[(IMes)2Pt(H)(ClBC5H4SiMe3)]: a Borabenzene–Platinum Adduct with an Unusual Pt-Cl-B Interaction**

André Languérand, Stephanie S. Barnes, Guillaume Bélanger-Chabot, Laurent Maron,

Philippe Berrouard, Pierre Audet, and Frédéric-Georges Fontaine*

[1] Département de Chimie, Université Laval, 1045 Avenue de la Médecine, Québec (Québec), Canada, G1V 0A6

2 Université de Toulouse, INSA, UPS, LPCNO, 135 avenue de Rangueil, 31077 Toulouse (France)

Email:

frederic.fontaine@chm.ulaval.ca

(IMes)₂Pt(H)(Chloroboratabenzene): a Borabenzene Platinum Adduct with an Unusual Pt-Cl-B interaction [**]

André Languérand, Stephanie S. Barnes, Guillaume Bélanger-Chabot, Laurent Maron, Philippe Berrouard, Pierre Audet, and Frédéric-Georges Fontaine

Since the first report of a metallaboratrane by Hill in 1999,[1] there has been a quest for transition metal complexes containing a dative interaction with group XIII Lewis acids. In a recent report, Braunschweig demonstrated that $[(PCy_3)_2Pt^0]$ interacts with alanes to form Lewis adducts $[(PCy_3)_2Pt(AlX_3)]$,[2] which are rare examples of well characterized alane (M→AlR₃) complexes.[3-4] However, the analogous reaction with haloboranes does not yield Lewis adducts, but instead forms platinum boryl complexes,[5] a class of anionic boron containing species with numerous examples reported to date.[6] The only compounds having an M→B dative interaction with boron are supported by ambiphilic ligands.[7-9] While metallaboratranes having bis- or tris(methimazolyl)boranes have the borane coordinating the transition metal selectively,[10] the Lewis acid moiety of phosphinoboranes, prepared by Bourissou,[11] in addition to interacting with a transition metal can interact with an anionic ligand within the coordination sphere, depending on the nature of the transition metal and the ambiphilic ligand. Such an interaction is seldom observed with Lewis acids and is supported by ambiphilic ligands,[12] with the exception of BF₄ adducts and halocarboranes where the Lewis acidity of the boron can no be longer considered. [13]

[*]   A. Languérand, S. S. Barnes, G. Bélanger-Chabot, P. Berrouard, P. Audet, F.-G. Fontaine

Département de Chimie
Université Laval
Cité Universitaire, Québec, Qc, Canada, G1R 7P4
Fax: (+) ((1-418-656-7916))
E-mail: frederic.fontaine@chm.ulaval.ca

L. Maron

Université de Toulouse, INSA, UPS, LPCNO, 135 avenue de Rangueil, F-31077 Toulouse, France, and CNRS, LPCNO, UMR 5215 CNRS-UPS-INSA, F-31077 Toulouse, France

While borabenzene adducts are the subject of continuing interest, mainly for their electronic properties,[14] the coordination modes of these heterocyclic molecules with transition metals are quite limited.
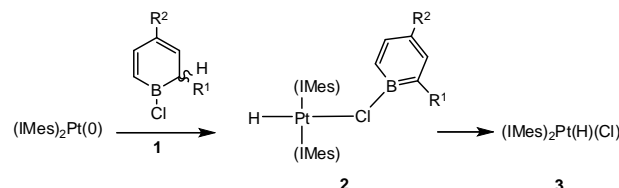
A common feature of borabenzenes (where L is a neutral Lewis base)[15] and boratabenzenes,[16] the analogue with anionic nucleophiles, is their coordination *via* the aromatic ring in a η⁶ fashion, analogous to arene and cyclopentadienyl ligands, respectively.[17] The exception is a phosphidoboratabenzene which binds transition metals by the phosphine moiety.[18] Using the efficient and general strategy of forming borabenzene organic adducts from boracyclohexadiene by the elimination of Me₃SiCl, first developed by Fu (Scheme 1),[19] we examined the possibility of
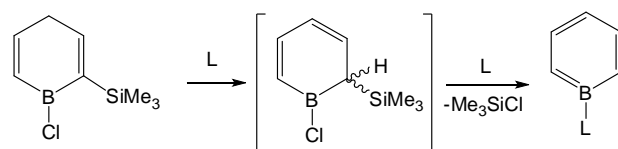
using a nucleophilic transition metal complex as a group to stabilize the Lewis acidic boron orbital on borabenzene. By applying this strategy, the isolation of an η¹-borabenzene transition metal adduct, and consequently of an unchelated borane having a dative interaction with a transition metal, could be possible. During these investigations, we observed that the B-Cl oxidative addition of the boracyclohexadiene with Pt⁰ does not occur, contrary to what was previously observed with haloboranes. Instead, formation of an μ-η¹-Cl-borabenzene adduct, which is a peculiar bonding mode for an unchelated Lewis acid, was observed.

Scheme 1. General scheme for formation of borabenzene adducts from boracyclohexadiene.

As evidenced by Braunschweig adducts (*vide supra*), $[(PCy_3)_2Pt^0]$ looked promising as a potent nucleophile for borabenzene formation; however, initial experiments with **1a** were problematic because of phosphine dissociation. Indeed, free phosphine was shown to interact with boracyclohexadiene precursors to form PCy₃-borabenzene adducts.[20] This result prompted us to use N-heterocyclic carbene ligands instead of phosphines since they are known to bind tightly to transition metals while offering good steric protection.[21]

Scheme 2. Formation of borabenzene adducts (**1a :** R¹ = TMS, R² = *i*Pr; **1b :** R¹ = TMS, R² = H; **1c :** R¹ = H, R² = H).

The addition of one equiv. of boracyclohexadiene **1a** to one equiv. of a yellow solution of $[(IMes)_2Pt^0]$ in benzene-d_6 gave a colorless reaction mixture. After 5 minutes, it was possible to observe one major compound, **2a,** in solution by ¹H NMR spectroscopy. In addition to resonances corresponding to the IMes carbene in the spectrum, the presence of a hydride signal at -22.41 ppm was observed, with a record breaking $^1J_{Pt-H}$ coupling constant of 1910 Hz.[22] Also present are resonances at 5.75 (d, $^3J_{H-H} = 10.4$

Hz), 7.25 (dd, $^3J_{H-H}$ = 10.4 Hz; $^4J_{H-H}$ = 2.1 Hz), and 7.80 ppm (d, $^4J_{H-H}$ = 2.1 Hz), for aromatic protons, at 3.25 (septet) and 1.64 ppm (d, $^3J_{H-H}$ = 6.9 Hz), for the iPr moiety bound to the aromatic group, and at 0.59 ppm for the trimethylsilyl (TMS) group. These resonances are characteristic of a 2-SiMe$_3$-4-iPr-borabenzene adduct. The integration of all resonances corresponds exactly to two IMes ligands for one hydride and one borabenzene moiety. A 2D ROESY NMR experiment was also carried out on **2a**. ROE correlations were observed between the borabenzene and the [(IMes)$_2$Pt(H)(Cl)] fragment. The methyl groups in the *ortho* position of the mesityl group were shown to have ROE correlations with both the resonances of TMS and the hydrogen at 5.75 ppm. Also, the methyl groups in the iPr moiety were shown to correlate with the aromatic proton in the *meta* position of the mesityl ring. Such correlations imply that the substituents in *ortho* and *meta* are in close proximity of the metal centre.

Compound **2a** was found to be unstable in solution and decomposes readily. Higher concentration, slight excess of **1a**, or removal of the solvent under reduced pressure increases the decomposition rate dramatically. Under dilute conditions ($\approx 10^{-6}$ M), compound **2a** was the major component in solution for up to three days. However, a single inorganic degradation product (**3**) was always present and was shown to be inversely proportional to **2a** in solution. All attempts to crystallize compound **2a** failed and only **3** was isolated. Compound **3** has very similar ^{1}H NMR spectroscopic features to **2a**, with the IMes resonances and the hydride (-17.96 ppm and $^1J_{Pt-H}$ = 1550 Hz) shifted slightly down field, although it contains no borabenzene moiety. Suitable crystals for x-ray crystallography were obtained from a saturated solution of **3** in benzene, which allowed its identification as [(IMes)$_2$Pt(H)(Cl)].[23]

The similarity of the spectroscopic features of **2a** and **3** suggest that the former complex should also be a hydrido chloro platinum[II] species, but with a borabenzene bound to it. Also, it is evident that the aromatization of the borabenzene does not involve the elimination of the TMSCl, but instead occurs *via* C-H bond activation by the Pt^0 precursor, forming the stable hydride complex. In order to account for the observed data, three different structures are proposed for the adduct, none of which has ever been reported with borabenzene. The first proposed structure involves an interaction between the hydride and the borabenzene, but can be ruled out since no broadening caused by the quadrupolar boron is observed for the hydride. Our second hypothetic structure has a Pt→B interaction, similarly to the phosphinoborane complex interaction reported by Bourrisou.[11c] The final hypothesis involves an interaction between the chloride and the borabenzene which is quite unusual for boron containing species other than BF$_4$ and halocarboranes. To gain more structural information, the synthesis of two other analogues, using precursors **1b** and **1c**, was undertaken.

The addition boracyclohexadienes **1b** and **1c** (see Scheme 2) to [(IMes)$_2$Pt^0] in benzene-d_6 gave similar reactivity to **1a**, affording **2b** and **2c**. The feasibility of the reaction with **2c** confirms that the elimination of TMSCl is not a requirement for the borabenzene adduct formation. It can also be observed by ^{1}H NMR that the borabenzene in **2c** is symmetric on an NMR time scale, since H^2/H^6 and H^3/H^5 are equivalent. However, the hydride and the IMes-bound ^{1}H NMR resonances are, within a margin of error, equivalent for all three complexes. Also equivalent are the ^{195}Pt resonances for all borabenzene complexes (**2a** = -4364 ppm, **2b** = **2c** = -4367 ppm), which are upfield from **3** (-4285 ppm). While the acquisition of an ^{11}B NMR spectrum proved difficult to obtain, especially for **2c** which decomposed during the acquisition, it was possible to observe that both **2a** and **2b** have similar chemical shifts (36.2 and 38.8 ppm,

respectively) which are in the expected range for borabenzene adducts.[19]

The similarity of the spectroscopic features of the (IMes)$_2$Pt(H)(Cl) core in **2a**–**2c** tends to favour the hypothesis of a bridging chloride adduct. Indeed, if a Pt-B interaction were present, a more significant shift in the ^{195}Pt and ^{1}H resonance should arise depending on the nature of the borabenzene. DFT calculations were done in order to credit or discredit the presence of a Pt-B or a Pt-Cl-B interaction. Modeling of **2b** show no minimum energy state that would account for any Pt-B interaction; however the Pt-Cl-B model did show an energy minimum (Figure 1).
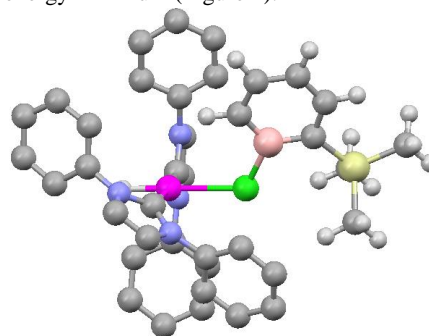

Figure 1. Optimized structure of the chloroboratabenzene complex **2b**. The hydrogen atoms and the methyl groups on the Mes were omitted for clarity.

In the complex **2b**, a marked interaction between the chlorine atom and the boron is obtained (B-Cl distance of 1.93Å). An NBO analysis indicates that a covalent bond is formed between these two atoms, and thus that a chloroboratabenzene ligand is obtained. At the same time, the Pt-Cl bond is elongated (2.47Å in [(IMes)$_2$PtHCl] and 2.56Å in **2b**) and the Pt-H bond is slightly shortened (1.53Å in **2b** and 1.56Å in [(IMes)$_2$PtHCl]), which could account for the large coupling constant between these two elements observed in the borabenzene complexes. At the NBO level, in **2b**, a remaining interaction between Cl and Pt is found at the second order donor-acceptor level (roughly 20 kcal.mol^{-1}). For comparison, a NBO analysis of [(IMes)$_2$PtHCl] already reveals a mainly ionic bond between Pt and Cl (second order interaction of more than 90 kcal.mol^{-1}). NMR calculations of the ^{11}B nuclear shift were carried out for the complex **2b** as well as for the "free" chloroboratabenzene. In complex **2b**, a ^{11}B nuclear shift of 35 ppm is obtained whereas a value of 51ppm is found for the "free" chloroboratabenzene. These values are in excellent agreement with the experimental data and clearly indicate that the chloroboratabenzene is coordinated to the platinum centre.

It was not possible to determine the nature of the organic fragment resulting from the dissociation of the borabenzene fragment from complex **2**.[24] However, the addition of 2 or 10 equiv. of pyridine to **2b** leads to the formation of the borabenzene adduct **4** with the silyl group still present. Formation of the same compound was observed in the addition of pyridine to chlorobora-bis(trimethylsilyl)cyclohexadiene, by elimination of TMSCl. The connectivity of **4** was confirmed using X-ray crystallography. It can be speculated that the boron is the subject of a nucleophilic attack, leading to the displacement of **3** by pyridine to form **4**. If such a mechanism occurs, it should be possible to use a chloride anion as a nucleophile to synthesize a chloroboratabenzene salt. 5 minutes after the addition of [NBu$_4$]Cl to **2b** in benzene-d_6, it was possible to observe in the ^{1}H NMR spectrum both the clean formation of **3** as the major inorganic compound (~90%) and new borabenzene

fragment (**5**). Although it was not possible to isolate the new borabenzene product, a significant upfield shift of the α and β methylene resonances of the butyl chains of the tetrabutyl ammonium cation, which integrates for a 1:1 ratio with the borabenzene fragment, was observed. The absence of such a shift when the only two other species present in solution, **3** and [NBu$_4$]Cl, are mixed together, suggests formation of a tetrabutylammonium salt of 1-chloro(2-trimethylsilyl)boratabenzene (**5**).
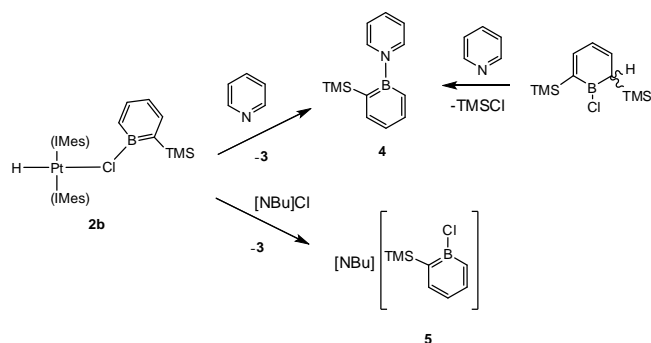
Scheme 3. Nucleophilic displacement of the borabenzene from **2b**.

Compounds **2a-2c** are, to our knowledge, the first examples of unsupported M-X-BR$_3$ complexes where the Lewis acidity of a borane is still available. The stability of the platinum-NHC, relative to usual Pt-L dative bonds, seems to be a requirement to prevent the weak [(IMes)$_2$Pt(H)(Cl)]-borabenzene adducts from dissociating to form L-borabenzene adducts. Whereas it might be economically more viable to use the Fu strategy to generate borabenzene adducts, the synthetic pathway we are reporting will favour the presence of additional functionalities on the borabenzene by not requiring a TMS group, and makes hypothetically possible the interaction with less donating L groups to form new and unusual borabenzene adducts, which we are currently examining.

Complete characterization and spectroscopic data of all new compounds can be found in the Supporting Information.

Experimental Section

[(IMes)$_2$Pt^0][25], **1a**[14a], **1b**[19], and **1c**[26] were synthesised according to literature procedures. In a typical experiment, a dilute solution of **1** (0.004 mmol) in C$_6$D$_6$ is added dropwise to a yellow solution of [(IMes)$_2$Pt^0] (0.0035g, 0.00425 mmol) in C$_6$D$_6$. NMR spectra show the formation of species **2**, which decomposes to give **3** over time. This decomposition is greatly accelerated if **1** is present in even minor excess.

2a: ^{1}H NMR (benzene-d_6): δ 7.78 (d, J = 2.1 Hz, 1H, H^3), 7.25 (dd, J = 10.3 Hz, 1 Hz, 1H, H^5), 6.76 (s, 8H, H^{meta}Mes), 5.94 (s, 4H, H^{imid}), 5.75 (d, J = 10.3 Hz, 1H, H^6), 3.25 (sept, J = 6.9 Hz, 1H, CH(CH$_3$)$_2$), 2.32 (s, 12H, Me^{para}Mes), 1.85 (s, 24H, Me^{ortho}Mes), 1.64 (d, J = 6.9 Hz, 6H, CH(CH_3)$_2$), 0.59 (s, 9H, TMS), -22.42 (s, $^1J_{P-tH}$ = 1910 Hz, 1H, Pt-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 137.8 (C^{para}Mes), 137.3 (C^3), 136.5 (C^{ipso}Mes), 135.7 (C^{ortho}Mes), 133.6 (C^5), 129.3 (C^{meta}Mes), 123.7 (C^6), 121.7 (C^{imid}), 26.6 (CH(CH_3)$_2$), 21.3 (Me^{para}Mes), 18.6 (Me^{ortho}Mes), 2.1 (TMS). C^2, C^4, and the carbenic carbon were not observed. ^{195}Pt (benzene-d_6): δ -4364 (d, $^1J_{Pt-H}$ = 1918 Hz). ^{11}B NMR (benzene-d_6): δ 36.2.

2b: ^{1}H NMR (benzene-d_6): δ 8.00 (dd, J = 7.2, 1.3 Hz, 1H, H^3), 7.41 (ddd, J = 10.3, 6.7, 1.4 Hz, 1H, H^5), 6.98 (td, J = 6.8, 0.7 Hz, 1H, H^4), 6.75 (s, 8H, H^{meta}Mes), 5.95 (s, 4H, H^{imid}), 5.80 (dt, J = 10.1, 0.7 Hz, 1H, H^6), 2.30 (s, 12H, Me^{para}Mes), 1.86 (s, 24H, Me^{ortho}Mes), 0.58 (s, 9H, TMS), -22.42 (s, $^1J_{Pt-H}$ = 1915 Hz, 1H, Pt-H). ^{13}C{^{1}H} NMR

(benzene-d_6): δ 139.3 (C^3), 137.8 (C^{para}Mes) 136.4 (C^{ipso}Mes), 135.6 (C^{ortho}Mes), 135.3 (C^5), 129.3 (C^{meta}Mes), 123.4 (C^6), 121.6 (C^{imid}), 112.5 (C^4), 21.3 (Me^{para}Mes), 18.5 (Me^{ortho}Mes), 2.0 (TMS). C^2, and the carbenic carbon were not observed. ^{195}Pt (benzene-d_6): δ -4367 (d, $^1J_{Pt-H}$ = 1960 Hz). ^{11}B NMR (benzene-d_6): δ 38.8.

2c: ^{1}H NMR (benzene-d_6): δ 7.76 (dd, J = 10.5, 7.1 Hz, 2H, H^3 and H^5), 7.00 (tt, J = 7.0, 1.1 Hz, 1H, H^4), 6.77 (s, 8H, H^{meta}Mes), 6.31 (dd, J = 10.5, 1.1 Hz, 2H, H^2 and H^6), 5.93 (s, 4H, H^{imid}), 2.30 (s, 12H, Me^{para}Mes), 1.88 (s, 24H, Me^{ortho}Mes), -22.44 (s, $^1J_{Pt-H}$ = 1905 Hz, 1H, Pt-H). ^{13}C{^{1}H} (HSQC) NMR (benzene-d_6): δ 133.6 (C^3 and C^5), 128.8 (C^{meta}Mes), 121.5 (C^{imid}), 120.4 (C^2 and C^6), 111.9 (C^4), 21.1 (Me^{para}Mes), 18.2 (Me^{ortho}Mes). C^{ipso}Mes, C^{ortho}Mes, C^{para}Mes and the carbenic carbon were not observed. ^{195}Pt (benzene-d_6) : δ -4367 (d, $^1J_{Pt-H}$ = 1910 Hz).

3: ^{1}H NMR (benzene-d_6): δ 6.80 (s, 8H, H^{meta}Mes), 6.08 (s, 4H, imidazol), 2.33 (s, 12H, Me^{para}Mes), 2.07 (s, 24H, Me^{ortho}Mes), -17.97 (s, $^1J_{Pt-H}$ = 1542 Hz, Pt-H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 180.1 (carbene), 137.3 (C^{ipso}Mes), 136.9 (C^{para}Mes), 136.1 (C^{ortho}Mes), 129.0 (C^{meta}Mes), 120.8 (C^{imid}), 21.4 (Me^{para}Mes), 18.9 (Me^{ortho}Mes). ^{195}Pt NMR (benzene-d_6): δ -4285 (d, $^1J_{Pt-H}$ = 1523 Hz).

[1] A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Angew. Chem.* **1999**, *111*, 2920-2923; *Angew. Chem. Int. Ed.* **1999**, *38*, 2759-2761.

[2] H. Braunschweig, K. Gruss, K. Radacki, *Angew. Chem.* **2007**, *119*, 7929-7931; *Angew. Chem. Int. Ed.* **2007**, *46*, 7782-7784.

[3] a) J. M. Burlitch, M. E. Leonowicz, R. B. Petersen, R. E. Hugues, *Inorg. Chem.* **1979**, *18*, 1097-1105; b) J. M. Mayer, J. C. Calabrese, *Organometallics* **1984**, *3*, 1292-1298.

[4] These compounds are supported by bridging hydrogen atoms: a) J. T. Golden, T. H. Peterson, P. L. Holland, R. G. Bergman, R. A. Andersen, *J. Am. Chem. Soc.* **1998**, *120*, 223-224; b) J. W. Bruno, J. C. Huffman, K. G. Caulton, *J. Am. Chem. Soc.* **1984**, *106*, 444-445.

[5] H. Braunschweig, K. Radacki, K. Uttinger, *Inorg. Chem.* **2007**, *46*, 8796-8800; and references therein.

[6] A few leading reviews: a) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380-5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254-5274; b) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535-559.

[7] a) F.-G. Fontaine, J. Boudreau, M-H. Thibault, *Eur. J. Inorg. Chem.* **2008**, 5439-5454; b) I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster, F. Breher, *Dalton Trans.* **2008**, 5836-5865.

[8] Wolczanski reported borane adducts with (silox)$_3$Ta that have some Ta→B dative character. J. B. Bonanno, T. P. Henry, P. T. Wolczanski, A. W. Pierpont, T. R. Cundari, *Inorg. Chem.* **2007**, *46*, 1222-1232.

[9] Other complexes reported having a M→B interaction have been discredited: a) H. Braunschweig, T. Wagner, *Chem. Ber.* **1994**, *127*, 1613-1614; b) H. Braunschweig, T. Wagner, *Z. Naturforsch. B* **1996**, *51*, 1618-1620; c) H. Braunschweig, C. Kollann, *Z. Naturforsch. B* **1999**, *54*, 839-842.

[10] A few leading references: a) M. R. St.-J. Foreman, A. F. Hill, G. R. Owen, A. J. P. White, D. J. Williams, *Organometallics* **2003**, *22*, 4446-4450; b) I. R. Crossley, A. F. Hill, *Organometallics* **2004**, *23*, 5656-5658; c) V. K. Landry, J. G. Melnick, D. Buccella, K. Pang, J. C. Ulichny, G. Parkin, *Inorg. Chem.* **2006**, *45*, 2588-2597; d) I. R. Crossley, A. F. Hill, A. C. Willis, *Organometallics* **2006**, *25*, 289-299; e) K. Pang, J. M. Tanski, G. Parkin, *Chem. Commun.* **2008**, 1008-1010; f) I. R. Crossley, A. F. Hill, A. C. Willis, *Organometallics* **2008**, *27*, 312-315; g) I. R. Crossley, A. F. Hill, *Dalton Trans.* **2008**, 201-203.

