Electronic Supplementary Material (ESI) for Chemical Science
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Supporting Information

Frustrated Lewis Pair-Like Splitting of Aromatic C-H bonds and Abstraction of Halogen Atoms by a Cationic $[(^{F}PNP)Pt]^{+}$ Species

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I. General considerations.

Unless otherwise noted, all manipulations and reactions were performed under argon, using standard glovebox and Schlenk line techniques. Toluene, triethylamine, pentane, C_6H_6 and C_6D_6 were dried over NaK/Ph_2CO/18-crown-6, distilled and stored over molecular sieves in an Ar-filled glovebox. Diethyl ether was dried and deoxygenated (by purging) using a solvent purification system and stored over molecular sieves in an Ar-filled glovebox. Fluorobenzene, 1,4-dioxane, acetonitrile, chlorobenzene, bromobenzene, CH_2Cl_2 and CD_2Cl_2 were dried over CaH_2, distilled or vacuum transferred and stored over molecular sieves in an Ar-filled glove box. 2-Bromotoluene, 3-bromotoluene and 4-bromotoluene were degassed and stored over molecular sieves in an Ar-filled glovebox. Triflic acid (HOTf) was vacuum transferred before use. Potassium tetrakis(pentafluorophenyl)borate (K-BARF) was dried under vacuum overnight at ambient temperature and stored in an Ar-filled glovebox. (^{F}PNP)PtCl, (^{F}PNP)PtH and (^{F}PNP)PtMe were prepared according to literature procedures.[1] All other chemicals were used as received from commercial vendors. NMR spectra were recorded on a Varian iNova 300 (^{1}H NMR, 299.951 MHz; ^{13}C NMR, 75.426 MHz; ^{31}P NMR, 121.422 MHz; ^{19}F NMR, 282.211 MHz), a Varian NMRS 500 (^{1}H NMR, 499.682 MHz; ^{13}C NMR, 125.660 MHz; ^{31}P NMR, 202.265 MHz; ^{19}F NMR, 470.111 MHz) or a Varian iNova 400 (^{1}H NMR, 399.532 MHz; ^{13}C NMR, 100.473 MHz). Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C NMR, the residual solvent peak was used to reference the spectra. ^{1}H NMR spectra in C_6D_5Br were referenced by setting the most downfield signal to 7.30 ppm. $^{13}C\{^1H\}$ NMR spectra in C_6D_5Br were referenced by setting the most downfield signal to 130.9 ppm. ^{19}F NMR signals (-134.3, -164.8, -168.7 ppm) and $^{13}C\{^1H\}$ NMR signals (149.5, 147.6, 139.6, 137.6, 135.7, 124.3 ppm) for $[BARF]^-$ were consistent between spectra and are not included below. ^{31}P NMR spectra were

referenced using 85% H_3PO_4 at δ 0 ppm. ^{19}F NMR spectra were referenced using CF_3CO_2H at δ -78.5 ppm. ^1H-^1H COSY experiments were used in the assignment of ^1H NMR signals. Elemental analysis was performed by Complete Analysis Laboratories Inc., Parsippany, NJ, USA. FT-IR spectra were collected using a Bruker ALPHA-P FT-IR spectrometer with a diamond ATR.

II. Synthetic Methods and Characterization.

II-A. Syntheses of starting and auxiliary materials.

(^{F}PNP)PtOTf (1). In a 50 mL Teflon screw-capped round-bottomed flask, (^{F}PNP)PtH (1.69 g, 2.67 mmol) was dissolved in 20 mL of toluene, forming a clear, yellow solution. MeOTf (332 μL, 2.94 mmol) was added via syringe, and the flask was placed in an oil bath at 110°C for 24 h. During the course of the reaction, a brown solid precipitate formed that is believed to be [(^{F}PN(Me)P)PtH][OTf]. With continued heating, this intermediate loses methane to generate the final product. The resulting orange solution was filtered over Celite, and the volatiles were removed, yielding an oily yellow residue. The residue was redissolved in a minimal amount of toluene and layered with pentane. After recrystallization at -35°C, yellow-orange crystals were collected, washed with cold pentane and dried under vacuum, yielding a yellow solid. Isolated yield: 1.88 g, 90%. ^{1}H NMR (C_6D_6): δ 7.22 (m, 2H, Ar-*H*), 6.70 (m, 2H, Ar-*H*), 6.52 (m, 2H, Ar-*H*), 2.50 (m, 4H, C*H*Me$_2$), 1.26 (vtd, J_{P-H} = 8.7 Hz, J_{H-H} = 7.0 Hz, 12H, CH*Me*$_2$), 0.90 (vtd, J_{P-H} = 8.1 Hz, J_{H-H} = 7.2 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.3 (vt, J_{P-C} = 9.4 Hz, C_{Ar}-N), 155.7 (d, J_{F-C} = 240 Hz, C_{Ar}-F), 119.0 (m, C_{Ar}-P), 118.8 (q, J_{F-C} = 318 Hz, *C*F$_3$), 118.4 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 118.1 (d, J_{F-C} = 22 Hz, C_{Ar}-H), 116.4 (m, C_{Ar}-H), 25.2 (vt, J_{P-C} = 15 Hz, *C*HMe$_2$), 18.1 (CH*Me*$_2$), 17.5 (CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -77.7, -126.9. ^{31}P{^{1}H} NMR (C_6D_6): δ 45.8 ($J_{195Pt-P}$ = 2,713 Hz).

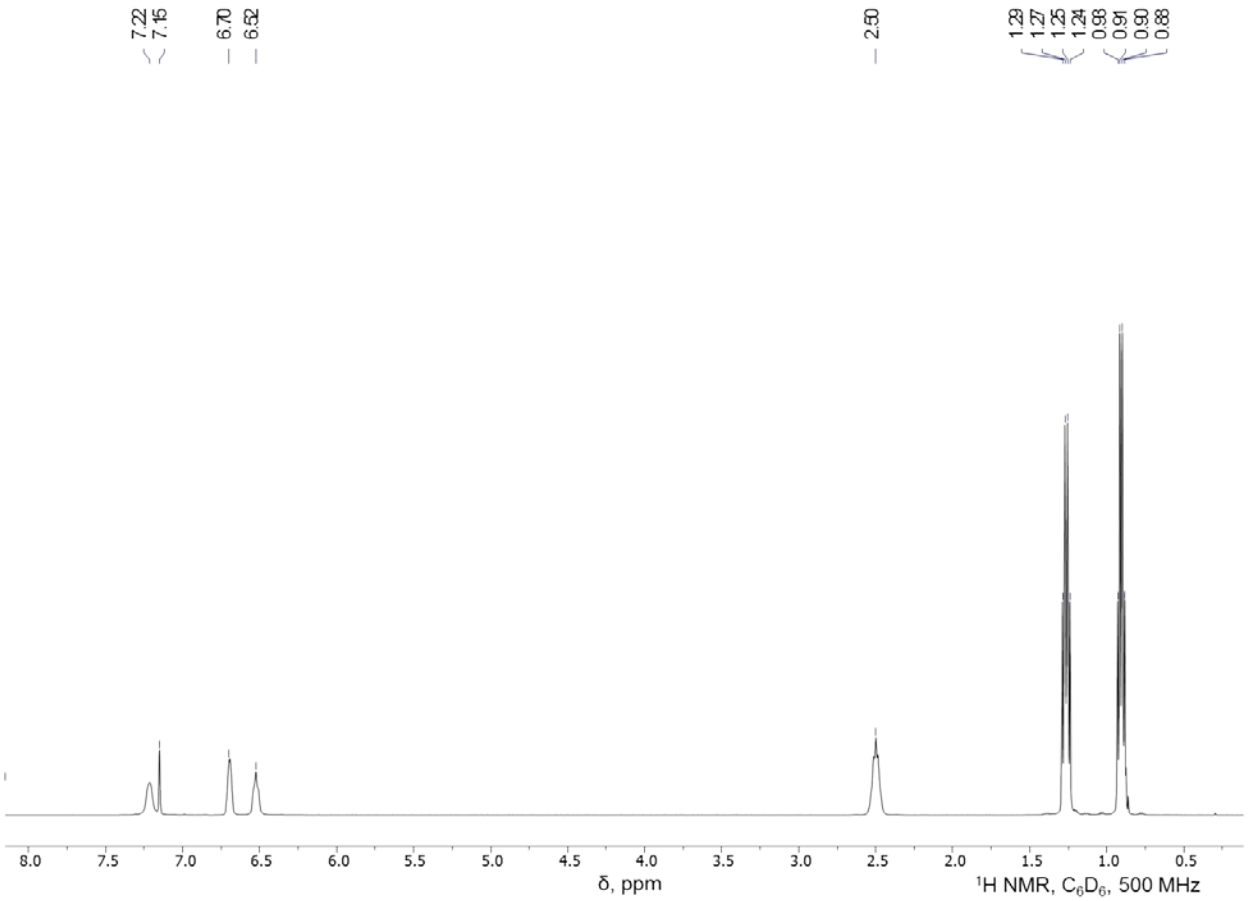


Figure S1. ^{1}H NMR spectrum of **1** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

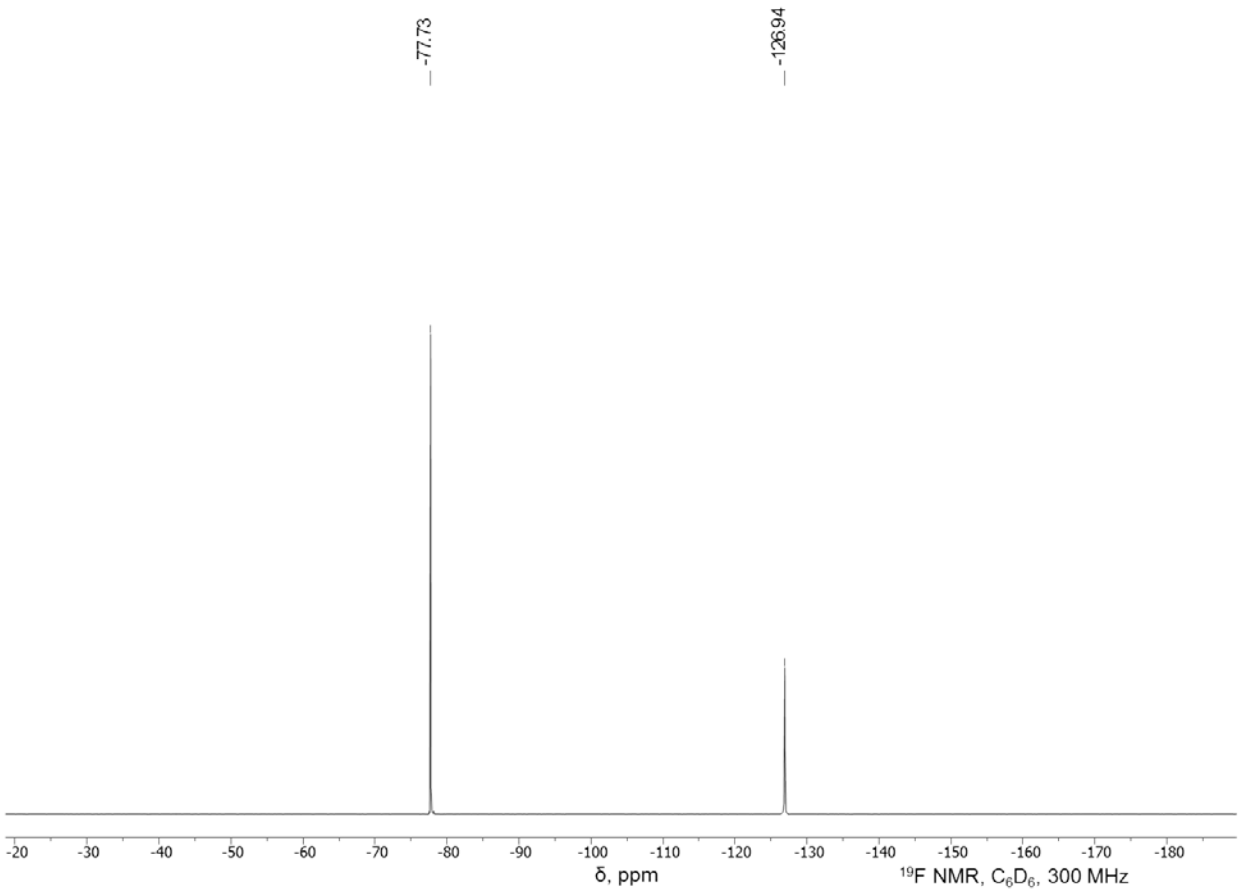


Figure S2. ^{19}F NMR spectrum of **1** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

