THESIS

Prepared at

UNIVERSITE BOURGOGNE FRANCHE-COMTE INSTITUTION

For the title of

DOCTOR'S DEGREE IN CHEMISTRY

By

Quentin BONNIN

Maître ès Sciences

New cationic group 4 metallocenes as potential organometallic frustrated Lewis pairs: synthesis, reactivity and catalysis

---

Thesis presented and defended in Dijon, on the 5th of December 2017

DOCTOR
EUROPEUS

Jury composition:

Pr. PIRIO, Nadine	Professor at UBFC	President
Dr. BOURISSOU, Didier	Directeur de Recherche CNRS	Reporter
Dr. AUFFRANT, Audrey	Chargée de Recherche CNRS	Reporter
Pr. LAURENCZY, Gábor	Professor at École polytechnique fédérale de Lausanne	Reporter
Pr. ERKER, Gerhard	Professor at WWU Münster	Examiner
Pr. LE GENDRE, Pierre	Professor at UBFC	Thesis supervisor
Dr. NORMAND Adrien	Chargé de Recherche CNRS	Co-supervisor

Acknowledgement / Remerciements

I would like to thank first Pr. Gerhard Erker for welcoming me in his group during my Ph-D, and for all the scientific discussions we had. I also warmly thank the Erker group for their kind welcoming, for helping me whenever I needed, and for their kind attention during my illness. I give a special thanks to Fatma who has kept in touch with me, even in my worst moments.

I also want to thank all members of my jury for agreeing to attend my thesis defence, to judge this work, and for their trip to Dijon regardless of the distance.

This work is supported by the CNRS, Université de Bourgogne, Conseil Régional de Bourgogne through the plan d'actions régional pour l'innovation (PARI) and the fonds européen de développement regional (FEDER) programs. All these organisations are sincerely thanked for their fundings.

J'aimerais ensuite remercier le Pr. Pierre Le Gendre pour m'avoir donné le goût pour la chimie organométallique en m'accordant l'opportunité d'aller chez le Pr. Gerhard Erker pour mon premier stage de Master, et en me faisant confiance en m'encadrant pour mon deuxième stage de Master et pour la présente thèse. J'ai ainsi eu la chance de réaliser mon doctorat sous la direction d'une personne ayant une culture scientifique « titanesque » qui m'a permis de développer la mienne, ainsi que mon esprit scientifique. Je sais que nos conversations de « 2 minutes » (plus ou moins 3 heures) me manqueront. J'ai conscience que je ne serais pas là où je suis à l'heure actuelle sans son soutien indéfectible, me permettant de finaliser ma thèse au-delà des trois années réglementaires suite à mon année thérapeutique. En résumé, j'ai eu autant de chance que de plaisir de travailler avec Pierre qui a su faire preuve de qualités tant scientifiques qu'humaines, et je l'en remercie très chaleureusement.

J'aimerais ensuite remercier tous les membres de l'équipe PLG (Michel, Ewen, Semra, Margot, Thien, Benoit, Pierre-Emmanuel ; Robin, Florian, Audrey, Océane mes quatre chers (futurs ex) collègues de bureau et de laboratoire , et tous les stagiaires qui sont passés au laboratoire) et SJ (Sylvain, Jérôme Baptiste et Julie mes binômes de badminton, Raluca et nos conversations en boite à gants, Marie-Joelle et ses dons récurrents de rhubarbe, Jean-Claude et nos conversations en salle RMN, Pauline, Julie, Mathieu, Marie-Laure, Pawel, Floriane et ses conseils avisés de mise en page, Antonin, Benjamin) anciens, comme actuels, permanents comme non permanents, pour leur aide au quotidien, leur bonne humeur, et les échanges que nous avons pu avoir au cours des cinq années passées ensemble. Grâce à vous tous j'ai eu plaisir à venir travailler chaque jour. Par ailleurs, je remercie Dr Virginie Comte pour m'avoir formé à Dijon pendant mon master et à la chimie des benzotriazoles. Je remercie également Cédric Balan pour son aide et sa participation dans la synthèse des composés de ce manuscrit ; ainsi que Sook Yen Wong pour m'avoir aidé à la paillasse pendant son stage de master.

Je souhaite également remercier tous les membres de l'institut qui m'ont aidé de près ou de loin, pendant ma thèse. J'ajoute une mention spéciale pour : la patience de Didier Poinsot pour les expériences sous pression de gaz, et l'aide qu'il m'a apporté pour la conception du montage d'hydrogénation à pression atmosphérique ; Nadine Pirio pour avoir participé à la partie zirconium de ce projet, et pour nos discussions à ce sujet ; Emmanuel Lerayer pour nos discussions scientifiques (et pas que), et toutes les galères qu'on a pu traverser ensemble sur les premières années ; Sylviane Royer pour ses conseils sur les précurseurs de zirconium, Marcel Soustelle, Dr. Fanny Picquet et Marie-José Penouilh-Suzette pour les analyses élémentaires, et de masses exactes. Je tiens aussi à remercier Marie-José pour nos nombreuses discussions de RMN, les problèmes récurrents résolus, et les réponses à toutes les questions existentielles de RMN que j'ai pu lui poser. Un grand merci à notre crystallographe Dr. Philippe Richard qui a eu la patience et l'énergie de s'occuper de mes « cristaux » parfois bien trop sensibles pour être analysés facilement, et sans qui nous n'aurions pas eu toutes les belles structures proposées dans ce manuscrit. Je remercie également l'équipe SI de l'institut et particulièrement Thierry Belloir qui m'est venu en aide à chaque fois que j'avais un problème. Je remercie aussi Véronique de Biasio pour son aide et sa patience lors de l'impression de ma thèse.

Je dois enfin remercier Dr Adrien Normand qui a, avec Pierre et Gerhard, encadré ces travaux de thèse durant ces cinq années ; jusqu'à me suivre à Münster, où je suis allé pour effectuer mes tests de réactivité. Il a été celui qui m'a « prodigué occasionnellement des conseils », un post-doc (parfois tyrannique), chargé de recherche anglophone correcteur de thèse, mais aussi et surtout un collègue et ami sur qui on peut compter pour vous aider et vous donner de bons conseils. Son sens de la critique et sa pédagogie m'ont permis de prendre le recul nécessaire à la finalisation de ma thèse. Pour toutes ses qualités et son aide apportée, je le remercie sincèrement. Je sais que sans lui je ne serais pas le chimiste que je suis aujourd'hui.

Je tiens tout particulièrement à remercier le directeur de l'institut de Chimie Moléculaire de Bourgogne Franck Denat, le président de l'Université de Bourgogne Alain Bonnin, et Pierre Le Gendre pour m'avoir octroyé cette dernière année de thèse sous la forme d'un contrat d'ingénieur d'étude, sans quoi je n'aurai pas pu aboutir ses travaux.

Je remercie enfin toute ma famille et mes amis (de l'ICMUB, du club de Jeunes de la SCF, ou d'ailleurs) qui m'ont soutenu et / ou supporté pendant ma thèse (et surtout sa rédaction pour André). C'est grâce à eux que j'ai pu reprendre le cours de ma thèse, là où elle s'était interrompue, et finaliser ses travaux sous la forme du présent manuscrit.

A tous merci

Abstract

In 2006, the concept of “frustrated Lewis pairs” (called FLPs) was introduced. The main characteristic of these compounds is their ability to activate cooperatively small molecules without the use of a metal (H_2, CO_2, alkene alkyne…). Initially based on P/B combination, the concept has been extended to several other main group elements (N/B, P/Al, N/Al…). Recently, FLPs have been extended to the transition metal realm. These organometallic FLPs (OmFLPs) are obviously non-metal free systems but they extend significantly the scope of FLP applications. Seeking to develop such systems, a research towards new OmFLP combinations (N/Ti^+, N/Zr^+) has been initiated in our group, based on the synthesis of N-based titanocene and zirconocene complexes. The first part of this manuscript deals with a survey of the literature on such compounds, and a more detailed presentation of FLPs and related concepts (metal-ligand cooperativity, ambiphilic ligands) is also developed. In a second chapter, the synthesis of new N-based cyclopentadienyl ligands and their coordination to group 4 metals is presented. The formation of a cationic complex is then developed in a third part on selected titanocenes. In these complexes, the amine function undergoes CH activation by the cationic metal centre, leading to unexpected rearrangements. Investigations on their plausible mechanism are also presented. In a fourth part, the synthesis of new cationic phosphido- and amidotitanocenes, discovered in the course of our study on OmFLPs, is developed. The cationic amidotitanocenes are shown to be catalytically active towards hydrogenation of small molecules. Lastly, the potential of cationic titanocenyl iminophosphoranes as OmFLPs, was developed.

Résumé

Le concept de "paires frustrées de Lewis" (plus communément désignées par l'acronyme anglais FLPs) a suscité un vif intérêt depuis sa formulation en 2006. Initialement décrit à partir d'une phosphine encombrée comme base de Lewis et d'un borane comme acide de Lewis pour l'activation coopérative d'hydrogène sans métal, ce concept a été ensuite très largement développé en utilisant divers éléments du groupe principal (N/B, P/Al, N/Al …). Le concept a ensuite été étendu aux métaux de transitions : sont ainsi apparues les premières paires frustrées de Lewis organométalliques (OmFLPs). Dans le but de développer de telles OmFLPs, nous nous sommes intéressés à la synthèse de complexes cationiques titanocèniques et zirconocèniques en présence d'une amine. La première partie de cette thèse présente les travaux précédemment décrits sur les ligands azotés, en vue de synthétiser des complexes du groupe 4 N-fonctionnalisés. Une description plus détaillée du concept de FLP est ensuite réalisée, et un parallèle est fait avec des concepts connexes (coopérativité métal-ligand, systèmes ambiphiles). La seconde partie de ce manuscrit développe la synthèse de nouveaux ligands (aminomethyl)cyclopentadiènylure de potassium ainsi qu'une étude de leur coordination aux métaux du groupe 4. Cette étude a permis d'accéder à toute une série de nouveaux complexes dichlorotitanocènes et zirconocènes porteurs d'une fonction amine tertiaire encombrée à proximité du centre métallique. Ces travaux ont montré que l'amine ne se coordine pas au centre métallique. Les métallocènes ainsi formés ont ensuite été transformés en cation afin de renforcer l' acidité de Lewis du centre métallique. Ces espèces ont montré une réactivité inattendue donnant lieu à des réarrangements par activation CH au voisinage de l'atome d'azote. Ces réarrangements ainsi que des études mécanistiques font l'objet du troisième chapitre. La quatrième partie de ce mémoire porte sur la synthèse de complexes amido- et phosphidotitanocènes cationiques. Ces complexes montrent une très bonne activité en catalyse d'hydrogénation de petites molécules dans des conditions relativement douces, vraisemblablement pour des raisons d'effets coopératifs entre le métal et le ligand. Dans une dernière partie, la synthèse de complexes titanocéniques cationiques portant une fonction iminophosphorane est développée, suivie d'une étude de réactivité de ces complexes en tant que paires frustrées de Lewis organométalliques.

General Remarks:

A. Operating conditions and source of reagents:

All reactions were carried out under an atmosphere of Ar using Schlenk techniques or an Ar glovebox. Alumina (Brockman grade II) and 3Å molecular sieves were activated by heating for at least 6 hours above 230°C under vacuum ($< 10^{-1}$ mbar), and stored in the glovebox in order to be used as drying agents (see below). Dichloromethane, diethyl ether, pentane, tetrahydrofuran and toluene were dried using a solvent purification system (MBraun SPS-800) whilst acetonitrile, benzonitrile, bromobenzene, chlorobenzene, and heptane were distilled over CaH_2 and stored over activate 3Å molecular sieves under Ar. Deuterated solvents were dried by passage through a short column of activated neutral alumina and stored over activated molecular sieves in the glovebox, either at room temperature (C_6D_6, C_6D_5Br, d_6-DMSO) or at -18°C (d_8-THF, CD_2Cl_2, $CDCl_3$, CD_3CN). A short column of activated neutral alumina and storage over activated molecular sieves in the glovebox were used for 1,4-cyclohexadiene, 3,3-dimethylbutene, perfluorostyrene, phenylacetylene and styrene. Chlorotrimethylsilane was distilled under atmospheric pressure before use. *Tert*-butanol was distilled under reduced pressure (7.5 mmHg) at 37°C before use. Diphenylacetylene was crystallized from warm ethanol or pentane. The following chemicals CpNa,[1] $TiCl_4(THF)_2$ and $ZrCl_4(THF)_2$,[2] $B(C_6F_5)_3$,[3] $[Li][B(C_6F_5)_4]$,[4] $[(Et_2O)_2H][B(C_6F_5)_4]$,[5] $[Ph_3C][B(C_6F_5)_4]$,[6] $[Et_3Si][B(C_6F_5)_4]$,[7] TTBPO• (TTBP = 2,4,6-tritertbutylphenyl),[8] and *N*-phenylbenzylimine,[9] were synthesized according to literature procedures. In addition, $[Cp_2Fe][BPh_4]$,[10] PPh_2Li (with a modified procedure: pentane as reaction solvent and isolation by filtration),[11] KC_8,[12] and $CpTiCl_3$,[13] Cp^*TiCl_3,[14] $Cp(CH_2CH_2PR_2)CpTiCl_2$ (R = Ph or Cy),[15a,b] were synthesized according to literature procedures by Dr. Adrien Normand or Cédric Balan respectively. Azides were synthesized by Dr. Laure Monnereau by using an adapted literature procedure.[16] Cp_2TiMe_2 was synthesized according to the procedure described by Petasis, and further stored in the

---

[1] Panda, T. K.; Gamer, M. T.; Roesky, P. W. *Organometallics.* **2003**, *22*, 877
[2] Manxzer, L. E.; Deaton, J.; Sharp, P.; Schrock, R. R.In *Inorganic Syntheses* Fackler, J. P., Ed.John Wiley & Sons, Inc.: Hoboken, NJ, USA 1982 Vol. 21 pp 135–140
[3] Koppe, K.; Bilir, V.; Frohn, H.-J.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **2007**, *46*, 9425
[4] Massey, A. G.; Park, A. J. *J. Organomet. Chem.* **1964**, *2*, 245
[5] Jutzi, P.; Müller, C.; Stammler, A.; Stammler, H.-G. *Organometallics.* **2000**, *19*, 1442
[6] Doellein, G.Method of producing ph3c[b(c6f5)4]. CA2108512 C, June 16, 1998
[7] Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics.* **1994**, *13*, 2430
[8] Manner, V. W.; Markle, T. F.; Freudenthal, J. H.; Roth, J. P.; Mayer, J. M. *Chem. Commun.* **2007**, 2, 256
[9] Dobbs, A. P.In *Encyclopedia of Reagents for Organic Synthesis* John Wiley & Sons, Ltd 2001
[10] Piglosiewicz, I. M.; Beckhaus, R.; Wittstock, G.; Saak, W.; Haase, D. *Inorg. Chem.* **2007**, *46*, 7610
[11] Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 1243
[12] Bergbreiter, D. E.; Killough, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 2126
[13] Reid, A. F.; Wailes, P. C. *J. Organomet. Chem.* **1964**, *2*, 329
[14] Llinás, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organomet. Chem.* **1988**, *340*, 37
[15] (a) : Le Gendre, P.; Richard, P.; Moïse, C. *J. Organomet. Chem.* **2000**, 605, (2), 151, (b): Le Gendre, P.; Picquet, M.; Richard, P.; Moïse, C. *J. Organomet. Chem.* **2002**, 643–644, 231
[16] R. O. Lindsay; Allen, C. H. *Org. Synth.* **1942**, *22*, 96

dark in the freezer (-18°C).[17] Benzotriazole derivatives were synthesized as described by Katritzky, or improved protocoles.[18a,b,c] $CpZrCl_3$ was sublimed ($1.9x10^{-2}$ mbar, 170°C). All other reagents were commercially available and used as received or purified according to the purification guide of laboratory chemicals if required.[19]

B. Gas specifications:

HCl (sigma Aldrich): Reagentplus > 99% 295426-230g-EU

The following gases were purified by passage through a column filled with P_2O_5 coupled with a coloured indicator (drierite). These home-made apparatuses were directly connected to a Schlenk line for H_2 or CO_2 reactions.

H_2: ALPHAGAZ^{TM} 2 (Air liquide) N60: 99.9999% purity, $H_2O < 0.5$ ppm/mol, $O_2 < 0.1$ ppm/mol

CO_2: N48 (Air liquide): 99.998% purity, $H_2O < 3$ ppm/mol, $O_2 < 2$ ppm/mol

C. Analyses

All of the analyses were performed at the "Plateforme d'Analyses Chimiques et de Synthèse Moléculaire de l'Université de Bourgogne". The identity and purity (> 95%) of the complexes were unambiguously established using elemental analysis, high-resolution mass spectrometry (Electrospray Ionization), NMR and IR spectroscopy. Elemental analyses were obtained on a Flash EA 1112 CHNS-O Thermo Electron Flash instrument by Marcel Soustelle. Exact masses of the isolated compounds were obtained on a Bruker micrOTOF-Q ESI-MS by Mari-José Penouilh-Suzette. ^1H (300.13, 500.03, or 600.23 MHz), ^{11}B (160.42 MHz), ^{13}C (125.77 or 150.94 MHz), ^{15}N (43.3 MHz) and ^{19}F (470.45 MHz) NMR spectra were recorded on Bruker 300 Avance III, 500 Avance III, or 600 Avance II spectrometers. Chemical shifts are quoted in parts per million (δ) relative to TMS (^1H and ^{13}C), $BF_3.Et_2O$ (for ^{19}F), CH_3NO_2 (for ^{15}N), or H_3PO_4 (for ^{31}P). For ^1H and ^{13}C spectra, values were determined by using solvent residual signals as internal standards. The ^{31}P, ^{19}F and ^{11}B NMR spectra were referenced according to IUPAC recommendations (absolute referencing), using the residual protonated solvent (^1H) or the deuterated solvent (^{13}C) as an internal standard.[20] IR spectra were recorded on a FT BRUKER Vertex 70v spectrophotometer (Glowbar MIR et Hg FIR sources, Ge/KBr (MIR) et silicium (FIR) dividing and Ge/KBr (MIR) and silicium (FIR) detectors). Continuous wave (CW) EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer. The instrument was equipped with a

---

[17] Petasis, N. A.; Morshed, M. M.; Ahmad, M. S.; Hossain, M. M.; Trippier, P. C.In *Encyclopedia of Reagents for Organic Synthesis* John Wiley & Sons, Ltd, Ed.John Wiley & Sons, Ltd: Chichester, UK 2012

[18] (a): Katritzky, A. R.; Rachwal, S.; Rachwal, B. *J. Chem. Soc. Perkin vol 1.* **1987**,, 799, (b): Katritzky, A. R.; Yannakopoulou, K.; Lue, P.; Rasala, D.; Urogdi, L. *J. Chem. Soc. Perkin vol 1.* **1989**, (2), 225, (c): Katritzky, A. R.; Lan, X.; Yang, J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, 98, (2), 409

[19] Armarego, W. L. F.; Chai, C. L. L.Purification of laboratory chemicals6th ed.Elsevier/Butterworth-Heinemann: Amsterdam ; Boston 2009

[20] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics*. **2010**, *29*, 2176

4122SHQE/0405 X-band resonant cavity operating at 9.43 GHz, a X-band high-power dual-gun-oscillator bridge, and a quartz cryostat cooled at 100 K with a stream of nitrogen. The temperature was regulated with an ER 4131VT accessory. All apparatus as well as data acquisition were controlled using Xepr software. The magnetic field was swept from 250 to 360 mT through 2048 points. EPR spectrometer BRUKER ELEXSYS 500 records X-band equipped with a 10” electromagnet. The irradiation experiments were operated with a medium pressure Hg lamp (Heraeus TQ 150).

D. Computational details:

The geometries of **Bq620** and the two fragments were taken directly from the X-ray analysis parameters without any optimization**.** The wavefunctions were computed using Density functional theory (DFT) based on Becke’s three parameter hybrid exchange functional and Perdew Wang 91 correlation functional (B3PW91) employing a 6-31+G(d,p) basis for all atoms. Three methods have been used to analyse the wavefunction and gain chemical insights: Atom In Molecules (AIM), Natural Bond Orbitals (NBO) and Electron Localization Function (ELF). Only the AIM and ELF results are presented in the text.

Abbreviations

ACACH: acetylacetone
AIM: atoms in molecules
Alk: alkyl
APTS: para-toluenesulfonic acid
ATR: attenuated total reflectance
Ar: aryl
Bn: benzyl
bs: broad signal
Bt: benzotriazolyl
Bu: butyl
cat: catalyst
COD: cyclooctadiene
COSY: correlation spectroscopy
Cp: cyclopentadienyl
Cp*: pentamethylcyclopentadienyl
Cy: cyclohexyl
d: doublet
DCC: dicyclohexylcarbodiimide
DFT: density functional theory
Dipp: 2,6-diisopropylphenyl
DMSO: dimethylsulfoxide
DTBP: 2,6-ditertbutylpyridine
ELF: electron localization function
EPR: electron paramagnetic resonance
ESI: electrospray ionization
Et: ethyl
Fc: ferrocene
FIR: far infrared
FLP: frustrated Lewis pairs
GC: gas chromatography
GCMS: gas chromatography coupled with mass spectrometry
h: heptet
HMBC: heteronuclear multiple-bond correlation
HMQC: heternuclear multiple-quantum correlation

HRMS: high-resolution mass spectrometry

IR: infrared

^{i}Pr: isopropyl

KHMDS: potassium hexamethyldisilazane

LA: Lewis acid

LB: Lewis base

LDA: lithium diisopropylamide

m: multiplet

MAO: methylaluminoxane

Me: methyl

MeLi: methyl lithium

Mes: mesityl

MIR: middle infra red

nb: norbornadiene

NBO: natural bond orbitals

NMR: nuclear magnetic resonance

NOESY: nuclear Overhauser effect spectroscopy

Nu: nucleophile

ORTEP: oak ridge thermal ellipsoid plot

Ph: phenyl

Pr: propyl

ppm: parts per millions

Py: pyridine

q: quartet

r.t.: room temperature

s: singlet

sext: sextet

t: triplet

Tf: triflate

THF: tetrahydrofuran

TLC: thin layer chromatography

TMP: tetramethylpiperidinyl

TMPH: tetramethylpiperidine

TMS: trymethylsilyl

TOF: turnover frequency

Ts: tosyl

XRD: X-ray diffraction

Foreword

This thesis has been accomplished in Dijon under the supervision of Pr. Pierre Le Gendre, Dr. Adrien Normand, and Pr. Gerhard Erker who kindly welcomed me in his working group in Münster for a three-month internship in order to test the potential of my compounds as OmFLPs.

During my thesis, I had the opportunity to teach chemistry to students for two years through practical and theoretical courses. In addition, I was secretary of the "Club de jeunes de la Société Chimique de France-section Bourgogne-Franche-Comté" during my 1st year of Ph-D and I evolved to the rank of vice president for my 2nd year. I have stayed active member of this association for the rest of my Ph-D.

Finally, I was doctoral student representative of the Institute for the "Conseil du département de Chimie" for 5 years.

Scientific communications

3 oral communications:

- 2014: Synthesis of new group 4 (aminomethyl)metallocenes: potential candidates as OmFLPs - Advances in the Synthesis of Molecularly Ordered Structures-X - Saint-Seine-l'Abbaye
- 2016: New cationic amino group 4 metallocenes: Towards organometallic frustrated Lewis pairs (OmFLPs) - International Conference on Coordination Chemistry - Brest
- 2016: Synthèse de nouveaux complexes (aminomethyl)métallocènes du groupe 4: vers des paires frustrées de Lewis organométalliques (OmFLP) – XVIIes Journées de l'École Doctorale Carnot Pasteur – Besançon

Poster communications:

- 2016: Ti and Zr based frustrated Lewis pairs – Core to core Japan Society for the Promotion of Science – Dijon
- 2017: CH-activation and unexpected rearrangements in cationic titanocenes – International Green Catalysis Symposium – Rennes; XVIIIes Journées de l'École Doctorale Carnot Pasteur – Dijon

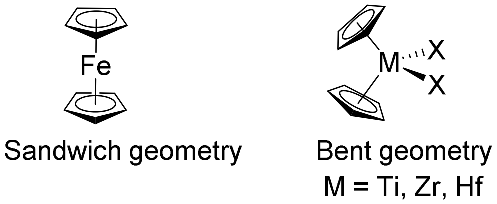
Publications:

- A. T. Normand, Q. Bonnin, The Taming of Redox-Labile Phosphidotitanocene Cations. Manuscript in preparation
- Q. Bonnin, Synthesis of new (aminomethyl)metallocenes, manuscript in preparation

Table of contents

General introduction

In 1951 Kealy and Pauson discovered a new organometallic molecule accidentally by attempting to synthesize fulvalene.[1] One year later, Woodward and Wilkinson rediscovered this ubiquitous molecule in the organometallic field, which was subsequently named "ferrocene".[2a,b] Fischer then described the synthesis of two analogous organometallic complexes based on nickel and cobalt: the new family of metallocenes was born. Wilkinson and Fischer obtained the Nobel Prize for their pioneering work on sandwich complexes of d-block metals in 1973.[3] A wide variety of metallocenes have been described over the years and exhibited various geometries and reactivity: one can cite cationic group 4 metallocenes used for Ziegler-Natta polymerization of alkenes which yield stereoregular polymers. Wilkinson and Birmingham described the first group 4 metallocenes in 1954 and the structure of Cp_2TiCl_2 was unambiguously established 21 years later.[4,5] Contrarily to ferrocene with its sandwich geometry, group 4 metallocenes adopt a "bent" or pseudo tetrahedral geometry, considering the centroids of both Cp and the two Cl atoms around the metal centre (Scheme 0-1).



Scheme 0-1: Sandwich and bent geometries of metallocenes

After the discovery of metallocenes, extensive work has been done in the organometallic field, in order to design functionalized cyclopentadienes, bringing functionalities in the proximity to the metal centre. Indeed, functionalization can confer specific properties to metallocenes: for example, incorporating a phosphanyl arm into a metallocene would be a useful tool for the synthesis of bimetallic complexes; or could favor a reaction in which a base is required in addition to the metallocene. Both donors such as O, N, P… or acceptors such as B have been incorporated into Cp rings. As illustrated below, recent works developed the synthesis of polyfunctionalized metallocenes in which several donor atoms were grafted on the Cp rings. In rarer cases, both donor and acceptor sites will be present. In the present manuscript, a survey of the literature is presented on the synthesis of N-functionalized

---

[1] T. J. Kealy; Pauson, P. L. *Nature.* **1951**, *168*, 1039

[2] (a):Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125, Woodward, R. B.; Rosenblum, M.; Whiting, M. C. *J. Am. Chem. Soc.* **1952**, *74*, 3458

[3] Pfab, W.; Fischer, E. O. *Z. Für Anorg. Allg. Chem.* **1953**, *274*, 316

[4] Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281

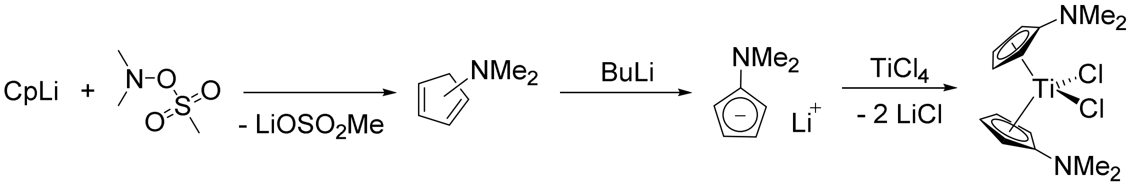
[5] Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622

cyclopentadienides and their coordination to group 4 metals over the past six decades. In the first part, particular attention will be devoted to the carbon-based spacer between the Cp ring and the N atom. Limitations of these syntheses will also be discussed. A second part will focus on the coordination of these ligands to group 4 metals. This bibliographic introduction will be followed by the discussion of the synthesis of new group 4 (aminomethyl)metallocenes as potential precursors for OmFLPs in a first chapter. A second chapter will then be developed on the generation of related cationic species and the study of their reactivity. A third chapter will describe the results obtained on the synthesis and the reactivity of new amido- and phosphidotitanocenes. Lastly, a brief chapter will focus on the reactivity of new titanocenyl iminophosphoranes previously developed in our group.

I. Bibliographic introduction

A. Aminocyclopentadienides: synthesis and coordination

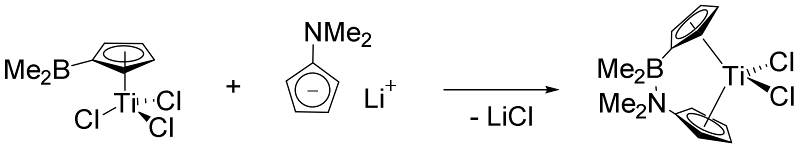
Aminocyclopentadienides can be synthesized according to two different procedures. Boche presented the first example described in the literature,[6] with the electrophilic amination of cyclopentadienyllithium (CpLi). The reaction required the synthesis of N,N-dimethyl-O-(methylsulfonyl)hydroxylamine **L1** which reacted with CpLi to form the corresponding aminocyclopentadiene **L2**. It was easily deprotonated with *n*-BuLi to yield **L3** (Scheme I-1).



L1 **L2** **L3** **L4**

Scheme I-1: synthesis of the first spacer-free aminocyclopentadienide L3

The coordination potential of this ligand was first proved by formation of the corresponding (bis amino)ferrocene; it was then coordinated to titanium in 1984 to form the (bisamino)titanocene dichloride **L4**.[7] This complex adopted a pseudo tetrahedral geometry in which both substituents were located on the open side of the bent metallocene so that both were as far as possible from each other due to steric effects. In 1999, Ostoja-Starzewski used **L3** for the synthesis of a new donor / acceptor titanocene dichloride **L5** (Scheme I-2).[8]



L3 **L5**

Scheme I-2: synthesis of B-N titanocene dichloride L5

The N-B interaction was proven to be strong in this structure with an interatomic distance of 1.74 Å. In this special case, substituents were in the closed side of the bent metallocene so that Lewis adduct formation was possible. This example illustrates how important it is to manage the nature of various substituents on Cp rings, and shows that steric hindrance can be overcome easily in front of stronger forces, such as Lewis adduct formation.

In 2000, the group of Bercaw used the previously described electrophilic amination to functionalize fluorene derivatives. The corresponding ligands **L7-a-b** were coordinated to zirconium and hafnium (Scheme I-3).[9] In the zirconocene structure of type **L9-a**, the

---

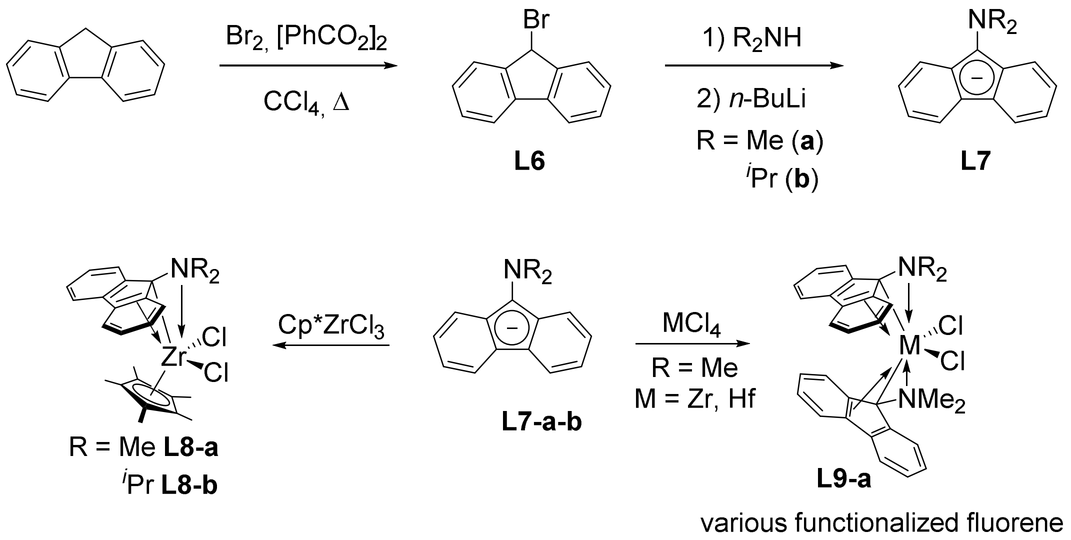
[6] Bernheim, M.; Boche, G. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 1010

[7] Stahl, K.-P.; Boche, G.; Massa, W. *J. Organomet. Chem.* **1984**, *277*, 113

[8] Ostoja Starzewski, K. A.; Kelly, W. M.; Stumpf, A.; Freitag, D. *Angew. Chem. Int. Ed.* **1999**, *38*, 2439

[9] Miller, S. A.; Bercaw, J. E. *Organometallics.* **2000**, *19*, 5608

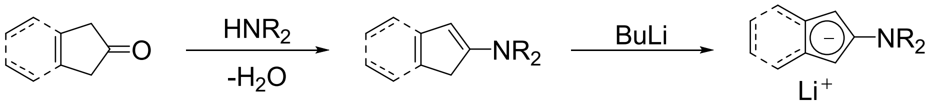
aminofluorene ligand was XL_2 according to Green formalism. Noteworthy, only one double bond from the Cp ring was coordinated to the titanium centre as the first L ligand whilst one amino group acted as the second. This feature conferred specific geometry to these zirconocenes.



Scheme I-3: synthesis of aminofluorenes and their coordination to group 4 metals

The narrow scope of the electrophilic amination reaction restricted its use in the literature, due to the low availability of hydroxylamines, and the associated danger of explosion.

The second procedure widely used in the literature was inspired from the work on enamines of cyclopentenones and indanones,[10a,b] which yielded aminocyclopentadienides or aminoindanylides after deprotonation (Scheme I-4).



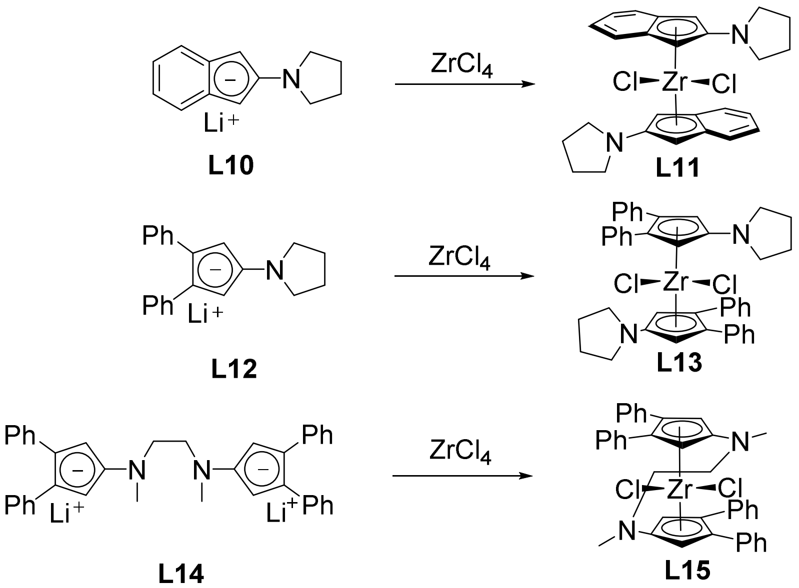
Scheme I-4: second route for aminocyclopentadienides

This type of ligand has been widely used to synthesize d-block metallocenes. In 1995, the first pyrrolidino-ligands **L10-12** were described by Plenio, and were used one year later, to form new bisaminozirconocenes **L11** and **L13**. This procedure was also used by Plenio with N,N'-dimethylethylene diamine to form the corresponding ligand **L14** which opened a straightforward procedure for a new ansametallocene series (e.g. compound **L15** Scheme I-5).[11]

---

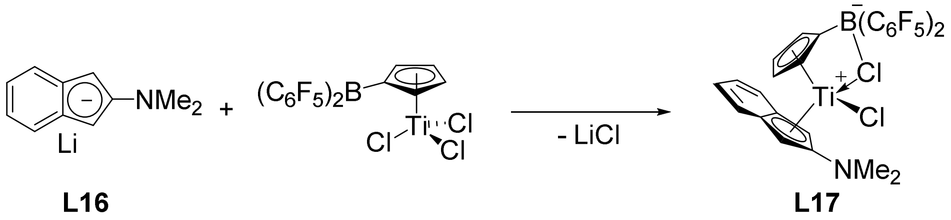
[10] (a): Treibs, W.; Schroth, W. *Justus Liebigs Ann. Chem.* **1961**, *639*, 204, Blomquist, A. T.; Moriconi, E. J. *J. Org. Chem.* **1961**, *26*, 3761, Edlund, U.; Esperås, S.; Songstad, J.; Lundblad, G.; Nimmich, W. *Acta Chem. Scand.* **1973**, *27*, 4027

[11] Plenio, H.; Burth, D. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 800



Scheme I-5: synthesis of Plenio's aminozirconocenes

Several other groups worked on this topic at the same time, such as Näsman,[12a,b] Britzinger,[13] and Bochmann,[14] using dimethylamine for the condensation reaction. Classical bis(aminoindenyl)zirconocene were quickly abandoned for the synthesis of mixed metallocenes and ansametallocenes. One example of the former is depicted in Scheme I-6 from Bochmann's work. All experimental analyses were in agreement with a B-Cl interaction instead of a B-N Lewis adduct as might be expected (compound **L17**).



Scheme I-6: intriguing boryl-(aminoindenyl)titanocene from Bochmann's work

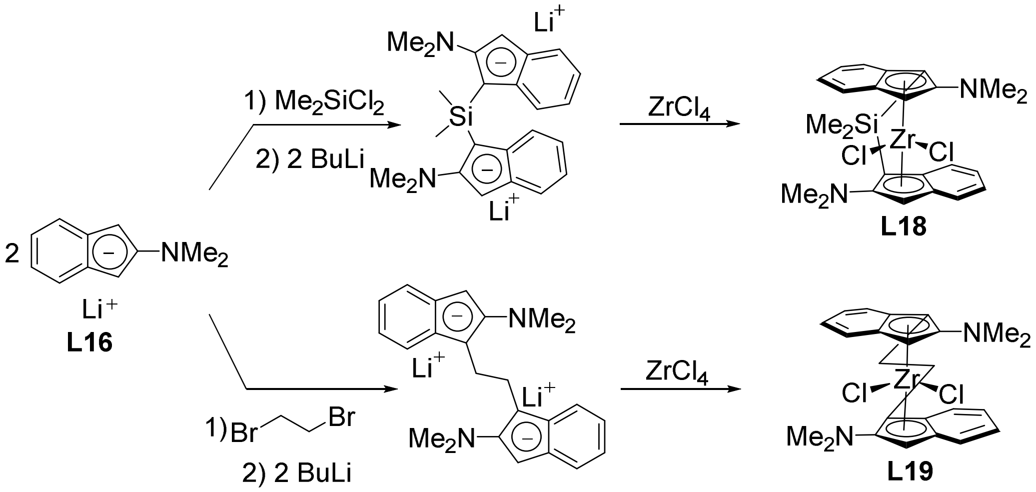
Two different ansabis(aminoindenyl)zirconocenes were also synthetized, described as good candidates for ethylene polymerization (**L18** and **L19** Scheme I-7).

---

[12] (a): Luttikhedde, H. J. G.; Leino, R. P.; Wilén, C.-E.; Näsman, J. H.; Ahlgrén, M. J.; Pakkanen, T. A. *Organometallics.* **1996**, *15*, 3092, (b): Luttikhedde, H. J. G.; Leino, R.; Ahlgrén, M. J.; Pakkanen, T. A.; Näsman, J. H. *J. Organomet. Chem.* **1998**, *557*, 227

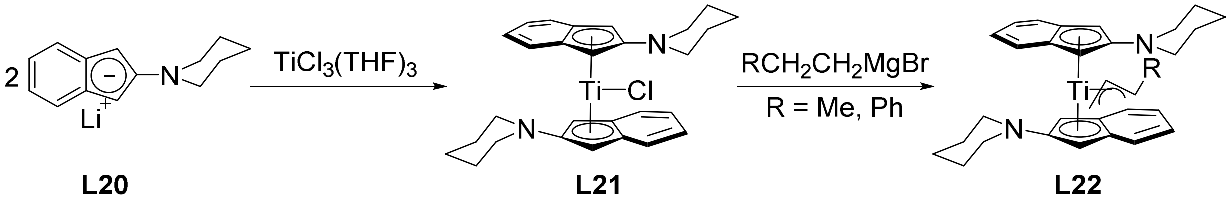
[13] Barsties, E.; Schaible, S.; Prosenc, M.-H.; Rief, U.; Röll, W.; Weyand, O.; Dorer, B.; Brintzinger, H.-H. *J. Organomet. Chem.* **1996**, *520*, 63, *J. Organomet. Chem.* **1996**, *520*, 63

[14] Lancaster, S. J.; Al-Benna, S.; Thornton-Pett, M.; Bochmann, M. *Organometallics.* **2000**, *19*, 1599



Scheme I-7: syntheses of ansabis(aminoindenyl)zirconocenes Brintzinger (top) and Näsman (bottom)

In 1999, the Ti (III) complex **L21** was described by Stryker, by reacting **L20** and TiCl$_3$(THF)$_3$ (Scheme I-8).[15a,b] The allyl-derivative **L23** was a precursor of stable titanocyclobutanes that were crystallized. Some of these complexes were used for homo- or co-polymerization of olefins such as ethylene. They were reviewed by Leino in his microreview of 2004 on group 4 bis(indenyl)metallocenes.[16]



Scheme I-8: synthesis of Stryker's bis(aminoindenyl)titanocenes

Between 2000 and 2002, Erker and Hämäläinen extended the synthesis to various amines and coordinated their ligand to zirconium (Scheme I-9, top).[17a,b,18] More complex amine can easily be introduced, such as morpholine (**L23-a** and **L24-a**) or allylethylamine (**L23-d** and **L24-d**). Erker also described a new series of aminocyclopentadienes (**L25-e-f**) derived from phenylcyclopentenone (Scheme I-9, bottom).

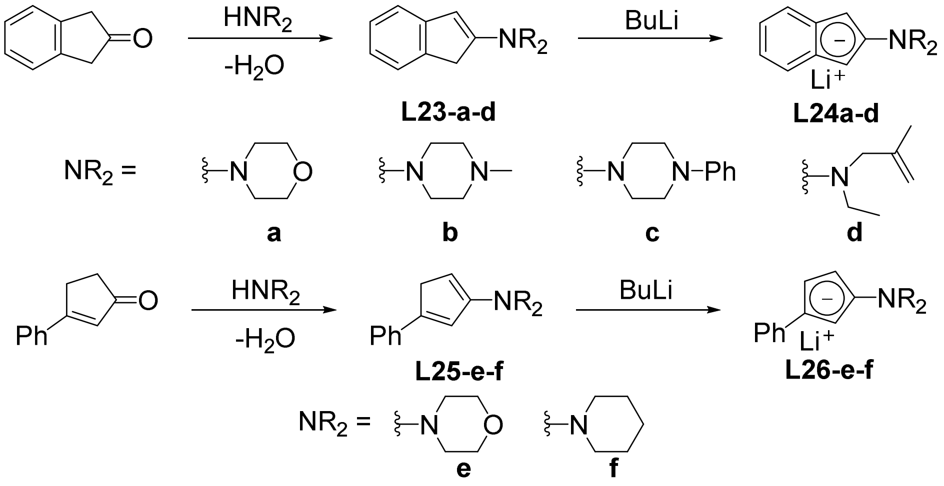
---

[15] (a): Carter, C. A. G.; McDonald, R.; Stryker, J. M. *Organometallics.* **1999**, *18*, 820, Greidanus, G.; McDonald, R.; Stryker, J. M. *Organometallics.* **2001**, *20*, 2492

[16] Leino, R.; Lehmus, P.; Lehtonen, A. *Eur. J. Inorg. Chem.* **2004**, 3201

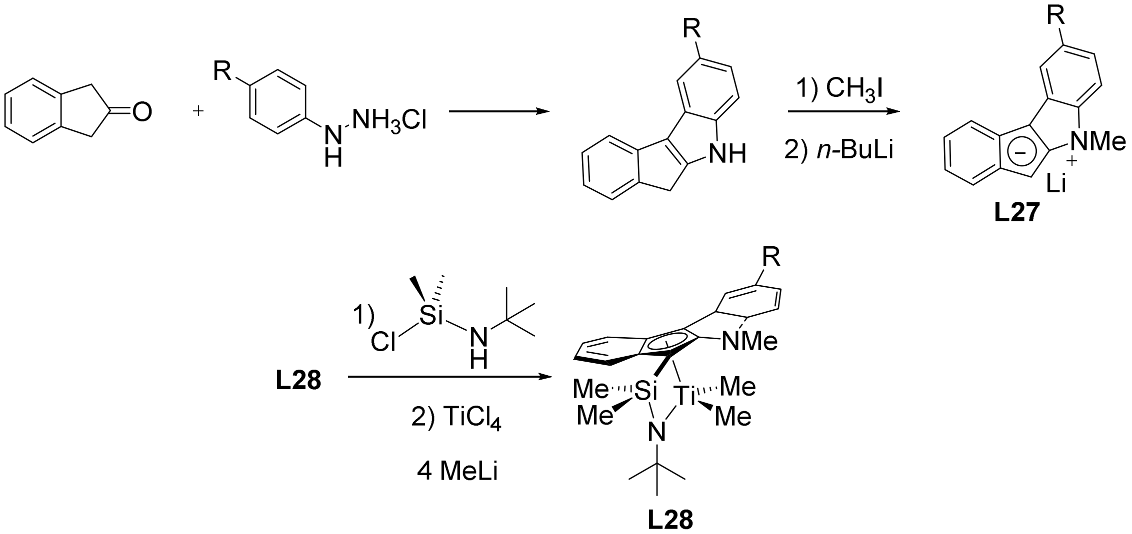
[17] (a): Fauré, J.-L.; Erker, G.; Fröhlich, R.; Bergander, K. *Eur. J. Inorg. Chem.* **2000**, *2000*, 2603, Knüppel, S.; Fauré, J.-L.; Erker, G.; Kehr, G.; Nissinen, M.; Fröhlich, R. *Organometallics.* **2000**, *19*, 1262

[18] Hämäläinen, M.; Korpi, H.; Polamo, M.; Leskelä, M. *J. Organomet. Chem.* **2002**, *659*, 64



Scheme I-9: aminocyclopentadienides reported by Erker and Hämäläinen

In the early 2000s, a news series of mixed constrained geometry titanocenes **L28** was described by Klosin,[19a,b] Resconi and De Rosa,[20a,b] for the synthesis of high-molecular-weight syndiotactic amorphous polypropylene. Resconi's synthesis is depicted in Scheme I-10. These ligands are rather elaborated, and their synthesis required three steps to form the four fused rings.



Scheme I-10: constrained geometry titanocenes with an amino(indenyl) ring

Many other examples could have been added to this part, such as syntheses of polyfunctionalized aminocyclopentadienes that were not used as ligands but were designed for other purposes (total synthesis of natural fused molecules).[21]

---

[19] (a): Klosin, J.; Kruper, W. J.; Nickias, P. N.; Roof, G. R.; De Waele, P.; Abboud, K. A. *Organometallics*. **2001**, *20*, 2663, Klosin, J.; Kruper, W. J.; Patton, J. T.; Abboud, K. A. *J. Organomet. Chem.* **2009**, *694*, 2581, Klosin, J.; Fontaine, P. P.; Figueroa, R. *Acc. Chem. Res.* **2015**, *48*, 2004

[20] (a): De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O.; Resconi, L.; Fait, A.; Ciaccia, E.; Camurati, I. *J. Am. Chem. Soc.* **2003**, *125*, 10913, Grandini, C.; Camurati, I.; Guidotti, S.; Mascellani, N.; Resconi, L.; Nifant'ev, I. E.; Kashulin, I. A.; Ivchenko, P. V.; Mercandelli, P.; Sironi, A. *Organometallics*. **2004**, *23*, 344

[21] Aumann, R.; Göttker-Schnetmann, I.; Fröhlich, R.; Meyer, O. *Eur. J. Org. Chem.* **1999**, 2545

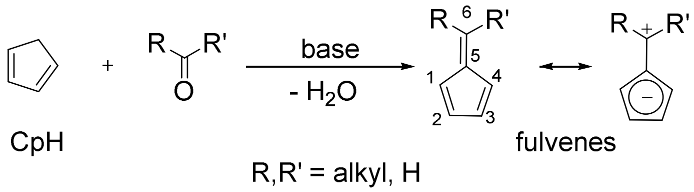
To summarize this first part, only two synthetic routes were found for the preparation of aminocyclopentadienides. The condensation of cyclopentenones and indanones with amines is a straightforward route to synthesize such ligands, which shows high versatility and tolerance towards various functionalized amines and ketones.

B. (Aminomethyl)cyclopentadienides

1. Synthesis

a. Fulvene route from Thiele

The fulvene route is a straightforward procedure to synthesize (aminomethyl)cyclopentadienes. The synthesis of fulvene, first reported by Thiele, has been widely improved over the years, in terms of yield and variety of substrates.[22] This reaction was based on a Mannich-type reaction involving the condensation of an aldehyde or a ketone with CpH in presence of a base (Scheme I-11).[23a,b]



Scheme I-11: general fulvene synthesis

Fulvenes exhibit two different kinds of reactivity: nucleophilic attack of the electrophilic carbon 6 is possible to form various functionalized cyclopentadienides of type **A.** With an enolizable fulvene, deprotonation is also possible to form vinylcyclopentadienides **B.** Depending on the nature of the nucleophile, these two reactions can be in competition and yield mixtures of both **A** and **B.** To circumvent this drawback, the use of a non-enolizable fulvene was chosen such as tetramethylfulvene **L29-Me** first reported by Jutzi, and 6-tertbutylfulvene **L30**,[24a,b,25] in which only substitution was able to occur to form **L31-a-b** or **c** respectively. In the fulvene chemistry, the synthesis of the easiest fulvene **L29-H** is known to be tedious. This is the reason for its rare use, contrarily to **L29-Me** as illustrated above.

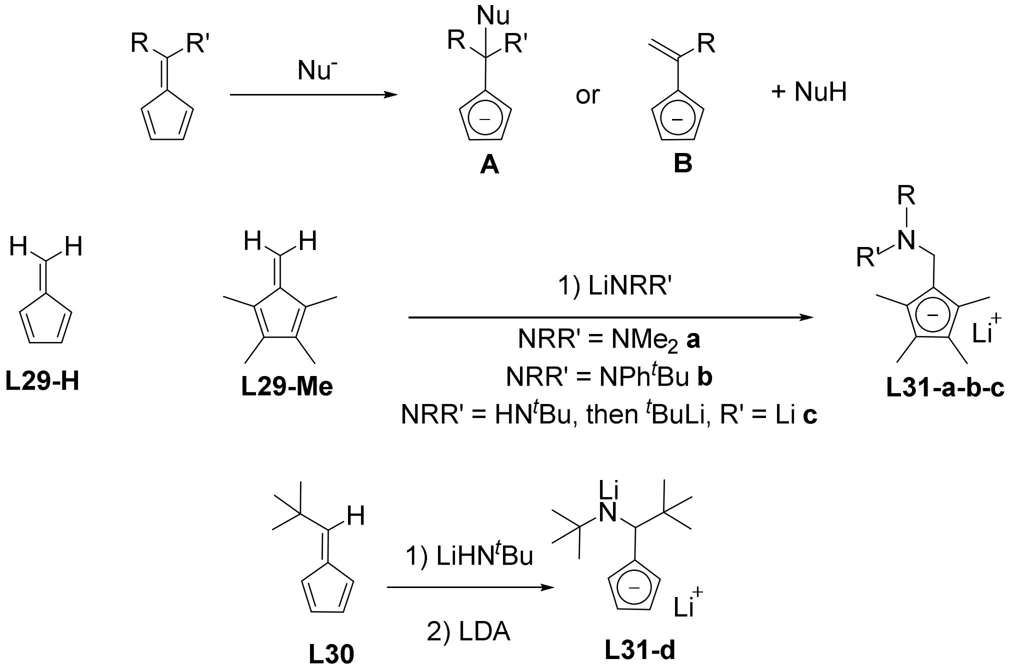
---

[22] Thiele, J. *Berichte Dtsch. Chem. Ges.* **1900**, *33*, 666

[23] (a): Freiesleben, W. *Angew. Chem.* **1963**, *75*, 576, (b): Buechi, G.; Berthet, D.; Decorzant, R.; Grieder, A.; Hauser, A. *J. Org. Chem.* **1976**, *41*, 3208, Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849

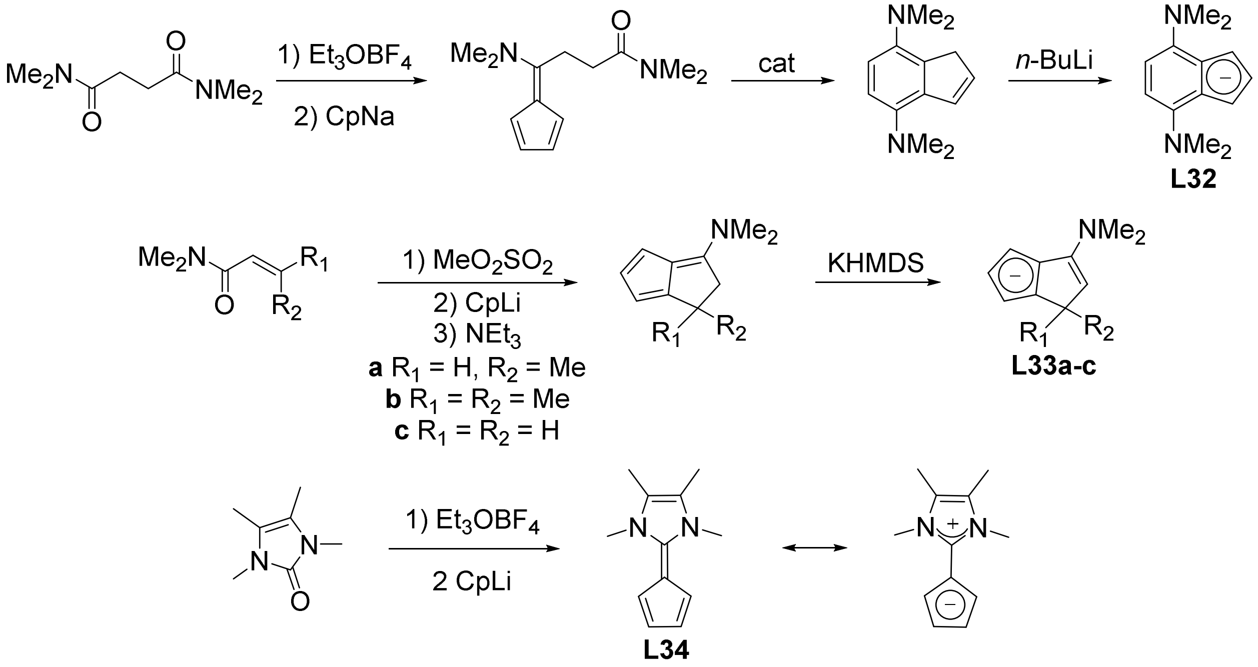
[24] (a): Jutzi, P.; Heidemann, T.; Neumann, B.; Stammler, H. G. *Synthesis.* **1992**, *1992*, 1096, (b): Heidemann, T.; Jutzi, P. *Synthesis.* **1994**, *1994*, 777

[25] Kunz, K.; Erker, G.; Döring, S.; Fröhlich, R.; Kehr, G. *J. Am. Chem. Soc.* **2001**, *123*, 6181



Scheme I-12: reactivity of fulvenes

The fulvene route was extended to amides, to form N-functionalized fulvenes. An unexpected rearrangement on newly obtained 6-aminofulvenes yielded bis(dimethylamino)indenyl ligand **L32** via an acid-catalysed ring closure reaction followed by deprotonation with *n*-BuLi. 3-dimethylamino-1,2-dihydropentalene **L33** could be obtained (Scheme I-13).[26,27]



Scheme I-13: (aminomethyl)cyclopentadienide formed via Thiele condensation

---

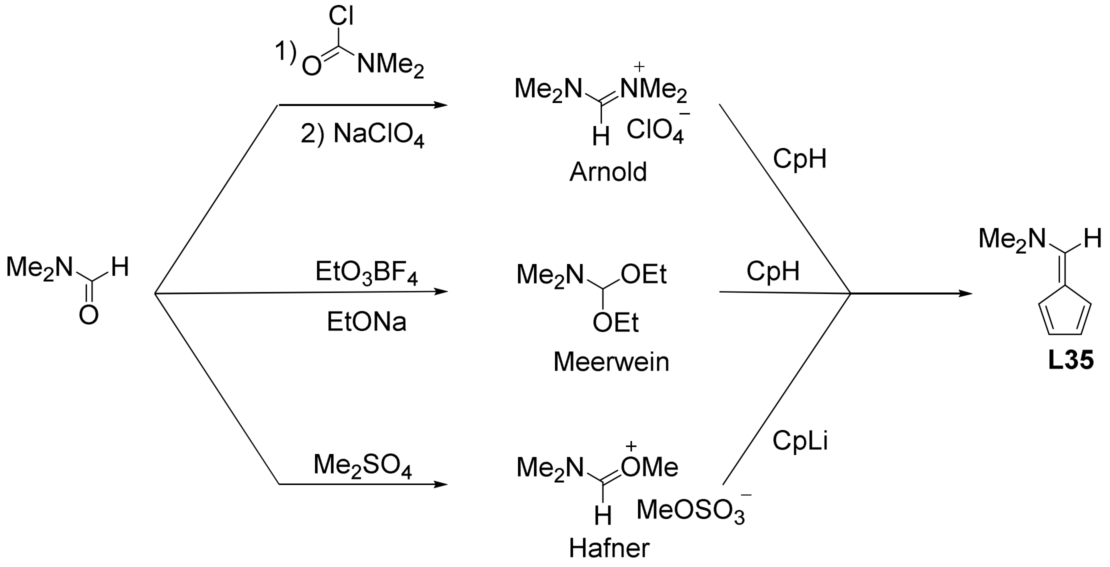
[26] Sierra, J. C.; Kehr, S. G.; Fröhlich, R.; Erker, G. *Eur. J. Inorg. Chem.* **2004**, 2260

[27] Xu, B.-H.; Kehr, G.; Fröhlich, R.; Nauha, E.; Erker, G. *Dalton Trans.* **2010**, *39*, 9973

With an imidazolone, Kunz described a new synthesis of imidazole-based fulvene **L34** via a Thiele condensation. **L34** was coordinated to group 8 metals, forming new metallocenes.[28]

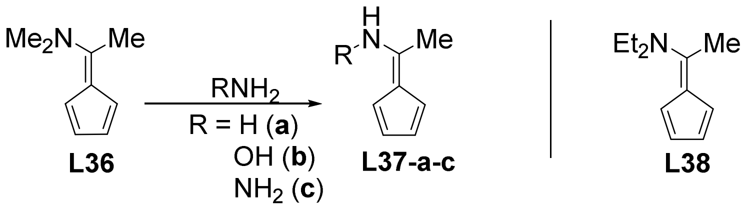
b. The Hafner route

During the 1960s, different syntheses of 6-dimethylaminofulvene **L35** were described which are based on the use of activated dimethylformamide (Scheme I-14). The Arnold procedure used a tetramethylformamidinium salt, which required harsh synthesis conditions.[29] Meerwein described a more straightforward route via an amidoacetal intermediate by using $[EtO_3][[BF_4]$,[30] whilst Hafner used dimethylsulfate.[31]



Scheme I-14: syntheses of 6-dimethylaminofulvene

The later procedure also worked with dimethylacetamide to form **L36** (Scheme I-15 left). **L36** was treated with primary amines to form 6-aminofulvenes of type **L37** by Hafner. This procedure has subsequently been used by numerous authors. Several analogues have been synthesized such as diethylacetamide-derived **L38** (Scheme I-15 right).[32]



Scheme I-15: 6-aminofulvenes obtained via Hafner's procedure

---

[28] Kunz, D.; Johnsen, E. Ø.; Monsler, B.; Rominger, F. *Chem. – Eur. J.* **2008**, *14*, 10909

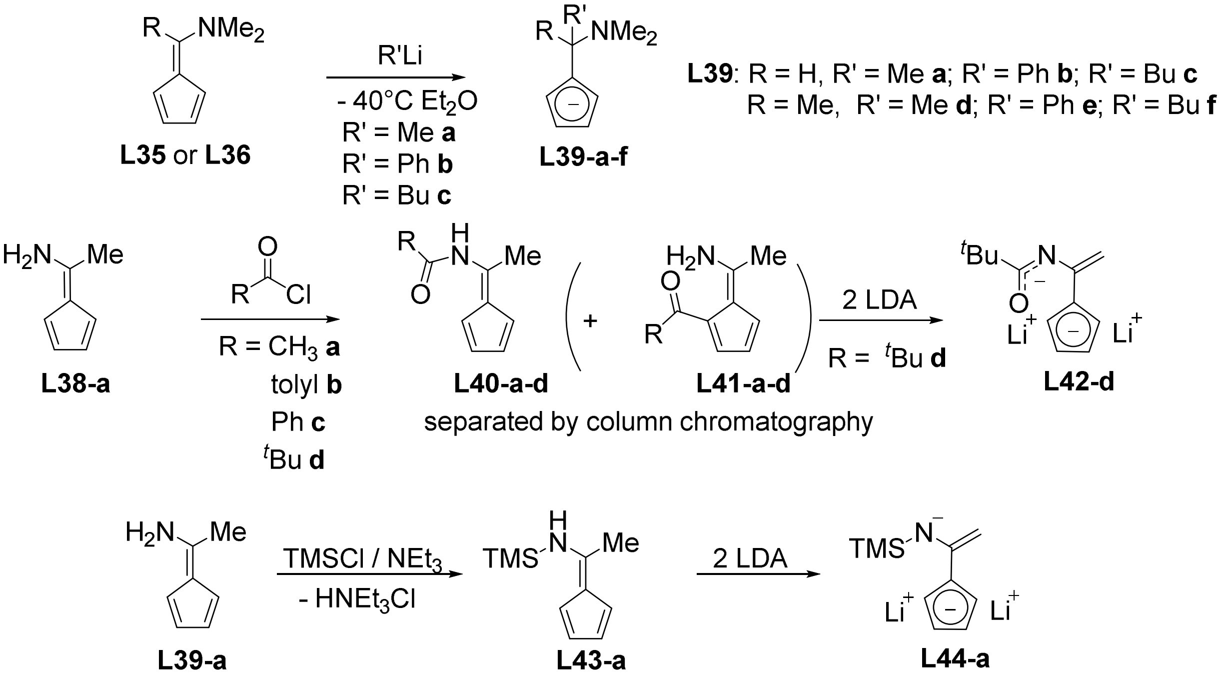
[29] (a): Arnold, Z. *Collect. Czechoslov. Chem. Commun.* **1959**, *24*, 760, (b): Arnold, Z.; Žemlička, J. *Collect. Czechoslov. Chem. Commun.* **1960**, *25*, 1302

[30] Meerwein, H.; Florian, W.; Schön, N.; Stopp, G. *Justus Liebigs Ann. Chem.* **1961**, *641*, 1

[31] (a): Hafner, K.; Schulz, G.; Wagner, K. *Justus Liebigs Ann. Chem.* **1964**, *678*, 39, (b): Hafner, K.*Organic syntheses*1967 p 52

[32] Venne-Dunker, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics.* **2003**, *22*, 948

These 6-aminofulvenes reacted as fulvene (Scheme I-12), depending on the presence of acidic H on the 7 position, or the nucleophile used (Scheme I-16). In 1997, the synthesis of six news ligands (**L39-a-f**) was described by Erker.[33] This was successfully achieved by a subtle control of the reaction conditions depending on the starting aminofulvene used (Scheme I-16 top). The same author described the synthesis of amidoyl fulvene **L40-a-d** by treatment of **L38-a** with various acyl chlorides.[34a,b] The coupling reaction was in competition with an electrophilic aromatic substitution on the Cp ring. A mixture of **L40** and **L41** was obtained, requiring a purification by column chromatography. The use of LDA as base on **L40-d** afforded **L42-d**, regioselectively. Some amines required activation or protection to avoid ortho C-acylation and enable N-acylation.[35] **L38-a** was also used by Erker to form the TMS-analogue (**L43-a**), which was deprotonated twice, affording **L44-a**.



Scheme I-16: Several examples of (aminomethyl)cyclopentadienide

In 1999, the scope of amines used for the formation of 6-aminofulvenes was improved by Erker, who synthesized the corresponding pyrrolidino- morpholino- and piperidino-methylcyclopentadienides **L49**-**L52** (Scheme I-17),[36,37] after deprotonation of **L45-L48** by MeLi respectively. The scope of nucleophiles used on **L35** was also extended to form **L53-a-d**.[38] In 2002, **L35** was substituted with lithium anilide to form **L54-a-b** after treatment with alkyl or aryl lithium nucleophiles.

---

[33] Bertuleit, A.; Fritze, C.; Erker, G.; Fröhlich, R. *Organometallics*. **1997**, *16*, 2891

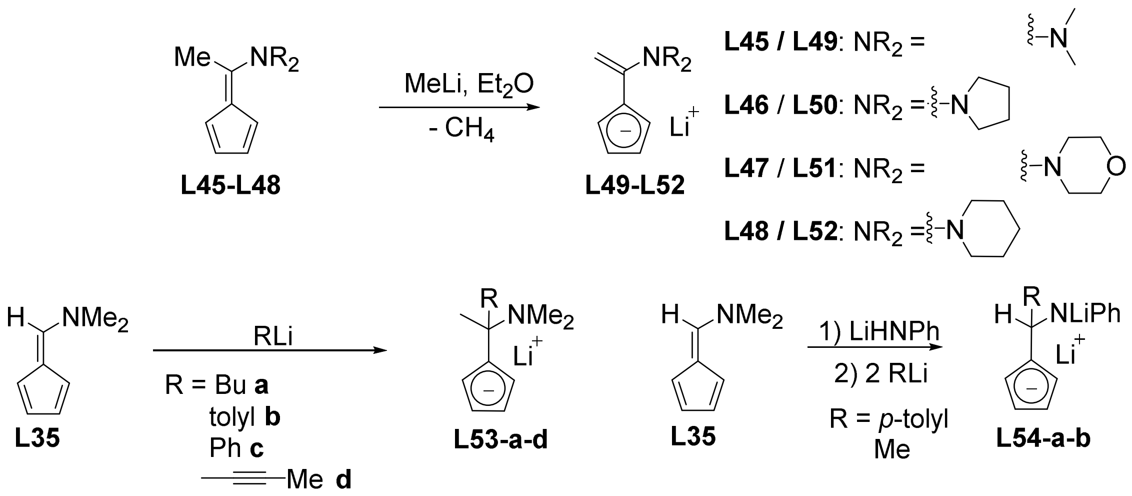
[34] (a): Duda, L.; Erker, G.; Fröhlich, R.; Zippel, F. *Eur. J. Inorg. Chem.* **1998**, 1153, (b): Kunz, D.; Erker, G.; Fröhlich, R.; Kehr, G. *Eur. J. Inorg. Chem.* **2000**, *2000*, 409

[35] Kunz, D.; Fröhlich, R.; Erker, G. *Eur. J. Org. Chem.* **2001**, 3531

[36] Knüppel, S.; Erker, G.; Fröhlich, R. *Angew. Chem. Int. Ed.* **1999**, *38*, 1923

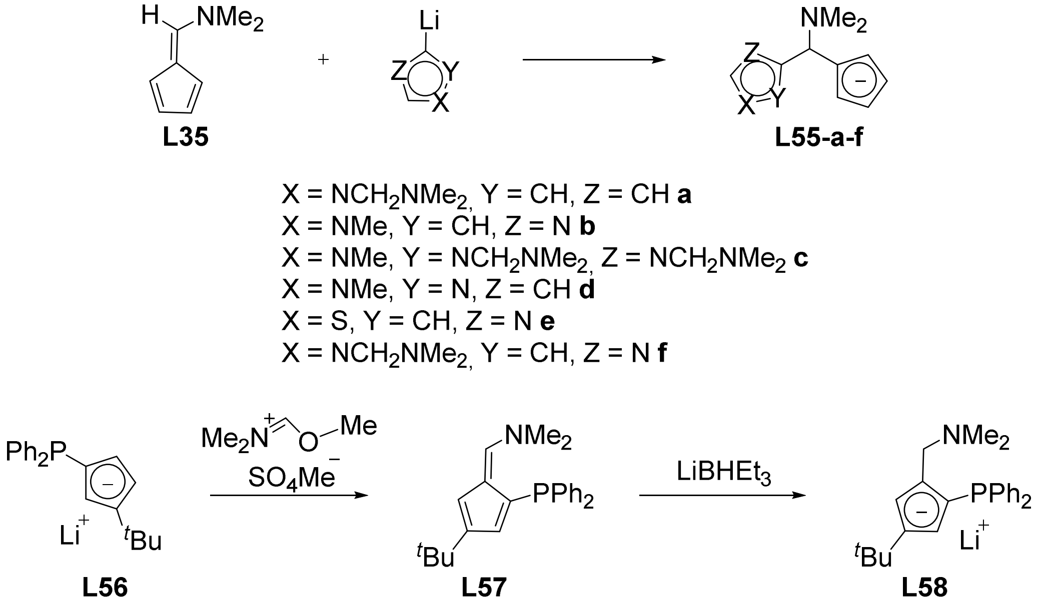
[37] Kotov, V. V.; Kehr, G.; Fröhlich, R.; Erker, G. *Z. Für Naturforschung B.* **2006**, *61*, 1319

[38] Kunz, K.; Pflug, J.; Bertuleit, A.; Fröhlich, R.; Wegelius, E.; Erker, G.; Würthwein, E.-U. *Organometallics*. **2000**, *19*, 4208



Scheme I-17: other examples of (aminomethyl)cyclopentadienides

After the 2000s many research groups worked on polyfunctionalized ligands. For example, new polyfunctionalized titanocenes for anticancer purpose were designed by Tacke. He showed that the fulvene route is versatile enough to get a new series of polyazaligands **L55-a-f** (Scheme I-18).[39]



X = NCH$_2$NMe$_2$, Y = CH, Z = CH **a**
X = NMe, Y = CH, Z = N **b**
X = NMe, Y = NCH$_2$NMe$_2$, Z = NCH$_2$NMe$_2$ **c**
X = NMe, Y = N, Z = CH **d**
X = S, Y = CH, Z = N **e**
X = NCH$_2$NMe$_2$, Y = CH, Z = N **f**

Scheme I-18: examples of polyfunctionalized (aminomethyl)cyclopentadienides

The Hafner procedure was also used by Hierso, with a disubstituted CpLi **L56** in order to form **L57**,[40] which yielded the new P-N ligand **L58** after reduction. This is one example of polyfunctionalized ligand. A new library of ferrocenes was designed by using **L58** on iron. Various procedures for the polyfunctionalization of the Cp framework were investigated over

---

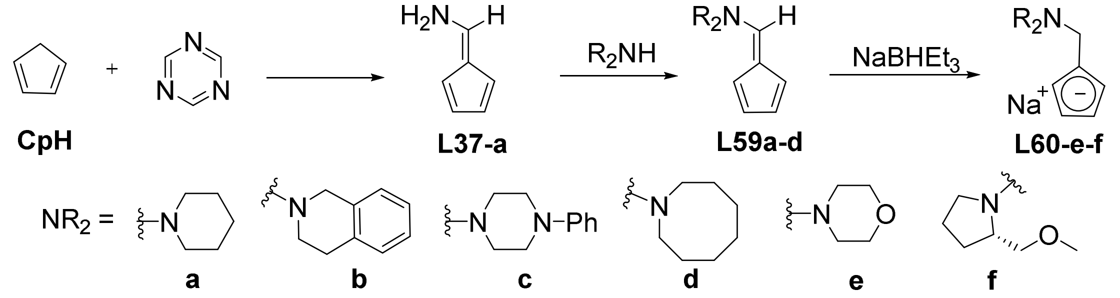
[39] (a): Hickey, T.; Claffey, J.; Fitzpatrick, E.; Hogan, M.; Pampillón, C.; Tacke, M. *Invest. New Drugs.* **2007**, *25*, 425, (b): Hogan, M.; Claffey, J.; Pampillón, C.; Watson, R. W. G.; Tacke, M. *Organometallics.* **2007**, *26*, 2501

[40] Allouch, F.; Dwadnia, N.; Vologdin, N. V.; Svyaschenko, Y. V.; Cattey, H.; Penouilh, M.-J.; Roger, J.; Naoufal, D.; Ben Salem, R.; Pirio, N.; Hierso, J.-C. *Organometallics.* **2015**, *34*, 5015

the years. Several examples could have been cited, would fall outside the scope of this dissertation.

c. Aminomethynylation of cyclopentadiene

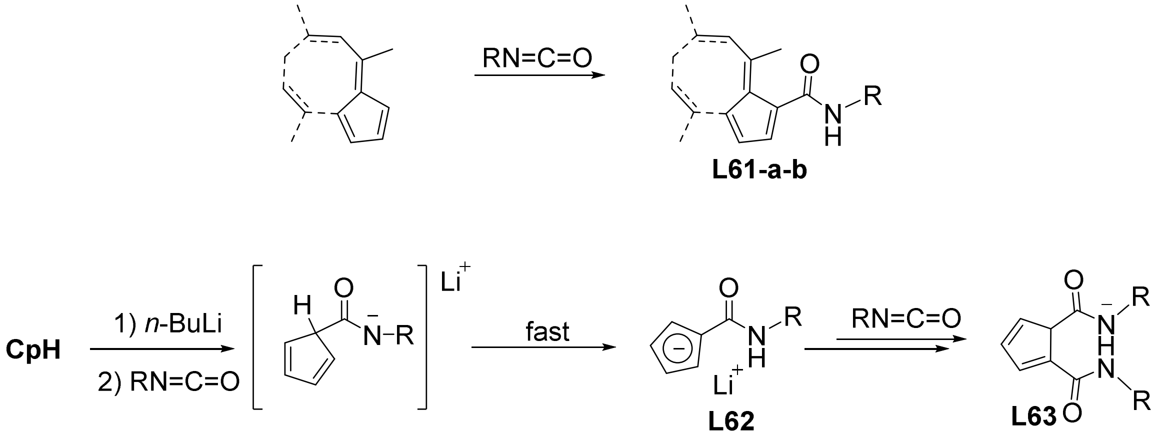
In 1986,[41] the aminomethynylation of CpH with 1-3-5-triazine was described by Kreutzberg, to form **L37-a** quantitatively. This compound was subsequently treated with cyclic secondary amines in order to form the corresponding 6-aminofulvene **L59-a-d** in moderate to good yield (28 to 72%). None of these cyclopentadienes was converted into an aminocyclopentadienide anion by Kreutzberg. Up to our knowledge, this procedure was used by only one group for ligand synthesis purpose: the 6-morpholinofulvene **L59-e** and a chiral 6-pyrrolidinofulvene **L59-f** were synthesized by Wirth by this manner; in higher yield than with Hafner's procedure.[42] The chiral ligand was used to form an enantiopure ruthenocene.



Scheme I-19: Kreutzberger synthesis

d. C-H activation of cyclopentadiene

In 1968, the potential of activated fulvenoid to undergo electrophilic aromatic substitution with isocyanates was shown by Effenberger, forming **L61-a-b** (Scheme I-20).[43]



Scheme I-20: reactivity of cyclopentadiene derivatives with isocyanates

---

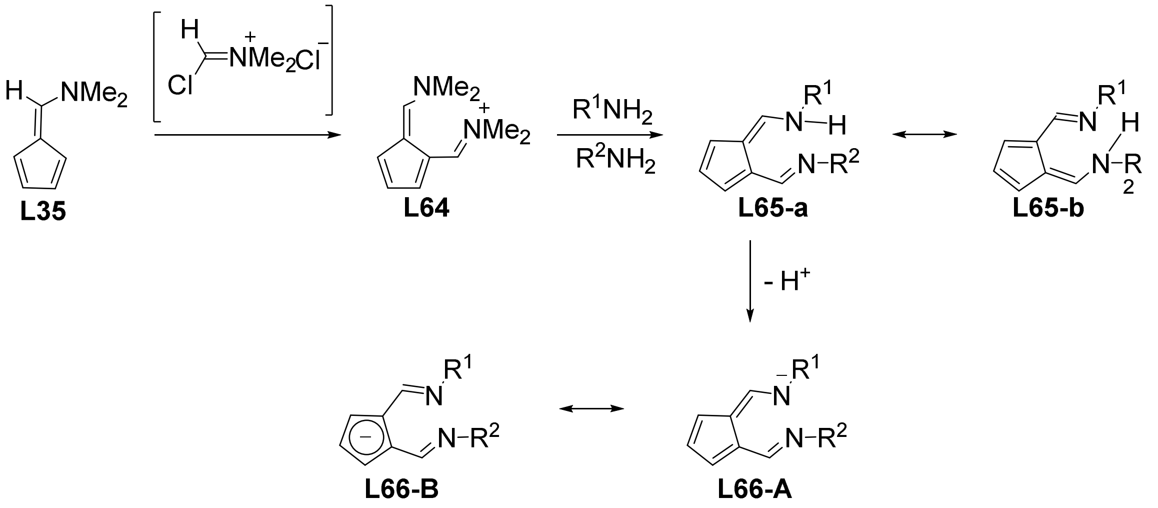
[41] Kreutzberger, A.; Kolter, K. *Liebigs Ann. Chem.* **1986**, 374

[42] Herberich, G. E.; Englert, U.; Wirth, T. *Eur. J. Inorg. Chem.* **2005**, 4924

[43] Effenberger, F.; Gleiter, R.; Heider, L.; Niess, R. *Chem. Ber.* **1968**, *101*, 502

This work was adapted by Erker to form new (aminomethyl)cyclopentadienides with a carbonyl function as a spacer.[44] The ligand **L62** formed by this manner was highly reactive towards the addition of another equivalent of isocyanate to form **L63**. Stoichiometry had to be carefully controlled to avoid or at least to limit the formation of **L63**.

Such kind of reactivity was also highlighted by Müller-Westerhoff in 1970,[45] with 6-dimethylaminofulvene **L35**. This compound reacted smoothly with Vilsmeier-type reagents to form intermediate **L64,** which yielded aldimine **L65** after further reaction with a primary amine (Scheme I-21).



Scheme I-21: first synthesis of aldimine from the work of Müller-Westerhoff

If two different amines were used to form aldimine by this procedure; and/or if the fulvene and the Vilsmeier complex were substituted, several isomers were observed (for example **L65-a** and **b**). According to Müller-Westerhoff, non-classical aromaticity in hydrogen-bonded systems was the course for this observation.[46a,b] After deprotonation of aldimines **L65**, these ligands can act as XL ligands under the form **L66-A** such as in copper,[47a,b] palladium or zinc complexes,[48] or as XL_2 ligands under the form **L66-B** in rarer cases.[49a,b]

In summary, four routes were found to synthesize (aminomethyl)cyclopentadienides based on the work of Thiele, Hafner, Kreutzberg and Effenberger. These ligands have been coordinated to several metal centres but only group 4 metallocenes will be described in the following part.

---

[44] Oberhoff, M.; Duda, L.; Karl, J.; Mohr, R.; Erker, G.; Fröhlich, R.; Grehl, M. *Organometallics.* **1996**, *15*, 4005

[45] Mueller-Westerhoff, U. *J. Am. Chem. Soc.* **1970**, *92*, 4849

[46] (a): Pietrzak, M.; Limbach, H.-H.; Pérez-Torralba, M.; Sanz, D.; Claramunt, R. M.; Elguero, J. *Magn. Reson. Chem.* **2001**, *39*, S100, (b): Perrin, C. L.; Ohta, B. K. *Bioorganic Chem.* **2002**, *30*, 3

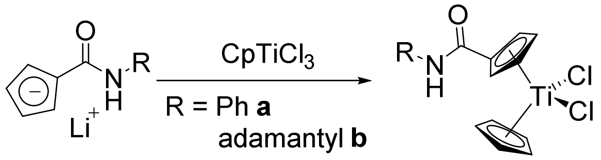
[47] (a): L. Johnson, A.; M. Willcocks, A.; R. Raithby, P.; R. Warren, M.; J. Kingsley, A.; Odedra, R. *Dalton Trans.* **2009**, 922, (b): Willcocks, A. M.; Gilbank, A.; Richards, S. P.; Brayshaw, S. K.; Kingsley, A. J.; Odedra, R.; Johnson, A. L. *Inorg. Chem.* **2011**, *50*, 937

[48] Bailey, P. J.; Collins, A.; Haack, P.; Parsons, S.; Rahman, M.; Smith, D.; White, F. J. *Dalton Trans.* **2010**, *39*, 1591

[49] (a): Willcocks, A. M.; Gilbank, A.; Richards, S. P.; Brayshaw, S. K.; Kingsley, A. J.; Odedra, R.; Johnson, A. L. *Inorg. Chem.* **2011**, *50*, 937, (b): Bailey, P. J.; Loroño-González, D.; Parsons, S. *Chem. Commun.* **2003**, 1426

2. Coordination to titanium, zirconium and hafnium

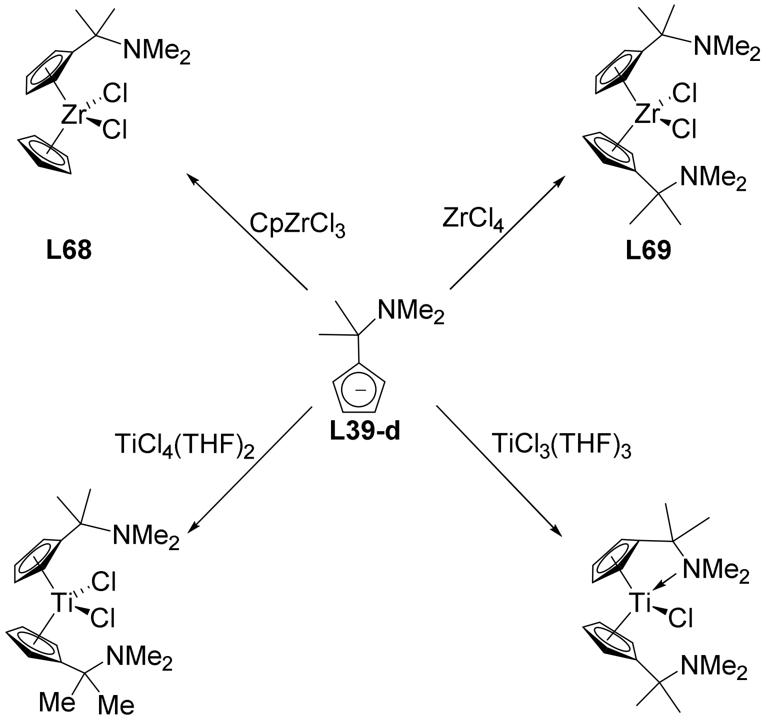
Some of the ligands described above were developed for constrained geometry complexes (e.g **L29** in Scheme I-10). Nevertheless, these complexes have already been reviewed elsewhere,[50,51] and will not be discussed in this section which will be therefore be limited to metallocenic or half-metallocenic fragments. In 1996, the synthesis of the first carboxamido titanocenes **L67-a-b** was described by Erker,[44] in which no coordination of the carboxamido moiety was observed to the titanium centre in the solid state (Scheme I-22).



L62 **L67-a-b**

Scheme I-22: synthesis of the first carboxamidotitanocenes

Between 1997 and 2003,[33,52] the ligand **L39-d** was used for the synthesis of new (aminomethyl)metallocenes (**L68**) or bis(aminomethyl)metallocenes (**L69-L71**).



Scheme I-23: coordination of L39-d to Ti and Zr

---

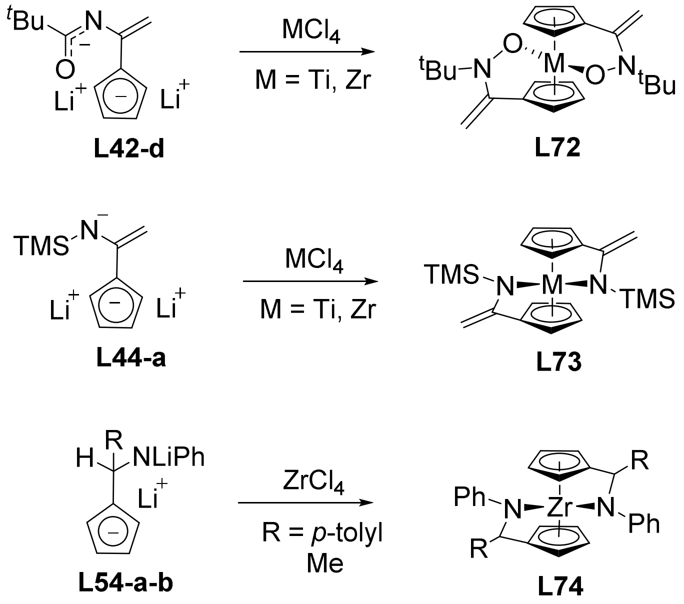
[50] Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691

[51] Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem. Int. Ed.* **1999**, *38*, 428

[52] Pflug, J.; Bertuleit, A.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics*. **1999**, *18*, 3818

The d^1- titanocene **L71** was the only example of this series exhibiting N coordination to the metal centre with a 2.420(2) Å Ti-N bond. [53] All complexes adopted a bent geometry in the solid state.

Another series of “spiro-metals” was also described by Erker (**L72**-**L74**),[25,34a,b] using dilithium (amido)cyclopentadienides **L42-d**, **L44-a** and **L54-a-b** (Scheme I-24).



Scheme I-24: synthesis of "spiro-metallocenes"

On the other hand, an interesting reaction based on bis(aminomethyl)metallocenes obtained from **L49** was fortuitously discovered at the same time by Zhou and Erker (Scheme I-25).[36,54] Depending on the reaction conditions, the expected bis(aminomethyl)metallocene **L75** was isolated (0°C, 1h stirring), and more surprisingly **L76** was finally formed after prolonged stirring of 12h at room temperature. The formation of this compound was based on an acid-catalysed Mannich-type reaction. This rearrangement was observed on various metals and even with several amines that are not depicted in this section for clarity.[55] In the case of NEt_2, the rearrangement needed several days to be completed in solution, and several weeks when the compound was stored as a solid.[32] These compounds underwent photochemical enamine [2+2] cycloaddition after irradiation.[56]

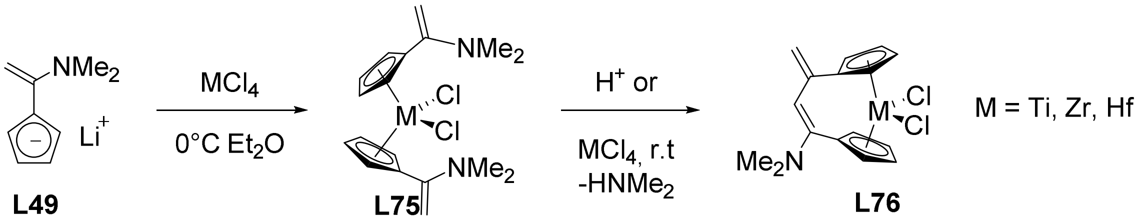
---

[53] Kotov, V. V.; Fröhlich, R.; Kehr, G.; Erker, G. *J. Organomet. Chem.* **2003**, *676*, 1

[54] Bai, S.-D.; Wei, X.-H.; Guo, J.-P.; Liu, D.-S.; Zhou, Z.-Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 1926

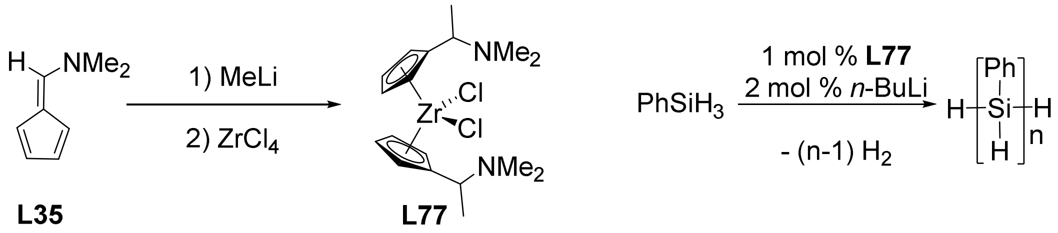
[55] Knüppel, S.; Wang, C.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Organomet. Chem.* **2005**, *690*, 14

[56] Tumay, T. A.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics.* **2009**, *28*, 4513



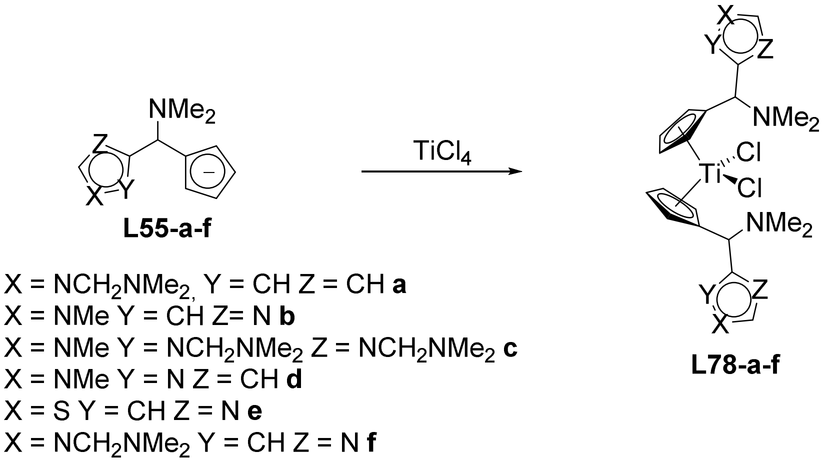
Scheme I-25: an acid-catalysed Mannich-type reaction on group 4 (aminomethyl)metallocenes

In 2002, Corey used a bis(aminomethyl)zirconocene for the dehydropolymerization of phenylsilane, and discovered a radical-based dehydrocoupling mechanism (Scheme I-26).[57]



Scheme I-26: dehydropolymerization of phenylsilane with a bis(aminomethyl)zirconocene

Since Cp_2TiCl_2 was shown to have good cytotoxicity towards cancers cells, many functionalized derivatives have been synthesized as new antitumor drug candidates. In 2007, new (aminomethyl)titanocenes **L78-a-f** were designed by Tacke (Scheme I-27). No coordination of nitrogen to the titanium centre was observed in the solid state.[39,58a,b,c,d,e,f]



X = NCH_2NMe_2, Y = CH Z = CH **a**
X = NMe Y = CH Z= N **b**
X = NMe Y = NCH_2NMe_2 Z = NCH_2NMe_2 **c**
X = NMe Y = N Z = CH **d**
X = S Y = CH Z = N **e**
X = NCH_2NMe_2 Y = CH Z = N **f**

Scheme I-27: (aminomethyl)titanocenes from Tacke's work

An interesting Bis(iminomethyl)zirconocene **L80** was synthesized in 2009 by treating the new 6-aminofulvene **L79** with $Cl_2Zr(NMe_2)_2THF_2$.[59] When **L80** was mixed with the Lewis acid

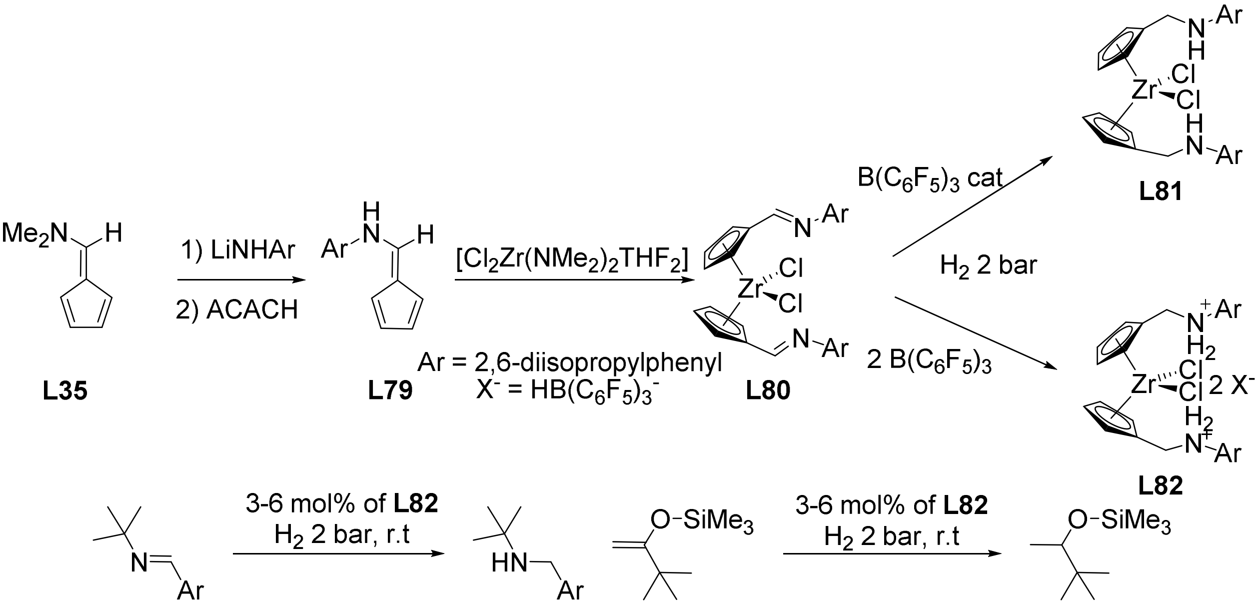
---

[57] Grimmond, B. J.; Corey, J. Y. *Inorganica Chim. Acta*. **2002**, *330*, 89

[58] (a): Hogan, M.; Cotter, J.; Claffey, J.; Gleeson, B.; Wallis, D.; O'Shea, D.; Tacke, M. *Helv. Chim. Acta*. **2008**, *91*, 1787, (b): Pampillón, C.; Claffey, J.; Strohfeldt, K.; Tacke, M. *Eur. J. Med. Chem.* **2008**, *43*, 122, (c): Pampillón, C.; Claffey, J.; Hogan, M.; Tacke, M. *BioMetals*. **2008**, *21*, 197, (d): Weber, H.; Claffey, J.; Hogan, M.; Pampillón, C.; Tacke, M. *Toxicol. In Vitro*. **2008**, *22*, 531, (e): Olszewski, U.; Claffey, J.; Hogan, M.; Tacke, M.; Zeillinger, R.; Bednarski, P. J.; Hamilton, G. *Invest. New Drugs*. **2010**, *29*, 607, (f): Cuffe, S.; Dowling, C. M.; Claffey, J.; Pampillón, C.; Hogan, M.; Fitzpatrick, J. M.; Carty, M. P.; Tacke, M.; Watson, R. W. G. *The Prostate*. **2011**, *71*, 111

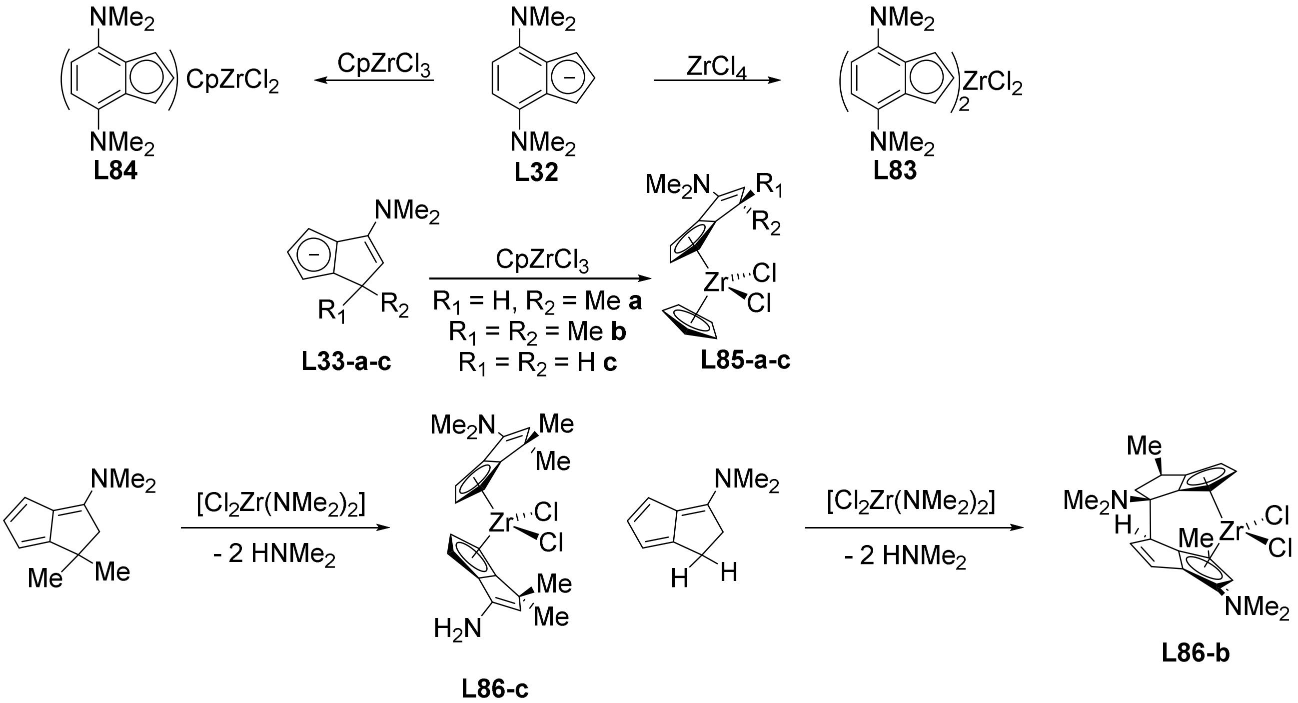
[59] Axenov, K. V.; Kehr, G.; Fröhlich, R.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 3454, *Organometallics*. **2009**, *28*, 5148

$B(C_6F_5)_3$ and dihydrogen, hydrogenation of the enamine occurred to form the bis(aminomethyl)zirconocene **L81**. The bis(ammoniummethyl)zirconocene **L82** can even be obtained by addition of two equivalents of $B(C_6F_5)_3$ were added (Scheme I-28). This complex was used for hydrogenation of imines and silyl enol ethers (2 bar of H_2, room temperature). This study shows an example of a frustrated Lewis pairs, a concept developed further in this introduction.



Scheme I-28: a new antagonist N/B Lewis pair for hydrogenation of imine and silyl enol ether

The two bicyclic ligands **L32** and **L33-a-c**, obtained by a fulvene route described in Scheme I-13, were also coordinated to Zirconium by using $ZrCl_4$ or $CpZrCl_3$, forming the corresponding bis(4,7-dimethylamino)indenylzirconocene **L83**, and the zirconocenes **L84** and **L85-a-c** (Scheme I-29).[26] The neutral form of **L33-c** was treated with $Cl_2Zr(NMe_2)_2$ to yield the expected zirconocene **L86-c**. In the case of $R_1 = R_2 = H$, carbon-carbon bond formation yielded the ansazirconocene **L86-b**. In the case of **L33-a** a mixture of three compounds was formed.[27]



Scheme I-29: synthesis of polycyclic zirconocenes

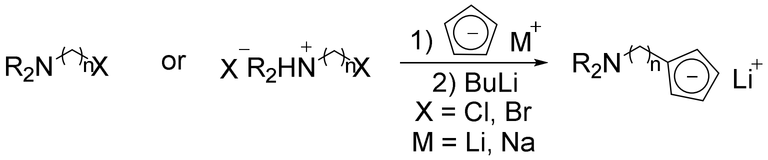
To resume this part, coordination of (aminomethyl)cyclopentadienides on group 4 metals is possible and yield stable functionalized metallocenes. Noteworthy, numerous unexpected reactions were observed during the formation of these metallocenes.

C. (Aminoalkyl)cyclopentadienides

In the following part, an overview of the synthesis of cyclopentadienides bearing an amino function with a hydrocarbon spacer longer than one atom is described. Their coordination to group 4 metallocenes will be discussed too. This section would include numerous examples, but the list will be limited to some examples in order to best illustrate the field of possibilities.

1. Synthesis

The main route used in the literature is based on the nucleophilic substitution of halogenoalkylamines (or their ammonium salt form) by CpNa or CpLi, first described by Wang in 1991.[60]

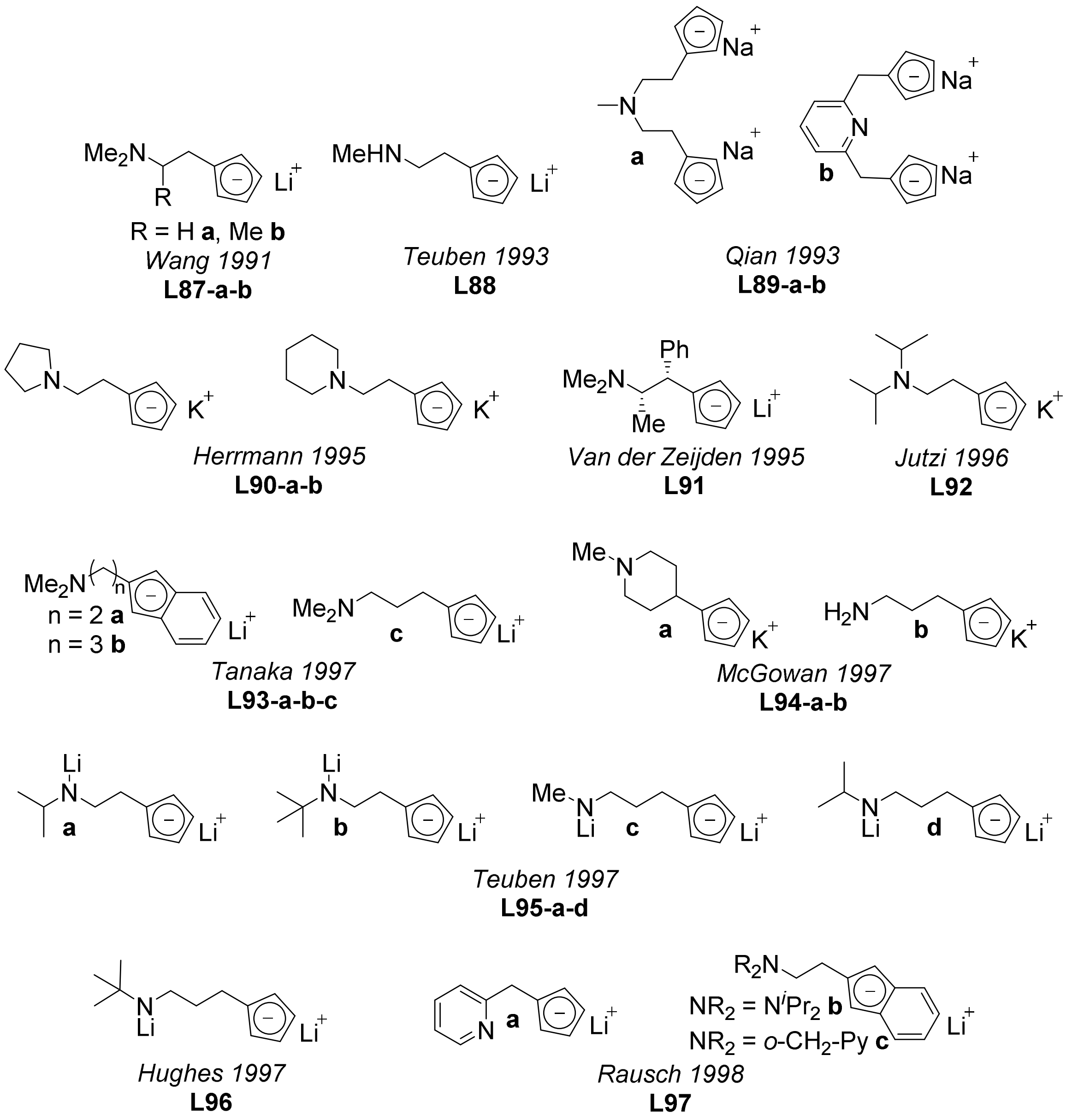


Scheme I-30: general procedure for the synthesis of (aminoalkyl)cyclopentadienides

---

[60] (a): Wang, T.-F.; Lee, T.-Y.; We, Y.-S.; Liou, L.-K. *J. Organomet. Chem.* **1991**, *403*, 353, (b): Tein-Fu, W.; Tsung-Yi, L.; Jim-Wen, C.; Chi-Wi, O. *J. Organomet. Chem.* **1992**, *423*, 31

The limitation of this reaction is the starting amine, which is not commercially available in most of the cases. The scope of this reaction is summarized in Scheme I-31 (compounds **L87-a-b-L97**).[61,62,63,64a,b,65,66,67,68,69,70]



Scheme I-31: Aminoligand synthesized over the years following Wang's synthesis

---

[61] Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics.* **1993**, *12*, 1936

[62] Qian, C.; Guo, J.; Ye, C.; Sun, J.; Zheng, P. *J Chem Soc Dalton Trans.* **1993**, 22, 3441

[63] Herrmann, W. A.; Morawietz, M. J. A.; Priermeier, T.; Mashima, K. *J. Organomet. Chem.* **1995**, *486*, 291

[64] (a): van der Zeijden, A. A. H. *Tetrahedron Asymmetry.* **1995**, *6*, 913, (b): *J. Organomet. Chem.* **1996**, *518*, 147

[65] Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *Organometallics.* **1996**, *15*, 4153

[66] Choi, N.; Onozawa, S.; Sakakura, T.; Tanaka, M. *Organometallics.* **1997**, *16*, 2765

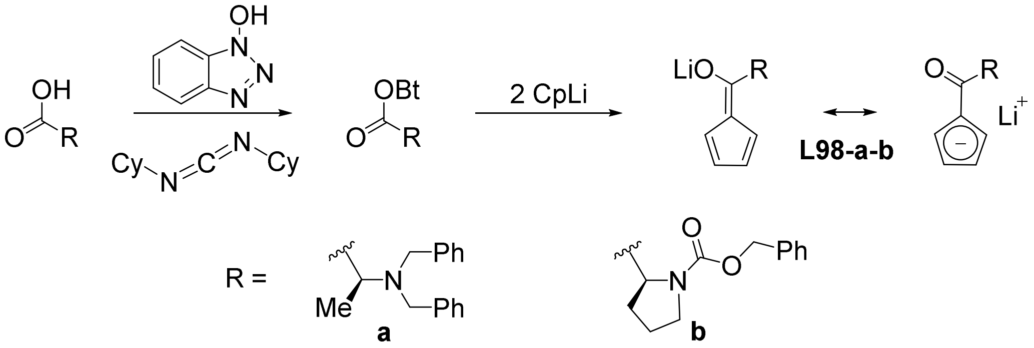
[67] McGowan, P. C.; Hart, C. E.; Donnadieu, B.; Poilblanc, R. *J. Organomet. Chem.* **1997**, *528*, 191

[68] Sinnema, P.-J.; van der Veen, L.; Spek, A. L.; Veldman, N.; Teuben, J. H. *Organometallics.* **1997**, *16*, 4245

[69] Hughes, A. K.; Marsh, S. M. B.; Howard, J. A. K.; Ford, P. S. *J. Organomet. Chem.* **1997**, *528*, 195

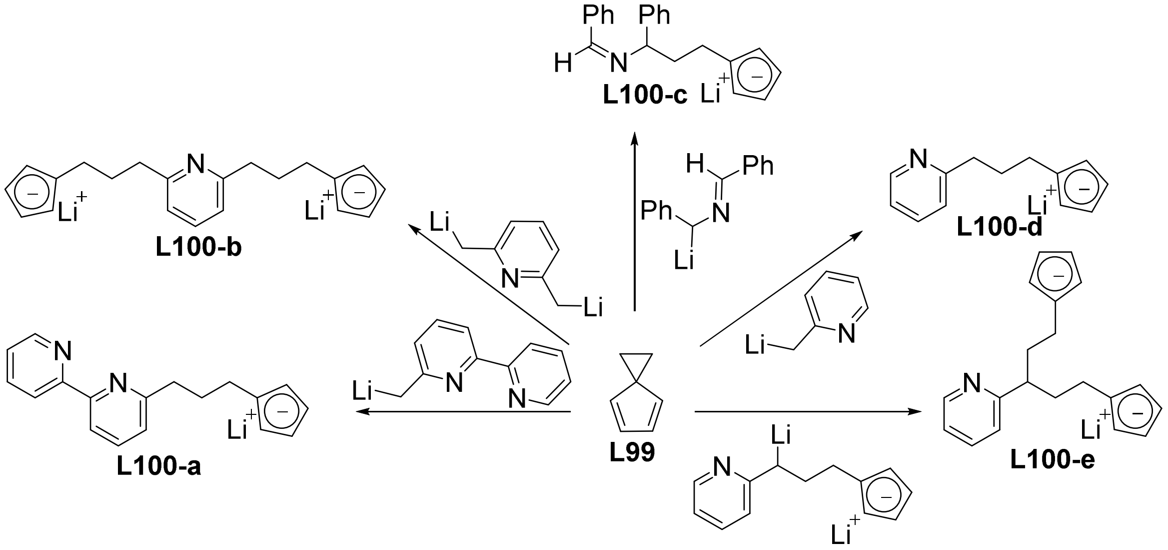
[70] Blais, M. S.; Chien, J. C.; Rausch, M. D. *Organometallics.* **1998**, *17*, 3775

This method is very convenient, and has been used for a wide range of amines as illustrated above. In 2001, a similar procedure was described by using activated carboxylic acids instead of chloroamines, in order to incorporate amino acids on metallocenes (Compound **L98-a-b** Scheme I-32).[71]



Scheme I-32: synthesis of amino-acid-based cyclopentadienides

An alternative route was described earlier in 1980 by Woltermann based on the use of spirane derivatives such as spiro[2.4]hepta-4-6-diene **L99**.[72,73] The treatment of this compound with a nucleophile yielded various (aminoalkyl)cyclopentadienides **L100-a-e** (Scheme I-33). The requirement for this synthesis was to synthesize the appropriate spirane derivative depending on the spacer required.

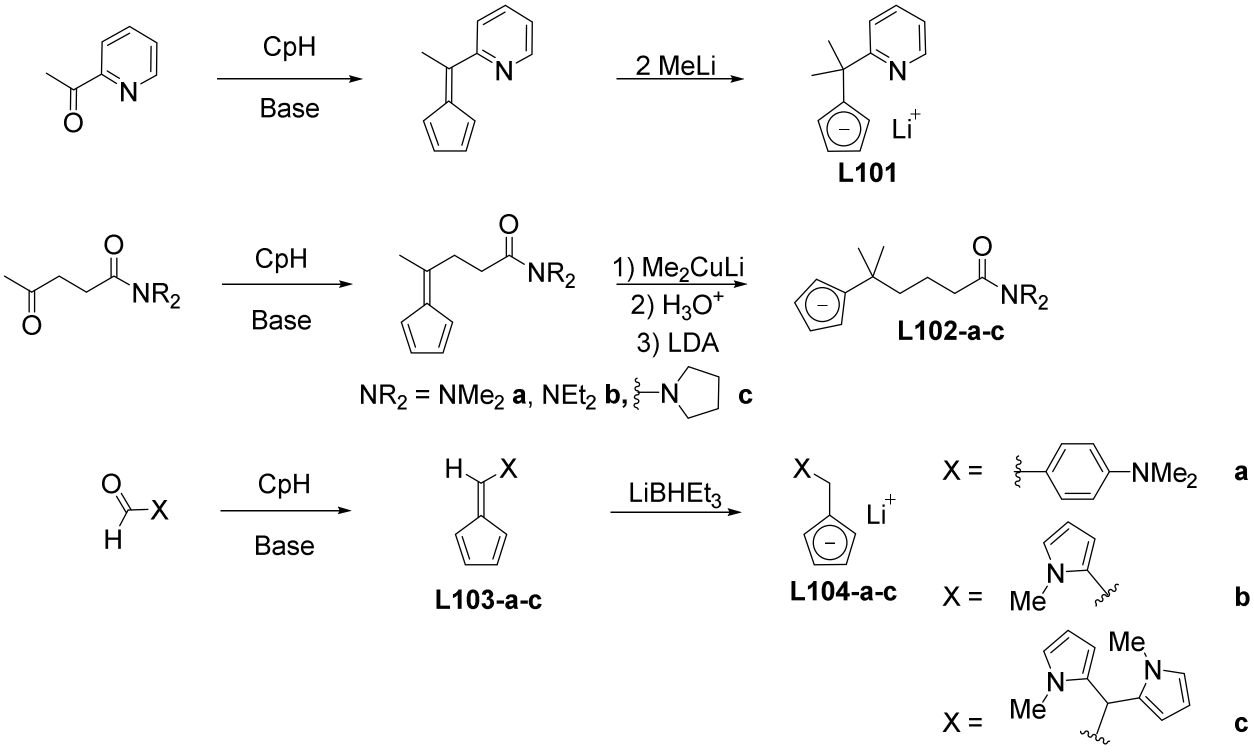


Scheme I-33: synthesis of (aminoalkyl)cyclopentadienides via the spirane route

---

[71] Kunz, D.; Fröhlich, R.; Erker, G. *Organometallics.* **2001**, *20*, 572
[72] Kauffmann, T.; Ennen, J.; Lhotak, H.; Rensing, A.; Steinseifer, F.; Woltermann, A. *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 328
[73] Wilcox, C. F.; Craig, R. R. *J. Am. Chem. Soc.* **1961**, *83*, 3866

The last synthesis found is based on the use of the already described procedure of Thiele: the condensation of CpH with a carbonylated amine. Three examples are depicted in Scheme I-34 with the synthesis of **L101**, **L102-a-c** and **L104-a-c**.[74,75a,b,c]



Scheme I-34: (aminoalkyl)cyclopentadienides synthesized via the synthesis of Thiele

Very recently, Lamač used 6,6-dimethylfulvene to synthesize new nitrile- and ketimide - containing ligands. Their synthesis is resumed in Scheme I-35.[76,77] The straightforward procedure started with the deprotonation of acetonitrile (or dimethylacetonitrile) followed by nucleophilic attack of the electrophilic carbon (C_6) of dimethylfulvene forming **L105** (**L106**).

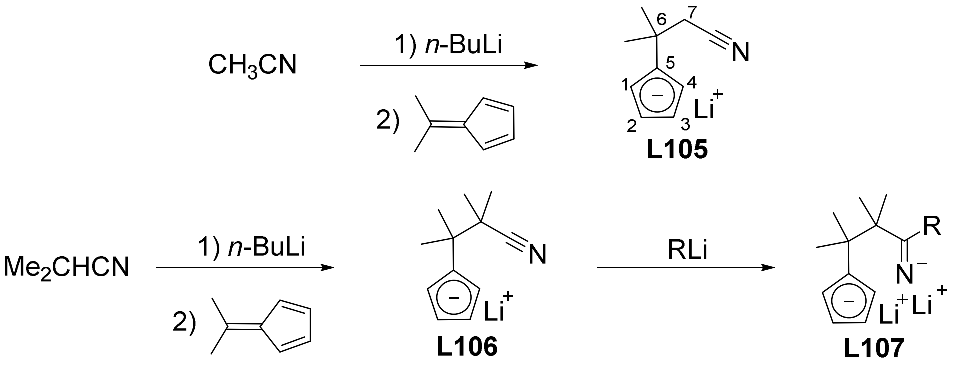
---

[74] Clark, T. J.; Nile, T. A.; McPhail, D.; McPhail, A. T. *Polyhedron.* **1989**, *8*, 1804

[75] (a): Tacke, M.; Allen, L. T.; Cuffe, L.; Gallagher, W. M.; Lou, Y.; Mendoza, O.; Müller-Bunz, H.; Rehmann, F.-J. K.; Sweeney, N. *J. Organomet. Chem.* **2004**, *689*, 2242, (b): Rehmann, F.-J. K.; Cuffe, L. P.; Mendoza, O.; Rai, D. K.; Sweeney, N.; Strohfeldt, K.; Gallagher, W. M.; Tacke, M. *Appl. Organomet. Chem.* **2005**, *19*, 293, (c): Sweeney, N. J.; Mendoza, O.; Müller-Bunz, H.; Pampillón, C.; Rehmann, F.-J. K.; Strohfeldt, K.; Tacke, M. *J. Organomet. Chem.* **2005**, *690*, 4537

[76] Pinkas, J.; Gyepes, R.; Kubišta, J.; Horáček, M.; Lamač, M. *J. Organomet. Chem.* **2011**, *696*, 2364

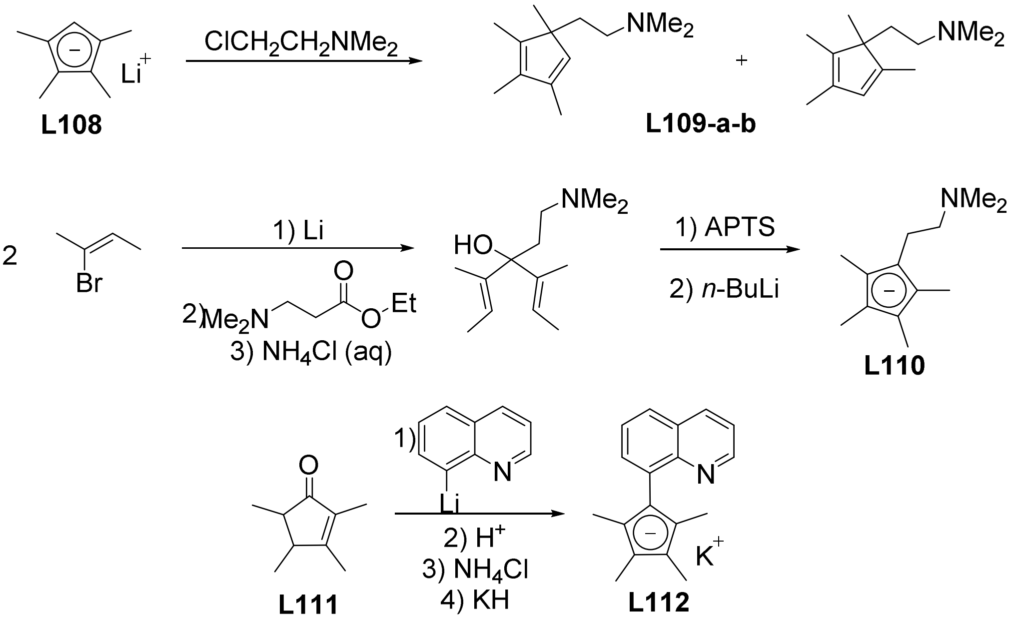
[77] Večeřa, M.; Varga, V.; Císařová, I.; Pinkas, J.; Kucharczyk, P.; Sedlařík, V.; Lamač, M. *Organometallics.* **2016**, *35*, 785



Scheme I-35: synthesis of nitrile-based and ketimide-based cyclopentadienides

Nucleophilic attack of the nitrile group on **L106** afforded new ketimide-based ligand **L107-a-c** depending on the nature of the alkyllithium used. The corresponding reaction on **L105** was tried but nucleophilic attack was shown to compete with deprotonation of C_7.

All syntheses described above were built on an unsubstituted cyclopentadiene. To incorporate substituents on the Cp moiety, depending on the nature of the ligand desired, the synthesis would be rather difficult to implement. As illustrated by Jutzi in 1993,[78] the synthesis of the tetramethylated (aminoethyl)cyclopentadienide **L110**, was not possible via the Wang route starting from **L108**. Indeed, a mixture of **L109-a** and **L109-b** was obtained with no desired methylated cyclopentadiene. The amino chain had to be introduced prior to the formation of the Cp ring to form **L110** (Scheme I-36). An alternative route was found by Enders in 1996, by reacting a lithium derivative with the 2,3,4,5-tetramethylcyclopent-2-ene-3-one **L111** in order to form **L112** (Scheme I-36).[79]



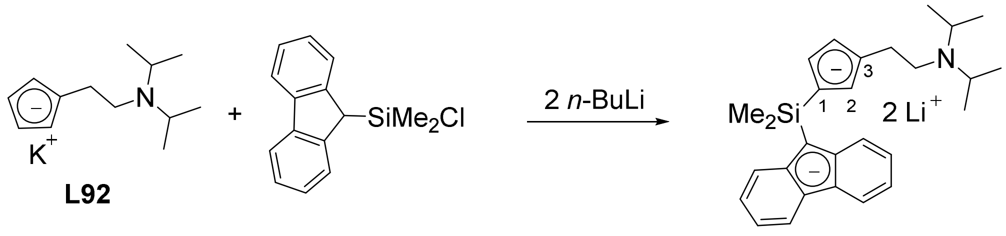
Scheme I-36: synthetic route for permethylated (aminoalkyl)cyclopentadienides

---

[78] Jutzi, P.; Dahlhaus, J. *Synthesis.* **1993** 684

[79] Enders, M.; Rudolph, R.; Pritzkow, H. *Chem. Ber.* **1996**, *129*, 459

Finally, it has to be noted that these ligands can be reacted with chlorosilane to form silylated Cp rings. In Scheme I-37, Jutzi described the synthesis of an ansa-ligand by using **L92,** with the appropriate chlorosilane to form **L113** regioselectively.[80] It is worth noting that several regioisomers could have been obtained (1-2 or 1-3 substitution).



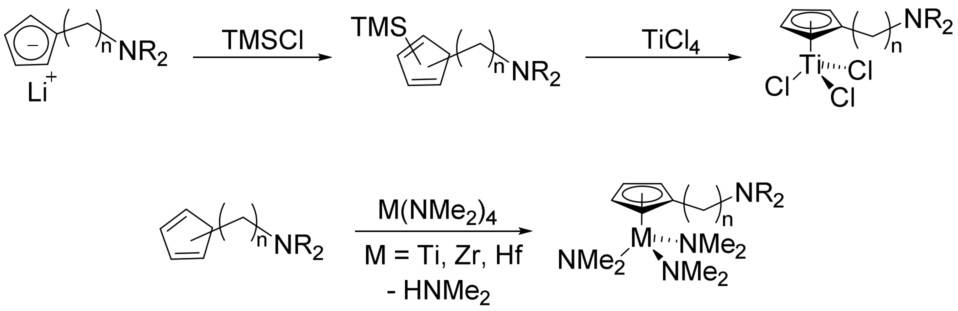
L92

L113

Scheme I-37: synthesis of an ansa precursor

2. Coordination to titanium, zirconium and hafnium

The use of TMSCl to silylate Cp rings has been exploited to form piano stool Ti(IV) (and more rarely zirconium and hafnium) complexes. The other route to synthesize piano stool group 4 metallocenes, was based on the work of Lappert and the protonolysis of $M(NMe_2)_4$ precursors (M= Ti, Zr, Hf - Scheme I-38).[81]



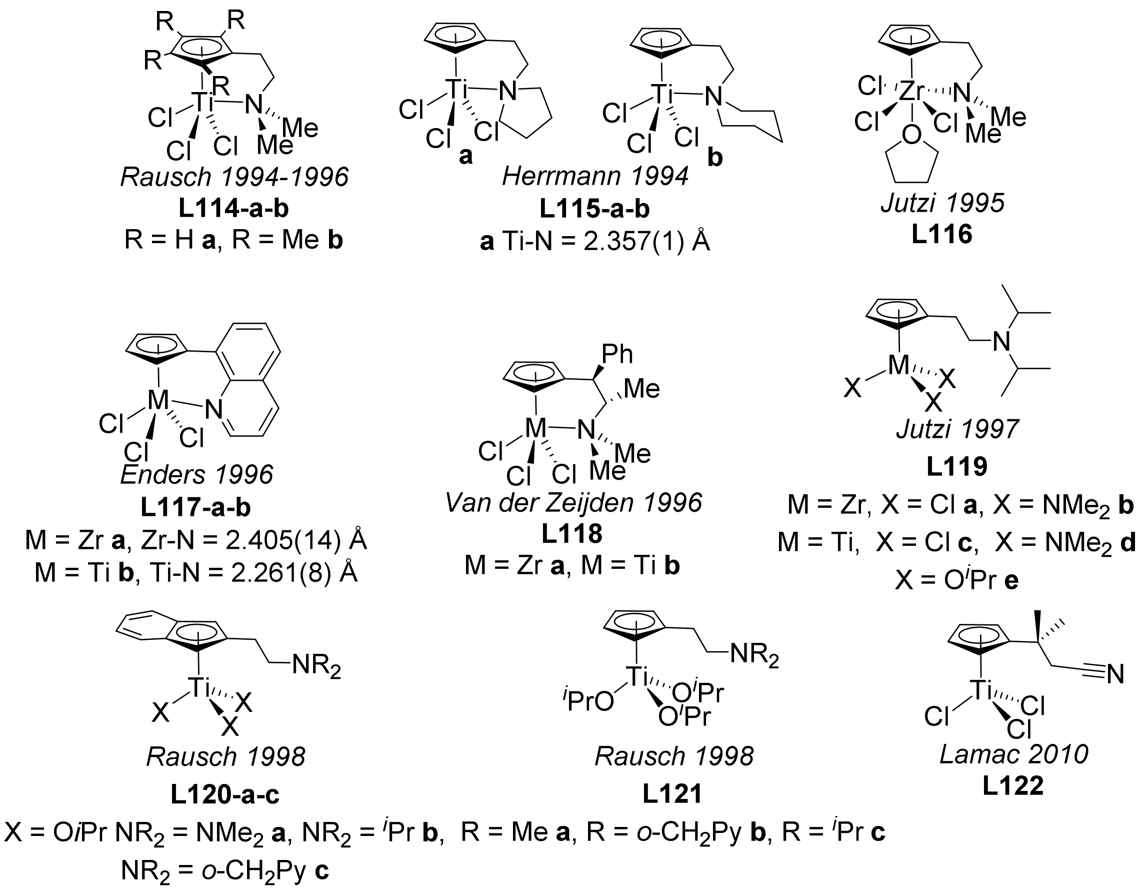
Scheme I-38: synthesis of piano stool group 4 complexes

Depending on the nature of the reaction, trichloro (e.g. **L114-118**) or tris(dimethylamino) complexes (**L119-b-d** and **L120**) were described in the following Scheme I-39.

---

[80] Müller, C.; Jutzi, P. *Synthesis.* **2000**, 389

[81] Chandra, G.; Lappert, M. F. *J. Chem. Soc. Inorg. Phys. Theor.* **1968**, 1940



Rausch 1994-1996
L114-a-b
R = H **a**, R = Me **b**

Herrmann 1994
L115-a-b
a Ti-N = 2.357(1) Å

Jutzi 1995
L116

Enders 1996
L117-a-b
M = Zr **a**, Zr-N = 2.405(14) Å
M = Ti **b**, Ti-N = 2.261(8) Å

Van der Zeijden 1996
L118
M = Zr **a**, M = Ti **b**

Jutzi 1997
L119
M = Zr, X = Cl **a**, X = NMe_2 **b**
M = Ti, X = Cl **c**, X = NMe_2 **d**
X = O^{i}Pr **e**

Rausch 1998
L120-a-c
X = O*i*Pr NR_2 = NMe_2 **a**, NR_2 = ^{i}Pr **b**,
NR_2 = *o*-CH_2Py **c**

Rausch 1998
L121
R = Me **a**, R = *o*-CH_2Py **b**, R = ^{i}Pr **c**

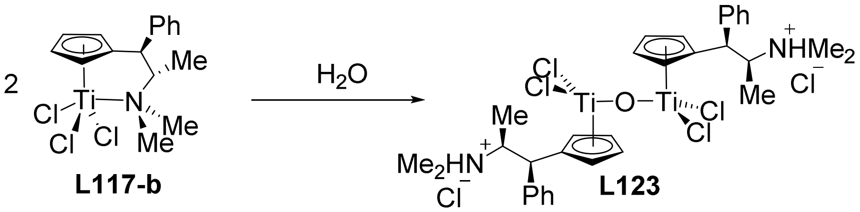
Lamac 2010
L122

Scheme I-39: overview of group 4 piano stool complexes with an amino-functionalized ligand

In most of these complexes, coordination of the amine is observed to the metal centre.[82] This was experimentally determined by NMR (^{1}H NMR signal of the CH_2 spacer group downfield compared to the free ligand) and / or by X-ray diffraction.[83a,b] The M-N bond length is specified if available.[63,77,79] The first complex exhibiting no M-N bond was described by Jutzi (**L119**), due to the steric hindrance of the amine; instead, coordination polymer formation was assumed by the authors.[84] The same observation was made by Rausch on compounds **L120-121**. This characteristic was assumed to be due to the presence of NMe_2 and isopropoxy ligands on titanium. These ligands were supposed to prevent coordination of the amino by a combination of steric hinderance and enhanced electron donation to the metal. Low purity of such kind of complexes was also observed and attributed to moisture sensitiveness. This was supposed to be directly connected to the non-coordinated pendant amine, which might act as a Brønsted base on water. Several μ-oxo complexes were obtained and characterized in this series. One example from the work of Van der Zeijden is depicted in Scheme I-40.[85]

---

[82] Jutzi, P.; Kleimeier, J. *J. Organomet. Chem.* **1995**, *486*, 287
[83] (a): Flores, J. C.; Chien, J. C. W.; Rausch, M. D. *Organometallics.* **1994**, *13*, 4140,(b): *Macromolecules.* **1996**, *29*, 8030
[84] Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **1997**, *533*, 237
[85] van der Zeijden, A. A. H. *J. Organomet. Chem.* **1996**, *518*, 147



Scheme I-40: hydrolysis product of a piano stool titanium complex

Most of the complexes described in Scheme I-39, were active in Ziegler Natta polymerization of alkenes. They have been widely studied due to the potential additional stabilization brought by the coordinating arm during catalysis. Numerous half sandwich complexes have been synthesized for this end, and based on other metals than those from group 4.

After describing half-sandwich complexes, the following section will develop the synthesis of some group 4 metallocenes. Some of the cyclopentadienides described previously on the synthesis of half-sandwich complexes have also been used for this purpose. Due to their tendency to form coordination polymers, and their moisture sensitivity, some of them were isolated as their hydrochloric salts: a large number of these complexes were tested as anticancer agents by the group of Tacke, [75a,b,c,86,87] McGowan,[88a,b,c,d] or Baird (**L132-133-L136-137**).[89a,b,c],[90] An overview of this type of metallocenes is depicted in Scheme I-41.

---

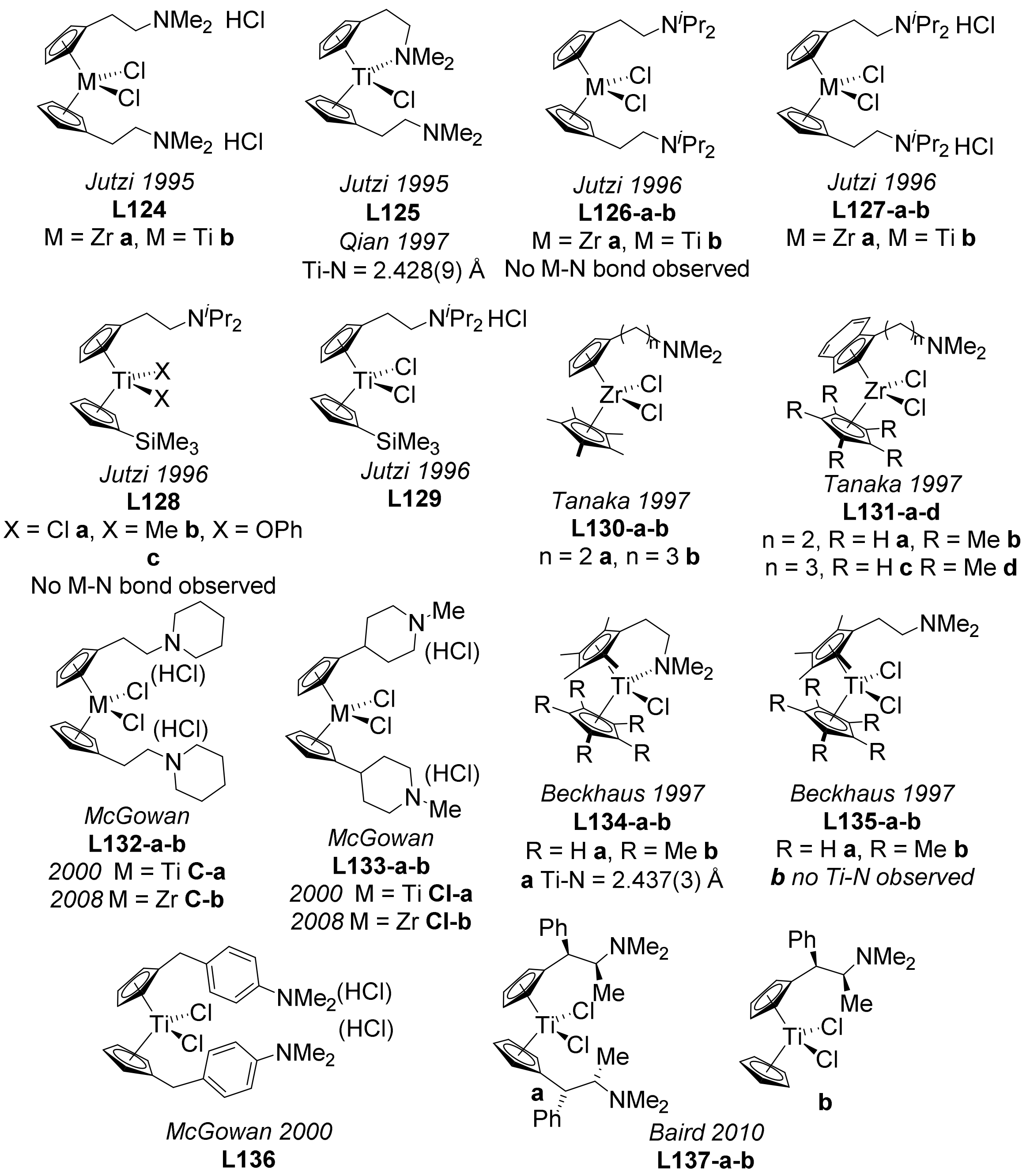
[86] Abeysinghe, P. M.; Harding, M. M. *Dalton Trans.* **2007**,32, 3474

[87] Deally, A.; Hackenberg, F.; Lally, G.; Tacke, M. *Int. J. Med. Chem.* **2012**, 2012, 1–13

[88] (a): Keinan, E.Novel Metallocenes as Anti-Tumor Drugs. WO9404142 (A1), March 3, 1994, McGowan, M. A. D.; McGowan, P. C. *Inorg. Chem. Commun.* **2000**, *3*, 337, Allen, O. R.; Croll, L.; Gott, A. L.; Knox, R. J.; McGowan, P. C. *Organometallics.* **2004**, *23*, 288, Allen, O. R.; Knox, R. J.; McGowan, P. C. *Dalton Trans.* **2008**,39, 5293

[89] (a): Causey, P. W.; Baird, M. C.; Cole, S. P. C. *Organometallics.* **2004**, *23*, 4486, (b): Potter, G. D.; Baird, M. C.; Chan, M.; Cole, S. P. C. *Inorg. Chem. Commun.* **2006**, *9*, 1114, (c): Potter, G. D.; Baird, M. C.; Cole, S. P. C. *Inorganica Chim. Acta.* **2010**, *364*, 16

[90] Hitchcock, P. B.; Leigh, G. J.; Togrou, M. *J. Organomet. Chem.* **2003**, *669*, 101



Scheme I-41: screening of various (aminoalkyl)metallocenes of group 4

Early work on metallocenes (IV), by Jutzi and Beckhaus, enabled a better comprehension of the coordination sphere of these metals in the solid state or in solution.[65,91,92,93,94,95] Usually, NMe_2 arms (e.g. in complex **L125**) were used to coordinate in an intra- or intermolecular mode, unless the steric bulk around the metal centre was too important.[93] As soon as the amino arm is hindered (e.g. in **L126** and **L128**),[65,92] no more

---

[91] Jutzi, P.; Dahlhaus, J. *Coord. Chem. Rev.* **1994**, *137*, 179

[92] Jutzi, P.; Kleimeier, J. *J. Organomet. Chem.* **1995**, *486*, 287

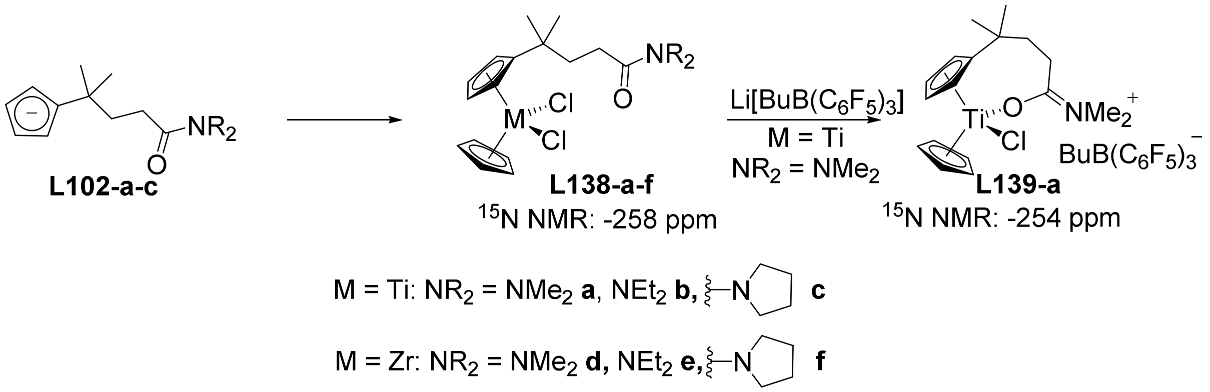
[93] Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175

[94] Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *Chem. Ber.* **1996**, *129*, 1509

[95] Beckhaus, R.; Oster, J.; Ganter, B.; Englert, U. *Organometallics.* **1997**, *16*, 3902

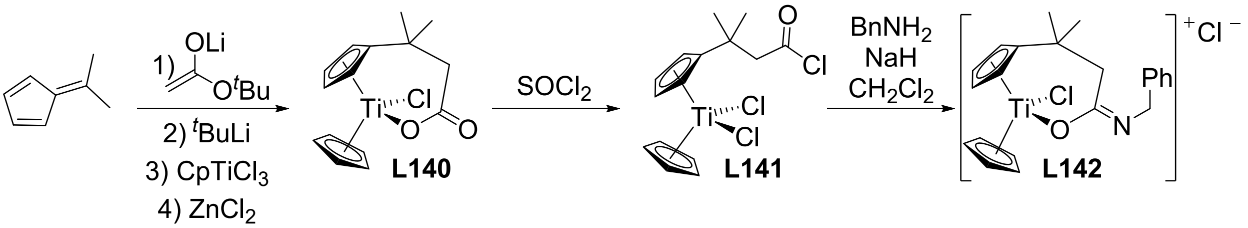
intramolecular coordination was observed. Nevertheless, the synthesis of the Ti(III) analogues (**L125** and **L134-a-b**),[96,93] proved the intramolecular coordination potential of this framework in the solid state (2.428(9) Å < Ti-N <2.437(3) Å), even with bulky amines; as soon as the metal presents a vacant coordination site. Whereas protonated metallocenes were tested as anticancer metallodrugs, their deprotonated analogues showed good activities in alkene or phenylsilane polymerizations.[97,65]

Carboxamide group 4 metallocenes showed no interaction between the amide part and the electrophilic metal centre, as described by Erker in 2002 (Scheme I-42).[98] Abstraction of a chloride from the corresponding titanocene yielded the formation of a cationic species in which oxygen from the amido function was coordinated to titanium.



Scheme I-42: carboxamide group 4 metallocenes synthesized by Erker

Complex **L139-a** is similar to the Gansäuer complexes of type **L142** but their synthesis and behaviour are quite different. Indeed, a post functionalization of titanocenes was achieved by Gansäuer, via a modular synthesis.[99] This reaction is depicted in Scheme I-43. Titanocenyl acyl chloride **L141** was first formed and reacted with an amine in the presence of NaH to form compound **L142**. This is a rare example of post functionalization of group 4 metallocenes, which is more common in group 8 metal chemistry.[100]



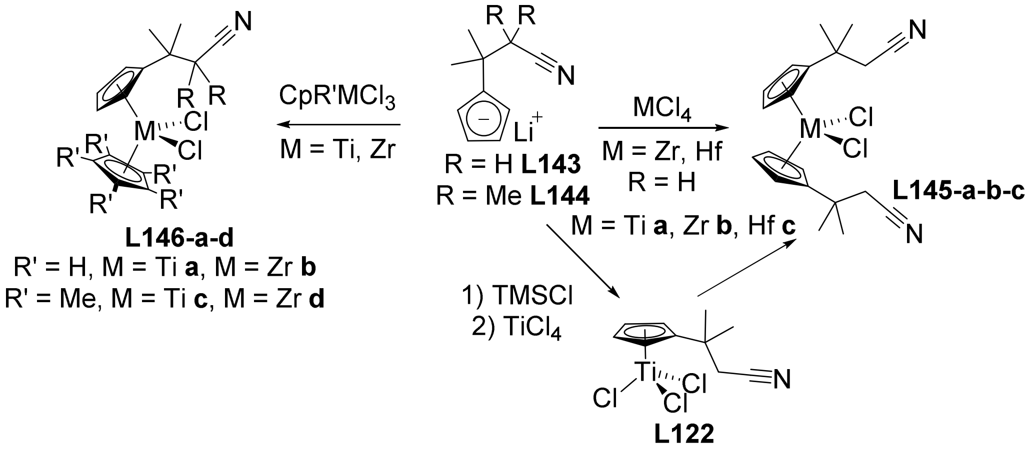
Scheme I-43: Gansäuer's synthesis of amido titanocenes

---

[96] Qian, Y.; Guo, R.; Huang, J.; Yang, Q. *Polyhedron.* **1997**, *16*, 195
[97] Jutzi, P.; Redeker, T. *Organometallics.* **1997**, *16*, 1343
[98] Hüerländer, D.; Fröhlich, R.; Erker, G. *J. Chem. Soc. Dalton Trans.* **2002**,7, 1513
[99] Gansäuer, A.; Franke, D.; Lauterbach, T.; Nieger, M. *J. Am. Chem. Soc.* **2005**, *127*, 11622
[100] See for example: Dwadnia, N.; Allouch, F.; Pirio, N.; Roger, J.; Cattey, H.; Fournier, S.; Penouilh, M.-J.; Devillers, C. H.; Lucas, D.; Naoufal, D.; Ben Salem, R.; Hierso, J.-C. *Organometallics.* **2013**, *32*, 5784

Some of these complexes were used as antitumor and antileukemic agents and some others were then reduced and used in hydrogen transfer catalysis for epoxide opening, and radical reduction.[101a,b]

Another atypic functionality incorporated into the cyclopentadienylide framework was described by Lamač: a nitrile. Coordination of compound **L143** to group 4 metals is straightforward. Bis(cyanoethyl)metallocenes **L145-a-c** were synthesized first (Scheme I-44).[74] In the case of titanium, better yields were obtained if the half sandwich **L122** was formed first. In these structures, no coordination of the nitrile to the titanium centre was observed. A second series of mono substituted (cyanoalkyl)metallocenes **L147-a-b** was synthesized (Scheme I-45).[102,103]



Scheme I-44: synthesis of cyano functionalized group 4 metallocenes

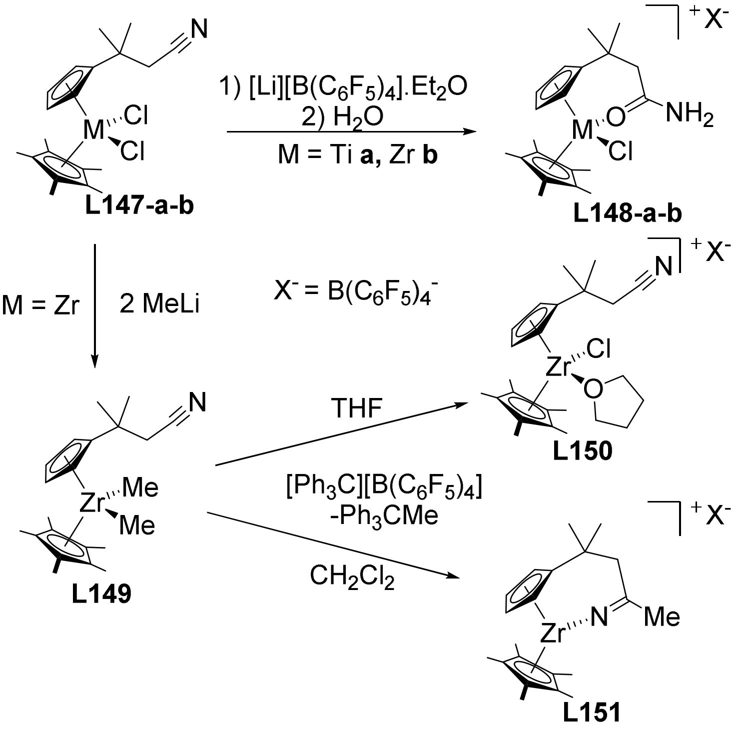
These nitrilo-based metallocenes were proved to be moisture sensitive. With the monofunctionalized metallocenes **L147-a-b**, water addition products were characterized for both titanium and zirconium complexes (**L148-a-b**). The dimethyl zirconocene **L149** was also synthesized, and abstraction of one methide with $[Ph_3C][B(C_6F_5)_4]$ yielded the cationic adduct **L150** in THF. In dichloromethane, the nitrile moiety was inserted into the Zr-Me bond to form **L151** (Scheme I-45 bottom).

---

[101] (a): Gansäuer, A.; Winkler, I.; Worgull, D.; Lauterbach, T.; Franke, D.; Selig, A.; Wagner, L.; Prokop, A. *Chem. – Eur. J.* **2008**, *14*, 4160, (b): Zhang, Y.-Q.; Jakoby, V.; Stainer, K.; Schmer, A.; Klare, S.; Bauer, M.; Grimme, S.; Cuerva, J. M.; Gansäuer, A. *Angew. Chem. Int. Ed.* **2016**, *55*, 1523

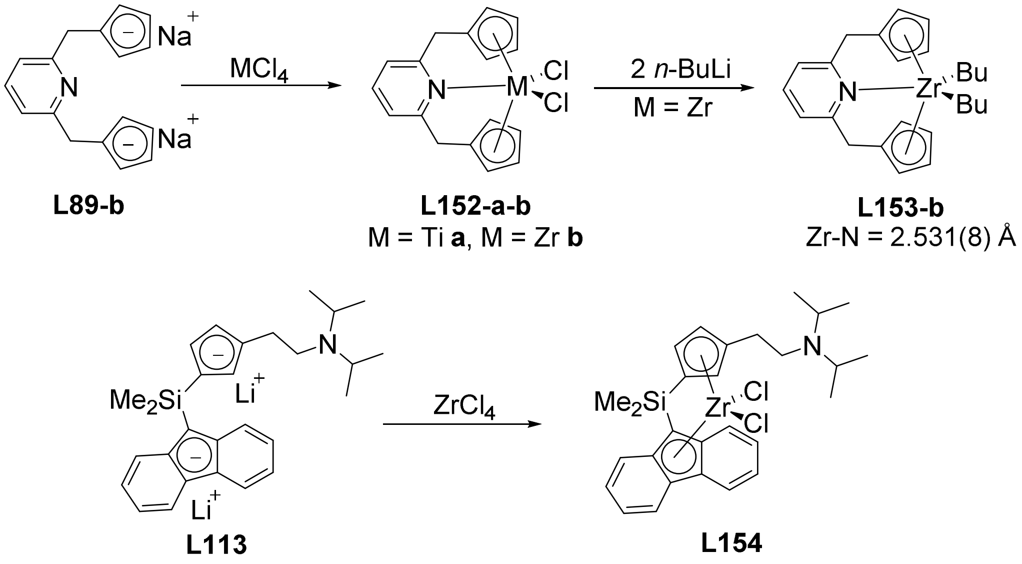
[102] Pinkas, J.; Císařová, I.; Kubišta, J.; Horáček, M.; Lamač, M. *Dalton Trans.* **2013**, *42*, 7101

[103] Horáček, M.; Gyepes, R.; Císařová, I.; Pinkas, J.; Kubišta, J.; Lamač, M. *J. Organomet. Chem.* **2015**, *787*, 56



Scheme I-45: reactivity of mono(cyanoethyl)zirconocene L147-a-b

Lastly, one can cite the synthesis of some ansametallocenes, based on the coordination of ligands **L89-b** and **L113** previously described (Scheme I-46). In 1997, Paolucci used **L89-b** (first designed by Qian),[104] for the synthesis of the new ansazirconocene **L152-b**.



Scheme I-46: synthesis of N-based ansazirconocenes

Complex **L153-b** is the first stable dialkyl zirconocene with β hydrogens which was characterized by X-ray diffraction. The pyridinyl moiety was coordinated to the metal centre (Zr-N = 2.531(8) Å). The analogous ansatitanocene **L152-a** was synthesized in 1997 by Qian

---

[104] Paolucci, G.; Pojana, G.; Zanon, J.; Lucchini, V.; Avtomonov, E. *Organometallics*. **1997**, *16*, 5312

but no crystal were obtained.[96] Jutzi described the synthesis of various ligands for the synthesis of ansazirconocenes. [80,105a,b] One example is depicted in Scheme I-46 (**L154**).

In conclusion to this part, it has been shown that a carbonated chain longer than one carbon enables coordination of the amine moiety to the metal centre if no steric effect are present to prevent it. This has been exploited to design N-stabilized metallocene complexes for polymerization catalysis. Several reviews have been published over the years on this topic for further information.[106]

The last part of this bibliographic introduction will deal with a new concept for activation of small molecules: the use of frustrated Lewis pairs (FLPs). After a short introduction to some of the main features of this concept and similar approaches (metal-ligand cooperativity and ambiphilic ligands), an overview of organometallic FLPs (OmFLPs) will be presented, with a focus on group 4 metals.

D. Frustrated Lewis Pairs

1. Concept and origins

Frustrated Lewis pairs were first introduced by Stephan,[107] and Erker.[108] These species consist of unquenched mixtures of Lewis acids and bases due to steric hindrance (Figure I-1). Compared to classical Lewis adducts, FLPs are less stable mixtures brought together by weak interactions, which reduces the activation energy required for small molecule activation. The concept has been extended to any combination capable of activating small molecules, even if a slight interaction between both partners is observed in less constrained pairs.

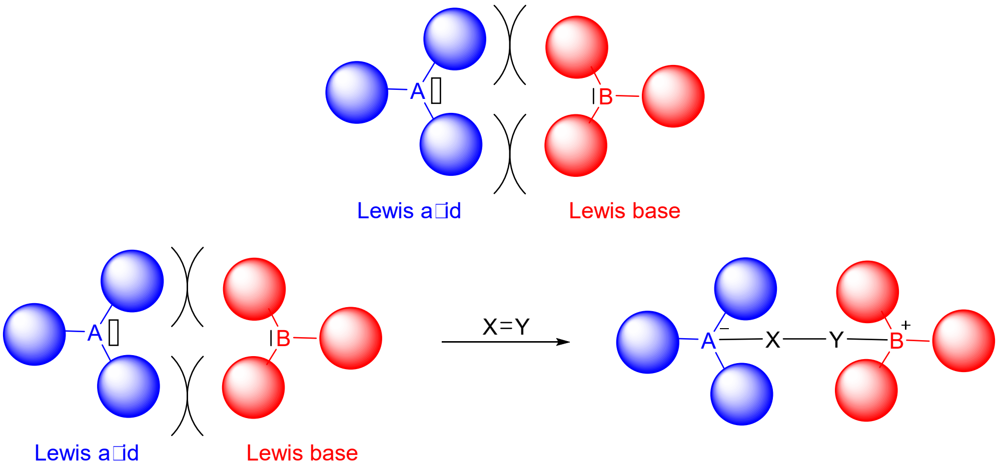


Figure I-1: illustration of an FLP

---

[105] (a): Jutzi, P.; Müller, C.; Neumann, B.; Stammler, H.-G. *J. Organomet. Chem.* **2001**, *625*, 180, (b): Hagemeister, T.; Jutzi, P.; Stammler, A.; Stammler, H.-G. *Can. J. Chem.* **2003**, *81*, 1255

[106] Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, *1998*, 663, Müller, C.; Vos, D.; Jutzi, P. *J. Organomet. Chem.* **2000**, *600*, 127

[107] Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science.* **2006**, *314*, 1124

[108] Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**,47, 5072

In a few cases, Lewis pairs are not frustrated anymore but are still able to activate several substrates. These aspects will be illustrated further.

a. Concept

These energetic considerations were put forth by Pápai in 2008,[109] with dihydrogen activation by a phosphine/borane FLP. Starting from a typical Lewis pair, quenching a Lewis acid with a Lewis base in the presence of dihydrogen will yield a Lewis adduct which is an potential energy well, precluding the activation of H_2 (Figure I-2). Indeed, the energy required to reach the activation transition state, which corresponds to the cleavage of the donor-acceptor-adduct cleavage and insertion of dihydrogen into the Lewis acid-Lewis base bond, is too high. In the case of FLPs, weak interaction between both partners causes a shallower energy well and hence a lower activation energy. Although no preactivation intermediates $LB\cdots H_2$ or $LA\cdots H_2$ were found when both are reacted alone with dihydrogen, it is no longer to be proved that several FLPs are able to split heterolitically H_2. This tends to prove that both Lewis acid and Lewis base are activating dihydrogen cooperatively, which can be illustrated as the TS FLP drawn in Figure I-2. This diagram is drawn by using dihydrogen but can be extended to any other small molecules such as CO_2, CO, NO_2, N_2O ... The nature of both partners will entail a certain energy supply which does not necessarily fit every substrate. Nevertheless some FLPs can activate (or react with) a variety of small molecules such as alkenes, alkynes, aldehydes, ketones and even ynones, as will be illustrated further.

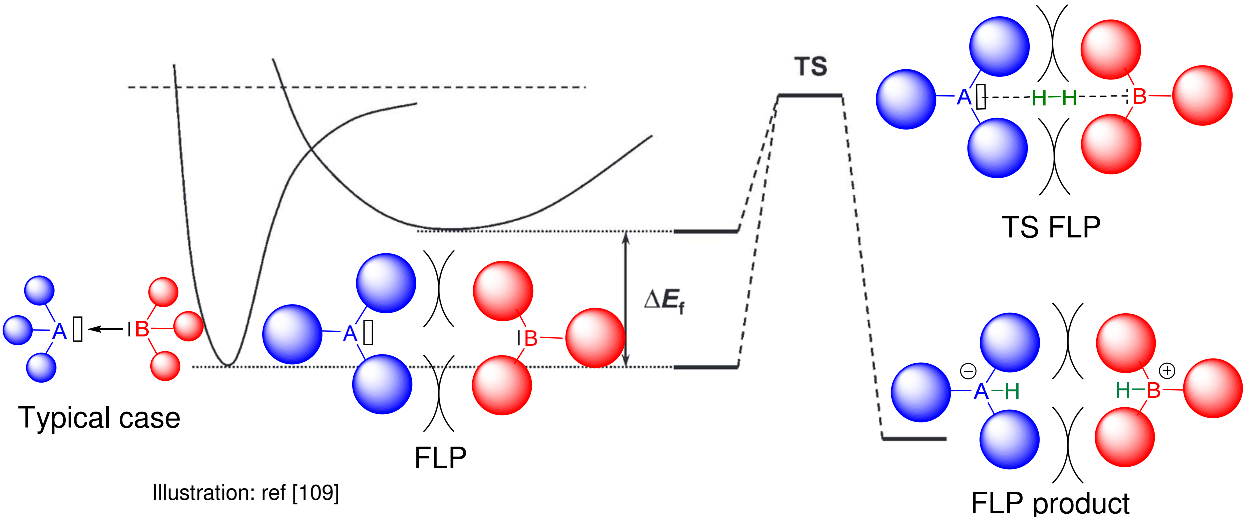


Illustration: ref [109]

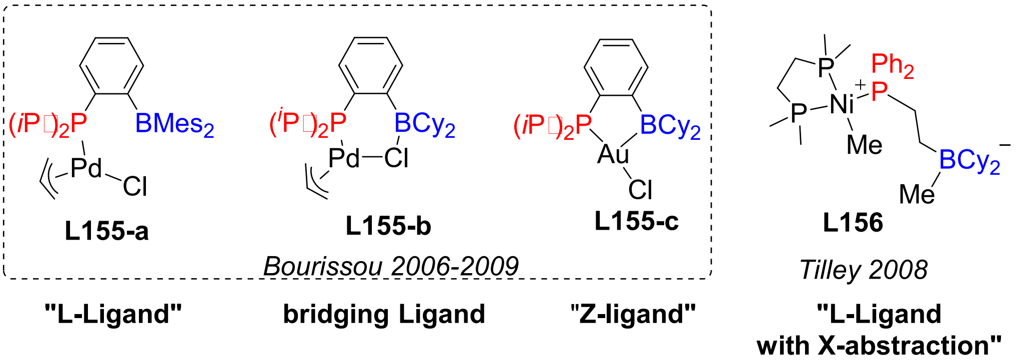
Figure I-2: Energetical illustration of the FLP concept adapted from Pápai

---

[109] Rokob, T. A.; Hamza, A.; Stirling, A.; Soós, T.; Pápai, I. *Angew. Chem. Int. Ed.* **2008**, *47*, 2435

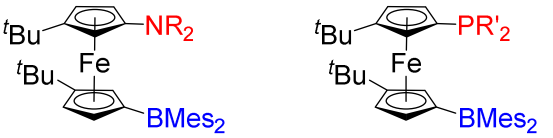
b. Ambiphilic molecules and metal-ligand cooperativity

Before developing the origins of FLPs, and the scope of their use, a parallel has to be done with two other noteworthy concepts described in the last decade. Indeed, extensive work has been done on ambiphilic (or amphoteric) derivatives over the past ten years. By definition, such kind of compounds are composed of two antagonistic moieties: an electron acceptor site (or Lewis acid) and an electron donor site (or a Lewis base). These two sites have to be separated by at least one atom. In other words, many intramolecular FLPs described further could be considered as ambiphilic derivatives. Ambiphilic compounds usually combining group 15 and 13 elements, were found to be able to act as L-ligand (**L155-a**), bridging ligand (**L155-b**), L-Ligand accompanied with a Ligand-X abstraction from the Lewis acid (**L156**), or more surprisingly as Z-Ligand (**L155-c**) as illustrated in Scheme I-47.[110,111,112]



Scheme I-47: the different coordination modes of ambiphilic ligands

Another example, based on a ferrocenic platform was developed in the group of Hierso as illustrated in Scheme I-48.[113,114]



L157-a-b
R = Et **a**, Pyrr **b**

L158-a-c
R' = Mes **a**, Ph **b**, ^{i}Pr **c**

Scheme I-48: ambiphilic P/B ferrocenes

Numerous example of ambiphilic ligands have already been reported elsewhere and will not be developed in more details.[115,116]

---

[110] Fischbach, A.; Bazinet, P. R.; Waterman, R.; Tilley, T. D. *Organometallics*. **2008**, *27*, 1135

[111] Bontemps, S.; Bouhadir, G.; Miqueu, K.; Bourissou, D. *J. Am. Chem. Soc.* **2006**, *128*, 12056

[112] Bontemps, S.; Bouhadir, G.; Apperley, D. C.; Dyer, P. W.; Miqueu, K.; Bourissou, D. *Chem. - Asian J.* **2009**, *4*, 428

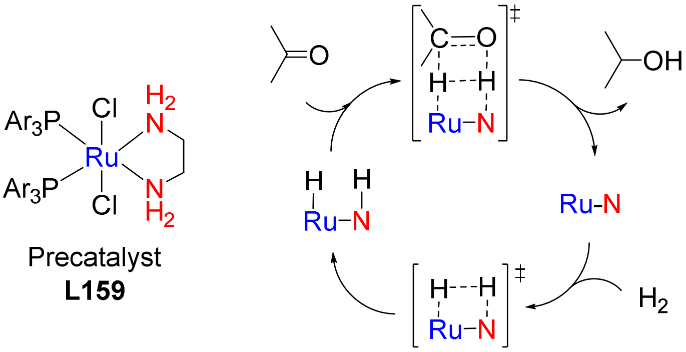
[113] (a): Lerayer, E.Synthèse et caractérisation de phosphine, borane, amine sur plateforme ferrocène polyfonctionnelle Bourgogne-Franche-Comté: Dijon 2016,

[114] Lerayer, E.; Renaut, P.; Roger, J.; Pirio, N.; Cattey, H.; Devillers, C. H.; Lucas, D.; Hierso, J.-C. *Chem. Commun.* **2017**, *53*, 6017

[115] Bouhadir, G.; Amgoune, A.; Bourissou, D. In *Advances in Organometallic Chemistry* Elsevier 2010 Vol. 58pp 1–107

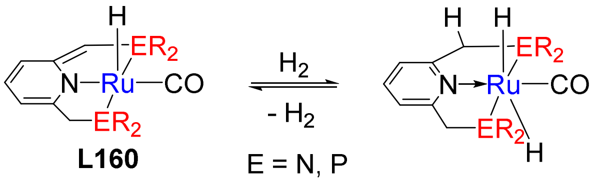
[116] Bouhadir, G.; Bourissou, D. *Chem. Soc. Rev.* **2016**, *45*, 1065

Another concept has emerged in the transition metals realm, based on similar antagonistic combinations. Noyori and Milstein have described the notion of metal-ligand cooperativity in catalysis. The first described ruthenium-based complexes bearing secondary amines. These systems are able to cooperatively activate H_2 before operating the enantioselective reduction of carbonylated derivatives (Scheme I-49).[117,118]



Scheme I-49: cooperative ketone hydrogenation reported by Noyori

The second showed the potential of non-innocent ligands such as PNP (di(phosphinomethyl)pyridines) in combination with ruthenium, in catalytic oxidation of alcohol by dehydrogenation (Scheme I-50). This catalysis was shown to process via metal-ligand cooperation based on an aromatization/de-aromatization process.



$$RCH_2OH \xrightarrow[- H_2]{\textbf{L160}} RCHO$$

Scheme I-50: non-innocent ligand for the dehydrogenation of alcohols

In both cases, the Ru played the role of a Lewis acid whilst the ligand acted as a Lewis Base. Their cooperativity led to the activation of H_2 in Noyori's catalysis or elimination of H_2 in Milstein's catalysis.[119] These two reactions are closely related to the FLP concept because they rely on the activation of small molecules by using synergistically a metal (Lewis acid) with a basic ligand (Lewis base).

c. Origins

Brown is generally recognized to have published, in 1942, the very first example of what would be described nowadays as an FLP.[120] Trimethylborane was mixed with 2,6-

---

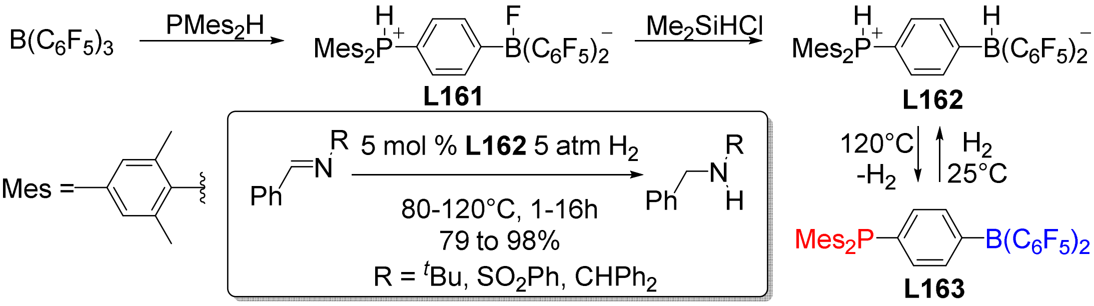
[117] Noyori, R.; Ohkuma, T. *Angew. Chem. Int. Ed.* **2001**, *40*, 40

[118] Peters, R.Cooperative Catalysis: Designing Efficient Catalysts for Synthesis John Wiley & Sons 2015

[119] Milstein, D. *Top. Catal.* **2010**, *53*, 915

[120] Brown, H. C.; Schlesinger, H. I.; Cardon, S. Z. *J. Am. Chem. Soc.* **1942**, *64*, 325

dimethylpyridine, and no adduct was observed. This unexpected behaviour was not investigated further at the time. Six decades later, whilst investigating phosphine-borane adducts,[107,] Stephan discovered the nucleophilic substitution of $B(C_6F_5)_3$ by $P(Mes)_2H$ to form the intermediate **L161** (Scheme I-51). After an H-for-F exchange with Me_2SiHCl, compound **L162** was obtained: at 120 °C a loss of H_2 was observed to liberate the FLP **L163**. H_2 could be easily activated by **L163** at 25°C in less than 5 min to recover **L162**. A new class of compounds was born, which led to the definition of the FLP concept shortly thereafter.[121] The discovery of compound **L163** was a milestone in metal-free hydrogenation and H_2 storage research.[122] It was first used as a catalyst for imine hydrogenation and benzaldehyde reduction.



Scheme I-51: first organic FLP from Stephan

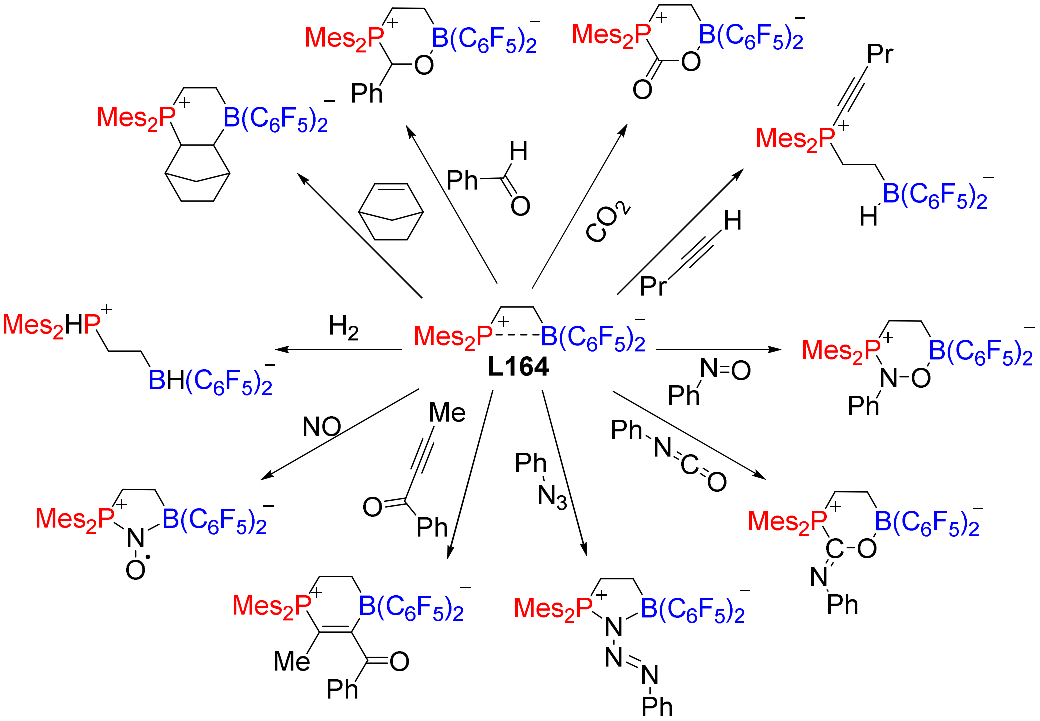
Following these results, another intramolecular FLP **L164** was decribed by Erker which was shown to activate various substrates in a number of papers (Scheme I-52).[108,123a,b,c,d]

---

[121] Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. *Dalton Trans.* **2007**,31, 3407

[122] Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2007**, *46*, 8050

[123] (a): Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**,47, 5072, (b): Mömming, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. *Angew. Chem. Int. Ed.* **2009**, *48*, 6643, (c): Mömming, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 12280, (d): Xu, B.-H.; Kehr, G.; Fröhlich, R.; Wibbeling, B.; Schirmer, B.; Grimme, S.; Erker, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 7183

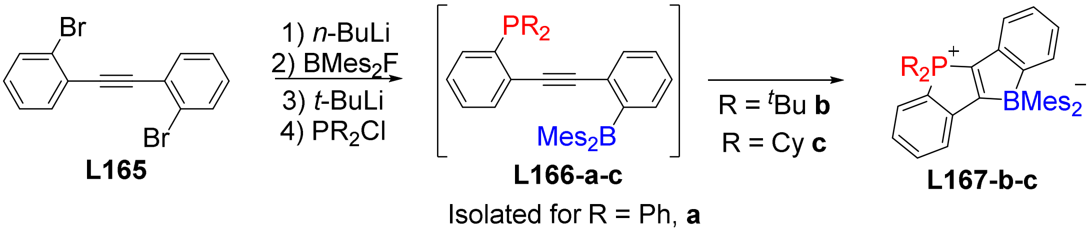


Scheme I-52: some examples of small molecule activation with L164

2. Scope of organic FLPs

a. Pionnering P/B systems

Intermolecular FLPs were then described by Stephan. The $P(^{t}Bu)_3$ / $B(C_6F_5)_3$ pair was shown to activate alkenes.[124] The FLP chemistry has been growing over the past decade. The concept was extended to various partners, and used to design new kind of compounds. For example, one can cite the synthesis of new P-B-diphenylacetylene derivatives (e.g. compound of type **L166**) developed by Yamaguchi.[125] The diphenylphosphine in compound **L166-a** was not nucleophilic enough to activate the alkynyl moiety, whilst **L166-b** and **c** underwent ring closing so quickly that they could not be isolated. **L167-b-c** were formed quantitatively without traces of the P-B-diphenylacetylene (Scheme I-53).



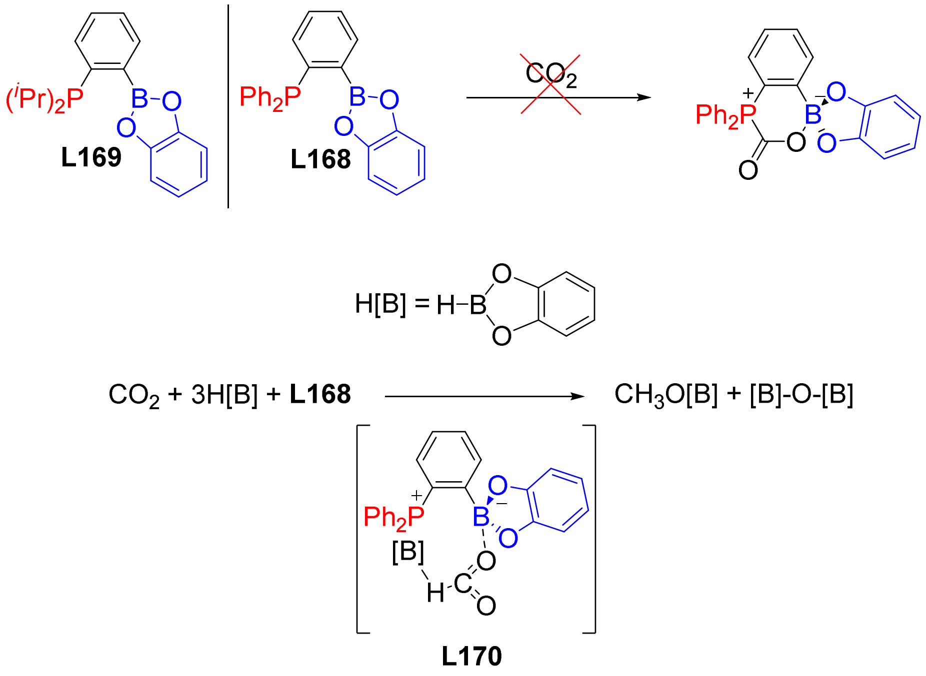
Scheme I-53: Yamaguchi's synthesis of π-ladder-conjugated skeleton

---

[124] (a): McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem. Int. Ed.* **2007**, *46*, 4968, (b): Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880

[125] Fukazawa, A.; Yamada, H.; Yamaguchi, S. *Angew. Chem. Int. Ed.* **2008**, *47*, 5582

After H_2-activation, much interest in FLP chemistry has been devoted to CO_2 binding. Indeed, due to its involvement in global warming via the greenhouse effect, numerous research groups have started working on its use as a C-1 feedstock. For instance, Fontaine devised a CO_2 reduction procedure involving the combination of **L168** and an hydroborane [H]B. Mechanistic studies involving DFT calculations and experimental evidence enable Fontaine to put forth a three-component mechanism (intermediate **L170**), instead of the more classical two-step sequence involving CO_2 activation followed by reduction. Indeed, compound **L168** was proved not to be able to bind CO_2 alone, according to NMR analyses.[126a,b] Nevertheless, the combination of **L168**, H[B] and CO_2 effected the reduction of CO_2 as illustrated in Scheme I-54. A simplified view of this mechanism involves H[B] activation by the phosphine, whilst the catechol borane moiety activates CO_2, in reality the mechanism is more complex.[127] A series of analogous P/B ambiphilic pairs was then tested against CO_2 reduction (with H[B] and $BH_3 \cdot Me_2S$). This study showed that **L168** and **L169** were the most active catalysts for CO_2 reduction.[128] Adducts of the ambiphilic system and CH_2O were shown to be the catalytically active species in this system.



Scheme I-54: FLP-catalysed reduction of CO_2

This example highlights both the complexity and the efficiency of ambiphilic pairs / FLPs in catalysis. Using a weakly acidic partner as in **L168**, does not enable CO_2 binding, but the combination of the P/B pair, H[B] and CO_2 creates a synergy to effect CO_2 reduction. The use

---

[126] (a): Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2013**, *135*, 9326, Fontaine, F.-G.; Courtemanche, M.-A.; Légaré, M.-A. *Chem. – Eur. J.* **2014**, *20*, 2990

[127] Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2014**, *136*, 10708

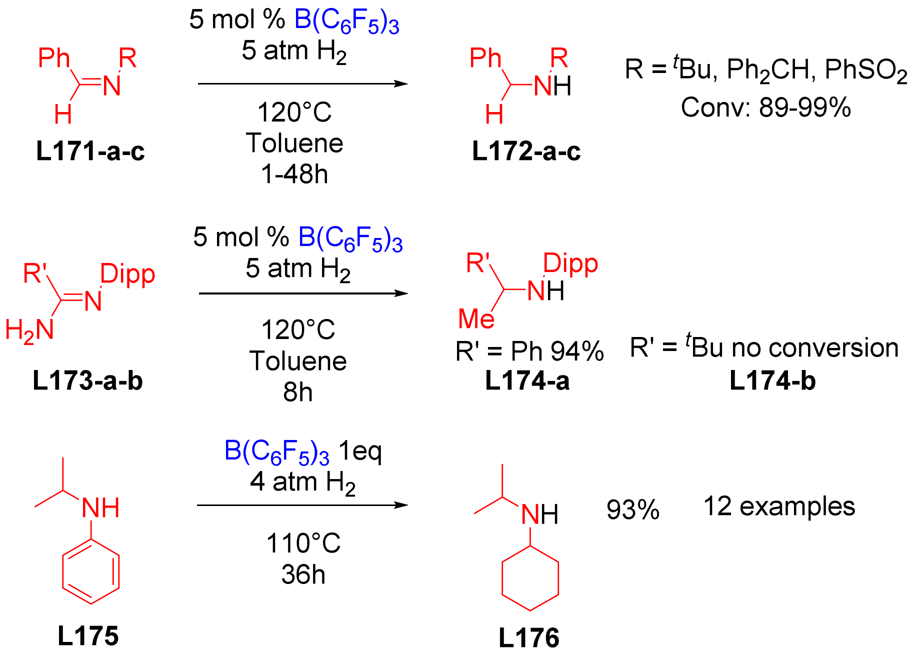
[128] Declercq, R.; Bouhadir, G.; Bourissou, D.; Légaré, M.-A.; Courtemanche, M.-A.; Nahi, K. S.; Bouchard, N.; Fontaine, F.-G.; Maron, L. *ACS Catal.* **2015**, *5*, 2513

of a more acidic and/or bulkier borane would lower the energy of some transition states, but would also over-stabilize some reaction intermediates, thus slowing down catalytic turnover.

Several other FLPs have been designed, not solely based on P/B systems, and advances in this field have already been reviewed elsewhere.[129a,b] Examples of N-based FLPs (generally with $B(C_6F_5)_3$ as the Lewis acid component) will now be presented, in an attempt to illustrate the wide range of FLPs and their applications.

b. N-based organic FLPs

Early work on N-based FLPs started with the catalytic hydrogenation of imines with $B(C_6F_5)_3$ described by Stephan (Scheme I-55).[130] By using only 5 mol % of this borane, very good conversion of imines into secondary amines was obtained in 1-8 h (**L172-a-c** and **L174-a**). The SO_2-based imine required 48h to get 94% of conversion. When the imine was too bulky, hydrogenation failed (**L174-b**).



Scheme I-55: FLP-hydrogenation of imines and aromatic amines

This pioneering work was the starting point of many developments in metal-free hydrogenation. In 2011, a diastereoselective version using chiral imines was described.[131] Besides, Stephan extended this type of reactivity to aromatic amines (**L175**) which were hydrogenated with one equivalent of $B(C_6F_5)_3$ (Scheme I-55-bottom).[132] In 2015, Oestreich extended this methodology by using cyclohexa-1,4-dienes as a source of hydrogen.[133]

---

[129] (a): Erker, G.; Douglas W. Stephan.Frustrated Lewis Pairs I - Uncovering and UnderstandingTopics in Current Chemistry Springer, Berlin, Heidelberg Vol. 332, Erker, G.; Stephan, D. W.Frustrated Lewis Pairs II - Expanding the Scope Topics in Current Chemistry Springer, Berlin, Heidelberg Vol. 334

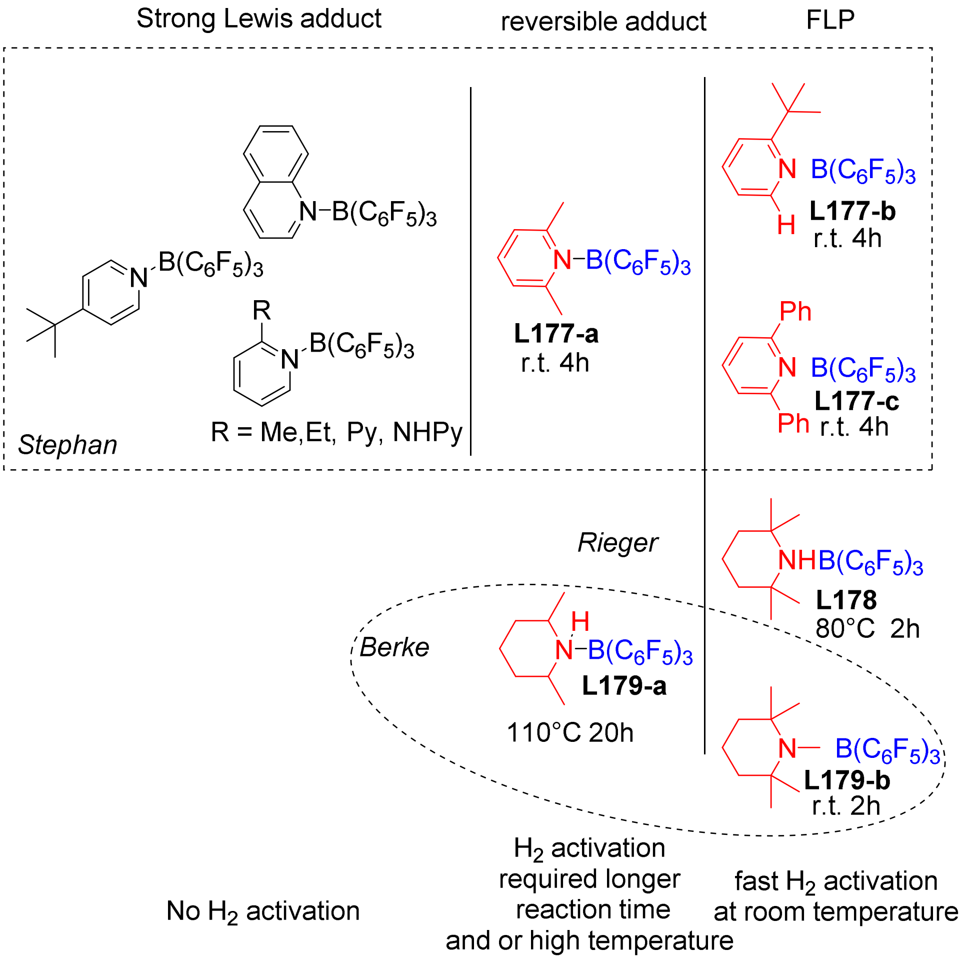
[130] Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, *14*, 1701

[131] Heiden, Z. M.; Stephan, D. W. *Chem. Commun.* **2011**, *47*, 5729

[132] Mahdi, T.; Heiden, Z. M.; Grimme, S.; Stephan, D. W. *J. Am. Chem. Soc.* **2012**, *134*, 4088

[133] Chatterjee, I.; Oestreich, M. *Angew. Chem. Int. Ed.* **2015**, *54*, 1965

Whilst Rieger and Repo[134] employed $B(C_6F_5)_3$ with TMPH (2,2,6,6-tetramethylpiperidine) and DIPA (Diisopropylamine) to activate dihydrogen, Stephan continued his investigations on N-based FLPs employing substituted pyridines treated with $B(C_6F_5)_3$ and studied the nature of the B-N adduct.[135] Whereas simple pyridines formed stable Lewis adducts, the bulkier 2,6-lutidine underwent reversible adduct formation with $B(C_6F_5)_3$, (forming **L167-a**) and was able to activate dihydrogen. Ring-opening THF was also observed with this adduct.[136] Bulkier 2-6 substituted pyridines showed no interaction whatsoever with $B(C_6F_5)_3$, forming FLP **L167-b-c,** and were also able to split H_2. In 2011, the conditions required for H_2 activation were explored by Berke with various bulky piperidines. Increasing bulkiness around piperidine reduced the energy required for activation (in the decreasing order: **L179-a**, **L178** and **L179-b**) as illustrated on Scheme I-56.[137]



Scheme I-56: overview of intermolecular N-based FLP studied, and their reactivity towards H_2 activation

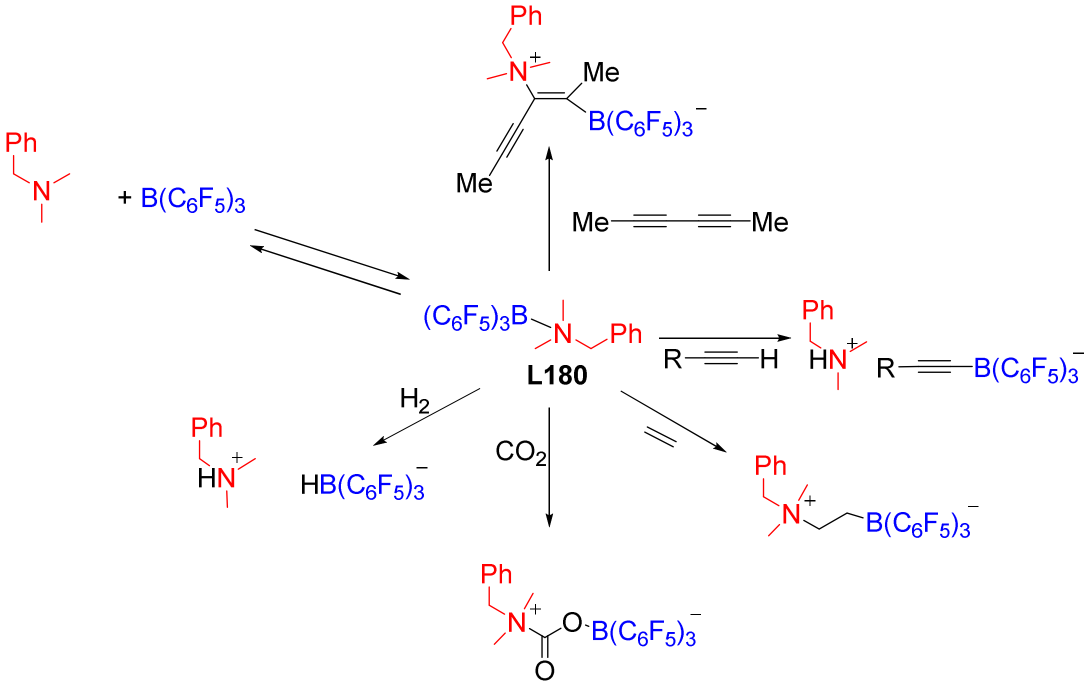
---

[134] Sumerin, V.; Schulz, F.; Nieger, M.; Leskelä, M.; Repo, T.; Rieger, B. *Angew. Chem. Int. Ed.* **2008**, *47*, 6001
[135] Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. *Inorg. Chem.* **2009**, *48*, 10466
[136] Geier, S. J.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 3476
[137] Jiang, C.; Blacque, O.; Fox, T.; Berke, H. *Organometallics.* **2011**, *30*, 2117

TMPH has been widely used in FLP chemistry. Various combinations with borane other than $B(C_6F_5)_3$ also showed H_2 activation.[138] Several studies on CO_2 reduction involving TMPH / $B(C_6F_5)_3$ mixture have been published. Indeed, as mentioned before, CO_2 reduction is an interesting way to use this greenhouse gas as C_1 feedstock. In 2009, O' Hare described the catalytic reduction of CO_2 by using H_2 in addition to **L178** to form methanol (after aqueous treatment).[139] Piers described the same kind of reactivity using Et_3SiH instead of H_2.[140] More surprisingly, TMPH was used in 2015 with a disguised silylium (silanetriflate) to activate CO_2.[141]

L178 and **L177-a** were used for alkyne activation. TMPH acted as Brønsted base whilst 2,6-lutidine was able to form the FLP-adduct.[142] The reactivity of primary alkyne with FLPs is dependent of the nature of the Lewis partner involved. Classical FLPs operate the carbon-carbon triple bond activation (e.g. 2,6-lutidine) whilst some Lewis base partners are too bulky to operate the same reactivity. In the latter case, deprotonation of the primary alkyne is observed (e.g. TMPH) which is a Brønsted type reactivity for a base. Berke showed the ability of **L179a-b** to activate cooperatively hydrogen.

In 2012, an FLP reactivity was described by Erker and Stephan by using a less hindered amine.[143] Various substrates were activated with the $BnMe_2N$ / $B(C_6F_5)_3$ pair (Scheme I-57). The N-B bond is very long and therefore adduct formation is reversible. This particularity must help small molecule activation as already illustrated.



Scheme I-57: low bulky N-based FLP

---

[138] (a): Binding, S. C.; Zaher, H.; Mark Chadwick, F.; O'Hare, D. *Dalton Trans.* **2012**, *41*, 9061, (b): Herrington, T. J.; Thom, A. J. W.; White, A. J. P.; Ashley, A. E. *Dalton Trans.* **2012**, *41*, 9019

[139] Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem. Int. Ed.* **2009**, *48*, 9839

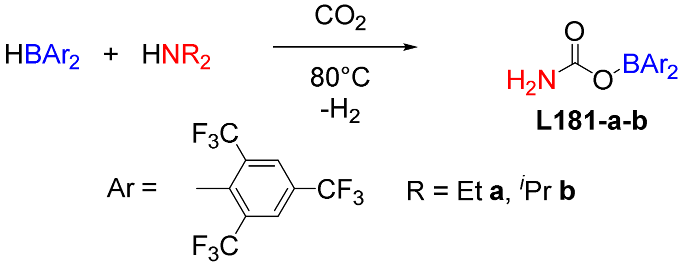
[140] Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 10660

[141] Weicker, S. A.; Stephan, D. W. *Chem. – Eur. J.* **2015**, *21*, 13027

[142] Jiang, C.; Blacque, O.; Berke, H. *Organometallics.* **2010**, *29*, 125

[143] Voss, T.; Mahdi, T.; Otten, E.; Fröhlich, R.; Kehr, G.; Stephan, D. W.; Erker, G. *Organometallics.* **2012**, *31*, 2367

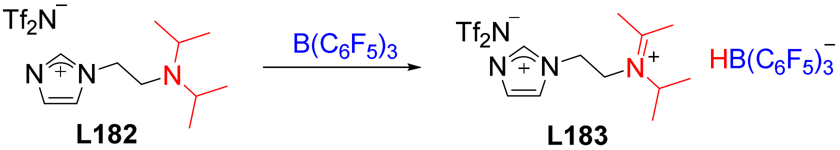
Wang described another example of less hindered amine than TMPH in 2013. Diethylamine or diisopropylamine were used in conjunction with an extremely bulky and Lewis acidic borane to activate CO_2 and form **L181-a-b** (Scheme I-58).[144]



L181-a-b

Scheme I-58: CO_2 activation from Wang's work

An unusual ionic liquid-based FLP was designed by Dyson in 2017 by using imidazolium **L182** with a pendant ethyldiisoproylamine in association with $B(C_6F_5)_3$.[145] The diisopropylamine moiety underwent an α-H abstraction to form an iminium hydrido borate. This ionic liquid-based FLP did not activate H_2, but both iminium and hydroborate were not observable anymore, according to NMR measurements. Nevertheless, at least partial reduction of CO_2 with H_2 was observed according to multinuclear NMR spectroscopic analyses (Scheme I-59).



L182 **L183**

Scheme I-59: an ionic liquid-based FLP

Many ambiphilic N/B systems have been reported over the years. Scheme I-60 summarizes the main advances in this field. Before the introduction of the FLP concept, Piers reported the synthesis the ambiphilic phenylene-based aminoborane **L184-a**. An attempt at stepwise addition of H^+ and H^- was also reported but failed. The expected H_2 addition product was unfortunately not obtained. [146] Inspired by this work, Rieger, Repo and Pápai have published (jointly or concurrently) several reports on related systems. Compound **L184-b-c-d** exhibited classical FLP-type chemistry, [147,148,149] with no B-N bond observed either in solid or

---

[144] Lu, Z.; Wang, Y.; Liu, J.; Lin, Y.; Li, Z. H.; Wang, H. *Organometallics.* **2013**, *32*, 6753

[145] Perrin, F. G.; Bobbink, F. D.; Păunescu, E.; Fei, Z.; Scopelliti, R.; Laurenczy, G.; Katsyuba, S.; Dyson, P. J. *Inorganica Chim. Acta.* **2018**, *470*, 270

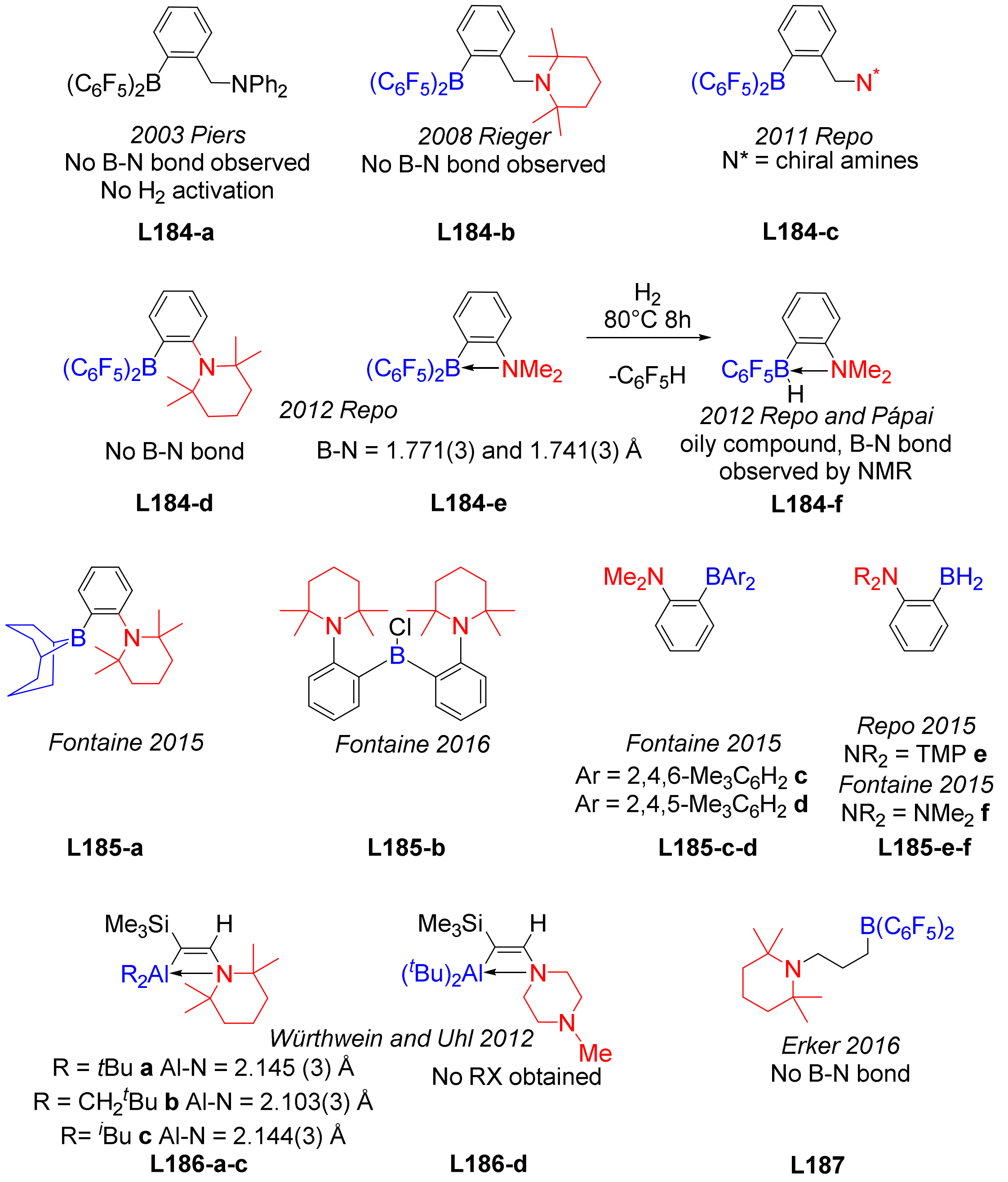
[146] Roesler, R.; Piers, W. E.; Parvez, M. *J. Organomet. Chem.* **2003**, *680*, 218

[147] (a): Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Rieger, B. *J. Am. Chem. Soc.* **2008**, *130*, 14117, (b): Schulz, F.; Sumerin, V.; Heikkinen, S.; Pedersen, B.; Wang, C.; Atsumi, M.; Leskelä, M.; Repo, T.; Pyykkö, P.; Petry, W.; Rieger, B. *J. Am. Chem. Soc.* **2011**, *133*, 20245

[148] Sumerin, V.; Chernichenko, K.; Nieger, M.; Leskelä, M.; Rieger, B.; Repo, T. *Adv. Synth. Catal.* **2011**, *353*, 2093

[149] Chernichenko, K.; Nieger, M.; Leskelä, M.; Repo, T. *Dalton Trans.* **2012**, *41*, 9029

liquid states; on the other hand, a less frustrated ambiphilic compound (**L184-e**) was reported to activate dihydrogen at 80°C.[148]



2003 Piers
No B-N bond observed
No H_2 activation
L184-a

2008 Rieger
No B-N bond observed
L184-b

2011 Repo
N* = chiral amines
L184-c

No B-N bond
L184-d

2012 Repo
B-N = 1.771(3) and 1.741(3) Å
L184-e

2012 Repo and Pápai
oily compound, B-N bond observed by NMR
L184-f

Fontaine 2015
L185-a

Fontaine 2016
L185-b

Fontaine 2015
Ar = 2,4,6-$Me_3C_6H_2$ **c**
Ar = 2,4,5-$Me_3C_6H_2$ **d**
L185-c-d

Repo 2015
NR_2 = TMP **e**
Fontaine 2015
NR_2 = NMe_2 **f**
L185-e-f

Würthwein and Uhl 2012
R = *t*Bu **a** Al-N = 2.145 (3) Å
R = $CH_2{}^tBu$ **b** Al-N = 2.103(3) Å
R= ^{i}Bu **c** Al-N = 2.144(3) Å
L186-a-c

No RX obtained
L186-d

Erker 2016
No B-N bond
L187

Scheme I-60: Scope of intramolecular N-based organic FLPs

Surprisingly, prolonged heating of the hydrogen-addition product led to the formation of a new ambiphilic aminoborane (**L184-f**),[150] which showed high potential in selective alkyne reduction for the first time. Interestingly, this compound was also used for aryl C-H activation.[151] As previously described, Fontaine explored ambiphilic phenylene-based complexes and

---

[150] Chernichenko, K.; Madarász, A.; Pápai, I.; Nieger, M.; Leskelä, M.; Repo, T. *Nat. Chem.* **2013**, *5*, 718
[151] Chernichenko, K.; Lindqvist, M.; Kótai, B.; Nieger, M.; Sorochkina, K.; Pápai, I.; Repo, T. *J. Am. Chem. Soc.* **2016**, *138*, 4860

synthesized various N/B systems of this type (**L185-a-d,f**).[152a,b,c,d] FLP-type reactivity was observed, along with C-H activation on heteroarenes,[153] and S-H bond borylation.[154a,b] Erker designed a TMP-based intramolecular FLP with a longer spacer (**L187**),[155] but no B-N interaction was found in the solid state. Würthwein and Uhl designed new N-based FLPs containing aluminum instead of a boron as the Lewis acid partner (**L-186-a-d**).[156]

In conclusion to this part on organic FLPs, they were able to be used in catalytic processes by activating small molecules as transition metals did earlier. With this new class of molecules, the main group elements were shown to react in a similar fashion as transition metal compounds as described by Power,[157] but remained used in stoichiometric conditions. Despite being widely presented as advantageous because of their "metal-free" nature, it was not long before FLP would enter the realm of organometallic chemistry. Important reviews on this topic have been written by Stephan,[158] Erker[159] and Wass.[160a,b,c] In this last part, only group 4 metal examples will be described.

3. Organometallic-based FLPs based on group 4 metals

Amongst other properties, group 4 metals are known for their Lewis acidity. This character has been widely exploited in organic chemistry especially with $TiCl_4$. The first example which comes to mind is the Knoevenagel reaction which is commonly performed with $TiCl_4$ and a base.[161] In fact, many reactions of this type use this combination of a Lewis pair in various reactions.

An early example was described by Jordan in 1991 who discovered the ring opening of THF with NMe_3 or PMe_2Ph in combination with a cationic zirconocene, forming **L189-a-b.**[162] Even if the FLP concept did not exist at the time, it is fair to say that this reaction would probably be described in terms of FLP chemistry nowadays (Scheme I-61). Stephan described a related

---

[152] (a): Rochette, É.; Courtemanche, M.-A.; Pulis, A. P.; Bi, W.; Fontaine, F.-G. *Molecules.* **2015**, *20*, 11902, (b): Courtemanche, M.-A.; Pulis, A. P.; Rochette, É.; Légaré, M.-A.; Stephan, D. W.; Fontaine, F.-G. *Chem. Commun.* **2015**, *51*, 9797, (c): Chernichenko, K.; Kótai, B.; Pápai, I.; Zhivonitko, V.; Nieger, M.; Leskelä, M.; Repo, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 1749, (d): Courtemanche, M.-A.; Rochette, É.; Légaré, M.-A.; Bi, W.; Fontaine, F.-G. *Dalton Trans.* **2016**, *45*, 6129, (e): Rochette, É.; Bouchard, N.; Légaré Lavergne, J.; Matta, C. F.; Fontaine, F.-G. *Angew. Chem. Int. Ed.* **2016**, *55*, 12722

[153] Légaré, M.-A.; Courtemanche, M.-A.; Rochette, É.; Fontaine, F.-G. *Science.* **2015**, *349*, 513

[154] (a): Rochette, É.; Boutin, H.; Fontaine, F.-G. *Organometallics.* **2017**, (b): Rochette, É.; Courtemanche, M.-A.; Fontaine, F.-G. *Chem. – Eur. J.* **2017**, *23*, 3567

[155] Wang, T.; Kehr, G.; Liu, L.; Grimme, S.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2016**, *138*, 4302

[156] Holtrichter-Rößmann, T.; Rösener, C.; Hellmann, J.; Uhl, W.; Würthwein, E.-U.; Fröhlich, R.; Wibbeling, B. *Organometallics.* **2012**, *31*, 3272

[157] Power, P. P. *Nature.* **2010**, *463*, 171

[158] Stephan, D. W. *J. Am. Chem. Soc.* **2015**, *137*, 10018

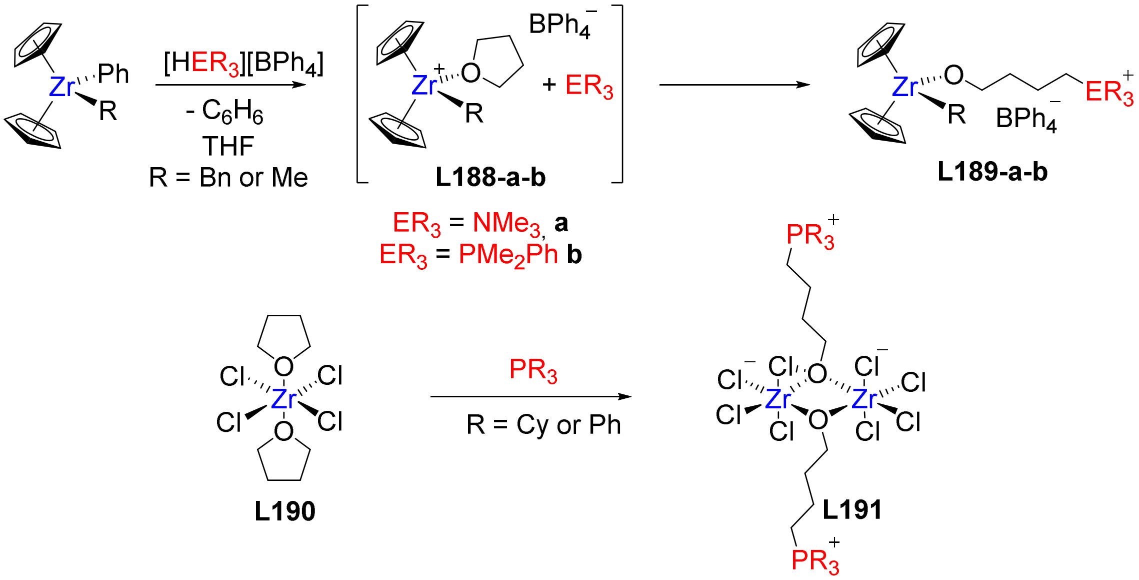
[159] Erker, G. *Dalton Trans.* **2011**, *40*, 7475

[160] (a): Wass, D. F.; Chapman, A. M.In *Frustrated Lewis Pairs II* Topics in Current Chemistry Springer, Berlin, Heidelberg 2013 pp 261–280, Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 18463, Flynn, S. R.; Wass, D. F. *ACS Catal.* **2013**, *3*, 2574

[161] Lehnert, W. *Tetrahedron.* **1974**, *30*, 301

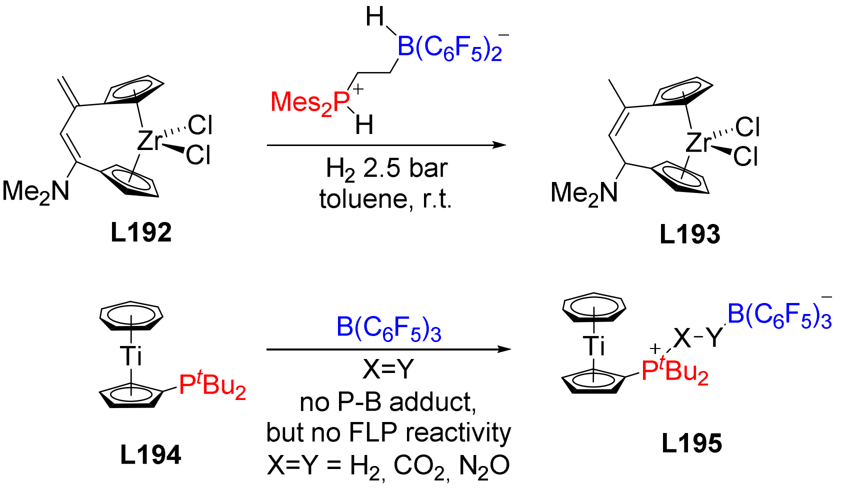
[162] Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics.* **1991**, *10*, 1268

reaction by starting with the THF adduct **L190** and formed **L191** by using a tertiary phosphine (Scheme I-61 down),[163] this was also observed in 1997 by Polamo.[164]



Scheme I-61: organometallic chemistry related to FLP chemistry

Following the emergence of FLP concept, two categories of group 4-based OmFLPs were designed. The first is composed of examples in which the metallocene fragment is a platform on which FLP reactivity occurs, but without involving necessarily the metal centre. Erker designed three zirconocenes of this type; the first has already been described in Scheme I-28. Compound **L80** was used in combination with $B(C_6F_5)_3$ to hydrogenate imines on the metallocene fragment.[58] In 2010 Erker described the hydrogenation of the enamino zirconocene **L192** by the organic FLP **L164** in presence of dihydrogen to form **L193** (Scheme I-62).[165]



Scheme I-62: Zr or Ti based complexes: potential platforms for FLP chemistry

---

[163] Breen, T. L.; Stephan, D. W. *Inorg. Chem.* **1992**, *31*, 4019

[164] Polamo, M.; Mutikainen, I.; Leskelä, M. *Acta Crystallogr. Sect. C.* **1997**, *53*, 1036

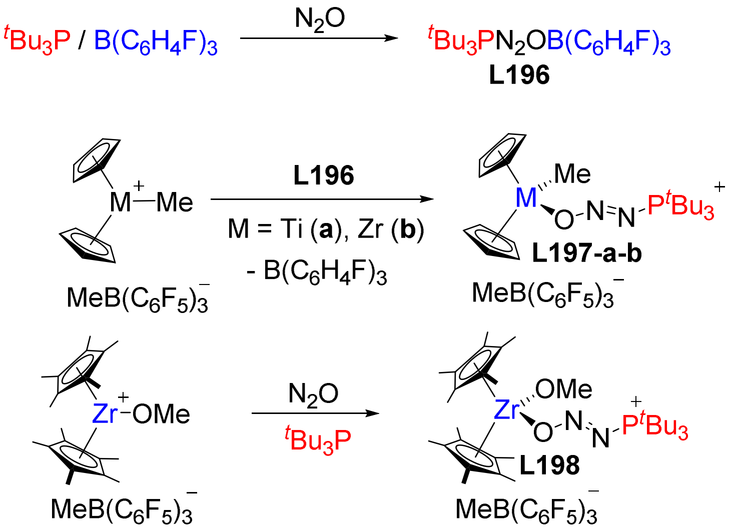
[165] Schwendemann, S.; Tumay, T. A.; Axenov, K. V.; Peuser, I.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics.* **2010**, *29*, 1067

On the other hand, a troticenyl phosphane was combined with $B(C_6F_5)_3$ by Tamm in 2015 to activate H_2, CO_2 and N_2O. The progress of these reactions was followed by a colorimetric detection.[166]

The second category is based on the use of the metal as a Lewis partner. As with organic FLPs, two strategies were employed to obtain these OmFLPs as intra- or intermolecular pairs.

a. Intermolecular OmFLPs

Early OmFLPs of this type have already been described in Scheme I-61, even if these examples were developed before the introduction of the concept of FLP. Stephan described the first N_2O addition product containing a group 4 metal.[167] By using a preactivated N_2O with an organic FLP **L196**, the possibility to exchange the Lewis acid by a cationic methyltitanocene or zirconocene to form **L197-a-b** respectively was shown by Stephan. Whilst all attempts at forming this adduct directly with the combination of P^tBu_3 and the corresponding cationic metallocene failed, combination of $[Cp^*_2ZrOMe][B(C_6F_5)_4]$ with P^tBu_3 was able to bind N_2O to form **L198** (Scheme I-63). This example highlights the importance of managing the acidity of the cationic metallocene, to use it as a Lewis partner. A similar example involving CO_2 was later reported.[168]



Scheme I-63: FLP exchange and first OmFLP reactivity

In 2016 Wass described the combination of cationic zirconocenes with phosphines (Scheme I-64).[169] Modification of the steric and electronic properties of these pairs enabled

---

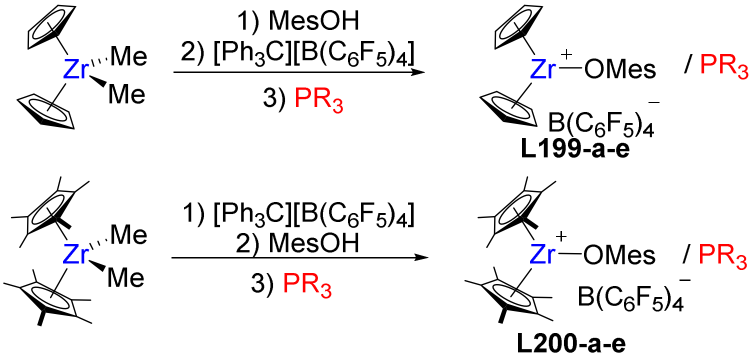
[166] Theuergarten, E.; Tagne Kuate, A. C.; Freytag, M.; Tamm, M. *Isr. J. Chem.* **2015**, *55*, 202

[167] Neu, R. C.; Otten, E.; Lough, A.; Stephan, D. W. *Chem. Sci.* **2011**, *2*, 170

[168] Neu, R. C.; Ménard, G.; Stephan, D. W. *Dalton Trans.* **2012**, *41*, 9016

[169] Metters, O. J.; Forrest, S. J. K.; Sparkes, H. A.; Manners, I.; Wass, D. F. *J. Am. Chem. Soc.* **2016**, *138*, 1994

FLP reactivity. For example, **L200-a-b** displayed no Zr/P interaction and are able to split D_2 quantitatively. Besides, **L199-e** and **L200-e** were OmFLPs in terms of frustration since no Zr/P interactions were observed; despite this, they were found to be completely unreactive towards any of the tested substrates. Surprisingly **L199-a** and **L199-b**, which showed strong Zr/P interactions, were able to activate CO_2, THF and phenylacetylene but were inert towards D_2.



PR_3 = **a** R = Cy, **b** R = Et, **c** R = Ph, **d** R = Mes, **e** R = C_6F_5

Scheme I-64: intermolecular OmFLPs from Wass

This highlights again the complexity of FLP chemistry: indeed, frustration is not always required for small molecule activation, as long as a pre-equilibrium exists between the Lewis adduct and its components. In another study, Wass used cationic zirconocene **L199** in combination with an imine and showed its activity in catalytic hydrogenation as Stephan did with $B(C_6F_5)_3$ (Scheme I-55). Surprisingly, the bulkier **L200** was completely inactive in catalytic hydrogenation most probably due to excessive steric hindrance at the metal centre. A series of analogous cationic zirconocenes were designed and tested towards hydrogenation of imines. It was found that the most sterically hindered and most electron rich bis(indenyl)zirconocene were the best catalyst of this study which remained limited to sterically hindered imines.[170]

b. Intramolecular OmFLPs

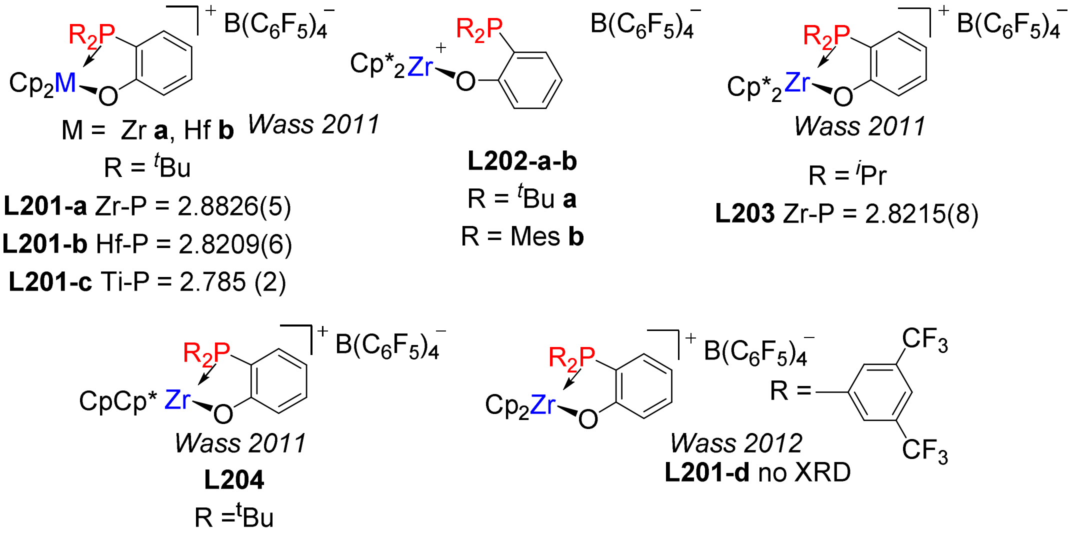
Several examples of intramolecular group 4 metal OmFLPs have been reported over the last decade. Early examples were reported by Wass in 2011: a phosphinophenate was grafted onto a metallocene fragment.[171] Coordination of the phosphine to zirconium is observed with Cp-based metallocenes (**L201-a-b-c, L203**), whilst Cp*-based complexes prevent coordination (**L202-a-b**). Likewise, mixed Cp/Cp* complexes containing relatively compact phosphane moiety displayed a Zr/P interaction. The potential of these compounds to act as OmFLPs was evaluated through their ability to activate H_2. Compounds **L202-a-b** are able to split H_2 quantitatively whereas **L201-a-c** do not react. More surprisingly, Zr compounds

---

[170] Flynn, S. R.; Metters, O. J.; Manners, I.; Wass, D. F. *Organometallics.* **2016**, *35*, 847

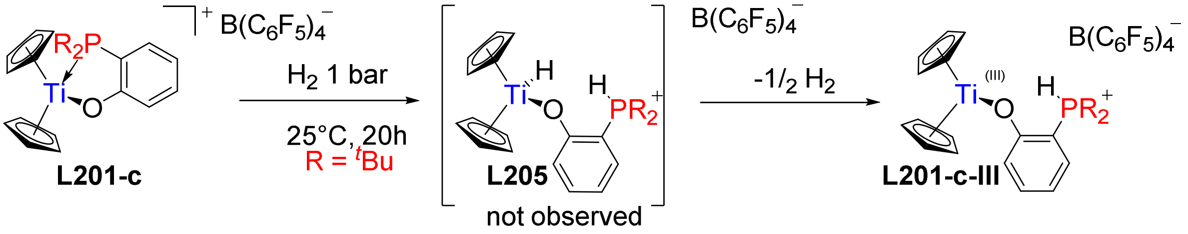
[171] Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 8826

L203 and **L204,** which are not frustrated, reacted as OmFLPs and were able to split H_2 too. Otherwise, the study of analogous titanocenes compounds gave unexpected results.



Scheme I-65: intramolecular phenate-based OmFLPs from Wass group

Thus, **L201-c** is able to split H_2 to form intermediately the phosphonium titanium hydride species **L205**. Ti-H bond are prone to rapid homolytic cleavage to form Ti (III) species along with H_2. In the case of Wass, this reduction process was revealed by crystallization of **L201-c-III** (Scheme I-66).[172]



Scheme I-66: Reactivity of 201-c towards dihydrogen

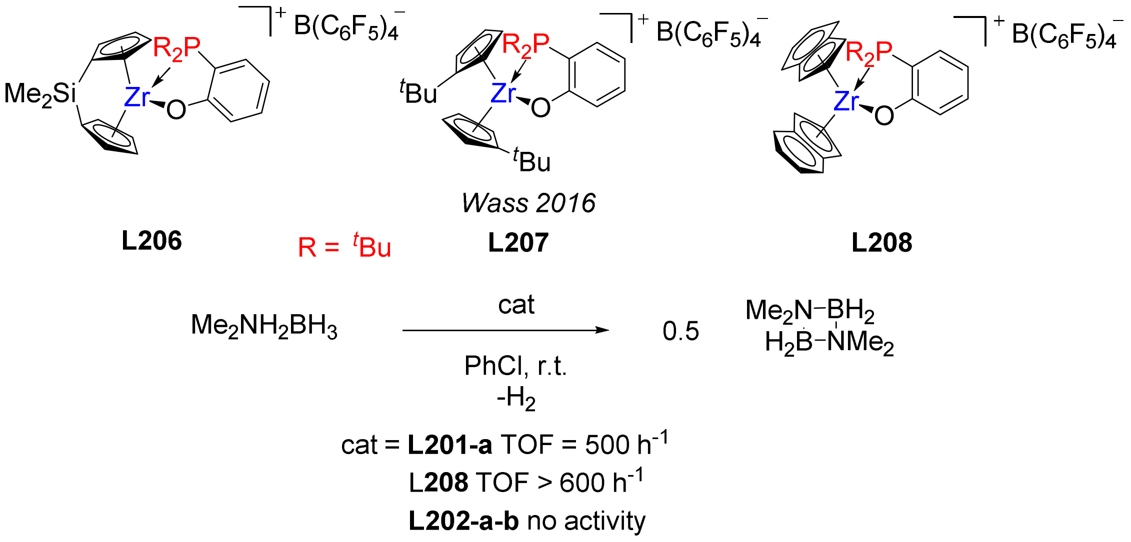
This work extended again the field of investigations to OmFLPs in which the “frustrated” character is not a requirement to observe FLP reactivity. The FLP reactivity of this series was mainly successful with **L202-a** for the activation of small molecules such as CO_2, alkenes, alkynes or THF; C-X bond cleavage (X = Cl, F, O), or CO and CO_2 reduction were also observed.[173]

Some of these complexes exhibited catalytic activity for the dehydrocoupling of dimethylamine borane. In a preliminary study, complex **L201-a** was more active than its Hf or Ti analogues **L201-b-c** respectively, whilst surprisingly, **L202-a** showed no activity (Scheme I-67).

---

[172] Chapman, A. M.; Wass, D. F. *Dalton Trans.* **2012**, *41*, 9067

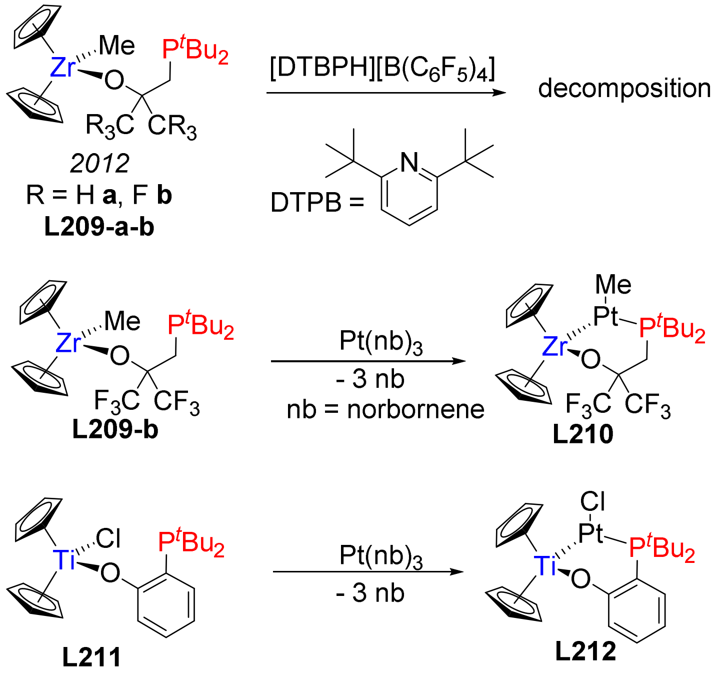
[173] Chapman, A. M.; Haddow, M. F.; Wass, D. F. *J. Am. Chem. Soc.* **2011**, *133*, 18463



Scheme I-67: catalytic dehydrocoupling of dimethylamine borane with various Zr-based OmFLPs

To better understand this mechanism, Wass designed new zirconocenes with a less basic phosphine with **L201-d** which was completely inactive; or less bulky Cp-based complexes with the last series **L206-L208.** The best candidate of this work was **L208,** which contained a basic phosphanyl group with an indenide-based metallocene fragment with a TOF > 600 h^{-1}.[174]

Wass also described (phosphinoalkoxy)zirconocenes[175] but this series was not stable enough in its cationic form to be used as OmFLPs as described in the previous series. Nevertheless, an interesting reactivity was observed in which the Zr/P **L209-b** binds to a platinum complex to form **L210** after methyl ligand migration to platinum (Scheme I-68).



Scheme I-68: new Early-Late heterobimetallic complexes with OmFLPs precursors

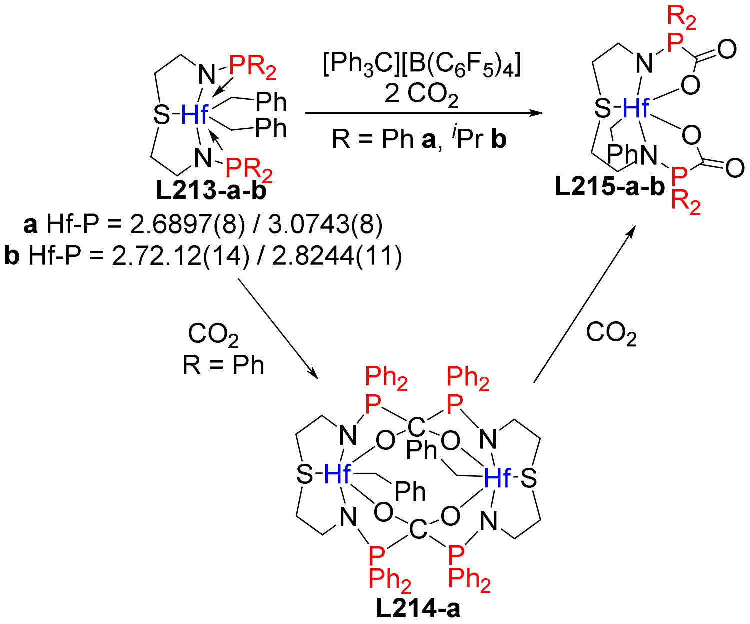
---

[174] Metters, O. J.; Flynn, S. R.; Dowds, C. K.; Sparkes, H. A.; Manners, I.; Wass, D. F. *ACS Catal.* **2016**, *6*, 6601

[175] Chapman, A. M.; Flynn, S. R.; Wass, D. F. *Inorg. Chem.* **2016**, *55*, 1017

To explore the limits of this unexpected reactivity, a chloro titanium-based precursor, **L211** was reacted as **L209-b** to form the unusual Early-Late heterobimetallic complex **L212.**[176]

A rare example of an Hf-based OmFLP was described in 2013 by Stephan (Scheme I-69).[177]



Scheme I-69: an Hf-based OmFLP

Compounds **L213-a-b** were able to bind two molecules of CO_2 to form **L215-a-b**. In the case of PPh_2 an intermediate was crystallized as a dimer (**L214-a**), which subsequently activated one more molecule of CO_2 to form **L215-a** (Scheme I-69).

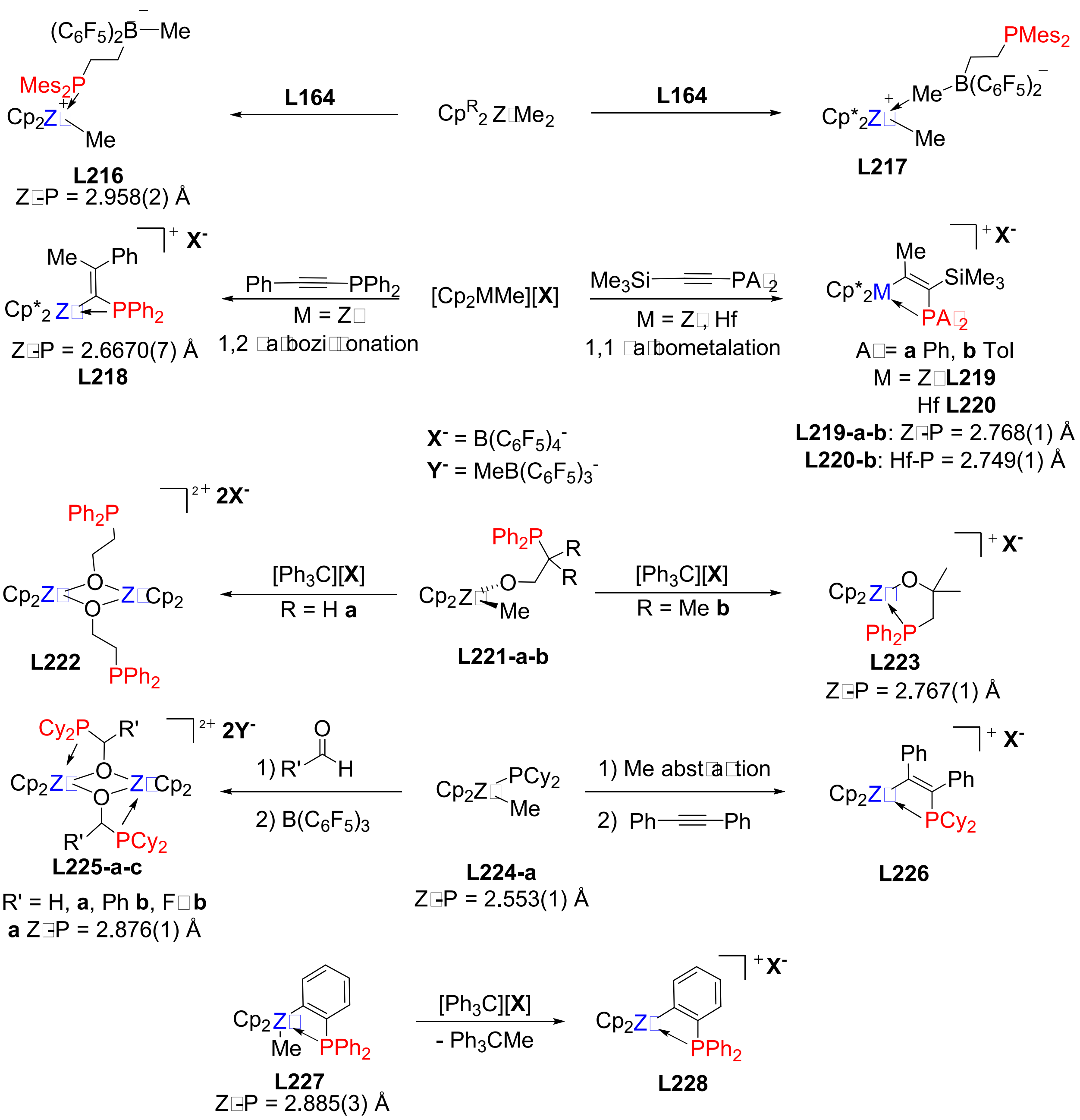
Numerous examples of zirconocene-based OmFLPs were described by Erker. Between 2013 and 2016, intramolecular P/Zr^+ OmFLPs, with different kinds of spacers, were described and are summarized in Scheme I-70. The zwitterionic species **L216** and **L217** were obtained by treating the already described organic FLPs **L164** with the corresponding dimethylziroconocene.[178] In the Cp_2 parent, methide is completely abstracted from the Zr centre and a Zr-P adduct formed, whilst coordination of $PMes_2$ is prevented with Cp^* ligands. Instead, the cationic zirconocenium complex was stabilized by electrostatic interactions with the B-CH_3 moiety. Nevertheless, both compounds were shown to act as OmFLPs.

---

[176] Chapman, A. M.; Flynn, S. R.; Wass, D. F. *Inorg. Chem.* **2016**, *55*, 1017

[177] Sgro, M. J.; Stephan, D. W. *Chem. Commun.* **2013**, *49*, 2610

[178] Frömel, S.; Kehr, G.; Fröhlich, R.; Daniliuc, C. G.; Erker, G. *Dalton Trans.* **2013**, *42*, 14531



Scheme I-70: P/Zr⁺ OmFLPs from Erker

Via a controlled 1,1 or 1,2 carbometalation of alkynes with cationic hafnio- or zirconocene, vicinal or geminal P/Zr⁺ OmFLPs were synthesized in a very convenient fashion (compounds **L218, L219** and **220** respectively).[179a,b,180a,b] Two other geminal OmFLPs were designed. **L228** was obtained by methide abstraction from **L227** whilst **L226** was obtained by reacting phosphidozirconocene **L224** with diphenylacetylene.[181,182] Carbonyl insertion in the

---

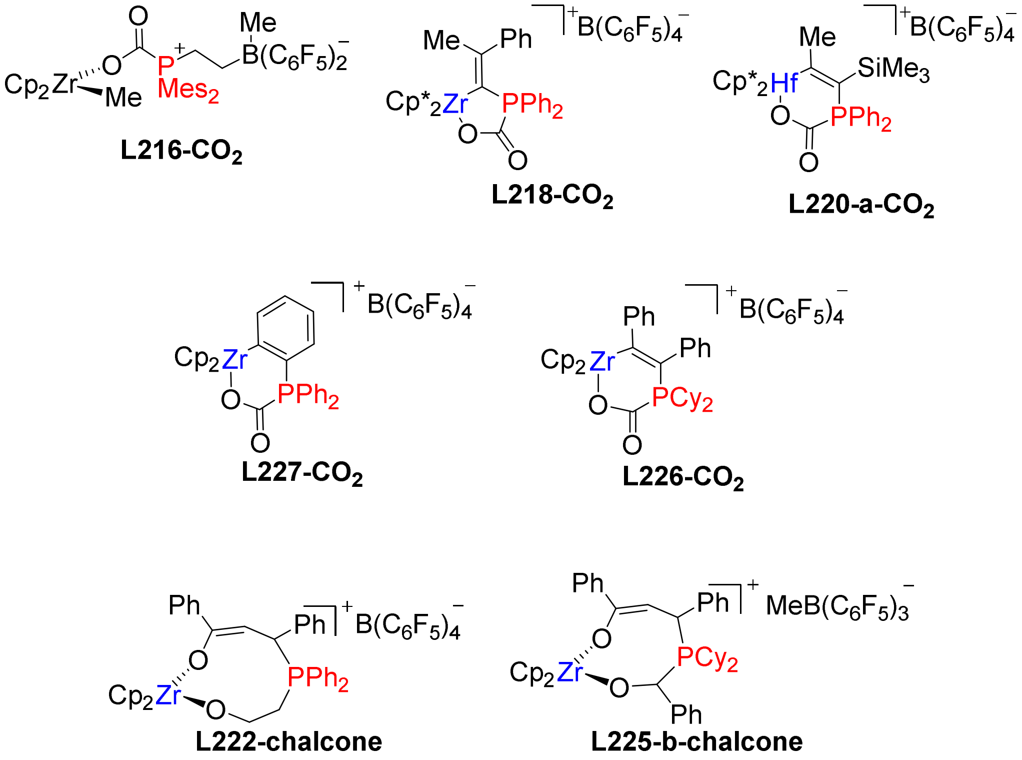
[179] (a): Xu, X.; Fröhlich, R.; Daniliuc, C. G.; Kehr, G.; Erker, G. *Chem. Commun.* **2012**, *48*, 6109, (b): Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2013**, *135*, 6465

[180] (a): Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2014**, *136*, 12431, (b) *Angew. Chem. Int. Ed.* **2013**, *52*, 13629

[181] Jian, Z.; Daniliuc, C. G.; Kehr, G.; Erker, G. *Organometallics.* **2017**, *36*, 424

[182] Normand, A. T.; Daniliuc, C. G.; Wibbeling, B.; Kehr, G.; Le Gendre, P.; Erker, G. *J. Am. Chem. Soc.* **2015**, *137*, 10796

Zr-P of **L224** was a straightforward route to form OmFLPs too.[183] These complexes were characterized as μ–alkoxy dimer, but were able to activate chalcone after dissociation. A similar dimer was also obtained after methide abstraction from **L221-a** forming **L222.**[184] Dimerization was prevented by increasing the bulk around oxygen as illustrated by **L223**. In all these examples, a relatively elongated Zr-P bond was observed (between 2.6670(7) and 2.958(2)Å). It can be compared to the distance of a single covalent Zr-P bond (2.82 ± 0.10 Å) estimated empirically from the analysis of X-ray diffraction data.[185] FLP reactivity was observed towards small molecules such as CO_2, or substrate such as aldehydes or chalcone. Several example of FLP adducts with CO_2 and chalcone are depicted in Scheme I-71.



Scheme I-71: FLP adducts with CO_2 and chalcone

Whilst numerous examples of P/Zr$^+$ OmFLPs have been described in the literature, N/Zr$^+$ OmFLPs are much rarer. To the best of our knowledge, Erker reported the only example in 2015. This pair was able to activate dichloromethane, primary alkynes, and H_2 (e.g. **L231**, **L232-a-b** or **L233** respectively). Noteworthy, complex **L230** was able to catalytically hydrogenate alkenes and alkynes in mild conditions (Scheme I-72).[186]

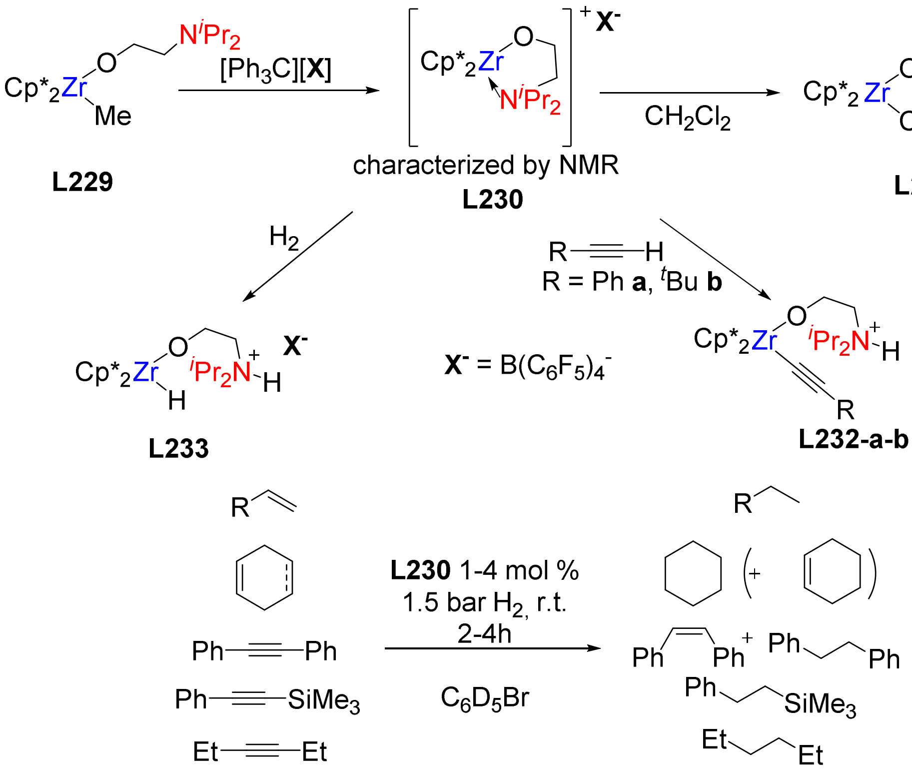
---

[183] Normand, A. T.; Daniliuc, C. G.; Wibbeling, B.; Kehr, G.; Le Gendre, P.; Erker, G. *Chem. – Eur. J.* **2016**, *22*, 4285

[184] Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *Organometallics*. **2015**, *34*, 2655

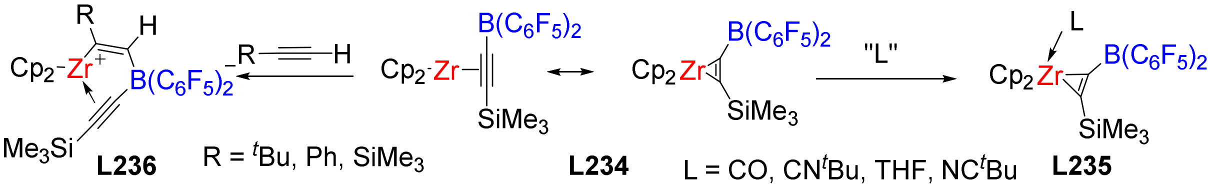
[185] Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832

[186] Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2015**, *137*, 4550



Scheme I-72: N/Zr⁺ OmFLP

Interestingly, whereas in the last examples reported above, the zirconium centre was used in its cationic form and reacted as a Lewis acid, Erker has described a Zr(II)/B system (**L234**) in which the zirconium (II) was found to react as the Lewis base.[187]. In this example, compound **L234** must be considered according to its limit form as a Zr(II) / alkyne complex (Scheme I-73).



Scheme I-73: an unusual Zr(II)/B OmFLP

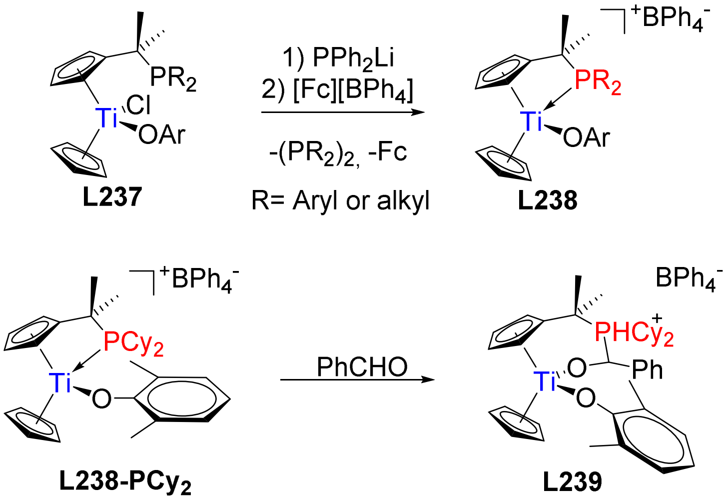
In this example, two different types of reactivity were observed depending on the substrate treated with **L234**. When the substrate was a single site donor, it was shown to act as a L-ligand, and stabilized the metallacyclopropene form (**L235** Scheme I-73 right). If the substrate was an alkyne, the Zr(II) / B pair was active and yielded the activated compound **L236** (Scheme I-73 left). The activation of H_2 was also observed and DFT calculation were conducted to determine that the more plausible mechanism implied an FLP reactivity.[188]

---

[187] Kumar Podiyanachari, S.; Kehr, G.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2013**, *135*, 17444

[188] Podiyanachari, S. K.; Fröhlich, R.; Daniliuc, C. G.; Petersen, J. L.; Mück-Lichtenfeld, C.; Kehr, G.; Erker, G. *Angew. Chem. Int. Ed.* **2012**, *51*, 8830

Interestingly only two examples of Ti-based OmFLP have been reported in the literature. The first one has already been described in Scheme I-66. The other one was reported by Erker and Le Gendre and consisted of a cationic titanocene fragment with a pendant phosphane. As Wass has already mentioned in 2012, titanium is more easily reduced than Zr and Hf due to lower-lying 3d orbitals.[189] This was the key to the reactivity of **L201-c** where the H_2 activation product was not stable due to Ti-H bond homolysis, which yielded a Ti(III) species. The reducibility of Ti was exploited in the synthesis of P/Ti$^+$ FLPs as illustrated in Scheme I-74. Thus, various complexes of type **L237** were converted to OmFLPs in a two-step reduction/oxidation sequence. Although an interaction between P and Ti$^+$ and no reactivity with classical gaseous substrates were observed in these complexes, FLP behaviour was demonstrated with benzaldehyde and forming **L239**. In this study, electronic and steric properties of both the phosphanyl group and the phenoxy ligand were investigated. Compound **L238-PCy$_2$** exhibited the best conditions of this series to activate a small molecule such as benzaldehyde (Scheme I-74).[190]



Scheme I-74: Ti-based OmFLP reported by Erker and Le Gendre

In light of these findings in FLP chemistry (organic or organometallic), many partners can be used to activate small molecules. Even if at first, frustration was a *sine qua non* condition to obtain reactivity, numerous examples have shown that some degree of interaction between the Lewis acid and Lewis base partners is not necessarily detrimental to reactivity. The bibliographic survey on group 4 OmFLPs showed that few examples of N-based or Ti-based OmFLPs are described in the literature. This bring us to the first chapter of this thesis, and the synthesis of potential N/Ti$^+$ or N/Zr$^+$ OmFLPs.

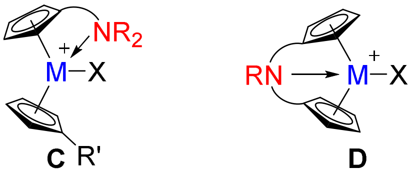
---

[189] Jean, Y.; Marsden, C. T. by: Molecular Orbitals of Transition Metal Complexes Oxford University Press: Oxford, New York 2005

[190] Normand, A. T.; Richard, P.; Balan, C.; Daniliuc, C. G.; Kehr, G.; Erker, G.; Le Gendre, P. *Organometallics*. **2015**, *34*, 2000

II. Chapter I: Synthesis of potential group 4 OmFLP precursors

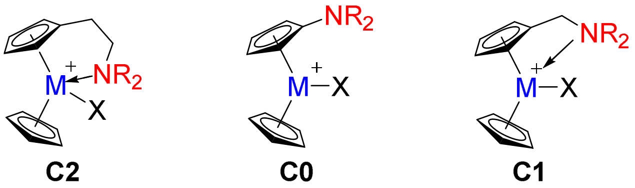
As previously described in the bibliographic introduction, group 4 transition metals have been used in the form of cationic metallocenes to act as Lewis acids in OmFLPs.[1a,b,c,d] In the present work, we propose to use an amine as the Lewis base partner. Two different strategies could have been followed: developing an intermolecular pair, or designing new intramolecular objects. The latter option has been chosen for this work. The general structures of the targeted complexes are composed of a cationic group 4 metallocene as Lewis acid, whilst the role of the Lewis base will be played by an amine grafted onto one of the cyclopentadienyl ring. These general structures are depicted in Scheme II-1.



R = alkyl groups
X = remaining X-ligand bound to the metal
R' = potential secondary functionality (e.g. phosphine, amine, alkyl groups, H)

Scheme II-1: illustration of targeted complexes

As shown before by Jutzi and others, two-carbon spacers or longer (e.g. in Scheme I-41) generally lead to coordination polymers or in some cases intramolecular coordination of the amine function to the metal centre (general structure of type **C2** Scheme II-2).



Scheme II-2: choice of the length of the spacer on the Cp ring

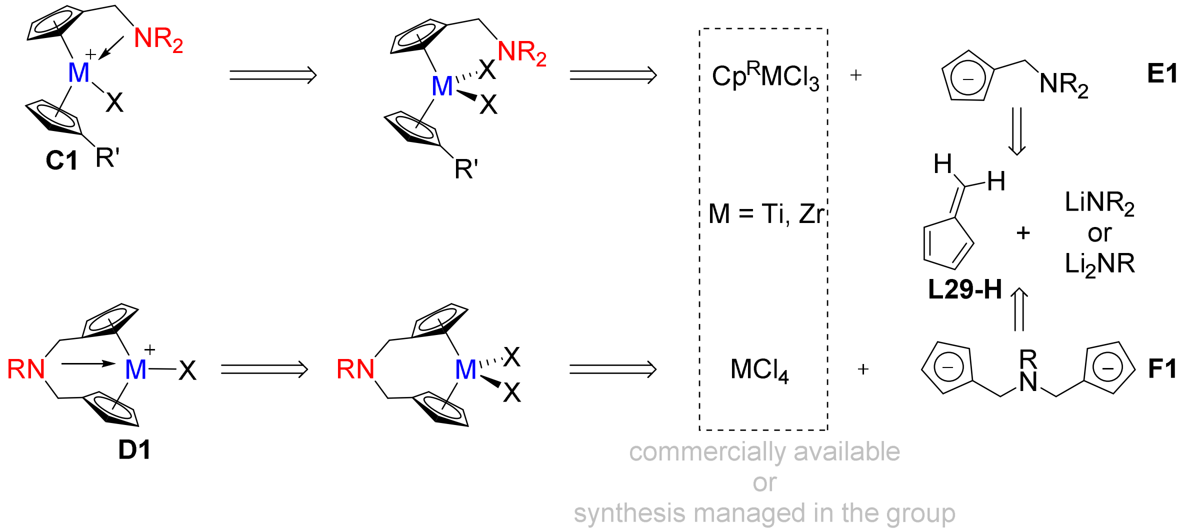
Incorporating an amine directly connected to the Cp ring without any spacer (**C0**) would completely prevent any interaction between both Lewis partner. The only possibility for such compounds to form Lewis pairs would be in an intermolecular manner, yielding dimeric species in which the interaction might be too strong. For effective FLP reactivity, the amine ligand would have to show at least some degree of hemilability; hence the choice of a CH_2 spacer, which should disfavour tight binding of the amine to titanium, whilst being flexible enough to activate a variety of substrates. This type of spacer (more generally one atom between the Cp ring and

---

[1] See for example: (a): Chapman, A. M.; Haddow, M. F.; Wass, D. F. *Eur. J. Inorg. Chem.* **2012**, 2012, 1546, (b): Xu, X.; Kehr, G.; Daniliuc, C. G.; Erker, G. *J. Am. Chem. Soc.* **2014**, 136, 12431, (c): *J. Am. Chem. Soc.* **2015**, 137, 4550, (d): Metters, O. J.; Forrest, S. J. K.; Sparkes, H. A.; Manners, I.; Wass, D. F. *J. Am. Chem. Soc.* **2016**, 138, 1994

the amide function) has already been employed for the design of constrained geometry complexes (CGc). The constraint is reflected by the bite angle of the (aminomethyl)cyclopentadienide ligand which is smaller than in comparable unbridged complexes.

With the general structure C1 in mind, the retrosynthetic Scheme II-3 leads us to the synthesis of (aminomethyl)cyclopentadienides or bis(cyclopentadienidemethyl)amines of type **E1** and **F1** respectively. It required formally the use of fulvene **L29-H** with a primary or secondary amide (*vide supra*, I.B.1).



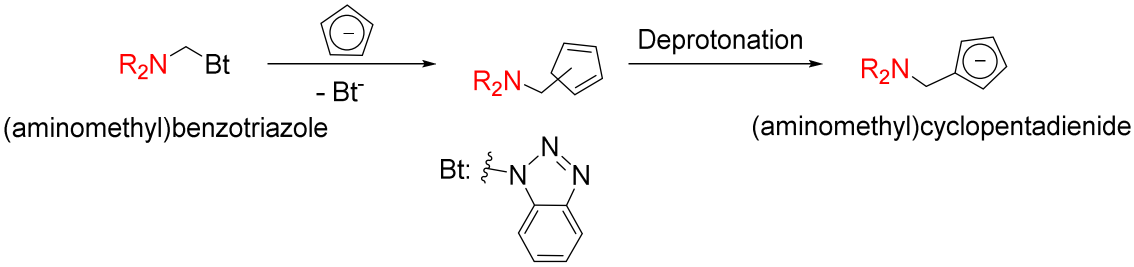
Scheme II-3: retrosynthetic scheme envisaged initially for the synthesis of aminomethyl-group 4-metallocenes

However **L29-H** is known to be difficult to handle due to its propensity to easily dimerise. It has to be used freshly and kept away from oxygen and heat.[2] The use of, e.g. 6,6-dimethylfulvene is proscribed, since the basic amides required for FLP reactivity would deprotonate the fulvene (*vide* supra, Scheme I-12) instead of adding to it. In addition, the use of the aminomethynylation route described by Kreutzberg (Scheme I-19), would be unfavoured. Indeed, in this case, the use of basic amines as nucleophiles is required. However, bulky amines as TMPH or diisopropylamine, required for this approach, are known to be poor nucleophiles.

An alternative route to (aminomethyl)cyclopentadienides has been envisioned by using (aminomethyl)benzotriazoles as starting material (Scheme II-4), in order to circumvent the use of **L29-H.** The use of benzotriazole derivatives will be explained in the following section.

---

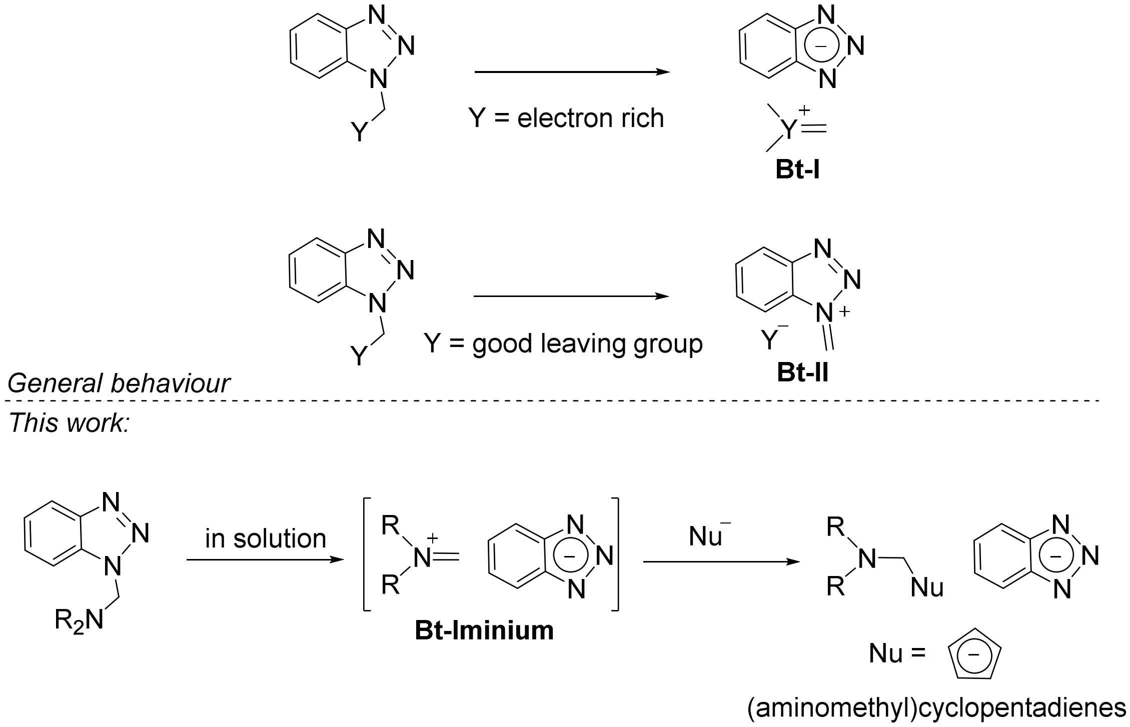
[2] Sturm, E.; Hafner, K. *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 749



Scheme II-4: synthetic route developed for (aminomethyl)cyclopentadienides

A. Synthesis of (aminomethyl)cyclopentadienides

The chemistry of benzotriazole (Bt-H) was widely investigated by Katritzky,[3] in the 1990s and has been a useful tool in organic chemistry. The Bt group was shown to behave differently depending on the nature of the Y-group in the α-position (Scheme II-5).



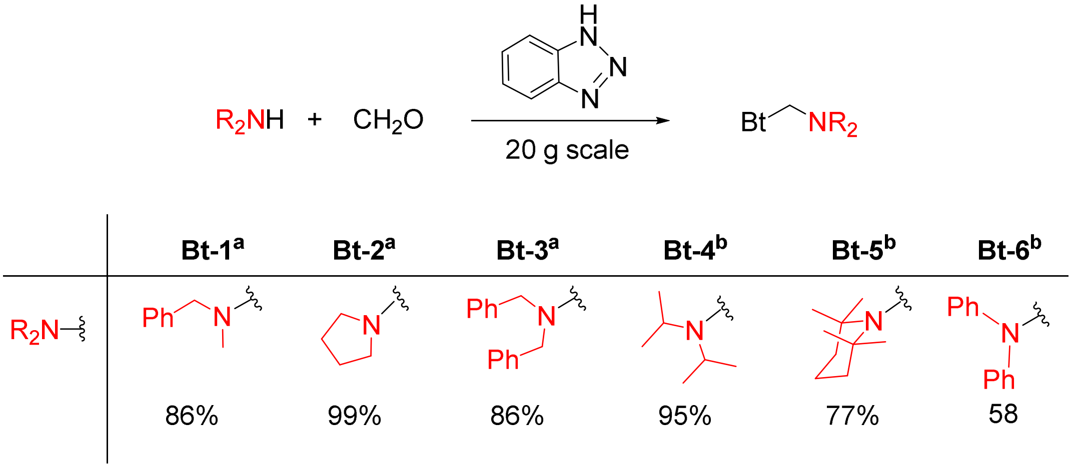
Scheme II-5: Behaviour of the benzotriazole group and synthetic strategy

If Y is electron rich, Bt will act as a good leaving group and form **Bt-I** in which the negative charge is well stabilized by the Bt system; whilst it will act as an electron donor if Y is a good nucleofuge and form **Bt-II**. In the case of (aminomethyl)benzotriazoles, **Bt-I** species was shown to prevail and to be in equilibrium with the iminium salt in solution (**Bt-Iminium**). Therefore, the Bt group may act as a leaving group in the reaction of (aminomethyl)benzotriazoles with the cyclopentadienide anion, as illustrated in Scheme II-5, forming (aminomethyl)cyclopentadienes.

---

[3] Katritzky, A. R.; Lan, X.; Yang, J. Z.; Denisko, O. V. *Chem. Rev.* **1998**, *98*, 409

This work started with the synthesis of desired (aminomethyl)benzotriazoles according to Katritzky's work.[4a,b] The benzotriazole derivatives **Bt-1-3** were synthesized by refluxing 6h in a mixture of diethyl ether and methanol, and further recrystallized as white crystals. The synthesis of **Bt-4-6** required harsher conditions, i.e. refluxing in toluene with a Dean-Stark apparatus. Both **Bt-4** and **Bt-5** were moisture sensitive and had to be stored under inert atmosphere as a light-yellow oil for the former and a white precipitate for the latter. These compounds were generally obtained in very good yields as described in the literature (Scheme II-6, 86-99%).



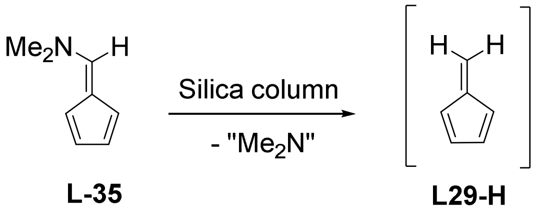
Scheme II-6: synthesis of (aminomethyl)benzotriazoles. ^{a}: refluxing Et$_2$O/Methanol 12h, ^{b}: Dean Stark apparatus, refluxing toluene 1h.

The proof of concept for the synthesis of related (aminomethyl)cyclopentadienides had to be obtained. With this goal in mind, reaction conditions were optimized with **Bt-1**. An homogeneous reaction was first tried in THF by cannulating **Bt-1** onto a solution of CpNa (1eq.) in THF at -25°C. The resulting solution became rapidly dim and yellowish. The reaction was followed by TLC (eluent 1:1 diethyl ether: pentane with several drops of methanol; stationary phase: silica) and GCMS. Whilst **Bt-1** exhibited a low migration (retention factor ~ 0.2) the desired diene **1-H** was observed almost in the solvent front. After 2 hours of stirring at room temperature, no more changes were observed by TLC and the residual **Bt-1** was still observed. All attempts at purification by column chromatography failed, yielding decomposition of the diene. This was in fact most probably due to the sensitivity of the diene towards silica. In fact, Trost described the synthesis of **L29-H** by degradation of **L35** on a silica column (Scheme II-7).[5]

---

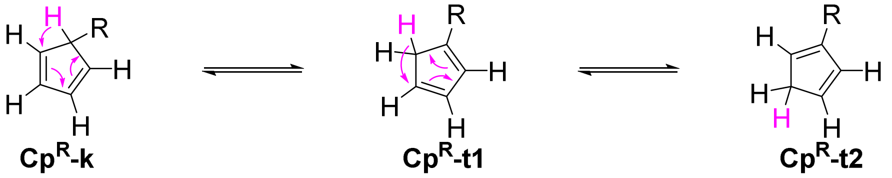
[4] (a): Katritzky, A. R.; Rachwal, S.; Rachwal, B. *J. Chem. Soc. Perkin vol 1.* **1987**, 799, (b): Katritzky, A. R.; Yannakopoulou, K.; Lue, P.; Rasala, D.; Urogdi, L. *J. Chem. Soc. Perkin vol 1.* **1989**, 225

[5] Trost, B. M.; Cory, R. M. *J. Org. Chem.* **1972**, *37*, 1106



Scheme II-7: decomposition process of L-35 described by Trost

With this information in hands, a heterogeneous synthesis was envisioned, in order to effect complete conversion of **Bt-1** with an excess of CpNa. For this purpose, 1.2 eq of CpNa was used, and the resulting suspension in Et_2O was refluxed for 12 hours. Analysis of the reaction mixture by TLC and GCMS revealed almost quantitative conversion of **Bt-1** into **1-H**. After filtration over a frit, and washing with Et_2O (see supporting information for details), **1-H** was isolated as a yellow oil, obtained after careful evaporation (25°C, mild vacuum). The ^1H NMR spectrum (300 MHz, 300 K, dichloromethane-d_2) of this oil showed a complex mixture of isomers. Monofunctionalized cyclopentadienes are known to exist as three isomers, as illustrated in Scheme II-8, due to [1,5] sigmatropic rearrangement of hydrogen.[6] The first form **Cp^R-k** is the kinetic form, known to rapidly be converted into the two thermodynamic forms **Cp^R-t1** and **Cp^{R}t2**.

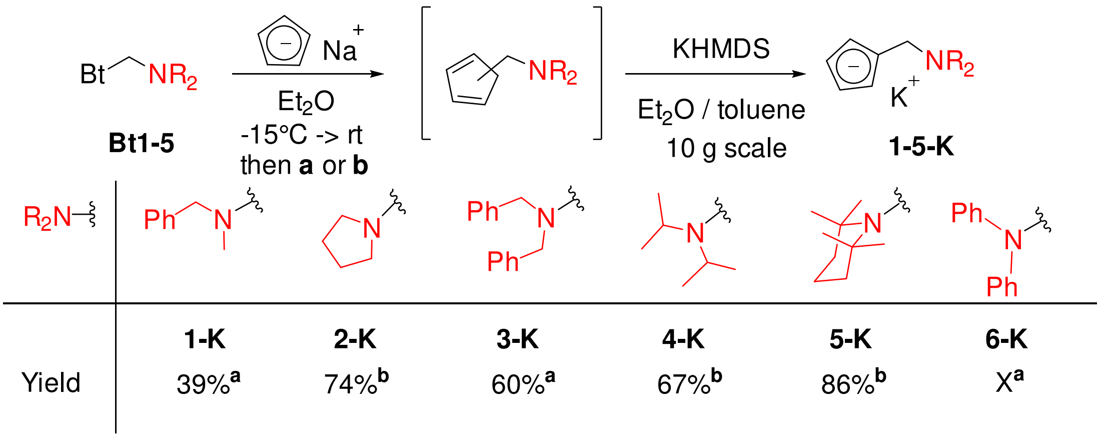


Scheme II-8: [1,5] sigmatropic rearrangement on a monosubstituted cyclopentadiene

The purity of the diene was checked by TLC and it was used freshly for deprotonation. Initial attempts at deprotonation with *n*-BuLi (THF, 0°C) yielded **1-Li**, however this compound was difficult to purify because of its oily nature. In order to circumvent this problem, the synthesis of **1-K** by deprotonation with potassium hexamethyldisilazane (KHMDS) was envisaged. After treatment of an etheral solution of **1-H** with KHMDS 1M in toluene at 0°C, followed by 2h of stirring at room temperature, a light brown precipitate formed. After filtration, washing and drying *in vacuo,* the desired product **1-K** was obtained as a beige powder. This procedure was successfully applied to **Bt-3**, whilst **Bt-6** was not converted and mainly yielded decomposition or starting material. The lone pair of the nitrogen atom, which is required for the iminium equilibrium depicted in Scheme II-5, may be partially delocalized into the phenyl rings, which could disfavour the reaction. Noteworthy, **Bt-2-4-5** did not require the refluxing period and were completely converted within 4h of stirring at room temperature, yielding **1-5-K** in moderate to good yield in a two-step synthesis (39-79% overall yield - Scheme II-9).

---

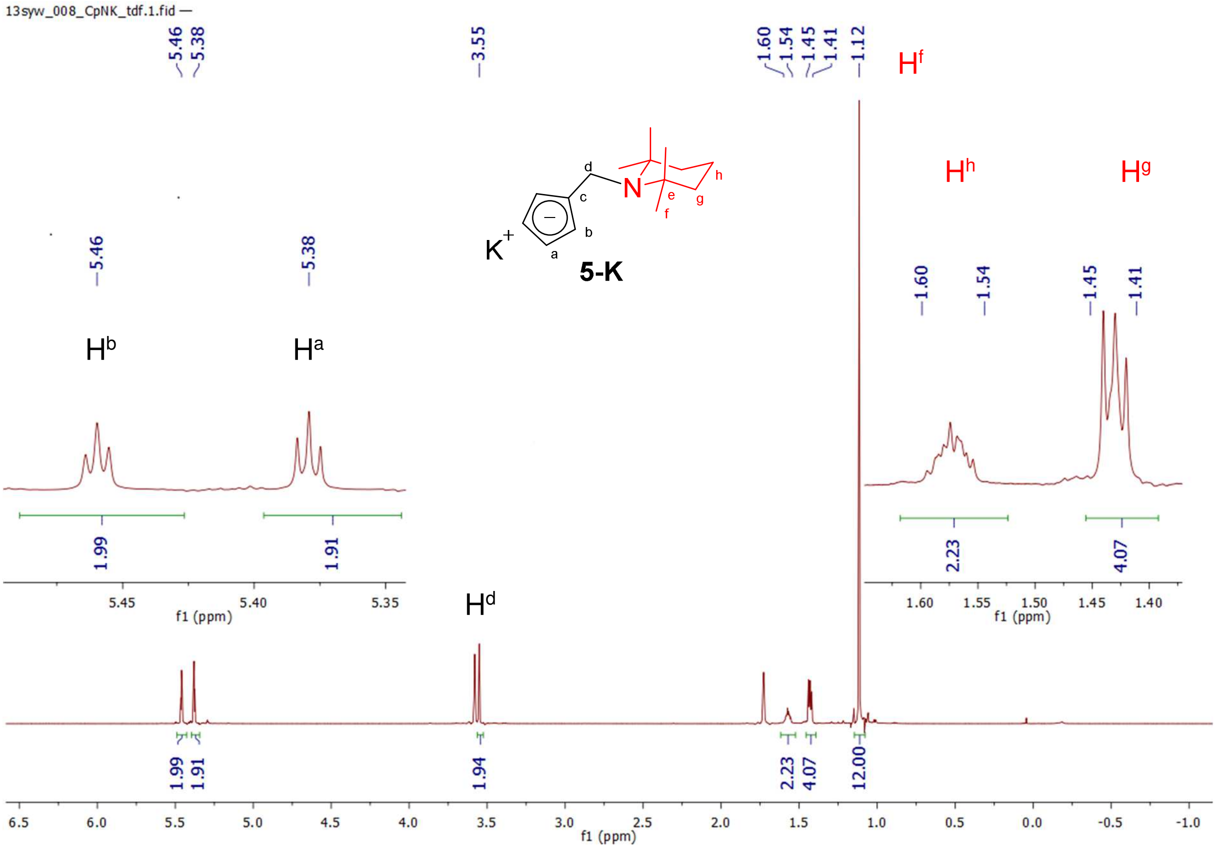
[6] McLean, S.; Haynes, P. *Tetrahedron*. **1965**, *21*, 2329



	1-K	2-K	3-K	4-K	5-K	6-K
Yield	39%[a]	74%[b]	60%[a]	67%[b]	86%[b]	X[a]

Scheme II-9: synthesis of potassium (aminomethyl)cyclopentadienides salts. Conditions of the nucleophilic substitution: [a]: refluxing Et_2O for 12h, [b]: room temperature for 4h.

These compounds were characterized by NMR spectroscopy (^1H, ^{13}C and 2D correlations) and negative mode ESI HRMS. The ^1H NMR spectra (600 MHz, 300 K, tetrahydrofuran-d_8 or DMSO-d_6) of compounds **1-5-K** showed a similar set of signals for the Cp ring and the bridging CH_2 protons, which resonate as two apparent triplets and one singlet in the 5.2-5.4 ppm and 3.3-3.5 ppm ranges, respectively. The ^1H NMR spectrum of **5-K** is depicted in Spectrum II-1. In this spectrum, the two apparent triplets for the Cp protons appear at 5.46 and 5.38 ppm, whilst the bridging CH_2 resonates at 3.55 ppm.



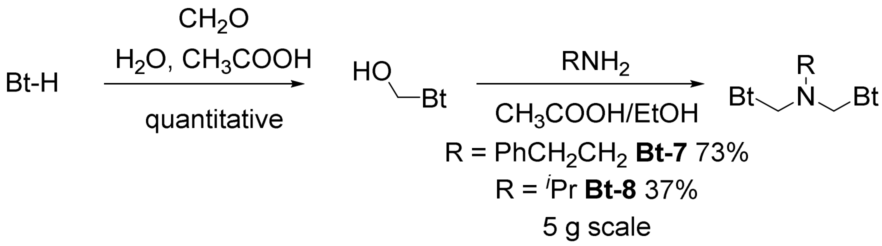
Spectrum II-1: ^{1}NMR spectrum of 5-K (600.23 MHz, 300 K, tetrahydrofuran-d_8)

All signals for the tetramethylpiperidine moiety are located in the 1.60 ppm - 1.12 ppm range as two multiplets for the CH_2 groups and one singlet for the four equivalents methyl groups. All attempt at crystallizing these ligands failed. This was most probably due to the potassium cation, which imparts a very low solubility in apolar solvents and a high propensity to precipitate as amorphous powders.

The successful synthesis of a new series of (aminomethyl)cyclopentadienide salts prompted us to try to synthesize bis(cyclopentadienidemethyl)amines via an analogous route.

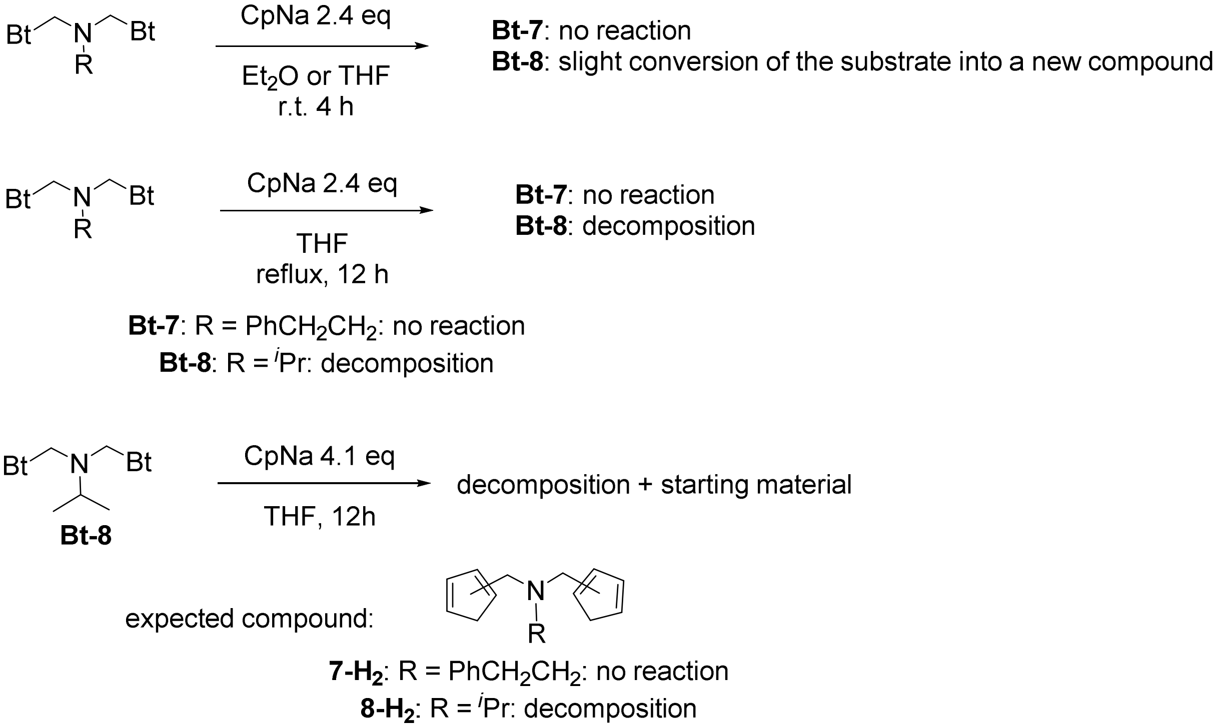
B. Attempted synthesis of bis (cyclopentadienylmethyl)amines

The first step of this route required the successful synthesis of the corresponding bis(benzotriazole) derivatives. In light of Katritzky's work,[3] two benzotriazole precursors (**Bt-7-8**) were synthesized for this topic, as illustrated in Scheme II-10.



Scheme II-10: synthesis of bis(benzotriazolylmethyl)amines

The substitution of the two benzotriazoles **Bt-7** and **Bt-8** by sodium cyclopentadienide was attempted. Initial trials were conducted under the same conditions as those used for the previous series (see Scheme II-9). Unfortunately, heterogeneous conditions did not convert the substrate into the desired molecule, only starting material was recovered after workup. The second strategy was to work under homogenous conditions by using THF, with a slight excess of CpNa. Whilst the reaction still did not work with **Bt-7** (even with a refluxing period of 12h), the desired compound was formed according to GCMS with 5h of stirring at room temperature for **Bt-8**. GCMS analysis was not very convenient for monitoring the reaction since substrates (i.e. benzotriazole derivatives) do not appear. Analysis of the reaction mixture by TLC (eluent 1:1 diethyl ether: pentane with several drops of methanol; mobile phase: silica) indicated the presence of residual starting material. Only traces of putative diene **8-H_2** were obtained, along with starting material, after workup. As illustrated in Scheme II-8, a monosubstituted Cp ring can be found in three forms (**Cp^R-k**, **Cp-t1** and **Cp-t2**), which means $3^2 = 9$ forms for **8-H_2**. Therefore, ^{1}H NMR spectroscopy is not the best analytical technique for purity determination in this case. In fact, cyclopentadienes are known to be temperature sensitive, and they easily dimerize via a [2+2] Diels-Alder process (for example, cyclopentadiene is commercially available under its dimeric stabilized form). If **8-H_2** is prone to easily be dimerized, refluxing period has to be avoided. As a last resort, the use of a four-fold excess of CpNa with **Bt-8** (both as a nucleophile and a base) was attempted, to no avail.



Scheme II-11: synthetic attempt at synthesis of bis(cyclopentadienylmethyl)amines

.

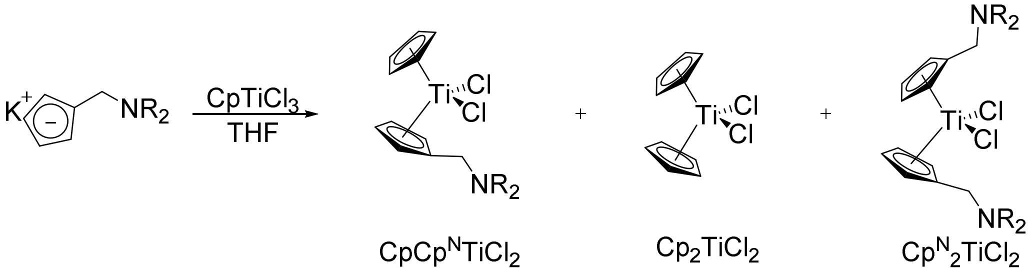
Despite our efforts to synthesize bis(cyclopentadienylmethyl)amines, no ligand of this type was obtained using our “benzotriazole” route, the corresponding synthesis of metallocenes of type **D1** (Scheme II-1) was abandoned.

C. Coordination chemistry to group 4 metals

With the (aminomethyl)cyclopentadienides **1-5-K** in hands, studying the coordination chemistry of these new ligands to group 4 metals was the next logical step.

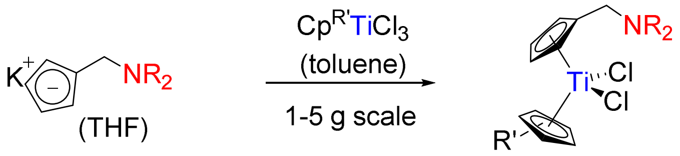
1. Titanium chemistry

Although THF is the usual solvent for this reaction, in our case, its use generally yielded a mixture of three compounds, as illustrated in Scheme II-12. It was evident that ligand scrambling was occurring, resulting in a statistical mixture of titanocene derivatives.

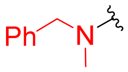
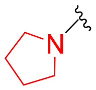
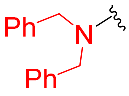
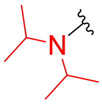
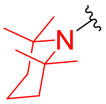


Scheme II-12: ligand scrambling during the synthesis of $CpCp^NTiCl_2$ derivatives

A mixture of toluene/THF was found to be the best choice to synthesize complexes **9-13** in moderate yield without ligand scrambling (54-80% - Scheme II-13). These complexes were characterized by NMR (^{1}H ^{13}C, ^{15}N, and 2D correlations) and IR spectroscopies, positive mode ESI HRMS and elemental analysis. The ^{1}H NMR spectra of complexes **9-13** show downfield signals for the Cp^N and bridging CH$_2$ protons compared to ligands **1-5-K** ($\Delta\delta$ = 0.2-1.25 ppm) (cf Table II-1). The unsubstituted Cp ring is in the 6.57-6.00 ppm range.



1-5-K **9-13**

R_2N–					
$Cp^{R'}$ = Cp	**9**	**10**	**11**	**12**	**13**
Yield	54 %	69 %	80 %	75 %	68 %
$Cp^{R'}$ = Cp*	-	-	-	**19**	-
Yield				46 %	

Scheme II-13: synthesis of Cp^{N}CpTiCl$_2$ complexes. ^{a}: only toluene was used for this procedure

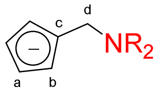
	d (ppm)	b (ppm)	a (ppm)	Cp (ppm)
1-K^a	3.30	5.47	5.45	x
9^b	3.74	6.26	5.68	5.98
2-K^c	3.34	5.27	5.22	x
10^d	3.67	6.52	6.46	6.57
3-K^c	3.40	5.42	5.32	x
11^d	3.60	6.52	6.43	6.38
4-K^c	3.41	5.28	5.22	x
12^d	3.71	6.52	6.44	6.54
5-K^a	3.55	5.46	5.38	x
13^d	4.02	6.26-6.20	5.73-5.67	6.01

Table II-1: relevant ^{1}H NMR signals (600 MHz, 300 K): NMR spectra recorded in ^{a} THF-d$_8$, ^{b} C$_6$D$_6$, ^{c} DMSO-d$_6$, ^{d} CD$_2$Cl$_2$

The $^{13}C\{^{1}H\}$ NMR spectra of these compounds showed that the chemical shift of the bridging CH_2 (d) was almost unaffected by the coordination to titanium, whilst the signals for the functionalized Cp (c,b,a) were shifted downfield ($\Delta\delta$ = 10-23.4 ppm) with respect to the anionic ligands **1-5-K** (cf Table II-2). The chemical shift for the unsubstituted Cp ring remained around 120.0 ppm.

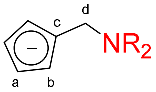
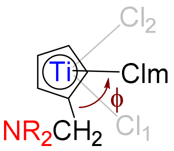
	d (ppm)	c (ppm)	b (ppm)	a (ppm)	Cp (ppm)
1-K^{a}	59.8	117.6	106.5	104.9	x
9^{b}	57.7	133.2	124.6	115.1	119.7
2-K^{c}	57.2	115.4	104.5	102.3	x
10^{d}	55.8	133.9	124.7	116.8	120.6
3-K^{c}	55.1	114.0	105.6	103.3	x
11^{d}	53.6	133.5	124.5	117.6	120.5
4-K^{c}	44.6	116.8	104.0	102.2	x
12^{d}	45.6	140.4	124.1	117.2	120.3
5-K^{a}	45.0	123.5	105.6	104.1	x
13^{d}	45.6	146.2	121.9	115.6	119.1

Table II-2: Relevant $^{13}C\{^{1}H\}$ NMR signals (600 MHz, 300 K): NMR spectra recorded on 600 MHz, 300 K, in ^{a} THF-d$_8$, ^{b} C_6D_6, ^{c} DMSO-d$_6$, ^{d} CD_2Cl_2

The ^{15}N NMR spectra of **6-10** display a single resonance between δ = -339 and δ = -309 ppm in a range comparable to that observed for other amino-functionalized group 4 organometallic complexes, consistent with the non-coordinating state of the amino group.[7]

Suitable crystals for X-ray diffraction analysis were obtained by slow diffusion of pentane into saturated CH_2Cl_2 solutions of **11** and **13**. For **13** two independent molecules were found in the asymmetric unit, only one is depicted for clarity in Figure II-1 (see experimental part, numbering up to C21 belongs to the second omitted molecule). The $CpCp^{N}TiCl_2$ fragments adopt a typically pseudo tetrahedral geometry in both structures with similar structural parameters. These two titanocene moieties show a difference in the position of the substituent held by the cyclopentadienyl ring. In order to illustrate this characteristic, torsions angles have been calculated as illustrated in Scheme II-14. Clm is the centroid of Cl1/Cl2.



Scheme II-14: top view of a dicloro(aminomethyl)titanocene and illustration of the torsion angle defined in this series

---

[7] Kotov, V. V.; Fröhlich, R.; Kehr, G.; Erker, G. *J. Organomet. Chem.* **2003**, *676*, 1

According to this illustration, the value of the torsion angle ϕ indicates the relative position of the amino arm compared to the bisecting plane of the dichlorotitanocene moiety comprising Ct1, Ti and Clm. If ϕ is far from 0 or 180°, the amino group is not located in this bisecting plane otherwise it is. In **11**, the latter situation is observed: the CH_2 bridge is located to the open side of the bent metallocene and lies above the $TiCl_2$ fragment (ϕ = C11-Ct1-Ti-Clm = -5.35(7)°), the lone pair of nitrogen is oriented to the opposite side of titanium (torsion angle C5-C1-C11-N = 88.14(26)°).

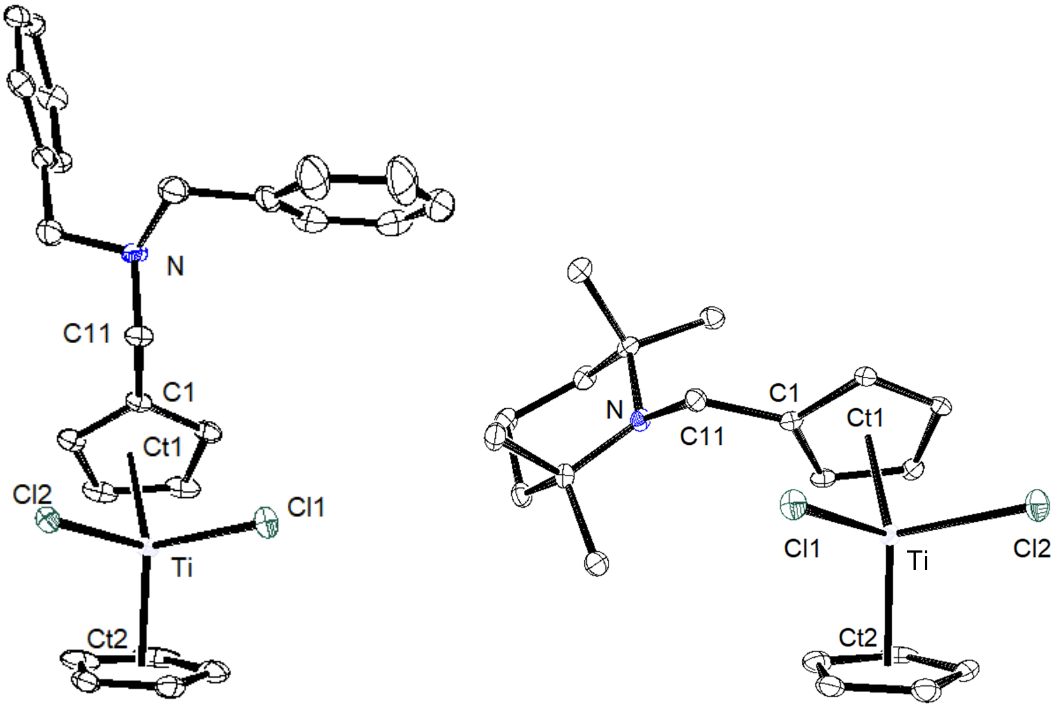
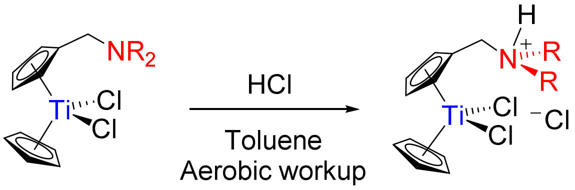


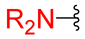
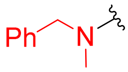
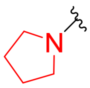
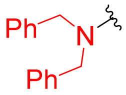
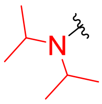
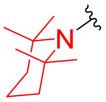
Figure II-1: ORTEP view of complex 11 (left) and 13 (right) (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity). Selected bond lengths (Å) and angles(°) *Ct1 and Ct2 are centroids of both Cp rings as illustrated above.* 11: Ct1-Ti = 2.0606(11), Ct2-Ti = 2.0598(12), Cl1-Ti = 2.3615(6), Cl2-Ti = 2.3768(6), C1-C11 = 1.494(3), C11-N = 1.481(3), Cl1-Ti-Cl2 = 93.89(2), Ct1-Ti-Ct2 = 131.12(5), C1-C11-N = 112.06(17). 13: Ct1-Ti = 2.074(2) / 2.069(2), Ct2-Ti = 2.061(2) / 2.064(2), Cl1-Ti = 2.3613(14) / 2.3539(14), Cl2-Ti = 2.3790(13) / 2.3718(13), C1-C11 = 1.509(6) / 1.508(6), C11-N = 1.468(5) / 1.470(5), Cl1-Ti-Cl2 = 94.05(5) / 94.26(5), Ct1-Ti-Ct2 = 131.39(9) / 131.73 (10), C1-C11-N = 113.9(4) / 112.3(4).

In contrast for compound **13**, the bulky (tetramethylpiperidino)methyl substituent is rotated from the bisecting position leading to torsion angles (ϕ) C11-Ct1-Ti-Clm equal to -81.25(12)° and -71.04(13)° for both independent molecules. The position of the nitrogen is particularly noteworthy with regard to complex **11** and the other complexes described in this manuscript. Indeed this atom is in the same plane as the Cp ring in **13** (torsion angles C2-C1-C11-N1 = -22.85(67)° and C23-C22-C32-N2 = -31.86(64)°), whereas the C11-N bond is more or less orthogonal to the Cp ring in **11** (as a reminder torsion angle C5-C1-C11-N = 88.14(26)°). These parameters will be used for comparison in all other tetramethylpiperidine-based structures.

It has been shown previously that the instability of amino titanocenes towards moisture could be attenuated by protonating the amine function.[8] This was particularly observed for **12** and **13.** The protonation of complexes **9-13** in hydrochloric acid-saturated solutions of toluene was conducted and yielded the corresponding ammonium salts **14-18** in 52-73% yield (Scheme II-15).



9-13 **14-18**

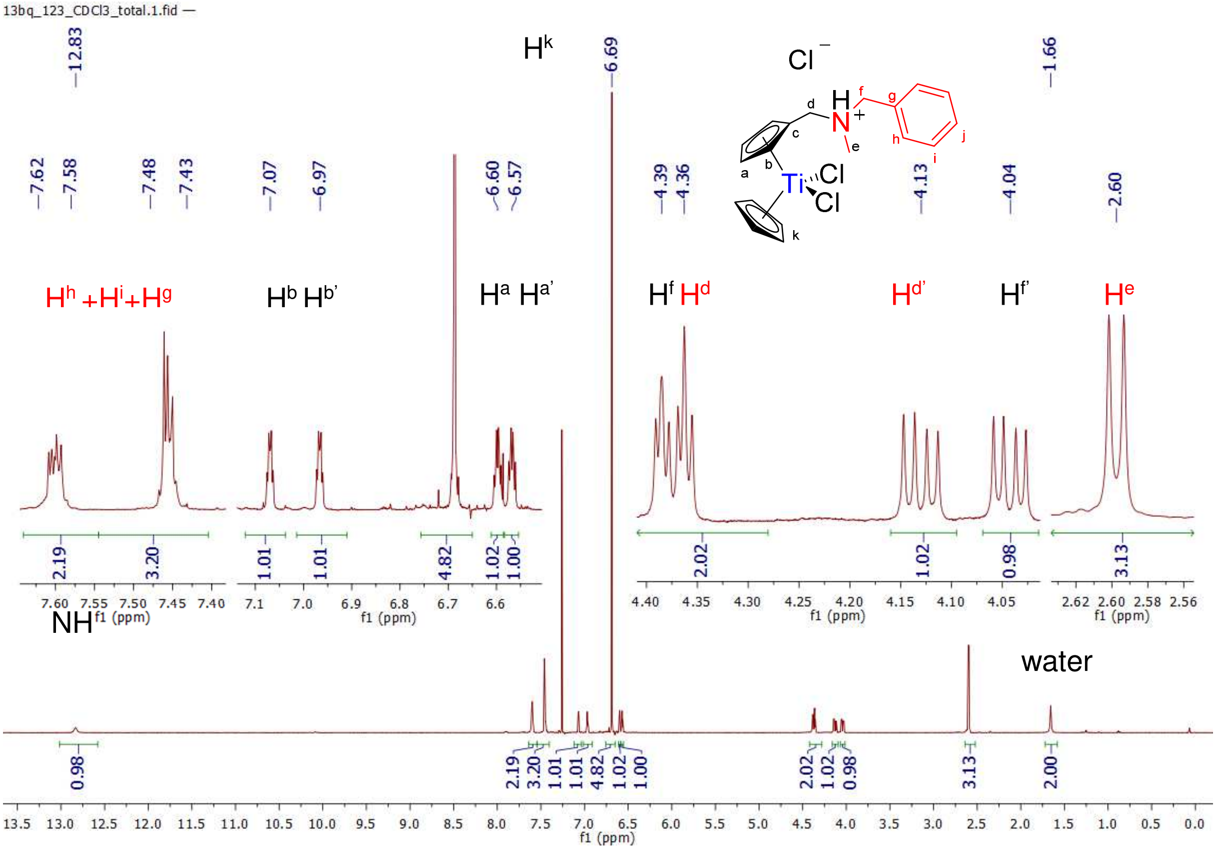
					
	14	**15**	**16**	**17**	**18**
	67 %	52 %	60 %	66 %	73 %

Scheme II-15: synthesis of titanocenyl ammonium chloride salts

These ammonium salts turned out to be air and moisture-stable, and even water-soluble. They were characterized by NMR (^{1}H ^{13}C, ^{15}N, and 2D correlations) and IR spectroscopies, positive mode ESI HRMS and elemental analysis. The protonation of the amine function affected deeply the shape of the ^{1}H NMR spectra of these complexes. Indeed, the nitrogen atom becomes prochiral (or chiral for **14**) and, as a result, changes the stereotopic relationships between atoms and/or groups. The ^{1}H NMR spectrum of **14** was shown to illustrate this diastereotopy (Spectrum II-2). The acidic proton responsible for the chirality is at 12.83 ppm. The aromatic CH signals appear in the 7.62 – 7.43 ppm range as two multiplets, whilst a set of four apparent quartets is observed for the signals of the protons from the Cp^{N} ring (7.07, 6.97, 6.60, 6.57, ppm). The signal of the unsubstituted Cp resonates as a singlet at 6.69 ppm, whilst diastereotopy is observed for the methylenic protons signals, which appear as four doublet of doublets at 4.39, 4.36, 4.13, 4.04 ppm (see appendix for details).

---

[8] Jutzi, P.; Redeker, T.; Neumann, B.; Stammler, H.-G. *Organometallics.* **1996**, *15*, 4153



Spectrum II-2: ^{1}**H NMR of 14 (600 MHz, 300K, CDCl$_3$)**

Splitting of the signals is also observed for the methylenic protons of the pyrrolidine ring in **15**, for the methylenic protons of the benzyl groups in **16**, for the methylic protons of the isopropyl groups in **17** and for both methylic and methylenic protons of the tetramethylpiperidine in **18** (due in these cases to the prochirality of the nitrogen). X-ray diffraction analysis of monocrystals of **15**, **17** and **18** allowed the determination of their solid-state structures. The pyrrolidinium methyl and diisopropylammonium methyl substituents, depicted in Figure II-3 (**15** and **17** respectively), adopt the same bisecting position as the neutral dibenzylamine group in **11** (ϕ = C11-Ct1-Ti-Clm = 0.90(22)° and C11-Ct1-Ti-Clm = 8.55(3)° respectively). The protonation does not change significantly the steric hindrance of the pendant group attached to the Cp ring. Both structures are comparable with respect to the position of the ammonium groups away, from the titanium atom (C7-C6-C11-N = 85.11(57)° for **15**, C5-C1-C11-N = 123.46(12)° for **17**).

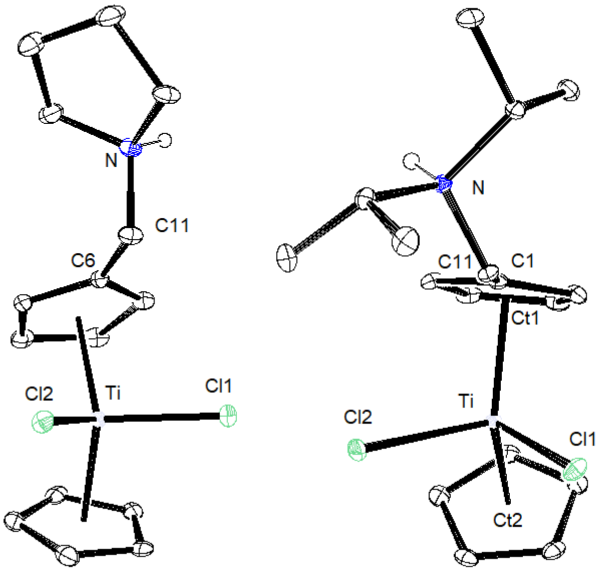
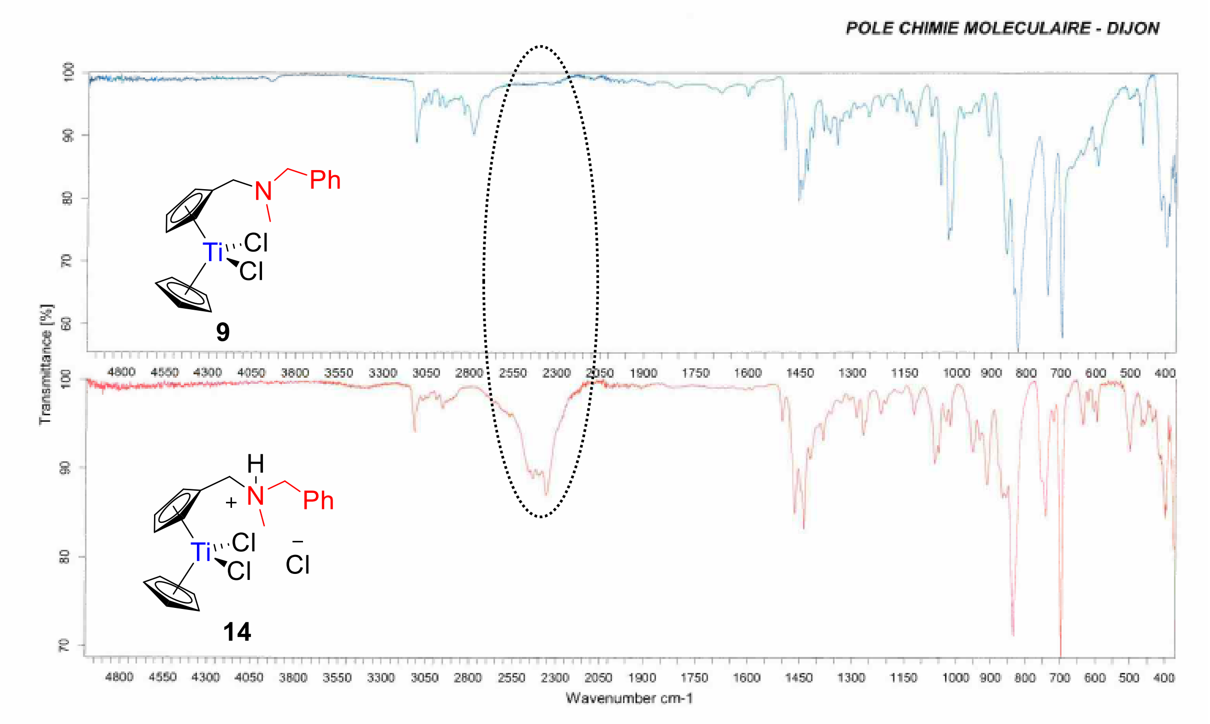


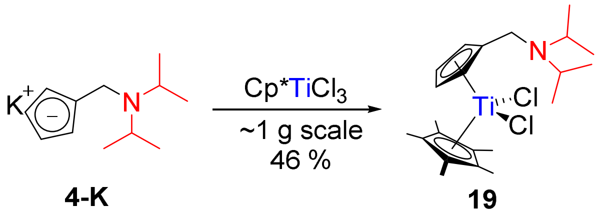
Figure II-2: ORTEP view of 15 (left) and 17 (right) (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity except NH as well as counter anion and solvent). Selected bond lengths (Å) and angles(°): 15: Ct1-Ti = 2.0606(11), Ct2-Ti = 2.0598(12), Cl1-Ti = 2.3477(17), Cl2-Ti = 2.3645(16), C1-C11 = 1.485(8), C11-N = 1.494(7), Cl1-Ti-Cl2 = 92.43(6), Ct1-Ti-Ct2 = 131.94(17), C1-C11-N = 111.2(5). 17: Ct1-Ti = 2.0617(6), Ct2-Ti = 2.0549(6), Cl1-Ti = 2.3660(4), Cl2-Ti = 2.3637(4), C1-C11 = 1.4988(15), C11-N = 1.5164(14), Cl1-Ti-Cl2 = 92.920(13), Ct1-Ti-Ct2 = 130.97(3), C1-C11-N = 113.72(9).

In the IR spectra, a characteristic middle intensity band was observed in the range of 2352-2588 cm^{-1} for ν-N-H compared to spectra from **9-13**. This is illustrated by the IR spectra superposition of **9** and **14** (Spectrum II-3).



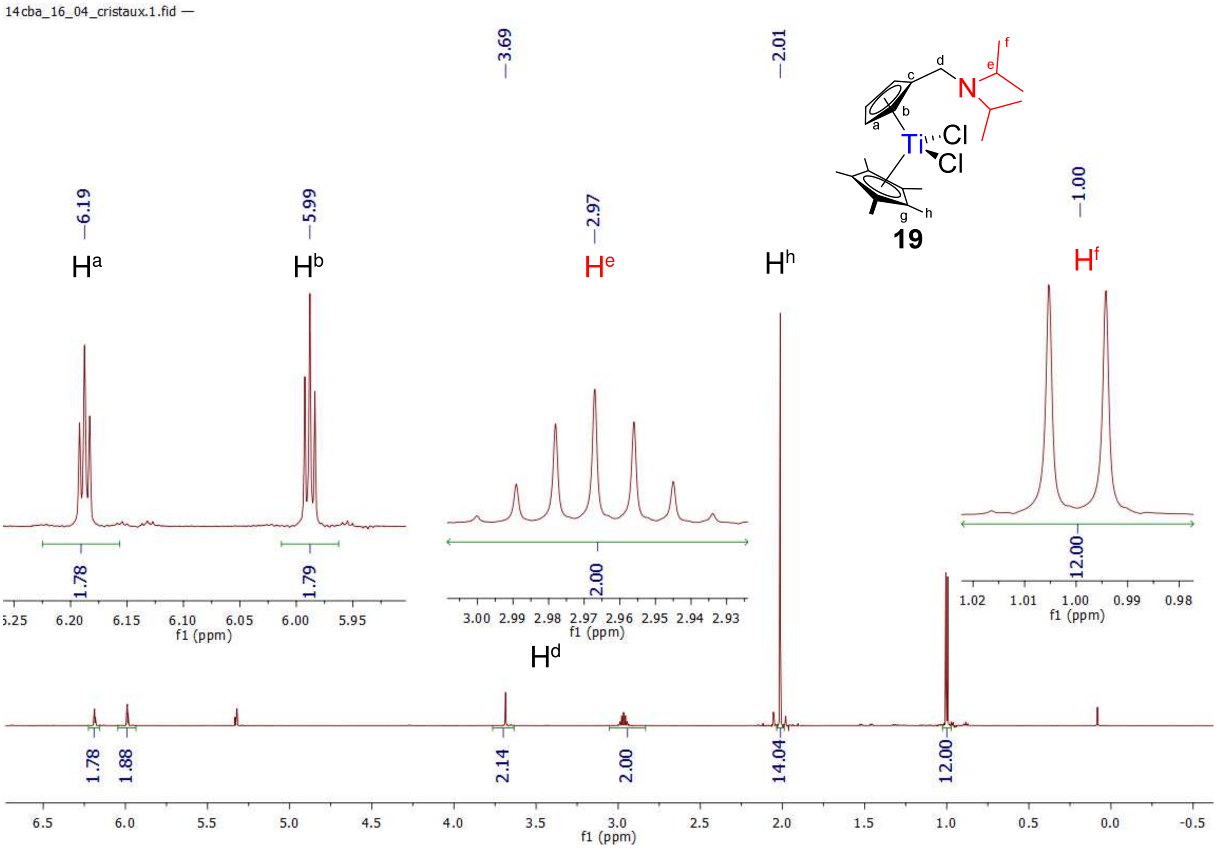
Spectrum II-3: superposition of the IR spectra of 9 and 14

To evaluate the coordination potential of our new ligands, other titanium complexes were synthesized. An electron-enriched titanocene was synthesized by reacting Cp*TiCl$_3$ with **4-K**, forming **19** in 46% yield. This synthesis was realised by Cédric Balan (Scheme II-16).



Scheme II-16: Synthesis of Cp*Cp^{N}TiCl$_2$ 19

As its Cp analogue, this compound was characterized by NMR and IR spectroscopies, positive mode ESI HRMS, elemental and X-ray diffraction anaylses. The ^{1}H NMR spectrum of this compound exhibits a set of two apparent triplets (6.19 and 5.99 ppm) for the signals of the monosubstituted Cp ring, and a singlet for the signal of the methyl groups of the Cp* ring at 2.01 ppm. Whilst a singlet at 3.69 ppm is observed for the signal of the bridging CH$_2$, a set of two signals appearing as an heptet and a doublet (2.97 and 1.00 ppm respectively) is observed for the two equivalent isopropyl groups (Spectrum II-4).



Spectrum II-4: ^{1}H NMR of 19 (600.23 MHz, 300 K, dichloromethane-d$_2$)

This compound was shown to undergo ligand scrambling in solution as illustrated in Scheme II-12. Nevertheless, it was easily purified by layering a dichloromethane solution with pentane at -15°C, eventually forming block-shaped crystals (Figure II-3).

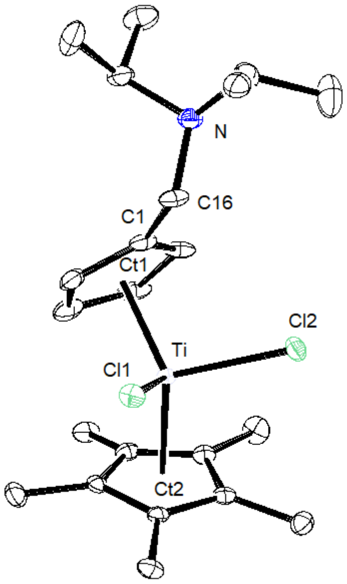
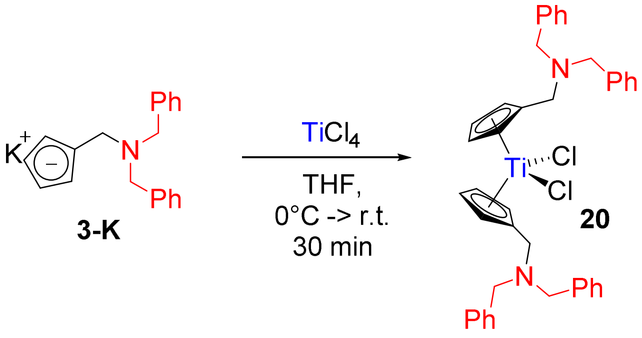


Figure II-3: ORTEP view of 19 (ellipsoids drawn at the 50% probability level, hydrogen atoms removed for clarity as well as the second molecule in the cell). Selected bond lengths (Å) and angles(°): Ti-Ct1 = 2.0743 / 2.0936, Ti-Ct2 = 2.0932(10) / 2.0690(11), Ti-Cl1 = 2.3527(6) / 2.361(6), Ti-Cl2 2.3602(6) / 2.3705(6), C1-C16 = 1.503(3) / 1.509(3), C16-N = 1.468(13) / 1.463(3), Ct1-Ti-Ct2 = 132.66(4) / 131.78(4), Cl1-Ti-Cl2 = 94.14(12) / 93.61(02), C1-C16-N = 109.94(16) / 111.97(16).

The structure is analogous to the one from **11** with respect to the calculated torsion angles (ϕ = C16-Ct1-Ti-Clm = -1.51(6)° / 1.94(6)° and C5-C1-C16-N = 56.26(3)° / 53.67(3)°) These parameters indicate that the amino substituent is almost in the bisecting plane of the metallocene.

Attempts at synthesizing bis(aminomethyl)titanocenes were also made, but was tedious and hardly reproducible. One of them was randomly obtained once and characterized with the 80 mg isolated (15 % yield). **3-K** was reacted in Et_2O with half an equivalent of $TiCl_4(THF)_2$ at 0°C. The mixture was briefly brought to room temperature before workup. The resulting brown oil was further purified by recrystallization from a dichloromethane solution layered with pentane. This workup eventually yielded **20** as orange prism-shaped crystals (Scheme II-17).



Scheme II-17:synthesis of 20

This compound was characterized as usual but elemental analysis and IR spectroscopy were not obtained due to a lack of compound.

The ^{1}H NMR spectrum of **20** shows one doublet at 7.36 ppm and two triplets at 7.32 and 7.24 ppm for the signals of the aromatic protons, two apparent triplets for the signal of the protons of the monofunctionalized Cp ring at 6.35 and 6.25 ppm and two overlapping singlets at 3.53 ppm corresponding to the signal of the twelve methylenic protons which fortuitously resonate at the same chemical shift (see appendix for details). The ^{15}N NMR spectrum of **20** displays a single resonance at almost the same chemical shift as the one observed for **11** (-328 ppm vs -327 ppm).

The X-ray structure of **20** is presented in Figure II-4 and shows a C2 symmetric conformation in the solid state (half a molecule was present in the asymmetric unit). The two amino methyl groups are located close to the bisecting plane of the bent metallocene (ϕ = C6-Ct1-Ti-Cl$_m$ = 0.93(4)°) and oriented away from each other in an antiperiplanar conformation (C2-C1-C6-N = 80.04(17)°).

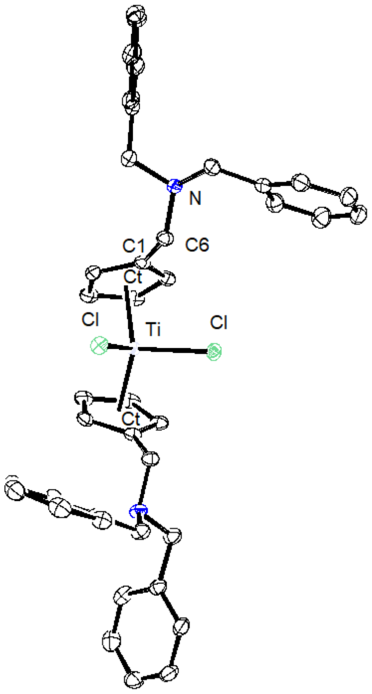
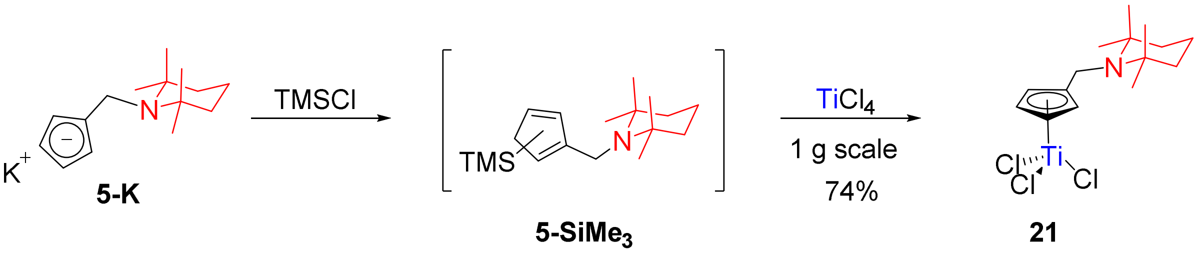


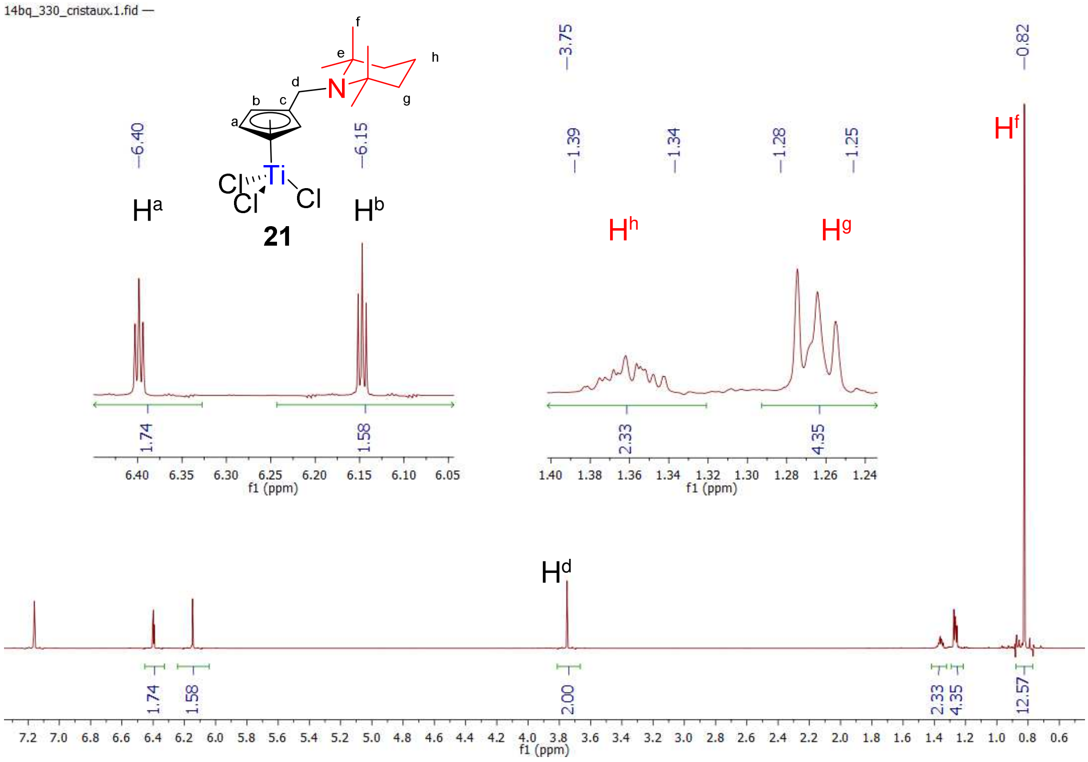
Figure II-4: ORTEP view of 20 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity). Selected bond lengths (Å) and angles(°): Ti-Cl = 2.3586(4), Ti-Ct = 2.3586(4), C1-C6 = 1.5006(18), C6-N = 1.4793(17), Cl-Ti-Cl = 94.38(2), Ct-Ti-Ct = 133.01(3), N-C6-C1 = 112.00(11).

A piano stool series was also envisioned. All attempt at forming such complexes failed except for the synthesis starting from **5-K** (Scheme II-18).



Scheme II-18: Synthesis of 21

Silylation of this compound was smoothly performed in THF with distilled Me_3SiCl. **5-SiMe3** was directly treated after purification with $TiCl_4$ in toluene at -30°C. The resulting brown solution yielded **21** as a dark brown powder. An amber solution in pentane was left to crystallize at -15°C, forming brown plates. This compound was fully characterized by standard techniques (NMR and IR spectrosocpies, HRMS, elemental and X-ray diffraction analyses). The ^{1}H NMR spectrum has roughly the same aspect as the one from **5-K** depicted in Spectrum II-2. The Cp signals are shifted downfield to 6.40 and 6.15 ppm (Spectrum II-5).



Spectrum II-5: ^{1}H NMR of 21 (600.23 MHz, 300K, benzene-d_6)

The signal of the bridging CH_2 appears as a singlet at 3.75 ppm. The signals of the tetramethylpiperidine ring are in the 1.39-1.25 ppm range and 0.82 ppm for the methylene and methyl groups, respectively. The electronic equivalence of the methylic signals from the tetramethylpiperidine moiety argues against the presence of the Ti-N interaction in solution.

Indeed, quaternisation of the N atom could block the conformation of the piperidine ring, which would translate in the ^{1}H NMR spectrum as a non-equivalence of the methyl groups as observed in **18.** The ^{15}N NMR signal of **21** resonates at -308 ppm (very close to the value of **13**: -309 ppm).The X-ray diffraction structure of **21** (Figure II-5) shows a typical pseudo tetrahedral geometry for the titanium centre (piano stool-like structure), and corroborated the absence of Ti-N interaction previously deduced from ^{1}H NMR spectroscopy in solution.

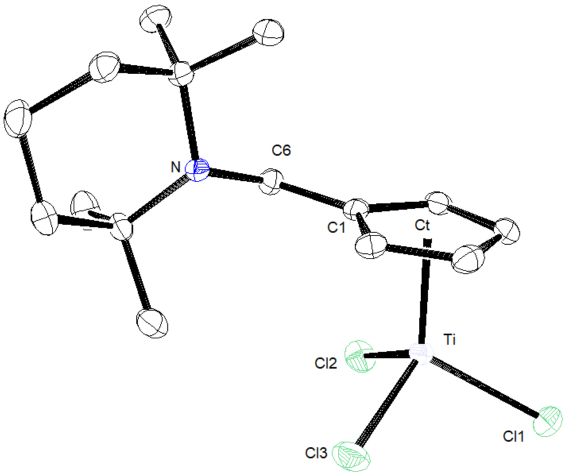


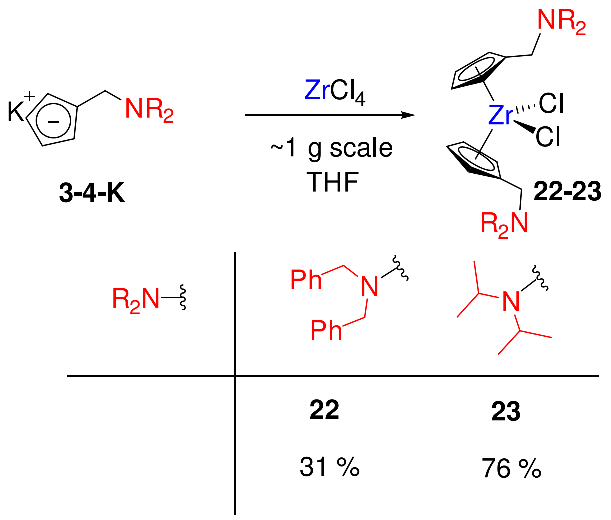
Figure II-5: ORTEP view of 21 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity). Selected bond lengths (Å) and angles(°): Ct-Ti = 2.0162(10), Cl1-Ti = 2.2360(6), Cl2-Ti = 2.2308(6), Cl3-Ti =2.2425(6) , C1-C6 = 1.519(3), C6-N = 1.461(2), Ct-Ti-Cl1 = 116.78(3), Ct-Ti-Cl2 = 115.36(3), Ct-Ti-Cl3 = 113.27(3), Cl1-Ti-Cl2 = 100.32(3), Cl1-Ti-Cl3 = 102.32(3), Cl2-Ti-Cl3 = 106.94(3)

The relevant torsion angles of **21** (Ti-Ct-C6- = 107.03(11)° and C5-C1-C6-N = 15.12(3)°) indicate that the tetramethylpiperidine moiety remains slightly tilted from the Cp ring as in the structure of **13.**

Several (aminomethyl)titanocenes and related compounds were synthesized and characterized. Before exploring their potential as OmFLPs, the synthesis of zirconium analogues was envisioned in collaboration with Pr. Nadine Pirio (ICMUB, Dijon).

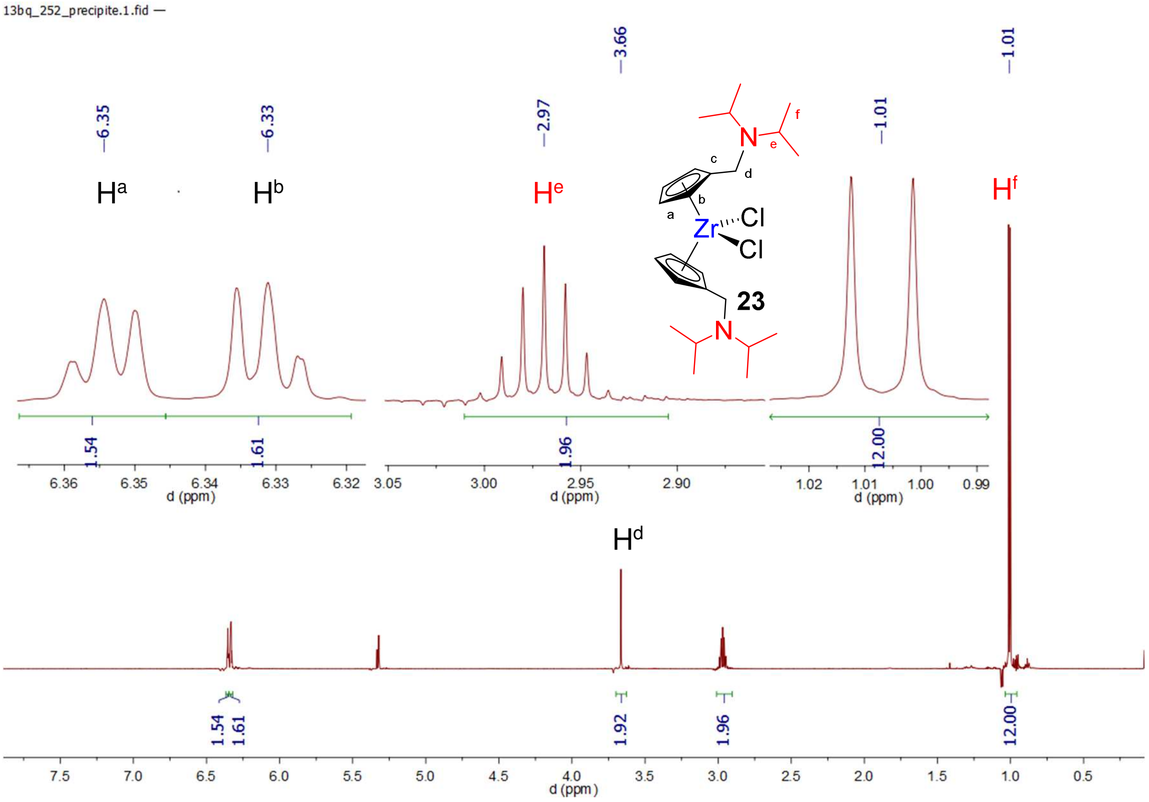
2. Zirconium chemistry

The synthesis of bis(aminomethyl)zirconocene derivatives was first attempted. By using half an equivalent of [$ZrCl_4(THF)_2$], with one equivalent of **3-4-K** in THF, two new zirconocenes **22** and **23** were obtained (Scheme II-19), whilst the last with **5-K** failed.



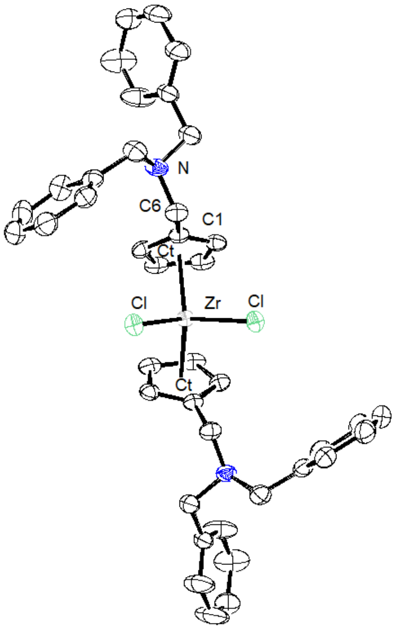
Scheme II-19: synthesis of bis(aminomethyl)zirconocenes

Even if the corresponding bis(aminomethyl)zirconocene was formed according to ^{1}H NMR, it could not be purified satisfactorily. All attempt at purification failed. Based on the observed behaviour with titanium compounds, one can assume that this complex is highly moisture sensitive and repeated workup only increased the extent of hydrolysis. Complexes **22** and **23** were characterized by NMR (^{1}H ^{13}C ^{15}N and 2D correlations) and IR spectroscopies and positive mode ESI HRMS. The elemental analyses were not satisfactory most probably due to the presence of remaining $ZrCl_4$ or residual inorganic salts. The ^{1}H NMR spectrum of **23** is presented on Spectrum II-6.



Spectrum II-6: ^{1}H NMR of 23 (600.23 MHz, 300 K, dichloromethane-d$_2$)

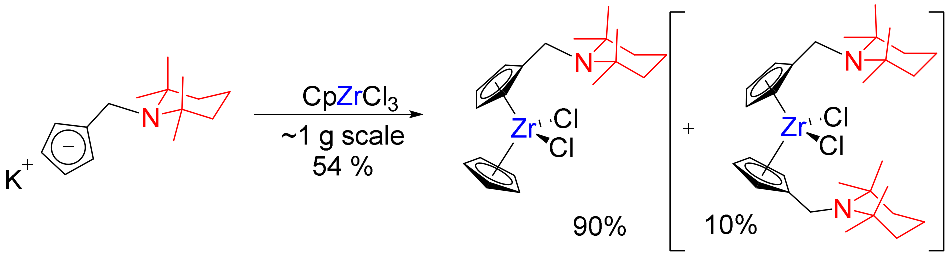
The signals of the protons from the Cp ring appears as two multiplets at 6.35 and 6.33 ppm, whilst the bridging CH_2 shows a singlet at 3.66 ppm. The four equivalent isopropyl groups exhibit a set of two signals at 2.97 and 1.01 ppm as an heptet and a doublet respectively.The solid-state structure of compound **22** was obtained by X-ray diffraction.



It adopts the same C2 symmetric conformation as **11** (Figure II-1) with similar parameters (C6-Ct1-Zr-Clm = -9.91(5)°), C5--C1C6-N = -68.89(22)°).

Figure II-6: ORTEP view of 20 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity). Selected bond lengths (Å) and angles(°): Zr-Cl = 2.4468(4), Zr-Ct = 2.2057(8), C1-C6 = 1.504 (2), C6-N = 1.475 (2), Cl-Zr-Cl = 94.42(2), Ct-Zr-Ct = 133.08(3), N-C6-C1 = 109.68(15).

The synthesis of the monosubstituted zirconocene **24** was also attempted with **5-K** and succeeded in one instance, but then after yielded a 90:10 mixture of the desired compound with the corresponding bis(aminomethyl)zirconocene (Scheme II-20). The commercial $CpZrCl_3$ most probably contained residual $ZrCl_4$, which was not completely removed even after sublimation. The best batch obtained at first was fully characterized by standard techniques, but never reproduced.



5-K **24** **bis-24**

Scheme II-20: Synthesis of 24

The $^{13}C\{^1H\}$ NMR chemical shifts of **13** are recalled in the following Table II-3. The nature of the metal in the metallocene does not change fundamentally the observed $^{13}C\{^1H\}$ NMR chemical shifts: $\Delta\delta$ = 4.3-1.7 ppm for the signal of the carbons from the Cp rings and $\Delta\delta$ = 0.3-0.8 ppm for the signals of the bridging CH_2 and the tetramethylpiperidine moiety. Suitable crystals for X-ray diffraction analysis were obtained by diffusion of pentane into a dichloromethane solution as colourless shaped needle at -15°C (Figure II-7).

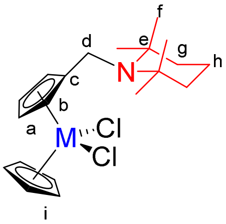
	M = Ti (**13**)[a] (δ in ppm)	M = Zr (**24**)[b] (δ in ppm)
c	142.6	146.2
b	117.6	121.9
I	116.6	119.1
a	113.9	115.6
e	56.2	55.6
d	45.9	45.6
g	42.7	41.9
h	28.9-28.2	28.6-27.9
f	18.9	18.2

Table II-3: $^{13}C\{^1H\}$ NMR (600 MHz, 300 K) chemical shifts of 13 and 24, NMR recorded in [a]: CD_2Cl_2, [b]:THF-d_8

A structural comparison of both structures of **24** and **13**, showed only one difference between the lengths of M-X bonds. These latter are longer for zirconium than titanium (Δ_{length} = 0.15-0.08 Å) due to the difference in their respective covalent radii (Ti = 1.60 ± 0.08 Å, Zr = 1.75 ± 0.07 Å).[9]

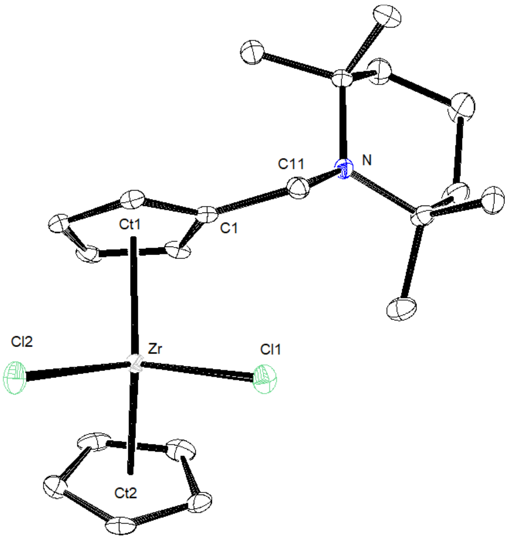


Figure II-7: ORTEP View of 24 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity). Selected bond lengths (Å) and angles(°): Zr-Cl1 = 24498(7), Zr-Cl2 = 2.4549(7), Zr-Ct1 = 2.2123(12), Zr-Ct2 = 2.2100(13), C1-C11 = 1.519(4), C11-N = 1.465(4), Cl1-Zr-Cl2 = 96.15(3), Ct1-Zr-Ct2 = 130.76(5), C1-C11-N = 113.1(2).

---

[9] Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832

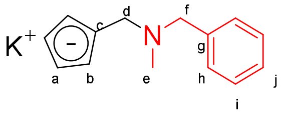
All synthesized zirconocenes were too impure to be used as OmFLPs precursors. Therefore none of them will appear in the following chapter II.

In conclusion to this chapter, a new series of (aminomethyl)cyclopentadienides and a new series of N-functionalized titanocenes was achieved in good yield and purity. (Aminomethyl)cyclopentadienides were coordinated to zirconium but the purity of the resulting complexes could not be improved.

With these complexes in hand, a cationic titanocene has to be generated to finally obtain the targeted complexes of type **C1** (Scheme II-2). This will be the topic of the following chapter II.

D. Experimental part:

3. Synthesis of 1-K:



Chemical Formula: $C_{14}H_{16}KN$
Molecular Weight: 237,4

To a suspension of CpNa (2.6 g, 0.024 mol, 1.2 eq) in 50 mL of Et_2O, was added dropwise by cannulation at -15°C, an etheral solution of N-benzotriazolylmethyl-N-methyl-1-phenylmethanamine (5 g, 0.02 mol, 1 eq). The resulting solution was left to warm up to room temperature and then refluxed overnight. Reaction progress was monitored by TLC (1: 1 Et_2O: pentane + several drops of methanol as eluent; mobile phase: silica). The white precipitate formed during the reaction was filtered off and extracted with 15 mL of Et_2O. The yellow filtrate was washed twice with 30 mL of deionized water. The combined organic phases were washed with a solution of saturated brine (30 mL) and dried over $MgSO_4$. After filtration and careful evaporation of the solvent, the yellow oil was dissolved in pentane (40 mL) and left 10 min during which time the residual starting material precipitated. After filtration and careful (25°C, middle depression) evaporation the corresponding diene was obtained as yellow oil (3.0 g, yield: 74 %). This unstable compound was directly used after dissolving in 50 mL of Et_2O. The resulting solution was cooled down to 0°C, and a freshly-prepared solution in toluene of KHMDS (2.7 g, 0.014 mol, 0.9 eq, 20 mL) was added dropwise. The cold bath was left to warm to room temperature over 5 h. The light brown precipitate formed during this time was filtered off, washed with 10 mL of cold Et_2O, 2 x 15 mL of pentane and resulted in a beige powder after drying (1.83 g, yield: 52 % overall yield: 39 %).[10]

---

[10] Elemental analysis was not obtained good enough due to residual presence of solvent, and their unpredictable distribution in the solid.

^{1}H NMR (600.23 MHz, 300 K, tetrahydrofuran-d$_8$): δ^{1}H: 7.31 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H, H^{h}), 7.23 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H, H^{i}), 7.13 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, H^{j}) 5.47 (m, 2H, H^{b}), 5.45 (2H, H^{a}), 3.46 (s, 2H, H^{f}), 3.30 (s, 2H, H^{d}), 2.09 (s, 3H, H^{e}).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, tetrahydrofuran-d$_8$): δ^{13}C: 142.2 (C^{g}), 129.8 (C^{h}), 128.8 (C^{i}), 127.1 (C^{j}), 117.6 (C^{c}), 106.5 (C^{b}), 104.9 (C^{a}), 63.5 (C^{f}), 59.8 (C^{d}), 43.0 (C^{e}).

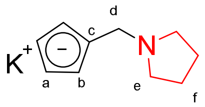
^{1}H ^{1}H COSY (600.23 MHz, 300 K, tetrahydrofuran-d$_8$): δ^{1}H / δ^{1}H: 7.31 / 7.23 (CH^{h} / CH^{i}), 7.23 / 7.31, 7.13 (CH^{i} / CH^{h}, CH^{j}), 7.13 / 7.23 (CH^{j} / CH^{i}) 5.47 / 5.45 (CH^{b} / CH^{a}), 5.45 / 5.47 (CH^{a} / CH^{b}).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d$_8$): δ^{1}H / δ^{13}C: 7.31 / 129.8 (CH^{h}), 7.23 / 128.8 (CH^{i}), 7.13 / 127.1 (CH^{j}) 5.47 / 106.5 (CH^{b}), 5.45 / 104.9 (CH^{a}), 3.46 / 63.5 (CH_2^{f}), 3.30 / 59.8 (CH_2^{d}), 2.09 / 43.0 (CH_3^{e}).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d$_8$): δ^{1}H / δ^{13}C: 7.31 / 129.8, 127.1, 63.5 (CH^{h} / CH^{h}, CH^{j}, CH_2^{f}), 7.23 / 142.2, 128.8 (CH^{i} / C^{g}, CH^{i}), 7.13 / 129.8 (CH^{j} / CH^{h}), 5.46 / 117.6, 104.9, 59.8 (CH^{b} / C^{c}, CH^{a}, CH_2^{d}), 5.45 / 117.6, 106.5, (CH^{a} / C^{c}, CH^{b}), 3.46 / 142.2, 129.8, 59.8, 43.1 (CH_2^{f} / C^{g}, CH^{h}, CH_2^{d}, CH_3^{e}), 3.30 / 117.6, 106.5, 63.5, 43.0 (CH_2^{d} / C^{c}, CH^{b}, CH_2^{f}, CH_3^{e}), 2.09 / 63.5, 59.8 (CH_3^{e} / CH_2^{f}, CH_2^{d}).

HMRS (ESI negative mode, dimethylsulfoxide): calcd. for $C_{14}H_{16}N$ [M-K]$^{-}$ 198.12869; found 198.12773 (Rel ab: 100%, -0.7 ppm)

4. Synthesis of **2-K**:



Chemical Formula: $C_{10}H_{14}KN$
Molecular Weight: 187,3

To a suspension of CpNa (0.06 mol, 1.2 eq) in 30 mL of Et$_2$O, was added dropwise by cannulation at -15°C an etheral solution of N-benzotriazolylmethyl-pyrrolidine (10.0 g, 0.05 mol, 1 eq). The resulting solution was stirred for 1 h at - 30°C and then brought to completion by an additional stirring of 3 h at room temperature. The resulting solution was left to warm up to room temperature and then refluxed overnight. Reaction progress was monitored by TLC (1: 1 Et$_2$O: pentane + several drops of methanol as eluent; mobile phase: silica). The white precipitate formed during the reaction was filtered off and extracted with 3x40mL mL of Et$_2$O. The yellow filtrate was washed twice with 50 mL of deionized water. The combined organic phases were washed with a solution of saturated brine (40 mL) and dried over MgSO$_4$. After filtration and careful evaporation (25°C, middle depression) of the solvent, the yellow oil was dissolved in pentane (40 mL) and left 10 min during which time the residual starting material precipitated. After filtration and careful evaporation the corresponding diene was obtained as yellow oil (5.8 g, yield: 78 %). This unstable compound was directly used after dissolving in 50 mL of Et$_2$O. The resulting solution was cooled down to 0°C, and a freshly-prepared solution in toluene of KHMDS (7.6 g, 0.038 mol, 0.98 eq, 80 mL) was added dropwise. The cold bath was left to warm to room temperature overnight. The light brown precipitate formed during this time was filtered off, washed with 2 x 20 mL of cold Et_2O, 2 x 30 mL of pentane and resulted in a beige powder after drying (4.58 g, yield: 96 % overall yield: 74 %).[10]

^{1}H NMR (600.23 MHz, 300 K, dimethylsulfoxide-d_6): δ^1H: 5.27 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.5$ Hz, 2H, H^b), 5.22 (m, 2H, H^a), 3.34 (s, 2H, H^d), 2.40-2.33 (bs, 4H, H^e), 1.61-1.53 (bs, 4H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dimethylsulfoxide-d_6): δ^{13}C: 115.4 (C^c), 104.5 (C^b), 102.3 (C^a), 57.2 (C^d), 53.2 (C^e), 23.1 (C^f).

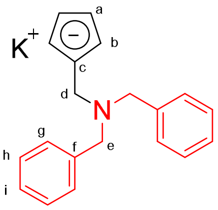
^{1}H ^{1}H COSY (600.23 MHz, 300 K, dimethylsulfoxide-d_6): δ^1H / δ^1H: 5.27 / 5.22 (CH^b / CH^a), 5.22 / 5.27 (CH^a/ CH^b), 2.40-2.33 / 1.61-1.53 (CH^e/ CH^f) , 1.61-1.53 / 2.40-2.33 (CH^f/ CH^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dimethylsulfoxide-d_6): δ^1H / δ^{13}C: 5.27 / 104.5 (CH^b), 5.22 / 102.3 (CH^a), 3.34 / 57.2 (CH_2^d), 2.40-2.33 / 53.2 (CH_2^e), 1.61-1.53 / 23.1 (CH_2^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dimethylsulfoxide-d_6): δ^1H / δ^{13}C: 5.27 / 115.4, 104.5, 102.3, 57.2 (CH^b/ C^c, CH^b, CH^a, CH_2^d), 5.22 / 115.4, 104.5, (CH^a / C^c, CH^b), 3.34 / 115.4, 104.5, 53.2 (CH_2^d / C^c, CH^b, CH_2^e), 2.40-2.33 / 53.2, 23.1 (CH_2^e / CH_2^e, CH_2^f), 1.61-1.53 / 53.2, 23.1 (CH_2^f / CH_2^e, CH_2^f).

HMRS (ESI negative mode, dimethylsulfoxide): calcd. For $C_{10}H_{14}N$ [M-K]$^-$ 148.11325; found 148.11323 (Rel ab: 100%, 0.5 ppm).

5. Synthesis of **3-K**:



Chemical Formula: $C_{20}H_{20}KN$
Molecular Weight: 313,5

To a solid mixture of CpNa (0.055 mol, 1.2 eq) and N-benzotriazolylmethyl-N-benzyl-1-phenylmethanamine (10 g, 0.030 mol, 1 eq) was added dropwise by cannulation at -15°C 500 mL of Et_2O. at -15°C. The resulting solution was left to warm up to room temperature and then refluxed overnight. TLC plate (1: 1 Et_2O: pentane as eluent+ several drops of MeOH as eluent) was done in order to check the completion of the reaction. The white precipitate formed during the reaction was filtered off and extracted with 2x100 mL of Et_2O. The yellow filtrate was washed twice with 50 mL of deionized water. The combined organic phases were washed with a solution of saturated brine (30 mL) and dried over $MgSO_4$. After filtration and careful evaporation of the solvent, the yellow oil was dissolved in pentane (40 mL) and left 10 min during which time the residual starting material precipitated. After filtration and careful evaporation (25°C, middle depression), the corresponding diene was obtained as yellow oil

(8.86 g, yield: 70 %). This unstable compound was directly used after dissolving in 50 mL of Et_2O. The resulting solution was cooled down to 0°C, and a freshly-prepared solution in toluene of KHMDS (5.77 g, 0.029 mol, 0.9 eq, 45 mL) was added dropwise. The cold bath was left to warm to room temperature overnight. A dark brown solution was obtained. After efficient evaporation, the sticky brown oil was triturated with 60 mL of Et_2O and 20 mL of pentane to form a white precipitate. The supernatant was cannulated, the precipitate was washed twice with 20 mL of pentane before drying *in* vacuo to remove residual traces of solvent. The light brown foam formed during this process was reduced in a thin powder in the Glove Box (8.52 g, yield: 84 %, overall yield: 60%).[10]

^{1}H NMR (500.13 MHz, 300 K, dimethylsulfoxide-d$_6$): δ^{1}H: 7.41 (d, $^{3}J_{HH}$ = 7.5 Hz, 4H, H^{g}), 7.29 (t, $^{3}J_{HH}$ = 7.5 Hz, 4H, H^{h}), 7.17 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, H^{i}) 5.42 (t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 2H, H^{b}), 5.32 (apparent t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 2H, H^{a}), 3.53 (s, 4H, H^{e}), 3.40 (s, 2H, H^{d}).

^{13}C{^{1}H} NMR (125.77 MHz, 300 K dimethylsulfoxide-d$_6$): δ^{13}C: 142.0 (C^{f}), 128.8 (C^{g}), 128.2 (C^{h}), 126.4 (C^{i}), 114.0 (C^{c}), 105.6 (C^{b}), 103.3 (C^{a}), 57.0 (C^{e}), 55.1 (C^{d}).

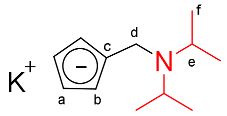
^{1}H ^{1}H COSY (500.13 MHz, 300 K, dimethylsulfoxide-d$_6$): δ^{1}H / δ^{1}H: 7.41 / 7.29, 7.17, 3.53 (CH^{g} / CH^{h}, CH^{i}, CH$_2^{e}$), 7.29 / 7.41, 7.17 (CH^{h} / CH^{g}, CH^{i}), 7.17 / 7.41, 7.29 (CH^{i} / CH^{g}, CH^{h}) 5.42 / 5.32 (CH^{b} / CH^{a}), 5.32 / 5.42 (CH^{a}/ CH^{b}), 3.53 / 7.41 (CH$_2^{e}$ / CH^{g}).

^{1}H ^{13}C HMQC (500.13 MHz / 125.77 MHz, 300 K, dimethylsulfoxide-d$_6$): δ^{1}H / δ^{13}C: 7.41 / 128.8 (CH^{g}), 7.29 / 128.2 (CH^{h}), 7.17 / 126.4 (CH^{i}), 5.42 / 105.6 (CH^{b}), 5.32 / 103.3 (CH^{a}), 3.53 / 57.0 (CH$_2^{f}$), 3.40 / 55.1 (CH$_2^{d}$).

^{1}H ^{13}C HMBC (500.13 MHz / 125.77 MHz, 300 K, dimethylsulfoxide-d$_6$): δ^{1}H / δ^{13}C: 7.41 / 128.8, 128.2, 126.4, 57.0 (CH^{g} / CH^{g}, CH^{h}, CH^{i}, CH$_2^{f}$), 7.29 / 142.0, 128.2 (CH^{h} / C^{f}, CH^{g}), 7.17 / 142.0, 128.3 (CH^{i} / C^{f}, CH^{g}), 5.42 / 114.0, 103.3, 55.1 (CH^{b} / C^{c}, CH^{b}, CH$_2^{d}$), 5.32 / 114.0, 105.6 (CH^{a} / C^{c}, CH^{b}), 3.53 / 142.0, 128.8, 57.0, 55.1 (CH$_2^{e}$/ C^{f}, CH^{g}, CH$_2^{e}$, CH$_2^{d}$), 3.40 / 114.0, 105.6, 57.0 (CH$_2^{d}$ / C^{c}, CH^{b}, CH$_2^{e}$).

HMRS (ESI negative mode, dimethylsulfoxide): calcd. For $C_{20}H_{20}N$ [M-K]$^{-}$ 274.15903; found 274.15967 (Rel. ab: 5%, -1.7 ppm).

6. Synthesis of **4-K**:



Chemical Formula: $C_{12}H_{20}KN$
Molecular Weight: 217,4

To a suspension of CpNa (0.043 mol, 1.3 eq) in 100 mL of Et_2O, was added dropwise via a syringe N-benzotriazolylmethyl-N,N-diisopropylamine (7.7 g, 0.033 mol, 1 eq). The resulting solution was left to warm up to room temperature over 2h and then stirred for 2 additional hours. The resulting solution was left to warm up to room temperature and then refluxed overnight. Reaction progress was monitored by TLC (1: 1 Et_2O: pentane + several drops of methanol as eluent; mobile phase: silica). The white precipitate formed during the reaction was filtered off and extracted with 15 mL of Et_2O. The combined organic phases were washed with deionized water (50 mL) and a solution of saturated brine (30 mL) and dried over $MgSO_4$. After filtration and careful evaporation of the solvent (25°C, middle depression), the yellow oil was dissolved in pentane (40 mL) and left 10 min during which time the residual starting material precipitated After filtration and careful evaporation, the corresponding diene was obtained as yellow oil (4.43 g, yield: 75 %). This unstable compound was directly used after dissolution in 50 mL of Et_2O. The resulting solution was cooled down to 0°C, and a freshly-prepared solution in toluene of KHMDS (4.8 g, 0.024 mol, 0.98 eq, 40 mL) was added dropwise. The cold bath was left to warm to room temperature overnight. A dark brown solution was obtained with eventually a white precipitate. After efficient evaporation, the sticky brown oil was triturated with 50 mL of Et_2O and 50 mL of pentane to form a white precipitate. The supernatant was cannulated; the precipitate was washed twice with 20 mL of pentane before drying *in* vacuo to remove residual traces of solvent. The desired compound was obtained as a beige powder (4.8 g, yield: 90%, overall yield 67%).[10]

^{1}H NMR (600.23 MHz, 300 K, dimethylsulfoxyde-d_6): δ^1H: 5.28 (apparent t, $^3J_{HH}$= $^4J_{HH}$ = 2.5 Hz, 2H, H^b), 5.22 (apparent t, $^3J_{HH}$= $^4J_{HH}$ = 2.5 Hz, 2H, H^a), 3.41 (s, 2H, H^d), 3.21 (hept, $^3J_{HH}$ = 6.5 Hz, 2H, H^e), 0.94 (s, 12H, $^3J_{HH}$ = 6.5 Hz, H^f). traces of toluene observed.

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dimethylsulfoxyde-d_6): δ^{13}C: 116.8 (C^c), 104.0 (C^b), 102.2 (C^a), 44.9 (C^e), 44.6 (C^d), 20.7 (C^f). traces of toluene observed.

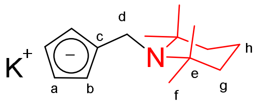
^{1}H ^{1}H COSY (600.23 MHz / 600 MHz, 300 K, dimethylsulfoxyde-d_6): δ^1H / δ^1H: 5.28 / 5.22 (CH^b / CH^a), 5.22 / 5.28 (CH^a/ CH^b), 3.21 / 0.94 (CH^e/ CH_3^f), 0.94 / 3.21 (CH_3^f/ CH^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dimethylsulfoxyde-d_6): δ^1H / δ^{13}C: 5.28 / 104.0 (CH^b), 5.22 / 102.2 (CH^a), 3.41 / 44.6 (CH_2^d), 3.21 / 44.9 (CH^e), 0.94 / 20.7 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dimethylsulfoxyde-d_6): δ^1H / δ^{13}C: 5.28 / 116.8, 104.0, 102.2, 44.6 (CH^b / C^c, CH^b, CH^a, CH_2^d), 5.22 / 116.8, 104.0 (CH^a / C^c, CH^b), 3.41 / 116.8, 104.0, 44.9 (CH^d / C^c, CH^b, CH^e), 3.21 / 44.9, 20.7 (CH^e / CH^e, CH_3^f), 0.94 / 44.9, 20.7 (CH_3^f / CH^e, CH_3^f).

HMRS (ESI negative mode, dimethylsulfoxide): calcd. For $C_{12}H_{16}N$ $[M-K]^-$ 178.15903; found 178.16042 (Rel. ab: 30%, 1.7 ppm).

7. Synthesis of **5-K**:



Chemical Formula: $C_{15}H_{24}KN$
Molecular Weight: 257,5

To a solid mixture of CpNa (0.068 mol, 1.4 eq) and N-benzotriazolylmethyl-2,2,6,6-tetramethylpiperidine (13.8 g, 0.050 mol, 1 eq) was added dropwise by cannulation at -15°C 500 mL of Et_2O. at -15°C. The resulting solution was stirred for 1 h at -15°C and then brought to completion by an additional stirring of 3 h at room temperature. The resulting solution was left to warm up to room temperature and then refluxed overnight. Reaction progress was monitored by TLC (1: 1 Et_2O: pentane + several drops of methanol as eluent; mobile phase: silica). The white precipitate formed during the reaction was filtered off and extracted with 40 mL of Et_2O twice. The combined organic phases were washed with a solution of saturated brine (30 mL) and dried over $MgSO_4$. After filtration and careful evaporation of the solvent, the corresponding diene was dissolved in 15 mL of pentane to precipitate the remaining Bt-derivative, filtered off and evaporated to yield a dark orange oil (9.83 g, yield: 90 %). This unstable compound was directly used after dissolving in 30 mL of Et_2O. The resulting solution was cooled down to 0°C, and a freshly-prepared solution in toluene of KHMDS (8.85 g, 0.044 mol, 0.98 eq, 80 mL) was added dropwise. The cold bath was left to warm to room temperature overnight. A dark brown solution was obtained. The solvent was first removed by vacuum pumping to yield a light brown precipitate. It was then dissolved in 20 mL of Et_2O 80 mL of pentane was added to yield a biphasic system. First layer was removed by cannulation and the remaining phase was dried under vacuum. The sticky oil was washed with pentane (2x20 mL) to yield a beige precipitate after drying (12.0 g, yield: 97%, overall yield 86%).[10]

^{1}H NMR (600.23 MHz, 300 K, tetrahydrofuran-d_8): δ^1H: 5.46 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 2H, H^b), 5.38 (apparent t, $^3J_{HH}$= $^4J_{HH}$ = 2.5 Hz, 2H, H^a), 3.55 (s, 2H, H^d), 1.60-1.54 (m, 2H, H^h), 1.45-1.41 (m, 4H, H^g), 1.12 (s, 12H, CH_3^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, tetrahydrofuran-d_8): δ^{13}C: 123.5 (C^c), 105.6 (C^b), 104.1 (C^a), 55.6 (C^e), 45.0 (C^d), 42.9 (C^g), 29.0 (C^f), 19.2 (C^h).

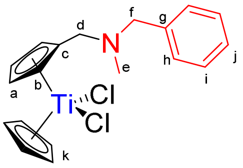
^{1}H ^{1}H COSY (600.23 MHz, 300 K, tetrahydrofuran-d_8): δ^1H / δ^1H: 5.46 / 5.38 (CH^b / CH^a), 5.38 / 5.46 (CH^a/ CH^b), 1.60-1.54 / 1.43 (CH_2^h/ CH_2^g) , 1.45-1.41 / 1.57 (CH_2^g/ CH_2^h).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d_8): δ^1H / δ^{13}C: 5.46 / 105.6 (CH^b), 5.38 / 104.1 (CH^a), 3.55 / 45.0 (CH_2^d), 1.60-1.54 / 19.2 (CH_2^h), 1.45-1.41 / 42.9 (CH_2^g), 1.12 / 29.0 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d_8): δ^1H / δ^{13}C 5.46 / 123.5, 105.6, 104.2, 45.0 (CH^b/ C^c, CH^b, CH^a, CH_2^d), 5.38 / 123.5, 105.6 (CH^a / C^c, CH^b), 3.55 / 123.5, 105.6, 55.6 (CH_2^d/ C^c, CH^b, C^e), 1.57 / 55.6, 42.9 (CH_2^h/ C^e, CH_2^g), 1.43 / 55.6, 42.9, 29.0, 19.2 (CH_2^g / C^e, CH_2^g, CH_3^f, CH_2^h), 1.12 / 55.6, 42.9, 29.0 (CH_3^f / C^e, CH_2^g, CH_3^f).

HMRS (ESI negative mode, dimethylsulfoxide): calcd. For $C_{10}H_{14}N$ $[M-K]^-$ 218.19033; found 218.19111 (Rel. ab: 100%, -1.4 ppm).

8. Synthesis of **9**:



Chemical Formula: $C_{19}H_{21}Cl_2NTi$
Molecular Weight: 382,2

A solution of **1-K** (818 mg, 3.4 mmol, 1.05 eq) in 25 mL of THF was added to a solution of $CpTiCl_3$ (718 mg, 3.2 mmol, 1 eq) in 20 mL of toluene, by cannulation at -30°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude red solution was first evaporated. The deep red oil obtained was dissolved in 20 mL of CH_2Cl_2, filtered through diatomaceous earth, which was then washed by 2 x 5 mL of CH_2Cl_2. The deep red extracts obtained were concentrated by evaporation of $^3/_4$ of the solvent and the compound was precipitate by addition of pentane with vigorous stirring. The orange-red precipitate was filtered off, and dried to yield the desired compound. (680 mg, yield = 54 %).

^{1}H NMR (600.23 MHz, 300 K, benzene-d_6): δ^1H: 7.29 (d, $^3J_{HH}$ = 7.4 Hz, 2H, H^h), 7.18 (t, $^3J_{HH}$ = 7.4 Hz, 2H, H^i), 7.10 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H^j) 6.26 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 5.98 (s, 5H, H^k), 5.68 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^a), 3.74 (s, 2H, H^d), 3.33 (s, 2H, H^f), 2.02 (s, 3H, H^e).

^{13}C{^{1}H} NMR (125.77 MHz, 300 K, benzene-d_6): δ^{13}C: 139.6 (C^g), 133.2 (C^c), 129.3 (C^h), 128.6 (C^i), 127.4 (C^j), 124.6 (C^b), 119.5 (C^k), 115.1 (C^a), 62.1 (C^f), 57.7 (C^d), 42.2 (C^e).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, benzene-d_6): δ^1H / δ^1H: 7.28 / 7.18 (CH^h / CH^i), 7.18 / 7.28, 7.10 (CH^i / CH^h, CH^j), 7.10 / 7.18 (CH^j / CH^i), 6.26 / 5.67 (CH^b / CH^a), 5.68 / 6.26 (CH^a / CH^b).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 7.28 / 129.3 (CH^h), 7.18 / 128.6 (CH^i), 7.10 / 127.4 (H^j) 6.26 / 124.6 (CH^b), 5.98 / 119.5 (CH^k), 5.68 / 115.1 (CH^a), 3.74 / 57.7 ($CH_2{}^d$), 3.33 / 62.1 ($CH_2{}^f$), 2.02 / 42.2 ($CH_3{}^e$).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 7.28 / 129.3, 128.6, 62.1 (CH^h / CH^h, CH^i, $CH_2{}^f$), 7.18 / 139.6, 128.6 (CH^i / C^g, CH^i), 7.10 / 129.3, 128.6 (CH^j / CH^h, CH^i) 6.26 / 124.6, 115.1 (CH^b / CH^b, CH^a), 5.98 / 119.5 (CH^k / CH^k), 5.68 / 133.2, 124.6, 115.1 (CH^a / C^c, CH^b, CH^a), 3.74 / 133.2, 124.6, 62.1, 42.2 ($CH_2{}^d$ / C^c, CH^b, $CH_2{}^f$, $CH_3{}^e$), 3.33 / 139.6, 129.3, 57.7, 42.2 ($CH_2{}^f$ / C^g, CH^h, $CH_2{}^d$, $CH_3{}^e$), 2.02 / 62.1, 57.7 ($CH_3{}^e$ / $CH_2{}^f$, $CH_2{}^d$).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{15}N: 2.02 / -339 (H^e / N).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{19}H_{21}NClTi$ $[M-Cl]^+$ 346.08388; found 346.08446 (Rel. ab: 90%, 2.3 ppm).

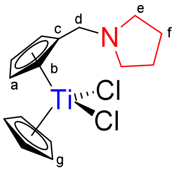
IR (ATR) ν [cm-1]

MIR: 3110; 2780; 1452; 1024; 824; 696.

FIR: 696; 610; 593; 465; 396; 361; 302; 256.

Elemental Analysis: % calcd for $C_{19}H_{19}NCl_2Ti$: C, 59.72; H, 5.54; N, 3.67; Found: C, 58.93; H, 5.50; N, 3.58.

9. Synthesis of **10**:



Chemical Formula:
$C_{15}H_{19}Cl_2NTi$
Molecular Weight: 332,1

A solution of **2-K** (2.25 g, 0.012 mol, 1 eq) in 150 mL of THF was added to a solution of $CpTiCl_3$ (2.60 g, 0.012 mol, 1 eq) dissolved in 180 mL of toluene, by cannulation at -30°C. The resulting red solution was left to warm up to room temperature and then stirred overnight. The crude dark-red solution was first evaporated. The deep red oil obtained was dissolved in 50 mL of CH_2Cl_2, filtered through diatomaceous earth which was then washed by 2 x 2 mL of CH_2Cl_2. The deep-red extracts obtained were concentrated by evaporation of $^3/_4$ of the solvent and the compound was precipitate by addition of pentane under vigorous stirring. The orange-red precipitate was filtered off, and dried to yield the desired compound. (2.74 g, yield = 69 %).

^{1}H NMR (600 MHz, 300 K, dichloromethane-d_2): δ^1H: 6.57 (s, 5H, H^g), 6.52 (m, 2H, H^b), 6.46 (apparent t, $^3J_{HH} = {}^4J_{HH}$ = 2.6 Hz, 2H, H^a), 3.67 (s, 2H, H^d), 2.61-2.49 (s, 4H, H^e), 1.83-1.70 (s, 4H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dichloromethane-d_2): δ^{13}C: 133.9 (C^c), 124.7 (C^b), 120.6 (C^g), 116.8 (C^a), 55.8 (C^d), 54.7 (C^e), 24.1 (C^f).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^1H 6.52 / 6.46 (CH^b / CH^a), 6.46 / 6.52 (CH^a / CH^b), 2.61-2.49 / 1.83-1.70 (CH_2^e / CH_2^f), 1.83-1.70 / 2.61-2.49 (CH_2^f / CH_2^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 6.57 / 120.6 (CH^g), 6.52 / 124.7 (CH^b), 6.46 / 116.8 (CH^a), 3.67 / 55.8 (CH_2^d), 2.61-2.49 / 54.7 (CH_2^e), 1.83-1.70 / 24.1 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 6.57 / 120.6 (CH^g / CH^g), 6.52 / 124.8, 116.8 (CH^i / C^g, CH^h, CH^j), 6.46 / 133.9, 124.7, 116.8 (CH^j / CH^h, CH^i) 3.67 / 133.9, 124.7, 54.7 (CH_2^d / C^c, CH^b, CH_2^e), 2.61-2.49 / 54.7, 24.1 (CH_2^e / CH_2^e, CH_2^f), 1.83-1.70 / 54.7, 24.1 (CH_2^f / CH_2^e, CH_2^f).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{15}N: 1.83-1.70 / -322 (H^f / N).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{15}H_{19}NClTi$ $[M\text{-}Cl]^+$ 296.06717; found 296.06819 (Rel. ab: 50%, -2.8 ppm).

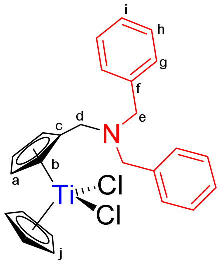
IR (ATR) ν [cm-1]

MIR: 3107; 2952; 2778; 2342; 1440; 1014; 828.

FIR: 640; 620; 587; 405; 362; 303; 252.

Elemental Analysis: % calcd for $C_{15}H_{19}NCl_2Ti$: C, 54.25; H, 5.77; N, 4.22; Found: C, 54.66; H, 5.51; N, 4.26.

10. Synthesis of **11**:



Chemical Formula: $C_{25}H_{25}Cl_2NTi$
Molecular Weight: 458,2

A solution of **3-K** (3.76 g, 0.012 mol, 1.05 eq) in 100 mL of THF was added to a solution of $CpTiCl_3$ (2.5 g, 0.011 mol, 1 eq) in 140 mL of toluene, by cannulation at -30°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude red solution was first evaporated. The deep red oil obtained was dissolved in 50 mL of CH_2Cl_2, filtered through diatomaceous earth which was then washed by 2 x 15 mL of CH_2Cl_2. The deep-red extracts obtained were concentrated by evaporation of $^3/_4$ of the solvent and the compound was precipitated by addition of pentane (70 mL) with vigorous stirring. The orange-red precipitate was filtered off, and dried to yield the desired compound. (4.0 g, yield = 80 %).

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H: 7.38 (d, $^3J_{HH}$ = 7.4 Hz, 4H, H^g), 7.33 (t, $^3J_{HH}$ = 7.4 Hz, 4H, H^h), 7.25 (t, $^3J_{HH}$ = 7.4 Hz, 2H, H^i), 6.52 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 6.43 (t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^a), 6.38 (s, 5H, H^j), 3.60 (s, 2H, H^d), 3.57 (s, 4H, H^e).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dichloromethane-d_2): δ^{13}C: 139.9 (C^f), 133.5 (C^c), 129.5 (C^g), 128.8 (C^h), 127.6 (C^i), 124.5 (C^b), 120.5 (C^j), 117.6 (C^a), 58.8 (C^e), 53.6 (C^d).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^1H: 7.38 / 7.33 (CH^g / CH^h), 7.33 / 7.38, 7.25 (CH^h / CH^g, CH^i), 7.25 / 7.33 (CH^i / CH^g), 6.52 / 6.43 (CH^b / CH^a), 6.43 / 6.52 (CH^a / CH^b).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 7.38 / 129.5 (CH^g), 7.33 / 128.8 (CH^h), 7.25 / 127.6 (H^i), 6.52 / 124.5 (CH^b), 6.43 / 117.6 (CH^a), 6.38 / 120.5 (CH^j), 3.60 / 53.6 (CH$_2$^{d}), 3.57 / 58.8 (CH$_2$^{e}).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 7.38 / 129.5, 127.6, 58.8 (CH^g / CH^g, CH^i, CH^e), 7.33 / 139.9, 128.8 (CH^h / C^f, CH^h), 7.25 / 129.5 (CH^i / CH^g)

6.52 / 117.6 (CH^b / CH^a), 6.43 / 133.5, 124.5 (CH^a / C^c, CH^b), 6.38 / 120.5 (CH^j / CH^j), 3.60 / 133.5, 124.5, 58.8 (CH_2^d / C^c, CH^b, CH_2^e), 3.57 / 139.9, 129.5, 58.8, 53.6 (CH_2^e / C^f, CH^g, CH_2^d, CH_2^e).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{15}N: 3.60 / -327 (H^d / N).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{25}H_{26}NCl_2Ti$ $[M+H]^+$ 458.09196; found 458.09393 (Rel. ab: 100%, 5.0 ppm).

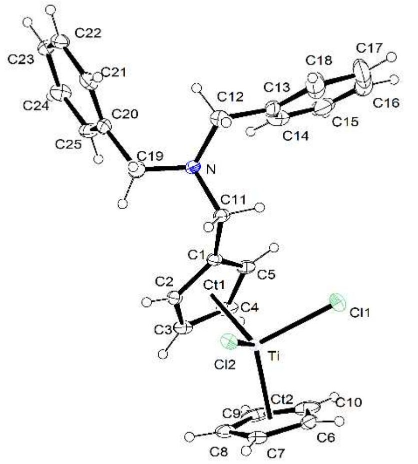
IR (ATR) ν [cm-1]

MIR: 3098; 3061; 2784; 1493; 1117; 1029; 856; 821; 738; 729.

FIR: 698; 612; 491; 473; 391; 375; 365; 306; 264.

Elemental Analysis: % calcd: C, 65.53; H, 5.50; N, 3.06; Found: C, 66.52; H, 5.57; N, 3.20.