[11] A few leading references: a) S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu, D. Bourissou, *Angew. Chem.* **2006,** *118,* 1641-1644*; Angew. Chem. Int. Ed.* **2006**, *45*, 1611-1614; b) M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron, D. Bourissou, *Angew. Chem.* **2007,** *119,* 8737-8740; *Angew. Chem. Int. Ed.* **2007**, *46*, 8583-8586; c) S. Bontemps, M. Sircoglou, G. Bouhadir, H. Puschmann, J. A. K. Howard, P. W. Dyer, K. Miqueu, D. Bourissou, *Chem. Eur. J.* **2008**, *14*, 731-740; d) M. Sircouglou, S. Bontemps, G. Boudhadir, N. Soffon, K. Miqueu, W. Gu, M, Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.* **2008**, *130*, 16729-16738; e) S. Bontemps, G. Bouhadir, D. C. Apperley, P. W. Dyer, K. Miqueu, D. Bourissou, *Chem. Asian. J.* **2009**, *4*, 428-435.

[12] To our knowledge, all compounds having an M-X-B interaction are supported by ambiphilic ligands. See ref. 7a and references within.

[13] According to SciFinder, more than 840 BF$_4$ and 64 halocarborane adducts have been reported.

[14] A few leading references: a) D. J. H. Emslie, W. E. Piers, M. Parvez, *Angew. Chem.* **2003***, 115,* 1290-1293*; Angew. Chem. Int. Ed.* **2003**, *42*, 1252-1255; b) M. J. D. Bosdet, W. E. Piers, T. S. Sorensen, M. Parvez, *Angew. Chem.* **2007***,119,* 5028-5031; *Angew. Chem. Int. Ed.* **2007**, *46*, 4940-4943; c) C. A. Jaska, W. E. Piers, R. McDonald, M. Parvez, *J. Org. Chem.* **2007**, *72*, 5234-5243.

[15] a) R. Boese, N. Finke, T. Keil, P. Paetzold, G. Schmid, *Z. Naturforsch., B: Chem. Sci.* **1985**, *40B,* 1327-1332; b) M. Amendola, K. E. Stockman, D. A. Hoic, W. M. Davis, G. C. Fu, *Angew. Chem. Int. Ed.* **1997**, *36*, 267-269.

[16] A few leading references: a) G. E. Herberich, H. Ohst, *Adv. Organomet. Chem.* **1986**, *25*, 199-236; b) G. C. Fu, *Adv. Organomet. Chem.* **2001**, *47*, 101-119; c) P. Cui, Y. Chen, G. Li, W. Xia, *Angew. Chem.* **2008***, 120,* 10092-10095*; Angew. Chem. Int. Ed.* **2008**, *47*, 9944-9947.

[17] Some of these complexes will exhibit different hapticities, but will still be analogous to arene complexes: a) G. E Herberich, U. Englert, A. Fischer, J. Ni, A. Schmitz, *Organometallics* **1996**, *15*, 5496-5501; b) P. Cui, Y. Chen, X. Zeng, J. Sun, G. Li, W. Xia, *Organometallics* **2007**, *26*, 6519-6521.

[18] D. A. Hoic, W. M. Davis, G. C. Fu, *J. Am. Chem. Soc.* **1996**, *118*, 8176-8177.

[19] D. A. Hoic, J. R. Wolf, W. M. Davis, G. C. Fu, *Organometallics* **1996**, *15*, 1315-1318.

[20] The addition of **1-*i*Pr** to [(PCy$_3$)$_2$Pt(0)] in benzene-*d*^{6} leads to a complex mixture where only *4-i*Pr-C$_5$H$_4$B-PCy$_3$ and [(PCy$_3$)$_2$Pt(H)(Cl)] were isolated (see Supporting Information).

[21] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39-91.

[22] Elsevier claimed to have the largest $^1J_{Pt-H}$ coupling reported of 1738 Hz. M. A. Duin, N. D. Clement, K. J. Cavell, C. J. Elsevier, *Chem. Commun.* **2003**, 400-401.

[23] The crystallographic data are given in the supporting information.

[24] It was not possible to isolate the boron containing species, but broad and large signals for the TMS and the *i*Pr indicate that oligomerization or Diels-Alder reactivity probably happen.

[25] A. J. Arduengo, S. F. Gamper, J. C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1994**, *116*, 4391-4294.

[26] G. Maier, H. Henkelmann, H. P. Reisenauer, *Angew. Chem.* **1985,** *97,* 1061-1063; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1065-1066.

André Languérand, Stephanie S. Barnes, Guillaume Bélanger-Chabot, Laurent Maron, Philippe Berrouard, Pierre Audet and Frédéric-Georges Fontaine*

(IMes)$_2$Pt(H)(Chloroboratabenzene): a Borabenzene Platinum Adduct with an Unusual Pt-Cl-B interaction

Borabenzene complexes are widely known to bind in an η^6 fashion to transition metals. It is observed that in the presence of a Pt^0 precursor with bulky N-heterocyclic carbenes, a new bonding mode is possible for a new boratabenzene-Pt^{II} species, where there is a presence of a Pt-Cl-B interaction.

6
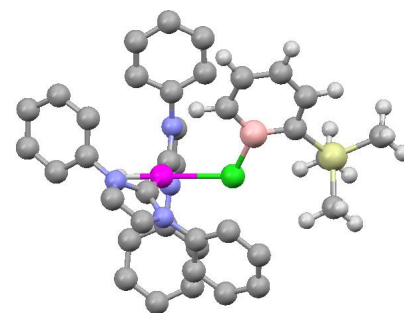
Supporting Information for:

(IMes)₂Pt(H)(Chloroboratabenzene): a Borabenzene Platinum Adduct with an Unusual Pt-Cl-B interaction

André Languérand, Stephanie S. Barnes, Guillaume Bélanger-Chabot, Laurent Maron[‡], Philippe Berrouard, Pierre Audet and Frédéric-Georges Fontaine*

Département de Chimie, Université Laval, Cité Universitaire,
Québec, QC, Canada, G1R 7P4.

[‡]Université de Toulouse, INSA, UPS, LPCNO, 135 avenue de Rangueil, F-31077 Toulouse, France, and CNRS, LPCNO, UMR 5215 CNRS-UPS-INSA, F-31077 Toulouse, France

*Email : frederic.fontaine@chm.ulaval.ca

<u>Contents</u>

1. General experimental

Unless otherwise specified, manipulations were carried out under an atmosphere of dinitrogen, using standard glovebox and Schlenk techniques. Dry, deoxygenated, distilled solvents were used for all manipulations. Toluene and benzene were distilled from sodium/benzophenone. Pyridine was dried over CaH_2. Deuterated solvents were dried over NaK, degassed using freeze-pump thaw cycles, and purified by vacuum transfer.

NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 100.580 MHz (^{13}C), 161.923 MHz (^{31}P), 85.987 MHz (^{195}Pt), Bruker Avance NMR 400 MHz spectrometer at 128.336 MHz (^{11}B), or on a Brucker NMR AC-300 at 300MHz (^{1}H), 75.435 MHz (^{13}C), 121.442 MHz (^{31}P). ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual protons in deuterated solvent. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), or overlapping (ov). Chemical shifts are reported in ppm. Coupling constants are reported in Hz.

2. Reactions involving PCy₃

2.1 Experimental

Reaction of [(PCy₃)₂Pt(0)] with boracycle 1a

Boracyclohexadiene **1a** (0.0056 g, 0.02 mmol) in C_6D_6 was added to [(PCy₃)₂Pt(0)] (0.015 g, 0.02 mmol) in a J-Young NMR tube. Several products were observable by NMR spectroscopy. ^{1}H NMR (C_6D_6, 25 °C) δ: 7.99 (d, $^3J_{\text{H-H}}$ = 10 Hz, 2H, **B**), 7.29 (d, $^3J_{\text{H-H}}$ = 10 Hz, 1H, **B**), 3.22 (sept., 1H, $^3J_{\text{HH}}$ = 6.8 Hz, **B**), 2.5-0.5 (m, Cy), 0.16 (s, $(CH_3)_3SiCl$), -17.78 (t, $^2J_{\text{P-H}}$ = 11 Hz, **C**), -18.66 (d, $^2J_{\text{P-H}}$ = 29 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C) δ: 62.8 (s, $^1J_{\text{P-Pt}}$ 4167 Hz, [(PCy₃)₂Pt(0)] (**A**)), 39.4 (s, $^1J_{\text{P-Pt}}$ 2814 Hz, [(PCy₃)₂Pt(H)(Cl)] (**C**)), 34.7 (s, $^1J_{\text{P-Pt}}$ 4922 Hz, **D**), 9.7 (bs, [C_8H_{11}B.PCy₃] **B**). Peaks for **C** were assigned to [(PCy₃)₂Pt(H)(Cl)], which has been previously reported in the literature.[1] A crystal structure for **C** was also obtained. (See page S51). The exact nature of **D** was not confirmed, but we suppose it to be [(PCy₃)(H)Pt(μ-Cl)]₂.[2]
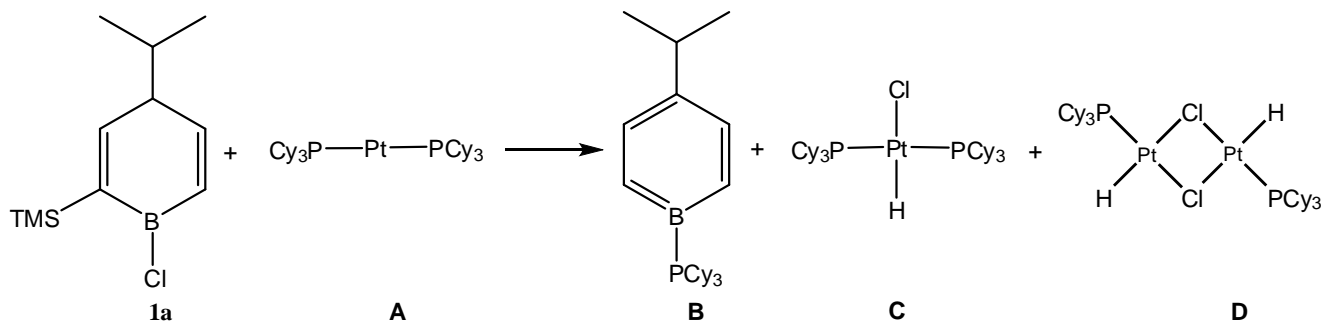

**Scheme S-1.** Reaction [(PCy₃)₂Pt(0)] with boracycle **1a**

Synthesis of 1-Tricyclohexylphosphine-4-(*iso*propyl)borabenzene (B)

Boracyclohexadiene **1a** (0.2704 g, 1.46 mmol) in toluene (3 mL) was added by cannulae to a solution of PCy₃ (0.4079 g, 1.46 mmol) in toluene (10 mL). The reaction proceeded for 3h to give a yellow solution. Solvent was removed under vacuum, and the resulting solid was recrystallized in pentane at -80°C. ^{1}H NMR (C_6D_6, 25°C) δ: 7.97 (d, $^3J_{\text{H-H}}$ = 10 Hz, 2H, H^3), 7.28 (d, $^3J_{\text{H-H}}$ = 10 Hz, 2H, H^2), 3.22 (sept, $^3J_{\text{H-H}}$ = 7 Hz, 1H, CH$^{i\text{Pr}}$), 2.35-1.10 (ov m, 33H, Cy), 1.53 (d, $^3J_{\text{H-H}}$ = 7 Hz, 6H, CH₃$^{i\text{Pr}}$). ^{31}P{^{1}H} NMR (C_6D_6, 25°C) δ: 9.3. ^{11}B{^{1}H} NMR (C_6D_6, 25°C) δ: 17.0.

2.2 NMR characterization

^{1}H NMR of the reaction of **1a** with [(PCy$_3$)$_2$Pt(0)] in C$_6$D$_6$ (300 MHz)
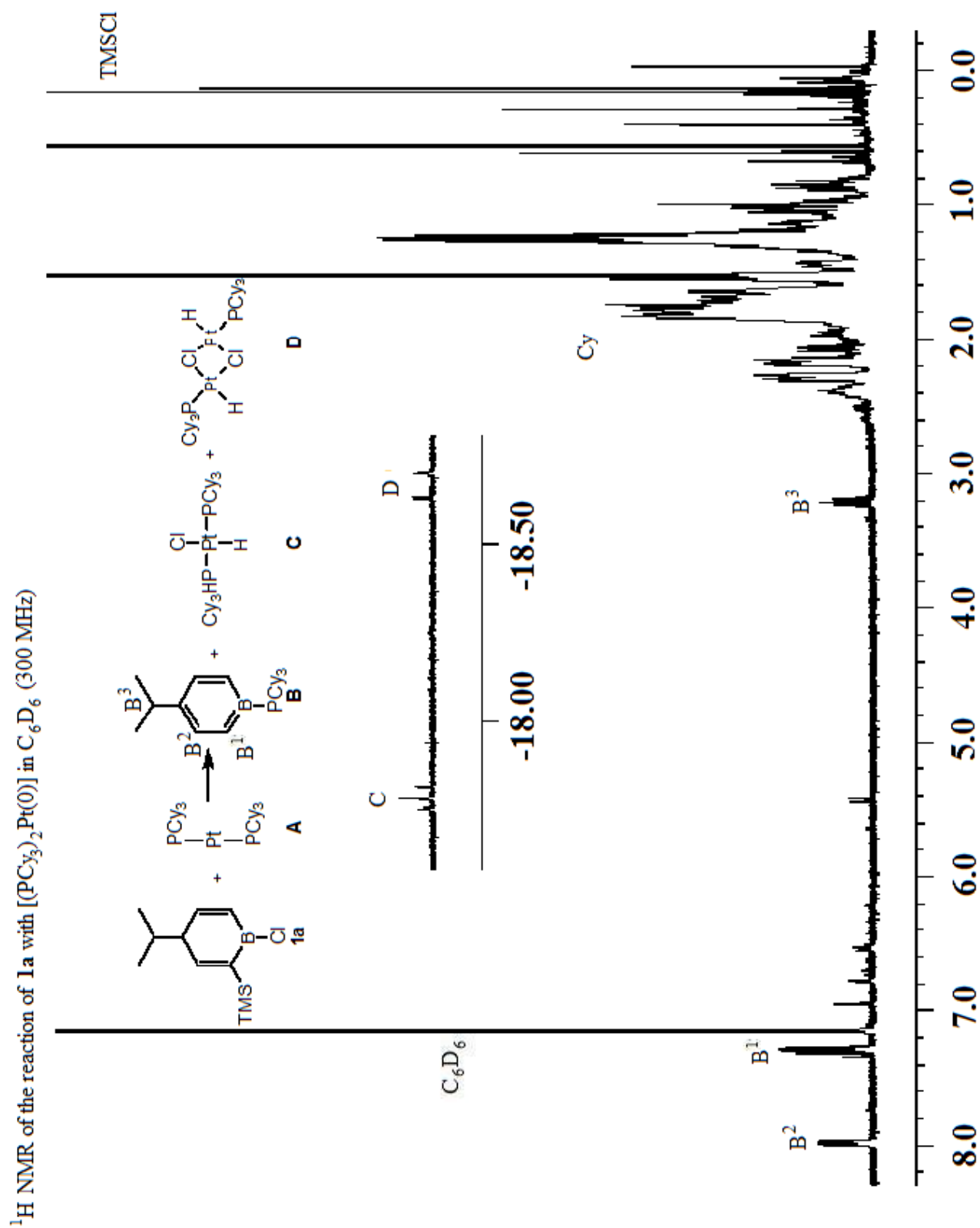
$^{31}P\{^{1}H\}NMR$ of the reaction of **1a** with [(PCy$_3$)$_2$Pt(0)] in C$_6$D$_6$ (121.4 MHz)
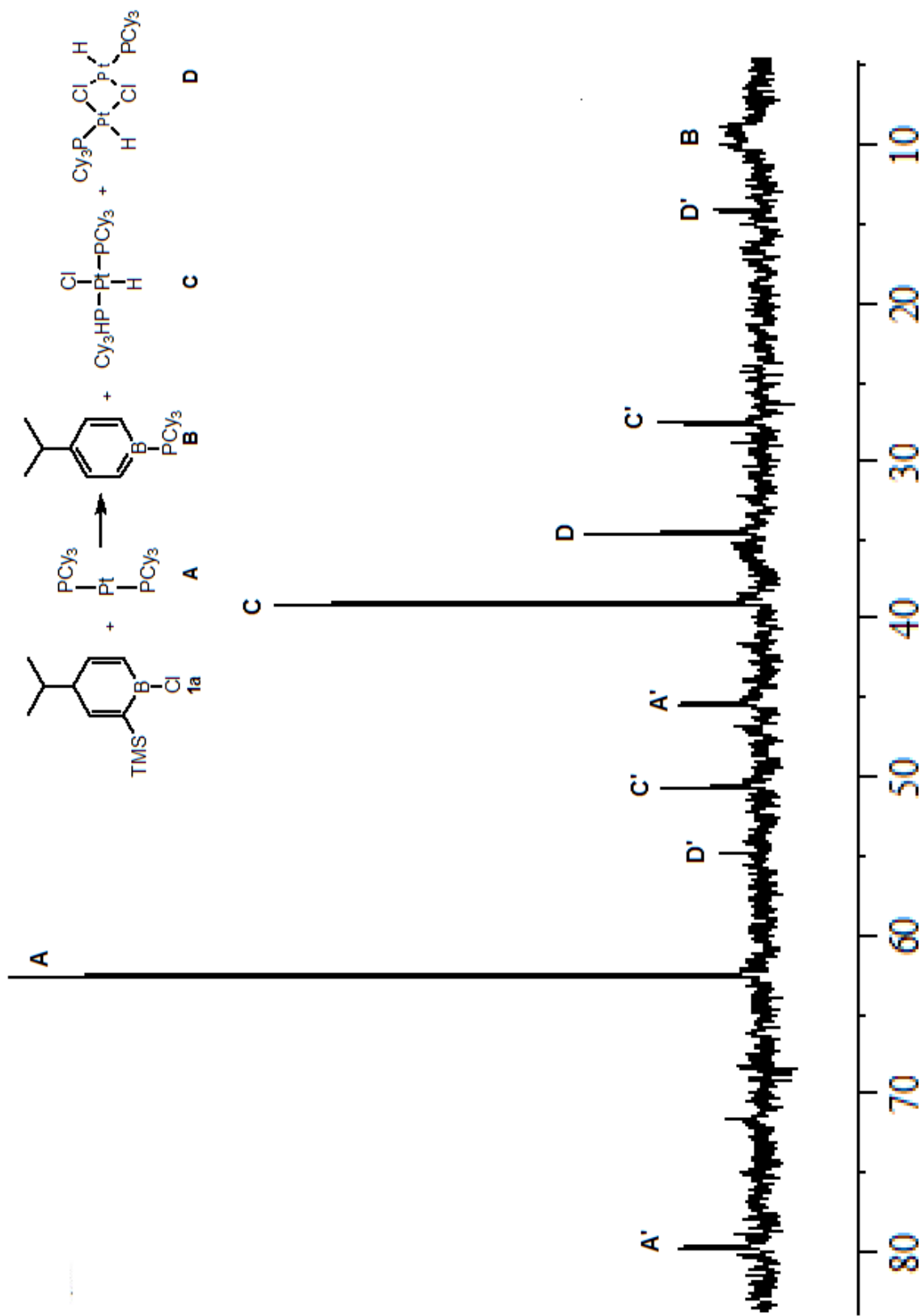
^{1}H NMR of 1-1-Tricyclohexylphosphine-4-(isopropyl)borabenzene in C_6D_6 (400 MHz)
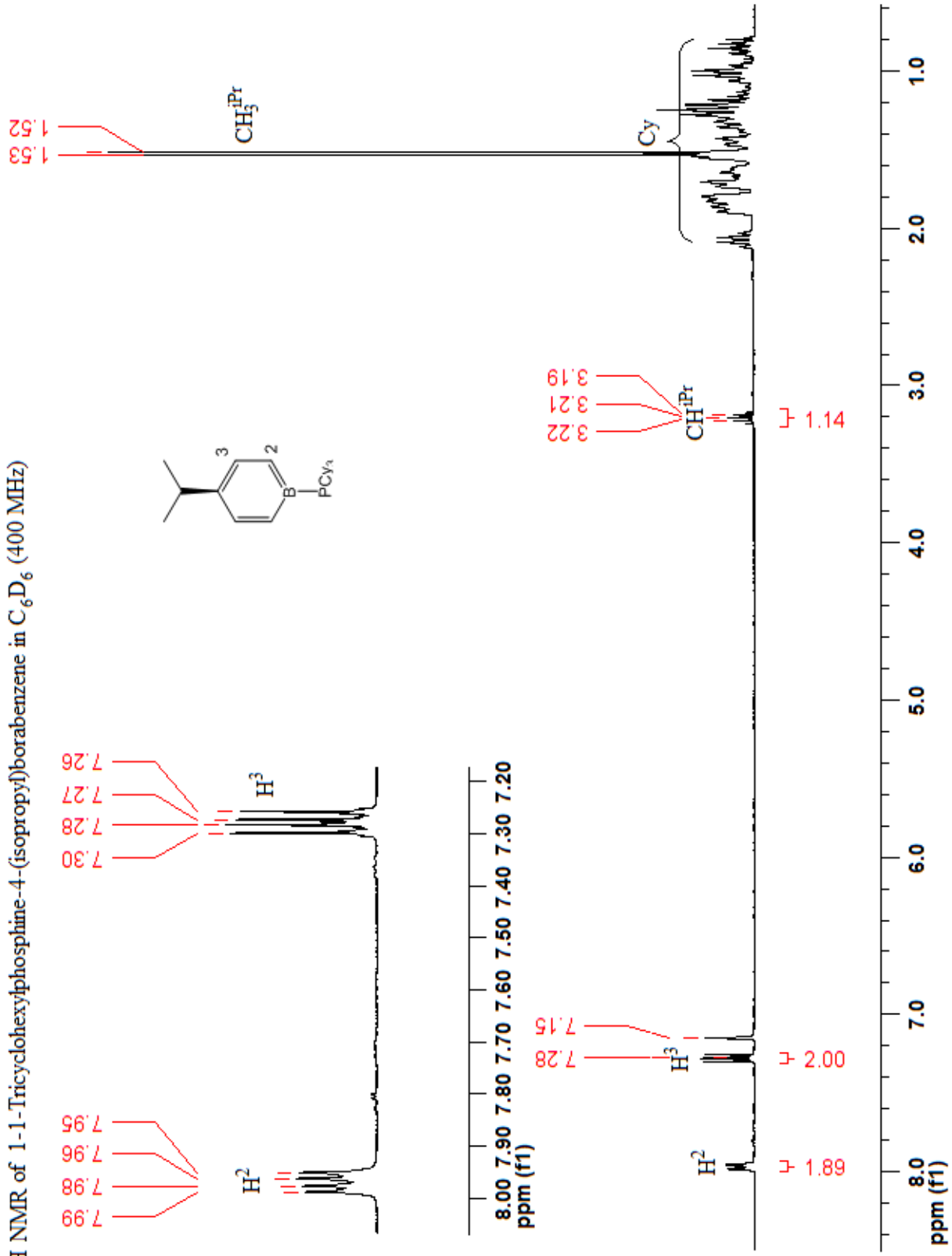
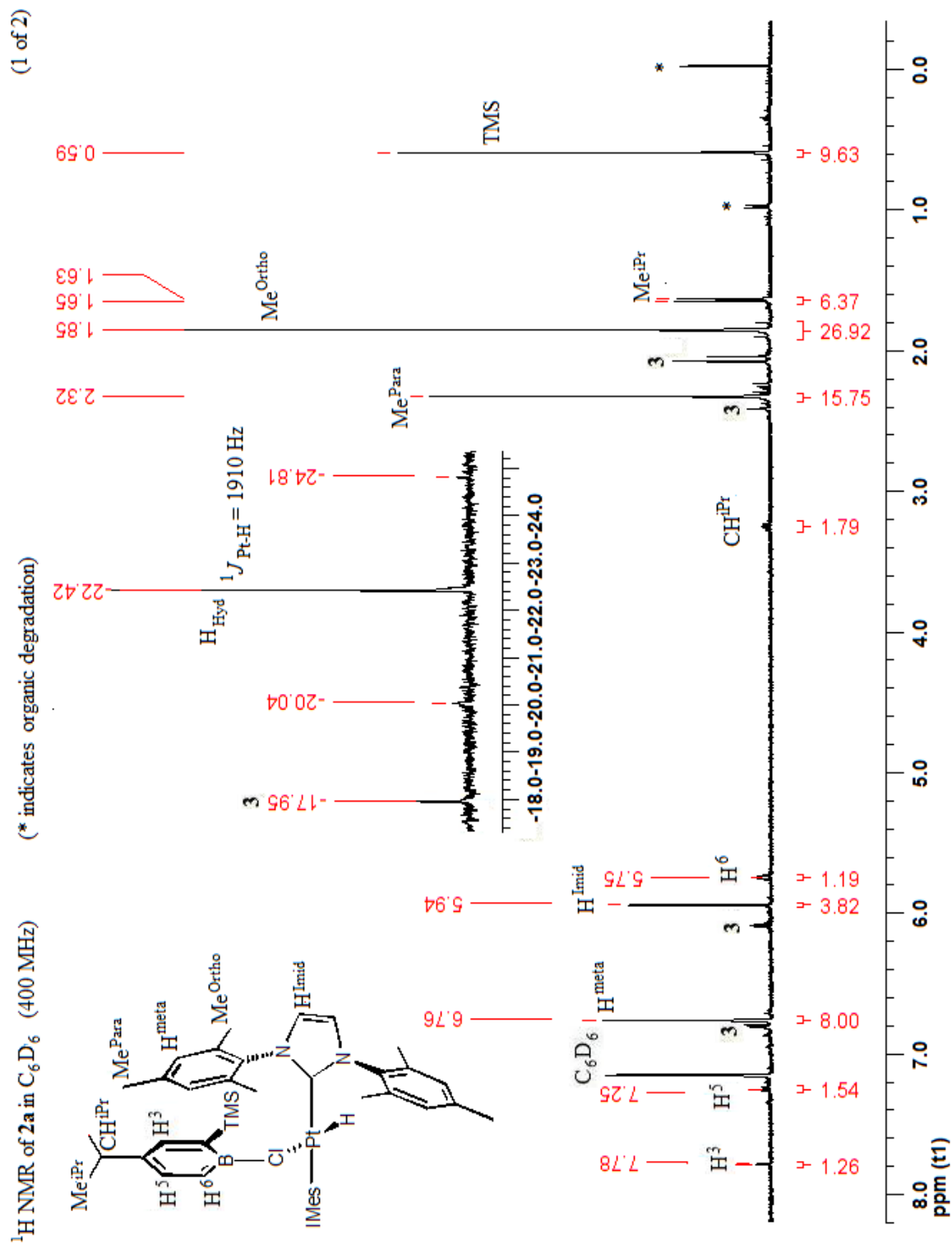^{31}P {^{1}H}NMR of 1-1-Tricyclohexylphosphine-4-(isopropyl)borabenzene in C$_6$D$_6$ (121.4 MHz)