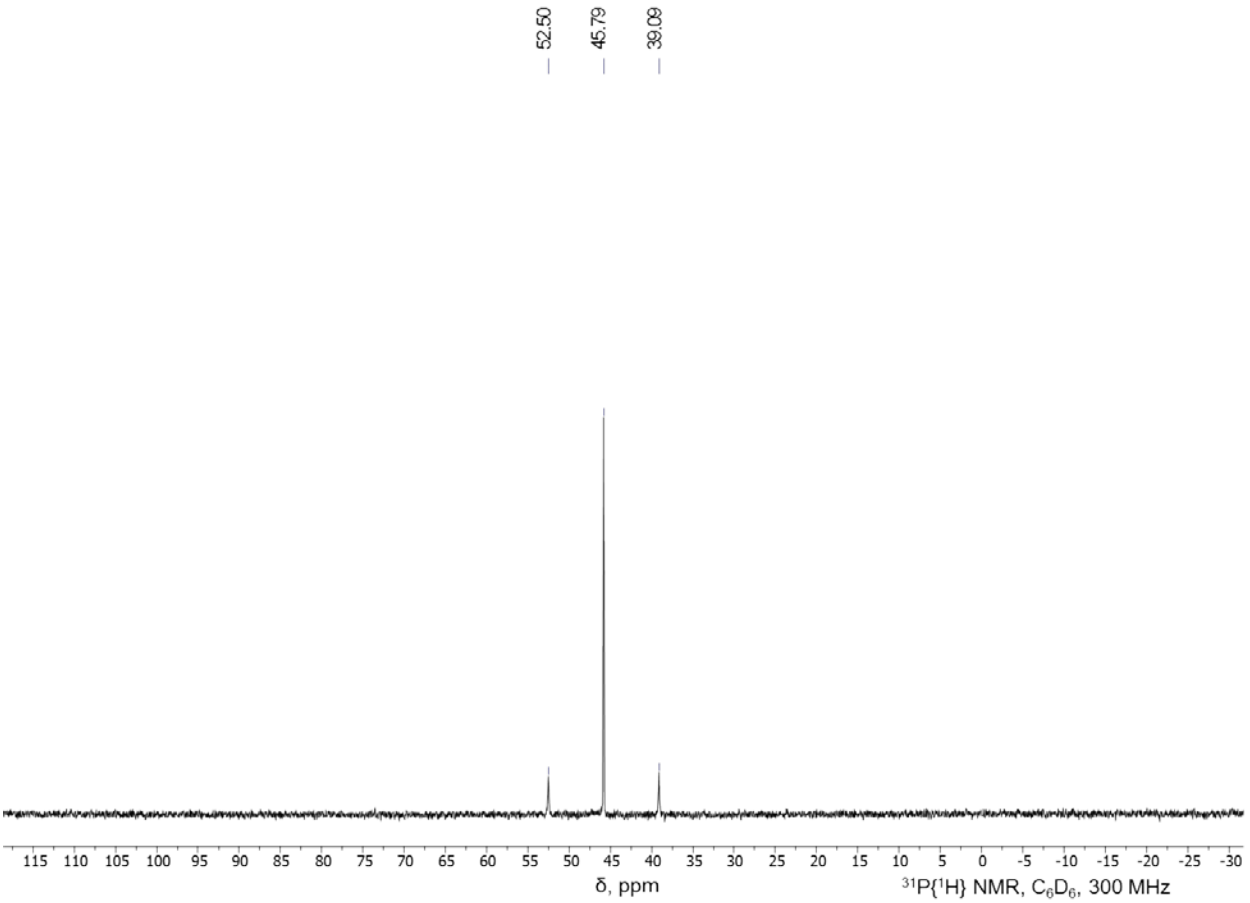


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

(PNP)PtBr (12). In a J. Young NMR tube, **1** (17.9 mg, 0.0229 mmol) was dissolved in C_6D_6. Me_3SiBr (3.0 µL, 0.023 mmol) was added via syringe, and the solution remained clear yellow with full conversion to **12** observed by NMR. ^{1}H NMR (C_6D_6): δ 7.38 (m, 2H, Ar-*H*), 6.75 (m, 2H, Ar-*H*), 6.63 (vtd, J_{P-H} = 8.5 Hz, J_{H-H} = 3 Hz, 2H, Ar-*H*), 2.35 (m, 4H, C*H*Me_2), 1.31 (vtd, J_{P-H} = 8 Hz, J_{H-H} = 7 Hz, 12H, CH*Me*$_2$), 0.96 (app q (dvt), J = 8 Hz, 12H CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -128.5. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 40.65 ($J_{195Pt-P}$ = 2,635 Hz).

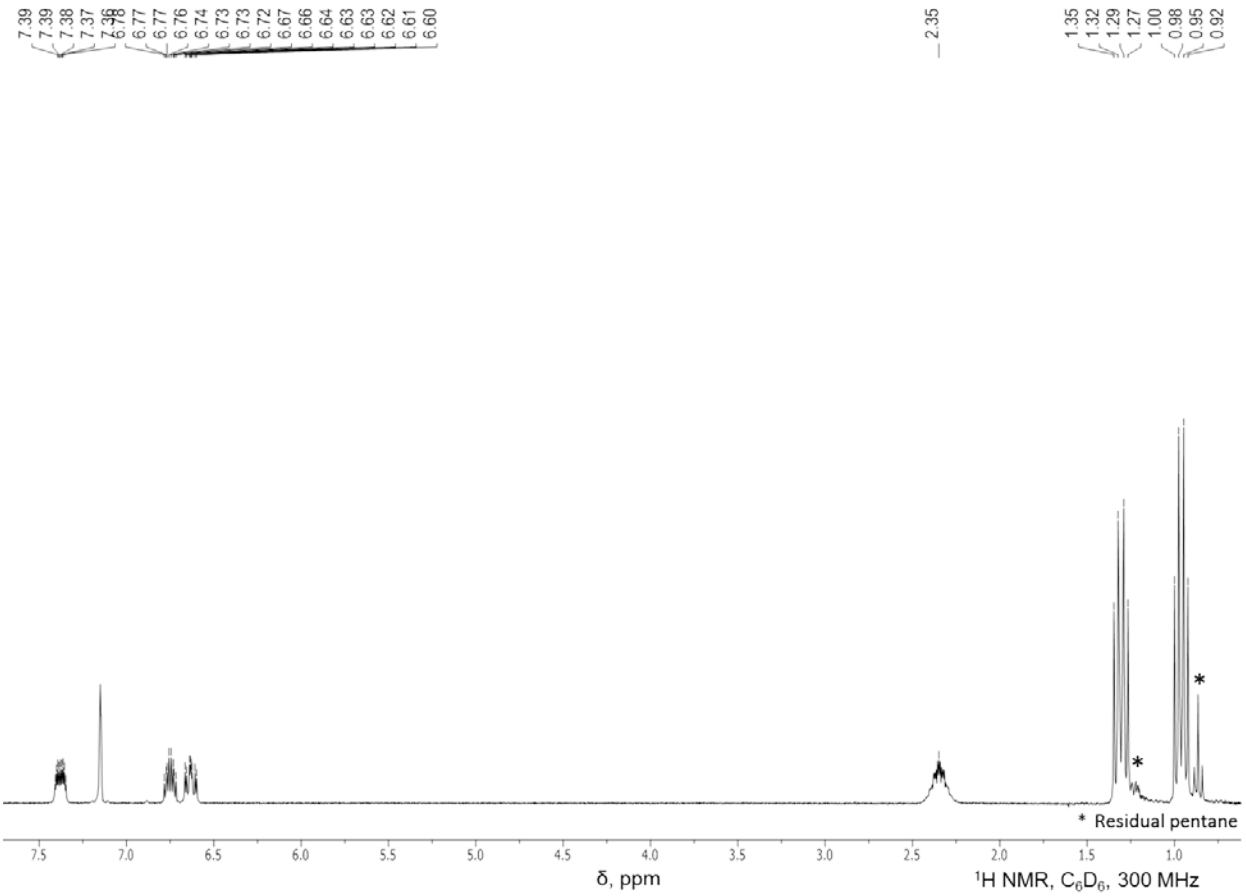


Figure S4. ^{1}H NMR spectrum of **12** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

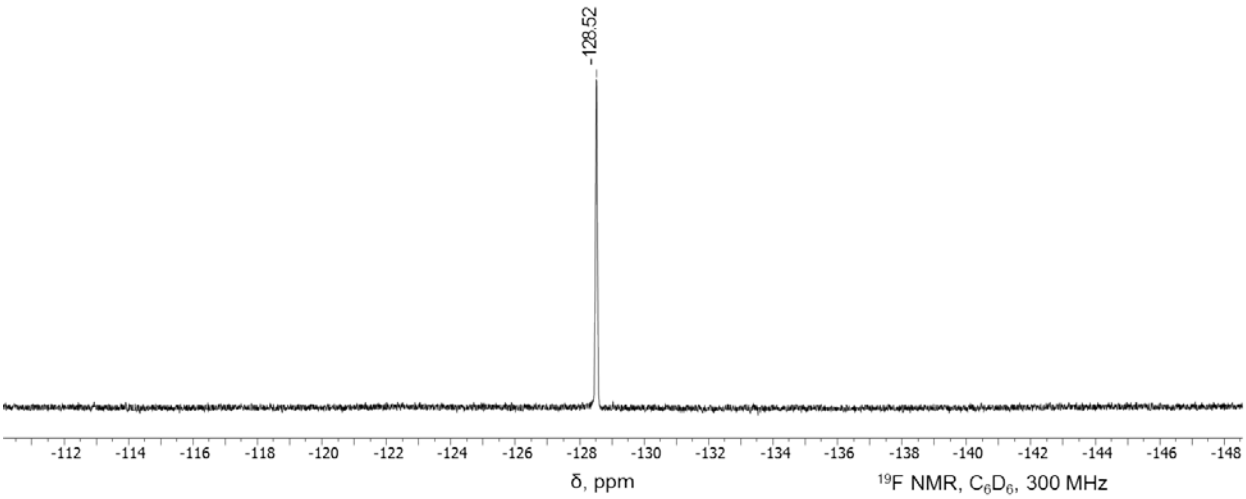


Figure S5. ^{19}F NMR spectrum of **12** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

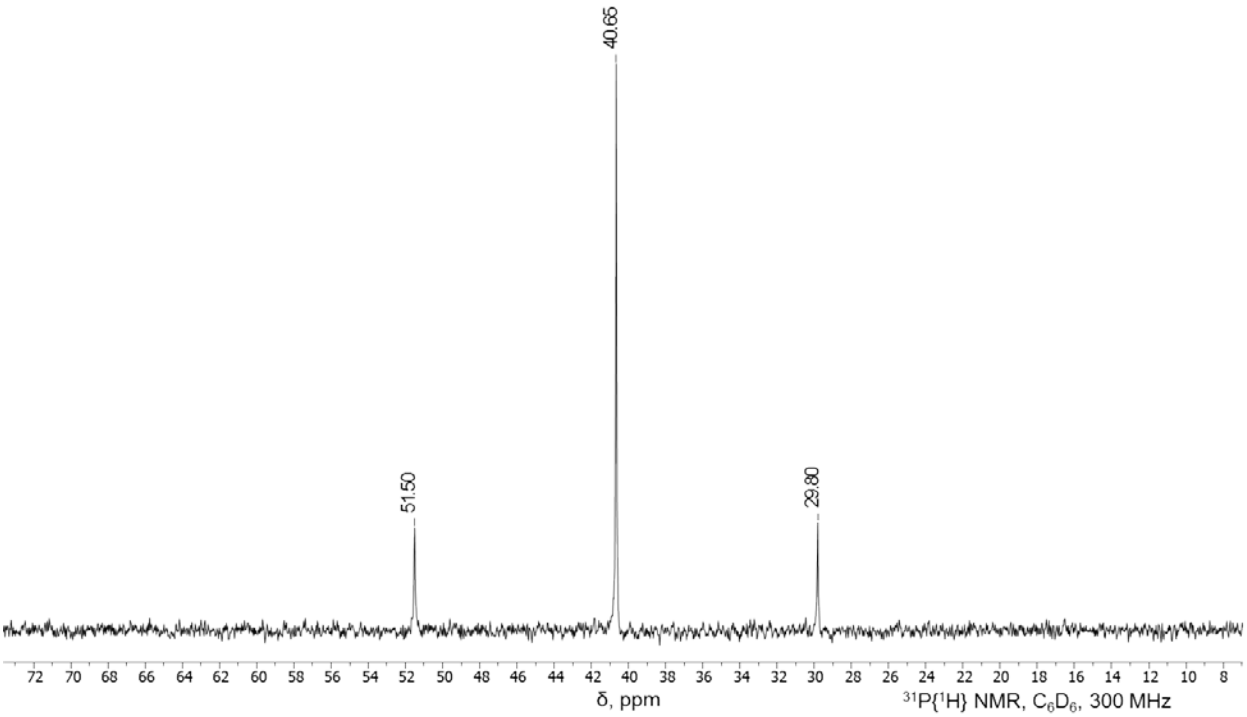


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **12** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