XRD:

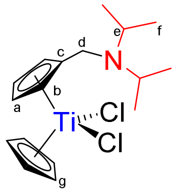


Compound	**q2**
Formula	$C_{25}H_{25}Cl_2NTi$
$D_{calc.}$/ g cm^{-3}	1.386
μ/mm^{-1}	0.645
Formula Weight	458.26
Colour	red
Shape	prism
Size/mm^3	0.30×0.25×0.20
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	6.5681(2)
b/Å	12.8473(4)
c/Å	13.7963(3)
α/°	73.684(2)
β/°	79.294(2)
γ/°	86.2190(10)
V/Å^3	1097.72(5)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.652
Θ_{max}/°	27.492
Measured Refl.	15014
Independent Refl.	4976
Reflections Used	4646
R_{int}	0.0202
Parameters	262
Restraints	0
Largest Peak	1.479
Deepest Hole	-0.550
GooF	1.057
wR_2 (all data)	0.1146
wR_2	0.1121
R_1 (all data)	0.0481
R_1	0.0452

Experimental. Single red prism-shaped crystals of (**q2**) were obtained by recrystallisation from diffusion of pentane into a concentrated dichloromethane solution at room temperature. A suitable crystal (0.30×0.25×0.20) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the SIR2004 (Burla et al., 2007) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{25}H_{25}Cl_2NTi$, M_r = 458.26, triclinic, P-1 (No. 2), a = 6.5681(2) Å, b = 12.8473(4) Å, c = 13.7963(3) Å, α = 73.684(2)°, β = 79.294(2)°, γ = 86.2190(10)°, V = 1097.72(5) Å^3, T = 115 K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 0.645, 15014 reflections measured, 4976 unique (R_{int} = 0.0202) which were used in all calculations. The final wR_2 was 0.1146 (all data) and R_1 was 0.0452 (I > 2(I)).

11. Synthesis of **12**:



Chemical Formula: $C_{17}H_{25}Cl_2NTi$
Molecular Weight: 362,2

A solution of **4-K** (1.19 g, 5.5 mmol, 1 eq) in 25 mL of THF was added to a solution of $CpTiCl_3$ (1.2 g, 5.5 mmol, 1 eq) in 25 mL of toluene, by cannulation at -30°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude red solution was first evaporated. The deep-red oil obtained was dissolved in 30 mL of CH_2Cl_2 and stirred 1h inside the glovebox to facilitate the following filtration. This solution was filtered through diatomaceous earth which was then washed by 2 x 5 mL of CH_2Cl_2. The deep red extracts obtained were concentrated by evaporation of $^3/_4$ of the solvent and the compound was precipitated by addition of pentane (40) with vigorous stirring. The orange-red precipitate was filtered off, washed with pentane twice (15 mL) and dried to yield the desired compound. (1.61 g, yield = 80 %).

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^1H: 6.54 (s, 5H, H^g), 6.52 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^b), 6.44 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^a), 3.71 (s, 2H, H^d), 2.97 (hept, $^3J_{HH} = 6.6$ Hz, 2H, H^e), 1.01 (d, $^3J_{HH} = 6.6$ Hz, 12H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 140.4 (C^c), 124.1 (C^b), 120.3 (C^g), 117.2 (C^a), 49.2 (C^e), 45.6 (C^d), 21.3 (C^f).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^1H / δ^1H: 6.52 / 6.44 (CH^b / CH^a), 6.44 / 6.52 (CH^a / CH^b), 2.97 / 1.01 (CH_2^e / CH_3^f), 1.01 / 2.97 (CH_3^f / CH_2^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$): δ^1H / δ^{13}C: 6.54 / 120.3 (CH^g), 6.52 / 124.1 (CH^b), 6.44 / 117.2 (CH^a), 3.71 / 45.6 (CH_2^d), 2.97 / 49.1 (CH^e), 1.01 / 21.3 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$): δ^1H / δ^{13}C: 6.54 / 120.3 (CH^g / CH^g), 6.52 / 140.4, 124.1, 117.2 (CH^b / C^c, CH^b, CH^a), 6.44 / 140.4, 124.1 (CH^a / C^c, CH^b), 3.71 / 140.4, 124.1, 49.1 (CH_2^d / C^c, CH^b, CH^e), 2.97 / 49.1, 45.6, 21.3 (CH^e / CH^e, CH_2^d, CH_3^f), 1.01 / 49.1, 21.3 (CH_3^f / CH^e, CH_3^f).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$): δ^1H / δ^{15}N: 1.01 / -322 (H^f / N).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{17}H_{26}NClTi$ $[M+H]^+$ 362.09189; found 362.09285 (Rel. ab: 100%, 3.4 ppm).

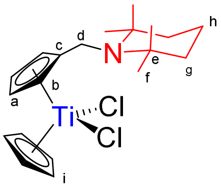
IR (ATR) ν [cm-1]

MIR: 3109; 2962; 1385; 1202; 1170; 859; 825.

FIR: 694; 619; 610; 522; 413; 387; 362; 302; 255.

Elemental Analysis: % calcd for $C_{17}H_{25}Cl_2NTi$: C, 56.38; H, 6.96; N, 3.87; Found: C, 55.99; H, 6.96; N, 3.88.

12. Synthesis of **13**:



Chemical Formula: $C_{20}H_{29}Cl_2NTi$
Molecular Weight: 402,2

A solution of **5-K** (693 mg, 3.17 mmol, 1.0 eq) in 20 mL of toluene was added to a solution of $CpTiCl_3$ (800 mg, 3.17 mmol, 1 eq) in 20 mL of toluene. Both solutions were cooled down at -15°C in the glovebox where the reaction was launched. The resulting solution was left to warm up to room temperature and then stirred overnight. Toluene was then evaporated and the red residue was dissolved in dichloromethane and filtered through diatomaceous earth in the glovebox. All volatiles were evaporated and the red precipitate was washed twice with pentane (20mL). An orange powder was obtained after drying *in vacuo*. (870 mg, yield = 68 %).

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d_2): δ^{1}H: 6.26-6.20 (bs, 2H, H^b), 6.01 (s, 5H, H^i), 5.73-5.67 (bs, 2H, H^a), 4.02 (s, 2H, H^d), 1.45-1.40 (m, 2H, H^h), 1.39-1.36 (m, 4H, H^g), 1.01 (s, 12H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dichloromethane-d_2): δ^{13}C: 146.2 (C^c), 121.9 (C^b), 119.1 (C^i), 115.6 (C^a), 55.6 (C^e), 45.6 (C^d), 41.9 (C^g), 28.6-27.9 (bs, C^f), 18.2 (C^h).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d_2): δ^{1}H / δ^{1}H: 6.26-6.20 / 5.73-5.67 (CH^a / CH^b), 5.73-5.67 / 6.26-6.20 (CH^b / CH^a), 1.45-1.40 / 1.39-1.36 (CH_2^h / CH_2^g), 1.39-1.36 / 1.45-1.40 (CH_2^g / CH_2^h).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^{1}H / δ^{13}C: 6.26-6.20 / 121.9 (CH^a), 6.01 / 119.1 (CH^i), 5.70 / 115.6 (CH^b), 4.02 / 45.6 (CH_2^d), 1.45-1.40 / 18.2 (CH_2^h), 1.39-1.36 / 41.9 (CH_2^g), 1.01 / 28.6-27.9 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^{1}H / δ^{13}C: 6.26-6.20 / 146.1, 121.9, 115.6 (CH^a / C^c, CH^a, CH^b), 6.01 / 119.1 (CH^i / CH^i), 5.70 / 146.1, 121.9 (CH^b / C^c, CH^a), 4.02 / 146.1, 121.1, 55.6 (CH_2^d / C^c, CH^a, C^e), 1.45-1.40 / 55.6, 41.9 (CH^h / C^e, CH_2^g), 1.39-1.36 / 55.6, 41.9, 18.2 (CH_2^h / C^e, CH_2^g, CH_2^h), 1.01 / 55.6, 41.9, 28.26-27.9 (CH_3^f / C^e, CH_2^h, CH_3^f).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^{1}H / δ^{15}N: 1.01 / -309 (H^f / N).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{20}H_{30}NCl_2Ti$ $[M+H]^+$ 402.12322; found 402.12089 (Rel. ab: 90%, -5.1 ppm).

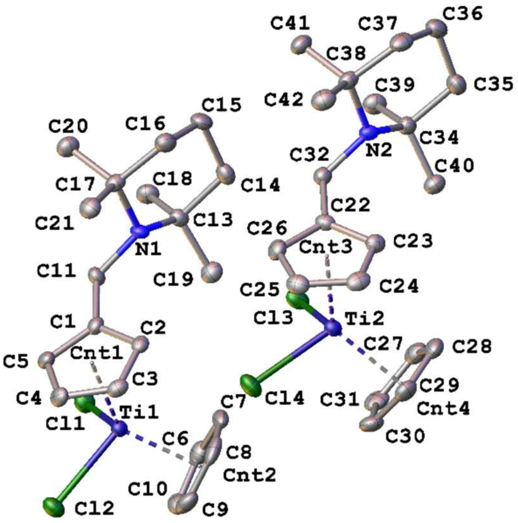
IR (ATR) ν [cm-1]

MIR: 3105; 2927; 1460; 1174; 1024; 816.

FIR: 694; 621; 631; 392; 332; 276; 144.

Elemental Analysis: % calcd for $C_{20}H_{29}NCl_2Ti$: C, 59.72; H, 7.27; N, 3.48; Found: C, 59.88; H, 7.71; N, 3.44.

XRD:

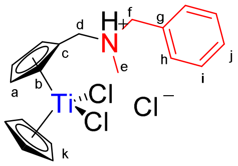


Experimental. Single light yellow needle-shaped crystals of (**ad10**) were obtained by slow diffusion of pentane into a concentrated dichloromethane solution at room temperature. A suitable crystal (0.17×0.05×0.02) mm³ was selected and mounted on a mylar loop with oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at T = 115 K during data collection. The structure was solved with the SIR2004 (Burla et al., 2007) structure solution program, using the Direct Methods solution method. Using **Olex2** (Dolomanov et al., 2009), the model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{20}H_{29}Cl_2NTi$, M_r = 402.24, triclinic, P-1 (No. 2), a = 7.7334(2) Å, b = 12.1253(4) Å, c = 20.8289(8) Å, α = 85.756(2)°, β = 85.836(2)°, γ = 78.471(2)°, V = 1905.12(11) Å³, T = 115 K, Z = 4, Z' = 2, $\mu(\mathrm{MoK}_\alpha)$ = 0.731, 24737 reflections measured, 8484 unique (R_{int} = 0.0789) which were used in all calculations. The final wR_2 was 0.1361 (all data) and R_1 was 0.0726 (I > 2(I)).

Compound	**ad10**
Formula	$C_{20}H_{29}Cl_2NTi$
$D_{calc.}$/ g cm^{-3}	1.402
μ/mm^{-1}	0.731
Formula Weight	402.24
Colour	light yellow
Shape	needle
Size/mm³	0.17×0.05×0.02
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	7.7334(2)
b/Å	12.1253(4)
c/Å	20.8289(8)
α/°	85.756(2)
β/°	85.836(2)
γ/°	78.471(2)
V/Å³	1905.12(11)
Z	4
Z'	2
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.030
Θ_{max}/°	27.453
Measured Refl.	24737
Independent Refl.	8484
Reflections Used	5551
R_{int}	0.0789
Parameters	433
Restraints	0
Largest Peak	0.610
Deepest Hole	-0.471
GooF	1.166
wR_2 (all data)	0.1361
wR_2	0.1154
R_1 (all data)	0.1294
R_1	0.0726

13. Synthesis of **14**:



Chemical Formula: $C_{19}H_{22}Cl_3NTi$
Molecular Weight: 418,6

To a solution of **9** (100 mg, 0.26 mmol, 1 eq, 5 mL toluene) was added dropwise a freshly-prepared HCl solution (5 mL of toluene). A red precipitate was directly formed. The reaction mixture was left to stir for 15 min. The precipitate was then filtered off and washed with 3 x 5 mL of pentane under aerobic conditions, yielding the desired precipitate as an orange solid (74 mg, yield: 67 %).

^{1}H NMR (600 MHz, 300 K, chloroform-d_1): δ^{1}H: 12.83 (s, 1H, 7.28, H^l), 7.62-7.58 (m, 2H, H^h), 7.48-7.43 (m, 3H, H^i / H^j), 7.07 (apparent q, $^3J_{HH} = {}^4J_{HH}$ = 2.6 Hz, 1H, H^b), 6.97 (apparent q, $^3J_{HH} = {}^4J_{HH}$ = 2.6 Hz,, 1H, $H^{b'}$), 6.69 (s, 5H, H^k), 6.60 (apparent q, $^3J_{HH} = {}^4J_{HH}$ = 2.6 Hz, 1H, H^a), 6.57 (apparent q, $^3J_{HH} = {}^4J_{HH}$ = 2.6 Hz, 1H, $H^{a'}$), 4.38 (overlapping dd with H^d, $^2J_{HH}$ = 13.2 Hz $^3J_{HH}$ = 3.6 Hz, 1H, H^f), 4.37 (overlapping dd with H^f, $^2J_{HH}$ = 13.7 Hz $^3J_{HH}$ = 4.6 Hz, 1H, H^d), 4.13 (dd, $^2J_{HH}$ = 13.7 Hz, $^3J_{HdHl}$ = 6.0 Hz, 1H, $H^{d'}$), 4.04 (dd, $^2J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, $H^{f'}$), 2.60 (d, $^3J_{HH}$ = 2.6 Hz, 3H, H^e).[11]

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, chloroform-d_1): δ^{13}C: 131.5 (C^h), 130.5 (C^i), 129.7 (C^j), 128.2 (C^g), 125.9 ($C^{b'}$), 124.8 (C^b), 122.0 (C^c), 121.3 (C^k), 117.0 ($C^{a'}$), 116.4 (C^a), 60.0 (C^f), 55.4 (C^d), 39.2 (C^e).

^{1}H ^{1}H COSY (500.13 MHz, 300 K, chloroform-d_1): δ^{1}H / δ^{1}H: 7.62-7.58 / 7.48-7.43 (CH^h / CH^i, CH^j), 7.48-7.43 / 7.62-7.58 (CH^i, CH^j / CH^h,), 7.07 / 6.60 (CH^b / CH^a), 6.97 / 6.57 (CH^b / CH^a), 6.60 / 7.07 (CH^a / CH^b), 6.57 / 6.97 (CH^a / CH^b), 4.39 / 4.04 (CH_2^f), 4.36 / 4.13 (CH_2^d), 4.13 / 4.36 (CH_2^d), 4.04 / 4.39 (CH_2^f).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1): δ^{1}H / δ^{13}C: 7.62-7.68 / 131.5 (CH^h), 7.48-7.43 / 130.5, 129.7 (CH^i, CH^j), 7.07 / 124.8 (CH^b) 6.96 / 125.9 ($CH^{b'}$), 6.69 / 121.3 (CH^k), 6.60 / 116.4 (CH^a), 6.57 / 117.0 ($CH^{a'}$), 4.39 / 60.0 (CH_2^f), 4.36 / 55.4 (CH_2^d), 4.13 / 55.4 (CH_2^d), 4.04 / 60.0 (CH_2^f), 2.60 / 39.2 (CH_3^e).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1): δ^{1}H / δ^{13}C: 7.62-7.68 / 131.5, 130.5, 129.7, 60.0 (CH^h / CH^h, CH^j, CH^i, CH_2^d), 7.48-7.43 / 131.5, 130.5, 129.7, 128.2 (CH^i, CH^j / CH^h, $Ch^{j/i}$, $CH^{i/j}$, C^g), 7.07 / 125.9, 117.0 (CH^b / $CH^{b'}$, $CH^{a'}$) 6.97 / 124.8, 116.4 ($CH^{b'}$ / CH^b, CH^a), 6.69 / 121.3 (CH^k / CH^k), 6.60 / 125.9, 122.0, 117.0 (CH^a / $CH^{b'}$, C^c, $CH^{a'}$), 6.57 / 124.8, 122.0, 116.4 ($CH^{a'}$ / CH^b, C^c, CH^a), 4.39 / 131.5, 128.2 (CH_2^f / CH^h, C^g), 4.36 / 125.9, 122.0,

---

[11] As the molecule is chiral, exact position of diastereotopic protons (x/x') on CH_2 groups was not determined, and noted.

39.2 (CH_2^d / CH^b, C^c, CH_3^e), 4.13 / 124.8, 122.0, 60.0, 39.2 (CH_2^d / CH^b, C^c, CH_2^f, CH_3^e), 4.04 / 131.6, 128.2, 55.4, 39.2 (CH_2^f / CH^h, C^g, CH_2^d, CH_3^e), 2.60 / 60.0, 55.4 (CH_3^e / CH_2^f, CH_2^d).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{19}H_{22}NCl_2Ti$ $[M]^+$ 382.06060; found 382.05935 (Rel. ab: 10%, -2.6 ppm).

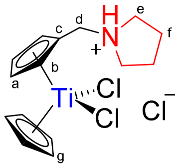
IR (ATR) ν [cm-1]

MIR: 3111; 2953; 2352 (N-H); 1461; 1434; 834; 696.

FIR: 696; 611; 497; 367; 304; 267.

Elemental Analysis: **%** calcd for $C_{19}H_{22}Cl_3NTi$: C, 54.51; H, 5.30; N, 3.35; Found: C, 54.50; H, 5.44; N, 3.69.

14. Synthesis of **15**:



Chemical Formula: $C_{15}H_{20}Cl_3NTi$
Molecular Weight: 368,6

To a solution of **10** (3.08 g, 0.008 mol, 1 eq, 20 mL dichloromethane) was added dropwise a freshly-prepared HCl solution (20 mL of toluene). The reaction mixture was left to stir for 15 min and the red precipitate was obtained by adding 20 mL of pentane. It was then filtered off and washed with 3 x 5 mL of pentane. (1.6 g, yield: 52 %).

^{1}H NMR (600 MHz, 300 K, chloroform-d$_1$): δ^{1}H: 12.77 (bs, 1H, H^h), 6.92 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 6.67 (s, 5H, H^g), 6.56 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^a), 4.27 (d, $^3J_{HH}$ = 6.0 Hz, 2H, H^d), 3.72-3.63 (m, 2H, H^e), 2.94-2.83 (m, 2H, H^e), 2.29-2.18 (m, 2H, H^f), 2.14-2.05 (m, 2H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, chloroform-d$_1$): δ^{13}C: 125.0 (C^b), 123.1 (C^c), 121.1 (C^g), 116.2 (C^a), 54.3 (C^d), 53.8 (C^e), 23.5 (C^f).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, chloroform-d$_1$): δ^{1}H / δ^{1}H: 6.92 / 6.56 (CH^b / CH^a), 6.56 / 6.92 (CH^a / CH^b), 3.72-3.63 / 2.94-2.83, 2.29-2.18 (CH_2^e / CH_2^e, CH_2^f), 2.94-2.83 / 3.72-3.63, 2.29-2.18, 2.14-2.05 (CH_2^e / CH_2^e, CH_2^f, CH_2^f), 2.29-2.18 / 3.72-3.63, 2.94-2.83, 2.12 (CH_2^f / CH_2^e, CH_2^e, CH_2^f), 2.14-2.05 / 3.72-3.63, 2.94-2.83, 2.29-2.18 (CH_2^f / CH_2^e, CH_2^e, CH_2^f).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$): δ^{1}H / δ^{13}C: 6.92 / 125.0 (CH^b), 6.67 / 121.1 (CH^g), 6.56 / 116.2 (CH^a), 4.27 / 54.3 (CH_2^d), 3.72-3.63 / 53.8 (CH_2^e), 2.94-2.83 / 53.8 (CH_2^e), 2.29-2.18 / 23.5 (CH_2^f), 2.14-2.05 / 23.5 (CH_2^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$): δ^{1}H / δ^{13}C: 6.92 / 125.0, 123.1, 116.2 (CH^a / CH^b, C^c, CH^a), 6.67 / 121.1 (CH^g / CH^g), 6.56 / 125.0, 123.1 (CH^b / CH^a, C^c) 4.27 / 125.0, 123.1, 53.8 (CH_2^d / CH^b, C^c,CH_2^e), 3.72-3.63 / 54.3, 53.8, 23.5 (CH_2^e / CH_2^d, CH_2^e,

CH_2^f), 2.94-2.83 / 54.3, 53.8, 23.5 (CH_2^e / CH_2^d CH_2^e, CH_2^f), 2.29-2.18 / 53.8, 23.5 (CH_2^f / CH_2^e, CH_2^f), 2.14-2.05 / 53.8, 23.5 (CH_2^f / CH_2^e, CH_2^f).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{15}H_{20}NCl_2Ti$ $[M-Cl+H]^+$ 332.04492; found 332.04335 (Rel. ab: 100%, -4.0 ppm).

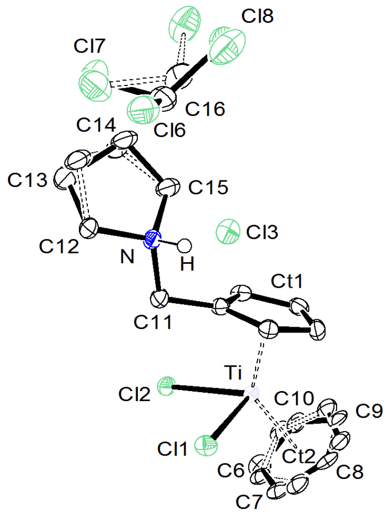
IR (ATR) ν [cm-1]

MIR: 3111; 2954; 2357 (N-H); 1433; 1015; 823.

FIR: 697; 642; 607; 597; 448; 401; 365; 303; 263; 257.

Elemental Analysis: % calcd for $C_{15}H_{20}Cl_3NTi$: C, 48.88; H, 5.44; N, 3.69; Found: C, 49.14; H, 5.82; N, 3.89.

XRD:

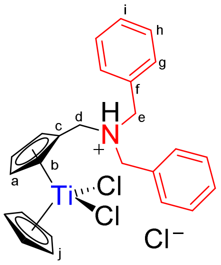


Experimental. Single orange plate-shaped crystals of (**quent1**) were obtained by slow diffusion of pentane into a chloroform solution at room temperature. A suitable crystal (0.25×0.10×0.05) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at T = 115 K during data collection., The structure was solved with the SIR2004 (Burla et al., 2007) structure solution program, using the Direct Methods solution method. Using **Olex2** (Dolomanov et al., 2009) the model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{16}H_{21}Cl_6NTi$, M_r = 487.94, triclinic, P-1 (No. 2), a = 6.3551(2) Å, b = 11.2920(4) Å, c = 15.2516(4) Å, α = 73.396(2)°, β = 79.317(2)°, γ = 78.9870(10)°, V = 1019.53(6) Å^3, T = 115 K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 1.205, 14702 reflections measured, 4602 unique (R_{int} = 0.0312) which were used in all calculations. The final wR_2 was 0.1911 (all data) and R_1 was 0.0798 (I > 2(I)).

Compound	**quent1**
Formula	$C_{16}H_{21}Cl_6NTi$
$D_{calc.}$/ g cm^{-3}	1.589
μ/mm^{-1}	1.205
Formula Weight	487.94
Colour	orange
Shape	plate
Size/mm^3	0.25×0.10×0.05
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	6.3551(2)
b/Å	11.2920(4)
c/Å	15.2516(4)
α/°	73.396(2)
β/°	79.317(2)
γ/°	78.9870(10)
V/Å^3	1019.53(6)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.902
Θ_{max}/°	27.505
Measured Refl.	14702
Independent Refl.	4602
Reflections Used	4354
R_{int}	0.0312
Parameters	300
Restraints	456
Largest Peak	0.851
Deepest Hole	-0.791
GooF	1.240
wR_2 (all data)	0.1911
wR_2	0.1894
R_1 (all data)	0.0832
R_1	0.0798

15. Synthesis of **16**:



Chemical Formula: $C_{25}H_{26}Cl_3NTi$
Molecular Weight: 494,7

To a solution of **11** (150 mg, 0.45 mmol, 1 eq, 5 mL toluene) was added dropwise a freshly-prepared HCl solution (5 mL). A red precipitate appeared from the red starting solution. The reaction mixture was left to stir for 15 min and the red precipitate was then filtered off and washed with 2 mL of toluene and 3 x 5 mL of pentane. (100 mg, yield: 60 %).

^{1}H NMR (600.23 MHz, 300 K, chloroform-d$_1$): δ^1H: 12.90 (s, 1H, H^k), 7.63-7.59 (m, 4H, H^g), 7.46-7.43 (m, 6H, H^h, H^i), 6.96 (apparent t, $^3J_{HH} = {}^4J_{HH}$ = 2.6 Hz, 2H, H^a), 6.61 (s, 5H, H^j), 6.47 (apparent t, $^3J_{HH} = {}^4J_{HH}$ = 2.6 Hz, 2H, H^b), 4.25 (dd, $^2J_{HH}$ = 13.3 Hz, $^3J_{HNIH}$ = 4.5 Hz, 2H, H^e), 4.18-4.15 (m overlapping with H^e, 2H, H^d), 4.15 (dd overlapping with H^d, $^2J_{HH}$ = 13.3 Hz, $^3J_{HNH}$ = 4.5 Hz, 2H, H^e).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, chloroform-d$_1$): δ^{13}C: 131.7 (C^g), 130.4 (C^i), 129.7 (C^h), 128.4 (C^f), 124.9 (C^a), 122.5 (C^c), 121.2 (C^j), 117.3 (C^b), 57.5 (C^e), 52.5 (C^d).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, chloroform-d$_1$): δ^1H / δ^1H: 7.63-7.59 / 7.46-7.43 (CH^g / CH^h, CH^i), 7.46-7.43 / 7.63-7.59 (CH^h, CH^i / CH^g), 6.96 / 6.47 (CH^a / CH^b), 6.47 / 6.96 (CH^b / CH^a), 4.25 / 4.14 (CH^e / CH^e), 4.14 / 4.25 (CH^e / CH^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$): δ^1H / δ^{13}C: 7.63-7.59 / 131.7 (CH^g), 7.46-7.43 / 130.4, 129.7 (CH^i, CH^h), 6.96 / 124.9 (CH^b), 6.61 / 121.2 (CH^j), 6.47 / 117.3 (CH^b), 4.25 / 57.5 (CH^e), 4.18-4.15 / 52.5 (CH$_2$^{d}), 4.14 / 57.5 (CH$_2$^{e}).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$): δ^1H / δ^{13}C: 7.63-7.59 / 131.7, 130.4, 129.7 (CH^g / CH^g, CH^i, CH^h), 7.46-7.43 / 131.7, 129.7, 128.4 (CH^h, CH^i / CH^g, CH$^{h/i}$, C^f), 6.96 / 124.9, 122.5, 117.3 (CH^a / CH^a, C^c, CH^b), 6.61 / 121.2 (CH^j / CH^j), 6.47 / 124.9, 122.5, 117.3 (CH^b / CH^a , C^c, CH^b), 4.25 / 131.7, 128.4 (CH$_2$^{e} / CH^g, C^f), 4.18-4.15 / 124.9, 122.5, 57.5 (CH$_2$^{d} / CH^a, C^c, CH$_2$^{d}, CH$_2$^{e}), 4.14 / 131.7, 128.4 (CH$_2$^{e} / CH^g, C^f).

HMRS (Positive mode ESI, dichloromethane-methanol): m/z calcd. for $C_{25}H_{26}NCl_2Ti$ [M-Cl]$^+$ 458.09196; found 458.09056 (Rel. ab: 15%, -2.3 ppm)

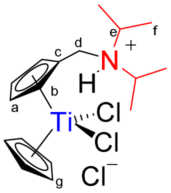
IR (ATR) ν [cm-1]

MIR: 3108; 2423 (N-H); 2354; 1445; 824.

FIR: 696; 615; 601; 506; 488; 363; 304; 256.

Elemental Analysis: % calcd for $C_{25}H_{26}Cl_3NTi$: C, 60.70; H, 5.30; N, 2.83; Found: C, 60.54; H, 5.13; N, 2.92.

16. Synthesis of **17**:



Chemical Formula: $C_{17}H_{26}Cl_3NTi$
Molecular Weight: 398,6

To a solution of **12** (725 mg, 1.82 mmol, 1 eq, 5 mL toluene) was added dropwise a freshly-prepared HCl solution (5 mL). A red precipitate appeared from the red starting solution. The reaction mixture was left to stir for 15 min and the red precipitate was then filtered off and washed with 2 mL of toluene and 3 x 5 mL of pentane. (490 mg, yield: 66 %).

^{1}H NMR (600.23 MHz, 300 K, chloroform-d$_1$): δ^1H: 11.62 (s, 1H, H^h), 7.00 (bs, 2H, H^a), 6.68 (s, 5H, H^g), 6.57 (bs, 2H, H^b), 4.35 (d, $^3J_{HNH}$ = 5.2 Hz, 2H, H^d), 3.71 (dhept, $^3J_{HH}$ = 6.7 Hz, $^3J_{HNH}$ = 3.4 Hz, 2H, H^e), 1.56 (d, $^3J_{HH}$ = 6.7 Hz, 6H, H^f), 1.51 (d, $^3J_{HH}$ = 6.7 Hz, 6H, H^f).[12]

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, chloroform-d$_1$): δ^{13}C: 127.0 (CH^a), 122.8 (C^c), 120.9 (C^g), 115.0 (C^b), 55.2 (C^e), 46.6 (C^d), 19.3 (C^f), 18.1 (C^f).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, chloroform-d$_1$): δ^1H / δ^1H: 7.00 / 6.57 (CH^a / CH^b), 6.57 / 7.00 (CH^b / CH^a), 3.71 / 1.56, 1.51 (CH_2^e / $CH_3^{f,}$ CH_3^f), 1.56 / 3.71 (CH_3^f / CH_2^e), 1.51 / 3.71 (CH_3^f / CH_2^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$): δ^1H / δ^{13}C: 7.00 / 127.0 (CH^a), 6.68 / 120.9 (CH^g), 6.57 / 115.0 (CH^b), 4.35 / 46.6 (CH_2^d), 3.71 / 55.2 (CH^e), 1.56 / 19.3 (CH_3^f), 1.56 / 19.3 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$): δ^1H / δ^{13}C: 7.00 / 127.0, 122.8 115.0 (CH^a / C^c, CH^a, CH^b), 6.68 / 120.9 (CH^g / CH^g), 6.57 / 127.0, 122.8, 55.2 (CH^b / CH^a, C^c, CH_2^e), 4.35 / 127.0, 122.8, 55.2 (CH_2^d / CH^a, C^c, CH^e), 1.56 / 55.2, 18.1 (CH^f / CH_2^d, CH_3^f), 1.51 / 55.2, 19.3 (CH_3^f / CH_2^d, CH_3^f).

HMRS (Positive mode ESI, dichloromethane-methanol): m/z calcd. for $C_{19}H_{21}NClTi$ [M-Cl]$^+$ 362.09189; found 362.09282 (Rel. ab: 85%, 3.3 ppm).

IR (ATR) ν [cm-1]

MIR: 3109; 3051; 2483 (N-H); 1423; 819.

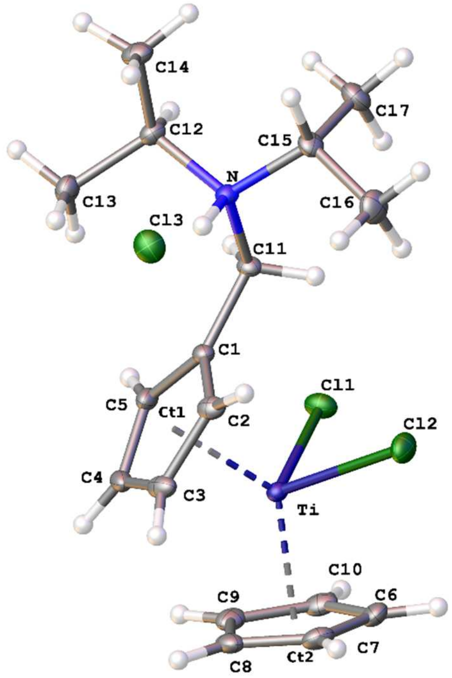
FIR: 631; 611; 554; 497; 402; 362; 304; 255.

---

[12] Methyl groups are diastereotopics, that's why, two different signals are observed.

Elemental Analysis: % calcd for $C_{25}H_{26}Cl_3NTi$: C, 51.22; H, 6.57; N, 3.51; Found: C, 50.95; H, 7.64; N, 3.52.

XRD:

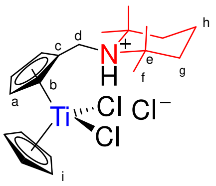


Compound	**quentin7_0m**
Formula	$C_{17}H_{26}Cl_3TiN$
$D_{calc.}$/ g cm^{-3}	1.456
μ/mm^{-1}	0.907
Formula Weight	398.64
Colour	red
Shape	plate
Size/mm^3	0.17×0.17×0.05
T/K	115
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	11.0641(6)
b/Å	10.2866(6)
c/Å	16.7645(9)
α/°	90
β/°	107.559(2)
γ/°	90
V/Å^3	1819.10(18)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.549
Θ_{max}/°	35.359
Measured Refl.	48780
Independent Refl.	8183
Reflections Used	6370
R_{int}	0.0459
Parameters	203
Restraints	0
Largest Peak	0.675
Deepest Hole	-0.343
GooF	1.060
wR_2 (all data)	0.0912
wR_2	0.0834
R_1 (all data)	0.0538
R_1	0.0361

Experimental. Single red plate-shaped crystals of (**quentin7_0m**) were obtained by recrystallisation from slow diffusion of pentane into a chloroform solution at -15°C. A suitable crystal (0.17×0.17×0.05) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa APEX II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the SIR2004 (Burla et al., 2007) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{17}H_{26}Cl_3TiN$, M_r = 398.64, monoclinic, $P2_1/n$ (No. 14), a = 11.0641(6) Å, b = 10.2866(6) Å, c = 16.7645(9) Å, β = 107.559(2)°, $\alpha = \gamma$ = 90°, V = 1819.10(18) Å^3, T = 115 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.907, 48780 reflections measured, 8183 unique (R_{int} = 0.0459) which were used in all calculations. The final wR_2 was 0.0912 (all data) and R_1 was 0.0361 (I > 2(I)).

17. Synthesis of **18**:



Chemical Formula: $C_{20}H_{30}Cl_3NTi$
Molecular Weight: 438,7

To a solution of **13** (2.55 g, 5.81 mmol, 1 eq, 5 mL toluene) was added dropwise a freshly-prepared HCl solution (5 mL). A red precipitate appeared from the red starting solution. The reaction mixture was left to stir for 15 min and the red precipitate was then filtered off and washed with 2 mL of $CHCl_3$. The compound was made precipitated by adding pentane on a concentrated $CHCl_3$ solution. (1.86 g, yield: 73 %).

^{1}H NMR (600.23 MHz, 300 K, chloroform-d_1): δ^1H: 10.77 (s, 1H, H^j), 6.75 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^a), 6.65 (s, 5H, H^i), 6.63 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 4.58 (d, $^3J_{HdHj}$ = 3.5, 2H, H^d), 2.81-2.73 (apparent td, 2H, H^g), 1.79 (s, 6H, H^f), 1.75-1.67 (m, 2H, H^h), 1.60-1.53 (m, 2H, H^g), 1.46 (s, 6H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, chloroform-d_1): δ^{13}C: 129.9 (C^a), 122.9 (C^i), 120.6 (C^b), 112.6 (C^c), 66.9 (C^e), 46.1 (C^d), 36.8 (C^g), 30.2 (C^f), 22.1 (C^f), 16.2 (C^h).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, chloroform-d_1): δ^1H / δ^1H: 10.77 / 4.58 (NH^j / CH_2^d), 6.75 / 6.63 (CH^a / CH^b), 6.63 / 6.75 (CH^b/ CH^a), 4.58 / 10.77 (CH_2^d / NH^j), 2.81-2.73 / 1.75-1.67, 1.60-1.53 (CH_2^g/ CH_2^h, CH_2^g), 1.75-1.67 / 2.81-2.73, 1.60-1.53 (CH_2^h / CH_2^g, CH_2^g), 1.60-1.53 / 2.81-2.73, 1.75-1.67 (CH_2^g / CH_2^g, CH_2^h).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1): δ^1H / δ^{13}C: 6.75 / 129.9 (CH^a), 6.65 / 122.9 (CH^i), 6.63 / 120.6 (CH^b), 4.58 / 46.1 (CH_2^d), 2.81-2.73 / 36.8 (CH_2^g), 1.79 / 30.2 (CH_3^f), 1.75-1.67 / 16.2 (CH_2^h), 1.60-1.53 / 36.8 (CH_2^g), 1.46 / 22.1 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1): δ^1H / δ^{13}C: 6.75 / 129.9, 122.9, 112.6 (CH^a/ C^c, CH^a, CH^b), 6.65 / 120.6 (CH^i/ CH^i), 6.63 / 129.9, 122.9, 112.6 (CH^b / C^c, CH^a, CH^b), 4.58 / 129.9, 122.9, 66.9 (CH_2^d/ C^c, CH^a, C^e), 2.81-2.73 / 66.9, 22.1 (CH^g/ C^e, CH_3^f), 1.79 / 66.9, 36.8, 22.1 (CH_3^f / C^e, CH_2^g, CH_3^f), 1.60-1.53 / 36.8 (CH_2^g / CH_2^g), 1.46 / 66.9, 36.8, 30.2 (CH_3^f / C^e, CH_2^g, CH_3^f).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{20}H_{30}NCl_2Ti$ $[M+H]^+$ 402.12322; found 402.12149 (Rel. ab: 85%, -3.6 ppm).

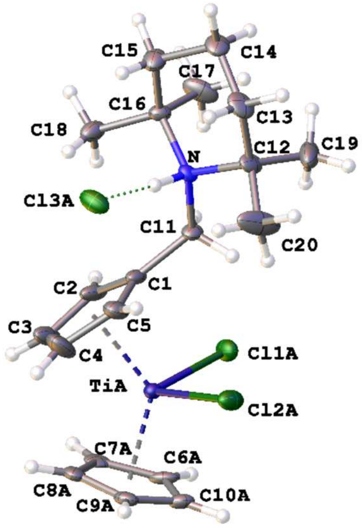
IR (ATR) ν [cm-1]

MIR: 3092; 3976; 2588(N-H); 2468; 1459; 1391; 820; 696.

FIR: 632; 601; 594; 484; 399; 363; 300; 255; 114.

Elemental Analysis: % calcd for $C_{20}H_{30}Cl_3NTi$: C, 54.76; H, 6.89; N, 3.19; Found: C, 54.57; H, 6.60; N, 2.87.

XRD:

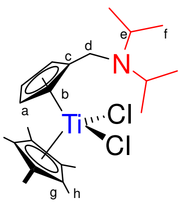


Experimental. Single red plate-shaped crystals of (**quentin21102013_0m**) were obtained by recrystallisation from slow diffusion of pentane into a chloroform solution at room temperature. A suitable crystal (0.17×0.07×0.03) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa APEX II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXS** (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{20}H_{30}Cl_3NTi$, M_r = 438.70, monoclinic, C2/c (No. 15), a = 33.057(3) Å, b = 7.0951(4) Å, c = 21.3626(15) Å, β = 123.711(2)°, $\alpha = \gamma$ = 90°, V = 4167.9(5) Å^3, T = 115 K, Z = 8, Z' = 1, $\mu(MoK_\alpha)$ = 0.799, 29692 reflections measured, 3369 unique (R_{int} = 0.0447) which were used in all calculations. The final wR_2 was 0.0821 (all data) and R_1 was 0.0332 (I > 2(I)).

Compound	**quentin21102013_0m**
Formula	$C_{20}H_{30}Cl_3NTi$
$D_{calc.}$/ g cm^{-3}	1.398
μ/mm^{-1}	0.799
Formula Weight	438.70
Colour	red
Shape	plate
Size/mm^3	0.17×0.07×0.03
T/K	115
Crystal System	monoclinic
Space Group	C2/c
a/Å	33.057(3)
b/Å	7.0951(4)
c/Å	21.3626(15)
α/°	90
β/°	123.711(2)
γ/°	90
V/Å^3	4167.9(5)
Z	8
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK_α
Θ_{min}/°	3.027
Θ_{max}/°	24.266
Measured Refl.	29692
Independent Refl.	3369
Reflections Used	2659
R_{int}	0.0447
Parameters	293
Restraints	60
Largest Peak	0.279
Deepest Hole	-0.218
GooF	1.038
wR_2 (all data)	0.0821
wR_2	0.0745
R_1 (all data)	0.0497
R_1	0.0332

18. Synthesis of **19**:



Chemical Formula: $C_{22}H_{35}Cl_2NTi$
Molecular Weight: 432,3

A solution of **4-K** (1.0 g, 4.6 mmol, 1 eq) in 70 mL of toluene was added to a solution of Cp*TiCl$_3$ (1.33 g, 4.6 mmol, 1 eq) in 50 mL of toluene, by cannulation at -30°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude red solution was first evaporated. The deep red oil obtained was dissolved in 10 mL of CH_2Cl_2, filtered through diatomaceous earth, which was then washed by 2 x 2 mL of CH_2Cl_2. The compound was concentrated and layered with pentane (15: 45 mL) to favored precipitation or crystallization at -15°C. The red precipitate was then filtered and dried in vacuo. (923 mg, yield = 46 %).

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H: 6.19 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^a), 5.99 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^b), 3.69 (s, 2H, H^d), 2.97 (hept, $^3J_{HH} = 6.7$ Hz, 2H, H^e), 2.01 (s, 15H, H^h), 1.00 (d, $^3J_{HH} = 6.7$ Hz, 12H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dichloromethane-d_2): δ^{13}C: 139.5 (C^c), 130.0 (C^g), 124.4 (C^a), 115.9 (C^b), 49.1 (C^e), 45.4 (C^d), 21.3 (C^f), 13.8 (C^h).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^1H: 6.19 / 5.99 (CH^a / CH^b), 5.99 / 6.19 (CH^b / CH^a), 2.97 / 1.00 (CH_2^e / CH_3^f), 1.00 / 2.97 (CH_3^f / CH_2^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 6.19 / 124.4 (CH^a), 5.99 / 115.9 (CH^b), 3.69 / 45.4 (CH_2^d), 2.97 / 49.1 (CH^e), 2.01 / 13.8 (CH_3^h), 1.00 / 21.3 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 6.19 / 124.4, 115.9 (CH^a / C^c, CH^a, CH^b), 5.99 / 139.5, 124.4 (CH^b / C^c, CH^a), 3.69 / 139.5, 124.4, 49.1 (CH_2^d / C^c, CH^a, CH^e), 2.97 / 49.1, 45.4, 21.3 (CH^e / CH^e, CH_2^d, CH_3^f), 2.01 / 130.0 (CH_3^h / C^g), 1.00 / 49.1, 21.3 (CH_3^f / CH^e, CH_3^f).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{15}N: 1.00 / -322.1 (H^f / N).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{22}H_{36}NCl_2Ti$ $[M+H]^+$ 432.17019; found 432.16878 (Rel. ab. 100%, -2.5 ppm).

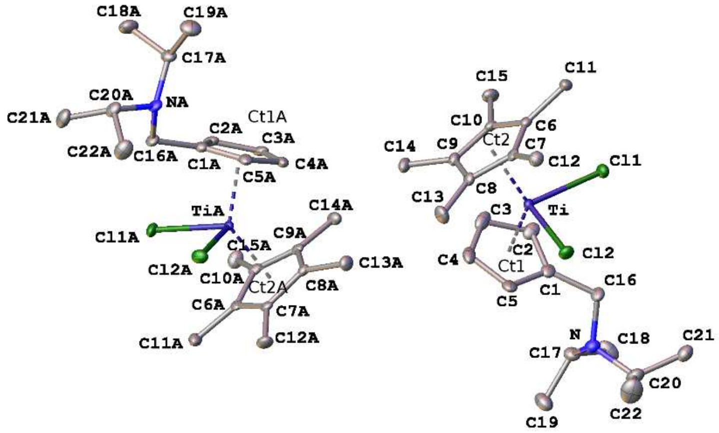
IR (ATR) ν [cm-1]

MIR: 2963; 1431; 1377; 1201; 1171; 1119; 1020; 895; 829; 789; 618.

FIR: 620; 614; 379; 348; 310; 274; 186; 126.

Elemental Analysis: % calcd for $C_{22}H_{35}NCl_2Ti$: C, 61.12; H, 8.16; N, 3.24; Found: C, 61.13; H, 8.26; N, 3.40.

XRD:

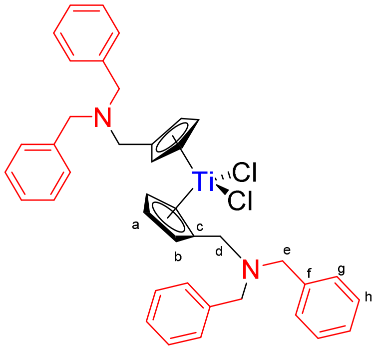


Compound	pierre090414bis_0m
Formula	$C_{22}H_{35}Cl_2NTi$
$D_{calc.}$/ g cm^{-3}	1.286
μ/mm^{-1}	0.629
Formula Weight	432.31
Colour	red
Shape	block
Size/mm^3	0.45×0.37×0.17
T/K	115
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	11.9003(7)
b/Å	24.9058(15)
c/Å	16.1960(10)
$\alpha/^\circ$	90
$\beta/^\circ$	111.552(2)
$\gamma/^\circ$	90
V/Å^3	4464.7(5)
Z	8
Z'	2
Wavelength/Å	0.71073
Radiation type	MoK_α
$\Theta_{min}/^\circ$	0.818
$\Theta_{max}/^\circ$	27.509
Measured Refl.	65479
Independent Refl.	10353
Reflections Used	9880
R_{int}	0.0360
Parameters	488
Restraints	0
Largest Peak	0.407
Deepest Hole	-0.321
GooF	1.118
wR_2 (all data)	0.0746
wR_2	0.0692
R_1 (all data)	0.0322
R_1	0.0291

Experimental. Single red block-shaped crystals of (**pierre090414bis_0m**) were obtained by recrystallisation from diffusion of pentane in a concentrated dichloromethane solution at -15°C. A suitable crystal (0.45×0.37×0.17) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{22}H_{35}Cl_2NTi$, $M_r = 432.31$, monoclinic, $P2_1/c$ (No. 14), a = 11.9003(7) Å, b = 24.9058(15) Å, c = 16.1960(10) Å, $\beta = 111.552(2)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 4464.7(5)$ Å^3, $T = 115$ K, $Z = 8$, $Z' = 2$, $\mu(MoK_\alpha) = 0.629$, 65479 reflections measured, 10353 unique ($R_{int} = 0.0360$) which were used in all calculations. The final wR_2 was 0.0746 (all data) and R_1 was 0.0291 (I > 2(I)).

19. Synthesis of **20**:



Chemical Formula: $C_{39}H_{38}Cl_2N_2Ti$
Molecular Weight: 653,5

$TiCl_4(THF)_2$ (268 mg, 0.8 mmol, 1 eq) dissolved in 5 mL of Et_2O was added dropwise at 0°C by cannulation on **3-K** (500 mg, 1.6 mmol, 2.0 eq) dissolved in 10 mL of Et_2O The resulting solution was left to warm up to room temperature and then stirred 30 min. The crude red/brown solution was filtered through diatomaceous earth which was then washed 2 x 5 mL of Et_2O and residual starting material. The brown solution was then evaporated to yield a dark brown oil. The compound was purified by crystallization thanks to a biphasic (Dichloromethane: Pentane 1: 3) in the Glove box. After removing the mother liquor, red crystals were obtained after washing with pentane and drying (80 mg, yield = 15 %).[13]

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H: 7.36 (d, $^3J_{HH}$ = 7.4 Hz, 8H, H^g), 7.32 (t, $^3J_{HH/I}$ = 7.4 Hz, 8H, H^h), 7.24 (t, $^3J_{HH}$ = 7.4 Hz, 4H, H^i), 6.35 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^a), 6.25 (apparent t, $^3J_{HH}$= $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 3.53 (s overlapping with H^d, 8H, H^e), 3.52 (s overlapping with H^e, 4H, H^d).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dichloromethane-d_2): δ^{13}C: 139.9 (C^f), 132.2 (C^c), 129.4 (C^g), 128.8 (C^h), 127.6 (C^i), 124.5 (C^a), 117.1 (C^b), 58.7 (C^e), 53.6 (C^d).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^1H: 7.36 / 7.32 (CH^g / CH^h), 7.32 / 7.36, 7.24 (CH^h / CH^g, CH^i), 7.24 / 7.32 (CH^i / CH^g), 6.35 / 6.25 (CH^a / CH^b), 6.25 / 6.35 (CH^b / CH^a).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 7.36 / 129.4 (CH^g), 7.32 / 128.8 (CH^h), 7.24 / 127.6 (H^i), 6.35 / 124.5 (CH^a), 6.25 / 117.1 (CH^b), 3.53 / 58.7 (CH$_2^e$), 3.52 / 53.6 (CH$_2^d$).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 7.36 / 129.4, 127.6, 58.7 (CH^g / CH^g, CH^i, CH^e), 7.32 / 139.9, 128.8 (CH^h / C^f, CH^h), 7.24 / 129.4 (CH^i / CH^g), 6.35 / 124.5, 117.7 (CH^a / CH^{a,} CH^b), 6.25 / 132.2, 124.5 (CH^b / C^c, CH^a), 3.53 / 132.2, 124.5, 53.6 (CH$_2^e$ / C^c, CH^a, CH$_2^d$), 3.52 / 139.9, 129.4, 58.7 (CH$_2^d$ / C^f, CH^g, CH$_2^e$).

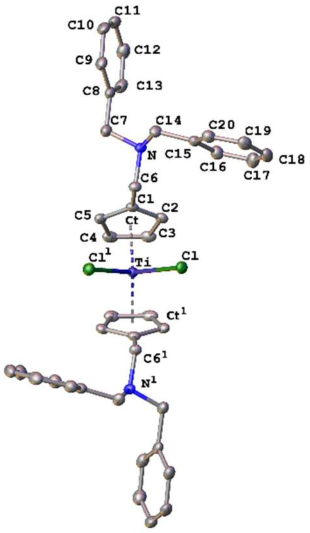
^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, benzene-d_6): δ^1H / δ^{15}N: 3.52 / -328 (H^d / N).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{40}H_{41}N_2Cl_2Ti$ $[M+H]^+$ 667.21258; found 667.21217 (Rel. ab: 35%, 0.137 ppm), $C_{40}H_{40}N_2ClTi$ $[M-Cl]^+$ 631.23586; found 631.23645 (Rel. ab: 5%, 1.7 ppm).

---

[13] IR spectroscopy and elemental analysis were not performed due to a lack of compound and the non-reproducible character of its synthesis

XRD:

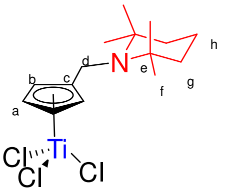


Compound	quentin21102013_0m
Formula	$C_{20}H_{30}Cl_3NTi$
$D_{calc.}$/ g cm^{-3}	1.398
μ/mm^{-1}	0.799
Formula Weight	438.70
Colour	red
Shape	plate
Size/mm^3	0.17×0.07×0.03
T/K	115
Crystal System	monoclinic
Space Group	C2/c
a/Å	33.057(3)
b/Å	7.0951(4)
c/Å	21.3626(15)
α/°	90
β/°	123.711(2)
γ/°	90
V/Å^3	4167.9(5)
Z	8
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	3.027
Θ_{max}/°	24.266
Measured Refl.	29692
Independent Refl.	3369
Reflections Used	2659
R_{int}	0.0447
Parameters	293
Restraints	60
Largest Peak	0.279
Deepest Hole	-0.218
GooF	1.038
wR_2 (all data)	0.0821
wR_2	0.0745
R_1 (all data)	0.0497
R_1	0.0332

Experimental. Single orange prism-shaped crystals of (**q3**) were obtained by recrystallisation from diffusion of pentane into a concentrated dichloromethane solution at room temperature. A suitable crystal (0.27×0.22×0.17) mm^3 was selected and mounted on a mylar loop with oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the SIR2004 (Burla et al., 2007) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{40}H_{40}Cl_2TiN_2$, M_r = 667.54, monoclinic, P2/c (No. 13), a = 13.2491(4) Å, b = 6.5269(2) Å, c = 20.2691(7) Å, β = 107.0590(10)°, $\alpha = \gamma$ = 90°, V = 1675.66(9) Å^3, T = 115 K, Z = 2, Z' = 0.5, μ(MoK$_\alpha$) = 0.446, 6022 reflections measured, 3813 unique (R_{int} = 0.0135) which were used in all calculations. The final wR_2 was 0.0725 (all data) and R_1 was 0.0316 (I > 2(I)).

20. Synthesis of **21**:



Chemical Formula: $C_{15}H_{24}Cl_3NTi$
Molecular Weight: 372,6

A solution of **5-K** (1.0 g, 3.9 mmol, 1.0 eq) in 30 mL of THF was cooled down at -70°C. Trimethylsilyl chloride (0.55 mL, 4.3mmol, 1.1 eq) was added dropwise to the solution and the resulting solution was warmed up to room temperature and stirred for 3h. All volatiles were removed by evaporation to yield a yellow sticky solid. Dissolution of the solid in 30 mL of pentane and filtration through diatomaceous earth were used to remove KCl salts. Pentane was evaporated to yield the corresponding silylated amino cyclopentadiene (970 mg, 3.33 mmol, 85 %) as a yellow solid. It was dissolved in 40 mL of toluene, and added at - 30°C to a toluenic solution of $TiCl_4$ (0.36 mL, 3.33 mmol, 1eq). The resulting brown solution was left to warm up to room temperature and stirred overnight. A dark brown solution with a black precipitate was obtained. The heterogeneous solution was dried *in vacuo*. The brownish residue was triturated in pentane (30 mL) and dried *in* vacuo. The sticky residue was triturated in cold pentane (10 mL) and filtered to yield a dark brown precipitate (1.08g, 87% step yield, 74% global yield).

^{1}H NMR (600.23 MHz, 300 K, benzene-d_6): δ^1H: 6.40 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^a), 6.15 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^b), 3.75 (s, 2H, H^d), 1.39-1.34 (m, 2H, H^h), 1.28-1.25 (m, 4H, H^g), 0.82 (s, 12H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, benzene-d_6): δ^{13}C: 151.0 (C^c), 123.9 (C^a), 123.5 (C^b), 55.3 (C^e), 45.5 (C^d), 41.2 (C^g), 29.0-27.2 (C^f), 17.8 (C^h).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, benzene-d_6): δ^1H / δ^1H: 6.40 / 6.15 (CH^a / CH^b), 6.15 / 6.40 (CH^b / CH^a), 1.39-1.34 / 1.28-1.25 (CH_2^h / CH_2^g), 1.28-1.25 / 1.39-1.34 (CH_2^g / CH_2^h).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 6.40 / 123.9 (CH^a), 6.15 / 123.5 (CH^b), 3.75 / 45.5 (CH_2^d), 1.39-1.34 / 17.8 (CH_2^h), 1.28-1.25 / 41.2 (CH_2^g), 0.82 / 29.0-27.2 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 6.40 / 123.5 (CH^a / CH^b), 6.15 / 151.0, 123.9 (CH^b / C^c, CH^a), 3.75 / 151.0, 124.0, 55.3 (CH_2^d / C^c, CH^a, C^e), 1.39-1.34 / 55.3, 41.3 (CH^h / C^e, CH_2^g), 1.28-1.25 / 55.3, 41.2, 17.8 (CH_2^g / C^e, CH_2^g, CH_2^h), 0.82 / 55.3, 41.3, 29.0-27.2 (CH_3^f / C^e, CH_2^h, CH_3^f).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, benzene-d_6): δ^1H / δ^{15}N: 0.82 / -308 (H^f / N).

HMRS (Positive mode ESI, dichloromethane / MeOH): m/z calcd. for $C_{16}H_{28}NCl_2TiO$ [M-Cl+OCH3+H]$^+$ 368.10244; found 368.1074 (Rel. ab: 100%, 2.3 ppm).

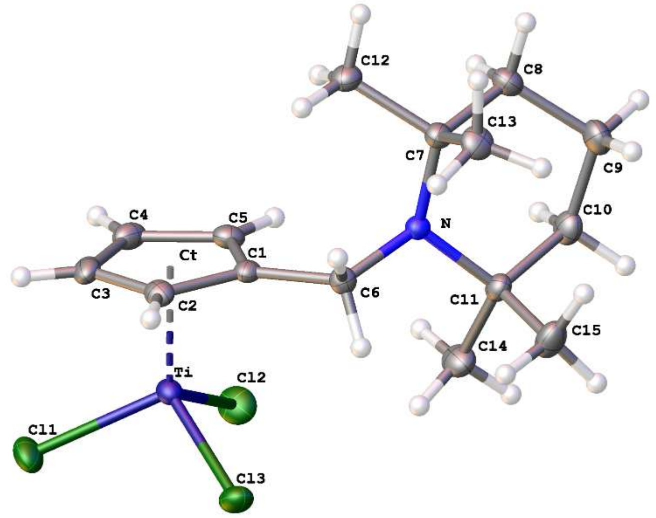
IR (ATR) ν [cm-1]

MIR:2942; 2586; 1409; 1224; 1115; 797.

FIR: 624; 535; 404; 287; 159; 121.

Elemental Analysis: % calcd for $C_{15}H_{24}NCl_3Ti$: C, 48.35; H, 6.49; N, 3.76; Found: C, 48.67; H, 6.69; N, 3.63.

XRD:

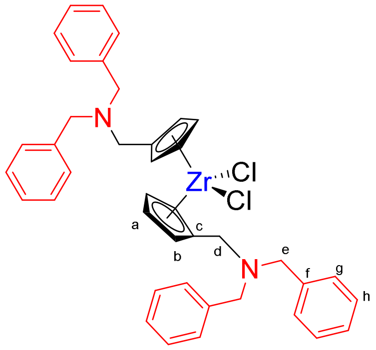


Compound	**mo_q110914_0m_a**
Formula	$C_{15}H_{24}Cl_3NTi$
$D_{calc.}$/ g cm^{-3}	1.420
μ/mm^{-1}	0.941
Formula Weight	372.60
Colour	brown
Shape	plate
Size/mm^3	0.50×0.36×0.03
T/K	100
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	7.8807(5)
b/Å	14.9295(9)
c/Å	14.8251(9)
$\alpha/^{\circ}$	90
$\beta/^{\circ}$	92.5190(19)
$\gamma/^{\circ}$	90
V/Å^3	1742.56(19)
Z	4
Z'	1
Wavelength/Å	0.710760
Radiation type	MoK$_{\alpha}$
$\Theta_{min}/^{\circ}$	3.056
$\Theta_{max}/^{\circ}$	27.571
Measured Refl.	37843
Independent Refl.	4005
Reflections Used	3395
R_{int}	0.0348
Parameters	185
Restraints	0
Largest Peak	0.472
Deepest Hole	-0.272
GooF	1.064
wR_2 (all data)	0.0858
wR_2	0.0777
R_1 (all data)	0.0472
R_1	0.0362

Experimental. Single brown plate-shaped crystals of (**mo_q110914_0m_a**) were obtained by introducing the filtrate at -15°C for several days. A suitable crystal (0.50×0.36×0.03) mm^3 was selected and mounted on a mylar loop with oil on a Bruker D8 Mo diffractometer. The crystal was kept at T = 100 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXS** (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{15}H_{24}Cl_3NTi$, M_r = 372.60, monoclinic, $P2_1/c$ (No. 14), a = 7.8807(5) Å, b = 14.9295(9) Å, c = 14.8251(9) Å, β = 92.5190(19)°, $\alpha = \gamma$ = 90°, V = 1742.56(19) Å^3, T = 100 K, Z = 4, Z' = 1, μ(MoK$_{\alpha}$) = 0.941, 37843 reflections measured, 4005 unique (R_{int} = 0.0348) which were used in all calculations. The final wR_2 was 0.0858 (all data) and R_1 was 0.0362 (I > 2(I)).

21. Synthesis of 22:



Chemical Formula: $C_{40}H_{41}Cl_2N_2Zr$
Molecular Weight: 711,9

A solution of **3-K** (1.2 g, 3.83 mmol, 2.1 eq) in 15 mL of THF was added to a freshly prepared solution of $ZrCl_4(THF)_2$ (425 mg of $ZrCl_4$ in 7 mL of THF, 1.83 mmol, 1 eq), by cannulation at -10°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude brown solution was first evaporated. The brown oil obtained was dissolved in 25 mL of toluene, filtered through diatomaceous earth which was then washed by 4 x 10 mL of toluene and residual starting material. The yellow solution was then evaporated to form a brown sticky oil which was stirred overnight in a mixture of Dichloromethane: pentane (1: 3) to yield a white precipitate. The precipitate was filtered off, washed with pentane (2 x 10 mL) and dried to yield the desired compound. (400 mg, yield = 31 %).[14]

^{1}H NMR (600.23 MHz, 300 K, benzene-d_6): δ^1H: 7.32 (d, $^3J_{HH}$ = 7.4 Hz, 8H, H^g), 7.20 (t, $^3J_{HH}$ = 7.4 Hz, 8H, H^h), 7.10 (t, $^3J_{HH}$ = 7.4 Hz, 4H, H^i), 6.06 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 4H, H^a), 5.72 (t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 4H, H^b), 3.62 (s, 4H, H^d), 3.38 (s, 8H, H^e).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, benzene-d_6): δ^{13}C: 139.6 (C^f), 129.2 (C^g), 128.7 (C^h), 128.6 (C^c), 127.4 (C^i), 118.4 (C^a), 113.2 (C^b), 58.1 (C^e), 52.7 (C^d).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, benzene-d_6): δ^1H / δ^1H: 7.32 / 7.20 (CH^g / CH^h), 7.20 / 7.32, 7.10 (CH^h / CH^g, CH^i), 7.10 / 7.20 (CH^i / CH^g), 6.06 / 5.72 (CH^a / CH^b), 5.72 / 6.06 (CH^b / CH^a).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 7.32 / 129.2 (CH^g), 7.20 / 128.7 (CH^h), 7.10 / 127.4 (CH^i), 6.06 / 118.4 (CH^a), 5.72 / 113.2 (CH^b), 3.62 / 52.7 (CH_2^d), 3.38 / 58.1 (CH_2^e).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 7.32 / 129.2, 128.7, 127.4, 58.1 (CH^g / CH^g, CH^h, CH^i, CH^e), 7.20 / 139.6, 128.7 (CH^h / C^f, CH^h), 7.10 / 129.2, 128.7 (CH^i / CH^g, CH^h) 6.06 / 128.6, 118.4, 113.2 (CH^a / C^c, $CH^{a,}$ CH^b), 5.72 / 128.6, 118.4 (CH^b / C^c, CH^a), 3.62 / 128.6, 118.4, 58.1 (CH_2^d / C^c, CH^a, CH_2^e), 3.38 / 139.6, 129.2, 58.1, 52.7 (CH_2^e / C^f, CH^g, CH_2^d, CH_2^e).

---

[14] A satisfactory elemental analysis could not be obtained (low C) due to remaining KCl salts or $ZrCl_4$

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, benzene-d$_6$): δ^{1}H / δ^{15}N: 3.62 / -328 (H^d / N).

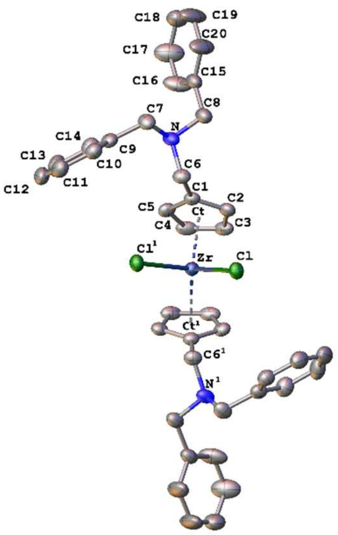
HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{40}H_{41}N_2Cl_2Zr$ [M+H]$^+$ 709.16884; found 709.16653 (Rel. ab: 15%, -3.3 ppm).

IR (ATR) ν [cm-1]

MIR: 3062, 3061, 2825, 1494, 1243, 1029, 834 , 747.

FIR: 698, 696, 638, 625, 504, 336, 278, 116.

XRD:



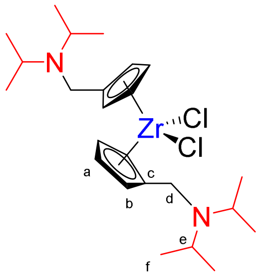
^{1}1-x,+y,1/2-z

Experimental. Single colourless plate-shaped crystals of (**shelx**) were obtained by recrystallisation from diffusion of pentane into a dichloromethane solution at -15°C. A suitable crystal (0.37×0.22×0.10) mm^3 was selected and mounted on a mylar loop with oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 115(2) K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the SIR2004 (Burla et al., 2007) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{40}H_{40}Cl_2N_2Zr$, M_r = 710.86, monoclinic, C2/c (No. 15), a = 26.4156(7) Å, b = 6.6533(2) Å, c = 20.1035(6) Å, β = 93.798(2)°, $\alpha = \gamma$ = 90°, V = 3525.45(18) Å^3, T = 115(2) K, Z = 4, Z' = 0.5, μ(MoK$_\alpha$) = 0.494, 7508 reflections measured, 4016 unique (R_{int} = 0.0199) which were used in all calculations. The final wR_2 was 0.0678 (all data) and R_1 was 0.0300 (I > 2(I)).

Compound	**shelx**
Formula	$C_{40}H_{40}Cl_2N_2Zr$
$D_{calc.}$/ g cm^{-3}	1.339
μ/mm^{-1}	0.494
Formula Weight	710.86
Colour	colourless
Shape	plate
Size/mm^3	0.37×0.22×0.10
T/K	115(2)
Crystal System	monoclinic
Space Group	C2/c
a/Å	26.4156(7)
b/Å	6.6533(2)
c/Å	20.1035(6)
α/°	90
β/°	93.798(2)
γ/°	90
V/Å^3	3525.45(18)
Z	4
Z'	0.5
Wavelength/Å	0.71073
Radiation type	MoK$_\alpha$
Θ_{min}/°	3.091
Θ_{max}/°	27.493
Measured Refl.	7508
Independent Refl.	4016
Reflections Used	3663
R_{int}	0.0199
Parameters	204
Restraints	0
Largest Peak	0.335
Deepest Hole	-0.266
GooF	1.094
wR_2 (all data)	0.0678
wR_2	0.0644
R_1 (all data)	0.0355
R_1	0.0300

22. Synthesis of **23**:



Chemical Formula: $C_{24}H_{40}Cl_2N_2Zr$
Molecular Weight: 518,7

A solution of **2-K** (3 g, 13.8 mmol, 2.0 eq) in 70 mL of THF was added to a freshly prepared solution of $ZrCl_4(THF)_2$ (1.77 g of $ZrCl_4$ in 30 mL of THF, 7.6 mmol, 1.1 eq), by cannulation at -10°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude brown solution was filtered through diatomaceous earth to remove KCl salts. Solvent was removed by vacuum pumping and the white precipitate obtained was wash with pentane (2 x 20 mL) to afford the desired compound in good yield .(2.75g, yield = 76 %).[14]

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H: 6.35 (m, 4H, H^a), 6.33 (m, 4H, H^b), 3.66 (s, 4H, H^d), 2.97 (hept, $^3J_{HH}$ = 6.5 Hz, 4H, H^e), 1.01 (d, $^3J_{HH}$ = 6.5 Hz, 24H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dichloromethane-d_2): δ^{13}C: 136.0 (C^c), 118.4 (C^a), 113.0 (C^b), 48.8 (C^e), 44.8 (C^d), 21.2 (C^f).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^1H: 6.35 / 6.33 (CH^a / CH^b), 6.33 / 6.35 (CH^b / CH^a), 2.97 / 1.01 (CH^e / CH$_3^f$), 1.01 / 2.97 (CH$_3^f$ / CH^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 6.35 / 118.4 (CH^a), 6.33 / 113.0 (CH^b), 3.66 / 44.8 (CH$_2^d$), 2.97 / 48.8 (CH$_2^e$), 1.01 / 21.2 (CH$_3^f$).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 6.35 / 113.0 (CH^a / CH^b), 6.33 / 136.0, 118.4 (CH^b / C^c, CH^a), 3.66 / 136.0, 118.4, 48.8 (CH$_2^d$ / C^c, CH^a, CH^e), 2.97 / 48.8, 44.8, 21.2 (CH$_2^e$ / C^e, CH$_2^d$, CH$_3^e$), 1.01 / 48.8, 21.2 (CH$_3^f$ / CH^e, CH$_3^f$).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{15}N: 1.01 / -322 (H^f / N).

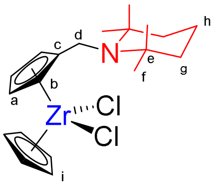
HMRS (Positive mode ESI, dichloromethane): not detected.

IR (ATR) ν [cm-1]

MIR: 2931; 1458; 1360; 1199; 1017; 848; 739.

FIR: 523; 359; 309; 277; 162; 105.

23. Synthesis of **24**:



Chemical Formula: $C_{20}H_{29}Cl_2NZr$
Molecular Weight: 445,6

A solution of **5-K** (586 mg, 2.66 mmol, 1.0 eq) in 35 mL of THF was added to a solution of $CpZrCl_3$ (700 mg, 2.66 mmol, 1 eq) in 35 mL of THF cooled down to -30°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude solution was evaporated and the residue was treated with 30 mL of dichloromethane. After filtration through diatomaceous earth, the filtrate was evaporated and the residue triturated with 15 mL of pentane in order to form a white powder. The supernatant was removed and the precipitate washed twice with 5 mL of pentane. The desired compound was obtained after removal of all volatiles as a white powder. (640 mg, 54%).[15]

^{1}H NMR (600.23 MHz, 300 K, tetrahydrofuran-d_8): δ^1H: 6.45 (s, 5H, H^i), 6.38 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^a), 6.31 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 3.82 (s, 2H, H^d), 1.59-1.53 (m, 2H, H^h), 1.44-1.39 (m, 4H, H^g), 1.03 (s, 12H, H^f).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, tetrahydrofuran-d_8): δ^{13}C: 142.6 (C^c), 117.6 (C^b), 116.6 (C^i), 113.9 (C^a), 56.2 (C^e), 45.4 (C^d), 42.7 (C^g), 28.9-28.2 (C^f), 18.9 (C^h).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, tetrahydrofuran-d_8): δ^1H / δ^1H: 6.38 / 6.31 (CH^a / CH^b), 6.31 / 6.38 (CH^b / CH^a), 1.59-1.53 / 1.44-1.39 (CH_2^h / CH_2^g), 1.44-1.39 / 1.59-1.53 (CH_2^g / CH_2^h).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d_8): δ^1H / δ^{13}C: 6.45 / 116.6 (CH^i), 6.38 / 113.9 (CH^a), , 6.31 / 117.6 (CH^b), 3.82 / 45.4 (CH_2^d), 1.59-1.53 / 18.9 (CH_2^h), 1.44-1.39 / 42.7 (CH_2^g), 1.03 / 28.9-28.2 (CH_3^f).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d_8): δ^1H / δ^{13}C: 6.45 / 116.6 (CH^i / CH^i), 6.38 / 142.6, 117.6 (CH^a / C^c, CH^b), 6.31 / 113.9 (CH^b / CH^a), 3.82 / 142.6, 117.6, 56.2 (CH_2^d / C^c, CH^b, C^e), 1.44-1.39 / 56.2, 42.7, 28.9-28.2, 18.9 (CH_2^h / C^e, CH_2^g, CH_2^h, CH_3^f), 1.03 / 56.2, 42.7, 28.9-28.2 (CH_3^f / C^e, CH_2^g, CH_3^f).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, tetrahydrofuran-d_8): δ^1H / δ^{15}N: 1.44-1.39, 1.03 / -311 (H^g, H^f / N).

HMRS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{20}H_{30}NCl_2Zr$ $[M+H]^+$ 444.07969; found 444.07893 (Rel. ab: 10%, -1.701 ppm), $C_{15}H_{26}N$ $[M-CpZrCl_2+H]^+$ 220.20652 found 220.20539 (Rel. ab: 100%, -5.1 ppm).

IR (ATR) ν [cm-1]

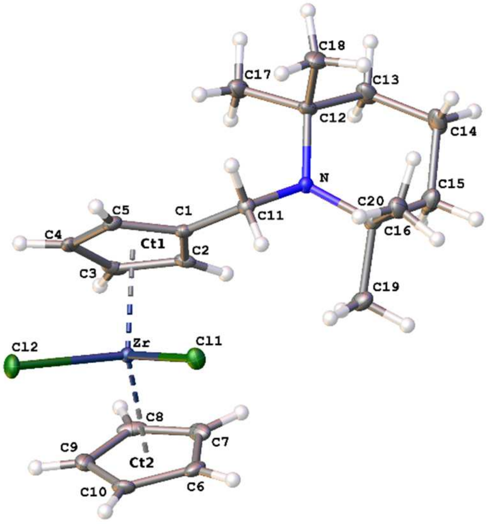
---

[15] A satisfactory elemental analysis could not be obtained du to the remaining presence of **bis-24**

MIR: 3100, 2926, 2869, 1460, 1376, 1261, 1131, 1022, 771, 737.

FIR: 627, 597, 535, 360, 309, 267, 153, 125.

XRD:



Experimental. Single colourless needle-shaped crystals of (**mo_q160714_0ma**) were obtained by recrystallisation from diffusion of pentane into a concentrated dichloromethane solution at -15°C. A suitable crystal (0.50×0.07×0.07) mm^3 was selected and mounted on a mylar loop with grease on a Bruker D8 Mo diffractometer. The crystal was kept at T = 100 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXS** (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{20}H_{29}Cl_2NZr$, M_r = 445.56, orthorhombic, Pna2$_1$ (No. 33), a = 21.2992(9) Å, b = 14.3145(7) Å, c = 6.5295(3) Å, $\alpha = \beta = \gamma =$ 90°, V = 1990.76(16) Å^3, T = 100 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.823, 19980 reflections measured, 4387 unique (R_{int} = 0.0351) which were used in all calculations. The final wR_2 was 0.0422 (all data) and R_1 was 0.0222 (I > 2(I)).

Compound	**mo_q160714_0ma**
Formula	$C_{20}H_{29}Cl_2NZr$
$D_{calc.}$/ g cm^{-3}	1.487
μ/mm^{-1}	0.823
Formula Weight	445.56
Colour	colourless
Shape	needle
Size/mm^3	0.50×0.07×0.07
T/K	100
Crystal System	orthorhombic
Flack Parameter	-0.017(19)
Hooft Parameter	0.011(18)
Space Group	Pna2$_1$
a/Å	21.2992(9)
b/Å	14.3145(7)
c/Å	6.5295(3)
α/°	90
β/°	90
γ/°	90
V/Å^3	1990.76(16)
Z	4
Z'	1
Wavelength/Å	0.710760
Radiation type	MoK$_\alpha$
Θ_{min}/°	3.002
Θ_{max}/°	27.508
Measured Refl.	19980
Independent Refl.	4387
Reflections Used	4026
R_{int}	0.0351
Parameters	221
Restraints	1
Largest Peak	0.330
Deepest Hole	-0.263
GooF	1.065
wR_2 (all data)	0.0422
wR_2	0.0406
R_1 (all data)	0.0286
R_1	0.0222

III. Chapter II: Generation of cationic species and study of their reactivity

Several methods for cationic group 4 metals generation have been developed in the literature. This chapter will be composed of two parts: the first will present a preliminary overview of the reagents traditionally used for ligand abstraction; a second part will then be developed on the synthesis of cationic (aminomethyl)titanocenes and the study of their reactivity.

A. Survey of the literature on X-ligand abstractors

The heterolytic cleavage of the M-X bond is usually called abstraction. Considering a group 4 metallocene fragment, one can abstract easily a chloride or a methide, as developed in this chapter. The first abstractor commonly used in catalysis was the organometallic aluminium-based polymer methylaluminoxane, usually called MAO. MAO was often used in Ziegler-Natta catalysis as both chloride and alkide abstractor. The two main drawbacks of MAO are its use in approximately hundredfold to ten-thousandfold excess due to its polymeric structure of type $[Al(CH_3)_xO]_n$; and its ill-defined action mechanism. As a result, numerous compounds with well-defined structures were further designed and used, in order to better understand the mechanisms involved in such reactions. These compounds are usually based on non-coordinating anions in order to prevent any coordination to the newly formed cationic species.[1]

1. Chloride abstraction

The first category of compounds described in the literature, are inorganic salts based on alkali metals with a non-coordinating, or at least weakly-coordinating counter anion. A highly valuable compound of this type was designed by Lapointe and Klosin in 2000,[2] and used on a dichloroziroconocene by Erker two years later (Scheme III-1).[3] The imidazolate **A**$^-$ showed no interaction with the cationic zirconocene. Tetrasubstituted borates BPh_4 and $B(C_6F_5)_4^-$ have also been used in conjunction with alkali metal cations.[4] The driving force for these reactions is the precipitation of MCl salts (M = Li, Na, K,…). It generally requires the use of an adapted solvent (e.g. dichloromethane) in which the inorganic salt will precipitate. Such reactivity has already been described in Scheme I-42 with the use of $[Li][BuB(C_6F_5)_3]$.[5]

---

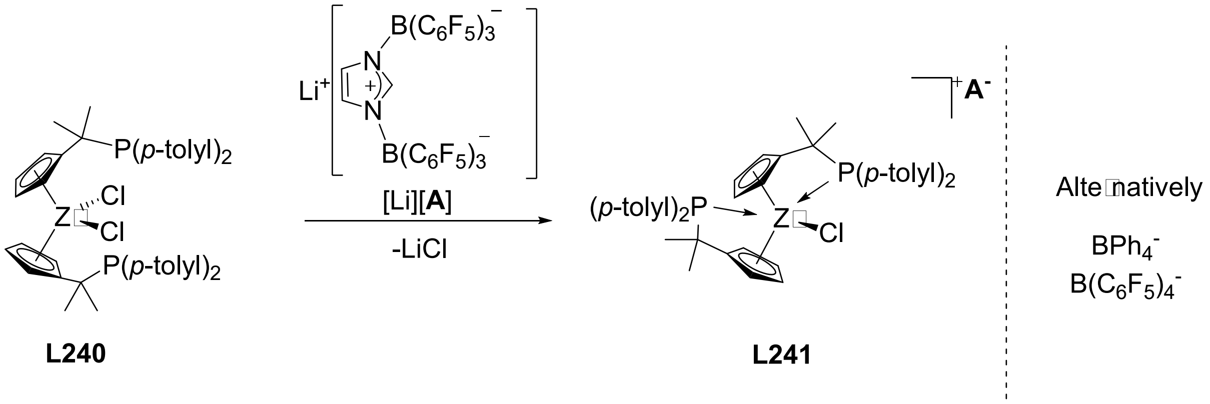
[1] See for example Focante, F.; Mercandelli, P.; Sironi, A.; Resconi, L. *Coord. Chem. Rev.* **2006**, *250*, 170 and publications herein

[2] LaPointe, R. E.; Roof, G. R.; Abboud, K. A.; Klosin, J. *J. Am. Chem. Soc.* **2000**, *122*, 9560

[3] Vagedes, D.; Erker, G.; Fröhlich, R. *J. Organomet. Chem.* **2002**, *641*, 148

[4] Döring, S.; Kotov, V. V.; Erker, G.; Kehr, G.; Bergander, K.; Kataeva, O.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2003**, 1599

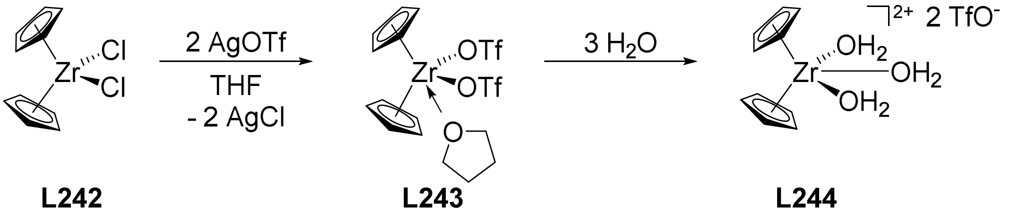
[5] Hüerländer, D.; Fröhlich, R.; Erker, G. *J. Chem. Soc. Dalton Trans.* **2002**,7, 1513



Scheme III-1: chloride abstraction from L240 by the alkali metal salt [Li][A]

An alternative reduction-oxidation process has been used for titanium complexes. By using an alkali metal with a reductive anion (PR_2^- or C_8^-), chloride abstraction is achieved concomitantly with reduction to Ti(III). Oxidation with a cationic oxidant containing a non-coordinating anion (e.g. $[Cp_2Fe][BPh_4]$) results in net chloride abstraction. An example of this type has already been described in Scheme I-74.

Furthermore, silver (I) salts have also been used to effect chloride abstraction. In that case, the high affinity of silver (I) for the chloride anion is the driving force of the abstraction reaction. Various salts are commercially available. One example with a zirconocene is depicted in Scheme III-2. The triflate ligand was shown to be substituted by water molecules due to the low basicity of the triflate ligand.[6] The same reactivity was also observed with titanium by Thewalt and Klein.[7]



Scheme III-2: synthesis of a ditriflate zirconocene with a silver-based abstractor

Noteworthy, the use of $[Ag][B(C_6F_5)_4]$ on **L211** by Wass led to the formation of the water addition compound **L245**, due to traces of water in the silver abstractor. In 1994, a new triethylsilyl cation was designed by Lambert,[8] and then used later by Wass to overcome the problem met with the silver derivative. A chloride from the chloro titanocene **L211** previously described (Scheme I-68) was successfully abstracted.[9] The use of the triphenylsilyl analogue was also found to effect chloride abstraction (Scheme III-3).[10]

---

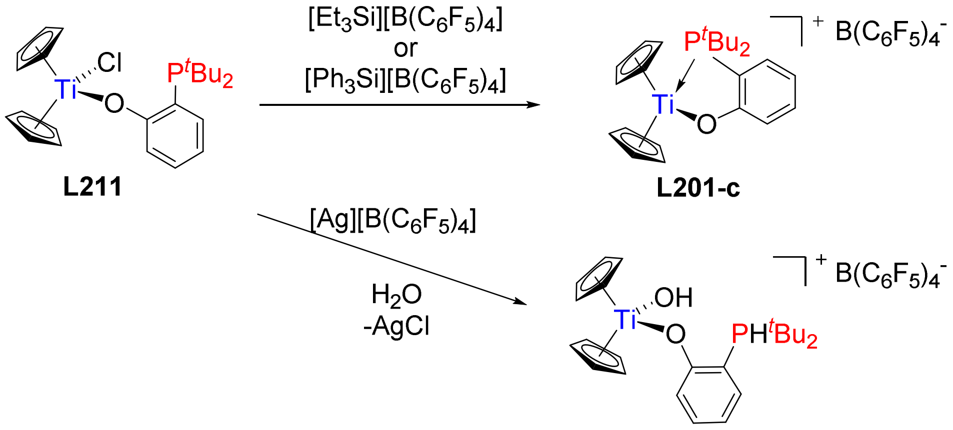
[6] Thewalt, U.; Wiltraud, L. *Z Naturforsch.* **1983**, *38b*, 1501

[7] Thewalt, U.; Klein, H.-P. *Z. Für Krist. - Cryst. Mater.* **1980**, *153*

[8] Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics.* **1994**, *13*, 2430

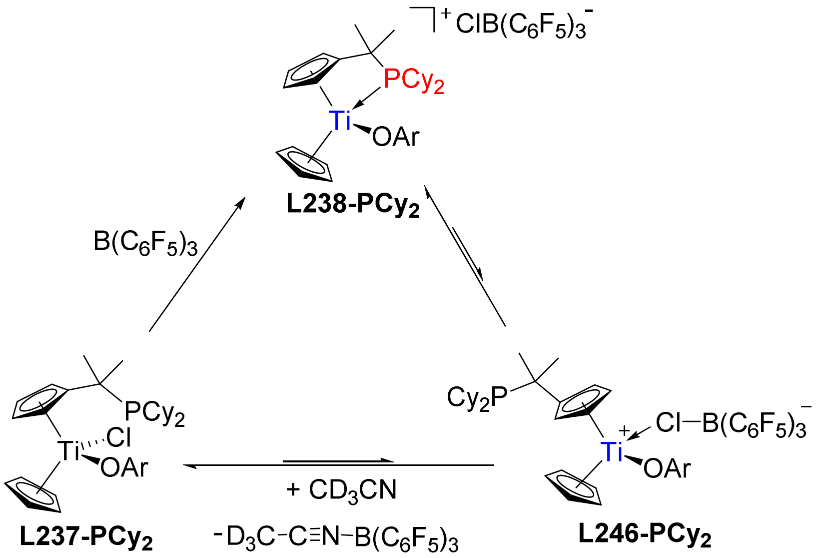
[9] Chapman, A. M.; Haddow, M. F.; Wass, D. F. *Eur. J. Inorg. Chem.* **2012**, *2012*, 1546

[10] Chapman, A. M.; Wass, D. F. *Dalton Trans.* **2012**, *41*, 9067



Scheme III-3: formation of cationic titanocene derivatives by silyl- or silver-based abstractors

The last category of compounds cited in this section are the Lewis acids based on group 13 elements. The most commonly used reagent in this category is MAO, as already been mentioned in the introduction. More recently, the perfluorinated borane $B(C_6F_5)_3$ was shown to be as competent chloride or methide abstractor.[11] The main disadvantage of its use is the reversibility of the abstraction. Indeed, several cationic transition metal complexes were isolated with the formation of a tight ion-pair between the cationic metal centre and the R-$B(C_6F_5)_3^-$ anion (R = Cl, or Me depending on the nature of the abstraction).[12] An example of this type of interaction was reported by Le Gendre and Erker on a titanocene complex. The use of $B(C_6F_5)_3$ on **L237-PCy$_2$** led to the formation of the desired cationic species in equilibrium with a tight ion-pair exhibiting a Cl between the cationic titanocene and the borane (**L246-PCy$_2$** Scheme III-4).



Scheme III-4: an example of chloride abstraction with $B(C_6F_5)_3$

---

[11] See for example: Bosch, B. E.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics.* **1997**, *16*, 5449

[12] For R=Me, see for example: Yang, X.; Stern, C.; Marks, T. J. *Organometallics.* **1991**, *10*, 840

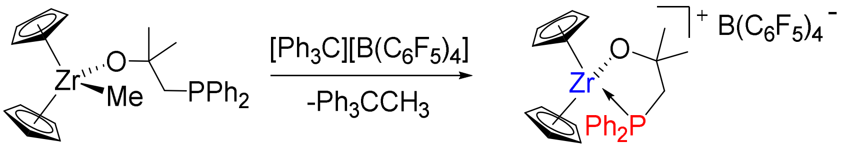
This equilibrium was inferred on the basis of NMR spectroscopic data. Addition of CD_3CN to the mixture led to the regeneration of the starting titanocene **L237-PCy$_2$** with the formation of the Lewis adduct of $CD_3CN \rightarrow B(C_6F_5)_3$ (Scheme III-4).[13]

The chloride abstraction was the first strategy envisioned in this project. The second was based on the abstraction of methide. This requires the synthesis of the corresponding methylated titanocenes, the synthesis of which will be presented in due course.

2. Methide abstraction

As mentioned above, group 13-based Lewis acids have been used for both methide and chloride abstractions. The principle being the same as for the chloride abstraction, it will not be developed in more detail.

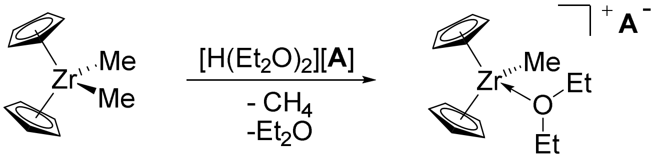
Trityl (or triphenylmethylcarbenium) derivatives have often been used alternatively to $B(C_6F_5)_3$. These compounds have the advantage of eliciting irreversible methide abstraction by forming 1,1,1-triphenylethane as a byproduct. This abstractor was shown to be compatible with group 4 dimethyl metallocenes. As illustrated in Scheme III-5, an OmFLP could be obtained in this way from **L221-b**.



L221-b **L223**

Scheme III-5: synthesis of an OmFLP with a trityl borate

A cationic group 4 metallocene was also generated by protonolysis of the M-Me bond with a Brønsted acid. This was done by using the super acid $H(Et_2O)_2^+$ or various ammonium salts combined with a non- or wealky-coordinating anion. The use of $H(Et_2O)_2^+$ entails the presence of Et_2O. In some cases, one molecule of diethyl ether was shown to coordinate to the cationic metallocenes as described by Erker with **L248.**[3]



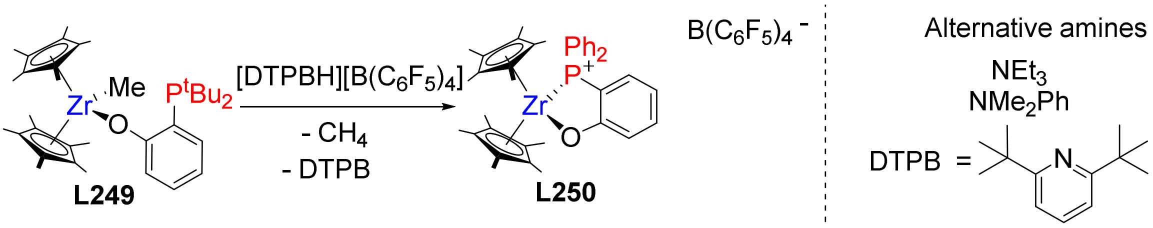
L247 **L248**

Scheme III-6: protonolysis of L247 with [H(Et$_2$O)$_2$][A]

---

[13] Normand, A. T.; Richard, P.; Balan, C.; Daniliuc, C. G.; Kehr, G.; Erker, G.; Le Gendre, P. *Organometallics.* **2015**, *34*, 2000

In the case of ammonium or pyridinium abstractors, the use of a bulky cation such as 2,6-di-tertbutylpyridinium prevents the coordination of the free N-base, such as in the example depicted in Scheme III-7.[9]



Scheme III-7: protonolysis of L249 by an ammonium borate salt

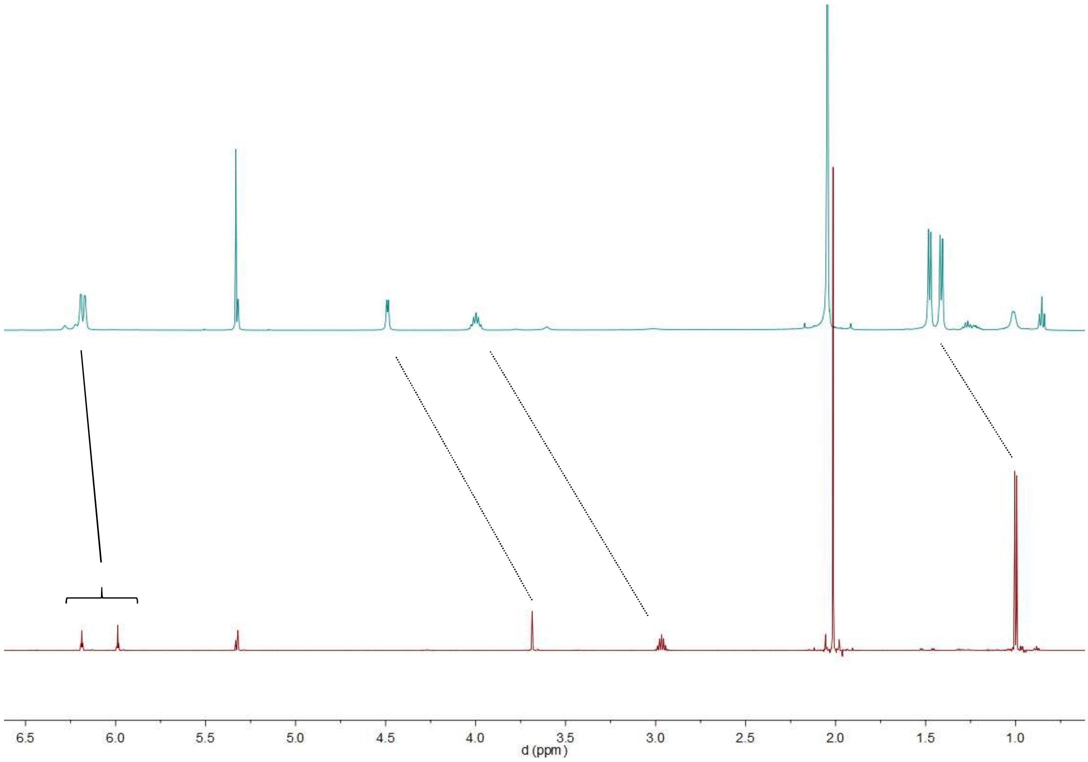
Most of these abstractors can be synthesized according to literature procedures, or purchased commercially in some cases (see general remarks). Their use to try to generate various cationic titanocenes will be illustrated in the following part.

B. Abstraction from (aminomethyl)titanocenes

In this section, the generation of some cationic species, (starting from the (aminomethyl)titanocenes described in section II.A.3.a.), will be discussed. The first part will deal with chloride abstraction, whilst the second will be focused on the synthesis of methylated (aminomethyl)titanocenes and methide abstraction therefrom.

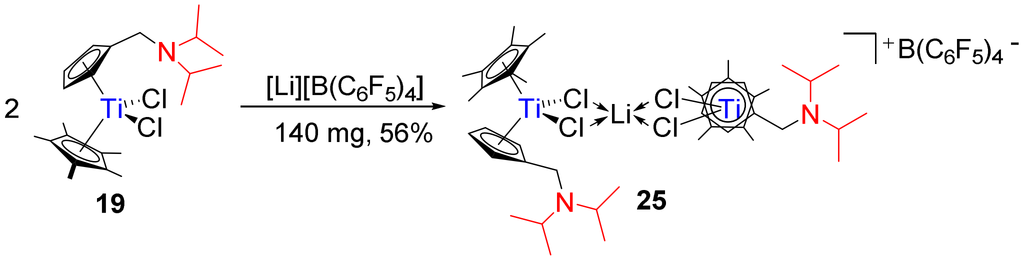
3. Chloride abstraction

As illustrated in the first part of this chapter, various reagents can be used for chloride abstraction. The first procedure envisioned was based on the use of alkali metal-based abstractors: $[Na][BPh_4]$ and $[Li][B(C_6F_5)_4]$ were used on the dichloro series **9-13** and **19** (section II.C.1), in various solvent conditions, in a 1: 1 ratio but did not effect the chloride abstraction. In one case however, we observed the formation of a new species upon reaction of **19** with $[Li][B(C_6F_5)_4]$ (Spectrum III-1). Indeed, the signals of the monosubstituted Cp ring were splitted, whilst the signals relative to the bridging CH_2 and the isopropyl groups were shifted downfield. In addition, a diastereotopic relationship appeared for the bridging CH_2, and the methyl groups of the isopropyl moieties. These observations were at first presumed to be a consequence of chloride abstraction from **19**, but the X-ray diffraction analysis rapidly contradicted this presumption.



Spectrum III-1: superposition of the ^{1}H NMR spectra of 19 (bottom) and after reaction with [Li][BC$_6$F$_5$)$_4$] (top) (600.23 MHz, 300 K, dichloromethane-d$_2$)

In fact a lithium adduct via μ-chloro bonds was obtained as illustrated in Scheme III-8.



Scheme III-8: synthesis of the Li adduct 25

This compound was additionally characterized by NMR spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{15}N, ^{19}F and 2D correlations), positive mode ESI HRMS and as mentioned before, X-ray diffraction analysis. The molecule crystallizes in a centrosymmetric space group (P-1) because of the presence of both enantiomers in the cell; only one is depicted in Figure III-1 for clarity. This unexpected heterotrimetallic complex exhibits an apparent tetrahedral geometry around both Ti centres and the Li atom. This concatenation gives to the molecule a spiranic-like structure, in which both titanocenes are orthogonal to each other (torsion angle Ct1-Ti1-Ti2-Ct3 = 83.94(6)°), responsible for the diastereotopy observed by NMR for **25**. Noteworthy, both nitrogens do not coordinate to Li, either intramolecularly or intermolecularly. This type of adduct could be formed in other reactions run with **9-13** as evidenced by ^{1}H NMR spectroscopy; but the corresponding adducts were not characterized further.

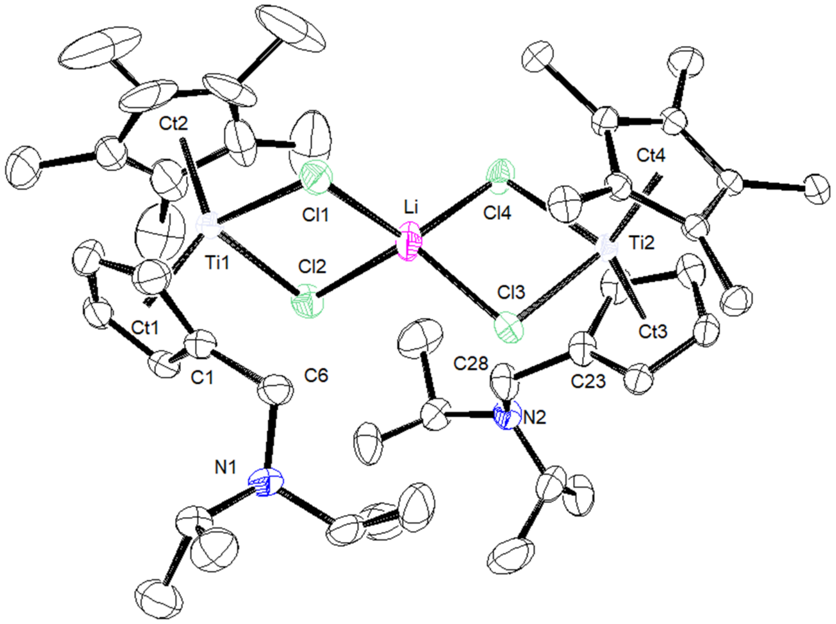


Figure III-1: ORTEP view of 25. (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity as well as the counter anion). Selected bond lengths (Å) and angles(°): Ti1-Ct1 = 2.0594(13), Ti1-Ct2 = 2.0720(11), Ti2-Ct3 = 2.0641(14), Ti2-Ct4 = 2.0714(13), Ti1-Cl1 = 2.3923, Ti1-Cl2 = 2.3862(7), Ti2-Cl3 = 2.3771(8), Ti2-Cl4 = 2.3990(8), C1-C6 = 1.507(4), C23-C28 = 1.506(4), C6-N1 = 1.457(3), C28-N2 = 1.456(3), Li-Cl1 = 2.348(5), Li-Cl2 = 2.323(5), Li-Cl3 = 2.301(5), Li-Cl4 = 2.357(5), Ct1-Ti1-Ct2 = 133.66(5), Ct3-Ti2-Ct4 = 133.41(5), Cl1-Ti1-Cl2 = 90.45(2), Cl3-Ti2-Cl4 = 89.79(3), C1-C6-N1 = 110.5(2), C23-C28-N2 = 110.0(2), Cl1-Li-Cl2 = 93.17(16), Cl3-Li-Cl4 = 92.72(16), Cl1-Li-Cl3 = 114.3(2), Cl1-Li-Cl4 = 126.3(2), Cl2-Li-Cl3 = 116.7(2), Cl2-Li-Cl4 = 115.7(2), Ct1-Ti1-Ti2-Ct3 = 83.94(6).

Two other examples of Li adduct formation by μ-chloro bonds have been also described in the literature with a Pd-based and a Co-based complex by Jordan and Roesky respectively.[14,15] The preparation of **25** with the correct stoichiometry (1 eq of $[Li][B(C_6F_5)_4]$ for 2 eq of **19**), yielded **25** in 56% yield in 90% purity after multiple recrystallization steps. Remaining unidentified by-products were still observed even after this workup (see experimental part).

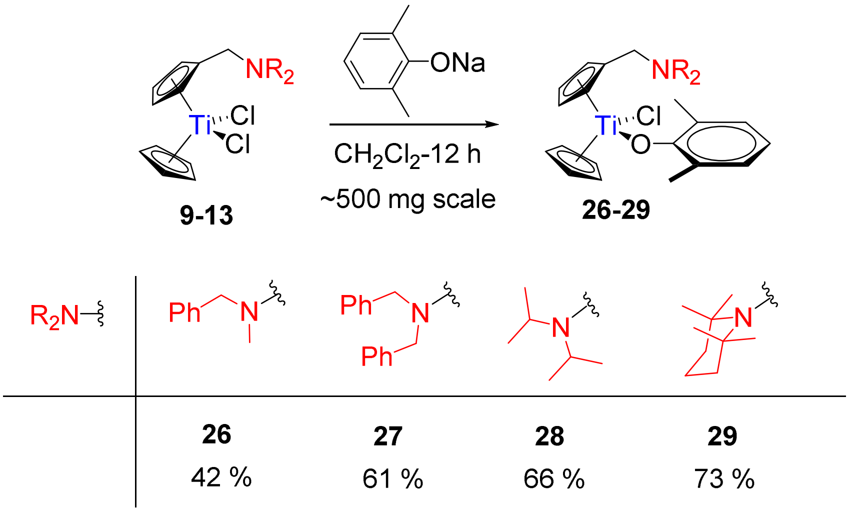
Despite our efforts, all attempts to generate cationic titanocenes from **9-13** failed whatever the choice of the chloride abstractor ($[Ag][BPh_4]$, $[Ag][NTf_2]$, $B(C_6F_5)_3$ or $[Et_3Si][B(C_6F_5)_4]$. The synthesis of electron-enriched titanocenes was then envisioned by substituting a chloride ligand by an aryloxy ligand. According to the results previously obtained in our group,[16] a 2,6-dimethylphenoxy ligand was chosen. A new series was thus synthesized according to the same procedure, yielding **26-29** in 42-73% yield (Scheme III-9).

---

[14] Shen, H.; Steele, I. M.; Jordan, R. F. *Acta Crystallogr. C.* **2003**, *59*, m 405

[15] Mondal, K. C.; Samuel, P. P.; Roesky, H. W.; Carl, E.; Herbst-Irmer, R.; Stalke, D.; Schwederski, B.; Kaim, W.; Ungur, L.; Chibotaru, L. F.; Hermann, M.; Frenking, G. *J. Am. Chem. Soc.* **2014**, *136*, 1770

[16] Normand, A. T.; Richard, P.; Balan, C.; Daniliuc, C. G.; Kehr, G.; Erker, G.; Le Gendre, P. *Organometallics.* **2015**, *34*, 2000

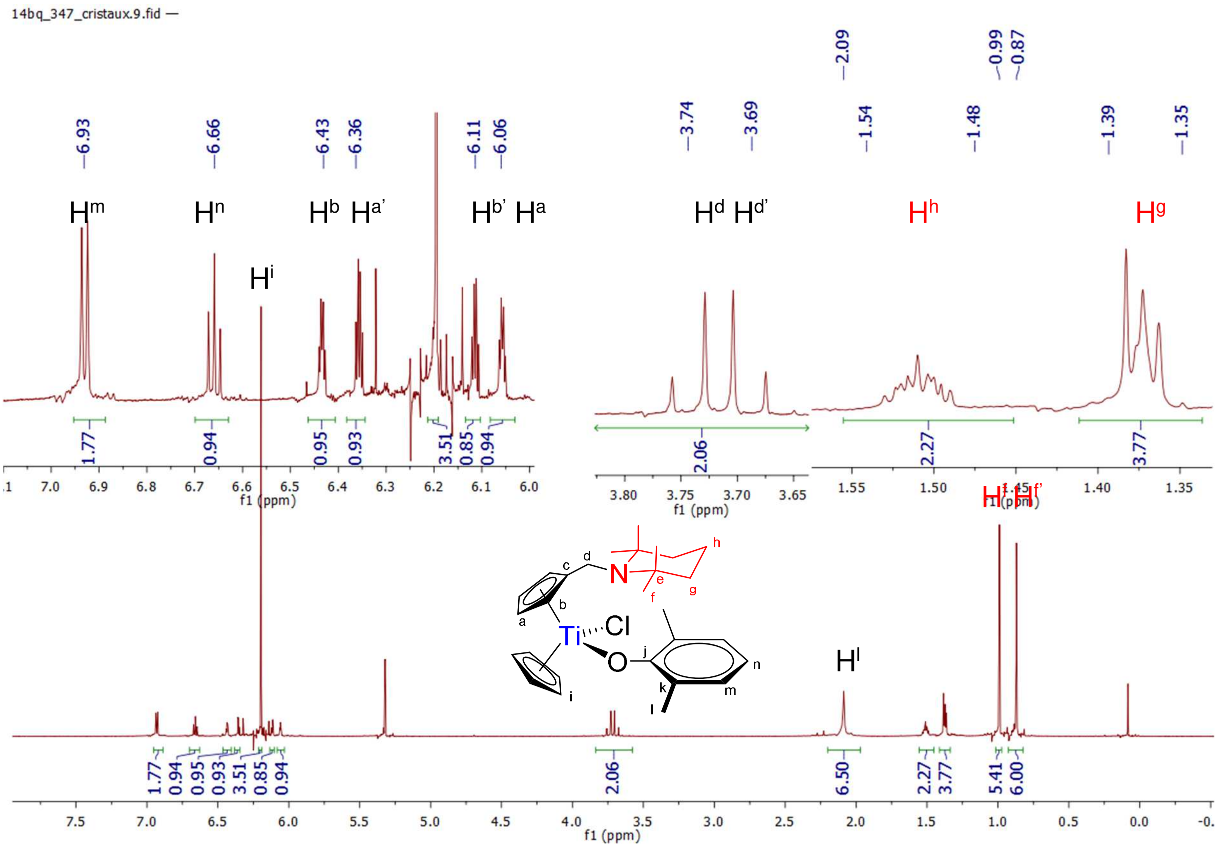


Scheme III-9: synthesis of 26-29

Stoichiometry was carefully controlled in order to avoid disubstitution of the titanocene. However, the chosen aryloxy ligand is quite bulky, which might prevent disubstitution due to steric hindrance. All these complexes were characterized at least by NMR spectroscopy, positive mode ESI HRMS and IR spectroscopy, except **26**.[17] Four different substituents of the titanium centre make these complexes chiral, which translates into diastereotopic relationships in the NMR spectra. For the protons on the monosubstituted Cp ring, a set of four apparent quartets is observed, whilst the signal of the bridging CH_2 exhibits an AB pattern. Methyl groups on **28** and **29** are also diastereotopic. The ^{1}H NMR of **29** is depicted in Spectrum III-2. The signals of the 2,6-dimethylphenoxy ligand appear as a set of one doublet and one triplet at 6.93 and 6.66 ppm respectively for aromatic signals, and one singlet for the methyl groups at 2.09 ppm. As explained above, a set of four apparent quartets (6.43, 6.36, 6.11 and 6.06 ppm) is observed for the signals of the monofunctionalized Cp ring, whilst the signal of the unsubstituted Cp appears as a singlet at 6.19 ppm. The signal of the bridging CH_2 exhibits a marked AB pattern (3.74 and 3.69 ppm, $^2J_{HH} = 15.2$ Hz). Finally, whilst the methyl groups from the tetramethylpiperidine moiety are diastereotopics (two singlets at 0.99 and 0.87 ppm), the signals for the methylene groups show two multiplets at 1.54-1.48 and 1.37-1.35 ppm.

---

[17] **26** was isolated as a sticky oil which prevented satisfactory IR measurement



Spectrum III-2: ^{1}H NMR of 29 (600.23 MHz, 300 K, dichloromethane-d$_2$)

Suitable crystals for X-ray diffraction analysis were obtained by diffusion of pentane into a dichloromethane solution of **29.** These crystals belong to the P2$_1$/c space group. Even if both enantiomers are present in the cell, the space group is chiral. Indeed, as illustrated in Figure III-2, both enantiomers do not adopt the same conformation. Whilst the tetramethylpiperidine moiety is located far away from both X ligand of the titanocene in the first enantiomer (left: C11-Ct1-Ti-Cl = -20.66(06), C11Ct1TiO = -122.70(07)); it is located almost above the oxygen atom in the second one (right: C11A-Ct1A-TiA-ClA = -94.33(06), C11A-Ct1A-TiA-OA = 7.37(08)). In both structures, the tetramethylpiperidine is located almost as in other tetramethylpiperidine-based structures described in chapter II (torsion angles ϕ: C5-C1-C11-N = -22.25(3)°, C5A-C1A-C11A-NA = 32.76°).

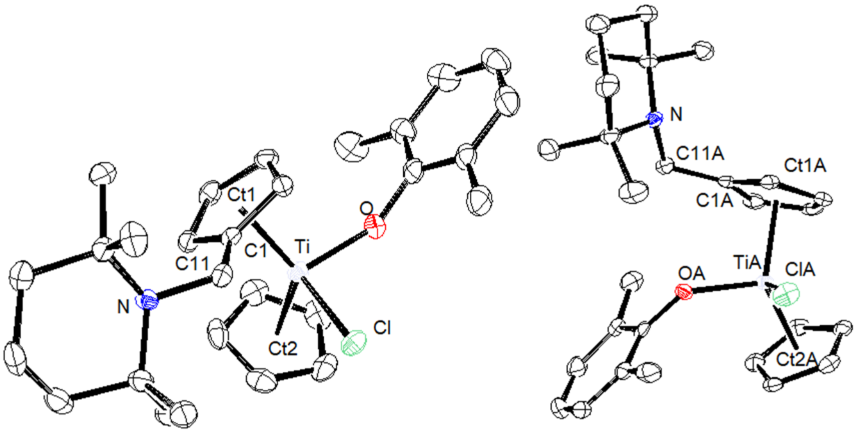
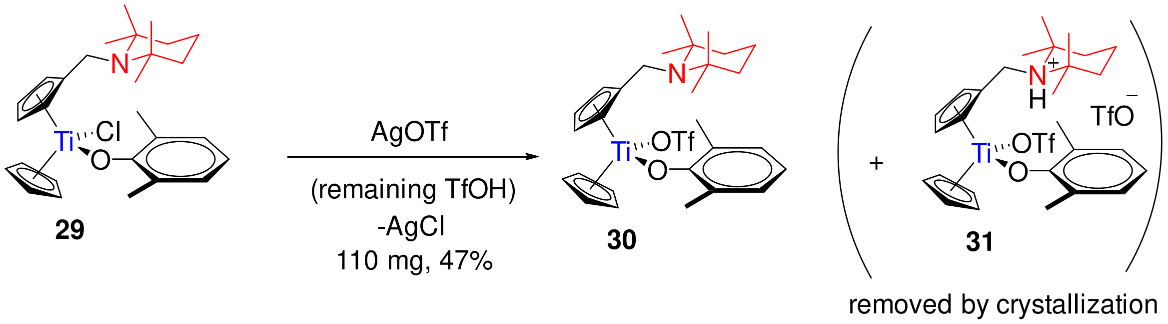


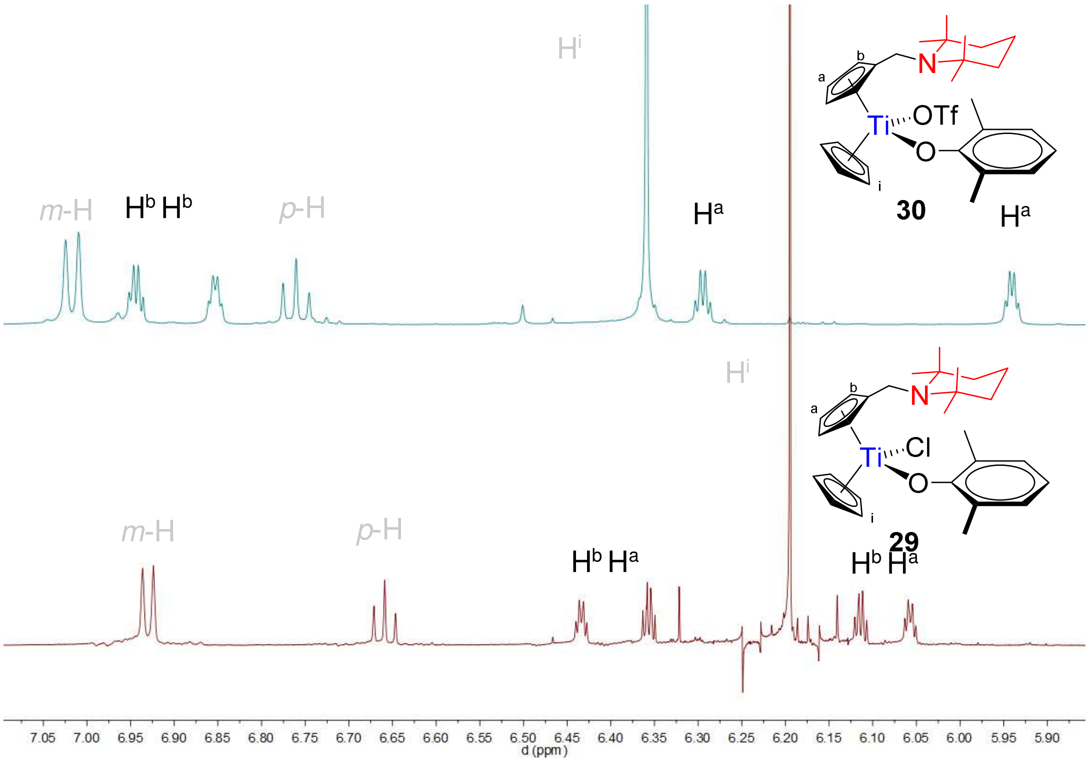
Figure III-2: ORTEP view of 29 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity). Selected bond lengths (Å) and angles(°): Ct1-Ti 2.0951(11) / 2.1053(9), Ct2-Ti = 2.0924(11) / 2.0721(10), Cl-Ti = 2.3864(7) / 2.3945(7), O-Ti = 1.8620(14) / 1.8835(15), C1-C11 = 1505(3), C11-N = 1.470(2) / 1.475(3), Ct1-Ti-Ct2 = 130.47(4) / 130.79(5), Cl-Ti-O = 96.17(5) / 96.94(5), C1-C11-N = 113.17(17) / 113.87(17)

For this series, the standard chloride abstractors were used to form the cationic titanocenes. Some of them did not react, and the starting titanocene was still observed in the ^{1}H NMR spectrum ([Li][B(C_6F_5)$_4$], [Ag][BPh_4]); or the cationic species formed was not stable, yielding only decomposition of the titanocene fragment according to NMR analyses ($AgNTf_2$, [Et_3Si][B(C_6F_5)$_4$]). However, the use of AgOTf was effective on **29** yielding **30** in moderate yield, with the presence of a side product. Indeed, the commercially available silver complex contained remaining triflic acid forming **31** (reaction of TfOH with **30**). Fortunately, purification by recrystallization was efficient (see experimental part) affording **30** in very good purity.



Scheme III-10: synthesis of 30

The compound was then characterized by the standard set of techniques (NMR, IR, HRMS, elemental and X-ray diffraction analyses). The ^{1}H NMR spectrum of **30** is similar to that of **29** (Spectrum III-2), the most noticeable change is that of the chemical shift of Cp rings. The signals of H^b and the unsubstituted Cp ring are shifted downfield, whilst the signals of H^a are shifted upfield.



Spectrum III-3: Superposition of the ^{1}H NMR spectra of 29 (bottom) and 30 (top) (600.23 MHz, 300K, dichloromethane-d$_2$)

Red plate-shaped crystals for X-ray measurement were obtained by cooling a concentrated pentane solution at -15°C over several days (Figure III-3).

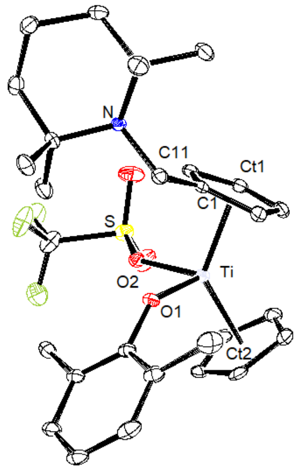
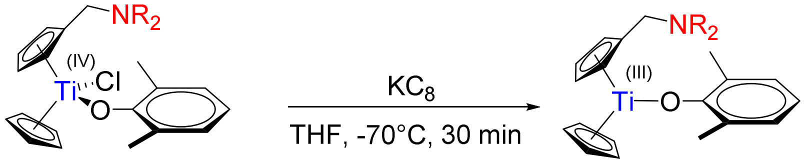


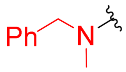
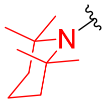
Figure III-3: ORTEP view of 30 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity, enantiomer omitted for clarity). Selected bond lengths (Å) and angles(°): Ti-Ct1 = 2.0931(14) / 2.0849(12), Ti-Ct2 = 2.0658(14) / 2.0585(12), Ti-O1 = 1.8748(17) / 1.8754(16), Ti-O2 = 2.0931(14) / 2.0887(17), C1-C11 = 1.514(4) / 1.503(3), C11-N 1.462(3) / 1.460(3), Ct1-Ti-Ct2 = 131.31(6) / 130.62(5), O1-Ti-O2 93.97(7) / 93.76(5), C1-C11-N = 113.0(2) / 112.7(2).

The elongated Ti-triflate bond observed for **30** (Ti-O2 = 2.0931(14) Å) suggests some degree of lability of the triflate. Indeed, complex $Cp_2Ti(OTf)_2$ (Ti-O = 2.003(7) and 2.000(7)Å) reported by Thewalt,[18] was shown to be labile in presence of coordinating solvents (DMF, H_2O).[19] This suggest that the titanocene triflate is a deguised cationic titanocene and could act as an OmFLP. Several attempts were made at activating small molecules (H_2, CO_2, phenylacetylene, acetophenone or benzophenone), but none of them succeeded, as evidenced by the unchanged ^1H NMR spectra of the reaction mixture. In fact, this complex turned out to be quite robust. This lack of reactivity prompted us to give up the triflate route.

Since silver-based and alkali-based abstractors failed, an alternative redox route was attempted. By using a phosphide as previously done in our group, all attempt to purify the Ti(III) species failed due to their high solubility even in apolar solvents and the resulting impossibility to separate them from the diphosphine byproduct. KC_8 was alternatively used to effect the reduction (Scheme III-11).



27 and **29** → **27-III** and **29-III**

R_2N–		
	27-III	**29-III**
	79%[a]	86 %[a]
	110 mg	135 mg

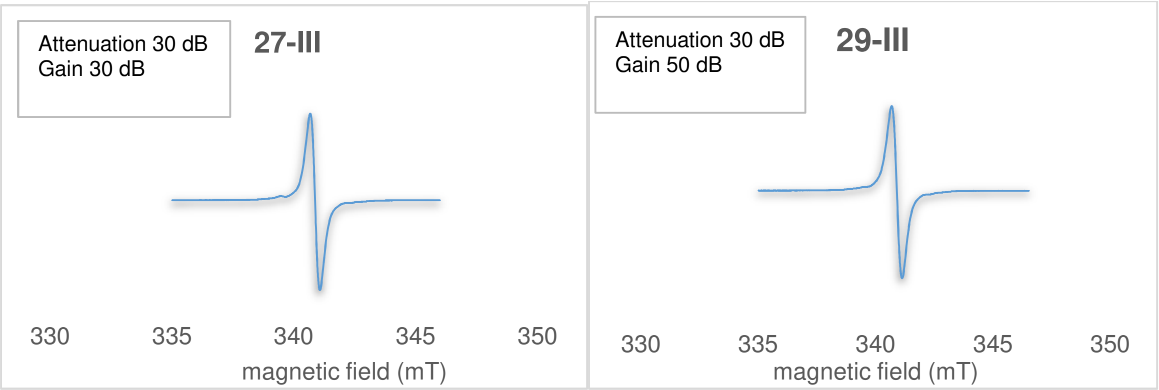
Scheme III-11: synthesis of Ti(III) species. [a]: crude yield determined by comparing the mass of isolated oil with the expected mass.

After evaporation of the crude solution, trituration in pentane helped removal of KCl salts and graphite easily from the product by filtration. Both Ti(III) species were obtained after evaporation of pentane as green sticky oils. They were characterized only by EPR and ^1H NMR spectroscopies (see Spectrum III-4 for the former, and the appendix for the latter).

---

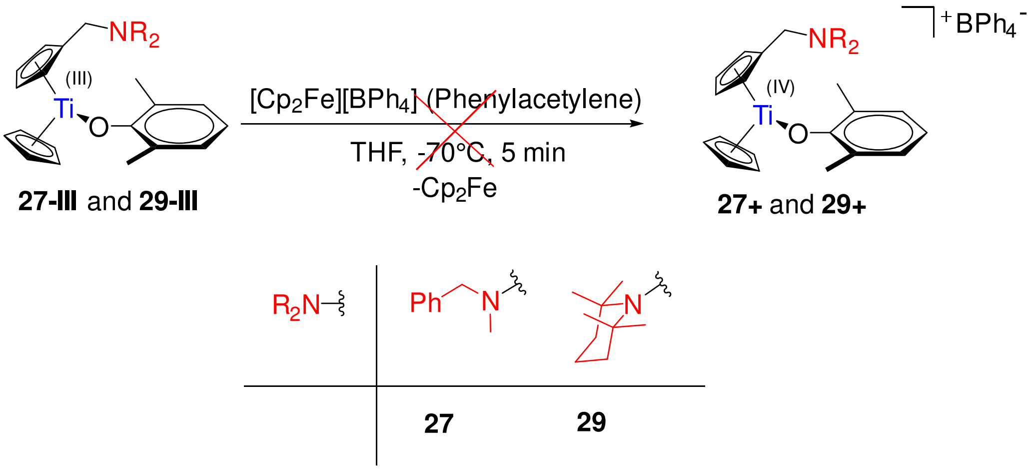
[18] Thewalt, U.; Klein, H.-P. *Z. Für Krist. - Cryst. Mater.* **1980**, *153*

[19] Honold, B.; Thewalt, U. *J. Organomet. Chem.* **1986**, *316*, 291



Spectrum III-4: EPR spectra of 27-III and 29-III (9.437952 and 9.437703 GHz, 295 K, pentane)

Both exhibits one peak at the same Lande factor (g = 1.9781) with no multiplicity. It does not indicate coordination of the nitrogen to the Ti centre. Nevertheless, N coupling are not always observed by EPR, even in cases where coordination is established by X-ray analysis.[20] The ^{1}H NMR spectra only showed traces of pentane and very broad signals, consistent with the paramagnetic nature of these species. These two Ti (III) species were engaged in an oxidation reaction with [Cp_2Fe][BPh_4] with (Scheme III-12) or without phenylacetylene (to trap the putative OmFLPs). These reactions only led to decomposition products. The reduction/oxidation process was then given up.



Scheme III-12: attempt at OmFLPs formation via a two steps reduction/oxidation process

In summary of this first part focused on chloride abstraction, all attempts at cationic titanocene generation failed with mild (alkali metals) or strong (silyl cation) chloride abstractors. Whilst the use of AgOTf (on a mono chlorotitanocene), yielded the stable neutral complex **30**, the apparent successful reduction of **27** and **29** unfortunately did not lead to the clean formation

---

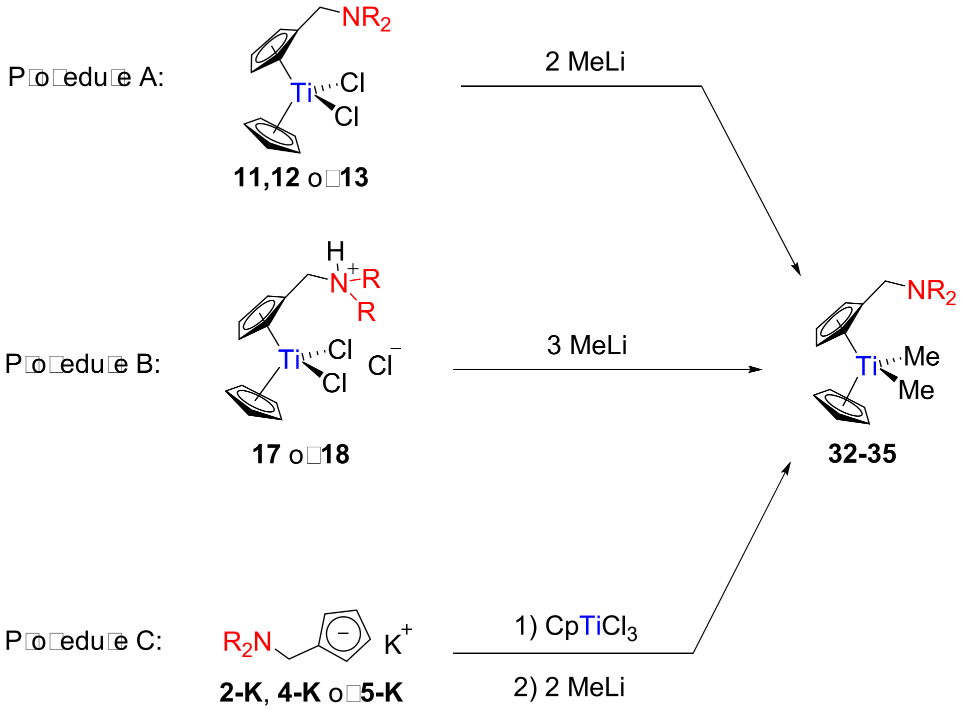
[20] Helten, H.; Dutta, B.; Vance, J. R.; Sloan, M. E.; Haddow, M. F.; Sproules, S.; Collison, D.; Whittell, G. R.; Lloyd-Jones, G. C.; Manners, I. *Angew. Chem. Int. Ed.* **2013**, *52*, 437

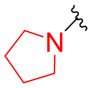
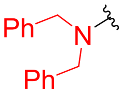
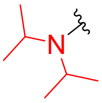
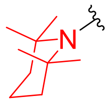
of a cationic species after oxidation. These results prompted us to envision an alternative route for cationic titanocene generation, by using methide abstractors.

4. Methide abstraction

a. Synthesis of dimethyl (aminomethyl)titanocenes

The first step required for this route was the formation of methylated titanocenes. For this purpose, the dimethyl titanocenes **32-35** were synthesized, first by using 2.0 equivalents of MeLi on complexes **10-13**. Complexes **32-35** were easily obtained in this manner in moderate yield as yellow light-, temperature- and moisture- sensitive solids (Scheme III-13).



R_2N–				
	32	**33**	**34**	**35**
Procedure A:	x	63% (228 mg)	68% (250 mg)	72% (260 mg)
Procedure B:	x	x	62% (120 mg)	63% (115 mg)
Procedure C:	47% (620 mg)	x	67% (830 mg)	77% (1.1 g)

x = not tried

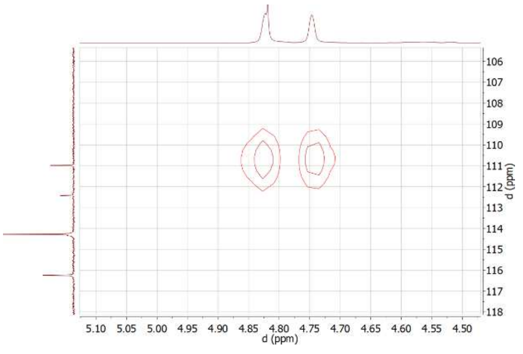
Scheme III-13: the three procedures used for the synthesis of dimethyltitanocenes

These compounds were stored at -15°C inside the glovebox to avoid their decomposition. The moisture sensitivity of the dichloro series (**9-13**) and the sensitivity of their dimethyl analogues (**32-35**) prompted us to find out a procedure for the generation of dimethyl titanocenes via the moisture stable ammonium complexes previously described in Scheme II-15. Indeed, the first FLP reactivity assays were conducted in Münster (Germany) in the group of Pr. Erker. The compounds had to be stable enough for a safe shipment. Thus, an alternative synthesis of complexes **34** and **35** was envisioned, starting from **17** and **18** by using 3.05 equivalents of MeLi. A third procedure was also developed, based on a one-pot synthesis starting from **2-K**, **4-K** and **5-K**, in order to increase the scale of dimethyl titanocene isolated. These complexes were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{15}N and 2D correlations) and positive mode ESI HRMS. Complexes **34** and **35**, isolated as yellow powders, were also characterized by IR spectroscopy. The ^{1}H NMR spectra of these species are similar to those of their dichloro analogues. Noteworthy, a new signal appears at -0.21 ppm, characteristic of the two equivalent methyl groups bound to a Ti centre. The ^{15}N chemical shit remained unchanged after methylation, as expected (e.g. -308 ppm vs -309 ppm for **13**).

In our hands, all attempts to synthesize mono methylated titanocenes failed. Only the dimethyl titanocenes described above could be isolated in sufficient purity and quantity.

b. Preliminary methide abstraction: en route to rearrangements

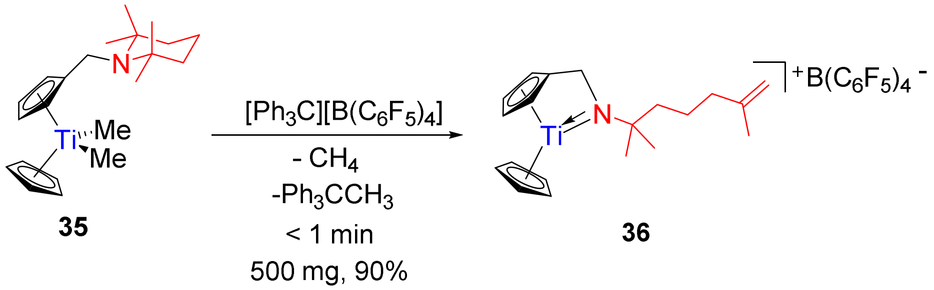
With complexes **17** and **18**, and the procedure B described in the previous section in hands, potential OmFLPs precursors were generated by forming **34** and **35** respectively. After achieving the synthesis of $B(C_6F_5)_3$, preliminary methide abstractions with this chemical were tried on **34** and **35**. Whilst the abstraction from **34** yielded a complex mixture of three titanocenes, the reaction of **35** led to an immediate gas release and a colour change from yellow to dark-red. A complete NMR study of this new molecule indicated that only one species had formed during this process (only one set of signals for a monosubstituted titanocene was observed) but that the TMP moiety had vanished. According to 2D NMR experiment (^{1}H ^{13}C HMQC NMR), a characteristic resonance was observed between a new carbon atom at 110.5 ppm (in the ethylenic region) with two different signals from the ^{1}H NMR spectrum at 4.83 and 4.73 ppm.



Spectrum III-5: ^{1}H ^{13}C HMQC of 36 (500.03 / 125.75 MHz, 300 K, bromobenzene-d_5)

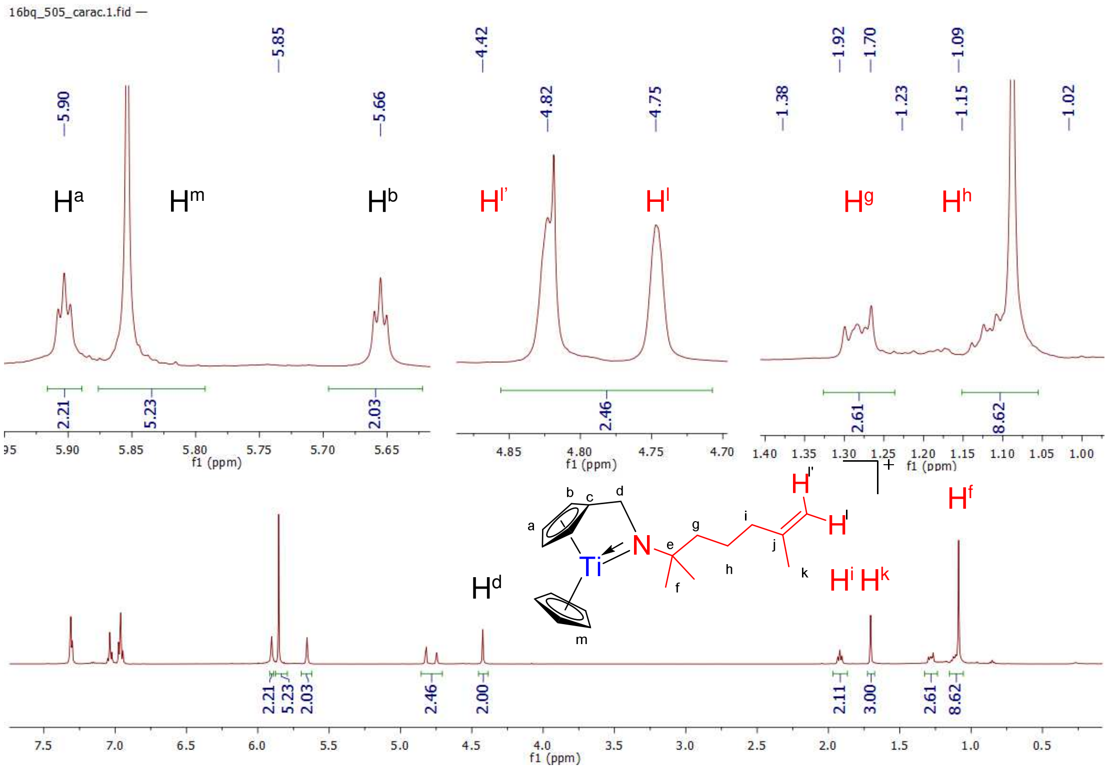
This strongly suggests the presence of a terminal alkene. Unfortunately, all crystallization attempts made at this compound failed. This lack of crystallinity might be a consequence of the Me-B$(C_6F_5)_3^-$ anion.[21]

Compound **36** was fully characterized by standard techniques (NMR spectroscopy, HRMS, and elemental analysis). The proposed structure for **36**, depicted in Scheme III-14 will be unambiguously proved below.



Scheme III-14: discovery of a new cationic titanocene

Considering this structure, all signals from the ^1H NMR spectrum (Spectrum III-6) can be assigned: the titanocene fragment appears as a set of two apparent triplets (5.90 and 5.66 ppm) for the monosubstituted Cp ring, and a singlet for the non-substituted Cp ring.



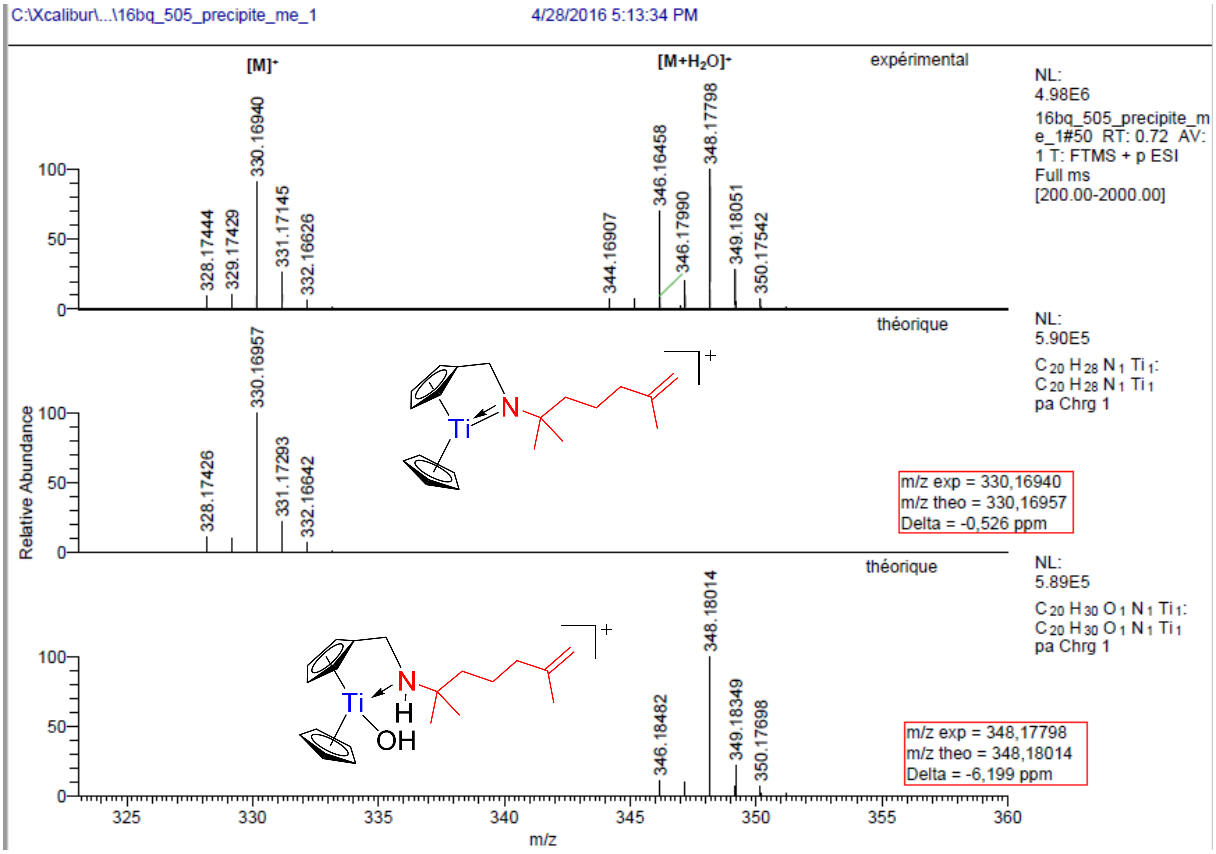
Spectrum III-6: ^1H NMR spectrum of 36 (500.03 MHz, 300 K, bromobenzene-d_5; counter anion omitted for clarity)

---

[21] A. Normand, personal communication

The bridging CH_2 resonates at 4.42 ppm, whilst two new multiplets are found at 4.82 and 4.75 ppm corresponding to the signals of the protons of the terminal akene. The signals of the aliphatic chain appear as one triplet and two multiplets (1.92, 1.38-1.23 and 1.15-1.02 ppm), and finally one can found two singlets in a 3 : 6 ratio for the two methyl groups (1.70 and 1.09 ppm respectively). Again, in the ^1H ^{13}C HMQC spectrum, a noteworthy correlation is found for the ethylenic protons with a carbon atom located at 111.0 ppm (see appendix). Both protons correlate to the same carbon atom.

In addition, the ^{15}N chemical shift was observed at -363 ppm, which represents a significant upfiled shift compared to **35** (-309 ppm $\Delta\delta$ = 54 ppm), indicating a change of the electronic and / or geometric environment of the nitrogen atom. Furthermore, a careful analysis of the ESI-MS spectrum showed the presence of two clusters of peaks with the molecular formula of $C_{20}H_{28}NTi$ and $C_{20}H_{30}ONTi$ corresponding to $[M]^+$ and $[M+H_2O]^+$ cations respectively (Spectrum III-7).



Spectrum III-7: HRMS spectrum of 36 (positive mode ESI, bromobenzene)

Nevertheless, these data do not prove the proposed structure, although they are in agreement with it. No crystals of **36** could be obtained. However, a $OPEt_3$-stabilised derivative (**37**) could be synthesized by trapping **36** *in situ*, and suitable crystals for X-ray diffraction were obtained by layering a dichloromethane solution with pentane at room temperature (Figure III-4). Due to the coordination of the phosphine oxide, the titanium centre is chiral. As a result, new diastereotopic relationships were observed by ^{1}H NMR spectroscopy between the signals of the protons of the monofunctionalized Cp ring, and those of the methylene and methyl groups along the aliphatic chain (see experimental part).

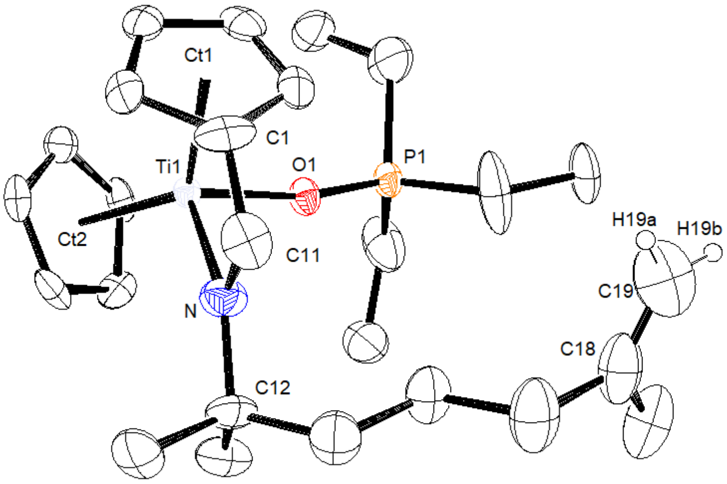


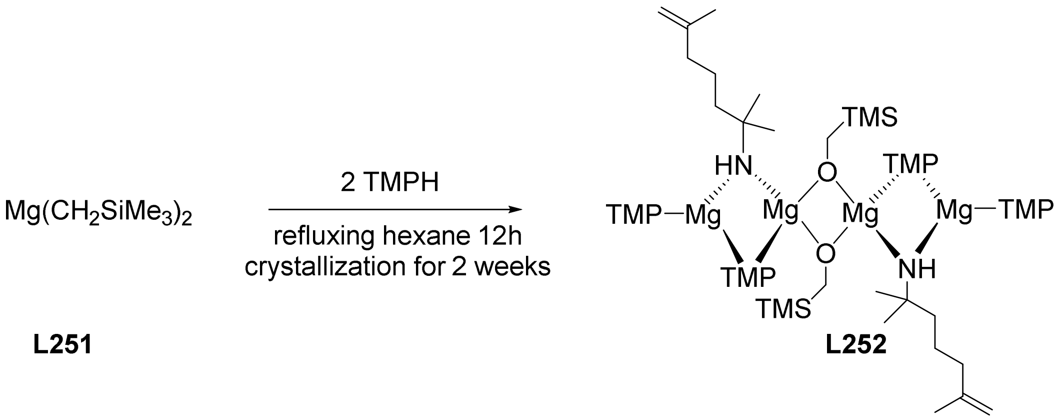
Figure III-4: ORTEP view of 37 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity except those from C19, enantiomer and counter anion omitted for clarity). Selected bond lengths (Å) and angles(°): Ti-Ct1 = 2.064(4), Ti-Ct2 = 2.078(4), O1-Ti = 2.023(4), N-Ti = 1.996(7), C1-C11 = 1.469(11), C18-C19 = 1.323(17), C18-C17 = 1.523(15), Ct1-Ti-Ct2 = 130.07(16), N1-Ti-O = 100.0(3), C1-C11-N = 99.3(6), C11-N-Ti = 104.9(5), Ti-N-C12 = 112.3(6), C11-N-C12 = 142.6(5), C-19-C18-C20 = 120.8(12), C19-C18-C17 = 121.8(12), C17-C18-C20 = 113.7(12), C18-C19-H19b = 120.01(11), C18-C19-H19a = 120.0(2), H19a-C19-H19b = 119.99(18).

The space group is achiral meaning that both enantiomers are present in the cell. The second molecule is omitted due to high disorder. It even confers a low-resolution factor to the global molecule. Nevertheless, the crystallographic analysis confirms the structure of the molecule. The Ti-N bond is relatively short (1.996(7) Å) and the nitrogen is planar ($\Sigma\alpha$(N) = 359.8(9)°) indicating sp2 hybridation. In addition, the calculated torsion angles (Ct1-Ti-N-C11 = 1.05(5)°, Ct2-Ti-N-C12 = 37.1(1)°) indicate that the orientation of the lone pair of the nitrogen is suitable for π-interaction with titanium. Moreover, the same hybridation is observed for C18 and C19 ($\Sigma\alpha$(C18) = 359.8(2)°, $\Sigma\alpha$(C19) = 360.0(2)° respectively), and the C18-C19 bond is also relatively short (1.323(17) Å vs 1.523(15) Å for C18-C17), which is in agreement with a terminal carbon-carbon double bond.

To the best of our knowledge, only one example of such rearrangement was observed by O'Hara by refluxing for 12h **L251**, forming the magnesium complex **L252** the structure of which was elucidated by X-ray diffraction analysis (Scheme III-15).[22]

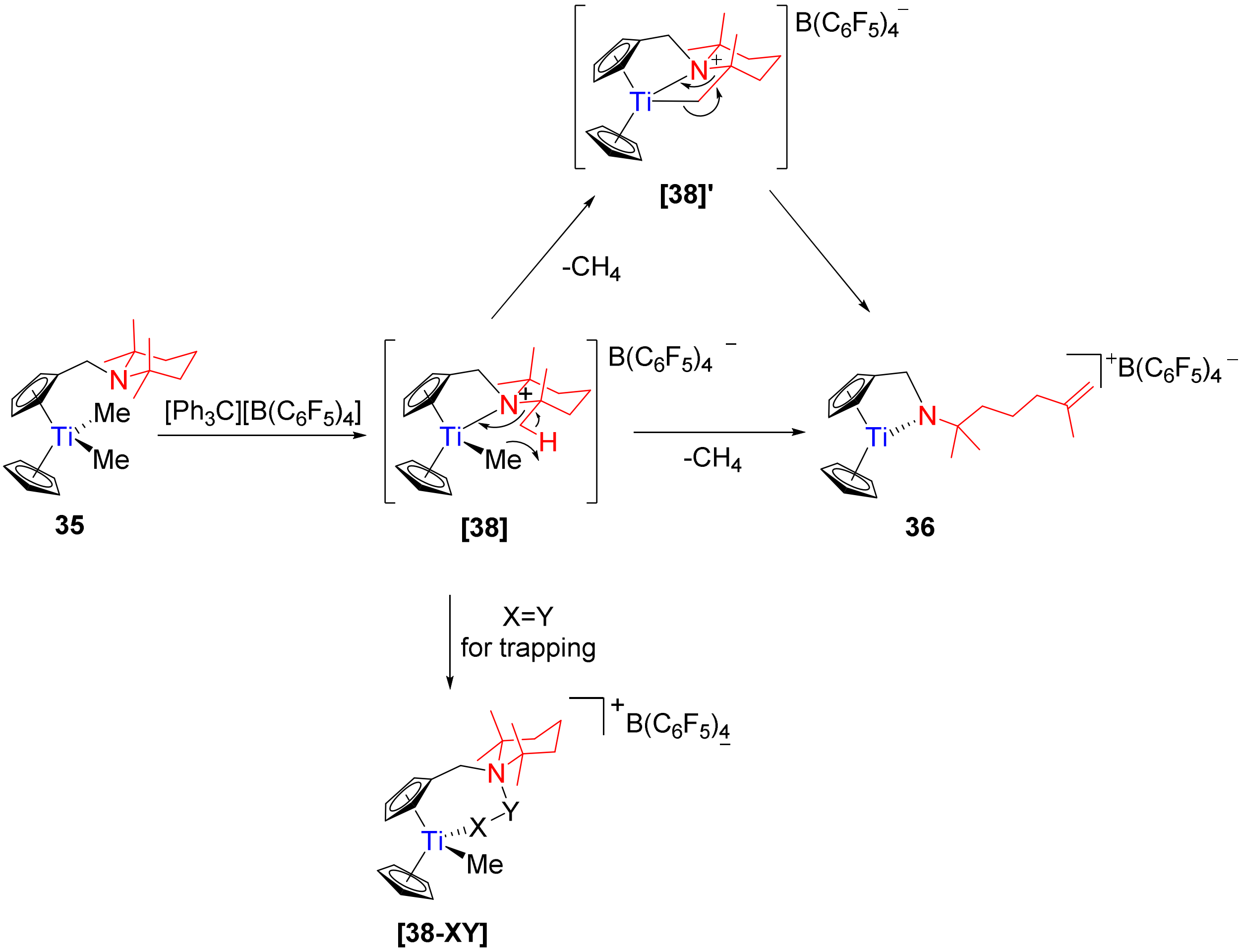
---

[22] Kennedy, A. R.; Klett, J.; McGrath, G.; Mulvey, R. E.; Robertson, G. M.; Robertson, S. D.; O'Hara, C. T. *Inorganica Chim. Acta.* **2014**, *411*, 1



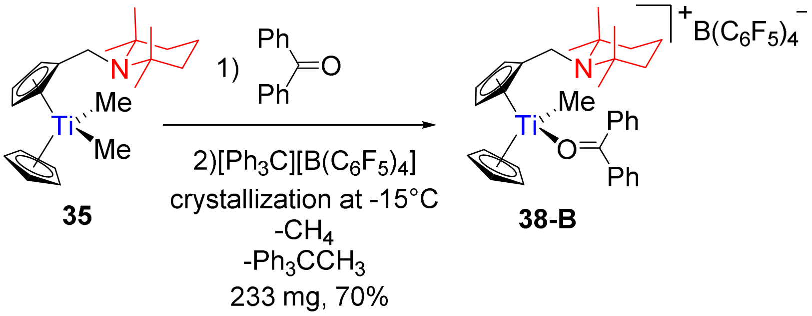
Scheme III-15: ring opening of TMP by a magnesium complex

This unexpected rearrangement was a consequence of the high reactivity and low stability of the cationic intermediate formed upon methide abstraction. Two mechanisms could be envisioned: complex **[38]** is presumed to be intermediately formed after methide abstraction, and then N-coordination of TMP is able to occur (Scheme III-16).



Scheme III-16: alternative strategy for the OmFLP concept with 35

This confers some degree of ammonium character to the nitrogen atom, which then undergoes intramolecular deprotonation by the remaining methide on titanium in a process akin to the Hofmann elimination in a concerted manner. Alternatively, a non-concerted mechanism can also be proposed: activation of one methyl of the TMP moiety could occur, forming **[38]'** intermediately. Considering that cationic amido titanocene can promote intramolecular hydroamination via a carbon-carbon double bond insertion into a Ti-N bond,[23] one might envisage the reverse desinsertion step as illustrated in Scheme III-16. A consequence of the mechanisms depicted in Scheme III-16 is that intermediate [**38**] could be trapped with a suitable reagent, e.g. an unsaturated substrate (X=Y). When **35** was reacted with $[Ph_3C][B(C_6F_5)_4]$ in the presence of nitriles or phenylacetylene, only **36** stabilized by the reagent (acting as L-Ligand) was observed. However, the same reaction in the presence of benzophenone prevented the rearrangement (presumably due to the high affinity of the titanocenium cation for oxygen) and adduct **38-B** was obtained (Scheme III-17).



Scheme III-17: synthesis of 38

This new compound was fully characterized by NMR spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{15}N, ^{19}F and 2D correlations), HRMS and elemental analysis.[24] Red prism-shaped crystals were obtained by slow diffusion of heptane into a chlorobenzene solution at -15°C. The X-ray diffraction study definitely established its structure (Figure III-5). As previously observed for other structures, the space group is achiral (P-1), both enantiomers are present in the cell but only one is presented for clarity. The structure exhibits a relatively short Ti-O bond (2.0008(13) Å vs 2.26 ± 0.10 Å for the empirical covalent bond length),[25] and the oxygen atom adopts a slight bent geometry (Ti-O-C22: 160.44(13) Å), whilst C22 retains a planar geometry ($\Sigma\alpha(C22) = 359.98(3)°$).

---

[23] Gribkov, D. V.; Hultzsch, K. C. *Angew. Chem. Int. Ed.* **2004**, *43*, 5542

[24] IR analysis did not show characteristic C=O absorptions due to the overwhelming bands of the borate anion.

[25] Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832

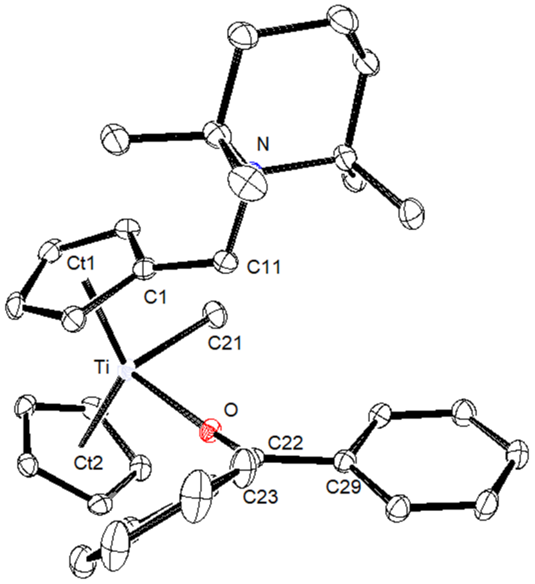
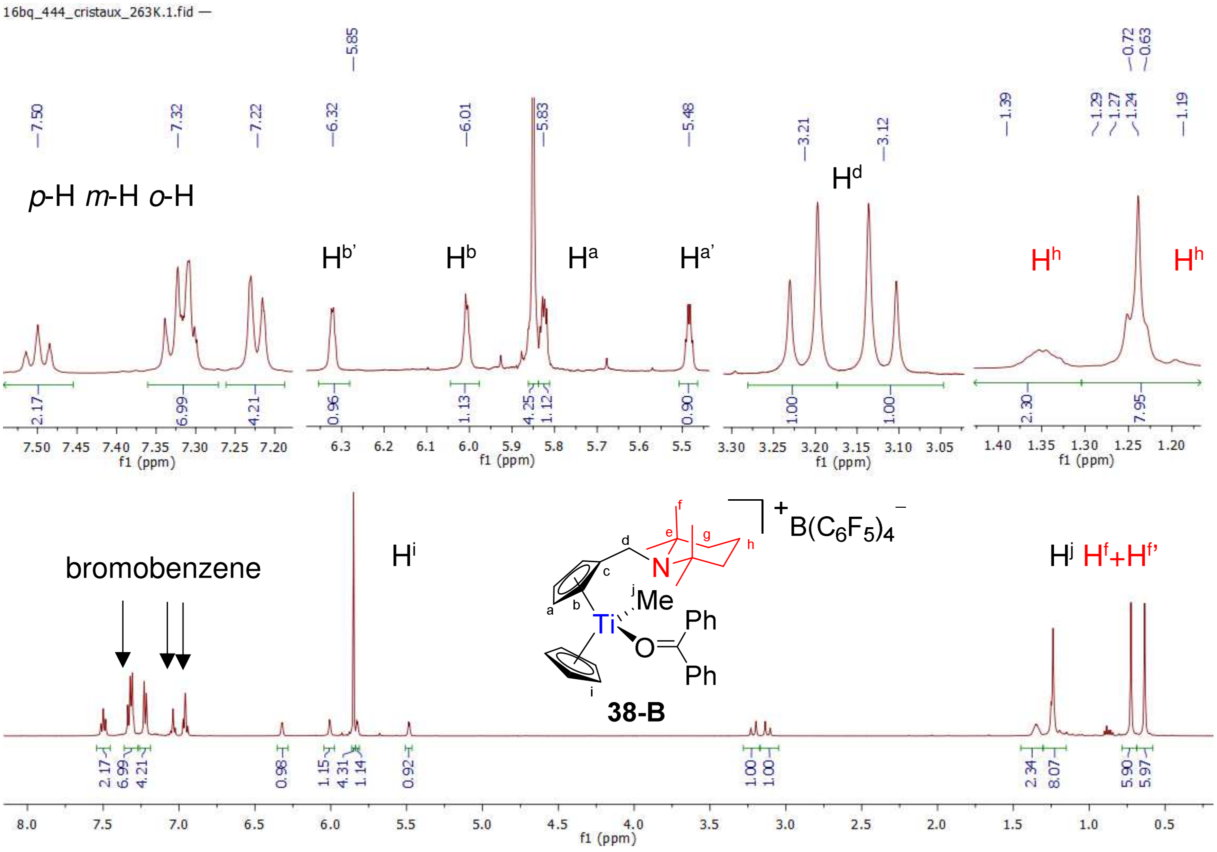


Figure III-5: ORTEP view of 38-B (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity, enantiomer, solvent and counter anion omitted for clarity). Selected bond lengths (Å) and angles(°): Ti-Ct1 = 2.0542(10), Ti-Ct2 = 2.0510(10), Ti-C21 = 2.1686(19), Ti-O = 2.0008(13), C1-C11 = 1.514(3), C11-N = 1.463(2), O-C22 = 1.252(2), Ct1-Ti-Ct2 = 134.78(4), O-Ti-C21 = 93.21(7), C1-C11-N = 114.73(16), Ti-O-C22 = 160.44(13), O-C22-C23 = 160.44(13), O-C22-C29 = 118.95(13), C23-C22-C29 = 121.75(17).

Additionnaly, the TMP arm is located between C21 and O but closer to the oxygen atom (torsion angles: C11-Ct1-Ti-O = 25.94(7)° and C11-Ct1-Ti-C21 -71.93(8)°).

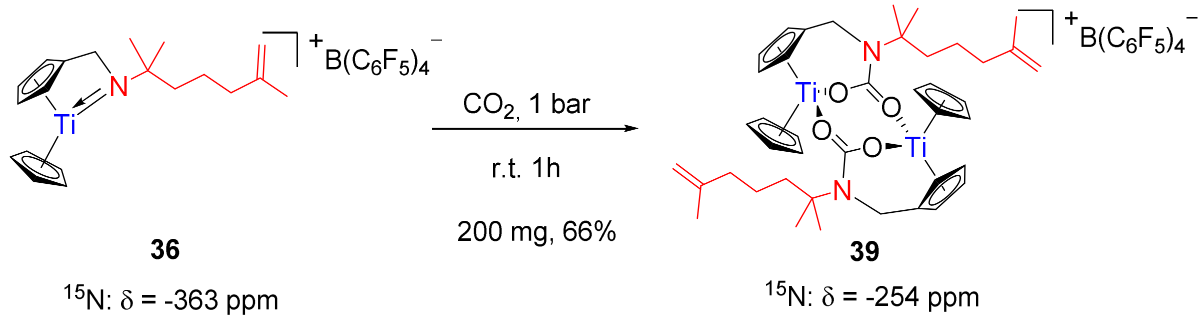
The coordination of benzophenone to titanium entails diastereotopic relationships in the ^{1}H NMR spectrum (Spectrum III-8). The ^{1}H NMR spectrum in bromobenzene-d$_5$ is presented in Spectrum III-8. In this particular case, residual non-deuterated chlorobenzene was still observed. One can observe the three signals of the phenyl rings of benzophenone as two triplets and one doublet in a 2 : 4 : 4 ratio at 7.50, 7.32 (overlapping with a signal of the deuterated solvent) and 7.22 ppm (for *para*-, *meta*- and *ortho*-H respectively). Then a characteristic set, for a chiral titanocene, of four apparent quartets with one singlet, are observed for the Cp rings, at 6.32, 6.01, 5.83 and 5.48 ppm and 5.85 ppm (monosubstituted and non-substituted Cp ring respectively). Diastereotopy is also observed at the bridging CH$_2$ and at the TMP moiety, with an AB pattern for the former ($^2J_{HH}$ = 16.4 Hz) at 3.21 and 3.12 ppm and a set of two multiplets and two singlets for the signals of the methylene and the methyl groups of the latter respectively (1.39-1.29, 1.27-1.19, 0.72 and 0.63 ppm). Lastly, the signal of the remaining methide on the titanium centre is observed at a rather downfield shift for a Ti-Me group (1.24 vs -0.21 ppm for the methide of **35** in benzene-d$_6$), indicative of the formation of a titanocenium cation.



Spectrum III-8: ^{1}H NMR of 38-B (500.03 MHz, 263 K, bromobenzene-d_5)

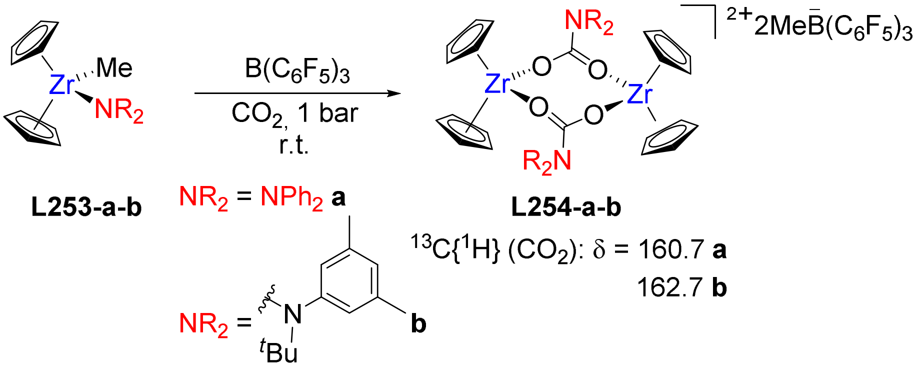
It has to be noted that compound **38-B** was isolated at low temperature, and characterized at 263 K. Indeed, a solution of **38-B** kept at room temperature, slowly turned into **36** with coordination of benzophenone in the course of several hours. The rearrangement occurred but in this case, unidentified side products were observed. The benzophenone-stabilized analogue of **36** was not characterized. In retrospect, one can conclude that **35** might not be the best precursor for OmFLP chemistry, due to the reactive nature of the TMP fragment.

With this new amidotitanocene in hand, the reactivity of the Ti-N bond in **36** was finally investigated. Several alkenes or alkynes were tested but none of them led to clean formation of a new species. Nevertheless, this species was able to react with CO_2, forming a new species, which we tentatively propose to be the dimeric complex **39** (Scheme III-18). A red solution of **36** in bromobenzene was stirred under 1 bar of CO_2 for 1h. Rapidly, a red oil had decanted from the organic layer. After workup, an orange precipitate was formed and was not soluble in bromobenzene anymore. This compound was characterized by NMR spectroscopy (^{1}H ^{11}B ^{13}C ^{15}N ^{19}F and 2D correlation), positive mode ESI HRMS and elemental analysis.



Scheme III-18: CO_2 activation with 36

Even if no suitable crystals for X-ray diffraction analysis were obtained, several pieces of evidence corroborate the dimeric structure. Indeed, similar examples for CO_2 activation by cationic amidozirconocenes have been reported in the literature, with ^{15}N chemical shifts around -363 ppm (vs -254 ppm for **39**). The mass spectrum of **39** is also consistent with the proposed dimeric structure, with a cluster of peaks at 374.16042 Da corresponding to $[2M]^{2+}$. Finally, the solubility profile of **39** is similar to its Zr analogues (**L254-a-b** Scheme III-19).[26]



Scheme III-19: CO_2 activation with amidozirconocenes[25]

The discovery of the unexpected rearrangement leading to **39** prompted further investigations into the reactivity of the pendant amine moiety in complexes **32-34**. Another consequence was the realisation that N/Ti⁺ OmFLPs are probably elusive targets due to the reactivity of the amine moiety in the presence of the titanocenium fragment. Before further developing the results of these investigations, this chapter will present a short survey of the literature on CH activation of amines. Particular attention will be devoted to group 4 metal examples.

c. CH activation of amines in the literature

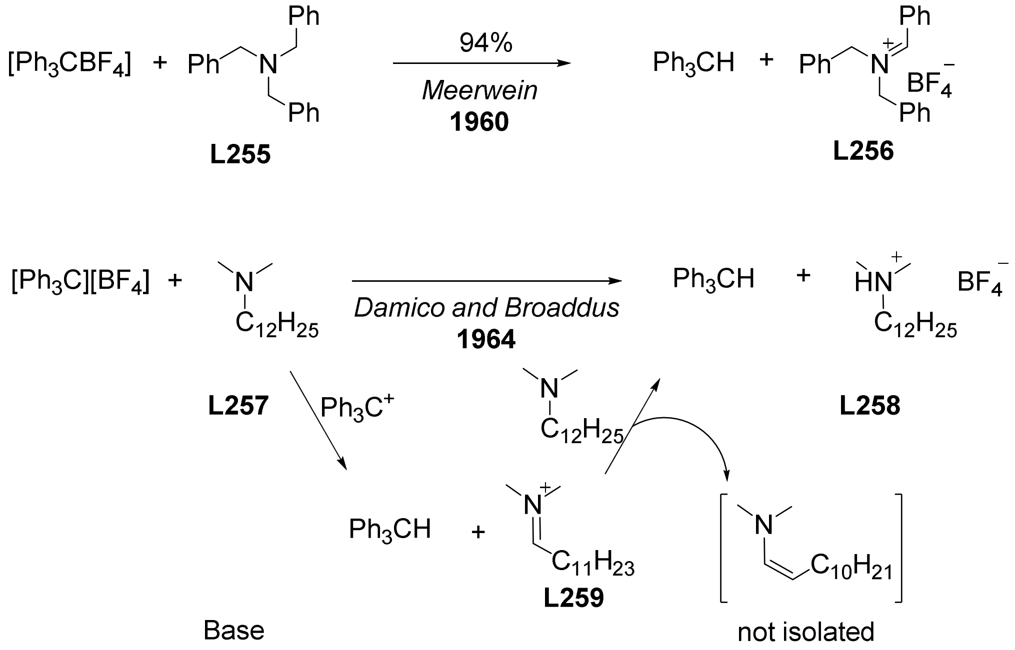
One of the earlier example in this category was described in 1960 by Meerwein,[27] who used the trityl cation to activate tribenzylamine. In this case, CH activation in the α position of the nitrogen atom occurred, yielding the **L256** iminium salt selectively (Scheme III-20). This

---

[26] Normand, A. T.; Daniliuc, C. G.; Wibbeling, B.; Kehr, G.; Le Gendre, P.; Erker, G. *J. Am. Chem. Soc.* **2015**, *137*, 10796

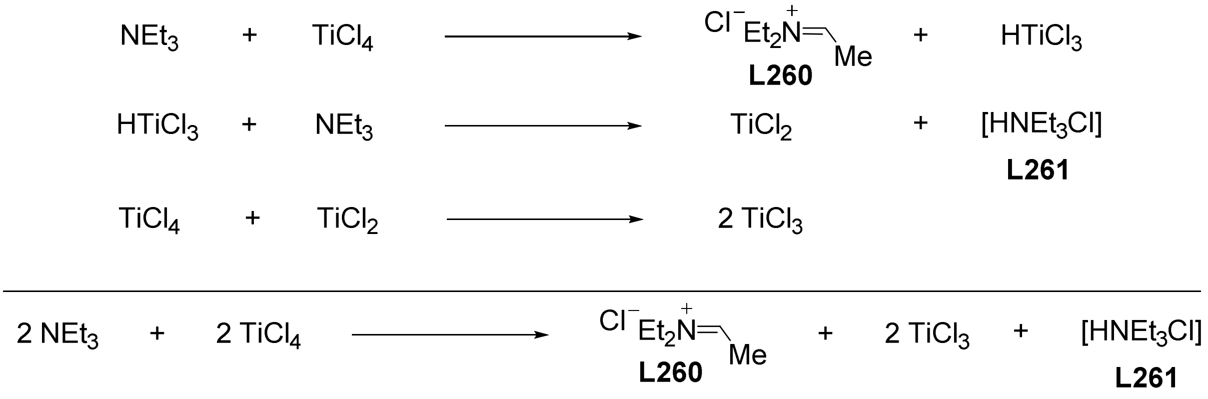
[27] Meerwein, H.; Hederich, V.; Morschel, H.; Wunderlich, K. *Justus Liebigs Ann. Chem.* **1960**, *635*, 1

reaction highlights one of the typical reactivity pattern of Ph_3C^+, i.e. hydride abstraction. The use of the trityl cation was further extended to β-H containing amines by Damico and Broaddus,[28] but they showed that another reaction occurred in their case. Indeed, the ammonium borate **L258** and triphenymethane were isolated in more than 60% yield, as if hydrogen activation had occurred, and no iminium salt was observed. A mechanism was proposed in which α-H abstraction by Ph_3C^+ yielded the iminium salt **L259**, which was deprotonated by the starting amine to yield **L258** and an enamine byproduct. This mechanism implies that some of the starting amine (~ 30%) is used as a sacrificial hydrogen source.



Scheme III-20: reactivity of amines with the trityl cation

Almost forty years later, a similar abstraction reaction was developed by Periasamy and Basset, using $TiCl_4$ or $B(C_6F_5)_3$ (Scheme III-21 and Scheme III-22).[29,30]



Scheme III-21: simplified mechanism of the CH activation of triethylamine with $TiCl_4$

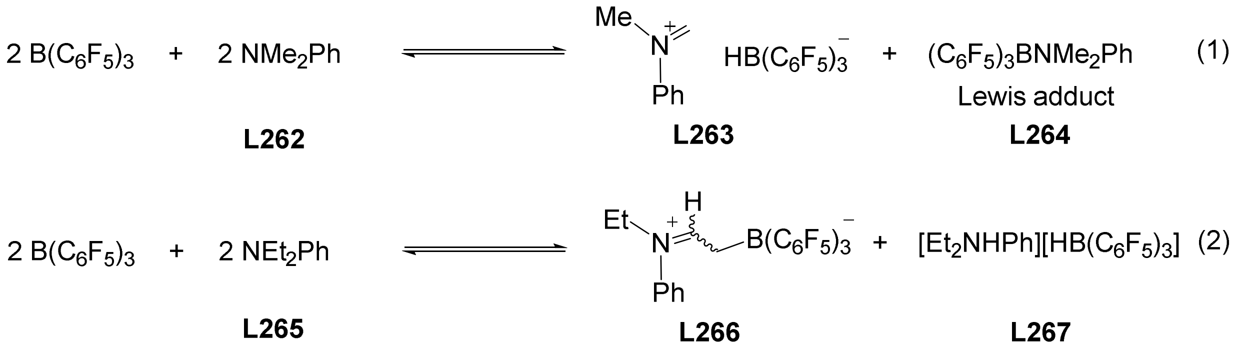
---

[28] Damico, R.; Broaddus, C. D. *J. Org. Chem.* **1966**, *31*, 1607

[29] Bharathi, P.; Periasamy, M. *Org. Lett.* **1999**, *1*, 857

[30] Millot, N.; Santini, C. C.; Fenet, B.; Basset, J. M. *Eur. J. Inorg. Chem.* **2002**, *2002*, 3328

Starting from dimethylaniline and $B(C_6F_5)_3$, equilibrium (1) was established, in which an iminium salt and a Lewis adduct are formed. In the case of diethylaniline, in which β-hydrogens are present, the iminium formed first, which was rapidly deprotonated by diethylaniline, to form the corresponding enamine, along with hydridoborate salt **L267.** The enamine reacted with $B(C_6F_5)_3$ to form a zwitterionic species (**L266**, Scheme III-22).



Scheme III-22: CH activation on tertiary amines by $B(C_6F_5)_3$

By using a borane, Basset showed that these reactions were in equilibrium, contrary to the reaction previously shown with the trityl cation. Nevertheless, a parallel can be established between both reactions, highlighting the reactivity of β-hydrogen-containing amines towards hydride abstraction. The formation of enamine is a key event in this type of reactivity. This feature was used by Stephan, to catalytically racemize amines with $B(C_6F_5)_3$ via the enamine form.[31]

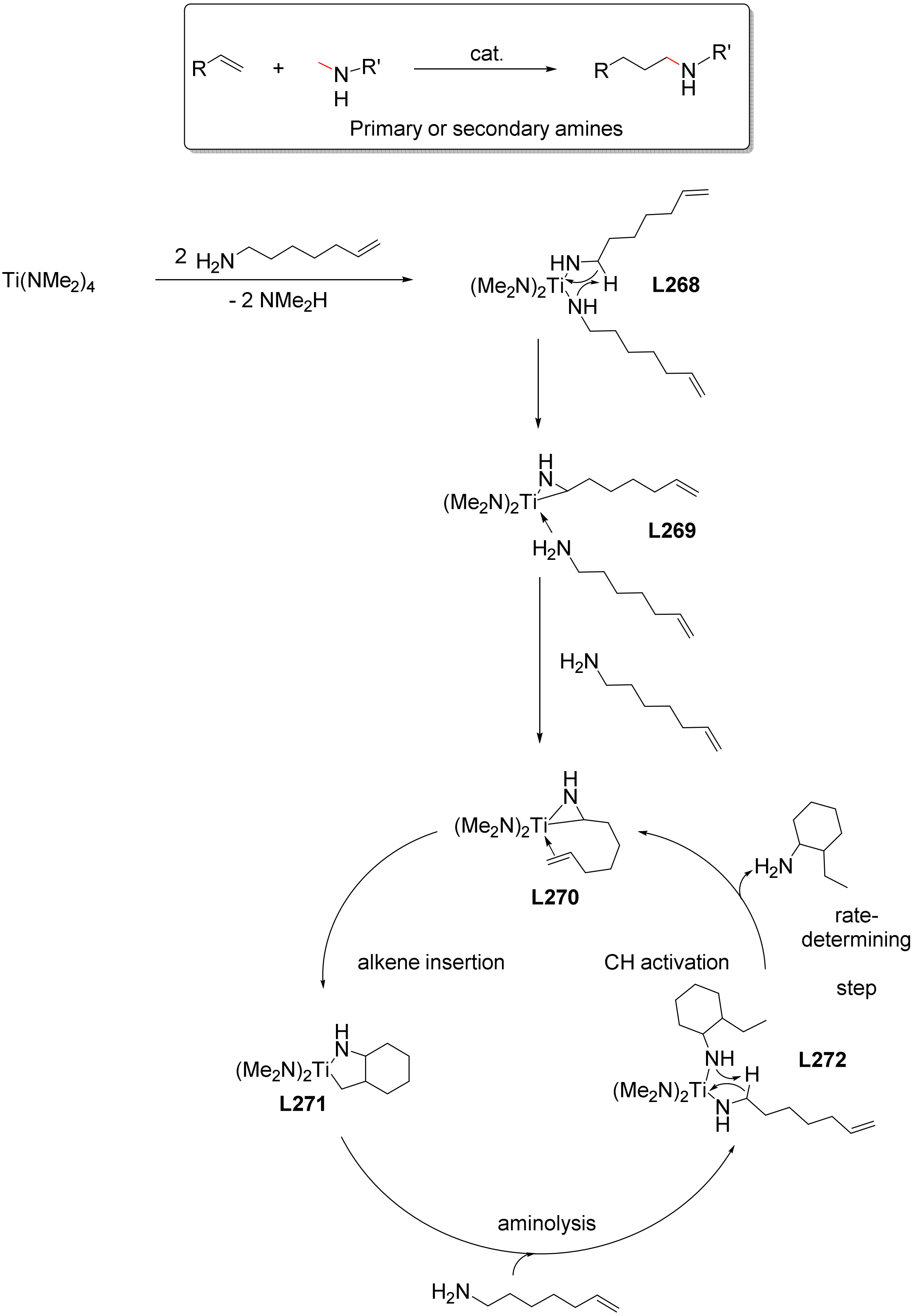
Numerous publications reported the potential of methylamine derivatives to undergo CH activation. The hydroaminoalkylation, first described by Hartwig in 2007 with thallium complexes,[32] enters in this category and was then developed with titanium by Doye. The mechanism of this reaction was investigated by D-labelling NMR spectroscopy experiments.[33]. The mechanism, depicted in Scheme III-23, suggests a rate-determining CH activation step to form **L270**, the active catalyst.

---

[31] Farrell, J. M.; Heiden, Z. M.; Stephan, D. W. *Organometallics.* **2011**, *30*, 4497

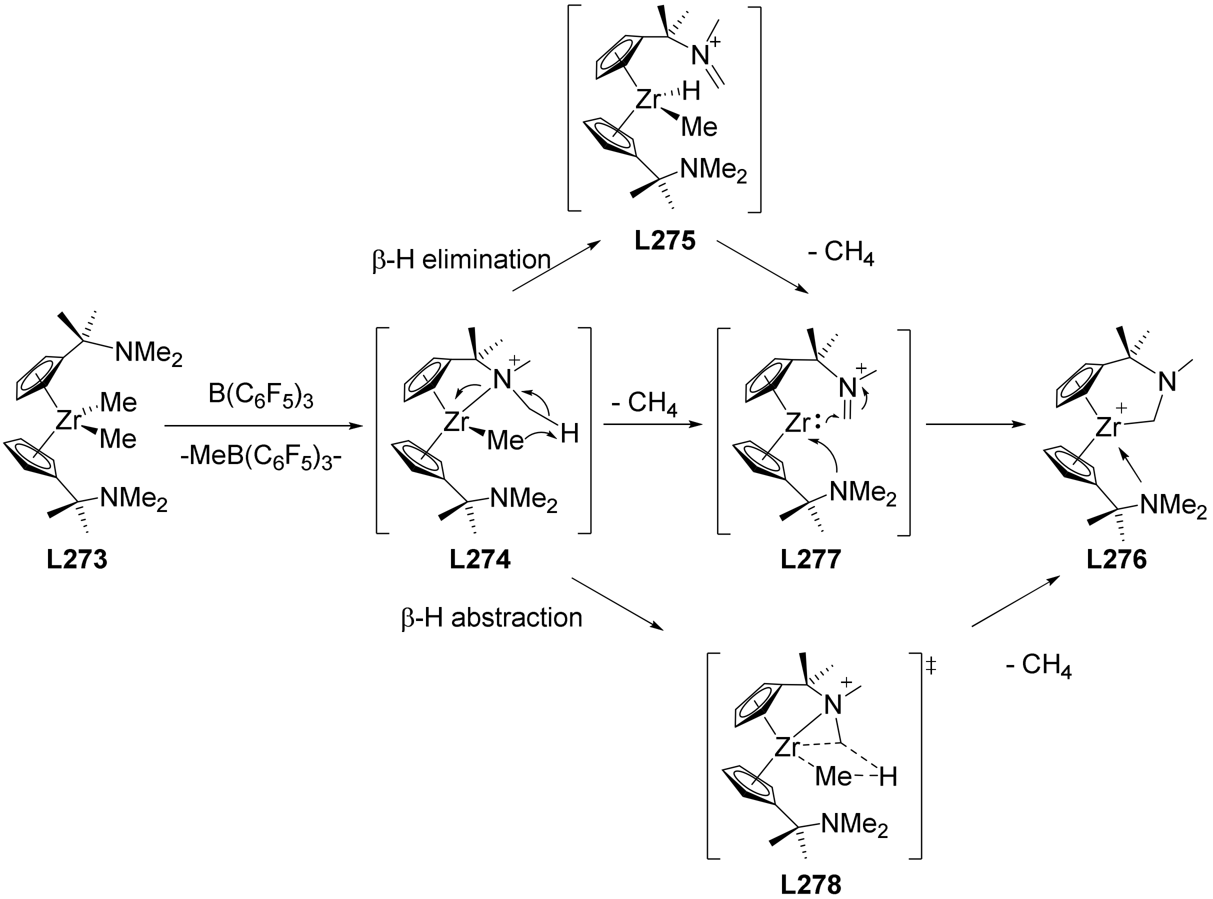
[32] Herzon, S. B.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 6690

[33] Prochnow, I.; Zark, P.; Müller, T.; Doye, S. *Angew. Chem. Int. Ed.* **2011**, *50*, 6401



Scheme III-23: proposed mechanism of Ti-catalysed hydroaminoalkylation

Erker reported CH activation processes in zirconocene complexes containing a pendant NMe_2 moiety.[34,35] Reaction of complex **L273** with $B(C_6F_5)_3$ rapidly yielded compound **L276.** Intermediate **L274**, in which the nitrogen atom coordinates to the zirconocenium cation, was proposed as the key species from which the final product evolved (Scheme III-24). The authors suggested three mechanisms to explain the formation of **L276**: *i/* β-H elimination leading to the species **L275**, followed by reductive elimination of methane, and *ii/* concerted deprotonation of the NMe_2 moiety by the methide ligand. In both cases, intermediate **L277** is formed, in which the metal is in the +II oxidation state. The last proposed mechanism would be a concerted σ-bond metathesis mechanism (β-H abstraction - **L278**) in which Zr remains in the +IV oxidation state.[35]



Scheme III-24: CH activation on a zirconocenyl amine, counter anion omitted for clarity

Krut'ko also observed analogous reactivity on a dichlorozirconocene. In reductive conditions (Mg/Hg) the zirconocene was shown to yield the same type of azametallacycle. In this case, a Zr(II) intermediate was probably involved in CH activation.[36]

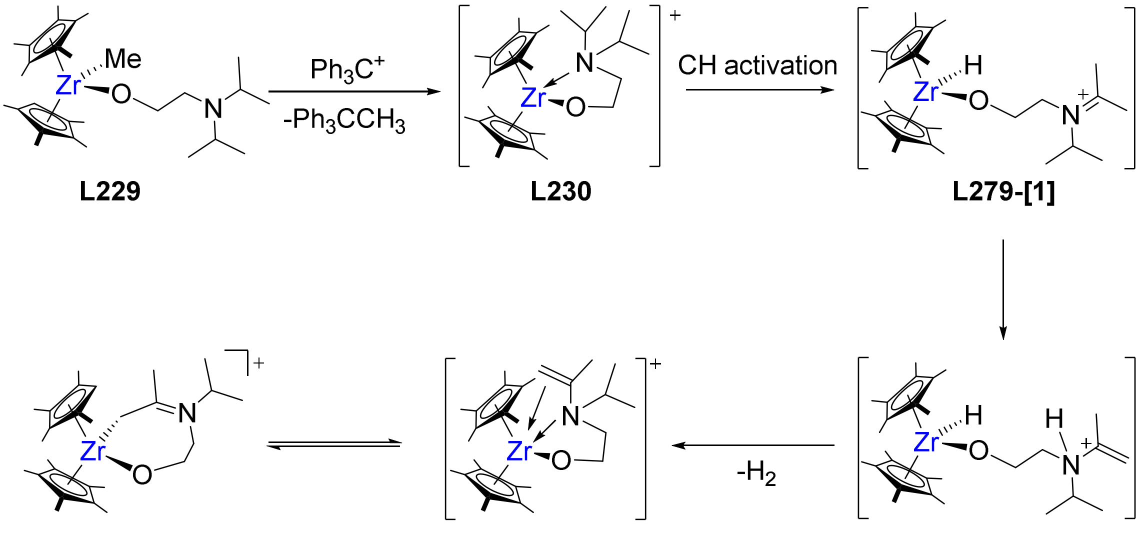
---

[34] Bertuleit, A.; Fritze, C.; Erker, G.; Fröhlich, R. *Organometallics.* **1997**, *16*, 2891

[35] Pflug, J.; Bertuleit, A.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics.* **1999**, *18*, 3818

[36] Krut'ko, D. P.; Borzov, M. V.; Kirsanov, R. S.; Churakov, A. V.; Kuz'mina, L. G. *J. Organomet. Chem.* **2005**, *690*, 3243

The last example of this survey is that of the reaction of complex **L229** with the trityl cation (Scheme III-25). The product of this reaction **L230**, was shown to activate various substratres following typical OmFLP reactivity, as illustrated in the bibliographic introduction (Scheme I-72). However, **L230** has limited stability in solution. When treated in bromobenzene at 60°C for 36h, it underwent β-H elimination to give iminium salt **L279-[1]**. The iminium enaminium tautomerization then yields **L279-[2]**, followed by H_2 loss and double bond isomerisation to give **L280** (identified by X-ray diffraction analysis). Dyson recently reported analogous reactivity in a diisopropylamine-containing ionic liquid. (Scheme I-59).[37]



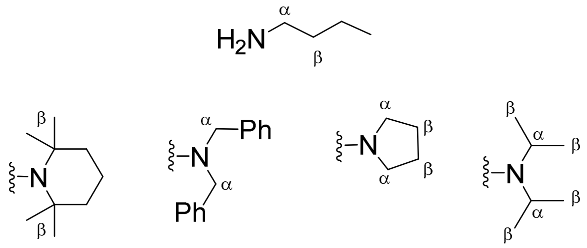
Scheme III-25: formation of azametallacycle L280 by intramolecular CH activation, counter anion omitted for clarity

A well-documented review has already been published by Resconi, discussing other examples not described above. Particular interest was devoted to the choice of methide abstractor and to the problems commonly faced with amine-based abstractors.[1] In the light of these results, CH activation of amines is not a rare occurence. Numerous examples have been reported, especially with tertiary amines. The dimethyl (aminomethyl)titanocenes **32-35** are good candidates for such reactivity, as previously observed for the rearrangement of **35+**. These observations will help the comprehension of the reactivity of **32-34** described in the following section.

---

[37] Perrin, F. G.; Bobbink, F. D.; Păunescu, E.; Fei, Z.; Scopelliti, R.; Laurenczy, G.; Katsyuba, S.; Dyson, P. J. *Inorganica Chim. Acta*. **2018**, *470*, 270

d. CH activation with cationic dimethyl (aminomethyl)titanocenes

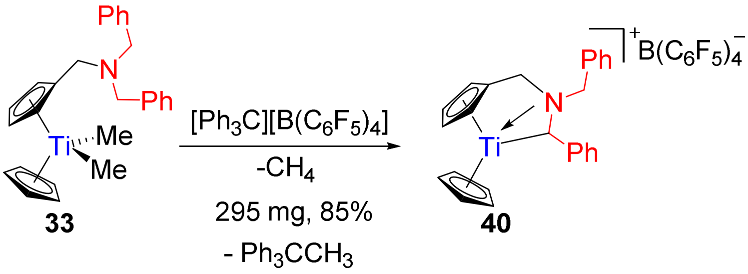


Scheme III-26: nomenclature used with amines

For this section, a general nomenclature will be used, as illustrated in Scheme III-26. The Greek symbols refer to the position of carbon atoms relative to the nitrogen atom (unless explicit noted otherwise). The bridging CH_2 of the titanocenes remained untouched in every reaction where CH activation was observed. As a result, the TMP moiety only possesses β-hydrogens whilst diphenylamine only has α-hydrogens. In the case of pyrrolidine and diisopropylamine, both α- and β-hydrogens are present.

(1) α–H activation

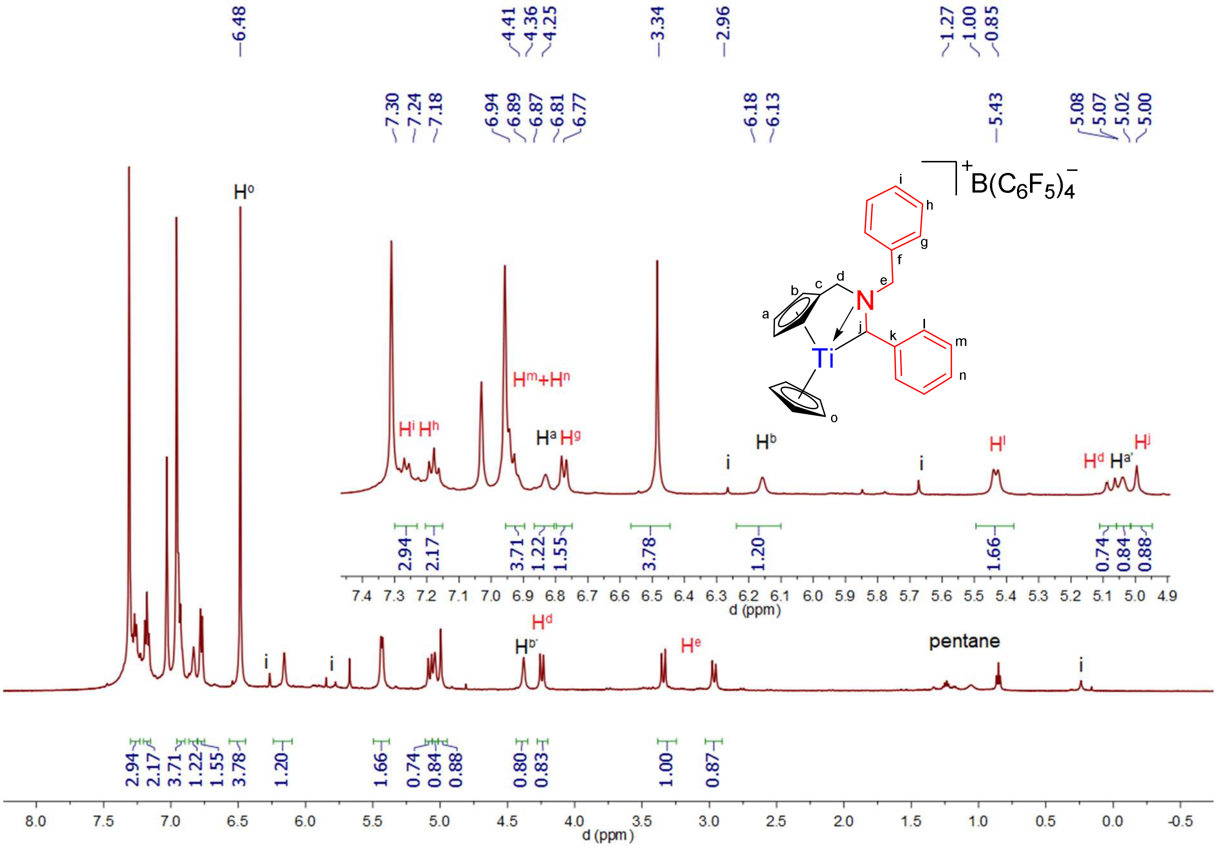
Since the case of TMP led to rearrangement via β-H activation, we were wondering if α-H activation would occur in the case of (dibenzylaminomethyl)titanocene. Indeed, after the formation of the cationic titanocene, gas evolution was observed and a deep green precipitate was obtained, identified as being **40** by spectroscopic analyses (NMR spectroscopy, positive mode ESI HRMS) and elemental analysis (Scheme III-27).



Scheme III-27: CH activation on 33

This compound is composed of 3 chiral centres (Ti, N, C), as a results, two diastereoisomers could have been formed (2 chirality centres, N and Ti are not independent). Nevertheless, according to the ^1H NMR spectrum (Spectrum III-9), only one diastereoisomer is formed. In this spectrum, two sets of signals are observed for the inequivalent phenyl rings (7.30-7.24, 7.18 and 6.77 ppm and 6.94-6.89 and 5.43 ppm respectively). The ^1H NMR spectrum shows several diastereotopic relationships. A set of four multiplets is observed for the monosubstituted Cp ring (6.87-6.81, 6.18-6.13, 5.08-5.02 and 4.41-4.36 ppm), and one singlet for the non-substituted Cp ring. The two remaining CH_2 groups exhibit an AB pattern (5.08 and

4.25 ppm, $^{2}J_{HH}$ = 12.0 Hz for the bridging CH_2, and 3.34 and 2.96 ppm, $^{2}J_{HH}$ = 13.0 Hz, for the benzylic CH_2), whilst a singlet appears at 5.00 ppm corresponding to the new CH group bound to titanium. This latter signal correlated with a shielded carbon signal at 92.3 ppm in the ^{1}H ^{13}C HMQC NMR spectrum, consistent with coordination to titanium.



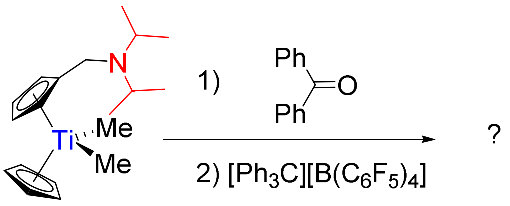
Spectrum III-9: ¹H NMR of 40 (500.03 MHz, 300 K, bromobenzene-d₅). ⁱ: unidentified impurities

The coordination of the nitrogen atom to the titanium can be inferred from the ^{15}N chemical shift observed for **40** compared to the one observed with **33** (-310 ppm, vs -328 ppm). It clearly indicates a change in electronic and / or geometric properties of the N atom, corresponding to the coordination to titanium. The last evidence of formation of this species was given by the HRMS analysis with a cluster of peaks at 386.13870 Da, characteristic of the cation (see experimental part).

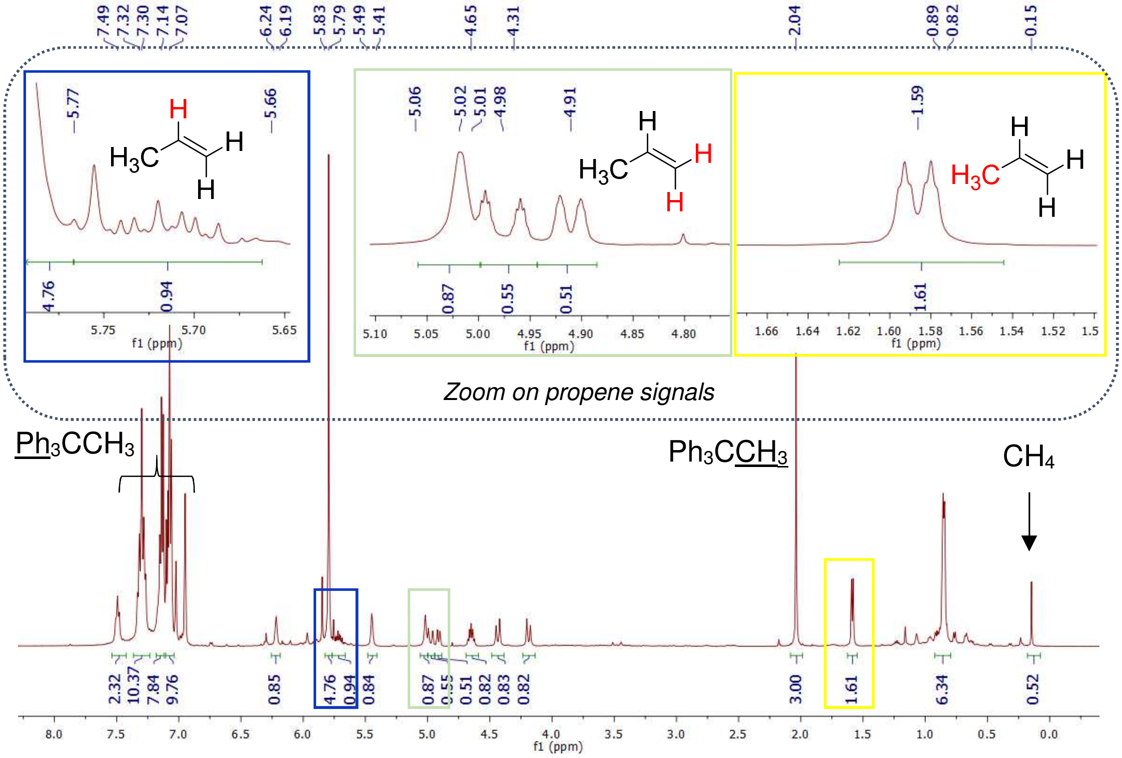
Since both α- and β-CH activations can be observed in two different complexes in which only one type of CH activation can occur, we wondered what kind of CH activation would occur if both α and β hydrogens were present in the amine moiety.

(2) α- and β-H activation

For this purpose, methide abstraction on the pirrolidinyl **32** and the diisopropylaminyl (**34**) dimethyltitanocene was performed with $[Ph_3C][B(C_6F_5)_4]$. Whilst in the case of pyrrolidine (**32**) only decomposition was observed, with the disappearance of any Cp signals in the ^{1}H NMR spectrum, two interesting, albeit complicated reactions occurred with the (diisopropylamino)titanocene **34**. Firstly, when benzophenone was used (in order to trap the potential cationic species generated by methide abstraction from **34** by $[Ph_3C][B(C_6F_5)_4]$), gas evolution was observed. A reaction mixture carried out in a J-Young NMR tube was directly brought to the spectrometer for NMR measurement. The following ^1H NMR spectrum was obtained (Spectrum III-10).

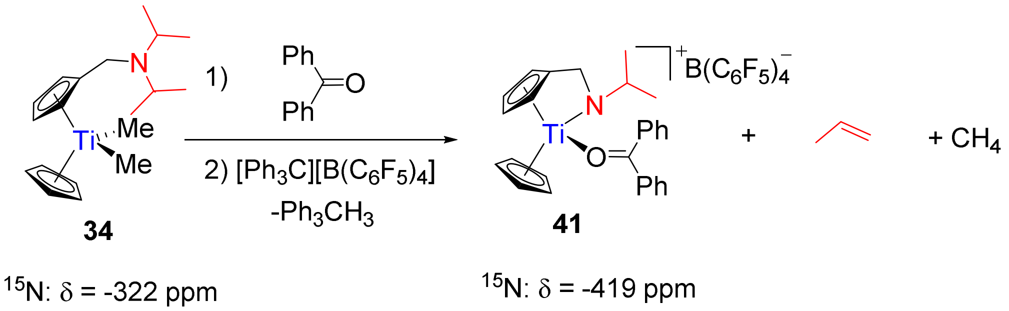


34



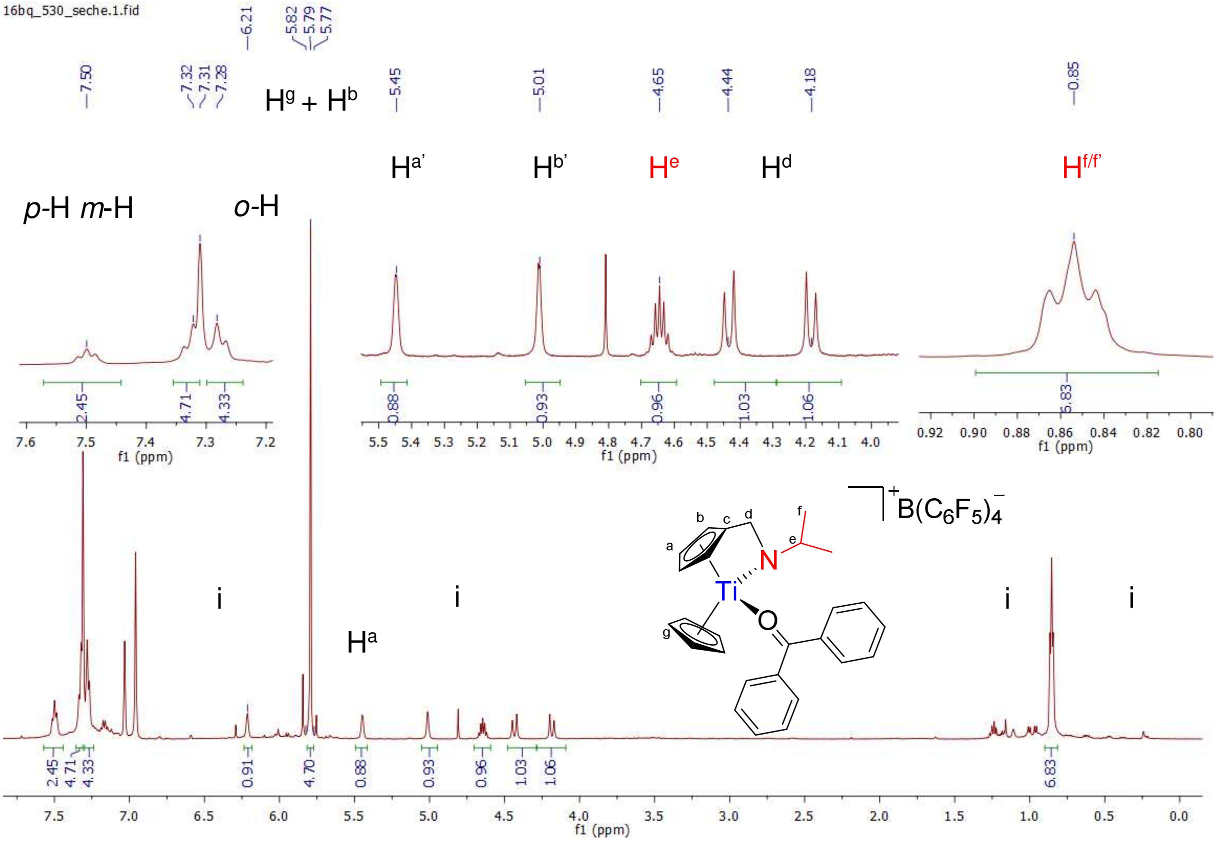
Spectrum III-10: crude ^1H NMR spectrum of the methide abstraction of 34 in presence of benzophenone

Careful analysis of the signals present in the crude ^1H NMR spectrum helped to understand the mechanism involved in this reaction, and as a result, to identify the product formed. Triphenylethane was observed as previously (30H in the aromatic region, signals overlapping with both solvent and benzophenone, and a singlet at 2.04 ppm for the signal of the methyl group). Traces of methane were also observed at 0.14 ppm. Finally, a set of four signals was also present in this spectrum as a multiplet, two doublets of multiplets and an apparent doublet of triplets (5.77-5.66, 4.98, 4.91 and 1.59 ppm respectively), all attributed to propene. Whilst the stoichiometry between the triphenylethane and the new compound seems to be respected according to the integrations of the respective signals, both methane and propene showed smaller integrations, probably because of their volatility. These observations suggest the formation of **41** (Scheme III-28).



Scheme III-28: formation of 41 by β-CH activation

This complex was isolated on a preparative scale, and its identity was unambiguously established by NMR experiments (multinuclear and 2D experiments), positive mode ESI HRMS, elemental and XRD analyses. The ^{1}H NMR spectrum of this compound after workup is presented below.



Spectrum III-11: ^{1}H NMR spectrum of 41 (500.03 MHz, 300 K, bromobenzene-d$_5$). ^{i}: unidentified impurities.

A set of three signals is observed in the aromatic region for the protons of the benzophenone. In this structure, the titanium centre is also chiral; the protons of the monosubstituted Cp ring are diastereotopic, and appear as a set of four apparent quartets (one is overlapping with the signal of the non-substituted Cp ring). The bridging CH_2 resonates at 4.44 and 4.18 ppm with an AB pattern ($^2J_{HH}$ = 15.4 Hz). For the isopropyl group, the CH group shows a heptet at 4.65 ppm, whilst the two methyl groups are diastereotopics and exhibit an apparent triplet at 0.85 ppm (a doublet of doublet was observed on the 600.23 MHz spectrometer). The mass spectrum showed a cluster of peaks at 248.09089 Da corresponding to the [M-benzophenone]$^+$ cation.

The structure was confirmed by X-ray diffraction analysis. The ORTEP view is presented in Figure III-6.

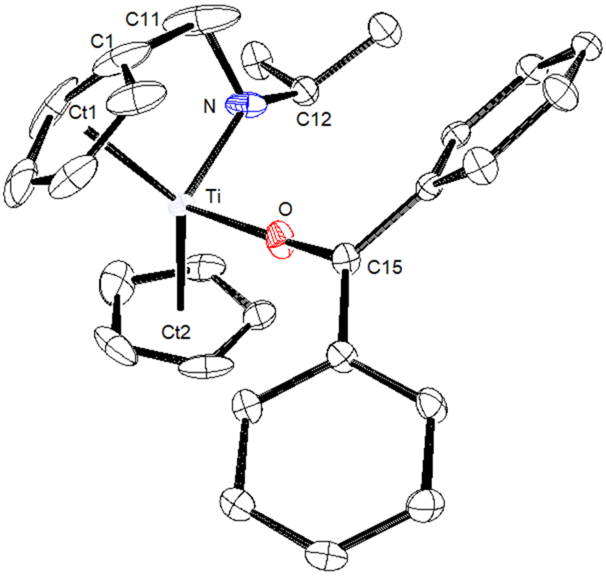
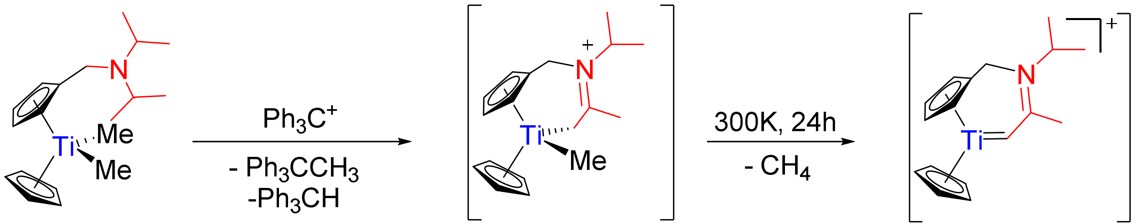


Figure III-6: ORTEP view of 41 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity, enantiomer and counter anion omitted for clarity). Selected bond lengths (Å) and angles(°): Ti-Ct1 = 2.037(2), Ti-Ct2 = 2.040(2), Ti-O = 2.078(2), Ti-N = 1.950(5) / 1.997(13), N-C11 = 1.463(9) / 1.463(15), C1-C11 = 1.593(10) / 1.662(10), Ct1-Ti-Ct2 = 136.09(9), O-Ti-N = 99.80(18) / 103.8(4), C1-C11-N = 101.6(5) / 101.6(8), C11-N-C12 = 113.7(5) / 115.7(10), C11-N-Ti = 104.3(5) / 103.9(8), C12-N-Ti = 140.6(5) / 140.0(9), Ti-O-C15 = 177.6(2).

The titanocene adopts a bent geometry, with a short Ti-N bond (1.950(5) / 1.997(13) Å). In both enantiomers, the nitrogen atom is planar ($\Sigma\alpha(N)$ = 358.6(2)° / 359.6(9)°). In addition, for this complex, Ti, O and C15 are almost aligned (Ti-O-C15 = 177.6(2)°).

In the absence of benzophenone, the reaction of **34** with $[Ph_3C][B(C_6F_5)_4]$ led to a completely different outcome. The formation of triphenylethane and methane was observed as previously, but triphenylmethane also appeared in the ^{1}H and ^{13}C NMR spectra. Besides these organic products, complex **43** was observed after ca 24h of reaction, whilst complex **42** was present initially (Scheme III-29). Interestingly, at no point during the reaction could we observe a well-defined stoichiometric ratio between organic and Ti-containing species. This is due to the parallel formation of paramagnetic Ti(III) species, which further complicates the analysis of reaction mixtures (*vide infra*). Although **42** and **43** are both unstable (all attempts at isolating them failed), we could characterize them *in situ* by NMR spectroscopy at 258 and 273 K, respectively. Complex **42** shows the common characteristics of a chiral titanium centre, with a set of four multiplets for the substituted Cp ring (6.66, 5.25, 5.02 and 4.97 ppm), an AB pattern for the signal of the bridging CH_2 (4.12 and 3.27 ppm, $^2J_{HH}$ = 15.0 Hz), and two doublets at 1.09 and 0.85 ppm for the two inequivalent methyl groups of the isopropyl moiety. Surprisingly, the methylene group bound to titanium resonates as a pronounced AB pattern (2.64, -0.86 ppm) was observed with no evaluable coupling constant, but a characteristic correlation for the same carbon atom in the ^1H ^{13}C HMQC NMR spectrum (δ ^{13}C = 67.8 ppm). In the ^1H NMR spectrum, the formation of **43** is accompanied by a loss of diastereotopic relationships previously observed for **42**. Indeed, only two broad signals are found for the substituted Cp ring (5.48-5.43 and 4.81-4.73 ppm), the bridging CH_2 signal resonates as a singlet at 3.76 ppm, and both methyl groups from the isopropyl moiety resonate as a doublet at 1.00 ppm. The loss of the pronounced AB pattern for the methylenic group boud to titanium for **42** is accompanied by the appearance of a new downfield-shifted signal at 11.44 ppm consistent with a carbenic signal for **43** (for more details, see experimental part and appendix). Besides, the ^{15}N chemical shift is notably modified during the process, as illustrated in Scheme III-29.



34 **42** **43**

^{15}N: δ = -322 ppm

^{15}N: δ = -197 ppm

^{15}N: δ = -242 ppm
δ Ti=CH: ^1H = 11.44 ppm
^{13}C: 266.2 ppm

Scheme III-29: *in situ* formation of 42 and 43 (counteranion omitted for clarity)

Titanium carbene complexes have previously been reported in the literature. These compounds are rarely stable, and often used directly as catalysts (e.g. ring opening metathesis polymerization of diene),[38] or stabilized with a phosphine for characterization purpose.[39] An interesting review was published on these species in 2001.[40] In addition to these reports, one can cite the studies published by Mindiola in the past six years (Scheme III-30).[41,42,43] All of these carbenes were characterized by ^1H and ^{13}C NMR spectroscopy (Table III-1).

Chemical shift	**L281**[a]	**L282**[a]	**L283**	**43**[c]	**L284**[d]	**L285**[c]
^1H: δ (ppm)	8.30	14.20	11.82[a]	11.44	-	-

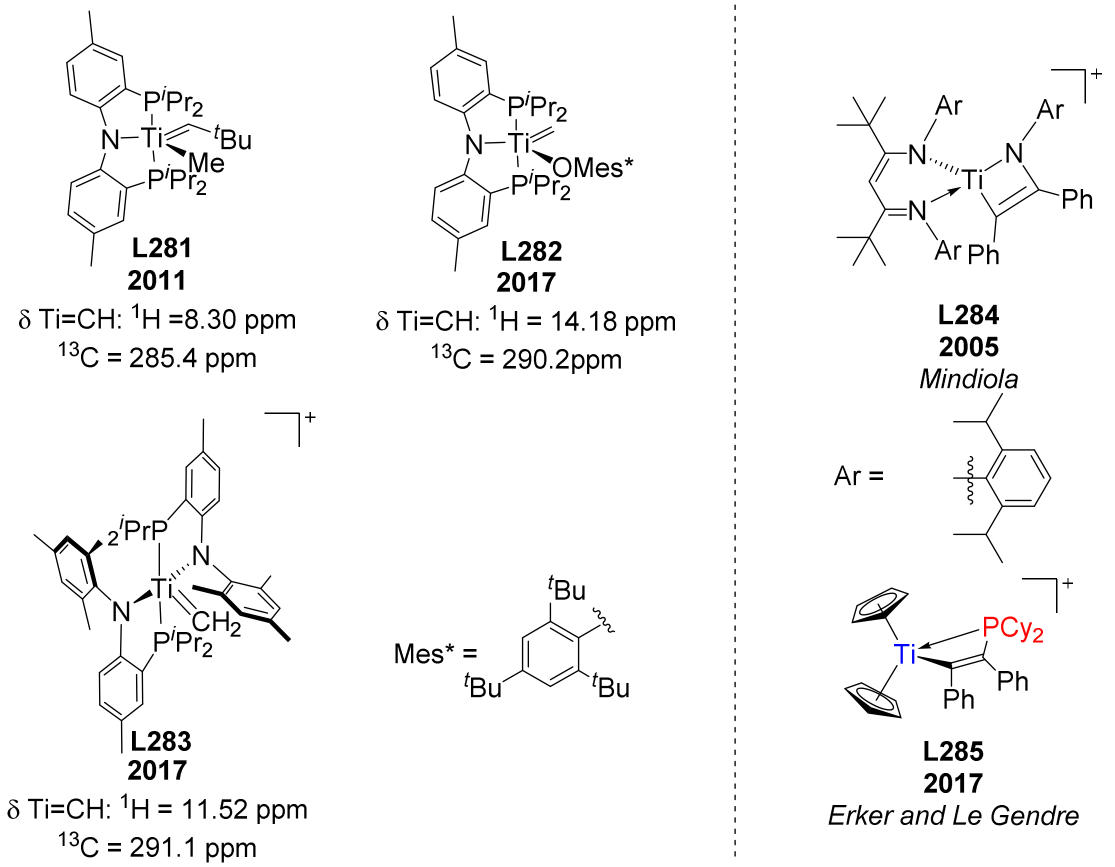
---

[38] Qian, Y.; Zhang, D.; Huang, J.; Ma, H.; Chan, A. S. C. *J. Mol. Catal. Chem.* **1998**, *133*, 135
[39] Meinhart, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics*. **1989**, *8*, 583
[40] Beckhaus, R.; Santamaría, C. *J. Organomet. Chem.* **2001**, *617–618*, 81
[41] Flores, J. A.; Cavaliere, V. N.; Buck, D.; Pintér, B.; Chen, G.; Crestani, M. G.; Baik, M.-H.; Mindiola, D. J. *Chem. Sci.* **2011**, *2*, 1457
[42] Grant, L. N.; Ahn, S.; Manor, B. C.; Baik, M.-H.; Mindiola, D. J. *Chem. Commun.* **2017**, *53*, 3415
[43] Kurogi, T.; Carroll, P. J.; Mindiola, D. J. *Chem. Commun.* **2017**, *53*, 3412

$^{13}C\{^1H\}$: δ (ppm)	285.4	290.3	291.1[b]	266.2	254.3	220.6

Table III-1: selected chemical shifts of carbenic or vinylic titanium complexes.[a]C_6D_6, [b]toluene-d_8, [c]C_6D_5Br, [d]CD_2Cl_2

The carbene CH reported by Mindiola, resonates between 8.30 and 14.18 ppm in the ^1H NMR spectrum depending on the carbon substituent, whilst the metal-bound carbon itself resonates between 285.4 and 291.1 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The ^1H NMR chemical shift of CH bound to titanium in **43** is consistent with those observed for carbenic species. However, the ^{13}C NMR chemical shift observed for **43** is relatively more upfield shifted compared to those of the carbenic titanium complexes described by Mindiola (Scheme III-30).



L281
2011
δ Ti=CH: ^1H =8.30 ppm
^{13}C = 285.4 ppm

L282
2017
δ Ti=CH: ^1H = 14.18 ppm
^{13}C = 290.2ppm

L284
2005
Mindiola

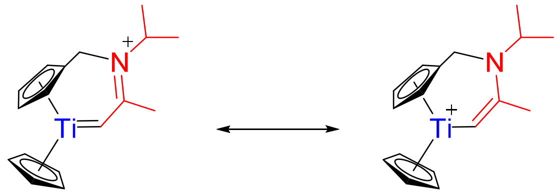
L283
2017
δ Ti=CH: ^1H = 11.52 ppm
^{13}C = 291.1 ppm

L285
2017
Erker and Le Gendre

Mindiola

Scheme III-30: carbenic and vinylic titanocenium. Counter anion omitted for clarity

Interestingly, **43** can be considered as two resonance forms; the carbenic form **A**, and the vinylic form **B**.

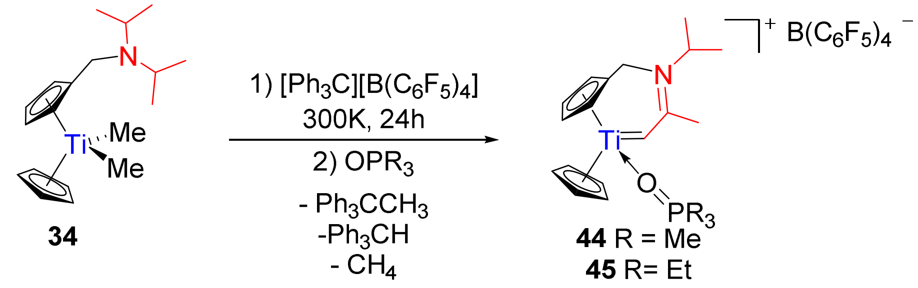


43-A **43-B**

Scheme III-31: the two limit forms of 43

Mindiola also reported a Ti-vinyl complex **L284**, the NMR spectroscopic signatures of which also appear in Table III-1. Additionnaly, we include the data for compound **L285,** a *bona fide* vinylic complex prepared by Dr. A. Normand.[44] The ^{13}C NMR chemical shift of **43** is relatively close to the one of the vinylic titanium complex **L284** reported by Mindiola but remains relatively dowfield-shifted compared to the one of **L285** ($\Delta\delta$ = 46 ppm). Therefore, it is difficult on the basis of the NMR spectroscopic evidence to ascribe form **A** or **B** to **43** with confidence. However, its reactivity is less ambiguous: metallacyclobutane formation, typical of Schrock carbenes, is observed upon reaction with olefins (*vide infra*), thus giving more credit to the carbenic form.

In order to obtain X-ray quality crystals of **43**, the reaction mixtures containing this complex were quenched with phosphine oxide $OPMe_3$ and $OPEt_3$. Two new species (**44** and **45**) were observed (Scheme III-32), which are more conducive to isolation. Nevertheless, they showed poor stability in dichloromethane, and consequently, isolated material always contained a large amount of bromo- or chlorobenzene.



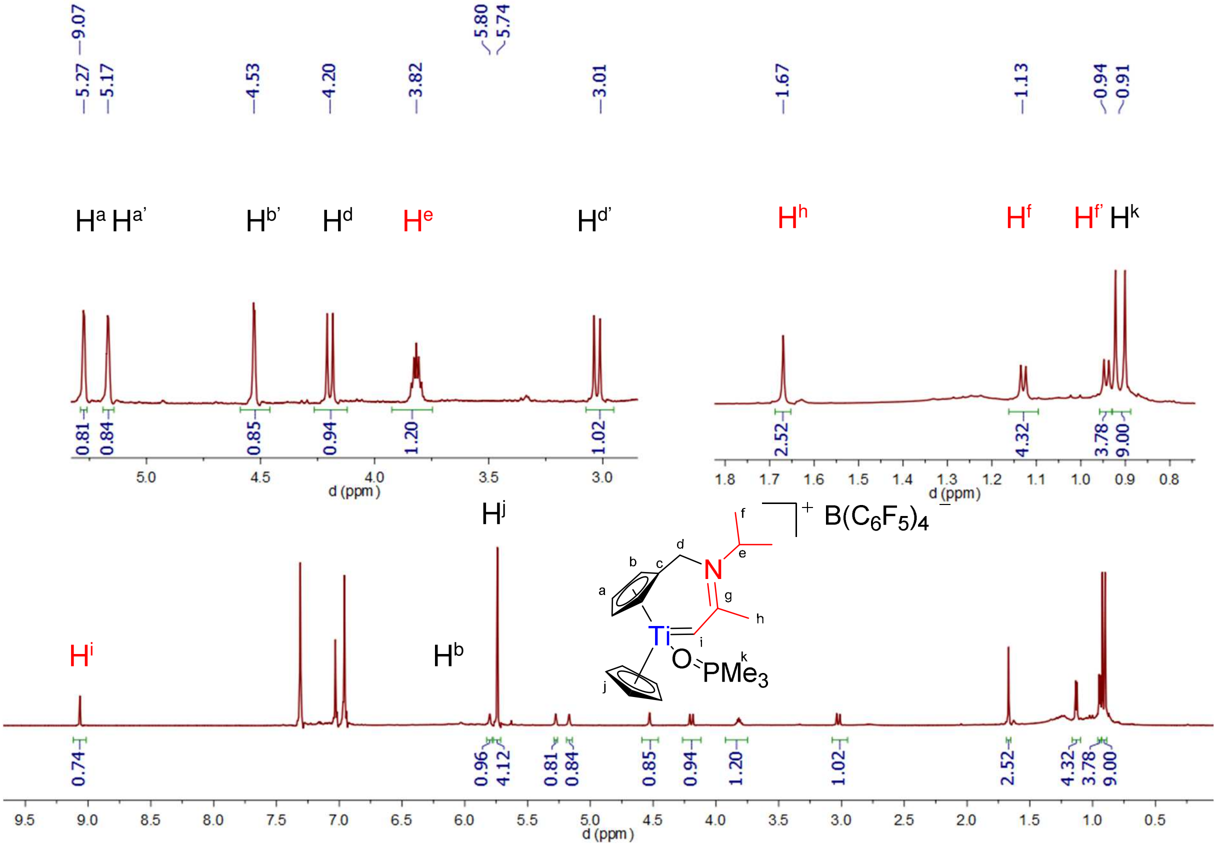
^{15}N: δ = -322 ppm ^{15}N: δ = -268 ppm

Scheme III-32: synthesis of new stabilized Ti-carbenes

In the ^{1}H NMR spectrum of **44** (Spectrum III-12), the first downfield signal at 9.07 ppm corresponds to the carbenic CH (vs 11.44 ppm in **43**). The signal of the non-substituted Cp ring appears as a singlet at 5.80 ppm, whilst the chirality of the titanium centre entails diasterotopic relationships between the signals of the monosubstituted Cp ring, with four apparent quartets (5.80, 5.27, 5.17 and 4.53 ppm).The signal of the bridging CH_2 exhibits a noteworthy AB pattern (4.20, 3.01 ppm $^{2}J_{HH}$ = 15.0 Hz). Then, only one isopropyl group is observed with a set of three signals due to the diastereotopy of the methyl groups showing an heptet and two doublets (3.82, 0.94 and 0.91 ppm respectively). Finally, a singlet (1.67 ppm) is observed for the isolated methyl group bound to the iminium carbon atom, whilst a doublet is found at 0.91 ppm for the three equivalents methyl groups bound to the phosphorus atom. Furthermore, the ^{1}H ^{13}C HMQC NMR spectrum shows a correlation between the signal at 9.70 ppm in the ^{1}H NMR spectrum with the signal of a CH carbon at δ = 221.9 ppm, consistent with a titanium-bound carbon atom.

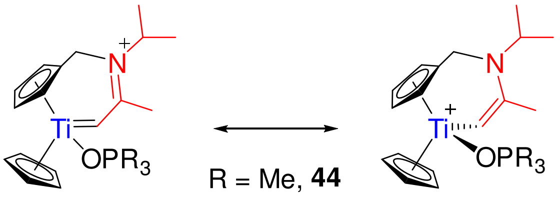
---

[44] Manuscript in preparation



Spectrum III-12: ^{1}H NMR of 44 (600.23 MHz, 300 K, bromobenzene-d_5)

The ^{15}N chemical shift was slightly downfield compared to the one observed for the free carbene (-268 vs -242 ppm). The large upfield shift of the ^{1}H and ^{13}C NMR signals of the Ti=CH moiety (^{1}H: $\Delta\delta = 2.4$ ppm, ^{13}C: $\Delta\delta = 44.3$ ppm) raises again the question of the appropriate resonance form of this compound (Scheme III-33).



44 or 45-A **44 or 45-B**

Scheme III-33: resonance forms of 44

Finally, the high-resolution ESI-MS spectrum of **44** showed a cluster of peaks corresponding to the cationic part at 380.16175 Da along with an H_2O-addition product at 388.17229 Da.

Suitable crystals for X-ray diffraction were obtained by diffusion of heptane into a bromobenzene solution of **45** (Figure III-7). Surprisingly, the structure obtained was not the one expected on the basis of NMR spectroscopic analysis. Indeed, as illustrated in the ORTEP view of the brown crystals obtained, a Ti(III)-alkyl compound was obtained instead (**46-OPEt$_3$**).

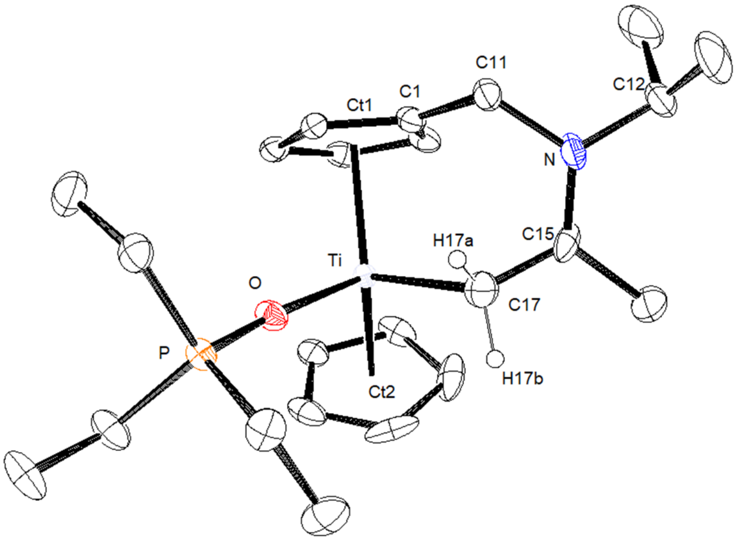
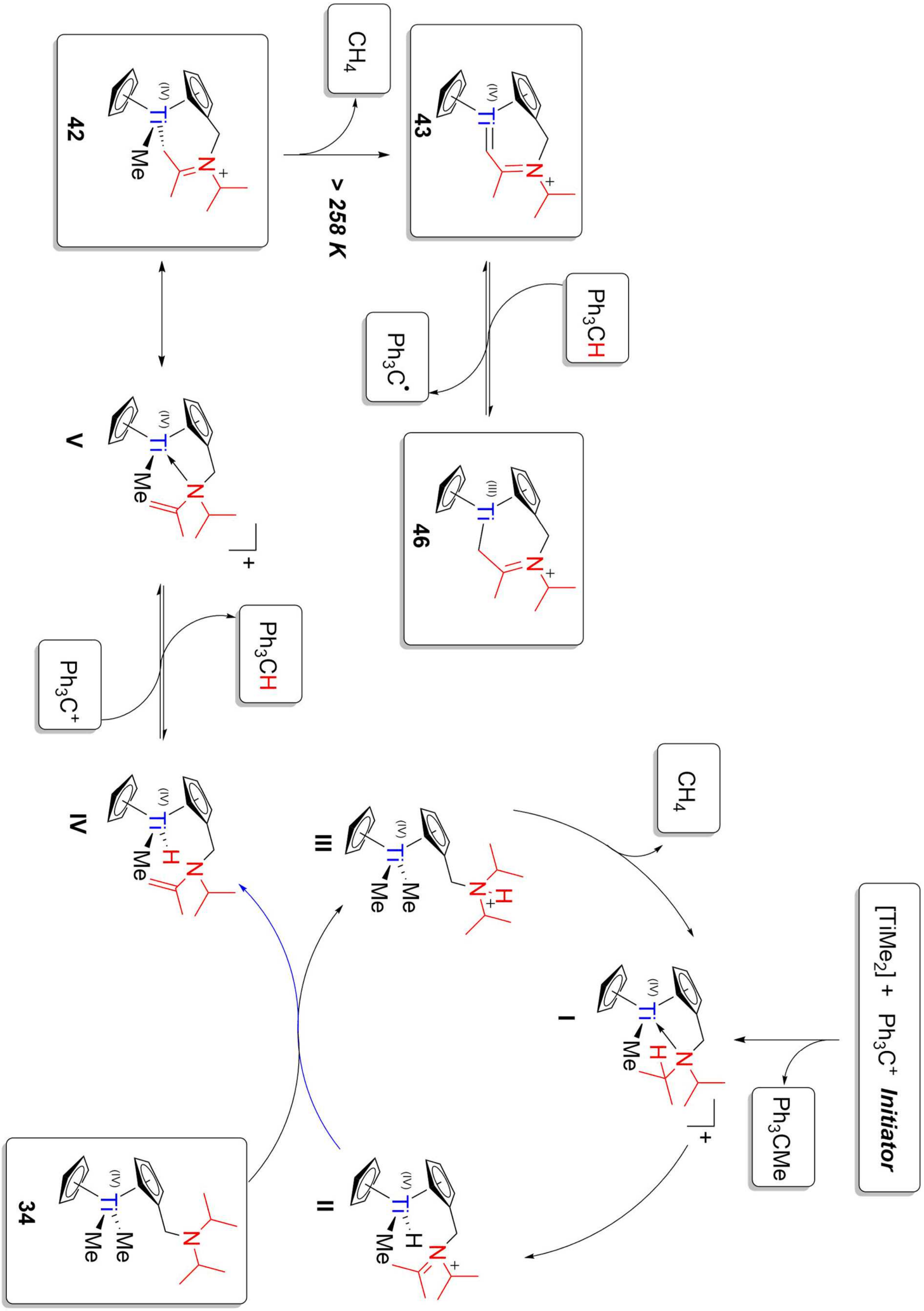


Figure III-7: ORTEP view of 46 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed for clarity except Ha and Hb, enantiomer and counter anion omitted for clarity). Selected bond lengths (Å) and angles(°): Ti-Ct1 = 2.0612(14), Ti-Ct2 = 2.0661(17), Ti-O = 2.106(2), Ti-C17 = 2.419(3), C1-C11 = 1.503(4), C11-N = 1.470(4), N-C15 = 1.291(4), Ct1-Ti-Ct2 = 133.91(7), O-Ti-C17 = 81.00(11), O-Ti-C17 = 81.00(11), C1-C11-N = 110.8(2), P-O-Ti = 175.71, C11-N-C15 = 117.3(3), C11-N-C12 = 117.7(3), C12-N-C15 = 124.8(3).

In accordance with this formulation, the Ti-C bond is relatively long (2.419(3) Å). On the other hand, a short distance is observed for N-C15 (1.291(4) Å vs 1.470(4) Å for N-C11), along with a trigonal-planar nitrogen atom (Σα(N) = 354.8(5)°), consistent with iminium formulation.

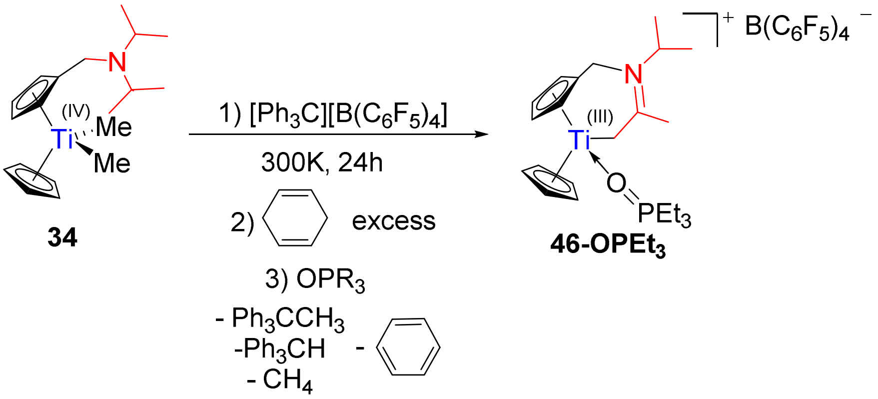
Since the presence of paramagnetic Ti(III) species could realistically be envisaged, NMR spectroscopic titration of these mixtures was performed (using tetramethylsilane as a standard). In fact, **44** and **45** only represent about 45% of the total amount of Ti introduced in the tube. The formation of **43** was also followed by EPR spectroscopy, and several paramagnetic species were observed (see appendix for details). The formation of these species explains the presence of unidentified broad signals in some of the ^{1}H NMR spectra recorded during the formation of **43**. It also explains the non-trivial stoichiometry between organic and Ti-containing species. Noteworthy, the presence of the trityl radical was observed during the late stages of the formation of **43**. The reaction sequence depicted below is an attempt at rationalizing the gathered spectroscopic and crystallographic evidence.



Scheme III-34: proposed mechanism of formation for 43, counter anion omitted for clarity

According to this mechanism, methide abstraction yields amine-coordinated methyltitanocenium intermediate **I** and triphenylethane. This reaction initiates the autocatalytic decomposition of **34**: intramolecular hydride abstraction of the α-H atom in **I** yields iminium salt **II**, which is deprotonated by **34** to give enamine complex **IV**. Ammonium salt **III** is also generated and converted into methane and intermediate **I**, thus closing the autocatalytic cycle. Intermediate **IV** competes with Ph_3C^+ for hydride abstraction, giving triphenylmethane and complex **V**. The iminium form of **V** is the observed species **42**, which undergoes methane extrusion to yield carbene **43**. This complex is then subject to decomposition, e.g. $H^\bullet$ abstraction from triphenylmethane to generate **46** and the trityl radical.

A consequence of this mechanism is that the presence of an excess of $H^\bullet$ donor should promote the formation of **46** by displacing the Ti(IV) carbene / Ti(III) alkyl equilibrium towards the right. Indeed, reacting **34** with $[Ph_3C][B(C_6F_5)_4]$ in the presence of an excess of cyclohexa-1,4-diene completely suppressed the formation of **43** and trityl radical (Scheme III-35). On the other hand, a signal at g = 1.9858 was observed by EPR spectroscopy (see appendix for details). Addition of $OPEt_3$ to the reaction mixture followed by workup afforded a new complex, which was characterized by EPR spectroscopy. Crystallization of the batch thus obtained yielded crystals with identical cell parameters as **46-OPEt₃**,[45] therefore we conclude that both compounds are identical and that **46** originates from reaction of **43** from an $H^\bullet$ donor.



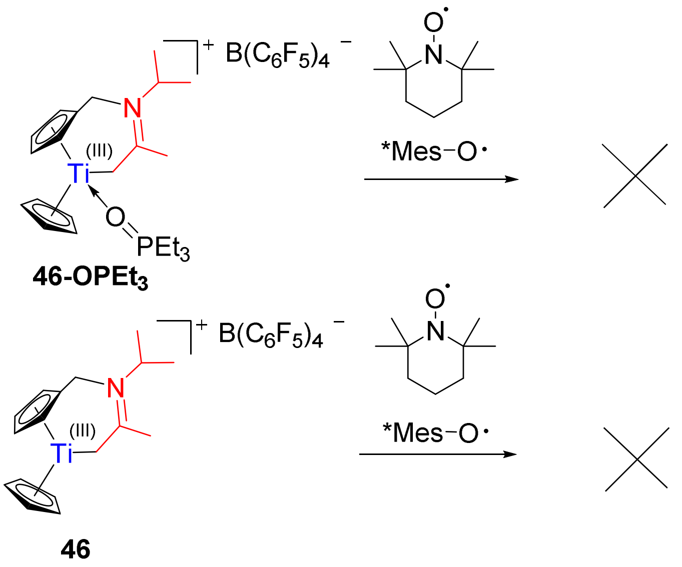
Scheme III-35: preparative scale synthesis of 46-OPEt₃

In the light of these findings, we also tried to prepare **45** and **43** from **46-OPEt₃** and (freshly generated) **46**, respectively but to no avail (Scheme III-36).

As mentioned above, the formulation of **43** as a Ti-carbene species rather than a titanocenium enamine cannot be grounded in spectroscopic evidence. In order to highlight the carbenic character of this compound, we reacted **34** with $[Ph_3C][B(C_6F_5)_4]$ in the presence of 3 eq of 3,3-dimethylbut-1-ene in the hope of generating a titanacyclobutane complex as illustrated in Scheme III-37.

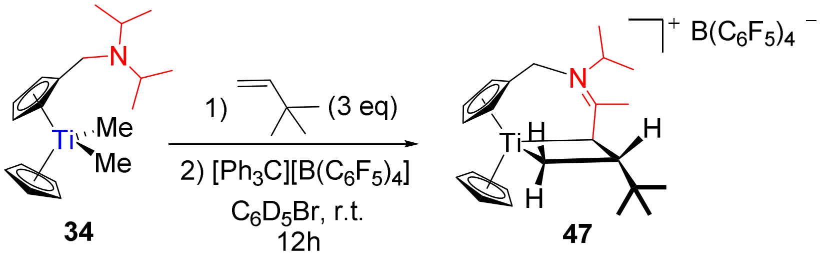
---

[45] Other crystals formed as well, which could be due to hydrolysis, or other decomposition reactions which commonly occur with Ti(III) species.



Scheme III-36: H· abstraction attempts

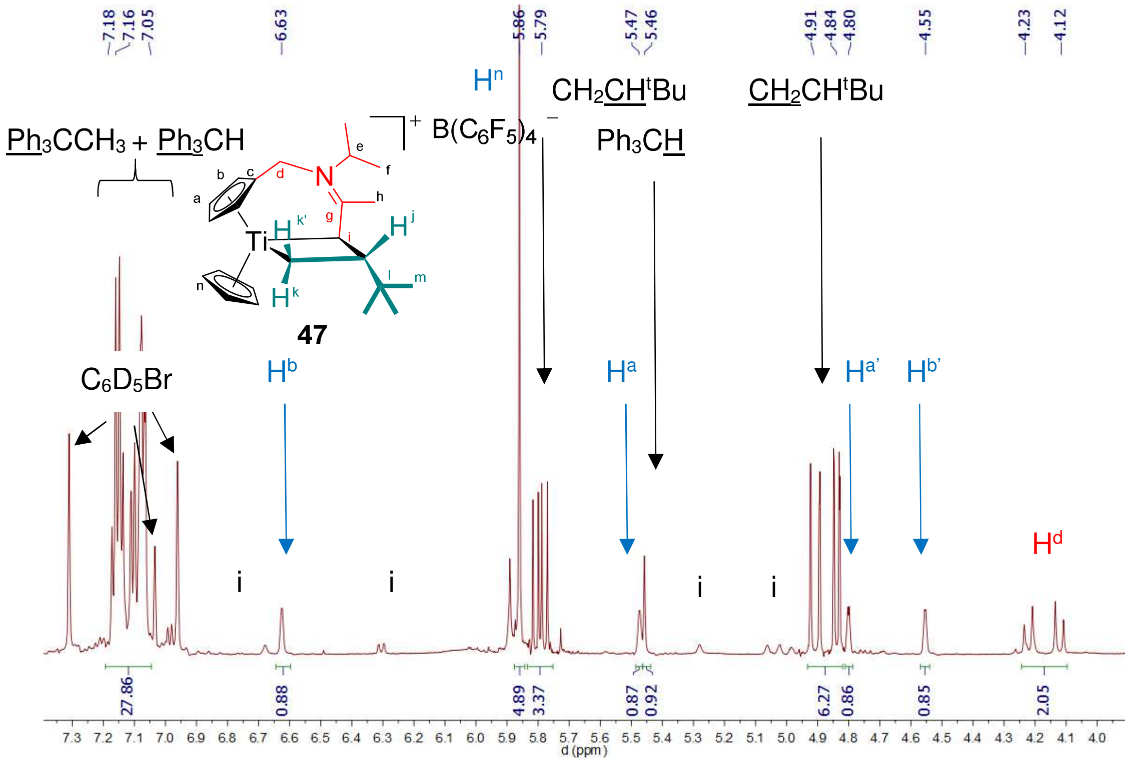
Indeed, the expected metallacycle **47** was observed and characterized spectroscopically.



Scheme III-37: formation of a Ti-metallacyclobutane complex

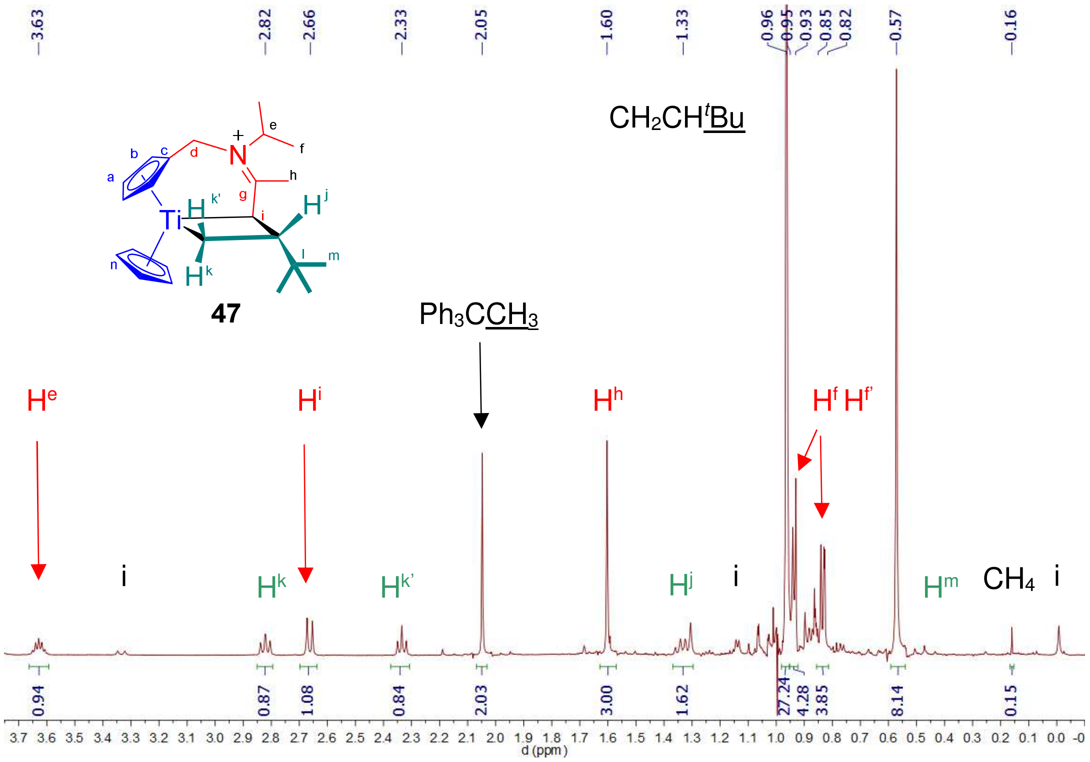
The first feature of the ^{1}H NMR spectrum, is the absence of a carbenic signal in the highfield region. According to 2D NMR experiments, all signals were assigned to **47** and the side products formed during the reaction. Four products were observed: triphenylethane (aromatic region and a singlet at 2.05 ppm), triphenylmethane (aromatic region and a singlet at 5.46 ppm), methane (s, 0.16 ppm) and excess 3-3-dimethylbut-1-ene, with three doublet of doublets and one singlet in a 1: 1: 1: 3 ratio (5.79, 4.91, 4.88 and 0.96 ppm respectively). Only one titanocene species is observed, exhibiting chirality as evidenced by the four apparent quartets observed for the monosubstituted Cp ring (6.63, 5.47, 4.80 and 4.55 ppm). A singlet is observed at 5.86 ppm for the non-substituted Cp ring. Diastereotopy is also observed at both the bridging CH_2 and the methyl groups of the isopropyl moeity; exhibiting an AB pattern at 4.23 and 4.12 ppm ($^2J_{HH}$ = 15.5 Hz), and two multiplets respectively (0.93-0.95 and 0.85-0.82). The methylene group of the isopropyl moiety shows an expected heptet at 3.63 ppm and the methyl group bound to the iminium shows a singlet at 1.60 ppm. The metallacycle exhibits a specific set of four signals: two triplets for the protons bound to C^k, a doublet for H^i and a quartet for H^j all in a 1: 1: 1: 1 ratio (2.82, 2.33, 2.66 and 1.33 ppm respectively).

The comparison of the signals observed in the $^{13}C\{^{1}H\}$ NMR spectrum for the carbon atom involved in the metallacyclobutane with those of the starting diene (C^{k} = 77.1 ppm and C^{l} = 36.4 ppm vs CH_2^{diene} = 149.6 ppm and CH^{diene} = 109.5 ppm) provides further evidence for **47**. In addition, the carbenic CH (C^{i} = 266.2 ppm for **43**) appears at 82.5 ppm in the newly formed metallacycle. These combined data are in agreement with the formation of a metallacyclobutane, according to the values observed in the literature.[39]

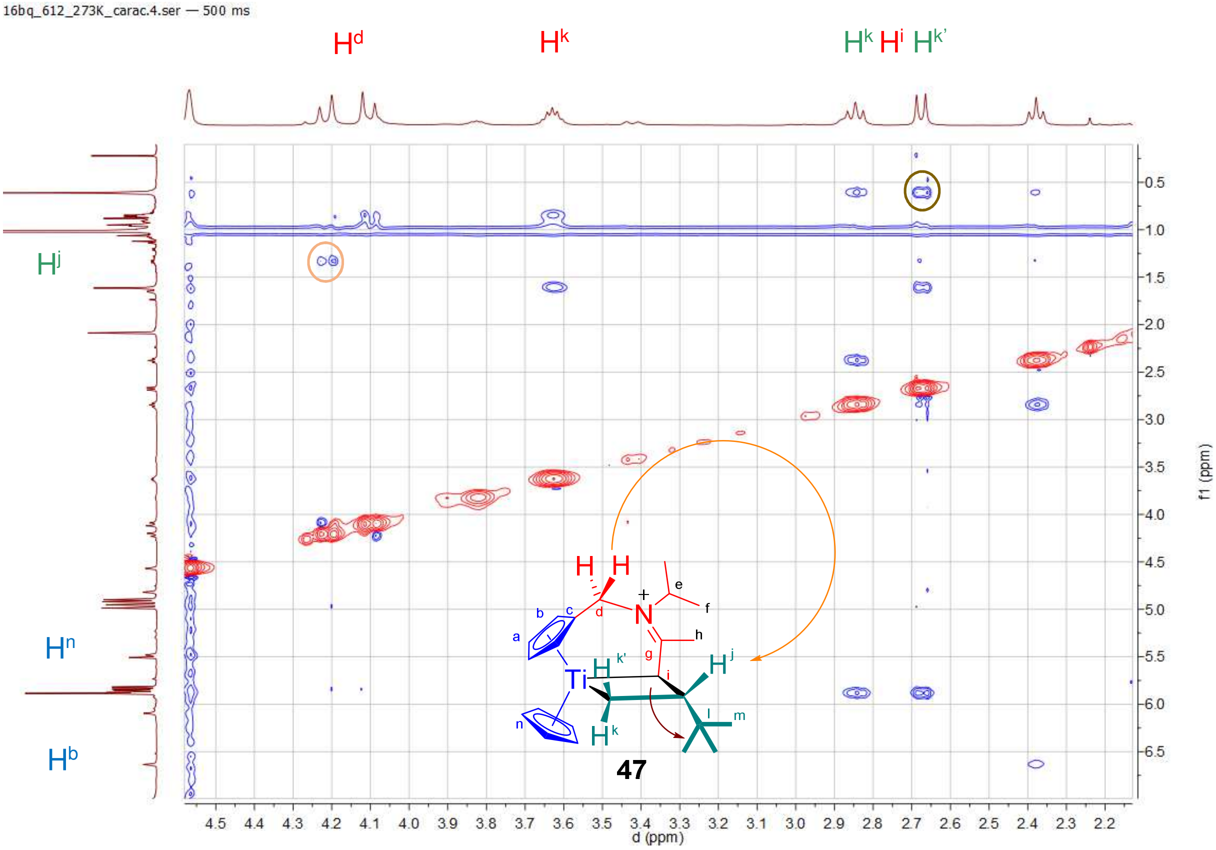


Spectrum III-13: ^{1}H NMR of 47 [7.5-3.9 ppm] (600.23 MHz, 300 K, bromobenzene-d_5). ^{i}: unidentified impurities

In the present case, the activation of the diene is regioselective, probably due to the steric hindrance of the tert-butyl group. Nevertheless, two diastereoisomers (*cis* / *trans)* would have been expected with this reaction, depending on which faces of 3,3-dimethylbutene and carbene react with each other preferentially. However, only one titanocene was observed by NMR spectroscopy, meaning that only one set of enantiomers was formed. A NOESY experiment was realised, to determine the relative position of the hydrogen atoms along the metallacyclobutane. With the two correlations described on the following Spectrum III-15, between H^{d} and H^{j} on the one hand, and H^{i} and ^{t}Bu on the other hand, the selective formation of **47**.

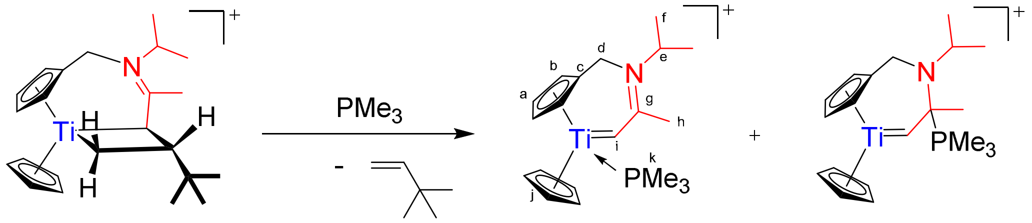


Spectrum III-14: ^{1}H NMR of 47 [3.9-0.0 ppm] (600.23 MHz, 300 K, bromobenzene-d_5)



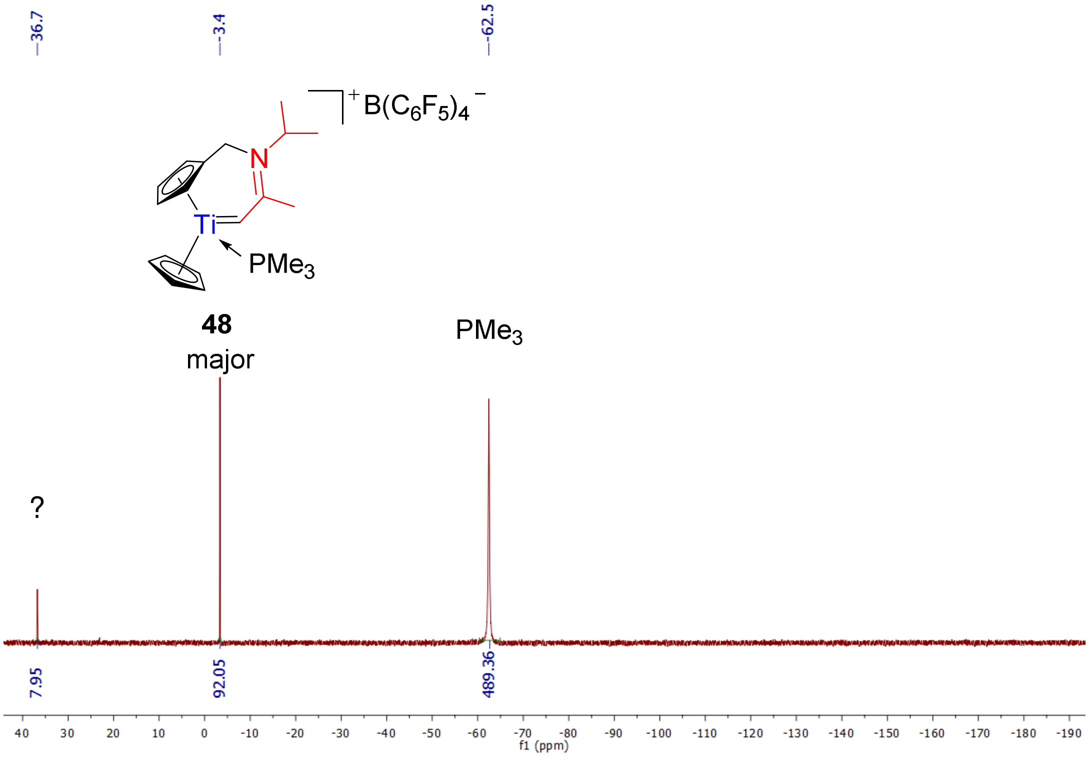
Spectrum III-15: ^{1}H ^{1}H NOESY of 47 (600.23 MHz, 273 K, bromobenzene-d_5)

Since attempts at isolating **47** failed, we surmised that this compound might be in equilibrium with the free alkene and carbene **43.** Others have successfully highlighted similar equilibria by adding PMe_3 to titanacyclobutanes.[39] Indeed, when PMe_3 was added to a mixture of **47** and 3,3-dimethylbut-1-ene, analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy indicated the presence of two species in addition to excess PMe_3 (Spectrum III-16). A possible explanation for this observation would be the nucleophilic addition of PMe_3 to the iminium moiety (signal at 36.7 ppm), besides the expected formation of a PMe_3-stabilized carbene species Scheme III-38.



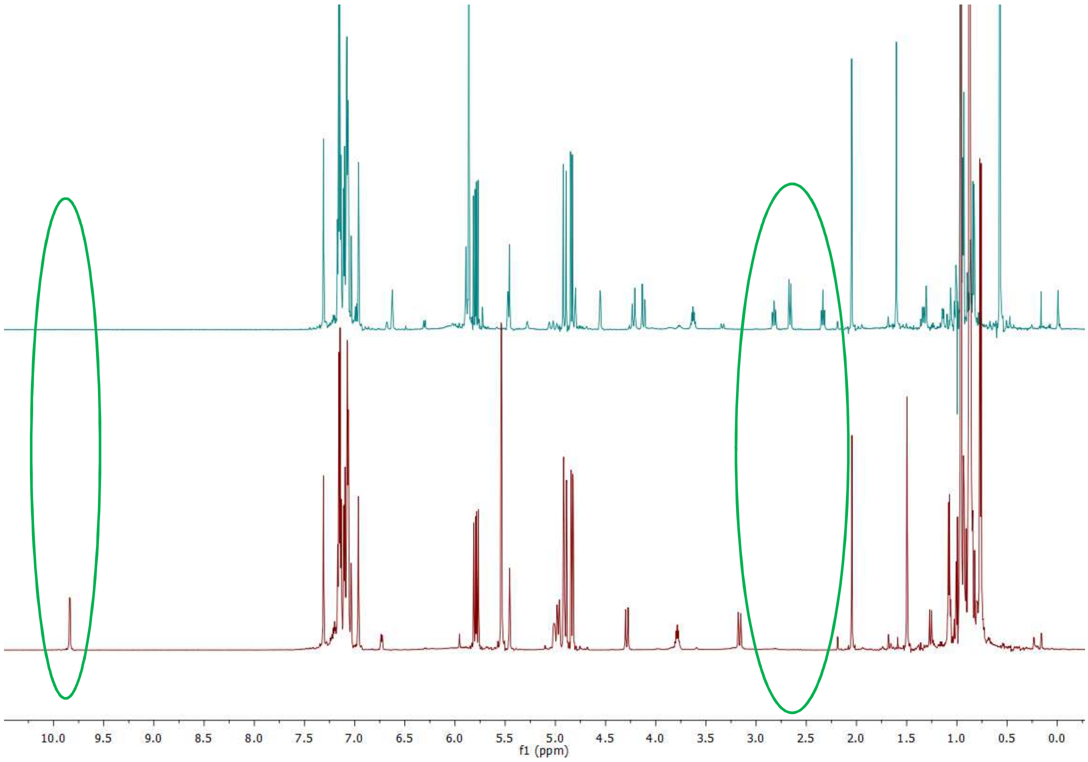
47 **48** major **48_bis** minor

Scheme III-38: putative species formed by reaction of 47 with PMe_3



Spectrum III-16: $^{31}P\{^1H\}$ NMR of crude 48 (600.23 MHz, 300 K, bromobenzene-d_5)

The ^1H NMR spectrum (Spectrum III-17) shows the disappearance of titanacyclobutane signals, along with the appearance of a characteristic downfield singlet at 9.84 ppm, which was ascribed to **48**. Therefore, the reversible nature of the cycloaddition of 3,3-dimethylbut-1-ene to Ti-carbene **43** is established.



Spectrum III-17: superposition of the ^{1}H NMR spectra of 48 (bottom) and 47 (top) (600.23 MHz, 300 K, bromobenzene-d_5)

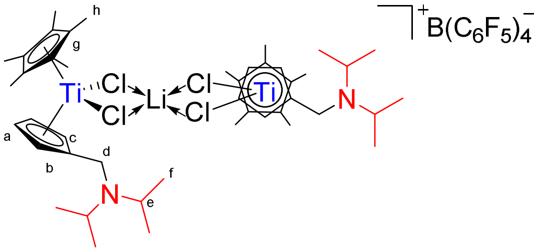
This spectrum will not be completely assigned since two species were present. This superposition just illustrates the complete and quick consumption of the previous titanacyclobutane (disappearance of the signals from the metallacycle) and formation of a major product with a downfield shifted signal (9.84 ppm) identified as **48**, by addition of PMe_3. This experiment is another proof of the formation of the metallacycle.

To resume this part on methide abstraction, the targeted OmFLPs were not obtained due to the high reactivity and activity of the titanocenium fragment, leading to novel unexpected species via CH activation pathways of the pendant amine arm.

In conclusion to this chapter, the synthetic approach towards N/Ti$^+$ based OmFLPs led us to shift our focus into new fields of investigations. Indeed, as previously described in the literature but rarely observed on titanium, new CH-activation of the tertiary amine moiety were highlighted and enabled us to synthesize two new cationic amidotitanocenes and an unexpected titanium carbene species. Their mechanisms of formation were also investigated. This work could help to understand the behaviour of cationic group 4 metallocenes towards N-based substrate in catalytic reaction, and could be used to synthesize new Ti-carbene species.

C. Experimental part:

1. Synthesis of **25**:



Chemical Formula: $C_{68}H_{70}BCl_4F_{20}LiN_2Ti_2$
Molecular Weight: 1550,6

A solution of **19** (150 mg, 0.35 mmol, 2 eq), and LiB(C_6F_5)$_4$ (121.6 mg, 0.17 mol, 1 eq) was prepared in dichloromethane for 5 minutes. The solution was then filtered through diatomaceous earth, and the compound was purified by fractional crystallization from diffusion of pentane in a concentrated dichloromethane solution at -15°C. The compound was dried *in vacuo* after the third time to afford the desired compound as a crystalline red solid with a 90% purity determined by NMR (140 mg, 56%).[46,47]

^{1}H NMR (500.03 MHz, 260 K, dichloromethane-d$_2$): δ^1H: 6.21-6.18 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 4H, H^a), 6.18-6.15 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 4H, H^b), 4.49 (s, 4H, $^2J_{HH}$ H$^{d/d'}$), 4.00 (hept, $^3J_{HH}$ = 6.7 Hz, 4H, H^e), 2.05 (s, 30H, H^h), 1.48 (d, $^3J_{HH}$ = 6.7 Hz, 12H, H^f), 1.41 (d, $^3J_{HH}$ = 6.7 Hz, 12H, H^f). Traces of pentane: 1.32-1.19 (m), 0.85 (t), and unidentified compound: 6.33-6.21 (bm), 3.68-3.54 (bm), 3.16-2.90 (bm), 1.10-0.91 (bm).

^{13}C{^{1}H} NMR (125.75 MHz, 260 K, dichloromethane-d$_2$): δ^{13}C: 148.2 (dm, $^1J_{FC}$ = 243 Hz, *o*-CF), 138.3 (dm, $^1J_{FC}$ = 243 Hz, *p*-CF), 136.5 (dm, $^1J_{FC}$ = 243 Hz, *m*-CF), 133.1 (C^g), 126.4 (C^b), 116.0 (C^c), 113.1 (C^a), 56.9 (C^e), 46.7 (C^d), 18.6 (C^f), 18.4 (C$^{f'}$), 13.9 (C^h). Pentane: 34.5, 22.8, 14.3

^{1}H ^{1}H COSY (500.03 MHz, 260 K, dichloromethane-d$_2$): δ^1H / δ^1H: 6.21-6.18 / 6.18-6.15 (CH^a / CH^b), 6.18-6.15 / 6.21-6.18 (CH^b / CH^a), 4.00 / 1.48, 1.41 (CH$_2^e$ / CH$_3^{f/f'}$), 1.48 / 4.00 (CH$_3^f$ / CH$_2^e$), 1.41 / 4.00 (CH$_3^{f'}$ / CH$_2^e$).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 260 K, dichloromethane-d$_2$): δ^1H / δ^{13}C: 6.21-6.18 / 113.1 (CH^a), 6.18-6.15 / 126.4 (CH^b), 4.49 / 46.7 (CH$_2^d$), 4.00 / 56.9 (CH^e), 2.05 / 13.9 (CH$_3^h$), 1.48 / 18.6 (CH$_3^f$), 1.41 / 18.4 (CH$_3^{f'}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 260 K, dichloromethane-d$_2$): δ^1H / δ^{13}C: 6.21-6.18 / 126.4 (CH^a / CH^b), 6.18-6.15 / 116.0, 113.1 (CH^b / C^c, CH^a), 4.49 / 126.4, 116.0, 56.9 (CH$_2^d$ /

---

[46] A satisfactory elemental analysis could not be obtained (low C) due to remaining [Li][B(C_6F_5)$_4$ salts

[47] IR spectroscopy was not measured due to the presence of the counter anion, hiding all structural parameters of the titanocene fragment.

CH^b, C^c, CH^e), 4.00 / 56.9, 46.7, 18.6, 18.4 (CH^e / CH^e, CH$_2^d$, CH$_3^{f/f'}$), 2.05 / 133.1 (CH$_3^h$ / C^g), 1.48 / 56.9, 18.4 (CH$_3^f$ / CH^e, CH$_3^{f'}$), 1.41 / 56.9, 18.6 (CH$_3^{f'}$ / CH^e, CH$_3^f$).

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, dichloromethane-d$_2$): δ^{11}B: -16.8 ($\nu_{1/2}$ = 21 Hz).

^{11}B NMR (160.42 MHz, 300 K, dichloromethane-d$_2$): δ^{11}B: -16.8 ($\nu_{1/2}$ = 21 Hz).

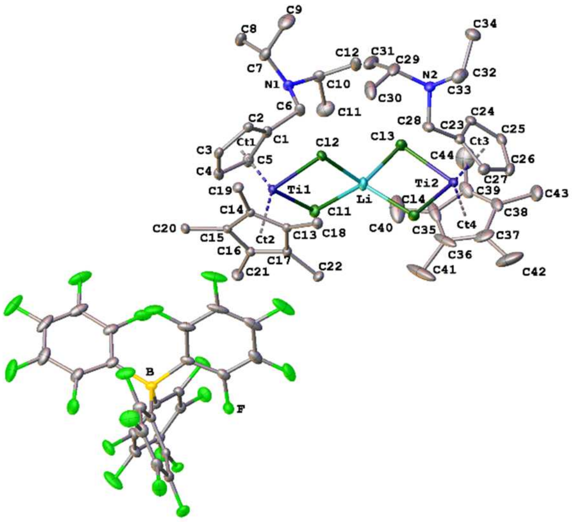
^{19}F{^{1}H} NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -133.2 (apparent d, $^3J_{FF}$ = 15 Hz, 8F, *o*-F), -163.3 (t, $^3J_{FF}$ = 19 Hz, 8F, *p*-F), -167.2 (apparent t, $^3J_{FF}$ = 17 Hz, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -133.2 (apparent d, $^3J_{FF}$ = 15 Hz, 8F, *o*-F), -163.3 (t, $^3J_{FF}$ = 19 Hz, 8F, *p*-F), -167.2 (apparent t, $^3J_{FF}$ = 17 Hz, 8F, *m*-F).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{15}N: 1.48, 1.41 / -309.0 (H^f / N).

HRMS (Positive mode ESI, dichloromethane) m/z: $C_{22}H_{36}Cl_2NTi$ [M-Cp^{N}CpTiCl$_2$-LiB(C$_6$F$_5$)$_4$+H]$^+$ 432.16988, found 432.17088 (Rel. Ab: 100%, 2.3 ppm).

XRD:



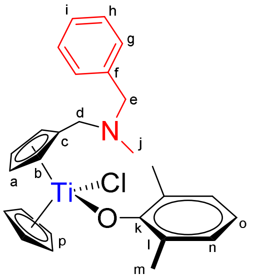
Compound	q28102015_0m_a
Formula	$C_{68}H_{70}BCl_4F_{20}LiN_2Ti_2$
$D_{calc.}$/ g cm^{-3}	1.353
μ/mm^{-1}	0.438
Formula Weight	1550.61
Colour	black
Shape	block
Size/mm^3	0.50×0.50×0.50
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	11.2304(6)
b/Å	17.2668(10)
c/Å	19.7419(11)
α/°	83.951(2)
β/°	89.789(2)
γ/°	88.199(2)
V/Å^3	3805.0(4)
Z	2
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.037
Θ_{max}/°	27.610
Measured Refl.	120519
Independent Refl.	17612
Reflections Used	13200
R_{int}	0.0366
Parameters	892
Restraints	30
Largest Peak	1.182
Deepest Hole	-0.654
GooF	1.047
wR_2 (all data)	0.1425
wR_2	0.1229
R_1 (all data)	0.0735
R_1	0.0501

Experimental. Single black block-shaped crystals of (**q28102015_0m_a**) were obtained by recrystallisation from .. A suitable crystal (0.50×0.50×0.50) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa APEX II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2017/1 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{68}H_{70}BCl_4F_{20}LiN_2Ti_2$, M_r = 1550.61, triclinic, P-1 (No. 2), a = 11.2304(6) Å, b = 17.2668(10) Å, c = 19.7419(11) Å, α = 83.951(2)°, β = 89.789(2)°, γ = 88.199(2)°, V = 3805.0(4) Å^3, T = 115 K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 0.438, 120519 reflections measured, 17612 unique (R_{int} = 0.0366) which were used in all calculations. The final wR_2 was 0.1425 (all data) and R_1 was 0.0501

(I > 2(I)).

2. Synthesis of **26**:



Chemical Formula: $C_{28}H_{38}ClNOTi$
Molecular Weight: 487,9

A solution of **9** (1.0 g, 2.6 mmol, 1.0 eq) and sodium 2,6-dimethylphenolate (430 mg, 2.6 mmol, 1.0 eq) in 40 mL of dichloromethane were stirred for 12h. The resulting red solution was filtered through diatomaceous earth to remove LiCl salts and all volatiles were removed. The red oil obtained was dissolved in Et_2O (30 mL), supernatant was syringed to remove insoluble impurities. After removal of all volatiles, the red oil was stirred in pentane. The desired compound was obtained as a red oil after removal of the supernatant and drying *in vacuo*. (510 mg, yield = 42 %).(Since grease can not be removed from this oily compound soluble in pentane, it was not characterized by elemental analysis and grease is observed in NMR spectra).[48]

^{1}H NMR (500.03 MHz, 300 K, dichloromethane-d_2): δ^{1}H: 7.29-7.18 (m, 5H, $H^{h,l,j}$), 6.93 (d, $^{3}J_{HH}$ = 6.9 Hz, 2H, H^{o}), 6.67 (t, $^{3}J_{HH}$ = 6.9 Hz, 1H, H^{p}), 6.46 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH'}$ = 2.8 Hz, 1H, H^{b}), 6.43 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH'}$ = 2.8 Hz, 1H, H^{a}), 6.23 (apparent q overlapping with H^{k}, $^{3}J_{HH}$ = $^{4}J_{HH'}$ = 2.8 Hz, 1H, $H^{b'}$), 6.22 (s overlapping with $H^{b'}$, 5H, H^{k}), 6.12 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.8 Hz, 1H, $H^{a'}$), 3.58 (d, $^{2}J_{HH}$ = 14.9 Hz, 1H, H^{d}), 3.51 (d, $^{2}J_{HH}$ = 14.9 Hz, 1H, $H^{d'}$), 3.47 (s, 2H, H^{f}), 2.12 (s, 3H, H^{e}), 2.06 (bs, 6H, H^{n}).

^{13}C{^{1}H} NMR (125.77 MHz, 300 K, dichloromethane-d_2): δ^{13}C: 169.4 (C^{l}), 139.8 (C^{g}), 132.2 (C^{c}), 129.4 ($^{h/i/j}$), 129.0 (C^{o}), 128.7 ($CH^{h/i/j}$), 127.5 ($C^{h/i/j}$), 123.3 (C^{b}), 123.2 ($C^{b'}$), 120.3 (C^{p}), 118.4 (C^{m}), 118.1 (C^{k}), 116.6 (C^{a}), 109.6 ($C^{a'}$), 62.3 (C^{f}), 57.2 (C^{d}), 42.6 (C^{e}), 19.3-18.5 (bs, C^{n}).

^{1}H ^{1}H COSY (500.03 MHz, 300 K, dichloromethane-d_2): δ^{1}H / δ^{1}H: 7.29-7.18 / 7.29-7.18 ($CH^{h,l,j}$), 6.93 / 6.67 (CH^{o} / CH^{p}), 6.67 / 6.93 (CH^{p} / CH^{o}), 6.46 / 6.43, 6.23, 6.12 (CH^{b} / CH^{a}, $CH^{b'}$, $CH^{a'}$), 6.43 / 6.46, 6.23, 6.12 (CH^{a} / CH^{b}, $CH^{b'}$, $CH^{a'}$), 6.23 / 6.46, 6.43, 6.12 ($CH^{b'}$ / CH^{b}, CH^{a}, $CH^{a'}$), 6.12 / 6.46, 6.43, 6.23 ($CH^{a'}$ / CH^{b}, CH^{a}, $CH^{b'}$), 3.58 / 3.51 ($CH_2^{d/d'}$), 3.51 / 3.58 ($CH_2^{d/d'}$).

---

[48] IR spectroscopy and elemental analysis were not performed due to the oily character of this compound.

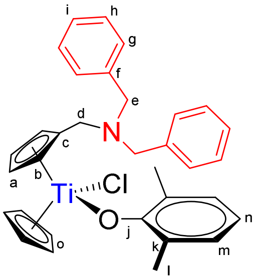
^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d_2): δ^{1}H / δ^{13}C: 7.29-7.18 / 129.4, 128.7, 127.5 (CH^{h,l,j}), 6.93 / 129.0 (CH^{o}), 6.67 / 120.3 (CH^{p}), 6.47 / 123.3 (CH^{b}), 6.43 / 116.6, (CH^{a}), 6.23 / 123.2 (CH$^{b'}$), 6.22 / 118.1 (CH^{k}), 6.12 / 109.6 (CH$^{a'}$), 3.58, 3.51 / 57.2 (CH$_2^{d/d'}$), 3.47 / 62.3,1 2.12 / 42.6 (CH$_3^{e}$), 2.06 / 19.3-18.5 (CH$_3^{n}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d_2): δ^{1}H / δ^{13}C: 7.29-7.18 / 139.8, 129.4, 128.7, 127.5 (CH^{i,j,k} / C^{g}, CH^{i,j,k}), 6.93 / 169.4, 129.0, 19.3-18.5 (CH^{o} / C^{m}, CH^{o}, CH$_3^{n}$), 6.67 / 169.4, 129.0 (CH^{p} / C^{m}, CH^{o}), 6.47 / 132.2, 123.2, 116.6, 109.6 (CH^{b} / C^{c}, CH$^{b'}$, CH^{a}, CH$^{a'}$), 6.43 / 132.2, 123.3, 123.2, 109.6 (CH^{a} / C^{c}, CH^{b}, CH$^{b'}$, CH$^{a'}$, CH), 6.23 / 132.2, 123.3, 123.2, 116.6, 109.6 (CH$^{b'}$ / C^{c}, CH, CH, CH), 6.22 / 118.1 (CH^{k} / CH^{k}), 6.12 / 132.2, 123.3, 123.2, 116.6 (CH$^{a'}$ / C^{c}, CH^{b}, CH$^{b'}$, CH^{a}), 3.58, 3.51 / 132.2, 123.3, 123.2, 62.3, 42.6 (CH$_2^{d}$ / C^{c}, CH^{b}, CH$^{b'}$, CH$_2^{f}$, CH$_3^{e}$), 3.47 / 139.8, 129.4, 57.2, 42.6 (CH$_2^{f}$ / C^{g}, CH^{h}, CH$_2^{d}$, CH$_3^{e}$) 2.12 / 62.3, 57.2 (CH$_3^{e}$ / CH$_2^{f}$, CH$_2^{d}$), 2.06 / 169.4, 129.0 (CH$_3^{n}$ / C^{m}, CH^{o}).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^{1}H / δ^{15}N: 2.12 / -340 (H^{e} / N).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{27}H_{31}ClNOTi$ $[M+H]^+$ 468.15682; found 468.15620 (Rel. ab: 100%, -1.3 ppm).

3. Synthesis of **27**:



Chemical Formula: $C_{33}H_{34}ClNOTi$
Molecular Weight: 544.0

A solution of **11** (810 mg, 1.8 mmol, 1.0 eq) and sodium 2,6-dimethylphenolate (290 mg, 1.8 mmol, 1.0 eq) in 15 mL of dichloromethane were stirred for 12h. The resulting red solution was filtered through diatomaceous earth to remove LiCl salts and all volatiles were removed. The red oil obtained was suspended in pentane (10 mL), and supernatant was removed at - 40 °C. The desired compound was obtained as a red sticky solid after drying *in vacuo*. (590 mg, yield = 61 %).[48]

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d_2): δ^{1}H: 7.32 (d, $^{3}J_{HH}$ = 7.3 Hz, 4H, H^{g}), 7.25 (t, $^{3}J_{HH}$ = $^{3}J_{HH}$ = 7.3 Hz 4H, H^{h}), 7.18 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, H^{i}), 6.89 (d, $^{3}J_{HnHo}$ = 7.4 Hz, 2H, H^{n}), 6.65 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, H^{o}), 6.44 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.2 Hz, 1H, H^{b}), 6.38 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.2 Hz, 1H, H$^{b'}$), 6.22 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.2 Hz, 1H, H^{a}), 6.12 (s, 5H, H^{j}), 6.08 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.2 Hz, 1H, H$^{a'}$), 3.56 (apparent d, $^{2}J_{HH}$ = 14.4 Hz, 2H, H$^{d+d'}$), 3.54 (d, $^{2}J_{HH}$ = 14.4 Hz, 2H, H^{e}), 3.48 (d, $^{2}J_{HH}$ = 14.4 Hz, 2H, H$^{e'}$), 1.96 (bs, 6H, H^{l}).

$^{13}C\{^{1}H\}$ NMR (125.77 MHz, 300 K, dichloromethane-d_2): $\delta^{13}C$: 169.4 (C^{k}), 140.1 (C^{f}), 131.8 (C^{c}), 129.3 (^{g}), 129.1 (C^{n}), 128.7 (C^{h}), 127.4 (C^{i}), 123.6 ($C^{b'}$), 123.0 (C^{b}), 120.7 (C^{l}), 120.3 (C^{o}), 118.5 (C^{l}), 118.1 (C^{j}), 117.5 (C^{a}), 109.4 ($C^{a'}$), 58.7 (C^{e}), 53.3 (C^{d}), 19.0-18.6 (C^{m}).

^{1}H ^{1}H COSY (500.03 MHz, 300 K, dichloromethane-d_2): $\delta^{1}H$ / $\delta^{1}H$: 7.32 / 7.25, 7.18 (H^{g} / H^{h}, H^{i}), 7.25 / 7.32, 7.18 (H^{h} / H^{g}, H^{i}), 7.18 / 7.32, 7.25 (H^{i} / H^{g}, H^{h}), 6.89 / 6.65 (H^{n} / H^{o}), 6.65 / 6.89 (H^{o} / H^{n}), 6.44 / 6.38, 6.22, 6.08 (H^{b} / $H^{b'}$, H^{a}, $H^{a'}$), 6.38 / 6.44, 6.22, 6.08 ($H^{b'}$ / H^{b}, H^{a} , $H^{a'}$), 6.22 / 6.44, 3.38, 6.08 (H^{a} / H^{b}, $H^{b'}$, $H^{a'}$), 6.08 / 6.44, 6.38, 6.22 ($H^{a'}$ / H^{b}, $H^{b'}$, H^{a}), 3.56 / 3.56 ($H^{d/d'}$), 3.54 / 3.48 ($H^{e/e'}$), 3.48 / 3.54 ($H^{e/e'}$).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): $\delta^{1}H$ / $\delta^{13}C$: 7.32 / 129.3 (CH^{g}), 7.25 / 128.7 (CH^{h}), 7.18 / 127.4 (CH^{i}), 6.89 / 129.1 (CH^{n}), 6.65 / 120.3 (CH^{o}), 6.44 / 123.0 (CH^{b}), 6.38 / 123.6 ($CH^{b'}$), 6.22 / 117.5 (CH^{a}), 6.12 / 118.1 (CH^{j}), 6.08 / 109.4 ($CH^{a'}$), 3.56 / 53.3 ($CH_2^{d/d'}$), 3.54, 3.48 / 58.7 ($CH_2^{e/e'}$), 1.96 / 19.0-18.6 (CH_3^{m}).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d_2): $\delta^{1}H$ / $\delta^{13}C$: 7.32 / 127.4, 58.7 (CH^{g} / CH^{i}, CH_2^{e}), 7.25 / 140.1, 128.7 (CH^{h} / C^{f}, CH^{h}), 7.18 / 129.3 (CH^{i} / CH^{g}), 6.89 / 169.4, 129.1, 19.0-18.6 (CH^{n} / C^{k}, CH^{n}, CH_3^{m}), 6.65 / 129.1 (CH^{o} / CH^{n}), 6.44 / 131.8, 123.6, 117.5, 109.4 (CH^{b} / C^{c}, $CH^{b'}$, CH^{a}, $CH^{a'}$), 6.38 / 131.8, 117.5, 109.4 ($CH^{b'}$ / C^{c}, CH^{a}, $CH^{a'}$), 6.22 / 131.8, 123.6, 123.0, 109.4 (CH^{a} / C^{c}, $CH^{b'}$, CH^{b}, $CH^{a'}$), 6.22 / 118.1 (CH^{k} / CH^{k}), 6.08 / 131.8, 123.6 ($CH^{a'}$ / C^{c}, $CH^{b'}$), 3.56 / 131.8, 123.6, 123.0, 58.7 (CH_2^{d} / C^{c}, $CH^{b'}$, CH^{b}, CH_2^{e}), 3.54, 3.48 / 140.0, 129.3, 58.7, 53.3 (CH_2^{e} / C^{f}, CH^{g}, CH_2^{d}, CH_2^{e}), 1.96 / 169.4, 129.1, 120.3 (CH_3^{m} / C^{k}, CH^{n}, CH^{o}).

^{1}H ^{15}N HMBC (600.23 MHz / 60.83 MHz, 300 K, dichloromethane-d_2): $\delta^{1}H$ / $\delta^{15}N$: 3.56 / -329 (H^{e} / N)

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{33}H_{35}ClNOTi$ $[M+H]^{+}$ 544.18812; found 544.18842 (Rel. ab: 100%, 0.6 ppm).

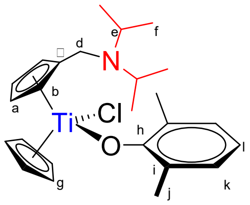
IR (ATR) ν [cm-1]

MIR: 3025; 2917; 1587; 1453; 1369; 1263; 1218; 1091; 1022; 873; 812; 732; 695.

FIR: 565; 545; 488; 386; 363; 241; 195, 128; 100.

Elemental Analysis: % calcd for $C_{33}H_{34}ClNOTi$: C, 72.87; H, 6.30; N, 2.58; Found: C, 71.68; H, 6.48; N, 2.89.

4. Synthesis of **28**:



Chemical Formula: $C_{25}H_{34}ClNOTi$
Molecular Weight: 447,9

A solution of **12** (200 mg, 0.55 mmol, 1.0 eq) and sodium 2,6-dimethylphenolate (97.5 mg, 0.55 mmol, 1.0 eq) in 5 mL of dichloromethane were stirred for 12h. The resulting red solution was filtered through diatomaceous earth to remove NaCl salts and all volatiles were removed. The red oil obtained was dissolved in Et$_2$O and left in the freezer (-30°C) for overnight crystallization. The desired compound was obtained as an orange microcrystalline solid after removal of the supernatant and drying *in vacuo*. (140 mg, yield = 57 %).

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 6.93 (d, $^3J_{HH}$ = 7.4, 2H, CH^{j}), 6.66 (t, $^3J_{HH}$ = 7.4, 1H, H^{k}), 6.44 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.3 Hz, 1H, H^{b}), 6.38 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.3 Hz, 1H, H$^{a'}$), 6.23 (s, 5H, H^{g}), 6.17 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.3 Hz, 1H, H$^{b'}$), 6.09 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.3 Hz, 1H, H^{a}), 3.68 (d, $^2J_{HH}$ = 15.7 Hz, 1H, H^{d}), 3.59 (d, $^2J_{HH}$ = 15.7 Hz, 1H,H$^{d'}$), 2.94 (hept, $^3J_{HH}$ = 6.6 Hz, 2H, H^{e}), 2.10 (bs, 6H, H^{j}), 0.96 (d, $^3J_{HH}$ = 6.6 Hz, 6H, H^{f}), 0.91 (d, $^3J_{HH}$ = 6.6 Hz, 6H, H$^{f'}$).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 169.3(C^{h}), 138.3 (C^{c}), 129.0 (C^{k}), 122.9 (C^{b}), 122.8 (C$^{b'}$), 120.1 (C^{l}), 118.4 (C^{i}), 117.8 (C^{g}), 116.6 (C$^{a'}$), 109.0 (C^{a}), 49.0 (C^{e}), 45.0 (C^{d}), 21.5 (C^{f}), 20.8 (C$^{f'}$), 19.0-18.7 (C^{j}).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{1}H: 6.93 / 6.66 (CH^{k} / CH^{l}), 6.66 / 6.92 (CH^{l} / CH^{k}), 6.44 / 6.09 (CH^{b} / CH^{a}), 6.38 / 6.17 (CH$^{a'}$ / CH$^{b'}$), 6.17 / 6.38, 6.09 (CH$^{b'}$ / CH$^{a'}$, CH^{a}), 6.09 / 6.44, 6.17 (CH^{a} / CH^{b}, CH$^{b'}$), 3.68 / 3.59 (CH$_2^{d/d'}$), 3.59 / 3.68 (CH$_2^{d/d'}$), 2.94 / 0.96, 0.91 (CH^{e} / CH$_3^{f}$, CH$_3^{f'}$), 0.96 / 2.94 (CH$_3^{f}$ / CH^{e}), 0.91 / 2.97 (CH$_3^{f'}$ / CH^{e}).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 6.93 / 129.0 (CH^{k}), 6.66 / 120.2 (CH^{l}), 6.44 / 122.9 (CH^{b}), 6.38 / 116.6 (CH$^{a'}$), 6.23 / 117.8 (CH^{g}), 6.17 / 122.8 (CH$^{b'}$), 6.09 / 109.0 (CH^{a}), 3.68, 3.59 / 45.0 (CH$_2^{d/d'}$), 2.94 / 49.0 (CH^{e}), 2.10 / 19.0-18.7 (CH$_3^{j}$), 0.96 / 21.5 (CH$_3^{f}$), 0.91 / 20.8 (CH$_3^{f'}$).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 6.93 / 169.3, 129.0, 120.2, 19.0-18.7 (CH^{k} / C^{i}, CH^{k}, CH^{l}, CH$_3^{j}$), 6.66 / 169.3, 129.0 (CH^{l} / C^{i}, CH^{k}), 6.44 / 138.3, 116.6, 109.0 (CH^{b} / C^{c}, CH$^{a'}$, CH^{a}), 6.38 / 138.3, 122.8, 109.0 (CH$^{a'}$ / C^{c}, CH$^{b'}$, CH^{a}), 6.23 / 117.8 (CH^{g} / CH^{g}), 6.17 / 138.3, 116.6, 109.0 (CH$^{b'}$ / C^{c}, CH$^{a'}$, CH^{a}), 6.09 / 138.3, 122.9, 122.8 (CH^{a} / C^{c}, CH^{b}, CH$^{b'}$), 3.68, 3.59 / 138.3, 122.9, 122.8, 49.0 (CH$_2^{d}$ / C^{c}, CH^{b}, CH$^{b'}$, CH^{e}), 2.94 / 49.0, 45.0, 21.5, 20.8 (CH^{e} / CH^{e}, CH$_2^{d}$, CH$_3^{f}$, CH$_3^{f'}$), 2.10 / 169.3, 129.0 (CH$_3^{j}$ / C^{i}, CH^{k}) 0.96 / 49.0, 20.8 (CH$_3^{f}$ / CH^{e}, CH$_3^{f'}$), 0.91 / 49.0, 21.5 (CH$_3^{f'}$ / CH^{e}, CH$_3^{f}$).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{15}N: 0.96 / -324 (H^{f} / N).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{25}H_{35}ClNOTi$ $[M+H]^+$ 448.18841; found 448.18899 (Rel. ab: 100%, 2.0 ppm).

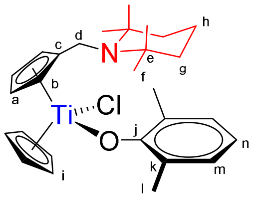
IR (ATR) ν [cm-1]

MIR: 2954; 1589; 1463; 1267; 1225; 1200; 1178; 1019; 876; 814; 753; 734; 716.

FIR: 716; 624; 563; 545; 392, 363, 270; 233; 189; 137.

Elemental Analysis: % calcd for $C_{25}H_{35}ClNOTi$: C, 67.05; H, 7.65; N, 3.13; Found: C, 66.15; H, 7.79; N, 3.12.

5. Synthesis of **29**:



Chemical Formula: $C_{28}H_{38}ClNOTi$
Molecular Weight: 487,9

A solution of **13** (300 mg, 0.75 mmol, 1.0 eq) and sodium 2,6-dimethylphenolate (131.7 mg, 0.75 mmol, 1.0 eq) in 5 mL of dichloromethane were stirred for 12h. The resulting red solution was filtered through diatomaceous earth to remove LiCl salts and all volatiles were removed. The red oil obtained was dissolved in dichloromethane and left in the freezer (-30°C) for crystallization by pentane diffusion. The desired compound was obtained as an orange microcrystalline solid after removal of the supernatant and drying *in vacuo*. (224 mg, yield = 58 %).

^{1}**H NMR** (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 6.93 (d, $^{3}J_{HH}$ = 7.4, 2H, CH^{m}), 6.66 (t, $^{3}J_{HH}$ = 7.4, 1H, H^{n}), 6.43 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.3 Hz, 1H, H^{b}), 6.36 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.3 Hz, 1H, H$^{a'}$), 6.19 (s, 5H, H^{i}), 6.11 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.3 Hz, 1H, H$^{b'}$), 6.06 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.3 Hz, 1H, H^{a}), 3.79 (d, $^{2}J_{HH}$ = 15.2 Hz, 1H, H^{d}), 3.74 (d, $^{2}J_{HH}$ = 15.2 Hz, 1H,H$^{d'}$), 2.09 (bs, 6H, H^{l}),1.54-1.48 (m, 2H, CH$_2^{h}$), 1.39-1.35 (m, 4H, CH$_2^{g}$), 0.99 (s, 6H, H^{f}), 0.87 (s, 6H, H$^{f'}$).

^{13}**C{**^{1}**H} NMR** (150.94 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 169.3 (C^{j}), 144.6 (C^{c}), 129.1 (C^{m}), 122.5 (C^{b}), 120.1 (C^{n}), 120.1 (C^{a}), 118.4 (C^{k}), 117.6 (C^{i}), 115.3 (C$^{a'}$), 109.7 (C$^{b'}$), 55.6 (C^{e}), 44.9 (C^{d}), 41.9 (C^{g}), 28.7-27.6 (C^{f}), 18.9-18.8 (C^{l}), 18.4 (C^{h}).

^{1}**H** ^{1}**H COSY** (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{1}H: 6.93 / 6.66 (CH^{m} / CH^{n}), 6.66 / 6.93 (CH^{n} / CH^{m}), 6.43 / 6.36, 6.11, 6.06 (CH^{b} / CH$^{a'}$, CH$^{b'}$, CH^{a}), 6.36 / 6.43, 6.11, 6.06 (CH$^{a'}$ / CH^{b}, CH$^{b'}$, CH^{a}), 6.11 / 6.43, 6.36, 6.06 (CH$^{b'}$ / CH^{b}, CH$^{a'}$, CH^{a}), 6.06 / 6.43, 6.36, 6.11 (CH^{a} / CH^{b}, CH$^{a'}$, CH$^{b'}$), 3.79 / 3.74 (CH$_2^{d/d'}$), 3.74 / 3.79 (CH$_2^{d'/d}$), 1.54-1.48 / 1.39-1.35 (CH$_2^{h}$ / CH$_2^{g}$), 1.39-1.35 / 1.54-1.48 (CH$_2^{g}$ / CH$_2^{h}$).

^{1}**H** ^{13}**C HMQC** (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 6.93 / 129.1 (CH^{m}), 6.66 / 120.2 (CH^{n}), 6.43 / 122.5 (CH^{b}), 6.36 / 115.3 (CH$^{a'}$), 6.19 / 117.6 (CH^{i}), 6.11 / 109.7 (CH$^{b'}$), 6.06 / 120.1 (CH^{a}), 3.79, 3.74 / 44.9 (CH$_2^{d/d'}$), 2.09 / 18.9-18.8 (CH^{l}), 1.54-1.48 / 18.4 (CH$_2^{h}$), 1.39-1.35 / 41.9 (CH$_2^{g}$), 0.99 / 28.3 (CH$_3^{f}$), 0.87 / 28.7-27.6 (CH$_3^{f'}$).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{13}C: 6.93 / 169.3, 129.1, 18.4 (CH^m / C^k, CH^m, CH_2^h), 6.19 / 117.6 (CH^i / CH^i), 3.79, 3.74 / 144.6, 120.1, 115.3, 44.9 (CH_2^d / C^c, CH^a, $CH^{a'}$, CH_2^d), 2.09 / 169.3, 129.1 (CH_3^l / C^k, CH^m) 1.54-1.48 / 55.6, 41.9 (CH_2^h / C^e, CH_2^g), 1.39-1.35 / 55.6, 41.9, 28.7-27.6, 18.4 (CH_2^g / C^e, CH_2^g, CH_3^f, CH_2^h), 0.99 / 55.6, 41.9, 28.7-27.6 (CH_3^f / C^e, CH_2^g, $CH_3^{f'}$), 0.87 / 55.6, 41.9, 28.7-27.6 ($CH_3^{f'}$ / C^e, CH_2^g, CH_3^f).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^{15}N: 0.99, 0.87 / -311 (H^f / N)

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{28}H_{39}ClNOTi$ $[M+H]^+$ 488.21974; found 488.21917 (Rel. ab: 100%, -0.5 ppm).

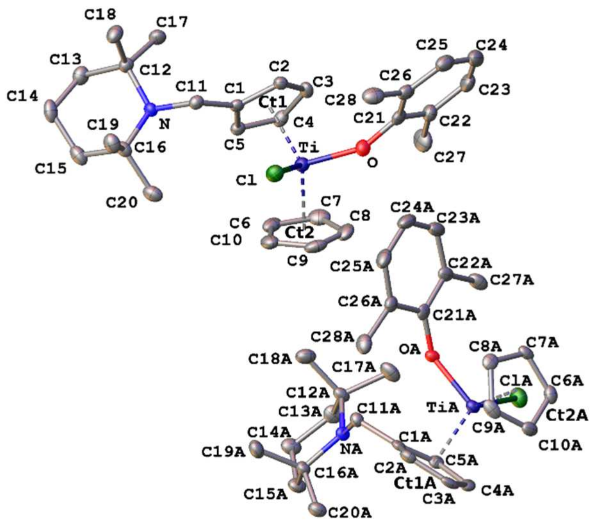
IR (ATR) ν [cm-1]

MIR: 3089; 2956; 1589; 1463; 1382; 1260; 1221; 1091; 1048; 870; 812; 739; 710.

FIR: 710; 620, 568, 542, 366, 280, 242, 195.

Elemental Analysis: % calcd for $C_{28}H_{38}ClNOTi$: C, 68.92; H, 7.85; N, 2.87; Found: C, 68.07; H, 7.56; N, 2.72.

XRD:

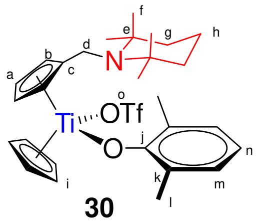


Experimental. Single red plate-shaped crystals of (**q060116_0ma_a**) were obtained by slow diffusion of pentane into a concentrated dichloromethane solution. A suitable crystal (0.20×0.20×0.02) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa APEX II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{28}H_{38}ClNOTi$, M_r = 487.94, monoclinic, P2$_1$/c (No. 14), a = 28.570(3) Å, b = 11.7824(11) Å, c = 14.9004(14) Å, β = 94.977(2)°, $\alpha = \gamma$ = 90°, V = 4997.0(8) Å^3, T = 115 K, Z = 8, Z' = 2, μ(MoK$_\alpha$) = 0.470, 64922 reflections measured, 11454 unique (R_{int} = 0.1148) which were used in all calculations. The final wR_2 was 0.0732 (all data) and R_1 was 0.0427 (I > 2(I)).

Compound	**q060116_0ma_a**
Formula	$C_{28}H_{38}ClNOTi$
$D_{calc.}$/ g cm^{-3}	1.297
μ/mm^{-1}	0.470
Formula Weight	487.94
Colour	red
Shape	plate
Size/mm^3	0.20×0.20×0.02
T/K	115
Crystal System	monoclinic
Space Group	P2$_1$/c
a/Å	28.570(3)
b/Å	11.7824(11)
c/Å	14.9004(14)
α/°	90
β/°	94.977(2)
γ/°	90
V/Å^3	4997.0(8)
Z	8
Z'	2
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.565
Θ_{max}/°	27.512
Measured Refl.	64922
Independent Refl.	11454
Reflections Used	6203
R_{int}	0.1148
Parameters	589
Restraints	0
Largest Peak	0.367
Deepest Hole	-0.473
GooF	0.858
wR_2 (all data)	0.0732
wR_2	0.0616
R_1 (all data)	0.1135
R_1	0.0427

6. Synthesis of **30**:



30

Chemical Formula: $C_{29}H_{39}F_3NO_4STi$
Molecular Weight: 602,6

A mixture of **29** (190 mg, 0.39 mmol, 1.0 eq) and silver triflate (98.3 mg, 0.38 mmol, 0.98 eq) was dissolved in 2 mL of THF for 12h. The resulting red solution was filtered over borosilicate to remove AgCl salts and all volatiles were removed. The red oil obtained was dissolved in dichloromethane (2 mL) and pentane (10 mL) and left in the freezer (-15°C) in order to crystalize the impurity. The desired compound was obtained by evaporation of the filtrate as a red solid. (110 mg, yield = 47 %).

^{1}H NMR (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 7.02 (d, $^{3}J_{HH}$ = 7.4, 2H, CH^{m}), 6.94 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H$^{b'}$), 6.85 (apparent q, $^{3}J_{H/H}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H^{b}), 6.76 (t, $^{3}J_{HH}$ = 7.4, 1H, H^{n}), 6.36 (s, 5H, H^{i}), 6.29 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H^{a}), 5.94 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.3 Hz, 1H, H$^{a'}$), 3.61 (d, $^{2}J_{HH}$ = 17.4 Hz, 1H, H^{d}), 3.52 (d, $^{2}J_{HH}$ = 17.4 Hz, 1H, H$^{d'}$), 2.04 (bs, 6H, H^{l}),1.53-1.45 (m, 2H, CH$_2^{h}$), 1.40-1.34 (m, 4H, CH$_2^{g}$), 0.96 (s, 6H, H^{f}), 0.77 (s, 6H, H$^{f'}$).

^{13}C{^{1}H} NMR (125.77 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 169.8 (C^{j}), 149.5 (C^{c}), 129.3 (C^{m}), 126.4 (C^{b}), 121.4 (C^{n}), 120.6 (C^{n}), 119.8 (q, $^{1}J_{CF}$ = 317.5 Hz, C^{o}), 118.8 (C^{i}), 116.1 (C$^{a'}$), 115.6 (C$^{b'}$), 111.5 (C^{a}), 55.5 (C^{e}), 44.4 (C^{d}), 41.8 (C^{g}), 28.6-28.0 (C$^{f'}$), 28.0-27.4 (C^{f}), 18.3 (C^{h}), 18.2-18.0 (C^{l}).

^{1}H ^{1}H COSY (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{1}H: 7.02 / 6.76 (CH^{m} / CH^{n}, 6.94 / 6.85, 6.29, 5.94 (CH$^{b'}$ / CH^{b}, CH^{a}, CH$^{a'}$), 6.85 / 6.94, 6.29, 5.94 (CH^{b} / CH$^{b'}$, CH^{a} , CH$^{a'}$), 6.76 / 7.02 (CH^{n} / CH^{m}), 6.29 / 6.94, 6.85, 5.94 (CH^{a} / CH^{b}, CH$^{b'}$, CH$^{a'}$), 5.94 / 6.94, 6.85, 6.29 (CH$^{a'}$ / CH$^{b'}$, CH^{b}, CH^{a}), 3.61 / 3.52 (CH$_2^{d/d'}$), 3.52 / 3.61 (CH$_2^{d/d'}$), 1.53-1.45 / 1.40-1.34 (CH$_2^{h}$ / CH$_2^{g}$), 1.40-1.34 / 1.53-1.45 (CH$_2^{g}$ / CH$_2^{h}$).

^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 7.02 / 129.3 (CH^{m}), 6.94 / 115.6 (CH$^{b'}$), 6.85 / 126.4 (CH^{b}), 6.76 / 121.4 (CH^{n}), 6.36 / 118.8 (CH^{i}), 6.29 / 111.5 (CH^{a}), 5.94 / 116.1 (CH$^{a'}$), 3.61, 3.52 / 44.4 (CH$_2^{d/d'}$), 2.04 / 18.2-18.0 (CH^{l}), 1.53-1.45 / 18.3 (CH$_2^{h}$), 1.40-1.34 / 41.8 (CH$_2^{g}$), 0.96 / 28.0-27.4 (CH$_3^{f}$), 0.77 / 28.6-28.0 (CH$_3^{f'}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 7.02 / 169.8, 129.3, 18.2-18.0 (CH^{m} / C^{k}, CH^{m}, CH$_3^{l}$), 6.94 / 149.5, (CH$^{b'}$ / C^{c}), 6.85 / 149.5, 115.6, 111.5 (CH^{b} / C^{c}, CH$^{b'}$, CH^{a}),, 6.76 / 129.3 (CH^{h} / CH^{m}), 6.36 / 118.8 (CH^{i} / CH^{i}), 6.29 / 115.6 (CH^{a} / CH$^{b'}$), 5.94 / 126.5, 115.6, 111.5 (CH$^{a'}$ / CH^{b}, CH$^{b'}$, CH^{a}), 3.61, 3.52 / 149.5, 126.4, 115.6, 55.5 (CH$_2^{d}$ / C^{c}, CH^{b}, CH$^{b'}$, CH$_2^{d}$), 2.04 / 169.8, 129.3 (CH$_3^{l}$ / C^{k}, CH^{m}) 1.53-1.45 / 55.5, 41.8 (CH$_2^{h}$ / C^{e}, CH$_2^{g}$), 1.40-1.34 / 55.5, 41.8, 28.6-28.0, 28.0-27.4, 18.3 (CH$_2^{g}$ / C^{e}, CH$_2^{g}$, CH$_3^{f'}$, CH$_3^{f'}$, CH$_2^{h}$), 0.96 / 55.5, 41.8, 28.6-28.0 (CH$_3^{f}$ / C^{e}, CH$_2^{g}$, CH$_3^{f'}$), 0.77 / 55.5, 41.8, 28.0-27.4 (CH$_3^{f'}$ / C^{e}, CH$_2^{g}$, CH$_3^{f}$).

^{19}F{^{1}H} NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -77.9.

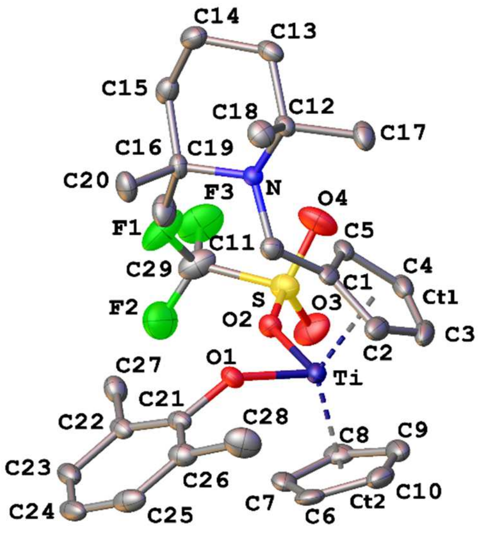
^{19}F NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -77.9.

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{15}N: 0.96, 0.77 / -311 (H^{f} / N).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{29}H_{39}NF_3SO_4Ti$ $[M+H]^+$ 602.20259 found 602.20082 (Rel. ab: 100%, -2.9 ppm), $C_{28}H_{38}NOTi$ $[M-OTf]^+$ 452.24274 found 452.24105 (Rel. ab: 5%, -3.7 ppm).

Elemental Analysis: % calcd for $C_{29}H_{39}F_3NO_4STi$: C, 57.90; H, 6.37; N, 2.33; S, 5.33; Found: C, 57.95; H, 6.74; N, 2.85; S, 4.73.

XRD:

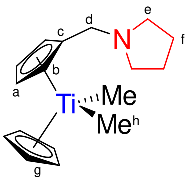


Experimental. Single red plate-shaped crystals of (**q220616_0m**) were obtained by recrystallisation from a saturated solution in pentane at -15°C. A suitable crystal (0.35×0.12×0.07) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa APEX II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{29}H_{38}F_3NO_4STi$, M_r = 601.56, triclinic, P-1 (No. 2), a = 11.8444(13) Å, b = 15.3636(17) Å, c = 17.702(2) Å, α = 76.761(2)°, β = 84.699(3)°, γ = 69.316(3)°, V = 2933.4(6) Å^3, T = 115 K, Z = 4, Z' = 2, μ(MoK$_\alpha$) = 0.416, 63699 reflections measured, 12796 unique (R_{int} = 0.0707) which were used in all calculations. The final wR_2 was 0.1054 (all data) and R_1 was 0.0477 (I > 2(I)).

Compound	**q220616_0m**
Formula	$C_{29}H_{38}F_3NO_4STi$
$D_{calc.}$/ g cm^{-3}	1.362
μ/mm^{-1}	0.416
Formula Weight	601.56
Colour	red
Shape	plate
Size/mm^3	0.35×0.12×0.07
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	11.8444(13)
b/Å	15.3636(17)
c/Å	17.702(2)
α/°	76.761(2)
β/°	84.699(3)
γ/°	69.316(3)
V/Å^3	2933.4(6)
Z	4
Z'	2
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.182
Θ_{max}/°	27.642
Measured Refl.	63699
Independent Refl.	12796
Reflections Used	7968
R_{int}	0.0707
Parameters	715
Restraints	0
Largest Peak	0.424
Deepest Hole	-0.460
GooF	1.009
wR_2 (all data)	0.1054
wR_2	0.0882
R_1 (all data)	0.1057
R_1	0.0477

7. Synthesis of **32**:



Chemical Formula: $C_{17}H_{25}NTi$
Molecular Weight: 291,3

A solution of **2-K** (0.85 g, 4.6 mmol, 1.1 eq) in 20 mL of toluene was added to a solution of $CpTiCl_3$ (1.0 g, 4.6 mmol, 1 eq) in 40 mL of toluene, by canulation at -30°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude red solution was first evaporated. The deep red oil obtained was triturated in pentane (20 mL), and the yellowish supernatant was removed. After drying *in vacuo*, the red residue was suspended in 60 mL of Et_2O. MeLi (1.1 mL, 1.6 M, 2.05 eq) was added dropwise to the etheral suspension cooled down to -70°C. After warming up to room temperature, the initial crude red suspension turned into a yellow solution with a white precipitate after 1h of stirring. The solvent was then removed and the residue was dissolved in 20 mL of pentane. LiCl salts were removed by filtration through diatomaceous earth. The desired compound was obtained after evaporation of all volatiles as a yellow sticky oil. (620 mg, yield = 47 %).[49,50]

^{1}H NMR (500.03 MHz, 300 K, benzene-d_6): δ^1H: 5.92 (br s, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^b), 5.75 (s, 5H, H^g), 5.37 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^a), 3.40 (s, 2H, H^d), 2.56-5.44 (m, 4H, H^e), 1.69-1.59 (m, 4H, H^f), 0.07 (s, 6H, H^h).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, benzene-d_6): δ^{13}C: 126.1 (C^c), 115.6 (C^b), 113.4 (C^g), 110.9 (C^a), 56.0 (C^d), 54.4 (C^e), 45.3 (C^h), 24.0 (C^f).

^{1}H ^{1}H GCOSY (500.03 MHz, 300 K, benzene-d_6): δ^1H / δ^1H 5.92 / 5.37 (CH^b / CH^a), 5.37 / 5.92 (CH^a / CH^b), 2.56-5.44 / 1.69-1.59 (CH_2^e / CH_2^f), 1.69-1.59 / 2.56-5.44 (CH_2^f / CH_2^e).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 5.92 / 115.6 (CH^g), 5.75 / 113.4 (CH^b), 5.37 / 110.9 (CH^a), 3.40 / 56.0 (CH_2^d), 2.56-5.44 / 54.4 (CH_2^e), 1.69-1.59 / 24.0 (CH_3^f), 0.07 / 45.3 (CH_3^h).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 5.92 / 126.1, 115.6, 110.9 (CH^b / C^c, CH^b, CH^a), 5.75 / 113.4, 45.3 (CH^g / CH^g, CH_3^h), 5.37 / 126.1, 115.6 (CH^a / C^c, CH^b) 3.40 / 126.1, 115.6, 54.4 (CH_2^d / C^c, CH^b, CH_2^e), 2.56-5.44 / 54.4, 24.0 (CH_2^e / CH_2^e, CH_2^f), 1.69-1.59 / 54.4, 24.0 (CH_2^f / CH_2^e, CH_2^f), 0.07 / 113.4 (CH_3^h / CH^g).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, benzene-d_6): δ^1H / δ^{15}N: 1.78 / -322 (H^f / N).

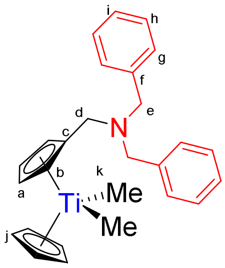
HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{16}H_{22}ONITi$ $[M-CH_4+CH_3OH]^+$ 292.11754 (Rel. ab: 65%, -2.0 ppm); found 292.11693, $C_{15}H_{18}NTi$, $[M-CH_3-CH_4]^+$ 260.09132; found 260.09106 (Rel. ab: 100%, -1.0 ppm).

---

[49] A satisfactory elemental analysis could not be obtained (low C) due to remaining LiCl salts.

[50] Ir spectroscopy was not measured due to the oily character of the compound.

8. Synthesis of **33**:



Chemical Formula: $C_{27}H_{31}NTi$
Molecular Weight: 417,4

An etheral solution of MeLi (1.1 mL, 1.6 M, 2.05 eq) was added dropwise to an etheral suspension of **11** (400 mg, 0.87 mmol, 1.0 eq) cooled down to -70°C. After warming up to room temperature, the initial crude red suspension turned into a yellow solution with a white precipitate after 1h of stirring. The solvent was then removed and the residue was dissolved in 20 mL of pentane. LiCl salts were removed by filtration through diatomaceous earth. The desired compound was obtained after evaporation of all volatiles as a yellow sticky oil. (228 mg, yield = 63 %).[49,50]

^{1}H NMR (500.03 MHz, 300 K, benzene-d_6): δ^1H: 7.41 (d, $^3J_{HH}$ = 7.2 Hz, 4H, H^g), 7.20 (t, $^3J_{HH}$ = 7.2 Hz, 4H, H^h), 7.10 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H^i), 5.89 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 5.63 (s, 5H, H^j), 5.53 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 3.58 (s, 4H, H^e), 3.30 (s, 4H, H^d), -0.06 (s, 6H, H^k). Traces of grease 0.29 (s) and pentane 1.31-1.14 (m), 0.87 (t).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, benzene-d_6): δ^{13}C: 140.0 (C^f), 129.2 (C^g), 128.6 (C^h), 127.3 (C^i), 124.0 (C^c), 115.6 (Cb^a), 113.4 (C^j), 111.9 (C^a), 58.2 (C^e), 52.9 (C^d), 45.6 (C^k). Traces of grease 1.4 (s) and pentane 34.4, 22.7, 14.3.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, benzene-d_6): δ^1H / δ^1H: 7.41 / 7.20 (CH^g / CH^h),7.20 / 7.41, 7.10 (CH^h / CH^g, CH^i), 7.10 / 7.20 (CH^i / CH^g), 5.89 / 5.53 (CH^b / CH^a), 5.53 / 5.89 (CH^a / CH^b).

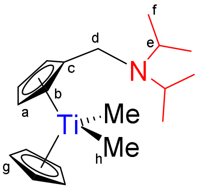
^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 7.41 / 129.2 (CH^g), 7.20 / 128.6 (CH^h), 7.10 / 127.3 (CH^i), 5.89 / 115.6 (CH^b), 5.63 / 113.4 (CH^j), 5.53 / 111.9 (CH^a), 3.58 / 58.2 (CH$_2^e$), 3.30 / 52.9 (CH$_2^d$), -0.06 / 45.6 (CH$_3^k$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 7.41 / 128.6, 58.2 (CH^g / CH^h, CH^e), 7.20 / 140.0, 129.2 (CH^h / C^f, CH^g), 7.10 / 129.2 (CH^i / CH^g) 5.89 / 124.0, 115.6, 111.9 (CH^b / C^c, CH^b, CH^a), 5.63 / 113.4, 45.6 (CH^j / CH^j, CH$_3^k$), 5.53 / 124.0, 115.6, 111.9 (CH^a/ C^c, CH^b CH^a), 3.58 / 140.0, 129.2, 128.6, 58.2, 52.9 (CH$_2^e$ / C^c, CH^g, CH^h, CH$_2^e$, CH$_2^d$), 3.30 / 124.0, 115.6, 58.2 (CH$_2^d$ / C^c, CH^b, CH$_2^e$), -0.06 / 113.4 (CH$_3^f$ / CH^j).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, benzene-d_6): δ^1H / δ^{15}N: 3.30 / -328 (H^d / N).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{27}H_{32}ONTi$ [M-CH_4+CH_3OH+H]$^+$ 434.19579; found 434.19598 (Rel. ab: 20%, 0.4 ppm); $C_{25}H_{24}NTi$ [M-2CH_4]$^+$ 386.13827, found 386.13899 (Rel. ab: 100%, 1.9 ppm).

9. Synthesis of **34**:



Chemical Formula: $C_{19}H_{31}NTi$
Molecular Weight: 321,3

Procedure A: An etheral solution of MeLi (1.8 mL, 1.53 M, 2 eq) was added dropwise to an etheral suspension of **12** (415 mg, 1.14 mmol, 1.0 eq) cooled down to -70°C. The crude red suspension turned into a yellow solution with a white precipitate after 1h of stirring at room temperature. The solvent was then removed and the residue was dissolved in 20 mL of pentane. LiCl salts were removed by filtration through diatomaceous earth. The desired compound was obtained after evaporation of all volatiles as a yellow precipitate. (250 mg, yield = 68 %).

Procedure B: An etheral solution of MeLi (1.0 mL, 1.67 M, 3.05 eq) was added dropwise to an etheral suspension **17** (218 mg, 0.5 mmol, 1 eq) cooled down to -70°C. The crude red suspension turned into a yellow solution with a white precipitate after 1h of stirring at room temperature. The solvent was then removed and the residue was dissolved in 20 mL of pentane. LiCl salts were removed by filtration through diatomaceous earth. Volatiles were removed *in vacuo*, yielding the **34** as a yellow precipitate. (120 mg, yield = 62 %).

Procedure C: A solution of **4-K** (840 mg, 3.86 mmol, 1 eq) in 25 mL of THF was added to a solution of $CpTiCl_3$ (840 mg, 3.86 mmol, 1 eq) in 25 mL of toluene, by cannulation at -30°C. The resulting solution was left to warm up to room temperature and then stirred overnight. The crude red solution was first evaporated. The deep-red oil obtained was dissolved in Et_2O, and MeLi (5.8 mL, 1.60 M, 2.4 eq) was added dropwise at -70°C. The crude red suspension turned into a yellow solution with a white precipitate after 1h of stirring at room temperature. The solvent was then removed and the residue was dissolved in 20 mL of pentane. LiCl salts were removed by filtration through diatomaceous earth. The desired compound was obtained after evaporation of all volatiles as a yellow precipitate. (830 mg, yield = 67 %).[49]

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^1H: 6.09 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^a), 6.05 (s, 5H, H^g), 5.76 (apparent t, $^3J_{HH} = {}^4J_{HH} = 2.6$ Hz, 2H, H^b), 3.38 (s, 2H, H^d), 3.11 (hept, $^3J_{HH} = 6.6$ Hz, 2H, H^e), 1.03 (d, $^3J_{HH} = 6.6$ Hz, 12H, H^f), -0.21 (s, 6H, H^h).

^{13}C{^{1}H} NMR (150.9 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 129.5 (C^c), 116.1 (C^a), 113.7 (C^g), 111.5 (C^b), 48.3 (C^e), 44.9 (C^d), 44.4 (C^h), 21.2 (C^f).

^1H ^1H COSY (600.23 MHz, 300 K, dichloromethane-d_2): δ^1H / δ^1H: 6.09 / 5.76 (CH^a / CH^b), 5.76 / 6.09 (CH^b / CH^a), 3.11 / 1.03 (CH_2^e / CH_3^f), 1.03 / 3.11 (CH_3^f / CH_2^e).

^1H ^{13}C HMQC (600.23 MHz / 150.9 MHz, 300 K, dichloromethane-d_2): δ^1H / $\delta^{13}C$: 6.09 / 116.1 (CH^a), 6.05 / 113.7 (CH^g), 5.76 / 111.5 (CH^b), 3.38 / 44.9 (CH_2^d), 3.11 / 48.3 (CH^e), 1.03 / 21.2 (CH_3^f), -0.21 / 44.4 (CH_3^h).

^1H ^{13}C HMBC (600.23 MHz / 150.9 MHz, 300 K, dichloromethane-d_2): δ^1H / $\delta^{13}C$: 6.09 / 116.1, 111.5 (CH^a / CH^a, CH^b), 6.05 / 113.7 (CH^g / CH^g), 5.76 / 129.5, 116.1 (CH^b / C^c, CH^a), 3.38 / 129.5, 116.1, 48.3 (CH_2^d / C^c, CH^a, CH^e), 3.11 / 21.2 (CH^e / CH_3^f), 1.03 / 48.3, 21.2 (CH_3^f / CH^e, CH_3^f), -0.21 / 44.4 (CH_3^h / CH_3^h).

^1H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^1H / $\delta^{15}N$: 1.03 / -322 (H^f / N).

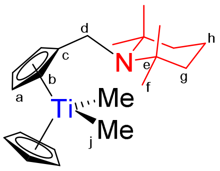
HRMS (Positive mode ESI, dichloromethane + methanol): m/z calcd. for $C_{19}H_{32}NTi$ [M - Me + MeOH]$^+$ 338.19578; found 338.19578 (Rel. ab: 40%, 0.02 ppm).

IR (ATR) ν [cm-1]

MIR: 2965; 2884; 1379; 1199; 1034; 813; 475.

FIR: 620; 566; 476; 399; 236; 165.

10. Synthesis of **35**:



Chemical Formula: $C_{22}H_{35}NTi$
Molecular Weight: 361,4

Procedure A: An etheral solution of MeLi (1.6 mL, 1.25 M, 2 eq) was added dropwise to an etheral suspension of **13** (400 mg, 1.0 mmol, 1 eq) cooled down to -70°C. The crude red suspension turned into a yellow solution with a white precipitate after 1h of stirring at room temperature. The solvent was then removed and the residue was dissolved in 20 mL of pentane. LiCl salts were removed by filtration through diatomaceous earth. The desired compound was obtained after evaporation of all volatiles as a yellow precipitate. (260 mg, yield = 72 %).

Procedure B: An etheral solution of MeLi (1.0 mL, 1.67 M, 3.05 eq) was added dropwise to an etheral suspension of **18** (240 mg, 0.54 mmol, 1.0 eq) cooled down to -70°C. The crude red suspension turned into a yellow solution with a white precipitate after 1h of stirring at room temperature. The solvent was then removed and the residue was dissolved in 20 mL of pentane. LiCl salts were removed by filtration through diatomaceous earth. The desired compound was obtained after evaporation of all volatiles as a yellow precipitate. (115 mg, yield = 63 %).

Procedure C: An etheral solution of **5-K** (1.53 g, 5.51 mmol, 1.0 eq) dissolved in 20 mL of toluene was added to a solution of CpTiCl$_3$ (1.2 g, 3.17 mmol, 1 eq) in 20 mL of toluene. Both solutions were cooled down at -15°C in the glovebox where the reaction was launched. The resulting solution was left to warm up to room temperature and then stirred overnight. Toluene was then evaporated and the red residue was dissolved in Et$_2$O, and MeLi (7.2 mL, 1.61 M, 2.1 eq) was added dropwise at -70°C. The crude red suspension turned into a yellow solution with a white precipitate after 1h of stirring at room temperature. The solvent was then removed and the residue was dissolved in 40 mL of pentane. LiCl salts were removed by filtration through diatomaceous earth. The desired compound was obtained after evaporation of all volatiles as a yellow precipitate. (1.1 g, overall yield = 57 %).[49]

^{1}H NMR (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^1H: 6.10 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^a), 6.05 (s, 5H, H^i), 5.76 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 3.43 (s, 2H, H^d), 1.60-1.52 (m, 2H, H^h), 1.48-1.40 (m, 4H, H^g), 1.07 (s, 12H, H^f), -0.21 (s, 6H, H^j).

^{13}C{^{1}H} NMR (150.9 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 134.6 (C^c), 115.1 (C^a), 113.6 (C^i), 112.2 (C^b), 55.7 (C^e), 44.8 (C^d), 44.5 (C^g), 42.1 (C^f), 25.7-28.1 (C^j), 18.4 (C^h).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, dichloromethane-d$_2$): δ^1H / δ^1H: 6.10 / 5.76 (CH^a / CH^b), 5.76 / 6.10 (CH^b / CH^a), 1.60-1.52 / 1.48-1.40 (CH$_2$^{h} / CH$_2$^{g}), 1.48-1.40 / 1.60-1.52 (CH$_2$^{g} / CH$_2$^{h}).

^{1}H ^{13}C HMQC (600.23 MHz / 150.9 MHz, 300 K, dichloromethane-d$_2$): δ^1H / δ^{13}C: 6.10 / 115.1 (CH^a), 6.05 / 113.6 (CH^i), 5.76 / 112.2 (CH^b), 3.43 / 44.5 (CH$_2$^{d}), 1.60-1.52 / 18.4 (CH$_2$^{h}), 1.48-1.40 / 42.1 (CH$_2$^{g}), 1.07: 25.7-28.1 (CH$_3$^{f}), -0.21 / 44.8 (CH$_3$^{j}).

^{1}H ^{13}C HMBC (600.23 MHz / 150.9 MHz, 300 K, dichloromethane-d$_2$): δ^1H / δ^{13}C: 6.10 / 134.6, 115.1, 112.2 (CH^a / C^c, CH^a, CH^b), 6.05 / 113.6 (CH^i / CH^i), 5.76 / 134.6, 115.1 (CH^b / C^c, CH^a), 3.43 / 134.6, 115.1, 55.7 (CH$_2$^{d} / C^c, CH^a, C^e), 1.60-1.52 / 55.7, 44.5 (CH^h / C^e, CH$_2$^{g}), 1.48-1.40 / 55.7, 44.5, 25.7-28.1, 18.4 (CH$_2$^{h} / C^e, CH$_2$^{g}, CH$_2$^{h}), 1.07 / 55.7, 44.5, 25.7-28.1 (CH$_3$^{f} / C^e, CH$_2$^{h}, CH$_3$^{f}), -0.21 / 44.8 (CH$_3$^{j}).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$): δ^1H / δ^{15}N: 1.07 / -308 (H^f / N).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for C$_{22}$H$_{36}$NTi [M+H]$^+$ 362.23238; found 362.23152 (Rel. ab: 65%, -1.8 ppm).

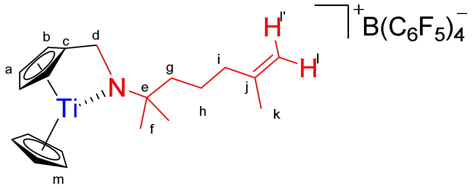
IR (ATR) ν [cm-1]

MIR: 2965; 1492; 1259; 1130; 1022; 810; 392.

FIR: 471; 403; 254; 187.

Elemental Analysis: % calcd. For C$_{22}$H$_{35}$NTi: C, 73.12; H, 9.76; N, 3.88; Found: C, 70.84; H, 9.50; N, 3.42.

11. Synthesis of **36**:



Chemical Formula: $C_{44}H_{28}BF_{20}NTi$
Molecular Weight: 1009,4

A solution of **35** (200 mg, 0.56 mmol, 1 eq) and $[Ph_3C][B(C_6F_5)_4]$ (511 mg, 0.56 mmol, 1 eq) was prepared in 2 mL of C_6H_5Br. The yellow solid mixture turned deep black-red in solution. After 5 min of stirring the solution was tried to precipitate in a vigorously stirred pentane solution (8 mL) but a red oil was formed instead. Precipitation attempt via C_6H_5Cl failed and a red oil was obtained again. A sticky red-brown precipitate was obtained after drying in vacuo (510 mg, 90 %).[47]

^{1}H NMR (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 5.90 (apparent t, $^{3}J_{HH} = {}^{4}J_{HH} = 2.5$ Hz, 2H, H^{a}), 5.85 (s, 5H, H^{m}), 5.66 (apparent t, $^{3}J_{HH} = {}^{4}J_{HH} = 2.6$ Hz, 2H, H^{b}), 4.82 (bs, 1H, H$^{l'}$), 4.75 (bs, 1H, H^{l}), 4.42 (s, 2H, H^{d}), 1.92 (t, $^{3}J_{HH} = 7.1$ Hz, 2H, H^{i}), 1.70 (s, 3H, H^{k}), 1.38-1.23 (m, 2H, H^{g}), 1.15-1.02 (m overlapping with H^{f}, 2H, H^{h}) 1.09 (s overlapping with H^{h}, 6H, H^{f}).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, bromobenzene-d$_5$): δ^{13}C: 148.8 (dm, $^{1}J_{CF} = 240$ Hz, o-CF), 144.8 (C^{j}), 138.5 (dm, $^{1}J_{CF} = 240$ Hz, *p*-CF), 136.9 (dm, $^{1}J_{CF} = 240$ Hz, *m*-CF), 125.6-123.6 (bs, *ipso*-C^{B}), 118.8 (C^{b}), 116.2 (C^{a}), 114.3 (C^{m}) 112.4 (C^{c}), 111.0 (C^{l}), 74.7 (C^{e}), 52.1 (C^{d}), 42.2 (C^{g}), 37.9 (C^{i}), 28.7 (C^{f}), 22.7 (C^{h}), 22.6 (C^{k}). (131.6, 130.2, 127.0, 122.7 belong to residual C_6H_5Cl).

^{1}H ^{1}H COSY (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 5.90 / 5.66 (CH^{a} / CH^{b}), 5.66 / 5.90 (CH^{b} / CH^{a}), 4.82 / 4.75, 1.70 (H$^{l'}$ / H^{l}, CH$_3^{k}$), 4.75 / 4.82, 1.92 (H^{l} / H$^{l'}$, CH$_2^{i}$), 1.92 / 1.15-1.02, 4.75 (CH$_2^{i}$ / CH$_2^{h}$, H^{l}), 1.70 / 4.82 (CH$_3^{k}$ / H$^{l'}$), 1.38-1.23 / 1.15-1.02 (CH$_2^{g}$/ CH$_2^{h}$), 1.15-1.02 / 1.92, 1.38-1.23 (CH$_2^{h}$ / CH$_2^{i}$, CH$_2^{g}$).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 5.90 / 116.2 (CH^{a}), 5.85 / 114.3 (CH^{m}), 5.66 / 118.8 (CH^{b}), 4.82, 4.75 / 111.0 (CH$_2^{l}$), 4.42 / 52.1 (CH$_2^{d}$), 1.92 / 37.9 (CH$_2^{i}$), 1.70 / 22.6 (CH$_3^{k}$), 1.38-1.23 / 42.2 (CH$_2^{g}$), 1.15-1.02 / 22.7 (CH$_2^{h}$), 1.09 / 28.7 (CH$_3^{f}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 4.82, 4.42 / 37.9, 22.7, 22.6 (H^{l}, H$^{l'}$ / CH$_2^{i}$, CH$_2^{h}$, CH$_3^{k}$), 4.42 / 118.8, 112.4, 74.7 (CH$_2^{d}$ / CH^{a}, C^{c}, C^{e}), 1.92 / 144.8, 111.0, 42.2, 22.6 (CH$_2^{i}$ / C^{j}, CH$_2^{l}$, CH$_2^{g}$, CH$_3^{k}$), 1.70 / 144.8, 111.0, 37.9 (CH$_3^{k}$ / C^{j}, CH$_2^{l}$, CH$_2^{i}$), 1.38-1.23 / 74.7, 28.7 (CH$_2^{g}$ / C^{e}, CH$_3^{f}$), 1.15-1.02 / 74.7, 42.2, 28.7 (CH$_2^{h}$/ C^{e}, CH$_2^{g}$, CH$_3^{f}$), 1.09 / 74.7, 42.2, 28.7 (CH$_3^{f}$ / C^{e}, CH$_2^{g}$, CH$_3^{f}$).

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -16.2 ($\nu_{1/2} = 21$ Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -16.2 ($\nu_{1/2}$ = 21 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.8 (m, 8F, *o*-F), -161.8 (t, $^3J_{FF}$ = 21 Hz, 8F, *p*-F), -165.7 (m, 8F, *m*-F).

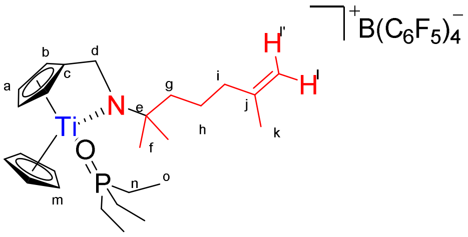
^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.8 (d, $^3J_{FF}$ = 11 Hz, 8F, *o*-F), -161.8 (t, $^3J_{FF}$ = 21 Hz, 8F, *p*-F), -165.7 (m, 8F, *m*-F).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 1.09 / -363 (H^f / N).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{20}H_{28}NTi$ [M]$^+$ 330.16957; found 330.16940 (Rel. ab: 100%, -6.2 ppm); for $C_{20}H_{30}ONTi$ [M+H$_2$O]$^+$ 348.18014; found 348.17798 (Rel. ab: 95%, -0.5 ppm).

Elemental Analysis: % calcd for $C_{28}H_{38}NClOTi$: C, 68.92; H, 7.85; N, 2.87; Found: C, 68.07; H, 7.56; N, 2.72.

12. Synthesis of **37:**



Chemical Formula: $C_{50}H_{43}BF_{20}NOPTi$
Molecular Weight: 1143,5

A solution of **35** (60 mg, 0.16 mmol, 1 eq) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (153.3 mg, 0.16 mmol, 1 eq) was prepared in 1 mL of C$_6$H$_5$Br. The yellow solid mixture turned deep black-red in solution. After 10 min of stirring OPEt$_3$ (22.3 mg, 0.16 mmol, 1eq) was added to the solution which was stirred for additional 30 min. The lighter red resulting solution was added in a vigorously stirred pentane solution (8 mL) and yield to a red oil. The whole solution was stored in the freezer (-15°C) for two days. The resulting red oil was isolated and dried after removing the yellow filtrate. The red precipitate obtained was dissolved in dichloromethane (1 mL) and layered with pentane (4 mL) and stored overnight in the freezer (-15°C). The microcrystalline red solid was isolated and dried *in vacuo* (160 mg, 84 %).[47]

^{1}H NMR (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 6.75 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H^a), 6.34 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H^b), 6.16 (s, 5H, H^m), 5.98 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H$^{a'}$), 5.48 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H$^{b'}$), 4.88 (d, $^2J_{HH}$ = 14.7 Hz , 1H, H^d), 4.76 (m, 1H, H$^{l'}$), 4.71 (m, 1H, H^l), 4.52 (d, $^2J_{HH}$ = 14.7 Hz , 1H, H$^{d'}$), 2.05 (t, $^3J_{HH}$ = 7.0 Hz, 2H, H^i), 1.83 (dq, $^2J_{HP}$ = 11.9 Hz, $^3J_{HH}$ = 7.7 Hz, 6H, H^n), 1.74 (s, 3H, H^k), 1.72-1.62 (m, 1H, CH^g), 1.45-1.26 (m overlapping with H^f and H$^{f'}$, 3H, H$^{g/h}$), 1.33 (s overlapping with H$^{g/h}$, 3H, H$^{f/f'}$), 1.30 (s overlapping with H$^{g/h}$, 3H, H$^{f'/f}$), 1.17 (dt, $^3J_{HP}$ = 17.8 Hz, $^3J_{HH}$ = 7.0 Hz, 9H, H^o).

^{1}H{^{31}P} NMR (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 6.75 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H^a), 6.34 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H^b), 6.16 (s, 5H, H^m), 5.98 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H$^{a'}$), 5.48 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H$^{b'}$), 4.88 (d, $^2J_{HH}$ = 14.7 Hz , 1H, H^d), 4.76 (br s, 1H, H$^{l'}$), 4.71 (br s, 1H, H^l), 4.52 (d, $^2J_{HH}$ = 14.7 Hz , 1H, H$^{d'}$), 2.05 (t, $^3J_{HH}$ = 7.0 Hz, 2H, H^i), 1.83 (bq, $^3J_{HH}$ = 7.7 Hz, 6H, H^n), 1.74 (s, 3H, H^k), 1.72-1.62 (m, 1H, CH^g), 1.45-1.26 (m overlapping with H^f and H$^{f'}$, 3H, H$^{g/h}$), 1.33 (s overlapping with H$^{g/h}$, 3H, H$^{f/f'}$), 1.30 (s overlapping with H$^{g/h}$, 3H, H$^{f'/f}$), 1.17 (bt, $^3J_{HH}$ = 7.0 Hz, 9H, H^o).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 148.7 (dm, $^1J_{CF}$ = 250 Hz, o-CF), 146.2 (C^j), 138.8 (dm, $^1J_{CF}$ = 250 Hz, *p*-CF), 136.9 (dm, $^1J_{CF}$ = 250 Hz, *m*-CF), 125.3-124.1 (bs overlapping with C^b, *ipso*-C^B), 124.3 (overlapping with ipso-C^B, C^b), 119.8 (C^a), 113.8 (C^m), 113.5 (C$^{a'}$), 112.0 (C^c), 110.8 (C^l), 110.5 (C$^{b'}$), 70.9 (C^e), 50.8 (C^d), 42.5 (C^g), 38.7 (C^i), 28.9 (C^f), 28.7 (C$^{f'}$), 23.6 (C^h), 22.6 (C^k), 18.9 (d, $^2J_{CP}$ = 67.1 Hz, C^n), 6.1 (d, $^3J_{CP}$ = 4.7 Hz, C^o). Pentane: 34.7, 22.9, 14.4.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{1}H: 6.75 / 6.34, 5.98, 5.48 (CH^a / CH^b, CH$^{a'}$, CH$^{b'}$), 6.34 / 6.75, 5.98, 5.48 (CH^b / CH^a, CH$^{a'}$, CH$^{b'}$), 6.16 / 113.8 (CH^m), 5.98 / 6.75, 6.34, 5.48 (CH$^{a'}$ / CH^a, CH^b, CH$^{b'}$), 5.48 / 6.75, 6.34, 5.98 (CH$^{b'}$ / CH^a, CH^b, CH$^{a'}$), 4.88 / 4.52 (CH$_2^{d/d'}$), 4.76 / 4.71, 1.74 (H$^{l'}$ / H^l, CH$_3^k$), 4.71 / 4.76 (H^l / H$^{l'}$), 4.52 / 4.88 (CH$_2^{d'/d}$), 2.05 / 4.71, 1.45-1.26 (H^i / H^l, CH$_2^{h/g}$), 1.83 / 1.17 (CH$_2^n$ / CH$_3^o$), 1.74 / 4.76 (CH$_3^k$ / H$^{l'}$), 1.72-1.62 / 1.45-1.26 (CH$_2^g$ / CH$_2^{h/g}$), 1.45-1.26 / 1.72-1.62, 1.45-1.26 (CH$_2^g$/ CH$_2^{h/g}$), 1.17 / 1.83 (CH$_3^o$ / CH$_2^n$).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 6.75 / 119.8 (CH^a), 6.34 / 124.3 (CH^b), 6.16 / 113.8 (CH^m), 5.98 / 113.5 (CH$^{a'}$), 5.48 / 110.5 (CH$^{b'}$), 4.88, 4.52 / 50.8 (CH$_2^d$), 4.76, 4.71 / 110.8 (CH$_2^l$), 2.05 / 38.7 (CH$_2^i$), 1.83 / 18.9 (CH$_2^n$), 1.74 / 22.6 (CH$_3^k$), 1.72-1.62 / 42.5 (CH$_2^g$), 1.45-1.26 / 42.5, 23.6 (CH$_2^{g/h}$), 1.33 / 23.6 (CH$_3^f$), 1.30 / 28.7 (CH$_3^{f'}$), 1.17 / 6.06 (CH$_3^o$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 6.75 / 124.3, 113.5, 112.0, 110.5 (CH^a / CH^b, CH$^{a'}$, C^c, CH$^{b'}$), 6.34 / 119.8, 113.5, 112.0, (CH^b / CH^a, CH$^{a'}$, C^c), 6.16 / 113.8 (CH^m / CH^m), 5.98 / 112.0, 110.5 (CH$^{a'}$ / C^c, CH$^{b'}$), 5.48 / 113.5, 112.0, 110.5 (CH$^{b'}$ / CH$^{a'}$, C^c, CH$^{b'}$), 4.88 / 124.3, 112.0, 110.5, 70.9 (CH$_2^d$ / CH^b, C^c, CH$^{b'}$, C^e), 4.76, 4.71 / 38.7, 22.6 (H^l, H$^{l'}$ / CH$_2^i$, CH$_3^k$), 4.52 / 124.3, 112.0, 110.5, 70.9 (CH$_2^d$ / CH^b, C^c, CH$^{b'}$, C^e), 2.05 / 146.2, 110.8, 42.5, 23.6, 22.6 (CH$_2^i$ / C^j, CH$_2^l$, CH$_2^g$, CH$_3^k$), 1.83 / 6.06 (CH$_2^n$ / CH$_3^o$), 1.74 / 146.2, 110.8, 42.5, 23.6 (CH$_3^k$ / C^j, CH$_2^l$, CH$_2^g$, CH$_2^h$), 1.72-1.62 / 70.9, 28.9, 28.7 (CH$_2^g$ / C^e, CH$_3^f$, CH$_3^{f'}$), 1.45-1.26 / 70.9, 28.9, 28.7, 22.6 (CH$_2^{g/h}$ / C^e, CH$_3^f$, CH3f', CH$_3^k$), 1.33 / 70.9, 42.5, 28.7 (CH$_3^f$/ C^e, CH$_2^g$, CH$_3^{f'}$), 1.30 / 70.9, 42.5, 28.9 (CH$_3^{f'}$ / C^e, CH$_2^g$, CH$_3^f$), 1.17 / 18.9 (CH$_3^o$ / CH$_2^n$).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, dichloromethane-d$_2$): δ^{31}P: s 79.5 ($\nu_{1/2}$ = 2.5 Hz)

^{31}P NMR (202.46 MHz, 300 K, dichloromethane-d$_2$): δ^{31}P: m 79.5 ($\nu_{1/2}$ = 74.5 Hz)

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, dichloromethane-d$_2$): δ^{11}B: -16.6 ($\nu_{1/2}$ = 21 Hz).

^{11}B NMR (160.42 MHz, 300 K, dichloromethane-d$_2$): δ^{11}B: -16.6 ($\nu_{1/2}$ = 21 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -133.1 (apparent d, $^{3}J_{FF}$ = 11 Hz, 8F, *o*-F), -163.7 (t, $^{3}J_{FF}$ = 21 Hz, 4F, *p*-F), -167.6 (apparent t, $^{3}J_{FF}$ = 21 Hz, 8F, *m*-F).

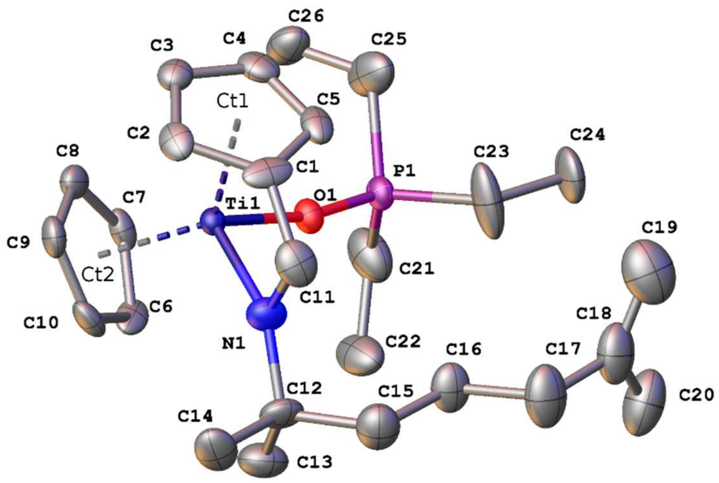
^{19}F NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -133.1 (apparent d, $^{3}J_{FF}$ = 11 Hz, 8F, *o*-F), -163.7 (t, $^{3}J_{FF}$ = 21 Hz, 4F, *p*-F), -167.6 (apparent t, $^{3}J_{FF}$ = 21 Hz, 8F, *m*-F).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{15}N: 4.88, 4.52, 1.33, 1.30 / -23.3 (H^{d}, H$^{d'}$, H^{f}, H$^{f'}$ / N).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{26}H_{43}NOPTi$ [M]$^{+}$ 464.25563; found 464.25493 (Rel. ab 65%, 1.8 ppm); for $C_{20}H_{37}NOPTi$ [M-C_6H_6]$^{+}$ 386.20867; found 386.20797 (Rel. ab 100%, -1.5 ppm).

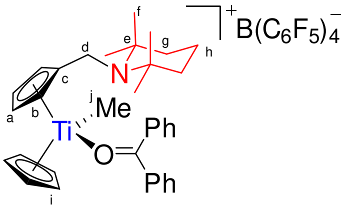
Elemental Analysis: % calcd for $C_{50}H_{43}BF_{20}NOPTi$ + $(C_5H_{12})_{0.2}$: C, 52.88; H, 3.94; N, 1.21; Found: C, 52.50; H, 4.15; N, 1.29.

XRD:



Crystal Data. $C_{50}H_{41}BF_{20}NOPTi$, M_r = 1140.01, triclinic, P-1 (No. 2), a = 16.747 Å, b = 17.135 Å, c = 19.906 Å, α = 71.61°, β = 66.61°, γ = 82.42°, V = 4975.0 Å^3, T = 115 K, Z = 4, Z' = 2, μ(MoK$_\alpha$) = 0.318, 68495 reflections measured, 17489 unique (R_{int} = 0.0735) which were used in all calculations. The final wR_2 was 0.3090 (all data) and R_1 was 0.0928 (I > 2(I)).

13. Synthesis of **38-B**:



Chemical Formula: $C_{58}H_{42}BF_{20}NOTi$
Molecular Weight: 1207,6

A solution of benzophenone (50.5 mg, 0.28 mmol, 1 eq) and **35** (100 mg, 0.28 mmol, 1 eq), was prepared in 1 mL of C_6H_5Br. Then, $[Ph_3C][B(C_6F_5)_4]$ was added to the yellow solution which turned red rapidly. After 5 mn of stirring, the compound was crystalized by slow diffusion of heptane at -15°C for two weeks. Crystals were isolated, washed twice with 2 mL of pentane and finally dried in vacuo to yield to a microcrystalline red powder (233 mg, 70%). Suitable crystals for XRD analysis were obtained by this process.[47]

^{1}H NMR (500.03 MHz, 263 K, bromobenzene-d$_5$): δ^{1}H: 7.50 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, *p*-CH^{benzo}), 7.32 (t overlapping with solvent signal, $^{3}J_{HH}$ = 7.2 Hz, 4H, *m*-CH^{benzo}), 7.22 (d, $^{3}J_{HH}$ = 7.2 Hz, 4H, *o*-CH^{benzo}), 6.32 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.6 Hz, 1H, H$^{b'}$), 6.01 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.6 Hz, 1H, H^{b}), 5.85 (s, 5H, H^{i}), 5.83 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.6 Hz, 1H, H^{a}), 5.48 (apparent q, $^{3}J_{HH}$= $^{4}J_{HH}$ = 2.6 Hz, 1H, H$^{a'}$), 3.21 (d, $^{2}J_{HH}$ = 16.4 Hz, 1H, H^{d}), 3.12 (d, $^{2}J_{HH}$ = 16.4 Hz, 1H, H$^{d'}$), 1.39-1.29 (m, 2H, H^{h}), 1.27-1.19 (m overlapping with H^{j}, 4H, H^{g}), 1.24 (s overlapping with H^{g}, 3H, H^{j}), 0.72 (s, 6H, H^{f}), 0.63 (s, 6H, H^{f}).

^{13}C{^{1}H} NMR (125.75 MHz, 263 K, bromobenzene-d$_5$): δ^{13}C: 211.0 (C=O), 148.8 (br d, $^{1}J_{CF}$ = 240 Hz, *o*-CF), 141.9 (C^{c}), 138.7 (br d, $^{1}J_{CF}$ = 240 Hz, *p*-CF), 137.7 (*p*-CH^{benzo}), 136.8 (br d, $^{1}J_{CF}$ = 240 Hz, *m*-CF), 133.2 (*ipso*-C^{benzo}), 132.6 (*o*-CH^{benzo}), 129.7 (*m*-CH^{benzo}), 125.6-123.9 (bs, *ipso*-C^{B}), 121.8 (CH$^{b'}$), 118.4 (CH^{b}), 116.0 (C^{i}), 112.7 (CH^{a}), 111.2 (CH$^{a'}$), 55.3 (C^{e}), 54.3 (C^{j}), 43.4 (C^{d}), 41.2 (C^{g}), 29.1-26.6 (C^{f}), 17.9 (C^{h}). C_6H_5Br 131.7, 130.4, 127.2, 122.8.

^{1}H ^{1}H COSY (500.03 MHz, 263 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 7.50 / 7.32 (*p*-CH^{benzo} / *m*-CH^{benzo}), 7.32 / 7.50, 7.22 (*m*-CH^{benzo} / *p*-CH^{benzo}, (*o*-CH^{benzo}), 7.22 / 7.32 (*o*-CH^{benzo} / *m*-CH^{benzo}), 6.32 / 5.48 (CH$^{b'}$ / CH$^{a'}$), 6.01 / 5.83 (CH^{b} / CH^{a}), 5.83 / 6.01 (CH^{a} / CH^{b}), 5.48 / 6.32 (CH$^{a'}$/ CH$^{b'}$), 3.21 / 3.12 (CH$_2^{d/d'}$), 3.12 / 3.21 (CH$_2^{d'/d}$), 1.39-1.29 / 1.27-1.19 (CH$_2^{h}$ / CH$_2^{g}$), 1.27-1.19 / 1.39-1.29 (CH$_2^{g}$ / CH$_2^{h}$).

^{1}H ^{13}C HMQC (500.03 MHz / 125.03 MHz, 263 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.50 / 137.7 (*p*-CH^{benzo}), 7.32 / 129.7 (*m*-CH^{benzo}), 7.22 / 132.6 (*o*-CH^{benzo}), 6.32 / 121.8 (CH$^{b'}$), 6.01 / 118.4 (CH^{b}), 5.85 / 116.0 (CH^{i}), 5.83 / 112.7 (CH^{a}), 5.48 / 111.2 (CH$^{a'}$), 3.21, 3.17 / 43.4 (CH$_2^{d}$), 1.39-1.29 / 17.9 (CH$_2^{h}$), 1.27-1.19 / 41.2 (CH$_2^{g}$), 1.24 / 54.3 (CH$_3^{j}$), 0.72 / 29.1-26.6 (CH$_3^{f}$), 0.63 / 29.1-26.6 (CH$_3^{f}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.03 MHz, 263 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.50 / 132.6 129.7 (*p*-CH^{benzo} / *o*-CH^{benzo},, *m*-CH^{benzo}), 7.32 / 137.7, 132.2, 129.7 (*m*-CH^{benzo} / *p*-CH^{benzo},, *ipso*-C^{benzo}, *m*-CH^{benzo}), 7.22 / 211.0, 137.7, 132.6 (*o*-CH^{benzo} / C=O, *p*-C^{benzo}, *o*-CH^{benzo}), 6.32 / 141.9, 118.4, 112.7, 111.2 (CH$^{b'}$ / C^{c}, CH^{b}, CH^{a}, CH$^{a'}$), 6.01 / 141.9, 121.8, 112.7, 111.2 (CH^{b} / C^{c}, CH$^{b'}$, CH^{a}), 5.85 / 116.0 (CH^{i} / CH^{i}), 5.83 / 141.9, 121.8, 111.2 (CH^{a} / C^{c}, CH$^{b'}$, CH$^{a'}$), 5.48 / 141.9, 121.8, 118.5, 112.7 (CH$^{b'}$ / C^{c}, CH$^{b'}$, CH^{b}, CH^{a}), 3.21, 3.17 / 141.9, 121.8, 118.5, 55.3 (CH$_2^{d}$ / C^{c}, CH^{b}, CH$^{b'}$, C^{e}), 1.39-1.29 / 55.3, 41.2 (CH$_2^{h}$ / C^{e}, CH$_2^{g}$), 1.27-1.19 / 55.3, 41.2, 17.3

(CH_2^g / C^e, CH_2^g, CH_2^h), 1.24 / 121.8, 116.0 (CH_3^f / CH^b, CH^i), 0.72, 0.63 / 55.3, 41.2, 29.1-26.6 ($CH_3^{f/f'}$ / C^e, CH_2^g, $CH_3^{f'/f}$).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 263 K, bromobenzene-d_5): δ^1H / δ^{15}N: 0.72, 0.63 / -306 (H^f, $H^{f'}$ / N).

^{11}B{^{1}H} NMR (160.42 MHz, 263 K, bromobenzene-d_5): δ^{11}B: -16.0 ($\nu_{1/2}$ = 24 Hz).

^{11}B NMR (160.42 MHz, 263 K, bromobenzene-d_5): δ^{11}B: -16.0 ($\nu_{1/2}$ = 24 Hz).

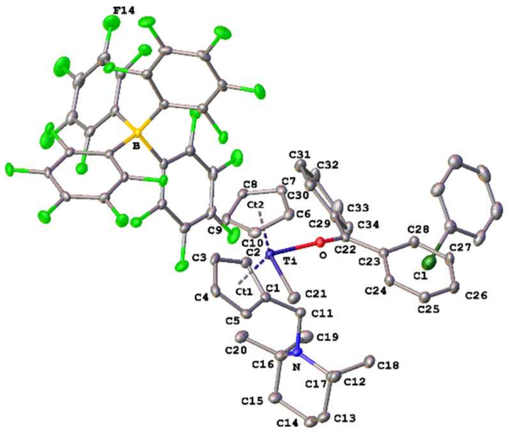
^{19}F{^{1}H} NMR (470.45 MHz, 263 K, bromobenzene-d_5): δ^{19}F: -131.5 (d, $^3J_{FF}$ = 15 Hz, 8F, *o*-F), -161.3 (t, $^3J_{FF}$ = 19 Hz, 8F, *p*-F), -165.2 (m, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 263 K, bromobenzene-d_5): δ^{19}F: -131.5 (d, $^3J_{FF}$ = 15 Hz, 8F, *o*-F), -161.3 (t, $^3J_{FF}$ = 19 Hz, 8F, *p*-F), -165.2 (m, 8F, *m*-F).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{20}H_{30}ONTi$ [M-benzophenone-CH_4+H_2O]$^+$ 348.18014; found 348.17798 (Rel. ab: 75%, -2.6 ppm).

Elemental Analysis: % calcd for $C_{20}H_{29}Cl_2NTi$: C, 57.59; H, 3.51; N, 1.16; Found: C, 57.58; H, 3.58; N, 1.00.

XRD:

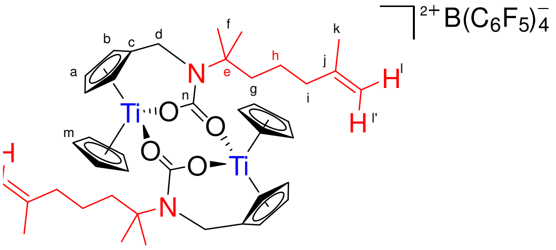


Compound	q121515_0m
Formula	$C_{61}H_{44.5}BCl_{0.5}F_{20}NOTi$
$D_{calc.}$/ g cm^{-3}	1.576
μ/mm^{-1}	0.302
Formula Weight	1263.91
Colour	red
Shape	prism
Size/mm^3	0.12×0.12×0.07
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	11.6624(6)
b/Å	12.6758(7)
c/Å	18.7399(12)
α/°	75.383(3)
β/°	83.631(3)
γ/°	87.410(3)
V/Å^3	2663.7(3)
Z	2
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.589
Θ_{max}/°	27.659
Measured Refl.	86538
Independent Refl.	12289
Reflections Used	6785
R_{int}	0.0732
Parameters	807
Restraints	36
Largest Peak	0.384
Deepest Hole	-0.394
GooF	0.880
wR_2 (all data)	0.0871
wR_2	0.0750
R_1 (all data)	0.0936
R_1	0.0385

Experimental. Single red prism-shaped crystals of (**q121515_0m**) were obtained by recrystallisation from diffusion of heptane in a bromobenzene solution at -15°C. A suitable crystal (0.12×0.12×0.07) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2017/1 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{61}H_{44.5}BCl_{0.5}F_{20}NOTi$, M_r = 1263.91, triclinic, P-1 (No. 2), a = 11.6624(6) Å, b = 12.6758(7) Å, c = 18.7399(12) Å, α = 75.383(3)°, β = 83.631(3)°, γ = 87.410(3)°, V = 2663.7(3) Å^3, T = 115 K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 0.302, 86538 reflections measured, 12289 unique (R_{int} = 0.0732) which were used in all calculations. The final wR_2 was 0.0871 (all data) and R_1 was 0.0385 (I > 2(I)).

14. Synthesis of **39**:



emical Formula: $C_{90}H_{56}BF_{40}N_2O_4Ti_2$
Molecular Weight: 2095,9

A solution of **36** (200 mg, 0.56 mmol, 1 eq) and $[Ph_3C][B(C_6F_5)_4]$ (511 mg, 0.56 mmol, 1 eq) was prepared in 2 mL of C_6H_5Br in a 15 mL Schlenk flask. The yellow solid mixture turned deep black-red in solution. After 5 mn of stirring the solution was degassed, 1 bar of dry CO_2 was introduced in the Schlenk tube and the solution was stirred at room temperature for 5 mn until a red oil was formed. Yellow supernatant was removed in the Glovebox, and the remaining oil was washed with 2 mL of C_6H_5Br and then twice with 5 mL of pentane. Traces of C_6H_5Br were removed by solubilisation of the residue in 2 mL of dichloromethane and precipitation with pentane (10 mL). 1h of decantation was required before removal of the supernatant. The red oil was finally dried in vacuo to yield a light-orange powder (200 mg, 66%).[47]

^{1}H NMR (500.03 MHz, 300 K, dichloromethane-d_2): $\delta^{1}H$: 7.50 (apparent q, $^{3}J_{HaHb}$ = $^{3}J_{HaHa'}$ = $^{4}J_{HaHb'}$ = 2.5 Hz, 2H, H^{a}), 6.92 (apparent q, $^{3}J_{HbHa}$ = $^{4}J_{HbHb'}$ = $^{4}J_{HbHa'}$ = 2.5 Hz, 2H, H^{b}), 6.80 (s, 10H, H^{m}), 6.07 (apparent q, $^{3}J_{Ha'Hb'}$ = $^{3}J_{Ha'Ha}$ = $^{4}J_{Ha'Hb}$ = 2.6 Hz, 2H, $H^{a'}$), 5.83 (apparent q, $^{3}J_{Hb'Ha'}$ = $^{4}J_{Hb'Ha}$ = $^{4}J_{Hb'Hb}$ = 2.5 Hz, 2H, $H^{b'}$), 4.74 (br s, 2H, $H^{l'}$), 4.66 (br s, 2H, H^{l}), 4.62 (d, $^{2}J_{HdHd'}$ = 16Hz, 2H, H^{d}), 3.94 (d, $^{2}J_{HdHd'}$ = 16 Hz, 2H, $H^{d'}$), 2.10-1.95 (m, 4H, H^{i}), 1.78-1.62 (m, 4H, H^{g}), 1.69 (s overlapping with H^{g}, 6H, H^{k}), 1.53-1.44 (m overlapping with $H^{f/f'}$, 4H, H^{h}) 1.47 (s overlapping with H^{h}, 6H, H^{f}), 1.44 (s overlapping with H^{h}, 6H, $H^{f'}$). Remaining pentane: 1.35-1.21 (m), 0.88 (t).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, dichloromethane-d_2): $\delta^{13}C$: 166.8 (C^{n}), 148.6 (br d, $^{1}J_{CF}$ = 240 Hz, o-CF), 145.8 (C^{c}), 145.2 (C^{j}) 138.6 (br d, $^{1}J_{CF}$ = 240 Hz, *p*-CF), 136.8 (br d, $^{1}J_{CF}$ = 240 Hz, *m*-CF), 126.7 ($C^{a'}$), 125.2-123.1 (*ipso*-C^{B}), 122.0 (C^{m}), 117.6 (C^{a}), 114.9 ($C^{b'}$), 111.9 (C^{b}), 111.0 (C^{l}), 63.6 (C^{e}), 45.4 (C^{d}), 40.8 (C^{g}), 37.9 (C^{i}), 27.7 (C^{f}), 27.6 ($C^{f'}$), 22.7 (C^{h}) 22.3 (C^{k}). C_6H_5Br: 131.9, 130.5, 128.7, 122.8; pentane: 34.6, 22.8, 14.2 belong to pentane.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, dichloromethane-d_2): $\delta^{1}H$ / $\delta^{1}H$: 7.50 / 6.92, 6.07, 5.83 (CH^{a} / CH^{b}, $CH^{a'}$, $CH^{b'}$), 6.92 / 7.50, 6.07, 5.83 (CH^{b} / CH^{a}, $CH^{a'}$, $CH^{b'}$), 6.07 / 7.50, 6.92, 5.83 ($CH^{a'}$ / CH^{a}, CH^{b}, $CH^{b'}$), 5.83 / 7.50, 6.92, 6.07 ($CH^{b'}$ / CH^{a}, CH^{b}, $CH^{a'}$), 4.74 / 4.66, 1.69 ($H^{l'}$ / H^{l}, CH_3^{k}), 4.66 / 4.74, 2.10-1.95, 1.69 (H^{l} / $H^{l'}$, CH_2^{i}, CH_3^{k}), 4.62 / 3.94 (H^{d} / $H^{d'}$), 3.94 / 4.62 ($H^{d'}$ / H^{d}), 2.10-1.95 / 4.74, 1.53-1.44 (CH_2^{i} / $H^{l'}$, CH_2^{h}), 1.78-1.62 / 4.74, 4.66, 1.53-1.44 (CH_2^{g} / $H^{l'}$, H^{l}, CH_2^{h}), 1.69 / 4.74, 4.66 (CH_3^{h} / $H^{l'}$, H^{l}), 1.53-1.44 / 2.10-1.95, 1.78-1.62 (CH_2^{h} / CH_2^{i}, CH_2^{g}).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d_2): $\delta^{1}H$ / $\delta^{13}C$: 7.50 / 117.6 (CH^{a}), 6.92 / 111.9 (CH^{b}), 6.80 / 122.0 (CH^{m}), 6.07 / 126.7 ($CH^{a'}$), 5.83 / 114.9 ($CH^{b'}$), 4.74, 4.66 /111.0 (CH_2^{l}), 4.62, 3.94 / 45.4 (CH_2^{d}), 2.10-1.95 / 37.9 (CH_2^{i}), 1.78-1.62 / 40.8 (CH_2^{g}), 1.69 / 22.3 (CH_3^{k}), 1.47 / 27.7 (CH_3^{f}), 1.53-1.44 / 22.7 (CH_2^{h}), 1.44 / 27.6 ($CH_3^{f'}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d_2): $\delta^{1}H$ / $\delta^{13}C$: 7.50 / 145.8, 126.7, 114.9, 111.9 (CH^{a} / C^{c}, $CH^{a'}$, $CH^{b'}$, CH^{b}), 6.92 / 145.8, 126.7, 117.6, 114.9 (CH^{b} / C^{c}, $CH^{a'}$, CH^{a}, $CH^{b'}$), 6.80 / 122.0 (CH^{m} / CH^{m}), 6.07 / 145.8, 117.6, 114.9, 111.9 ($CH^{a'}$ / C^{c}, CH^{a}, $CH^{b'}$, CH^{b}), 5.83 / 145.8, 126.7, 117.6, 111.9 ($CH^{b'}$ / C^{c}, $CH^{a'}$, CH^{a}, CH^{b}), 4.74, 4.66 / 37.9, 22.3 ($CH_2^{l'/l}$ / CH_2^{i}, CH_3^{k}), 4.62 / 166.8, 145.8, 63.6 (H^{d} / C^{n}, C^{c}, C^{e}), 3.94 / 145.8, 114.9, 111.9 ($H^{d'}$ / C^{c}, $CH^{b'}$, CH^{b}), 2.10-1.95 / 145.2, 111.0, 40.8, 22.7 (CH_2^{i} / C^{j}, CH_2^{l}, CH_2^{g}, CH_3^{k}), 1.78-1.62 /

63.6, 27.7, 22.7 (CH_2^g / C^e, CH_3^f), 1.69 / 145.2, 111.0, 37.9 (CH_3^k / C^j, CH_2^l, CH_2^i), 1.47 / 145.2 63.6, 40.8, 27.6 (CH_3^f / C^j, C^e, CH_2^g, $CH_3^{f'}$), 1.53-1.44 / 145.2, 40.8, 27.7, 27.6 (CH_2^h/ C^e, CH_2^g, CH_3^f, $CH_3^{f'}$), 1.44 / 145.2, 63.6, 40.8, 27.7 ($CH_3^{f'}$ / C^j, C^e, CH_2^g, CH_3^f).

$^{11}B\{^1H\}$ NMR (160.42 MHz, 300 K, dichloromethane-d_2): $\delta^{11}B$: -16.6($\nu_{1/2}$ = 21 Hz).

^{11}B NMR (160.42 MHz, 300 K, dichloromethane-d_2): $\delta^{11}B$: -16.6 ($\nu_{1/2}$ = 21 Hz).

$^{19}F\{^1H\}$ NMR (470.45 MHz, 300 K, dichloromethane-d_2): $\delta^{19}F$: -132.8 (d, $^3J_{FF}$ = 11 Hz, 8F, *o*-F), -163.2 (t, $^3J_{FF}$ = 21 Hz, 8F, *p*-F), -167.1 (m, 8F, *m*-F).

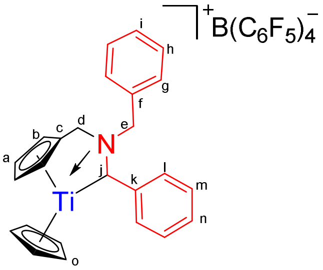
^{19}F NMR (470.45 MHz, 300 K, dichloromethane-d_2): $\delta^{19}F$: -132.8 (d, $^3J_{FF}$ = 11 Hz, 8F, *o*-F), -163.2 (t, $^3J_{FF}$ = 21 Hz, 8F, *p*-F), -167.1 (m, 8F, *m*-F).

^1H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2): δ^1H / $\delta^{15}N$: 1.47, 1.44 / -254 ($H^{f/f'}$ / N).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{42}H_{56}N_2Ti_2O_4$ $[2M]^{2+}$ 374.15940; found 374.16042 (Rel. ab: 10%, 2.7 ppm).

Elemental Analysis: % calcd for $C_{93.65}H_{64.76}N_2F_{40}O_4Ti_2$ (with 73% pentane): C, 52.09; H, 3.02; N, 1.30; Found: C, 52.43; H, 2.89; N, 1.29.