9.3

ppm (t1)

40   30   20   10   0   -10   -20   -30   -40
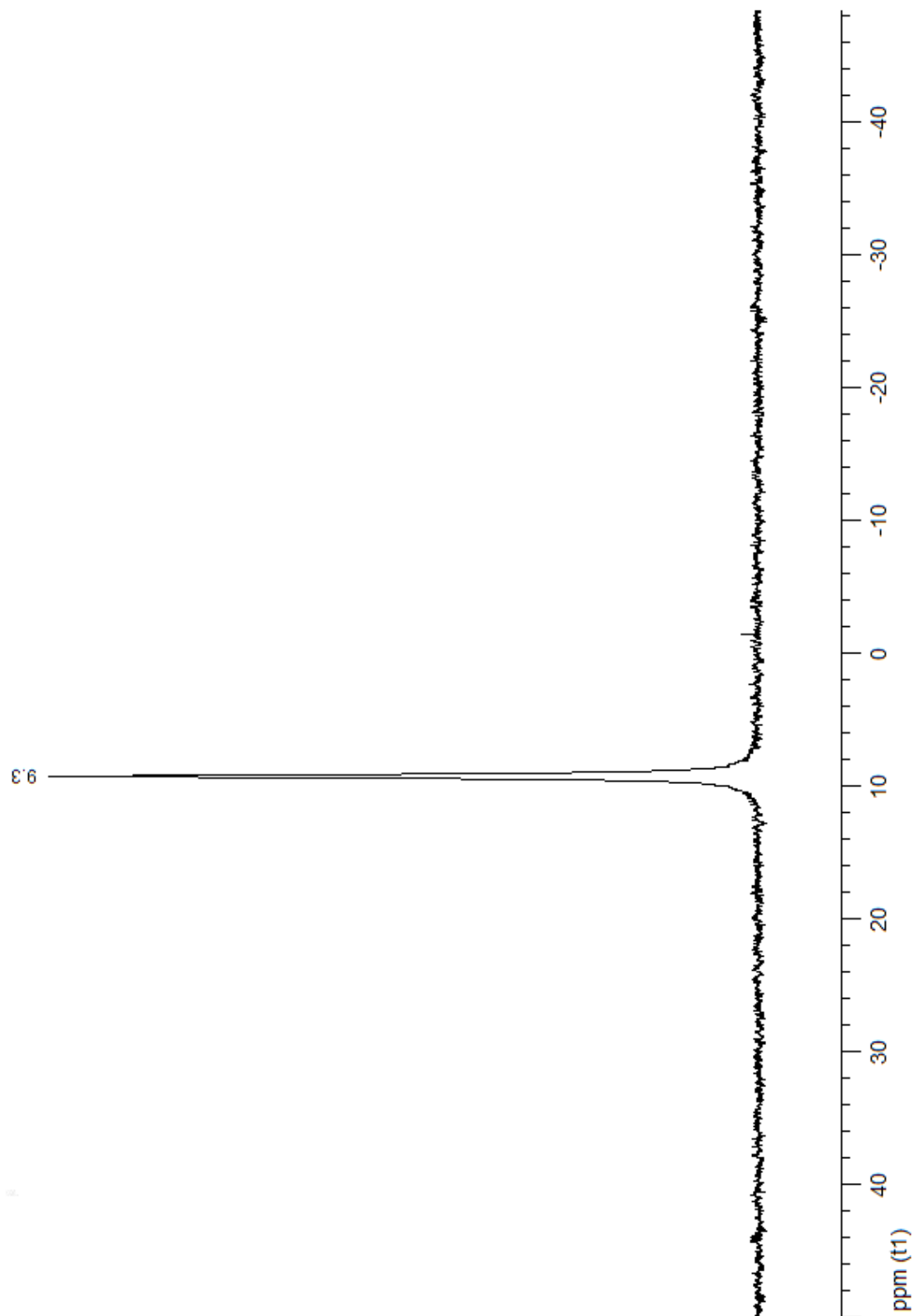
3. Multinuclear NMR characterization

3.1 Compounds 2a-2c

Compound 2a

^{1}H NMR of **2a** in C_6D_6 (400 MHz)

(1 of 2)

(* indicates organic degradation)

^{1}H NMR of **2a** in C_6D_6 (400 MHz)

(* Indicates Pt(IMes)$_2$)

^{13}C{^{1}H} NMR of **2a** in C$_6$D$_6$ (75.4 MHz)
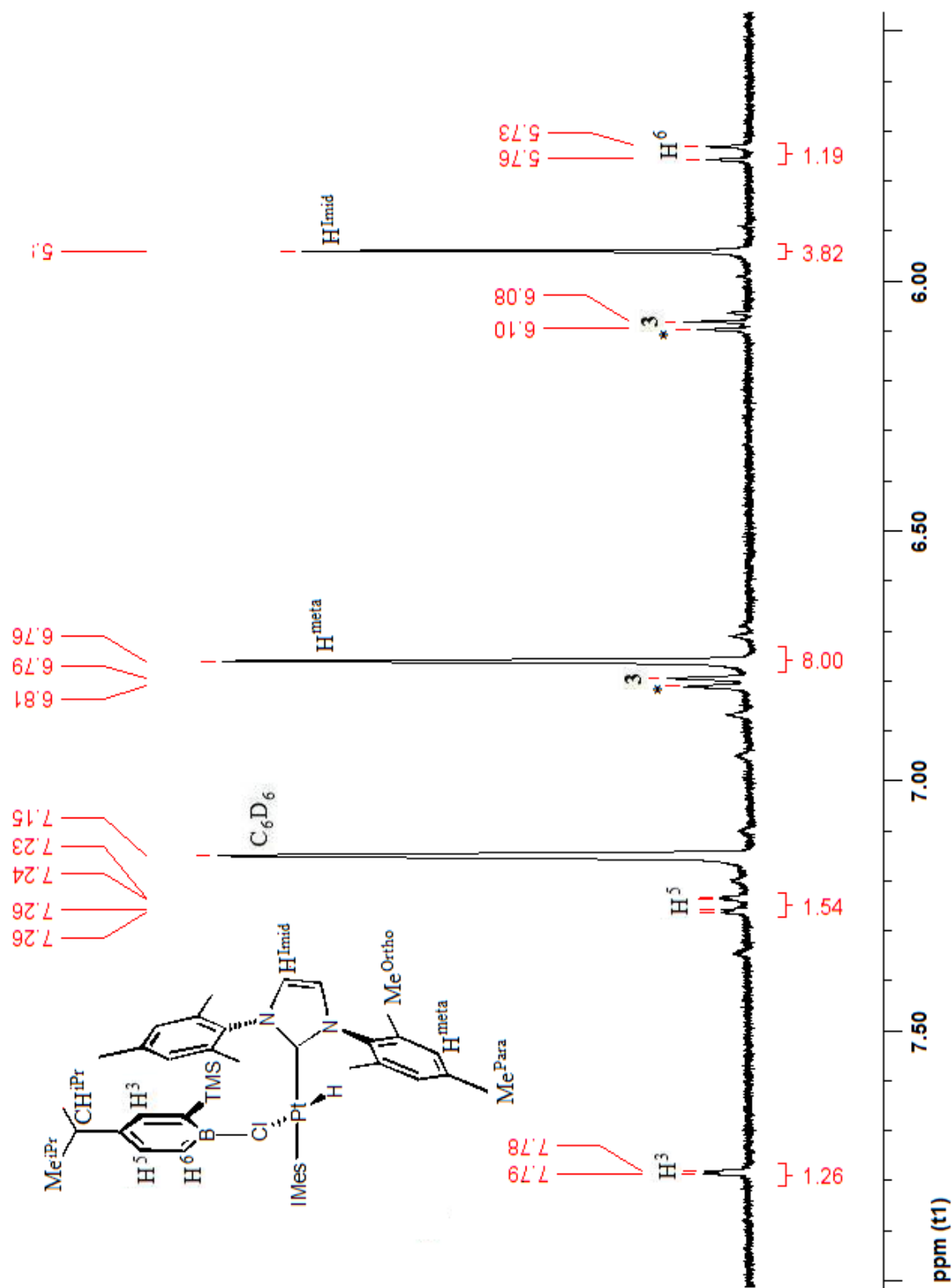
^{13}C{^{1}H} NMR of **2a** in C$_6$D$_6$ (75.4 MHz)
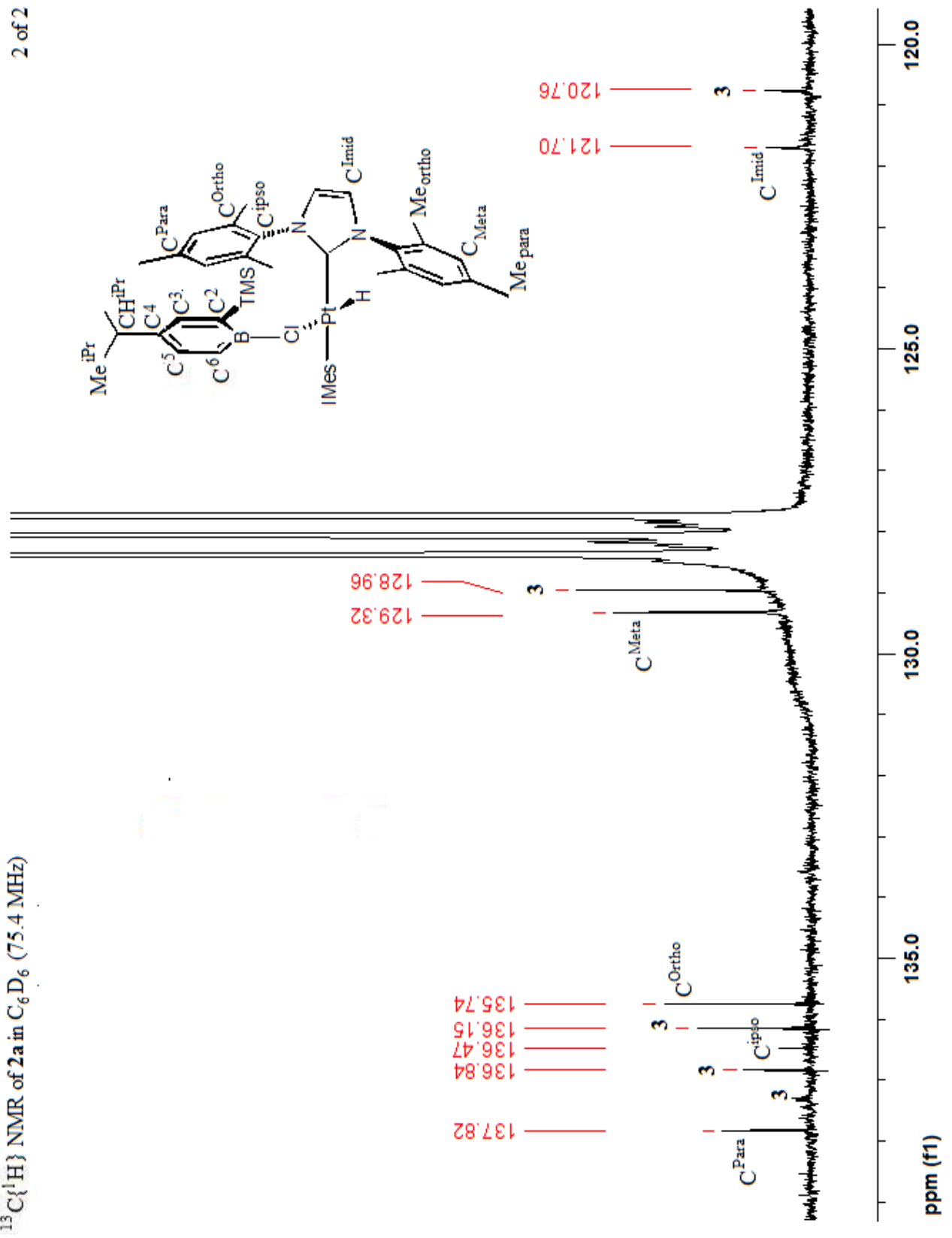
^{195}Pt NMR of **2a** in C_6D_6 (85.99 MHz)

$^1J_{\text{Pt-H}} = 1918$ Hz

-4375

-4353

-4400

-4350

-4300

ppm (t1)

S12
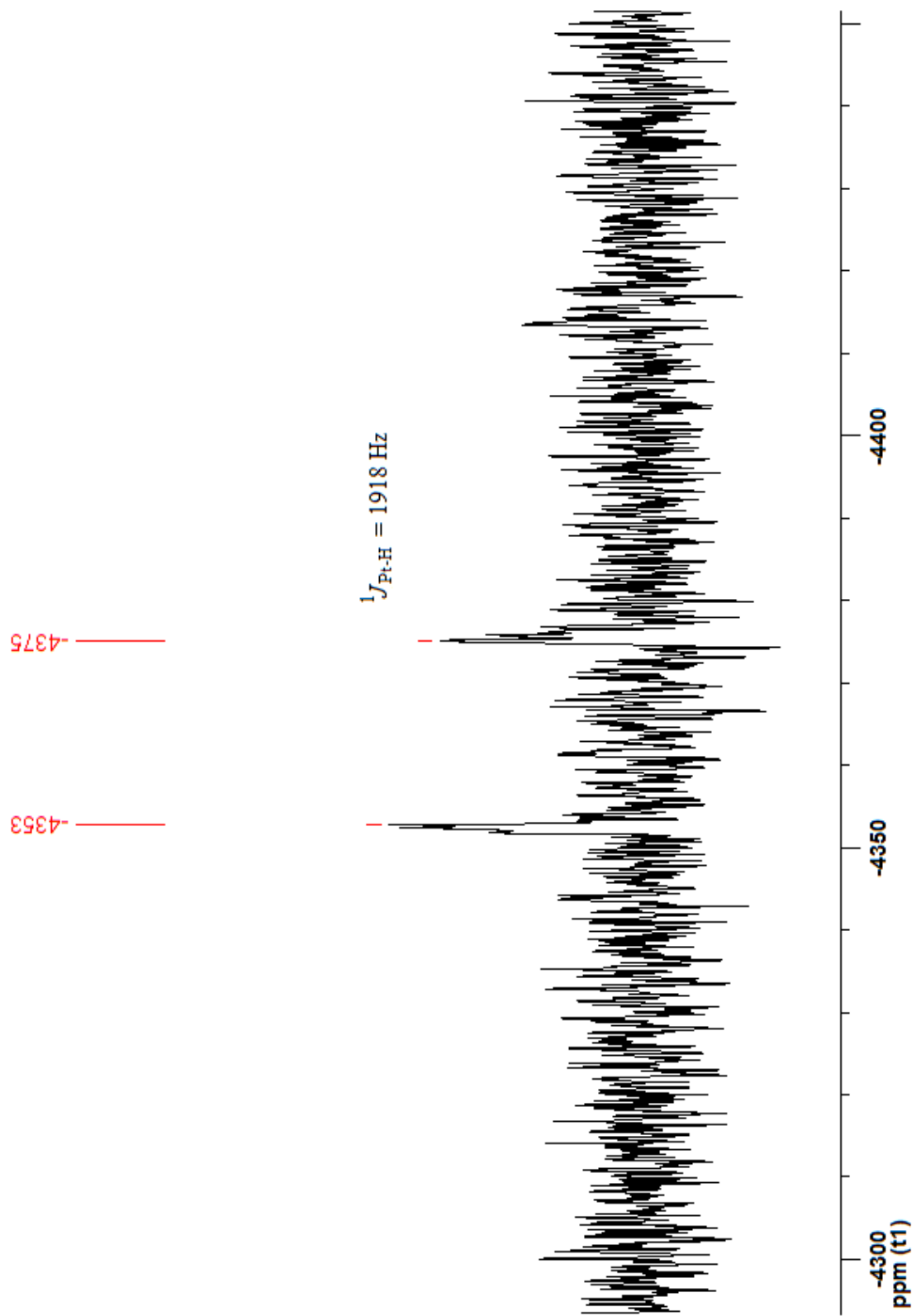
^{11}B NMR of **2a** in C_6D_6 (128.34 MHz)

(* Indicates degradation)
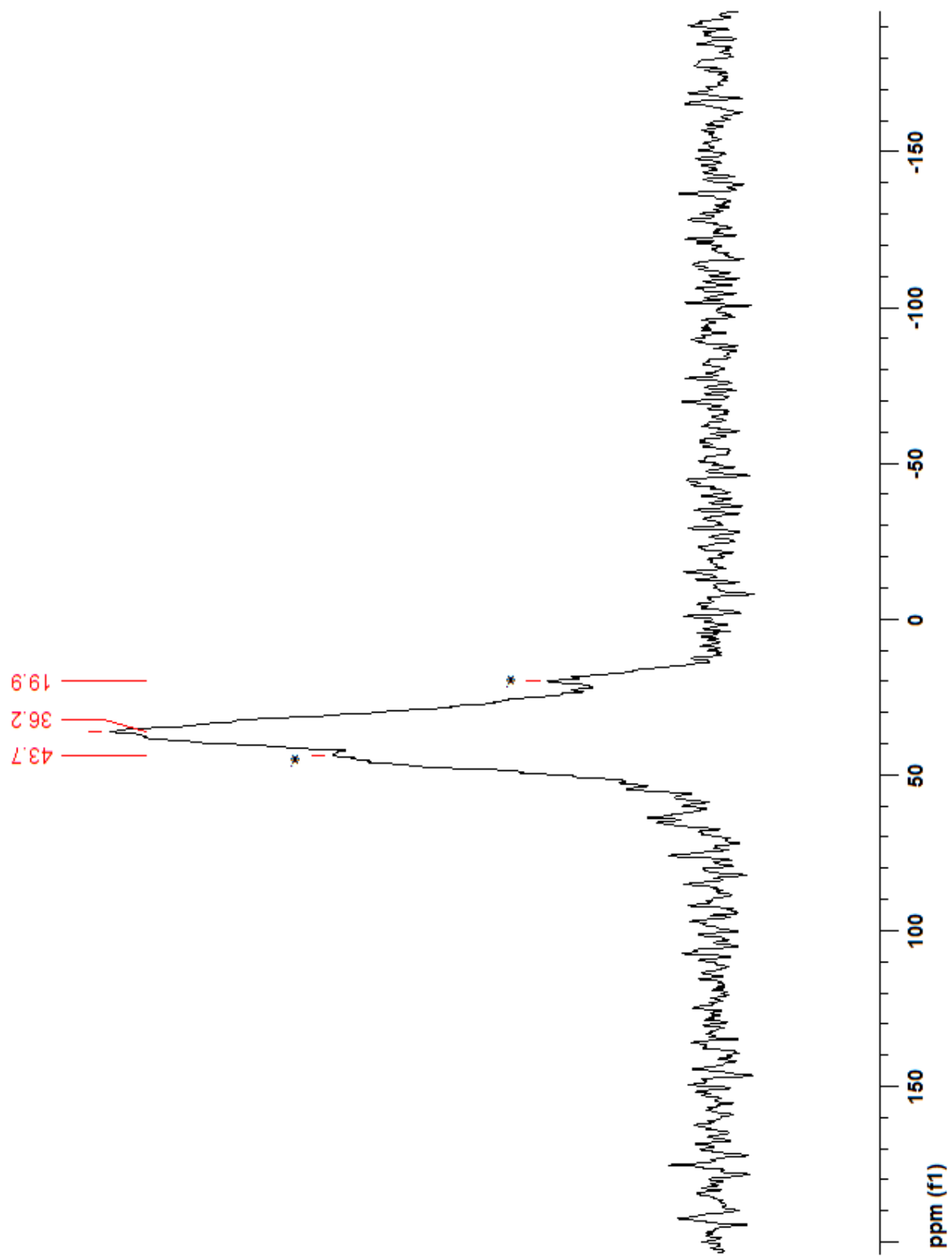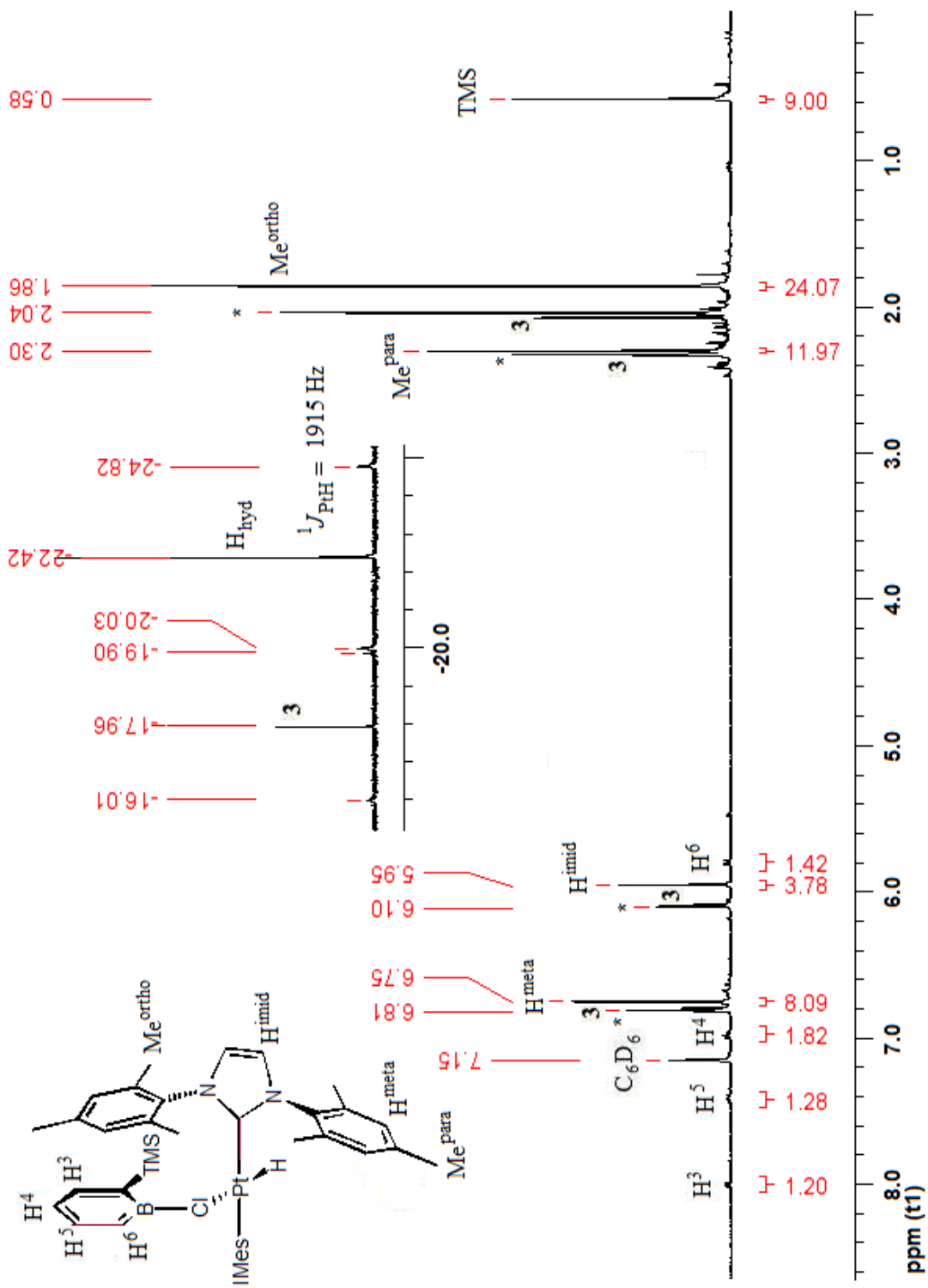
19.9
36.2
43.7

ppm (f1)