Independent synthesis of [(^{F}PN(H)P)PtOTf][BARF] (8). 1 (26.2 mg, 0.0335 mmol) was dissolved in about 4 mL of pentane and 1 mL of Et_2O, forming a clear yellow solution. $[H(OEt_2)_2]$[BARF] (24.2 mg, 0.0292 mmol) was added, and a solid immediately precipitated out of the solution. The volatiles were removed, and the pale blue solid was washed 3 times with pentane and then redissolved in CD_2Cl_2. This solution was filtered over Celite into a J. Young NMR tube and characterized by NMR. Please note that **8** is believed to decompose over time in CD_2Cl_2, resulting in the formation of **9**. ^{1}H NMR (CD_2Cl_2): δ 8.31 (s, $J_{195Pt\text{-}H}$ = 114Hz, 1H, N-*H),* 7.52 (m, 2H, Ar-*H*), 7.45-7.35 (m, 4H, Ar-*H*), 3.12 (m, 2H, C*H*Me_2), 2.98 (m, 2H, C*H*Me_2), 1.47 (app q (dvt), J = 8 Hz, 6H, CH*Me*$_2$), 1.45 (app q (dvt), J = 8 Hz, 6H, CH*Me*$_2$), 1.25 (app q (dvt), J

= 9 Hz, 6H, CH*Me*$_2$), 1.24 (app q (dvt), J = 9 Hz, 6H, CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -77.3, -107.5. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 47.1 ($J_{195Pt-P}$ = 2,474 Hz).

Independent synthesis of [(^{F}PN(H)P)PtCl][BARF] (9). (^{F}PNP)PtCl (32.7 mg, 0.0491 mmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a clear yellow solution. [H(OEt$_2$)$_2$][BARF] (41.2 mg, 0.0498) was added, and upon shaking, the solution became a clear, very pale blue. After a few minutes, a small amount of white precipitate was also observed. ^{1}H NMR (CD_2Cl_2): δ 8.01 (s, $J_{195Pt-H}$ = 86 Hz, 1H, N-*H*), 7.44 (m, 2H, Ar-*H*), 7.40 (m, 2H, Ar-*H*), 7.36 (m, 2H, Ar-*H*), 3.05 (m, 2H, C*H*Me$_2$), 2.88 (m, 2H, C*H*Me$_2$), 1.50 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$), 1.42 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$), 1.33 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$), 1.28 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -109.4. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.7 ($J_{195Pt-P}$ = 2,445 Hz).

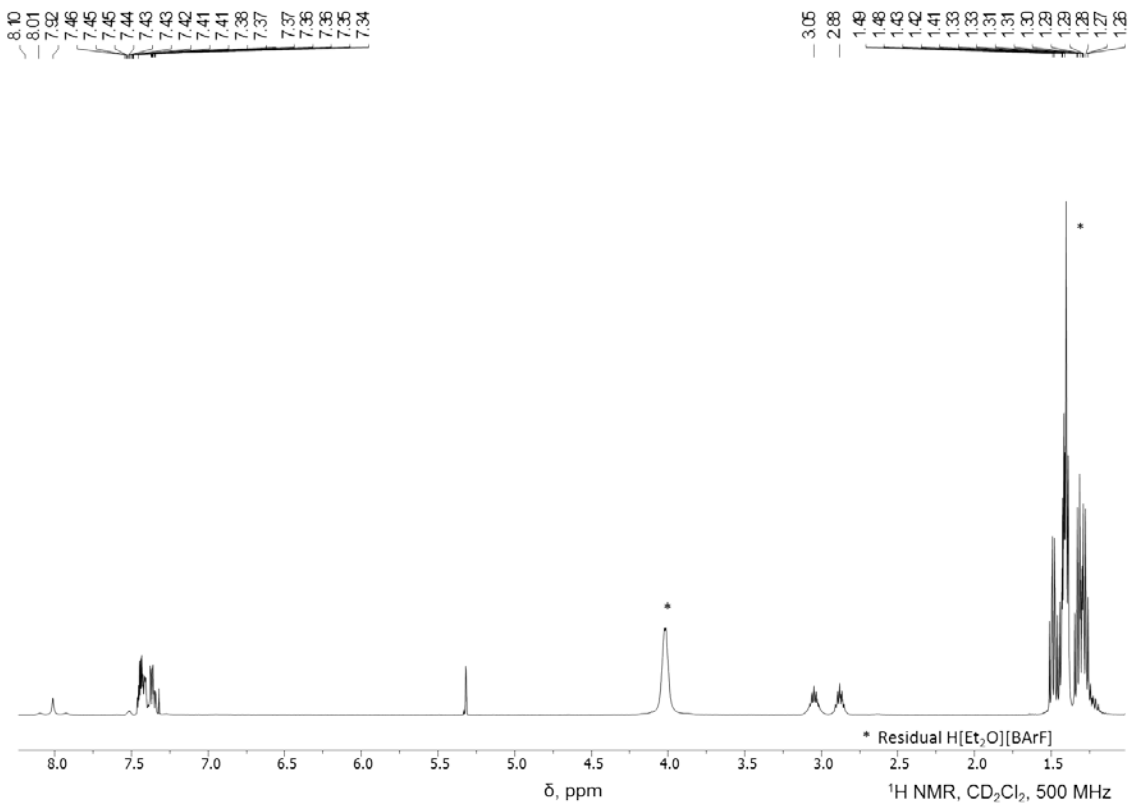


Figure S7. ^{1}H NMR spectrum of **9** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

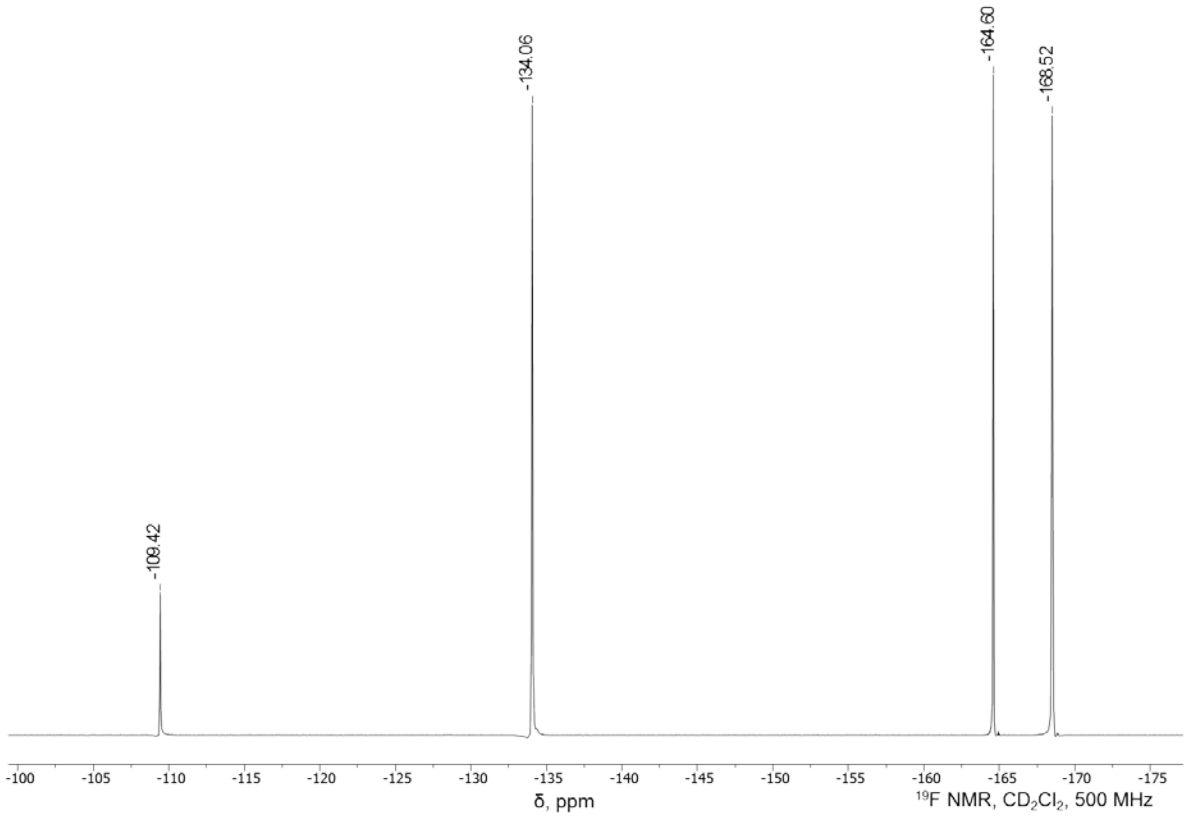


Figure S8. ^{19}F NMR spectrum of **9** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

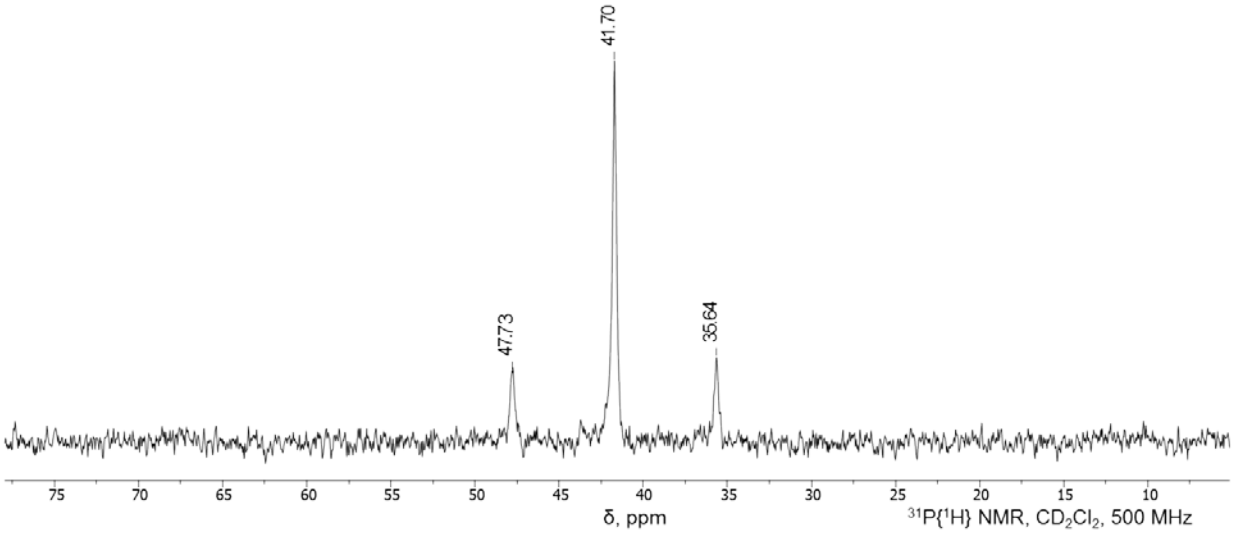
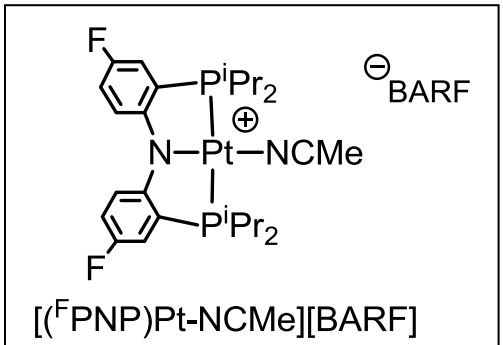


Figure S9. $^{31}P\{^1H\}$ NMR spectrum of **9** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

[(^{F}PNP)Pt-NCMe][BARF] (6). **1** (14.6 mg, 0.0187 mmol) and KBARF (13.4 mg, 0.0187 mmol) were added to a J. Young NMR tube. MeCN was added, forming an orange solution containing some undissolved K-BARF. The NMR tube was placed on an NMR tube rotator overnight, after which the ^{19}F NMR spectrum showed full conversion to the product. The contents were transferred to a 10 mL Schlenk flask, and the volatiles were removed. The resulting oily solid was washed with isooctane and dried, yielding a yellow solid that was somewhat soluble in C_6D_6. ^{1}H NMR (C_6D_6): δ 7.06-7.02 (m, 2H, Ar-*H*), 6.58-6.53 (m, 4H, Ar-*H*), 1.96 (m, 4H, C*H*Me$_2$), 1.41 (s, 3H, NC*Me*), 0.92 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, 12H, CH*Me*$_2$), 0.76 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 159.8 (vt, J_{P-C} = 10 Hz, C_{Ar}-N), 156.1 (dvt, J_{F-C} = 242 Hz, J_{P-C} = 5 Hz, C_{Ar}-F), 137.7 (t, J_{P-C} = 14 Hz), 119.7 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 118.0 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 116.8 (m), 116.6 (app q, J = 6.4 Hz, C_{Ar}-H), 25.3 (vt, J_{P-C} = 16 Hz, *C*HMe$_2$), 17.6 (CH*Me*$_2$), 17.2 (CH*Me*$_2$), 1.29 (NC*Me*). ^{19}F NMR (C_6D_6): δ -125.1. ^{31}P{^{1}H} NMR (C_6D_6): δ 48.9 ($J_{195Pt-P}$ = 2,474 Hz).