15. Synthesis of **40**:



Chemical Formula: $C_{49}H_{24}BF_{20}NTi$
Molecular Weight: 1065,4

A solid mixture of **33** (400 mg, 0.32 mmol, 1 eq) and $[Ph_3C][B(C_6F_5)_4]$ (294.2 mg, 0.34 mmol, 0.95 eq) was introduced in a Schlenk tube an dissolved in 5 mL of C_6H_5Br. The solution turned rapidly dark green and gas was released. After 1h of stirring, pentane (15 mL) was added to the solution and a green precipitate formed after 30 min of stirring. The supernatant was then removed and the green residue was washed with 5 mL of pentane. The green residue was dissolved in dichloromethane (3mL) and precipitated by pentane (5 mL). After removal of the supernatant, washing by pentane (5 mL), the desired compound was obtained after evaporation of all volatiles as a green powder. (295 mg, 0.28 mmol, yield = 87 %).[47]

^1H NMR (500.03 MHz, 300 K, bromobenzene-d_5): δ^1H: 7.30-7.24 (m, 1H, H^i), 7.18 (t, $^3J_{HH}$ = 7.2 Hz, 2H, H^h), 6.94-6.89 (m, 3H, H^m+H^n), 6.87-6.81 (m, 1H, H^a), 6.77 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H^g), 6.48 (s, 5H, H^o), 6.18-6.13 (m, 1H, H^b), 5.43 (d, $^3J_{HH}$ = 7.5 Hz, 2H, H^l), 5.07 (d overlapping with $H^{a'}$, $^2J_{HH}$ = 12.0 Hz, 1H, H^d), 5.08-5.02 (m overlapping with H^d, 1H, $H^{a'}$), 5.00 (s, 1H, H^j), 4.25

(d, $^{2}J_{HH}$ = 12.0 Hz, 1H, H$^{d'}$), 4.41-4.36 (m, 1H, H$^{b'}$), 3.34 (d, $^{2}J_{HH}$ = 13.0 Hz, 1H, H^{e}), 2.96 (d, $^{2}J_{HH}$ = 13.0 Hz, 1H, H$^{e'}$). Pentane: 1.27-1.00 (m), 0.85 (t).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, bromobenzene-d$_5$) correlated with **dept135**: δ^{13}C: 148.8 (br d, $^{1}J_{CF}$ = 240 Hz, o-CF), 141.9 (C^{k}), 138.6 (br d, $^{1}J_{CF}$ = 240 Hz, *p*-CF), 136.9 (br d, $^{1}J_{CF}$ = 240 Hz, *m*-CF), 132.8 (C^{f}), 130.4 (C^{i}), 129.8 (C^{h}), 129.5 (C^{g}), 129.0 (C$^{m/n}$), 127.6 (C$^{n/m}$), 127.2 (C^{b}), 126.7 (C^{l}), 125.0 (C^{a}), 121.0 (C$^{b'}$), 119.8 (C^{o}), 115.6 (C$^{a'}$), 111.1 (C^{c}), 92.3 (C^{j}), 68.0 (C^{e}), 49,1 (C^{d}). *ispo*-C^{B} n.o. (C$_6$H$_5$Br: 131.6, 130.0, 126.8 and 122.8).[51]

^{1}H ^{1}H COSY (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 7.30-7.24 / 7.18 (CH^{i} / CH^{h}), 7.18 / 7.30-7.24, 6.77 (CH^{h} / CH^{i}, CH^{g}), 6.94-6.89 / 5.43 (CH$^{m/n}$ / CH^{l}), 6.87-6.81 / 6.18-6.13, 5.08-5.02, 4.41-4.36 (CH^{a} / CH^{b}, CH$^{a'}$, CH$^{b'}$), 6.18-6.13 / 6.87-6.81, 5.08-5.02, 4.41-4.36 (CH^{b} / CH^{a}, CH$^{a'}$, CH$^{b'}$), 5.43 / 6.94-6.89 (CH^{l} / CH$^{m/n}$), 5.08-5.02 / 6.87-6.81, 6.18-6.13, 4.41-4.36 (CH$^{a'}$ / CH^{a}, CH^{b}, CH$^{b'}$), 5.07 / 4.25 (CH$_2$$^{d/d'}$) 4.25 / 5.07 (CH$_2$$^{d'/d}$), 4.41-4.36 / 6.87-6.81, 6.18-6.13, 5.08-5.02 (CH$^{b'}$ / CH^{a}, CH^{b}, CH$^{a'}$), 3.34 / 2.96 and 2.96 / 3.34 (CH$_2$$^{e/e'}$).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.30-7.24 / 130.4 (CH^{i}), 7.18 / 129.7 (CH^{h}), 6.94-6.89 / 127.6, 129.0 (CH$^{m/n}$), 6.87-6.81 / 125.0 (CH^{a}), 6.77 / 129.5 (CH^{g}), 6.48 / 119.8 (CH^{o}), 6.18-6.13 / 127.6 (CH^{b}), 5.43 / 126.7 (CH^{l}), 5.07, 4.25 / 49.0 (CH$_2$^{d}), 5.00 / 92.3 (CH^{j}), 4.41-4.36 / 121.0 (CH$^{b'}$), 3.34, 2.96 / 68.0 (CH$_2$$^{e/e'}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.30-7.24 / 129.8, 129.5 (CH^{g} / CH^{h}, CH^{g}), 7.18 / 132.8, 130.4 (CH^{h} / C^{f}, CH^{i}), 6.94-6.89 / 141.9 (CH$^{m/n}$ / C^{k}) 6.77 / 130.4, 129.8, 68.0 (CH^{g} / CH^{i}, CH^{h}, CH$_2$^{e}), 6.48 / 119.8 (CH^{j} / CH^{j}), 6.18-6.13 / 125.0, 121.0, 115.6, 111.1 (CH^{b} / CH^{a}, CH$^{b'}$, CH$^{a'}$ C^{c}), 5.43 / 127.6, 92.3 (CH^{l} / CH$^{m/n,}$ CH^{j}), 5.08-5.02 / 111.1 (CH^{a} / C^{c}), 5.07, 4.25 / 127.2, 121.0, 111.1, 92.3, 68.0 (CH$_2$^{d} / CH^{b}, CH$^{b'}$, C^{c}, CH^{j}, CH$_2$^{e}), 5.00 / 141.8, 129.0, 126.7, 68.0, 49.0 (CH^{j} / C^{k}, CH$^{m/n}$, CH$_2$^{e}, CH$_2$^{d}), 4.41-4.36 / 127.2, 115.6 (CH$^{b'}$ / CH^{b}, CH$^{a'}$), 3.34, 2.96 / 132.8, 130.4, 129.8, 92.3, 49.0 (CH^{b} / C^{f}, CH^{i}, CH^{h}, CH^{j}, CH$_2$^{d}).

^{1}H ^{15}N HMBC (600.13 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 5.00 / -309.8 (H^{j} / N).

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 19 Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 19 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (bs, 8F, *o*-F), -161.2 (bs, 4F, *p*-F), -165.1 (bs, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (bs, 8F, *o*-F), -161.2 (bs, 4F, *p*-F), -165.1 (bs, 8F, *m*-F).

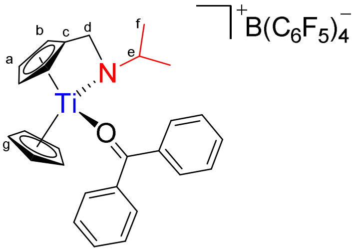
HRMS (Positive mode ESI, bromobenzene): m/z calcd. for C$_{25}$H$_{24}$NTi [M]$^{+}$ 386.13827 found 386.13870 (Rel. ab: 100%, 1.105 ppm).

---

[51] Satelite peaks were unfortunately observed.

Elemental Analysis: % calcd for $C_{44}H_{31}BF_{20}NOPTi$: C, 55.24; H, 2.27; N, 1.31; Found: C, 54.66; H, 2.51; N, 1.34.

16. Synthesis of **41**:



Chemical Formula: $C_{51}H_{28}BF_{20}NOTi$
Molecular Weight: 1109,4

A solution of benzophenone (57 mg, 0.31 mmol, 1 eq) and **34** (100 mg, 0.31 mmol, 1 eq), was prepared in 1 mL of C_6H_5Br. Then $[Ph_3C][B(C_6F_5)_4]$ (237 mg, 0.31 mmol, 1 eq) was added to the yellow solution which turned red rapidly. After 30 min of stirring, the red solution was precipitated by transferring in a stirred pentane solution (10 mL). A sticky red oil was formed. The yellow supernatant was removed and the red residue was stirred in pentane (10 mL) for 1h, until it was fully solidified. After removing supernatant, the red precipitate was dissolved in 2 mL of CH_2Cl_2, and made precipitate by addition of 4 eq of pentane. The red solid was isolated and triturated in pentane to get an orange precipitate. The desired compound was isolated as a light orange powder after drying *in* vacuo. (195 mg, 57%).[47]

^{1}H NMR (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^1H: 7.50 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *p*-CH^{benzo}), 7.32 (m overlapping with solvent, 4H, *m*-CH^{benzo}), 7.28 (d, $^3J_{HH}$ = 7.5 Hz, 4H, *o*-CH^{benzo}), 6.21 (apparent q, $^3J_{HH} = {}^4J_{HH}$ = 2.7 Hz, 1H, H^a), 5.82-5.77 (m overlapping with H^i, 1H, H^b), 5.79 (s overlapping with H^b, 5H, H^i), 5.45 (apparent q, $^3J_{HHH} = {}^4J_{HH}$ = 2.7 Hz, 1H, H$^{a'}$), 5.01 (apparent q, $^3J_{HH} = {}^4J_{HH}$ = 2.7 Hz, 1H, H$^{b'}$), 4.65 (hept, $^3J_{HH}$ = 6.7 Hz, 1H, CH^e), 4.44 (d, $^2J_{HH}$ = 15.4 Hz, 1H, H$^{d'}$), 4.18 (d, $^2J_{HH}$ = 15.4 Hz, 1H, H$^{d'}$), 0.89-0.81 (m, 6H, H$^{f/f'}$).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, bromobenzene-d$_5$) correlated with **dept135**: δ^{13}C: 209.5 (C=O), 148.8 (br d, $^1J_{CF}$ = 240 Hz, *o*-CF), 138.7 (br d, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.8 (br d, $^1J_{CF}$ = 240 Hz, *m*-CF), 136.3 (*p*-CH^{benzo}), 134.6 (*ipso*-C^{benzo}), 131.3 (*o*-CH^{benzo}), 129.4 (*m*-CH^{benzo}), 125.5-123.7 (*ipso*-C^B), 123.5 (C^b), 117.4 (C^a), 113.1 (C^g), 112.4 (C$^{a'}$), 111.0 (C^c), 110.6 (C$^{b'}$), 66.8 (C^e), 47.7 (C^d), 22.0 and 21.7 (C^f). *ipso*-C^B n.o.(C_6H_5Br: 131.6, 130.0, 126.8 and 122.6; pentane: 34.4, 22.8, 14.5).

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 300 K, bromobenzene-d$_5$): δ^1H / δ^1H: 7.50 / 7.32 (*p*-H^{benzo} / *m*-H^{benzo}), 7.32 / 7.50, 7.28 (*m*-H^{benzo} / *p*-H^{benzo}, (*o*-H^{benzo}), 7.28 / 7.32 (*o*-H^{benzo} / *m*-H^{benzo}), 6.21 / 5.82-5.77, 5.45, 5.01 (H^b / H^a, CH$^{a'}$, H$^{b'}$), 5.82-5.77 / 6.21, 5.45, 5.01 (H^a / H^b, H$^{a'}$, H$^{b'}$), 5.45 / 6.21, 5.82-5.77, 5.01 (H$^{a'}$ / H^b, H^a, H$^{b'}$),5.01 / 6.21, 5.82-5.77, 5.45 (H$^{b'}$ / H^b, H^a, H$^{a'}$), 4.65 / 0.89-0.81 (H^e / H^f), 4.44 / 4.18 (H$^{d/d'}$), 4.18 / 4.44 (H$^{d'/d}$), 0.89-0.81 / 4.65 (H^f / H^e).

^{1}H ^{13}C HMQC (500.03 MHz / 125.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.50 / 136.3 (*p*-CH$^{\mathrm{benzo}}$), 7.32 / 129.4 (*m*-CH$^{\mathrm{benzo}}$), 7.28 / 131.3 (*o*-CH$^{\mathrm{benzo}}$), 6.21 / 117.4 (CH^{a}), 5.82-5.77 / 123.5 (CH^{b}), 5.79 / 113.1 (CH^{g}), 5.45 / 112.4 (CH$^{a'}$), 5.01 / 110.6 (CH$^{b'}$), 4.65 / 66.8 (CH^{e}), 4.44, 4.18 / 47.7 (CH$_2^{d}$), 0.89-0.81 / 22.0, 21.7 (CH$_3^{f/f'}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.50 / 131.3 (*p*-CH$^{\mathrm{benzo}}$ / *o*-CH$^{\mathrm{benzo}}$), 7.32 / 134.6, 129.4 (*m*-CH$^{\mathrm{benzo}}$ / *ipso*-C$^{\mathrm{benzo}}$,, *m*-C$^{\mathrm{benzo}}$), 7.28 / 209.5, 136.3, 131.3 (*o*-CH$^{\mathrm{benzo}}$ / C=O, *p*-C$^{\mathrm{benzo}}$, *o*-CH$^{\mathrm{benzo}}$), 6.21 / 123.5, 112.4, 111.0, 110.6 (CH^{a} / CH^{b}, CH$^{a'}$, C^{c}, CH$^{b'}$), 5.79 / 113.1 (CH^{g} / CH^{g}), 5.45 / 111.0, 110.6 (CH$^{a'}$ / C^{c}, CH$^{b'}$), 5.01 / 123.5, 112.4, 117.4, 111.0 (CH$^{b'}$ / CH^{b}, CH$^{a'}$, CH^{a}, C^{c}), 4.65 / 47.7, 22.0, 21.7 (CH^{e} / CH$_2^{d}$, CH$_3^{f/f'}$), 4.44, 4.18 / 123.5, 111.0, 110.6, 66.8 (CH$_2^{d}$ / CH^{b}, C^{c}, CH$^{b'}$, CH^{e}), 0.89-0.82 / 66.8, 22.0, 21.7 (CH$_3^{f/f'}$ / C^{e}, CH$_3^{f'/f}$).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 0.89-0.81 / -419 (H^{f}, H$^{f'}$ / N).

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -16.2 ($\nu_{1/2}$ = 24 Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -16.2 ($\nu_{1/2}$ = 24 Hz).

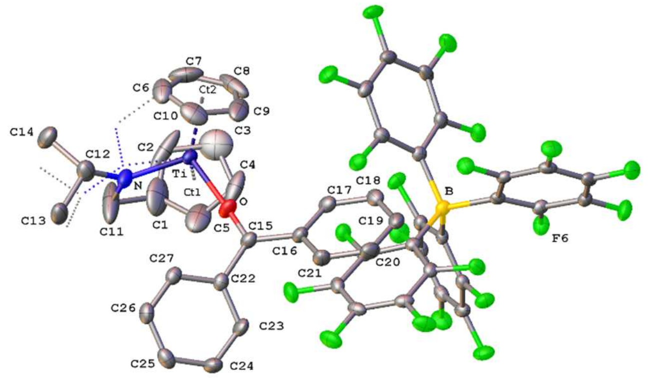
^{19}F{^{1}H} NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.7 (dm, $^{3}J_{\mathrm{FF}}$ = 15 Hz, 8F, *o*-F), -161.9 (t, $^{3}J_{\mathrm{FF}}$ = 19 Hz, 8F, *p*-F), -165.8 (m, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.7 (dm, $^{3}J_{\mathrm{FF}}$ = 15 Hz, 8F, *o*-F), -161.9 (t, $^{3}J_{\mathrm{FF}}$ = 19 Hz, 8F, *p*-F), -165.8 (m, 8F, *m*-F).

Elemental Analysis: % calcd for $C_{51}H_{28}BF_{20}NOTi$: C, 55.21; H, 2.54; N, 1.26; Found: C, 55.10; H, 2.93; N, 1.28

HRMS (Positive mode ESI, bromobenzene): m/z calcd. for $C_{14}H_{18}NTi$ [M-benzophenone]$^{+}$ 248.09132 found 248.09089 (Rel. ab: 35%, -1.8 ppm).

XRD analysis:

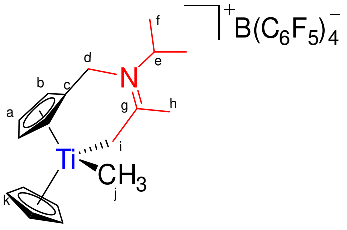


Experimental. Single plate-shaped crystals of (**cu_q09262016_0m**) were obtained by recrystallisation from diffusion of methylcyclohexane in a chlorobenzene solution at -15°C. A suitable crystal (0.25×0.18×0.08) mm^3 was selected and mounted on a mylar loop with oil on a Bruker D8 VENTURE diffractometer. The crystal was kept at T = 100 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the XT (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2017/1 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{51}H_{28}BF_{20}NOTi$, M_r = 1109.45, monoclinic, $P2_1/n$ (No. 14), a = 7.7585(2) Å, b = 29.6034(8) Å, c = 19.1746(5) Å, β = 91.662(2)°, $\alpha = \gamma$ = 90°, V = 4402.1(2) Å^3, T = 100 K, Z = 4, Z' = 1, $\mu(CuK_\alpha)$ = 2.815, 29330 reflections measured, 7771 unique (R_{int} = 0.0554) which were used in all calculations. The final wR_2 was 0.1124 (all data) and R_1 was 0.0478 (I > 2(I)).

Compound	**cu_q09262016_0m**
Formula	$C_{51}H_{28}BF_{20}NOTi$
$D_{calc.}$/ g cm^{-3}	1.674
μ/mm^{-1}	2.815
Formula Weight	1109.45
Colour	None None None
Shape	plate
Size/mm^3	0.25×0.18×0.08
T/K	100
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	7.7585(2)
b/Å	29.6034(8)
c/Å	19.1746(5)
α/°	90
β/°	91.662(2)
γ/°	90
V/Å^3	4402.1(2)
Z	4
Z'	1
Wavelength/Å	1.541840
Radiation type	CuK_α
Θ_{min}/°	2.985
Θ_{max}/°	66.838
Measured Refl.	29330
Independent Refl.	7771
Reflections Used	6116
R_{int}	0.0554
Parameters	701
Restraints	750
Largest Peak	0.562
Deepest Hole	-0.402
GooF	1.028
wR_2 (all data)	0.1124
wR_2	0.1034
R_1 (all data)	0.0665
R_1	0.0478

17. *In situ* characterization of **42**:



Chemical Formula: $C_{42}H_{26}BF_{20}NTi$
Molecular Weight: 983,3

A J-Young NMR-tube was loaded with **34** (20 mg, 62.3 µmol, 1 eq) and $[Ph_3C][B(C_6F_5)_4]$ (57.5, 62.3 µmol, 1 eq) and stored in the freezer for 10 min (258 K). Cold C_6D_5Br was added (0.7 mL) in the Young-tube and tightly closed. The initial yellow solution turned rapidly dark red. The tube was brought then on the spectrometer and kept at 258 K for analysis.

^{1}H NMR (500.03 MHz, 258 K, bromobenzene-d$_5$): δ^{1}H: 7.24-7.01 (m, ~ 30H, CH$^{Ph3CH,\ Ph3CCH3}$), 6.66 (m, 1H, H^{b}), 5.87 (s, 5H, H^{k}), 5.46 (s, ~ 1H, CH^{CHCPh3}), 5.25 (m, 1H, H^{a}), 5.02 (m, 1H, H$^{b'}$), 4.97 (m, 1H, H$^{a'}$), 4.12 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, H$^{d/d'}$), 3.27 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, H$^{d'/d}$), 3.69 (bs, 1H, CH^{e}), 2.03 (s, 3H, CH$_3$^{CH3CPh3}), 2.64 (s, $^{2}J_{HH}$ = not observed, 2H, H$^{i/i'}$), 1.25 (s, 3H, H^{h}), 1.09 (d, $^{3}J_{H'H}$ = 6.5 Hz, 3H, H^{f}), 0.85 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, H$^{f'}$), 0.18 (s, methane), -0.04 (H^{j}), -0.86 (s, $^{2}J_{HH}$ = not observed, 1H, H$^{i'/i}$).

^{13}C{^{1}H} NMR (125.75 MHz, 258 K, bromobenzene-d$_5$): δ^{13}C: 192.3 (C^{g}), 148.4 (dm, $^{1}J_{CF}$ = 240 Hz, *o*-CF), 146.2 (C^{c}), 138.3 (dm, $^{1}J_{CF}$ = 240 Hz, *p*-CF), 136.4 (dm, $^{1}J_{CF}$ = 240 Hz, *m*-CF), 125.2-123.2 (bs, *ipso*-C^{B}), 120.9 (C^{b}), 116.1 (C^{k}), 112.3 (C$^{a'}$), 110.5 (C^{a}), 108.5 (C$^{b'}$), 67.8 (C^{i}), 59.9 (C^{j}), 52.8 (C^{e}), 43.7 (C^{d}), 21.1 (C^{h}), 20.5 (C$^{f'}$), 19.7(C^{f}).

Side product of the crude: C_6H_5Br: 131.2, 129.8, 126.6; Ph_3CCH_3: 148.9 (*ipso*-C), 128.7, 127.9, 126.0 (CH^{Ph}), 52.3 (Cq), 30.3 (CH$_3$); Ph_3CH: 143.8 (*ipso*-C), 129.5, 128.3, 126.3 (CH^{Ph}), 56.7 (CH); CH_4: -3.6.

Side products are omitted for clarity on the following description.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 258 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 6.66 / 5.25, 5.02, 4.97 (CH^{b} / CH^{a}, CH$^{b'}$, CH$^{a'}$), 5.25 / 6.66, 5.02, 4.97 (CH^{a} / CH^{b}, CH$^{b'}$, CH$^{a'}$), 5.02 / 6.66, 5.02, 4.97 (CH$^{b'}$ / CH^{b}, CH^{a}, CH$^{a'}$),4.97 / 6.66, 5.25, 5.02 (CH$^{a'}$ / CH^{b}, CH^{a}, CH$^{b'}$), 4.12 / 3.27 (CH$_2$$^{d'}$ / CH$_2$^{d}), 3.69 / 1.09, 0.85 (CH^{e} / CH$_3$^{f}, CH$_3$$^{f'}$), 3.27 / 4.12 (CH$_2$^{d} / CH$_2$$^{d'}$), 2.64 / -0.86 (CH$_2$^{i} / CH$_2$$^{i'}$), 1.09, 0.85 / 3.69 (CH$_3$^{f},CH$_3$$^{f'}$ / CH^{e}), -0.86 / 2.64 (CH$_2$$^{d'}$ / CH$_2$^{d}).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 258 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 6.66 / 120.9 (CH^{b}), 5.87 / 116.1 (CH^{k}), 5.25 / 110.5 (CH^{a}), 5.02 / 108.5 (CH$^{b'}$), 4.97 / 112.3 (CH$^{a'}$), 4.12, 3.27 / 43.7 (CH$_2$^{d}), 3.69 / 52.8 (CH^{e}), 2.64 / 67.8 (CH$_2$^{i}), 1.25 / 21.1 (CH$_3$^{h}), 1.09 / 19.7 (CH$_3$^{f}), 0.85 / 20.5 (CH$_3$$^{f'}$), -0.04 / 59.9 (CH$_3$^{j}), -0.86 / 67.8 (CH$_2$^{i}).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 258 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 6.66 / 146.2, 110.5, 108.5 (CH^{b} / C^{c}, CH^{a}, CH$^{b''}$), 5.87 / 116.1 (CH^{k}/ CH^{k}), 5.25 / 146.2, 120.9, 112.3, 110.5 (CH^{a} / C^{c}, CH^{b}, CH$^{a'}$, CH^{a}), 5.02 / 146.2, 120.9, 112.3, 110.5 (CH$^{b'}$ / C^{c}, CH^{b}, CH$^{a'}$, CH^{a}), 4.97 / 146.2, 120.9, 110.5, 108.5 (CH$^{a'}$ / C^{c}, CH^{b}, CH^{a}, CH$^{b'}$), 4.12, 3.27 / 192.3, 146.2, 120.9, 108.5, 52.8 (CH$_2$^{d} / C^{g}, C^{c}, CH^{b}, CH$^{b'}$, CH^{e}), 2.64 / 21.1 (CH$_2$^{i} / CH$_3$^{h}), 1.25 / 192.2, 67.8 (CH$_3$^{h} / C^{g}, CH$_2$^{i}), 1.09 / 52.8, 20.5 (CH$_3$^{f} / CH^{e}, CH$_3$$^{f'}$) 0.85 / 52.8, 19.7 (CH$_3$$^{f'}$ / C^{e}, CH$_3$^{f}), -0.04 / 120.9 (CH$_3$^{j} / CH^{b}), -0.86 / 21.1 (CH$_2$^{i} / CH$_3$^{h}).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 258 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 1.25, 1.09, 0.85 / -197 (H^{h}, H^{f}, H$^{f'}$ / N).

^{11}B{^{1}H} NMR (160.42 MHz, 258 K, bromobenzene-d$_5$): δ^{11}B: -16.3 ($\nu_{1/2}$ = 19 Hz).

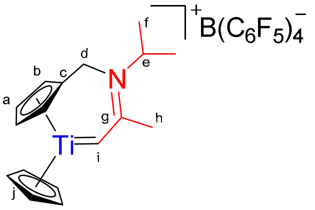
^{11}B NMR (160.42 MHz, 258 K, bromobenzene-d$_5$): δ^{11}B: -16.3 ($\nu_{1/2}$ = 19 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 258 K, bromobenzene-d_5): δ^{19}F: -131.6 (bs, 8F, *o*-F), -161.2 (bs, 8F, *p*-F), -164.6 (m, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 258 K, bromobenzene-d_5): δ^{19}F: -131.6 (bs, 8F, *o*-F), -161.2 (bs, 8F, *p*-F), -164.6 (bs, 8F, *m*-F).

HRMS (Positive mode ESI, bromobenzene): m/z calcd. for $C_{14}H_{18}NTi$ [M-propene]$^{+}$ 248.09132 found 248.09119 (Rel. ab: 60%, -0.5 ppm).

18. *In situ* characterization of **43**:



Chemical Formula: $C_{41}H_{22}BF_{20}NTi$
Molecular Weight: 967,3

The Young-type NMR-tube was left to warm up to room temperature and turned slowly dark green. The desired compound was completely formed after 24h and characterized by NMR at 273 K in order to obtain a decent ^{13}C{^{1}H} NMR spectrum.

^{1}H NMR (500.03 MHz, 273 K, bromobenzene-d_5): δ^{1}H: 11.44 (s, 1H, CH^{i}), 7.23-7.05 (m, ~ 40H, CH$^{Ph3CH,\ Ph3CCH3}$), 5.86 (s, 5H, H^{k}), 5.48-5.43 (br s, 2H, H^{a}), 5.43 (s, ~ 1.8H, CH^{CHCPh3}), 4.81-4.73 (br s, 2H, H^{b}), 3.84 (m, 1H, CH^{e}), 3.76 (s, 2H, H^{d}), 2.05 (s, ~ 3.7H, $CH_3^{CH3CPh3}$), 1.55 (s, 3H, H^{h}), 1.00 (d, $^{3}J_{HH}$ = 7.0 Hz, 6H, H^{f}), 0.16 (s, methane).

^{13}C{^{1}H} NMR (125.75 MHz, 273 K, bromobenzene-d_5): δ^{13}C: 266.2 (C^{i}), 156.9 (C^{g}), 148.8 (dm, $^{1}J_{CF}$ = 240 Hz, *o*-CF), , 138.7 (dm, $^{1}J_{CF}$ = 240 Hz, *p*-CF), 136.9 (dm, $^{1}J_{CF}$ = 240 Hz, *m*-CF), 125.6-123.7 (bs, *ipso*-B^{C}), 115.9 (C^{c}), 111.9 (C^{b}), 111.7 (C^{j}), 106.9 (C^{a}), 52.0 (C^{e}), 42.6 (C^{d}), 20.7(C^{f}), 19.9 (C^{h}).

Side product of the crude: C_6H_5Br: 131.6, 130.1, 127.0; Ph_3CCH_3: 149.3 (*ipso*-C), 129.1, 128.3, 126.3 (CH^{Ph}), 52.7 (Cq), 30.7 (CH_3); Ph_3CH: 144.2 (*ipso*-C), 129.8, 128.7, 126.7 (CH^{Ph}), 57.2 (CH); CH_4: -3.4.

Side products are omitted for clarity on the following description.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, bromobenzene-d_5): δ^{1}H / δ^{1}H: 5.86 / 4.81-4.73 (CH^{a} / CH^{b}), 4.81-4.73 / 5.86 (CH^{b} / CH^{a}), 3.84 / 1.00 (CH^{e} / CH_3^{f}), 1.00 / 3.84 (CH_3^{f} / CH^{e}).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 273 K, bromobenzene-d_5): δ^{1}H / δ^{13}C: 11.44 / 266.2 (CH^{i}), 5.86 / 111.7 (CH^{j}), 5.48-5.43 / 111.9 (CH^{a}), 4.81-4.73 / 106.9 (CH^{b}), 3.84 / 52.0 (CH^{e}), 3.76 / 42.6 (CH_2^{d}), 1.55 / 19.9 (CH_3^{h}), 1.00 / 20.7 (CH_3^{f}).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 273 K, bromobenzene-d_5): δ^{1}H / δ^{13}C: 11.44 / 19.9 (CH^{i} / CH_3^{h}), 5.86 / 111.7 (CH^{j}/ CH^{j}), 5.48-5.43 / 115.9, 106.9 (CH^{a} / C^{c}, CH^{b}), 4.81-4.73 / 115.9, 111.9, 106.9 (CH^b / C^c, CH^a, CH^b), 3.84 / 20.7 (CH^e / CH$_3^f$), 3.76 / 156.9, 115.9, 106.9, 52.0 (CH$_2^d$ / C^g, C^c, CH^b, CH^e), 1.55 / 266.2, 156.9 (CH$_3^h$ / CH^i, C^g), 1.00 / 52.0, 20.7 (CH$_3^f$ / CH^e, CH$_3^f$).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^1H / δ^{15}N: 1.55, 1.00 / -242.6 (H^h, H^f / N).

^{11}B{^{1}H} NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -16.0 ($\nu_{1/2}$ = 20 Hz).

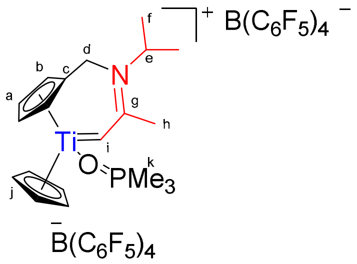
^{11}B NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -16.0 ($\nu_{1/2}$ = 20 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (br s, 8F, *o*-F), -160.9 (br s, 4F, *p*-F), -164.5 (br s, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (br s, 8F, *o*-F), --160.9 (br s, 4F, *p*-F), -164.5 (m, 8F, *m*-F).

HRMS (Positive mode ESI, bromobenzene): m/z calcd. for $C_{17}H_{22}NTi$ [M]$^+$ 288.12262 found 288.12323 (Rel. ab: 65%, 2.1 ppm); $C_{14}H_{18}NTi$ [M-propene]$^+$ 248.09132 found 248.09150 (Rel. ab: 100%, 0.7 ppm).

19. Attempted synthesis of **44**:



Chemical Formula: $C_{44}H_{31}BF_{20}NOPTi$
Molecular Weight: 1059,4

A solution of **34** (100 mg, 0.31 mmol, 1 eq) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (287.6, 0.31 mmol, 1 eq) in 3 mL of C$_6$H$_5$Cl was prepared in a vial inside the glovebox. The solution turned rapidly red and gaz releasing was observed. The solution was stirred for 24h until the color turned to dark green, due to the formation of the carbene. OPMe$_3$ (28.7 mg, 0.31 mmol, 1 eq) was incorporated to the solution which became dark purple. After 10 min of stirring, the solution was transferred in a Schlenk tubecontaining 25 mL of vigorously stirred pentane. A dark purple oil slowly decanted after freezing at -15°C overnight. Supernatant was removed and the dark purple oil was washed twice with pentane (2x5 mL). A dark purple precipitate (205 mg) was obtained *in vacuo*. EPR spectrum revealed that the material was contaminated with considerable amount of paramagnetic material.

^{1}H NMR (600.23 MHz, 300 K, bromobenzene-d$_5$): δ^1H: 9.07 (s, 1H, CH^i), 5.80 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H^b), 5.74 (s, 5H, H^j), 5.27 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H^a), 5.17 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H$^{a'}$), 4.53 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H$^{b'}$), 3.82 (hept $^3J_{HH}$ = 6.6 Hz, 1H, CH^e), 4.20 (d, $^2J_{HH}$ = 15.0 Hz, 1H, H^d), 3.01 (d, $^2J_{HH}$ = 15.0 Hz, 1H, H$^{d'}$), 1.67 (s, 3H, H^{h}), 1.13 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, H^{f}), 0.94 (d overlapping with H^{k}, $^{3}J_{HH}$ = 6.6 Hz, 3H, H$^{f'}$), 0.91 (d overlapping with H$^{f'}$, $^{2}J_{HP}$ = 12.8 Hz, 9H, H^{k}).

^{1}H{^{31}P} NMR (500.03 MHz, 300 K, bromobenzene-d$_{5}$): δ^{1}H: 9.07 (s, 1H, CH^{i}), 5.80 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H^{b}), 5.74 (s, 5H, H^{j}), 5.27 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H^{a}), 5.17 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H$^{a'}$), 4.53 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H$^{b'}$), 3.82 (hept $^{3}J_{HH}$ = 6.6 Hz, 1H, CH^{e}), 4.20 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, H^{d}), 3.01 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, H$^{d'}$), 1.67 (s, 3H, H^{h}), 1.13 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, H^{f}), 0.94 (d overlapping with H^{k}, $^{3}J_{HH}$ = 6.6 Hz, 3H, H$^{f'}$), 0.91 (soverlapping with H$^{f'}$, 9H, H^{k}).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, bromobenzene-d$_{5}$): δ^{13}C: 221.9 (C^{i}), 149.0 (C^{g}), 148.4 (dm, $^{1}J_{CF}$ = 240 Hz, *o*-CF), 138.3 (dm, $^{1}J_{CF}$ = 240 Hz, *p*-CF), 136.3 (dm, $^{1}J_{CF}$ = 240 Hz, *m*-CF), 125.9-123.3 (bs, *ipso*-C^{B}), 118.8 (C$^{a'}$), 116.6 (C^{c}), 112.0 (C^{j}), 109.3 (C^{a}), 108.0 (C^{b}), 103.6 (C$^{b'}$), 49.8 (C^{e}), 41.8 (C^{d}), 22.4 (C^{f}), 21.1 (C^{h}), 19.4 (C$^{f'}$), 14.1 (d, $^{1}J_{PC}$ = 72 Hz, C^{k}). C_6H_5Cl: 131.3, 129.9, 126.8, 124.7

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 300 K, bromobenzene-d$_{5}$): δ^{1}H / δ^{1}H: 5.80 / 5.27, 5.17, 4.53 (CH^{b} / CH^{a}, CH$^{a'}$, CH$^{b'}$), 5.27 / 5.80, 5.17, 4.53 (CH^{a} / CH^{b}, CH$^{a'}$, CH$^{b'}$), 5.17 / 5.80, 5.27, 4.53 (CH$^{a'}$ / CH^{b}, CH^{a}, CH$^{b'}$), 4.53 / 5.80, 5.27, 5.17 (CH$^{b'}$ / CH^{b}, CH^{a}, CH$^{a'}$), 4.20 / 3.01 (CH$_2^{d'/d}$), 3.82 / 0.94, 0.91(CH^{e} / CH$_3^{f/f'}$),3.01/ 4.20 (CH$_2^{d'/d}$), 1.13 / 3.82 (CH$_3^{f}$ / CH^{e}), 0.94 / 3.82 (CH$_3^{f'}$ / CH^{e}).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_{5}$): δ^{1}H / δ^{13}C: 9.07 / 221.9 (CH^{i}), 5.80 / 108.0 (CH^{b}), 5.74 / 112.0 (CH^{j}), 5.27 / 109.3 (CH^{a}), 5.17 / 118.8 (CH$^{a'}$), 4.53 / 103.6 (CH$^{b'}$), 4.20 / 41.8 (CH$_2^{d}$), 3.82 / 49.8 (CH^{e}), 3.01 / 41.8 (CH$_2^{d}$), 1.67 / 21.1 (CH$_3^{h}$), 1.13 / 22.4 (CH$_3^{f}$), 0.94 / 19.4 (CH$_3^{f'}$), 0.91 / 14.1 (CH$_3^{k}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_{5}$): δ^{1}H / δ^{13}C: 9.07 / 21.1 (CH^{i} / CH$_3^{h}$), 5.74 / 221.9, 112.0 (CH^{j}/ CH^{i}, CH^{j}), 5.27 / 118.8, 116.6, 108.0, 103.6 (CH^{a} / CH$^{a'}$, C^{c}, CH^{b}, CH$^{b'}$), 5.17 / 116.6, 108.0, 103.6 (CH$^{b'}$ / C^{c}, CH^{b}, CH$^{b'}$), 4.53 / 118.8, 116.6, 109.3 (CH$^{b'}$ / CH$^{a'}$, C^{c}, CH^{a}), 3.82 / 149.0, 41.8, 22.4, 19.4 (CH^{e} / C^{g}, CH$_2^{d}$, CH$_3^{f}$, CH$_3^{f'}$), 4.20, 3.01 / 221.9, 149.0, 116.6, 108.0, 103.6, (CH$_2^{d}$ / CH^{i}, C^{g}, C^{c}, CH^{b}, CH$^{b'}$), 1.67 / 221.9, 149.0, 49.8 (CH$_3^{h}$ / CH^{i}, C^{g}, CH^{e}), 1.13 / 49.8, 19.4 (CH$_3^{f}$ / CH^{e}, CH$_3^{f'}$), 0.94 / 49.8, 22,4 (CH$_3^{f'}$ / CH^{e}, CH$_3^{f}$), 0.91 / 14.1 (CH$_3^{k}$).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, bromobenzene-d$_{5}$): δ^{31}P: 63.5 ($\nu_{1/2}$ = 3.0 Hz)

^{31}P NMR (202.46 MHz, 300 K, bromobenzene-d$_{5}$): δ^{31}P: apparent hex 63.5 ($\nu_{1/2}$ = 44.6 Hz)

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_{5}$): δ^{1}H / δ^{15}N: 9.07, 1.13, 0.94 / -268 (H$^{'}$, H$^{f/f'}$ / N).

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d$_{5}$): δ^{11}B: -16.2 ($\nu_{1/2}$ = 22 Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d$_{5}$): δ^{11}B: -16.2 ($\nu_{1/2}$ = 22 Hz).

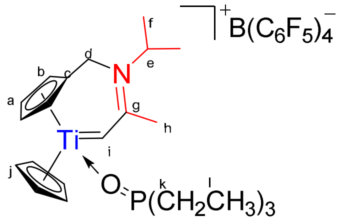
$^{19}F\{^1H\}$ NMR (470.45 MHz, 300 K, bromobenzene-d_5): δ^{19}F: -131.6 (bs, 8F, *o*-F), -161.8 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.6 (bs, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d_5): δ^{19}F: -131.6 (bs, 8F, *o*-F), -161.8 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.6 (bs, 8F, *m*-F).

HRMS (Positive mode ESI, bromobenzene): m/z calcd. for $C_{20}H_{31}NOPTi$ $[M]^+$ 380.16172 found 380.16175 (Re. ab: 100%, 0.07 ppm); $C_{20}H_{33}NO_2PTi$ $[M+H_2O]^+$ 398.17229 found 380.17230 (Rel. ab 48%, 0.03 ppm).

Elemental Analysis: % calcd for $C_{44}H_{31}BF_{20}NOPTi$: C, 49.31; H, 2.98; N, 1.34; Found: C, 49.44; H, 3.25; N, 1.30.

20. Attempted synthesis of **45**:



Chemical Formula: $C_{47}H_{37}BF_{20}NOPTi$
Molecular Weight: 1101,44

Asolution of **34** (100 mg, 0.31 mmol, 1 eq) and $[Ph_3C][B(C_6F_5)_4]$ (287.6, 0.31 mmol, 1 eq) in 3 mL of C_6H_5Br was prepared in a vial inside the glovebox. The solution turned rapidly red and gaz releasing was observed. The solution was stirred for 24h until the color turned to dark green, due to the formation of the carbene. $OPet_3$ (42 mg, 0.31 mmol, 1 eq) was incorporated to the solution which became dark purple. After 10 min of stirring, the solution was transferred in a Schlenk tube containing 25 mL of vigorously stirred pentane. A dark purple oil slowly decanted after freezing at -15°C overnight. Supernatant was removed and the dark purple oil was washed twice with pentane (2x5 mL). A dark purple precipitate (210 mg) was obtained *in vacuo*. EPR spectrum revealed that the material was contaminated with considerable amount of paramagnetic material.

^1H NMR (500.03 MHz, 300 K, bromobenzene-d_5): δ^1H: 9.04 (s, 1H, CH^i), 5.82 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H^a), 5.76 (s, 5H, H^j), 5.35 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H^b), 5.18 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H$^{a'}$), 4.55 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 1H, H$^{b'}$), 4.21 (d, $^2J_{HH}$ = 15.0 Hz, 1H, H^d), 3.81 (hept $^3J_{HH}$ = 6.6 Hz, 1H, CH^e), 3.03 (d, $^2J_{HH}$ = 15.0 Hz, 1H, H$^{d'}$), 1.66 (s, 3H, H^h), 1.21-1.13 (m overlapping with H^f, 6H, H^k), 1.13 (d overlapping with H^k, $^3J_{HH}$ = 6.6 Hz, 3H, H^f), 0.95 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H$^{f'}$), 0.66 (dt, $^3J_{HP}$ = 17.8 Hz, $^3J_{HH}$ = 7.7 Hz, 9H, H^l).

^{1}H{^{31}P} NMR (600.23 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 9.04 (s, 1H, CH^{i}), 5.82 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H^{a}), 5.76 (s, 5H, H^{j}), 5.35 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H^{b}), 5.18 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H$^{a'}$), 4.55 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.5 Hz, 1H, H$^{b'}$), 4.21 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, H^{d}), 3.81 (hept $^{3}J_{HH}$ = 6.6 Hz, 1H, CH^{e}), 3.03 (d, $^{2}J_{HH}$ = 15.0 Hz, 1H, H$^{d'}$), 1.66 (s, 3H, H^{h}), 1.21-1.13 (bm overlapping with H^{f}, $^{3}J_{HH}$ = 7.7 Hz, 6H, H^{k}), 1.13 (d overlapping with H^{k}, $^{3}J_{HH}$ = 6.6 Hz, 3H, H^{f}), 0.95 (d, $^{3}J_{HH}$ = 6.6 Hz, 3H, H$^{f'}$), 0.66 (bm, $^{3}J_{HP}$ = 17.8 Hz, $^{3}J_{HH}$ = 7.7 Hz, 9H, H^{l}).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, bromobenzene-d$_5$): δ^{13}C: 221.1 (C^{i}), 149.0 (C^{g}), 148.8 (dm, $^{1}J_{CF}$ = 245 Hz, *o*-CF), 138.7 (dm $^{1}J_{CF}$ = 245 Hz, *p*-CF), 136.8 (dm, $^{1}J_{CF}$ = 245 Hz, *m*-CF), 125.8-123.7 (bs, *ipso*-C^{B}), 118.9 (C$^{a'}$), 117.1 (C^{c}), 112.3 (C^{j}), 109.7 (C^{b}), 108.0 (C^{a}), 104.4 (C$^{b'}$), 50.1 (C^{e}), 42.1 (C^{d}), 22.8 (C^{f}), 21.5 (C^{h}), 19.8 (C$^{f'}$), 17.4 (d, $^{1}J_{PC}$ = 72 Hz, C^{k}), 5.2 (d, $^{1}J_{PC}$ = 4.7 Hz, C^{l}).

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 4.21 / 3.03 (CH$_2^{d}$), 3.81 / 1.13, 0.95 (CH^{e} / CH$_3^{f/f'}$), 3.03 / 4.21 (CH$_2^{d}$), 1.21-1.13 / 0.66 (CH$_3^{l}$ / CH$_2^{k}$), 1.13 / 3.81 (CH$_3^{f}$ / CH^{e}), 0.95 / 3.81 (CH$_3^{f'}$ / CH^{e}), 0.66 / 1.21-1.13 (CH$_2^{k}$ / CH$_3^{l}$).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 9.04 / 221.1 (CH^{i}), 5.82 / 108.0 (CH^{a}), 5.76 / 112.3 (CH^{j}), 5.35 / 109.7 (CH^{b}), 5.18 / 118.9 (CH$^{a'}$), 4.55 / 104.4 (CH$^{b'}$), 4.21 / 42.1 (CH$_2^{d}$), 3.81 / 50.1 (CH^{e}), 3.03 / 42.1 (CH$_2^{d}$), 1.66 / 21.5 (CH$_3^{h}$), 1.21-1.13 / 17.4 (CH$_2^{k}$), 1.13 / 22.8 (CH$_3^{f}$), 0.95 / 19.8 (CH$_3^{f'}$), 0.95 / 14.1 (CH$_3^{l}$), 0.66 / 5.2 (CH$_2^{l}$).

^{1}H ^{13}C HMBC (600.23 MHz / 150.86 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 9.04 / 21.5 (CH^{i} / CH$_3^{h}$), 5.82 / 117.1 (CH^{a}/ C^{c}), 5.76 / 112.3 (CH^{j}), 5.35 / 118.9, 117.1, 108.0, 104.4 (CH^{b} / CH$^{a'}$, C^{c}, CH^{a}, CH$^{b'}$), 5.18 / 117.1, 104.4 (CH$^{a'}$ / C^{c}, CH$^{a'}$), 4.55 / 118.9, 117.1, 109.7 (CH$^{b'}$ / CH$^{a'}$, C^{c}, CH^{a}), 4.21 / 149.0, 117.1, 109.7, 104.4, 50.1, 22.8, 19.8 (CH$_2^{d}$ / C^{g}, C^{c}, CH^{b}, CH$^{b'}$, CH^{e}, CH$_3^{f/f'}$) 3.81 / 149.0, 42.1 (CH^{e} / C^{g}, CH$_2^{d}$), 3.03 / 149.0, 117.1, 109.7, 104.4, 50.1, 22.8, 19.8 (CH$_2^{d'}$ / C^{g}, C^{c}, CH^{b}, CH$^{b'}$, CH^{e}, CH$_3^{f/f'}$), 1.66 / 149.0, 50.1 (CH$_3^{h}$ / C^{g}, CH^{e}), 1.21-1.13 / 5.2 (CH$_2^{k}$ / CH$_3^{l}$), 1.13, 0.95 / 50.1, 22.8, 19.8 (CH$_3^{f/f'}$ / CH^{e}, CH$_3^{f/f'}$), 0.66 / 17.4 (CH$_3^{l}$ / CH$_2^{k}$).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: 76.7 ($\nu_{1/2}$ = 2.8 Hz)

^{31}P NMR (202.46 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: m 77.1-76.3 ($\nu_{1/2}$ = 70.0 Hz)

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 9.04, 1.66, 1.13, 0.95 / -268 (H^{i}, H^{h}, H$^{f/f'}$ / N).

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 20 Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 20 Hz).

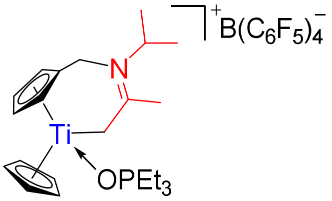
^{19}F{^{1}H} NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.2 (bm, 8F, *o*-F), -161.2 (bm, 4F, *p*-F), -164.8 (bm, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.2 (bm, 8F, *o*-F), -161.2 (bm, 4F, *p*-F), -164.8 (bm, 8F, *m*-F).

HRMS (Positive mode ESI, bromobenzene): m/z calcd. for $C_{23}H_{37}NOPTi$ $[M]^+$ 422.20890 found 422.20718 (Rel. ab: 20%, -3.5 ppm), $C_{17}H_{23}NTi$ [M + H°- $OPEt_3$] $^+$ 289.13060 found 289.12712 (Rel. ab: 70%, -11.5 ppm); $C_{17}H_{22}NTi$ [M - $OPEt_3$] $^+$ 288.12278 found 288.12222 (Rel. ab: 75%, -1.4 ppm); $C_{14}H_{18}NTi$ [M - $OPEt_3$ - propene]: 248.09145 found 248.09060 (Rel. ab: 45 %, -2.9 ppm)

Elemental Analysis: % calcd for $C_{47}H_{37}BF_{20}NOPTi$: C, 51.25; H, 3.39; N, 1.27; Found: C, 51.13; H, 3.18; N, 1.15.

21. Synthesis of **46-OPEt$_3$**:



Chemical Formula: $C_{47}H_{38}BF_{20}NOPTi$
Molecular Weight: 1102,4

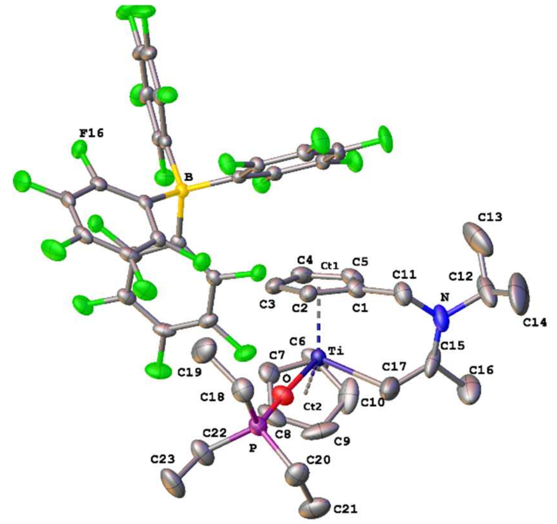
A solution of **34** (50 mg, 0.16 mmol, 1 eq) and $[Ph_3C][B(C_6F_5)_4]$ (923.4, 0.16 mmol, 1 eq) in 3 mL of C_6H_5Br was prepared in a vial inside the glovebox.The solution turned rapidly red and gaz releasing was observed. The solution was stirred for 8h until the color turned to dark green, due to the formation of the carbene. 1,4-cyclohexadiene (80 mg, 0.93 mmol, 6.4 eq), was added to the solution and stirred overnight. $OPet_3$ (42 mg, 0.31 mmol, 1 eq) was incorporated to the maroon solution. After 10 min of stirring, the solution was transferred in a Schlenk tube containing 25 mL of vigorously stirred pentane. A dark purple oil slowly decanted after freezing at -15°C overnight. Supernatant was removed and the dark purple oil was washed twice with pentane (2x5 mL). The desired compound was obtained after evaporation of all volatiles *in vacuo* as a maroon precipitate (73 mg, 43%). Suitable crystals for X-ray diffraction were obtained by diffusion of heptane into a bromobenzene solution at -15°C.

Positive mode ESI HRMS (Positive mode ESI, bromobenzene): m/z calcd. for $C_{17}H_{22}NTi$ [M - $OPEt_3$] $^+$ 289.13060 found 289.12895 (Rel. ab: 37%, -3.5 ppm); $C_{14}H_{18}NTi$ [M - $OPEt_3$ – propene-H°]: 248.09145 found 248.09055 (Rel. ab: 32%, -3.5 ppm).

Elemental Analysis: % calcd for $C_{47}H_{38}BF_{20}NOPTi$: C, 51.21; H, 3.47; N, 1.27; Found: C, 51.13; H, 4.11; N, 1.15.

EPR (9.439232 GHz, 295 K, bromobenzene): the spectrum was too compled to be simulated.

XRD:

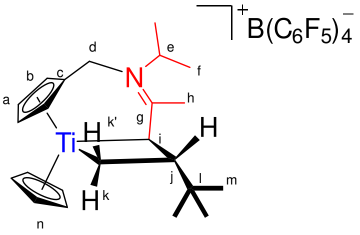


Compound	**q060317_0m_a**
Formula	$C_{47}H_{38}BF_{20}NOPTi$
$D_{calc.}$/ g cm^{-3}	1.598
μ/mm^{-1}	0.342
Formula Weight	1102.46
Colour	brown
Shape	plate
Size/mm^3	0.17×0.12×0.03
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	12.9659(13)
b/Å	13.1590(13)
c/Å	15.5256(15)
α/°	113.182(2)
β/°	107.789(2)
γ/°	90.732(3)
V/Å^3	2291.7(4)
Z	2
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.669
Θ_{max}/°	27.563
Measured Refl.	58682
Independent Refl.	10547
Reflections Used	7282
R_{int}	0.0497
Parameters	655
Restraints	0
Largest Peak	0.831
Deepest Hole	-0.540
GooF	1.021
wR_2 (all data)	0.1296
wR_2	0.1125
R_1 (all data)	0.0845
R_1	0.0495

Experimental. Single brown plate-shaped crystals of (**q060317_0m_a**) were obtained by recrystallisation from diffusion of heptane in a chlorobenzene solution at -15°C. A suitable crystal (0.17×0.12×0.03) mm^3 was selected and mounted on a mylar loop with oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2017/1 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{47}H_{38}BF_{20}NOPTi$, M_r = 1102.46, triclinic, P-1 (No. 2), a = 12.9659(13) Å, b = 13.1590(13) Å, c = 15.5256(15) Å, α = 113.182(2)°, β = 107.789(2)°, γ = 90.732(3)°, V = 2291.7(4) Å^3, T = 115 K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 0.342, 58682 reflections measured, 10547 unique (R_{int} = 0.0497) which were used in all calculations. The final wR_2 was 0.1296 (all data) and R_1 was 0.0495 (I > 2(I)).

22. *In situ* characterization of **47**:



Chemical Formula: $C_{47}H_{34}BF_{20}NTi$
Molecular Weight: 1051,4

A solution of **34** (10 mg, 31.2 µmol, 1 eq) and 3,3-dimethylbut-1-ene (8 mg, 95.0 µmol, 3 eq) was prepared in 1 mL of cold C_6D_5Br. This yellow solution was added in a J-Young NMR tube where [Ph_3C][$B(C_6F_5)_4$] (28.8 mg, 31.2 µmol, 1 eq) was introduced before. The initial yellow solution turned rapidly dark red. The tube was then brought to the spectrometer. After 12h, the reaction was completed, and the reaction mixture was characterized by NMR spectroscopy.

^{1}H NMR (600.23 MHz, 273 K, bromobenzene-d_5): δ^{1}H: 7.18 – 7.05 (m, ~ 30H, CH$^{Ph3CH,\ Ph3CCH3}$), 6.63 (s, 1H, H$^{b/b'}$), 5.86 (s, 5H, H^{n}), 5.79 (dd, $^{trans}J_{HH}$ = 17.4 Hz, $^{cis}J_{HH}$ = 10.6 Hz, ~ 3H, CH^{alkene}), 5.47 (bs, 1H, H$^{a/a'}$), 5.46 (s, ~ 1H, CH^{CHCPh3}), 4.91 (dd, $^{trans}J_{HH}$ = 17.4 Hz, $^{gem}J_{HH}$ = 1.4 Hz, ~ 3H, trans-H^{CH2alkene}), 4.84 (dd, $^{cis}J_{HH}$ = 10.6 Hz, $^{gem}J_{HH}$ = 1.4 Hz, ~ 3H, cis-H^{CH2alkene}), j 4.80 (bs, 1H, H$^{a'/a}$), 4.55 (bs, 1H, H$^{b'/b}$), 4.23 (d, $^{2}J_{HH}$ = 15.5 Hz, 1H, H^{d}), 4.12 (d, $^{2}J_{HH}$ = 15.5 Hz, 1H, H$^{d'}$), 3.63 (hept, $^{3}J_{HH}$ = 7.4 Hz, 1H, H^{e}), 2.82 (t, $^{3}J_{HH}$ = 10.1 Hz, 1H, H^{k}), 2.66 (d, $^{3}J_{HH}$ = 10.1 Hz, 1H, H^{i}), 2.33 (t, $^{3}J_{HH}$ = 10.1 Hz, 1H, H$^{k'}$), 2.05 (s, ~ 2H, $CH_3^{CH3CPh3}$), 1.60 (s, 3H, H^{h}), 1.33 (q, $^{3}J_{HH}$ = 10.1 Hz, 1H, H^{j}), 0.96 (s, ~ 27iH, ^{t}Bu^{alkene}), 0.93-0.95 (m, 3H, H$^{f/f'}$), 0.85-0.82 (m, 3H, H$^{f'/f}$), 0.57 (m, 9H, H^{m}), 0.16 (s, methane).

^{13}C{^{1}H} NMR (125.75 MHz, 273 K, bromobenzene-d_5): δ^{13}C: 185.9 (C^{g}), 148.8 (dm, $^{1}J_{CF}$ = 240 Hz, *o*-CF), 138.7 (dm, $^{1}J_{CF}$ = 240 Hz, *p*-CF), 138.6 (C^{c}), 136.8 (dm, $^{1}J_{CF}$ = 240 Hz, *m*-CF), 127.0 (C$^{b/b'}$), 125.6-123.5 (bs, *ipso*-C^{B}), 115.3 (C^{n}), 113.1 (C$^{a/a'}$), 108.2 (C$^{a'/a}$), 105.2 (C$^{b'/b}$), 82.5 (C^{i}), 77.1 (C^{k}), 53.7 (C^{e}), 44.8 (C^{d}), 36.4(C^{l}), 29.6 (C^{j}), 27.9 (C^{m}) 25.1 (C^{h}), 20.9 (C$^{f/f'}$), 18.7 (C$^{f'/f}$).

Side product of the crude: C_6H_5Br: 131.6, 130.1, 126.9, 122.8; Ph_3CCH_3: 149.3 (*ipso*-C), 129.0, 128.2, 126.3 (CH^{Ph}), 52.7 (Cq), 30.7 (CH_3); Ph_3CH: 144.2 (*ipso*-C), 129.8, 128.6, 126.6 (CH^{Ph}), 57.1 (CH); CH_4: -3.4. $CH_2CHC(CH_3)_3$: 149.6 (CH_2), 109.5 (CH), 33.8 (C), 29.4 (CH_3).

Side products are omitted for clarity on the following description.

^{1}H ^{1}H COSY (500.03 MHz, 273 K, bromobenzene-d_5): δ^{1}H / δ^{1}H: 6.63 / 5.47, 4.80, 4.55 (H$^{b/b'}$ / H$^{a/a'}$, H$^{a'/a}$, H$^{b'/b}$), 5.47 / 6.63, 4.80, 4.55 (H$^{a/a'}$ / H$^{b/b'}$, H$^{a'/a}$, H$^{b'/b}$), 4.80 / 6.63, 5.47, 4.55 (H$^{a'/a}$ / H$^{b/b'}$, H$^{a/a'}$, H$^{b'/b}$), 4.55 / 6.63, 5.47, 4.80 (H$^{b'/b'}$ / H$^{b/}$b', H$^{a/a'}$, H$^{a'/a}$), 4.23 / 4.12 (H^{d}), 4.12 / 4.23 (H^{d}), 3.63 / 0.95-0.93, 0.85-0.82 (H^{e}/ H$^{f/f'}$), 2.82 / 2.33, 1.33 (H^{k} / H$^{k'}$, H^{j}), 2.66 / 1.33 (H^{i} / H^{j}), 2.33 / 2.82, 1.33 (H$^{k'}$ / H^{k}, H^{j}), 1.33 / 2.82, 2.66, 2.33 (H^{j} / H^{k}, H^{i}, H$^{k'}$), 0.95-0.93 / 3.63 (H$^{f/f'}$ / H^{e}), 0.85-0.82 / 3.63 (H$^{f'/f}$ / H^{e}).

^{1}H ^{1}H NOESY (600.23 MHz, 273 K, bromobenzene-d_5): δ^{1}H / δ^{1}H: 4.17 / 1.33, 0.85-0.82 (H^{d} / H^{j}, H$^{f'/f}$), 3.63 / 1.60, 0.85-0.82 (H^{e} / H^{h}, H$^{f'/f}$), 2.82 / 5.86, 2.33, 0.5 (H^{k} / H^{n}, H$^{k'}$, H^{m}), 2.66 / 5.86, 1.60, 0.57 (H^{i} / H^{n}, H^{h}, H^{m}), 2.33 / 6.63, 2.82, 0.57 (H$^{k'}$ / H$^{b/b'}$, H^{k}, H^{m}).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 273 K, bromobenzene-d_5): δ^{1}H / δ^{13}C: 6.59 / 127.0 (CH$^{b/b'}$), 5.86 / 115.2 (CH^{n}), 5.43 / 113.1 (CH$^{a/a'}$), 4.76 / 108.2 (CH$^{a'/a}$), 4.51 / 105.2 (C$^{b'/b}$), 4.23, 4.12 / 44.8 (C^{d}), 3.58 / 53.7 (C^{e}), 2.80 / 77.1 (C^{k}), 2.62 / 82.5 (C^{i}), 2.33 / 77.1 (C^{k}), 1.56 / 25.1 (C^{h}), 1.33 / 29.6 (C^{j}), 0.90 / 18.7 (C$^{f/f'}$), 0.81 (C$^{f'/f}$), 0.56 / 27.9 (C^{m}).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 273 K, bromobenzene-d_5): δ^{1}H / δ^{13}C: 6.59 / 138.6, 113.1, 108.2, 105.2 (CH$^{b/b'}$/ C^{c}, CH$^{a/a'}$, CH$^{a'/a}$, CH$^{b'/b}$), 5.86 / 115.2 (CH^{n}), 5.43 / 138.6, 127.0,

108.2, 105.2 (CH$^{a/a'}$ / C^{c}, CH$^{b/b'}$, CH$^{a'/a}$, CH$^{b'/b}$), 4.77 / 138.6, 127.0, 108.2, 105.2 (CH$^{a'/a}$ / C^{c}, CH$^{b/b'}$, CH$^{a/a'}$, CH$^{b'/b}$), 4.52 / 138.6, 127.0, 113.1, 108.2 (CH$^{b'/b}$ / C^{c}, CH$^{b/b'}$, CH$^{a/a'}$, CH$^{b'/b}$), 4.23, 4.12 / 185.9, 138.6, 127.0, 105.2, 53.7 (CH$_2^{d}$ / C^{g}, C^{c}, CH$^{b/b'}$, CH$^{b'/b}$, CH^{e}), 3.63 / 185.9, 44.8, 20.9, 18.7 (CH^{e} / C^{g}, CH$_2^{d}$, CH$_3^{f/f'}$, CH$_3^{f'/f}$), 2.80 / 36.4, 29.6 (H^{k} / C^{l}, CH^{j}), 2.62 / 36.4, 25.1 (CH^{i} / C^{l}, CH$_3^{f/f'}$), 2.33 / 82.5, 29.6 (H$^{k'}$ / CH^{i}, CH^{j}), 1.60 / 185.9, 82.5 (CH$_3^{h}$ / C^{g}, CH^{i}), 1.33 / 82.5, 77.2, 36.4, 27.9 (CH^{j} / CH^{i}, CH$_2^{k}$, C^{l}, C^{m}), 0.90 / 53.7, 20.9 (CH$_3^{f/f'}$ / CH^{e}, CH$_3^{f'/f}$), 0.80 / 53.7, 18.6 (CH$_3^{f}$ / CH^{e}, CH$_3^{f'/f}$), 0.55 / 36.4, 27.9 (CH$_3^{m}$ / C^{l}, CH$_3^{m}$).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 2.66, 1.60, 0.95-0.93, 0.85-0.82 / -220 (H^{i}, H^{g}, H$^{f/f'}$/ N).

^{11}B{^{1}H} NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -16.0 ($\nu_{1/2}$ = 23 Hz).

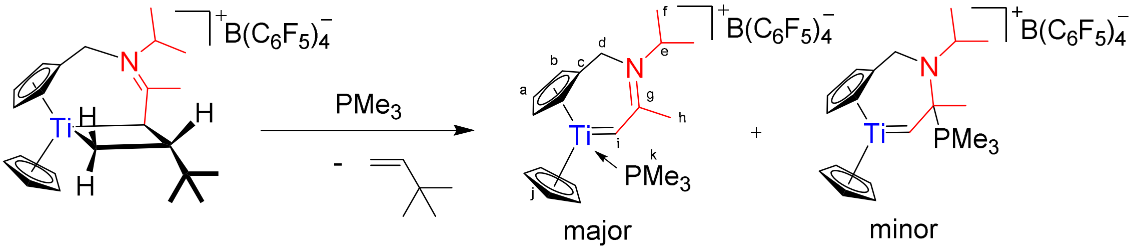
^{11}B NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -16.0 ($\nu_{1/2}$ = 23 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (bs, 8F, *o*-F), -161.1 (bs, 8F, *p*-F), -164.8 (bs, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (bs, 8F, *o*-F), -161.1 (bs, 8F, *p*-F), -164.8 (bs, 8F, *m*-F).

HRMS (Positive mode ESI, bromobenzene): m/z calcd. for $C_{23}H_{36}NOTi$ [M+H$_2$O]$^+$ 390.22709 found 390.22726 (Rel. ab: 65%, 0.4 ppm), $C_{14}H_{18}NTi$ [M-3,3-dimethylbutene-propene]$^+$ 248.09132 found 248.09148 (Rel. ab: 100%, -0.6 ppm).

23. *In situ* characterization of **48**:



A solution of **34** (19.1 mg, 59.5 µmol, 1 eq) and 3,3-dimethylbut-1ene (13 mg, 154 µmol, 2.6 eq) was prepared in 1 mL of cold C_6D_5Br. This yellow solution was added in a Young-type NMR-tube where [Ph$_3$C][B(C$_6$F$_5$)$_4$] (54.8 mg, 59.5 µmol, 1 eq) was introduced before. The initial yellow solution turned rapidly dark red. The tube was then brought on the spectrometer in order to check complete formation of the titanocyclobutane species. PMe$_3$ (4.5 mg, 59.5 µmol, 1 eq) was added to the red solution inside the glovebox and a dark “blood” red solution was obtained. NMR measurements have been carried out on the tube.

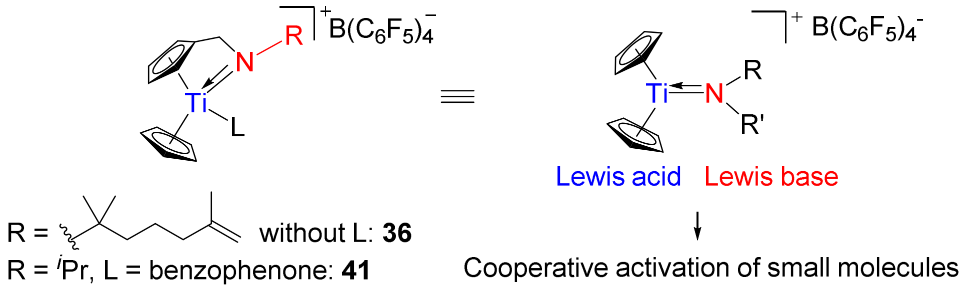
^{1}H NMR (600.23 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 9.84 (d, $^3J_{PH}$ = 4.5 Hz, 1H, H^{i}), 7.20 – 7.05 (m, ~ 30H, CH$^{Ph3CH,\ Ph3CCH3}$), , 5.81 (dd, $^3J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 10.6 Hz, ~ 4H, CH^{alkene}), 5.54 (d, $^3J_{PH}$ = 2.5 Hz, 5H, H^{j}) 5.46 (s, ~ 1H, CH^{CHCPh3}), 5.04 – 4.90 (m overlapping with CH$_2^{alkene}$, 4H, H$^{a/b}$) 4.91 (dd overlapping with H$^{a/b}$, $^3J_{HH}$ = 17.4 Hz, , $^2J_{HH}$ = 1.5 Hz, ~ 4H, CH$_2^{alkene}$), 4.83 (dd, $^3J_{HH}$ = $^3J_{HH}$ = 10.6 Hz, $^2J_{HH}$ = 1.5 Hz, ~ 4H, CH$_2^{alkene}$), 4.29 (d, $^2J_{HH}$ = 15.3 Hz, 1H, H^d), 3.79 (hept, $^3J_{HH}$ = 6.5 Hz, 1H, H^e), 3.16 (d, $^2J_{HH}$ = 15.3 Hz, 1H, H$^{d'}$), 2.05 (s, 1.7 H, CH$_3^{CH3CPh3}$), 1.50 (s, 3H, H^h), 1.08 (m, 3H, CH$_3^f$), 0.96 (s, ~ 36H, ^{t}Bu^{alkene}), 0.92 (m, 3H, CH$_3^f$), 0.87 (br s, 67H, free PMe$_3$), 0.76 (d, $^3J_{PHm}$ = 7.6 Hz, 9H, H^m).

^{1}H {^{31}P} NMR (600.23 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 9.84 (s, 1H, H^i), 7.20 – 7.05 (m, ~ 30H, CH$^{Ph3CH, Ph3CCH3}$), , 5.81 (dd, $^3J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 10.6 Hz, ~ 4H, CH^{alkene}), 5.54 (s, 5H, H^j) 5.46 (s, ~ 1H, CH^{CHCPh3}), 5.04 – 4.90 (m overlapping with CH$_2^{alkene}$, 4H, H$^{a/b}$) 4.91 (dd overlapping with H$^{a/b}$, $^3J_{HH}$ = 17.4 Hz, , $^2J_{HH}$ = 1.5 Hz, ~ 4H, CH$_2^{alkene}$), 4.83 (dd, $^3J_{HH}$ = $^3J_{HH}$ = 10.6 Hz, $^2J_{HH}$ = 1.5 Hz, ~ 4H, CH$_2^{alkene}$), 4.29 (d, $^2J_{HH}$ = 15.3 Hz, 1H, H^d), 3.79 (hept, $^3J_{HH}$ = 6.5 Hz, 1H, H^e), 3.16 (d, $^2J_{HH}$ = 15.3 Hz, 1H, H$^{d'}$), 2.05 (s, 1.7 H, CH$_3^{CH3CPh3}$), 1.50 (s, 3H, H^h), 1.08 (m, 3H, CH$_3^f$), 0.96 (s, ~ 36H, ^{t}Bu^{alkene}), 0.92 (m, 3H, CH$_3^f$), 0.87 (br s, 67H, free PMe$_3$), 0.76 (s, 9H, H^m).

^{31}P{^{1}H} NMR (243.0 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: 36.7 (minor), -3.3 (major), 62.5 (free PMe$_3$).

IV. Chapter III: Cationic amido- and phosphidotitanocenes: exploring the frontier of the FLP concept

As illustrated in the previous chapter, the intramolecular combination of a titanocenium cation with a tertiary amine is not a suitable target for FLP chemistry, due to the reactivity of CH bonds in the amine moiety with strong Lewis acids. However, since this reactivity leads to stable amidotitanocene cations such as **36** and **41** (Scheme IV-1), we spotted an opportunity for the development of cooperative systems based on the combination of a titanocenium cation with simple amido ligands.



Scheme IV-1 illustration of the new approach

In fact, this approach has already been explored successfully by Le Gendre and Erker with cationic amido- and phosphidozirconocene complexes.[1] As a result, the synthesis of new titanocene analogues was envisioned. In the following chapter, a brief overview of cationic group 4 metals with amido or phosphido ligands will be described, before developing the results obtained with the new cationic titanocenes, synthesized during this thesis.

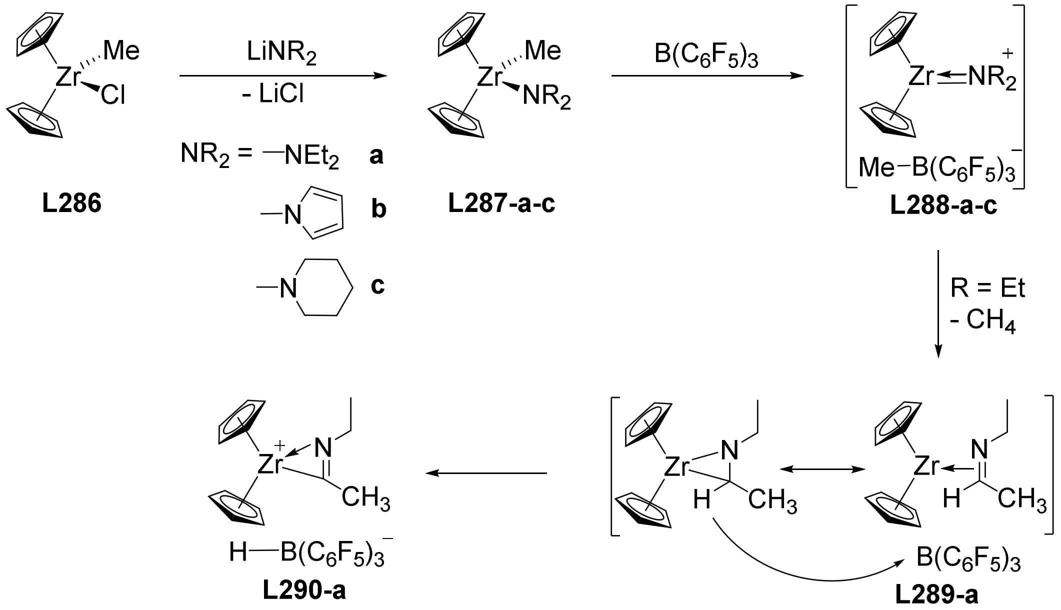
A. Bibliographic introduction

Numerous example of neutral group 4 amido- or phosphidometallocenes have been reported over the years,[2,3,4] but only a few examples of cationic analogues have been described until now. Some of them will be presented in the following section. Early examples of amidozirconocene cations were described by Erker in 1995 (Scheme IV-2).[5] These compounds were shown to be unstable. For example, the cationic (diethylamido)zirconocene **L288-a**, characterized by ^{1}H NMR spectroscopy, was shown to be highly unstable in the course of several hours, yielding cationic (η^2-iminoacyl)zirconocene **L290-a**. The proposed mechanism of formation of **L290-a** involves CH activation at the α-position of nitrogen, followed by methane elimination (by reaction with the methyl-borate anion) and hydride abstraction with

---

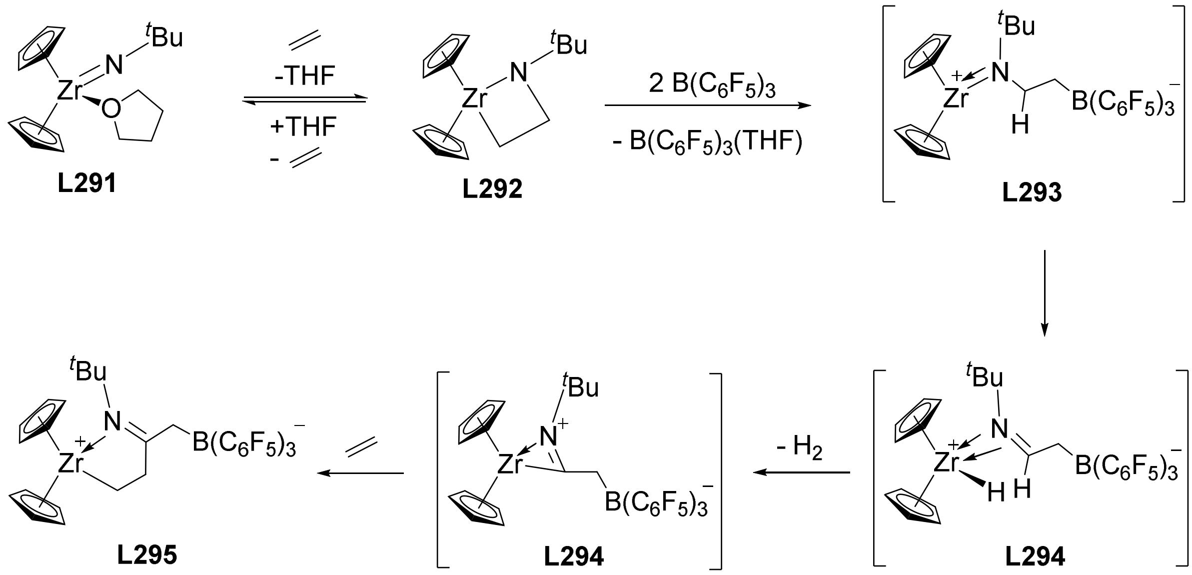
[1] Normand, A. T.; Daniliuc, C. G.; Wibbeling, B.; Kehr, G.; Le Gendre, P.; Erker, G. *J. Am. Chem. Soc.* **2015**, *137*, 10796
[2] Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661
[3] Stephan, D. W. *Angew. Chem. Int. Ed.* **2000**, *39*, 314
[4] Rosenberg, L. *Coord. Chem. Rev.* **2012**, *256*, 606
[5] Temme, B.; Erker, G. *J. Organomet. Chem.* **1995**, *488*, 177

$B(C_6F_5)_3$ thus regenerated. This reactivity is in line with some processes described in the previous chapter (III.B.2.c).



Scheme IV-2: synthesis of the (η^2-iminoacyl)zirconocene via an amidozirconocene

In 1999, another example was reported by Norton (Scheme IV-3).[6] A neutral imidozirconocene was reacted with ethylene in order to form the azametallacycle **L292** after [2+2] cycloaddition. Treatment of this compound with $B(C_6F_5)_3$ afforded the cationic amidozirconocene **L293** by alkide abstraction. Compound **L293** was shown to be highly sensitive and was not characterized. Nevertheless, its formation was proved by further reaction with ethylene, forming **L295** after H_2 loss and ethylene insertion.

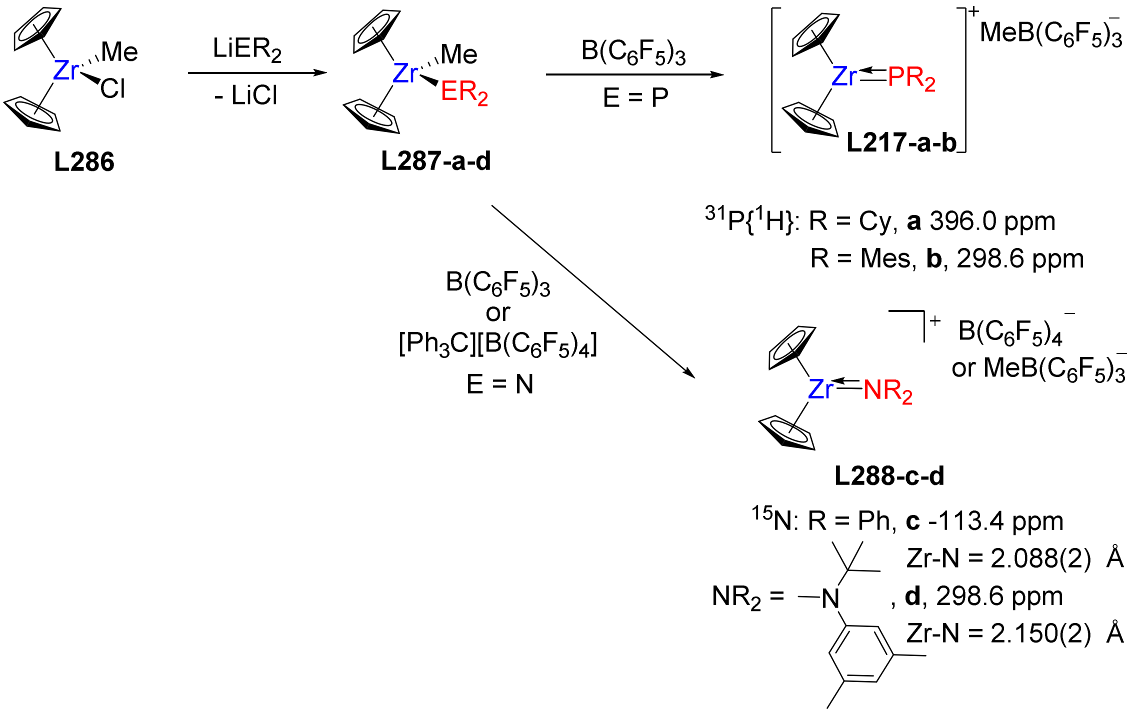


Scheme IV-3: reactivity of an azazirconacycle with $B(C_6F_5)_3$

---

[6] Harlan, C. J.; Bridgewater, B. M.; Hascall, T.; Norton, J. R. *Organometallics.* **1999**, *18*, 3827

Recently, Le Gendre and Erker reported the synthesis of cationic Zr amido and phosphido complexes as previously mentioned in the introduction (Scheme IV-4).[1] Starting from chloro methyl zirconocene **L286**, the target compounds were synthesized in two steps (Scheme IV-4). In the case of amidozirconocenes, the cationic species were isolated and fully characterized, whilst the phospidozirconocenes were shown to be too reactive species to be isolated, and were used *in situ*. Furthermore, both series were shown to be active for small molecule activation. Both N and P atoms exhibited a marked nucleophilic character, conferring to these molecules the ability to react with dihydrogen, CO_2, benzaldehyde.

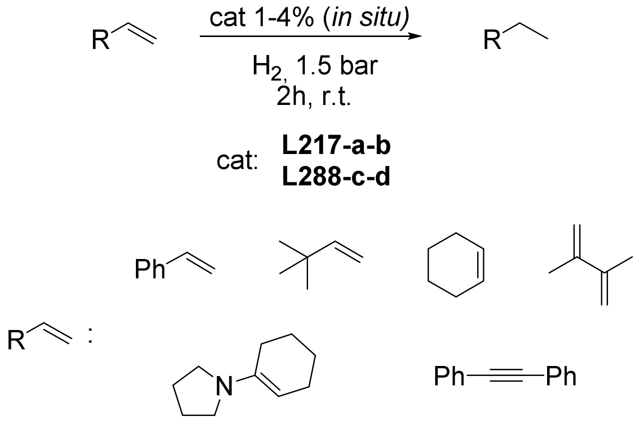


Scheme IV-4: synthesis of cationic amido and phosphido zirconocene complexes

The insertion product of diphenylacetylene with **L217-a** was shown to act as an OmFLP (I.D.3: Scheme I-68),[1] whilst **L217-a** was also used for the direct P-functionalization of azobenzene.[7] Additionnaly, these Zr phosphido and amido complexes were used for the catalytic hydrogenation of alkenes, alkynes, and enamines. Complexes **L217-b** and **L288-d** were shown to be the most active species in this series (Scheme IV-5).

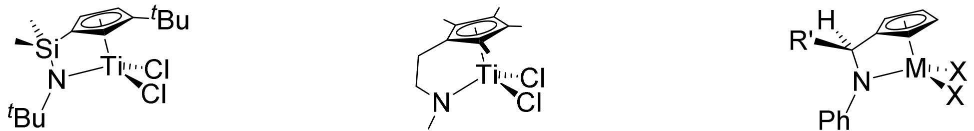
---

[7] Normand, A. T.; Daniliuc, C. G.; Kehr, G.; Gendre, P. L.; Erker, G. *Dalton Trans.* **2016**, *45*, 3711



Scheme IV-5: catalytic hydrogenation of various substrates

To the best of my knowledge, no analogous titanocenes complexes have been reported in the literature. Nevertheless, one can cite the widely reported family of constrained geometry complex, with a M-bound nitrogen, mainly composed of Ti-based examples. These complexes have often been used in combination with an X-Ligand abstractor such as MAO to generate the cationic active species *in situ* in Ziegler-Natta polymerization. Three examples of neutral precursors from the work of Okuda,[8] Teuben,[9] and Erker,[10] are illustrated in Scheme IV-6.



L289 *Okuda* **1990**

L290-a-c *Teuben* **2000**
R = ^{t}Bu **a**, ^{i}Pr **b**, Me **c**

L291-a-b *Erker* **2001**
R' = *p*-tolyl, $MX_2 = Zr(NEt_2)_2$ **a**
R' = Me, $MX_2 = TiN(Me_2)_2$ **b**

Scheme IV-6: selected examples of CGC complexes

Although these complexes have been mainly characterized under their neutral form, the activity of the cationic CGC complexes have been widely developed over the years and could not be avoided in this section. Their use in catalytic processes has already been reviewed elsewhere.[11,12] Working on a metallocenic platform, we were interested in synthesizing cationic amido- and phosphido titanocenes, in order to study their reactivity, and extend the scope of cationic group 4 metallocenes of this category previously initiated in our group.[1]

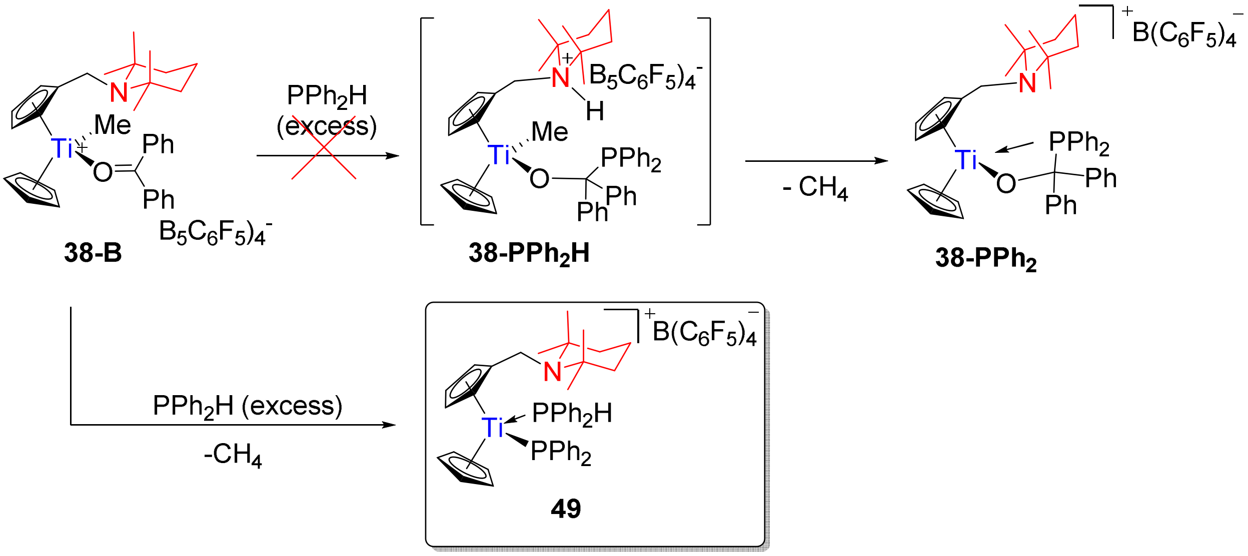
---

[8] Okuda, J. *Chem. Ber.* **1990**, *123*, 1649
[9] van Leusen, D.; Beetstra, D. J.; Hessen, B.; Teuben, J. H. *Organometallics.* **2000**, *19*, 4084
[10] Kunz, K.; Erker, G.; Döring, S.; Fröhlich, R.; Kehr, G. *J. Am. Chem. Soc.* **2001**, *123*, 6181
[11] For example: Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691 and publications cited herein
[12] Collins, R. A.; Russell, A. F.; Mountford, P. *Appl. Petrochem. Res.* **2015**, *5*, 153

B. Synthesis of cationic phosphidotitanocenes

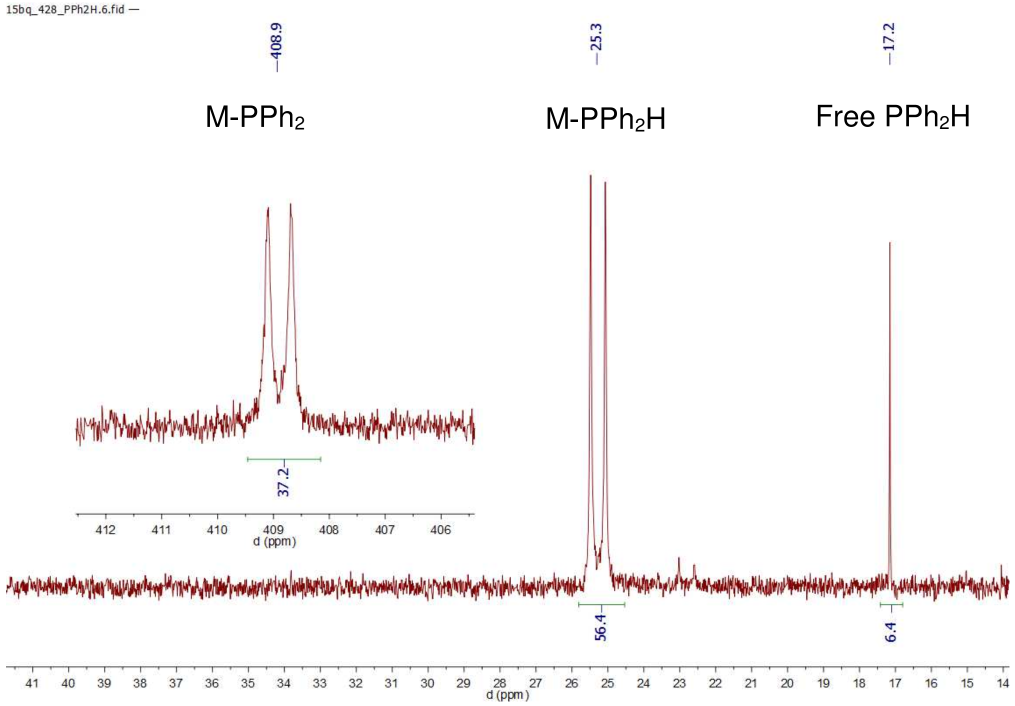
1. Preliminary results

In the course of our studies on OmFLPs, we were interested in the reactivity of secondary phosphines with compound **38-B** in order to form a species of type **38-PPh₂**. The nucleophilic attack of the carbonyl group envisioned initially did not occur. Indeed, protonation of the methide ligand was observed instead, as illustrated in Scheme IV-7.



Scheme IV-7: unexpected formation of a cationic phosphido phosphine titanocene

According to a no lock $^{31}P\{^{1}H\}$ NMR spectrum, a new cationic phosphido titanocene was identified (Spectrum IV-1).

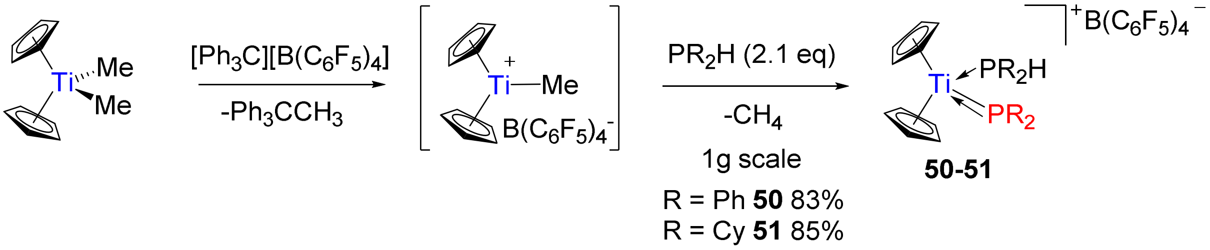


Spectrum IV-1: no lock $^{31}P\{^{1}H\}$ NMR spectrum of 49 (202.46 MHz, 300 K, bromobenzene-d_5)

Indeed, two doublets ($^2J_{PP}$ = 82.7 Hz: coupling through the titanium atom) are observed with one signal shifted strongly downfield (408.9 ppm), similar to the phosphidozirconocene cations (previously described in Scheme IV-4). The other doublet at δ = 17.2 ppm turns into a doublet of doublets in the ^{31}P NMR spectrum, indicative of the presence of a secondary phosphine ($^1J_{PH}$ = 340 Hz). The presumed structure of **49** is depicted in Scheme IV-7. This compound was not isolated, but this unexpected result was the starting point of new investigations.

2. A straightforward route to phosphidotitanocenes

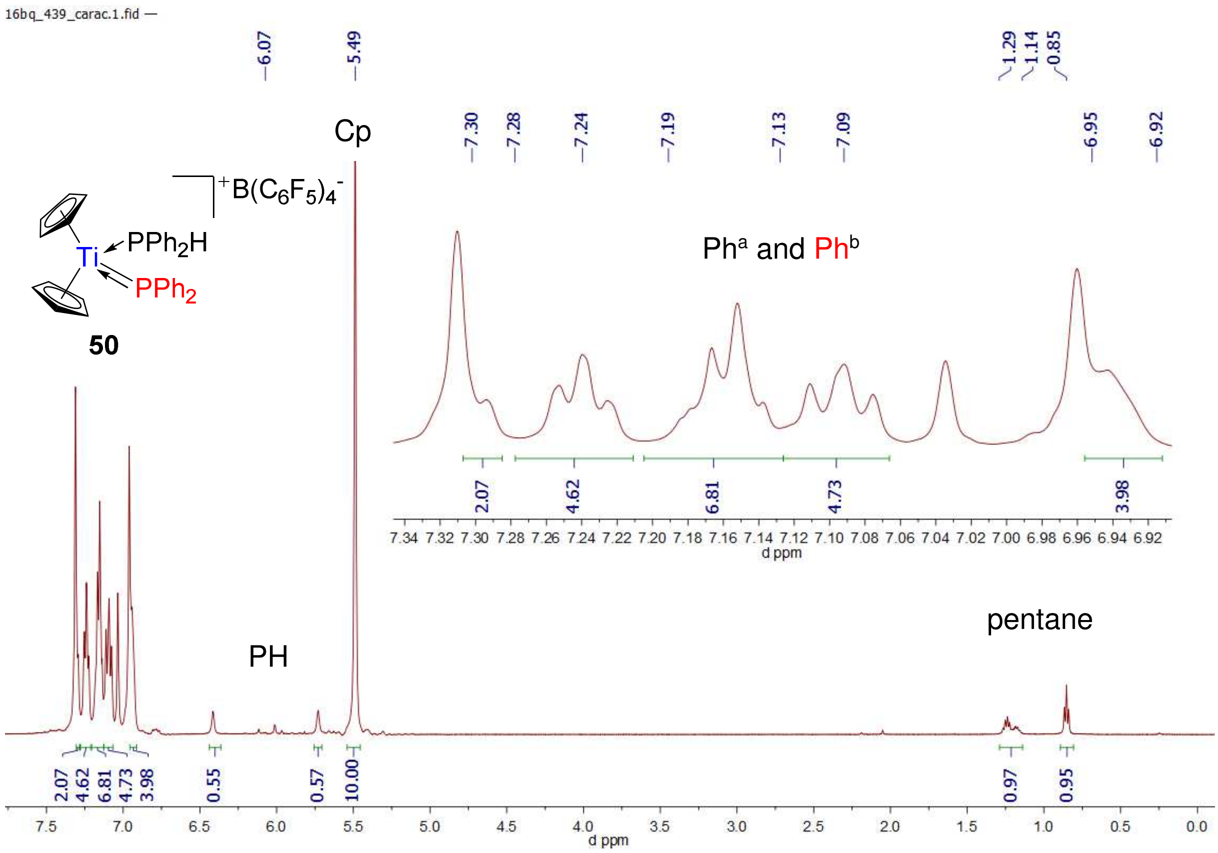
A new procedure was developed according to the preliminary results described above. Starting from dimethyltitanocene, $[Ph_3C][B(C_6F_5)_4]$ was used to abstract a methide from the titanium centre, forming $[Cp_2TiMe][B(C_6F_5)_4]$ intermediately. Attempts at isolating this compound failed. As a result, this compound was always used *in situ*. Addition of a secondary phosphine yielded the corresponding cationic phosphido phosphine titanocene in very good yield as dark-red precipitates (Scheme IV-8).



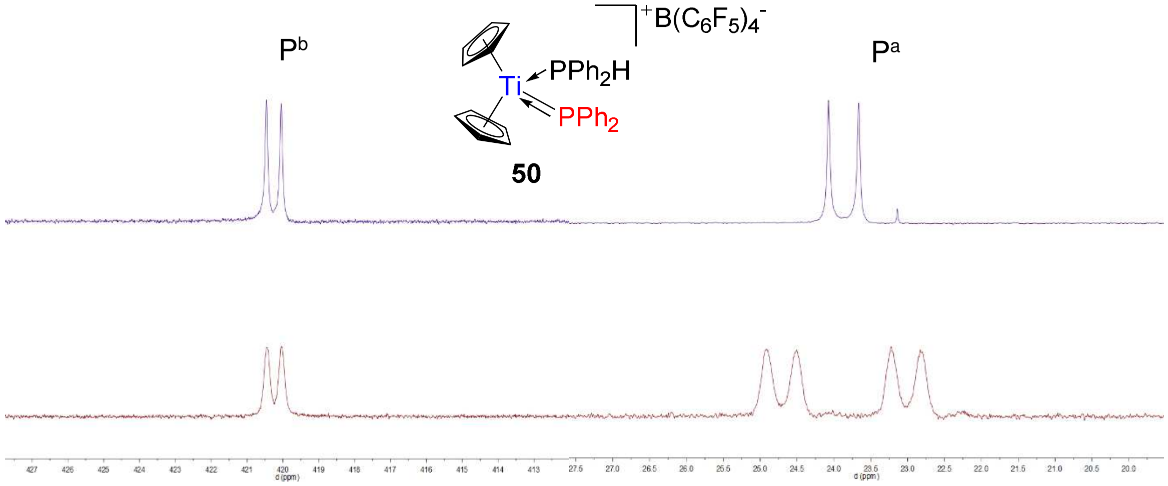
Scheme IV-8: one-pot synthesis of cationic phosphidotitanocenes

The ^{1}H NMR spectra of **50** shows several multiplet for the aromatic signals (7.30-7.28, 7.24, 7.19-7.13, 7.09 and 6.95-6.92 ppm), and one doublet ($^3J_{PH}$ = 2.4 Hz) for the signal of the Cp rings (5.49 ppm). The coupling observed for the signal of the Cp rings is indicative of the coordination of at least one phosphorous atom to the titanocenium fragment.

A characteristic doublet with a large coupling ($^1J_{PH}$ = 342 Hz) is observed at δ = 6.07 ppm for the signal of the phosphorous-bound hydrogen. As previously shown for **49**, a characteristic set of two doublets is observed in the ^{31}P{^{1}H} NMR. The upfield doublet corresponding to the secondary phosphine turns into a doublet of doublets in the ^{31}P NMR (Spectrum IV-3).



Spectrum IV-2: ^{1}H NMR of 50 (500.03 MHz, 300 K, bromobenzene-d$_5$)



Spectrum IV-3: superposition of the ^{31}P{^{1}H} (top) and ^{31}P (bottom) NMR spectra of 50 (202.46 MHz, 300 K, bromobenzene-d$_5$)

In addition, both compounds were characterized by positive mode ESI HRMS, in which a characteristic cluster of peaks corresponding to $[M\text{-}PR_2H]^+$ was observed (at 363.07672 Da for **50** and 375. 17001 Da for **51**). Finally, suitable crystals for X-ray diffraction analysis were obtained for **50**. The ORTEP view is depicted in Figure IV-1.

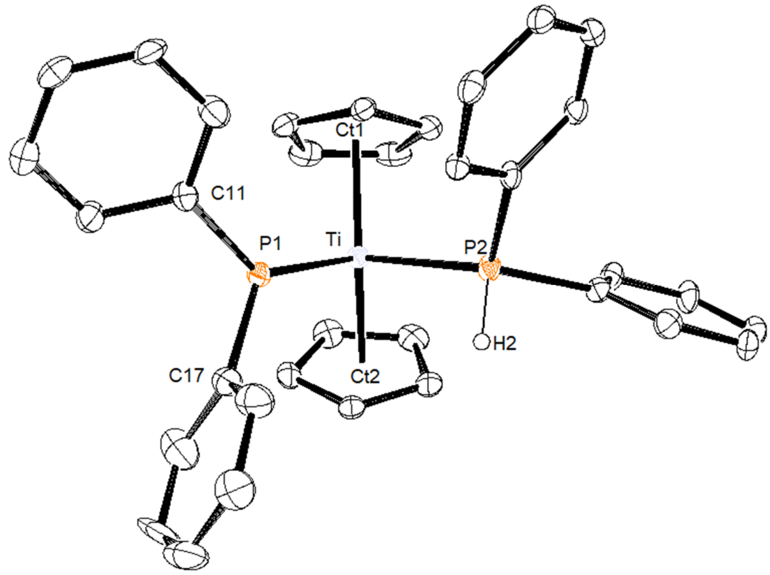


Figure IV-1: ORTEP view of 50 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed as the counter anion, except H2). Selected bond lengths (Å) and angles(°):Ct1-Ti = 2.051(3), Ct2-Ti = 2.042(3), P1-Ti = 2.3607(16), P2-Ti = 2.5864(16), P2-H2 = 1.36(5), P2-Ti-P1 = 88.85(5), Ct1-Ti-Ct2 = 134.85(12), Ti-P1-C11 = 126.16(18), Ti-P1-C17 = 133.52(19), C1-P1-C17 = 100.3(2).

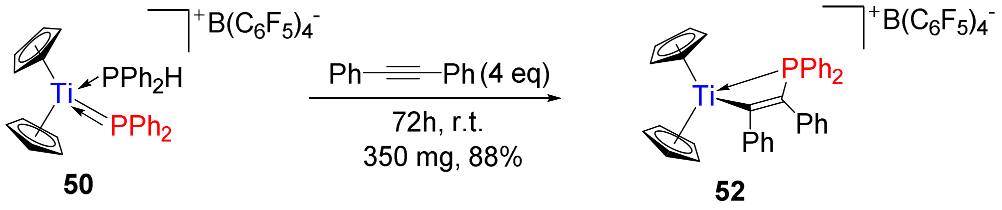
The titanocene fragment adopts a classical bent geometry. Both Ti-P bonds are relatively short compared to the sum of covalent radii (Ti-PPh_2 = 2.3607(16) Å and Ti-PPh_2H = 2.5864(16) vs 2.67 ± 0.11 Å).[13] In addition, the phosphido ligand adopts an almost planar geometry according to the sum of angles around P1 ($\Sigma\alpha$(P1) = 359.9(3)°). The phosphido ligand is well oriented for π-orbital overlap with Ti-based empty orbitals (Torsion angles: C17-P1-Ti-Ct2 = -2.26(3)° and C11-P1-Ti-Ct1 = 24.74(3)°).[14] These results suggest a potential double bond character of the Ti-P1 bond.

The reactivity of these compounds was then investigated. The presence of a lone electron pair on the phosphorus atom of the phosphido ligand, suggests that the formation of heterobimetallic complexes could be feasible. However, all attempts at preparing such compounds failed, whichever late-metal precursor was used: ([Pd-Cl_2], $[(COD)Rh-Cl]_2$, $[Pd(PPh_3)_4]$, [Pt(allyl)$PPh_3)_3$]). The reactivity of the Ti-PR_2 bond was then investigated: no reactivity towards CO_2 or H_2 (2 atm and 1 atm respectively) was observed at room temperature over 24h. Barely any change was observed according to ^{31}P NMR experiments. Since no reactivity was observed with gaseous substrates, diphenylacetylene was tested on **50**. When this complex was reacted with 1 eq of alkyne for 12h at room temperature, a new compound was observed (according to no lock ^{31}P NMR spectroscopy). However, only 30% of conversion was observed. The reaction was then carried out with 4 equivalents of diphenylacetylene, and shown to be completed after 72h of stirring at room temperature (Scheme IV-9).

---

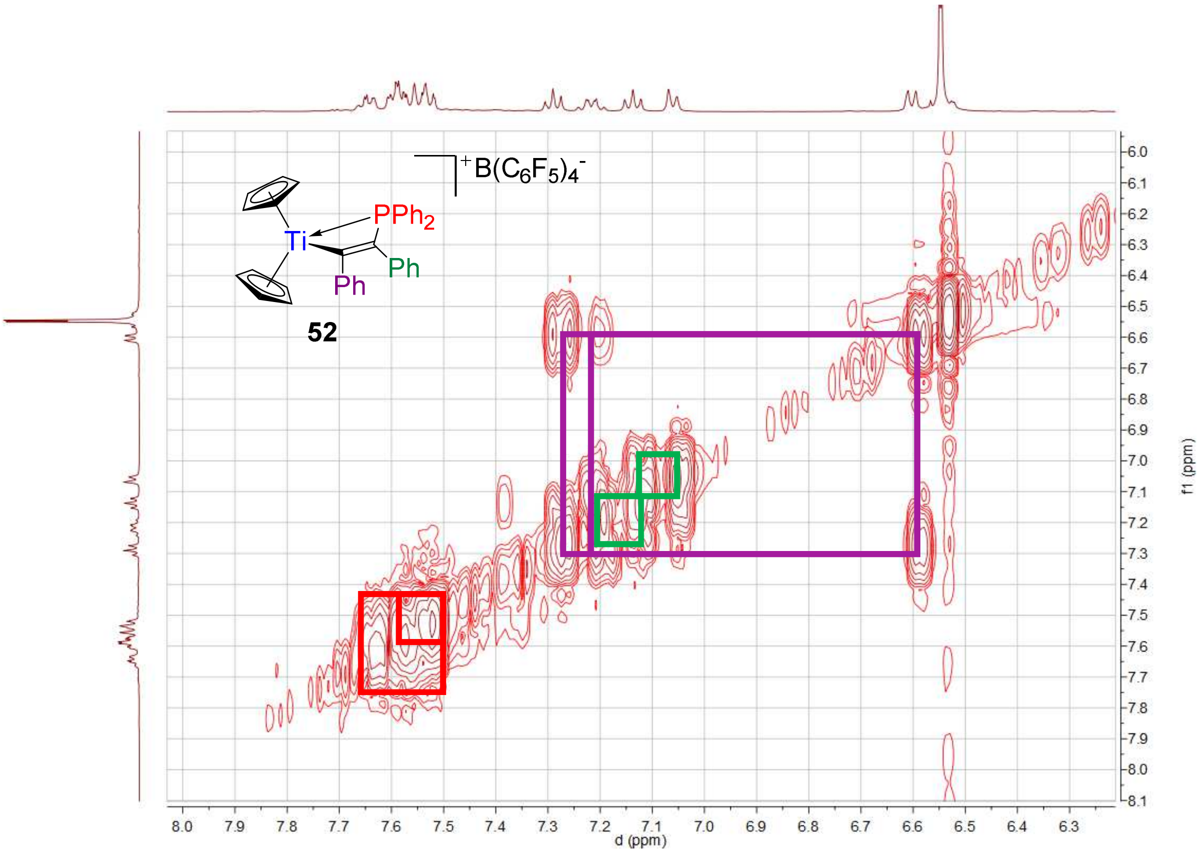
[13] Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832

[14] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729



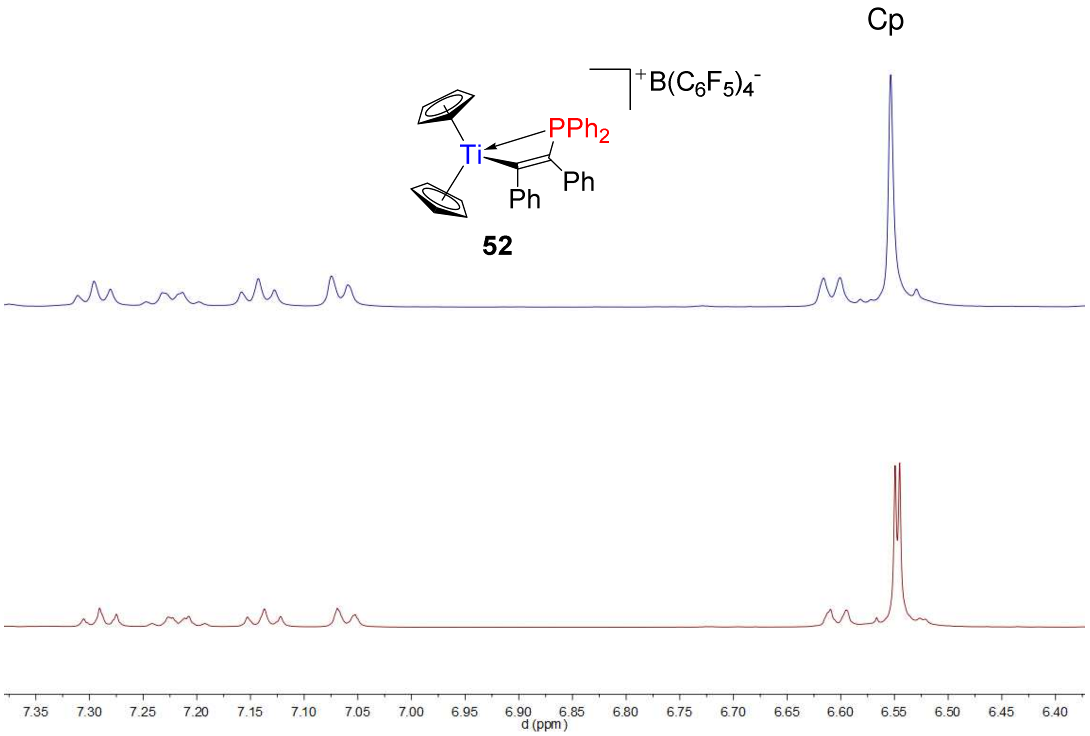
Scheme IV-9: synthesis of 52

The new cationic titanocene compound was identified as being **52**, formed by insertion of the diphenylacetylene into the Ti-PPh_2 bond. This compound was isolated and characterized by NMR (^1H, ^{11}B, ^{13}C, ^{19}F, ^{31}P and 2D correlations) positive mode ESI HRMS and elemental analysis. The ^1H ^1H COSY NMR spectrum shows three different phenyl rings, as illustrated in Spectrum IV-4.



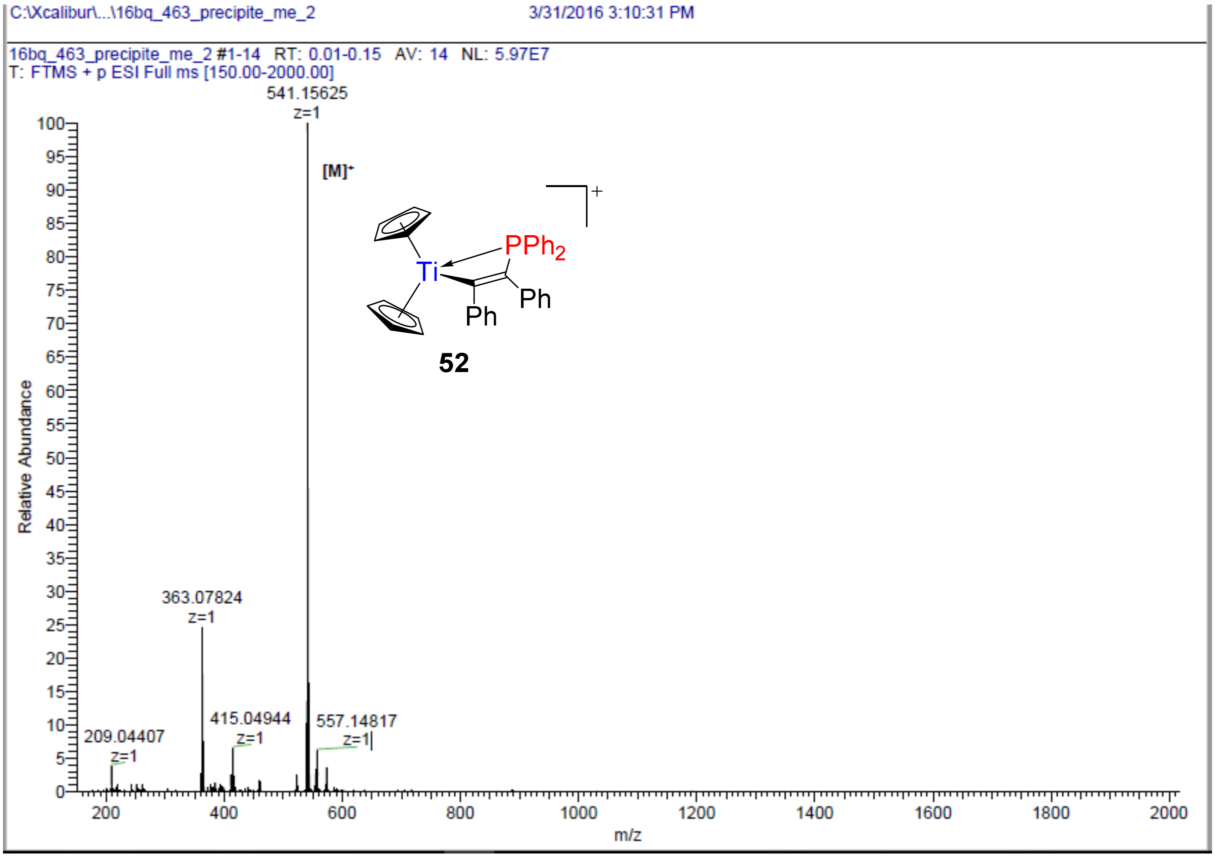
Spectrum IV-4: ^1H ^1H COSY NMR spectrum of 52 (500.03 MHz, 300 K, dichloromethane-d_2)

Furthermore, the signal of the Cp rings resonates as a doublet ($^3J_{PH}$ = 2.0 Hz), the coupling of which was attributed to the phosphorous atom according to $^1H\{^{31}P\}$ NMR spectroscopy (see Spectrum IV-5).



Spectrum IV-5: superposition of $^1H\{^{31}P\}$ (top) and ^1H (bottom) NMR of 52

Lastly, the mass spectrum of **52** shows a cluster of peaks corresponding to the cationic species, at 541.15625 Da, as illustrated in Spectrum IV-6.



Spectrum IV-6: HRMS spectrum of 52 (Positive mode ESI, dichloromethane)

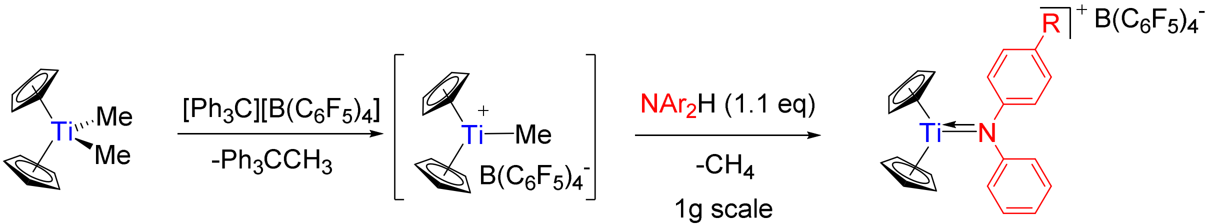
This compound was tested towards standard substrates for FLP reactivity, but turned out to be completely unreactive. The PCy_2 analogue of **52** was not synthesized, since it had been prepared by Dr. Adrien Normand using a different synthetic route. Of note, the structure of this compound was elucidated by X-ray diffraction analysis, which gives further support to the proposed connectivity of **52**.

The successful synthesis of cationic phosphidotitanocenes led us to investigate the extension of this methodology to cationic amidotitanocenes by reacting $[Cp_2TiMe][B(C_6F_5)_4]$ with secondary amines.

C. Synthesis of cationic amidotitanocenes

1. Synthesis

By using the above described procedure, three new amidotitanocenes were obtained in very good yield and purity as illustrated in Scheme IV-10. With secondary amines, no amine coordination was observed, even in the presence of an excess of amine. The dark-red solution of $[Cp_2TiMe][B(C_6F_5)_4]$ turned rapidly dark-green after addition of the amine.

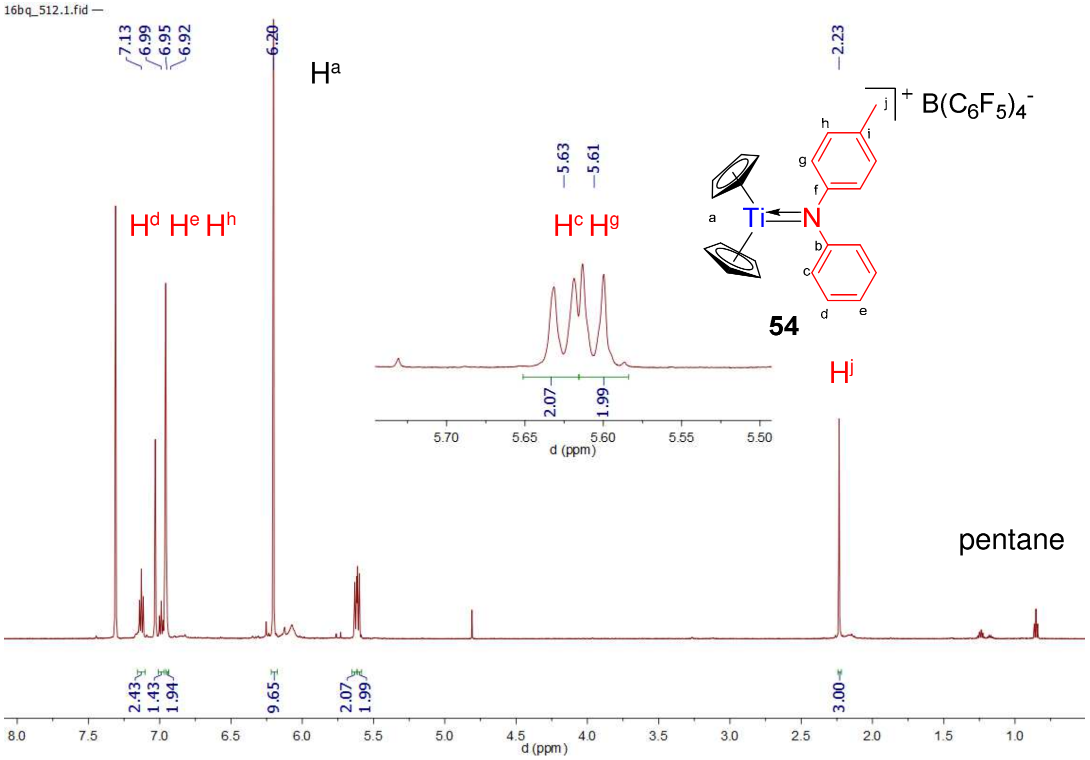


53-55

R = H **53** 88% δ: ^{15}N NMR: -35 ppm
R = Me **54** 85% -32 ppm
R = OMe **55** 97% -30 ppm

Scheme IV-10: a one-pot synthesis for cationic amidotitanocenes

Compounds **53-55** were characterized by NMR spectroscopy (^1H, ^{11}B, ^{13}C, ^{15}N, ^{19}F and 2D correlations) and elemental analysis. Despite their ionic form, these compounds could not be characterized by mass spectrometry, presumably due to their high sensitivity, and rapid decomposition. The ^1H NMR spectrum of **54** is depicted in Spectrum IV-7.



Spectrum IV-7: ^{1}H NMR of 54 (600.23 MHz, 300 K, bromobenzene-d$_5$)

Two sets of aromatic signals are observed: one monosubstituted phenyl ring with a set of two triplets and one doublet (7.13, 6.99 and 5.63 ppm respectively), and one para-disubstituted phenyl ring with two doublets (one at 6.95-6.92 ppm overlapping with the solvent peak, and one at 5.61 ppm). Lastly, one can find one singlet for the signals of the Cp rings and one singlet for the methyl of the tolyl group (6.20 and 2.23 ppm respectively). The structure of this compound was elucidated by X-ray diffraction analysis of green needle-shaped crystals.

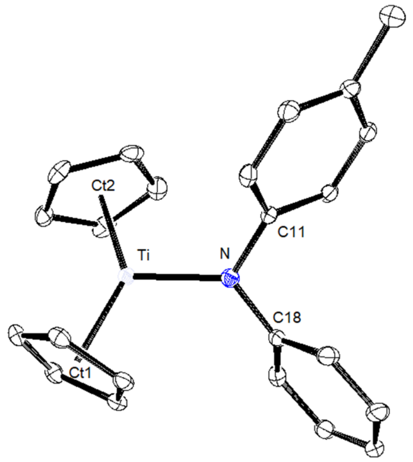
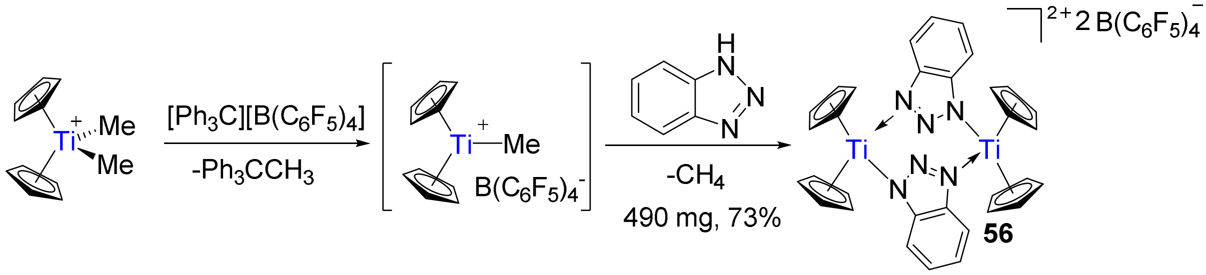


Figure IV-2: ORTEP view of 54 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed as the counter anion). Selected bond lengths (Å) and angles(°): Ct1-Ti = 2.0308(12), Ct2-Ti = 2.0282(11), N-Ti = 1.9791(19), N-C11 = 1.433(3), N-C18 = 1.432(3), Ct1-Ti-Ct2 = 135.41(6), Ct1-Ti-N = 111.56(6), Ct2-Ti-N = 112.99(6), Ti-N-C18 = 127.01(14), Ti-N-C11 = 122.31(14), C11-N-C18 = 110.67(17).

In this structure, the titanocene adopts a bent geometry. The Ti-N bond is relatively short compared to the sum of covalent radii for Ti and N (1.9791(19) vs 2.31 ± 0.09 Å). Besides, the sum of angles around nitrogen indicates a planar geometry ($\Sigma\alpha(N) = 359.9(3)°$). The selected torsion angles calculated (C11-N-Ti-Ct2 = 43.82(18)°, C18-N-Ti-Ct1 = 41.46(19)°) show that the tolyl and phenyl groups bound to the amido ligand are neither in the bisecting plane of the titanocene moiety, nor orthogonal to it, but somewhere in between. Nevertheless partial π-orbitals overlap between the titanocenium fragment and the amido ligand may confer a certain degree of double bond character to the Ti-N interaction. This assumption should be investigated by theoretical calculations.

This synthesis was also attempted on alkyl-substituted amines such as dibenzylamine, tetramethylpiperidine or tert-butyl-meta-dimethylaniline. The green color observed for the aryl analogues was also observed, but rapid decomposition occurred forming brownish solution containing unidentified compounds. As previously shown in chapter II, CH activation on the amine fragment might occur, yielding decomposition of the desired product. Nevertheless, an additional Ti amido complex was obtained by using benzotriazole. In this case, dimeric species **56** was obtained with two bridging benzotriazolides, as a light-orange powder (Scheme IV-11).



Scheme IV-11: synthesis of the homobimetallic complex 56

This compound was characterized by NMR (^1H, ^{11}B, ^{13}C, ^{19}F and 2D correlation) and IR spectroscopies, positive mode ESI HRMS and elemental analysis. The positive mode ESI HRMS spectrum shows the cationic species derived from the splitting of the dimer as a cluster of peaks at 296.06660 Da (calculated for $C_{16}H_{14}N_3Ti^+$), and more surprisingly, another cluster of peaks is observed at 1271.11567 Da, corresponding to a monocationic adduct of the dimer with only one borate (calculated for $C_{32}H_{28}N_6Ti_2BC_{24}F_{20}^+$). An additional dimeric mixed valence (Ti(III) and Ti(IV)) species was identified with a cluster of peaks at 592.13433 Da (calculated for $C_{32}H_{28}N_6Ti_2^+$). The dimeric nature of **56** was definitely established by X-ray diffraction analysis (Figure IV-3).

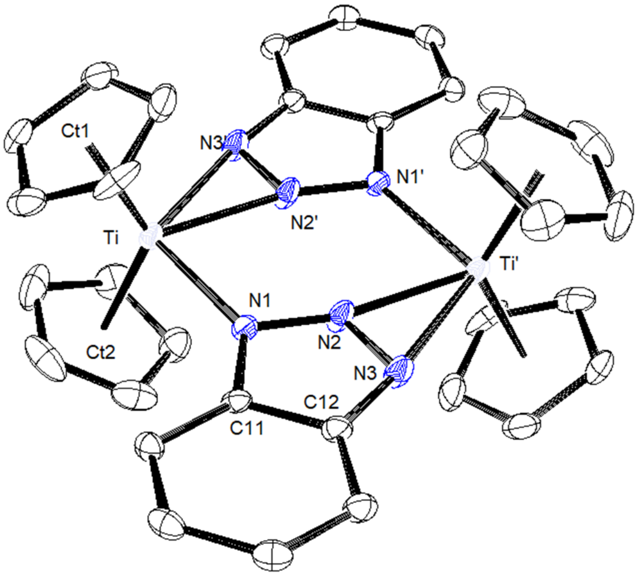


Figure IV-3: ORTEP view of 56 (ellipsoids drawn at the 30% probability level, hydrogen atoms removed as the counter anion and the molecules of solvent for clarity). Selected bond lengths (Å) and angles(°): Ti-N1 = 2.235(3), Ti-N2 = 2.086(3), Ti’-N3 = 2.236(3), N1-N2 = 1.303(4), N2-N3 = 1.326(4), Ct1-Ti = 2.061(2), Ct2-Ti = 2.055(2), Ct1-Ti-Ct2 = 133.17(10), N3’-Ti-Cln = 95.49(10), N1-N2-N3 = 114.1(2), N2-N3-C12 = 104.8(2), N3-C12-C11 = 107.3(3), C12-C11-N1 = 107.0(3), C11-N1-N2 = 106.8(3), Ti-N2-N3 = 166.8(2), Ti-N3’-N2’ = 115.54(18), N2-Ti-N3’ = 77.45(10).

The molecule present a symmetric centre in the solid state. As a result, the numbering with the superscript prime was used to describe the whole structure. The geometry of the titanocene moiety remains pseudo tetrahedral as illustrated by the ORTEP view. This structure clearly shows that the benzotriazolide group acts as a bridging XL ligand. The geometry of the triazole pentagon remains planar in this structure ($\Sigma\alpha$(triazole) = 540.0(6)°). As a result, both benzotriazolide ligands lie in the bisecting plane of the titanocenes.

This compound was shown to be highly stable, in various solvents (dichloromethane, tetrahydrofuran….) contrary to the cationic amidotitanocene analogues, only stable in bromo- or chlorobenzene. It has to be mentioned that these cationic amidotitanocenes are prone to decomposition if stored at room temperature and ambient light over several weeks. We suspected that decomposition might be a result of exposure to light, therefore we conducted a study to verify this assumption.

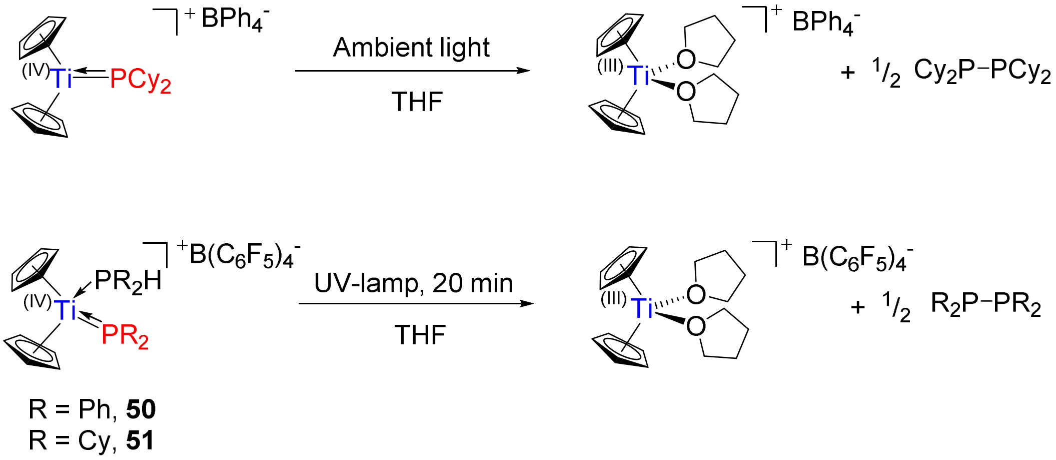
2. Irradiation study

These results were collected in collaboration with Dr. Adrien Normand, who had previously developed the general procedure for the reactivity studies of cationic phosphido titanocenes he designed.[15] According to this procedure, complexes **50** and **51** on the one hand, and **53-54** on the other hand, were irradiated with an Heraeus TQ 150 UV lamp in THF (purple-coloured solution). Reaction mixtures were analysed by EPR and NMR spectroscopies (and GCMS analysis for the amido series) and compared to the solution before irradiation. A

---

[15] Manuscript in preparation

characteristic cation had been prepared separately as its BPh_4^- salt and characterized by EPR spectroscopy XRD analysis, and elemental analysis by Dr. Adrien Normand. This paramagnetic complex was used as reference for the following study. As a matter of fact, $[Cp_2Ti(THF)_2][BPh_4]$ can be made by decomposition of $[Cp_2Ti(PCy_2)][BPh_4]$ under ambient light (established by Dr. Adrien Normand). As a result for the phosphido series, a 20 min-period of irradiation was sufficient to obtain a blue-coloured solution, characteristic of the paramagnetic species $Cp_2Ti(THF)_2^+$ (g = 1.9758), further confirmed by EPR spectroscopy and X-ray diffraction analysis. In addition, multinuclear NMR spectroscopy corroborates the formation of $(PR_2)_2$, the side product in such decomposition process (see appendix for more details). Of note, Ti-P bond homolysis has been previously observed by Stephan with neutral phosphidotitanocenes.[16]

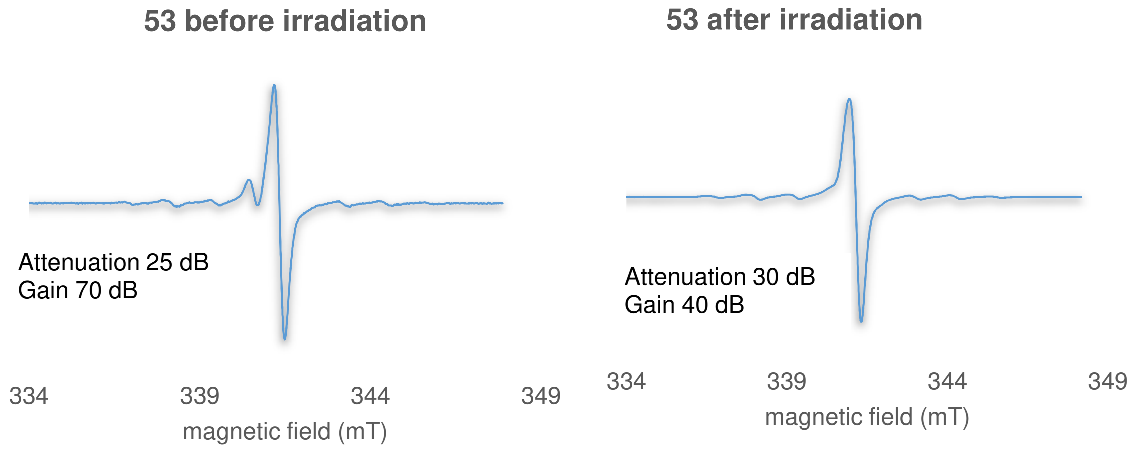


Scheme IV-12: homolytic cleavage of the Ti-N bond from cationic phosphidotitanocenes

On the other hand, for the amido series, whilst a 20-min-period of irradiation was sufficient to obtain a blue-coloured solution for **55**, an additional period of 20 min was required for **53** and **54**. The EPR spectra of **53** before and after irradiation are depicted in Spectrum IV-8, showing the presence of $Cp_2Ti(THF)_2^+$ in both cases.

---

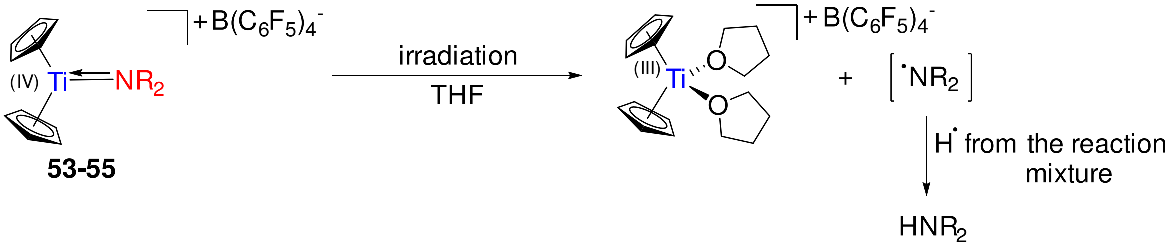
[16] Dick, D. G.; Stephan, D. W. *Organometallics.* **1991**, *10*, 2811



Spectrum IV-8: EPR spectra of 53 before (left) and after irradiation (right) (9.438876 GHz / 9.435437 GHz, 295 K, THF)

Note that the attenuation has been increased and the gain has been diminished in the spectrum recorded after irradiation, which indicates that the concentration of $Cp_2Ti(THF)_2^+$ has increased. The calculated Lande factor (g = 1.9758) is consistent with that measured by Dr. A. Normand and to the literature value. [17]

For the amido series, no $(NR_2)_2$ coupling products were observed by NMR spectroscopy or by GCMS analysis. $B(C_6F_5)_4^-$ was the only species identified by NMR spectroscopies, whilst secondary amines were identified by GCMS analysis (see experimental part). According to the literature, aminyl radicals do not dimerize like phosphanyl radicals, but tend to abstract $H^•$ (e.g. from solvent molecules),[18] as illustrated in Scheme IV-13.



Scheme IV-13: homolytic cleavage of the Ti-N bond from cationic amidotitanocenes

3. Reactivity study

After this irradiation study, the reactivity of this amido series was also studied. Dimeric **56** did not react towards CO_2 or H_2 under mild conditions. The starting product was recovered after these reactions. Similarly, all attempts to insert unsaturated substrates (diphenylacetylene, phenylacetylene, imines) also failed, highlighting the high stability of **56.**

Conversely, insertion reaction of the same unsaturated substrates with cationic amidotitanocenes **53-55** only yielded decomposition of the complexes. These compounds

---

[17] Borkowsky, S. L.; Baenziger, N. C.; Jordan, R. F. *Organometallics.* **1993**, *12*, 486

[18] Wang, Y.; Olankitwanit, A.; Rajca, S.; Rajca, A. *J. Am. Chem. Soc.* **2017**, *139*, 7144

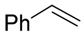
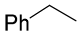
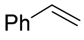
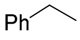
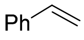
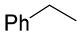
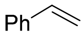
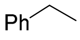
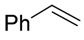
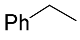
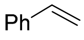
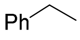
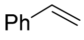
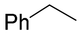
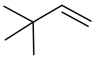
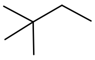
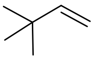
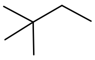
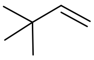
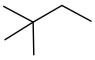
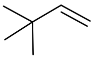
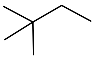
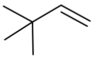
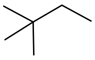
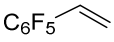
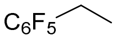
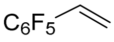
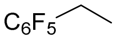
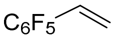
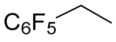
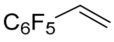
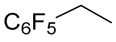
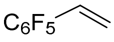
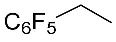
were shown to react with CO_2, but these reactions did not yield well-defined species, according to the recorded spectra, indicating a mixture of several products. The same observation was made with H_2. These compounds were shown to be too reactive to form viable complexes whatever the type of reactivity attempted. Thus, these complexes were tested as catalysts for the hydrogenation of unsaturated substrates, due to their ability to react with H_2.

D. Catalytic hydrogenation of unsaturated molecules

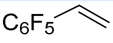
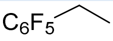
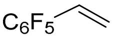
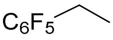
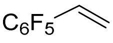
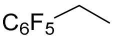
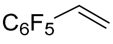
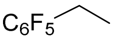
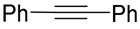
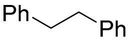
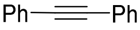
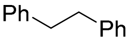
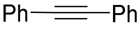
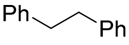
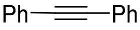
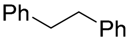
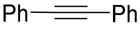
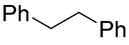
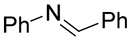
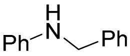
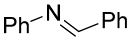
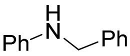
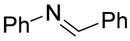
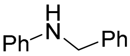
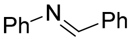
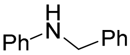
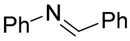
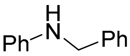
The previously described amido and phosphido Zr complexes reported by Erker and Le Gendre, showed good catalytic activity in the hydrogenation of unsaturated substrates (Scheme IV-5).[1]

Thus, the activity of **50-51** and **53-56** was tested by reacting a range of substrate in an atmosphere of dry H_2 (see the appendix for details), in bromobenzene over a period of 3h. Trimethoxybenzene (TMB) was used as internal standard, in order to quantify the conversion of the reaction by ^{1}H NMR spectroscopy. The results obtained are summarized in Table IV-1.

$$\text{Substrate} \xrightarrow[\text{TMB 5 mol \%},\ C_6H_5Br]{\text{cat.},\ H_2 \text{ 1 atm, 3h, r.t.}} \text{Product}$$

Entry	Substrate	Product	conditions	catalyst	Loading (mol %)	Conversion (%)
1			a	x	X	0
2			a	**50**	4	0
3			a	**51**	4	0
4			a	**53**	2	97
5			a	**54**	2	87
6			a	**55**	2	79
7			a	**56**	2	0
8			a	x	x	0
9			a	**53**	2	69
10			a	**54**	2	74
11			a	**55**	2	55
12			a	**56**	2	0
13			a	x	x	0
14			a	**53**	2	1
15			a	**54**	2	1.2
16			a	**55**	2	0
17			a	x	x	0

$$\text{Substrate} \xrightarrow[\text{TMB 5 mol \%}\ C_6H_5Br]{\text{cat.}\ H_2\ \text{1 atm, 3h, r.t.}} \text{Product}$$

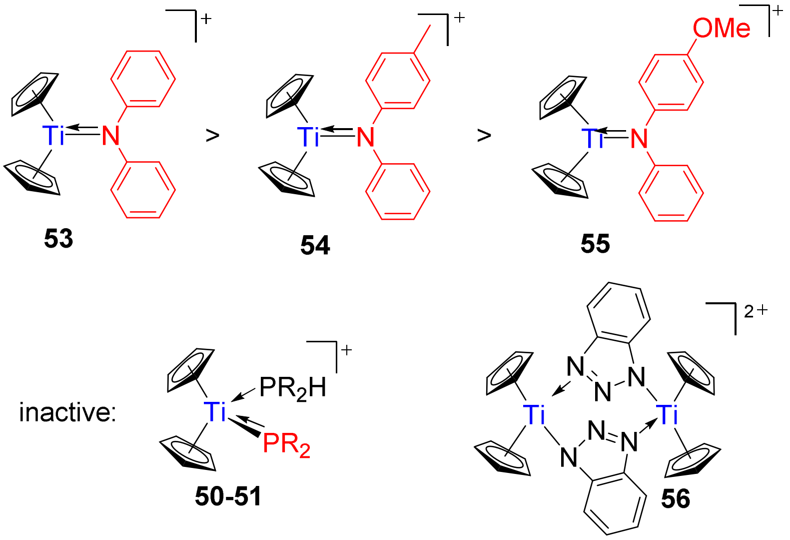
Entry	Substrate	Product	conditions	catalyst	Loading (mol %)	Conversion (%)
18			b	**53**	4	4.5
19			b	**54**	4	3.2
20			b	**55**	4	traces
21			b	**56**	4	0
22			b	x	x	0
23			b	**53**	4	95
24			b	**54**	4	53
25			b	**55**	4	14
26			b	**56**	4	0
27			b	x	x	0
28			b	**53**	4	12[c]
29			b	**54**	4	8[c]
30			b	**55**	4	4[c]
31			b	**56**	4	0

Conversion to product (average of two runs) determined by integration *versus* trimethoxybenzene (TMB) standard [a]: 960 µmol of substrate, 5 mol% TMB, 2 mol% catalyst ; [b]: 480 µmol of substrate, 5 mol% TMB, 4 mol% catalyst; [c] conversion determined by integration vs starting material.

Table IV-1: results of the hydrogenation catalysis

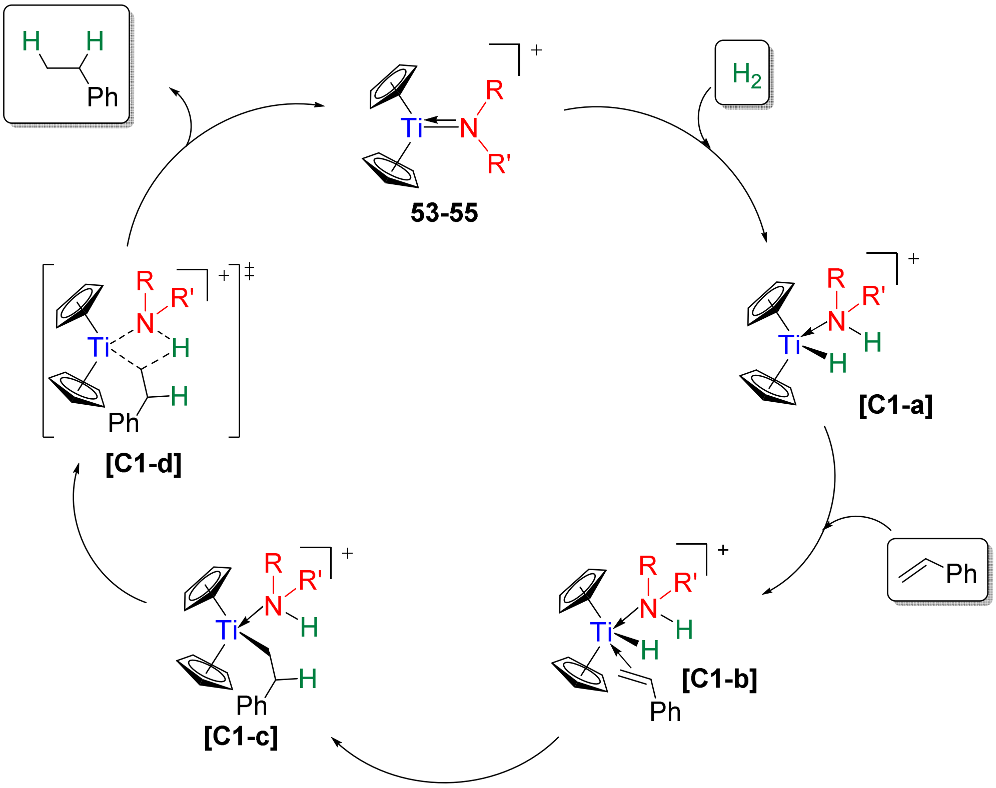
The first catalytic assays were conducted on alkenes with the cationic phosphido and amidotitanocenes. The Ti phosphido series (Table IV-1: entry 2-3) turned out to be completely inactive, contrary to the phosphido zirconocene complexes previously reported by Le Gendre and Erker (**L217-a-b** Scheme IV-4).[1] This difference might be explained considering that the vacant site on **L217-a-b** is occupied by PR_2H in **50-51,** even if this phosphine was found to be labile in polar solvents (e.g. THF, see appendix). The benzotriazolido titanocenium was also completely inactive. Nevertheless, the Ti amido series was active against a range of substrates. Indeed, comparable conversions to those obtained with the zirconocene series described by Le Gendre and Erker, were observed for the cationic amidotitanocenes in the hydrogenation of styrene, 3,3-dimethybut-1-ene, and diphenylacetylene (Table IV-1 Entry 4-6, 9-11 and 23-25 respectively). The best catalyst in this series is compound **53.** However, the hydrogenation of an electron-deprived substrate such as the perfluorostyrene was completely ineffective with this, even with higher loading and concentration (Table IV-1 Entry 14-20). The limitation of the system was also observed with benzalaniline (Table IV-1 Entry 28-30). For this substrate, complicated ^{1}H NMR spectra were recorded. In some cases, the TMB signals were even almost vanished from the ^{1}H NMR spectrum. Nevertheless, the starting imine and the corresponding hydrogenated product benzylaniline (corroborated with GCMS analysis for qualitative purpose) were observed and identified by ^{1}H NMR spectra, showing very low conversion (entry 28-30). Catalyst poisoning by the imine substrate or by the amine product is likely the cause of this lack of catalytic activity.

To summarize the results obtained in the titanocenium series, the phosphido series was completely inactive contrary to their Zr analogues in catalytic hydrogenation. More surprisingly for the amido Ti series, comparable activity to the most basic Zr analogues were observed. Indeed, the diphenylamido zirconocenium complex was relatively poorly active compared to the 3,5-dimethylphenyl-*tert*-butylamido zirconocenium complex and the amido Ti series reported in this manuscript.



Scheme IV-14: comparison of the activity of cationic amido- and phosphido titanocenes in catalytic hydrogenation (counter anion $B(C_6F_5)_4^-$ omitted for clarity)

For this catalytic reaction, the following mechanisms are proposed based on a metal-ligand cooperativity, but remain subject to debate without further experimental evidence, and / or DFT calculations. The first proposal is analogous to the mechanism proposed for the Zr-based systems previously described by Le Gendre and Erker, in which the active species is a cationic amido Ti (IV) complex. For clarity, it has been exemplified with styrene but it could be extended to any substrates used in this catalytic reaction. The first step of this mechanism is the cooperative H_2 activation by the cationic Ti amido complex, forming **[C1-a]**. The resulting formation of a labile secondary amine may favour the styrene approach in the coordination sphere of the titanium **[C1-b]**, a requirement for the insertion step of the carbon-carbon double into the Ti-H bond. The cationic alkyl titanocene formed (**[C1-c]**) may then be able to undergo protonolysis by the Ti-bound secondary amine via transition state **[C1-d]**, liberating ethylbenzene, and regenerating the cationic amidotitanocene complex.

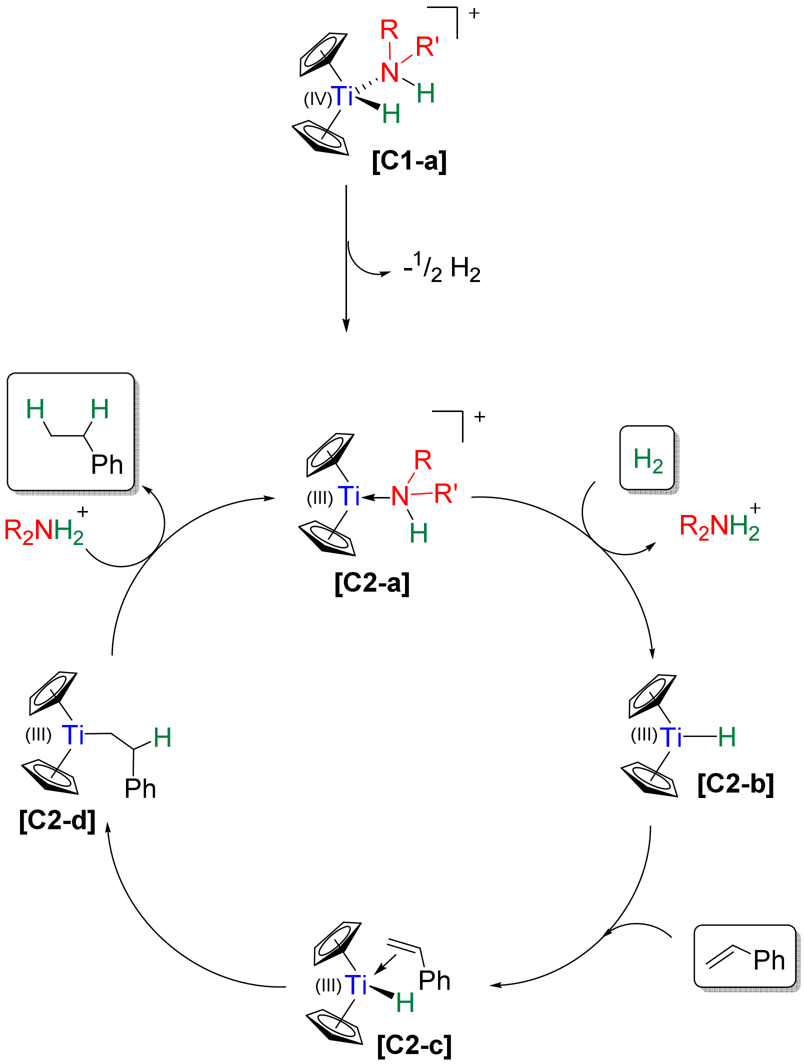


Scheme IV-15: catalytic mechanism via a cationic Ti(IV) species: first proposal

Alternatively, a mechanism based on Ti(III) species may be envisioned. Indeed, Ti(IV)-H species are known to undergo homolytic Ti-H cleavage, thus generating Ti(III) species along with H_2.[19] One can then draw the catalytic cycle depicted in Scheme IV-16. Starting from the cationic titanium hydride **[C1-a]**, the second catalytically active species **[C2-a]** is generated by homolytic cleavage of the Ti-H bond forming **[C2-a]**. From this stage, an analogous mechanism to the one depicted in Scheme IV-15 may operate, except that the ammonium acts as an external Brønsted acid to protonate Ti-alkyl species. Of note, both mechanisms could operate simultaneously, or the formation of Ti(III) species could just be a catalyst decomposition pathway, if one step of the following mechanism is energetically unfavoured.

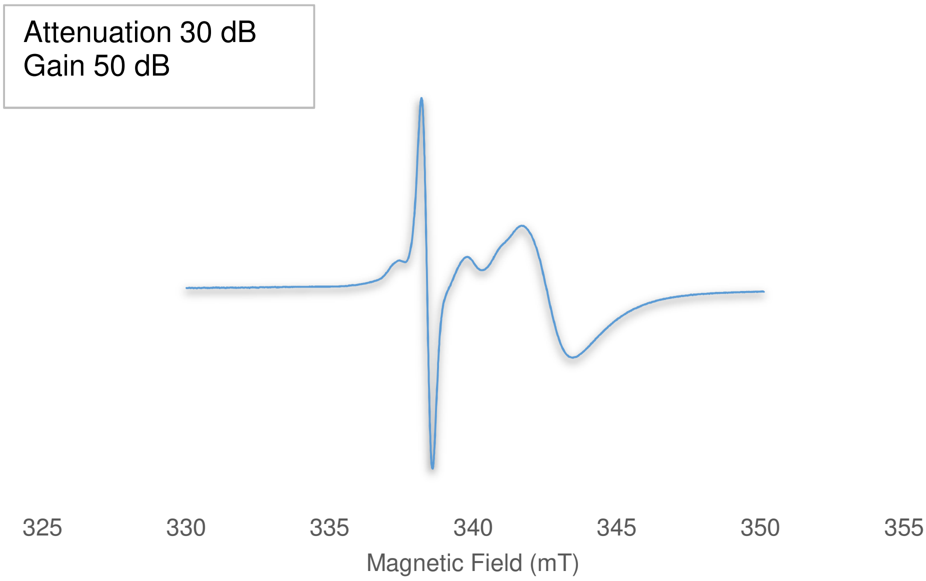
---

[19] Chapman, A. M.; Wass, D. F. *Dalton Trans.* **2012**, *41*, 9067



Scheme IV-16: catalytic mechanism via a cationic Ti(III) species: second proposal

A preliminary clue was obtained, by measuring an EPR spectrum during the catalytic hydrogenation of styrene with **53** (Spectrum IV-9). The presence of Ti(III) species was detected, but this is definitely not sufficient to demonstrate the second mechanism without a better characterization of the detected Ti(III) species. Indeed, Ti(IV) compounds often contain residual Ti(III) species.

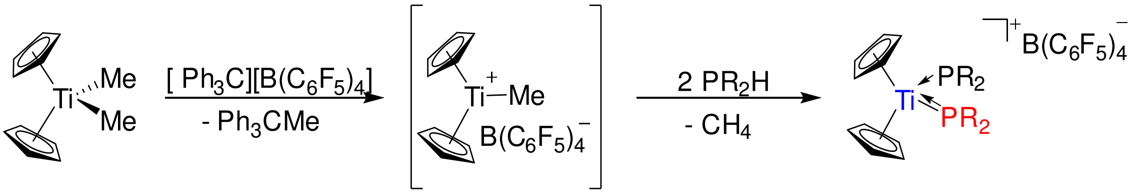


Spectrum IV-9: EPR spectrum of the catalytic hydrogenation of diphenylacetylene with 53 (9.430654 GHz, 295 K, bromobenzene)

In conclusion to this chapter, a straightforward synthesis of cationic phosphido and amidotitanocenes was developed with commercially available starting material in a one-pot synthesis. The cationic phosphidotitanocenes series was shown to be poorly reactive compared to the amido series. The latter were used in catalytic hydrogenation (possibly following a mechanism involving metal ligand cooperativity) of unsaturated substrates in mild conditions and showed relatively good activity.

E. Experimental part

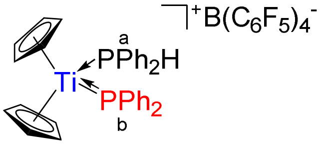
1. Synthesis of phosphido-titanocenes:



General procedure:

In an Ar glovebox, Cp_2TiMe_2 (200 mg, 0.96 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (888 mg, 0.96 mmol, 1 eq) were mixed for 5 min in 2 mL of C_6H_5Br at room temperature. A solution of PR_2H (376 mg, 2.02 mmol) in C_6H_5Br was added dropwise to the reaction mixture. The resulting deep-red solution was stirred for 3h until a red precipitate was formed. The heterogeneous solution was added dropwise to 8 mL pf pentane under vigorous agitation to complete the precipitation of the desired red compound. The supernatant was removed and the red precipitate was washed twice with 5 mL of pentane. After removal of traces of pentane *in vacuo*, the red precipitate was dissolved in CH_2Cl_2 and precipitated from pentane as described above (*N.B.: compound* ***50*** *and* ***51*** *slowly decompose in* CH_2Cl_2*, therefore this step must be performed quickly*).

a. $PR_2H = PPh_2H$ **50**:



Chemical Formula: $C_{58}H_{31}BF_{20}P_2Ti$
Molecular Weight: 1228,5

Yield: 0.98 g, 83%

^{1}H NMR (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 7.30-7.28 (m overlapping with bromobenzene signal, 2H, *p*-H^b), 7.24 (tm, $^3J_{HH}$ = 7.0 Hz, 4H, *o*-H^b), 7.19-7.13 (m, 6H, *m*-H^b, *p*-H^a), 7.09 (apparent tm, $^3J_{HH}$ = 7.0 Hz, 4H, *m*-H^b, *o*-H^a), 6.95-6.92 (m, 4H, *m*-H^b, *m*-H^a), 6.07 (d, $^1J_{PH}$ = 342 Hz, 1H, H^{P-H}), 5.49 (d, $^3J_{PH}$ = 2.4 Hz, 10H, H^{Cp}). Residual pentane 1.29-1.14 (m), 0.85 (t).

^{1}H{^{31}P} NMR (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 7.30-7.28 (m, 2H, *p*-H^b), 7.24 (t, $^3J_{HH}$ = 7.0 Hz, 4H, *o*-H^a), 7.19-7.13 (m, 6H, *m*-H^b, *p*-H^a), 7.09 (t, $^3J_{HH}$ = 7.0 Hz, 4H, *m*-H^b, *o*-H^b), 6.95-6.92 (m, 4H, *m*-H^b, *m*-H^a), 6.06 (s, 1H, H^{P-H}), 5.49 (s, 10H, H^{Cp}).

^{13}C{^{1}H} NMR (125.77 MHz, 300 K, bromobenzene-d$_5$) correlated with **dept 135**: δ^{13}C: 148.8 (dm, $^1J_{CF}$ = 240 Hz, o-CF), 144.8 (dm, $^1J_{CP}$ = 11 Hz, ipso-C^b), 138.8 (dm, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.6 (dm, $^1J_{CF}$ = 240 Hz, *m*-CF), 132.8 (d, $^2J_{PC}$ = 9 Hz, *o*-C^a), 131.7 (d, $^4J_{PC}$ = 2 Hz, *p*-C^a), 131.4 (d, $^4J_{PC}$ = 6 Hz, *m*-C^b), 130.4 (*p*-C^b), 129.9 (d overlapping with bromobenzene signal, visible in DEPT 135 spectrum, $^2J_{PC}$ = 3 Hz, *m*-C^a), 129.2 (*o*-C^b), 125.5-123.3 (bs, *ipso*-C^{BCF}), 104.4 (C^{Cp}). C_6H_5Br: 131.5, 129.8, 126.7, 122.5 ; pentane: 34.3, 22.7, 14.4. *ipso*-C^a not identified.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 7.30-7.28 / 7.24 (*p*-CH^a / *m*-CH^a), 7.24 / 7.30-7.28, 7.09 (*m*-CH^a / *p*-CH^a, *o*-CH^a), 7.19-7.13 / 6.95-6.91 (*o*-CH^b, *p*-CH^b / *m*-CH^b), 7.09 / 7.24 (*o*-CH^a / *m*-CH^a), 6.95-6.91 / 7.19-7.13 (*m*-CH^b / *p*-CH^b, *o*-CH^b).

^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.30-7.28 / 131.7 (*p*-CH^a), 7.24 / 129.9 (*o*-CH^b), 7.19-7.13 / 131.4, 129.2 (*p*-CH^b, *m*-CH^a), 7.09 / 132.8 (*o*-CH^a), 6.95-6.92 / 131.5 (*m*-CH^a), 5.5 / 104.4 (CH^{Cp}).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.30-7.28 / 132.8 (*p*-CH^a / *o*-CH^a), 7.24 / 131.4 (*o*-CH^b / *p*-CH^b), 7.19-7.13 / 144.8, 131.7, 129.2 (*p*-CH^b , *m*-CH^a / ips*o*-C, *p*-CH^a, *m*-CH^a), 7.09 / 132.8, 131.7 (*o*-CH^a / o-CH^a, *p*-CH^a), 6.95-6.92 / 131.5, 131.4 (*m*-CH^b/ m-CH^b, *p*-CH^b), 6.06 / 132.8 (H^{PH} / o-CH^a), 5.5 / 104.4 (CH^{Cp} / CH^{Cp}).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: 420.3 (d, $^2J_{PP}$ = 83 Hz, P^b), 23.8 (d, $^2J_{PP}$ = 85 Hz, P^a).

^{31}P NMR (202.46 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: 420.3 (d, $^2J_{PP}$ = 83 Hz, P^b), 23.8 (dd, $^1J_{PH}$ = 342 Hz, $^2J_{PP}$ = 83 Hz, P^a).

^{31}P{^{1}H} NMR (121.48 MHz, 300 K, tetrahydrofuran-d$_8$): δ^{31}P: 413.7 (d, $^2J_{PP}$ = 83 Hz, P^b), 388.8, 19.1 (d, $^2J_{PP}$ = 83 Hz, P^a), -17.4, -42.8.

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.8 (w = 21 Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.8 (w = 21 Hz).

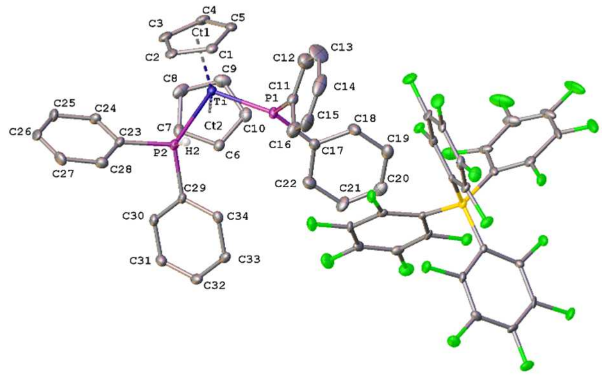
^{19}F{^{1}H} NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (d, $^3J_{FF}$ = 11 Hz, 8F, *o*-F), -161.6 (t, $^3J_{FF}$ = 21 Hz, 8F, *p*-F), -165.4 (m, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (d, $^3J_{FF}$ = 11 Hz, 8F, *o*-F), -161.6 (t, $^3J_{FF}$ = 21 Hz, 8F, *p*-F), -165.4 (m, 8F, *m*-F).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{22}H_{20}PTi$ [M-PPh$_2$H]$^+$ 363.07766; found 363.07672 (Rel. ab: 40%, -0.8 ppm).

Elemental Analysis: % calcd: C, 57.07; H, 2.45; Found: C, 56.71; H, 2.54.

XRD:

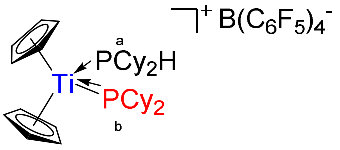


Experimental. Single red needle-shaped crystals of (**q02022016_0m**) were obtained by recrystallisation from diffusion of pentane in a bromobenzene solution. A suitable crystal (0.30×0.07×0.02) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the XT (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2017/1 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{58}H_{31}BF_{20}P_2Ti$, M_r = 1228.48, monoclinic, P2$_1$/c (No. 14), a = 9.0275(6) Å, b = 33.3407(18) Å, c = 17.1603(11) Å, β = 103.855(4)°, α = γ = 90°, V = 5014.7(5) Å^3, T = 115 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.351, 76800 reflections measured, 7870 unique (R_{int} = 0.1827) which were used in all calculations. The final wR_2 was 0.1194 (all data) and R_1 was 0.0609 (I > 2(I)).

Compound	**q02022016_0m**
Formula	$C_{58}H_{31}BF_{20}P_2Ti$
$D_{calc.}$/ g cm^{-3}	1.627
μ/mm^{-1}	0.351
Formula Weight	1228.48
Colour	red
Shape	needle
Size/mm^3	0.30×0.07×0.02
T/K	115
Crystal System	monoclinic
Space Group	P2$_1$/c
a/Å	9.0275(6)
b/Å	33.3407(18)
c/Å	17.1603(11)
α/°	90
β/°	103.855(4)
γ/°	90
V/Å^3	5014.7(5)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.520
Θ_{max}/°	23.998
Measured Refl.	76800
Independent Refl.	7870
Reflections Used	4343
R_{int}	0.1827
Parameters	742
Restraints	0
Largest Peak	0.608
Deepest Hole	-0.603
GooF	1.044
wR_2 (all data)	0.1194
wR_2	0.0947
R_1 (all data)	0.1559
R_1	0.0609

b. PR_2H = PCy_2H **51**:



Chemical Formula: $C_{58}H_{55}BF_{20}P_2Ti$
Molecular Weight: 1252,7

Yield: 1.05 g, 83%, with 85% pentane

^{1}H NMR (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 5.48 (d, $^3J_{PH}$ = 2.5 Hz, 10H, H^{Cp}), 3.50 (d, $^1J_{PH}$ = 320 Hz, 1H, $H^{P\text{-}H}$), 3.01 (m, 2H, CH^b), 1.84-1.48 (m, 26H, $CH_2^{a/b}$ and CH^a), 1.39-0.96 (m, overlapping with pentane, 16H, $CH_2^{a}/^{b}$). pentane: 0.85 (t).

^{1}H{^{31}P} NMR (300.0 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 5.48 (s, 10H, H^{Cp}), 3.50 (s, 1H, $H^{P\text{-}H}$), 3.01 (m, 2H, CH^b), 1.84-1.48 (m, 26H, $CH_2^{a/b}$ and CH^a), 1.39-0.96 (m, 16H, $CH_2^{a}/^{b}$).

^{13}C{^{1}H} NMR (125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{13}C: 149.0 (dm, $^1J_{CF}$ = 243 Hz, *o*-CF), 138.7 (dm, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.7 (dm, $^1J_{CF}$ = 238 Hz, *m*-CF), 125.7-123.8 (*ipso*-C^B), 102.5 (CH^{Cp}), 53.2 (CH^b), 39.6 (d, $^1J_{PC}$ = 13 Hz, CH^a), 33.7 (br s, CH_2 of Cy), 33.6 (br s, CH_2 of Cy), 33.2 (br s, CH_2 of Cy), 32.4 (br s, CH_2 of Cy), 28.5 (br s, CH_2 of Cy), 28.0 (br s, CH_2 of Cy), 27.8 (br s, CH_2 of Cy), 26.0 (br s, CH_2 of Cy), 25.8 (br s, CH_2 of Cy). Pentane: 34.4, 22.7 and 14.5.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 3.0 / 1.84-1.48 (CH^b / CH_2^b), 1.84-1.48 / 3.0, 1.39-0.96 ($CH_2^{a/b}$, CH^a/ CH_2^a, CH^b), 1.39-0.96 / 1.84-1.48 ($CH_2^{b/a}$ / CH^b, CH_2^a).

^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 5.48 / 102.5 (CH^{Cp}), 3.0 / 53.2 (CH^b), 3.0 / 39.6, 33.7, 33.2, 32.4, 28.5, 28.0, 26.0, 25.8 (CH^a, $CH_2^{a/b}$), 1.84-1.48 / 34.4, 33.6, 33.2, 28.5, 27.8, 26.0, 25.8 ($CH_2^{a/b}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 5.48 / 102.5 (CH^{Cp}), 3.50 / 33.2 (H^{PH} / CH_2^a), 3.0 / 53.2 (CH^b), 3.0 / 53.2, 39.6, 33.7, 33.2, 32.4, 28.5, 28.0, 26.0, 25.8 (CH^a, $CH_2^{a/b}$ / CH^b, CH^a, $CH_2^{a/b}$), 1.84-1.48 / 53.2, 34.4, 33.6, 33.2, 28.5, 27.8, 26.0, 25.8 ($CH_2^{a/b}$).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: 500.8 (d, $^2J_{PP}$ =76.7 Hz, P^b), 39.2 (d, $^2J_{PP}$ = 76.7 Hz, P^a).

^{31}P NMR (202.46 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: 500.8 (d, $^2J_{PP}$ = 76.7 Hz, P^b), 39.2 (dd, $^1J_{PH}$ = 320 Hz, $^2J_{PP}$ = 76.7 Hz, P^a).

^{31}P{^{1}H} NMR no lock (242.95 MHz, 300 K, tetrahydrofuran): δ^{31}P: 492.0 (d, $^2J_{PP}$ = 85 Hz, P^b), 486.5, 34.6 (d, $^2J_{PP}$ = 85 Hz, P^a) , -31.3.

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.9 (w = 21 Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.9 (w = 21 Hz).

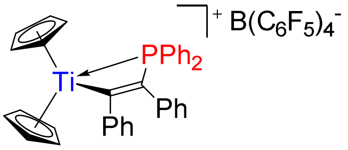
^{19}F{^{1}H} NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (d, $^3J_{FF}$ = 11 Hz, 8F, *o*-F), -161.8 (t, $^3J_{FF}$ = 21 Hz, 8F, *p*-F), -165.6 (m, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.3 (d, $^3J_{FF}$ = 11 Hz, 8F, *o*-F), -161.8 (t, $^3J_{FF}$ = 21 Hz, 8F, *p*-F), -165.6 (m, 8F, *m*-F).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{22}H_{32}PTi$ [M-PCy$_2$H]$^+$ 375.17266; found 375.17001 (Rel. ab: 60%, -4.1 ppm).

Elemental Analysis: % calcd with 85% of pentane: C, 57.57; H, 4.37; Found: C, 57.00; H, 5.00.

2. Synthesis of **52**:



Chemical Formula: $C_{60}H_{30}BF_{20}PTi$
Molecular Weight: 1220,5

In an Ar glovebox, compound **50** (400 mg, 0.32 mmol) was dissolved in C_6H_5Br (3 mL) with an excess of diphenylacetylene (232 mg, 1.3 mmol) at room temperature and stirred for 72H. The evolution of the reaction was followed by ^{31}P{^{1}H} no lock NMR experiments. The starting red solution became green. The compound was precipitated by addition to 6 mL of pentane under vigorous agitation. An oil formed, the supernatant was discarded and the oil extracted twice with pentane. The black-green residue was dissolved in 2 mL of dichloromethane and precipitated as described above. Compound **52** was obtained as a light brown powder containing 30 mol% of pentane after drying *in vacuo* (350 mg, 88 %).

^{1}H NMR (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 7.65 (tm, $^3J_{HH}$ = 7.5 Hz, 2H, *p*-H^P), 7.59 (apparent td, $^3J_{HH}$ = 7.5 Hz, $^4J_{PH}$ = 2.0 Hz, 4H, *m*-H^P), 7.54 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 11.0 Hz, 4H, *o*-H^P), 7.29 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-H^1), 7.23 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-H^2), 7.21 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-H^1), 7.14 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-H^2), 7.06 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *o*-H^2), 6.60 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *o*-H^1), 6.55 (d, $^3J_{PH}$ = 2.0 Hz, 10H, H^{Cp}). Pentane: 1.21-1.00 (m), 0.85 (t).

^{1}H{^{31}P} NMR (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 7.65 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *p*-H^P), 7.59 (t, $^3J_{HH}$ = 7.5 Hz, 4H, *m*-H^P), 7.54 (d, $^3J_{HH}$ = 7.5 Hz, 4H, *o*-H^P), 7.29 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-H^1), 7.23 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-H^2), 7.21 (t, $^3J_{HH}$ = 7.7 Hz, 1H, *p*-H^1), 7.14 (t, $^3J_{HH}$ = 7.7 Hz, 2H, *m*-H^2), 7.06 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *o*-H^2), 6.60 (d, $^3J_{HH}$ = 7.7 Hz, 2H, *o*-H^1), 6.55 (s, H^{Cp}).

^{13}C{^{1}H} NMR (125.77 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 223.1 (s, C-Ti), 148.7 (d, $^1J_{FC}$ = 243 Hz, *o*-CF), 142.0 (d, $^2J_{PC}$ = 25 Hz, *ipso*-C^1), 138.7 (d, $^1J_{FC}$ = 243 Hz, *p*-CF), 136.8 (br d, $^1J_{FC}$ = 243 Hz, *m*-CF), 132.7 (d, $^2J_{PC}$ = 3.0 Hz, i*pso*-C^2), 132.5 (d, $^2J_{PC}$ = 3.0 Hz, *p*-C^P), 132.4

(d, $^2J_{PC}$ = 9.0 Hz, *o*-C^P), 130.6 (d overlapping with *C*H of PPh, $^1J_{PC}$ = 34.6 Hz, *ipso*-C^P), 130.5 (d overlapping with CH o PPh, $^3J_{PC}$ = 10.0 Hz, *m*-C^P), 130.0 (*m*-C^1), 129.6 (d, $^3J_{PC}$ = 4.0 Hz, *o*-C^2), 129.3 (*m*-C^2), 128.8 (*p*-C^2), 128.3 (*p*-C^1), 126.0 (d, $^4J_{PC}$ = 2.0 Hz, *o*-C^1), 125.8-123.5 (bs, *ipso*-C^B), 120.9 (C^{Cp}), 116.2 (d, $^1J_{PC}$ = 45.0 Hz, =CPPh$_2$). Pentane: 34.6, 22.7, 14.2.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{1}H: 7.65 / 7.59 (*p*-CH^P / *m*-CH^P), 7.59 / 7.65, 7.54 (*m*-CH^P / *p*-CH^P, *o*-CH^P), 7.54 / 7.59 (*o*-CH^P / *m*-CH^P), 7.29 / 7.21, 6.60 (*m*-CH^1 / *p*-CH^1, *o*-CH^1), 7.23 / 7.14, 7.06 (*p*-CH^2 / *m*-CH^2, *o*-CH^2), 7.21 / 7.29 (*p*-CH^1 / *m*-CH^1), 7.14 / 7.23, 7.06 (*m*-CH^2 / *p*-CH^2, *o*-CH^2), 7.06 / 7.23, 7.14 (*o*-CH^2 / *p*-CH^2, *m*-CH^2), 6.60 / 7.29, 7.21 (*o*-CH^1 / *m*-CH^1, *p*-CH^1).

^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 7.65 / 132.7 (*p*-CH^P), 7.59 / 130.5 (*m*-CH^P), 7.54 / 132.4(*o*-CH^P), 7.29 / 130.0 (*m*-CH^1), 7.23 / 128.8 (*p*-CH^2), 7.21 / 128.3 (*p*-CH^1), 7.14 / 129.3 (*m*-CH^2), 7.06 / 129.6 (*o*-CH^2), 6.60 / 126.0 (*o*-CH^1), 6.55 / 120.9 (CH^{Cp}).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 7.65 / 132.4 (*p*-CH^P / *o*-CH^P), 7.59 / 132.7, 132.4, 130.5 (*m*-CH^P / *o*-CH^P, *m*-CH^P), 7.54 / 132.7 (*o*-CH^P / *p*-CH^P), 7.29 / 142.0, 130.0, 126.0 (*m*-CH^1 / *ipso*-C^1, *m*-CH^1, *o*-CH^1), 7.23 / 129.6 (p-CH^2 / *o*-CH^2), 7.21 / 142.0, 126.0 (*p*-CH^1 / *ipso*-C^1, *o*-CH^1), 7.14 / 132.5, 129.6, 116.2 (*m*-CH^2 / *o*-CH^2, =C-P), 7.06 / 128.8, 116.2 (*o*-CH^2 / *p*-CH^2, =C-P), 6.60 / 223.1, 128.3, 126.0 (*o*-CH^1 / C-Ti, *p*-CH^1,*o*-CH^1), 6.55 / 120.9 (CH^{Cp}).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, dichloromethane-d$_2$): δ^{31}P: -26.9 ($\nu_{1/2}$ = 3.3 Hz).

^{31}P NMR (202.46 MHz, 300 K, dichloromethane-d$_2$): δ^{31}P: -26.9 ($\nu_{1/2}$ = 34.7 Hz).

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, dichloromethane-d$_2$): δ^{11}B: -16.6 ($\nu_{1/2}$ = 21 Hz).

^{11}B NMR (160.42 MHz, 300 K, dichloromethane-d$_2$): δ^{11}B: -16.6 ($\nu_{1/2}$ = 21 Hz).

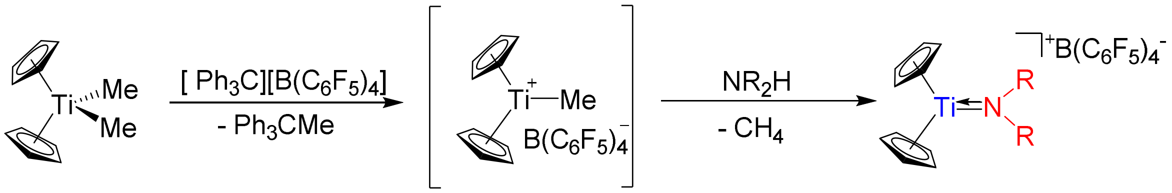
^{19}F{^{1}H} NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -131.3 (d, $^3J_{FF}$ = 15 Hz, 8F, *o*-F), -163.7 (t, $^3J_{FF}$ = 29 Hz, 8F, *p*-F), -167.5 (m, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -133.0 (d, $^3J_{FF}$ = 15 Hz, 8F, *o*-F), -163.7 (t, $^3J_{FF}$ = 19 Hz, 8F, *p*-F), -167.5 (m, 8F, *m*-F).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. for $C_{36}H_{30}PTi$ [M]$^+$ 541.15591; found 541.15625 (Rel. ab: 100%, 0.6 ppm).

Elemental Analysis: % calcd: C, 59.05; H, 2.48; Found: C, 59.73; H, 2.44.

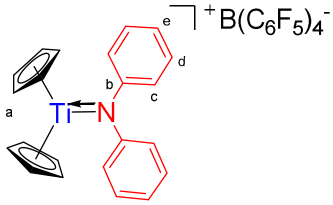
3. General procedure for the synthesis of amidotitanocenes:



Cp_2TiMe_2 (X mmol, 1 eq) and $[Ph_3C][B(C_6F_5)_4]$ (1 eq) were combined in a vial inside the glovebox and dissolved in 3 mL of C_6H_5Br. The resulting red solution was stirred for 5 min and arylamine (1.1 eq) was added. The solution was stirred for 1h until the color turned to dark green. The solution was transferred in a schlenk vessel containing 10 mL of vigorously stirred pentane. An heavy green precipitate was formed and left to decant for 5min. The red supernatant solution was removed and the green powder was washed twice with pentane (2 x 5 mL). After drying *in vacuo* the green powder was dissolved in dichloromethane (2 mL) and precipitated again with pentane (10 mL). The light green supernatant solution was removed and the desired compound was obtained as a dark green precipitate after evaporation of all volatiles *in vacuo*.

NB: these compounds were shown to be light sensitive. They were stored in the freezer at -18°C.[20]

c. Synthesis of **53**:



Chemical Formula: $C_{46}H_{20}BF_{20}NTi$
Molecular Weight: 1025,3

X = 0.96 mmol, Yield: 876 mg, 88 %.

^{1}H NMR (500.03 MHz, 300 K, bromobenzene-d_5): δ^1H: 7.13 (t, $^3J_{HdHe}$ = $^3J_{HdHc}$ 7.2 Hz, 4H, H^d), 7.00 (t, $^3J_{HeHd}$ = 7.2 Hz, 2H, H^e), 6.15 (s, 10H, H^a), 5.75 (d, $^3J_{HcHd}$ = 7.2 Hz, 4H, H^c). Pentane t, 0.85 (t).

^{13}C{^{1}H} NMR (125.77 MHz, 300 K, bromobenzene-d_5): δ^{13}C: 156.1 (C^b), 148.6 (dm, $^1J_{CF}$ = 240 Hz, *o*-CF), 138.6 (dm, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.7 (dm, $^1J_{CF}$ = 240 Hz, *m*-CF), 131.7 (C^d), 129.1 (C^e), 122.6 (C^a), 117.9 (C^c), *i*-C$^{B(C6F5)4}$ *n.o.*

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, bromobenzene-d_5): δ^1H / δ^1H: 7.13 / 7.00, 5.75 (H^d / H^e, H^c), 7.00 / 7.13 (H^e / H^d), 5.75 / 7.13 H^c / H^d).

^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 300 K, bromobenzene-d_5): δ^1H / δ^{13}C: 7.13 / 131.7 (CH^d), 7.00 /129.1 (CH^e), 6.15 / 122.6 (CH^a), 5.75 / 117.9 (CH^c).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 273 K, bromobenzene-d_5): δ^1H / δ^{13}C: 7.13 / 156.1, 131.7, 117.9 (CH^d / C^b, CH^d, CH^c), 7.00 / 156.1, 117.9 (CH^e / C^b, CH^c), 6.15 / 122.6 (CH^a), 5.75 / 156.1, 129.1, 117.9 (CH^c / C^b, CH^e, CH^c).

---

[20] These complexes were presumed to be too reactive to be observed by ESI HMRS

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 5.75 / -35 (H^c / N).

^{11}B{^{1}H} NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 22 Hz).

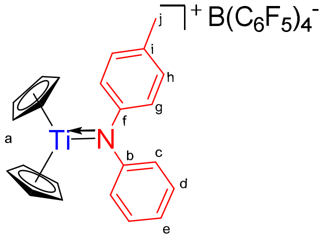
^{11}B NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 22 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.4 (br s, 8F, *o*-F), -161.4 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.3 (br s, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.4 (br s, 8F, *o*-F), -161.4 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.3 (m, 8F, *m*-F).

Elemental Analysis: % calcd for $C_{46}H_{20}BF_{20}NTi$: C, 53.89; H, 1.97; N, 1.37; Found: C, 53.89; H, 1.97; N, 1.38.

d. Synthesis of **54**:



Chemical Formula: $C_{47}H_{22}BF_{20}NTi$
Molecular Weight: 1039,3

X= 0.72 mmol, Yield: 635 mg, 85 %.

^{1}H NMR (600.23 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 7.13 (t, $^3J_{HdHe}$ = $^3J_{HdHc}$ 7.3 Hz, 2H, H^d), 6.99 (t, $^3J_{HeHd}$ = 7.3 Hz, 1H, H^e), 6.95-6.92 (m, 2H,H^h), 6.20 (s, 10H, H^a), 5.63 (d, $^3J_{HcHd}$ = 7.3 Hz, 2H, H^c), 5.61 (d, $^3J_{HgHh}$ = 8.0 Hz, 2H, H^g), 2.23 (s, 3H, H^j). *traces of pentane were observed (m, 1.20; t, 0.85).*

^{13}C{^{1}H} NMR correlated with **dept 135** (125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{13}C: 156.0 (C^b), 152.7 (C^f), 148.9 (dm, $^1J_{CF}$ = 240 Hz, *o*-CF), 140.7 (C^i), 138.7 (dm, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.9 (dm, $^1J_{CF}$ = 240 Hz, *m*-CF), 133.0 (C^h), 130.9 (C^d), 128.7 (C^e), 123.0 (C^a), 118.7 (C^c), 116.4 (C^g), 21.3 (C^j) *i*-C$^{B(C6F5)4}$ *n.o.*

^{1}H ^{1}H COSY (600.23 MHz, 300 K, 273 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 7.13 / 6.99, 5.63 (H^d / H^e, H^c), 6.99 / 7.13 (H^e / H^d), 6.95-6.92 / 5.61 (H^h / H^g), 5.63 / 7.13 (H^c / H^d), 5.61 / 6.95-6.92 (H^g / H^h).

^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.13 / 130.9 (CH^d), 6.99 / 128.7 (CH^e), 6.95-6.92 / 133.0 (CH^h), 6.20 / 123.0 (CH^a), 5.63 / 118.7 (CH^c), 5.61 / 116.4 (CH^g), 2.23 / 21.3 (CH$_3^j$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 273 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.13 / 156.0, 130.9, 118.7 (CH^d / C^b, CH^d, CH^c), 6.99 / 118.7 (CH^e / CH^c), 6.95-6.92 / 152.7, 133.0, 21.3 (CH^h / C^f, CH^h, CH$_3^j$), 6.20 / 123.0 (CH^a), 5.63 / 128.7, 118.7 (CH^c / CH^e, CH^c), 5.61 / 140.7, 116.4 (CH^g / C^i, CH^g), 2.23 / 140.7, 133.0 (CH$_3^j$ / C^i, CH^h).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 5.63, 5.61 / -32 (H^c, H^g / N).

^{11}B{^{1}H} NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 22 Hz).

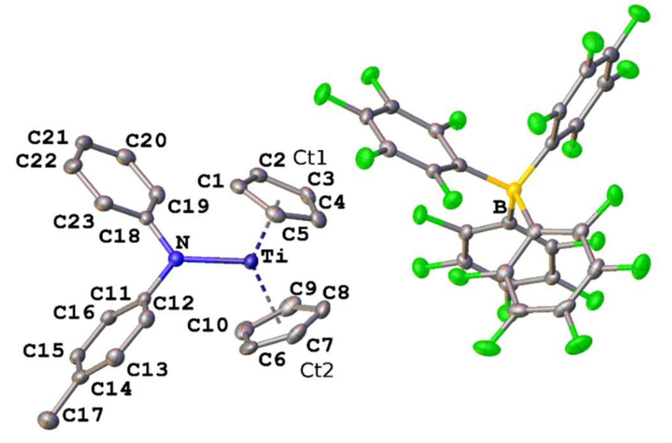
^{11}B NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 22 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.8 (br s, 8F, *o*-F), -161.8 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.7 (br s, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.8 (br s, 8F, *o*-F), -161.8 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.7 (m, 8F, *m*-F).

Elemental Analysis: % calcd for $C_{46}H_{20}BF_{20}NTi$: C, 54.31; H, 2.13; N, 1.35; Found: C, 53.65; H, 2.86; N, 1.26.

XRD:

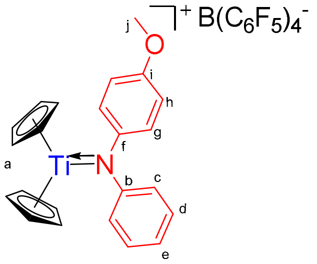


Compound	**cu_q010616_0m_a**
Formula	$C_{47}H_{22}BF_{20}NTi$
$D_{calc.}$/ g cm^{-3}	1.716
μ/mm^{-1}	3.015
Formula Weight	1039.36
Colour	dark green
Shape	needle
Size/mm^3	0.15×0.04×0.03
T/K	100
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	8.0825(6)
b/Å	14.1366(10)
c/Å	35.406(3)
α/°	90
β/°	96.136(4)
γ/°	90
V/Å^3	4022.3(5)
Z	4
Z'	1
Wavelength/Å	1.541840
Radiation type	CuK$_\alpha$
Θ_{min}/°	2.510
Θ_{max}/°	66.681
Measured Refl.	48078
Independent Refl.	7074
Reflections Used	5458
R_{int}	0.0656
Parameters	632
Restraints	0
Largest Peak	0.284
Deepest Hole	-0.402
GooF	1.018
wR_2 (all data)	0.0797
wR_2	0.0725
R_1 (all data)	0.0568
R_1	0.0363

Experimental. Single dark green needle-shaped crystals of (**cu_q010616_0m_a**) were obtained by recrystallisation from slow diffusion of heptane in a concentrated C_6H_5Cl solution. A suitable crystal (0.15×0.04×0.03) mm^3 was selected and mounted on a mylar loop with oil on a Bruker D8 VENTURE diffractometer. The crystal was kept at T = 100 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{47}H_{22}BF_{20}NTi$, M_r = 1039.36, monoclinic, $P2_1/n$ (No. 14), a = 8.0825(6) Å, b = 14.1366(10) Å, c = 35.406(3) Å, β = 96.136(4)°, $\alpha = \gamma$ = 90°, V = 4022.3(5) Å^3, T = 100 K, Z = 4, Z' = 1, μ(CuK$_\alpha$) = 3.015, 48078 reflections measured, 7074 unique (R_{int} = 0.0656) which were used in all calculations. The final wR_2 was 0.0797 (all data) and R_1 was 0.0363 (I > 2(I)).

e. Synthesis of **55**:



Chemical Formula: $C_{47}H_{22}BF_{20}NOTi$
Molecular Weight: 1055,3

X= 0.96 mmol, 970 mg, 97 %.

^{1}H NMR (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H: 7.12 (t, $^3J_{HdHe}$ = $^3J_{HdHc}$ = 7.9 Hz, 2H, H^d), 6.98 (t, $^3J_{HeHd}$ = 7.9 Hz, 1H, H^e), 6.68 (d, $^3J_{HgHh}$ = 9.0 Hz, 2H,H^g), 6.24 (s, 10H, H^a), 5.47 (d, $^3J_{HhHg}$ = 9 Hz, 2H, H^h), 5.43 (d, $^3J_{HcHd}$ = 7.9 Hz, 2H, H^c), 3.54 (s, 3H, H^j). *traces of pentane were observed (m, 1.20; t, 0.85).*

^{13}C{^{1}H} NMR correlated with **dept 135** (125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{13}C: 161.6 (C^i), 155.7 (C^b), 148.8 (dm, $^1J_{CF}$ = 240 Hz, *o*-CF), 147.1 (C^f), 138.7 (dm, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.8 (dm, $^1J_{CF}$ = 240 Hz, *m*-CF), 130.4 (C^d), 128.6 (C^e), 125.7-123.9 (*ipso*-C^B), 123.3 (C^a), 119.2 (C^c), 117.6 (C^h),117.4 (C^g), 55.7 (C^j).

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 7.12 / 6.98, 5.43 (H^d / H^e, H^c), 6.98 / 7.12 (H^e / H^d), 6.68 / 5.47 (H^g / H^h), 5.47 / 6.68 (H^h / H^g), 5.43 / 7.12 (H^c / H^d).

^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.12 / 130.4 (CH^d), 6.98 / 128.6 (CH^e), 6.68 / 117.4 (CH^g), 6.24 / 123.3 (CH^a), 5.47 / 117.6 (CH^h), 5.43 / 119.2 (CH^c), 3.54 / 55.7 (CH$_3^j$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 273 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.12 / 155.7, 130.4, 119.2 (CH^d / C^b, CH^d, CH^c), 6.98 / 119.2 (CH^e / CH^c), 66.68 / 161.6, 147.1, 117.6 (CH^g / C^i, C^f, CH^h), 6.24 / 123.3 (CH^a), 5.47 / 161.6, 117.4 (CH^h / C^i, CH^g), 5.43 / 128.6, 119.2 (CH^c / CH^e, CH^c), 3.54 / 161.6 (CH$_3^j$ / C^i).

^{1}H ^{15}N HMBC (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{15}N: 5.43 / -30 (H^c / N).

^{11}B{^{1}H} NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 21 Hz).

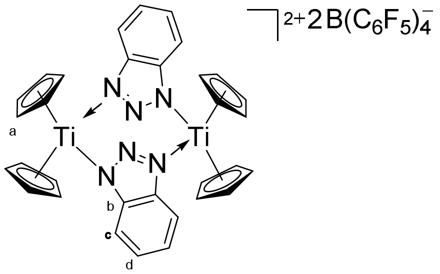
^{11}B NMR (160.42 MHz, 273 K, bromobenzene-d$_5$): δ^{11}B: -15.9 (ν$_{1/2}$ = 21 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.4 (br s, 8F, *o*-F), -161.3 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.2 (br s, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 273 K, bromobenzene-d$_5$): δ^{19}F: -131.4 (br s, 8F, *o*-F), -161.3 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.2 (br s, 8F, *m*-F).

Elemental Analysis: % calcd for $C_{47}H_{22}BF_{20}NOTi$: C, 53.49; H, 2.10; N, 1.33; Found: C, 53.14; H, 2.12; N, 1.25.

f. Synthesis of **56**:



Chemical Formula: $C_{80}H_{28}B_2F_{40}N_6Ti_2$
Molecular Weight: 1950,4

X= 0.58 mmol, Yield: light orange powder 490 mg, 73 % - with 16% of C_6H_5Br.

^{1}H NMR (500.03 MHz, 263 K, tetrahydrofuran-d$_8$): δ^{1}H: 8.12 (m, 4H, H^c), 7.89 (m, 4H, H^d), 6.82 (s, 10H, H^a). C_6H_5Br: 7.52, 7.35-7.26, pentane 1.36-1.20 (m), 0.85 (t).

^{3}C{^{1}H} NMR (125.77 MHz, 263 K, tetrahydrofuran-d$_8$): δ^{13}C: 148.8 (dm, $^1J_{CF}$ = 240 Hz, *o*-CF), 147.7, 138.8 (dm, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.8 (dm, $^1J_{CF}$ = 240 Hz, *m*-CF) 130.4 (C^d), 126.1-124.0 (*ipso*-C^B), 120.7 (C^a), 117.8 (C^c). C_6H_5Br: 132.1, 130.9, 127.7, 122.9, pentane: 34.9, 23.2, 14.3).

Traces of solvents were omitted for clarity in the following description.

^{1}H ^{1}H COSY (500.03 MHz, 263 K, 273 K, tetrahydrofuran-d$_8$): δ^{1}H / δ^{1}H: 8.12 / 7.89 (H^c / H^d).

^{1}H ^{13}C HMQC (500.03 MHz / 125.77 MHz, 263 K, tetrahydrofuran-d$_8$): δ^{1}H / δ^{13}C: 8.12 / 117.8 (CH^c), 7.89 / 130.4 (CH^d), 6.82 / 120.7 (CH^a).

^{1}H ^{13}C HMBC (500.03 MHz / 125.77 MHz, 263 K, tetrahydrofuran-d$_8$): δ^{1}H / δ^{13}C: 8.12 / 130.4 (CH^c / CH^d), 7.89 / 147.7, 117.8 (CH^d / C^b, CH^c), 6.82 / 120.7 (CH^a).

^{11}B{^{1}H} NMR (160.42 MHz, 263 K, tetrahydrofuran-d$_8$): δ^{11}B: -18.6 (ν$_{1/2}$ = 22 Hz).

^{11}B NMR (160.42 MHz, 263 K, tetrahydrofuran-d$_8$): δ^{11}B: -18.6 (ν$_{1/2}$ = 22 Hz).

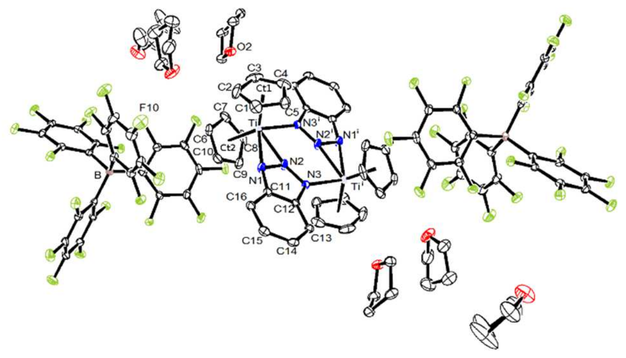
^{19}F{^{1}H} NMR (470.45 MHz, 263 K, tetrahydrofuran-d$_8$): δ^{19}F: -134.7(dm, $^3J_{FF}$ = 8 Hz, 8F, *o*-F), -166.4 (t, $^3J_{FF}$ = 20 Hz, 4F, *p*-F), -170.0 (br t, $^3J_{FF}$ = 17 Hz, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 263 K, tetrahydrofuran-d$_8$): δ^{19}F: -137.4(dm, $^3J_{FF}$ = 8 Hz, 8F, *o*-F), -166.4 (t, $^3J_{FF}$ = 20 Hz, 4F, *p*-F), -170.0 (br t, $^3J_{FF}$ = 17 Hz, 8F, *m*-F).

Positive mode ESI HRMS (Positive mode ESI, tetrahydrofuran): m/z calcd. for $C_{56}H_{28}BF_{20}N_6Ti_2$ $[M\text{-}B(C_6F_5)_4]^+$ 1271.11026, found 1271.11567 (Rel. ab: 15%, 4.3 ppm), $C_{32}H_{28}N_6Ti_2$ $[M\text{+}e^-\text{-}2B(C_6F_5)_4]^+$ 592.13289; found 592.13433 (Rel. ab: 35%, 2.4 ppm); $C_{16}H_{14}N_3Ti$ $[M\text{-}B(C_6F_5)_4]/2^+$ 296.06672 found 296.06660 (Rel. ab: 40%, 1.4 ppm).

Elemental Analysis: % calcd for $C_{80}H_{28}B_2F_{40}N_6Ti_2$+2THF with dried crystals: C, 50.46; H, 2.12; N, 4.01; Found: C, 50.72; H, 1.89; N, 3.95.

XRD:



Experimental. Single yellow prism-shaped crystals of (**q130617_0m**) were obtained by recrystallisation from layering a bromobenzene solution, by pentane. A suitable crystal (0.07×0.07×0.05) mm³ was selected and mounted on a mylar loop with oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at *T* = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2017/1 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

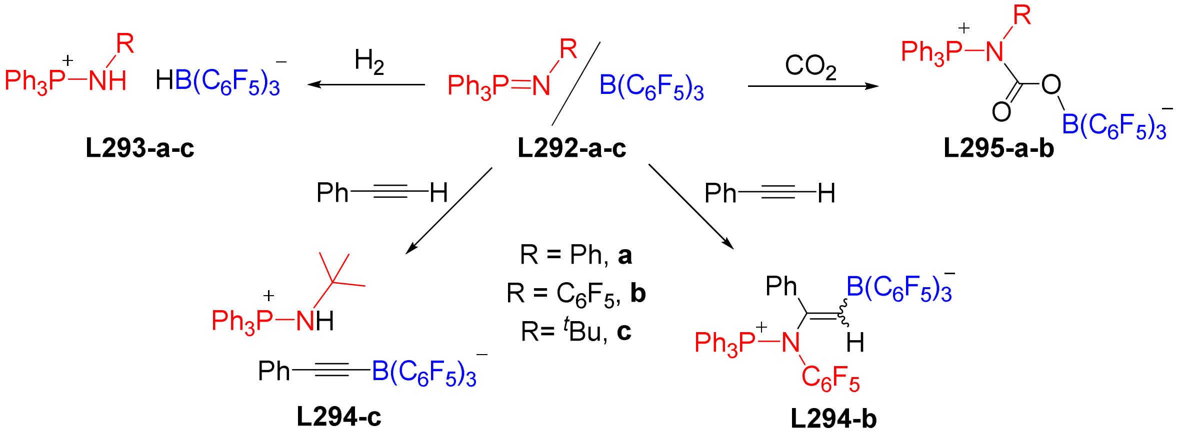
Crystal Data. $C_{104}H_{76}B_2F_{40}N_6O_6Ti_2$, M_r = 2383.12, triclinic, P-1 (No. 2), a = 11.7809(18) Å, b = 15.422(2) Å, c = 16.293(3) Å, α = 117.416(4)°, β = 107.695(4)°, γ = 91.433(4)°, V = 2455.3(7) Å³, T = 115 K, Z = 1, Z' = 0.5, $\mu(\text{MoK}_\alpha)$ = 0.299, 64017 reflections measured, 11266 unique (R_{int} = 0.0932) which were used in all calculations. The final wR_2 was 0.1518 (all data) and R_1 was 0.0556 (I > 2(I)).

Compound	**q130617_0m**
Formula	$C_{104}H_{76}B_2F_{40}N_6O_6Ti_2$
$D_{calc.}$/ g cm^{-3}	1.612
μ/mm^{-1}	0.299
Formula Weight	2383.12
Colour	yellow
Shape	prism
Size/mm³	0.07×0.07×0.05
T/K	115
Crystal System	triclinic
Space Group	P-1
a/Å	11.7809(18)
b/Å	15.422(2)
c/Å	16.293(3)
α/°	117.416(4)
β/°	107.695(4)
γ/°	91.433(4)
V/Å³	2455.3(7)
Z	1
Z'	0.5
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.728
Θ_{max}/°	27.544
Measured Refl.	64017
Independent Refl.	11266
Reflections Used	6099
R_{int}	0.0932
Parameters	721
Restraints	13
Largest Peak	0.662
Deepest Hole	-0.469
GooF	1.006
wR_2 (all data)	0.1518
wR_2	0.1201
R_1 (all data)	0.1325
R_1	0.0556

V. Chapter IV: Synthesis and reactivity of titanocenyl iminophosphoranes

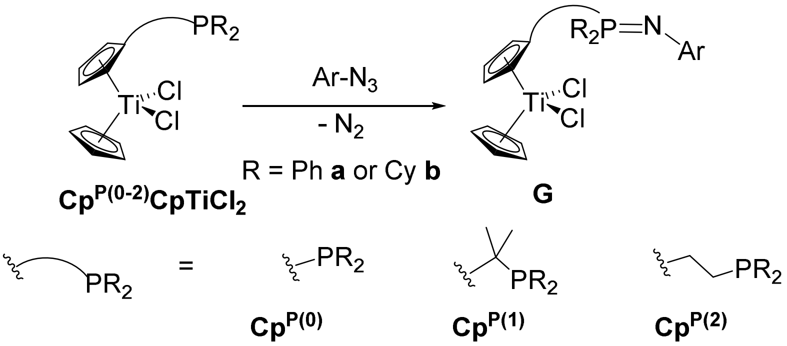
A. Bibliographic introduction

In 2013, Stephan described new organic FLPs based on the use of iminophosphoranes. Their combination with the Lewis acid $B(C_6F_5)_3$ demonstrated their ability to activate several small molecules (H_2, CO_2 and phenylacetylene) as illustrated in Scheme V-1.[1]



Scheme V-1: an iminophosphorane-based organic FLP

In addition, among the numerous OmFLPs previously reported in I.D.3., two examples of cationic Ti-based metallocenes have been described (Scheme I-66 and Scheme I-74).[2,3] Furthermore, in 2015, Dr. Laure Monnereau had investigated the synthesis of titanocenyl iminophosphorane of type **G** in our group (Scheme V-2).[4]



Scheme V-2: synthetic approach to titanocenyl iminophosphoranes

---

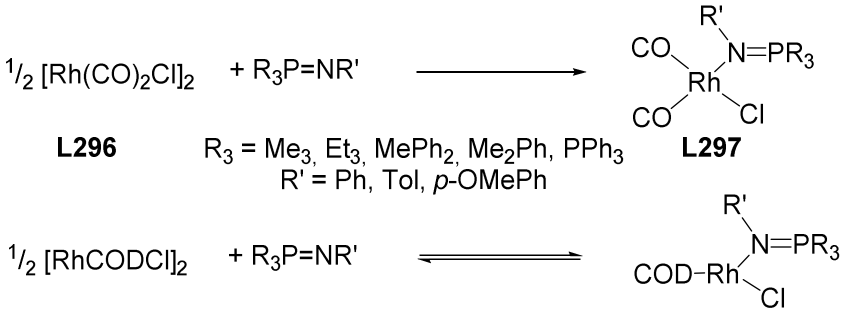
[1] Jiang, C.; Stephan, D. W. *Dalton Trans.* **2013**, *42*, 630

[2] Chapman, A. M.; Wass, D. F. *Dalton Trans.* **2012**, *41*, 9067

[3] Normand, A. T.; Richard, P.; Balan, C.; Daniliuc, C. G.; Kehr, G.; Erker, G.; Le Gendre, P. *Organometallics*. **2015**, *34*, 2000

[4] Unpublished results

At the time, the incentive for this research was to establish whether the Staudinger reaction was applicable to organometallic phosphanes, to synthesize a new series of bimetallic complexes.[5] In fact, Dr. Monnereau found a straightforward route to titanocenyl iminophosphoranes starting from titanocenyl phosphanes of type **CpCp$^{P(2)}$TiCl$_2$**. All other combinations tested (with **CpCp$^{P(0)}$TiCl$_2$** and **CpCp$^{P(1)}$TiCl$_2$**) yielded decomposition of the titanocenyl phosphane. The coordination potential of this new series of titanocenyl iminophosphorane was tested but all attempt to form heterobimetallic complexes (Rh, Ru, Pt, Pd) failed. Taken alone, the iminophosphorane ligand seems to be a weak coordinating ligand. As illustrated above, some examples of κ-N coordination of an iminophosphorane to a metallic centre have already been described with no additional "chelate" effect. One example was described by Elsevier in 1990. With CO ligands, the complexes were quantitatively formed and the X-ray structure of one of them was even obtained. Nevertheless, coordination of the iminophosphorane was shown to be reversible with **L299**.[6]



Scheme V-3: coordination behaviour of a simple iminophosphorane to Rh

Nevertheless, in the light of the publication of Stephan (Scheme V-1), the titanocenyl iminophosphoranes were considered under a new light: we were wondering if these organometallic iminophophoranes would be able to show FLP-like reactivity as reported for organic parents by Stephan. This study is the topic of the following chapter.

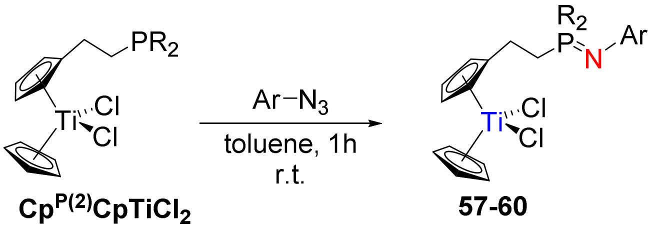
B. Dichloro titanocenyl iminophosphoranes

The procedure described by Dr. Monnereau was used to synthesize new batches of four complexes, to complete their characterization, and try to test them in typical OmFLP reactions. Reaction of complexes **Cp$^{P(2)}$CpTiCl$_2$** with aryl azides in toluene (1h reaction) yielded the corresponding titanocenyl iminophosphorane (**57-60**) in good yield (Scheme V-4).

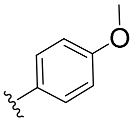
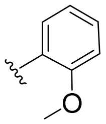
---

[5] Staudinger, H.; Meyer, J. *Helv. Chim. Acta.* **1919**, *2*, 635

[6] Imhoff, P.; Elsevier, C. J.; Stam, C. H. *Inorganica Chim. Acta.* **1990**, *175*, 209



$Cp^{P(2)}CpTiCl_2$ **57-60**

Ar / PR2		
PPh_2	**57** 80 %	**58** 73 %
PCy_2	**59** 84 %	**60** 73 %

Scheme V-4: synthesis of titanocenyl iminophosphorane 57-60

All compounds were characterized by NMR (^1H, ^{13}C, ^{31}P and 2D correlations) and IR spectroscopies, positive mode ESI HRMS and elemental analysis.

The $^{31}P\{^1H\}$ NMR chemical shift and the shape of the signals are characteristic of the formation of these complexes: much broader than the corresponding titanocenyl phosphanes and shifted upfield by about 20 ppm for PPh_2 derivatives (**$Cp^{PPh2}CpTiCl_2$** = 30.7 ppm: **57** = 5.3-3.6 ppm, **58** = 7.5-0.5 ppm), whilst downfield by about 10 ppm for the PCy_2 derivatives (**$Cp^{PCy2}CpTiCl_2$** = -7.0 ppm **59** = 22.3-14.0 ppm, **60** = 19.9-13.7 ppm). The ^1H NMR spectra of these complexes exhibit the same set of signals for the titanocene fragment with two broad signals in the 6.31-5.91 and 5.98-5.53 ppm ranges for the substituted Cp ring, and 6.22-5.93 for the unsubstituted Cp ring. The two signals of the bridging CH_2 appear as two multiplets in the 3.04-2.34 and 3.42-3.12 ppm ranges for the one bearing the phosphanyl group, and the one next to the Cp ring respectively. Relevant chemical shifts are summarized in Table V-1.

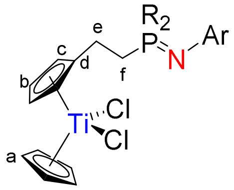
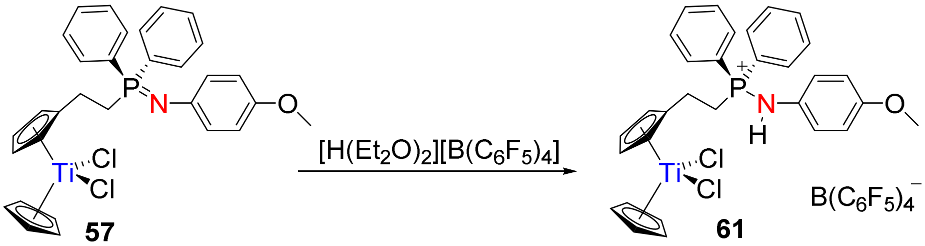
	a (ppm)	b (ppm)	c (ppm)	e (ppm)	f (ppm)
57 PPh$_2$-*p*-OMe	5.94	5.53	5.91	2.95-2.58	3.18-3.12
58 PPh$_2$-*o*-OMe	5.99-5.93	5.64-5.55	6.09-5.99	3.04-2.91	3.26-3.05
59 PCy$_2$-*p*-OMe	6.12-6.07	5.80-5.73	6.17-6.12	2.48-2.34	3.40-3.31
60 PCy$_2$-*o*-OMe	6.22-6.11	5.98-5.82	6.31-6.22	2.59-2.53	3.42-3.32

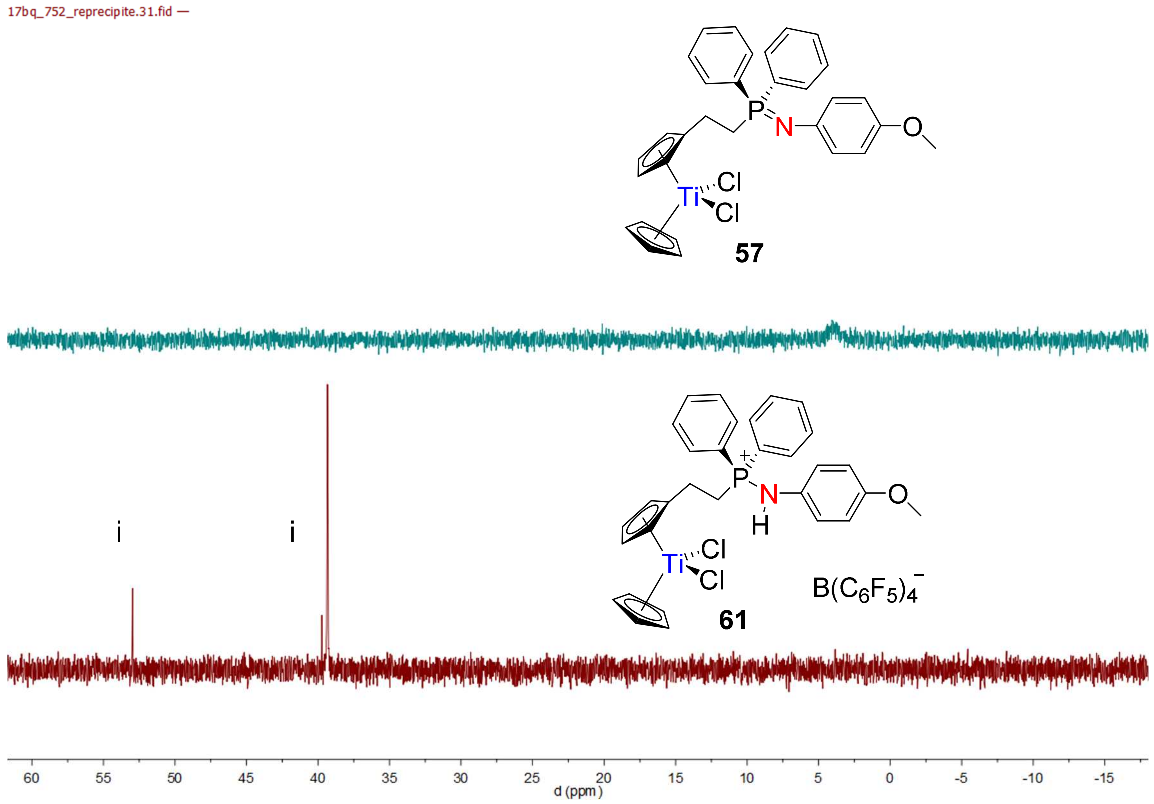
Table V-1: selected ^{1}H NMR chemical shifts (600.23 or 500.03 MHz, 300K, C_6D_6)

The broadness observed for some signals in the ^{1}H or ^{31}P NMR spectra was studied by ^{31}P{^{1}H} NMR spectroscopy by changing the deuterated solvent and by variable temperature analyses, but no decoalescing or narrowing of the signals as observed. This may be a characteristic of this series of compounds. All our efforts to crystallize one of these titanocenyl iminophosphoranes failed and yielded precipitation or oily residues. To help crystallization, **57** was protonated with $H(Et_2O)_2B(C_6F_5)_4$ in dichloromethane (Scheme V-5).



Scheme V-5: protonation reaction of 57

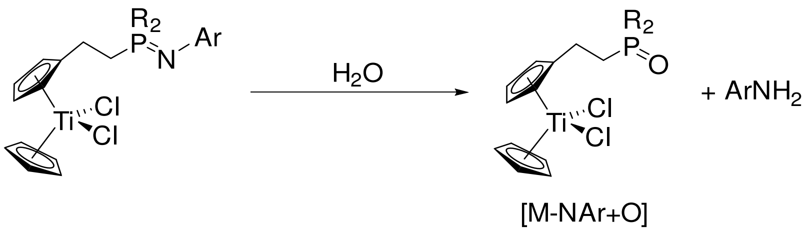
The aminophosphonium **61** was obtained after workup as a brick-red solid. NMR (^{1}H, ^{11}B, ^{13}C, ^{19}F, ^{31}P and 2D correlation) and IR spectroscopies, positive mode ESI HRMS and elemental analysis were performed on this compound. Unfortunately, it did not crystalize either. Nevertheless, the ^{31}P{^{1}H} NMR signal in its spectrum is narrower than in **57** as illustrated in Spectrum V-1.



Spectrum V-1: superposition of $^{31}P\{^1H\}$ NMR spectra of 61 (bottom) and 57(top) (500 MHz, 300K, C_6D_6) ^{i}: unidentified impurities

In the light of this result, one can hypothesize that an interaction exists between the P=N moiety and Ti which translates into NMR spectroscopy by the observation of broad signals in the $^{31}P\{^1H\}$ spectra of the titanocenyl iminophosphoranes (**57-60**). The protonation of **57** clearly prevents this interaction.

All these complexes exhibited in their mass spectra the presence of the cluster of peaks from [M-NAr+O] (see the experimental part and appendix for details). According to the bibliography, iminophosphoranes are well known to form the corresponding phosphine oxide / primary amine by hydrolysis, as illustrated in Scheme V-6.[5]



Scheme V-6: hydrolysis process of the titanocenyl iminophosphoranes

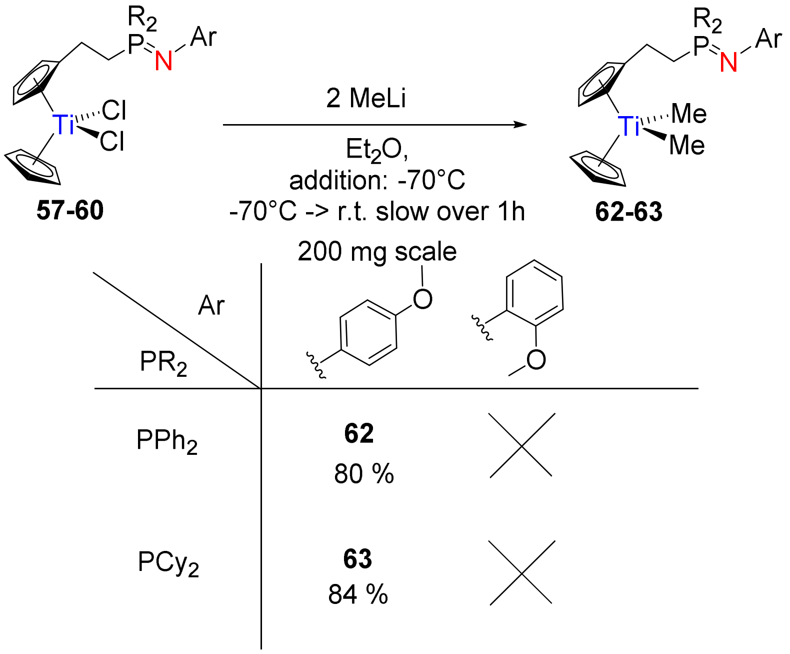
The synthesis of these titanocenyl phosphane oxides were attempted with compounds **57-60**, in various solvent conditions, but none of them yielded a clean product. The final mixture always contained two or more compounds according to $^{31}P\{^1H\}$ NMR. Consequently, their synthesis was abandoned. The synthesis of the four new dichloro titanocenyl iminophosphoranes has been successfully achieved. Nevertheless, the iminophosphorane function did not exhibit clean hydrolysis as might be expected for this class of compounds.

On the other hand, the potential as OmFLPs of these titanocenyl iminophosphoranes has been evaluated. Preliminary chloride abstraction with silver-based reagents ([Ag][BPh_4] or $AgNTf_2$) did not lead to effective or clean abstraction. As a result, and considering the ineffective chloride abstraction on the (aminomethyl)titanocenes, whichever the chloride abstractor, we focused our attention on methide abstraction.

C. Dimethyl titanocenyl iminophosphoranes

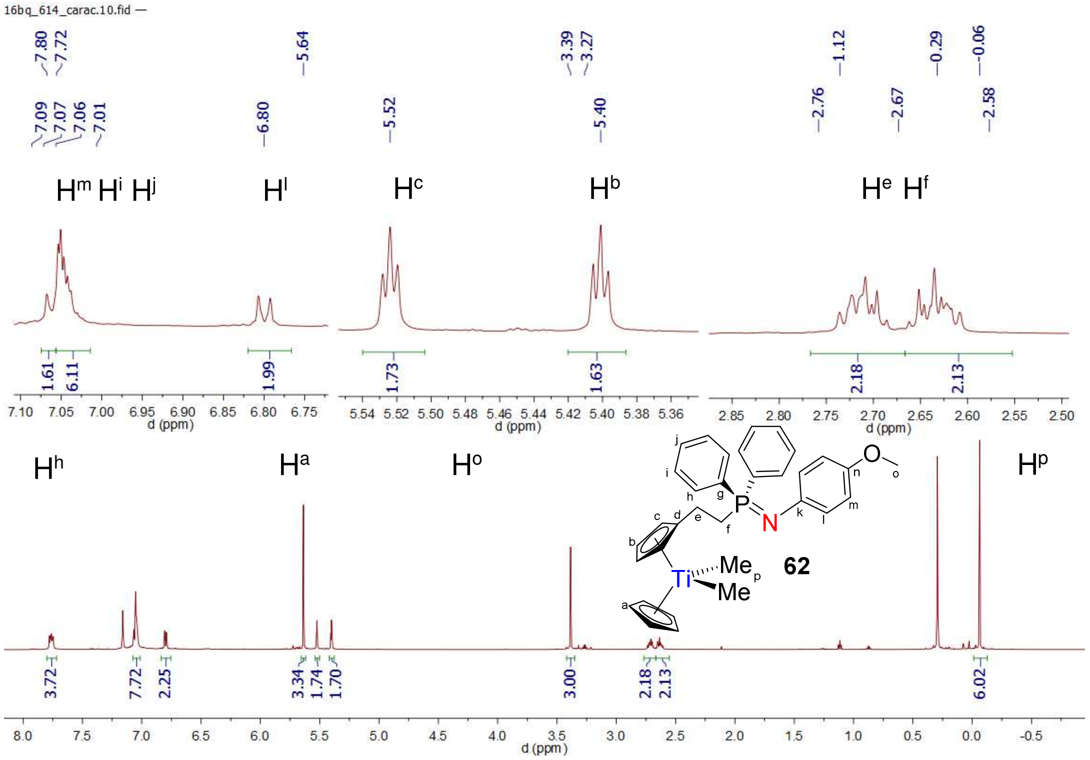
1. Synthesis

The question was, after the successful synthesis of potential OmFLPs by generating a cationic titanocene fragment, whether any rearrangement would occur after titanocenium cation formation. Starting from **57-60**, methylation was conducted in the same conditions as for other dimethyl titanocenes previously described. Despite repeated attempts, both compound **58** and **60** failed to be methylated. The ortho methoxy group seemed to prevent clean methylation. Nevertheless, compound **62** and **63** were obtained in good yields (Scheme V-7).



Scheme V-7: methylation of the titanocenyl iminophosphoranes

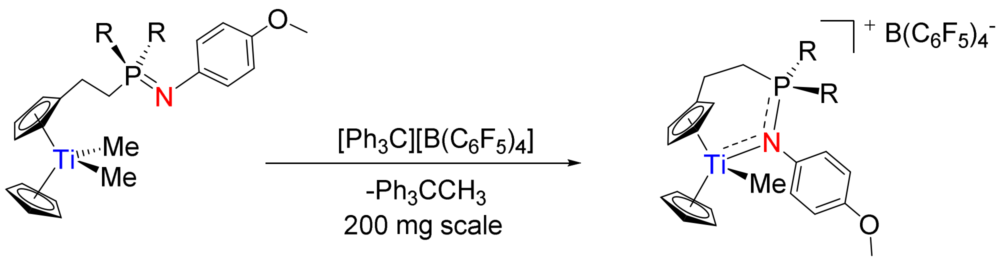
These compounds were characterized by NMR (^1H, ^{13}C, ^{31}P and 2D correlations) and IR spectroscopies, positive mode ESI HRMS and elemental analysis. By contrast with the dichloro precursors, **62** and **63** exhibited much narrower $^{31}P\{^1H\}$ NMR signals ($\nu_{1/2}$: 38 and 25 Hz for **62** and **63** vs 240 and 1300 Hz for **57** and **59**). As illustrated in Spectrum V-2, a set of two multiplets is observed for the phenyl rings bound to the phosphorus atom (7.80-7.72 and 7.06-7.01 ppm). The para-substituted phenyl ring showed two multiplets (7.09-7.07 and 6.80 ppm), whilst two apparent triplets are observed for the monosubstituted Cp ring. The non-substituted Cp ring exhibits a singlet at 5.64 ppm, as do the methoxy group at 3.39 ppm, and the methide groups at -0.06 ppm. The two bridging CH_2 groups show two multiplets at 2.76-2.67 and 2.67-2.58 ppm. These complexes were found to be light- and temperature-sensitive, and had to be stored in the glovebox at -18°C.



Spectrum V-2: ^1H NMR of 62 (500.03 MHz, 300 K, benzene-d_6)

2. Reactivity

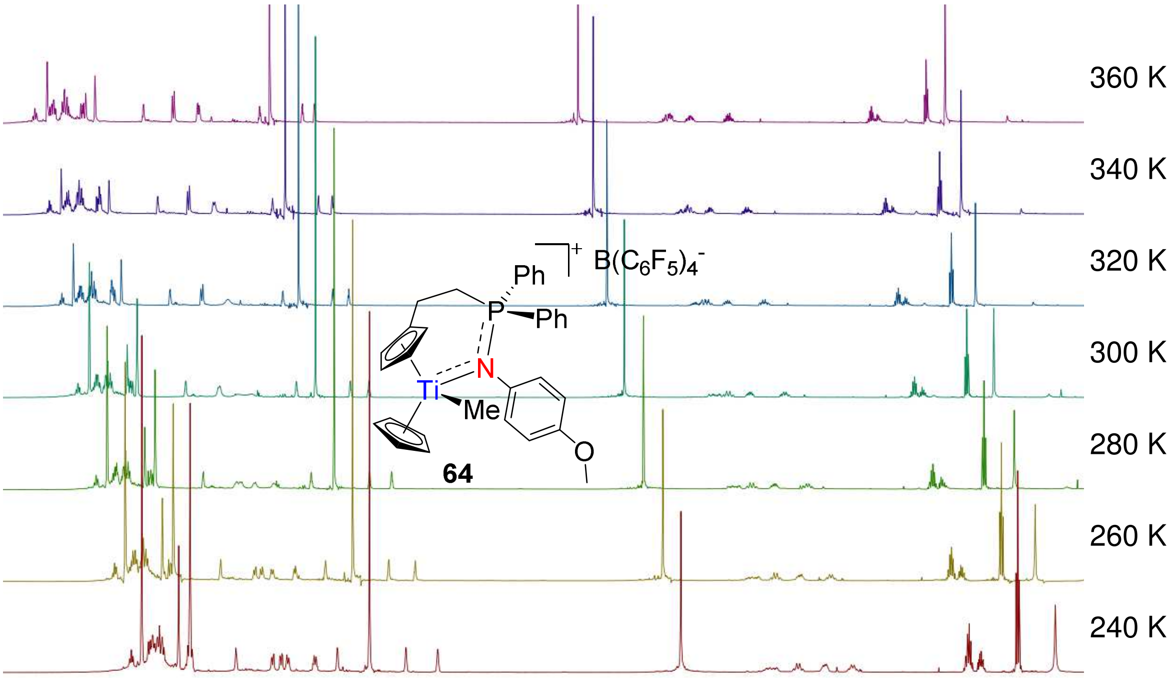
Methide abstraction with $[Ph_3C][B(C_6F_5)_4]$ afforded complexes **64** and **65** in moderate to good yields (Scheme V-8).



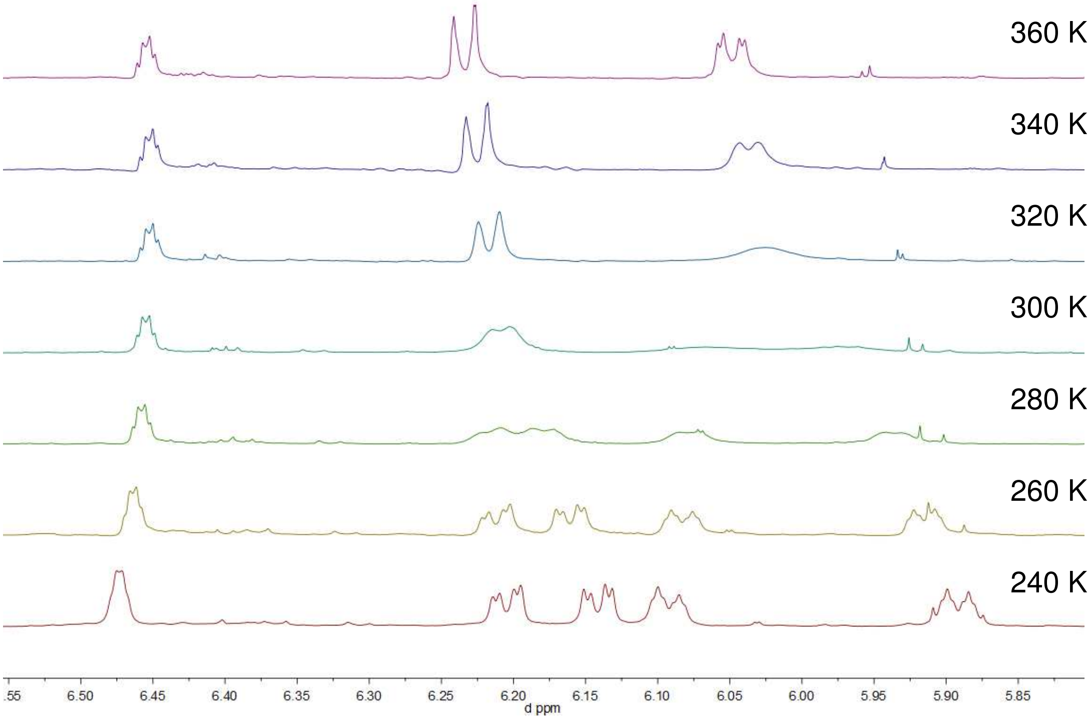
R = Ph, **64** 62%
R = Cy, **65** 81%

Scheme V-8: synthesis of the cationic species 64 and 65

No CH activation was observed for both compounds. They were characterized with standard techniques (NMR spectroscopy, HRMS, elemental analysis and X-ray diffraction). The ^{1}H NMR spectrum of **64** showed broad signals for the disubstituted phenyl ring at 300 K, due to a coalescence phenomenon. The superposition of the ^{1}H NMR spectra obtained between 240 and 360 K is shown in Spectrum V-3 and Spectrum V-4.

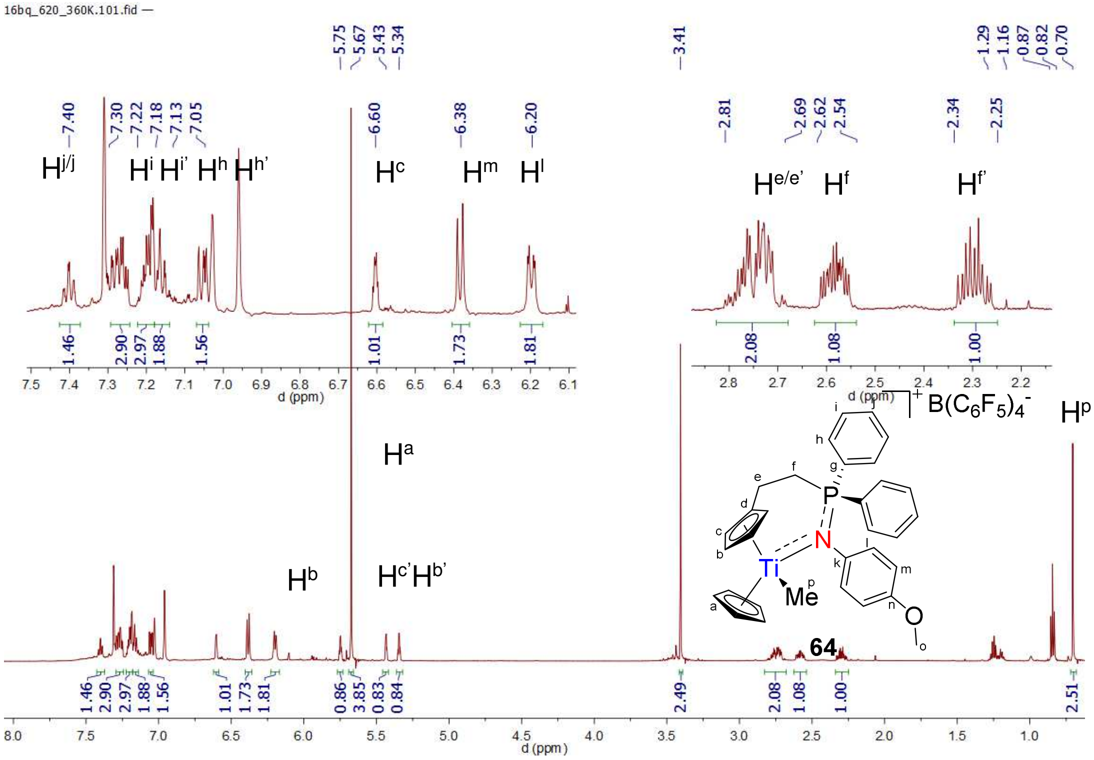


Spectrum V-3: superposition of the ^{1}H NMR spectra of 64 (600.23 MHz, 240 (bottom)-360 K (top), bromobenzene-d$_5$)



Spectrum V-4: superposition of the ^{1}H NMR spectra of 64, 6.50-5.80 ppm (600.23 MHz, 240 (bottom)-360 K (top), bromobenzene-d$_5$)

This coalescence phenomenon is observed for the signals of the phenyl ring bound to nitrogen. Steric hindrance around the nitrogen is probably responsible for this phenomenon, and as a consequence the rotation of the *p*-methoxyphenyl ring is slow on the NMR time scale at temperatures below 280 K. This compound was fully characterized by NMR spectroscopy at 360 K. The corresponding ^{1}H NMR spectrum is depicted in Spectrum V-5.



Spectrum V-5: ^{1}H NMR spectrum of 64 (600.23 MHz, 360 K, bromobenzene-d$_5$)

Chirality at titanium is observed as previously, hence the presence of several diastereotopic relationships in the ^{1}H NMR spectrum. In these structures, the phosphorous atom is prochiral. As a result, the two phenyl rings bound to P are diastereotopic. A set of five signals is observed for these two phenyl rings (7.40, 7.30-7.22, 7.22-7.18, 7.18-7.13 and 7.05 ppm), and a set of two signals is observed for the para substituted phenyl ring (6.38 and 6.20 ppm, a doublet and a doublet of doublets respectively). The classical set of four apparent quartets is observed for the signal of the protons of the monosubstituted Cp ring (6.60, 5.75, 5.43 and 5.34 ppm), whilst a singlet is observed for the non-substituted Cp ring at 5.67 ppm. The methoxy group and the remaining methide exhibit a singlet at 3.41 and 0.70 ppm respectively. Finally, the signals of the two bridging CH_2 are diasterotopic and appear as two more complex multiplets (2.62-2.54 and 2.34-2.25 ppm). The $^{31}P\{^1H\}$ chemical shift is shifted downfield by 36 ppm compared to the dimethyl titanocene (**62**), in agreement with the charge transfer from the iminophosphorane moiety to titanium.

The structure of both cationic species was established by X-ray diffraction analysis. An ORTEP view is presented in Figure V-1, and a table resumes selected parameters (Table V-2).

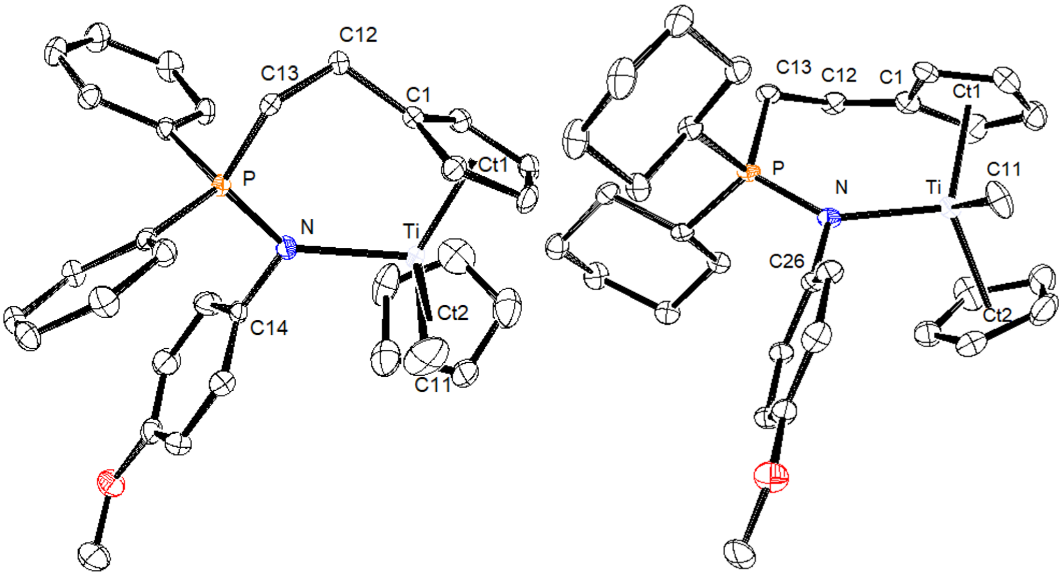
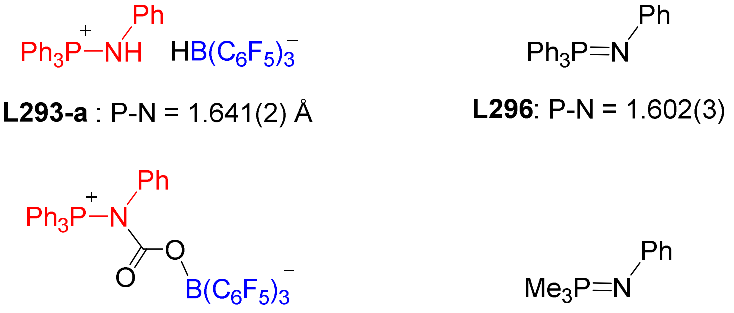


Figure V-1: ORTEP view of 64 (left) and 65 (right), counter anions omitted for clarity

	64	**65**
Selected bond length (Å)		
Ti-Ct1	2.084(3)	2.0621(13)
Ti-Ct2	2.090(4)	2.0733(16)
Ti-C11	2.181(6)	2.192(2)
Ti-N	2.143(4)	2.1555(19)
P-N	1.643(4)	1.6481(19)
C1-C12	1.497(6)	1.497(4)
C12-C13	1.522(6)	1.521(3)
C13-P	1.793(4)	1.804(2)
Selected angles (°)		
Ct1-Ti-Ct2	127.36(12)	130.83(6)
N-Ti-C11	92.0(2)	96.28(9)
P-N-Ti	135.9(2)	136.68(10)
Ti-N-C14/C26	117.6(3)	113.17(13)
C14/26-N-P	106.4(3)	110.09(14)
Σα(N)	359.9(5)	349.93(2)
P-N-Ti-Ct1	19.20(18)	52.74(16)
C14/C26-N-Ti-Ct2	-8.0(4)	30.2(4)

Table V-2: selected parameters from the crystallographic structures of 64 and 65

On one hand, the titanocene adopts a bent geometry in both structures, and on the other hand, the general parameters of both structures are relatively similar between both structures. The P-N bond length can be compared to that of the literature (Scheme V-9). No simple analogue of **65** has been found in the Cambridge Crystallographic Data Centre;[7] as a results, it will be compared to **L297** (although this choice can be debatable, since the steric influence of the cyclohexyl groups is not taken into account). The P-N bond length observed for **64** and **65** is longer than the one reported for **L296** and **L297** respectively (1.643(4) vs 1.602(3) Å and 1.6481(19) vs 1.572(3) Å).[8][9] In fact this parameter is closely related to the one observed by Stephan on **L293-a.**



L293-a : P-N = 1.641(2) Å

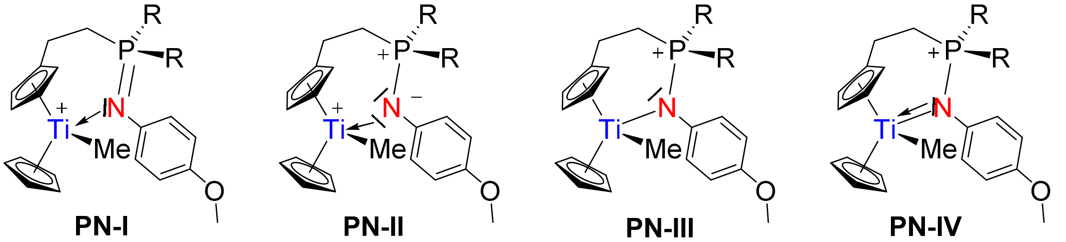
L296: P-N = 1.602(3)

L295-a : P-N = 1.671(2) Å

L297: P-N =1.572(3)

Scheme V-9: P-N bond lenghs reported in the literature

Considering these structural parameters and notably the short Ti-N bond distances compared to the sum of the covalent radii (2.143(4) / 2.1555(19) Å , covalent radii Ti-N = 2.31 ± 0.09 Å),[10] the question of the nature of the Ti-N bond within these complexes is raised (Scheme V-10).



PN-I **PN-II** **PN-III** **PN-IV**

Scheme V-10: the four potential resonance forms for 64 and 65 (counter anion omitted for clarity)

In other words, which resonance form **PN-I-IV** has the greatest contribution? Similar considerations have previously been envisioned by Bourissou on Zr-based constrained geometry complexes.[11] Furthermore, previous theoretical studies conducted on

---

[7] https://www.ccdc.cam.ac.uk/

[8] Böhm, E.; Dehnicke, K.; Beck, J.; Hiller, W.; Strähle, J.; Maurer, A.; Fenske, D. *Z. Für Naturforschung B.* **1988**, *43*

[9] Abboud, K. A.; Villanueva, L. A.; Boncella, J. M. *Acta Crystallogr. C.* **1993**, *49*, 1848

[10] Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832

[11] Truflandier, L.; Marsden, C. J.; Freund, C.; Martin-Vaca, B.; Bourissou, D. *Eur. J. Inorg. Chem.* **2004**, *2004*, 1939, Oulié, P.; Freund, C.; Saffon, N.; Martin-Vaca, B.; Maron, L.; Bourissou, D. *Organometallics.* **2007**, *26*, 6793

aminophosphonium salts,[12] have shown that the dipolar form (R_3P^+-NR^-) is dominant and that electrostatic interactions greatly contribute to strengthening the P-N bond. Considering that the P-N bond lengths in **L296** and **L297** are closer to that of aminophosphonium (**L293-a**), one can presume that the P-N bond weakening is correlated to a partial charge transfert from the iminophosphorane to the Ti centre tantamount to covalent bonding. DFT calculations were then undertaken by Pr. Paul Fleurat-Lessart and Pr. Marek Kubicki, in order to better understand the nature of the Ti-N bond in these complexes.

For this study, two different methods have been used: the Atoms In Molecules theory of Bader (AIM) and the Electron Localization Function (ELF) (see general remarks for computational details). The AIM method analyses the electron density based on its second derivative. It decomposes the electronic density of molecules into atomic basins. Two linked atoms share a common surface between their atomic basin. If a covalent bond is observed, a red point is represented on the bond path (represented in maroon in Figure V-2) between the two basins. Considering the Ti-N bond characterized by the AIM method, a covalent contribution is clearly observed.

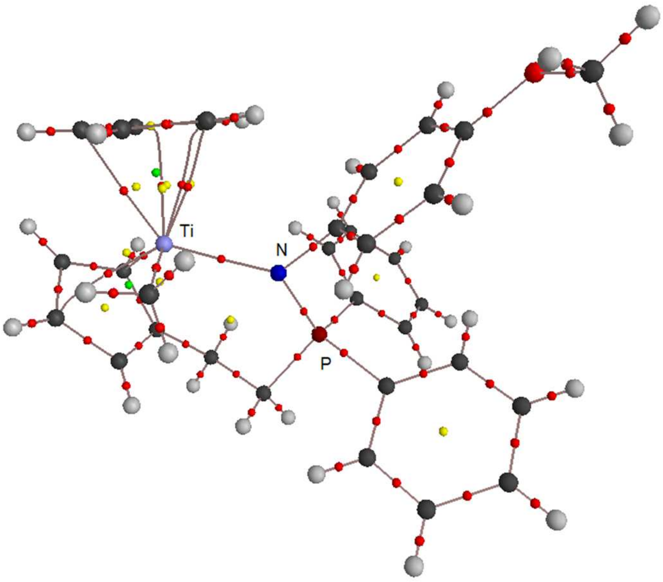


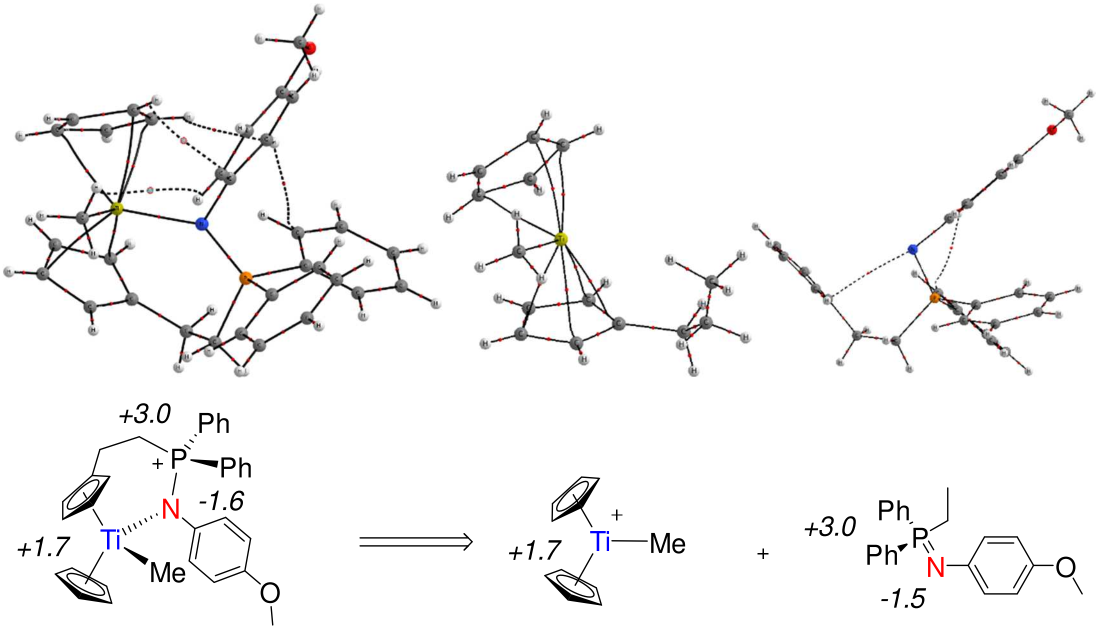
Figure V-2: calculated structure with the AIM method: covalent contribution (red point), bonding path (maroon) conjugation (yellow)

In addition to indications as to the covalent nature of the bonds, the AIM method gives the value of electronic charges: it has been calculated for the titanium (+1.7), the nitrogen (-1.6) and the phosphorus atom (+3) in **64**. Analogous calculations have been conducted on two split models as illustrated in Scheme-V-11. Considering first a cationic titanocene fragment **64-Ti+**, the electronic charge value found for the titanium atom is +1.7. For the iminophosphorane moiety (**64-PN**), the respective electronic charge of the N and P atoms are -1.5 and +3.0.

---

[12] Orzechowski, L.; Jansen, G.; Harder, S. *J. Am. Chem. Soc.* **2006**, *128*, 14676

These values are very close to those obtained on the complete model of **64** with AIM methods. Surprisingly, whilst the Bond Critical Point along the Ti-N bond indicates a covalent bond, there is barely any charge transfer between both atoms. This is shown by the fact that both titanium and nitrogen charges do not vary between the split models calculations and the complete molecule.



64 **64-Ti+** **64-PN**

Complete model Split models

Scheme-V-11: models considered in for the NBO calculations

Last, the topology of the ELF was analysed (Figure V-3). In this method, the electronic density is split into core electrons, bonding electrons and non-bonding pairs.

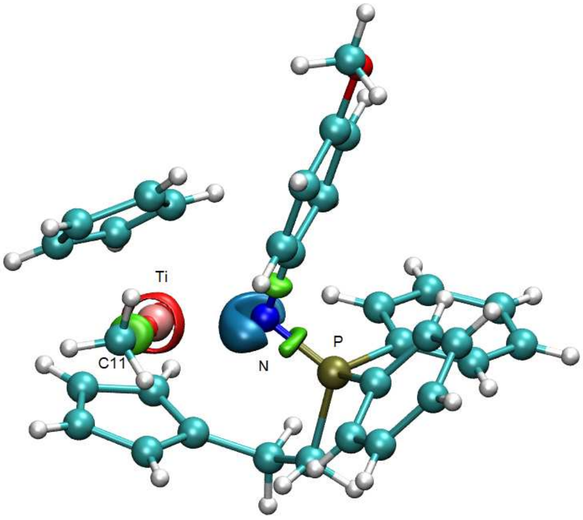


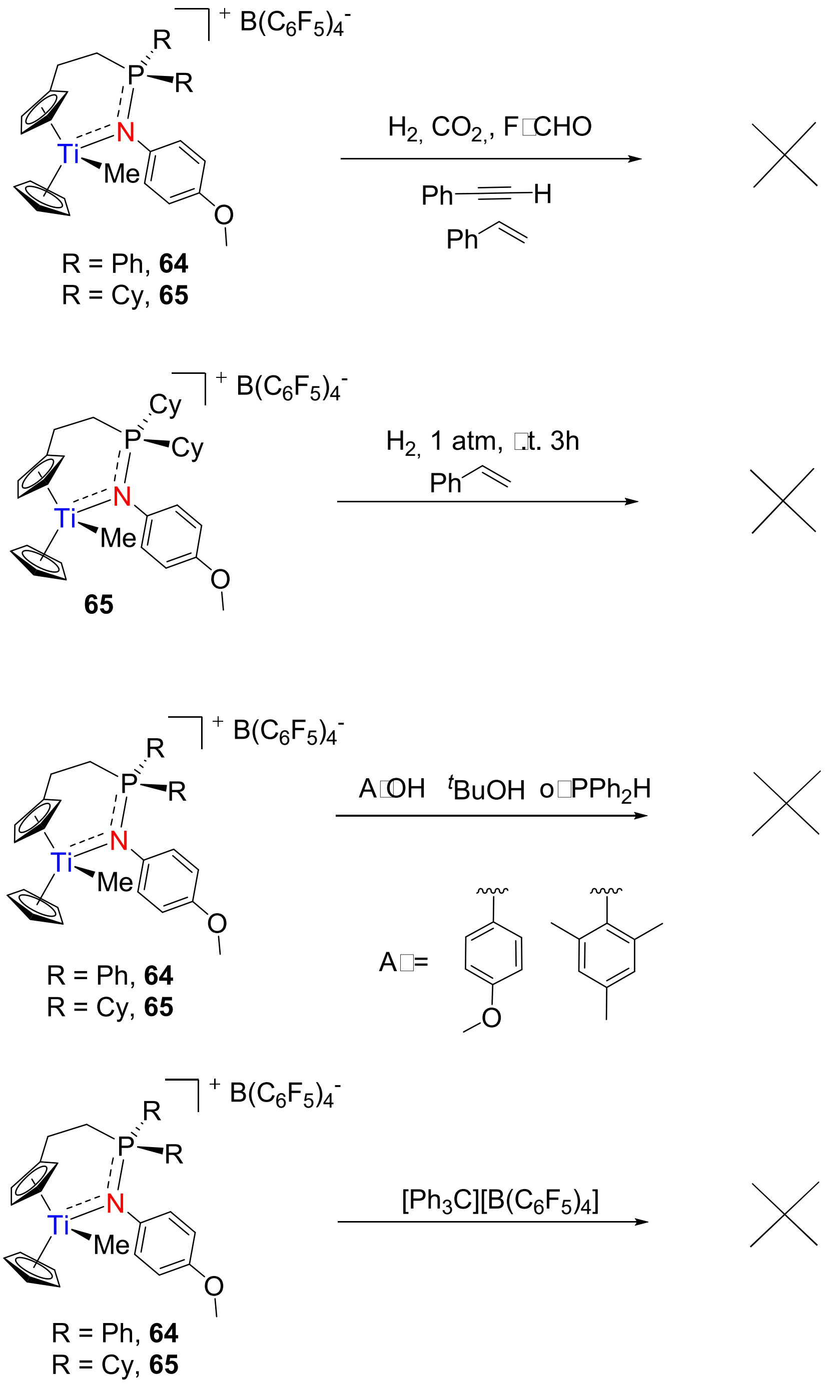
Figure V-3: simplified calculated structure of 64 by the ELF method: bonding electron (green), non-bonding electron (blue) and core electron (red) (only selected covalent contribution are depicted for clarity)

The resulting structure is depicted in Figure V-3. When a bond is covalent, a green ring between both atoms is observed: in our case, the Ti-C11 bond has a high covalent contribution. Considering the Ti-N bond on this structure, such a ring is not observed: instead, a blue electronic basin is present. This basin represent the two indistinguishable lone pairs of the nitrogen atom. This means that the nature of the bond is more ionic than covalent according to the ELF method. This is very similar to the AIM results: the bonding basin indicates covalent character, but in practice, the interaction looks like a weak dative bond between nitrogen and titanium. This suggests that the structure of **64** is somewhere in between **PN-II** and **PN-IV** for **64** in the solid state (Scheme V-10).

To resume these preliminary results, the nature of the Ti-N bond in **64** seems to be quite complex, since AIM and ELF methods are not fully concordant. Some additional calculations have to be carried out to exemplify this type of bond by simulating various structures. A more precise picture of the nature of this bond cannot be definitively putforth without further investigations.

The reactivity of **64** and **65** towards small molecules was finally investigated in order to determine their potential as OmFLPs (Scheme V-12). Compound **64** was found to be completely unreactive towards various substrates (H_2, CO_2, FcCHO,…) as evidenced by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Compound **65** was only reactive towards H_2. Unfortunately, the reaction was not clean, and mainly decomposition of **65** was observed. This complex was also tested as a catalyst for hydrogenation of styrene. No evidence of phenylethane formation was observed by NMR spectroscopy or GCMS analysis.

Since small molecule activations did not work at all with these complexes, modification of the coordination sphere of titanium was attempted. Protonolysis of the methide bound to the titanocene was attempted. However, no reaction was observed with alcohols or diphenylphosphine. Alternatively, methide abstraction of the second methide bound to titanium was attempted, by using $[Ph_3C][B(C_6F_5)_4]$ from **64** and **65**. As previously described, such abstraction are relatievely quick when favoured. The methide abstraction did not occur after 30 min of reaction, according to ^1H and $^{31}P\{^1H\}$ NMR spectra of both mixtures. The starting aminophosphonium were observed with concomittent presence of the methide abstractor. The reaction mixture was then left to stir for 12h. Only decomposition products were observed after this period of stirring.



Scheme V-12: reactivity studies of 64 and 65

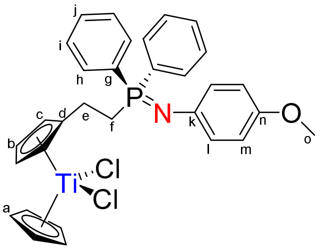
In conclusion to this last chapter, a series of dichloro titanocenyl iminophosphoranes was achieved according to the procedure previously developed in our group, and two dimethyl analogues were obtained. Methide abstraction was effective on both compounds yielding two new cationic complexes whose robustness prevented any reactivity to occur. As a result, a DFT study has been initiated in order to better understand the nature of the Ti-N bond involved in such structures. The preliminary results have to be compared with calculations computed on other molecules than **64** in order to highlight a trend for this type of bond.

D. Experimental part

1. Iminophosphorane synthesis

To a suspension of the desired $Cp^PCpTiCl_2$ (X mmol, 1 eq) in toluene, 1.1 eq of the corresponding *p/o*-methoxyazide was added slowly at room temperature. The resulting red heterogeneous suspension was stirred for 2h, became homogeneous before finishing heterogeneous again. A small degassing was observed. The resulting solution was evaporated, and the red crude precipitate was dissolved in a few amount of dichloromethane before being precipitated by 10 eq of pentane. Supernatant was cannulated at -40°C and washed twice with pentane. The resulting red precipitate was finally dried *in vacuo* to yield the desired compound as a brick-red solid.

a. Synthesis of **57**:



Chemical Formula: $C_{31}H_{30}Cl_2NOPTi$
Molecular Weight: 582,3

X= 0.87 mmol, Yield: 400 mg, 80%

^{1}H NMR (500.03 MHz, 300 K, benzene-d$_6$): δ^1H: 7.89-7.82 (m, 4H, H^h), 7.09 (d, $^3J_{HH}$= 9.0 Hz, 2H, H^m), 7.07-7.01 (m, 6H, $H^{i/j}$), 6.79 (dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{PH}$ = 1.0 Hz, 2H, H^l), 5.94 (s, 5H, H^a), 5.91 (m, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 2H, H^c), 5.53 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 2H, H^b), 3.38 (s, 3H, H^o), 3.18-3.12 (m, 2H, H^e), 2.95-2.88 (m, 2H, H^f).

^{1}H{^{31}P} NMR (600.23 MHz, 300 K, benzene-d$_6$): δ^1H: 7.89-7.82 (m, 4H, H^h), 7.09 (d, $^3J_{HH}$= 9.0 Hz, 2H, H^m), 7.07-7.01 (m, 6H, $H^{i/j}$), 6.79 (dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{PH}$ = 1.0 Hz, 2H, H^l), 5.94 (s, 5H, H^a), 5.91 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 2H, H^c), 5.53 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.5 Hz, 2H, H^b), 3.38 (s, 3H, H^o), 3.18-3.12 (m, 2H, H^e), 2.95-2.88 (m, 2H, H^f).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, benzene-d$_6$): δ^{13}C: 152.9 (C^n), 144.9-144.5 (C^k), 136.6 (d, $^3J_{PC}$ = 15.2 Hz, C^d), 132.0 (d, $^3J_{PC}$ = 9.2 Hz, C^i), 131.5 (C^h), 128.8 (d, $^2J_{PC}$ = 11.5 Hz, C^i), 123.7 (d, $^4J_{PC}$ = 17.3 Hz, C^m), 122.2 (C^c), 119.4 (C^a), 115.0 (C^b), 114.9 (br s, C^l), 55.2 (C^o), 27.2 (d, $^1J_{PC}$ = 67.6 Hz C^f), 23.6 (d, $^2J_{PC}$ = 1.8 Hz C^e). Traces of toluene (129.2, 128.4, 125.6, 21.3) and pentane (34.3, 22.6, 14.2) observed, C^g n.o.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, benzene-d$_6$): δ^1H / δ^1H: 7.89-7.82 / 7.07-7.01 (H^h / $H^{i/j}$), 7.09 / 6.79 (H^m / H^l), 7.07-7.01 / 7.89-7.82 ($H^{i/j}$ / H^h), 6.79 / 7.09 (H^l / H^m), 5.91 / 5.53 (H^c / H^b), 5.53 / 5.91 (H^b / H^c), 3.18-3.12 / 2.95-2.88 (H^e / H^f), 2.95-2.88 / 3.18-3.12 (H^f / H^e).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6): $\delta^{1}H$ / $\delta^{13}C$: 7.89-7.82 / 132.0 (CH^{h}), 7.09 / 123.7 (CH^{m}), 7.07-7.01 / 131.5, 128.8 (CH^{j}, CH^{i}), 6.79 / 114.9 (CH^{l}), 5.94 / 119.4 (CH^{a}), 5.91 / 122.2 (CH^{c}), 5.53 / 115.0 (CH^{b}), 3.38 / 55.2 (CH_3^{o}), 3.18-3.12 / 23.6 (CH_2^{e}), 2.95-2.88 / 27.2 (CH_2^{f}).

^{1}H ^{13}C HMBC (600.23 MHz / 150.86 MHz, 300 K, benzene-d_6): $\delta^{1}H$ / $\delta^{13}C$: 7.89-7.82 / 131.5 (CH^{h} / CH^{j}), 7.09 / 152.9, 123.7 (CH^{m} / C^{n}, CH^{m}), 7.07-7.01 / 132.0, 128.8 ($CH^{i/j}$ / CH^{h}, CH^{i}), 6.79 / 152.9, 144.9-144.5, 114.9 (CH^{l} / C^{n}, C^{k}, CH^{l}), 5.94 / 119.4 (CH^{a}), 5.91 / 136.9, 115.0 (CH^{c} / C^{d}, CH^{b}), 5.53 / 136.9, 122.2, 115.0 (CH^{b} / C^{d}, CH^{c}, CH^{b}), 3.38 / 152.9 (CH_3^{o} / CH^{n}), 3.18-3.12 / 136.9, 122.2, 27.2 (CH_2^{e} / C^{d}, CH^{c}, CH_2^{f}), 2.95-2.88 / 136.8, 23.6 (CH_2^{f} / C^{d}, CH_2^{e}).

$^{31}P\{^{1}H\}$ NMR (202.41 MHz, 300 K, benzene-d_6): $\delta^{31}P$: bs 5.3-3.6 (w = 240Hz)

^{31}P NMR (202.41 MHz, 300 K, benzene-d_6): $\delta^{31}P$: bs 6.4-1.4 (w = 270 Hz)

HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{31}H_{31}ONCl_2PTi$ $[M+H]^+$ 582.09983, found 582.09733 (Rel. ab: 35%, -4.9 ppm); $C_{24}H_{23}ClOPTi$ $[M+H_2O-ArNH_2]^+$ 441.0649, found 441.06278 (Rel. ab: 80%, -4.8 ppm); $C_{26}H_{27}NOP$ $[M-CpTiCl_2]^+$ 400.18248, found 400.18041 (Rel. ab: 100%, -5.2 ppm).

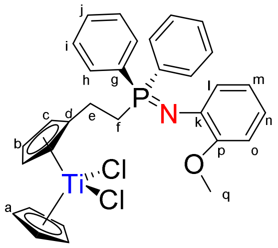
IR (ATR) ν [cm-1]

MIR: 2922; 1498 (P=N); 1442; 1229; 1054; 854; 524.

FIR: 484; 366; 303; 265; 190; 144

Elemental Analysis: % calcd for $C_{31}H_{30}Cl_2NOPTi$: C, 63.94; H, 5.19; N, 2.41; found: C, 63.37; H, 5.24; N, 2.31.

b. Synthesis of **58**:



Chemical Formula: $C_{31}H_{30}Cl_2NOPTi$
Molecular Weight: 582,3

X=1.08 mmol, Yield: 460 mg, 73%

^{1}H NMR (500.03 MHz, 300 K, benzene-d_6): $\delta^{1}H$: 7.83 (apparent dd, $^{3}J_{PH}$ = 11.7 Hz, $^{3}J_{HH}$= 7.2 Hz, 4H, H^{h}), 7.71-7.61 (bs, 1H, H^{l}), 7.08-7.01 (m overlapping with H^{m}, 6H, $H^{i/j}$), 7.01-6.97 (m overlapping with $H^{i/j}$, 1H, H^{m}), 6.77 (t, $^{3}J_{HH}$ = $^{3}J_{HH}$ = 7.6 Hz, 1H, H^{n}), 6.56 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H^{o}), 6.06-5.99 (bs overlapping with H^{a}, 2H, H^{c}), 5.99-5.93 (s overlapping with H^{c}, 5H, H^{a}), 5.64-5.55 (bs, 2H, H^{b}), 3.16-3.05 (m, 2H, H^{e}), 2.98 (s overlapping with H^{f}, 3H, H^{q}), 3.04-2.91 (bm overlapping with H^{q}, 2H, H^{f}).

^{1}H{^{31}P} NMR (500.03 MHz, 300 K, benzene-d$_6$): δ^{1}H: 7.83 (apparent dd, $^{3}J_{PH}$ = 11.7 Hz, $^{3}J_{HH}$= 7.2 Hz, 4H, H^{h}), 7.71-7.61 (bs, 1H, H^{l}), 7.08-7.01 (m overlapping with H^{m}, 6H, H$^{i/j}$), 7.01-6.97 (m overlapping with H$^{i/j}$, 1H, H^{m}), 6.77 (t, $^{3}J_{HH}$ = $^{3}J_{HH}$ = 7.6 Hz, 1H, H^{n}), 6.56 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H^{o}), 6.06-5.99 (bs overlapping with H, 2H^{a}, H^{c}), 5.99-5.93 (s overlapping with H^{c}, 5H, H^{a}), 5.64-5.55 (bs, 2H, H^{b}), 3.16-3.05 (m, 2H, H^{e}), 2.98 (s overlapping with H^{f}, 3H, H^{q}), 3.04-2.91 (bm overlapping with H^{q}, 2H, H^{f}).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, benzene-d$_6$): δ^{13}C: 152.4 (C^{p}), 136.6 (C^{d}), 136.5 (C^{k}), 131.5 (d, $^{2}J_{PC}$ = 9.2 Hz, C^{h}), 131.0 (br s, C^{j}), 128.6 (d, $^{3}J_{PC}$ = 11.1 Hz, C^{i}), 127.5 (a part of the doublet from C^{g}) 126.0 (d, $^{3}J_{PC}$ = 21.6 Hz, C^{l}), 122.4 (C^{c}), 122.3 (d, $^{4}J_{PC}$ = 3.0 Hz C^{m}) 119.5 (C^{a}), 119.0 (C^{n}), 115.6 (br s, C^{b}), 111.8 (C^{o}), 54.4 (C^{q}), 29.8 (d, $^{1}J_{PC}$ = 64.4 Hz C^{f}), 23.8 (d, $^{2}J_{PC}$ = 1.6 Hz C^{e}). Traces of pentane (34.5, 22.7, 14.1) observed.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, benzene-d$_6$): δ^{1}H / δ^{1}H: 7.83 / 7.08-7.01 (H^{h} / H$^{i/j}$), 7.71-7.61 / 7.01-6.97 (H^{l} / H^{m}), 7.08-7.01 / 7.83 (H$^{i/j}$ / H^{h}), 7.01-6.97 / 7.71-7.61, 6.77 (H^{m}, H^{l}, H^{n}), 6.77 / 7.01-6.97, 6.56 (H^{n} / H^{m}, H^{o}), 6.06-5.99 / 5.64-5.55 (H^{c} / H^{b}), 5.64-5.55 / 6.06-5.99 (H^{b} / H^{c}), 3.16-3.05 / 3.04-2.91 (H^{e} / H^{f}), 3.04-2.91 / 3.16-3.05 (H^{f} / H^{e}).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$): δ^{1}H / δ^{13}C: 7.83 / 131.5 (CH^{h}), 7.71-7.61 / 126.0 (CH^{l}), 7.08-7.01 / 131.0, 128.6 (CH^{j}, CH^{i}), 7.01-6.97 / 122.3 (CH^{m}), 6.77 / 119.0 (CH^{n}), 6.56 / 111.8 (CH^{o}), 6.06-5.99 / 122.4 (CH^{c}), 5.99-5.93 / 119.5 (CH^{a}), 5.64-5.55 / 115.6 (CH^{b}), 3.16-3.05 / 23.9 (CH$_2^{e}$), 2.98 / 54.4 (CH$_3^{o}$), 3.04-2.91 / 29.8 (CH$_2^{f}$).

^{1}H ^{13}C HMBC (600.23 MHz / 150.86 MHz, 300 K, benzene-d$_6$): δ^{1}H / δ^{13}C: 7.83 / 131.0 (CH^{h} / CH^{j}), 7.08-7.01 / 131.5, 128.6 (CH$^{i/j}$ / CH^{h}, CH^{i}), 7.01-6.97 / 111.8 (CH^{m} / CH^{n}), 6.77 / 152.4, 126.0, 111.8 (CH^{n} / C^{p}, CH^{l}, CH^{n}), 6.56 / 122.3 (CH^{o} / CH^{m}), 5.99-5.93 / 119.5 (CH^{a}), 5.64-5.55 / 136.6, 122.4 (CH^{b} / C^{d}, CH^{c}), 3.16-3.05 / 136.6, 122.4, 29.8 (CH$_2^{e}$ / C^{d}, CH^{c}, CH$_2^{f}$), 2.98 / 152.4 (CH$_3^{o}$ / C^{p}), 3.04-2.91 / 23.9 (CH$_2^{f}$ / CH$_2^{e}$).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, benzene-d$_6$): δ^{31}P: bs 7.5-0.5 (ν$_{1/2}$ = 1100 Hz).

^{31}P NMR (202.46 MHz, 300 K, benzene-d$_6$): δ^{31}P: bs 7.9 - -0.3 (ν$_{1/2}$ = 2100 Hz).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{31}H_{31}ONCl_2PTi$ [M+H]$^{+}$ 582.09983, found 582.09733 (Rel ab: 100%, -3.6 ppm); $C_{24}H_{23}ClOPTi$ [M+H$_2$O-ArNH$_2$]$^{+}$ 441.06490, found 441.06285 (Rel. ab: 20%, -4.7 ppm).

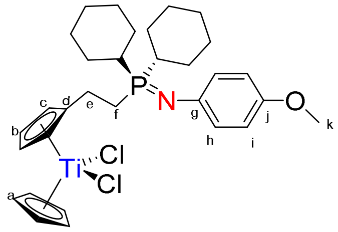
IR (ATR) ν [cm-1]

MIR: 3050; 1490 (P=N); 1433; 1342; 1259; 1112; 1019; 816; 693.

FIR: 498; 398; 302; 247; 134.

Elemental Analysis: % calcd for $C_{31}H_{30}Cl_2NOPTi$: C, 63.94; H, 5.19; N, 2.41; found: C, 63.53; H, 5.02; N, 2.46.

c. Synthesis of **59**:



Chemical Formula: $C_{31}H_{42}Cl_2NOPTi$
Molecular Weight: 594,4

X= 1.06 mmol, Yield: 530 mg, 84%

^{1}H NMR (500.03 MHz, 300 K, benzene-d_6): δ^1H: 7.15-7.10 (m, 2H, H^h), 6.90 (apparent d, $^3J_{HH}$ = 6.4 Hz, $^5J_{PH}$ = 3.4 Hz, 2H, H^i), 6.17-6.12 (bs, 2H, H^c), 6.12-6.07 (s, 5H, H^a), 5.80-5.73 (br s, 2H, H^b), 3.45 (s, 3H, H^k), 3.40-3.31 (m, 2H, H^e), 2.48-2.34 (m, 2H, H^f), 2.09-2.02 (bm, 2H, CH_2 of Cy), 2.02-1.94 (bm, 2H, CH of Cy), 1.94-1.97 (apparent d, $^3J_{HH}$ = 13.0 Hz, 2H, CH_2 of Cy), 1.70-1.60 (m, 4H, CH_2 of Cy), 1.59-1.45 (bm, 6H, CH_2 of Cy), 1.13-1.02 (m, 6H, CH_2 of Cy).

^{1}H{^{31}P} NMR (600.23 MHz, 300 K, benzene-d_6): δ^1H: 7.15-7.10 (m, 2H, H^h), 6.90 (apparent d, $^3J_{HH}$ = 6.4 Hz, $^5J_{PH}$ = 3.4 Hz, 2H, H^i), 6.17-6.12 (bs, 2H, H^c), 6.12-6.07 (s, 5H, H^a), 5.80-5.73 (br s, 2H, H^b), 3.45 (s, 3H, H^k), 3.40-3.31 (m, 2H, H^e), 2.48-2.34 (m, 2H, H^f), 2.09-2.02 (bm, 2H, CH_2 of Cy), 2.02-1.94 (bm, 2H, CH of Cy), 1.94-1.97 (apparent d, $^3J_{HH}$ = 13.0 Hz, 2H, CH_2 of Cy), 1.70-1.60 (m, 4H, CH_2 of Cy), 1.59-1.45 (bm, 6H, CH_2 of Cy), 1.13-1.02 (m, 6H, CH_2 of Cy).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, benzene-d_6): δ^{13}C: 152.7 (C^j), 145.9-144.9 (C^g), 137.8 (d, $^3J_{PC}$ = 14.1 Hz, C^d), 123.8 (d, $^3J_{PC}$ = 13.2 Hz, C^h), 122.7 (C^c), 119.7 (C^a), 115.1 (C^i), 114.8 (C^b), 55.4 (C^k), 37.3 (d, $^1J_{PC}$ = 59.7 Hz, CH of Cy), 27.4-27.1 (m, CH_2 of Cy), 27.0 (d, J_{PC} = 3.2 Hz, CH_2 of Cy), 26.3 (CH_2 of Cy), 24.4 (d, $^2J_{PC}$ = 2.8 Hz, CH_2^e), 22.3 (d, $^1J_{PC}$ = 57.4 Hz, CH_2^f). Pentane (34.4, 22.7, 14.1) observed.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, benzene-d_6): δ^1H / δ^1H: 7.15-7.10 / 6.90 (H^h / H^i), 6.90 / 7.15-7.10 (H^i / H^h), 6.17-6.12 / 5.80-5.73 (H^c / H^b), 5.80-5.73 / 6.17-6.12 (H^b / H^c), 3.40-3.31 / 2.48-2.34 (H^e / H^f), 2.48-2.34 / 3.40-3.31 (H^f / H^e), 2.09-2.02 / 1.70-1.60, 1.59-1.45 (CH_2 of Cy), 2.02-1.94 / 1.51 (CH of Cy / CH_2 of Cy), 1.94-1.97 / 1.70-1.60, 1.59-1.45 (CH_2 of Cy), 1.70-1.60 / 2.09-2.02, 1.94-1.97, 1.59-1.45, 1.13-1.02 (CH_2 of Cy), 1.59-1.45 / 2.09-2.02, 1.94-1.97, 1.70-1.60, 1.13-1.02 (CH_2 of Cy), 1.13-1.02 / 1.70-1.60, 1.59-1.45 (CH_2 of Cy).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6): δ^1H / δ^{13}C: 7.15-7.10 / 123.8 (CH^h), 6.90 / 115.1 (CH^i), 6.17-6.12 / 122.7 (CH^c), 6.12-6.07 / 119.7 (CH^a), 5.80-5.73 / 114.8 (CH^b), 3.45 / 55.4 (CH_3^k), 3.40-3.31 / 24.4 (CH_2^e), 2.48-2.34 / 22.3 (CH_2^f), 2.09-2.02 / 27.0 (CH_2 of Cy), 2.02-1.94 / 37.3 (CH of Cy), 1.94-1.97 / 27.0 (CH_2 of Cy), 1.70-1.60 / 27.4-27.1, 26.3, 24.4 (CH_2 of Cy), 1.59-1.45 / 27.4-27.1, 26.3, 24.4 (CH_2 of Cy), 1.13-1.02 / 27.4-27.1, 26.3, 24.4 (CH_2 of Cy).

^{1}H ^{13}C HMBC (600.23 MHz / 150.86 MHz, 300 K, benzene-d$_6$): δ^1H / δ^{13}C: 7.15-7.10 / 152.7, 123.8, 115.1 (CH^h / C^j, CH^h, CH^i), 6.90 / 152.7, 145.9-144.9, 123.8, 115.1 (CH^i / C^j, C^g, CH^h, CH^i), 6.17-6.12 / 137.8, 122.7, 114.8 (CH^c / C^d, CH^c, CH^b), 6.12-6.07 / 119.7 (CH^a), 5.80-5.73 / 137.8, 122.7, 114.8 (CH^b / C^d, CH^b), 3.45 / 152.7 (CH_3^k / C^j), 3.40-3.31 / 137.8, 122.7, 22.3 (CH_2^e / C^d, CH^c, CH_2^f), 2.48-2.34 / 24.4 (CH_2^f / CH_2^e), 2.09-2.02 / 37.3, 27.4-27.1 (CH_2 of Cy / CH of Cy, CH_2 of Cy), 2.02-1.94 / 27.4-27.1 (CH of Cy / CH_2 of Cy), 1.94-1.97, 1.70-1.60, 1.59-1.45 / 37.3, 27.4-27.1 (CH_2 of Cy / CH_2 of Cy), 1.13-1.02 / 27.4-27.1, 27.0 (CH_2 of Cy / CH_2 of Cy).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, benzene-d$_6$): δ^{31}P: br 22.3-14.0 ($\nu_{1/2}$ = 1300 Hz)

^{31}P NMR (202.46 MHz, 300 K, benzene-d$_6$): δ^{31}P: br 26.3-14.2 ($\nu_{1/2}$ = 3020 Hz)

HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{31}H_{43}ONCl_2PTi$ $[M+H]^+$ 594.19373, found 594.19135 (Rel. ab: 100%, -3.333 ppm); $C_{24}H_{35}ClOPTi$ $[M+H_2O-ArNH_2]^+$ 453.15880, found 453.15689 (Rel. ab: 55%, -4.223 ppm); $C_{26}H_{39}NOP$ $[M-CpTiCl_2]^+$ 412.27638, found 412.27443 (Rel. ab: 75%, -4.725 ppm).

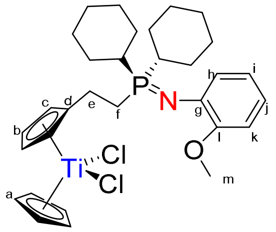
IR (ATR) ν [cm-1]

MIR: 2922; 1583; 1498 (P=N); 1442; 1367; 1262; 1053; 817.

FIR: 524; 407; 366; 304; 267.

Elemental Analysis: % calcd for $C_{31}H_{42}Cl_2NOPTi$: C, 62.64; H, 7.12; N, 2.36; found: C, 60.37; H, 7.45; N, 2.44.

d. Synthesis of **60**:



Chemical Formula: $C_{31}H_{42}Cl_2NOPTi$
Molecular Weight: 594,4

X= 1.06 mmol, Yield: 460 mg, 73%

^{1}H NMR (600.23 MHz, 300 K, benzene-d$_6$): δ^1H: 7.60-7.39 (bs, 1H, H^h), 6.98 (t, $^3J_{HH}$ = $^3J_{HH}$ = 7.6 Hz, 1H, H^i), 6.80 (td, $^3J_{HH}$ = $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H^j), 6.70 (apparent d, $^3J_{HH}$ = 7.6 Hz, 1H, H^k), 6.31-6.22 (bs, 2H, H^c), 6.22-6.11 (s, 5H, H^a), 5.98-5.82 (bs, 2H, H^b), 3.48 (s, 3H, H^m), 3.42-3.32 (bs, 2H, H^e), 2.59-2.53 (bm, 2H, H^f), 2.15-2.05 (bm, CH of Cy), 1.96 (ddm, J_{HH} = 65.1 Hz, J_{HH} = 8.6 Hz, 4H, CH_2 of Cy), 1.73-1.58 (dm, 4H, CH_2 of Cy), 1.57-1.41 (dm, 6H, CH_2 of Cy), 1.14-1.01 (m, 6H, CH_2 of Cy). Traces of pentane 1.29-1.16 (m), 0.85 (t).

^{1}H{^{31}P} NMR (600.23 MHz, 300 K, benzene-d$_6$): δ^1H: 7.60-7.39 (bs, 1H, H^h), 6.98 (t, $^3J_{HH}$ = $^3J_{HH}$ = 7.6 Hz, 1H, H^i), 6.80 (td, $^3J_{HH}$ = $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H^j), 6.70 (br d, $^3J_{HH}$ = 7.6

Hz, 1H, H^k), 6.31-6.22 (bs, 2H, H^c), 6.22-6.11 (s, 5H, H^a), 5.98-5.82 (bs, 2H, H^b), 3.48 (s, 3H, H^m), 3.42-3.32 (br AB system, $^2J_{HH}$ = 8.0 Hz, 2H, H^e), 2.59-2.53 (br m, 2H, H^f), 2.15-2.05 (br m, CH of Cy), 1.96 (br dd, J_{HH} = 65.1 Hz, J_{HH} = 8.6 Hz, 4H, CH$_2$ of Cy), 1.73-1.58 (br m, 4H, CH$_2$ of Cy), 1.57-1.41 (br m, 6H, CH$_2$ of Cy), 1.14-1.01 (br m, 6H, CH$_2$ of Cy). Traces of pentane 1.29-1.16 (m), 0.85 (t).

^{13}C{^{1}H} NMR (150.94 MHz, 300 K, benzene-d$_6$): δ^{13}C: 152.1 (C^l), 138.0-137.2 (C^{g+d}), 125.4 (d, $^3J_{PC}$ = 14.8 Hz, C^h), 122.3 (C^c), 121.8 (C^i), 119.4 (C^a), 119.3 (C^j), 115.2-114.6 (bs, C^b), 111.5 (C^k), 54.6 (C^m), 39.0-37.4 (bs, CH of Cy), 27.1-26.6 (m, C^f, CH2 of Cy), 26.0 (CH$_2$ of Cy), 24.1 (d, $^3J_{PC}$ = 3.5 Hz, C^e). Traces of pentane (34.1, 22.3, 13.9).

^{1}H ^{1}H COSY (600.23 MHz, 300 K, 273 K, benzene-d$_6$): δ^{1}H / δ^{1}H: 7.60-7.39 / 6.98 (H^h / H^i), 6.98 / 7.60-7.39, 6.80 (H^i / H^h, H^j), 6.80 / 6.98, 6.70 (H^j / H^i, H^k), 6.70 / 6.80 (H^k / H^j), 6.31-6.22 / 5.98-5.82 (H^c / H^b), 5.98-5.82 / 6.31-6.22 (H^b / H^c), 3.42-3.32 / 1.51 (H^e / H^f), 1.51 / 3.42-3.32 (H^f / H^e), 2.15-2.05 / 1.57-1.41 (CH of Cy / CH$_2$ of Cy), 1.96 / 1.73-1.58, 1.57-1.41 (CH$_2$ of Cy), 1.73-1.58 / 1.96, 1.57-1.41, 1.14-1.01 (CH$_2$ of Cy), 1.57-1.41 / 2.15-2.05, 1.96, 1.73-1.58, 1.14-1.01 (CH$_2$ of Cy / CH of Cy, CH$_2$ of Cy), 1.14-1.01 / 1.73-1.58, 1.57-1.41 (CH$_2$ of Cy).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, benzene-d$_6$): δ^{1}H / δ^{13}C: 7.60-7.39 / 125.4 (CH^h), 6.98 / 121.8 (CH^i), 6.80 / 119.3 (CH^j), 6.70 / 111.5 (CH^k), 6.31-6.22 / 112.3 (CH^a), 6.22-6.11 / 119.4 (CH^c), 5.98-5.829 / 115.2-114.6 (CH^b), 3.48 / 54.6 (CH$_3$^{o}), 3.42-3.32 / 24.1 (CH$_2$^{e}), 2.59-2.53 / 27.1-26.6 (CH$_2$^{f}), 2.15-2.05 / 39.0-37.4 (CH of Cy), 1.96 / 27.1-26.6 (CH$_2$ of Cy), 1.73-1.58 / 27.1-26.6, 26.0 (CH$_2$ of Cy), 1.57-1.41 / 27.1-26.6, 26.0 (CH$_2$ of Cy), 1.14-1.01 / 27.1-26.6 (CH$_2$ of Cy).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, benzene-d$_6$): δ^{1}H / δ^{13}C: 6.98 / 111.5 (CH^i / CH^k), 6.80 / 152.4, 125.4, 121.8 (CH^j / C^l, CH^h, CH^i), 6.70 / 121.8 (CH^k / CH^i), 6.22-6.11 / 119.4 (CH^a), 2.15-2.05 / 27.1-26.6 (CH of Cy / CH$_2$ of Cy), 1.96 - 1.14-1.01 / 27.1-26.6 (CH$_2$ of Cy).

^{31}P{^{1}H} NMR (202.41 MHz, 300 K, benzene-d$_6$): δ^{31}P: br 18.9-15.0 ($\nu_{1/2}$ = 360 Hz)

^{31}P NMR (202.41 MHz, 300 K, benzene-d$_6$): δ^{31}P: br 19.9-13.7 ($\nu_{1/2}$ = 540 Hz)

HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{31}H_{43}ONCl_2PTi$ [M+H]$^+$ 594.19373, found 594.19128 (Rel ab: 100%, -3.451 ppm);); $C_{24}H_{35}ClOPTi$ [M+H$_2$O-ArNH$_2$]$^+$ 453.15880, found 453.15667 (Rel. ab: 50%, -4.814 ppm); $C_{26}H_{39}NOP$ [M-CpTiCl$_2$]$^+$ 412.27638, found 412.27426 (Rel. ab: 75%, -5.166 ppm).

IR (ATR) ν [cm-1]

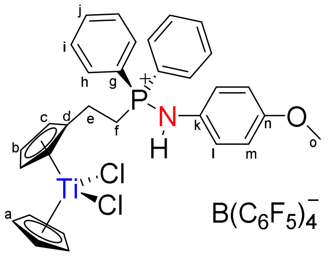
MIR: 3050; 1583; 1490 (P=N); 1433; 1342; 1223; 1112;; 1019; 819; 737; 693; 517.

FIR: 518; 488; 395; 245; 132.

Elemental Analysis: % calcd for $C_{31}H_{42}Cl_2NOPTi$: C, 62.64; H, 7.12; N, 2.36; found: C, 61.76; H, 7.63; N, 2.46.

2. Synthesis of **61**:

A solution of **57** (50 mg, 86.0 µmol, 1 eq) and $H(Et_2O)_2B(C_6F_5)_4$ (71.3 mg, 86.0 µmol, 1 eq) were mixed in dichloromethane (2 mL) at 10°C and stirred for 2h. The solution was evaporated, and the red residue redissolved in 1 mL of dichloromethane and precipitated by addition of pentane (6 mL). The supernatant was removed by cannulation and the red precipitate was washed twice with pentane (2 mL) before being dried *in vacuo*. The desired compound was obtained as a red solid (70 mg, 64%).



Chemical Formula: $C_{55}H_{31}BCl_2F_{20}NOPTi$
Molecular Weight: 1262,4

^{1}H NMR (500.03 MHz, 300 K, benzene-d$_6$): δ^{1}H: 7.31 (apparent dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.3 Hz, 4H, H^h), 7.06 (apparent t, $^3J_{HH}$= 7.6 Hz, 2H, H^j), 7.00 (apparent td, $^3J_{HH}$ = $^3J_{HH}$ = 7.6 Hz, $^4J_{PH}$ = 3.9 Hz, 4H, H^i), 6.58 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H^l), 6.45 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H^m), 5.95 (s, 5H, H^a), 5.82 (ps t, $^3J_{HH}$ = $^4J_{HH}$ = 2.8 Hz, 2H, H^c), 5.56 (ps t, $^3J_{HH}$ = $^4J_{HH}$ = 2.8 Hz, 2H, H^b), 3.28-3.19 (m, 2H, H^f), 3.13 (s, 3H, H^o), 3.03-2.94 (m, 2H, H^e).

^{1}H{^{31}P} NMR (500.03 MHz, 300 K, benzene-d$_6$): δ^{1}H: 7.31 (m, $^4J_{HH}$ = 1.3 Hz, 4H, H^h), 7.06 (apparent t, $^3J_{HH}$= 7.6 Hz, 2H, H^j), 7.00 (apparent t, $^3J_{HH}$ = $^3J_{HH}$ = 7.6 Hz, 4H, H^i), 6.58 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H^l), 6.45 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H^m), 5.95 (s, 5H, H^a), 5.82 (ps t, $^3J_{HH}$ = $^4J_{HH}$ = 2.8 Hz, 2H, H^c), 5.56 (ps t, $^3J_{HH}$ = $^4J_{HH}$ = 2.8 Hz, 2H, H^b), 3.28-3.19 (bm, 2H, H^f), 3.13 (s, 3H, H^o), 3.03-2.94 (bm, 2H, H^e).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, benzene-d$_6$) correlated with **dept 135**: δ^{13}C: 158.0 (C^n), 149.2 (dm, $^1J_{CF}$ = 240 Hz, *o*-CF), 138.9 (dm, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.8 (dm, $^1J_{CF}$ = 240 Hz, *m*-CF), 135.7 (d, $^4J_{PC}$ = 3.3 Hz Hz, C^j), 132.6 (d, $^2J_{PC}$ = 11.0 Hz Hz, C^h) 131.2 (d, $^3J_{PC}$ = 18.1 Hz Hz, C^d), 130.3 (d, $^3J_{PC}$ = 13.0 Hz, C^i), 128.0 (overlapping with solvent peak, C^k) 125.2 (C^c), 124.0 (d, $^3J_{PC}$ = 5.3 Hz, C^l), 121.3 (br, C^B), 120.4 (C^a), 118.6 (d, $^1J_{PC}$ = 98.2 Hz, C^g), 115.3 (C^m), 112.0 (C^b), 55.0 (C^o), 23.4 (d, $^1J_{PC}$ = 65.0 Hz C^f), 22.1 (br s, C^e). Traces of pentane (34.5, 22.7, 14.1) observed.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, benzene-d$_6$): δ^{1}H / δ^{1}H: 7.31 / 7.00 (H^h / H^i), 7.06 / 7.00 (H^j / H^i), 7.00 / 7.31, 7.06 (H^i / H^h, H^j), 6.58 / 6.45 (H^l / H^m), 6.45 / 6.58 (H^m / H^l), 5.82 / 5.56 (H^c / H^b), 5.56 / 5.42 (H^b / H^c), 3.28-3.19 / 3.03-2.94 (H^f / H^e), 3.03-2.94 / 3.28-3.19 (H^e / H^f).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6): δ^{1}H / δ^{13}C: 7.31 / 132.6 (CH^h), 7.06 / 135.7 (CH^j), 7.00 / 130.3 (CH^i), 6.58 / 124.0 (CH^l), 6.45 / 115.3 (CH^a), 5.95 / 120.4 (CH^c), 5.82 / 125.2 (CH^b), 5.56 / 112.0 (CH_3^o), 3.28-3.19 / 23.4 (CH_2^f), 3.13 / 55.0 (CH_3^o), 3.03-2.94 / 22.1 (CH_2^e).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6): δ^{1}H / δ^{13}C: 7.31 / 135.7, 132.6, 118.6 (CH^h / CH^j, CH^h, C^g), 7.06 / 132.6, 130.3 (CH^j / CH^h, CH^i), 7.00 / 132.6, 130.3, 118.6 (CH^i / CH^h, CH^i, C^g), 6.58 / 158.0, 128.0, 124.0, 115.3 (CH^l / C^n, C^k, CH^l, CH^m), 6.45 / 158.0, 128.0, 124.0, 115.3 (CH^m / C^n, C^k, CH^l, CH^m), 5.95 / 120.4 (CH^a), 5.82 / 131.2, 112.0 (CH^c / C^d, CH^b), 5.56 / 131.2, 125.2 (CH^b / C^d, CH^c), 3.28-3.19 / 22.1 (CH_2^f / CH_2^e), 3.13 / 158.0 (CH_3^o / C^n), 131.2, 125.2, 23.4 (CH_2^e / C^d, CH^c, CH_2^e).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, benzene-d_6): δ^{31}P: 39.3 ($\nu_{1/2}$ = 10.3 Hz)

^{31}P NMR (202.46 MHz, 300 K, benzene-d_6): δ^{31}P: br 39.3 ($\nu_{1/2}$ = 53.6 Hz)

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d_5): δ^{11}B: -15.9 ($\nu_{1/2}$ = 22 Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d_5): δ^{11}B: -15.9 ($\nu_{1/2}$ = 22 Hz).

^{19}F{^{1}H} NMR (470.45 MHz, 300 K, bromobenzene-d_5): δ^{19}F: -131.8 (apparent d, $^{3}J_{FF}$ = 20.0 Hz, 8F, *o*-F), -162.1 (t, $^{3}J_{FF}$ = 20 Hz, 4F, *p*-F), -166.1 (apparent t, $^{3}J_{FF}$ = 20 Hz, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d_5): δ^{19}F: -131.8 (apparent d, $^{3}J_{FF}$ = 20.0 Hz, 8F, *o*-F), -162.1 (t, $^{3}J_{FF}$ = 20 Hz, 4F, *p*-F), -166.1 (apparent t, $^{3}J_{FF}$ = 20 Hz, 8F, *m*-F).

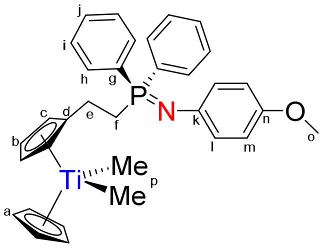
HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{31}H_{31}ONCl_2PTi$ $[M]^+$ 582.09943, found 582.09911 (Rel. ab: 100%, -0.550 ppm); $C_{24}H_{23}ClOPTi$ $[M\text{-}ArNH_2+H_2O]^+$ 441.06490, found 441.06430 (Rel. ab: 15%, -1.368 ppm); $C_{26}H_{27}NOP$ $[M\text{-}CpTiCl_2]^+$ 400.18248, found 400.18088 (Rel. ab: 30%, -3.992 ppm).

Elemental Analysis: % calcd for $C_{55}H_{31}BF_{20}Cl_2NOPTi$: C, 52.33; H, 2.48; N, 1.11; found: C, 51.33; H, 2.86; N, 1.07.

3. General protocole for the synthesis of dimethyl-iminophosphoranyl-titanocenes:

To an ethereal suspension of $Cp^{PN}CpTiCl_2$ (X mmol, 1 eq), was added dropwise MeLi (2.1 eq) at -78°C protected from light. The resulting solution was stirred 1h at -78°C until an yellow clear solution was obtained and left to warm up to room temperature over 30 min. The resulting heterogeneous solution was completed with 1 volume of pentane and filtered through diatomaceous earth. The yellow filtrate was evaporated *in vacuo* yielding a light sensitive light maroon solid. It has to be stored at -15°C and light protected

a. Synthesis of **62**:



Chemical Formula: $C_{33}H_{36}NOPTi$
Molecular Weight: 541,5

X= 0.51 mmol, Yield: 180 mg, 65%

^{1}H NMR (500.03 MHz, 300 K, benzene-d$_6$): δ^{1}H: 7.80-7.72 (m, 4H, H^{h}), 7.09-7.07 (m, 2H, H^{m}), 7.06-7.01 (m, 6H, H$^{i/j}$), 6.80 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{PH}$ = 1.0 Hz, 2H, H^{l}), 5.64 (s, 5H, H^{a}), 5.52 (apparent t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.6 Hz, 2H, H^{c}), 5.40 (apparent t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.6 Hz, 2H, H^{b}), 3.39 (s, 3H, H^{o}), 2.76-2.67 (m, 2H, H^{e}), 2.67-2.58 (m, 2H, H^{f}), -0.06 (s, 6H, H^{p}). Diethyl ether: 3.27 (q), 1.12 (t), grease: 0.29 (s).

H{^{31}P} NMR (600.23 MHz, 300 K, benzene-d$_6$): δ^{1}H: 7.80-7.72 (m, 4H, H^{h}), 7.09-7.07 (m, 2H, H^{m}), 7.06-7.01 (m, 6H, H$^{i/j}$), 6.80 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{PH}$ = 1.0 Hz, 2H, H^{l}), 5.64 (s, 5H, H^{a}), 5.52 (apparent t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.6 Hz, 2H, H^{c}), 5.40 (apparent t, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.6 Hz, 2H, H^{b}), 3.39 (s, 3H, H^{o}), 2.76-2.67 (m, 2H, H^{e}), 2.67-2.58 (m, 2H, H^{f}), -0.06 (s, 6H, H^{p}). Diethyl ether: 3.27 (q), 1.12 (t), grease: 0.29 (s).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, benzene-d$_6$): δ^{13}C: 152.8 (C^{n}), 145.7 (C^{k}), 132.6 (d, $^{1}J_{PC}$ = 92 Hz, C^{g}), 131.9 (d, $^{3}J_{PC}$ = 8.9 Hz, C^{h}), 131.4 (d, $^{3}J_{PC}$ = 2.8 Hz, C^{j}), 128.8 (d, $^{2}J_{PC}$ = 11.1 Hz, C^{i}), 127.7 (C^{d} determined by HMBC), 124.0 (d, $^{4}J_{PC}$ = 18.2 Hz, C^{m}), 115.1 (C^{c}), 113.7 (C^{c}), 113.5 (C^{a}), 111.9 (C^{b}), 55.3 (C^{o}), 45.9 (C^{p}), 30.3 (d, $^{4}J_{PC}$ = 68 Hz, C^{f}), 23.0 (C^{e}). Traces of diethyl ether (65.9, 15.6) and grease (1.4) observed.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, benzene-d$_6$): δ^{1}H / δ^{1}H: 7.80-7.72 / 7.06-7.01 (H^{h} / H$^{i/j}$), 7.09-7.07 / 6.80 (H^{m} / H^{l}), 7.06-7.01 / 7.80-7.72 (H$^{i/j}$ / H^{h}), 6.80 / 7.09-7.07 (H^{l} / H^{m}), 5.52 / 5.40 (H^{c} / H^{b}), 5.40 / 5.52 (H^{b} / H^{c}), 2.76-2.67 / 2.67-2.58 (H^{e} / H^{f}), 2.67-2.58 / 2.76-2.67 (H^{f} / H^{e}).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$): δ^{1}H / δ^{13}C: 7.80-7.72 / 131.9 (CH^{h}), 7.09-7.07 / 124.0 (CH^{m}), 7.06-7.01 / 131.4, 128.8 (CH^{j}, CH^{i}), 6.80 / 115.1 (CH^{l}), 5.64 / 113.5 (CH^{a}), 5.52 / 113.7 (CH^{c}), 5.40 / 111.9 (CH^{b}), 3.39 / 55.3 (CH$_3$^{o}), 2.76-2.67 / 23.0 (CH$_2$^{e}), 2.67-2.58 / 30.3 (CH$_2$^{f}), -0.06 / 45.9 (CH$_3$^{p}).

^{1}H ^{13}C HMBC (600.23 MHz / 150.86 MHz, 300 K, benzene-d$_6$): δ^{1}H / δ^{13}C: 7.80-7.72 / 131.9 (CH^{h} / CH^{j}), 7.09-7.07 / 152.8, 145.7, 124.0, 115.1 (CH^{m} / C^{n}, C^{k}, CH^{m}, CH^{l}), 7.06-7.01 / 131.9, 128.8 (CH$^{i/j}$ / CH^{h}, CH^{i}), 6.80 / 152.8, 145.7, 115.1 (CH^{l} / C^{n}, C^{k}, CH^{l}), 5.64 / 113.5, 46.6 (CH^{a}, CH$_3$^{p}), 5.52 / 127.7, 111.9 (CH^{c} / C^{d}, CH^{b}), 5.40 / 127.7, 113.7 (CH^{b} / C^{d}, CH^{c}), 3.39 / 152.8

(CH_3^o / CH^n), 2.76-2.67 / 127.7, 113.7, 30.3 (CH_2^e / C^d, CH^c, CH_2^f), 2.67-2.58 / 127.7, 23.0 (CH_2^f / C^d, CH_2^e), -0.06 / 113.5 (CH_3^p / CH^a).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, benzene-d$_6$): δ^{31}P: 1.5 ($\nu_{1/2}$ = 38 Hz).

^{31}P NMR (202.46 MHz, 300 K, benzene-d$_6$): δ^{31}P: bs 1.5 ($\nu_{1/2}$ = 63.4 Hz).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{33}H_{37}ONPTi$ $[M+H]^+$ 542.20867, found 542.20604 (Rel. ab: 35%, -4.9 ppm); $C_{31}H_{30}ONPTi$ $[M-ArNH_2+H_2O]^+$ 511.15390, found 511.15217 (Rel ab: 100%, -3.4), $C_{26}H_{27}NOP$ $[M-CpTiCl_2]^+$ 400.18248, found 400.18109 (Rel. ab: 65%, -3.5 ppm).

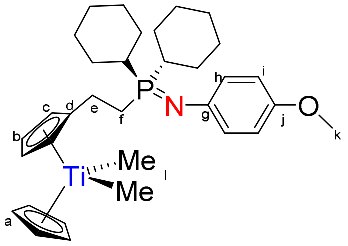
IR (ATR) ν [cm-1]

MIR: 2925; 1496 (P=N); 1443; 1338; 1227; 1049; 809; 524; 471.

FIR: 520; 470; 402; 304; 178.

Elemental Analysis: % calcd for $C_{33}H_{36}NOPTi$: C, 73.20; H, 6.70; N, 2.59; found: C, 66.02; H, 6.60; N, 2.21.

b. Synthesis of **63**:



Chemical Formula: $C_{33}H_{48}NOPTi$
Molecular Weight: 553,6

X= 0.60 mmol, Yield: 200 mg, 62%

^{1}H NMR (600.23 MHz, 300 K, benzene-d$_6$): δ^{1}H: 7.02 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H^h), 6.89 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H^i), 5.74 (s overlapping with H^c, 5H, H^a), 5.74-5.72 (m overlapping with H^a, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 5H, H^c), 5.44 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 3.46 (s, 3H, H^k), 2.90-2.83 (m, 2H, H^e), 2.10-2.02 (m overlapping with CH_2 of Cy, 2H, H^f), 2.02-1.96 (m overlapping with H^f, 2H, CH_2 of Cy), 1.90-1.77 (m, CH and CH_2 of Cy), 1.68-1.58 (m, 4H, CH_2 of Cy), 1.57-1.48 (m, 2H, CH_2 of Cy), 11.47-1.33 (m, 4H, CH_2 of Cy), 1.14-0.95 (m, 6H, CH_2 of Cy), 0.05 (s, 6H, H^l).Pentane 1.33-1.29 (m), 0.87 (t).

^{1}H{^{31}P} NMR (600.23 MHz, 300 K, benzene-d$_6$): δ^{1}H: 7.02 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H^h), 6.89 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H^i), 5.74 (s overlapping with H^c, 5H, H^a), 5.74-5.72 (m overlapping with H^a, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 5H, H^c), 5.44 (apparent t, $^3J_{HH}$ = $^4J_{HH}$ = 2.6 Hz, 2H, H^b), 3.46 (s, 3H, H^k), 2.90-2.83 (m, 2H, H^e), 2.10-2.02 (m overlapping with CH_2 of Cy, 2H, H^f), 2.02-1.96 (m overlapping with H^f, 2H, CH_2 of Cy), 1.90-1.77 (m, CH and CH_2 of Cy), 1.68-1.58 (m, 4H, CH_2 of Cy), 1.57-1.48 (m, 2H, CH_2 of Cy), 11.47-1.33 (m, 4H, CH_2 of Cy), 1.14-0.95 (m, 6H, CH_2 of Cy), 0.05 (s, 6H, H^l).Pentane 1.33-1.29 (m), 0.87 (t).

$^{13}C\{^{1}H\}$ NMR (150.94 MHz, 300 K, benzene-d_6): $\delta^{13}C$: 152.2 (br s, C^j), 147.1 (C^g), 129.3 (d, $^3J_{PC}$ = 13.8 Hz, C^c), 123.9 (d, $^3J_{PC}$ = 14.5 Hz, C^h), 115.0 (C^i), 113.9 (C^c), 113.6 (C^a), 111.6 (C^b), 55.5 (C^k), 45.8 (C^l), 37.9 (d, $^1J_{PC}$ = 61.2 Hz, CH of Cy), 27.3 (d, J_{PC} = 3.1 Hz CH_2 of Cy), 27.2 (d, J_{PC} = 3.7 Hz CH_2 of Cy), 27.1 (d, J_{PC} = 3.8 Hz, CH_2 of Cy), 26.4 (CH_2 of Cy), 25.7 (d, $^1J_{PC}$ = 56.2 Hz, $CH_2{}^f$), 24.0 (d, $^2J_{PC}$ = 3.3 Hz, $CH_2{}^e$). Pentane 34.4, 22.7, 14.1.

^1H ^1H COSY (600.23 MHz, 300 K, 273 K, benzene-d_6): δ^1H / δ^1H: 7.02 / 6.89 (H^h / H^i), 6.89 / 7.02 (H^i / H^h), 5.74-5.72 / 5.44 (H^c / H^b), 5.44 / 5.74-5.72 (H^b / H^c), 2.90-2.83 / 2.10-2.02 (H^e / H^f), 2.10-2.02 / 2.90-2.83 (H^f / H^e), 2.02-1.96 / 1.90-1.77, 1.68-1.58, 11.47-1.33 (CH_2 of Cy / CH and CH_2 of Cy), 1.90-1.77 / 2.02-1.96, 1.68-1.58, 11.47-1.33 (CH and CH_2 of Cy / CH_2 of Cy), 1.68-1.58 / 1.14-0.95 (CH_2 of Cy), 1.57-1.48 / 1.14-0.95 (CH_2 of Cy), 11.47-1.33 / 2.02-1.96, 1.90-1.77, 1.14-0.95 (CH_2 of Cy / CH and CH_2 of Cy), 1.14-0.95 / 1.68-1.58, 1.57-1.48, 1.38 (CH_2 of Cy).

^1H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6): δ^1H / $\delta^{13}C$ 7.02 / 123.9 (CH^h), 6.89 / 115.0 (CH^i), 5.74 / 113.6 (CH^a), 5.74-5.72 / 113.9 (CH^c), 5.44 / 111.6 (CH^b), 3.46 / 55.5 ($CH_3{}^k$), 2.90-2.83 / 24.0 ($CH_2{}^e$), 2.10-2.02 / 25.7 ($CH_2{}^f$), 2.02-1.96 / 27.3, 27.2, 27.1 (CH_2 of Cy), 1.90-1.77 / 37.9, 27.1 (CH and CH_2 of Cy), 1.68-1.58 / 27.3, 27.2, 27.1, 25.1 (CH_2 of Cy), 1.57-1.48 / 26.4 (CH_2 of Cy), 11.47-1.33 / 27.3, 27.2, 27.1 (CH_2 of Cy), 1.14-0.95 / 27.3, 27.2, 27.1 (CH_2 of Cy), 0.05 / 45.8 ($CH_3{}^l$).

^1H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6): δ^1H / $\delta^{13}C$: 7.02 / 152.2, 147.1, 123.9 (CH^h / C^j, C^g, CH^h), 6.89 / 152.2, 147.1, 123.9, 115.0 (CH^i / C^j, C^g, CH^h, CH^i), 5.74 / 113.6 (CH^a), 5.74-5.72 / 129.3, 111.6 (CH^c / C^d, CH^b), 5.44 / 129.3, 113.9, 111.6 (CH^b / C^d, CH^c, CH^b), 3.46 / 152.2 ($CH_3{}^k$ / C^j), 2.90-2.83 / 129.3, 113.9, 25.7 ($CH_2{}^e$ / C^d, CH^c, $CH_2{}^f$), 2.10-2.02 / 129.3, 24.0 ($CH_2{}^f$ / C^d, $CH_2{}^e$), 2.02-1.96 / 37.9, 27.3 - 26.4 (CH_2 of Cy / CH of Cy, CH_2 of Cy), 1.90-1.77 / 37.9, 27.3 - 26.4 (CH and CH_2 of Cy / CH and CH_2 of Cy), 1.68-1.58 / 37.9, 27.3 - 26.4 (CH_2 of Cy / CH of Cy and CH_2 of Cy), 1.57-1.48 - 1.14-0.95 / 27.3 - 26.4 (CH_2 of Cy / CH_2 of Cy).

$^{31}P\{^1H\}$ NMR (242.97 MHz, 300 K, benzene-d_6): $\delta^{31}P$: 15.3 ($\nu_{1/2}$ = 25 Hz).

^{31}P NMR (242.97 MHz, 300 K, benzene-d_6): $\delta^{31}P$: br 15.3 ($\nu_{1/2}$ = 30 Hz).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{33}H_{49}ONPTi$ $[M+H]^+$ 554.30258, found 554.30218 (Rel. ab 70%, -0.7 ppm); $C_{26}H_{39}NOP$ $[M-CpTiCl_2]^+$ 412.27638, 412.27659 (Rel. ab: 75%, 0.5 ppm).

IR (ATR) ν [cm-1]

MIR: 2926; 1496 (P=N); 1443; 1339; 1227; 1050; 810.

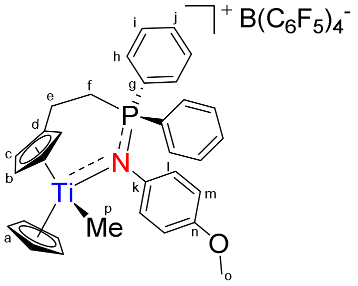
FIR: 520; 466; 400; 253; 176.

Elemental Analysis: % calcd for $C_{33}H_{48}NOPTi$: C, 66.52; H, 8.90; N, 2.90; found: C, 71.60; H, 8.74; N, 2.53.

4. General protocole for the synthesis of the aminophosphonium:

A solution of $Cp^{PN}CpTiMe_2$ (X mmol, 1 eq) and $[Ph_3C][B(C_6F_5)_4]$ (1 eq) in C_6H_5Br (2 mL) wasstirred 10 min. The solution which kept a light maroon color, was transferred in a Schlenk containing vigourously stirred pentane (15 mL). Yellow supernatant was removed and the marron oil was then triturated in pentane (3 mL). The resulting maroon precipitate was isolated and dried *in vacuo*. A small amount of dichloromethane was used to dissolve the compound, and pentane (15 mL) was added to the stirred solution. Light yellow supernatant was removed and the residue was triturated again in pentane. The resulting maroon solid was dried *in vacuo* yielding the desired compound as a maroon powder.[13]

a. Synthesis of **64**:



Chemical Formula: $C_{56}H_{33}BF_{20}NOPTi$
Molecular Weight: 1205,5

X= 0.185 mmol, 180 mg, 81%

This compound exhibits dynamic signal in ^{1}H NMR. A variable temperature study has been carried out in order to find out the best temperature for characterization.

The compound was characterized at 360 K for ^{1}H and ^{13}C NMR and at 300 K for others.

^{1}H NMR (600.23 MHz, 360 K, bromobenzene-d_5): δ^1H: 7.40 (tm, $^3J_{HH}$ = 7.5 Hz, 2H, $H^{j/j'}$), 7.30-7.22 (m, 2H, H^i), 7.22-7.18 (m, 2H, $H^{i'}$), 7.18-7.13 (m, 2H, H^h), 7.05 (dm overlapping with the one solvent peak, $^4J_{PH}$ = 11.9 Hz, 2H, $H^{h'}$), 6.60 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.4 Hz, 1H, H^c), 6.38 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H^m), 6.20 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{PH}$ = 2.5 Hz, 2H, H^l), 5.75 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.4 Hz, 1H, H^b), 5.67 (s, 5H, H^a), 5.43 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.4 Hz, 1H, $H^{c'}$), 5.34 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.4 Hz, 1H, $H^{b'}$), 3.41 (s, 3H, H^o), 2.81-2.69 (m, 2H, H^e), 2.62-2.54 (m, 1H, H^f), 2.34-2.25 (m, 1H, H^f), 0.70 (s, 3H, H^p). pentane: 1.29-1.16 (m), 0.85 (t).

^{1}H{^{31}P} NMR (600.23 MHz, 360 K, bromobenzene-d_5): δ^1H: 7.40 (t, $^3J_{HH}$ = 7.5 Hz, 2H, $H^{j/j'}$), 7.30-7.24 (m, 2H, H^i), 7.21-7.18 (m, 2H, $H^{i'}$), 7.18-7.15 (m, 2H, H^h), 7.05 (d overlapping with the one solvent peak, $^3J_{HH}$ = 8.1 Hz, 2H, $H^{h'}$), 6.60 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.4 Hz, 1H, H^c),

---

[13] IR spectroscopy was not measured due to the presence of the counter anion.

6.38 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H^m), 6.19 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H^l), 5.75 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.4 Hz, 1H, H^b), 5.67 (s, 5H, H^a), 5.43 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.4 Hz, 1H, $H^{c'}$), 5.34 (apparent q, $^3J_{HH}$ = $^4J_{HH}$ = 2.4 Hz, 1H, $H^{b'}$), 3.40 (s, 3H, H^o), 2.79-2.68 (m, 2H, H^e), 2.61-2.53 (m, 1H, H^f), 2.33-2.24 (m, 1H, H^f), 0.70 (s, 3H, H^p). pentane: 1.29-1.16 (m), 0.87 (t).

^{13}C{^{1}H} NMR (150.94 MHz, 360 K, bromobenzene-d$_5$): correlated with **dept 135**: δ^{13}C: 157.8 (C^n), 148.8 (br d, $^1J_{CF}$ = 240 Hz, *o*-CF), 139.2 (br s, C^k), 138.7 (br d, $^1J_{CF}$ = 240 Hz, *p*-CF), 136.8 (br d, $^1J_{CF}$ = 240 Hz, *m*-CF), 134.2 (d, $^4J_{PC}$ = 2.9 Hz, C^j), 133.8 (d, $^4J_{PC}$ = 2.6 Hz, $C^{j'}$), 132.7(d, $^3J_{PC}$ = 9.2 Hz, C^h), 132.2 (d, $^3J_{PC}$ = 9.2 Hz, $C^{h'}$), 131.0 (n.o. C^l), 129.5 (d, $^3J_{PC}$ = 9.2 Hz, C^i), 129.4 (d, $^3J_{PC}$ = 11.9 Hz, $C^{i'}$), 128.9 (d, $^3J_{PC}$ = 3.1Hz, C^d), 124.8 (d, $^3J_{PC}$ = 94.1 Hz, $C^{g+g'}$), 121.6 (C^c), 117.8 (C^b), 115.9 (C^a), 114.3 (C^m), 111.1 ($C^{b'}$), 106.7 ($C^{c'}$), 55.3(C^o), 55.2 (C^p), 28.9 (d, $^1J_{PC}$ = 71.0 Hz, C^f), 20.6 (d, $^2J_{PC}$ = 5.4 Hz, C^e). Pentane (34.2, 22.4, 14.1), iapparento-C^B not observed.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, bromobenzene-d$_5$): δ^{1}H / δ^{1}H: 7.40 / 7.30-7.22, 7.22-7.18, 7.18-7.13, 7.05 ($H^{j/j'}$ / H^i, $H^{i'}$, H^h, $H^{h'}$), 7.30-7.22 / 7.40 7, 7.18-7.13 (H^i / H^j, H^h), 7.22-7.18 / 7.40, 7.05 ($H^{i'}$ / $H^{j'}$, $H^{h'}$), 7.18-7.13 / 7.40, 7.30-7.22 (H^h / H^j, H^i), 7.05 / 7.40 , 7.22-7.18 ($H^{h'}$ / $H^{j'}$, $H^{i'}$), 6.60 / 5.75, 5.43, 5.34 (H^c / H^b, $H^{c'}$, $H^{b'}$), 6.38 / 6.20 (H^m / H^l), 6.20 / 6.38 (H^l / H^m), 5.75 / 6.60, 5.43, 5.34 (H^b / H^c, $H^{c'}$, $H^{b'}$), 5.43 / 6.60, 5.75, 5.34 ($H^{c'}$ / H^c, H^b, $H^{b'}$), 5.34 / 6.60, 5.75, 5.43 ($H^{b'}$ / H^c, H^b, $H^{c'}$), 2.81-2.69 / 2.62-2.54, 2.34-2.25 (CH_2^e / CH_2^f), 2.62-2.54, 2.34-2.25 / 2.81-2.69 (CH_2^f / CH_2^e).

^{1}H ^{13}C HMQC (600.23 MHz / 150.94 MHz, 360 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.40 / 134.2, 133.8 ($CH^{j/j'}$), 7.30-7.22 / 129.5 (CH^i), 7.22-7.18 / 129.4 ($CH^{i'}$), 7.18-7.13 / 132.7 ($CH^{h'}$), 7.05 / 132.2 ($CH^{h'}$), 6.60 / 121.1 (CH^c), 6.38 / 114.3 (CH^m), 6.20 / 131.6 (CH^l), 5.75 / 117.8 (CH^b), 5.67 / 115.9 (CH^a), 5.43 / 106.7 ($CH^{c'}$), 5.34 / 111.1 ($CH^{b'}$), 3.41 / 55.3 (CH_3^o), 2.81-2.69 / 20.6 (CH_2^e), 2.62-2.54, 2.34-2.25 / 27.3 (CH_2^f), 0.70 / 55.2 (CH_3^p).

^{1}H ^{13}C HMBC (600.23 MHz / 150.94 MHz, 360 K, bromobenzene-d$_5$): δ^{1}H / δ^{13}C: 7.40 / 132.7, 132.2 ($CH^{j/j'}$ / CH^i, $CH^{i'}$), 7.30-7.22 / 134.2, 132.7, 129.5, 124.8 (CH^i / CH^j, CH^h, CH^i, C^g), 7.05 / 134.2, 132.2, 129.5 ($CH^{h'}$ / $CH^{j'}$, $CH^{h'}$, $CH^{i'}$), 6.60 / 128.9, 117.8, 111.1, 106.7 (CH^c / C^d, CH^b, $CH^{b'}$, $CH^{c'}$), 6.38 / 157.8, 139.2, 114.3 (CH^m / C^n, C^k, CH^m), 6.20 / 157.8, 139.2, 131.6 (CH^l / C^n, C^k, CH^l), 5.75 / 128.9, 121.6, 111.1, 106.7 (CH^b / C^d, CH^c, $CH^{b'}$, $CH^{c'}$), 5.67 / 115.9 (CH^a), 5.43 / 129.8, 121.6, 117.8, 111.1 ($CH^{c'}$ / C^d, CH^c, CH^b, $CH^{b'}$), 5.34 / 128.9, 121.6, 117.8, 106.7 ($CH^{b'}$ / C^d, CH^c, CH^b, $CH^{c'}$), 3.41 / 157.8 (CH_3^o / CH^n), 2.81-2.69 / 128.9, 121.6, 106.7 (CH_2^e / C^d, CH^c, $CH^{c'}$), 2.62-2.54, 2.34-2.25 / 128.9, 20.6 (CH_2^f / C^d, CH_2^f).

^{31}P{^{1}H} NMR (202.46 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: 36.6 ($\nu_{1/2}$. = 2.6 Hz).

^{31}P NMR (202.46 MHz, 300 K, bromobenzene-d$_5$): δ^{31}P: br 36.6 $\nu_{1/2}$ = 66.8 Hz).

^{11}B{^{1}H} NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 21 Hz).

^{11}B NMR (160.42 MHz, 300 K, bromobenzene-d$_5$): δ^{11}B: -15.9 ($\nu_{1/2}$ = 21 Hz).

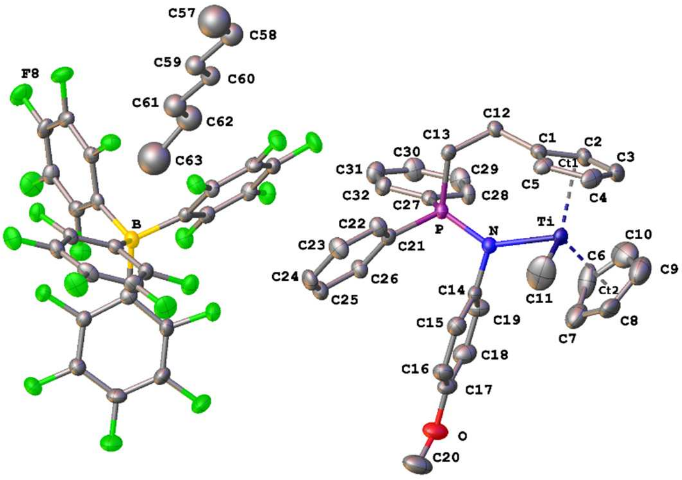
^{19}F{^{1}H} NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.4 (br d, $^3J_{FF}$ = 18.1 Hz, 8F, *o*-F), -161.5 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.4 (br t, $^3J_{FF}$ = 21 Hz, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 300 K, bromobenzene-d$_5$): δ^{19}F: -131.4 (br d, $^3J_{FF}$ = 18.1 Hz, 8F, *o*-F), -161.5 (t, $^3J_{FF}$ = 21 Hz, 4F, *p*-F), -165.4 (br t, $^3J_{FF}$ = 21 Hz, 8F, *m*-F).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{31}H_{30}NOPTi$: $[M-CH_3]^+$ 511.15390, found 511.15262 (Rel. ab: 100%, -2.5 ppm).

Elemental Analysis: % calcd for $C_{56}H_{33}BF_{20}NOPTi$: C, 55.88; H, 2.31; N, 1.06; found: C, 55.80; H, 2.76; N, 1.16.

XRD:

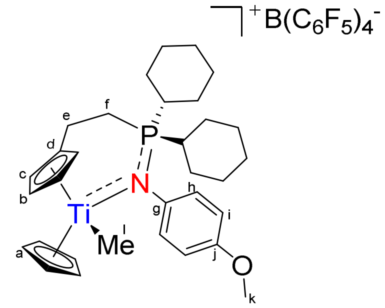


Experimental. Single orange needle-shaped crystals of (**q090117_0ma_a**) were obtained by recrystallisation from diffusion of pentane in a dichloromethane solution at -15°C. A suitable crystal (0.37×0.05×0.03) mm^3 was selected and mounted on a mylar loop with oil on a Nonius Kappa Apex II diffractometer. The crystal was kept at *T* = 115115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the ? structure solution program, using the ? methods solution method. The model was refined with version 2017/1 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{59.5}H_{41}BF_{20}NOPTi$, M_r = 1255.61, monoclinic, C2/c (No. 15), a = 39.807(7) Å, b = 12.4929(18) Å, c = 30.542(5) Å, β = 129.687(7)°, $\alpha = \gamma$ = 90°, V = 11688(3) Å^3, T = 115115 K, Z = 8, Z' = 1, μ(MoK$_\alpha$) = 0.278, 116678 reflections measured, 10212 unique (R_{int} = 0.0972) which were used in all calculations. The final wR_2 was 0.2002 (all data) and R_1 was 0.0655 (I > 2(I)).

Compound	**q090117_0ma_a**
Formula	$C_{59.5}H_{41}BF_{20}NOPTi$
$D_{calc.}$/ g cm^{-3}	1.427
μ/mm^{-1}	0.278
Formula Weight	1255.61
Colour	orange
Shape	needle
Size/mm^3	0.37×0.05×0.03
T/K	115
Crystal System	monoclinic
Space Group	C2/c
a/Å	39.807(7)
b/Å	12.4929(18)
c/Å	30.542(5)
α/°	90
β/°	129.687(7)
γ/°	90
V/Å^3	11688(3)
Z	8
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.576
Θ_{max}/°	25.000
Measured Refl.	116678
Independent Refl.	10212
Reflections Used	6917
R_{int}	0.0972
Parameters	762
Restraints	3
Largest Peak	1.482
Deepest Hole	-0.540
GooF	1.053
wR_2 (all data)	0.2002
wR_2	0.1693
R_1 (all data)	0.1076
R_1	0.0655

b. Synthesis of **65**:



Chemical Formula: $C_{56}H_{45}BF_{20}NOPTi$
Molecular Weight: 1217,6

X=0.180 mmol, 140 mg; 64%

^{1}H NMR (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 6.97 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = 3.1 Hz, 1H, H^{i}), 6.85 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = 3.1 Hz, 1H, H$^{i'}$ overlapping with H^{b}), 6.84 (m, 1H, H^{b} overlapping with H$^{i'}$), 6.75 (dt, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = $^{4}J_{PH}$ = 3.1 Hz, 1H, H^{h}), 6.59 (dt, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = $^{4}J_{PH}$ = 3.1 Hz, 1H, H$^{h'}$), 5.85 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.9 Hz, 1H, H^{c}), 5.75 (s overlapping with H$^{b'}$, 5H, H^{a}), 5.73 (apparent q overlapping with H^{a}, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.9 Hz, 1H, H$^{b'}$), 5.56 (apparent q, $^{3}J_{HH}$ = $^{4}J_{HH}$ = 2.9 Hz, 1H, H$^{c'}$), 3.84 (s, 3H, H^{k}), 3.35-3.08 (m, 2H, H^{e}), 2.54-2.38 (m, 2H, H^{f}), 2.35-2.12 (m, 1H, CH of Cy), 2.08-0.94 (m overlapping with pentane, CH' of Cy and CH$_2$ of Cy), 0.86 (s, 3H, H^{l}). pentane: 1.35-1.12 (m), 0.88 (t).

^{1}H{^{31}P} NMR (500.03 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H: 6.97 (dd, $^{3}J_{HiHh}$ = 9.0 Hz, $^{4}J_{HiHi'}$ = 3.1 Hz, 1H, H^{i}), 6.85 (dd, $^{3}J_{Hi'Hh'}$ = 9.0 Hz, $^{4}J_{Hi'Hi}$ = 3.1 Hz, 1H, H$^{i'}$ overlapping with H^{b}), 6.84 (m, 1H, H^{b} overlapping with H$^{i'}$), 6.75 (dd, $^{3}J_{HhHi}$ = 9.0 Hz, $^{4}J_{HhHi'}$ = 3.1 Hz, 1H, H^{h}), 6.59 (dd, $^{3}J_{Hh'Hi'}$ = 9.0 Hz, $^{4}J_{Hh'Hi}$ = 3.1 Hz, 1H, H$^{h'}$), 5.85 (apparent q, $^{3}J_{HcHb}$ = $^{4}J_{HcHb/Hb'}$ = 2.9 Hz, 1H, H^{c}), 5.75 (s, 5H, H^{a}), 5.73 (apparent q, $^{3}J_{Hb'Hc'/Hb}$ = $^{4}J_{Hb'Hc}$ = 2.9 Hz, 1H, H$^{b'}$), 5.56 (apparent q, $^{3}J_{Hc'Hb'}$ = $^{4}J_{Hc'Hb/Hc}$ = 2.9 Hz, 1H, H$^{c'}$), 3.84 (s, 3H, H^{k}), 3.35-3.08 (m, 2H, H^{e}), 2.54-2.38 (m, 2H, H^{f}), 2.35-2.12i (m, 1H, CH of Cy), 2.08-0.94 (m, CH' of Cy and CH$_2$ of Cy), 0.86 (s, 3H, H^{l}).

^{13}C{^{1}H} NMR (125.75 MHz, 300 K, dichloromethane-d$_2$): δ^{13}C: 158.7 (C^{j}), 148.8 (dm, $^{1}J_{CF}$ = 240 Hz, *o*-CF), 140.8 (d, $^{2}J_{PC}$ = 6.8 Hz, C^{g}), 138.8 (dm, $^{1}J_{CF}$ = 240 Hz, *p*-CF), 136.9 (dm, $^{1}J_{CF}$ = 240 Hz, *m*-CF), 133.4 (d, $^{3}J_{PC}$ = 5.7 Hz, C$^{h'}$), 129.2 (d, $^{3}J_{PC}$ = 4.0 Hz, C^{h}), 126.6 (d, $^{3}J_{PC}$ = 1.9 Hz, C^{d}), 125.4-123.6 (ipso-C^{B} overlapping with C^{b}) 124.9 (C^{b} Overlapping with *ipso*-C^{B}), 116.2 (C^{a}), 115.2 (d, $^{4}J_{PC}$ = 2.7 Hz, C^{i}), 114.8 (d, $^{4}J_{PC}$ = 2.7 Hz, C$^{i'}$), 113.2 (C$^{c'}$), 112.3 (C^{c}), 104.1 (C$^{b'}$), 56.2 (C^{k}), 50.9 (C^{l}), 40.2 (d, $^{1}J_{PC}$ = 53.3 Hz, CH' of Cy'), 36.4 (d, $^{1}J_{PC}$ = 51.1 Hz, CH of Cy), 28.1 – 25.7 (m, CH$_2$ of Cy and Cy'), 21.3 (d, $^{2}J_{PC}$ = 6.2 Hz, C^{e}), 18.0 (d, $^{1}J_{PC}$ = 59.3 Hz, C^{f}). Pentane 34.7, 22.9, 14.4.

^{1}H ^{1}H COSY (500.03 MHz, 300 K, 273 K, dichloromethane-d$_2$): δ^{1}H / δ^{1}H: 6.97 / 6.75 (H^{i} / H^{h}), 6.85 / 6.59 (H$^{i'}$ / H$^{h'}$), 6.84 / 5.85, 5.73, 5.56 (H^{b}/ H^{c}, H$^{b'}$, H$^{c'}$), 6.75 / 6.97 (H^{h} / H^{i}), 6.59 / 6.85 (H$^{h'}$ / H$^{i'}$), 5.85 / 6.84, 5.73, 5.56 (H^{c}/ H^{b}, H$^{b'}$, H$^{c'}$), 5.73 / 6.84, 5.85, 5.56 (H$^{b'}$/ H^{b}, H^{c}, H$^{c'}$), 5.56

/ 6.84, 5.85, 5.73 (H$^{c'}$/ H^{b}, H^{c}, H$^{b'}$), 3.35-3.08 / 2.54-2.38 (H^{e} / H^{f}), 2.54-2.38 / 3.35-3.08 (H^{f} / H^{e}), 2.35-2.12 / 2.08 - 0.95 (CH of Cy / CH$_2$ of Cy), 2.08 - 0.95 / 2.35-2.12, 2.08 - 0.95 (CH' and CH$_2$ of Cy / CH of Cy, CH' and CH$_2$ of Cy).

^{1}H ^{13}C HMQC (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 6.97 / 115.2 (CH^{i}), 6.85 / 114.8 (CH$^{i'}$), 6.84 / 124.9 (CH^{b}), 6.75 / 129.2 (CH^{h}), 6.59 / 133.4 (CH$^{h'}$), 5.85 / 112.3 (CH^{c}), 5.75 / 116.2 (CH^{a}), 5.73 / 104.1 (CH$^{b'}$), 5.56 / 113.2 (CH$^{c'}$), 3.84 / 56.2 (CH$_3^{k}$), 3.35-3.08 / 21.3 (CH$_2^{e}$), 2.54-2.38 / 18.0 (CH$_2^{f}$), 2.35-2.12 / 36.4 (CH of Cy), 2.08 – 0.95 / 40.2, 28.1-25.7 (CH of Cy' and CH$_2$ of Cy and Cy'), 0.86 / 50.9 (CH$_3^{l}$).

^{1}H ^{13}C HMBC (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$): δ^{1}H / δ^{13}C: 6.97 / 140.8, 114.8 (CH^{i} / C^{g}, CH$^{i'}$), 6.85 / 140.8, 115.2 (CH$^{i'}$ / C^{g}, CH^{i}), 6.84 / 112.3, 104.1 (CH^{b}/ CH^{c}, CH$^{b'}$), 6.75 / 158.7, 133.4 (CH^{h} / C^{j}, CH$^{h'}$), 6.59 / 158.7, 129.2 (CH$^{h'}$ / C^{j}, CH^{h}), 5.85 / 126.6 (CH^{c} / C^{d}), 5.75 / 116.2 (CH^{a} / CH^{a}), 5.73 / 126.6, 124.9 (CH$^{b'}$ / C^{d}, CH^{b}), 5.56 / 126.6, 104.1 (CH$^{c'}$ / C^{d}, CH$^{b'}$), 3.84 / 158.7 (CH$_3^{k}$ / C^{j}), 3.35-3.08 / 126.6, 124.9, 104.1, 18.8 (CH$_2^{e}$ / C^{d}, CH^{b}, CH$^{b'}$,CH$_2^{f}$), 2.54-2.38 / 126.6, 21.3 (CH$_2^{f}$ / C^{d}, CH$_2^{e}$), 2.35-2.12, 2.08 - 0.95 / 28.1 – 25.7 (CH and CH$_2$ of Cy and Cy'), 0.86 / 124.9 (CH$_3^{l}$ / CH^{b}).

^{31}P{^{1}H} NMR (202.41 MHz, 300 K, dichloromethane-d$_2$): δ^{31}P: 48.3 ($\nu_{1/2.}$ = 60.3 Hz).

^{31}P NMR (202.41 MHz, 300 K, dichloromethane-d$_2$): δ^{31}P: br 48.3 ($\nu_{1/2}$ = 3.3 Hz).

^{11}B{^{1}H} NMR (160.43 MHz, 300 K, dichloromethane-d$_2$): δ^{11}B: -16.6 ($\nu_{1/2}$ = 22 Hz).

^{11}B NMR (160.43 MHz, 300 K, dichloromethane-d$_2$): δ^{11}B: -16.6 ($\nu_{1/2}$ = 22 Hz).

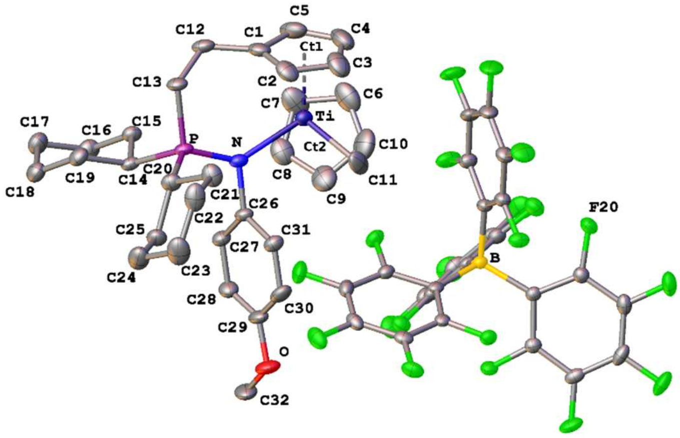
^{19}F{^{1}H} NMR (470.45 MHz, 300 K, dichloromethane-d$_2$): δ^{19}F: -133.1 (apparent d, $^3J_{FF}$ = 19 Hz, 8F, *o*-F), -163.6 (t, $^3J_{FF}$ = 19 Hz, 4F, *p*-F), -167.5 (apparent t, $^3J_{FF}$ = 19 Hz, 8F, *m*-F).

^{19}F NMR (470.45 MHz, 273 K, dichloromethane-d$_2$): δ^{19}F: -133.1 (br d, $^3J_{FF}$ = 19 Hz, 8F, *o*-F), -163.6 (t, $^3J_{FF}$ = 19 Hz, 4F, *p*-F), -167.5 (br t, $^3J_{FF}$ = 19 Hz, 8F, *m*-F).

HRMS (Positive mode ESI, dichloromethane): m/z calcd. For: $C_{32}H_{45}ONPTi$ [M]$^+$ 538.27128, found 538.27059 (Rel. ab: 60%, -1.3 ppm); $C_{31}H_{42}ONPTi$ [M-CH$_3$]$^+$ 523.24780, found 523.24775 (Rel. ab: 100%, -0.1ppm); $C_{26}H_{39}NOP$ [M-ArNH$_2$-H$_2$O]$^+$ 412.27638, 412.27644 ppm (Rel. ab: 30%, 0.2 ppm).

Elemental Analysis: % calcd for $C_{56}H_{45}BF_{20}NOPTi$: C, 55.24; H, 3.73; N, 1.15; found: C, 55.04; H, 3.30; N, 1.10.

XRD:



Compound	**q300317_0m_a**
Formula	$C_{56}H_{45}BF_{20}NOPTi$
$D_{calc.}$/ g cm^{-3}	1.447
μ/mm^{-1}	0.288
Formula Weight	1217.61
Colour	orange
Shape	block
Size/mm^3	0.37×0.25×0.25
T/K	115
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	12.069(2)
b/Å	16.790(3)
c/Å	28.184(5)
α/°	90
β/°	101.793(3)
γ/°	90
V/Å^3	5590.9(18)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	2.114
Θ_{max}/°	27.623
Measured Refl.	68733
Independent Refl.	12917
Reflections Used	10244
R_{int}	0.0300
Parameters	732
Restraints	0
Largest Peak	0.979
Deepest Hole	-0.681
GooF	1.030
wR_2 (all data)	0.1396
wR_2	0.1296
R_1 (all data)	0.0645
R_1	0.0493

Experimental. Single orange block-shaped crystals of (**q300317_0m_a**) were obtained by recrystallisation by diffusion of pentane to a dichloromethane solution at -15°C. A suitable crystal (0.37×0.25×0.25) mm^3 was selected and mounted on a mylar loop with oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 115 K during data collection. Using **Olex2** (Dolomanov et al., 2009), the structure was solved with the **ShelXT** (Sheldrick, 2015) structure solution program, using the Intrinsic Phasing solution method. The model was refined with version 2017/1 of **XL** (Sheldrick, 2008) using Least Squares minimisation.

Crystal Data. $C_{56}H_{45}BF_{20}NOPTi$, M_r = 1217.61, monoclinic, $P2_1/c$ (No. 14), a = 12.069(2) Å, b = 16.790(3) Å, c = 28.184(5) Å, β = 101.793(3)°, $\alpha = \gamma$ = 90°, V = 5590.9(18) Å^3, T = 115 K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.288, 68733 reflections measured, 12917 unique (R_{int} = 0.0300) which were used in all calculations. The final wR_2 was 0.1396 (all data) and R_1 was 0.0493 (I > 2(I)).

General conclusion

In summary, the present manuscript deals with several new aspects of nitrogen-functionalized titanocene chemistry. Firstly, it describes a new procedure for the synthesis of (aminomethyl)cyclopentadienylides via a benzotriazole route. The five new synthesized ligands have been coordinated to titanium or zirconium, forming N-functionalized dichlorotitanocenes or dichlororzirconocenes in moderate to good yields, and in satisfactory purity for the formers, but in moderate purity for the latters. The (aminomethyl)titanocenes have been further derivatized with various X-Ligand (OAr, Me, OTf). Secondly, various procedures for the generation of cationic (aminomethyl)titanocenes have been attempted. In particular, methide abstraction from dimethyl titanocene complexes led to unexpected rearrangements of the amine moiety via CH activation, leading to the discovery of i) a cationic amidotitanocene (**36** and **41**), and ii) an unprecedented iminium carbene titanocene (**43**). The mechanism of the first reactions was not investigated, considering that it is reminiscent of Hofmann degradation. The formation of the titanium carbene species has been investigated in details and it appears that the mechanism of this reaction is quite complex. The evidence gathered so far, suggests an autocatalytic process (potentially accompanied by side reactions), in which the methide abstractor is induced in more than one step. In light of these results, amines are not the best choice for FLP chemistry since the literature is rife with similar cases of CH activation reactions of amine compounds.

The third part of this thesis develops a straightforward synthesis of cationic phosphido-phosphine and amido-titanocenes. The latter show very good activity in the catalytic hydrogenation of various unsaturated substrates such as styrene, 3,3-dimethylbut-1-ene and diphenylacetylene. Nevertheless, the catalysts are poorly active towards electron-deficient substrates such as perfluorostyrene, and they do not seem to tolerate N-containing substrates such as imines. It would be interesting to investigate the selectivity of these catalysts on prochiral substrates, in order to develop an asymmetric hydrogenation. One could further develop this family of catalyst by modifying the steric and electronic properties of the metallocenic fragment.

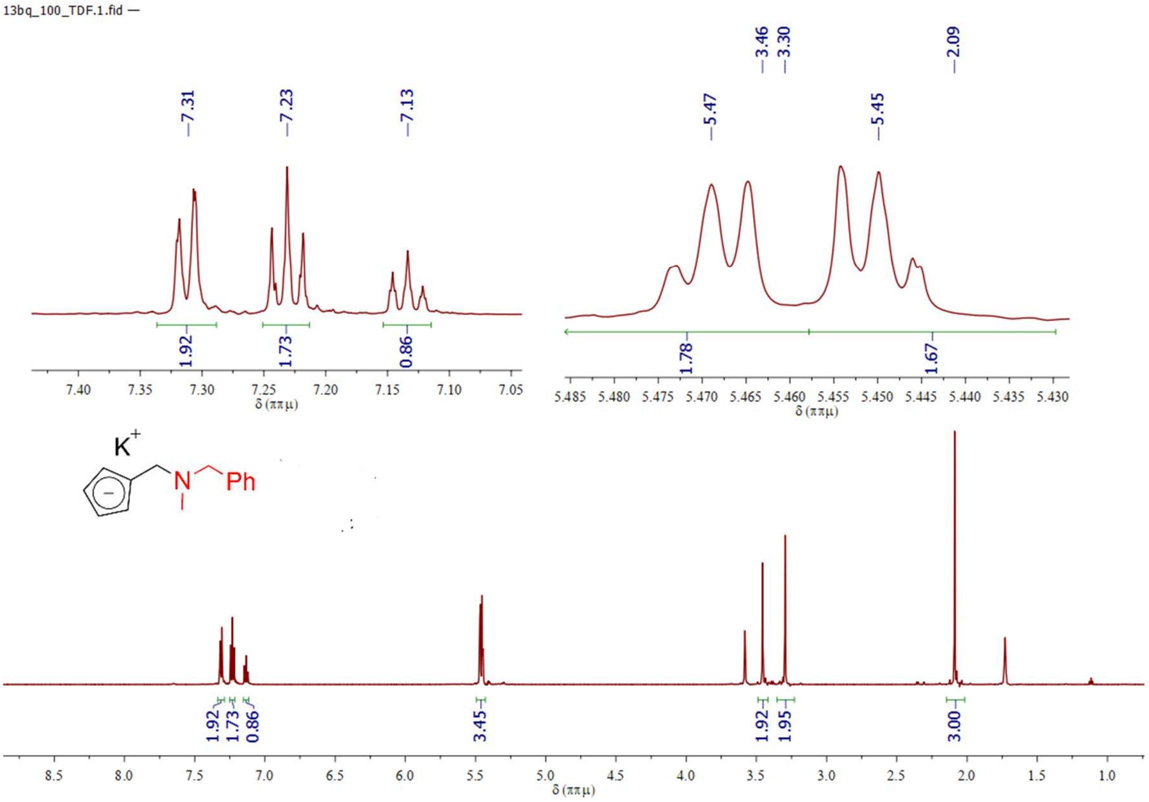
In parallel to this work, an alternative synthesis of titanocenyl iminophosphoranes (**57-60**) has been further explored, following preliminary results obtained by Dr. Monnereau in the laboratory of Pr. Pierre Le Gendre. After methylation of dichloro titanocene precursors, methide abstraction yields **64** and **65**, two titanocenyl iminophosphoniums presenting a very strong Ti-N bond, the nature of which has been studied theoretically; further investigations are currently underway.

In this study of OmFLPs based on N/Ti$^+$ combinations, none of the obtained cationic complexes showed FLP reactivity. Nevertheless, some new aspects of the organometallic chemistry of titanium have been discovered along the way. Frustrated Lewis pairs are not always an achievable goal, but in the case of this thesis, they were just as a good starting point as any.