Compound **2b**

^{1}H NMR of **2b** in C$_6$D$_6$ (400 MHz)

(* Indicates starting material)

$^1J_{PtH}$ = 1915 Hz

TMS

Me^{ortho}

Me^{para}

H$_{hyd}$

H^{imid}

H^6

H^{meta}

H^4

C$_6$D$_6$

H^5

H^3

Me^{ortho}

H^{imid}

H^{meta}

Me^{para}

H^4

H^5

H^3

H^6

0.58

1.86
2.04
2.30

-24.82

-22.42

-20.03
-19.90

-17.96

-16.01

5.95
6.10

6.75
6.81

7.15

-20.0

9.00

24.07

11.97

1.42
3.78

8.09

1.82

1.28

1.20

1.0   2.0   3.0   4.0   5.0   6.0   7.0   8.0

ppm (t1)

^{1}H NMR of **2b** in C$_6$D$_6$ (400 MHz)

(* Indicates starting material)

ppm (t1)

$^{13}C\{^1H\}$ NMR of **2b** in C_6D_6 (100.58 MHz)

(* Indicates starting material)

(1 of 2)

S16

$^{13}C\{^1H\}$ NMR of **2b** in C_6D_6 (100.58 MHz)

(* Indicates starting material)

(2 of 2)

138.65
137.84
137.23
136.79
136.40
136.18
136.09
135.68
135.64

129.27
128.91
128.57

130.0

135.0

ppm (f1)

S17
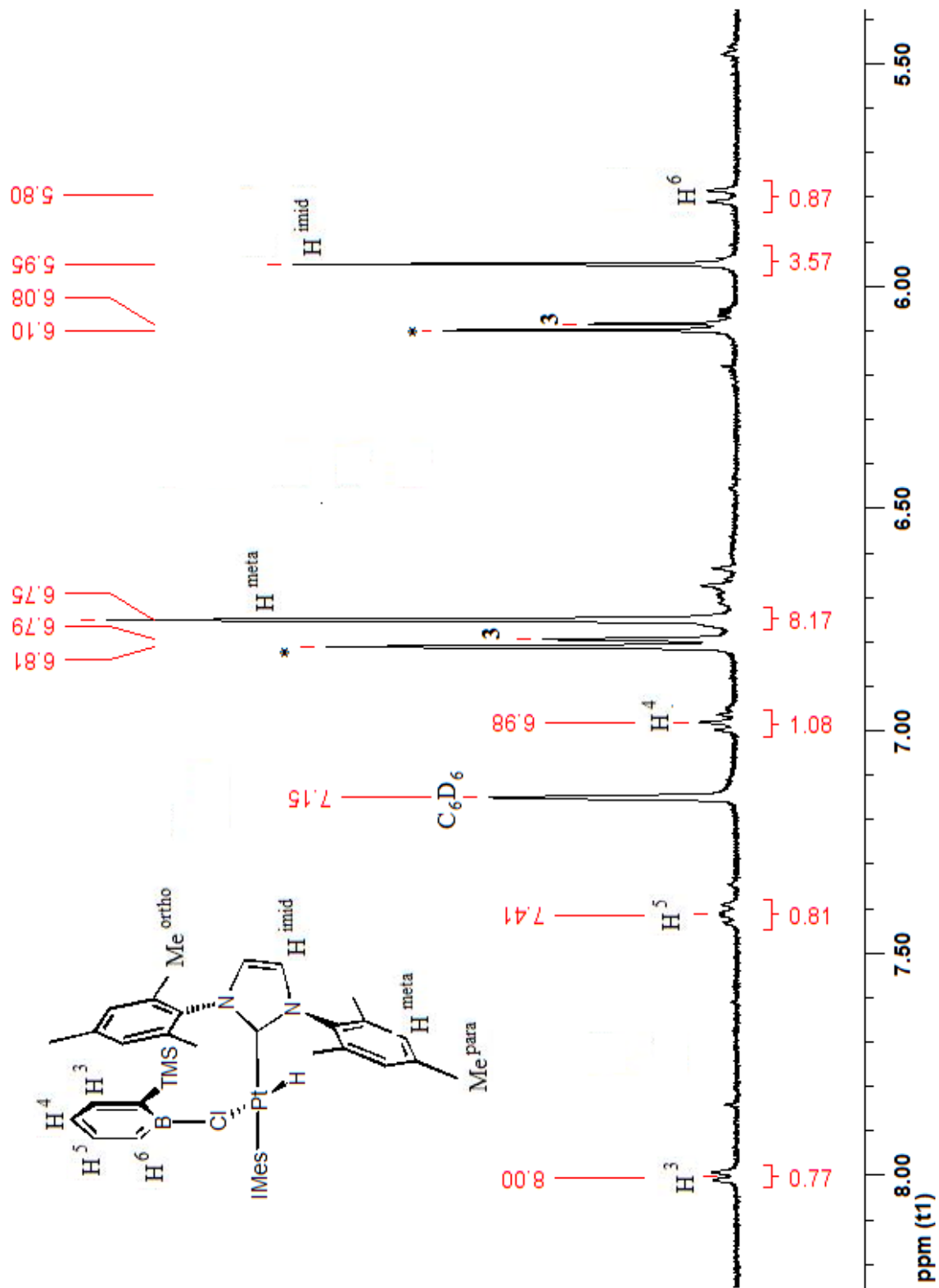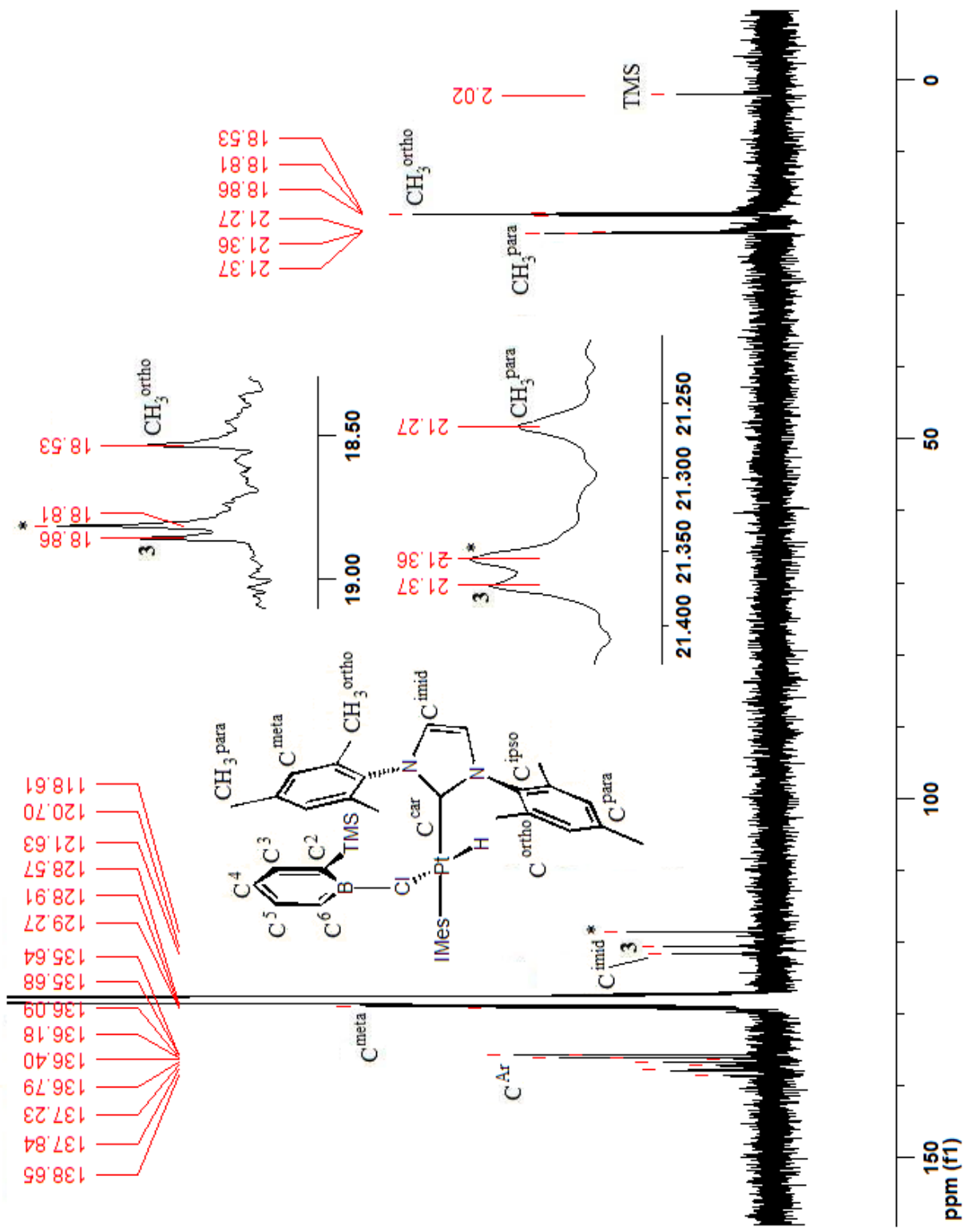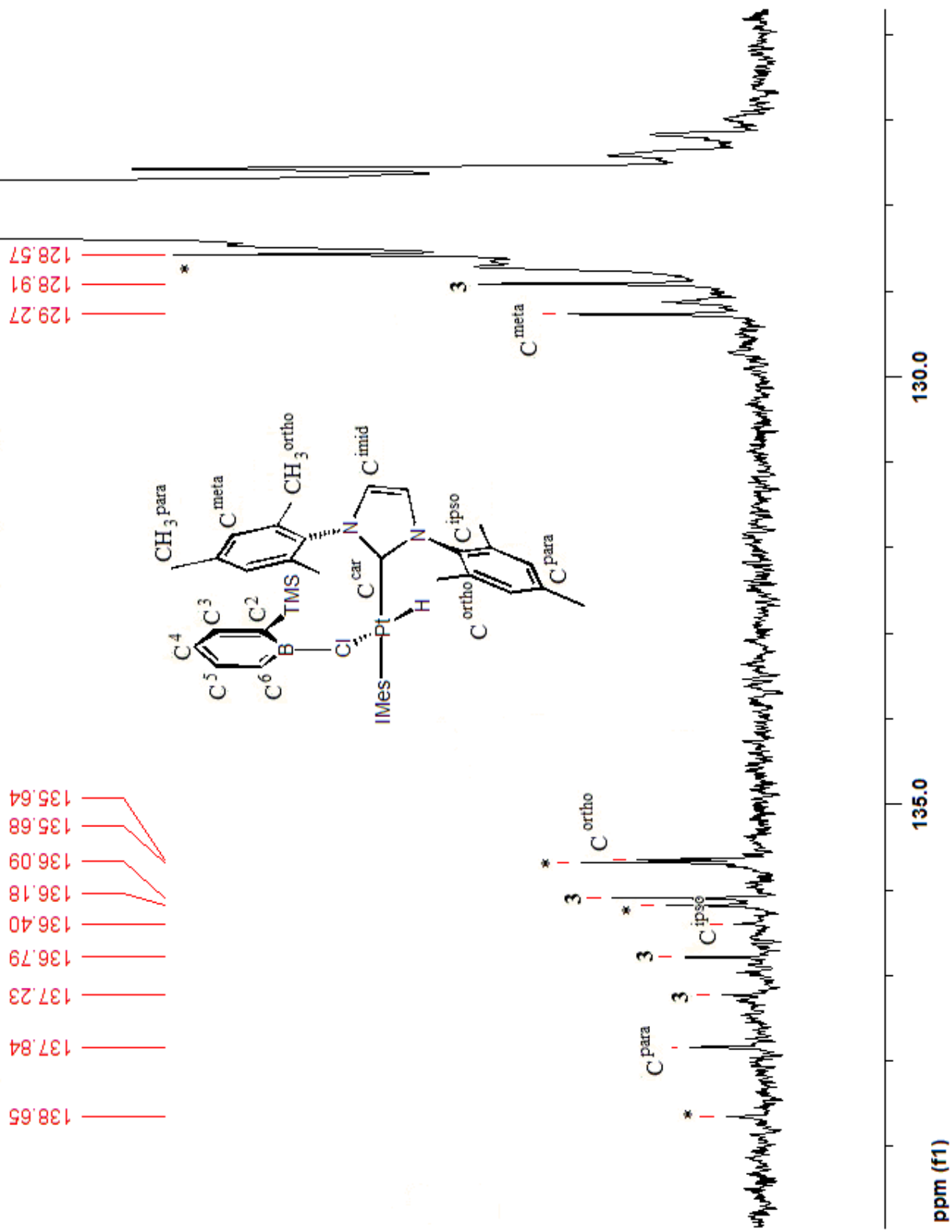
195Pt NMR of **2b** in C_6D_6 (85.99 MHz)

-4276.5

-4294.7

$^1J_{PtH}$ = 1560 Hz

3

-4355.5

$^1J_{PtH}$ = 1960 Hz

-4378.4

-4400

-4350

-4300

ppm (f1)
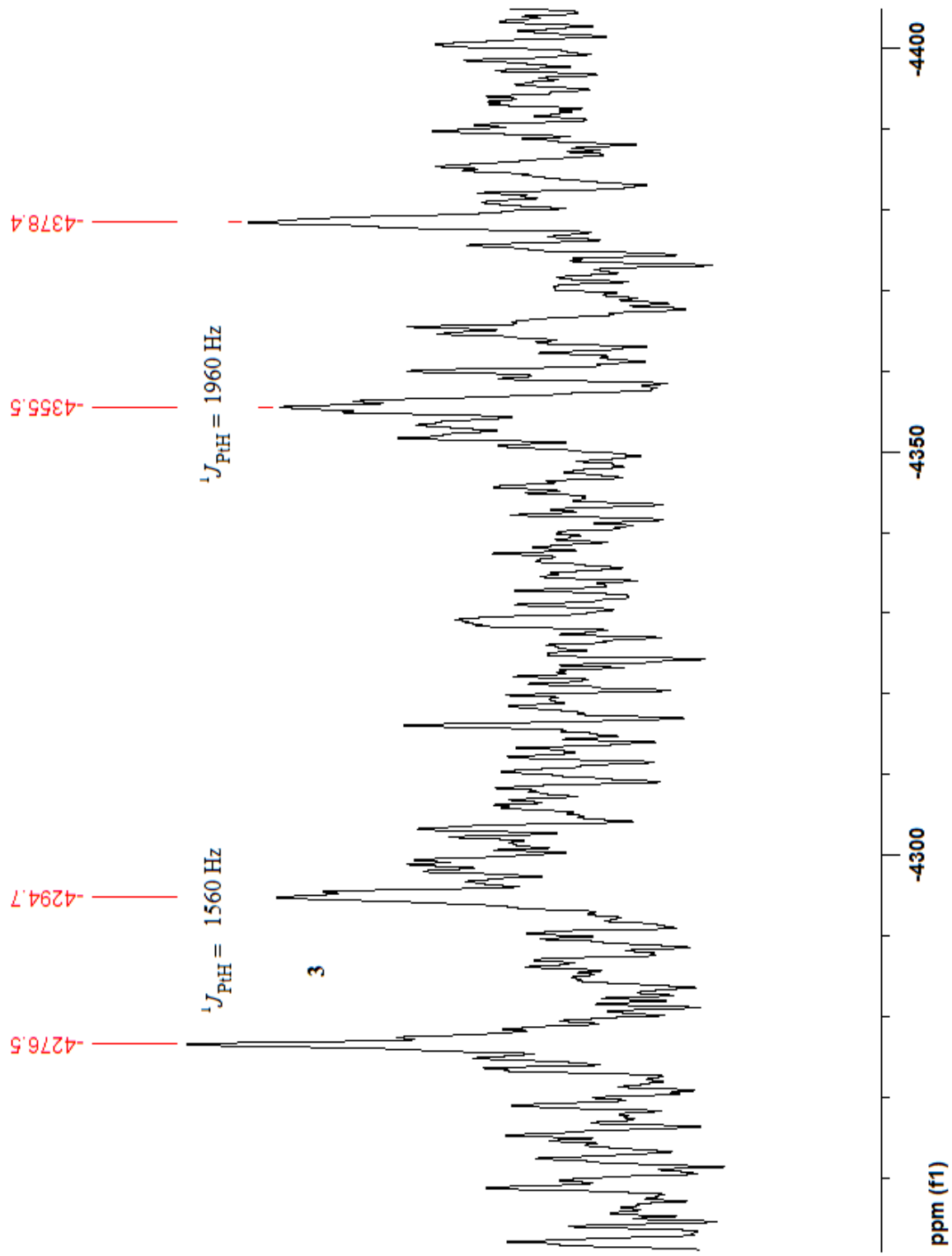
^{11}B NMR of **2b** in C$_6$D$_6$ (128.3 MHz)

(* Indicates degredation product)

21.1
38.8
45.9

ppm (f1)

Compound **2c**

^{1}H NMR of **2c** in C$_6$D$_6$ (400 MHz)

(* Indicates starting material)

Me^{ortho}

^{1}J$_{PtH}$ = 1905 Hz

1.88
2.04
2.08
2.30
2.32
2.33

−24.83
−22.44
−20.06
−19.90
−17.96
−16.02

5.93
6.08
6.10
6.10
6.29
6.32

6.77
6.80
6.81
7.00

Me^{para}

H^{imid}

H^{meta}

H^2

H^4

H^3

C$_6$D$_6$

Me^{para}

H^{meta}

Me^{ortho}

H^{imid}

H^4
H^3
H^2 B Cl Pt H
IMes

23.49
13.67
4.00
7.41

ppm (t1)

−25.0   −20.0

2.0   3.0   4.0   5.0   6.0   7.0

ppm (t1)

S20
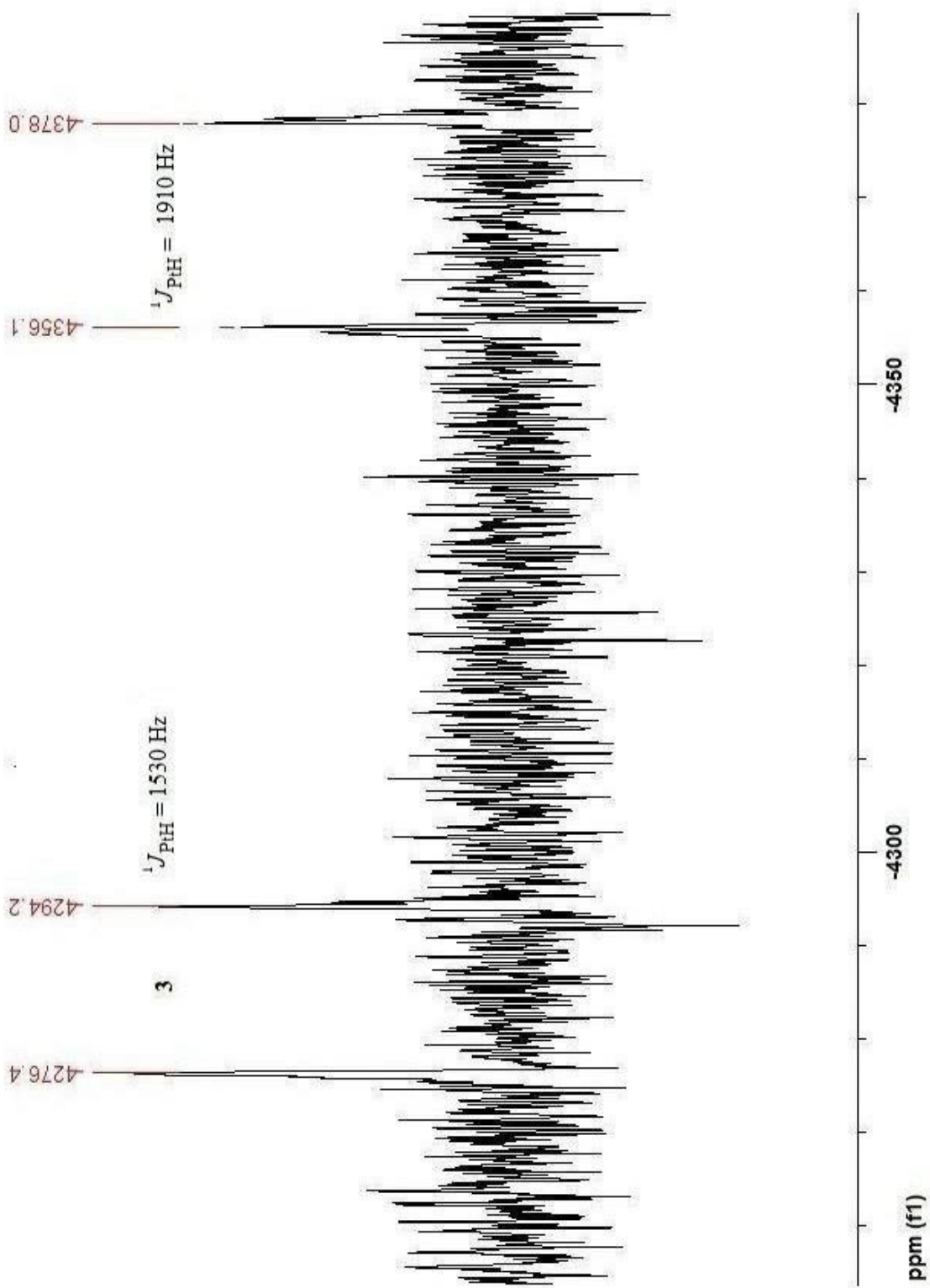
^{1}H NMR of **2c** in C_6D_6 (400 MHz)