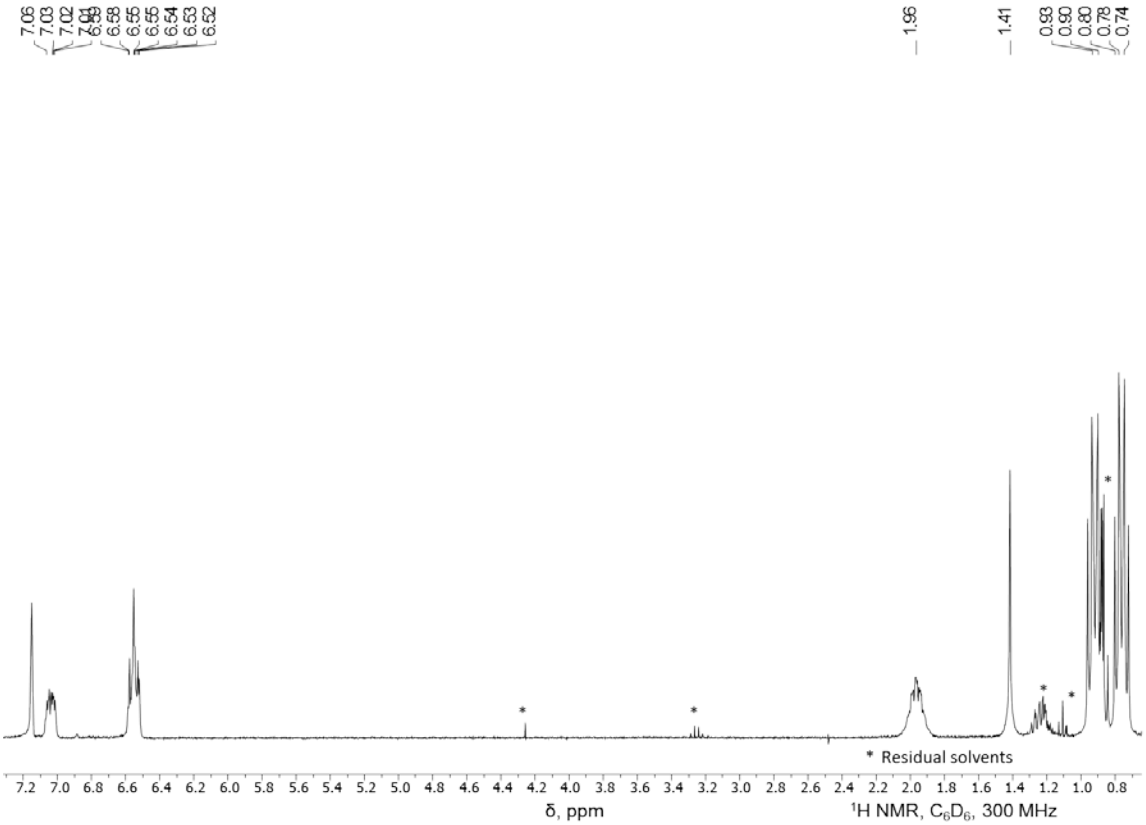


Figure S10. ^{1}H NMR spectrum of **6** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

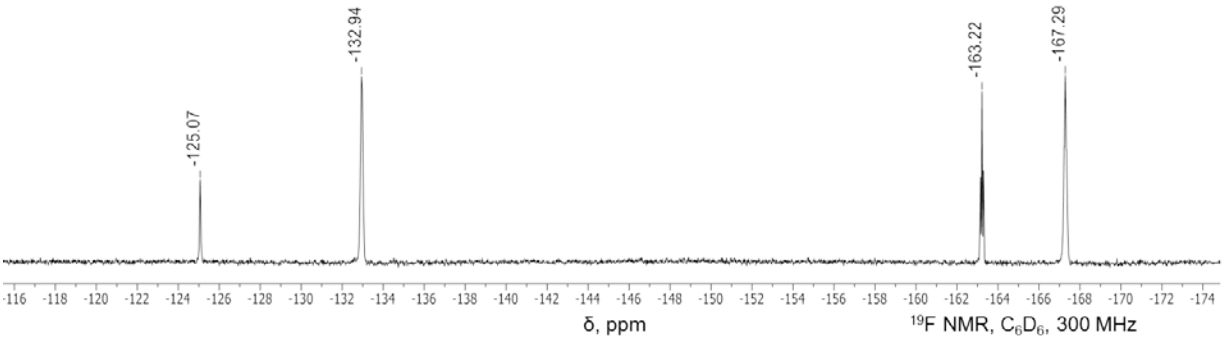


Figure S11. ^{19}F NMR spectrum of **6** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

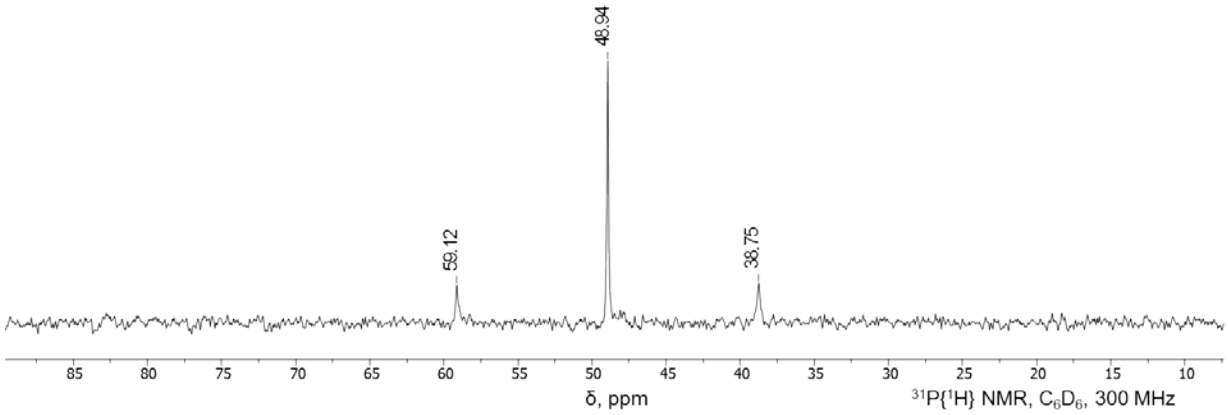


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

***o*-Tolyllithium.** 2-bromotoluene (173 mg, 1.01 mmol) was transferred to a small vial. About 5 mL of pentane was added, and the solution was chilled to -35°C in a glovebox freezer. ^{n}BuLi (310 µL, 2.5 M solution in hexanes, 0.775 mmol) was added via syringe. The solution was allowed to stir at RT overnight, resulting in the formation of a white precipitate. The solvent was decanted off of the solid, and the solid was washed with 3x 3 mL of pentane and then dried under vacuum. The solid was stored at -35°C. For NMR characterization, an aliquot of the solid was transferred to an NMR tube and mixed with a ~4:1 C_6D_6:Et_2O solution. Isolated yield: 62 mg, 81%. ^{1}H NMR (C_6D_6/Et_2O): δ 8.19 (m, 1H, Ar-*H*), 7.32-7.23 (m, 3H, Ar-*H*), 2.74 (s, 3H, C*H*$_3$).

***m*-Tolyllithium.** 3-bromotoluene (154 mg, 0.901 mmol) was transferred to a small vial. About 5 mL of pentane was added, and the solution was chilled to -35°C in a glovebox freezer. ^{n}BuLi (280 µL, 2.5 M solution in hexanes, 0.700 mmol) was added via syringe. The solution was allowed to stir at RT overnight, resulting in the formation of a white precipitate. The solvent was decanted off of the solid, and the solid was washed with 3x 3 mL of pentane and then dried under vacuum. The solid was stored at -35°C. For NMR characterization, an aliquot of the solid was

transferred to an NMR tube and mixed with a ~4:1 C_6D_6:Et_2O solution. Isolated yield: 59.7 mg, 87%. ^{1}H NMR (C_6D_6/Et_2O): δ 8.04 (br s, 1H, Ar-*H*), 8.00 (d, J = 6.6 Hz, 1H, Ar-*H*), 7.18 (overlapping with C_6D_6 signal, 1H, Ar-*H*), 6.97 (d of multiplets, J = 7.5 Hz, 1H, Ar-*H*), 2.30 (s, 3H, C*H*$_3$).

***p*-Tolyllithium.** 4-bromotoluene (208 mg, 1.22 mmol) was transferred to a small vial. About 5 mL of pentane was added, and the solution was chilled to -35°C in a glovebox freezer. ^{n}BuLi (370 μL, 2.5 M solution in hexanes, 0.925 mmol) was added via syringe. The solution was allowed to stir at RT overnight, resulting in the formation of a white precipitate. The solvent was decanted off of the solid, and the solid was washed with 3x 3 mL of pentane and then dried under vacuum. The solid was stored at -35°C. For NMR characterization, an aliquot of the solid was transferred to an NMR tube and mixed with a ~4:1 C_6D_6:Et_2O solution. Isolated yield: 77 mg, 85%. ^{1}H NMR (C_6D_6/Et_2O): δ 8.04 (d, J = 7 Hz, 2H, Ar-*H*), 7.08 (d, J = 7 Hz, 2H, Ar-*H*), 2.24 (s, 3H, C*H*$_3$).

[H(OEt$_2$)$_2$][BARF]. This procedure was modified from the one reported in the literature.[2] K-BARF (412 mg, 0.574 mmol) was dissolved in approximately 10 mL of dry Et_2O under Ar. A 100 mL Schlenk flask was filled with HCl gas, and the K-BARF solution was transferred into this flask via syringe. The flask was opened to an Ar atmosphere and allowed to stand in an ice bath. After 30 min, the clear colorless supernatant was cannula transferred through a filter away from the precipitated KCl. Washes were also cannula transferred into the final vessel containing the product solution. The volatiles were removed, and the flask was transferred into a glovebox. The resulting white solid was collected, dried under vacuum and stored at -35°C. Isolated yield: 378 mg, 79.5%. ^{1}H NMR (CD_2Cl_2): δ 16.4 (br s, 1H, Et_2O-*H*), 4.06 (br s, 8H, C*H*$_2$), 1.42 (t, J = 6.5 Hz, 12H, C*H*$_3$).

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II-B. Syntheses of neutral (PNP)Pt-R complexes from (PNP)PtCl.

