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Intermolecular Oxidative Addition of Aryl Halides to Platinum(II) Alkyl Complexes

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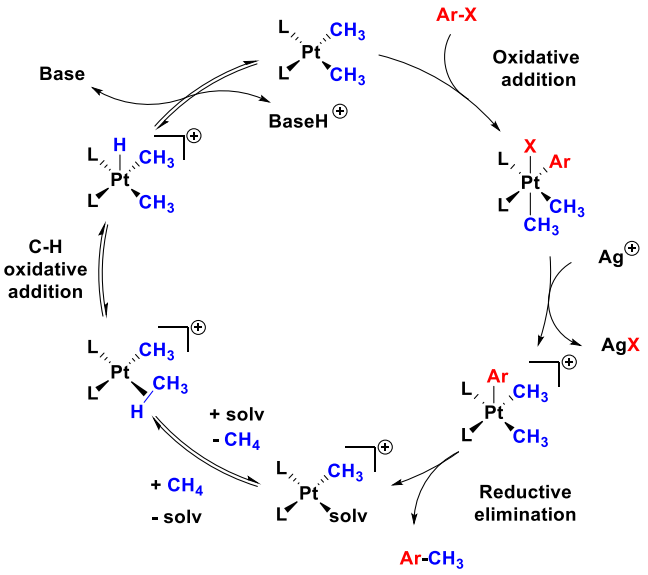
ABSTRACT: We report the first well-defined example of intermolecular aryl halide oxidative addition (OA) to Pt(II). Complexes of the type (IMes)$PtMe_2$(L) and (IMes')PtMe(L) (L = SMe_2, pyridine; IMes = *N*,*N*-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; IMes' = cyclometalated IMes) undergo intermolecular OA of phenyl iodide (PhI) at 60 °C, producing toluene *via* reductive elimination from a proposed Pt(IV)-phenyl species. Isolation of a model Pt(IV) OA product provides evidence for a Pt(II)/(IV) pathway. The OA of PhI is not limited to Pt(II)-IMes complexes;analogous reactions also proceed with phosphine-ligated Pt(II) dialkyl complexes, demonstrating that this reaction is feasible for a variety of electron-rich Pt(II) complexes bearing labile ligands.

Oxidative addition (OA) is a fundamental reaction that is a critical step in catalytic processes such as Suzuki-Miyaura coupling,[1] Buchwald-Hartwig amination,[2] olefin hydrogenation,[3] and the Monsanto process.[4] The OA of a variety of oxidants to low valent metals is well established; the aforementioned processes often rely on OA of carbon-(pseudo)halide (C-X) bonds to M(0) or M(I) species.[5] The OA of alkyl halides to group 10 M(II) species has been well studied stoichiometrically and catalytically.[4,6–16] Despite the increasing prevalence of M(II)/M(IV) (M = Ni, Pd) catalytic processes invoking Csp^2-X OA in the literature,[17] few well-defined examples of such reactivity have been reported.[18–23] While many Pt(II) complexes undergo facile S_N2-type Csp^3-X OA, these complexes are inactive toward intermolecular Csp^2-X OA which typically occurs in a concerted fashion.[24] With the exception of a poorly defined example from 1967,[25] efforts to achieve intermolecular C(aryl)-X oxidative addition have necessitated incorporation of the oxidant into the ligand scaffold (intramolecular OA).[16,22,26–32]

As part of our ongoing efforts in Pt(II)/(IV) catalysis,[33–36] we were interested in exploring the potential of aryl halides as oxidants in a proposed process for methane functionalization (Scheme 1). Our initial efforts in this area were reliant on a strategy developed by Puddephatt and coworkers, wherein Csp^2-X activation is facilitated by tethering an aryl halide to the ancillary ligand scaffold.[22,26–31,37] This approach provides well-defined Pt(IV) intermediates from which C-C reductive elimination (RE) can be induced, but tethering the aryl group prevents product dissociation and facilitates decomposition *via* ligand C-H activation.[38] As intermolecular Csp^2-X activation would obviate this problem, it became crucial to develop a Pt(II) system capable of intermolecular oxidative addition of aryl halides. In this work we describe a *N*-heterocyclic carbene (NHC) ligated dimethyl Pt(II) complex capable of intermolecular oxidative addition of PhX (X= I, Br). Through a combined experimental and computational study, we demonstrate the feasibility of concerted Csp^2-X OA to electron-rich Pt(II) complexes and extend this reactivity to several other L_2PtMe_2 complexes featuring common ligands.

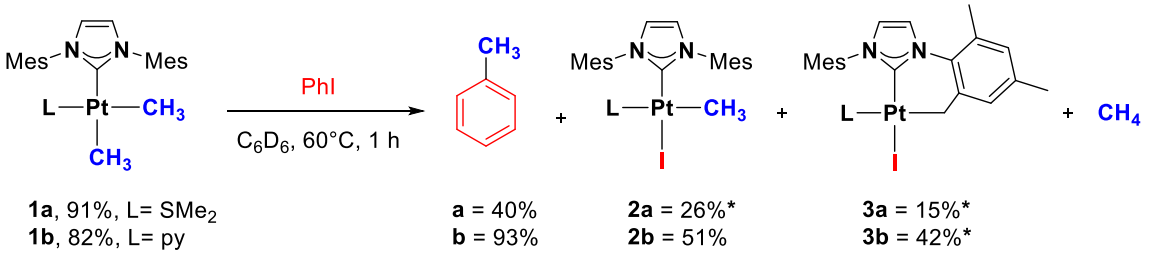
Scheme 1. Proposed catalytic cycle for methane functionalization.



We initially hypothesised that intermolecular Csp^2-X OA would be possible at sufficiently electron rich Pt(II) centres. As such, we aimed to prepare a series of Pt(II) dialkyl complexes using *N*-heterocyclic carbene (NHC) ligands. Complexes bearing an NHC in addition to SMe_2 (**1a**) or pyridine (**1b**) donors were readily prepared from $Pt_2Me_4(\mu\text{-}SMe_2)_2$ and $PtMe_2COD$, respectively. Heating **1a,b** at 60 °C in the presence of one equivalent of PhI generated toluene and new Pt(II) complexes **2a,b** and **3a,b** (Scheme 2). Deuterium labelling experiments with PhI-d_5 revealed exclusive formation of toluene-d_5, indicating that the phenyl group in the observed toluene was derived from PhI.

In-situ ^{1}H NMR spectroscopic analysis of the reaction mixtures of **1a,b** with PhI resulted in the detection of toluene and a single new Pt-CH_3 signal in each case. The Pt-CH_3 coupling constants (**2a**; $^2J_{Pt\text{-}H}$ = 80 Hz, **2b**; $^2J_{Pt\text{-}H}$ = 84 Hz) are consistent for methyl and NHC ligands being in a *cis* configuration. Additionally, the detection of methane in the ^{1}H NMR suggested that a C-H activation event occurred, which was confirmed by the presence of diastereotopic methylene

Scheme 2. Reaction of complexes 1a,b with PhI at 60 °C.



(*) Indicates the presence of an additional isomer (see experimental section of SI for details). Percentages correspond to sum of yields of both isomers. Major isomers shown except for **3b**.[50]

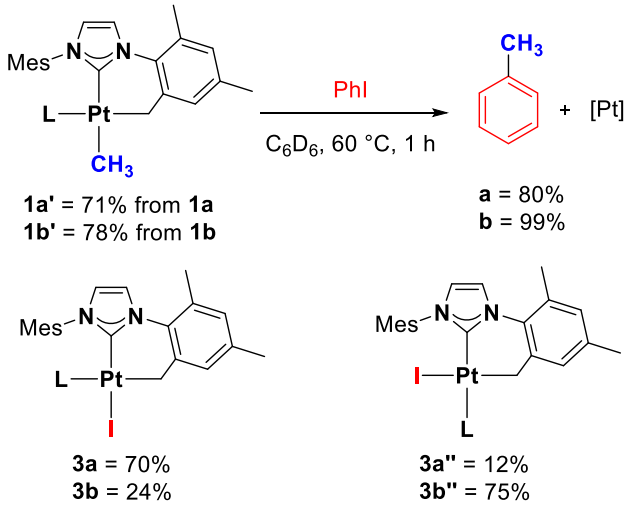
resonances characteristic of IMes cyclometallation at the *ortho*-methyl position (**3a,b**).[39,40]

The independent synthesis and full characterization (^{1}H, ^{13}C{^{1}H} NMR spectroscopy, ESI-MS) of all Pt(II) species presumed to have formed in the reaction of **1a,b** with PhI corroborated our assignments. The conversion of PhI to toluene is consistent with a mechanism in which PhI OA is followed by Csp^2-Csp^3 RE to provide **2a,b**, but the mechanism by which **3a,b** are formed is less clear. Cyclometalation of organoplatinum(II) NHC complexes *via* Csp^3-H activation and subsequent reductive elimination of methane is well established.[39–43] Thus we reasoned that **3a,b** was formed directly from **1a,b** or from the less electron-rich products, **2a,b**. To probe these possibilities, product mixtures containing **2a,b** and **3a,b** were heated for two hours at 100 °C. No changes in product ratios were observed. Heating an independently prepared sample of **2b** at 100 °C for one hour did not afford any conversion to **3b**, nor did heating in the presence of PhI. These results indicate that cyclometalated complexes are formed by an initial C-H activation process at **1a,b**, followed by PhI OA and reductive elimination of toluene. Gratifyingly, heating **1a,1b** at 60 °C for two hours in C_6H_6 was found to provide cyclometalated complexes **1a'** and **1b'** in 71% and 78% yield, respectively (see SI for solid state structures). Comparison of τ_4 values for **1a** (0.057) and **1a'** (0.070) shows that both complexes adopt square planar geometries[44] as expected for Pt(II) complexes. Cyclometallation results in minor distortions of the square plane for **1b** (0.034) and **1b'** (0.061).

The isolated complexes **1a',b'** were heated at 60 °C for 1 hour in the presence of PhI, resulting in the formation of toluene in excellent yields (80, 99% by ^{1}H NMR spectroscopy, respectively). Phenyl bromide also reacts with **1a'** to form toluene in ~37% yield, but this reaction is slower (16 h) and requires an excess of PhBr to achieve appreciable conversion (further details in Figure S57). The reaction of PhI with SMe$_2$ complex **1a'** provides toluene quantitatively if longer reaction times are employed (2 h). The higher reactivity of pyridine derivative **1b'** compared to SMe$_2$ complex **1a'** may be attributed to the ability of nitrogen to stabilize the Pt(IV) oxidation state, or to a higher barrier for SMe$_2$ dissociation due to the soft nature of sulfur. To explore this, the reaction of **1a'** with PhI was performed in the presence of excess SMe$_2$ at 60 °C. Added SMe$_2$ was found to inhibit the reaction, affording toluene and **3a** in only 4% yield over a one-hour period (*c.f.* 80% yield in the absence of added SMe$_2$). Similar inhibition was observed when **1b** and PhI were heated in the presence of excess pyridine (See SI for details). These observations are consistent with a mechanism in which dissociation of L creates a coordinative vacancy for interaction with PhI. The steric bulk of NHC ligands is known to stabilize low-coordinate, T-shaped complexes.[39,41,45] Furthermore, Crespo and Martinez have shown with several studies that dissociation of ligand, to create a vacant site, must occur prior to OA of the Csp^2-X bond.[24,28,37]

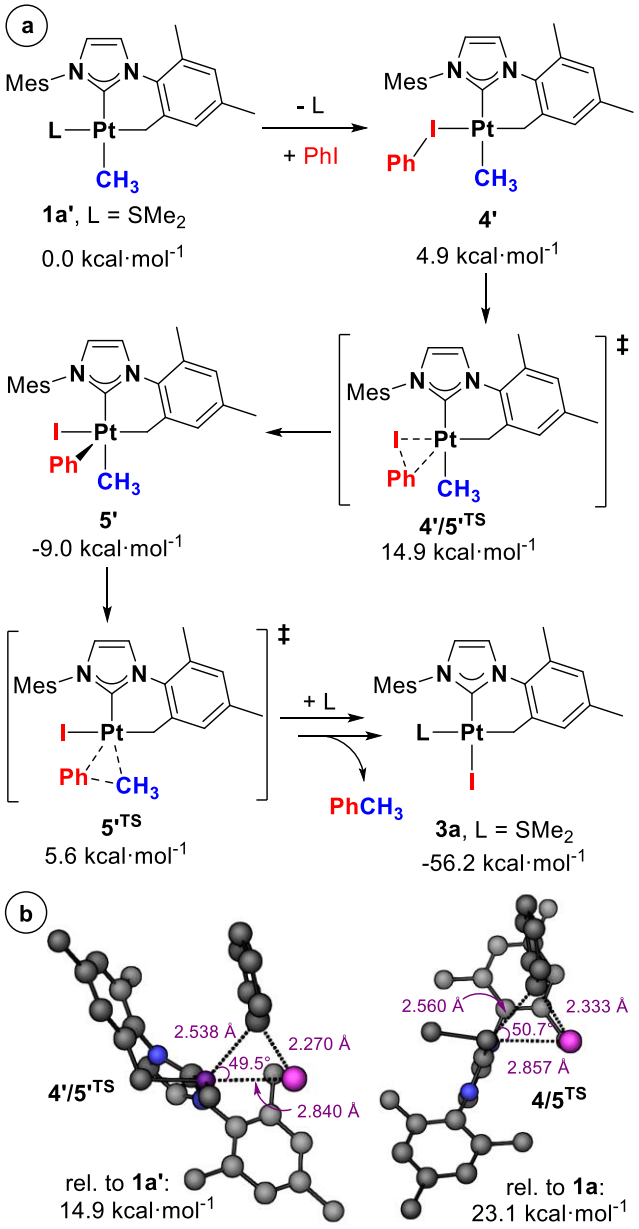
On this basis, we tentatively propose a mechanism in which ligand L dissociates to facilitate the concerted OA of PhI (Scheme 4a). DFT calculations support this proposal, establishing that a concerted OA process is energetically feasible for both complexes **1a** and **1a'**. Starting from **1a'**, the dissociation of SMe$_2$ results in the formation of a weak PhI adduct **4'**, 4.9 kcal·mol^{-1} uphill in energy due to the relatively weak donor ability of PhI. These interactions have previously been demonstrated through computational calculations.[46–48] The oxidative addition barrier ($\Delta G^{\ddagger}$) was calculated to be 14.9 kcal·mol^{-1} relative to **1a'** in benzene, which is in general agreement with our experimental observations. The OA transition state geometry **4'/5'^{TS}** is characterized by a 'face-on' approach of the aryl halide to Pt and a single imaginary frequency corresponding to cleavage of the Ph-I bond. The Csp^2-I addition occurs in a manner that positions the Ph group *trans* to a vacant coordination site in the resultant Pt(IV) complex **5'**, which exhibits a square pyramidal geometry (τ_5 = 0.04). Toluene reductive elimination from Pt(IV) intermediate **5'** proceeds through transition state **5'^{TS}** with a barrier of 14.6 kcal·mol^{-1}, accounting for the lack of Pt(IV) intermediates detected experimentally.

Scheme 3. Reactivity of cyclometalated 1a',b' with PhI.



Consistent with observed differences in reactivity between **1a** and **1a'**, the Csp^2-I OA pathway starting from non-cyclometallated **1a** proceeds with a significantly higher OA barrier ($\Delta G^{\ddagger}$ = 23.1 kcal·mol^{-1} relative to **1a**) than **1a'**. As the free energy (ΔG) for formation of Pt(IV) intermediates **5**/**5'** is similar in both systems (ΔG = -10.3 kcal·mol^{-1}, **5**; -9.0 kcal·mol^{-1}, **5'**), we attribute the difference in transition state energies to greater steric repulsion between the NHC and PhI in the non-cyclometalated complex (Scheme 4b).

Scheme 4. Proposed mechanism of OA of PhI to Pt(II) NHC complexes. DFT energies (ΔG) reported in C_6H_6 relative to 1a'.



We hypothesized that a chelating aryl iodide could be employed to trap the putative Pt(IV) OA product by disfavouring the formation of 5-coordinate Pt(IV) species that undergo C-C RE. To this end, we treated **1a'** with 2-(2-iodophenyl)pyridine in a 1:1 ratio in C_6H_6. After 36 h at room temperature, octahedral Pt(IV) complex **6** was isolated from the reaction mixture. An X-ray crystal structure of **6** was obtained, unambiguously confirming OA of the Csp^2-X bond (Figure 1).

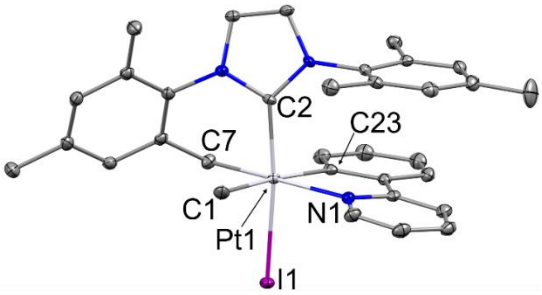
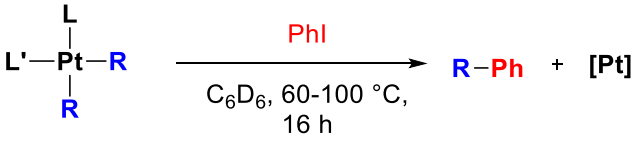


Figure 1. ORTEP representation of the solid-state structure of 7. (Thermal ellipsoids set at 50% probability, hydrogen atoms as well as solvent molecules omitted for clarity).

We are aware of only one report providing evidence for intermolecular OA of aryl halides to Pt(II), reported by Kistner and coworkers in 1967.[25] In this paper, a solution of Pt(*o*-tol)$_2$(pyridine)$_2$ (**8**; *o*-tol = *ortho*-tolyl) in neat PhI was reported to produce PtI(*o*-tol)(pyridine)$_2$ over a period of 6 d at 25 °C. Only limited characterization data were provided for the Pt product, and the formation of the organic product was inferred from that data. We reasoned that the formation of the observed PtI(o-tol)(pyridine)$_{2\ complex}$ could be attributed to a Csp^2-I OA/Csp^2-Csp^2 RE process, which would also result in formation of the presumed organic product. As this would suggest that the intermolecular Csp^2-I reaction is generalizable to other electron-rich Pt(II) complexes with labile ligands, we sought to reproduce the reported reactivity. Indeed, we found that the treatment of **8** with one equivalent of PhI afforded 2-methylbiphenyl in 42% yield (Table 1), confirming the hypothesis of the original paper.

To further establish the generality of this reaction, we prepared a series of mono- and diphosphine complexes (**9** – **11**, Table 1). Treatment of monophosphine complexes **9** and **10** with one equivalent of PhI at 60 and 100 °C, respectively, resulted in the formation of toluene in ~50% yield (^{1}H NMR spectroscopy, 1,3,5-trimethoxybenzene internal standard) along with methane, ethane, and ethylene.

Table 1. Reaction of L_2Pt(II) derivatives 8-10 with phenyl iodide.



complex	R	T (°C)	L, L'	Yield (%)[a]	side products[d]
8[b]	*o*-tol	60	pyridine	42	-
9[b]	Me	60	L' = SMe_2, L = PCy_3	49	C_2H_6, CH_4
10[c]	Me	100	L' = SMe_2, L = $P(C_6F_5)_3$	52	C_2H_6, C_2H_4, CH_4
11[b]	Me	100	L' = L = $P(^nBu)_3$	-	-

[a]Yields correspond to formation of R-Ph (^{1}H NMR spectroscopy, 1,3,5-trimethoxybenzene internal standard). [b]No reaction in the absence of PhI. [c]Reaction conducted without PhI resulted in metallic

Pt, as well as methane and ethylene; no ethane or toluene were observed. [d]Gaseous products identified by comparison with literature data.[49]

Unexpectedly, we found that changing the electron density at Pt(II) did not inhibit toluene formation completely (complexes **9** and **10**, Table 1). Notably, however, higher temperatures were required to see any toluene formation with complex **10**, indicating a higher activation barrier for less electron rich metal centres. According to our proposed mechanism, replacement of the labile SMe_2 ligand with a second strongly donating phosphine was expected to inhibit toluene formation. This hypothesis was supported by experiments with bisphosphine complex **11** (Table 1), which does not react with PhI at temperatures up to 100 °C.

In summary, we have demonstrated that simple Pt(II) complexes featuring NHC, pyridine and phosphine ligands indeed undergo intermolecular aryl halide oxidative addition and that this process is more general than previously thought. DFT calculations were performed to demonstrate the feasibility of a concerted OA pathway. Trapping of a Pt(IV) complex was achieved using a chelating aryl iodide, providing experimental evidence for a Pt(II)/(IV) pathway. The results described herein pave the way for the development of new reactions utilizing simple aryl halides as oxidants in Pt(II)/Pt(IV) catalytic cycles.

ASSOCIATED CONTENT

Supporting Information

CCDC 1873760-1873766 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures

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Notes

The authors declare no competing financial interests.

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(50) The major isomer of **3b** formed during the reaction has the iodide ligand trans to the methylene group and the pyridine ligand trans to the NHC as seen in scheme 3.

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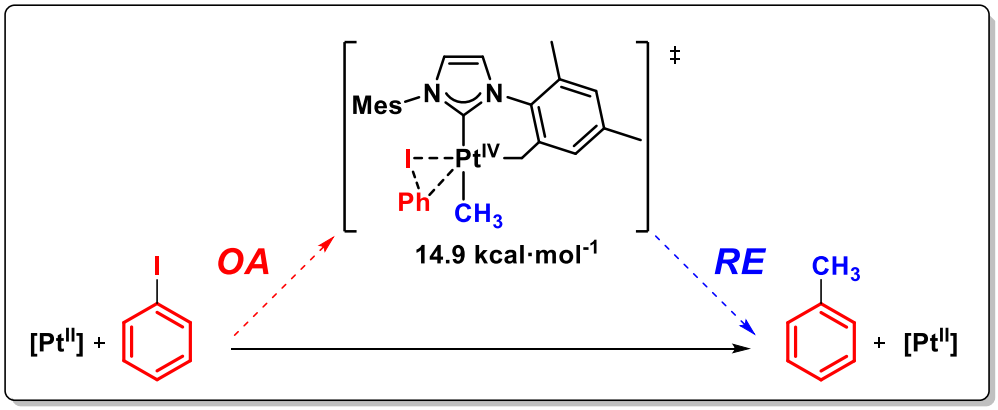

Supporting information for

Intermolecular Oxidative Addition of Aryl Halides to Platinum(II) Alkyl Complexes

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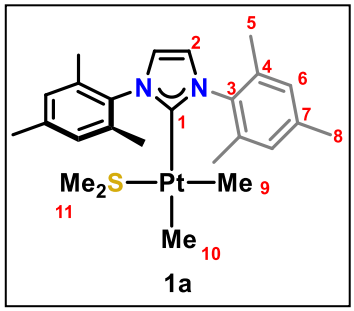
1. Experimental

A. General considerations.

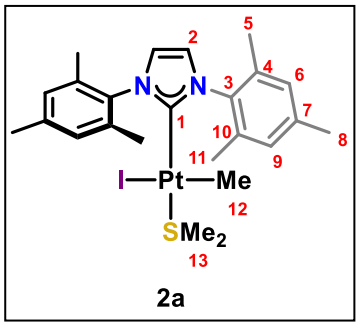
All manipulations were carried out using standard glove box/Schlenk techniques under an atmosphere of N_2. All deuterated solvents and chemicals that are not described herein were purchased from commercial vendors (Sigma Aldrich, TCI, Strem Chemicals, Alfa-Aesar, Pressure Chemicals and Acros) and used without further purification. Solvents, phenyl iodide (PhI), and phenyl bromide (PhBr) were stored over activated 3 Å molecular sieves, PhI and PhBr were stored in the glove box freezer at -35 °C. ^{1}H, $^{1}H\{^{31}P\}$, $^{13}C\{^{1}H\}$, ^{31}P, $^{31}P\{^{1}H\}$ and ^{19}F NMR spectra were recorded on 300, 400 or 600 MHz spectrometers. Chemical shifts are reported in ppm and referenced to residual protio-solvent resonance peaks for ^{1}H NMR spectroscopy, and to solvent peaks for $^{13}C\{^{1}H\}$ NMR spectroscopy. Multiplicity abbreviations: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), multiplet (m). Coupling constants are designated as $^{n}J_{X\text{-}Y}$ for each respective nucleus. The term 'Pt satellites' refers to the doublet observed due to coupling to the ^{195}Pt nucleus, whereas 'Pt shoulders' refers to signals exhibiting coupling to ^{195}Pt where the satellites are not resolved from the parent signal. Elemental analyses were performed by Analytical Services at the Department of Chemistry at the University of British Columbia. ESI-MS was recorded on waters LCMS. ESI-MS data was recorded by dissolving a sample of the complex in acetonitrile or methanol, in some cases acetonitrile was observed to exchange for SMe_2/pyridine and has been specified when observed as the m/z peak. The synthesis of $Pt_2Me_4(SMe_2)_2$/$Pt_2(CD_3)_4(SMe_2)_2$,[1] $PtMe_2COD$,[2] 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene,[3] 2-(2-iodophenyl)pyridine,[4] perdeuterated phenyl iodide[5] and Pt(*o*-tolyl)$_2$(pyridine)$_2$[6] were performed according to literature procedures. All NMR assignments for complexes were made on the basis of 1D and 2D NMR data.

B. Synthesis of Pt Complexes.



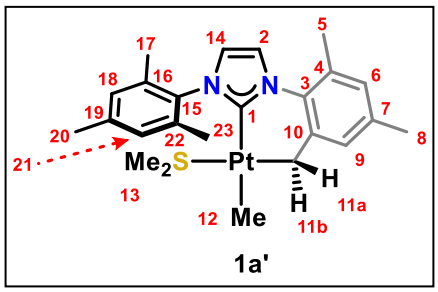
$PtMe_2(IMes)(SMe_2)$ (1a): To 5-dram vial was added $Pt_2Me_4(SMe_2)_2$ (194 mg, 0.327 mmol), benzene (3 mL) and dimethyl sulfide (48.0 µL, 0.654 mmol). The solution was stirred for five minutes at room temperature before the addition of IMes (200 mg, 0.654 mmol) which was added as a solution in benzene (10 mL) at once, the solution was then stirred for 10 minutes. The solution was concentrated and the product precipitated with pentane (15 mL). The supernatant was removed and the solid washed further with pentane (2 x 5 mL), it was then dried under vacuum to remove any remaining solvent to give 356 mg of **1a** as a white powder in 91% yield. **1a** was stored at -35°C to prevent thermal decomposition. Colourless X-ray quality crystals were grown from a dilute solution of hexane at -35°C.

^{1}H NMR (600 MHz, CD_2Cl_2, 25 °C) δ 6.99 (s, broad, 6 , 4H), 6.94 (s, 2, 2H), 2.33 (s, 8, 6H), 2.18-2.26 (m, broad, 5, 12H), 1.77 (s, Pt-satellites, $^3J_{Pt-H}$ = 24 Hz, 11, 6H), 0.06 (s, Pt satellites, $^2J_{Pt-H}$ = 87 Hz, 9, 3H), -0.23 (s, Pt satellites, $^2J_{Pt-H}$ = 60 Hz, 10, 3H). **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 25 °C) δ 187.65 (1), 138.73 (7), 137.46 (3), 136.30 (broad, 4), 129.41 (broad, m, 6), 122.47 (s, Pt satellites, $^1J_{Pt-C}$ = 25 Hz, 2), 21.36 (8), 19.65 (11), 18.98 (5), -3.52 (s, Pt satellites, $^1J_{Pt-C}$ = 596 Hz, 10), -11.61 (s, Pt satellites, $^1J_{Pt-C}$ = 763 Hz, 9). **Elemental analysis for $C_{25}H_{36}N_2PtS$** (C, H, N,): Calculated C, 50.75; H, 6.13; N, 4.73; Found C, 50.70; H, 6.02; N, 4.73. **ESI-MS**: 576.4 $(M\text{-}CH_3)^+$.



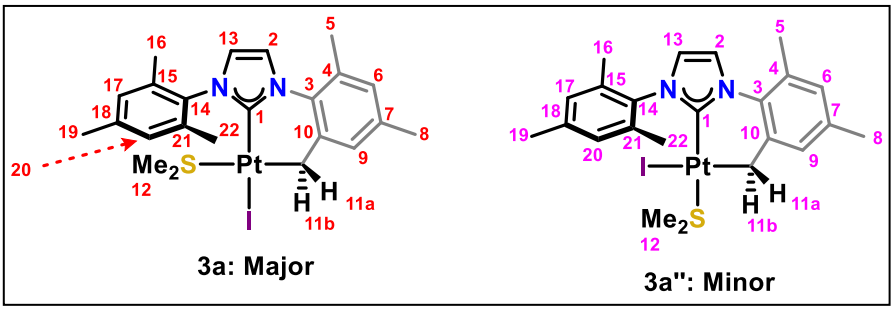
$PtIMe(IMes)(SMe_2)$ (2a): To a 5-dram vial was added **1a** $PtMe_2(IMes)(SMe_2)$ (50.0 mg, 0.0860 mmol). The complex was dissolved in C_6H_6 and followed by addition of methyl iodide as a solution in benzene over one minute (57.3 µL, 1M, 0.0860 mmol). The solution was stirred for 20 minutes before the volatiles were removed under reduced pressure. The white solid was washed with hexane (2 x 5 mL) and dried under reduced pressure to yield 60.5 mg of **2a** in 99% yield. X-ray quality crystals were grown from a THF/pentane layer over a period of three days at room temperature. The solid-state X-ray structure and solution-state structure differ with respect to the positions of the iodide and dimethyl sulfide. The solution-state structure is as shown above which was confirmed by ^{1}H-^{1}H NOESY.

^{1}H NMR (400 MHz, C_6D_6, 35 °C) **Major Isomer** δ 6.81 (s, 6/9, 2H), 6.75 (s, 6/9, 2H), 6.19 (s, 2, 2H), 2.66 (s, 5/11, 6H), 2.22 (s, 5/11, 6H), 2.05 (S, 8, 6H), 1.79 (s, Pt satellites, $^3J_{Pt-H}$ = 33 Hz, 13, 6H), 0.65 (s, Pt satellites, $^2J_{Pt-H}$ = 80 Hz, 12, 3H). **^{13}C{^{1}H} NMR** (100 MHz, C_6D_6, 35 °C) δ 165.9 (Pt satellites not resolved, 1) 138.5 (7), 137.0 (4/10), 136.8 (3), 134.6 (4/10), 130.17 (6/9), 128.9 (6/9), 122.5 (2), 22.12 (5/11), 21.80 (13), 21.04 (8), 18.99 (5/11), -10.69 (12). **Minor Isomer** peaks were not well resolved. **Elemental analysis for $C_{24}H_{34}IN_2PtS$** (C, H, N): Calculated C, 40.97; H, 4.73; N, 3.98; Found C, 40.62; H, 4.50; N, 3.90. **ESI-MS**: 555.2 $[M\text{-}I]^+$ - (C_2H_6S) + (C_2H_3N).



PtMe(IMes')(SMe$_2$) (1a'): To a flame dried Schlenk flask was added a **1a** PtMe$_2$(IMes)(SMe$_2$) (102 mg, 0.170 mmol) and benzene (20 mL). The solution was then heated at 60 °C for 2 hours. The solution was allowed to cool to room temperature where the solvent was concentrated to the point of product precipitation. Hexane was added, and the remaining product immediately precipitates. The supernatant was decanted, and the product washed with hexane (2 x 5 mL) to give 69 mg of **1a'** as a white powder in 71% yield. It is noteworthy that this reaction has a tendency to darken significantly due to Pt(0) formation, Pt(0) was removed by dissolving the solid in THF and adding hexane (half the amount of THF) and leaving at -30 °C overnight. The solution was then filtered through a glass microfibre filter with celite. X-ray quality crystals were grown from a THF solution layered with hexane.

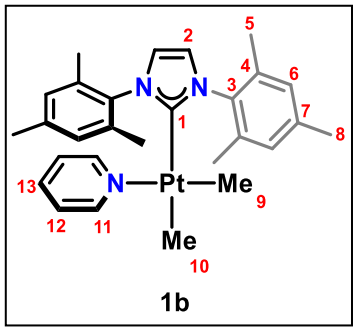
^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 7.42 (d, $^3J_{H-H}$ = 1.9 Hz, 14, 1H) , 6.99 (s, broad, 18/21, 1H), 6.97 (s, broad, 18/21, 1H), 6.89 (s, Pt shoulders, 9, 1H), 6.86 (d, $^3J_{H-H}$ = 1.9 Hz, 2, 1H), 6.73 (s, Pt shoulders, 6, 1H), 2.82 (d, $^2J_{H-H}$ = 9 Hz, Pt satellites; $^2J_{Pt-H}$ = 142 Hz, 11a, 1H), 2.33 (s, 17/23, 6H), 2.33 (s, overlapping, 5, 3H), 2.25 (s, 8, 3H), 2.15 (s, 20, 3H), 2.02 (d, $^2J_{H-H}$ = 9 Hz, Pt satellites; $^2J_{Pt-H}$ = 74 Hz, 11b, 1H), 1.71(s, v broad, 13, 6H), 0.14 (s, Pt satellites; $^2J_{Pt-H}$ = 62 Hz, 12, 3H). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 25 °C) δ 187.04 (1), 146.87 (10), 139.37, 137.39, 137.15, 137.09, 136.62, 136.35 (3), 129.25 (18/21), 129.02 (18/21), 128.99, 126.76 (Pt satellites, $^5J_{Pt-C}$ = 21 Hz, 6), 125.66 (Pt satellites, $^3J_{Pt-C}$ = 43 Hz, 9), 121.93 (Pt satellites, $^3J_{Pt-C}$ = 30 Hz, 2), 120.30 (Pt satellites, $^3J_{Pt-C}$ = 12 Hz, 14), 21.32 (17/23), 21.20 (8), 20.18 (13), 20.02, 18.96, 18.26 (17/23), 14.62 (Pt satellites, $^1J_{Pt-C}$ = 668 Hz, 11a/b), -4.41 (Pt satellites, $^1J_{Pt-C}$ = 617 Hz, 12). **Elemental analysis calculated for $C_{24}H_{32}N_2PtS$** (C, H, N): Calculated C, 50.07; H, 5.60; N, 4.87; Found C, 50.08; H, 5.80; N, 4.88. **ESI-MS**: 560.4 $(M\text{-}CH_3)^+$.



PtIMe(IMes')(SMe$_2$) (3a/3a''): To a 5 dram vial was added **1a'** PtMe(IMes')(SMe2) (50.0 mg, 0.0860 mmol). this was dissolved in C_6H_6 and kept stirring while MeI (57.3 µL, 1M, 0.0860 mmol) was added as a solution in benzene over one minute. The solution was allowed to stir for 20 minutes before the volatiles were removed under reduced pressure. The solid was washed with hexane (2 x 5 mL) and dried to give 59.1 mg of a mixture containing **3a/3a''** in 4:1 ratio in 99% yield. X-ray quality crystals were grown from a THF/hexane diffusion over several days.

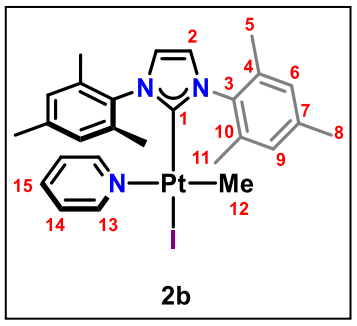
^{1}H NMR major isomer (400 MHz, C_6D_6, 55°C) δ 7.26 (s, 9, 1H), 6.75 (d, $^3J_{H-H}$ = 2 Hz, Pt satellites, $^4J_{Pt-H}$ = 13 Hz, 2, 1H), 6.67 (s, 17/20, 2H), 6.53 (s, 6, 1H), 6.05 (d, $^3J_{H-H}$ = 2 Hz, Pt satellites, $^4J_{Pt-H}$ = 15 Hz, 13, 1H), 4.34 (d, $^2J_{H-H}$ = 10 Hz, Pt satellites; $^2J_{Pt-H}$ = 105 Hz, 11b, 1H), 2.91 (d, $^2J_{H-H}$ = 10 Hz, Pt satellites; $^2J_{Pt-H}$ = 105 Hz, 11a, 1H), 2.36 (s, 22, 3H), 2.06 (s, overlapping, 16/19, 3H), 2.06 (s, overlapping, 16/19, 3H), 2.04 (s, 8, 3H), 1.96 (s, 5, 3H), 1.72 (m, very broad, 12, 6H). **^{1}H NMR minor isomer** (400 MHz, C_6D_6, 55°C) δ 6.96 (s, 9, 1H), 6.88 (s, 17, 1H), 6.82 (s, 20, 1H), 6.73 (d, $^3J_{H-H}$ = 2 Hz, Pt shoulders, 2, 1H), 6.58 (s, 6, 1H), 6.21 (d, $^3J_{H-H}$ = 2Hz, Pt satellites; $^4J_{Pt-H}$ = 15 Hz, 13, 1H), 2.97 (d, $^2J_{H-H}$ = 10 Hz, Pt satellites overlapping, 11a, 1H), 2.51 (s, 22, 3H), 2.47 (d, $^2J_{H-H}$ = 10 Hz, Pt

satellites not resolved, 11b, 1H), 2.39 (s, 16, 3H), 2.17 (s, 8, 3H), 2.12 (s, 19, 3H), 1.90 (s, 5, 3H), 1.76 (s, 12, 6H). **$^{13}C\{^{1}H\}$ NMR major isomer** (101 MHz, C_6D_6, 55 °C) δ 162.80 (1), 143.34 (10), 139.32 (15/18), 137.95 (7), 137.76 (21), 136.09 (15/18), 135.75 (3),135.67 (14), 129.69 (17/20), 128.70 (17/20), 127.55 (6), 126.88 (9), 121.97 (13), 119.53 (2), 22.86 (broad, 12), 20.91(8), 20.82 (16/19), 19.27(5), 19.01 (22), 18.23 (16/19), 8.03 (11a/b). **$^{13}C\{^{1}H\}$ NMR minor isomer** (peaks could not be resolved). **Elemental analysis calculated for $C_{23}H_{29}IN_2PtS$** (C, H, N): Calculated C, 40.18; H, 4.25; N, 4.07; Found C, 40.07; H, 4.38; N, 3.76. **ESI-MS**: 539.2 $[M\text{-}I]^+$ - (C_2H_6S) + (C_2H_3N).



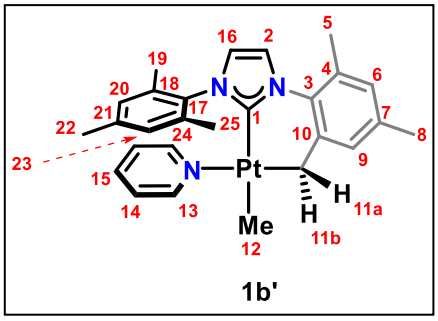
$PtMe_2$(IMes)(Pyridine) (1b): To a 5-dram vial was added $PtMe_2COD$ (250 mg, 0.750 mmol), pyridine (118 mg, 1.50 mmol) and IMes (228 mg, 0.750 mmol). This mixture was dissolved in THF (15 mL) and stirred for 30 minutes at room temperature. The solution was then concentrated, and the product precipitated with Et_2O (10 mL). The supernatant was decanted, the product was washed twice further with Et_2O (2 x 5 mL). The solid was dried under reduced pressure to give 373 mg of **1b** in 82% yield.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 7.97 (m, Pt satellites, $^{3}J_{Pt\text{-}H}$ = 26 Hz, 11, 2H) 7.49 (t, 13, 1H), 6.96 (s, 6, 4H), 6.92 (m, 12, 2H), 6.85 (s, 2, 2H), 2.38 (s, 8, 6H), 2.07 (s, 5, 12H), 0.07 (s, Pt satellites, $^{2}J_{Pt\text{-}H}$ = 89 Hz, 9, 3H), -0.52 (s, Pt satellites, $^{2}J_{Pt\text{-}H}$= 60 Hz, 10, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, CD_2Cl_2, 25 °C) δ 188.49 (1), 152.50 (Pt satellites, $^{2}J_{Pt\text{-}C}$ = 15 Hz, 11), 138.63, 137.78, 136.03, 134.70 (13), 129.41 (6), 124.81 (Pt satellites, $^{3}J_{Pt\text{-}C}$= 23 Hz, 12), 122.26 (Pt satellites, $^{3}J_{Pt\text{-}C}$ = 25 Hz, 2), 21.40 (8), 18.73 (5), 2.22 (Pt satellites, $^{1}J_{Pt\text{-}C}$ = 604 Hz, 10), -26.49 (Pt satellites, $^{1}J_{Pt\text{-}C}$ = 755 Hz, 9). **Elemental analysis for $C_{28}H_{35}N_3Pt$** (C, H, N): Calculated C, 55.25; H, 5.80; N, 6.90; Found C, 55.38; H, 6.06; N, 6.79. **ESI-MS**: 555.2 $[M\text{-}CH_3]^+$ - (C_5H_5N) + (C_2H_3N).



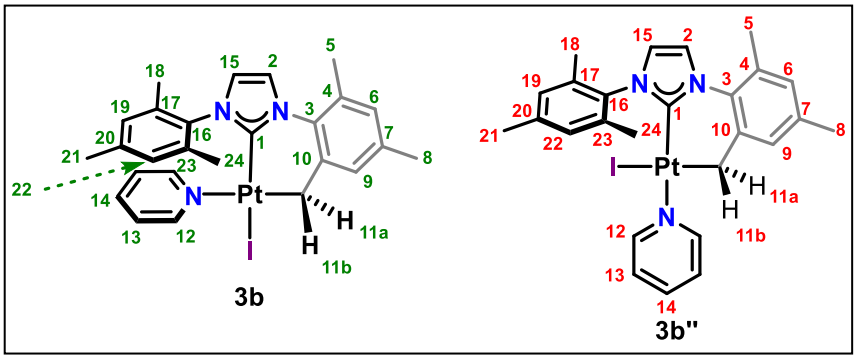
PtIMe(IMes)(pyridine) (2b): a 5-dram vial was charged with **1b** $PtMe_2$(IMes)(Pyridine) (39.2 mg, 0.0640 mmol). After dissolving the **1a** in benzene (5 mL), MeI (64.0 uL, 0.0640 mmol, 1M) was then added as a solution in benzene over one minute. A white solid starts to precipitate from the solution, the mixture was kept stirring until all the solid became dissolved (10-15 min). Once dissolved the solvent was evaporated under reduced pressure and pentane (5 mL) was added and subsequently evaporated to remove any remaining volatiles to give 44.6 mg of **2b** as a white powder in 97% yield.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 8.51 (d, $^{3}J_{H\text{-}H}$ = 5.6 Hz, Pt satellites, $^{3}J_{Pt\text{-}H}$ = 24 Hz, 13, 2H), 7.60 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 15, 1H), 7.14 (m, 14, 2H), 7.02 (s, broad, 6/9, 2H), 7.01 (s, broad, overlapping, 6/9, 2H), 6.98 (s, 2, 2H), 2.44 (s, 5/11, 6H), 2.37 (s, 8, 6H), 2.25 (s, 5/11, 6H), 0.25 (s, Pt satellites, $^{3}J_{Pt\text{-}H}$ = 84 Hz, 12, 3H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, CD_2Cl_2, 25 °C) δ 157.16 (1), 152.89 (13), 138.83 (7), 137.06 (4/10), 136.89 (15), 135.47 (3), 129.83 (6/9), 129.15 (6/9), 125.11 (Pt satellites, $^{3}J_{Pt\text{-}C}$ = 33 Hz, 14), 123.12 ($^{3}J_{Pt\text{-}C}$= 46 Hz, 2), 21.57 (5/11), 21.44 (8), 19.18 (5/11), -7.03 (Pt- satellites not observed, 12). **Elemental analysis calculated for $C_{27}H_{32}IN_3Pt$** (C, H, N): Calculated C, 45.01; H, 4.48; N, 5.83; Found C, 45.81; H, 4.76; N, 5.55 (best after three attempts). **ESI-MS**: 593.2 $[M\text{-}I]^+$.



PtMe(IMes')(pyridine) (1b'): To a Schlenk flask was added **1b** $PtMe_2$(IMes)(Pyridine) (215 mg, 0.350 mmol). The solid was dissolved in benzene (25 mL) and heated at 60°C for two hours. the solution was concentrated to 5 mL where then pentane (20 mL) was added. A precipitate starts to form immediately and the Schlenk flask placed at -30°C to precipitate the remaining solid. the supernatant was removed and the solid washed one further time with pentane (5 mL) to give 161 mg of **1b'** as pale yellow solid in 78% yield.

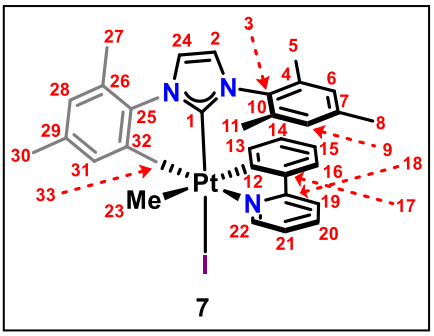
^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 8.10 (m, Pt satellites, $^3J_{Pt-H}$ = 28 Hz, 13, 2H), 7.42 (d, $^3J_{H-H}$ = 2 Hz, 2/16 ,1H), 7.41(m, overlapping, 15, 1H) , 6.91-6.97 (m, 9 & 20/23, 2H), 6.76-6.84 (m, 14 & 6 & 2/16 ,4H), 6.25 (s, 20/23, 1H), 3.02 (d, $^2J_{H-H}$ = 9 Hz, Pt satellites; $^2J_{Pt-H}$ = 146 Hz, 11a, 2H), 2.50 (s, broad, 19/25, 3H), 2.36 (s, 5, 3H), 2.28 (s, 8, 3H), 2.20 (s, 22, 3H), 2.01 (d, $^2J_{H-H}$ = 9 Hz, Pt satellites; $^2J_{Pt-H}$ = 72 Hz, 11b, 1H), 1.58 (s, broad, 19/25, 3H), -0.04 (s, Pt satellites, $^2J_{Pt-H}$ = 63 Hz, 12). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 25 °C) δ 189.78 (1), 152.14 (Pt satellites, J_{Pt-C} = 18 Hz, 13), 148.34, 138.61, 136.88, 136.63 (3), 136.58, 134.51 (15), 129.25 (20/23), 128.98, 128.87 (4), 128.71 (20/23), 126.89 (Pt satellites, $^5J_{Pt-C}$ = 21 Hz, 6), 125.80 (Pt satellites, $^3J_{Pt-C}$ = 42 Hz, 9), 124.50 (Pt satellites, $^3J_{Pt-C}$= 25 Hz, 14), 120.98 (Pt satellites, $^3J_{Pt-C}$= 30 Hz, 2/16), 120.07 (Pt satellites, $^3J_{Pt-C}$ = 12 Hz, 2/16), 21.19 (8), 21.15 (22), 20.27 (6),18.89 (19/25), 17.65 (19/25), 1.12 (11a/b), 0.79 (Pt satellites, $^1J_{Pt-C}$ = 619 Hz, 12). **Elemental analysis for $C_{27}H_{31}N_3Pt$** (C, H, N): Calculated C, 54.72; H, 5.27; N, 7.09; Found C, 54.43; H, 5.28; N, 7.14. **ESI-MS**: 498.1 $[M-C_6H_8N]^+$.



PtI(IMes')(pyridine), (3b/3b''): To a 5 dram vial was added **1b'** (64.0 mg, 0.108 mmol), which was dissolved in benzene (5 mL). MeI (118 µL, 1M, 0.188 mmol) was added as a solution in benzene to the stirring solution of **1b'** and allowed to stir at room temperature for five minutes. The solvent was removed fully, acetone (5 mL) was then added followed by hexane (5 mL). The supernatant was removed and the remaining solid washed with hexane (2 x 5 mL). Finally, the solid was dried under reduced pressure to yield 72.0 mg of a mixture of **3b/3b''** as white solid in 1:1 ratio in 94% yield.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 8.72 (d, $^3J_{H-H}$ = 5 Hz, Pt shoulders, 12, 2H), 8.11 (d, $^3J_{H-H}$ = 5 Hz, Pt shoulders, 12), 7.74 (t, $^3J_{H-H}$ = 8 Hz, 14, 1H), 7.55 (d, $^3J_{H-H}$ = 2 Hz, overlapping, 1H), 7.52 (d, $^3J_{H-H}$ = 2 Hz, overlapping, 1H), 7.48 (t, $^3J_{H-H}$ = 8 Hz, 14, 1H), 7.30 (t, $^3J_{H-H}$ = 7 Hz, 13, 2H), 7.05 (s, 3H), 6.95 (s, 2H), 6.87-6.9 (m, 6H), 6.30 (s, 1H), 3.27 (d, $^2J_{H-H}$ = 10 Hz, Pt satellites, $^2J_{Pt-H}$ = 108 Hz, 11a, 1H), 2.93 (d, $^2J_{H-H}$ = 10 Hz, Pt satellites, $^2J_{Pt-H}$ = 124 Hz, 11b, 1H) 2.77 (d, $^2J_{H-H}$ = 10 Hz, Pt satellites not resolved, 11b, 1H), 2.58 (s, 8/12, 3H), 2.54 (s, 3H), 2.44 (s, overlapping, 3H), 2.43 (s, overlapping, 3H), 2.37 (s, 3H), 2.31(m, 6H), 2.25 (s, 3H), 2.22 (s, 3H), 1.82 (d, $^3J_{H-H}$ = 10 Hz, Pt satellites, $^2J_{Pt-H}$ = 105 Hz, 1b, 1H), 1.47 (s, 18/24, 3H). **^{13}C{^{1}H} NMR** (100 MHz, CD_2Cl_2, 25 °C) δ 161.6 (1), 157.21 (1), 152.61 (12), 151.88 (12), 143.80 (10), 142.29 (10), 138.88, 138.50, 137.36, 137.27, 136.78 (14),

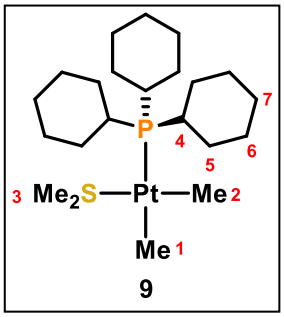
136.40, 136.38, 136.10, 135.92, 135.77, 135.63 (14), 135.42, 134.76, 134.05, 129.31, 128.90, 128.80, 128.51, 128.46, 128.25, 127.56, 127.51, 125.20, 124.97 (13), 124.07, 123.85, 123.63, 121.80, 119.64, 119.49, 20.92, 20.70, 20.66, 20.60, 19.52, 19.48, 1937, 18.90, 18.68, 17.27 (18/24), 16.62 (11a/b), -4.57 (11a/b) . **Elemental analysis for $C_{26}H_{28}IN_3Pt$** (C, H, N): Calculated C, 44.33; H, 4.01; N, 5.96; Found C, 44.48; H, 4.30; N, 5.75 **ESI-MS**: 577.2 $[M-I]^+$.