(* Indicates starting material)

(2 of 2)

S21

^{195}Pt NMR of **2c** in C_6D_6 (85.99 MHz)

-4378.0

-4356.1

$^1J_{PtH} = 1910$ Hz

-4294.2

$^1J_{PtH} = 1530$ Hz

3

-4276.4

-4350

-4300

ppm (f1)

S22

3.2 Compound **3**

^{1}H NMR of **3** in C_6D_6 (400 MHz)

$^1J_{Pt-H}$ = 1542 Hz
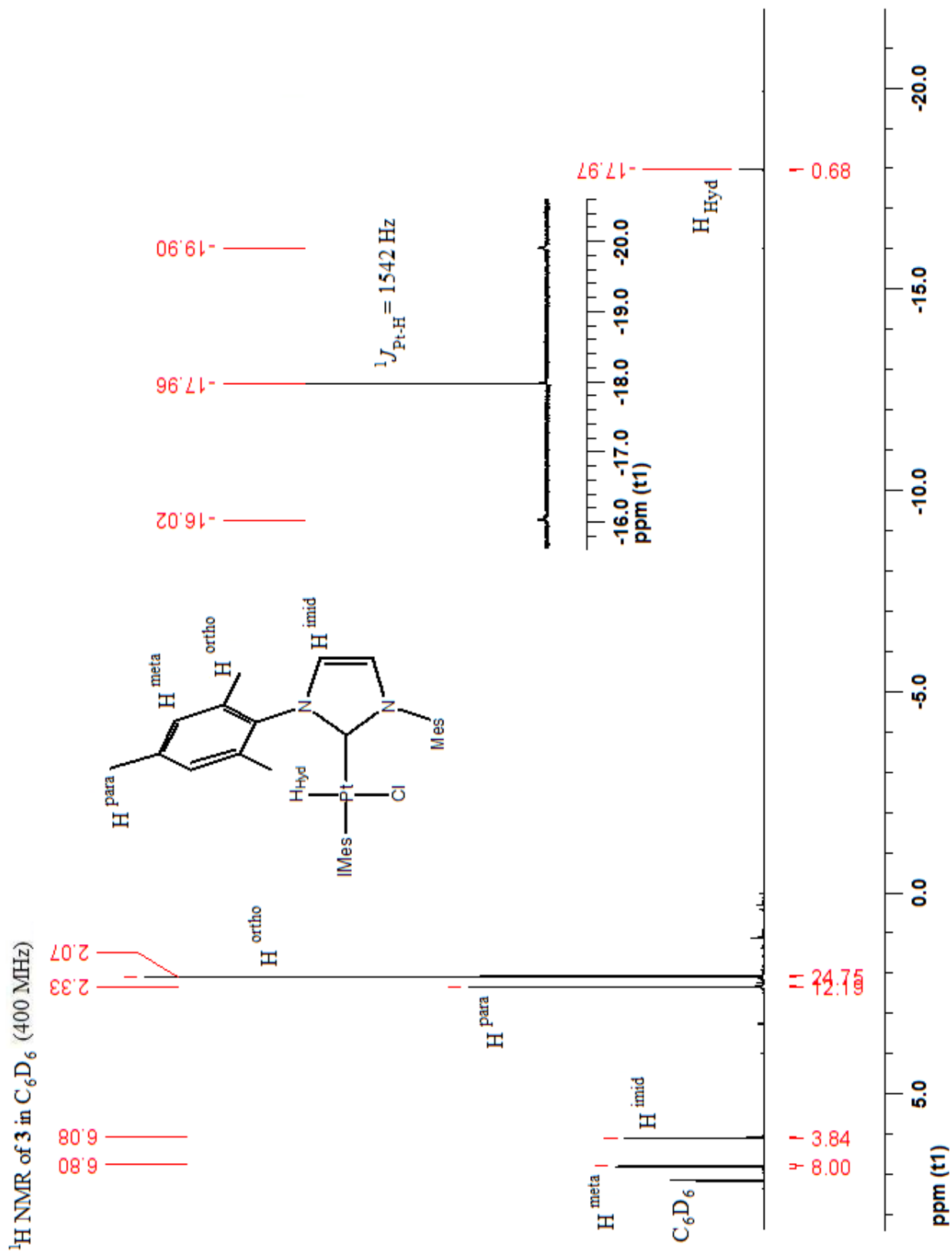
$^{13}C\{^1H\}$ NMR of **3** in C_6D_6 (75.42 MHz)

ppm (f1)

S24
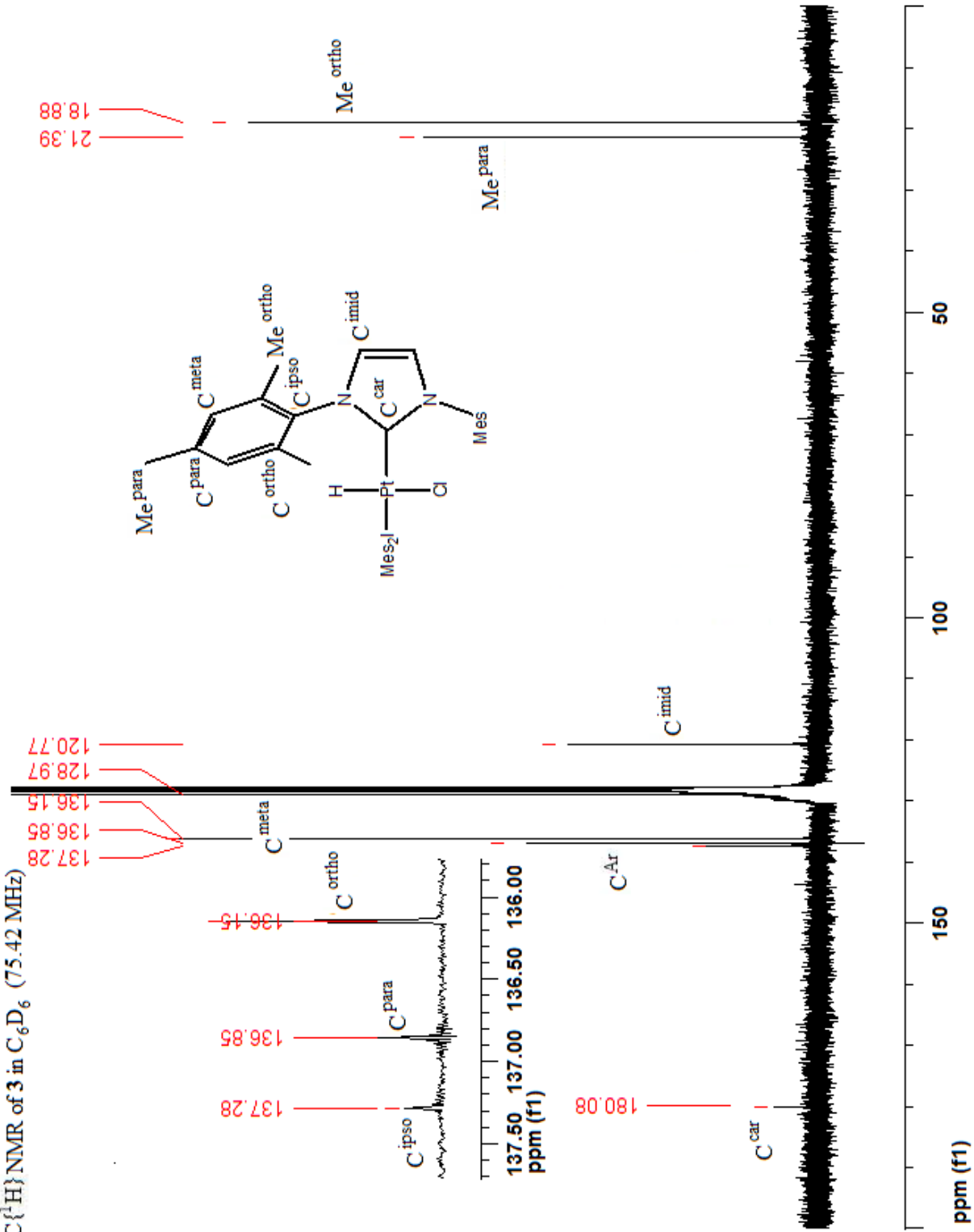
^{195}Pt NMR of **3** in C$_6$D$_6$ (85.99 MHz)

$^1J_{\text{Pt-H}}$ = 1523 Hz

−4294

−4276

-4200   -4250   -4300   -4350   -4400   -4450

ppm (t1)
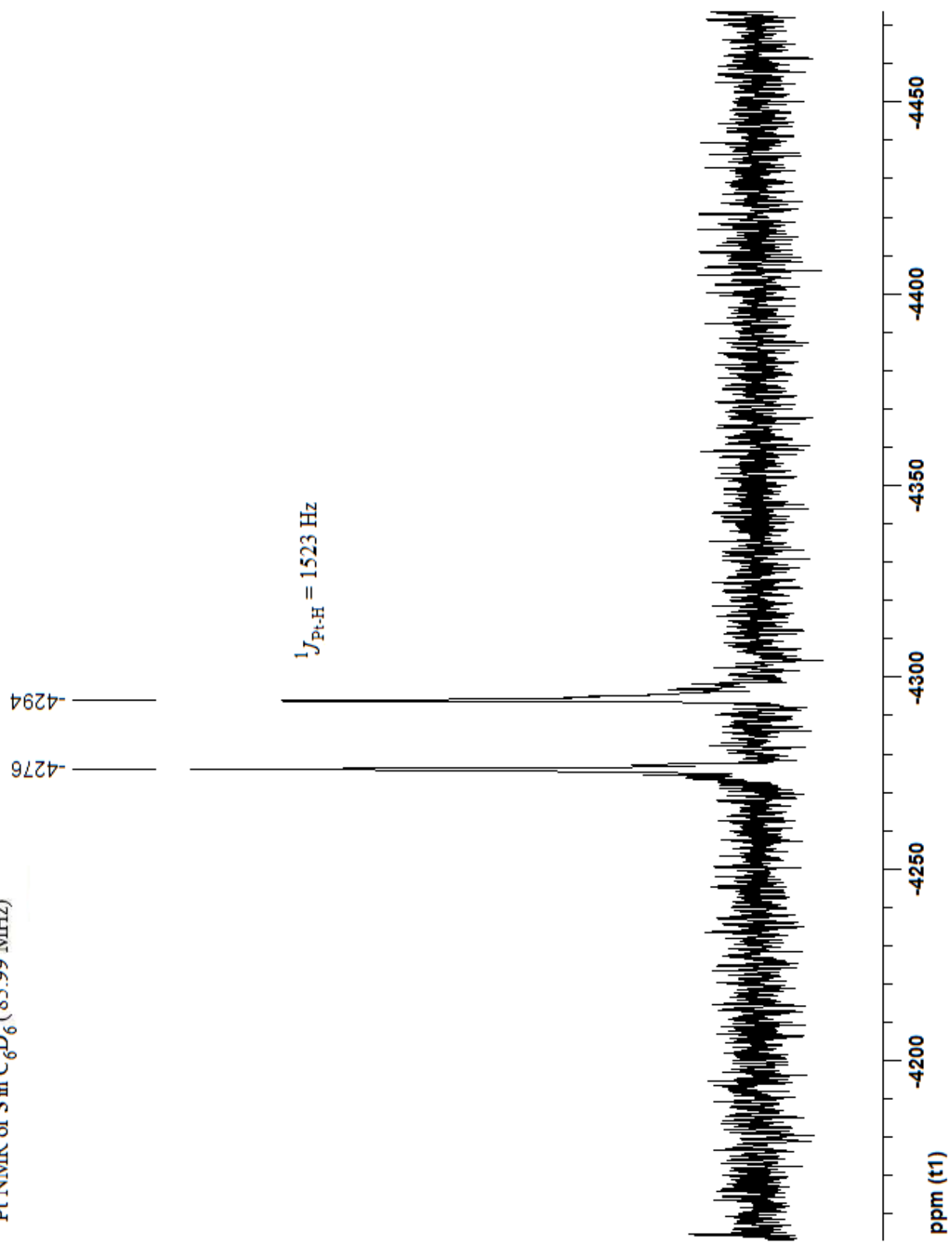
4. Reactions with Pyridine

4.1 Experimental

Reaction of 2b with Pyridine

Boracyclohexadiene **1b** (0.00045 g, 0.0024 mmol) and [(IMes)$_2$Pt(0)] (0.0021 g, 0.0026 mmol) were combined in C$_6$D$_6$ (1 mL) in a J-Young NMR tube, to generate **2b**, as previously described. After five minutes, a dilute solution of pyridine (0.0004 g, 0.005 mmol) in C$_6$D$_6$ was added by syringe. Several species were observable by NMR spectroscopy, but after 24 hours **3** and **4** were the principal species remaining in solution. ^{1}H NMR (C$_6$D$_6$, 25 ^{o}C) δ: 8.52 (d, J = 4.2 Hz, Py), 8.23 - 8.10 (ovm, 2H, **4**), 8.08 (dm, J = 6.7 Hz, 2H, **4**), 7.35 (td, J = 7.2, 1.1 Hz, 1H, **4**), 6.97 (app.tt, J = 7.6, 1.7 Hz, Py), 6.80 (s, **3**), 6.65 (ov, ddd, J = 7.5, 4.2, 1.2 Hz, **4**, Py), 6.48 (app.tt, J = 7.8, 1.5 Hz, 1H, **4**), 6.12 (dd, J = 7.8, 6.7 Hz, 2H, **4**), 6.08 (s, **3**), 5.84 (s,*), 2.33 (s, **3**), 2.07 (s, **3**), 1.49 (s, *), 0.91 (s, *), 0.18 (s, TMS **4**), -17.97 (d, $^1J_{Pt-H}$ = 1546 Hz, **3**). * is for unidentified species.
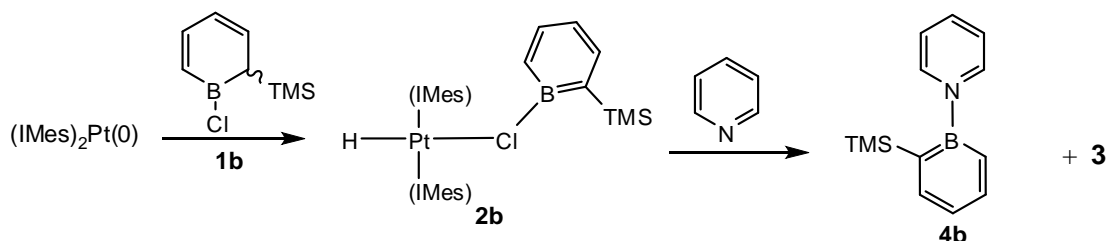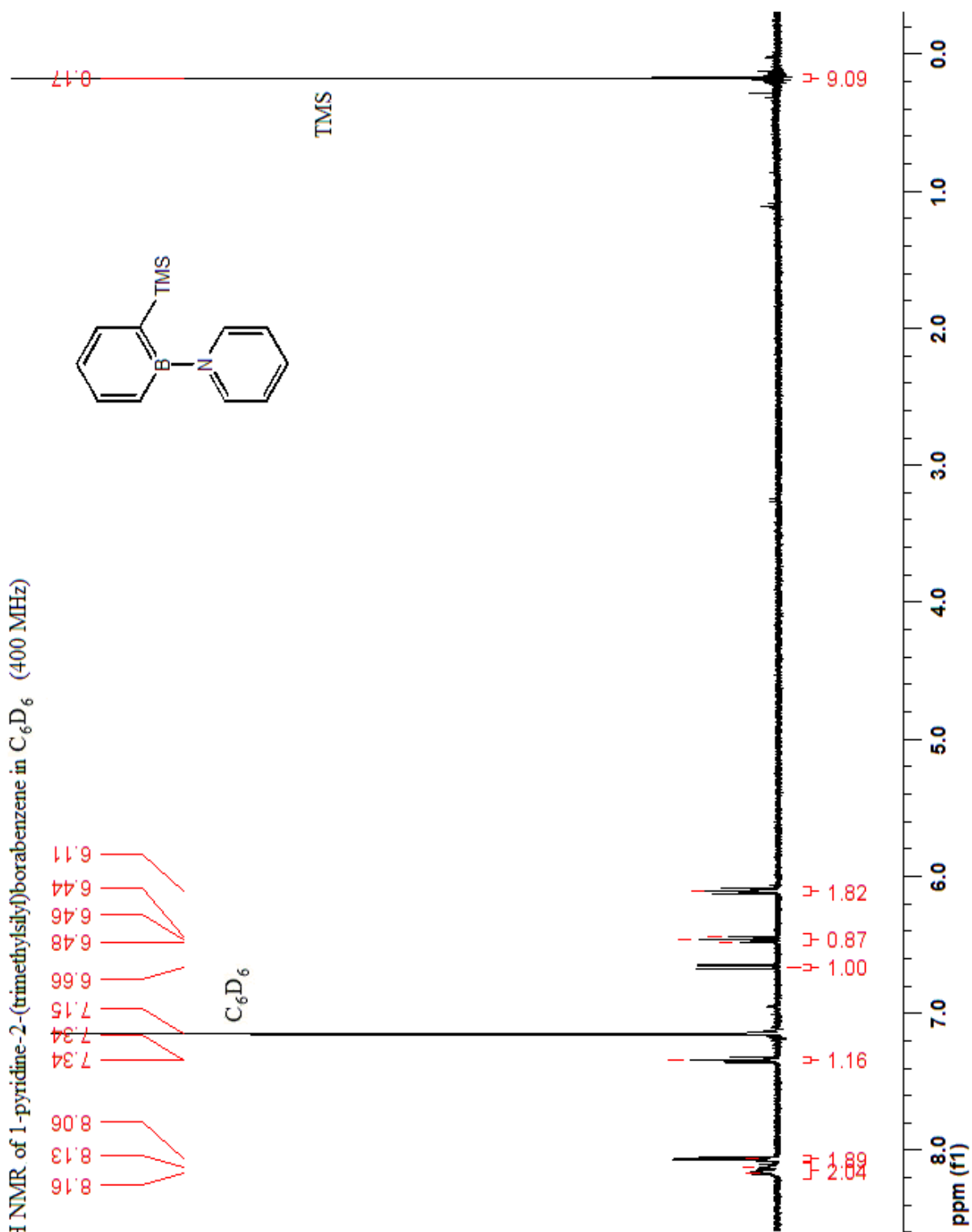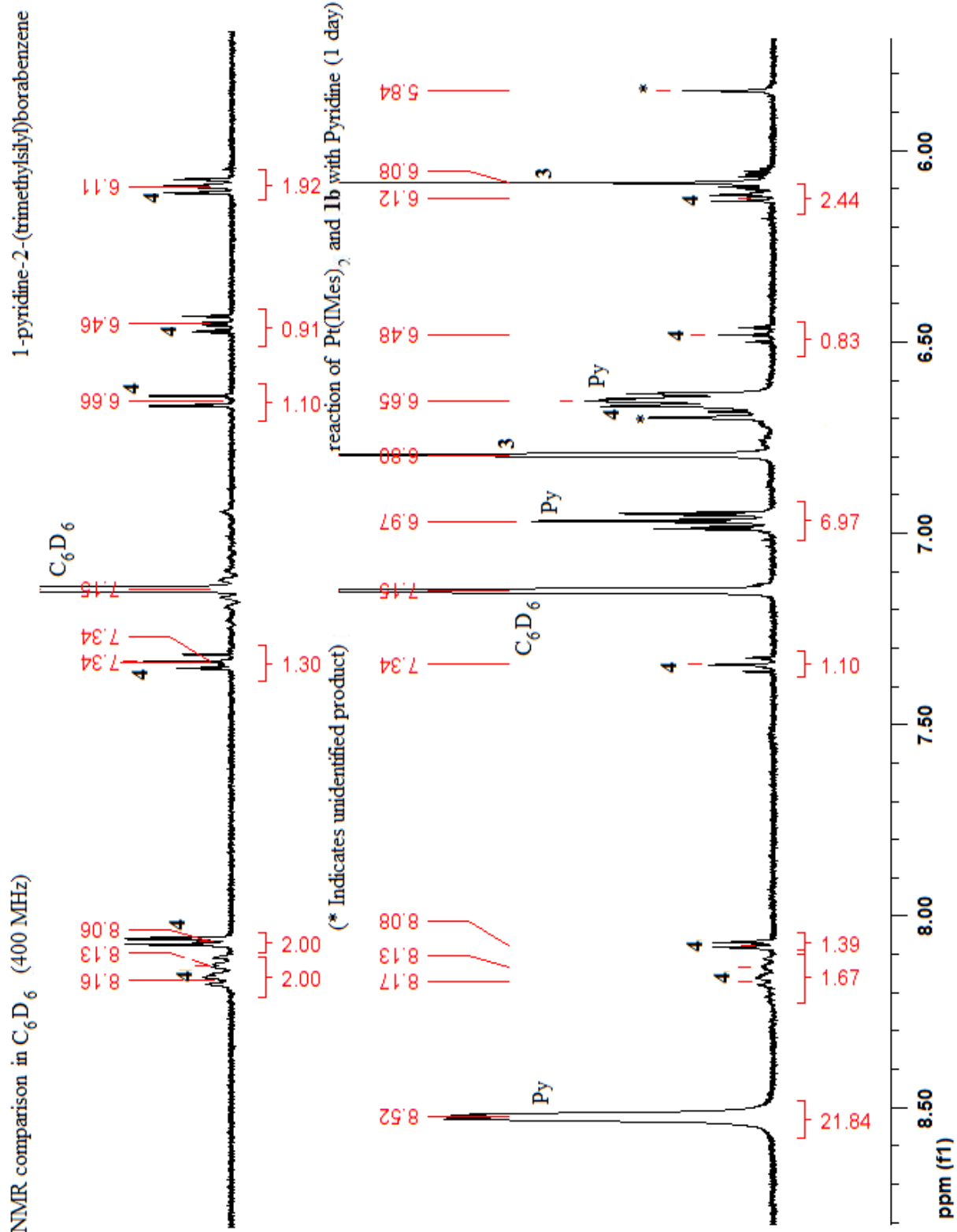

Scheme S-2. Reaction of **2b** with pyridine.