(^{F}PNP)PtC_6H_5 (2a). (^{F}PNP)PtCl (40.7 mg, 0.0610 mmol) was dissolved in C_6D_6 in a J. Young NMR tube. PhLi (41 μL, 1.8 M solution in Et_2O, 0.077 mmol) was added via syringe. After 10 min, the ^{19}F NMR spectrum showed full conversion to the product. The solution was filtered over a pad of Celite and silica gel and washed through with toluene. The volatiles were then removed, and the resulting yellow solid was redissolved in C_6D_6 for characterization. Isolated yield: 35 mg, 82%. ^{1}H NMR (C_6D_6): δ 7.64 (dd, J = 7.6 Hz, 1.9 Hz, $J_{195Pt-H}$ = 54 Hz, 2H, *o*-Ph-*H*), 7.55 (m, 2H, Ar-*H*), 7.14 (m, 2H, *m*-Ph-*H*), 6.98 (td, J = 7.6 Hz, 1.9 Hz, 1H, *p*-Ph-*H*), 6.75 (m, 4H, Ar-*H*), 2.08 (m, 4H, C*H*Me_2), 0.90-0.83 (m, 24H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.7 (vt, J_{P-C} = 9 Hz, C_{Ar}-N), 154.5 (dvt, J_{F-C} = 236 Hz, J_{P-C} = 5 Hz, C_{Ar}-F), 139.5 (t, J_{P-C} = 2.3 Hz, $J_{195Pt-C}$ = 28 Hz), 136.9 (t, J_{P-C} = 9 Hz), 127.9 (overlapping with C_6D_6 signal), 122.1 (t, J_{P-C} = 1.3 Hz), 121.4 (vtd, J_{P-C} = 21 Hz, J_{F-C} = 4.5 Hz, C_{Ar}-P), 118.6 (d, J_{F-C} = 21 Hz, C_{Ar}-H), 118.2 (d, J_{F-C} = 22 Hz, C_{Ar}-H), 115.2 (app q, J = 6 Hz, C_{Ar}-H), 24.1 (vt, J_{P-C} = 15 Hz, *C*HMe_2), 17.7 (CH*Me*$_2$), 17.0 (CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -130.5. ^{31}P{^{1}H} NMR (C_6D_6): δ 40.1 ($J_{195Pt-P}$ = 2,848 Hz).

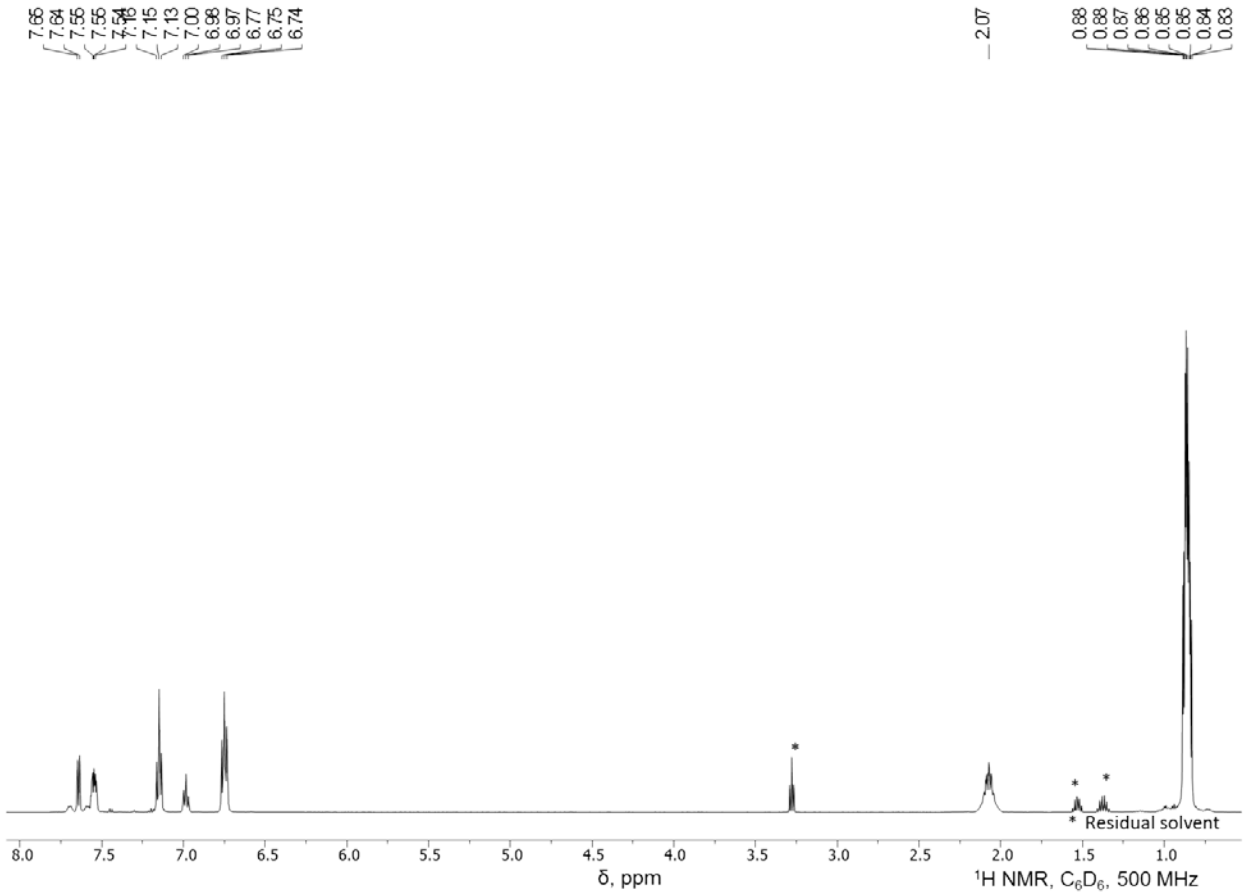


Figure S13. ^{1}H NMR spectrum of **2a** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

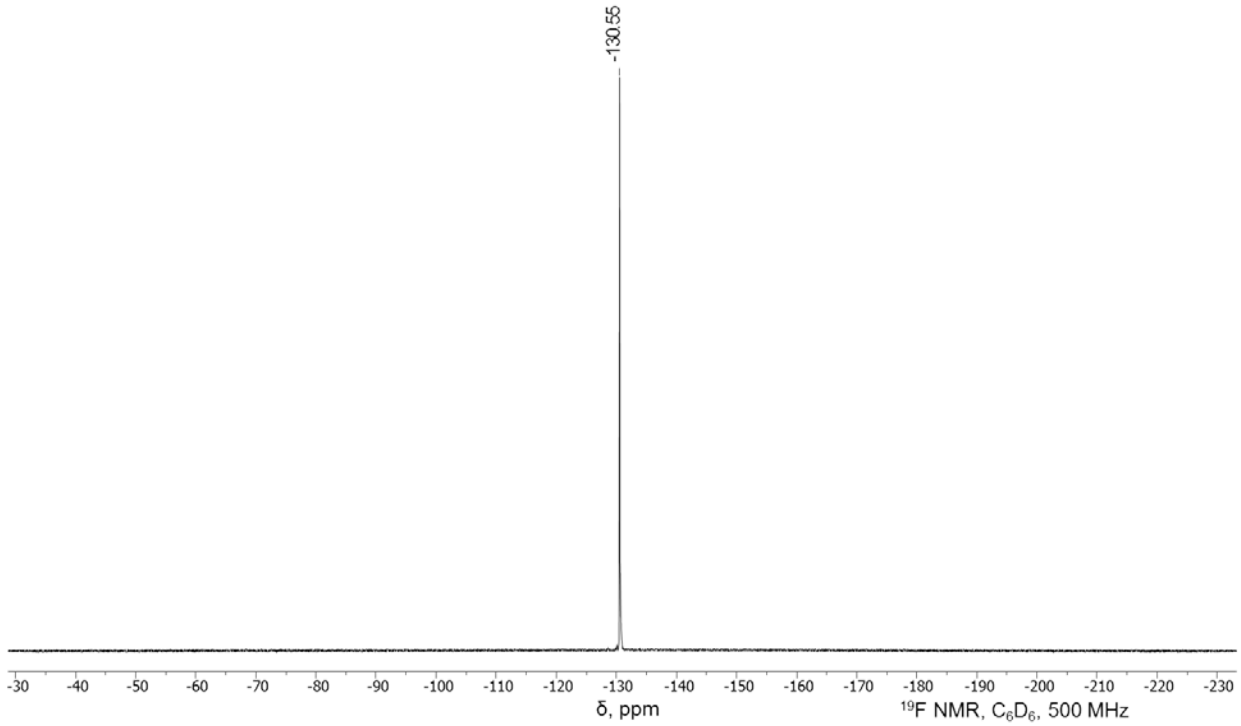


Figure S14. ^{19}F NMR spectrum of **2a** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

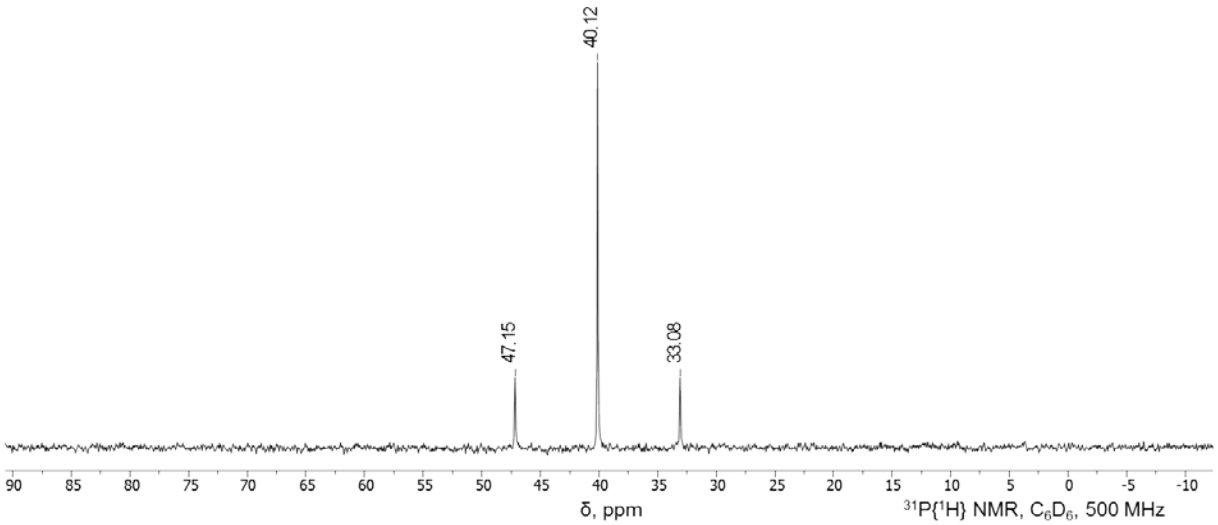


Figure S15. $^{31}P\{^1H\}$ NMR spectrum of **2a** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

(^{F}PNP)Pt-*o*-C_6H_4Me (2b). (^{F}PNP)PtCl (52.2 mg, 0.0783 mmol) and *o*-tolyllithium (9.8 mg, 0.10 mmol) were combined in a 10 mL Schlenk flask and stirred overnight in about 4 mL of toluene. The solution was then filtered over a pad of Celite and silica gel, the volatiles were removed and the resulting oily yellow solid was redissolved in pentane. The solution was filtered a second time over Celite and silica gel and eluted with pentane. The resulting pale blue solid was recrystallized from pentane at -35°C, washed with cold pentane and dried under vacuum. Isolated yield: 32 mg, 57%. ^{1}H NMR (C_6D_6): δ 7.65 (m, $J_{195Pt-H}$ = 52.9 Hz, 1H, ortho C-*H* of C_6H_4Me), 7.48 (dquint, J = 9.2 Hz, 2.3 Hz, 2H, Ar-*H*), 7.13 (m, 1H, meta C-*H* of C_6H_4Me), 7.03 (m, 2H, meta and para C-*H* of C_6H_4Me), 6.73 (m, 4H, Ar-*H*), 2.68 (s, 3H, C_6H_4*Me*), 2.06 (m, 4H, C*H*Me_2), 0.83 (m, 24H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.2 (vt, J_{P-C} = 9 Hz, C_{Ar}-N), 154.5 (dvt, J_{F-C} = 236 Hz, J_{P-C} = 5 Hz, C_{Ar}-F), 143.4 (t, J_{P-C} = 2.3 Hz), 138.8 (t, J_{P-C} = 2.4 Hz), 136.5, 125.0 ($J_{195Pt-C}$ = 55 Hz), 122.5, 121.5 (vt, J_{P-C} = 22 Hz, C_{Ar}-P), 118.4 (d, J_{F-C} = 22 Hz, C_{Ar}-H), 118.3 (d, J_{F-C} = 22 Hz, C_{Ar}-H), 115.2 (app q, J = 6 Hz, C_{Ar}-H), 28.0 ($C_6H_4CH_3$), 24.9 (vt, J_{P-C} = 15 Hz, *C*HMe_2), 23.4 (vt, J_{P-C} = 15 Hz, *C*HMe_2), 17.37 (CH*Me*$_2$), 17.35 (CH*Me*$_2$), 17.0 (CH*Me*$_2$), 16.5 (CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -130.5. ^{31}P{^{1}H} NMR (C_6D_6): δ 40.3 ($J_{195Pt-P}$ = 2,901 Hz).