7

PtIMe(phenyl-pyridine)(IMes') (7): To a 5 dram vile was added **1b'** (100 mg, 0.168 mmol) and 2(2-iodophenyl)pyridine (47.3 mg, 0.168 mmol). This was dissolved in THF (10 ml). After three days a white precipitate had formed. This precipitate was filtered and washed with acetone (2 x 1 mL). All volatiles were removed to yield 51.0 mg of **7** as a white powder in 38% yield. X-ray quality crystals were grown from an acetonitrile solution layered with Et_2O at -30 °C. These crystals were obtained by replacing THF with benzene and stirring or 36 h at room temperature. Pentane was added to precipitate a solid which was then recrystallised from acetonitrile/diethyl ether giving suitable crystals for X-ray diffraction.

^{1}H NMR (400 MHz, CD_2Cl_2 25°C): δ 8.55 (d, $^3J_{H-H}$ = 6 Hz, Pt satellites, $^3J_{Pt-H}$ = 20 Hz, 22, 1H), 7.60-7.55 (m, , 3H), 7.49 (d, $^3J_{H-H}$ = 8 Hz, , 1H), 7.42 (d, $^3J_{H-H}$ = 8 Hz), 7.22-7.19 (m, , 2H), 7.12-7.04 (m, 21 , 2H), 6.96 (s, , 1H), 6.61 (d, $^3J_{H-H}$ = 2 Hz, Pt satellites, $^4J_{Pt-H}$ = 10 Hz, 2/24, 1H), 6.64 (s, , 1H), 6.00 (s, , 1H), 4.43 (d, $^2J_{H-H}$ = 10 Hz, Pt satellites, $^3J_{Pt-H}$ = 89 Hz, 33a/b, 1H), 3.82 (d, $^2J_{H-H}$ = 10 Hz, Pt satellites, $^3J_{Pt-H}$ = 90 Hz, 33a/b, 1H), 2.40 (s, , 3H), 2.39 (s, , 3H), 2.11 (s, , 3H), 1.61 (s, 11, 3H), 1.06 (s, , 3H), 0.24 (s, Pt satellites, $^2J_{Pt-H}$ = 44 Hz, 23). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 25 °C): δ 167.11 (Pt satellites, $^1J_{Pt-C}$ = 29 Hz ,1), 162.91 (), 147.08 (Pt satellites, J_{Pt-C} = 9 Hz, 22), 146.70 (), 142.23 (), 141.97 (), 138.90 (), 137.03 (), 136.44 (), 135.77 (), 135.01 (), 134.82 (), 132.66 (), 131.93 (Pt satellites, J_{Pt-C} = 27 Hz), 129.07 (Pt satellites, J_{Pt-C} = 28 Hz,), 129.05 (), 128.58 (), 128.56 (), 127.25 (), 125.40 (Pt satellites, J_{Pt-C} = 24 Hz), 125.23 (Pt satellites, J_{Pt-C} = 19 Hz), 123.60 (), 122.76 (Pt satellites, J_{Pt-C} = 39 Hz), 121.28 (Pt satellites, J_{Pt-C} = 12 Hz), 121.02 (Pt satellites, J_{Pt-C} = 23 Hz), 119.70 (Pt satellites, J_{Pt-C} = 14 Hz), 20.71 (), 20.55 (), 20.10 (), 17.69 (), 15.77 (), 7.34 (Pt satellites, $^2J_{Pt-C}$ = 511 Hz, 33a/b), -8.05 (Pt satellites not resolved, 23).

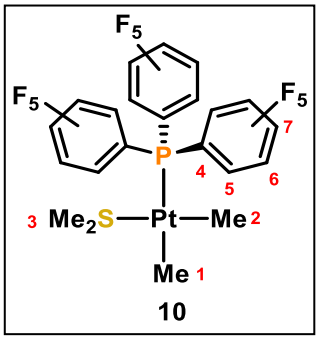


9

$PtMe_2(SMe_2)(PCy_3)$ (9): To a 5 dram vial was added $Pt_2Me_4(SMe_2)_2$ (47.9 mg, 0.830 mmol) and THF (5 mL). To this solution was added PCy_3 (46.8 mg, 0.166 mmol) as a solution in THF (5 mL) at once. After allowing the solution to stir for 30 minutes, the solvents were removed under the reduced pressure and solid suspended in pentane (3 mL), the pentane was then removed along with any remaining volatiles to yield 94.7 mg of **9** as a white powder in 99% yield.

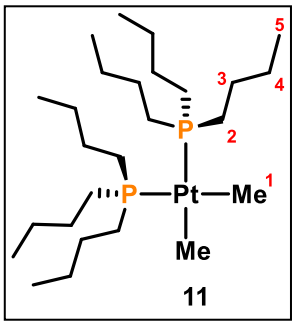
^{1}H{^{31}P} NMR (300 MHz, C_6D_6, 25 °C) δ 2.22-2.38 (m, 4, 3H), 2.02 (s, Pt satellites, $^3J_{Pt-H}$ = 24 Hz, 3, 6H), 1.96 (d, broad overlapping, $^2J_{H-H}$ = 12 Hz, 5, 6H), 1.46-178 (m 5, 6H & 6, 6H & 7, 3H), 1.27 (s, Pt satellites, $^2J_{Pt-H}$ = 83 Hz, 1, 3H), 1.14-125 (m, 6, 6H & 7, 3H), 1.10 (s, Pt satellites, $^2J_{Pt-H}$ = 66 Hz, 2, 3H). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 25 °C) δ 32.01 (d, $^1J_{P-C}$ = 20 Hz, Pt satellites, $^2J_{Pt-C}$ = 16 Hz, 4),

30.08 (Pt satellites, $^{3}J_{Pt\text{-}C}$ = 15 Hz, 5), 28. 08 (d, $^{3}J_{P\text{-}C}$ = 9 Hz, 6), 27.14 (7), 19.43 (d, $^{3}J_{P\text{-}C}$ = 3 Hz, Pt- satellites not resolved, 3), 8.65 (d, $^{2}J_{P\text{-}C}$ = 103 Hz, Pt-satellites not resolved, 2), -7.82 (d, $^{2}J_{P\text{-}C}$ = 6 Hz, Pt-satellites not resolved, 1). **^{31}P{1H) NMR** (121 MHz, C_6D_6, 25 °C) δ 22.20 (Pt satellites, $^{1}J_{Pt\text{-}P}$ = 1852 Hz). **Elemental analysis for $C_{22}H_{45}PPtS$** (C, H, N): Calculated C, 46.54; H, 7.83; Found C, 46.92; H, 7.83. **ESI-MS**: 531.2 $[M\text{-}CH_3]^+$ - (C_2H_6S) + (C_2H_3N).



$PtMe_2(SMe_2)(P(C_6F_5)_3)$ (10): To a 5 dram vial was added $Pt_2Me_4(SMe_2)_2$ (53.2 mg, 0.0930 mmol) and THF (5 mL). To this solution was added $P(C_6F_5)_3$ (98.5 mg, 0.185 mmol) as a solution in THF (5 mL) at once. After allowing the solution to stir for 30 minutes, the solvents were removed under reduced pressure to yield a white powder. This complex is soluble in hexane and was therefore dissolved and filtered before the solvent was removed to yield 145 mg of **10** as a white powder in 94% yield.

^{1}H NMR (600 MHz, C_6D_6, 25 °C) δ 1.78 (s, Pt satellites, $^{3}J_{Pt\text{-}H}$ = 26 Hz, 3, 6H), 1.24 (d, $^{3}J_{P\text{-}H}$ = 9 Hz, Pt satellites, $^{2}J_{Pt\text{-}H}$ = 74 Hz, 1, 3H), 0.97 (d, $^{3}J_{P\text{-}H}$ = 12 Hz, Pt satellites, $^{2}J_{Pt\text{-}H}$ = 83 Hz, 2, 3H). **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6, 25 °C) δ 147.22 (d, $^{3}J_{P\text{-}C}$ = 250 Hz, 5/6), 143.26 (d, $^{1}J_{P\text{-}C}$ = 259 Hz, Pt satellites not resolved, 4), 137.78 (d, $^{2}J_{P\text{-}C}$ = 255 Hz, 5/6), 104.10 (7), 19.35 (d, $^{3}J_{P\text{-}C}$ = 3 Hz, Pt-satellites not resolved, 3), 9.05 (d, $^{2}J_{P\text{-}C}$ = 132 Hz, Pt satellites, $^{1}J_{Pt\text{-}C}$ = 719 Hz, 1), 1.38 (silicone grease) -9.00 (Pt satellites, $^{2}J_{P\text{-}C}$ = 2.32 Hz, $^{1}J_{Pt\text{-}C}$ = 724 Hz, 2). **^{31}P NMR** (162 MHz, C_6D_6, 25 °C) δ -19.55 (Pt satellites, $^{1}J_{Pt\text{-}P}$ = 1582 Hz). **^{19}F NMR** (282 MHz, C_6D_6, 25 °C) δ -130.15, -146.88 (7), -159.76. **Elemental analysis for $C_{22}H_{12}F_{15}PPtS$** (C, H): Calculated C, 32.25; H, 1.48; Found C, 32.40; H, 1.41.



$PtMe_2(P^nBu_3)_2$ (11): To a 5 dram vial was added $Pt_2Me_4(SMe_2)_2$ (101.8 mg, 0.177 mmol) which was dissolved in THF (5 mL), to this was added a solution of $P(^nBu)_3$ (174 µL, 0.708 mmol, 4 equiv.) in THF (5 mL) and allowed to stir for 10 minutes before the solvent was removed forming a colourless oil, which under prolonged exposure to vacuum becomes a greasy white solid, 147.6 mg, 97% yield. The solid was recrystallised from a concentrated acetone solution at -30°C.

^{1}H NMR (600 MHz, C_6D_6, 25 °C) δ 1.72-1.76 (m, 2, 12H), 1.47-1.57 (m, 3, 12H), 1.35 (m, $^{3}J_{H\text{-}H}$ = 7 Hz, 4, 12H), 1.02 (dd, $^{3}J_{P\text{-}H}$ = 6 Hz, Pt satellites, $^{2}J_{Pt\text{-}H}$ = 66 Hz, 1, 6H), 0.89 (t, $^{3}J_{H\text{-}H}$ = 7 Hz, 5). **^{13}C{^{1}H} NMR** (150 MHz, C_6D_6, 25 °C) δ 27.09 (t, Pt satellites, $^{3}J_{Pt\text{-}C}$ = 18 Hz, 3) 24.81-25.18 (m, Pt and P coupling could not be resolved, 2 & 4), 14.12 (5), 4.33 (dd, *cis*-$^{2}J_{P\text{-}C}$ = 10 Hz, *trans*-$^{2}J_{P\text{-}C}$ = 103 Hz, Pt satellites, $^{1}J_{P\text{-}C}$ = 597 Hz, 1, 6H) .**^{31}P{^{1}H} NMR** (121 MHz, C_6D_6) δ -3.56 (Pt satellites, $^{1}J_{Pt\text{-}P}$ = 1821 Hz. **Elemental analysis for $C_{26}H_{60}P_2Pt$** (C, H): Calculated C, 49.59; H, 9.60. Found C, 49.46; H, 9.28.

2. NMR Spectra

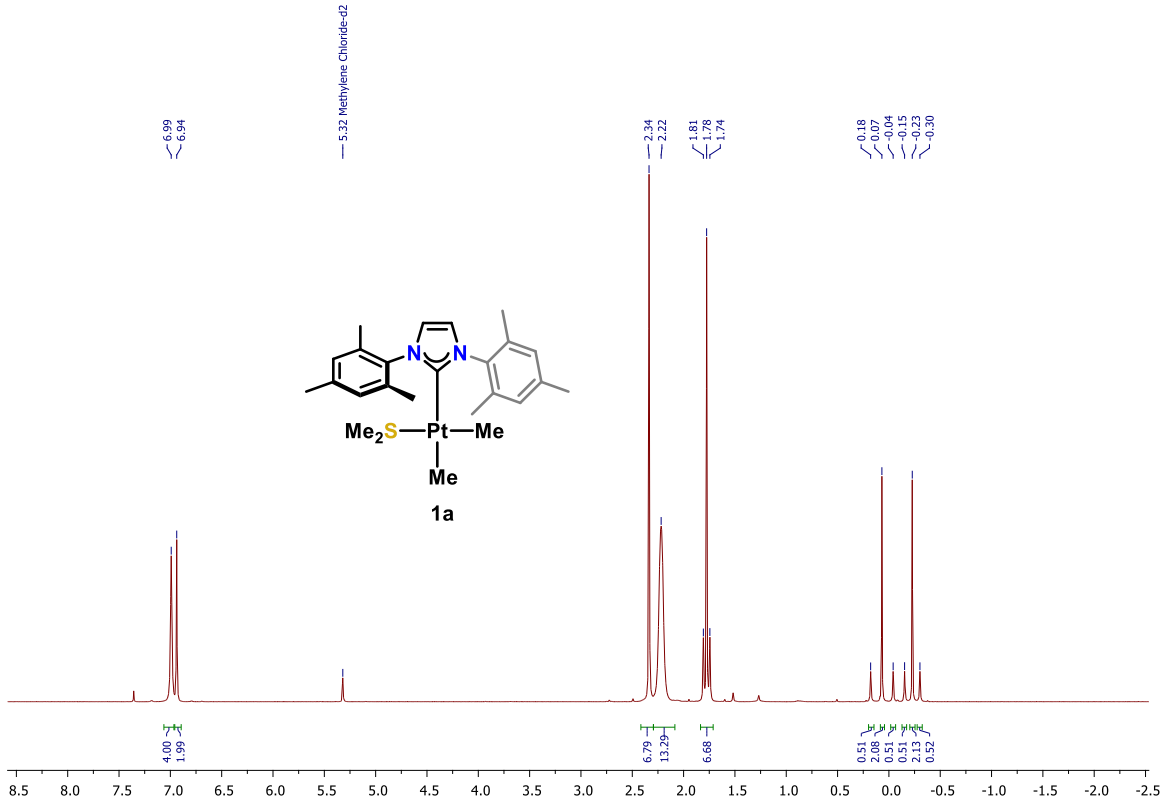


Figure S1: 1a, ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C)

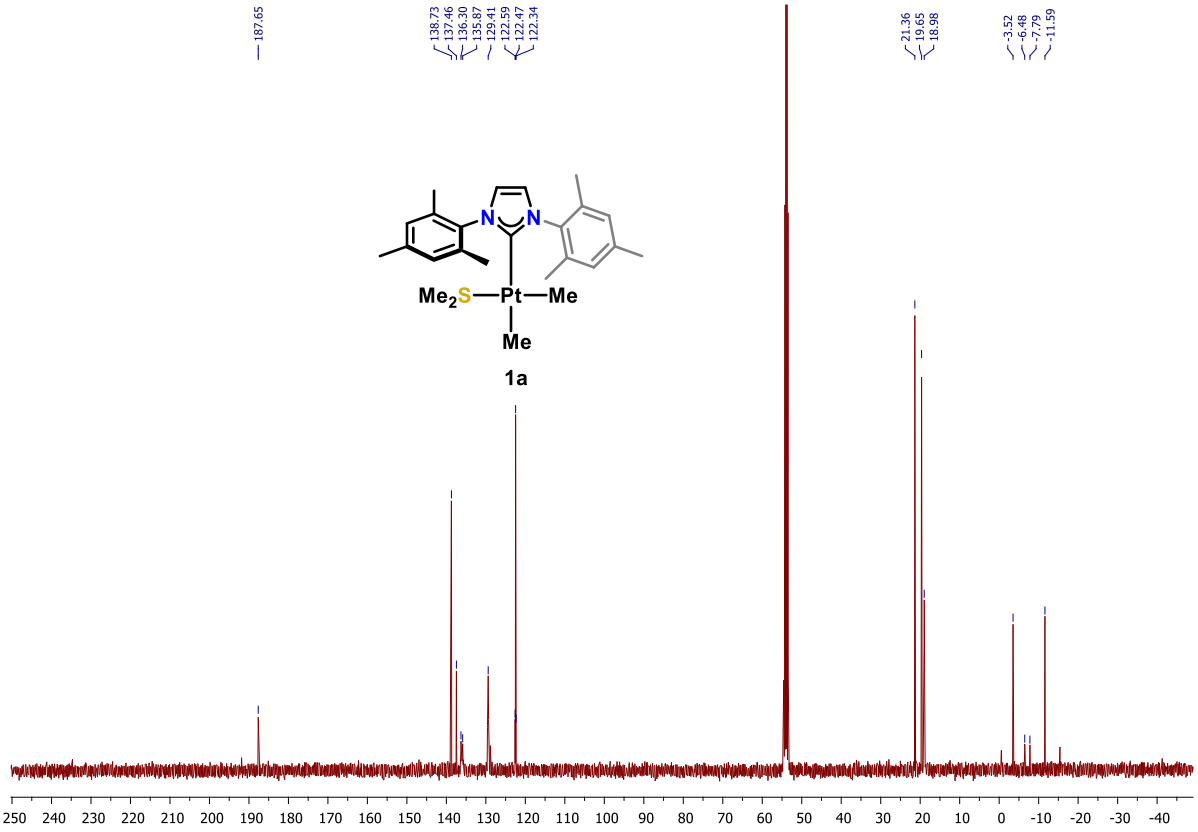


Figure S2: 1a, $^{13}C\{^{1}H\}$ (CD_2Cl_2, 100 MHz, 25 °C)

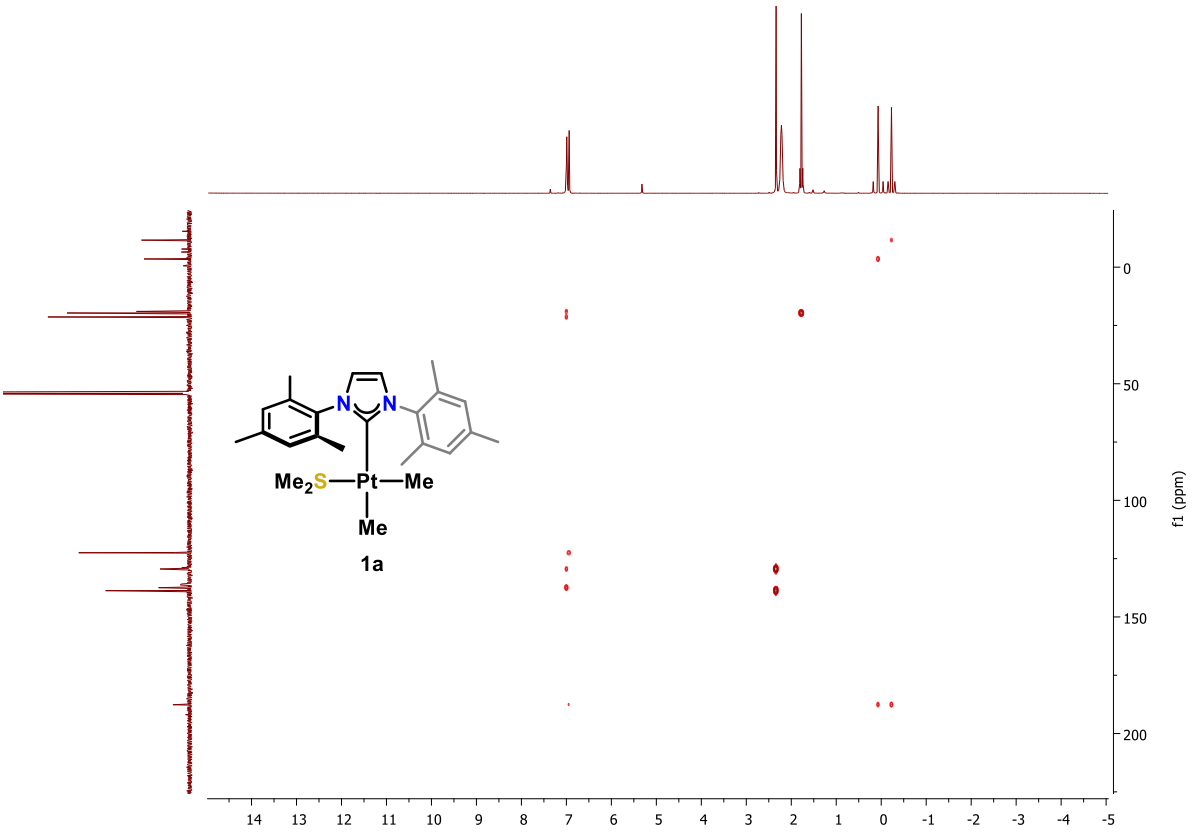


Figure S3: 1a, ^{1}H-^{13}C HMBC (CD_2Cl_2, 400/100 MHz, 25 °C)

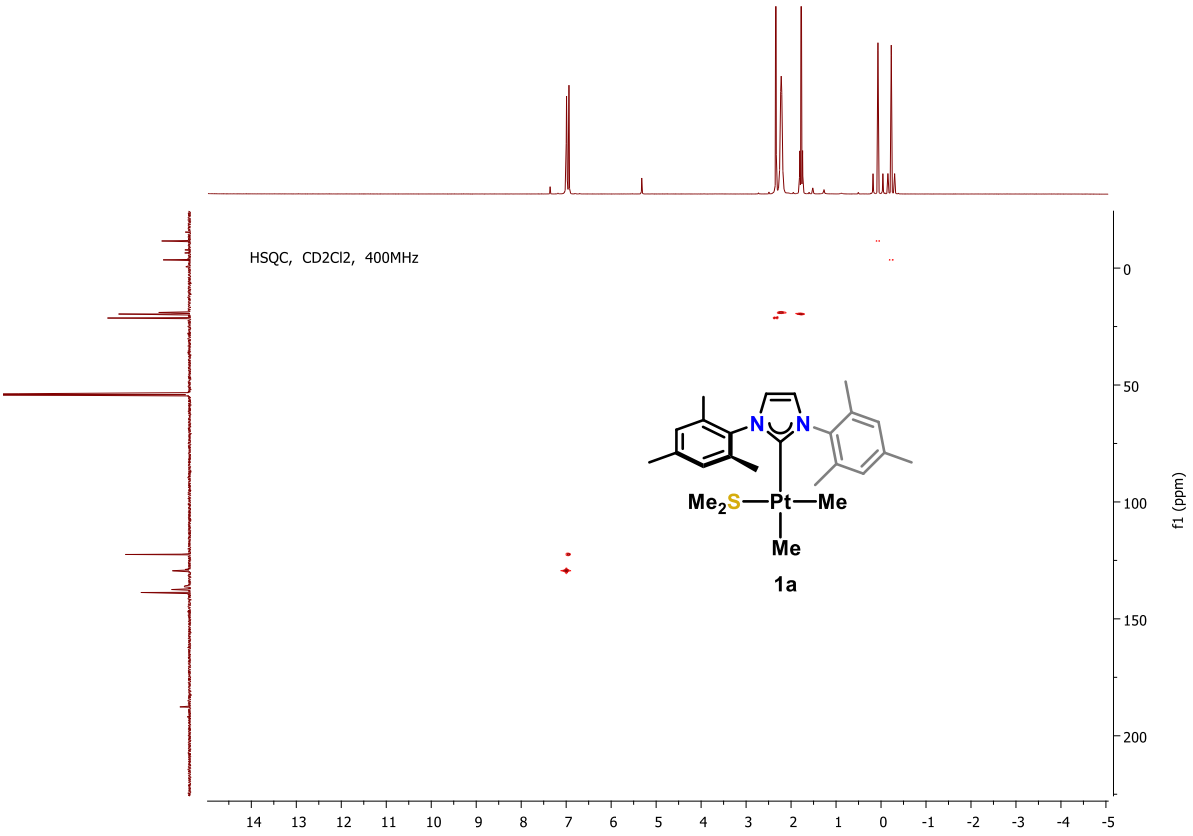


Figure S4: 1a, HSQC (CD_2Cl_2, 400 MHz, 25 °C)

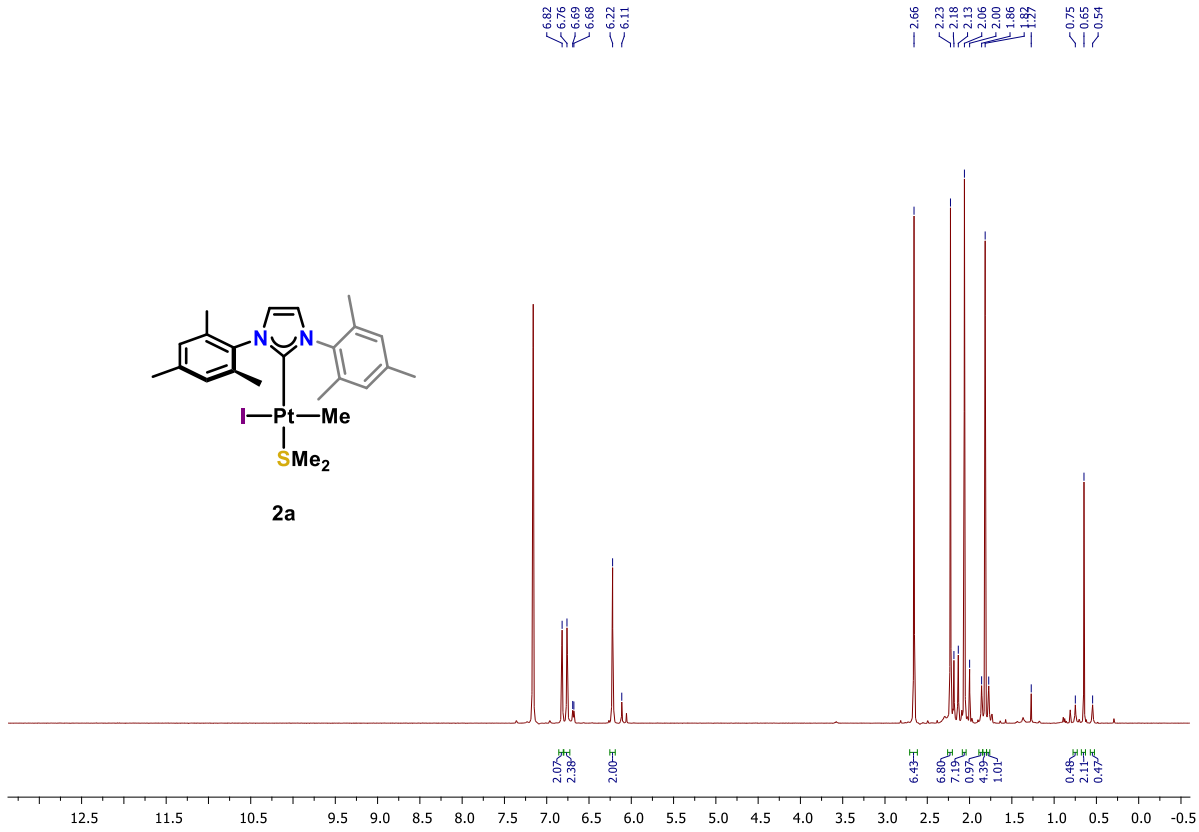


Figure S5: 2a, ^{1}H NMR (C_6D_6, 400 MHz, 35°C)

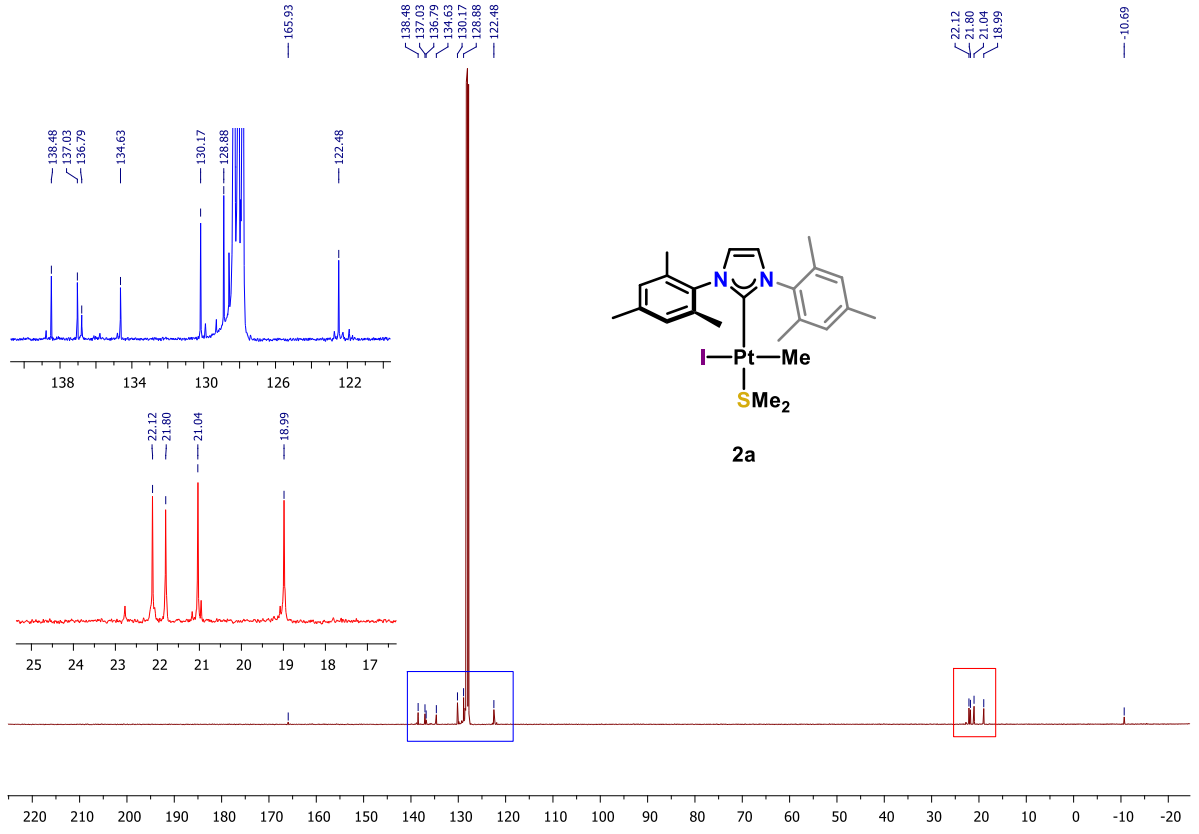


Figure S6: 2a, $^{13}C\{^{1}H\}$ NMR (C_6D_6, 100 MHz, 35°C)

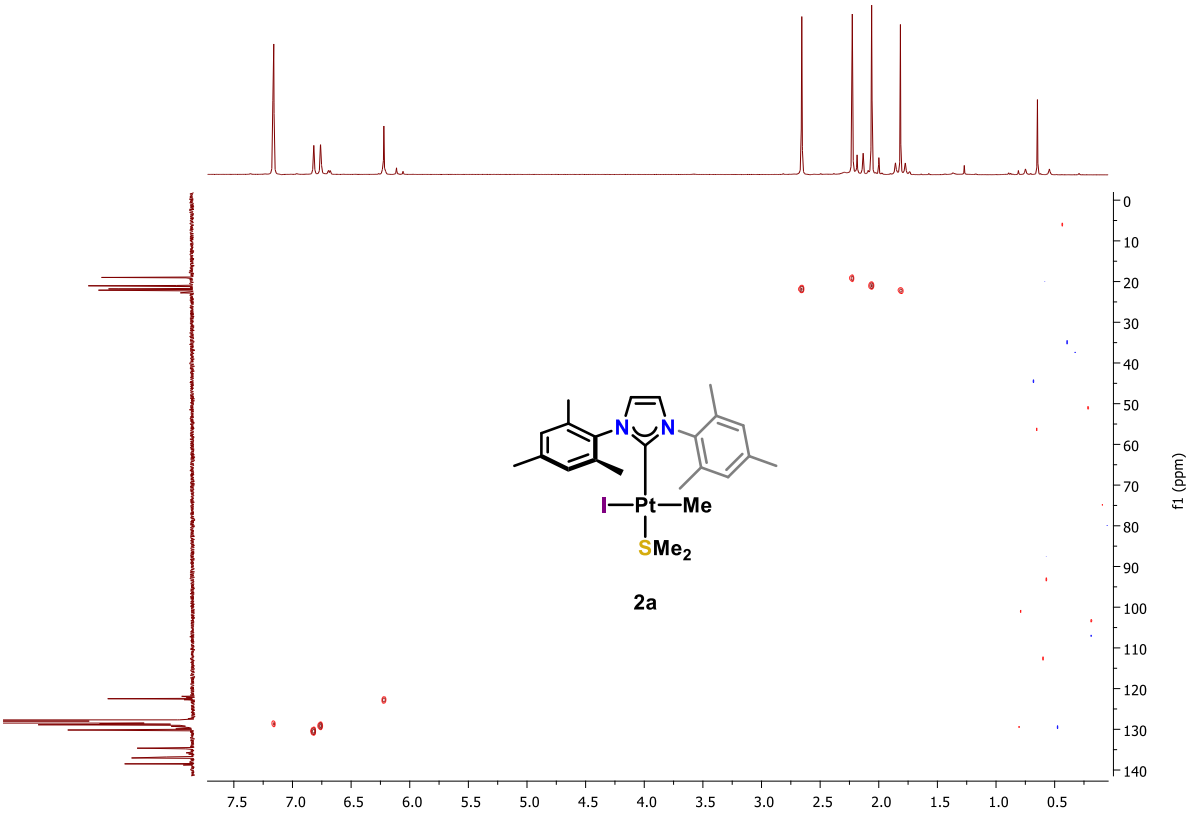


Figure S7: 2a, HSQC (C_6D_6, 400/100 MHz, 35 °C)

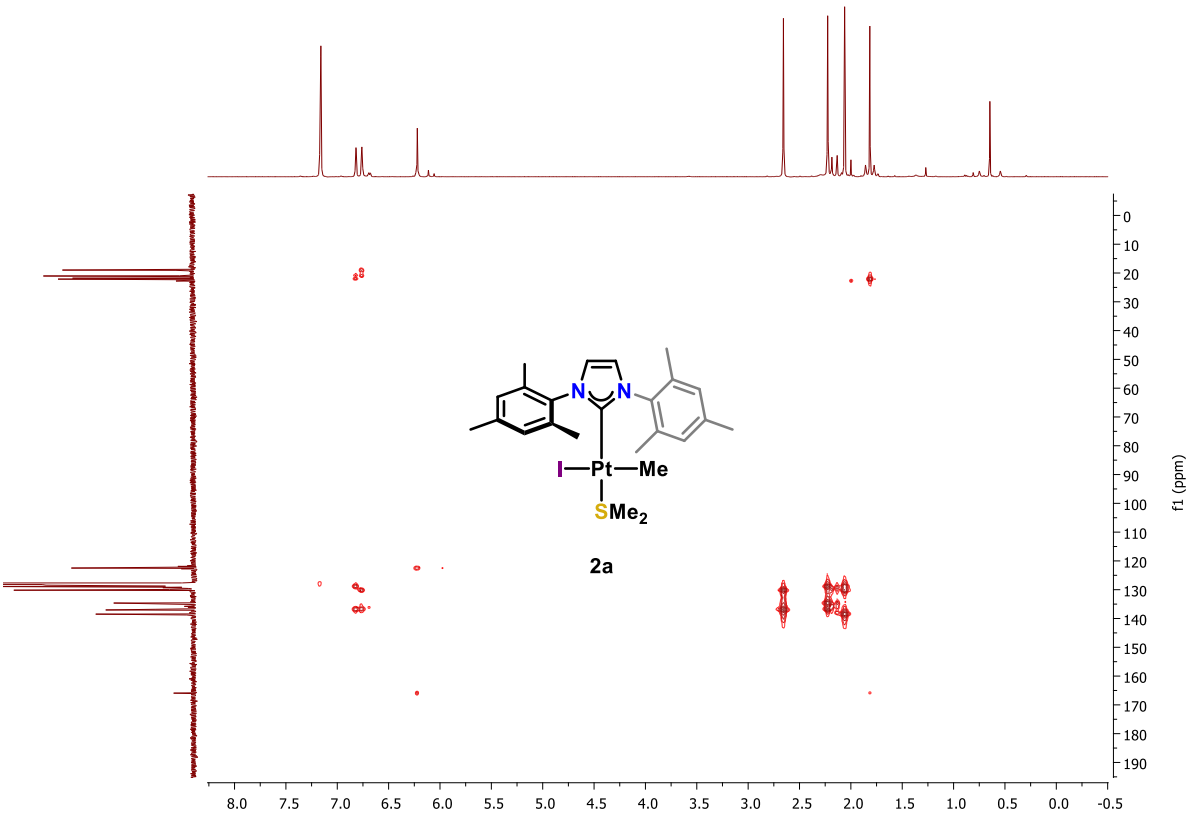


Figure S8: 2a, ^{1}H-^{13}C HMBC (C_6D_6, 400/100 MHz, 35 °C)

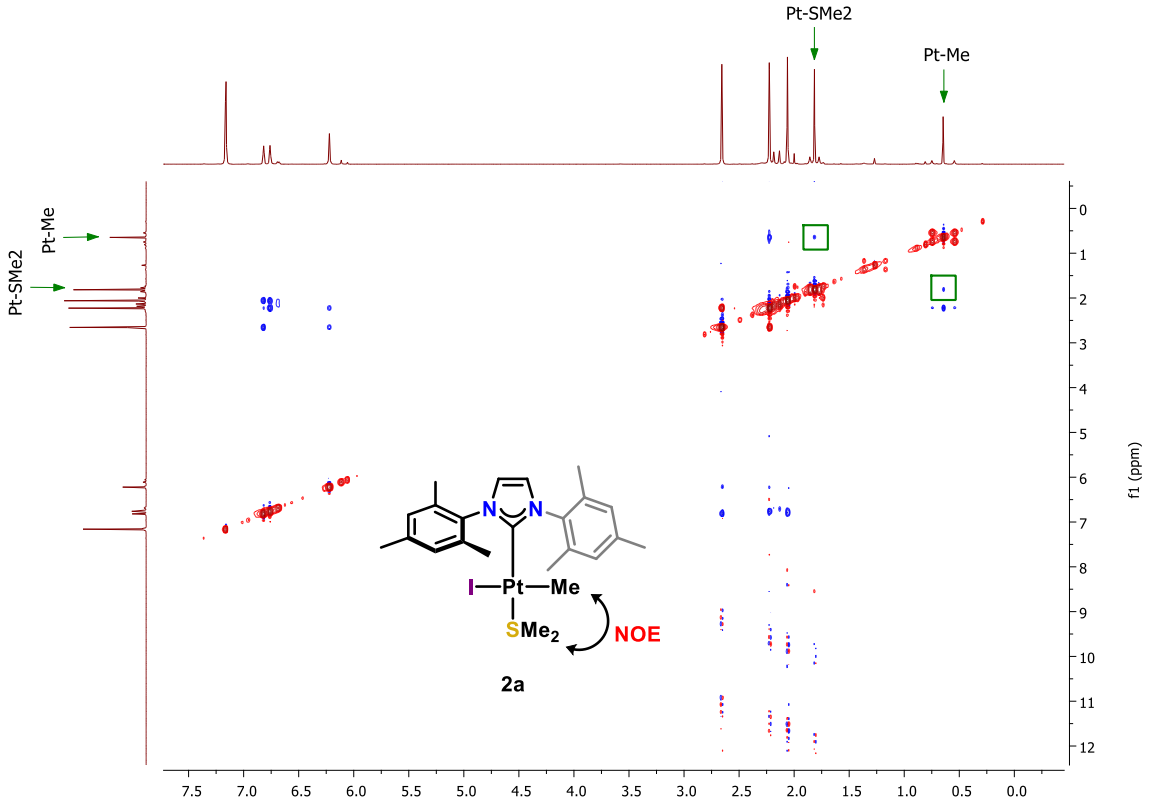


Figure S9: 2a, ^{1}H-^{1}H NOESY (C_6D_6, 400 MHz, 35 °C)

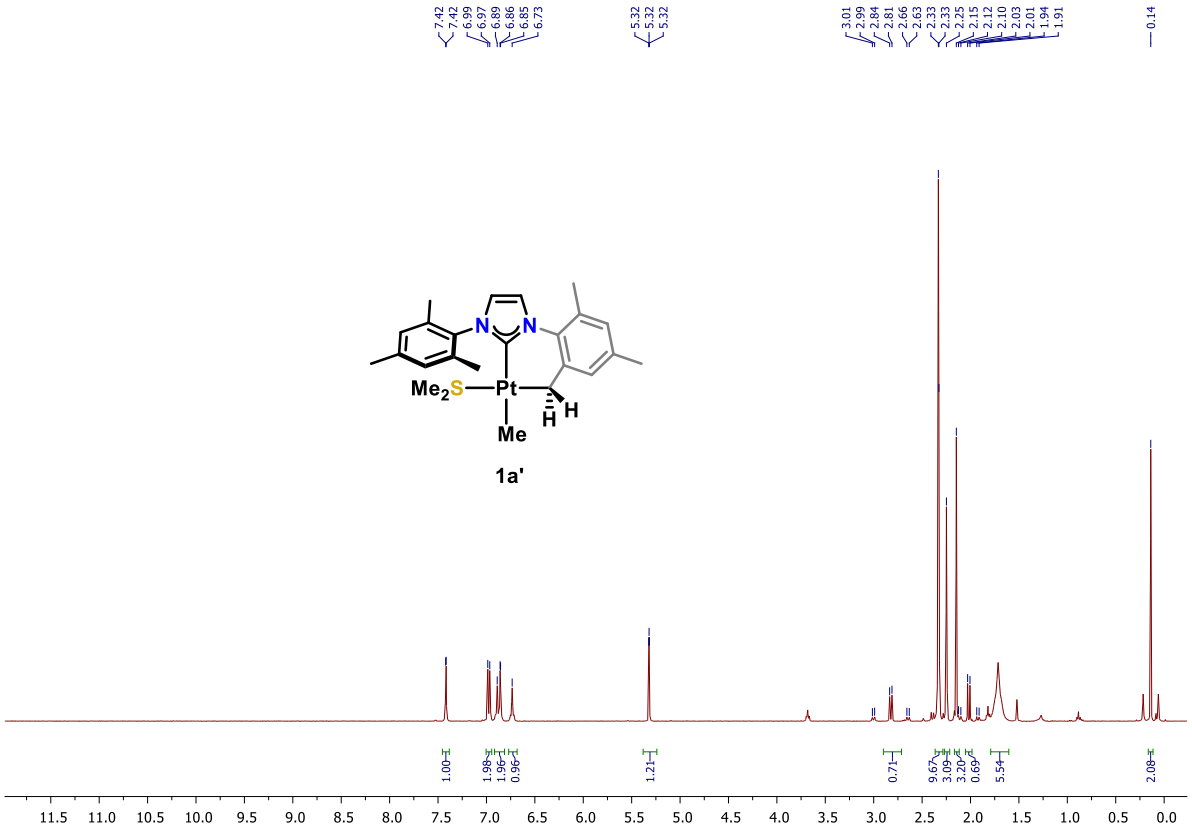


Figure S10: 1a', ^{1}H (CD_2Cl_2, 400 MHz, 25 °C)

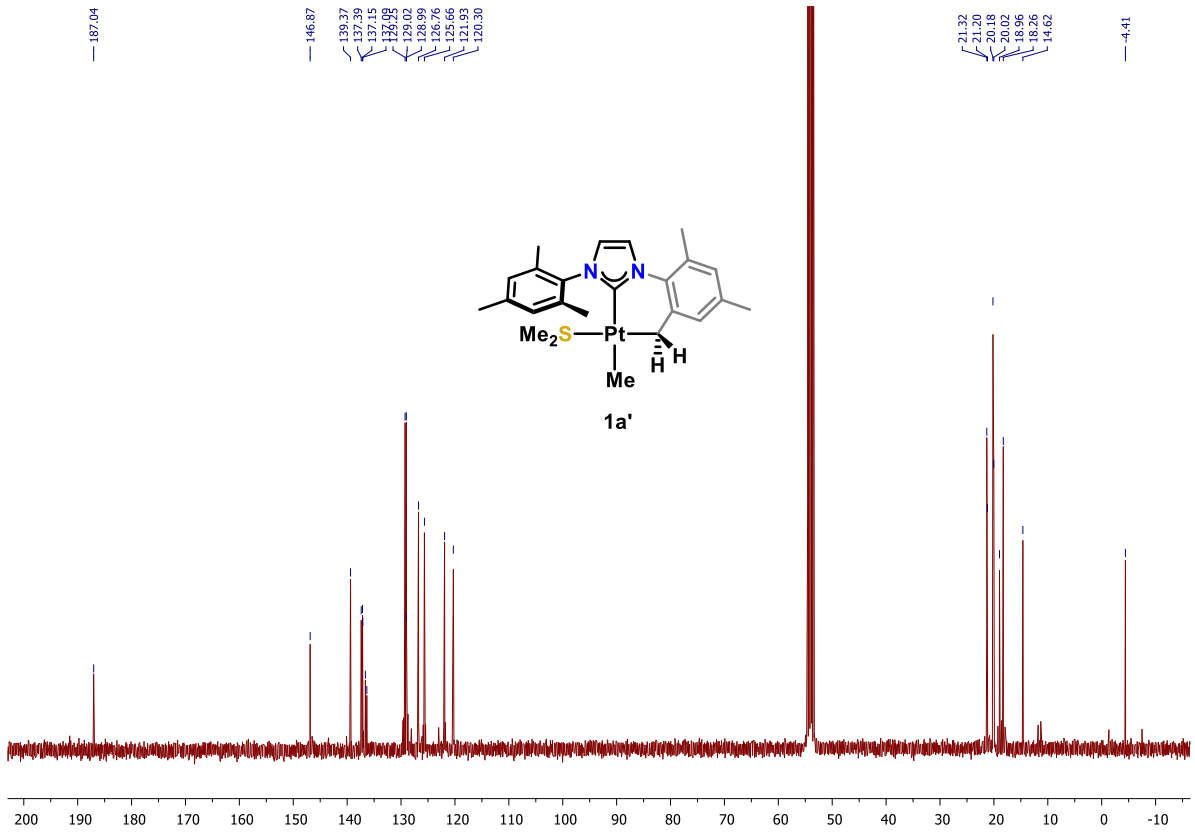


Figure S11: **1a'**, $^{13}C\{^{1}H\}$ (CD_2Cl_2, 100 MHz, 25 °C)