Synthesis of 1-pyridine-2-(trimethylsilyl)borabenzene (4)

1-chloro-2,6-bis(trimethylsilyl)-2,4-boracyclohexadiene and 1-chloro-2,2-bis(tri-methylsilyl)-3,5-boracyclohexadiene were combined in a 1:1 mixture, according to a known procedure.[3] Pyridine (0.4 mL, 4.95 mmol) was slowly added to a stirring solution of the boracycles (1.36 g, 5.3 mmol) in Et$_2$O (2 mL). Volatiles were removed under vacuum, and the resulting red precipitate was recrystallized from a saturated solution of Et$_2$O, filtered at -70°C, and dried under vacuum, to give a yellow crystalline solid. ^{1}H NMR (C$_6$D$_6$, 25 ^{o}C) δ: 8.20-8.07 (ovm, 2H), 8.03 (dm, J = 7.1 Hz, 2H), 7.32 (td, J = 7.1, 1.1 Hz, 1H), 6.66 (dd, J = 10.1, 1.1 Hz, 1H), 6.48 (app.tt, J = 7.8, 1.5 Hz, 1H), 6.15 (m, 2H), , 0.17 (s, 9H, TMS); ^{11}B NMR (C$_6$D$_6$, 25 ^{o}C) δ: 37.5 ppm. A crystal structure of **4** was also obtained (See S54)

4.2 NMR characterization

^{1}H NMR of the reaction of Pt(IMes)$_2$ and **1b** with Pyridine (1 day)

(* Indicates unidentified product)

^{1}H NMR of 1-pyridine-2-(trimethylsilyl)borabenzene in C_6D_6 (400 MHz)

^{1}H NMR comparison in C_6D_6 (400 MHz)

1-pyridine-2-(trimethylsilyl)borabenzene

reaction of Pt(IMes)$_2$ and **1b** with Pyridine (1 day)
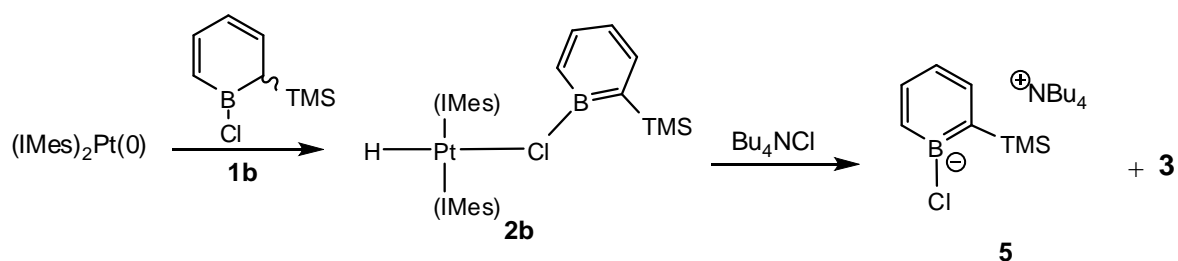
(* Indicates unidentified product)

## 5. Reactions with tetrabutylammonium chloride

5.1 Experimental

Reaction of 2b with tetrabutylammonium chloride

Boracyclohexadiene **1b** (0.00045 g, 0.0024 mmol) and [(IMes)$_2$Pt(0)] (0.0021 g, 0.0026 mmol) were combined in C$_6$D$_6$ (1 mL) in a J-Young NMR tube, to generate **2b**, as previously described. Tetrabutylammonium chloride (0.0005g, 0.0022 mmol) was dissolved in C$_6$D$_6$, and added dropwise. Two species, **3** and **5** were the major species observable by NMR spectroscopy. ^{1}H NMR (C$_6$D$_6$, 25 °C) δ: 7.84 (dd, J = 6.8, 1.4 Hz, 1H, **5**), 7.62 (ddd, J = 10.1, 6.8, 1.5 Hz, 1H, **5**), 6.81 (s, [Pt(0)IMes$_2$]), 6.80 (s, **3**), 6.78 (s, *), 6.70 (td, J = 6.9, 1.1, 1H, **5**), 6.66 (dd, J = 10.1, 1.0, 1H, **5**), 6.10 (s, [Pt(0)IMes$_2$]), 6.09 (s, **3**), 6.09 (s, *), 2.75 (m, 8H, **5**), 2.33 (s, **3**), 2.32 (s, [Pt(0)IMes$_2$]), 2.10 (s, *), 2.07 (s, **3**), 2.04 (s, [Pt(0)IMes$_2$]), 1.24 (ov m, 16H, **5**), 0.92 (t, J = 7.0, 12H, **5**), 0.74 (s, 9H, **5**), 0.29 (s, *), -16.70 (s, *), -17.96 (s, **3**). ^{13}C{^{1}H} (HSQC) NMR (C$_6$D$_6$, 25 °C) δ: 128.7 (**3**), 120.5 (**3**), 58.5 (Bu, **5**), 24.1 (Bu, **5**), 21.1 (**3**), 19.8 (Bu, **5**), 18.5 (**3**), 13.7 (Bu, **5**), 1.6 (TMS, **5**) * is for unidentified species.

Scheme S-3. Reaction of **2b** with [NBu$_4$]Cl.

5.2 NMR characterization
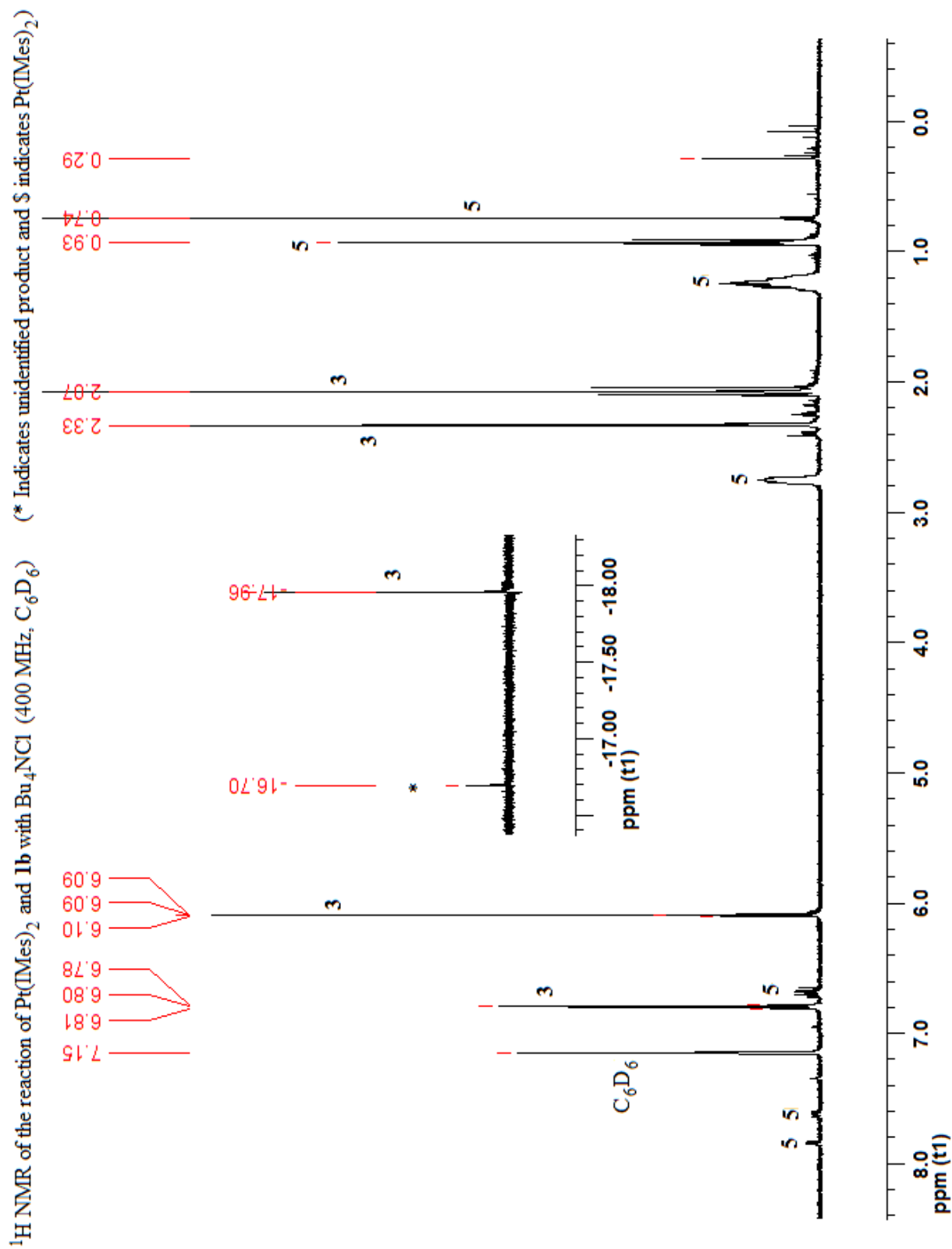
^{1}H NMR of the reaction of Pt(IMes)$_2$ and **1b** with Bu$_4$NCl (400 MHz, C$_6$D$_6$) (* Indicates unidentified product and $ indicates Pt(IMes)$_2$)

^{1}H NMR of the reaction of Pt(IMes)$_2$ and **1b** with Bu$_4$NCl (400 MHz, C$_6$D$_6$)

(* Indicates unidentified product and $ indicates Pt(IMes)$_2$)
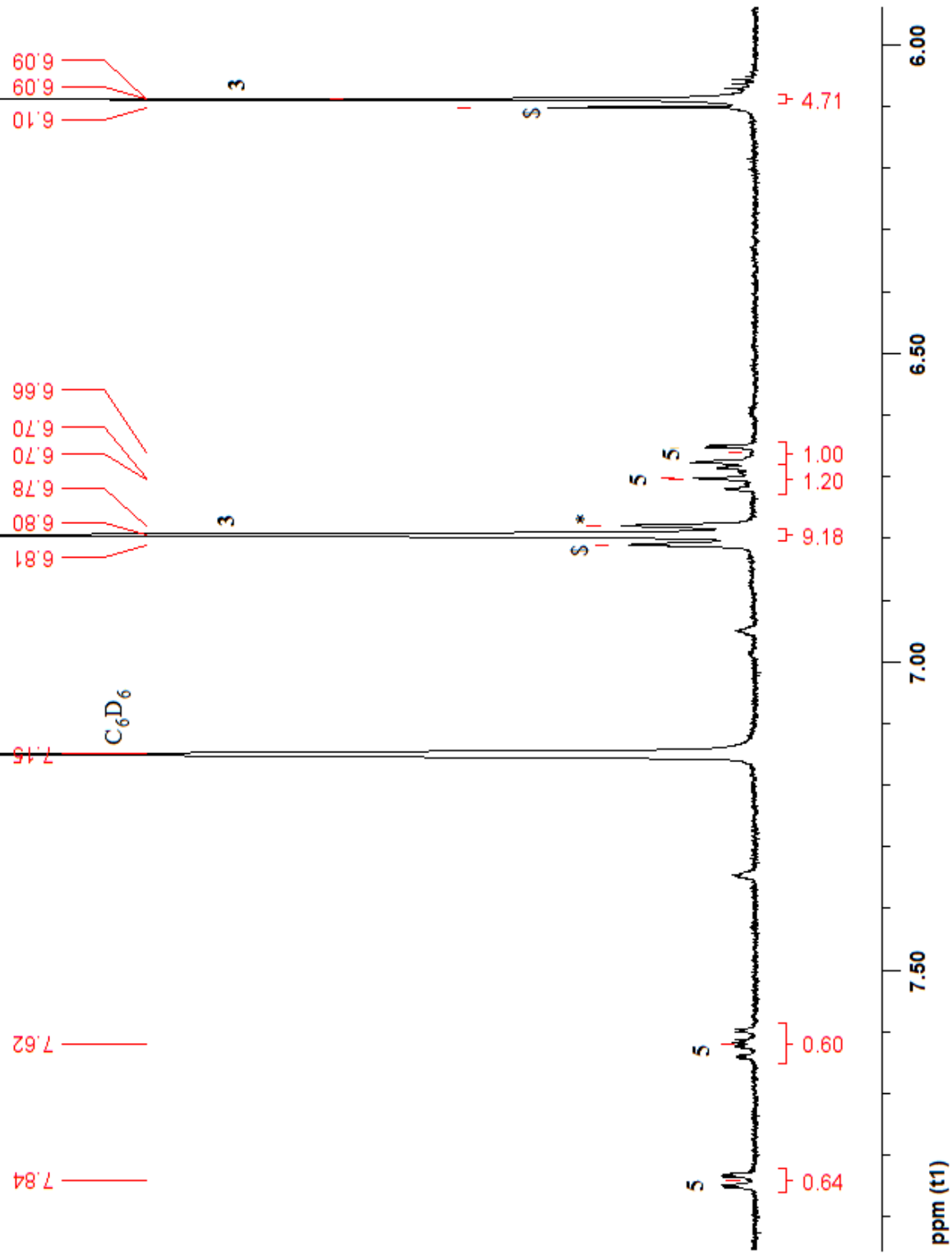
Comparison of the reaction of $Pt(IMes)_2$ and **1b** with NBu_4Cl, with the mixture of **3** with NBu_4Cl

$Pt(IMes)_2$ + **1b** + NBu_4Cl

$(IMes)_2Pt(H)(Cl)$ (**3**) + NBu_4Cl
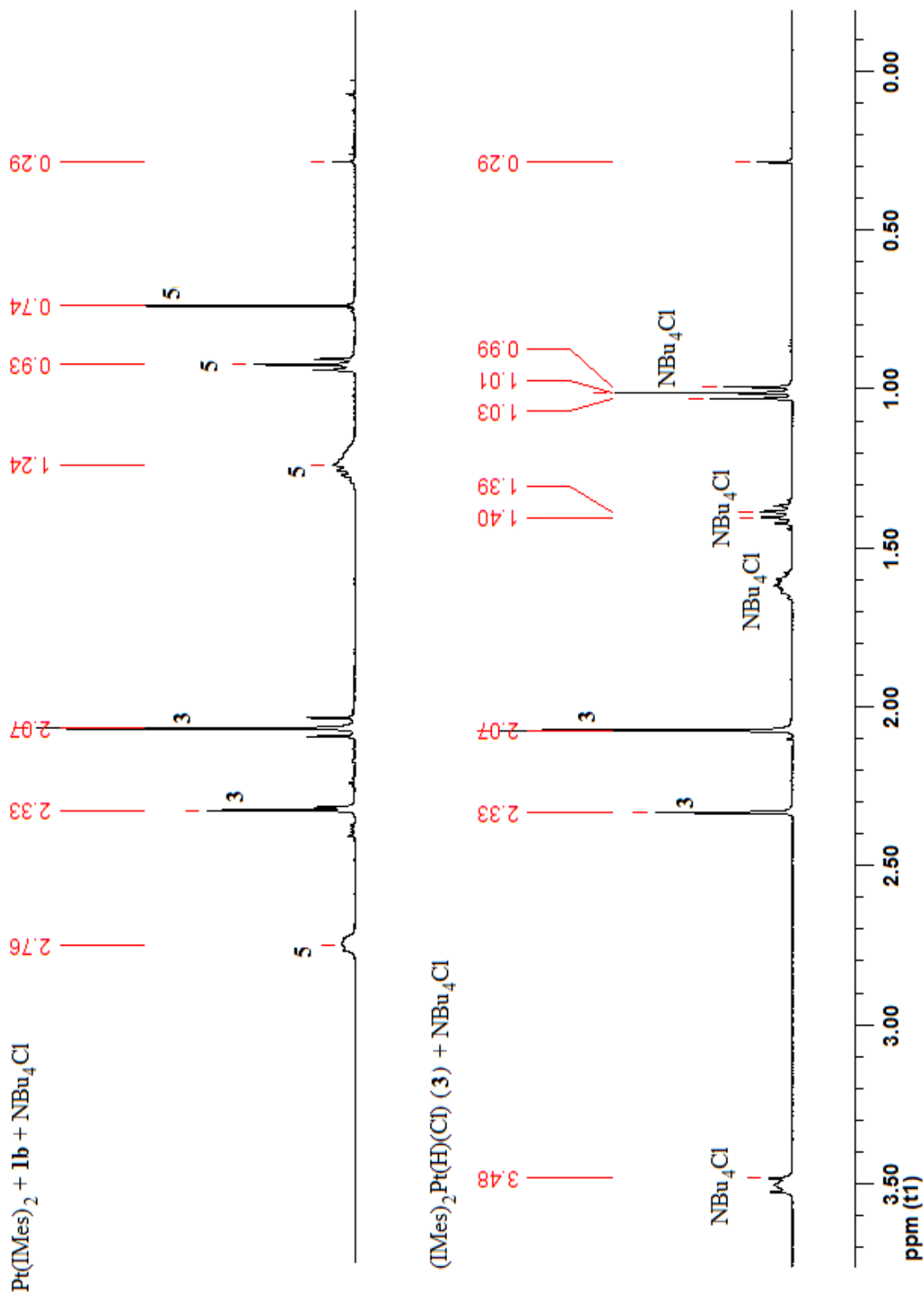
^{1}H NMR of the reaction of Pt(IMes)$_2$ with **1b**, before and after NBu$_4$Cl addition (400 MHz, C$_6$D$_6$) (* indicates Pt(Imes)$_2$)
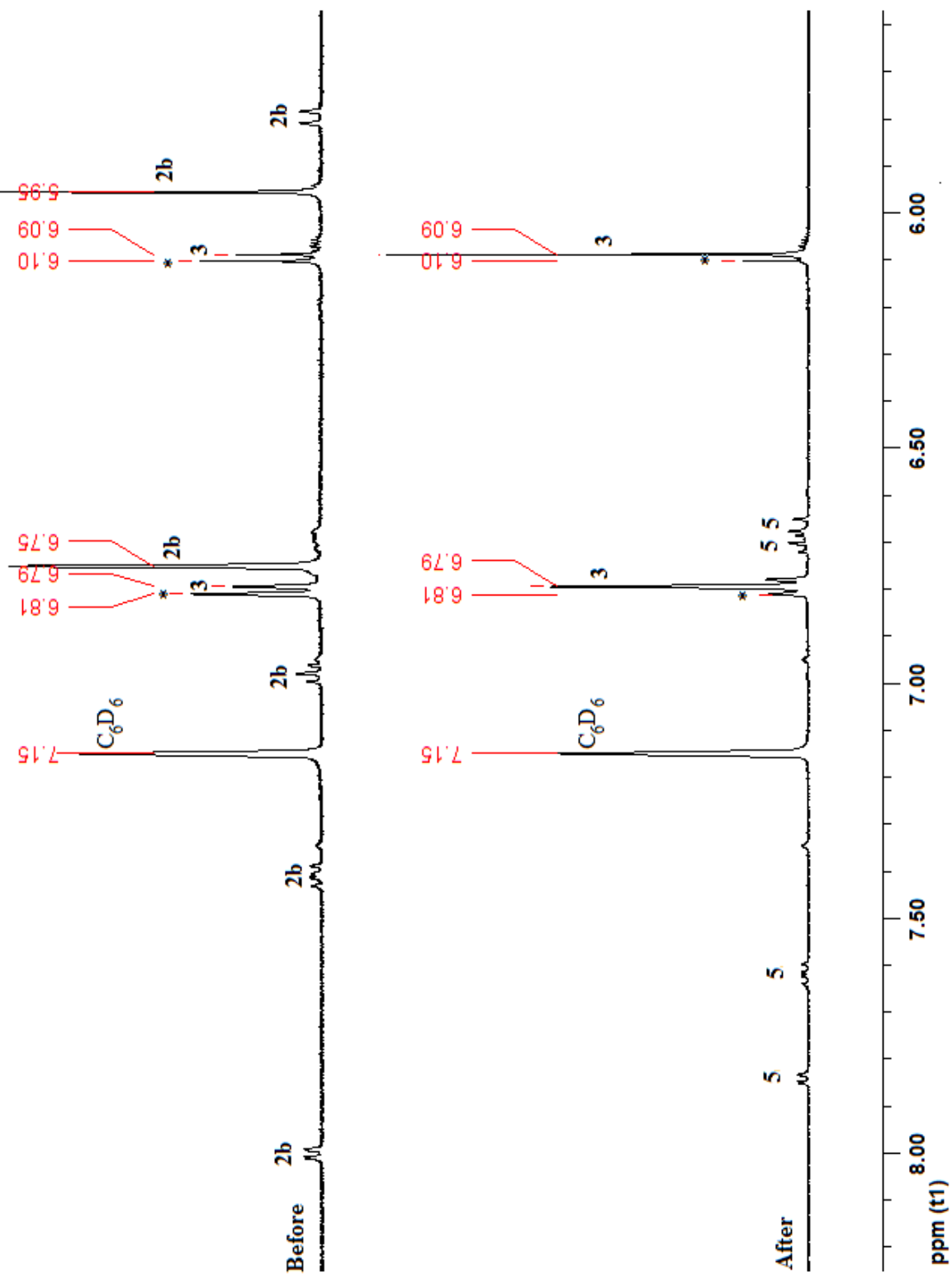
gHMQC of the reaction of Pt(IMes)$_2$ and **1b** with Bu$_4$NCl
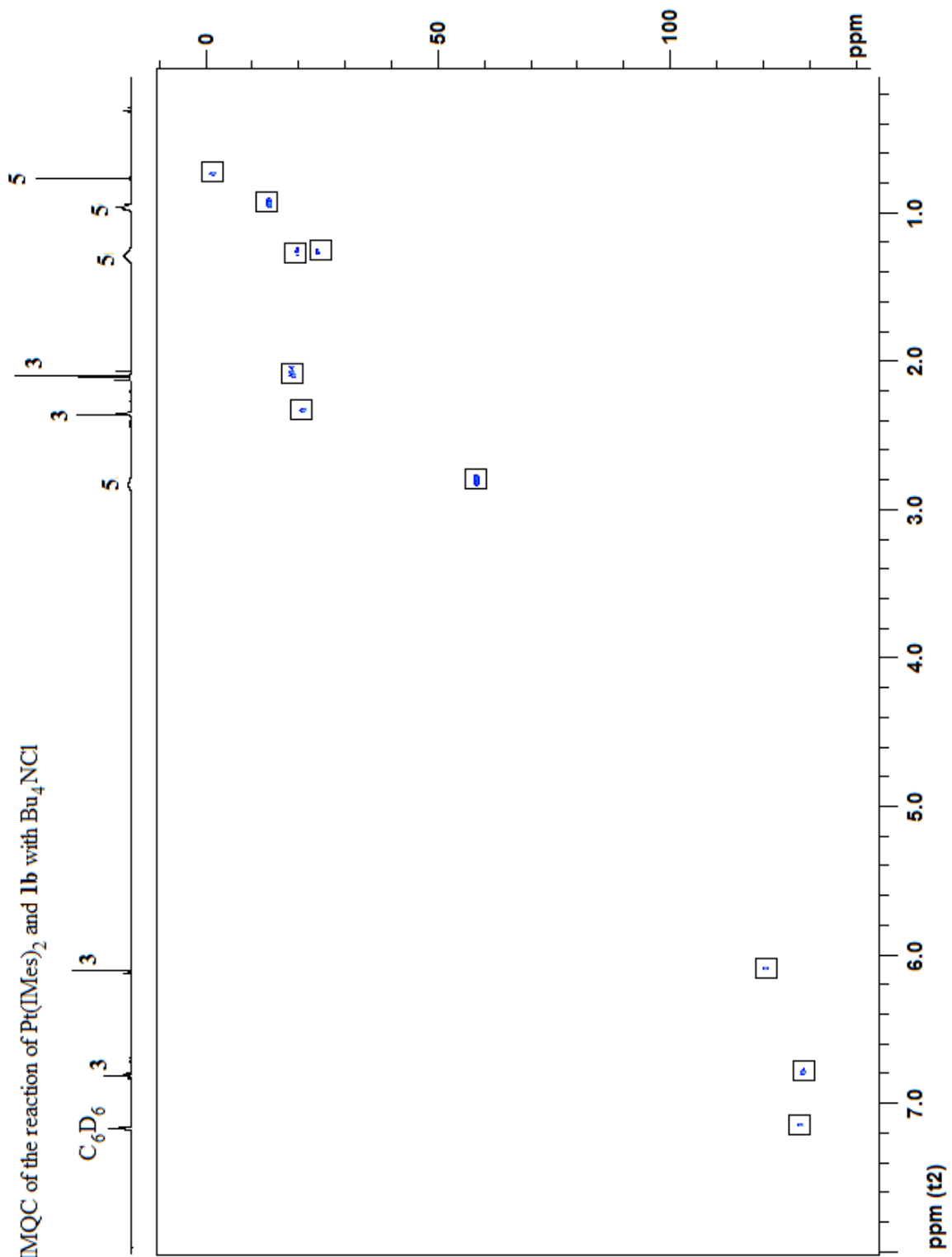
6. 2D NMR experiments