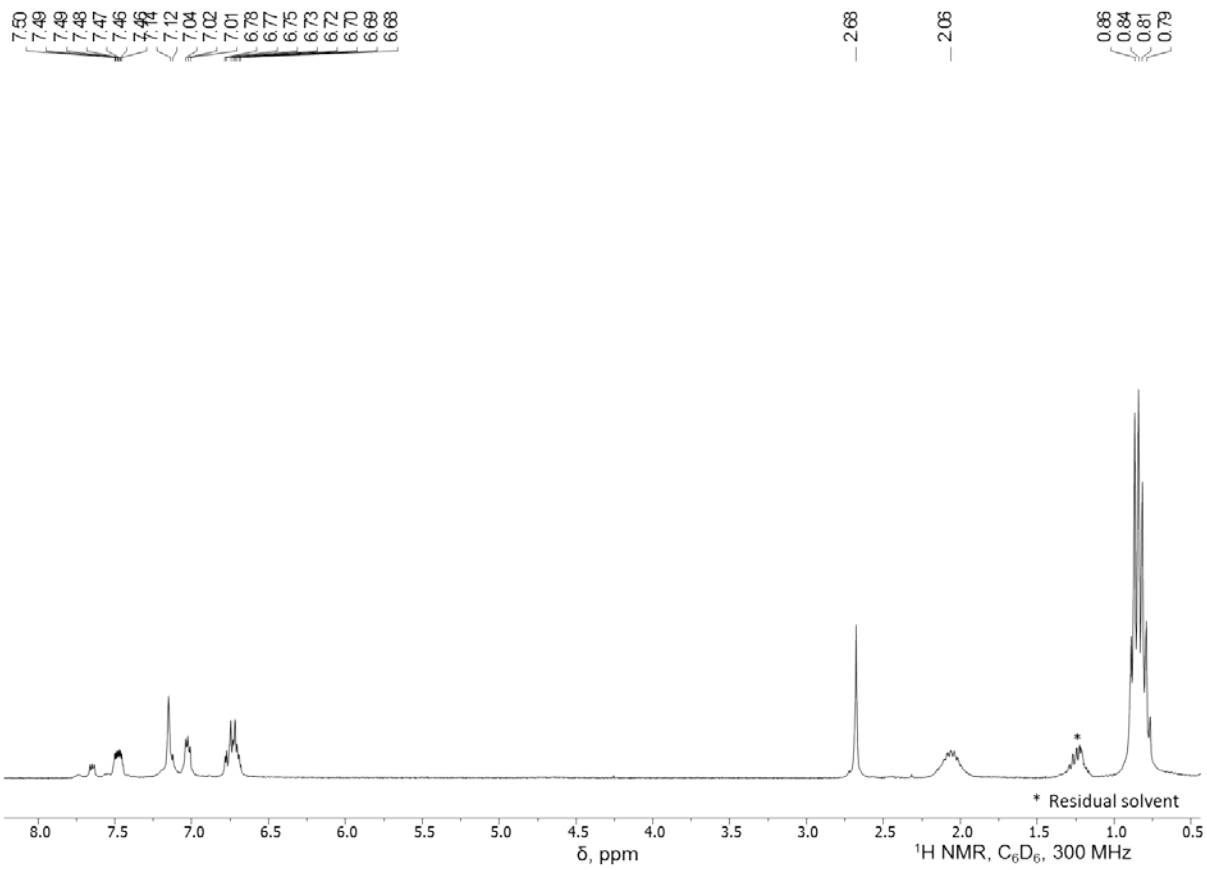


Figure S16. ^{1}H NMR spectrum of **2b** in C_6D_6 at RT measured on a 300 MHz Varian iNova.

(^{F}PNP)Pt-*m*-C_6H_4Me (2c). (^{F}PNP)PtCl (50.2 mg, 0.075 mmol) and *m*-tolyllithium (9.0 mg, 0.10 mmol) were combined in a 10 mL Schlenk flask and stirred overnight in about 4 mL of toluene. The solution was then filtered over a pad of Celite and silica gel, the volatiles were removed and the resulting oily yellow solid was redissolved in pentane. The solution was filtered a second time over Celite and silica gel and eluted with pentane. The resulting pale blue solid was recrystallized from pentane at -35°C, washed with cold pentane and dried under vacuum. Isolated yield: 36 mg, 66%. ^{1}H NMR (C_6D_6): δ 7.57 (br s, $J_{195Pt-H}$ = 54.6 Hz, 1H, C-*H* ortho to Pt and Me), 7.56 (m, 2H, Ar-*H*), 7.48 (d, J = 7.4 Hz, $J_{195Pt-H}$ = 53.6 Hz, 1H, C-*H* ortho to Pt, para to Me), 7.10 (t, J = 7.4 Hz, 1H, meta C-*H* of C_6H_4Me), 6.82 (d, J = 7.4 Hz, 1H, para C-*H* of C_6H_4Me), 6.76 (m, 4H, Ar-*H*), 2.31 (s, 3H, C_6H_4*Me*), 2.11 (m, 4H, C*H*Me_2), 0.89 (m, 24H,

CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.7 (vt, J_{P-C} = 10 Hz, C_{Ar}-N), 154.5 (dvt, J_{F-C} = 231 Hz, J_{P-C} = 5 Hz, C_{Ar}-F), 140.3 (t, J_{P-C} = 2.5 Hz), 136.7 (t, J_{P-C} = 9 Hz), 136.6 (t, J_{P-C} = 2.4 Hz), 136.4, 123.0, 121.5 (vtd, J_{P-C} = 22 Hz, J_{F-C} = 4 Hz, C_{Ar}-P), 118.7 (d, J_{F-C} = 22 Hz, C_{Ar}-H), 118.3 (d, J_{F-C} = 22 Hz, C_{Ar}-H), 115.2 (app q, J = 6 Hz, C_{Ar}-H), 24.2 (vt, J_{P-C} = 16 Hz, *C*HMe$_2$), 22.7 (C_6H_4*C*H$_3$), 17.8 (CH*Me*$_2$), 17.0 (CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -130.3. ^{31}P{^{1}H} NMR (C_6D_6): δ 40.0 ($J_{195Pt-P}$ = 2,855 Hz).

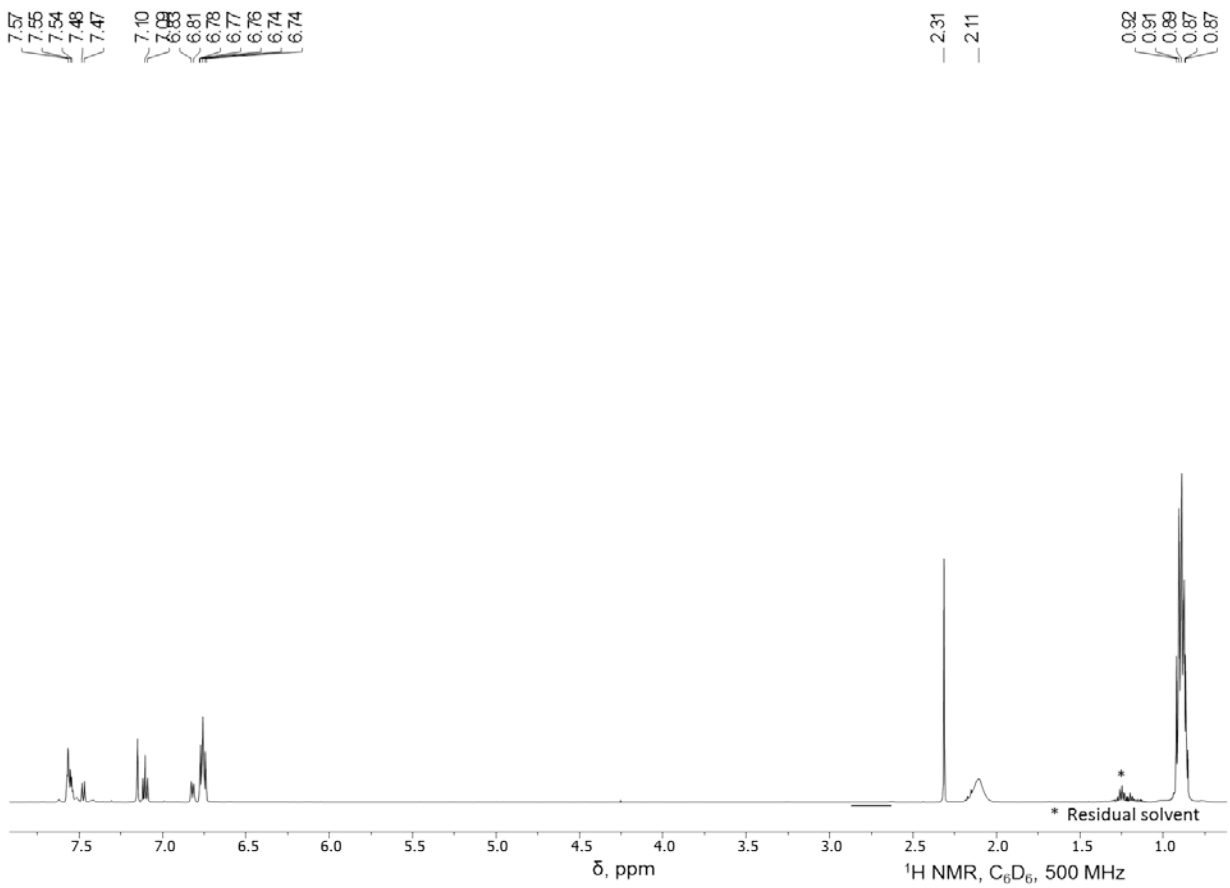


Figure S17. ^{1}H NMR spectrum of **2c** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

(^{F}PNP)Pt-*p*-C$_6$H$_4$Me (2d). (^{F}PNP)PtCl (118 mg, 0.177 mmol) and *p*-tolyllithium (19.5 mg, 0.199 mmol) were combined in a 25 mL Schlenk flask and stirred overnight in about 7 mL of toluene. The solution was then filtered over a pad of Celite and silica gel, the volatiles were removed and the resulting oily yellow solid was redissolved in pentane. The solution was filtered

a second time over Celite and silica gel and eluted with pentane. The resulting pale blue solid was recrystallized from pentane at -35°C, washed with cold pentane and dried under vacuum. Isolated yield: 94 mg, 72%. ^{1}H NMR (C_6D_6): δ 7.56 (m, $J_{195Pt-H}$ = 51.9 Hz, 4H, ortho C-*H* of C_6H_4Me and Ar-*H*), 7.04 (d, J = 7.6 Hz, 2H, meta C-*H* of C_6H_4Me), 6.76 (m, 4H, Ar-*H*), 2.27 (s, 3H, C_6H_4*Me*), 2.10 (m, 4H, C*H*Me_2), 0.88 (m, 24H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 160.8 (vt, J_{P-C} = 8.8 Hz, C_{Ar}-N), 154.5 (dvt, J_{F-C} = 237 Hz, J_{P-C} = 5 Hz, C_{Ar}-F), 139.2 (t, J_{P-C} = 9.3 Hz, $J_{195Pt-C}$ = 30 Hz), 132.0 (t, J_{P-C} = 9 Hz), 130.5 (t, J_{P-C} = 1.5 Hz), 129.0 ($J_{195Pt-C}$ = 60 Hz, C_{Ar}-Pt), 121.6 (vtd, J_{P-C} = 22.4 Hz, J_{F-C} = 4 Hz, C_{Ar}-P), 118.7 (d, J_{F-C} = 21 Hz, C_{Ar}-H), 118.3 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 115.2 (app q, J = 6 Hz, C_{Ar}-H), 24.2 (vt, J_{P-C} = 15.4 Hz, *C*HMe_2), 21.2 (C_6H_4*C*H_3), 17.8 (CH*Me*$_2$), 17.0 (CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -130.6. ^{31}P{^{1}H} NMR (C_6D_6): δ 40.0 ($J_{195Pt-P}$ = 2,853 Hz).