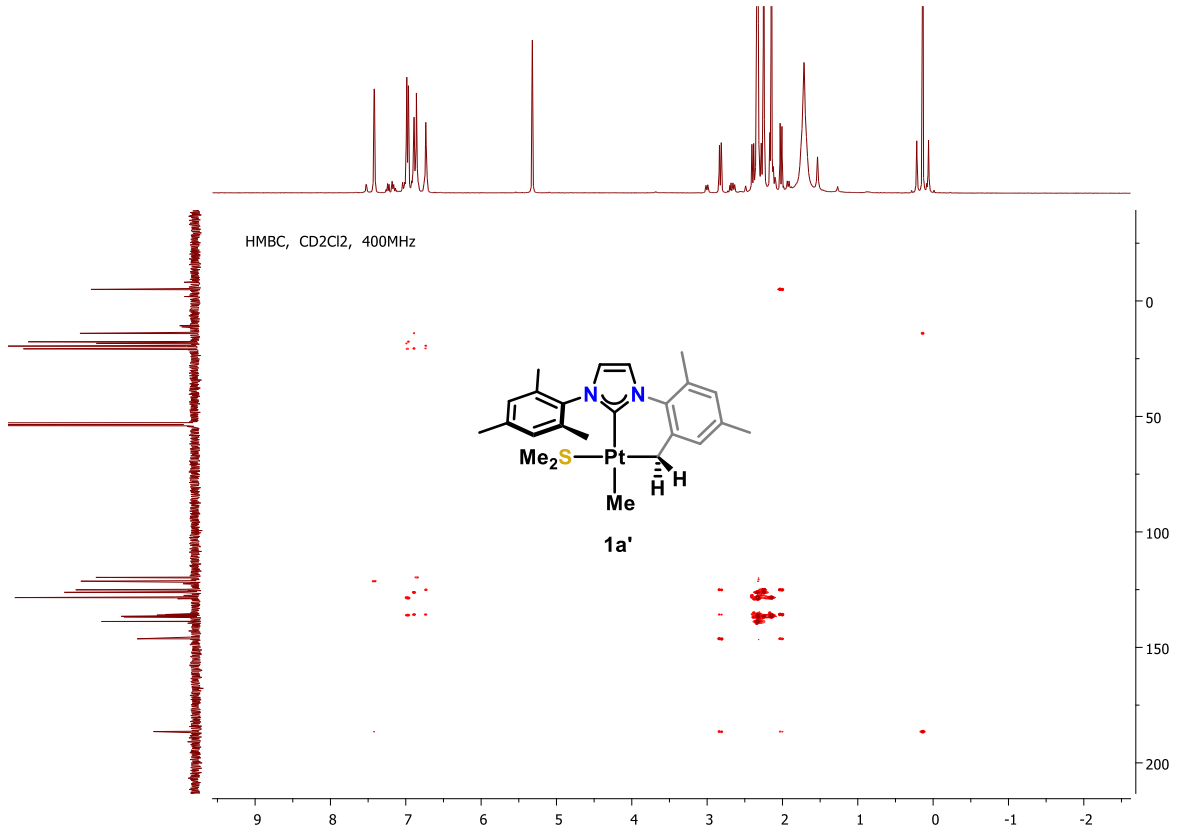


Figure S12: 1a', ^{1}H-^{13}C HMBC (CD_2Cl_2, 400/100 MHz, 25 °C)

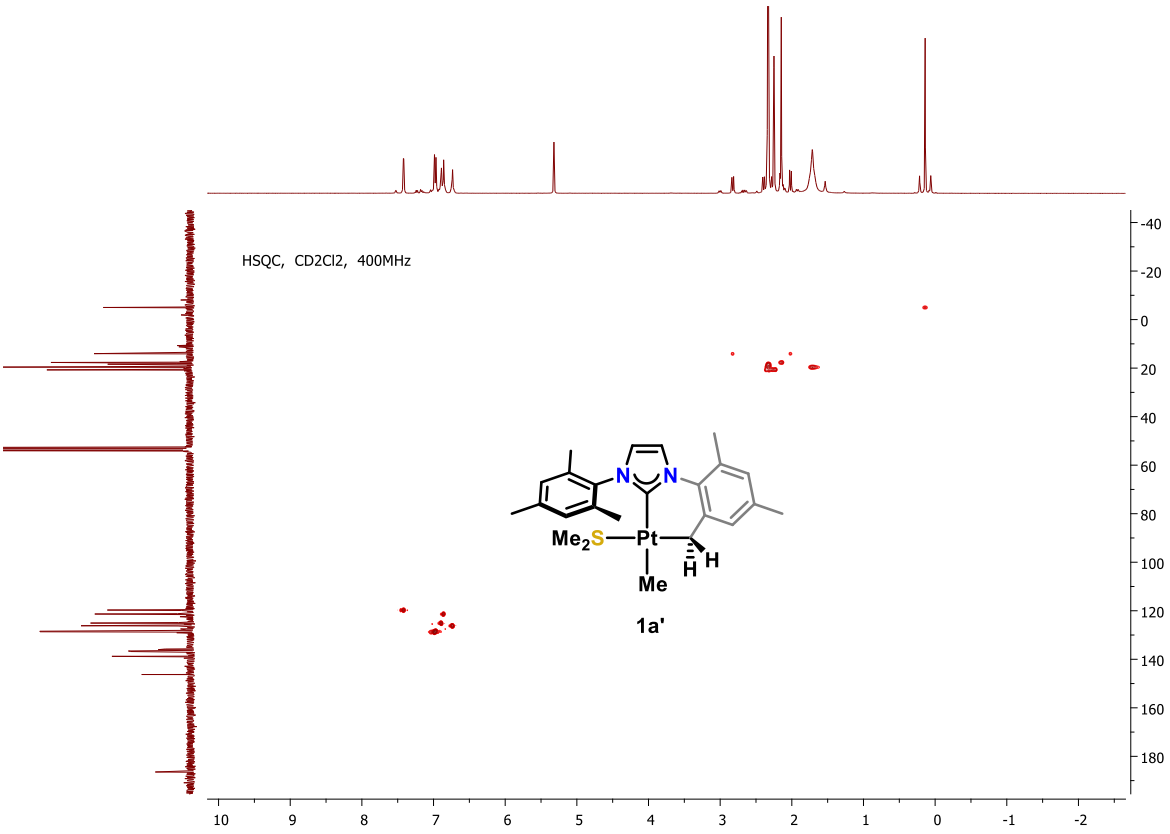


Figure S13: 1a', HSQC (CD_2Cl_2, 400/100 MHz, 25 °C)

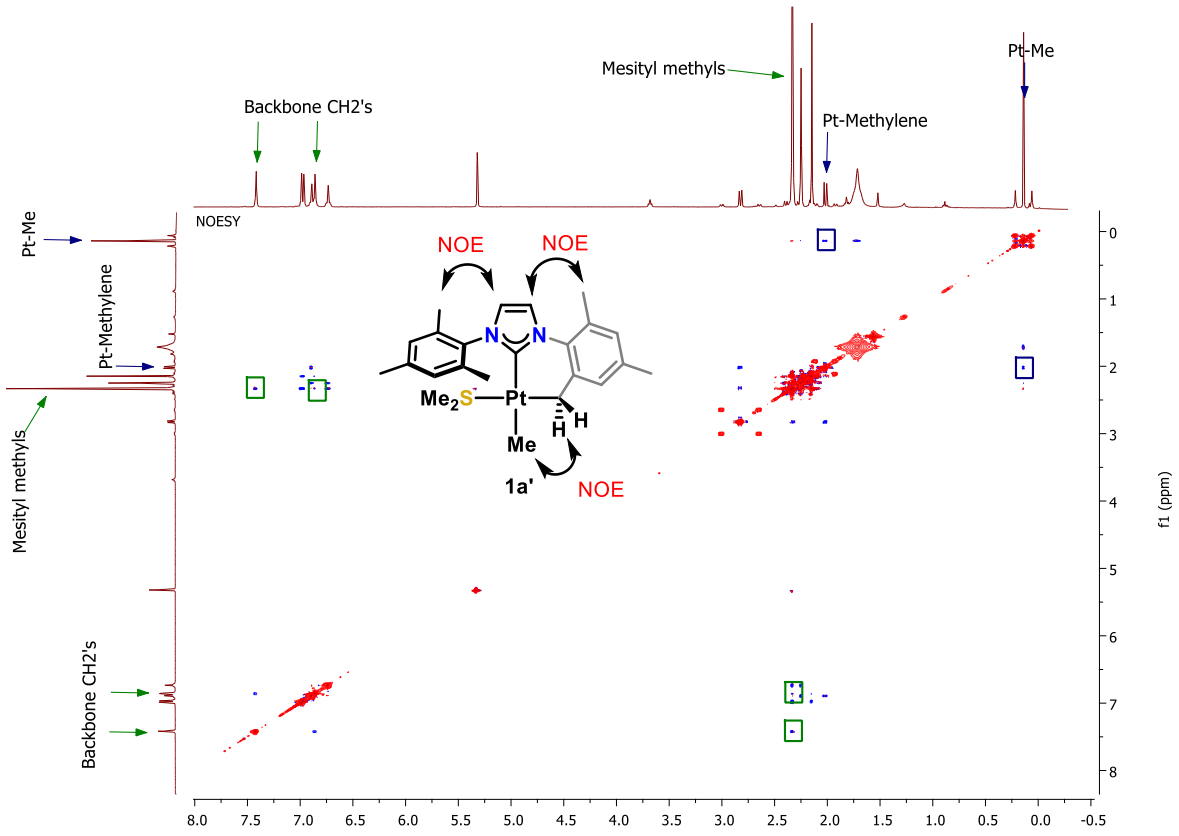


Figure S14: 1a', 1H-1H NOESY, (CD_2Cl_2, 400 MHz, 25 °C)

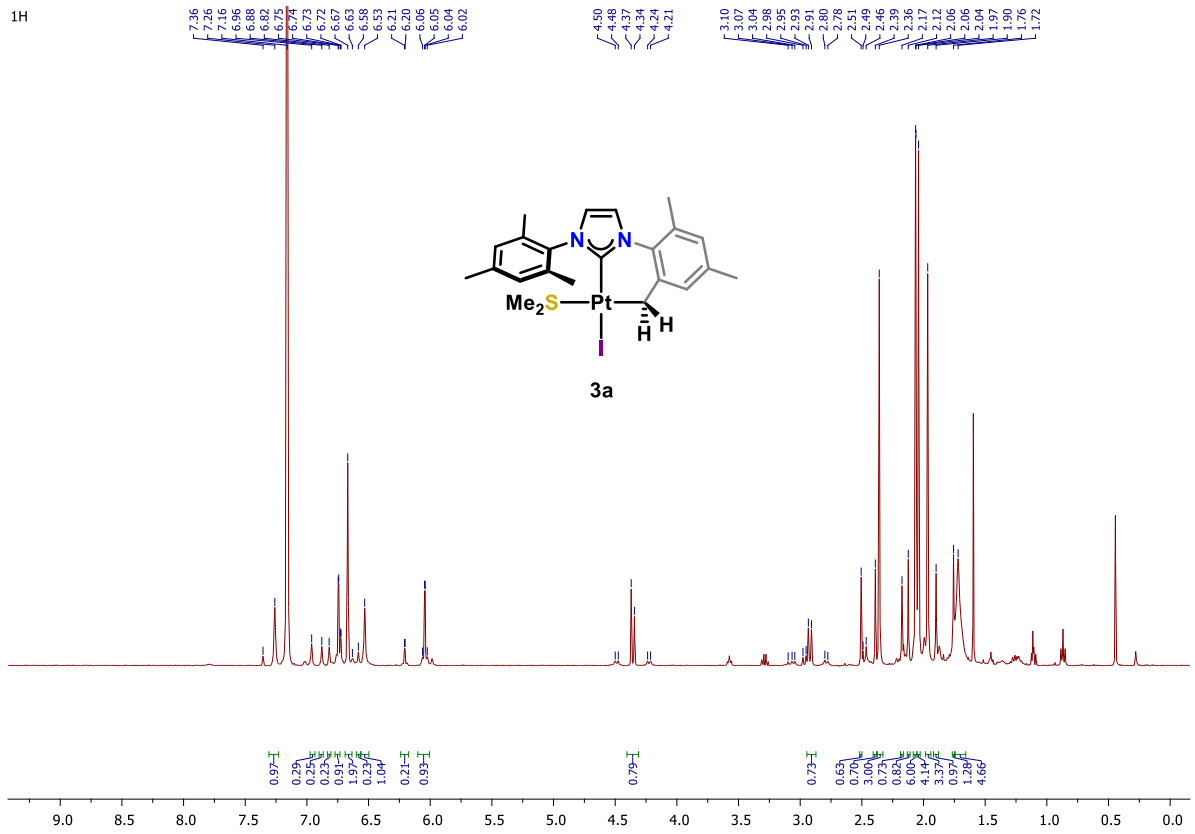


Figure S15: 3a, ^{1}H (C_6D_6, 400 MHz, 55 °C)

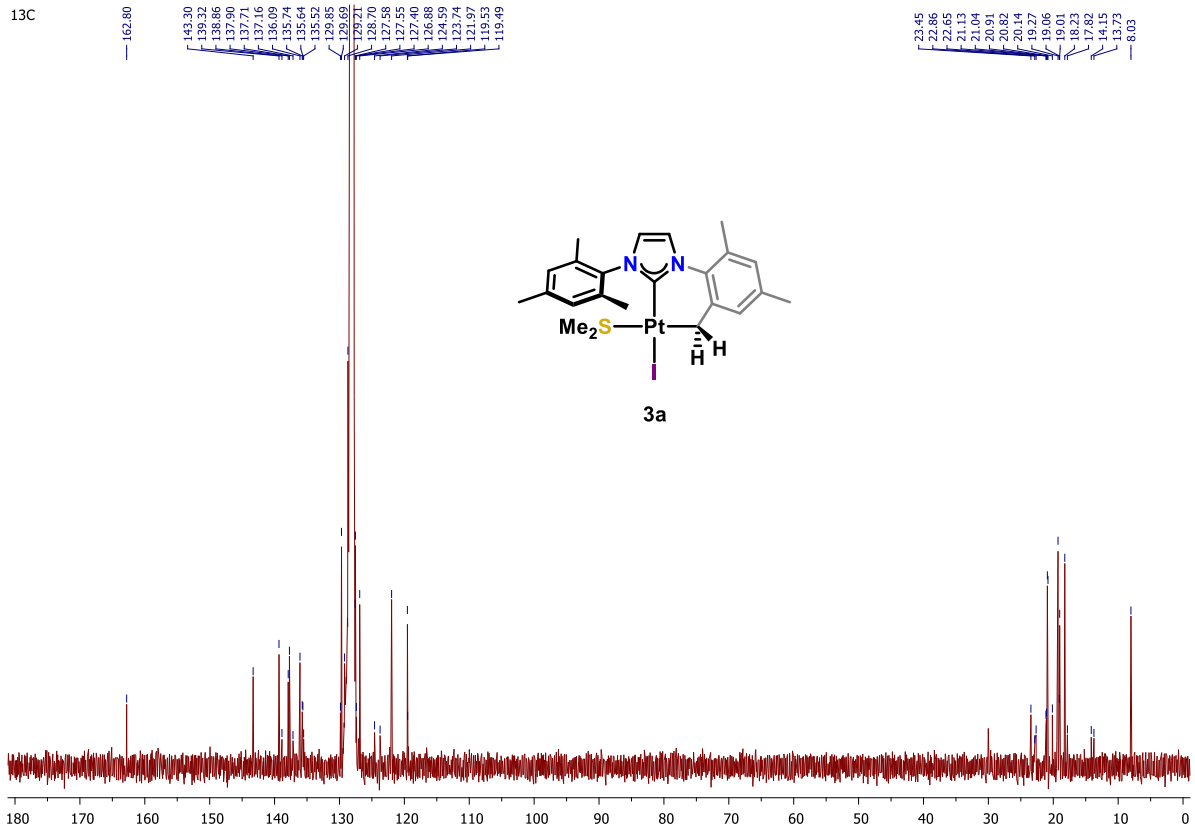


Figure S16: 3a, $^{13}C\{^{1}H\}$ (C_6D_6, 100 MHz, 55 °C)

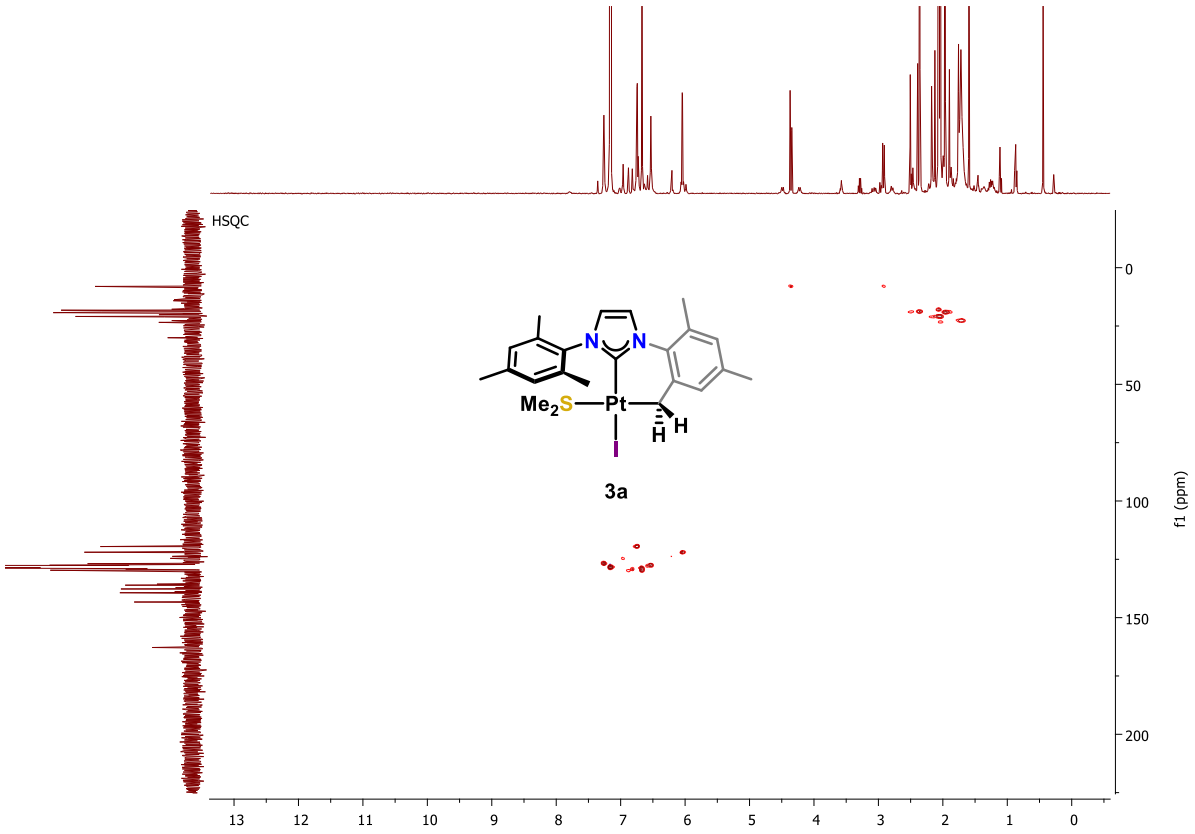


Figure S17: 3a, HSQC (C_6D_6, 400/100 MHz, 55 °C)

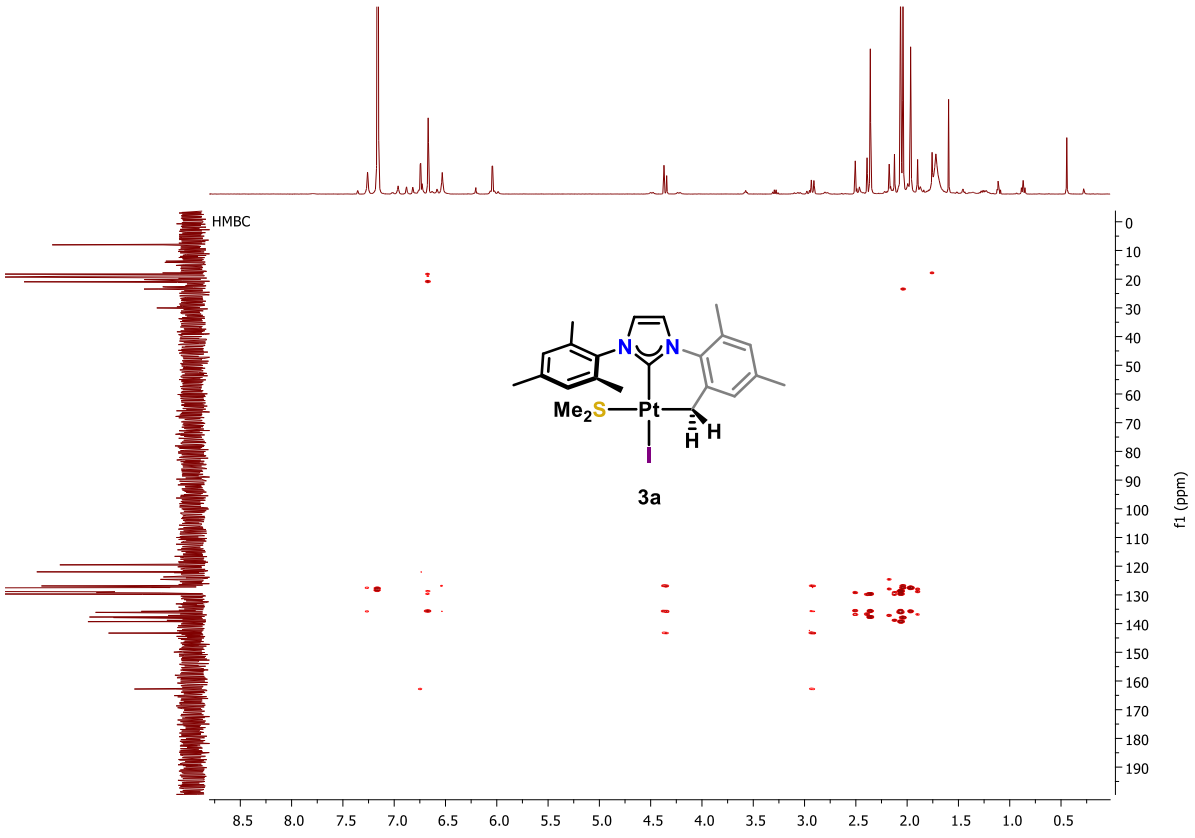


Figure S18: 3a, ^{1}H-^{13}C HMBC (C_6D_6, 400/100 MHz, 55 °C)

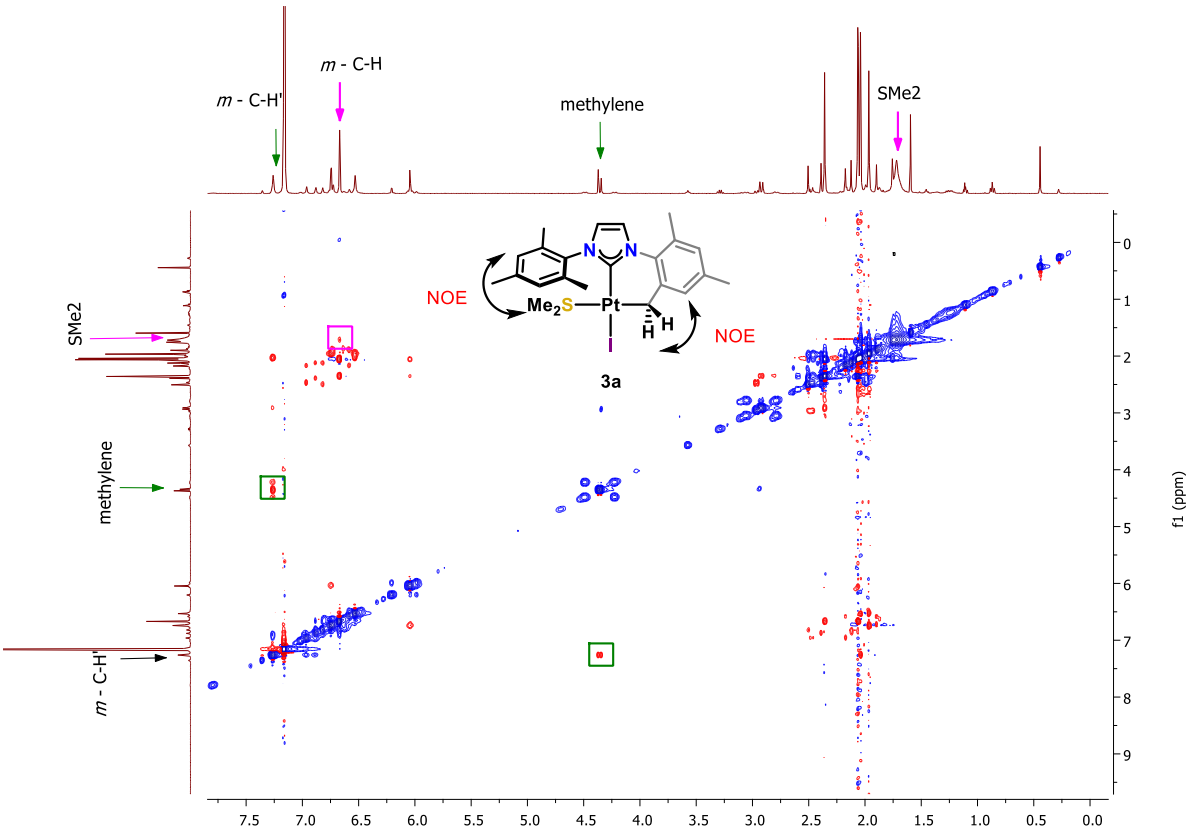


Figure S19: 3a, ^{1}H-^{1}H NOESY (C_6D_6, 400 MHz, 55 °C)

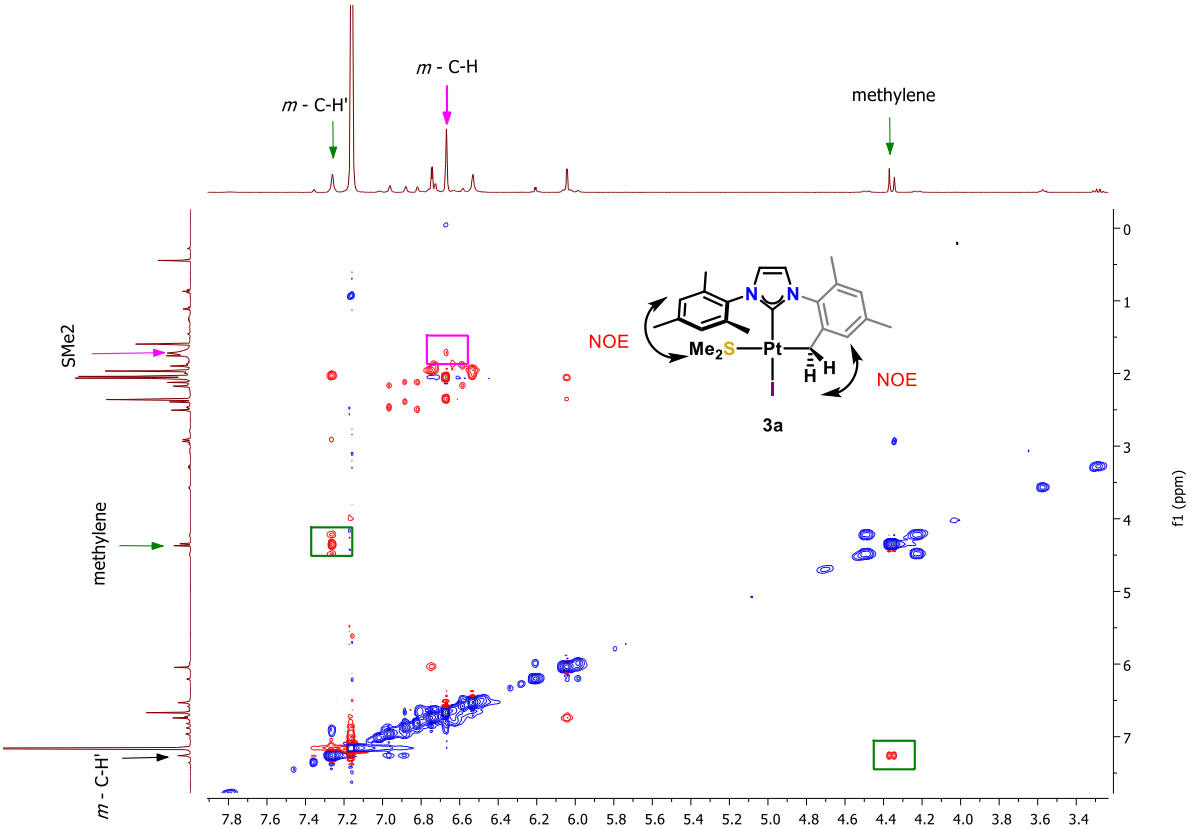


Figure S20: 3a, region showing NOE between SMe_2 and aryl C-H (C_6D_6, 400 MHz, 55 °C)

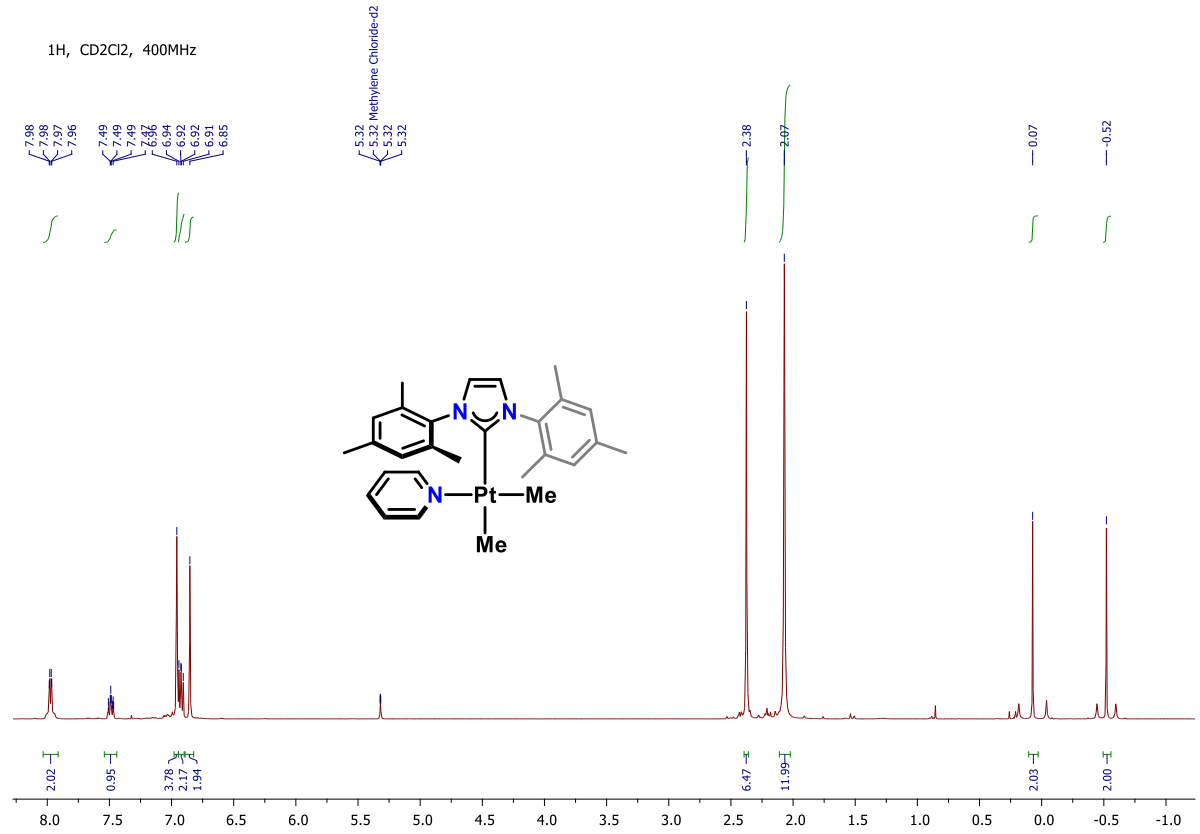


Figure S21: 1b, ^{1}H (CD_2Cl_2, 400 MHz, 25 °C)

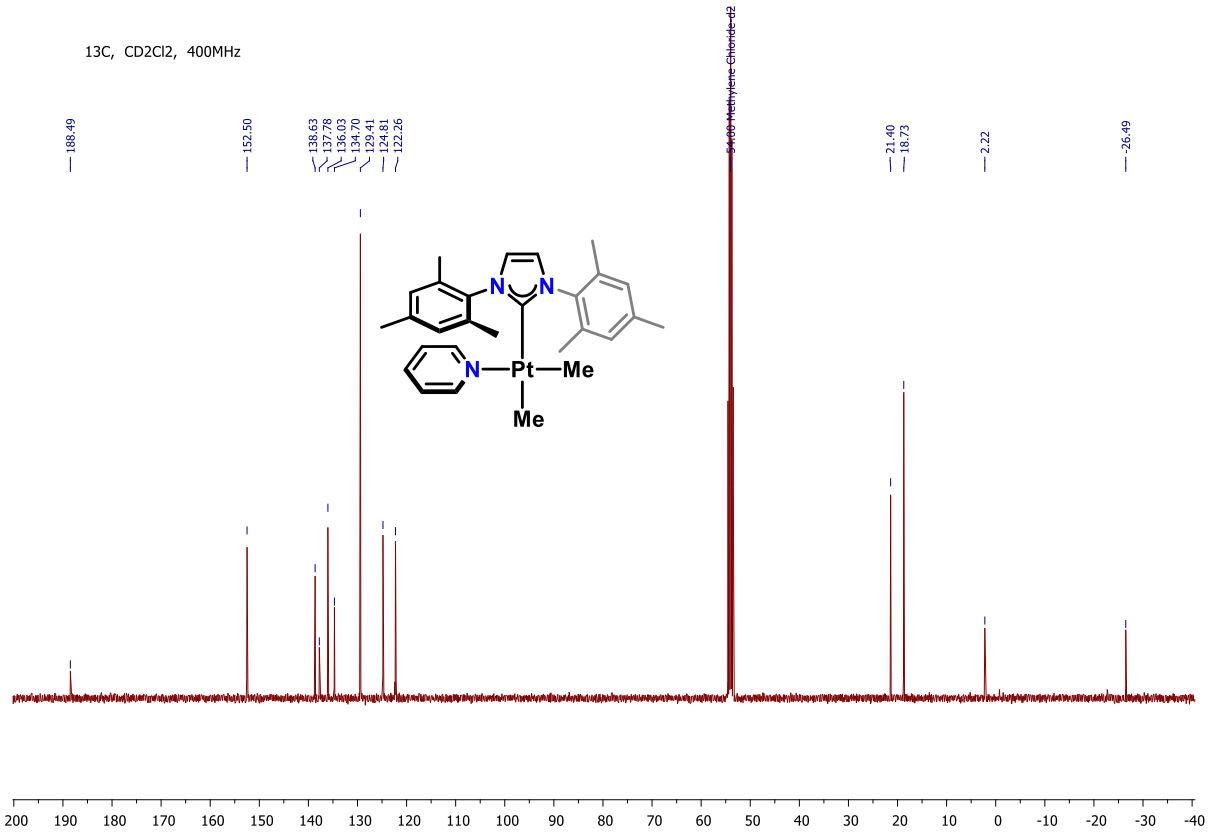


Figure S22: 1b, $^{13}C\{^{1}H\}$ (CD_2Cl_2, 100 MHz, 25 °C)

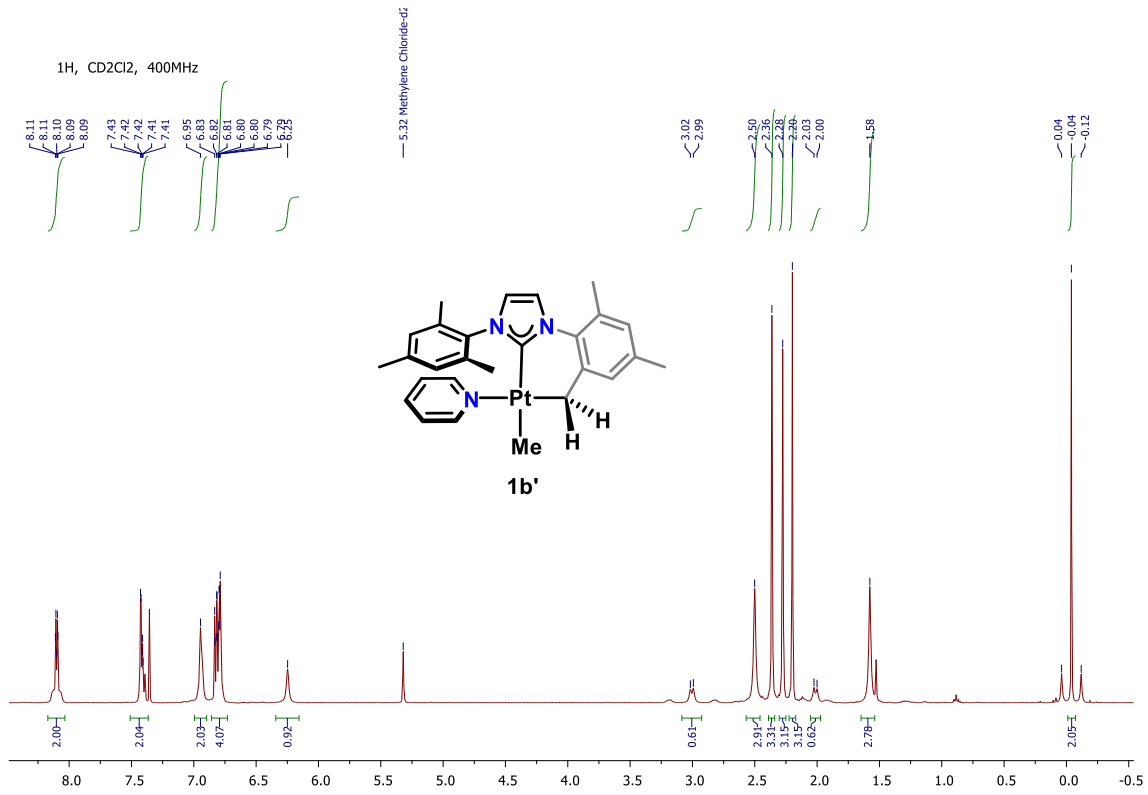


Figure S23: 1b', ^{1}H (CD_2Cl_2, 400 MHz, 25 °C)

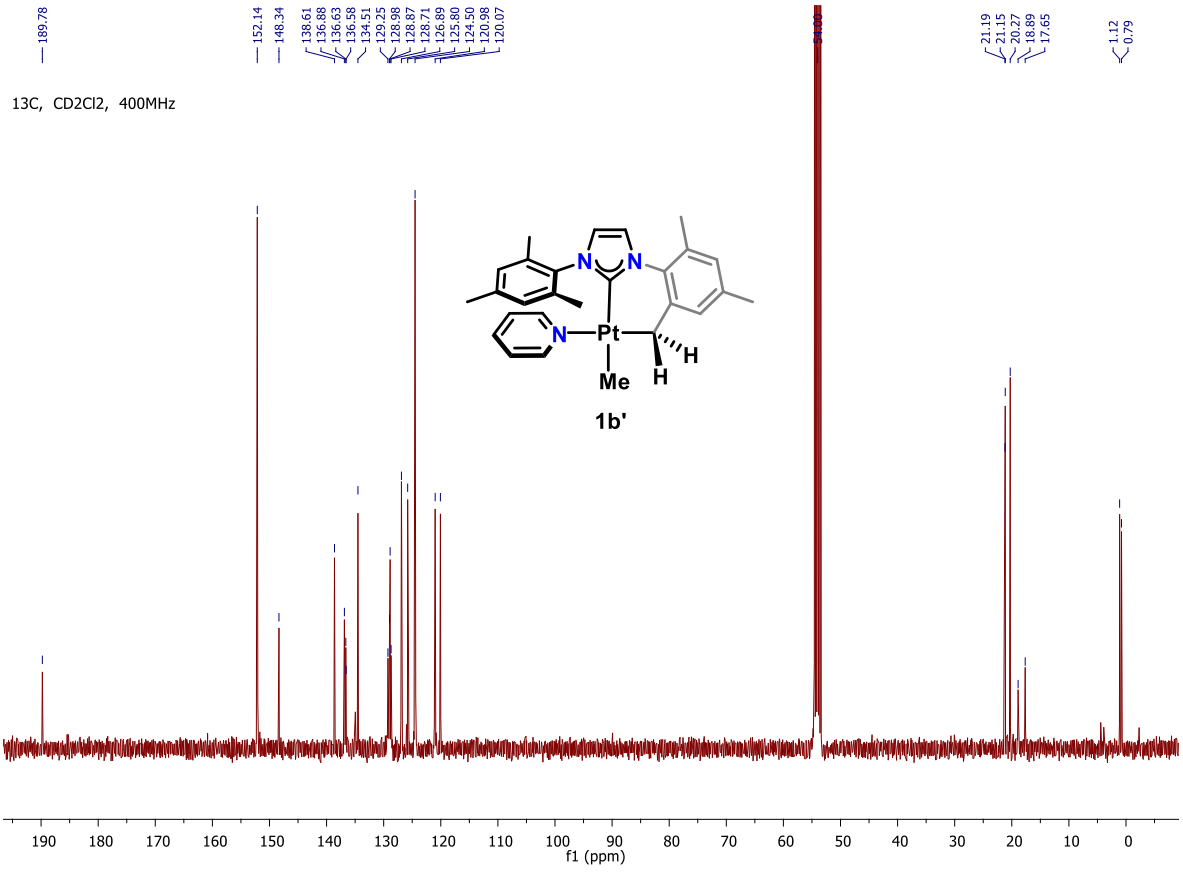


Figure S24: 1b', $^{13}C\{^{1}H\}$ (CD_2Cl_2, 100 MHz, 25 °C)

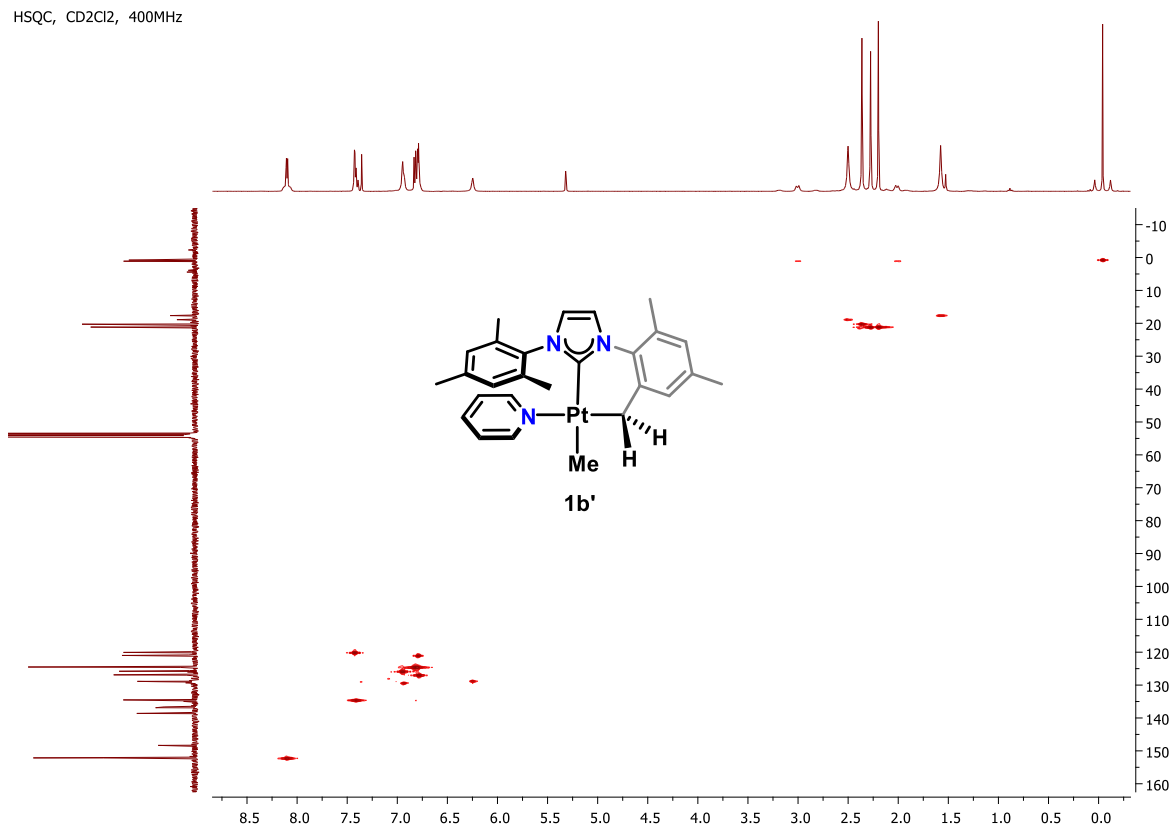


Figure S25: 1b', HSQC (CD_2Cl_2, 400/100 MHz, 25 °C)

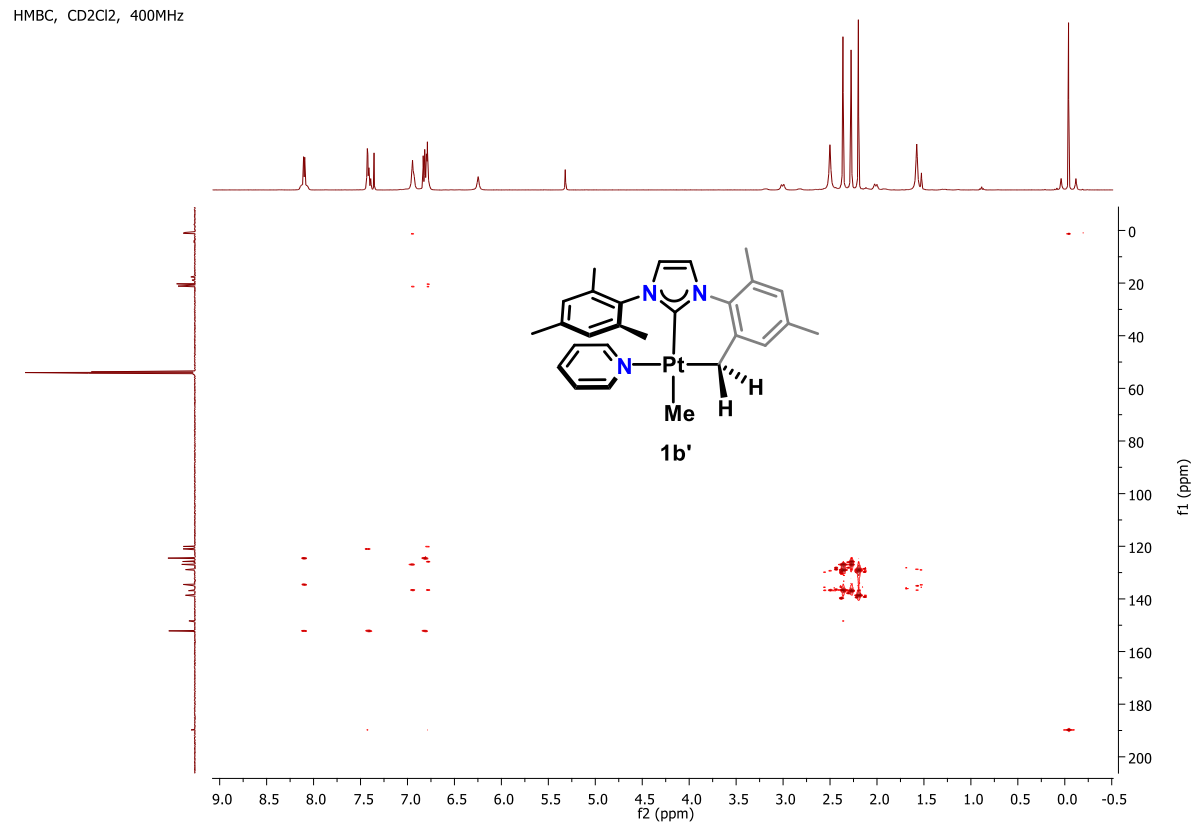


Figure S26: 1b', ^{1}H-^{13}C HMBC (CD_2Cl_2, 400/100 MHz, 25 °C)

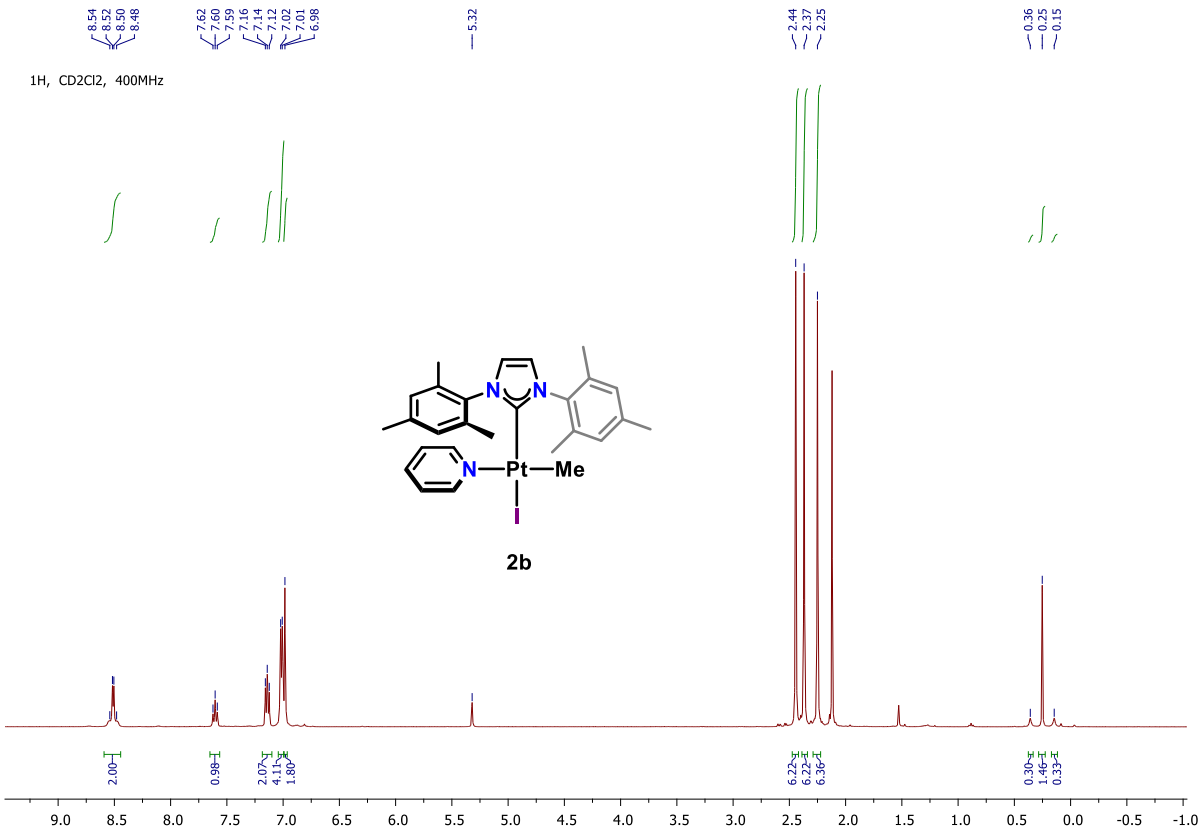


Figure S27: 2b, ^{1}H (CD_2Cl_2, 400 MHz, 25 °C), peak at 2.1 corresponds to acetone from recrystallisation.