6.1 ROESY-2D of **2a**

ROESY-2D of **2a** in C_6D_6 (400 MHz)
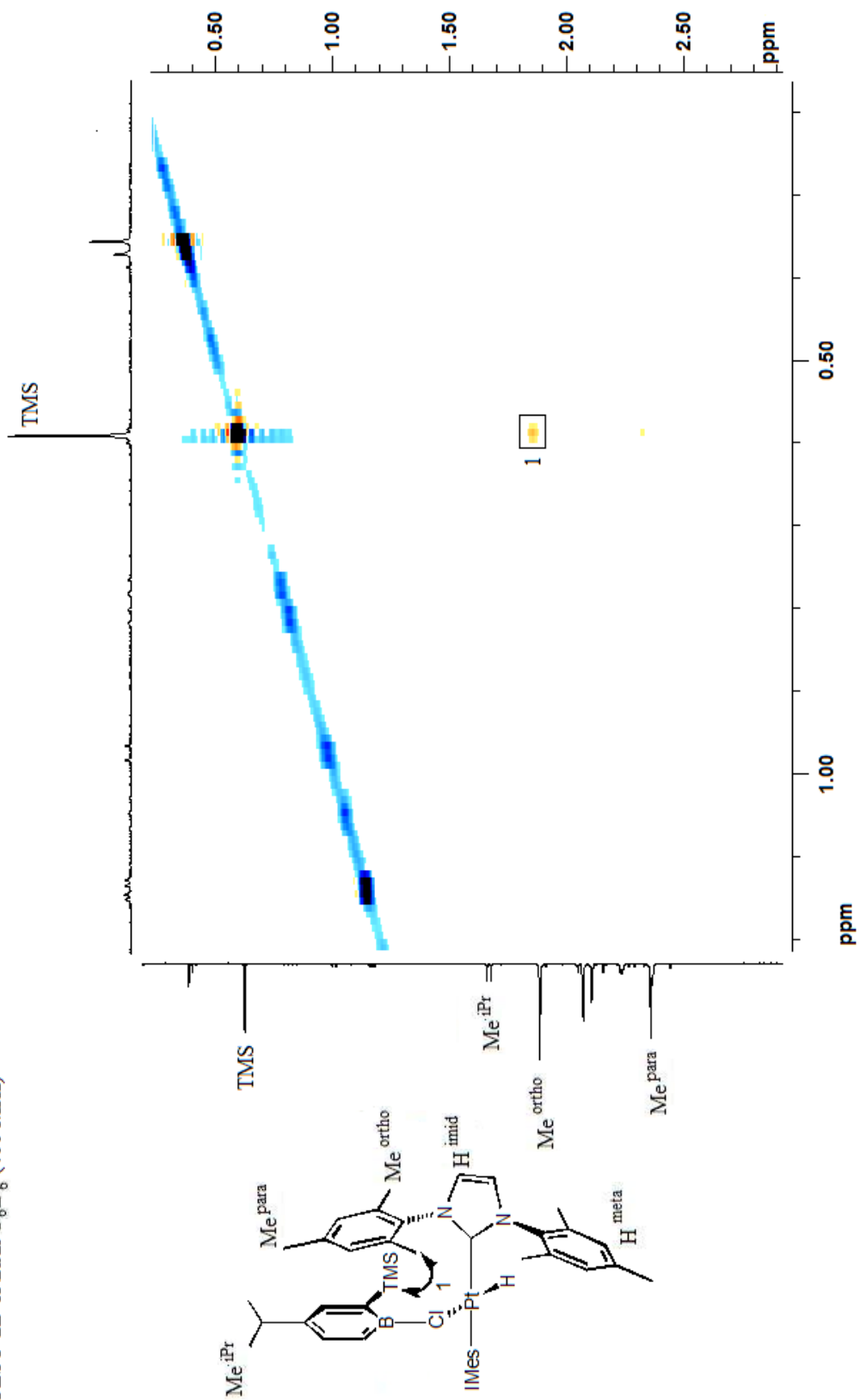
6.2 gHMQC of **2a, 2b, 2c** and **3**

gHMQC of **2a** in C_6D_6 (400 MHz)
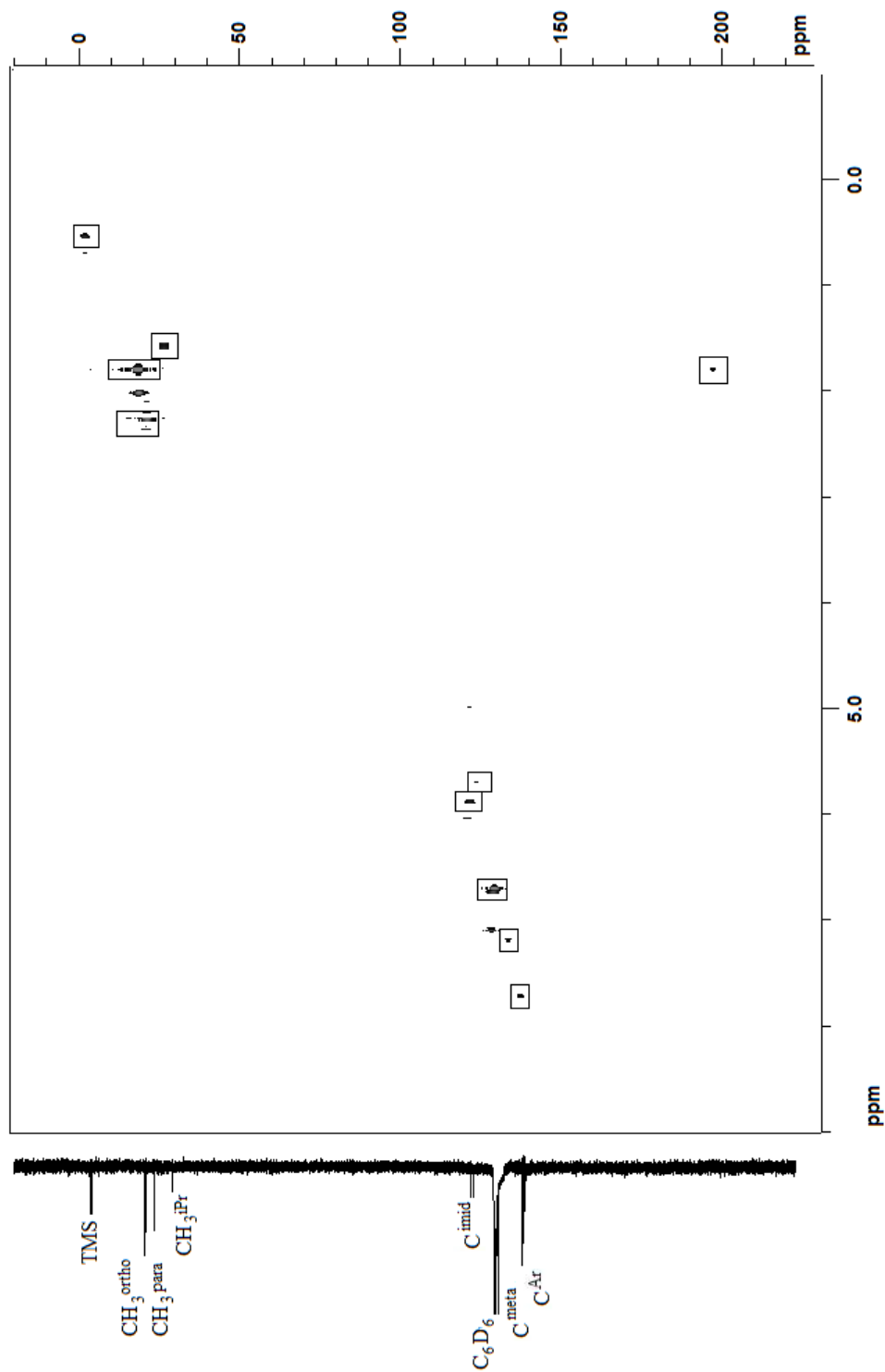
gHMQC of **2a** in C_6D_6 (400 MHz)

TMS

Me_{iPr}

Me^{ortho}

Me^{para}

TMS

C^{ortho}

C^{para}

CH_3^{iPr}

gHMQC of **2a** in C_6D_6 (400 MHz)

(* Indicates starting material)

(3 of 3)

S40

gHMQC of **2b** in C_6D_6 (400 MHz)

gHMQC of **2b** in C$_6$D$_6$ (400 MHz)

(* Indicates starting material)

TMS

Me^{ortho}

Me^{para}
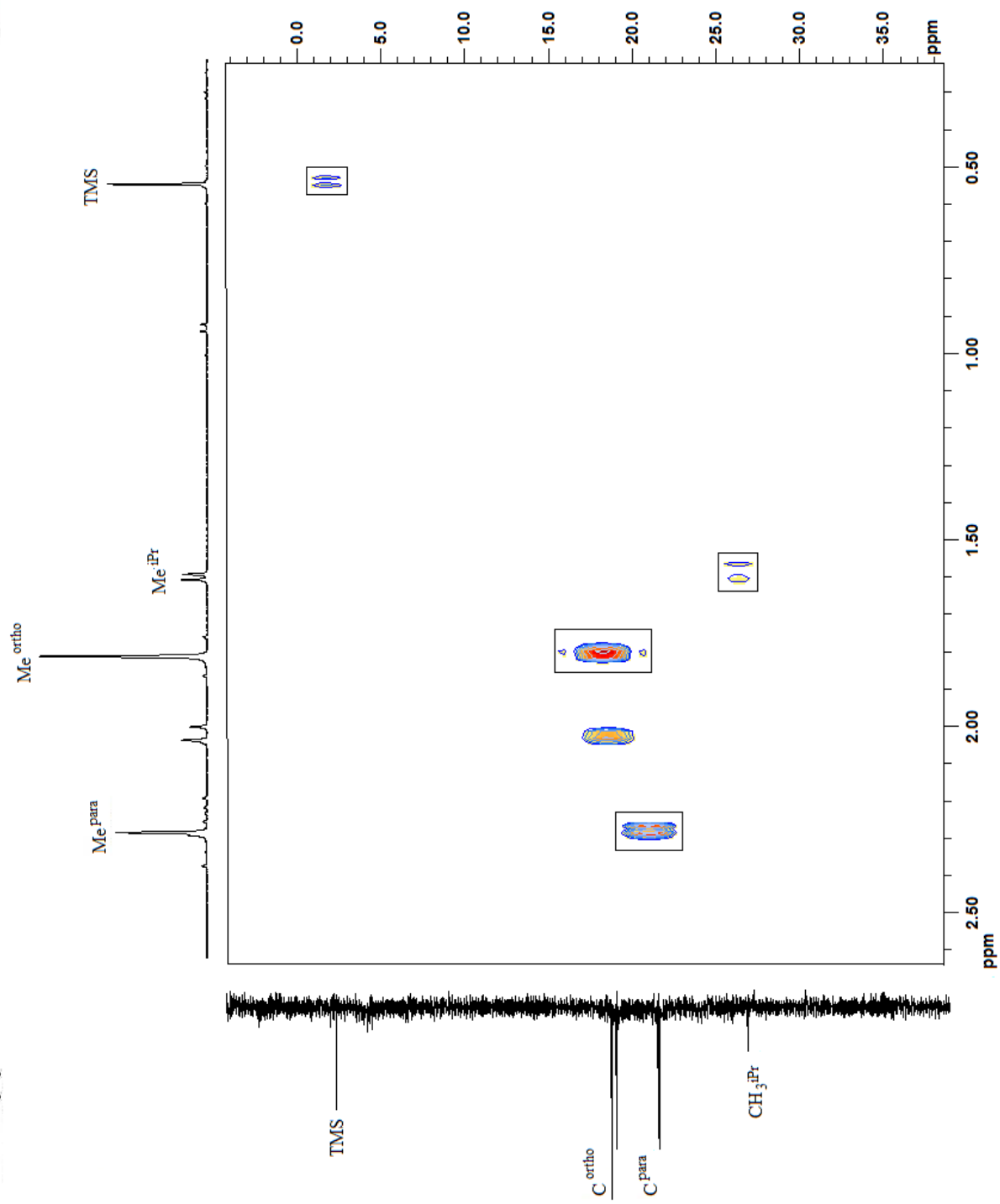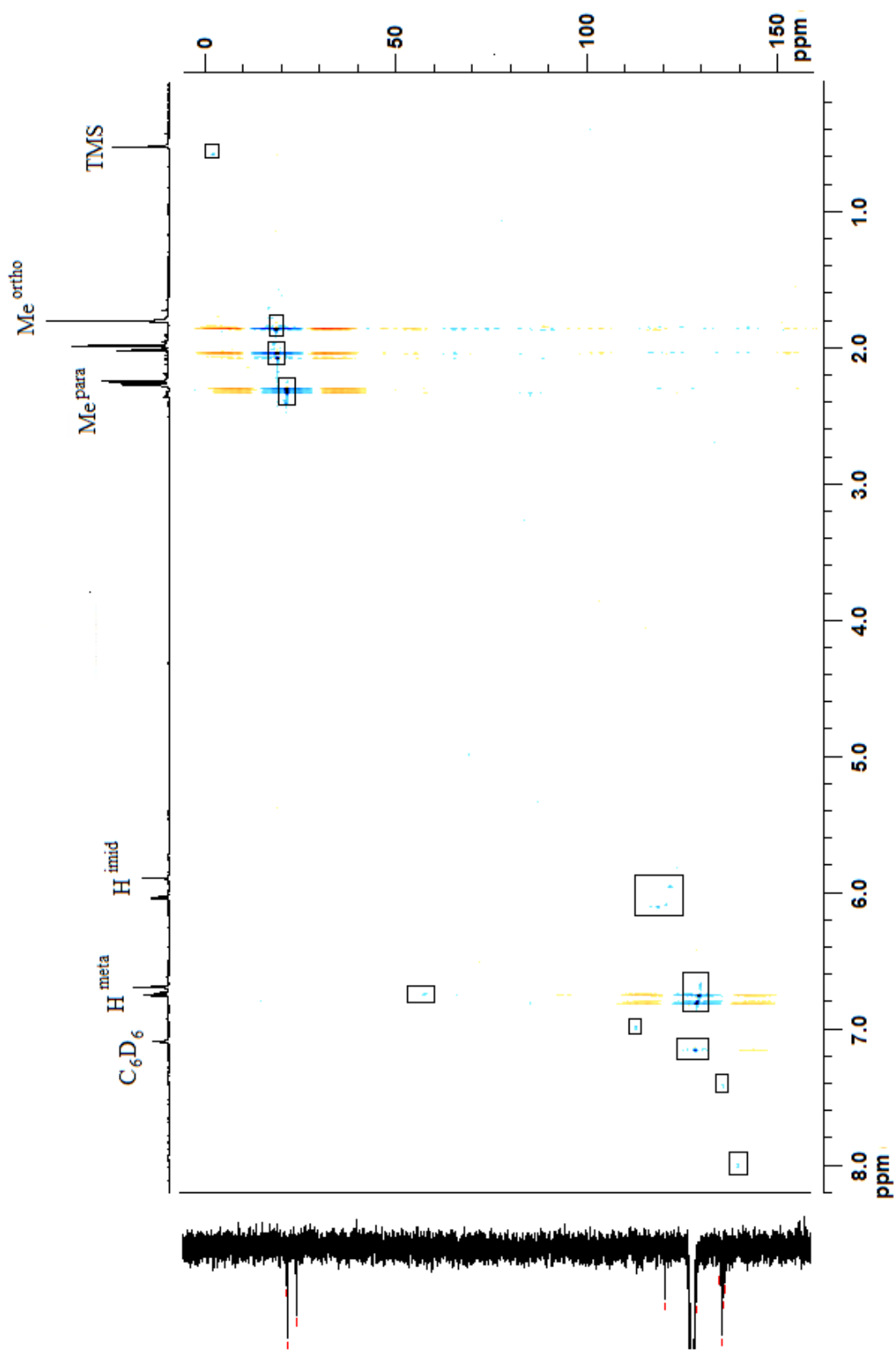
gHMQC of **2b** in C_6D_6 (400 MHz)

(* Indicates starting material)

gHMQC of **2c** in C$_6$D$_6$ (400 MHz)

(1 of 3)

gHMQC of **2c** in C_6D_6 (400 MHz)

(* Indicates starting material)

Me^{ortho}

Me^{para}

3

*

* **3**

gHMQC of **2c** in C_6D_6 (400 MHz)

(* Indicates starting material)
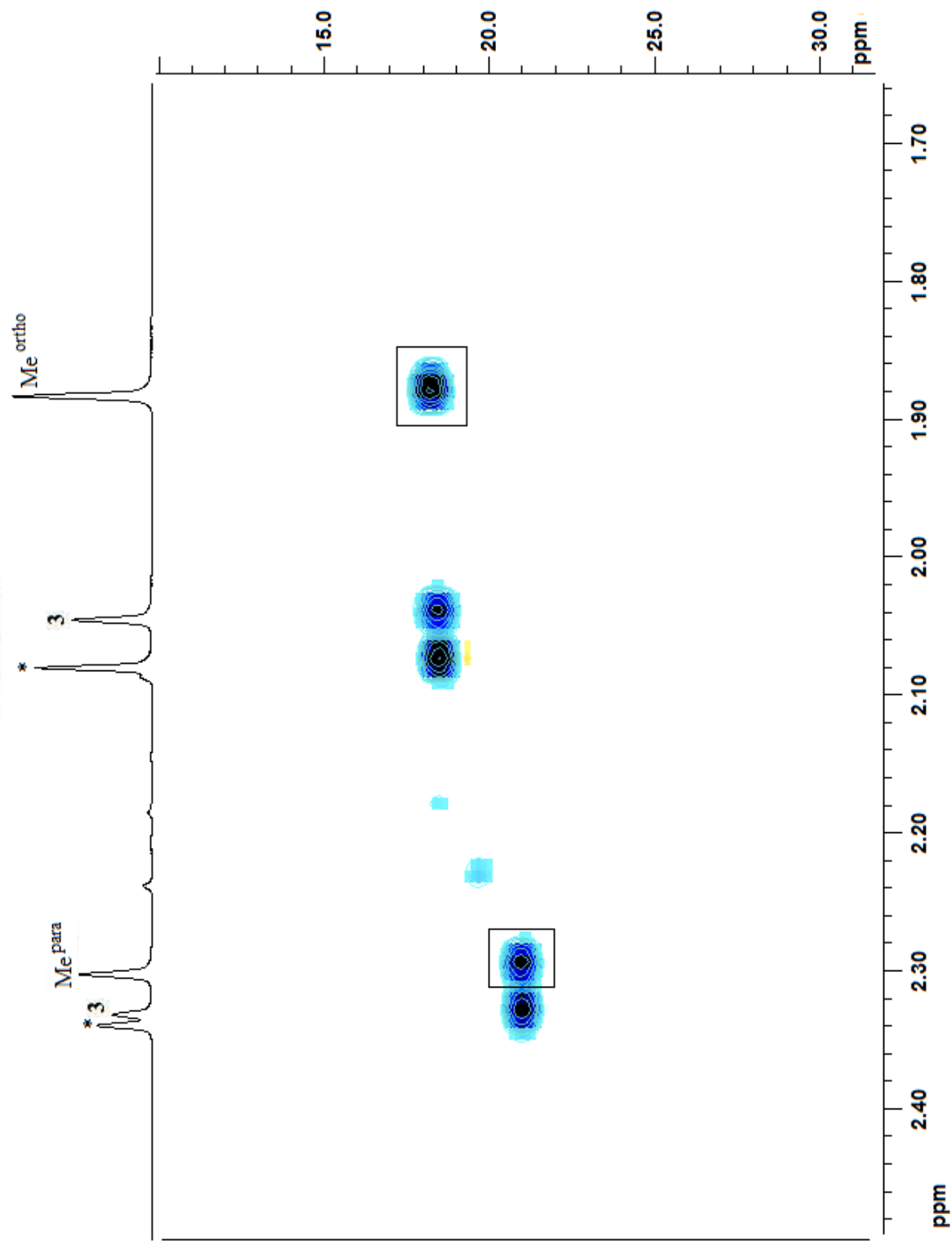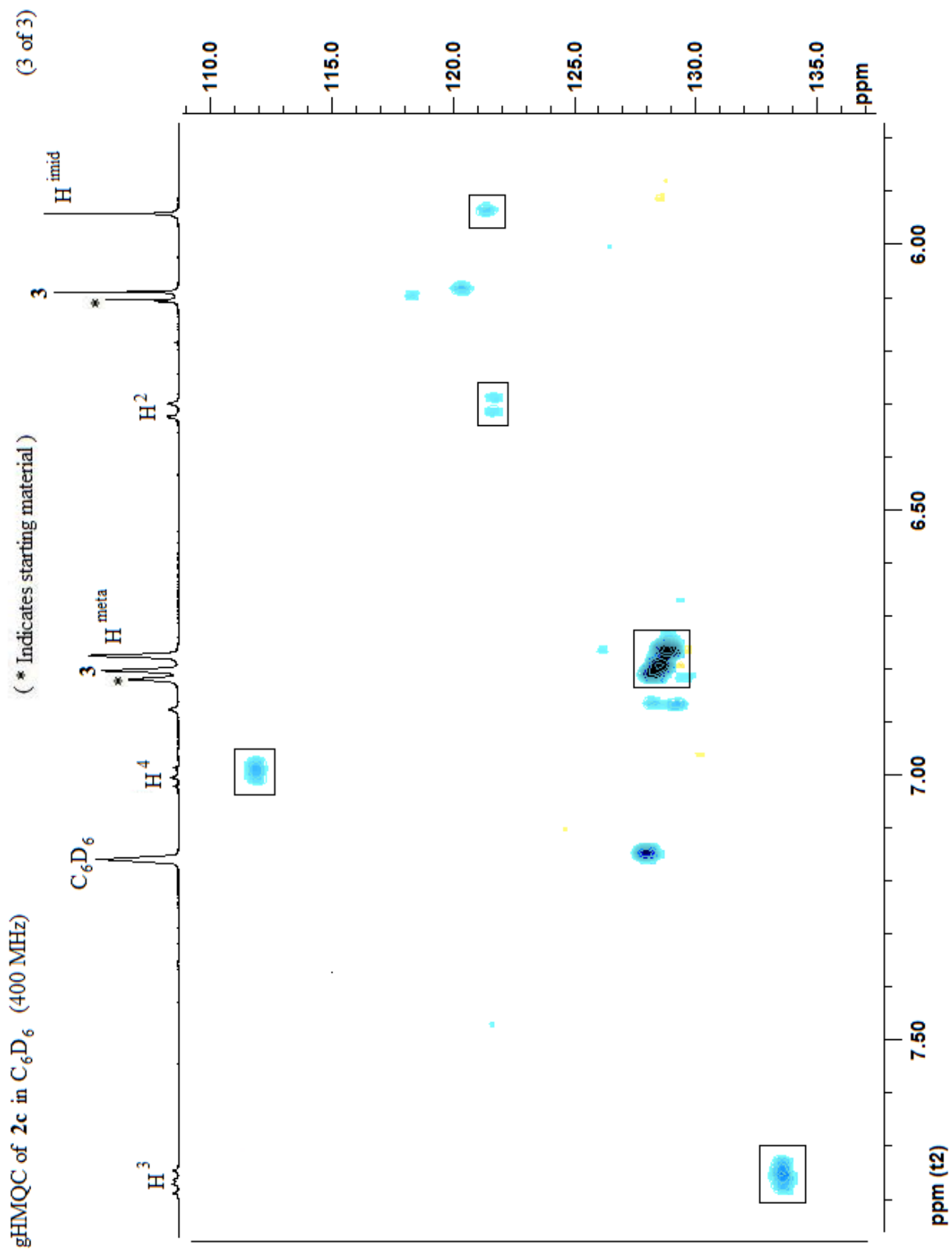
gHMQC (^{1}H^{13}C) of **3** in C$_6$D$_6$ (400 MHz)