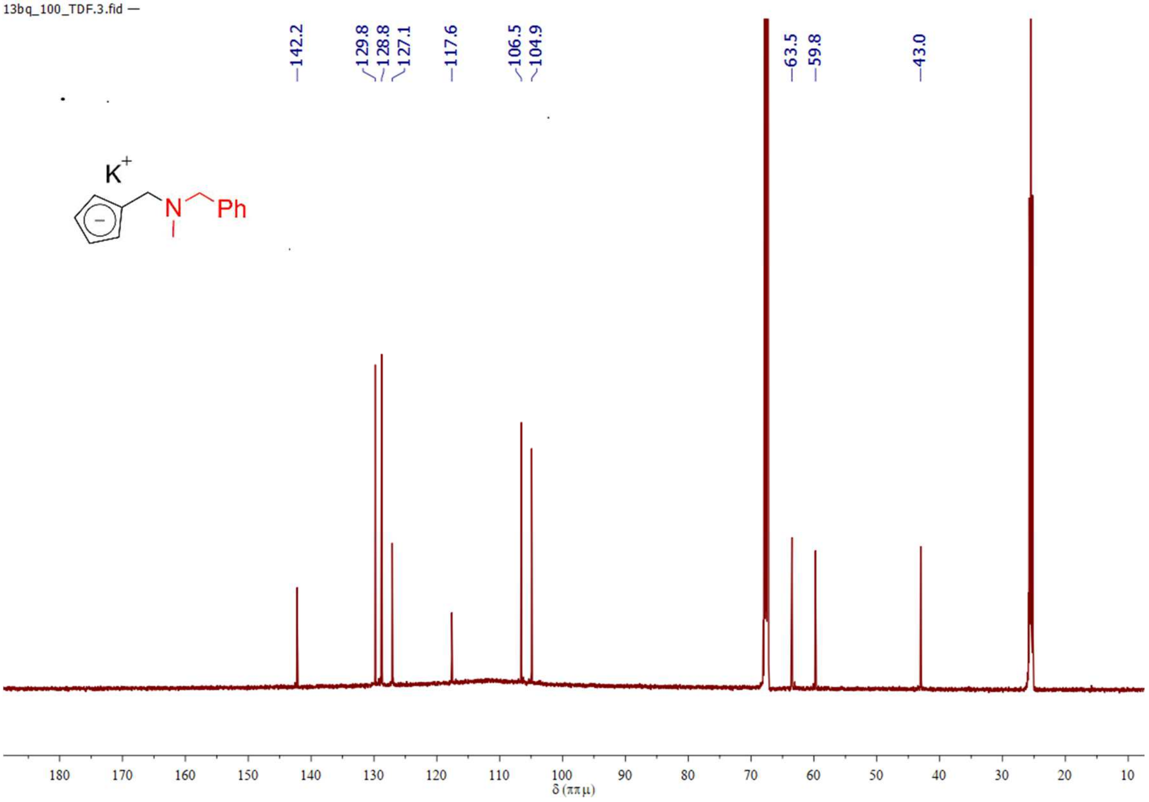
Appendix

A. Appendix Chapter II

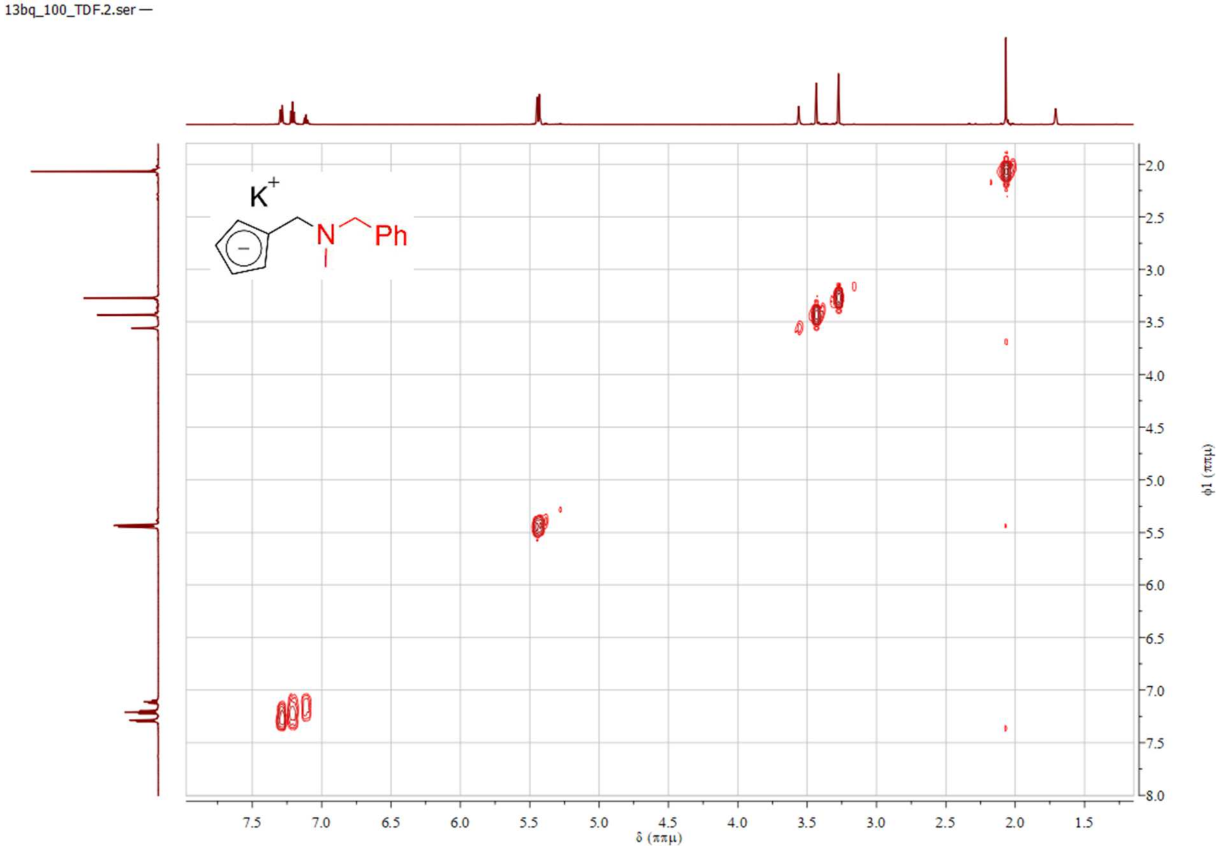
1. Coupound **1-K**:



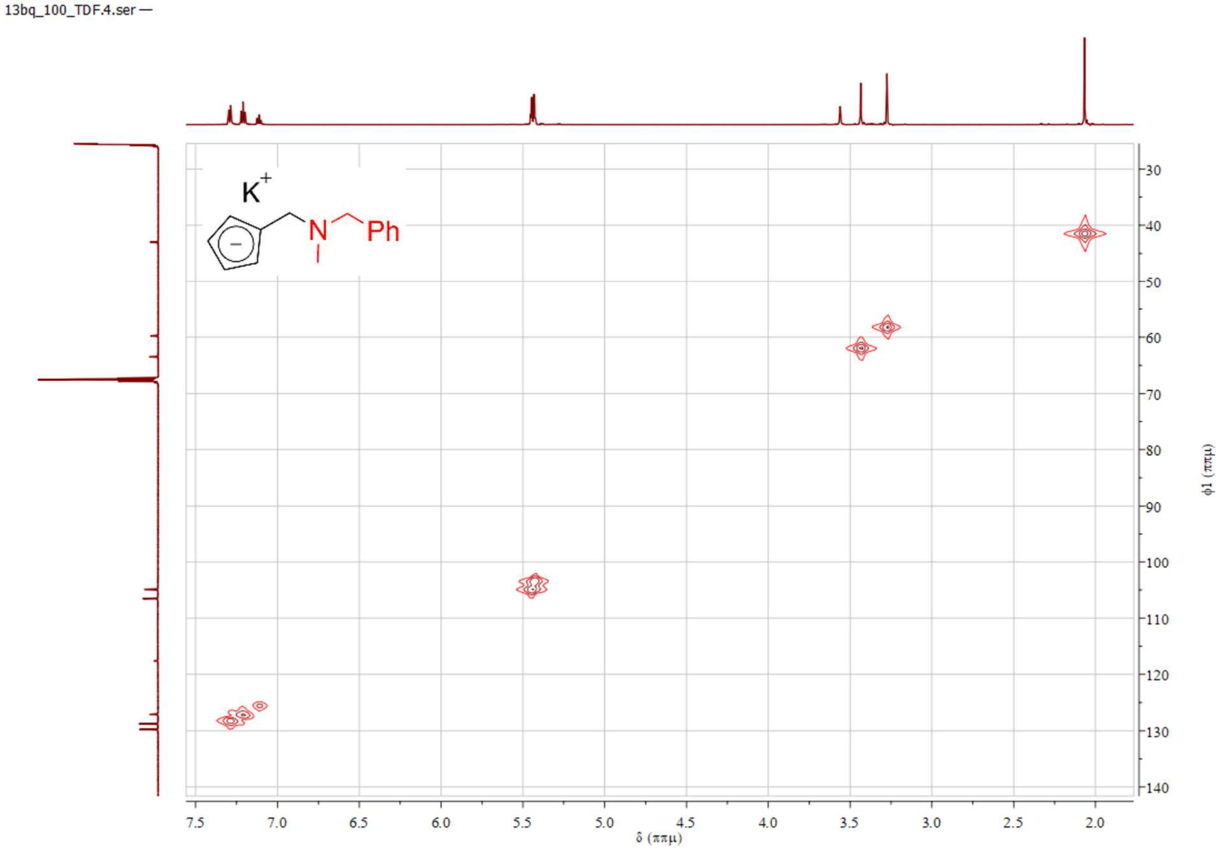
Spectrum 0-1: ^{1}H NMR of 1-K (600.23 MHz, 300K, tetrahydrofuran-d_8)



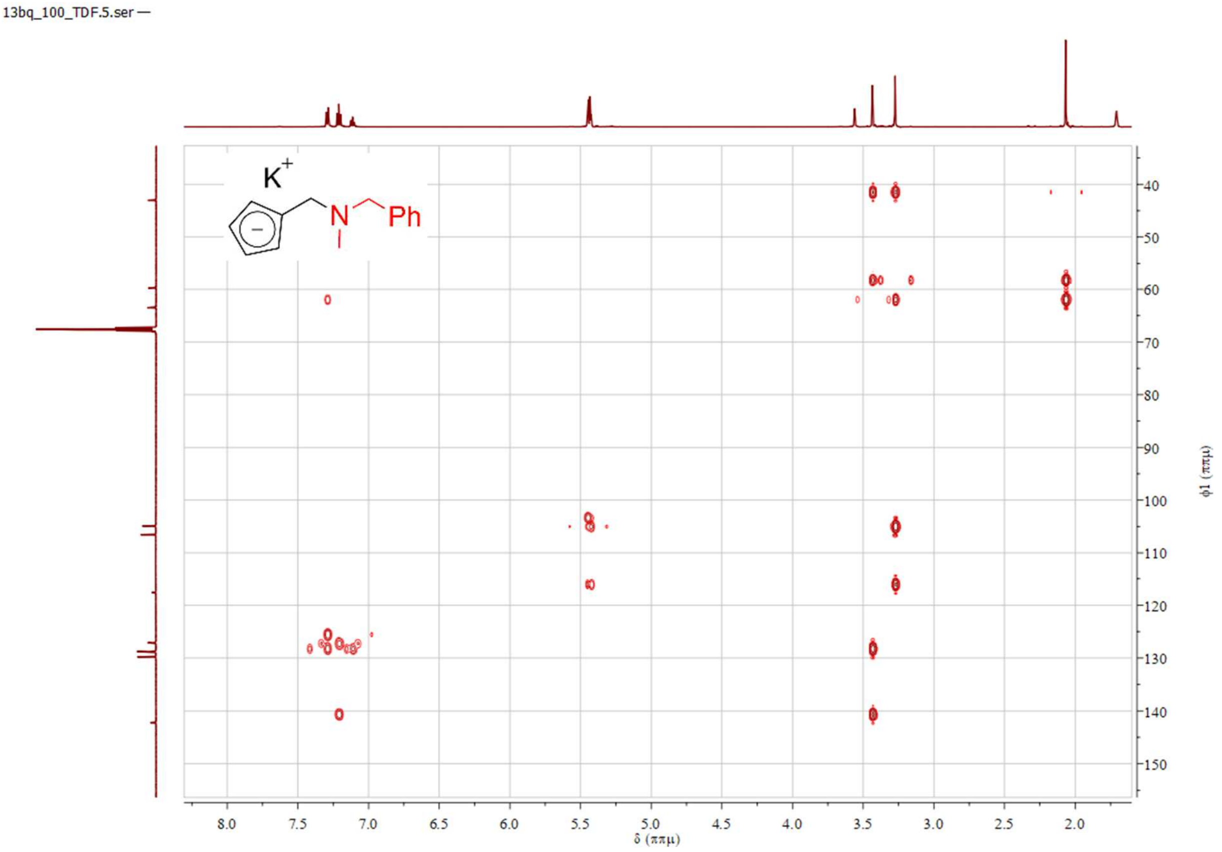
Spectrum 0-2: $^{13}C\{^1H\}$ NMR of 1-K (150.94 MHz, 300 K, tetrahydrofuran-d_8)



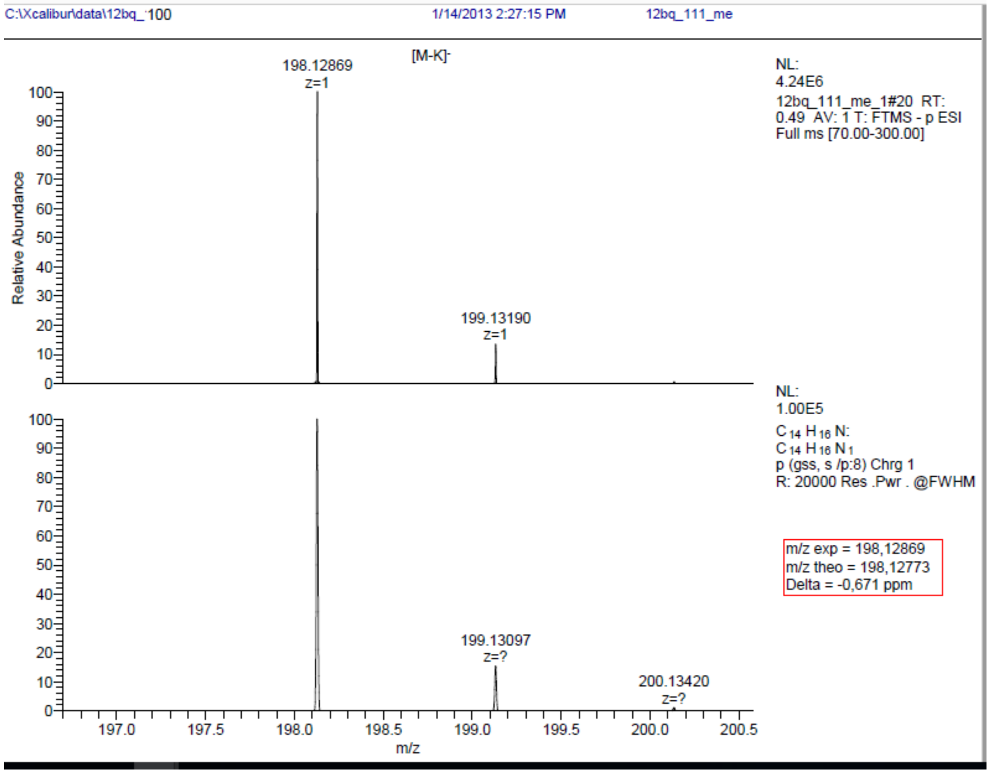
Spectrum 0-3: ^1H ^1H COSY of 1-K (600.23 MHz, 300 K, tetrahydrofuran-d_8)



Spectrum 0-4: ^1H ^{13}C HMQC of 1-K (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d_8)

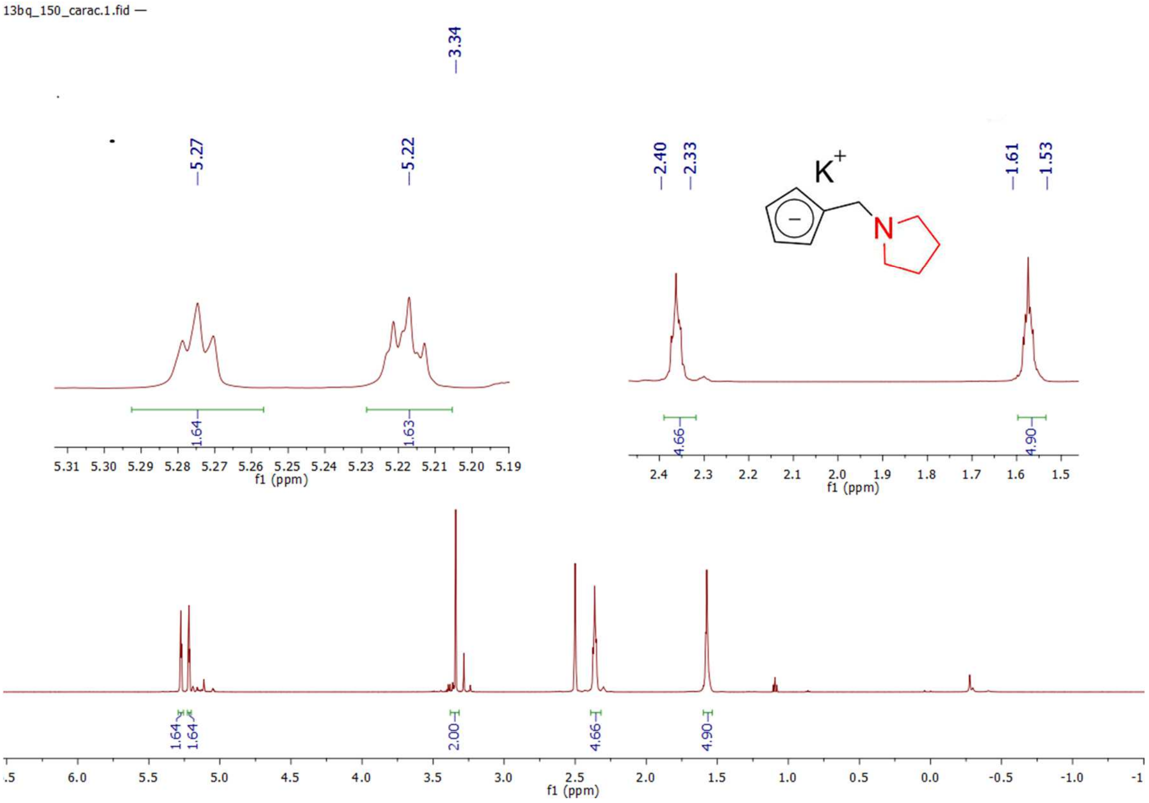


Spectrum 0-5: ^{1}H ^{13}C HMBC of 1-K (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d$_8$)

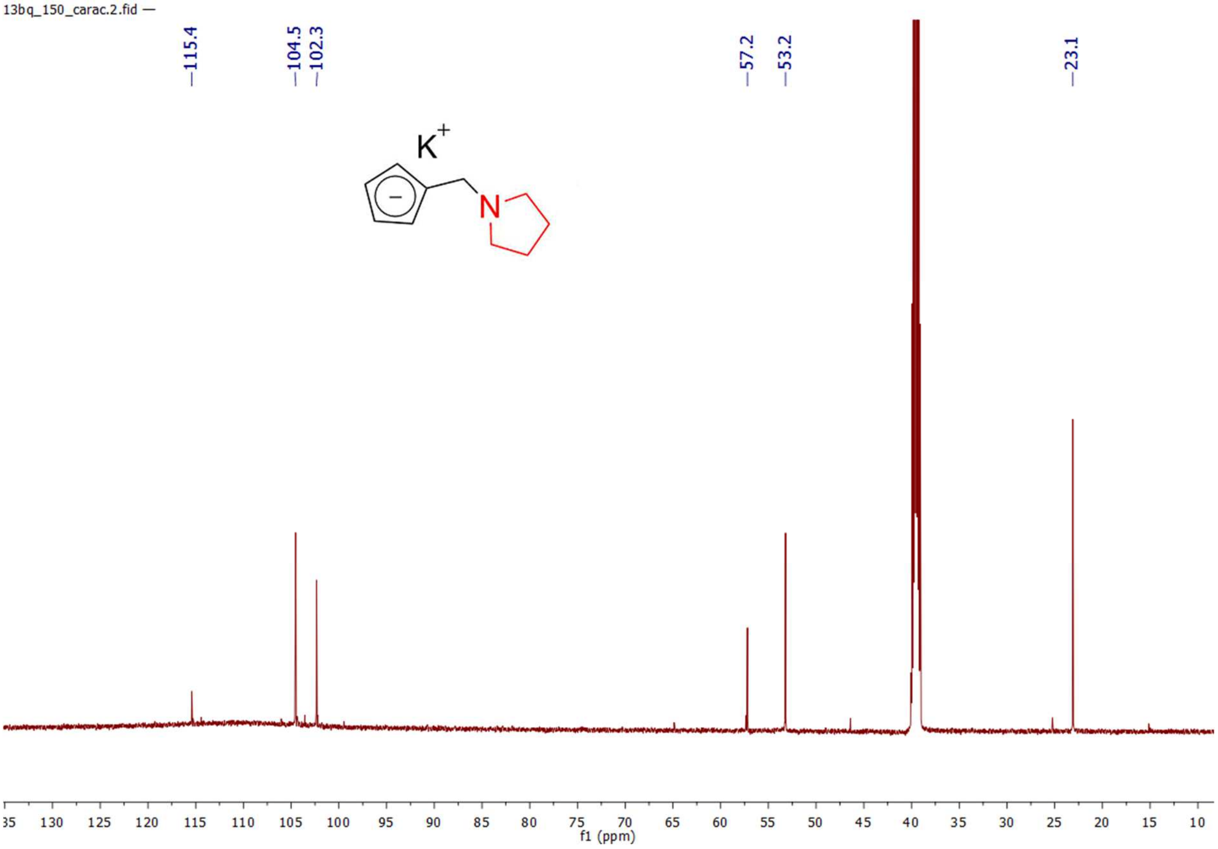


Spectrum 0-6: HRMS of 1-K (Negative mode ESI, dimethylsulfoxide)

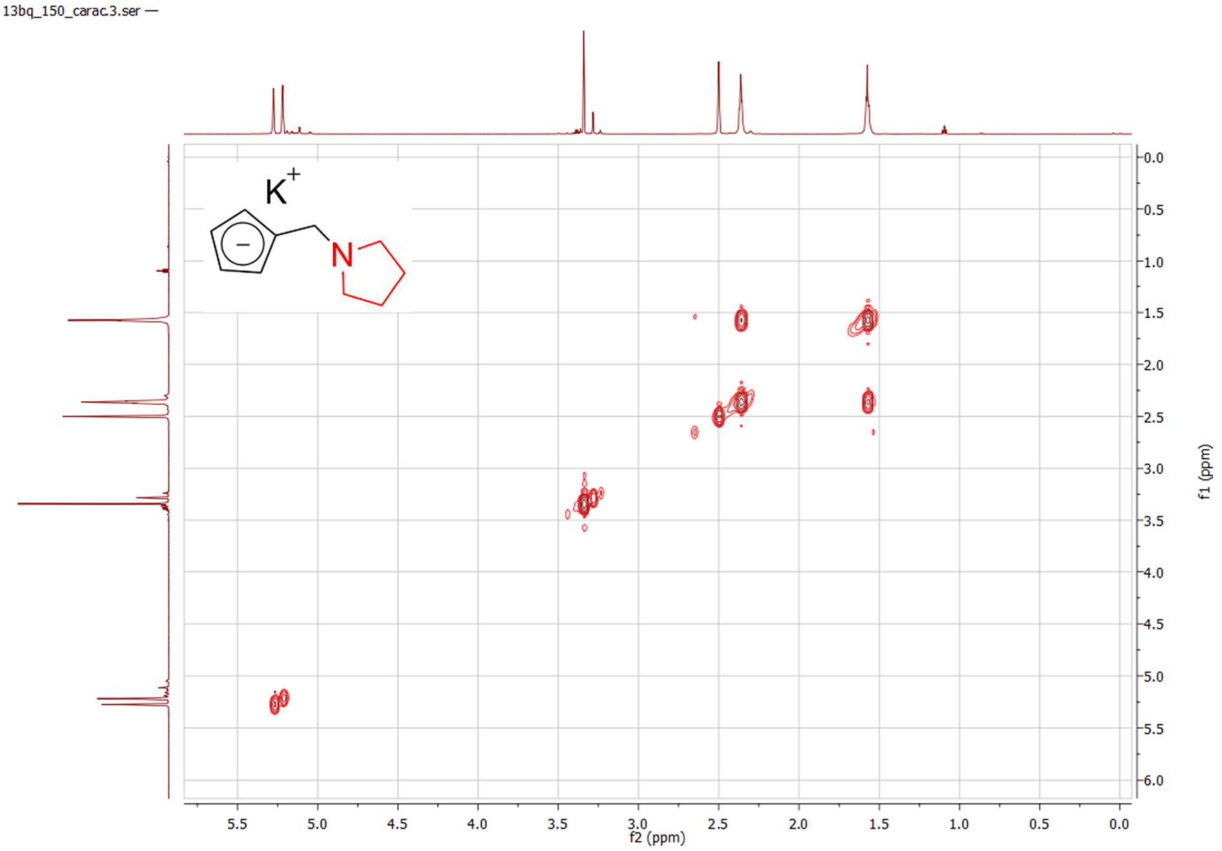
2. Compound **2-K**:



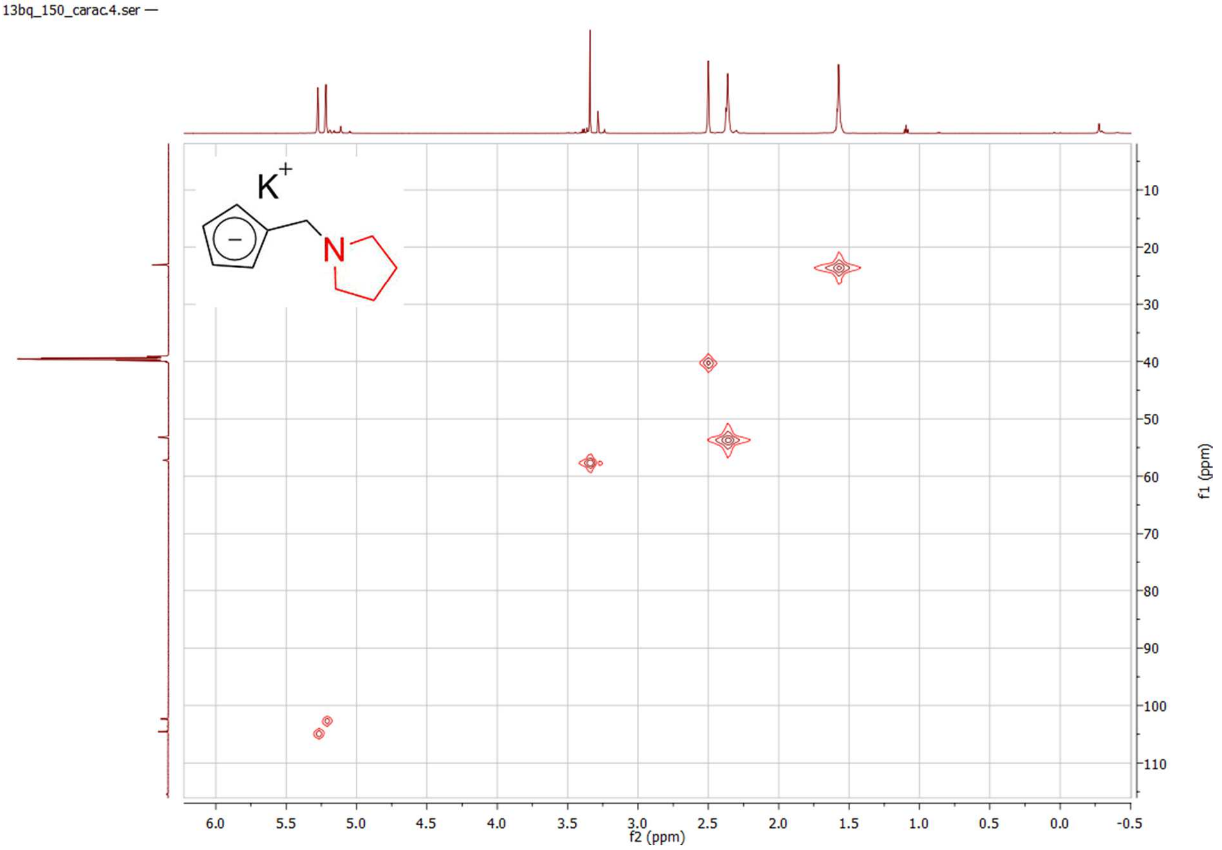
Spectrum 0-7: ^{1}H NMR of 2-K (600.23 MHz, 300 K, dimethylsulfoxide-d$_{6}$)



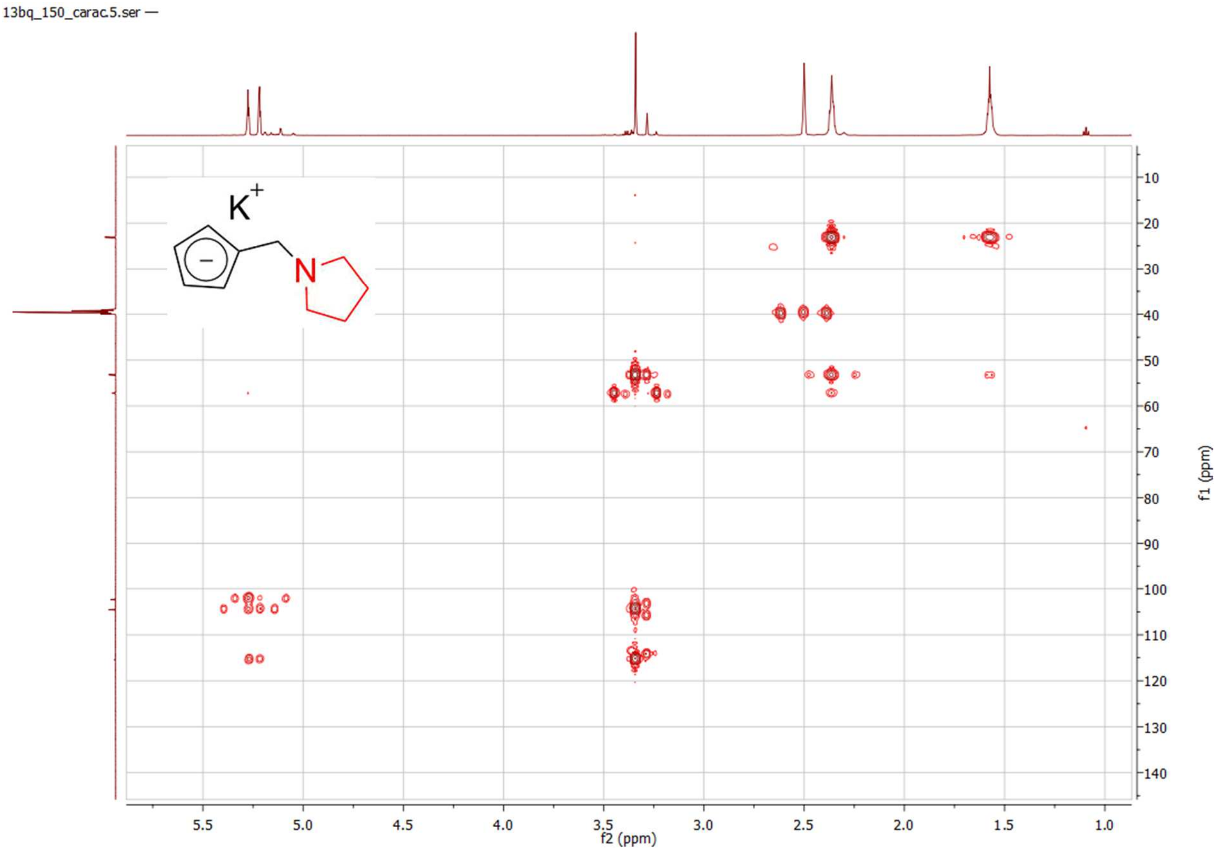
Spectrum 0-8: ^{13}C{^{1}H} NMR of 2-K (150.94 MHz, 300 K, dimethylsulfoxide-d$_{6}$)



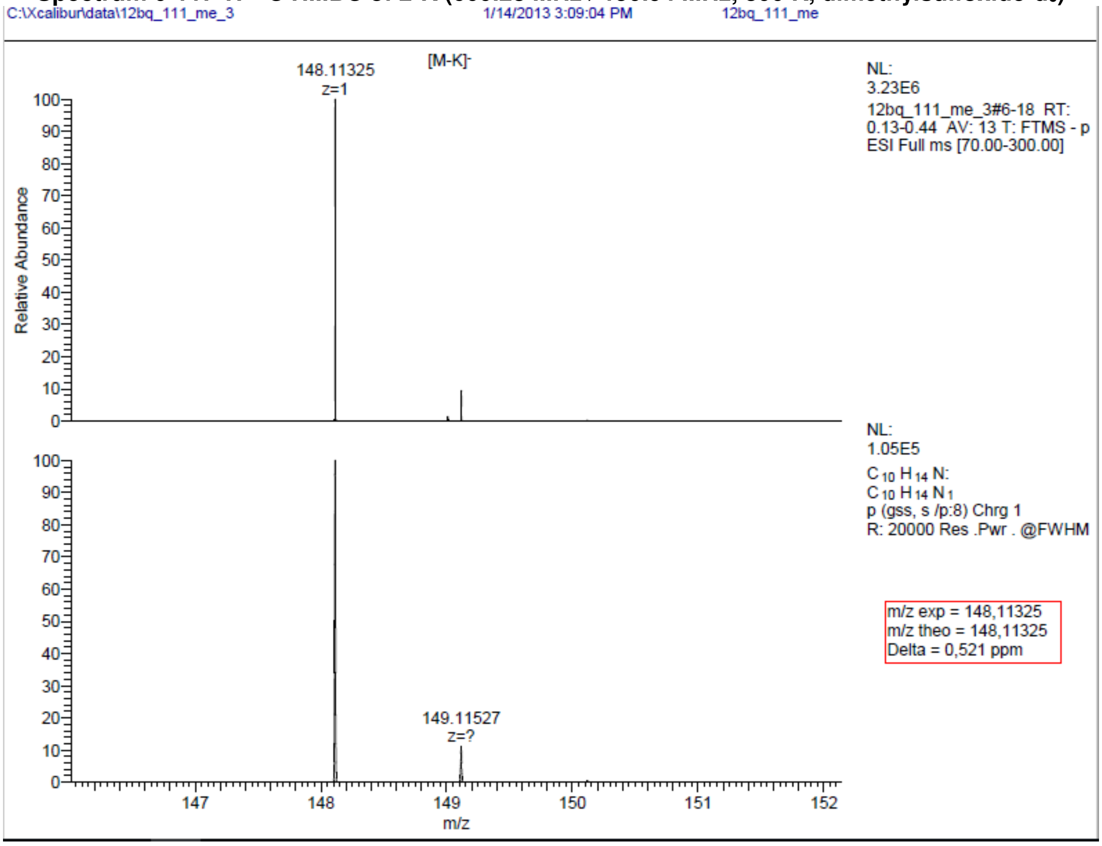
Spectrum 0-9: ^{1}H ^{1}H COSY of 2-K (600.23 MHz, 300 K, dimethylsulfoxide-d$_6$)



Spectrum 0-10: ^{1}H ^{13}C HMQC of 2-K (600.23 MHz / 150.94 MHz, 300 K, dimethylsulfoxide-d$_6$)

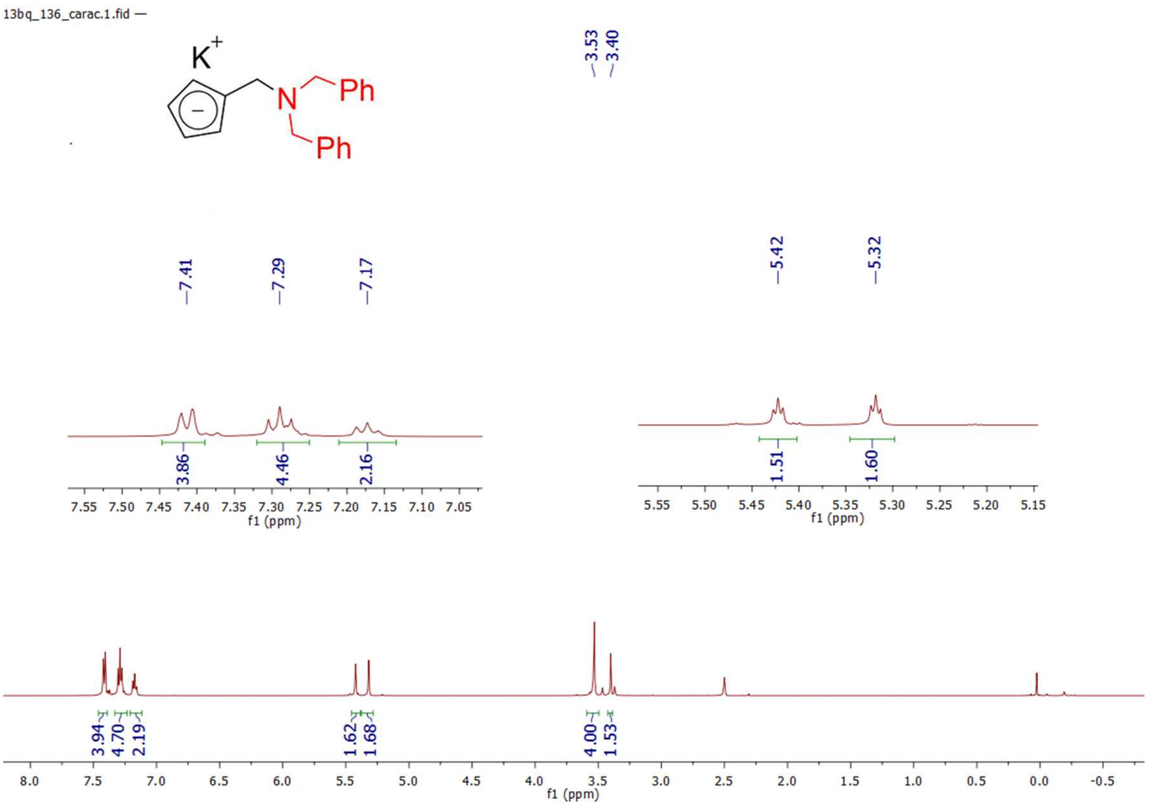


Spectrum 0-11: ^{1}H ^{13}C HMBC of 2-K (600.23 MHz / 150.94 MHz, 300 K, dimethylsulfoxide-d$_6$)

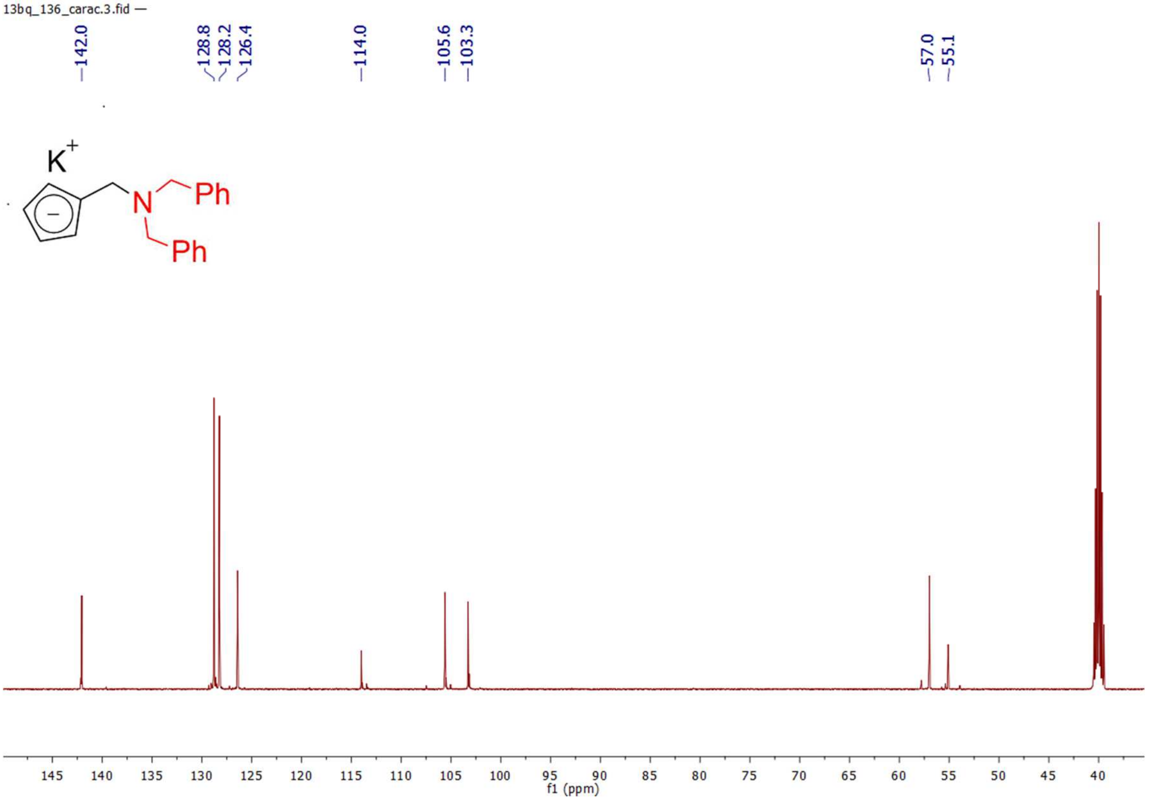


Spectrum 0-12: HRMS of 2-K (Negative mode ESI, dimethylsulfoxide)

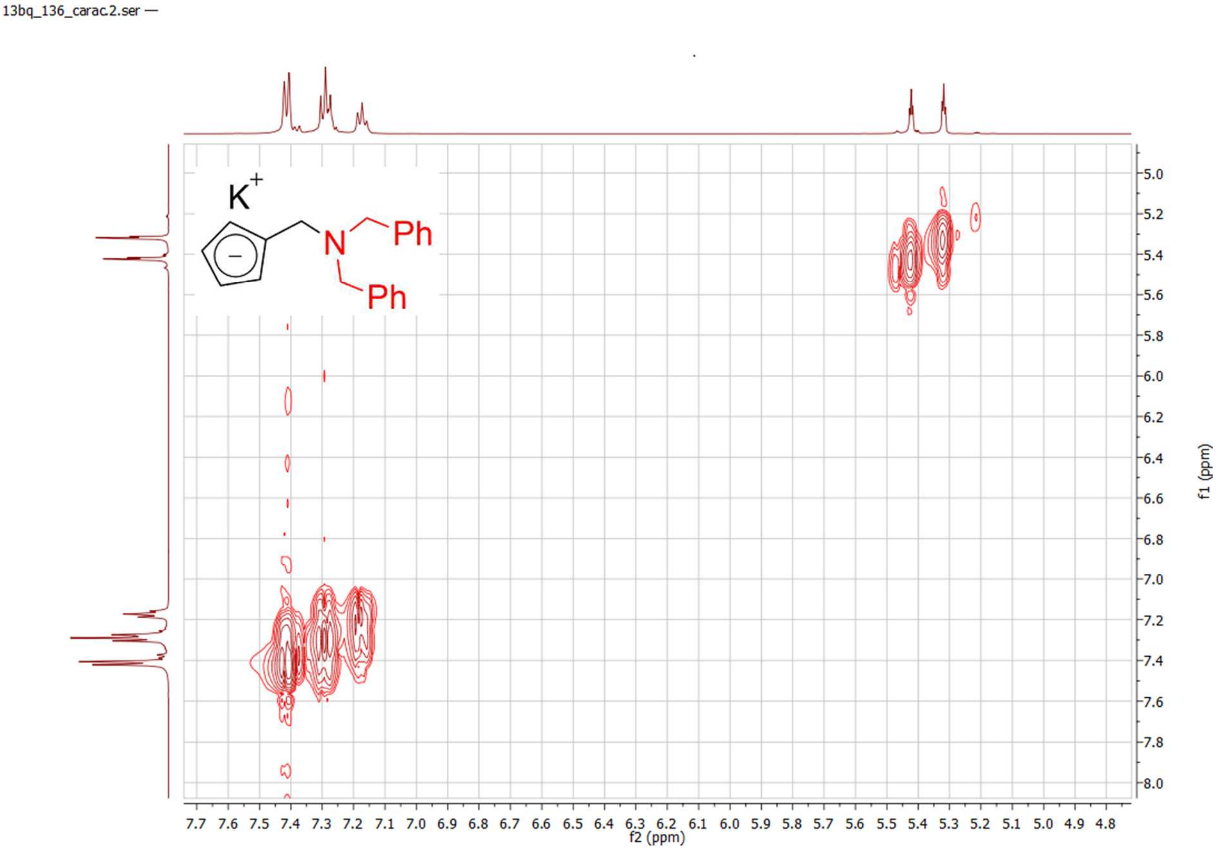
3. Compound **3-K:**



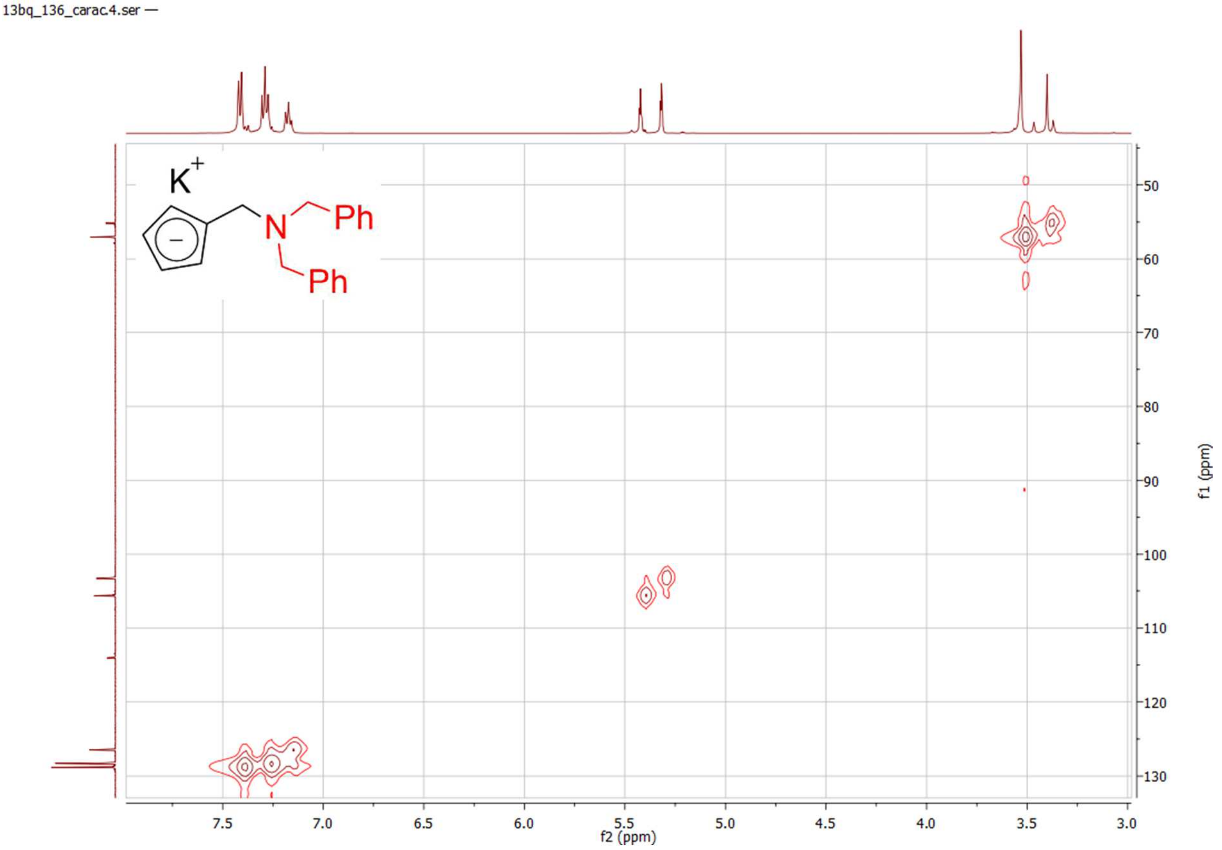
Spectrum 0-13: ^{1}H NMR of 3-K (500.03 MHz, 300 K, dimethylsulfoxide-d_6)



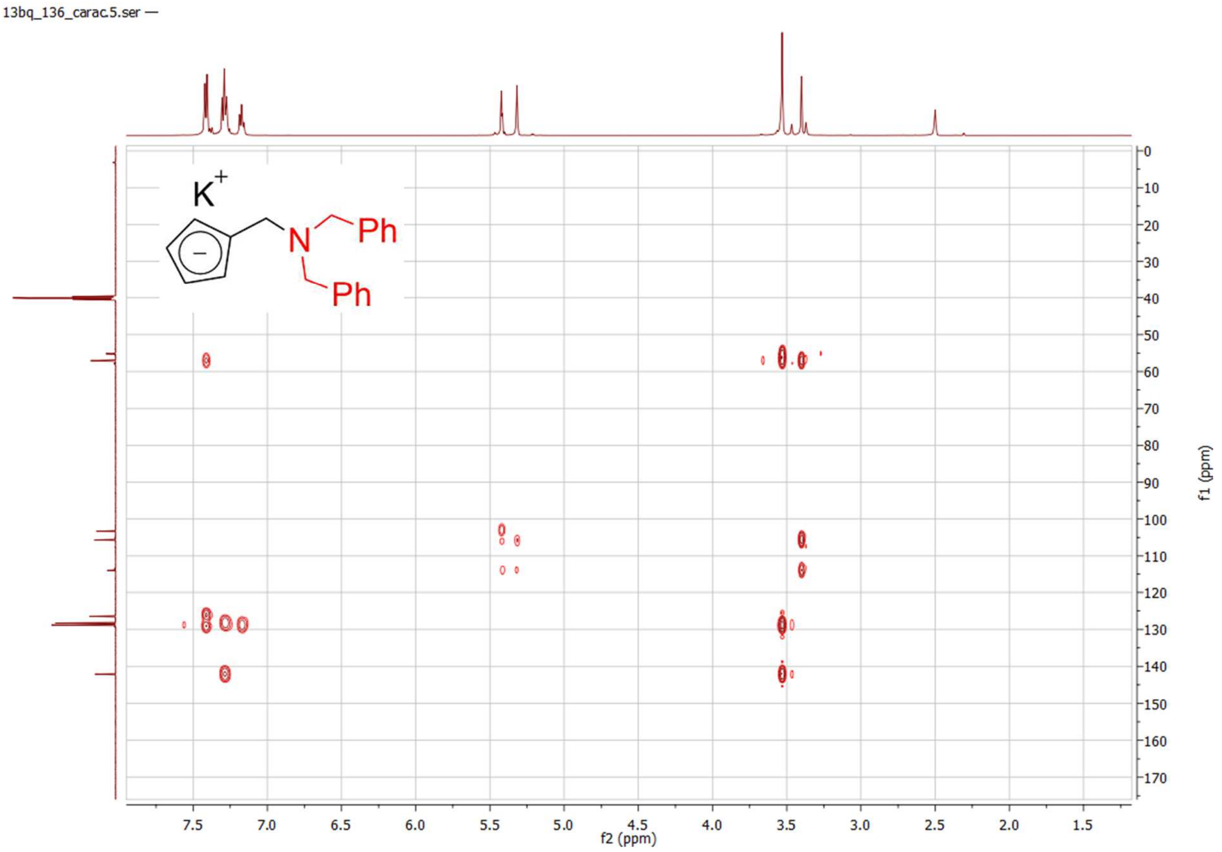
Spectrum 0-14: ^{13}C{^{1}H} NMR of 3-K (125.77 MHz, 300 K dimethylsulfoxide-d_6)



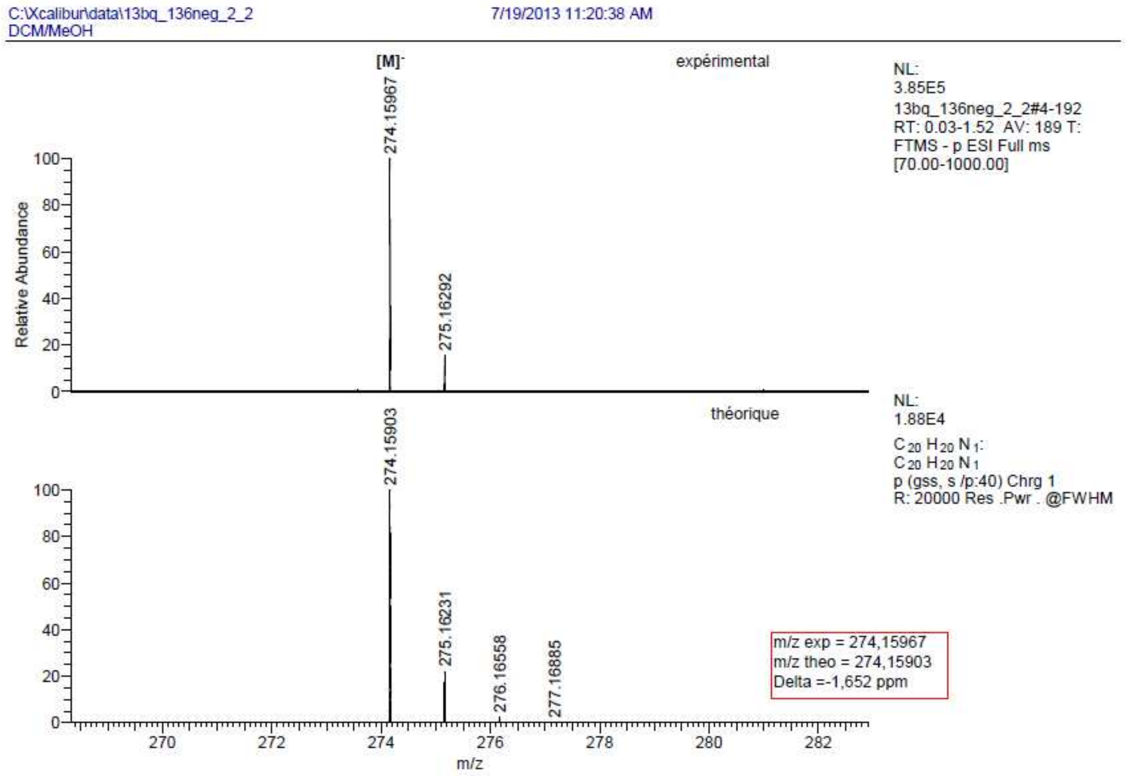
Spectrum 0-15: ^{1}H ^{1}H COSY of 3-K (500.03 MHz, 300 K, dimethylsulfoxide-d$_6$)



Spectrum 0-16: ^{1}H ^{13}C HMQC of 3-K (500.03 MHz / 125.77 MHz, 300 K, dimethylsulfoxide-d$_6$)

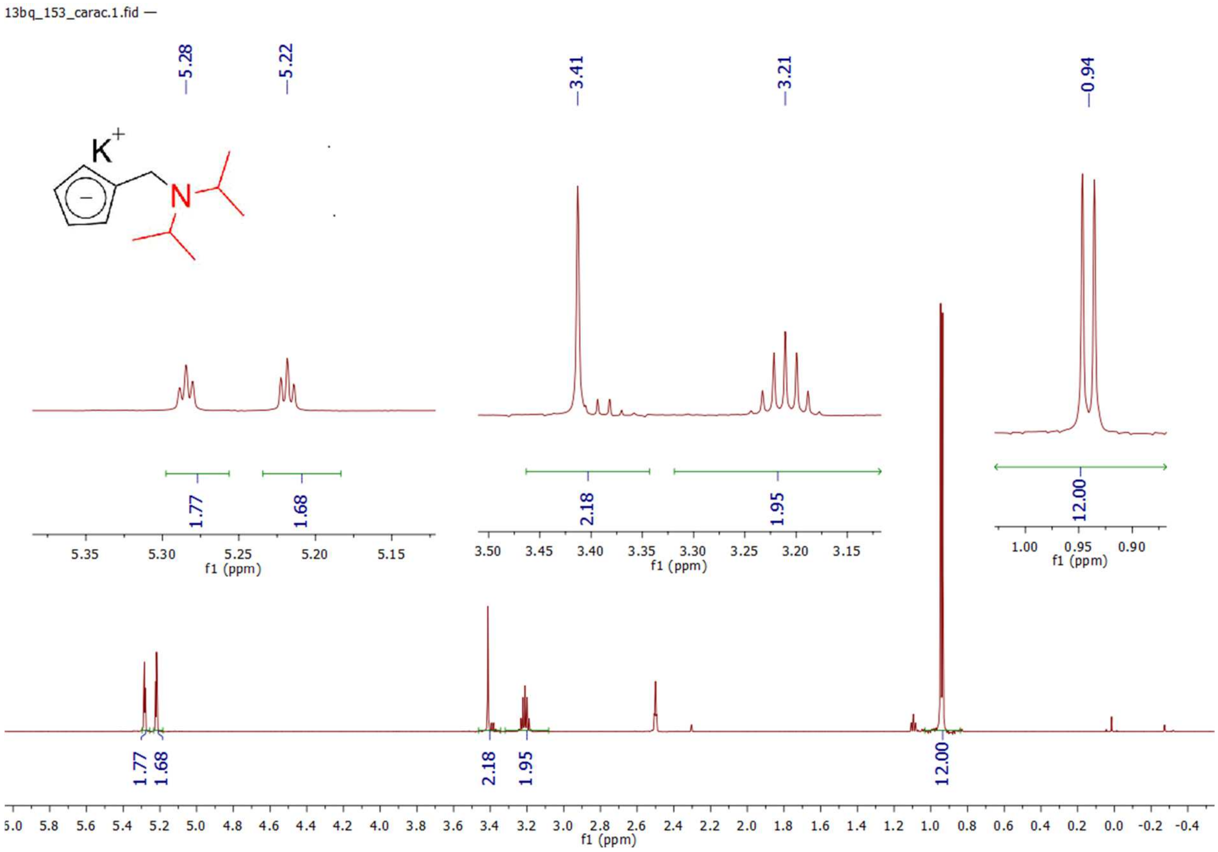


Spectrum 0-17: ^{1}H ^{13}C HMBC of 3-K (500.03 MHz / 125.77 MHz, 300 K, dimethylsulfoxide-d$_6$

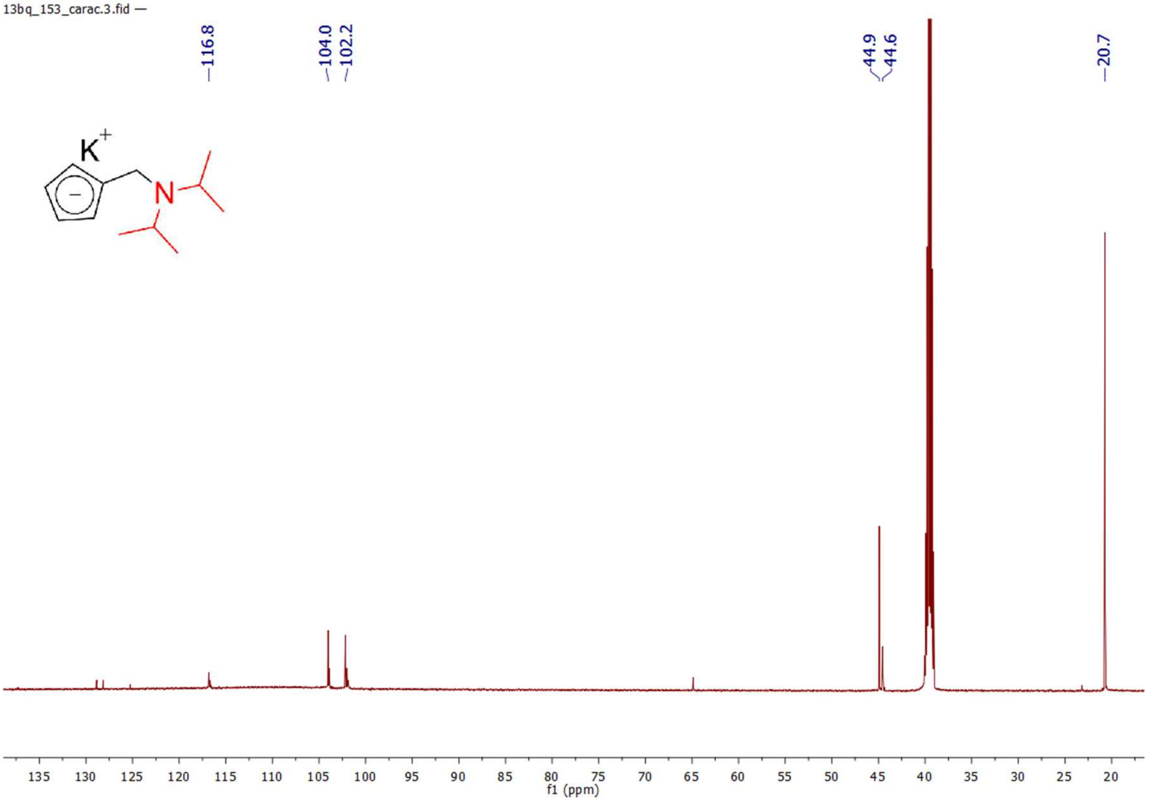


Spectrum 0-18: HRMS of 3-K (Negative mode ESI, dimethylsulfoxide)

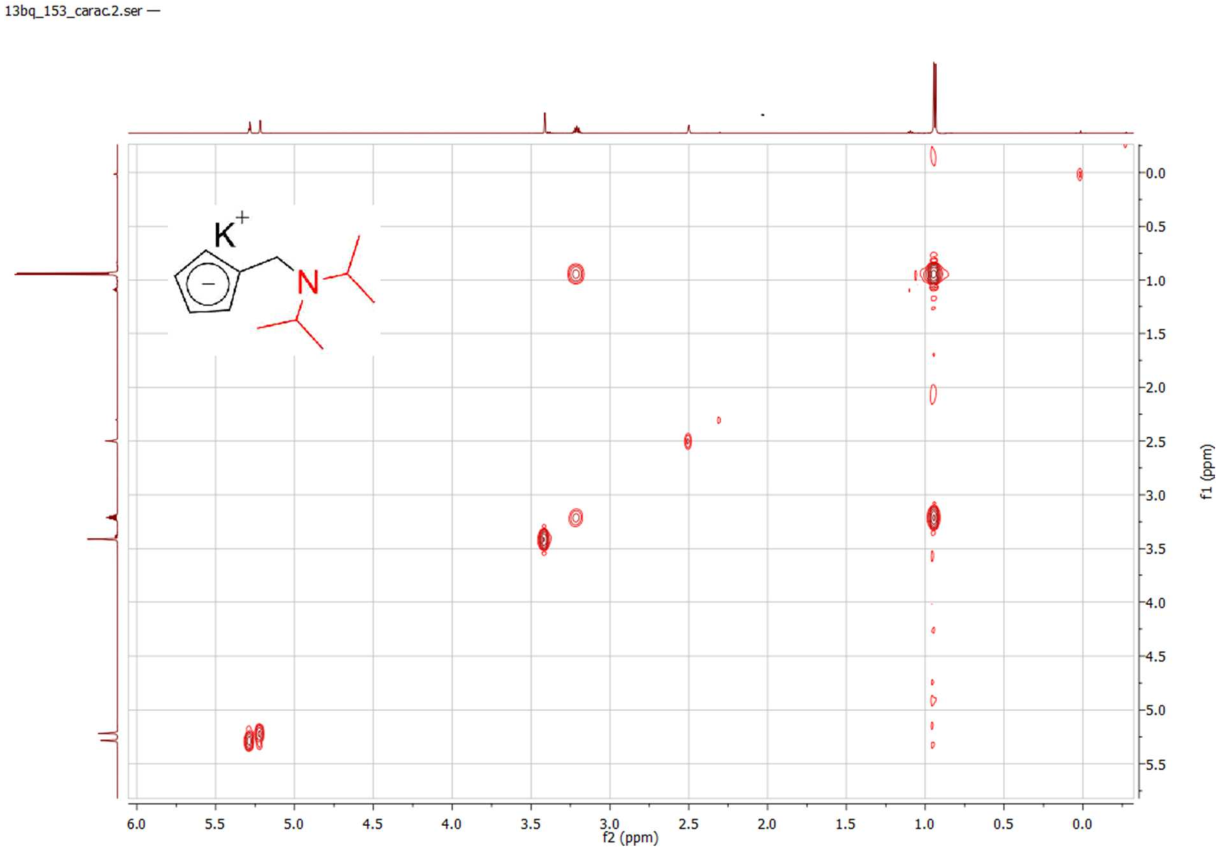
4. Compound **4-K**:



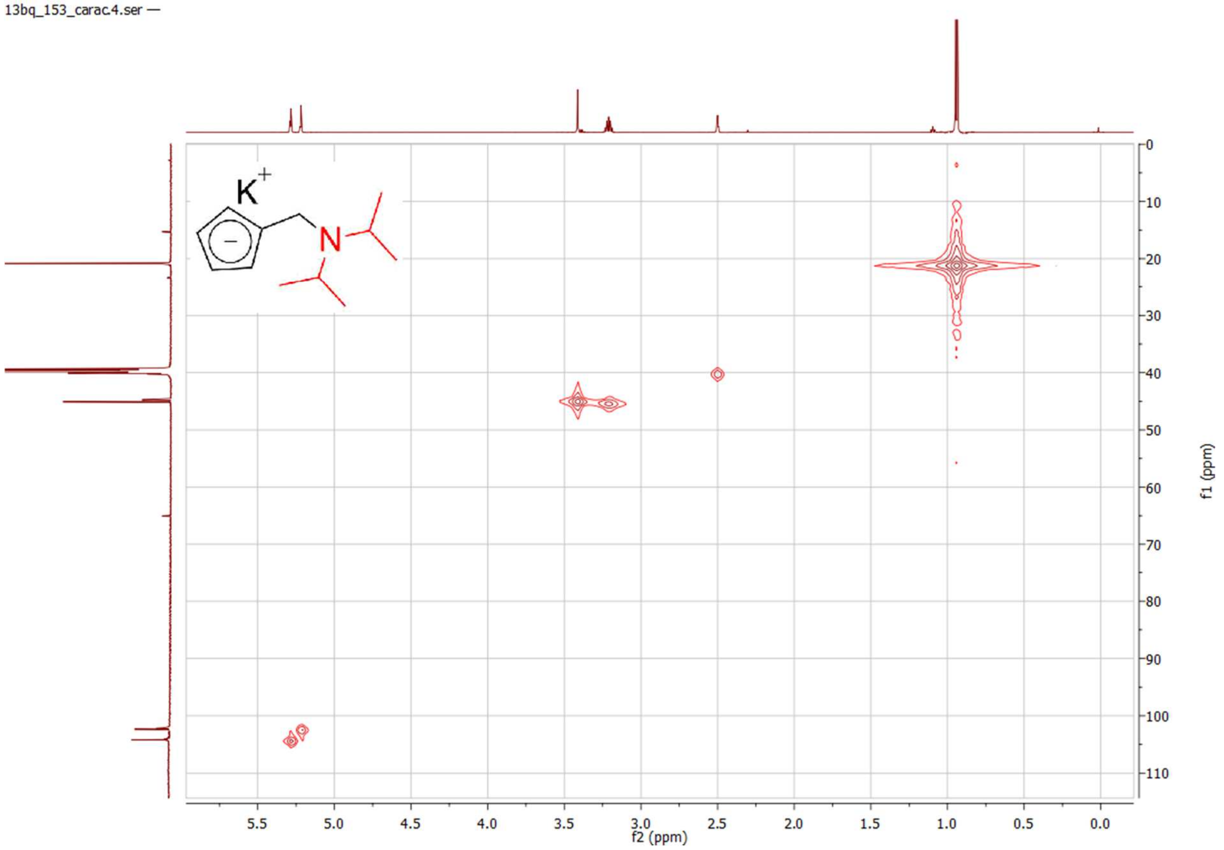
Spectrum 0-19: ^{1}H NMR of 4-K (600.23 MHz, 300 K, dimethylsulfoxyde-d$_6$)



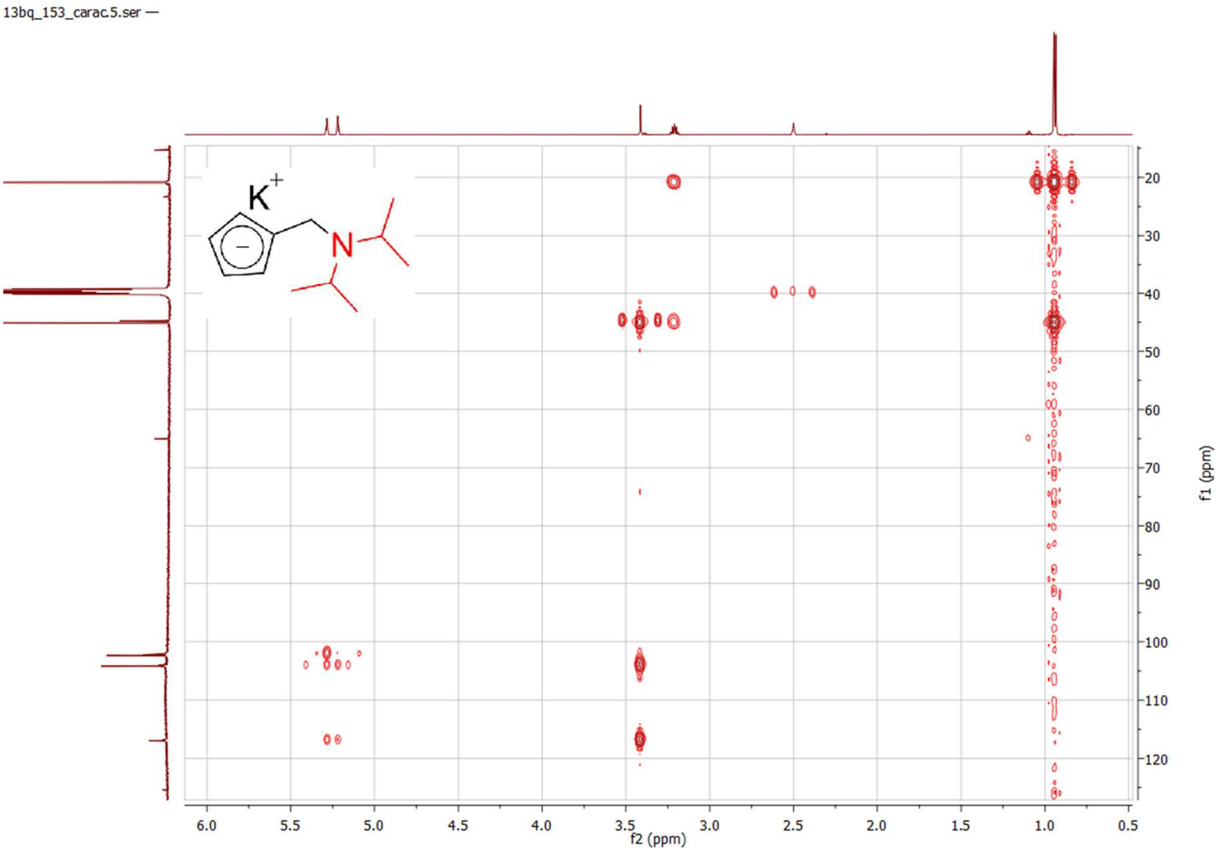
Spectrum 0-20: ^{13}C{^{1}H} NMR of 4-K (150.94 MHz, 300 K, dimethylsulfoxyde-d$_6$)



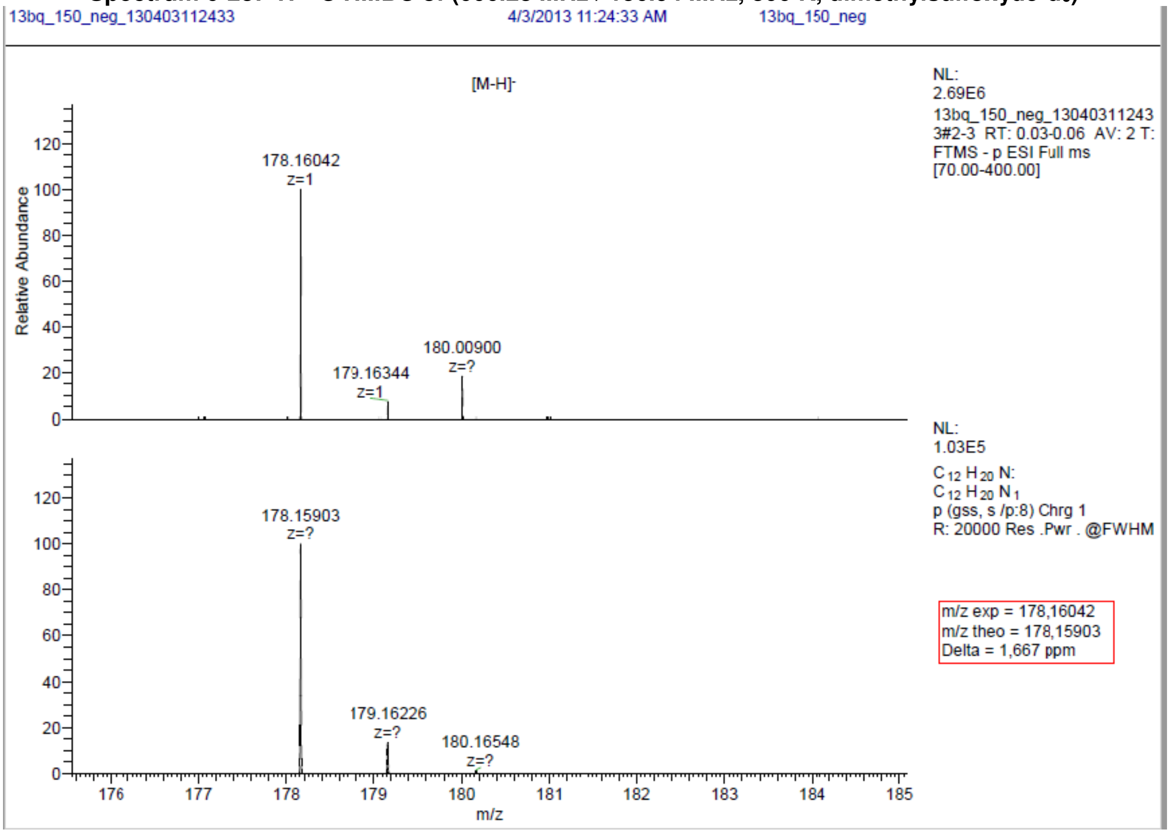
Spectrum 0-21: ^{1}H ^{1}H COSY of 4-K (600.23 MHz / 600 MHz, 300 K, dimethylsulfoxyde-d$_6$)



Spectrum 0-22: ^{1}H ^{13}C HMQC of 4-K (600.23 MHz / 150.94 MHz, 300 K, dimethylsulfoxyde-d$_6$)

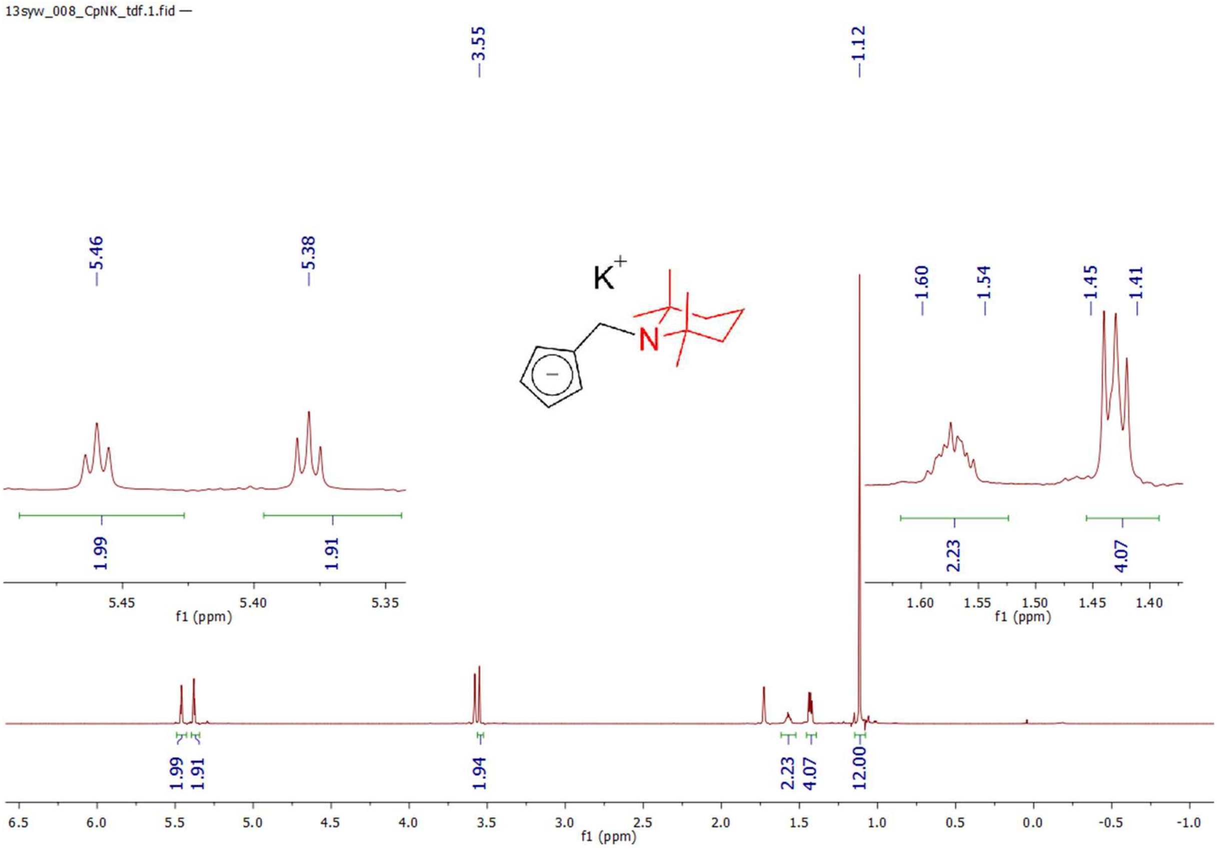


Spectrum 0-23: ^1H ^{13}C HMBC of (600.23 MHz / 150.94 MHz, 300 K, dimethylsulfoxyde-d_6)

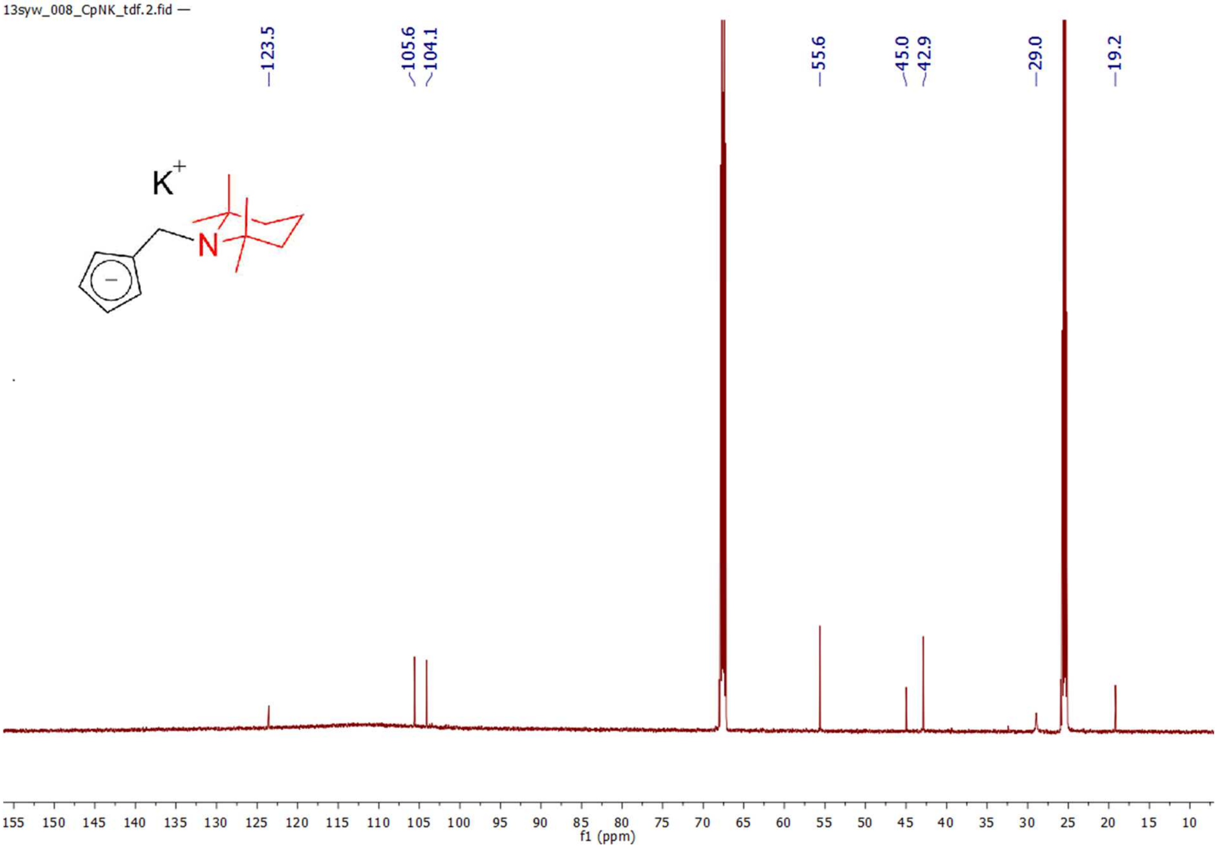


Spectrum 0-24: HRMS of 4-K (Negative mode ESI, dimethylsulfoxide)

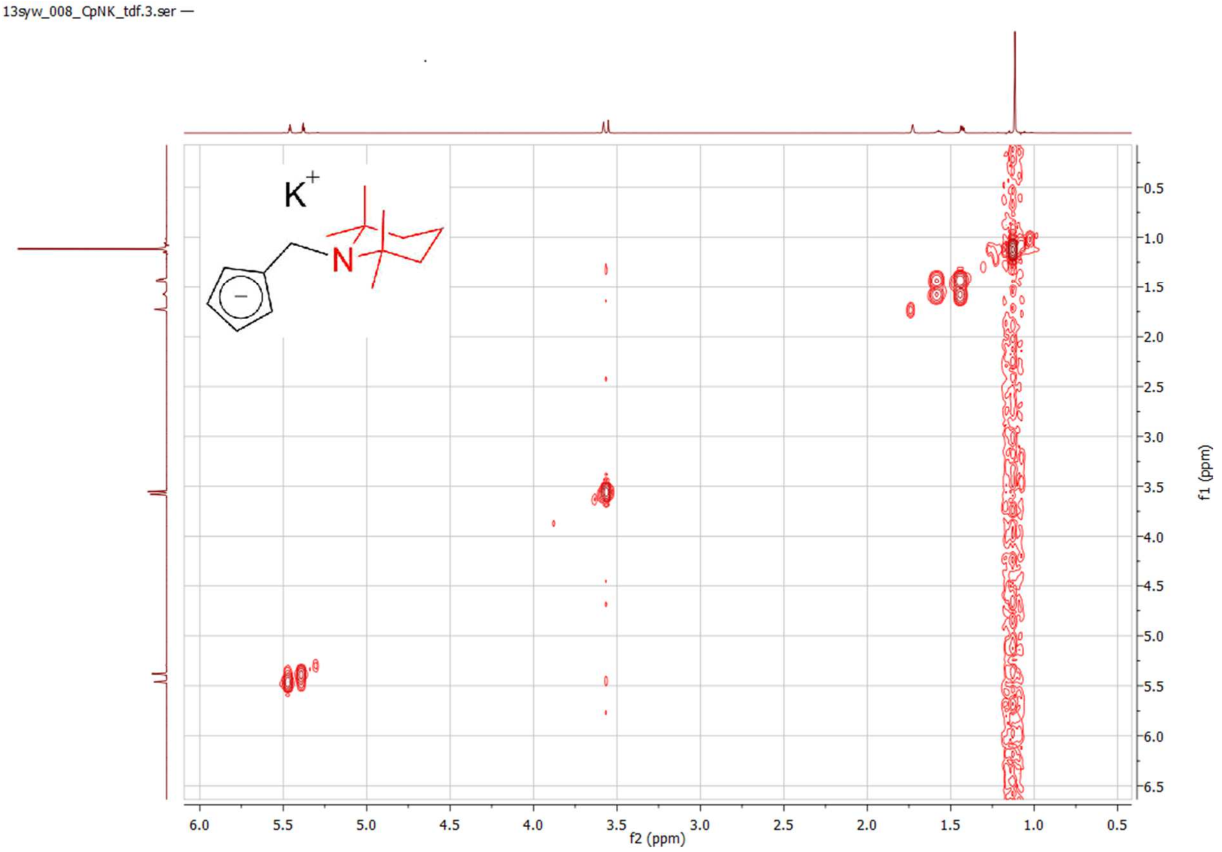
5. Compound **5-K**



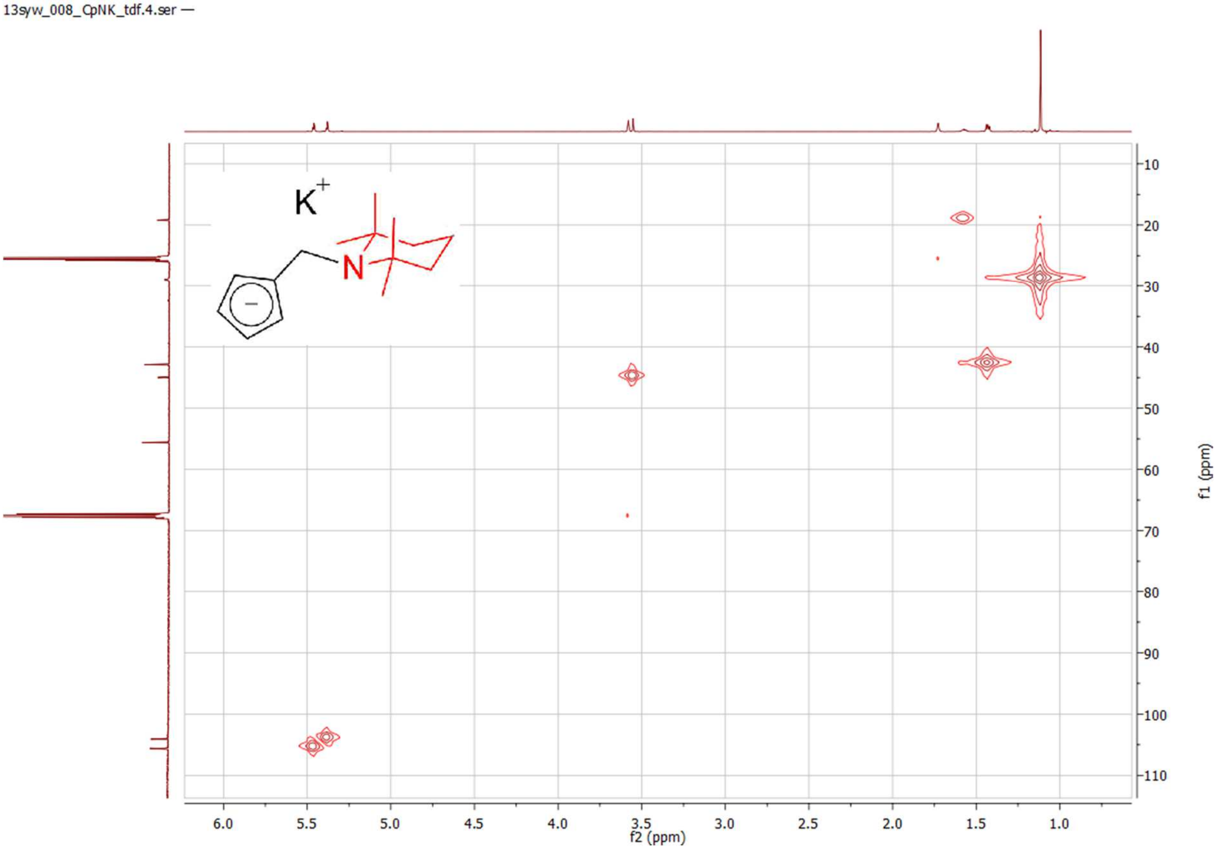
Spectrum 0-25: ^{1}H NMR of 5-K (600.23 MHz, 300 K, tetrahydrofuran-d$_8$)



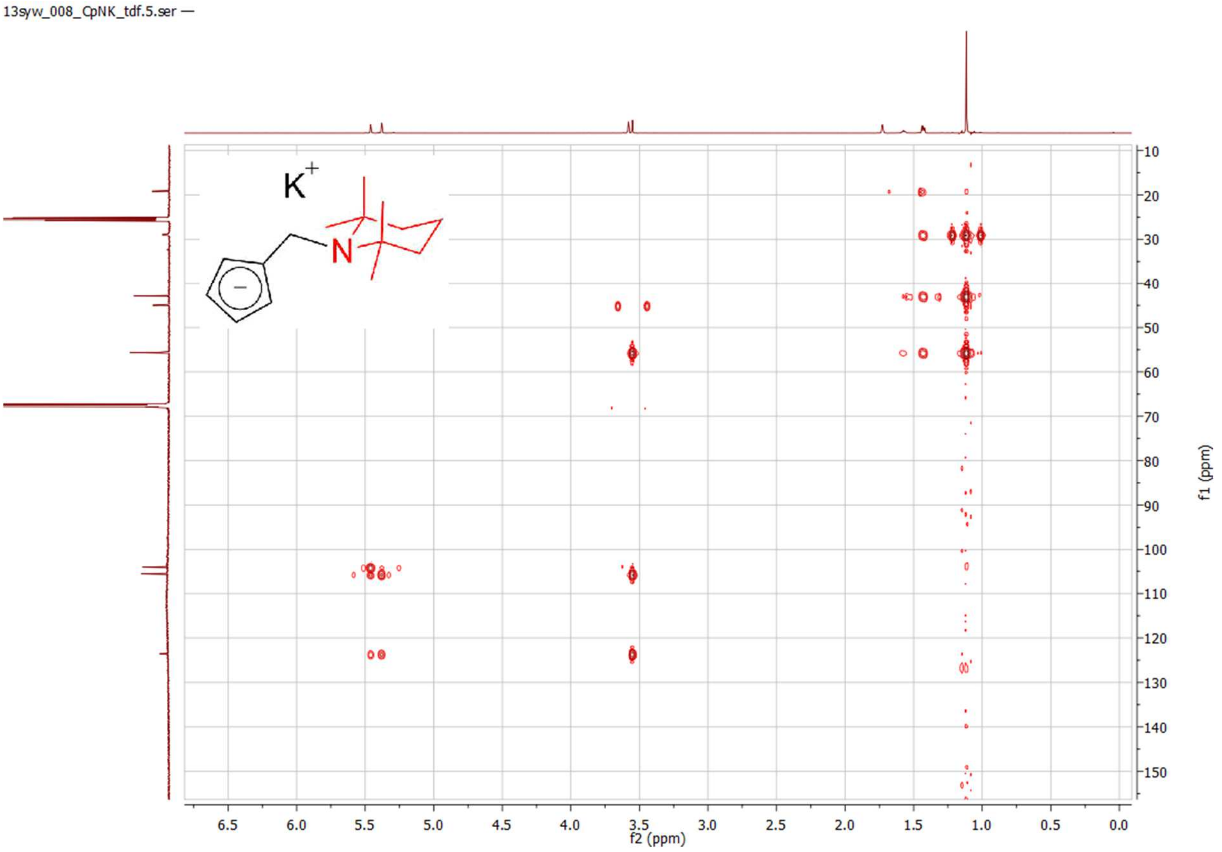
Spectrum 0-26: ^{13}C{^{1}H} NMR of 5-K (150.94 MHz, 300 K, tetrahydrofuran-d$_8$)



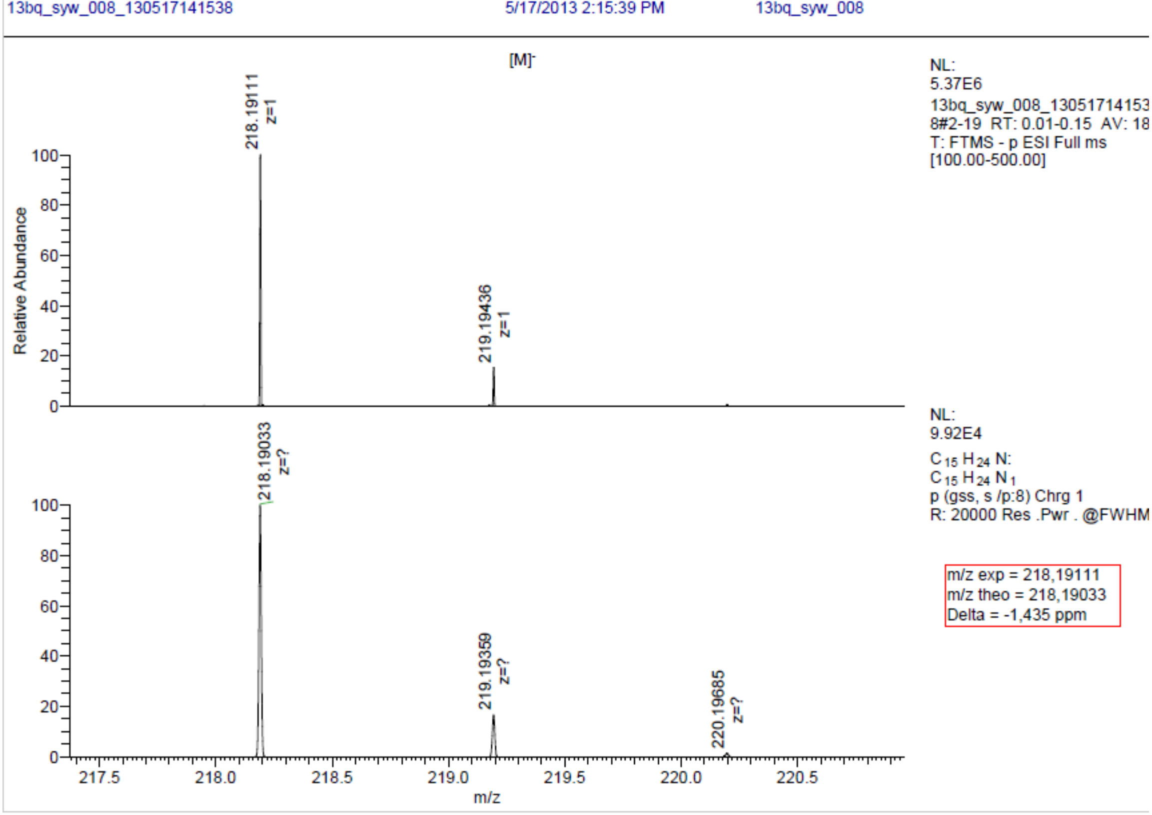
Spectrum 0-27: ^{1}H ^{1}H COSY of 5-K (600.23 MHz, 300 K, tetrahydrofuran-d_8)



Spectrum 0-28: ^{1}H ^{13}C HMQC of 5-K (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d_8)

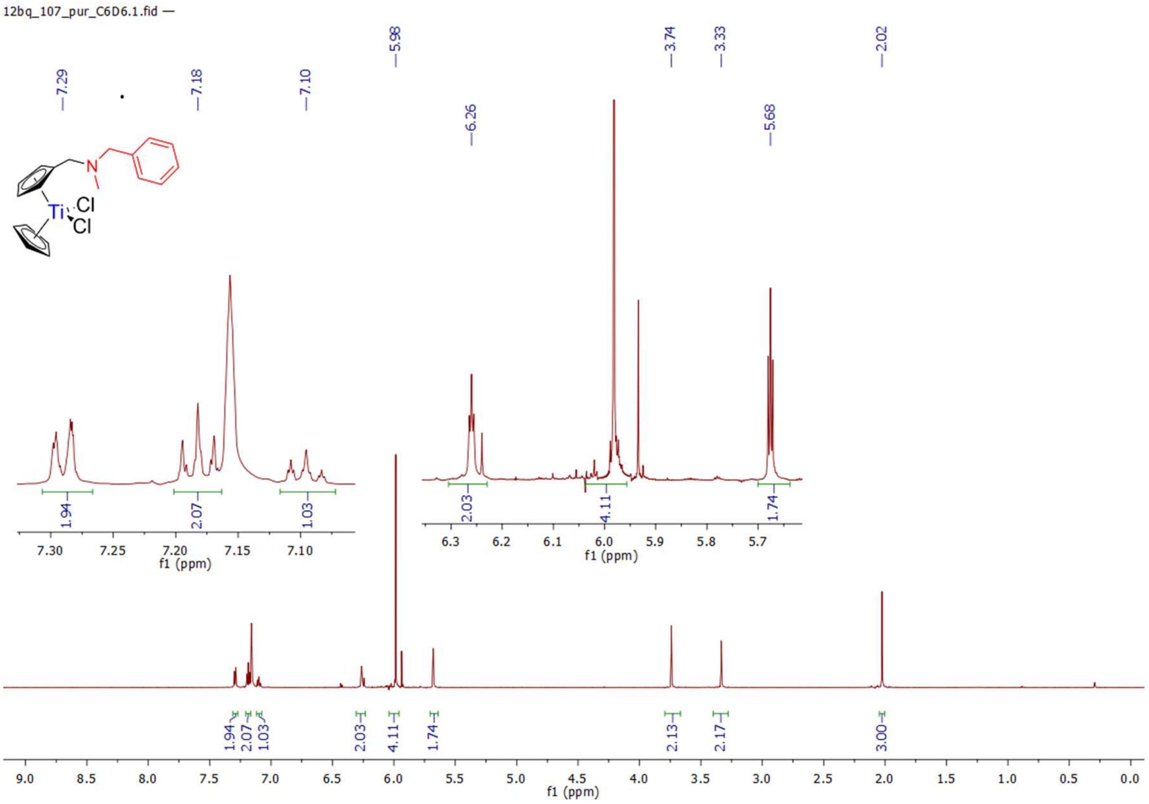


Spectrum 0-29: ^{1}H ^{13}C HMBC of 5-K (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d_8)

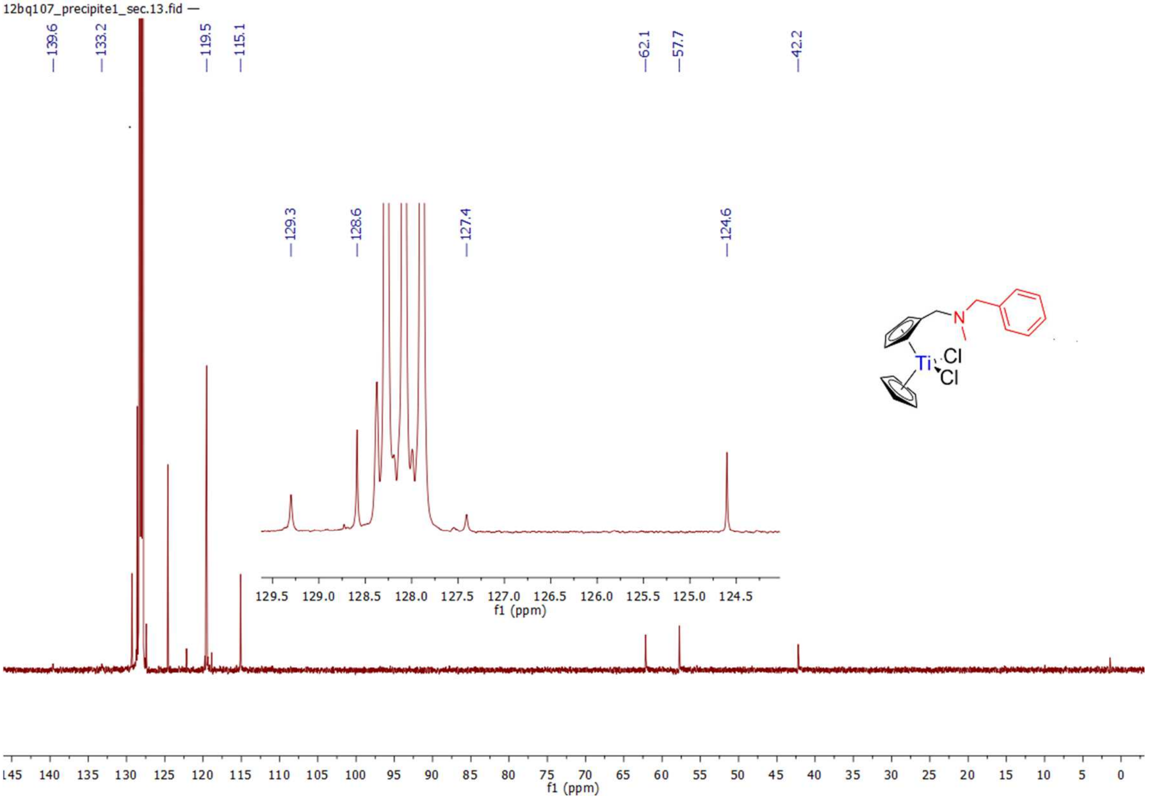


Spectrum 0-30: HRMS of 5-K (Negative mode ESI, dimethylsulfoxide)

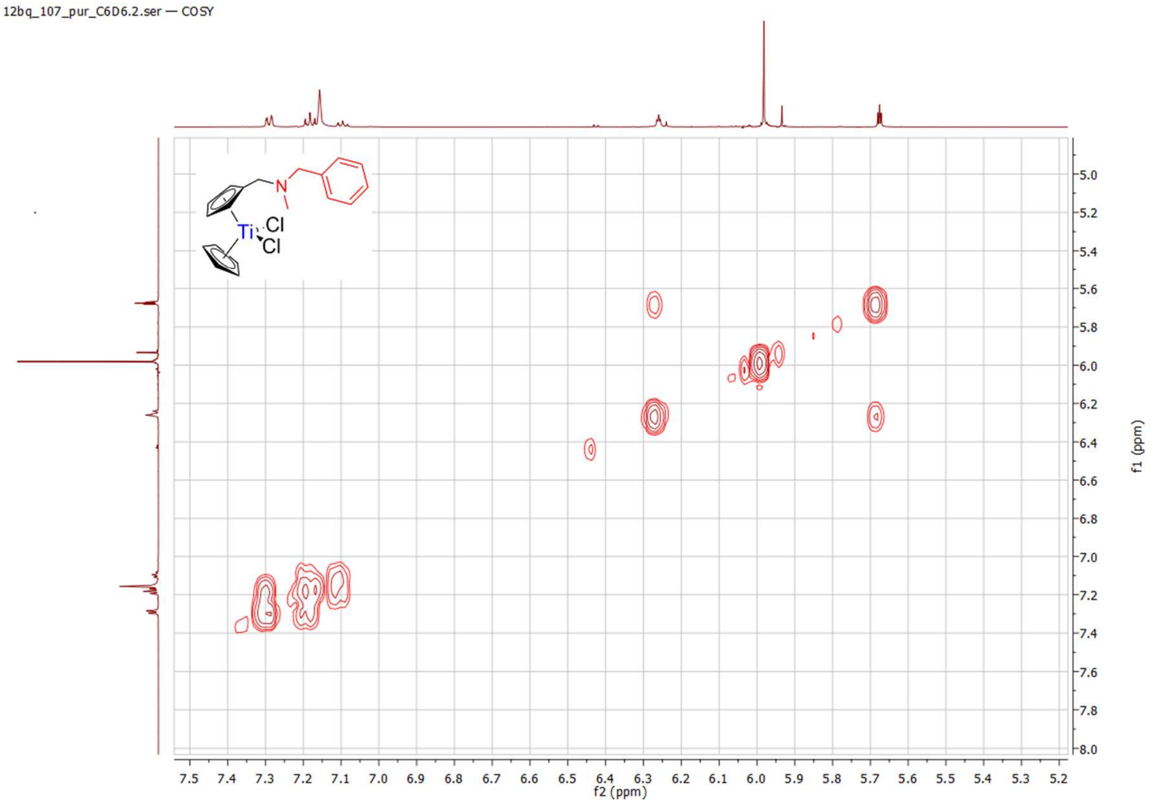
6. Compound **9**:



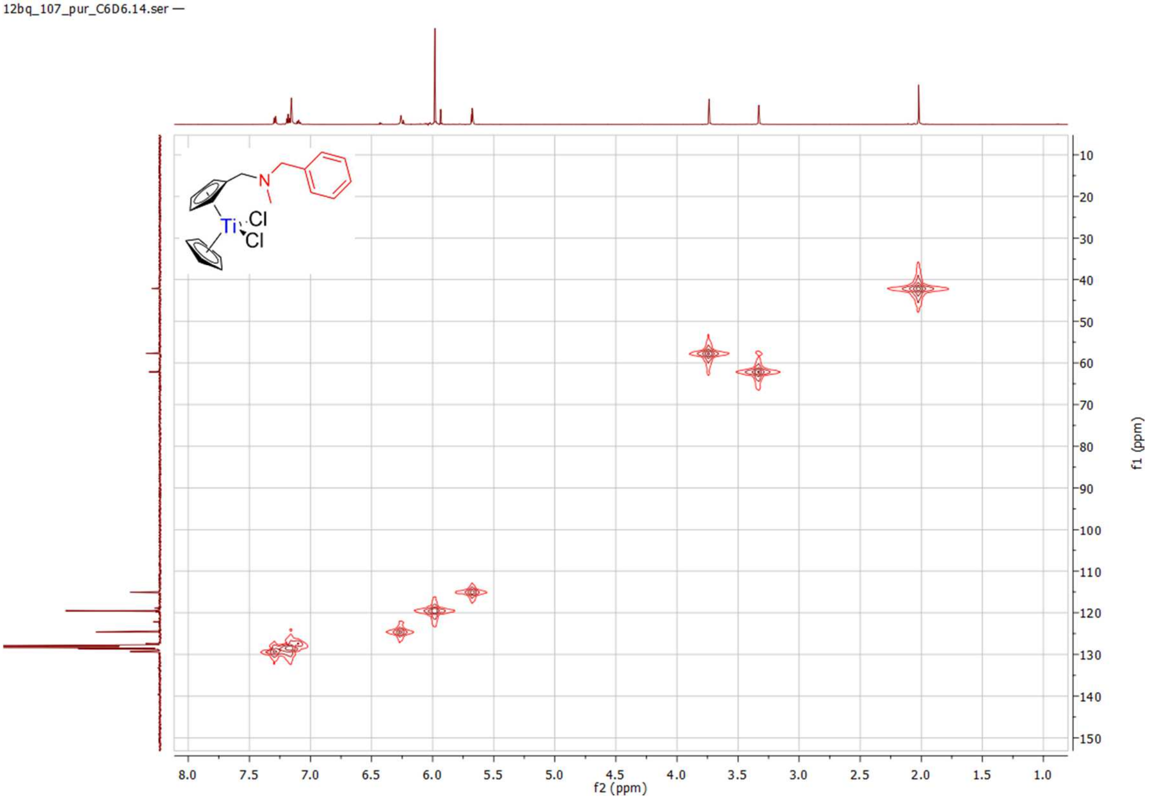
Spectrum 0-31: ^{1}H NMR of 9 (600.23 MHz, 300 K, benzene-d$_6$)



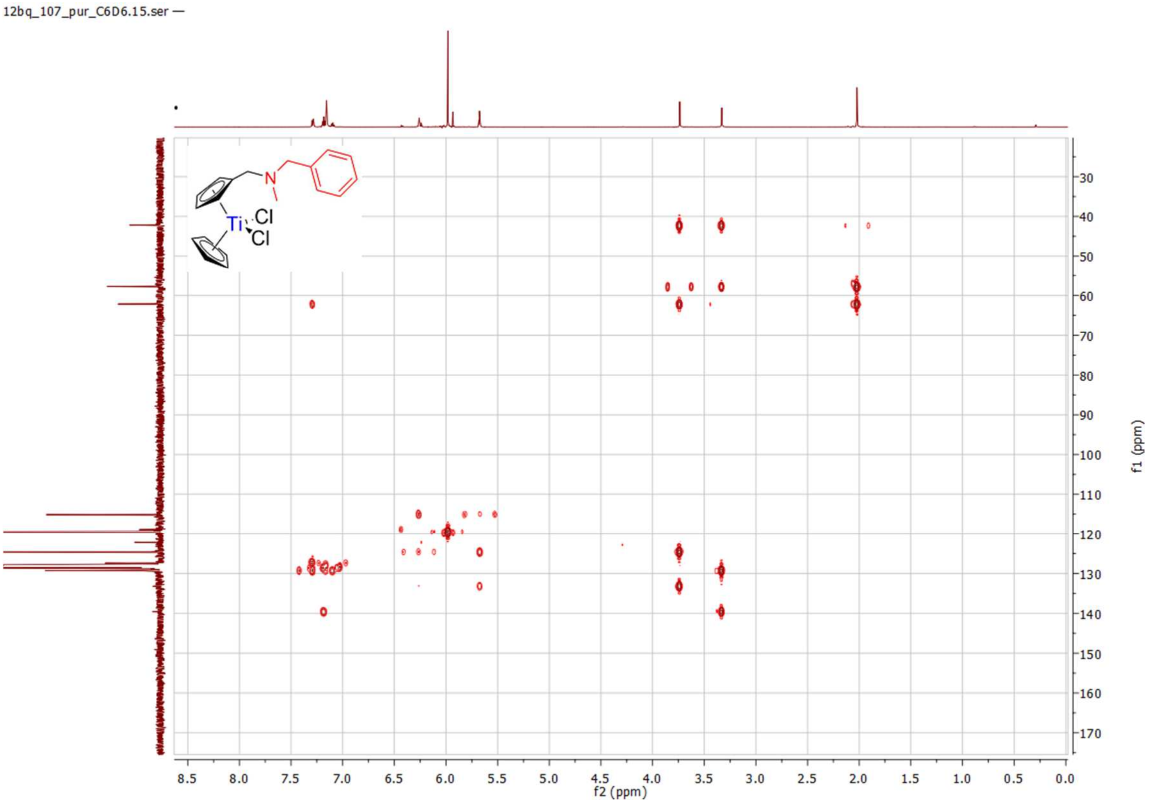
Spectrum 0-32: ^{13}C{^{1}H} NMR of 9 (125.77 MHz, 300 K, benzene-d$_6$)



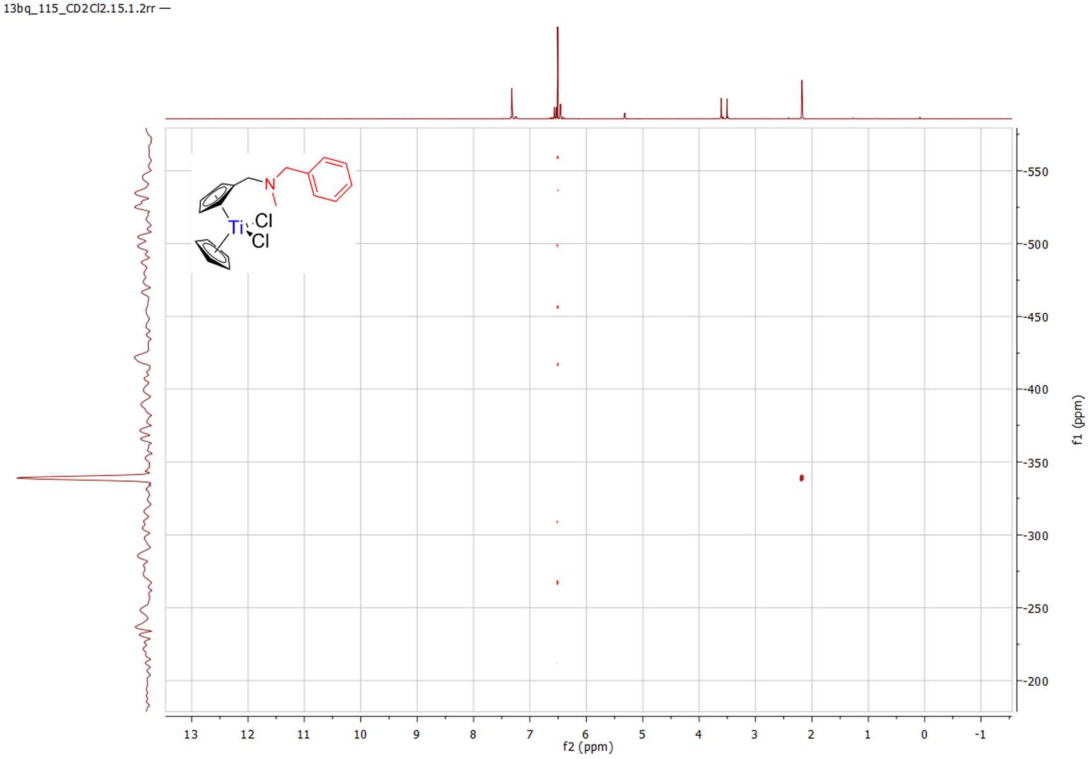
Spectrum 0-33: ^{1}H ^{1}H COSY of 9 (600.23 MHz, 300 K, benzene-d$_6$)



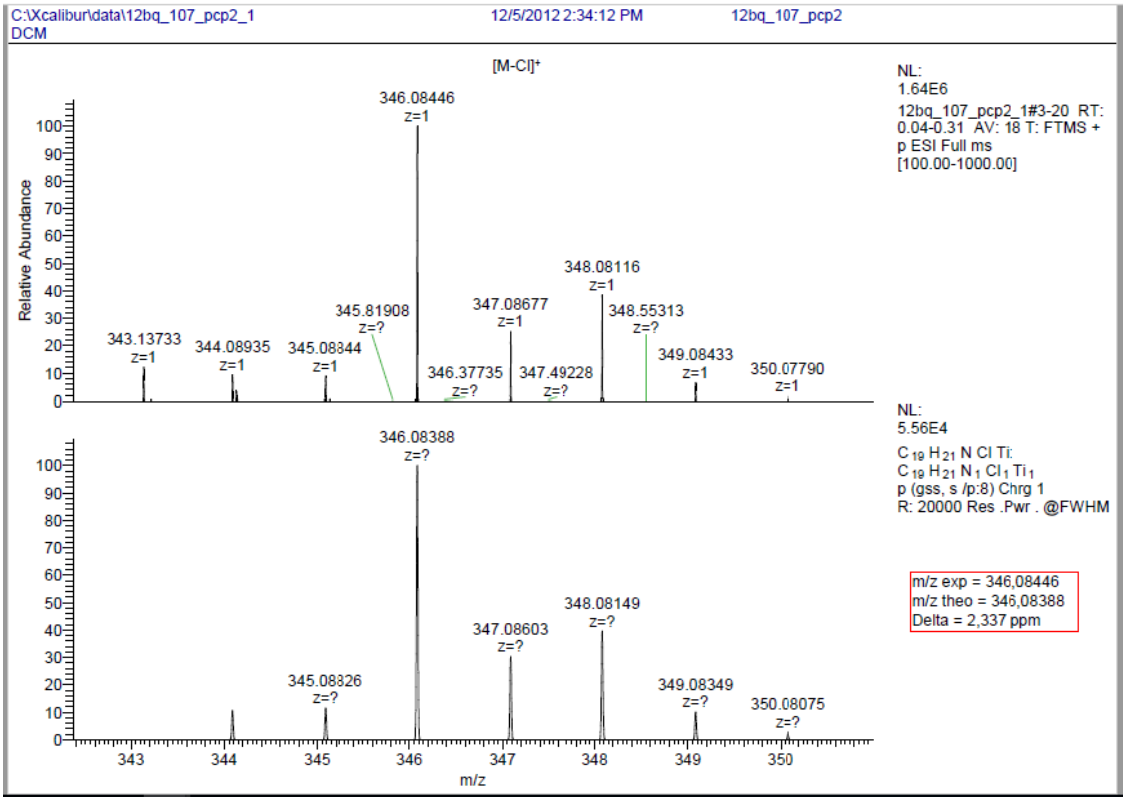
Spectrum 0-34: ^{1}H ^{13}C HMQC of 9 (600.23 MHz / 150.94 MHz, 300 K, benzene-d$_6$)



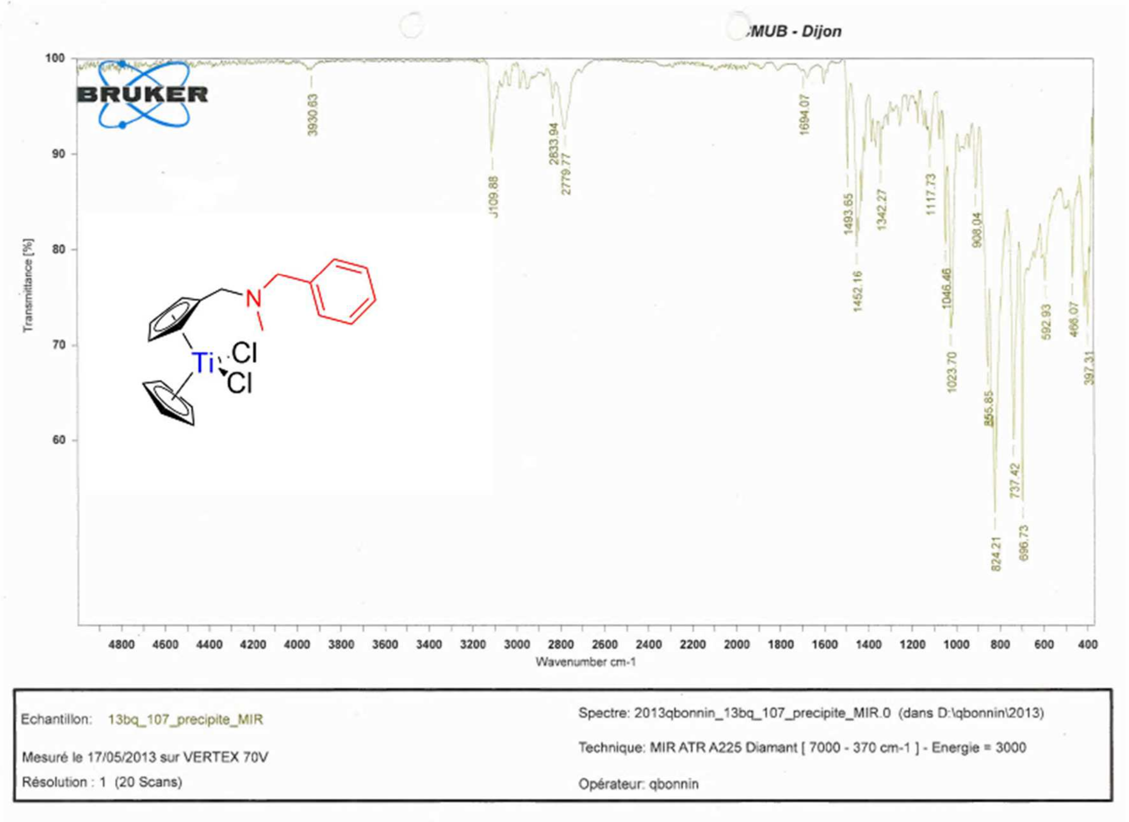
Spectrum 0-35: ^1H ^{13}C HMBC of 9 (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6)



Spectrum 0-36: ^1H ^{15}N HMBC of 9 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-37: HRMS of 9 (Positive mode ESI, dichloromethane)



Echantillon: 13bq_107_precipite_MIR

Mesuré le 17/05/2013 sur VERTEX 70V

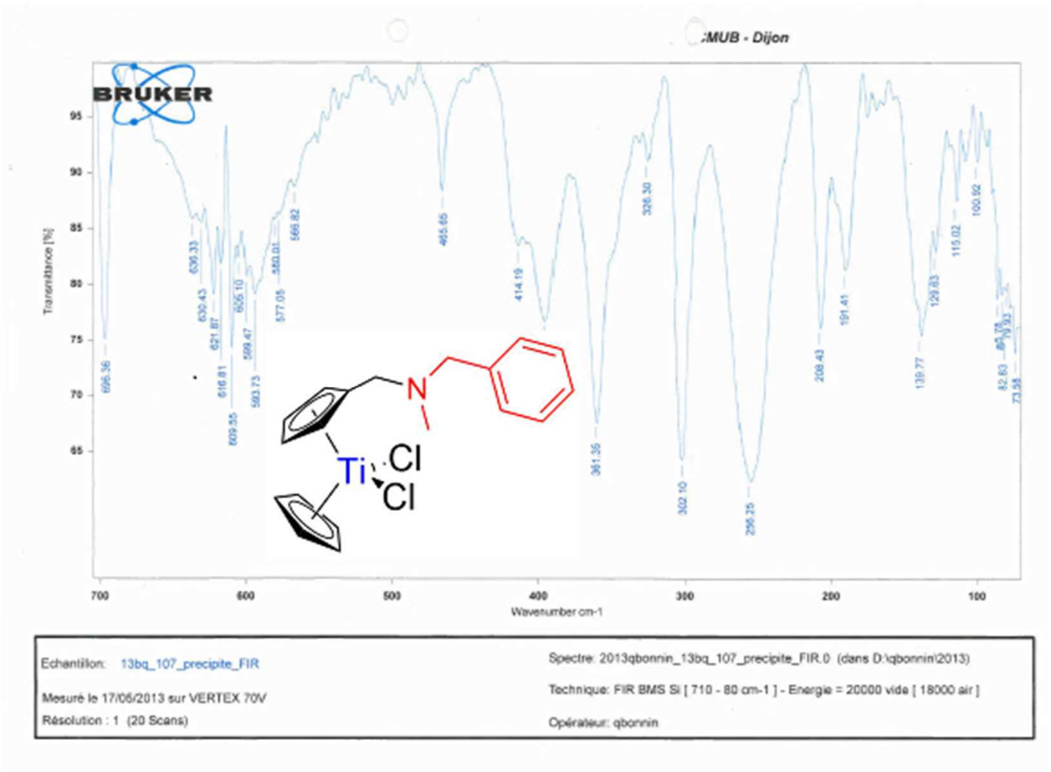
Résolution : 1 (20 Scans)

Spectre: 2013qbonnin_13bq_107_precipite_MIR.0 (dans D:\qbonnin\2013)

Technique: MIR ATR A225 Diamant [7000 - 370 cm-1] - Energie = 3000

Opérateur: qbonnin

Spectrum 0-38: MIR of 9



Echantillon: 13bq_107_precipite_FIR

Mesuré le 17/06/2013 sur VERTEX 70V

Résolution : 1 (20 Scans)

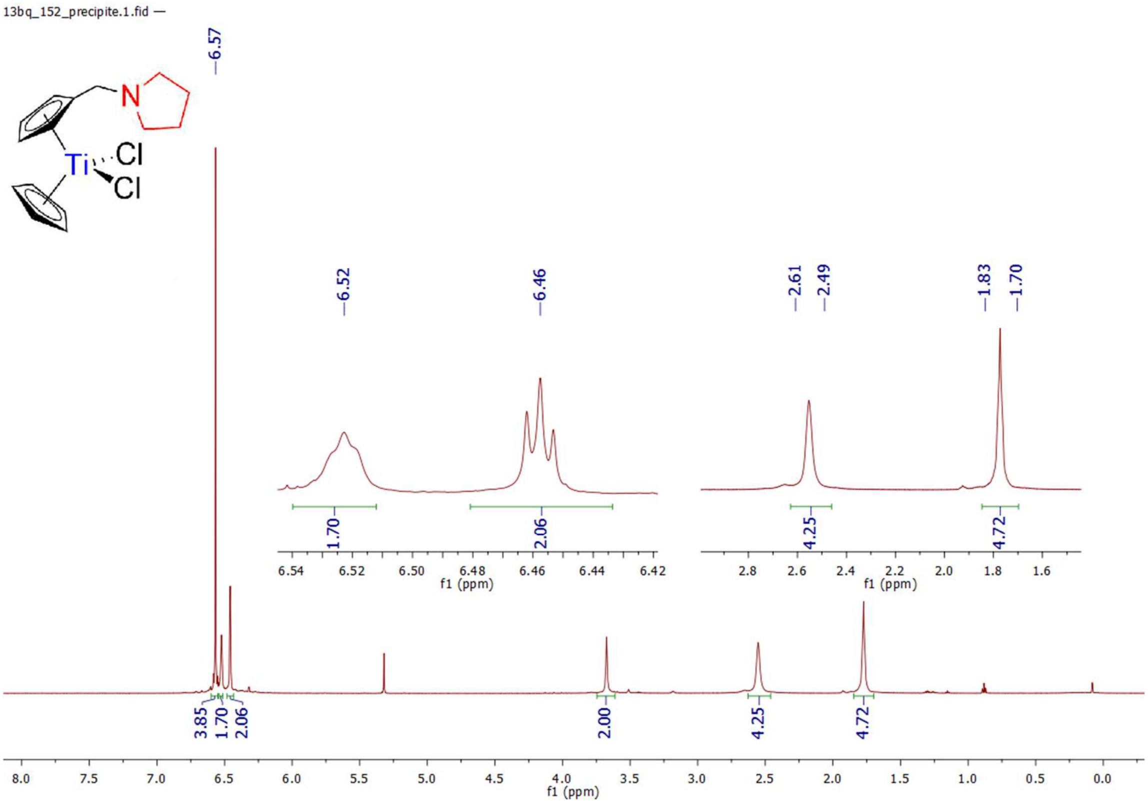
Spectre: 2013qbonnin_13bq_107_precipite_FIR.0 (dans D:\qbonnin\2013)

Technique: FIR BMS Si [710 - 80 cm-1] - Energie = 20000 vide [18000 air]

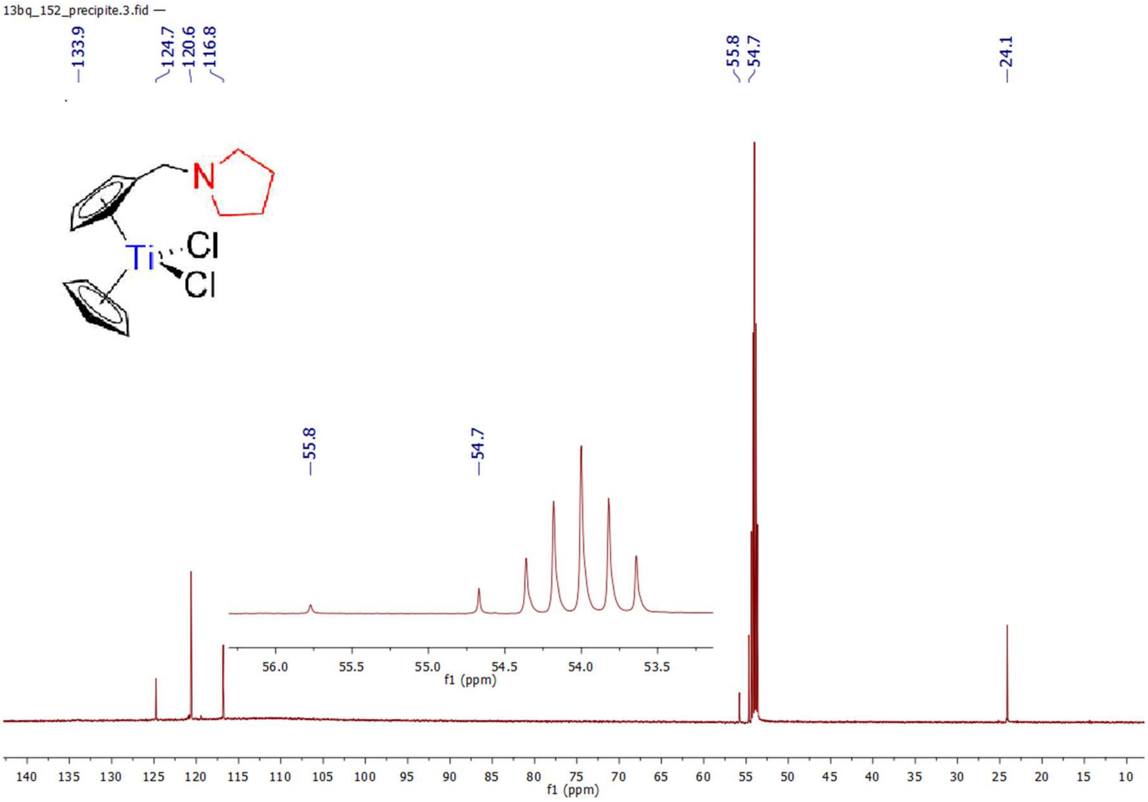
Opérateur: qbonnin

Spectrum 0-39: FIR of 9

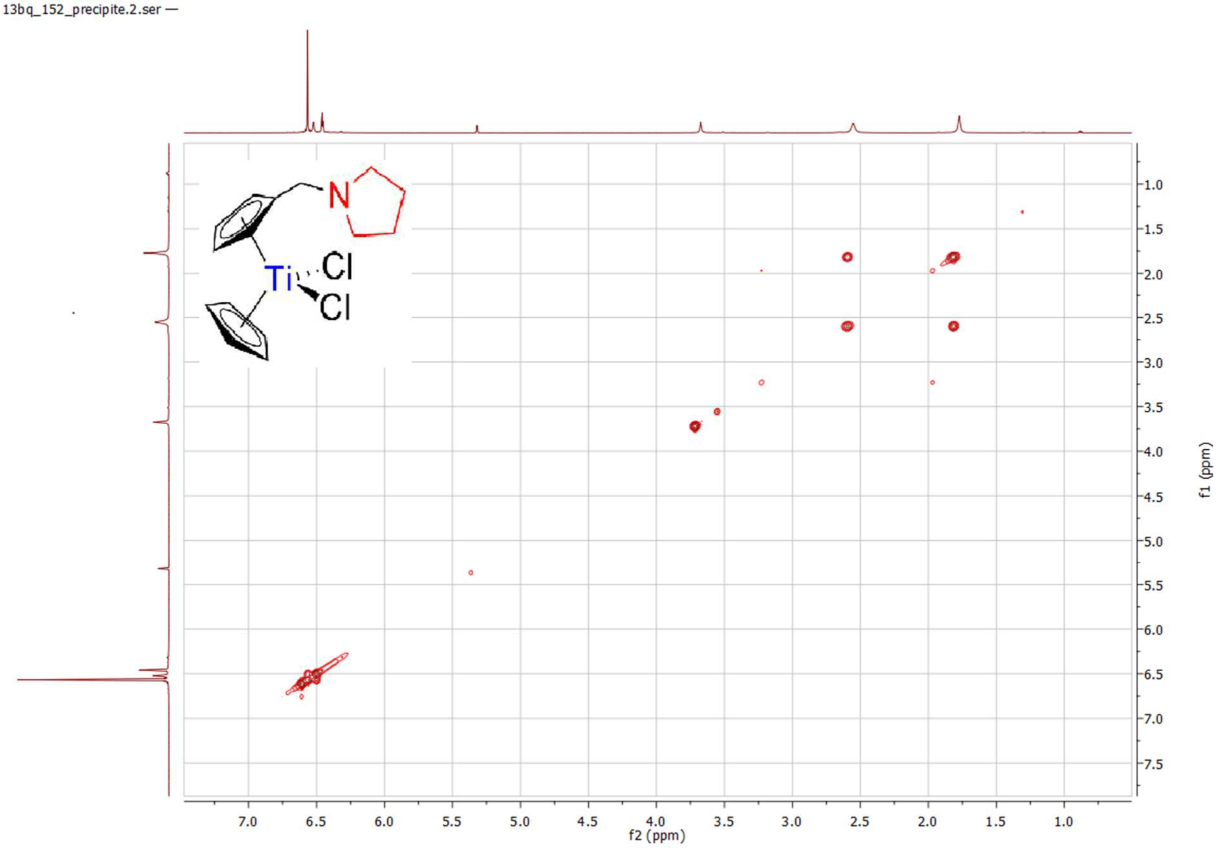
7. Compound **10**:



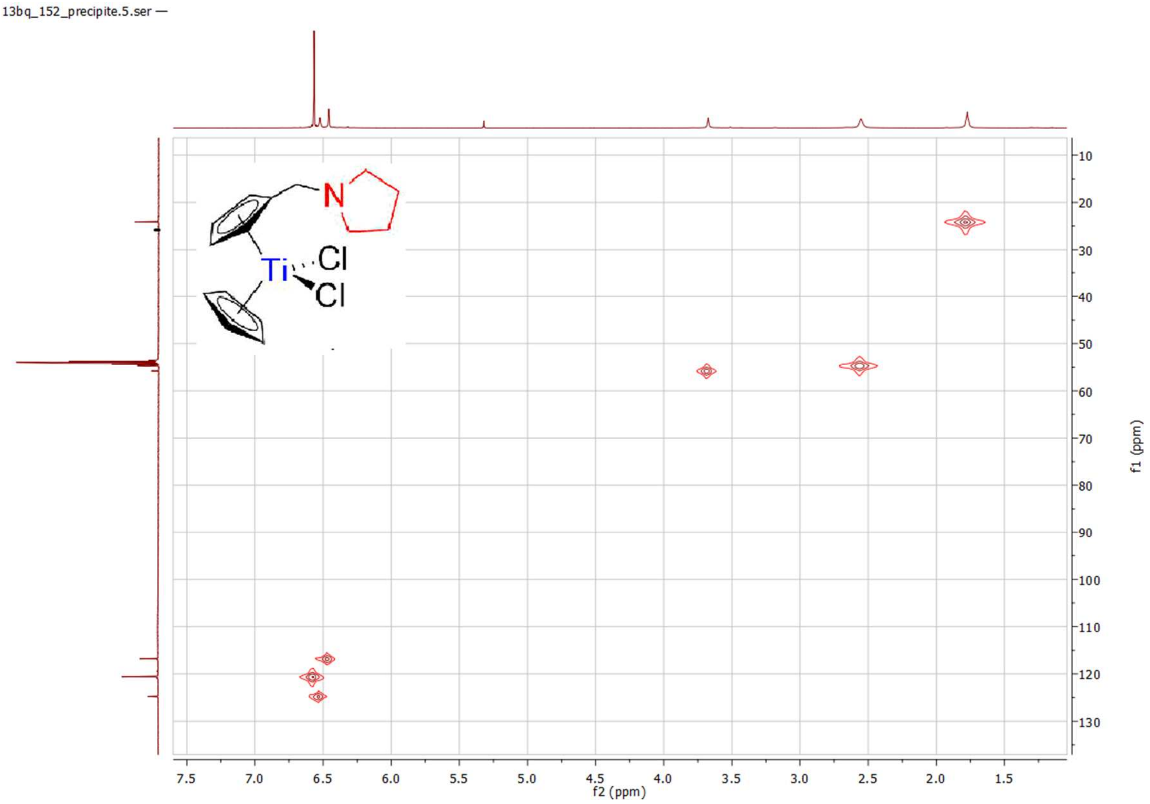
Spectrum 0-40: ^{1}H NMR of 10 (600 MHz, 300 K, dichloromethane-d_2)



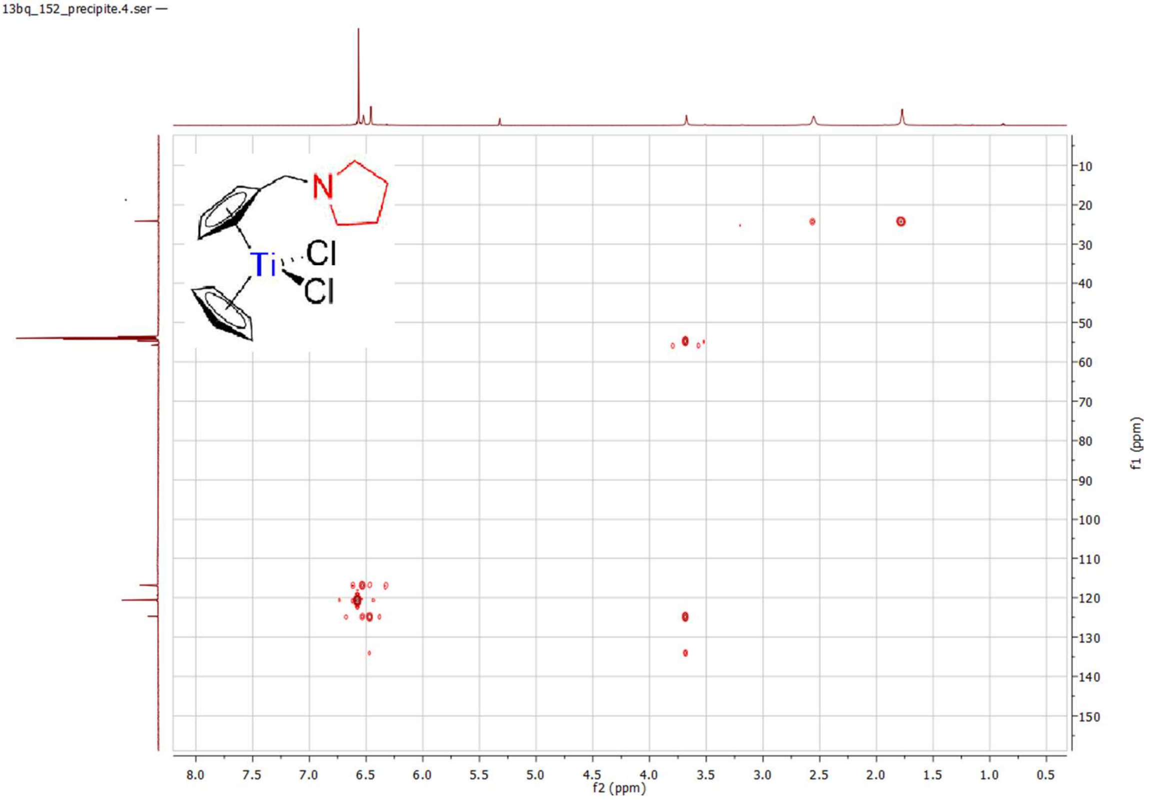
Spectrum 0-41: $^{13}C\{^1H\}$ NMR of 10 (150.94 MHz, 300 K, dichloromethane-d_2)



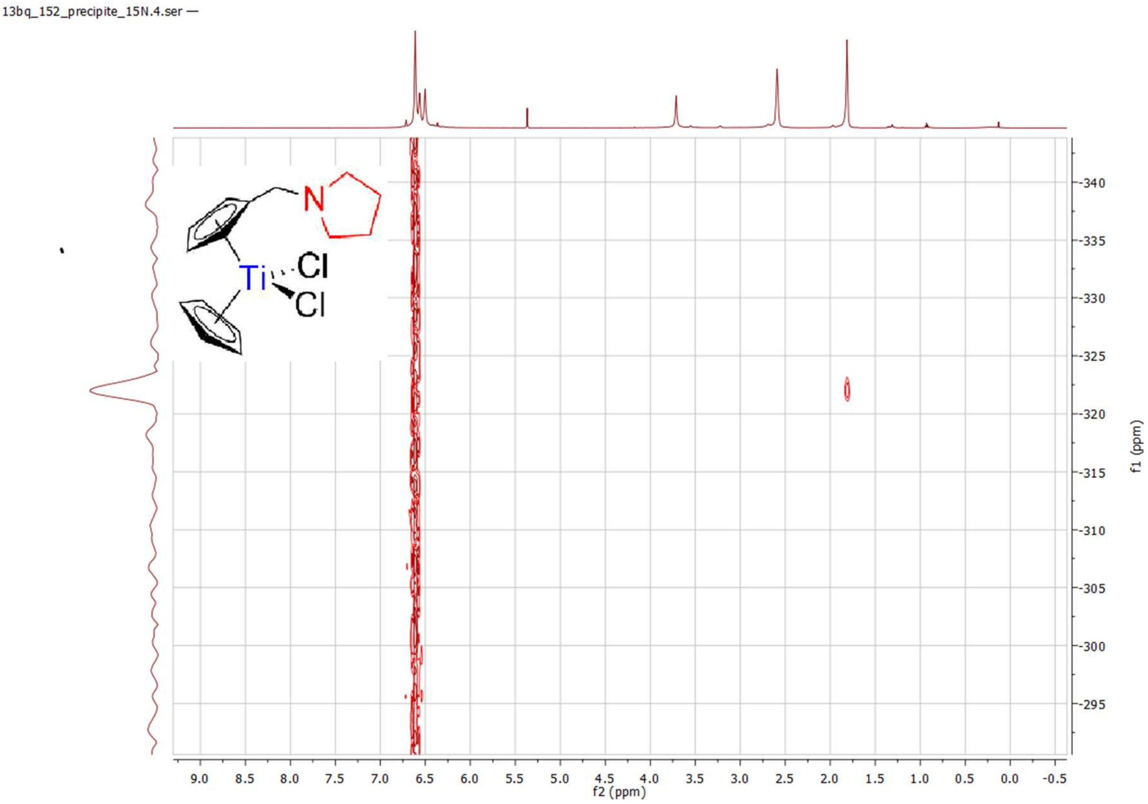
Spectrum 0-42: ^1H ^1H COSY of 10 (600.23 MHz, 300 K, dichloromethane-d_2)



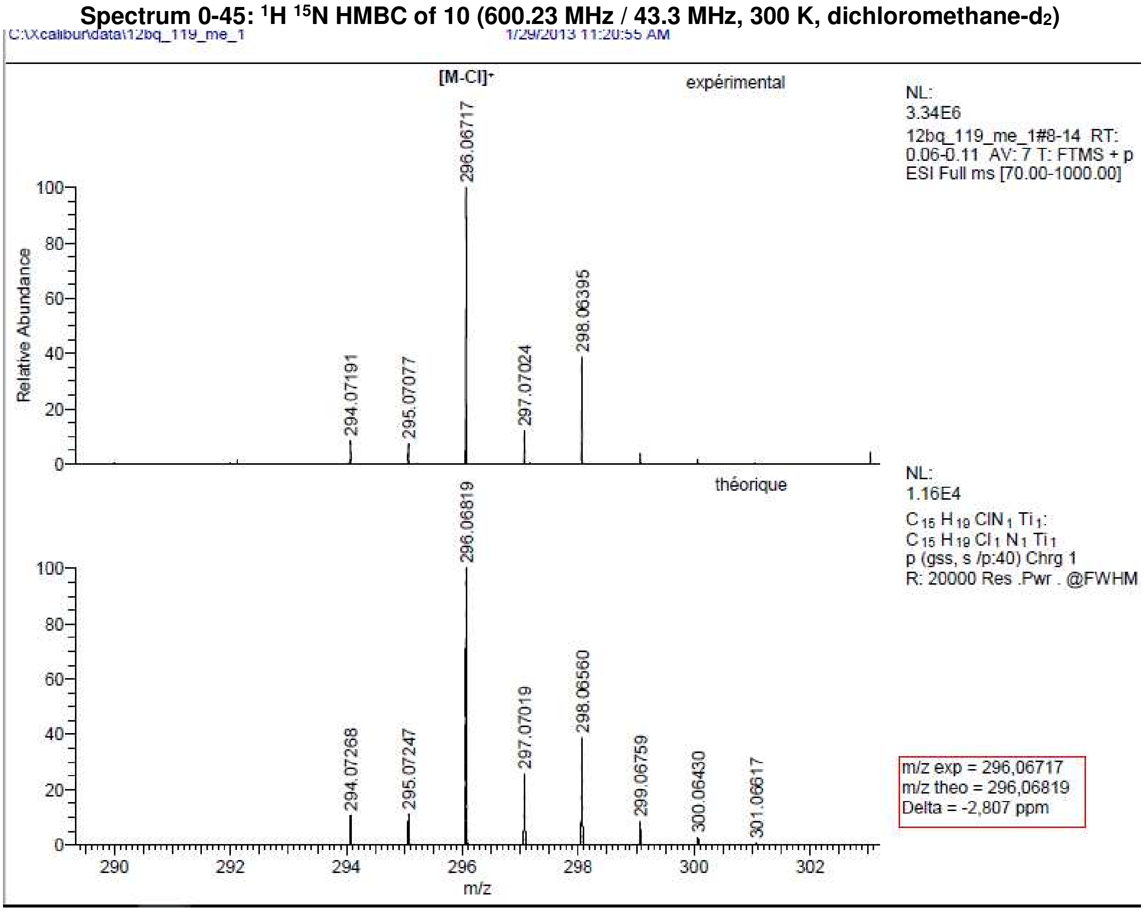
Spectrum 0-43: ^{1}H ^{13}C HMQC of 10 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-44: ^{1}H ^{13}C HMBC of 10 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)

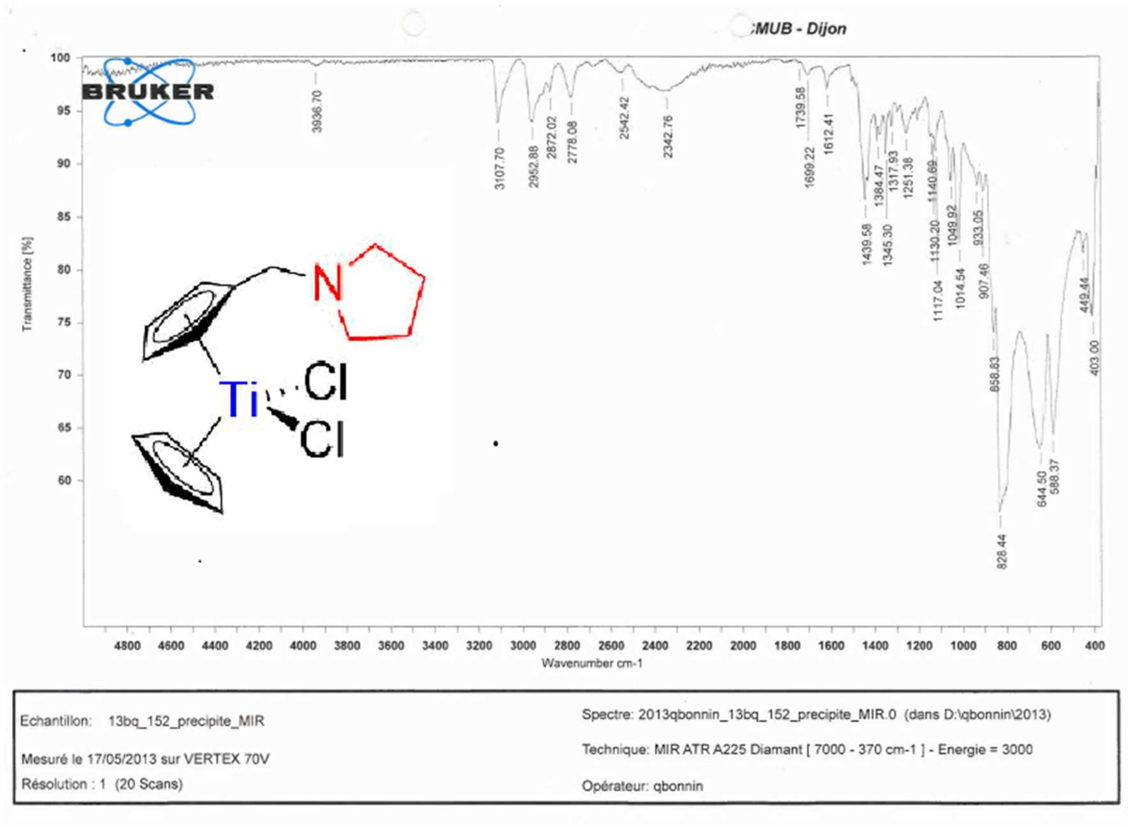


Spectrum 0-45: ^1H ^{15}N HMBC of 10 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2)



m/z exp = 296,06717
m/z theo = 296,06819
Delta = -2,807 ppm

Spectrum 0-46: HRMS of 10 (Positive mode ESI, dichloromethane)



Echantillon: 13bq_152_precipite_MIR

Mesuré le 17/05/2013 sur VERTEX 70V

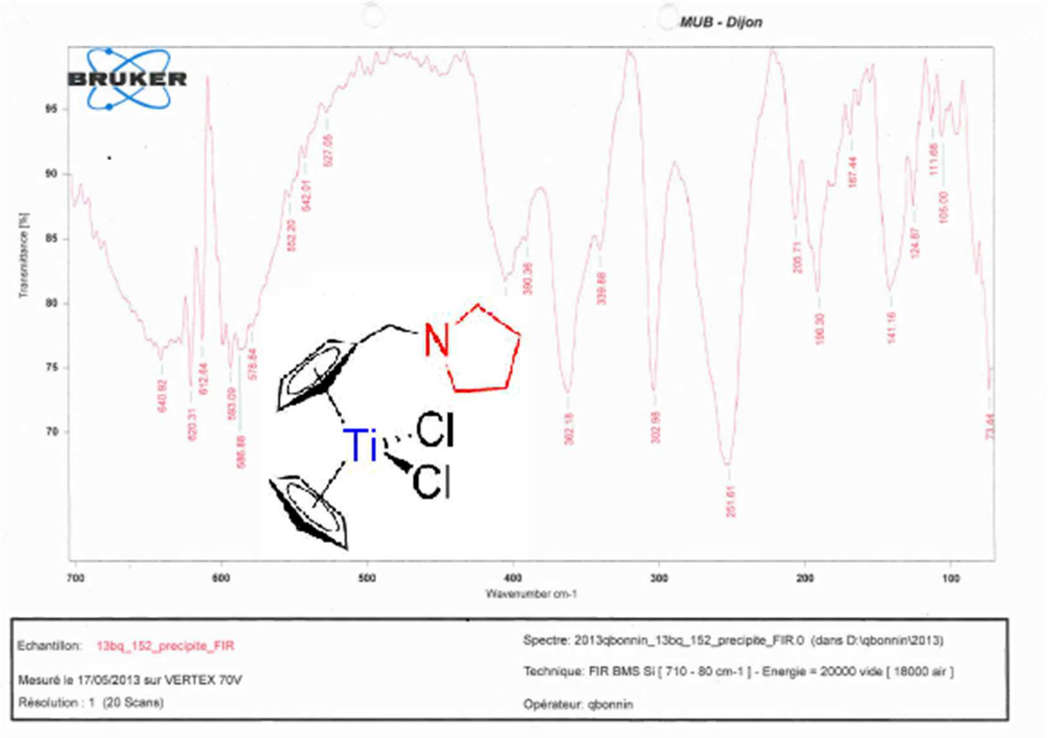
Résolution : 1 (20 Scans)

Spectre: 2013qbonnin_13bq_152_precipite_MIR.0 (dans D:\qbonnin\2013)

Technique: MIR ATR A225 Diamant [7000 - 370 cm-1] - Energie = 3000

Opérateur: qbonnin

Spectrum 0-47: MIR of 10



Echantillon: 13bq_152_precipite_FIR

Mesuré le 17/05/2013 sur VERTEX 70V

Résolution : 1 (20 Scans)

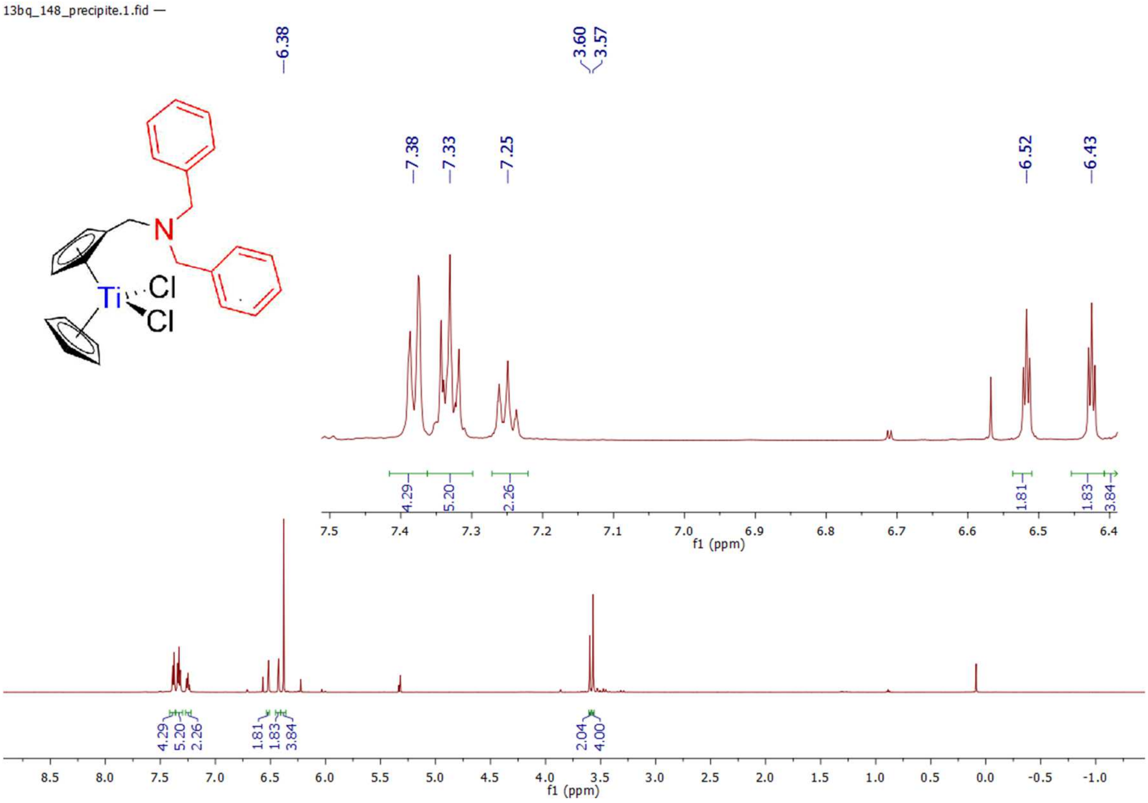
Spectre: 2013qbonnin_13bq_152_precipite_FIR.0 (dans D:\qbonnin\2013)

Technique: FIR BMS Si [710 - 80 cm-1] - Energie = 20000 vide [18000 air]

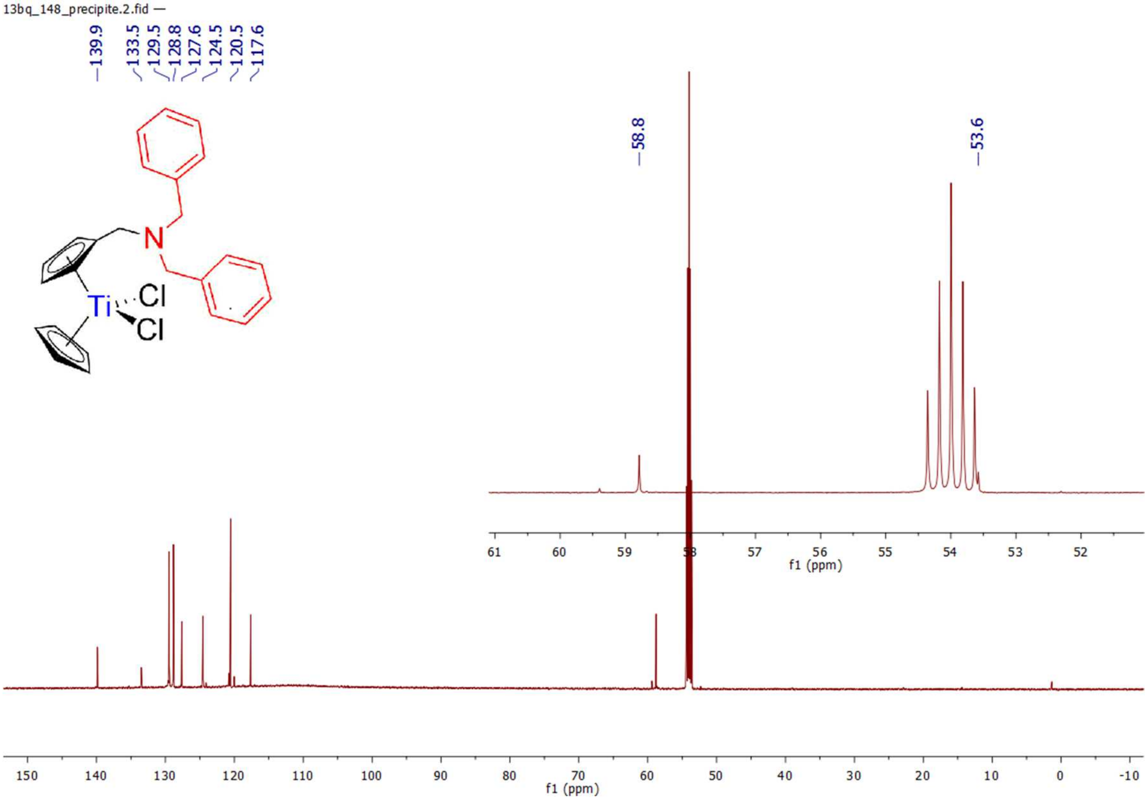
Opérateur: qbonnin

Spectrum 0-48: FIR of 10

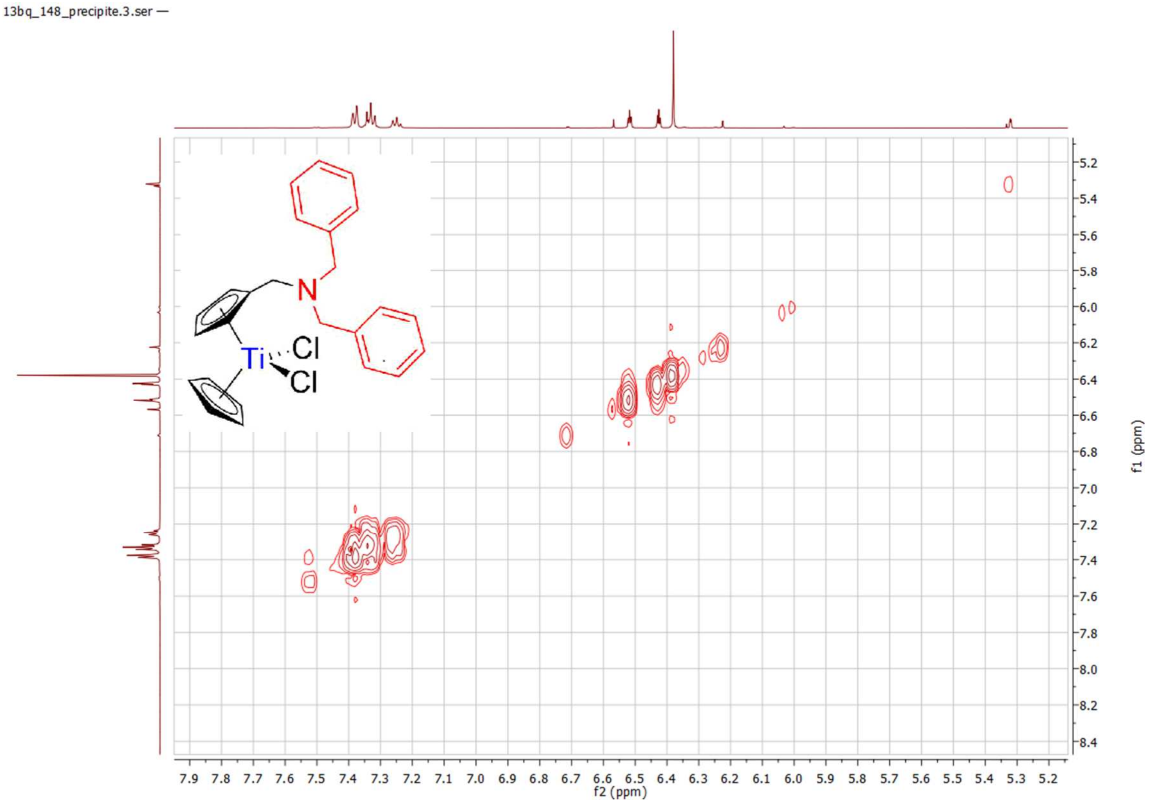
8. Compound **11**:



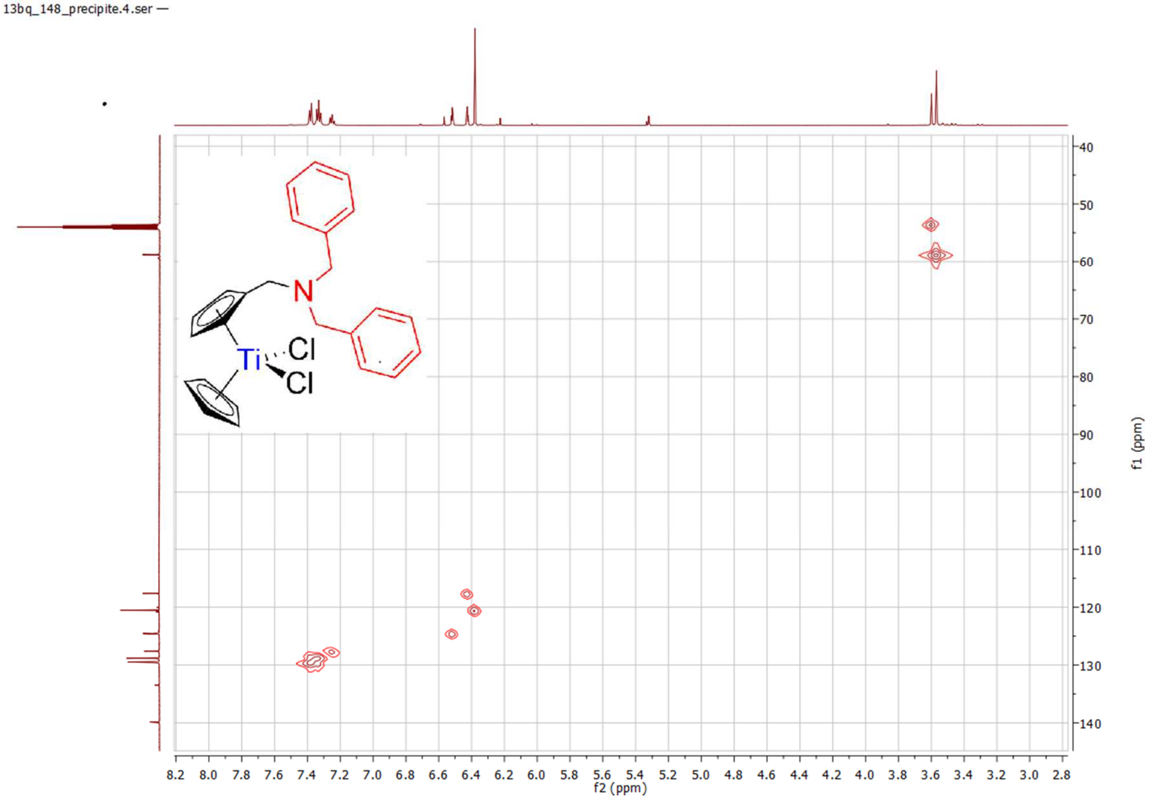
Spectrum 0-49: ^{1}H NMR of 11 (600.23 MHz, 300 K, dichloromethane-d$_2$)



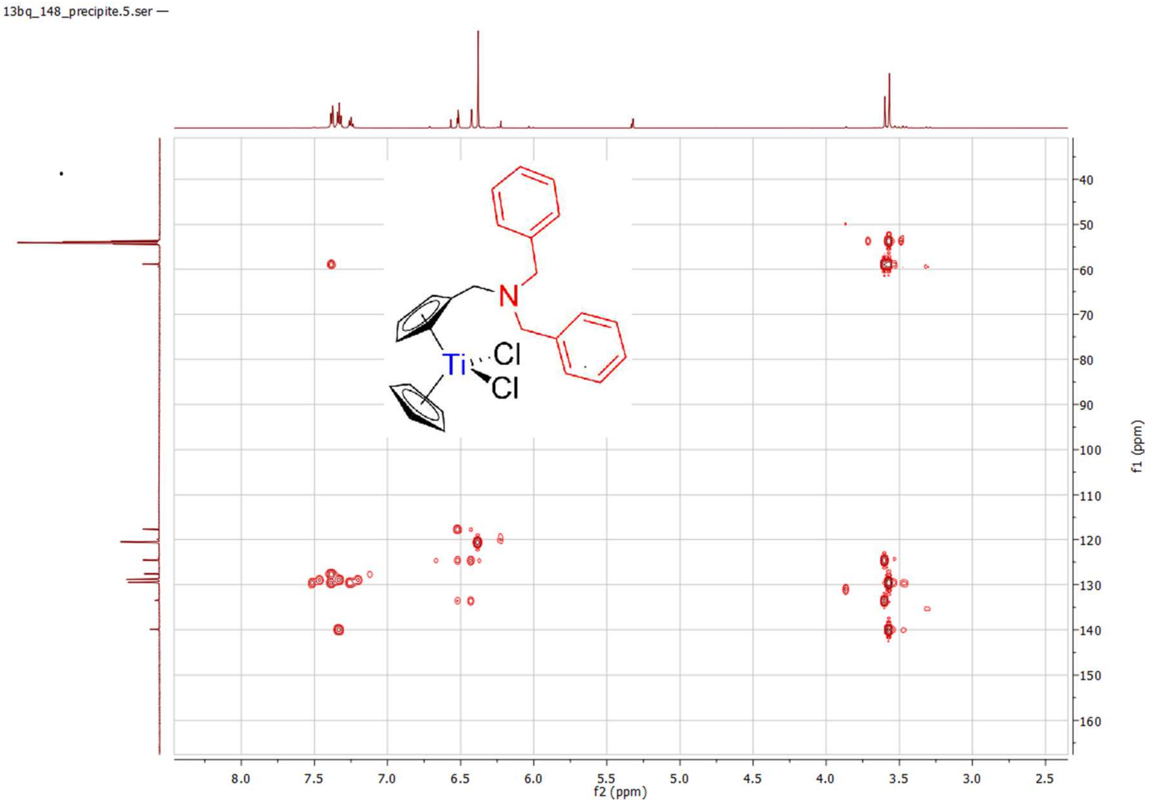
Spectrum 0-50: ^{13}C{^{1}H} NMR of 11 (150.94 MHz, 300 K, dichloromethane-d$_2$)



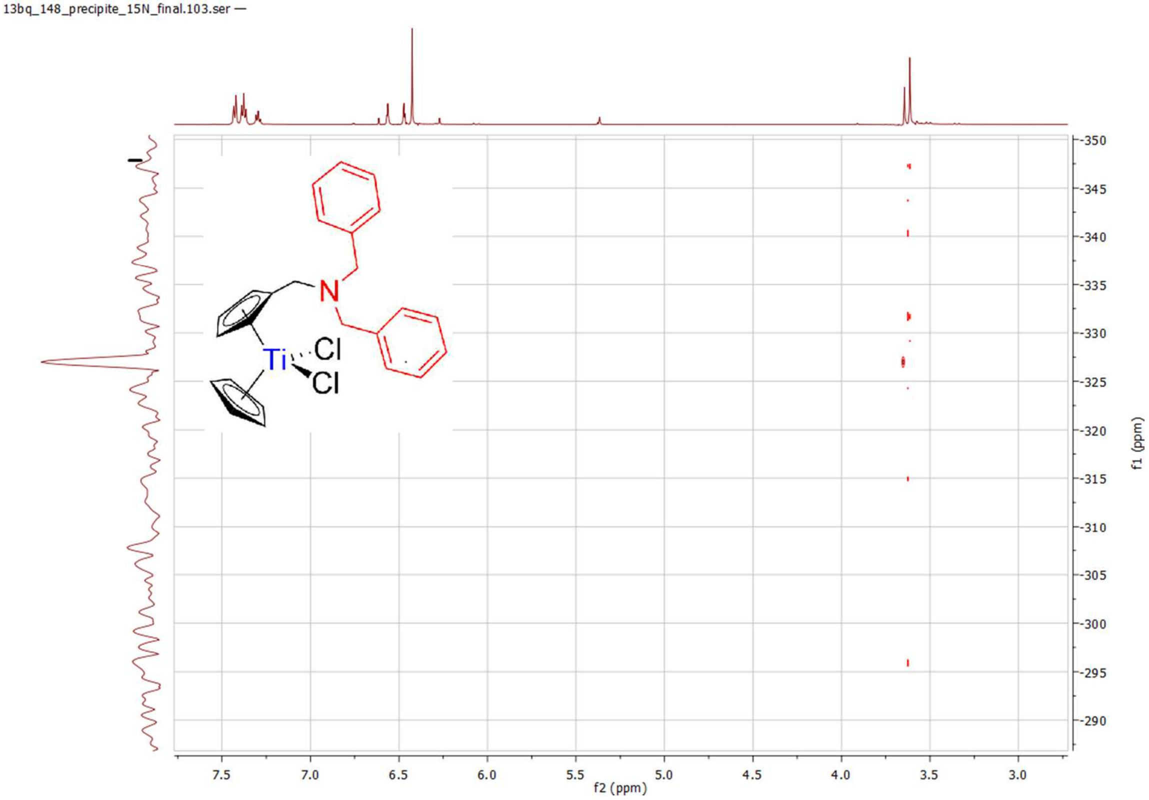
Spectrum 0-51: ^{1}H ^{1}H COSY of 11 (600.23 MHz, 300 K, dichloromethane-d_2)



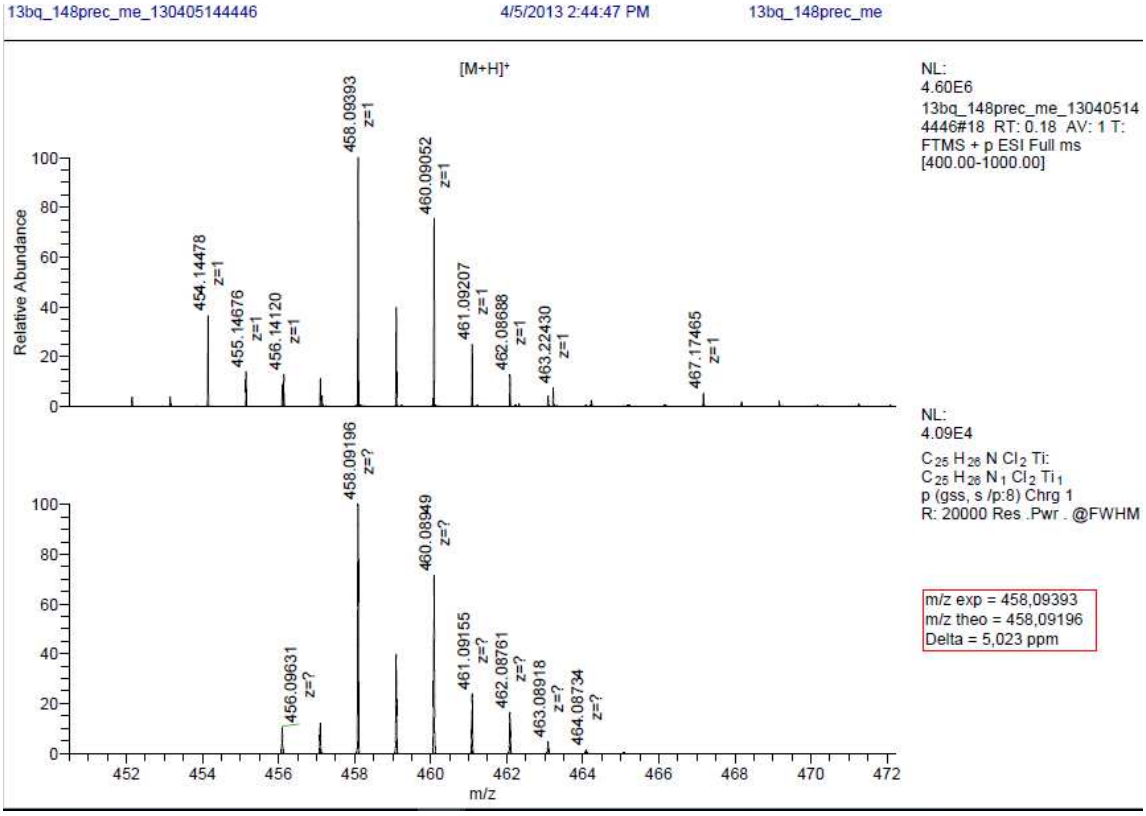
Spectrum 0-52: ^{1}H ^{13}C HMQC of 11 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-53: ^{1}H ^{13}C HMBC of 11 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)

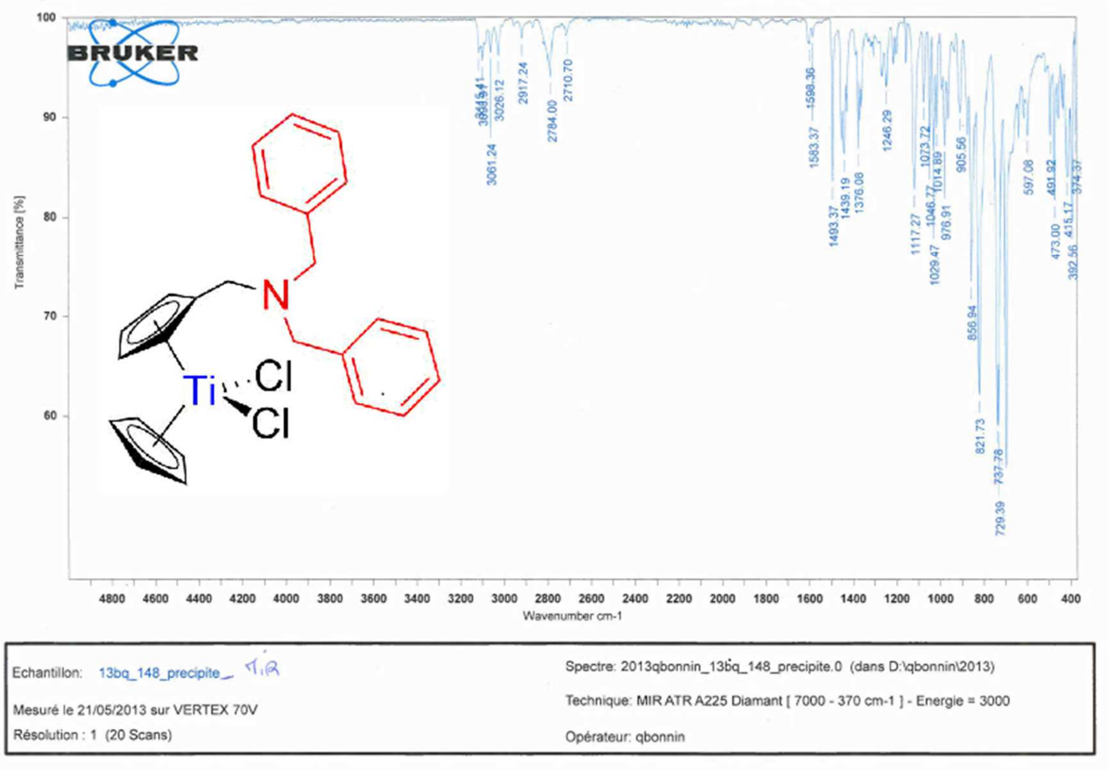


Spectrum 0-54: ^{1}H ^{15}N HMBC of 11 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2)



m/z exp = 458,09393
m/z theo = 458,09196
Delta = 5,023 ppm

Spectrum 0-55: HRMS of 11 (Positive mode ESI, dichloromethane)



Echantillon: 13bq_148_precipite_ Ti,R

Mesuré le 21/05/2013 sur VERTEX 70V

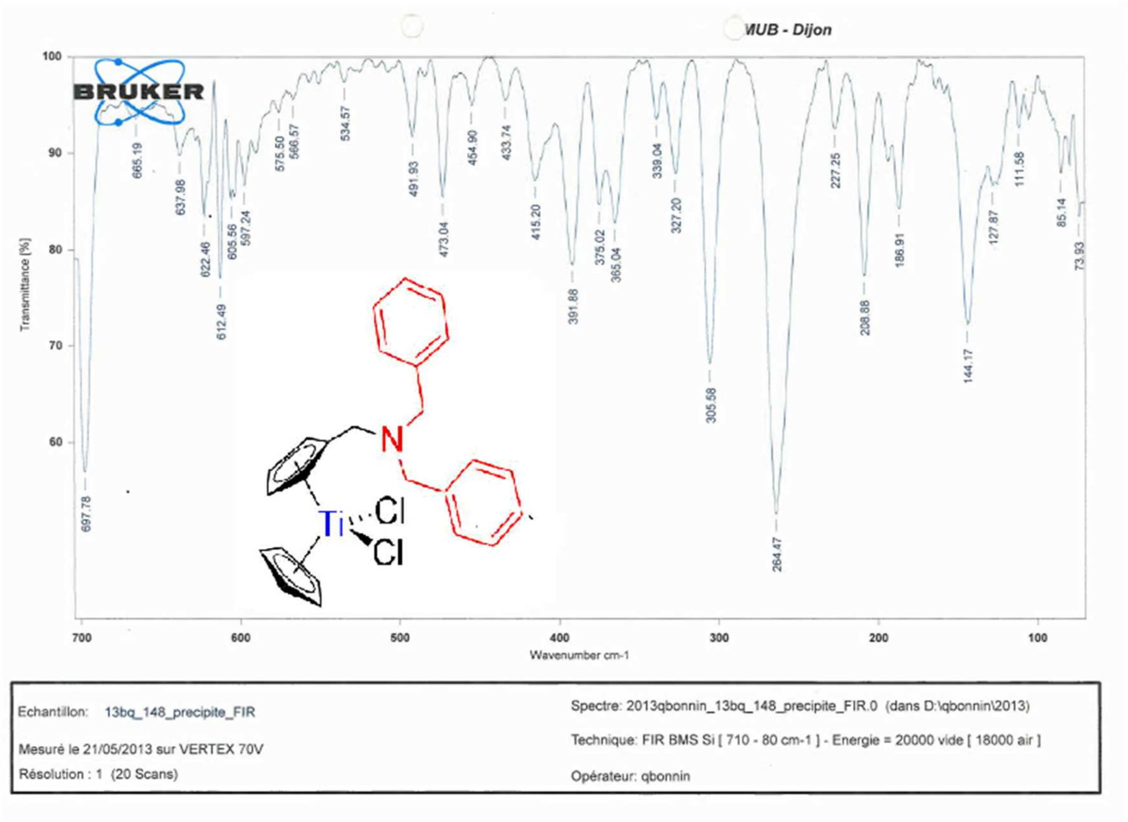
Résolution : 1 (20 Scans)

Spectre: 2013qbonnin_13bq_148_precipite.0 (dans D:\qbonnin\2013)

Technique: MIR ATR A225 Diamant [7000 - 370 cm-1] - Energie = 3000

Opérateur: qbonnin

Spectrum 0-56: MIR of 11



Echantillon: 13bq_148_precipite_FIR

Mesuré le 21/05/2013 sur VERTEX 70V

Résolution : 1 (20 Scans)

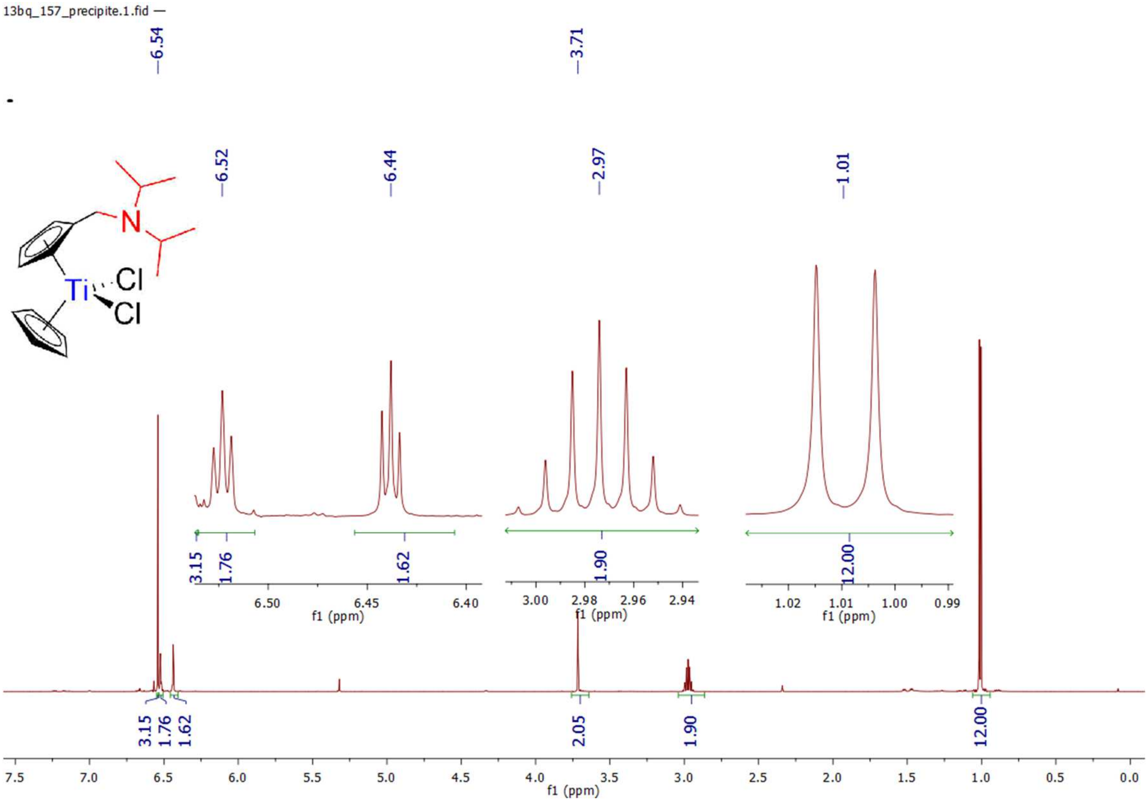
Spectre: 2013qbonnin_13bq_148_precipite_FIR.0 (dans D:\qbonnin\2013)

Technique: FIR BMS Si [710 - 80 cm-1] - Energie = 20000 vide [18000 air]

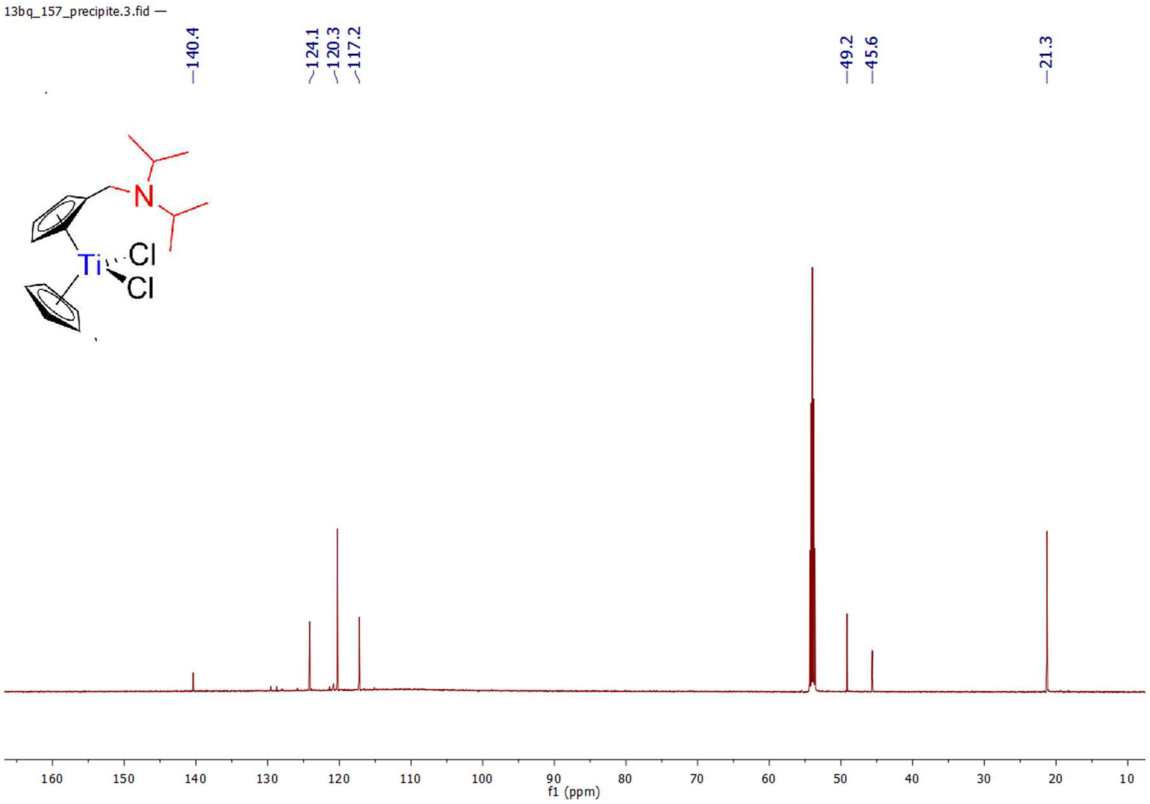
Opérateur: qbonnin

Spectrum 0-57: FIR of 11

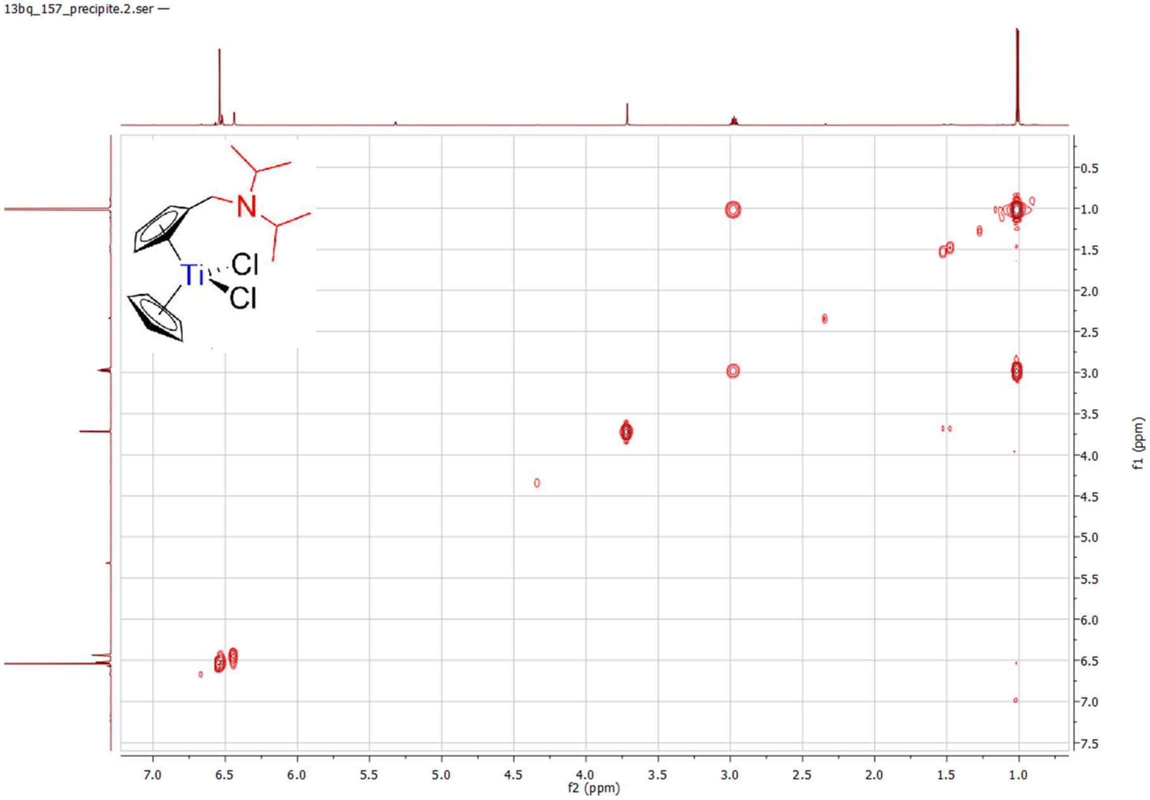
9. Compound **12**:



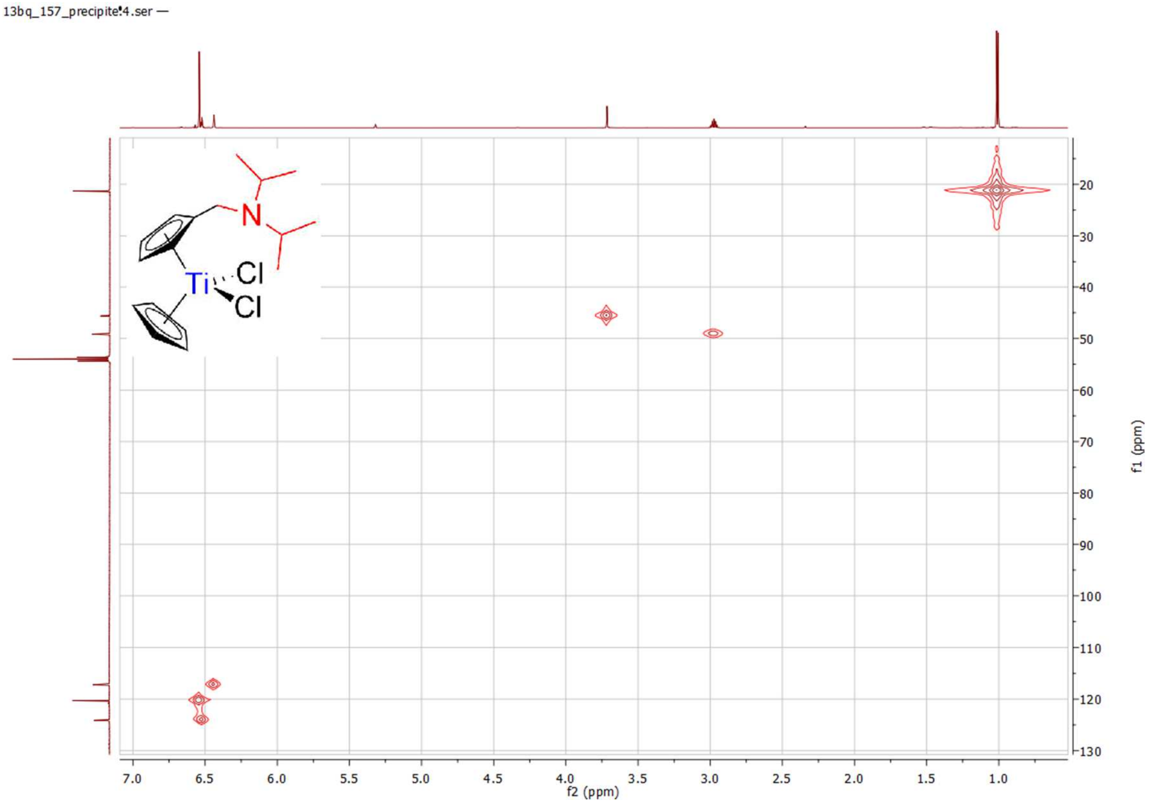
Spectrum 0-58: ^{1}H NMR of 12 (600.23 MHz, 300 K, dichloromethane-d$_2$)



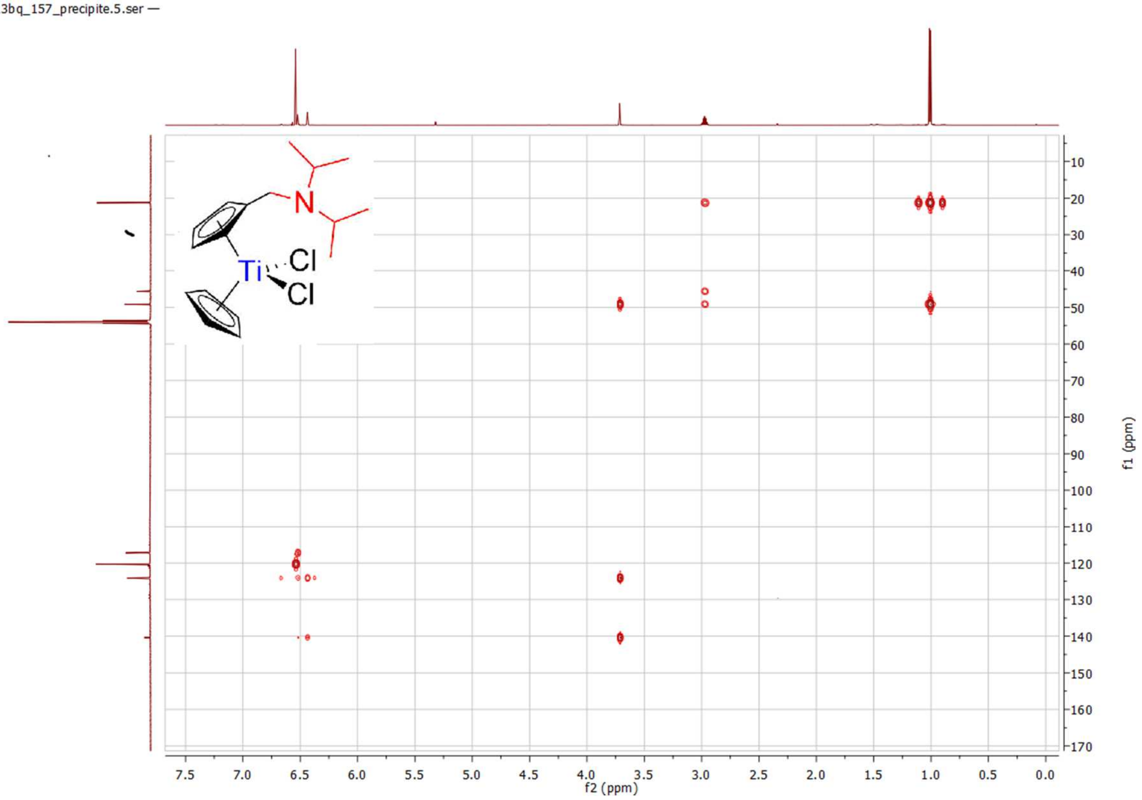
Spectrum 0-59: $^{13}C\{^{1}H\}$ NMR of 12 (150.94 MHz, 300 K, dichloromethane-d_2)



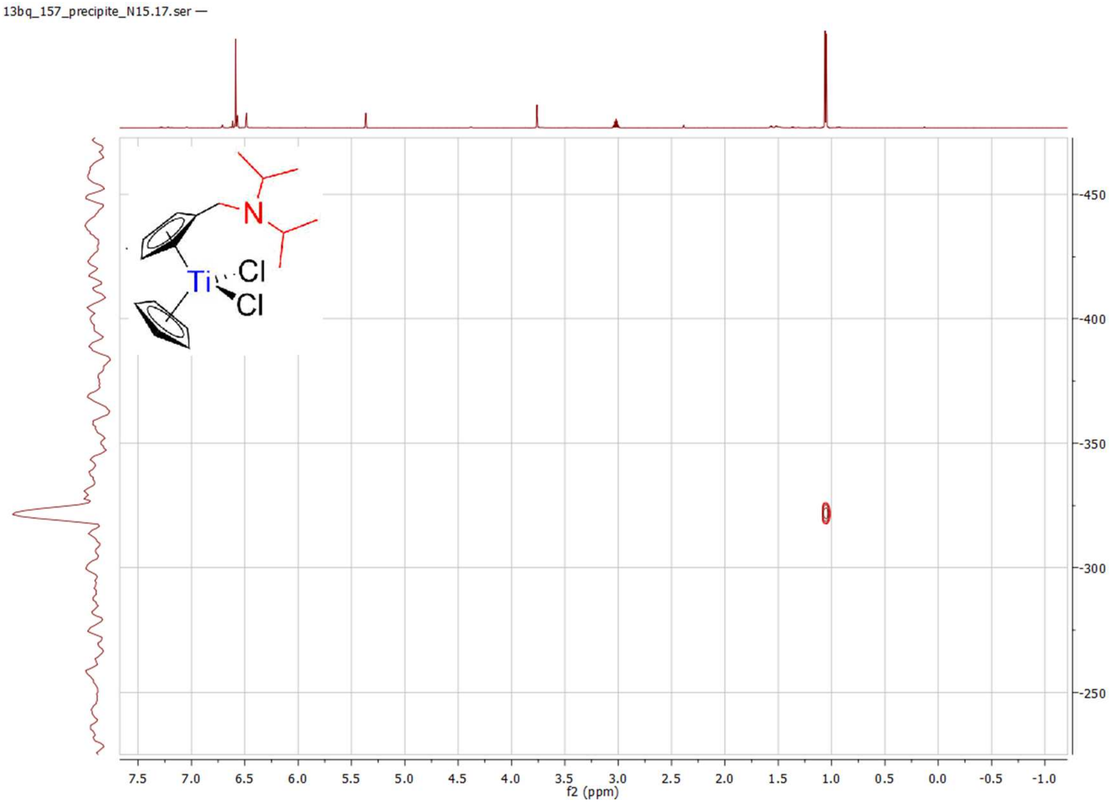
Spectrum 0-60: ^{1}H ^{1}H COSY of 12 (600.23 MHz, 300 K, dichloromethane-d_2)



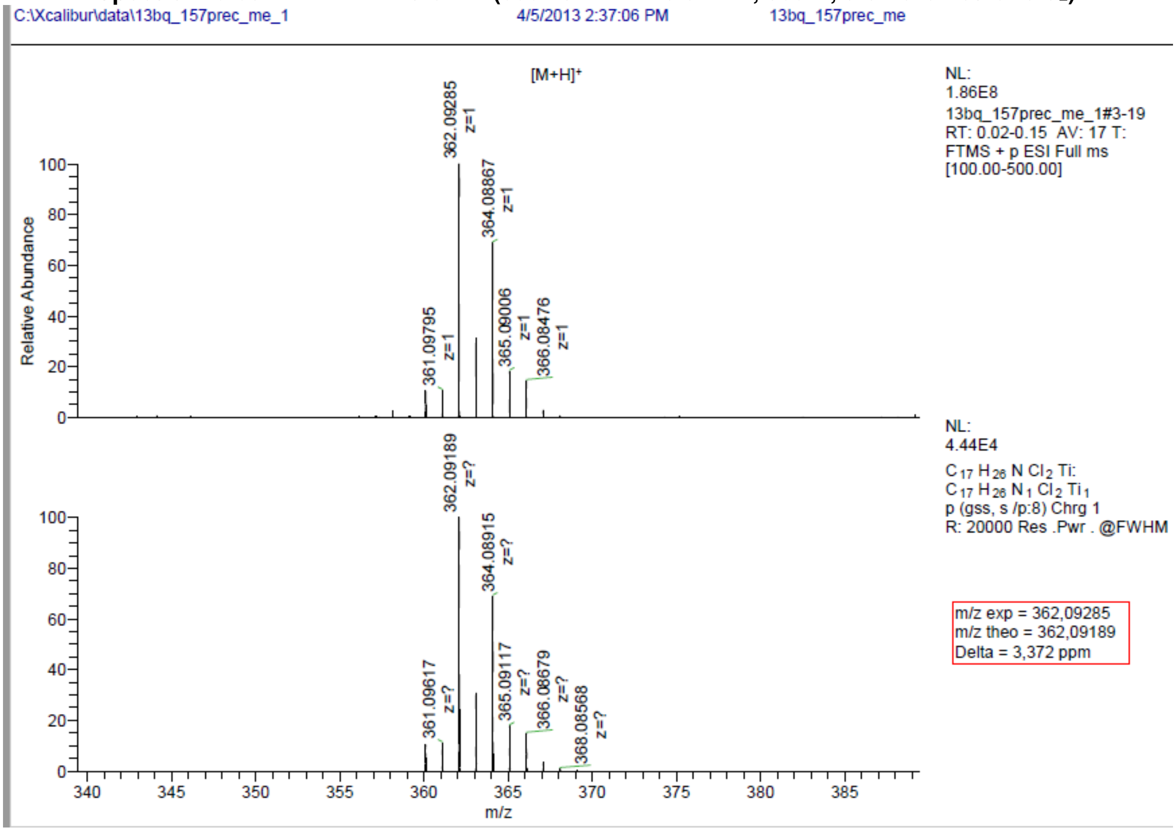
Spectrum 0-61: ^1H ^{13}C HMQC of 12 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-62: ^1H ^{13}C HMBC of 12 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-63: ^{1}H ^{15}N HMBC of 12 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2)

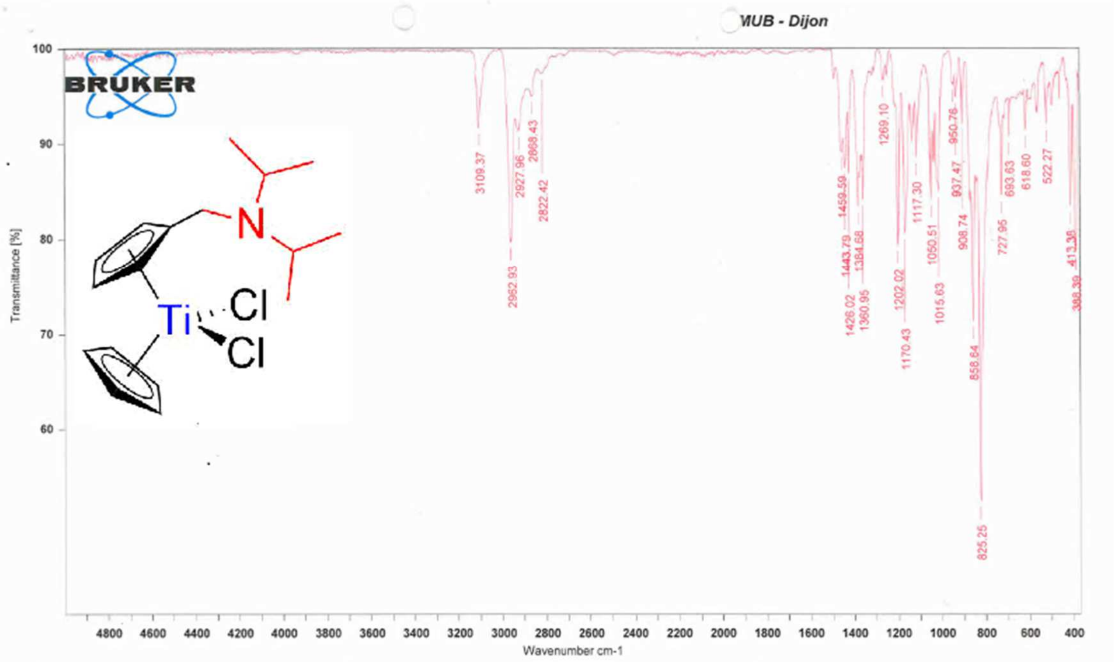

C:\Xcalibur\data\13bq_157prec_me_1 4/5/2013 2:37:06 PM 13bq_157prec_me

NL:
1.86E8
13bq_157prec_me_1#3-19
RT: 0.02-0.15 AV: 17 T:
FTMS + p ESI Full ms
[100.00-500.00]

NL:
4.44E4
$C_{17}H_{26}NCl_2Ti$:
$C_{17}H_{26}N_1Cl_2Ti_1$
p (gss, s /p:8) Chrg 1
R: 20000 Res .Pwr . @FWHM

m/z exp = 362,09285
m/z theo = 362,09189
Delta = 3,372 ppm

Spectrum 0-64 : HRMS of 12 (Positive mode ESI, dichloromethane)



Echantillon: 13bq_157_precipite _ MIR

Mesuré le 21/05/2013 sur VERTEX 70V

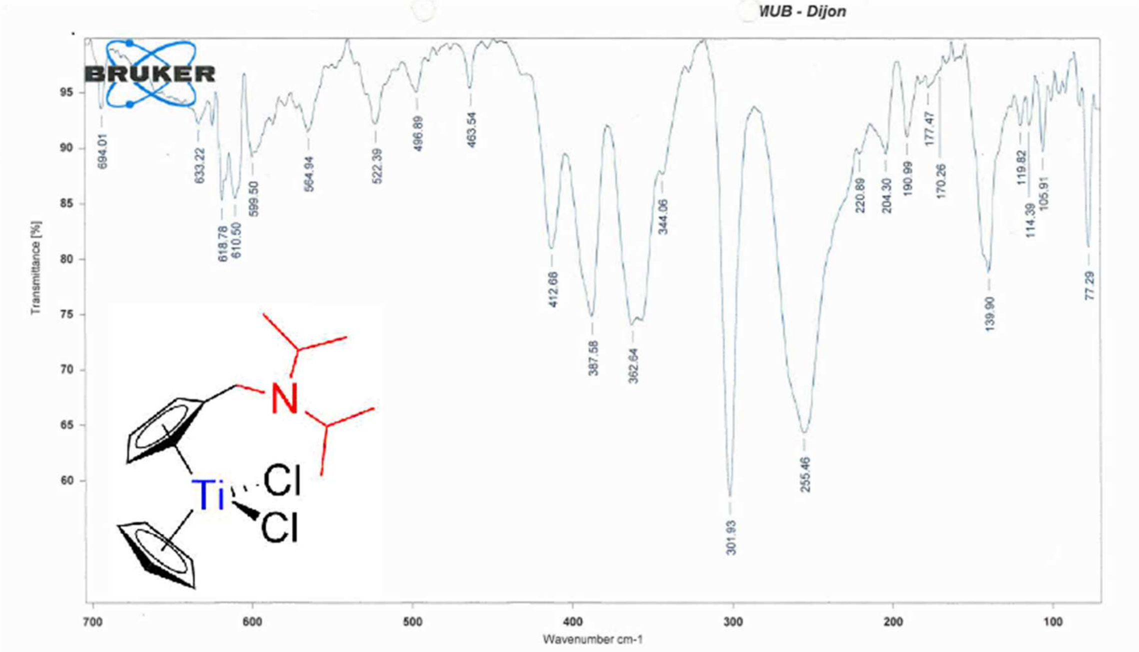
Résolution : 1 (20 Scans)

Spectre: 2013qbonnin_13bq_157_precipite.0 (dans D:\qbonnin\2013)

Technique: MIR ATR A225 Diamant [7000 - 370 cm-1] - Energie = 3000

Opérateur: qbonnin

Spectrum 0-65 : MIR of 12



Echantillon: 13bq_157_precipite_FIR

Mesuré le 21/05/2013 sur VERTEX 70V

Résolution : 1 (20 Scans)

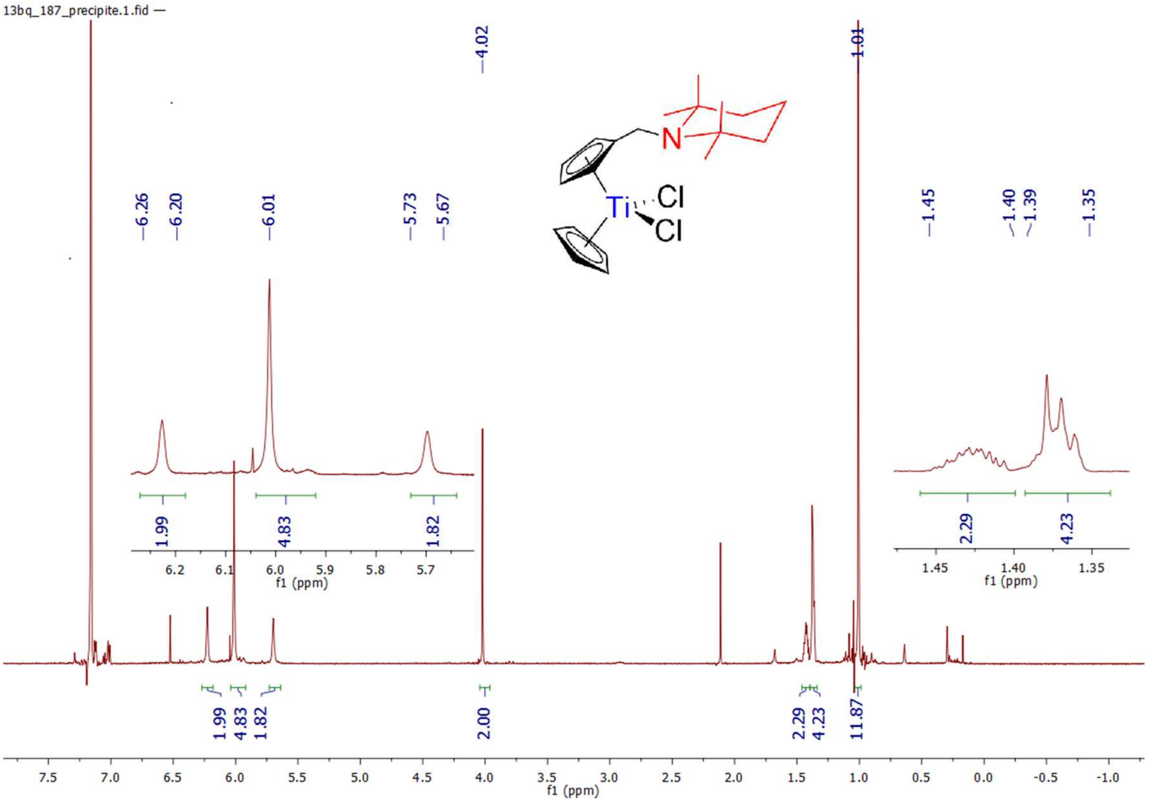
Spectre: 2013qbonnin_13bq_157_precipite_FIR00.0 (dans D:\qbonnin\2013)

Technique: FIR BMS Si [710 - 80 cm-1] - Energie = 20000 vide [18000 air]

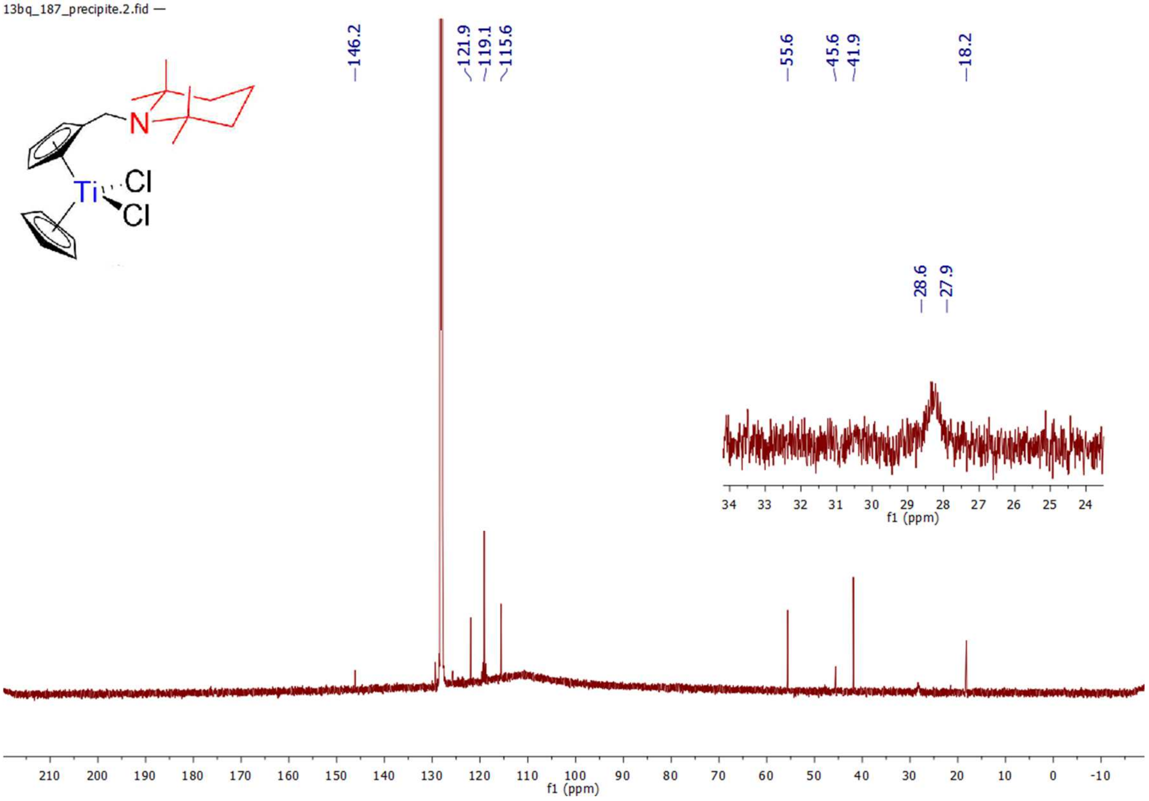
Opérateur: qbonnin

Spectrum 0-66 : FIR of 12

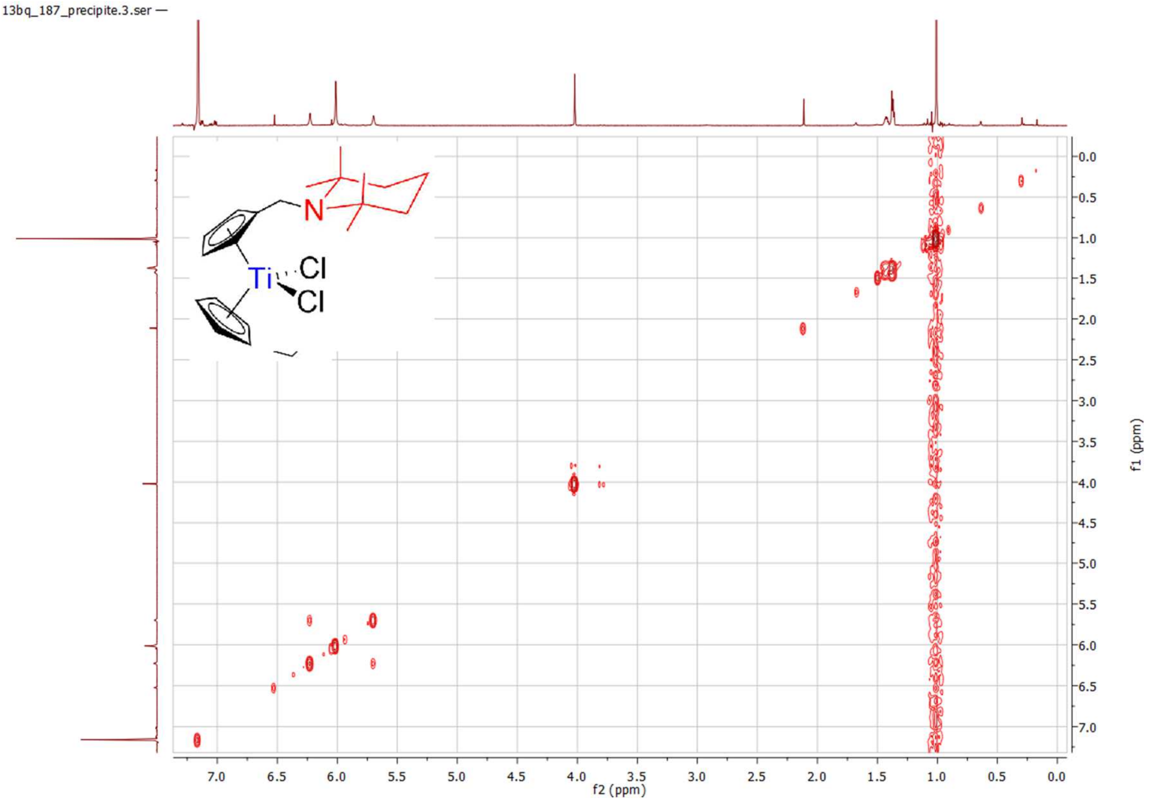
10. Compound **13**:



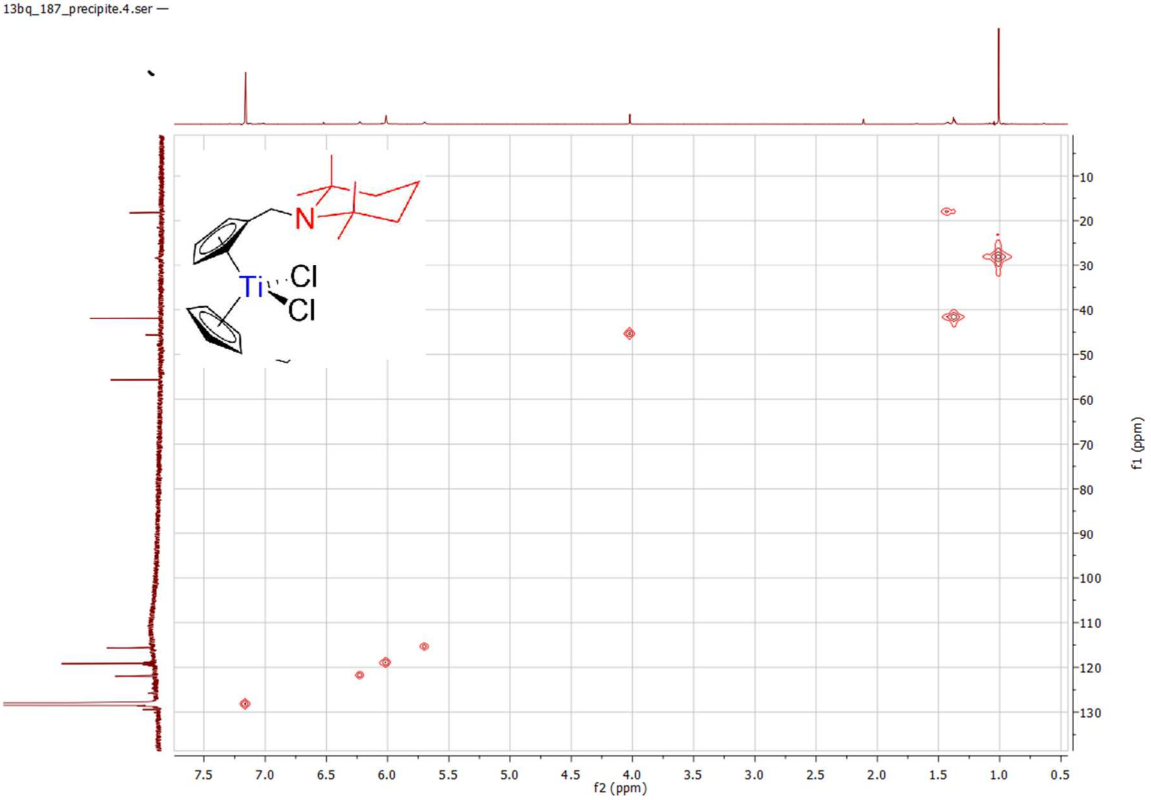
Spectrum 0-67: ^{1}H NMR of 13 (600.23 MHz, 300 K, dichloromethane-d_2)



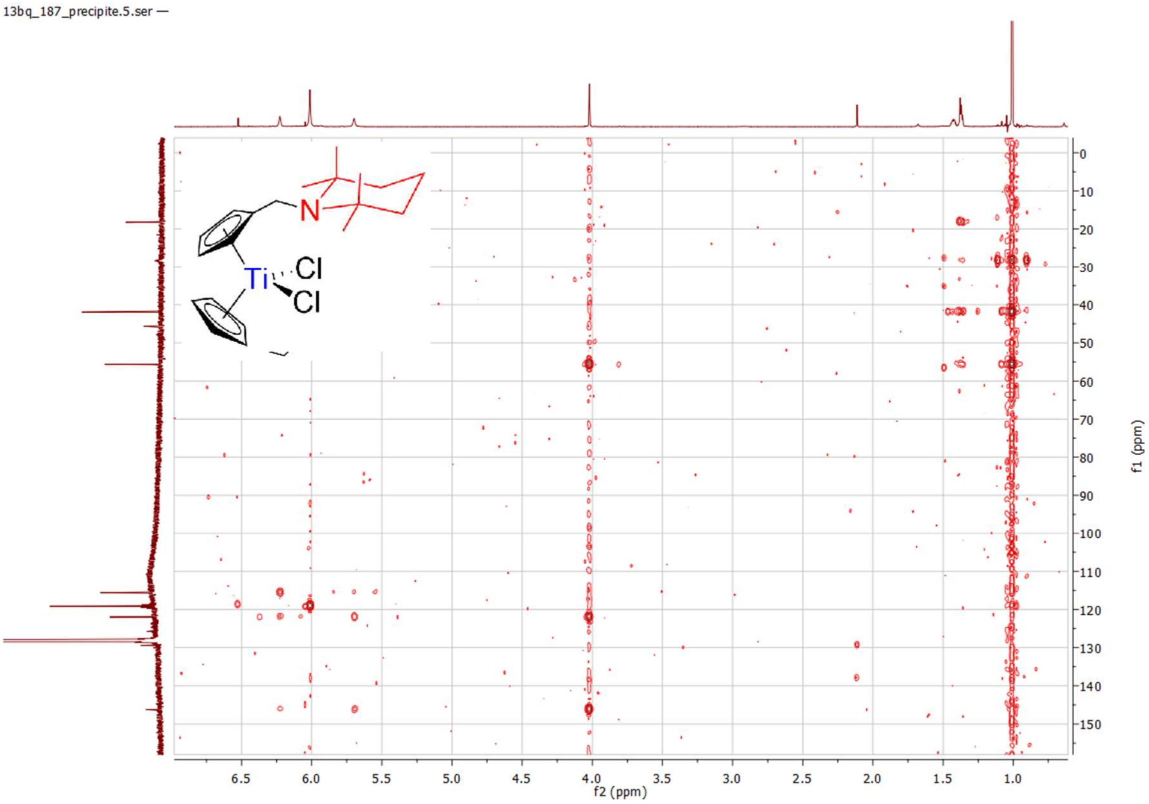
Spectrum 0-68: ^{13}C{^{1}H} NMR of 13 (150.94 MHz, 300 K, dichloromethane-d_2)



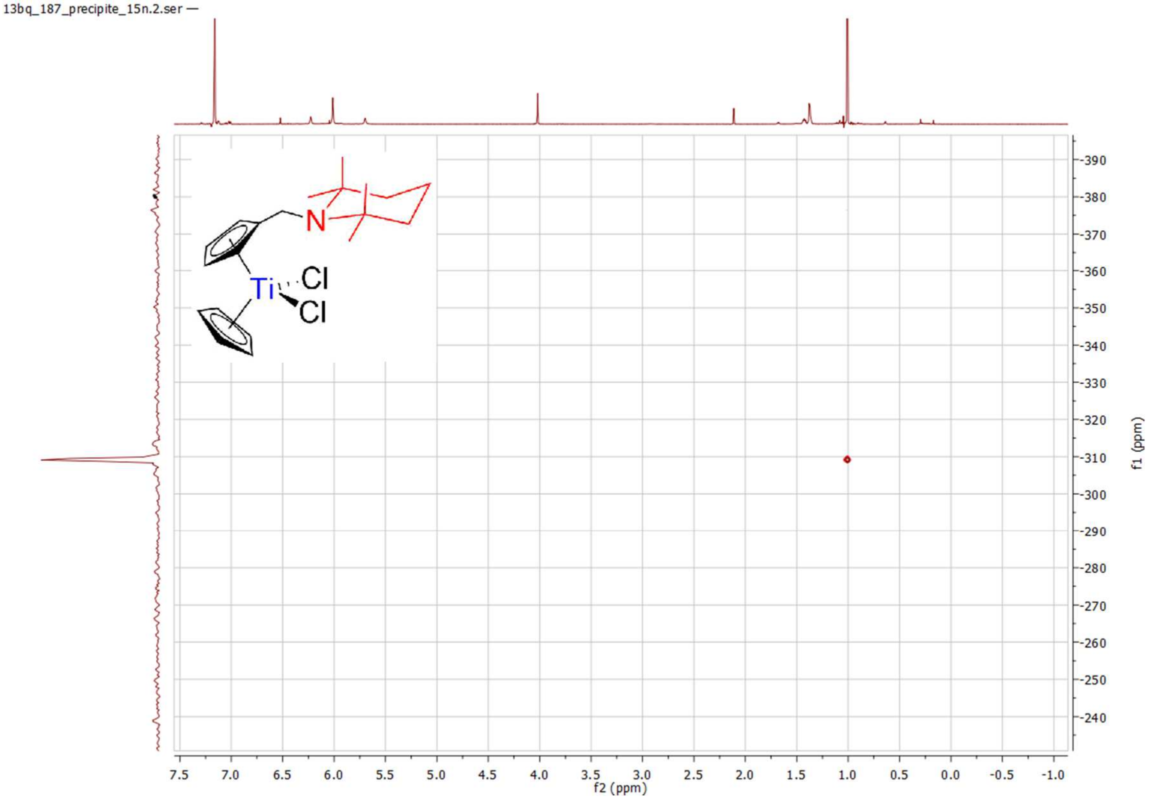
Spectrum 0-69: ^{1}H ^{1}H COSY of 13 (600.23 MHz, 300 K, dichloromethane-d_2)



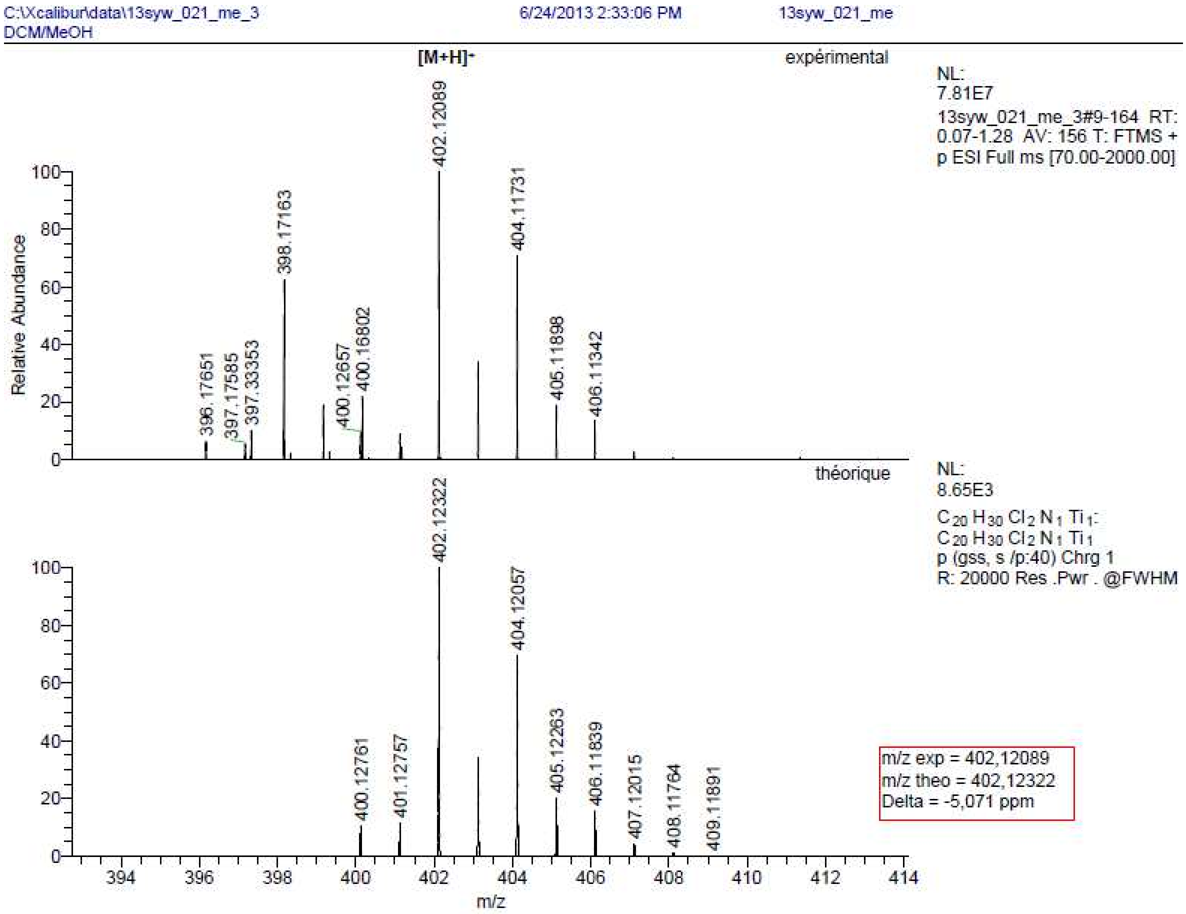
Spectrum 0-70: ^{1}H ^{13}C HMQC of 13 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



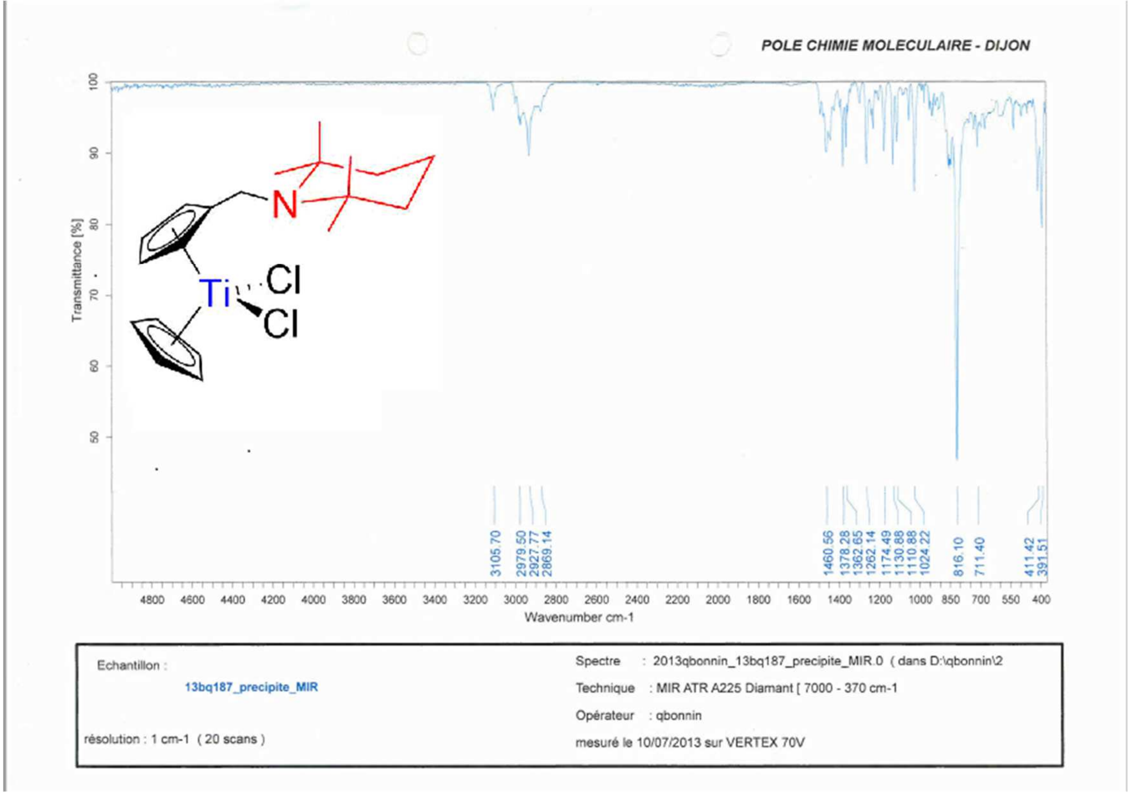
Spectrum 0-71: ^{1}H ^{13}C HMBC of 13 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



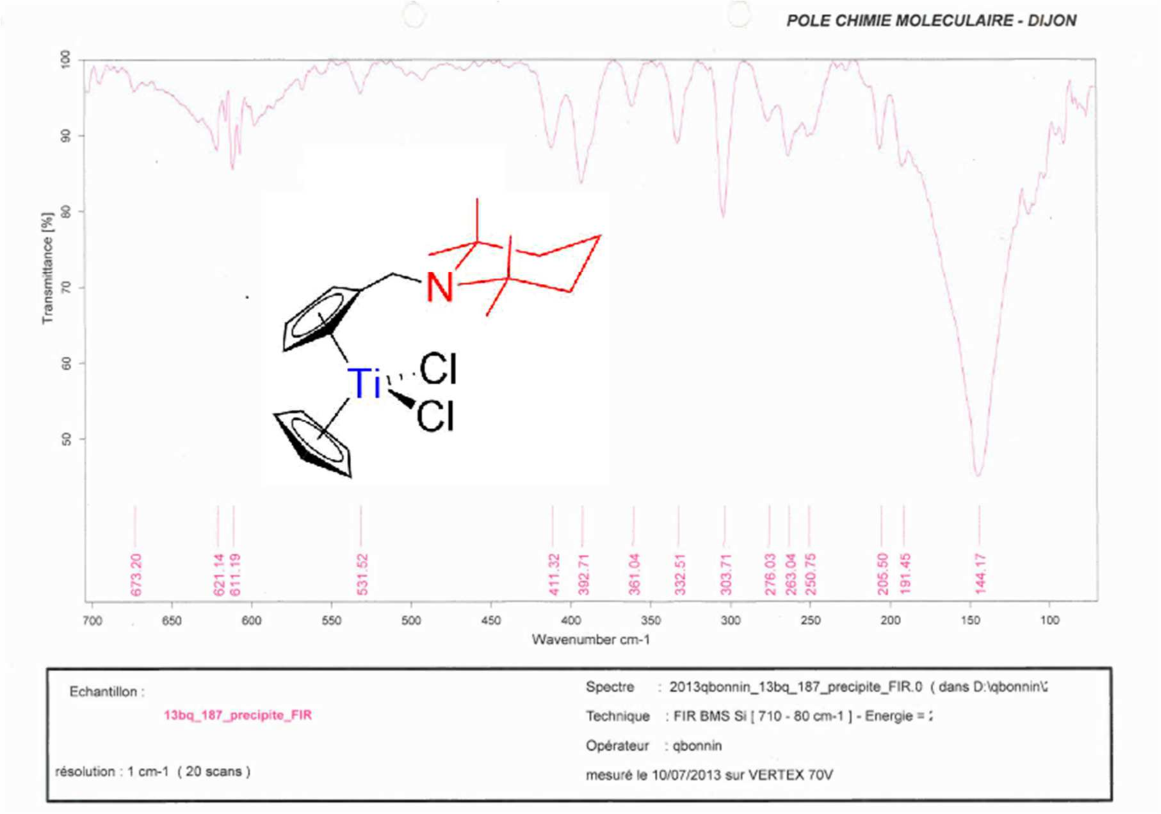
Spectrum 0-72: ^{1}H ^{15}N HMBC of 13 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-73: HRMS of 13 (Positive mode ESI, dichloromethane)

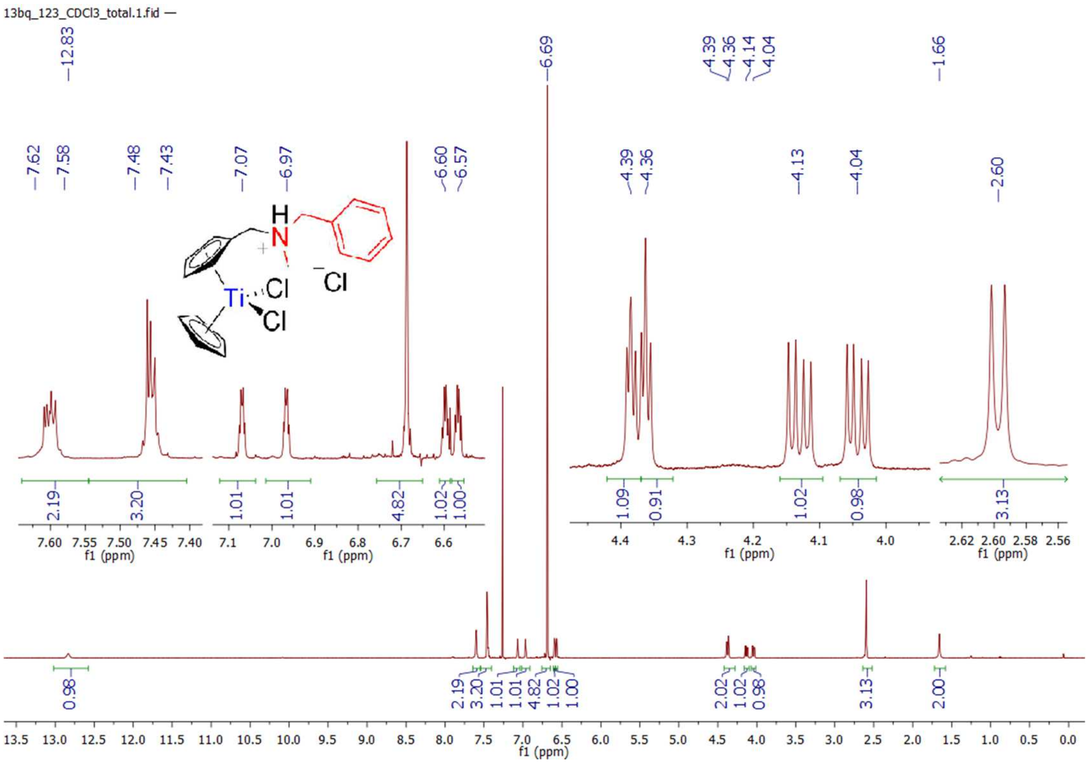


Spectrum 0-74: MIR of 13

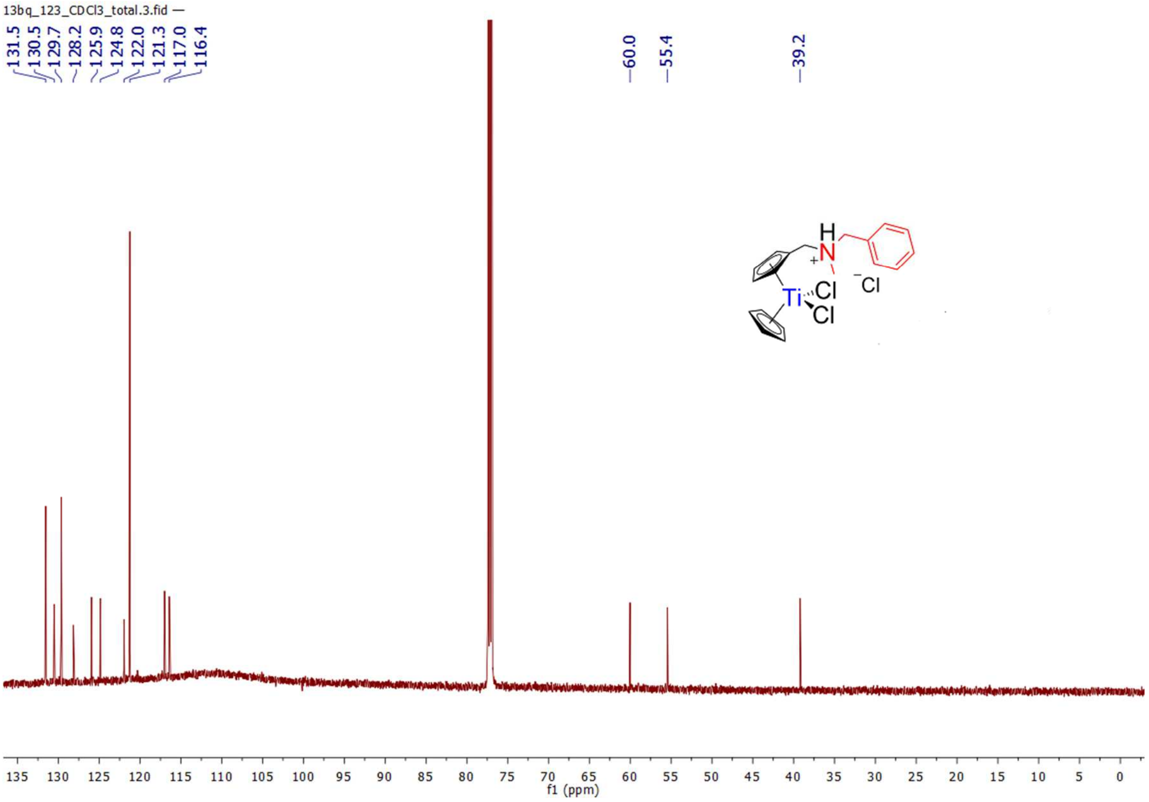


Spectrum 0-75: FIR of 13

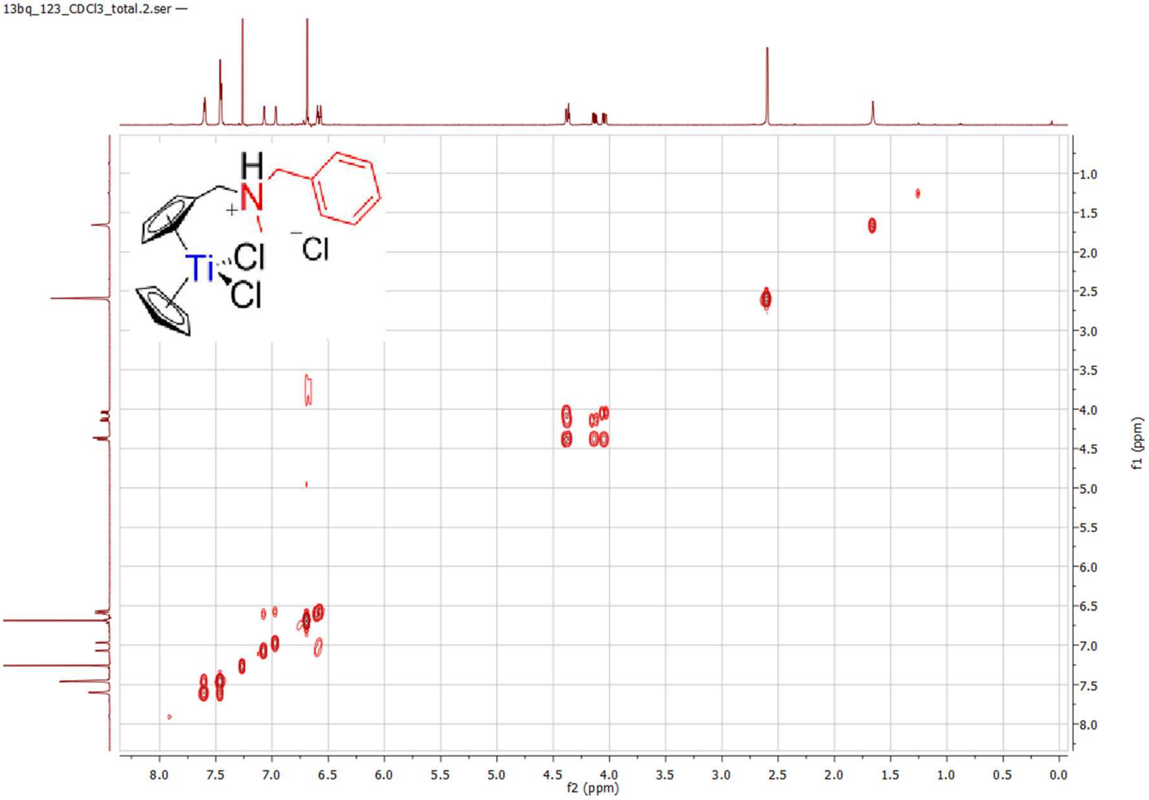
11. Compound **14**:



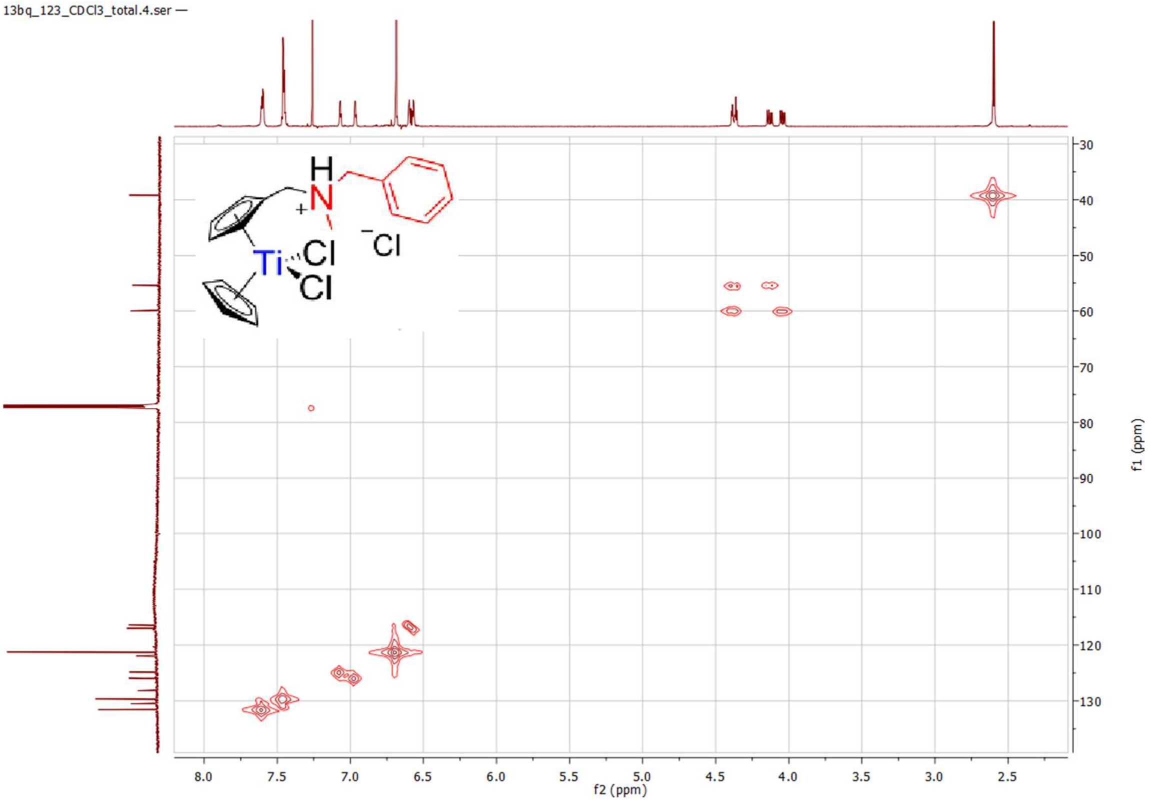
Spectrum 0-76: ^{1}H NMR of 14 (600 MHz, 300 K, chloroform-d$_1$)



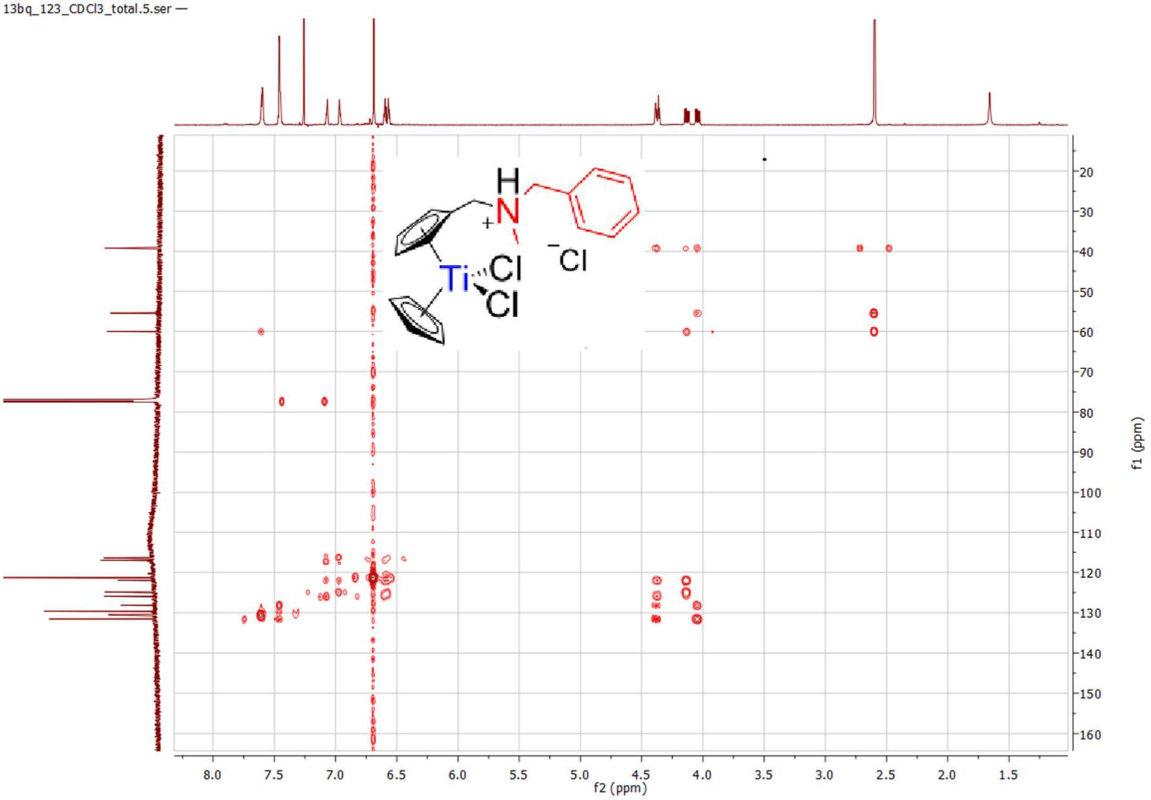
Spectrum 0-77: $^{13}C\{^1H\}$ NMR of 14 (150.94 MHz, 300 K, chloroform-d_1)



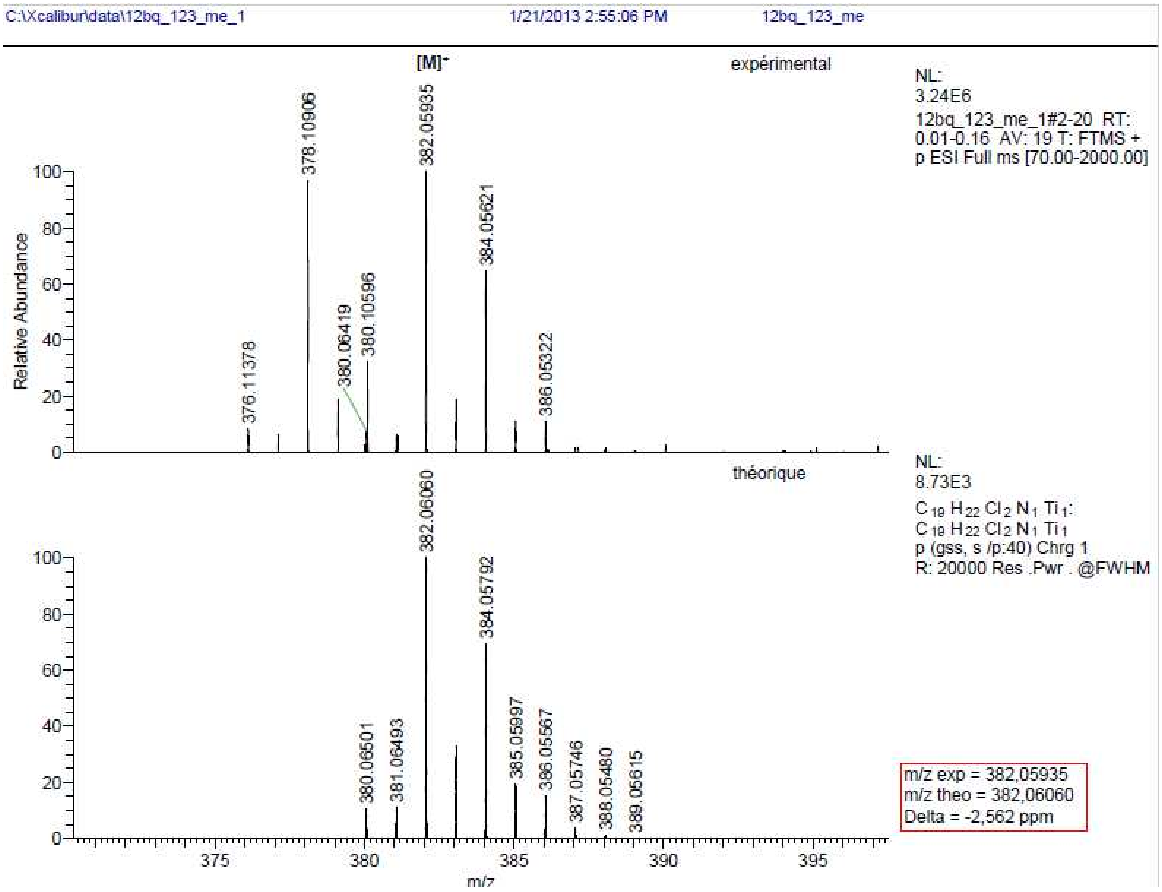
Spectrum 0-78: ^1H ^1H COSY of 14 (500.03 MHz, 300 K, chloroform-d_1)



Spectrum 0-79: ^{1}H ^{13}C HMQC of 14 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$)



Spectrum 0-80: ^{1}H ^{13}C HMBC of 14 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$)



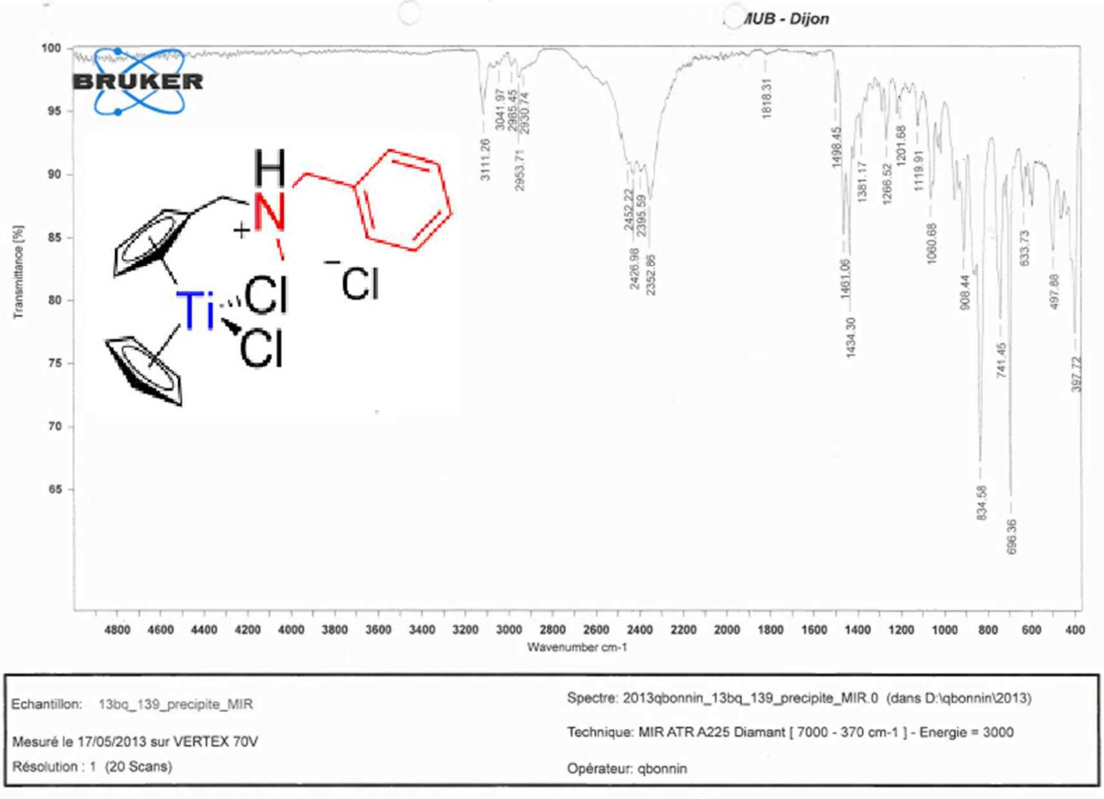
C:\Xcalibur\data\12bq_123_me_1 1/21/2013 2:55:06 PM 12bq_123_me

NL:
3.24E6
12bq_123_me_1#2-20 RT: 0.01-0.16 AV: 19 T: FTMS + p ESI Full ms [70.00-2000.00]

NL:
8.73E3
$C_{19}H_{22}Cl_2N_1Ti_1$:
$C_{19}H_{22}Cl_2N_1Ti_1$
p (gss, s /p:40) Chrg 1
R: 20000 Res .Pwr . @FWHM

m/z exp = 382,05935
m/z theo = 382,06060
Delta = -2,562 ppm

Spectrum 0-81: HRMS of 14 (Positive mode ESI, dichloromethane)



Echantillon: 13bq_139_precipite_MIR

Mesuré le 17/05/2013 sur VERTEX 70V

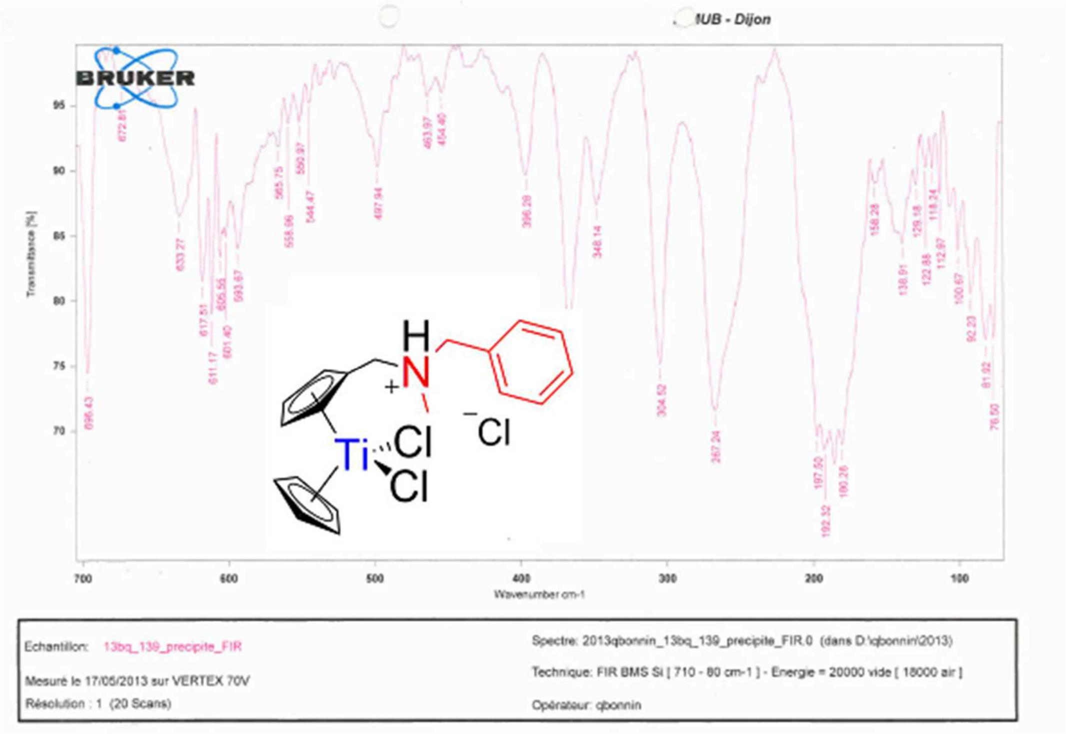
Résolution : 1 (20 Scans)

Spectre: 2013qbonnin_13bq_139_precipite_MIR.0 (dans D:\qbonnin\2013)

Technique: MIR ATR A225 Diamant [7000 - 370 cm-1] - Energie = 3000

Opérateur: qbonnin

Spectrum 0-82: MIR of 14



Echantillon: 13bq_139_precipite_FIR

Mesuré le 17/05/2013 sur VERTEX 70V

Résolution : 1 (20 Scans)

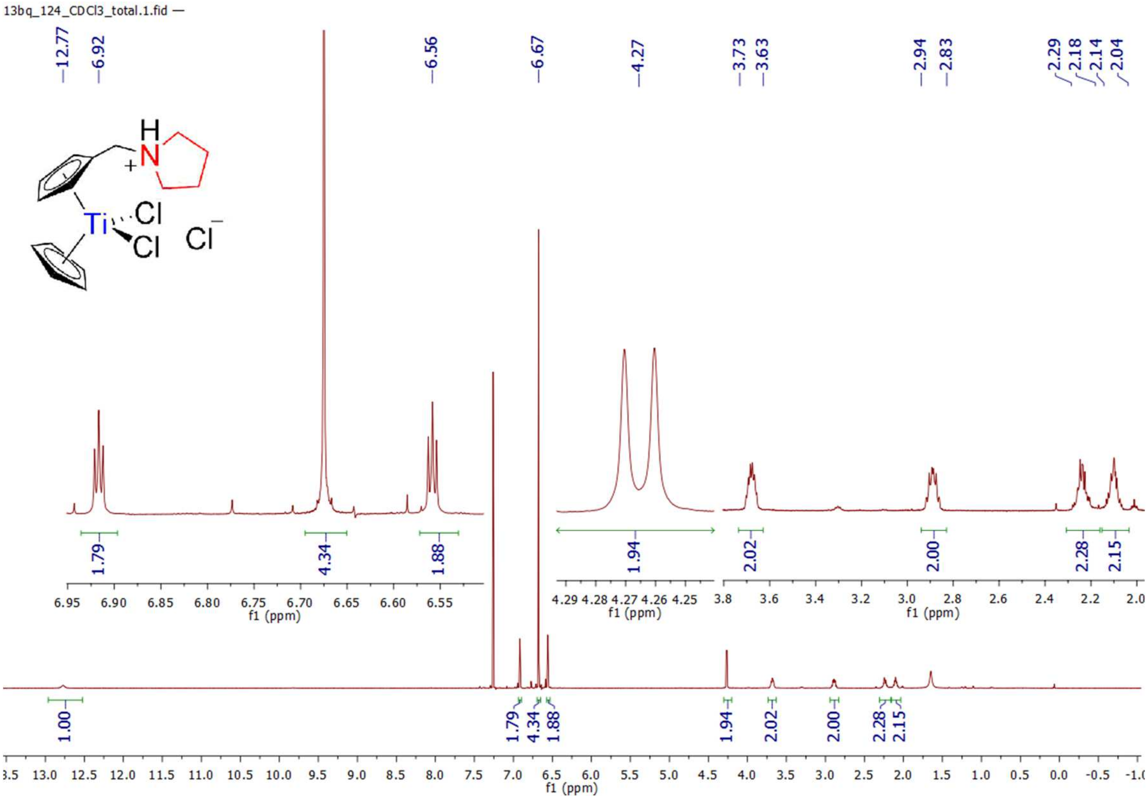
Spectre: 2013qbonnin_13bq_139_precipite_FIR.0 (dans D:\qbonnin\2013)

Technique: FIR BMS Si [710 - 80 cm-1] - Energie = 20000 vide [18000 air]

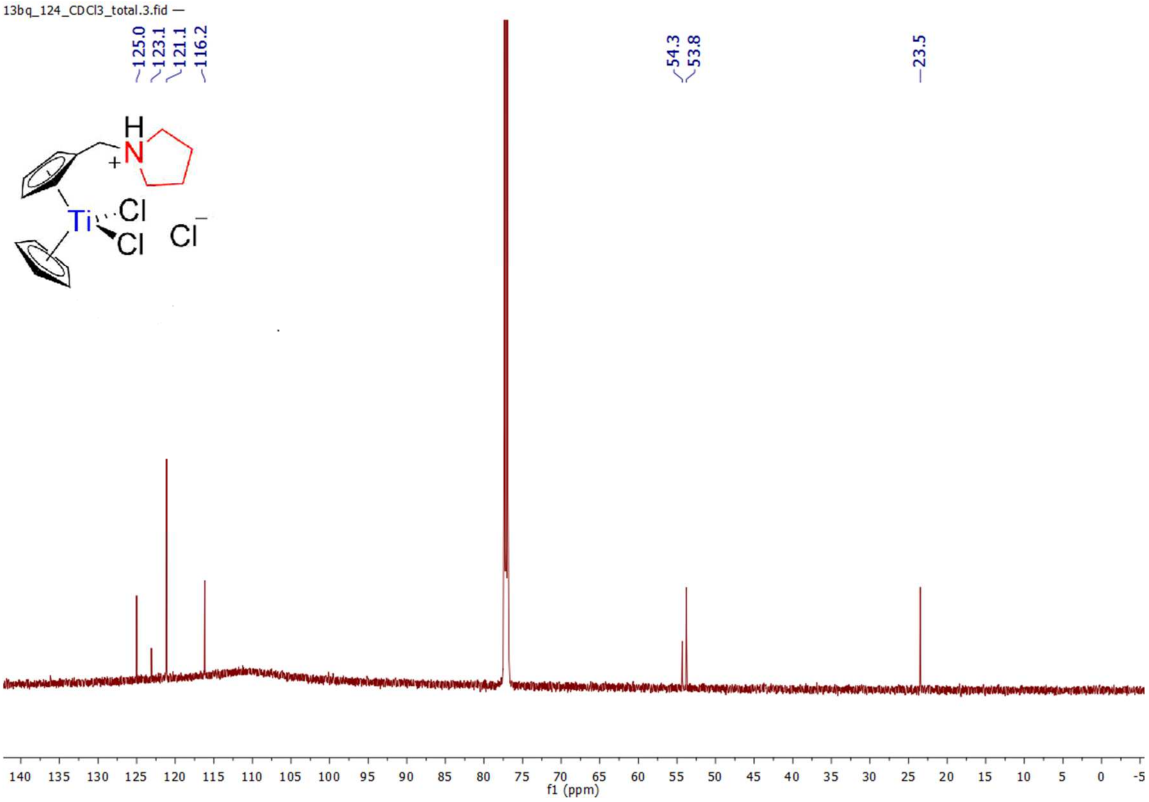
Opérateur: qbonnin

Spectrum 0-83: FIR of 14

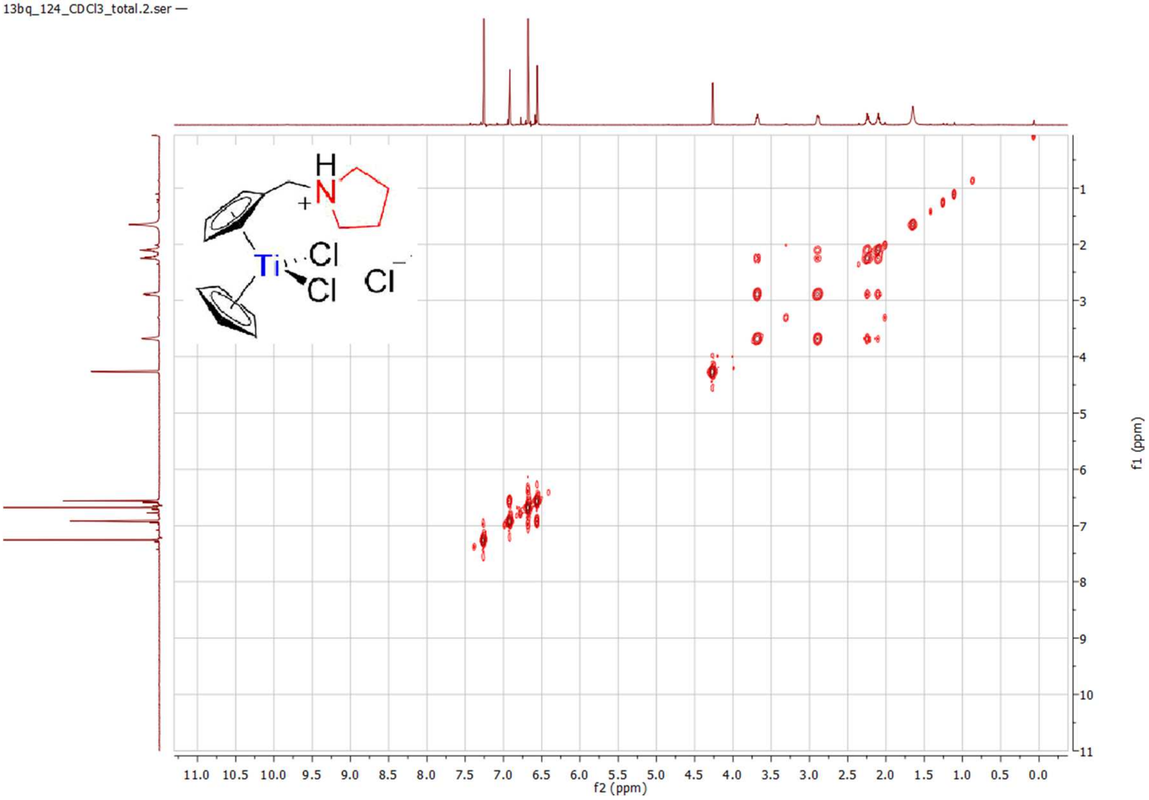
12. Compound **15**:



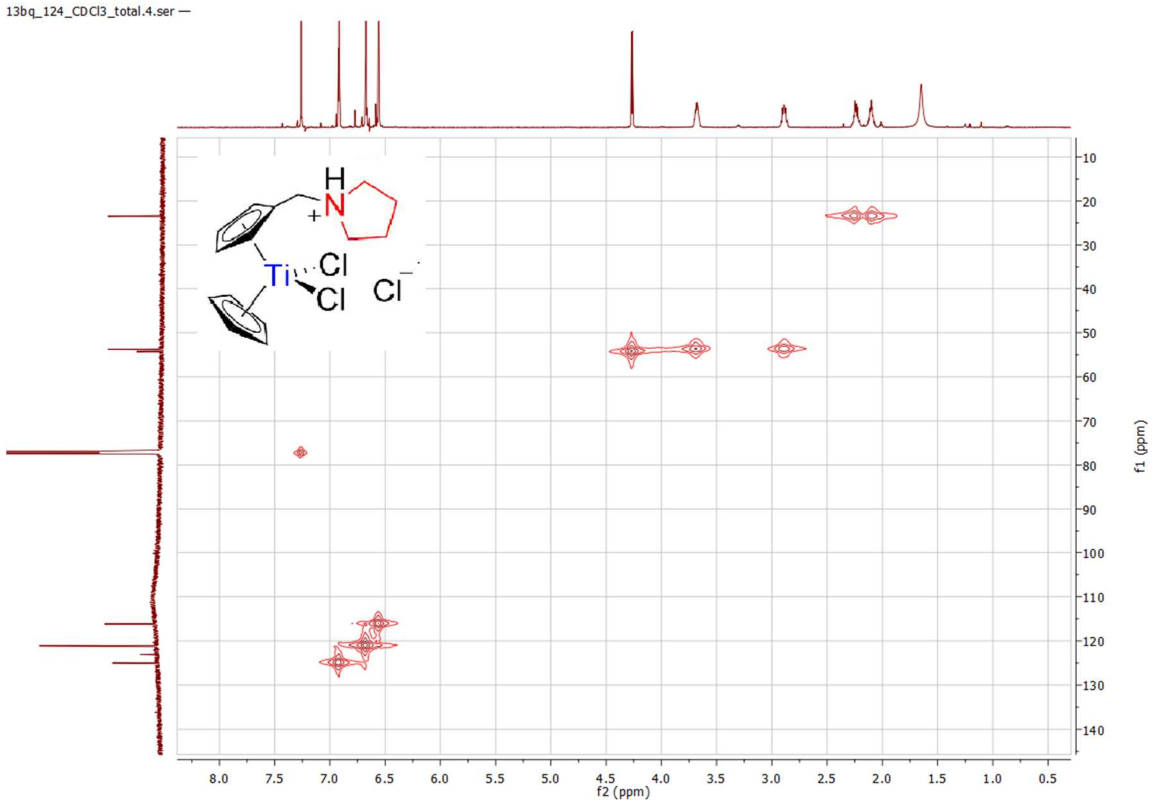
Spectrum 0-84: ^{1}H NMR of 15 (600 MHz, 300 K, chloroform-d$_1$)



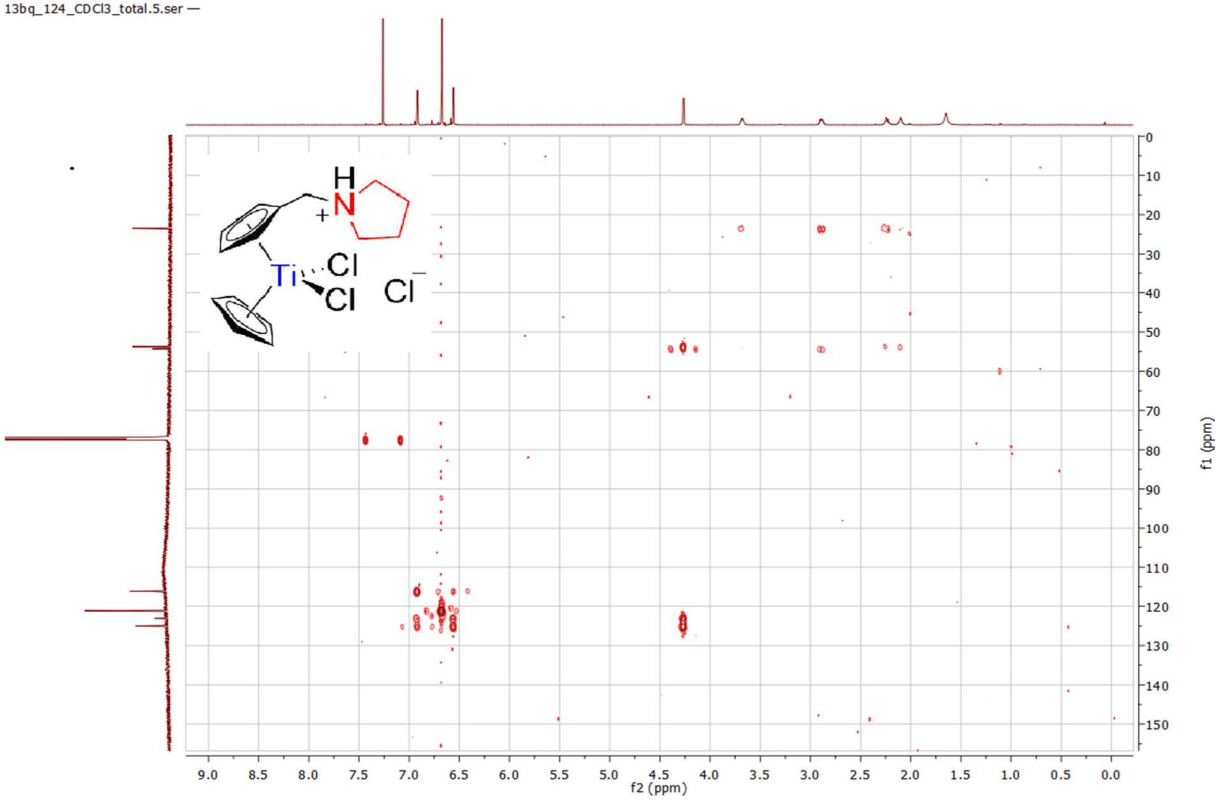
Spectrum 0-85: $^{13}C\{^{1}H\}$ NMR of 15 (150.94 MHz, 300 K, chloroform-d_1)



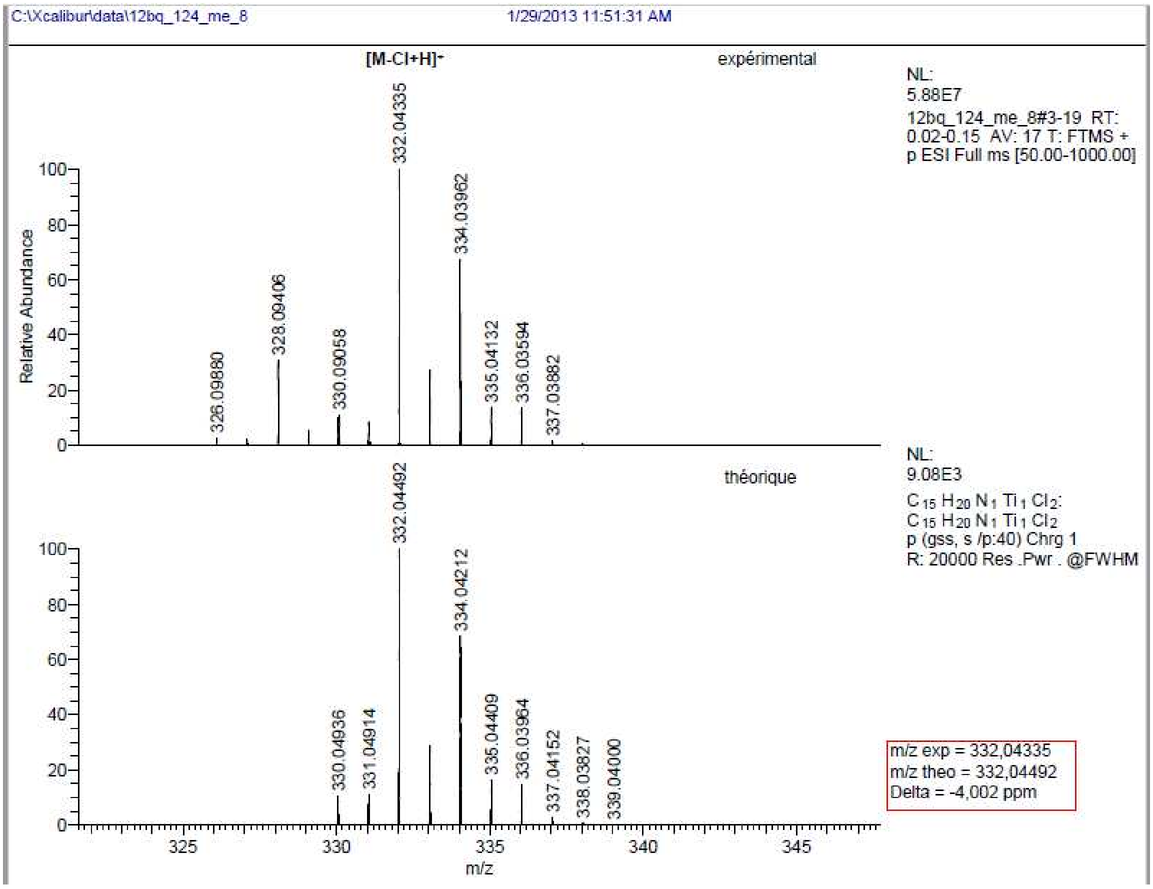
Spectrum 0-86: ^{1}H ^{1}H COSY of 15 (600.23 MHz, 300 K, chloroform-d_1



Spectrum 0-87: ^{1}H ^{13}C HMQC of 15 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$)

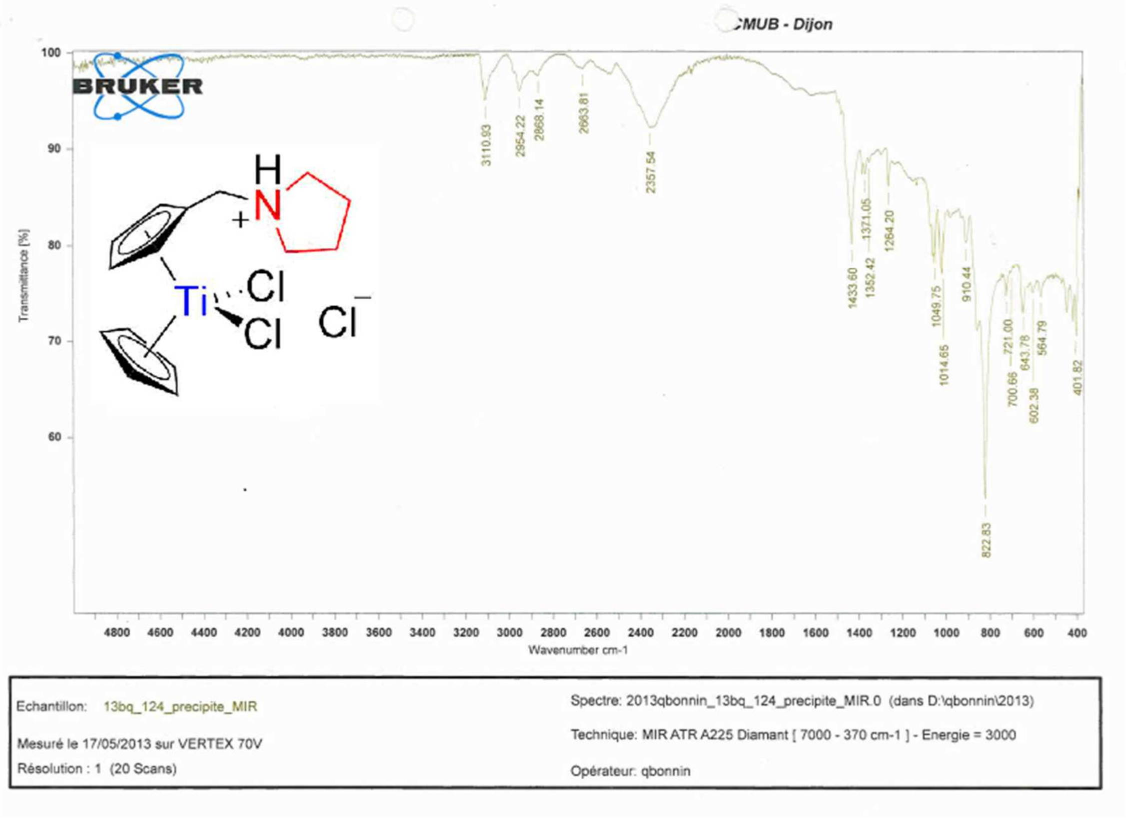


Spectrum 0-88: ^{1}H ^{13}C HMBC of 15 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d$_1$)



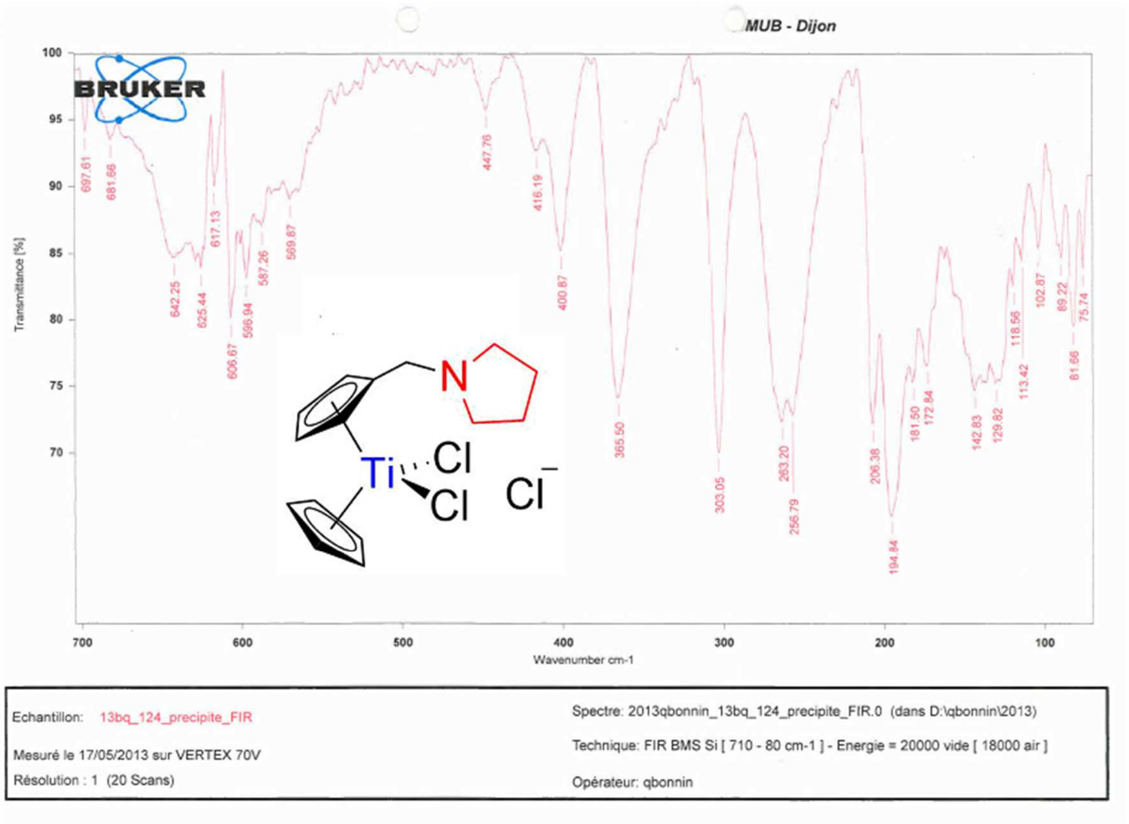
m/z exp = 332,04335
m/z theo = 332,04492
Delta = -4,002 ppm

Spectrum 0-89: HRMS of 15 (Positive mode ESI, dichloromethane)



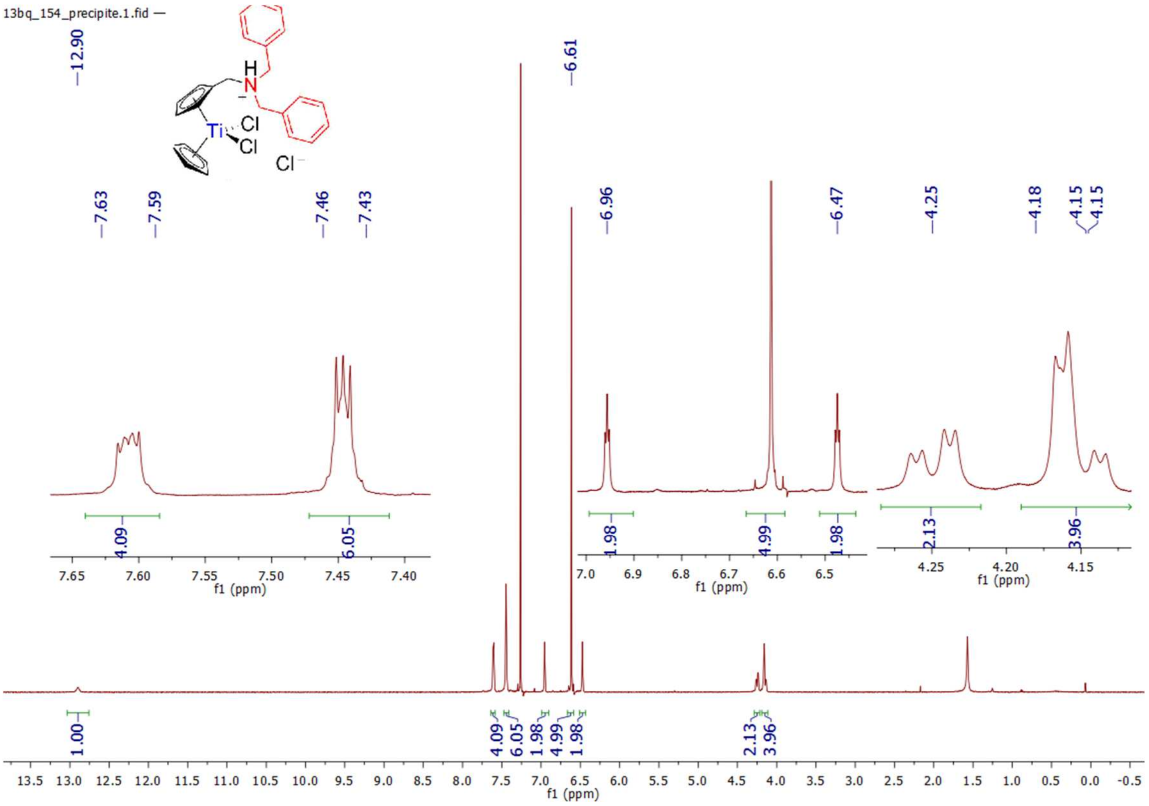
Echantillon: 13bq_124_precipite_MIR
Mesuré le 17/05/2013 sur VERTEX 70V
Résolution : 1 (20 Scans)
Spectre: 2013qbonnin_13bq_124_precipite_MIR.0 (dans D:\qbonnin\2013)
Technique: MIR ATR A225 Diamant [7000 - 370 cm-1] - Energie = 3000
Opérateur: qbonnin

Spectrum 0-90: MIR of 15

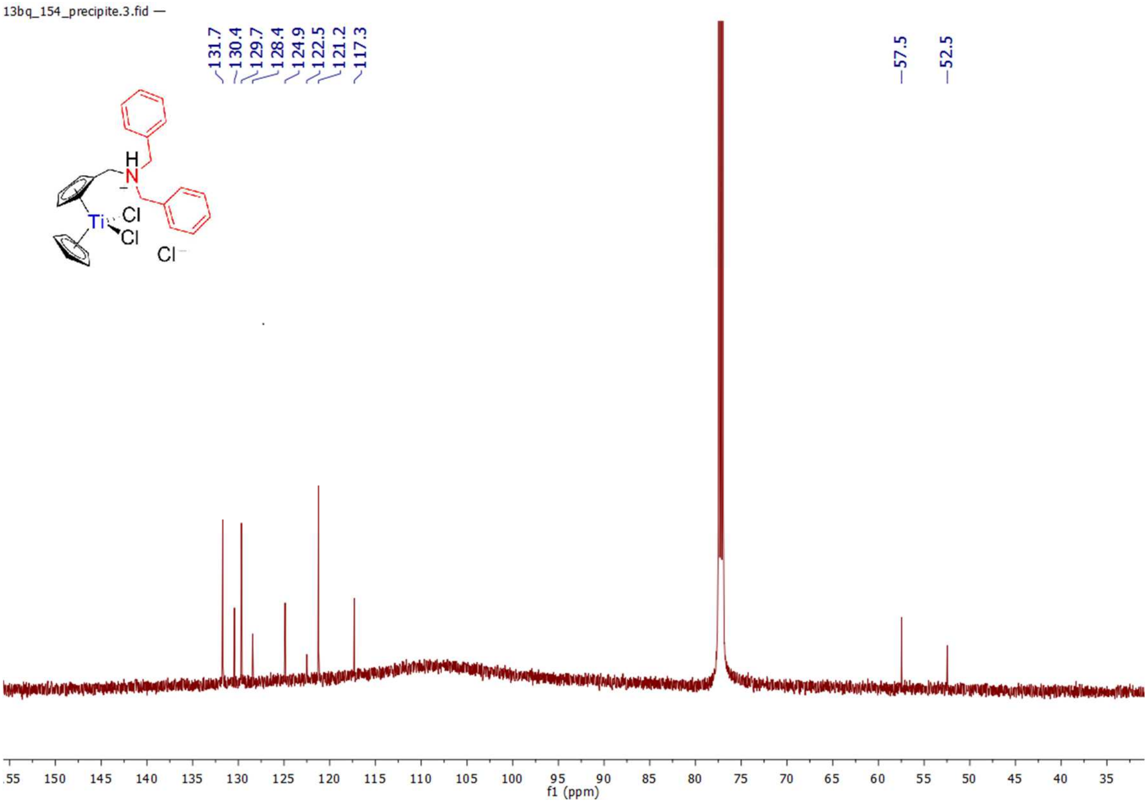


Spectrum 0-91: FIR of 15

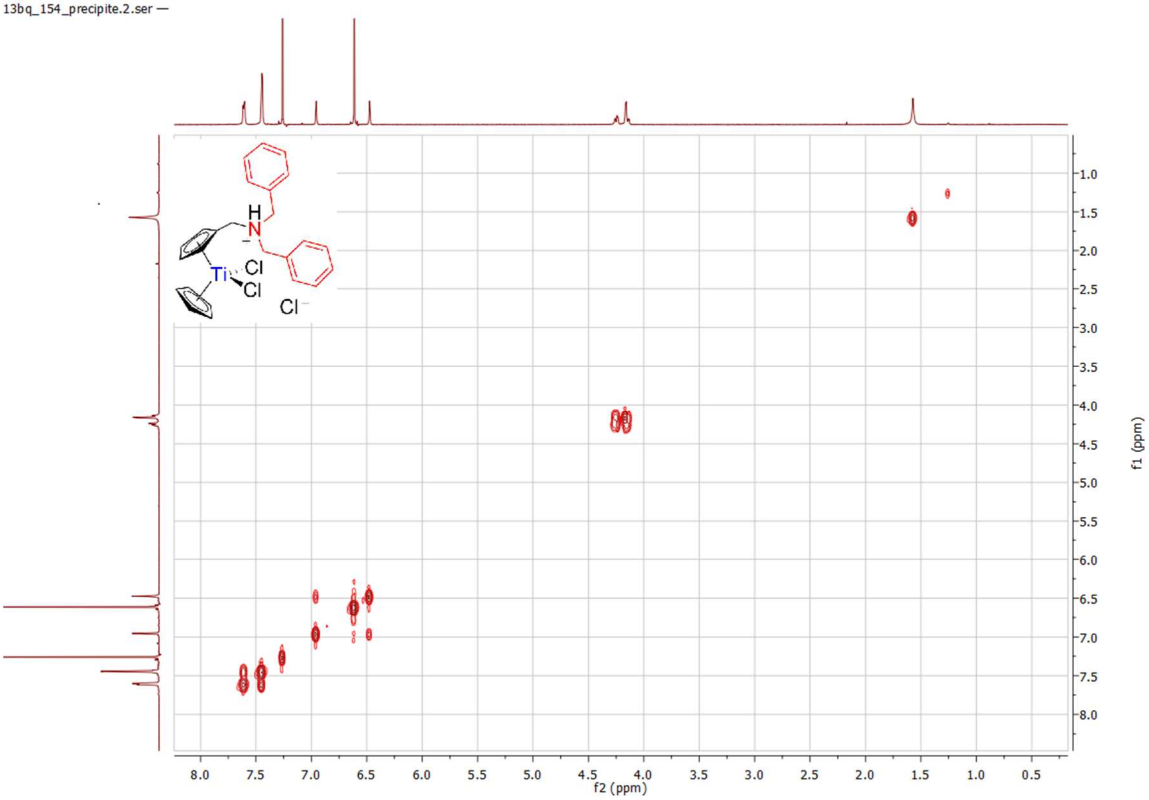
13. Compound **16**:



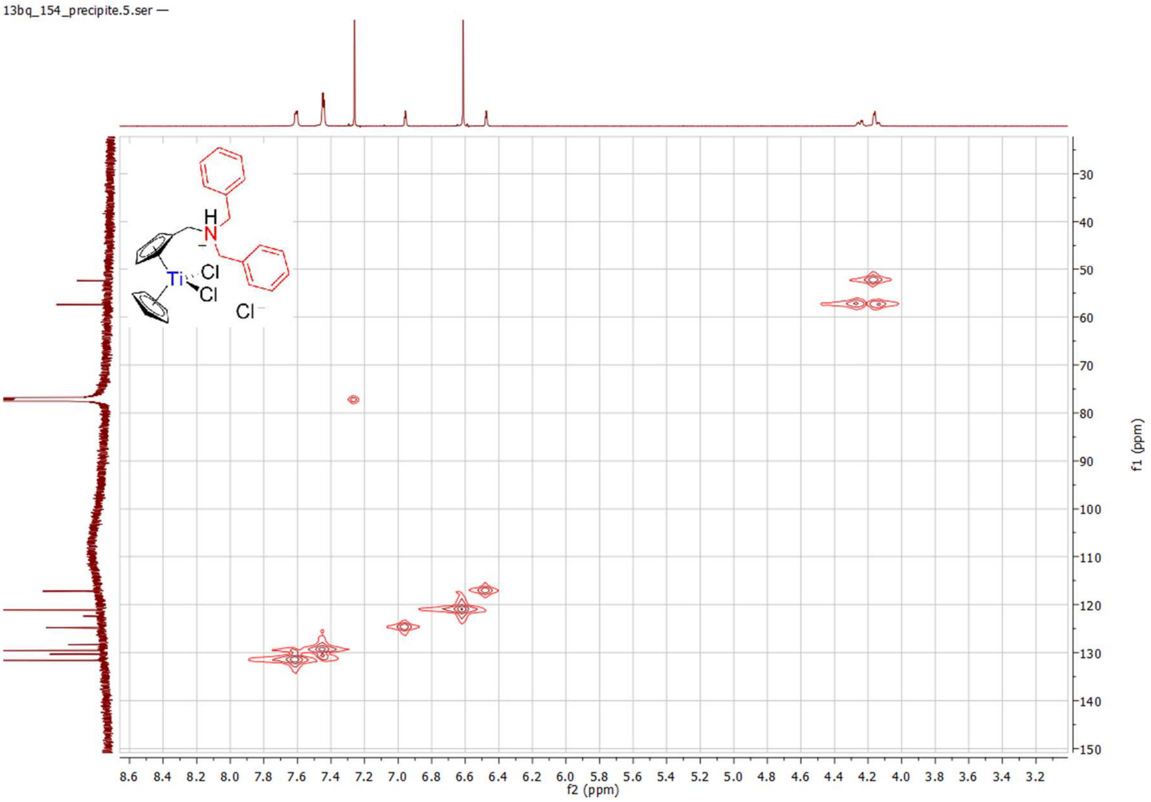
Spectrum 0-92: ^{1}H NMR of 16 (600.23 MHz, 300 K, chloroform-d$_1$)



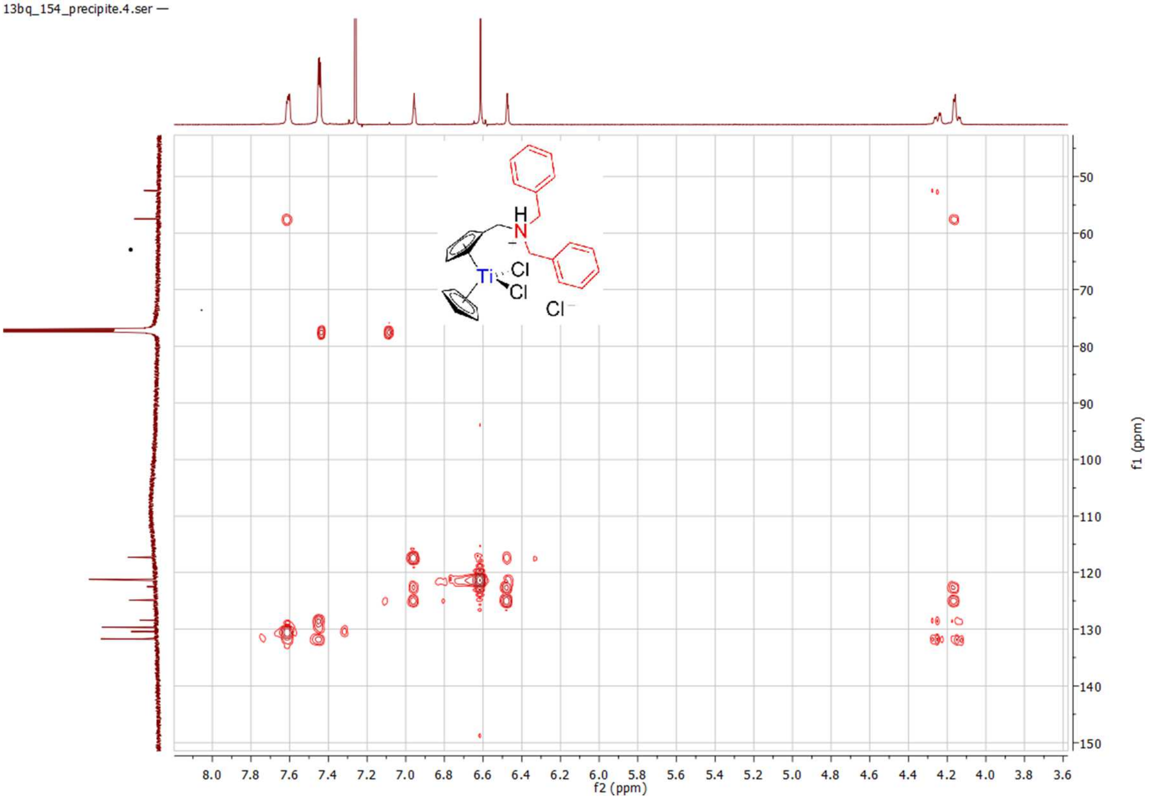
Spectrum 0-93: ^{13}C{^{1}H} NMR of 16 (150.94 MHz, 300 K, chloroform-d$_1$)



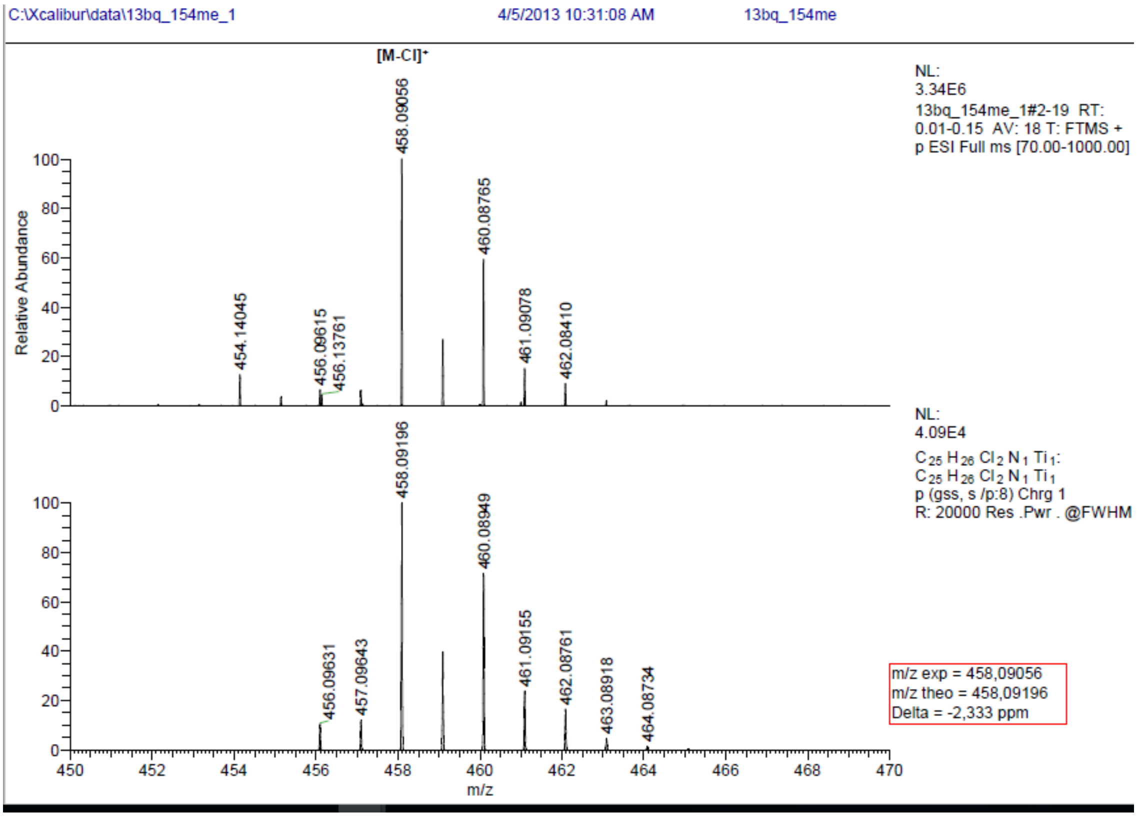
Spectrum 0-94: ^{1}H ^{1}H COSY of 16 (600.23 MHz, 300 K, chloroform-d$_1$)



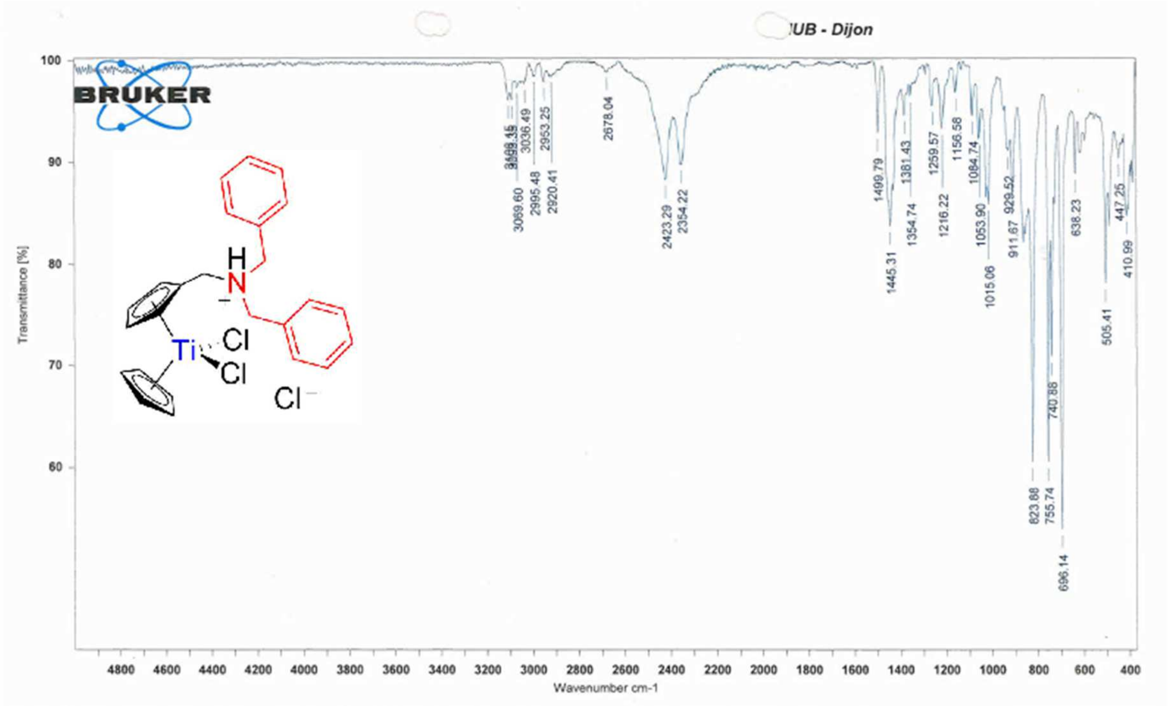
Spectrum 0-95: ^{1}H ^{13}C HMQC of 16 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1)



Spectrum 0-96: ^{1}H ^{13}C HMBC of 16 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1)



Spectrum 0-97: HRMS of 16 (Positive mode ESI, dichloromethane-methanol)



Echantillon: 13bq_154_precipite_MIR

Mesuré le 17/05/2013 sur VERTEX 70V

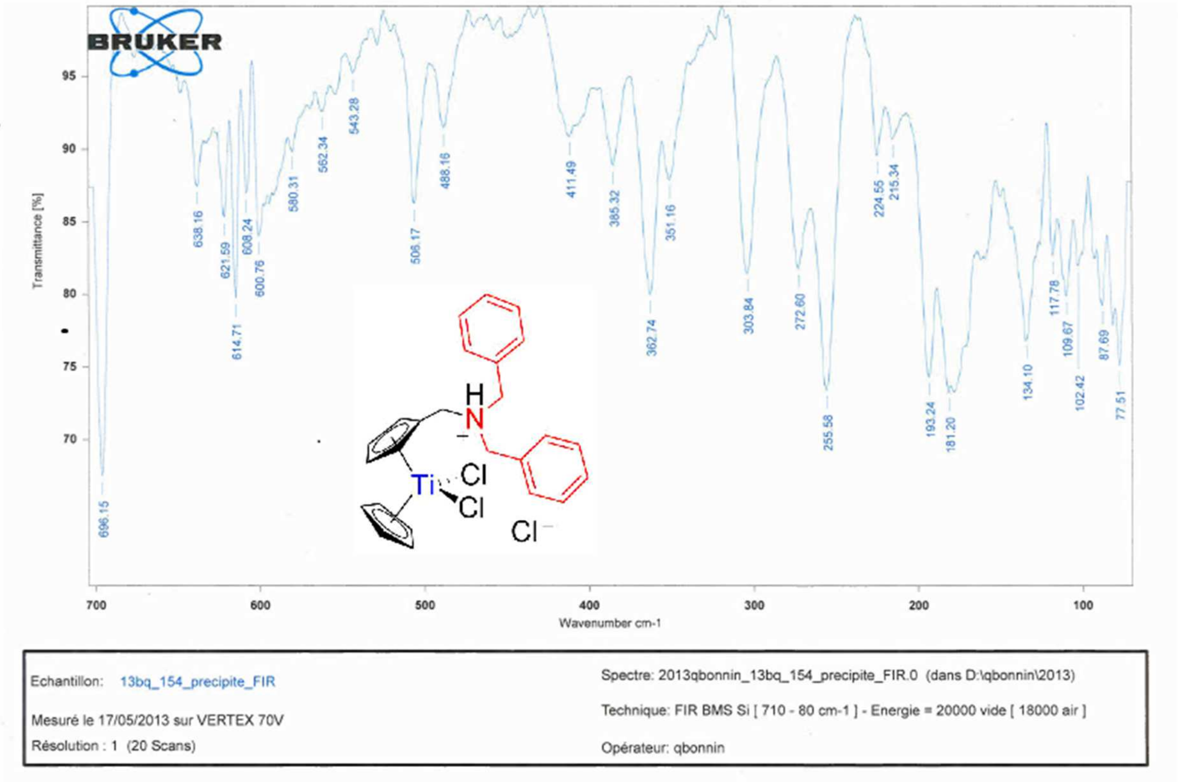
Résolution : 1 (20 Scans)

Spectre: 2013qbonnin_13bq_154_precipite_MIR.0 (dans D:\qbonnin\2013)

Technique: MIR ATR A225 Diamant [7000 - 370 cm-1] - Energie = 3000

Opérateur: qbonnin

Spectrum 0-98: MIR of 16



Echantillon: 13bq_154_precipite_FIR

Mesuré le 17/05/2013 sur VERTEX 70V

Résolution : 1 (20 Scans)

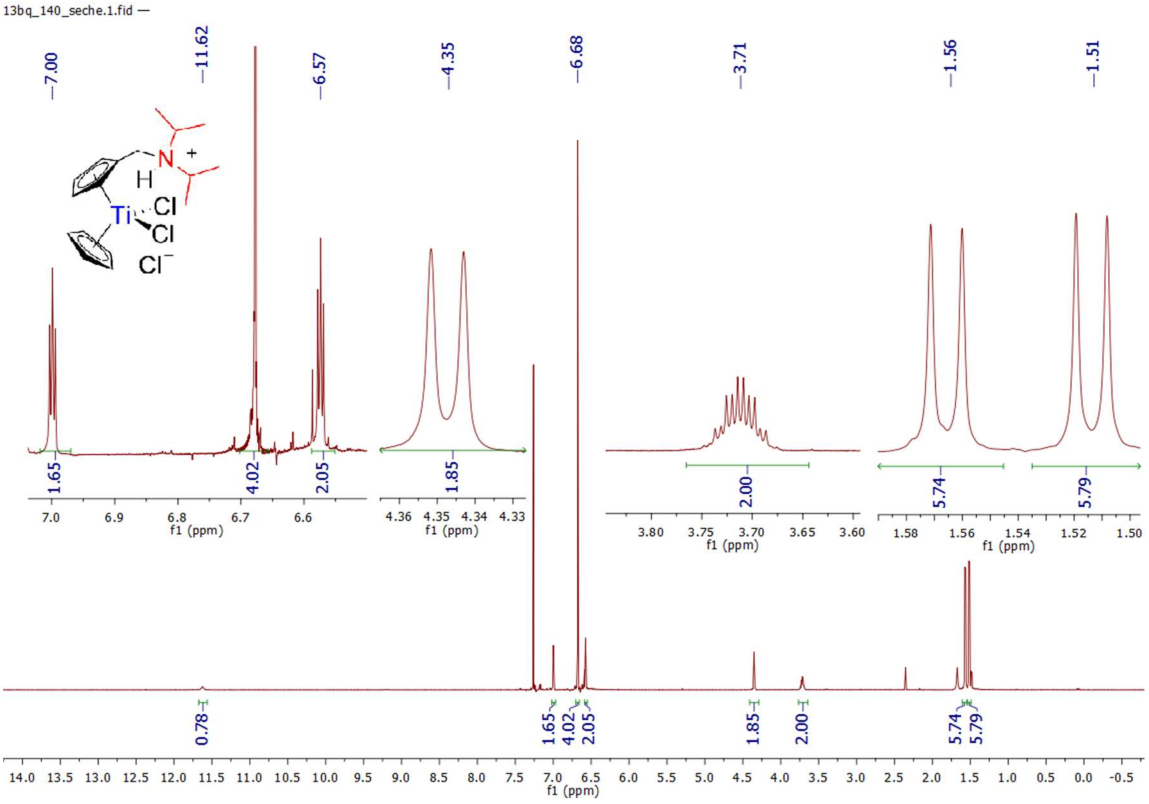
Spectre: 2013qbonnin_13bq_154_precipite_FIR.0 (dans D:\qbonnin\2013)

Technique: FIR BMS Si [710 - 80 cm-1] - Energie = 20000 vide [18000 air]

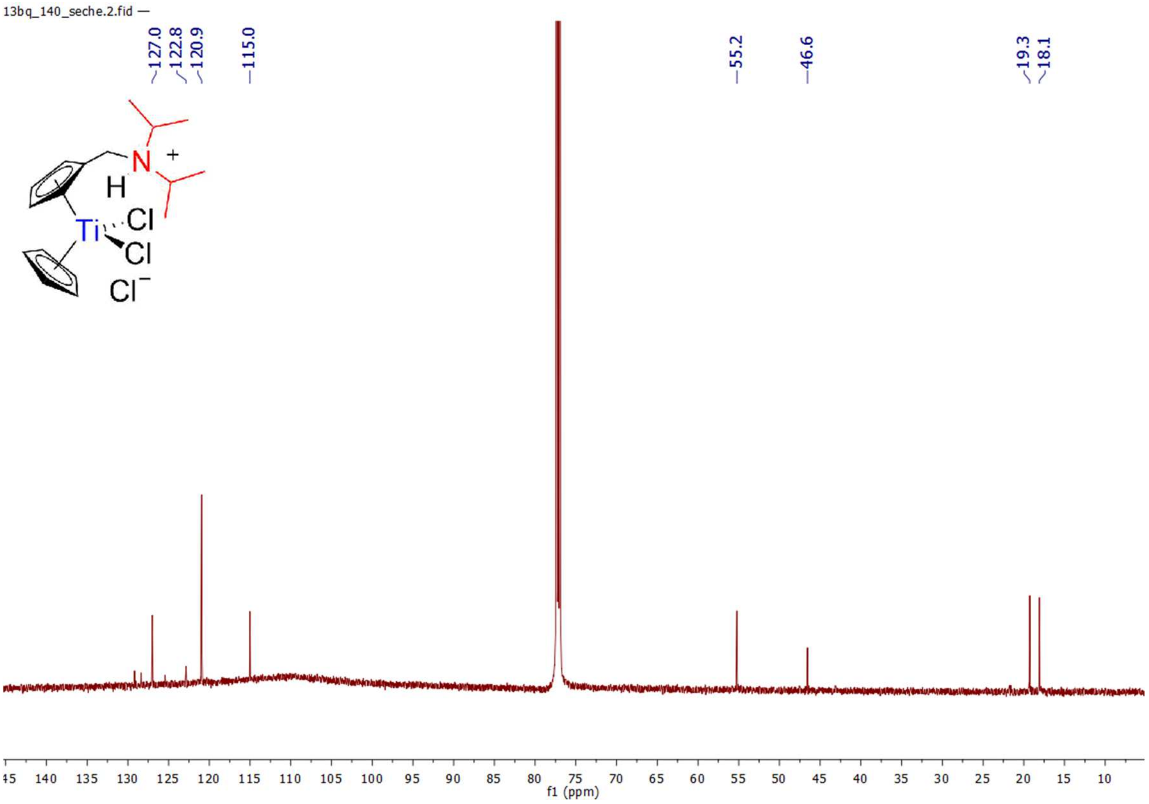
Opérateur: qbonnin

Spectrum 0-99: FIR of 16

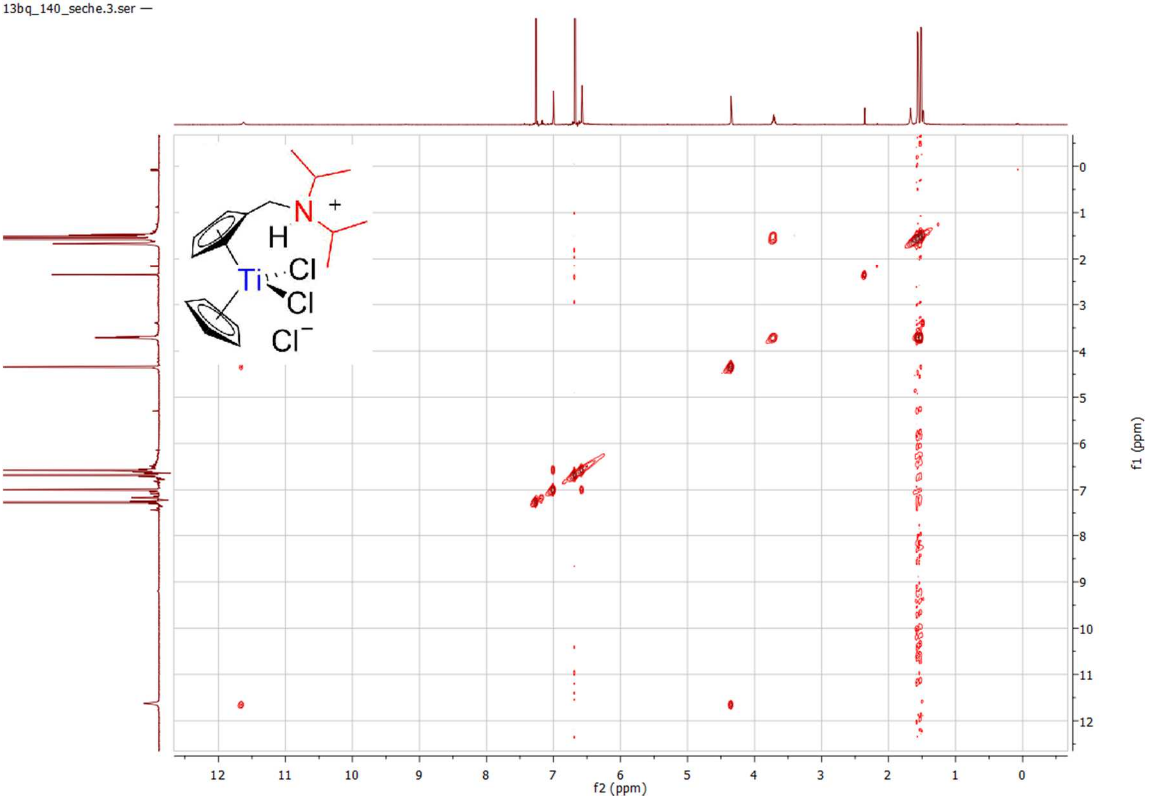
14. Compound **17**:



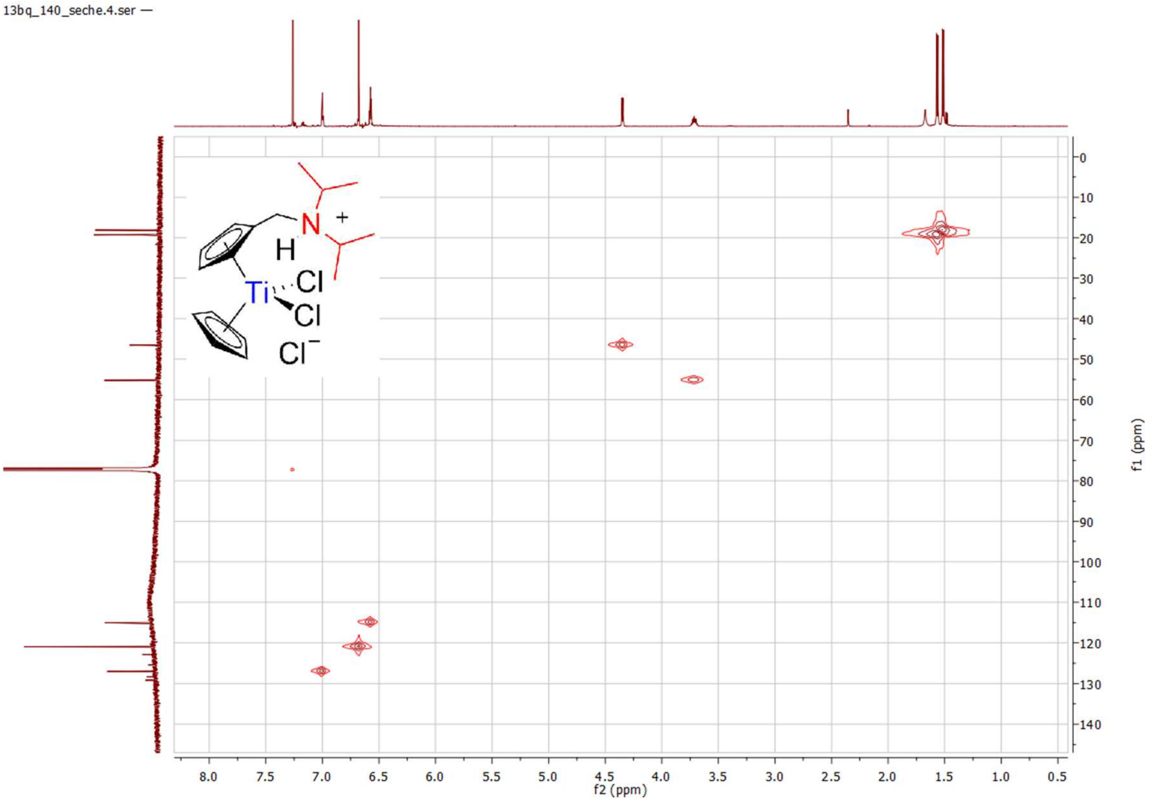
Spectrum 0-100: ^{1}H NMR of 17 (600.23 MHz, 300 K, chloroform-d_1)



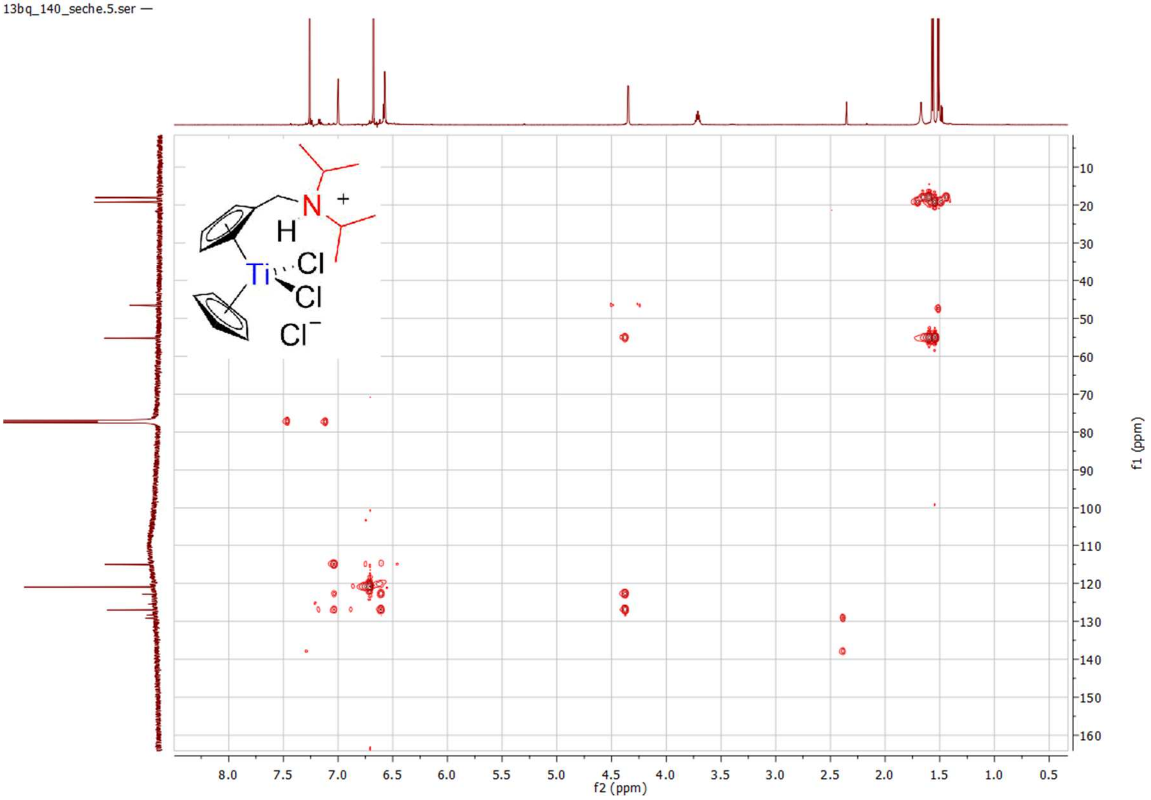
Spectrum 0-101: $^{13}C\{^1H\}$ NMR of 17 (150.94 MHz, 300 K, chloroform-d_1)



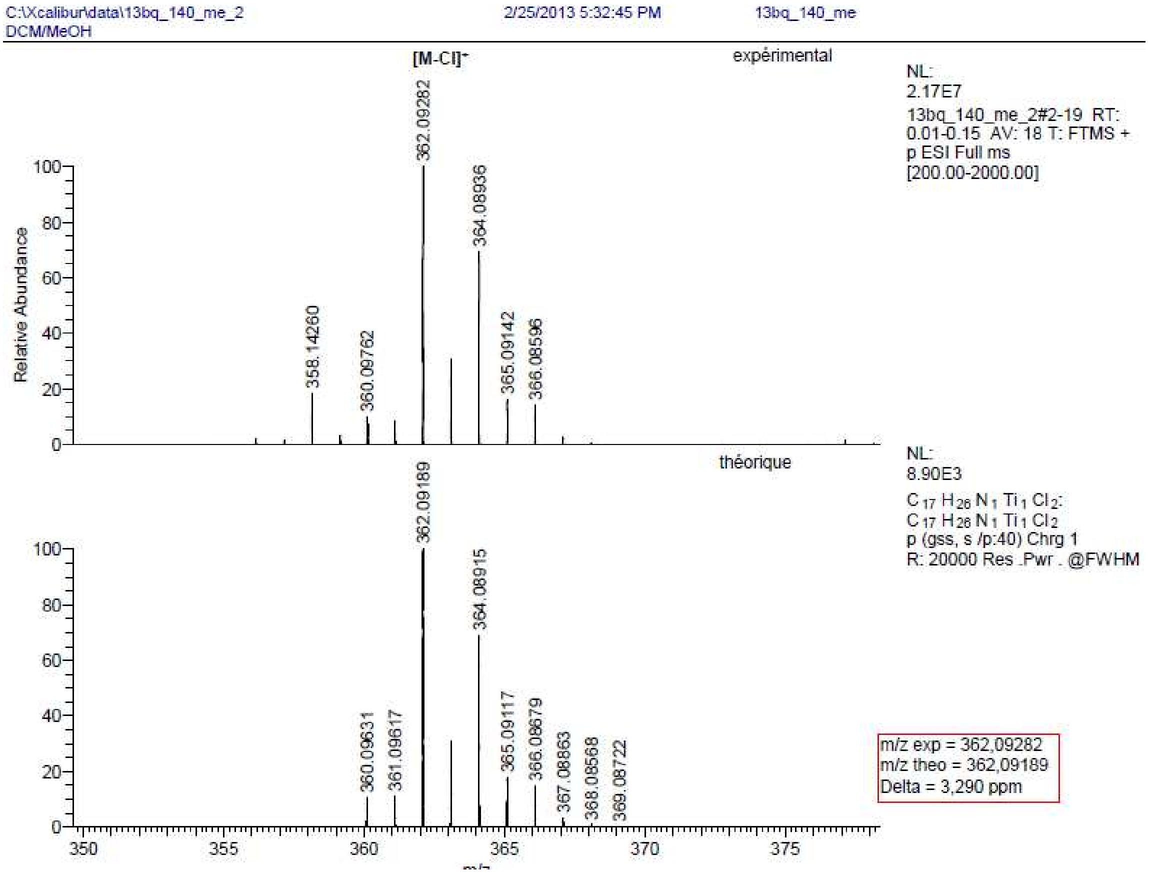
Spectrum 0-102: ^1H ^1H COSY of 17 (600.23 MHz, 300 K, chloroform-d_1)



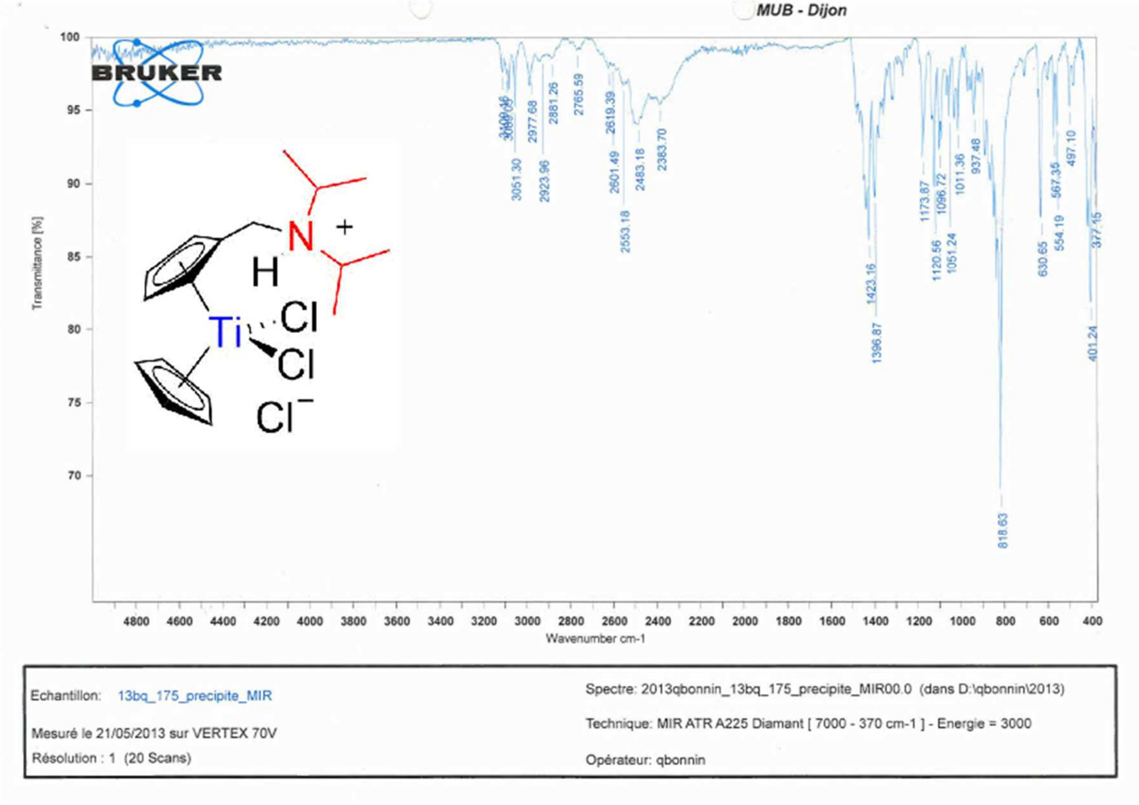
Spectrum 0-103: ^{1}H ^{13}C HMQC of 17 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1)



Spectrum 0-104: ^{1}H ^{13}C HMBC of 17 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1)

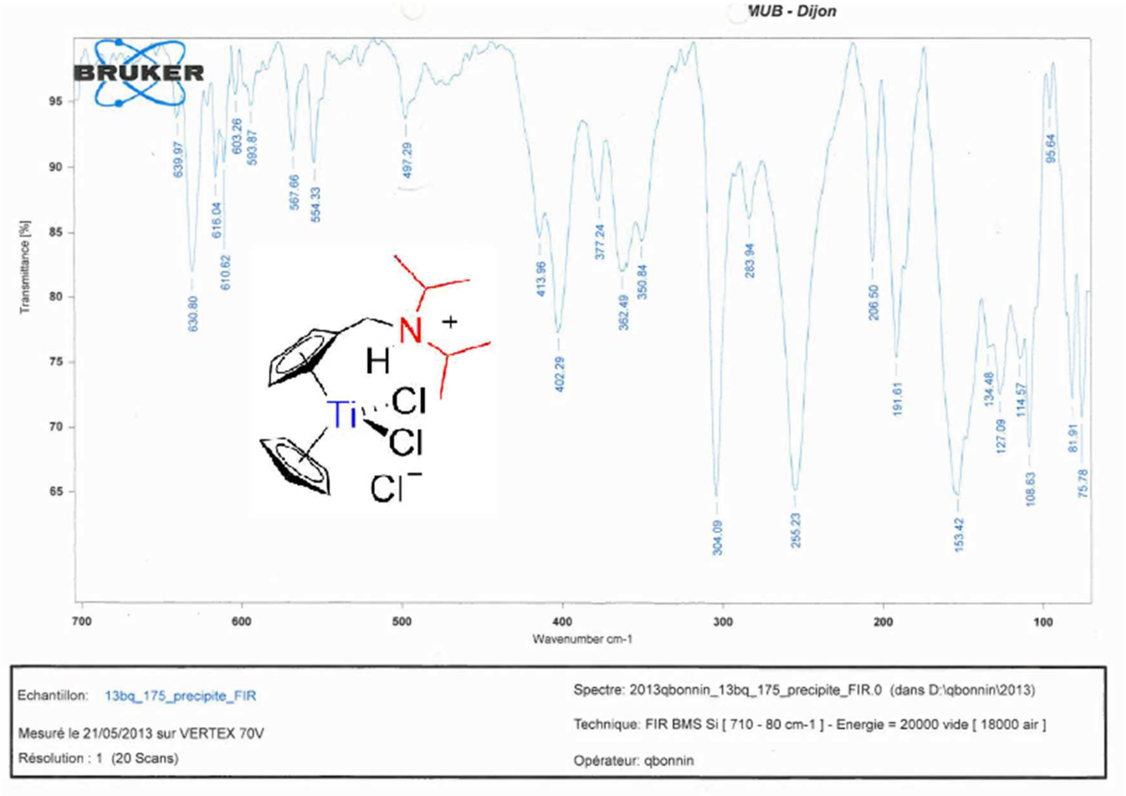


Spectrum 0-105: HRMS of 17 (Positive mode ESI, dichloromethane-methanol)



Echantillon: 13bq_175_precipite_MIR
Spectre: 2013qbonnin_13bq_175_precipite_MIR00.0 (dans D:\qbonnin\2013)
Mesuré le 21/05/2013 sur VERTEX 70V
Technique: MIR ATR A225 Diamant [7000 - 370 cm-1] - Energie = 3000
Résolution : 1 (20 Scans)
Opérateur: qbonnin

Spectrum 0-106: MIR of 17



Echantillon: 13bq_175_precipite_FIR

Mesuré le 21/05/2013 sur VERTEX 70V

Résolution : 1 (20 Scans)

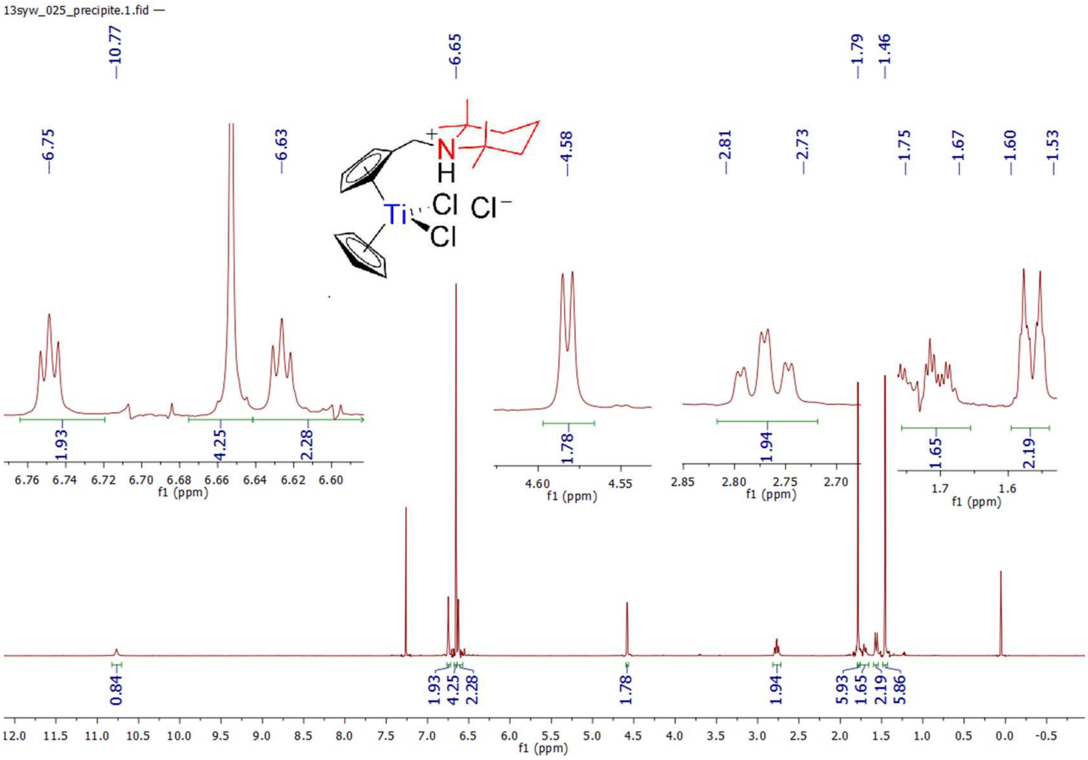
Spectre: 2013qbonnin_13bq_175_precipite_FIR.0 (dans D:\qbonnin\2013)

Technique: FIR BMS Si [710 - 80 cm-1] - Energie = 20000 vide [18000 air]

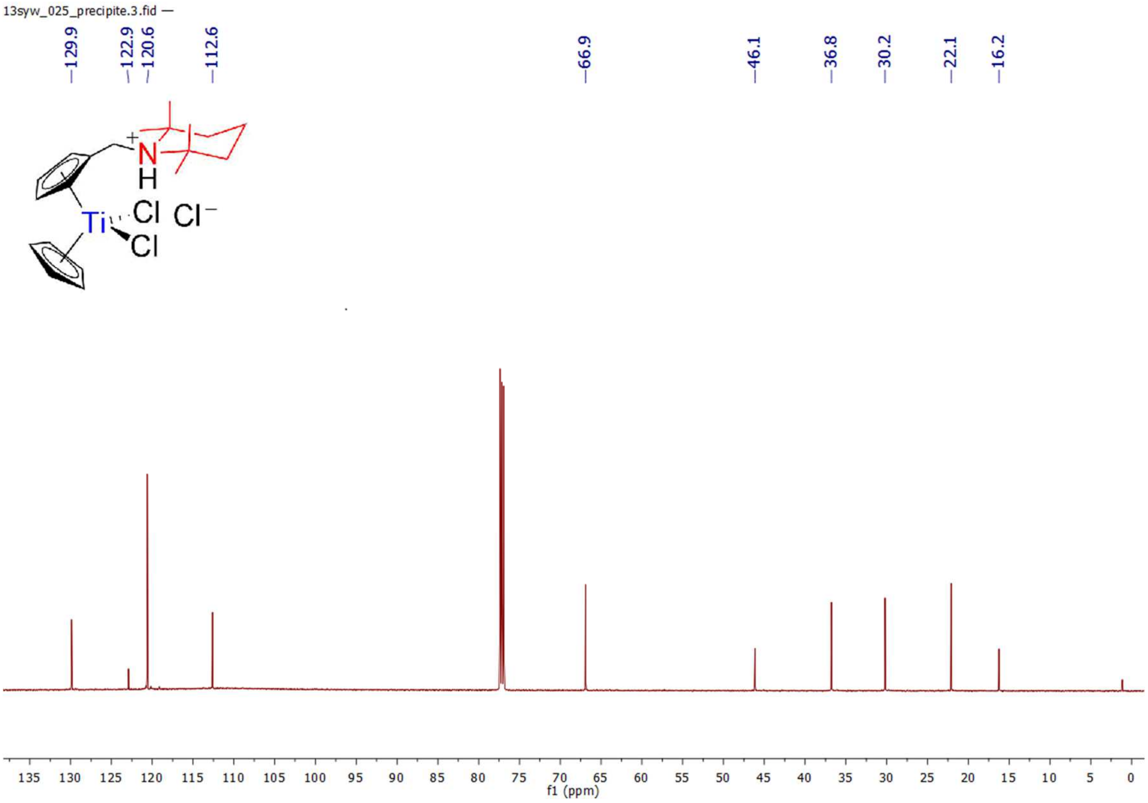
Opérateur: qbonnin

Spectrum 0-107: FIR of 17

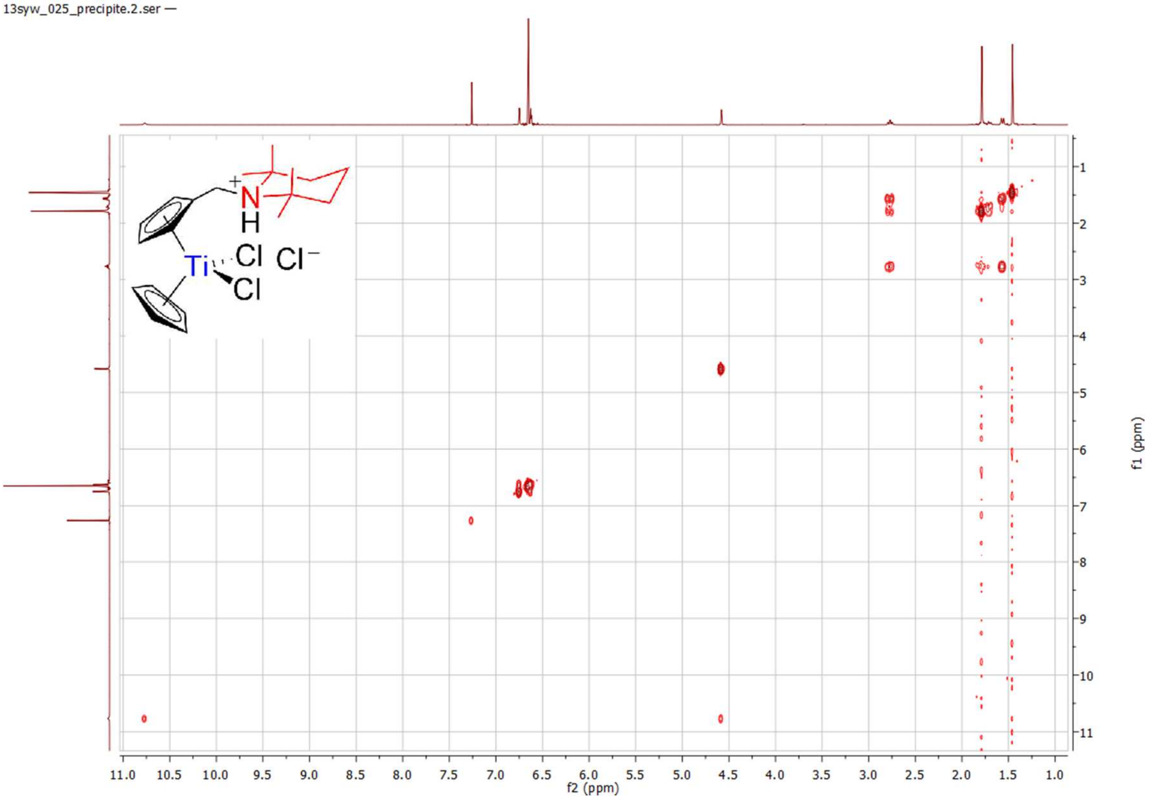
15. Compound **18**:



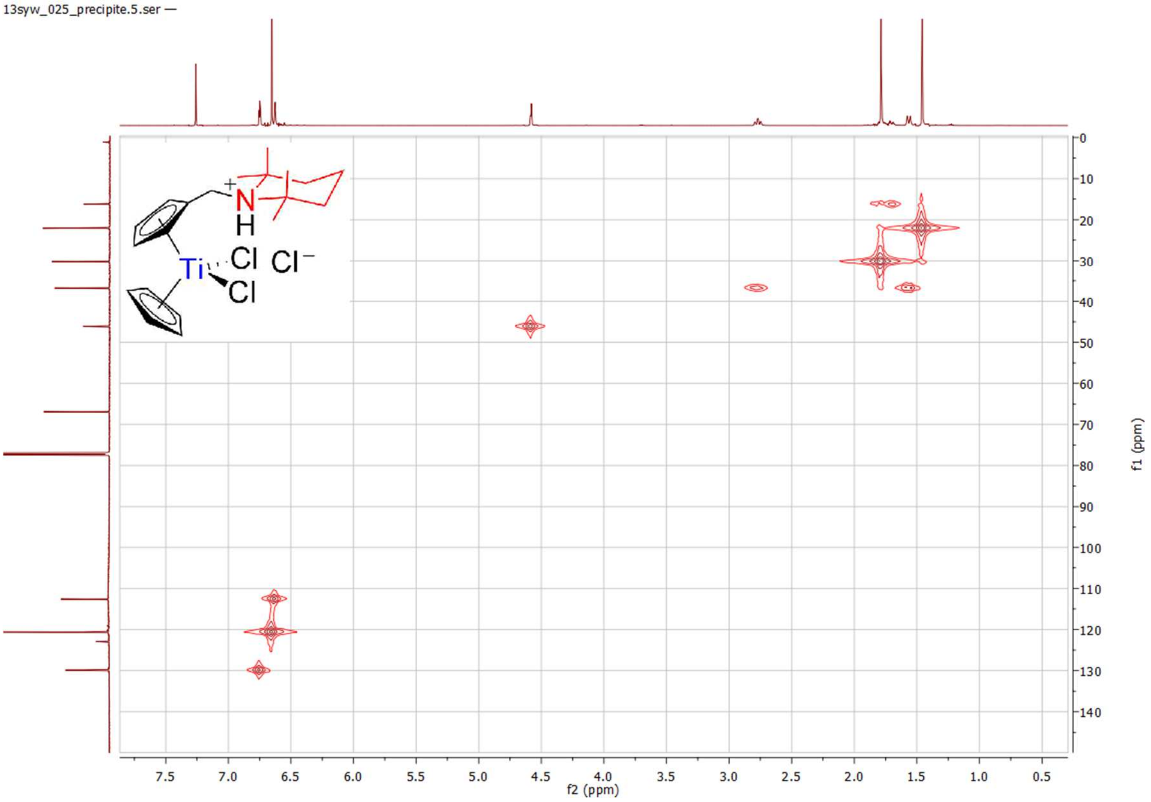
Spectrum 0-108: ^{1}H NMR of 18 (600.23 MHz, 300 K, chloroform-d$_1$)



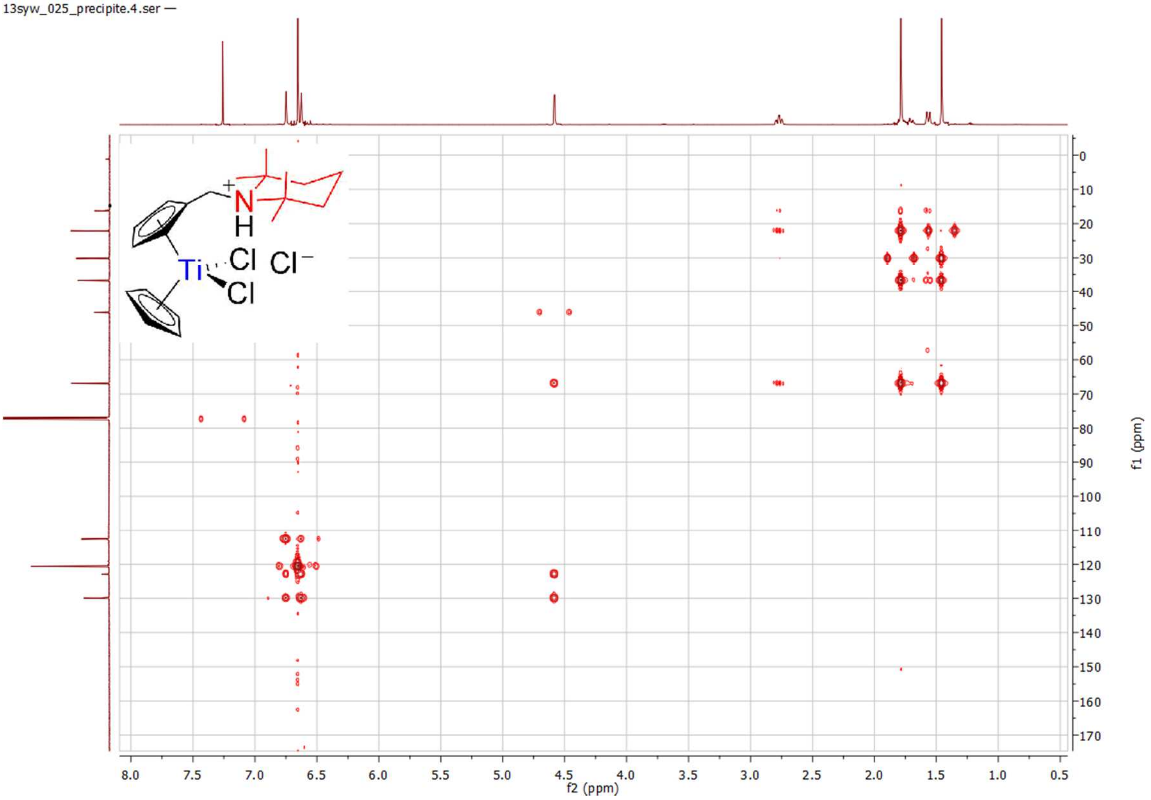
Spectrum 0-109: $^{13}C\{^{1}H\}$ NMR of 18 (150.94 MHz, 300 K, chloroform-d_1)



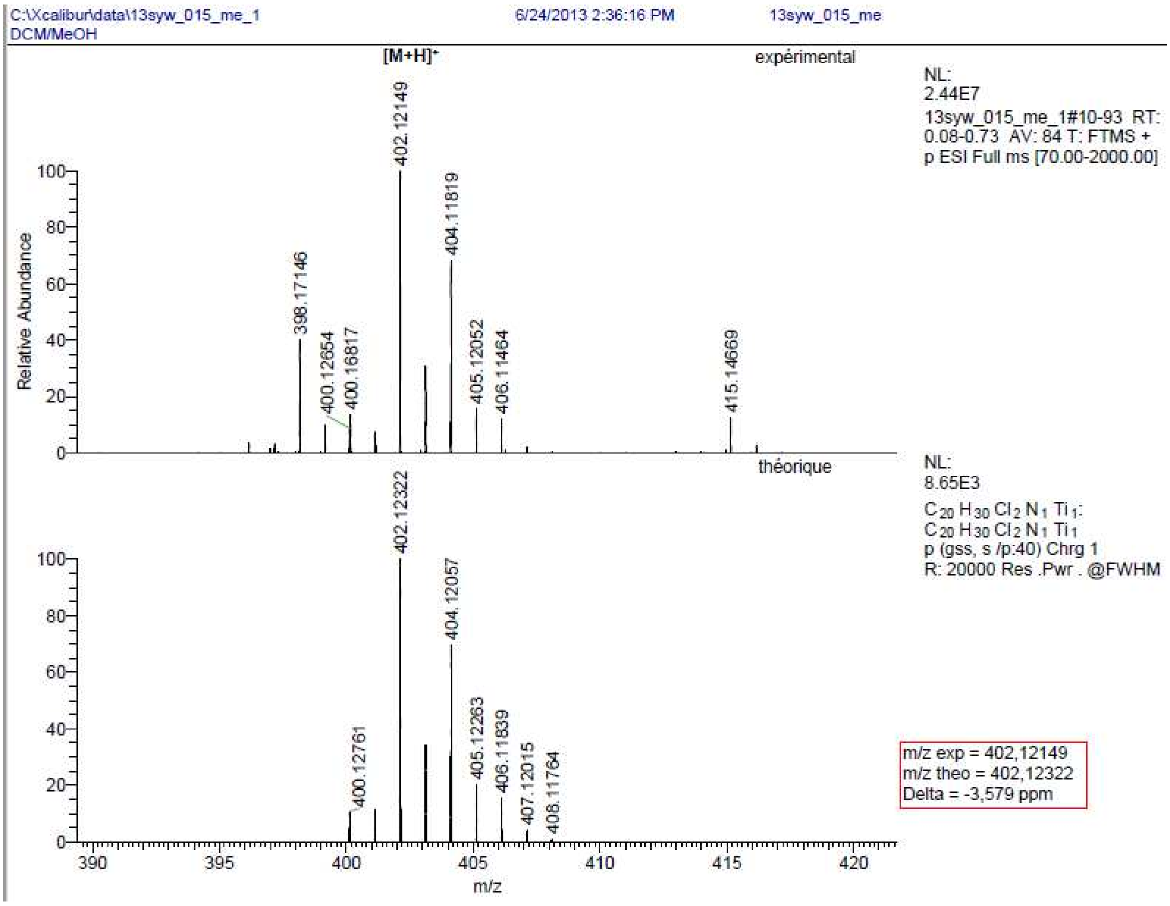
Spectrum 0-110: ^{1}H ^{1}H COSY of 18 (600.23 MHz, 300 K, chloroform-d_1)



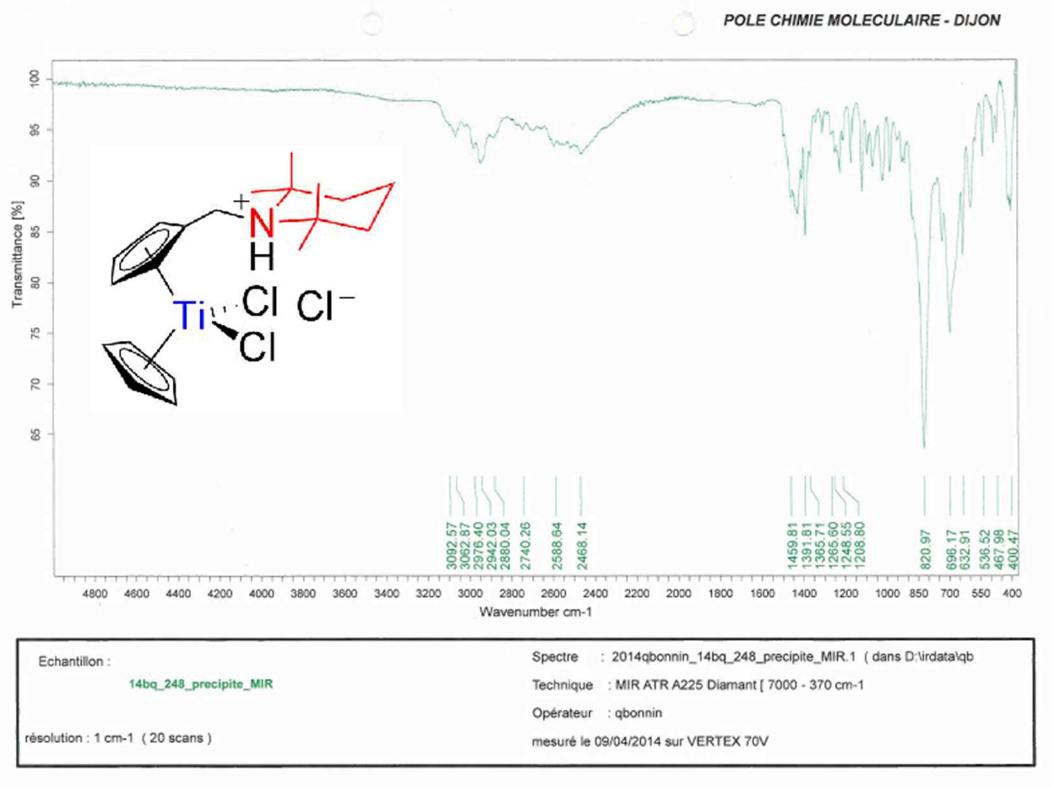
Spectrum 0-111: ^{1}H ^{13}C HMQC of 18 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1)



Spectrum 0-112: ^{1}H ^{13}C HMBC of 18 (600.23 MHz / 150.94 MHz, 300 K, chloroform-d_1)



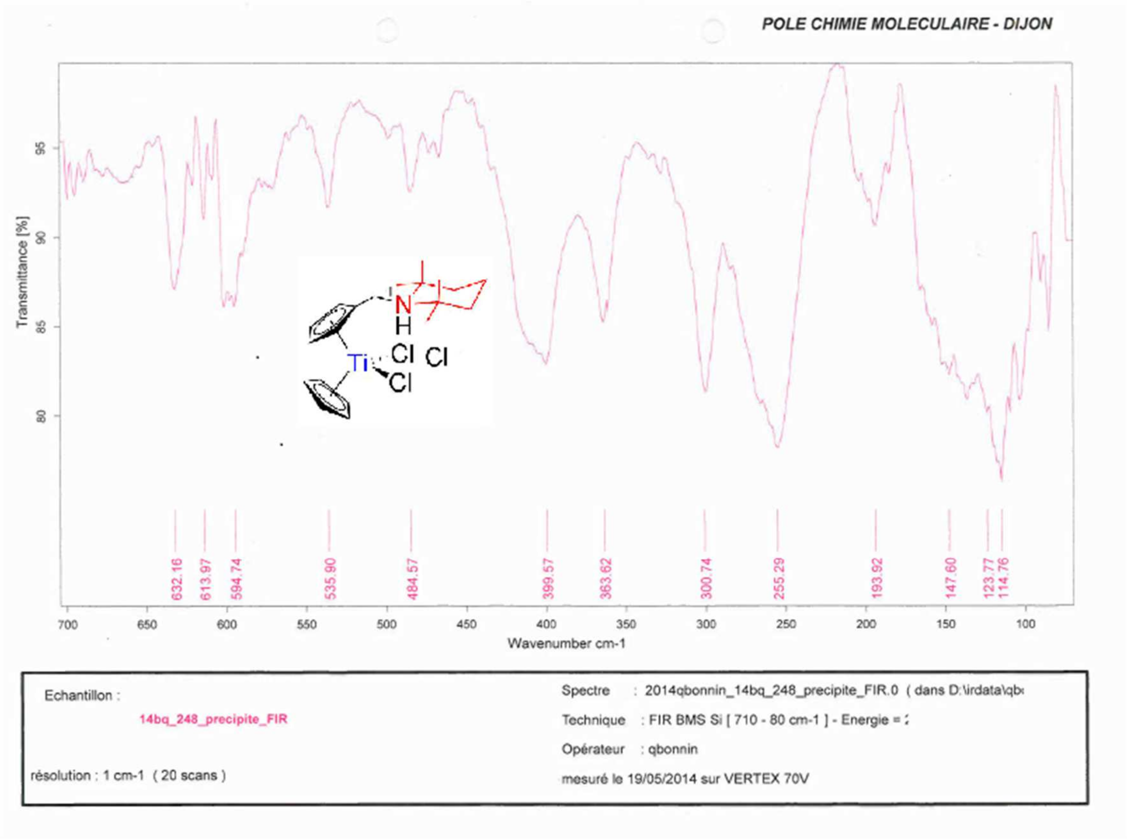
Spectrum 0-113: HRMS of 18 (Positive mode ESI, dichloromethane)



Echantillon :
14bq_248_precipite_MIR
résolution : 1 cm-1 (20 scans)

Spectre : 2014qbonnin_14bq_248_precipite_MIR.1 (dans D:\irdata\qb
Technique : MIR ATR A225 Diamant [7000 - 370 cm-1
Opérateur : qbonnin
mesuré le 09/04/2014 sur VERTEX 70V

Spectrum 0-114: MIR of 18



Echantillon :

14bq_248_precipite_FIR

résolution : 1 cm-1 (20 scans)

Spectre : 2014qbonnin_14bq_248_precipite_FIR.0 (dans D:\irdata\qb

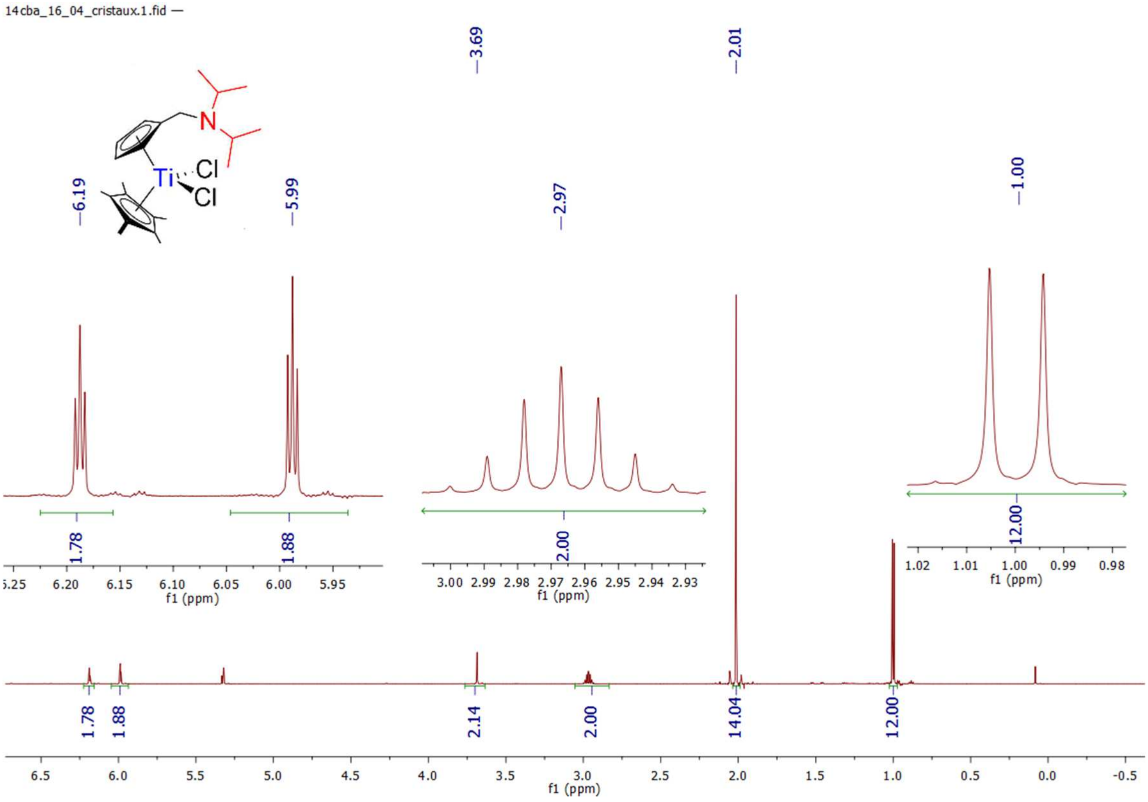
Technique : FIR BMS Si [710 - 80 cm-1] - Energie =

Opérateur : qbonnin

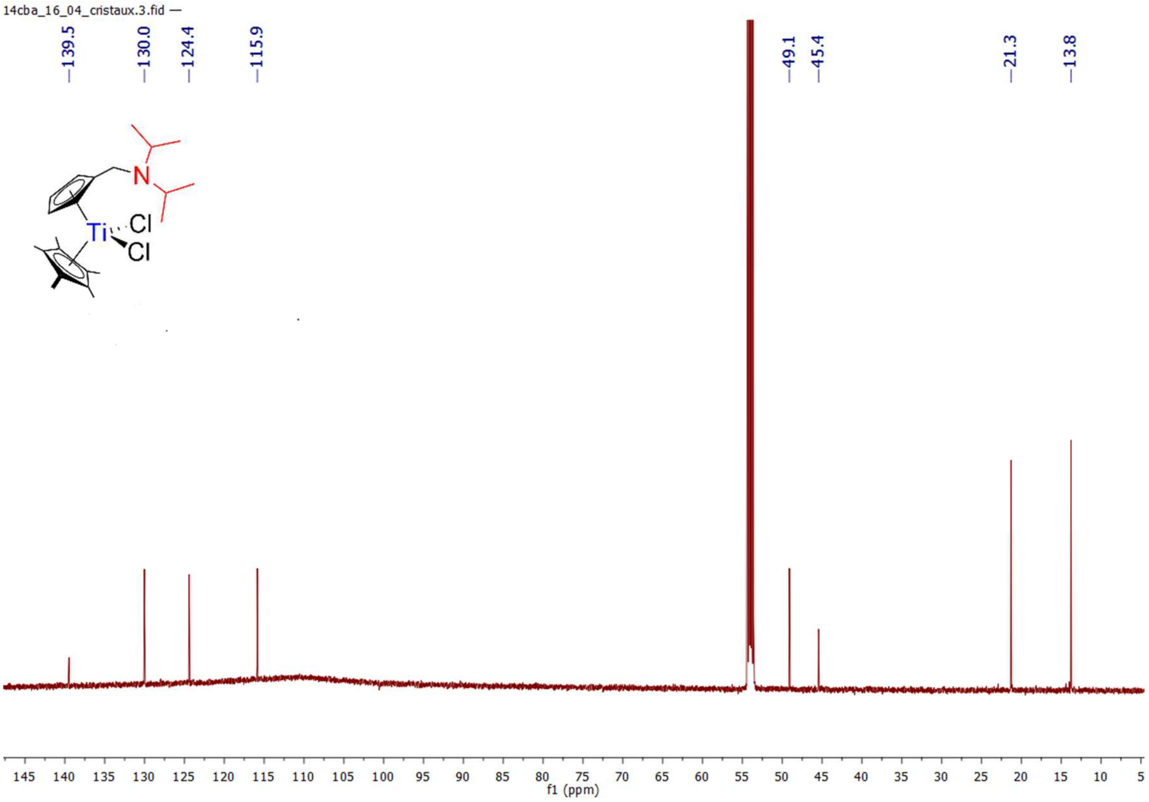
mesuré le 19/05/2014 sur VERTEX 70V

Spectrum 0-115: FIR of 18

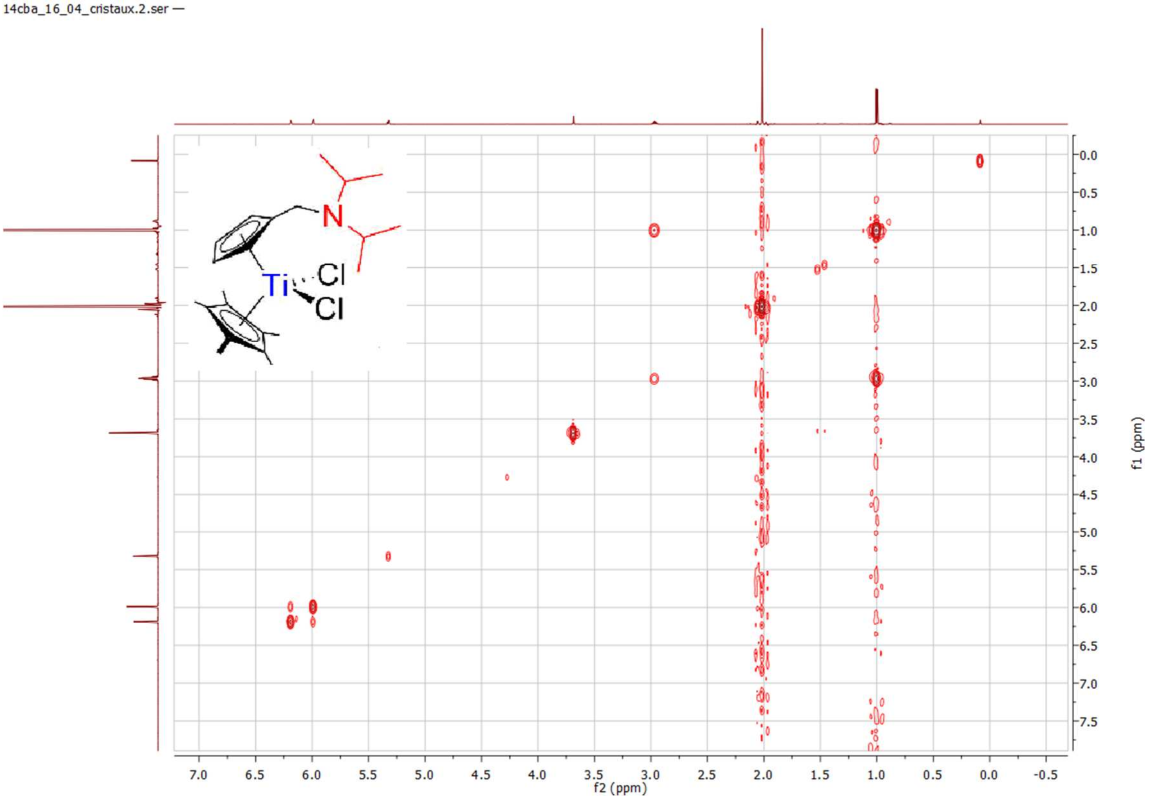
16. Compound **19**:



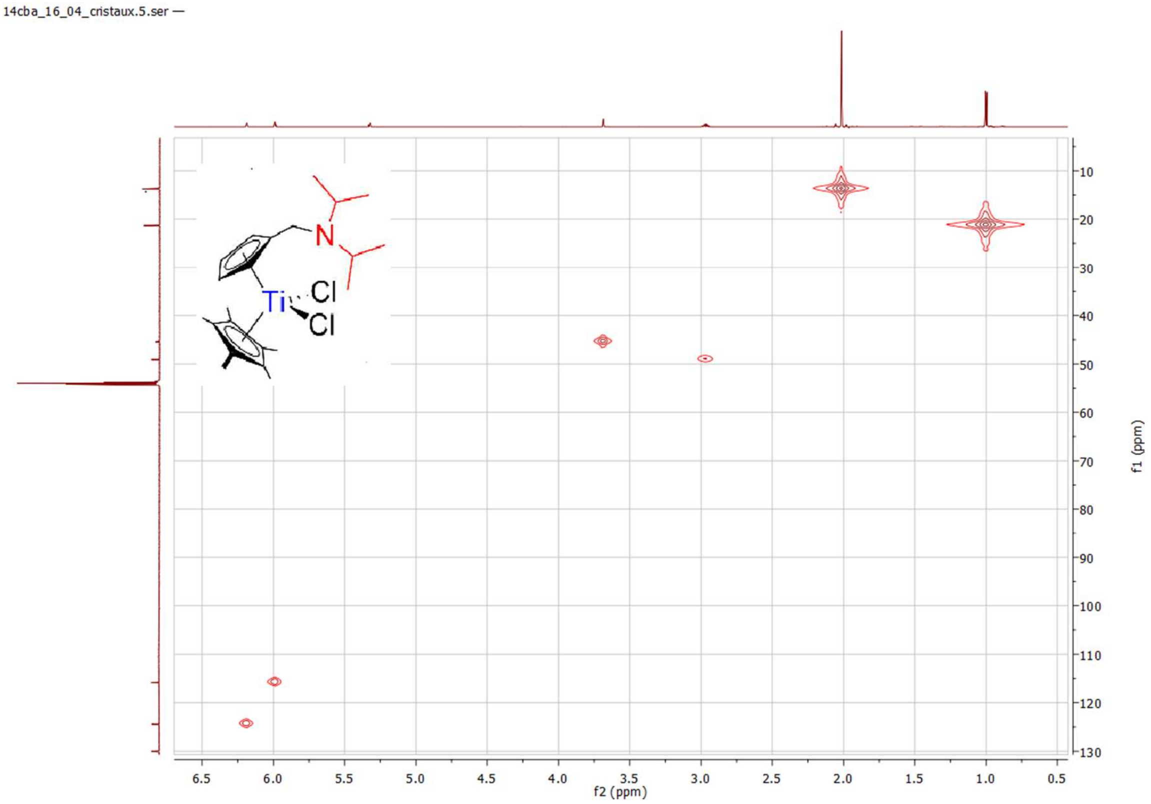
Spectrum 0-116: ^{1}H NMR of 19 (600.23 MHz, 300 K, dichloromethane-d_2)



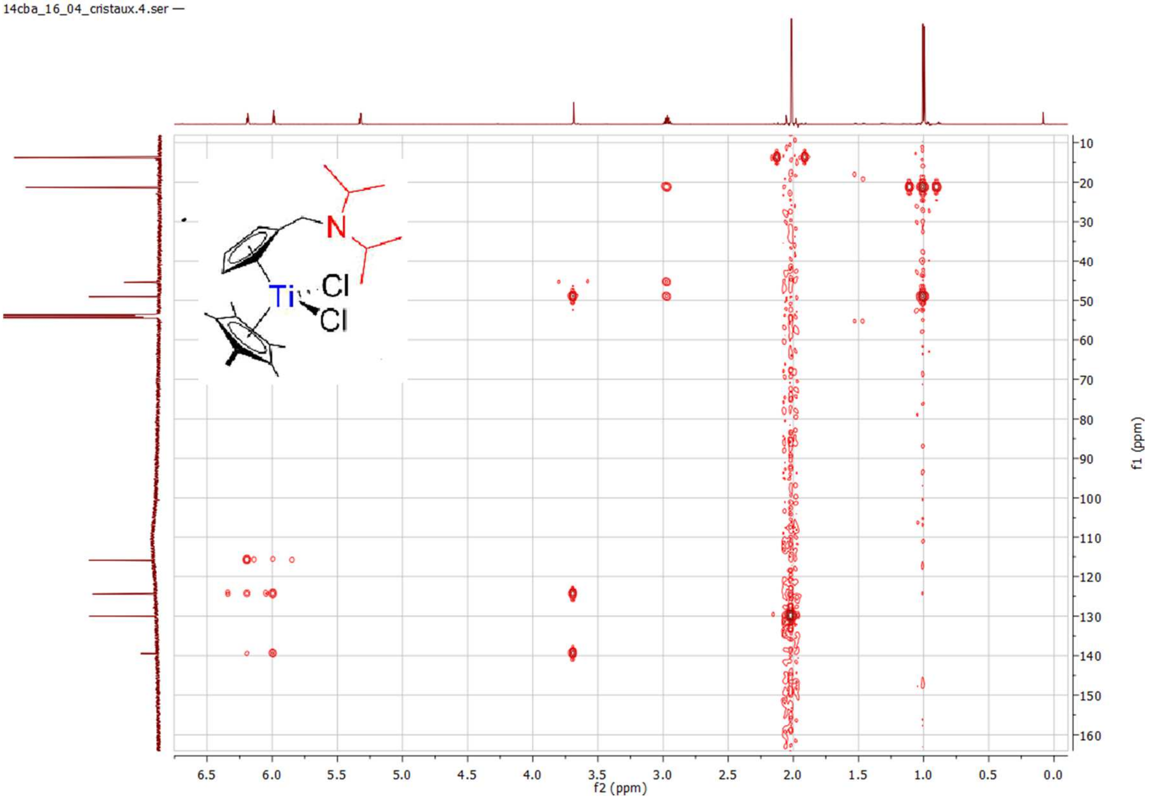
Spectrum 0-117: $^{13}C\{^{1}H\}$ NMR of 19 (150.94 MHz, 300 K, dichloromethane-d_2)



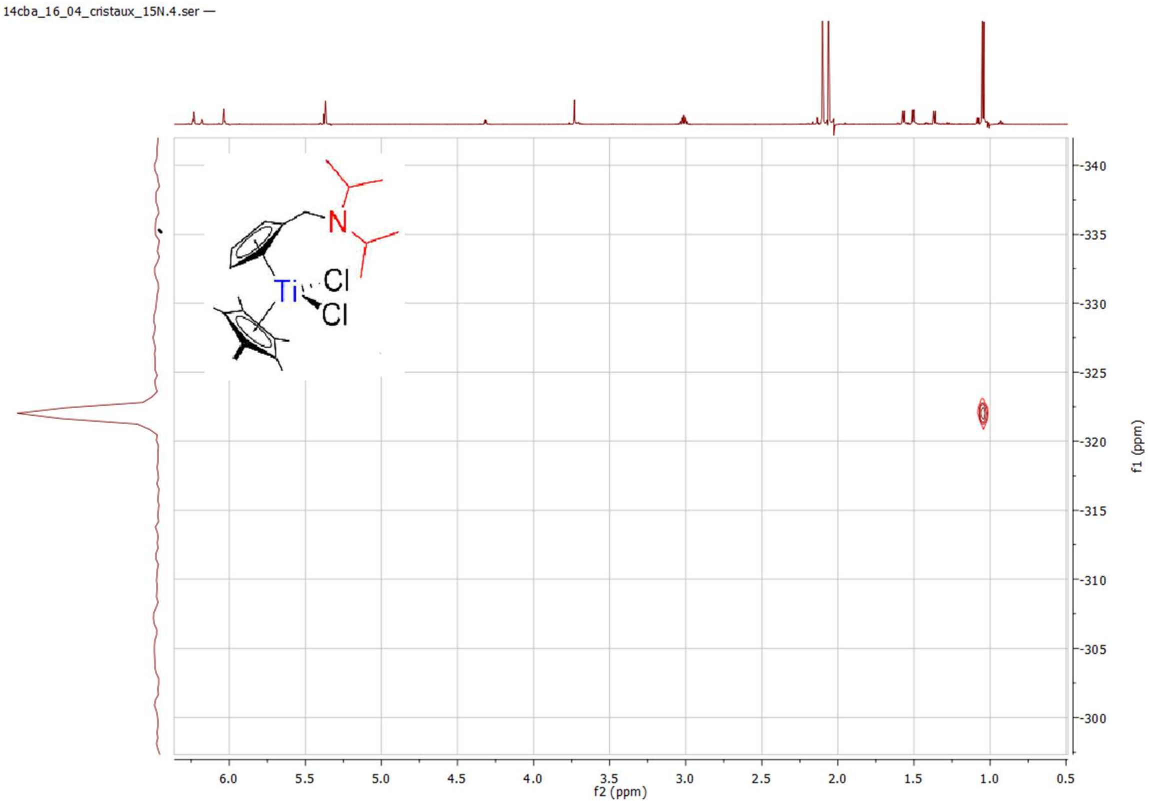
Spectrum 0-118: ^{1}H ^{1}H COSY of 19 (600.23 MHz, 300 K, dichloromethane-d_2)



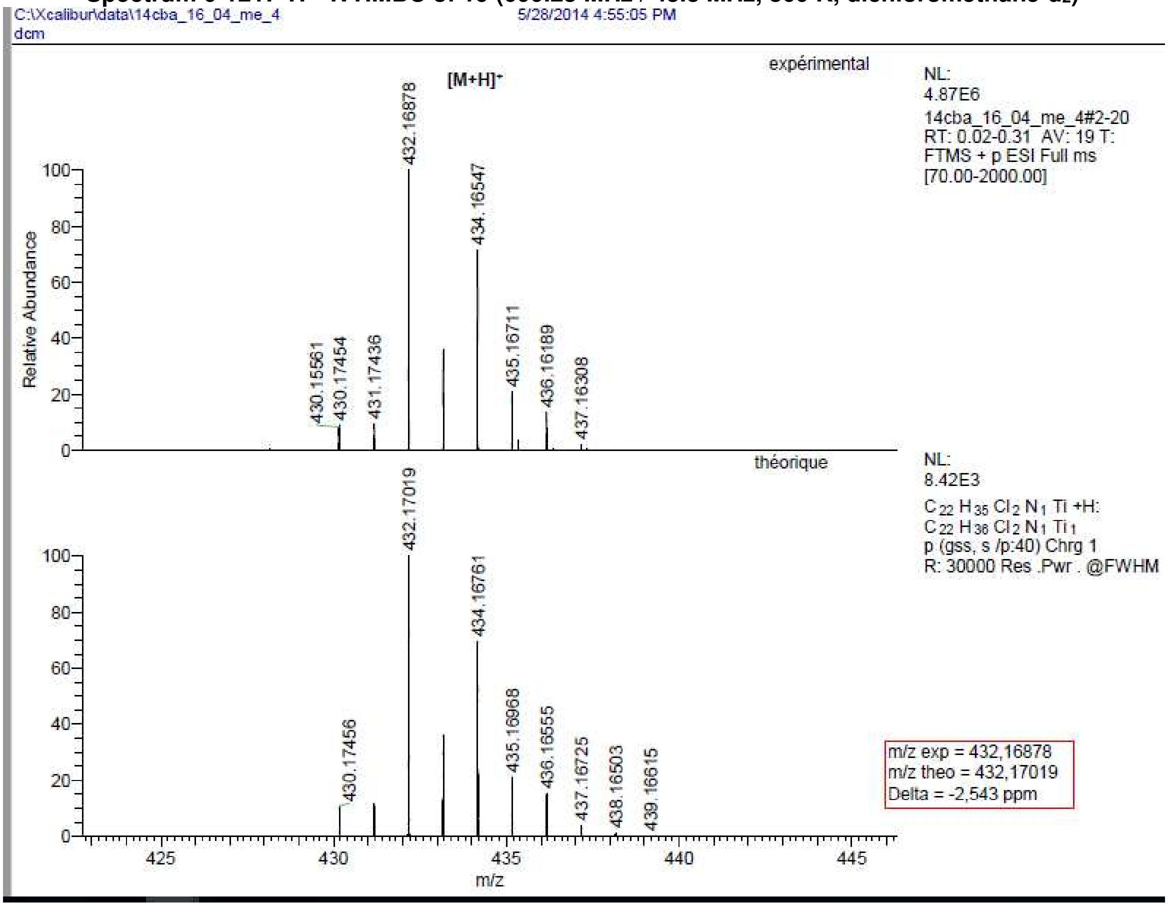
Spectrum 0-119: ^{1}H ^{13}C HMQC of 19 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