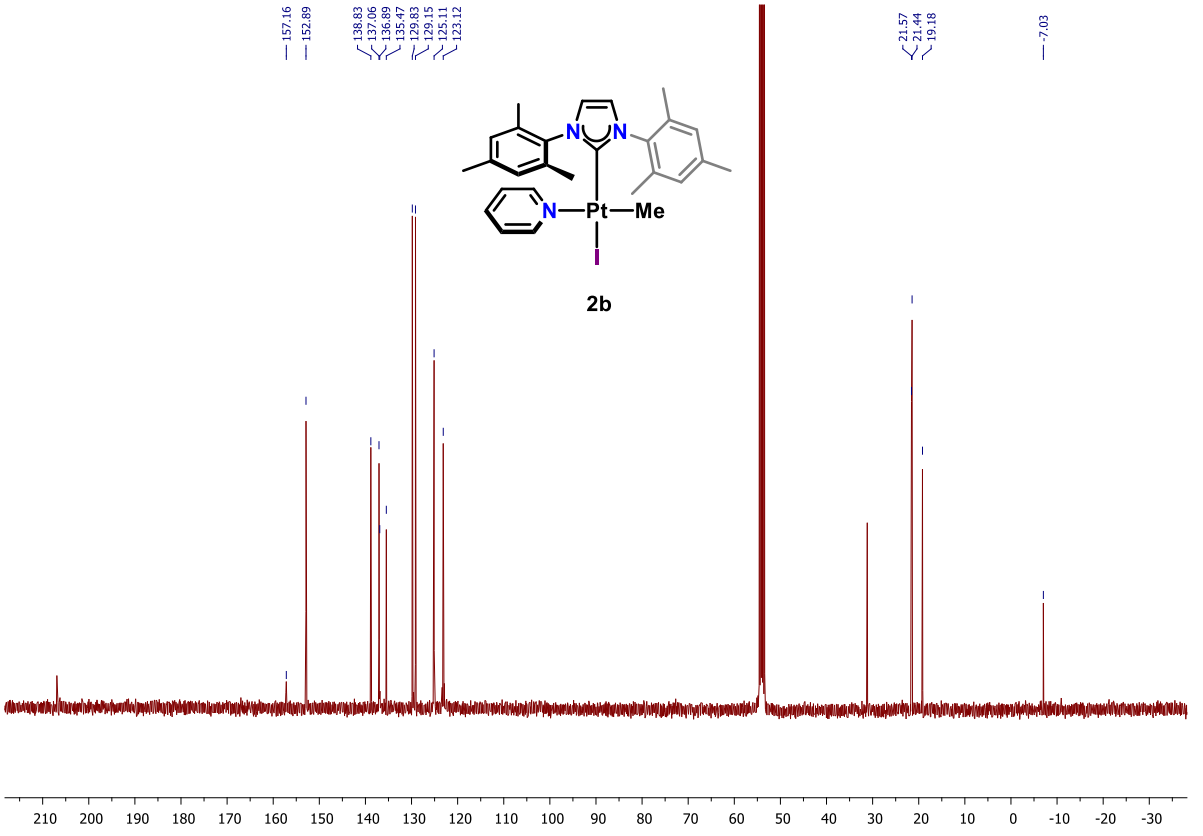


Figure S28: 2b, $^{13}C\{^{1}H\}$ (CD_2Cl_2, 100 MHz, 25 °C), peaks at 31ppm and 206ppm correspond to acetone.

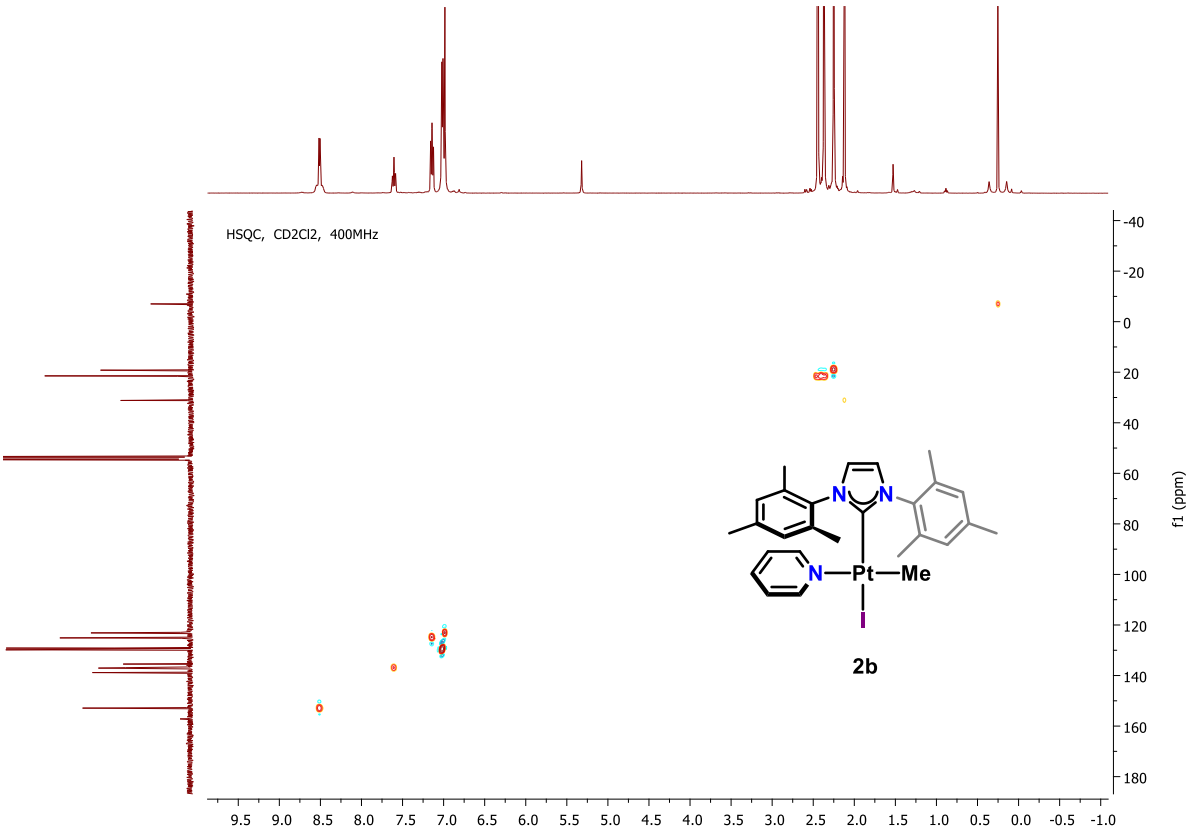


Figure S29: 2b, HSQC (CD_2Cl_2, 400/100 MHz, 25 °C)

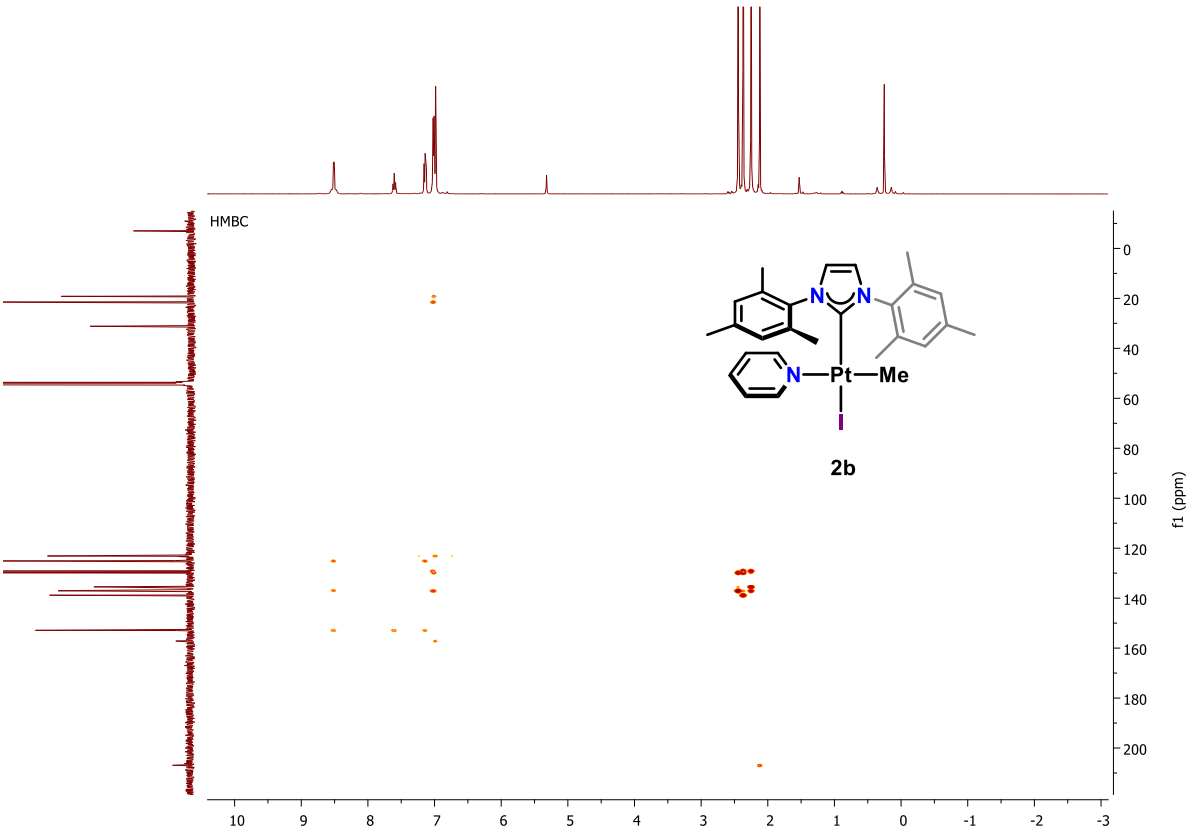


Figure S30: 2b, ^{1}H-^{13}C HMBC (CD_2Cl_2, 400/100 MHz, 25 °C)

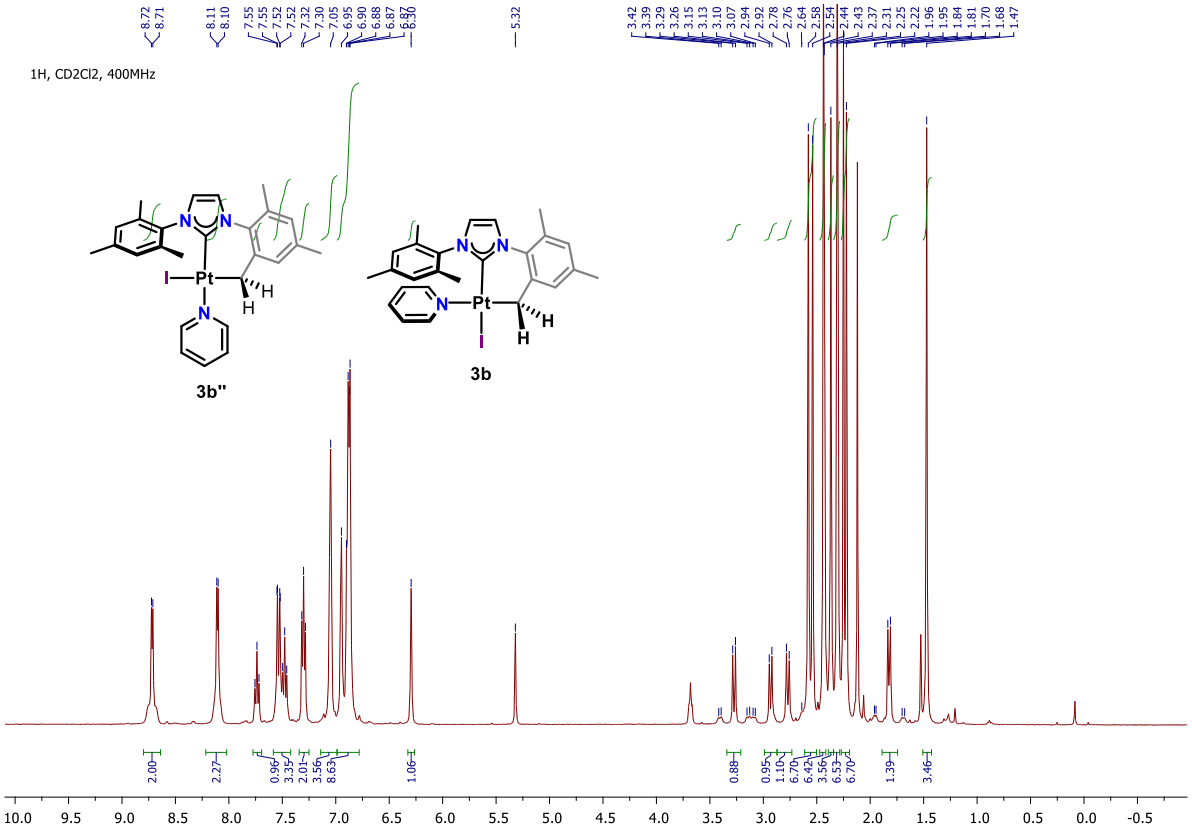


Figure S31: 3b and 3b', ^{1}H (CD_2Cl_2, 400 MHz, 25 °C)

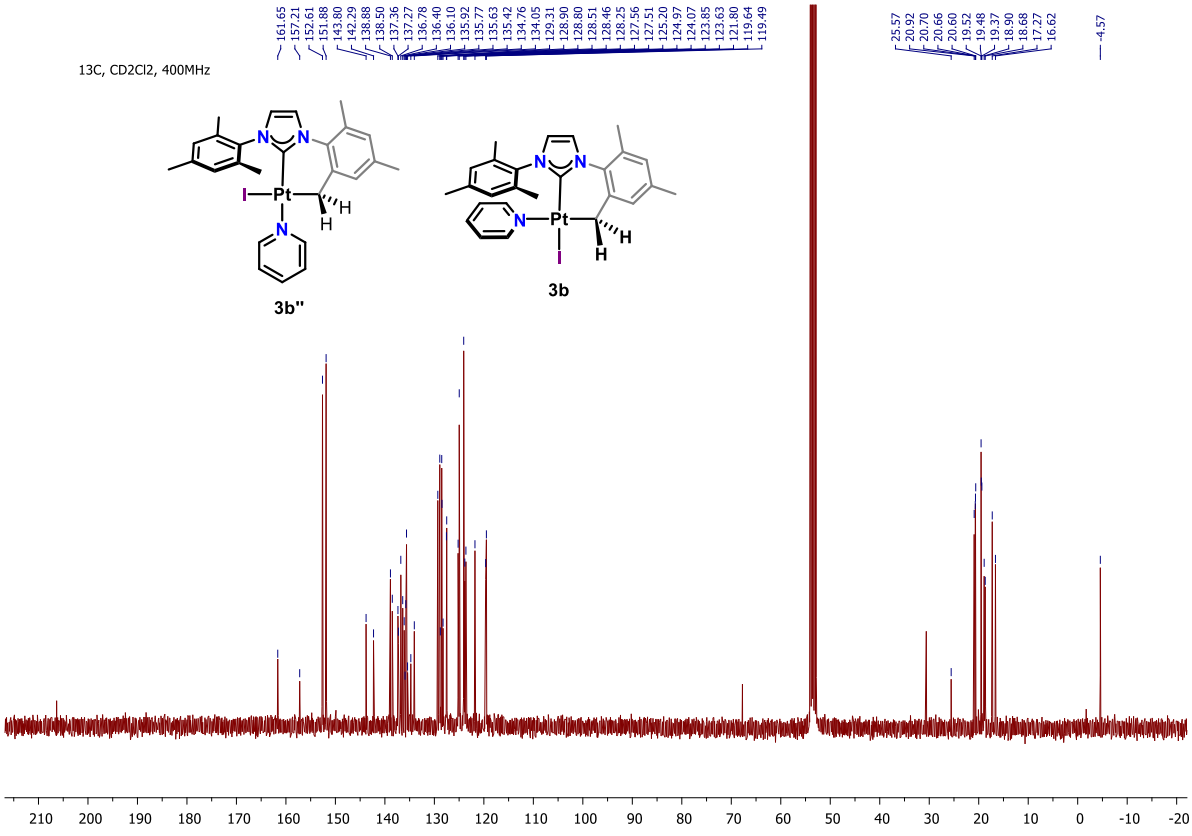


Figure S32: 3b and **3b',** $^{13}C\{^{1}H\}$ (CD_2Cl_2, 100 MHz, 25 °C)

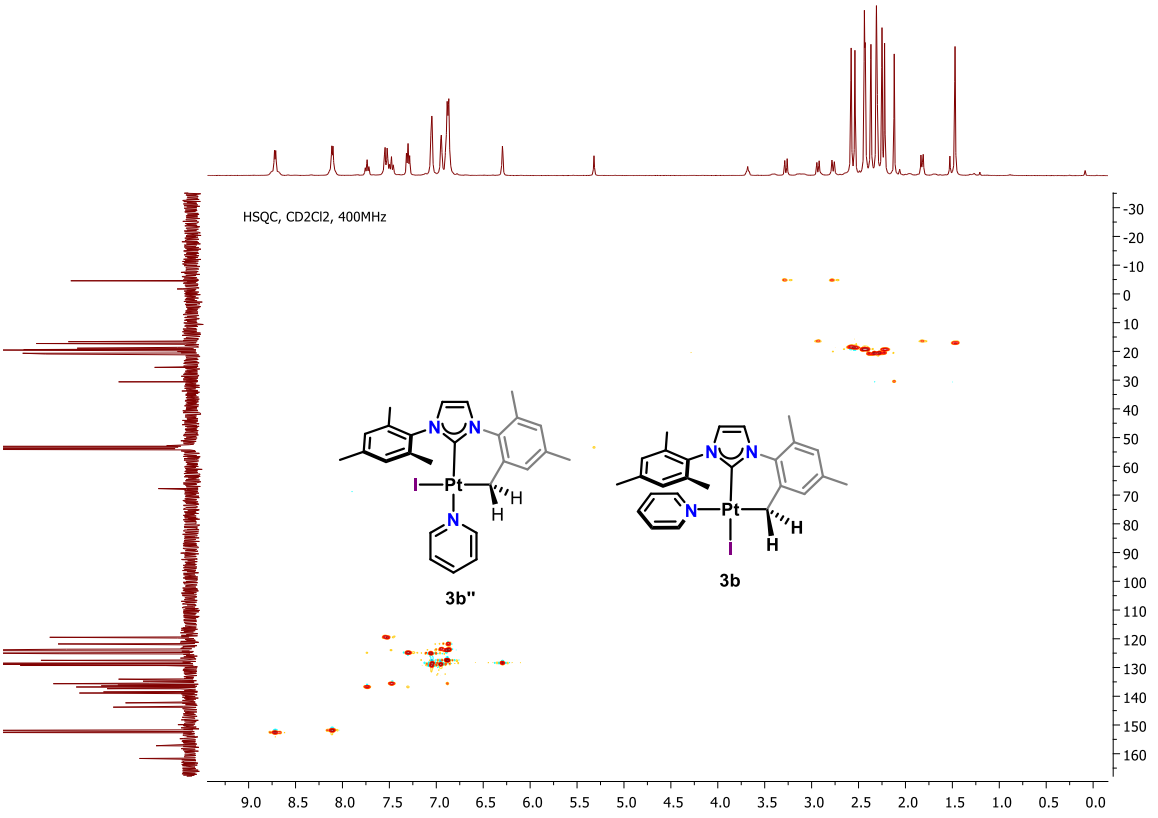


Figure S33: 3b and **3b',** HSQC (CD_2Cl_2, 400/100 MHz, 25 °C)

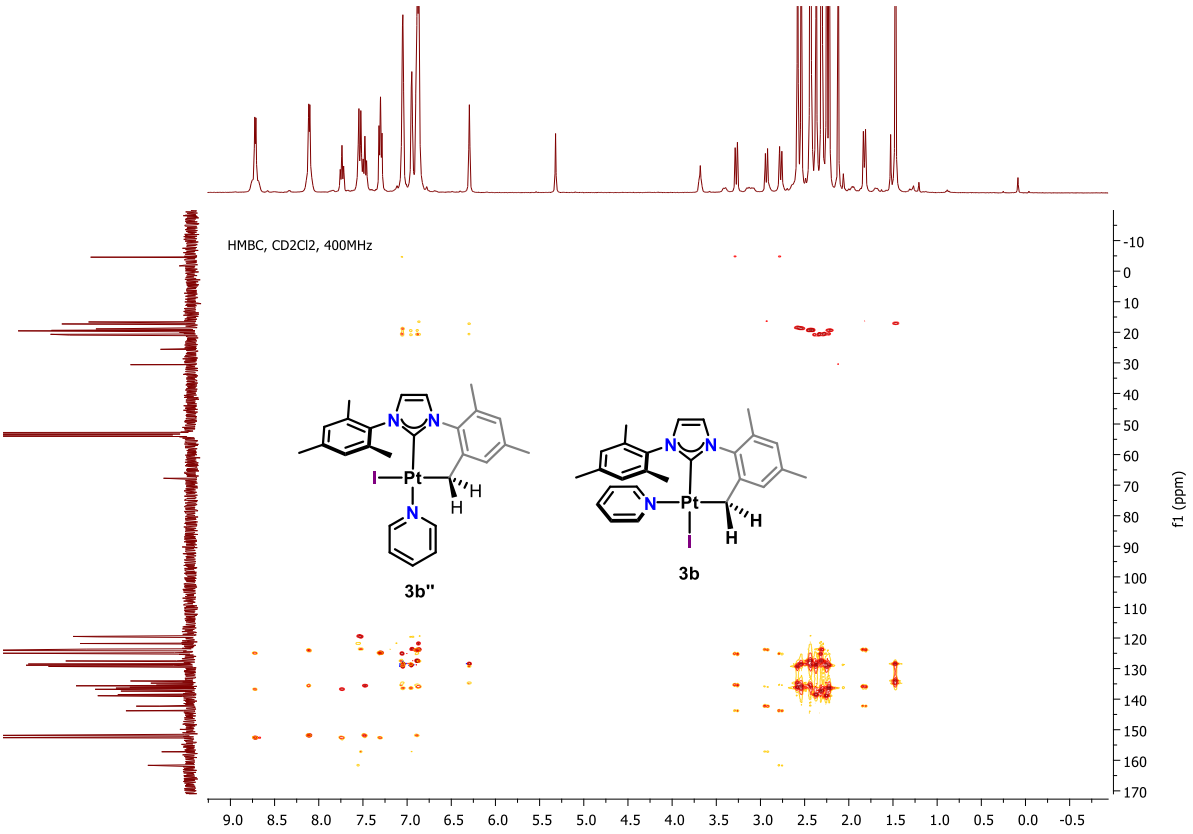


Figure S34: **3b and 3b',** ^{1}H-^{13}C HMBC (CD_2Cl_2, 400/100 MHz, 25 °C)

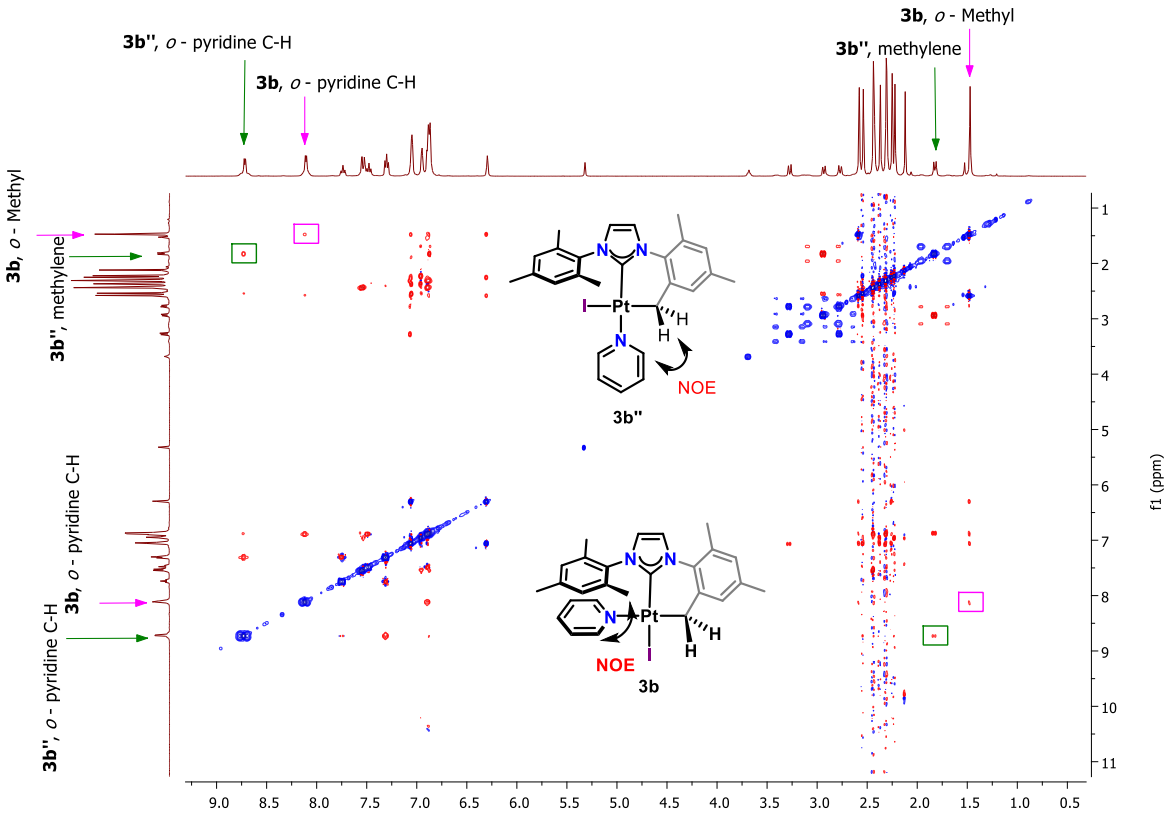


Figure S35: 3b and **3b'',** ^{1}H-^{1}H NOESY (CD_2Cl_2, 400 MHz, 25 °C)

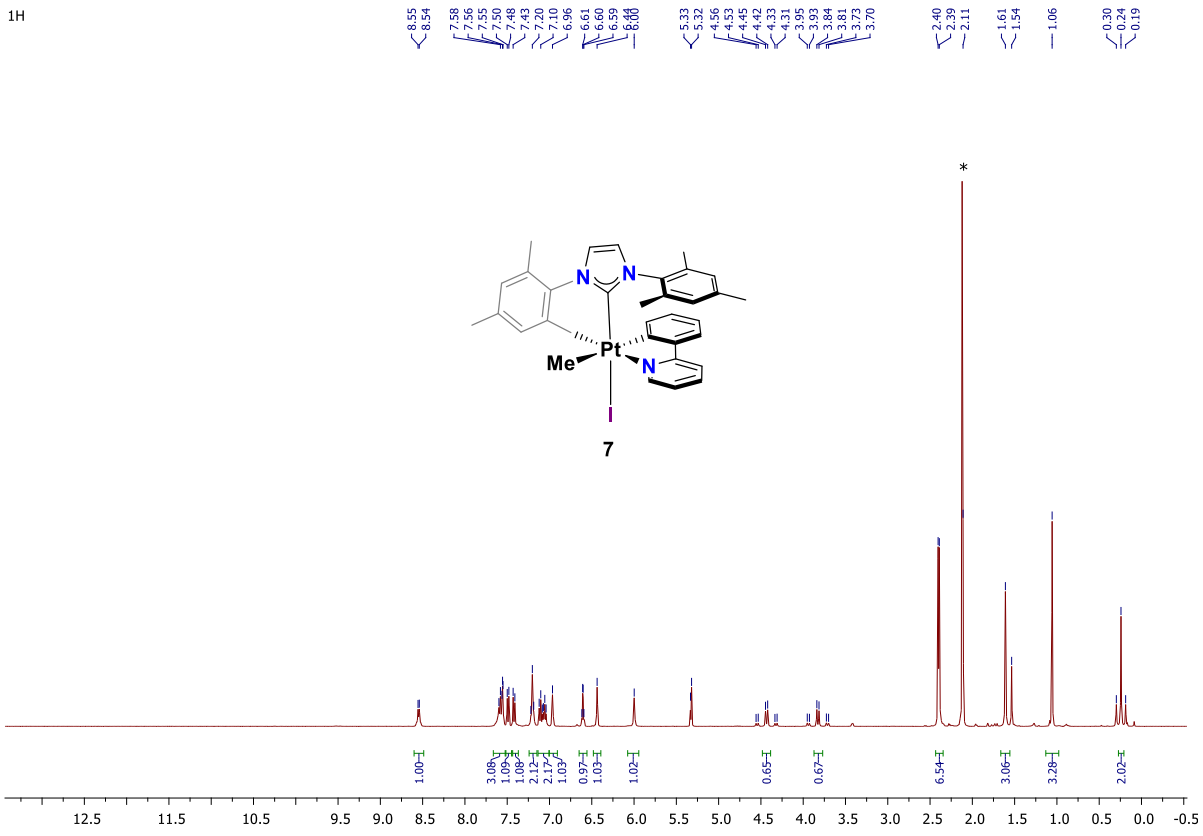


Figure S36: **7**, ^{1}H NMR (CD_2Cl_2, 400 MHz, 25 °C). * Acetone from recrystallisation

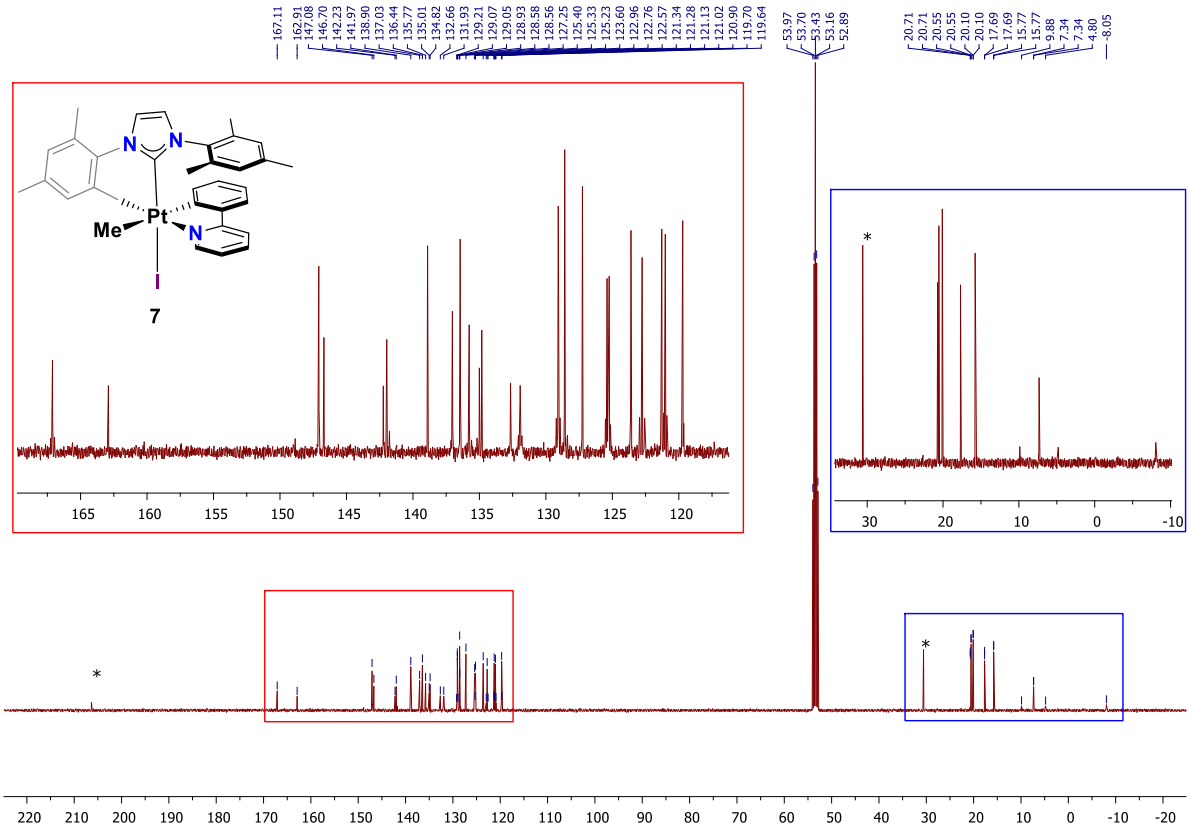


Figure S37: 7,$^{13}C\{^{1}H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C). * Acetone from recrystallisation

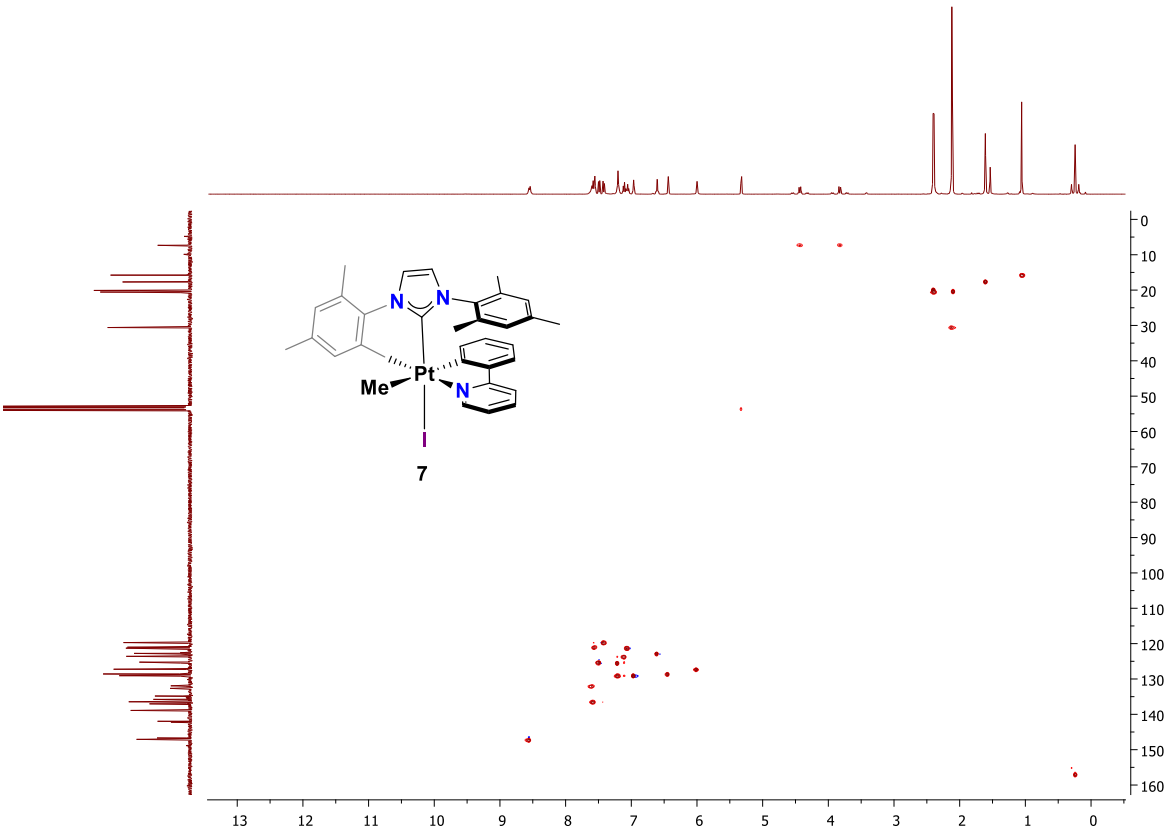


Figure S38: **7**, HSQC (400/100 MHZ, CD_2Cl_2, 25 °C)

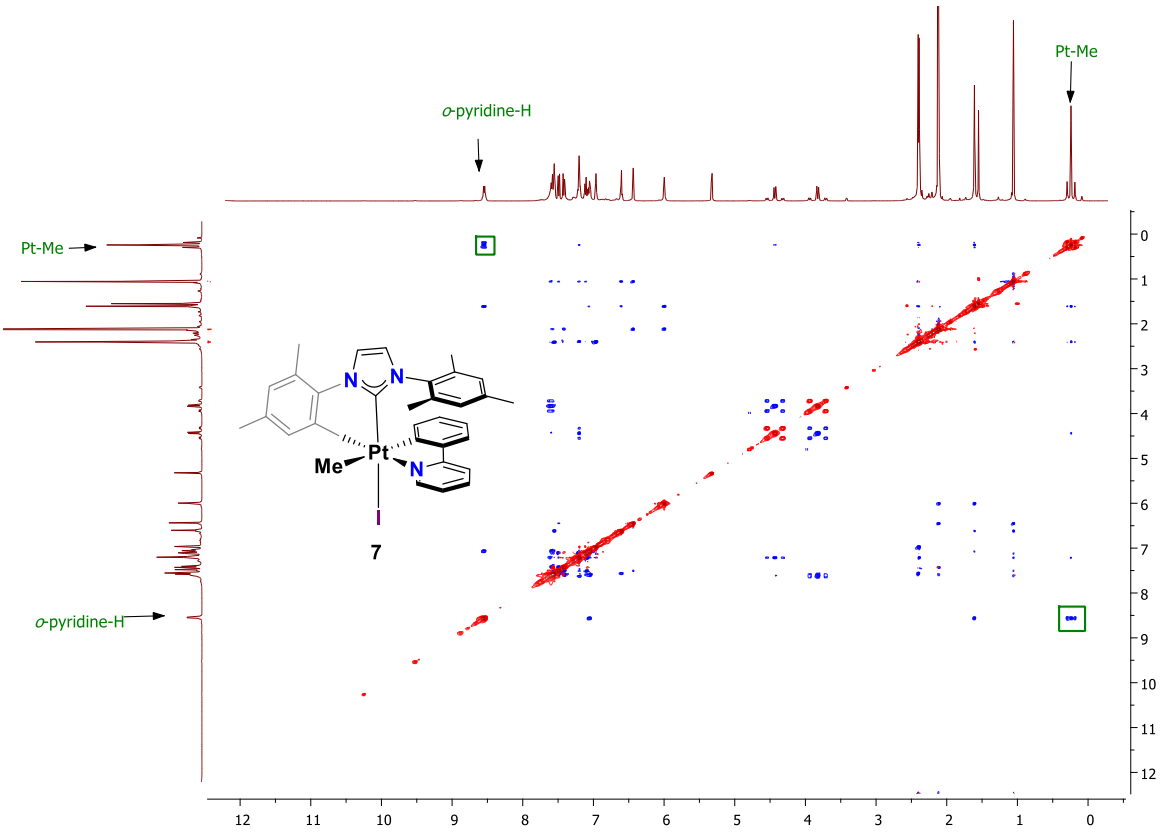


Figure S39: **7**, ^{1}H-^{1}H NOESY (400 MHz, CD_2Cl_2, 25 °C)

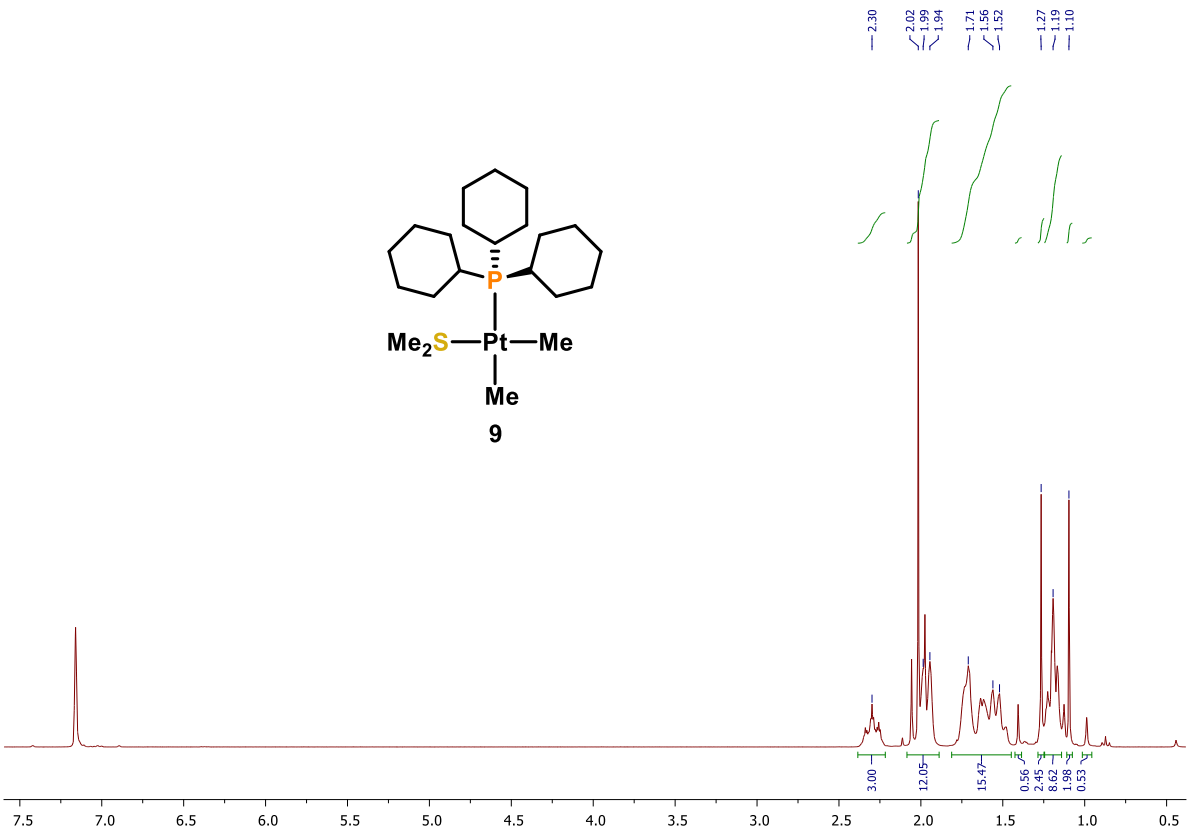


Figure S40: 9, ^{1}H (C_6D_6, 300 MHz, 25 °C)

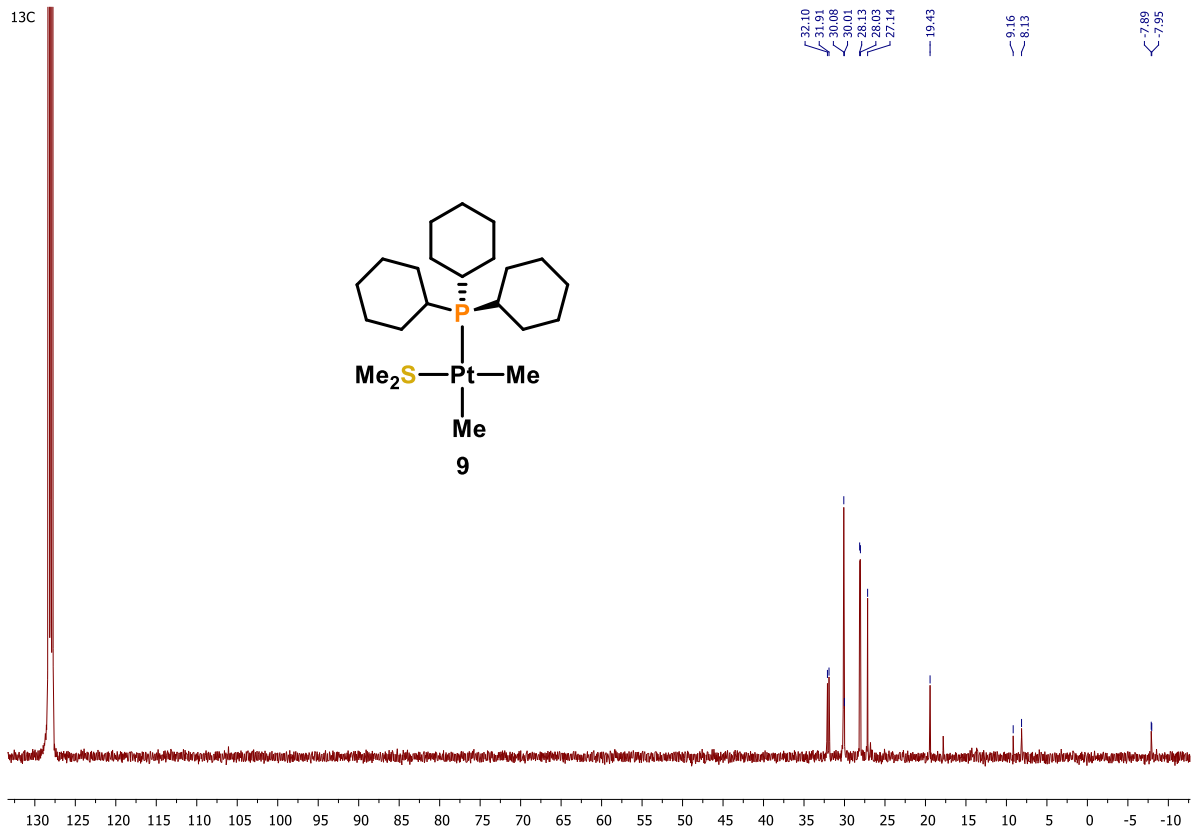


Figure S41: 9, $^{13}C\{^{1}H\}$ (C_6D_6, 100 MHz, 25 °C)

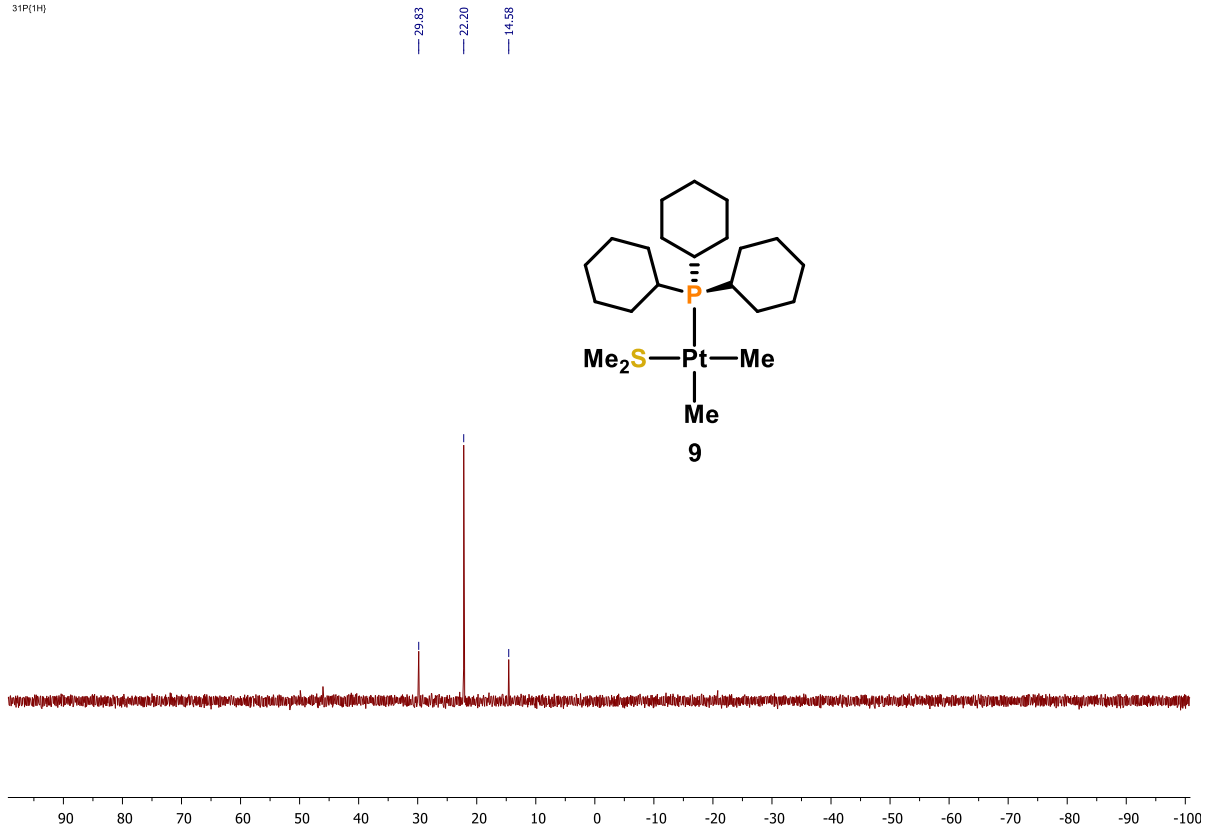


Figure S42: 9, $^{31}P\{^{1}H\}$ (C_6D_6, 121 MHz, 25 °C)