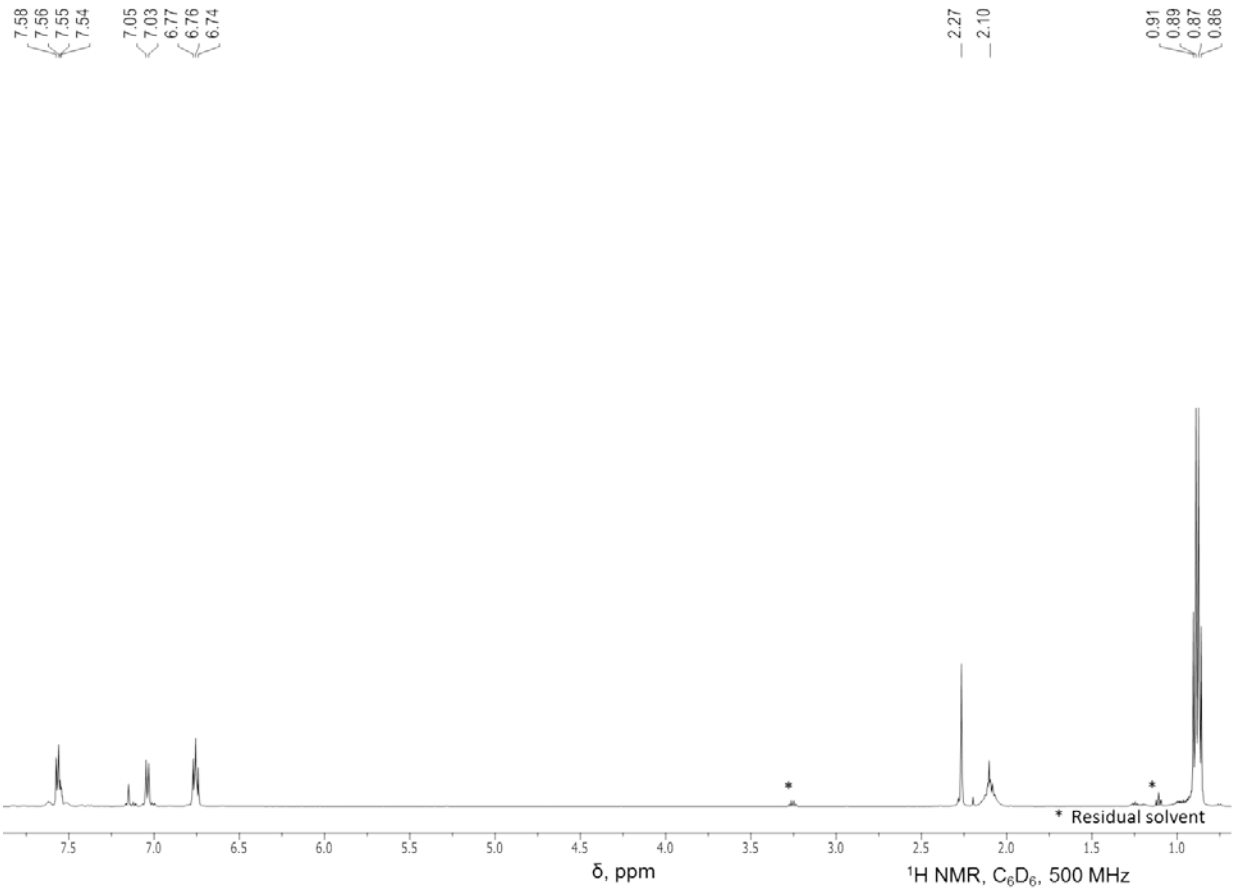


Figure S18. ^{1}H NMR spectrum of **2d** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

(^{F}PNP)PtCH$_2$C$_6$H$_5$ (2g). (^{F}PNP)PtCl (40.8 mg, 0.0612 mmol) was dissolved in C_6D_6 in a J. Young NMR tube, producing a clear yellow solution. About 0.5 mL of dioxane was added, followed by BnMgCl (73 μL, 1.0 M solution in Et_2O, 0.073 mmol). A white precipitate was immediately generated. The NMR tube was covered with Al foil and placed on an NMR tube rotator for 16 h, after which the ^{19}F NMR spectrum showed full conversion to the product. The solution was filtered through a pad of Celite and silica gel, yielding a clear yellow solution. The volatiles were removed, and the product was recrystallized from pentane at -35°C. The resulting yellow solid was collected and dried under vacuum. Isolated yield: 18.6 mg, 42.1%. ^{1}H NMR (C_6D_6): δ 7.52 (t, J = 9 Hz, 2H, Ar-*H*), 7.49 (d, J = 7.5 Hz, 2H, Ar-*H*), 7.17 (t, J = 7.6 Hz, 2H, Ar-*H*), 6.97 (t, J = 7.5 Hz, 1H, $CH_2C_6H_5$), 6.81 (m, 2H, $CH_2C_6H_5$), 6.73 (m, 2H, $CH_2C_6H_5$), 3.32

(t, $J_{P\text{-}H}$ = 6 Hz, $J_{195Pt\text{-}H}$ = 95 Hz, 2H, C*H*$_2$C$_6$H$_5$), 1.94 (m, 4H, C*H*Me$_2$), 1.02 (app q (dvt), J = 8 Hz, 12H, CH*Me*$_2$), 0.90 (app q (dvt), J = 7.7 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 160.3 (vt, $J_{P\text{-}C}$ = 10 Hz, *C*$_{Ar}$-N), 154.5 (dvt, $J_{F\text{-}C}$ = 236 Hz, $J_{P\text{-}C}$ = 5 Hz, *C*$_{Ar}$-F), 152.5 (t, $J_{P\text{-}C}$ = 2 Hz, $J_{195Pt\text{-}C}$ = 39 Hz), 130.6 ($J_{195Pt\text{-}C}$ = 46 Hz), 127.6, 123.6, 121.9 (vtd, $J_{P\text{-}C}$ = 23 Hz, $J_{F\text{-}C}$ = 5 Hz, *C*$_{Ar}$-P), 118.2 (d, $J_{F\text{-}C}$ = 11 Hz, *C*$_{Ar}$-H), 117.9 (d, $J_{F\text{-}C}$ = 22 Hz, *C*$_{Ar}$-H), 115.3 (app q, J = 6 Hz, *C*$_{Ar}$-H), 24.9 (vt, $J_{P\text{-}C}$ = 15 Hz, *C*HMe$_2$), 18.3 (CH*Me*$_2$), 17.6 (CH*Me*$_2$), -3.4 (t, $J_{P\text{-}C}$ = 6 Hz, $J_{195Pt\text{-}C}$ = 602 Hz, *C*H$_2$C$_6$H$_5$). ^{19}F NMR (C$_6$D$_6$): δ -130.6. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 38.7 ($J_{195Pt\text{-}P}$ = 2,910 Hz).

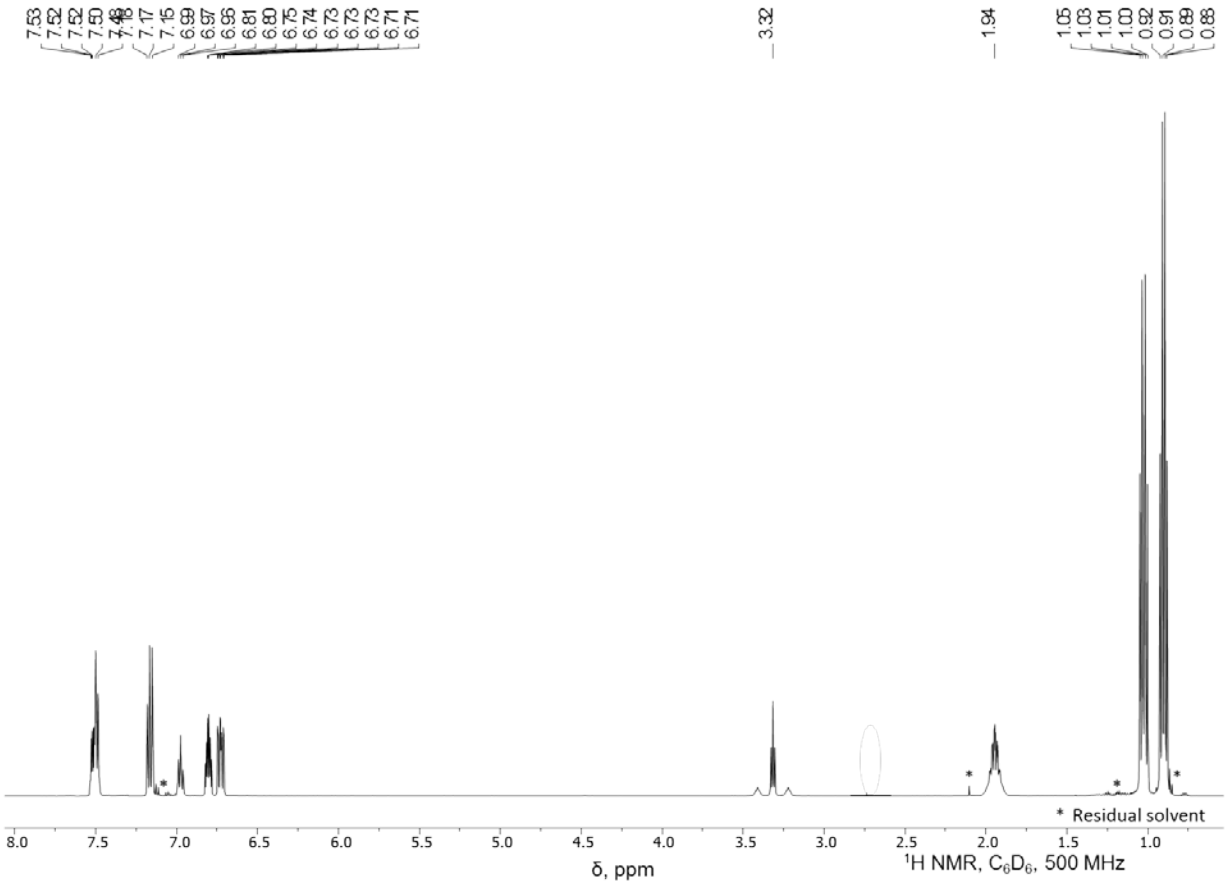


Figure S19. ^{1}H NMR spectrum of **2g** in C$_6$D$_6$ at RT measured on a 500 MHz Varian NMRS.

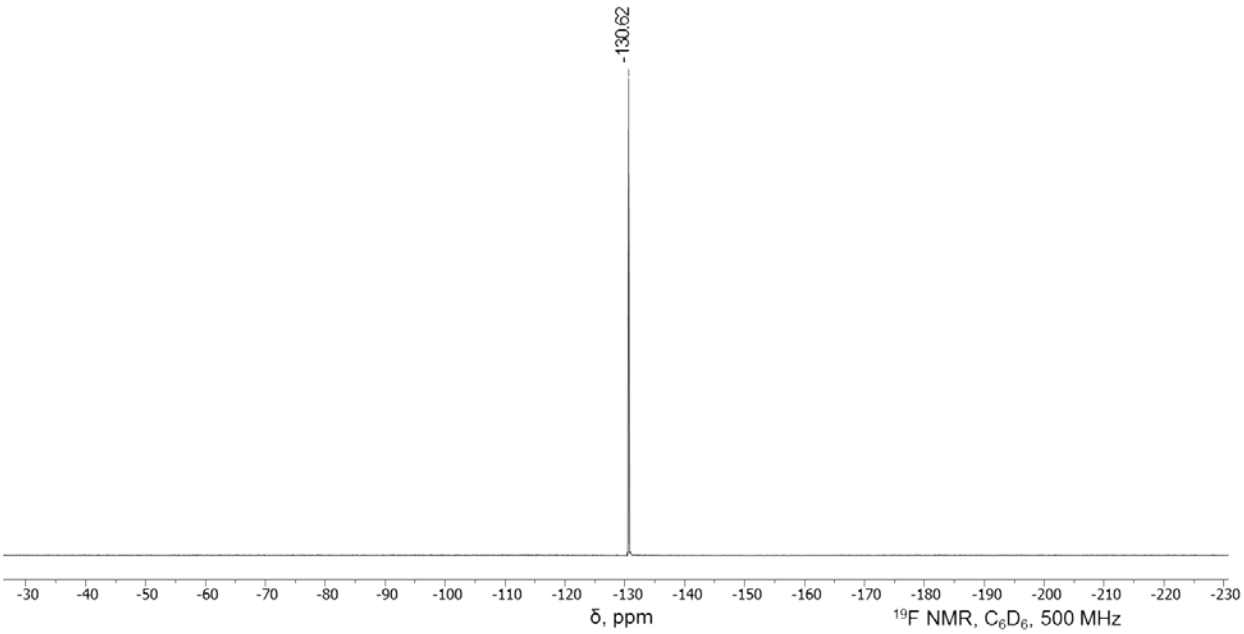


Figure S20. ^{19}F NMR spectrum of **2g** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