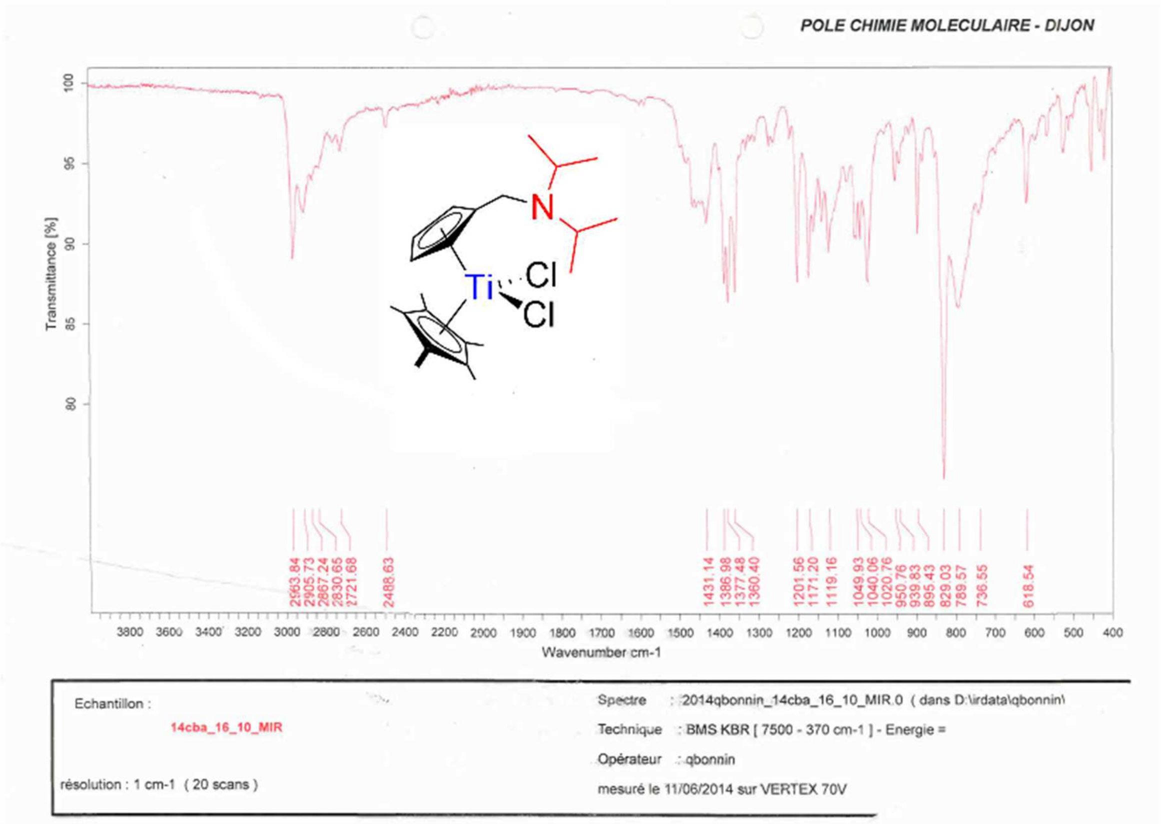
Spectrum 0-120: ^{1}H ^{13}C HMBC of 19 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-121: ^{1}H ^{15}N HMBC of 19 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-122: HRMS of 19 (Positive mode ESI, dichloromethane)



Echantillon :

14cba_16_10_MIR

résolution : 1 cm-1 (20 scans)

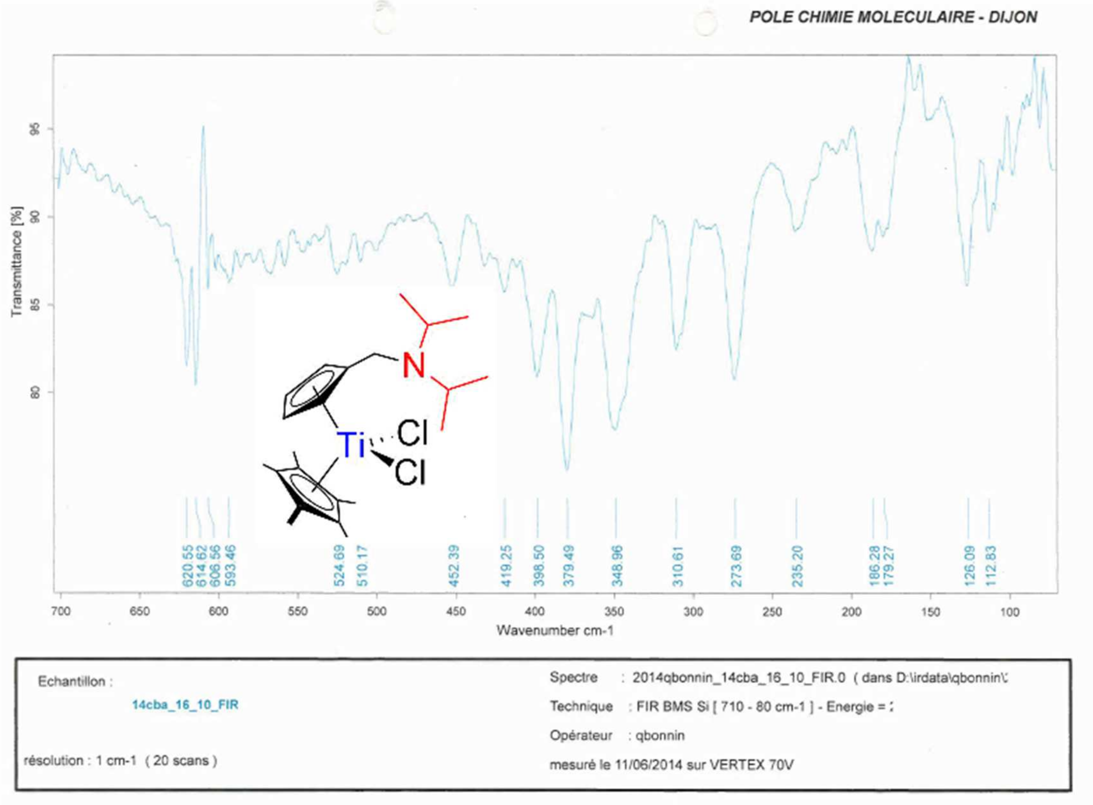
Spectre : 2014qbonnin_14cba_16_10_MIR.0 (dans D:\irdata\qbonnin\

Technique : BMS KBR [7500 - 370 cm-1] - Energie =

Opérateur : qbonnin

mesuré le 11/06/2014 sur VERTEX 70V

Spectrum 0-123: MIR of 19



Echantillon :

14cba_16_10_FIR

résolution : 1 cm-1 (20 scans)

Spectre : 2014qbonnin_14cba_16_10_FIR.0 (dans D:\irdata\qbonnin\

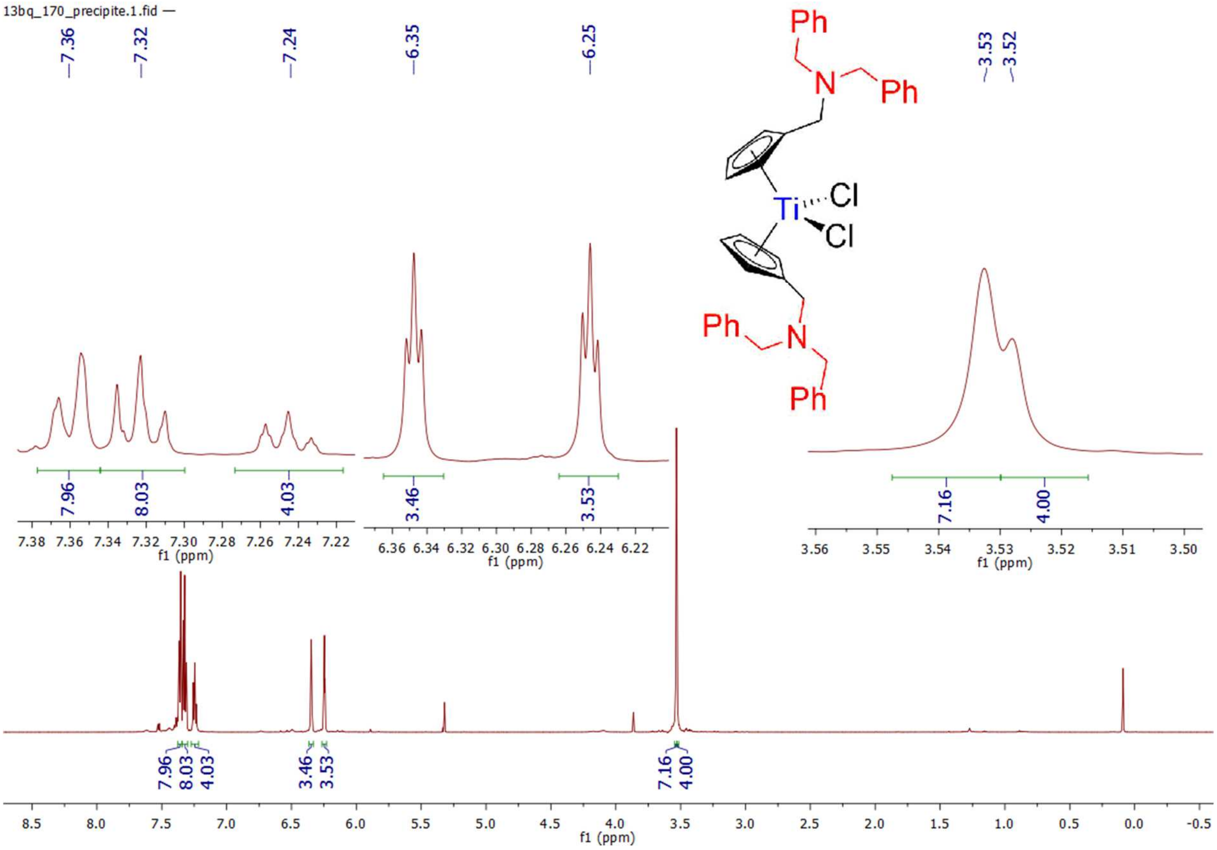
Technique : FIR BMS Si [710 - 80 cm-1] - Energie =

Opérateur : qbonnin

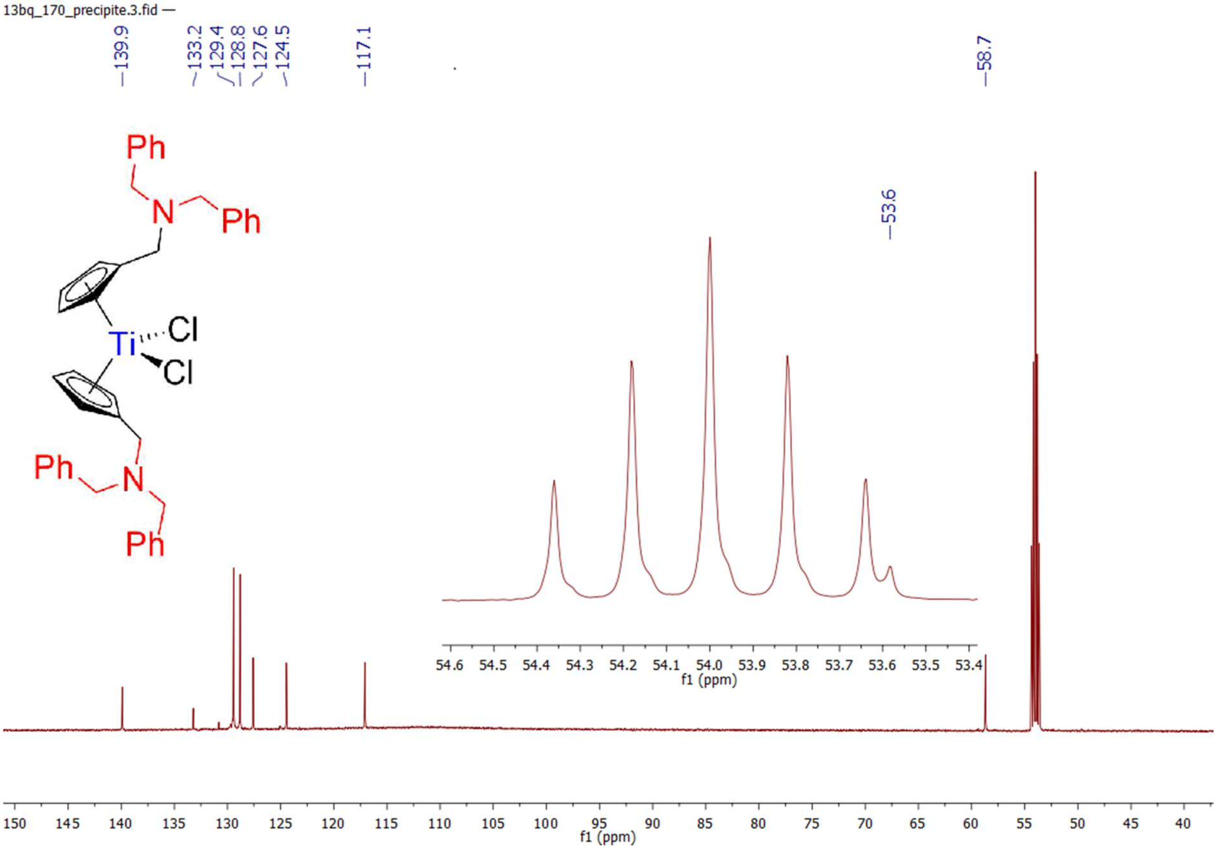
mesuré le 11/06/2014 sur VERTEX 70V

Spectrum 0-124: FIR of 19

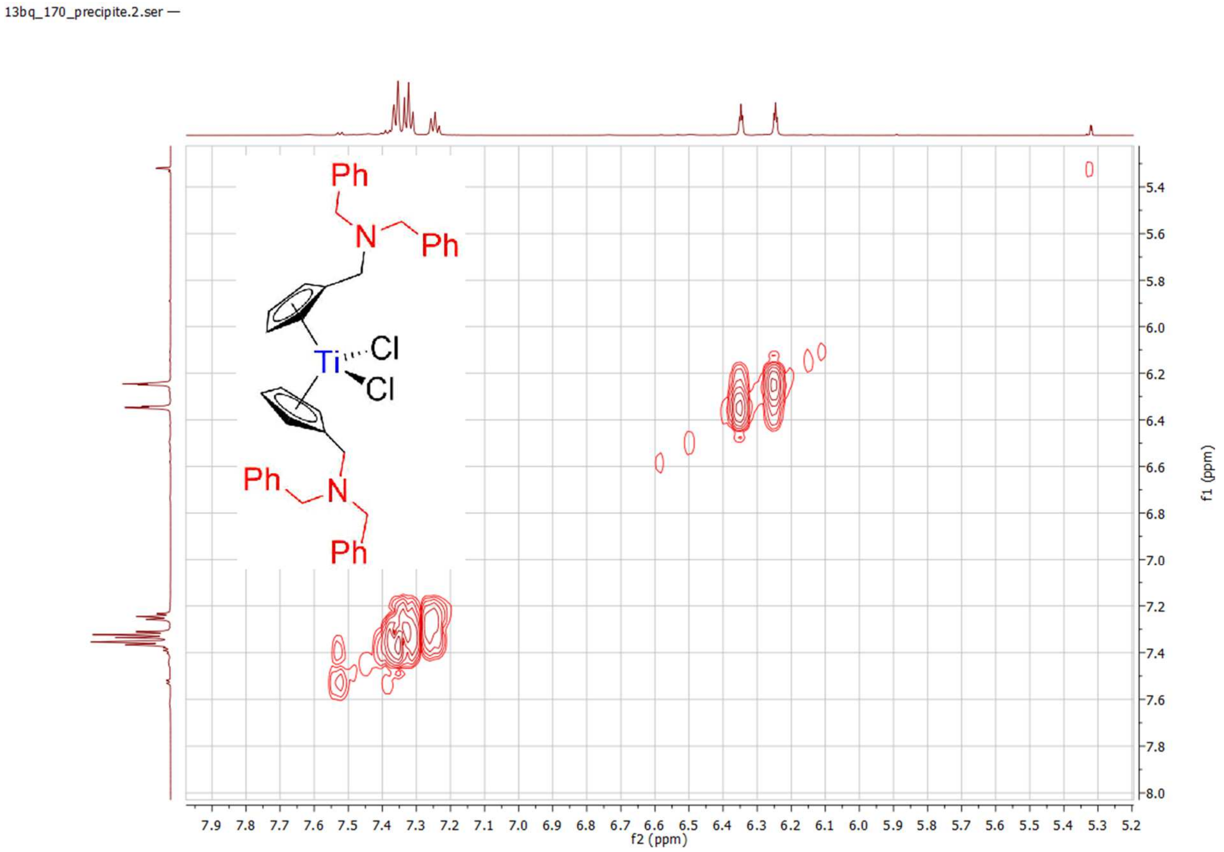
17. Compound **20**:



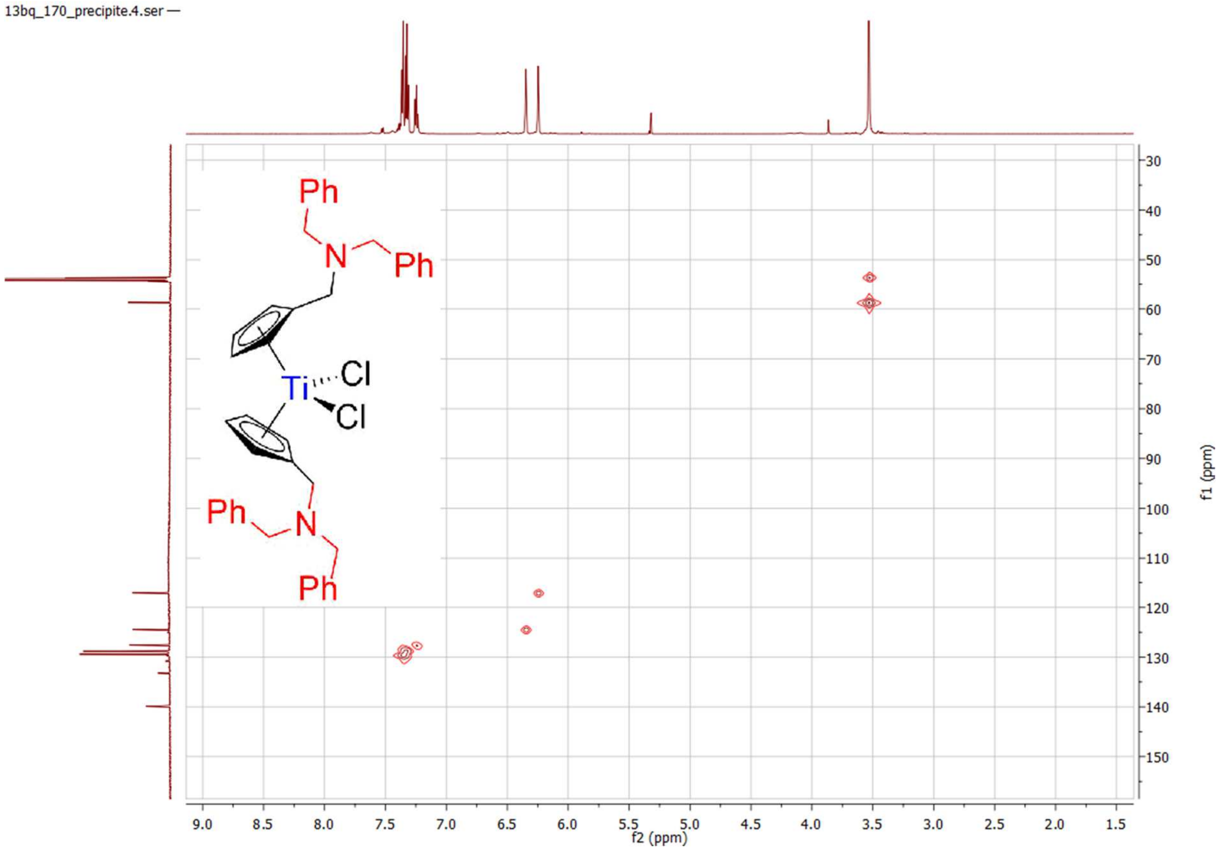
Spectrum 0-125: ^{1}H NMR of 20 (600.23 MHz, 300 K, dichloromethane-d$_2$)



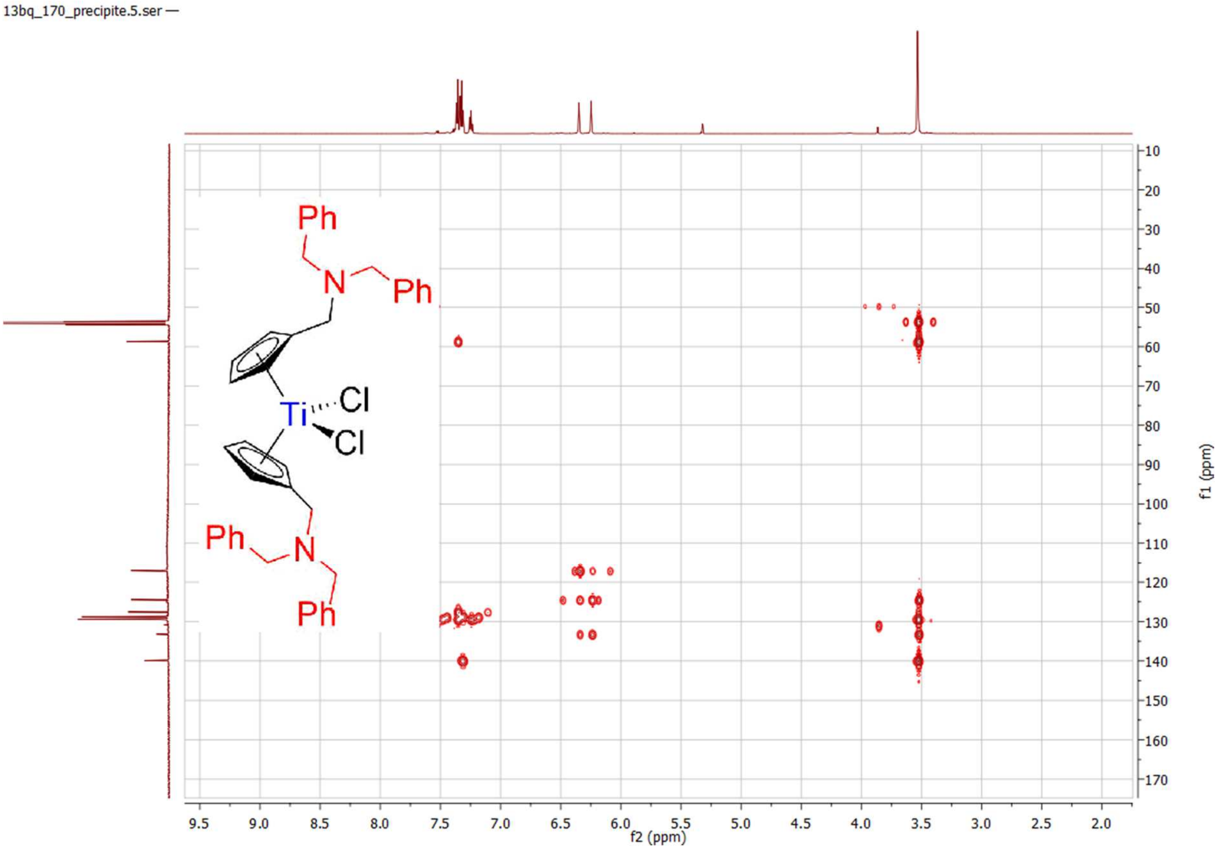
Spectrum 0-126: ^{13}C{^{1}H} NMR of 20 (150.94 MHz, 300 K, dichloromethane-d$_2$)



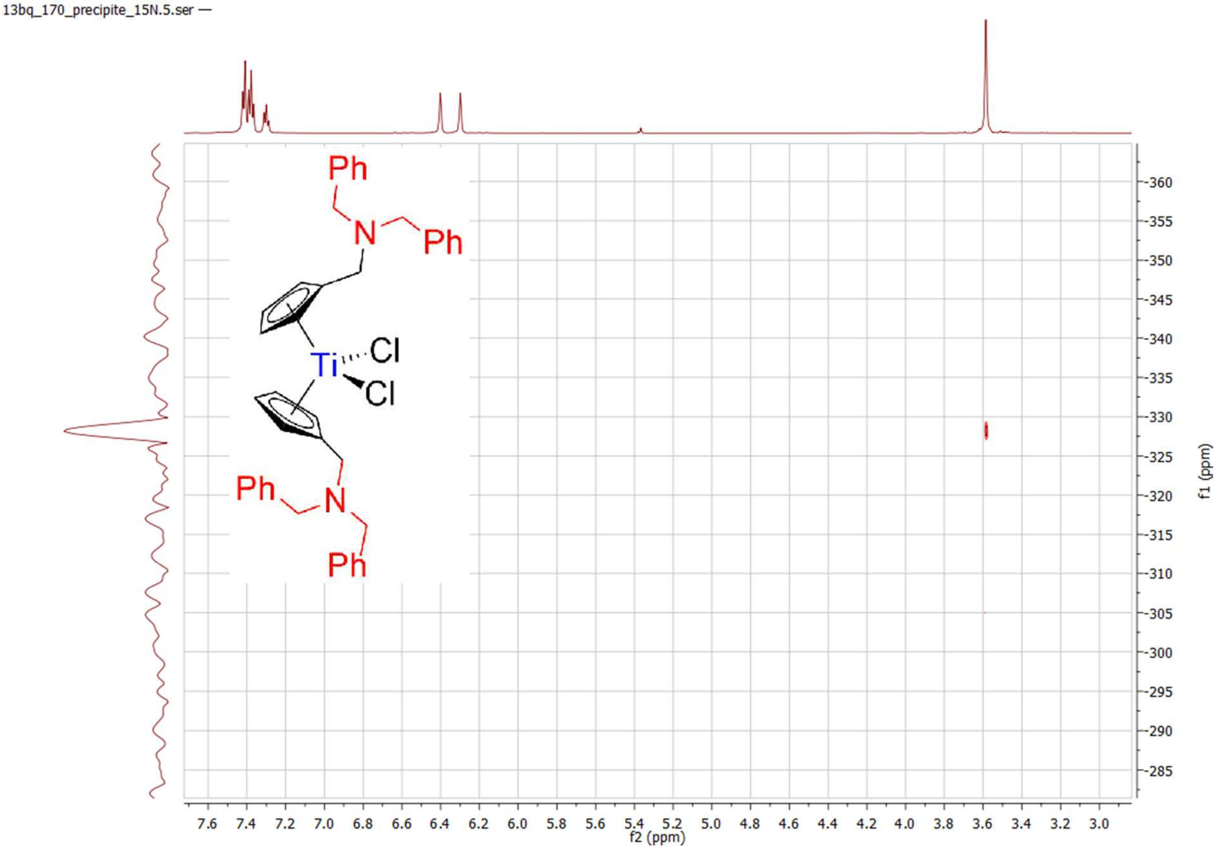
Spectrum 0-127: ^{1}H ^{1}H COSY of 20 (600.23 MHz, 300 K, dichloromethane-d_2)



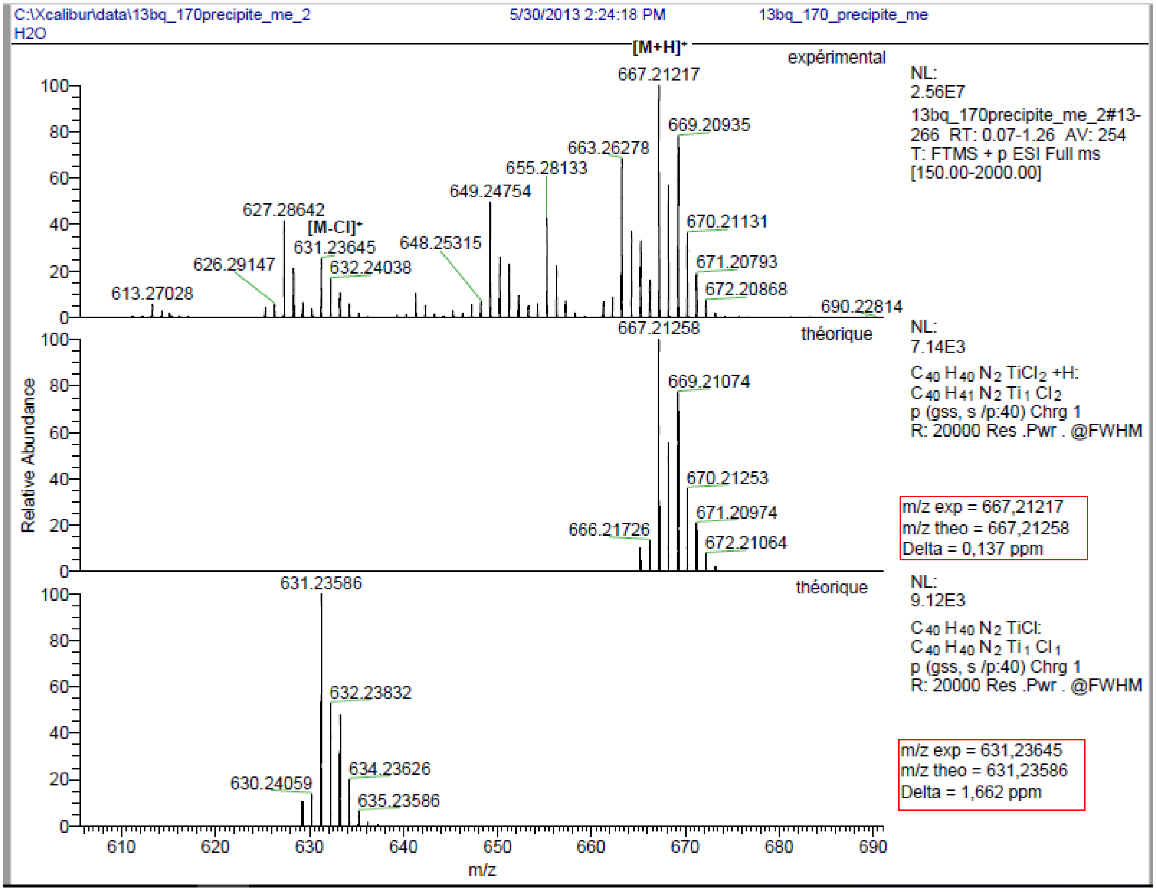
Spectrum 0-128: ^{1}H ^{13}C HMQC of 20 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-129: ^{1}H ^{13}C HMBC of 20 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)

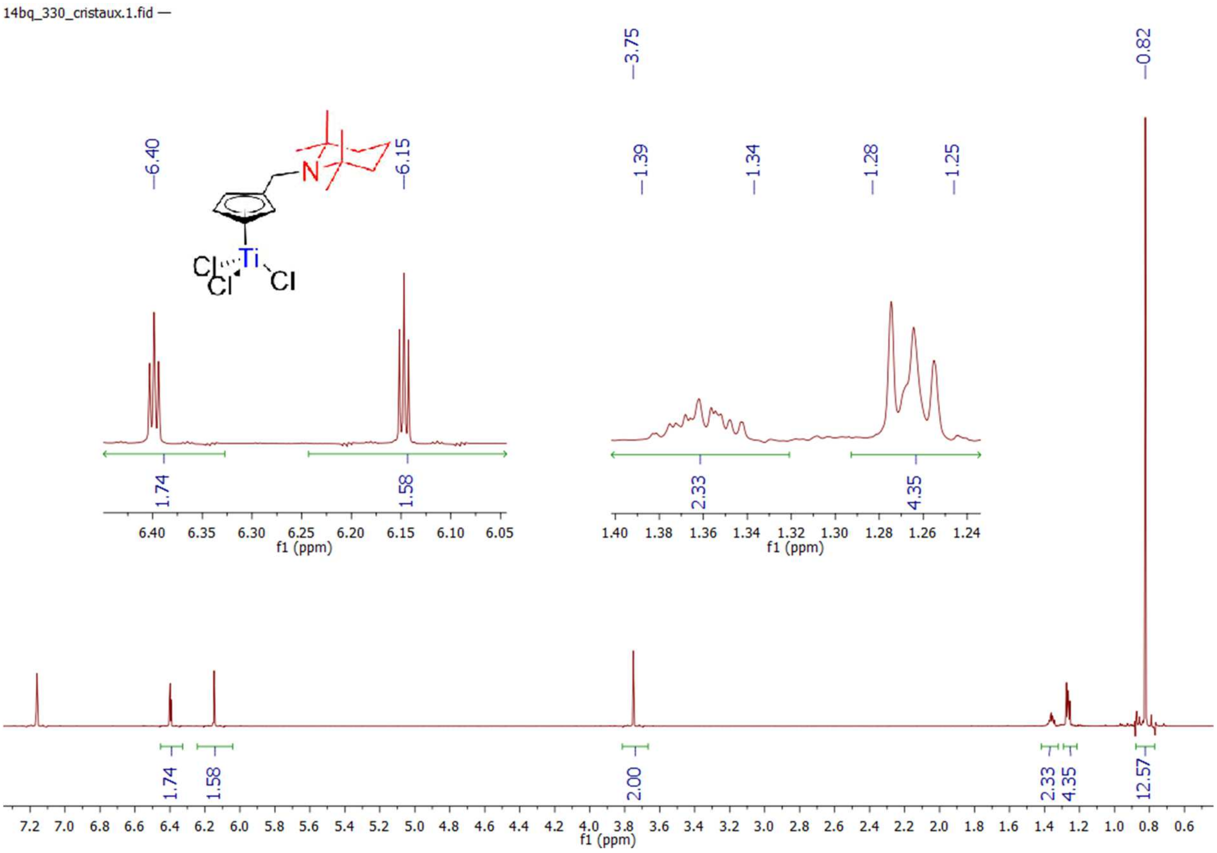


Spectrum 0-130: ^{1}H ^{15}N HMBC of 20 (600.23 MHz / 43.3 MHz, 300 K, benzene-d_6)

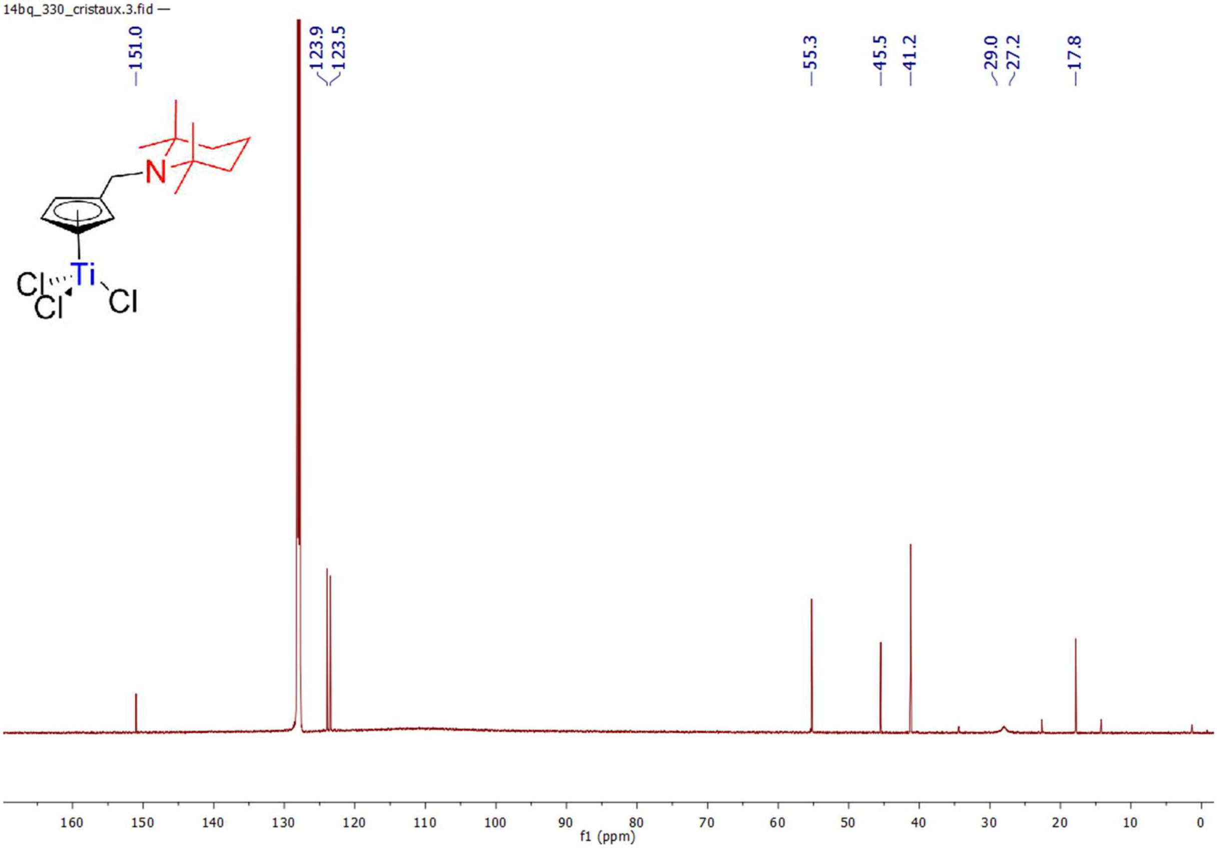


Spectrum 0-131: HRMS of 20 (Positive mode ESI, dichloromethane)

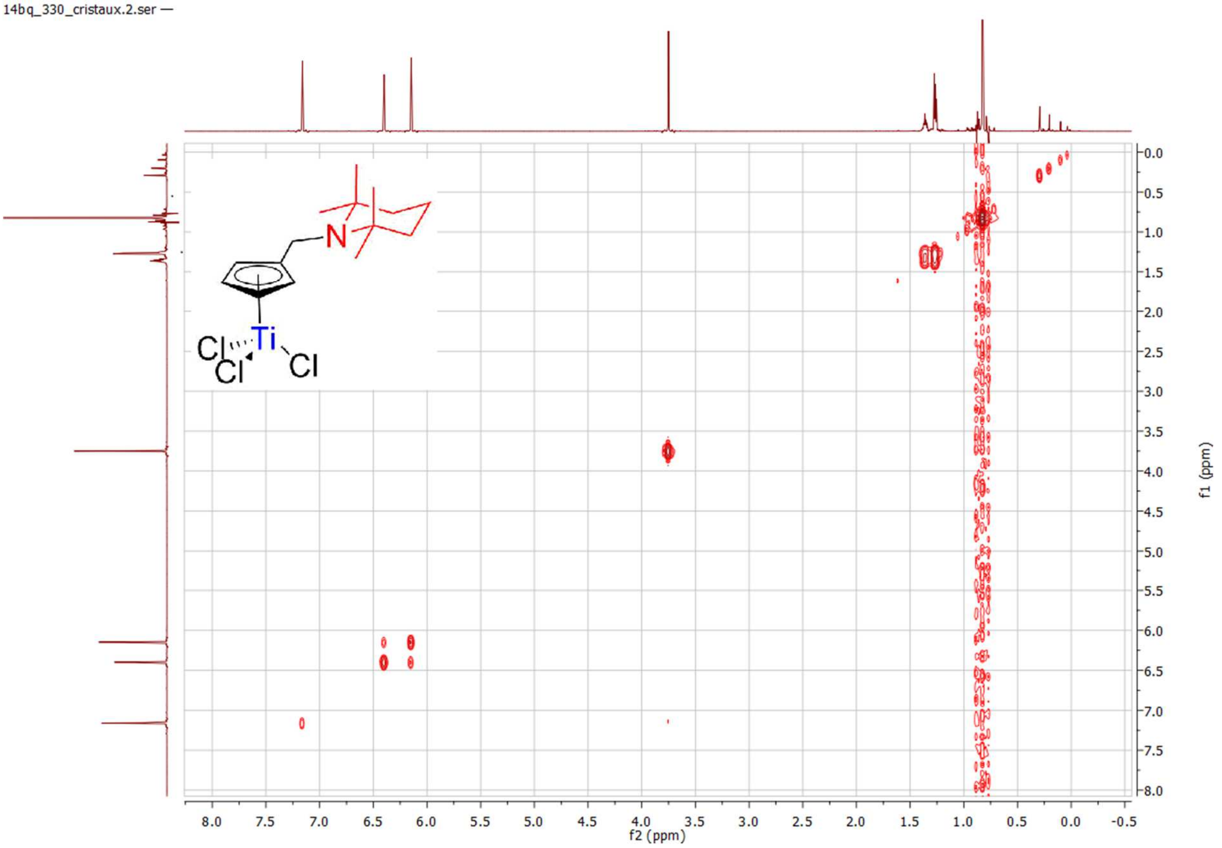
18. Compound **21**:



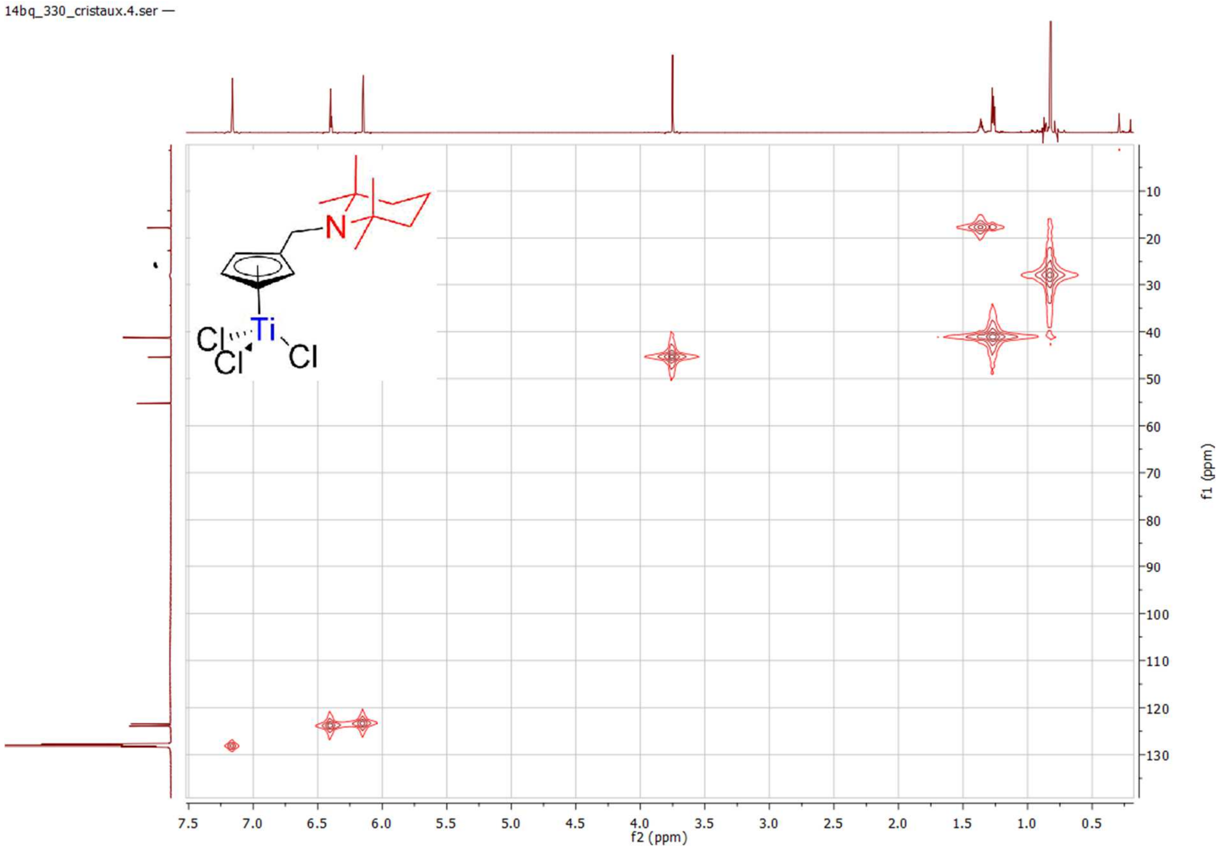
Spectrum 0-132: ^{1}H NMR of 21 (600.23 MHz, 300 K, benzene-d$_6$)



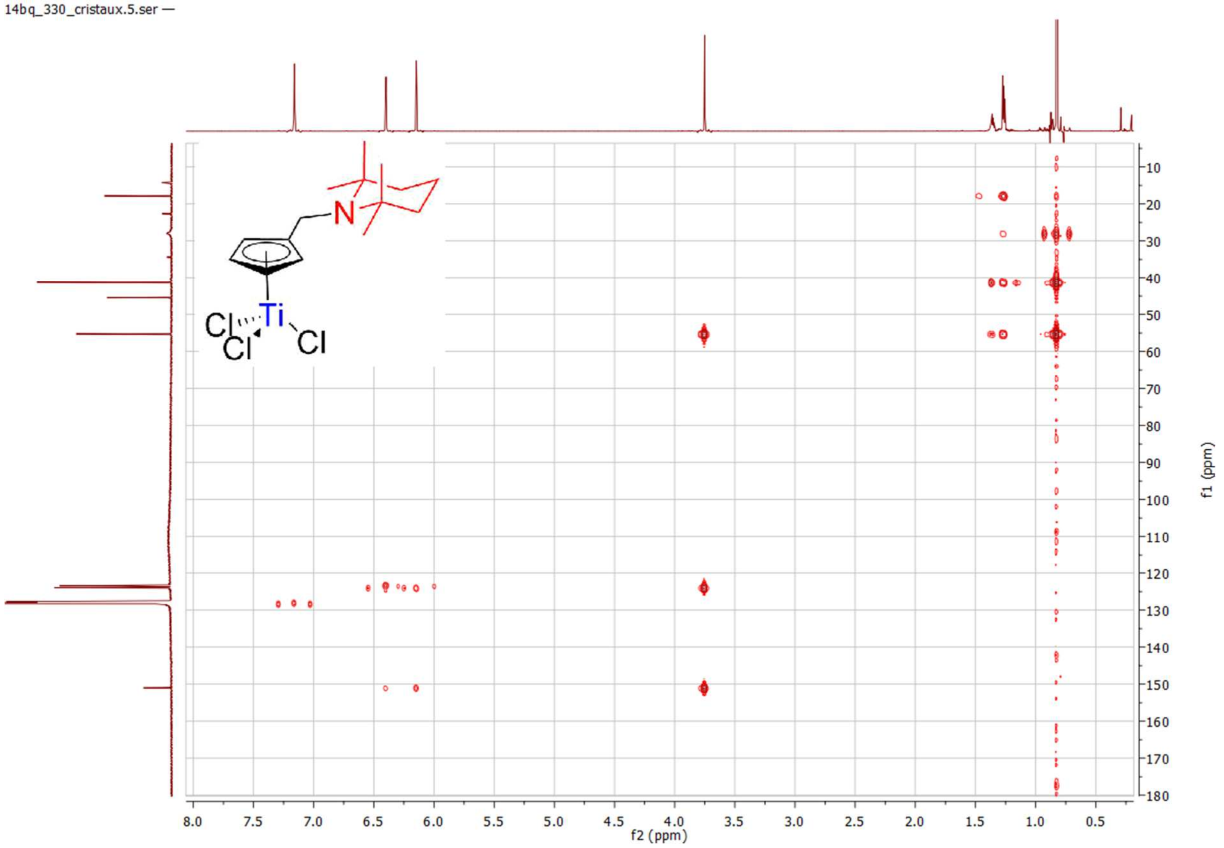
Spectrum 0-133: ^{13}C{^{1}H} NMR of 21 (150.94 MHz, 300 K, benzene-d$_6$)



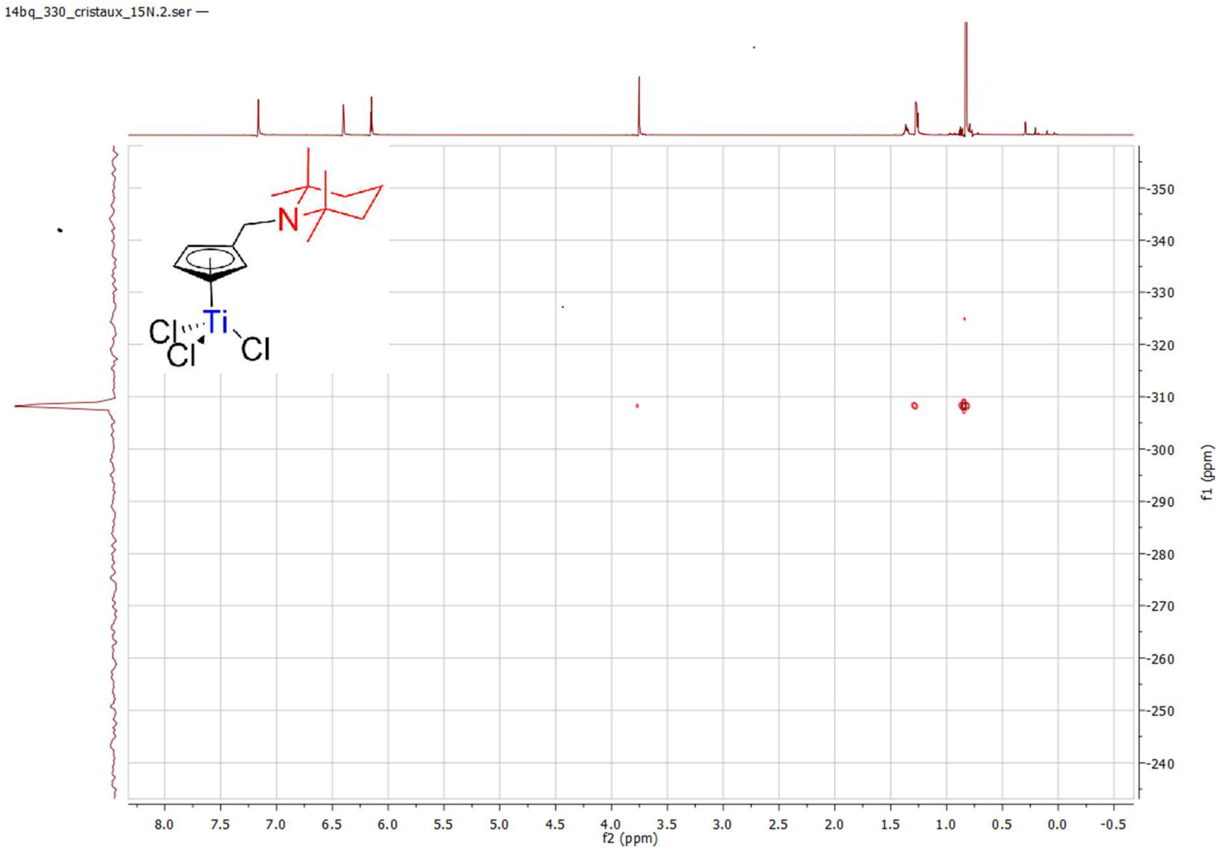
Spectrum 0-134: ^{1}H ^{1}H COSY of 21 (600.23 MHz, 300 K, benzene-d$_6$)



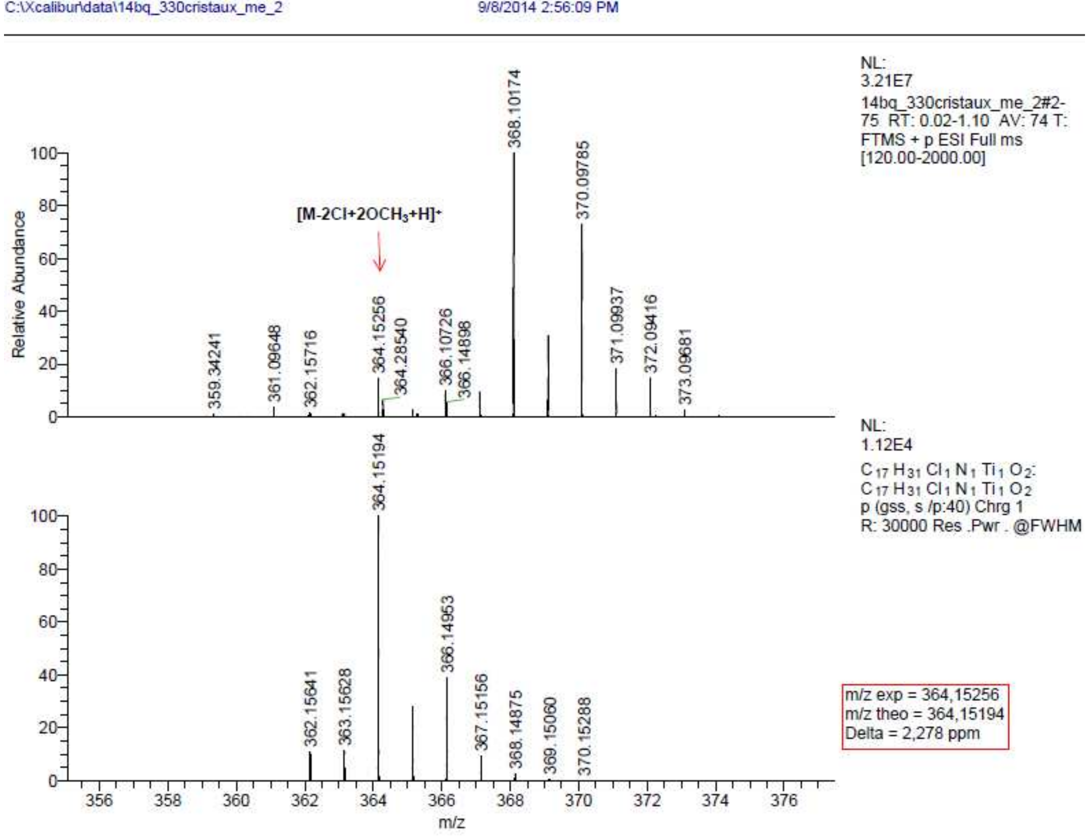
Spectrum 0-135: ^{1}H ^{13}C HMQC of 21 (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6)



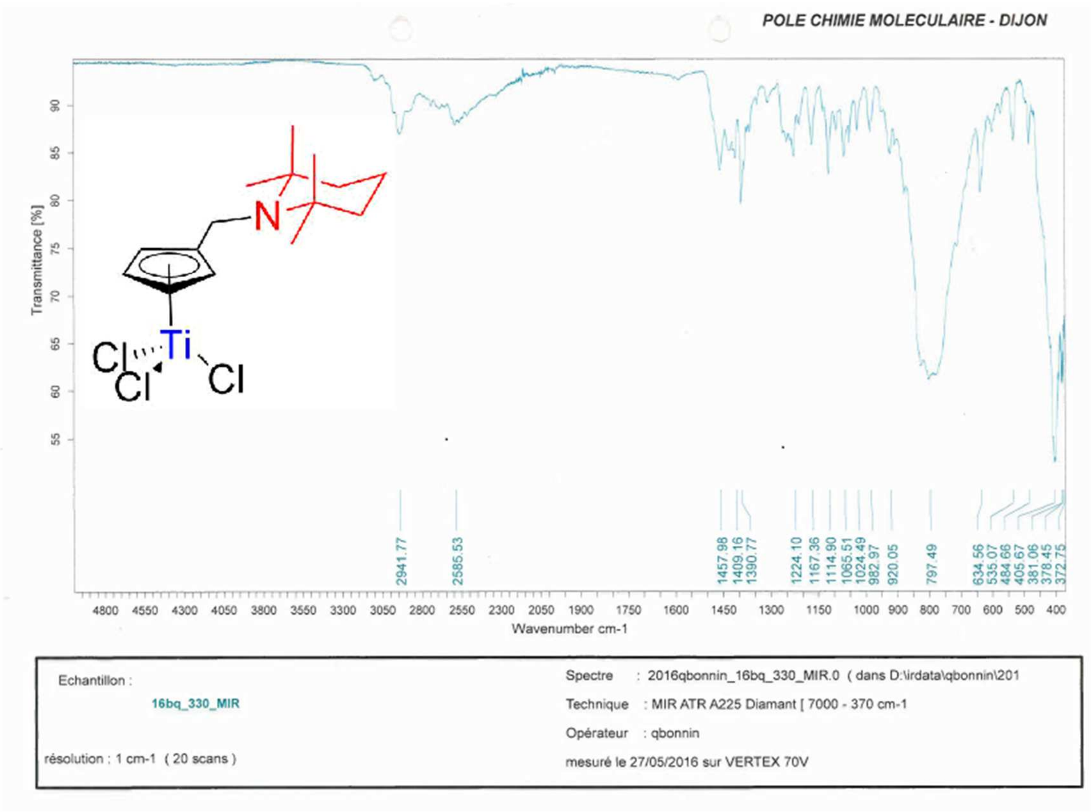
Spectrum 0-136: ^{1}H ^{13}C HMBC of 21 (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6)



Spectrum 0-137: ^{1}H ^{15}N HMBC of 21 (600.23 MHz / 43.3 MHz, 300 K, benzene-d$_6$)



Spectrum 0-138: HRMS (Positive mode ESI, dichloromethane / MeOH)



Echantillon :

16bq_330_MIR

résolution : 1 cm-1 (20 scans)

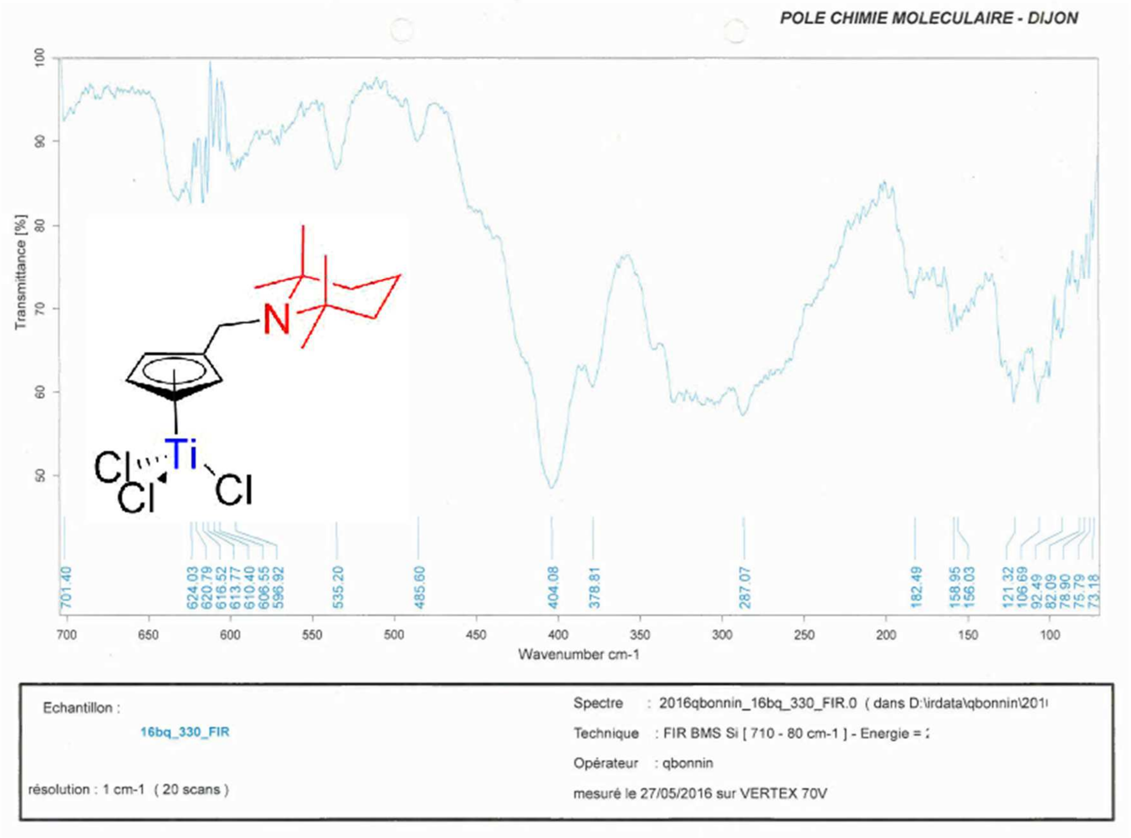
Spectre : 2016qbonnin_16bq_330_MIR.0 (dans D:\irdata\qbonnin\201

Technique : MIR ATR A225 Diamant [7000 - 370 cm-1

Opérateur : qbonnin

mesuré le 27/05/2016 sur VERTEX 70V

Spectrum 0-139: MIR of 21



Echantillon :

16bq_330_FIR

résolution : 1 cm-1 (20 scans)

Spectre : 2016qbonnin_16bq_330_FIR.0 (dans D:\irdata\qbonnin\201

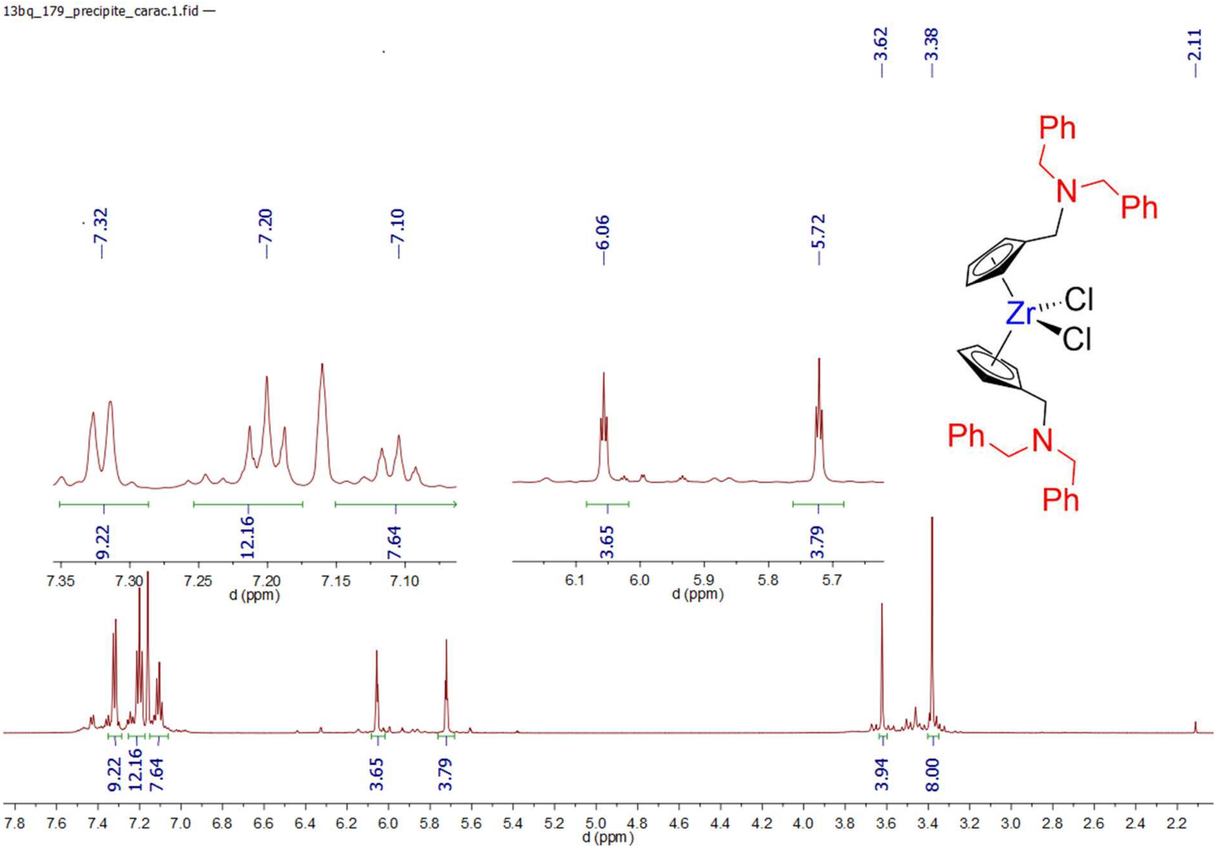
Technique : FIR BMS Si [710 - 80 cm-1] - Energie =

Opérateur : qbonnin

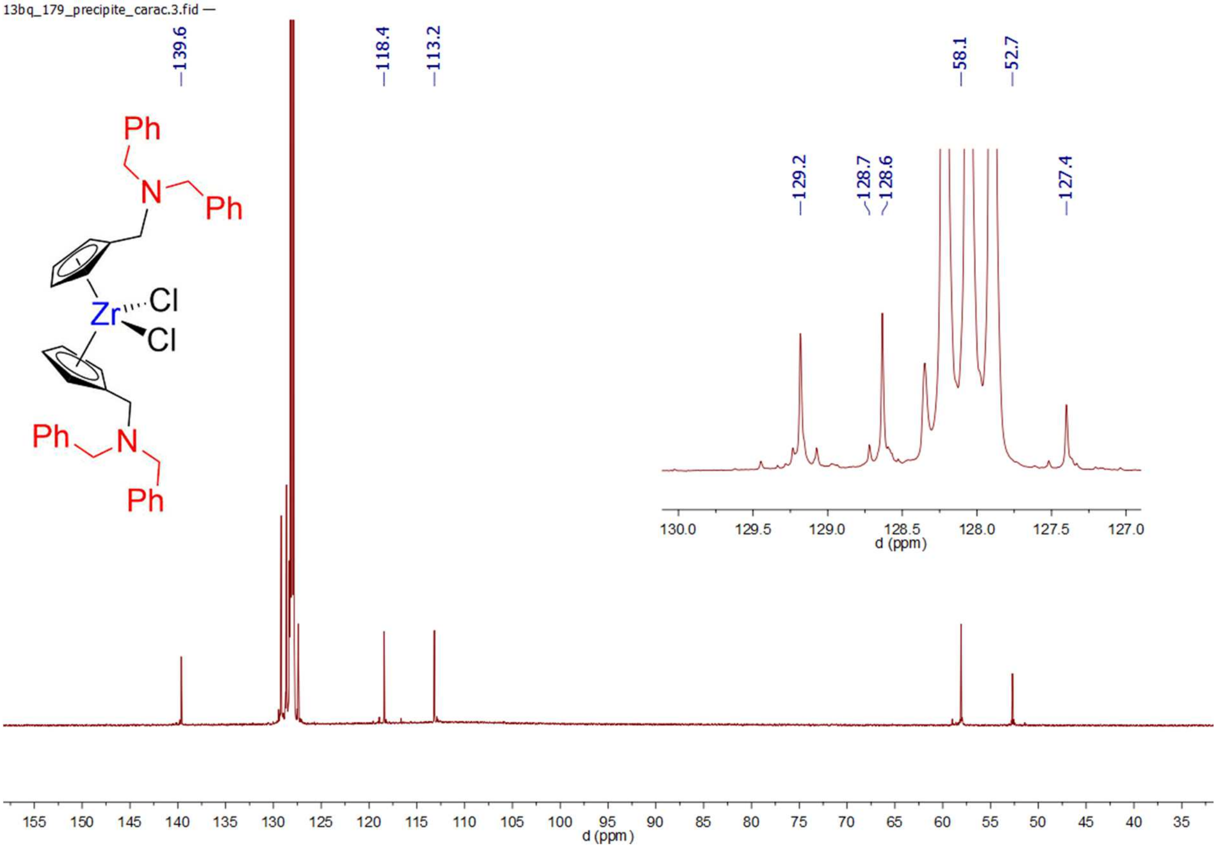
mesuré le 27/05/2016 sur VERTEX 70V

Spectrum 0-140: FIR of 21

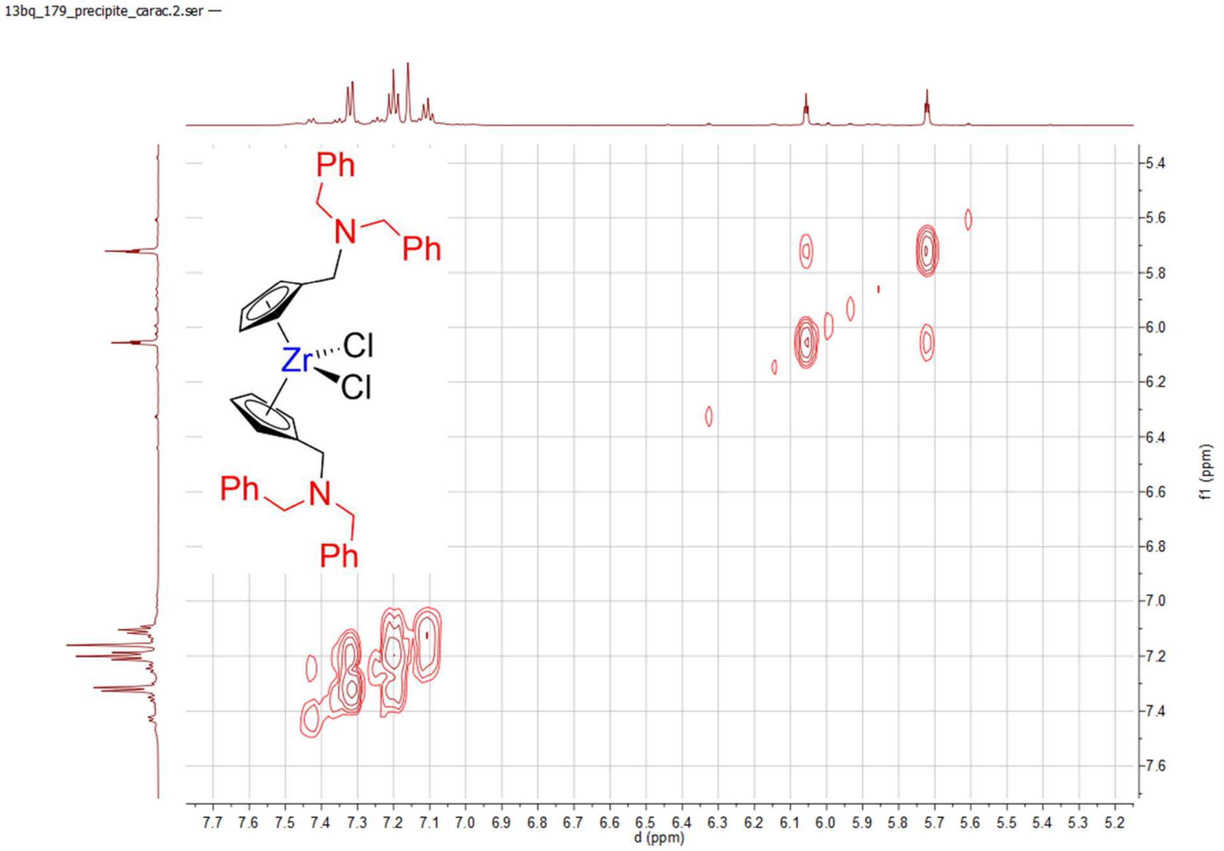
19. Compound **22**:



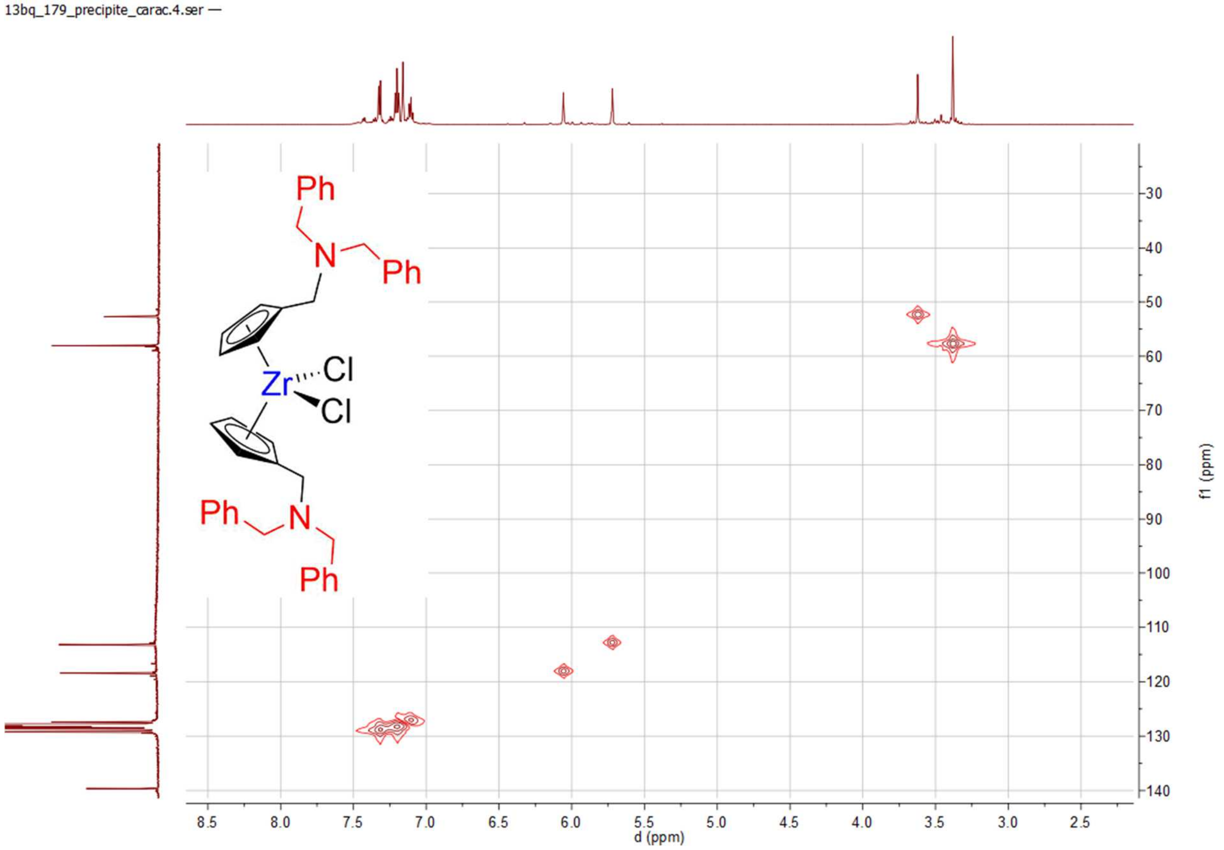
Spectrum 0-141: ^{1}H NMR of 22 (600.23 MHz, 300 K, benzene-d$_6$)



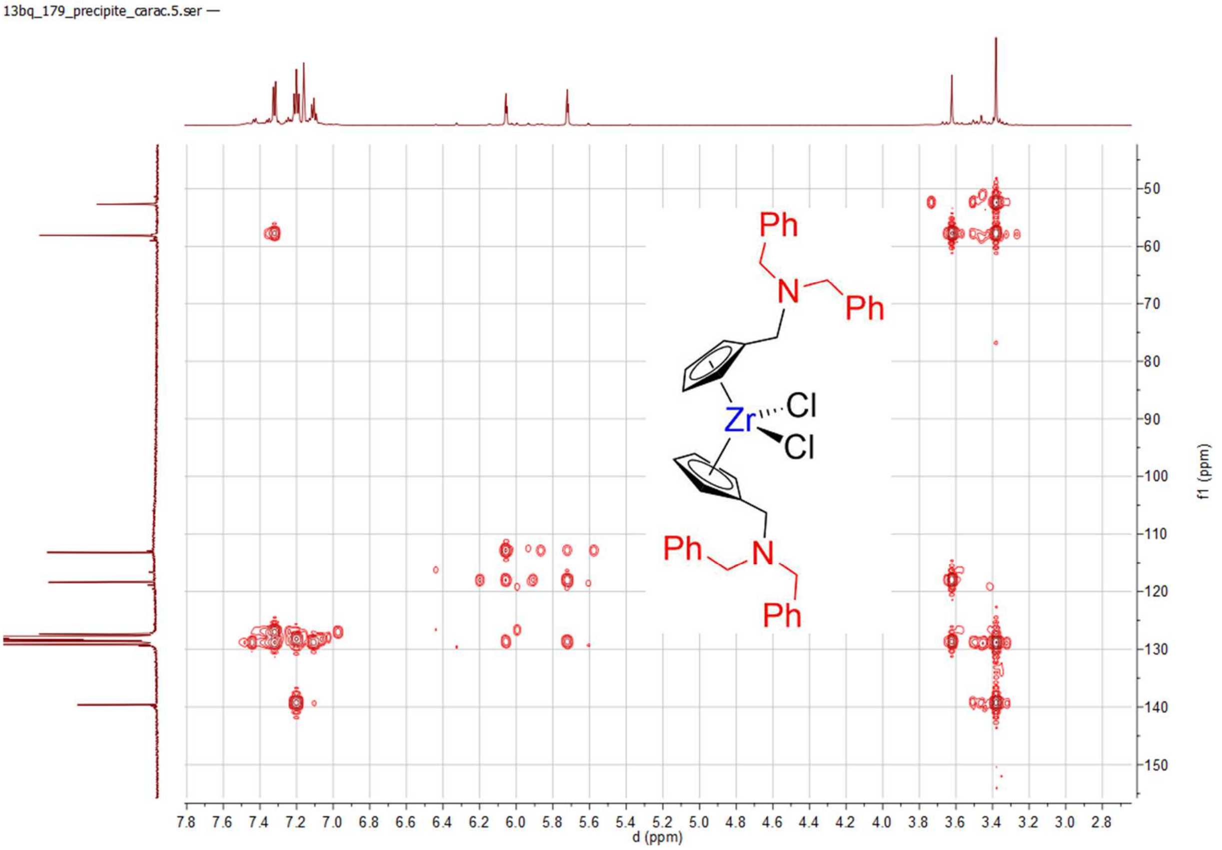
Spectrum 0-142: ^{13}C{^{1}H} NMR of 22 (150.94 MHz, 300 K, benzene-d$_6$)



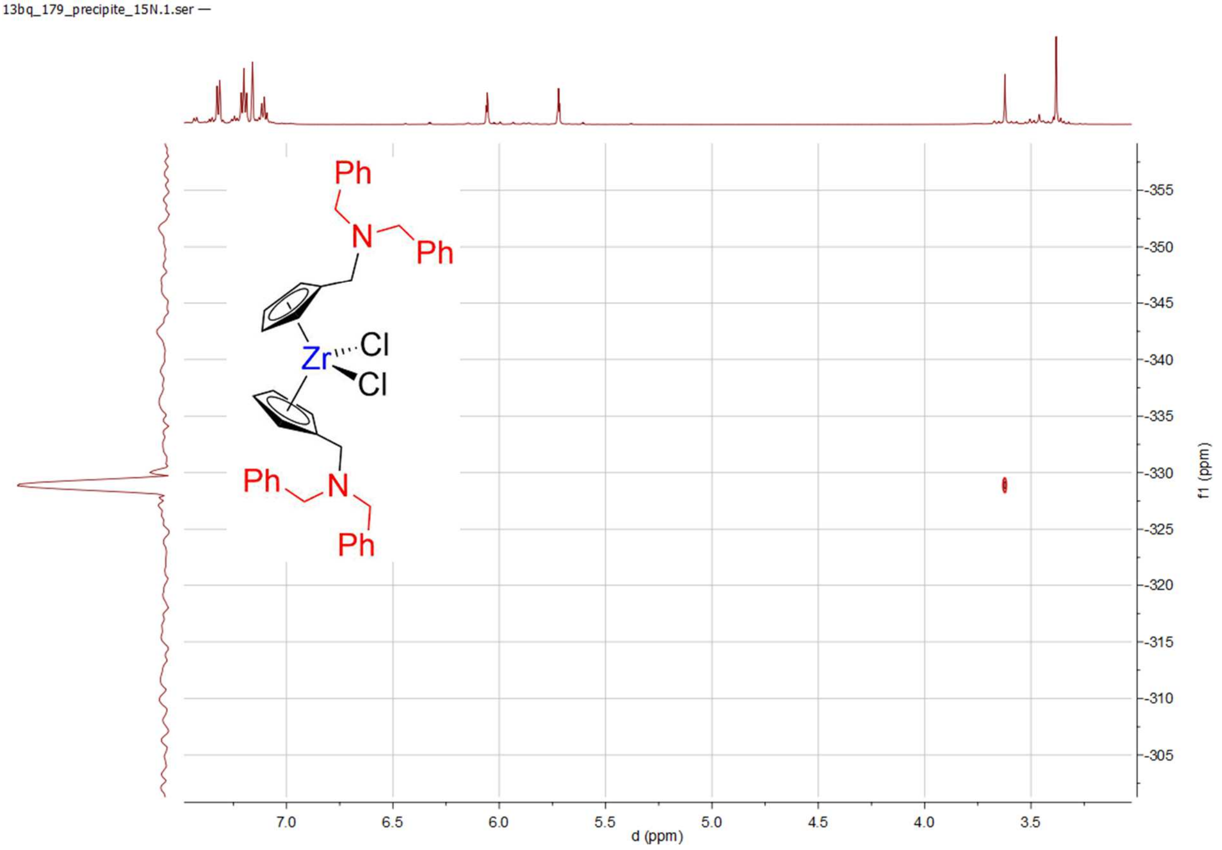
Spectrum 0-143: ^{1}H ^{1}H COSY of 22 (600.23 MHz, 300 K, benzene-d_6)



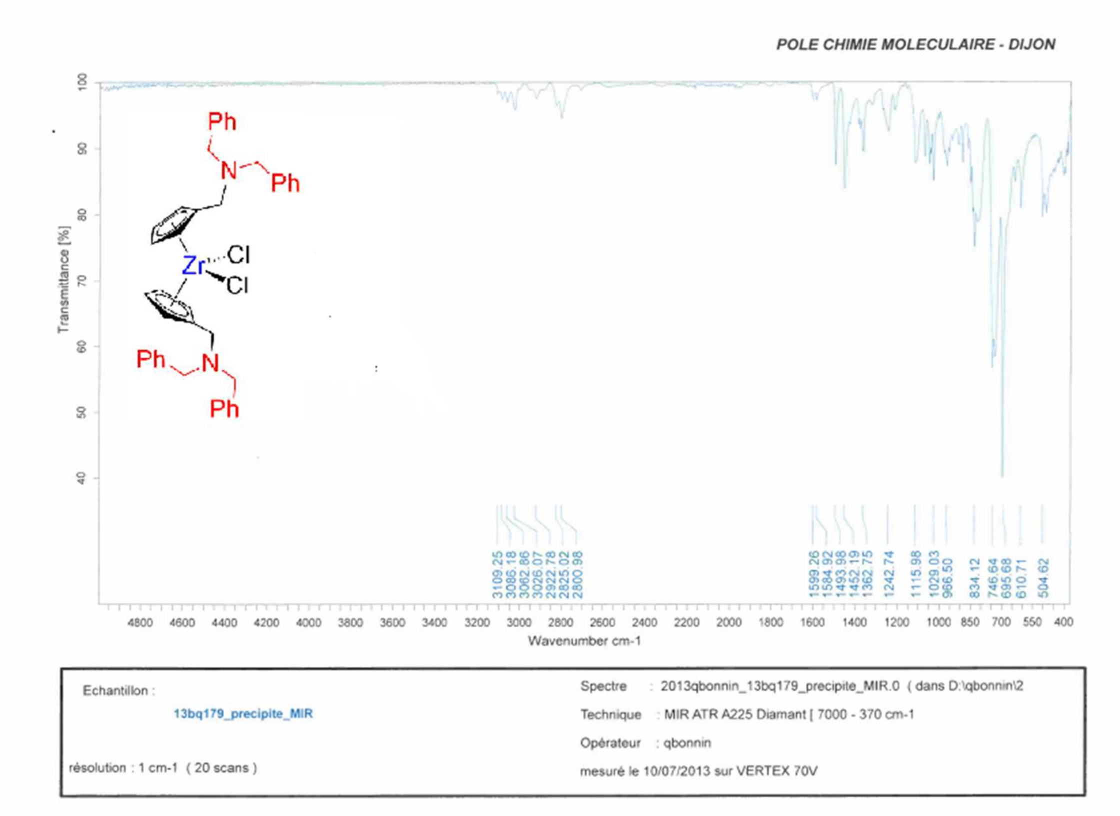
Spectrum 0-144: ^{1}H ^{13}C HMQC of 22 (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6



Spectrum 0-145: ^{1}H ^{13}C HMBC of 22 (600.23 MHz / 150.94 MHz, 300 K, benzene-d$_6$)



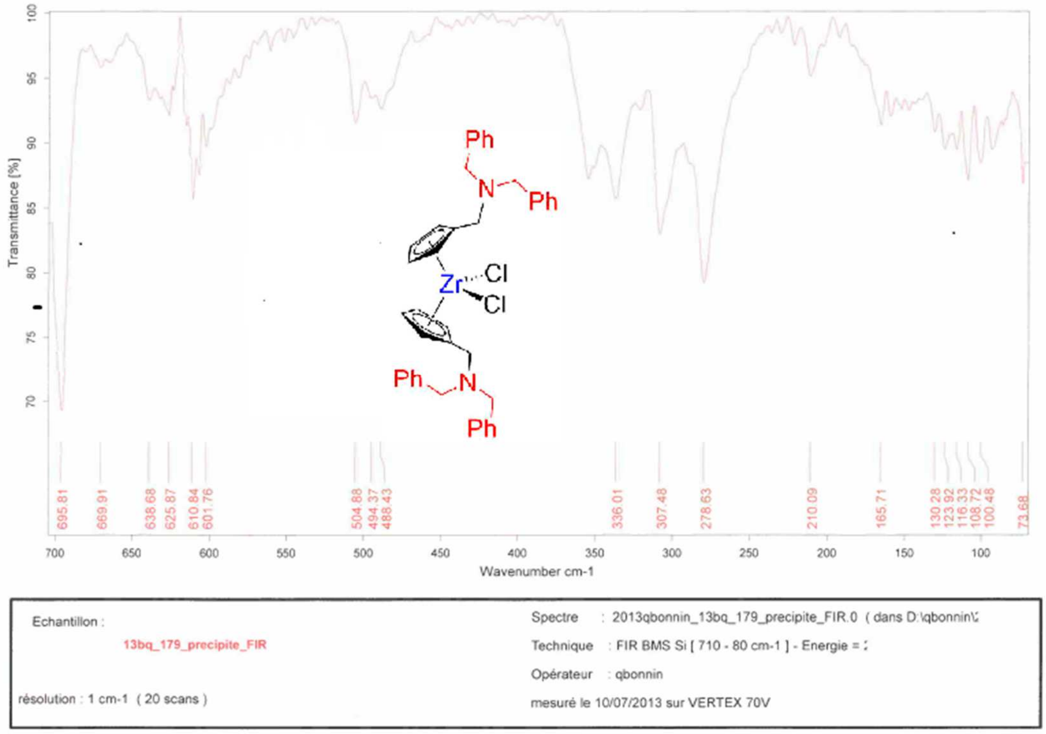
Spectrum 0-146: ^{1}H ^{15}N HMBC of 22 (600.23 MHz / 43.3 MHz, 300 K, benzene-d$_6$)



Echantillon :
13bq179_precipite_MIR
résolution : 1 cm-1 (20 scans)

Spectre : 2013qbonnin_13bq179_precipite_MIR.0 (dans D:\qbonnin\2
Technique : MIR ATR A225 Diamant [7000 - 370 cm-1
Opérateur : qbonnin
mesuré le 10/07/2013 sur VERTEX 70V

Spectrum 0-147: MIR of 22

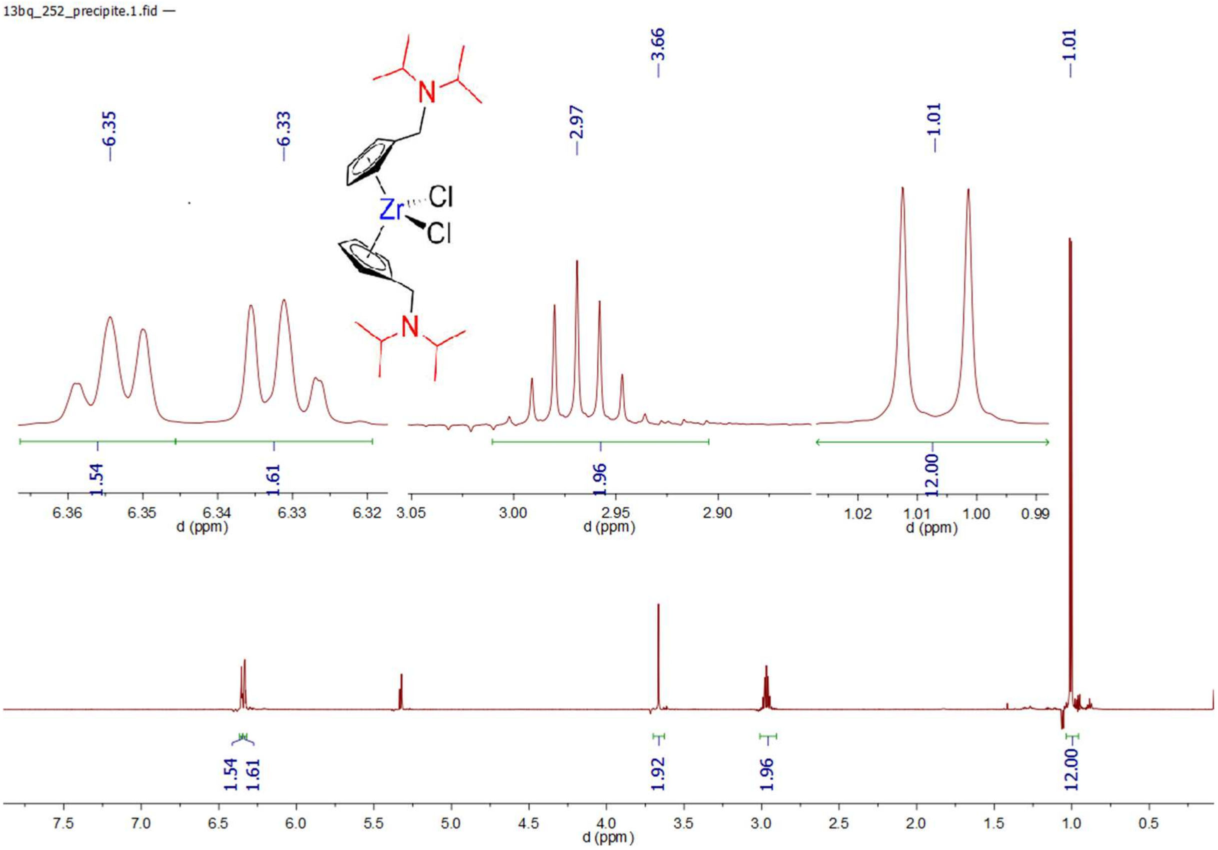


Echantillon :
13bq_179_precipite_FIR
résolution : 1 cm-1 (20 scans)

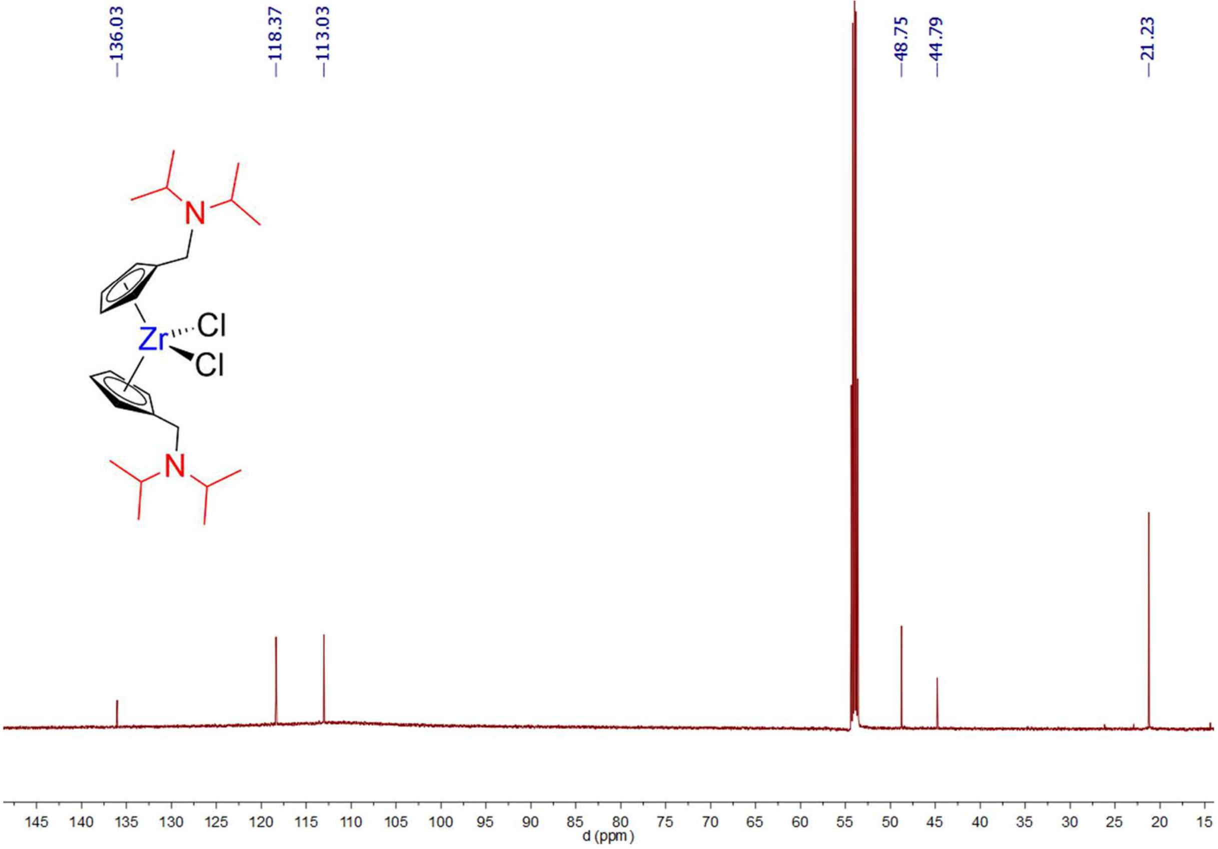
Spectre : 2013qbonnin_13bq_179_precipite_FIR.0 (dans D:\qbonnin\
Technique : FIR BMS Si [710 - 80 cm-1] - Energie =
Opérateur : qbonnin
mesuré le 10/07/2013 sur VERTEX 70V

Spectrum 0-148: FIR of 22

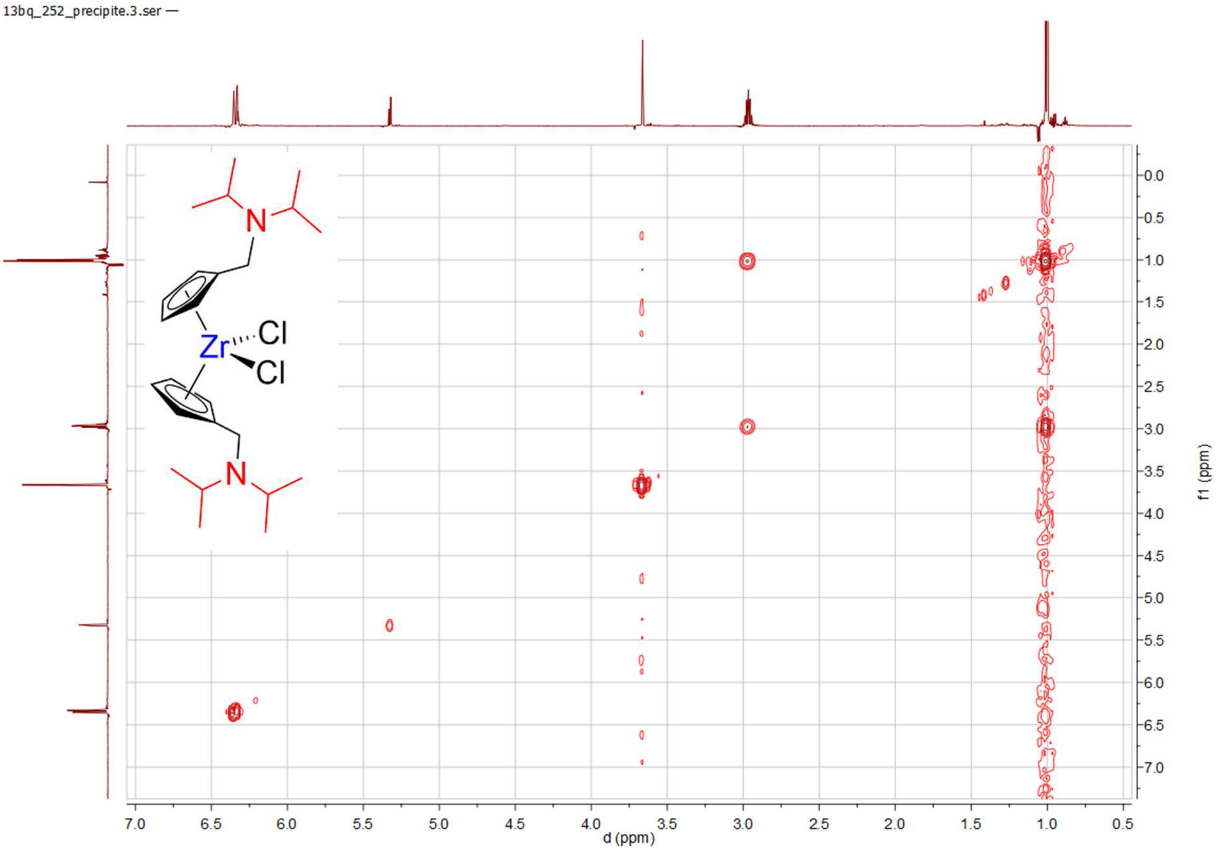
20. Compound **23**:



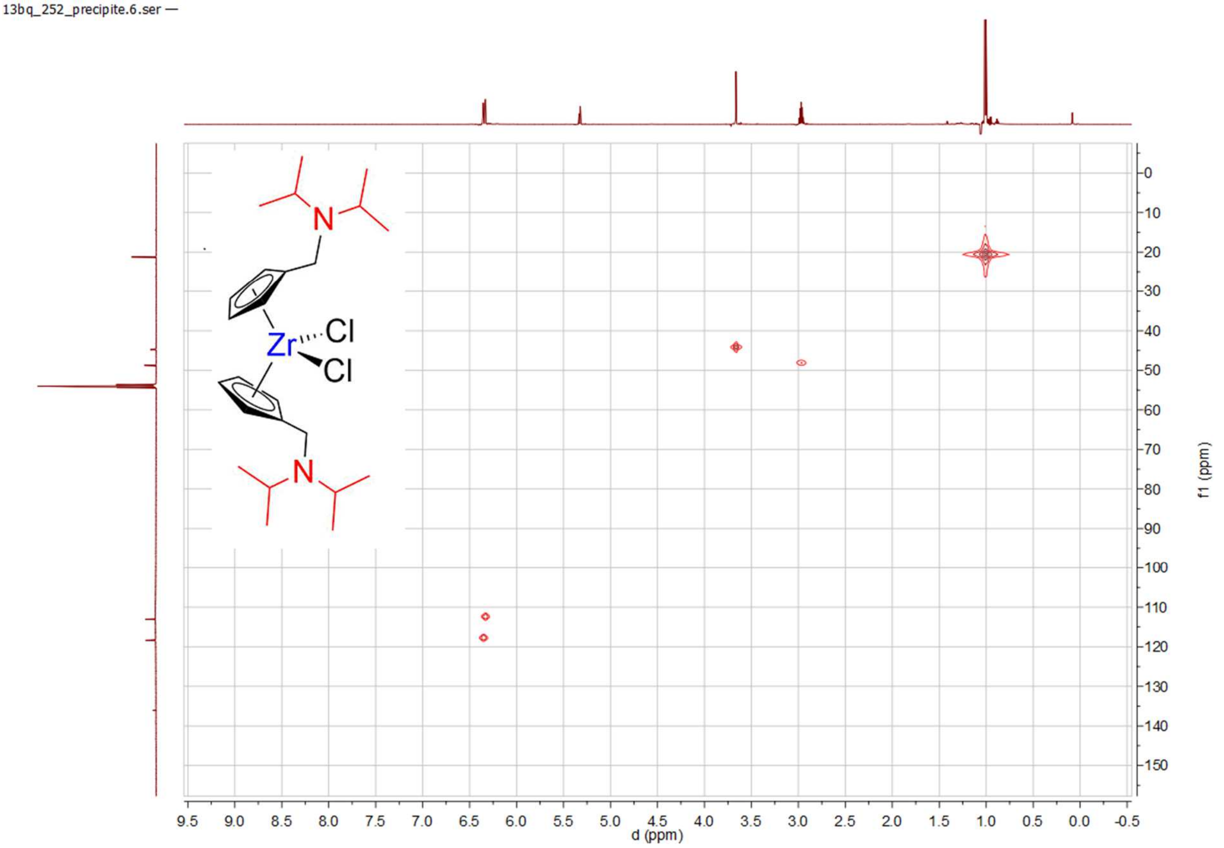
Spectrum 0-149: ^{1}H NMR of 23 (600.23 MHz, 300 K, dichloromethane-d$_2$)



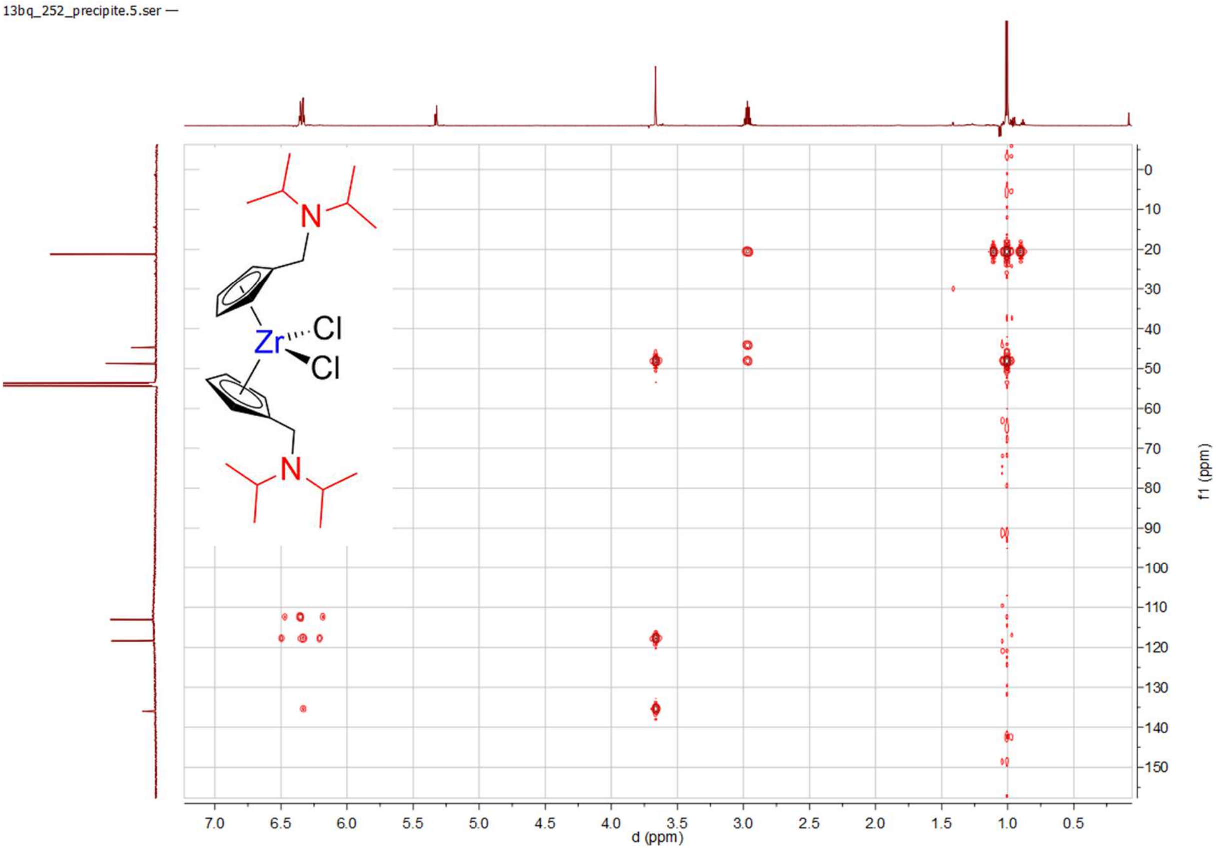
Spectrum 0-150: ^{13}C{^{1}H} NMR of 23 (150.94 MHz, 300 K, dichloromethane-d$_2$)



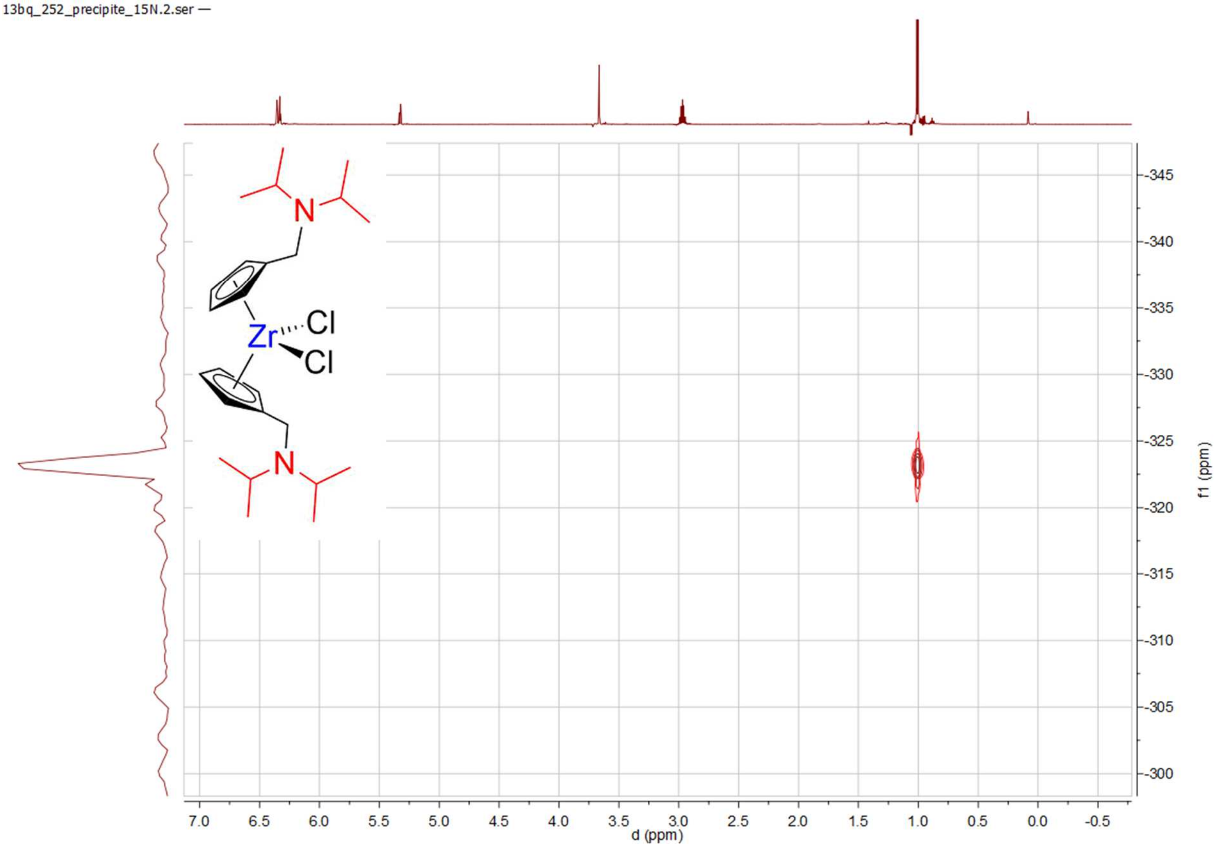
Spectrum 0-151: ^{1}H ^{1}H COSY of 23 (600.23 MHz, 300 K, dichloromethane-d_2)



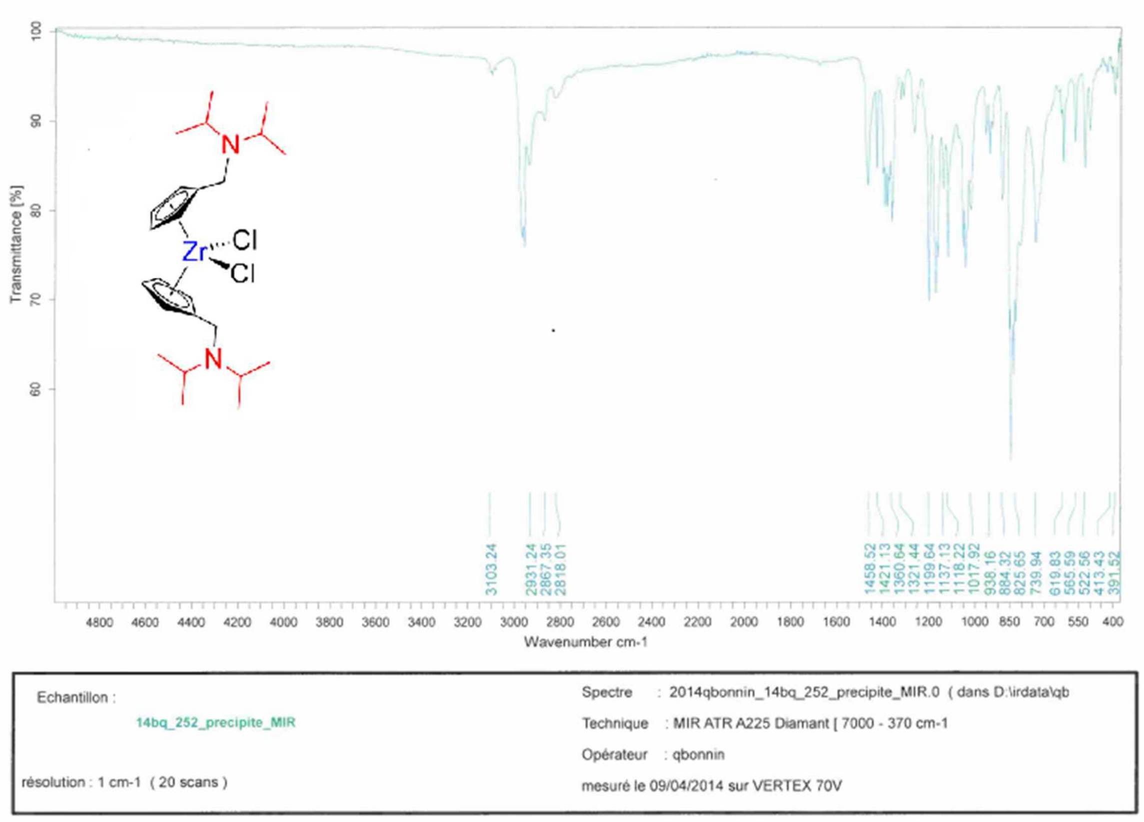
Spectrum 0-152: ^{1}H ^{13}C HMQC of 23 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-153: ^{1}H ^{13}C HMBC of 23 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-154: ^{1}H ^{15}N HMBC of 23 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)



Echantillon :

14bq_252_precipite_MIR

résolution : 1 cm-1 (20 scans)

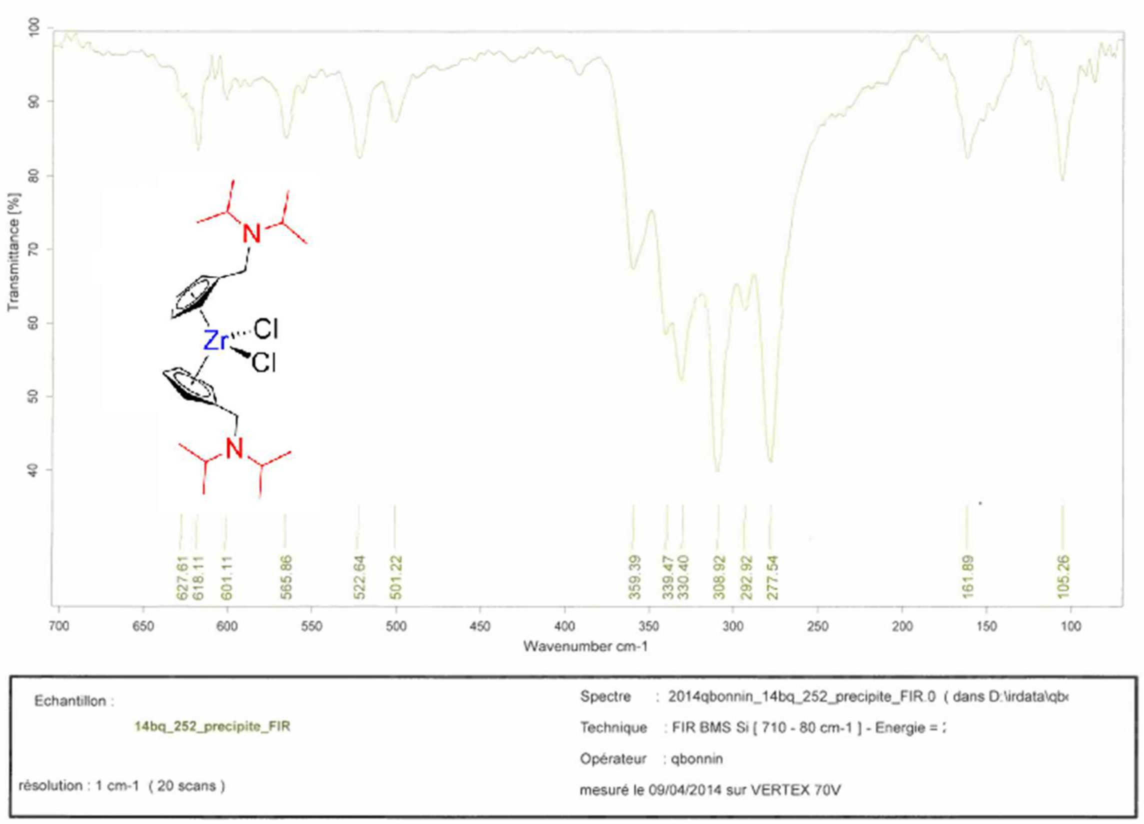
Spectre : 2014qbonnin_14bq_252_precipite_MIR.0 (dans D:\irdata\qb

Technique : MIR ATR A225 Diamant [7000 - 370 cm-1

Opérateur : qbonnin

mesuré le 09/04/2014 sur VERTEX 70V

Spectrum 0-155: MIR of 23



Echantillon :

14bq_252_precipite_FIR

résolution : 1 cm-1 (20 scans)

Spectre : 2014qbonnin_14bq_252_precipite_FIR.0 (dans D:\irdata\qb

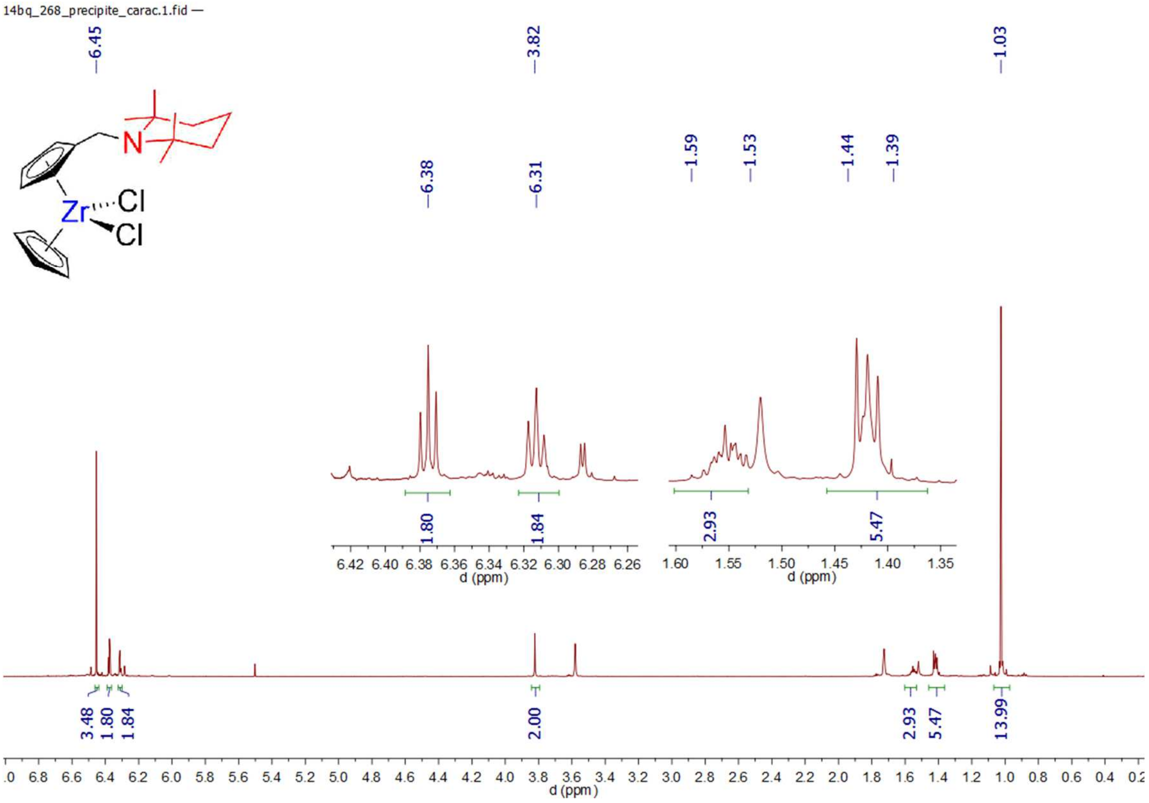
Technique : FIR BMS Si [710 - 80 cm-1] - Energie = :

Opérateur : qbonnin

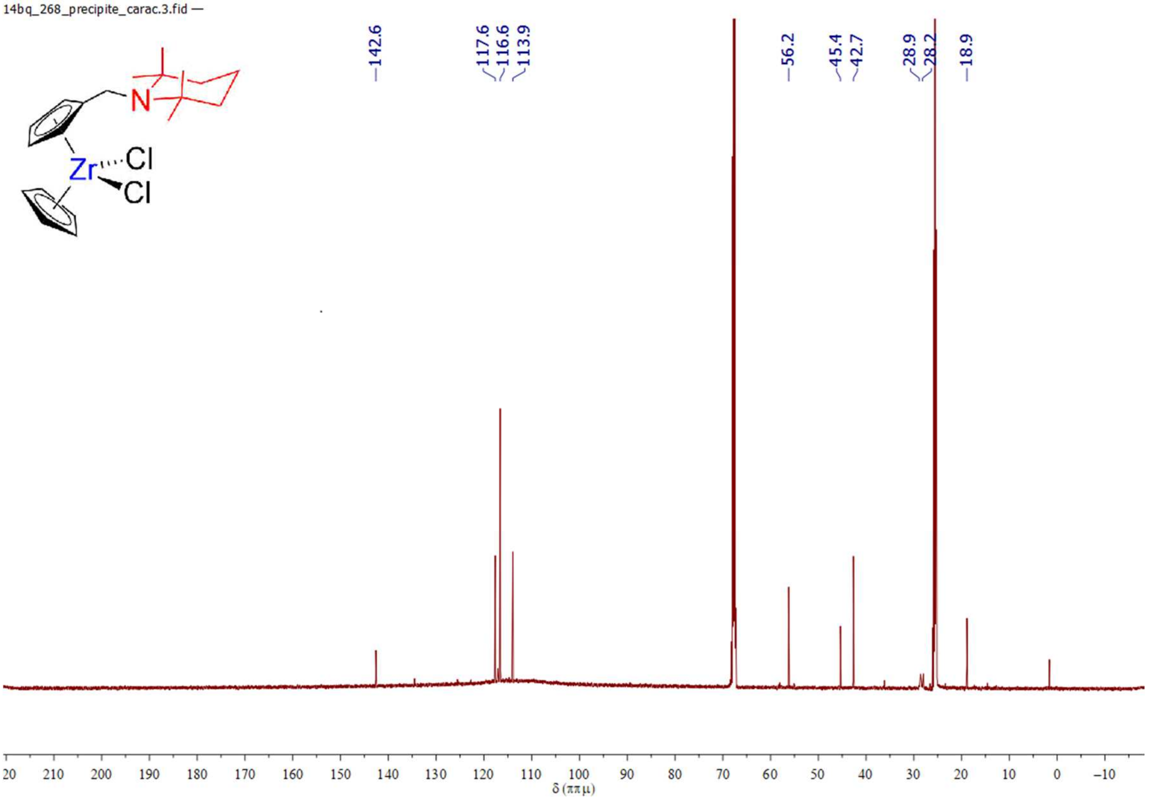
mesuré le 09/04/2014 sur VERTEX 70V

Spectrum 0-156: FIR of 23

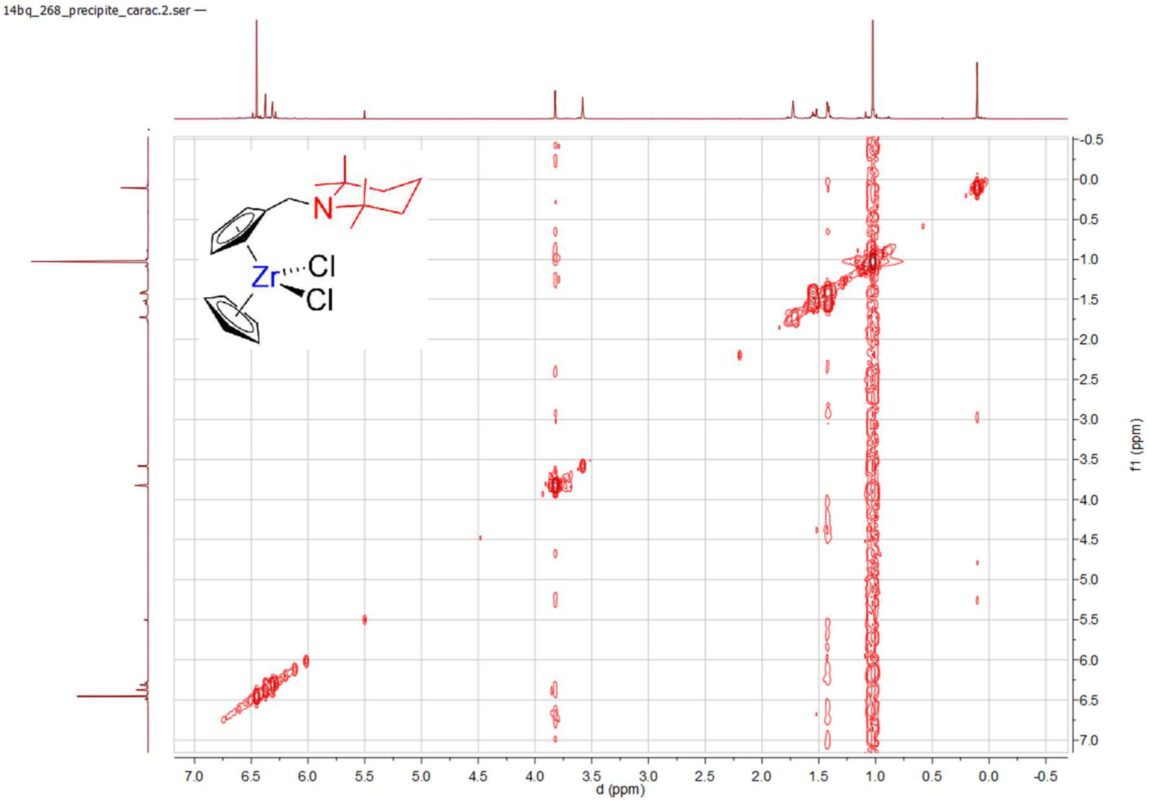
21. Compound **24**:



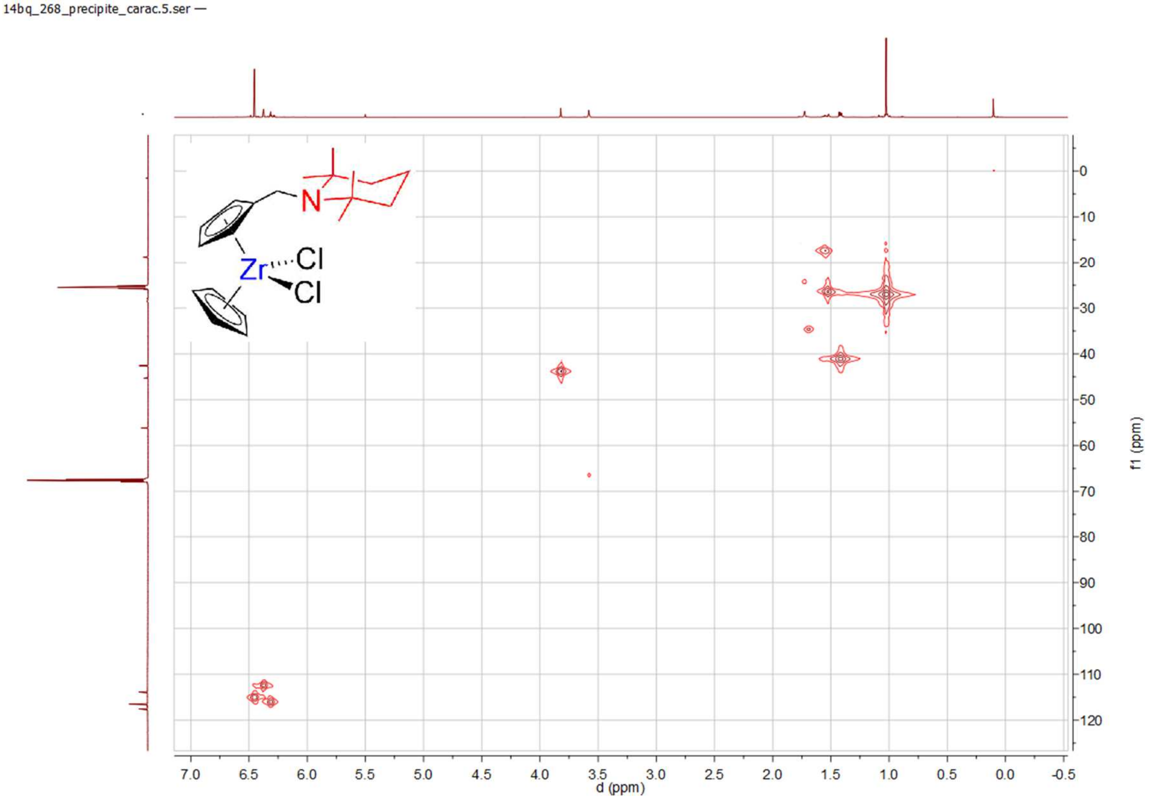
Spectrum 0-157: ^{1}H NMR of 24 (600.23 MHz, 300 K, tetrahydrofuran-d$_8$)



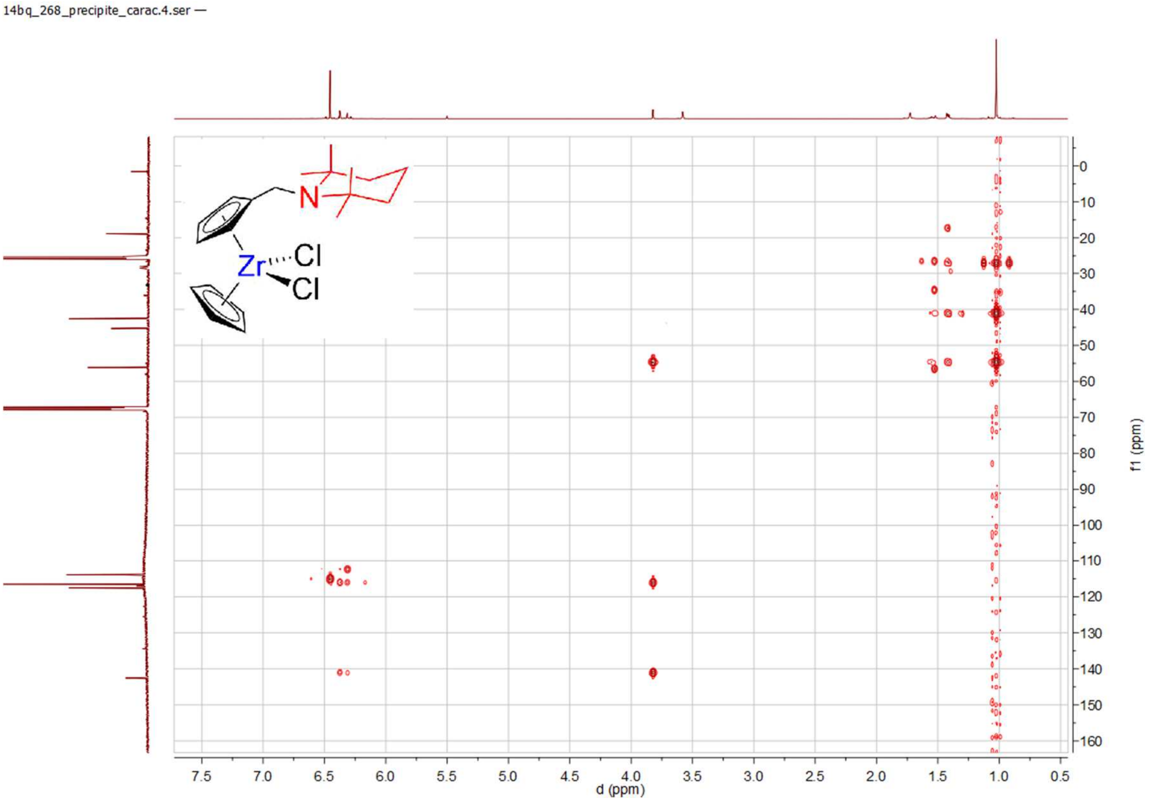
Spectrum 0-158: ^{13}C{^{1}H} NMR of 24 (150.94 MHz, 300 K, tetrahydrofuran-d$_8$)



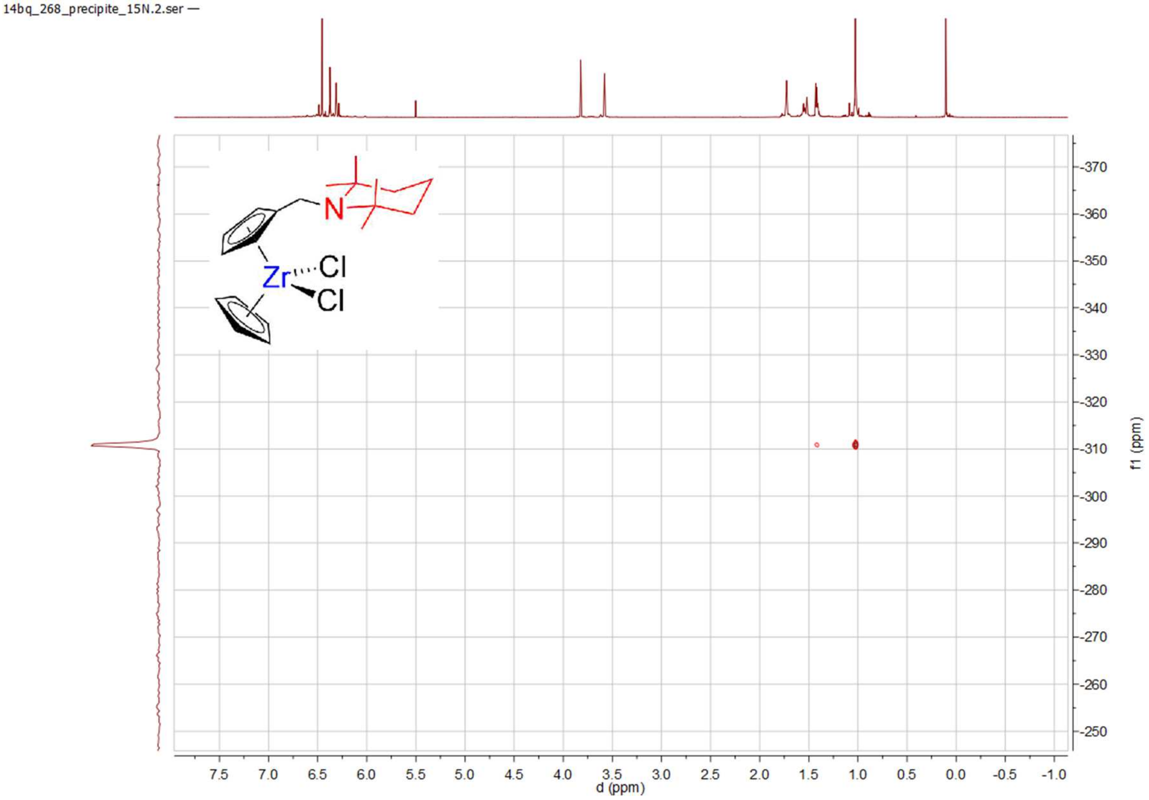
Spectrum 0-159: ^{1}H ^{1}H COSY of 24 (600.23 MHz, 300 K, tetrahydrofuran-d_8)



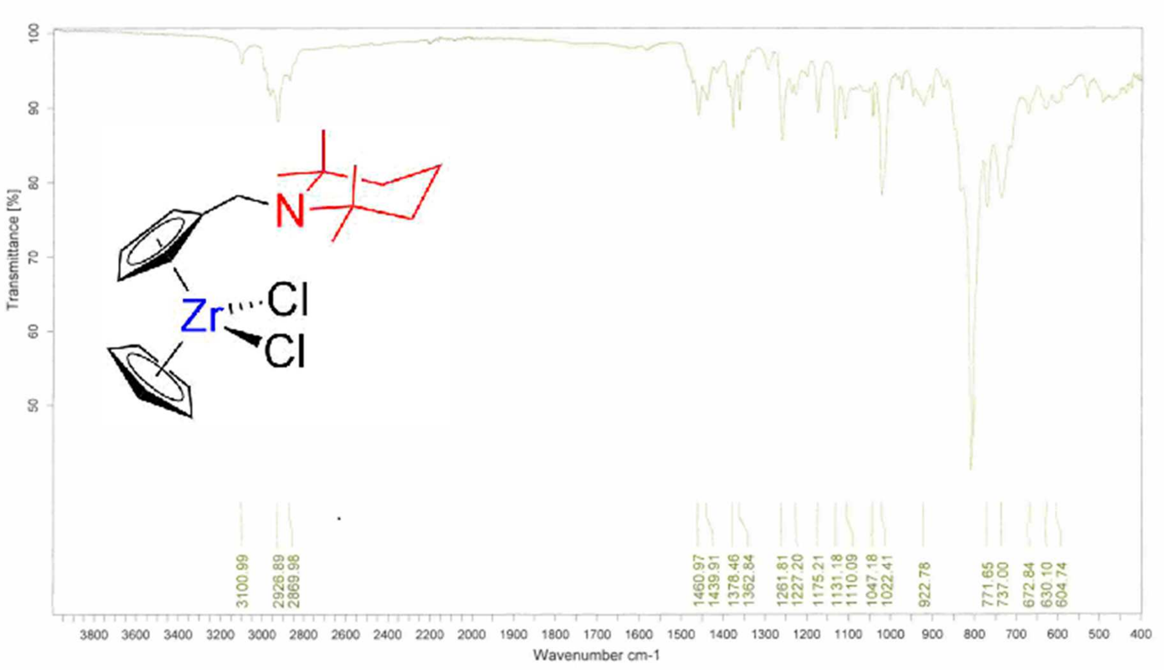
Spectrum 0-160: ^{1}H ^{13}C HMQC of 24 (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d_8)



Spectrum 0-161: ^{1}H ^{13}C HMBC of 24 (600.23 MHz / 150.94 MHz, 300 K, tetrahydrofuran-d$_8$)



Spectrum 0-162: ^{1}H ^{15}N HMBC of 24 (600.23 MHz / 43.3 MHz, 300 K, tetrahydrofuran-d$_8$)



Echantillon :

14bq_268_precipite_MIR

résolution : 1 cm-1 (20 scans)

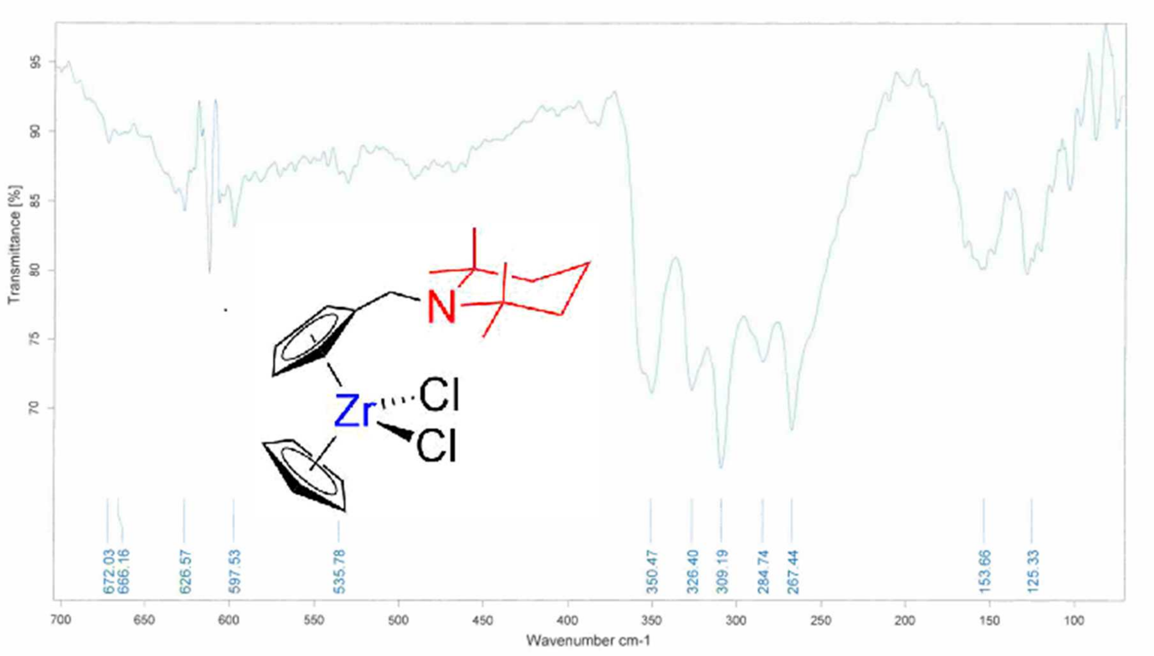
Spectre : 2014qbonnin_14bq_268_precipite_MIR.0 (dans D:\irdata\qb

Technique : BMS KBR [7500 - 370 cm-1] - Energie =

Opérateur : qbonnin

mesuré le 19/05/2014 sur VERTEX 70V

Spectrum 0-163: MIR of 24



Echantillon :

14bq_268_precipite_FIR

résolution : 1 cm-1 (20 scans)

Spectre : 2014qbonnin_14bq_268_precipite_FIR.0 (dans D:\irdata\qb

Technique : FIR BMS Si [710 - 80 cm-1] - Energie = :

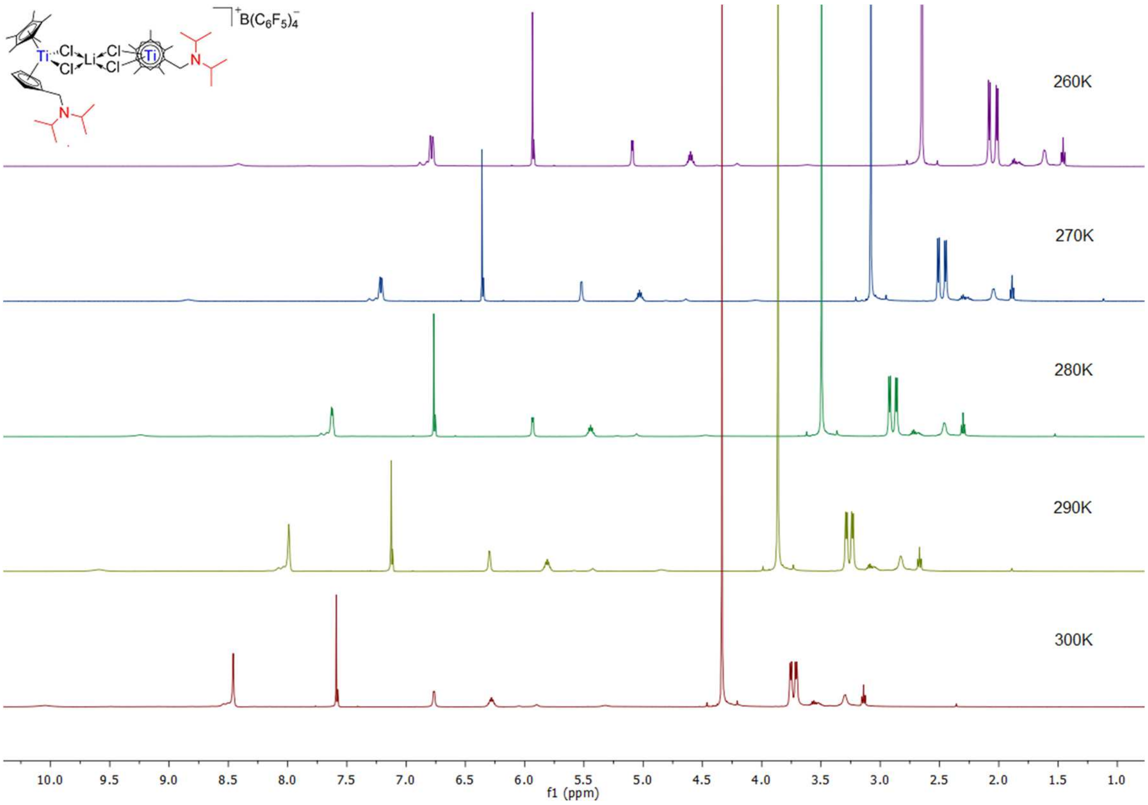
Opérateur : qbonnin

mesuré le 19/05/2014 sur VERTEX 70V

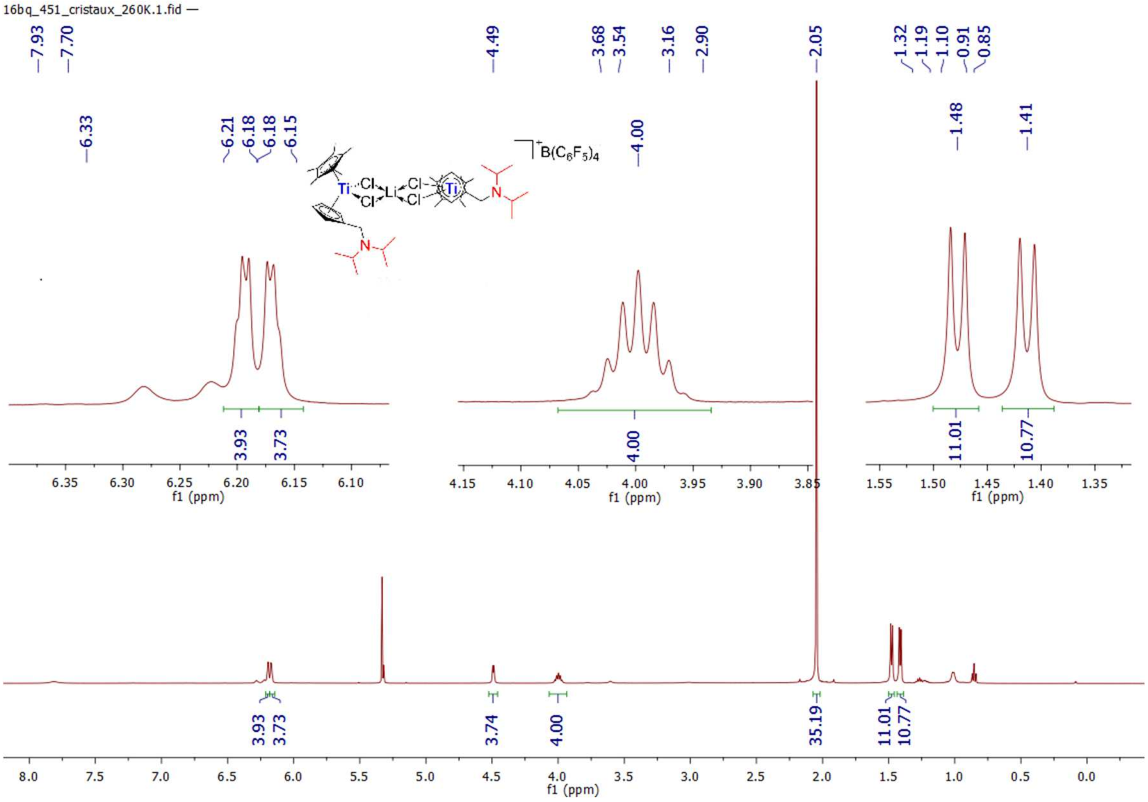
Spectrum 0-164: FIR of 24

B. Appendix Chapter III

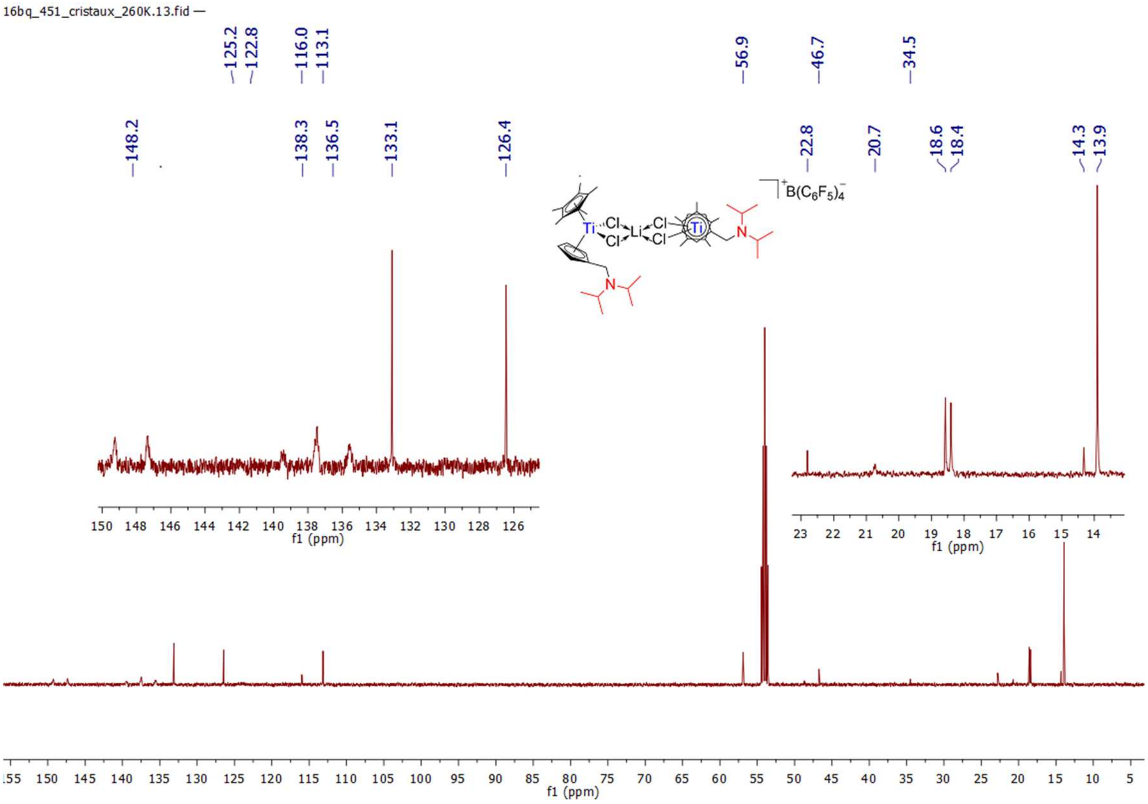
1. Compound **25**:



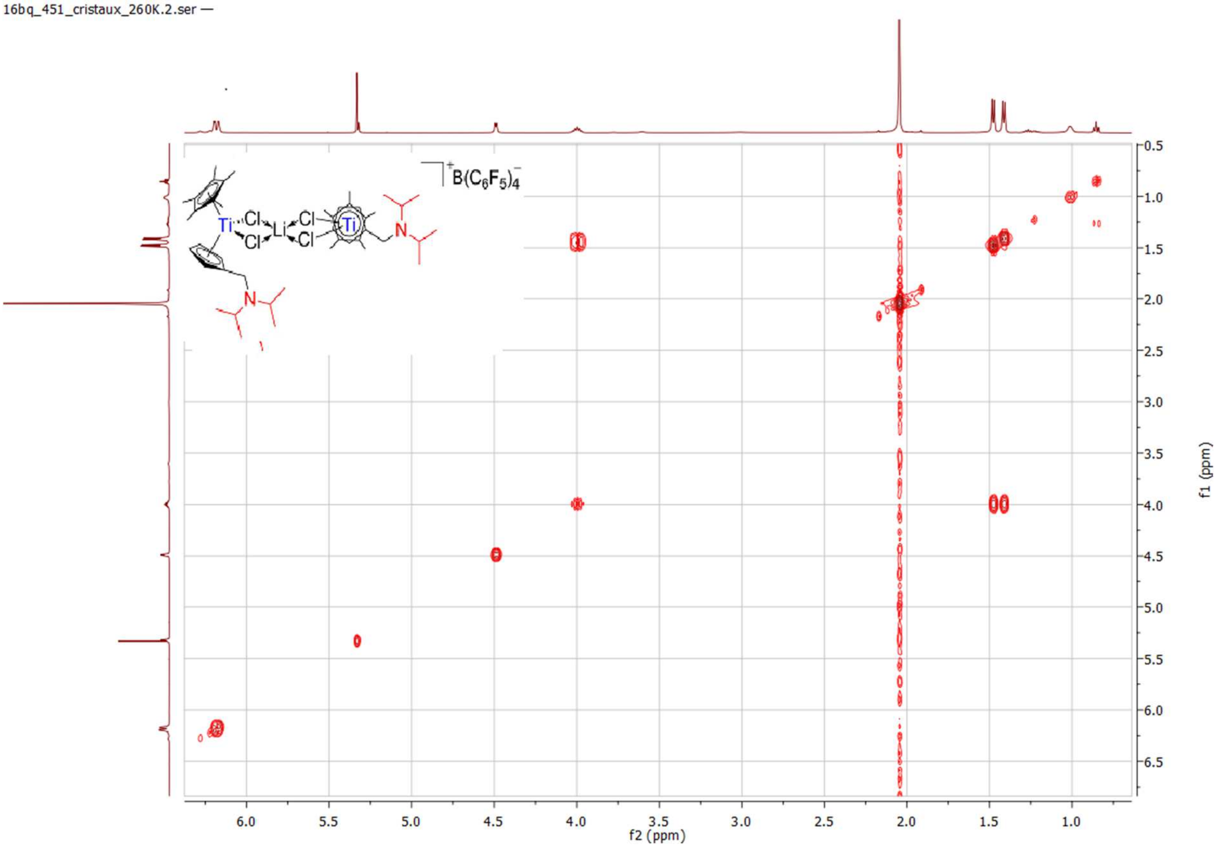
Spectrum 0-165: superposition of the ^{1}H NMR spectra from 300K to 260 K (500.03 MHz, 260 K, dichloromethane-d_2)



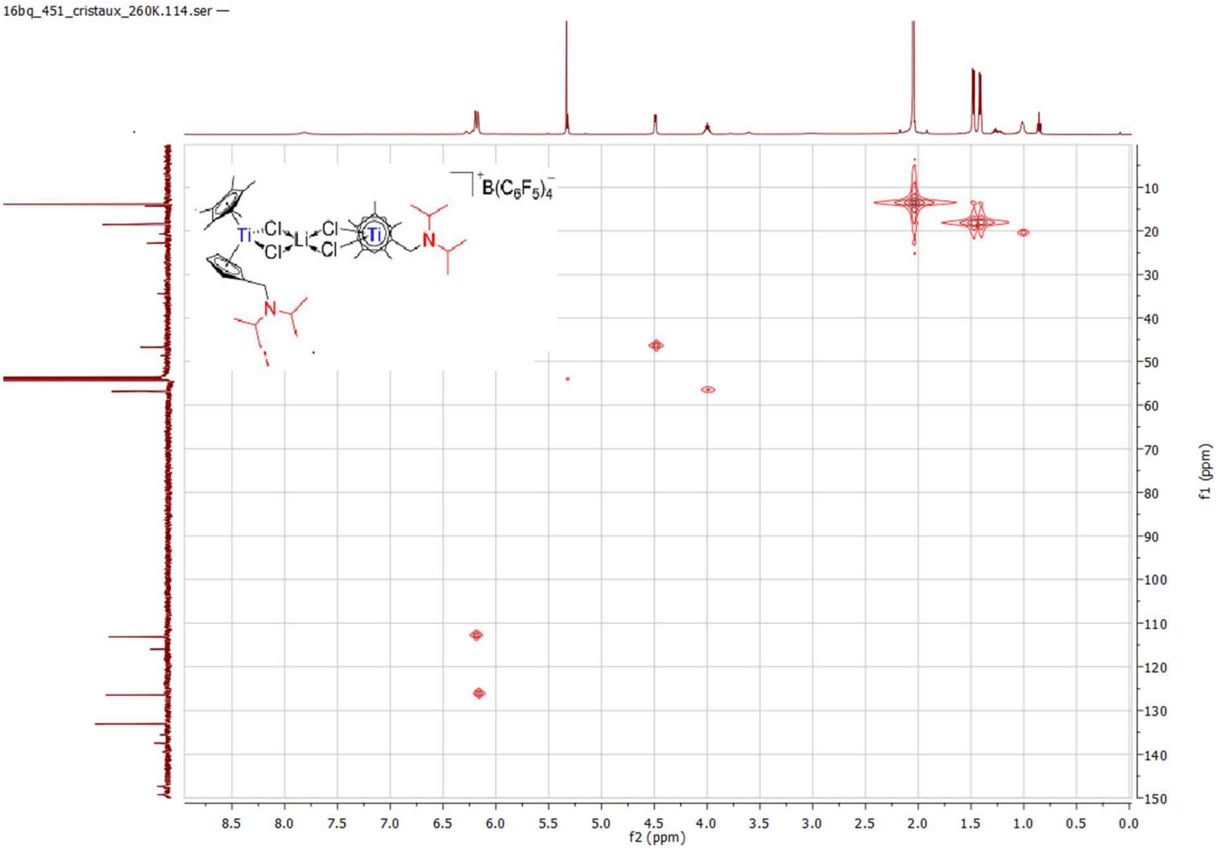
Spectrum 0-166: ^{1}H NMR of 25 (500.03 MHz, 260 K, dichloromethane-d_2)



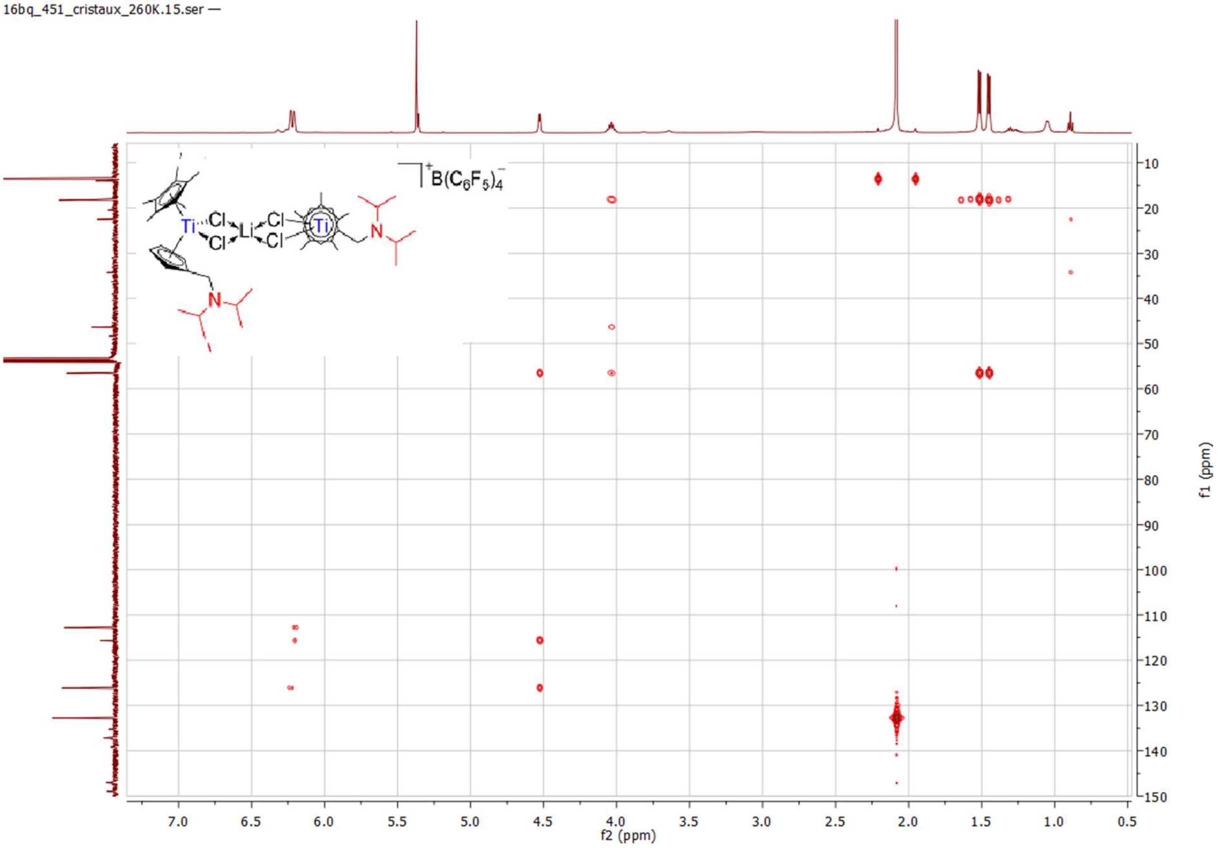
Spectrum 0-167: $^{13}C\{^{1}H\}$ NMR of 25 (125.75 MHz, 260 K, dichloromethane-d_2)



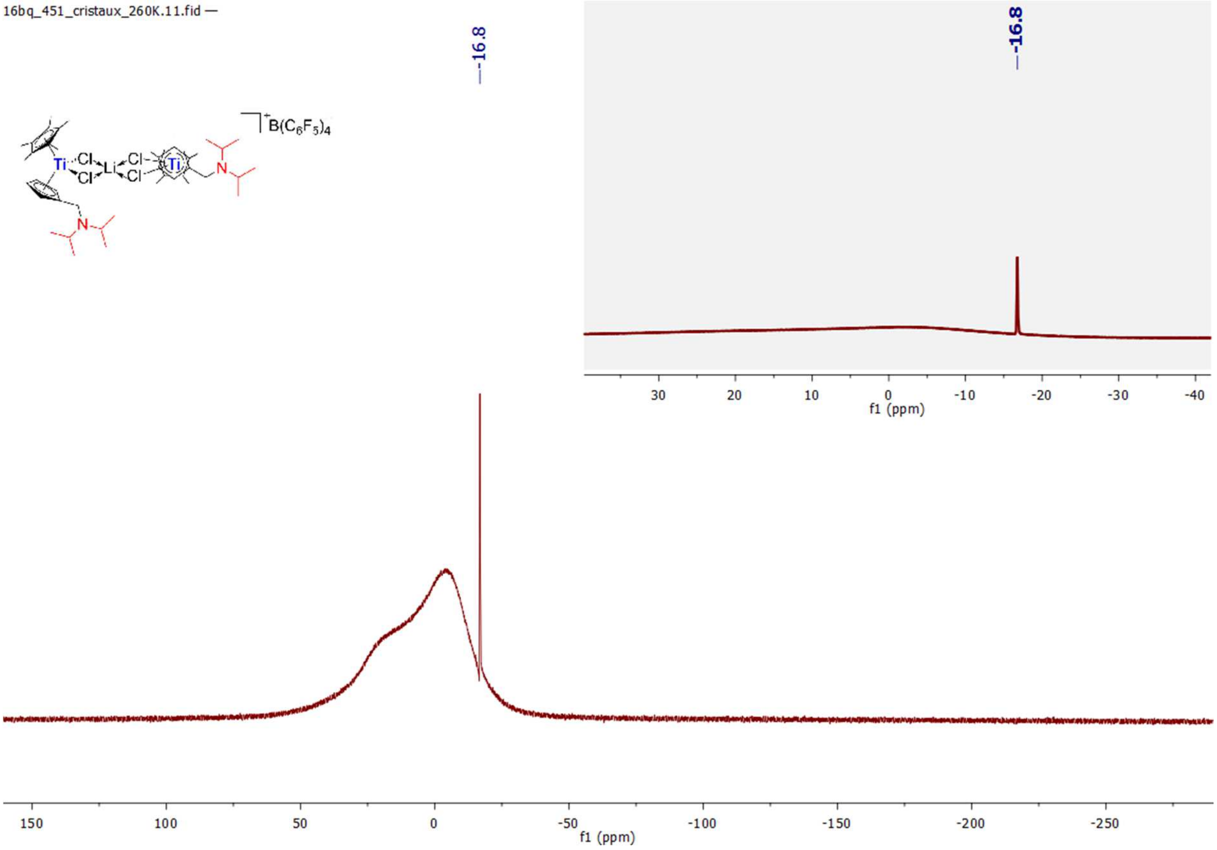
Spectrum 0-168: ^{1}H ^{1}H COSY of 25 (500.03 MHz, 260 K, dichloromethane-d_2)



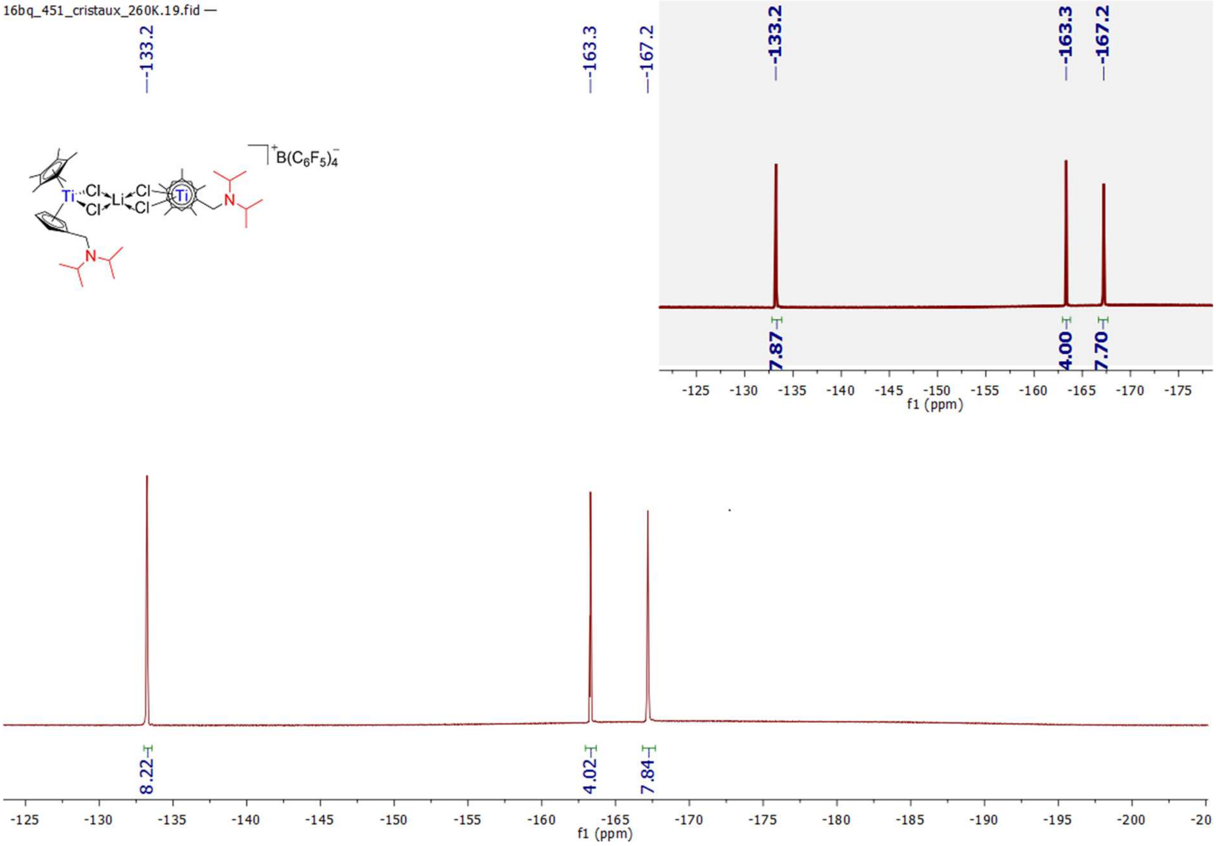
Spectrum 0-169: ^{1}H ^{13}C HMQC of 25 (500.03 MHz / 125.75 MHz, 260 K, dichloromethane-d$_2$)



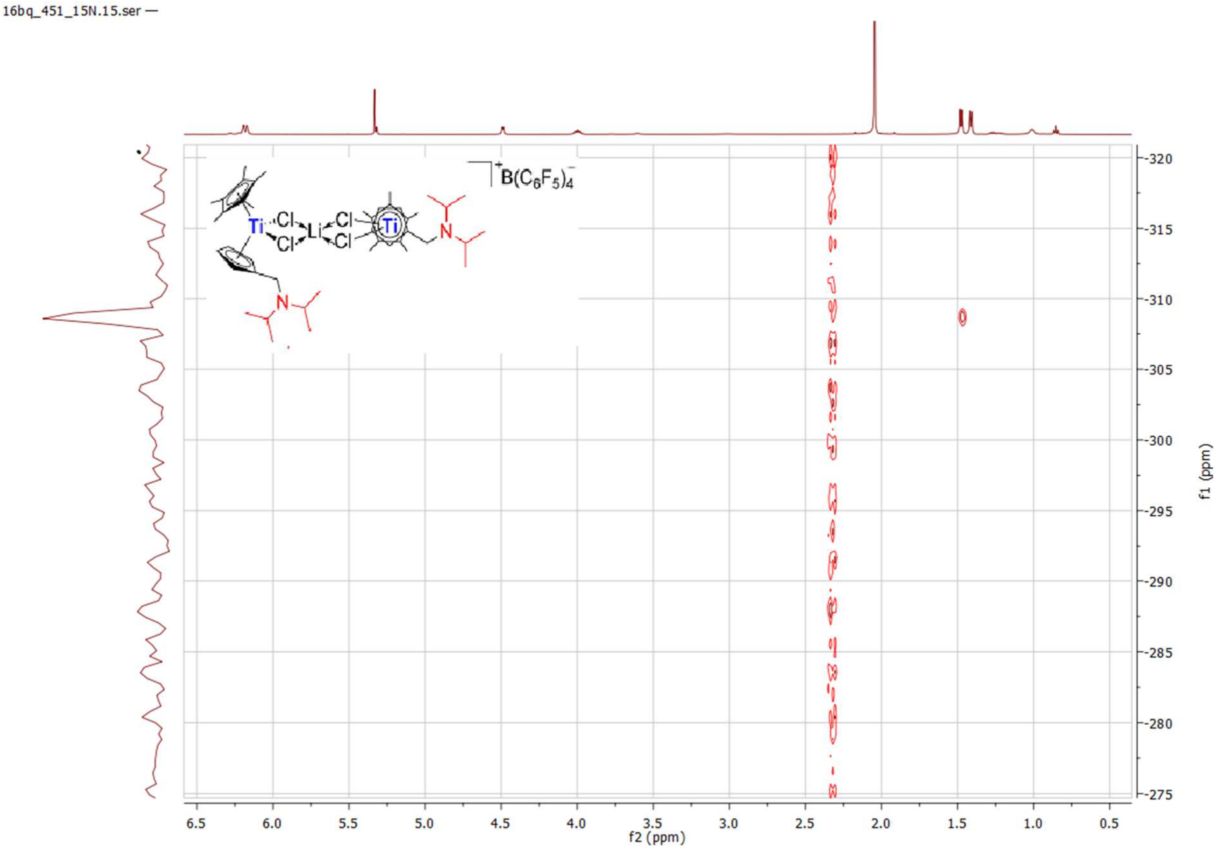
Spectrum 0-170: H ^{13}C HMBC of 25 (500.03 MHz / 125.75 MHz, 260 K, dichloromethane-d$_2$)



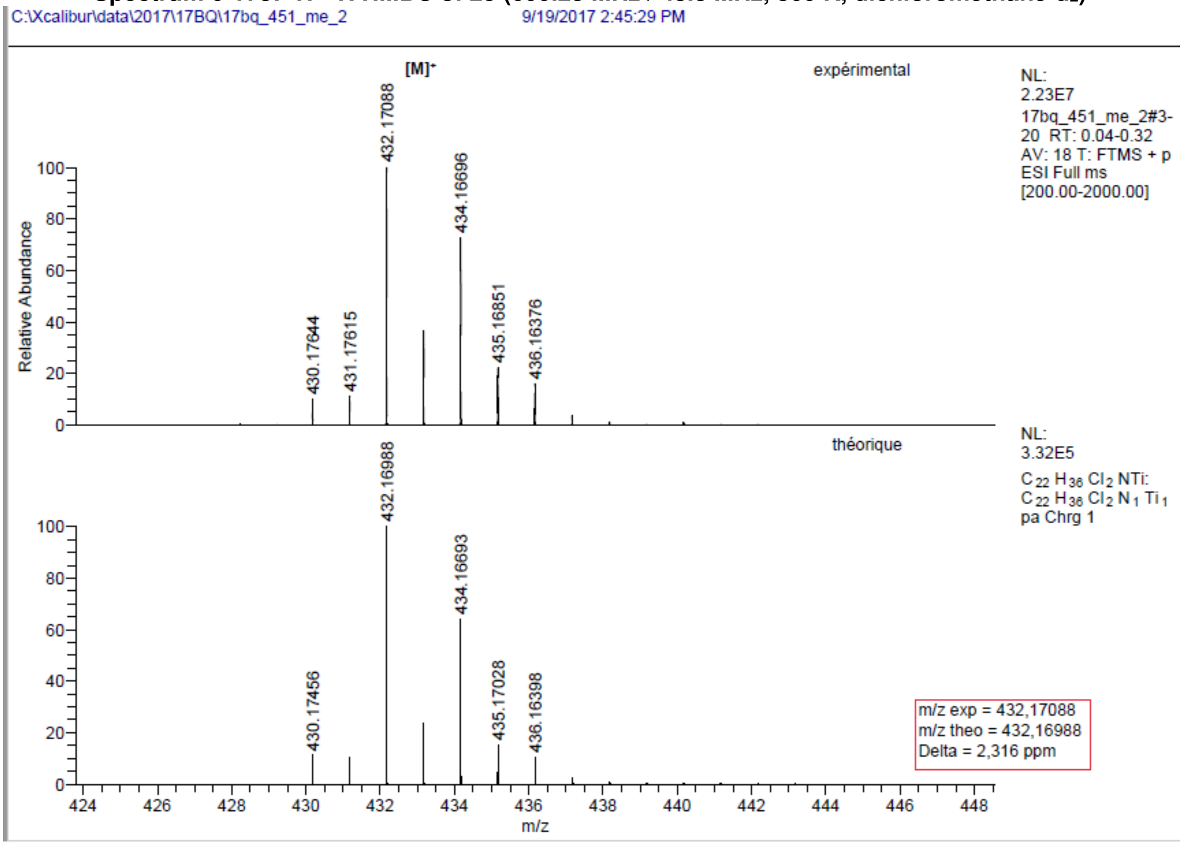
Spectrum 0-171: ^{11}B{^{1}H} and ^{11}B (οπαχιφιεδ) of 25 (160.42 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-172: ^{19}F{^{1}H} and ^{19}F NMR of 25 (470.45 MHz, 300 K, dichloromethane-d$_2$)

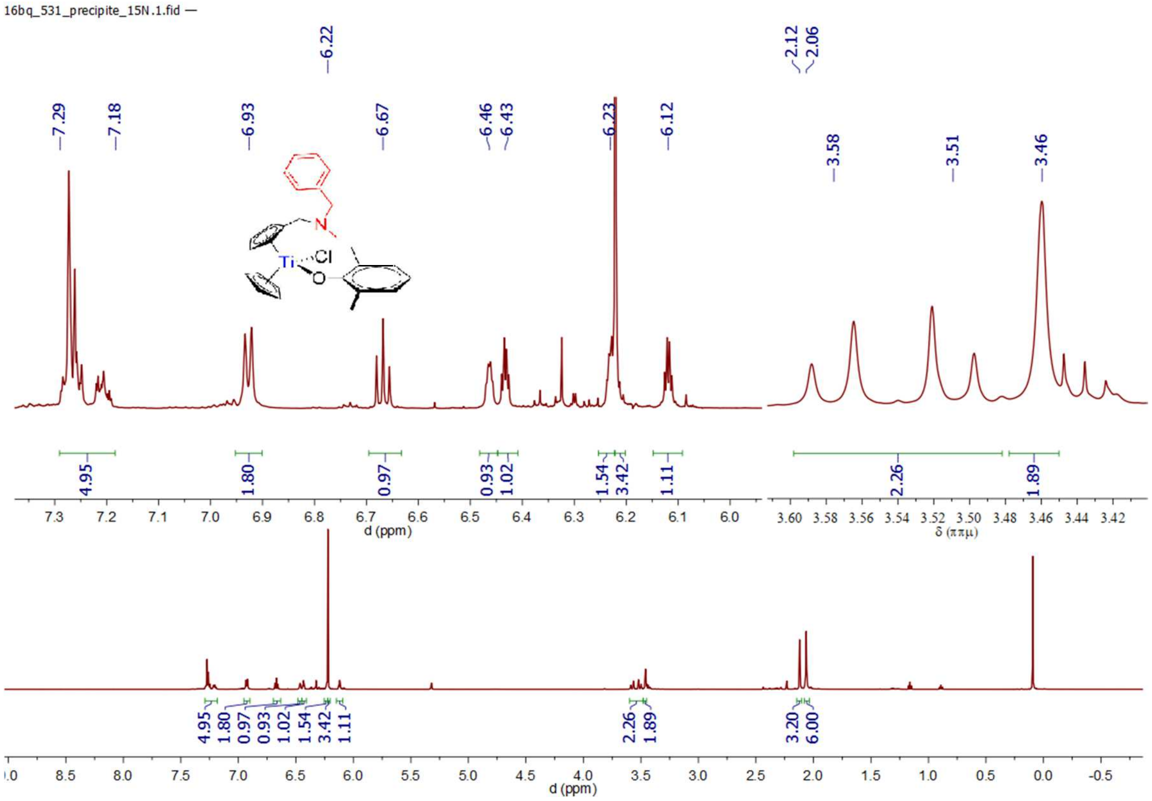


Spectrum 0-173: ^{1}H ^{15}N HMBC of 25 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)

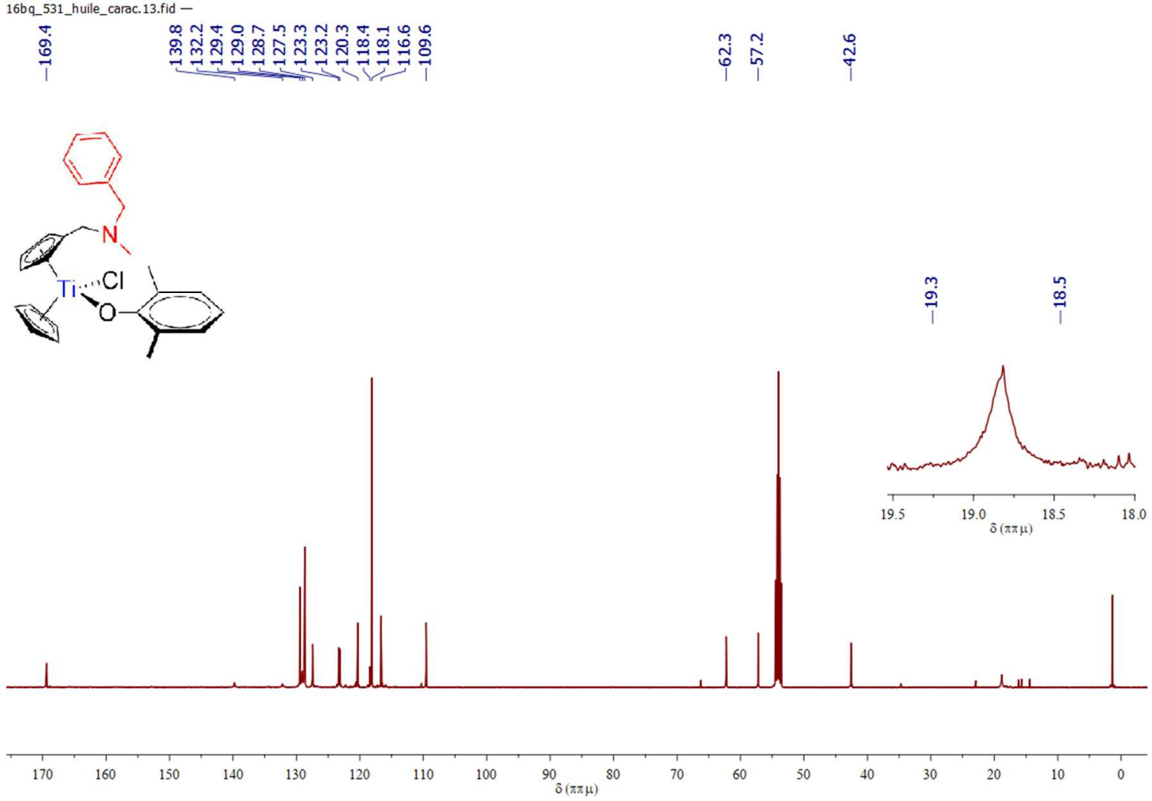


Spectrum 0-174: HRMS of 25 (Positive mode ESI, dichloromethane)

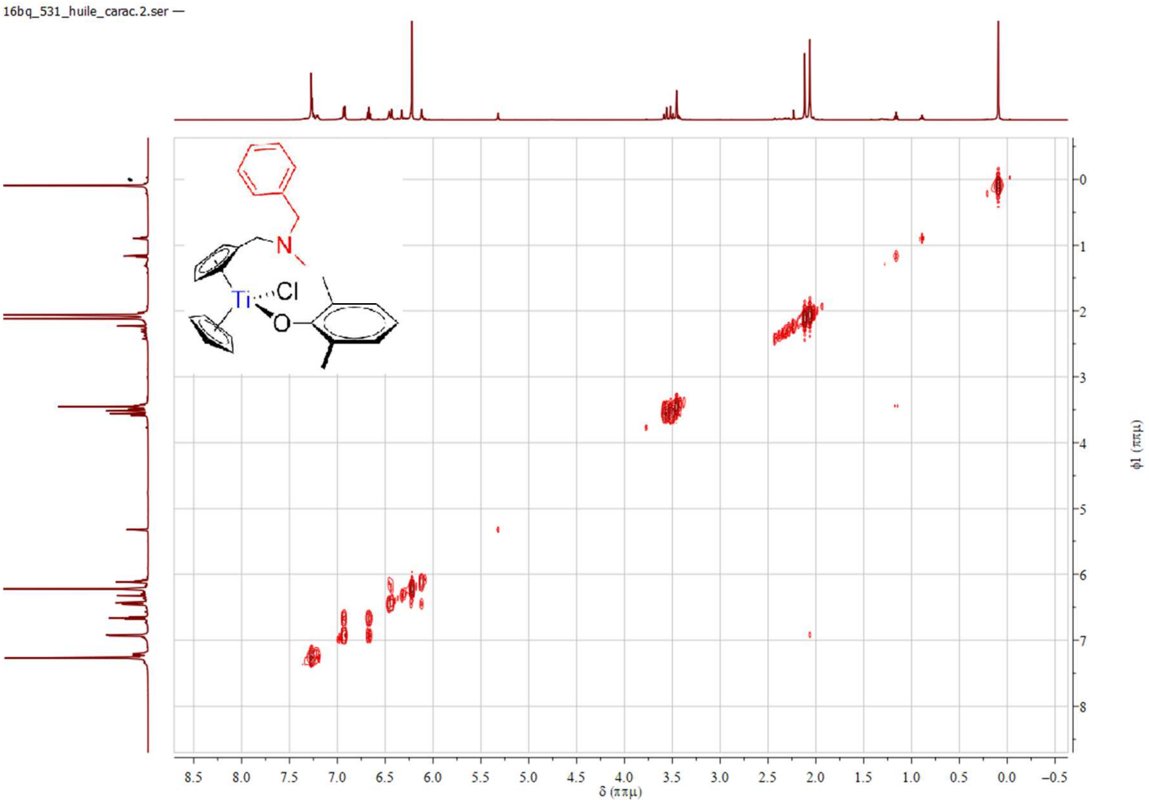
2. Compound **26**:



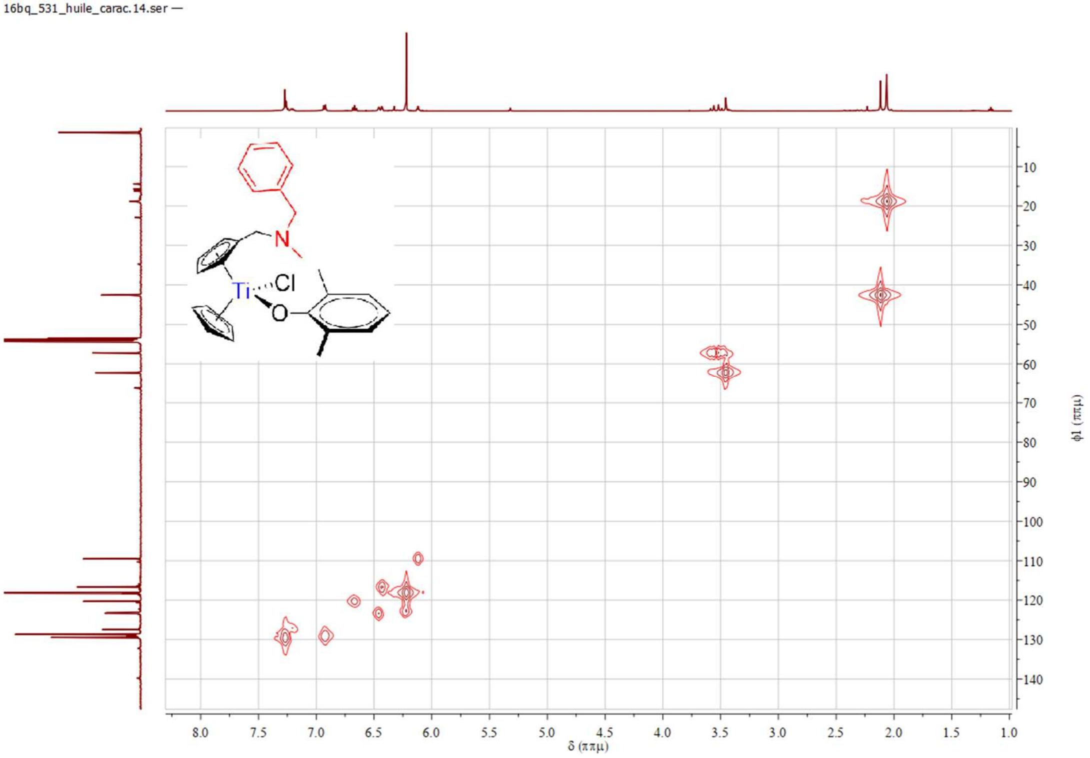
Spectrum 0-175: ^{1}H NMR of 26 (500.03 MHz, 300 K, dichloromethane-d$_2$)



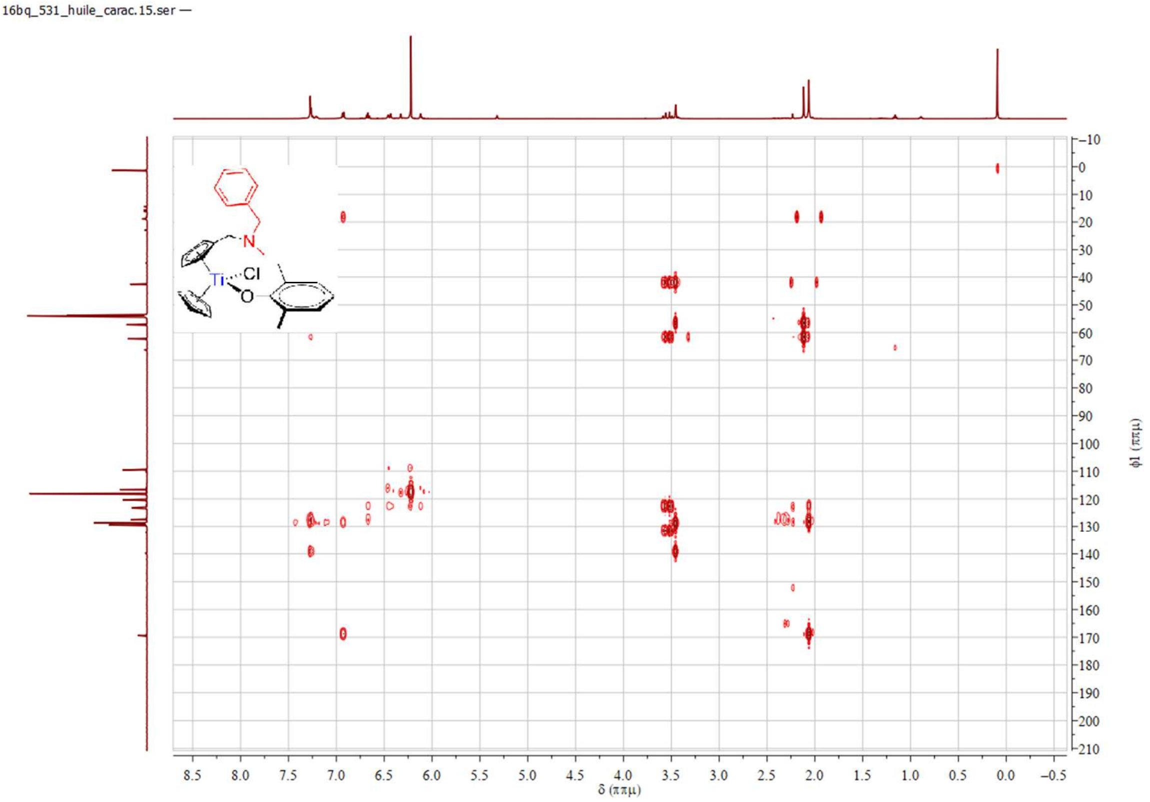
Spectrum 0-176: ^{13}C{^{1}H} NMR of 26 (125.77 MHz, 300 K, dichloromethane-d$_2$)



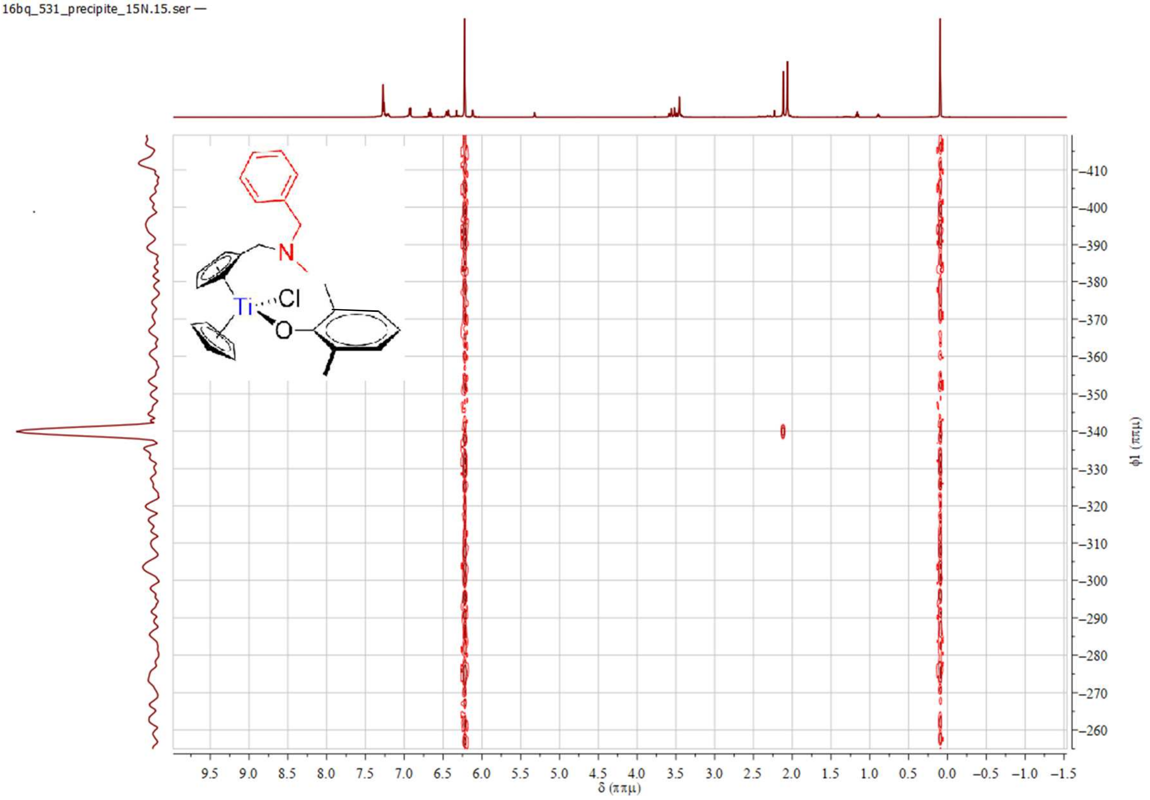
Spectrum 0-177: ^{1}H ^{1}H COSY of 26 (500.03 MHz, 300 K, dichloromethane-d$_2$)



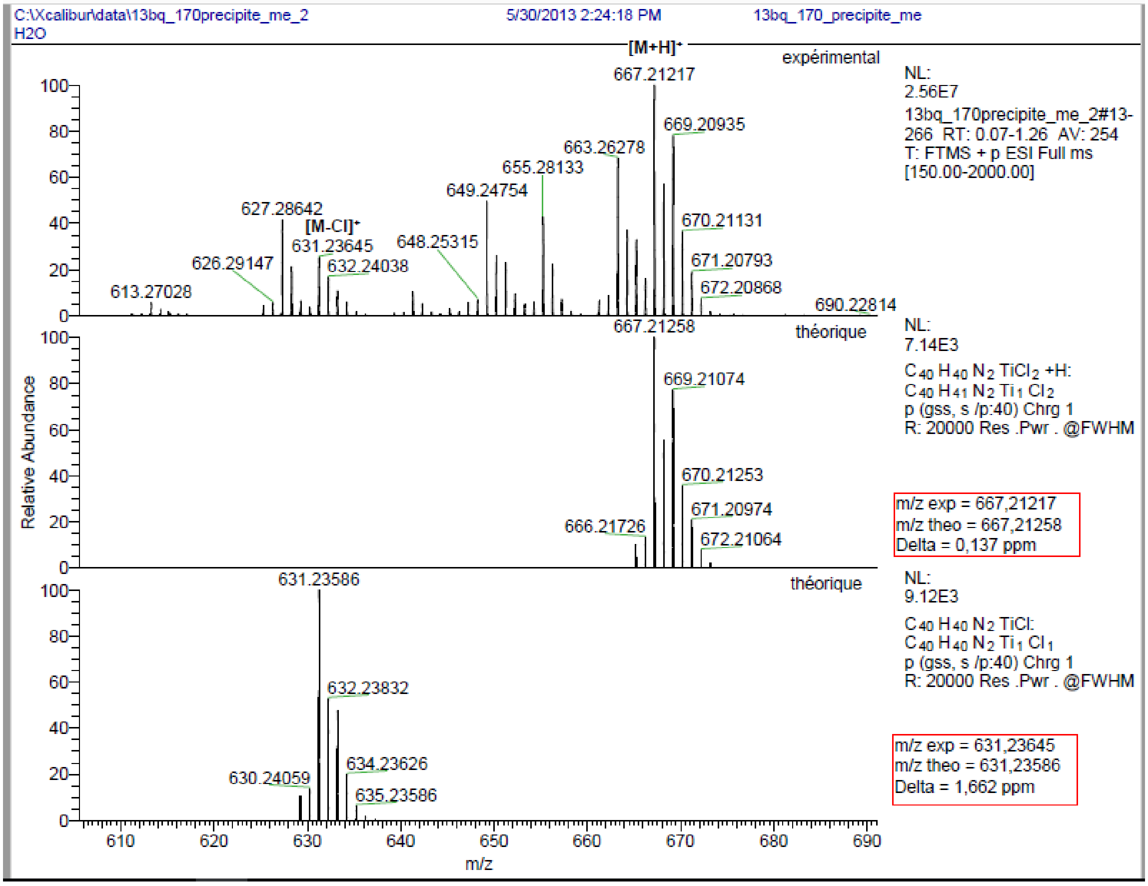
Spectrum 0-178: ^{1}H ^{13}C HMQC of 26 (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-179: ^{1}H ^{13}C HMBC of 26 (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d$_2$)

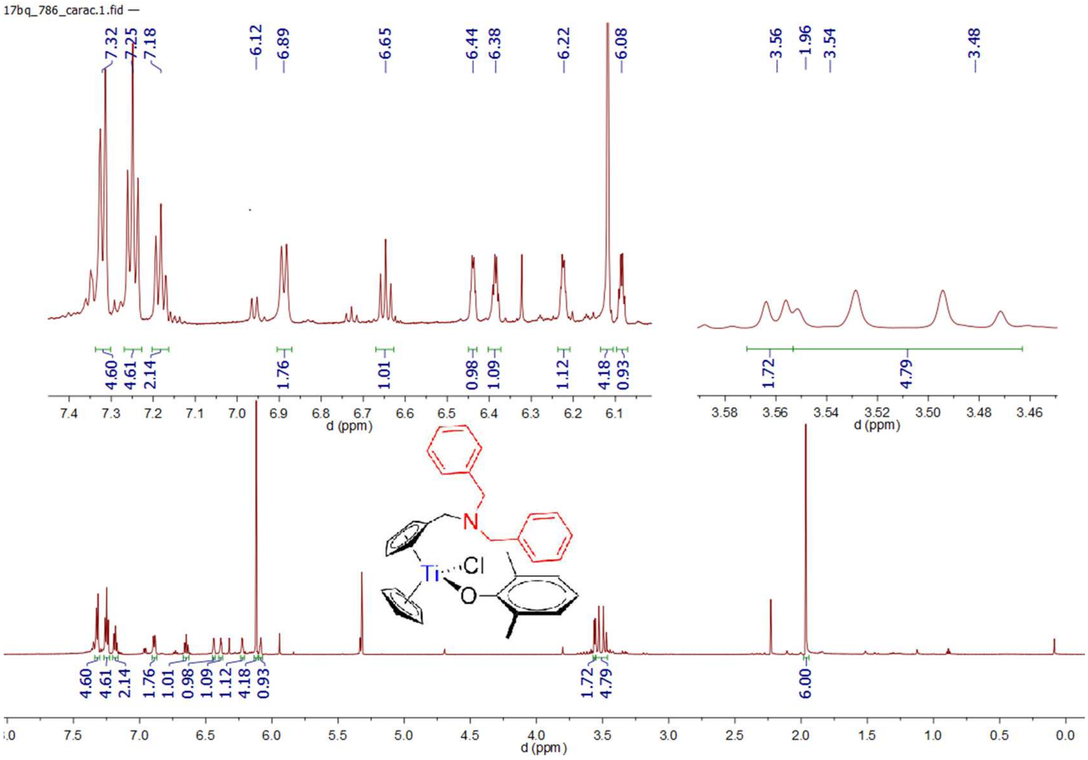


Spectrum 0-180: ^{1}H ^{15}N HMBC of 26 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)

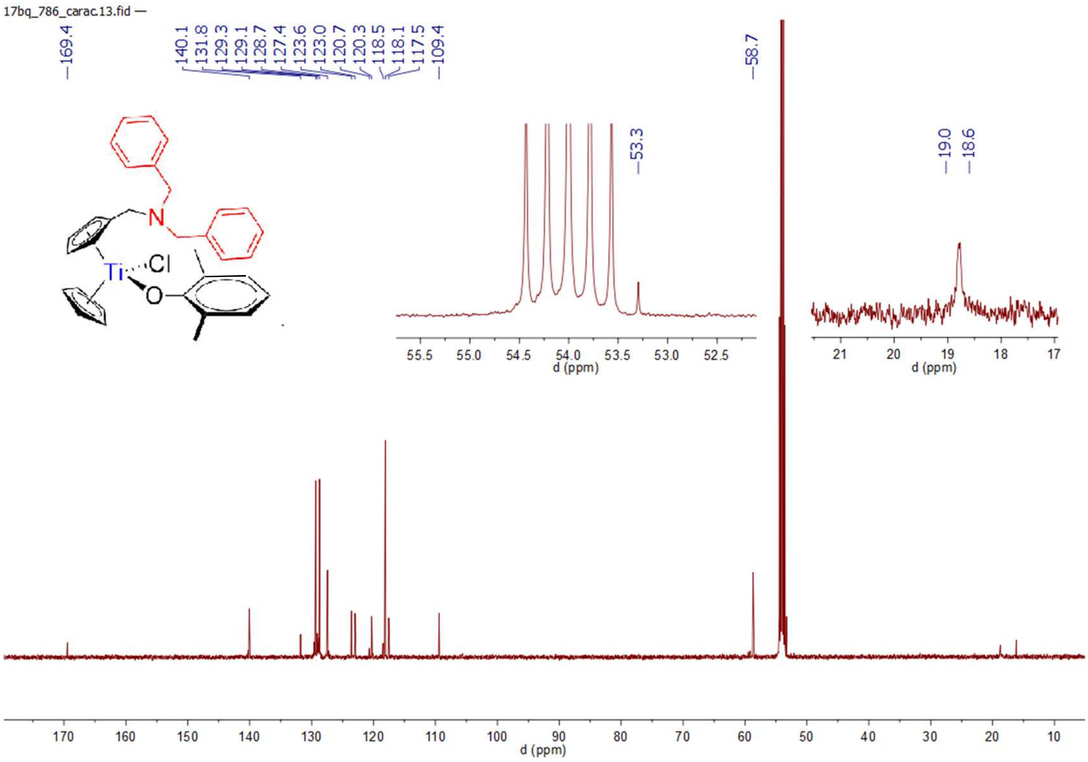


Spectrum 0-181: HRMS of 26 (Positive mode ESI, dichloromethane)

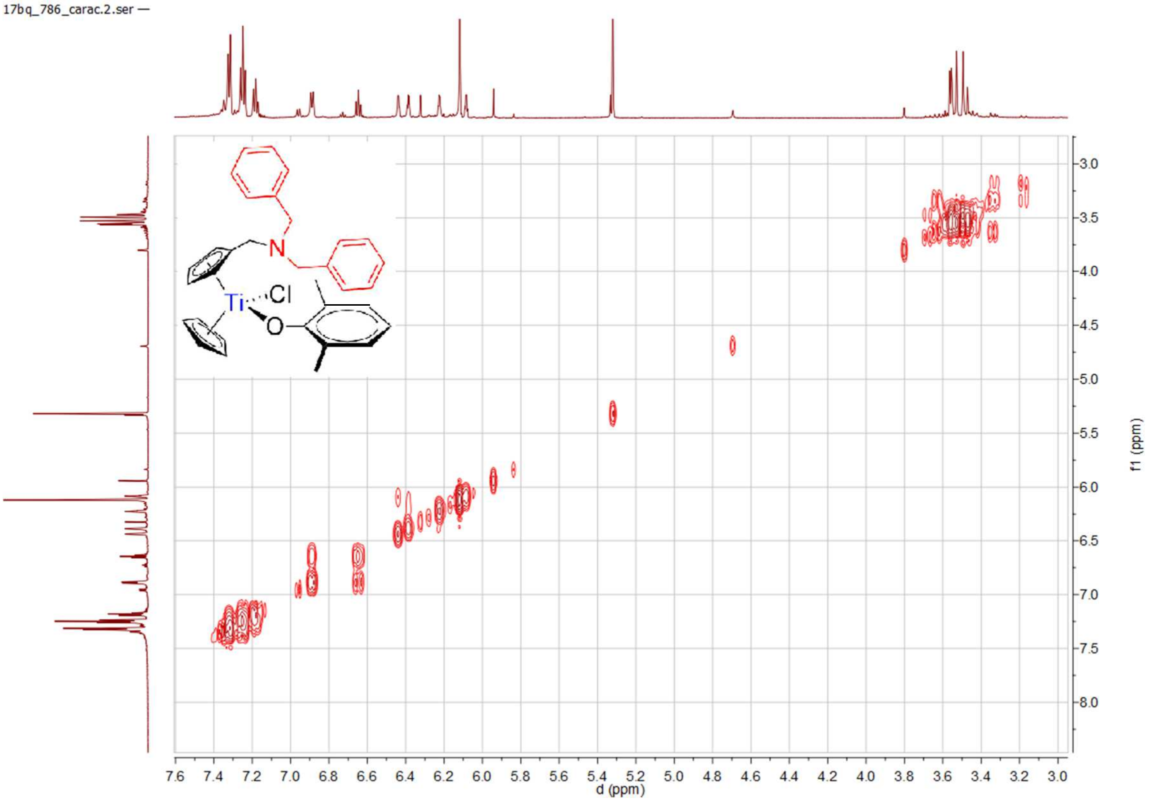
3. Compound **27**:



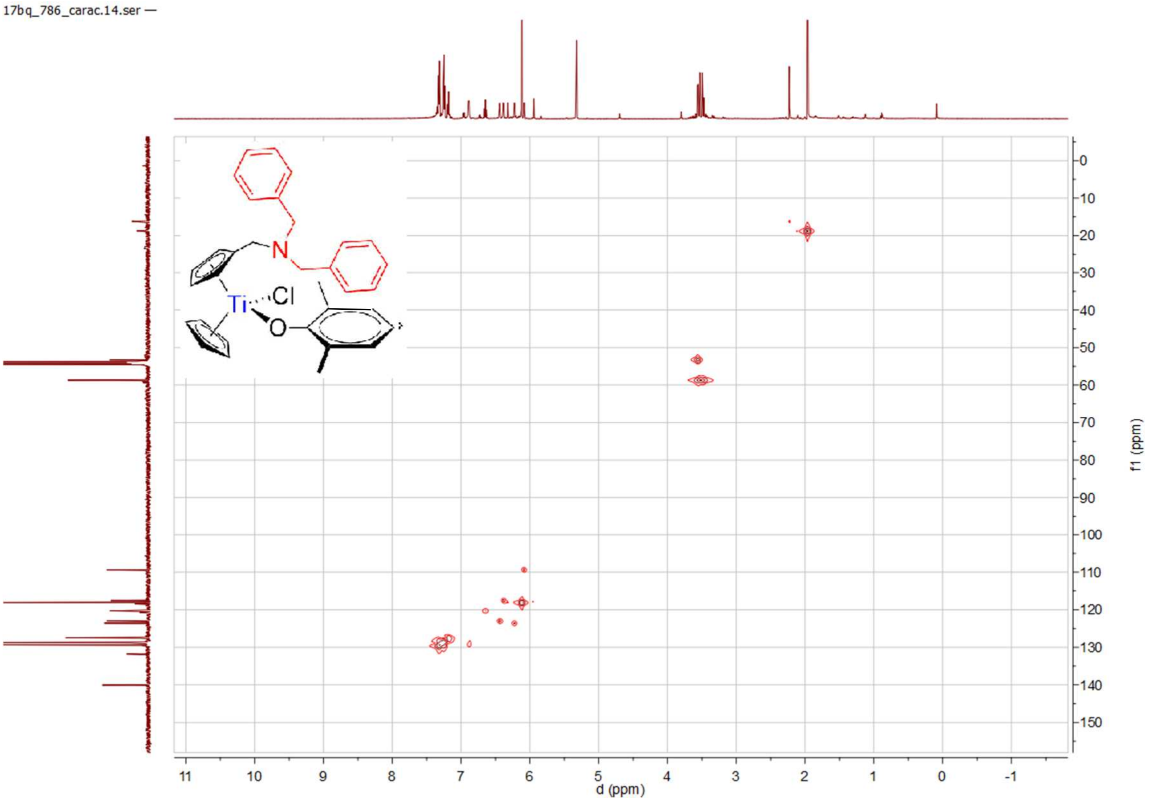
Spectrum 0-182: ^{1}H NMR of 27 (600.23 MHz, 300 K, dichloromethane-d$_2$)



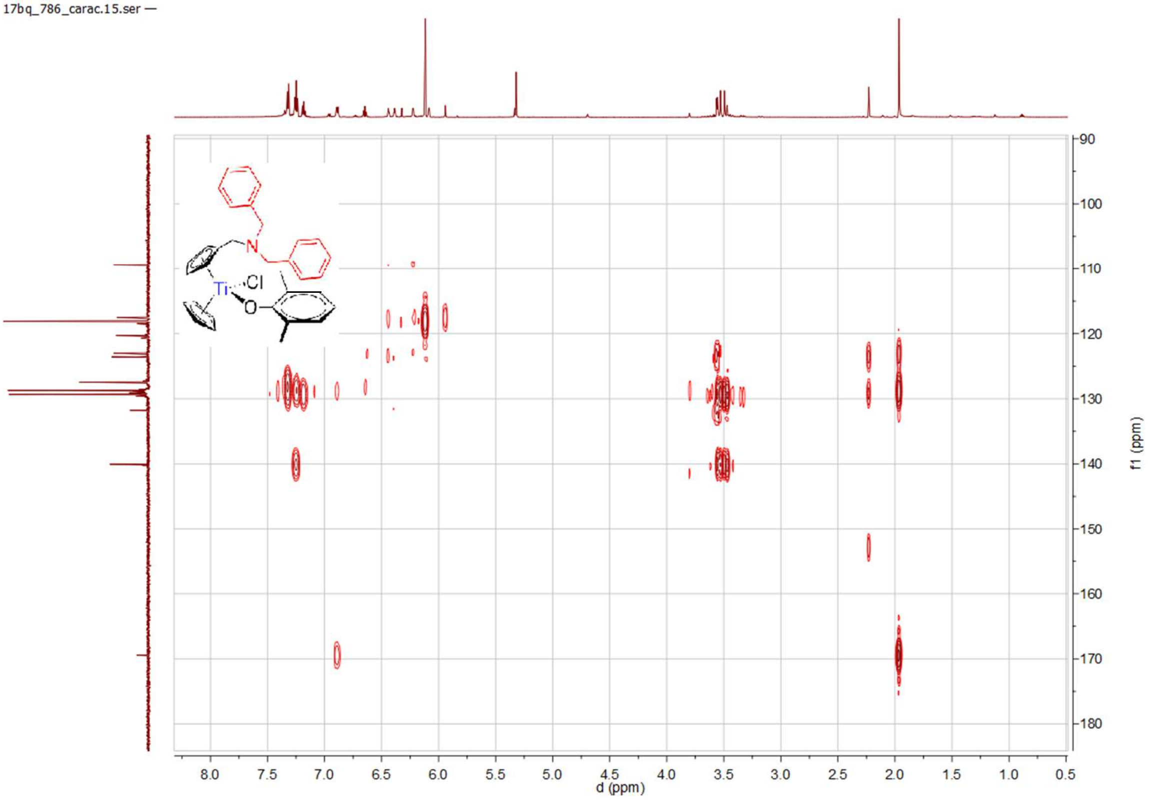
Spectrum 0-183: $^{13}C\{^{1}H\}$ NMR of 27 (125.77 MHz, 300 K, dichloromethane-d$_2$)



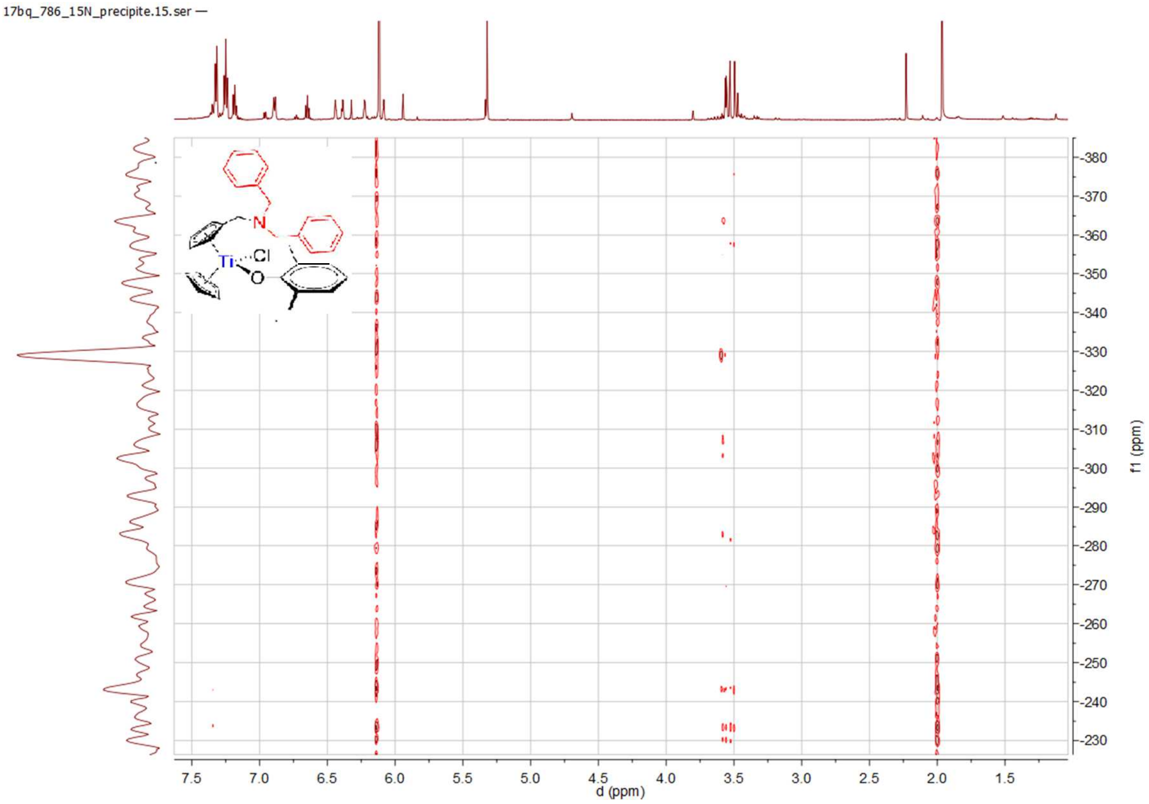
Spectrum 0-184: ^{1}H ^{1}H COSY of 27 (500.03 MHz, 300 K, dichloromethane-d$_2$)



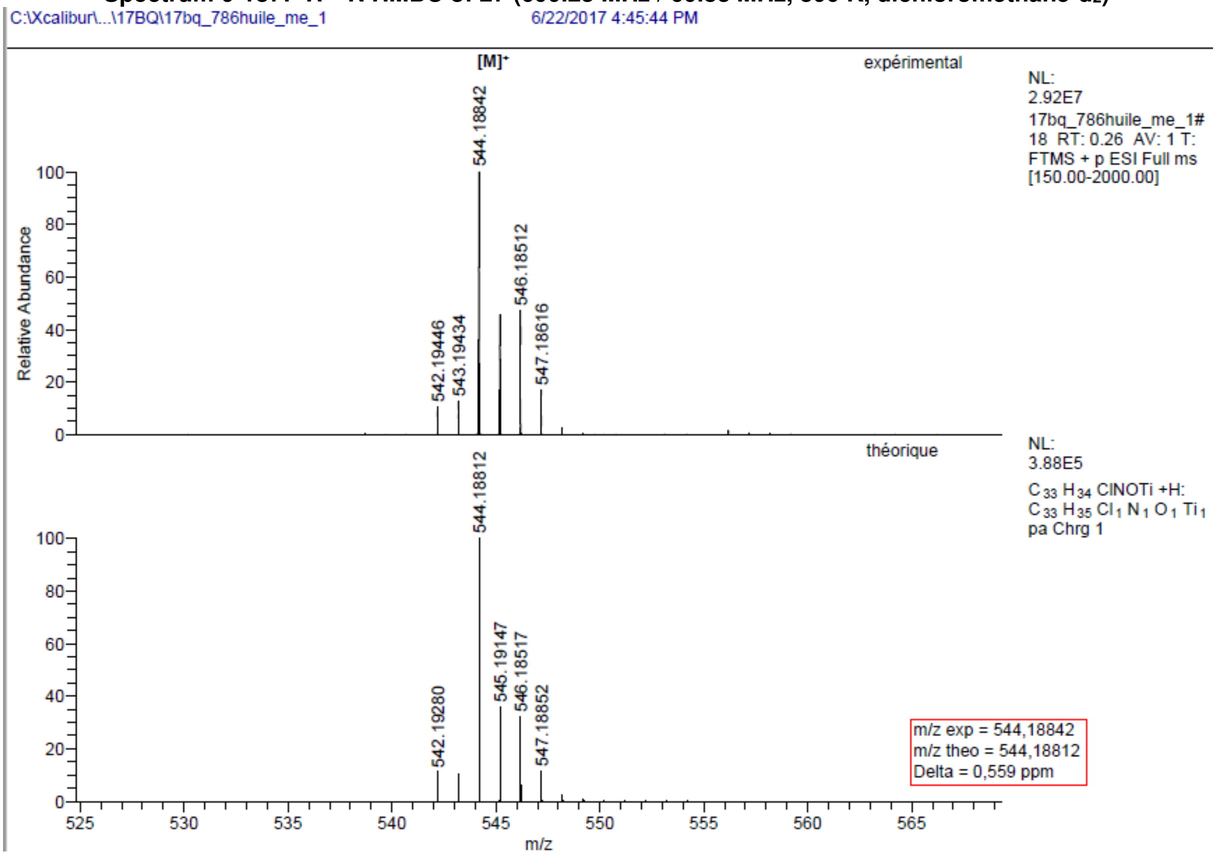
Spectrum 0-185: ^1H ^{13}C HMQC of 27 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



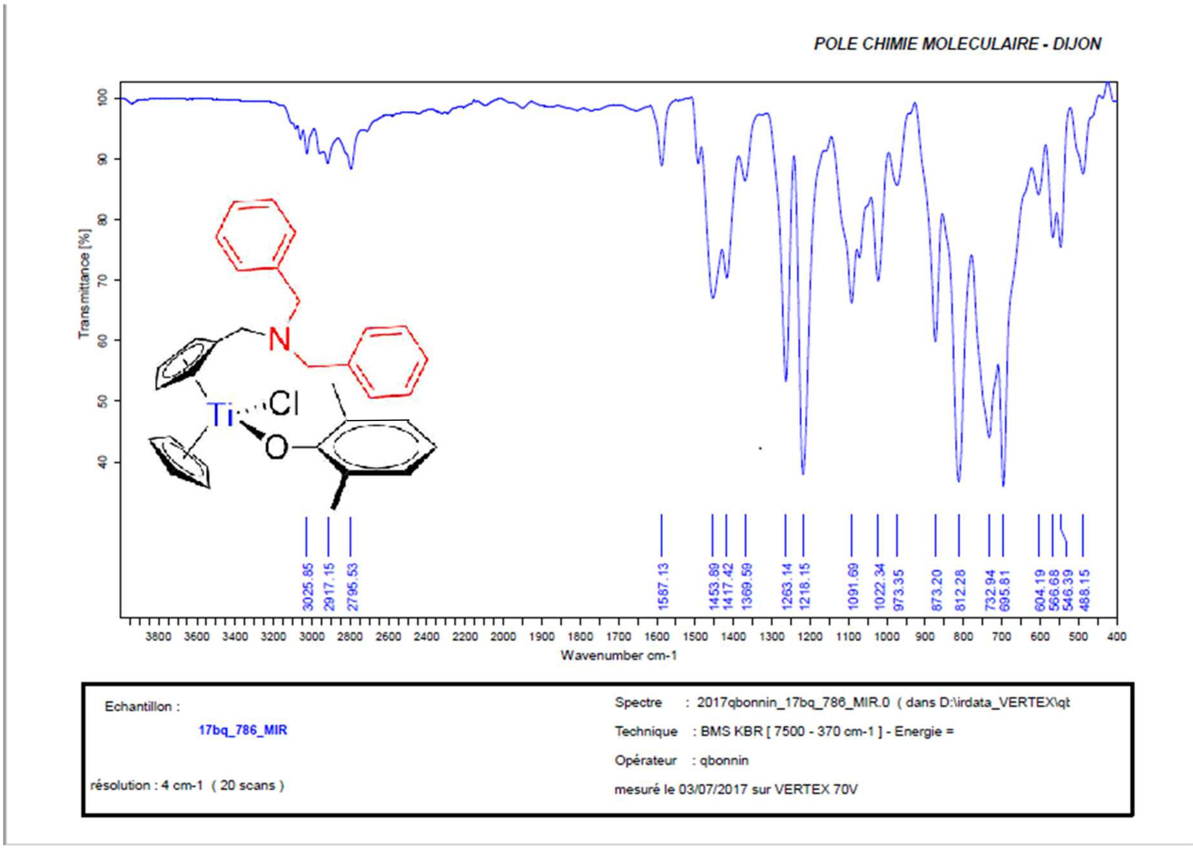
Spectrum 0-186: ^1H ^{13}C HMBC of 27 (600.23 MHz / 150.944 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-187: ^{1}H ^{15}N HMBC of 27 (600.23 MHz / 60.83 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-188: HRMS of 27 (Positive mode ESI, dichloromethane)



Echantillon :

17bq_786_MIR

résolution : 4 cm-1 (20 scans)

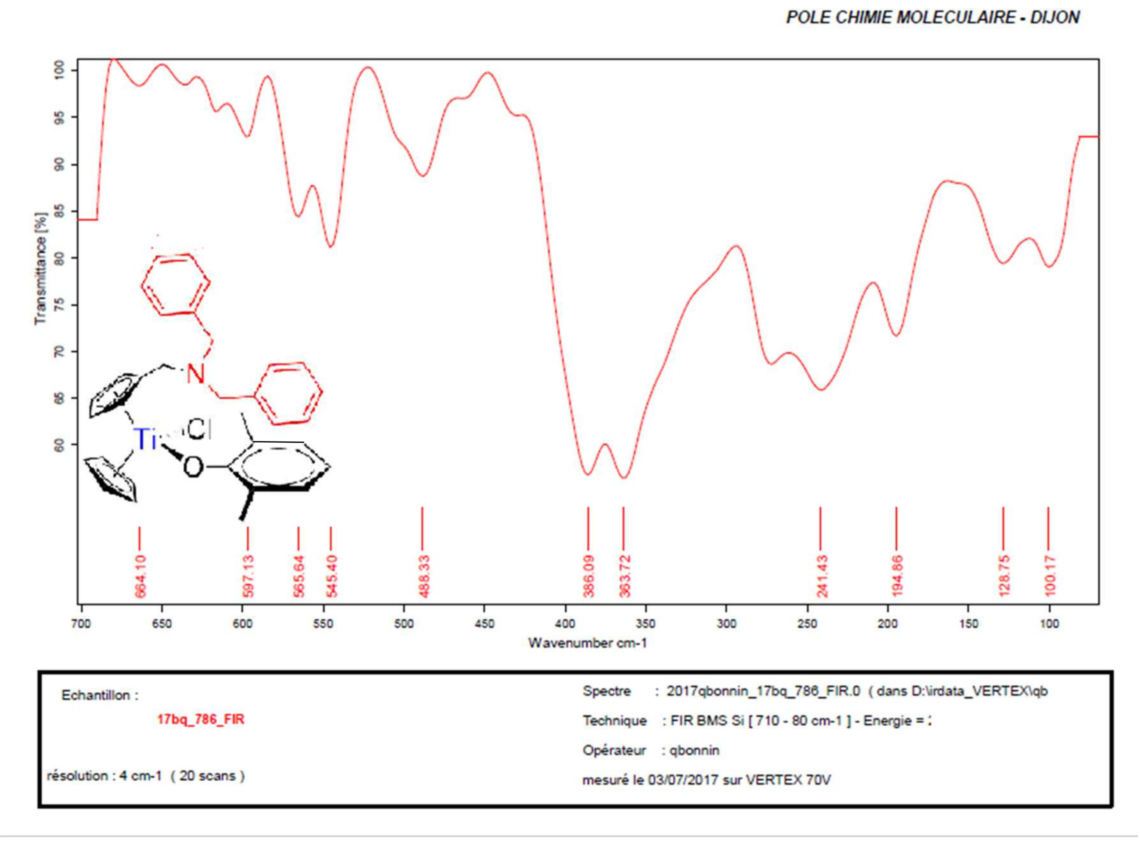
Spectre : 2017qbonnin_17bq_786_MIR.0 (dans D:\irdata_VERTEX\qt

Technique : BMS KBR [7500 - 370 cm-1] - Energie =

Opérateur : qbonnin

mesuré le 03/07/2017 sur VERTEX 70V

Spectrum 0-189: MIR of 27



Echantillon :

17bq_786_FIR

résolution : 4 cm-1 (20 scans)

Spectre : 2017qbonnin_17bq_786_FIR.0 (dans D:\irdata_VERTEX\qb

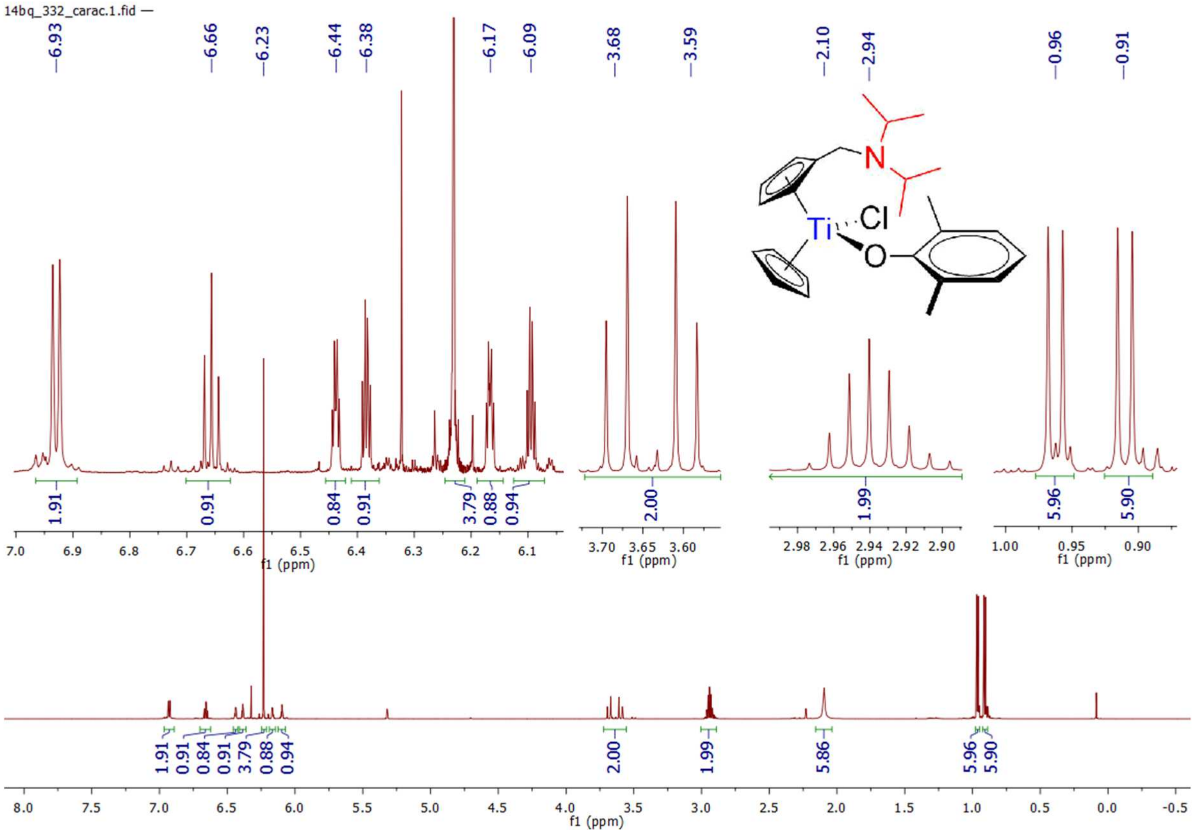
Technique : FIR BMS Si [710 - 80 cm-1] - Energie = :

Opérateur : qbonnin

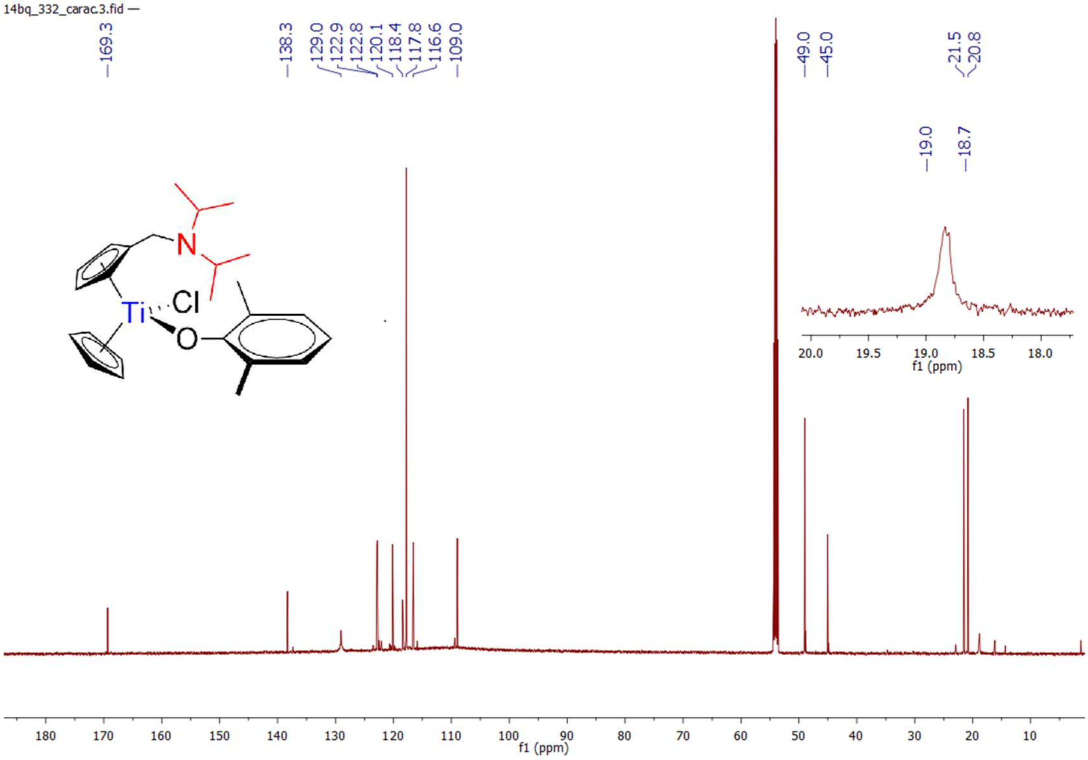
mesuré le 03/07/2017 sur VERTEX 70V

Spectrum 0-190: FIR of 27

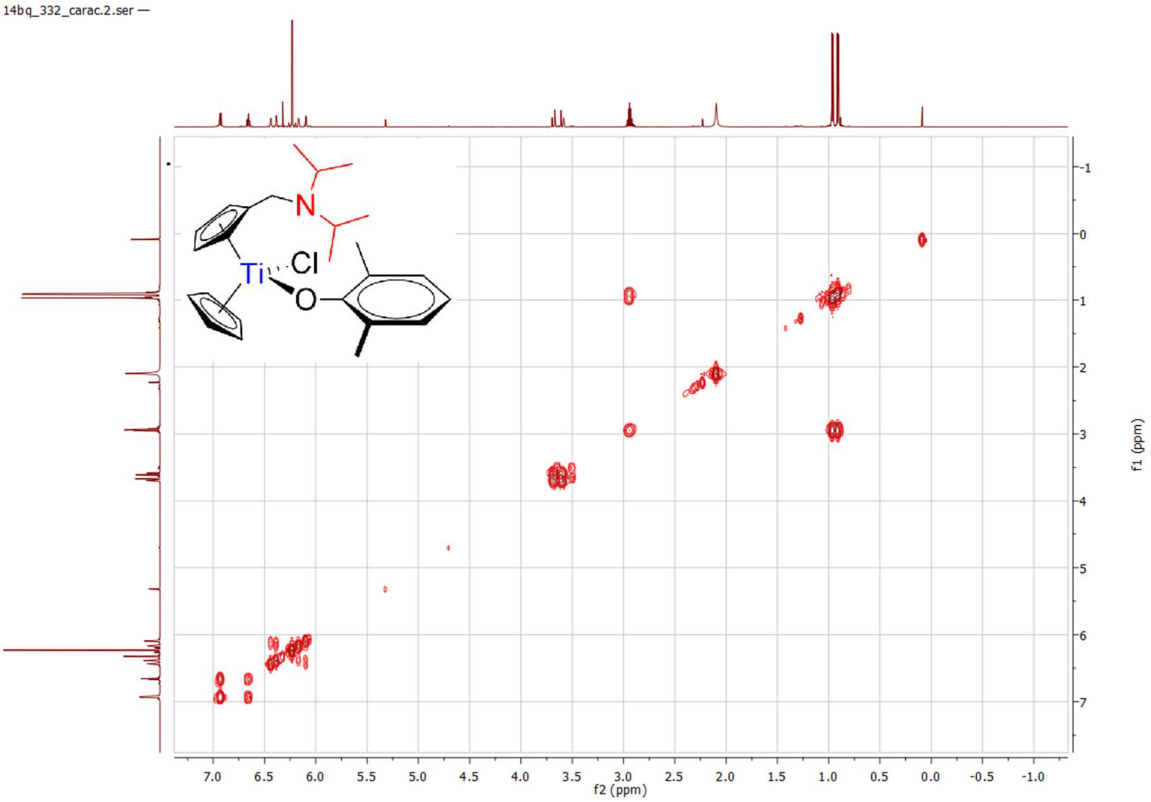
4. Compound **28**:



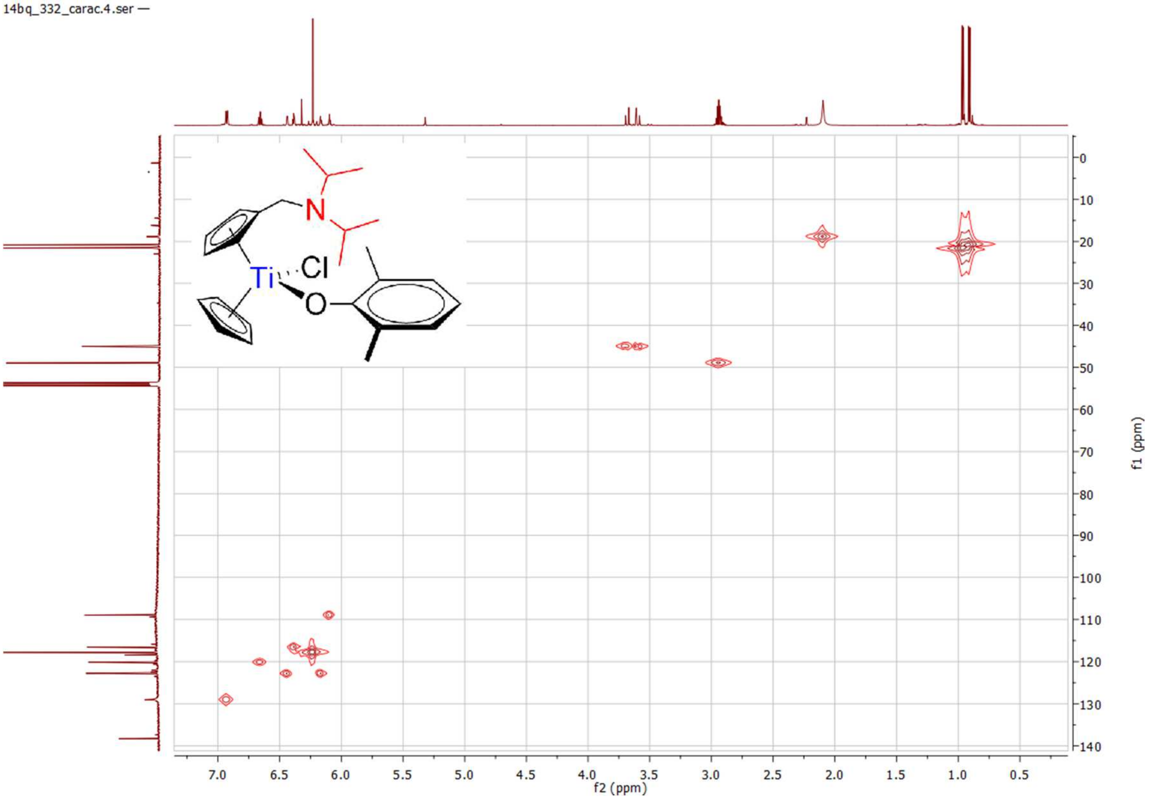
Spectrum 0-191: ^{1}H NMR of 28 (600.23 MHz, 300 K, dichloromethane-d$_2$)



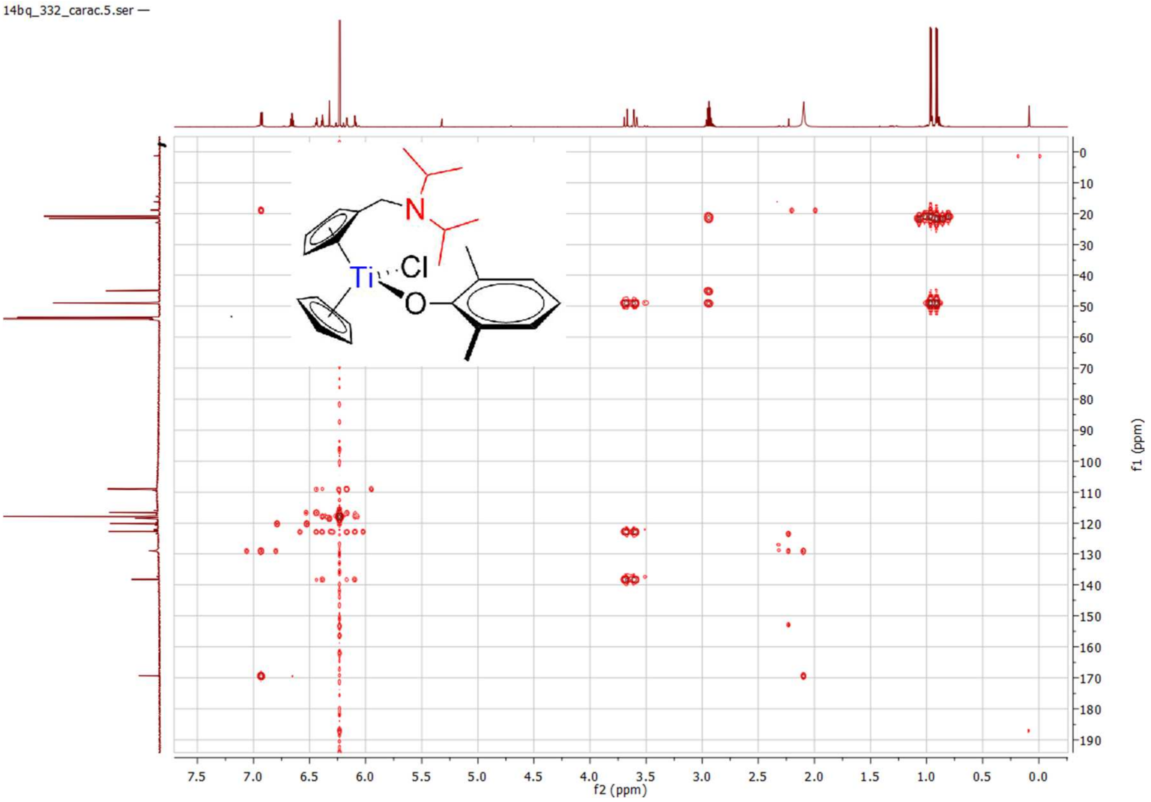
Spectrum 0-192: ^{13}C{^{1}H} NMR of 28 (150.94 MHz, 300 K, dichloromethane-d$_2$)



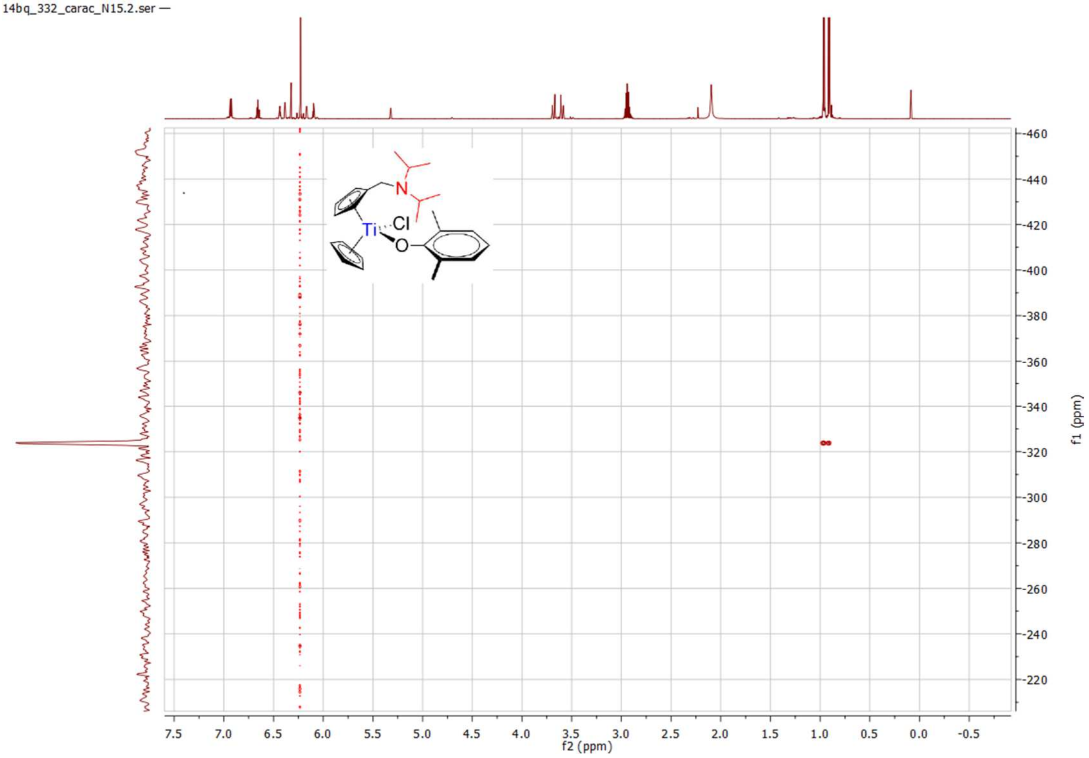
Spectrum 0-193: ^{1}H ^{1}H COSY of 28 (600.23 MHz, 300 K, dichloromethane-d_2)



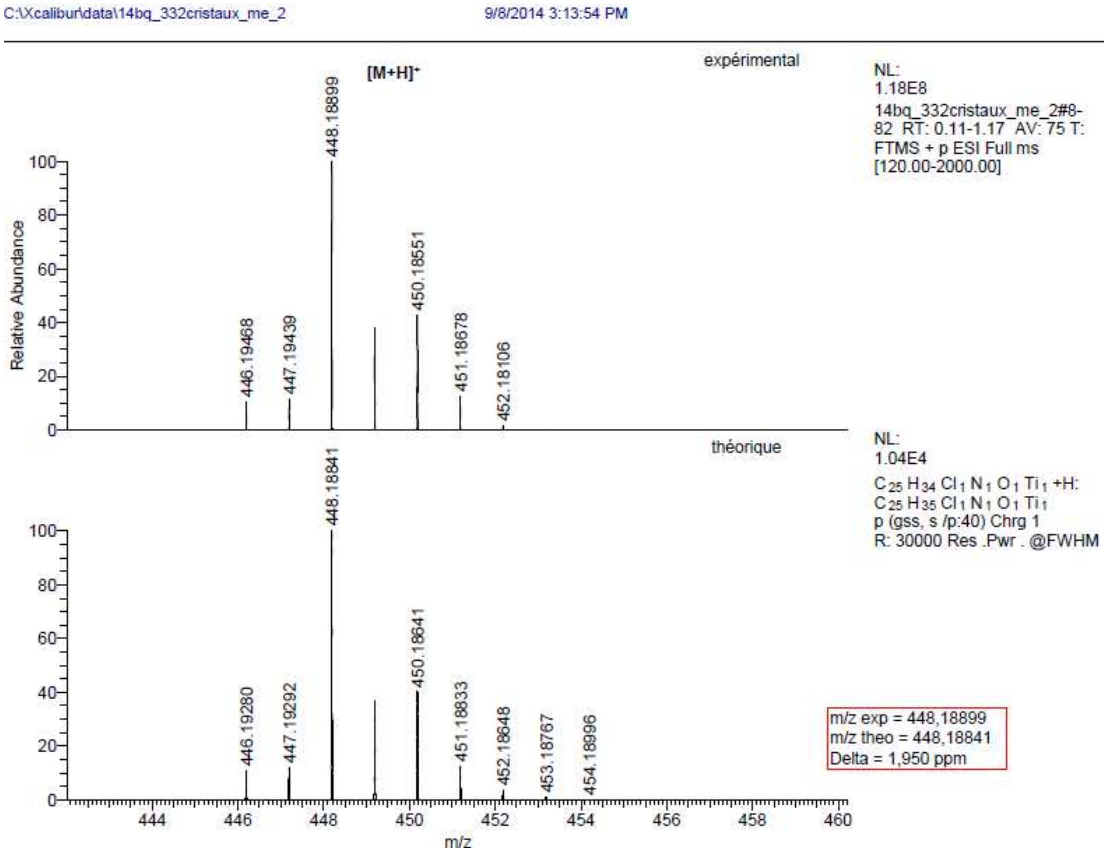
Spectrum 0-194: ^{1}H ^{13}C HMQC of 28 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d_2)



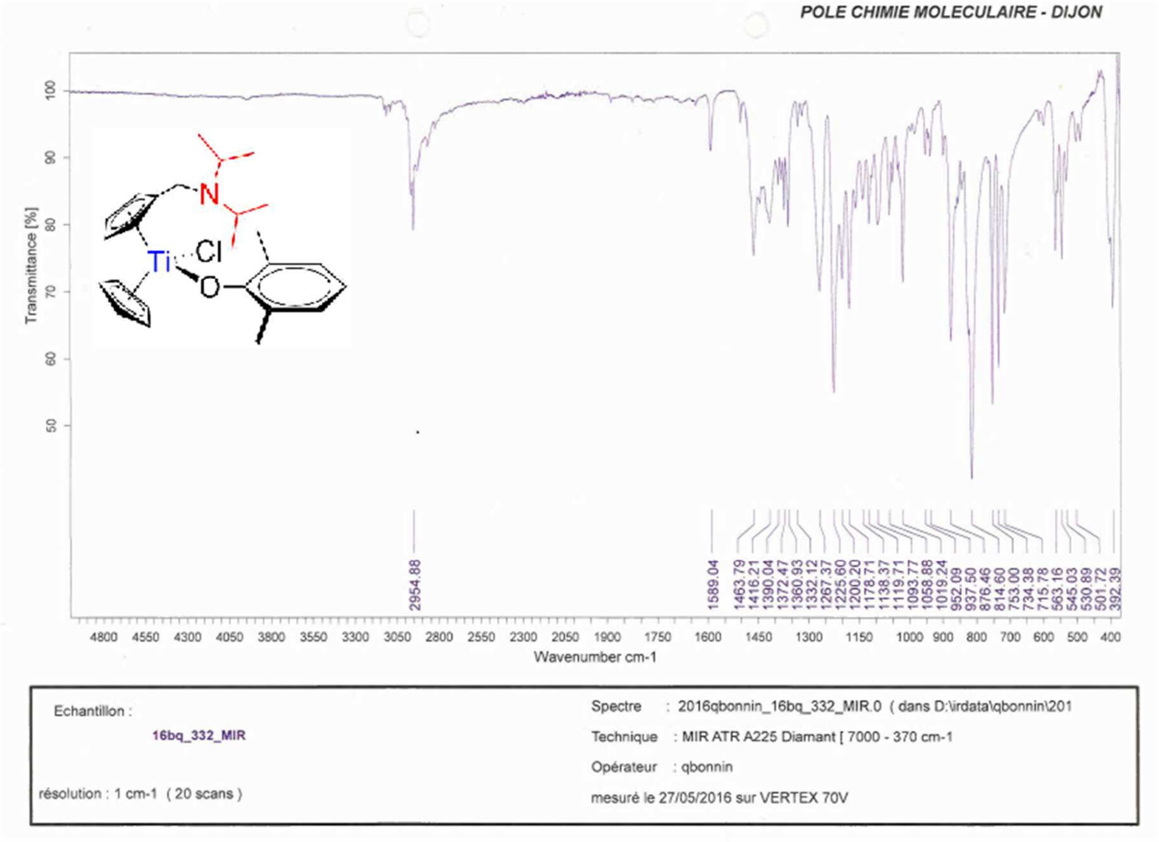
Spectrum 0-195: ^{1}H ^{13}C HMBC of 28 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-196: ^{1}H ^{15}N HMBC of 28 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-197: HRMS of 28 (Positive mode ESI, dichloromethane)



Echantillon :

16bq_332_MIR

résolution : 1 cm-1 (20 scans)

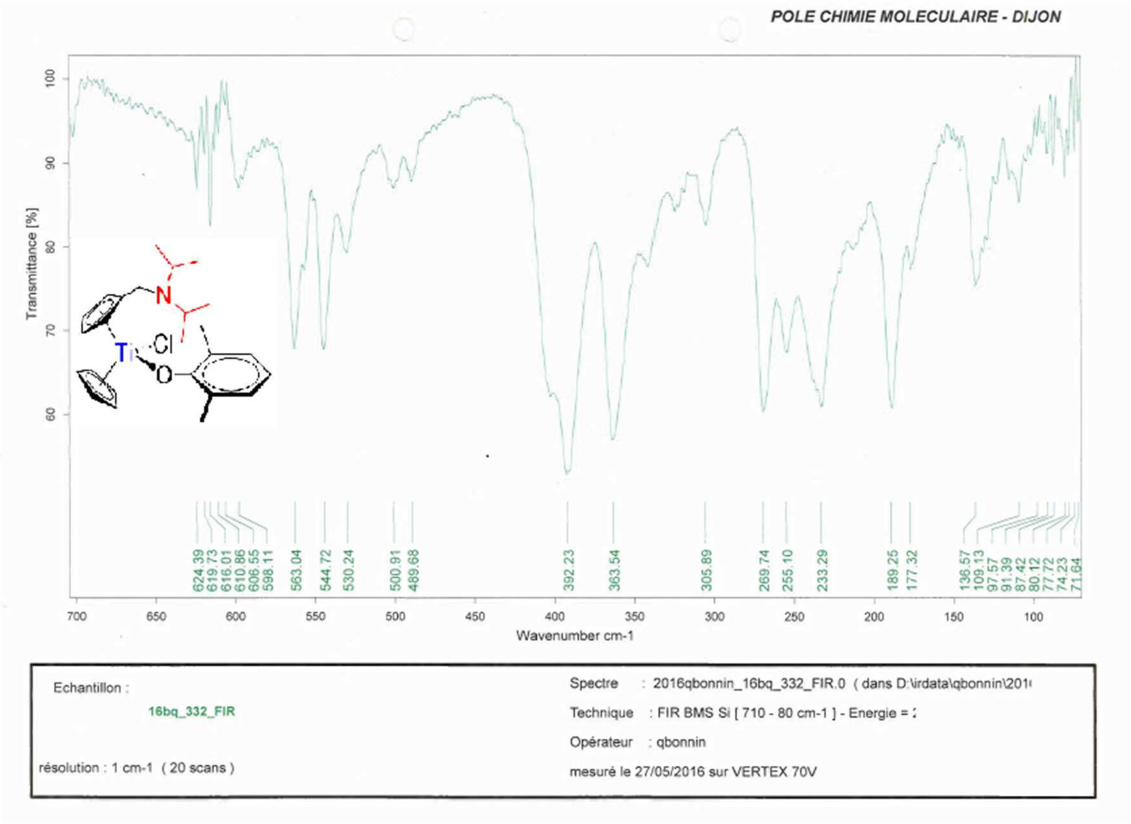
Spectre : 2016qbonnin_16bq_332_MIR.0 (dans D:\irdata\qbonnin\201

Technique : MIR ATR A225 Diamant [7000 - 370 cm-1

Opérateur : qbonnin

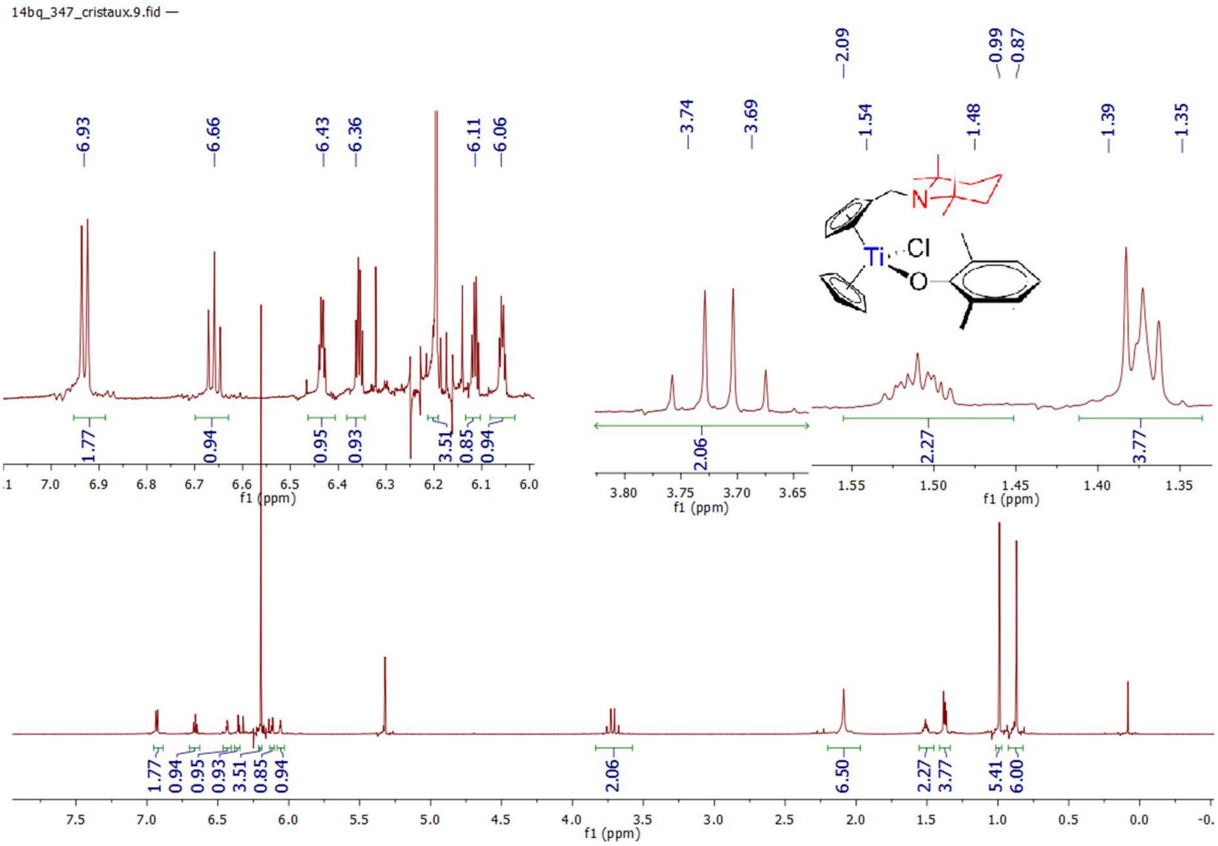
mesuré le 27/05/2016 sur VERTEX 70V

Spectrum 0-198: MIR of 28

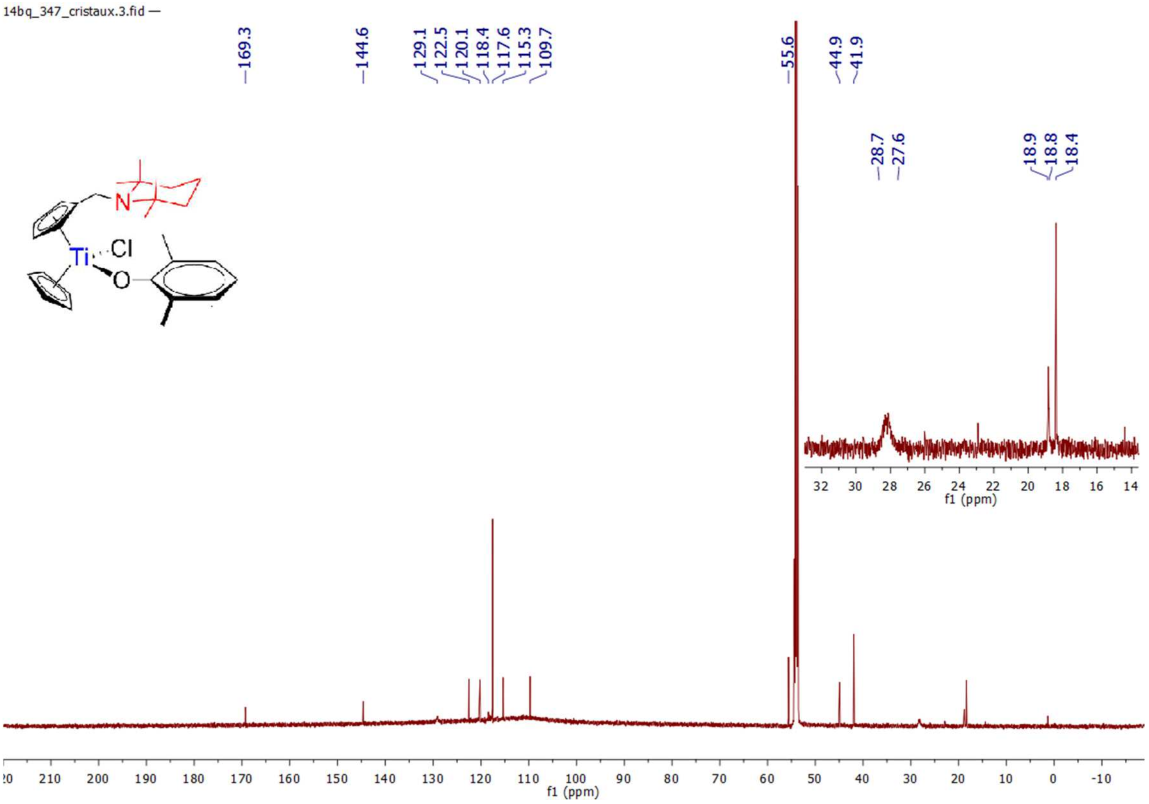


Spectrum 0-199: FIR of 28

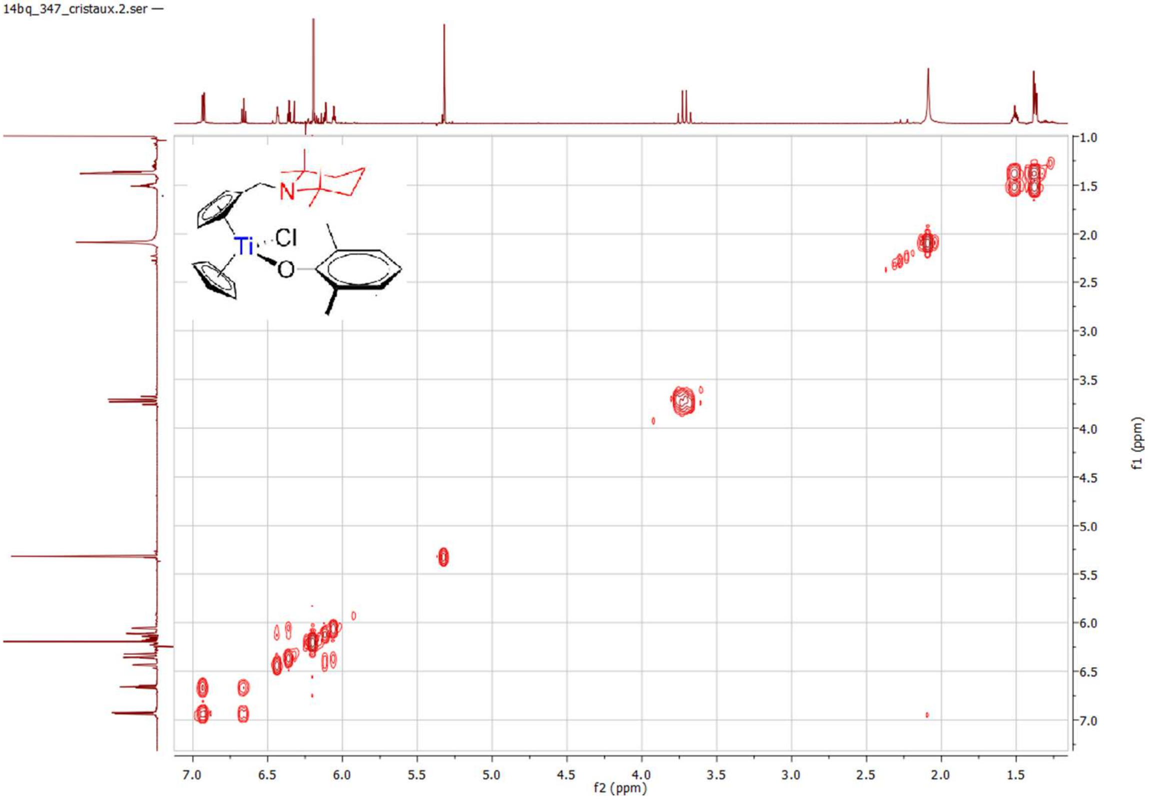
5. Compound **29**:



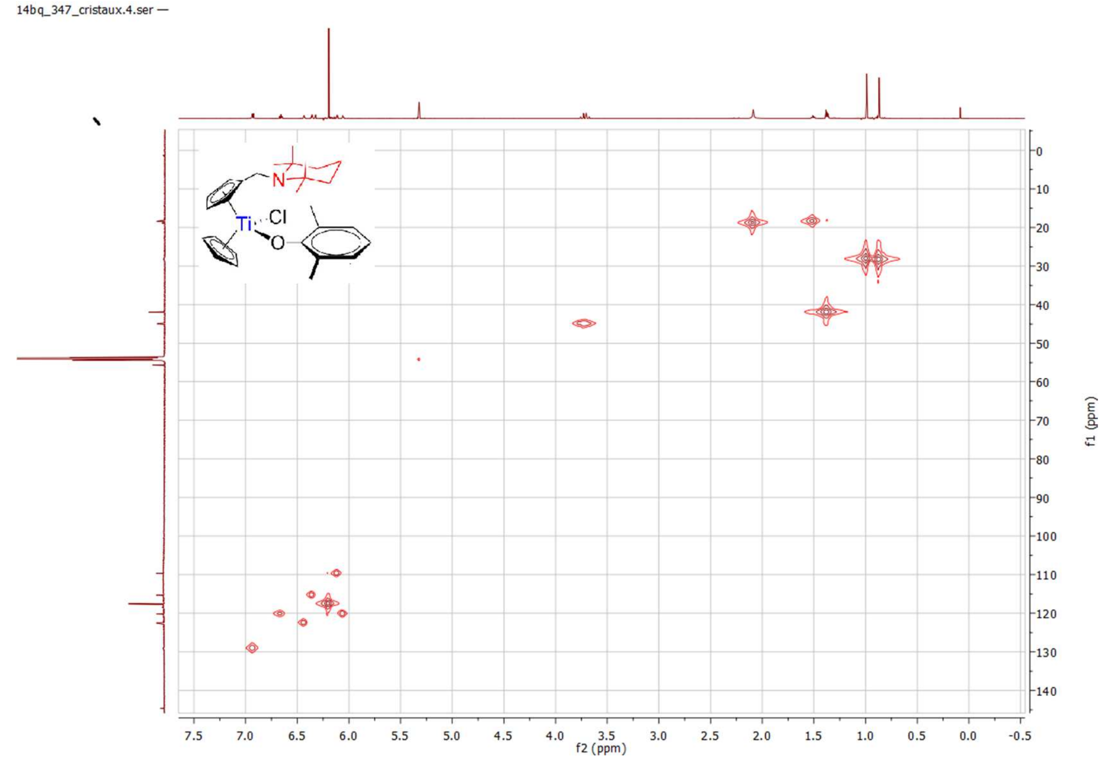
Spectrum 0-200: ^{1}H NMR of 29 (600.23 MHz, 300 K, dichloromethane-d_2)



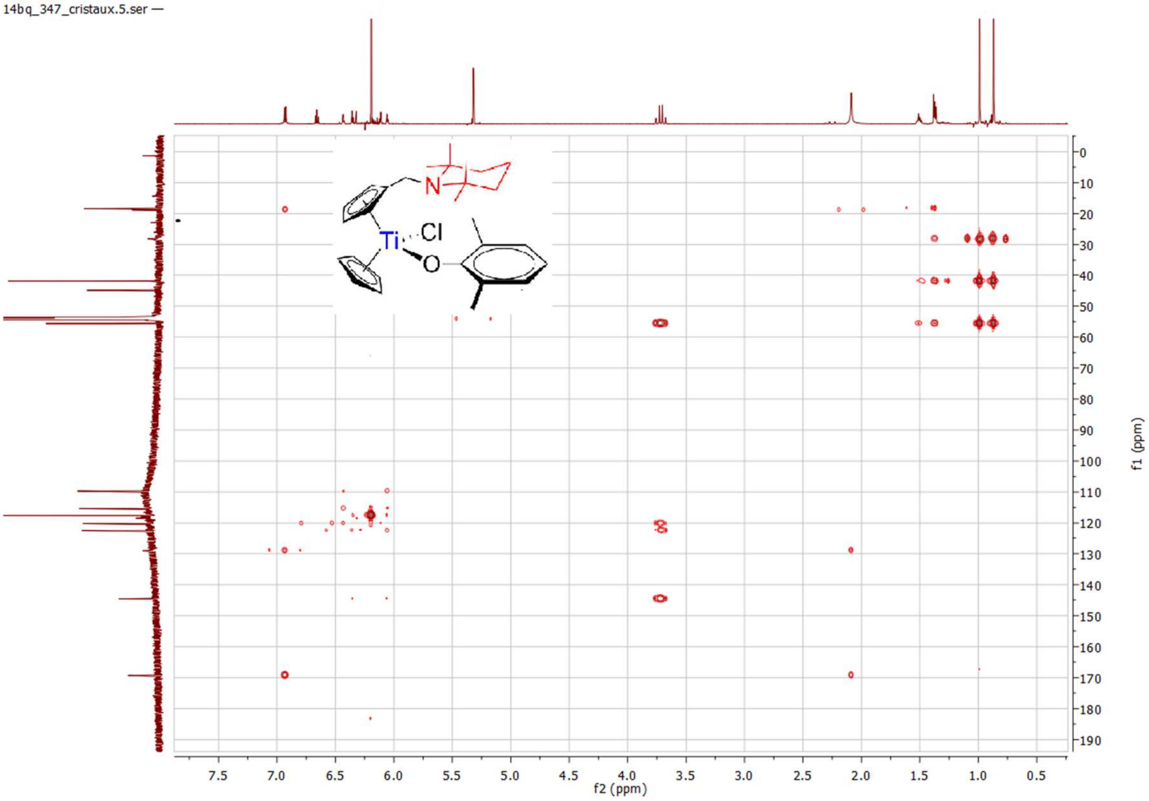
Spectrum 0-201: $^{13}C\{^{1}H\}$ NMR of 29 (150.94 MHz, 300 K, dichloromethane-d_2)



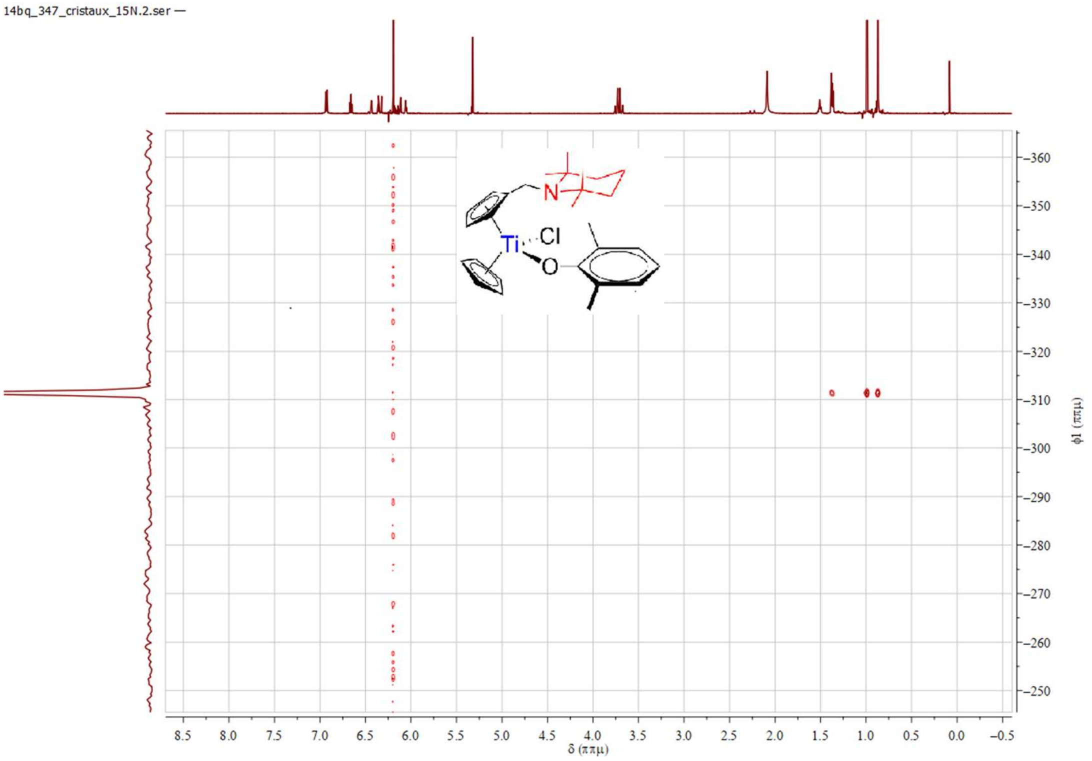
Spectrum 0-202: ^{1}H ^{1}H COSY of 29 (600.23 MHz, 300 K, dichloromethane-d_2)



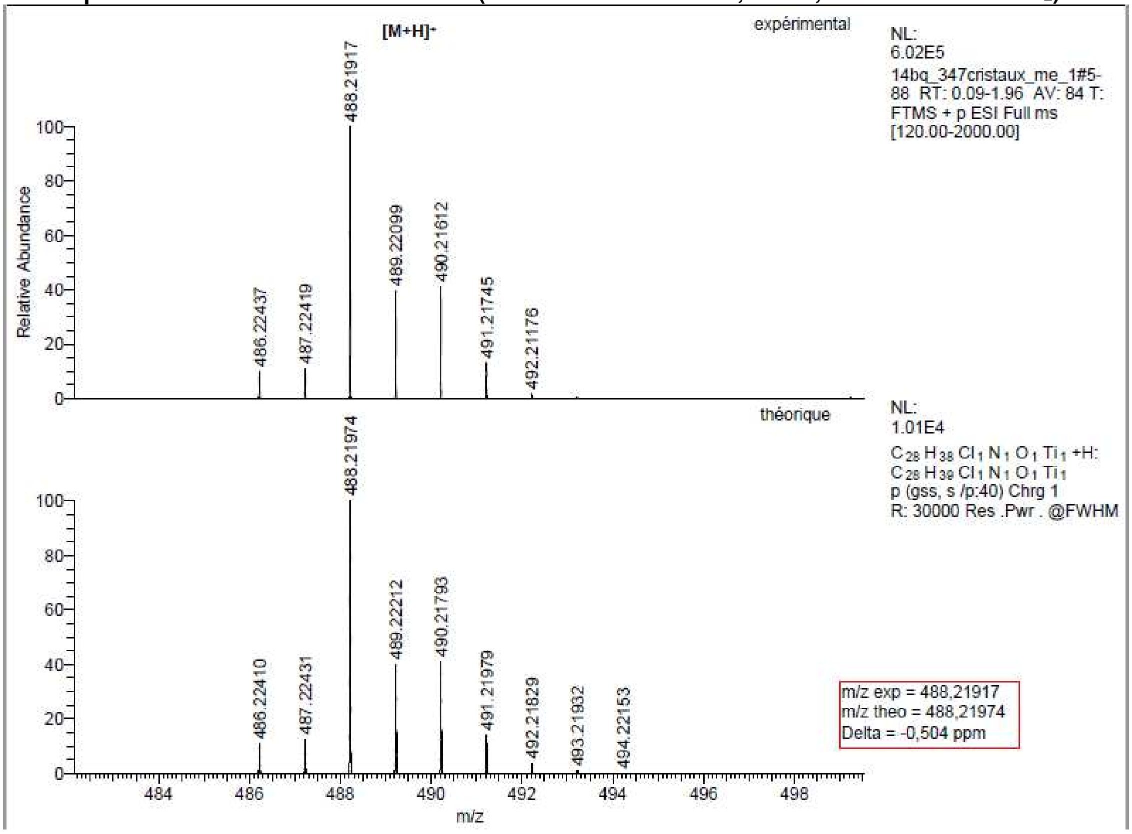
Spectrum 0-203: ^{1}H ^{13}C HMQC of 29 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$)



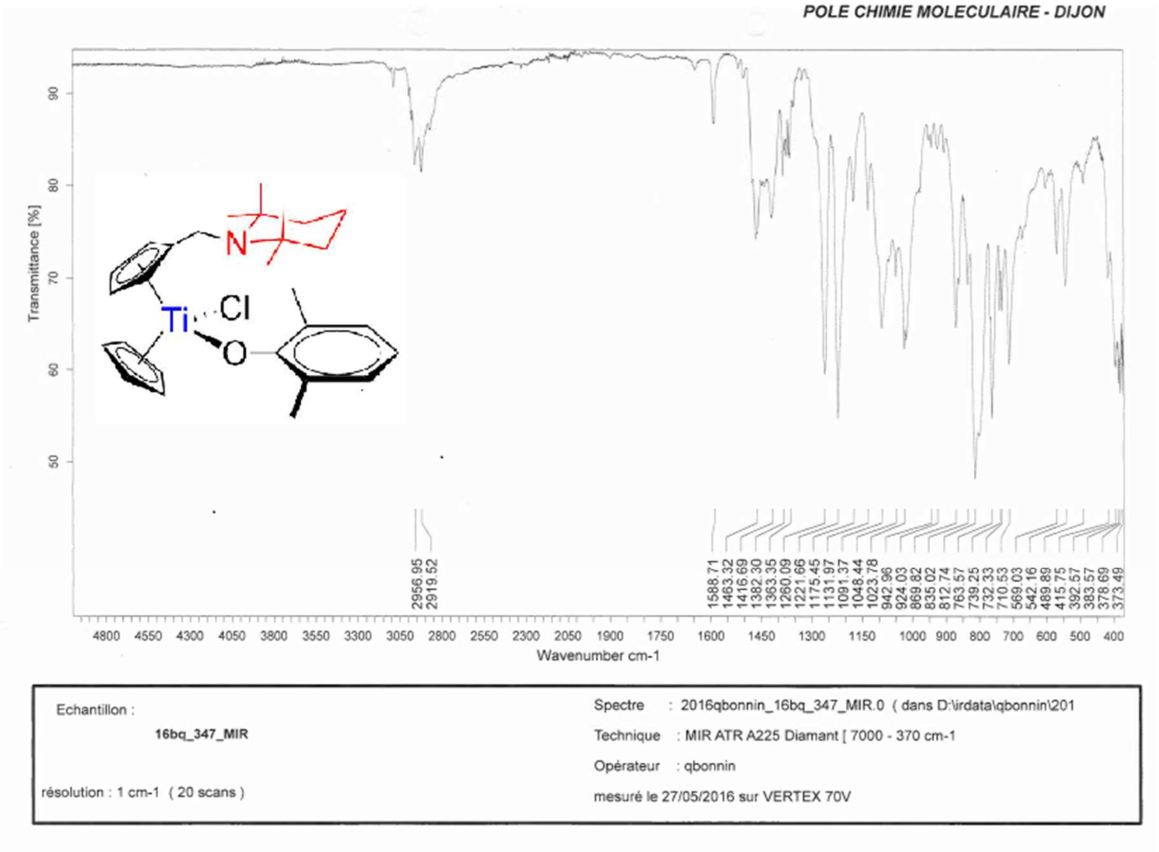
Spectrum 0-204: ^{1}H ^{13}C HMBC of 29 (600.23 MHz / 150.94 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-205: ^{1}H ^{15}N HMBC of 29 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-206: HRMS of 29 (Positive mode ESI, dichloromethane)



POLE CHIMIE MOLECULAIRE - DIJON

Echantillon :

16bq_347_MIR

résolution : 1 cm-1 (20 scans)

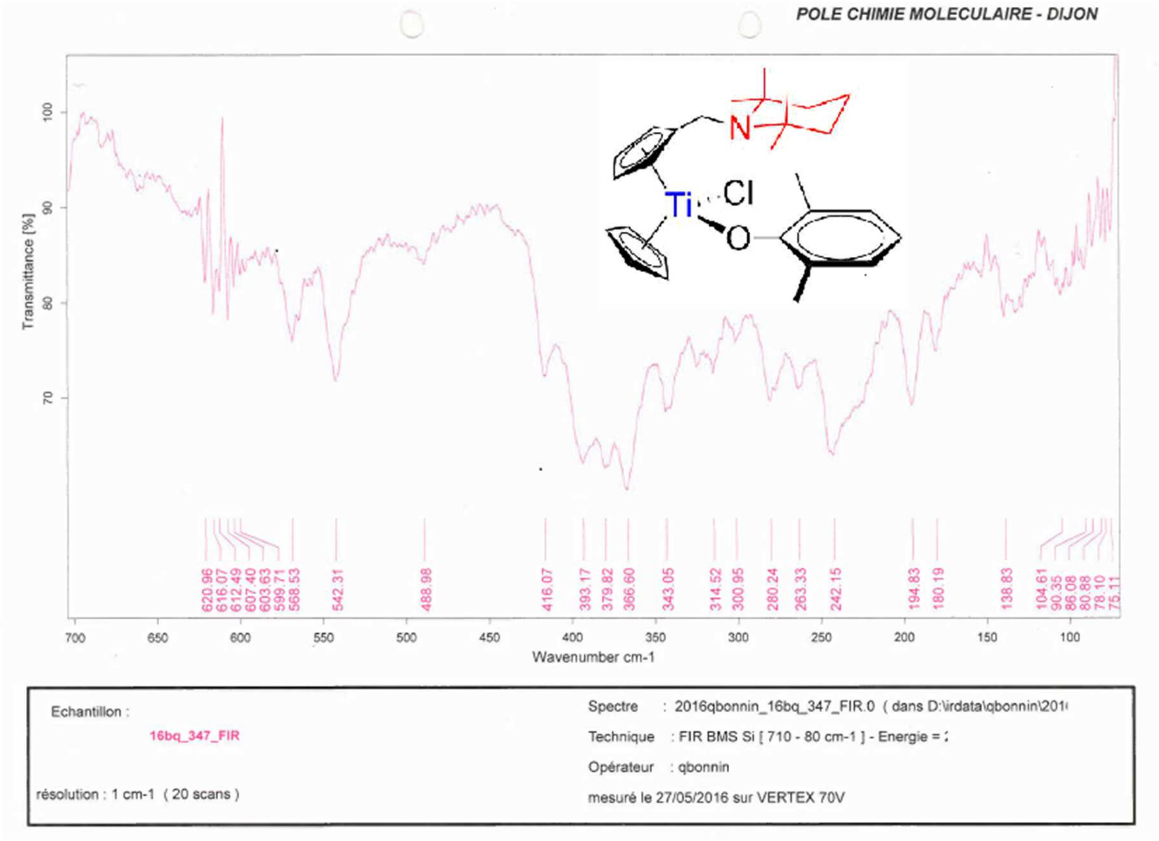
Spectre : 2016qbonnin_16bq_347_MIR.0 (dans D:\irdata\qbonnin\201

Technique : MIR ATR A225 Diamant [7000 - 370 cm-1

Opérateur : qbonnin

mesuré le 27/05/2016 sur VERTEX 70V

Spectrum 0-207: MIR of 29



POLE CHIMIE MOLECULAIRE - DIJON

Echantillon :

16bq_347_FIR

résolution : 1 cm-1 (20 scans)

Spectre : 2016qbonnin_16bq_347_FIR.0 (dans D:\irdata\qbonnin\201

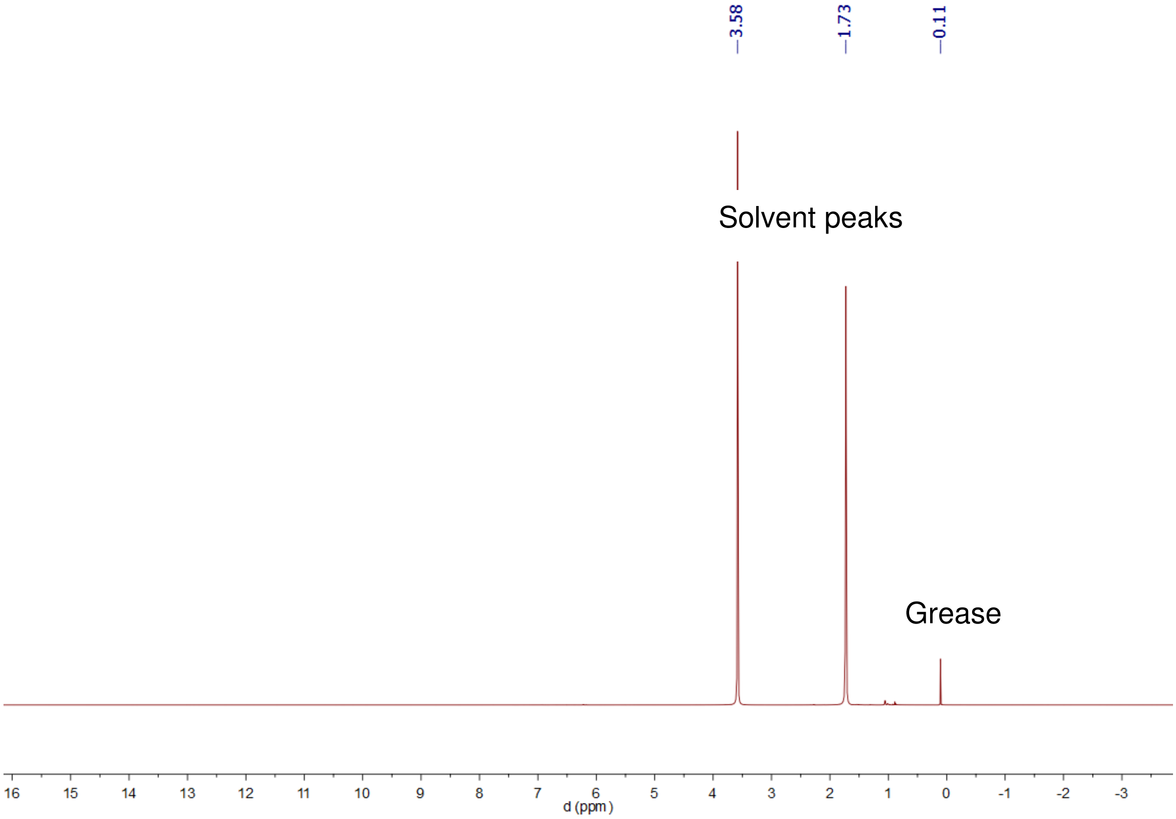
Technique : FIR BMS Si [710 - 80 cm-1] - Energie =

Opérateur : qbonnin

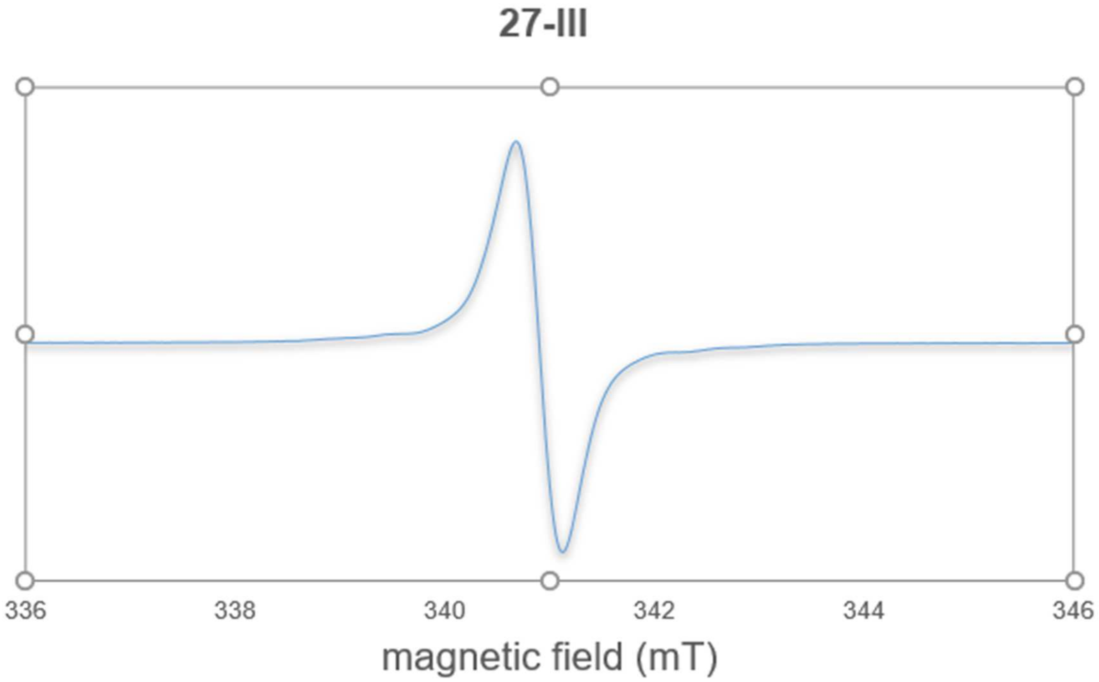
mesuré le 27/05/2016 sur VERTEX 70V

Spectrum 0-208: FIR of 29

6. Attempted synthesis **27-III**:

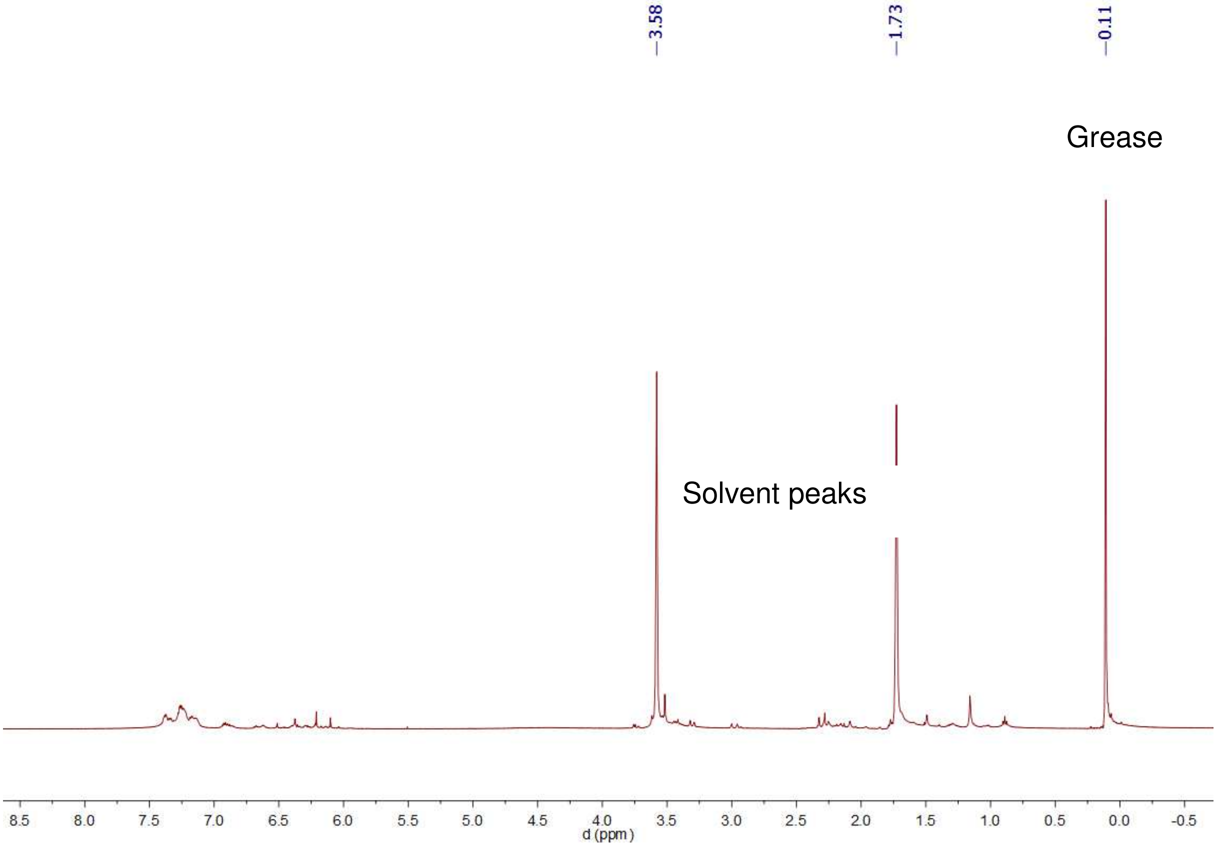


Spectrum 0-209: ^{1}H NMR spectrum of 27-III (600.23 MHz, 300K, tetrahydrofuran-d$_8$)

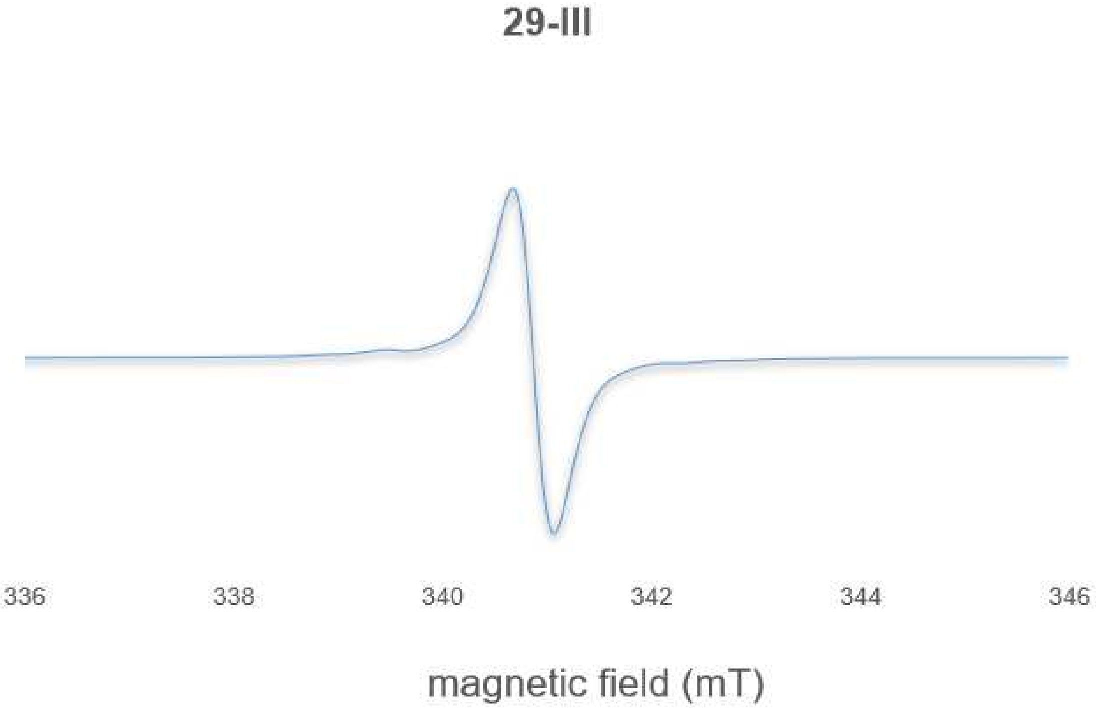


Spectrum 0-210: EPR spectrum of 27-III (9.437703 GHz, 295 K, pentane)

7. Attempted synthesis of **29-III**:

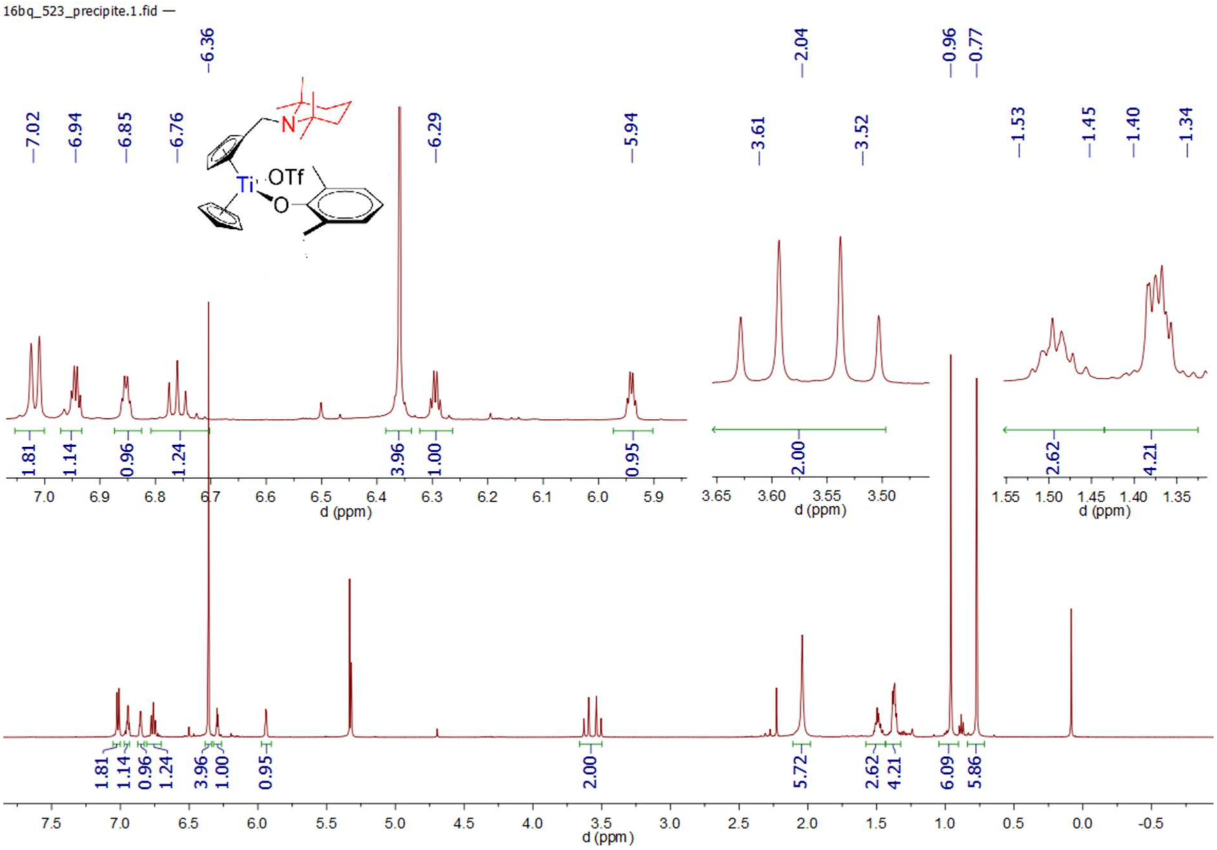


Spectrum 0-211: ^{1}H NMR spectrum of 29-III (500.53 MHz, 300K, tetrahydrofuran-d$_{8}$)

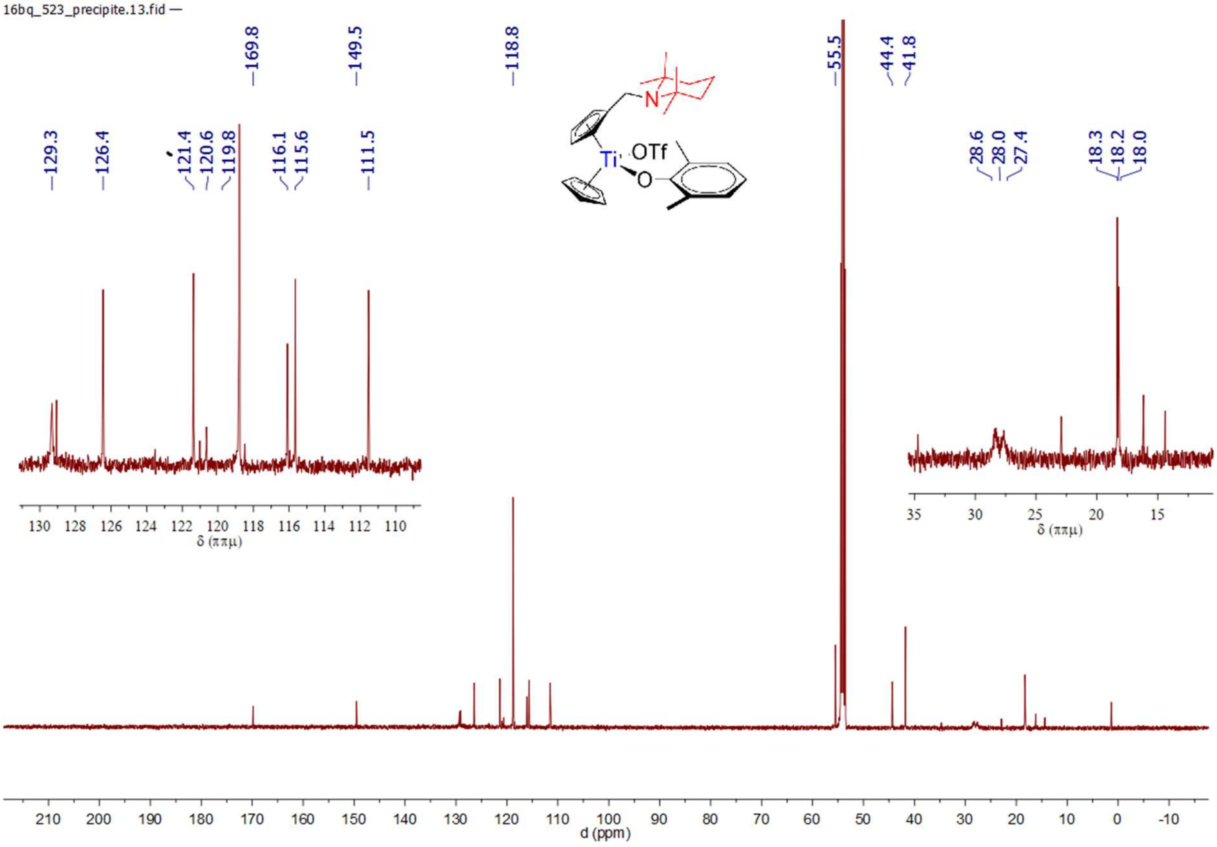


Spectrum 0-212: EPR spectrum of 29-III (9.437952 GHz, 295 K, pentane)

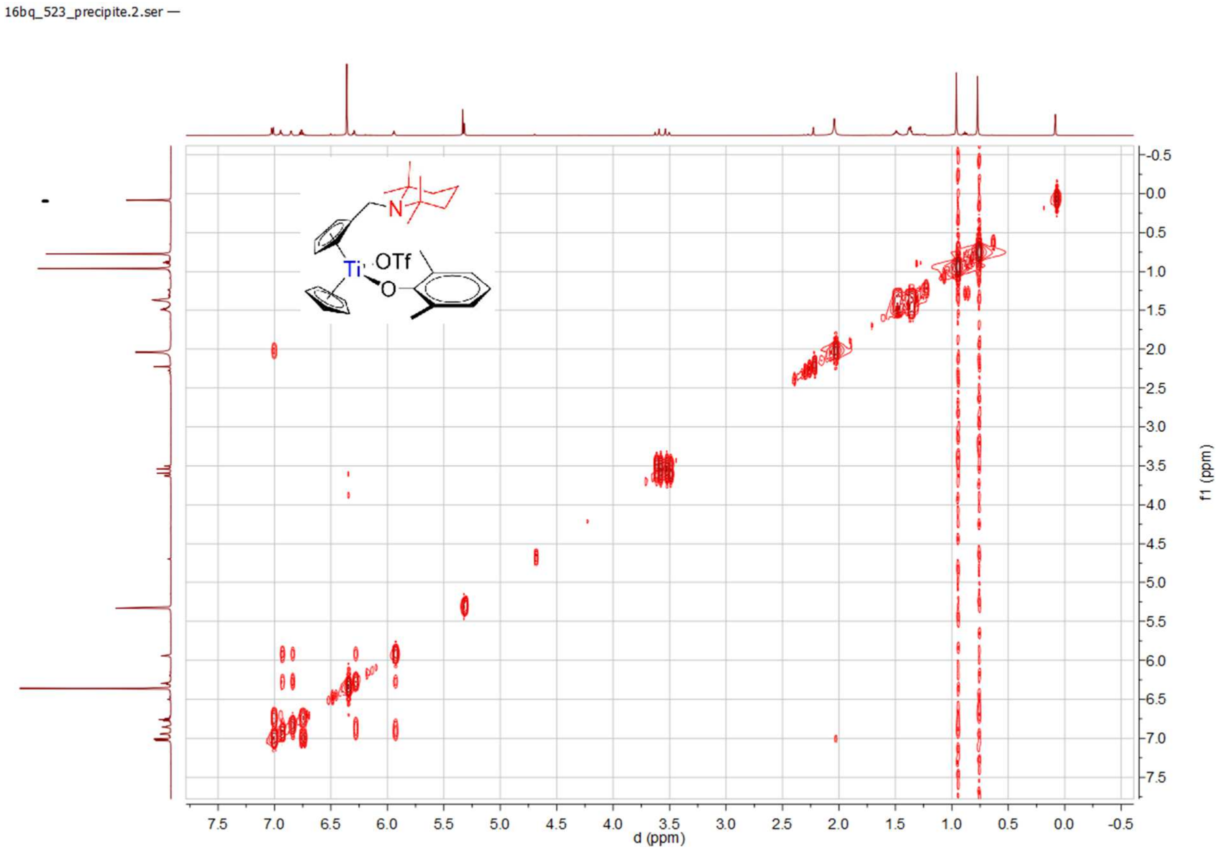
8. Compound **30**:



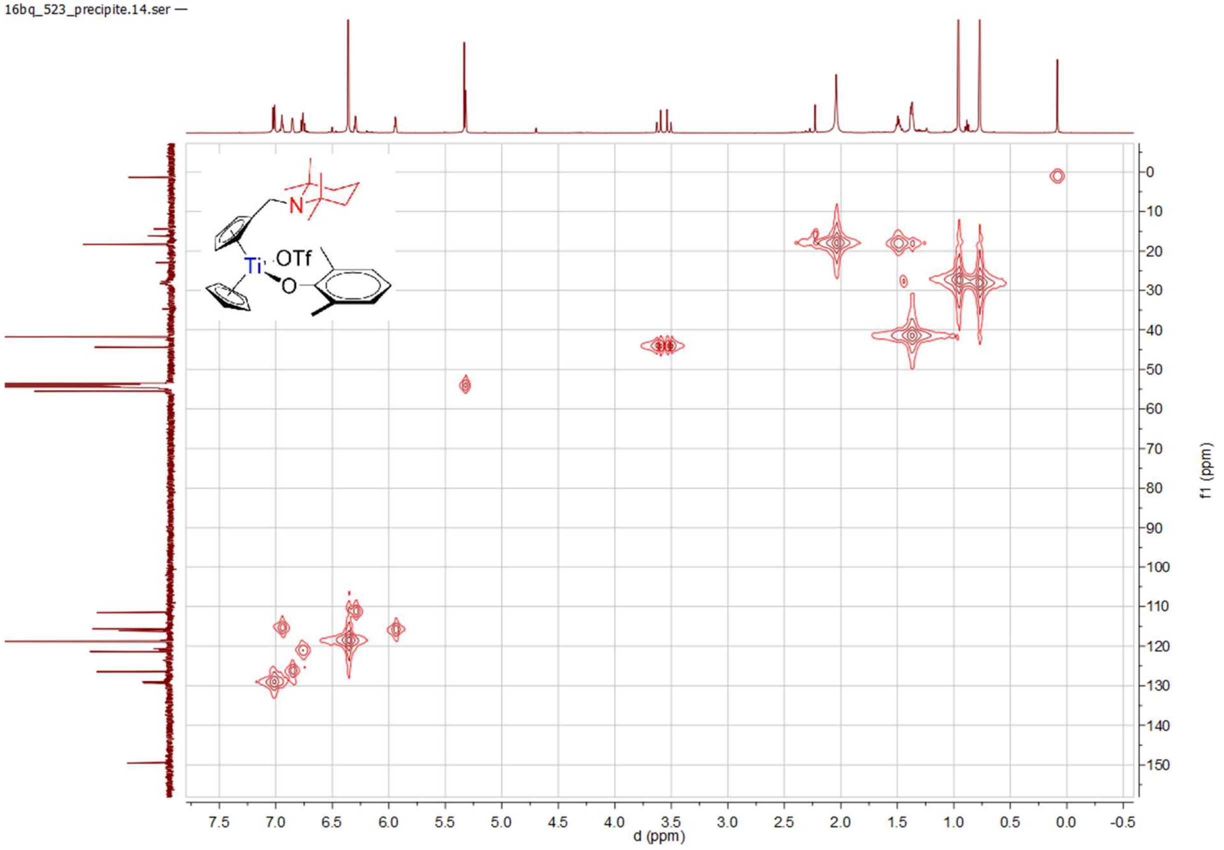
Spectrum 0-213: ^{1}H NMR of 30 (500.03 MHz, 300 K, dichloromethane-d$_2$)



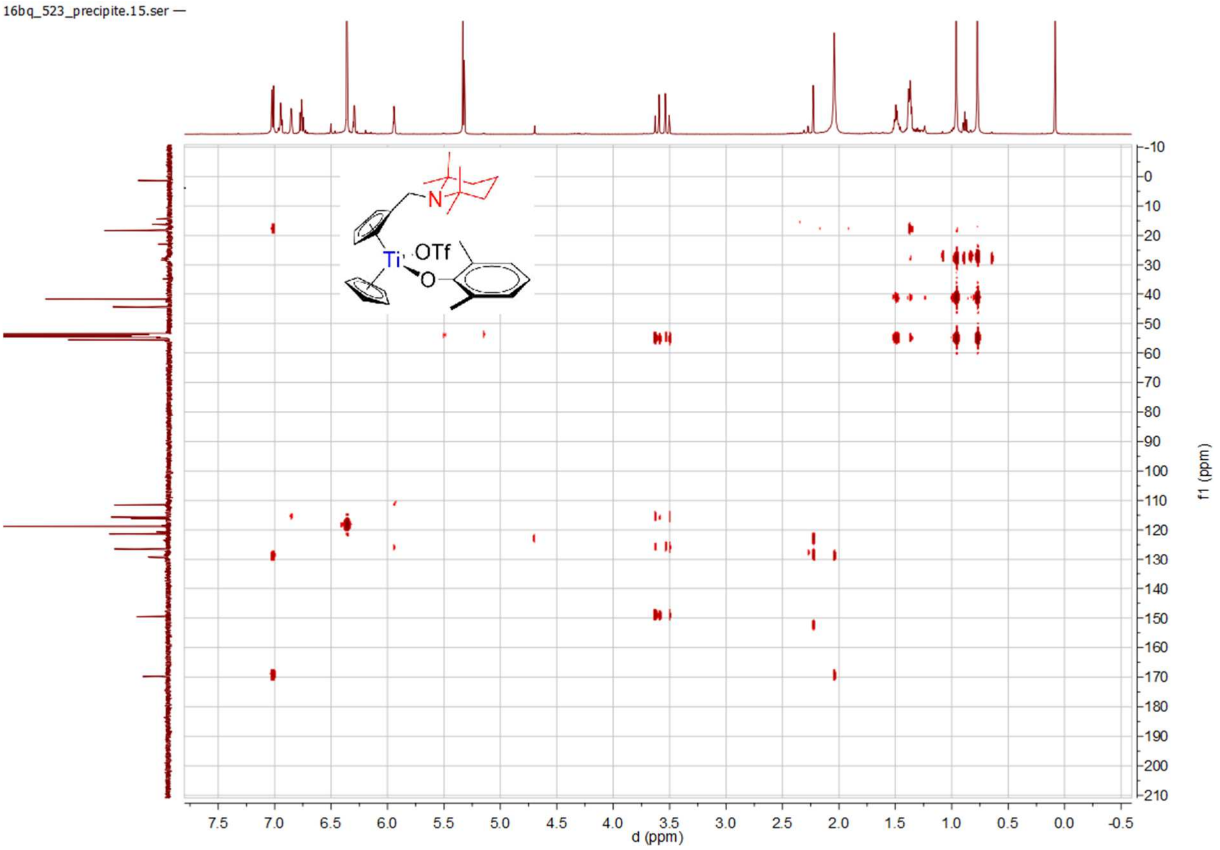
Spectrum 0-214: ^{13}C{^{1}H} NMR of 30 (125.77 MHz, 300 K, dichloromethane-d$_2$)



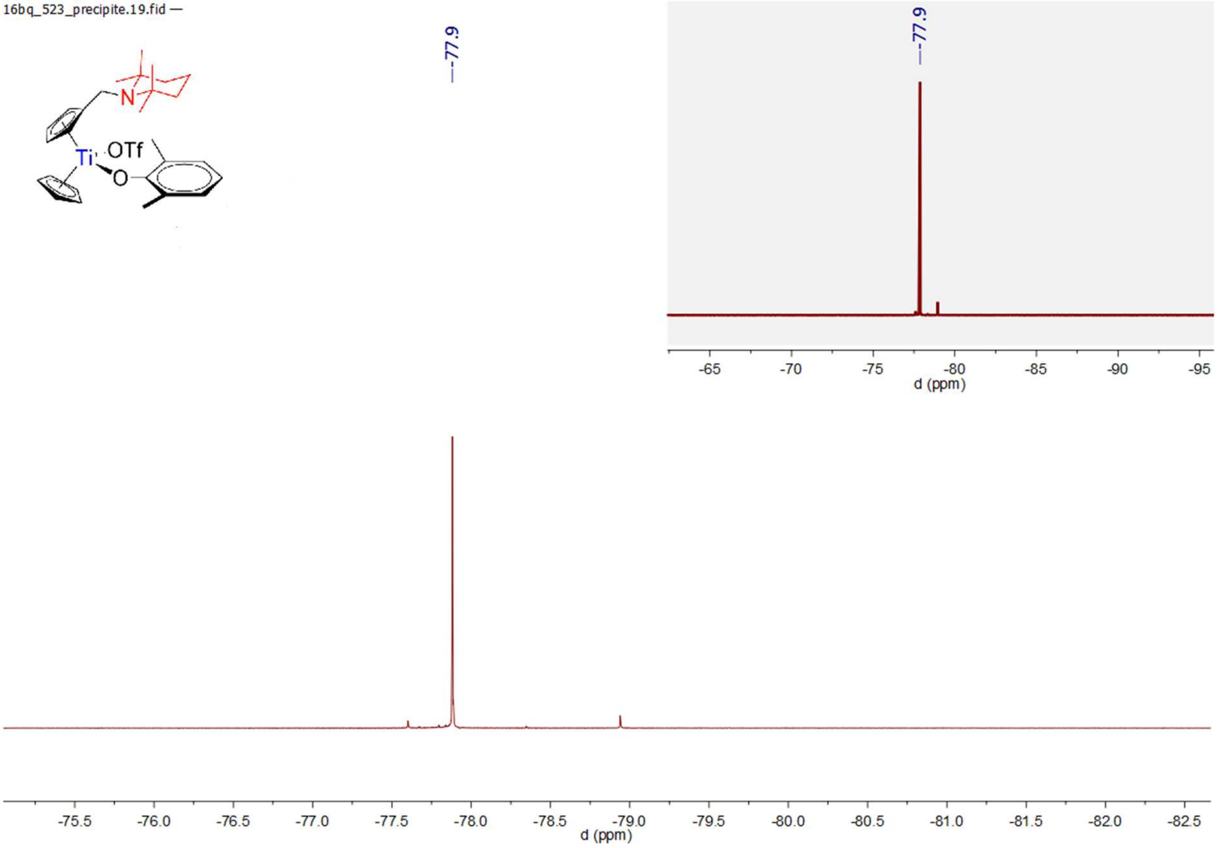
Spectrum 0-215: ^1H ^1H COSY of 30 (500.03 MHz, 300 K, dichloromethane-d_2)



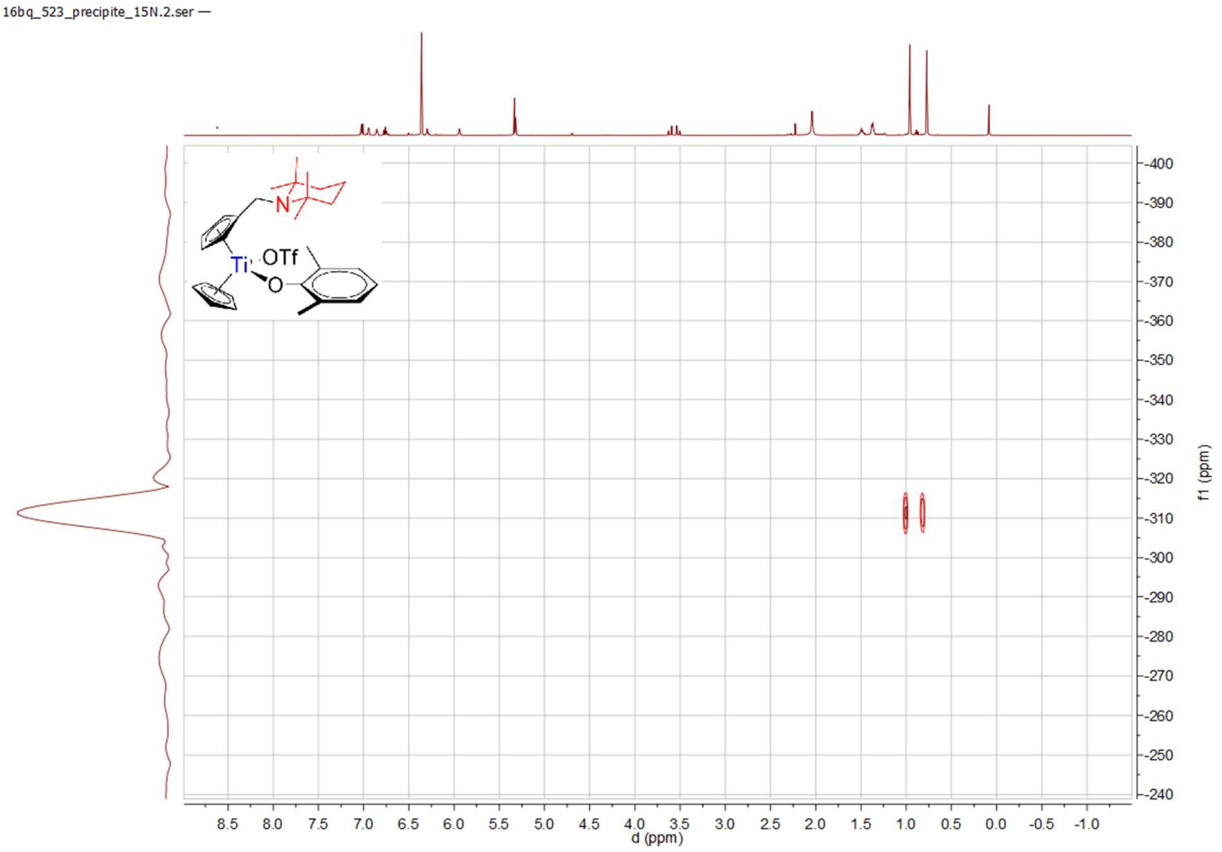
Spectrum 0-216: ^1H ^{13}C HMQC of 30 (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d_2)



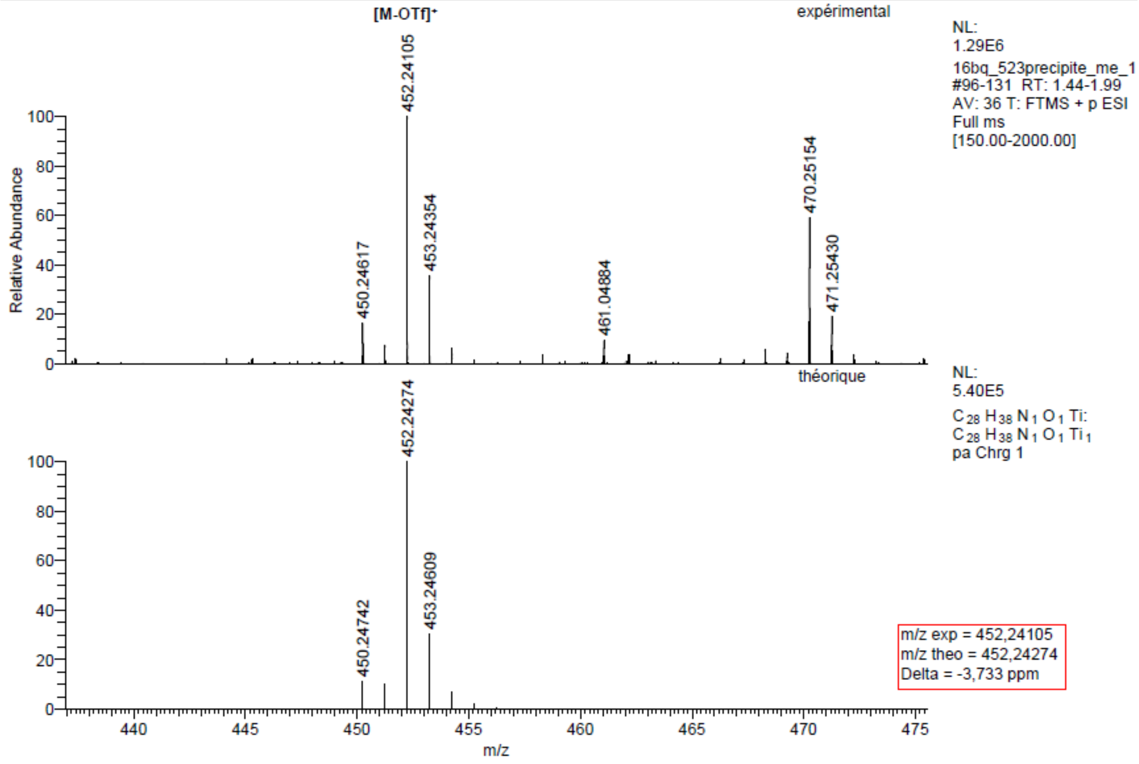
Spectrum 0-217: ^{1}H ^{13}C HMBC of 30 (500.03 MHz / 125.77 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-218: ^{19}F{^{1}H} and ^{19}F(οπαχιφιεδ) NMR of 30 (470.45 MHz, 300 K, dichloromethane-d$_2$)

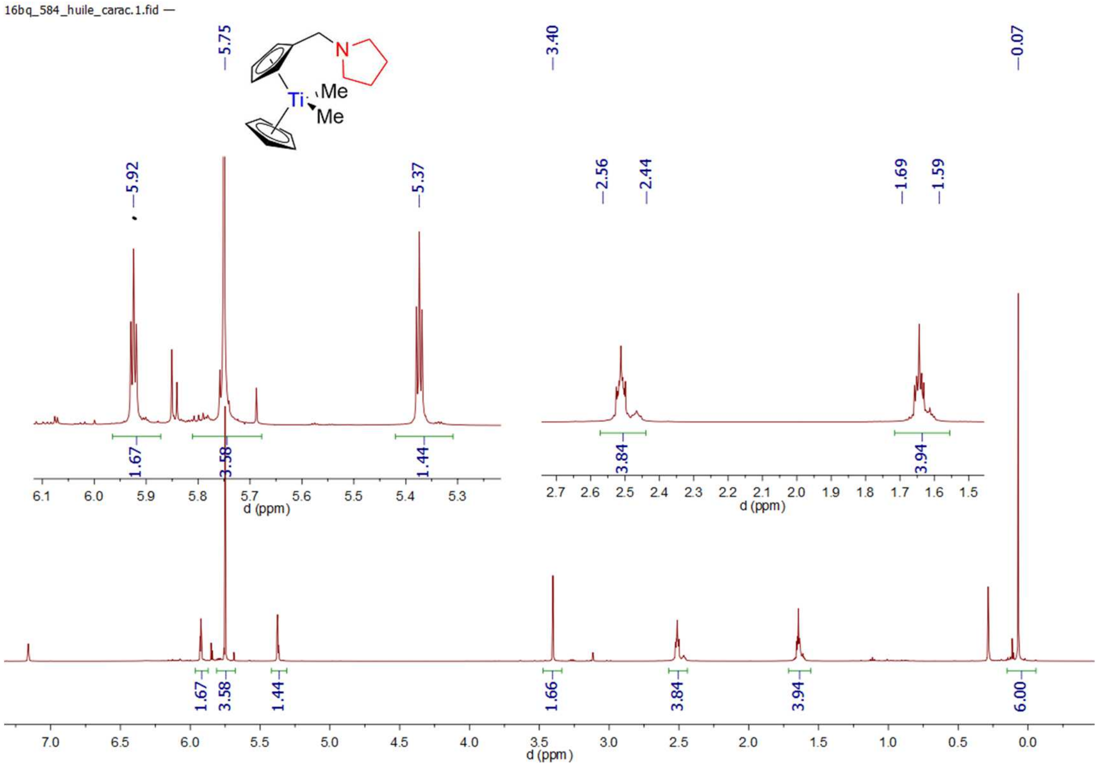


Spectrum 0-219: ^{1}H ^{15}N HMBC of 30 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)

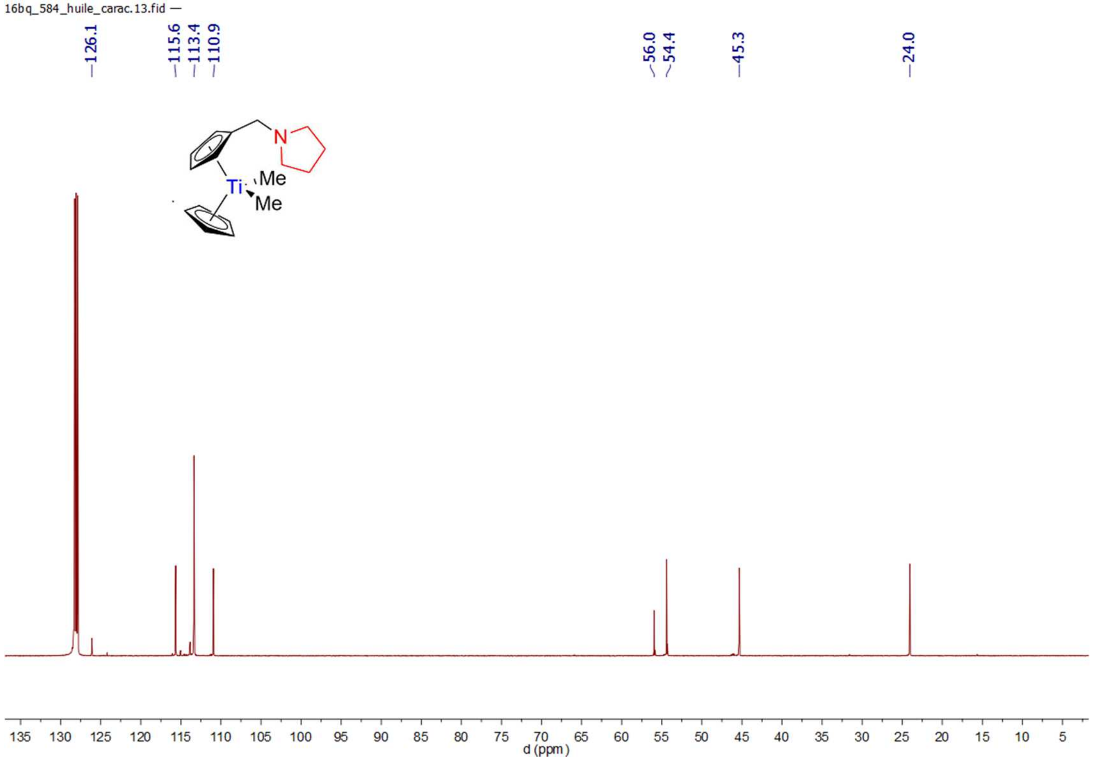


Spectrum 0-220: HRMS of 30 (Positive mode ESI, dichloromethane)

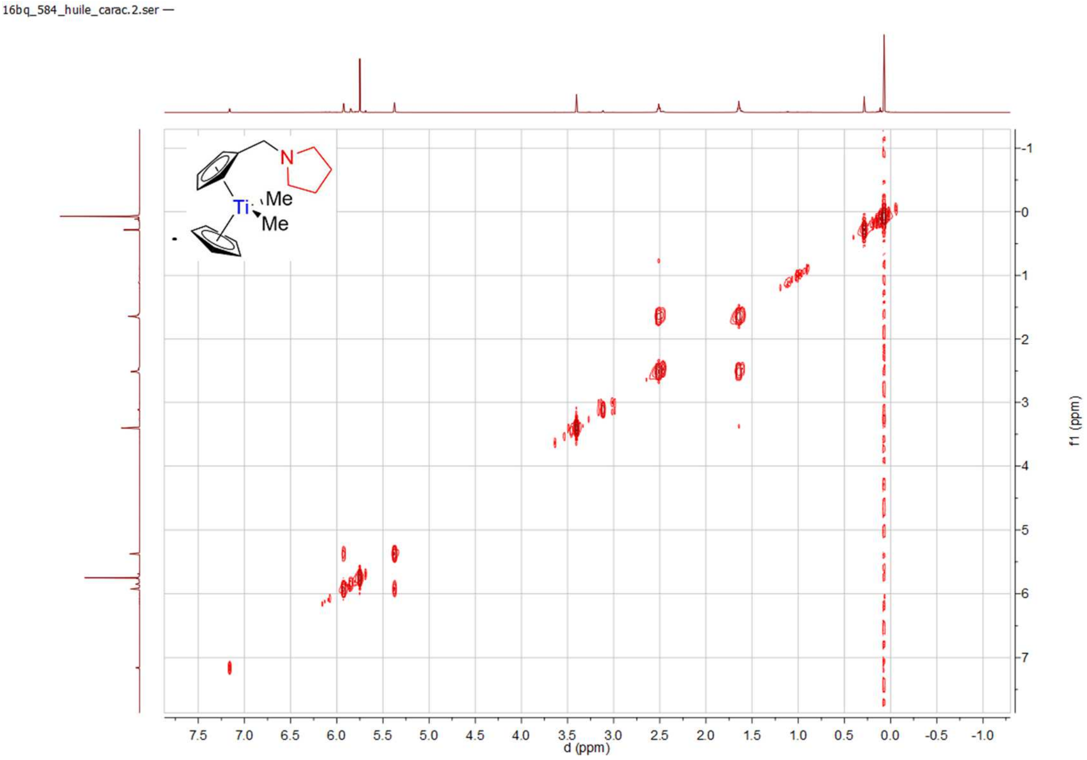
9. Compound **32:**



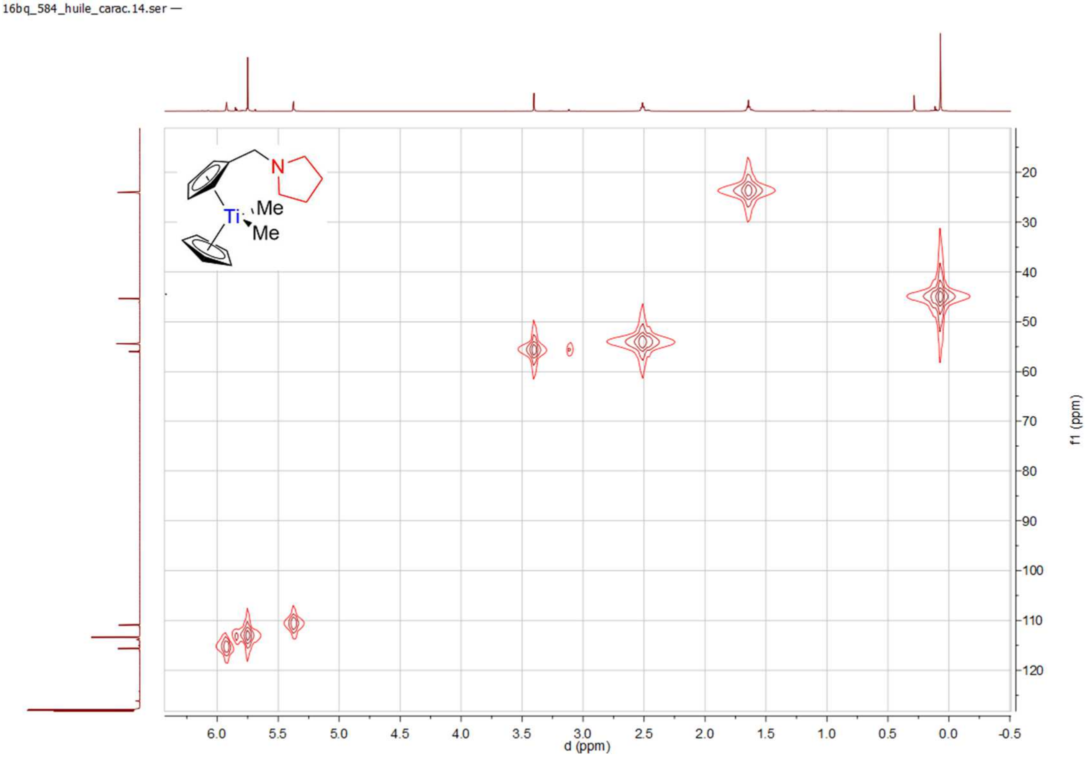
Spectrum 0-221: ^{1}H NMR of 32 (500.03 MHz, 300 K, benzene-d_6)



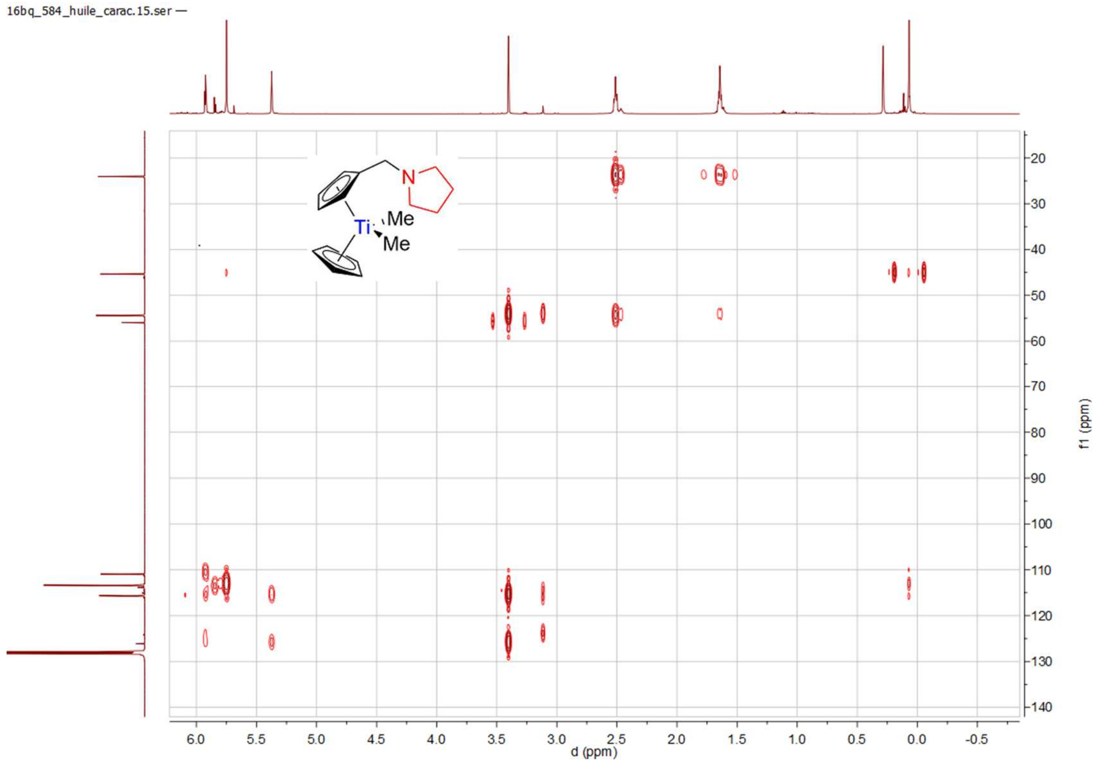
Spectrum 0-222: ^{13}C{^{1}H} NMR of 32 (125.75 MHz, 300 K, benzene-d_6)



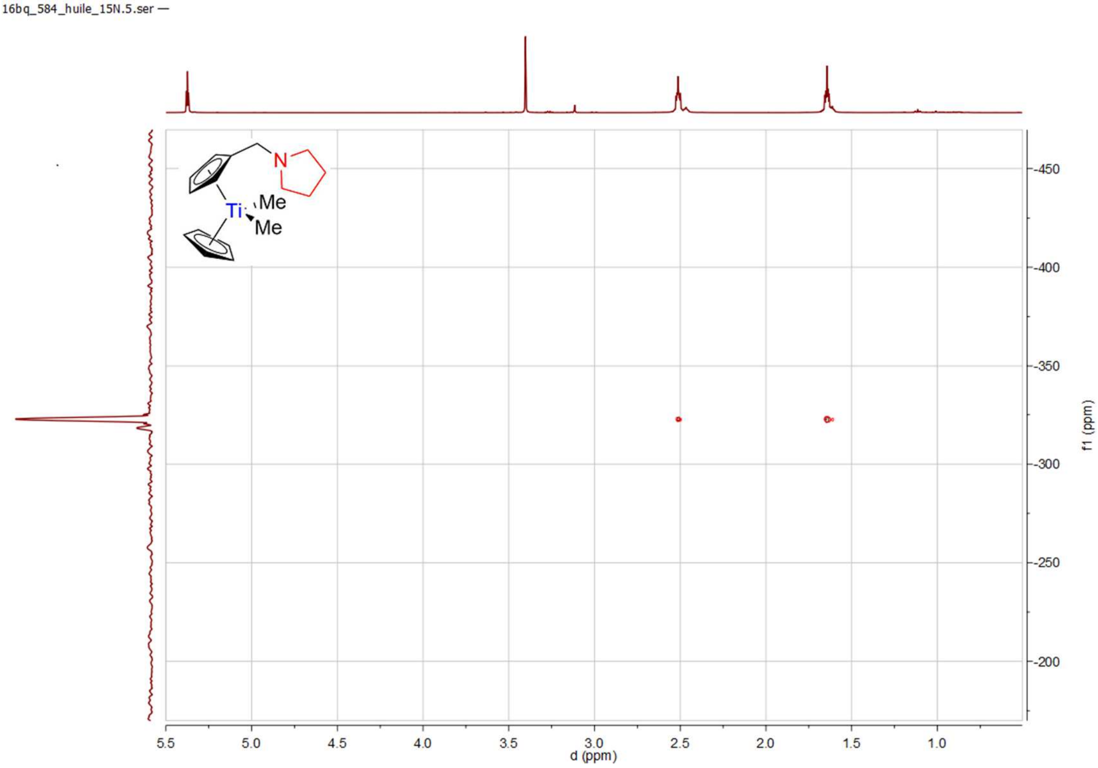
Spectrum 0-223: ^{1}H ^{1}H GCOSY of 32 (500.03 MHz, 300 K, benzene-d$_6$)



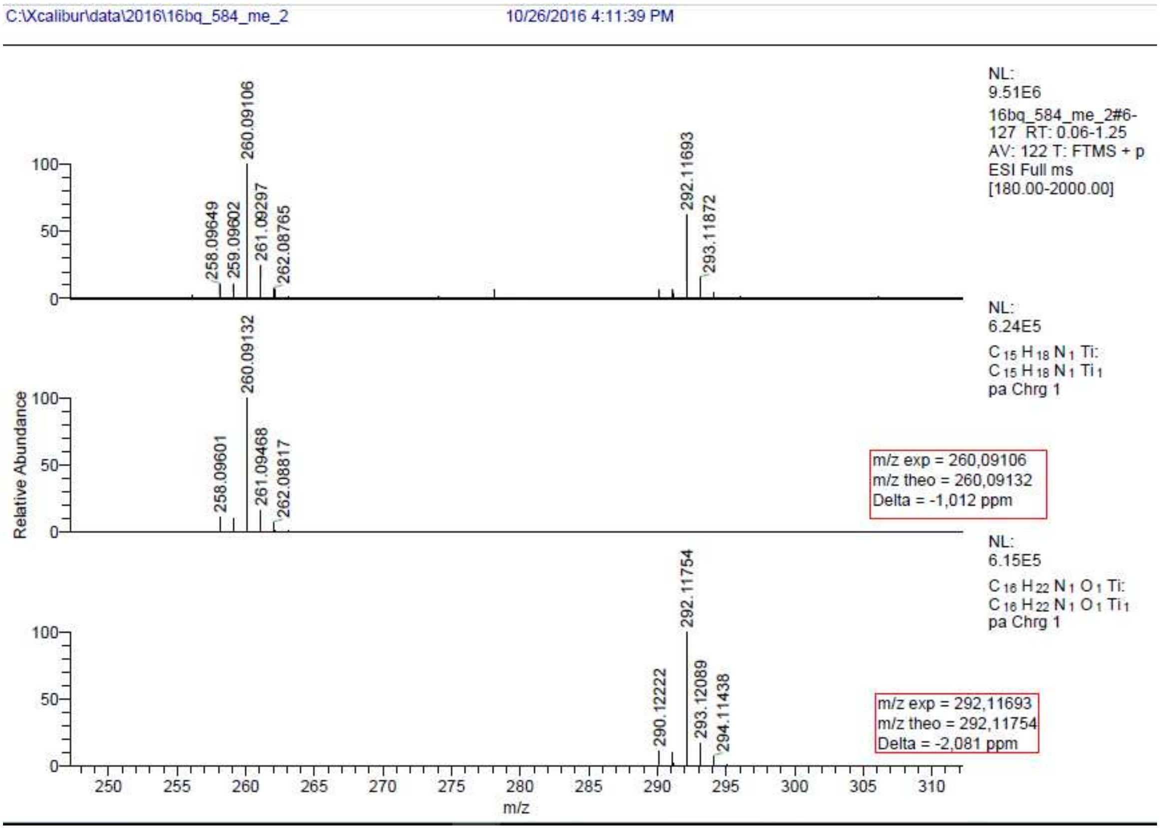
Spectrum 0-224: ^{1}H ^{13}C HMQC of 32 (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$)



Spectrum 0-225: ^{1}H ^{13}C HMBC of 32 (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$)

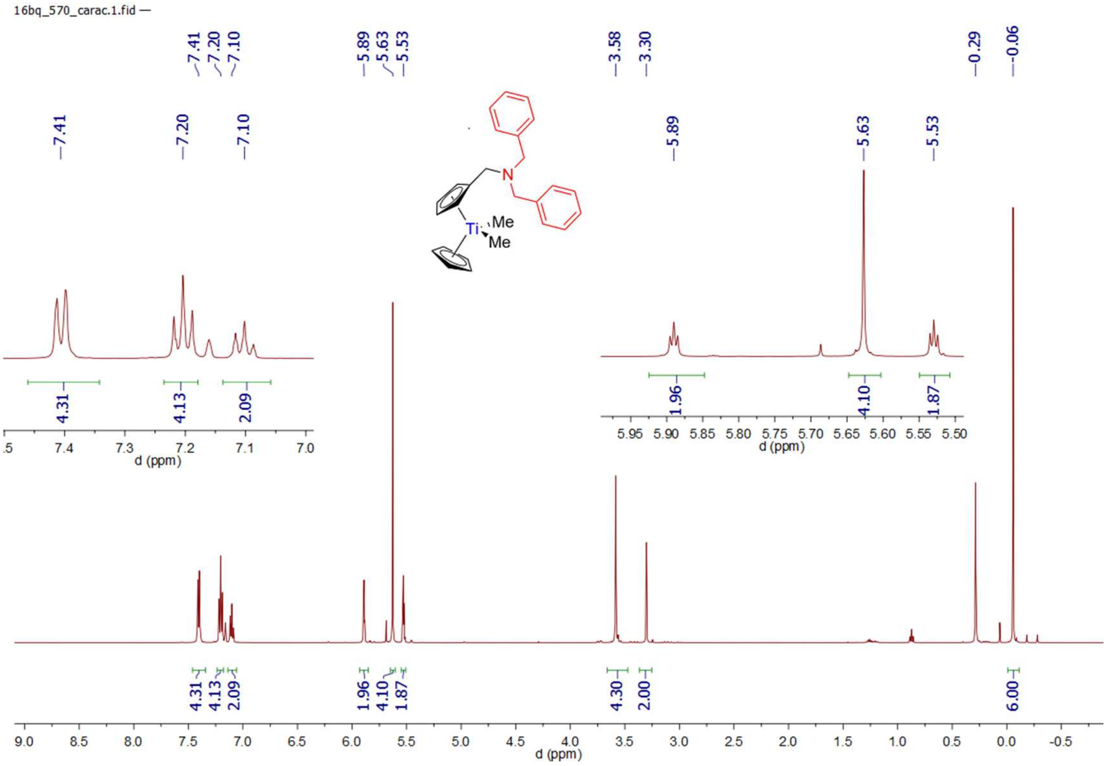


Spectrum 0-226: ^{1}H ^{15}N HMBC of 32 (600.23 MHz / 43.3 MHz, 300 K, benzene-d$_6$)

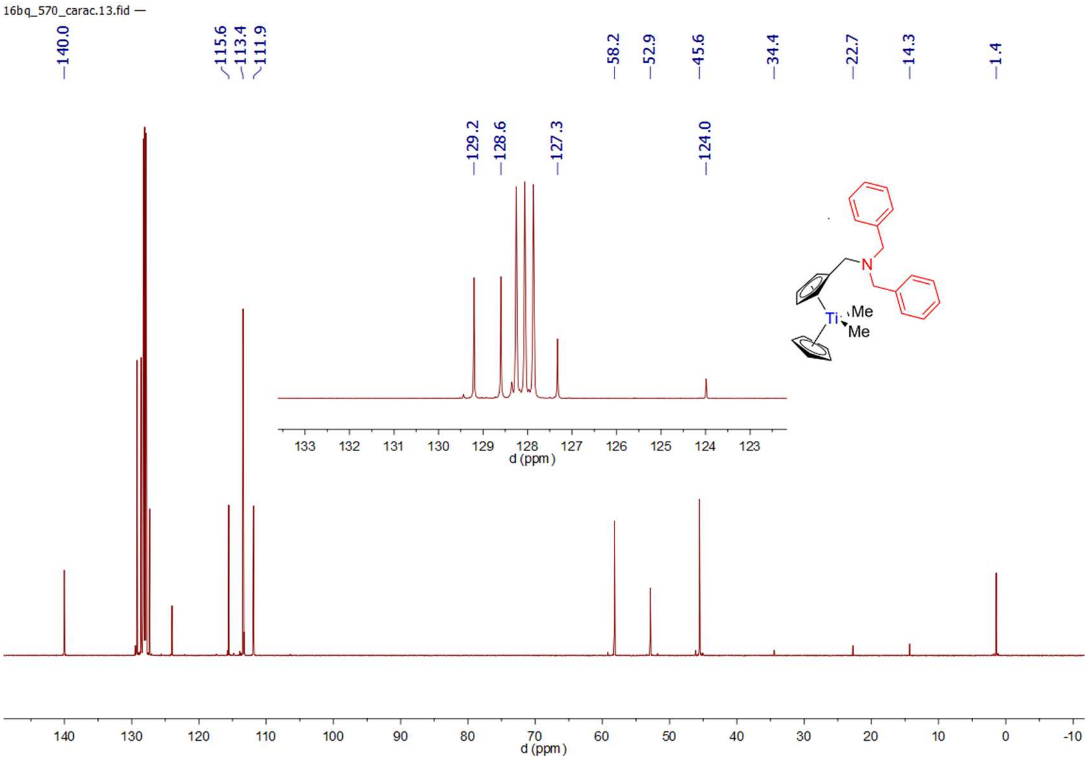


Spectrum 0-227: HRMS of 32 (Positive mode ESI, dichloromethane + methanol)

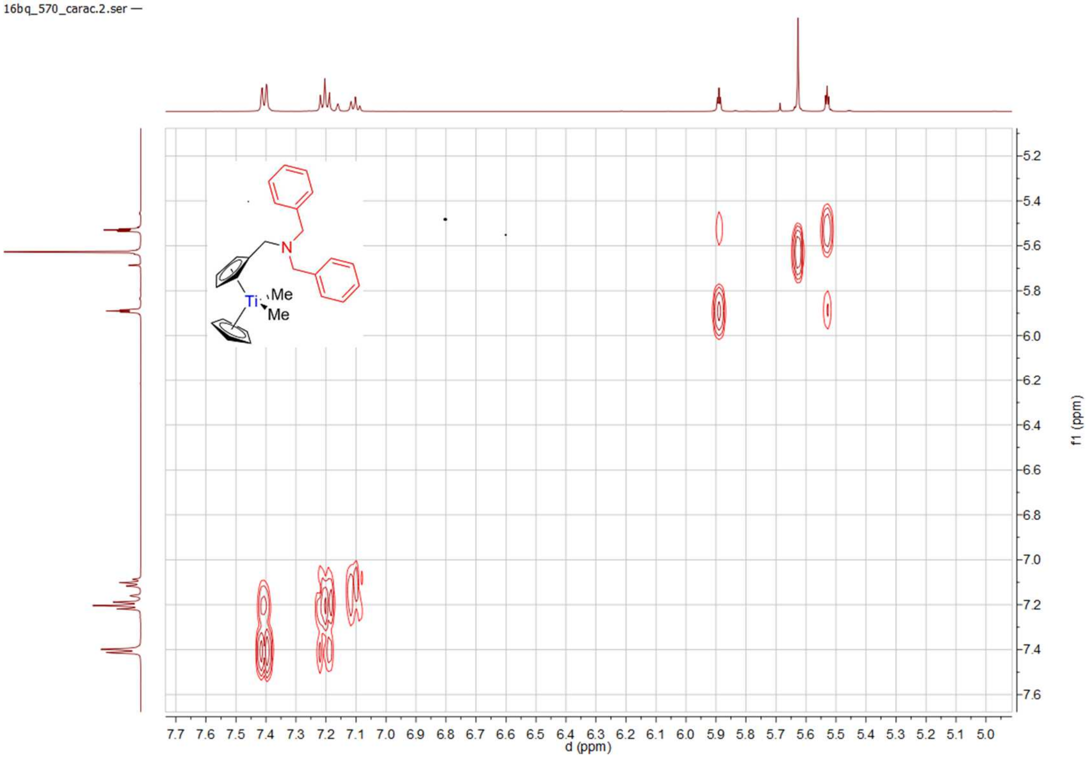
10. Compound **33:**



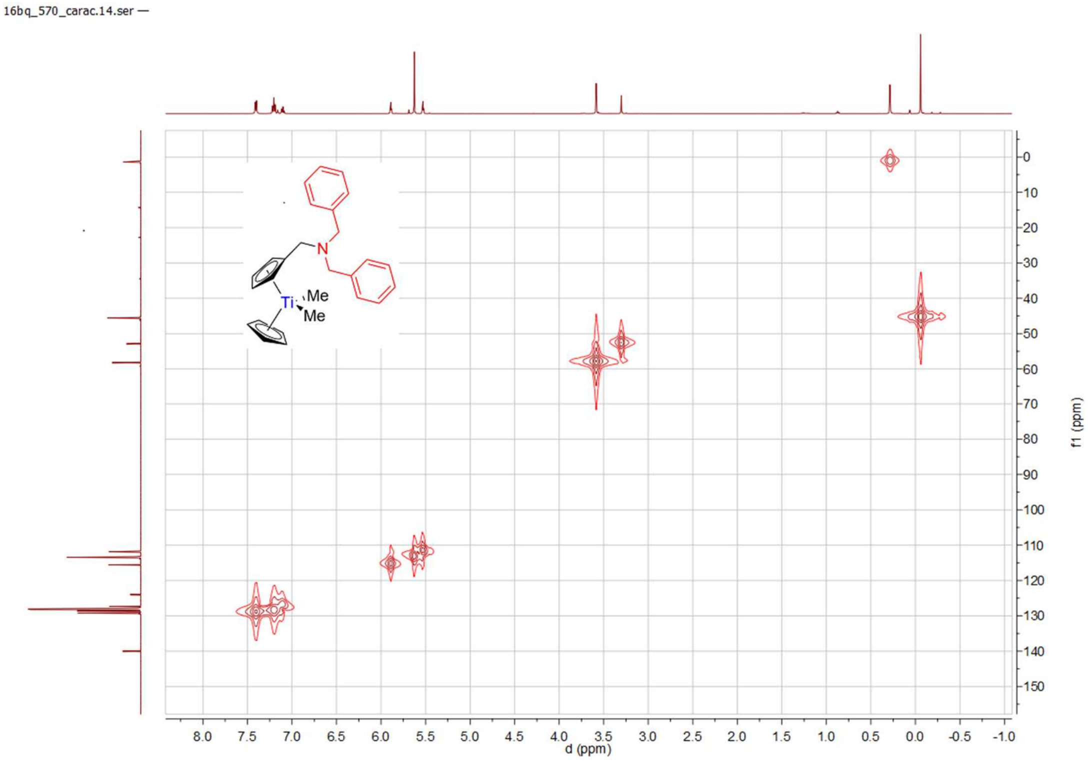
Spectrum 0-228: ^{1}H NMR of 33 (500.03 MHz, 300 K, benzene-d_6)



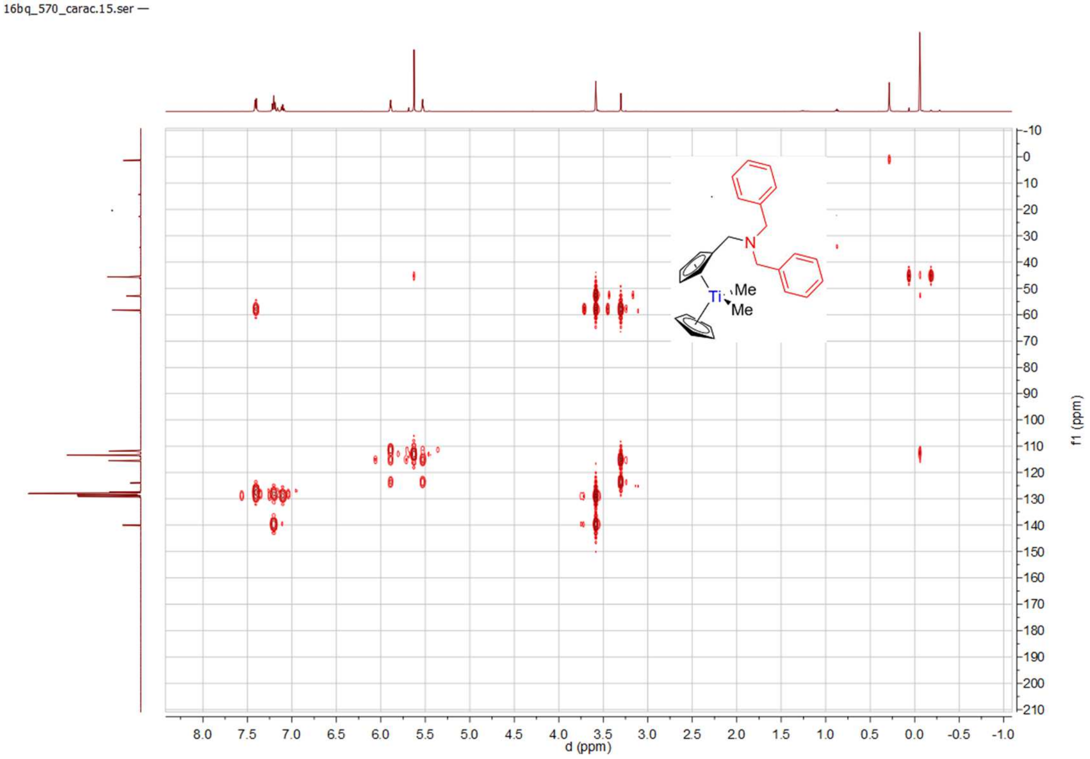
Spectrum 0-229: $^{13}C\{^1H\}$ NMR of 33 (125.75 MHz, 300 K, benzene-d_6)



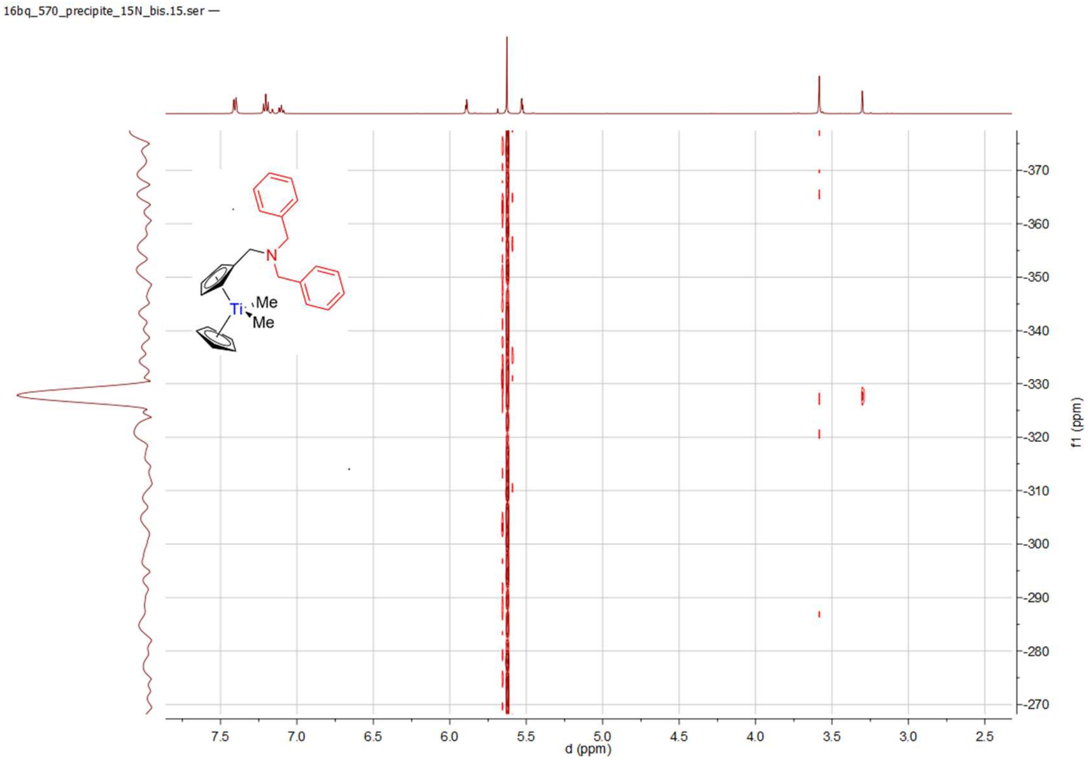
Spectrum 0-230: ^1H ^1H COSY of 33 (500.03 MHz, 300 K, benzene-d_6)



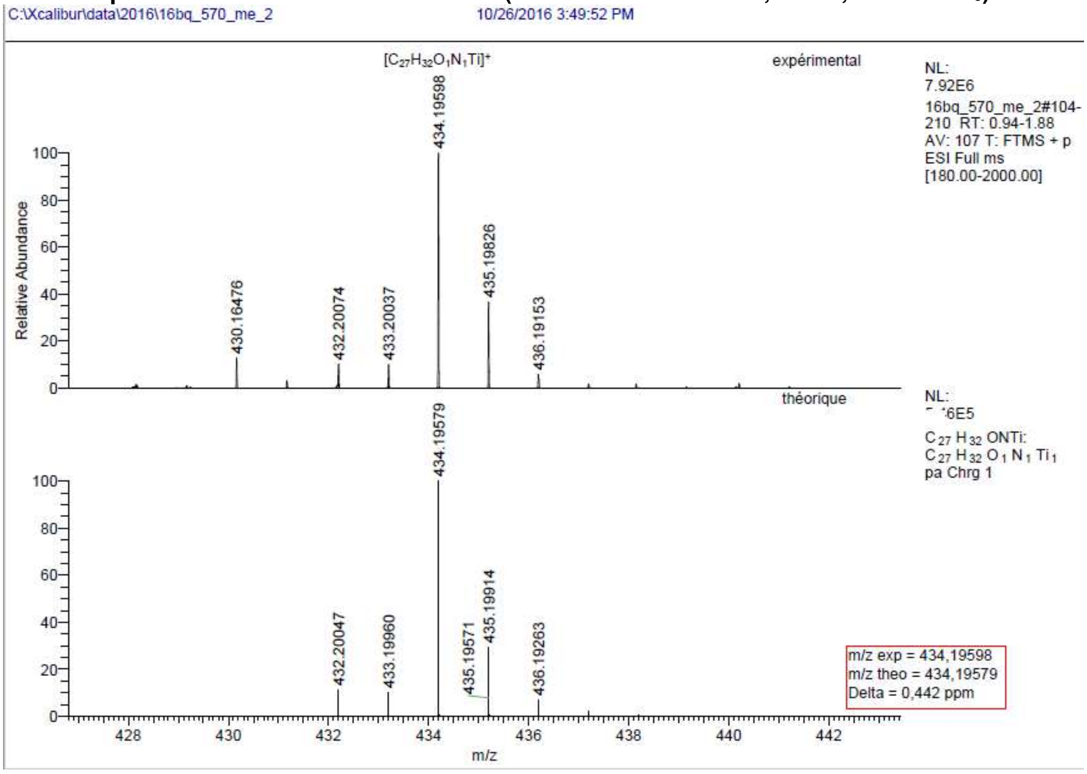
Spectrum 0-231: ^{1}H ^{13}C HMQC of 33 (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6)



Spectrum 0-232: ^{1}H ^{13}C HMBC of 33 (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6)

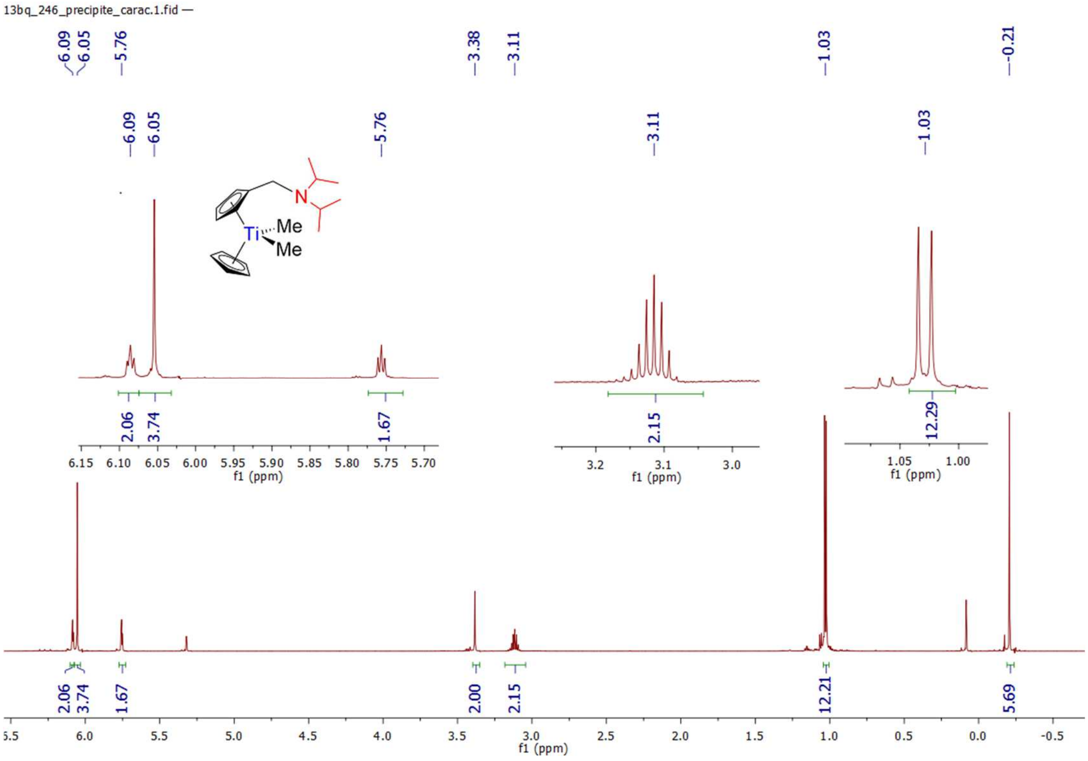


Spectrum 0-233: ^{1}H ^{15}N HMBC of 33 (600.23 MHz / 43.3 MHz, 300 K, benzene-d$_6$)