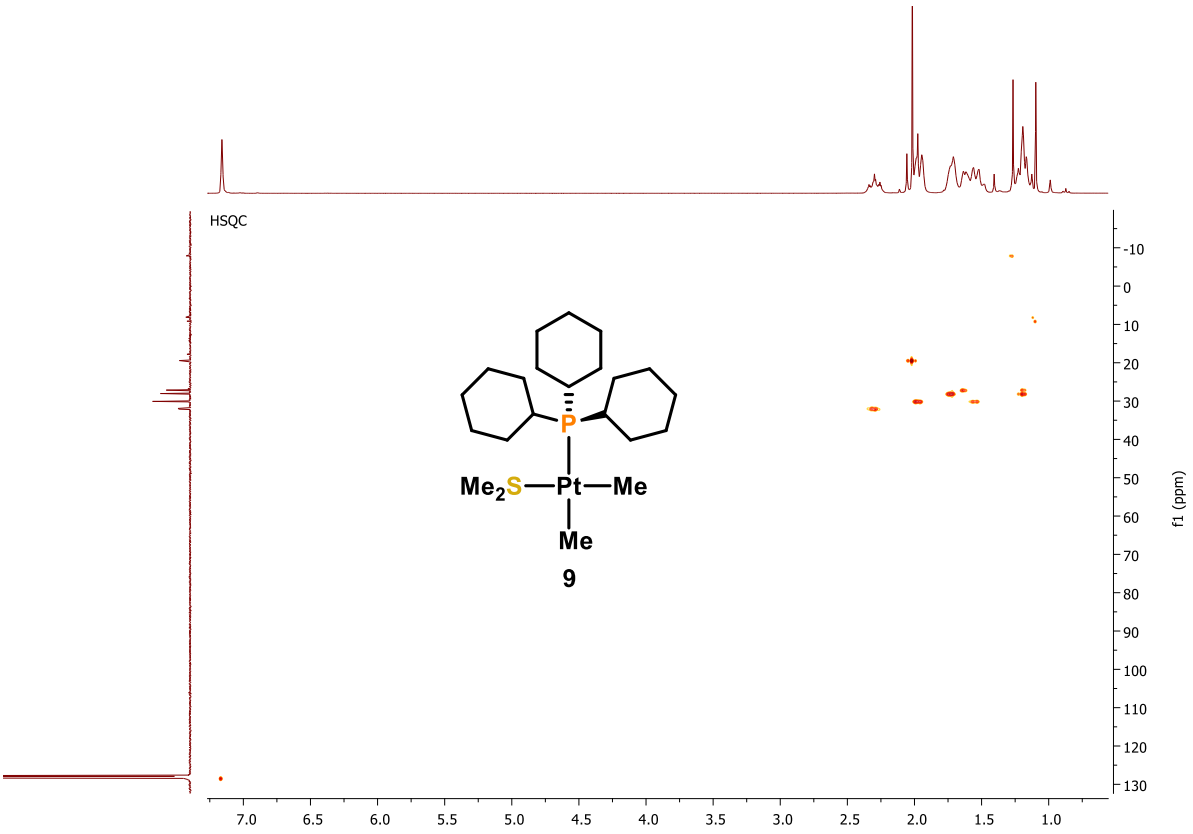


Figure S43: 9, HSQC (C_6D_6, 300/100 MHz, 25 °C)

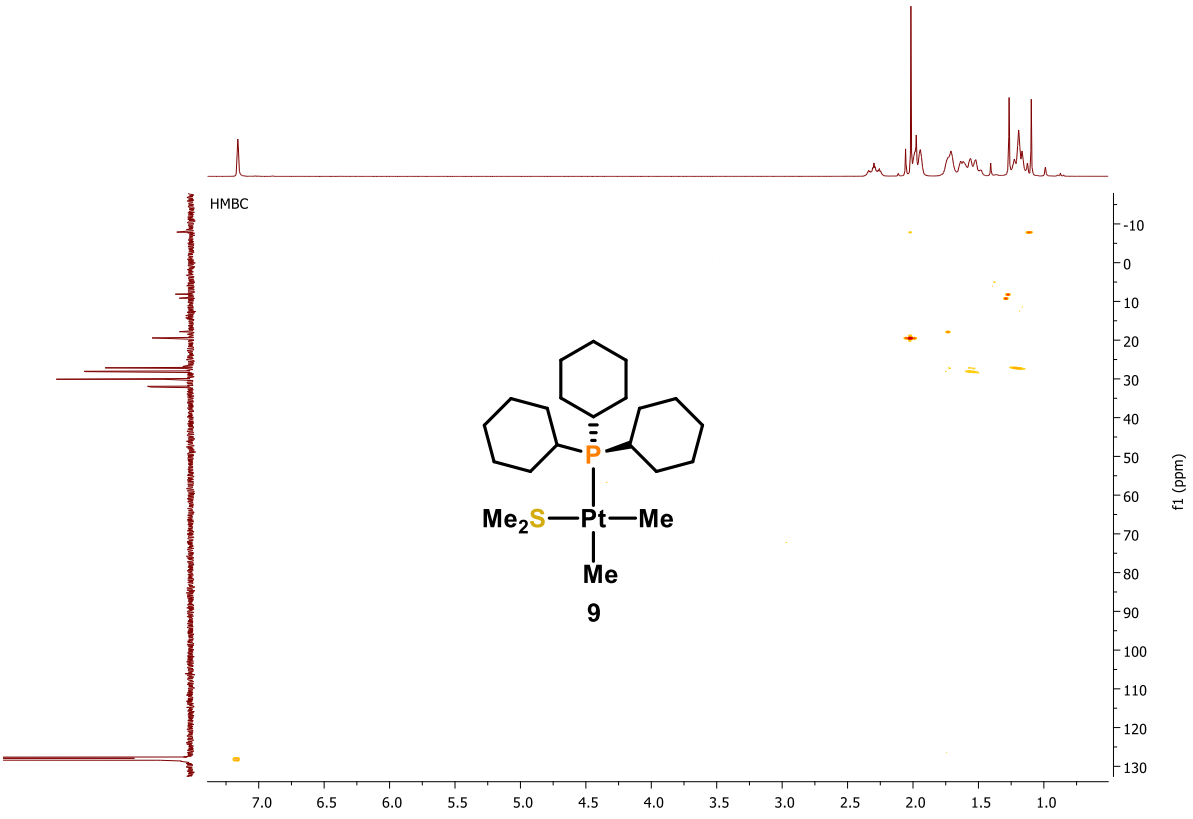


Figure S44: 9, ^{1}H-^{13}C HMBC (C_6D_6, 300/100 MHz, 25 °C)

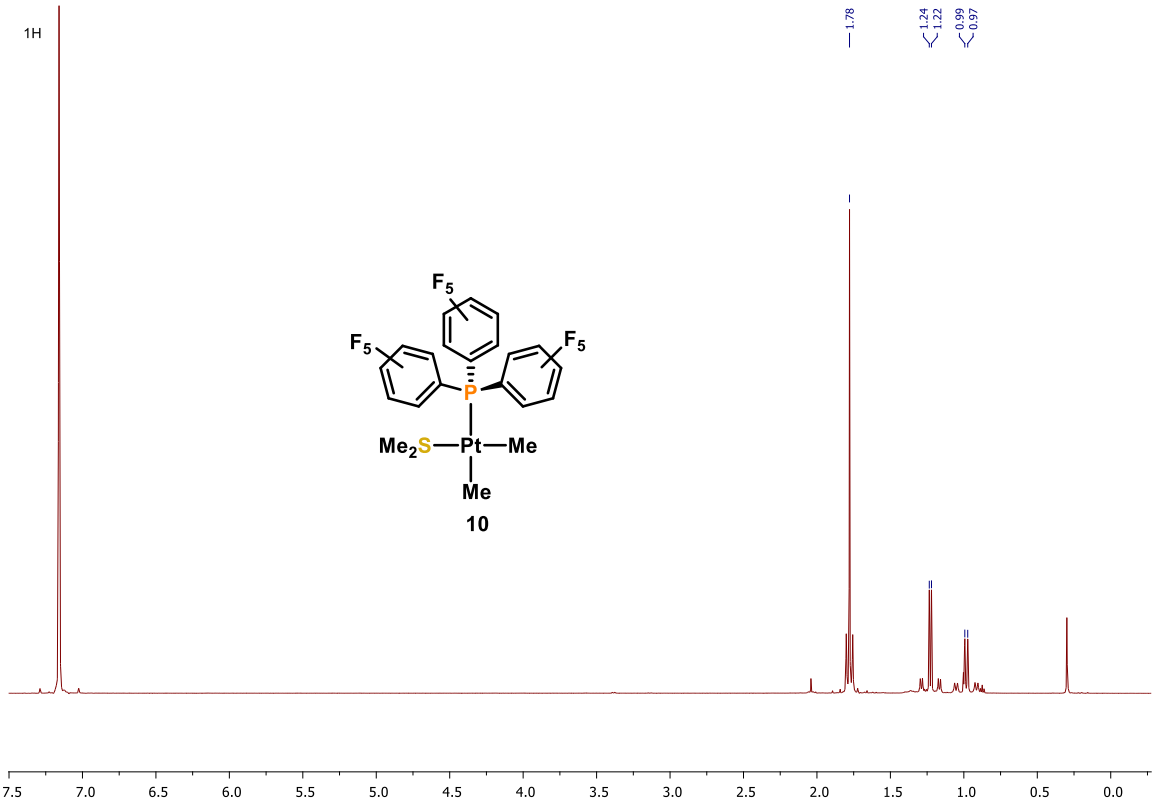


Figure S45: 10, ^{1}H NMR (C_6D_6, 600 MHz, 25 °C)

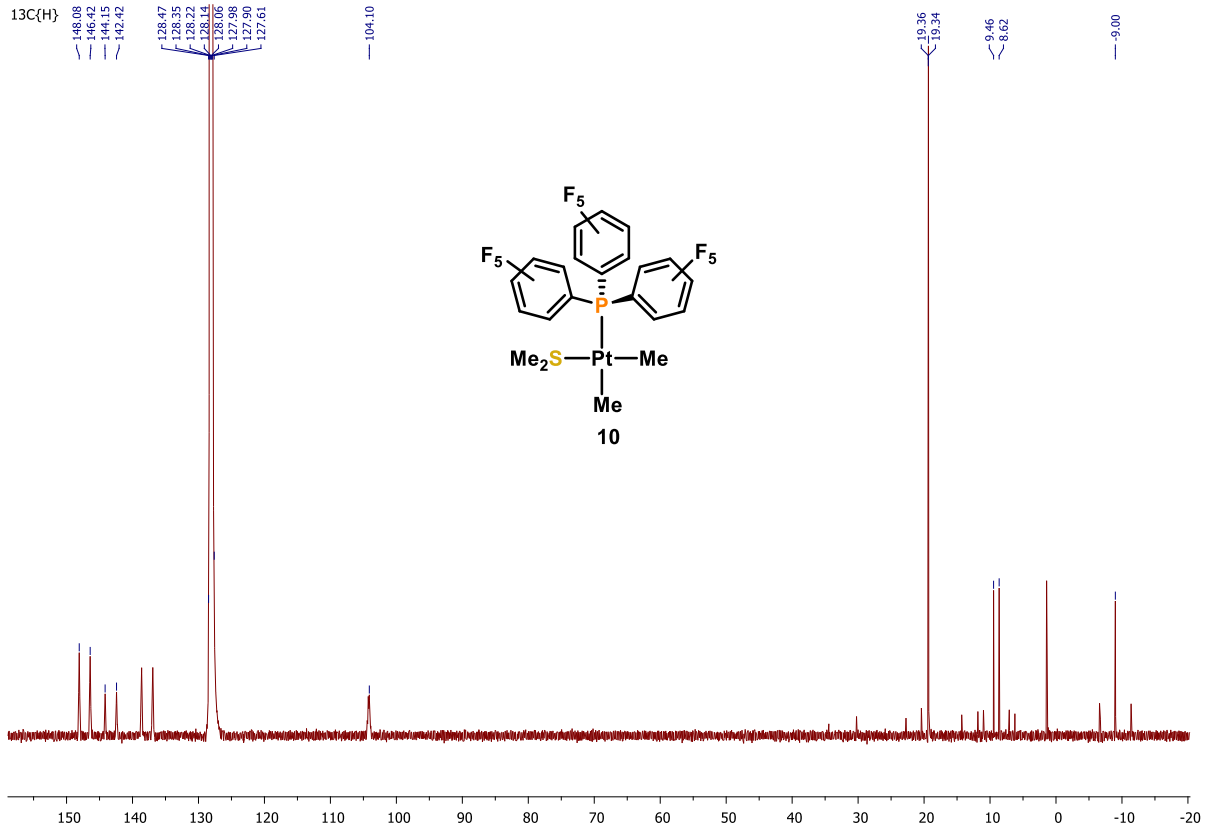


Figure S46: 10, $^{13}C\{^{1}H\}$ (C_6D_6, 150 MHz, 25 °C)

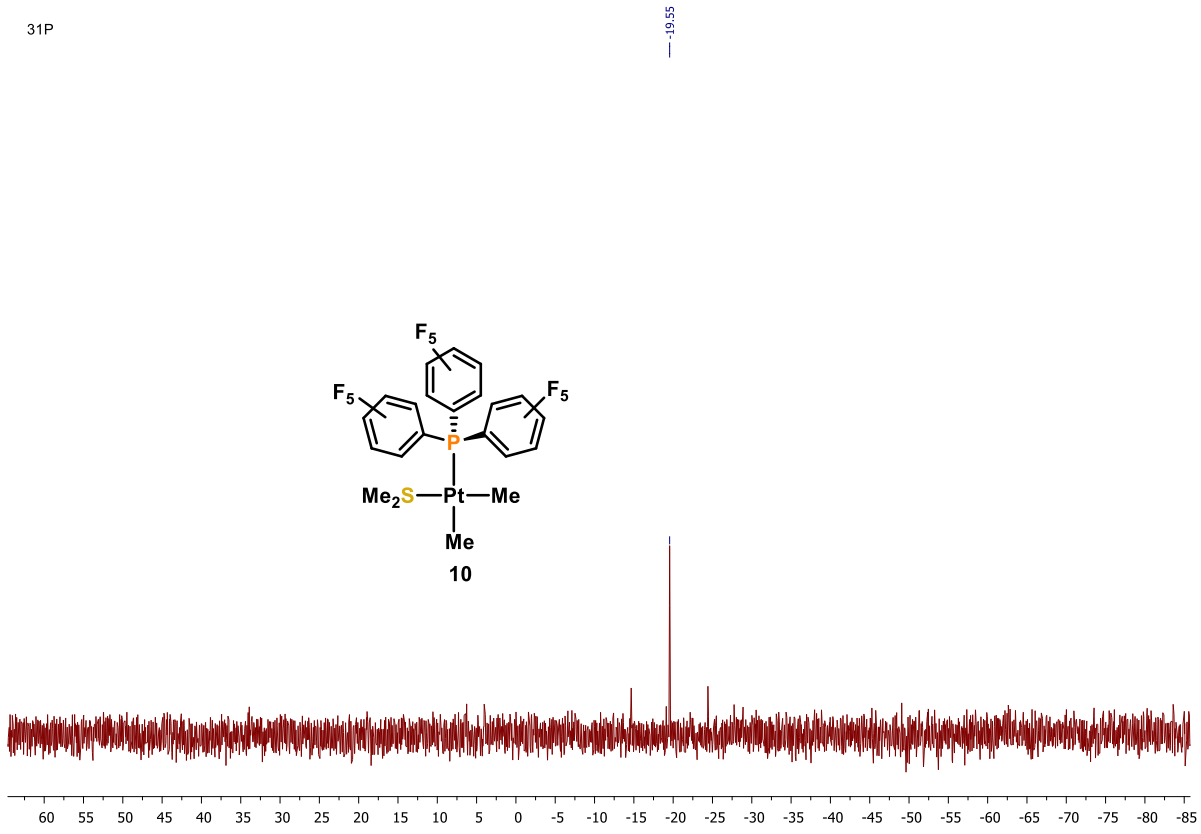


Figure S47: 10, ^{31}P (C_6D_6, 162 MHz, 25 °C)

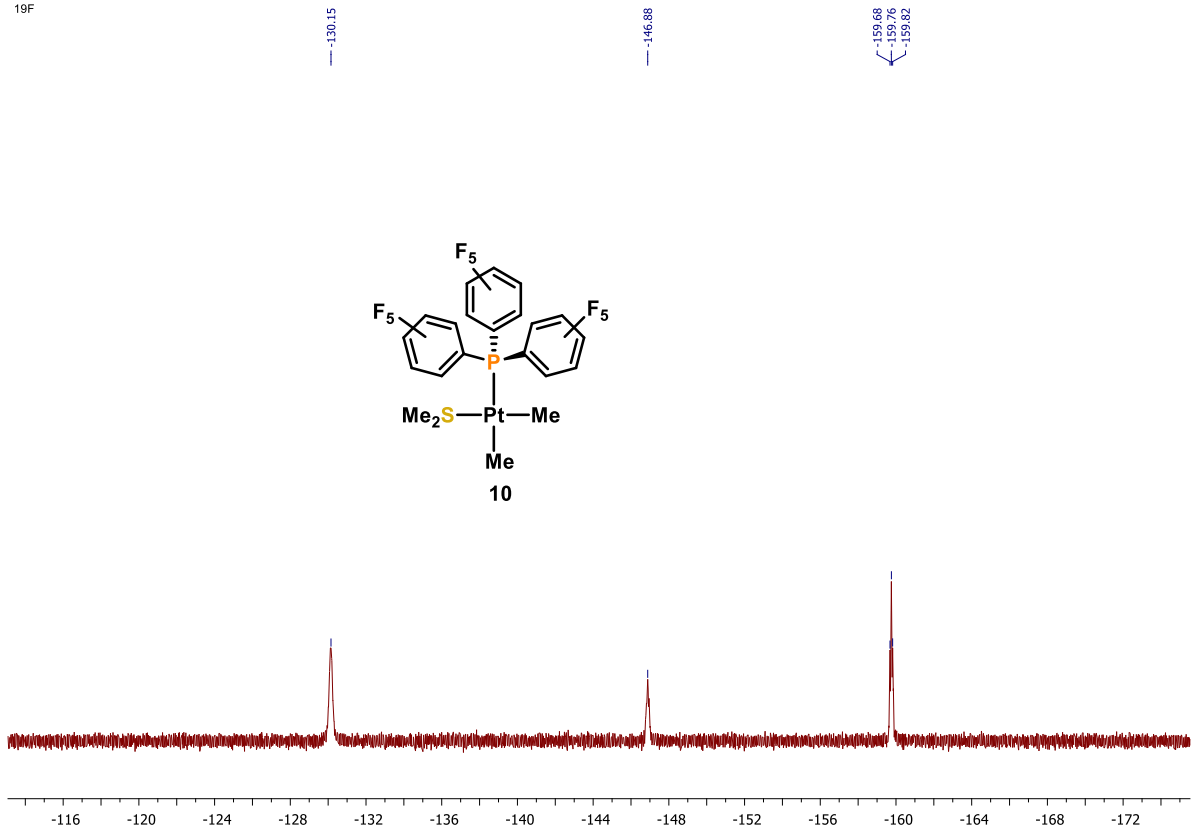


Figure S48: 10, ^{19}F (C_6D_6, 282 MHz, 25 °C)

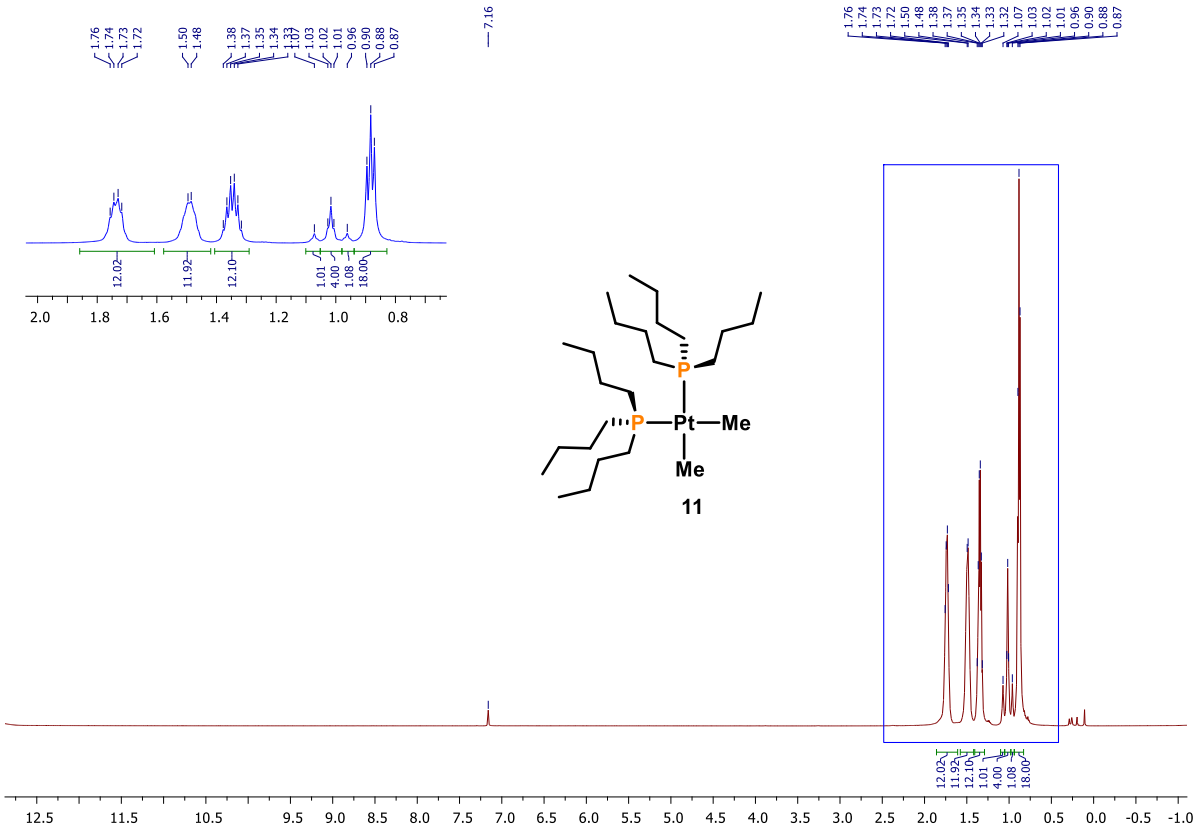


Figure S49: 11, ^{1}H (C_6D_6, 600 MHz, 25 °C)

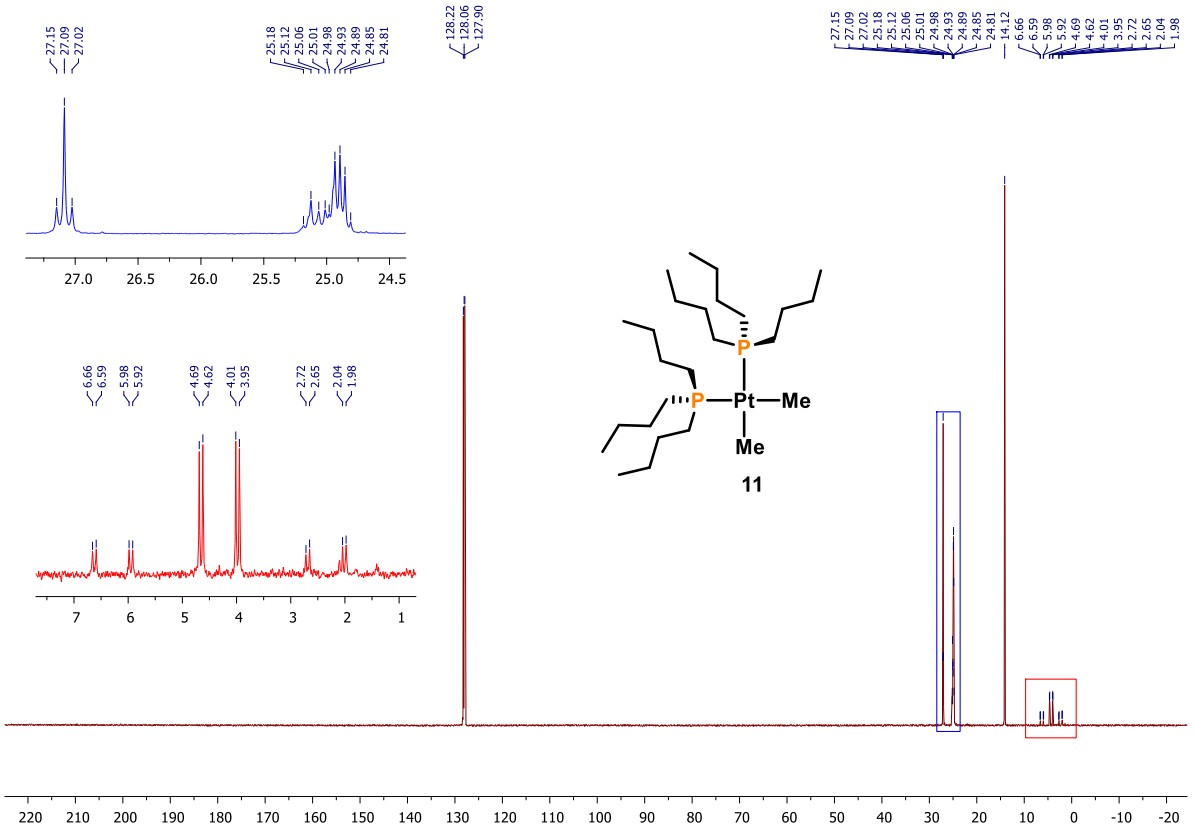


Figure S50: 11, $^{13}C\{^{1}H\}$ NMR (C_6D_6, 150 MHz, 25 °C)

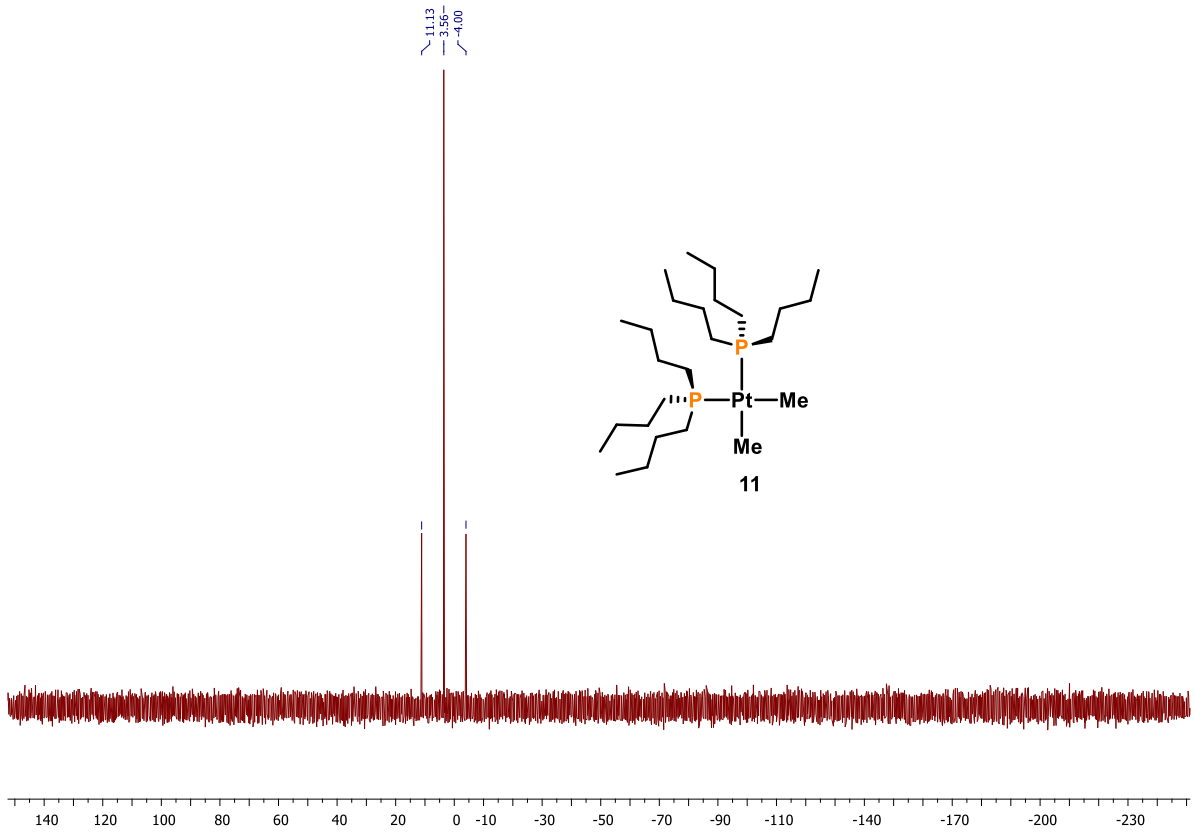


Figure S51: 11, $^{31}P\{^{1}H\}$ NMR (C_6D_6, 121 MHz, 25 °C)

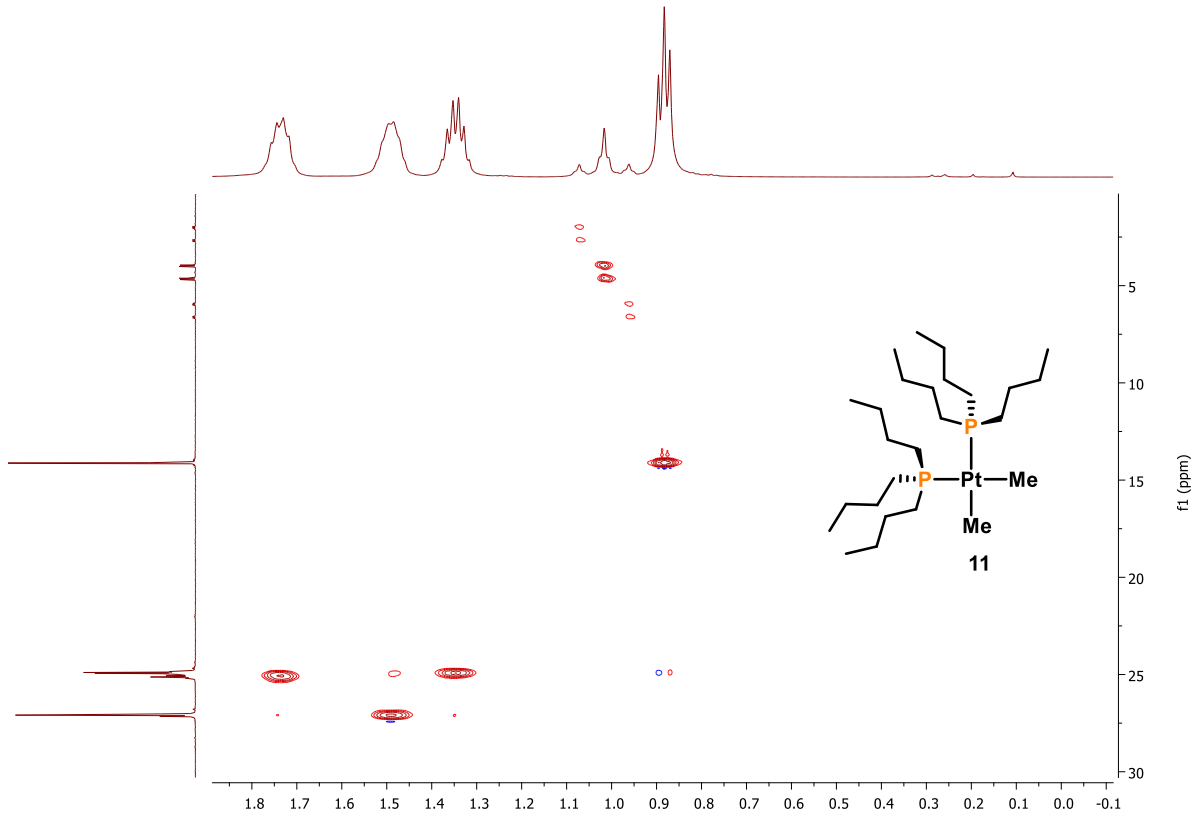


Figure S52: 11, HSQC, (C_6D_6, 600/150 MHz, 25 °C)

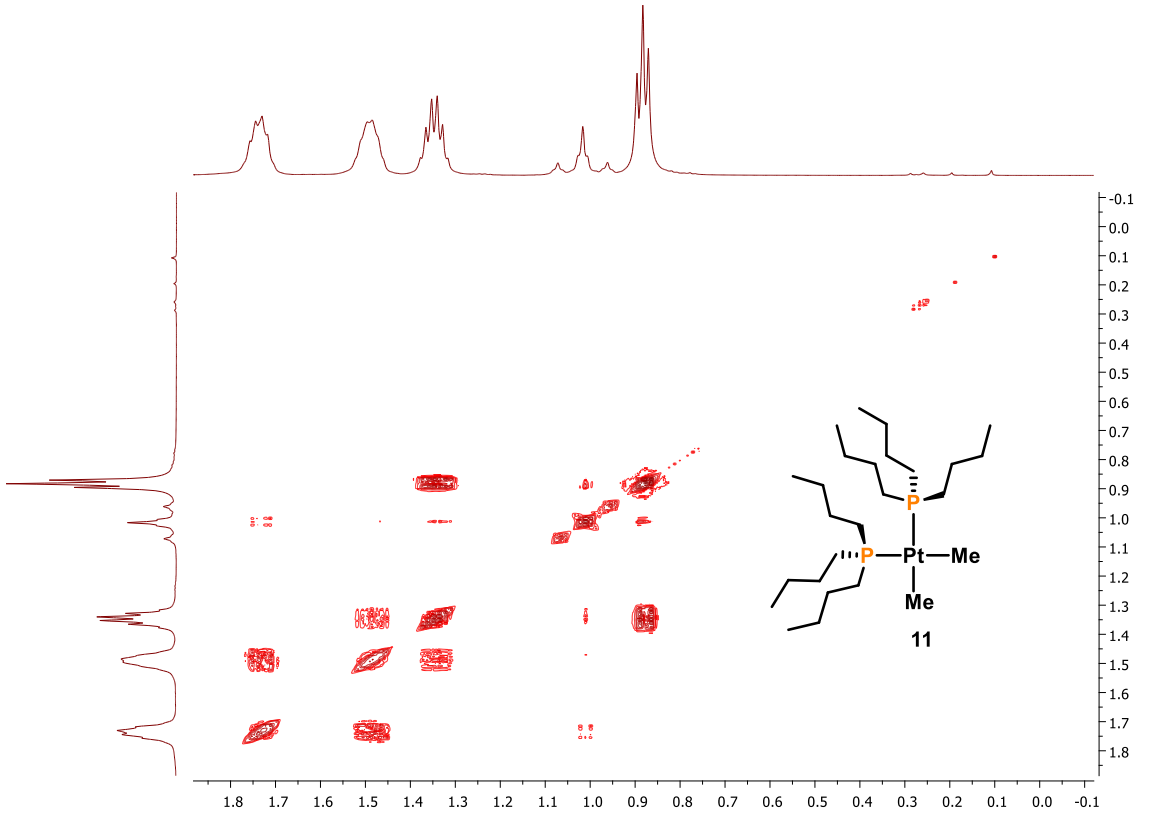


Figure S53: **11**, COSY (400 MHz, C_6D_6, 25 °C)

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3. In situ reactivity studies

A. Identification of Pt(II) complexes from the reaction mixture.

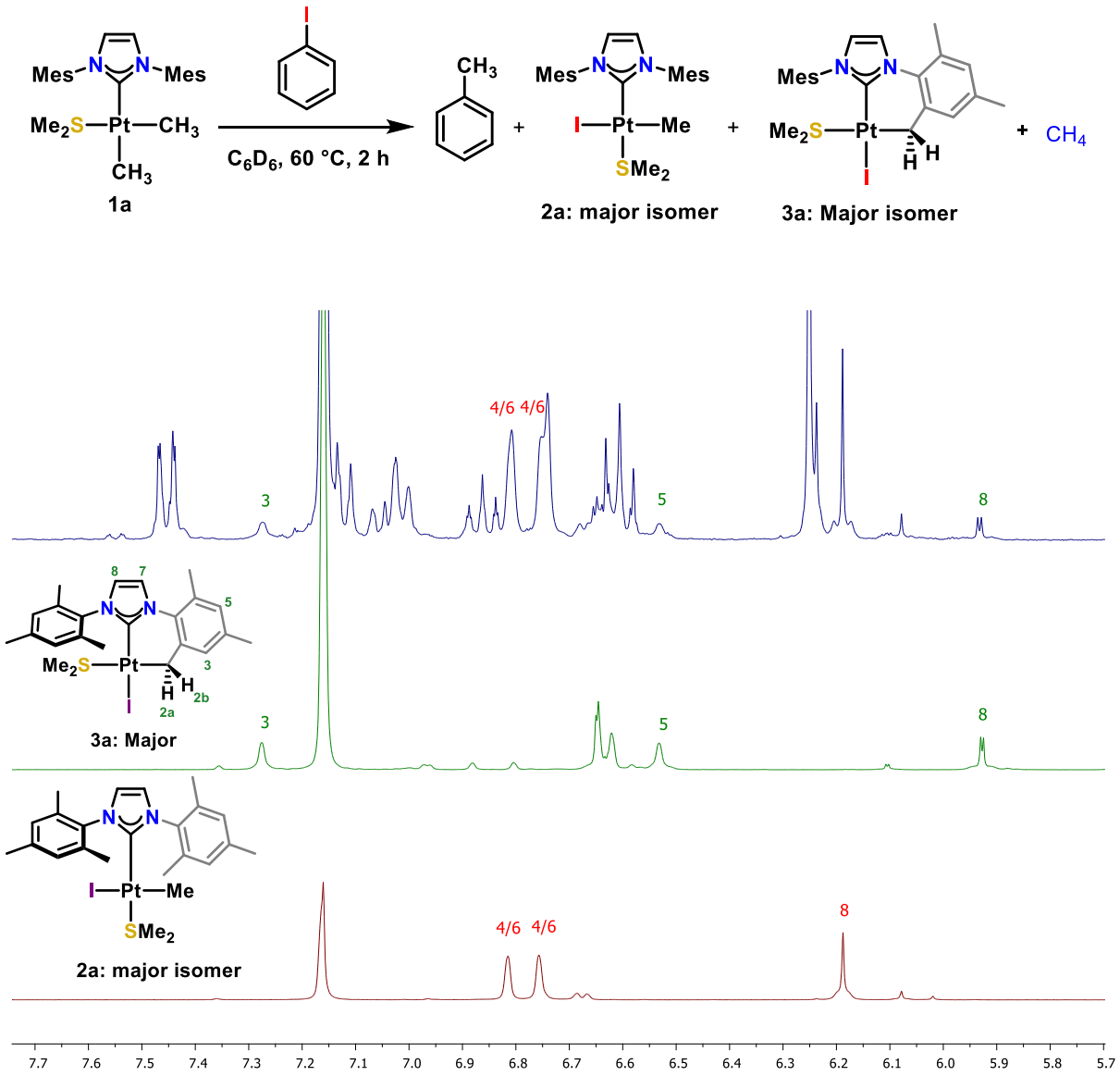


Figure S54: Stacked ^{1}H NMR ($C^{6}D^{6}$, 400 MHz, 25 °C) of 1a with PhI after two hours at 60 °C (top/blue) and independently synthesised complexes 1a' (middle/green) and 2a (bottom/red) to show the formation of the platinum complexes during the reaction (Aromatic region shown).

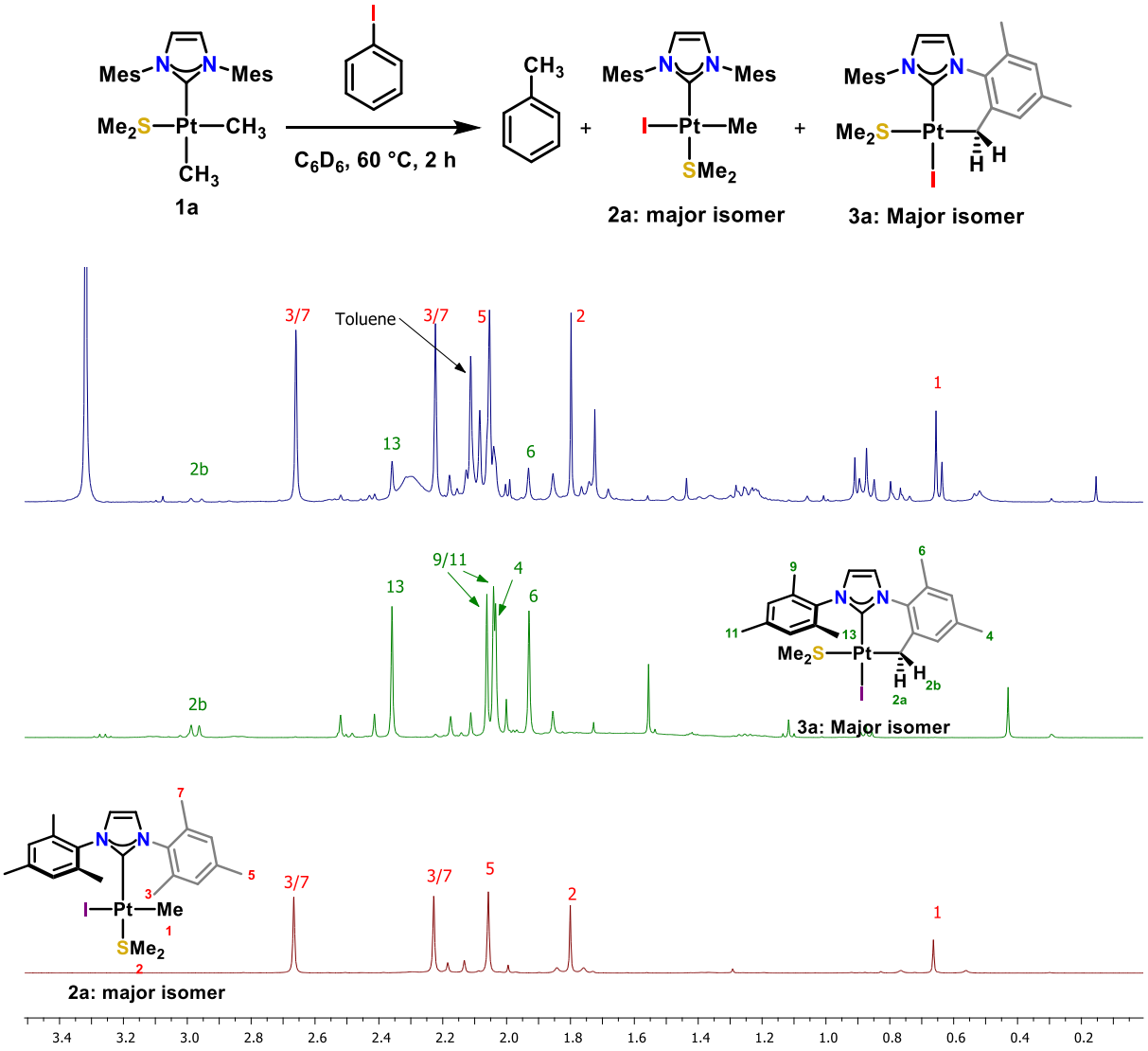


Figure S55: Stacked ^{1}H NMR (C_6D_6, 400 MHz, 25 °C) of **1a** with PhI after two hours at 60 °C (top/blue) and independently synthesised complexes **1a'** (middle/green) and **2a** (bottom/red) to show the formation of the platinum complexes during the reaction (aliphatic region shown).

B. Isotopic labelling experiment with PhI-d_5 showing the origin of toluene.

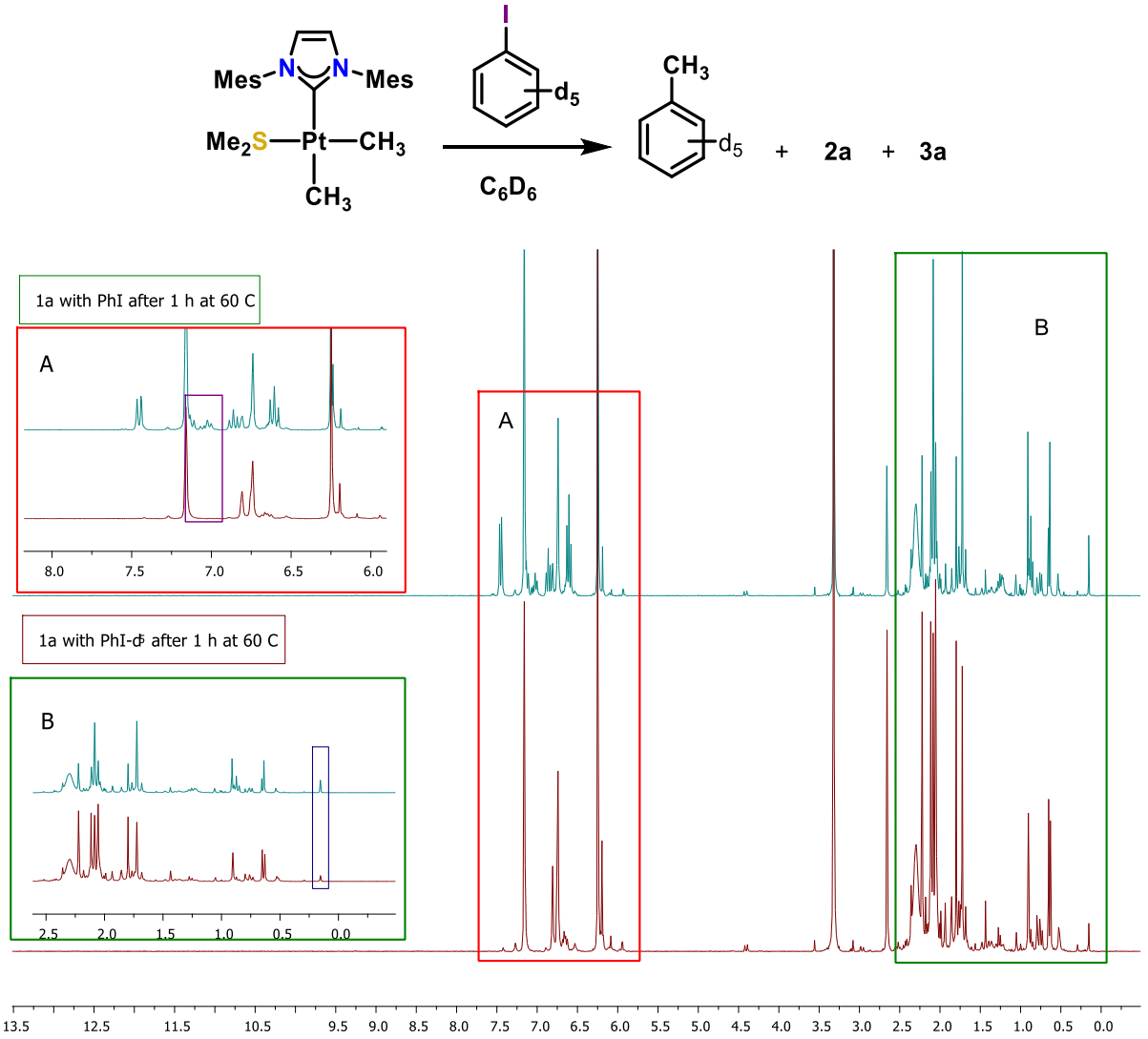


Figure S56: Deuterium labelling experiment showing the formation of complex 2a (red box) and complex 3a (blue box) from the reaction of 1a and deuterated phenyl iodide (^{1}H NMR, C_6D_6, 300 MHz, 25 °C).

Additional discussion (Figure S53):

The reaction between **1a** and PhI-d_5 produces toluene-d_5 and complexes **2a** and **3a**. However, the aromatic signals corresponding to toluene are no longer visible in the experiment with PhI-d_5 (inset **A**). Furthermore, the detection of methane (0.15ppm) in the NMR tube of both experiments (inset **B**) along with the diagnostic doublets at 4.5 ppm provide the evidence for the formation of **3a**. Isotopic labelling of the aryl halide has thus provided evidence that toluene formation is a direct result of the OA of PhI and not from the solvent.