Me^{ortho}

Me^{para}

H^{imid}

H^{meta}

C$_6$D$_6$

Me^{ortho}

Me^{para}

C$_6$D$_6$

C^{imid}

C^{meta}

C^{car}
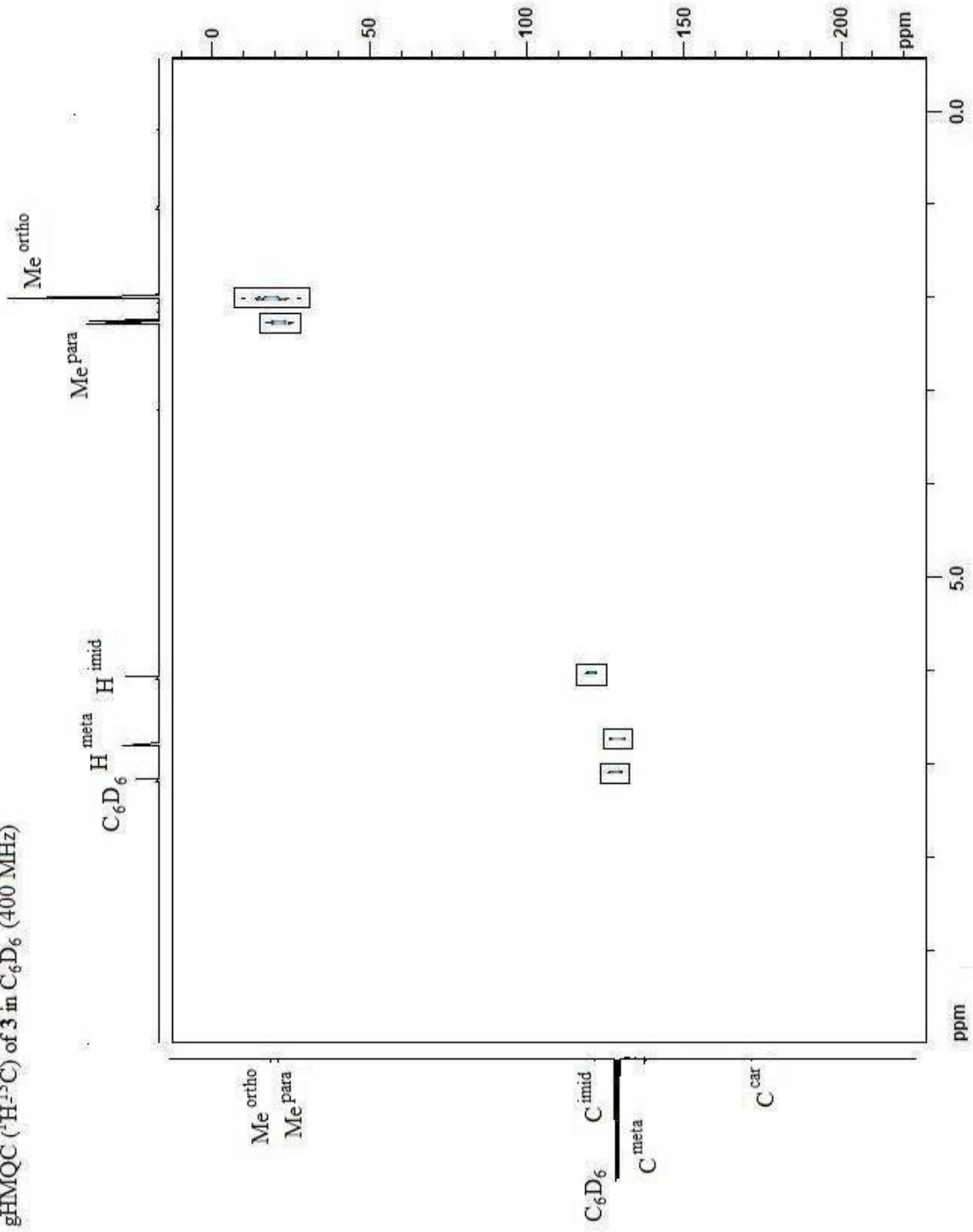
7. DFT calculations

Pt and Cl were treated with a Stuttgart-Dresden pseudopotential in combination with their adapted basis set.[4,5] In all cases, the basis set has been augmented by a set of polarization functions (f for Pt d for Cl).[6] Carbon, Nitrogen, Boron and Hydrogen atoms have been described with a 6-31G(d,p) double-ζ basis set.[7] Calculations were carried out at the DFT level of theory using the hybrid functional B3PW91.[8,9] Geometry optimisations were carried out without any symmetry restrictions, the nature of the *extrema* (*minimum*) was verified with analytical frequency calculations. All these computations have been performed with the Gaussian 03[10] suite of programs. ^{11}B NMR chemical shifts were evaluated by employing the direct implementation of the Gauge Including Atomic Orbitals (GIAO) method[11] at the B3PW91 density functional level of theory, using as reference the corresponding $BF_3 \cdot OEt_2$ ($\delta^{11}B = 0$ ppm) shielding constant calculated at the same level of theory.

Table S-1 - Complex **2b**

120
E=-2324.29407 a.u.

C	0.262000	0.585000	0.517000
C	0.204000	0.861000	1.891000
C	1.037000	0.214000	2.817000
C	1.965000	-0.708000	2.329000
C	2.070000	-0.999000	0.967000
C	1.208000	-0.348000	0.082000
N	-0.803000	1.760000	2.384000
C	-0.647000	3.095000	2.630000
N	-1.849000	3.477000	3.147000
C	-2.730000	2.409000	3.215000
C	-2.074000	1.328000	2.734000
Pt	1.033000	4.200000	2.355000
Cl	0.155000	4.904000	0.050000
C	-2.202000	4.790000	3.621000
C	-2.991000	5.623000	2.816000
C	-3.353000	6.869000	3.336000
C	-2.969000	7.283000	4.610000
C	-2.211000	6.406000	5.391000
C	-1.819000	5.153000	4.923000
C	-3.444000	5.250000	1.433000

C	-3.356000	8.645000	5.122000
C	-1.022000	4.226000	5.799000
C	0.929000	0.490000	4.292000
C	3.094000	-1.983000	0.465000
C	-0.662000	1.256000	-0.460000
C	2.818000	5.184000	2.300000
N	3.462000	5.734000	3.379000
C	4.698000	6.251000	3.025000
C	4.847000	6.021000	1.702000
N	3.699000	5.374000	1.273000
C	3.028000	5.733000	4.749000
C	3.408000	4.658000	5.570000
C	3.038000	4.701000	6.915000
C	2.328000	5.780000	7.451000
C	1.989000	6.836000	6.605000
C	2.335000	6.842000	5.250000
C	3.583000	4.935000	-0.093000
C	3.370000	5.899000	-1.092000
C	3.374000	5.464000	-2.417000
C	3.567000	4.123000	-2.760000
C	3.775000	3.202000	-1.734000
C	3.799000	3.584000	-0.389000

C	3.107000	7.343000	-0.765000	H	-1.434000	3.211000	5.797000
C	3.540000	3.694000	-4.202000	H	0.016000	4.159000	5.455000
C	4.052000	2.568000	0.689000	H	-1.013000	4.587000	6.830000
C	4.200000	3.502000	5.024000	H	-3.152000	8.746000	6.192000
C	1.977000	5.816000	8.915000	H	-2.798000	9.429000	4.598000
C	1.998000	8.016000	4.375000	H	-4.421000	8.845000	4.959000
H	5.342000	6.729000	3.746000	H	1.612000	-0.151000	4.856000
H	5.653000	6.248000	1.022000	H	1.173000	1.534000	4.513000
H	3.204000	6.196000	-3.203000	H	-0.086000	0.312000	4.663000
H	3.939000	2.155000	-1.981000	H	-0.491000	2.337000	-0.486000
H	3.320000	3.873000	7.562000	H	-0.509000	0.864000	-1.468000
H	1.445000	7.688000	7.006000	H	-1.713000	1.103000	-0.194000
H	4.401000	2.766000	5.807000	H	2.776000	-2.449000	-0.472000
H	3.663000	3.003000	4.211000	H	4.054000	-1.489000	0.275000
H	5.162000	3.832000	4.617000	H	3.278000	-2.777000	1.195000
H	1.496000	7.704000	3.456000	H	1.500000	3.682000	3.725000
H	1.343000	8.715000	4.900000	B	-0.541000	6.697000	-0.084000
H	2.901000	8.562000	4.078000	C	-0.335000	7.590000	1.087000
H	1.131000	6.483000	9.108000	C	-0.807000	8.899000	0.968000
H	1.718000	4.822000	9.291000	C	-1.451000	9.346000	-0.192000
H	2.822000	6.179000	9.513000	C	-1.666000	8.491000	-1.278000
H	3.146000	2.393000	1.281000	C	-1.255000	7.140000	-1.325000
H	4.366000	1.616000	0.254000	H	0.121000	7.277000	2.024000
H	4.834000	2.900000	1.382000	H	-0.685000	9.603000	1.795000
H	3.071000	7.941000	-1.679000	H	-1.802000	10.375000	-0.250000
H	2.140000	7.456000	-0.259000	H	-2.193000	8.917000	-2.134000
H	3.873000	7.772000	-0.111000	Si	-1.690000	6.137000	-2.851000
H	3.807000	2.639000	-4.313000	C	-2.659000	7.189000	-4.111000
H	2.541000	3.835000	-4.629000	C	-0.149000	5.476000	-3.755000
H	4.236000	4.284000	-4.808000	C	-2.789000	4.639000	-2.425000
H	-3.734000	2.527000	3.592000	H	-2.910000	6.584000	-4.989000
H	-2.382000	0.303000	2.604000	H	-3.595000	7.568000	-3.688000
H	-3.944000	7.536000	2.712000	H	-2.074000	8.048000	-4.456000
H	-1.923000	6.701000	6.398000	H	-3.005000	4.042000	-3.319000
H	2.615000	-1.219000	3.036000	H	-2.299000	3.992000	-1.691000
H	1.263000	-0.574000	-0.980000	H	-3.743000	4.970000	-2.000000
H	-2.914000	5.863000	0.694000	H	-0.434000	4.849000	-4.608000
H	-3.255000	4.203000	1.191000	H	0.457000	6.307000	-4.131000
H	-4.516000	5.442000	1.317000	H	0.474000	4.884000	-3.078000

8. Crystallographic analyses

Data Reduction

Data were integrated using the program SAINT.[12] The data were corrected for Lorentz and polarization effects. Face-indexed and multiscan absorption corrections were both performed, respectively using the XPREP[13] and SADABS[14] programs.

Structure Solution and Refinement

The structures were solved and refined using SHELXS-97 and SHELXL-97.[15] All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions, except for the hydrides that were located in the Fourier map. Neutral atom scattering factors were taken from the International Tables for X-Ray Crystallography.[16] All calculations and drawings were performed using the SHELXTL package.[17] The final model was checked either for missed symmetry or voids in the crystal structure using the PLATON software.[18] None were found. All crystal structures give satisfactory chekcif reports.

Data Collection

Crystals were mounted on a glass fiber using Paratone N hydrocarbon oil. Measurements were made at 200(2) K on a Bruker APEX II area detector diffractometer equipped with graphite monochromated MoKα radiation. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.5° counted for a total of 30 seconds per frame.

Orientation matrixes corresponding to cell constants listed in Tables S-2 and S-3 were obtained from a least-squares refinement using the measured positions of *n* centered reflections. The program used for retrieving cell parameters and data collection was APEX 2.[19]

Table S-2. Crystal data and structure refinement for **C** and **3**

|	[(PCy$_3$)$_2$Pt(H)(Cl)] (**C**)	[(IMes)$_2$Pt(H)(Cl)] (**3**)
Empirical formula	C36 H67 Cl P2 Pt	C42 H49 Cl N4 Pt
Formula weight	792.38	840.39
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	P2(1)/C	Pbca
Unit cell dimensions	a = 10.0446(11) Å	a = 17.0333(16) Å
	b = 15.7442(17) Å; β= 109.880(4)°	b = 19.0943(18) Å
	c = 24.5102(19) Å	c = 23.214(2) Å
Volume	3645.2(6) Å^3	7550.1(12) Å^3
Z	4	8
Density (calculated)	1.444 Mg/m^3	1.479 Mg/m^3
Absorption coefficient	4.033 mm^{-1}	3.822 mm^{-1}
F(000)	1632	3392
Crystal size	0.20 x 0.14 x 0.02 mm^3	0.30 x 0.20 x 0.20 mm^3
θ range for data collection	1.77 to 27.00°	1.75 to 29.11°
Reflections collected	41578	90507
Independent reflections	7932 [R(int) = 0.0512]	9696 [R(int) = 0.0373]
Max. and min. transmission	0.9237 and 0.4993	0.5153 and 0.3935
Data / restraints / parameters	7932 / 0 / 365	9696 / 0 / 449
Goodness-of-fit on F^2	1.119	1.213
Final R indices [I>2σ(I)]	R1 = 0.0298,	R1 = 0.0217,
	wR2 = 0.0621	wR2 = 0.0525
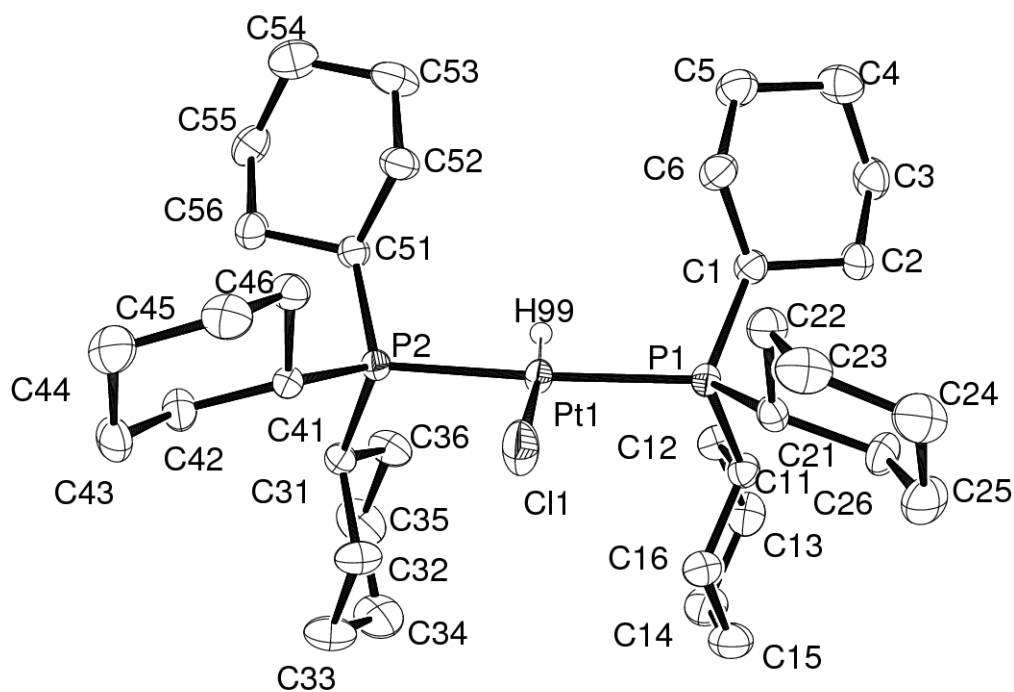
Figure S-1. Molecular structure of [(PCy$_3$)$_2$Pt(H)(Cl)] (**C**) Selected bond lengths (Å) and bond angles (°): Pt(1)-Cl(1) 2.4043(10), Pt(1)-H(99) 1.38(4), Pt(1)-P(1)/P(2) 2.2859(9)/2.2840(9), P(1)-Pt(1)-P(2) 162.77(3), Cl(1)-Pt(1)-H(99) 174.5(17), Cl(1)-Pt(1)-P(1)/P(2) 96.69(3)/95.36(3), H(99)-Pt(1)-P(1)/P(2) 87.7(15)/80.4(15). Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Hydrides are represented by spheres of arbitrary size. (CCDC deposition No. 724579)
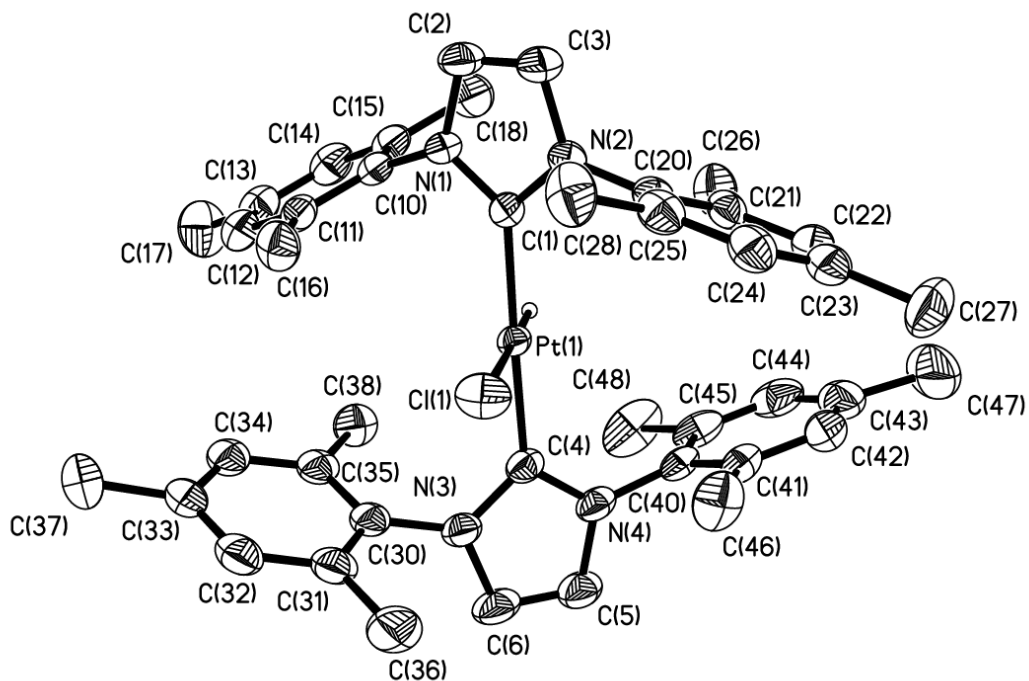
Figure S-2. Molecular structure of [(IMes$_2$)$_2$Pt(H)(Cl)] (**3**). Selected bond lengths (Å) and bond angles (°): Pt(1)-C(1)/C(4) 1.995(2)/1.998(2), Pt(1)-Cl(1) 2.4174(7), Pt(1)-H(1) 1.54(3), C(1)-Pt(1)-C(4) 177.22(9), Cl(1)-Pt(1)-C(1)/C(4) 92.48(7)/90.18(7), H(1)-Pt(1)-C(1)/C(4) 85.5(9)/91.8(9), Cl(1)-Pt(1)-H(1) 179.6(10). Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Hydrides are represented by spheres of arbitrary size. (CCDC deposition No. 724579)

Table S-3 Crystal data and structure refinement for **(4)**

|	
Empirical formula	C26 H35 B2 N2 Si2
Formula weight	453.36
Crystal system	Monoclinic
Space group	c2/c
Unit cell dimensions	a = 18.842(5) Å $\qquad \alpha = 90°$.
	b = 9.016(3) Å $\qquad \beta = 117.481(14)°$.
	c = 18.201(6) Å $\qquad \gamma = 90°$.
Volume	2743.1(15) Å^3
Z	4
Density (calculated)	1.098 Mg/m^3
Absorption coefficient	0.145 mm^{-1}
F(000)	972
Crystal size	0.13 x 0.12 x 0.02 mm^3
θ range for data collection	2.44 to 24.25°.
Reflections collected	12430
Independent reflections	2220 [R(int) = 0.1380]
Data / restraints / parameters	2220 / 0 / 148
Goodness-of-fit on F^2	1.004
Final R indices [I>2σ(I)]	R1 = 0.0573, wR2 = 0.0931
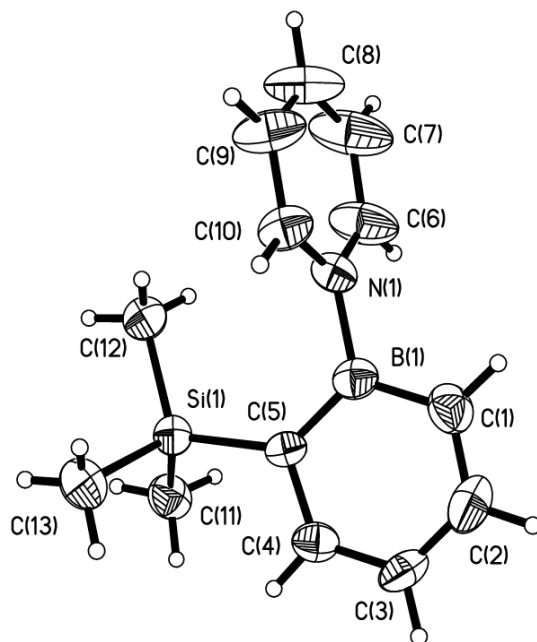
Figure S-3. Molecular Structure of 1-pyridine-2-(trimethylsilyl)borabenzene **(4).** Selected bond length (Å): B(1)-N(1)   1.555(5). Anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 50% probability level. Hydrogen atoms are represented by spheres of arbitrary size.(CCDC Deposition number 737237)

9. References

[1] N. A. Jasim, R. N. Rerutz, *J. Am. Chem. Soc*. **2000**, *122*, 8685–8693.

[2] H. Braunschweig, K. Radacki, K. Uttinger, *Inorg. Chem*. **2007**, 46, 8796–8800.

[3] J. Tweddell, D. A. Hoic, G. C. Fu, *J. Org. Chem.* **1997**, *62*, 8286–287.

[4] D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.

[5] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431–1441.

[6] A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1993**, *208*, 111–114.

[7] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213–222.

[8] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[9] K. Burke, J. P. Perdew, W. Yang, *Electronic Density Functional Theory: Recent Progress and New Directions*, Eds.: J. F. Dobson, G. Vignale, M. P. Das, **1998**.

[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratman, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui,

K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowswi, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Jonhson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 03*; C.02 ed. Pittsburgh PA, **2006**.
[11] (a) F. London, *J. Phys. Radium* **1937**, *8*, 3974–3976; (b) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789–807; (c) K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260.
[12] Bruker, *SAINT* Version 7.07a, **2003,** Bruker AXS Inc., Madison, Wisconsin, USA.
[13] Bruker, *XPREP* Version 2005/2, **2005,** Bruker AXS Inc., Madison, Wisconsin, USA.
[14] G.M. Sheldrick, *SADABS* Version 2004/1, **2004,** Bruker AXS Inc., Madison, Wisconsin, USA.
[15] G.M. Sheldrick, *SHELXS-97 and SHELXL-97* Programs for the refinement of crystal structures. **1997,** University of Gottingen, Germany.
[16] International Tables for Crystallography, Vol C. **1992**, Ed. A.J.C. Wilson, Kluwer Academic Publishers, Dordecht: Tables 4.2.6.8 (pp 219-222) and 6.1.1.4 (pp. 500-502).
[17] Bruker, *SHELXTL* Version 6.12 **2001,** Bruker AXS, Madison, Wisconsin, USA.
[18] A. L. Spek, *Acta Cryst.* **1990,** A46, C-34.
[19] Bruker. *APEX 2* Version 2.0.2 **2005,** Bruker AXS Inc., Madison, Wisconsin, USA.