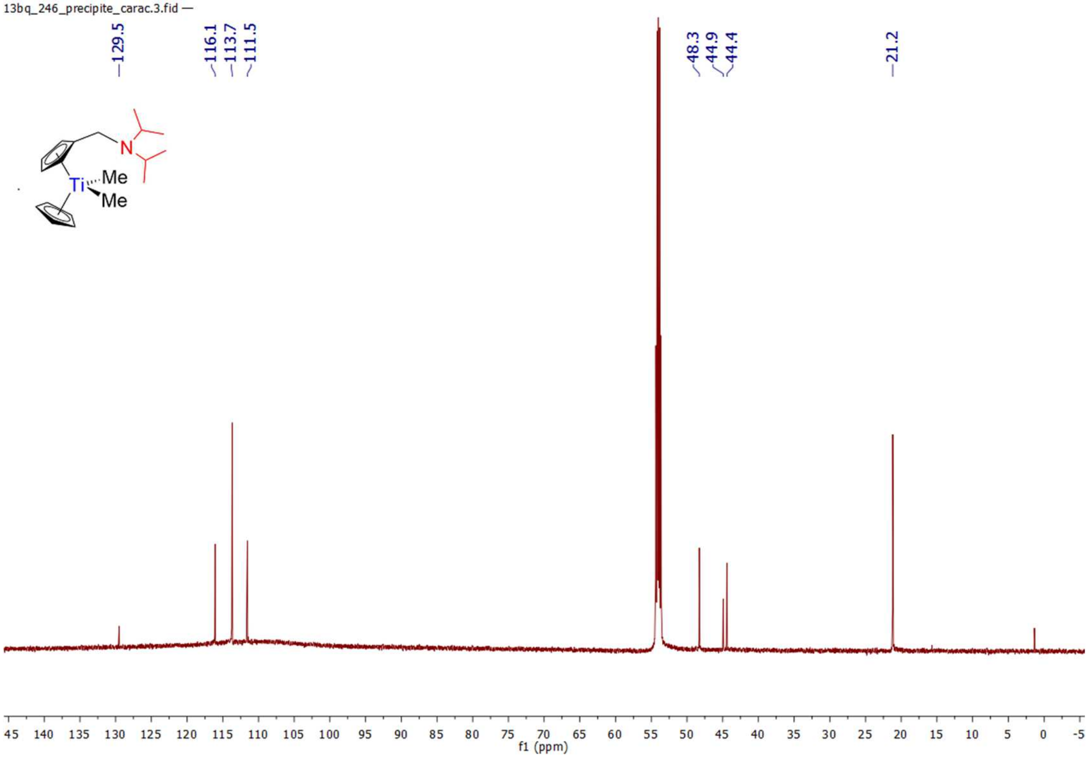


Spectrum 0-234: HRMS of 33 (Positive mode ESI, dichloromethane)

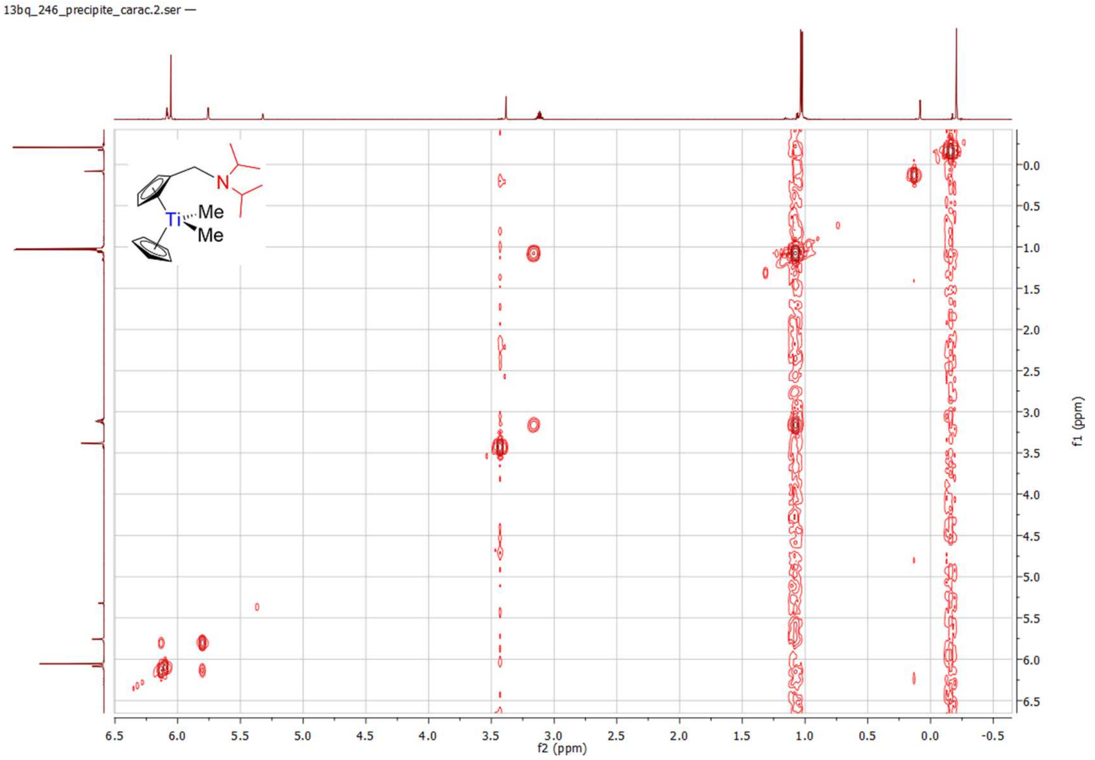
11. Compound **34:**



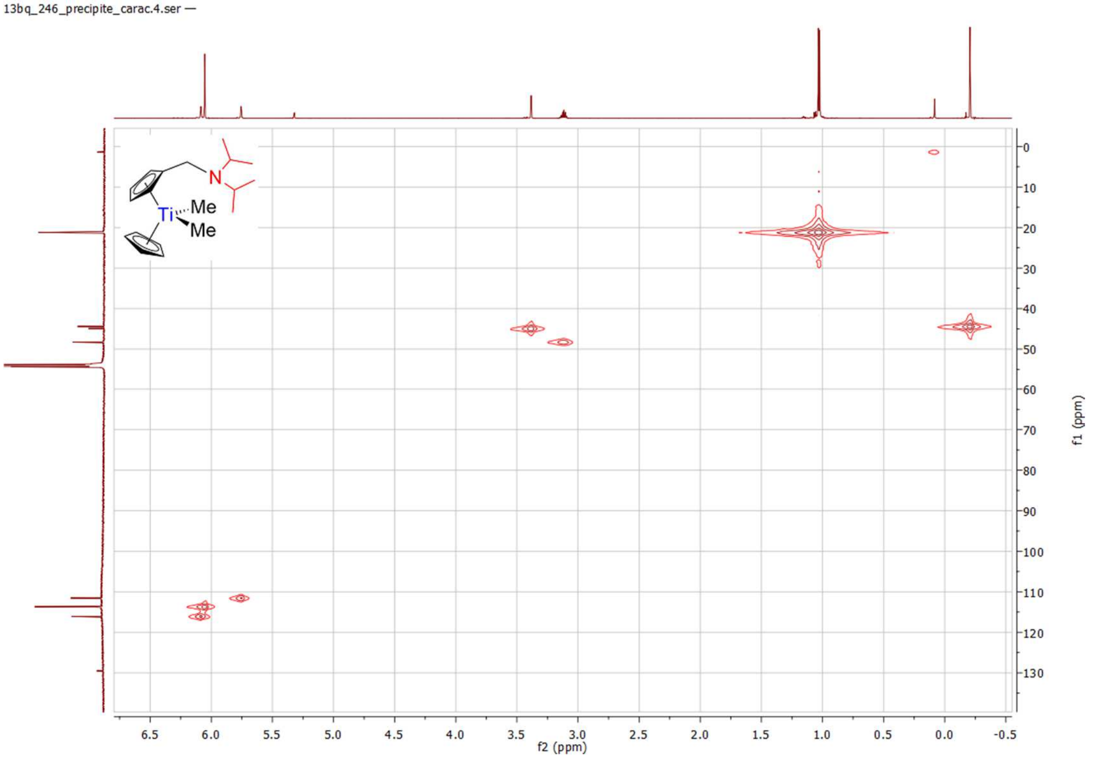
Spectrum 0-235: ^{1}H NMR of 34 (600.23 MHz, 300 K, dichloromethane-d_2)



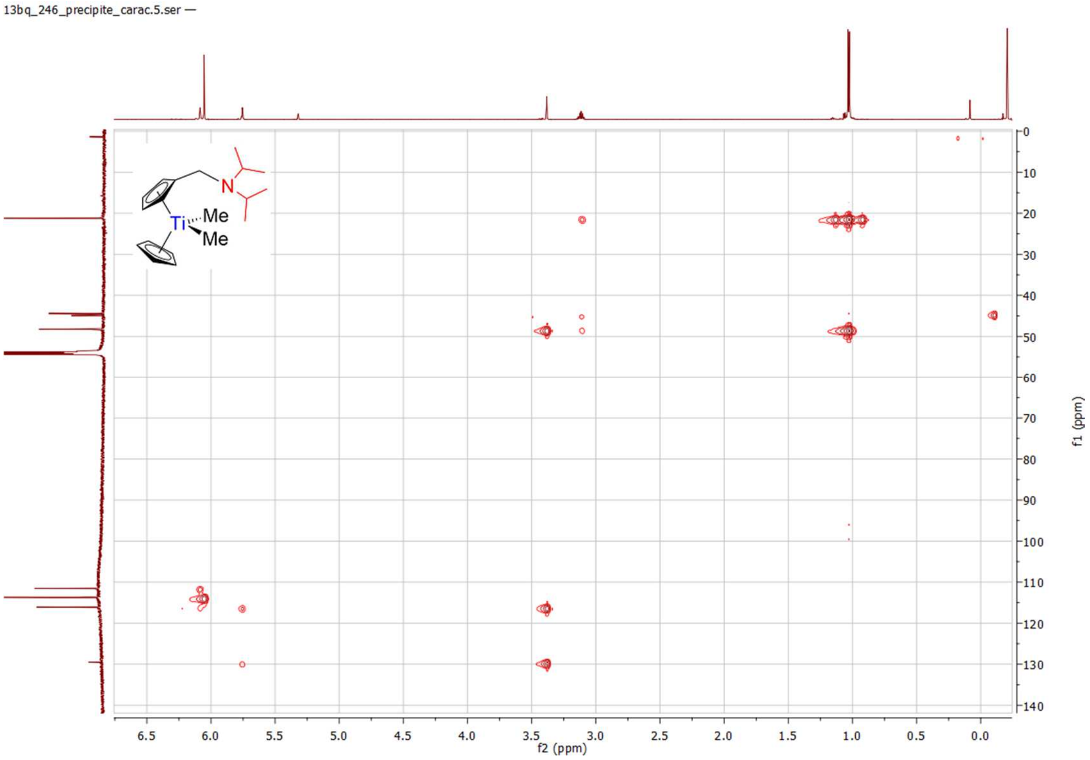
Spectrum 0-236: ^{13}C{^{1}H} NMR of 34 (150.9 MHz, 300 K, dichloromethane-d_2)



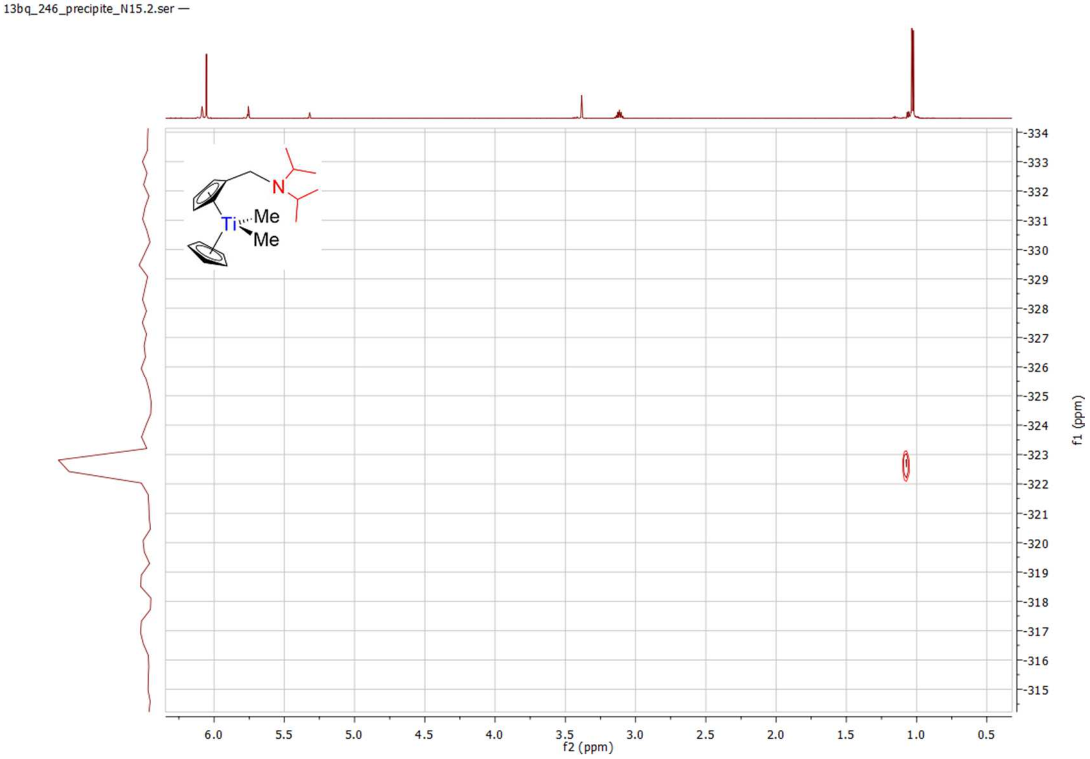
Spectrum 0-237: ^1H ^1H COSY of 34 (600.23 MHz, 300 K, dichloromethane-d_2)



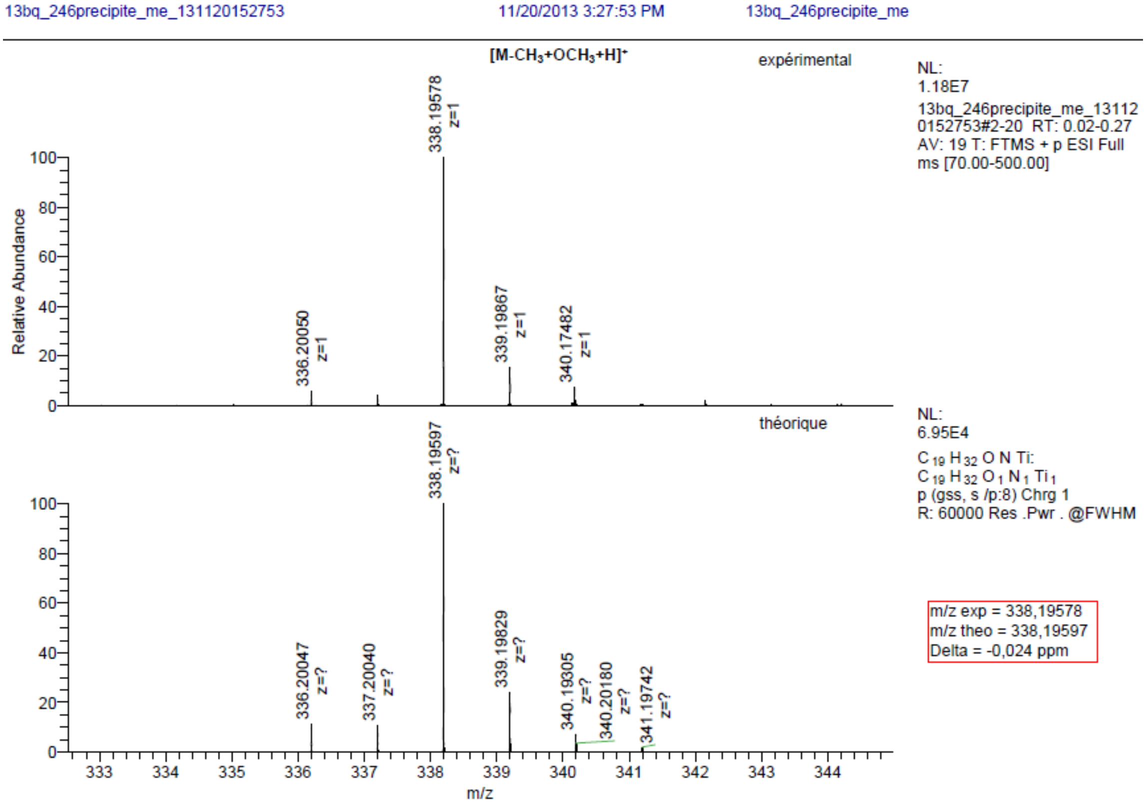
Spectrum 0-238: ^1H ^{13}C HMQC of 34 (600.23 MHz / 150.9 MHz, 300 K, dichloromethane-d_2)



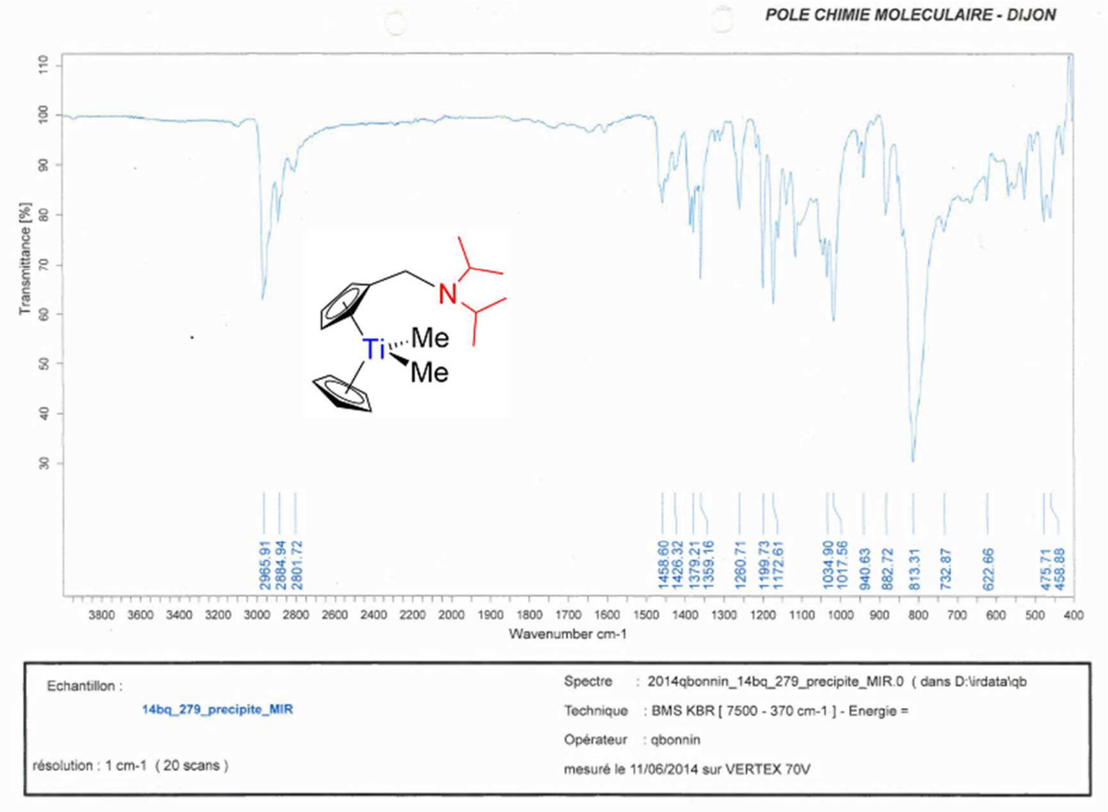
Spectrum 0-239: ^{1}H ^{13}C HMBC of 34 (600.23 MHz / 150.9 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-240: ^{1}H ^{15}N HMBC of 34 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-241: HRMS of 34 (Positive mode ESI, dichloromethane + methanol)



Echantillon : 14bq_279_precipite_MIR

résolution : 1 cm-1 (20 scans)

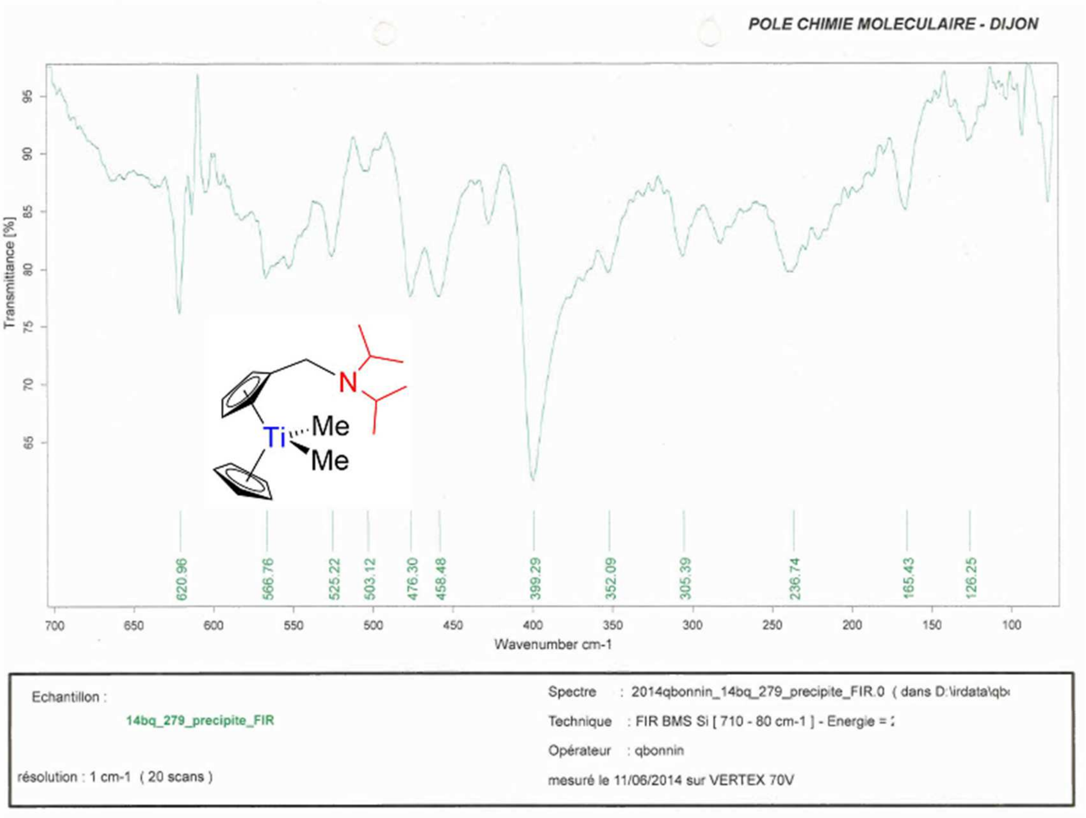
Spectre : 2014qbonnin_14bq_279_precipite_MIR.0 (dans D:\irdata\qb

Technique : BMS KBR [7500 - 370 cm-1] - Energie =

Opérateur : qbonnin

mesuré le 11/06/2014 sur VERTEX 70V

Spectrum 0-242: MIR of 34

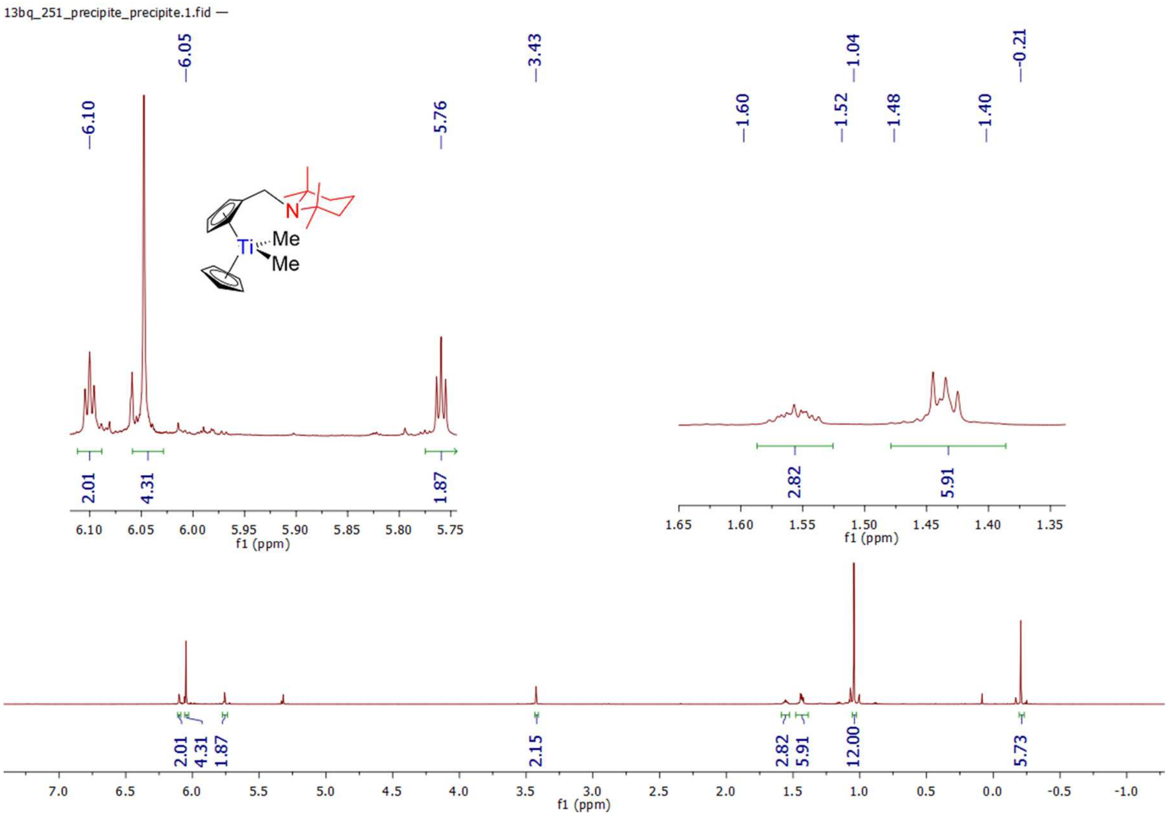


Echantillon :
14bq_279_precipite_FIR
résolution : 1 cm-1 (20 scans)

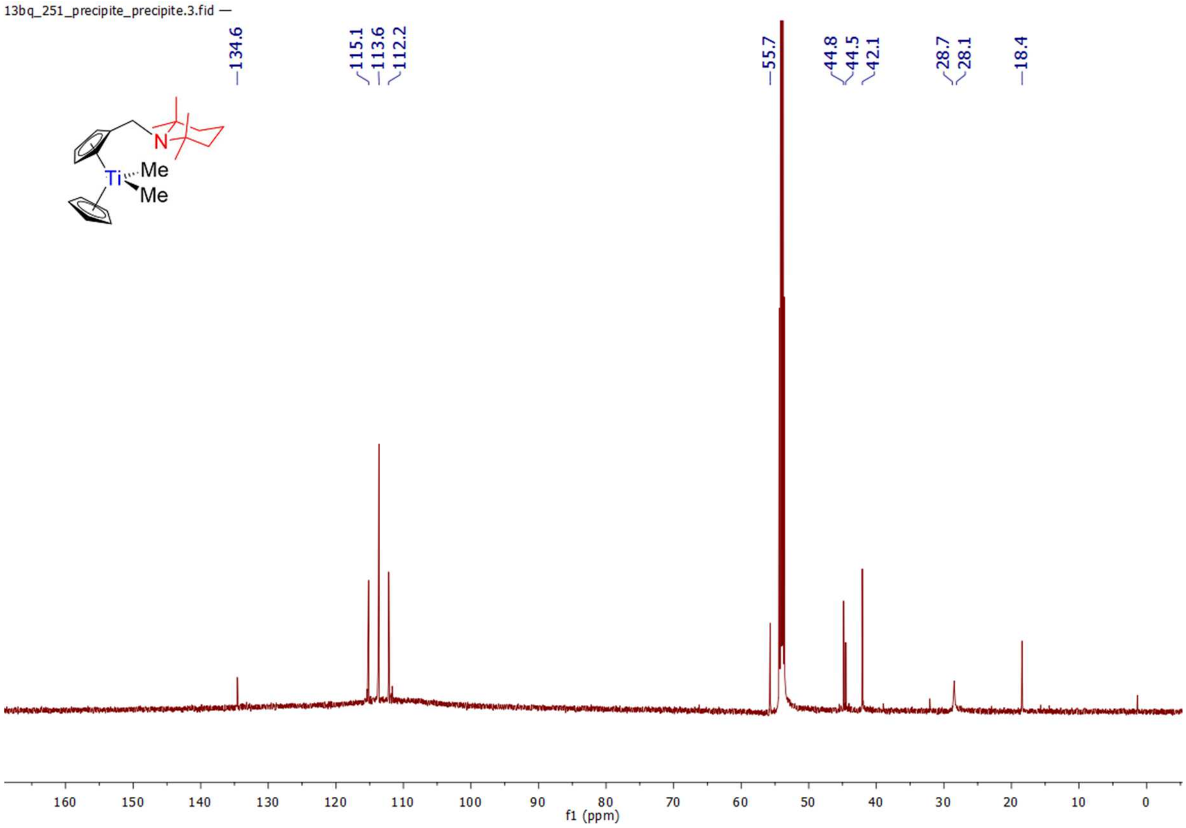
Spectre : 2014qbonnin_14bq_279_precipite_FIR.0 (dans D:\irdata\qb
Technique : FIR BMS Si [710 - 80 cm-1] - Energie =
Opérateur : qbonnin
mesuré le 11/06/2014 sur VERTEX 70V

Spectrum 0-243: FIR of 34

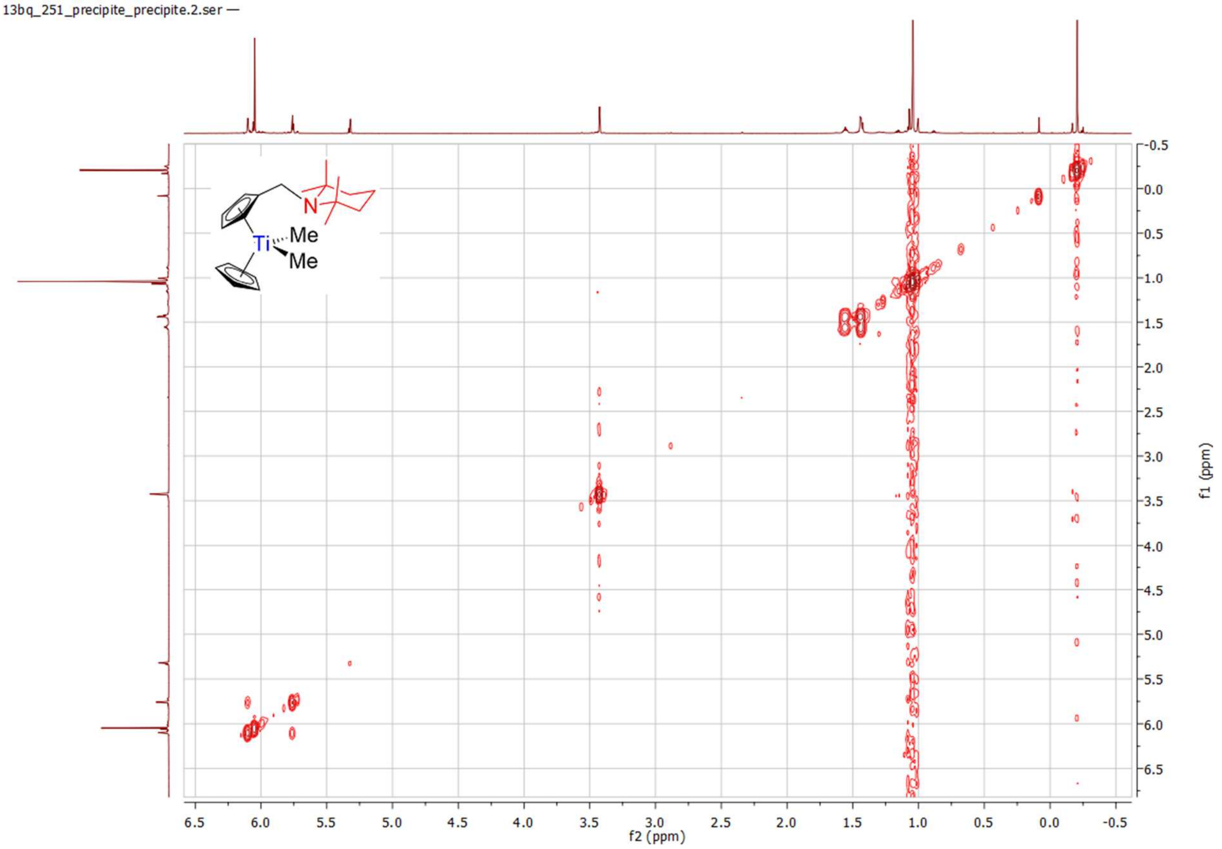
12. Compound **35**:



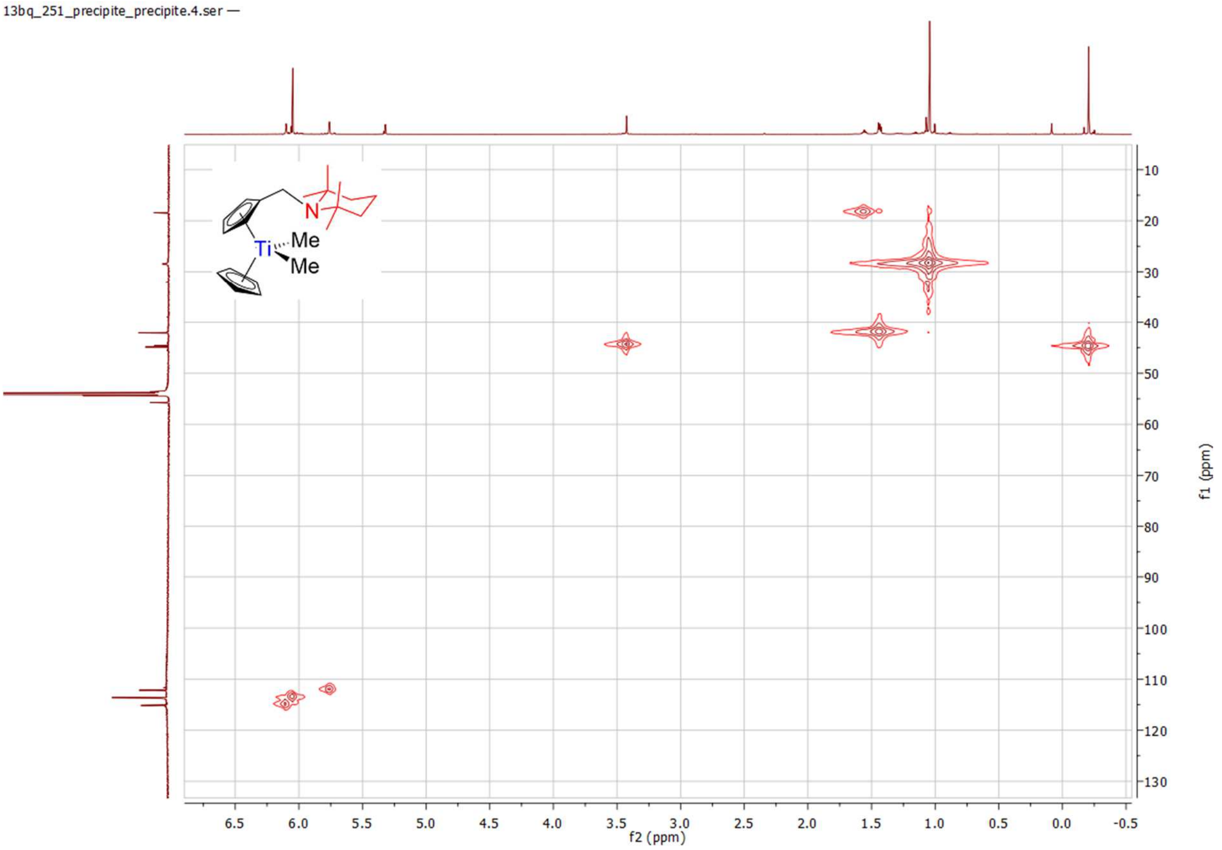
Spectrum 0-244: ^{1}H NMR of 35 (600.23 MHz, 300 K, dichloromethane-d_2)



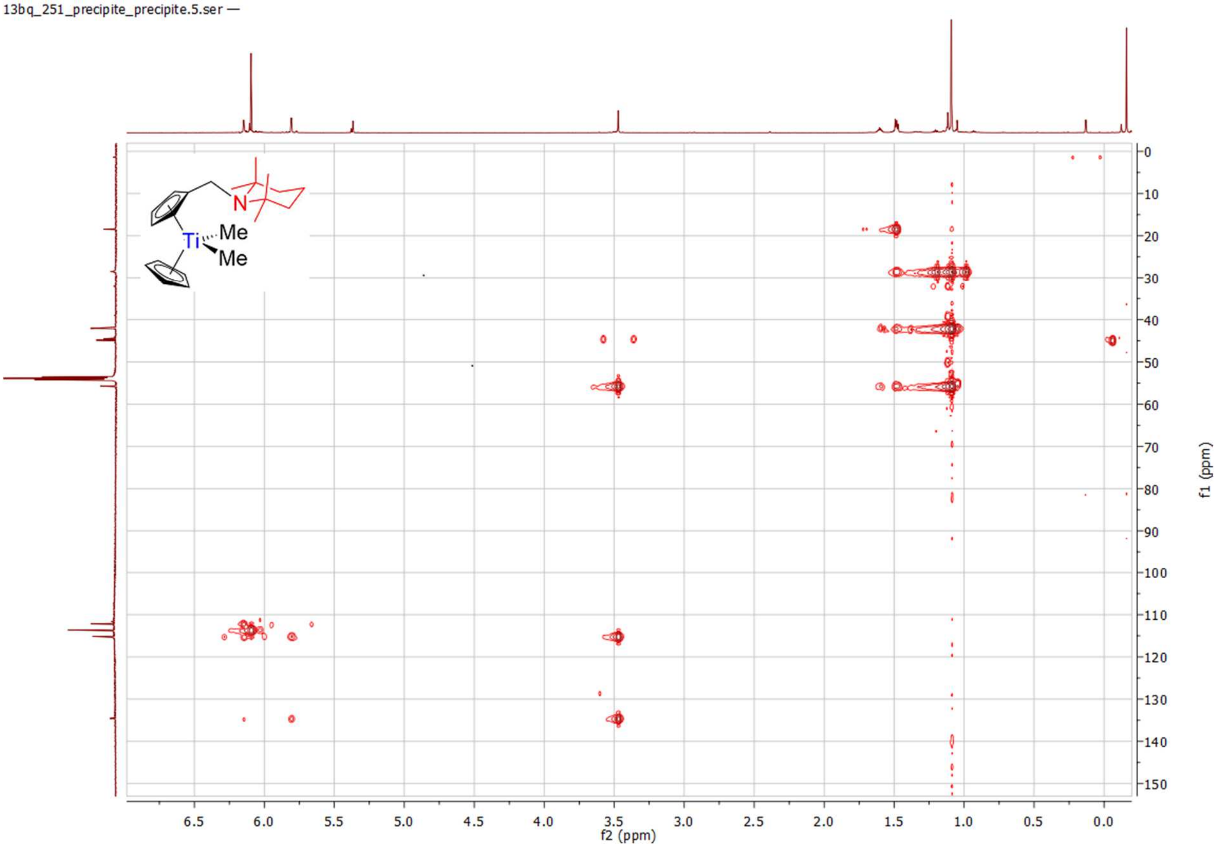
Spectrum 0-245: $^{13}C\{^1H\}$ NMR of 35 (150.9 MHz, 300 K, dichloromethane-d_2)



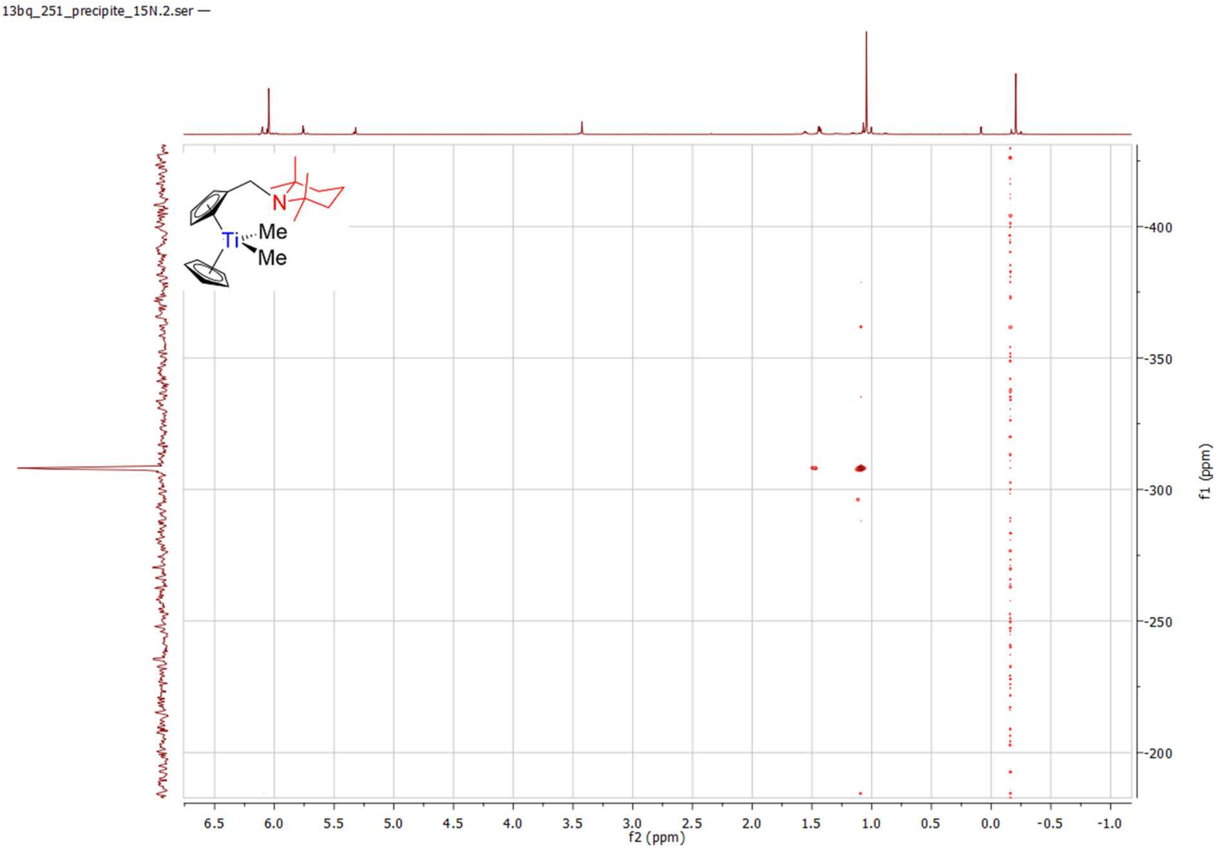
Spectrum 0-246: ^1H ^1H COSY of 35 (600.23 MHz, 300 K, dichloromethane-d_2):



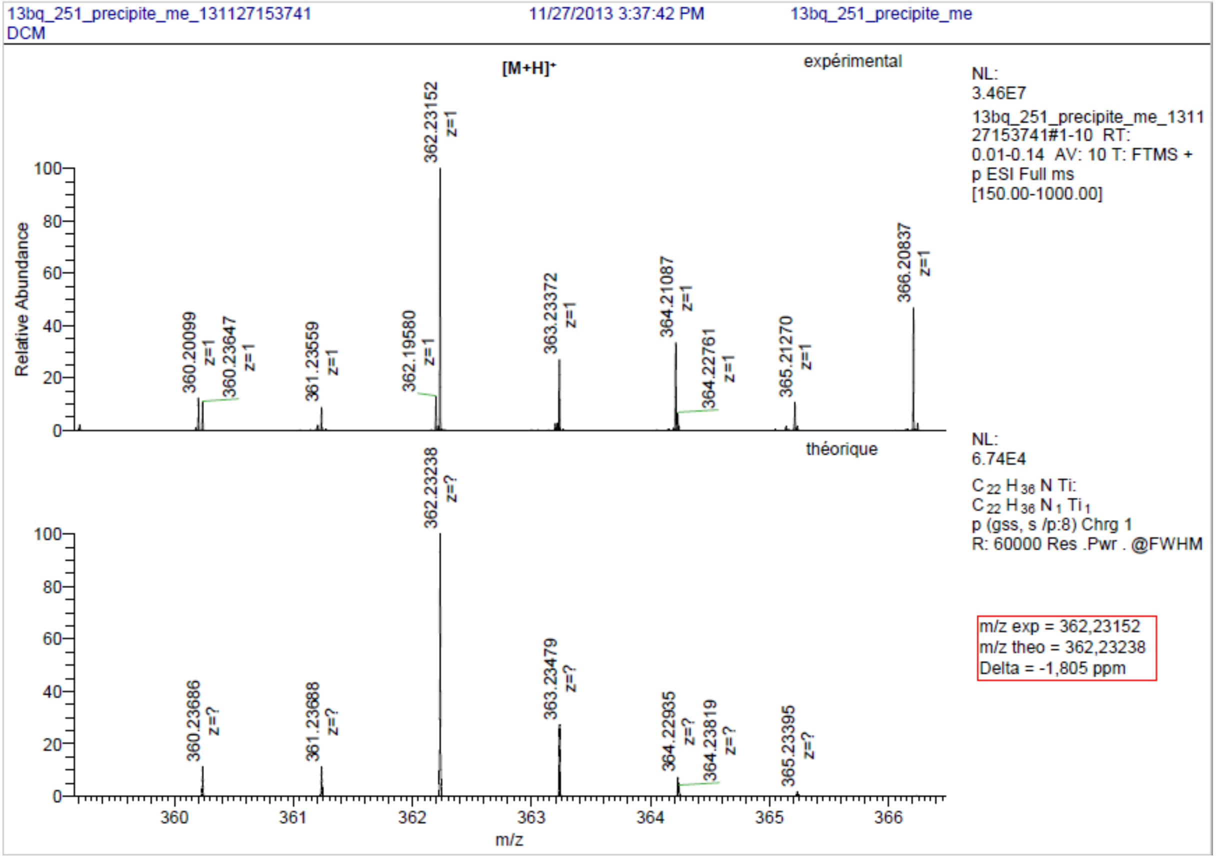
Spectrum 0-247: ^{1}H ^{13}C HMQC of 35 (600.23 MHz / 150.9 MHz, 300 K, dichloromethane-d_2)



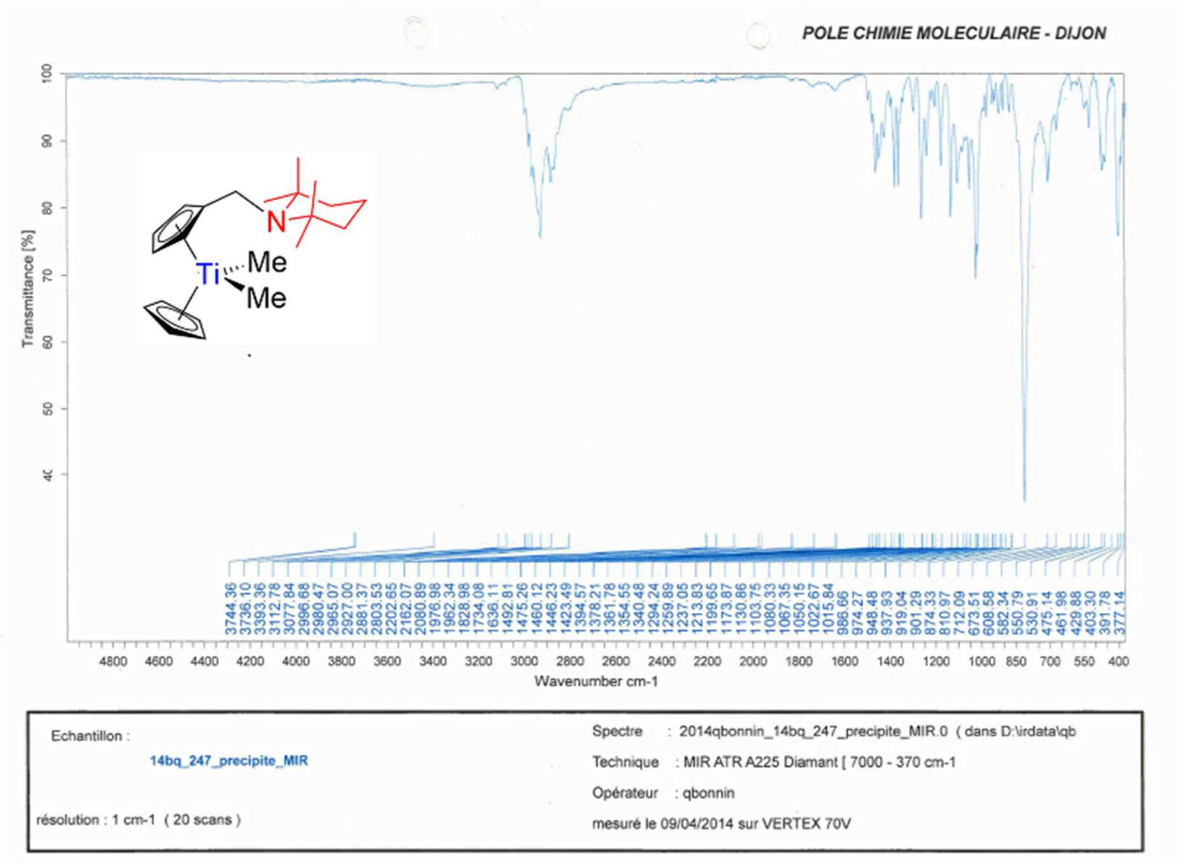
Spectrum 0-248: ^{1}H ^{13}C HMBC of 35 (600.23 MHz / 150.9 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-249: ^{1}H ^{15}N HMBC of 35 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-250: HRMS of 35 (Positive mode ESI, dichloromethane + methanol)



Echantillon :

14bq_247_precipite_MIR

résolution : 1 cm-1 (20 scans)

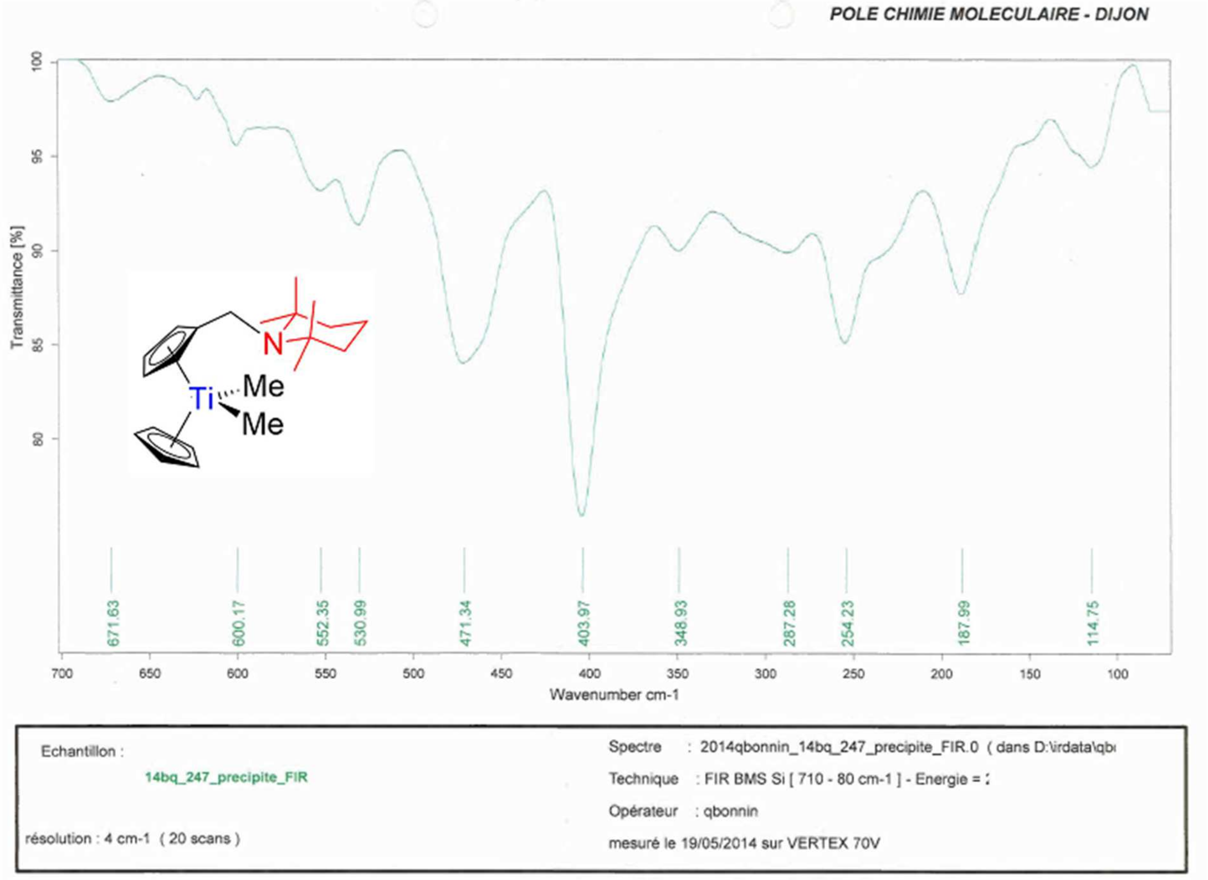
Spectre : 2014qbonnin_14bq_247_precipite_MIR.0 (dans D:\irdata\qb

Technique : MIR ATR A225 Diamant [7000 - 370 cm-1

Opérateur : qbonnin

mesuré le 09/04/2014 sur VERTEX 70V

Spectrum 0-251: MIR of 35



Echantillon :

14bq_247_precipite_FIR

résolution : 4 cm-1 (20 scans)

Spectre : 2014qbonnin_14bq_247_precipite_FIR.0 (dans D:\irdata\qb

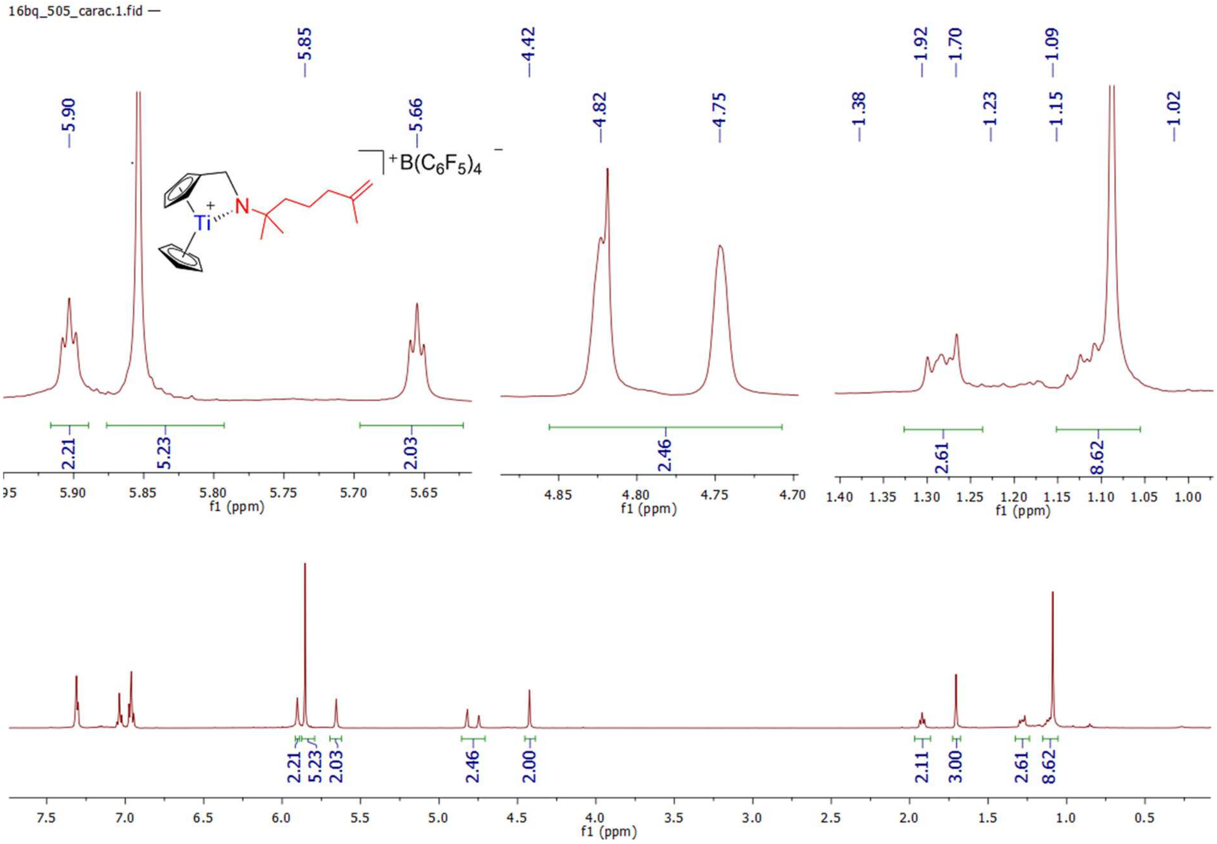
Technique : FIR BMS Si [710 - 80 cm-1] - Energie =

Opérateur : qbonnin

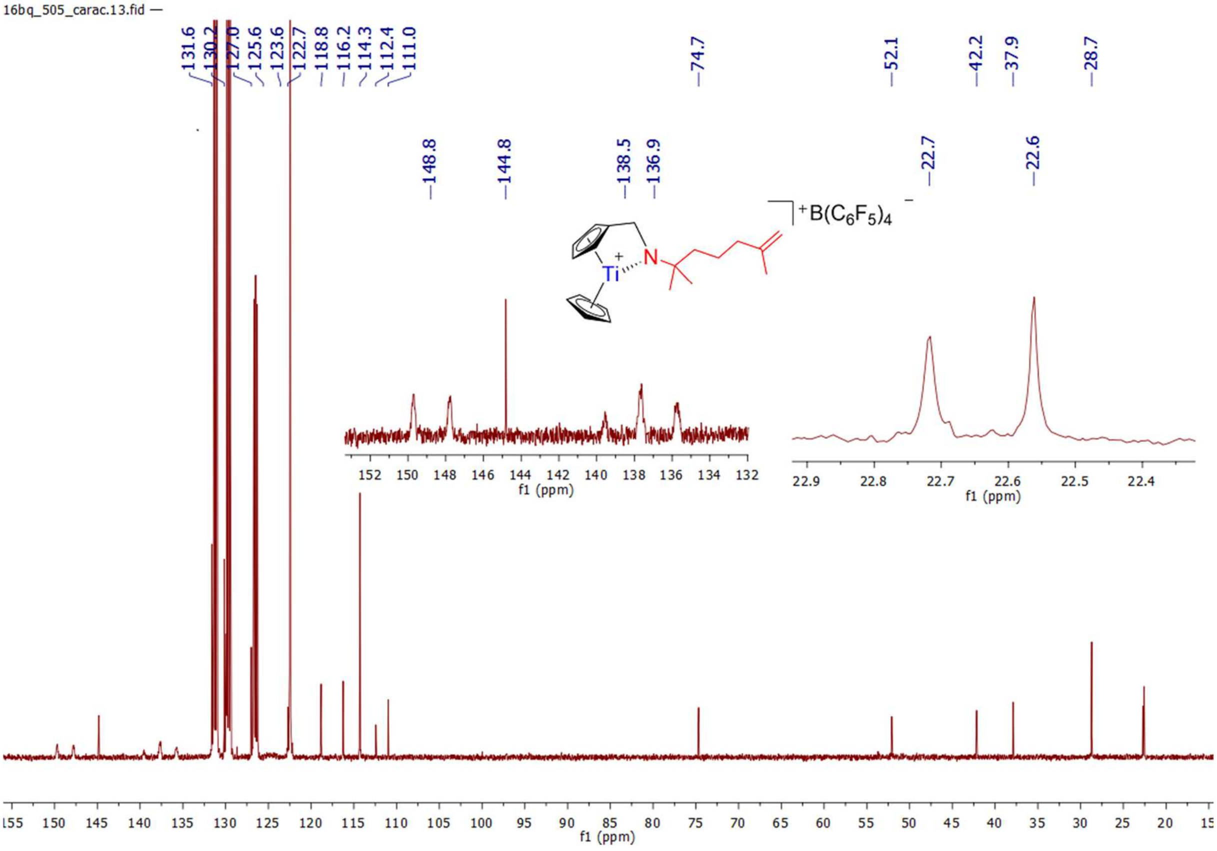
mesuré le 19/05/2014 sur VERTEX 70V

Spectrum 0-252: FIIR of 35

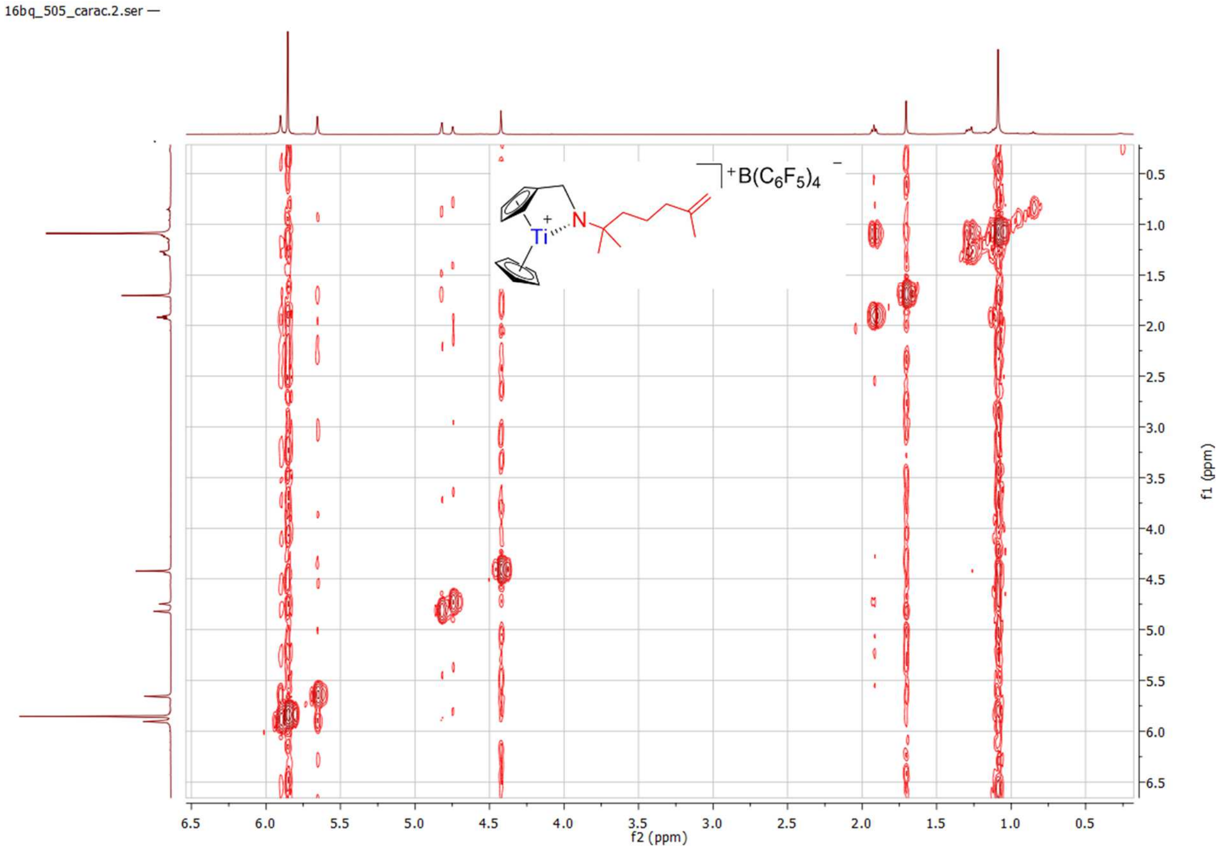
13. Compound **36**:



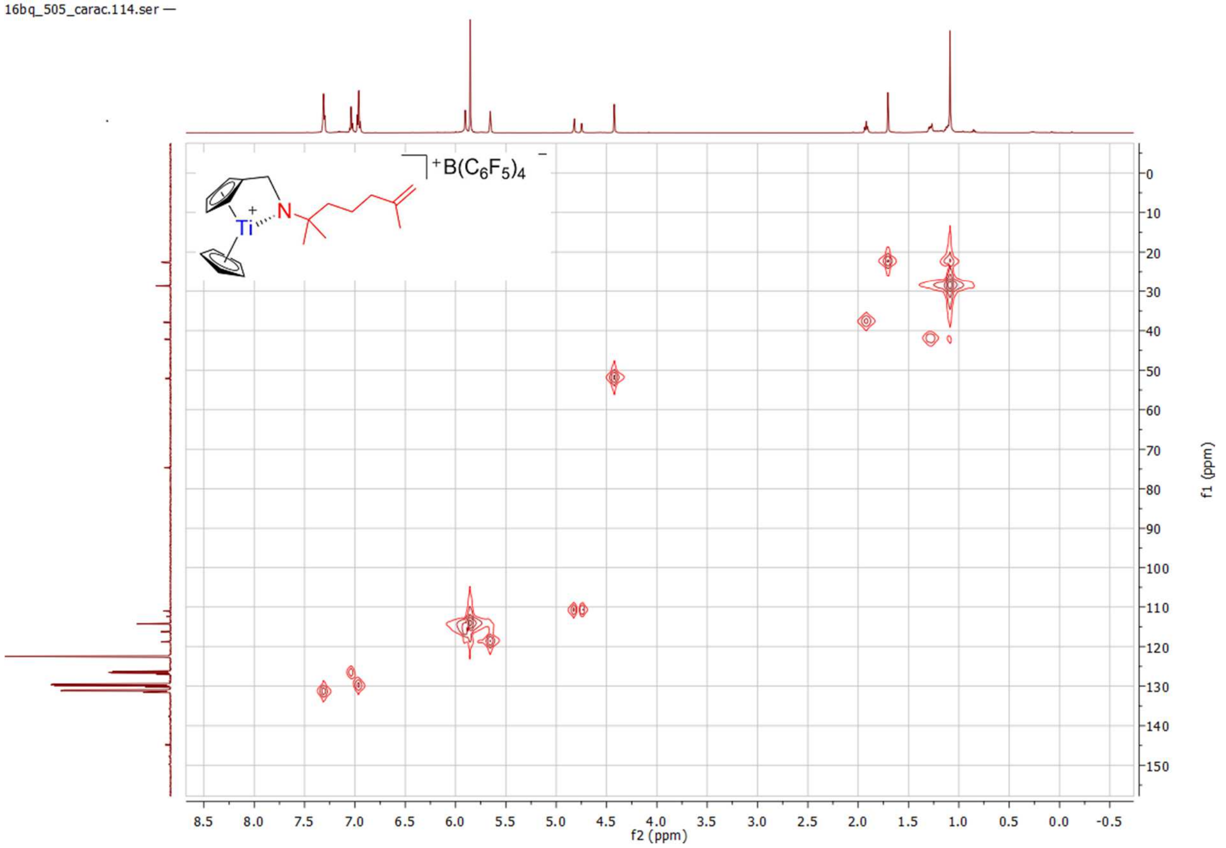
Spectrum 0-253: ^{1}H NMR of 36 (500.03 MHz, 300 K, bromobenzene-d_5)



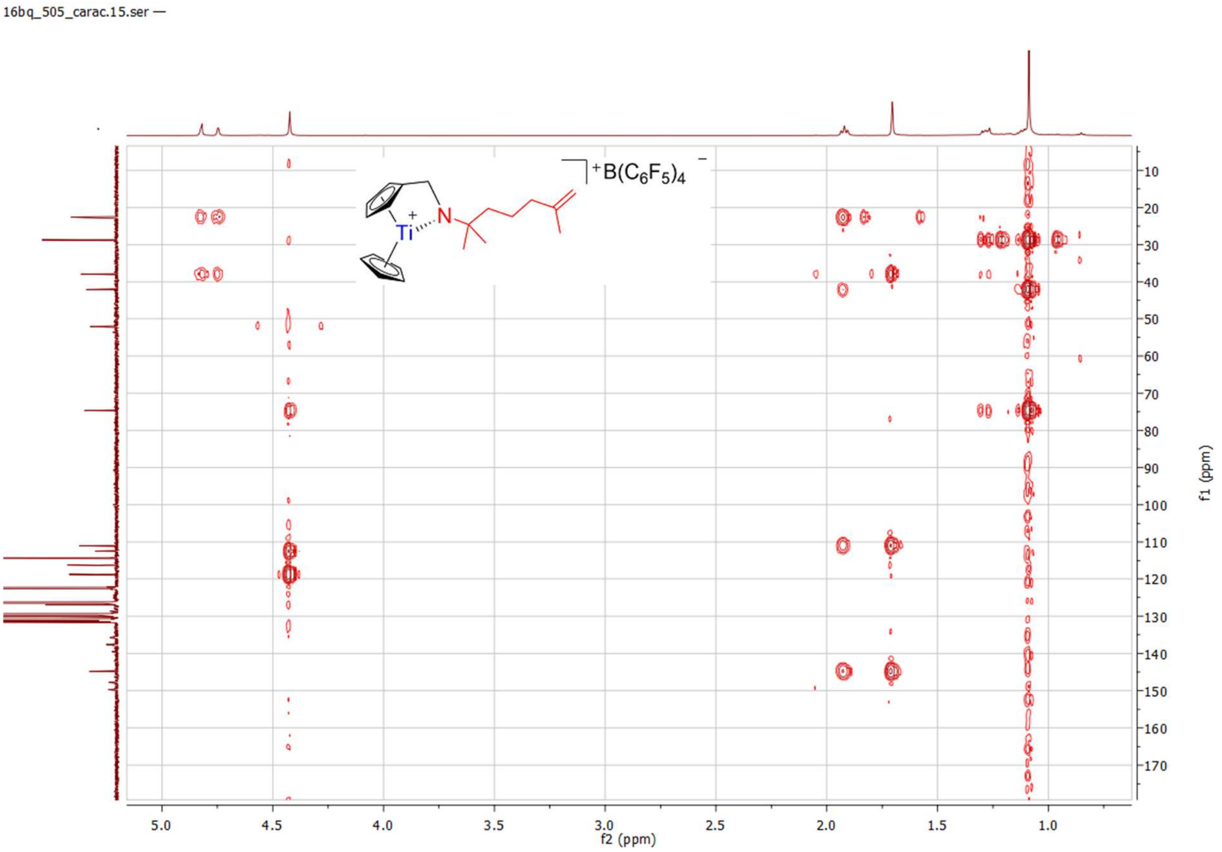
Spectrum 0-254: ^{13}C{^{1}H} NMR of 36 (125.75 MHz, 300 K, bromobenzene-d_5)



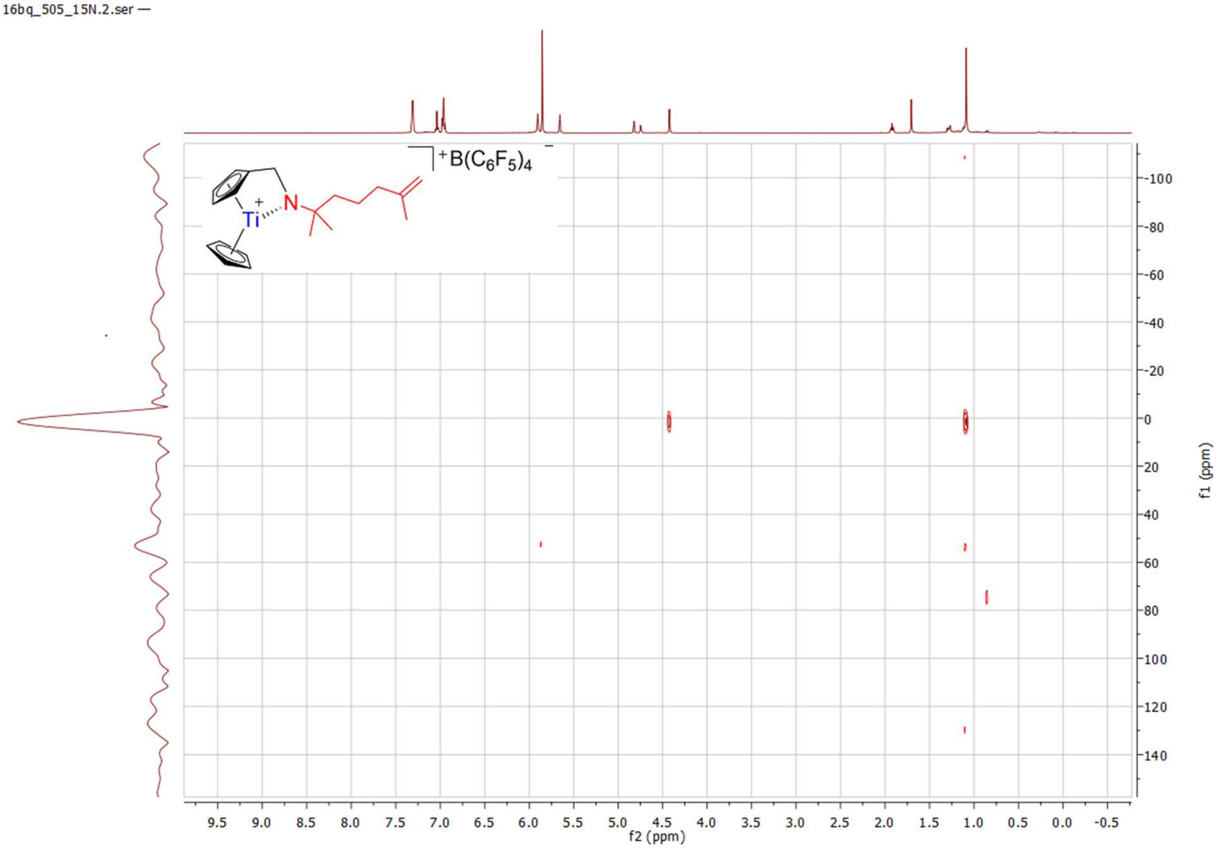
Spectrum 0-255: ^{1}H ^{1}H COSY of 36 (500.03 MHz, 300 K, bromobenzene-d_5)



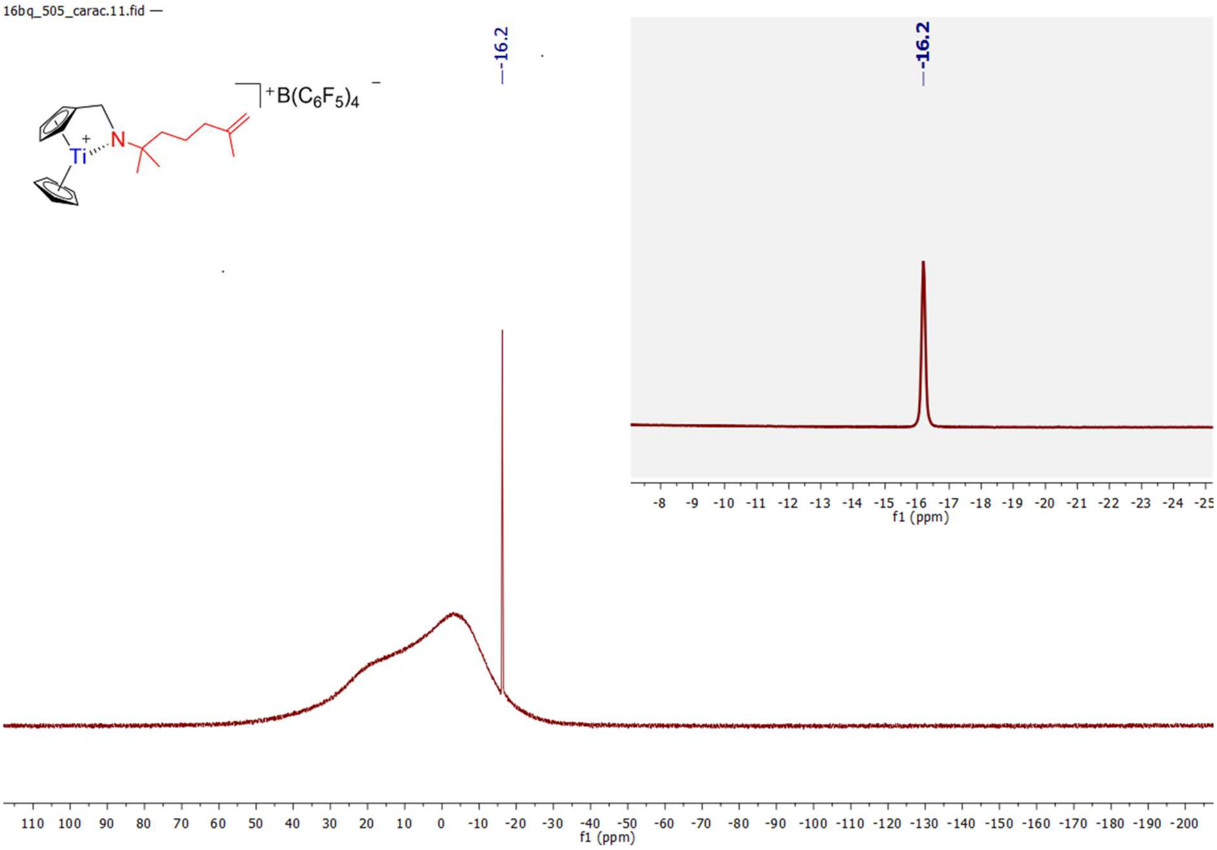
Spectrum 0-256: ^{1}H ^{13}C HMQC of 36 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d_5)



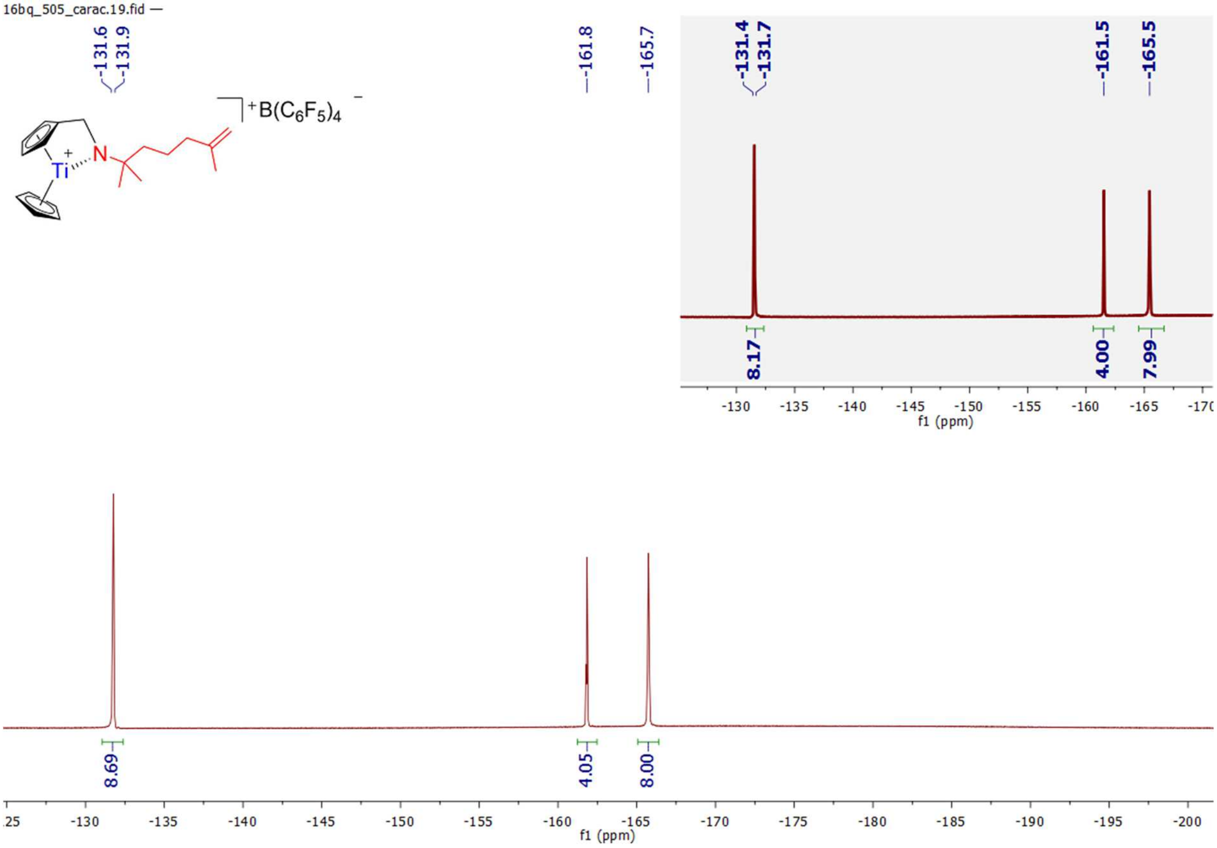
Spectrum 0-257: ^{1}H ^{13}C HMBC of 36 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



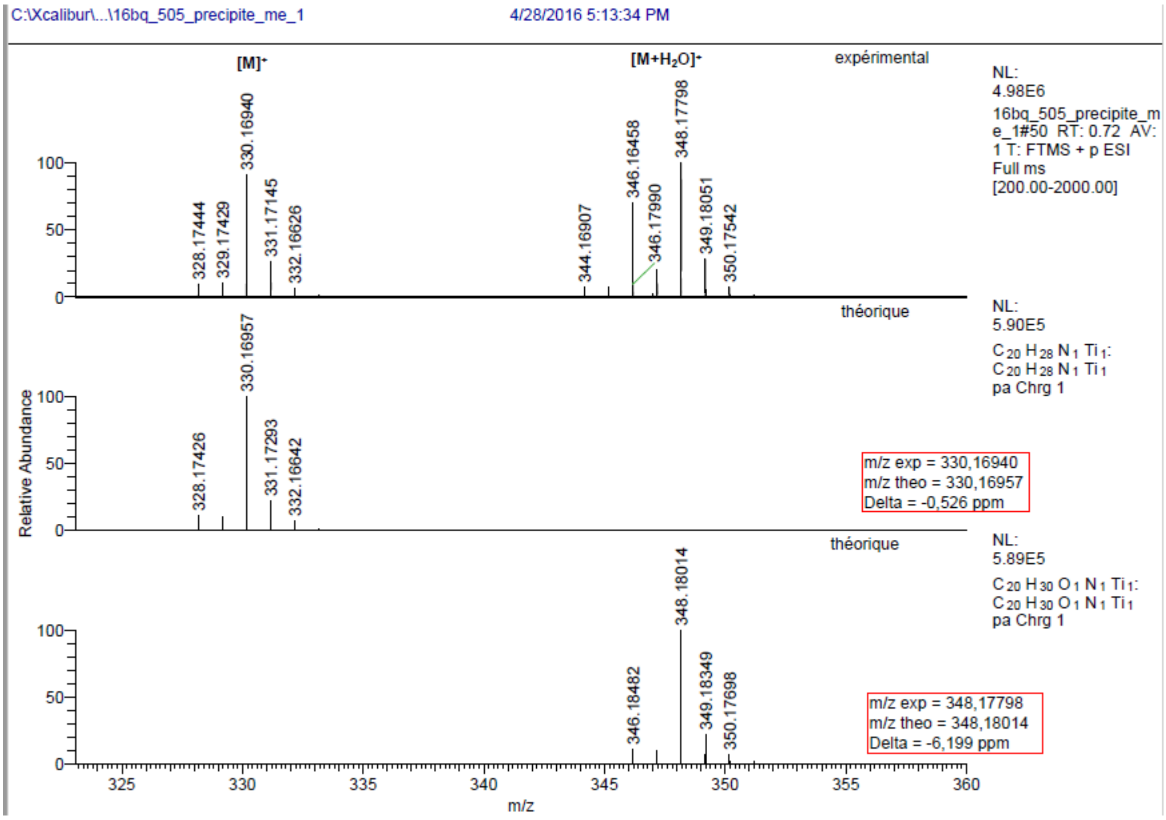
Spectrum 0-258: ^{1}H ^{15}N HMBC of 36 (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-259: $^{11}B\{^{1}H\}$ and ^{11}B (opacified) NMR of 36 (160.42 MHz, 300 K, bromobenzene-d5)

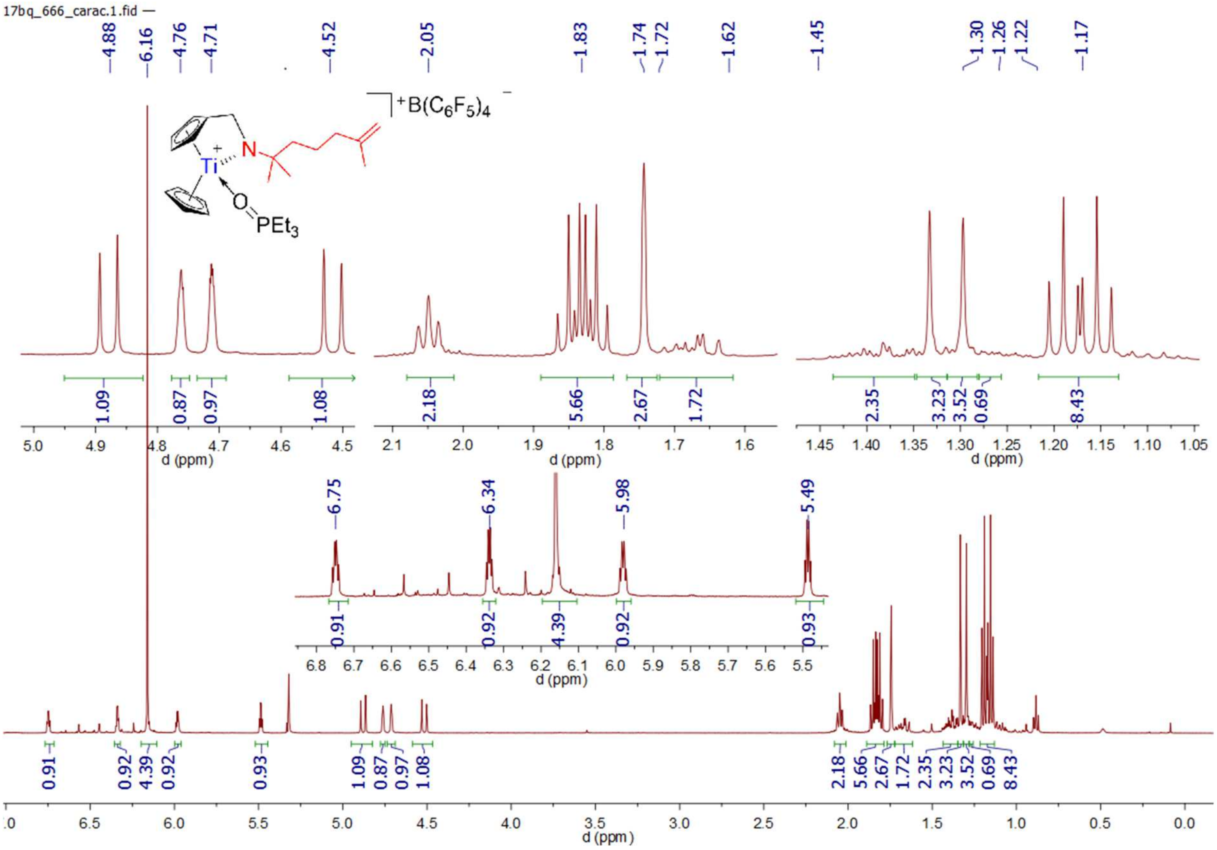


Spectrum 0-260: $^{19}F\{^{1}H\}$ and ^{19}F(opacified) NMR of 36 (470.45 MHz, 300 K, bromobenzene-d5)

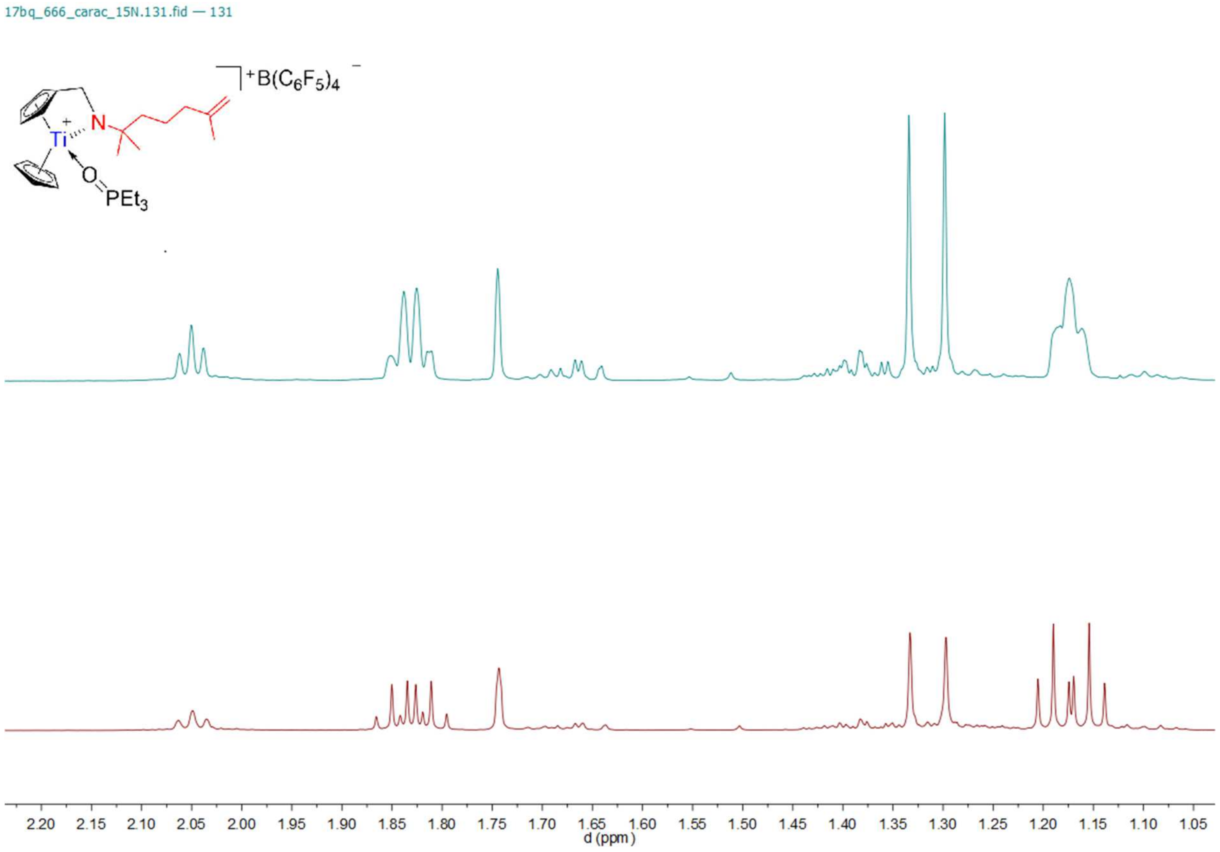


Spectrum 0-261: HRMS of 36 (Positive mode ESI, bromobenzene)

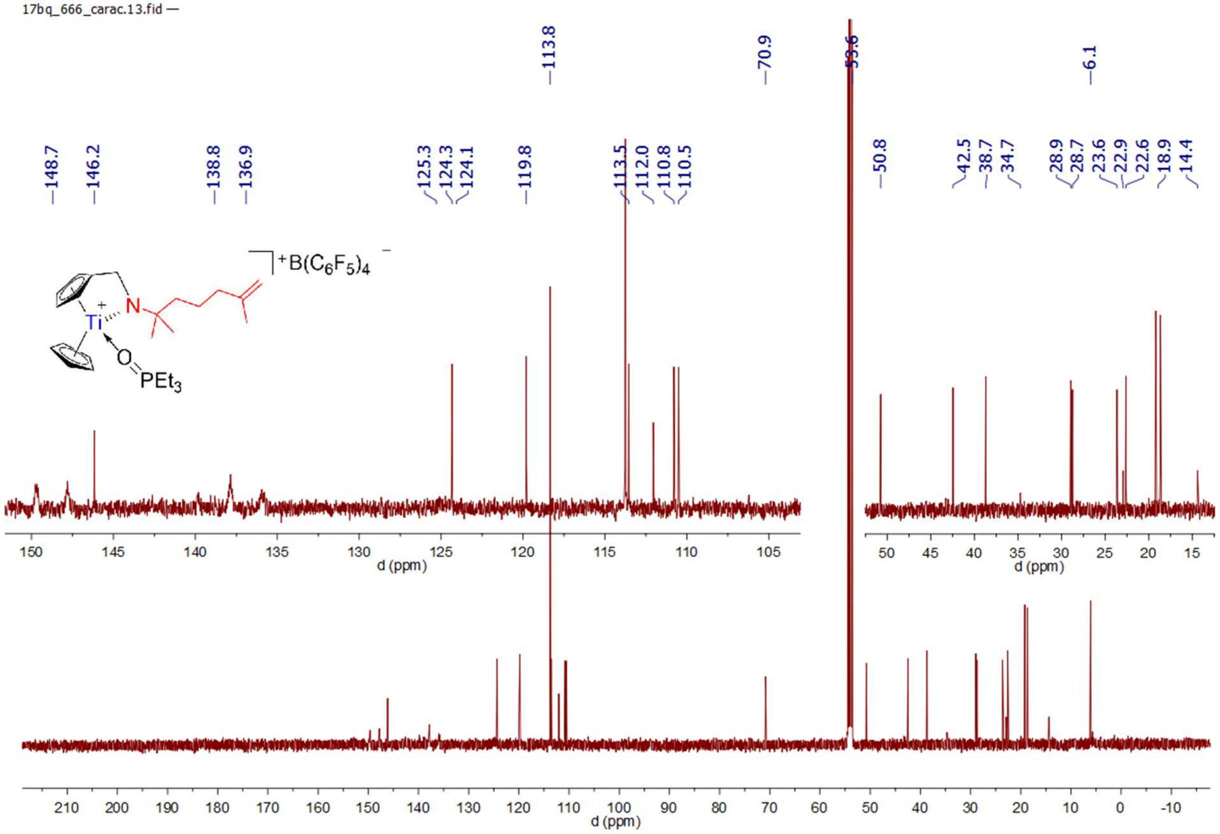
14. Compound **37**:



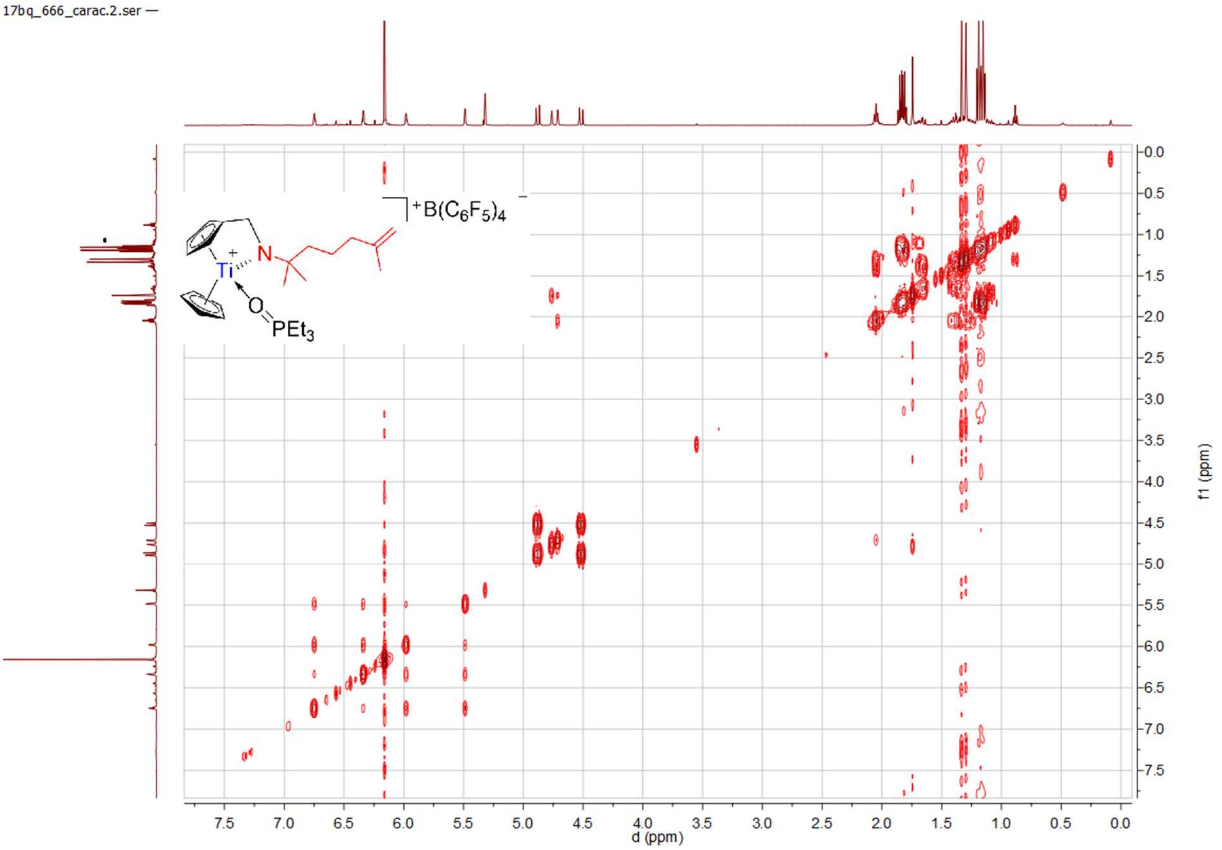
Spectrum 0-262: ^{1}H NMR of 37 (500.03 MHz, 300 K, dichloromethane-d$_2$)



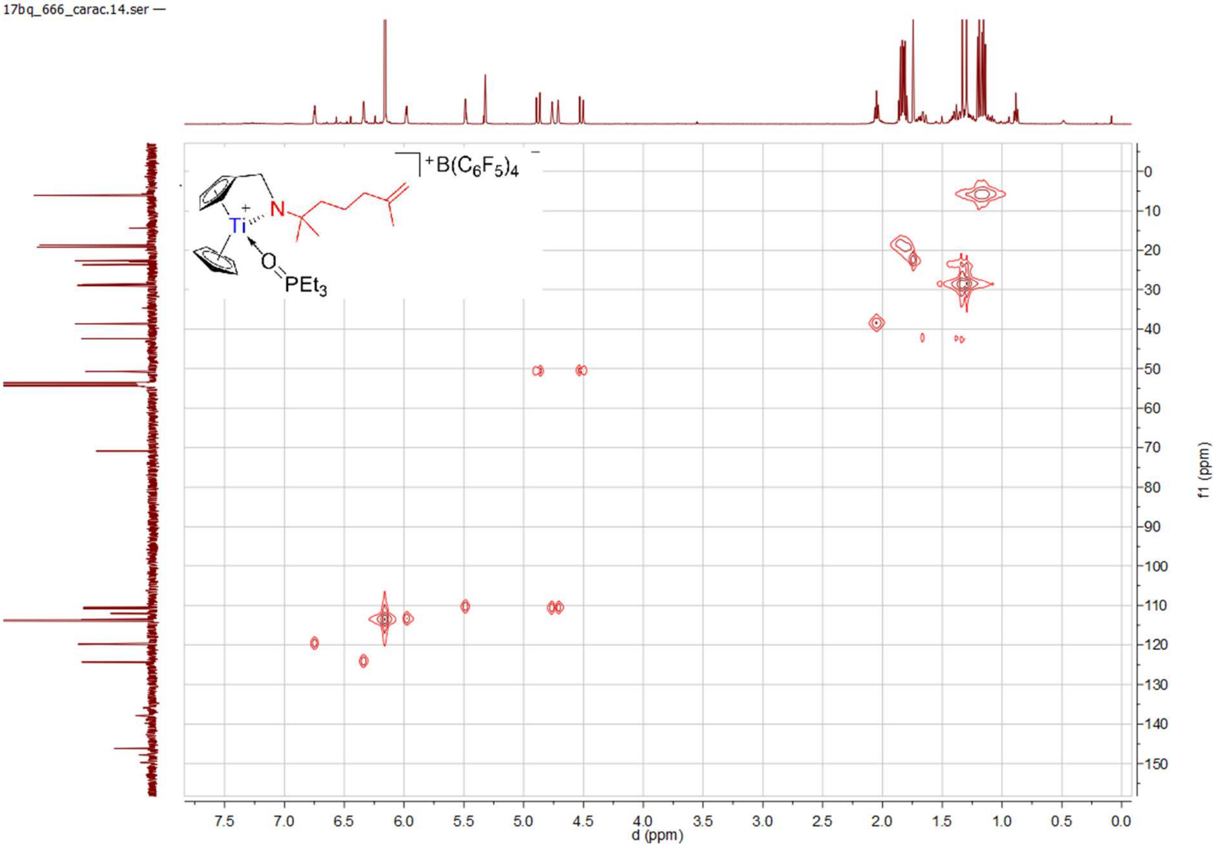
Spectrum 0-263: Superposition of ^{1}H NMR spectrum (bottom) and ^{1}H{^{31}P} spectrum (top) of 37



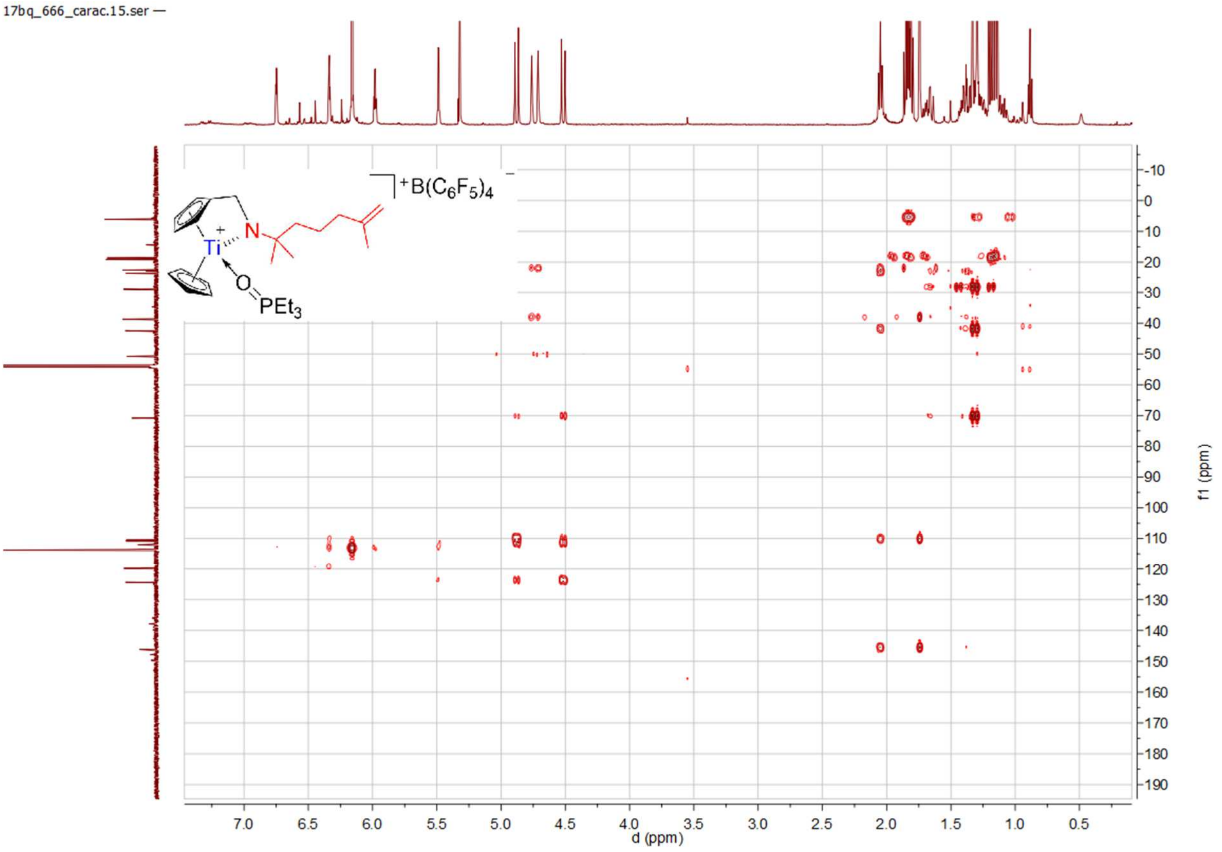
Spectrum 0-264: ^{13}C{^{1}H} NMR of 37 (125.75 MHz, 300 K, dichloromethane-d_2)



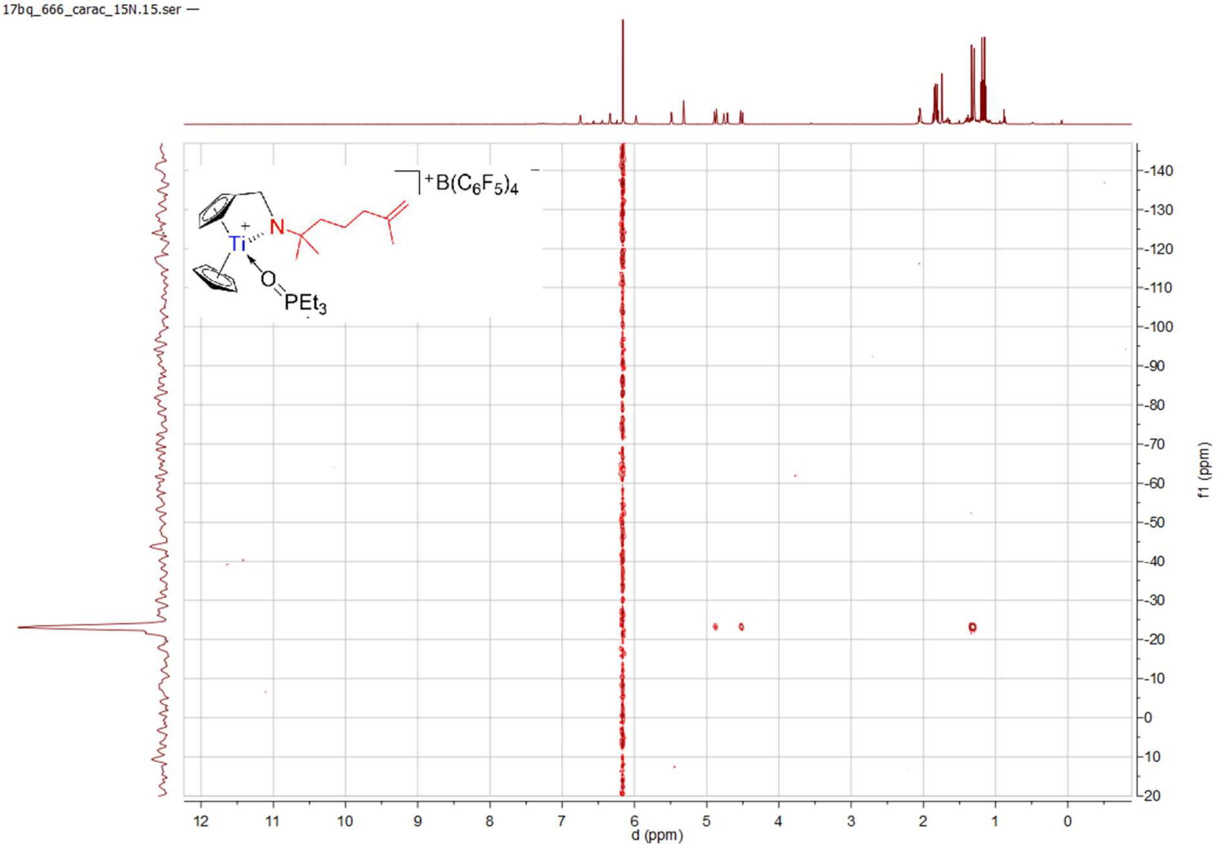
Spectrum 0-265: ^1H ^1H COSY of 37 (500.03 MHz, 300 K, dichloromethane-d_2)



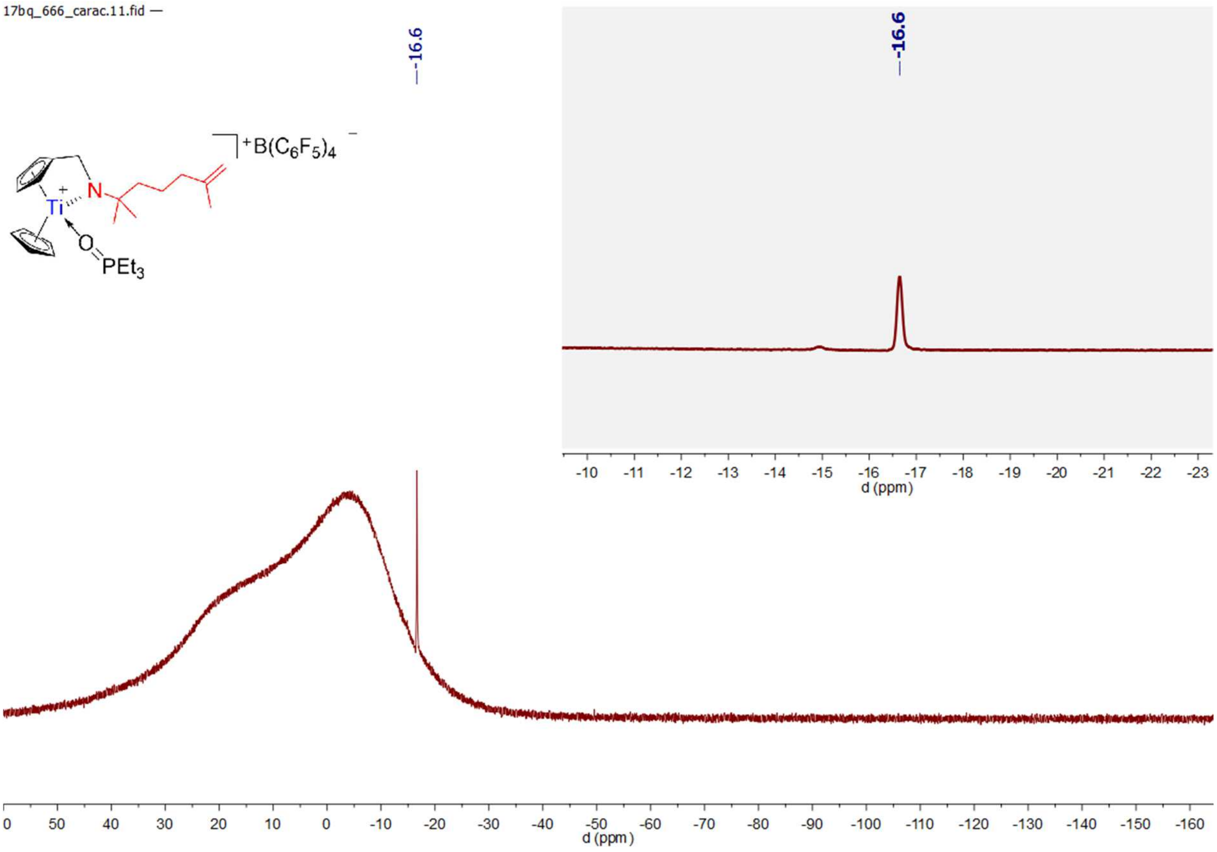
Spectrum 0-266: ^1H ^{13}C HMBC of 37 (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d_2)



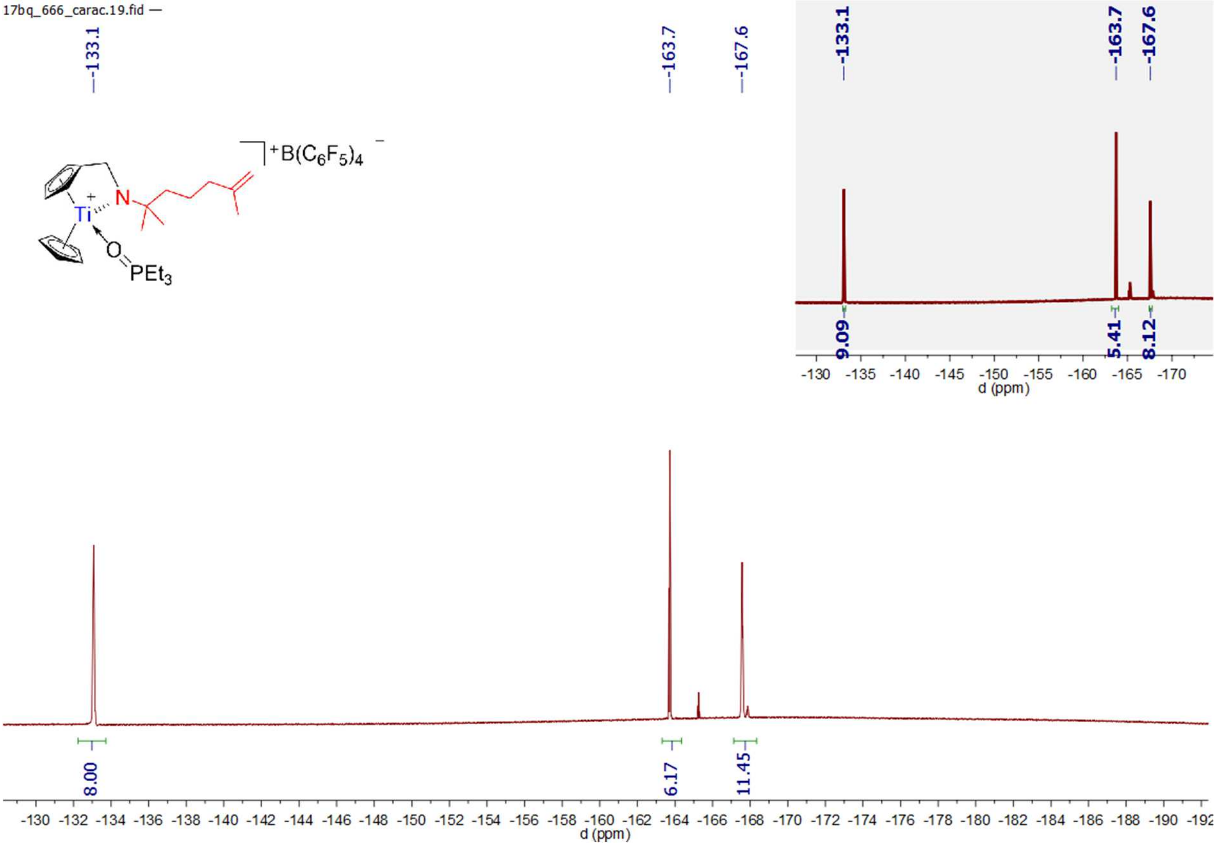
Spectrum 0-267: ^{1}H ^{13}C HMBC of 37 (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$)



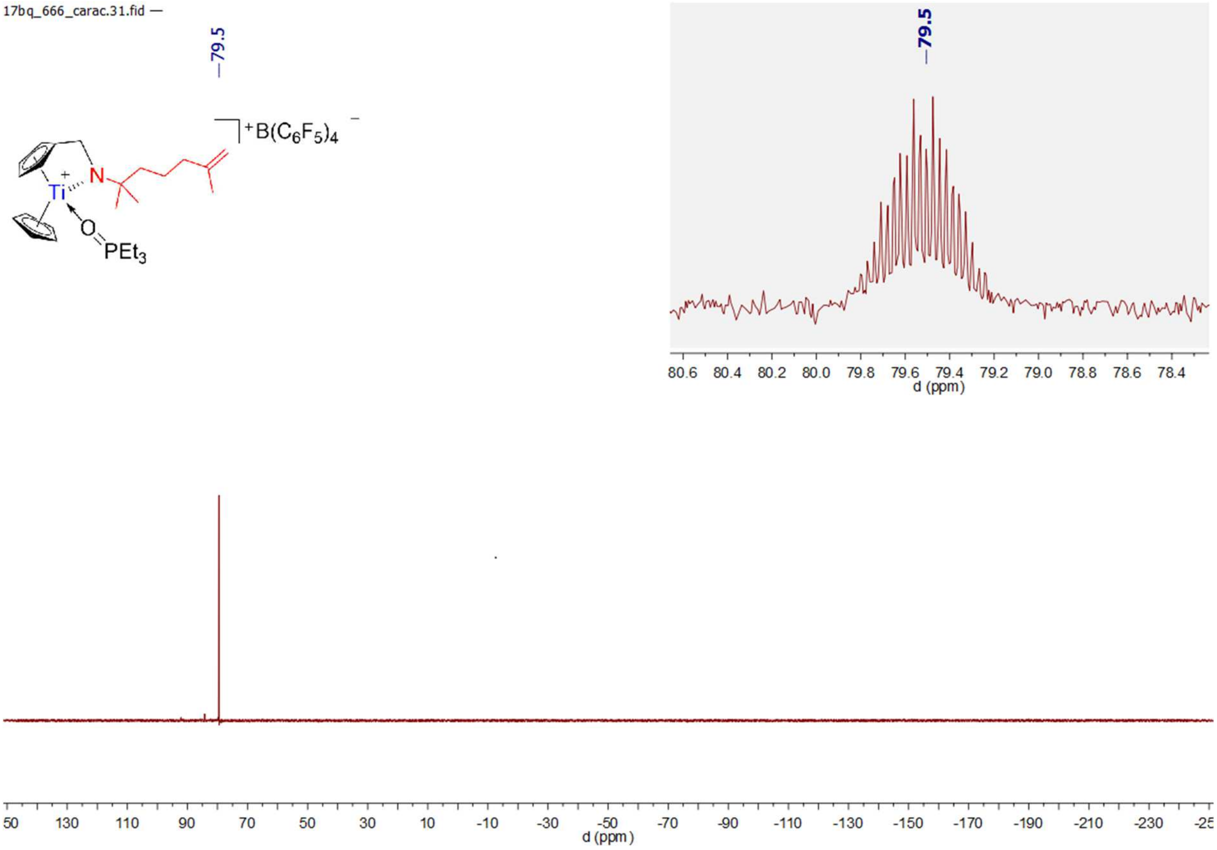
Spectrum 0-268: ^{1}H ^{15}N HMBC of 37 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)



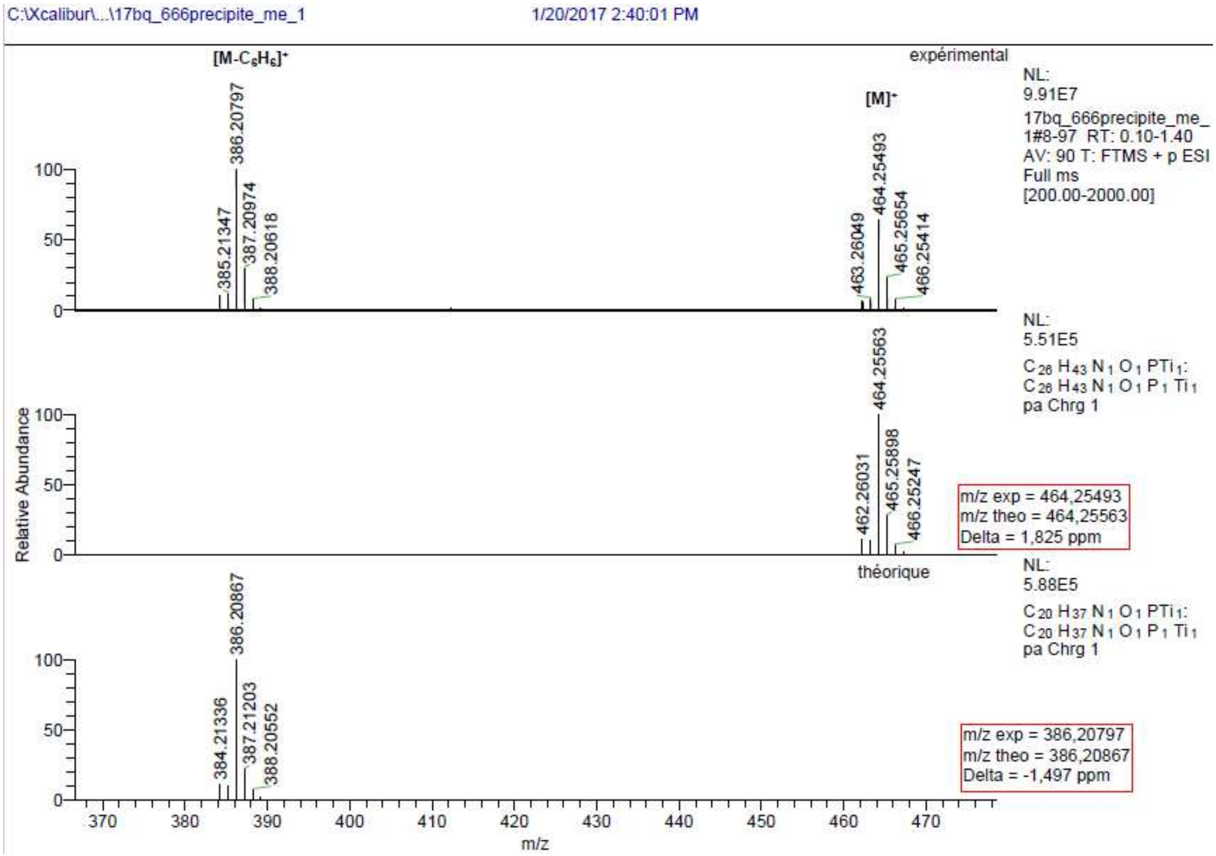
Spectrum 0-269: $^{11}B\{^1H\}$ NMR and ^{11}B (opacified) of 37 (160.42 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-270: $^{19}F\{^1H\}$ NMR and ^{19}F (opacified) of 37 (470.45 MHz, 300 K, dichloromethane-d_2)

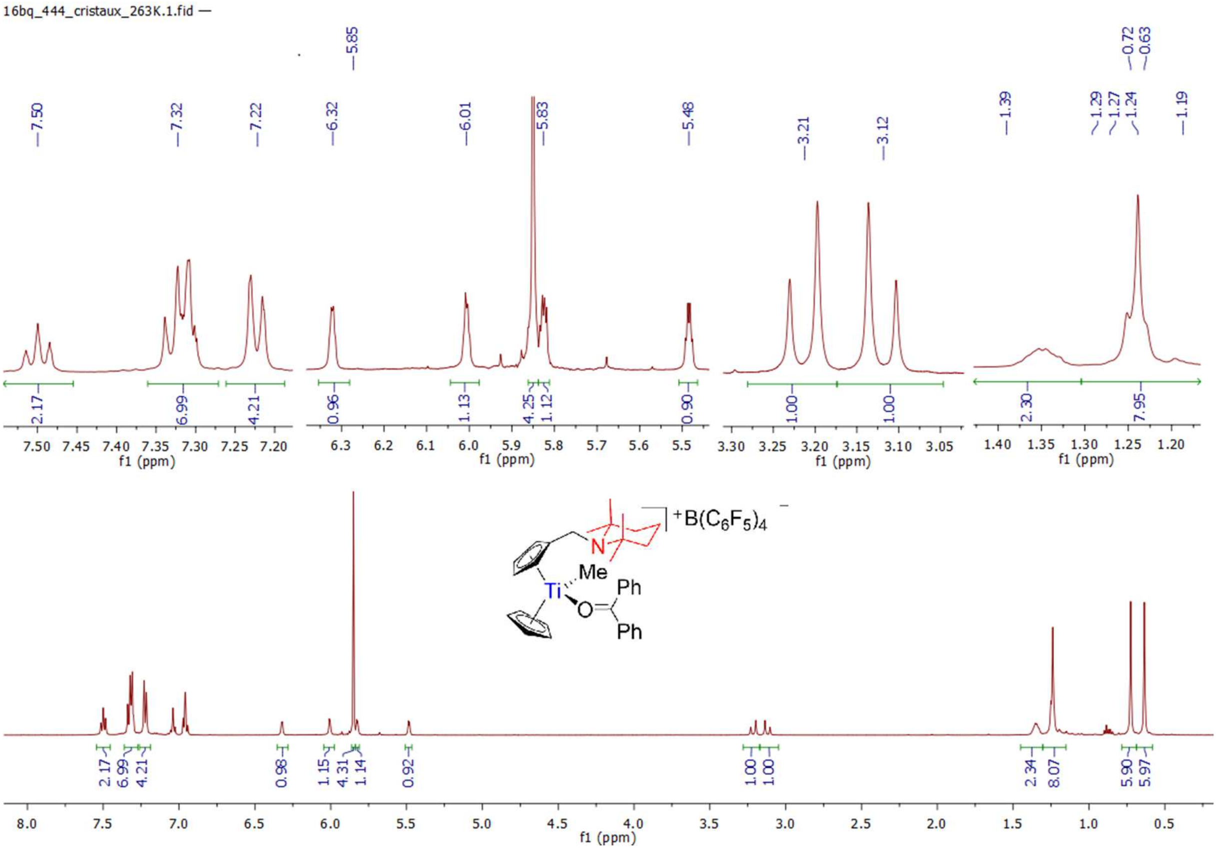


Spectrum 0-271: $^{31}P\{^{1}H\}$ NMR and ^{31}P (opacified) of 37 (202.46 MHz, 300 K, dichloromethane-d$_2$)

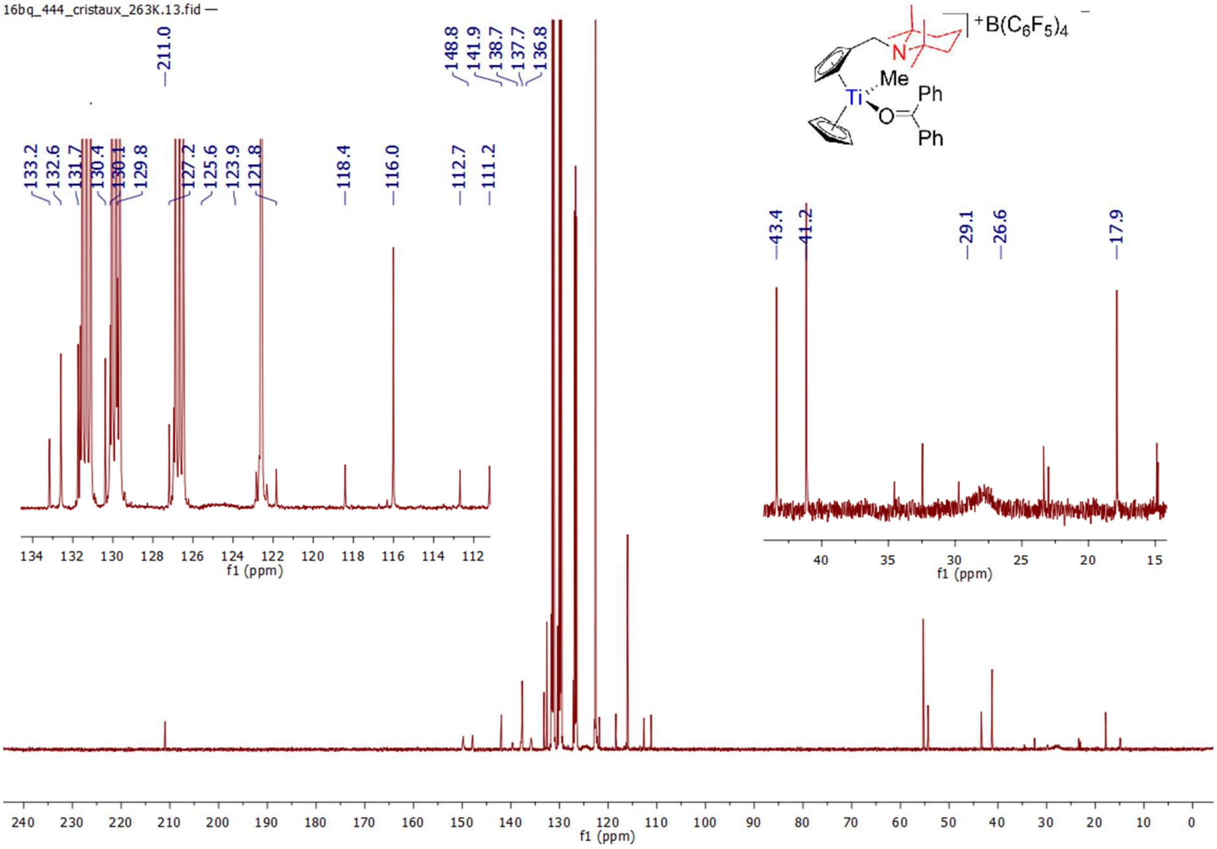


Spectrum 0-272: HRMS of 37 (Positive mode ESI, dichloromethane)

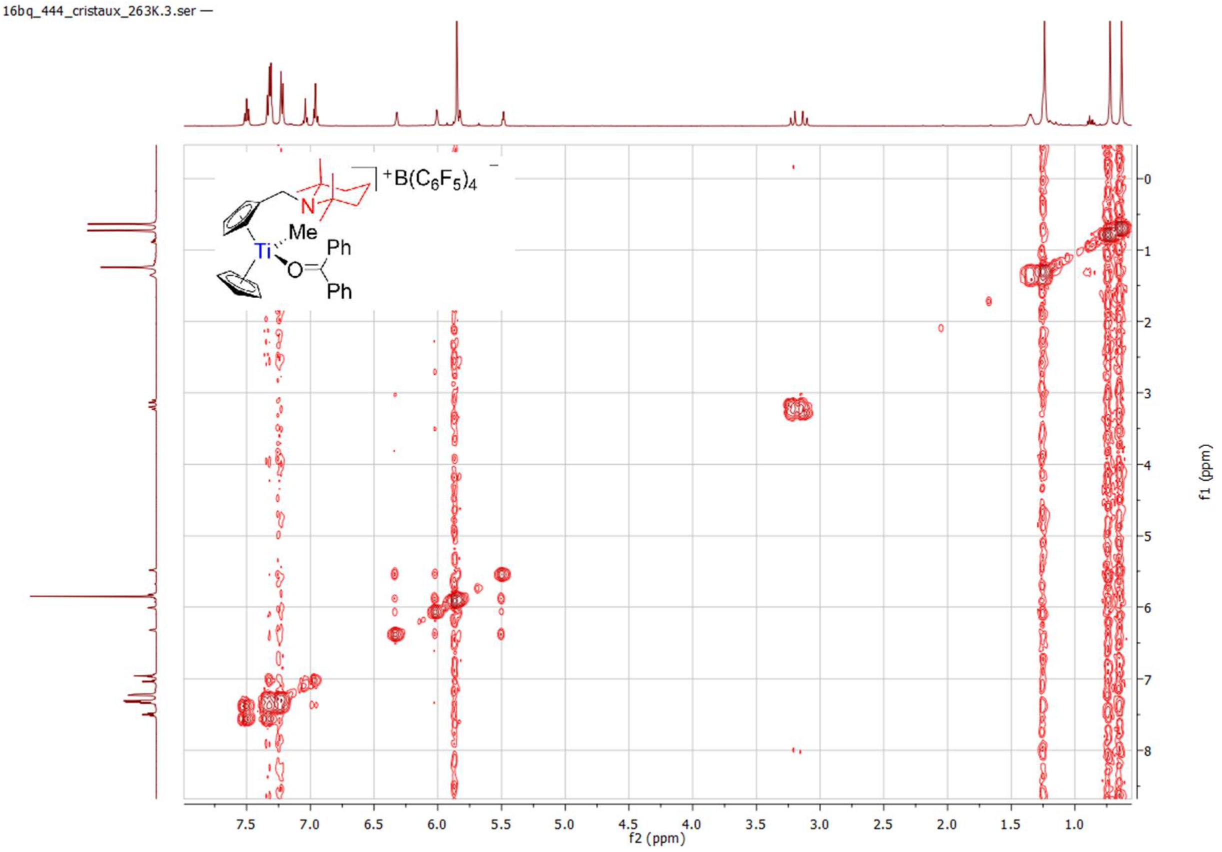
15. Compound **38**:



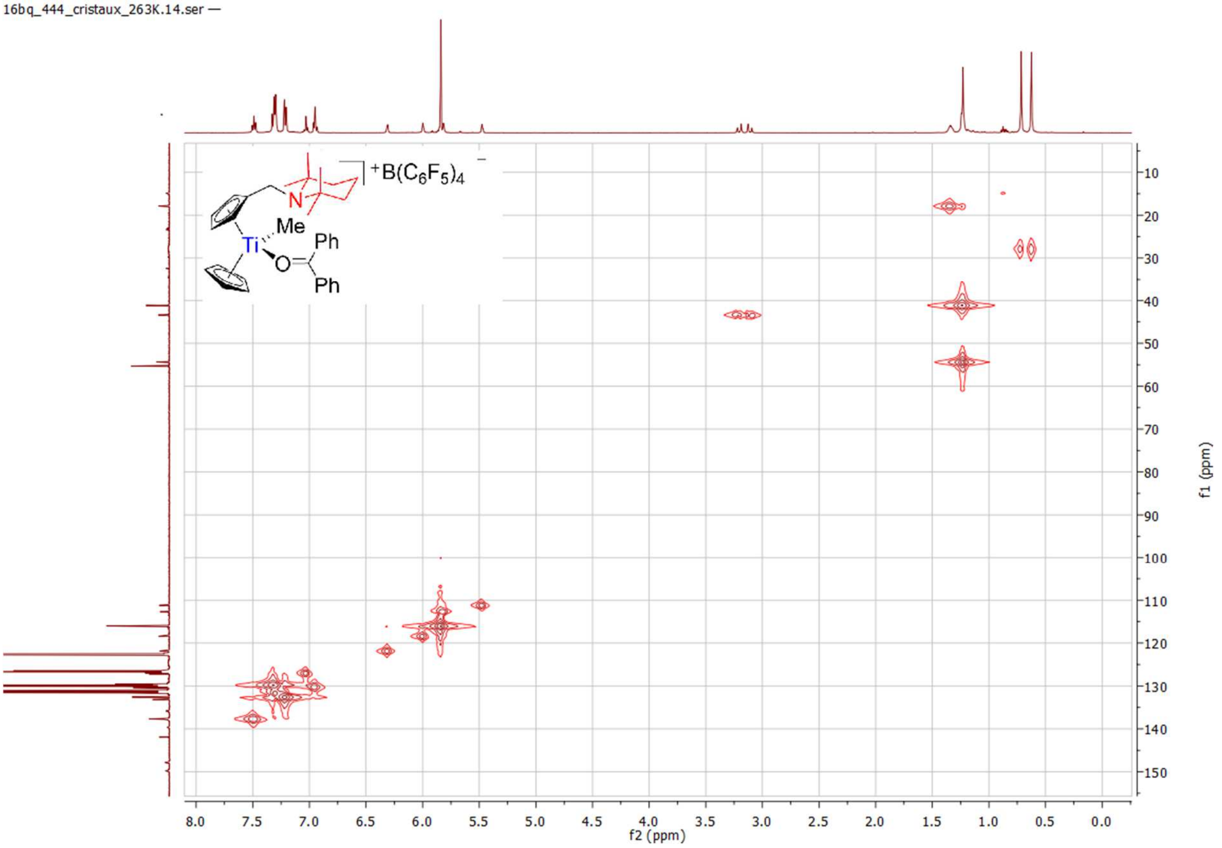
Spectrum 0-273: ^{1}H NMR of 38 (500.03 MHz, 263 K, bromobenzene-d$_5$)



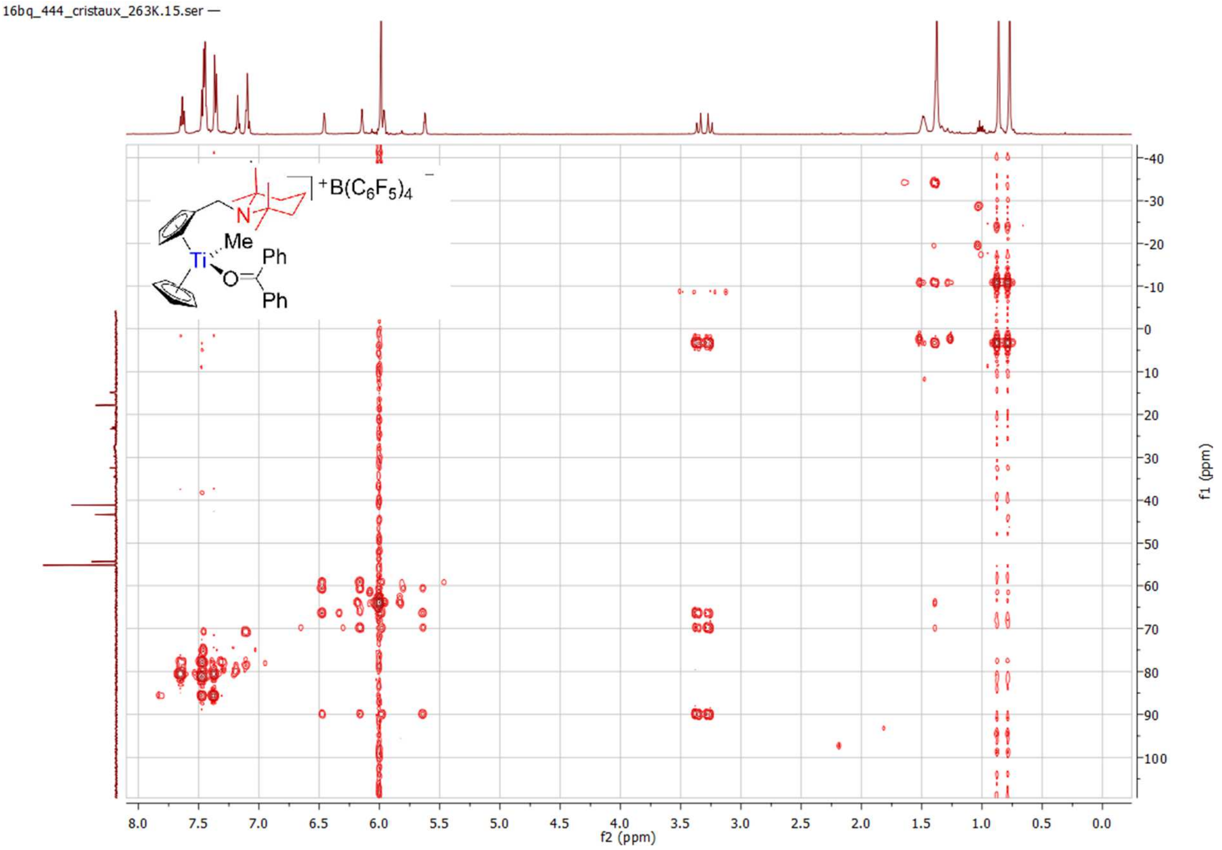
Spectrum 0-274: ^{13}C{^{1}H} NMR of 38 (125.75 MHz, 263 K, bromobenzene-d$_5$)



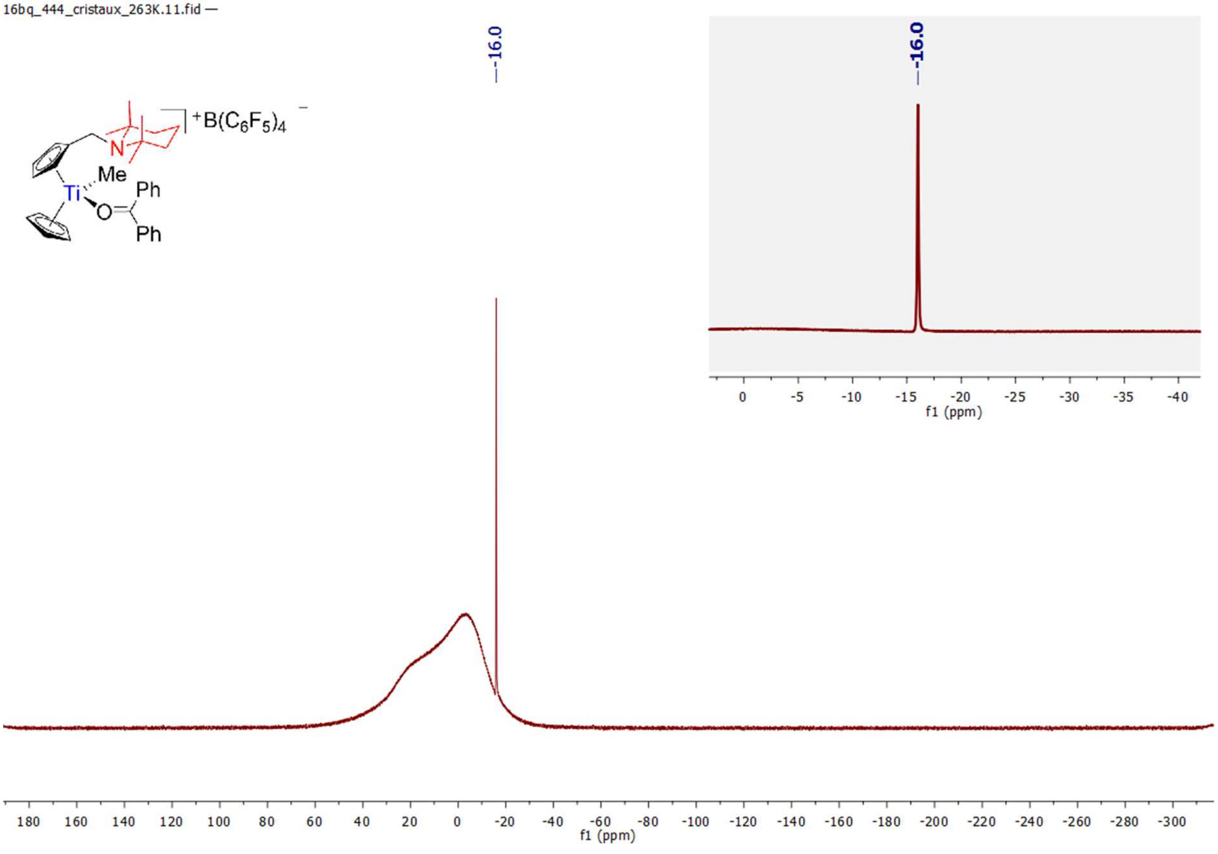
Spectrum 0-275: ^{1}H ^{1}H COSY of 38 (500.03 MHz, 263 K, bromobenzene-d_5)



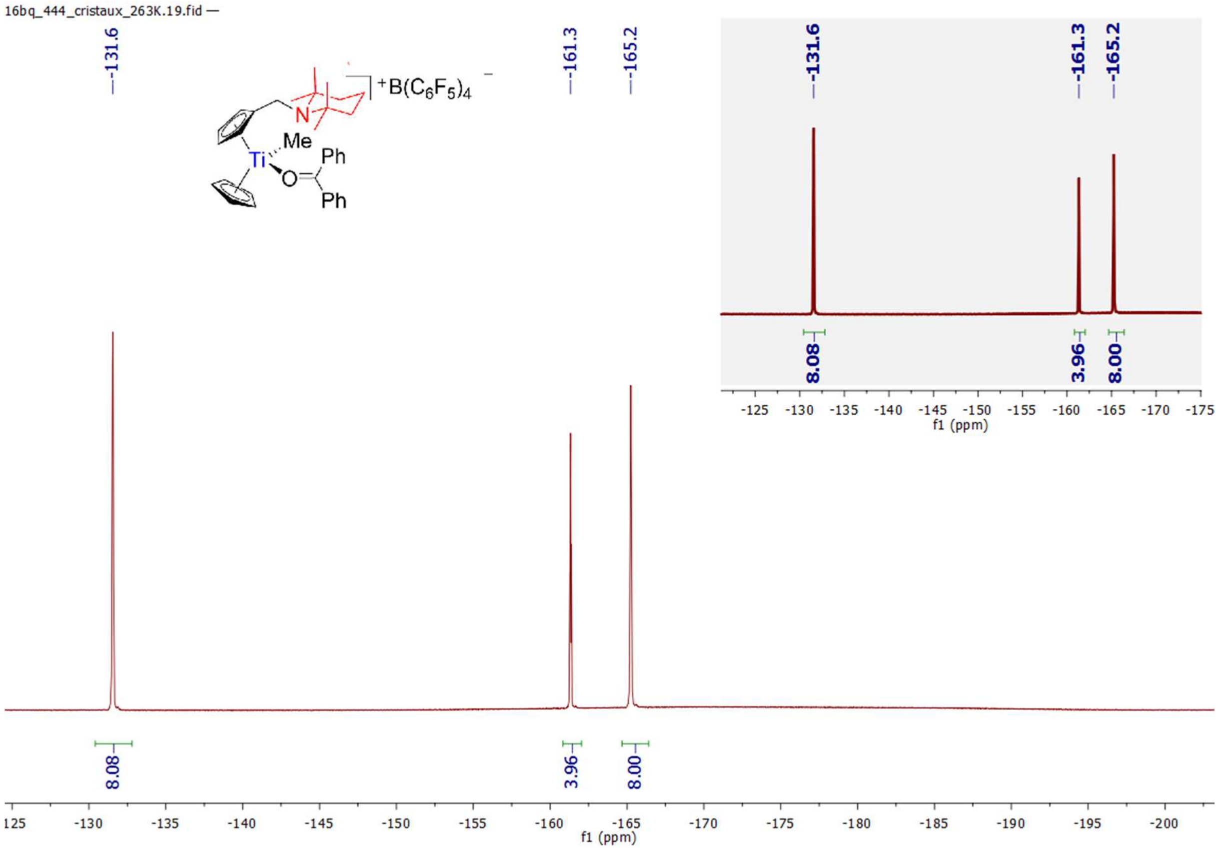
Spectrum 0-276: ^{1}H ^{13}C HMQC 38 (500.03 MHz / 125.03 MHz, 263 K, bromobenzene-d_5)



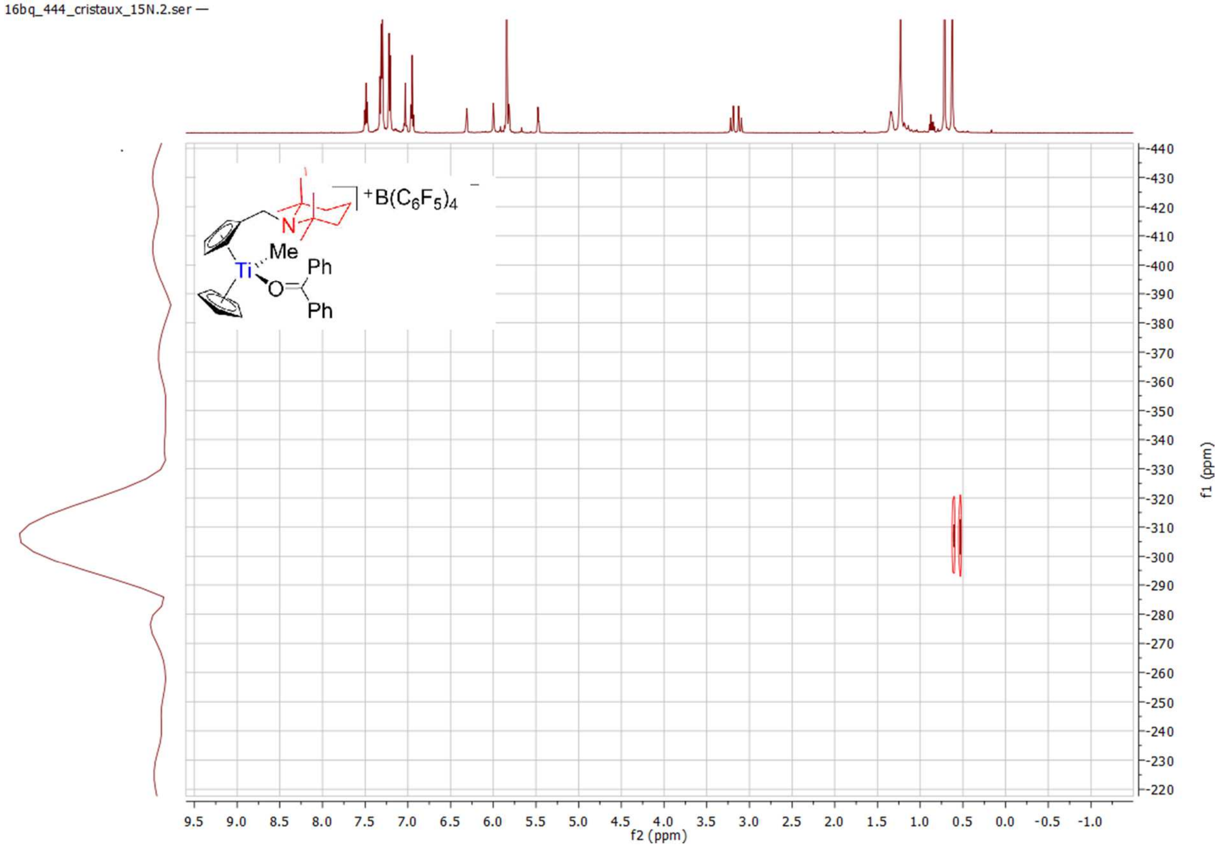
Spectrum 0-277: ^{1}H ^{13}C HMBC of 38 (500.03 MHz / 125.03 MHz, 263 K, bromobenzene-d$_5$)



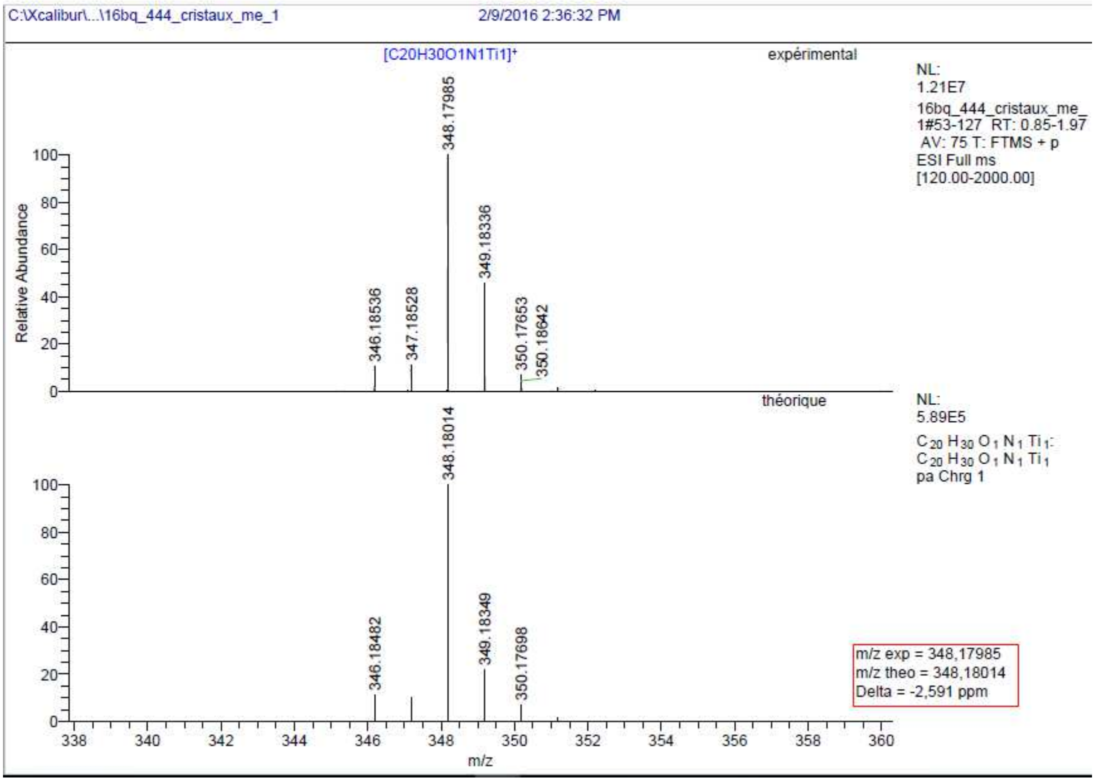
Spectrum 0-278: ^{11}B{^{1}H} and ^{11}B (opacified) NMR of 38 (160.42 MHz, 263 K, bromobenzene-d$_5$)



Spectrum 0-279: $^{19}F\{^{1}H\}$ and ^{19}F (opacified) NMR of 38 (470.45 MHz, 263 K, bromobenzene-d_5)

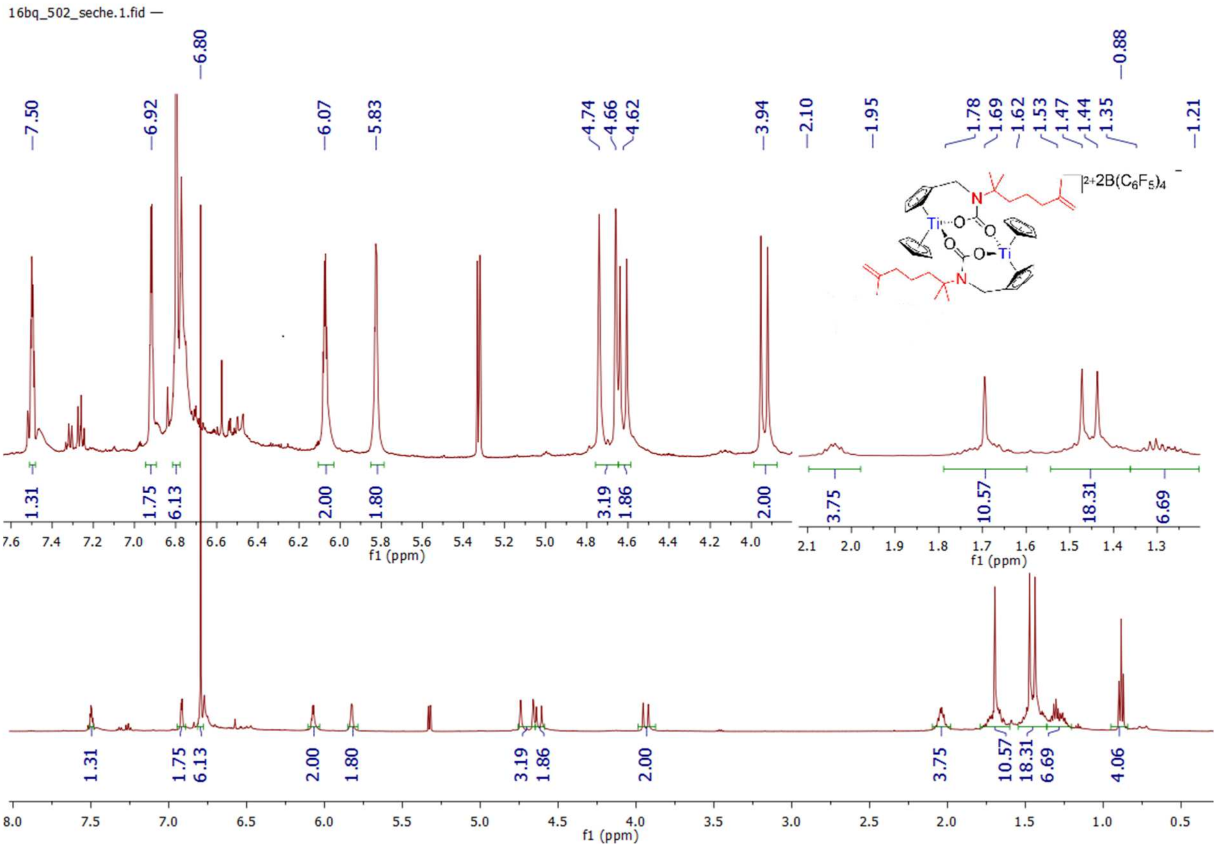


Spectrum 0-280: ^{1}H ^{15}N HMBC of 38 (600.23 MHz / 43.3 MHz, 263 K, bromobenzene-d_5)

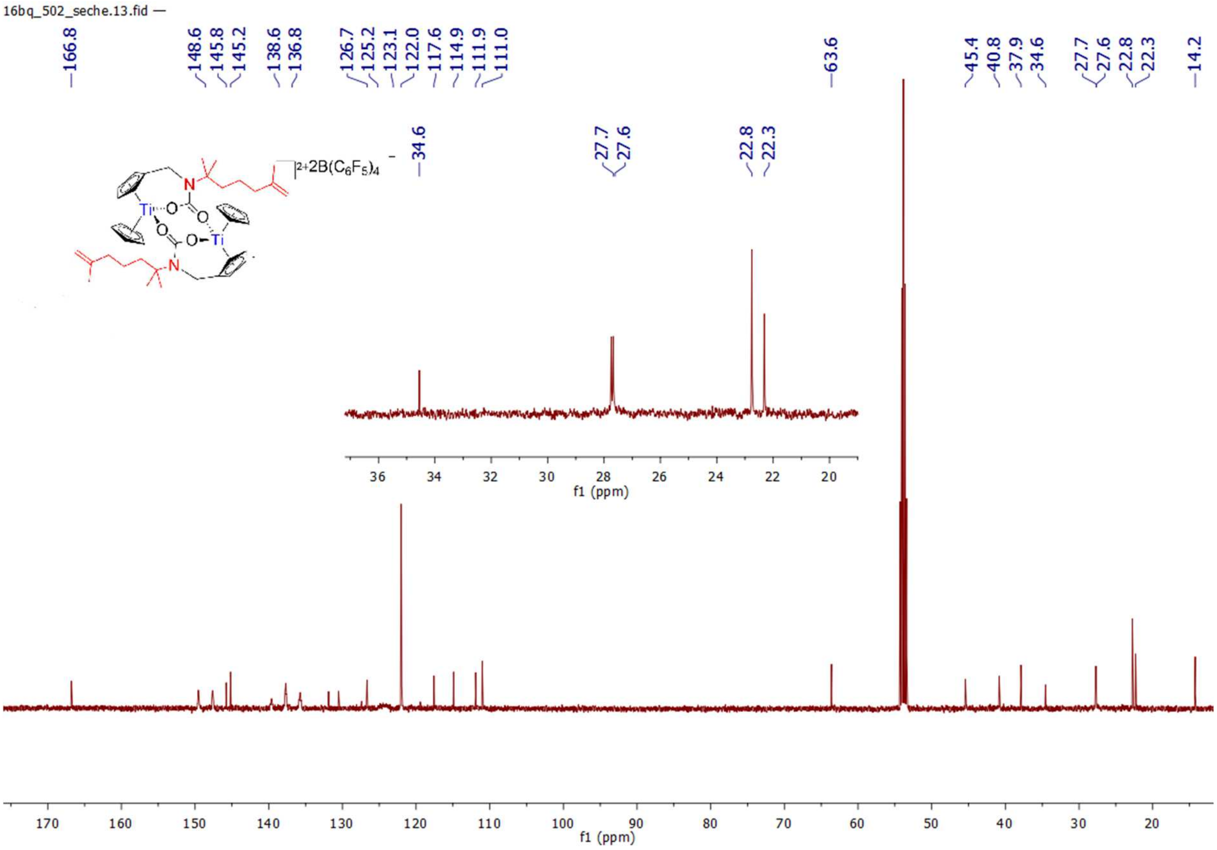


Spectrum 0-281: HRMS of 38 (Positive mode ESI, bromobenzene)

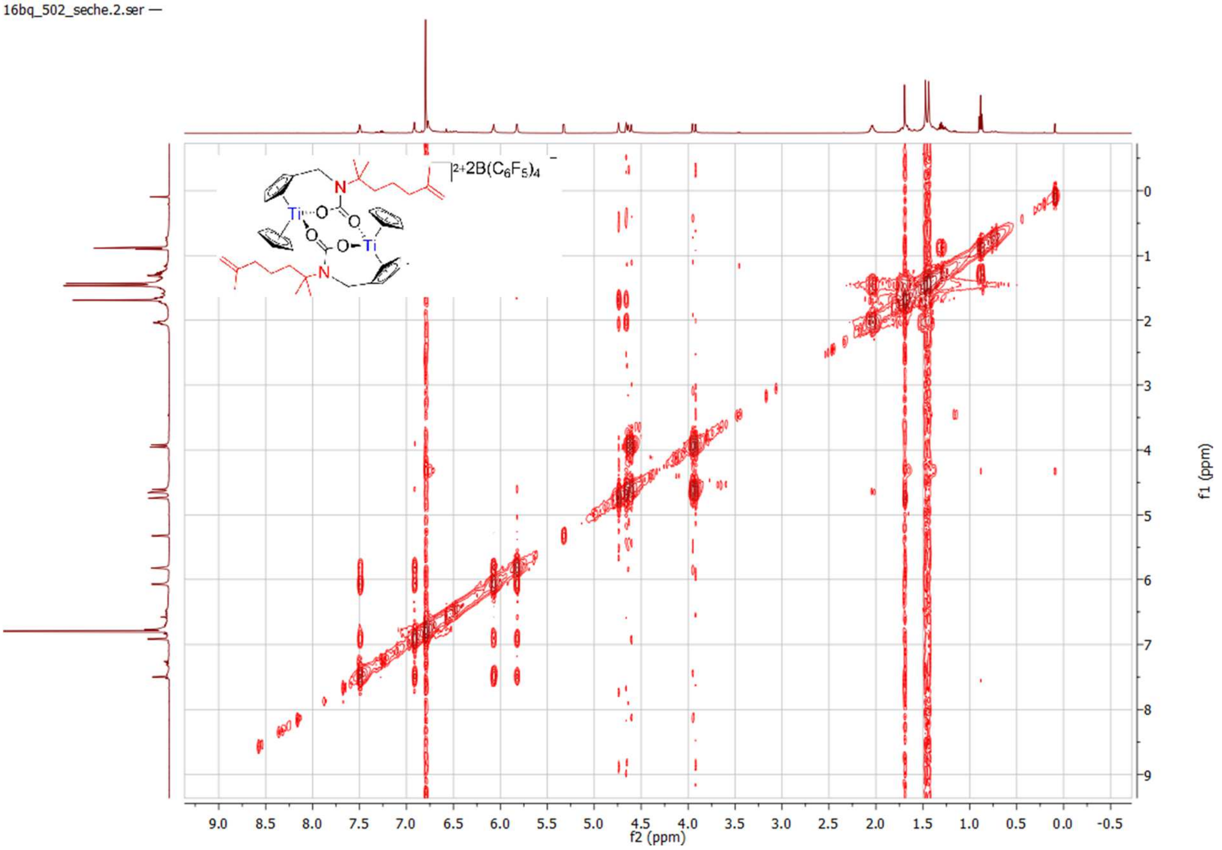
16. Compound **39**:



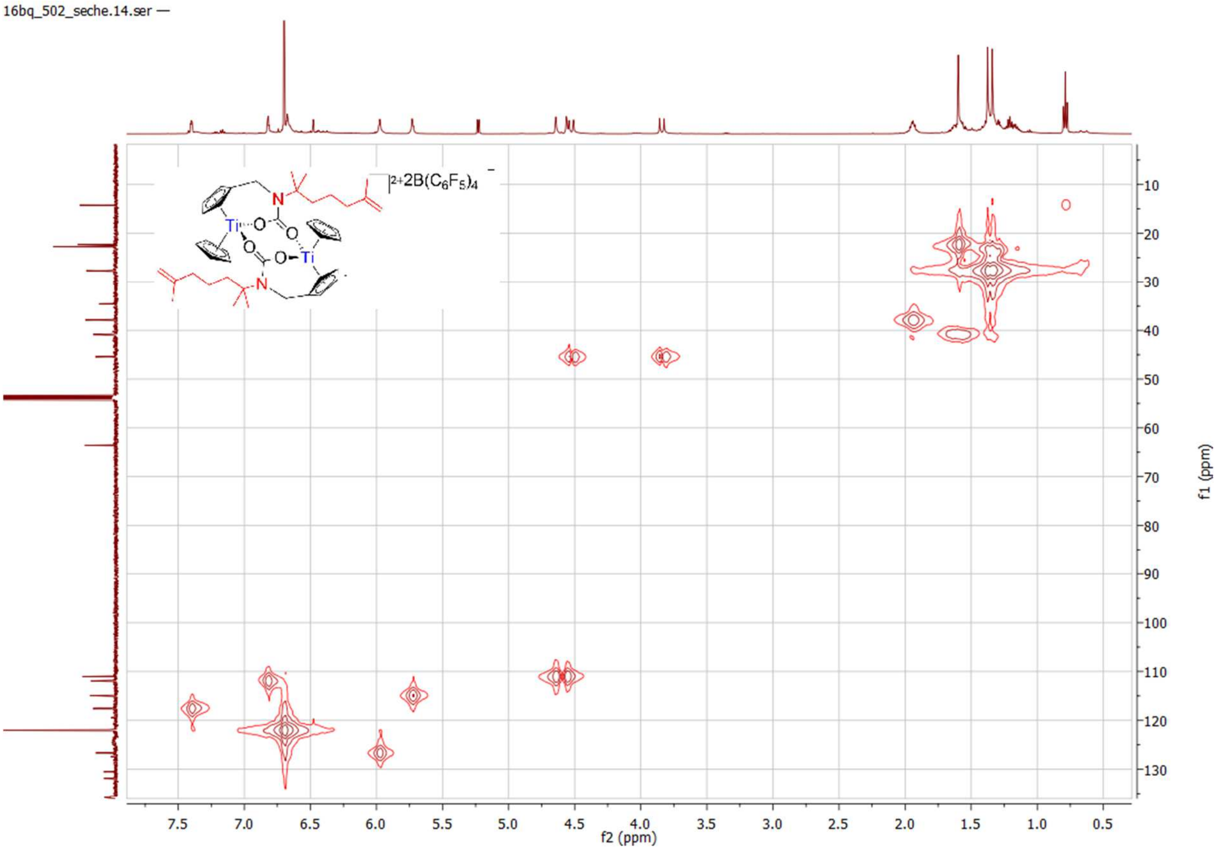
Spectrum 0-282: ^{1}H NMR of 39 (500.03 MHz, 300 K, dichloromethane-d_2)



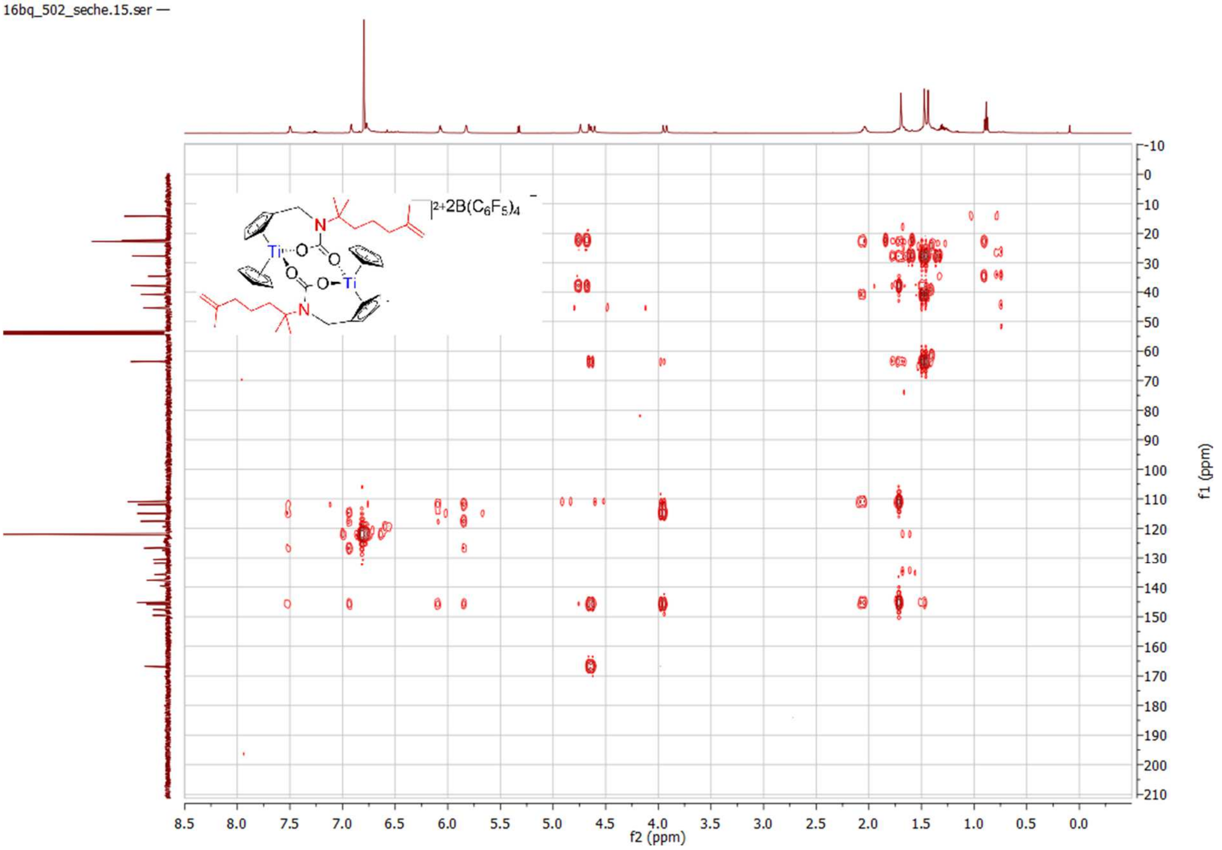
Spectrum 0-283: $^{13}C\{^1H\}$ NMR of 39 (125.75 MHz, 300 K, dichloromethane-d_2)



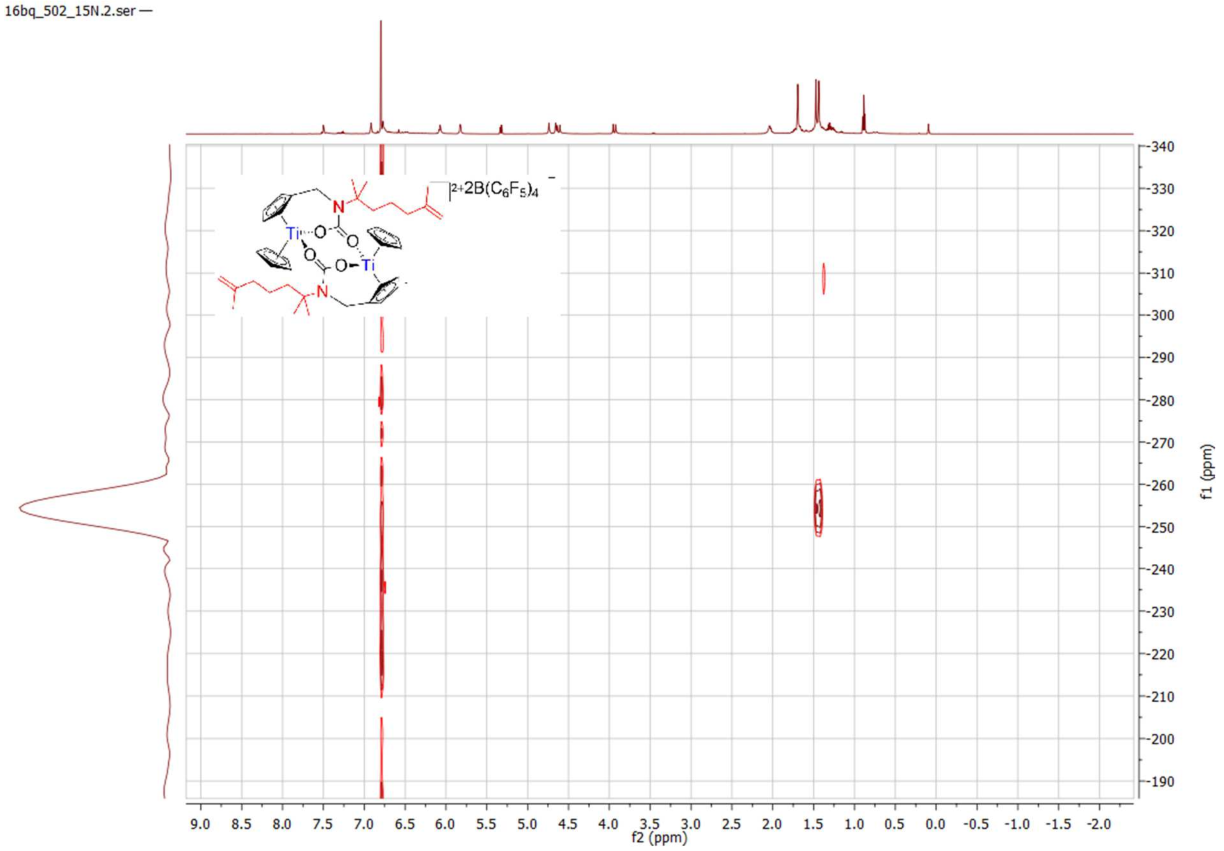
Spectrum 0-284: $^{13}C\{^1H\}$ NMR of 39 (125.75 MHz, 300 K, dichloromethane-d_2)



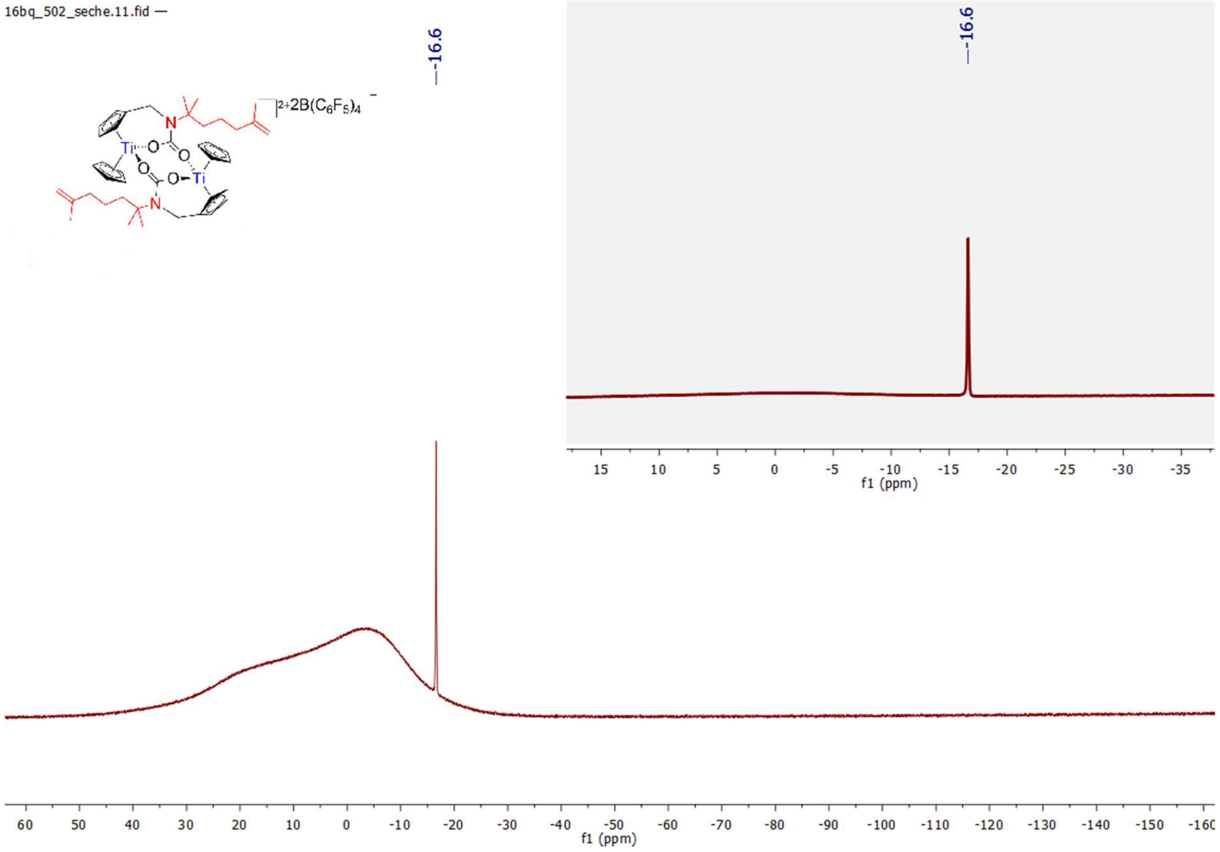
Spectrum 0-285: ^{1}H ^{13}C HMQC of 39 (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$)



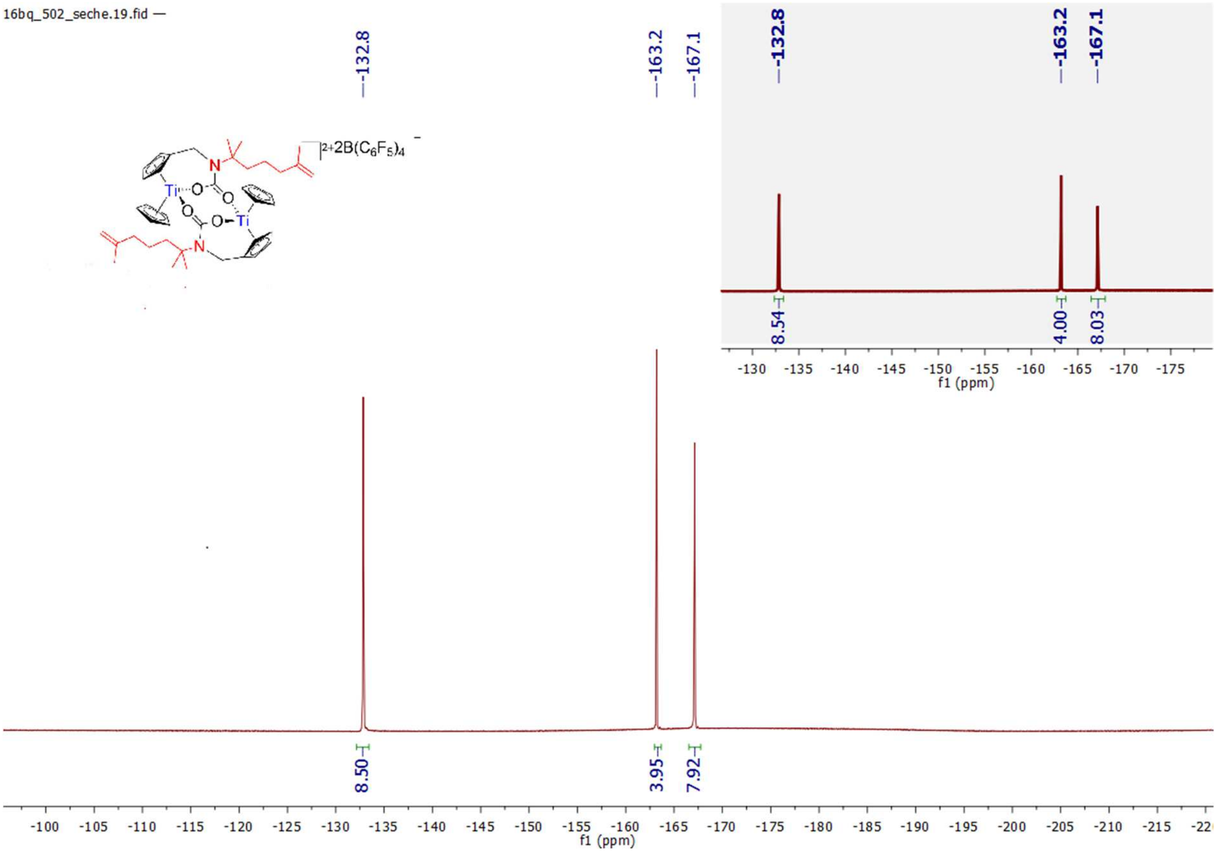
Spectrum 0-286: ^{1}H ^{13}C HMBC of 39 (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$)



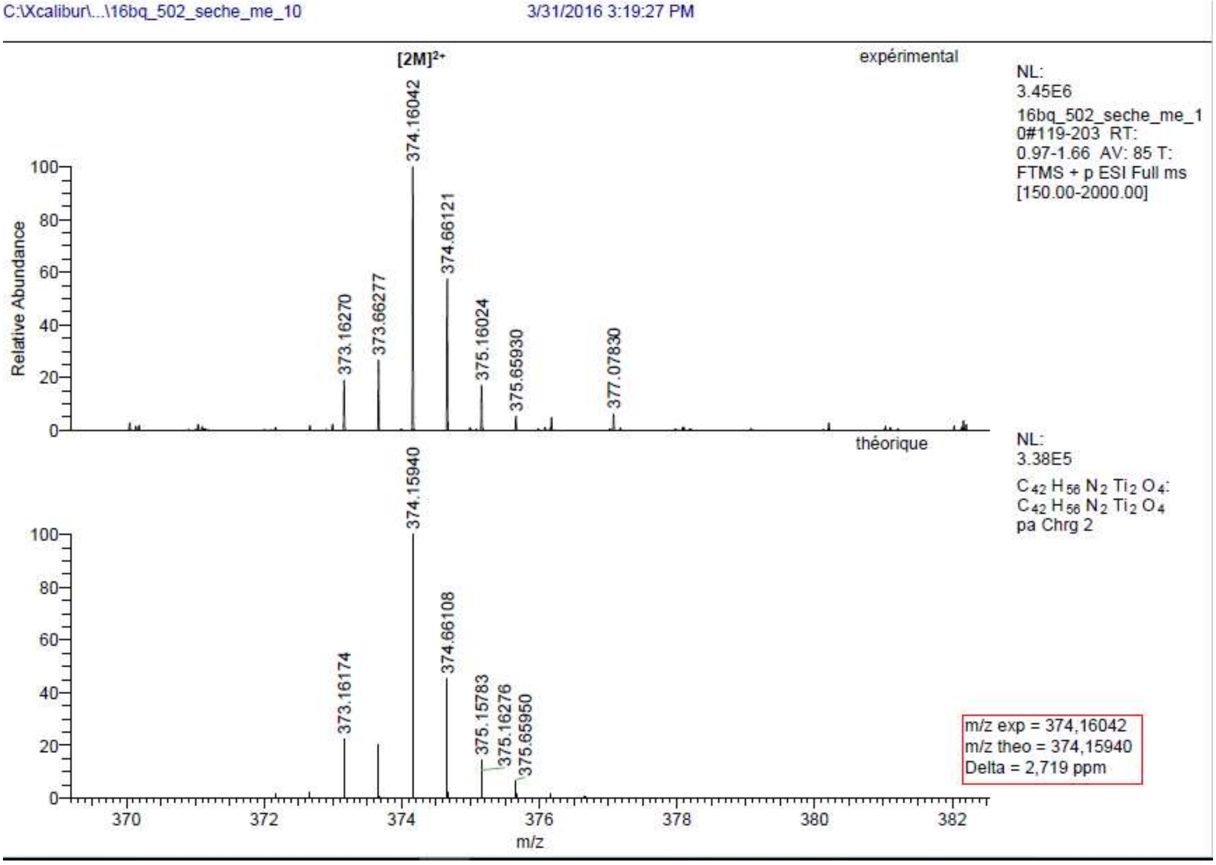
Spectrum 0-287: ^{1}H ^{15}N HMBC of 39 (600.23 MHz / 43.3 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-288: ^{11}B{^{1}H} and ^{11}B (opacified) NMR of 39 (160.42 MHz, 300 K, dichloromethane-d$_2$)



Spectrum 0-289: $^{19}F\{^{1}H\}$ and ^{19}F (opacified) NMR of 39 (470.45 MHz, 300 K, dichloromethane-d_2)


C:\Xcalibur\...\16bq_502_seche_me_10 3/31/2016 3:19:27 PM

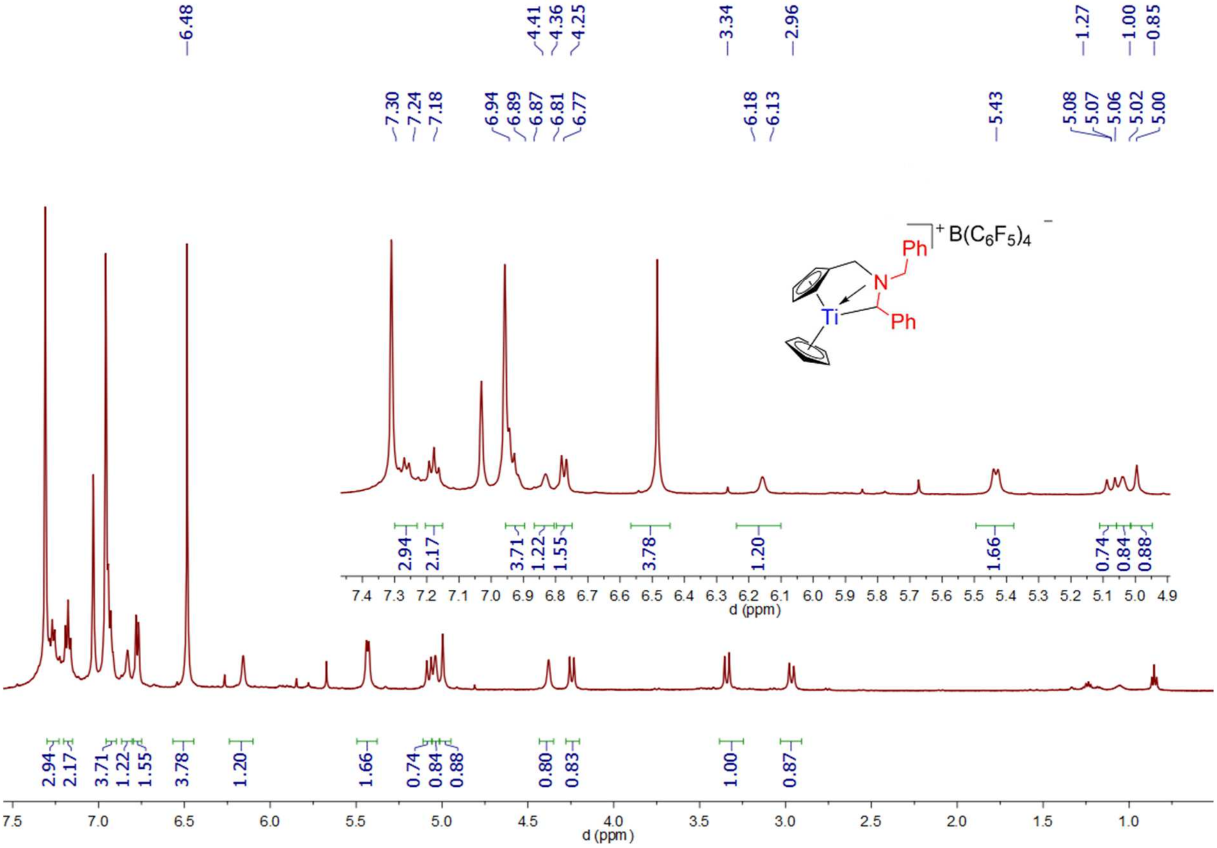
NL:
3.45E6
16bq_502_seche_me_10#119-203 RT:
0.97-1.66 AV: 85 T:
FTMS + p ESI Full ms
[150.00-2000.00]

NL:
3.38E5
$C_{42}H_{56}N_2Ti_2O_4$:
$C_{42}H_{56}N_2Ti_2O_4$
pa Chrg 2

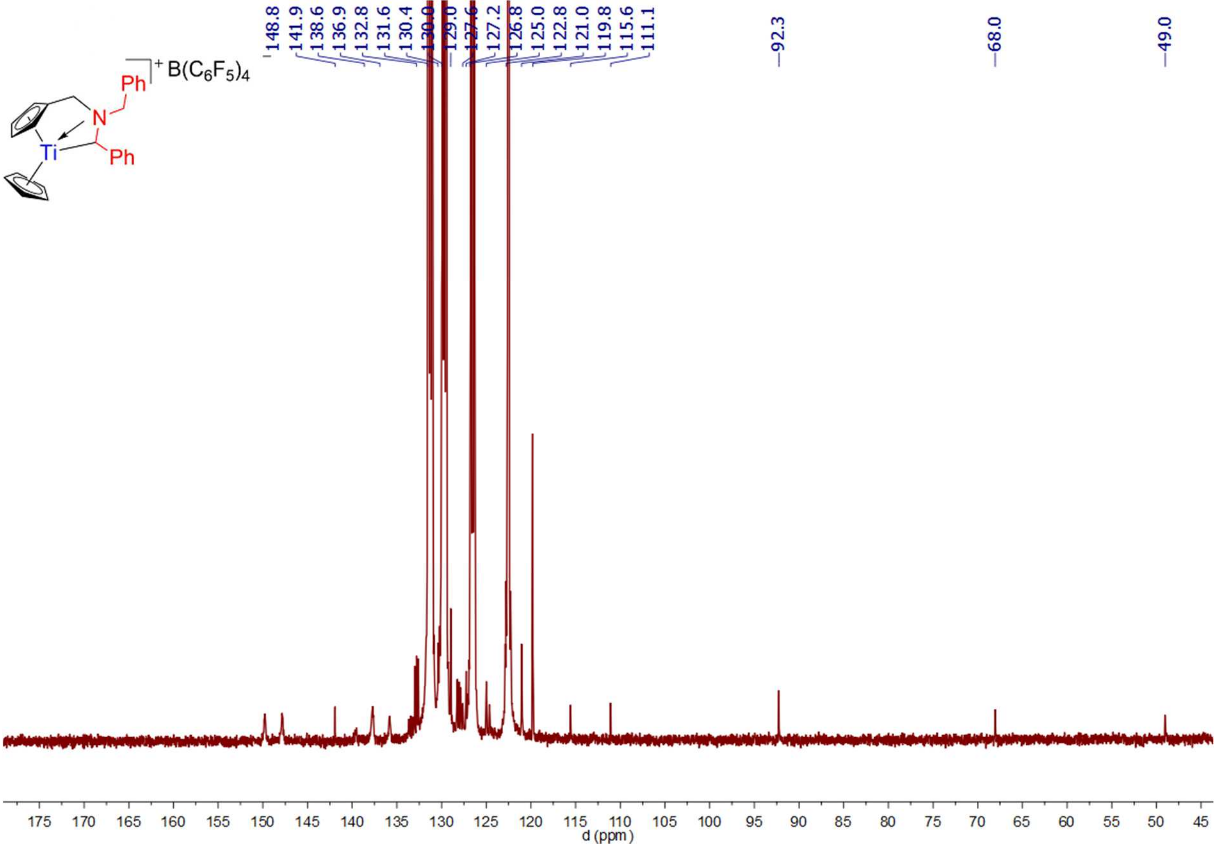
m/z exp = 374,16042
m/z theo = 374,15940
Delta = 2,719 ppm

Spectrum 0-290 HRMS of 39 (Positive mode ESI, tetrahydrofuran)

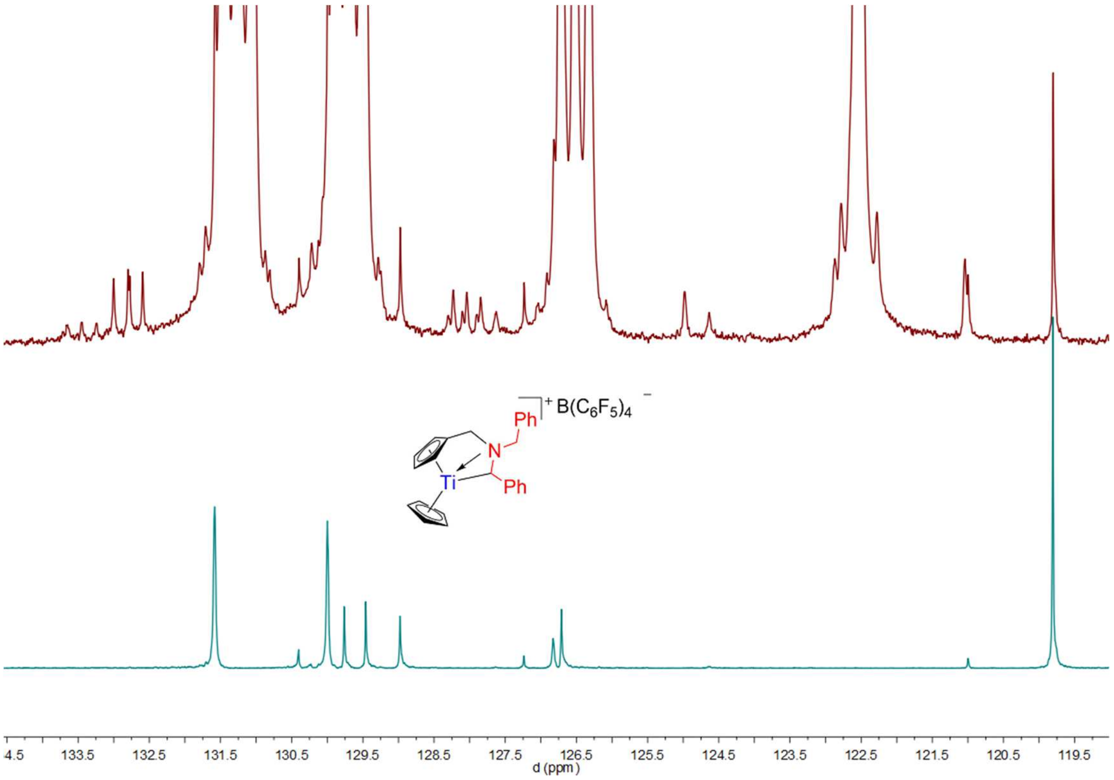
17. Compound **40**:



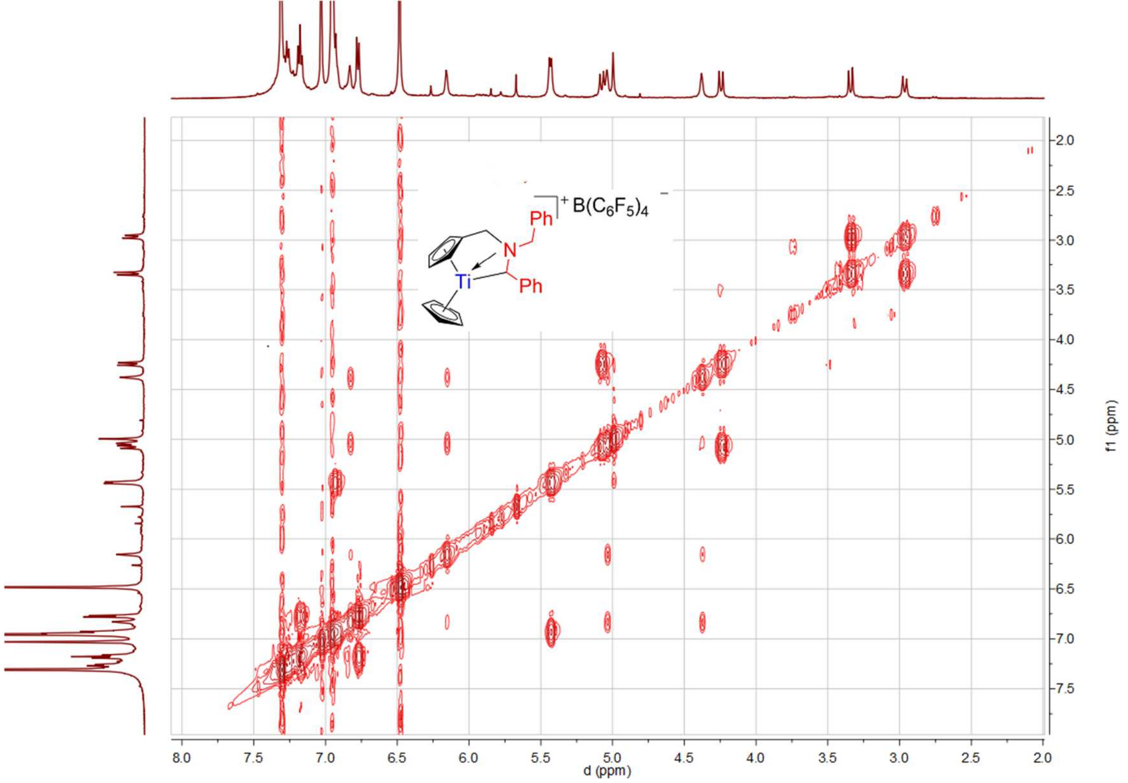
Spectrum 0-291: ^{1}H NMR of 40 (500.03 MHz, 300 K, bromobenzene-d$_5$)



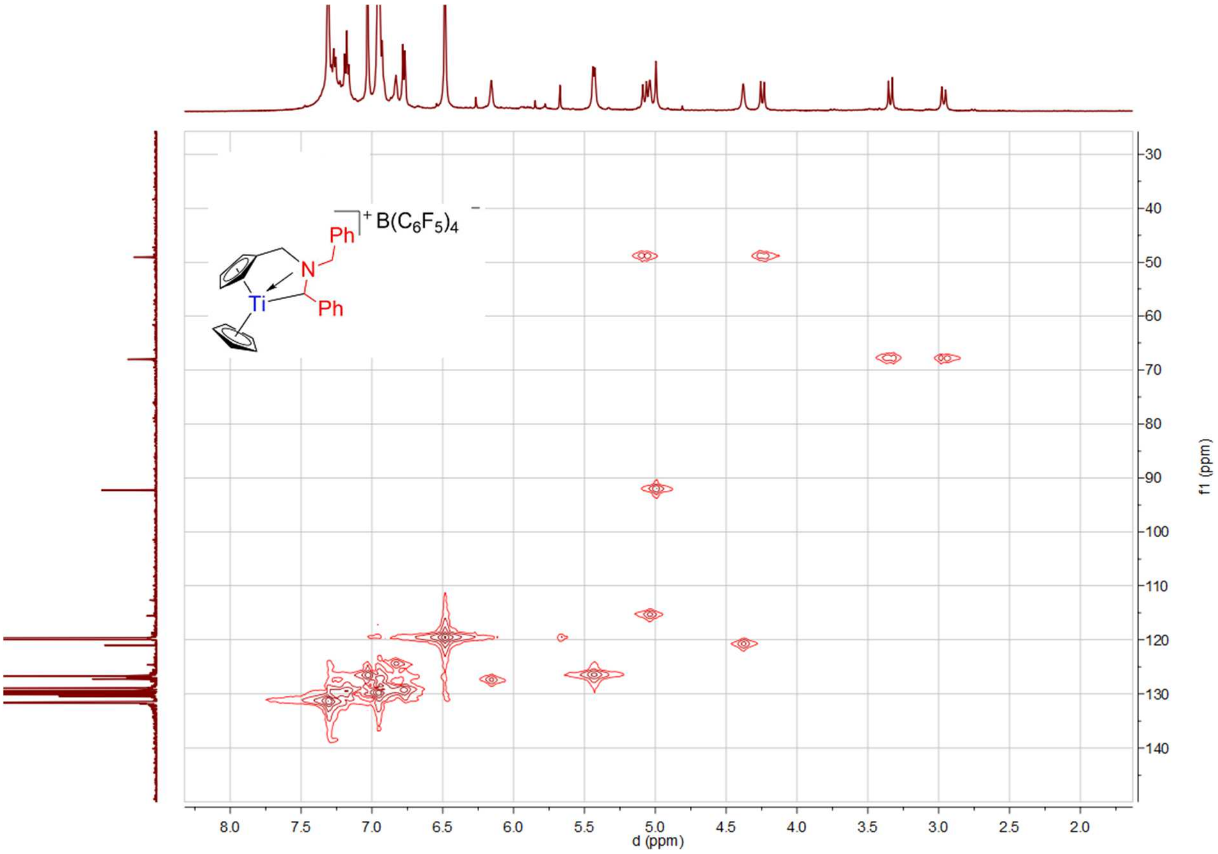
Spectrum 0-292: ^{13}C{^{1}H} NMR of 40 (125.75 MHz, 300 K, bromobenzene-d$_5$)



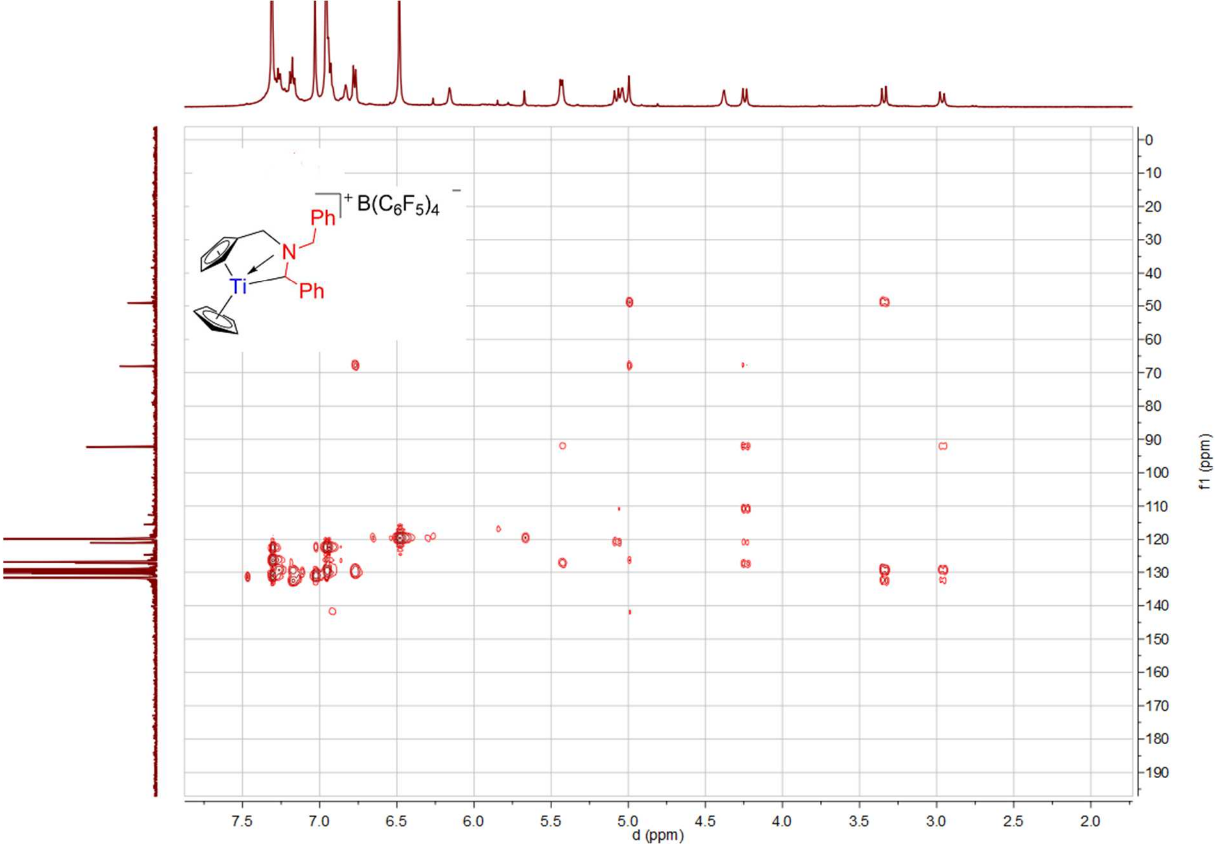
Spectrum 0-293: $^{13}C\{^{1}H\}$ NMR (top) superposed with dept135 NMR (bottom) of 40 (125.75 MHz, 300 K, bromobenzene-d_5)



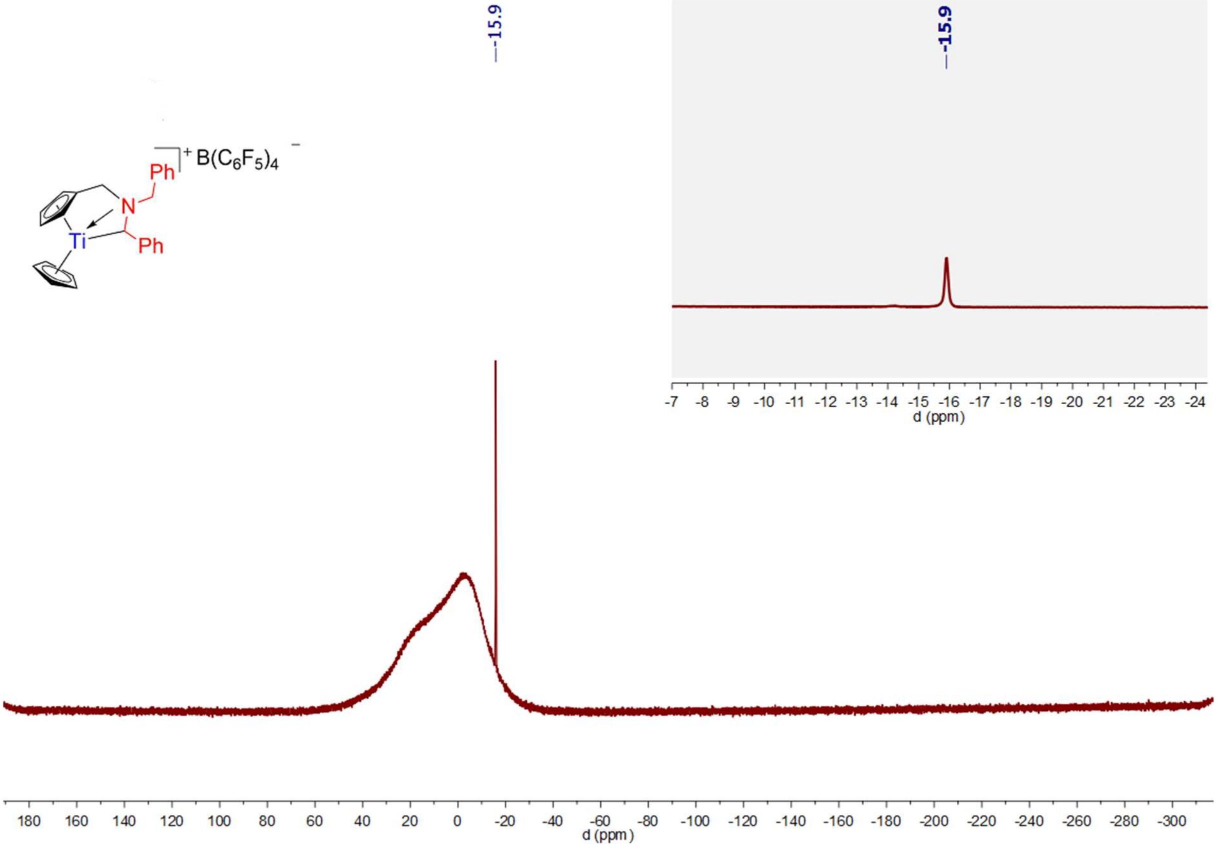
Spectrum 0-294: ^{1}H ^{1}H COSY of 40 (500.03 MHz, 300 K, bromobenzene-d_5)



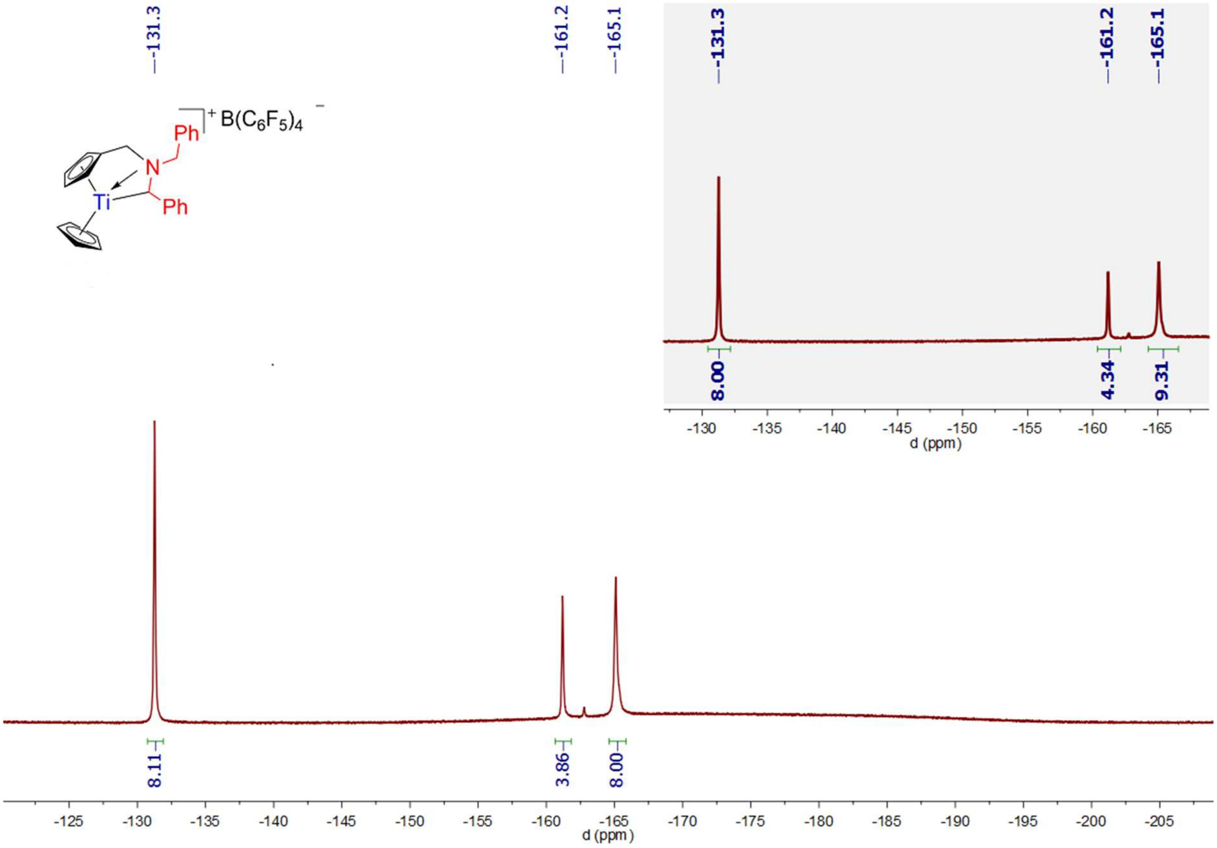
Spectrum 0-295: ^1H ^{13}C HMQC of 40 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d_5)



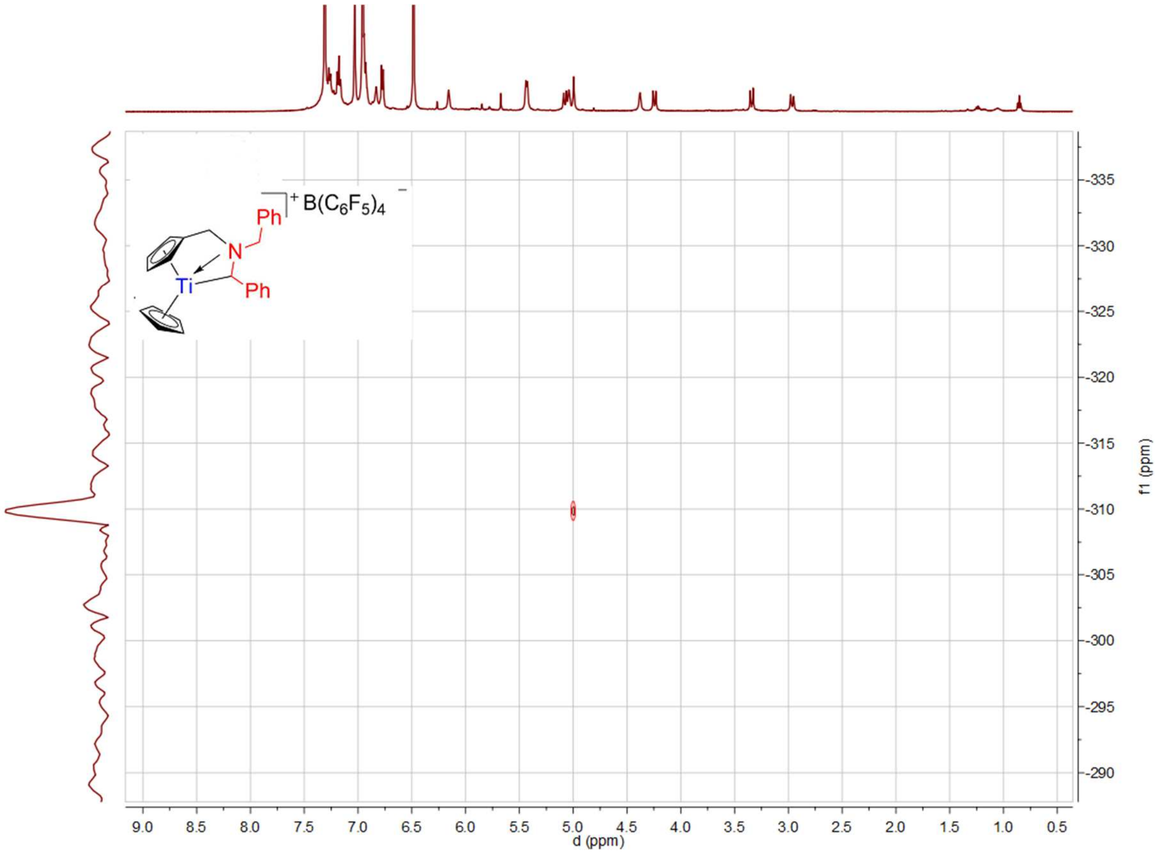
Spectrum 0-296: ^1H ^{13}C HMBC of 40 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d_5)



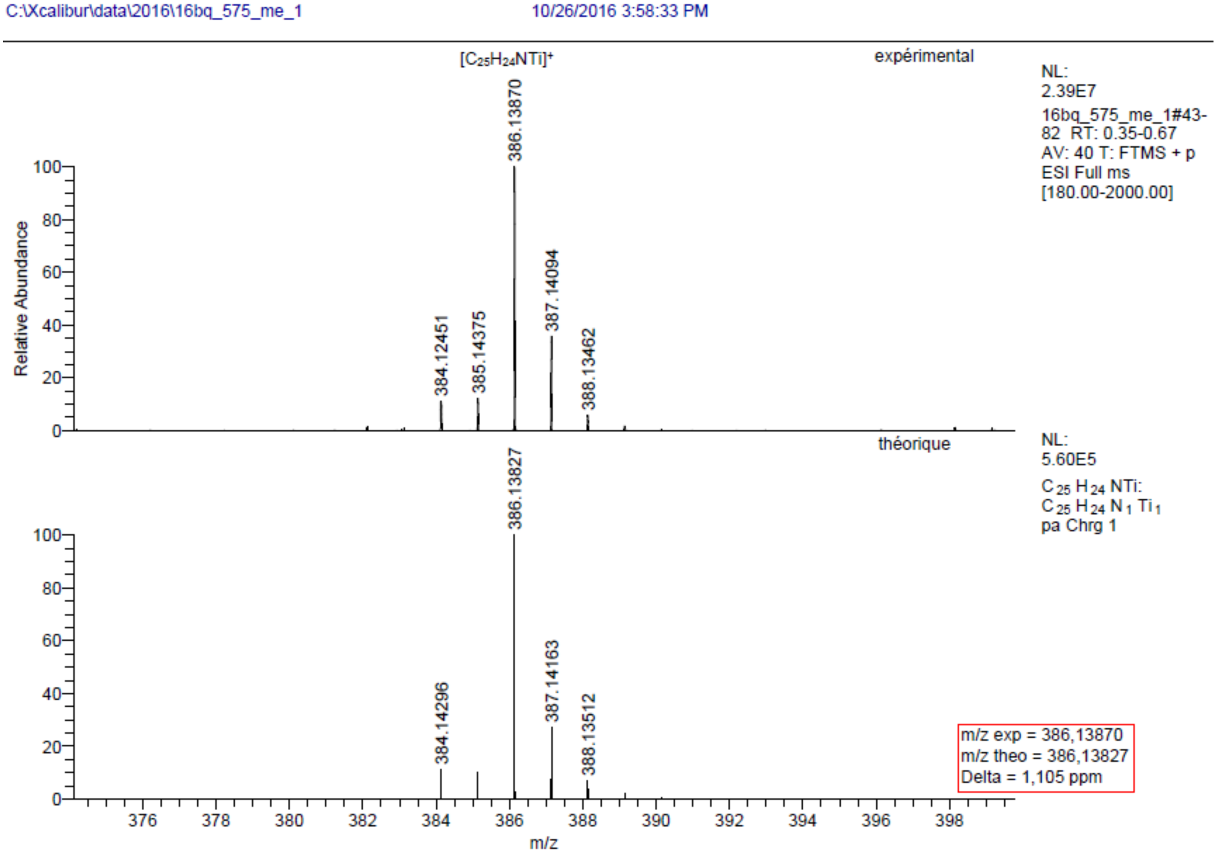
Spectrum 0-297: $^{11}B\{^{1}H\}$ and ^{11}B (opacified) NMR of 40 (160.42 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-298: $^{19}F\{^{1}H\}$ and ^{19}F (opacified) NMR of 40 (470.45 MHz, 300 K, bromobenzene-d$_5$)

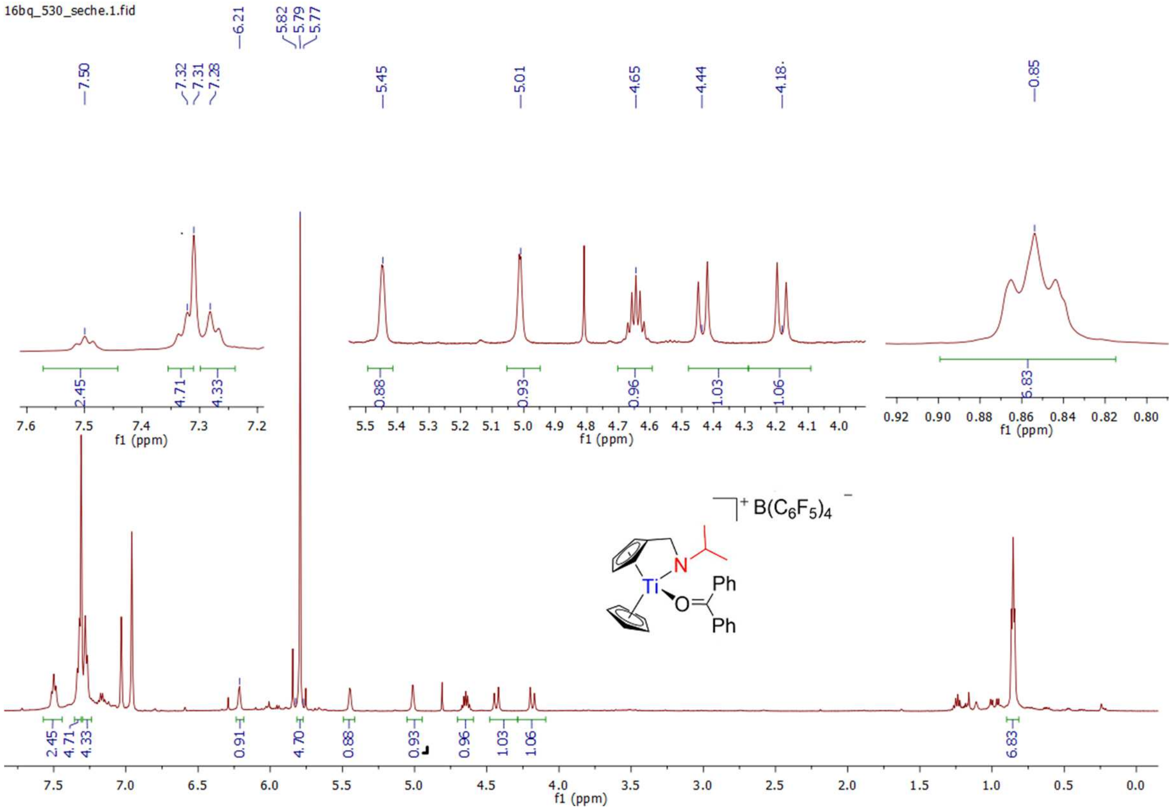


Spectrum 0-299: ^{1}H ^{15}N HMBC of 40 (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)

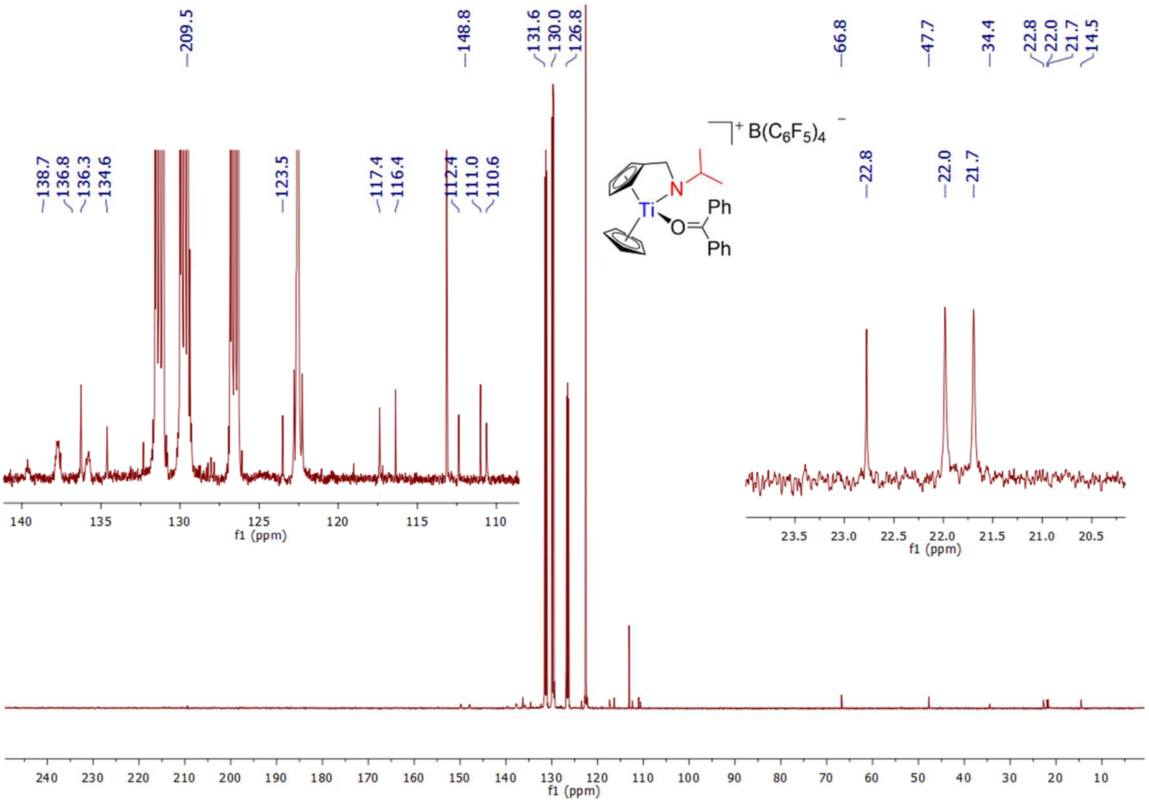


Spectrum 0-300: HRMS of 40 (Positive mode ESI, bromobenzene)

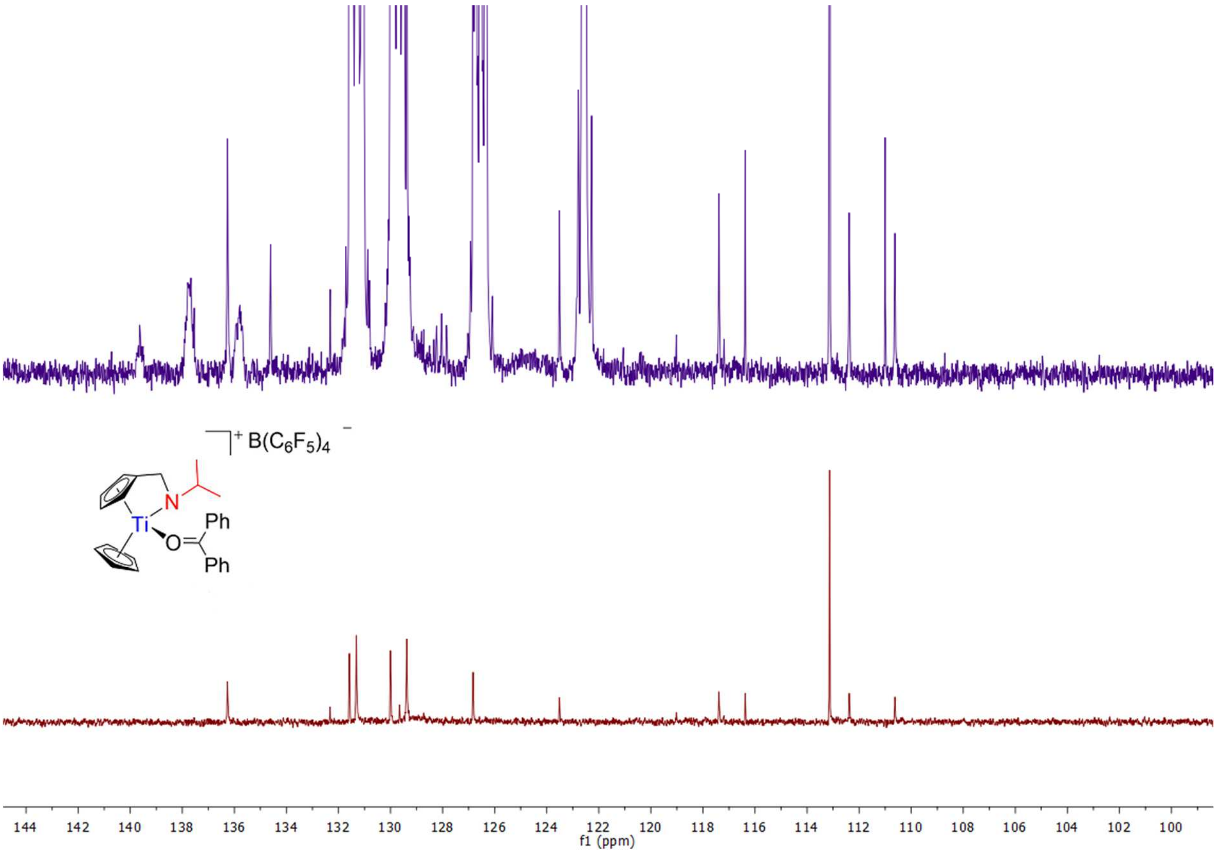
18. Compound **41**:



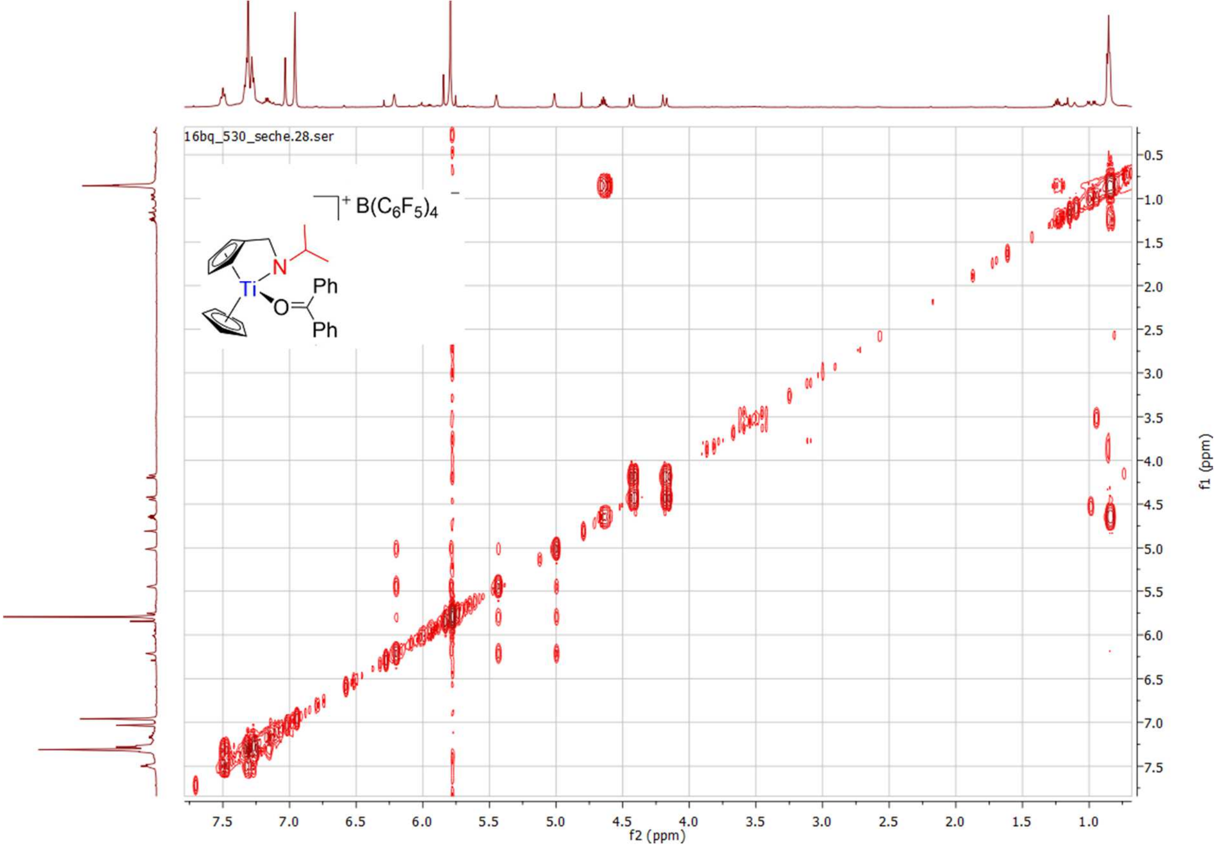
Spectrum 0-301: ^{1}H NMR of 41 (500.03 MHz, 300 K, bromobenzene-d_5)



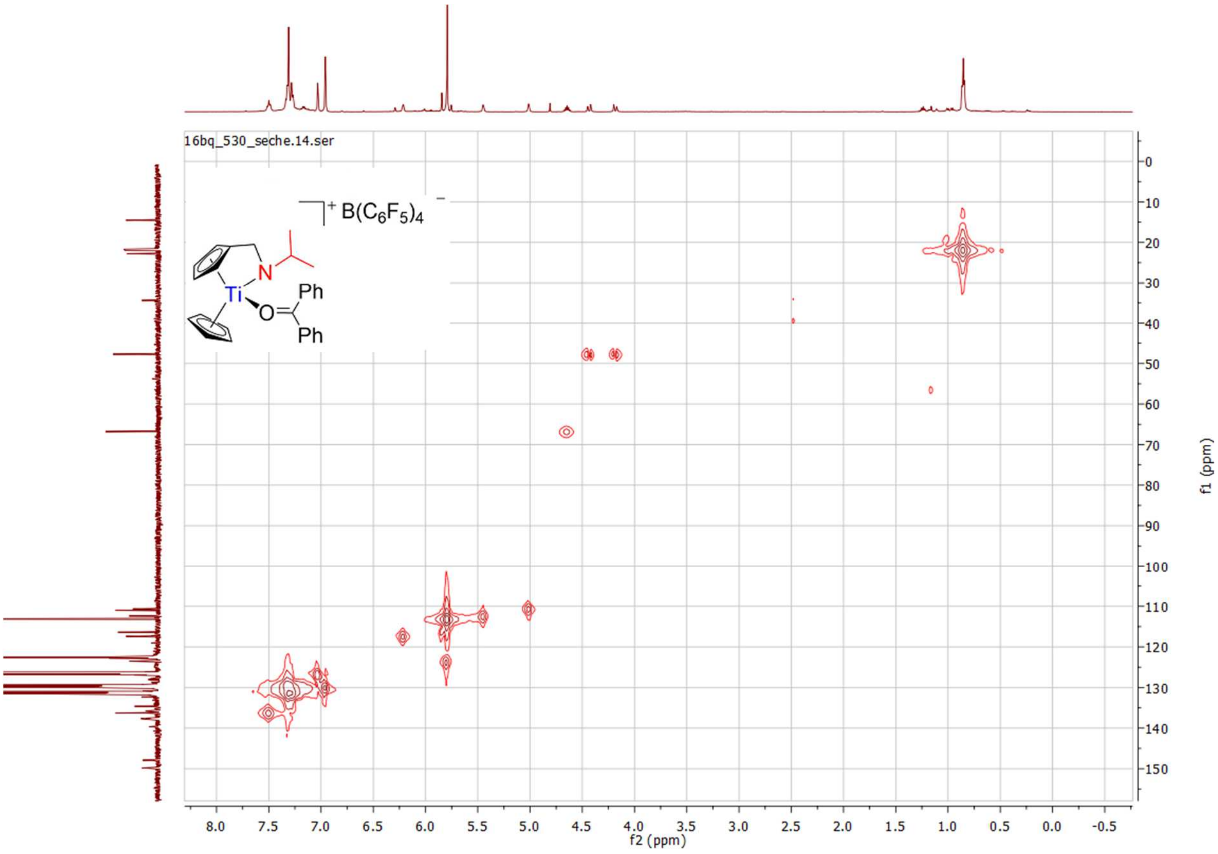
Spectrum 0-302: $^{13}C\{^1H\}$ NMR of 41 (125.75 MHz, 300 K, bromobenzene-d_5)



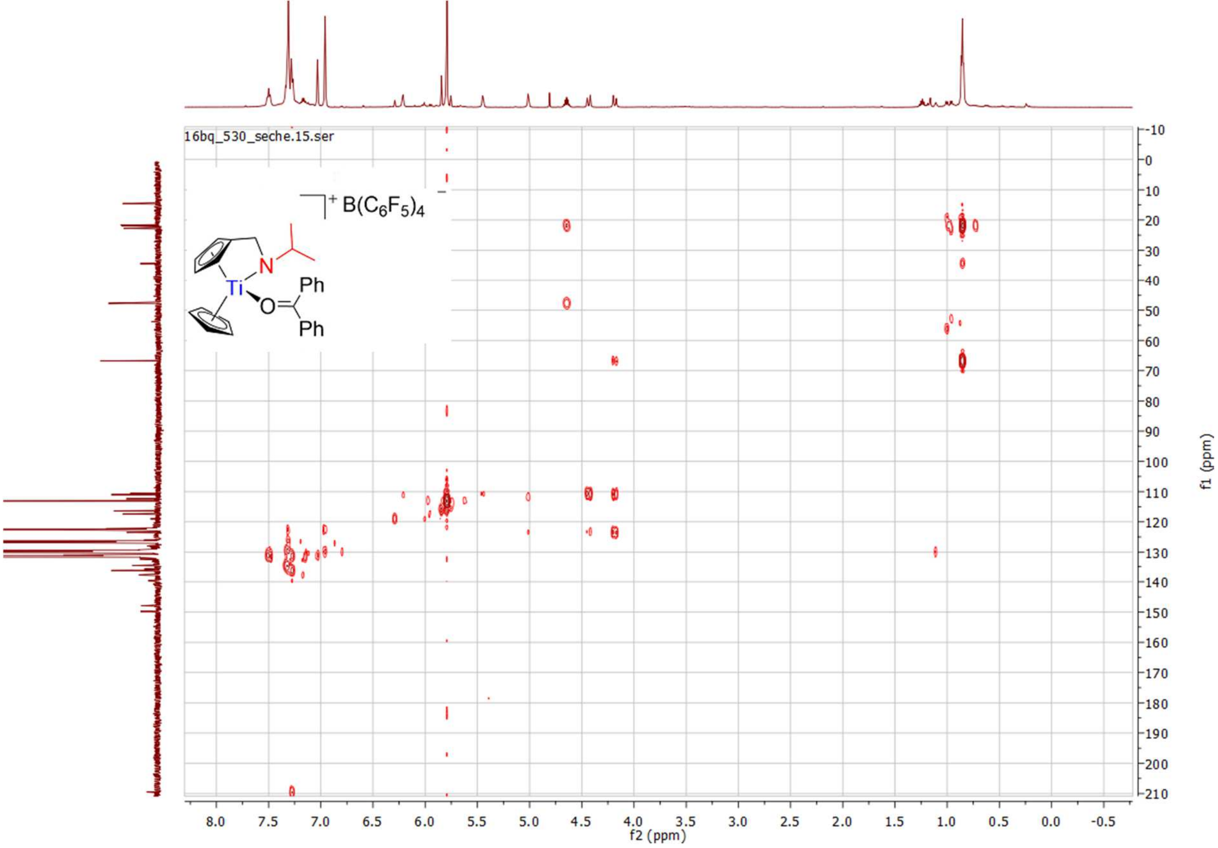
Spectrum 0-303: $^{13}C\{^{1}H\}$ (top) correlated with dept135 (bottom) NMR of 41 (125.75 MHz, 300 K, bromobenzene-d_5)



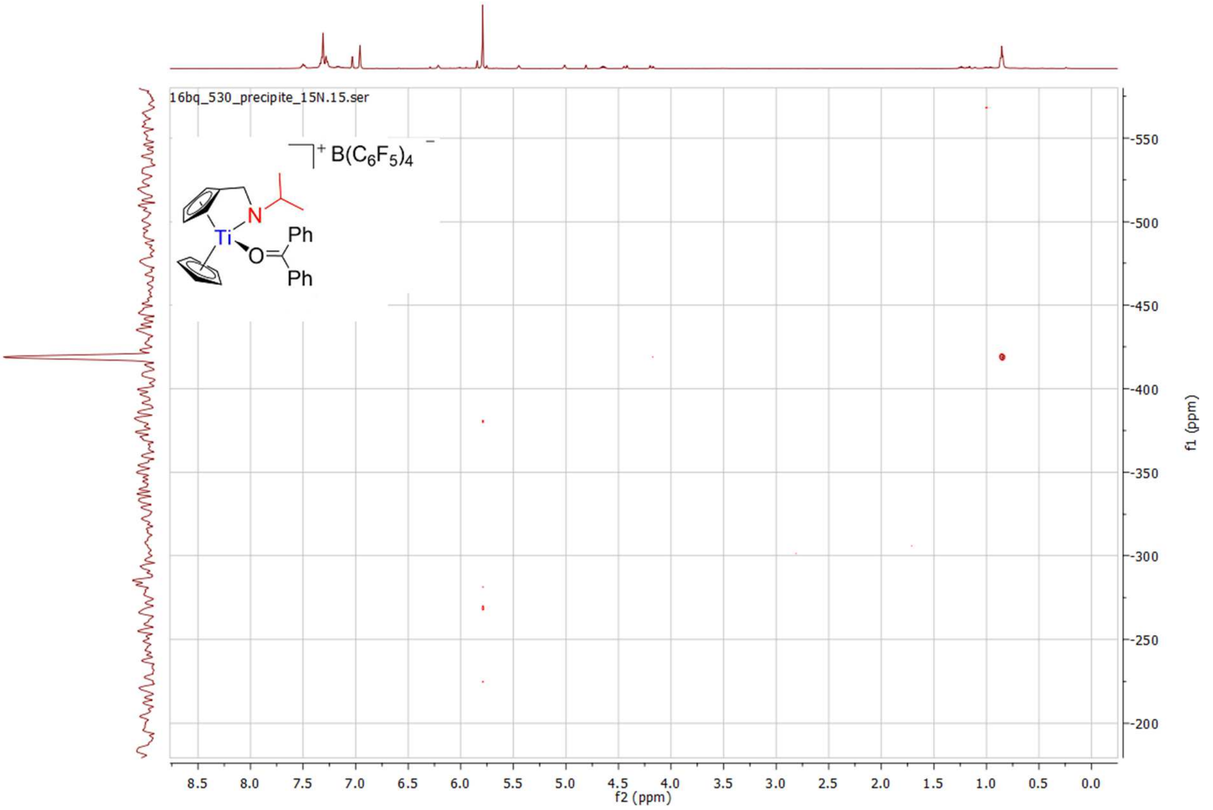
Spectrum 0-304: ^{1}H ^{1}H COSY of 41 (500.03 MHz, 300 K, 300 K, bromobenzene-d_5)



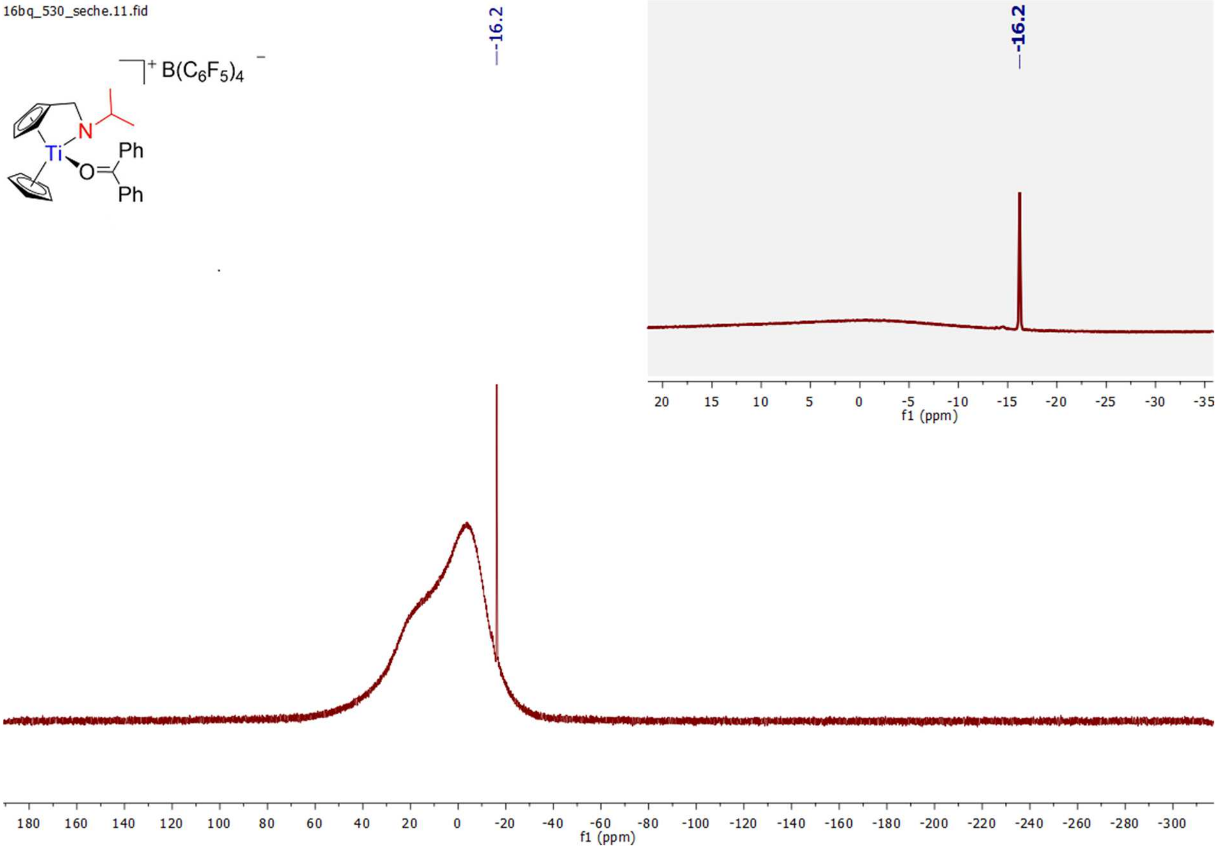
Spectrum 0-305: ^{1}H ^{13}C HMQC of 41 (500.03 MHz / 125.03 MHz, 300 K, bromobenzene-d$_5$)



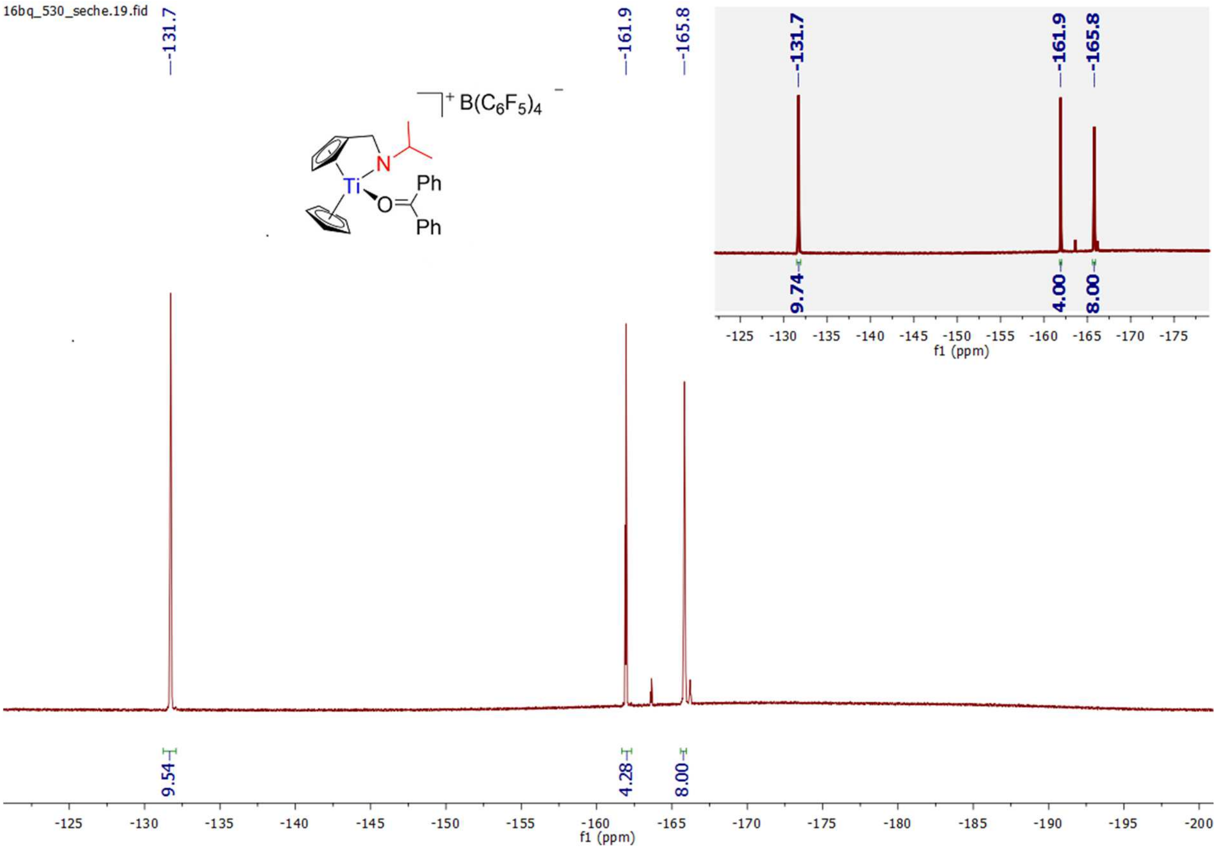
Spectrum 0-306: ^{1}H ^{13}C HMBC of 41 (500.03 MHz / 125.03 MHz, 300 K, bromobenzene-d$_5$)



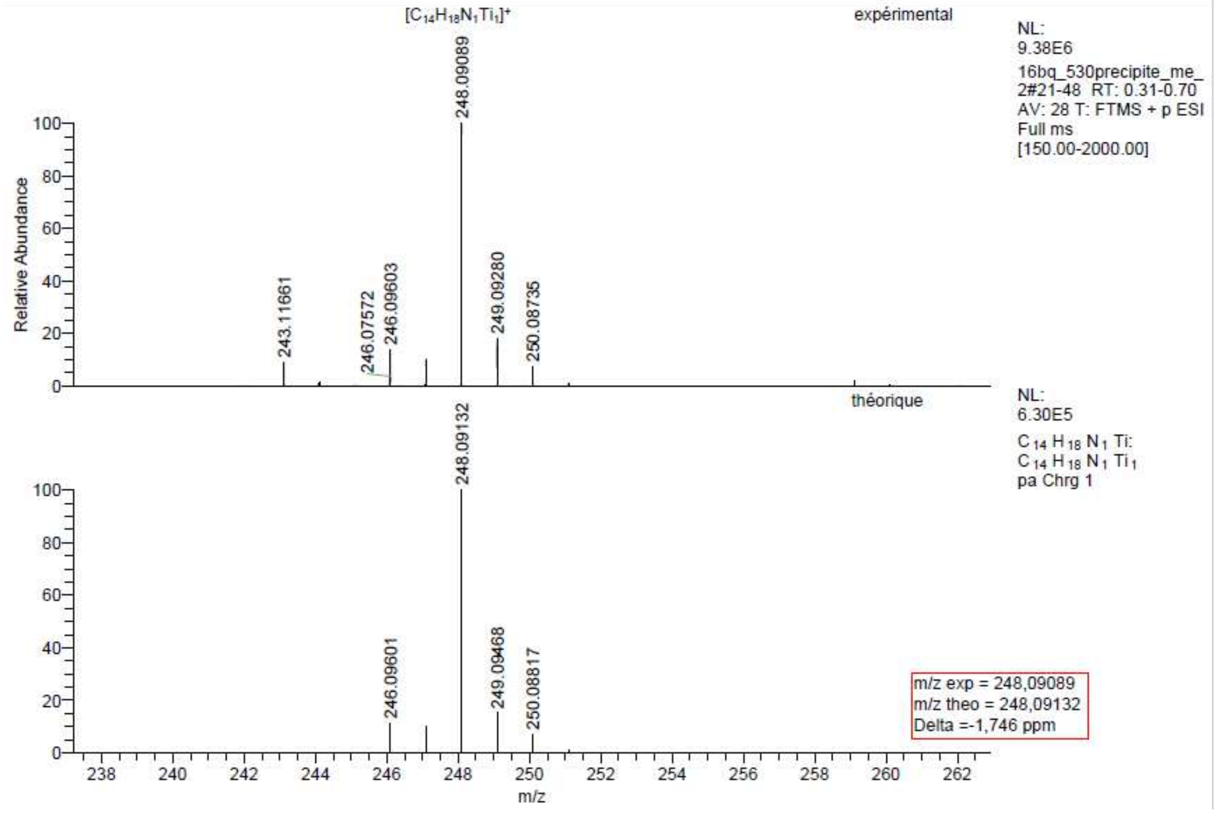
Spectrum 0-307: ^{1}H ^{15}N HMBC of 41 (500.03 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-308: ^{11}B{^{1}H} and ^{11}B (opacified) NMR of 41 (160.42 MHz, 300 K, bromobenzene-d$_5$)

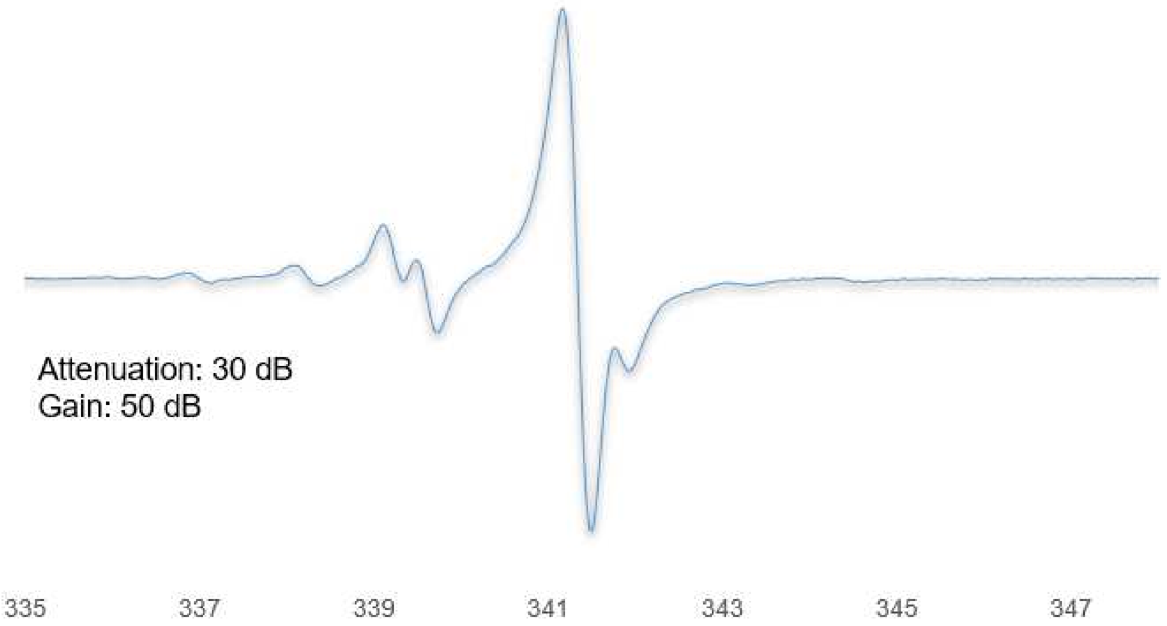


Spectrum 0-309: $^{19}F\{^1H\}$ and ^{19}F (opacified) NMR of 41 (470.45 MHz, 300 K, bromobenzene-d_5)

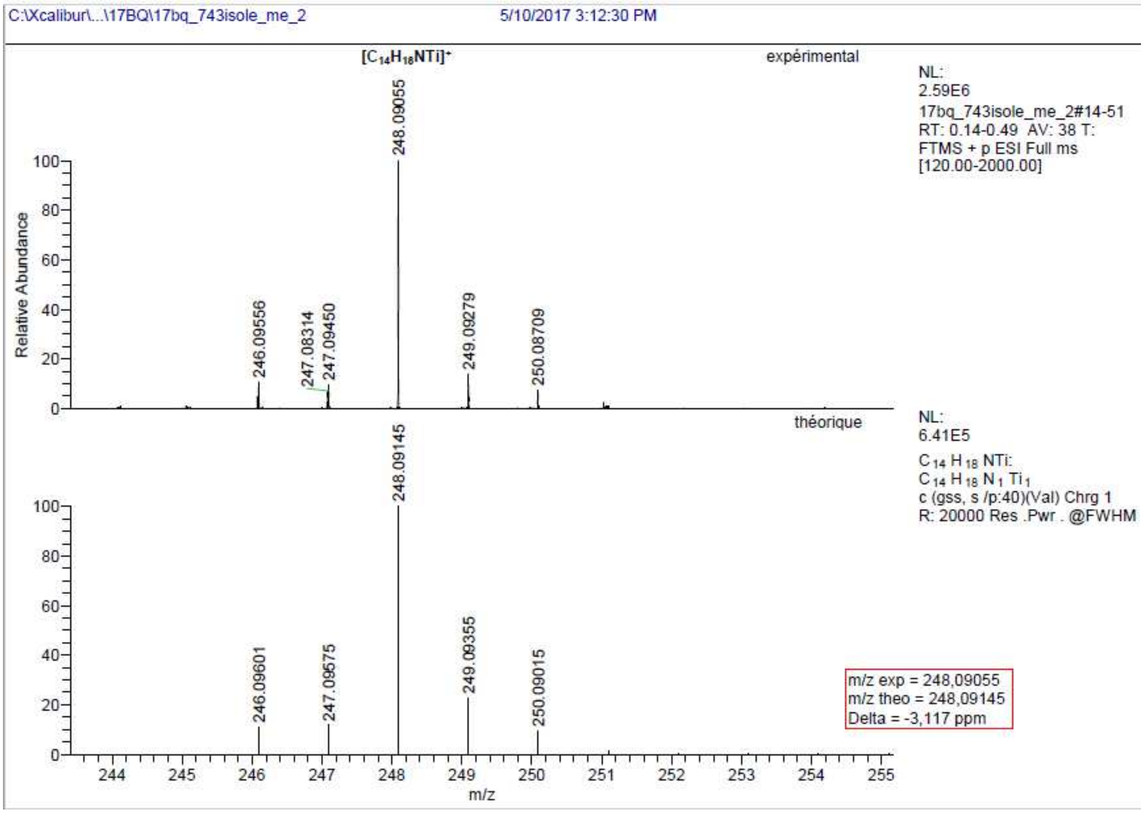


Spectrum 0-310: HRMS of 41

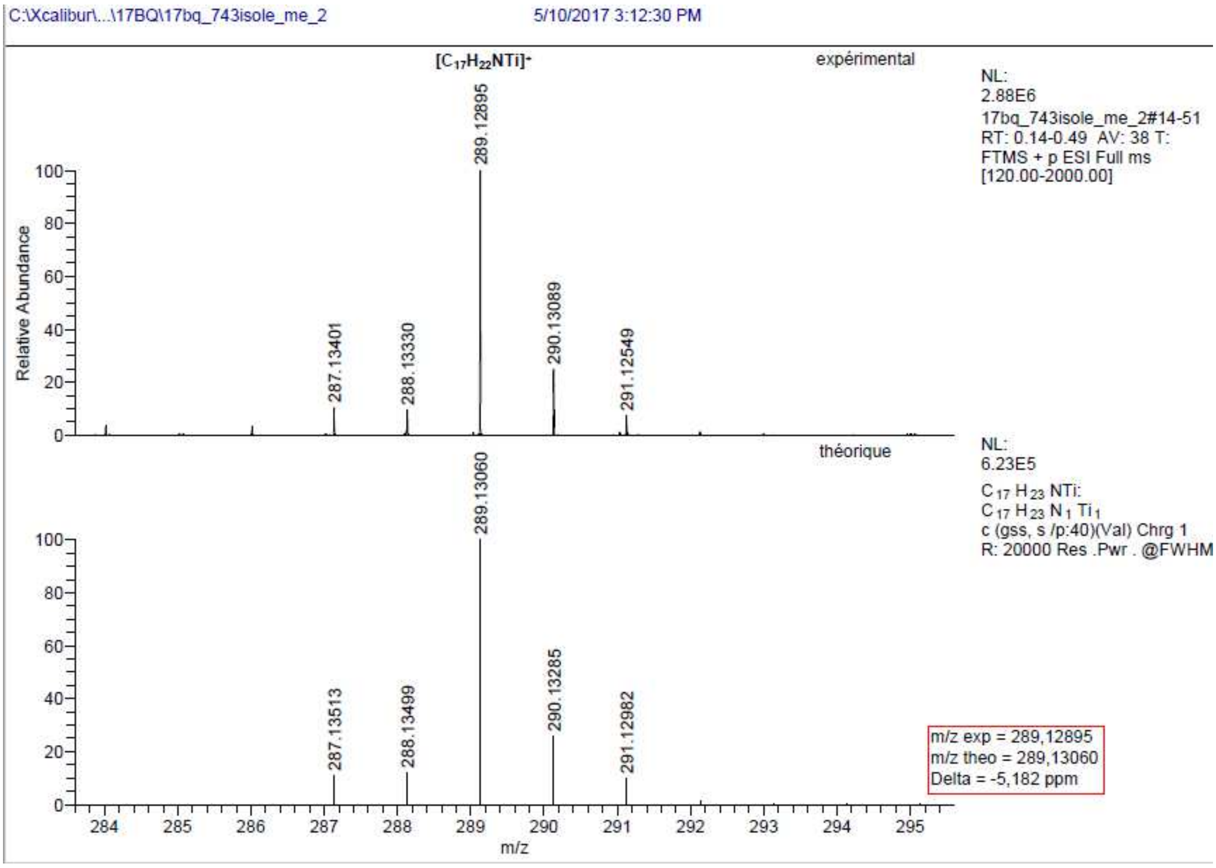
19. Compound **46**-OPEt$_3$:



Spectrum 0-311: EPR of 46-OPEt$_3$ (9.439232 GHz, 300K, bromobenzene)



Spectrum 0-312: HRMS of 46-OPEt$_3$ (Positive mode ESI, bromobenzene)

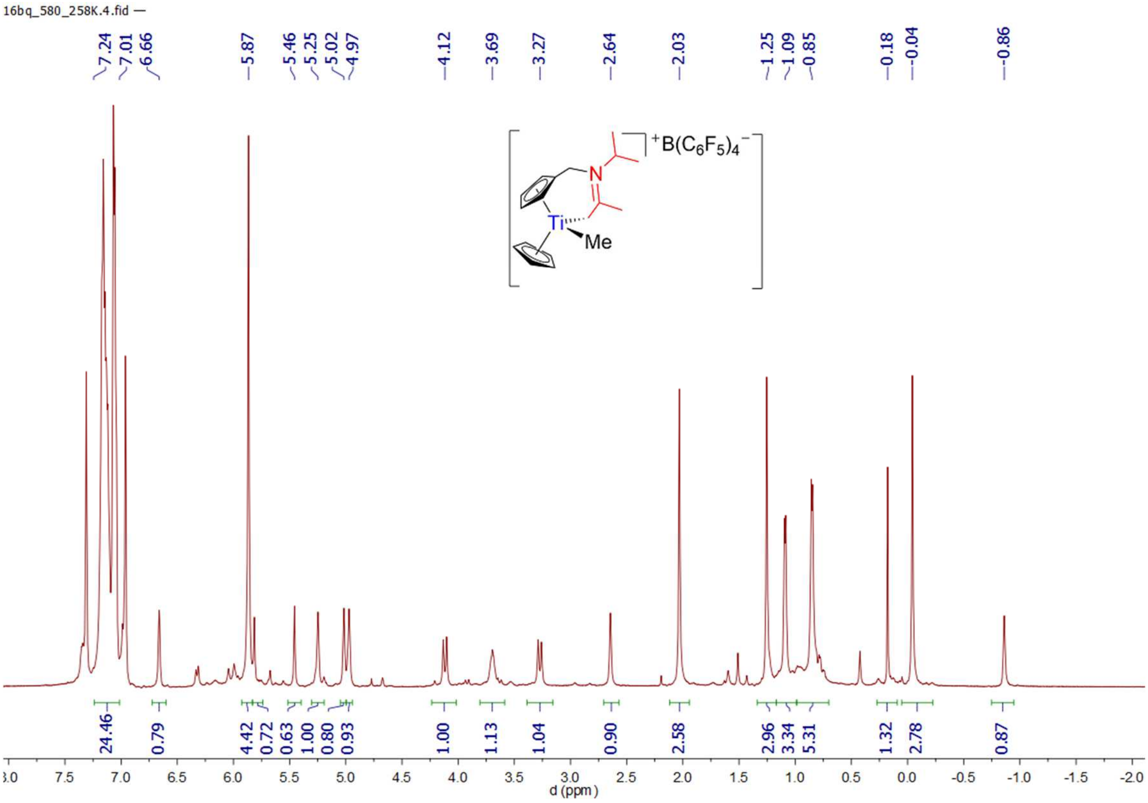


m/z exp = 289,12895
m/z theo = 289,13060
Delta = -5,182 ppm

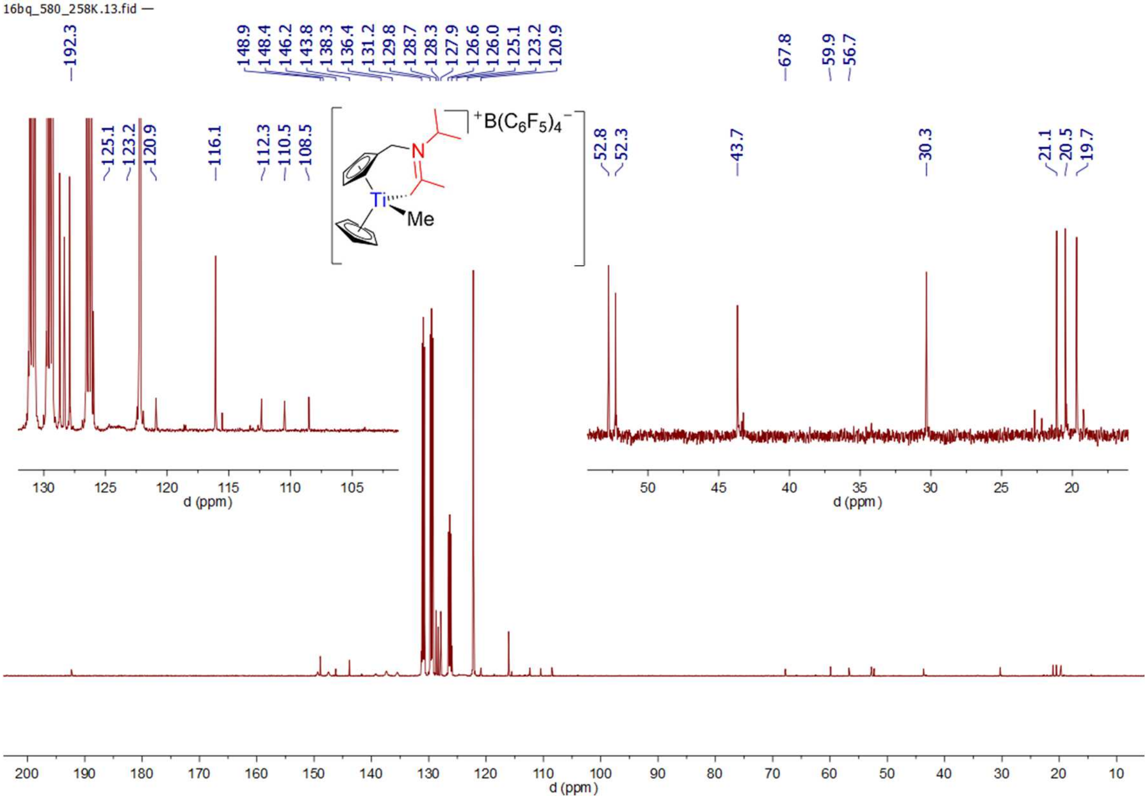
Spectrum 0-313: HRMS of 46-OPEt$_3$ (Positive mode ESI, bromobenzene)

20. Reactivity studies:

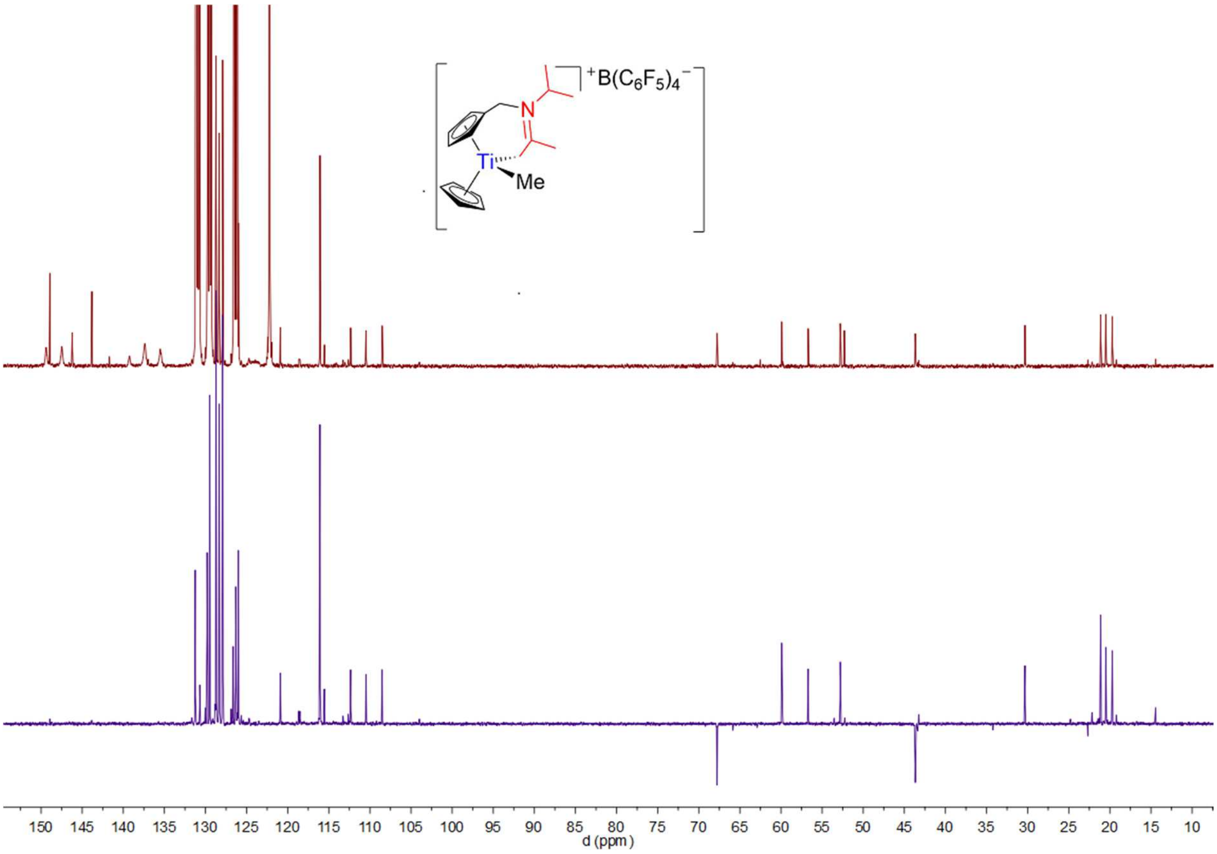
a. In situ characterization of **42**:



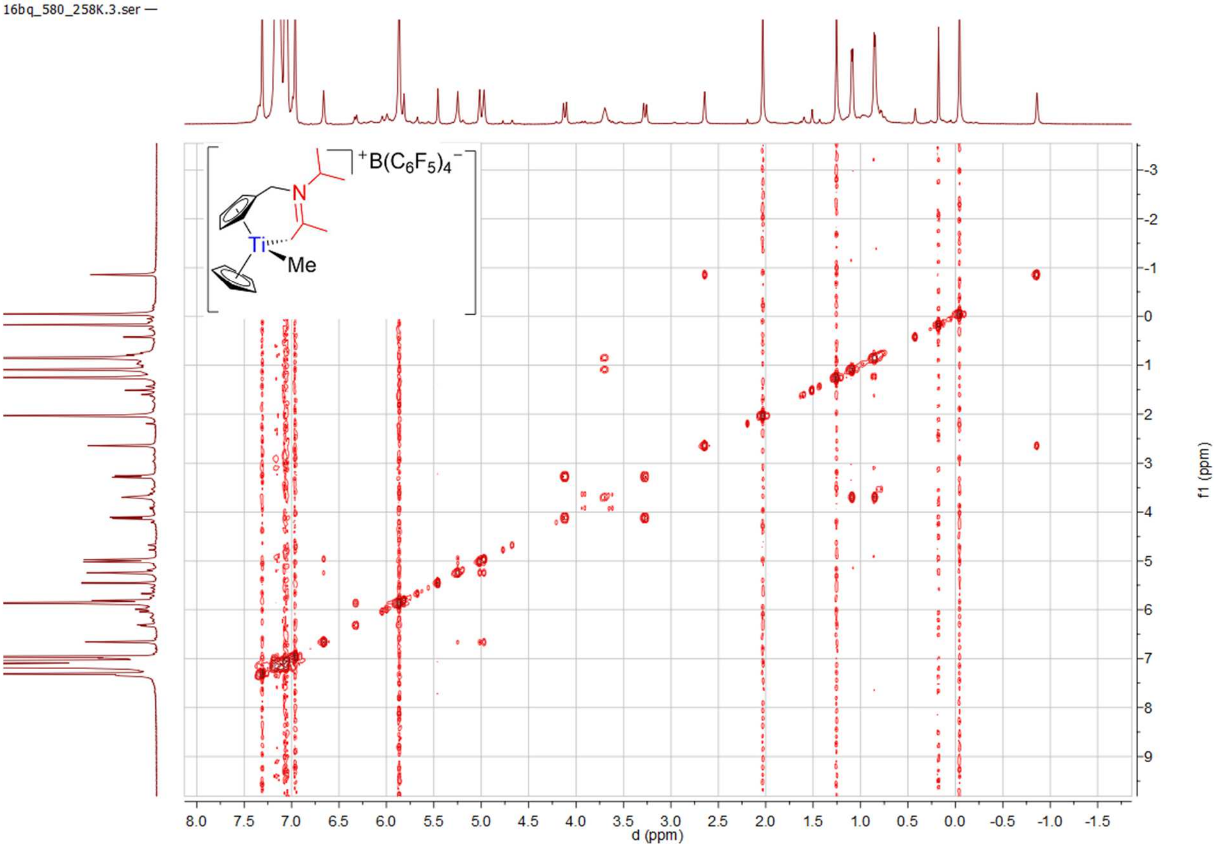
Spectrum 0-314: ^{1}H NMR of 42 (500.03 MHz, 258 K, bromobenzene-d$_5$)



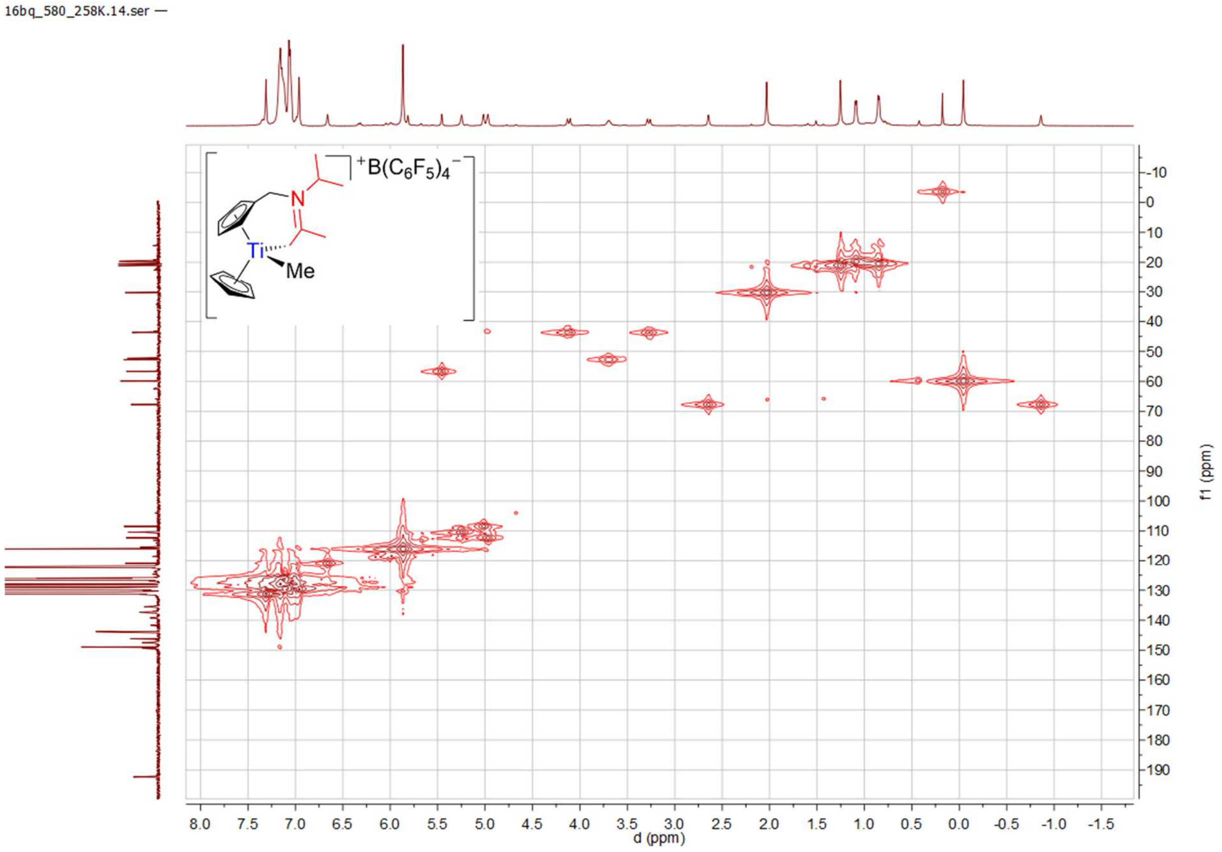
Spectrum 0-315: ^{13}C{^{1}H} NMR of 42 (125.75 MHz, 258 K, bromobenzene-d$_5$)



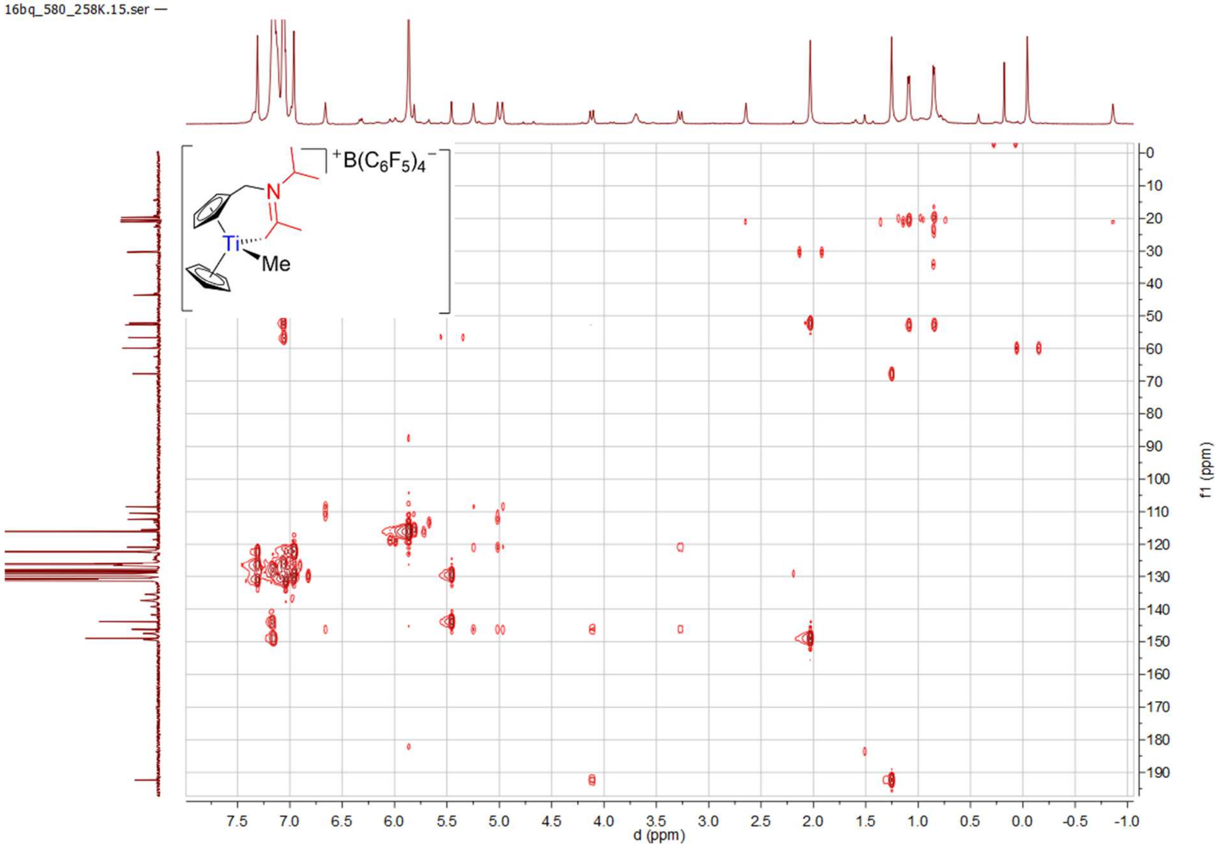
Spectrum 0-316: $^{13}C\{^1H\}$ NMR (top) of 42 correlated with dept135 (bottom) (125.75 MHz, 258 K, bromobenzene-d_5)



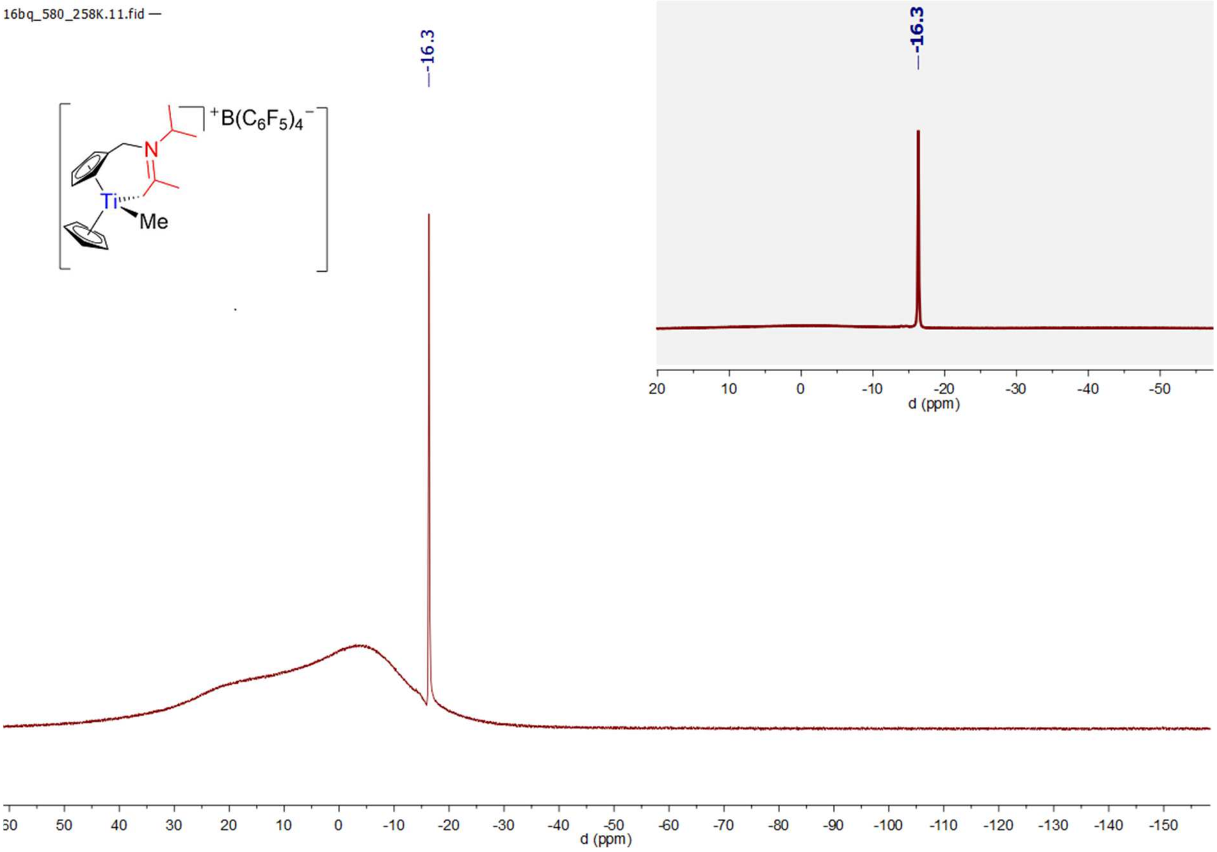
Spectrum 0-317: ^1H ^1H COSY of 42 (500.03 MHz, 300 K, 258 K, bromobenzene-d_5)



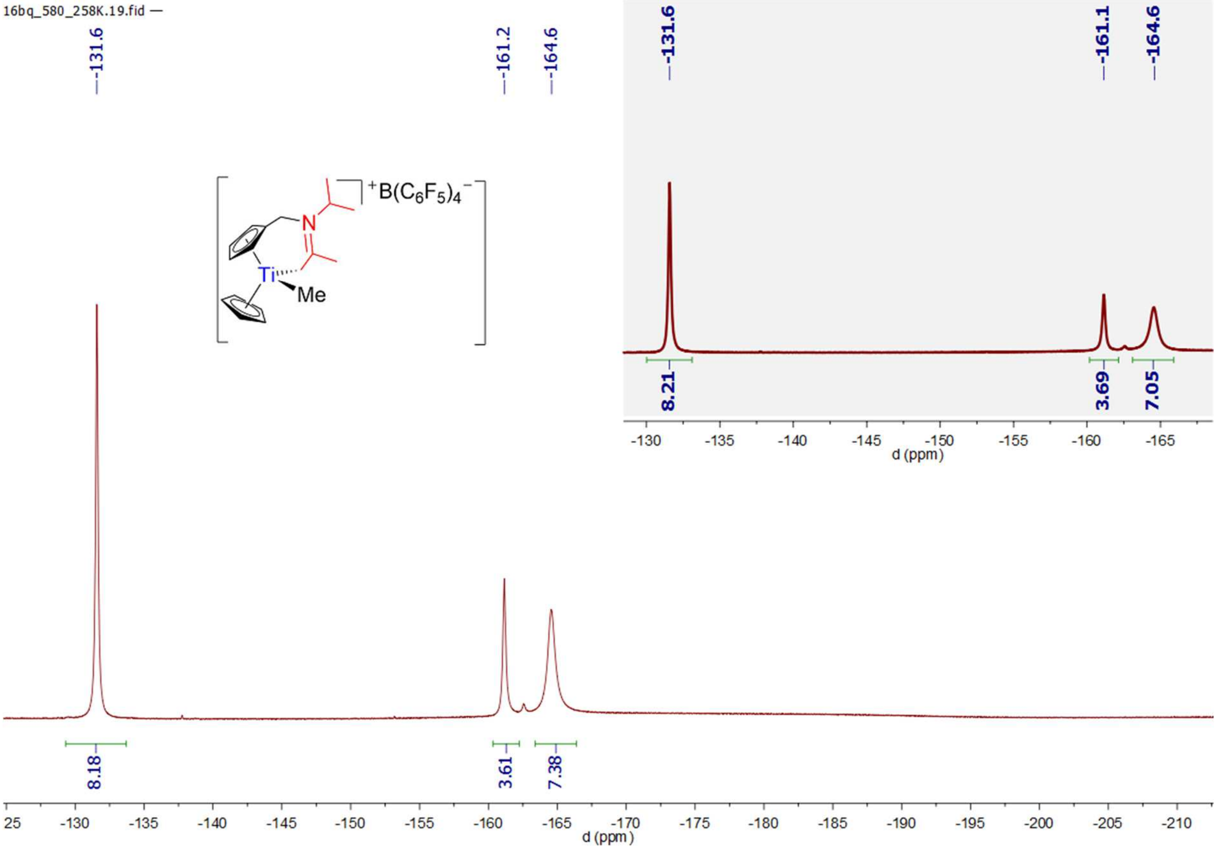
Spectrum 0-318: ^{1}H ^{13}C HMQC of 42 (600.23 MHz / 150.94 MHz, 258 K, bromobenzene-d$_5$)



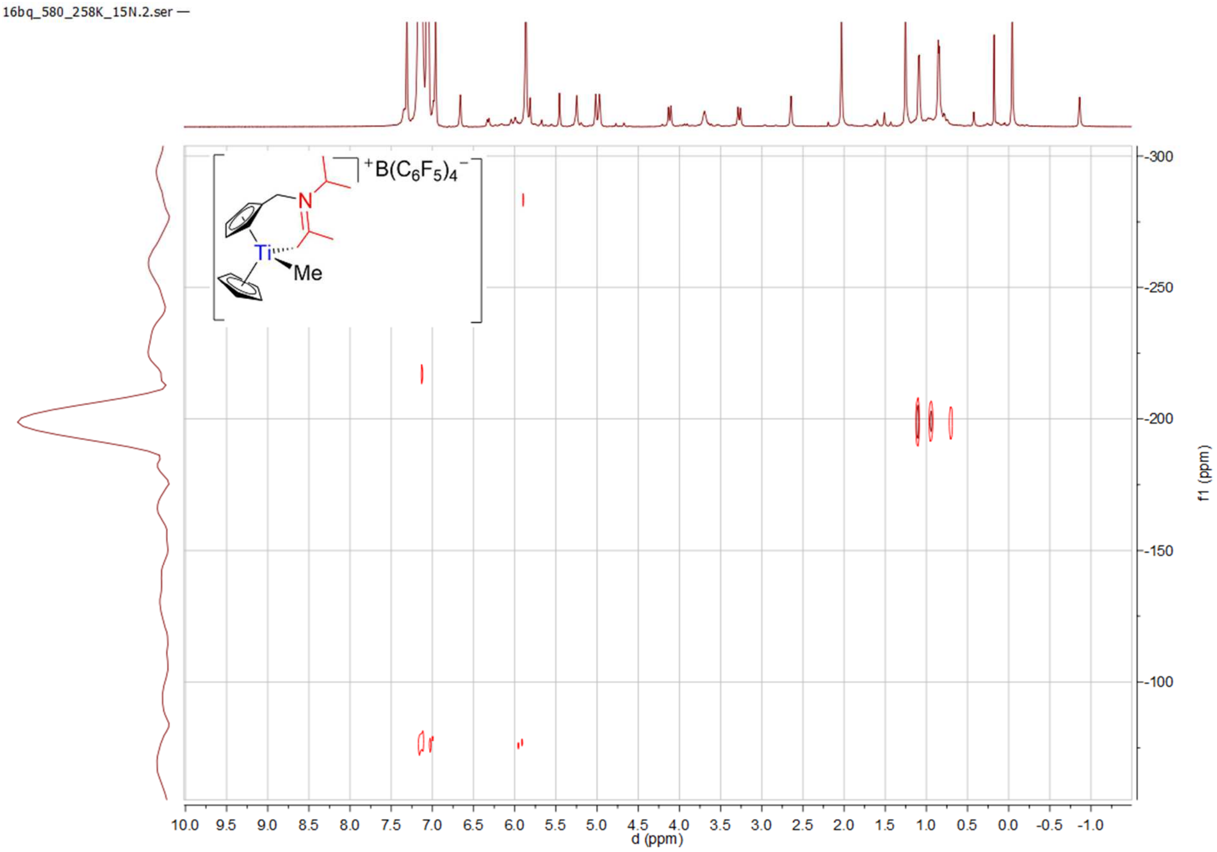
Spectrum 0-319: ^{1}H ^{13}C HMBC of 42 (600.23 MHz / 150.94 MHz, 258 K, bromobenzene-d$_5$)



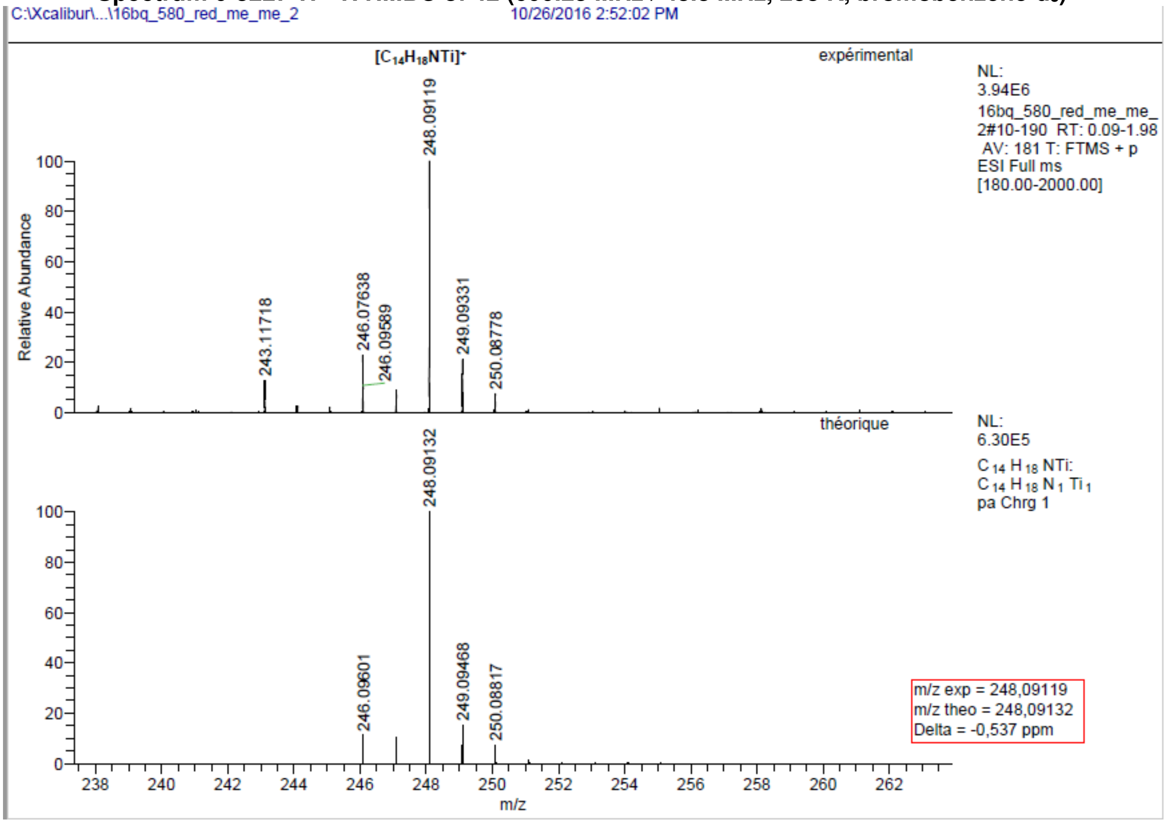
Spectrum 0-320: $^{11}B\{^1H\}$ and ^{11}B(opacified) NMR of 42 (160.42 MHz, 258 K, bromobenzene-d$_5$)



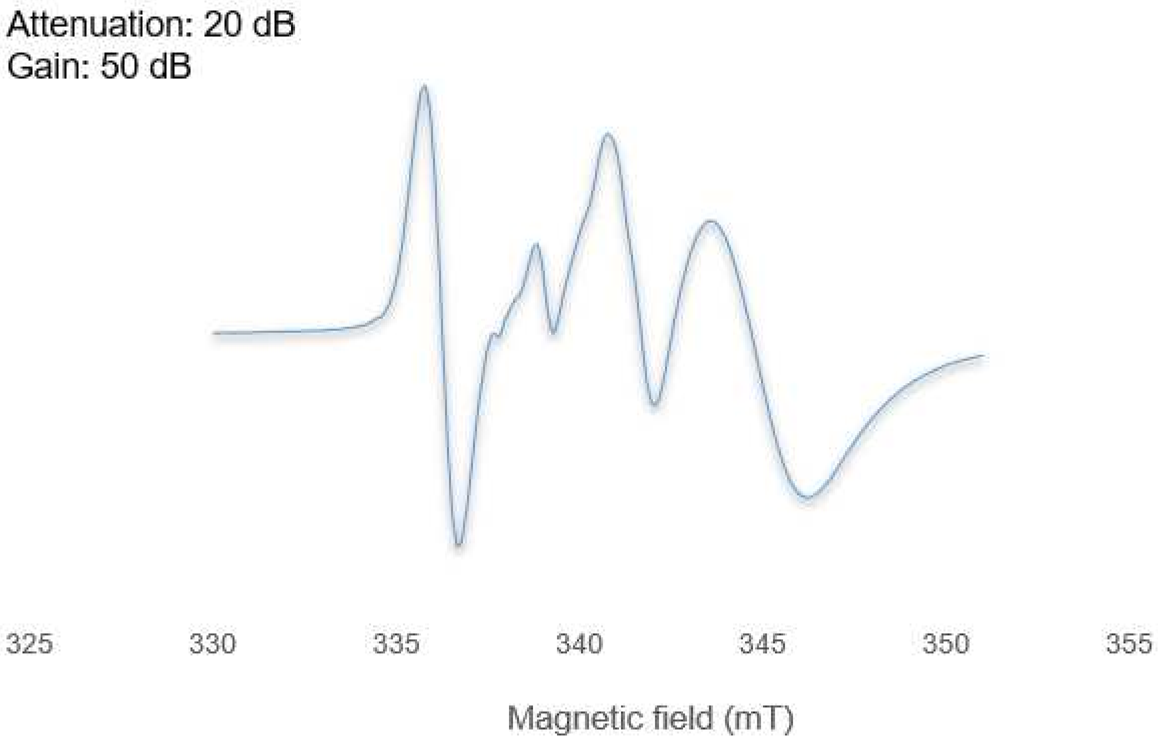
Spectrum 0-321: $^{19}F\{^1H\}$ and ^{19}F(opacified) NMR of 42 (470.45 MHz, 258 K, bromobenzene-d$_5$)



Spectrum 0-322: ^{1}H ^{15}N HMBC of 42 (600.23 MHz / 43.3 MHz, 258 K, bromobenzene-d$_5$)

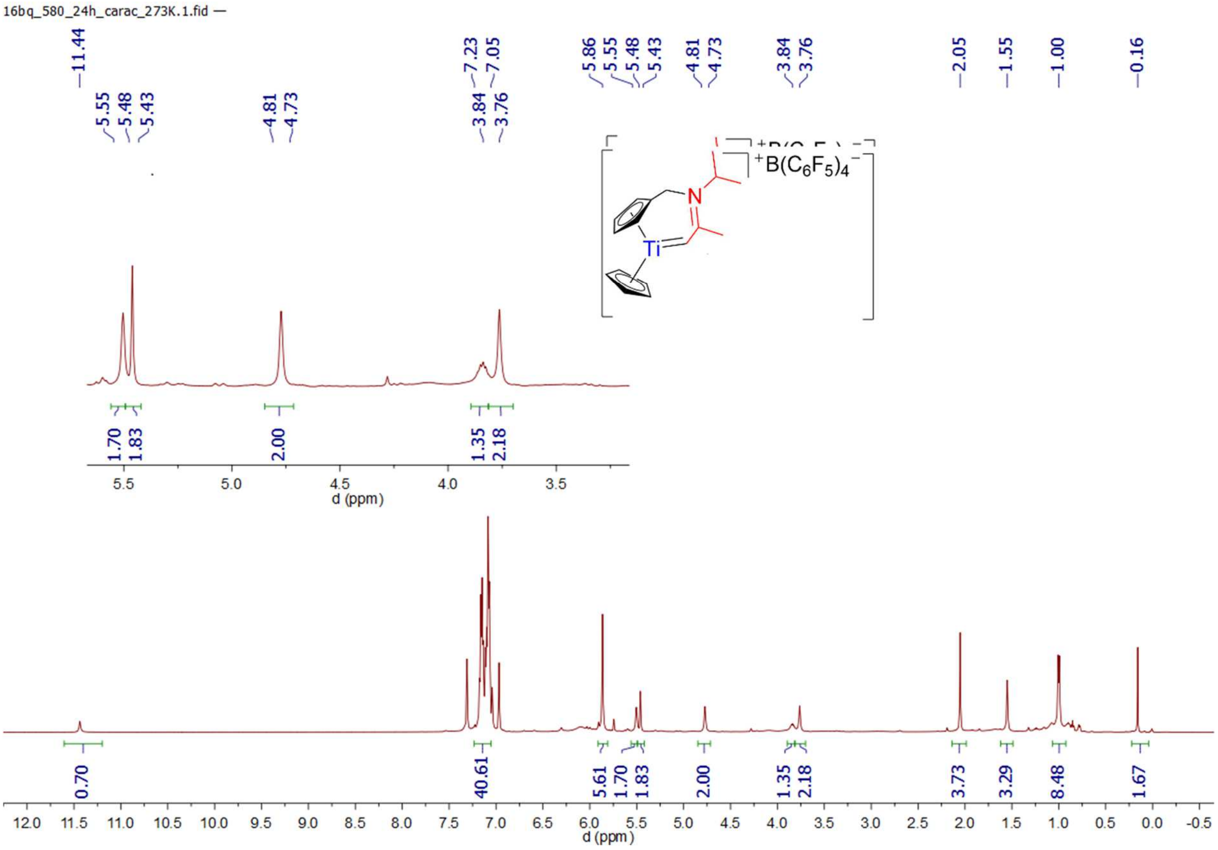


Spectrum 0-323: HRMS of 42 (Positive mode ESI, bromobenzene)

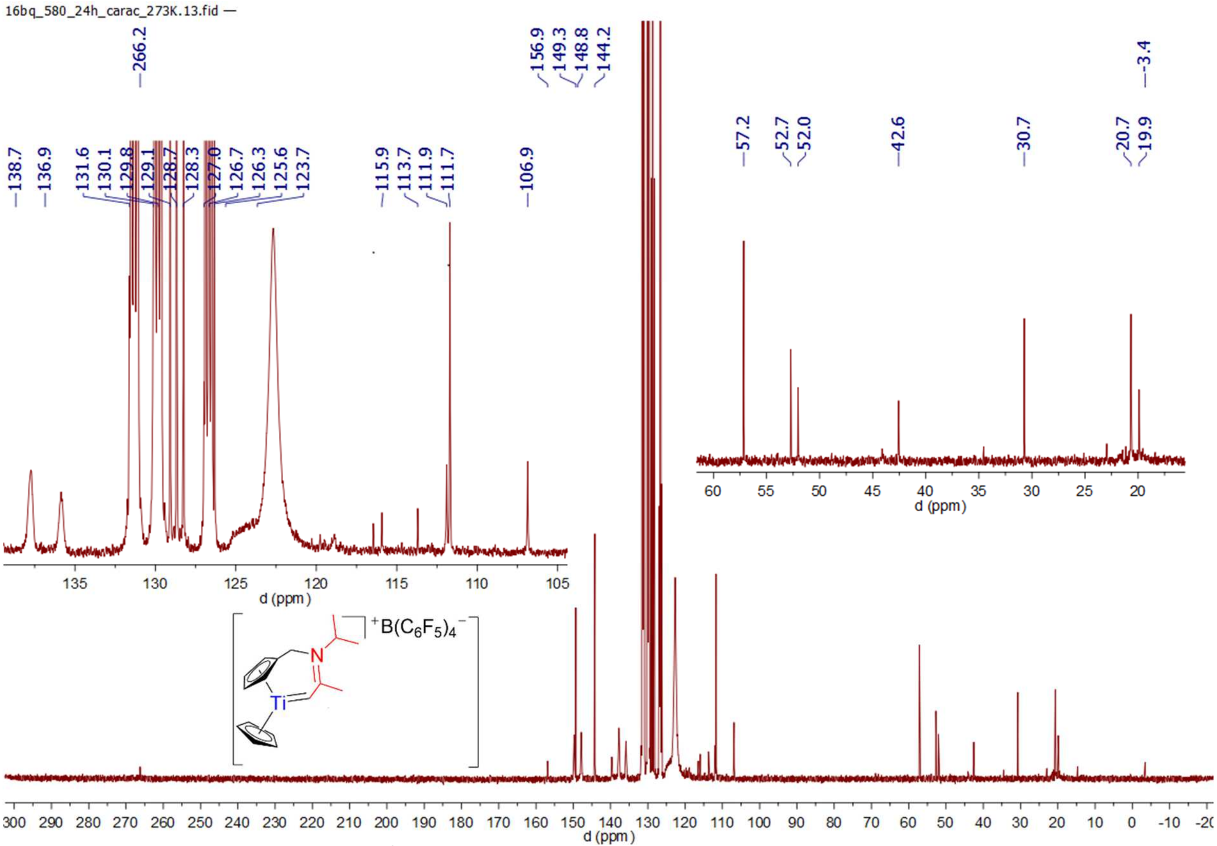


Spectrum 0-324: EPR spectrum of 42 (9.9.428487 GHz, 295K, bromobenzene)

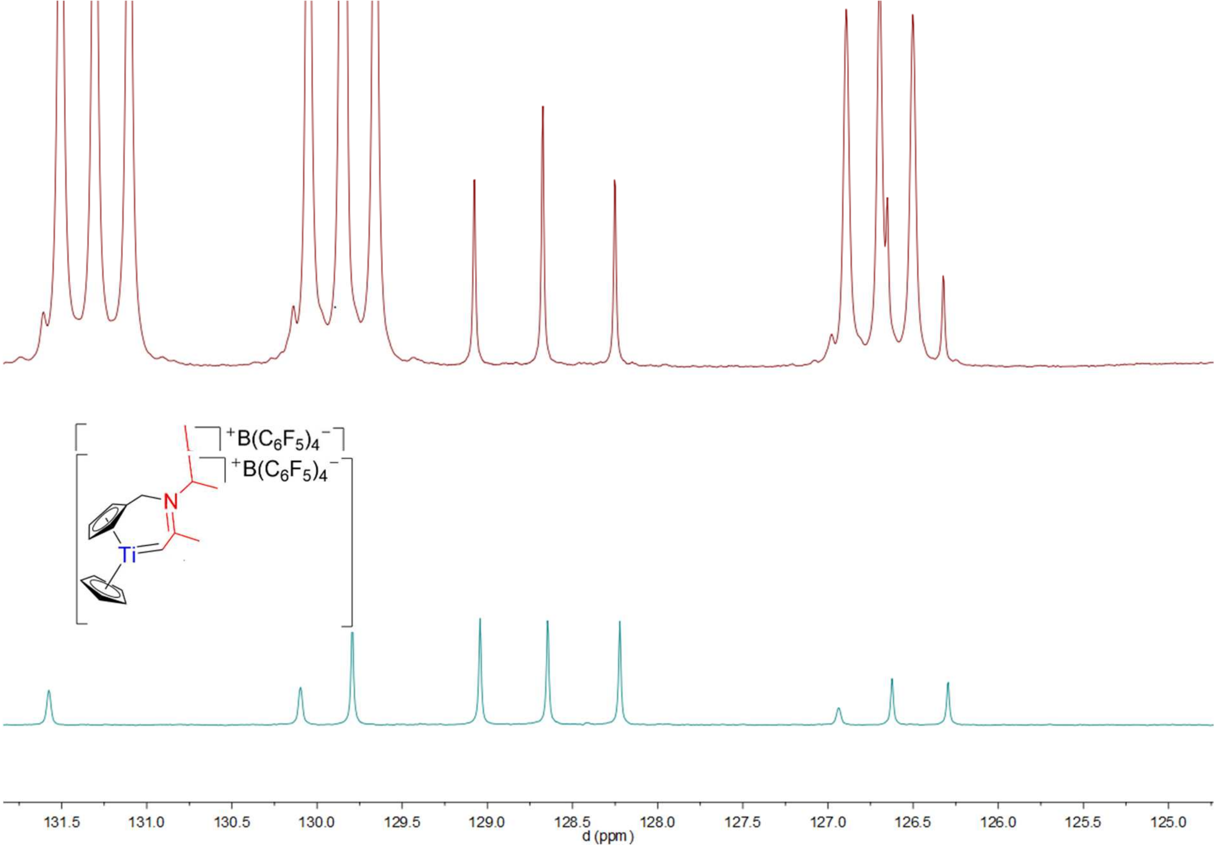
b. In situ characterization of **43**:



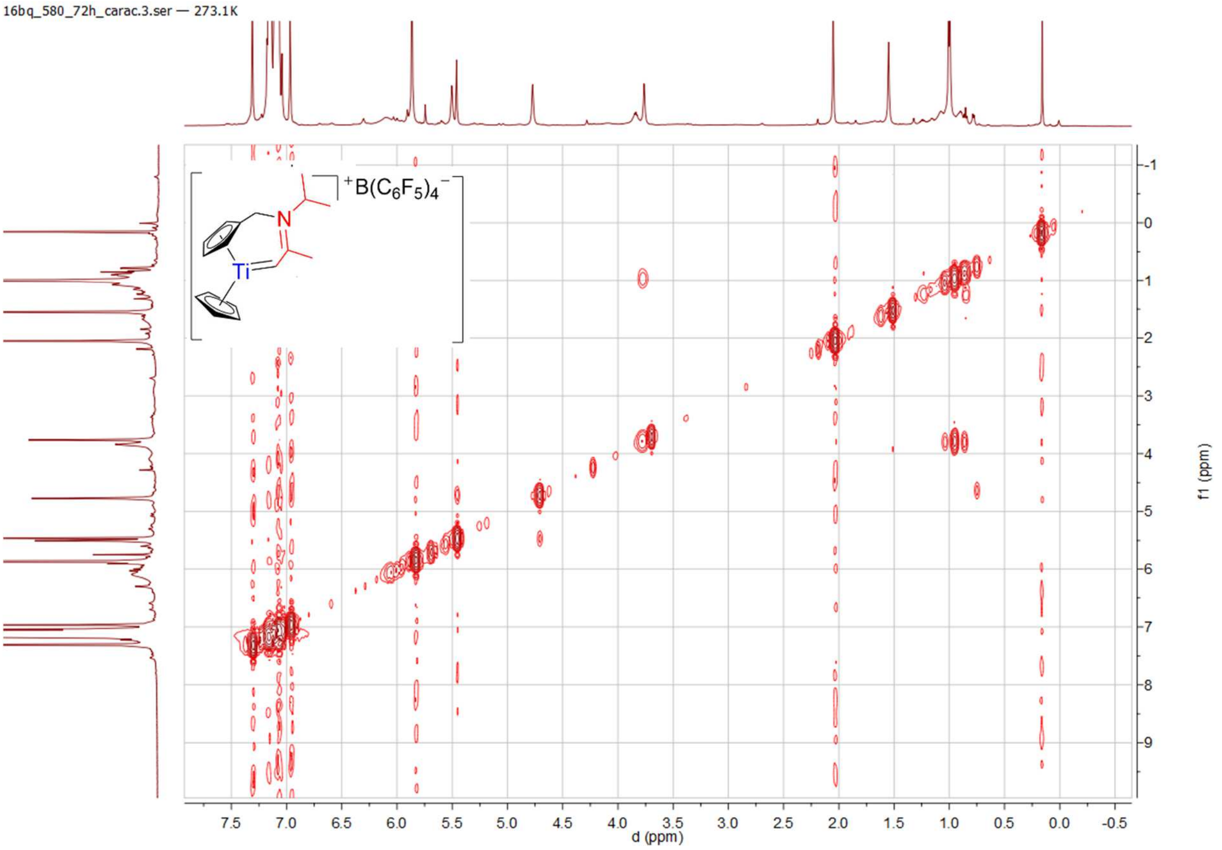
Spectrum 0-325: ^{1}H NMR of 43 (500.03 MHz, 273 K, bromobenzene-d$_5$)



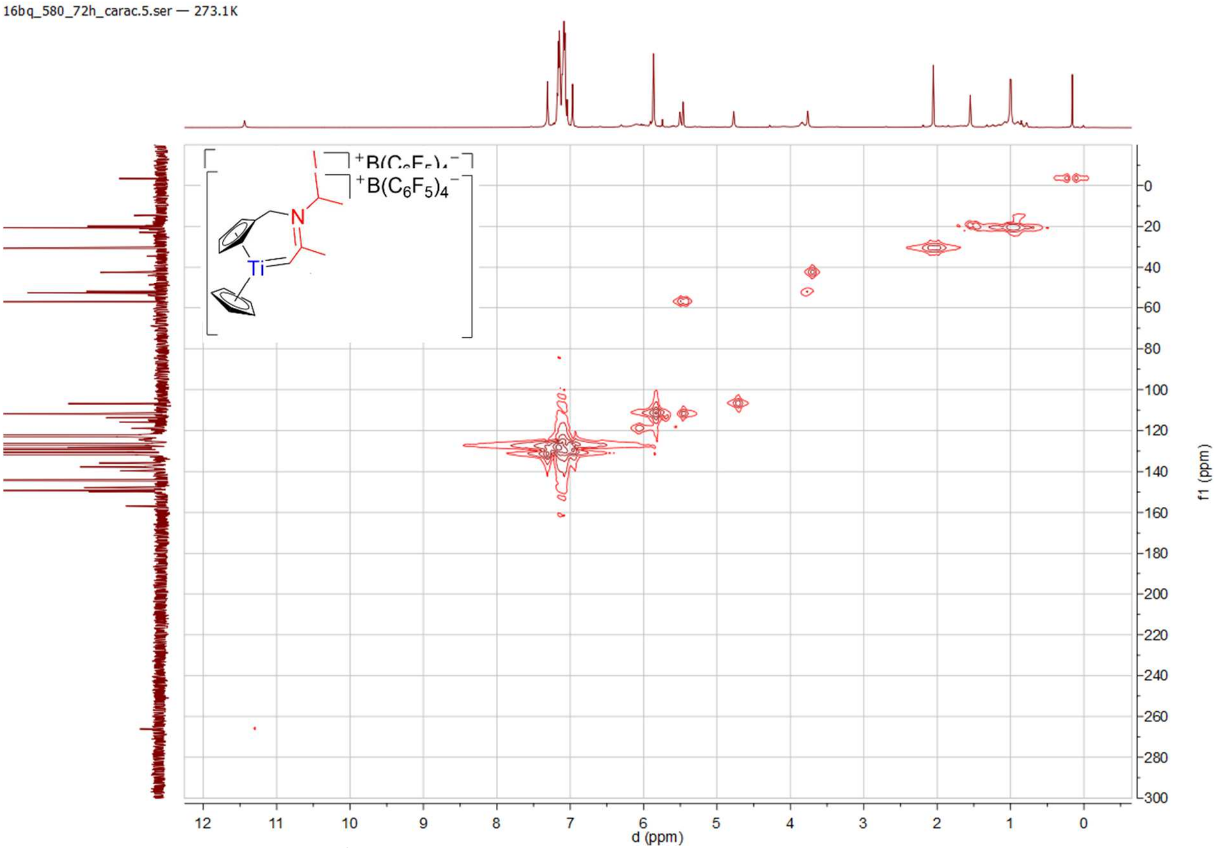
Spectrum 0-326: $^{13}C\{^{1}H\}$ NMR of 43 (125.75 MHz, 273 K, bromobenzene-d_5)



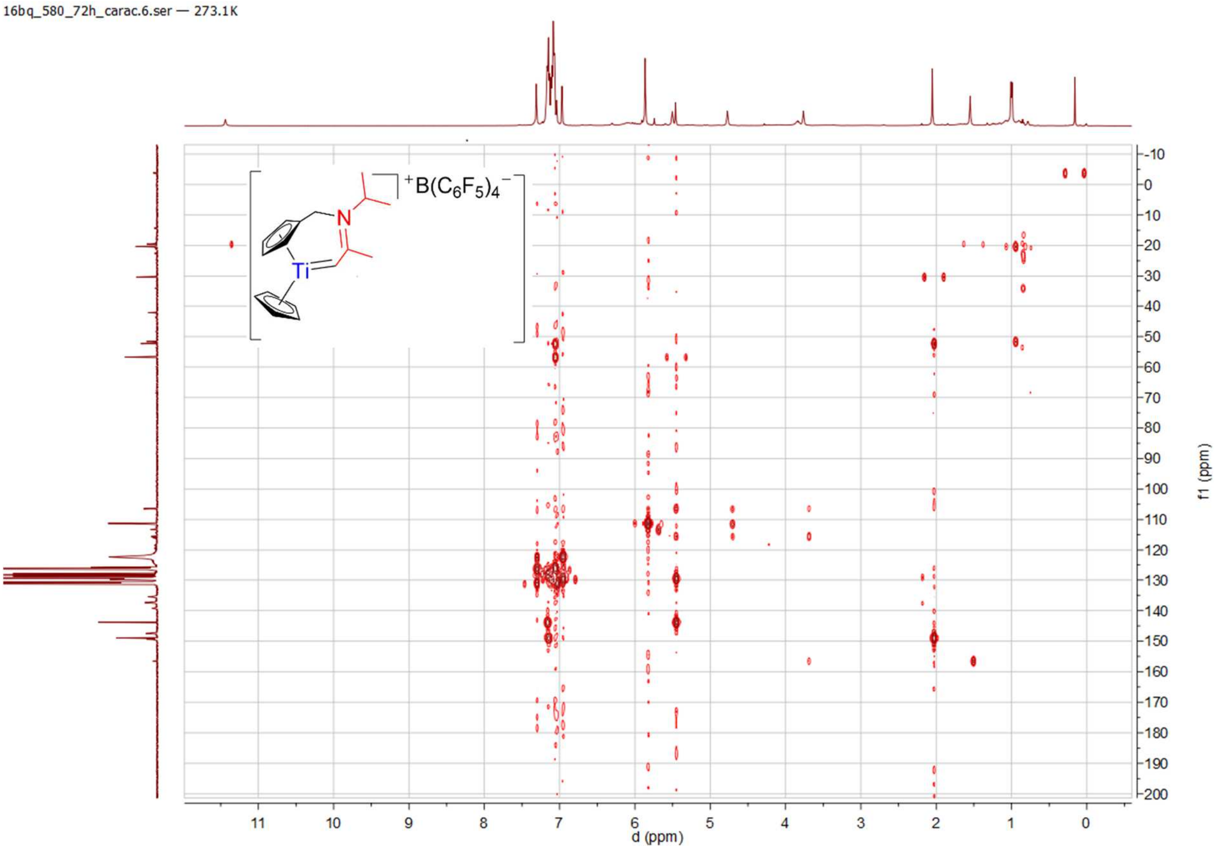
Spectrum 0-327: $^{13}C\{^{1}H\}$ NMR of 43 (top) correlated with dept 135 (bottom) (25.75 MHz, 273 K, bromobenzene-d_5)



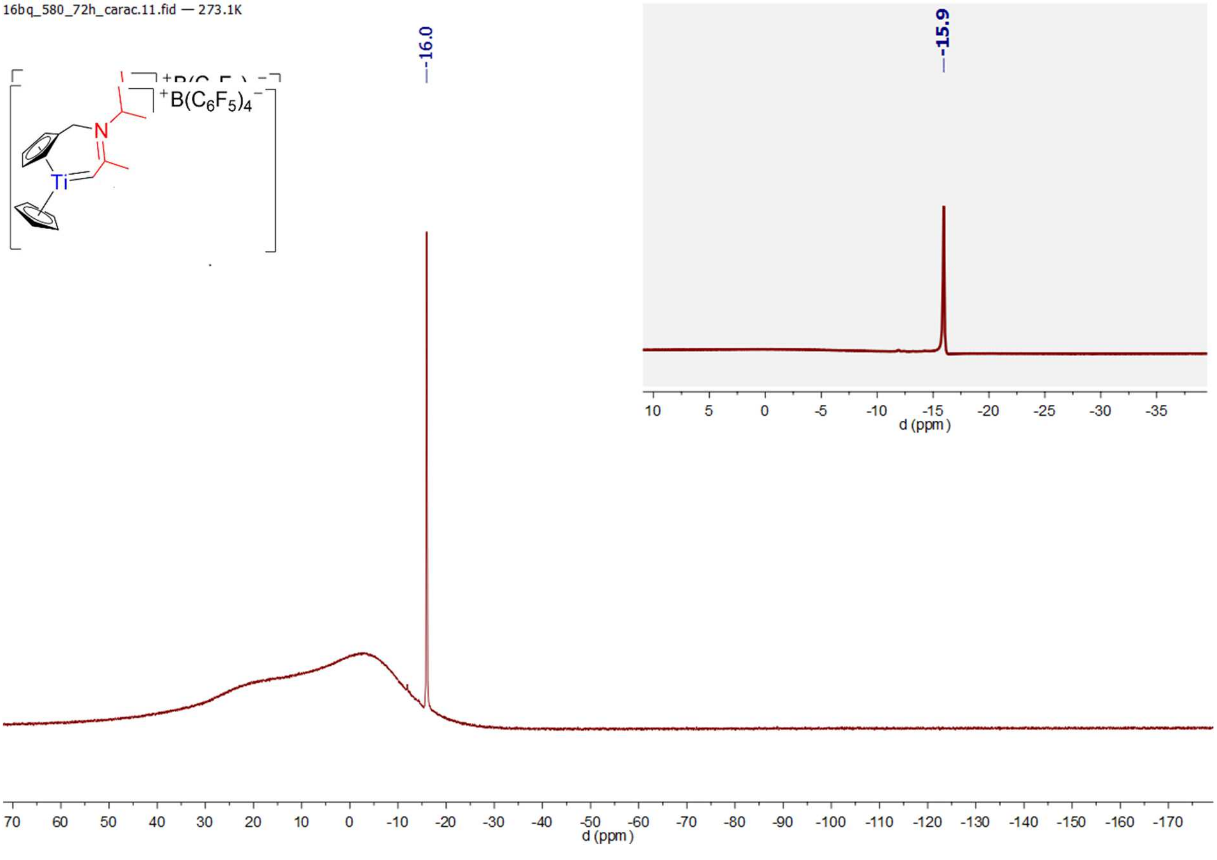
Spectrum 0-328: ^{1}H ^{1}H COSY of 43 (500.03 MHz, 273 K, bromobenzene-d$_5$)



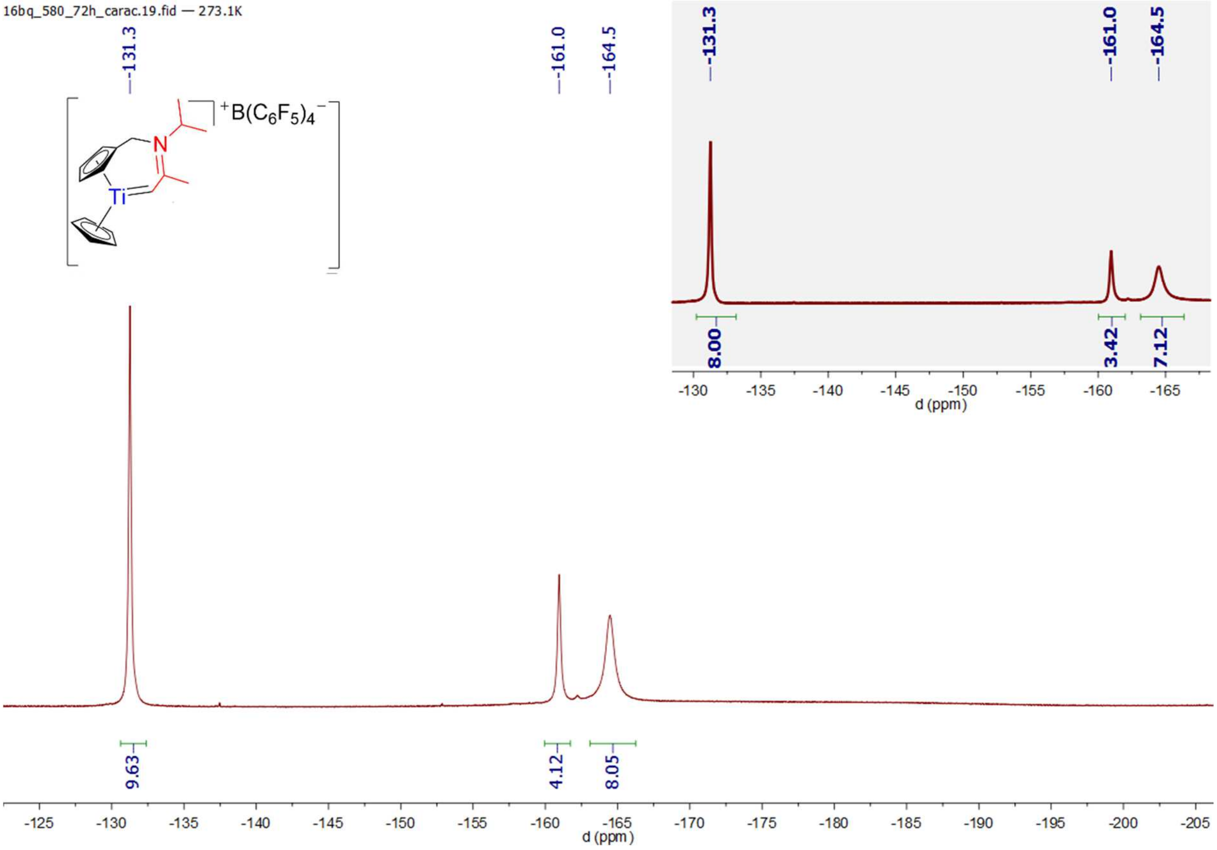
Spectrum 0-329: ^{1}H ^{13}C HMQC of 43 (600.23 MHz / 150.94 MHz, 273 K, bromobenzene-d$_5$)



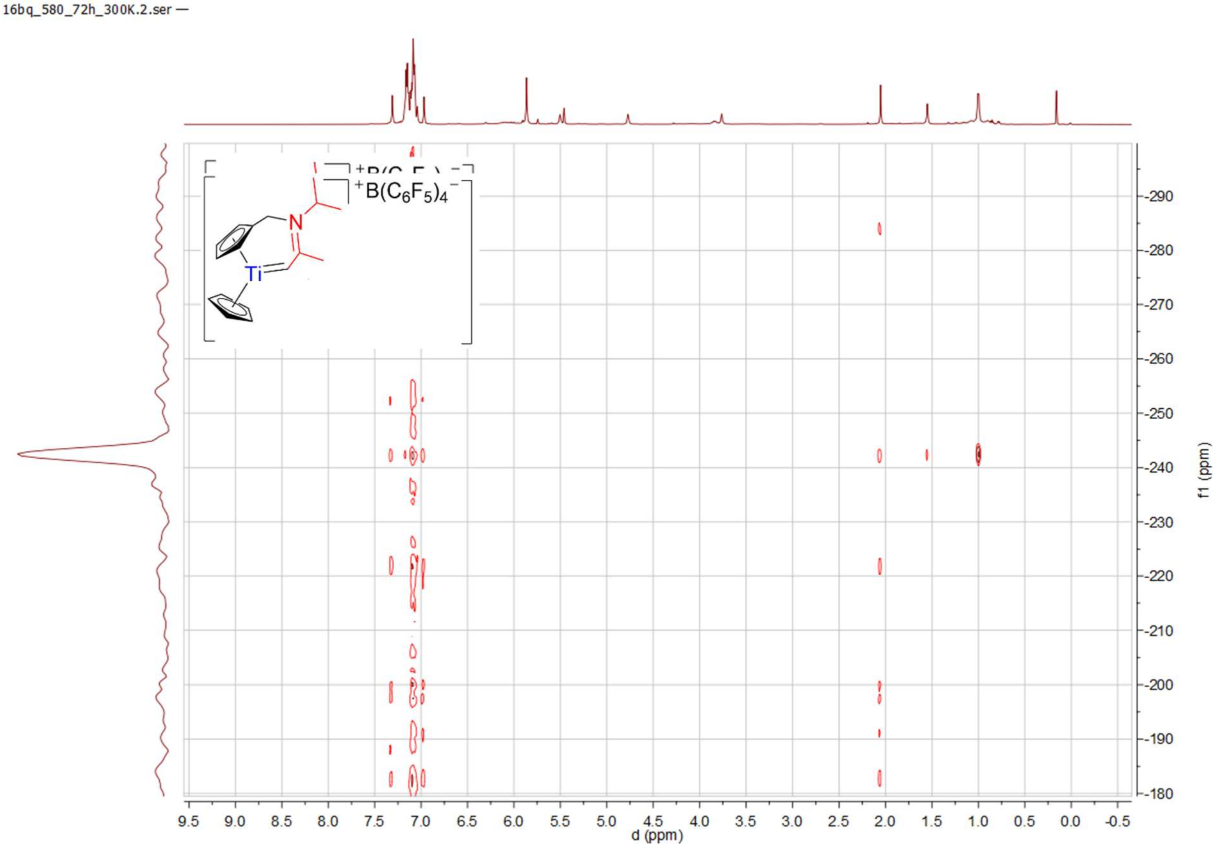
Spectrum 0-330: ^{1}H ^{13}C HMBC of 43 (600.23 MHz / 150.94 MHz, 273 K, bromobenzene-d_5)



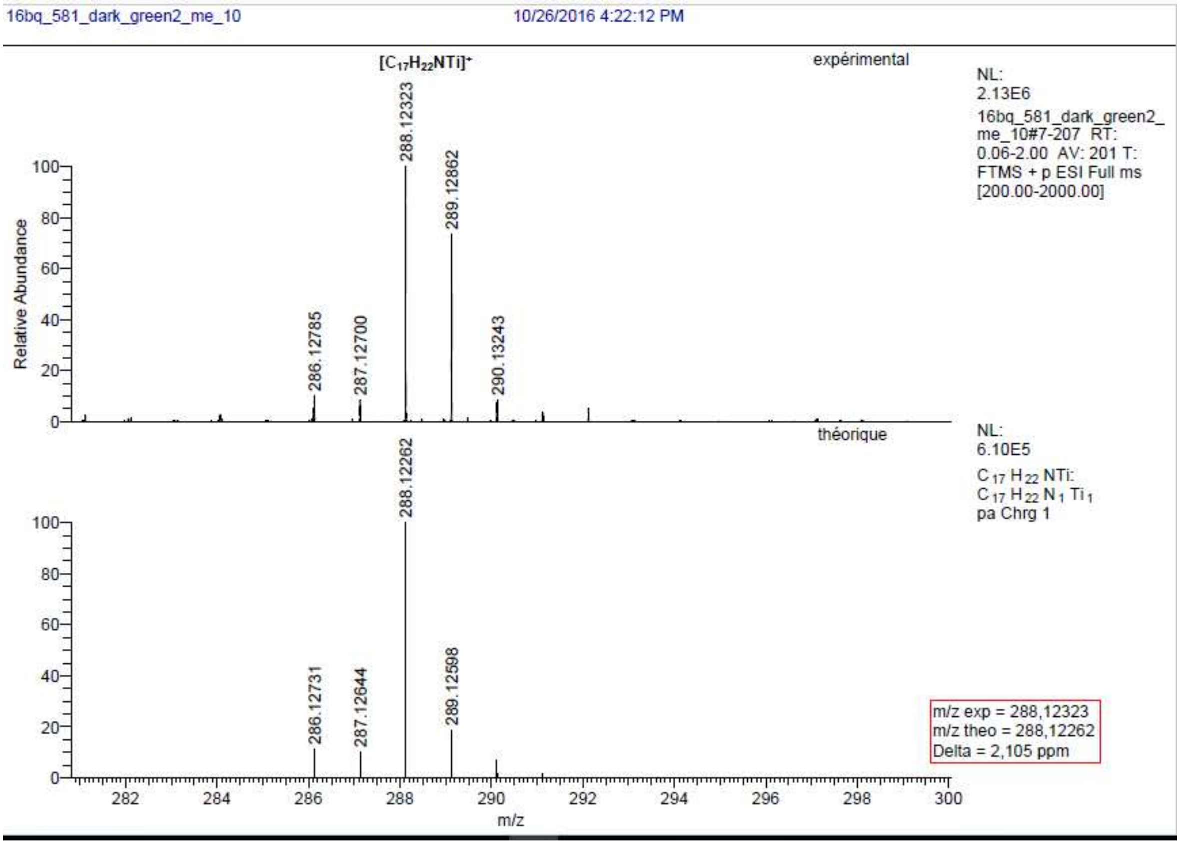
Spectrum 0-331: ^{11}B{^{1}H} and ^{11}B(opacified) NMR of 43 (160.42 MHz, 273 K, bromobenzene-d_5)



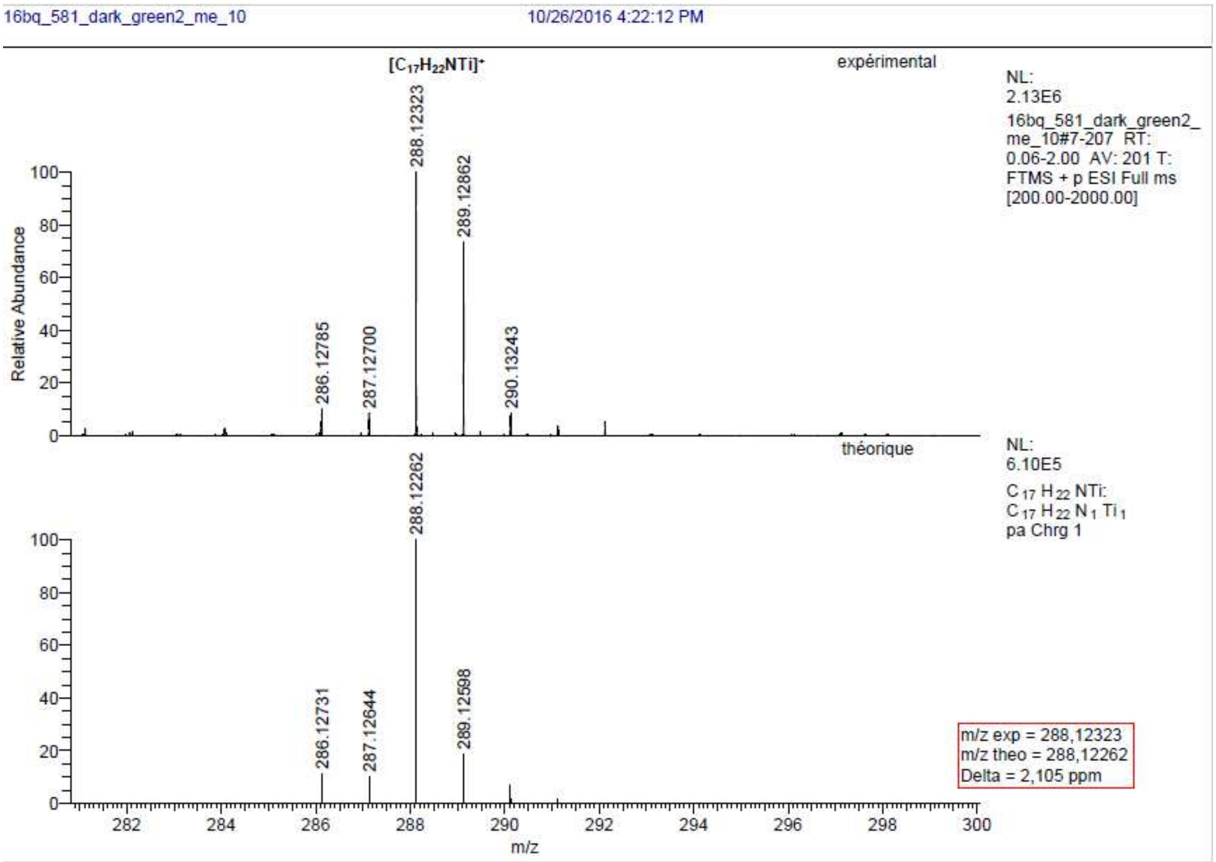
Spectrum 0-332: $^{19}F\{^{1}H\}$ and ^{19}F(opacified) NMR of 43 (470.45 MHz, 273 K, bromobenzene-d_5)



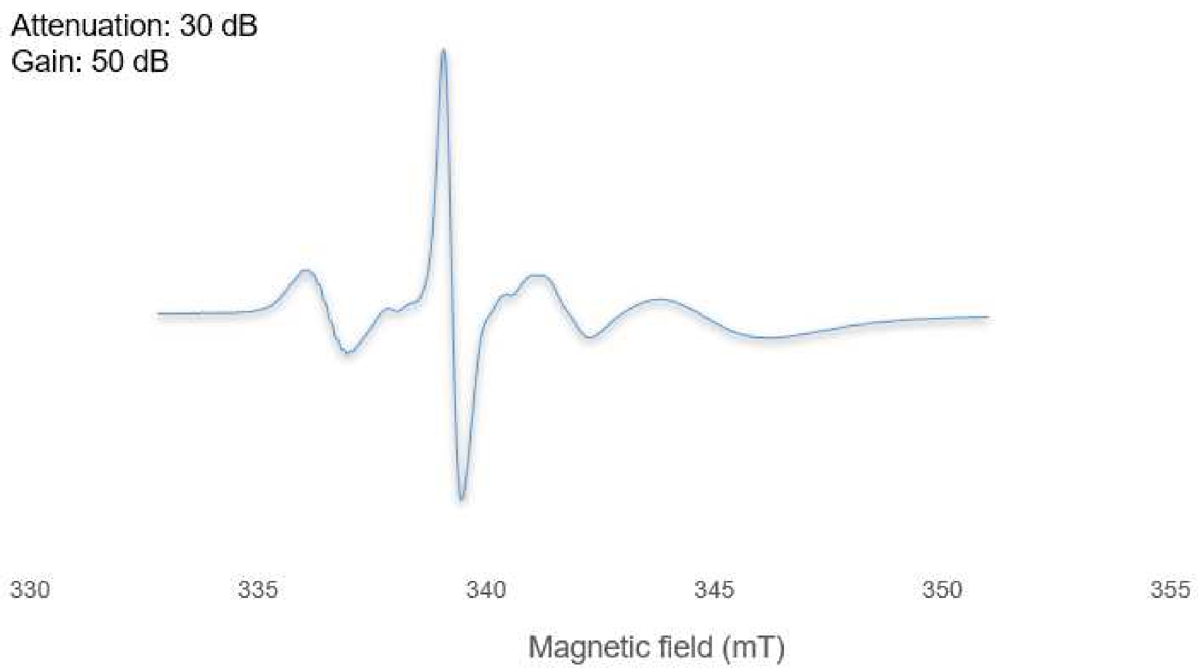
Spectrum 0-333: ^{1}H ^{15}N HMBC of 43 (600.23 MHz / 43.3 MHz, 273 K, bromobenzene-d_5)



Spectrum 0-334: HRMS of 43 (Positive mode ESI, bromobenzene)

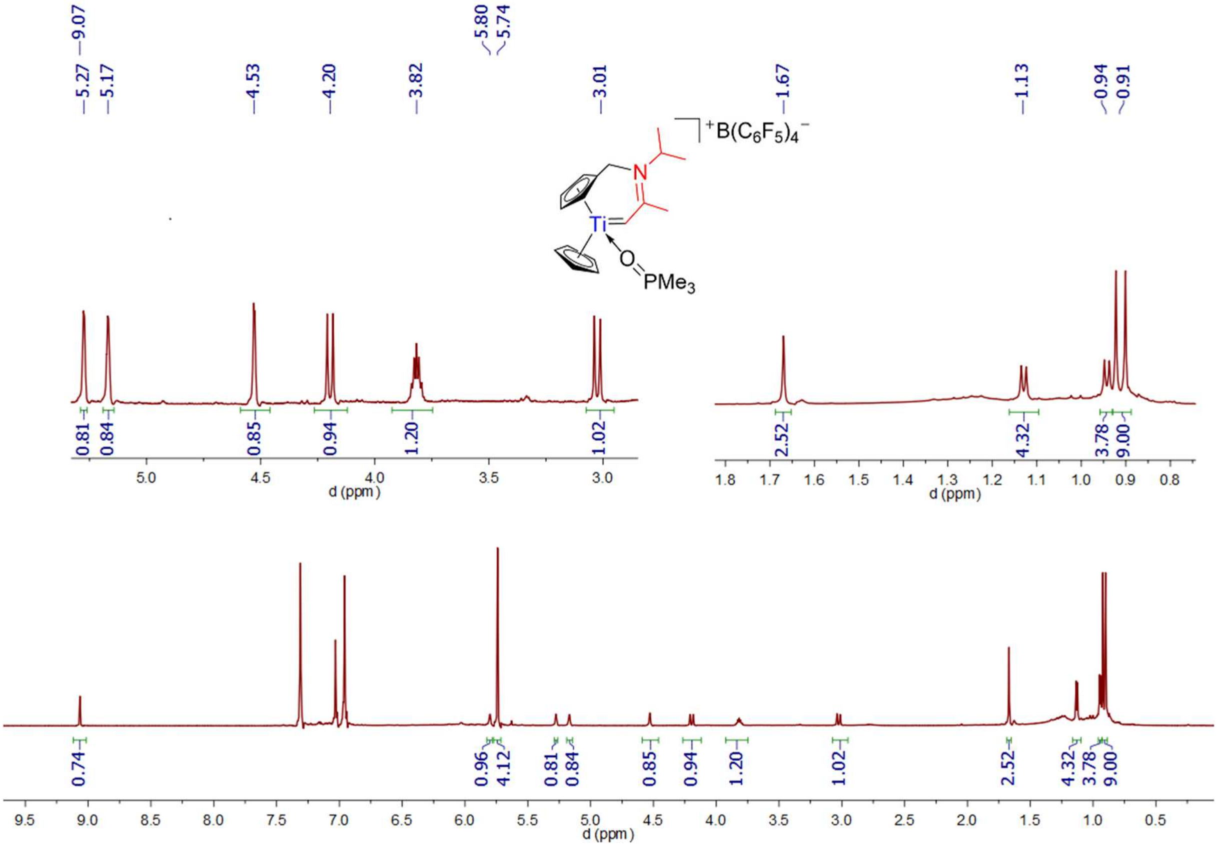


Spectrum 0-335: HRMS of 43 (Positive mode ESI, bromobenzene)

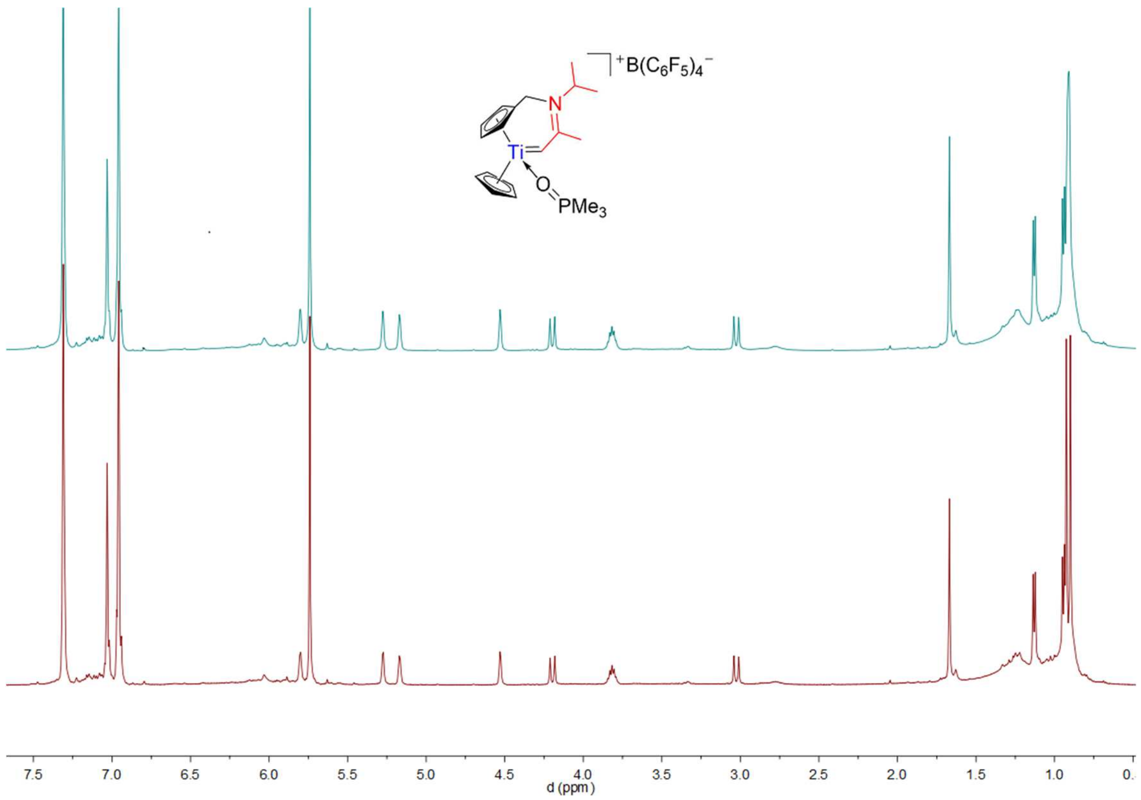


Spectrum 0-336: EPR spectrum of 43 (9.436937 GHz, 295K, bromobenzene)

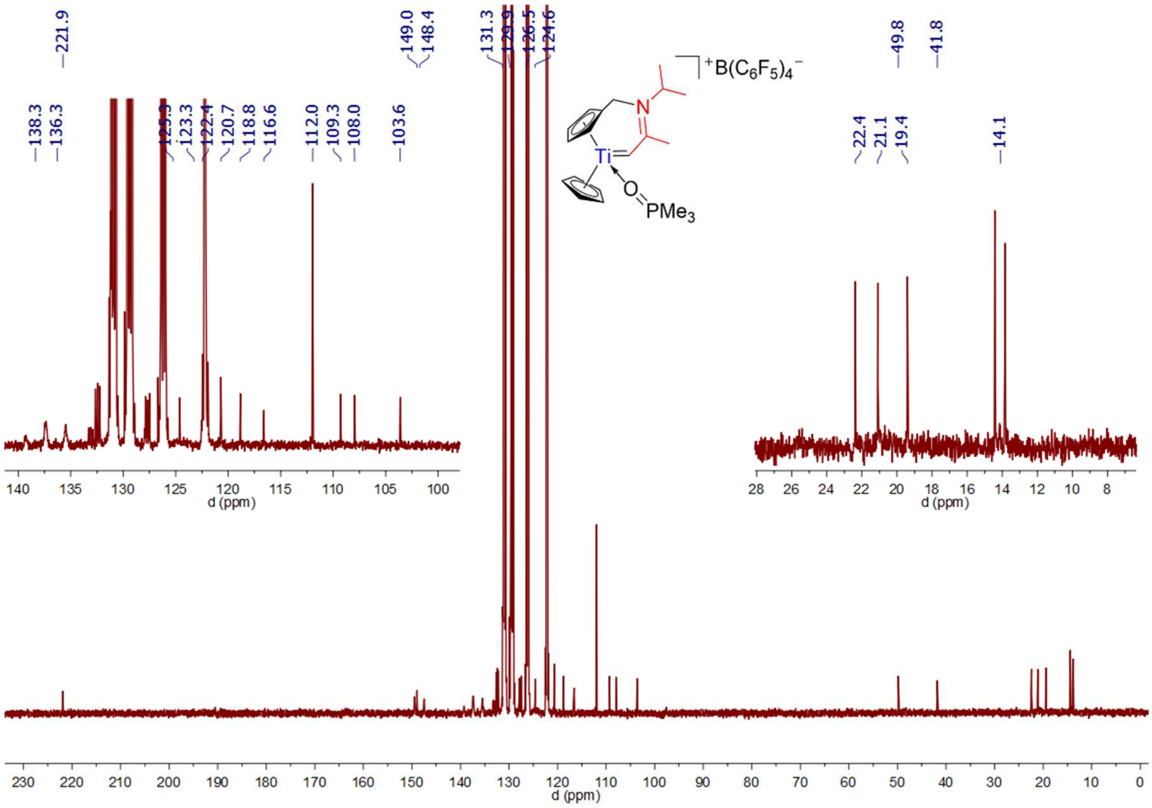
c. Attempted synthesis **44:**



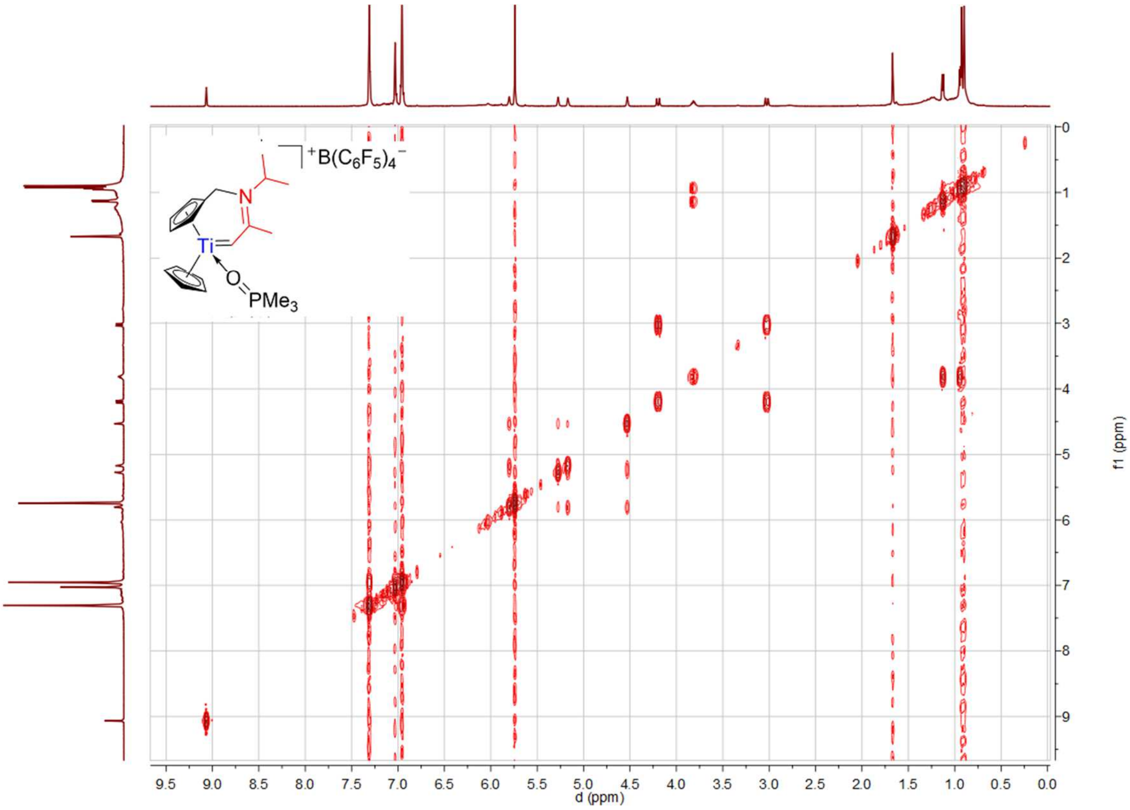
Spectrum 0-337: ^{1}H NMR of 44 (600.23 MHz, 300 K, bromobenzene-d$_5$)



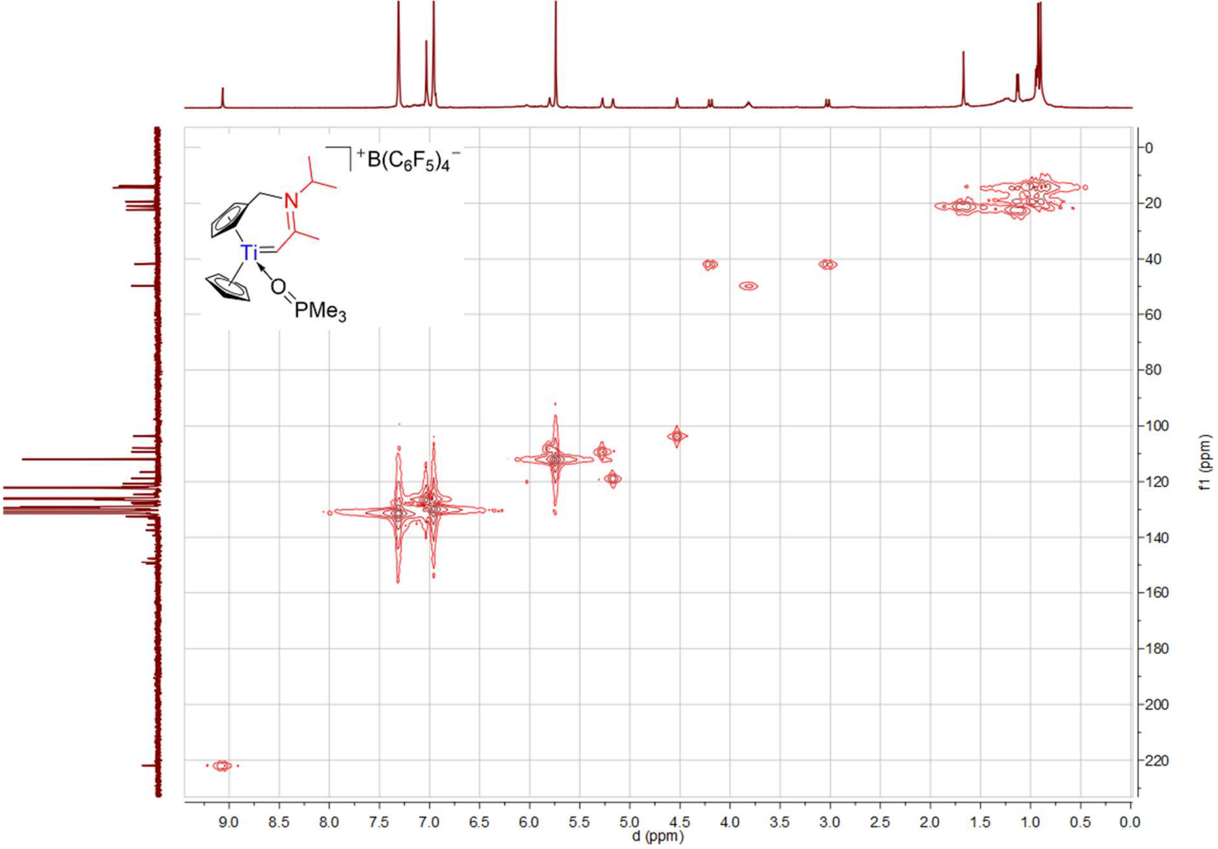
Spectrum 0-338: $^1H\{^{31}P\}$ NMR (top) superposed with ^1H NMR (bottom) of 44 (500.03 MHz, 300 K, bromobenzene-d$_5$)



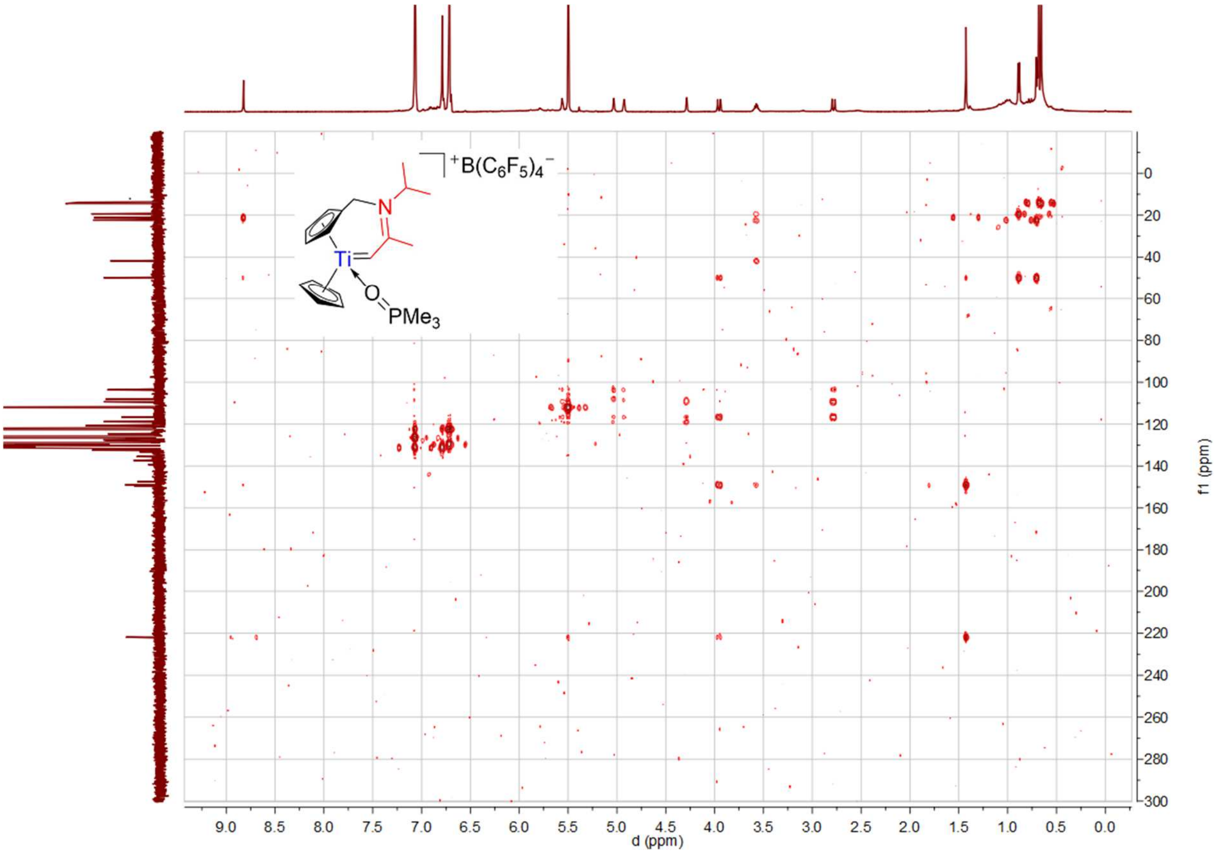
Spectrum 0-339: $^{13}C\{^1H\}$ NMR of 44 (125.75 MHz, 300 K, bromobenzene-d$_5$)



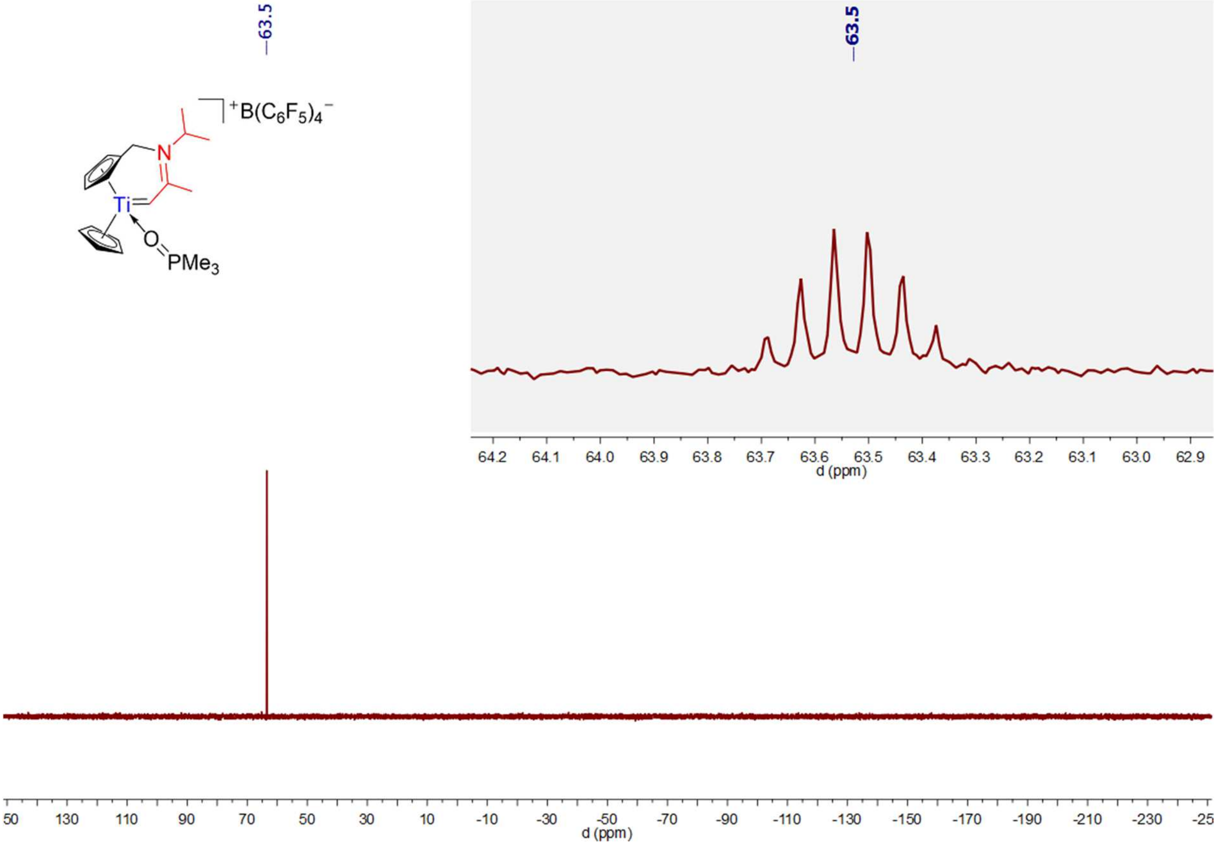
Spectrum 0-340: ^{1}H ^{1}H COSY of 44 (500.03 MHz, 300 K, bromobenzene-d$_5$)