C. Reactivity of 1a' with phenyl bromide.

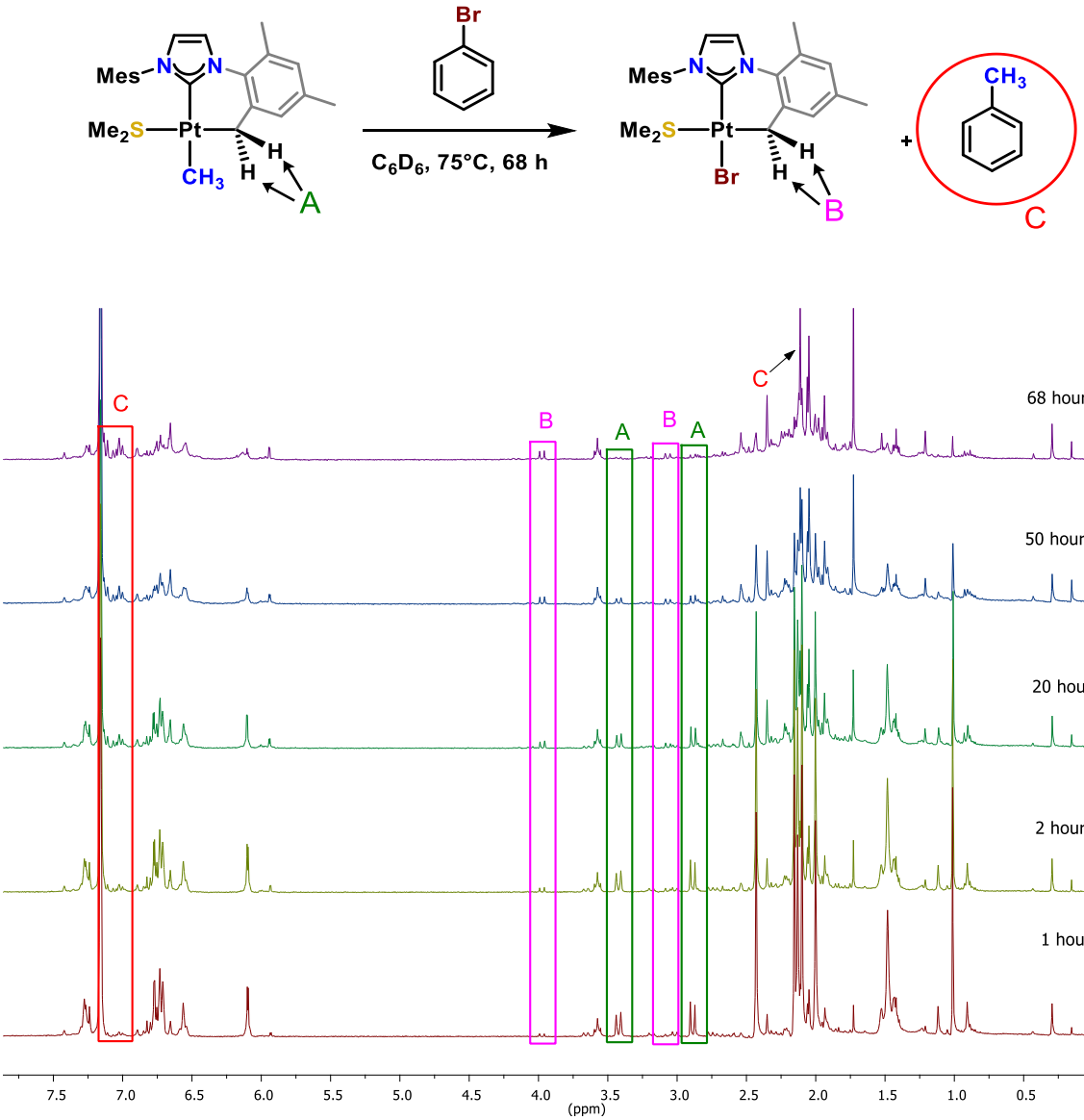
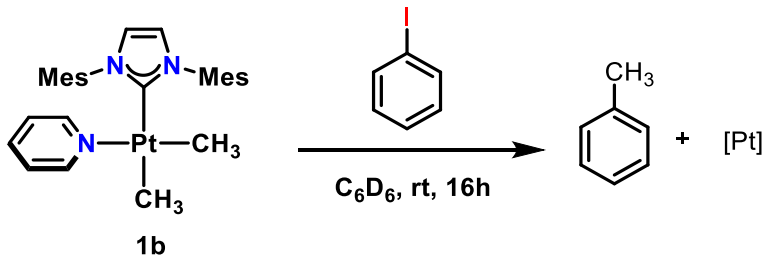


Figure S57: ^{1}H NMR (C_6D_6, 300 MHz, 25 °C) analysis of **1a'** with PhBr at 75°C

Additional discussion (Figure S54):

Complex **1a'** (Green box (**A**)) and PhBr were reacted at 75°C, and ^{1}H NMR data was recorded at certain time intervals. In the above Figure, each spectrum over the course of 68 hours is stacked with the relevant product peaks being highlighted (pink box (**B**) = **3a-Br** methylene protons; red box (**C**) = toluene). Formation of both toluene and **3a-Br** is evidenced by diagnostic shifts at 4.00 and 3.20 ppm. However, continued heating at 75°C results decomposition of the starting material. Better results were obtained by using an excess of phenyl bromide (37%; toluene and **3a-Br** after 16 h at 60°C) and decreasing the temperature to 60°C.

D. Reactivity of PhI with 1b at different temperatures and the identification of isolated Pt(II)-pyridine products during the reaction.



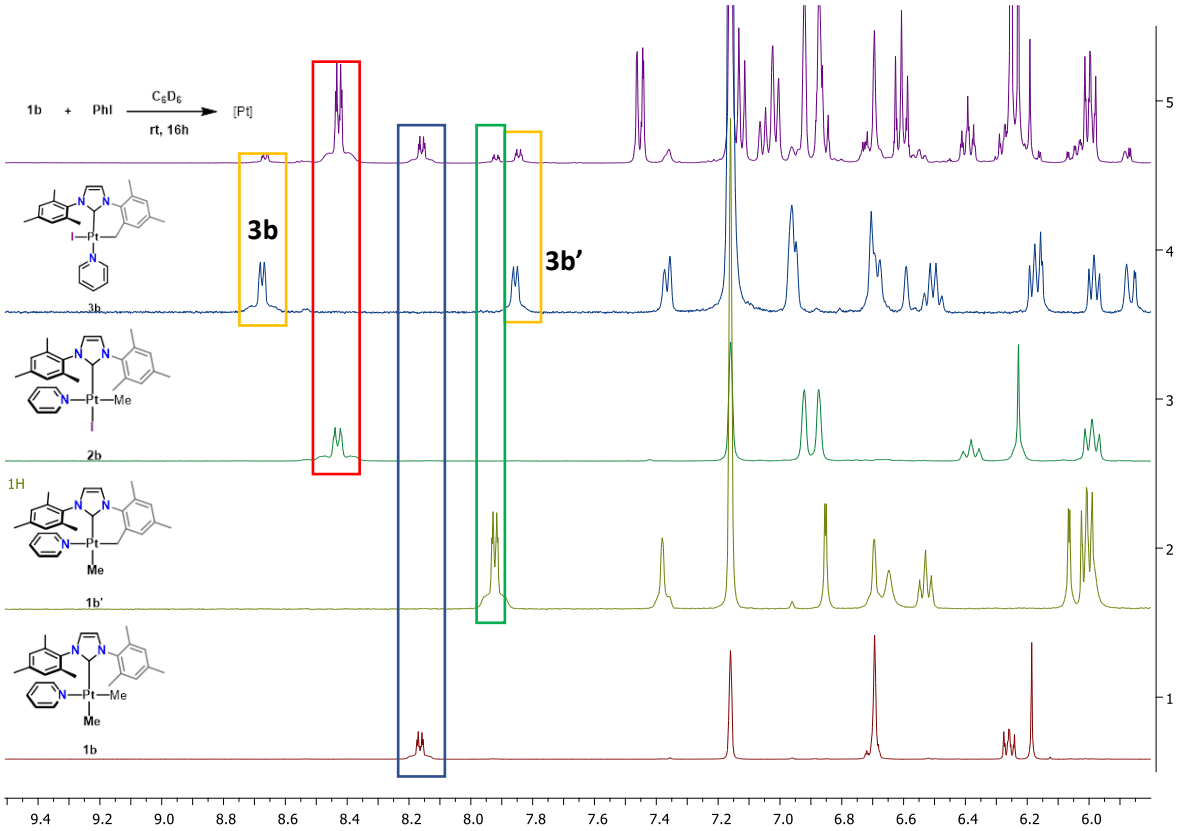


Figure S58: ^{1}H NMR (C_6D_6, 400 MHz, 25°C) of reaction mixture after 16 h between **1b** and PhI at rt and comparison of aromatic regions with isolated complexes.

Additional discussion (Figure S55):

The Figure above shows the reaction between **1b** and PhI at room temperature after 16 h (spectrum 5, purple). The remaining stacked spectra are of each independently synthesised complex discussed in the main text. the pyridine analogues were favoured compared to the SMe_2 analogue, due to the unique chemical shifts of the *ortho*-pyridine protons. This allowed us to systematically follow reactions by ^{1}H NMR and confidently identify which species were present. Furthermore, the reaction shown above is good evidence that both OA of phenyl iodide as well as C-H activation of the NHC mesityl methyl occurs during the reaction. **3b** and **3b'** are isomers whereby the pyridine is either trans to the NHC (**3b**) or trans to the methylene (**3b'**), this was confirmed by a NOSEY experiment see Figure **S35** for NOESY spectrum.

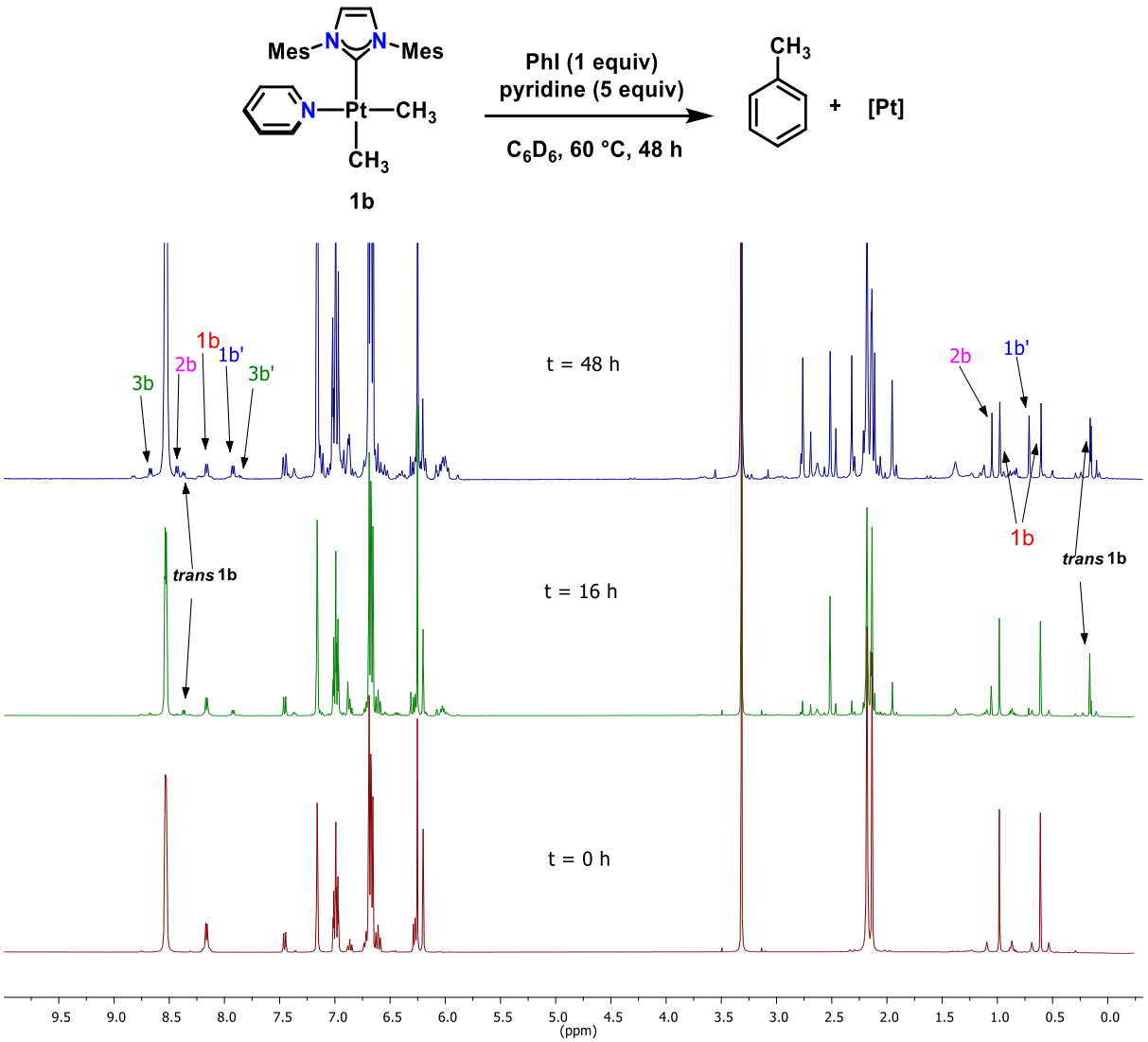


Figure S59: Stacked ^{1}H NMR (C_6D_6, 300 MHz, 25 °C) reaction of **1b** with PhI and excess pyridine at 60 °C for 48 h.

Additional discussion (Figure S56):

Addition of excess pyridine to the reaction resulted in a significant inhibition in efficacy. Furthermore, a peak at 0.25ppm is observed that has characteristic Pt(IV)-C*H*$_3$ coupling ($^{2}J_{Pt\text{-}H}$= 48 Hz). Addition of $AgBF_4$ did not generate the expected spike in toluene or ethane that would result from abstraction of the halide from a Pt(IV) octahedral intermediate. A ^{1}H NMR spectrum was obtained, precluding identification of species present. Due to the lack of aromatic Pt-C*H* coupling, a Pt(IV) species was ruled out and the *trans* isomer of **1b** was proposed instead. We were not able to confirm the signals as the trans isomer, as isolation of this species was non-trivial.

4. Reactivity of simple $L_2Pt(II)$ complexes with PhI.

A. Replication of Kistner example, OA of PhI with Pt(*o*-tolyl)$_2$(py).

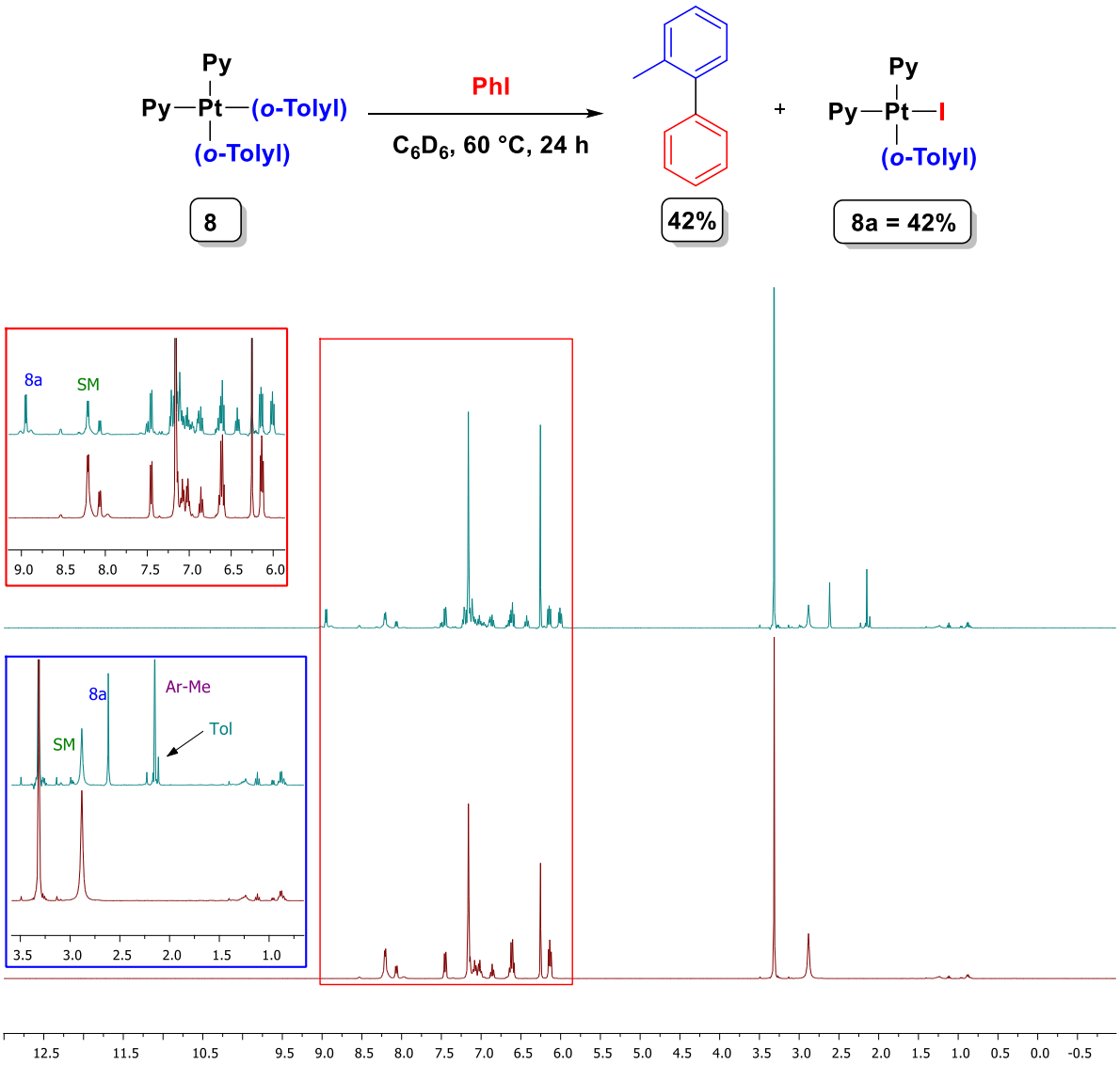


Figure S60: ^{1}H NMR (C_6D_6, 400 MHz, 25 °C) of Repeat of Kistner example, OA of PhI to Pt(II) diaryl species.

Additional discussion (Figure S62):

The reaction conditions disclosed by Kistner *et al*. in their report from 1967,[8] "Reacting Pt(*o*-tolyl)$_2$(pyridine)$_2$ (300 mg) in neat iodobenzene (7 mL) for 6 days", left us questioning whether generation of the resultant PtI(*o*-tolyl)(pyridine)$_2$ complex could have arisen from formation of iodine/iodide. After all, no discussion of the reaction or the organic products was given by the authors. With a large volume of phenyl iodide being left for 6 days in light, generation of a variety of iodine and iodide species may have been responsible for the resultant products. Never the less, repeating the experiment in a stoichiometric fashion in C_6D_6 at 60 °C showed the formation of new methyl signals corresponding to 2-methylbiphenyl (2.14 ppm, green/top spectrum). New Pt-py signals (9.0, 6.4 and 6 ppm) were also observed, which integrated well with respect to the methyl resonances in the sp^3 region.

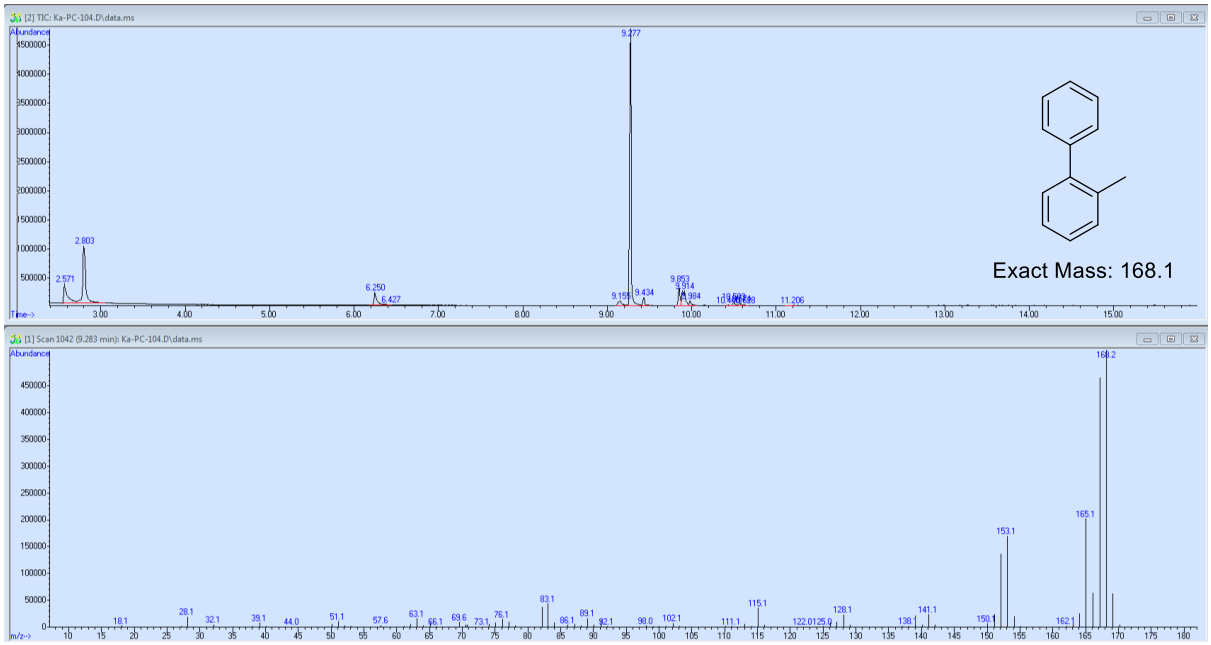


Figure S61: GCMS (EI) chromatogram showing the mass values for the signal at 9.283 minutes.

Additional discussion (Figure S65):

The GCMS trace shows the most intense signal to have a retention time of 9.283 minutes. The EI mass spectrum shows the base peak to have a m/z value of 168.2 and good agreement with the calculated mass of 2-methylbiphenyl (168.1). The data acquired from ^{1}H NMR and GCMS shows good evidence for oxidative addition of PhI to **8**.

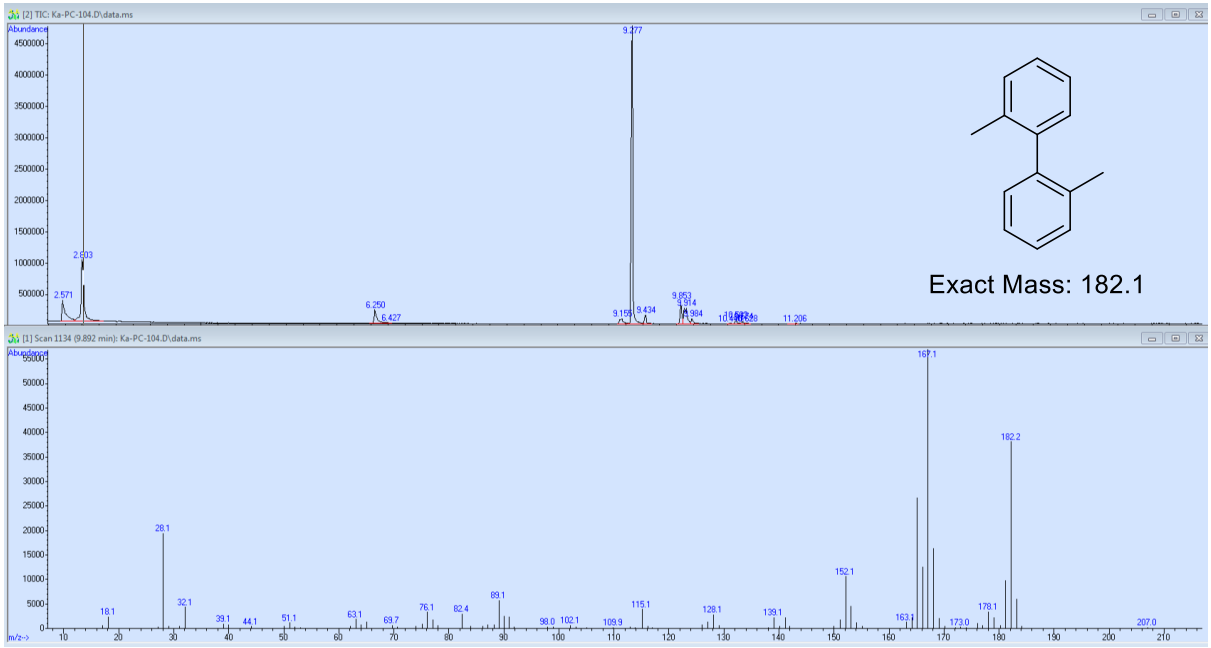


Figure S62: GCMS (EI) chromatogram showing the mass values for the signal at 9.892 minutes.

Additional discussion (Figure S66):

A much less intense signal at 9.892 minutes revealed a mass of 182.2 which is good agreement with the mass of 2,2'-dimethyl-1,1'-biphenyl (182.1). The observation of this mass is good evidence that the oxidative addition of PhI to **8** can also result in the coupling of the two *o*-Tolyl groups.

B. Complex 9 with PhI and *in situ* analysis.

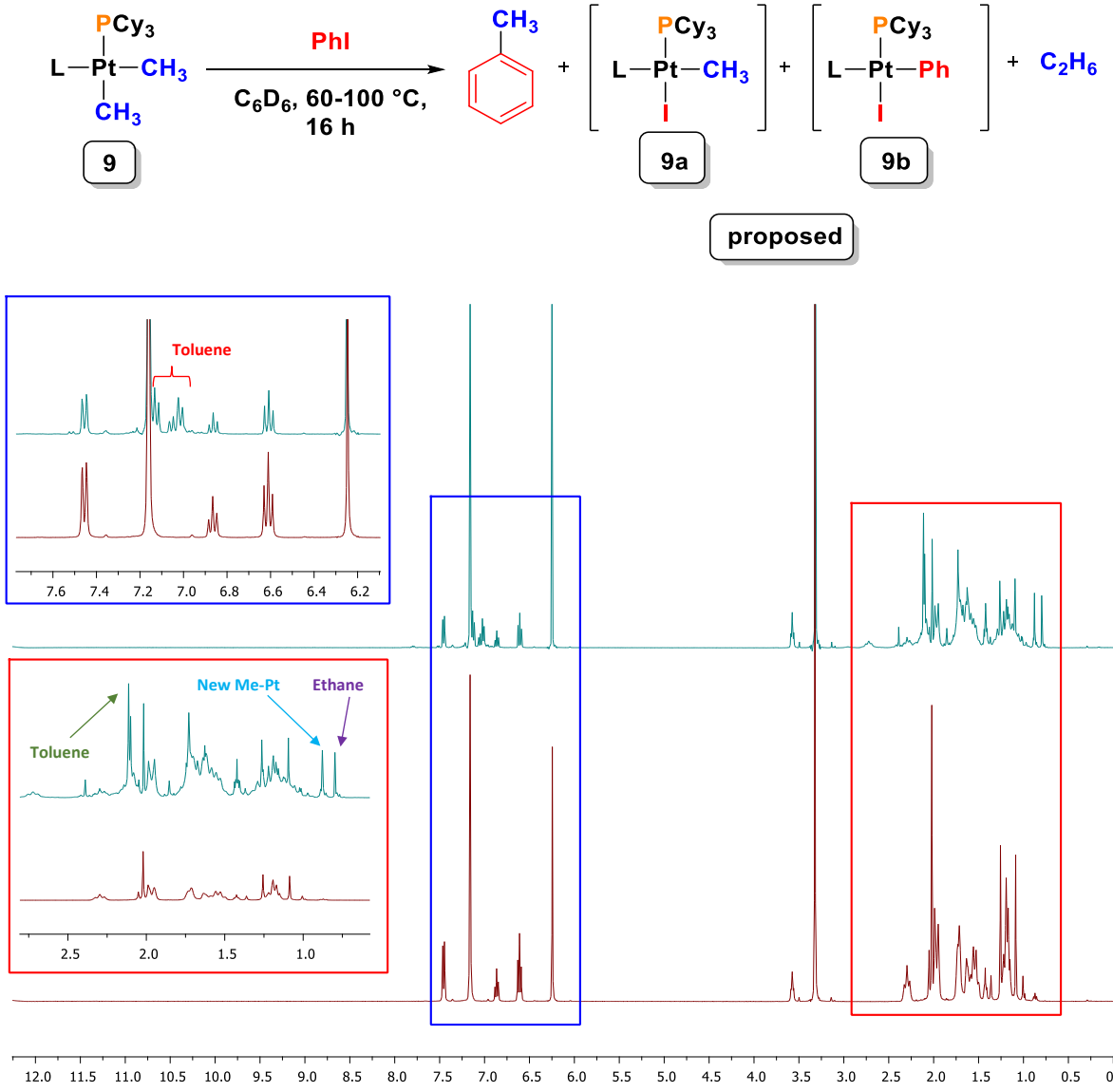


Figure S63: Stacked ^{1}H NMR (400 MHz, C_6D_6, 25 °C) of the reaction between complex **9** and PhI at 60 °C. bottom spectrum of stack shows the reaction mixture before heating. Top spectrum of stack shows the reaction mixture after heating at 100 °C for 16 h.

Additional discussion (Figure S57):

The reaction of PhI with complex **9** is slow but produces toluene (49%), ethane and new Pt species. Starting material is still observed in both the $^{1}H\{^{31}P\}$ and $^{31}P\{^{1}H\}$ NMR suggesting that longer reaction lengths are required when only one equivalent of phenyl iodide is used. Ethane was the only gaseous product observed in significant amount, a trace amount of methane was also observed. Methane could be due to protonation from adventitious water in the solvent or from C-H activation of ethane. A new methyl-Pt signal is observed which shows Pt-H coupling, $^{2}J_{Pt\text{-}H}$= 75 Hz, consistent with a Pt(II) methyl (satellites buried in ^{1}H NMR but were elucidated from 2D NOESY). The coupling constant is halfway between those exhibited by both methyl's from **9** (66 Hz and 83 Hz), this change can be attributed to the addition of an iodide atom and the $^{31}P\{^{1}H\}$ NMR confirms a Pt-P signal with a coupling constant of 3920 Hz consistent with an iodine atom trans to a phosphine.

Structure **9b** is invoked due to the presence of ethane in the ^{1}H NMR, although, the only signal that suggests this structure is an aromatic resonance (7.55 ppm) observed as doublet with Pt satellites ($^{3}J_{Pt\text{-}H}$= 54 Hz). When PhI is not included in the reaction, no change in either ^{31}P or ^{1}H NMR is observed therefore ruling out formation of **9b** via OA to a Pt(0) species.

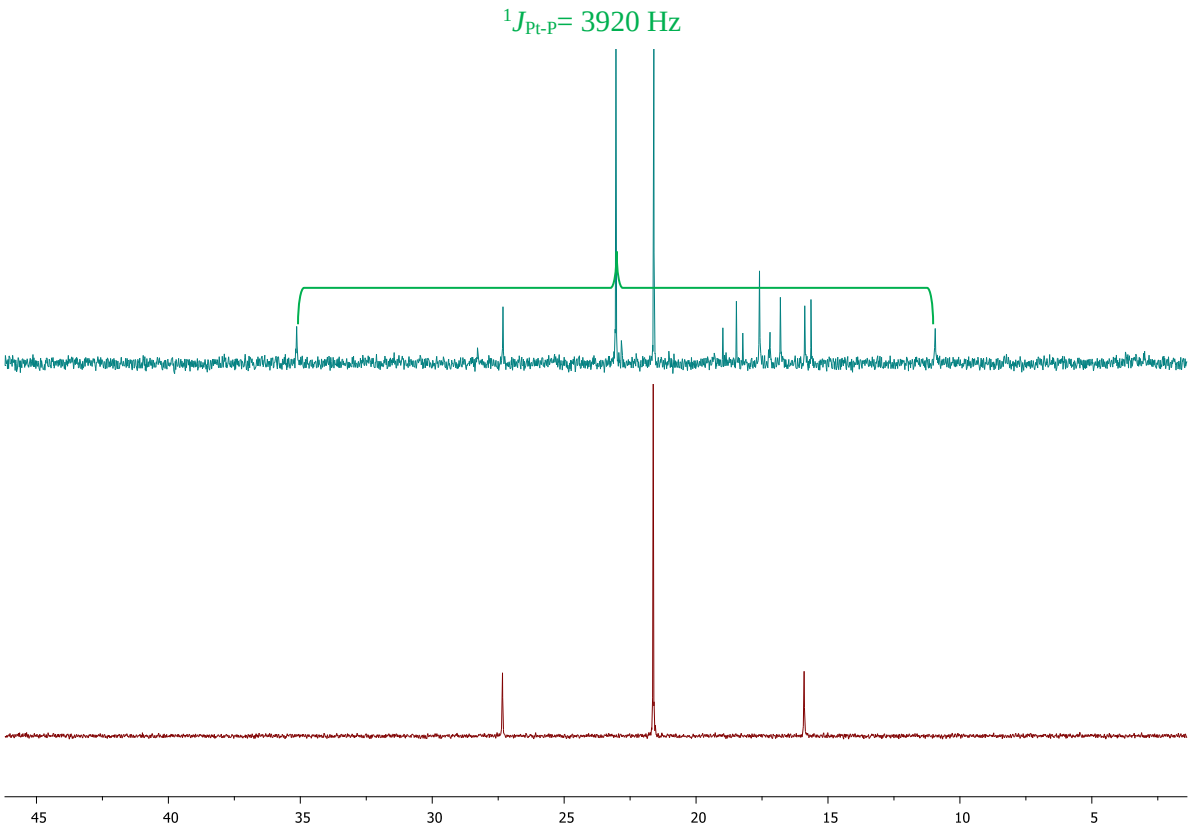


Figure S64: Stacked $^{31}P\{^1H\}$ NMR of reaction between PhI and complex **9**. Bottom spectrum shows reaction mixture before heating. Top spectrum shows reaction mixture after 16 h heating at 100 °C.

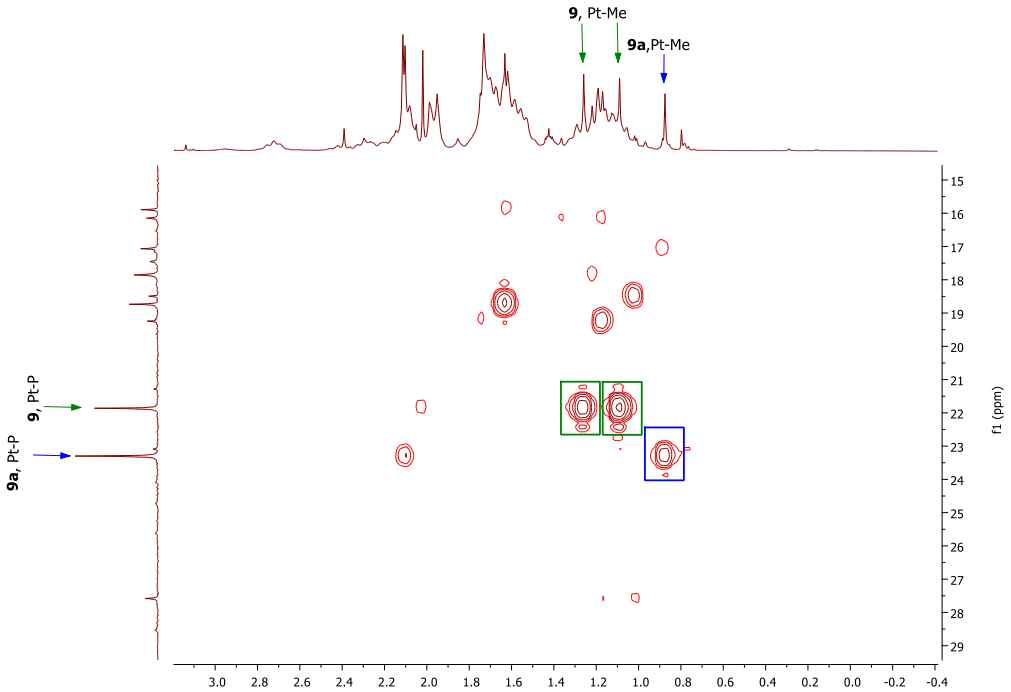
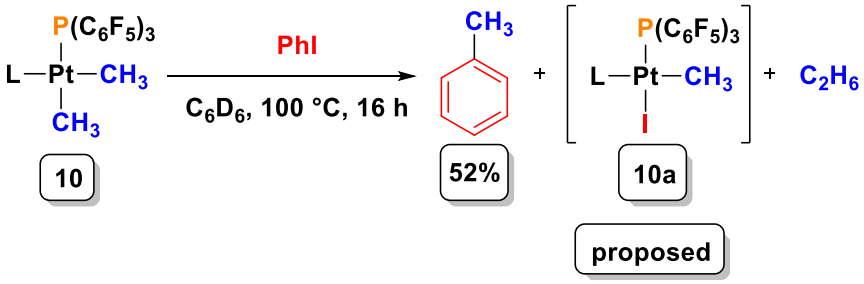


Figure S65: ^{31}P-^1H HMBC (400/160 MHz, C_6D_6, 25 °C) showing the $^3J_{P-H}$ coupling between methyl and phosphine ligands. The phosphorus signal with the Pt-P coupling constant of 3920 Hz observes correlation to the new methyl peak observed in the ^1H NMR spectrum (vide supra).

Addition discussion (Figure S58 & S59):

Several new peaks are observable in the ^{31}P NMR spectrum, however, the signal at 23 ppm shows large Pt-P (3920 Hz) coupling consistent with a weak *trans* influence ligand *trans* to the phosphine. Furthermore, ^{31}P-^{1}H HMBC shows the expected correlation between the phosphine ligand and the methyl group expected for the structure of **9a.**

C. Complex 10 with PhI and *in-situ* analysis



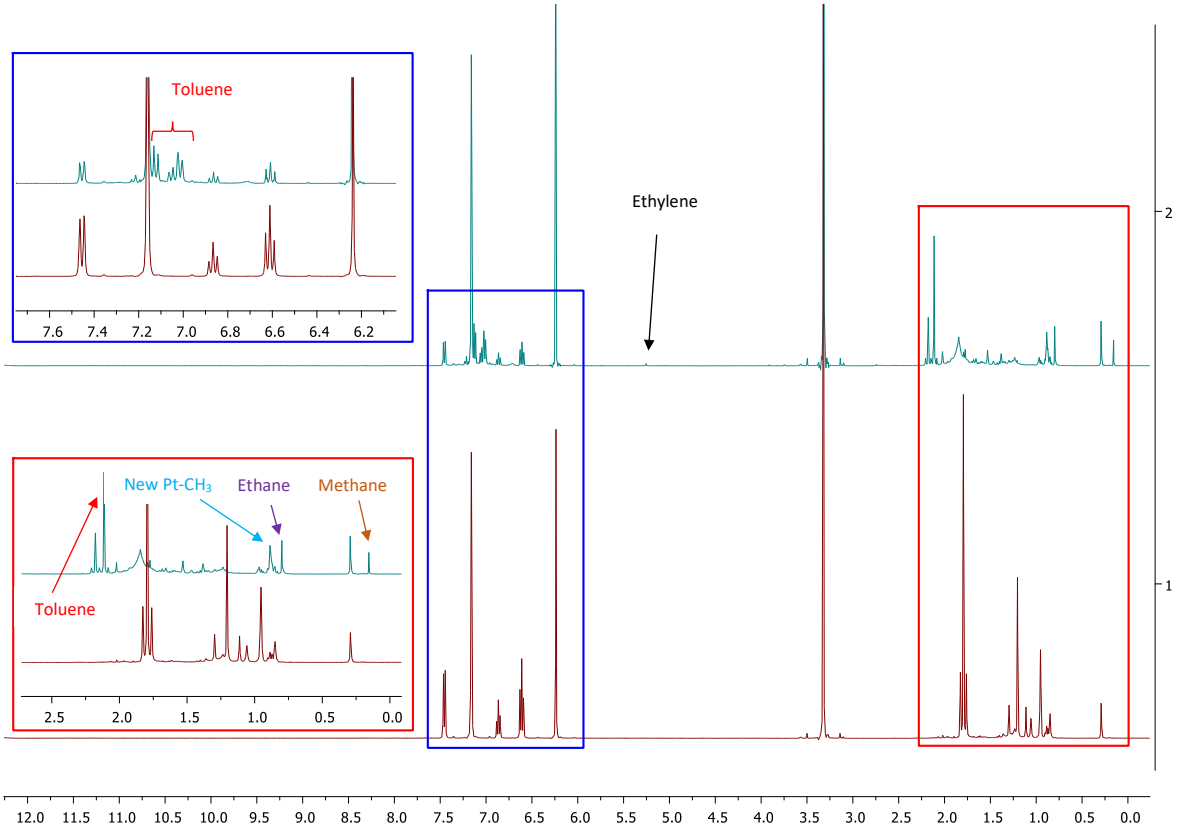


Figure S66: Stacked ^{1}H NMR (400 MHz, C_6D_6, 25 C) of the reaction between PhI and complex **10**, before heating (bottom) and after heating for 16 hours at 100 C (Top).

Additional discussion (Figure S60):

The reaction between PhI and complex **10** proceeds to complete conversion in 16 hours. A significant amount of metallic Pt is precipitated onto the walls of the NMR J-Young tube. Furthermore, 52% toluene is produced at the end of the reaction with significant amount of both methane and ethane as well as trace amounts of ethylene. Unlike complex **9**, there were no aromatic signals detected corresponding to the formation of a Pt-Ph complex, thus we have proposed that the major product from this reaction is metallic Pt and a new Pt-Me complex, **10a**, which shows Pt-C*H* coupling, $^{2}J_{Pt\text{-}H}$= 75 Hz, consistent with a methyl *cis* to both phosphine and iodide. ^{31}P-^{1}H HMBC provides evidence for the structure *via* correlation between the phosphorus and the methyl-H (*vide infra*)

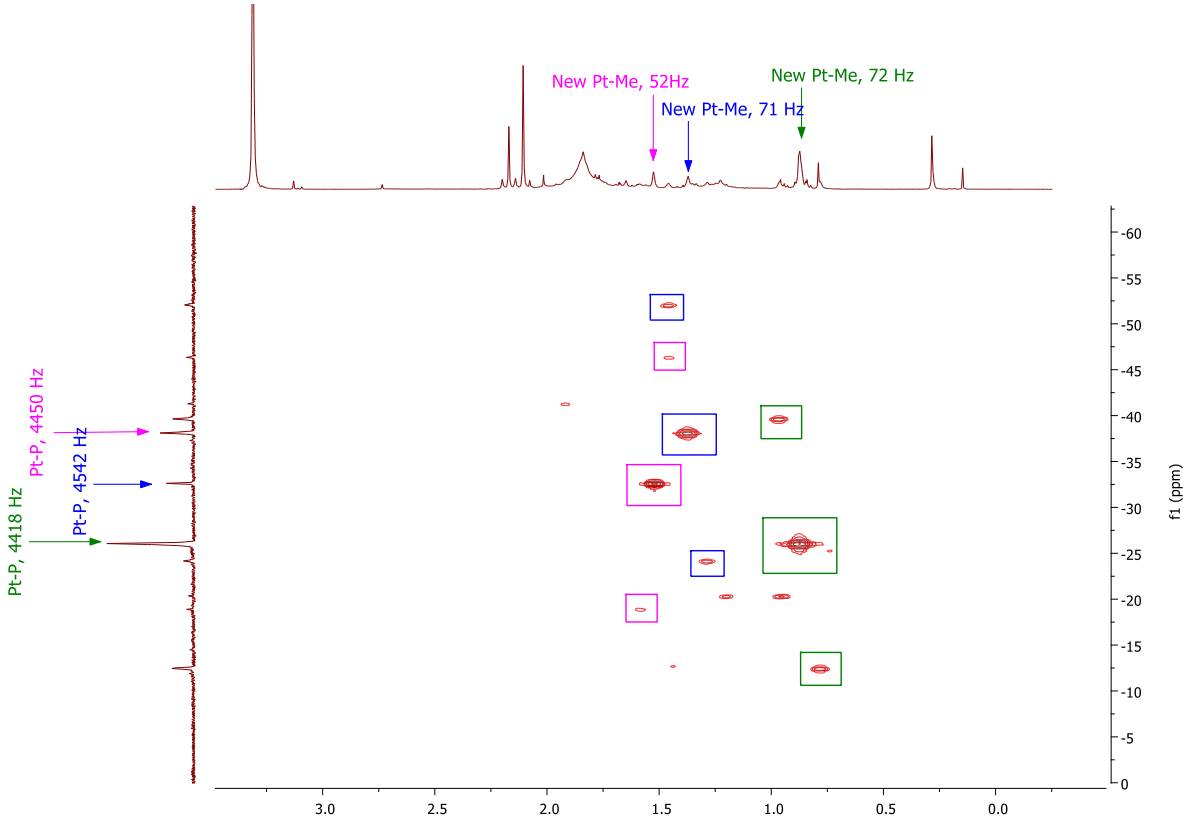
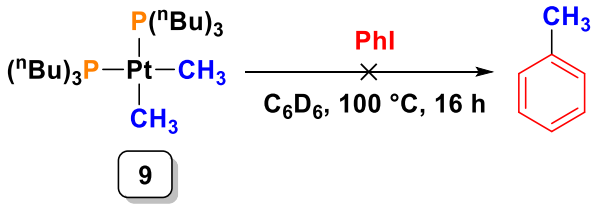


Figure S67: ^{31}P-^{1}H HMBC (400 MHz, C_6D_6, 25 °C) of the reaction between PhI and complex **10** after heating for 16 hours at 100 °C.

Additional discussion (Figure S61):

The ^{31}P-^{1}H HMBC shows correlation for three distinct pairs of R_3P-Pt-C*H*$_3$ fragments. Coupling constants for both Pt-P and Pt-C*H*$_3$ were elucidated from this data as the corresponding 1D spectra were not conclusive. The major signal corresponding to a new Pt-Me (~0.8ppm, green) peak showed strong correlation with the major signal in the ^{31}P NMR (26 ppm, green) spectrum. The coupling constants for Pt-P ($^{1}J_{Pt\text{-}P}$ = 4418 Hz) and Pt-C*H*$_3$ ($^{2}J_{Pt\text{-}H}$ = 72 Hz) are indicative of a *cis* relationship between these two ligands. Furthermore, the large coupling constant of 4418 Hz in the ^{31}P NMR is highly suggestive of a weak *trans* influence ligand, supporting the notion for complex **10a**.[7]

D. Reaction with complex 11 and PhI



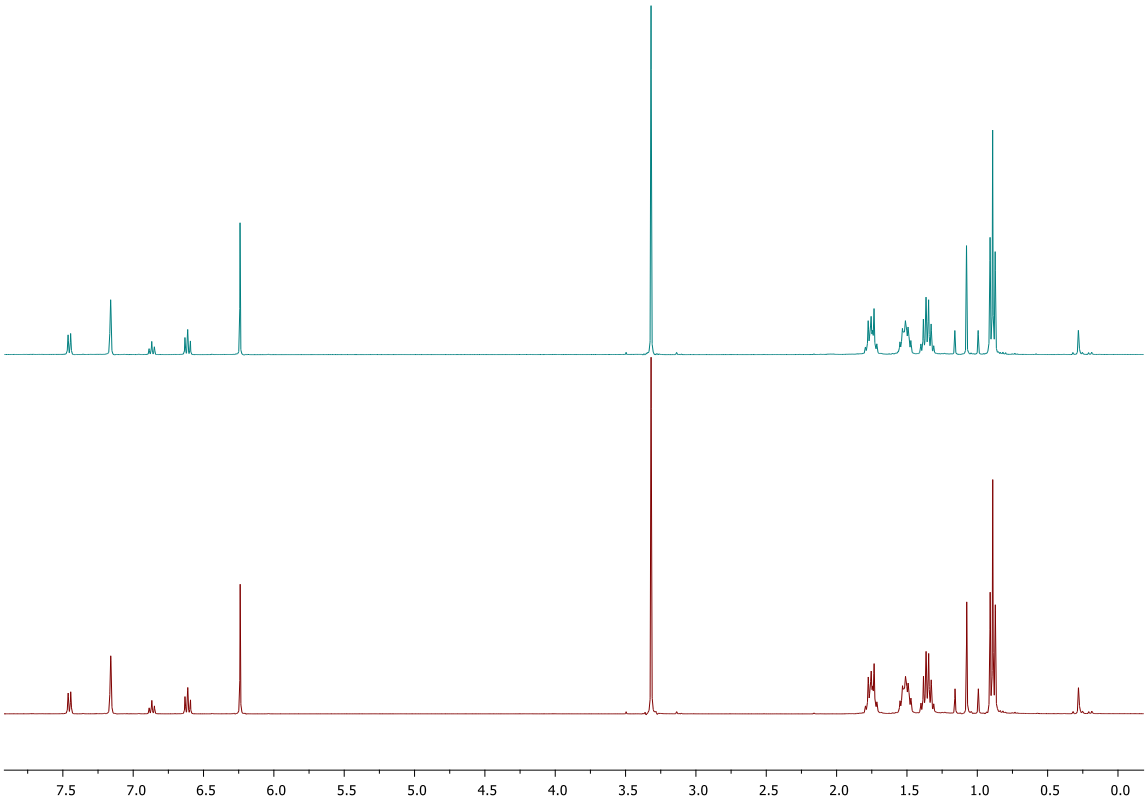


Figure S68: Stacked $^{1}H\{^{31}P\}$ NMR of reaction between PhI and complex 11 before heating (red/bottom) and after heating (green/top).

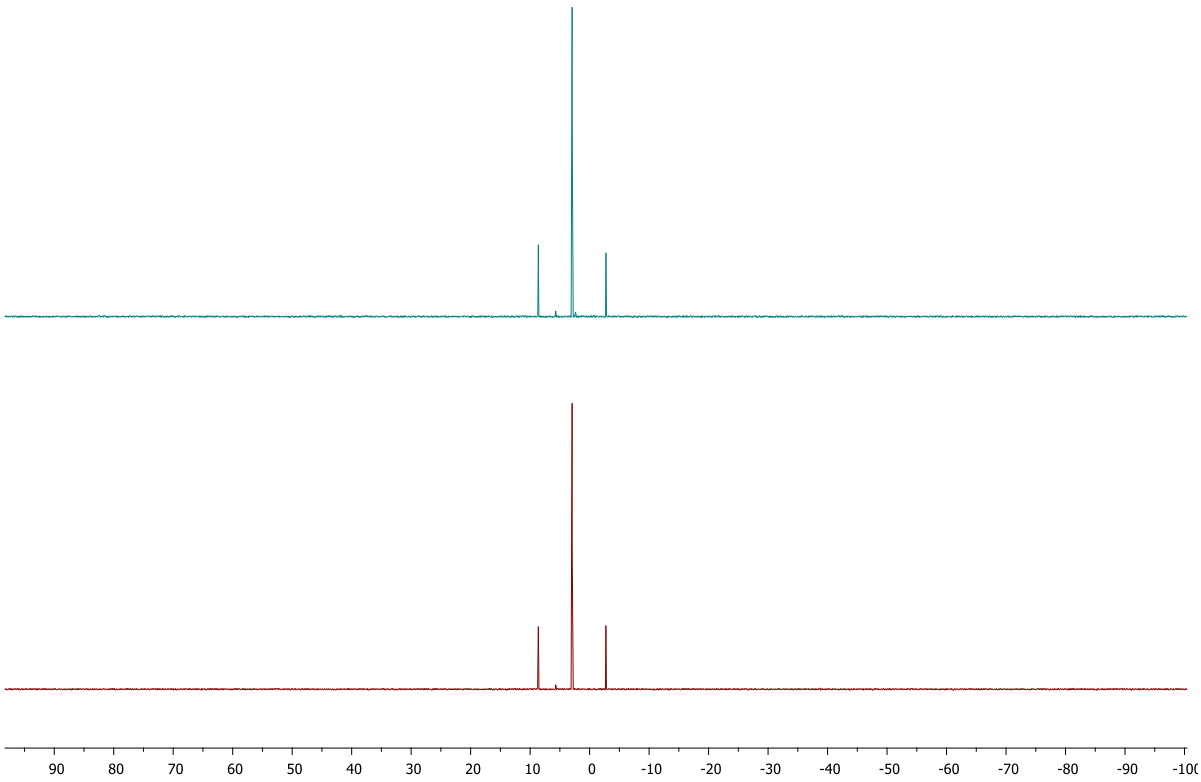


Figure S69: Stacked ^{31}P NMR of the reaction between PhI and complex **11** before heating (bottom/red) and after heating (top/green).

Additional discussion regarding Figures S62 and S63:

No reaction was observed at any temperature up to 100 °C over a period of 16 h. This observed lack of reactivity is in keeping with our proposed mechanism of dissociation of a labile ligand

5. Crystallographic data.

Data for **1a**, **1a'**, **1b**, **1b'**, **2a**, **3a**, and **6** were collected using graphite-monochromated Mo Kα radiation (λ=0.71073 Å) on a Bruker APEX Duo or X8 diffractometer. This analysis was carried out at the Department of Chemistry, The University of British Columbia by Mr. D. Dawson Beattie. The structures were solved by intrinsic phasing (ShelXT) and refined by full-matrix least-squares procedures on F2 (SHELXL-2013)[9] using the OLEX2 interface.[10]

CCDC 1873760-1873766 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/structures

Additional Notes on Refinement:

Complex 6: Two disordered molecules of acetonitrile are found in the unit cell, and were modelled successfully. Additionally, RIGU, SIMU, EADP (2), and SADI (1) restraints were used in the refinement process. All restraints led to improved model statistics.

Complex 1a **Complex 1a'**

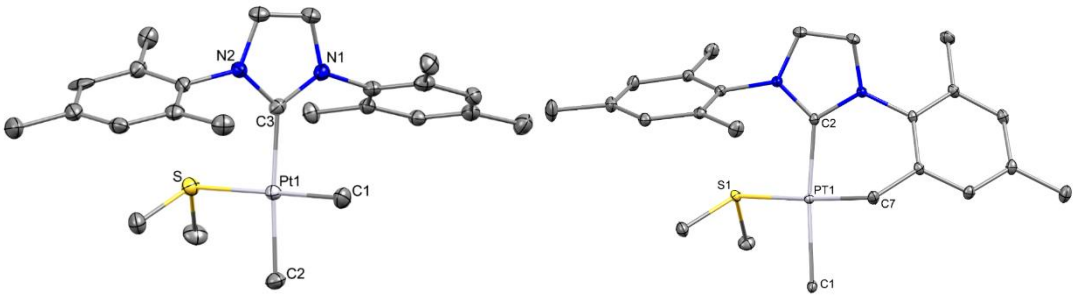


Figure S70: ORTEP depiction of the solid-state molecular structure of complex **1a** and **1a'** (ellipsoids are set at 50% probability; H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°) **1a**: Pt-C1 2.068(3), Pt-C2 2.099(3), Pt-C3 2.039(3), Pt-S 2.367(1), S-Pt-C3 91.73(9), C2-Pt-C1 88.03, C1-Pt1-C3 88.42, S1-Pt1-C2 91.98. **1a'**: Pt-C1 2.103(1), Pt-C2 2.010(5), Pt-C7 2.063(6), Pt-S1 2.351(3), C1-Pt1-C7 90.11, S1-Pt1-C2 94.60, C2-Pt1-C7 82.66, C1-Pt-1-S1 92.63.

Compound	**1a**	**1a'**
Empirical formula	$C_{31}H_{48}N_2PtS$	$C_{24}H_{32}N_2PtS$
Formula weight	675.86	575.66
Temperature/K	100	90
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	12.4820(19)	9.3602(8)
b/Å	19.106(3)	14.9581(13)
c/Å	12.859(2)	16.3919(13)
α/°	90	90
β/°	90.059(4)	104.308(2)
γ/°	90	90
Volume/Å^3	3066.6(8)	2223.9(3)
Z	4	4
ρ_{calc}g/cm^3	1.464	1.719
μ/mm^{-1}	4.664	6.415
F(000)	1368	1136
Crystal size/mm^3	0.13 × 0.1 × 0.09	0.2 × 0.08 × 0.08
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.818 to 63.326	3.74 to 63.008
Index ranges	-10 ≤ h ≤ 18, -27 ≤ k ≤ 28, -18 ≤ l ≤ 18	-13 ≤ h ≤ 11, -21 ≤ k ≤ 21, -16 ≤ l ≤ 23
Reflections collected	74991	20232
Independent reflections	10320 [R_{int} = 0.0405, R_{sigma} = 0.0277]	7060 [R_{int} = 0.0652, R_{sigma} = 0.0773]
Data/restraints/parameters	10320/0/328	7060/0/261
Goodness-of-fit on F^2	1.022	1.002
Final R indexes [I>=2σ (I)]	R_1 = 0.0198, wR_2 = 0.0385	R_1 = 0.0359, wR_2 = 0.0595
Final R indexes [all data]	R_1 = 0.0278, wR_2 = 0.0407	R_1 = 0.0651, wR_2 = 0.0666
Largest diff. peak/hole / e Å^{-3}	0.81/-0.66	2.37/-0.97
Flack Parameter	$C_{31}H_{48}N_2PtS$	$C_{24}H_{32}N_2PtS$

Complex 1b **Complex 1b'**

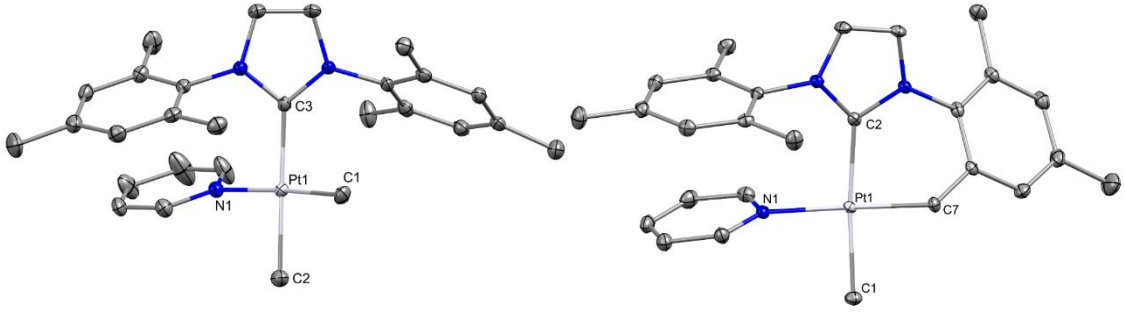


Figure S71: ORTEP depiction of the solid-state molecular structure of complex **1b** and **1b'** (ellipsoids are set at 50% probability; H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°) **1b**: C1-Pt1 2.049(3), C2-Pt1 2.084(2), C3-Pt1 2.027(2), N1-Pt1 2.126(2), C1-Pt1-C2 88.8(1), C2-Pt1-N1 88.28(9), C3-Pt1-C1 90.11(9), N1-Pt1-C3 92.77(8). **1b'**: C1-Pt1 2.079(2), C2-Pt1 2.021(2), C7-Pt1 2.045(2), N1-Pt1 2.102(2), C1-Pt1-N1 88.57(7), C2-Pt1-C7 83.49(8), C7-Pt1-C1 90.07(8), N1-Pt1-C2 97.83(7).

Compound	**1b**	**1b'**
Empirical formula	$C_{28}H_{35}N_3Pt$	$C_{27}H_{31}N_3Pt$
Formula weight	608.68	592.64
Temperature/K	90	90
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	12.4804(11)	11.780(2)
b/Å	15.4521(14)	17.027(3)
c/Å	14.1248(13)	11.769(2)
α/°	90	90
β/°	112.659(2)	96.54(3)
γ/°	90	90
Volume/Å^3	2513.7(4)	2345.1(7)
Z	4	4
ρ_{calc}g/cm^3	1.608	1.679
μ/mm^{-1}	5.602	6.002
F(000)	1208	1168
Crystal size/mm^3	0.24 × 0.18 × 0.02	0.2 × 0.15 × 0.019
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.088 to 61.038	4.224 to 61.488
Index ranges	-17 ≤ h ≤ 17, -21 ≤ k ≤ 22, -20 ≤ l ≤ 20	-16 ≤ h ≤ 16, -24 ≤ k ≤ 24, -16 ≤ l ≤ 16
Reflections collected	32960	81847
Independent reflections	7663 [R_{int} = 0.0351, R_{sigma} = 0.0306]	7270 [R_{int} = 0.0480, R_{sigma} = 0.0242]
Data/restraints/parameters	7663/0/297	7270/0/286
Goodness-of-fit on F^2	1.023	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0210, wR_2 = 0.0416	R_1 = 0.0177, wR_2 = 0.0342
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0447	R_1 = 0.0262, wR_2 = 0.0364
Largest diff. peak/hole / e Å^{-3}	0.87/-0.89	0.56/-0.70
Flack Parameter	$C_{28}H_{35}N_3Pt$	$C_{27}H_{31}N_3Pt$

Complex 2a **Complex 3a**

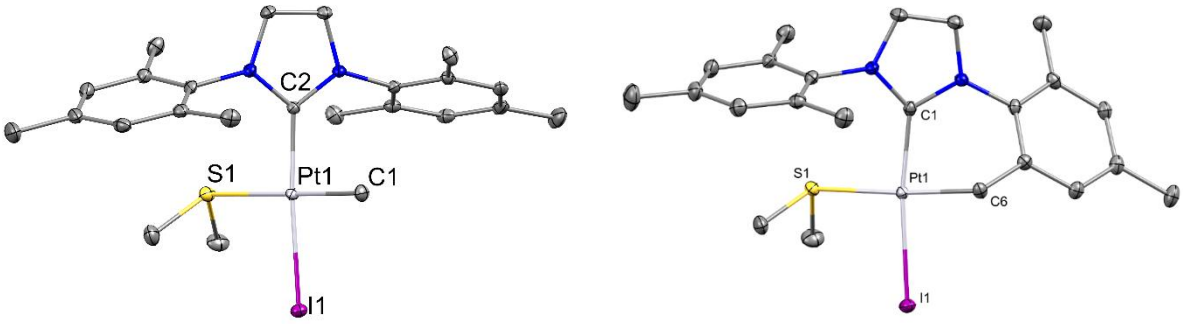


Figure S72: ORTEP depiction of the solid-state molecular structure of complex **2a** and **3a** (ellipsoids are set at 50% probability; H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°) **2a**:Pt1-C1 2.064(2), Pt1-C2 1.972(2), Pt1-S1 2.3941(5), Pt1-I1 2.6631(5), C1-Pt1-C2 87.69(7), C2-Pt1-S1 91.69(5), S1-Pt1-I1 92.31(1), I1-Pt1-C188.44(5). **3a**: Pt1-C1 1.972(2), Pt1-C6 2.068(2), Pt1-I1 2.6350(4), Pt1-S1 2.3871(6), S1-Pt1-C1 94.66(6), C1-Pt1-C6 81.61(8), C6-Pt1-I 90.21(6), I1-Pt-1-S1 93.53(2).

Compound	**2a**	**3a**
Empirical formula	$C_{24}H_{33}IN_2PtS$	$C_{23}H_{29}IN_2PtS$
Formula weight	703.57	687.53
Temperature/K	90	90
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.4632(10)	9.5034(7)
b/Å	14.6453(14)	15.2304(11)
c/Å	16.4371(15)	16.3957(11)
α/°	90	90
β/°	93.941(2)	102.914(2)
γ/°	90	90
Volume/Å^3	2512.8(4)	2313.1(3)
Z	4	4
ρ_{calc}g/cm^3	1.86	1.974
μ/mm^{-1}	6.908	7.502
F(000)	1352	1312
Crystal size/mm^3	0.29 × 0.29 × 0.28	0.26 × 0.22 × 0.14
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.728 to 63.564	3.694 to 66.324
Index ranges	-15 ≤ h ≤ 15, -21 ≤ k ≤ 21, -24 ≤ l ≤ 24	-14 ≤ h ≤ 14, -19 ≤ k ≤ 23, -25 ≤ l ≤ 25
Reflections collected	166812	35721
Independent reflections	8517 [R_{int} = 0.0406, R_{sigma} = 0.0136]	8839 [R_{int} = 0.0325, R_{sigma} = 0.0281]
Data/restraints/parameters	8517/0/271	8839/0/260
Goodness-of-fit on F^2	1.157	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0146, wR_2 = 0.0305	R_1 = 0.0209, wR_2 = 0.0493
Final R indexes [all data]	R_1 = 0.0176, wR_2 = 0.0316	R_1 = 0.0247, wR_2 = 0.0506
Largest diff. peak/hole / e Å^{-3}	0.69/-0.72	2.98/-1.18

Complex 7

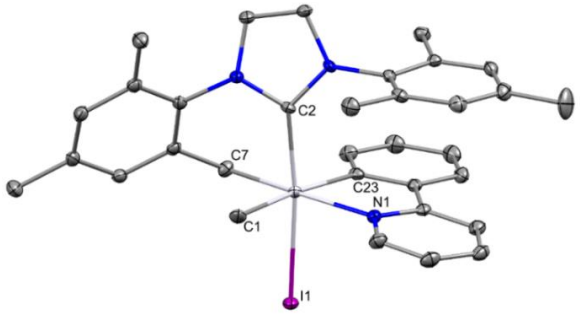


Figure S73: Ortep depiction of the solid-state molecular structure of complex **7** (ellipsoids are set at 50% probability; H atoms and two acetonitrile molecules have been omitted for clarity). The complex is substitutionally disordered at C1 (0.8) and I1 (0.8), with the alternate positions of iodide and methyl holding occupancies of (0.2). Only the major occupancy is shown. Selected bond lengths (Å) and angles (°): C1-Pt 2.161(6), C2-Pt1 2.015(3), C23-Pt1 2.076(3), C7-Pt1 2.083(3), I1-Pt1 2.6849(6), N1-P1 2.164(2), C2-Pt1-N1 100.4(1), C23-Pt1-N1 79.1(1), C2-Pt1-C7 82.4(1), N1-Pt1-I1 86.19(7).

Compound	**7**
Empirical formula	$C_{37}H_{40}IN_5Pt$
Formula weight	876.73
Temperature/K	90
Crystal system	triclinic
Space group	P-1
a/Å	9.8998(17)
b/Å	11.630(2)
c/Å	15.561(3)
α/°	75.326(4)
β/°	77.955(4)
γ/°	78.978(4)
Volume/Å^3	1676.7(5)
Z	2
ρ_{calc}g/cm^3	1.737
μ/mm^{-1}	5.139
F(000)	856
Crystal size/mm^3	0.23 × 0.22 × 0.025
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.744 to 61.08
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 15, -22 ≤ l ≤ 22
Reflections collected	38751
Independent reflections	10237 [R_{int} = 0.0347, R_{sigma} = 0.0330]
Data/restraints/parameters	10237/724/443
Goodness-of-fit on F^2	1.271
Final R indexes [I>=2σ (I)]	R_1 = 0.0259, wR_2 = 0.0576
Final R indexes [all data]	R_1 = 0.0287, wR_2 = 0.0584
Largest diff. peak/hole / e Å^{-3}	1.06/-1.64
Flack Parameter	$C_{37}H_{40}IN_5Pt$

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6. Computational details.

Density functional theory was employed using Gaussian 09, revision D.01.[1] The gradient-corrected functional BP86 (incorporating Becke's exchange functional[2] and the correlation functional of Perdew[3]) was used in all calculations, and geometry optimizations were performed with no symmetry restrictions. The double-ζ basis set 6-31G(*d*,*p*) was used for non-metal atoms in all calculations, and the SDD basis set and associated effective core-potentials were used for S, I and Pt. Additional *d* (S, I) and *f* (Pt) polarization functions were added as recommended by Frenking *et al*.[4] Analytical computation of the Hessian matrix was performed on each output geometry to ensure the presence of local minima (no imaginary frequencies) or transition states (one imaginary frequency). Single point energy calculations were performed on the optimized coordinates with the same basis set and inclusion of solvent (PCM, solvent = benzene) and dispersion corrections.[5] Statistical mechanics calculations of entropic and thermal effects were performed using the rigid rotor and harmonic oscillator approximations at 298.15 K and 1 atm. Connectivity between transition states and intermediates was established by means of intrinsic reaction coordinate (IRC) calculations. NBO analysis was performed using the NBO 3.1 program as implemented in Gaussian 09.[6]

Full pathways for Csp^2-I cleavage starting from **1a** and **1a'** are shown in Figures S74 and S75, respectively. Attempts to locate Csp^2-I OA transition states with PhI in the opposite orientation (*i.e.* to give the square pyramidal Pt(IV) product with I in the apical position) were not successful. A variety of reductive elimination (RE) pathways yielding toluene are possible from **5**/**5'** due to facile isomerization of the 5-coordinate intermediate.[7] As such, only one pathway – Csp^2-Csp^3 RE of the apical Ph group and the alkyl group *trans* to the NHC donor - was considered. Pathways for PhI OA that involved a *trans*-configuration of anionic C donors were considered, and in all cases were found to be higher in energy than OA to isomers in which anionic C donors were in a *cis* configuration. This is illustrated in Figure S76, which shows the relative energies of Csp^2-I OA transition states for different isomers of the cyclometallated and dimethyl NHC complexes. The barriers ($\Delta G^{\ddagger}$) to Csp^2-I OA to **1a** are significantly higher than those for **1a'** as a consequence of greater steric repulsion between the NHC mesityl substituents and the PhI moiety when the NHC is not cyclometallated (Figure S77). In the Csp^2-I OA step, the PhI group interacts with Pt in a face-on fashion, resulting in strong steric repulsion with the *cis* NHC group in the non-cyclometallated complex. The ΔG values for the OA step are similar in both systems due to reorientation of the Ph group after the OA step, which results in a parallel arrangement of the NHC-mesityl and Pt-Ph aromatic rings. Attempts were made to identify other rotameric transition states such as **4/5_rot^{TS}** (+1.5 kcal·mol^{-1} relative to **4/5^{TS}**) which would have fewer repulsive interactions, but no lower energy transition states were found using several different input geometries. The difference in $\Delta G^{\ddagger}$ values for **4/5^{TS}** and **4/5_*trans*alkyl^{TS}** (4.6 kcal·mol^{-1}) are smaller than $\Delta\Delta G^{\ddagger}$ for cyclometallated transition states **4'/5'^{TS}** and **4'/5'_*trans*alkyl^{TS}** (9.2 kcal·mol^{-1}).

This observation is attributed to the relief of steric repulsion between PhI and the NHC upon moving from **4/5^{TS}** to **4/5_*trans*alkyl^{TS}**, which partially offsets the higher energy of the *trans*-alkyl arrangement.

IRC calculations in the reverse direction for Csp^2-Csp^3 reductive elimination transition states **5/6^{TS}** and **5'/6'^{TS}** confirmed connectivity of the transition state to the Pt(IV) intermediates **5** and **5'**, respectively. The IRC calculations in the forward direction were consistent with the intermediacy of σ-(Csp^3-H) complexes **6** and **6'**, in line with expectations based on our previous work[7] and evidenced by elongation of the interacting Csp^3-H bond throughout the reaction coordinate (Figure S78). IR C calculations in the forward direction (to **6**/**6'**) failed after 25-40 steps of 0.1 $(amu)^{1/2}$Bohr for both systems, and attempts to optimize the geometry of the structures late in the reaction coordinate resulted in dissociation of toluene – no minima corresponding to **6**/**6'** were found. This observation may be attributed to a shallow potential energy surface surrounding the σ-toluene intermediates **6**/**6'**, or in these systems it is possible that they do not exist as intermediates due to steric repulsion with the NHC. In Figures S74 and S75, complexes **6**/**6'** are shown as proposed intermediates for clarity, along with upper energy bounds estimated from the electronic energies of the furthest point obtained in the IRC starting from **5/6^{TS}** and **5'/6'^{TS}**.

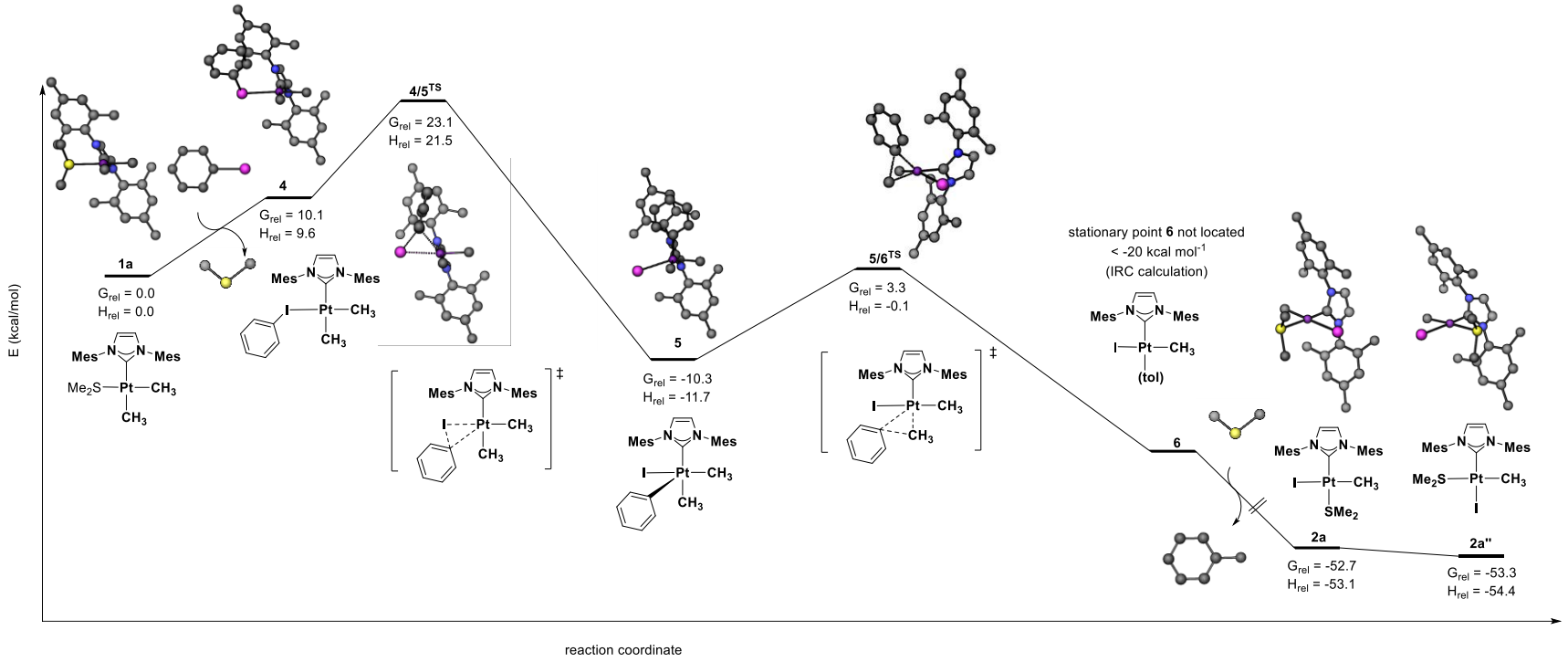

Figure S74: Reaction coordinate for Csp^2-I oxidative addition starting from the Pt(II) dimethyl complex **1a.**

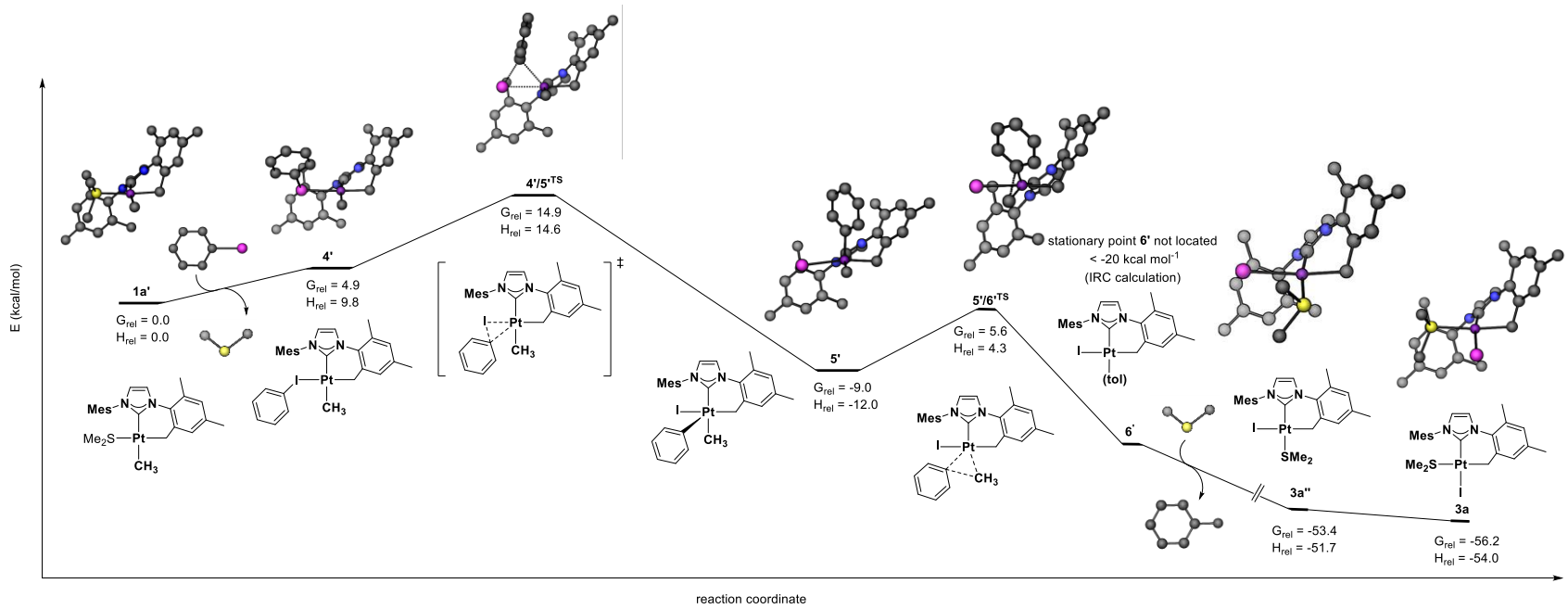

Figure S75: Reaction coordinate for Csp^2-I oxidative addition starting from cyclometallated complex **1a'**.

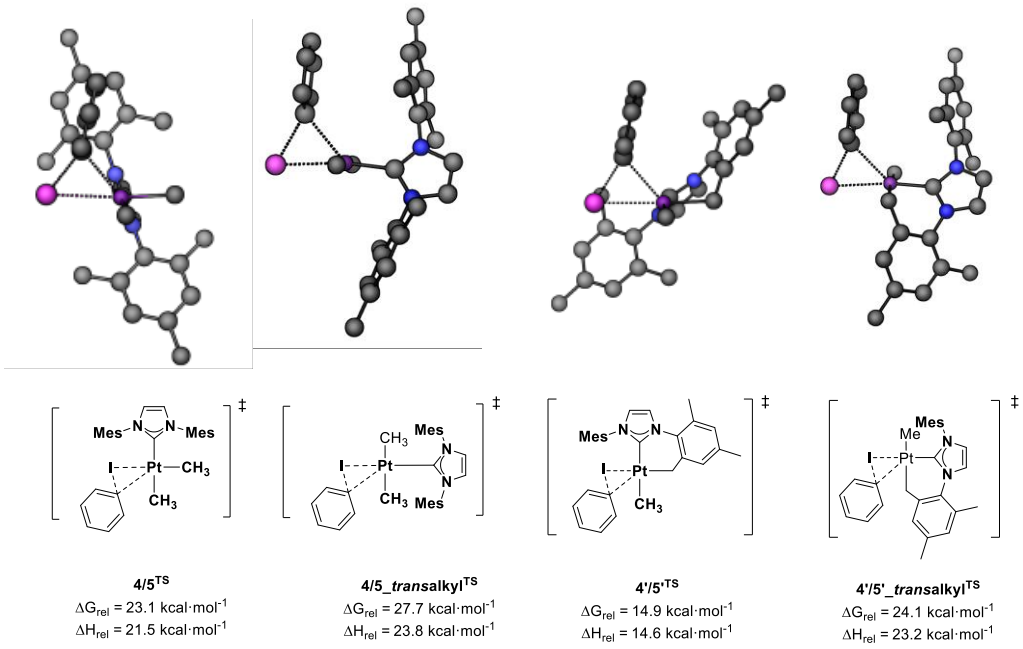

Figure S 76: Transition states for Csp^2-I OA showing higher energies when Pt-alkyl groups are in a mutally trans configuration. Relative energies reported relative to **1a** for **4/5TS** and **4/5_transalkyl^{TS}**, relative to **1a'** for **4'/5'^{TS}** and **4'/5'_transalkyl^{TS}**.

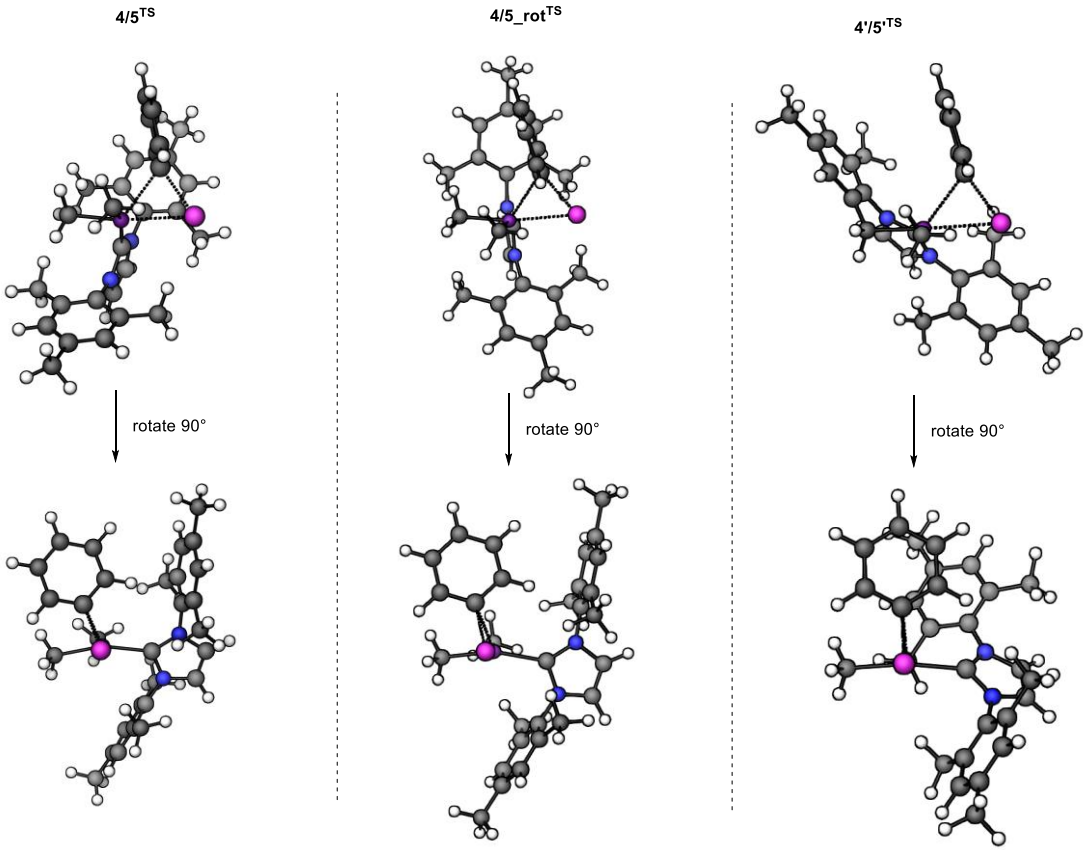

Figure S77: Csp^2-I OA transition state geometries.

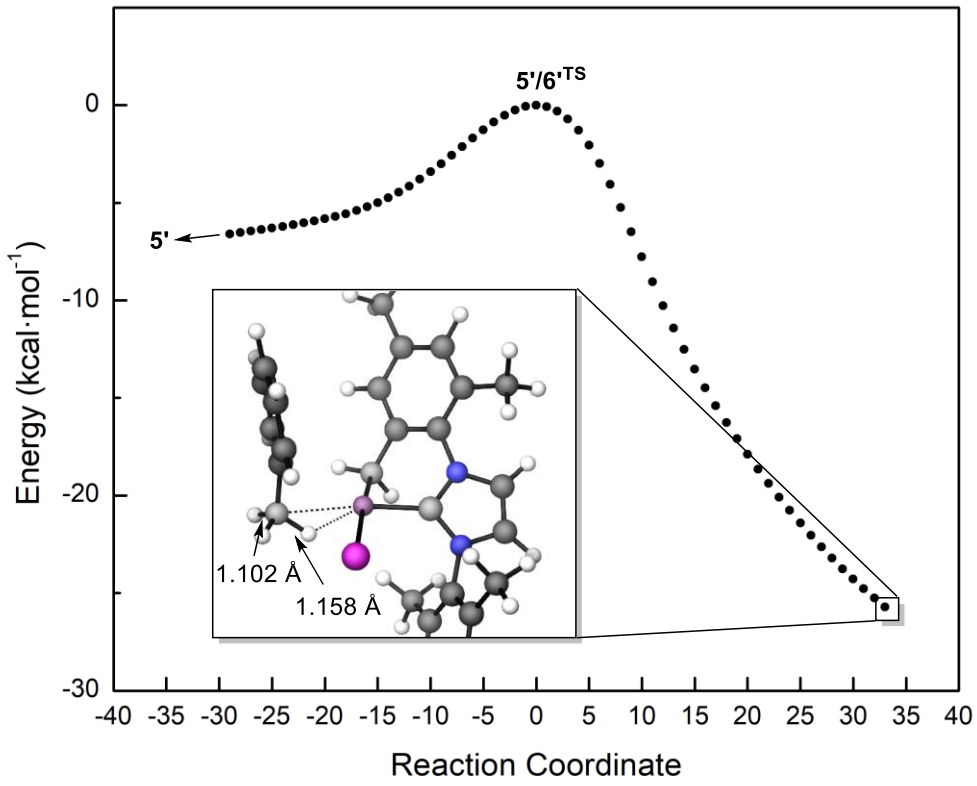

Figure S 78: Representative PES for Csp^2-Csp^3 RE obtained from IRC calculations on **5'/6'^{TS}**. Electronic energy reported relative to **5'/6'^{TS}**, with C-H bond distances for interacting and noninteracting C-H bonds labelled.

References

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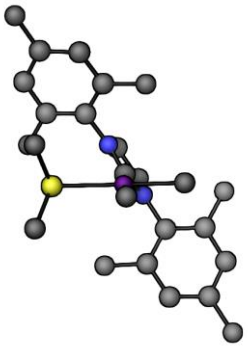
XYZ Coordinates of Optimized Structures (hydrogen atoms omitted from images)

1a

imaginary frequencies = 0
Sum of electronic & zero-point Energies= -1213.257397
Sum of electronic & thermal Energies= -1213.220613
Sum of electronic & thermal Enthalpies= -1213.219669
Sum of electronic & thermal Free Energies=-1213.328462



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4

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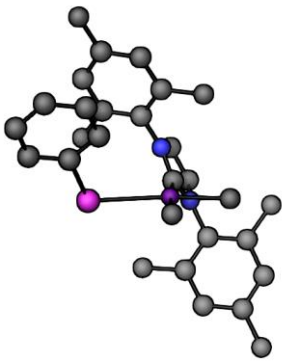
Sum of electronic & thermal Free Energies=-1366.369488



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4/5^{TS}

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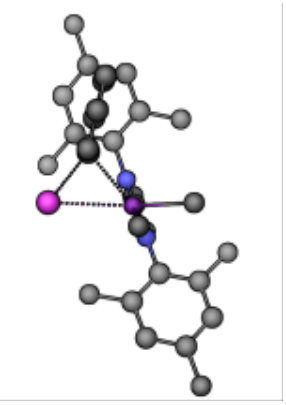
Sum of electronic & thermal Enthalpies= -1366.236062

Sum of electronic & thermal Free Energies=-1366.348743



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C	-3.85451199	2.42352807	-1.15625751
C	-6.16437519	2.38010172	-0.09374740
C	-2.44886908	2.37099432	-1.09881549
C	3.81294735	1.57520022	-0.97920077
C	5.10106562	1.01834062	-1.07102619
C	-4.65358317	2.35279626	-0.00084570
C	-1.84593703	2.23794284	0.17257147
C	0.23623127	3.45294505	0.66181405
C	-4.01116947	2.23953607	1.24654404
C	1.57255901	3.18929548	0.66728017
C	0.49534768	1.23774478	0.03241814
C	3.03311118	1.25622430	0.15811662
C	7.00141961	-0.43450559	-0.21224268
C	-2.61040707	2.18787479	1.36354283
C	5.62888787	0.18682980	-0.06664098
C	-1.95635182	2.07584602	2.72252077
C	4.84307409	-0.05502416	1.07401975
C	3.54784873	0.47490038	1.21815726
C	2.75659011	0.22273235	2.47878834
H	3.27068005	3.55700667	-1.70258516
H	2.29397129	2.24186498	-2.38711952
H	-0.79701050	3.16043979	-2.27361916
H	3.97432719	2.48258574	-2.93484350
H	-2.24685903	2.72124956	-3.22283838
H	-6.61079594	2.94597687	0.74108445
H	-4.33480388	2.52894207	-2.13649226
H	5.70962275	1.24764469	-1.95418373
H	-6.50359194	2.83636180	-1.03797987
H	-6.58261900	1.35772761	-0.05190610
H	7.66673930	0.19083009	-0.83043402
H	-0.32176829	4.35903025	0.88245005
H	7.48377261	-0.58558256	0.76777693
H	2.42896189	3.81286812	0.90914154
H	-4.61538098	2.19339611	2.16044595
H	-1.30097960	2.93764577	2.93895965
H	6.93684237	-1.42460781	-0.69980479
H	-1.33075279	1.16825945	2.78472726
H	-2.71843627	2.02122809	3.51554914
H	5.24963448	-0.66933761	1.88646061

H	2.28761315	1.14631945	2.85937932
H	1.94164294	-0.49856087	2.28961756
H	3.40468120	-0.18818013	3.26906221
N	-0.40533109	2.26861113	0.27714476
N	1.71934525	1.85441558	0.28564963
Pt	0.47089841	-0.79261547	-0.54909357
C	1.11889983	-2.71445338	-1.07443831
H	2.19469553	-2.66475303	-1.32526313
H	1.00728382	-3.41502582	-0.22489996
H	0.58061539	-3.12708199	-1.94659903
C	-3.74152422	-1.43575721	-1.47499330
C	-3.79650262	-2.73514014	-2.00168470
C	-2.84436342	-3.68317959	-1.58906414
C	-1.83291163	-3.33977708	-0.67888756
C	-1.75561251	-2.01145262	-0.22002599
C	-2.74214858	-1.07050190	-0.55528492
H	-4.48553043	-0.68512753	-1.76295800
H	-4.58673214	-3.01537757	-2.70538898
H	-2.88651342	-4.71119796	-1.96587785
H	-1.10442369	-4.08737598	-0.36104192
H	-2.72605511	-0.06887886	-0.12791537
I	-0.72489783	-1.76239750	1.85796077
H	-1.16898782	1.45099327	-2.57366857
C	1.16979338	-0.34997346	-2.43955593
H	0.77801046	-1.09223228	-3.15399568
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H	2.27254459	-0.40331698	-2.43565305

5

imaginary frequencies = 0

Sum of electronic & zero-point Energies= -1366.327772

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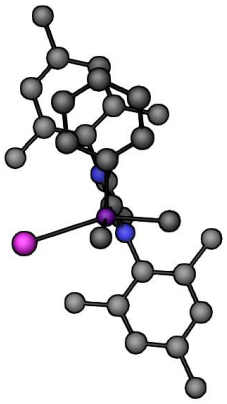
Sum of electronic & thermal Enthalpies= -1366.288957

Sum of electronic & thermal Free Energies=-1366.401948



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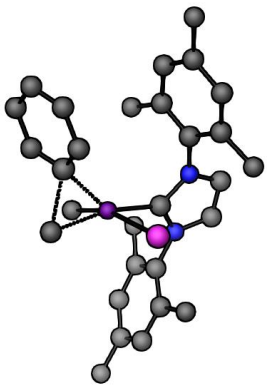
C	-2.66200000	2.23400000	-0.11600000
C	3.44200000	2.03000000	0.60900000
C	4.73800000	1.72200000	1.06600000
C	-4.79200000	1.40400000	-1.02000000
C	-1.99100000	1.53200000	-1.14300000
C	0.00900000	2.64400000	-2.07700000
C	-4.08500000	0.76200000	-2.05100000
C	1.35900000	2.58700000	-1.89800000
C	0.41500000	0.98900000	-0.53100000
C	2.93200000	1.28800000	-0.48200000
C	6.90000000	0.39000000	0.99100000
C	-2.68100000	0.81600000	-2.14500000
C	5.53000000	0.73700000	0.44900000
C	-1.95900000	0.15000000	-3.29300000
C	5.01600000	0.08600000	-0.68700000
C	3.72700000	0.35000000	-1.18600000
C	3.24800000	-0.30800000	-2.45700000
H	2.89400000	4.12300000	0.71100000
H	1.58600000	3.02300000	1.19600000
H	-1.21200000	3.77300000	0.40100000
H	2.96600000	3.31100000	2.29000000
H	-2.60700000	3.65700000	1.50900000
H	-6.74500000	0.97200000	-1.87600000
H	-4.59800000	2.67600000	0.72500000
H	5.13900000	2.27700000	1.92200000
H	-6.75600000	2.26300000	-0.64300000
H	-6.59000000	0.56500000	-0.15000000
H	7.35200000	1.23900000	1.52800000
H	-0.61100000	3.27900000	-2.70400000
H	7.58900000	0.08500000	0.18500000
H	2.17200000	3.15600000	-2.34000000
H	-4.63900000	0.20300000	-2.81500000
H	-1.39300000	0.88100000	-3.89900000
H	6.83900000	-0.45400000	1.70200000
H	-1.23400000	-0.60100000	-2.92900000

H	-2.67400000	-0.35800000	-3.95800000
H	5.63800000	-0.64700000	-1.21300000
H	2.91700000	0.44100000	-3.19800000
H	2.39000000	-0.98100000	-2.27400000
H	4.05700000	-0.90300000	-2.91100000
N	-0.55100000	1.67200000	-1.24300000
N	1.59400000	1.58200000	-0.95700000
Pt	0.25800000	-0.69800000	0.82000000
C	0.41100000	-2.38700000	2.04200000
H	1.47300000	-2.69100000	1.97300000
H	-0.21800000	-3.21200000	1.67500000
H	0.15700000	-2.17200000	3.09400000
C	-3.28800000	0.06200000	3.26900000
C	-4.27100000	-0.66000000	2.58200000
C	-3.91300000	-1.36200000	1.42000000
C	-2.59000000	-1.34200000	0.94600000
C	-1.60500000	-0.60100000	1.63300000
C	-1.95600000	0.08700000	2.81000000
H	-3.54100000	0.61000000	4.18400000
H	-5.30100000	-0.68800000	2.95300000
H	-4.66000000	-1.94700000	0.87100000
H	-2.32500000	-1.90600000	0.04900000
H	-1.21800000	0.64400000	3.38800000
I	0.25300000	-2.50700000	-1.34600000
H	-1.31600000	2.43200000	1.56900000
C	1.01500000	0.38900000	2.41600000
H	0.80700000	-0.12700000	3.36600000
H	0.62200000	1.41700000	2.45000000
H	2.10500000	0.41500000	2.24200000

5/6^{TS}

imaginary frequencies = 1 (-364.9 cm^{-1})
Sum of electronic & zero-point Energies= -1366.308721
Sum of electronic & thermal Energies= -1366.271437
Sum of electronic & thermal Enthalpies= -1366.270492
Sum of electronic & thermal Free Energies=-1366.380303



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C	-3.75995000	1.36411600	-1.83808500
C	-6.02643100	1.94142100	-0.84809900
C	-2.35382600	1.34610400	-1.81922600
C	3.86388000	0.67203600	-1.71288000
C	5.14043000	0.08859000	-1.62422400
C	-4.51344500	1.97294300	-0.81977500
C	-1.70263500	1.95658400	-0.72274700
C	0.41949200	3.20587400	-1.00214000
C	-3.82268800	2.60704700	0.22795300
C	1.75323000	2.93892600	-0.92394200
C	0.63533300	0.99252500	-0.44518800
C	3.18360300	0.96094900	-0.50469200
C	7.10402000	-0.85966600	-0.31880900
C	-2.41811300	2.62623200	0.29896200
C	5.74766000	-0.19140600	-0.38644300
C	-1.72647000	3.36295700	1.42399900
C	5.05724100	0.16139900	0.78658500
C	3.77881600	0.75151000	0.76075000
C	3.10521800	1.17462100	2.04264300
H	3.23289500	2.07226900	-3.26069500
H	2.22715900	0.61435800	-3.14936900
H	-0.70663600	1.29438100	-3.24504000
H	3.85673400	0.52077300	-3.86923300
H	-2.23864100	0.59337000	-3.83946300
H	-6.46026300	2.79890000	-0.30772000
H	-4.27674600	0.89184300	-2.68193200
H	5.67292900	-0.15226700	-2.55206600
H	-6.41248400	1.95370000	-1.88107300
H	-6.41065200	1.02309300	-0.36754800
H	7.69351200	-0.67419800	-1.23166700
H	-0.12083700	4.11589800	-1.24572200
H	7.68784000	-0.50390200	0.54632900
H	2.62593200	3.57087400	-1.06198100
H	-4.39068700	3.11043600	1.01924200
H	-1.18026200	4.25362700	1.06373500
H	6.99986600	-1.95507700	-0.21216000
H	-1.00456500	2.70775100	1.94147600
H	-2.46535800	3.70374100	2.16600500
H	5.52944700	-0.01192200	1.76094400
H	2.74499000	2.21643700	1.98426400
H	2.21991800	0.55434600	2.27469000
H	3.80575600	1.10076100	2.88921800
N	-0.25339000	2.01809600	-0.70807100
N	1.87786500	1.58663400	-0.59148200
Pt	0.14507400	-0.92163800	0.05225400

C	0.06102400	-2.99439500	0.84800600
H	1.04294000	-2.66827900	1.25659200
H	-0.60016600	-3.23110500	1.68834300
H	0.22158600	-3.85544900	0.18762600
C	-2.80194300	-3.39681800	-2.01465800
C	-3.97894300	-3.09077400	-1.31343700
C	-3.88043200	-2.41226500	-0.08928500
C	-2.63157900	-2.03271100	0.42778900
C	-1.44195400	-2.29902200	-0.29460100
C	-1.54810800	-3.02365200	-1.50763300
H	-2.84984800	-3.94151700	-2.96447600
H	-4.95508500	-3.39290100	-1.70696200
H	-4.78192900	-2.17974200	0.48842500
H	-2.57471600	-1.51571100	1.38890000
H	-0.65232200	-3.29920400	-2.06794600
I	-0.55817800	-0.09264500	2.68890900
H	-1.23733800	-0.29953000	-2.66168500
C	1.17429400	-1.61186400	-1.62533100
H	1.23263700	-2.71263800	-1.57695500
H	0.69194000	-1.31940700	-2.57279000
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2a

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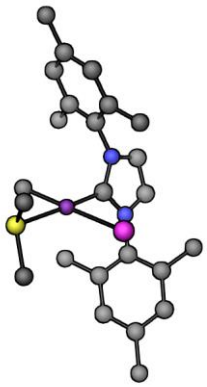
Sum of electronic & thermal Enthalpies= -1184.876119
Sum of electronic & thermal Free Energies=-1184.984930