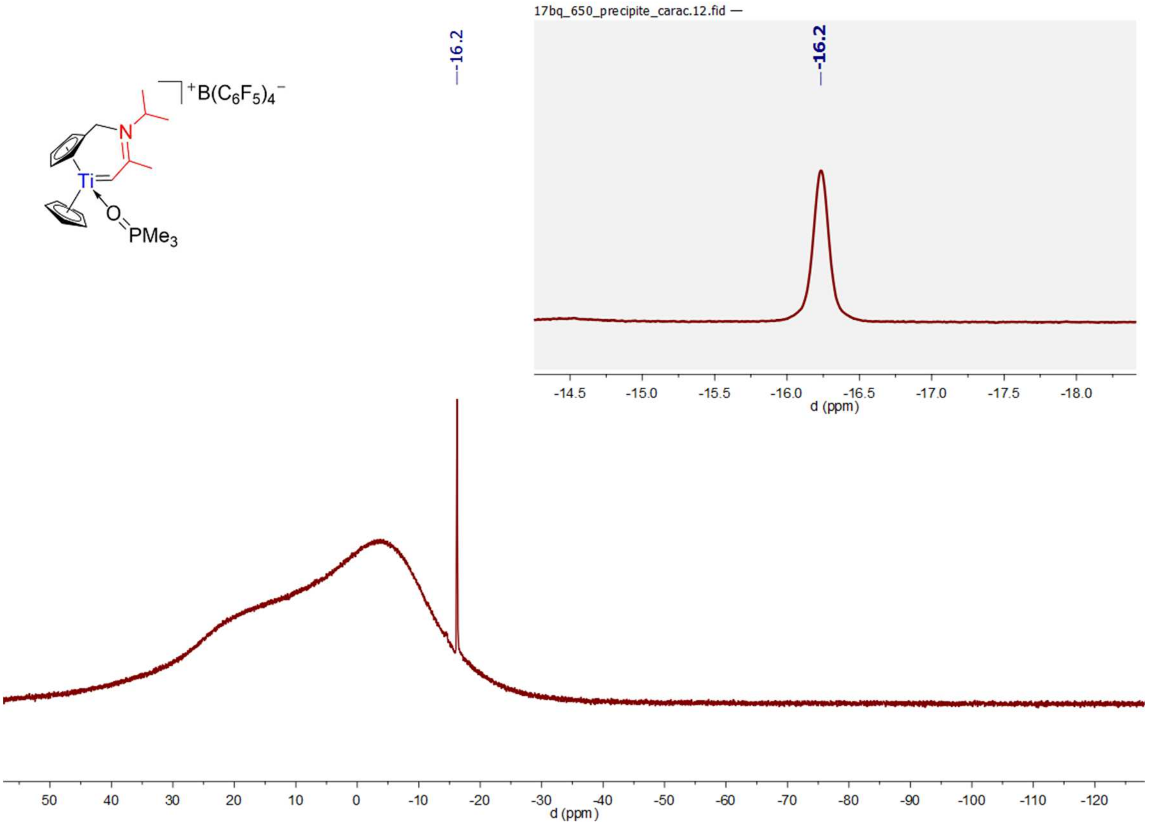
Spectrum 0-341: ^{1}H ^{13}C HMQC of 44 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



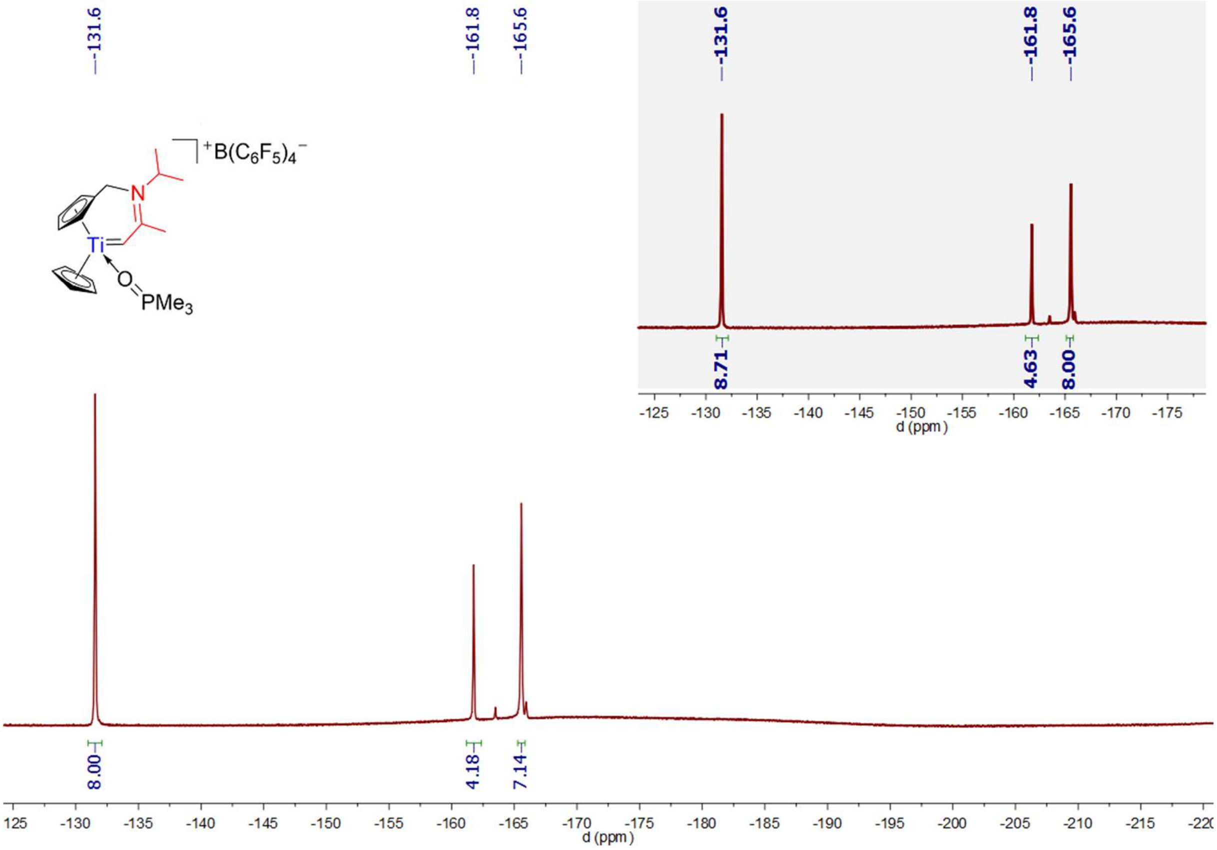
Spectrum 0-342: ^{1}H ^{13}C HMBC of 44 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



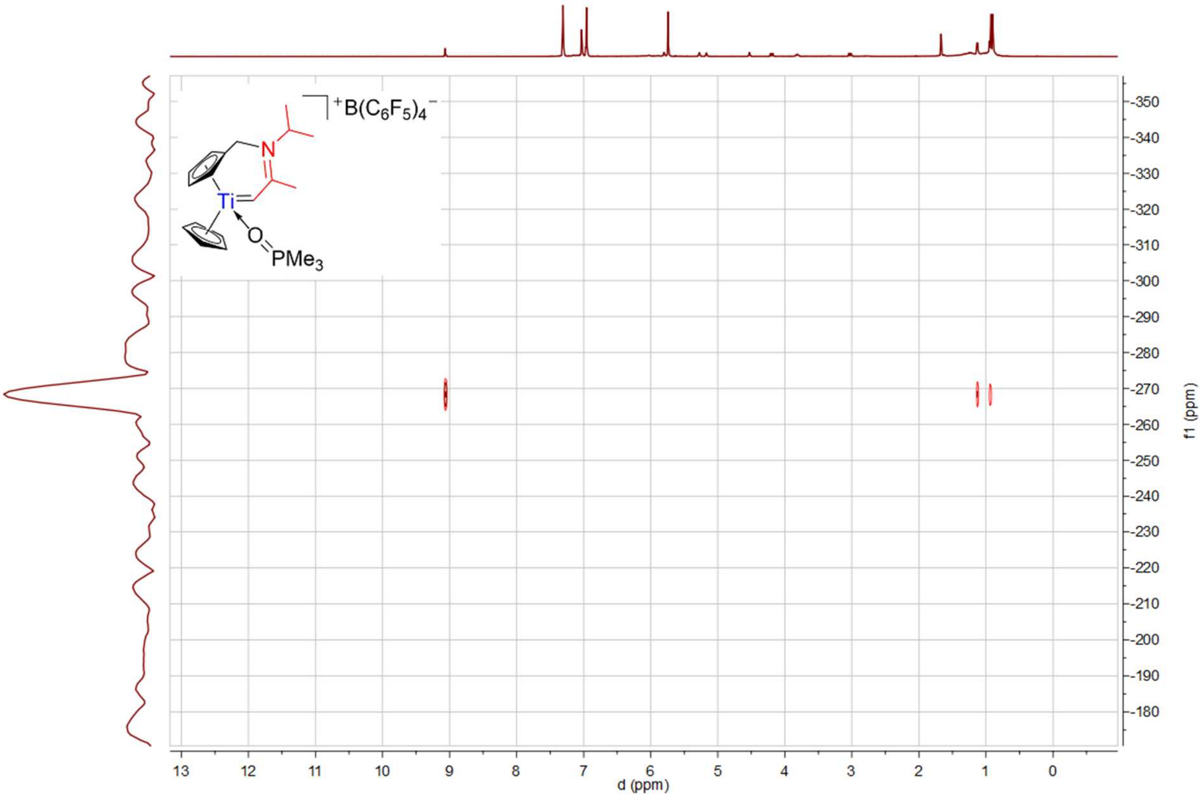
Spectrum 0-343: ^{31}P{^{1}H} and ^{31}P (opacified) NMR of 44 (202.46 MHz, 300 K, bromobenzene-d$_5$)



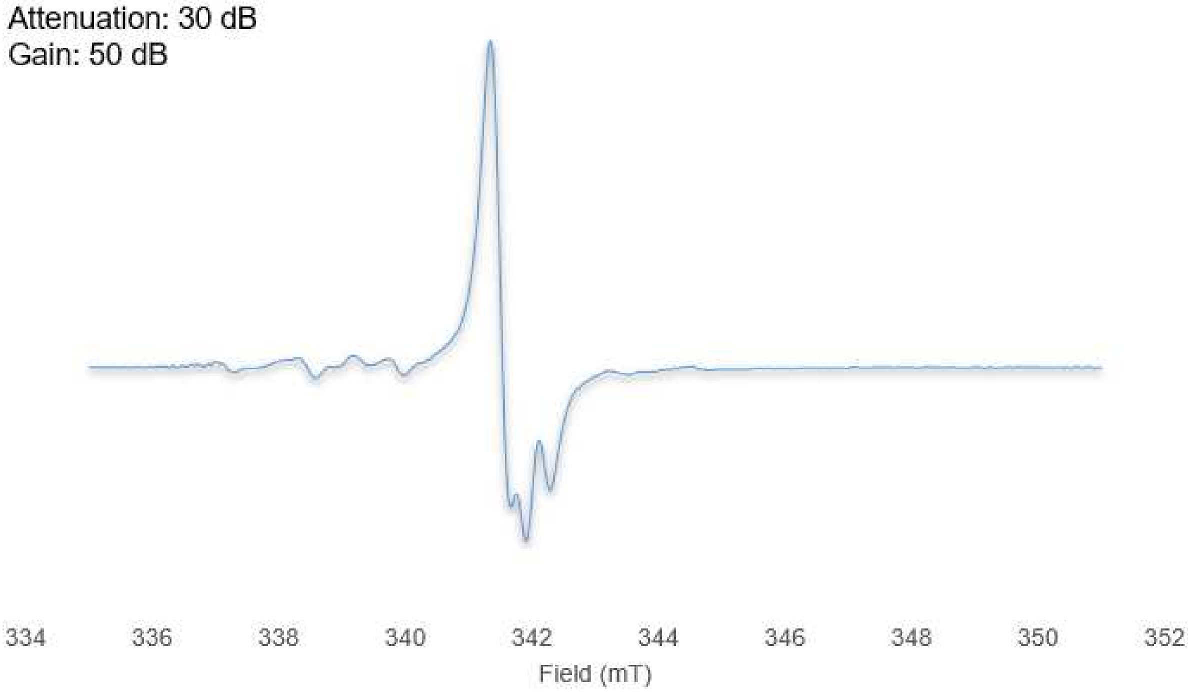
Spectrum 0-344: $^{11}B\{1H\}$ **and** ^{11}B **(opacified) NMR of 44 (160.42 MHz, 300 K, bromobenzene-** d_5 **)**



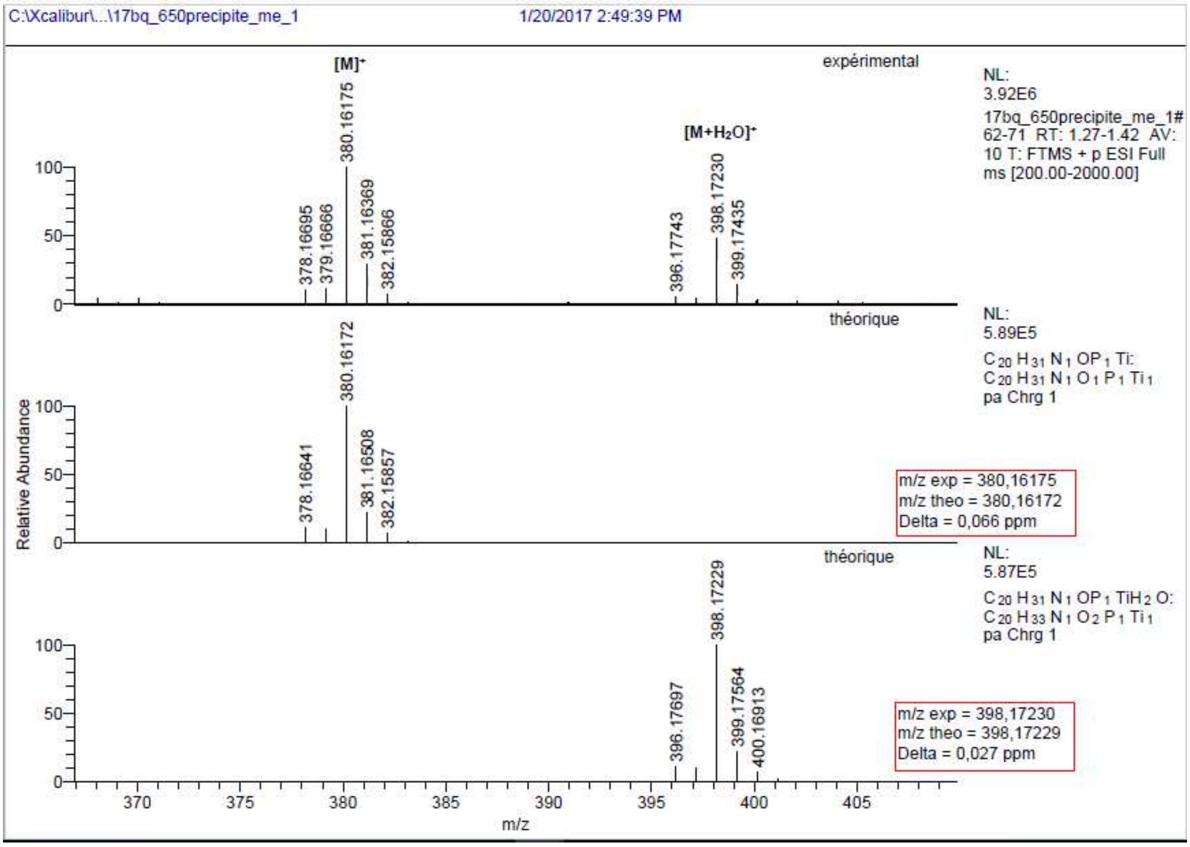
Spectrum 0-345: $^{19}F\{^1H\}$ **and** ^{19}F **(opacified) NMR of 44 (470.45 MHz, 300 K, bromobenzene-** d_5 **)**



Spectrum 0-346: ^{1}H ^{15}N HMBC of 44 (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)

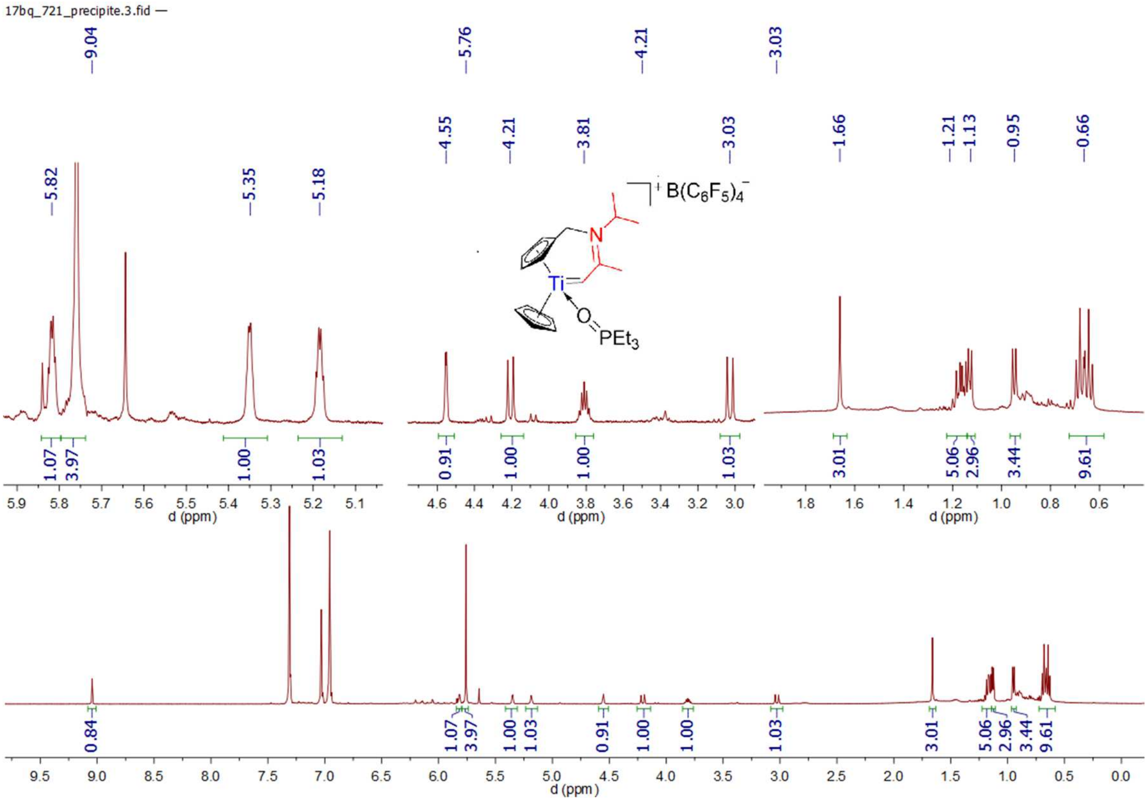


Spectrum 0-347: EPR of 44 (9.444823 GHz, 295K, bromobenzene)

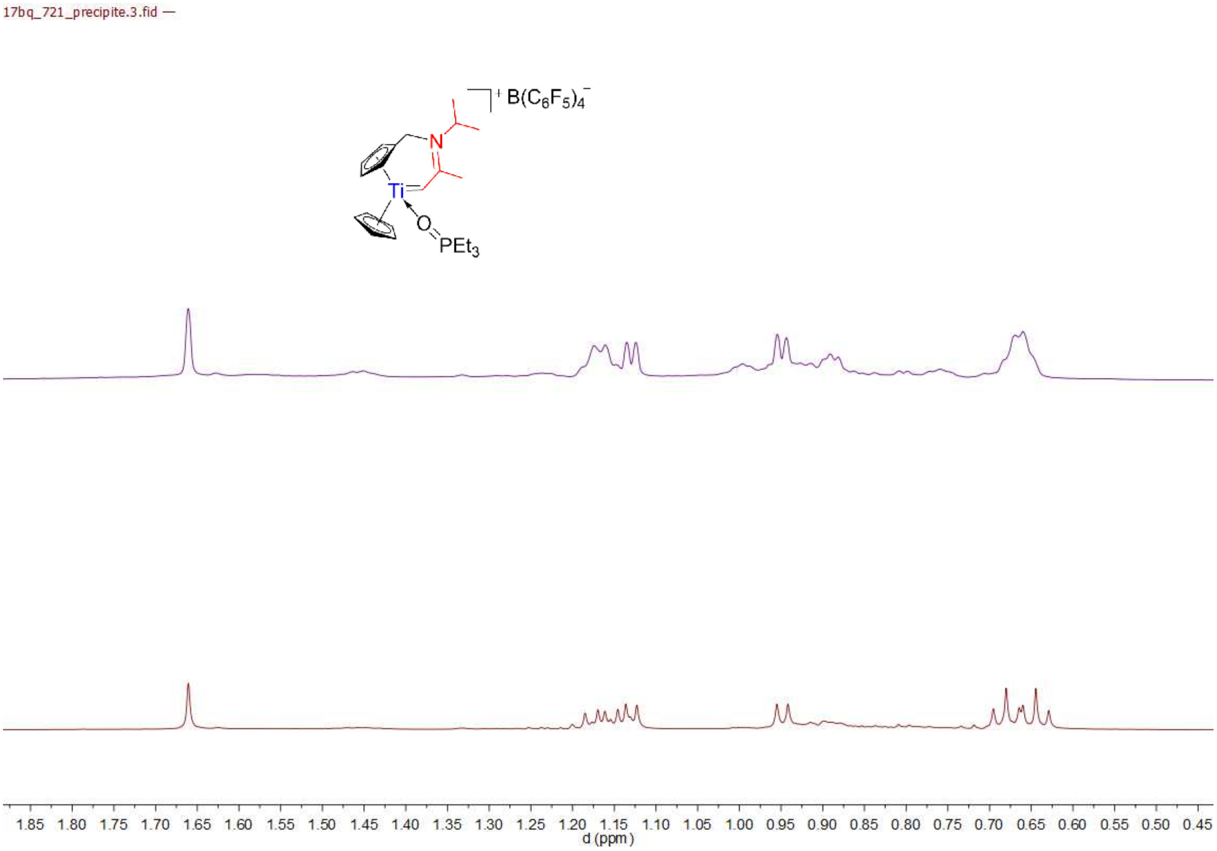


Spectrum 0-348: HRMS of 44 (Positive mode ESI, bromobenzene)

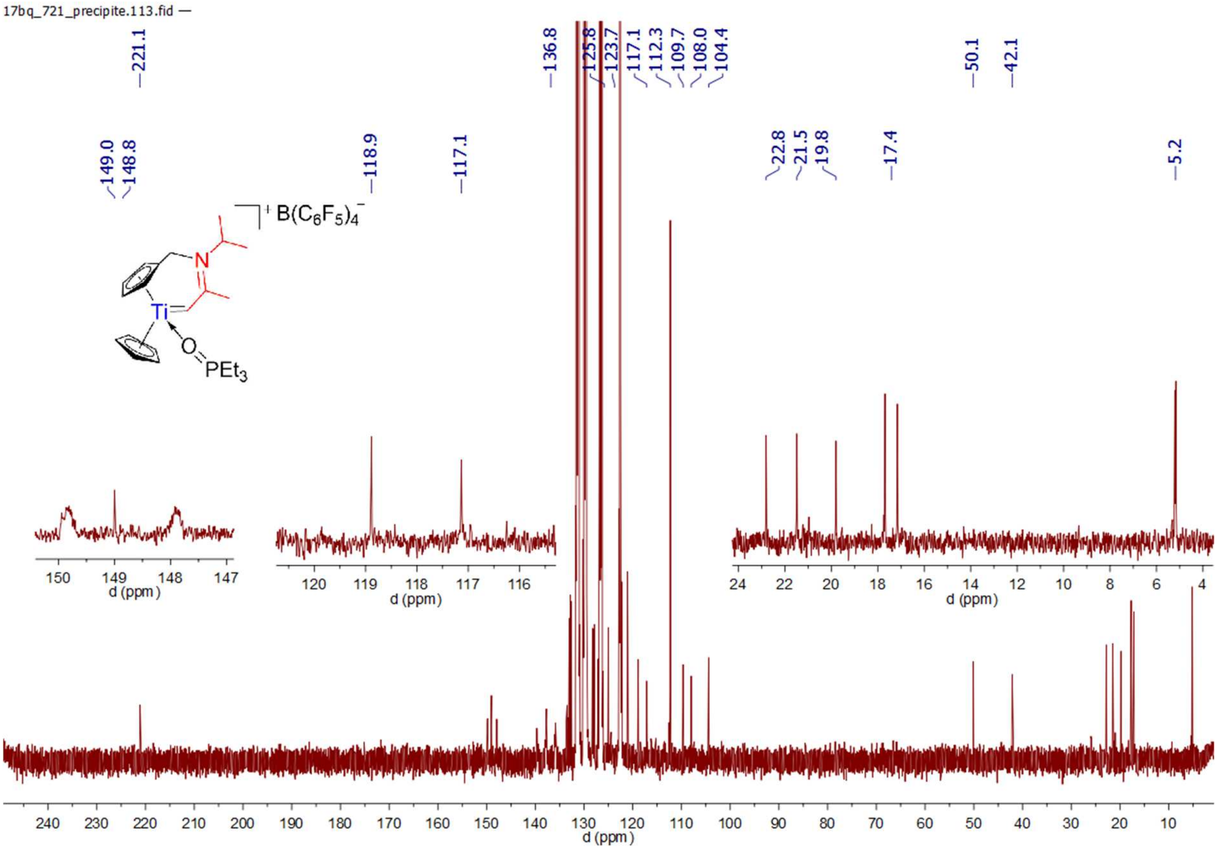
d. Attempted synthesis **45:**



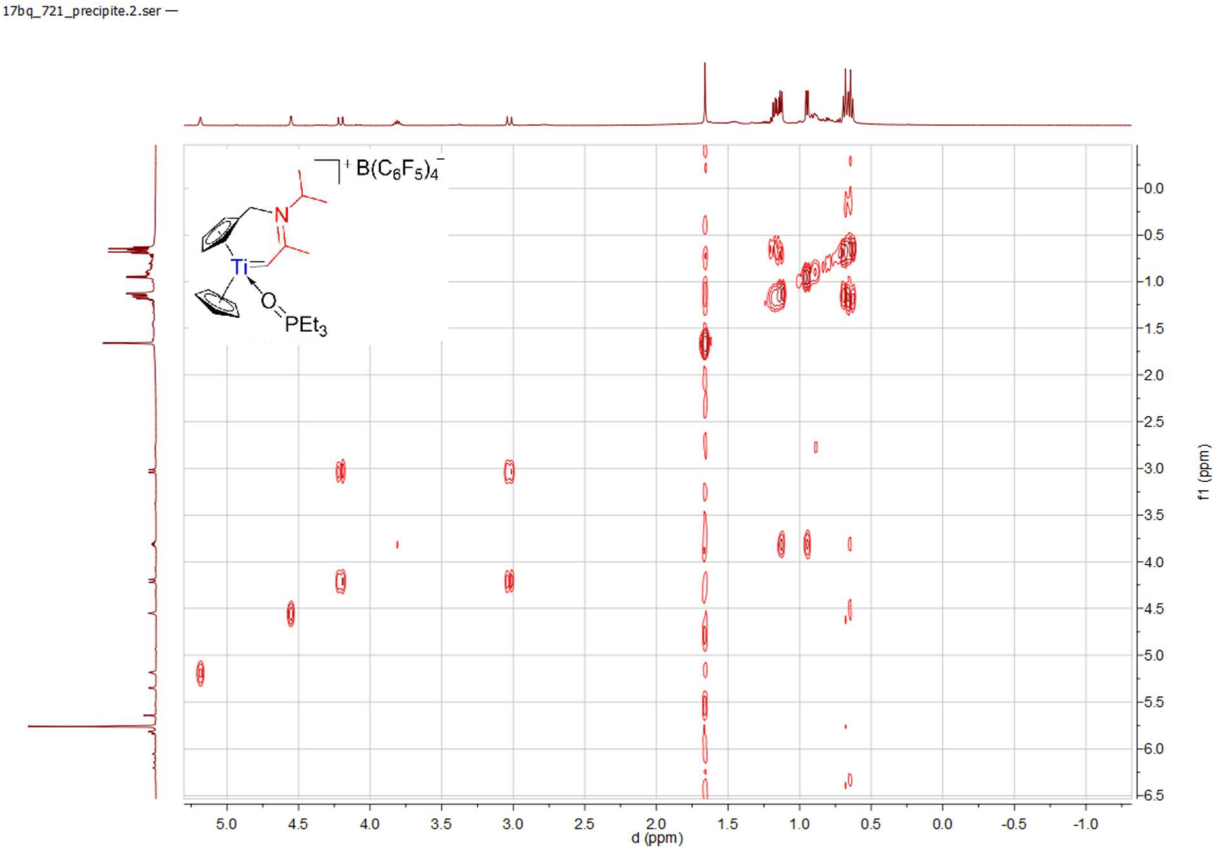
Spectrum 0-349: ^{1}H NMR of 45 (500.03 MHz, 300 K, bromobenzene-d_5)



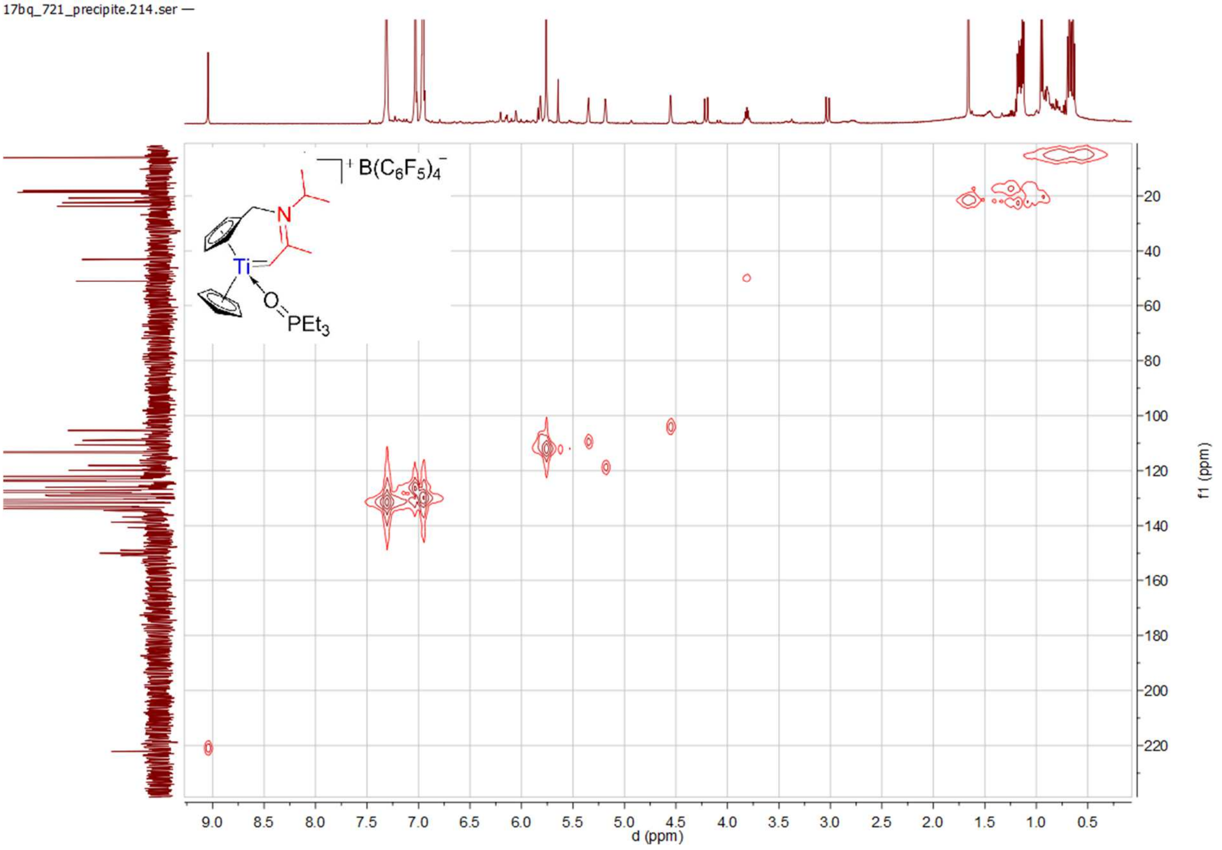
Spectrum 0-350: $^{1}H\{^{31}P\}$ NMR (top) superposed with ^{1}H NMR (bottom) of 45 (600.23 MHz, 300 K, bromobenzene-d_5)



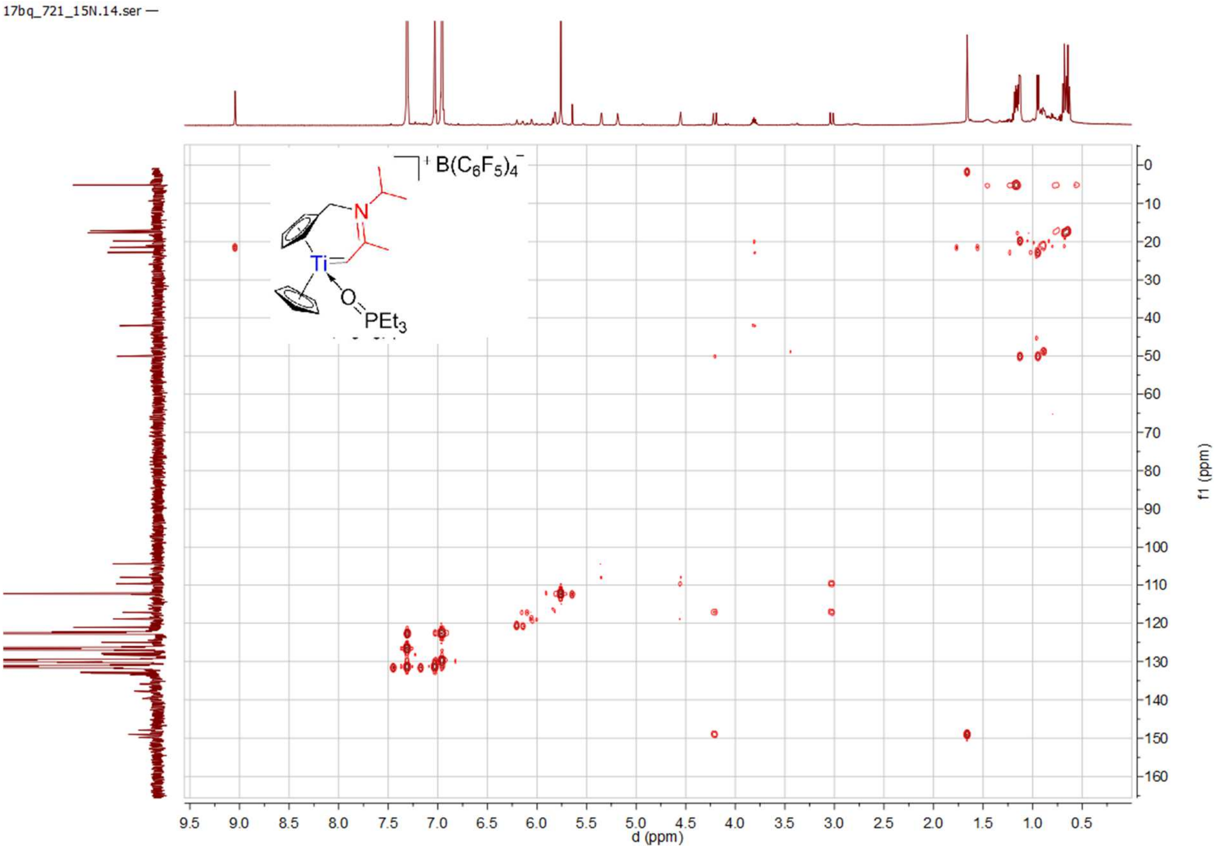
Spectrum 0-351: $^{13}C\{^{1}H\}$ NMR of 45 (125.75 MHz, 300 K, bromobenzene-d_5)



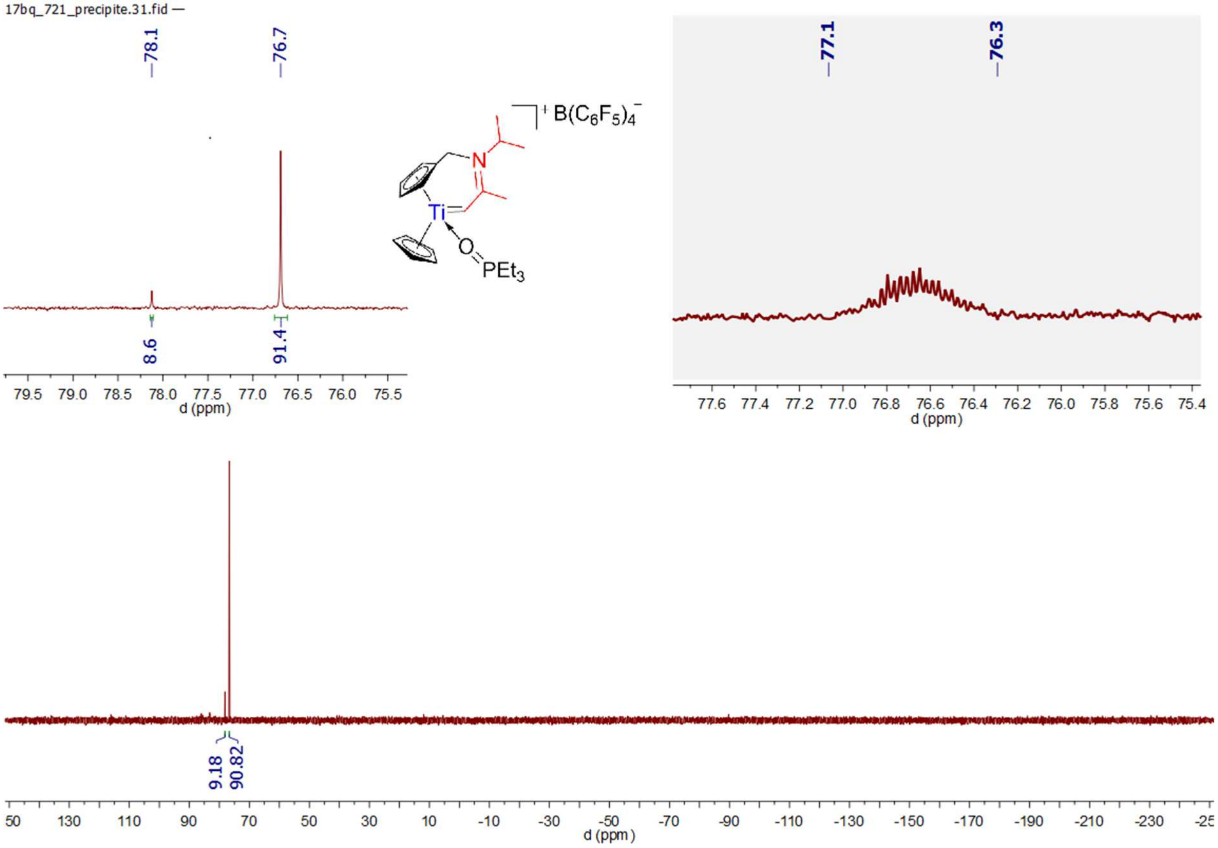
Spectrum 0-352: ^{1}H ^{1}H COSY of 45 (500.03 MHz, 300 K, bromobenzene-d$_5$)



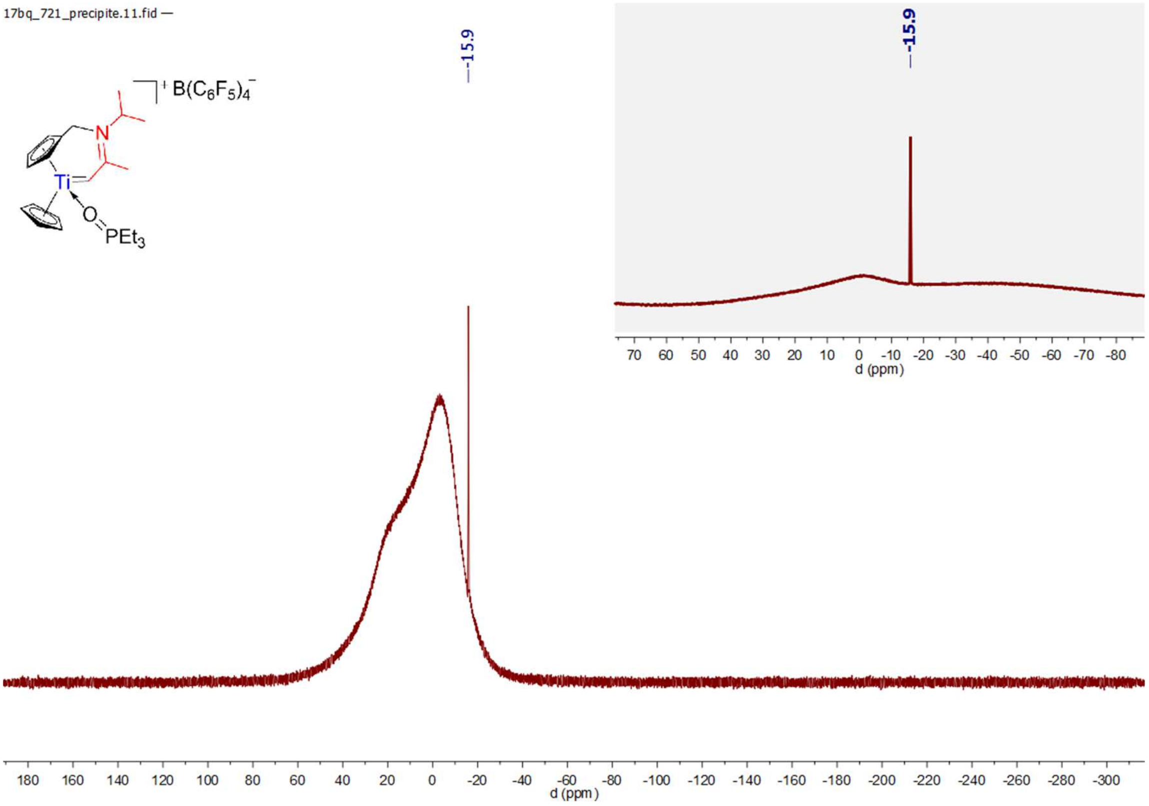
Spectrum 0-353: ^{1}H ^{13}C HMQC of 45 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



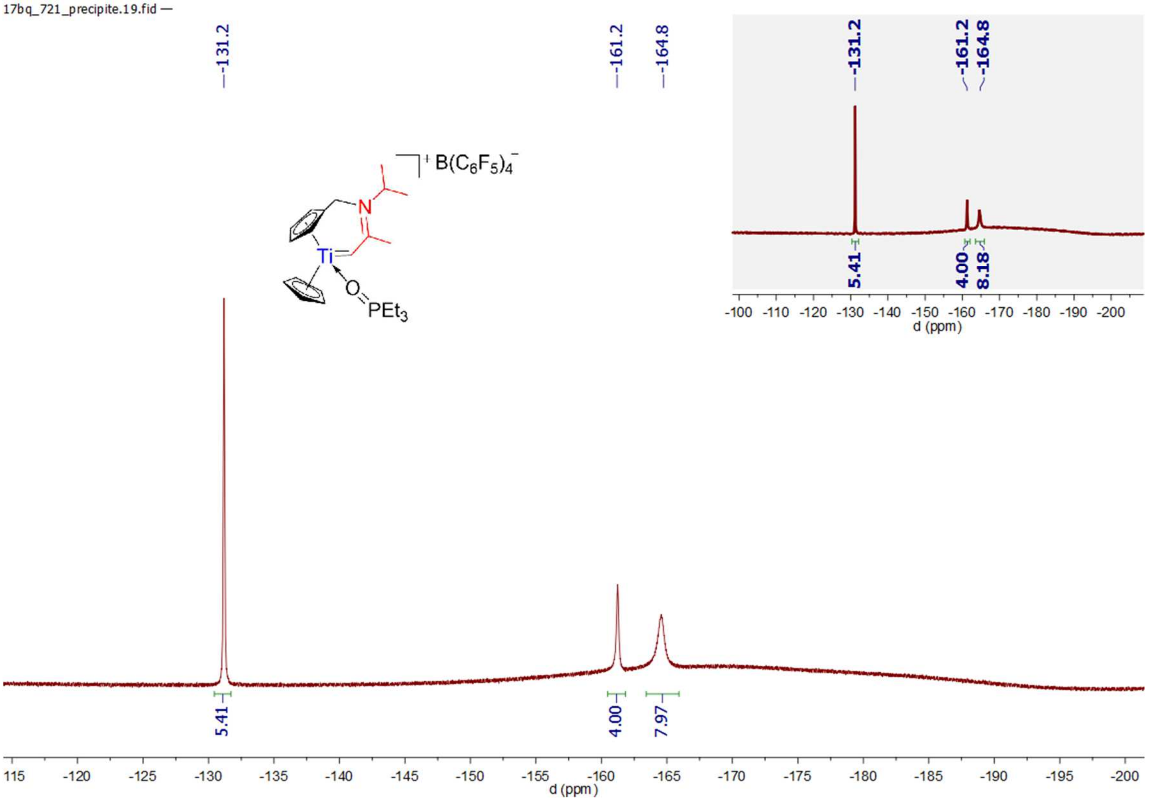
Spectrum 0-354: ^{1}H ^{13}C HMBC of 45 (600.23 MHz / 150.86 MHz, 300 K, bromobenzene-d$_5$)



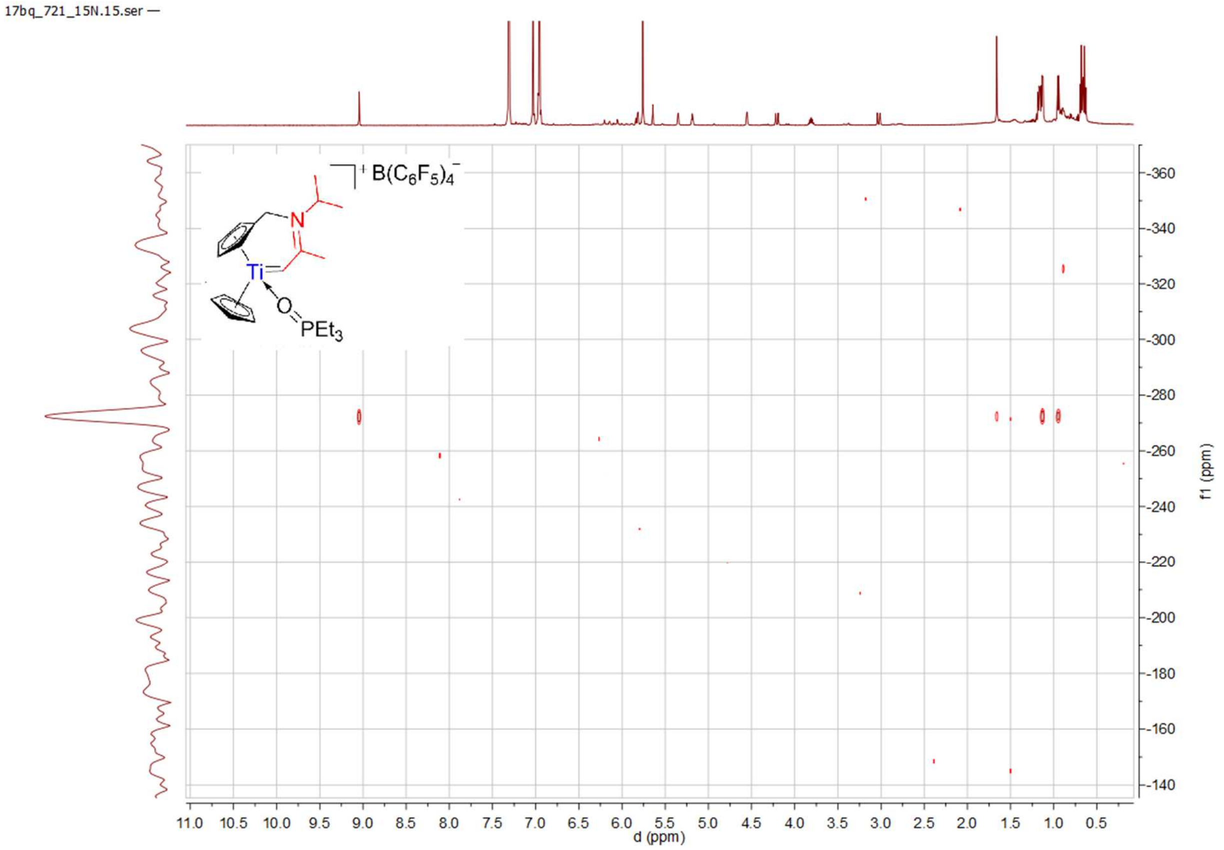
Spectrum 0-355: ^{31}P{^{1}H} and ^{31}P (opacified) NMR of 45 (202.46 MHz, 300 K, bromobenzene-d$_5$)



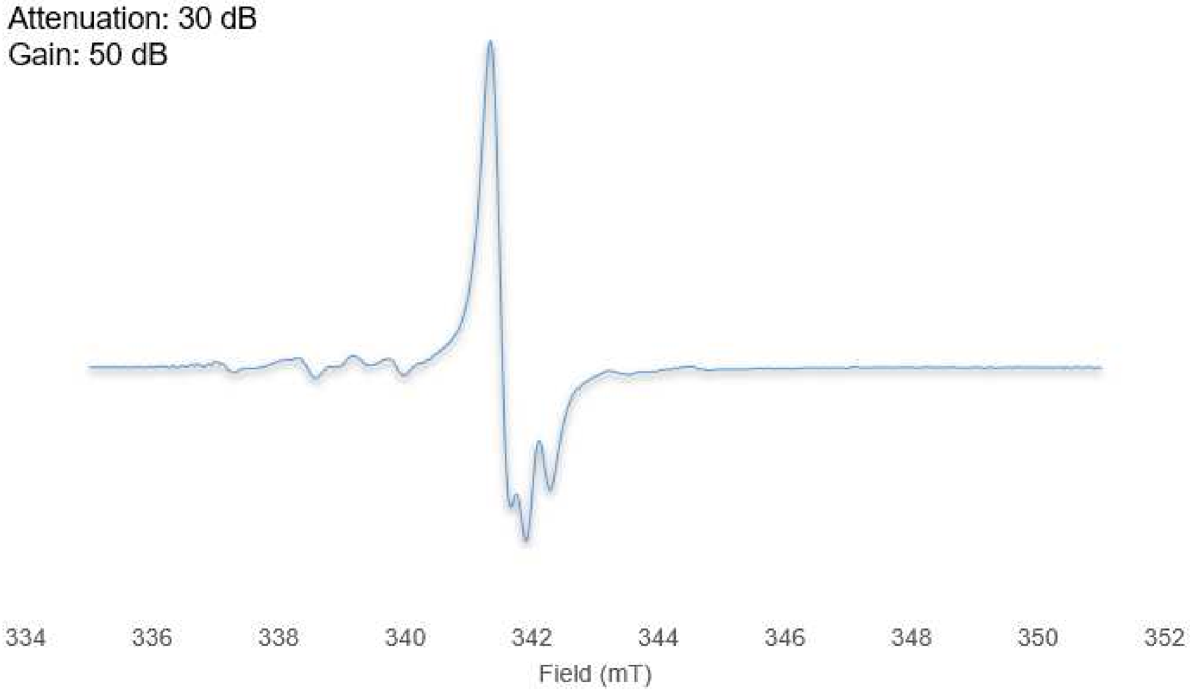
Spectrum 0-356: ^{11}B{1H} and ^{11}B (opacified) NMR of 45 (160.42 MHz, 300 K, bromobenzene-d$_5$)



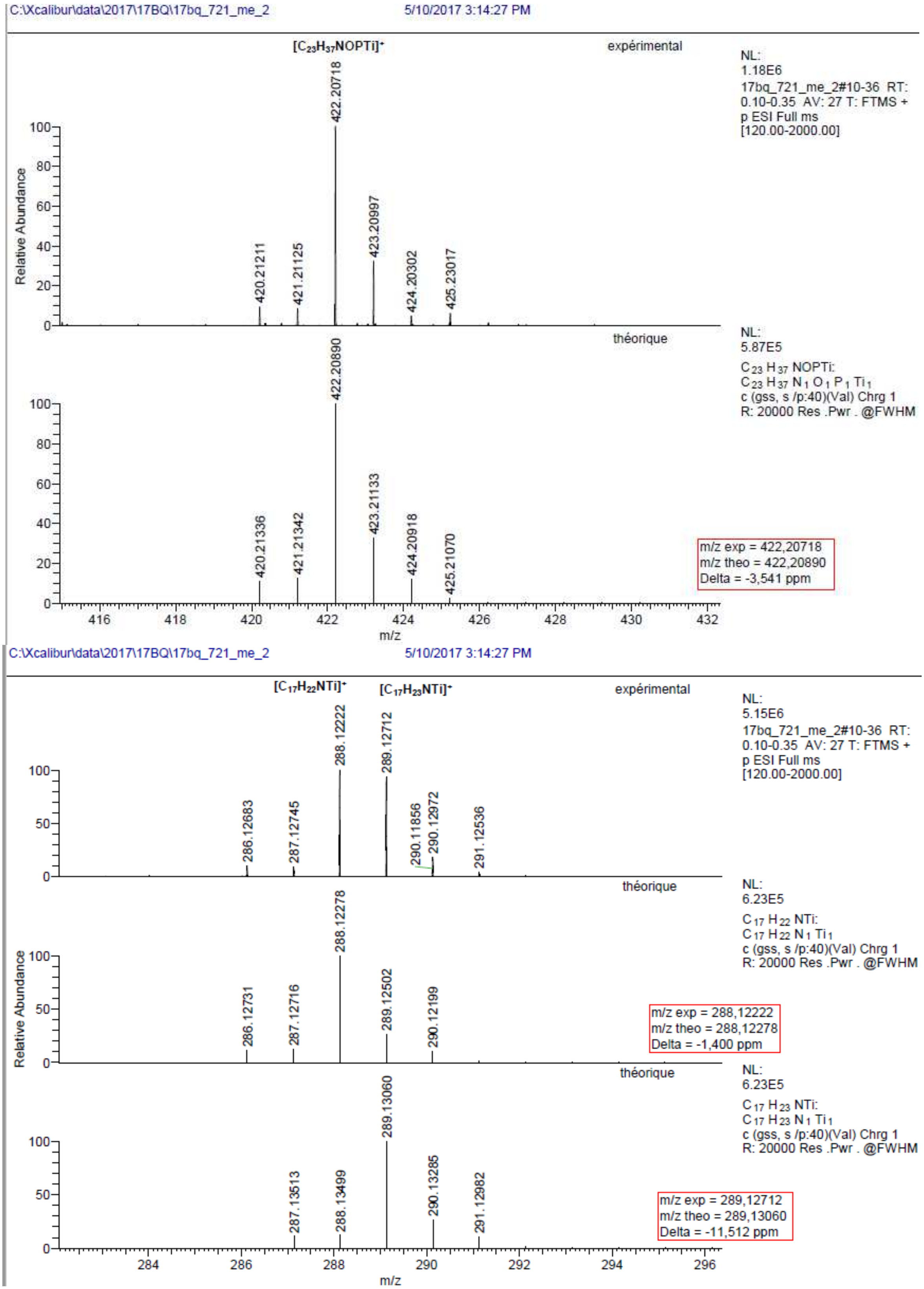
Spectrum 0-357: ^{19}F{^{1}H} and ^{19}F (opacified) NMR of 45 (470.45 MHz, 300 K, bromobenzene-d$_5$)



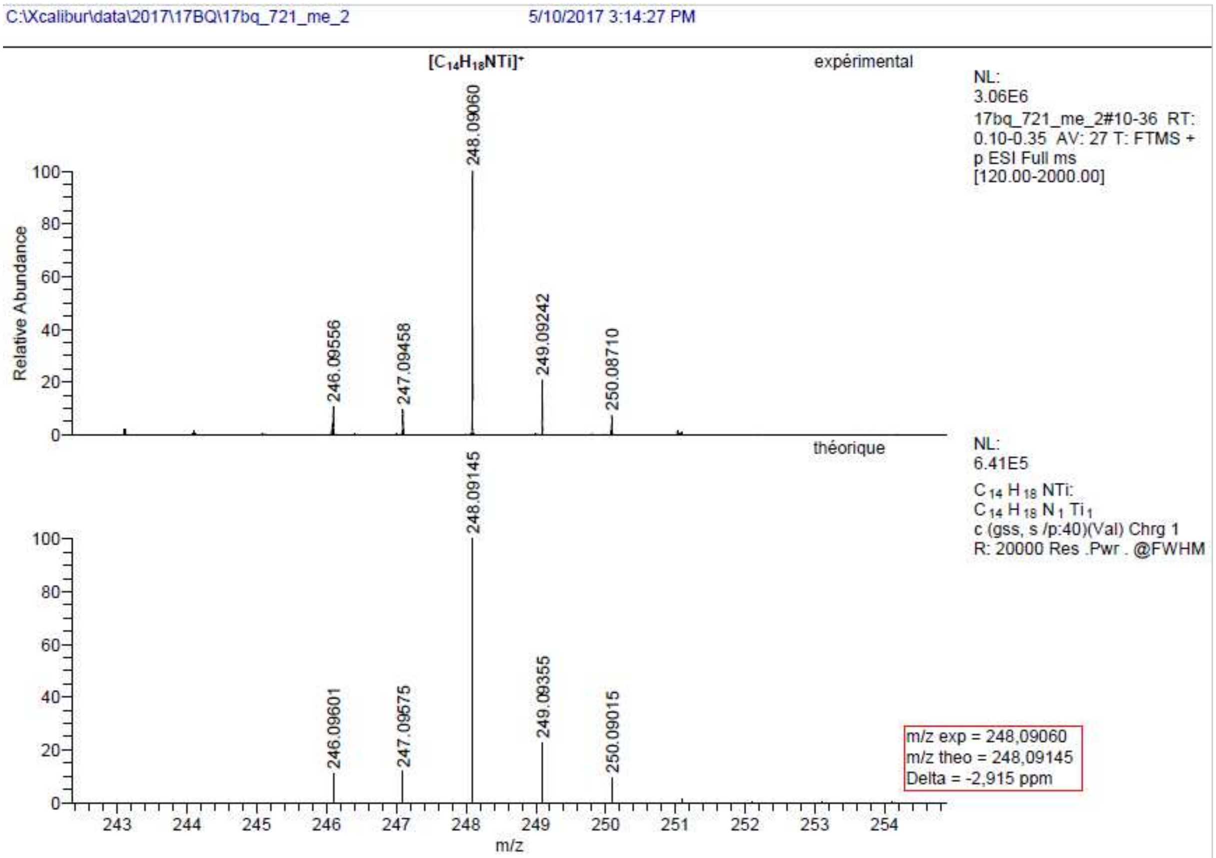
Spectrum 0-358: ^{1}H ^{15}N HMBC of 45 (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)



Sectrum 0-359: EPR of 45 (9.445560 GHz, 300K, bromobenzene)

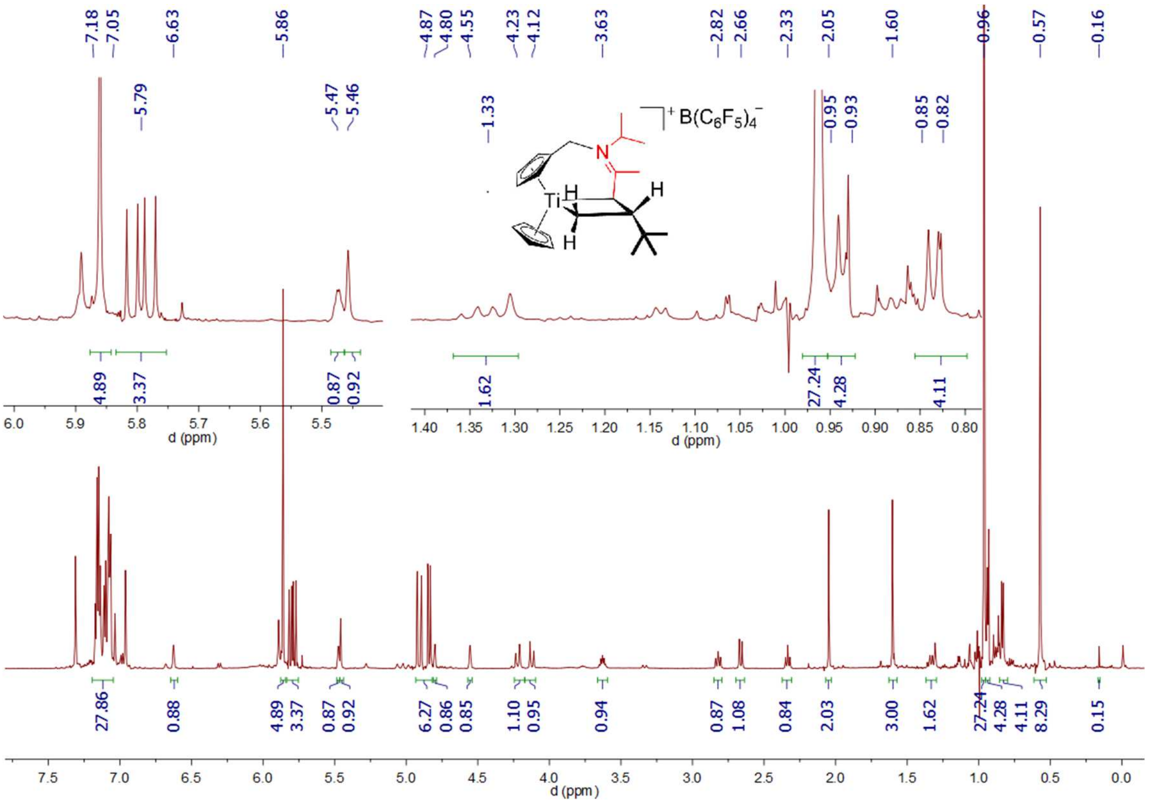


Spectrum 0-360: HRMS of 45 (Positive mode ESI, bromobenzene)



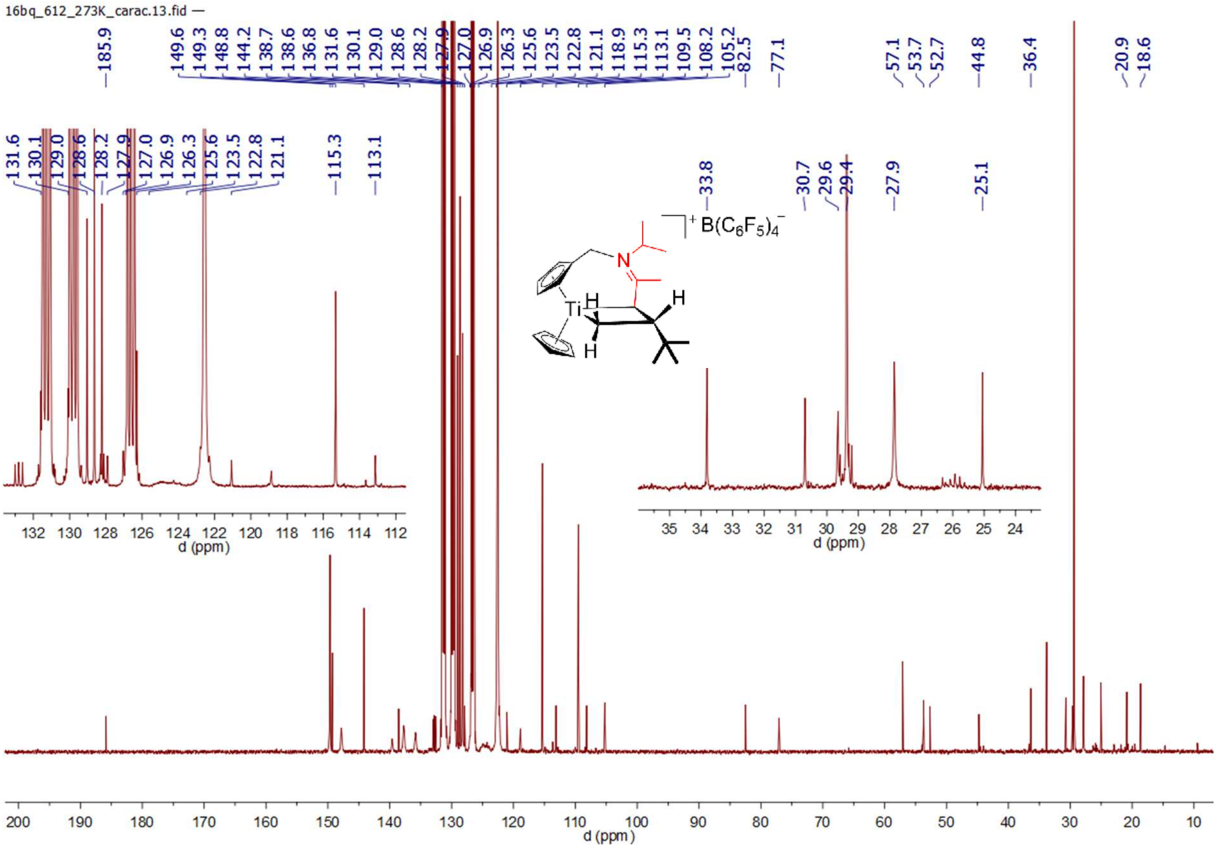
Spectrum 0-361: HRMS of 45 (Positive mode ESI, bromobenzene)

e. In situ characterization of **47**:

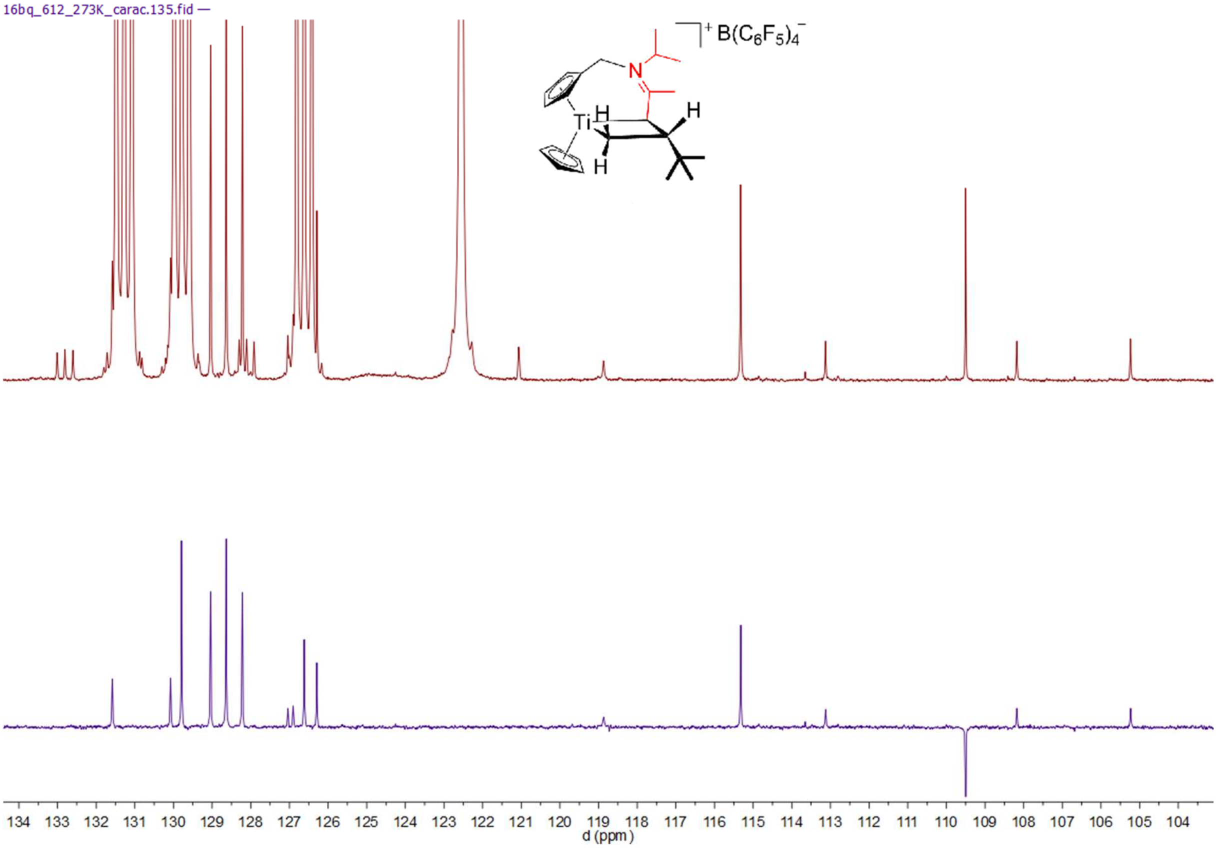


Spectrum 0-362: ^{1}H NMR of 47 (600.23 MHz, 273 K, bromobenzene-d_5)

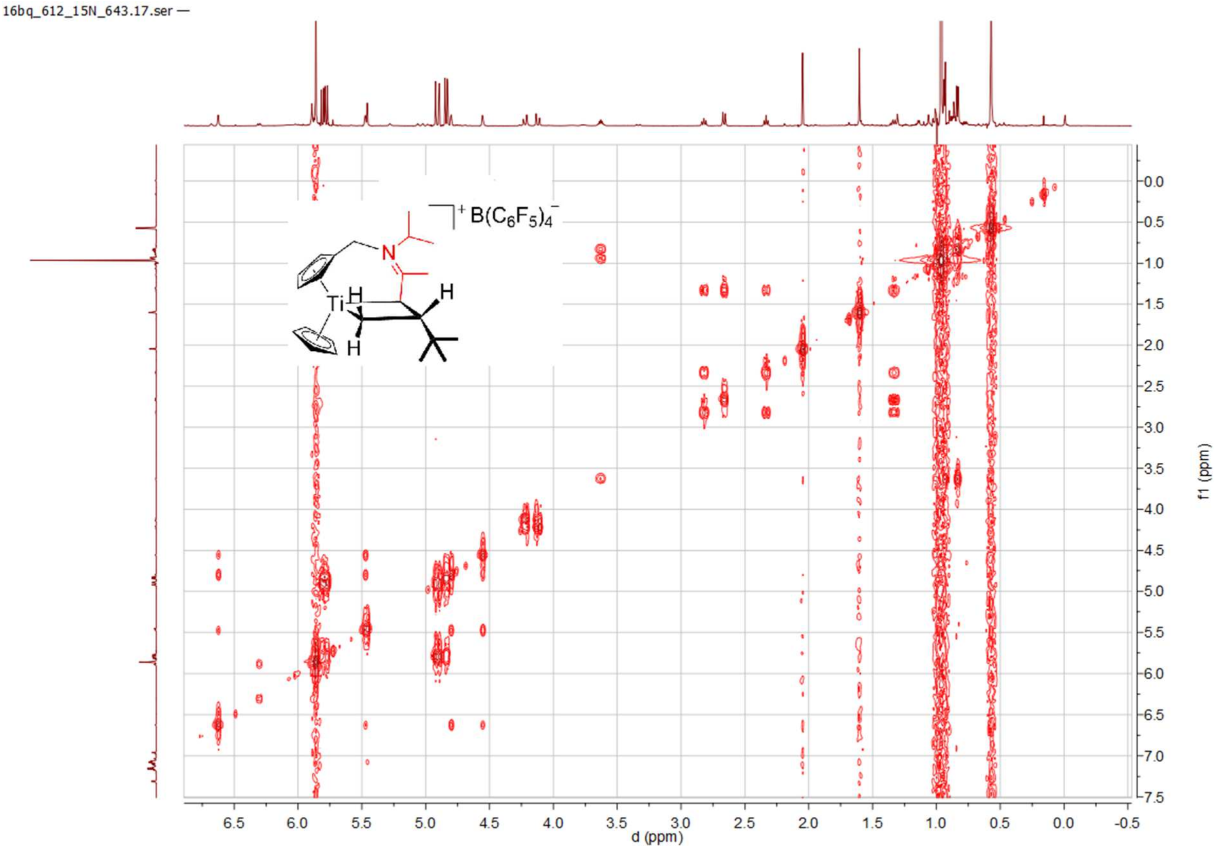
re



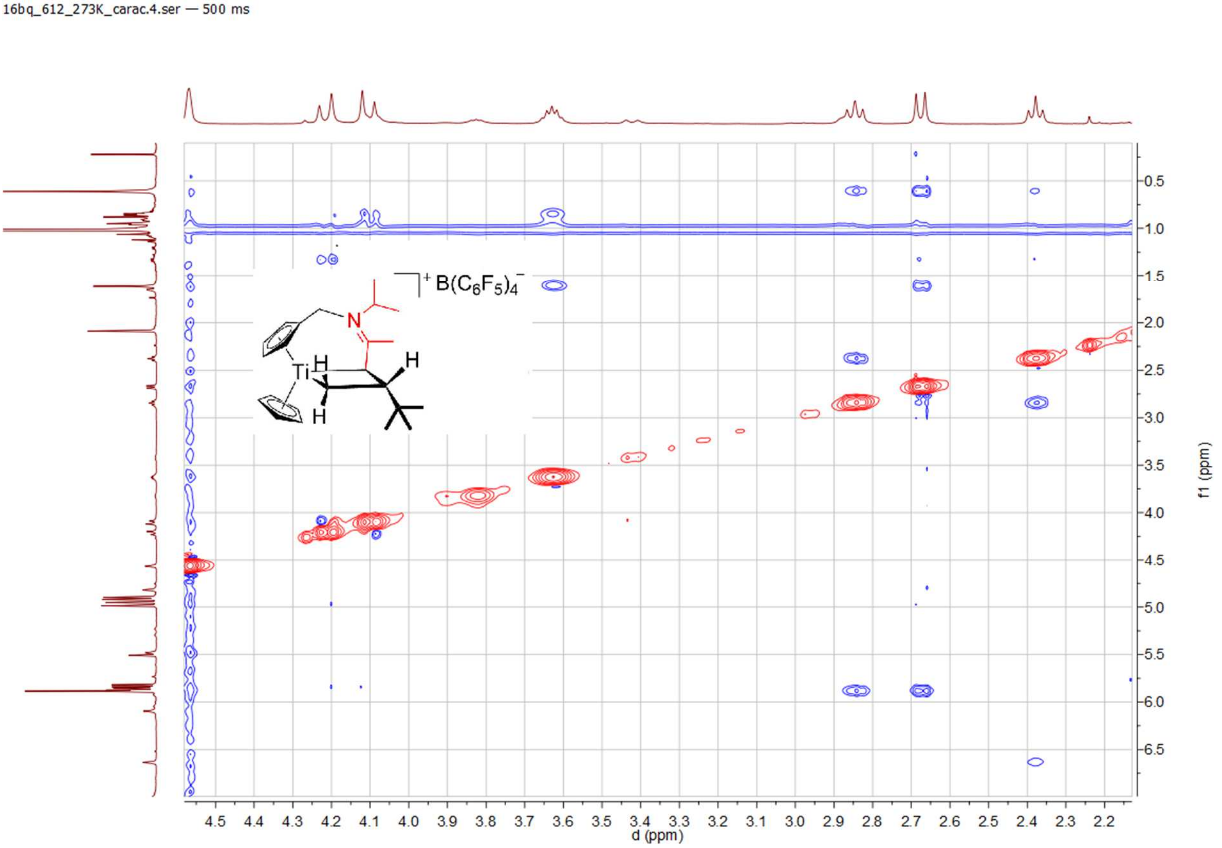
Spectrum 0-363: $^{13}C\{^1H\}$ NMR of 47 (125.75 MHz, 273 K, bromobenzene-d_5)



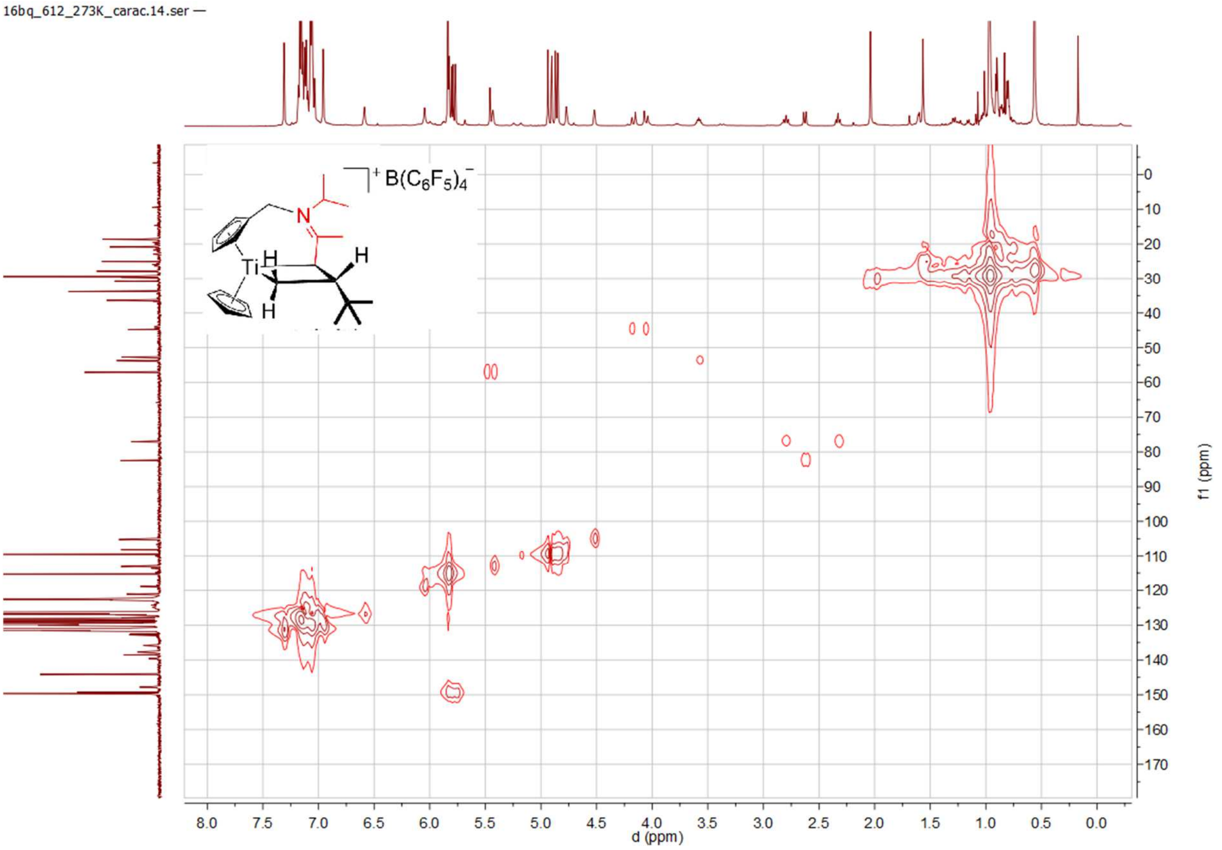
Spectrum 0-364: $^{13}C\{^1H\}$ NMR (top) correlated with dept135 (bottom) of 47 (125.75 MHz, 273 K, bromobenzene-d_5)



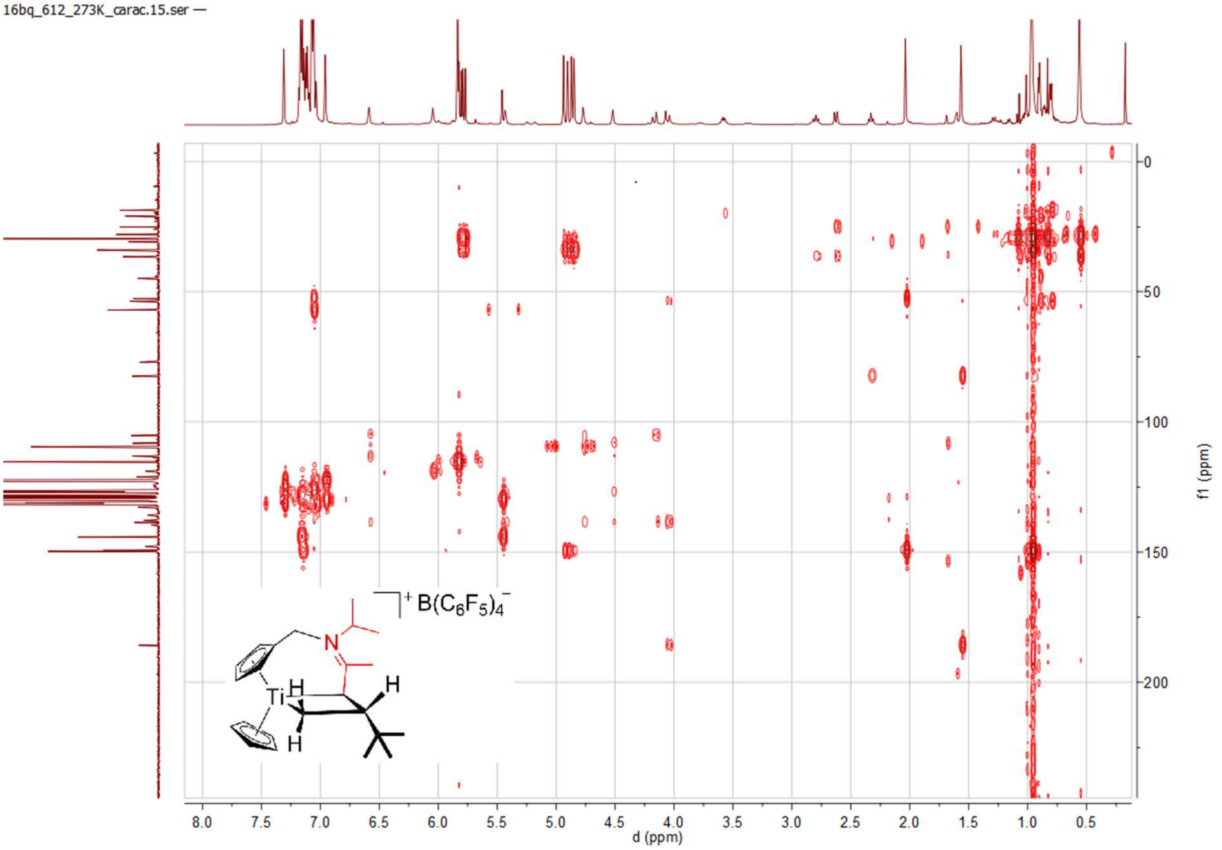
Spectrum 0-365: ^{1}H ^{1}H COSY of 47 (500.03 MHz, 273 K, bromobenzene-d$_5$)



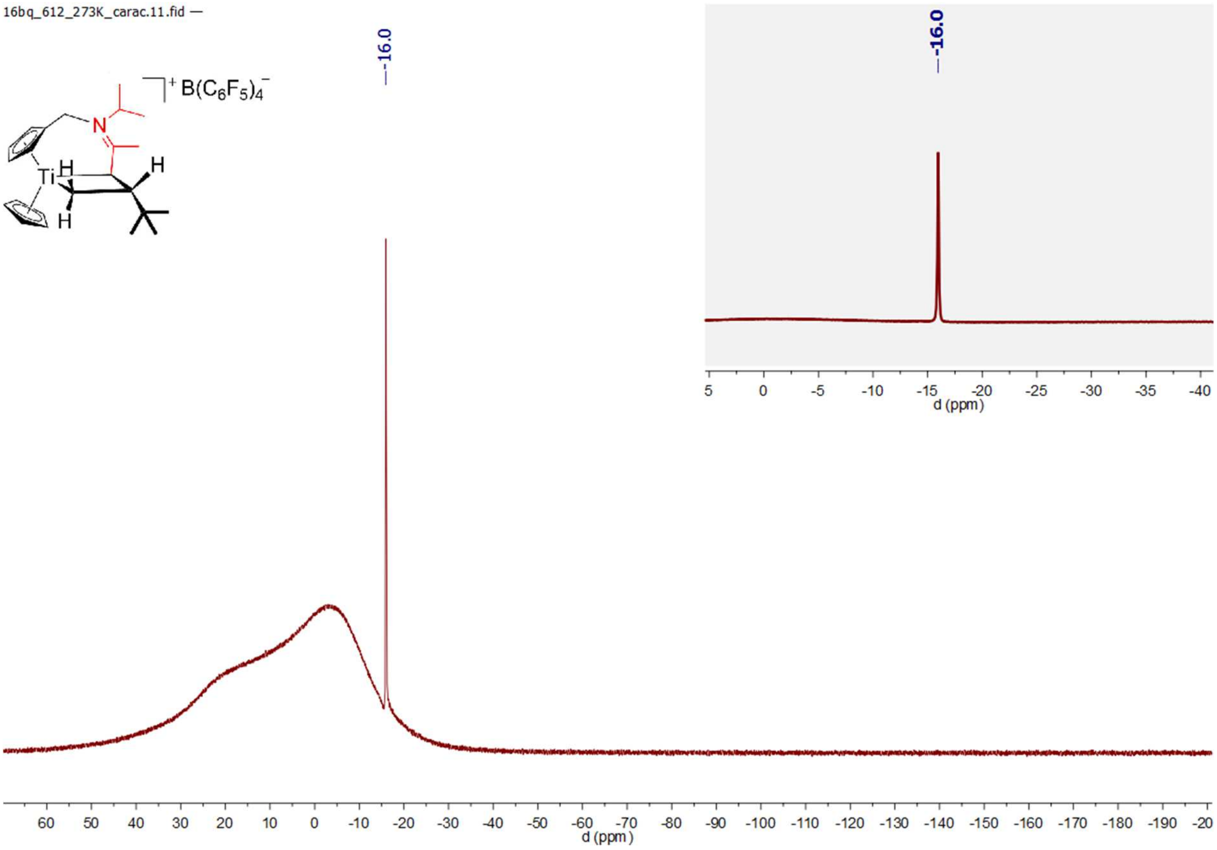
Spectrum 0-366: ^{1}H ^{1}H NOESY of 47 (600.23 MHz, 273 K, bromobenzene-d$_5$



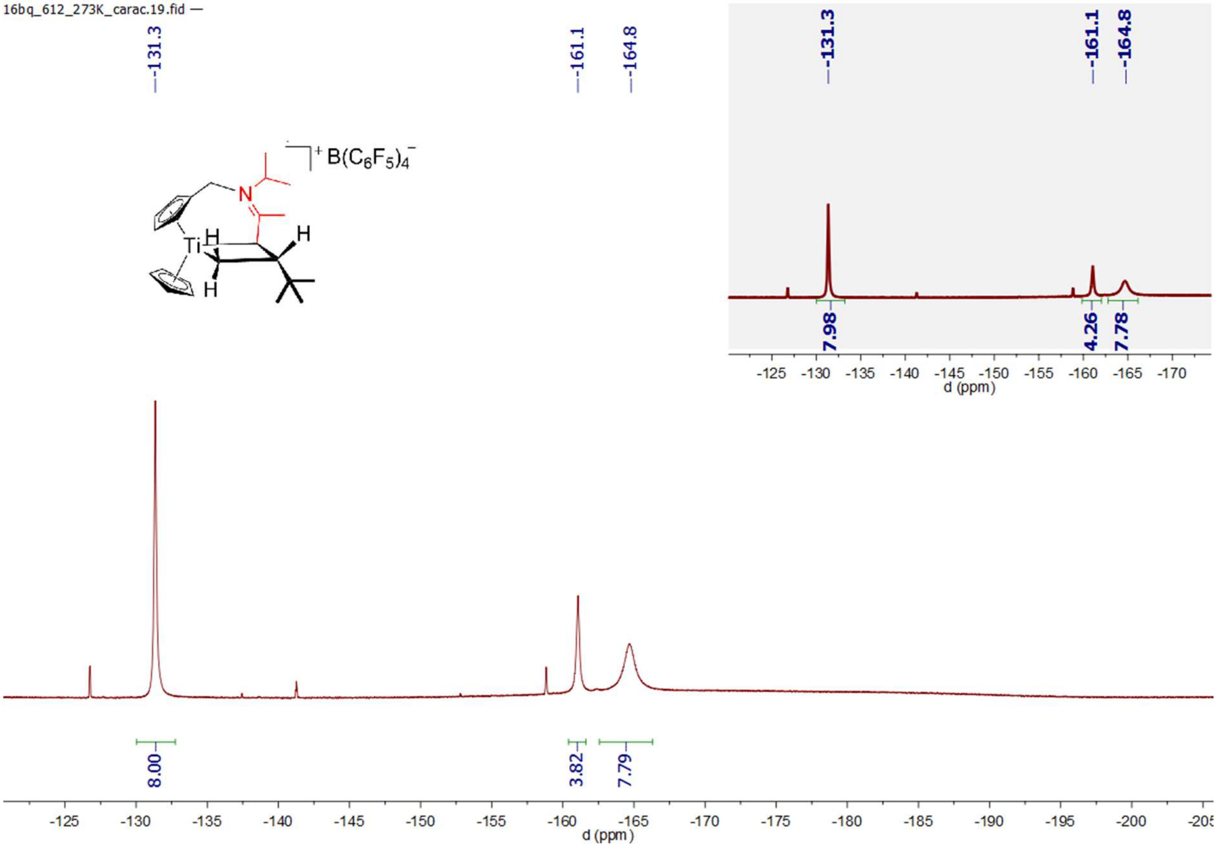
Spectrum 0-367: ^{1}H ^{13}C HMQC of 47 (500.03 MHz / 125.75 MHz, 273 K, bromobenzene-d$_5$)



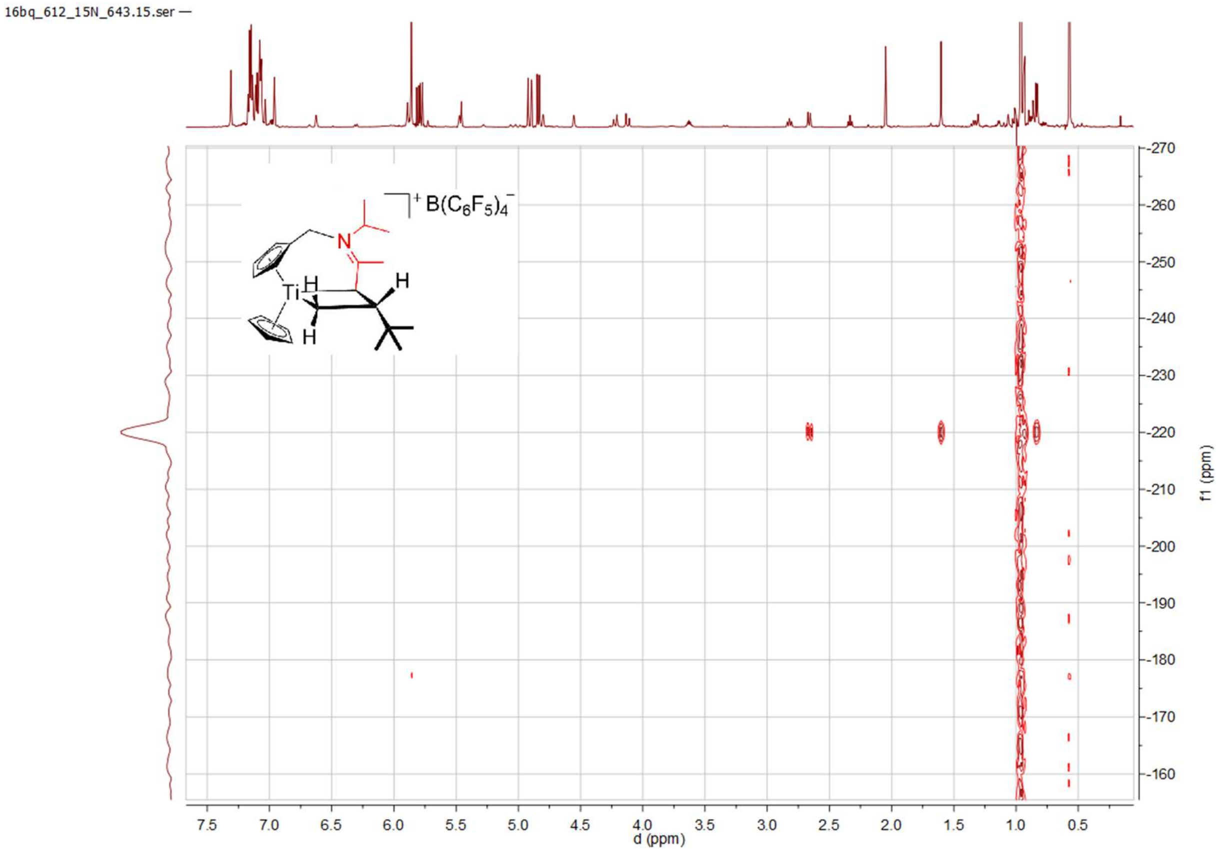
Spectrum 0-368: ^{1}H ^{13}C HMBC of 47 (500.03 MHz / 125.75 MHz, 273 K, bromobenzene-d$_5$)



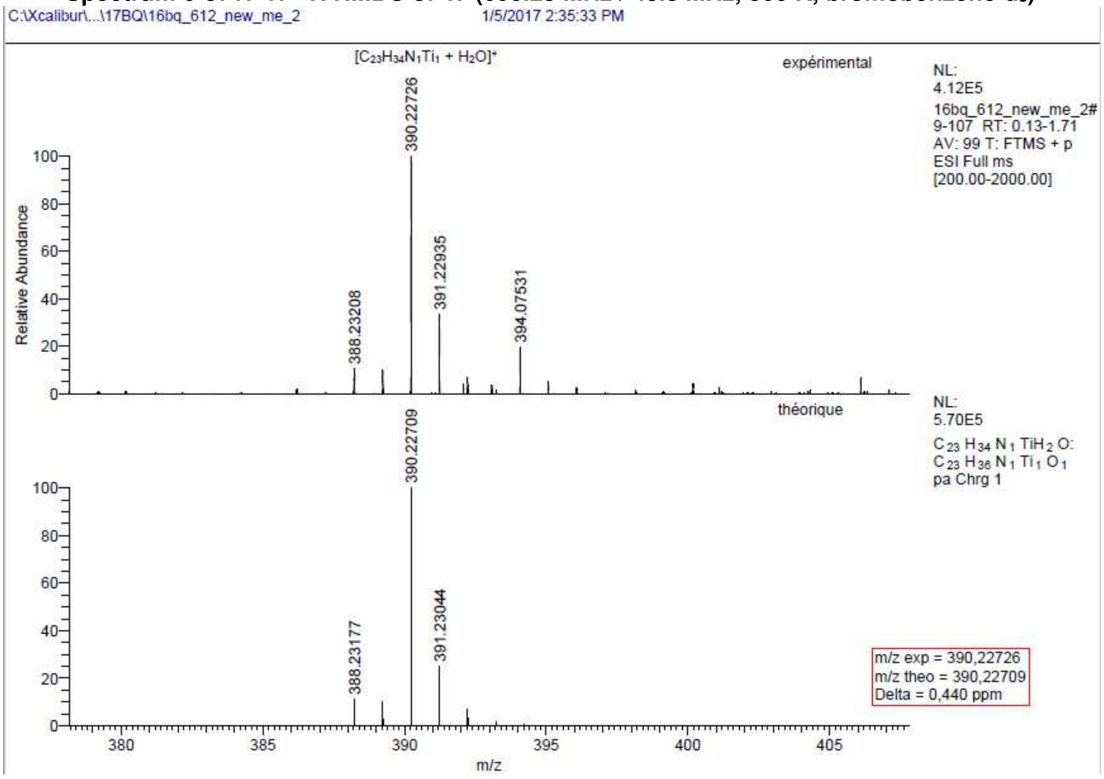
Spectrum 0-369: $^{11}B\{^1H\}$ and ^{11}B (opacified) NMR of 47 (160.42 MHz, 273 K, bromobenzene-d_5)



Spectrum 0-370: $^{19}F\{^1H\}$ and ^{19}F (opacified) NMR of 47 (470.45 MHz, 273 K, bromobenzene-d_5)

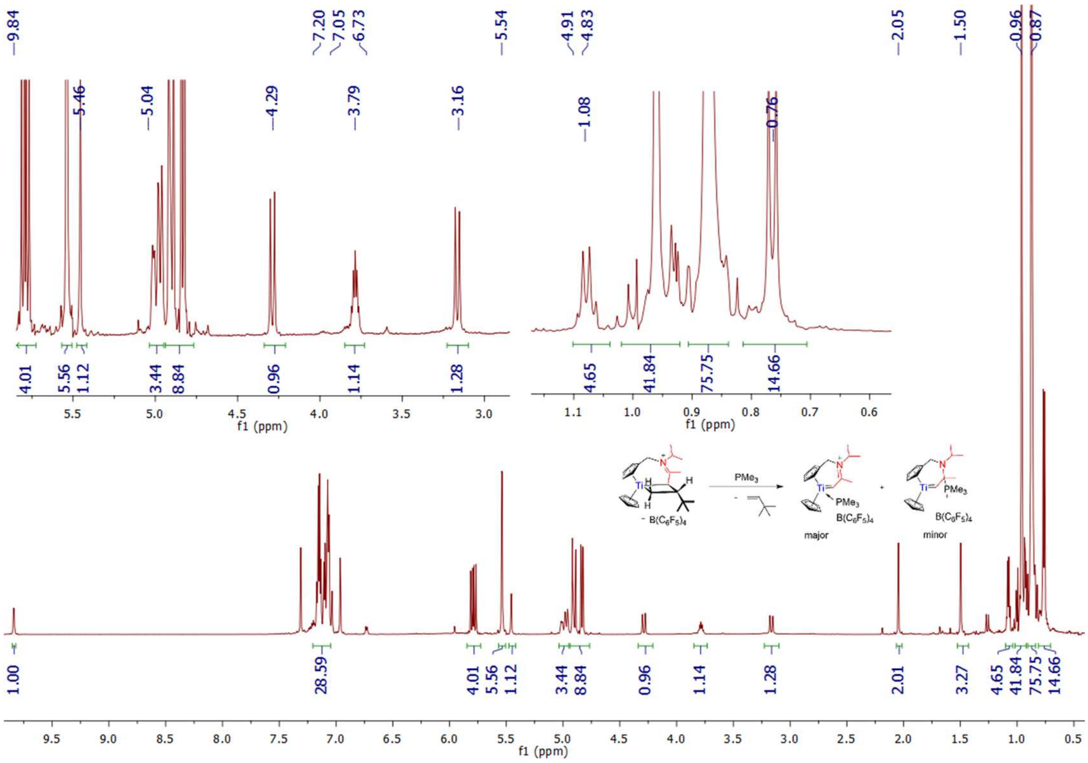


Spectrum 0-371: ^{1}H ^{15}N HMBC of 47 (600.23 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)

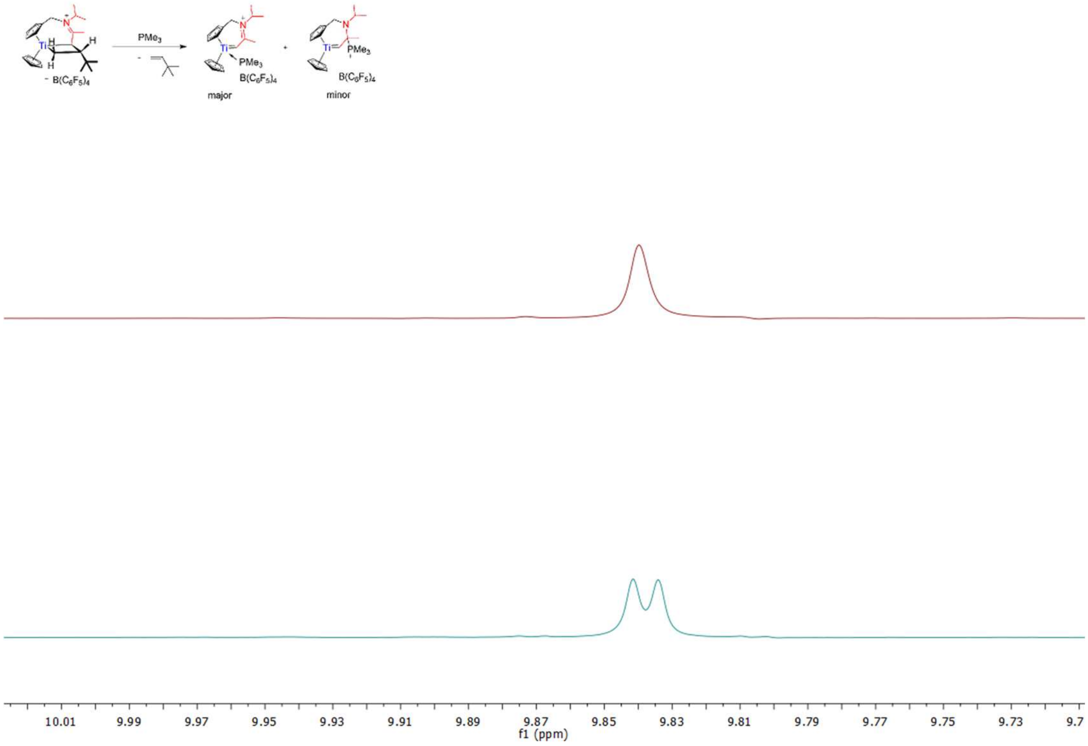


Spectrum 0-372: HRMS of 47 (Positive mode ESI, bromobenzene)

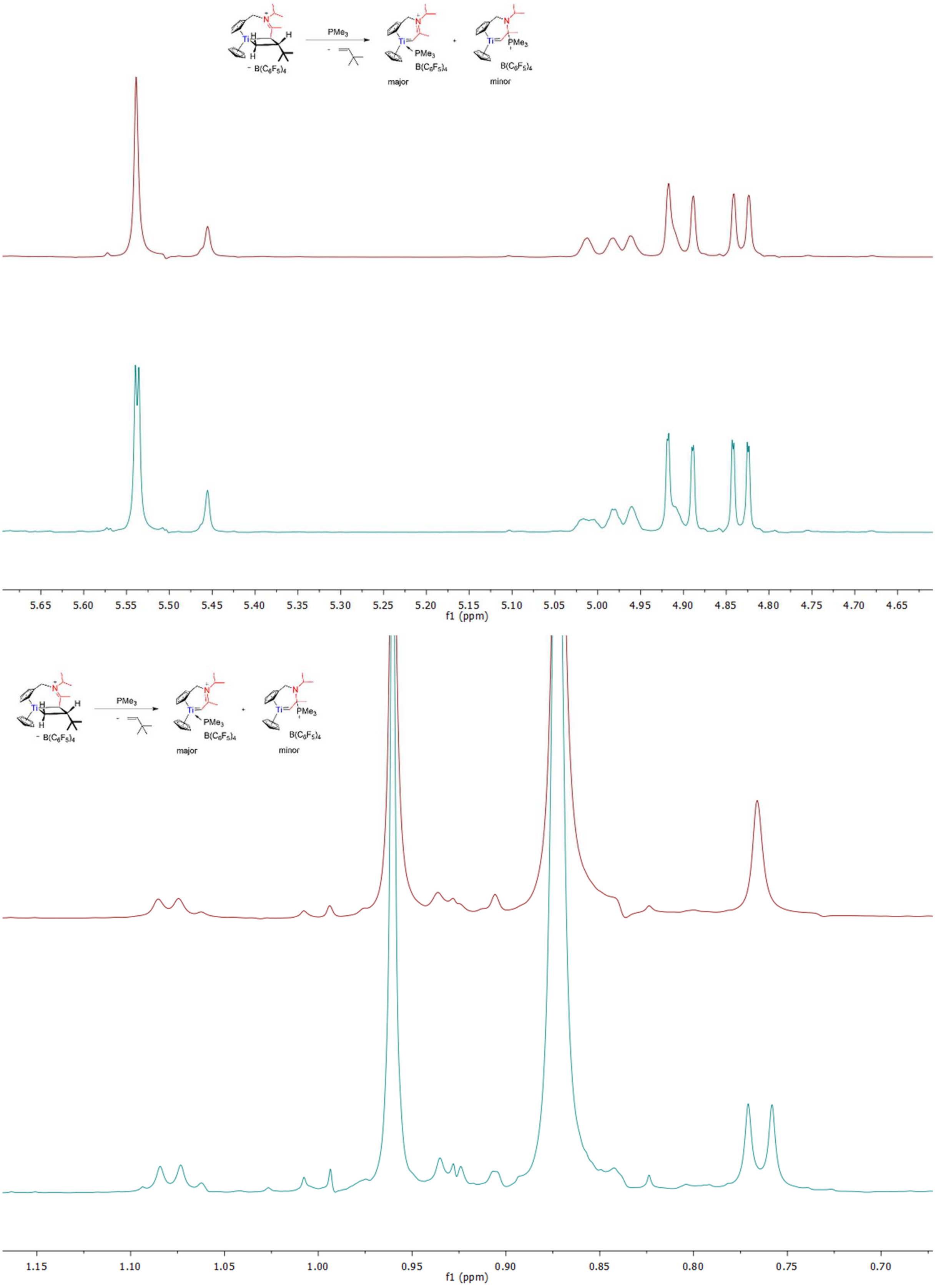
f. In situ characterization of **48**:



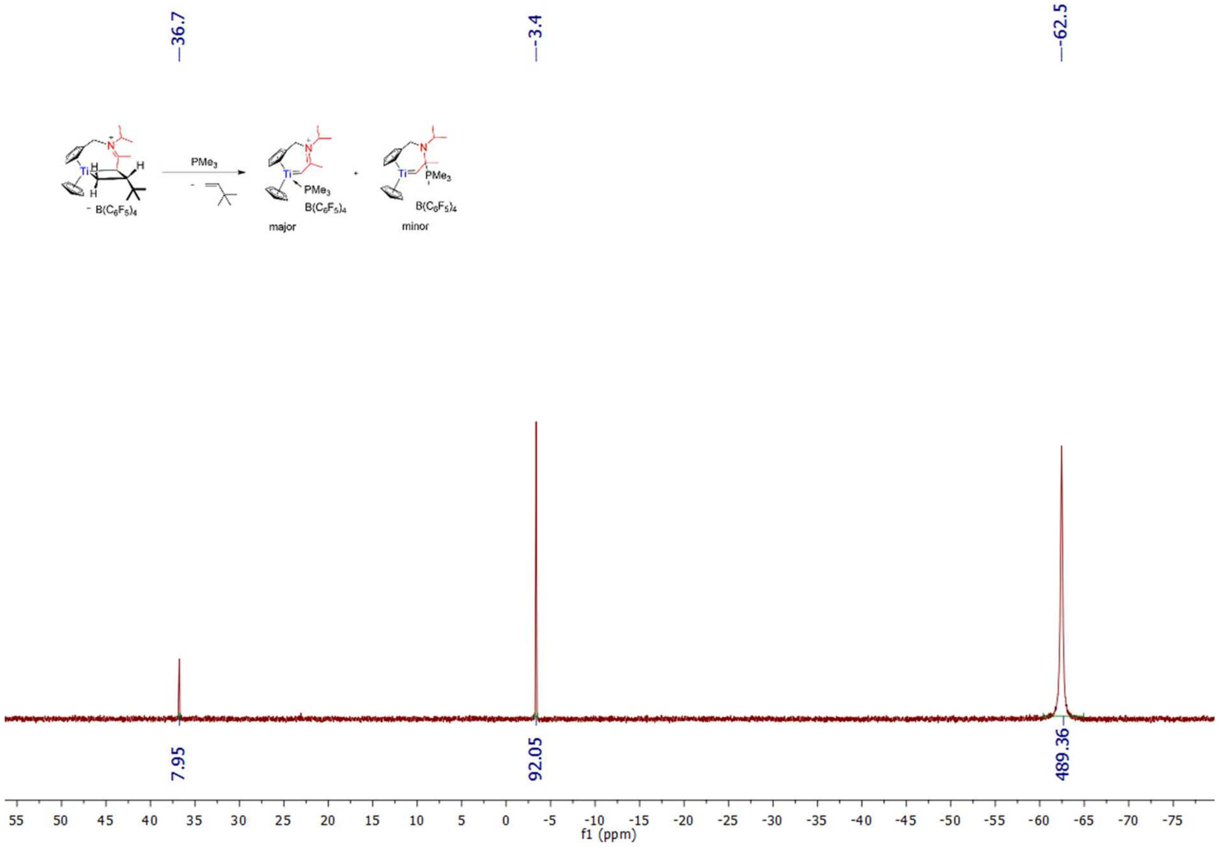
Spectrum 0-373: ^{1}H NMR of 48 (600.23 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-374: ^{1}H{^{31}P} NMR of 48 (600.23 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-375: $^{1}H\{^{31}P\}$ NMR of 48 (600.23 MHz, 300 K, bromobenzene-d_5)

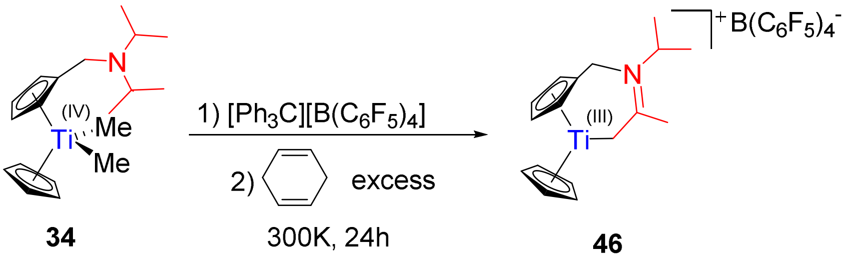


Spectrum 0-376: $^{31}\text{P}\{^{1}\text{H}\}$ NMR of 48 (243.0 MHz, 300 K, bromobenzene-d_5)

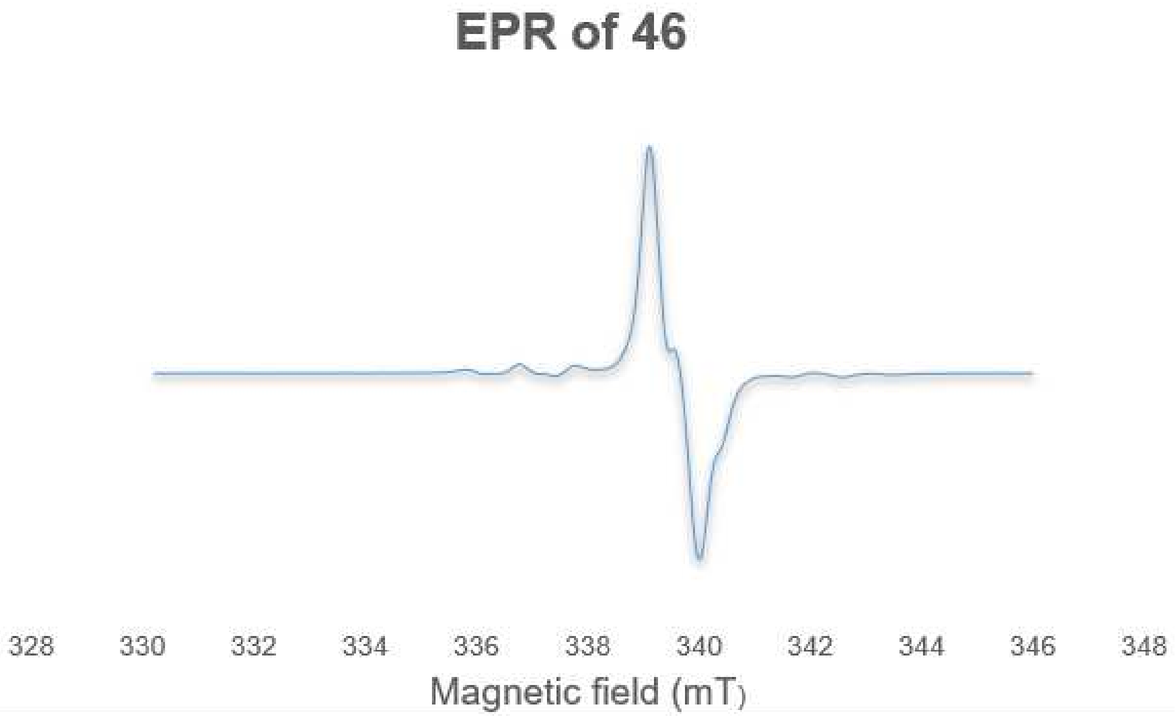
21. EPR study:

a. In situ characterization of **46**:

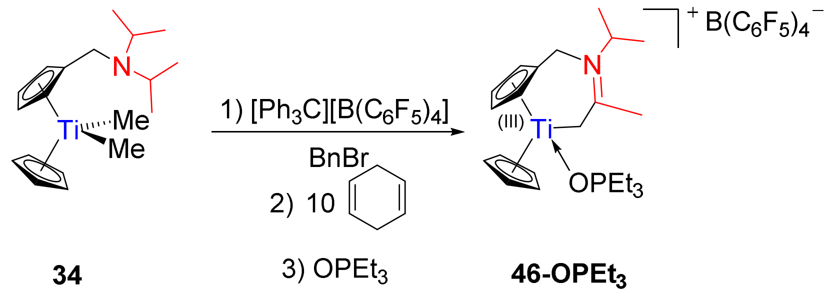
The same procedure as **46-OPEt3** was followed but EPR spectroscopy was recorded without stabilization with any phosphine oide.



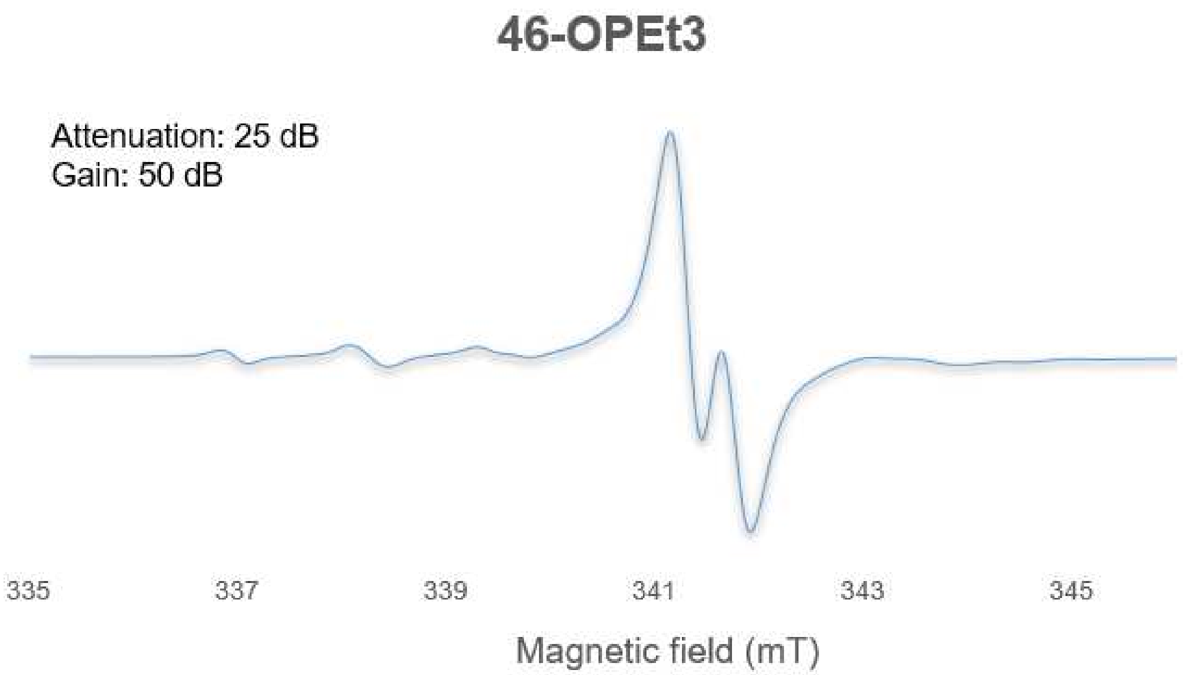
34 **46**



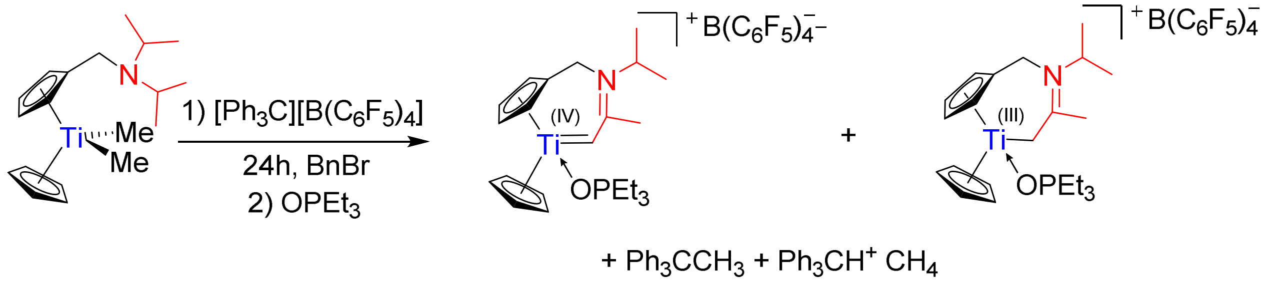
b. Crude EPR of **46-OPEt$_3$:**

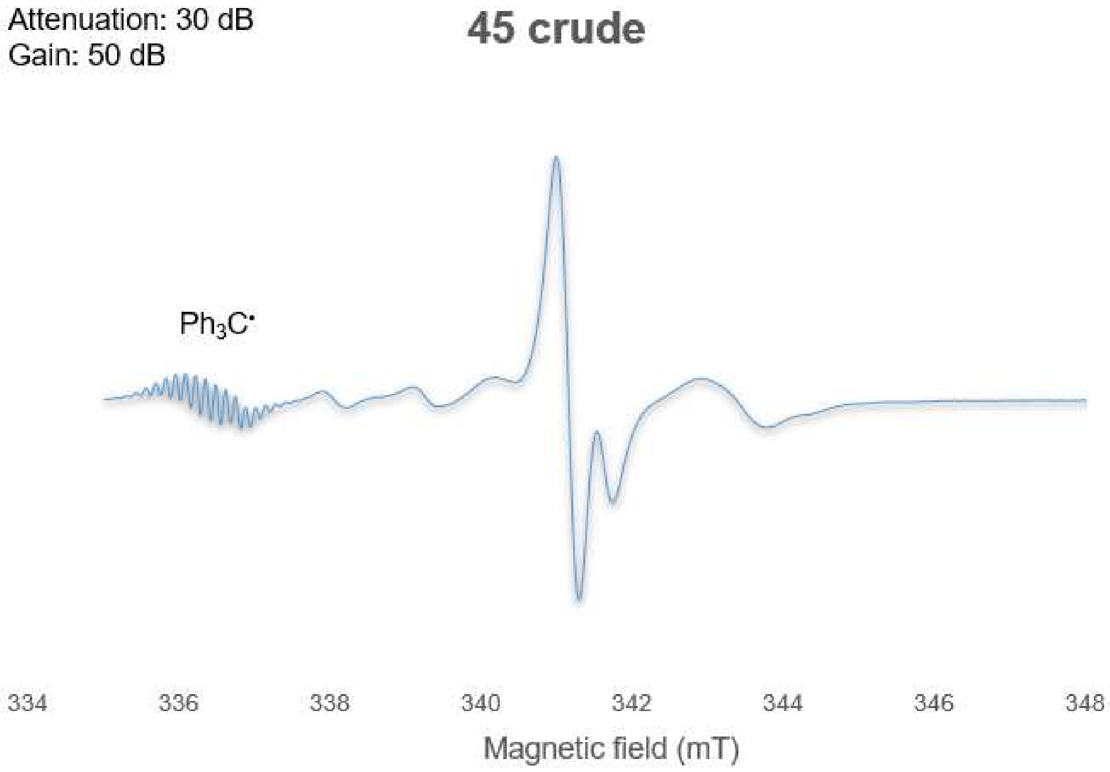


34 **46-OPEt$_3$**



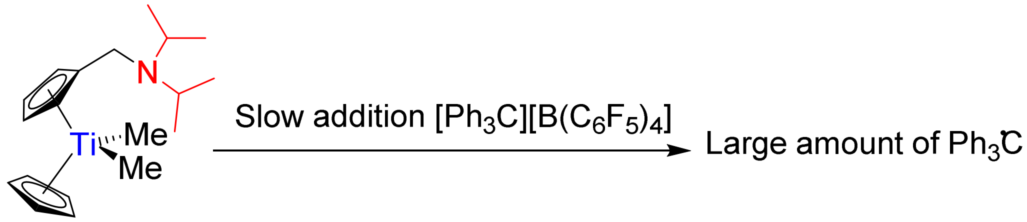
c. Crude EPR of **45:**

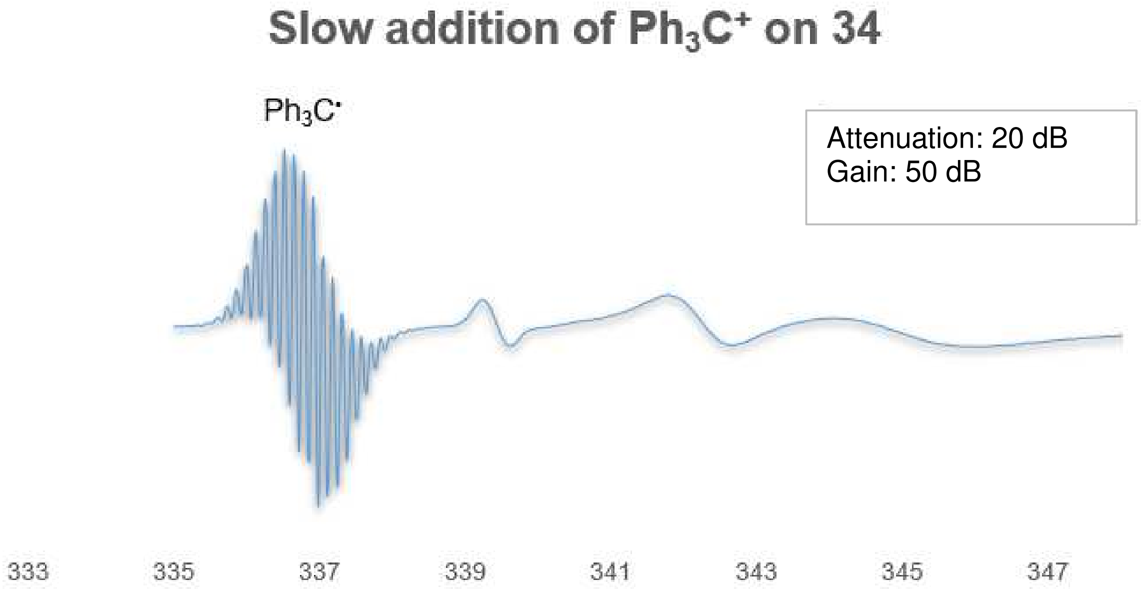




d. Additional experiment:

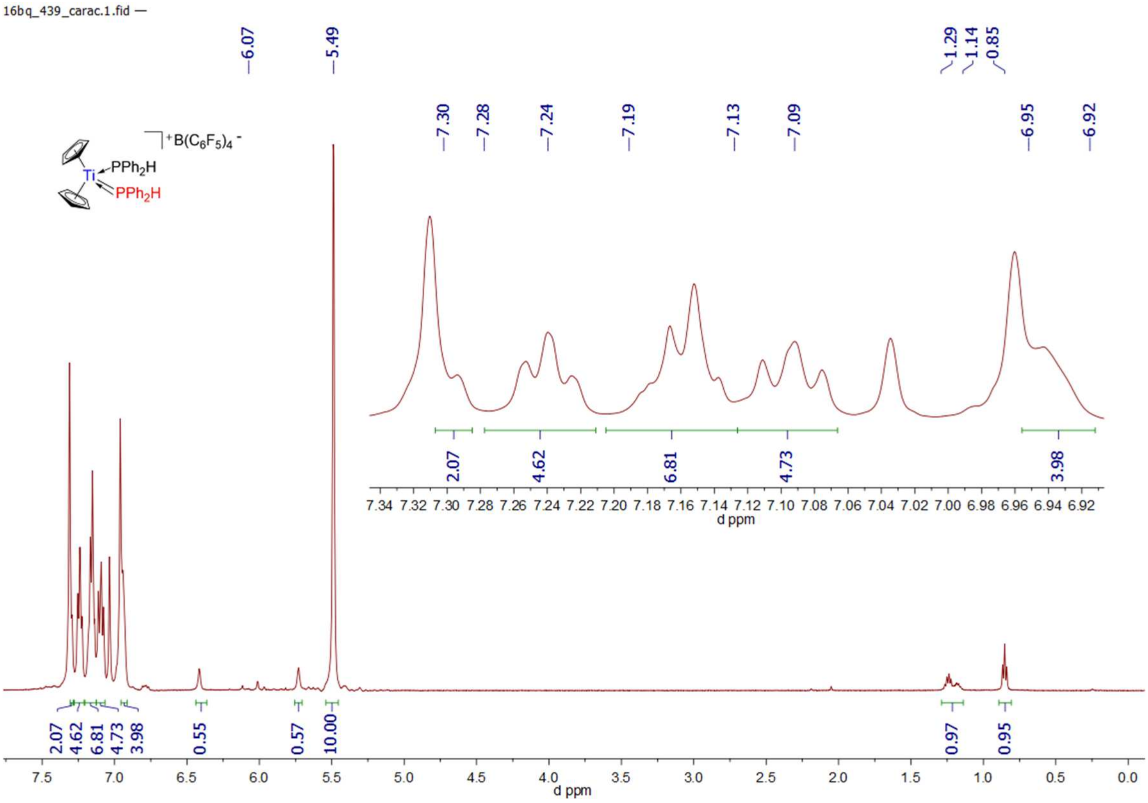
Slow addition of Ph_3C+ on **34** then EPR measurement:



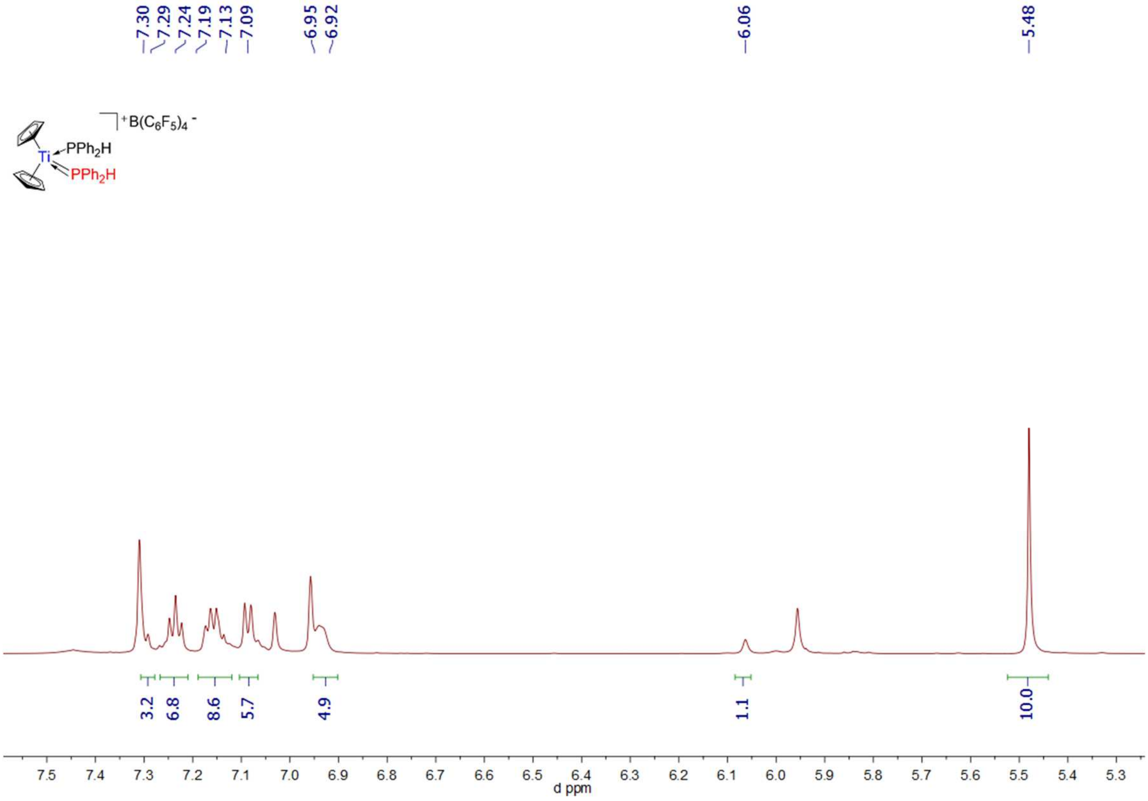


C. Appendix Chapter IV

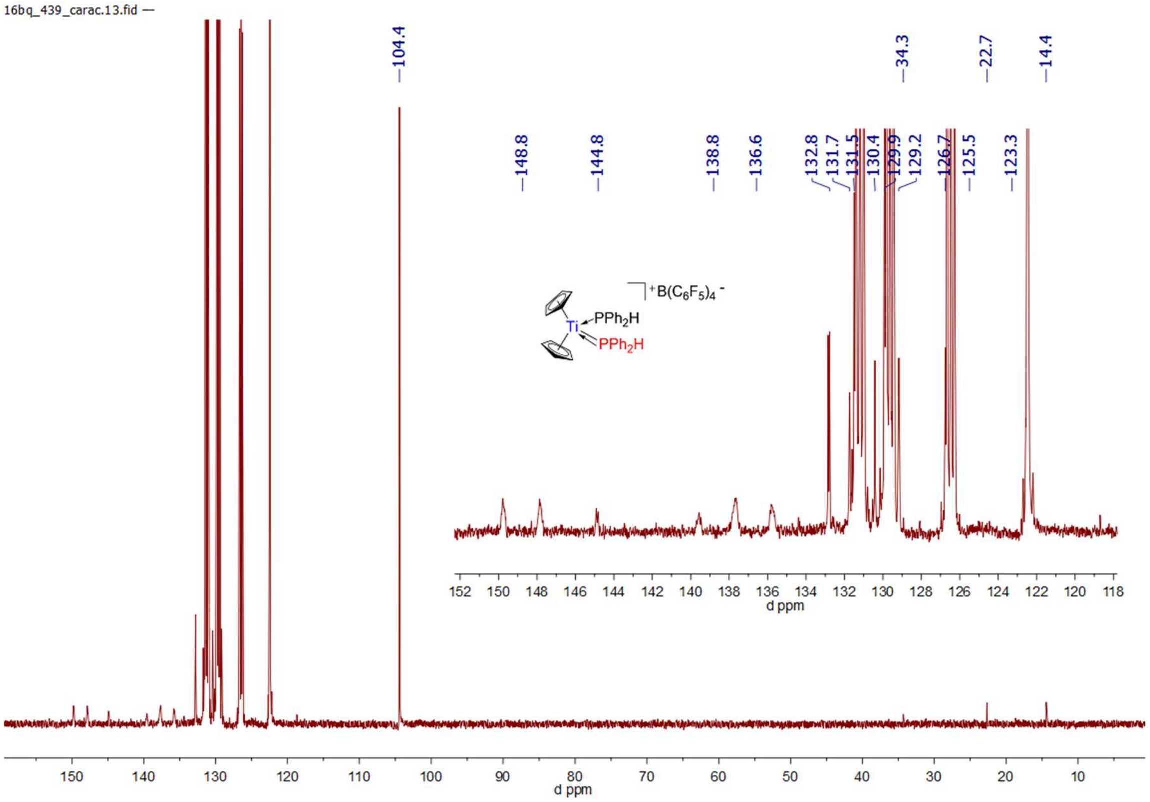
22. Compound **50**:



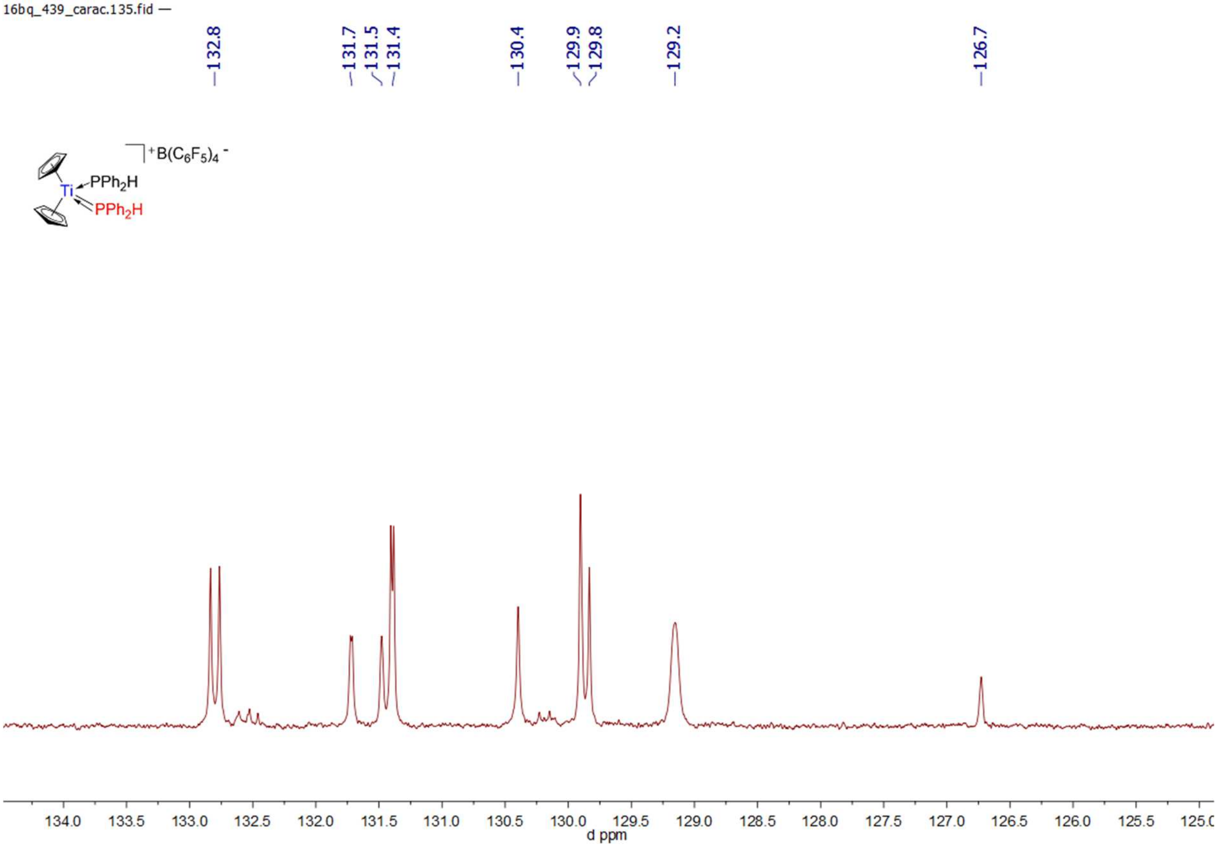
Spectrum 0-377: ^{1}H NMR of 50 (500.03 MHz, 300 K, bromobenzene-d_5)



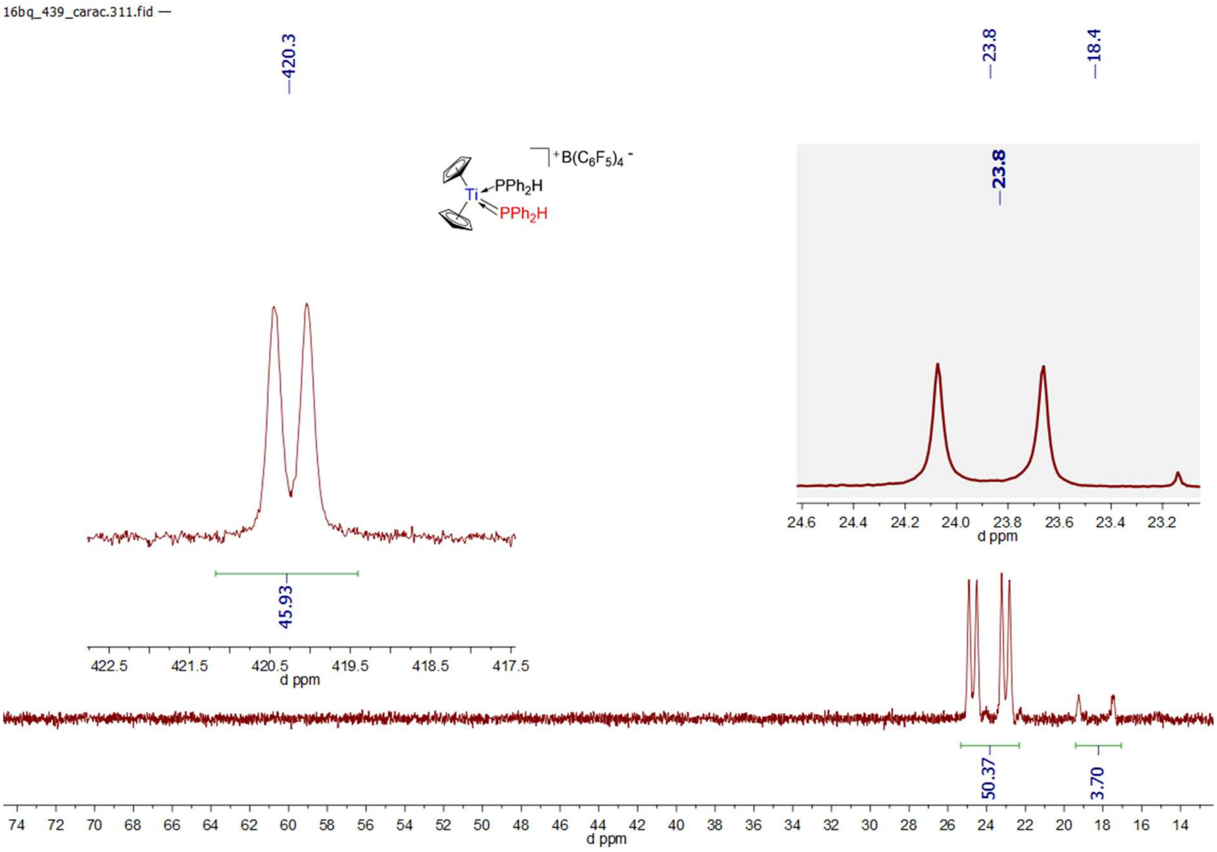
Spectrum 0-378: $^{1}H\{^{31}P\}$ NMR (top) correlated with ^{1}H (bottom) of 50 (500.03 MHz, 300 K, bromobenzene-d_5)



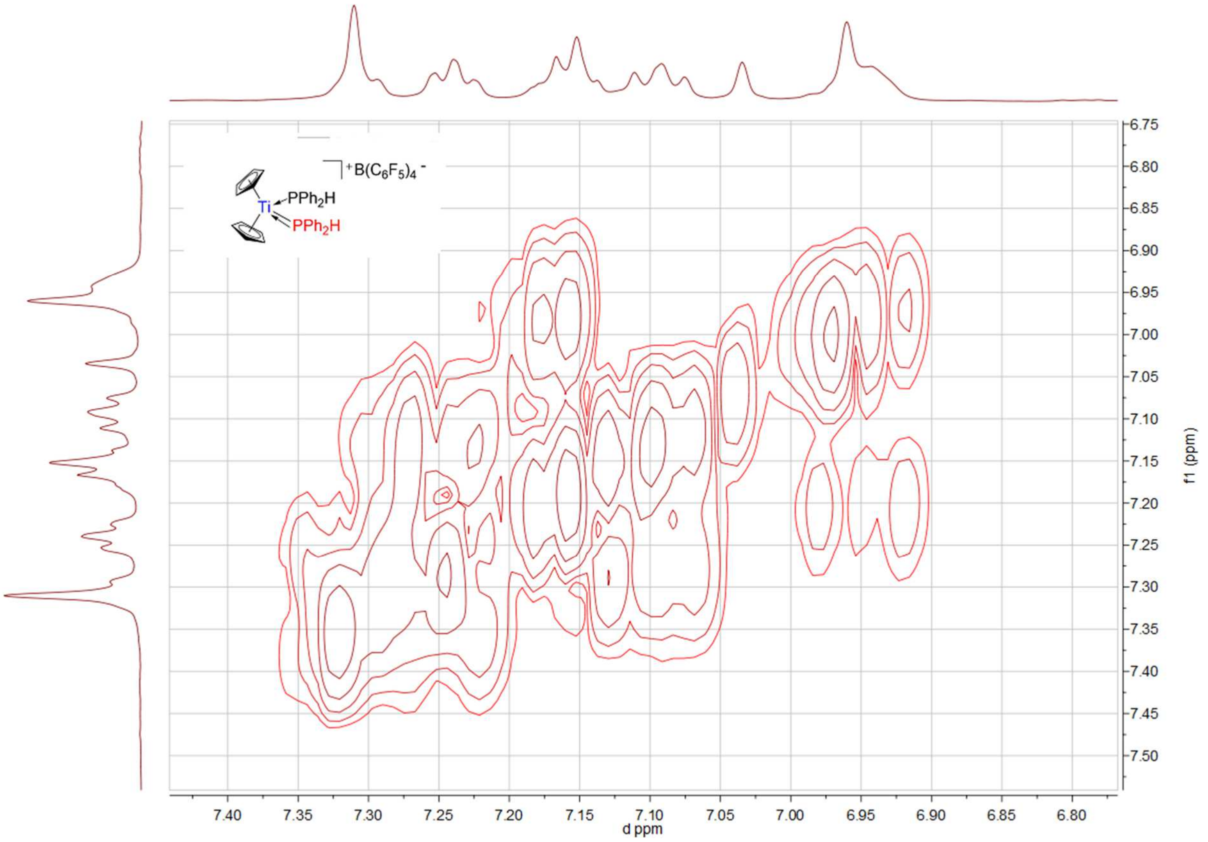
Spectrum 0-379: $^{13}C\{^{1}H\}$ NMR of 50 (125.75 MHz, 300 K, bromobenzene-d_5)



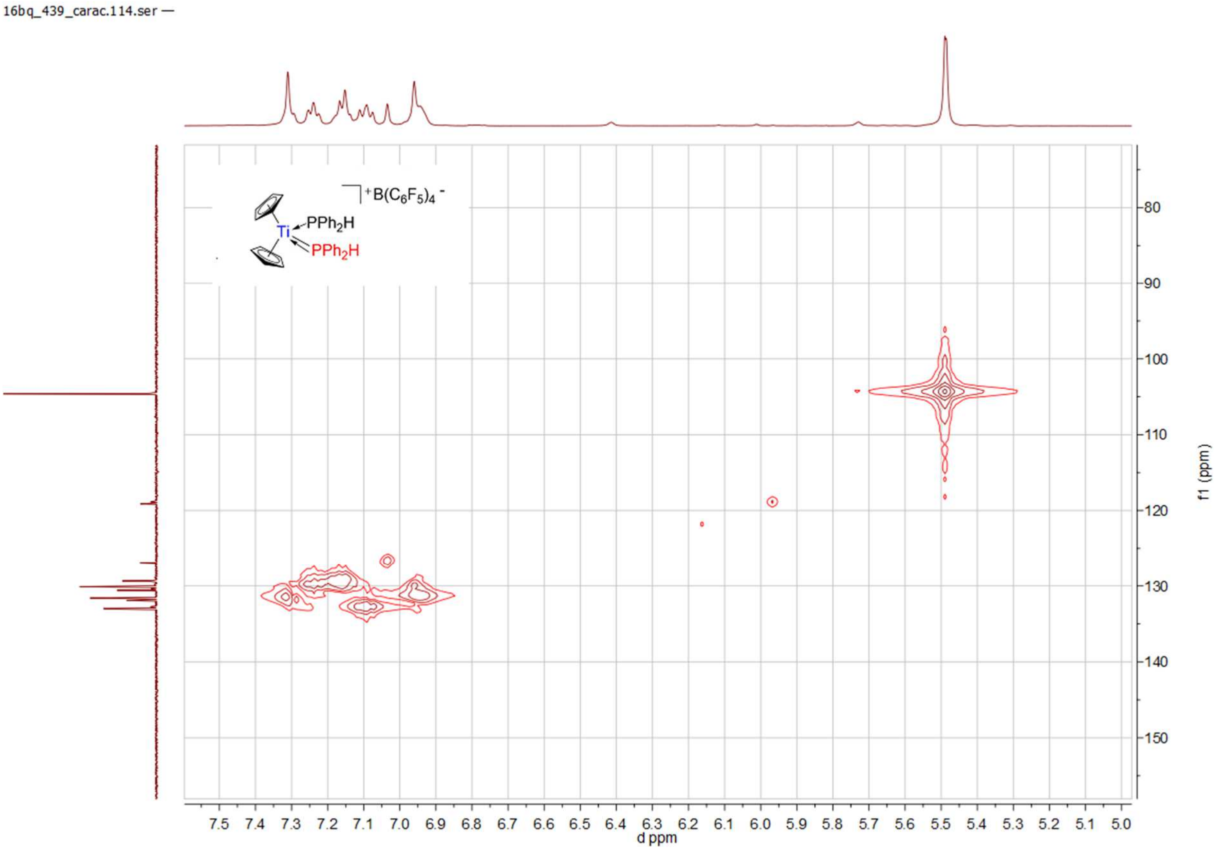
Spectrum 0-380: dept135 NMR of 50 (125.75 MHz, 300 K, bromobenzene-d_5)



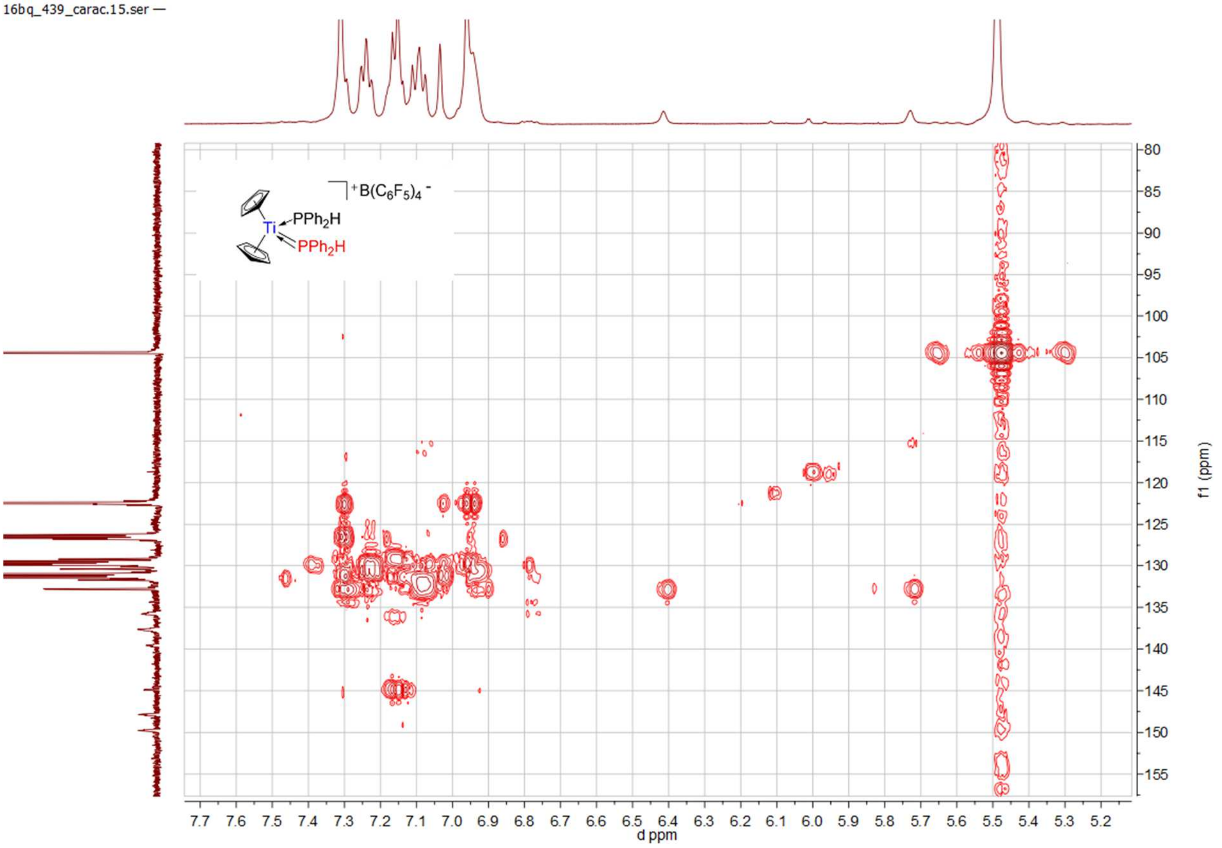
Spectrum 0-381: $^{31}P\{^1H\}$ and ^{31}P (opacified) NMR of 50 (202.41 MHz, 300 K, bromobenzene-d_5)



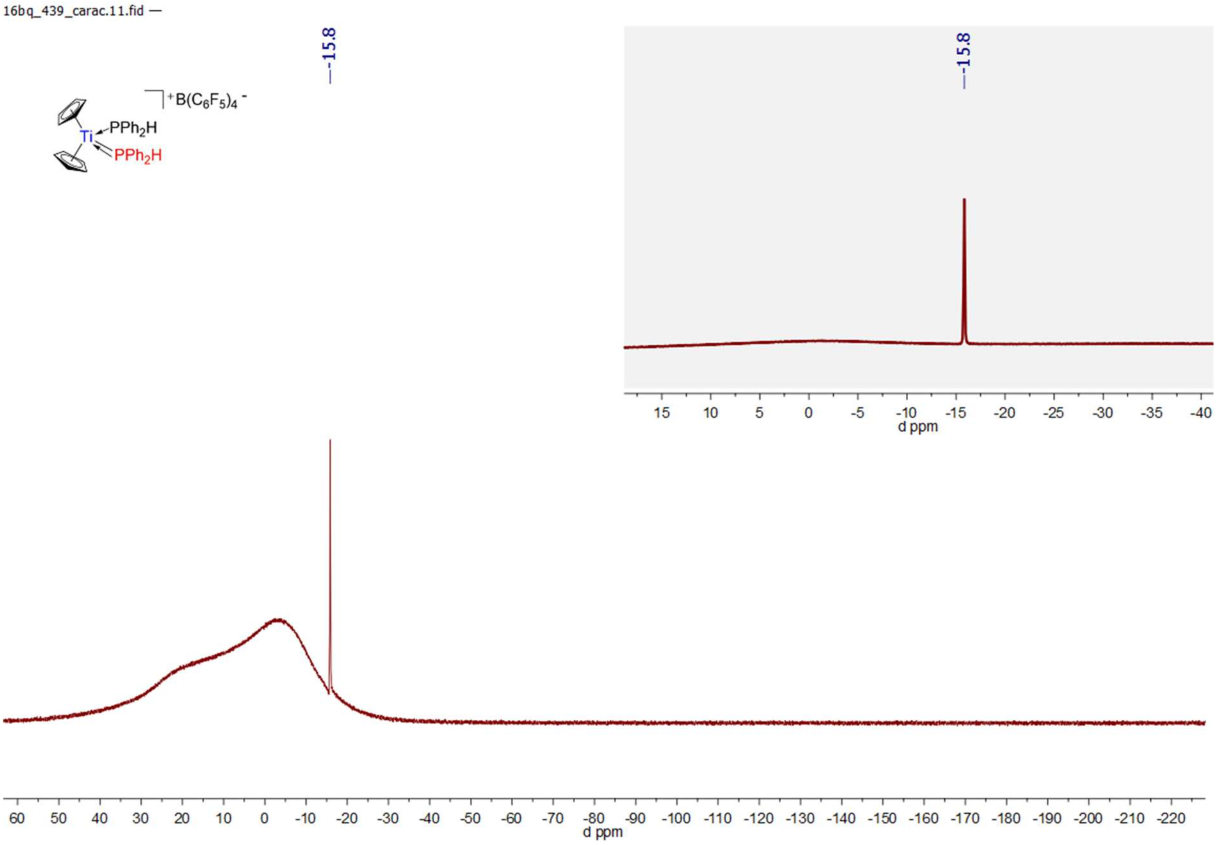
Spectrum 0-382: ^1H ^1H COSY of 50 (500.03 MHz, 300 K, 273 K, bromobenzene-d_5)



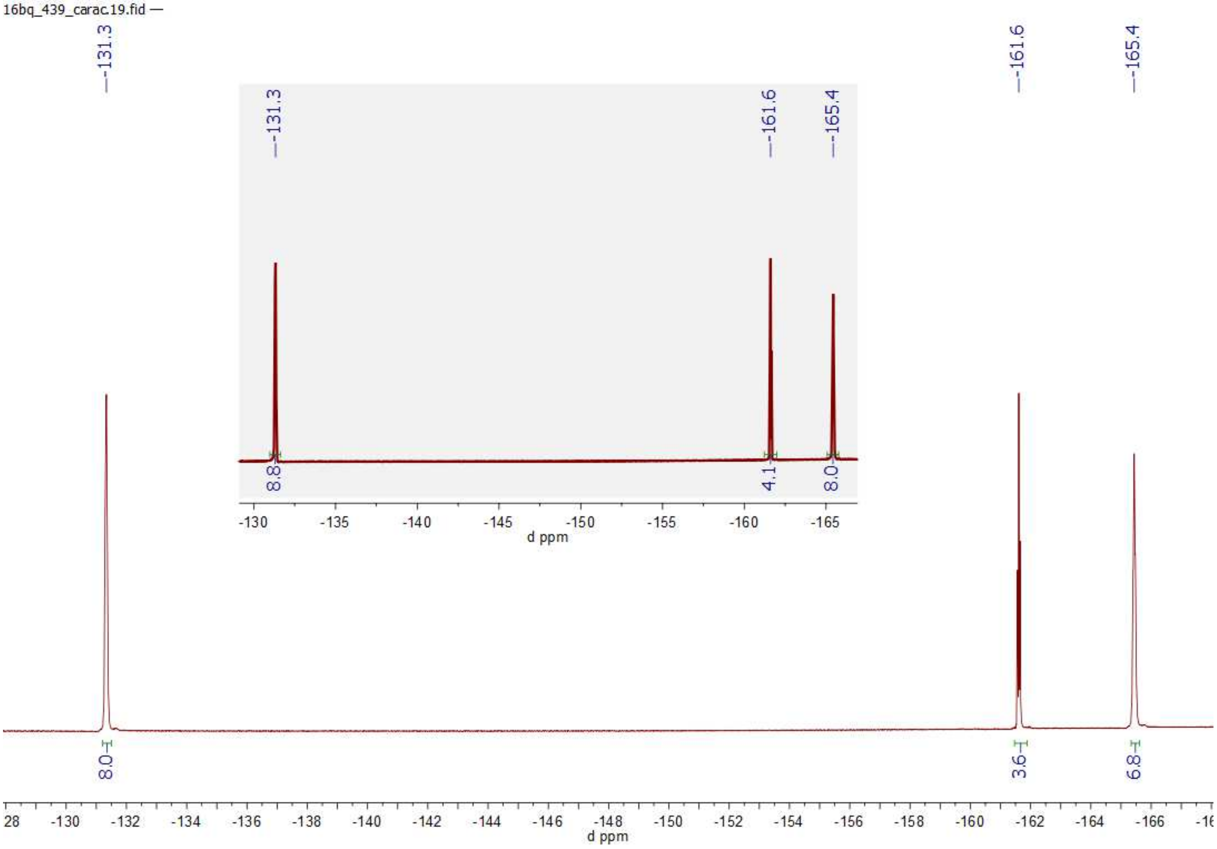
Spectrum 0-383: ^1H ^{13}C HMQC of 50 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d_5)



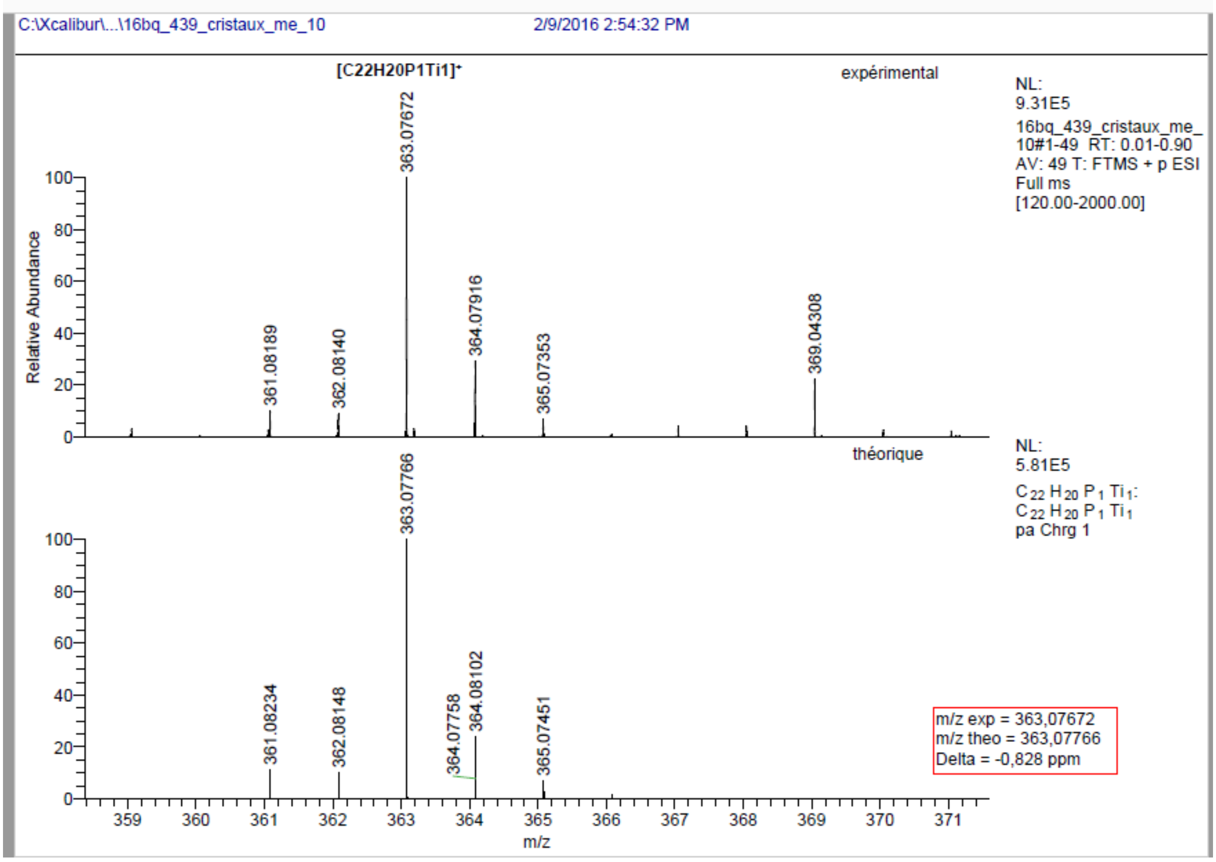
Spectrum 0-384: ^1H ^{13}C HMBC of 50 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d_5)



Spectrum 0-385: $^{11}B\{^1H\}$ and ^{11}B NMR of 50 (160.43 MHz, 300 K, bromobenzene-d$_5$)

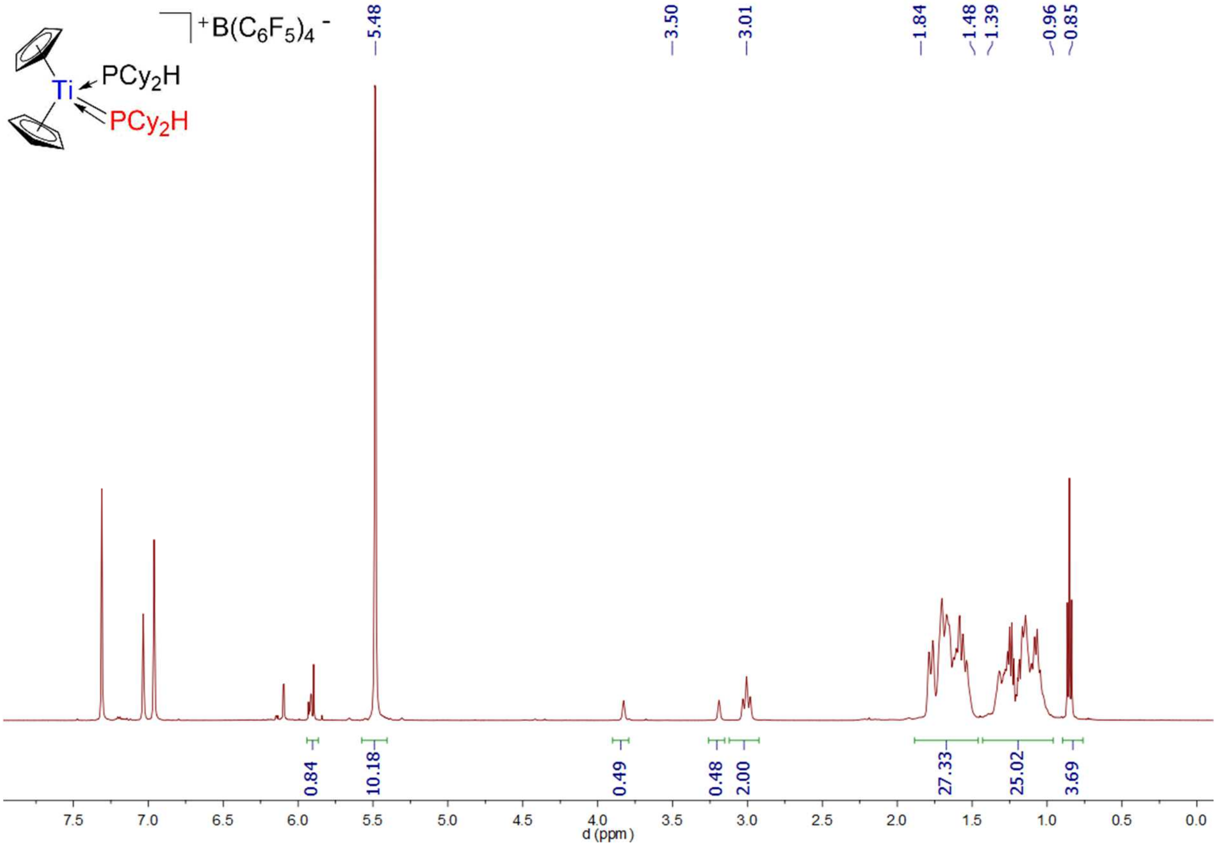


Spectrum 0-386: $^{19}F\{^1H\}$ and ^{19}F NMR of 50 (470.45 MHz, 300 K, bromobenzene-d$_5$)

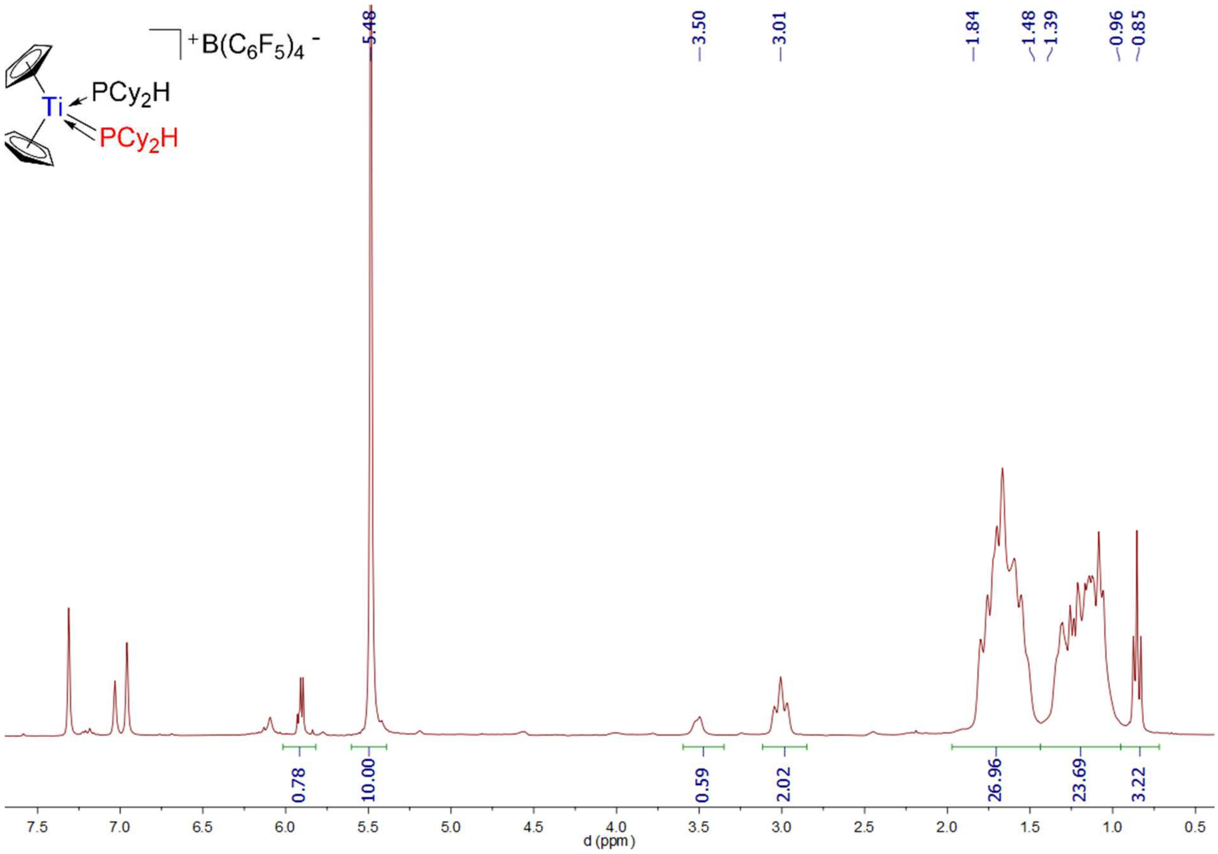


Spectrum 0-387: HRMS of 50 (Positive mode ESI, dichloromethane)

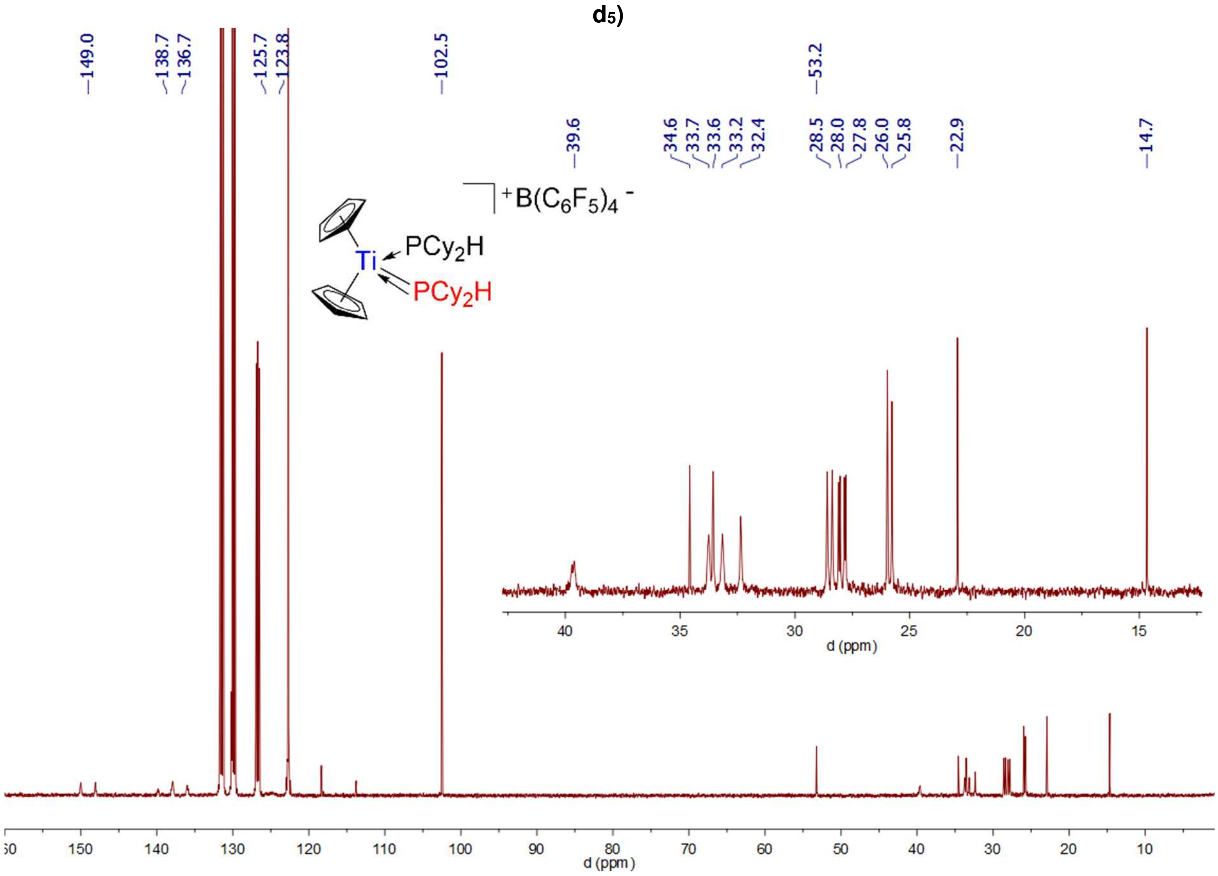
23. Compound **51**:



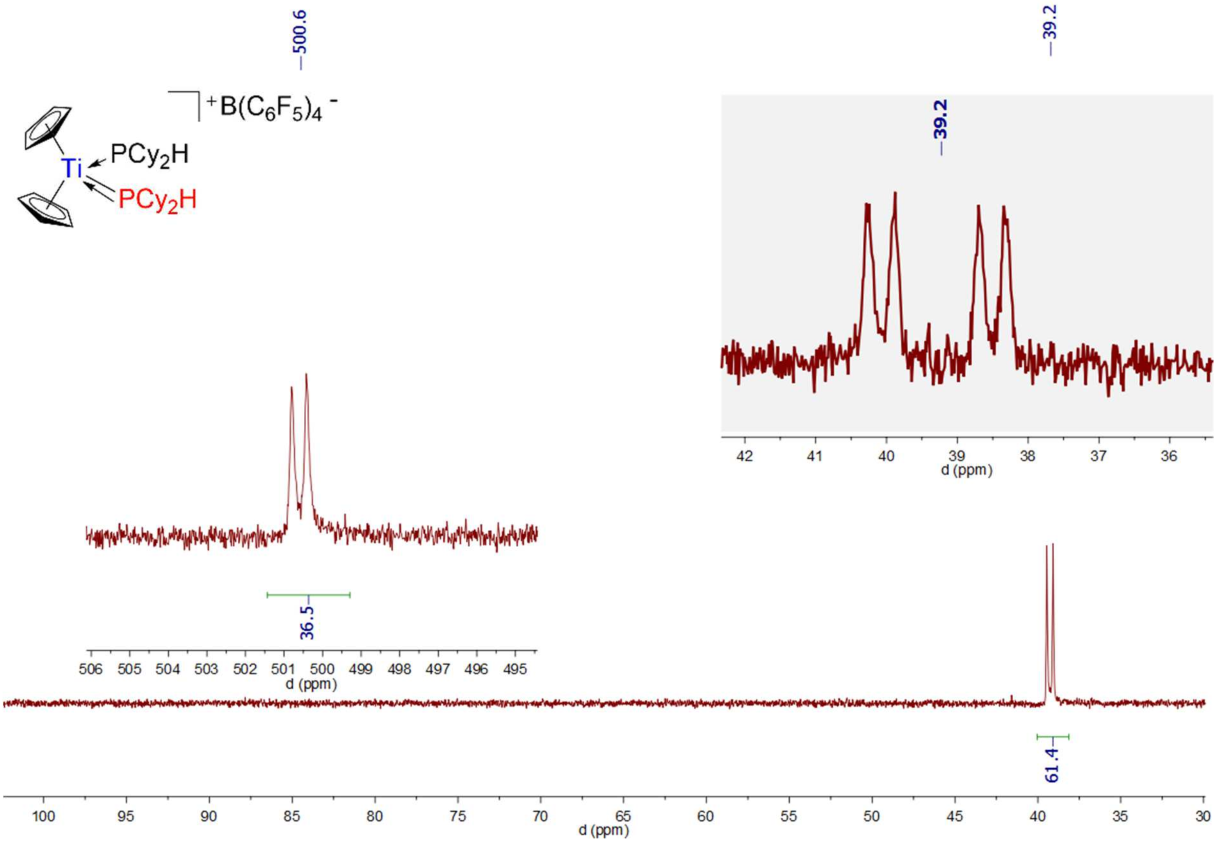
Spectrum 0-388: ^{1}H NMR of 51 (500.03 MHz, 300 K, bromobenzene-d$_5$)



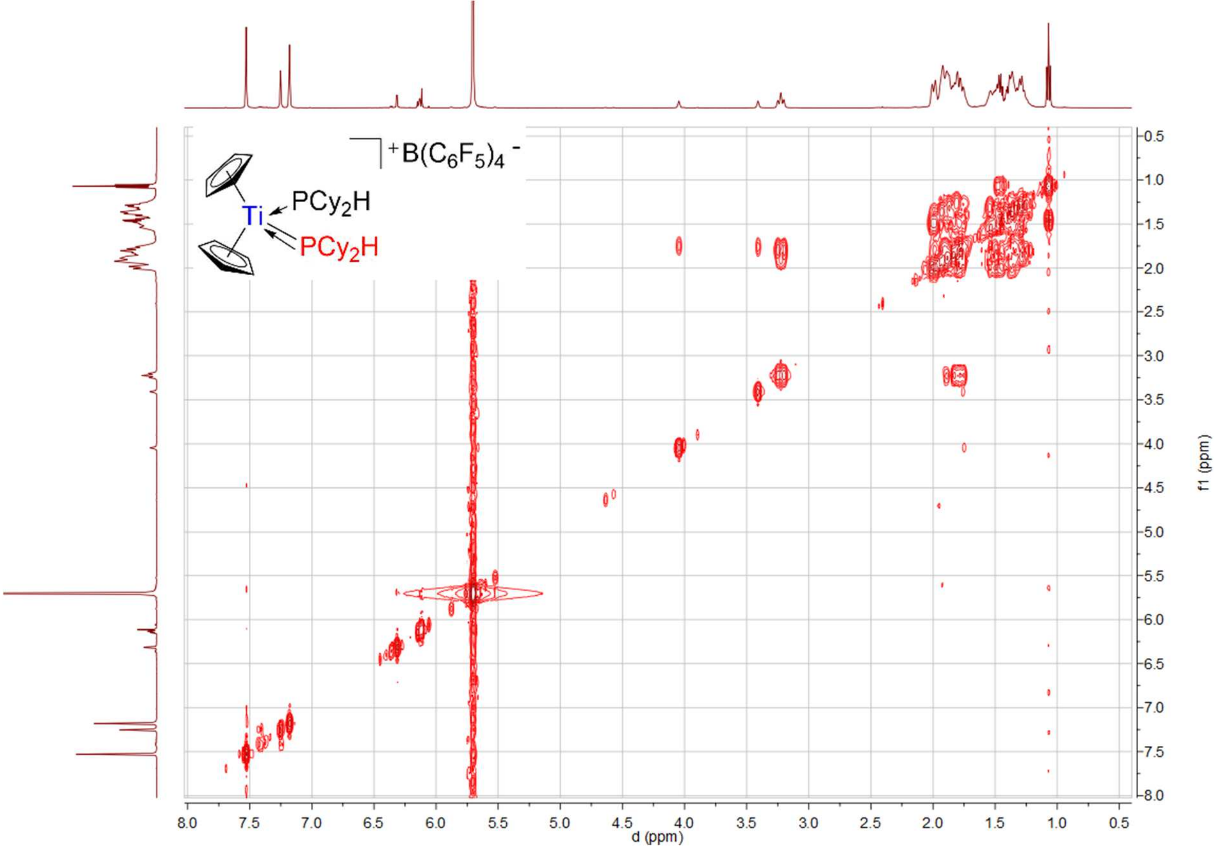
Spectrum 0-389: ^{1}H{^{31}P} NMR (top) correlated with ^{1}H (bottom) of 51 (500.03 MHz, 300 K, bromobenzene-d$_5$)



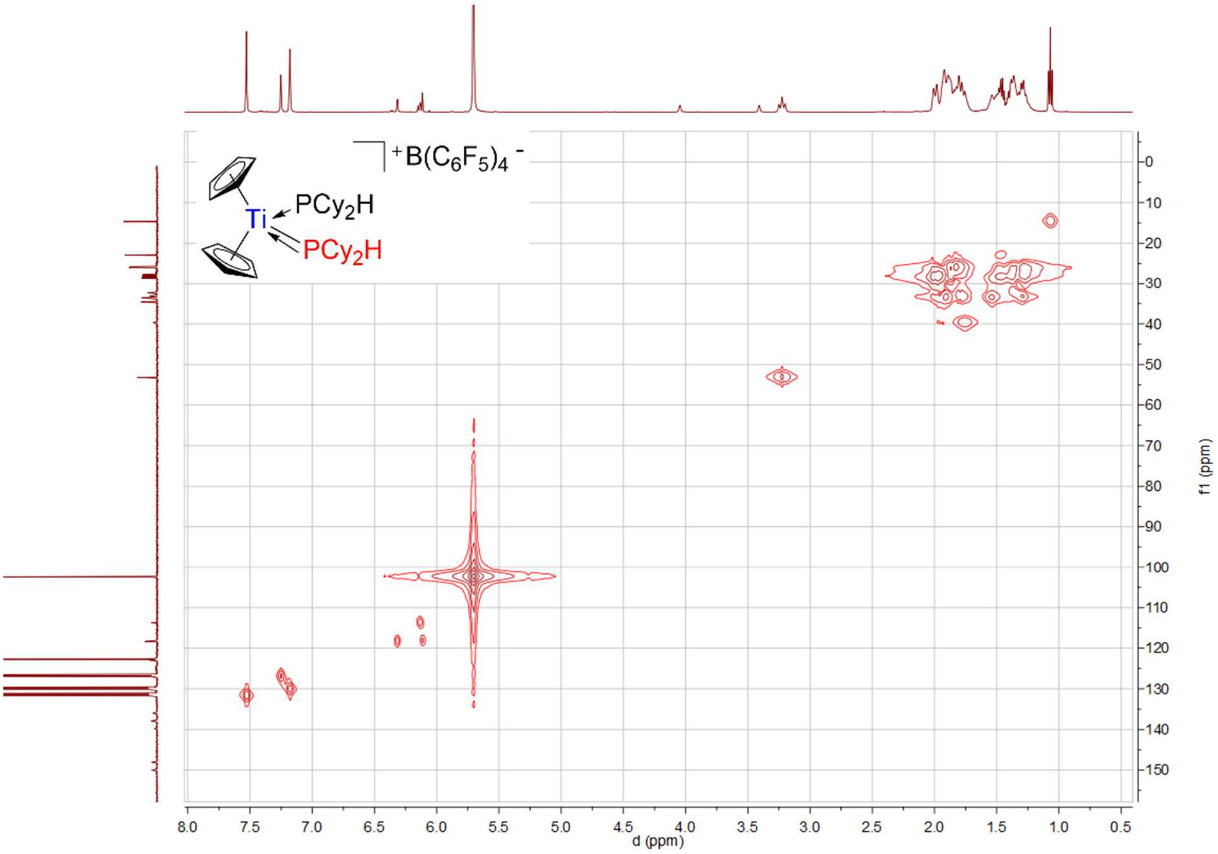
Spectrum 0-390: ^{13}C{^{1}H} NMR of 51 (125.75 MHz, 300 K, bromobenzene-d$_5$)



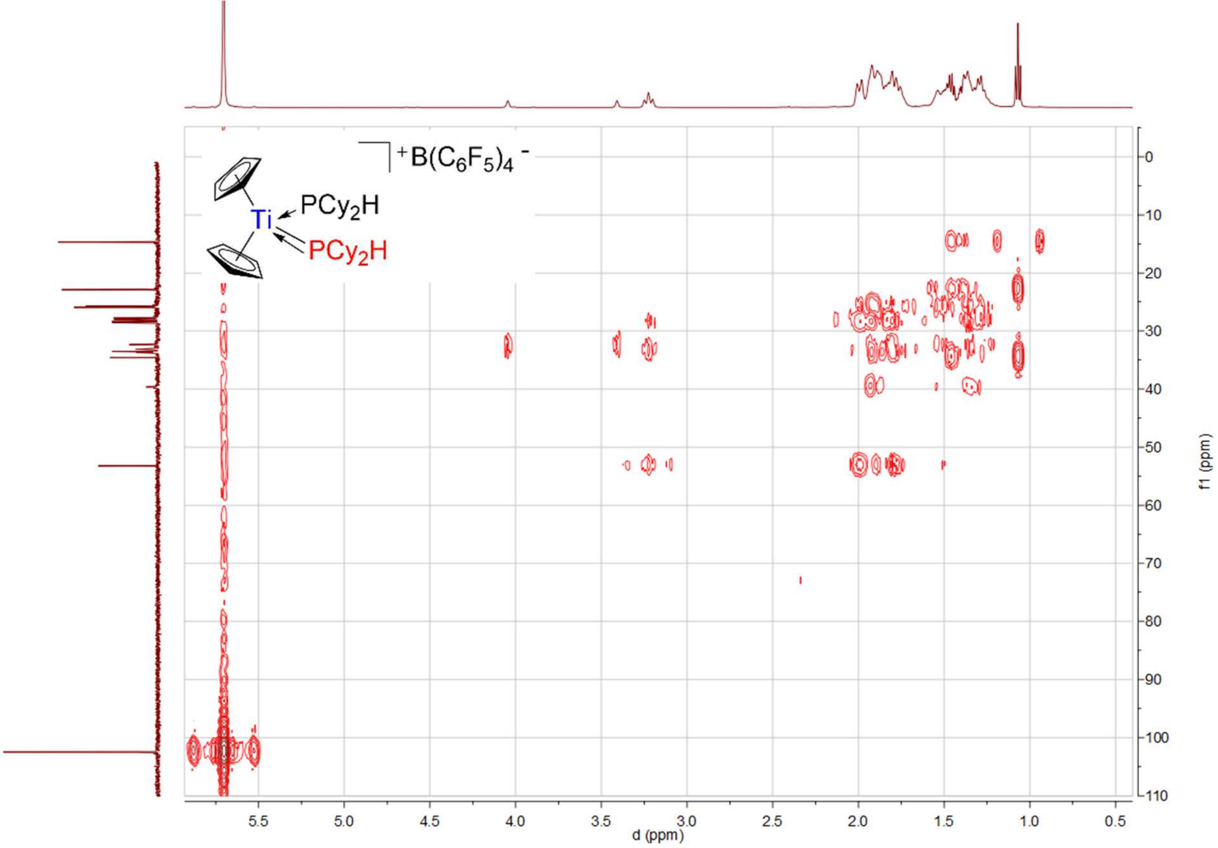
Spectrum 0-391: $^{31}P\{^1H\}$ and ^{31}P (opacified) NMR of 51 (202.41 MHz, 300 K, bromobenzene-d_5)



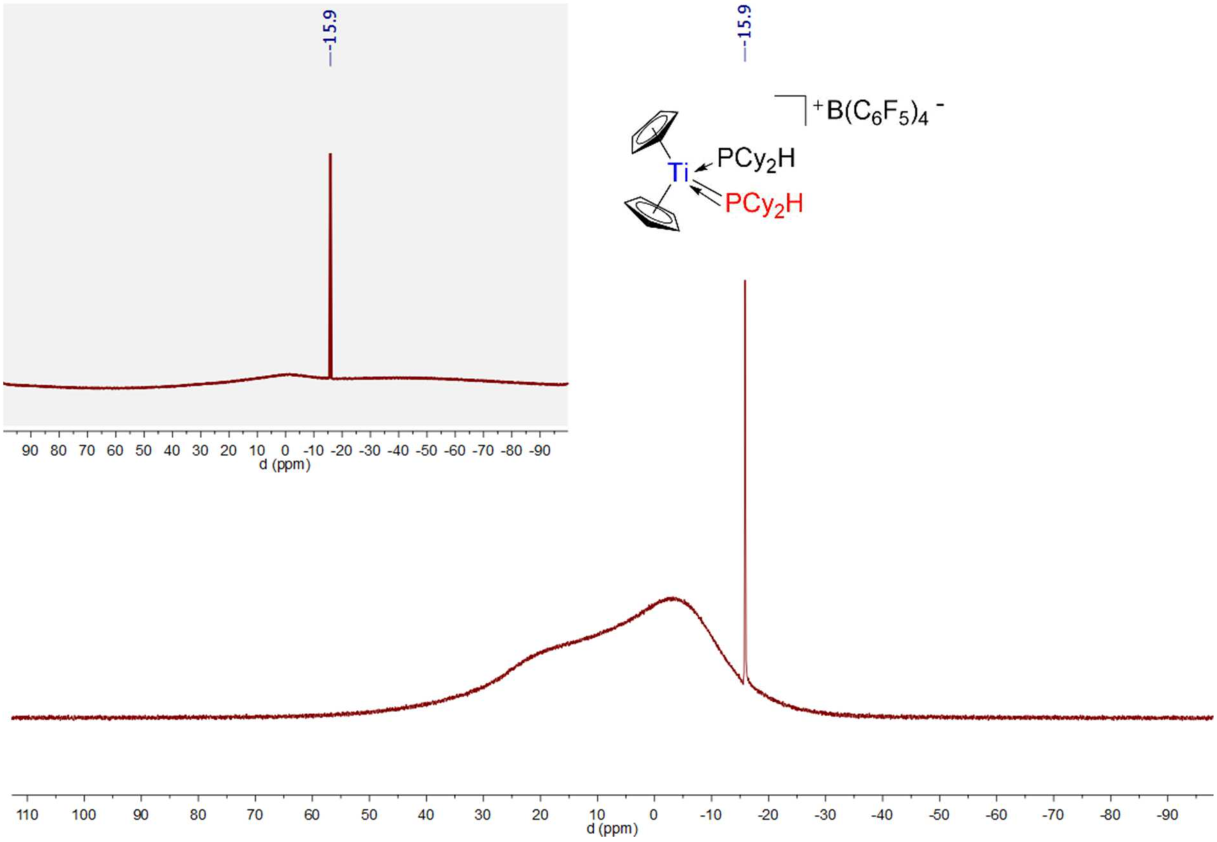
Spectrum 0-392: ^1H ^1H COSY of 51 (500.03 MHz, 300 K, 273 K, bromobenzene-d_5)



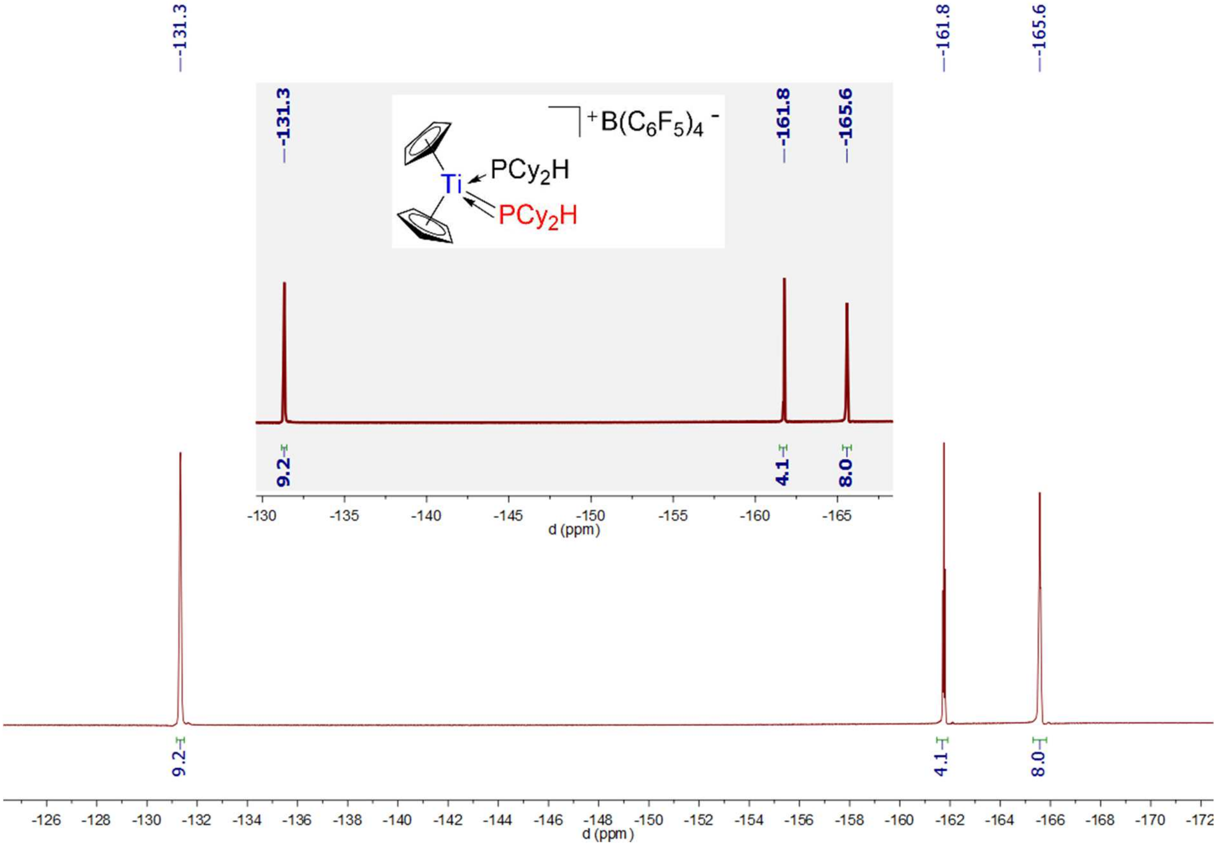
Spectrum 0-393: ^{1}H ^{13}C HMQC of 51 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



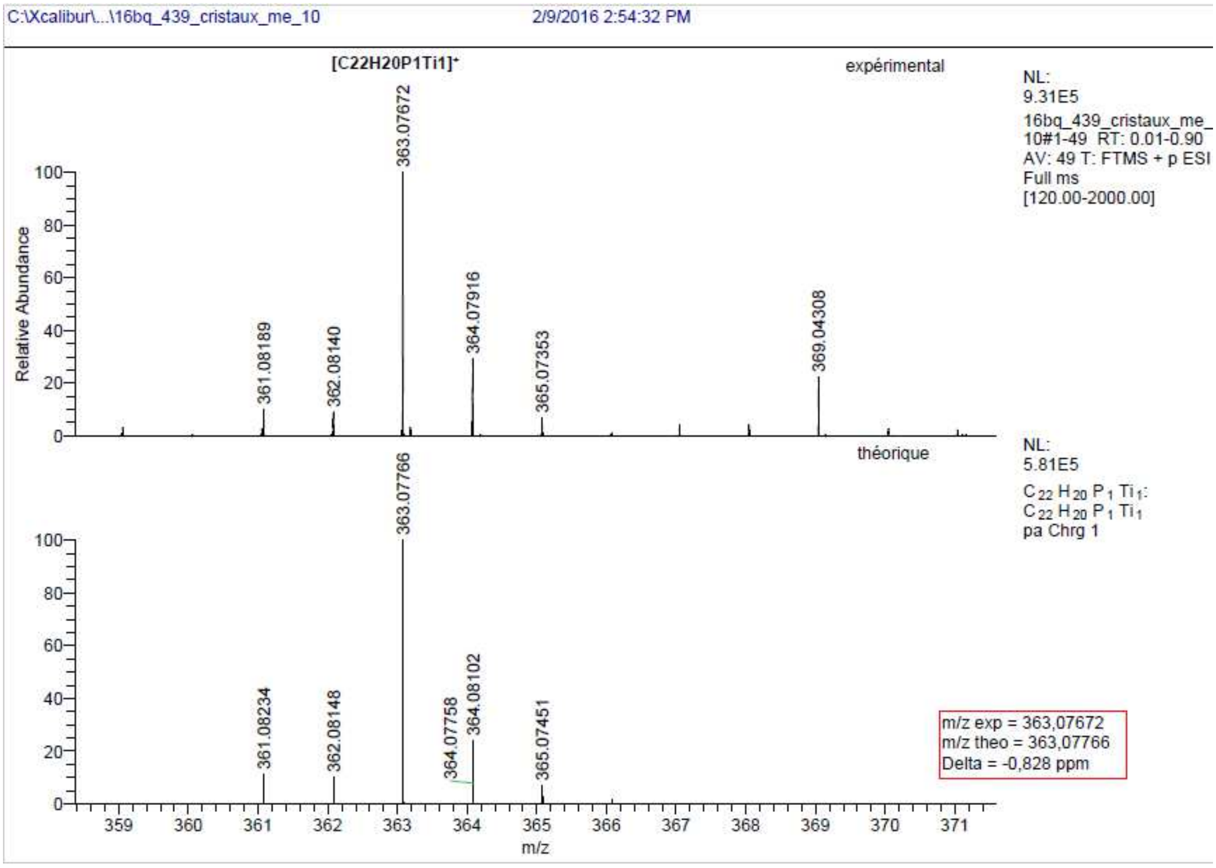
Spectrum 0-394: ^{1}H ^{13}C HMBC of 51 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-395: $^{11}B\{^1H\}$ and ^{11}B NMR of 51 (160.43 MHz, 300 K, bromobenzene-d_5)

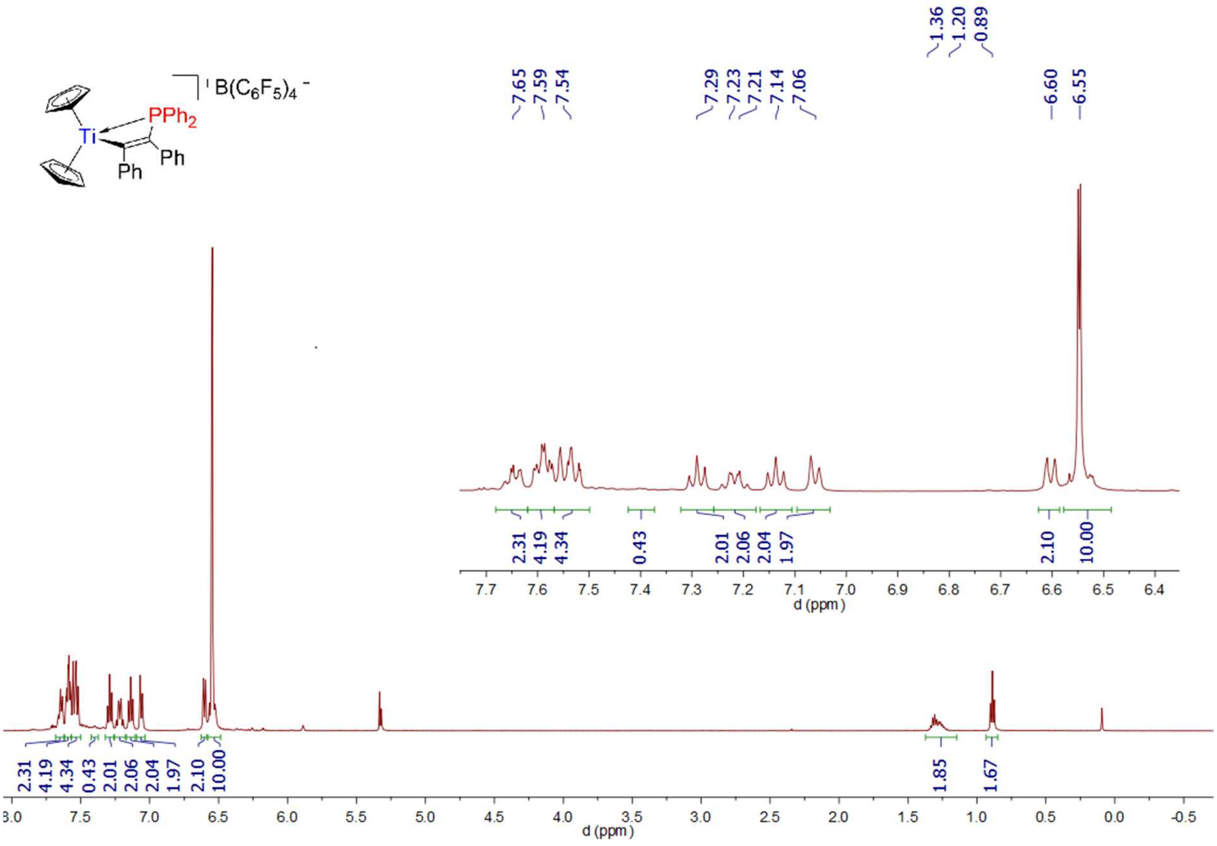


Spectrum 0-396: $^{19}F\{^1H\}$ and ^{19}F NMR of 51 (470.45 MHz, 300 K, bromobenzene-d_5)

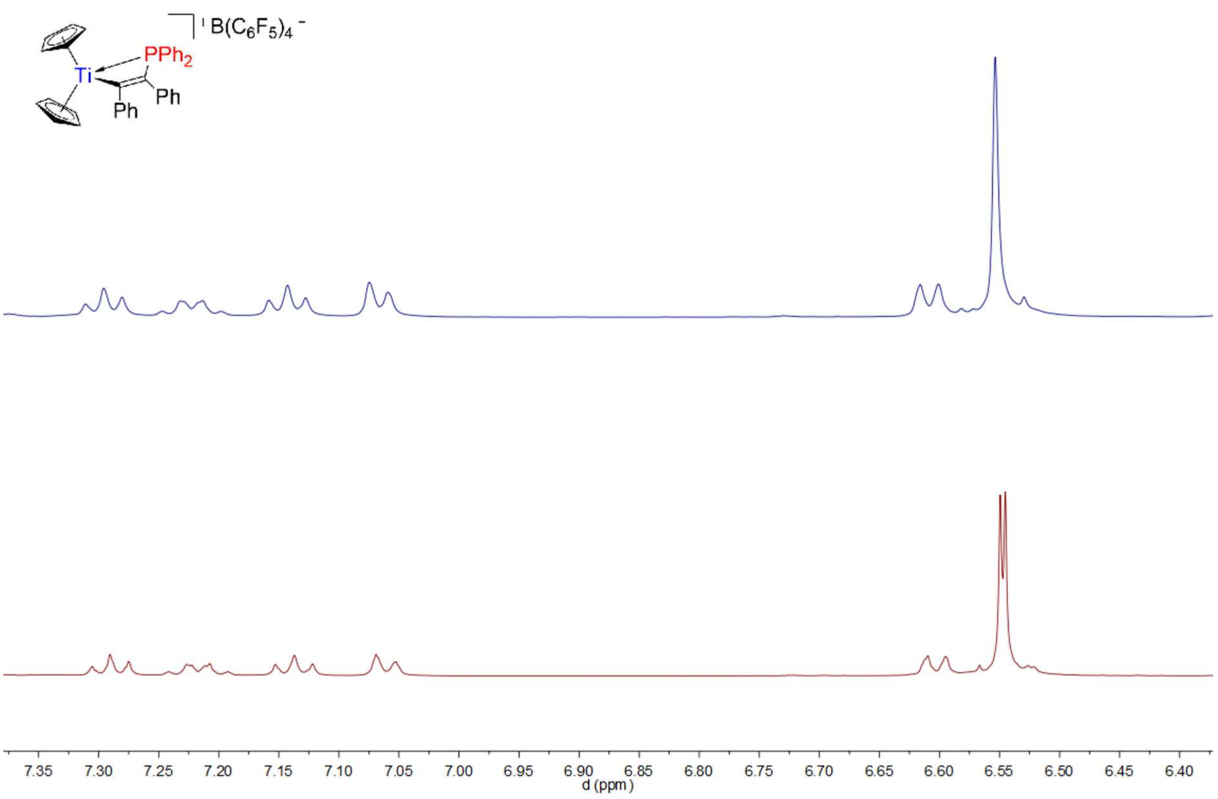


Spectrum 0-397: HRMS of 51 (Positive mode ESI, dichloromethane)

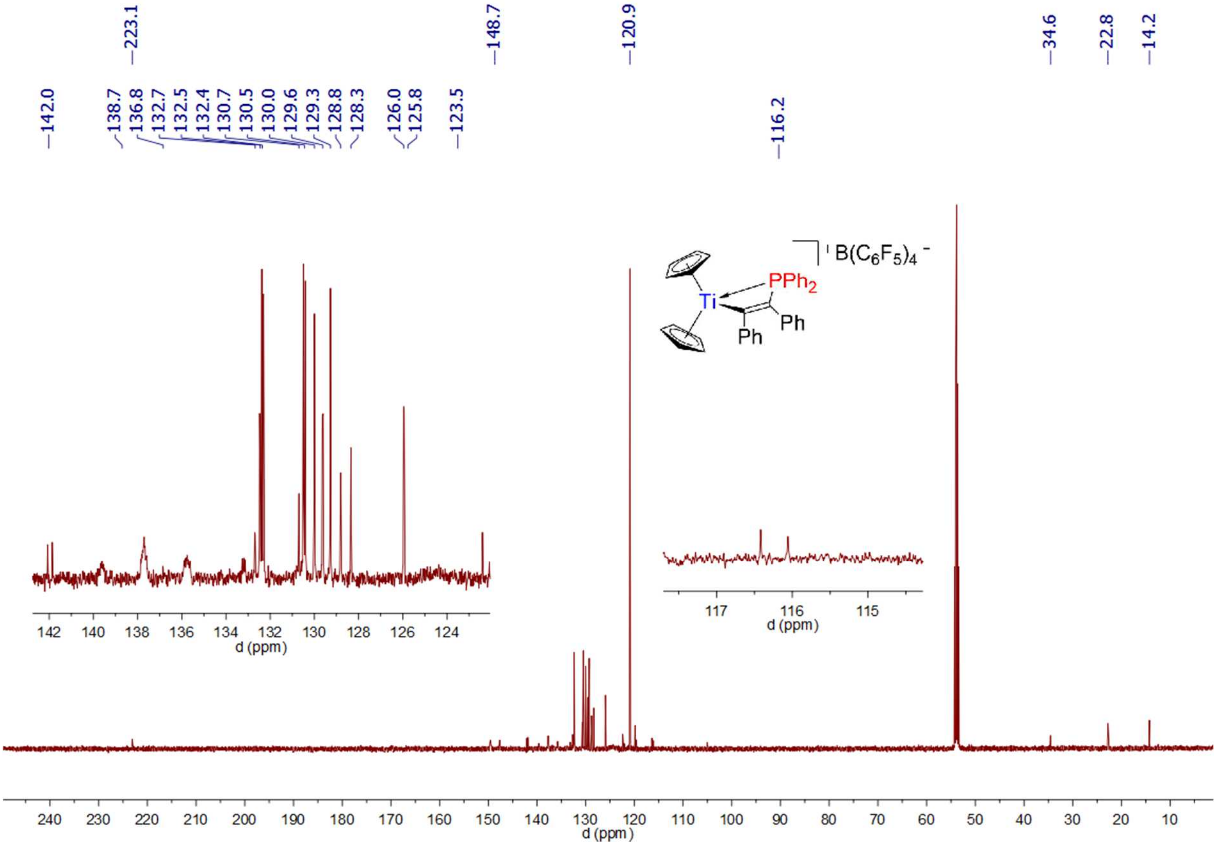
24. Compound **52**:



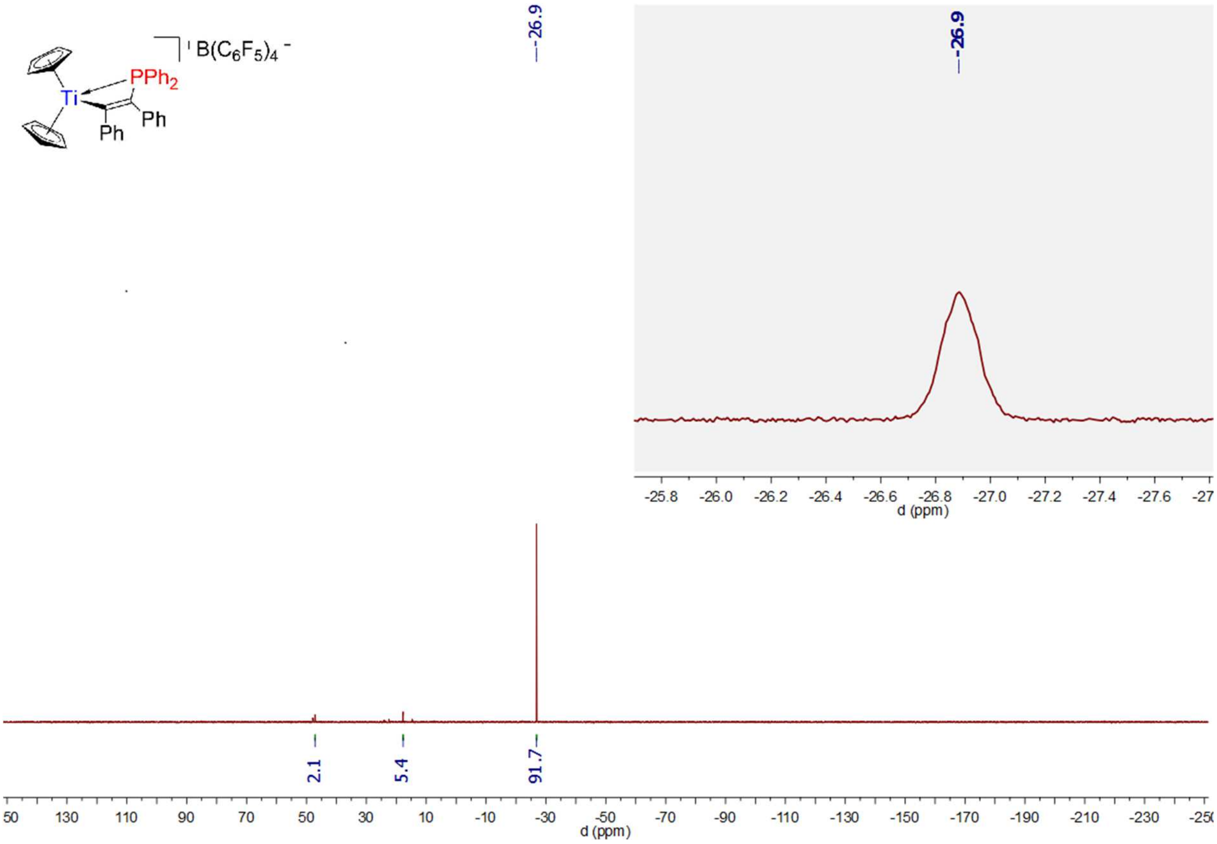
Spectrum 0-398: ^{1}H NMR of 52 (500.03 MHz, 300 K, bromobenzene-d_5)



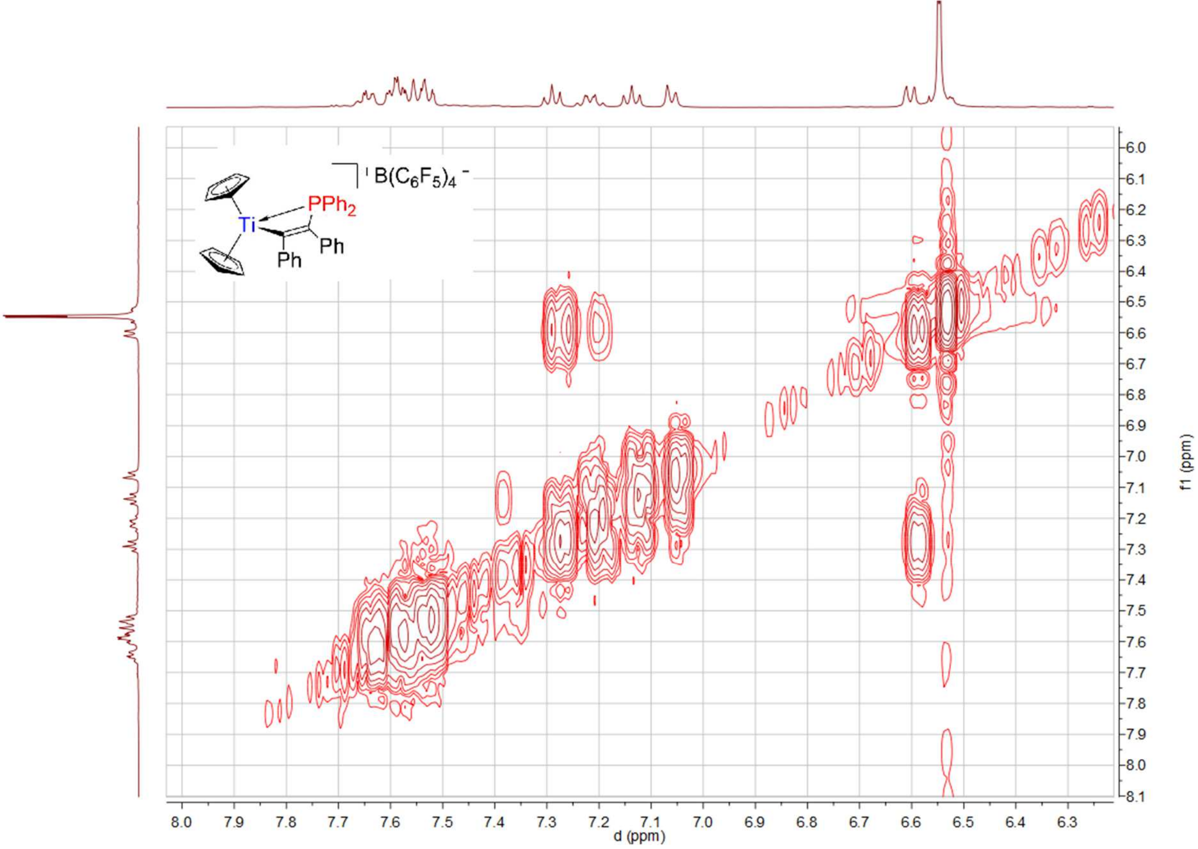
Spectrum 0-399: ^{1}H{^{31}P} NMR (top) correlated with ^{1}H (bottom) of 52 (500.03 MHz, 300 K, bromobenzene-d$_5$)



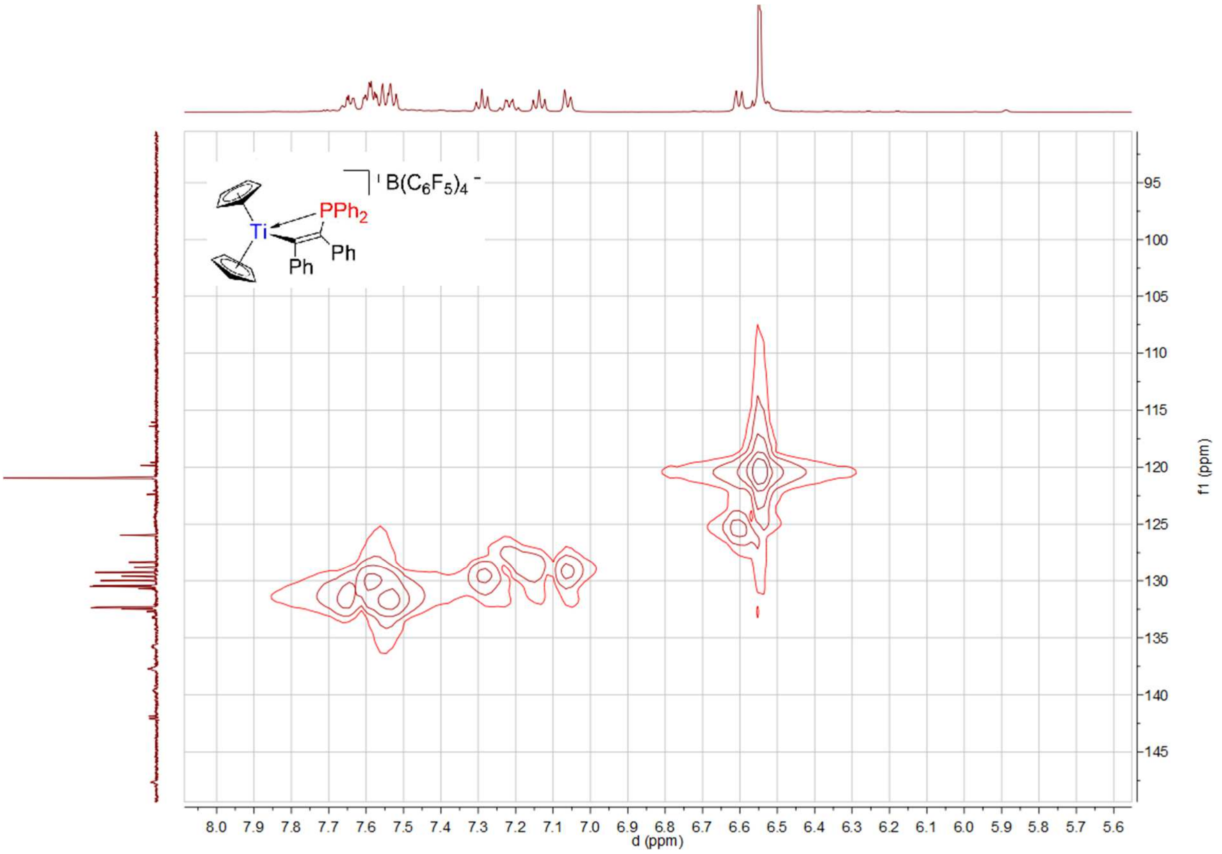
Spectrum 0-400: ^{13}C{^{1}H} NMR of 52 (125.75 MHz, 300 K, bromobenzene-d$_5$)



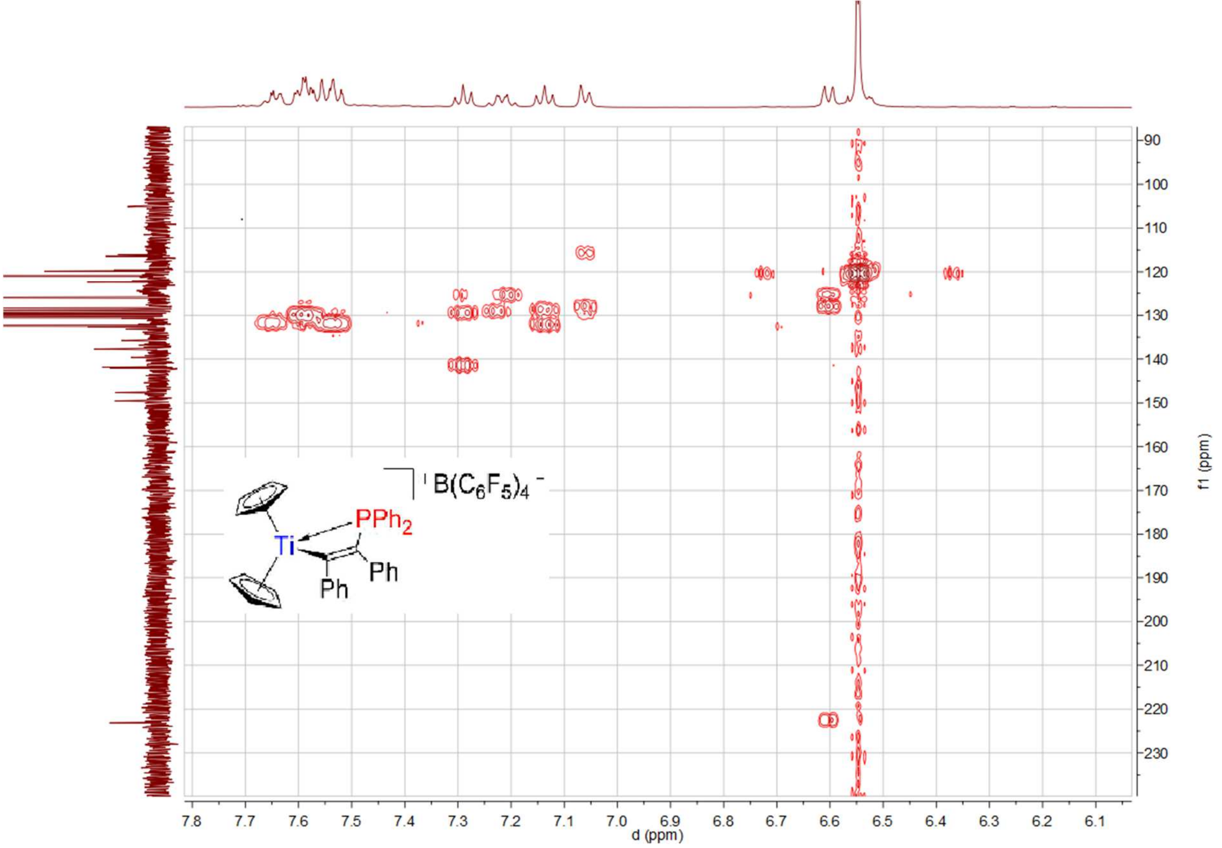
Spectrum 0-401: ^{31}P{^{1}H} and ^{31}P (opacified) NMR of 52 (202.41 MHz, 300 K, bromobenzene-d$_5$)



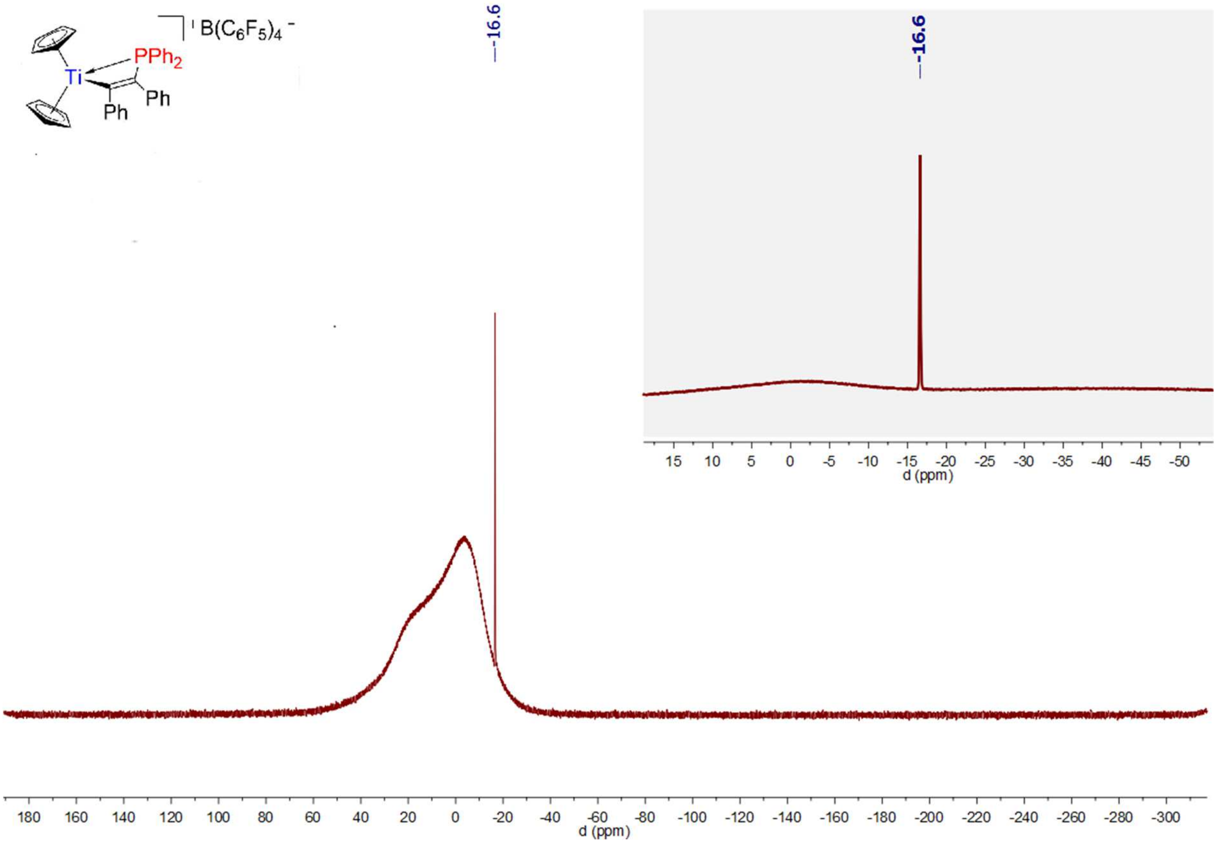
Spectrum 0-402: ^{1}H ^{1}H COSY of 52 (500.03 MHz, 300 K, 273 K, bromobenzene-d$_5$)



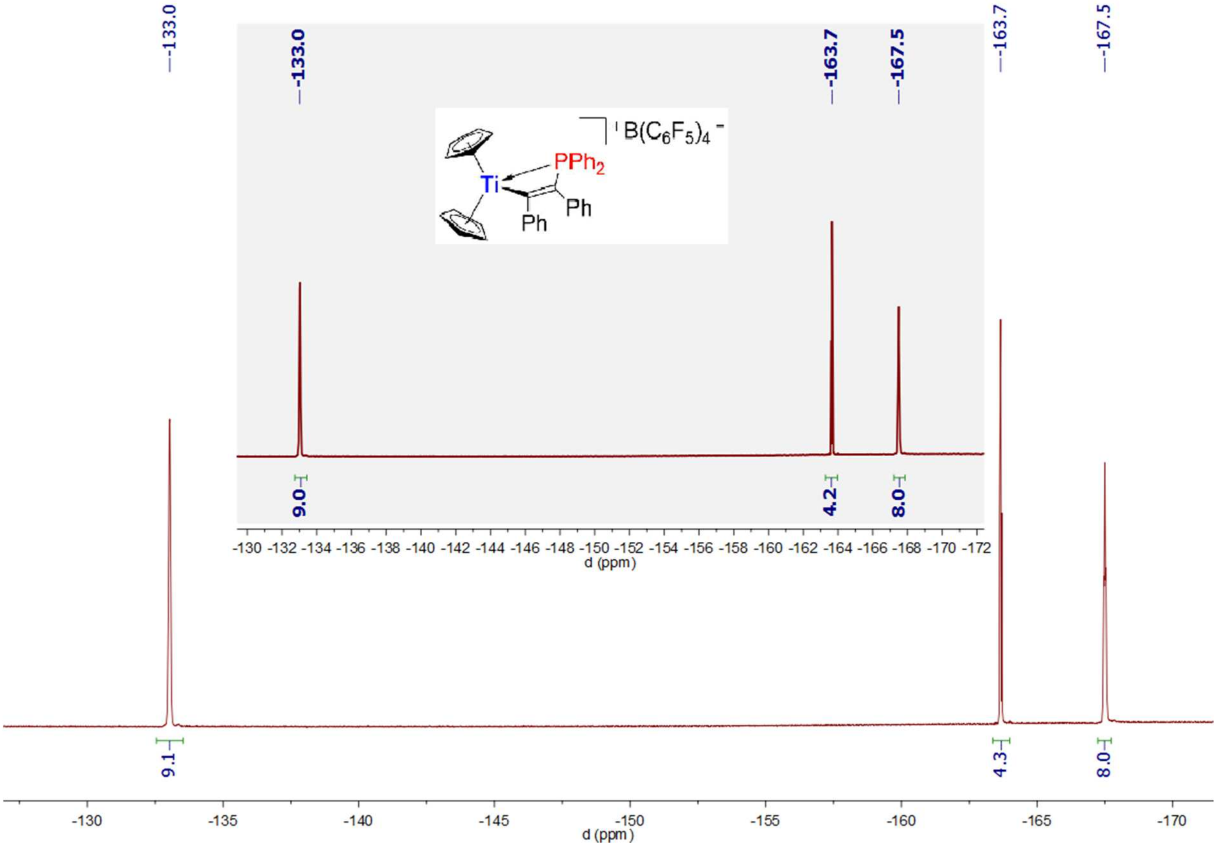
Spectrum 0-403: ^{1}H ^{13}C HMQC of 52 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



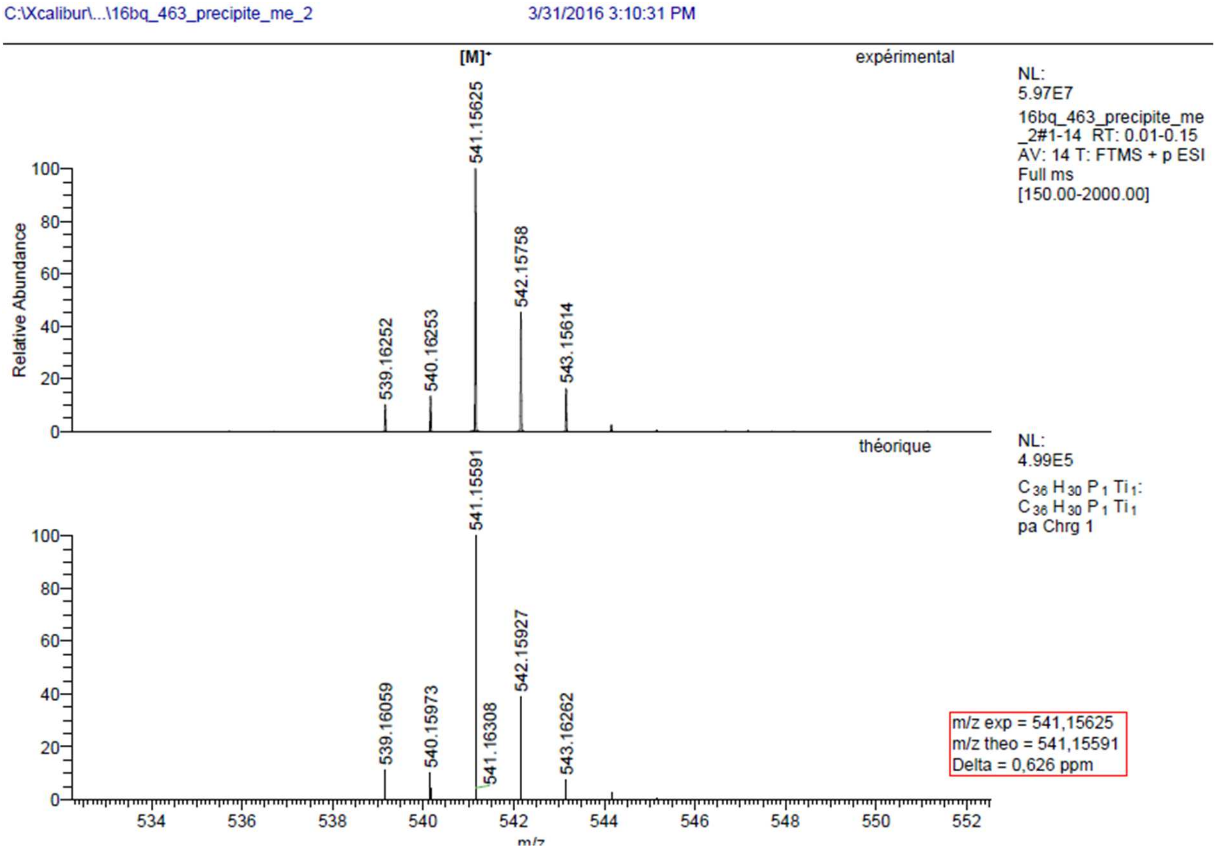
Spectrum 0-404: ^{1}H ^{13}C HMBC of 52 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-405: $^{11}B\{^1H\}$ and ^{11}B NMR of 52 (160.43 MHz, 300 K, bromobenzene-d_5)

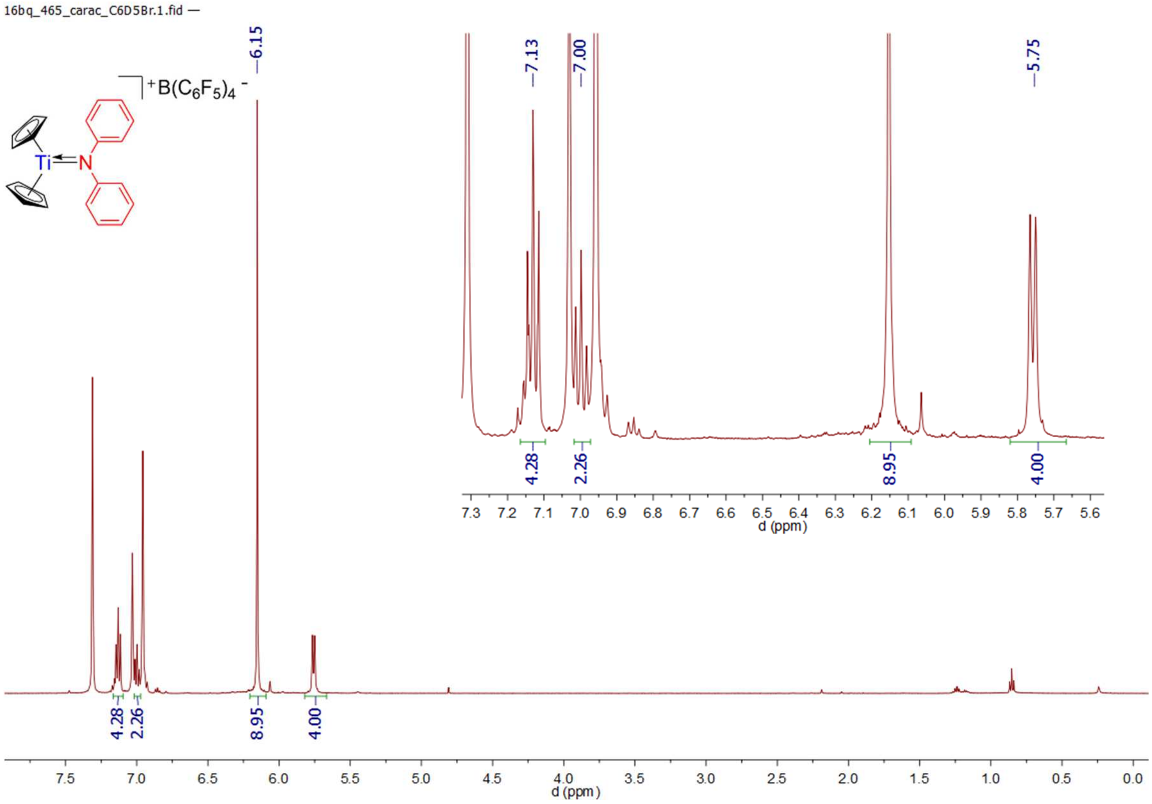


Spectrum 0-406: $^{19}F\{^1H\}$ and ^{19}F NMR of 52 (470.45 MHz, 300 K, bromobenzene-d_5)

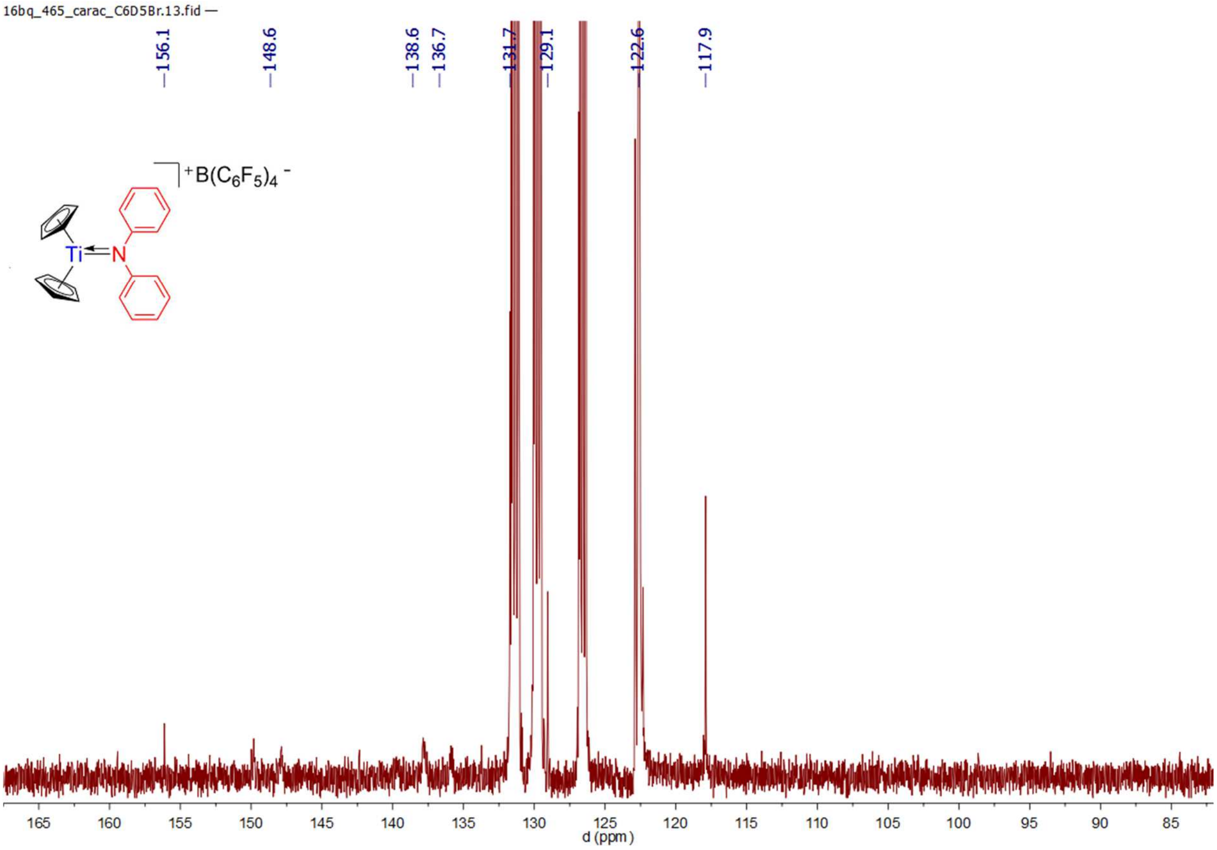


Spectrum 0-407: HRMS of 52 (Positive mode ESI, bromobenzene)

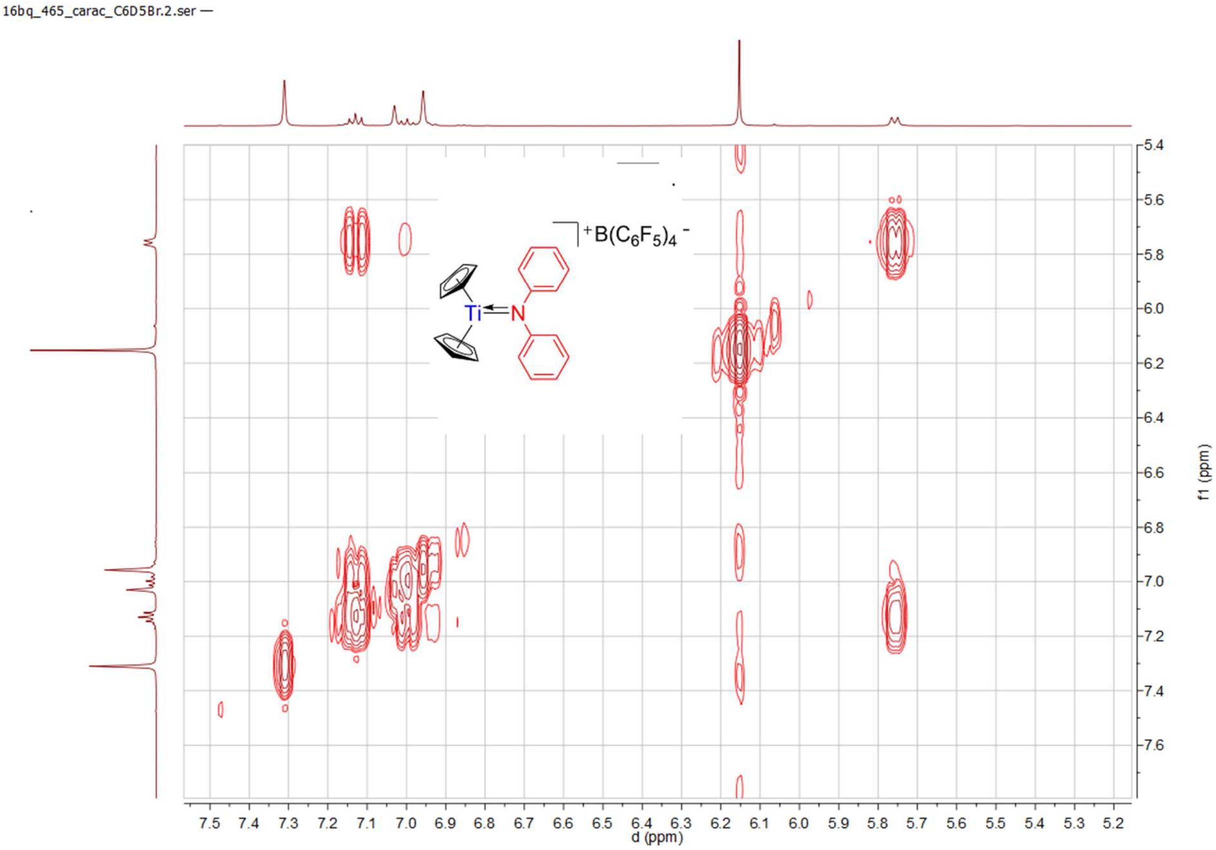
25. Compound **53**:



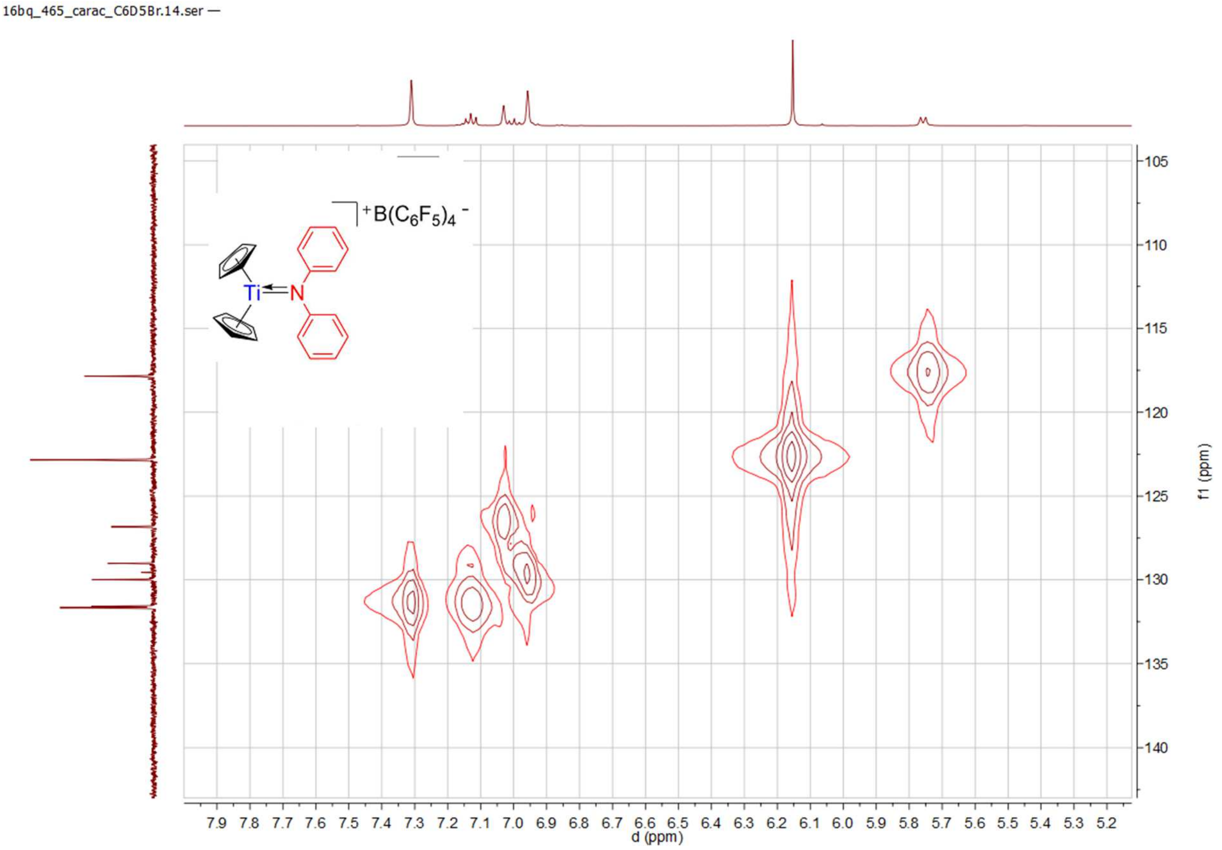
Spectrum 0-408: ^{1}H NMR of 53 (500.03 MHz, 300 K, bromobenzene-d$_5$)



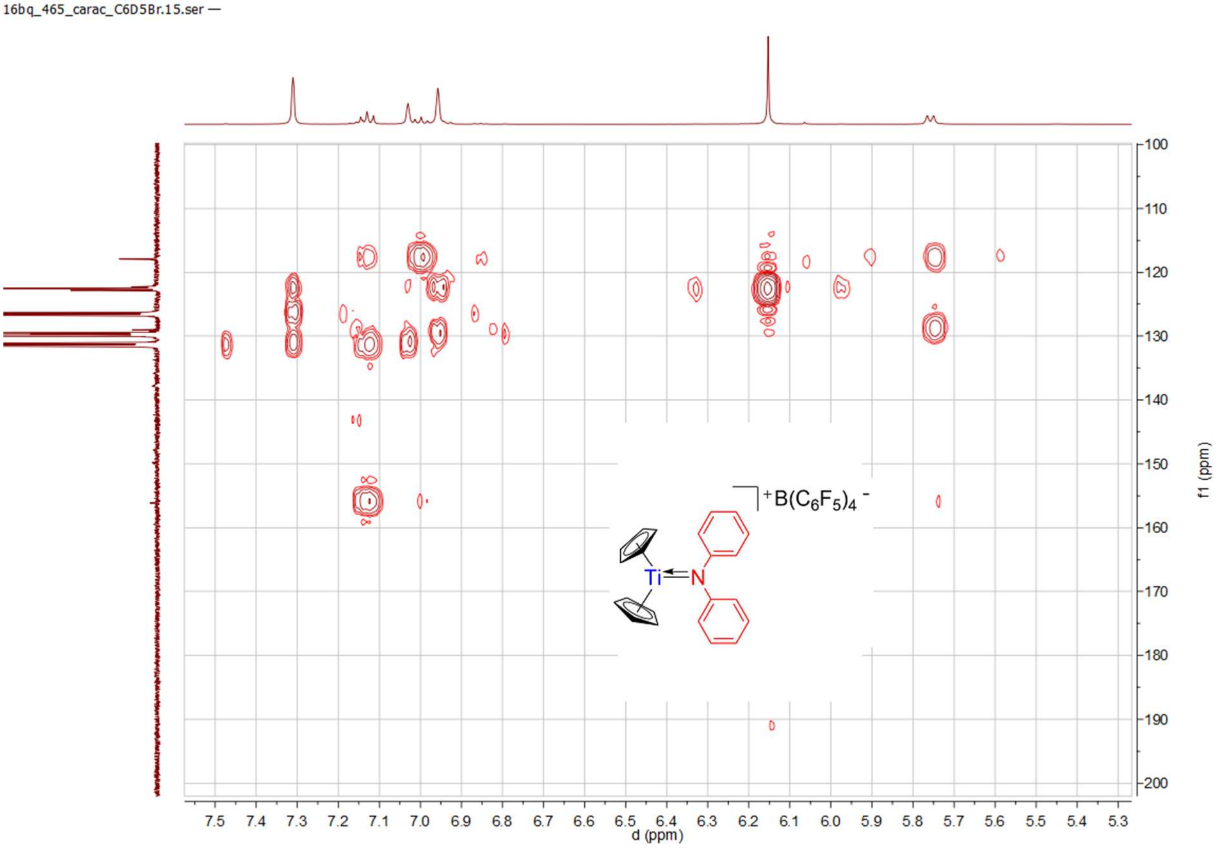
Spectrum 0-409: $^{13}C\{^{1}H\}$ NMR of 53 (125.75 MHz, 300 K, bromobenzene-d$_5$)



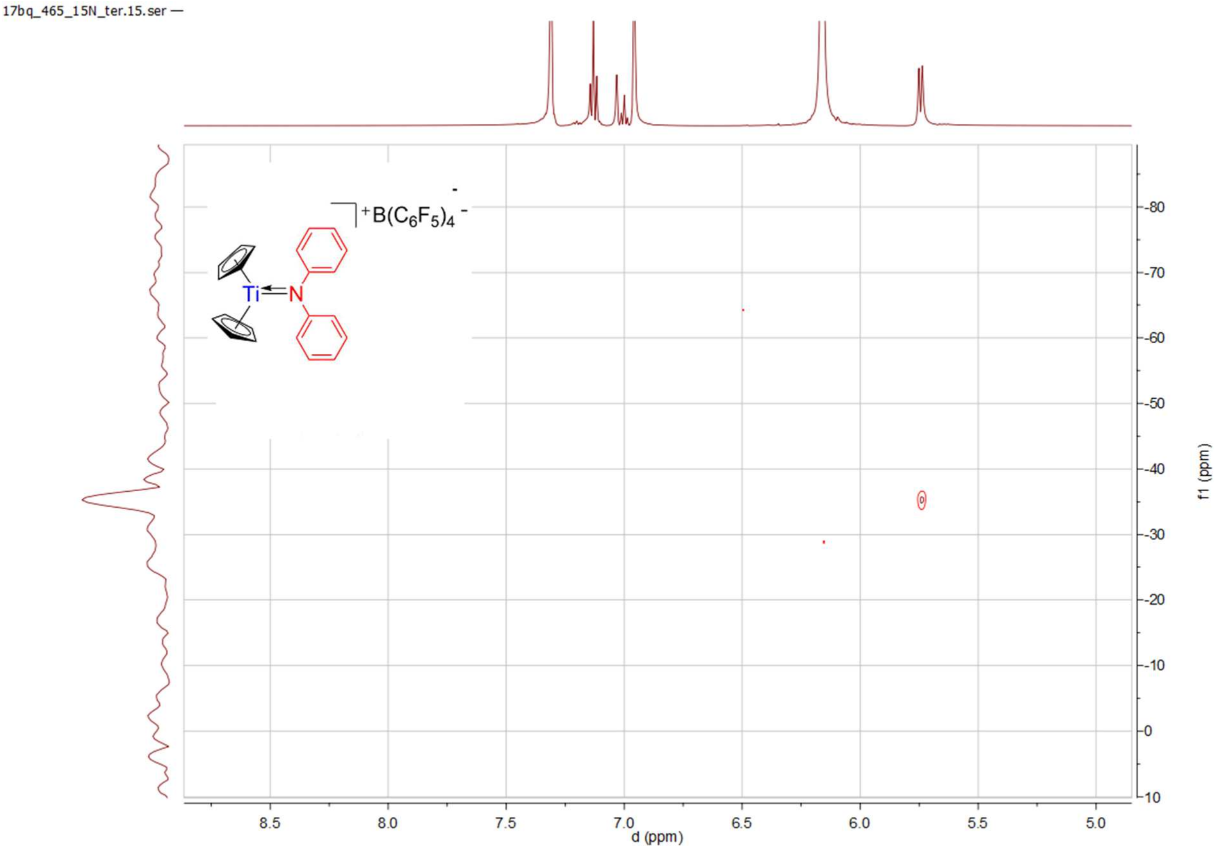
Spectrum 0-410: ^{1}H ^{1}H COSY of 53 (500.03 MHz, 300 K, 273 K, bromobenzene-d$_5$)



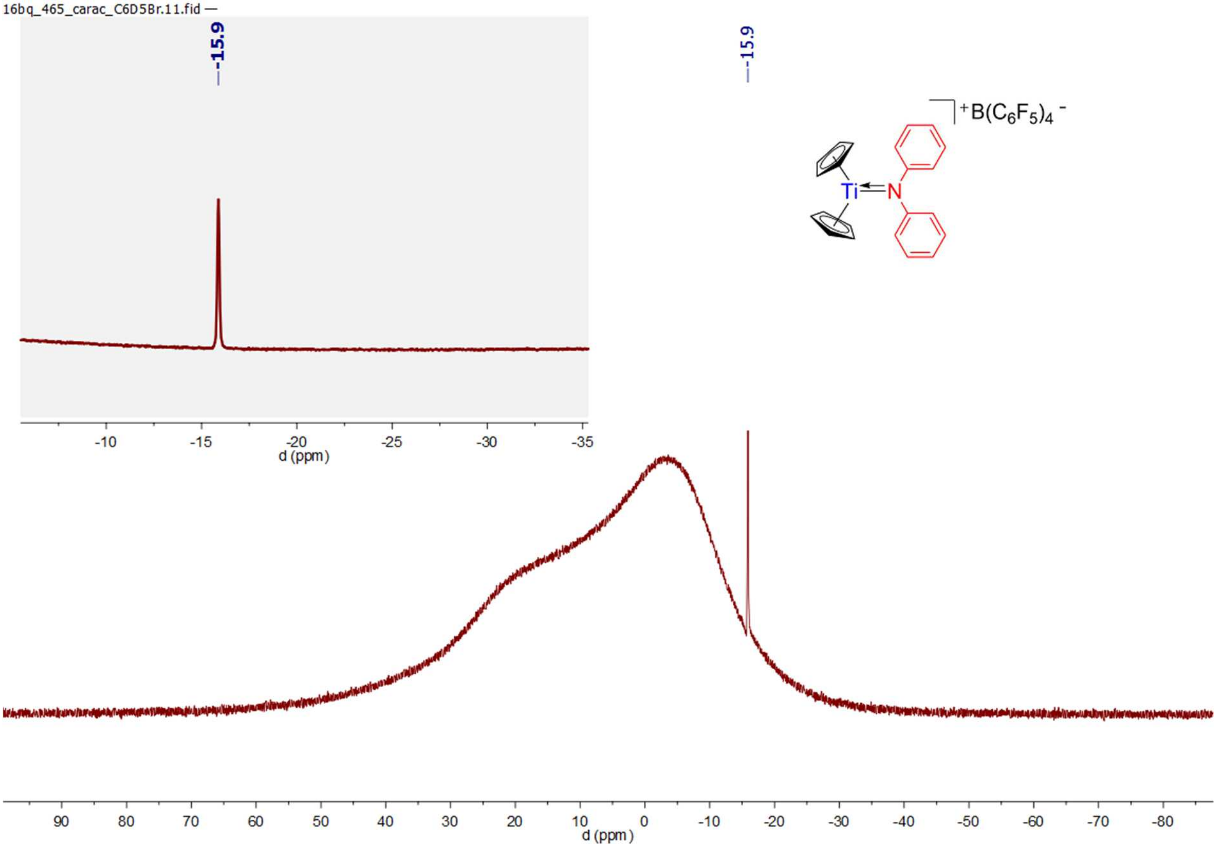
Spectrum 0-411: ^{1}H ^{13}C HMQC of 53 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



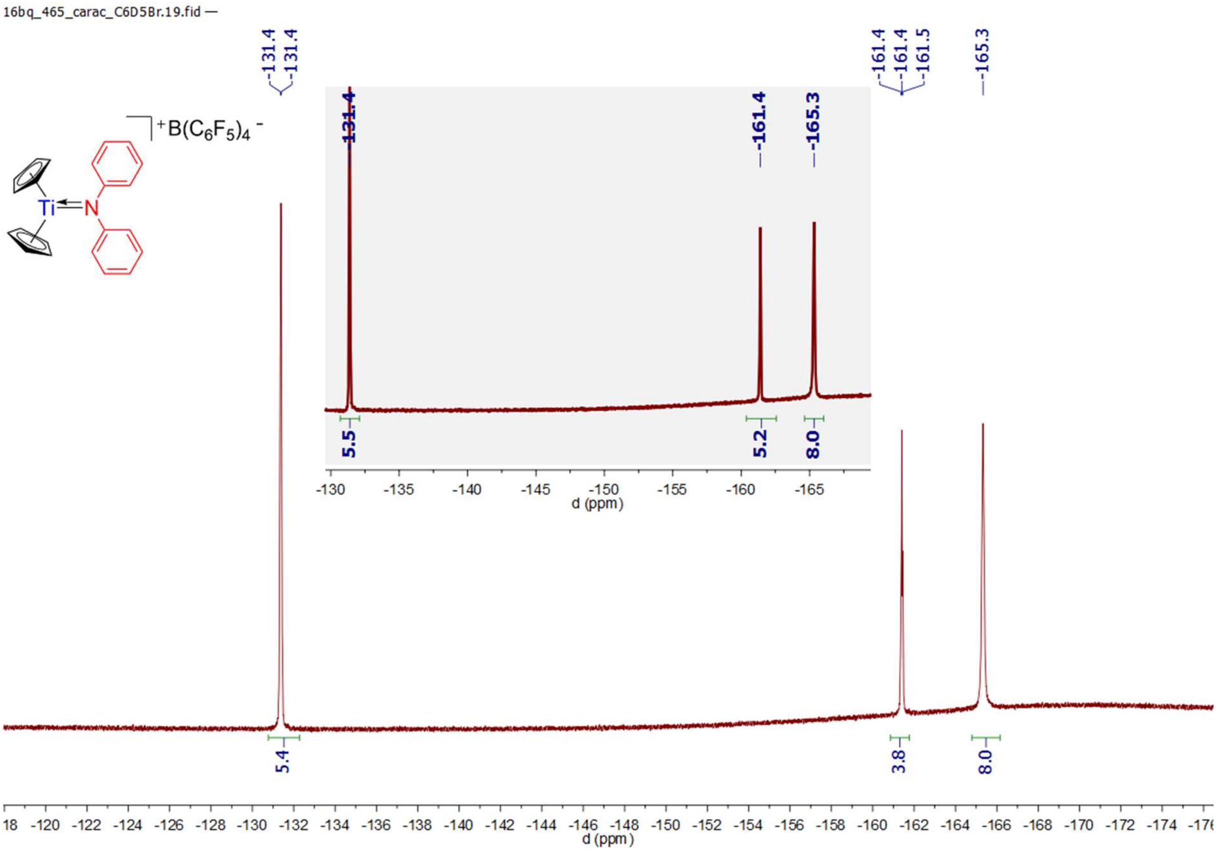
Spectrum 0-412: ^{1}H ^{13}C HMBC of 53 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



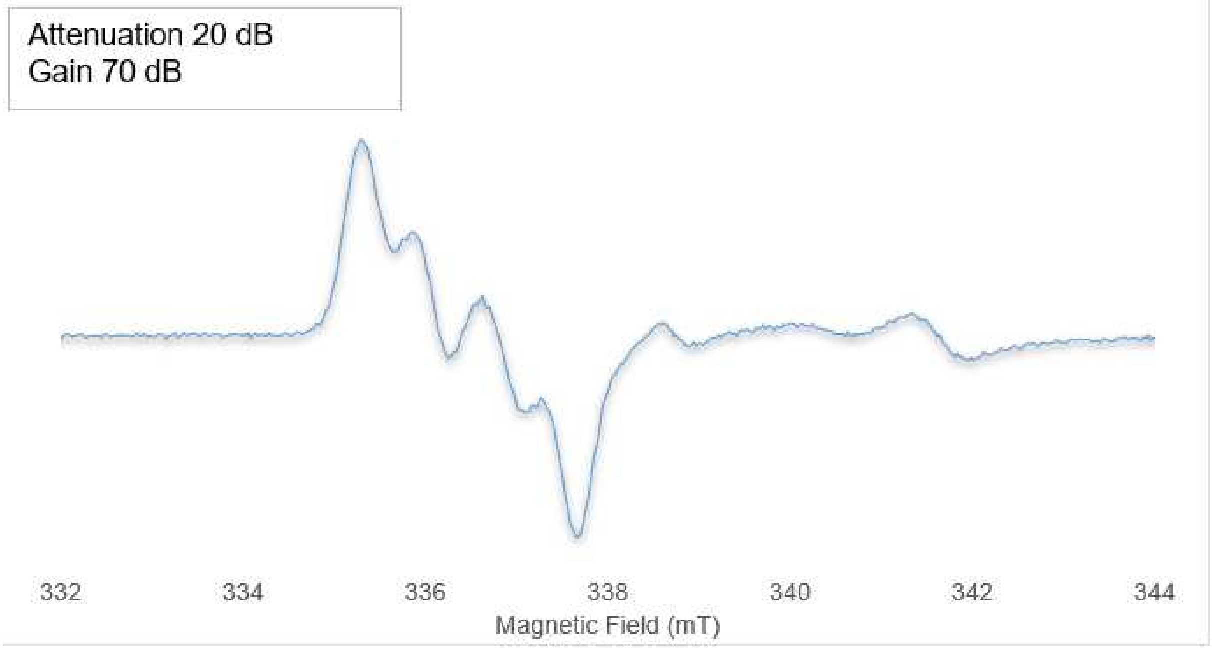
Spectrum 0-413: ^{1}H ^{15}N HMBC of 53 (500.03 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-414: ^{11}B{^{1}H} and ^{11}B NMR of 53 (160.43 MHz, 300 K, bromobenzene-d$_5$)

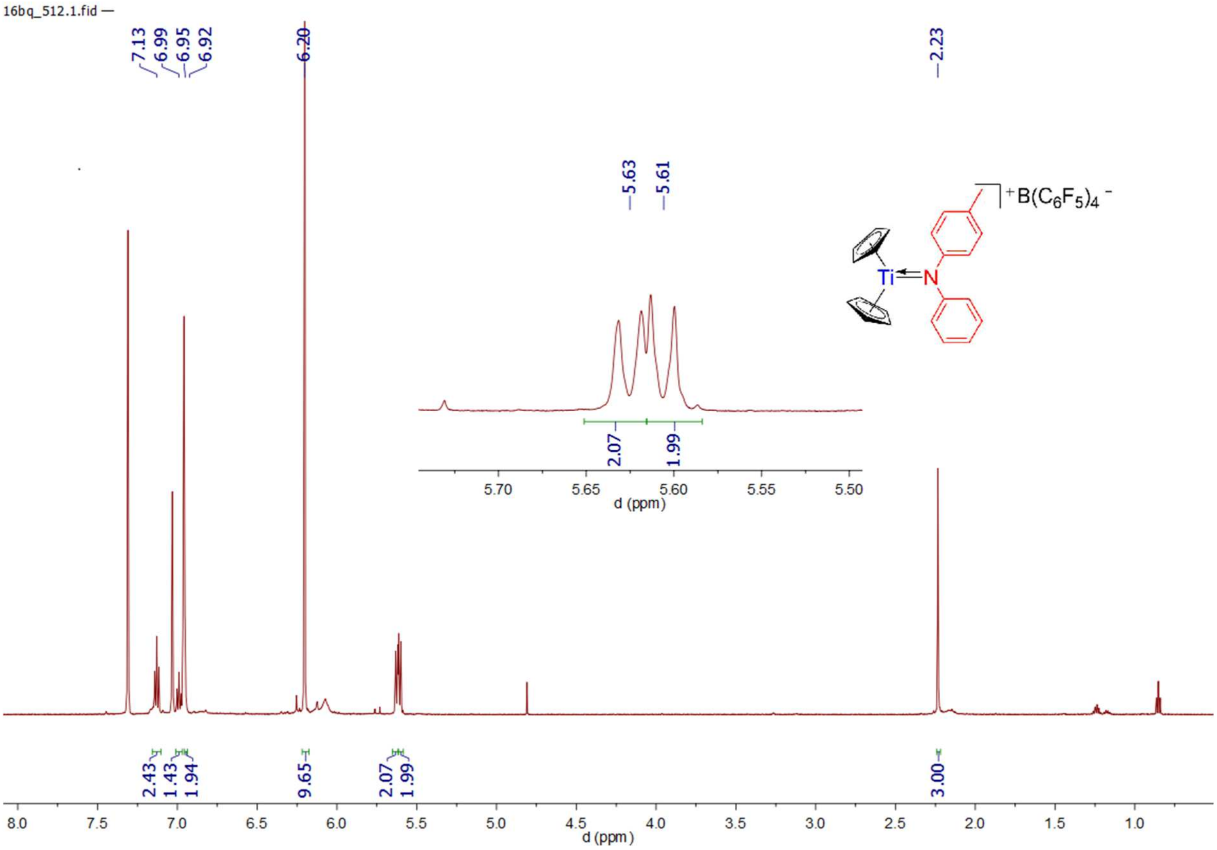


Spectrum 0-415: $^{19}F\{^{1}H\}$ and ^{19}F NMR of 53 (470.45 MHz, 300 K, bromobenzene-d_5)

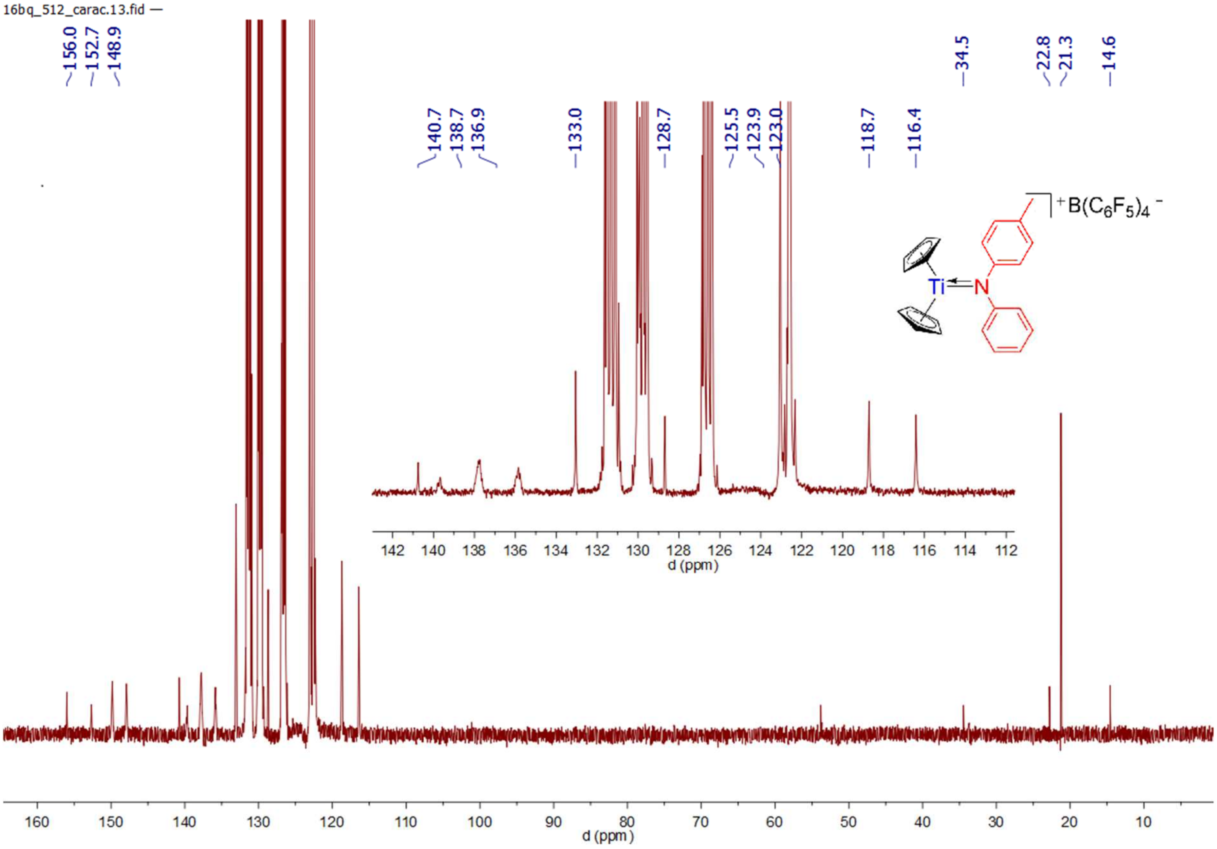


Spectrum 0-416: EPR spectrum of 53 (9.440489 GHz, 295 K, Bromobenzene)

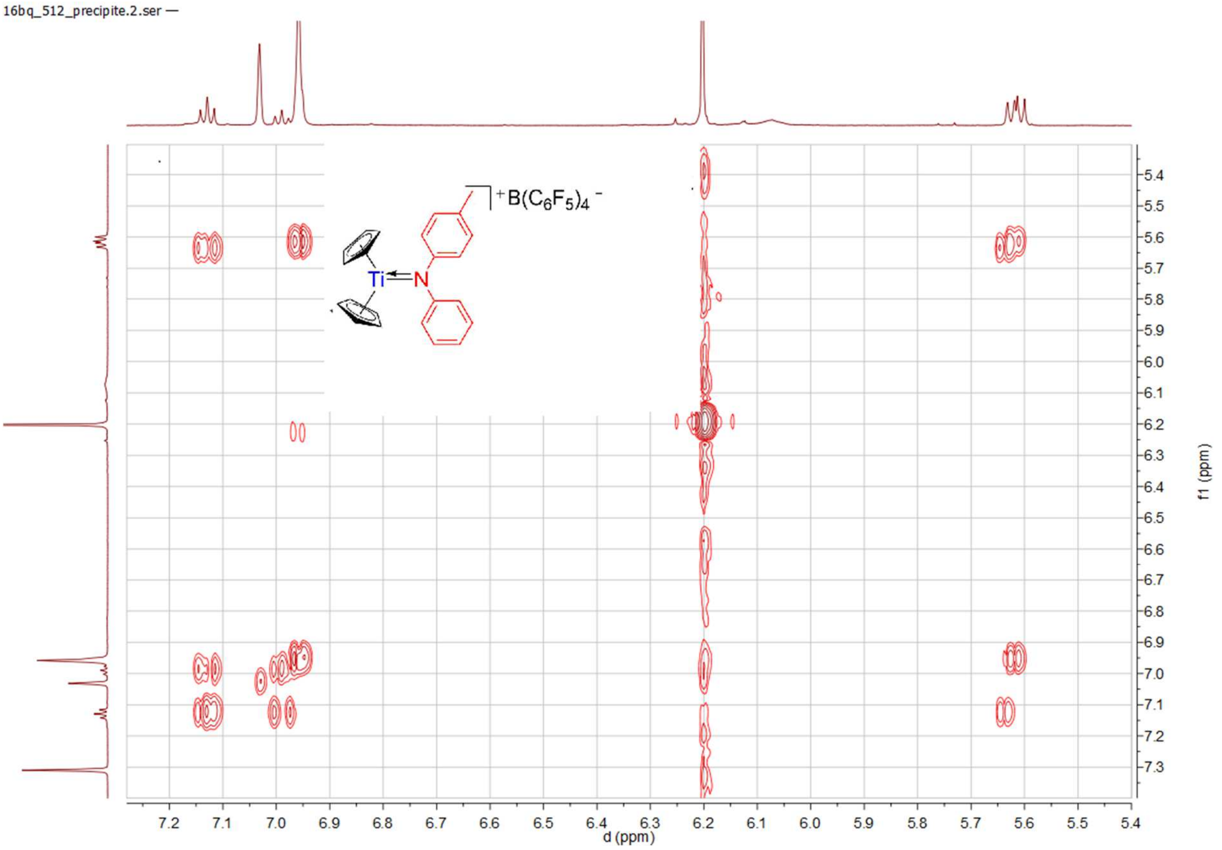
26. Compound **54**:



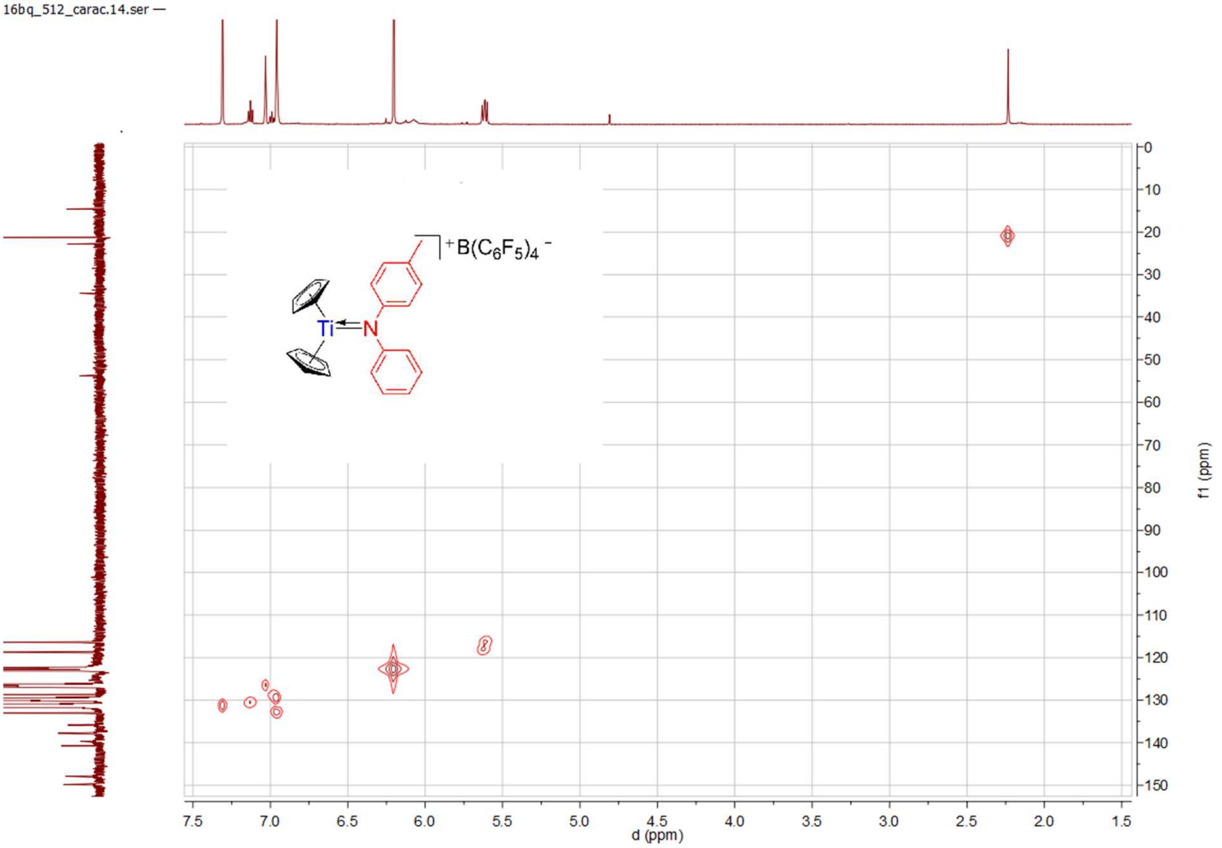
Spectrum 0-417: ^{1}H NMR of 54 (500.03 MHz, 300 K, bromobenzene-d$_5$)



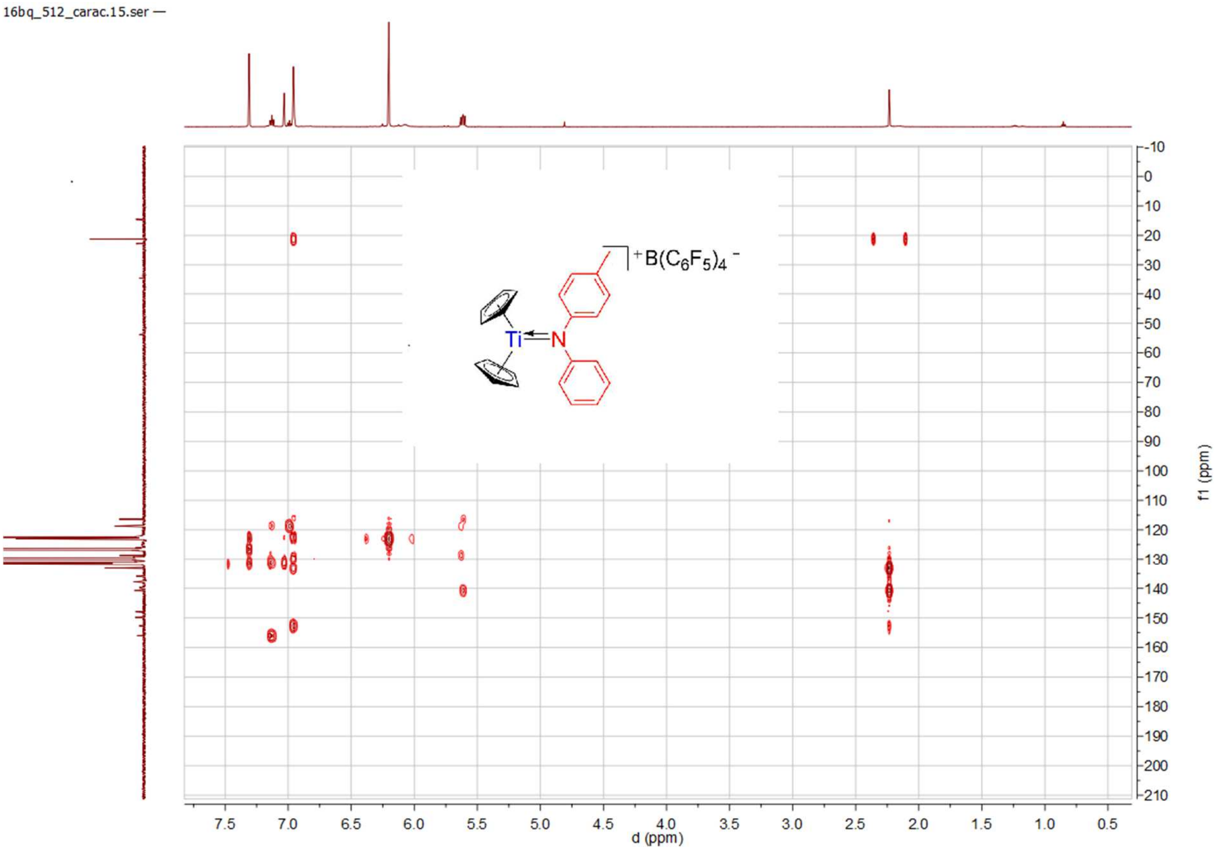
Spectrum 0-418: ^{13}C{^{1}H} NMR of 54 (125.75 MHz, 300 K, bromobenzene-d$_5$)



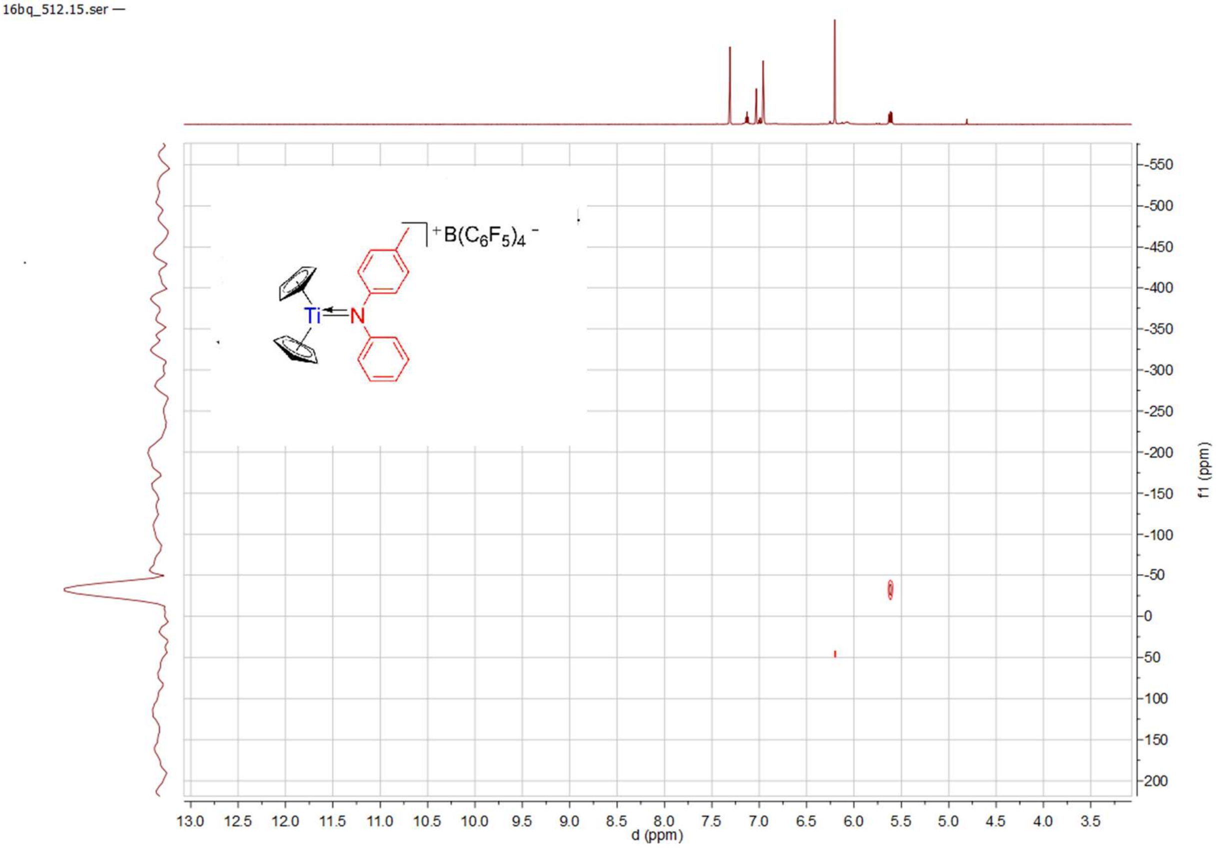
Spectrum 0-419: ^{1}H ^{1}H COSY of 54 (500.03 MHz, 300 K, 273 K, bromobenzene-d$_5$)



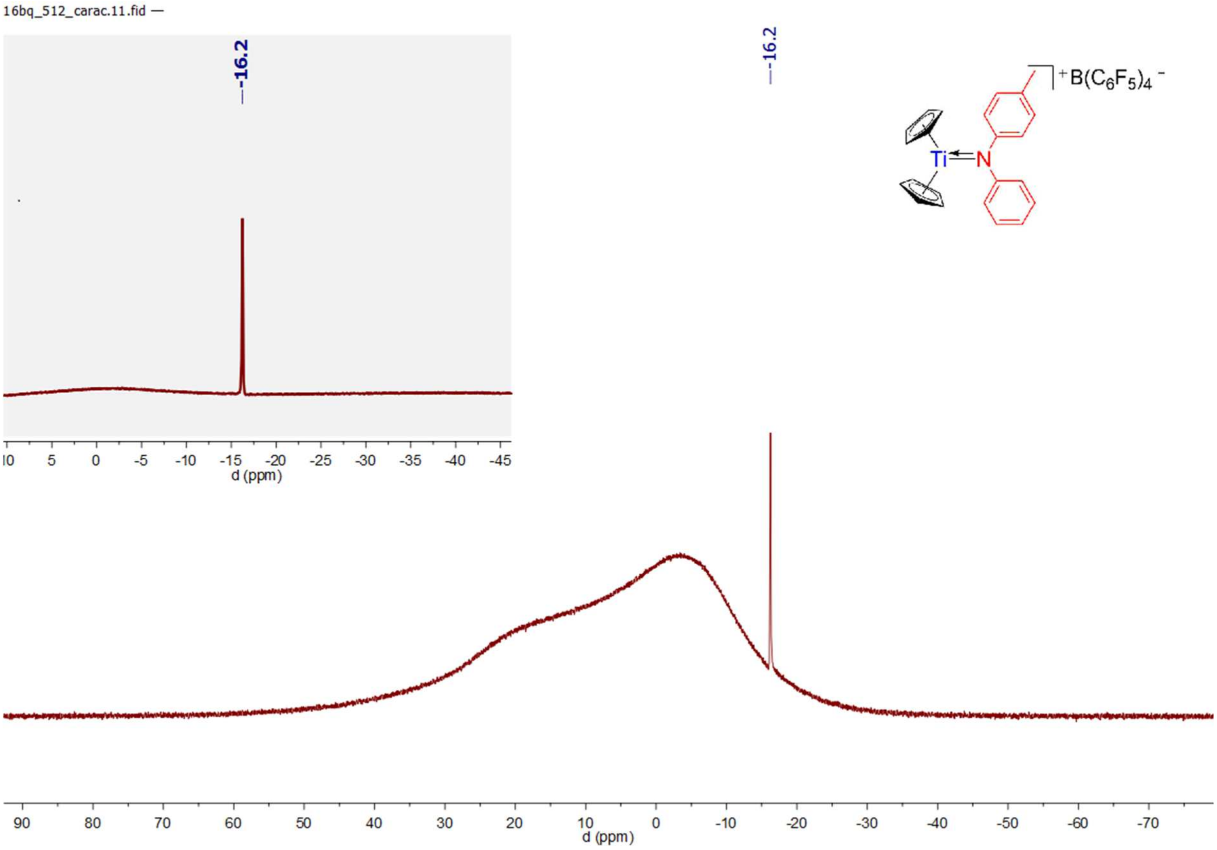
Spectrum 0-420: ^{1}H ^{13}C HMQC of 54 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



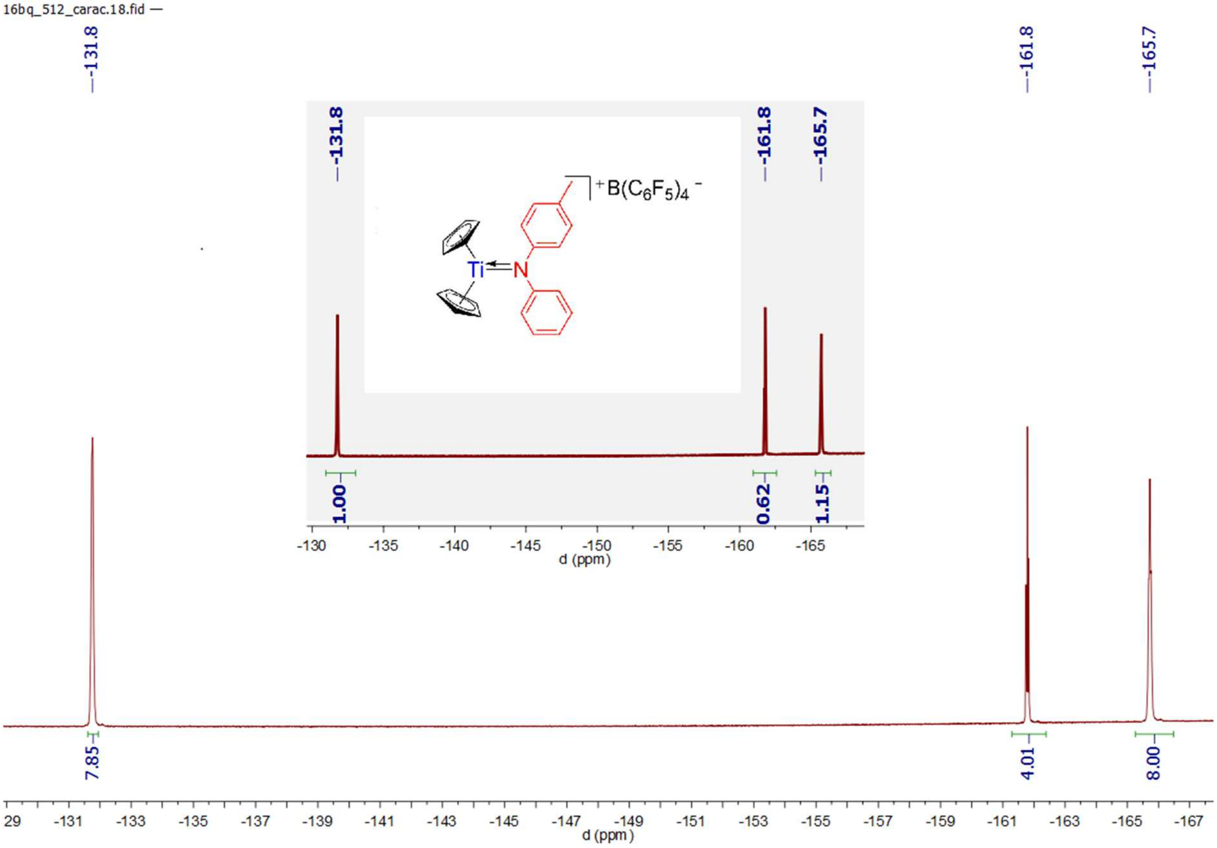
Spectrum 0-421: ^{1}H ^{13}C HMBC of 54 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



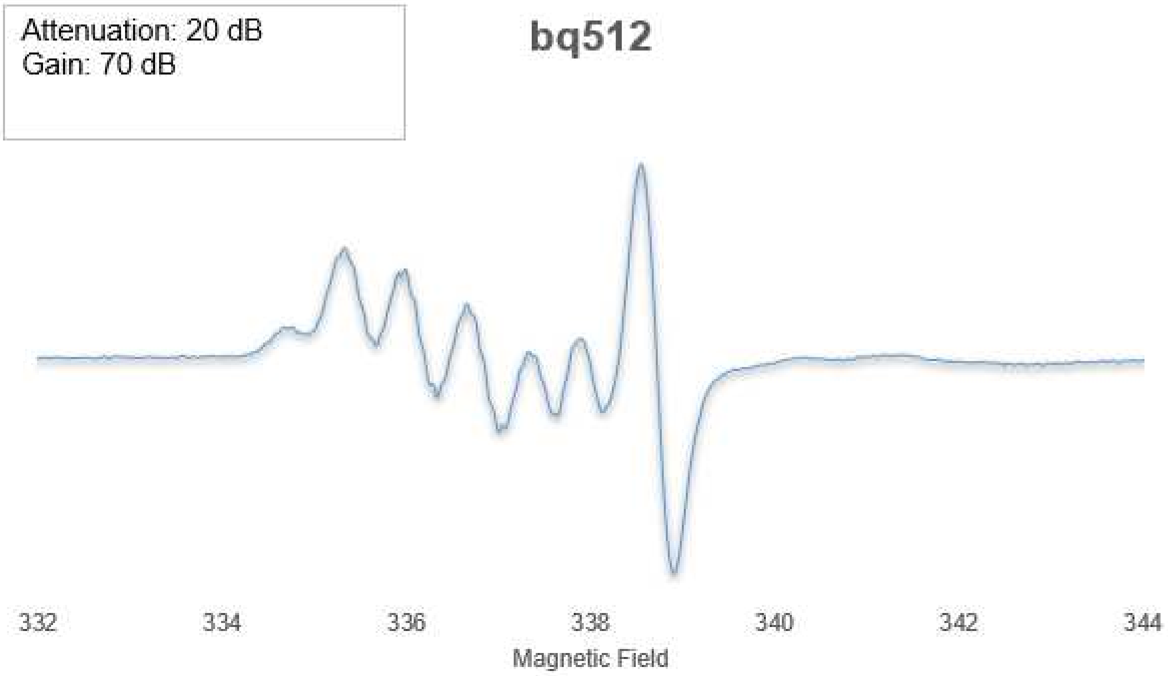
Spectrum 0-422: ^{1}H ^{15}N HMBC of 54 (500.03 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-423: $^{11}B\{^{1}H\}$ and ^{11}B NMR of 54 (160.43 MHz, 300 K, bromobenzene-d5)

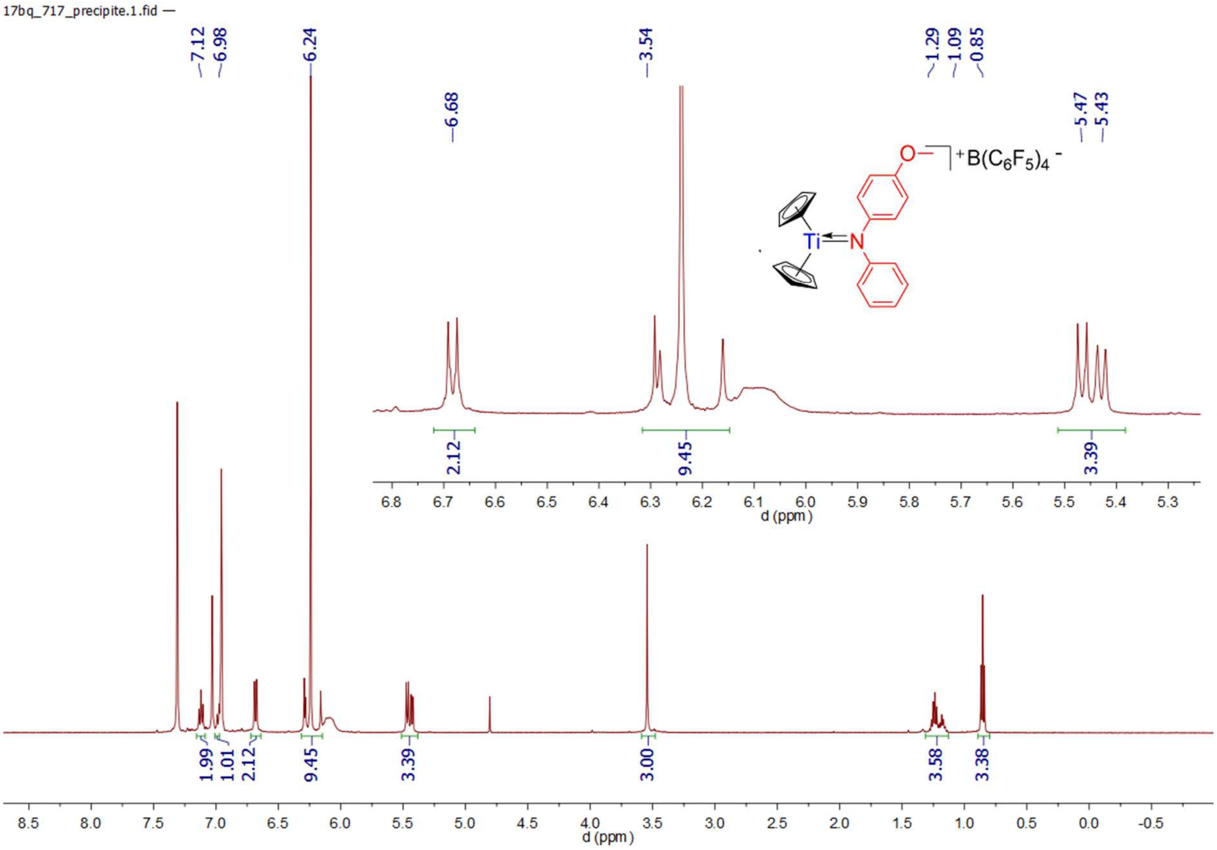


Spectrum 0-424: $^{19}F\{^{1}H\}$ and ^{19}F NMR of 54 (470.45 MHz, 300 K, bromobenzene-d5)

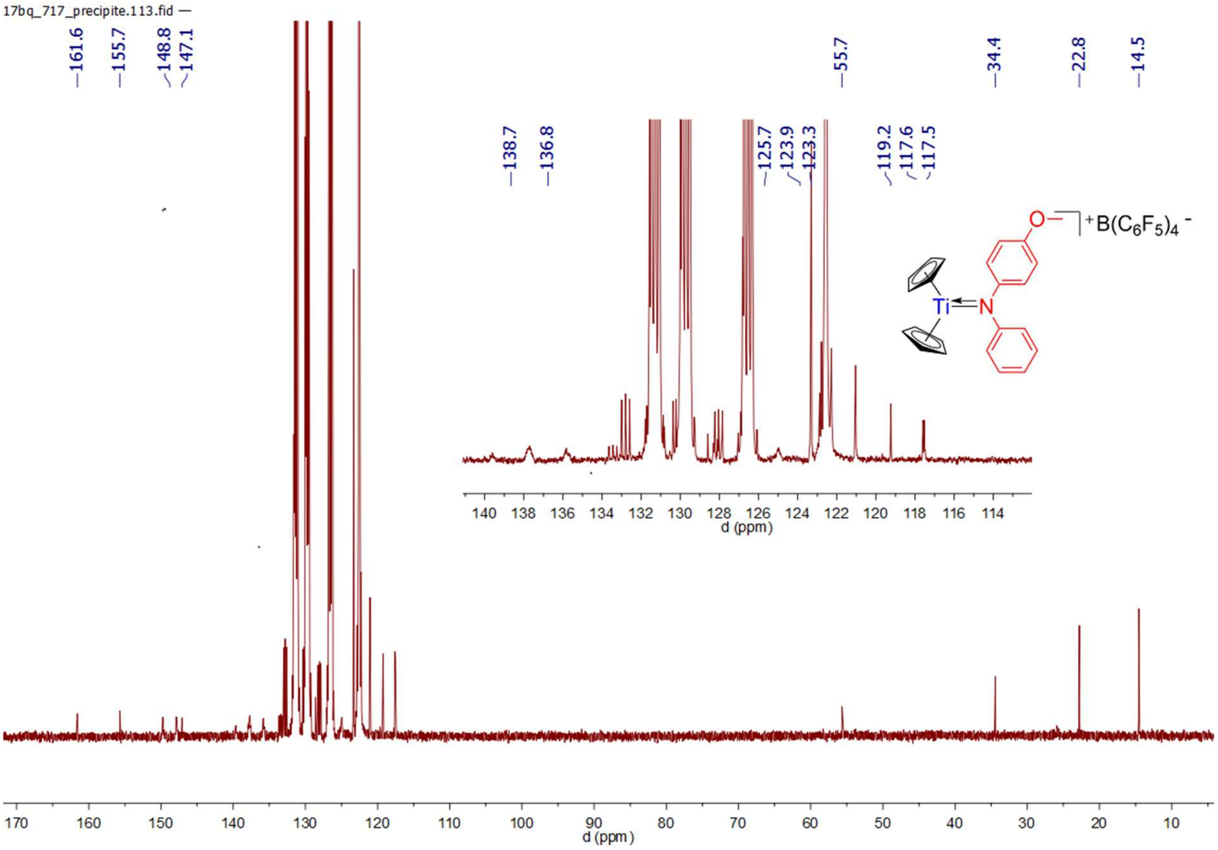


Spectrum 0-425: EPR spectrum of 54 (9.439933 GHz, 295 K, Bromobenzene)

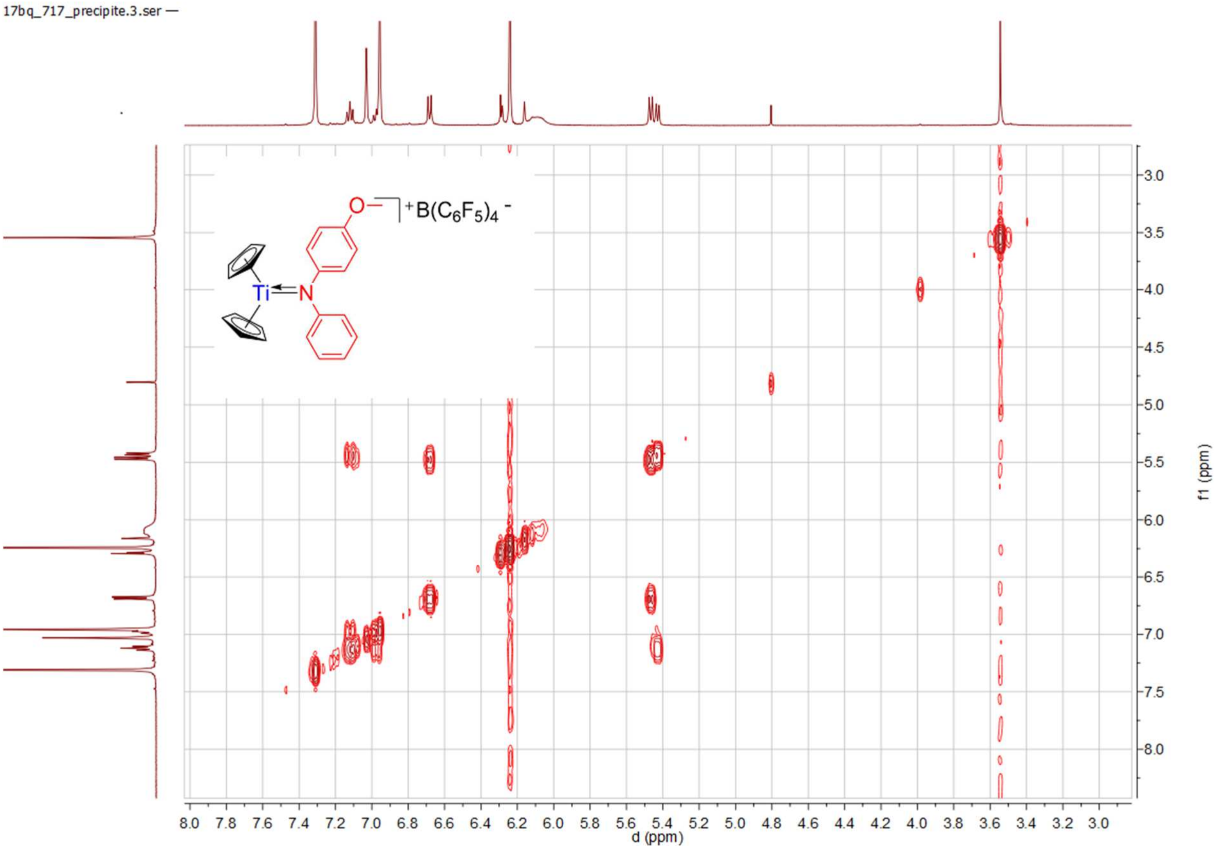
27. Compound **55**:



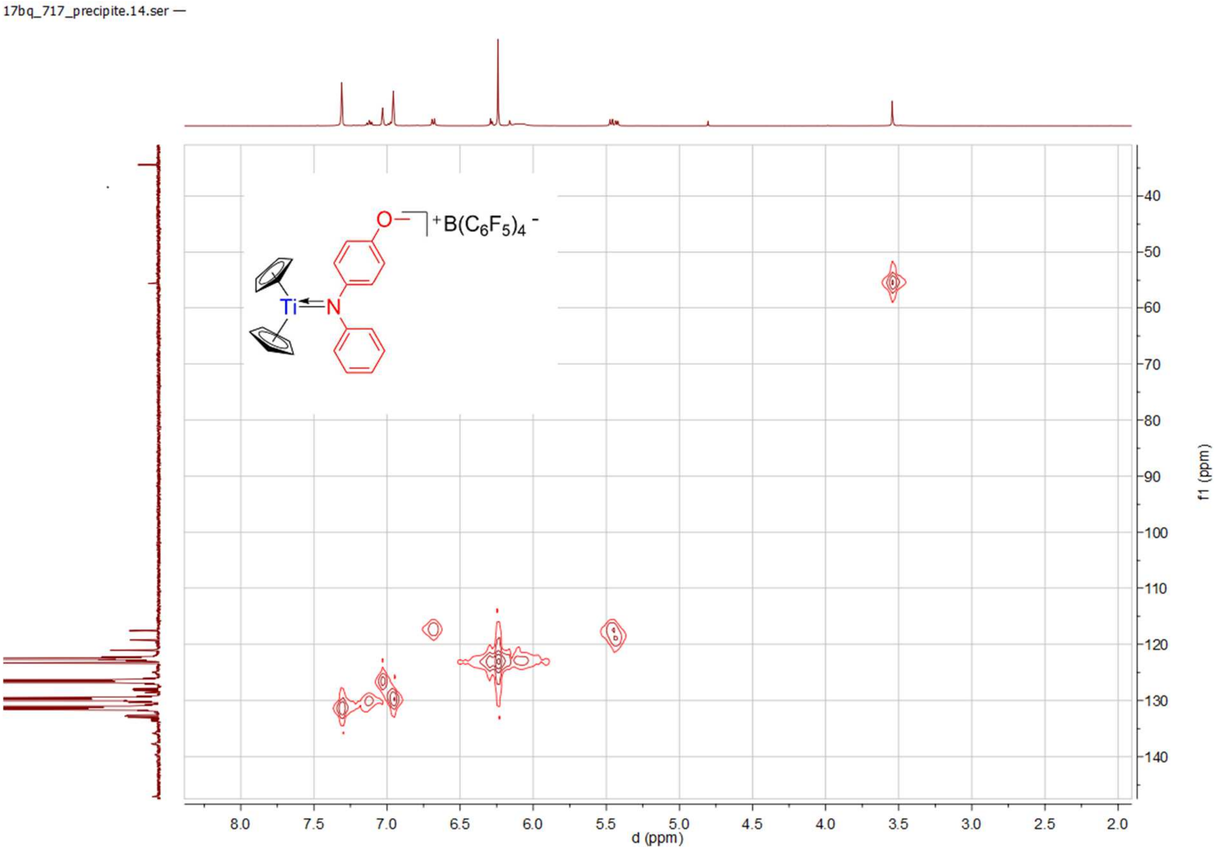
Spectrum 0-426: ^{1}H NMR of 55 (500.03 MHz, 300 K, bromobenzene-d_5)



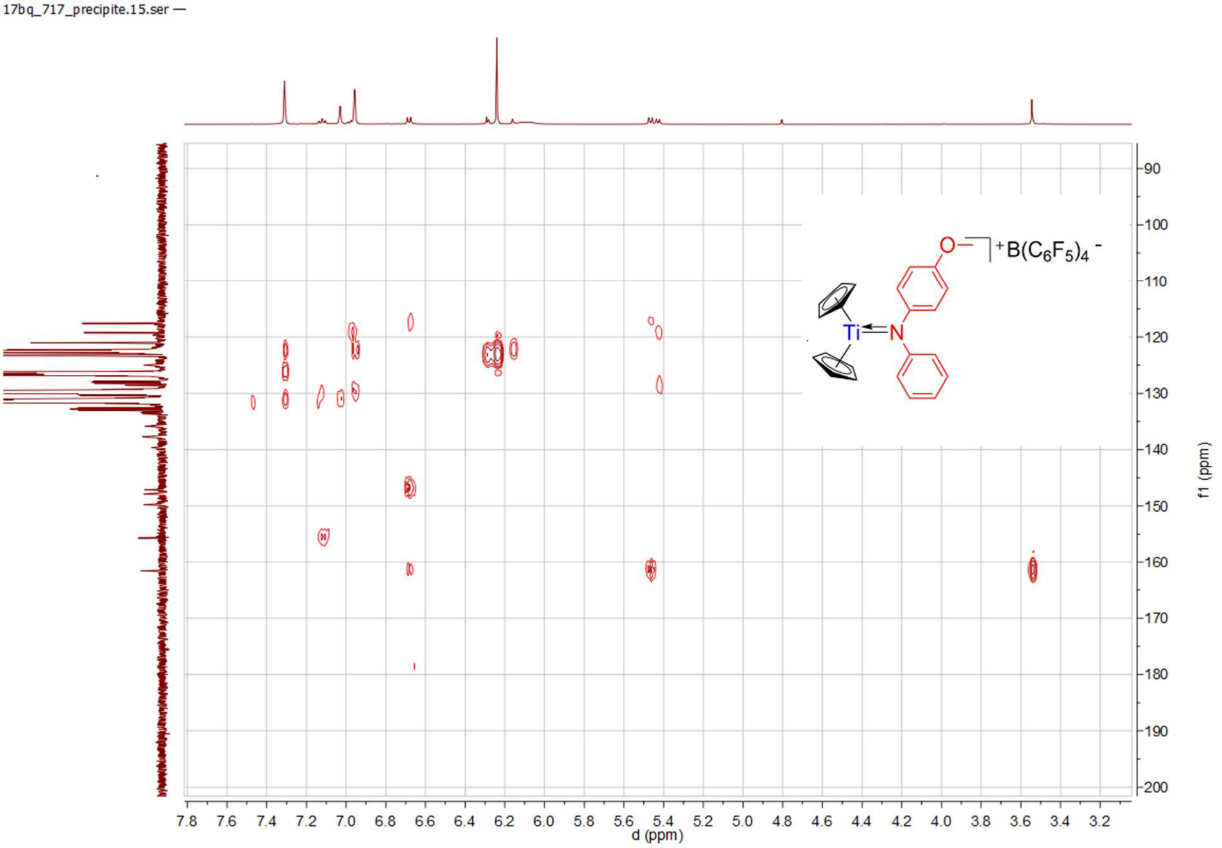
Spectrum 0-427: $^{13}C\{^1H\}$ NMR of 55 (125.75 MHz, 300 K, bromobenzene-d_5)



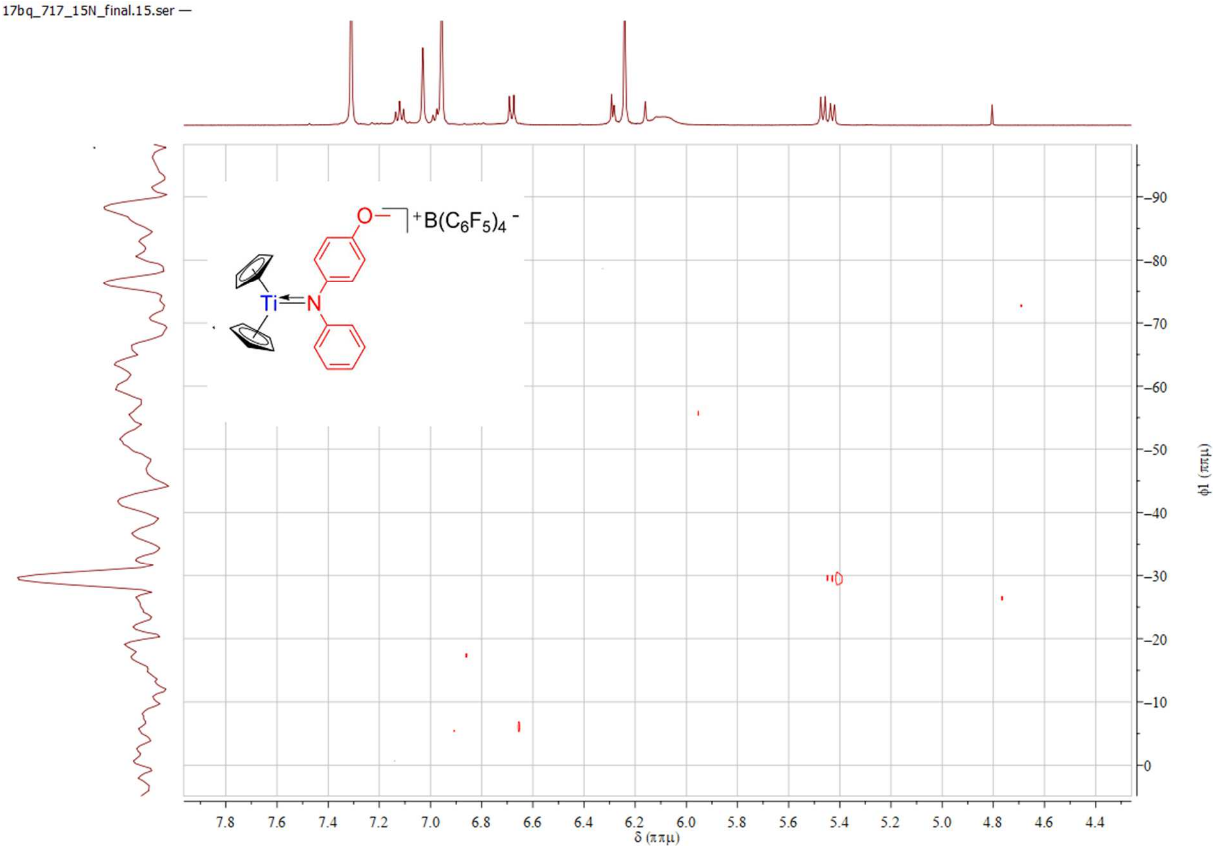
Spectrum 0-428: ^1H ^1H COSY of 55 (500.03 MHz, 300 K, 273 K, bromobenzene-d_5)



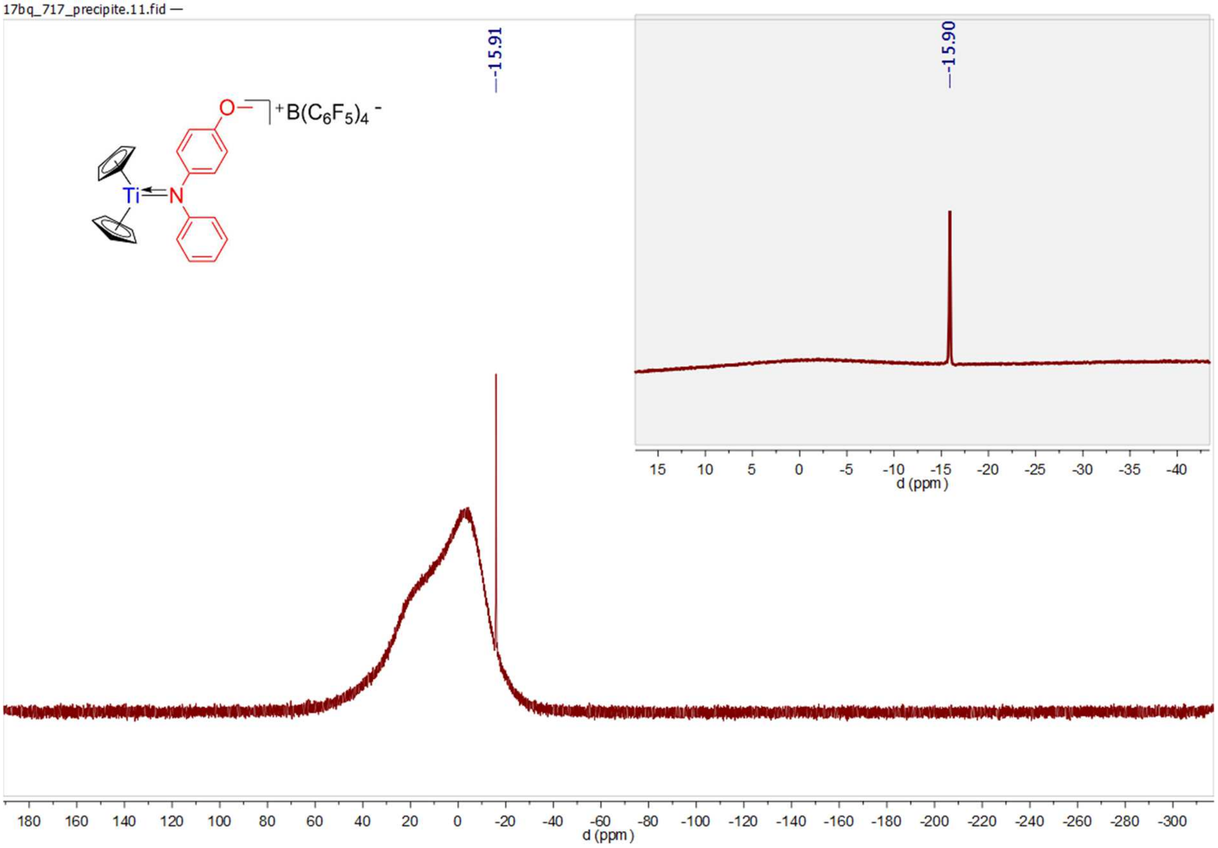
Spectrum 0-429: ^{1}H ^{13}C HMQC of 55 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



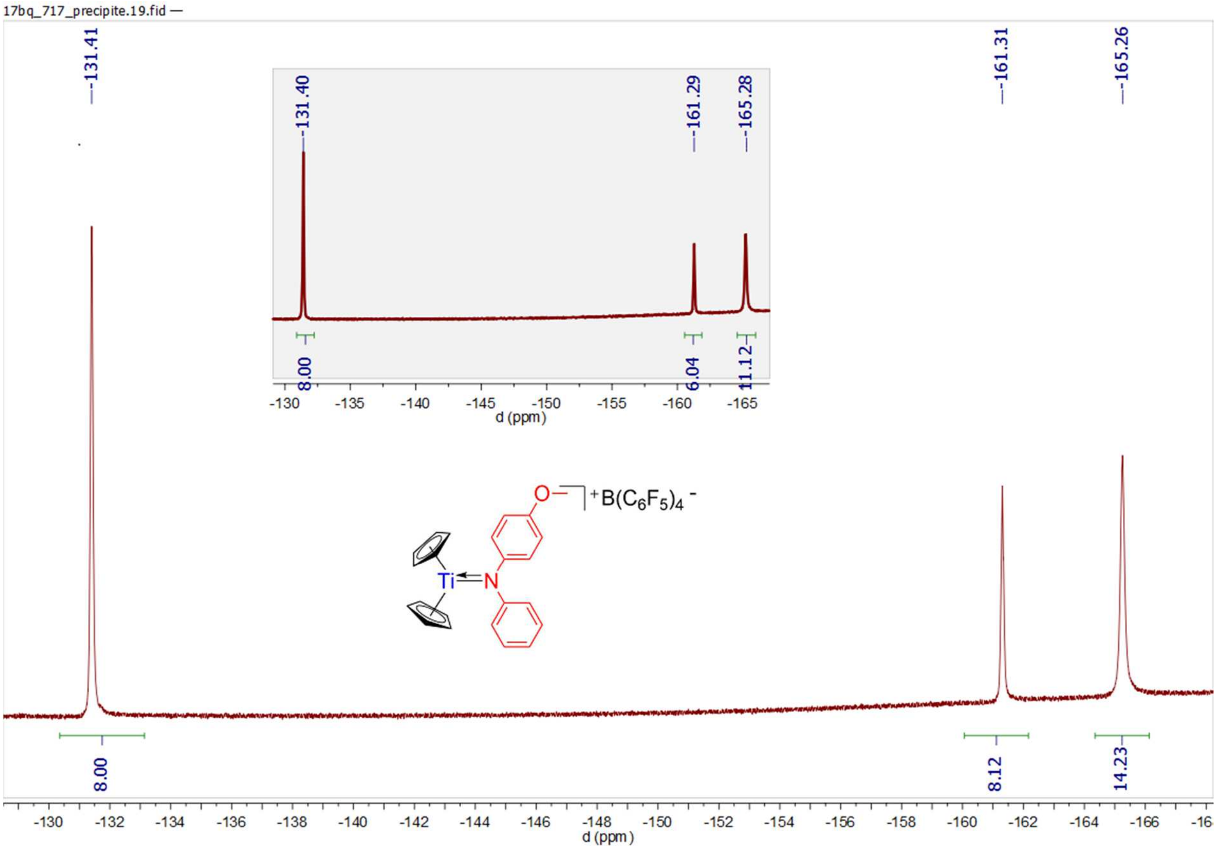
Spectrum 0-430: ^{1}H ^{13}C HMBC of 55 (500.03 MHz / 125.75 MHz, 300 K, bromobenzene-d$_5$)



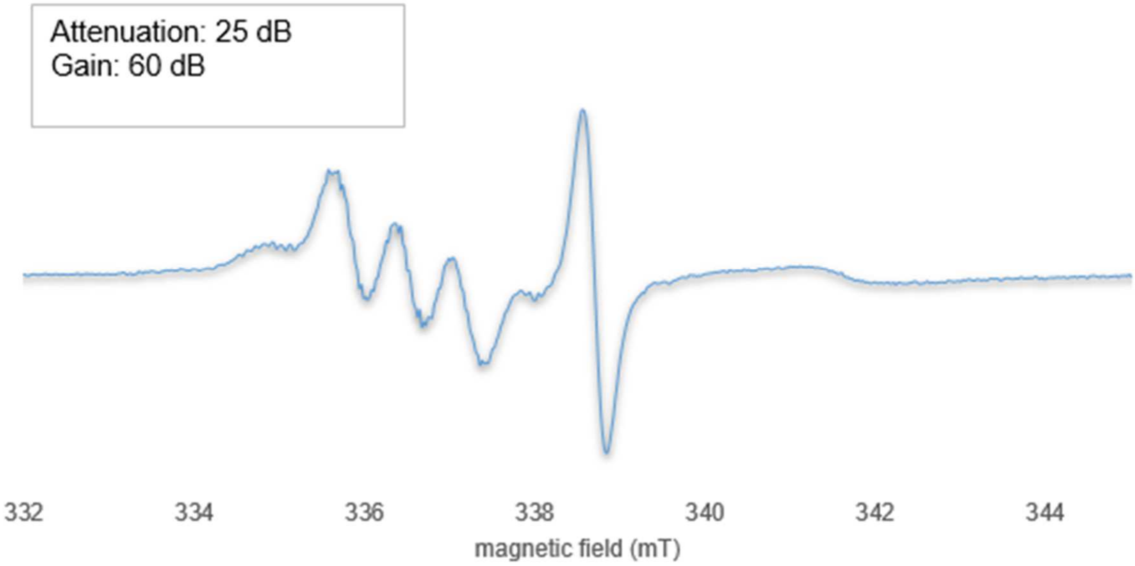
Spectrum 0-431: ^{1}H ^{15}N HMBC of 55 (500.03 MHz / 43.3 MHz, 300 K, bromobenzene-d$_5$)



Spectrum 0-432: ^{11}B{^{1}H} and ^{11}B NMR of 55 (160.43 MHz, 300 K, bromobenzene-d$_5$)

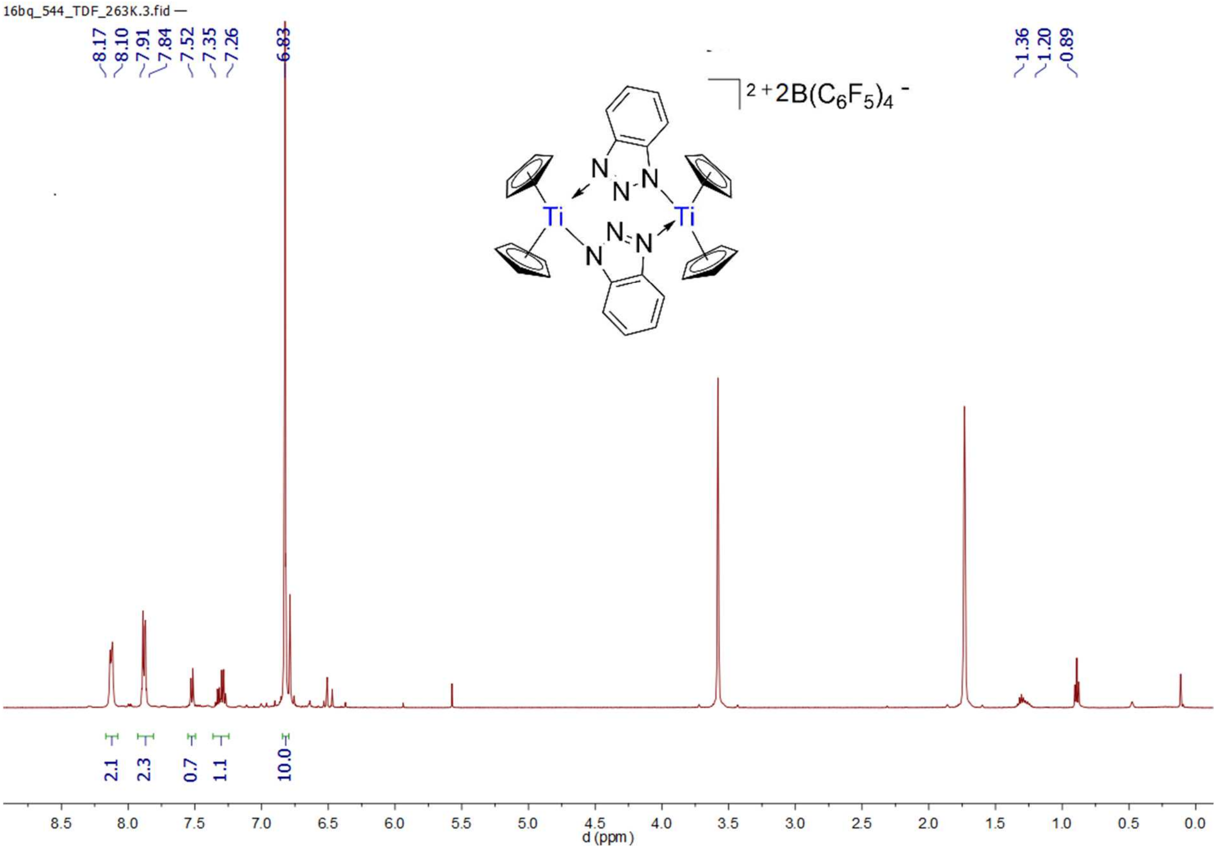


Spectrum 0-433: ^{19}F{^{1}H} and ^{19}F NMR of 55 (470.45 MHz, 300 K, bromobenzene-d$_5$)

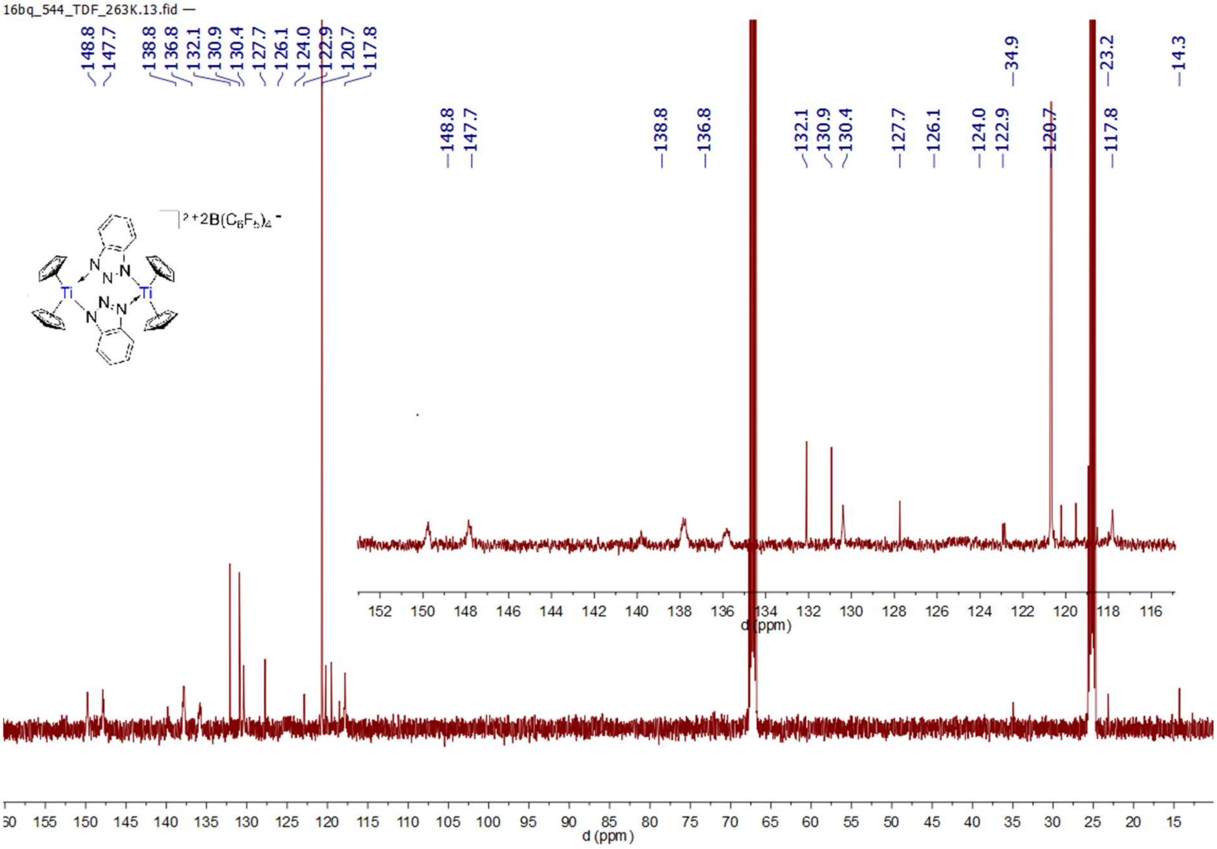


Spectrum 0-434: EPR spectrum of 55 (9.439554 GHz, 295 K, Bromobenzene)

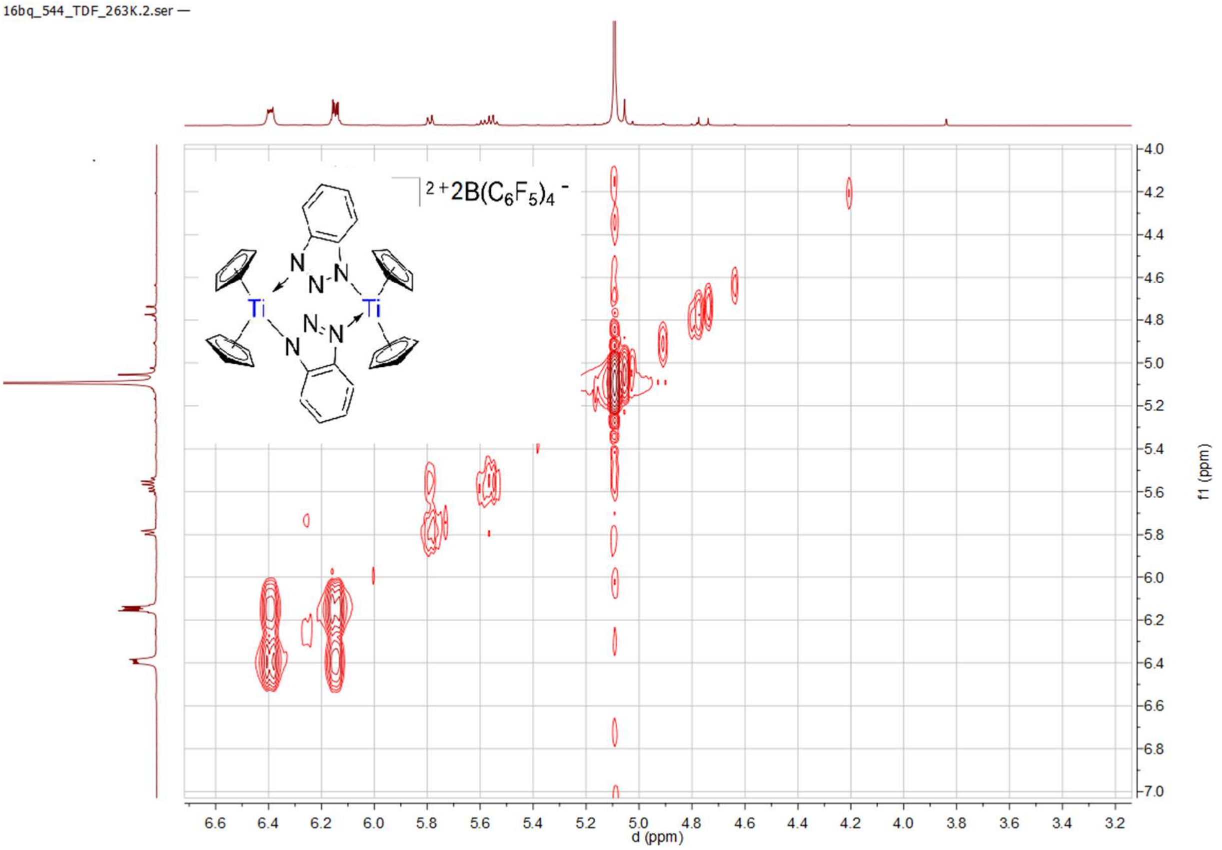
28. Compound **56**:



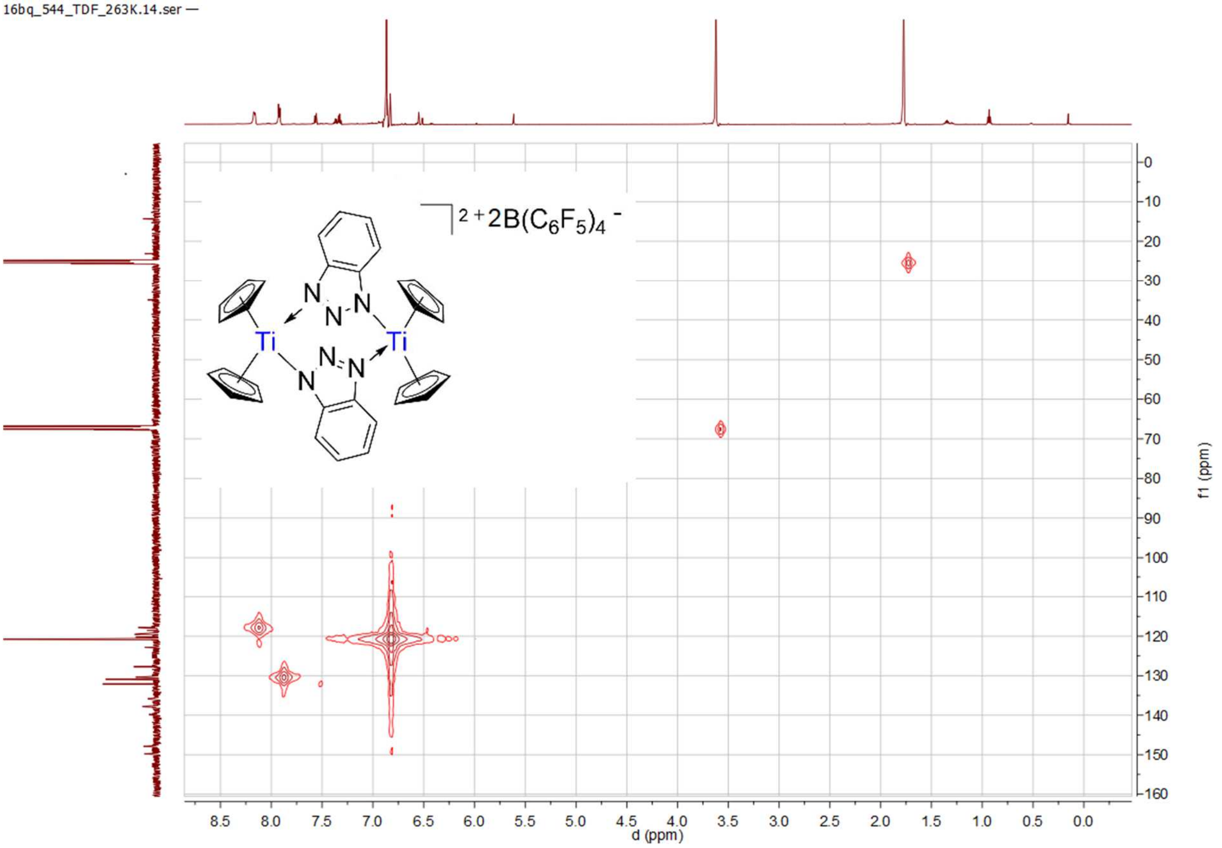
Spectrum 0-435: ^{1}H NMR of 56 (500.03 MHz, 300 K, tetrahydrofuran-d$_5$)



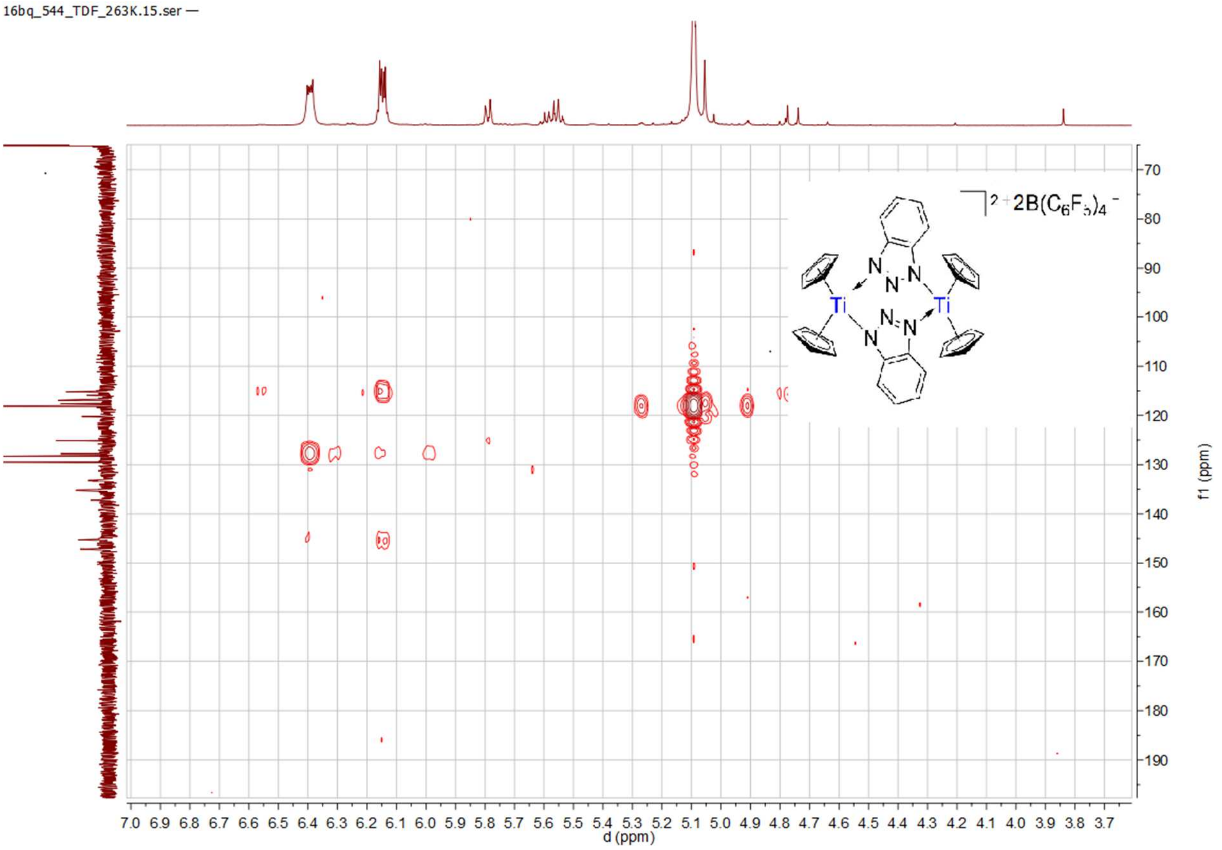
Spectrum 0-436: ^{13}C{^{1}H} NMR of 56 (125.75 MHz, 300 K, tetrahydrofuran-d$_5$)



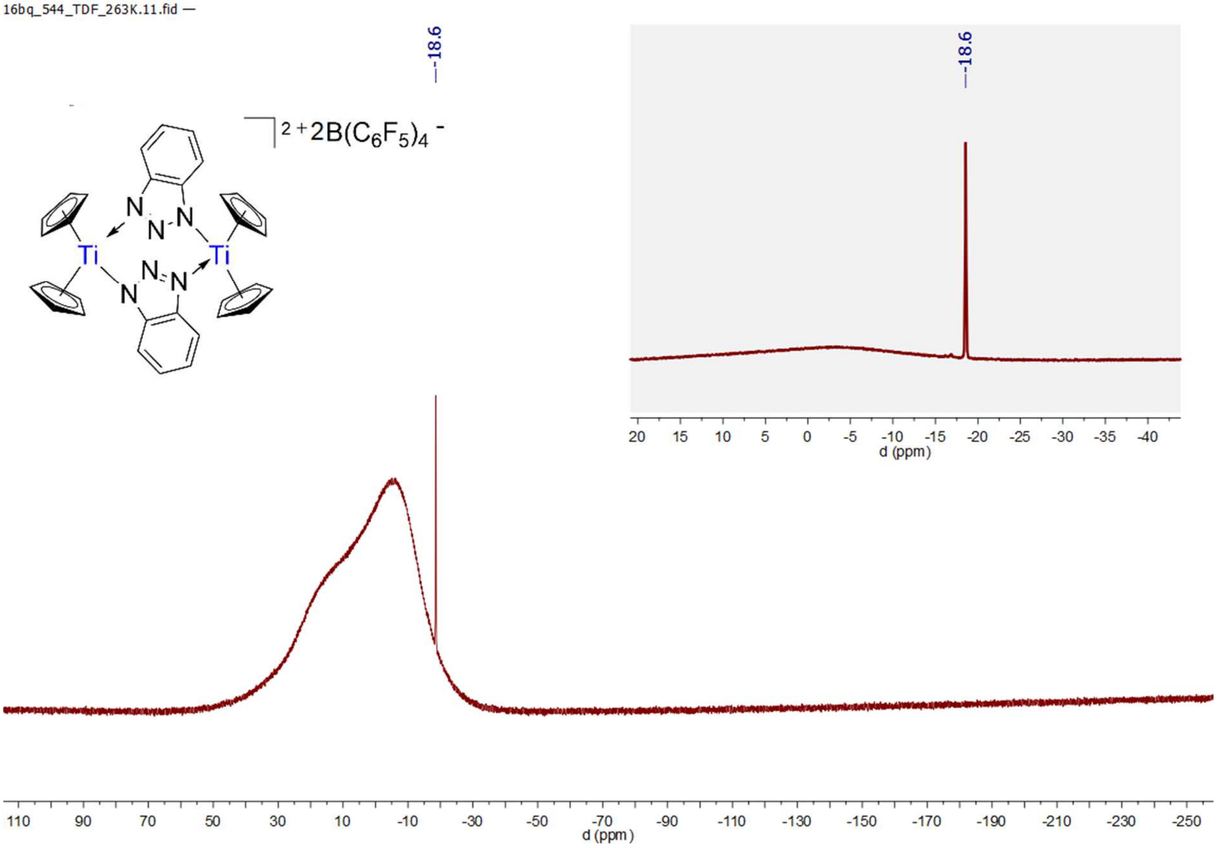
Spectrum 0-437: ^{1}H ^{1}H COSY of 56 (500.03 MHz, 300 K, 273 K, tetrahydrofuran-d$_5$)



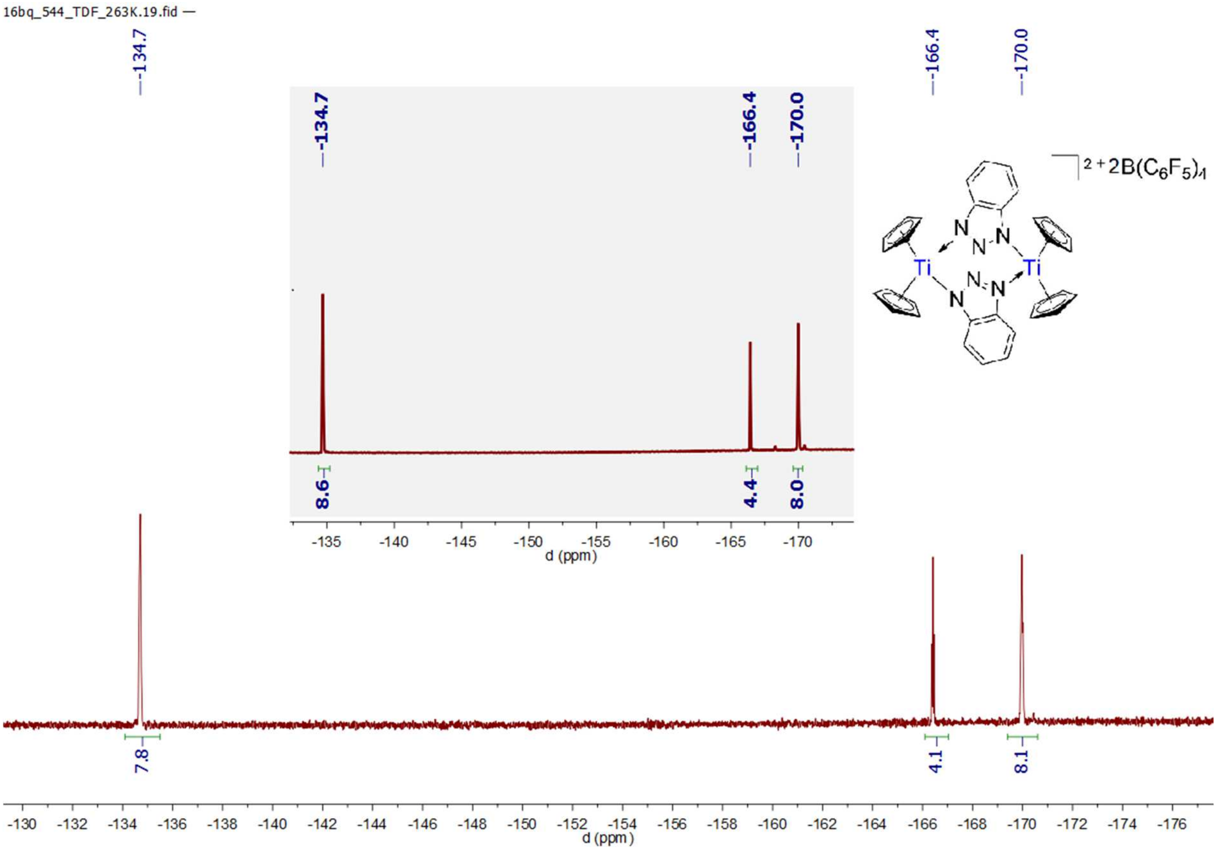
Spectrum 0-438: ^{1}H ^{13}C HMQC of 56 (500.03 MHz / 125.75 MHz, 300 K, tetrahydrofuran-d$_5$)



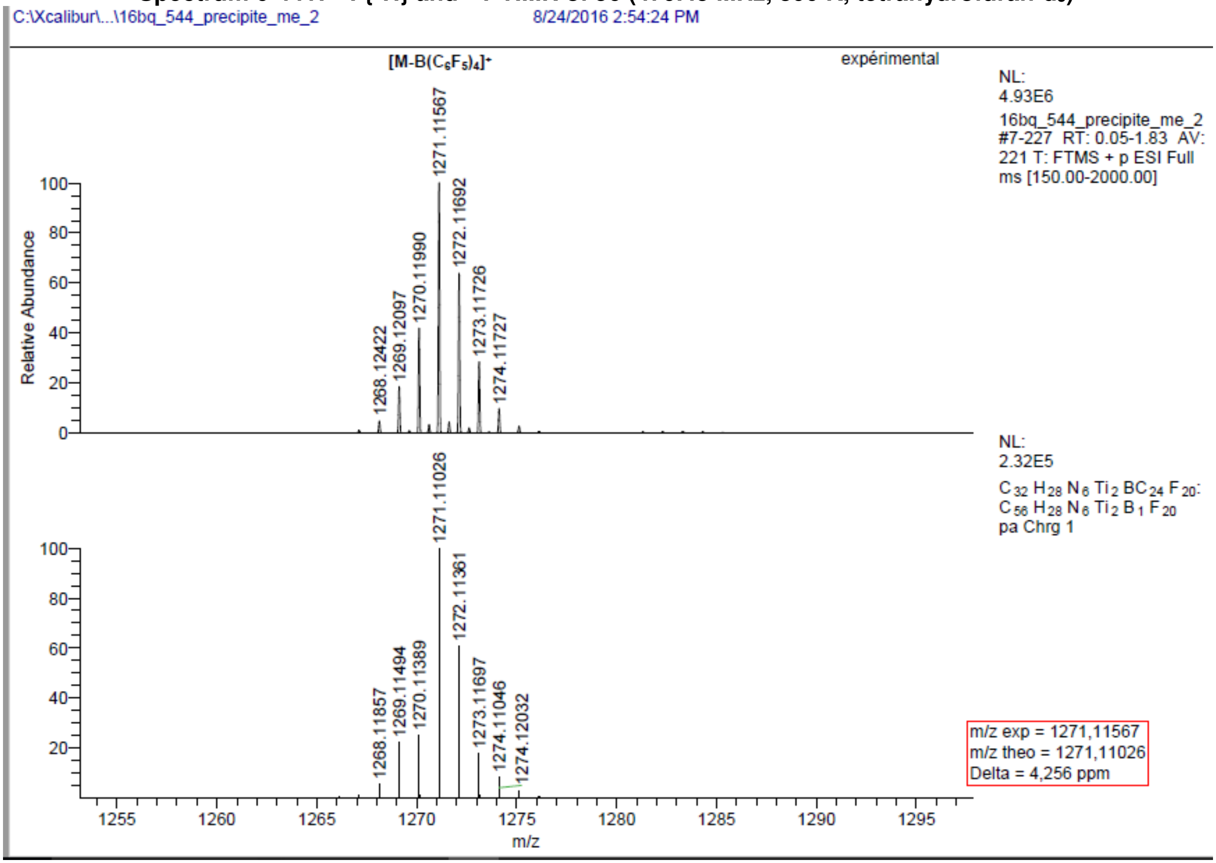
Spectrum 0-439: ^{1}H ^{13}C HMBC of 56 (500.03 MHz / 125.75 MHz, 300 K, tetrahydrofuran-d$_5$)



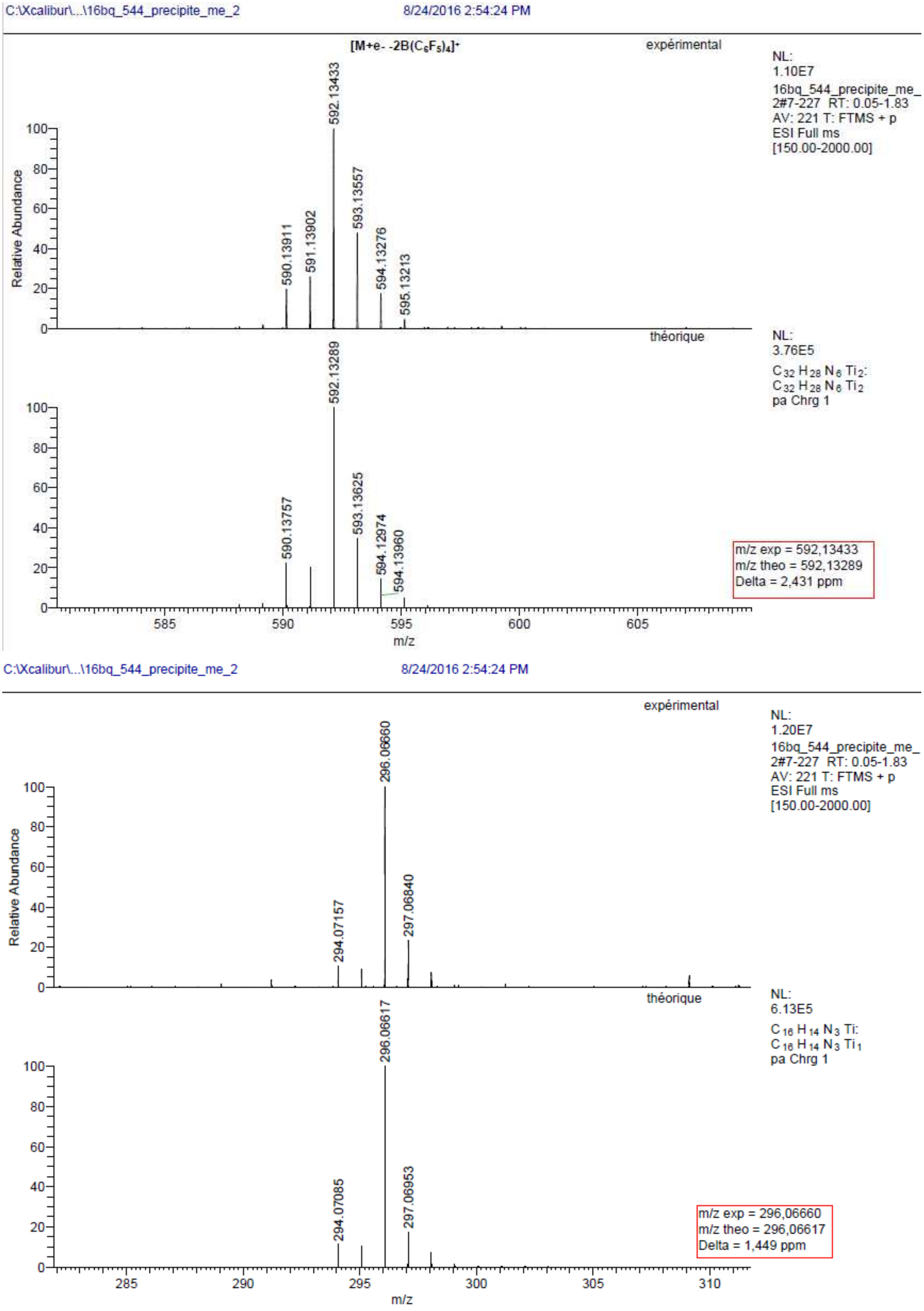
Spectrum 0-440: ^{11}B{^{1}H} and ^{11}B NMR of 56 (160.43 MHz, 300 K, tetrahydrofuran-d$_5$)



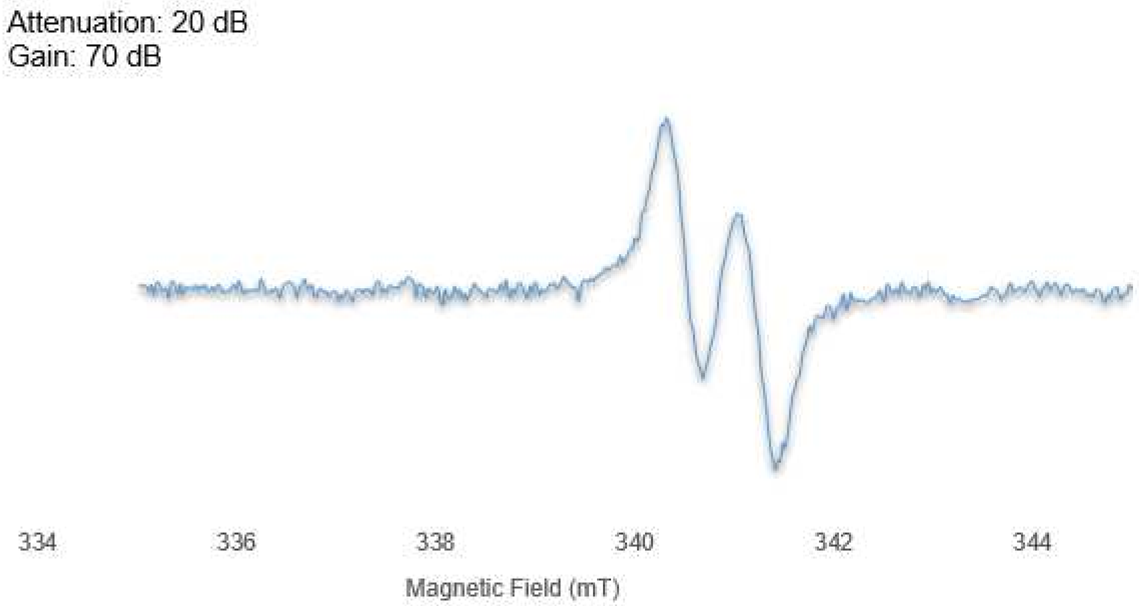
Spectrum 0-441: $^{19}F\{^{1}H\}$ and ^{19}F NMR of 56 (470.45 MHz, 300 K, tetrahydrofuran-d_5)



Spectrum 0-442: HRMS of 56 (Positive mode ESI, tetrahydrofuran)



Spectrum 0-443: HRMS of 56 (Positive mode ESI, tetrahydrofuran)



Spectrum 0-444: EPR spectrum of 56 (9.439554 GHz, 295 K, Bromobenzene)

29. Reactivity studies:

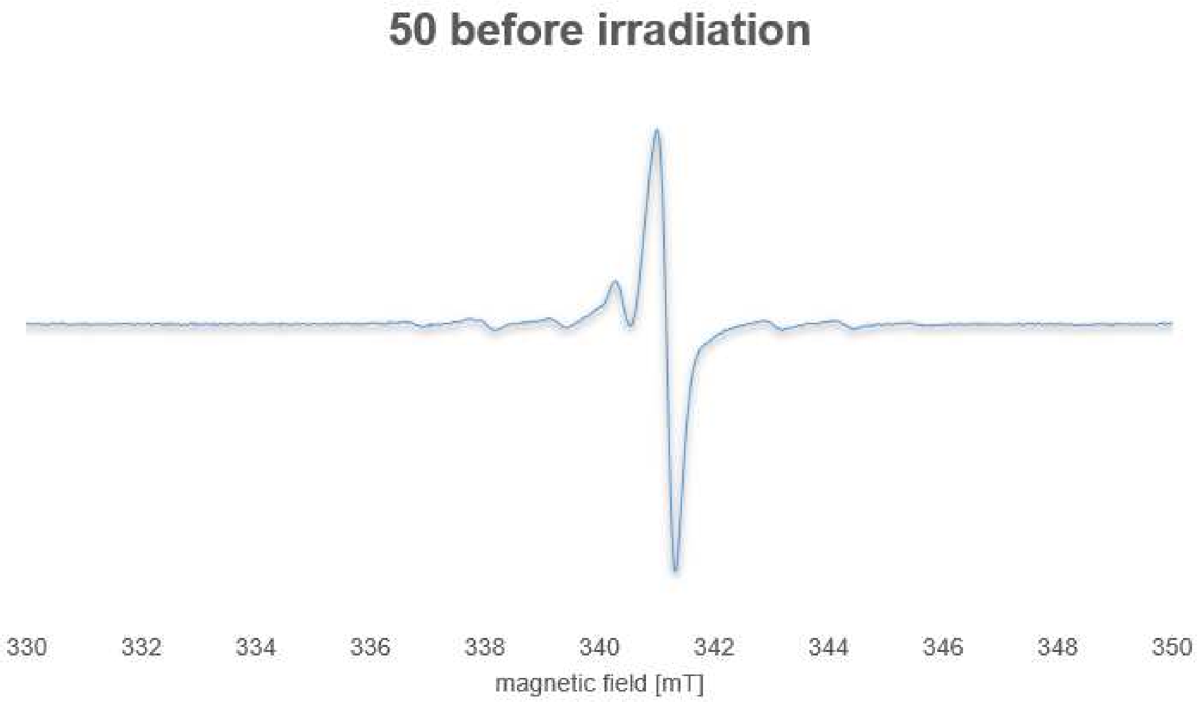
a. EPR study:

A 0.02M solution of amido Ti(IV) complexes in THF was irradiated in three sequences of 20 min with a medium pressure Hg lamp (Heraeus TQ 150).

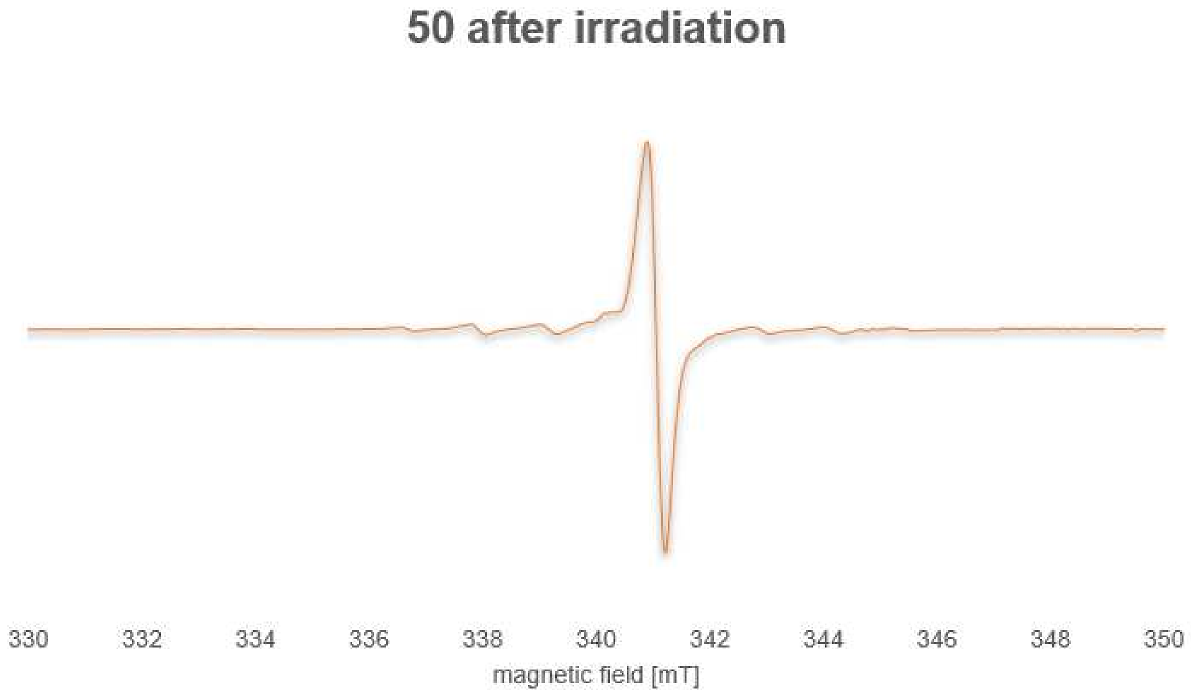
The EPR spectrum before irradiation revealed the presence of the $[Cp_2Ti(THF)_2]^+$ cation along with an unknown, minor product. After irradiation, only $[Cp_2Ti(THF)_2]^+$ was observed. The NMR indicated that the only P-containing NMR active species were $HPPh_2$ and $(PPh_2)_2$, while the only B-containing NMR active species was $B(C_6F_5)_4^-$.