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C	-6.84267000	-0.12433700	-0.22604500
C	-3.56519300	-1.92220700	0.68409600
C	2.74626000	-1.77007500	1.30838300
C	4.13204100	-1.58244000	1.46367400
C	-5.41210900	-0.61607600	-0.28571100
C	-2.72370900	-1.45002100	-0.35030100
C	-1.00576000	-3.20296500	-0.77498800
C	-4.55428100	-0.21565900	-1.32679200
C	0.34814000	-3.30635900	-0.65876900
C	-0.22465300	-1.17266400	-0.03788500
C	2.23179400	-1.82152800	-0.00705100
C	6.48128900	-1.22949500	0.56126700
C	-3.20991300	-0.62381700	-1.39165300
C	4.99928600	-1.46591400	0.36354000
C	-2.34057300	-0.21483700	-2.55487800
C	4.44956900	-1.56486400	-0.92708200
C	3.07195300	-1.74542500	-1.14395900
C	2.52982200	-1.84203500	-2.55202400
H	2.46734200	-2.08564900	3.42753100
H	1.16173900	-2.76863300	2.41801900
H	-3.23785700	-3.95315900	1.38544400
H	1.24677600	-1.01521500	2.66995700
H	-3.67161300	-2.79519700	2.66071300
H	-7.26487900	0.01448300	-1.23533600
H	-5.56089500	-1.82981200	1.50183800
H	4.54285400	-1.54059000	2.47985800
H	-7.49070900	-0.82656800	0.32382000
H	-6.90537100	0.85172100	0.28946500
H	6.82878900	-1.62292500	1.53095700
H	-1.75799800	-3.91734600	-1.09692400
H	7.07743600	-1.70410400	-0.23592300
H	1.02499400	-4.13594200	-0.84157000
H	-4.94255300	0.42651000	-2.12660700
H	-1.81415700	-1.08171800	-2.99089700
H	6.71543000	-0.14916800	0.54272100
H	-1.55914300	0.50448100	-2.24868800
H	-2.94757200	0.25199300	-3.34668600
H	5.10947700	-1.49395300	-1.79985700
H	2.04931900	-2.81588300	-2.75264000
H	1.77811500	-1.05268700	-2.73053400
H	3.34120200	-1.71022400	-3.28481500
N	-1.34873400	-1.90300600	-0.39035900
N	0.81823100	-2.06750200	-0.21099800
Pt	-0.14872500	0.69209800	0.62988800
H	-2.02779800	-2.79176500	1.96953000
S	-0.10300400	2.86442000	1.64638900
C	-0.87881000	4.06203300	0.48325000
H	-0.41004300	3.96424200	-0.50828000
H	-1.94368400	3.79429000	0.42366500
H	-0.76727200	5.07777200	0.89486200
C	1.63748600	3.45804500	1.56907200
H	1.67597500	4.49354900	1.94305900
H	2.22222000	2.79712000	2.22516200
H	2.00352600	3.37674500	0.53389700
C	-1.14008800	0.11855300	2.36607400
H	-2.20088800	0.41587500	2.26868700
H	-1.09926800	-0.96559300	2.55377100
H	-0.71046700	0.63506800	3.24429400
I	1.06537600	1.67737800	-1.70610300

2a''

imaginary frequencies = 0
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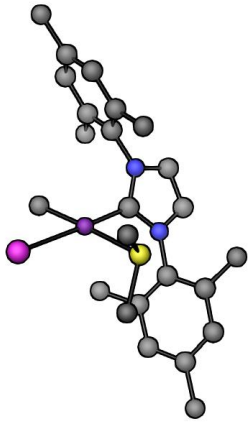
Sum of electronic & thermal Enthalpies= -1184.878249
Sum of electronic & thermal Free Energies=-1184.986029



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C	-6.52069000	-1.30523400	-0.56700100
C	-3.09040900	-2.17094900	0.94861100
C	3.16961000	-0.97451700	1.33028100
C	4.52198300	-0.59377000	1.36832800
C	-5.02763500	-1.50821100	-0.42025300
C	-2.25310500	-1.93593400	-0.16932600
C	-0.36662900	-3.53547500	0.08465000
C	-4.15993200	-1.29687800	-1.50815200
C	0.98907600	-3.45743400	0.19162800
C	0.20026900	-1.30565100	-0.02261700
C	2.70731700	-1.66168300	0.18325700
C	6.85112500	-0.41634100	0.36846000
C	-2.77242600	-1.51253700	-1.41675100
C	5.41190100	-0.88183500	0.31755700
C	-1.88542000	-1.28837200	-2.61715000
C	4.91983100	-1.59467800	-0.78887500
C	3.57570800	-2.00083500	-0.88121900
C	3.11580400	-2.78857600	-2.09045000
H	2.83508700	-0.30152300	3.35648800
H	1.65094600	-1.51922400	2.79336300
H	-2.25963200	-3.71631000	2.24999300
H	1.54836500	0.14923900	2.18817900
H	-3.30329100	-2.53079300	3.06715300
H	-7.00304600	-2.20223600	-0.99751700
H	-5.12821100	-2.11431200	1.65727400
H	4.88857600	-0.05577200	2.25073000
H	-7.00016700	-1.11092800	0.40624000
H	-6.74979300	-0.46069300	-1.23774900
H	6.94541400	0.61504600	-0.01799200
H	-1.03875900	-4.38877300	0.07440800
H	7.23959100	-0.41287400	1.40055300
H	1.74448400	-4.22726400	0.31953700
H	-4.57205700	-0.96131900	-2.46727400
H	-1.18824800	-2.13008900	-2.77144100
H	7.50691000	-1.05683800	-0.24390900
H	-1.26874200	-0.38267700	-2.47203300
H	-2.48873100	-1.16488800	-3.53017700
H	5.59841700	-1.83956300	-1.61487900
H	3.16622200	-3.87881400	-1.91200600
H	2.07697200	-2.55206500	-2.36983200
H	3.76053500	-2.57163300	-2.95689000
N	-0.84112400	-2.22521300	-0.04377300
N	1.32972200	-2.10214300	0.12200500
Pt	0.08917500	0.65983500	-0.19659700
C	1.30282100	0.57236700	-1.87361700
H	2.27636300	1.02379400	-1.61609200
H	1.46722700	-0.45287600	-2.24245200
H	0.84168300	1.17253300	-2.67583900
H	-1.65167000	-2.07531000	2.57377900
S	-1.42192000	0.84207900	1.76188400
C	-2.94094100	1.66844700	1.13587500
H	-2.65414100	2.58114400	0.59043600
H	-3.42318200	0.95340200	0.45372400
H	-3.60720700	1.88920000	1.98518800
C	-0.80649100	2.17213500	2.87699300
H	-1.56294000	2.36430600	3.65467700
H	0.11709500	1.79783200	3.34238900
H	-0.58646100	3.07501100	2.28525500
I	0.02099000	3.36186600	-0.58460500

1a'

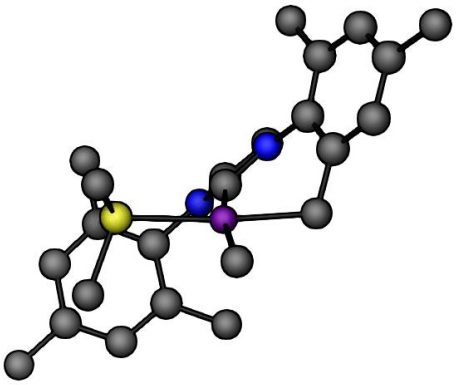
imaginary frequencies = 0

Sum of electronic & zero-point Energies= -1172.785881

Sum of electronic & thermal Energies= -1172.753722

Sum of electronic & thermal Enthalpies= -1172.752778

Sum of electronic & thermal Free Energies=-1172.849826



C	-2.01900000	0.62700000	2.64600000
C	1.84500000	-0.72800000	1.54900000
C	4.23300000	-0.50600000	0.72200000
C	6.65500000	-0.42100000	-0.03800000
C	2.92400000	0.00500000	0.80600000
C	-2.85100000	0.90800000	1.41800000
C	-4.23100000	0.63100000	1.39700000
C	5.25100000	0.14400000	-0.00100000
C	2.65400000	1.22500000	0.12600000
C	0.94300000	3.05600000	0.43000000
C	4.93000000	1.33100000	-0.67900000
C	-0.42100000	3.09800000	0.45500000
C	0.18900000	0.90400000	0.10000000
C	-2.26800000	1.43500000	0.24200000

C	-6.51800000	0.61300000	0.28700000
C	3.63400000	1.88800000	-0.64500000
C	-5.02600000	0.87300000	0.26100000
C	3.35300000	3.13100000	-1.46700000
C	-4.40400000	1.39300000	-0.88900000
C	-3.02700000	1.68300000	-0.92500000
C	-2.38000000	2.21000000	-2.18600000
H	-2.65400000	0.31500000	3.49000000
H	-1.43800000	1.51400000	2.95600000
H	1.42900000	-0.10100000	2.36300000
H	-1.28800000	-0.17600000	2.42900000
H	2.25200000	-1.64600000	2.00300000
H	7.19300000	-0.22300000	0.90800000
H	4.45500000	-1.44500000	1.24200000
H	-4.69700000	0.22300000	2.30300000
H	6.64700000	-1.51600000	-0.17900000
H	7.24900000	0.02300000	-0.85400000
H	-6.77100000	-0.22500000	0.95800000
H	1.67700000	3.84200000	0.57900000
H	-7.07000000	1.49900000	0.65200000
H	-1.11200000	3.92300000	0.60800000
H	5.69900000	1.83500000	-1.27600000
H	3.47000000	4.06400000	-0.88200000
H	-6.90600000	0.37800000	-0.71700000
H	2.33300000	3.13400000	-1.88400000
H	4.06400000	3.19300000	-2.30700000
H	-5.00400000	1.58000000	-1.78800000
H	-1.83200000	3.15200000	-2.01000000
H	-1.65000000	1.48100000	-2.58000000
H	-3.13600000	2.39400000	-2.96600000
N	1.30600000	1.72700000	0.19600000
N	-0.86700000	1.78600000	0.24600000
Pt	0.28400000	-1.13600000	0.23100000
C	0.54200000	-3.16700000	0.66900000
H	1.49900000	-3.53200000	0.24400000
H	0.59900000	-3.32500000	1.76400000
H	-0.25700000	-3.84000000	0.29600000
S	-1.40000000	-1.55400000	-1.43900000
C	-0.70100000	-2.86100000	-2.53400000
H	-1.46300000	-3.17500000	-3.26600000
H	0.15300000	-2.40400000	-3.05300000
H	-0.35100000	-3.71300000	-1.93300000
C	-2.77400000	-2.51900000	-0.67900000
H	-3.30300000	-1.82300000	-0.01200000
H	-3.45600000	-2.87300000	-1.46900000
H	-2.36900000	-3.36100000	-0.09800000

4'

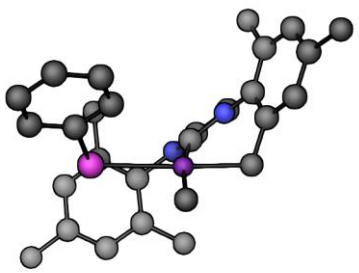
imaginary frequencies = 0

Sum of electronic & zero-point Energies= -1325.823740

Sum of electronic & thermal Energies= -1325.788666

Sum of electronic & thermal Enthalpies= -1325.787722

Sum of electronic & thermal Free Energies=-1325.899029



C	-1.71000000	-2.79100000	-2.09300000
C	2.10600000	-0.80300000	-1.81800000

C	4.41600000	-0.31200000	-0.90300000
C	6.76600000	0.25000000	-0.11900000
C	3.15200000	-0.91100000	-0.74700000
C	-2.56600000	-2.43200000	-0.90200000
C	-3.95900000	-2.27700000	-1.03000000
C	5.40600000	-0.37800000	0.09600000
C	2.89200000	-1.59800000	0.47000000
C	1.30400000	-3.43500000	1.16100000
C	5.09600000	-1.04600000	1.29200000
C	-0.05200000	-3.59000000	1.12700000
C	0.41900000	-1.52300000	0.22300000
C	-1.99600000	-2.22000000	0.37600000
C	-6.27900000	-1.81900000	-0.10300000
C	3.84200000	-1.65300000	1.51400000
C	-4.77800000	-1.93700000	0.06300000
C	3.56900000	-2.28500000	2.86500000
C	-4.17000000	-1.73500000	1.31500000
C	-2.78100000	-1.87000000	1.49900000
C	-2.15100000	-1.61200000	2.85000000
H	-2.33500000	-3.02800000	-2.96900000
H	-1.06200000	-3.65900000	-1.88100000
H	1.78200000	-1.80300000	-2.16600000
H	-1.04300000	-1.94400000	-2.34700000
H	2.49300000	-0.24200000	-2.68300000
H	7.38800000	-0.36100000	-0.79900000
H	4.62400000	0.22200000	-1.83800000
H	-4.41300000	-2.43400000	-2.01500000
H	6.68100000	1.25200000	-0.57400000
H	7.31900000	0.35300000	0.83000000
H	-6.54300000	-1.35000000	-1.06500000
H	2.08500000	-4.11400000	1.48800000
H	-6.76100000	-2.81400000	-0.08300000
H	-0.68700000	-4.41600000	1.43600000
H	5.84100000	-1.08000000	2.09600000
H	3.78600000	-3.36900000	2.87900000
H	-6.72900000	-1.21900000	0.70500000
H	2.52000000	-2.15600000	3.18100000
H	4.21300000	-1.82300000	3.63100000
H	-4.79000000	-1.46000000	2.17700000
H	-1.57400000	-2.47900000	3.21400000
H	-1.45000000	-0.76000000	2.79800000
H	-2.92200000	-1.37400000	3.60000000
N	1.58100000	-2.17200000	0.62900000
N	-0.57800000	-2.42200000	0.56200000
Pt	0.43200000	0.10400000	-1.02800000
C	0.60700000	1.55900000	-2.52200000
H	0.41100000	1.09100000	-3.50800000
H	-0.09500000	2.40800000	-2.42200000
H	1.63200000	1.97900000	-2.56400000
C	1.03900000	4.75900000	0.81700000
C	0.21300000	5.81600000	1.23100000
C	-1.17700000	5.62900000	1.31200000
C	-1.74800000	4.38700000	0.98300000
C	-0.89900000	3.34900000	0.57400000
C	0.49000000	3.50900000	0.48400000
H	2.12300000	4.90000000	0.74900000
H	0.65000000	6.78600000	1.48900000
H	-1.82700000	6.45000000	1.63200000
H	-2.83100000	4.24100000	1.04400000
H	1.11500000	2.67300000	0.14700000
I	-1.74700000	1.42200000	0.10500000

4'/5'^{TS}

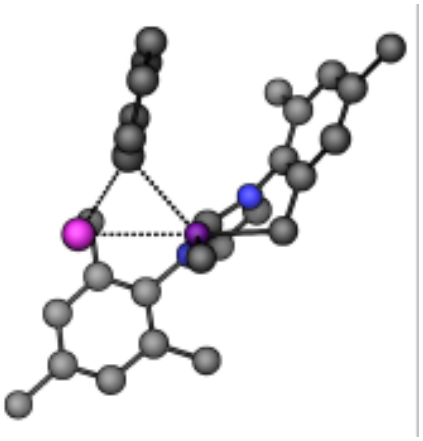
imaginary frequencies = 1 (-157 cm^{-1})

Sum of electronic & zero-point Energies= -1325.814475

Sum of electronic & thermal Energies= -1325.781006

Sum of electronic & thermal Enthalpies= -1325.780062

Sum of electronic & thermal Free Energies=-1325.883193



C	2.35978052	1.86345689	-2.31005938
C	-1.64776617	0.63144541	-2.03433808
C	-4.06415950	0.68832105	-1.28379274
C	-6.52702618	0.67676051	-0.66421965
C	-2.72295097	1.06138510	-1.08147300
C	3.12758032	1.58228905	-1.04081570
C	4.48219742	1.20588325	-1.08496945
C	-5.08950492	1.07143688	-0.39926868
C	-2.42055447	1.84574973	0.06437820
C	-0.57828650	3.47639347	0.60559444
C	-4.74165055	1.82952528	0.73041756
C	0.78368904	3.40408789	0.64248111
C	0.00979173	1.31355034	0.05974779
C	2.50891325	1.66133839	0.22784326
C	6.68949598	0.56907522	0.00042366
C	-3.41259210	2.22044466	0.99621219
C	5.22126260	0.93049772	0.08050477
C	-3.11521941	2.98055370	2.27430883
C	4.56806853	1.03147898	1.32262540
C	3.21242897	1.39306952	1.42370674
C	2.52864509	1.44287940	2.77179470
H	3.03251516	1.87679692	-3.18205304
H	1.83112136	2.83171060	-2.26283634
H	-1.11650449	1.50334141	-2.46454803
H	1.58965870	1.08135456	-2.46580052
H	-2.07159646	0.03843915	-2.85978966
H	-6.95429077	1.25806334	-1.50194946
H	-4.30596765	0.07940980	-2.16309553
H	4.97296443	1.13207929	-2.06294653
H	-6.60787795	-0.38914331	-0.93823378
H	-7.16378680	0.85111457	0.21844339
H	6.91226595	-0.01622440	-0.90705283
H	-1.24800862	4.31547676	0.76380805
H	7.32188200	1.47566573	-0.03354169
H	1.53721989	4.15656995	0.85901687
H	-5.52143303	2.11187485	1.44829456
H	-3.13357460	4.07709630	2.12937239
H	7.00936590	-0.02025197	0.87532642
H	-2.12834230	2.72346780	2.69245011
H	-3.87858351	2.74966332	3.03493222
H	5.12461247	0.81511771	2.24252849
H	1.99810711	2.39558908	2.93985055
H	1.77801506	0.63614866	2.85564754
H	3.25881306	1.30854828	3.58525355
N	-1.04070993	2.20107172	0.26789724
N	1.12918320	2.08712721	0.31406438
Pt	-0.22120106	-0.45224685	-1.00110991
C	-0.45226510	-1.94518183	-2.45269523
H	-0.18850943	-1.54352158	-3.45043298
H	0.20190639	-2.81968466	-2.27069025
H	-1.49849690	-2.30288370	-2.50636448
C	-2.27648449	-1.75919422	2.57633442
C	-3.00612149	-2.85689441	2.09160880
C	-2.50130279	-3.59932938	1.01051794
C	-1.28147244	-3.25562831	0.40758775
C	-0.58982482	-2.12088904	0.87478119
C	-1.05409486	-1.39432261	1.98987462
H	-2.64997432	-1.17942888	3.42736679
H	-3.95237280	-3.14125354	2.56228735
H	-3.05199002	-4.46673891	0.63039095
H	-0.89086683	-3.83850470	-0.42864058
H	-0.48251536	-0.54635509	2.37318842
I	1.63862555	-2.02990134	0.45430171

5'

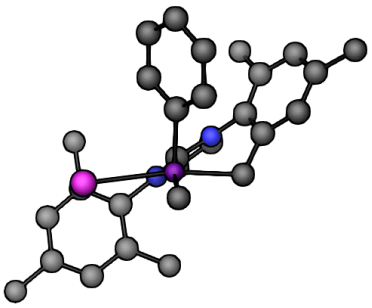
imaginary frequencies = 0

Sum of electronic & zero-point Energies=-1325.855841

Sum of electronic & thermal Energies= -1325.823413

Sum of electronic & thermal Enthalpies= -1325.822469

Sum of electronic & thermal Free Energies=-1325.921274



C	2.34900000	1.48800000	2.43100000
C	-1.64400000	0.19800000	1.93300000
C	-4.07000000	0.63800000	1.39100000
C	-6.54900000	0.95500000	0.94000000
C	-2.70900000	0.90100000	1.15100000
C	3.16400000	1.43000000	1.15900000
C	4.54100000	1.15500000	1.20400000
C	-5.09300000	1.23300000	0.63100000
C	-2.38400000	1.80400000	0.10700000
C	-0.52300000	3.42600000	-0.26500000
C	-4.72300000	2.08100000	-0.42500000
C	0.83800000	3.34900000	-0.32100000
C	0.05400000	1.21400000	-0.02700000

C	2.57100000	1.61000000	-0.10900000
C	6.81000000	0.80200000	0.11600000
C	-3.37700000	2.37600000	-0.72100000
C	5.32100000	1.06700000	0.03700000
C	-3.07000000	3.24300000	-1.92700000
C	4.68700000	1.25200000	-1.20500000
C	3.31100000	1.52000000	-1.30800000
C	2.64400000	1.62700000	-2.66000000
H	3.00400000	1.54100000	3.31500000
H	1.66600000	2.35400000	2.45300000
H	-1.03100000	0.91300000	2.52000000
H	1.72700000	0.57700000	2.54000000
H	-2.09200000	-0.52800000	2.63000000
H	-6.87600000	1.50100000	1.84400000
H	-4.32900000	-0.05900000	2.19700000
H	5.01500000	1.00200000	2.18100000
H	-6.72300000	-0.11700000	1.13100000
H	-7.20500000	1.26500000	0.11000000
H	7.06100000	0.17800000	0.99000000
H	-1.18800000	4.28200000	-0.30200000
H	7.38000000	1.74500000	0.21100000
H	1.59800000	4.11600000	-0.43600000
H	-5.50300000	2.51500000	-1.06200000
H	-3.02700000	4.32000000	-1.67700000
H	7.17500000	0.28700000	-0.78700000
H	-2.11300000	2.97500000	-2.40200000
H	-3.86600000	3.12600000	-2.68000000
H	5.27400000	1.16800000	-2.12700000
H	1.98600000	2.50900000	-2.74300000
H	2.02300000	0.73100000	-2.84000000
H	3.39600000	1.68300000	-3.46300000
N	-0.99300000	2.12200000	-0.09400000
N	1.17600000	2.00000000	-0.17700000
Pt	-0.19500000	-0.75900000	0.74000000
C	-0.36300000	-2.50800000	1.86700000
H	0.52200000	-2.52700000	2.53200000
H	-0.33500000	-3.41400000	1.24200000
H	-1.27800000	-2.51700000	2.48800000
C	-2.31300000	-1.69800000	-2.85200000
C	-3.44000000	-2.42500000	-2.43900000
C	-3.63300000	-2.67300000	-1.07300000
C	-2.71000000	-2.20400000	-0.11900000
C	-1.58800000	-1.47400000	-0.54200000
C	-1.38100000	-1.22200000	-1.91200000
H	-2.13800000	-1.50400000	-3.91600000
H	-4.15900000	-2.79700000	-3.17700000
H	-4.50700000	-3.24000000	-0.73100000
H	-2.87700000	-2.41000000	0.94000000
H	-0.49400000	-0.67900000	-2.24400000
I	1.99100000	-1.95600000	-0.47100000

5'/6'^{TS}

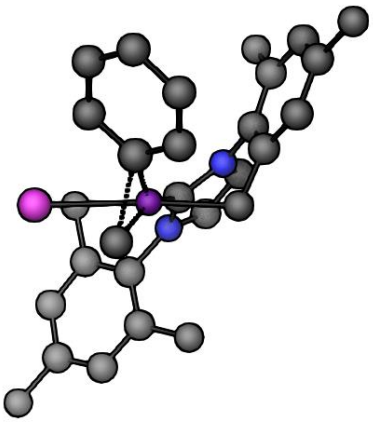
imaginary frequencies = 0

Sum of electronic & zero-point Energies= -1325.831110

Sum of electronic & thermal Energies= -1325.797482

Sum of electronic & thermal Enthalpies= -1325.796538

Sum of electronic & thermal Free Energies=-1325.897912



C	-2.31100000	1.16200000	2.66200000
C	1.52400000	0.57600000	1.77300000
C	3.89200000	1.22400000	1.09300000
C	6.29100000	1.72800000	0.43800000
C	2.50100000	1.33400000	0.92800000
C	-3.25000000	1.01600000	1.48700000
C	-4.56300000	0.54900000	1.67700000
C	4.79900000	1.88600000	0.24200000
C	2.02700000	2.16700000	-0.12000000
C	-0.05700000	3.53600000	-0.37000000
C	4.28200000	2.66000000	-0.80800000
C	-1.39200000	3.28300000	-0.26300000
C	-0.30900000	1.28600000	-0.02100000
C	-2.85600000	1.34200000	0.17100000
C	-6.86900000	-0.11400000	0.84200000
C	2.89600000	2.81400000	-1.02300000
C	-5.47200000	0.42300000	0.61300000
C	2.41800000	3.61900000	-2.21500000
C	-5.04400000	0.79100000	-0.67600000
C	-3.74100000	1.25100000	-0.92800000
C	-3.30000000	1.57900000	-2.33600000
H	-2.85200000	1.02500000	3.61200000
H	-1.82900000	2.15600000	2.68400000
H	0.84300000	1.26000000	2.31300000
H	-1.50100000	0.41100000	2.61400000
H	2.03800000	-0.04600000	2.52200000
H	6.58500000	1.94000000	1.48100000
H	4.27500000	0.59600000	1.90500000
H	-4.88300000	0.28700000	2.69300000
H	6.61400000	0.69500000	0.21600000
H	6.86000000	2.40600000	-0.21900000
H	-7.20600000	0.06100000	1.87700000
H	0.48100000	4.46700000	-0.50800000
H	-7.59900000	0.35000000	0.15800000
H	-2.25500000	3.94200000	-0.30400000
H	4.97300000	3.15300000	-1.50200000
H	2.25700000	4.68600000	-1.97000000
H	-6.90400000	-1.20500000	0.66500000
H	1.47600000	3.22800000	-2.63100000
H	3.17700000	3.59000000	-3.01300000
H	-5.74000000	0.70400000	-1.51800000
H	-2.91700000	2.61000000	-2.43500000
H	-2.49100000	0.89200000	-2.64300000
H	-4.13700000	1.45900000	-3.04100000
N	0.59800000	2.31300000	-0.22300000
N	-1.53800000	1.90800000	-0.05200000
Pt	0.29900000	-0.58300000	0.49400000
C	0.35900000	-2.51700000	1.58200000
H	-0.63500000	-2.15200000	1.91400000
H	0.20900000	-3.47800000	1.07600000
H	1.02900000	-2.60600000	2.44500000
C	3.07000000	-3.14500000	-1.52900000
C	4.26000000	-3.11500000	-0.78600000
C	4.23500000	-2.58600000	0.51300000
C	3.04400000	-2.07600000	1.05100000
C	1.84800000	-2.05700000	0.29400000
C	1.87000000	-2.64800000	-0.99400000
H	3.05900000	-3.57200000	-2.53800000

H	5.18900000	-3.51700000	-1.20500000
H	5.14300000	-2.57700000	1.12500000
H	3.05400000	-1.70200000	2.07800000
H	0.95100000	-2.70300000	-1.58100000
I	-1.60300000	-1.81600000	-1.18300000

3a

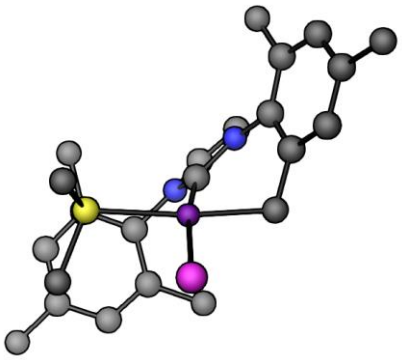
imaginary frequencies = 0

Sum of electronic & zero-point Energies= -1144.444479

Sum of electronic & thermal Energies= -1144.411625

Sum of electronic & thermal Enthalpies= -1144.410681

Sum of electronic & thermal Free Energies=-1144.511960



C	2.07492795	0.66232543	-2.68837357
C	-1.76638718	-0.20744365	-1.44685413
C	-4.14944520	0.20979596	-0.67627380
C	-6.56587774	0.50583306	0.04511887
C	-2.81364201	0.63617665	-0.78184476
C	2.95842464	1.00244825	-1.51151896
C	4.31408602	0.62353523	-1.49729123
C	-5.13043328	0.98177242	-0.02555927
C	-2.47335558	1.88698847	-0.20066301
C	-0.62088637	3.55629886	-0.61456194
C	-4.74145180	2.20069571	0.55440314
C	0.74083961	3.48153784	-0.66324179
C	-0.03883093	1.38403964	-0.16547294
C	2.45981061	1.69573640	-0.38355874
C	6.63190424	0.54829139	-0.45775411
C	-3.41409461	2.67479267	0.49675191
C	5.16659615	0.92747240	-0.41922651
C	2.68767265	-2.04705474	1.16455517
C	-3.06447452	3.96404809	1.21439188
C	4.62863411	1.62338977	0.67939783
C	3.27948509	2.02027265	0.72312014
C	0.58643990	-1.88318588	3.01975211
C	2.72784511	2.74175640	1.93269929
H	2.67274881	0.27326409	-3.52735245
H	1.51033379	1.54246653	-3.04227550
H	-1.30999722	0.32180441	-2.30603171
H	1.33093976	-0.10398045	-2.39850576
H	-2.19477582	-1.15312960	-1.81013595
H	-7.06935872	0.60812310	-0.93380010
H	-4.42071589	-0.75782288	-1.11416393
H	4.71425806	0.08333690	-2.36364248
H	-6.62250108	-0.55966765	0.32596676
H	-7.14906917	1.08467156	0.77979277
H	6.79396541	-0.38415578	-1.02307060
H	-1.29019898	4.38957579	-0.79971022
H	7.23244729	1.33584065	-0.94949515
H	1.49391006	4.23463678	-0.87797209
H	3.26900751	-1.52803064	0.38835127
H	-5.48482053	2.79938879	1.09468614
H	2.19473928	-2.93600477	0.74051905
H	-3.11337362	4.84731204	0.54988591
H	7.04156078	0.41110007	0.55638281
H	3.34036685	-2.30690827	2.01316306
H	-2.05263581	3.93752852	1.65148804
H	-3.78132177	4.14391691	2.03169027
H	0.19048984	-2.80241815	2.56049202
H	5.27492730	1.86603741	1.53147615
H	2.25918231	3.70538104	1.66898962
H	1.95463708	2.12918185	2.42941473
H	-0.24396471	-1.28204037	3.41814393
H	1.31173040	-2.10307470	3.81957147
H	3.52688733	2.94088885	2.66388453
I	-0.66091668	-3.25122852	-0.29012982
N	-1.09130112	2.28004275	-0.29559734
N	1.08790312	2.15382948	-0.38504545
Pt	-0.25260201	-0.57595860	-0.05687427
S	1.40682545	-0.85447397	1.73199108

3a''

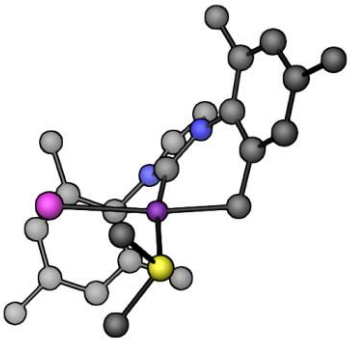
imaginary frequencies = 0

Sum of electronic & zero-point Energies= -1144.440614

Sum of electronic & thermal Energies= -1144.407972

Sum of electronic & thermal Enthalpies= -1144.407028

Sum of electronic & thermal Free Energies=-1144.507449

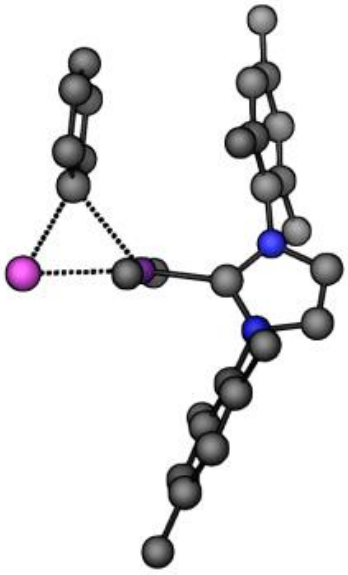


C	1.84679668	-0.97172285	2.82238472
C	-1.88302928	0.18162374	1.70251874
C	-4.28485273	-0.02726172	0.89123149
C	-6.71028285	-0.12612138	0.14041865
C	-2.96002680	-0.49932880	0.90946417
C	2.76664810	-1.20022769	1.64550021
C	4.14013701	-0.91322869	1.74135559
C	-5.28463670	-0.63478319	0.10720029

C	-2.65286812	-1.62907785	0.10364535
C	-0.87894878	-3.41811128	0.25020033
C	-4.92514897	-1.72769759	-0.69803901
C	0.48146149	-3.40755735	0.35054959
C	-0.19652428	-1.23239236	0.17705888
C	2.28608775	-1.69755334	0.41407410
C	6.49053607	-0.76862714	0.78684383
C	-3.61079237	-2.24038818	-0.73165690
C	5.02254623	-1.11773622	0.66561937
C	-3.28775177	-3.37495923	-1.68386707
C	4.50164382	-1.63420579	-0.53452661
C	3.13611237	-1.92876419	-0.69118298
C	2.60291453	-2.42388051	-2.01593144
H	2.42316087	-0.71098721	3.72424317
H	1.23815328	-1.86513323	3.04909311
H	-1.43700797	-0.50107326	2.45080898
H	1.14074089	-0.14835125	2.60111089
H	-2.28874213	1.05643316	2.23839656
H	-7.24193417	-0.48655176	1.04055893
H	-4.53697225	0.84011194	1.51357186
H	4.52939128	-0.52534505	2.69053948
H	-6.74589003	0.97625249	0.16508066
H	-7.28221403	-0.46692536	-0.73806668
H	6.83570024	-0.82337939	1.83259861
H	-1.58596596	-4.24043062	0.27218543
H	7.11903439	-1.44285234	0.18139398
H	1.20027744	-4.21489992	0.45765407
H	-5.68100606	-2.19055776	-1.34388692
H	-3.37353768	-4.36833674	-1.20464828
H	6.68110735	0.26066176	0.43149931
H	-2.26876642	-3.29370895	-2.09597954
H	-3.99587380	-3.36861110	-2.52798652
H	5.17364763	-1.80157263	-1.38463329
H	2.01379408	-3.35203674	-1.91850649
H	1.94375338	-1.65670579	-2.46233769
H	3.42866054	-2.61574690	-2.71885824
N	-1.28755013	-2.08729997	0.13414351
N	0.88994584	-2.06963076	0.30193581
Pt	-0.38384806	0.73210889	0.34031817
I	1.37992757	1.37849524	-1.70670268
S	-0.82031188	3.02441639	0.85078001
C	0.80159736	3.85645634	1.11036548
H	0.62941527	4.93699664	1.23804751
H	1.22745887	3.43130522	2.03067195
H	1.46239621	3.64023317	0.25632389
C	-1.33039814	3.85056820	-0.71531885
H	-1.44544901	4.92962318	-0.52577658
H	-0.58112807	3.64360758	-1.49550919
H	-2.29732047	3.41095516	-0.99964706

4/5_*trans*alkyl^{TS}

imaginary frequencies = 1 (-163 cm^{-1})
Sum of electronic & zero-point Energies= -1366.269752
Sum of electronic & thermal Energies= -1366.233319
Sum of electronic & thermal Enthalpies= -1366.232375
Sum of electronic & thermal Free Energies=-1366.341403



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C	-3.06224964	-2.18074190	2.56092708
C	-5.02182132	-1.09221998	1.38468582
C	-7.05540019	0.04233997	0.36760616
C	-3.70938683	-1.59289346	1.32592082
C	2.57785778	-1.95396025	1.12134310
C	3.98342021	-1.92662237	1.09195225
C	-5.65618622	-0.52588774	0.26407797
C	-3.02402918	-1.51125287	0.08930131
C	-1.50404619	-3.46878483	0.02343797
C	-4.94784889	-0.48761265	-0.94936826
C	-0.16062382	-3.68739125	-0.00130716
C	-0.47896106	-1.41128320	-0.03924049
C	1.90136833	-2.31421689	-0.06632623
C	6.22638667	-2.18781967	-0.07129429
C	-3.63405415	-0.97832763	-1.06823676
C	4.71404903	-2.25546069	-0.06385694
C	-2.92028296	-0.92662130	-2.39734223
C	4.00137068	-2.63705201	-1.21417109
C	2.59522192	-2.68133925	-1.24313662
C	1.87284913	-3.12255270	-2.49743198
H	2.52367248	-1.51516214	3.23606890
H	1.10164437	-2.42190478	2.64679918
H	-2.84559475	-3.25779012	2.44887105
H	1.25633207	-0.69212978	2.27562048
H	-3.72122698	-2.06051934	3.43503071
H	-7.65669234	-0.49469291	1.11997335
H	-5.55943606	-1.14256115	2.33919807
H	4.51937514	-1.64751245	2.00671957
H	-7.02905457	1.10559889	0.66934814
H	-7.58599003	-0.00948021	-0.59750093

H	6.57651685	-1.16072680	-0.28292317
H	-2.34581048	-4.15510158	0.04277387
H	6.64962094	-2.47920036	0.90470775
H	0.42068203	-4.60472745	0.01907564
H	-5.43105120	-0.07011132	-1.84097147
H	-2.41865541	-1.88142388	-2.63132562
H	6.65836104	-2.84617207	-0.84286251
H	-2.13574700	-0.14983330	-2.38354249
H	-3.62738349	-0.69821912	-3.21054584
H	4.55239898	-2.91383086	-2.12115473
H	1.34913818	-4.08528375	-2.35853080
H	1.11701209	-2.38041110	-2.80275261
H	2.58557871	-3.24844937	-3.32762439
N	-1.69530624	-2.08252062	0.00661822
N	0.45935744	-2.43313896	-0.04508418
Pt	-0.20999591	0.52451484	-0.16313922
C	0.57604818	0.26240766	-2.15524361
H	1.61072967	-0.12469360	-2.13006032
H	-0.02178952	-0.44276953	-2.76322602
H	0.58542978	1.22098354	-2.70943194
H	-2.10608301	-1.67656915	2.78070321
C	-1.12382058	0.83365679	1.76464658
H	-2.20788200	0.63124863	1.69862261
H	-0.71288907	0.19055111	2.56747789
H	-1.02634031	1.88117584	2.10729197
I	-0.20060666	3.25308590	-0.50407148
C	2.72627204	2.01829378	-0.54968113
C	4.02212675	1.90078270	-0.02336293
C	4.24107971	1.93918718	1.36395091
C	3.14900529	2.09692582	2.23265828
C	1.84233573	2.21783821	1.73046874
C	1.64271927	2.13599002	0.33991492
H	2.56097704	2.00261607	-1.62807701
H	4.86471922	1.79171004	-0.71468002
H	5.25734990	1.86540644	1.76403605
H	3.30442467	2.14222753	3.31622648
H	0.99766884	2.35622366	2.40698096

4'/5' *trans*alkyl^{TS}

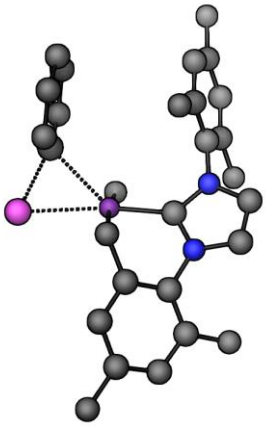
imaginary frequencies = 1 (-145 cm^{-1})

Sum of electronic & zero-point Energies= -1325.800906

Sum of electronic & thermal Energies= -1325.767347

Sum of electronic & thermal Enthalpies= -1325.766403

Sum of electronic & thermal Free Energies-1325.868511

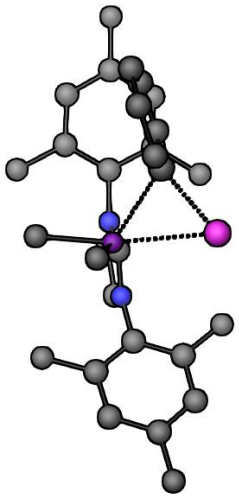


C	-2.36306100	0.81007900	2.36879100
C	1.65570600	-0.37764800	1.37239600
C	4.13741400	-0.00517900	0.94036400
C	6.62466200	0.23118300	0.48846500
C	2.81398600	0.47802300	0.98436500
C	-3.04381600	1.33345500	1.12621400
C	-4.41649400	1.11790500	0.90290700
C	5.21339800	0.78082400	0.48733000
C	2.60490300	1.81868400	0.55184600
C	0.82817500	3.53676300	1.06270100
C	4.94840000	2.08749600	0.04557600
C	-0.53017700	3.58318200	0.94090600
C	0.15200500	1.53848400	0.17255800
C	-2.32923100	2.06149800	0.15117000
C	-6.54612800	1.34151800	-0.46710100
C	3.64515900	2.62911600	0.05272700
C	-5.07345000	1.60988400	-0.23906600
C	3.42776400	4.02061500	-0.51018000
C	-4.32398800	2.34726300	-1.17511900
C	-2.94956500	2.58920500	-1.00427100
C	-2.16642900	3.37335100	-2.03340000
H	-3.09629000	0.36196300	3.05682800
H	-1.82832600	1.61229900	2.90763600
H	1.11510500	0.03948000	2.24398100
H	-1.61677300	0.03905200	2.10808600
H	2.00834700	-1.38899800	1.63889300
H	7.05015300	0.22187900	1.50915000
H	4.32321700	-1.03340700	1.27406700
H	-4.98668100	0.55527600	1.65163600
H	6.65322100	-0.80809500	0.11872300
H	7.29563300	0.83651500	-0.14293700
H	-7.06734300	1.11492600	0.47742300
H	1.52978100	4.26138600	1.46209900
H	-7.04725700	2.20468800	-0.93663000
H	-1.25067000	4.35486600	1.19646300
H	5.76941700	2.70452900	-0.33890000
H	3.45930000	4.80545600	0.26909400
H	-6.69343200	0.47674700	-1.14003900
H	2.46037300	4.11368100	-1.03067100
H	4.22466800	4.26033600	-1.23256500
H	-4.82034400	2.74704000	-2.06760900
H	-1.66611200	4.25337700	-1.59279800
H	-1.37964300	2.74496800	-2.48542900
H	-2.82827200	3.72643000	-2.83961200
N	1.24278800	2.29649600	0.57830200
N	-0.93430600	2.36150700	0.38789400

Pt	0.30668500	-0.34084400	-0.34536800
C	-0.81145200	-0.11495700	-2.15091100
H	-1.84232400	0.24182100	-1.97755700
H	-0.30470300	0.61557600	-2.81113500
H	-0.87361900	-1.06242400	-2.72049600
I	0.90399700	-2.94379100	-1.00854000
C	-0.83828200	-2.49417200	0.38678100
C	-0.63727500	-2.79618200	1.74700200
C	-2.12595400	-2.47311200	-0.18039900
C	-1.75989300	-3.01291900	2.56248500
H	0.37051300	-2.85109600	2.16302300
C	-3.23221300	-2.69109800	0.65749700
H	-2.26118900	-2.26796400	-1.24371200
C	-3.05721700	-2.96322900	2.02461700
H	-1.60828300	-3.23466300	3.62445700
H	-4.23737800	-2.65464100	0.22449600
H	-3.92539800	-3.15044700	2.66450200

4/5_rotTS

imaginary frequencies = 1 (-184.7 cm^{-1})
Sum of electronic & zero-point Energies= -1366.272608
Sum of electronic & thermal Energies= -1366.234883
Sum of electronic & thermal Enthalpies= -1366.233939
Sum of electronic & thermal Free Energies=-1366.346373

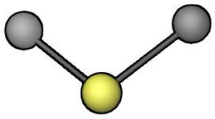


C	-2.94180000	-2.06489700	-2.32487600
C	2.47694500	-2.85067000	-2.17623400
C	4.42066100	-2.24617300	-0.67574500
C	6.48793400	-1.69163200	0.69443000
C	3.02981600	-2.38399200	-0.84928700
C	-3.49933400	-1.54565000	-1.02078400
C	-4.81836700	-1.05929700	-0.95814900
C	4.98957500	-1.85215900	0.54771100
C	2.19731500	-2.09305800	0.25430200
C	0.22270000	-3.54765700	0.48606100
C	4.12717400	-1.61110700	1.63380900
C	-1.13207900	-3.39630800	0.48865400
C	-0.21700000	-1.33760400	-0.04745400
C	-2.73415400	-1.52689200	0.16680500
C	-6.78930800	-0.01670200	0.25992900
C	2.73067000	-1.73209100	1.51615100
C	-5.38295600	-0.57563400	0.23504500
C	1.83464800	-1.48800400	2.71088300
C	-4.60238200	-0.62081600	1.40486300
C	-3.28162500	-1.10142800	1.40061600
C	-2.48555400	-1.17286900	2.68363300
H	-2.35341300	-2.98737800	-2.18455100
H	-2.26900800	-1.31977000	-2.78164000
H	3.26885200	-3.31963300	-2.78166500
H	-3.75442900	-2.27840600	-3.03742200
H	2.06224800	-2.00700500	-2.75264400
H	6.82267100	-1.93294100	1.71696300
H	5.07760800	-2.46955800	-1.52500600
H	-5.42121400	-1.06462200	-1.87434200
H	7.03509700	-2.34067200	-0.00885800
H	6.79984200	-0.65122600	0.48774100
H	-7.42357300	-0.48030700	-0.51374900
H	0.85292400	-4.40996300	0.68754900
H	-7.27138600	-0.17327800	1.23929900
H	-1.93617700	-4.10123300	0.68282100
H	4.55051000	-1.33269900	2.60642400
H	1.15401300	-2.33868400	2.88918400
H	-6.78415300	1.07214000	0.06886700
H	1.19804200	-0.59608400	2.56540600
H	2.43457200	-1.33154400	3.62107900
H	-5.03456600	-0.28087300	2.35382500
H	-2.15801600	-2.20412400	2.90615800
H	-1.57443800	-0.55189100	2.62248700
H	-3.08675100	-0.81706400	3.53517900
N	0.76751900	-2.29810500	0.16001500
N	-1.38610800	-2.06128200	0.16728900
Pt	-0.34166700	0.58152100	-0.90027300
C	-1.03323900	2.21878600	-2.00530200
H	-1.92319400	1.89977000	-2.57935800
H	-1.34906700	3.04365600	-1.33887000
H	-0.28193900	2.60572600	-2.71754600
C	3.67165300	2.02839400	-0.13935100
C	3.75694500	3.24283000	-0.83781600
C	2.59008100	3.99833600	-1.04470100
C	1.34580000	3.54667600	-0.57829700
C	1.27446200	2.29528400	0.06228600
C	2.43746800	1.55954000	0.34290500
H	4.56838800	1.42900600	0.05095700
H	4.72377400	3.60948600	-1.19687500
H	2.63876500	4.96113500	-1.56551100
H	0.44892400	4.14659000	-0.74167100
H	2.38750600	0.62446600	0.89861800
I	-0.51183400	2.04661000	1.53343800
H	1.66131900	-3.58157100	-2.04826100
C	0.07675900	-0.17988600	-2.77505700
H	1.10250600	0.15016400	-3.02060500
H	0.03313700	-1.28069500	-2.79628400
H	-0.60891600	0.22389400	-3.53989800

SMe_2

imaginary frequencies = 0
Sum of electronic & zero-point Energies= -89.983511

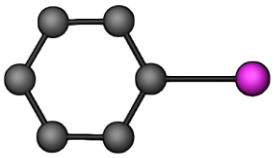
Sum of electronic & thermal Energies= -89.978529
Sum of electronic & thermal Enthalpies= -89.977585
Sum of electronic & thermal Free Energies= -90.010006



S	0.00000000	0.00000000	0.66870704
C	-0.00000000	-1.40126403	-0.52079791
C	0.00000000	1.40126403	-0.52079791
H	0.90239896	-1.38703034	-1.15274531
H	-0.00032656	-2.32349110	0.08041462
H	-0.90255250	-1.38668047	-1.15253818
H	-0.90239896	1.38703034	-1.15274531
H	0.00032656	2.32349110	0.08041462
H	0.90255250	1.38668047	-1.15253818

PhI

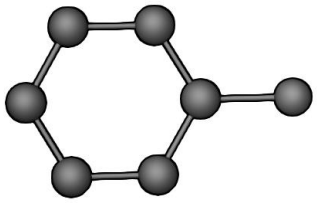
imaginary frequencies = 0
Sum of electronic & zero-point Energies= -243.035188
Sum of electronic & thermal Energies= -243.029122
Sum of electronic & thermal Enthalpies= -243.028177
Sum of electronic & thermal Free Energies= -243.067092



C	-2.66648171	-1.21420358	0.00000027
C	-1.26108271	-1.22491689	-0.00000061
C	-0.57687604	-0.00002588	-0.00000104
C	-1.26106037	1.22489919	-0.00000034
C	-2.66643761	1.21423018	-0.00000085
C	-3.37070611	0.00001425	0.00000036
H	-3.20729143	-2.16641364	0.00000523
H	-0.71254188	-2.17020115	-0.00000503
H	-0.71245542	2.17014697	-0.00000211
H	-3.20725954	2.16643314	0.00000514
H	-4.46516619	0.00005103	0.00000009
I	1.56831287	0.00000000	0.00000019

Toluene

imaginary frequencies = 0
Sum of electronic & zero-point Energies= -271.463634
Sum of electronic & thermal Energies= -271.457233
Sum of electronic & thermal Enthalpies= -271.456289
Sum of electronic & thermal Free Energies= -271.494542



C	-1.20714273	1.21221647	0.00229161
C	0.19605501	1.20931537	-0.00916538
C	0.92040507	0.00002931	-0.01193512
C	0.19606714	-1.20937098	-0.00918833
C	-1.20700288	-1.21226096	0.00233655
C	-1.91481165	0.00001685	0.00875433
H	-1.74859517	2.16435051	0.00128798
H	0.74106716	2.16069395	-0.01818164
H	0.74127038	-2.16064581	-0.01827771
H	-1.74862607	-2.16429397	0.00130063
H	-3.00971317	-0.00014683	0.01391610
C	2.43473027	0.00003672	0.00943106
H	2.82089612	0.00015855	1.04563076
H	2.84699062	-0.89219832	-0.49030433
H	2.84690878	0.89218526	-0.49052009