N.B.: The $^{31}P\{^1H\}$ NMR spectrum of ***50*** *in d_8-THF was also recorded, suggesting the presence (in addition to* ***50****) of free $HPPh_2$ (δ = -42.9 ppm) and of the putative phosphidotitanocene cation $[Cp_2Ti(PPh_2)(THF)_n]^+$ (δ = 388.7 ppm).*

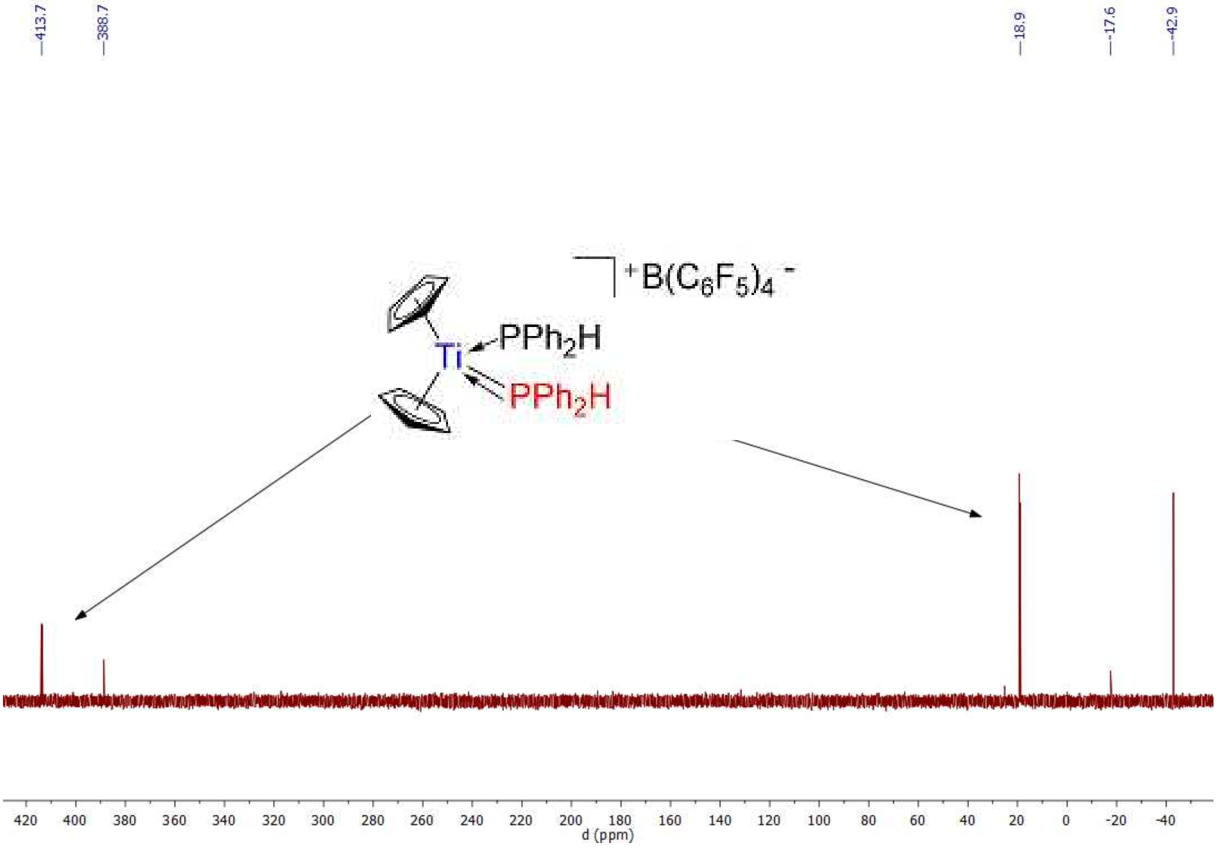
*(1) Compound **50:***



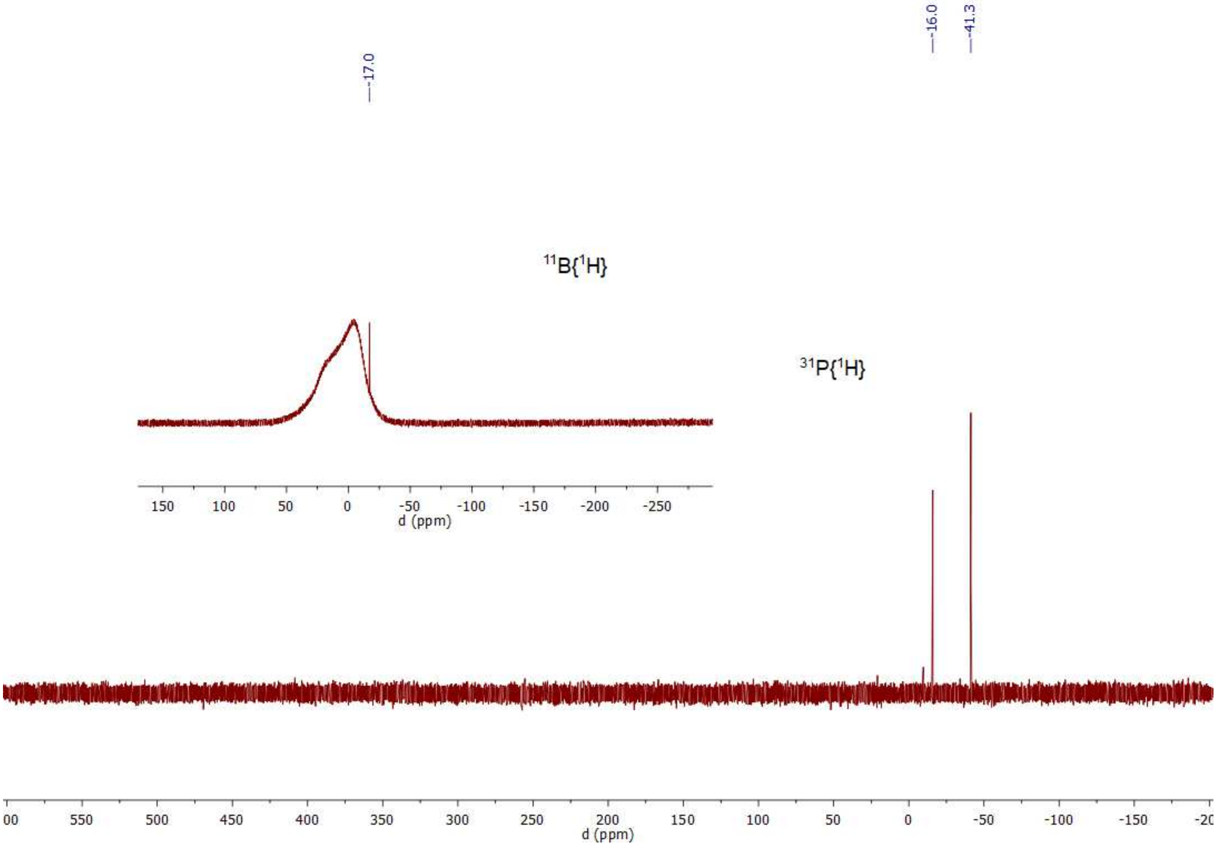
Spectrum 0-445 : EPR before irradiation (THF, 295 K)



Spectrum 0-446: EPR after irradiation (THF, 295 K)



Spectrum 0-447: $^{31}P\{^1H\}$ NMR (202 MHz, d_8-THF, 300K), no irradiation.

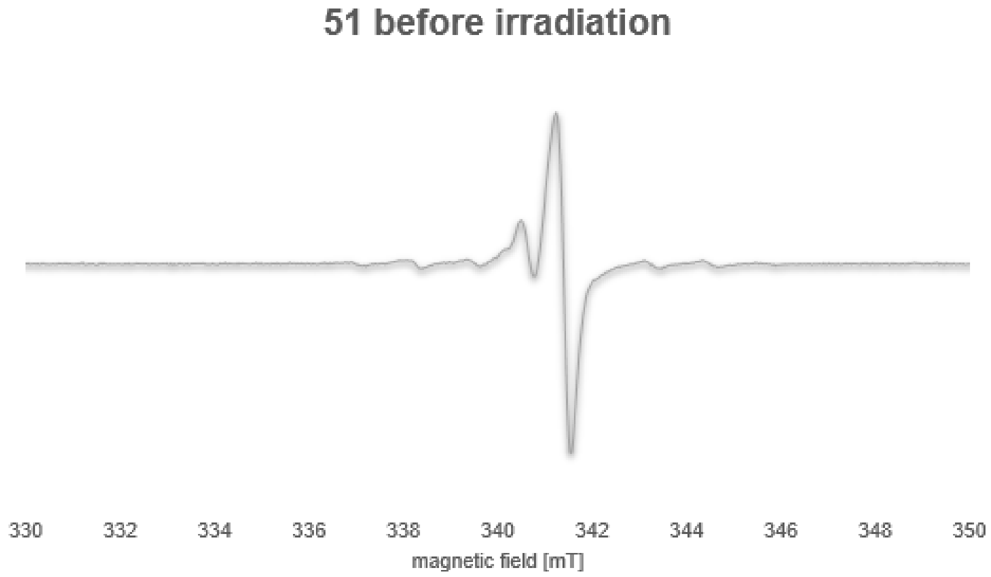


Spectrum 0-448: $^{11}B\{^1H\}$ NMR (160 MHz) and $^{31}P\{^1H\}$ NMR (202 MHz) (THF, 300K, no lock) after irradiation

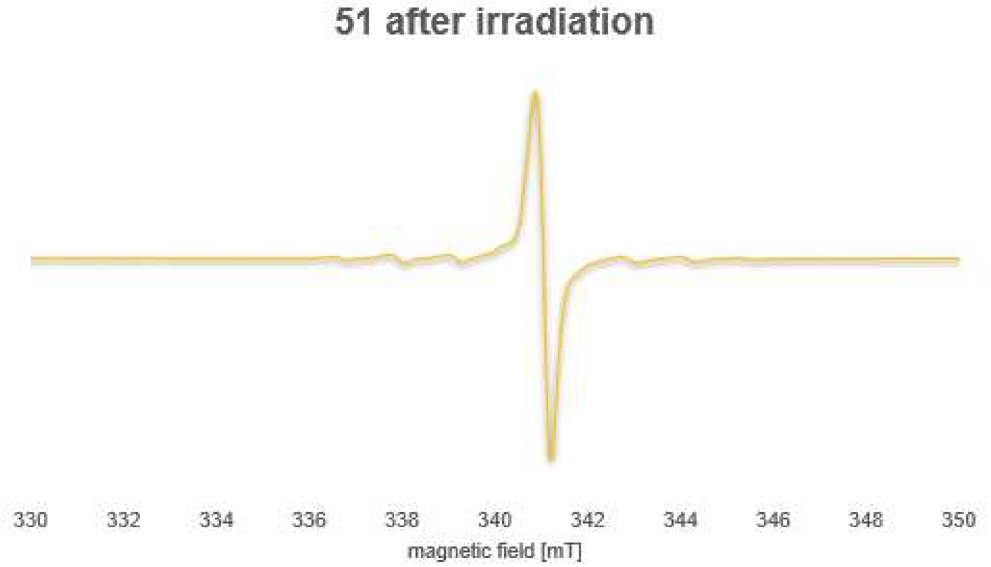
*(2) Compound **51**:*

The EPR spectrum before irradiation revealed the presence of the $[Cp_2Ti(THF)_2]^+$ cation along with an unknown, minor product. After irradiation, only $[Cp_2Ti(THF)_2]^+$ was observed. The NMR indicated that the main P-containing NMR active species was $HPCy_2$, while the only B-containing NMR active species was $B(C_6F_5)_4^-$.

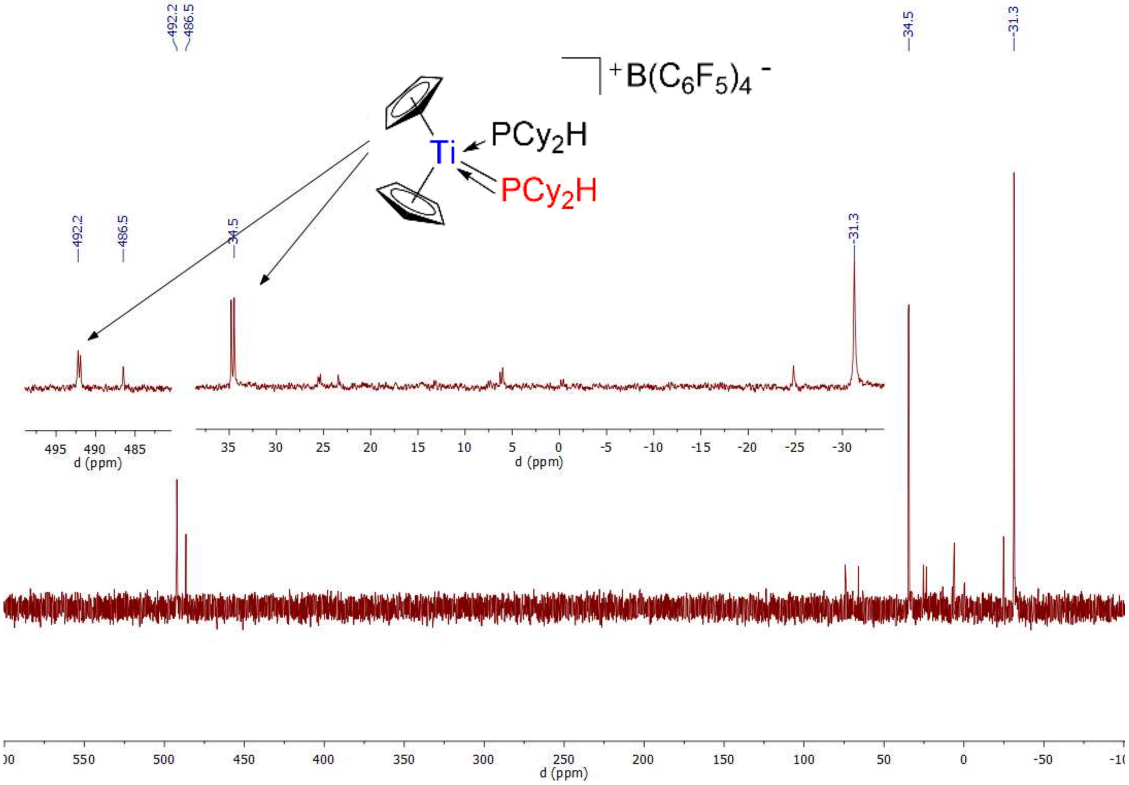
*N.B.: The $^{31}P\{^1H\}$ NMR spectrum of **3f** in THF (no lock) was also recorded, showing extensive decomposition.*



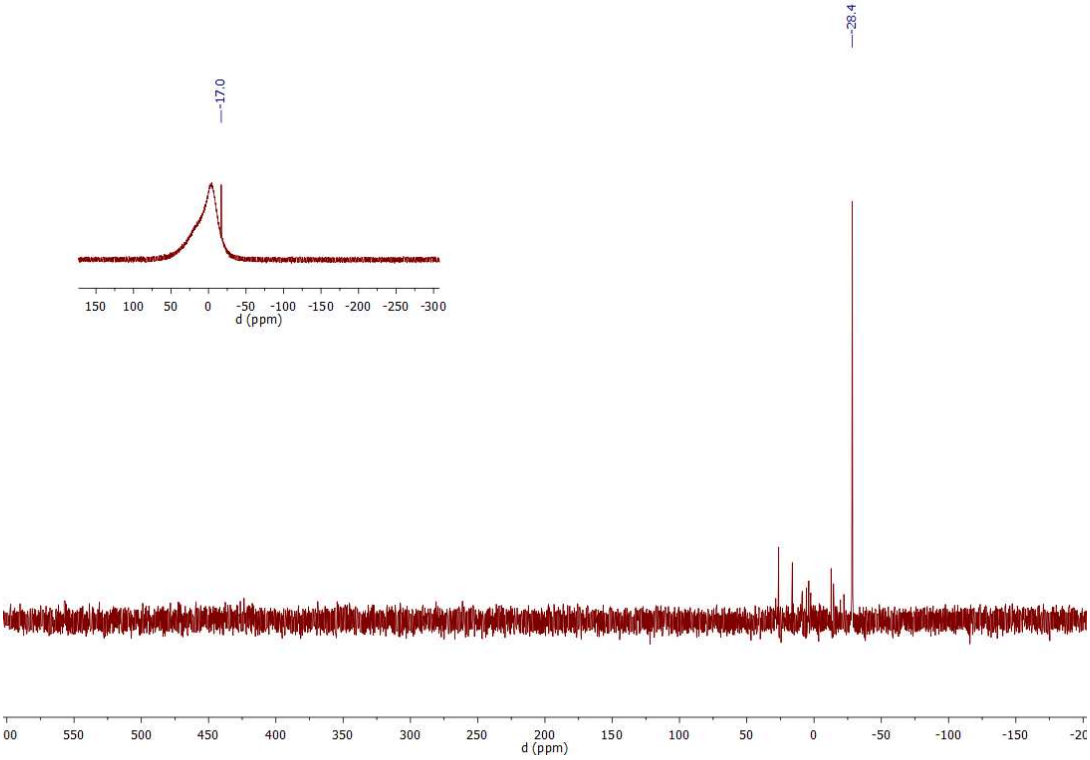
Spectrum 0-449:EPR before irradiation (THF, 295 K)



Spectrum 0-450: EPR after irradiation (THF, 295 K)



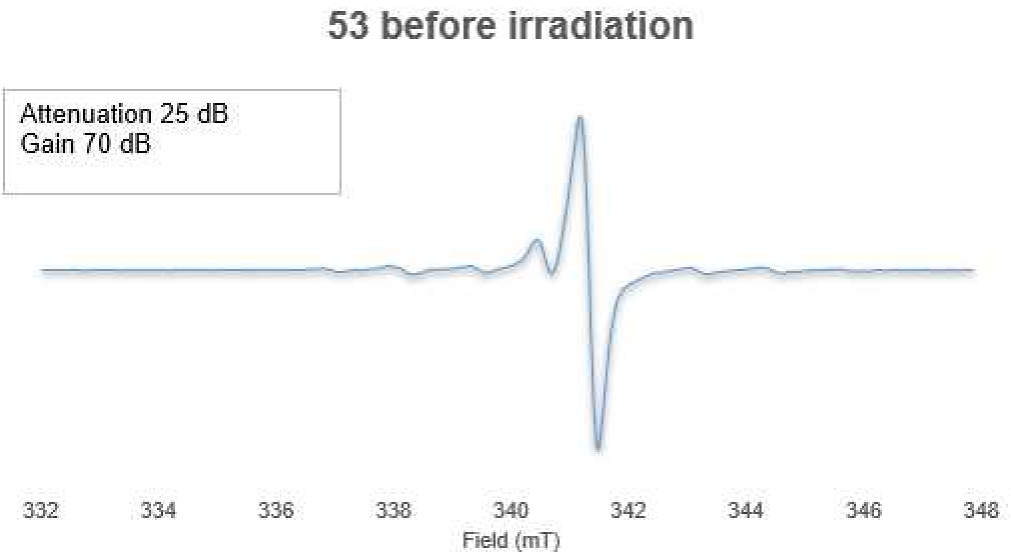
Spectrum 0-451: $^{31}P\{^1H\}$ NMR (243 MHz, THF, 300K, no lock), no irradiation.



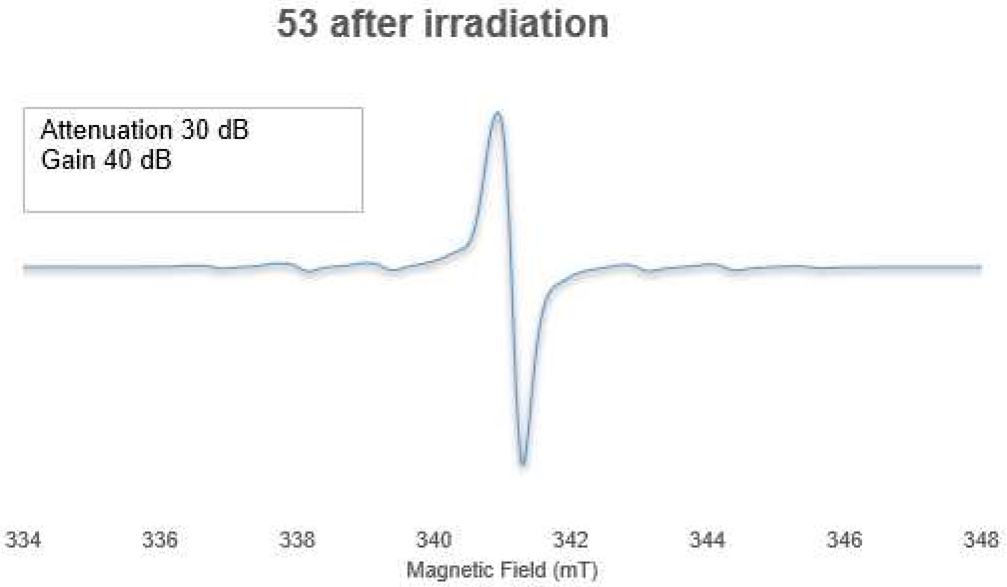
Spectrum 0-452: $^{11}B\{^1H\}$ NMR (160 MHz) and $^{31}P\{^1H\}$ NMR (202 MHz) (THF, 300K, no lock) after irradiation

The final irradiated residue after evaporation was analysed by NMR spectroscopy. While all 1H NMR showed complex mixture, the only B- and F-containing NMR active species was $B(C_6F_5)_4^-$.

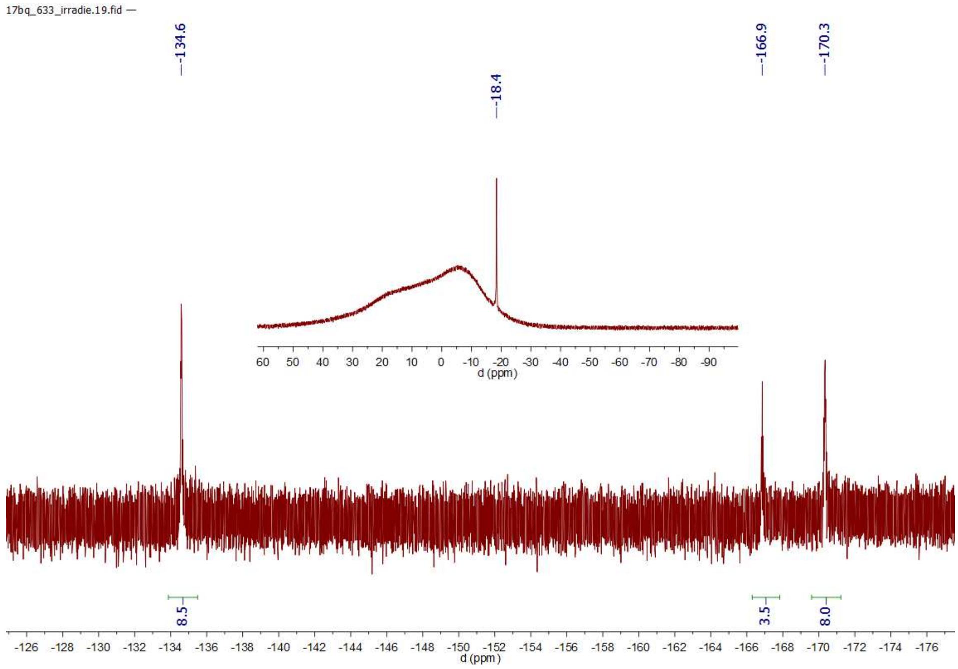
*(3) Compound **53:***



Spectrum 0-453: EPR before irradiation (9.439089GHz, 295 K, THF)

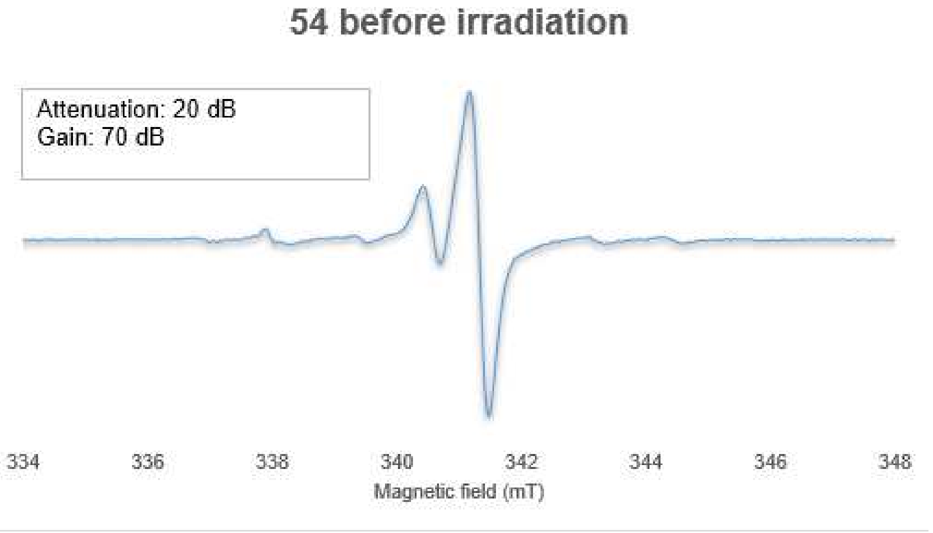


Spectrum 0-454: EPR spectrum after irradiation (9.434780 GHz, 295 K, THF)



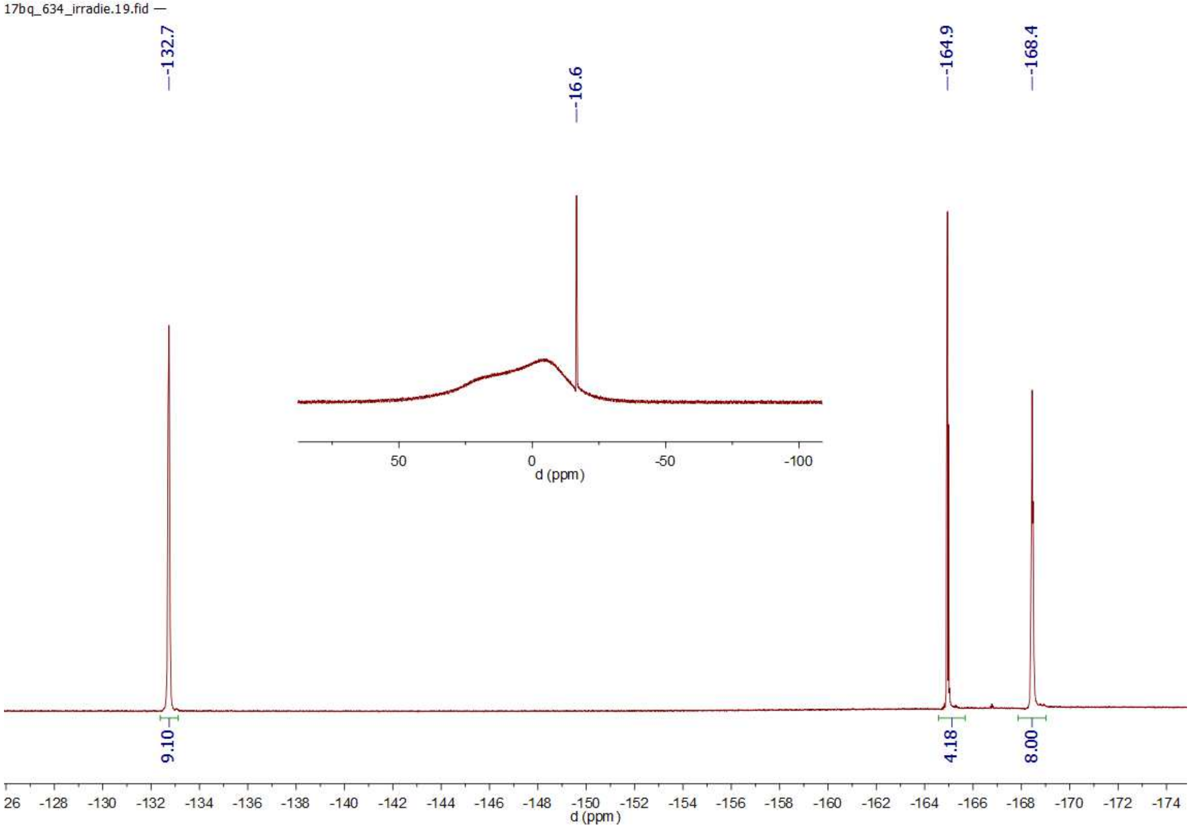
Spectrum 0-455 : $^{11}B\{^1H\}$ and 19F{^{1}H} NMR spectra of 53 after irradiation (500.03 MHz, 300 K, tetrahydrofuran-d$_8$)

(4) *Compound* **54:**



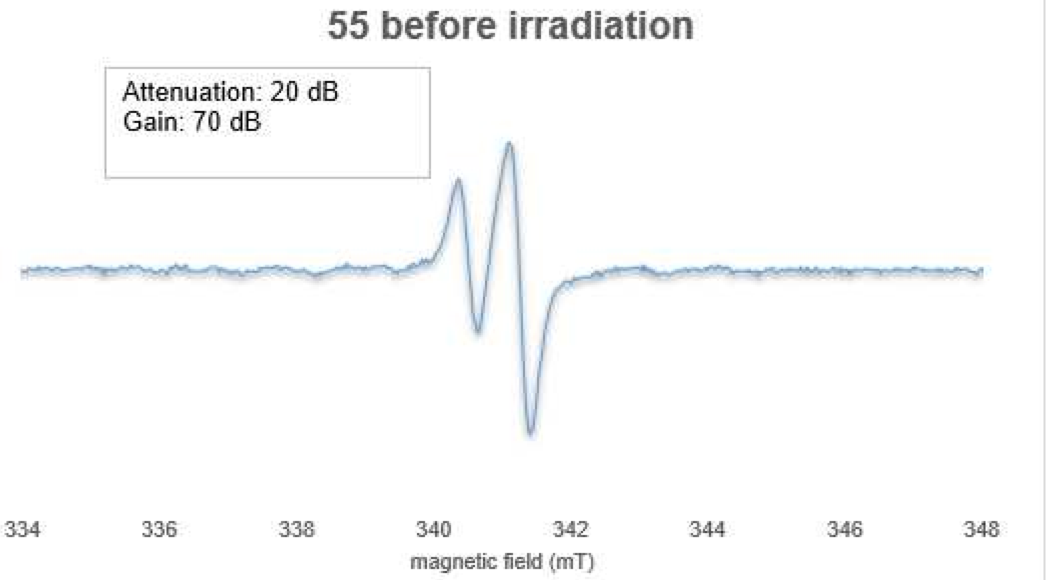
Spectrum 0-456: EPR spectrum of 54 before irradiation (9.438876 GHZ, 295 K THF)

Spectrum 0-457: EPR spectrum of 54 after irradiation (9.435437, 295 K, THF)

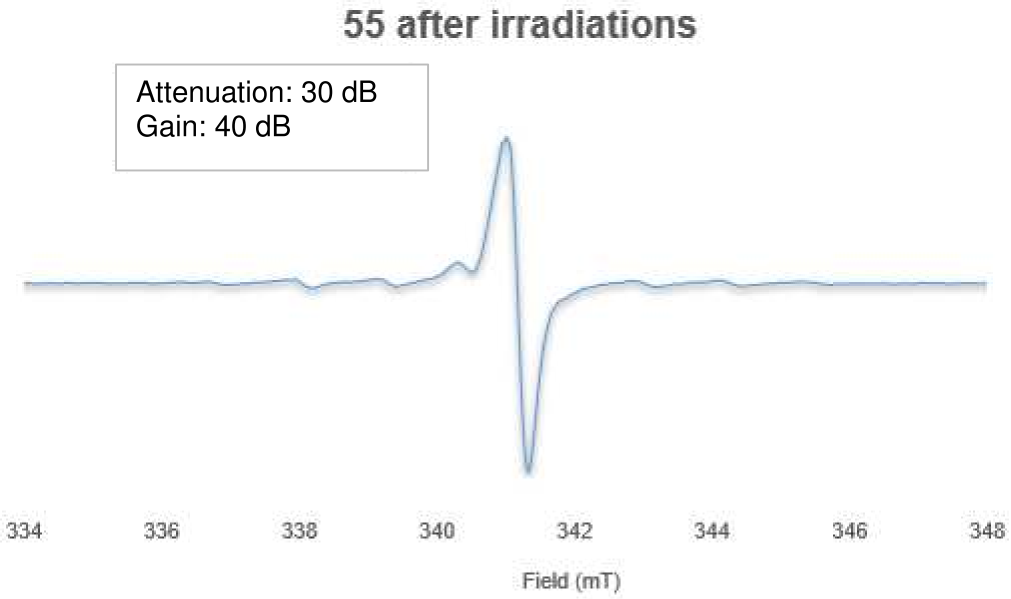


Spectrum 0-458: ^{11}B{^{1}H} and 19F{^{1}H} NMR spectra of 54 after irradiation (500.03 MHz, 300 K, tetrahydrofuran-d_8)

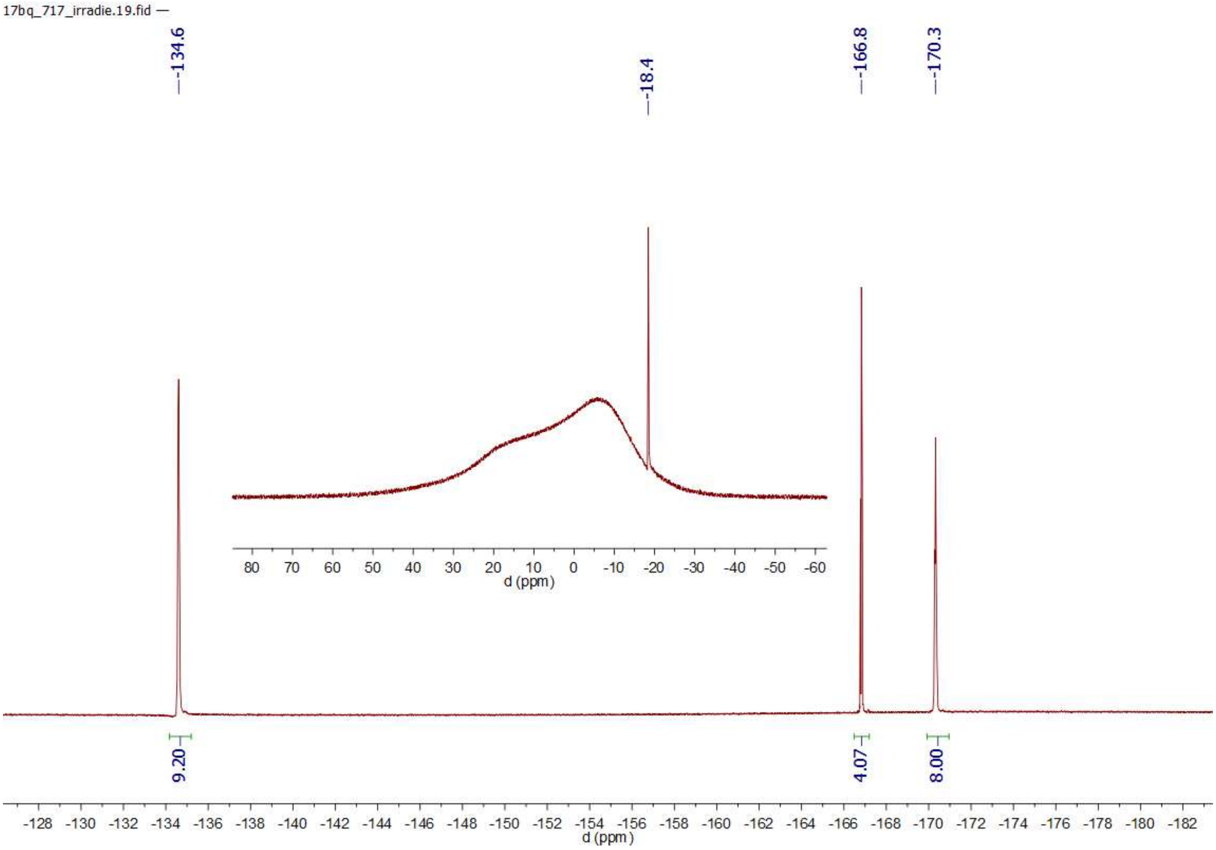
*(5) Compound **55:***



Spectrum 0-459 : EPR spectrum of 55 before irradiation (9.437043, 295 k, THF)



Spectrum 0-460: EPR spectra of 55 after irradiation (9.435333, 295 K, THF)



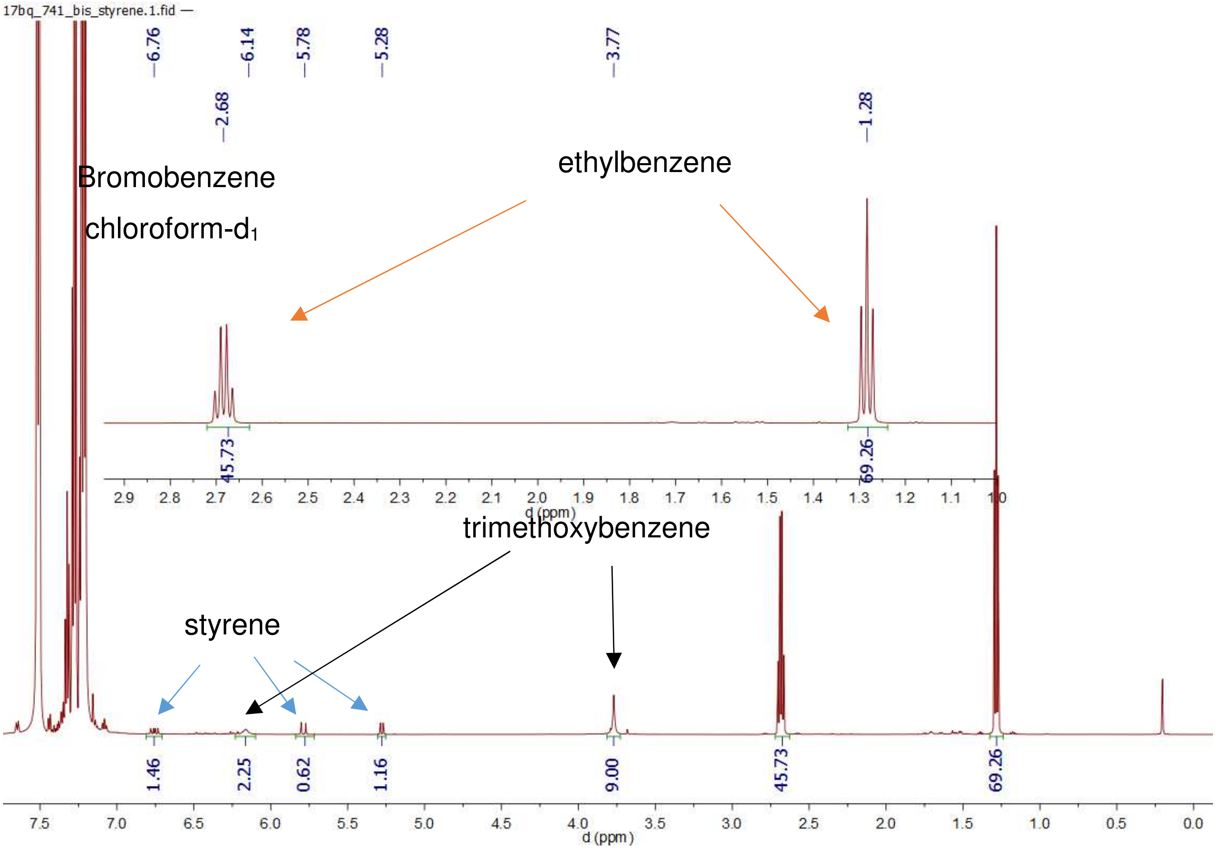
Spectrum 0-461: $^{11}B\{^{1}H\}$ and $19F\{^{1}H\}$ NMR spectra of 55 after irradiation (500.03 MHz, 300 K, tetrahydrofuran-d_8)

b. Catalytic hydrogenation

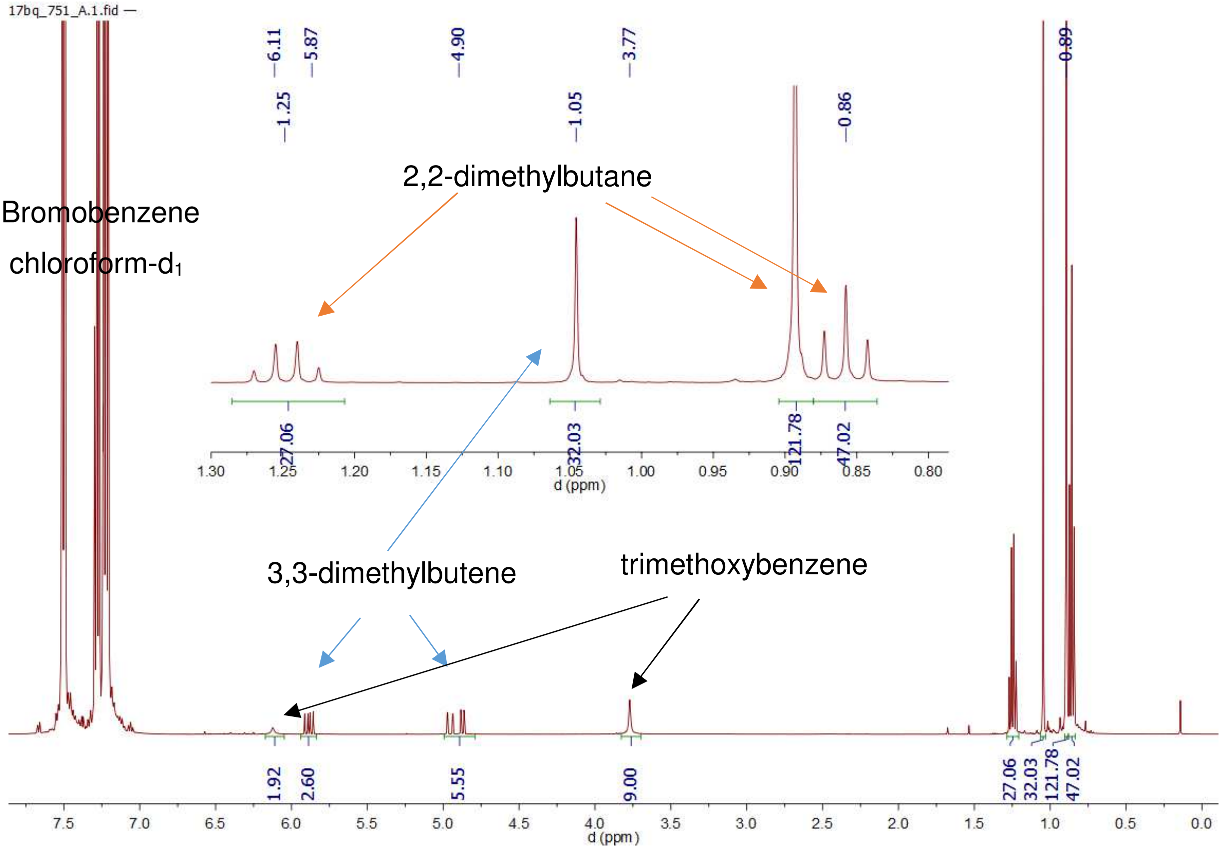
Procedure A: for catalytic hydrogenation: A 0.048 M solution of trimethoxybenzene (TMB) was prepared in C_6H_5Br. Protocol for a classical run: The substrate (960.0 μmol) and the catalyst (19.2 μmol, 2 mol%) were introduced in a 25 mL Schlenk tube and 1.0 mL of the TMB solution was added οπαχιφιεδ the Glovebox. The resulting solution was frozen, and degassed. An aliquot of the resulting solution was collected mixed up with $CDCl_3$ and the mixture was analyzed by ^1H NMR spectroscopy.

Procedure B: (for higher loading and concentration run) The substrate (480.0 μmol) and the catalyst (19.2 μmol, 4 mol%) were introduced in a 25 mL Schlenk tube and 0.50 mL of the TMB solution was added οπαχιφιεδ the Glovebox. The resulting solution was frozen, and degassed. An aliquot of the resulting solution was collected mixed up with $CDCl_3$ and the mixture was analyzed by ^1H NMR spectroscopy.

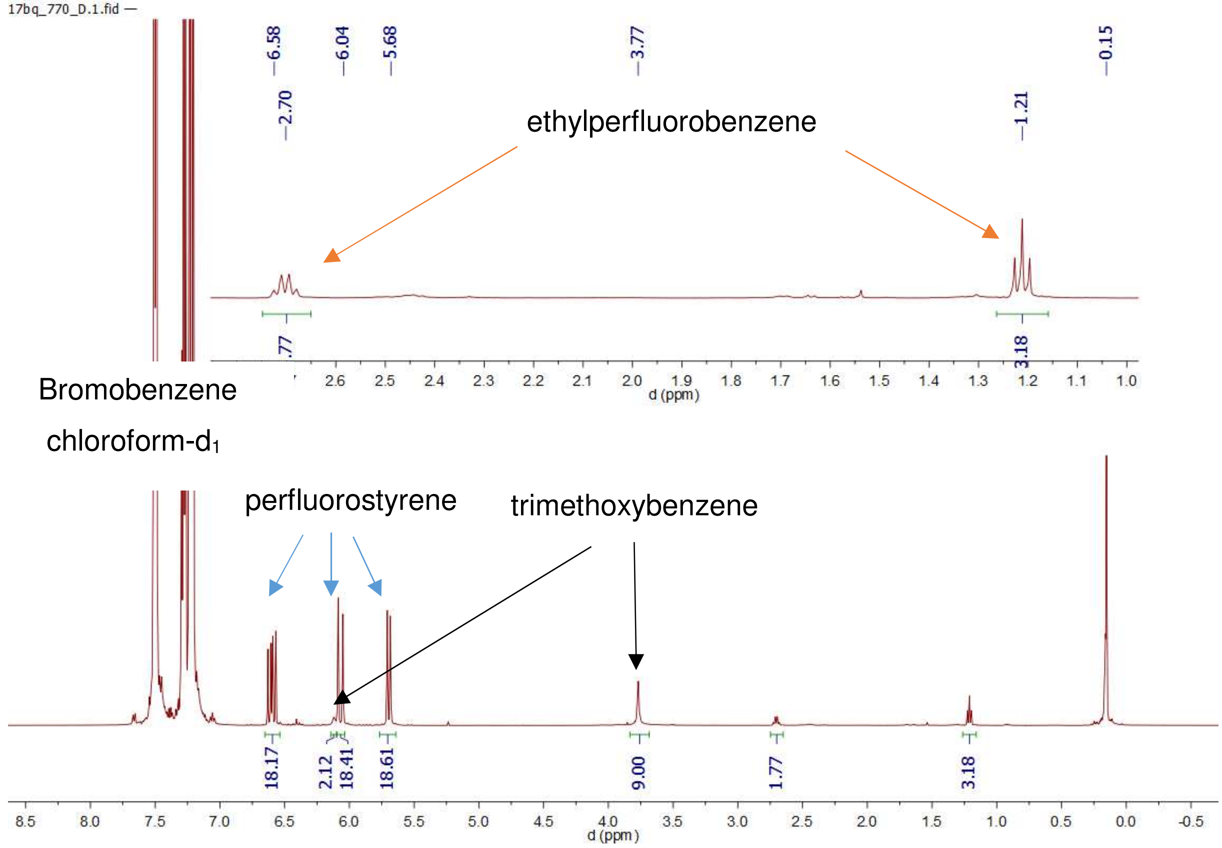
^1H NMR spectra of representative catalytic runs:



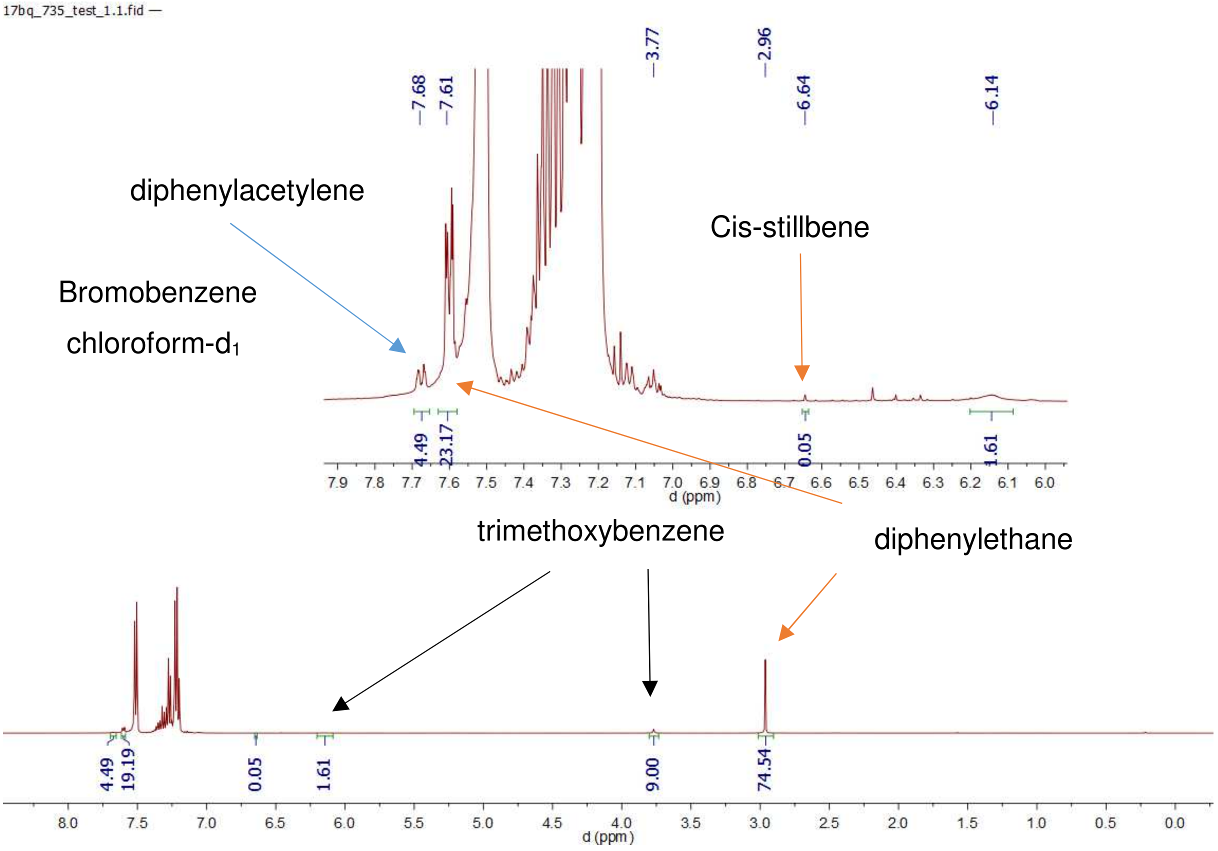
Spectrum 0-462: Hydrogenation of styrene with 53 (600.23 MHz, 300K, Chloroform-d$_1$)



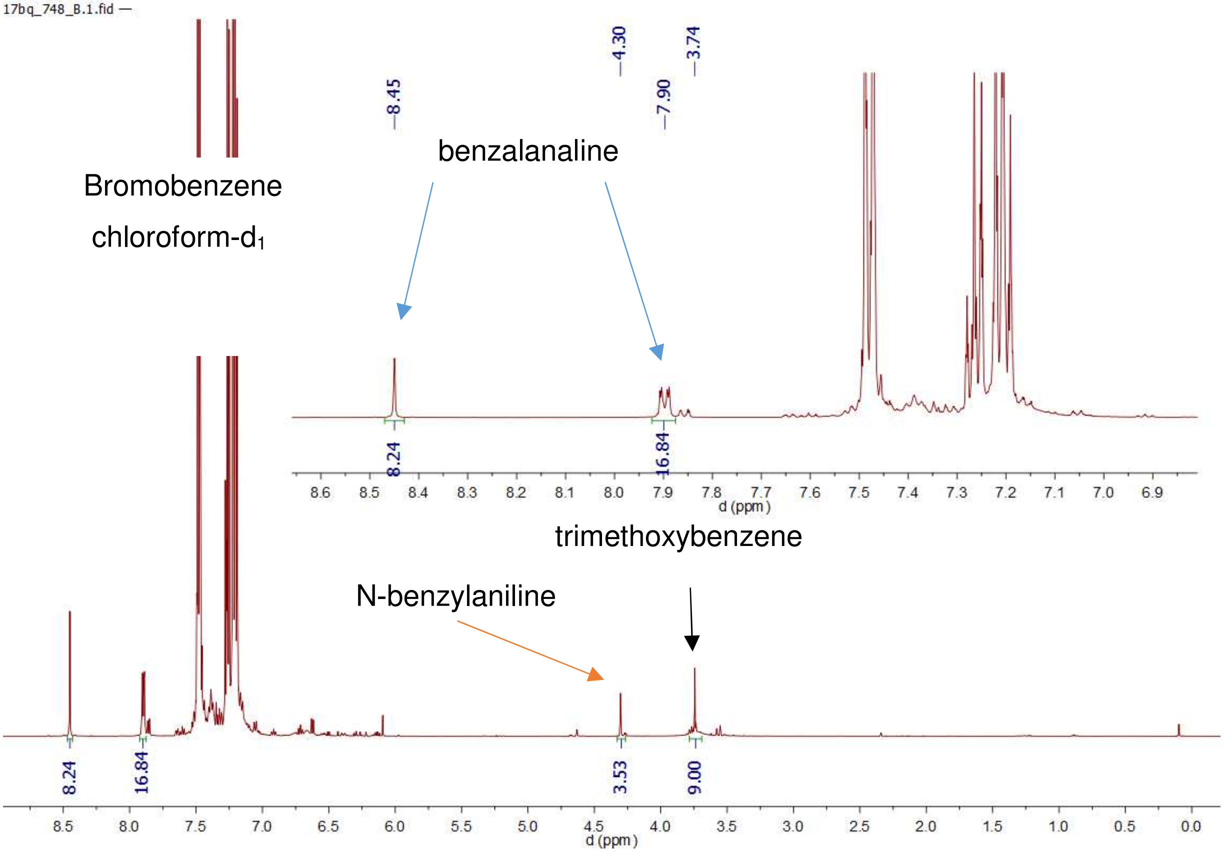
Spectrum 0-463 : Hydogenation of 3,3-dimethylbutene with 53 (500.03 MHz, 300K, Chloroform-d₁)



Spectrum 0-464: Hydogenation of perfluorostyrene with 53 (500.03 MHz, 300K, Chloroform-d₁)



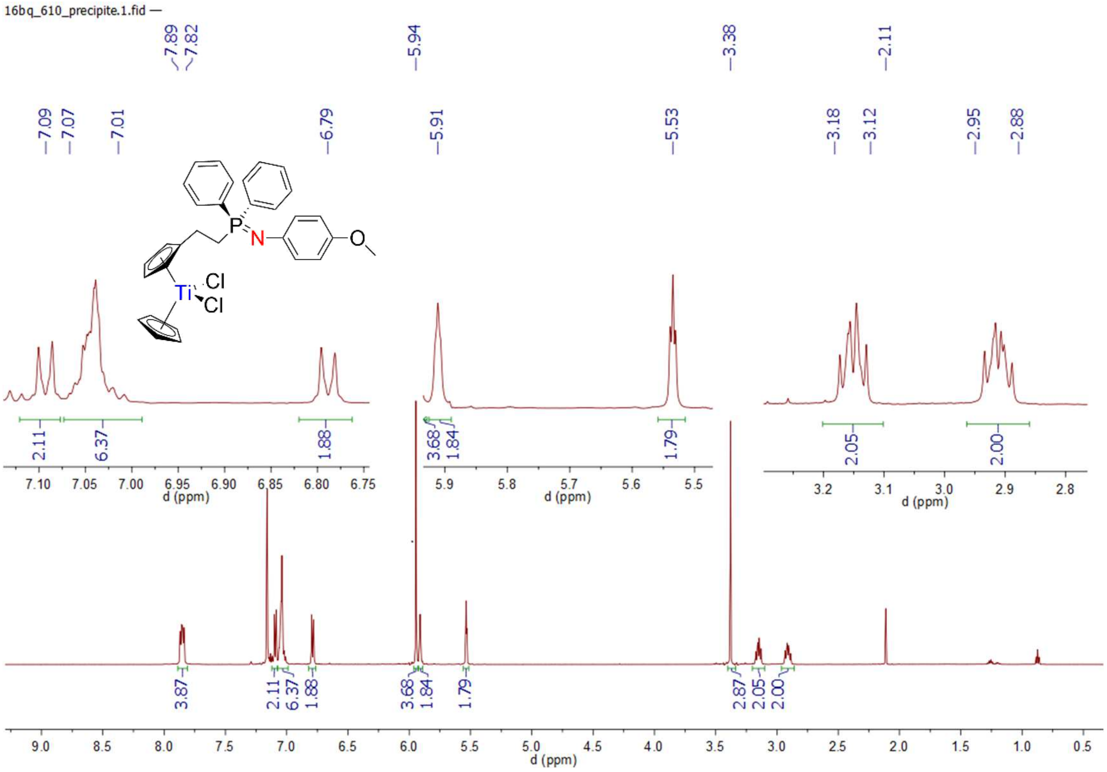
Spectrum 0-465: Hydogenation of diphenylacetylene with 53 (500.03 MHz, 300K, Chloroform-d₁)



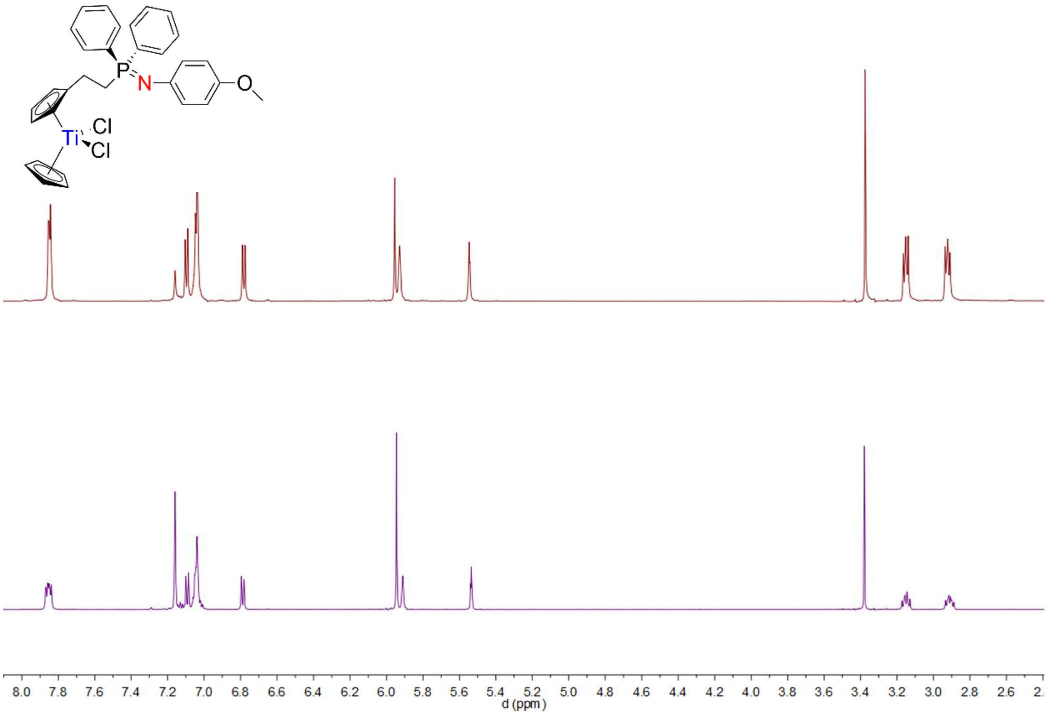
Spectrum 0-466: Hydogenation of benzalanaline with 53 (500.03 MHz, 300K, Chloroform-d₁)

D. Appendix Chapter V

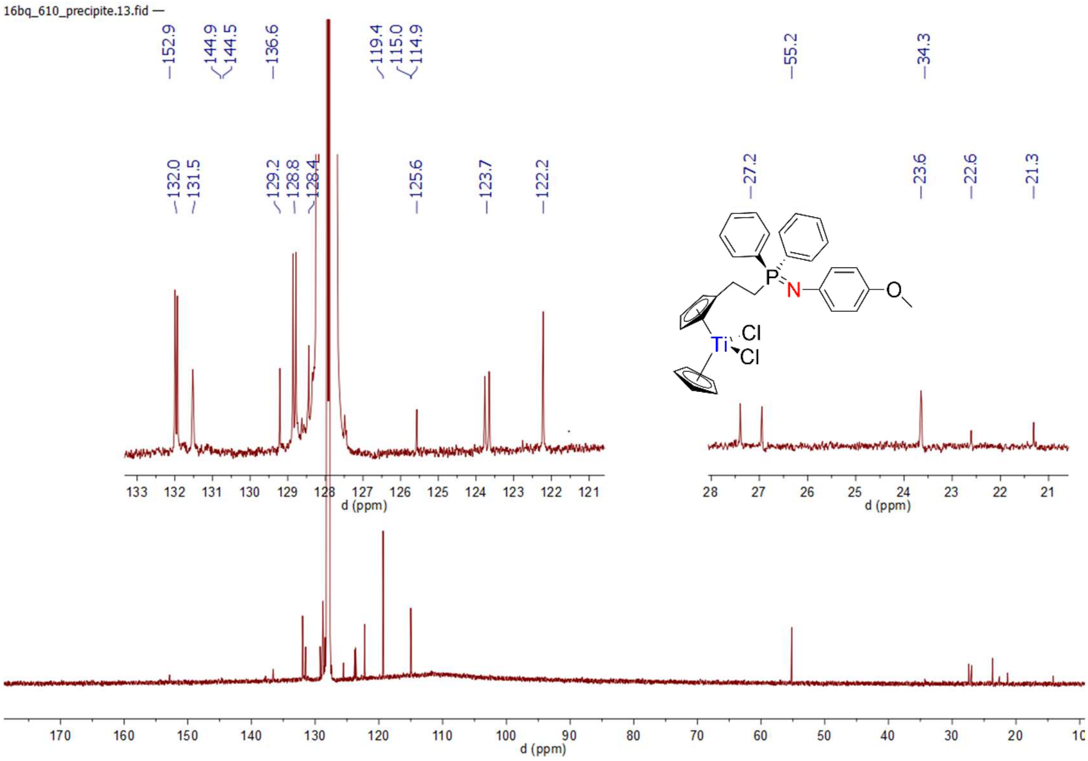
30. Compound **57**:



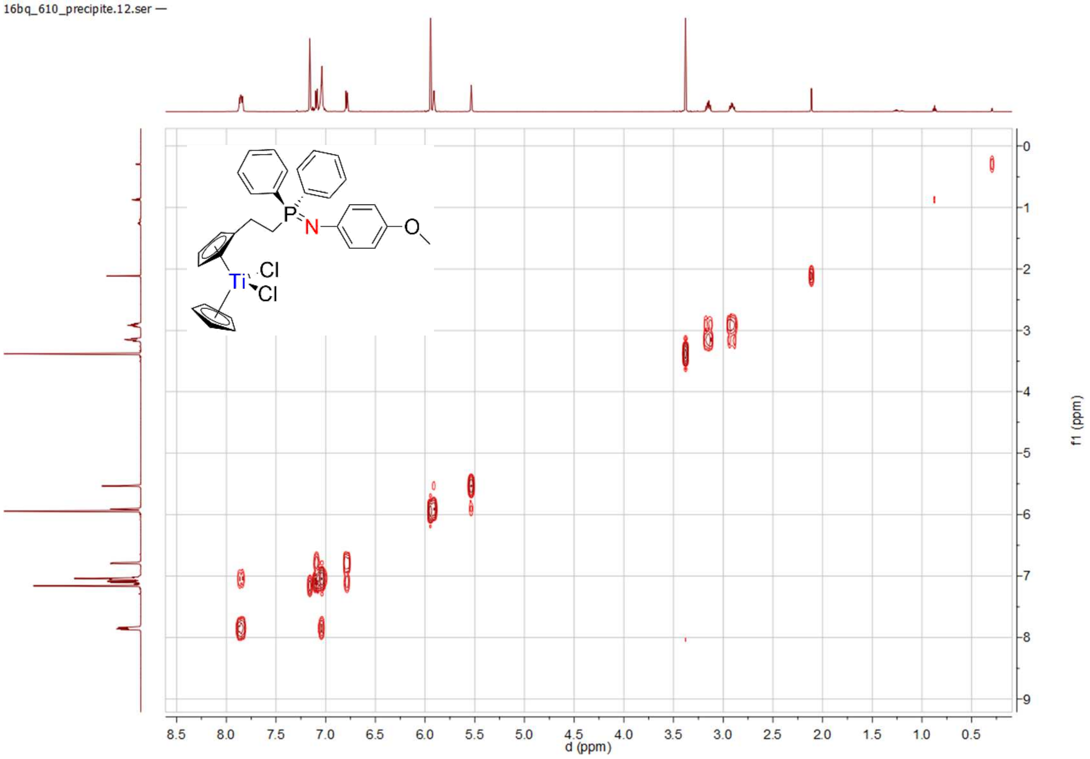
Spectrum 0-467: ^{1}H NMR of 57 (500.03 MHz, 300 K, benzene-d$_6$)



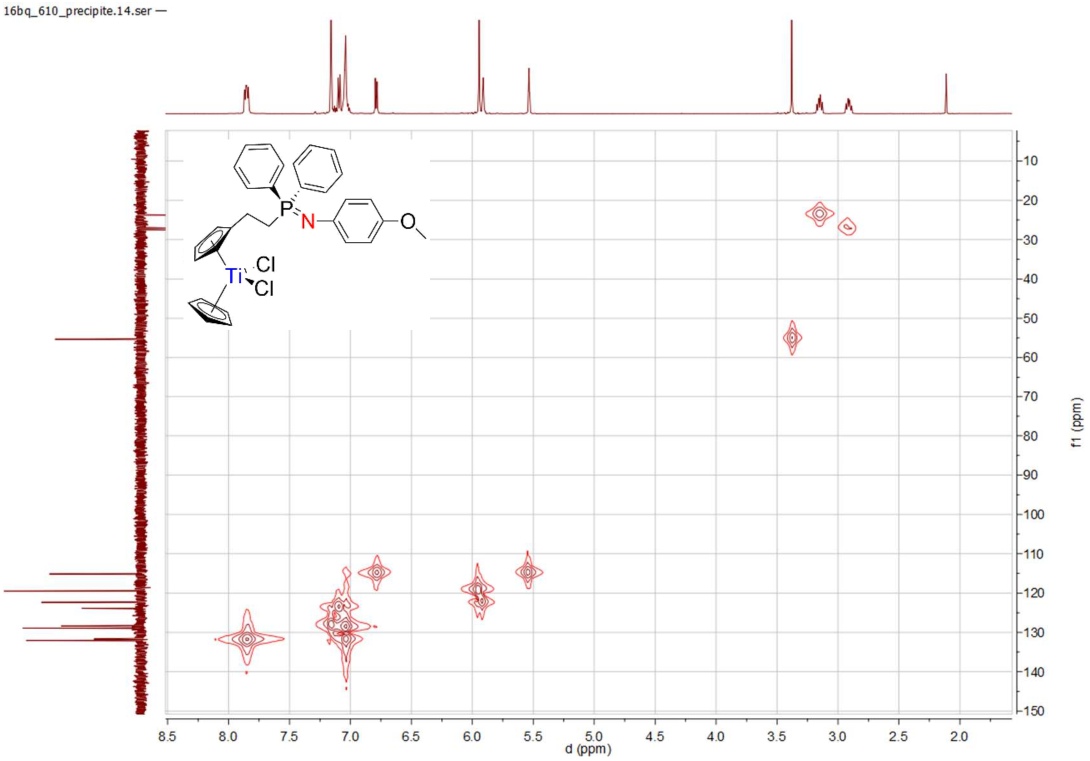
Spectrum 0-468: ^{1}H{^{31}P} NMR (top) correlated with ^{1}H NMR (bottom) of 57 (600.23 MHz, 300 K, benzene-d$_6$)



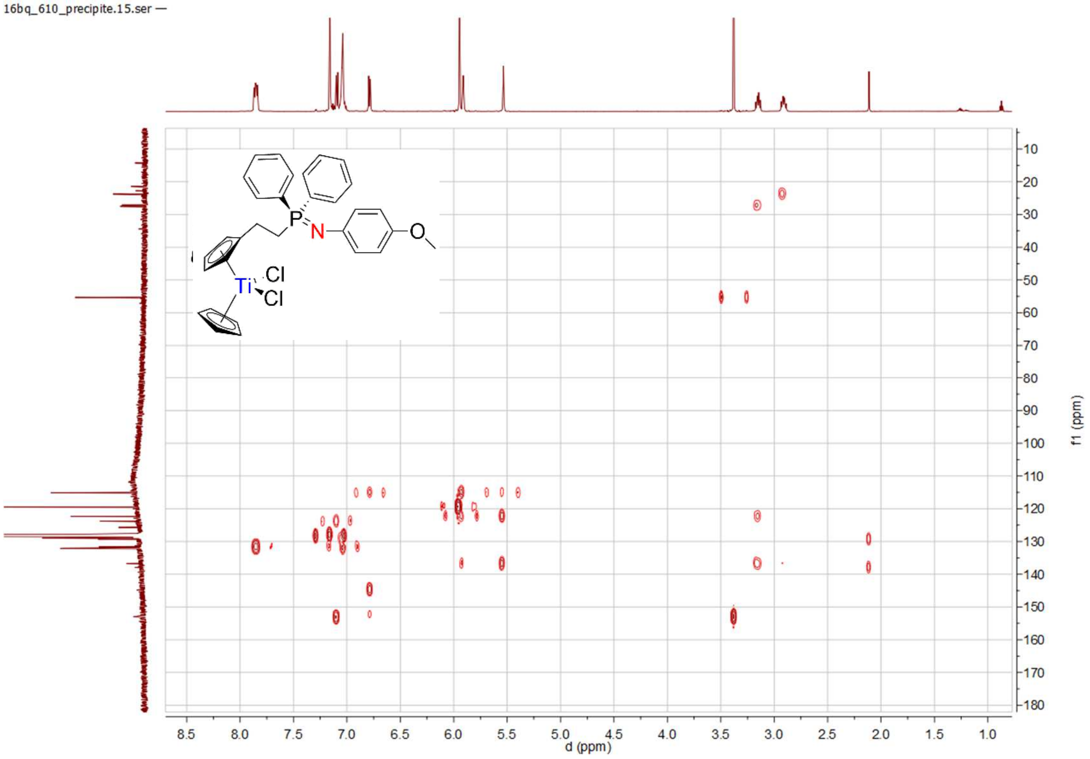
Spectrum 0-469: $^{13}C\{^{1}H\}$ NMR of 57 (125.75 MHz, 300 K, benzene-d_6)



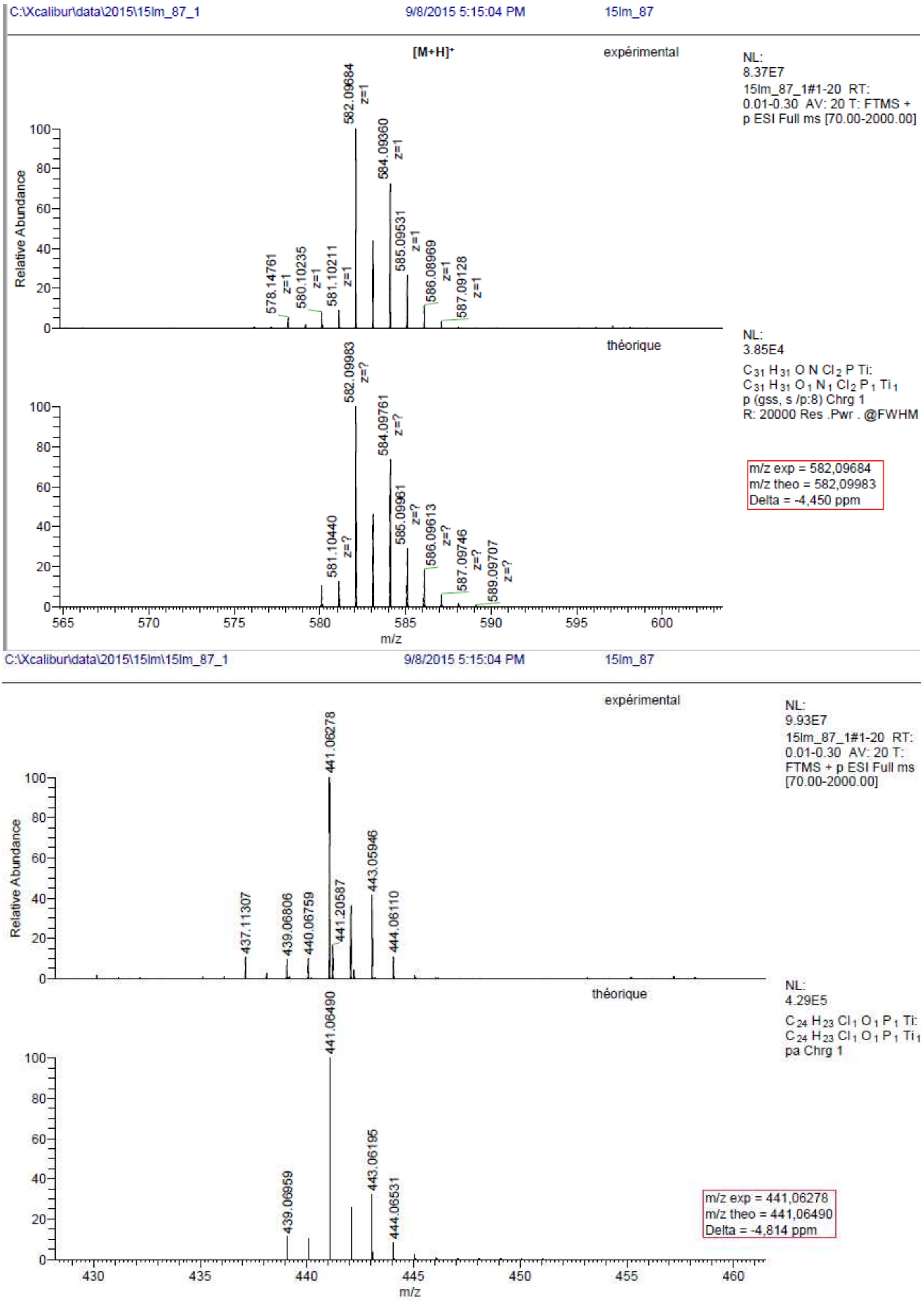
Spectrum 0-470: ^{1}H ^{1}H COSY of 57 (500.03 MHz, 300 K, 273 K, benzene-d_6)



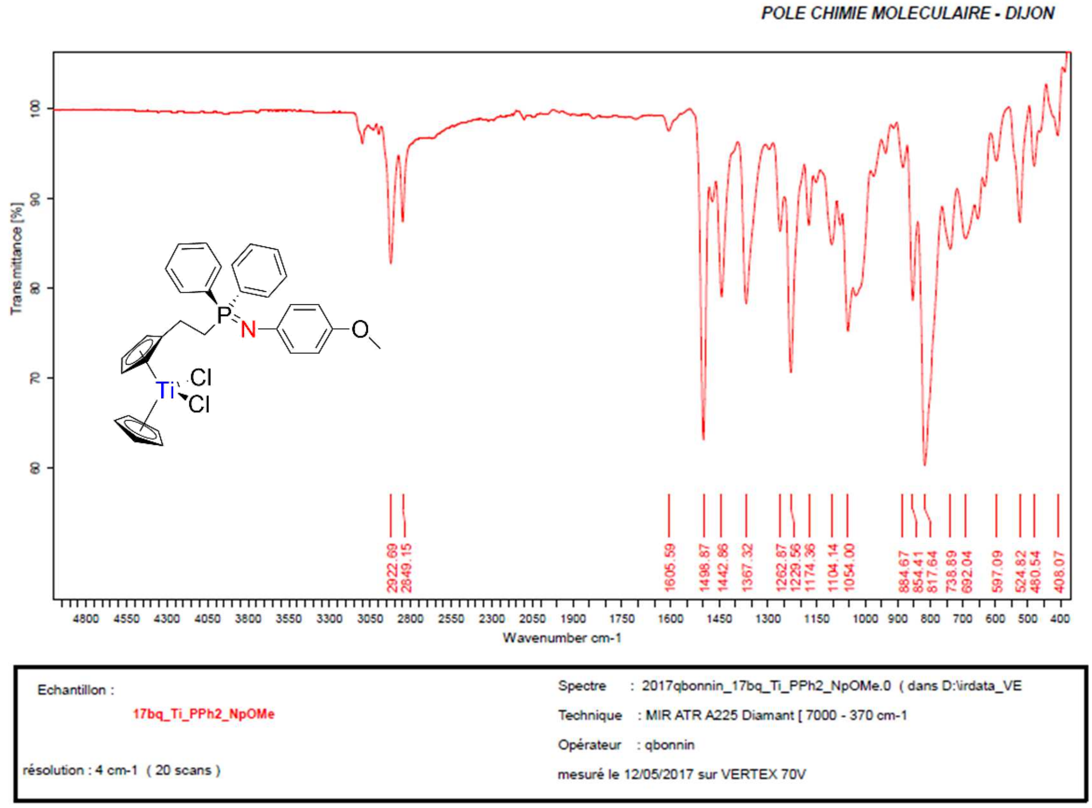
Spectrum 0-471: ^{1}H ^{13}C HMQC of 57 (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$)



Spectrum 0-472: ^{1}H ^{13}C HMBC of 57 (600.23 MHz / 150.86 MHz, 300 K, benzene-d$_6$)



Spectrum 0-473: HRMS of 57 (Positive mode ESI, dichloromethane)



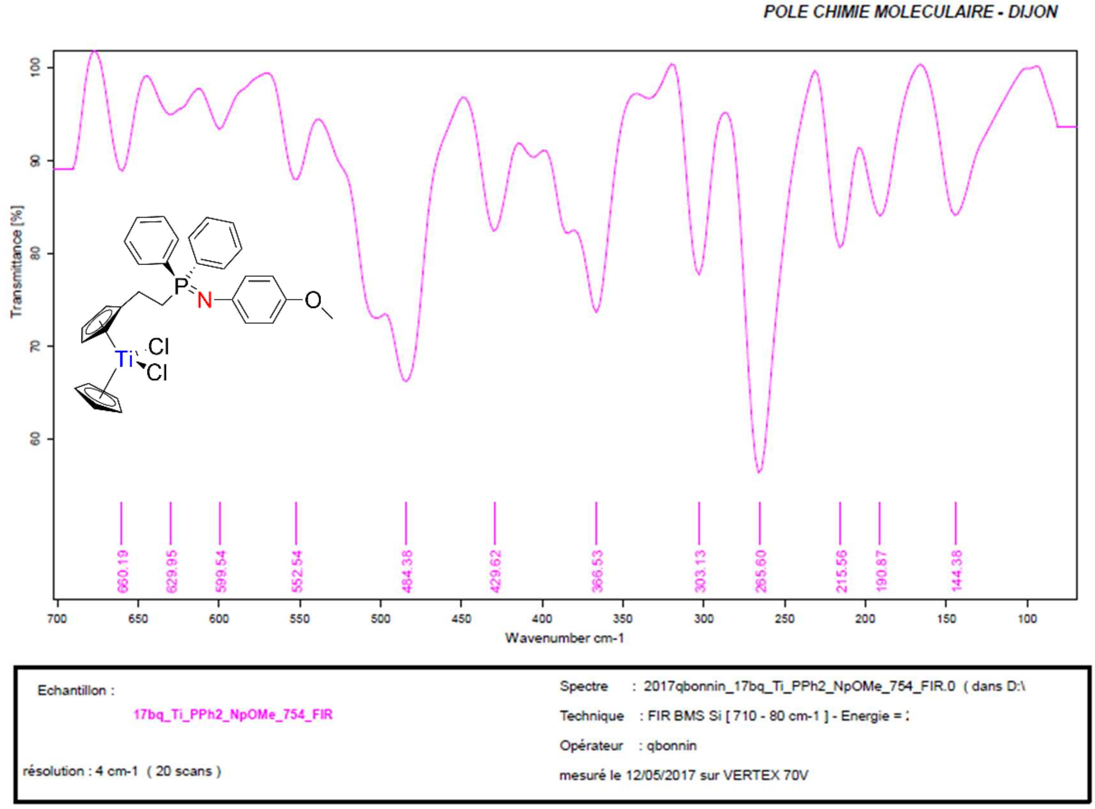
POLE CHIMIE MOLECULAIRE - DIJON

Echantillon :
17bq_Ti_PPh2_NpOMe

résolution : 4 cm-1 (20 scans)

Spectre : 2017qbonnin_17bq_Ti_PPh2_NpOMe.0 (dans D:\irdata_VE
Technique : MIR ATR A225 Diamant [7000 - 370 cm-1
Opérateur : qbonnin
mesuré le 12/05/2017 sur VERTEX 70V

Spectrum 0-474: MIR of 57



POLE CHIMIE MOLECULAIRE - DIJON

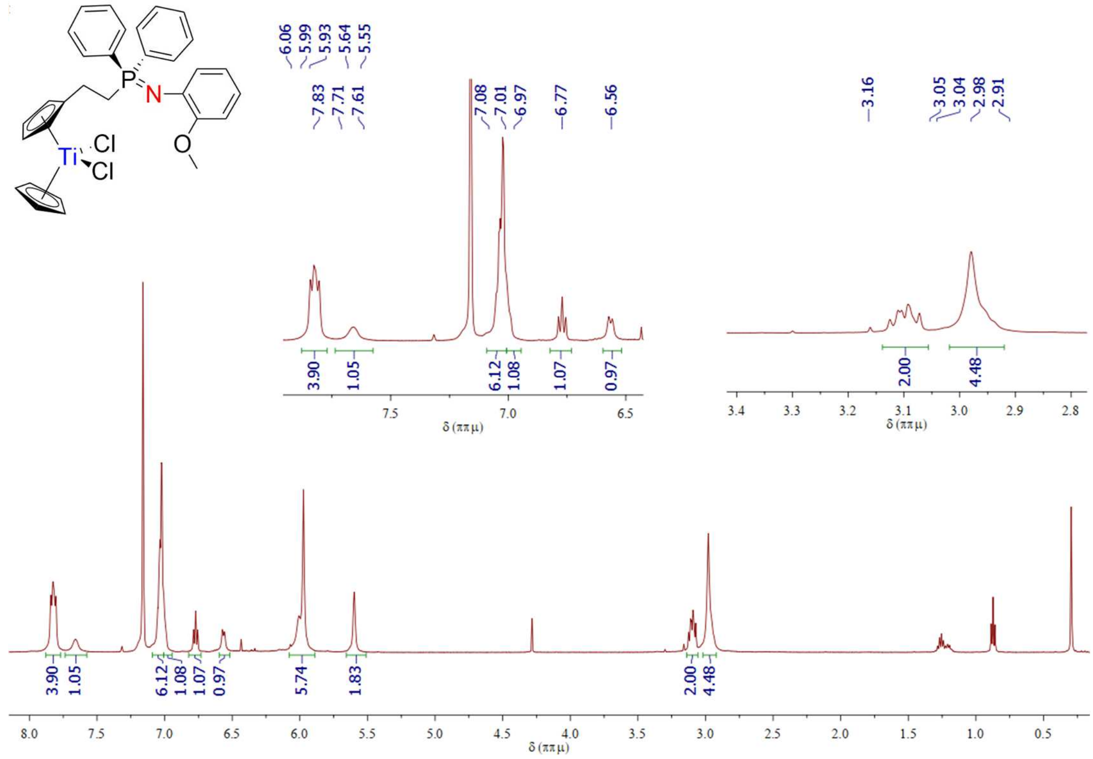
Echantillon :
17bq_Ti_PPh2_NpOMe_754_FIR

résolution : 4 cm-1 (20 scans)

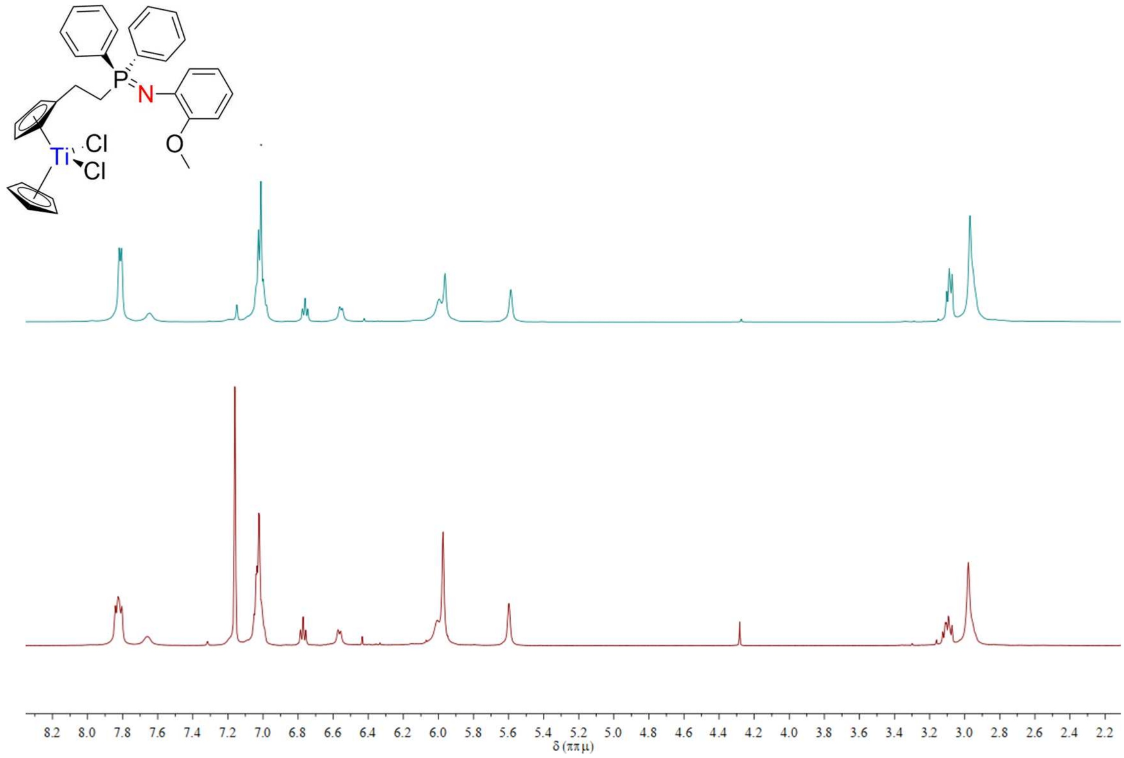
Spectre : 2017qbonnin_17bq_Ti_PPh2_NpOMe_754_FIR.0 (dans D:\
Technique : FIR BMS Si [710 - 80 cm-1] - Energie = :
Opérateur : qbonnin
mesuré le 12/05/2017 sur VERTEX 70V

Spectrum 0-475: FIR of 57

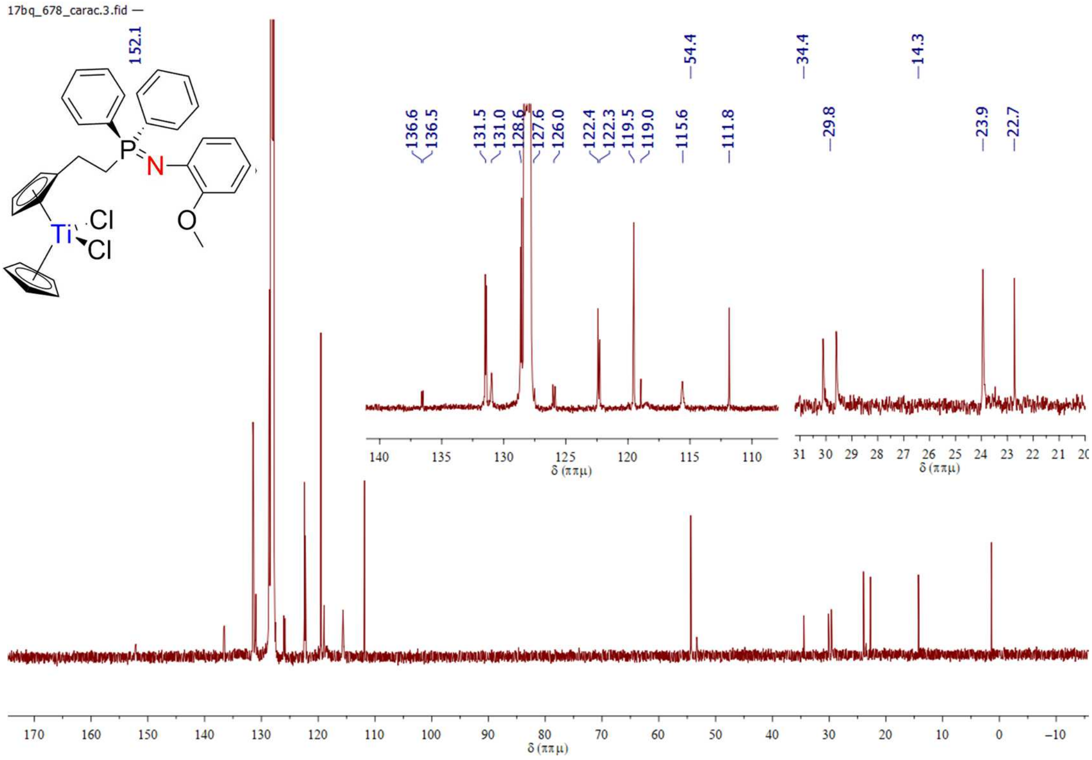
31. Compound **58**:



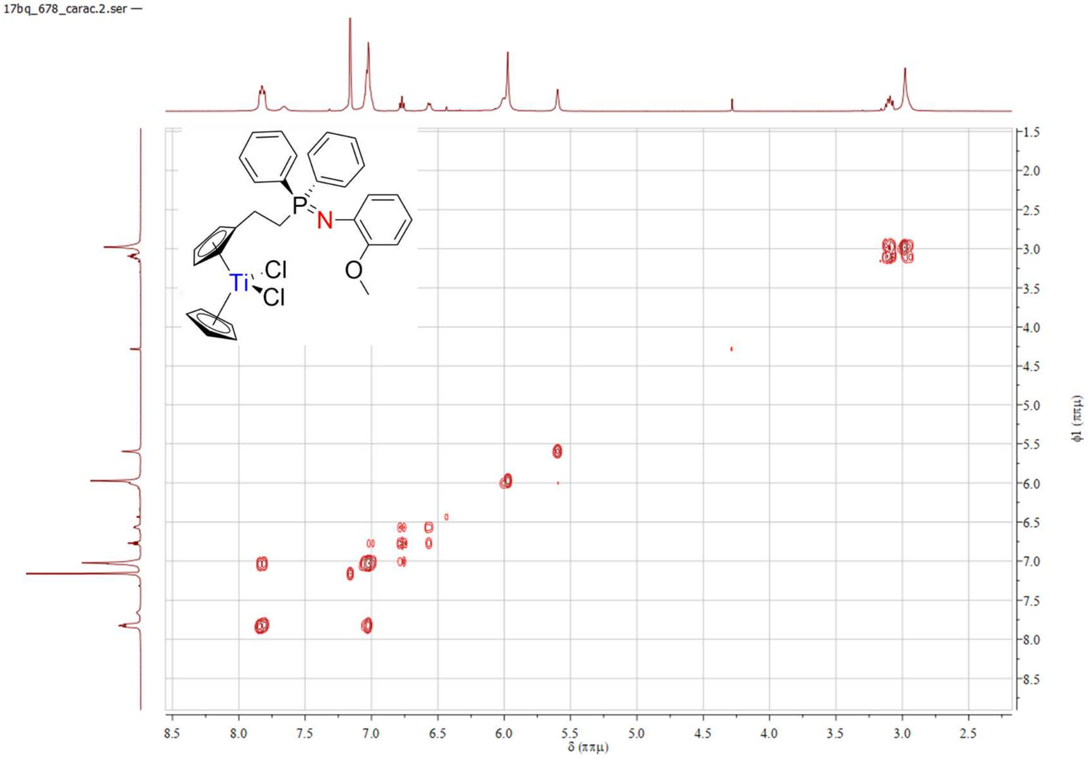
Spectrum 0-476: ^{1}H NMR of 58 (500.03 MHz, 300 K, benzene-d_6)



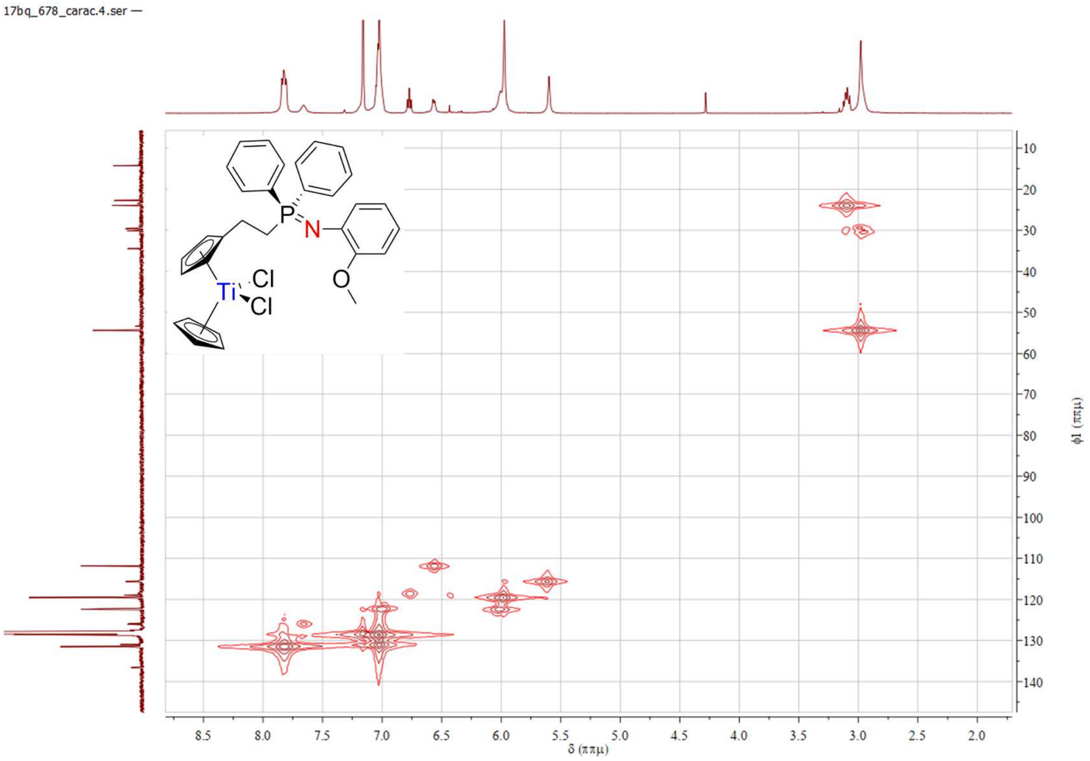
Spectrum 0-477: ^{1}H{^{31}P} NMR (top) superposed with ^{1}H NMR (bottom) of 58 (500.03 MHz, 300 K, benzene-d_6)



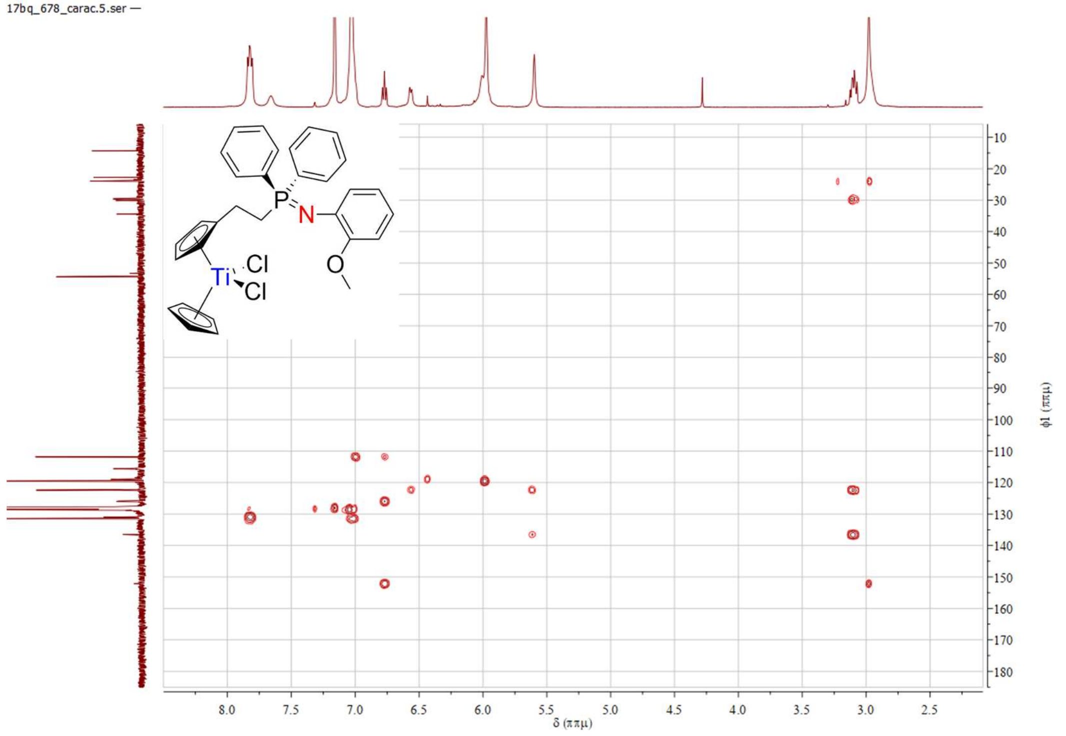
Spectrum 0-478: ^{13}C{^{1}H} NMR of 58 (125.75 MHz, 300 K, benzene-d$_6$)



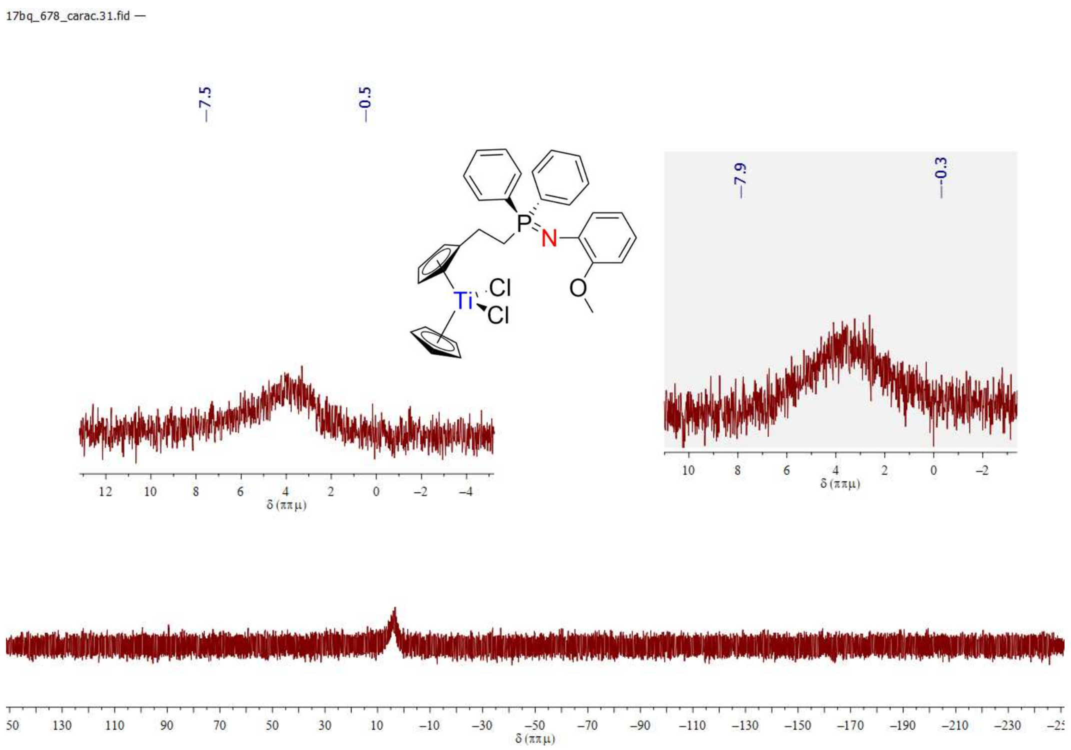
Spectrum 0-479: ^{1}H ^{1}H COSY of 58 (500.03 MHz, 300 K, 273 K, benzene-d$_6$)



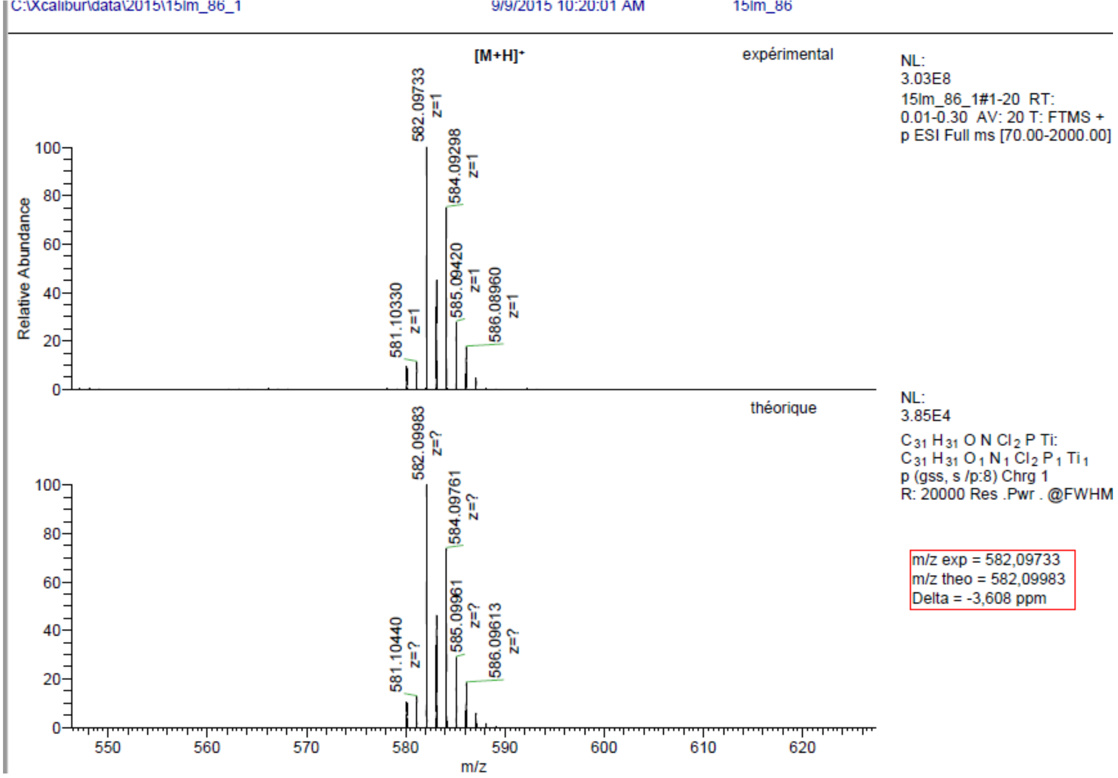
Spectrum 0-480: ^{1}H ^{13}C HMQC of 58 (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6)



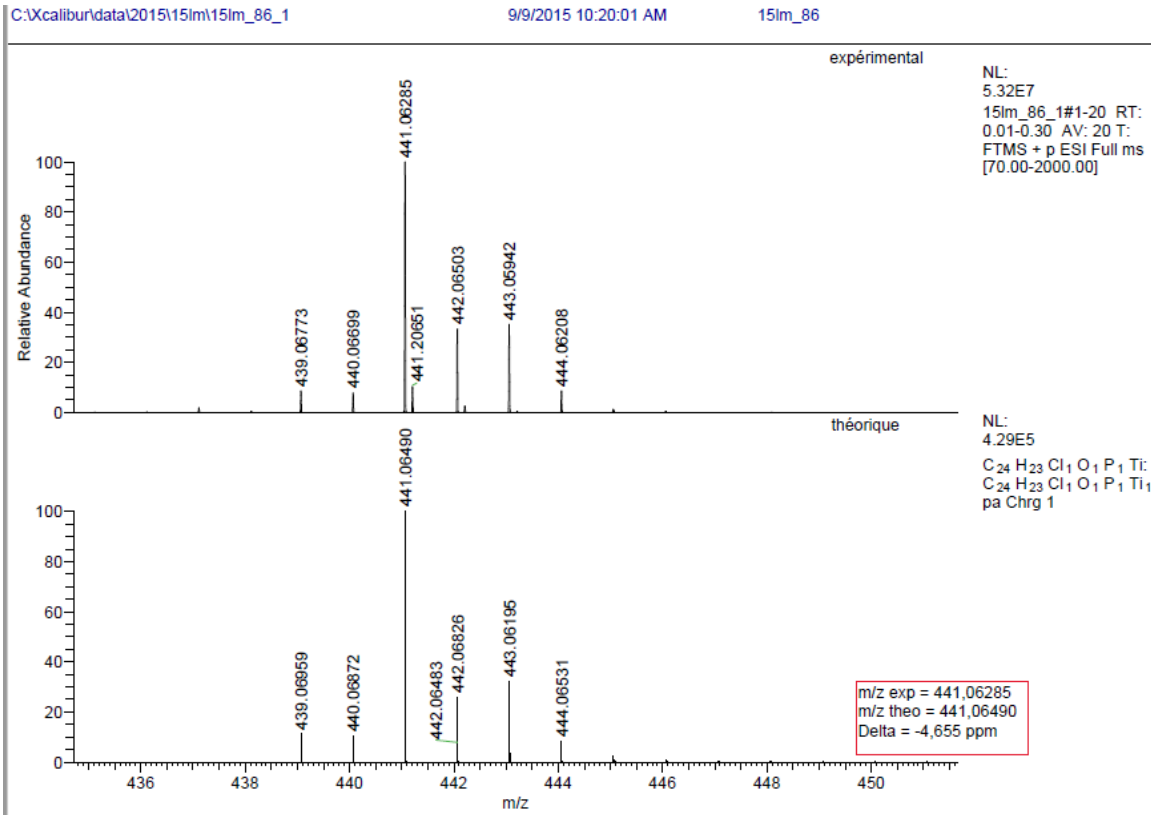
Spectrum 0-481: ^{1}H ^{13}C HMBC of 58 (600.23 MHz / 150.86 MHz, 300 K, benzene-d_6)



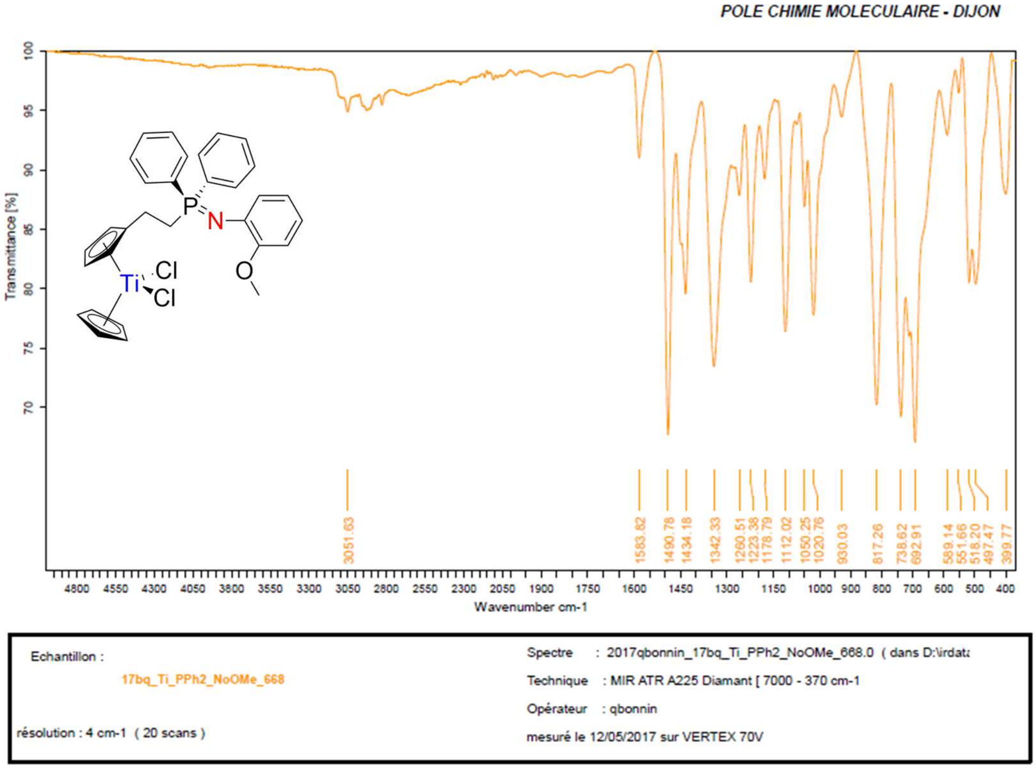
Spectrum 0-482: $^{31}P\{^{1}H\}$ and ^{31}P (opacified) NMR of 58 (202.46 MHz, 300 K, benzene-d_6)



Spectrum 0-483: HRMS of 58 (Positive mode ESI, dichloromethane)



Spectrum 0-484: HRMS of 58 (Positive mode ESI, dichloromethane)



Echantillon :

17bq_Ti_PPh2_NoOMe_668

résolution : 4 cm-1 (20 scans)

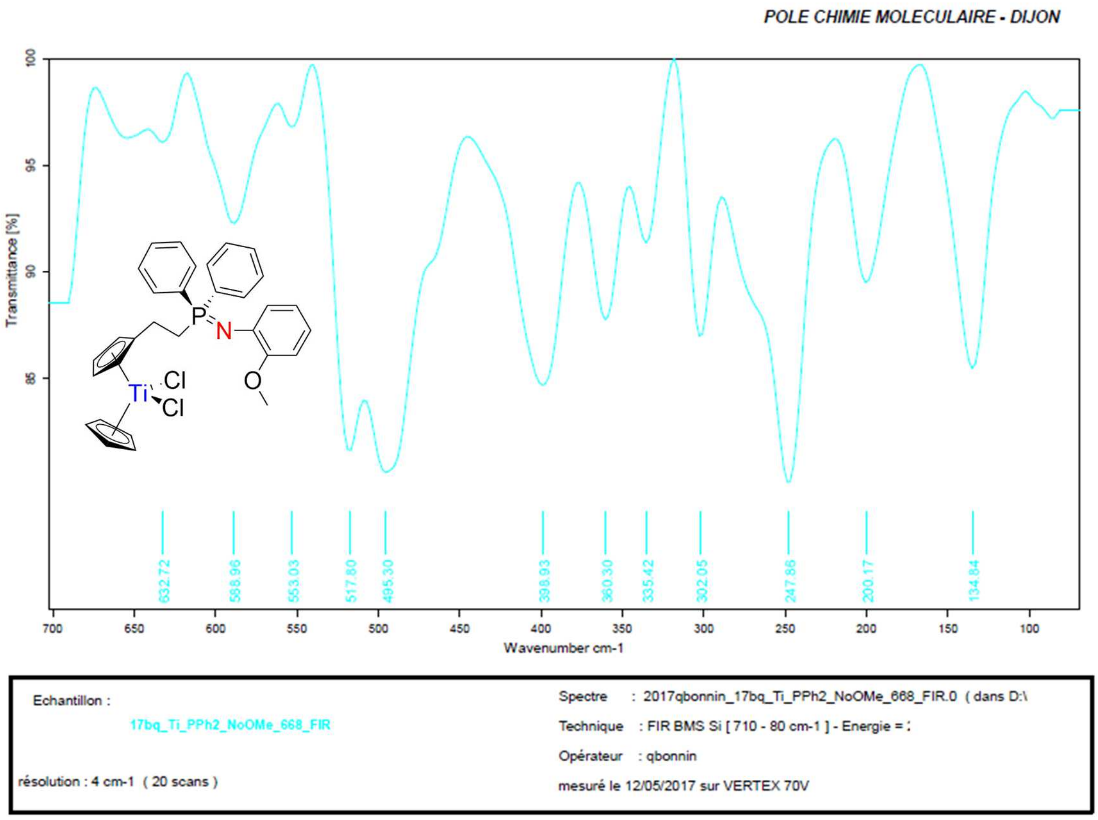
Spectre : 2017qbonnin_17bq_Ti_PPh2_NoOMe_668.0 (dans D:\irdat

Technique : MIR ATR A225 Diamant [7000 - 370 cm-1

Opérateur : qbonnin

mesuré le 12/05/2017 sur VERTEX 70V

Spectrum 0-485: MIR of 58

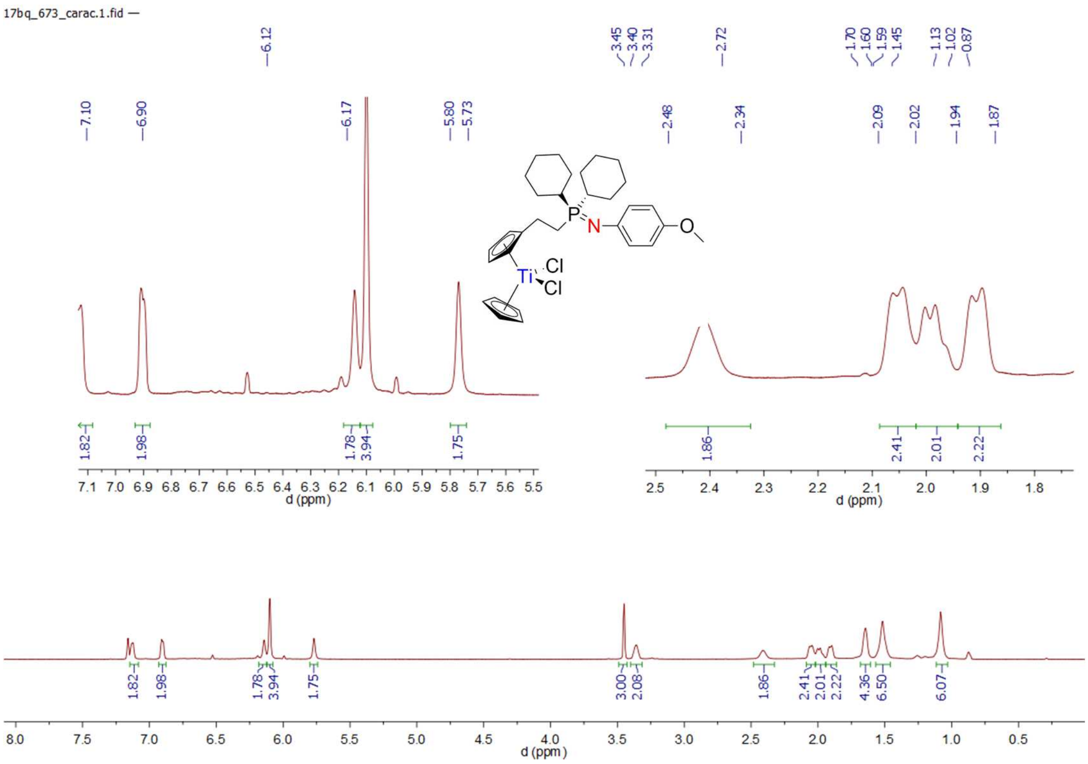


Echantillon :
17bq_Ti_PPh2_NoOMe_668_FIR
résolution : 4 cm-1 (20 scans)

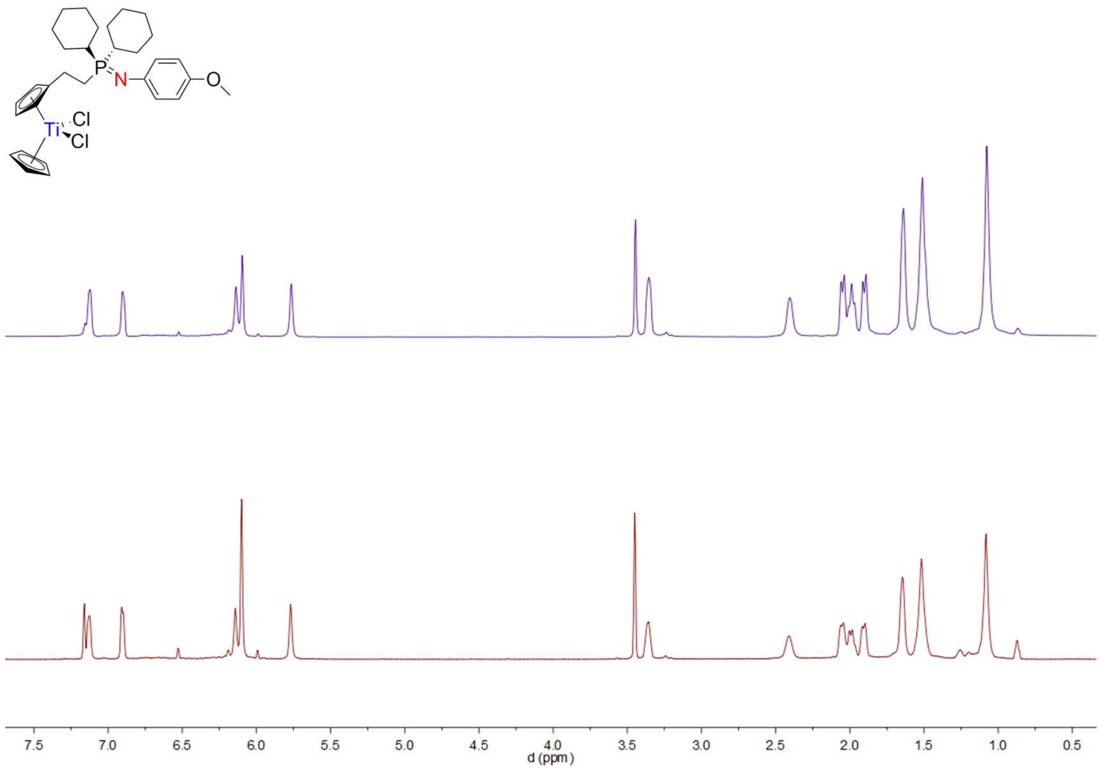
Spectre : 2017qbonnin_17bq_Ti_PPh2_NoOMe_668_FIR.0 (dans D:\
Technique : FIR BMS Si [710 - 80 cm-1] - Energie = :
Opérateur : qbonnin
mesuré le 12/05/2017 sur VERTEX 70V

Spectrum 0-486: FIR of 58

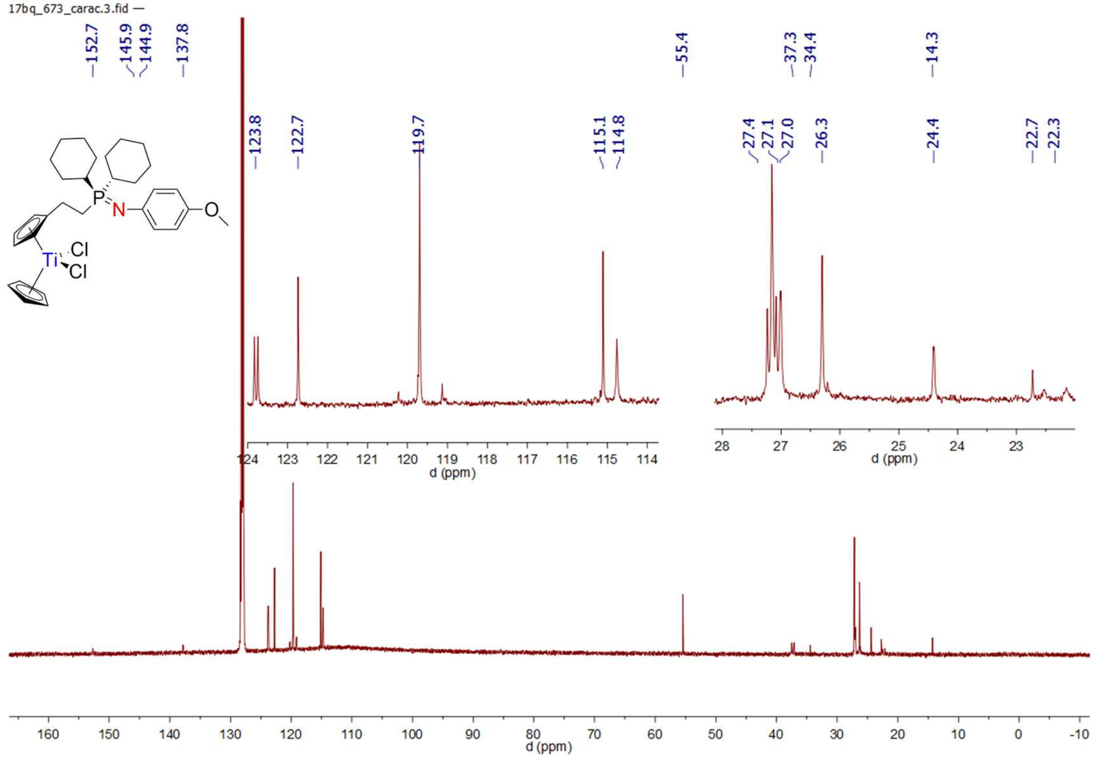
32. Compound **59:**



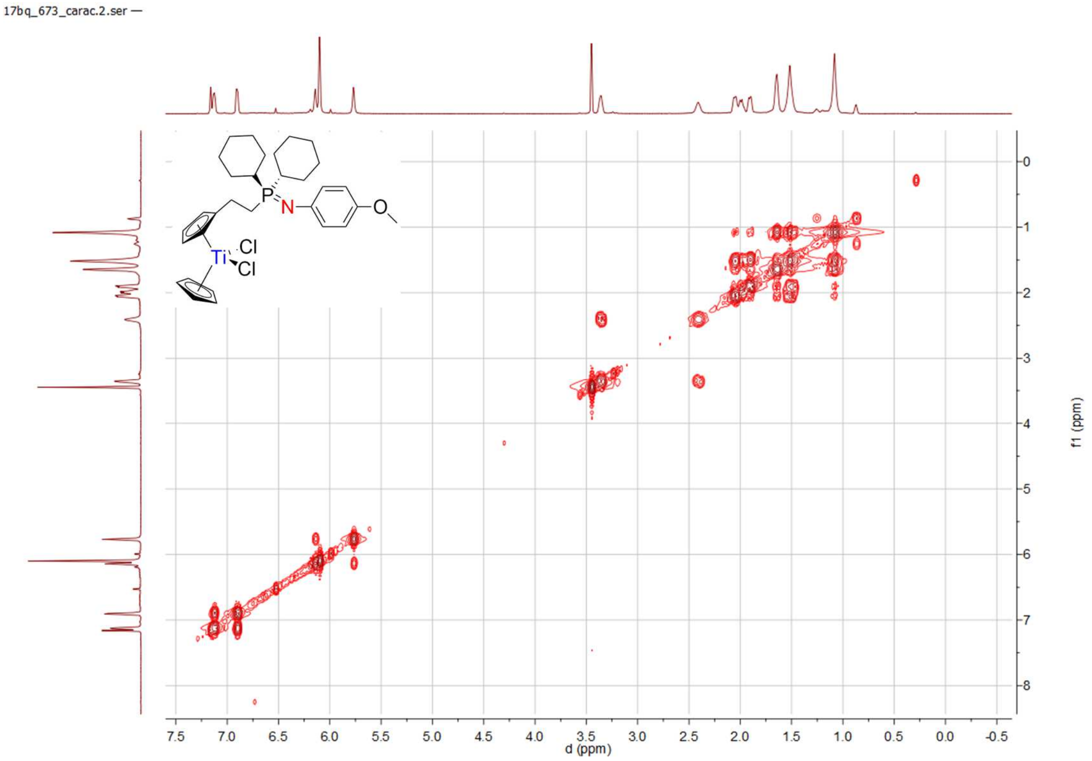
Spectrum 0-487: ^{1}H NMR of 59 (500.03 MHz, 300 K, benzene-d$_6$)



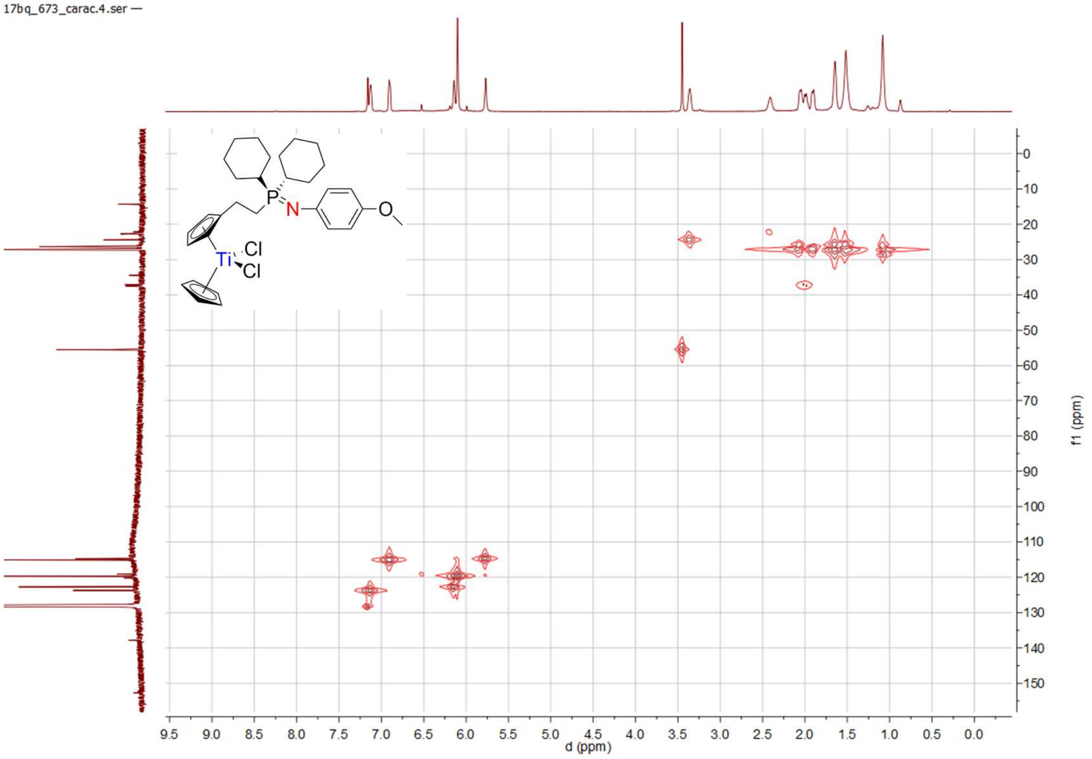
Spectrum 0-488: $^1H\{^{31}P\}$ NMR (top) correlated with ^1H NMR (bottom) of 59 (500.03 MHz, 300 K, benzene-d_6)



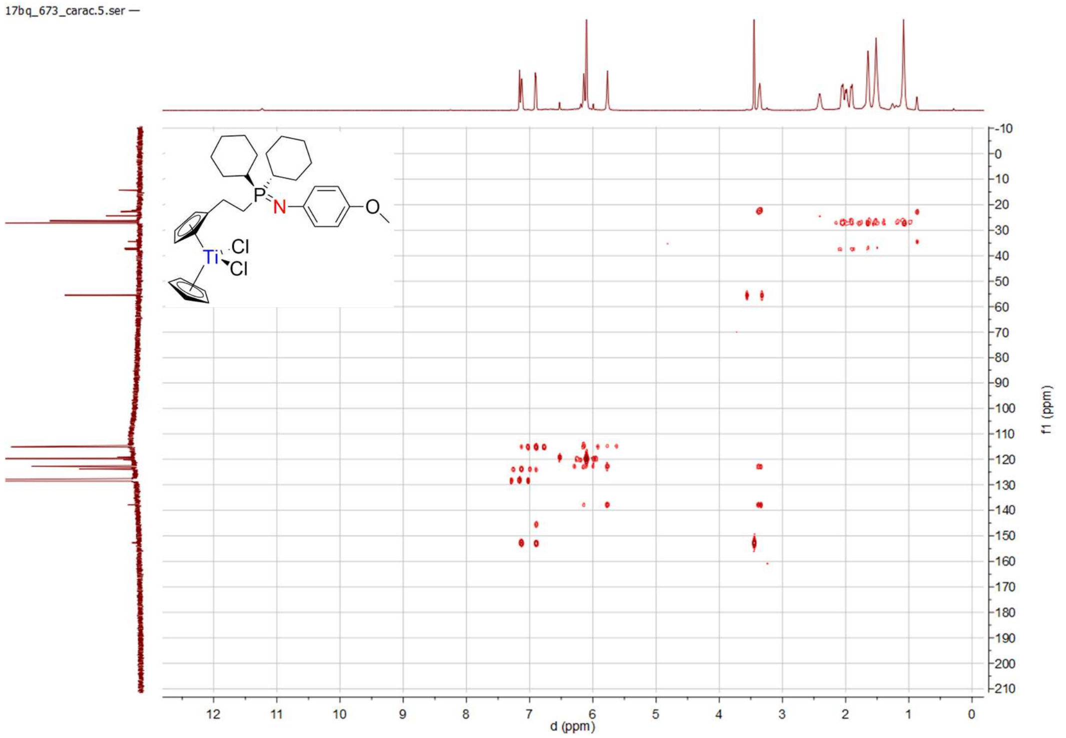
Spectrum 0-489: $^{13}C\{^1H\}$ NMR of 59 (125.75 MHz, 300 K, benzene-d6)



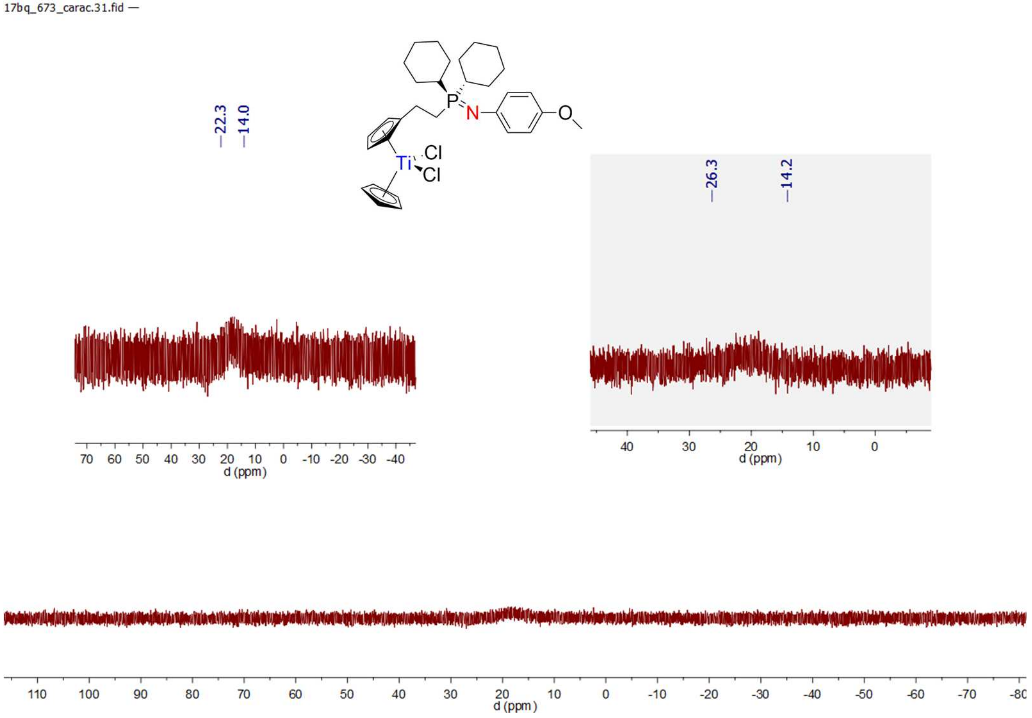
Spectrum 0-490: ^{1}H ^{1}H COSY of 59 (500.03 MHz, 300 K, 273 K, benzene-d$_6$)



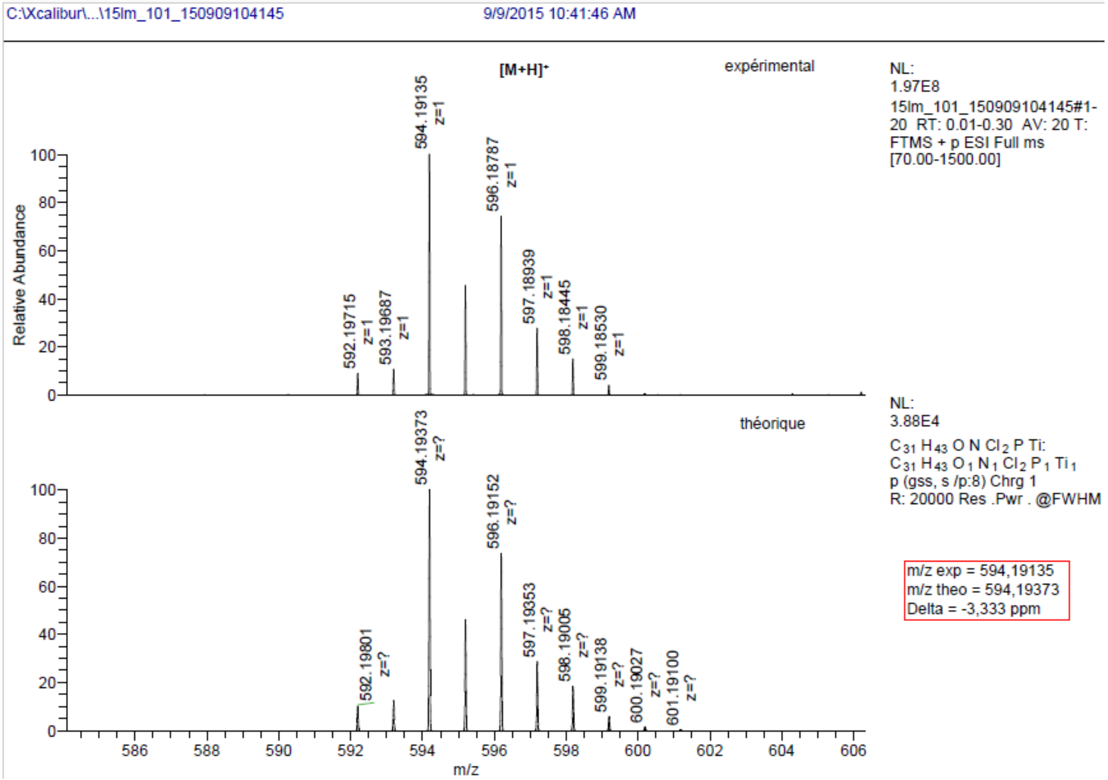
Spectrum 0-491: ^{1}H ^{13}C HMQC of 59 (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$)



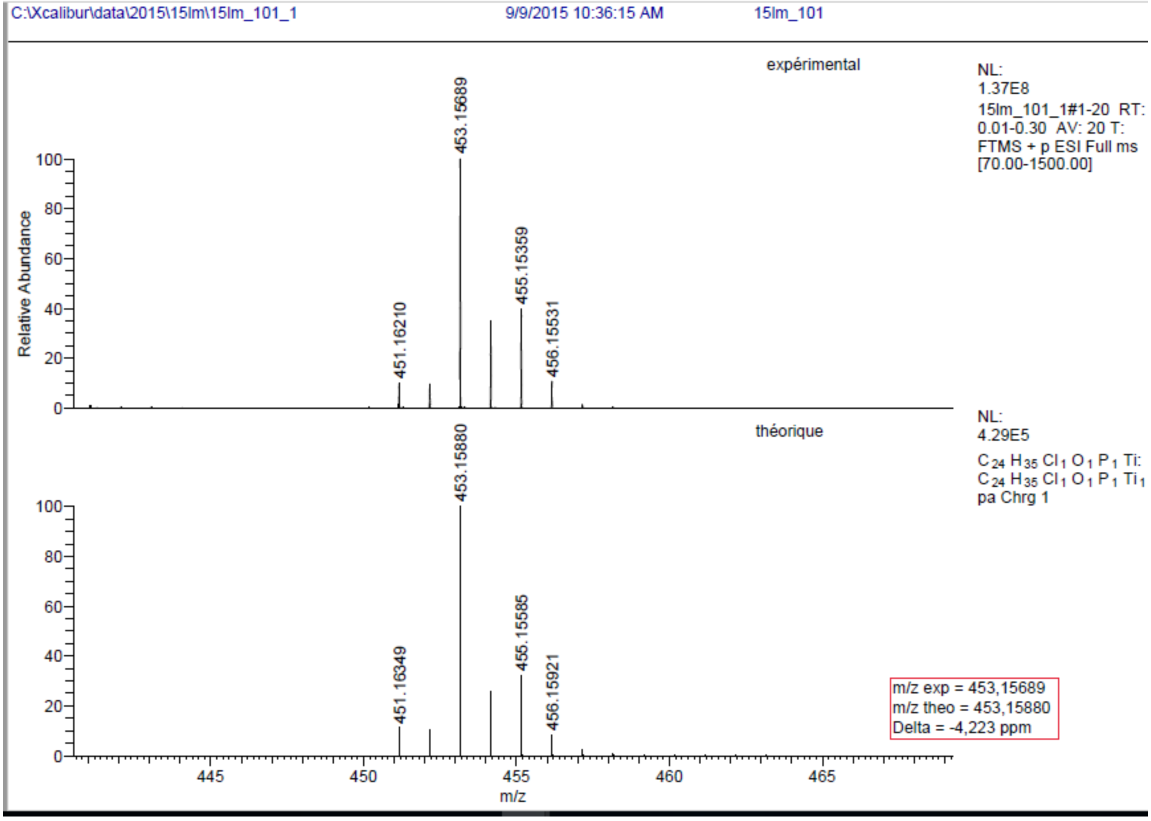
Spectrum 0-492: ^{1}H ^{13}C HMBC of 59 (600.23 MHz / 150.86 MHz, 300 K, benzene-d_6)



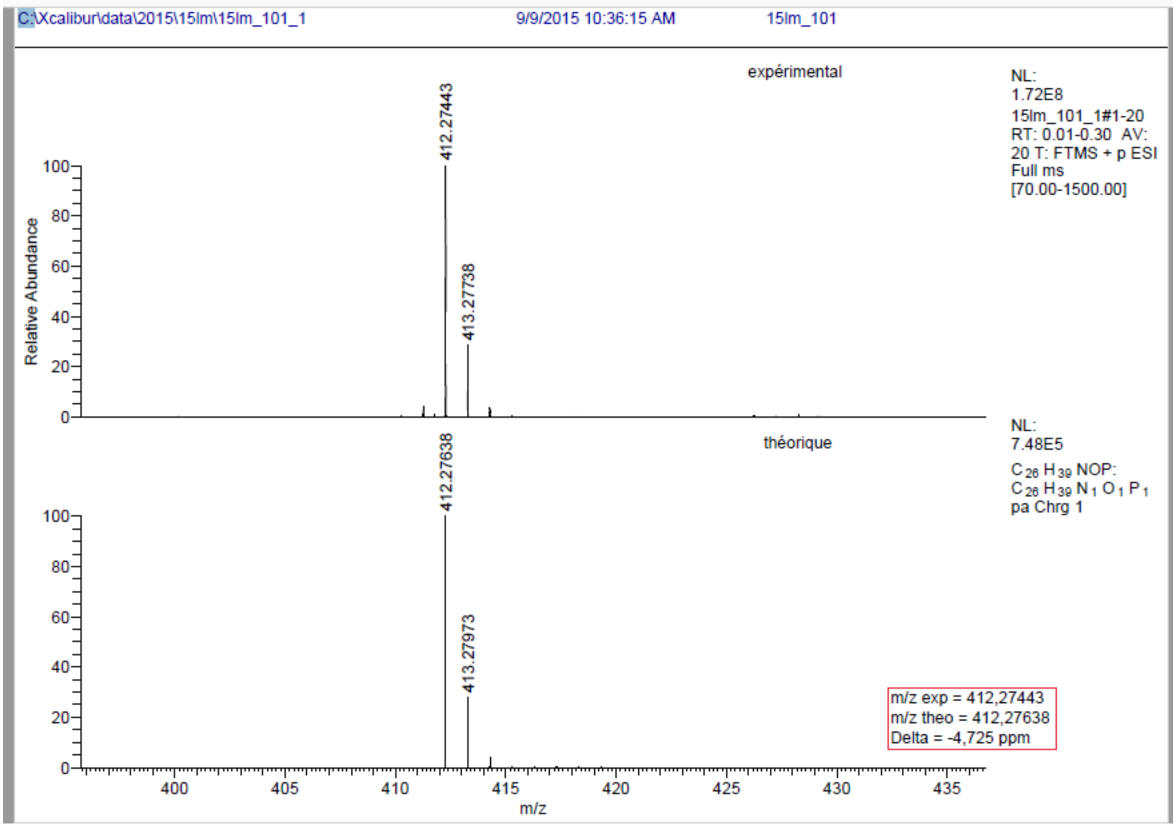
Spectrum 0-493: $^{31}P\{^{1}H\}$ and ^{31}P(opacified) NMR of 59 (202.46 MHz, 300 K, benzene-d_6)



Spectrum 0-494: HRMS of 59 (Positive mode ESI, dichloromethane)

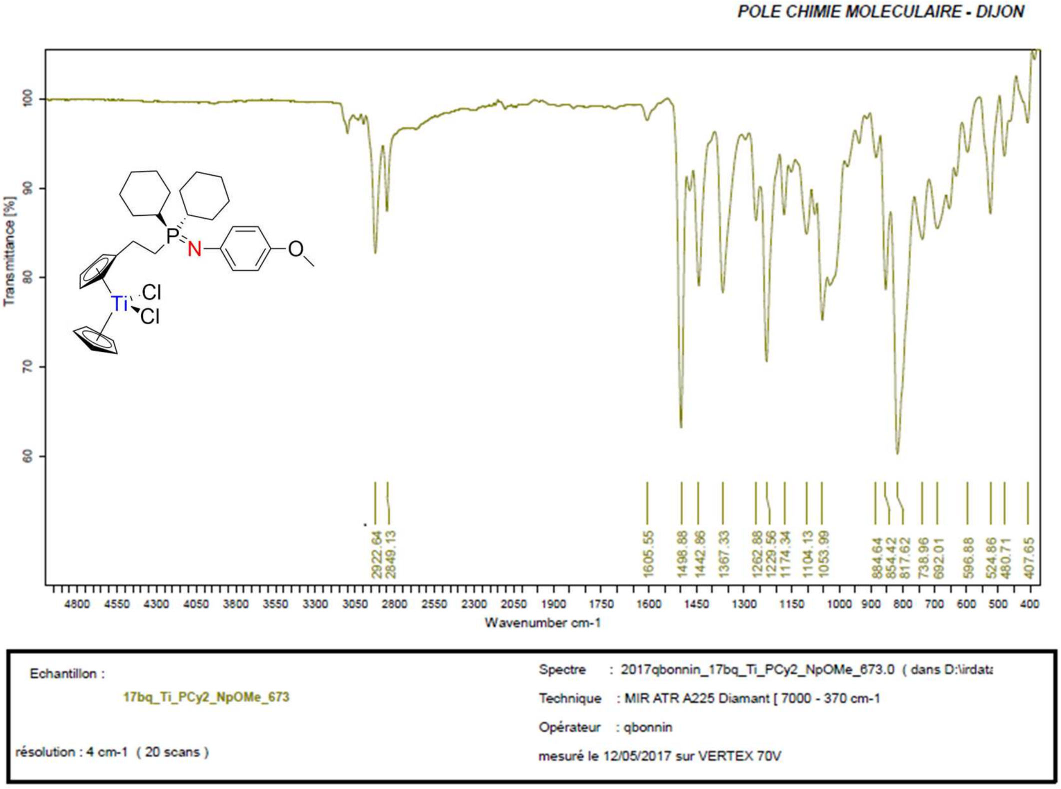


Spectrum 0-495: HRMS of 59 (Positive mode ESI, dichloromethane)



m/z exp = 412,27443
m/z theo = 412,27638
Delta = -4,725 ppm

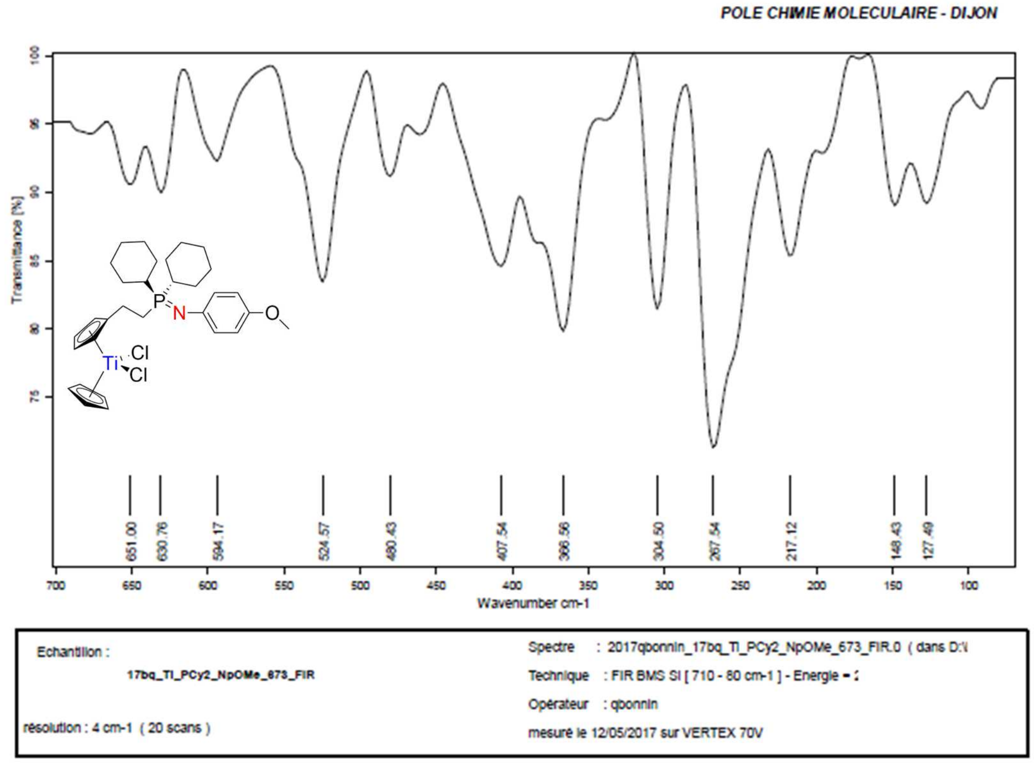
Spectrum 0-496: HRMS of 59 (Positive mode ESI, dichloromethane)



Echantillon :
17bq_Ti_PCy2_NpOMe_673
résolution : 4 cm-1 (20 scans)

Spectre : 2017qbonnin_17bq_Ti_PCy2_NpOMe_673.0 (dans D:\irdata
Technique : MIR ATR A225 Diamant [7000 - 370 cm-1
Opérateur : qbonnin
mesuré le 12/05/2017 sur VERTEX 70V

Spectrum 0-497: MIR of 59



Echantillon :

17bq_Ti_PCy2_NpOMe_673_FIR

résolution : 4 cm-1 (20 scans)

Spectre : 2017qbonnin_17bq_Ti_PCy2_NpOMe_673_FIR.0 (dans D:\

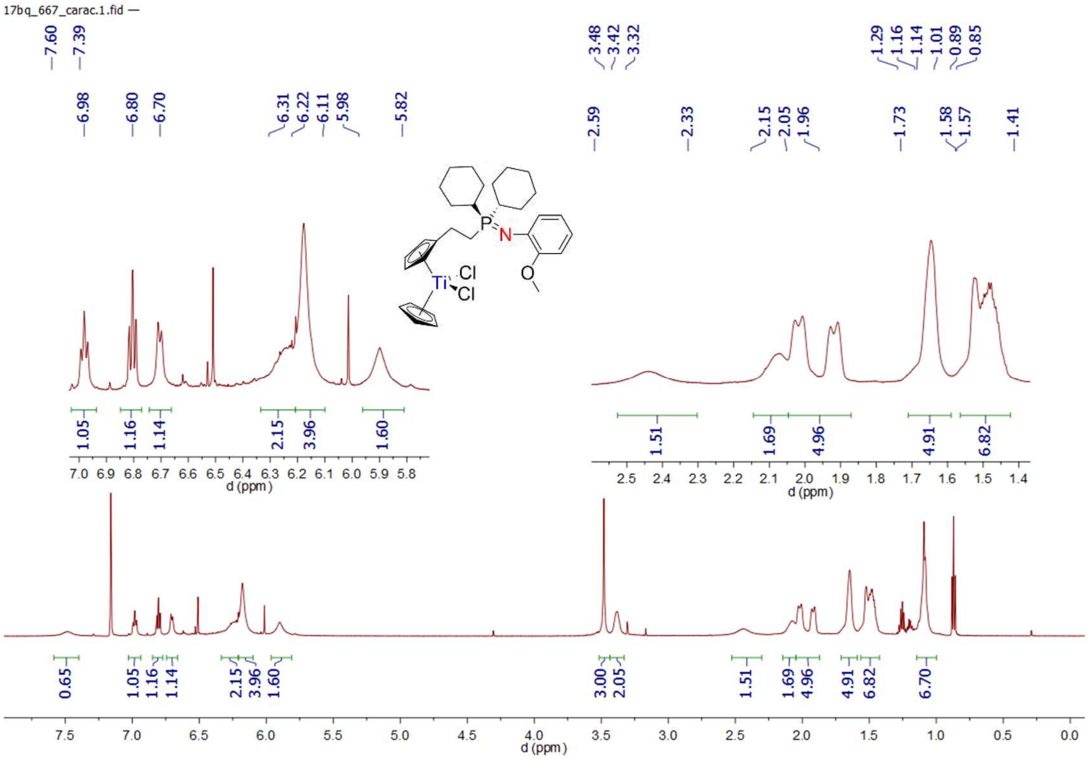
Technique : FIR BMS SI [710 - 80 cm-1] - Energie = 2

Opérateur : qbonnin

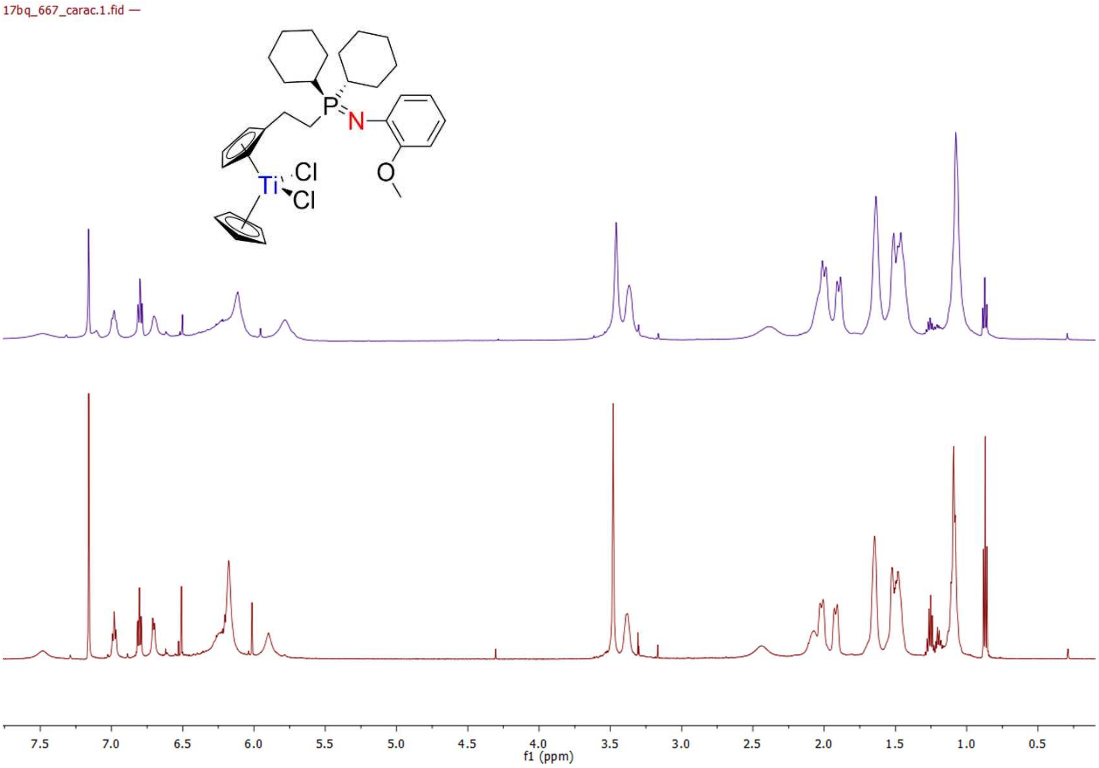
mesuré le 12/05/2017 sur VERTEX 70V

Spectrum 0-498: FIR of 59

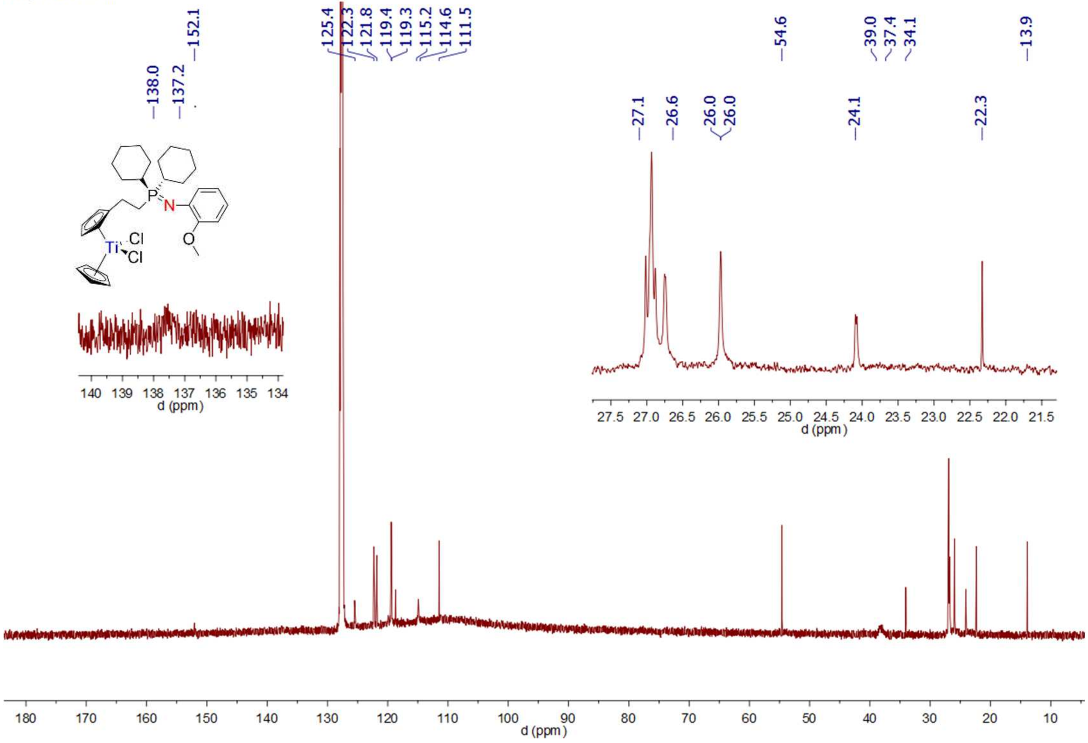
33. Compound **60**:



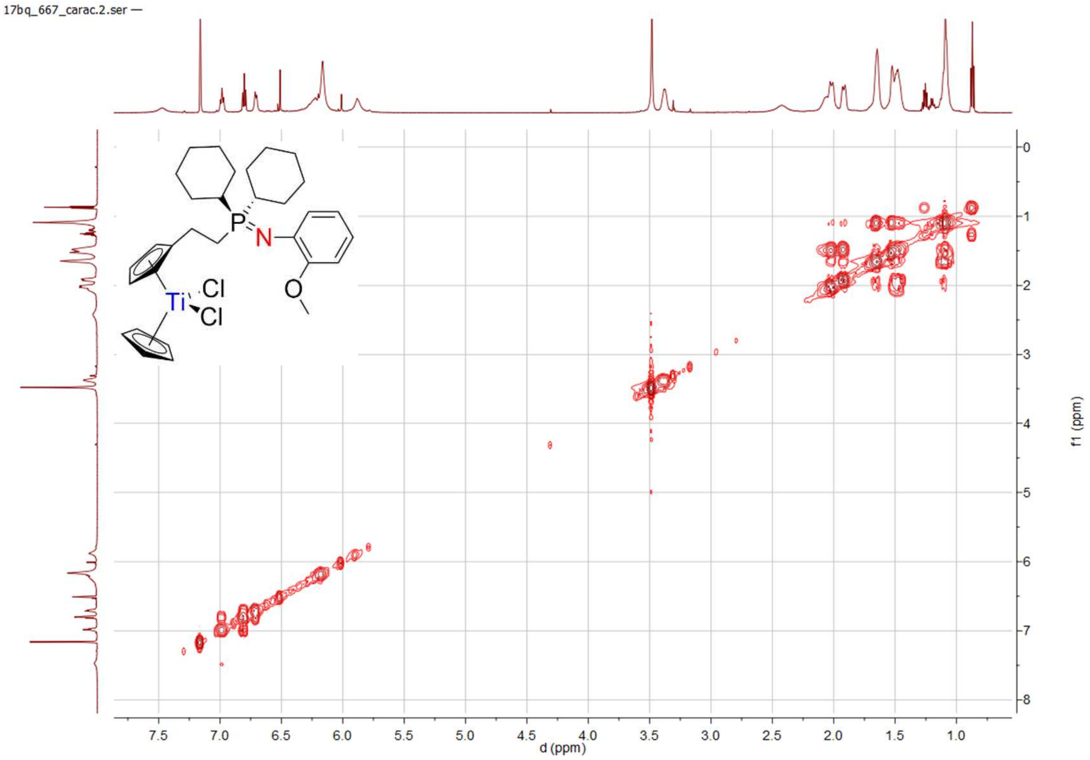
Spectrum 0-499: ^{1}H NMR of 60 (600.23 MHz, 300 K, benzene-d$_6$)



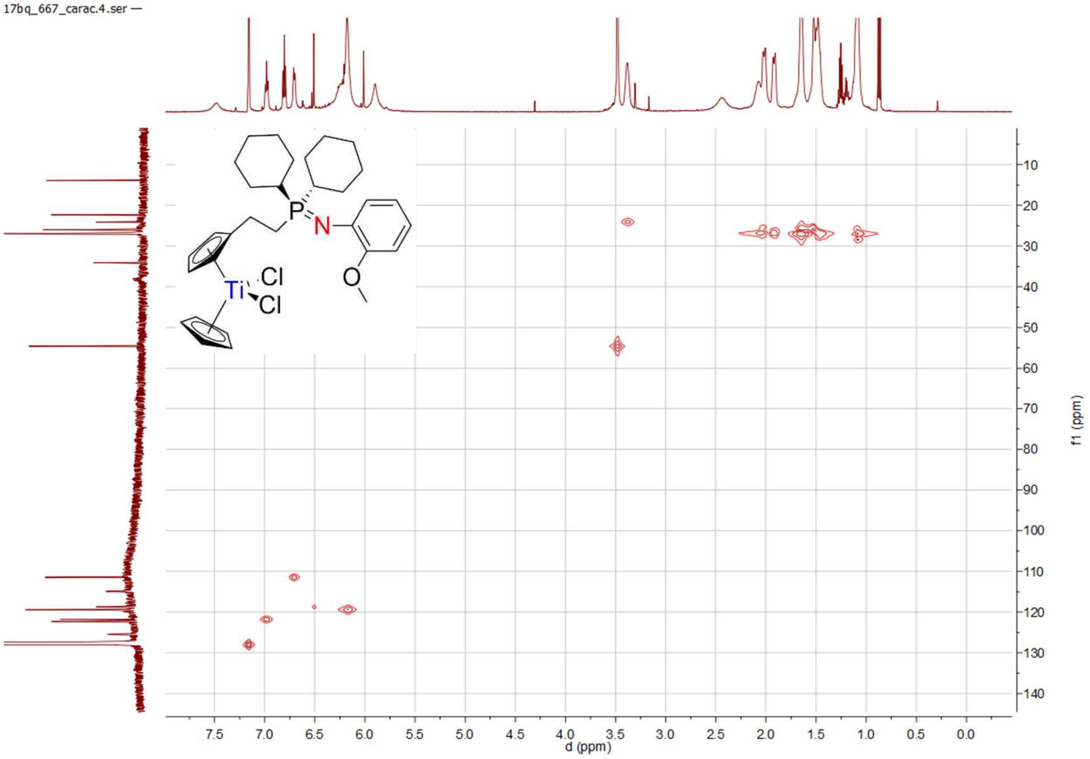
Spectrum 0-500: $^1H\{^{31}P\}$ NMR (top) correlated with ^1H NMR (bottom) of 60 (600.23 MHz, 300 K, benzene-d_6)



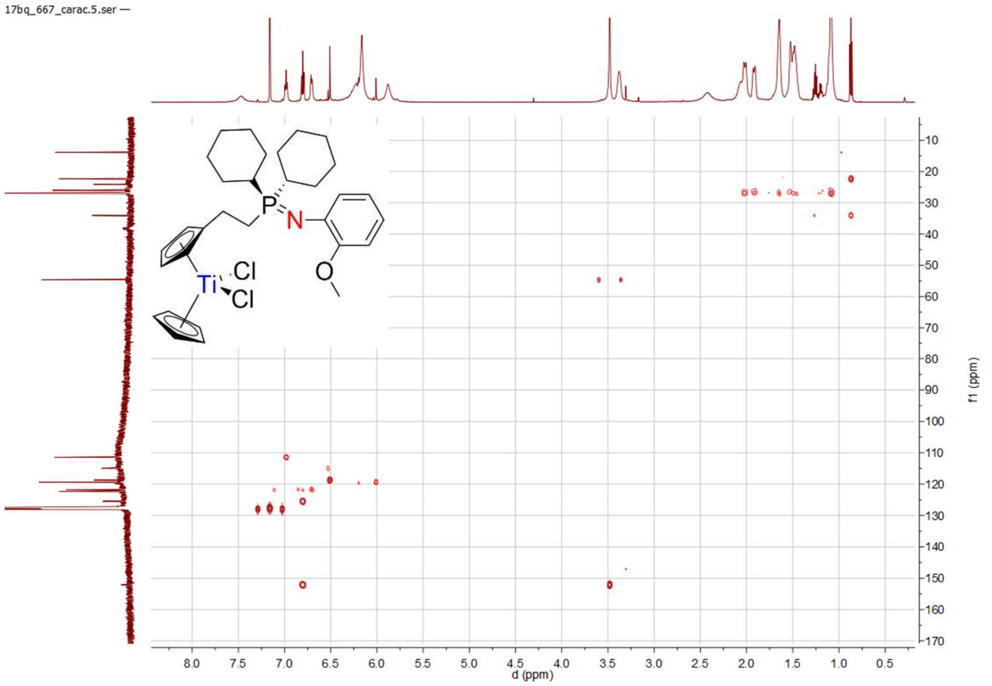
Spectrum 0-501: $^{13}C\{^1H\}$ NMR of 60 (150.94 MHz, 300 K, benzene-d_6)



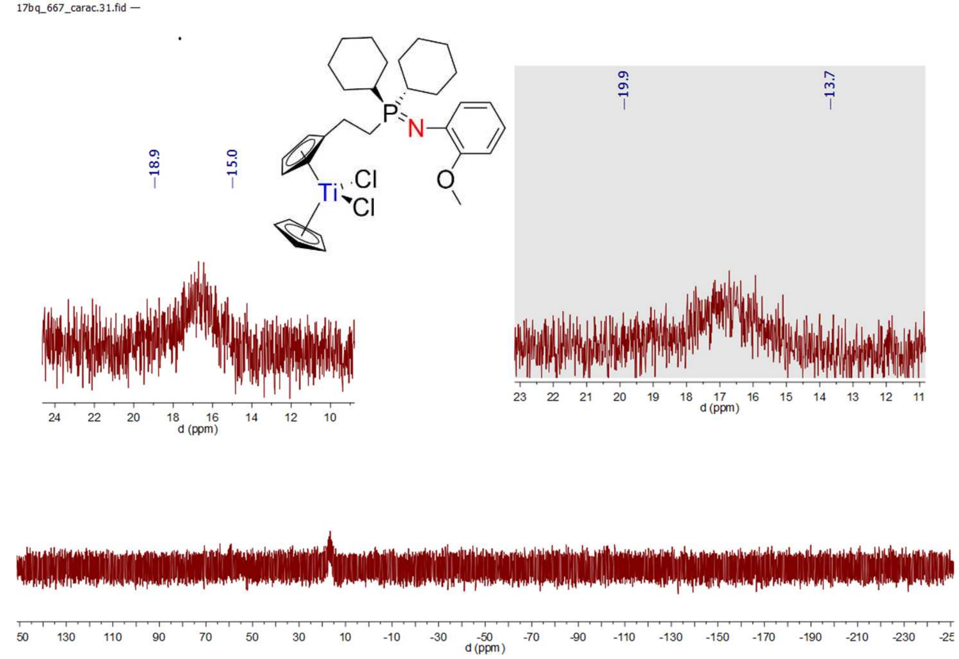
Spectrum 0-502: ^{1}H ^{1}H COSY of 60 (600.23 MHz, 300 K, 273 K, benzene-d_6)



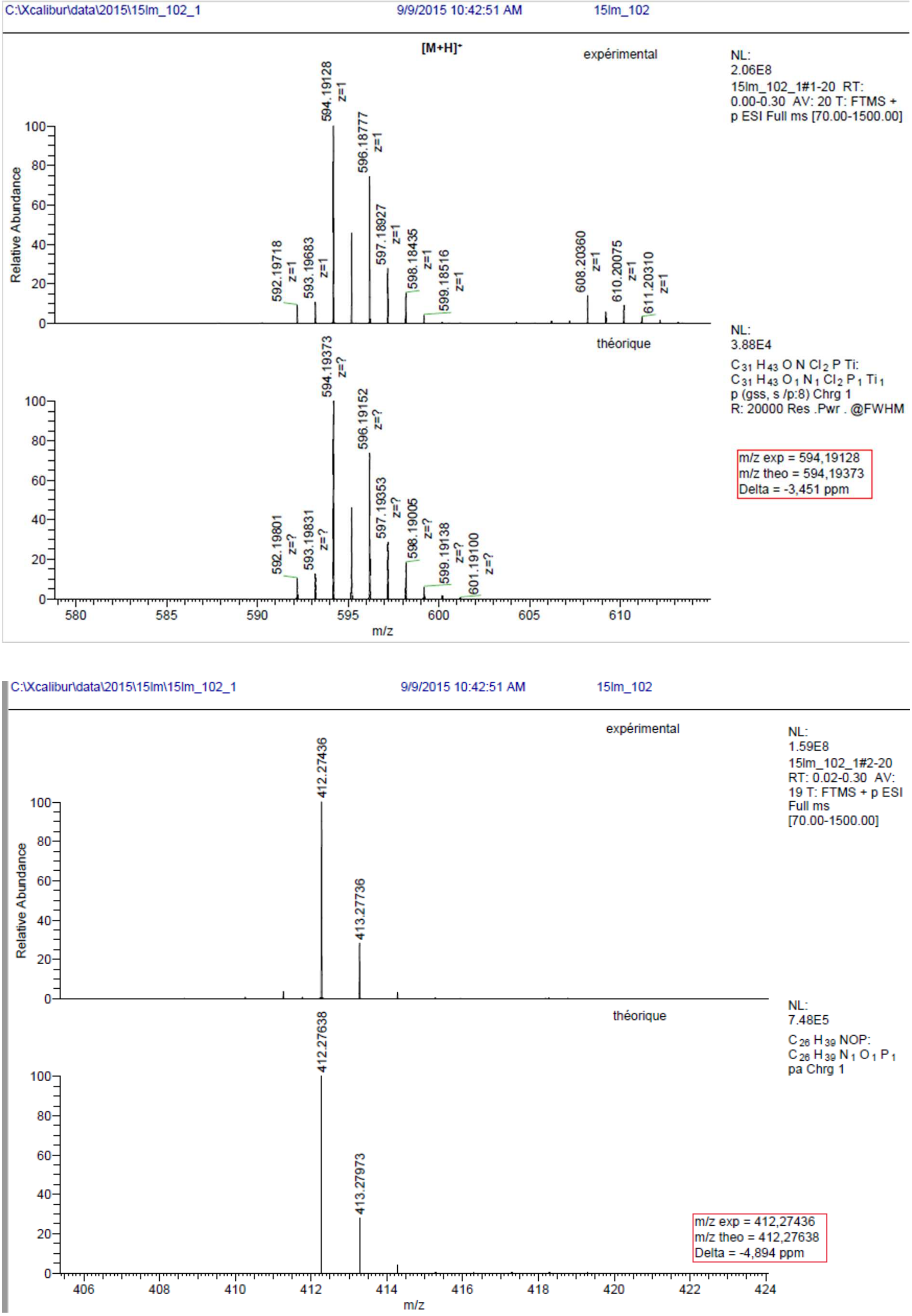
Spectrum 0-503: ^{1}H ^{13}C HMQC of 60 (600.23 MHz / 150.94 MHz, 300 K, benzene-d_6)



Spectrum 0-504: ^{1}H ^{13}C HMBC of 60 (600.23 MHz / 150.94 MHz, 300 K, benzene-d$_6$)



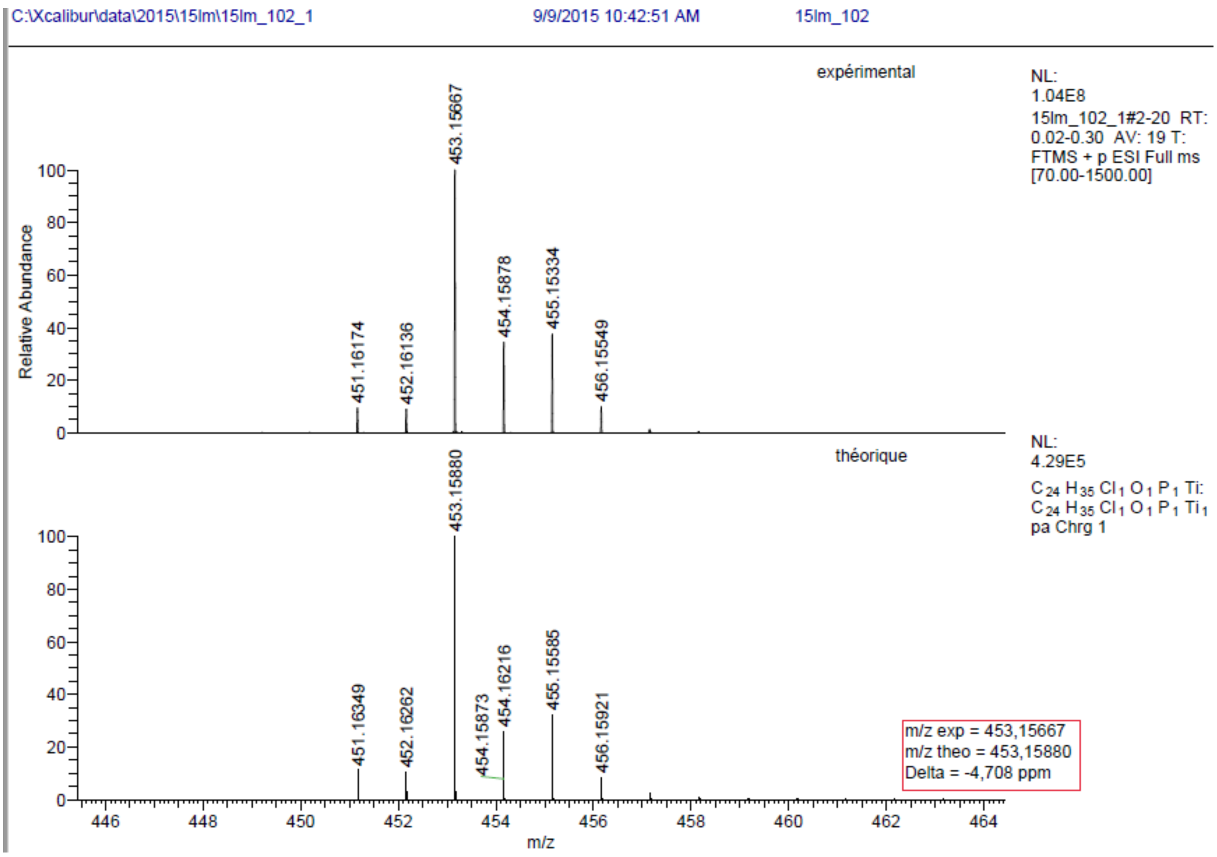
Spectrum 0-505: ^{31}P{^{1}H} and ^{31}P(opacified) NMR of 60 (202.41 MHz, 300 K, benzene-d$_6$)



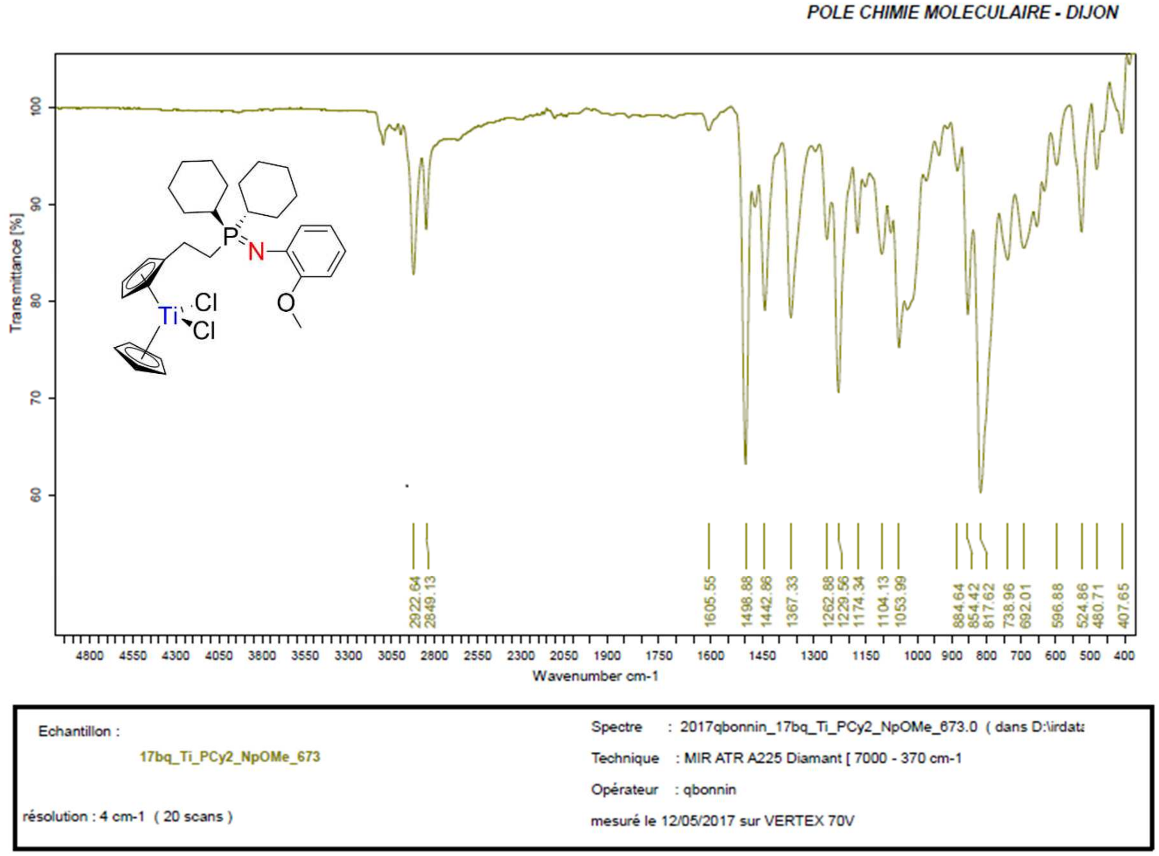
m/z exp = 594,19128
m/z theo = 594,19373
Delta = -3,451 ppm

m/z exp = 412,27436
m/z theo = 412,27638
Delta = -4,894 ppm

Spectrum 0-506: HRMS of 60 (Positive mode ESI, dichloromethane)



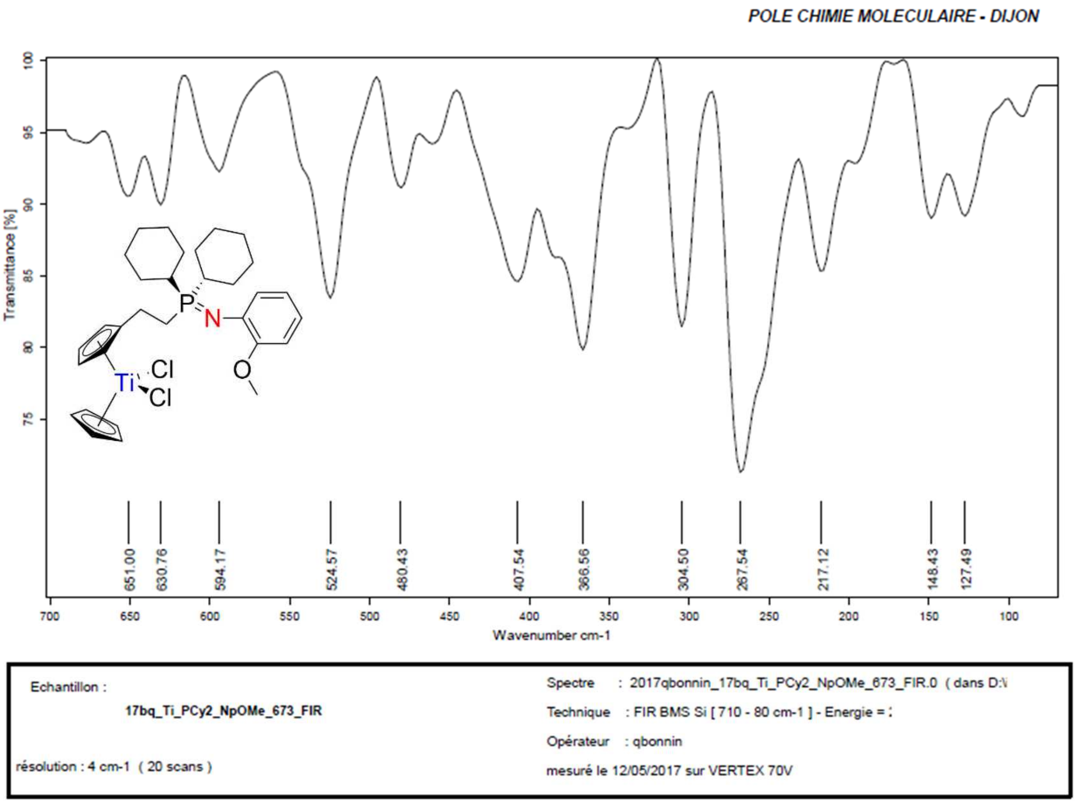
Spectrum 0-507: HRMS of 60 (Positive mode ESI, dichloromethane)



Echantillon :
17bq_Ti_PCy2_NpOMe_673
résolution : 4 cm-1 (20 scans)

Spectre : 2017qbonnin_17bq_Ti_PCy2_NpOMe_673.0 (dans D:\irdat
Technique : MIR ATR A225 Diamant [7000 - 370 cm-1
Opérateur : qbonnin
mesuré le 12/05/2017 sur VERTEX 70V

Spectrum 0-508: MIR of 60



Echantillon :
17bq_Ti_PCy2_NpOMe_673_FIR

résolution : 4 cm-1 (20 scans)

Spectre : 2017qbonnin_17bq_Ti_PCy2_NpOMe_673_FIR.0 (dans D:\

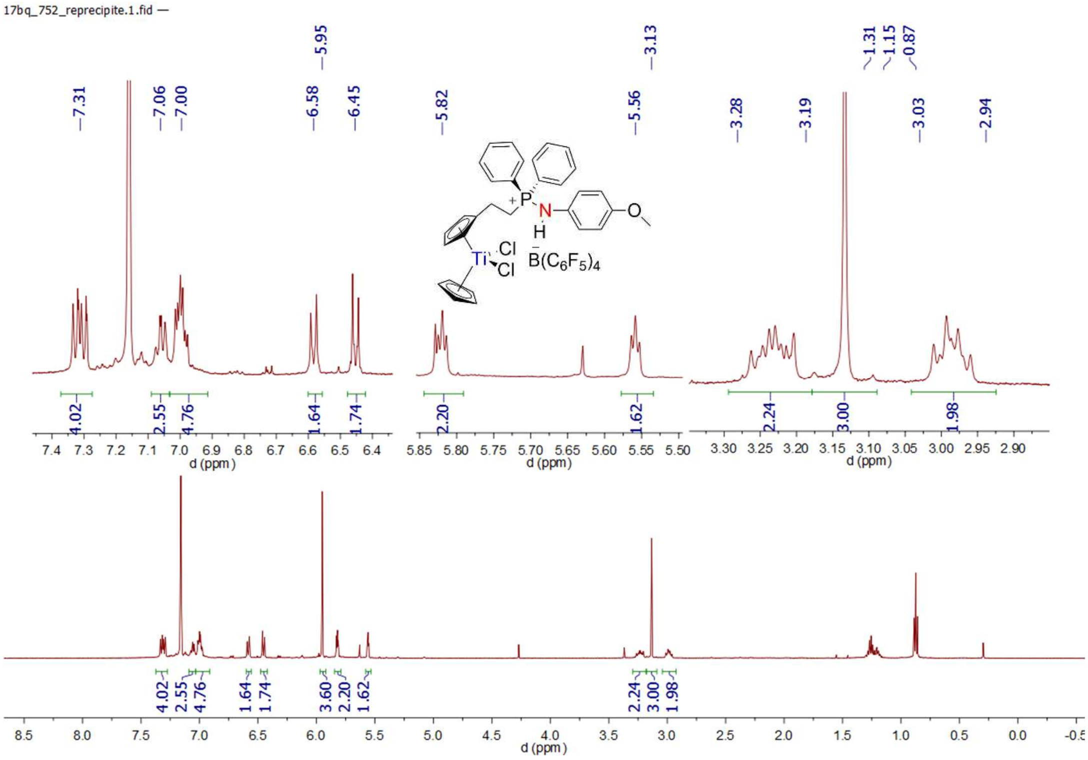
Technique : FIR BMS Si [710 - 80 cm-1] - Energie = :

Opérateur : qbonnin

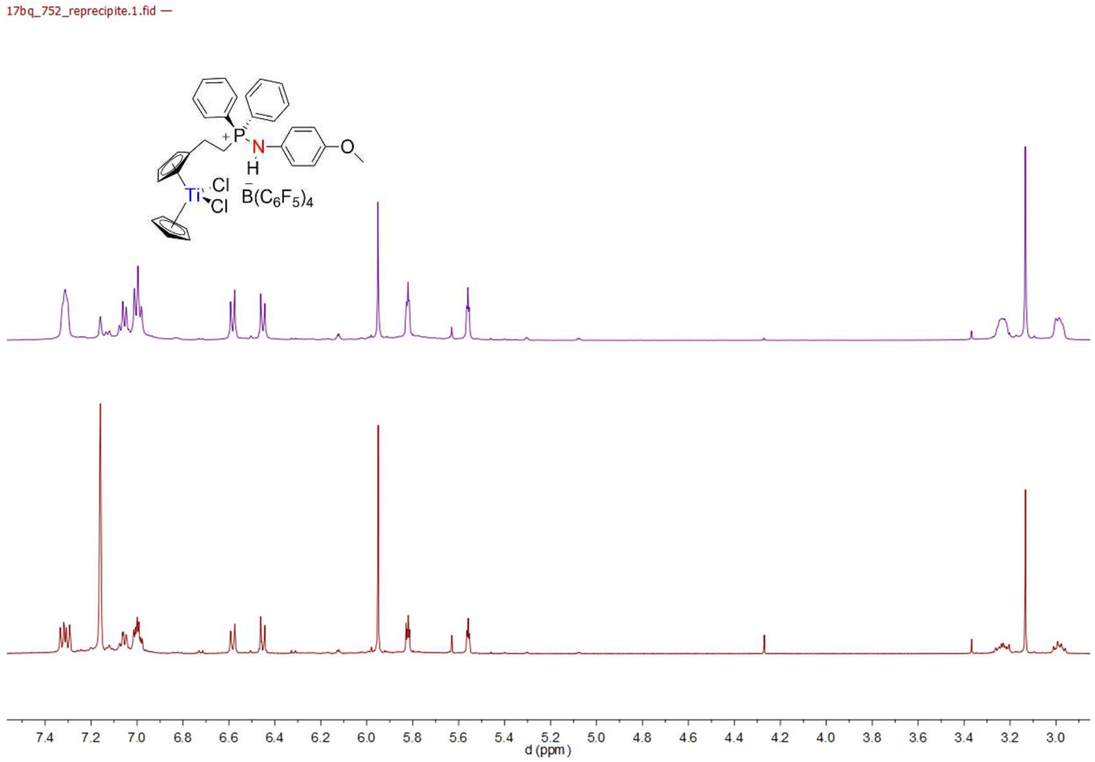
mesuré le 12/05/2017 sur VERTEX 70V

Spectrum 0-509: FIR of 60

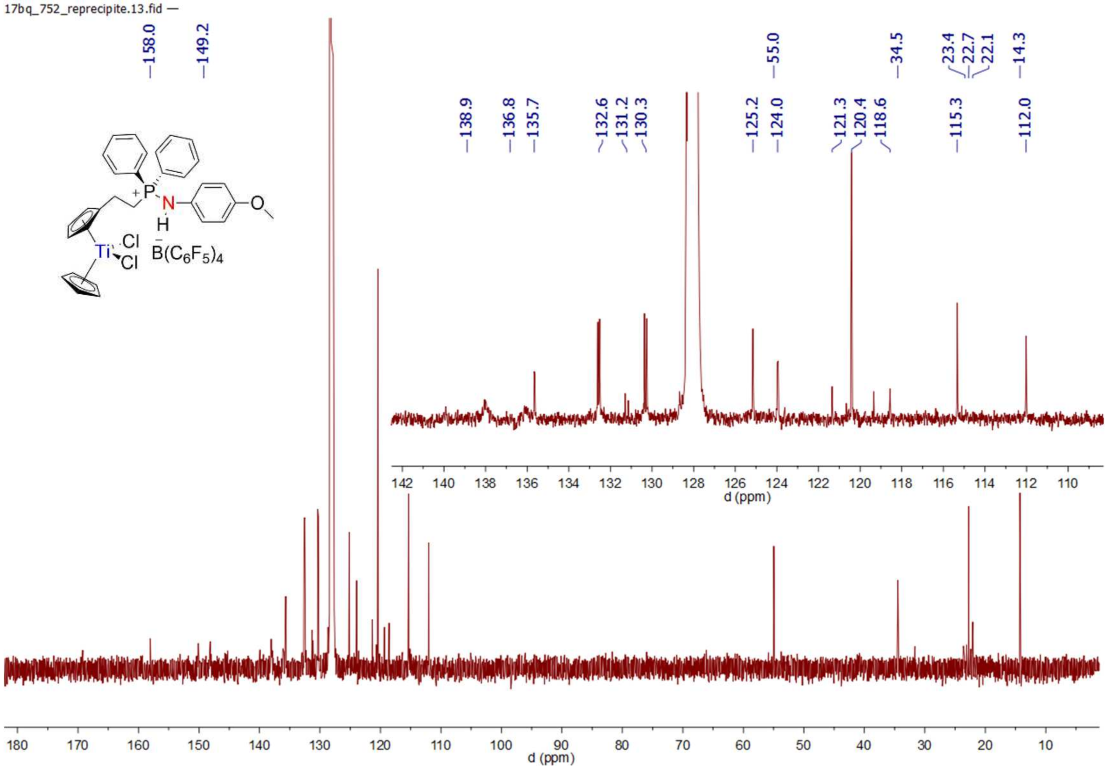
34. Compound **61**:



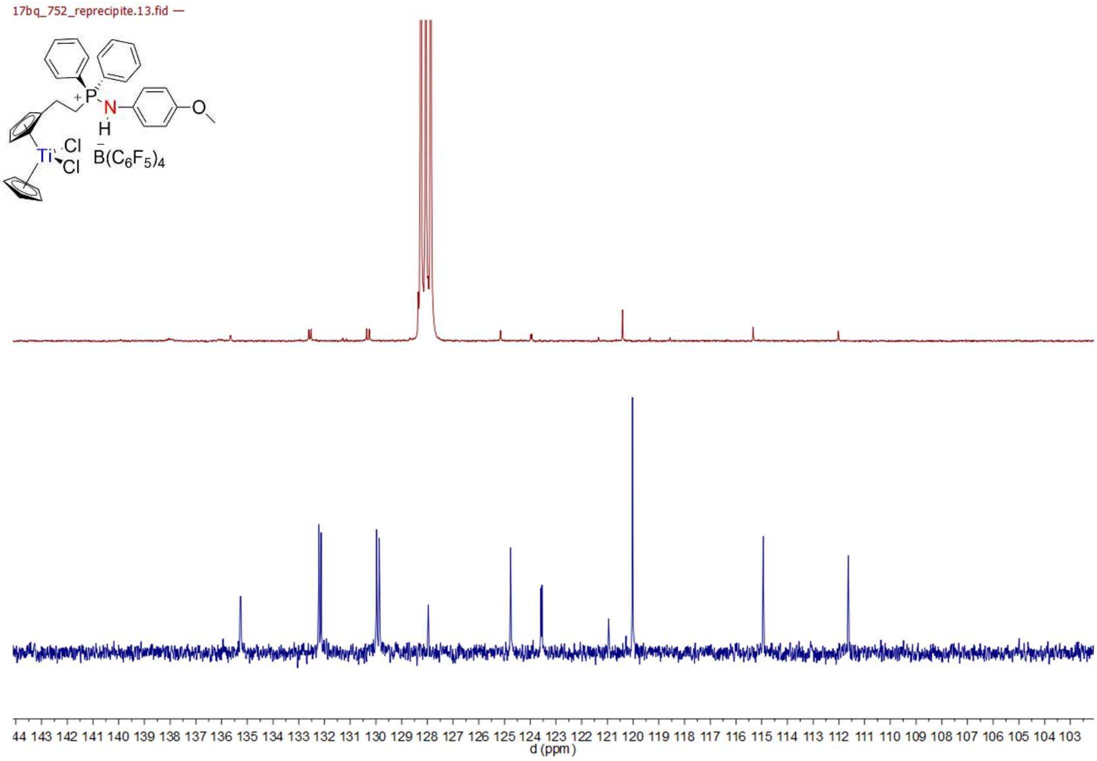
Spectrum 0-510: ^{1}H NMR of 61 (500.03 MHz, 300 K, benzene-d$_6$)



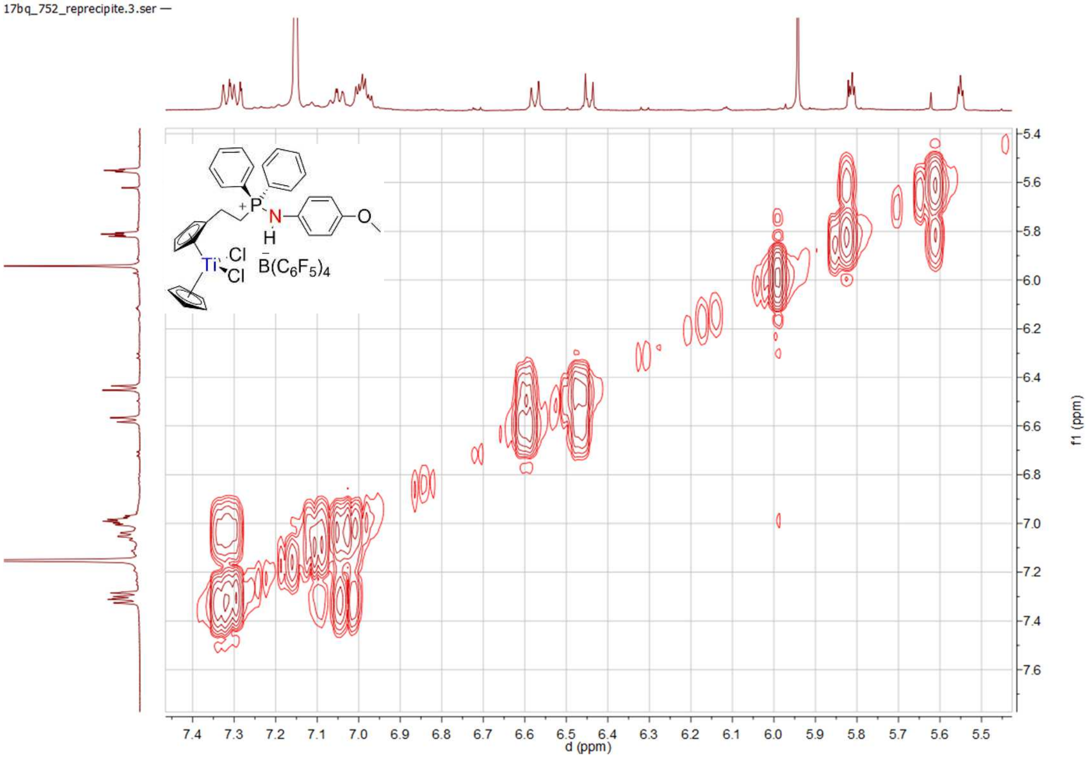
Spectrum 0-511: ^{1}H{^{31}P} NMR (top) correlated with ^{1}H NMR (bottom) of 61 (500.03 MHz, 300 K, benzene-d$_6$)



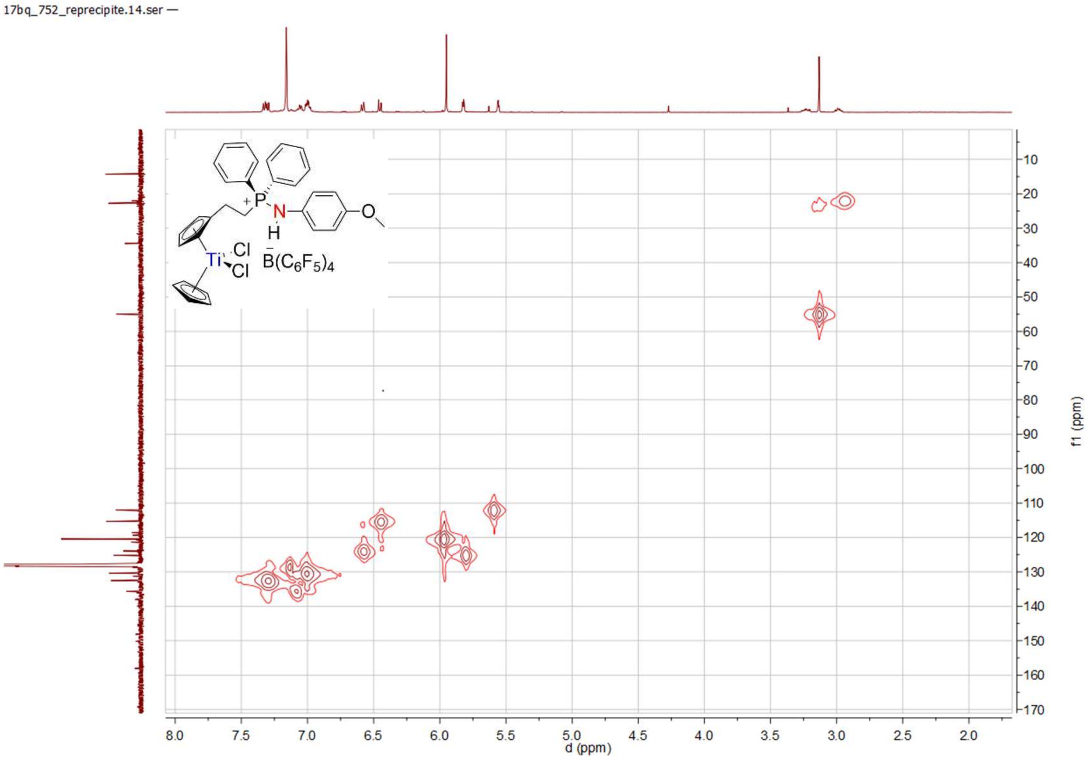
Spectrum 0-512: ^{13}C{^{1}H} NMR of 61 (125.75 MHz, 300 K, benzene-d$_6$)



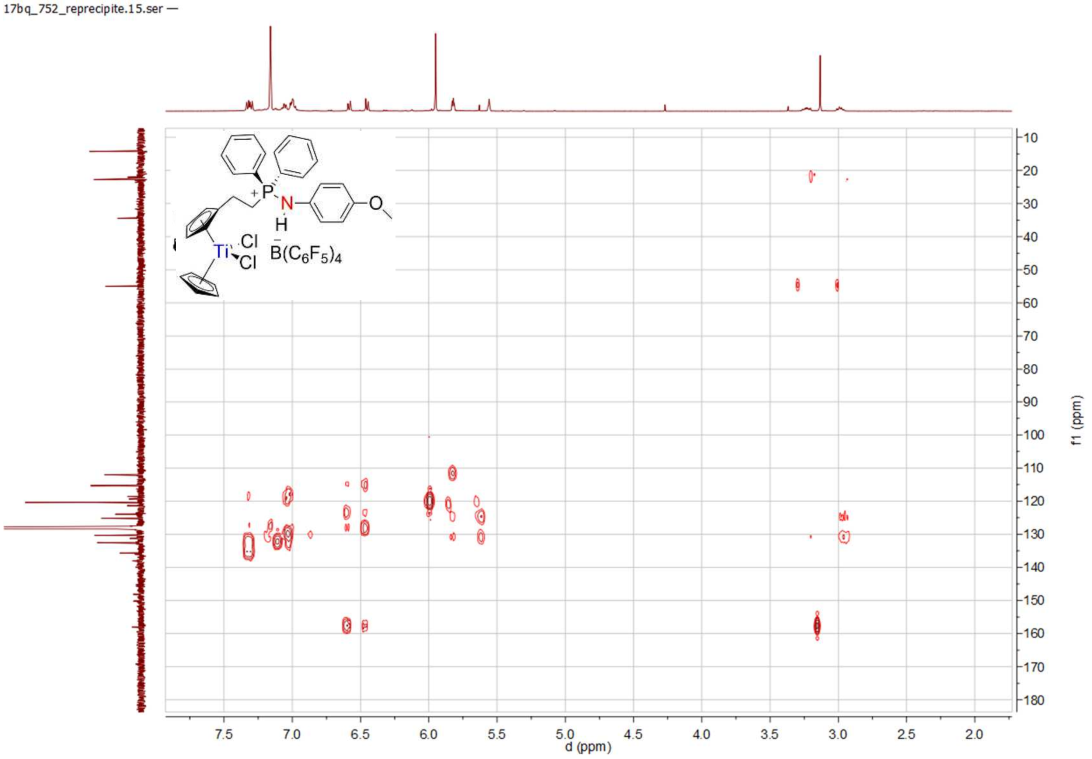
Spectrum 0-513: ^{13}C{^{1}H} and dept135 NMR superposition of 61 (125.75 MHz, 300 K, benzene-d$_6$)



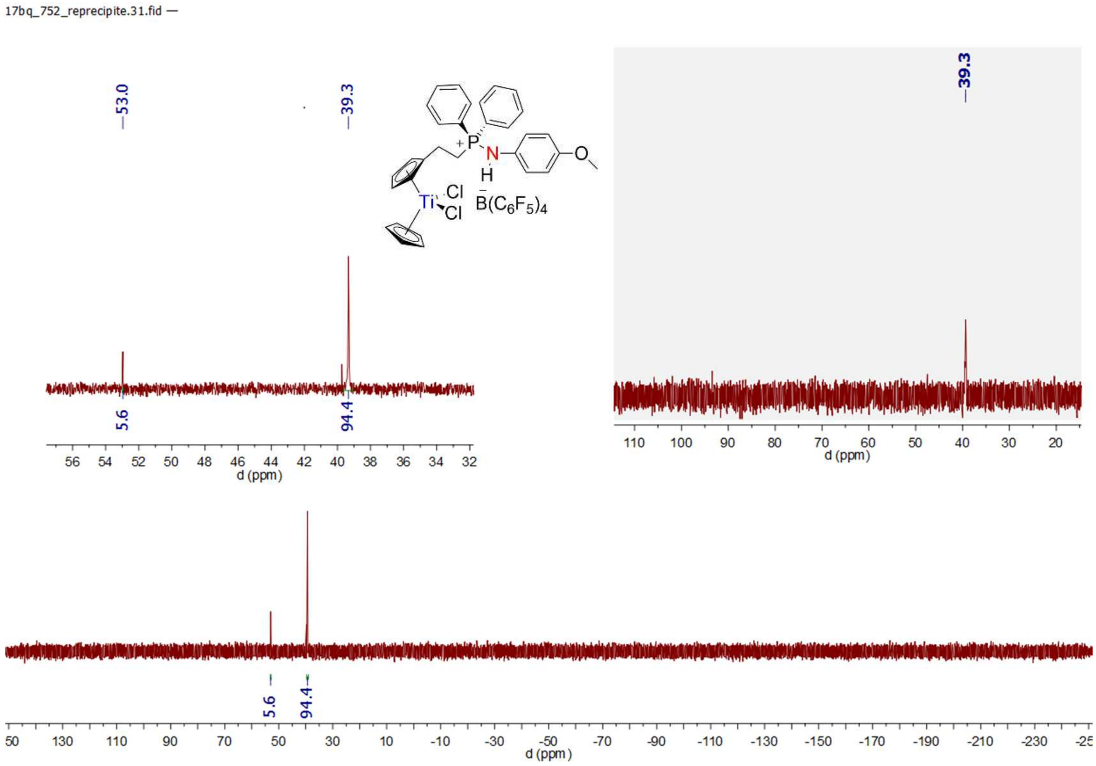
Spectrum 0-514: ^{1}H ^{1}H COSY of 61 (500.03 MHz, 300 K, 273 K, benzene-d$_6$)



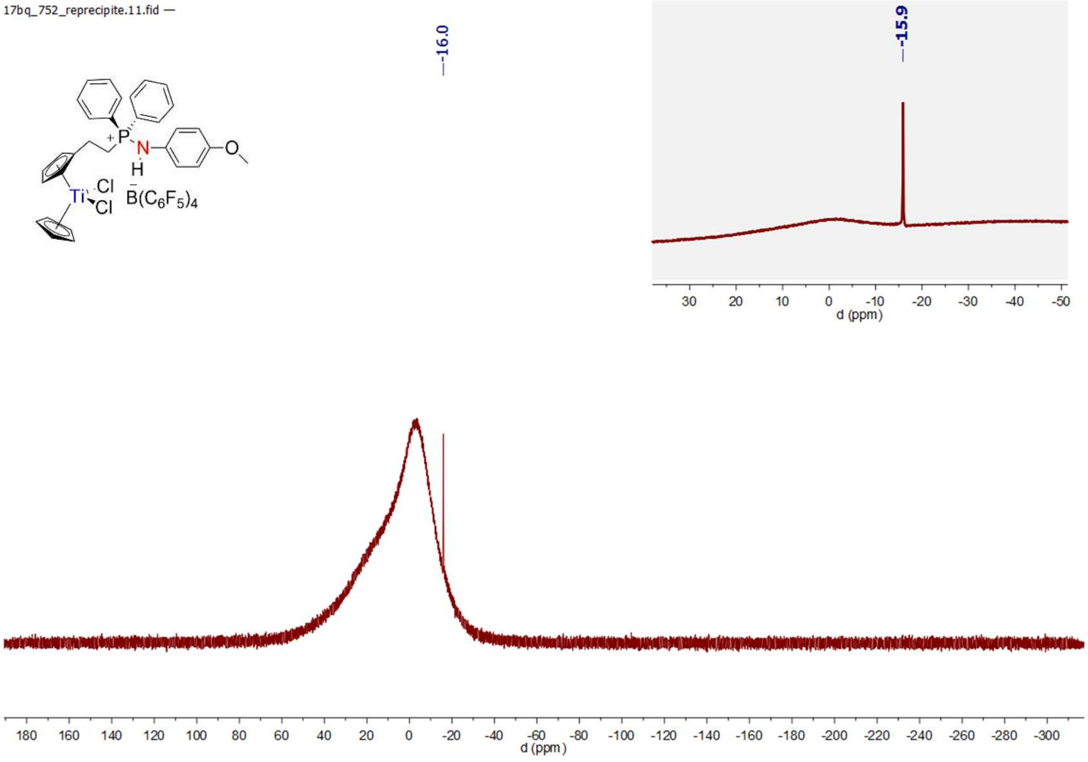
Spectrum 0-515: ^{1}H ^{13}C HMQC of 61 (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$)



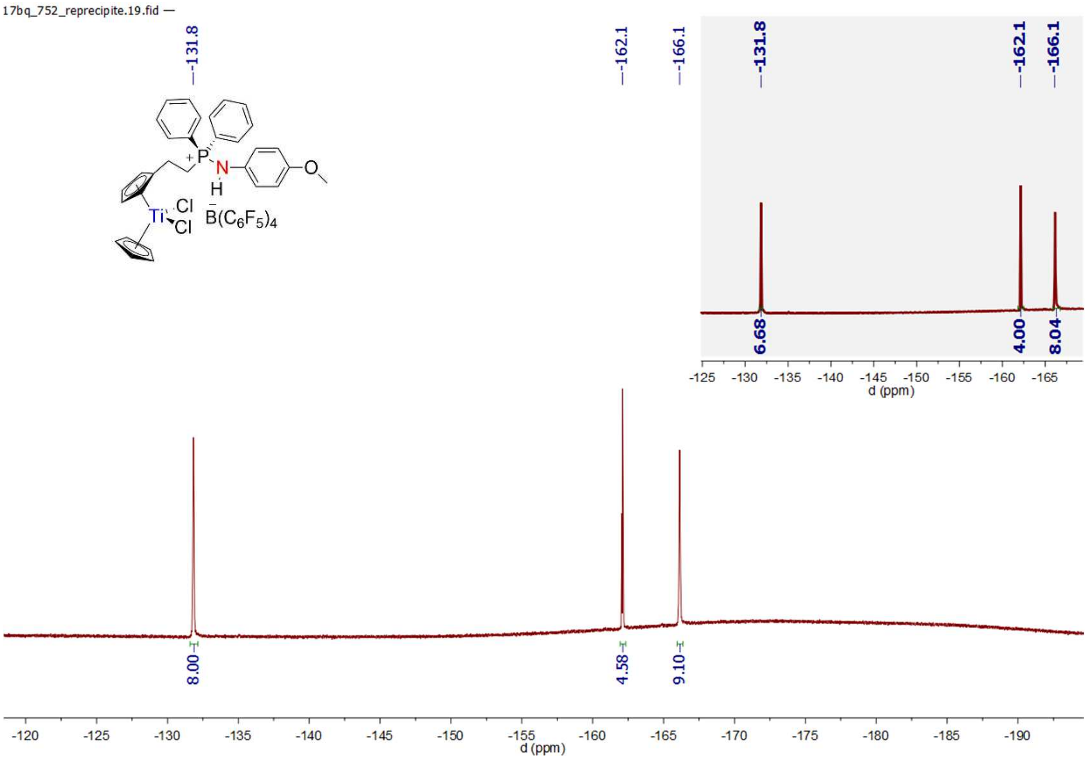
Spectrum 0-516: ^{1}H ^{13}C HMBC of 61 (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$)



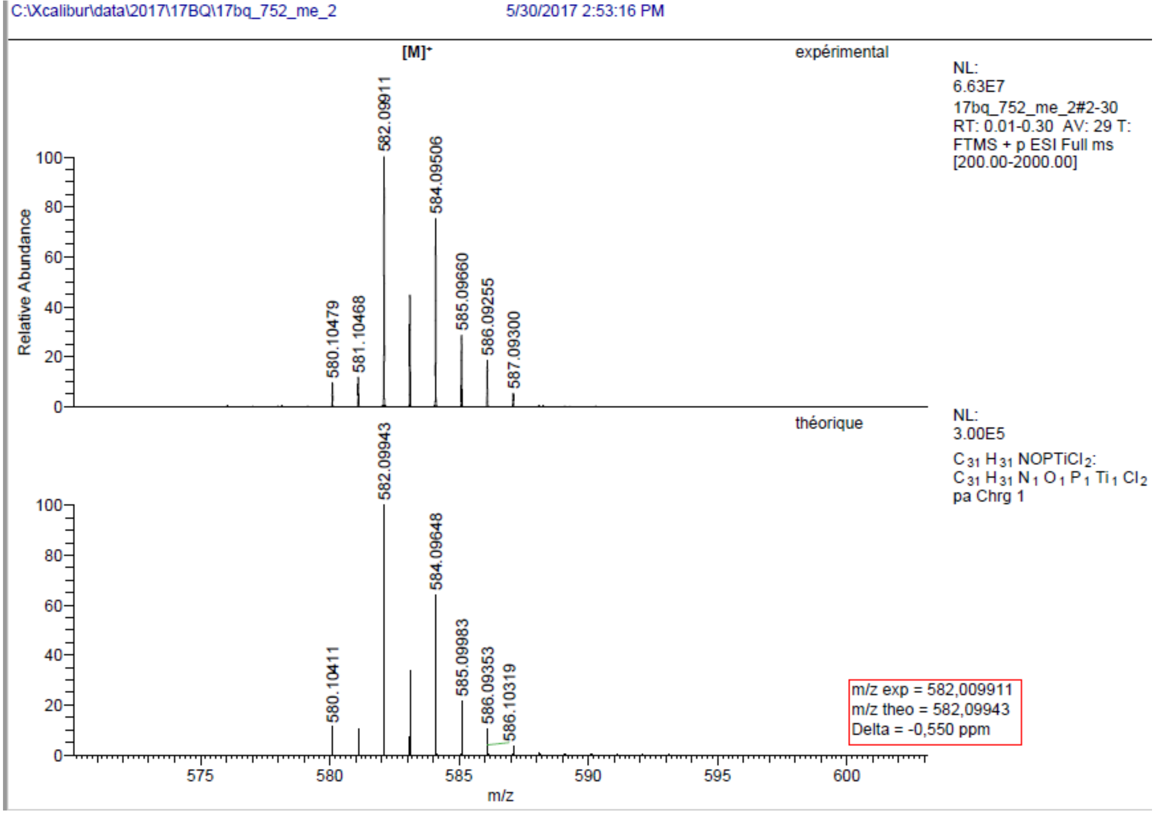
Spectrum 0-517: $^{31}P\{^{1}H\}$ and ^{31}P (opacified) NMR of 61 (202.46 MHz, 300 K, benzene-d_6)



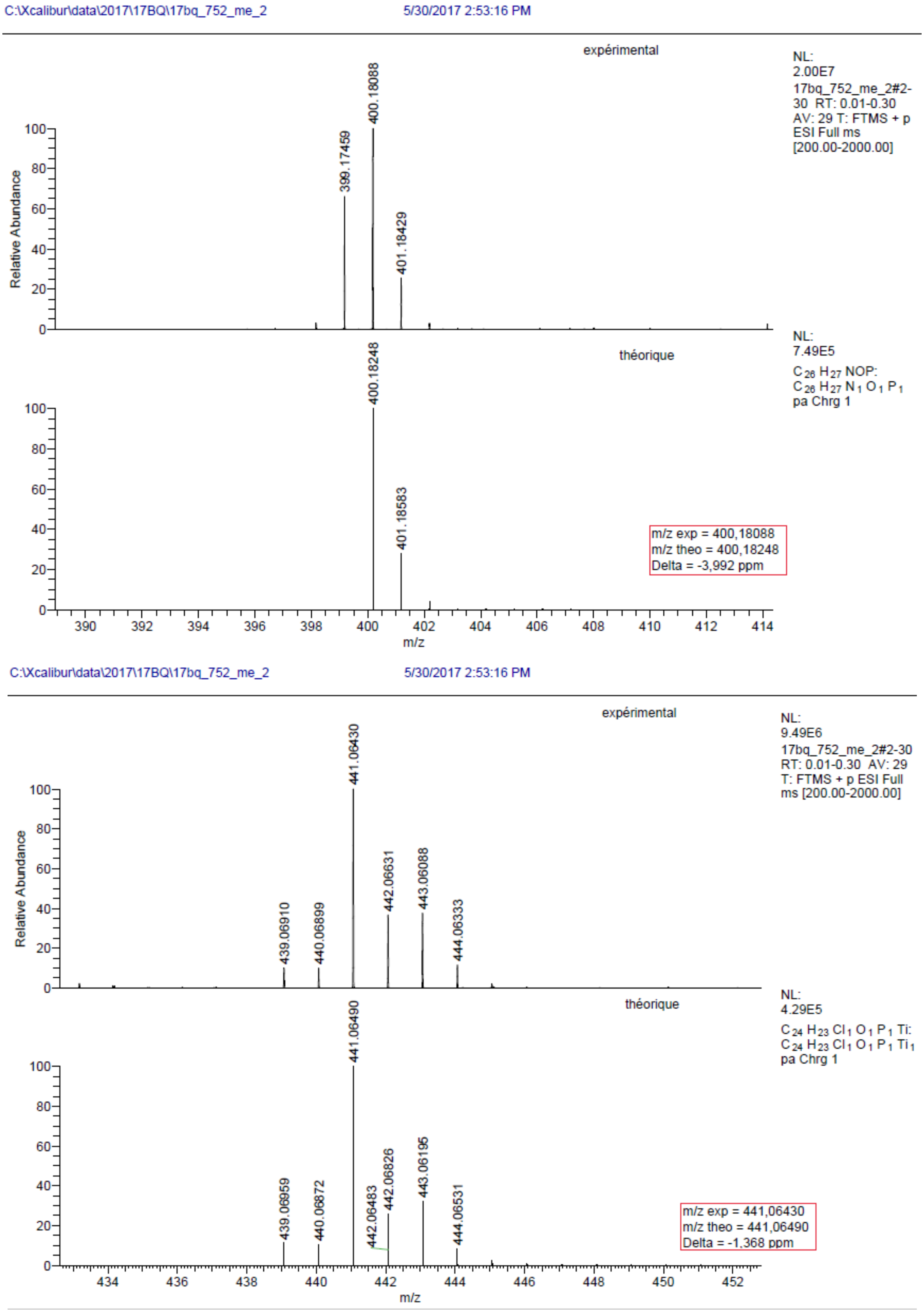
Spectrum 0-518: $^{11}B\{^{1}H\}$ and ^{11}B NMR(opacified) of 61 (160.42 MHz, 300 K, bromobenzene-d_5)



Spectrum 0-519: $^{19}F\{^1H\}$ and ^{19}F NMR(opacified) of 61 (470.45 MHz, 300 K, bromobenzene-d$_5$)

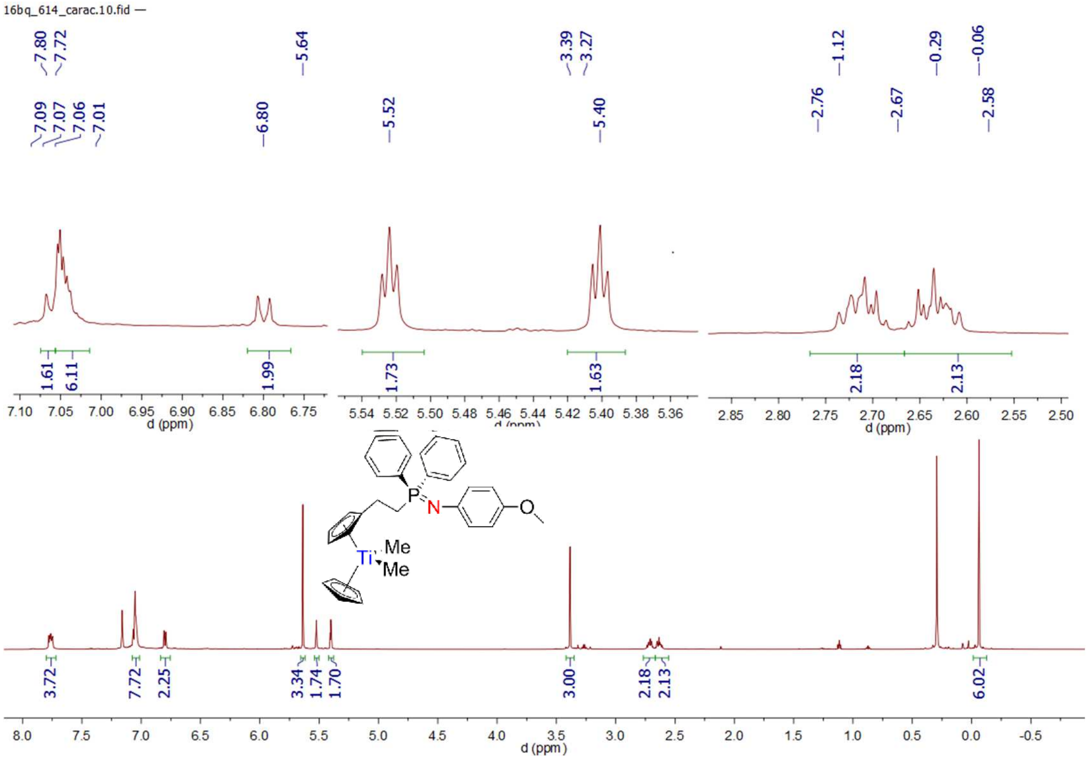


Spectrum 0-520: HRMS of 61 (Positive mode ESI, dichloromethane)

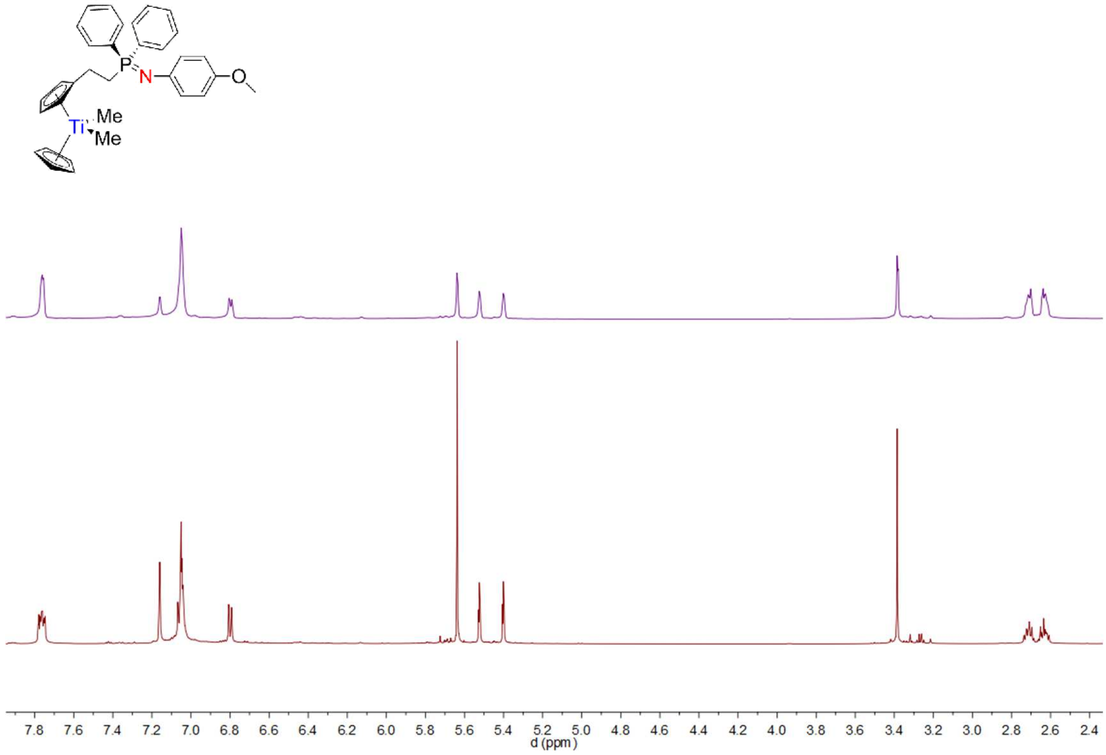


Spectrum 0-521: HRMS of 61 (Positive mode ESI, dichloromethane)

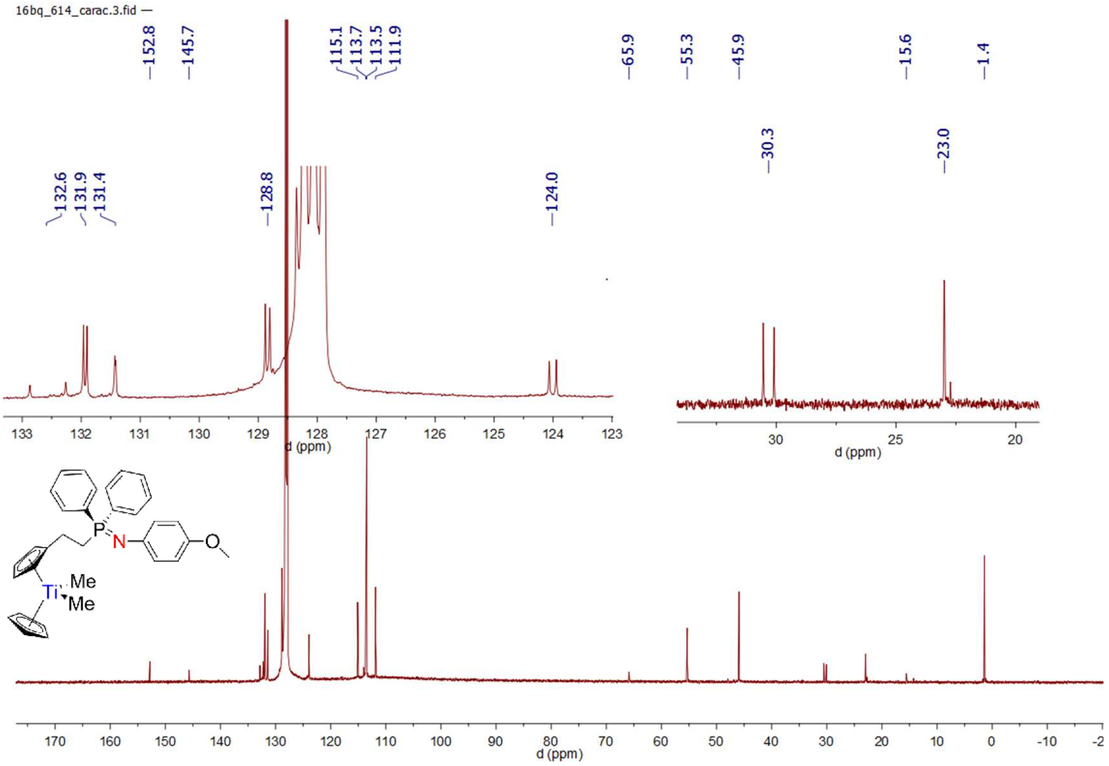
35. Compound **62**:



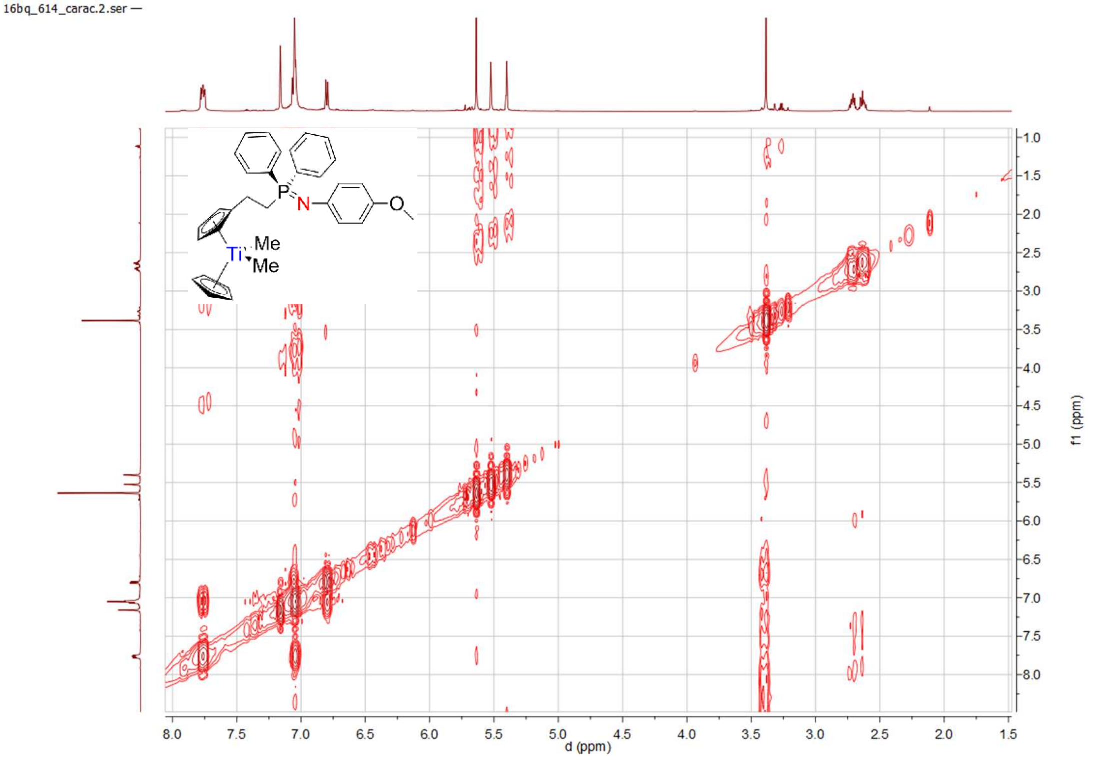
Spectrum 0-522: ^1H NMR of 62 (500.03 MHz, 300 K, benzene-d_6)



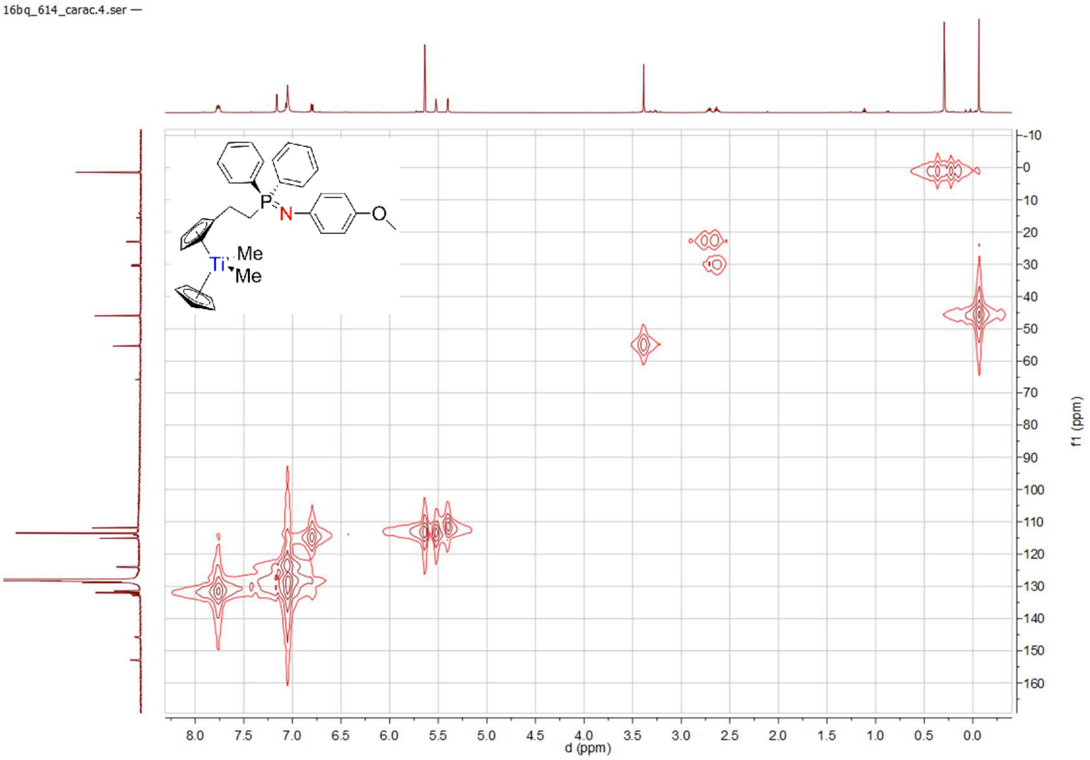
Spectrum 0-523: $^1H\{^{31}P\}$ NMR (top) correlated with ^1H (bottom) of 62 (600.23 MHz, 300 K, benzene-d_6)



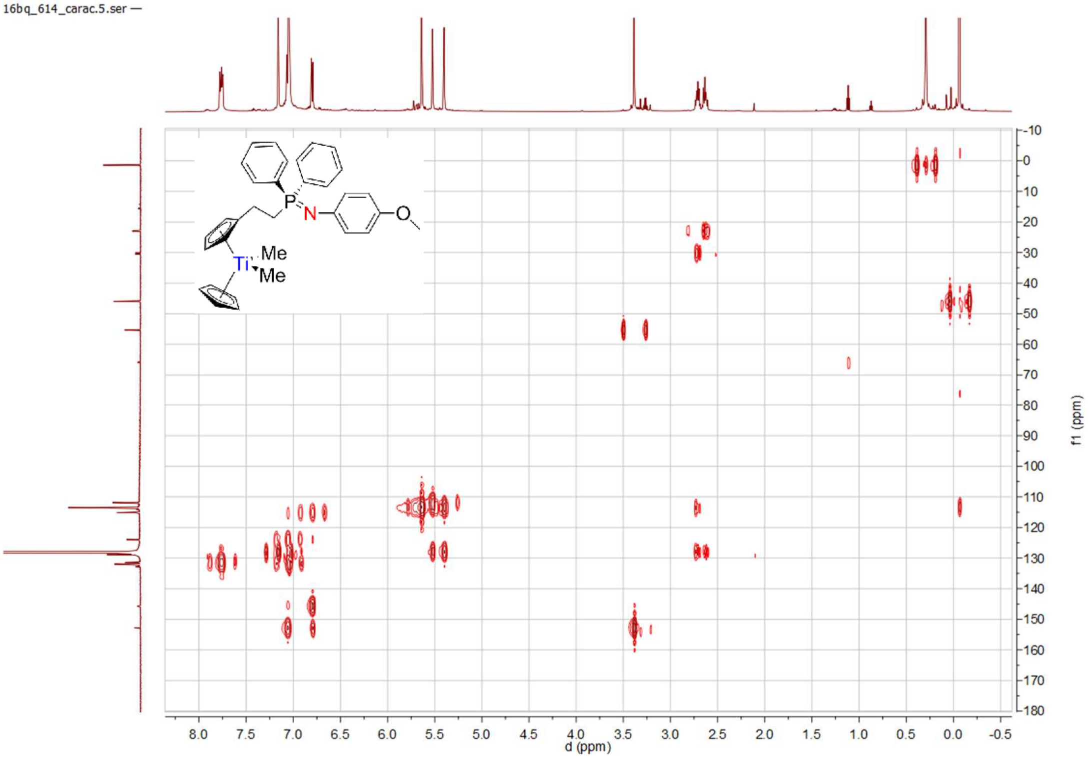
Spectrum 0-524: ^{13}C{^{1}H} NMR of 62 (125.75 MHz, 300 K, benzene-d$_6$)



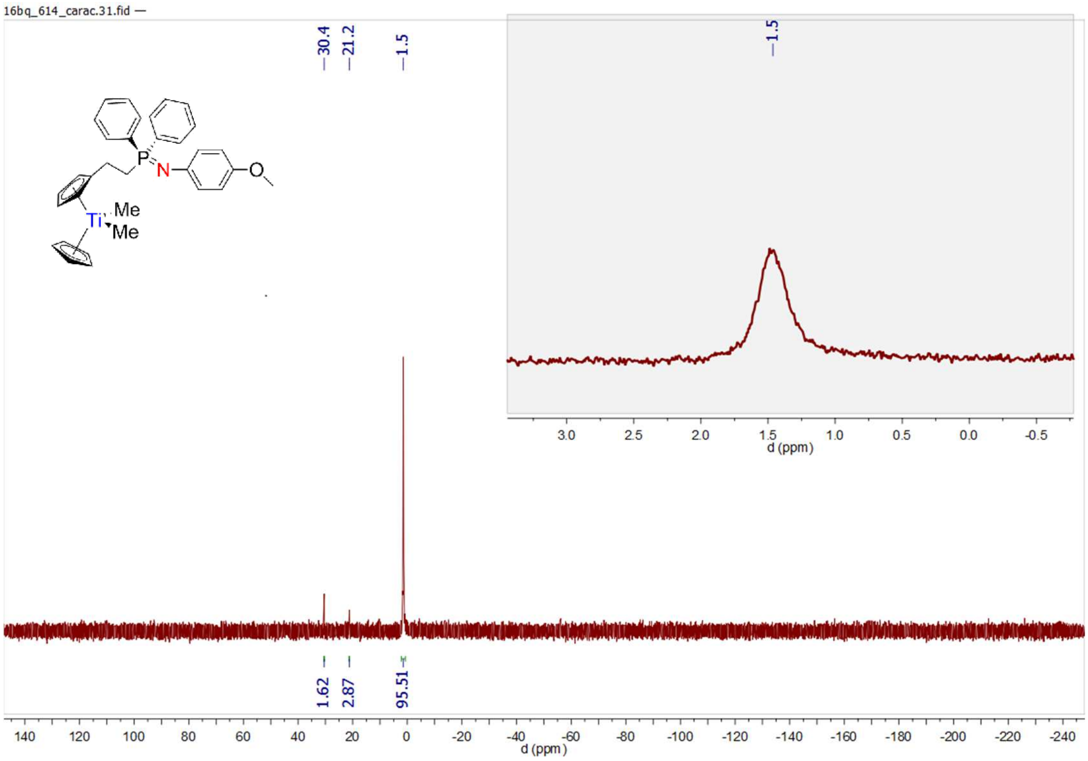
Spectrum 0-525: ^{1}H ^{1}H COSY of 62 (500.03 MHz, 300 K, 273 K, benzene-d$_6$)



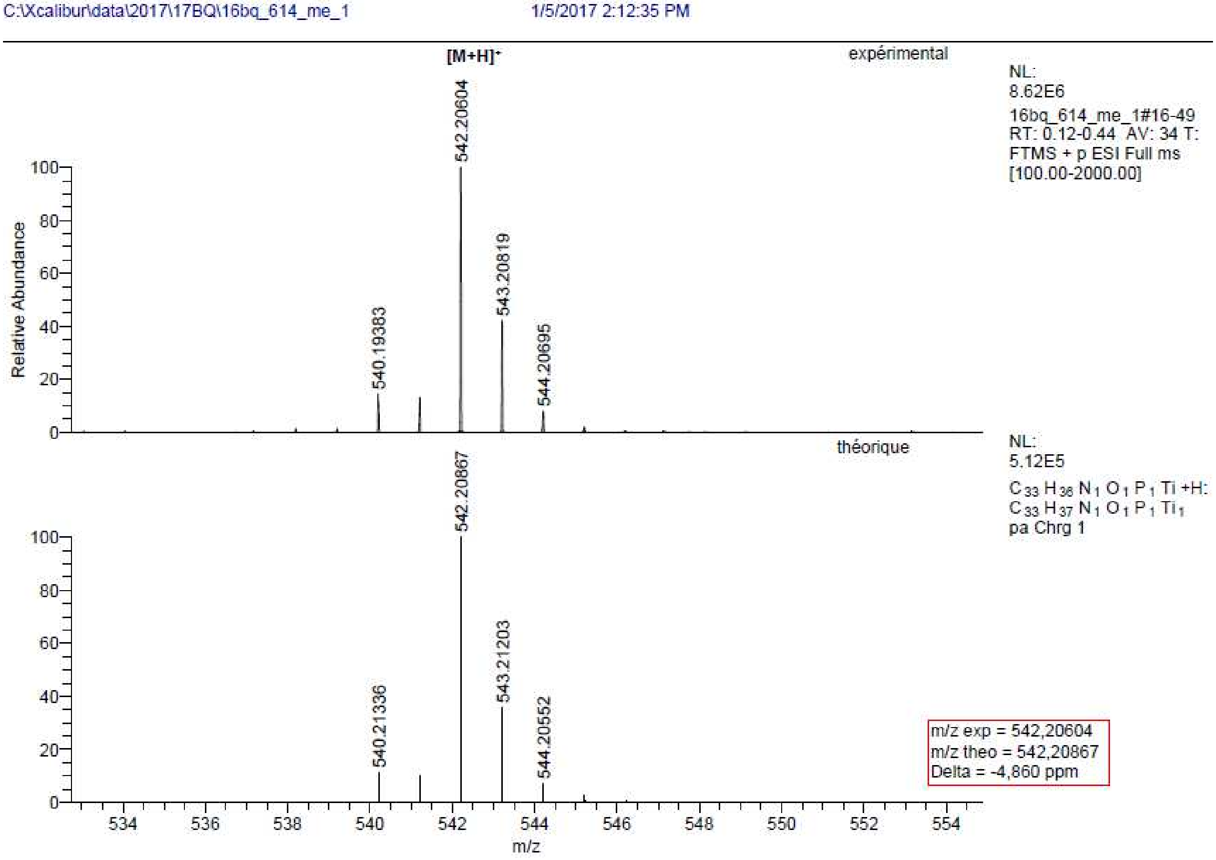
Spectrum 0-526: ^1H ^{13}C HMQC of 62 (500.03 MHz / 125.75 MHz, 300 K, benzene-d_6)



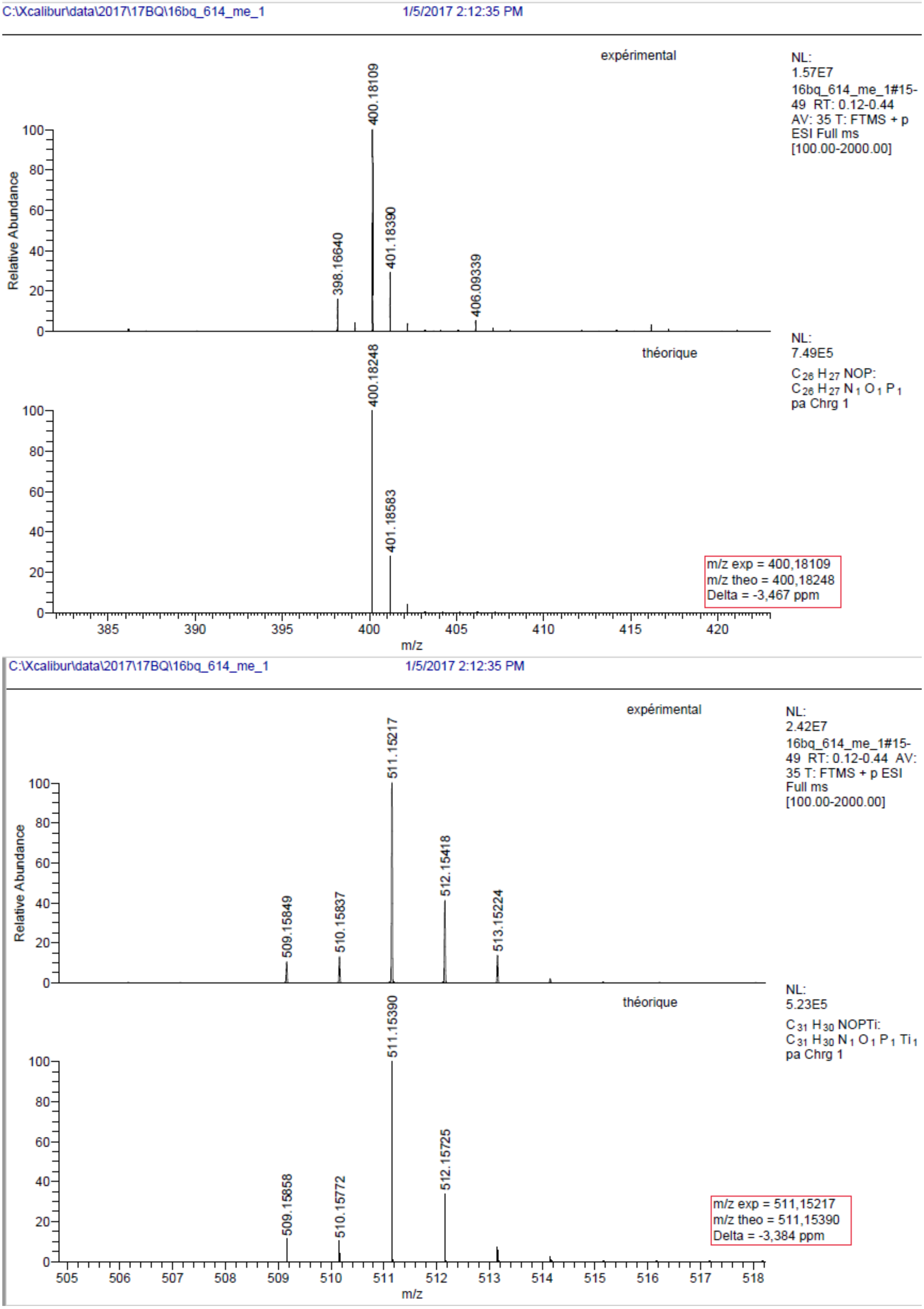
Spectrum 0-527: ^1H ^{13}C HMBC of 62 (600.23 MHz / 150.86 MHz, 300 K, benzene-d_6)



Spectrum 0-528: $^{31}P\{^1H\}$ and ^{31}P (opacified) NMR of 62 (202.46 MHz, 300 K, benzene-d_6)

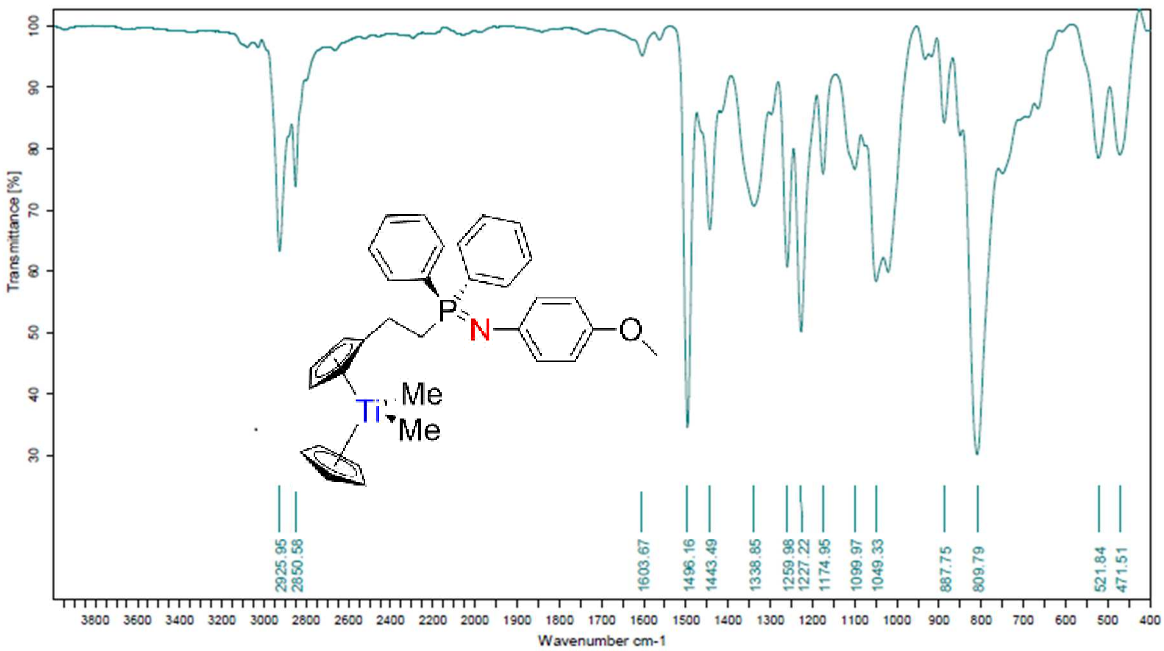


Spectrum 0-529: HRMS of 62 (Positive mode ESI, dichloromethane)



Spectrum 0-530: HRMS of 62 (Positive mode ESI, dichloromethane)

POLE CHIMIE MOLECULAIRE - DIJON

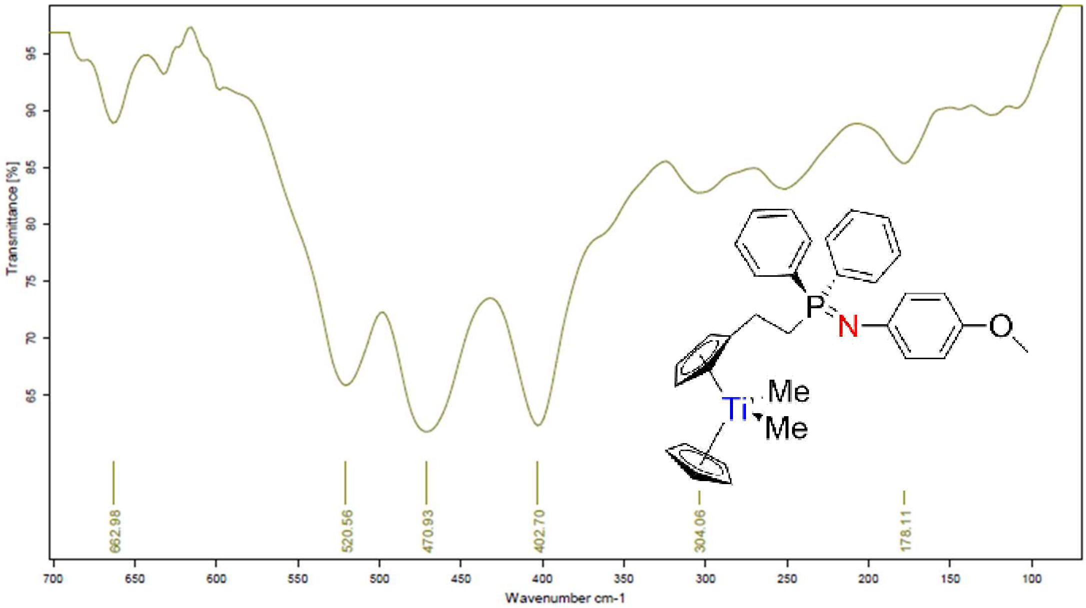


Echantillon :
17bq_614_MIR
résolution : 4 cm-1 (20 scans)

Spectre : 2017qbonnin_17bq_614_MIR.0 (dans D:\irdata_VERTEX\qt
Technique : BMS KBR [7500 - 370 cm-1] - Energie =
Opérateur : qbonnin
mesuré le 23/06/2017 sur VERTEX 70V

Spectrum 0-531: MIR of 62

POLE CHIMIE MOLECULAIRE - DIJON

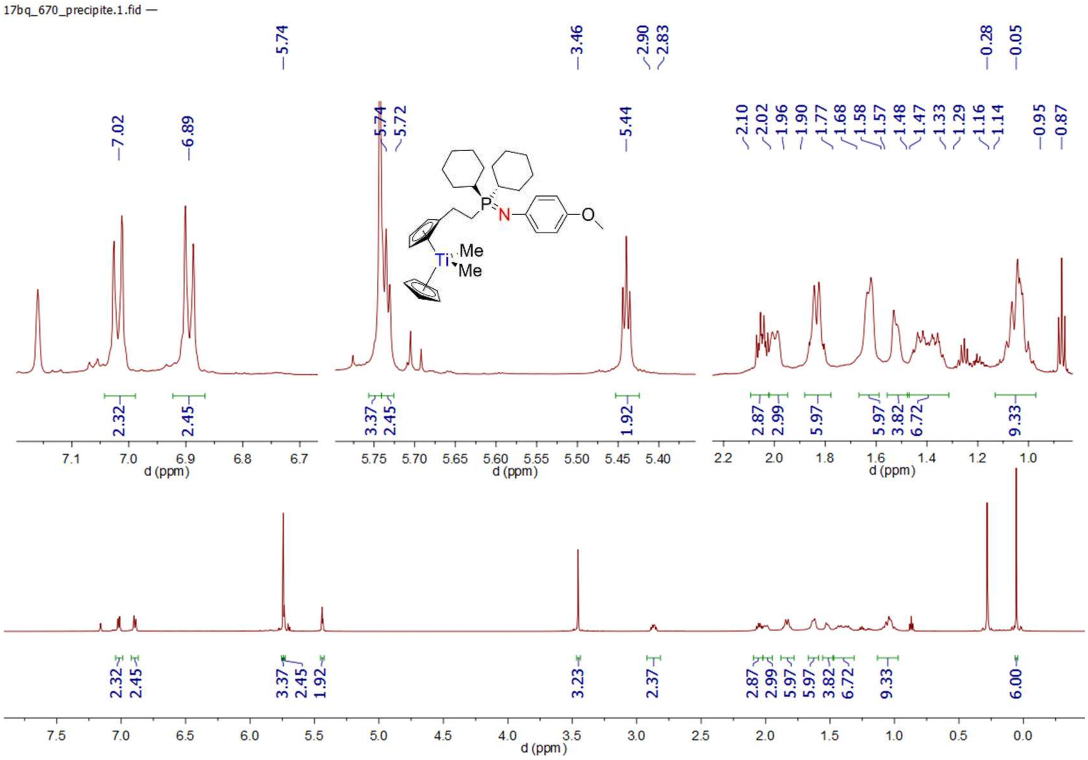


Echantillon :
17bq_614_FIR
résolution : 4 cm-1 (20 scans)

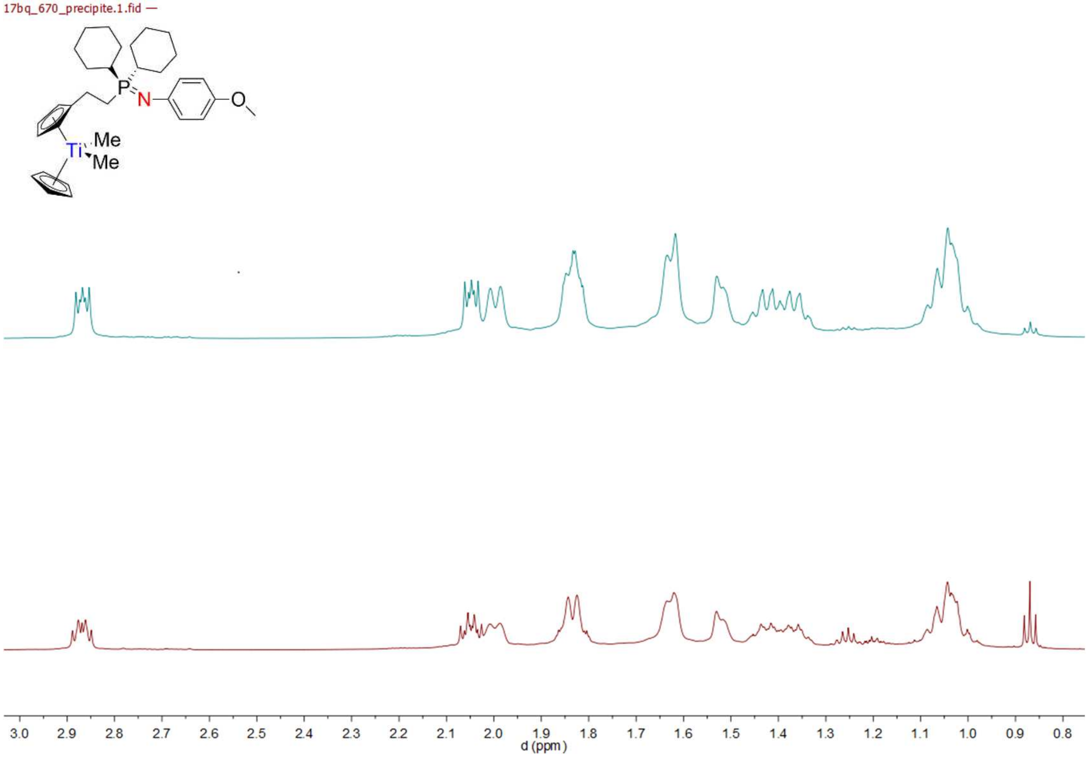
Spectre : 2017qbonnin_17bq_614_FIR.0 (dans D:\irdata_VERTEX\qb
Technique : FIR BMS Si [710 - 80 cm-1] - Energie = :
Opérateur : qbonnin
mesuré le 23/06/2017 sur VERTEX 70V

Spectrum 0-532: FIR of 62

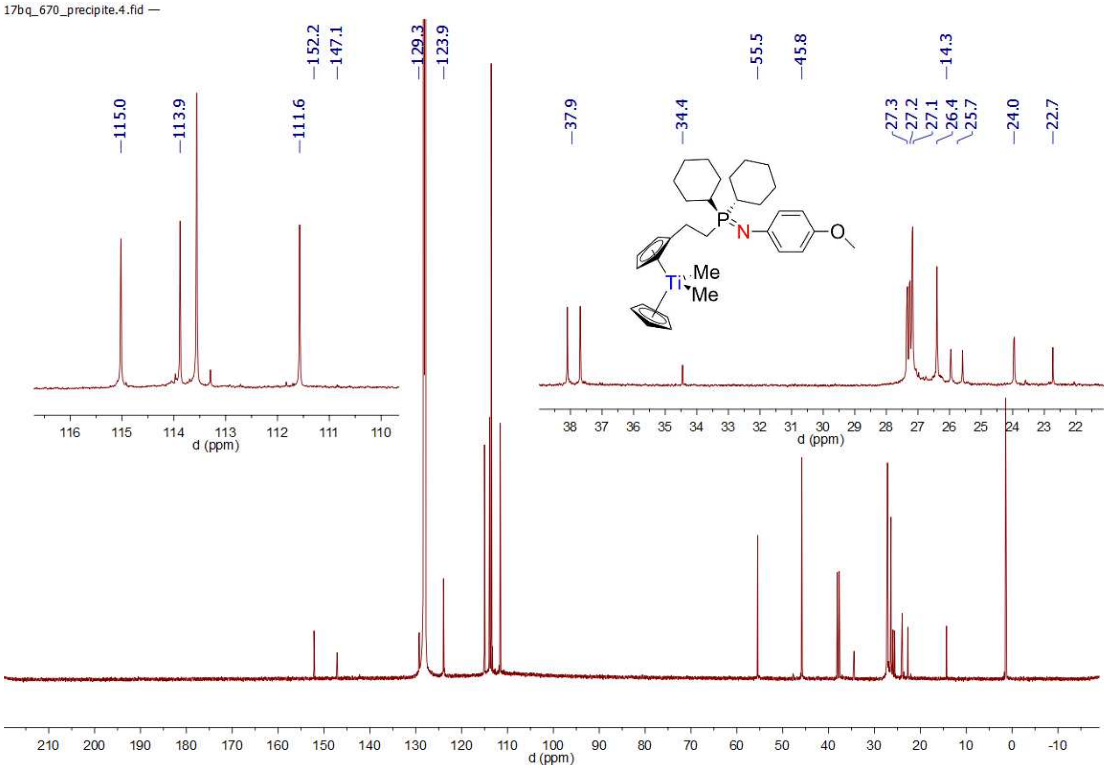
36. Compound **63**:



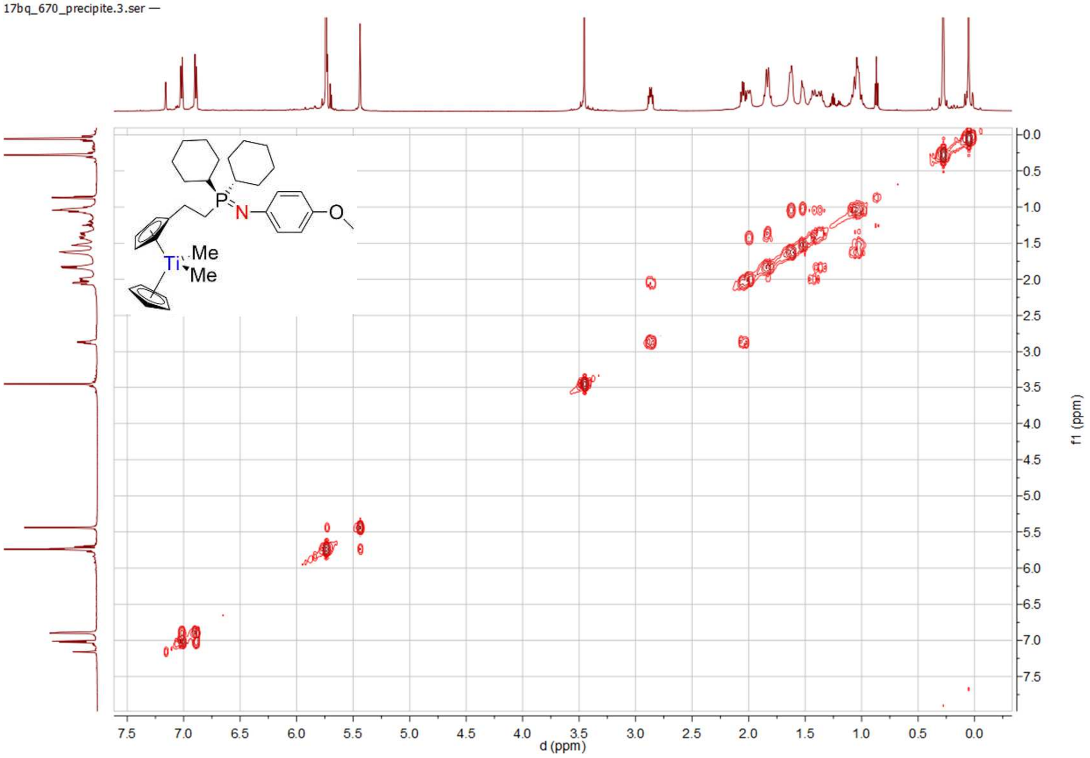
Spectrum 0-533: ^{1}H NMR of 63 (500.03 MHz, 300 K, benzene-d_6)



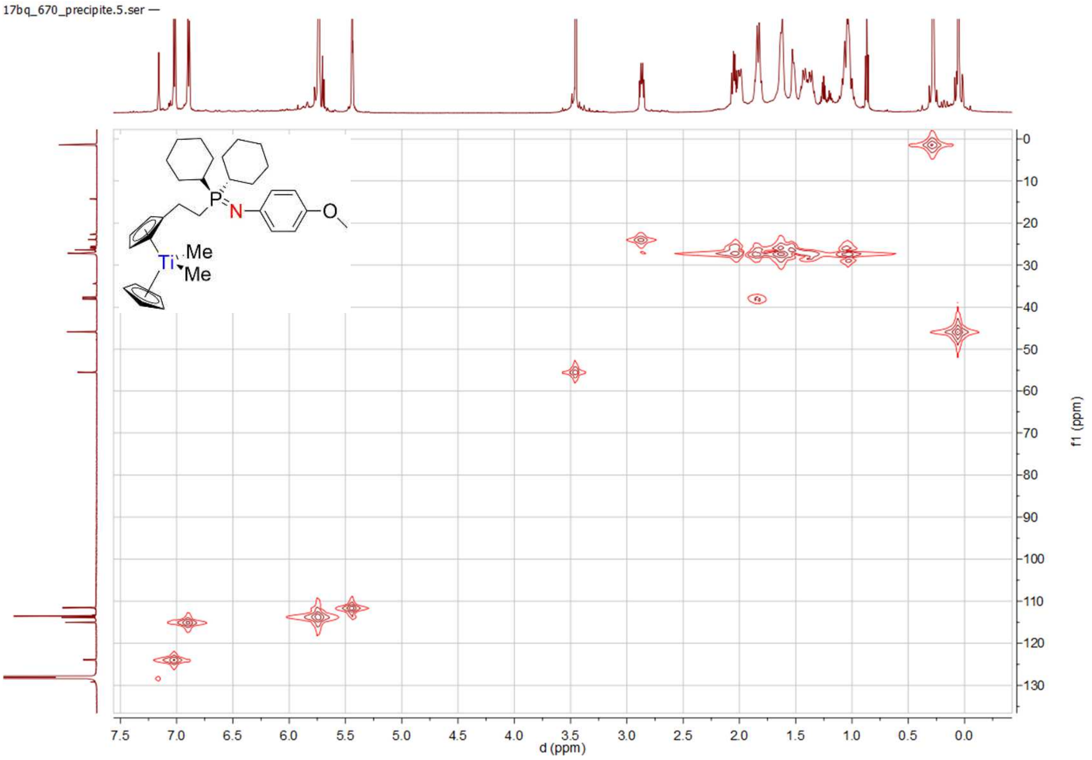
Spectrum 0-534: ^{1}H{^{31}P} NMR (top) correlated with ^{1}H (bottom) of 63 (600.23 MHz, 300 K, benzene-d_6)



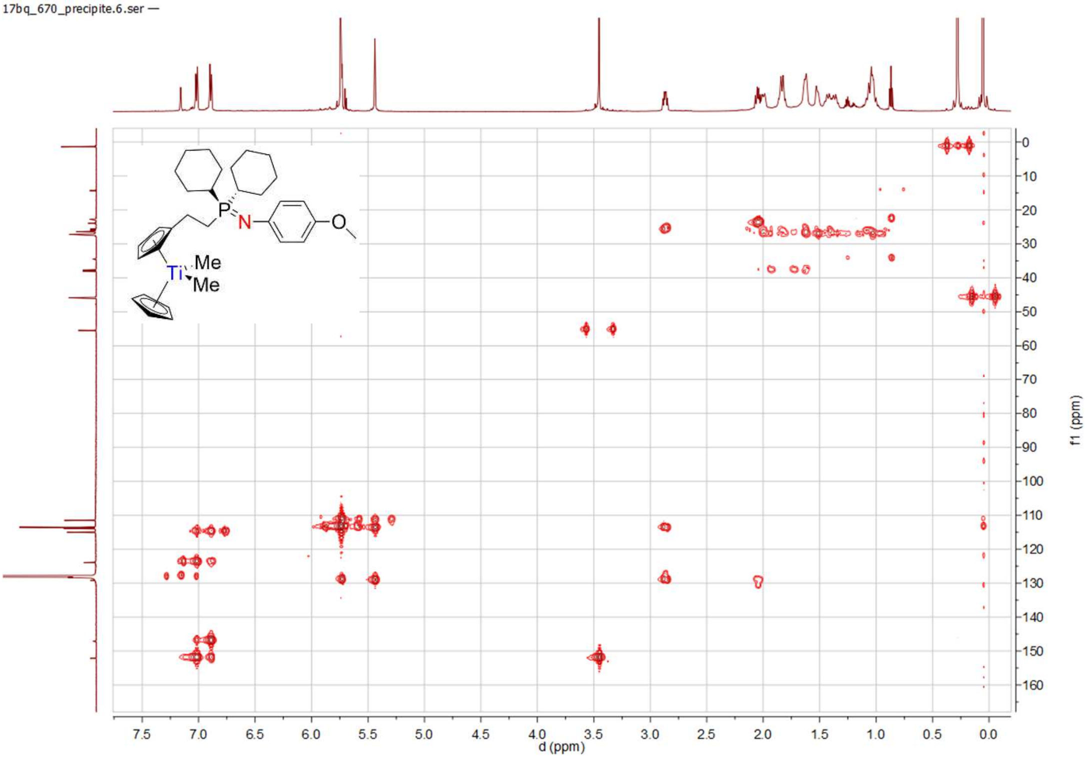
Spectrum 0-535: ^{13}C{^{1}H} NMR of 63 (125.75 MHz, 300 K, benzene-d$_6$)



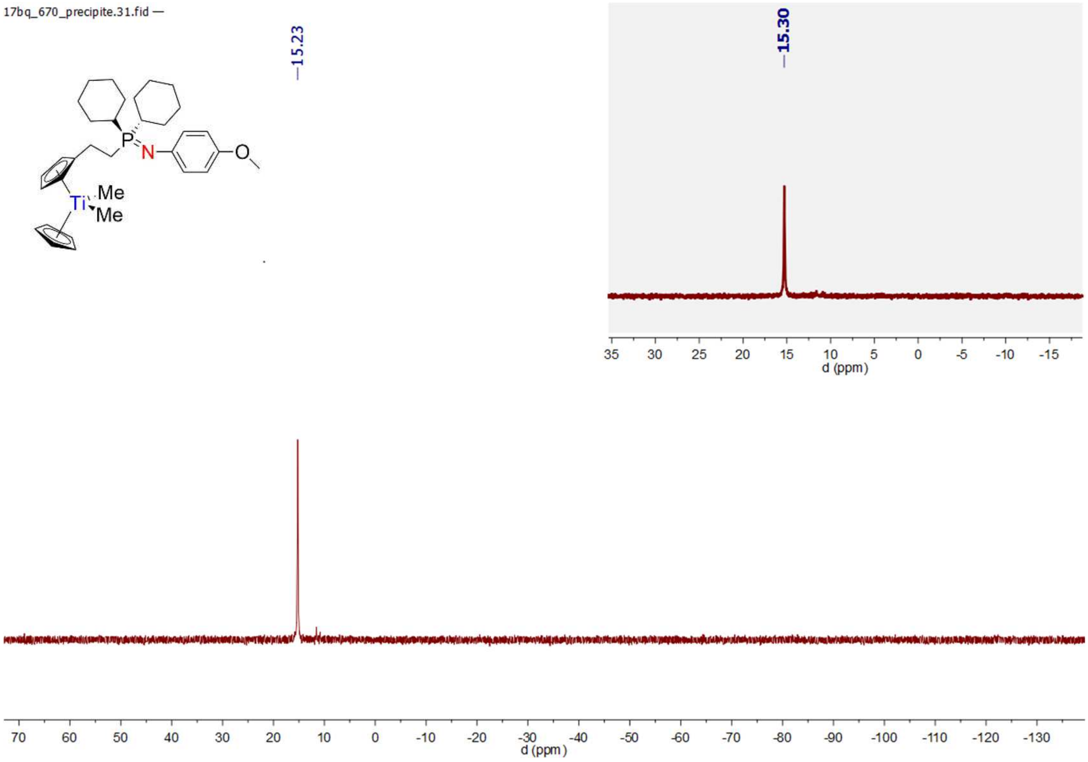
Spectrum 0-536: ^{1}H ^{1}H COSY of 63 (500.03 MHz, 300 K, 273 K, benzene-d$_6$)



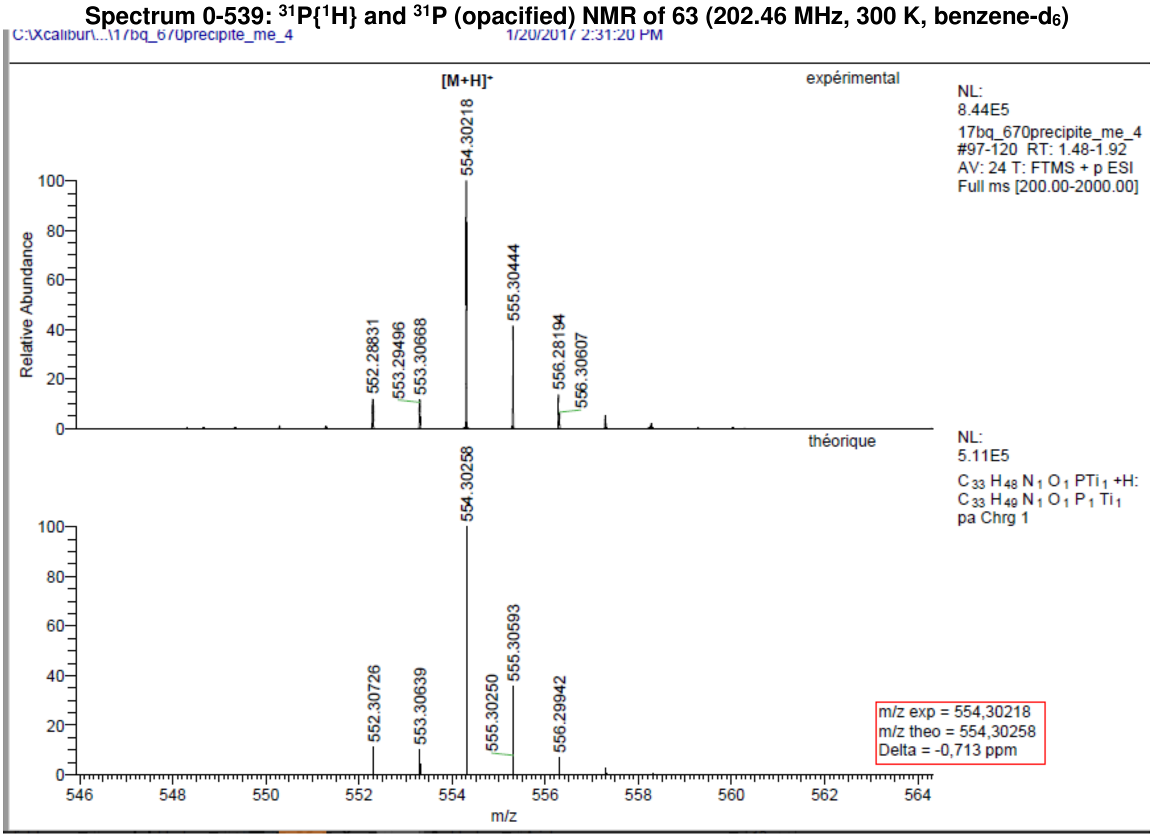
Spectrum 0-537: ^{1}H ^{13}C HMQC of 63 (500.03 MHz / 125.75 MHz, 300 K, benzene-d$_6$)



Spectrum 0-538: ^{1}H ^{13}C HMBC of 63 (600.23 MHz / 150.86 MHz, 300 K, benzene-d$_6$)

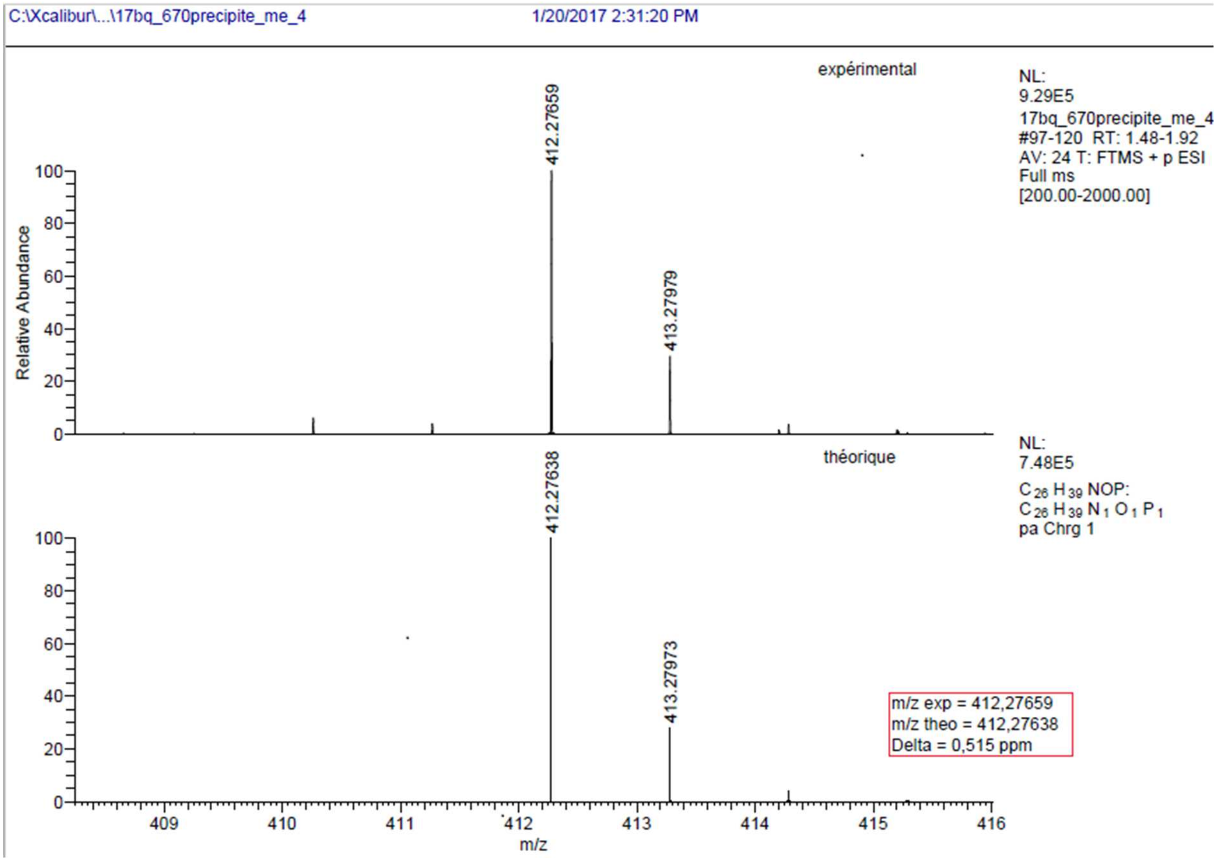


Spectrum 0-539: $^{31}P\{^{1}H\}$ and ^{31}P (opacified) NMR of 63 (202.46 MHz, 300 K, benzene-d_6)



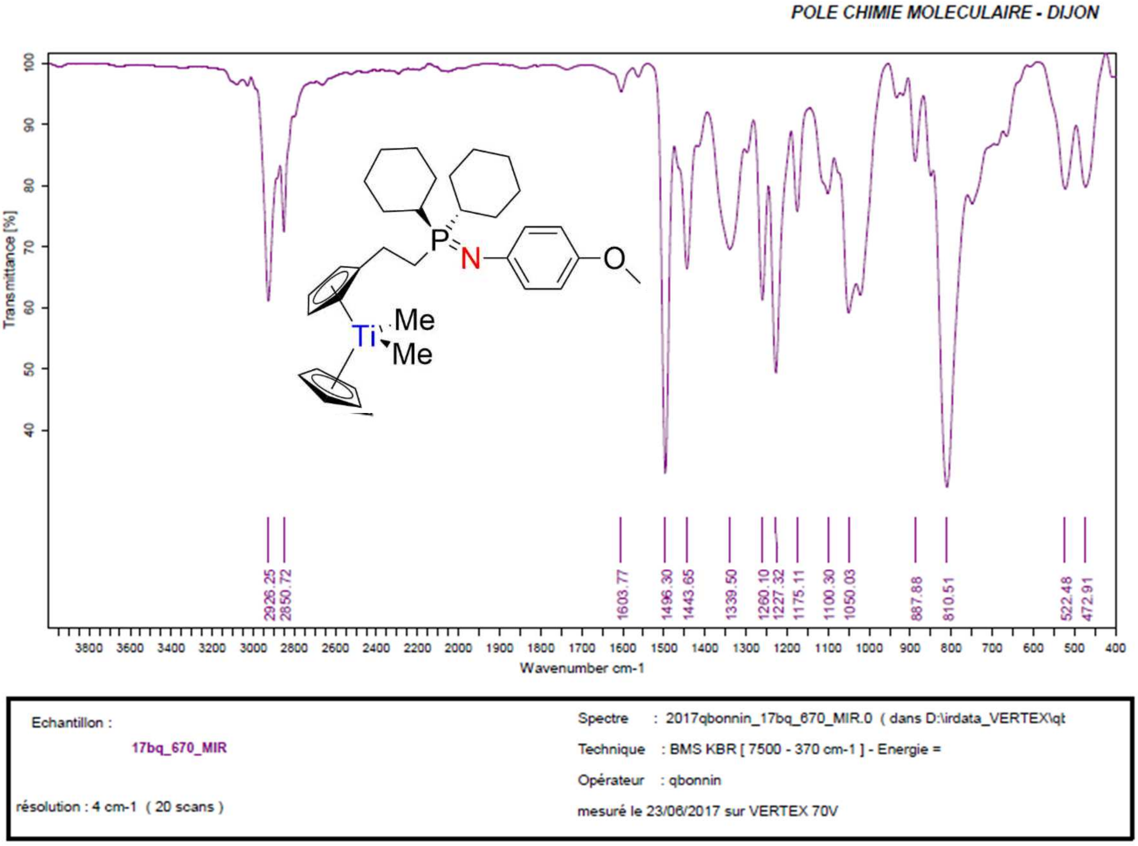
m/z exp = 554,30218
m/z theo = 554,30258
Delta = -0,713 ppm

Spectrum 0-540: HRMS of 63 (Positive mode ESI, dichloromethane)



m/z exp = 412,27659
m/z theo = 412,27638
Delta = 0,515 ppm

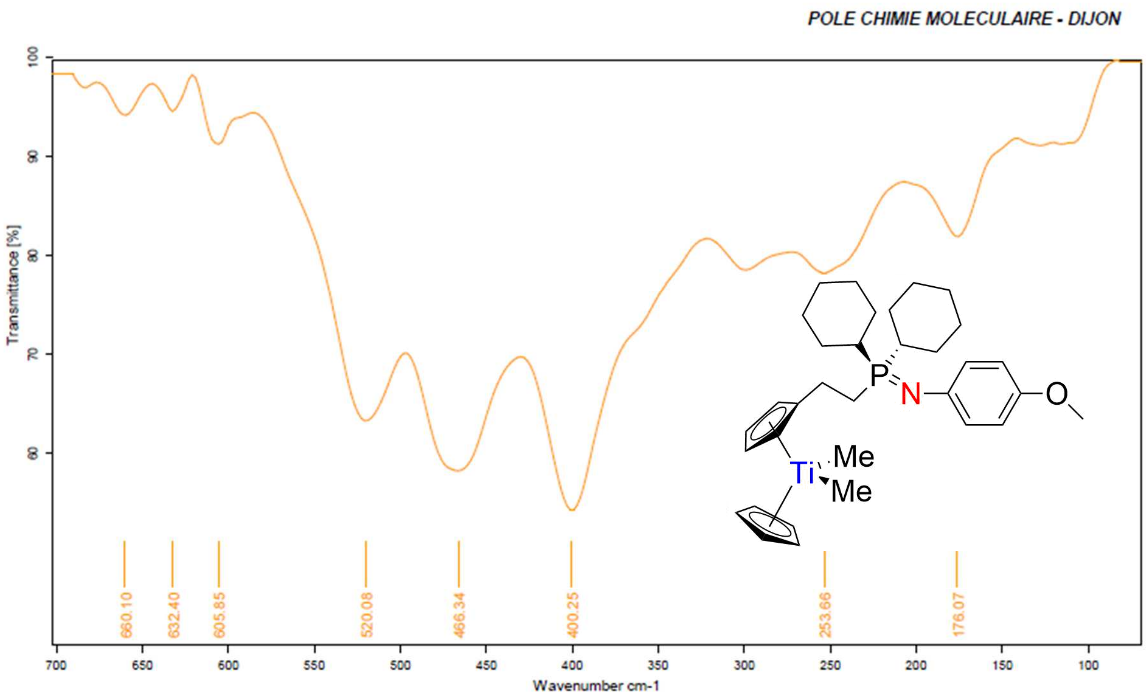
Spectrum 0-541: HRMS of 63 (Positive mode ESI, dichloromethane)



Echantillon :
17bq_670_MIR
résolution : 4 cm-1 (20 scans)

Spectre : 2017qbonnin_17bq_670_MIR.0 (dans D:\irdata_VERTEX\qt
Technique : BMS KBR [7500 - 370 cm-1] - Energie =
Opérateur : qbonnin
mesuré le 23/06/2017 sur VERTEX 70V

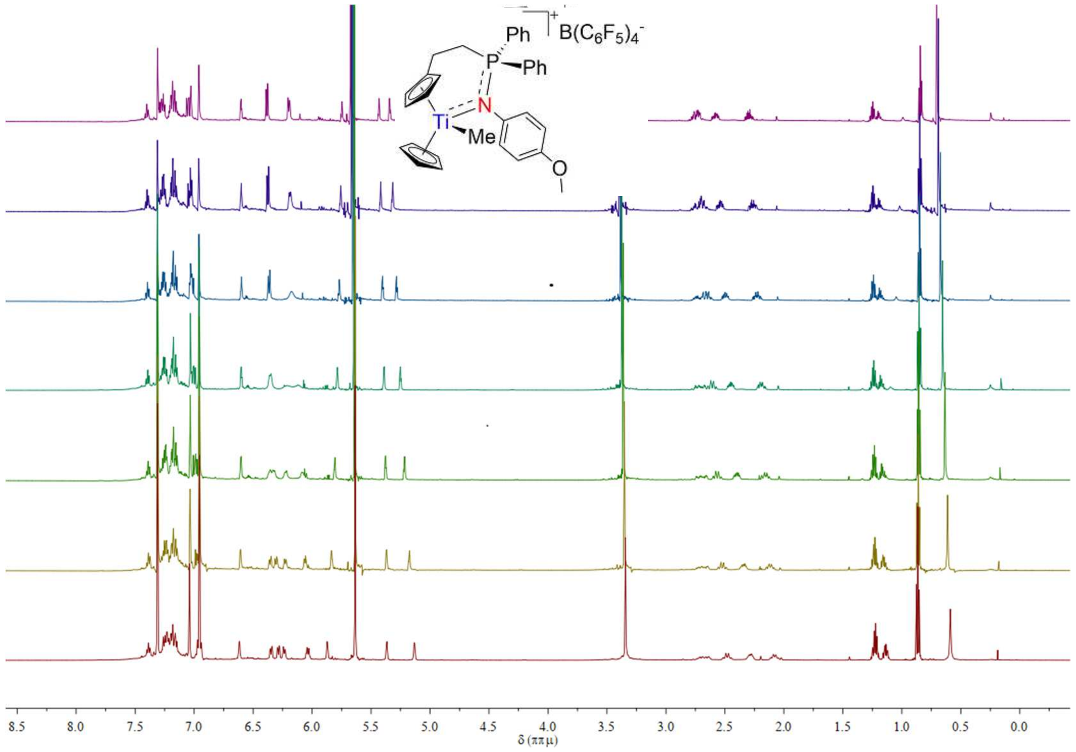
Spectrum 0-542: MIR of 63



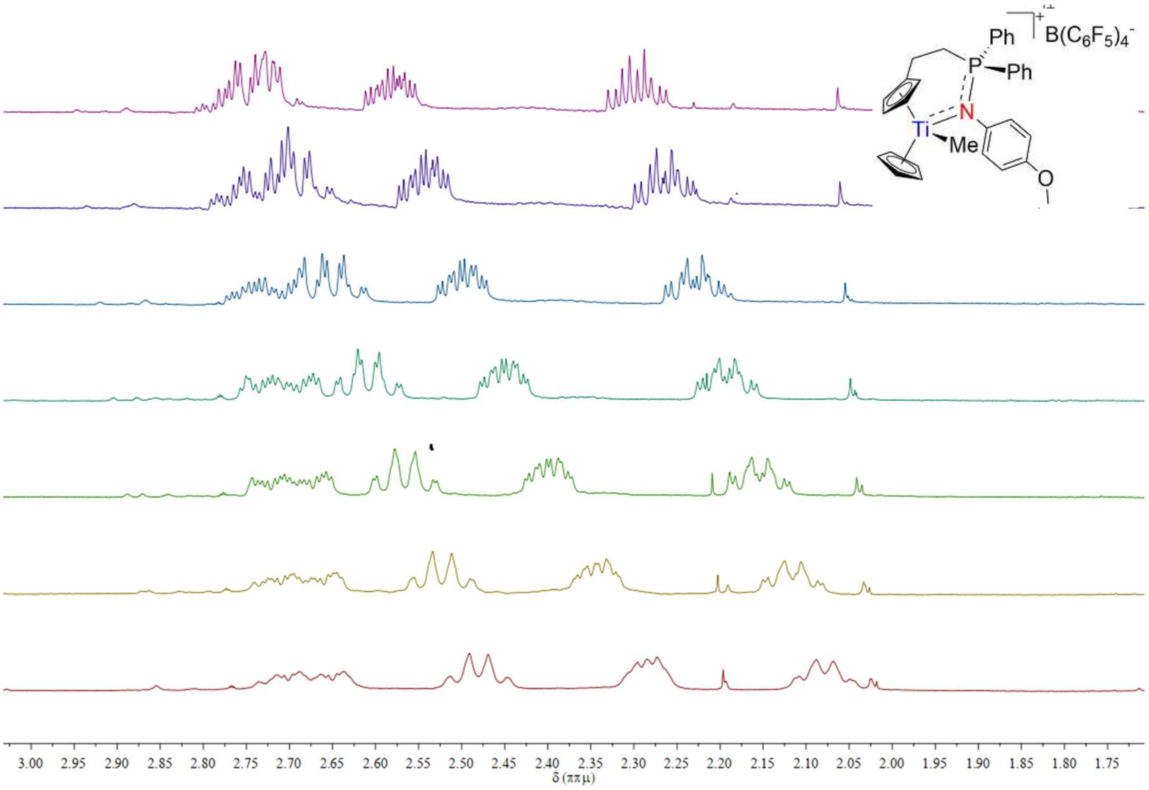
Echantillon :	Spectre : 2017qbonnin_17bq_670_FIR.0 (dans D:\irdata_VERTEX\qb
17bq_670_FIR	Technique : FIR BMS Si [710 - 80 cm-1] - Energie = :
	Opérateur : qbonnin
résolution : 4 cm-1 (20 scans)	mesuré le 23/06/2017 sur VERTEX 70V

Spectrum 0-543: FIR of 63

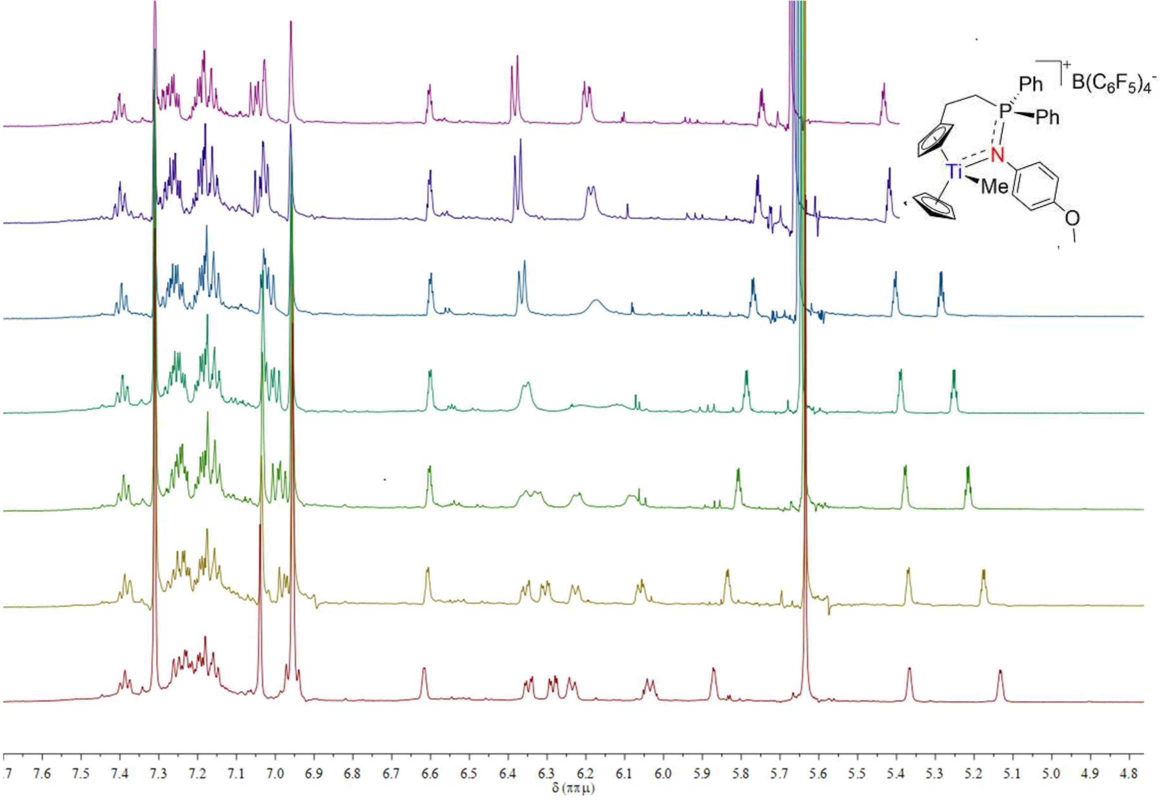
37. Compound **64**:



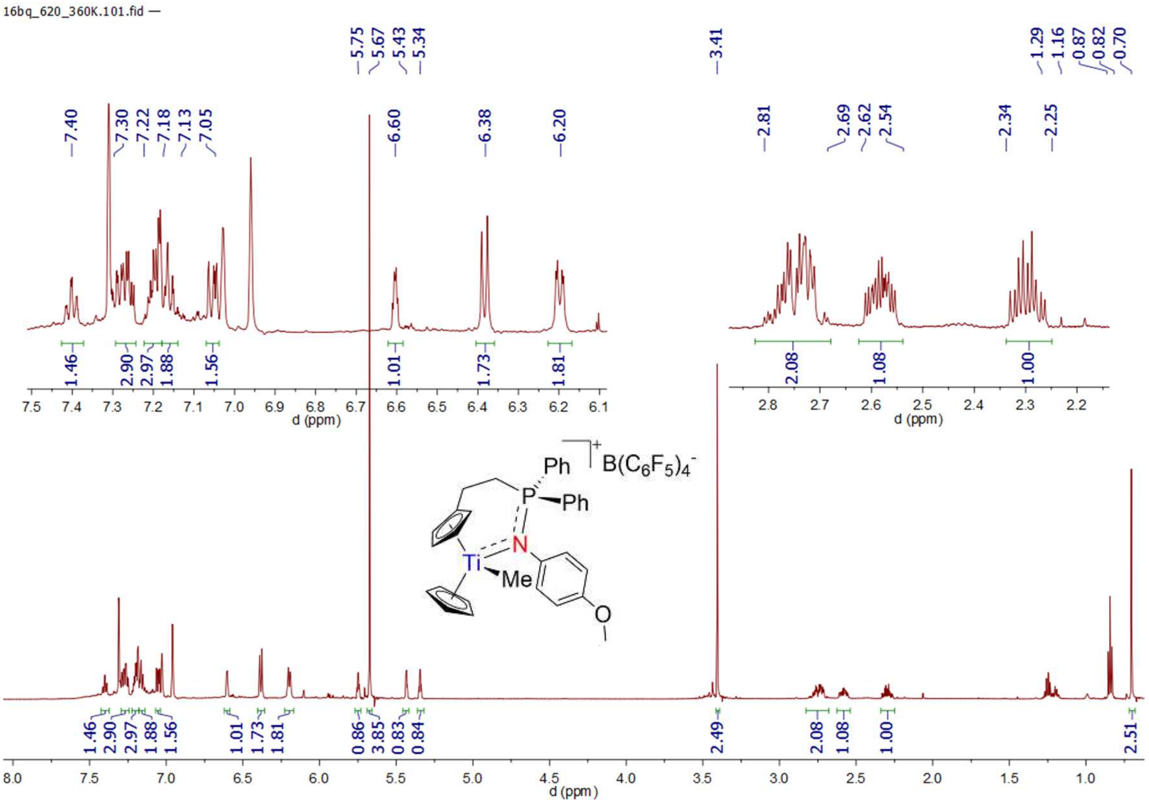
Spectrum 0-544 ^{1}H NMR superposition of 64 (600 MHz, 240-360K, bromobenzene-d_5)



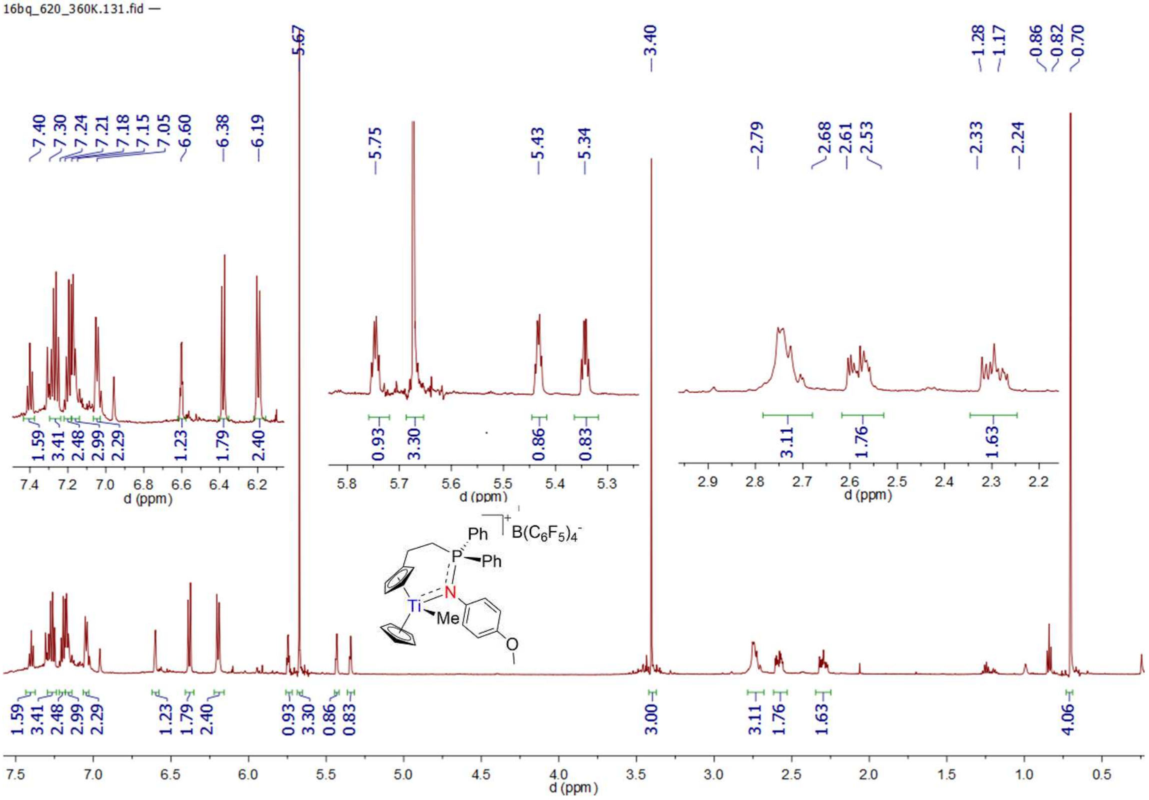
Spectrum 0-545: ^{1}H NMR superposition 3.00-1.75 ppm of 64 (600 MHz, 240-360K, bromobenzene-d_5)



Spectrum 0-546: ^{1}H NMR superposition 7.6-4.8 ppm of 64 (600 MHz, 240-360K, bromobenzene-d_5)

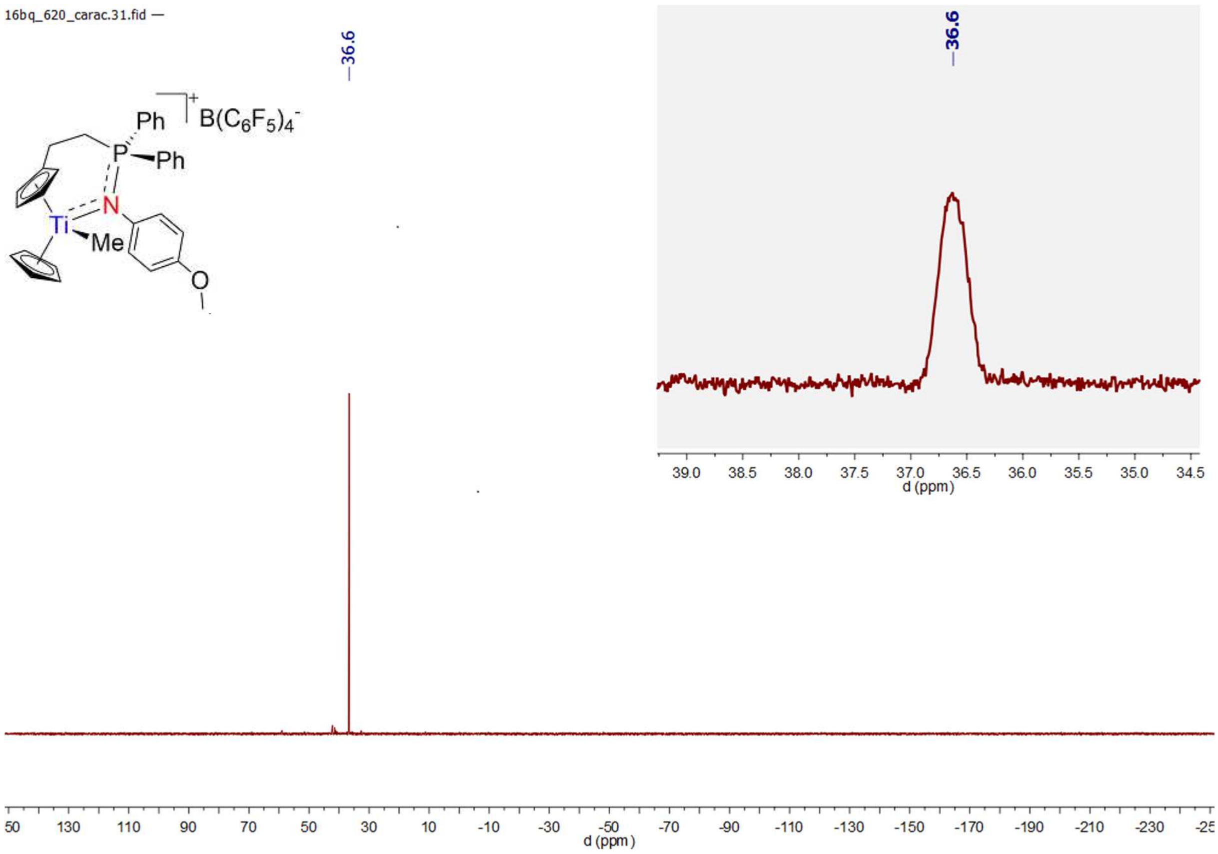


Spectrum 0-547: ^{1}H NMR of 64 (600.23 MHz, 360 K, bromobenzene-d$_5$)

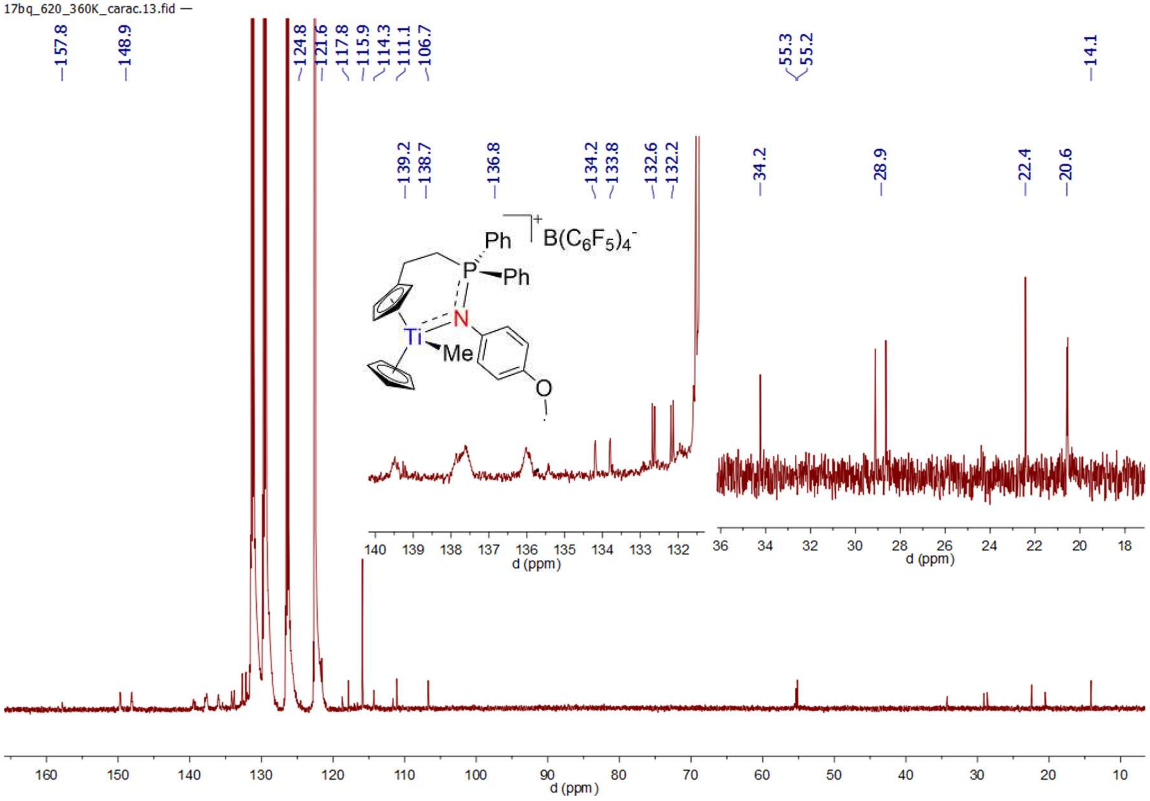


Spectrum 0-548: ^{1}H{^{31}P} NMR of 64 (600.23 MHz, 360 K, bromobenzene-d$_5$)

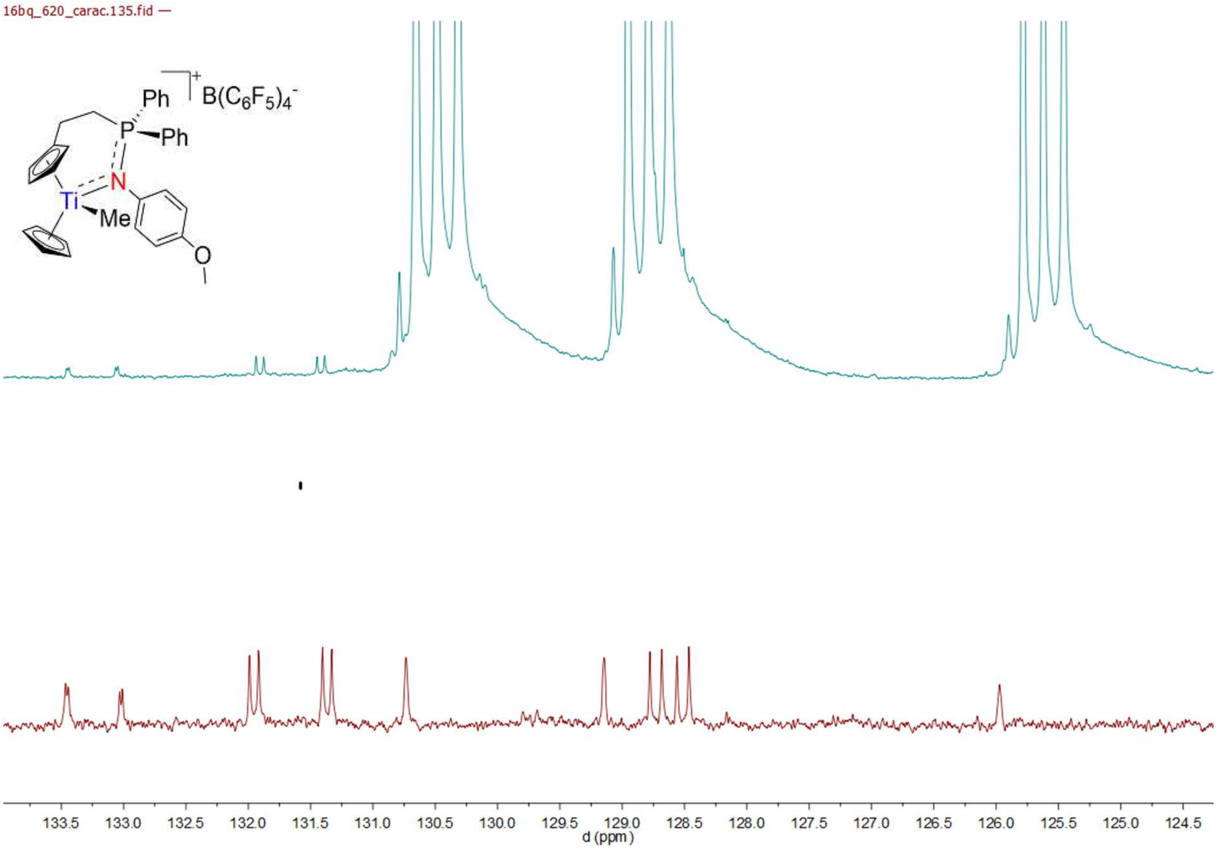
v



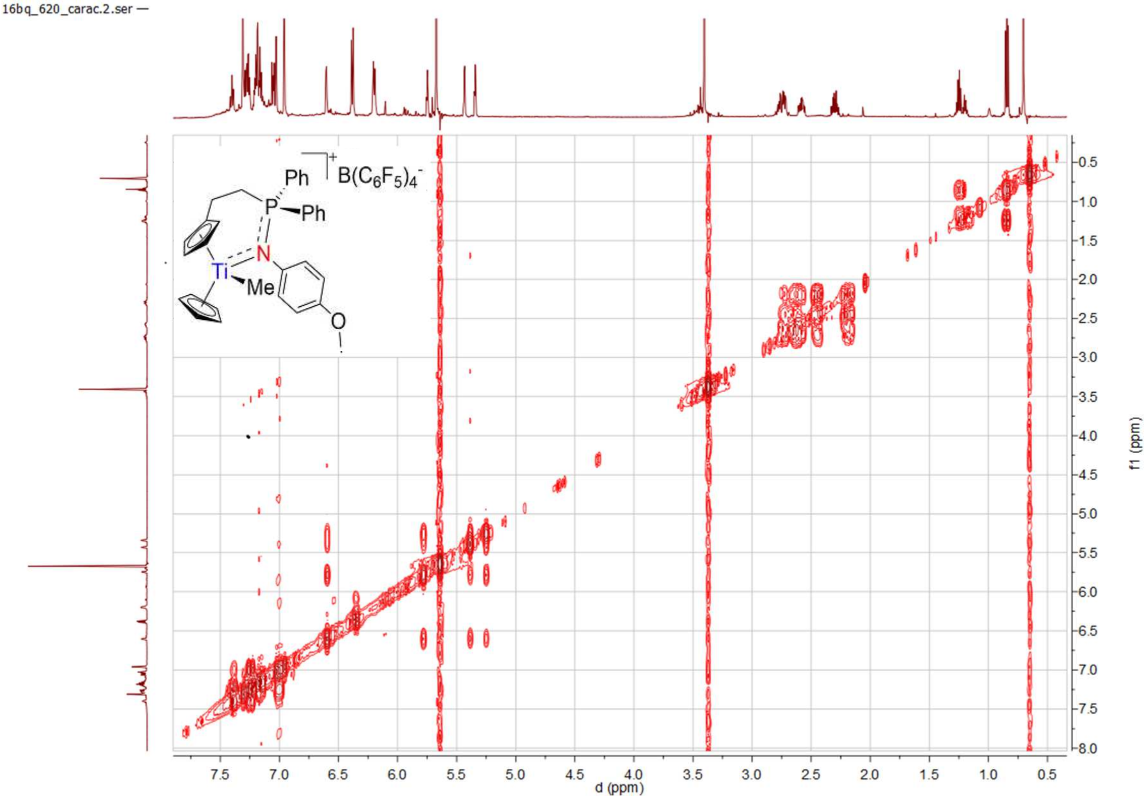
Spectrum 0-549: $^{31}P\{^1H\}$ NMR of 64 (202.46 MHz, 300 K, bromobenzene-d_5)



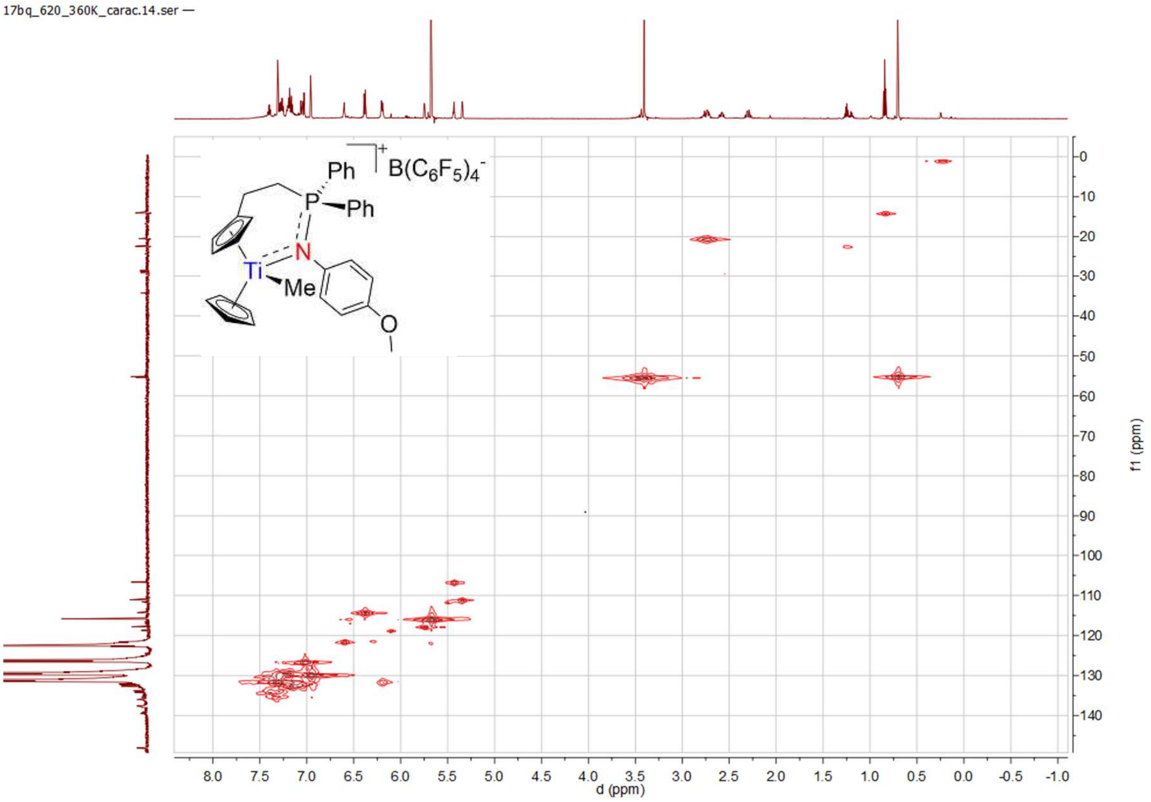
Spectrum 0-550: $^{13}C\{^1H\}$ NMR of 64 (150.94 MHz, 360 K, bromobenzene-d_5)



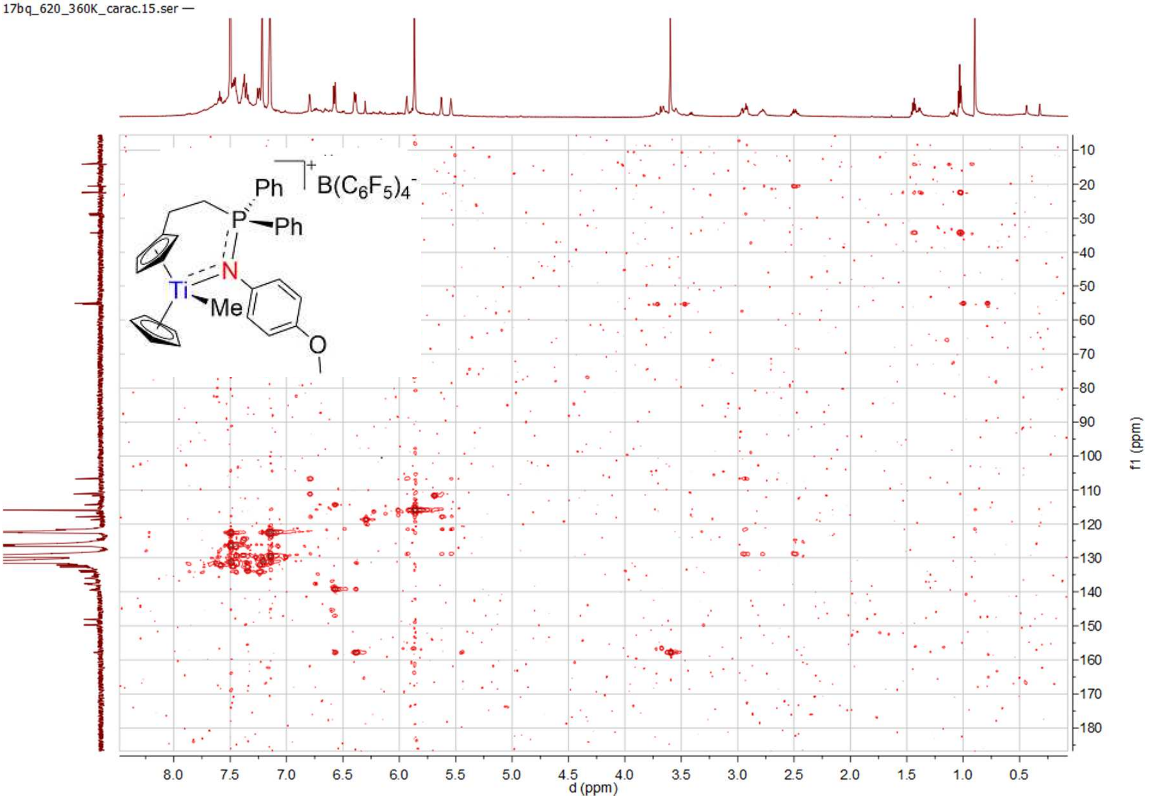
Spectrum 0-551: $^{13}C\{^1H\}$ NMR (top) correlated with dep135 (bottom) of 64 (150.94 MHz, 360 K, bromobenzene-d_5)



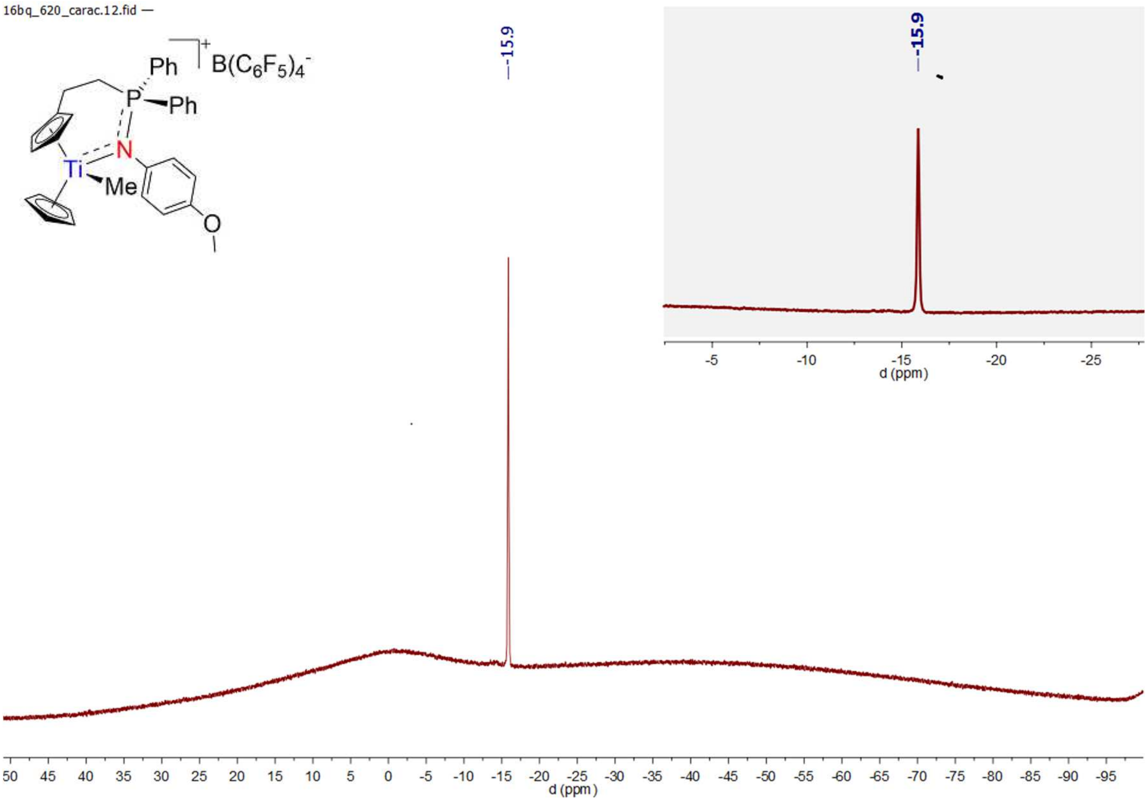
Spectrum 0-552: ^1H ^1H COSY of 64 (500.03 MHz, 300 K, bromobenzene-d_5)



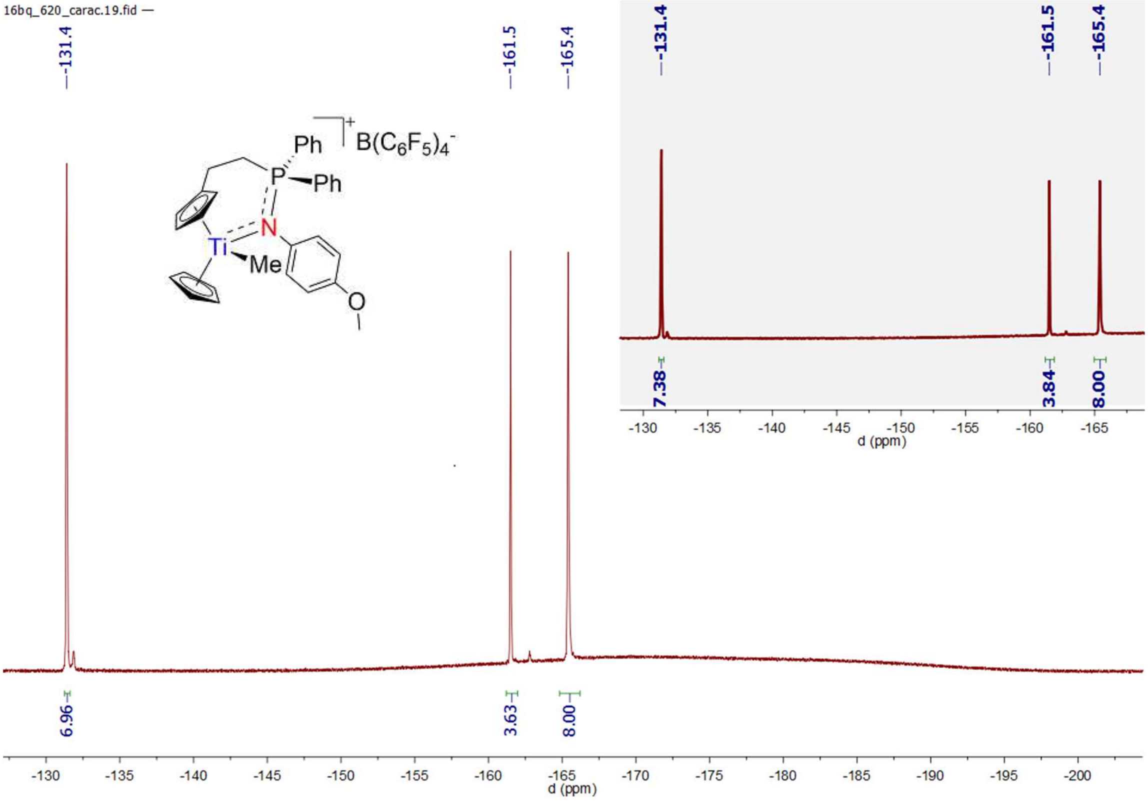
Spectrum 0-553: ^{1}H ^{13}C HMQC of 64 (600.23 MHz / 150.94 MHz, 360 K, bromobenzene-d$_5$)



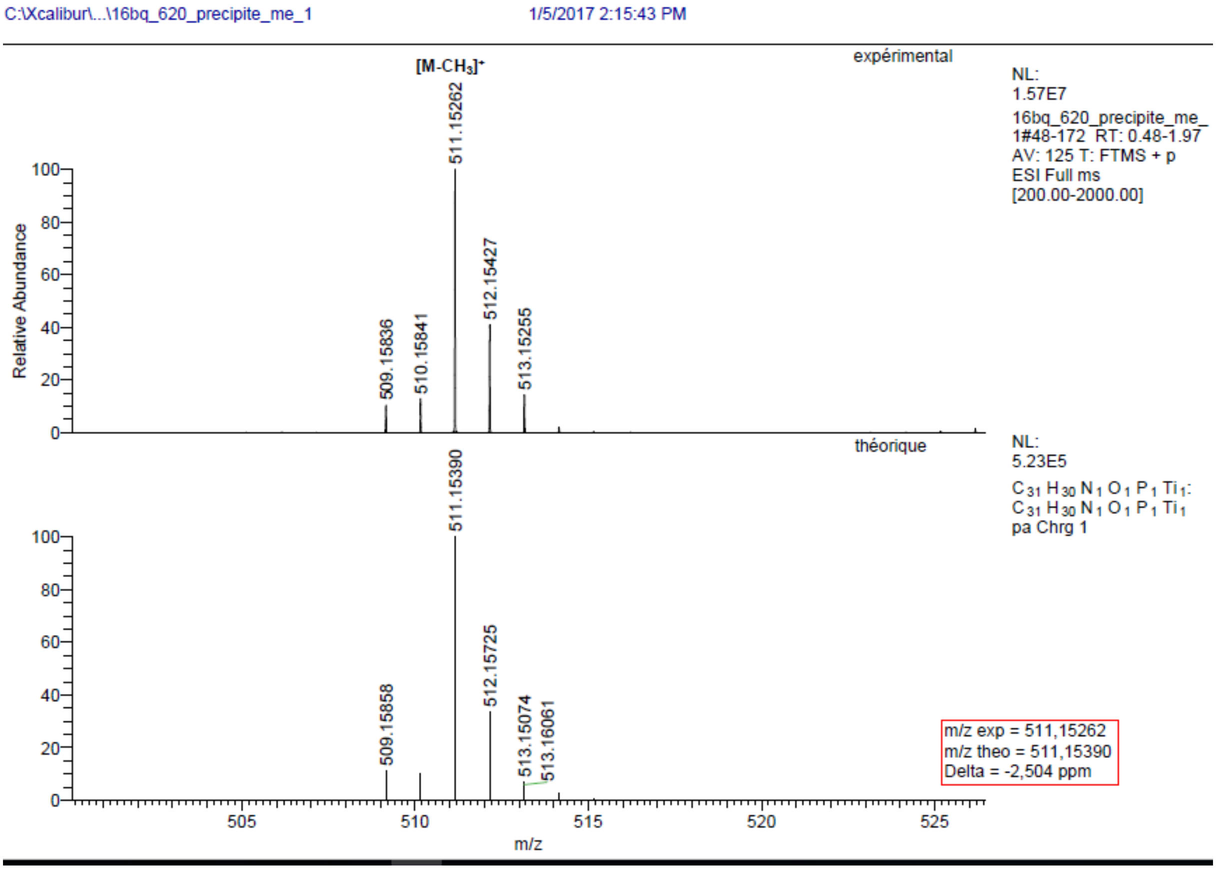
Spectrum 0-554: ^{1}H ^{13}C HMBC of 64 (600.23 MHz / 150.94 MHz, 360 K, bromobenzene-d$_5$)



Spectrum 0-555: $^{11}B\{^{1}H\}$ **and** ^{11}B **(opacified) NMR of 64 (160.42 MHz, 300 K, bromobenzene-d$_5$)**

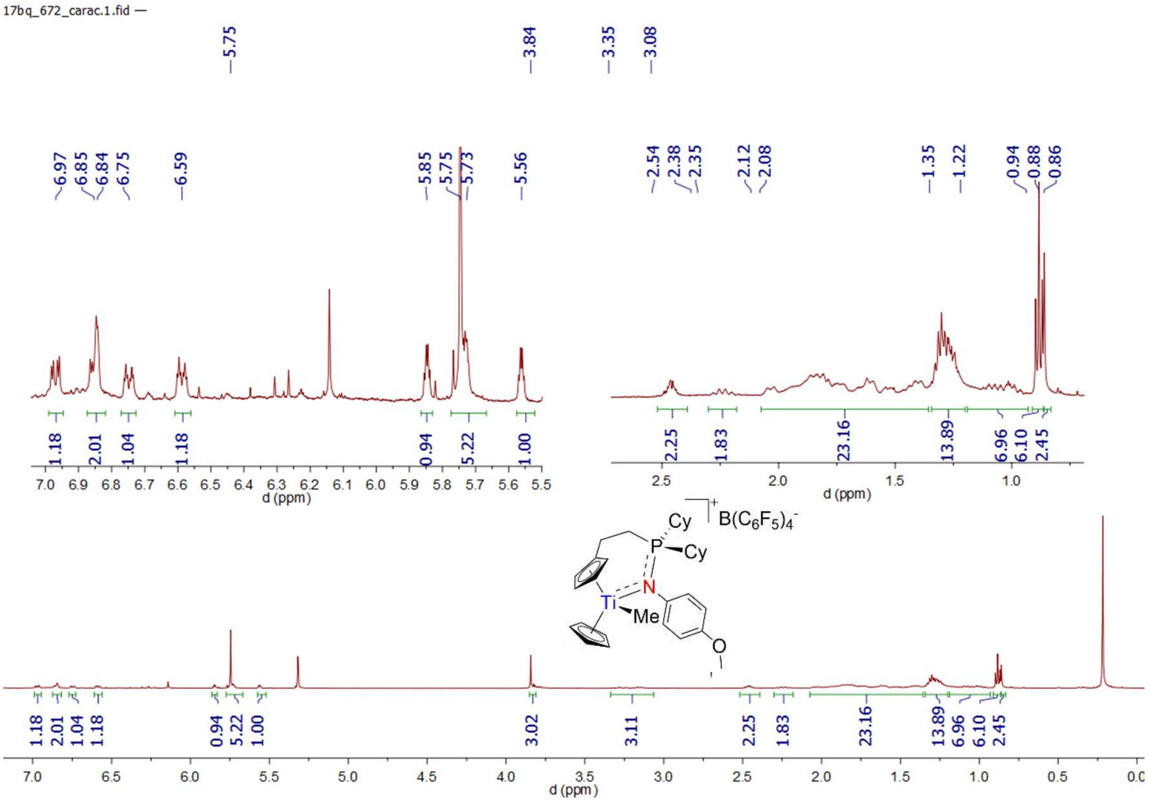


Spectrum 0-556: $^{19}F\{^{1}H\}$ **and** ^{19}F **(opacified) NMR of 64 (470.45 MHz, 300 K, bromobenzene-d$_5$)**

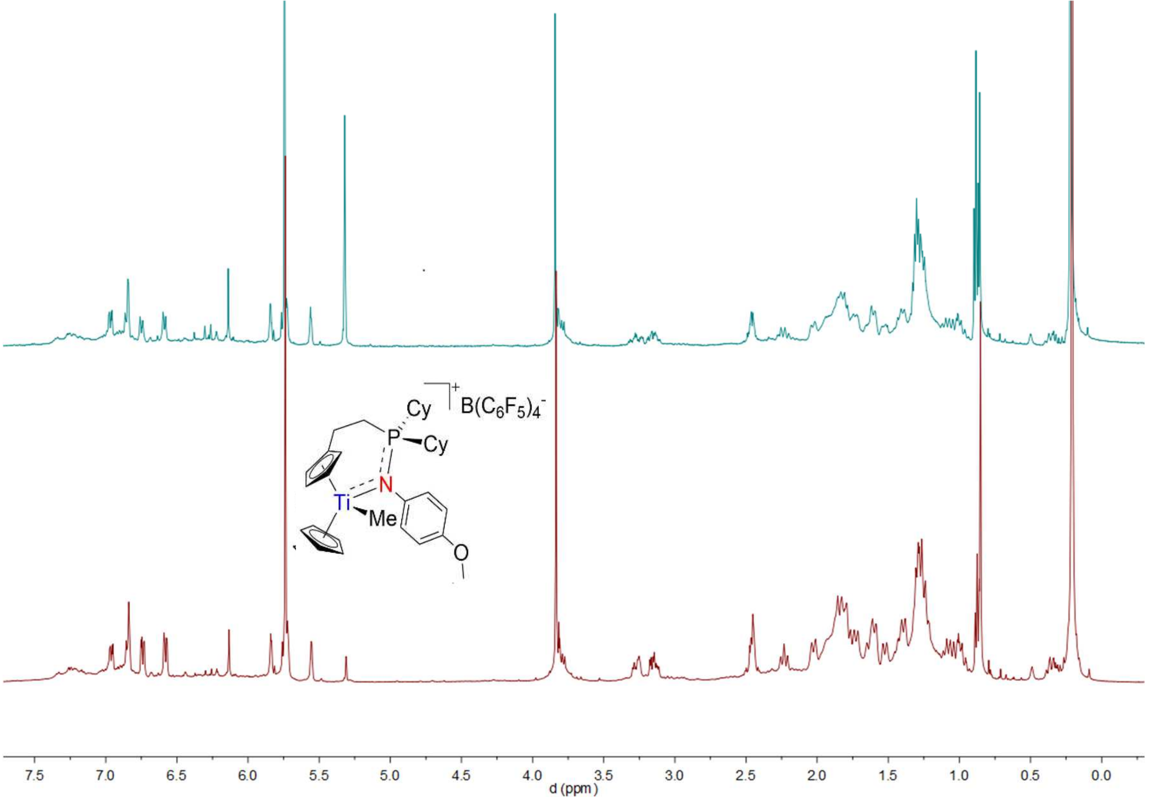


Spectrum 0-557: HRMS of 64 (ESI positive mod, dichloromethane)

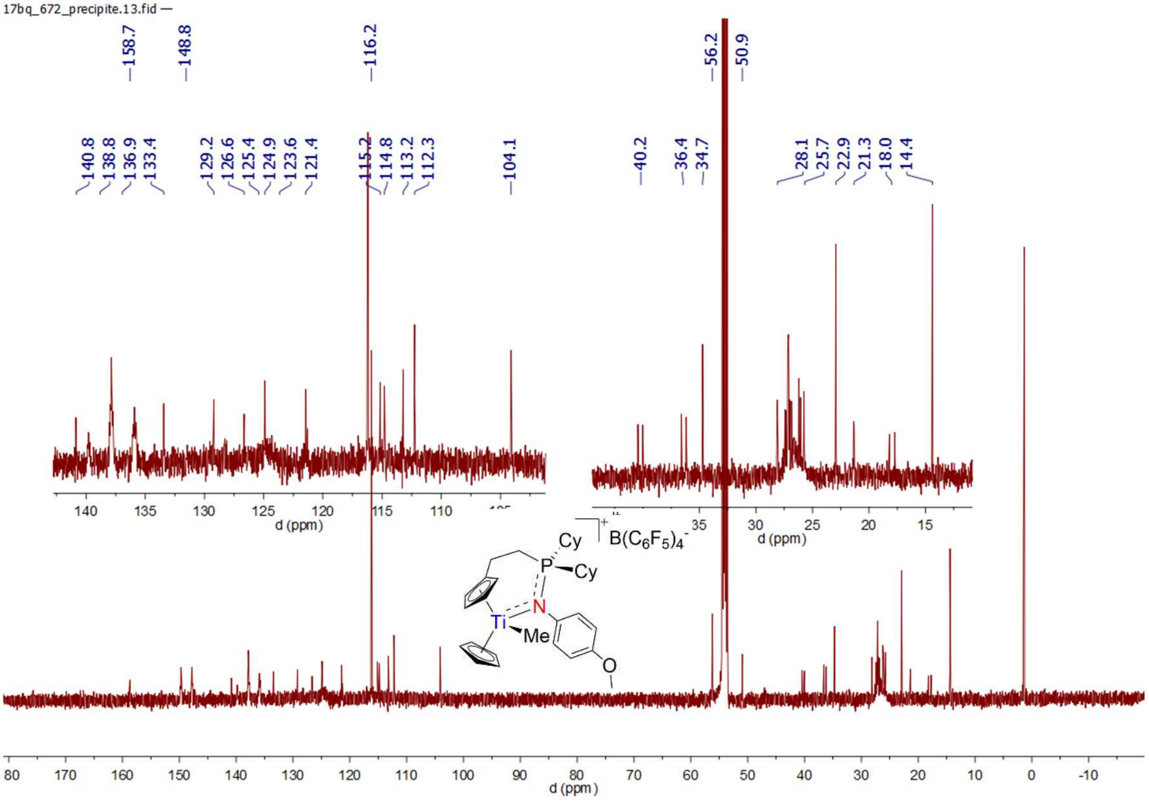
38. Compound **65**:



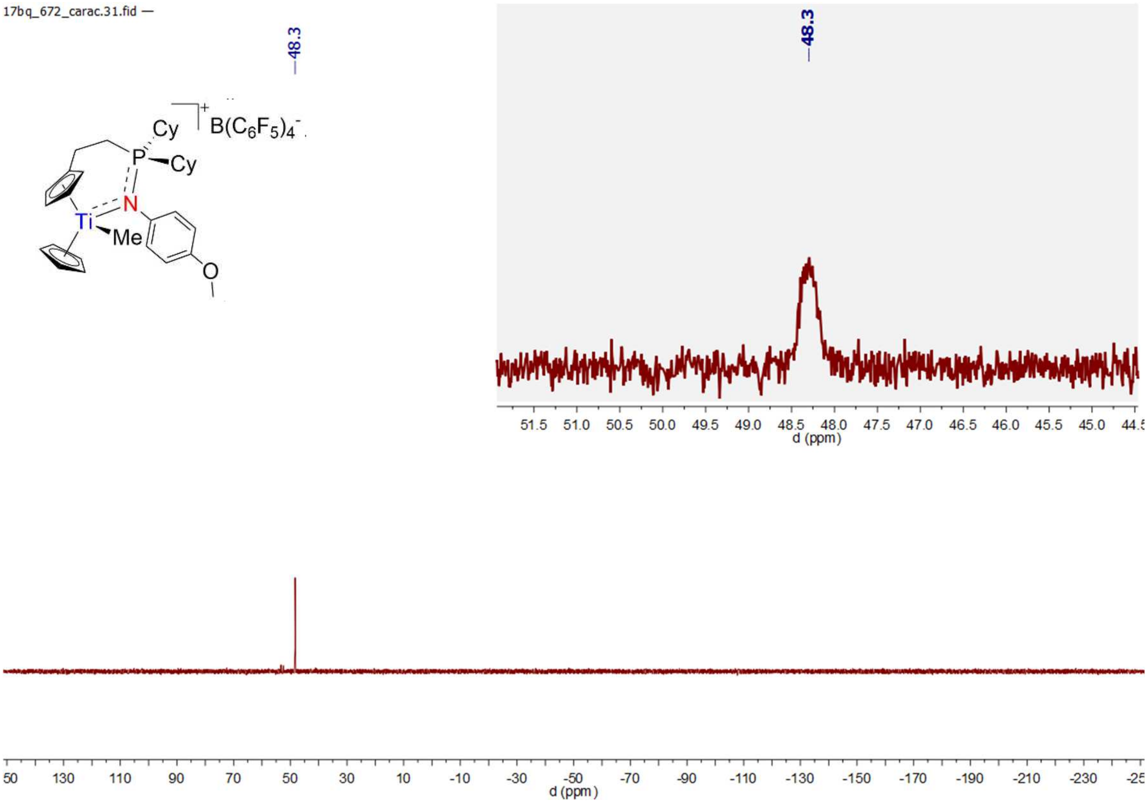
Spectrum 0-558: ^{1}H NMR of 65 (500.03 MHz, 300 K, dichloromethane-d$_2$)



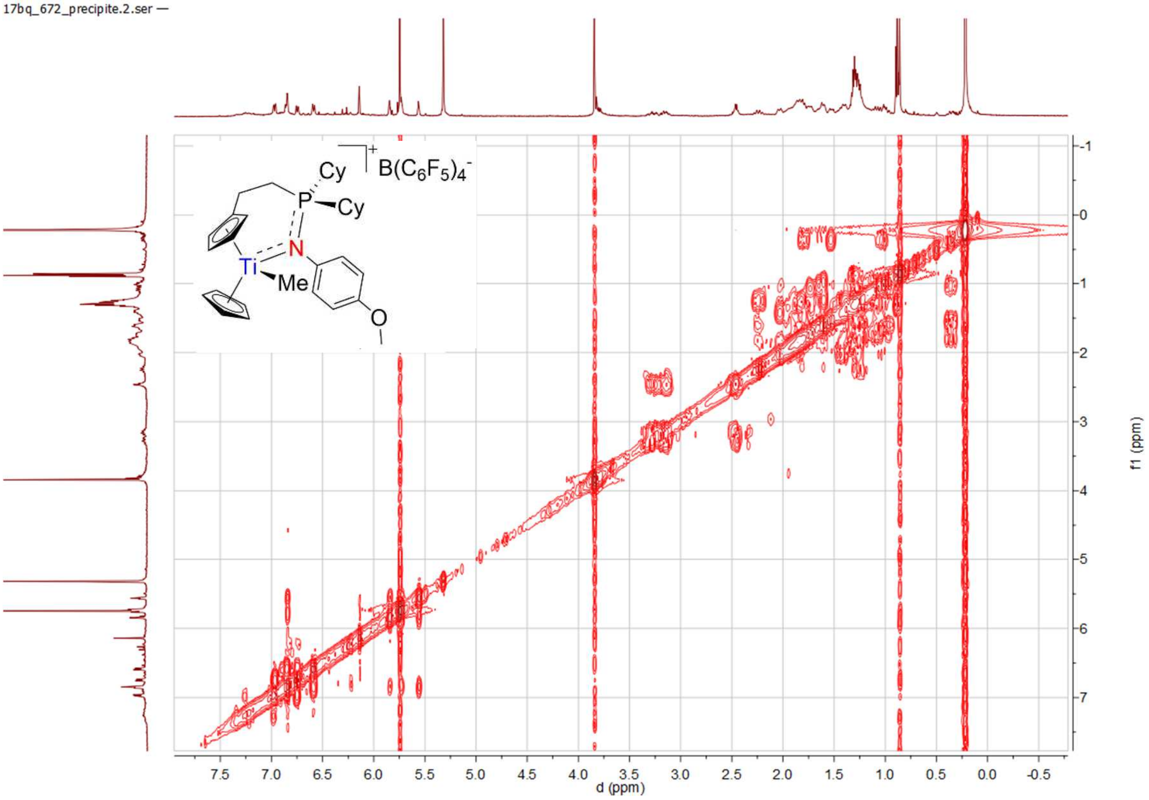
Spectrum 0-559: ^{1}H{^{31}P} NMR (top) correlated with ^{1}H (bottom) of 65 (500.03 MHz, 300 K, dichloromethane-d$_2$)



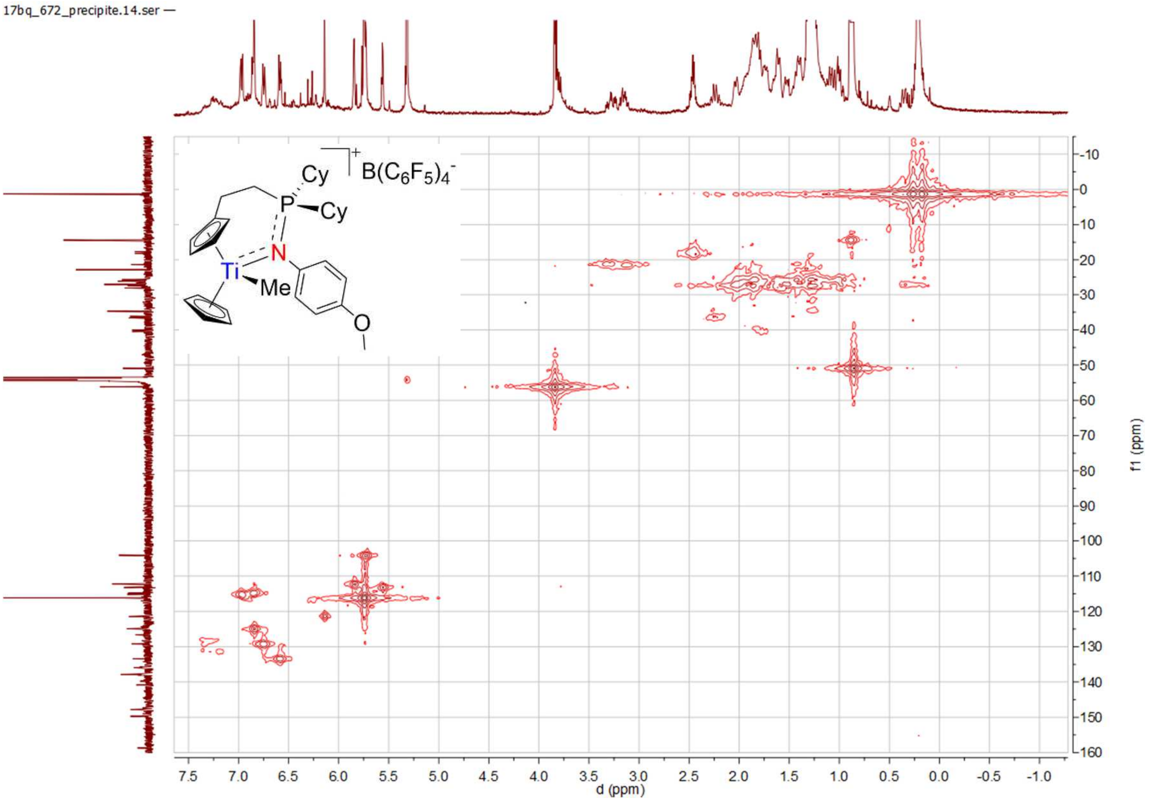
Spectrum 0-560: ^{13}C{^{1}H} NMR of 65 (125.75 MHz, 300 K, dichloromethane-d$_2$)



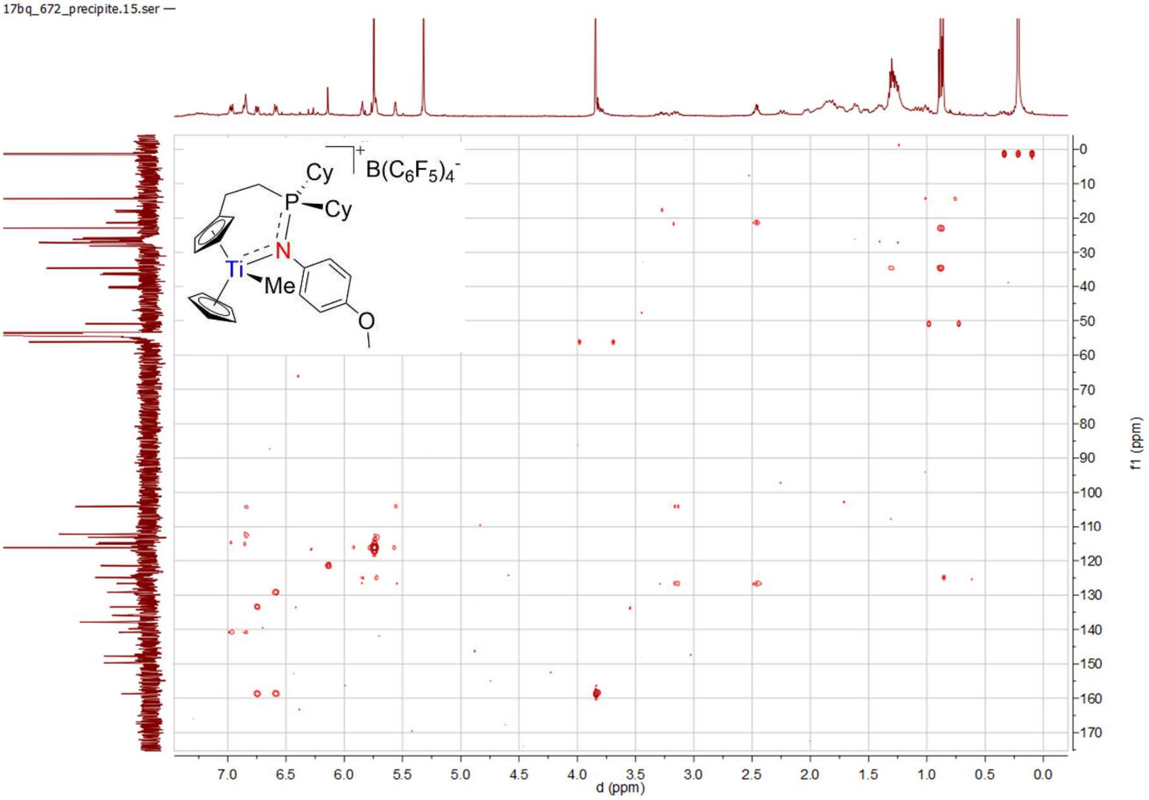
Spectrum 0-561: ^{31}P{^{1}H} and ^{31}P (opacified) NMR of 65 (202.41 MHz, 300 K, dichloromethane-d$_2$)



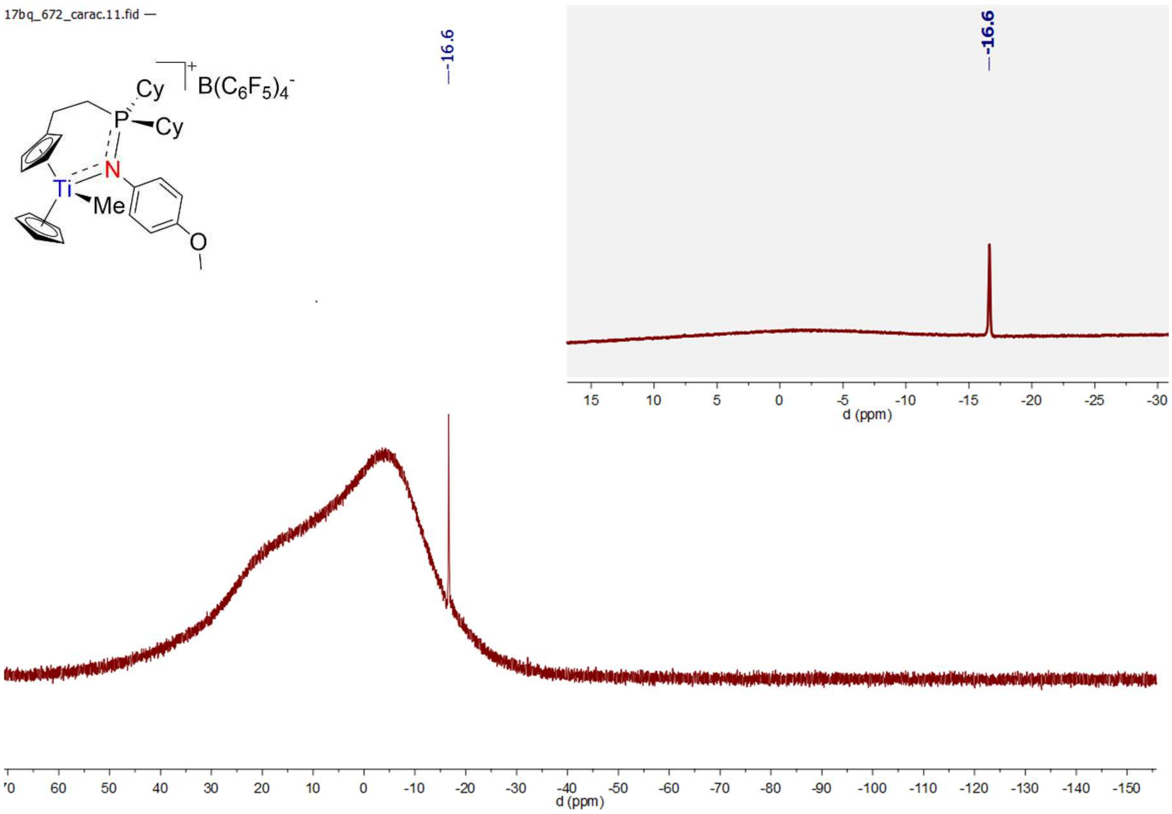
Spectrum 0-562: ^{1}H ^{1}H COSY of 65 (500.03 MHz, 300 K, 273 K, dichloromethane-d$_2$)



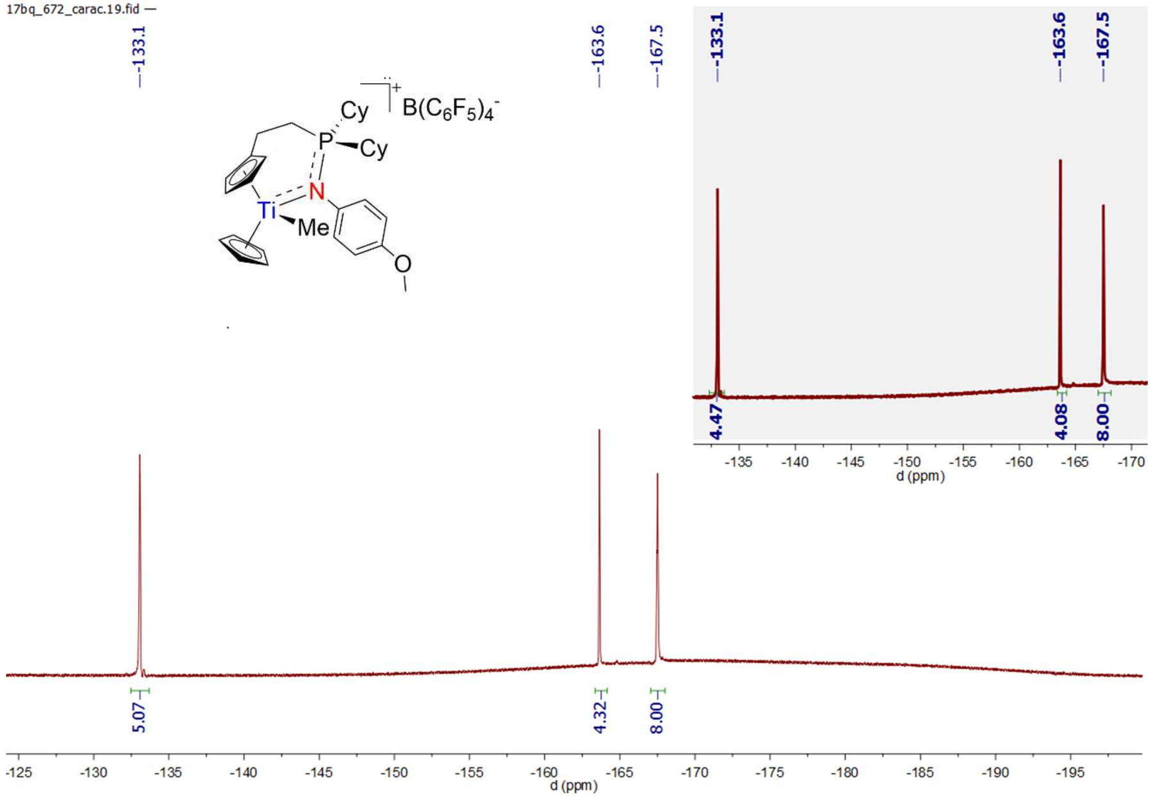
Spectrum 0-563: ^{1}H ^{13}C HMQC of 65 (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$



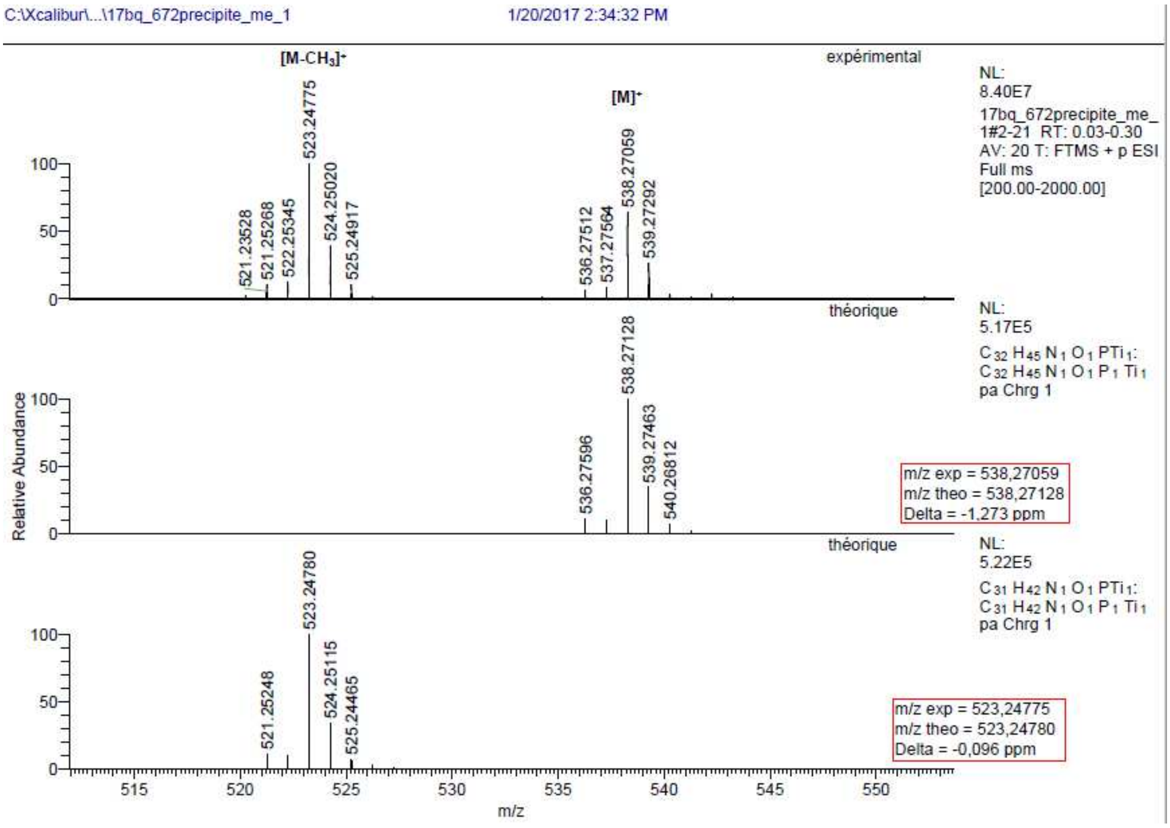
Spectrum 0-564: ^{1}H ^{13}C HMBC of 65 (500.03 MHz / 125.75 MHz, 300 K, dichloromethane-d$_2$)



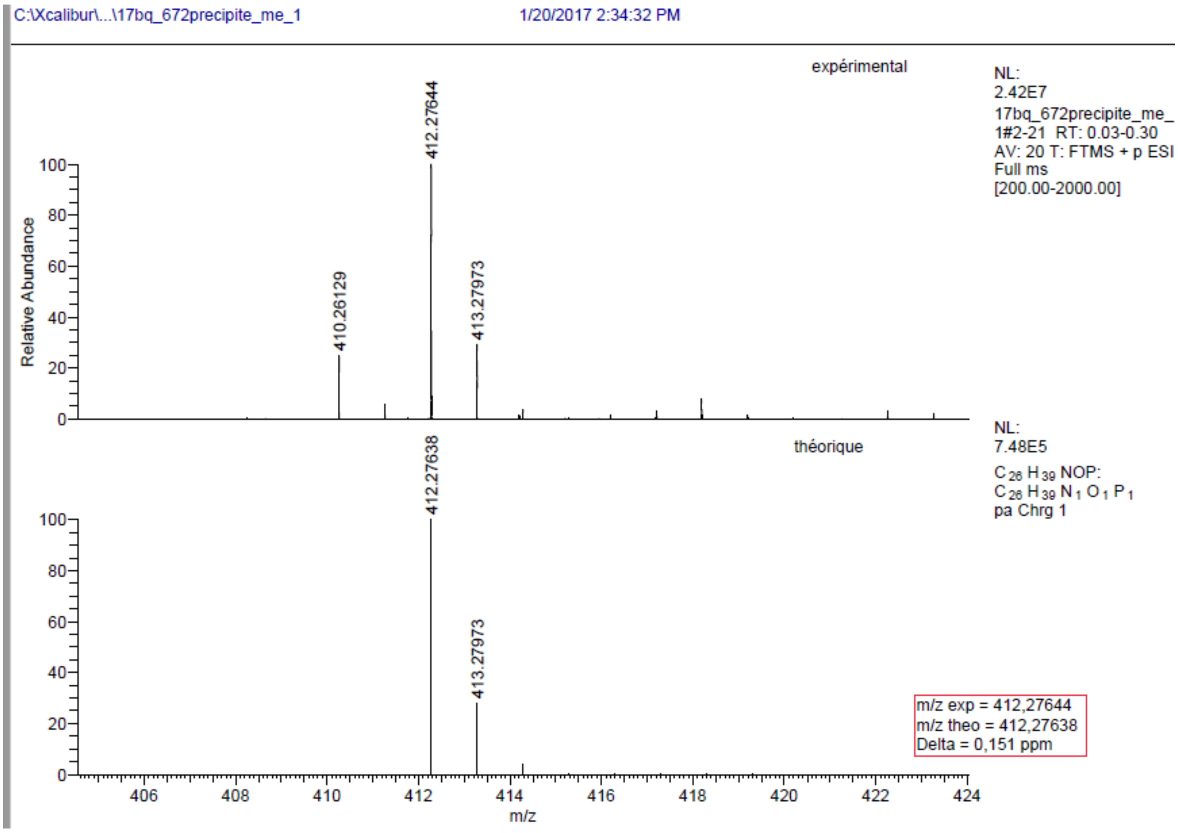
Spectrum 0-565: $^{11}B\{^1H\}$ and ^{11}B NMR of 65 (160.43 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-566: $^{19}F\{^1H\}$ and ^{19}F NMR of 65 (470.45 MHz, 300 K, dichloromethane-d_2)



Spectrum 0-567: HRMS of 65 (Positive mode ESI, dichloromethane)



Spectrum 0-568: HRMS of 65 (Positive mode ESI, dichloromethane)

Titre: Nouveaux complexes cationiques du groupe 4 comme potentielles paires frustrées de Lewis organométalliques: synthèse, réactivité, catalyse.

Mot-Clés: groupe 4, métallocènes, amine, paires frustrées de Lewis, catalyse, activation CH

Résumé:L'association d'une base de Lewis et d'un acide de Lewis tous deux encombrés a montré une réactivité nouvelle à l'égard de petites molécules telles que le dihydrogène. Un nouveau concept, appelé « paires frustrées de Lewis », a ainsi vu le jour en 2006. Initialement basé sur l'emploi de réactifs organiques issus des éléments principaux du tableau périodique (P/B, N/B, P/Al, N/Al …), ce concept a ensuite été étendu aux métaux de transition. Nous nous sommes intéressés à la synthèse de complexes de titane et de zirconium cationiques (acide de Lewis) associés à une amine en guise de base de Lewis. Le premier chapitre développe les travaux précédemment effectués sur la synthèse de complexes de titane ou de zirconium comportant une fonction amine, ainsi que les concepts clefs nécessaires à la compréhension de ce mémoire. La seconde partie de ce manuscrit porte sur la synthèse de nouveaux complexes de titane ou de zirconium ayant une fonction amine pendante. L'étude de ces composés ne montre aucune interaction entre l'atome d'azote et le métal. La réactivité de ces complexes organométalliques (N/Ti^+) a été ensuite étudiée dans un troisième chapitre. Le concept initialement envisagé n'a pu être appliqué sur ces complexes, car ils ont démontré une forte instabilité. En effet, des réarrangements ont lieu par activation de liaison CH au voisinage de l'azote. La quatrième partie de ce mémoire développe la synthèse de nouveaux complexes cationiques de titane directement liés à une phosphine ou une amine. Certains de ces complexes se sont montrés actifs vis-à-vis de l'hydrogénation catalytique de petites molécules. Dans une dernière partie, la synthèse de complexes titanocéniques cationiques portant une fonction iminophosphorane est développée, suivie d'une étude de leur réactivité en tant que paires frustrées de Lewis organométalliques.

Title: New cationic group 4 metallocenes as potential organometallic frustrated Lewis pairs: synthesis, reactivity and catalysis.

Keywords: group 4, metallocenes, amine, frustrated Lewis pair, catalysis, CH activation

Abstract: The concept of "frustrated Lewis pairs", developed in 2006, is based on the cooperative use of a bulky Lewis acid with a bulky Lewis base in order to activate small molecules such as dihydrogen. Numerous examples based on purely organic derivatives (e.g. phosphine/borane), have been developed over the years. More recently, new organometallic frustrated Lewis pairs have been described. In such system, one of the Lewis partner is a transition metal. The introduction of transition metals and hence of coordination chemistry, in the frustrated Lewis pair systems, broaden considerably the scope. of the possibilities in this field, particularly for catalytic purpose. The present manuscript describes the synthesis of potential organometallic frustrated Lewis pairs based on the combination of an amine and a cationic titanium or zirconium complex. Their synthesis and reactivity are the topic of the second and the third chapter respectively. The fourth part of this thesis deals with the synthesis of new cationic titanium complexes directly bound to a phosphane or an amine. Some of these compounds are shown to be catalytically active towards hydrogenation of small molecules. Lastly, the potential as organometallic frustrated Lewis pairs of cationic titanium complexes bearing an iminophosphorane function, was developed.