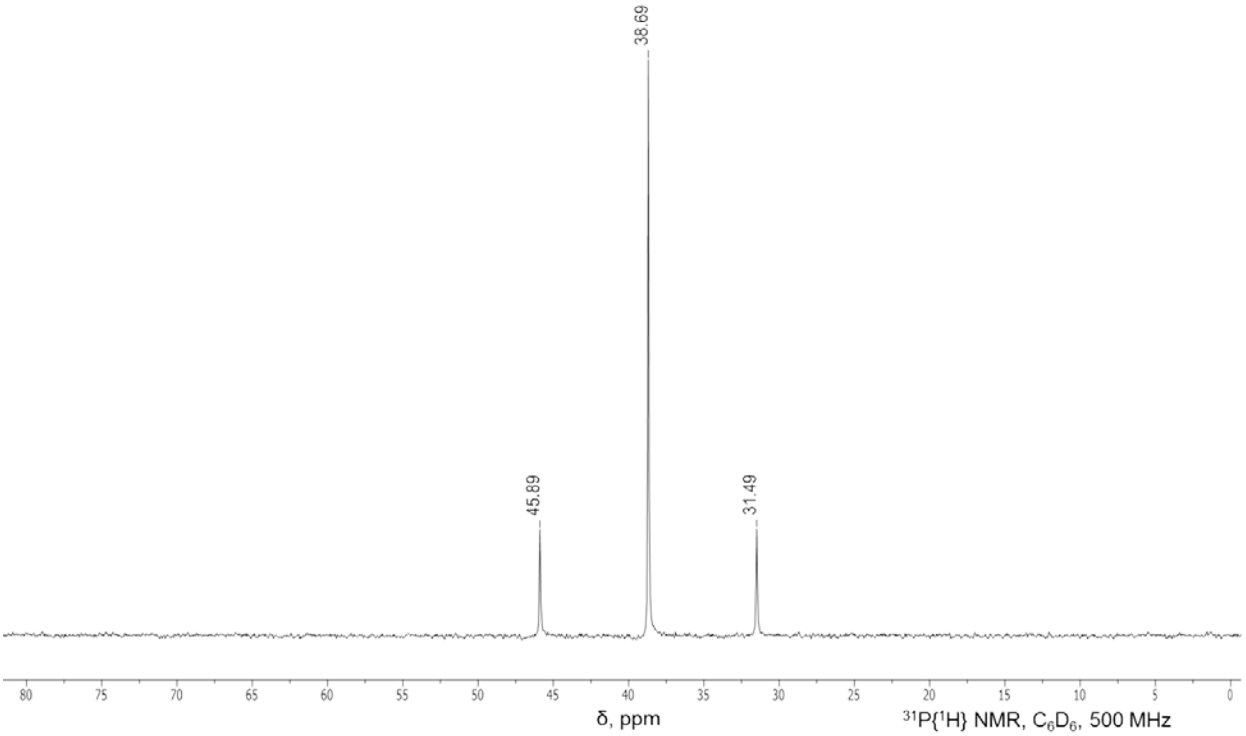


Figure S21. $^{31}P\{^1H\}$ NMR spectrum of **2g** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

II-C. C-H Activation of arenes with 1/NEt_3.

1 plus NEt_3 in C_6D_6. 1 (22.0 mg, 0.0280 mmol) was transferred to a J. Young NMR tube and dissolved in toluene, forming a clear, yellow solution. NEt_3 (5.0 µL, 0.036 mmol) was added via syringe, and the NMR tube was placed in an oil bath at 115°C. The reaction was monitored by ^{19}F NMR. After 2 weeks, about 17% of the original (^{F}PNP)PtOTf remained, with approximately 79% conversion of the total starting material to (^{F}PNP)PtC_6D_5 (**2a-D**) and 4% conversion to (^{F}PNP)PtH.

1 plus NEt_3 in toluene. 1 (23.0 mg, 0.0294 mmol) was transferred to a J. Young NMR tube and dissolved in toluene, forming a clear, yellow solution. NEt_3 (5.0 µL, 0.036 mmol) was added via syringe, and the NMR tube was placed in an oil bath at 115°C. The reaction was monitored by ^{19}F NMR. After 7 days, the complete disappearance of (^{F}PNP)PtOTf was noted, with about 90% conversion to (^{F}PNP)PtC_6H_4Me (**2b-d**) and 10% conversion to (^{F}PNP)PtH. The volatiles were removed, and the residual solid was redissolved in C_6D_6, filtered over Celite and silica gel and characterized by NMR. The ^{1}H NMR spectrum showed an **2b:2c:2d** tolyl isomeric ratio of approximately 1%:68%:31%.

II-D. Reactions of 1 with K-BARF in arene solvents.

[(^{F}PN(H)P)PtC$_6$H$_5$][BARF] (3a). 1 (18.1 mg, 0.0232 mmol) and K-BARF (17.1 mg, 0.0238 mmol) were added to a 5 mL round-bottomed Teflon screw-capped flask. C_6H_6 (2 mL) was added, forming an orange solution containing some undissolved K-BARF. The solution was left to stir at RT. After 24 h, the solution had become a brownish green, and after 4 days, the solution had become a pale green. The complete disappearance of starting material was confirmed by ^{19}F NMR. The volatiles were removed, yielding a pale blue-green solid. The solid was washed with pentane, dried, extracted with CD_2Cl_2 and filtered through a pad of Celite into a J. Young NMR tube for characterization. ^{1}H NMR (CD_2Cl_2): δ 7.52 and 7.51 (overlapping br signals, 2H, Ar-*H*), 7.38 (td, J = 8.4 Hz, 3 Hz, 2H, *o*-Ph-*H*, ^{195}Pt coupling buried), 7.36 (t, J = 7.5 Hz, 2H, Ar-*H*), 7.35 (d, J = 7.5 Hz, 2H, Ar-*H*), 7.26 (br s, $J_{195Pt-H}$ = 37 Hz, 1H, N-*H*), 7.05 (t, J = 7.8 Hz, 2H, *m*-Ph-*H*), 6.94 (t, J = 7.2 Hz, 1H, *p*-Ph-*H*), 2.81 (m, 2H, C*H*Me$_2$), 2.68 (m, 2H, C*H*Me$_2$), 1.20 (m, 12H, CH*Me*$_2$), 1.07 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7.5 Hz, 6H, CH*Me*$_2$), 0.88 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7.3 Hz, 6H, CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -111.7. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.3 ($J_{195Pt-P}$ = 2,819 Hz). IR (solid): 3240 cm^{-1} (N-H).

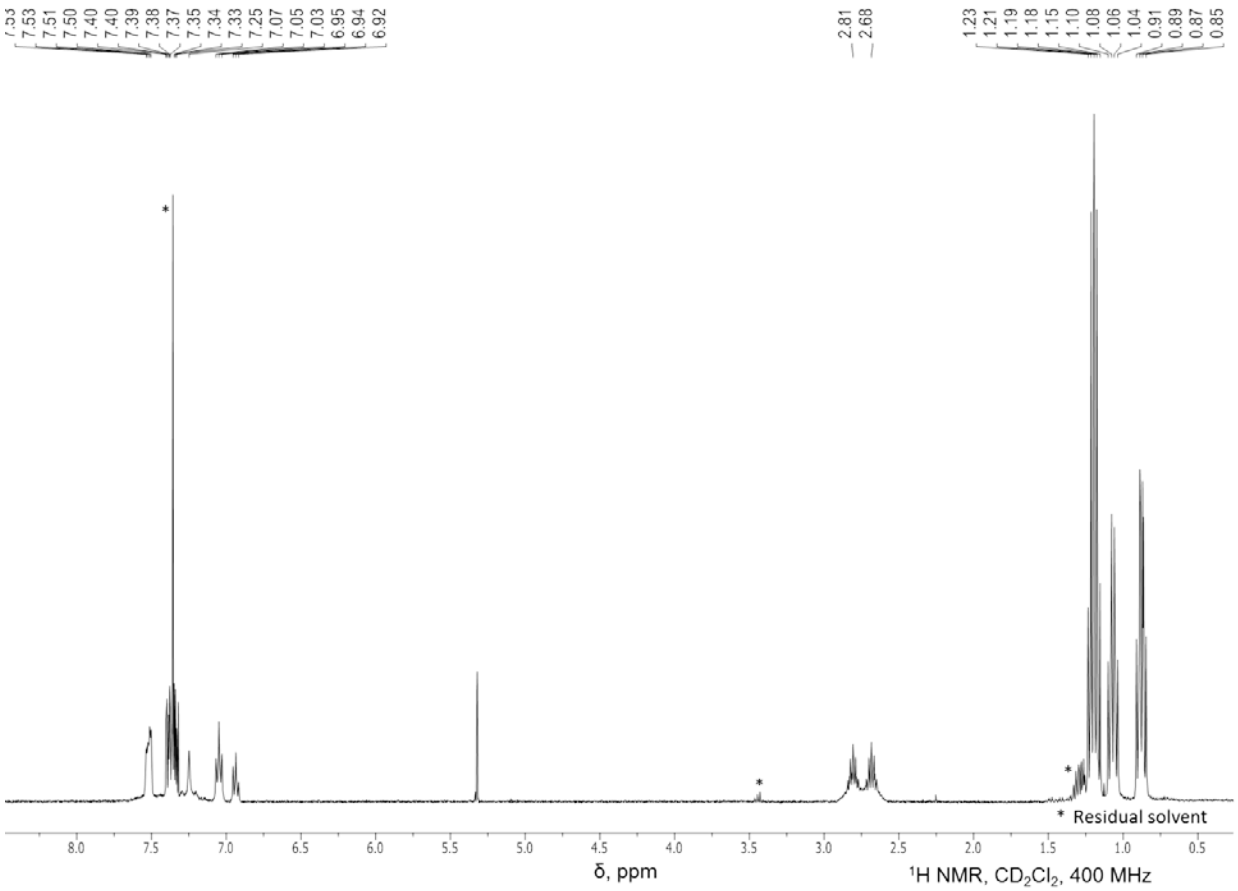


Figure S22. ^{1}H NMR spectrum of **3a** in CD_2Cl_2 at RT measured on a 400 MHz Varian iNova.

[(^{F}PN(D)P)PtC$_6$D$_5$][BARF] (3a-D). **1** (100 mg, 0.128 mmol) and K-BARF (93.0 mg, 0.130 mmol) were added to a round-bottomed Teflon screw-capped flask. About 3 mL of C_6D_6 was added, forming an orange solution containing some undissolved K-BARF. The flask was then placed in an oil bath at 80°C. After 2 h, the solution had a cloudy orange appearance, and after 16 h, the reaction became a cloudy green. Conversion to the product was confirmed by NMR. The solution was filtered over a pad of Celite and rinsed through with CH_2Cl_2. The volatiles were removed under vacuum, yielding a pale green solid that was recrystallized from a CH_2Cl_2 solution layered with pentane at -35°C. The crystals were collected, washed with pentane and dried under vacuum, yielding a pale blue solid. Conversion to the final product was also

achieved by performing this reaction at RT for 4 days. Isolated yield: 111 mg, 61%. ^{1}H NMR (CD_2Cl_2): δ 7.52 and 7.51 (overlapping br signals, 2H, Ar-*H*), 7.36 (t, J = 7.5 Hz, 2H, Ar-*H*), 7.35 (d, J = 7.5 Hz, 2H, Ar-*H*), 2.81 (m, 2H, C*H*Me$_2$), 2.68 (m, 2H, C*H*Me$_2$), 1.23 (m, 12H, CH*Me*$_2$), 1.07 (app q (dvt), J = 8 Hz, 6H, CH*Me*$_2$), 0.88 (app q (dvt), J = 8 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.4 (dvt, J_{F-C} = 256 Hz, J_{P-C} = 4 Hz, C_{Ar}-F), 144.6 (vtd, J_{P-C} = 7 Hz, J_{F-C} = 3 Hz, C_{Ar}-N), 136.2 (overlapping with BARF signal), 132.3 (vtd, J_{P-C} = 18 Hz, J_{F-C} = 6 Hz, C_{Ar}-P), 128.4 (br s), 126.1, 124.5 (t, J_{P-C} = 8 Hz), 121.5 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 120.0 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 26.5 (vt, J_{P-C} = 14 Hz, *C*HMe$_2$), 23.6 (vt, J_{P-C} = 15 Hz, *C*HMe$_2$), 18.0 (CH*Me*$_2$), 17.8 (CH*Me*$_2$), 17.6 (CH*Me*$_2$), 16.9 (CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -111.7. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.2 ($J_{195Pt-P}$ = 2,820 Hz). Elemental analysis, found (calculated) for $C_{54}H_{34}D_6BF_{22}NP_2Pt$: C, 46.25 (46.50); H, 2.09 (2.34). IR (solid): 2405 cm^{-1} (N-D).

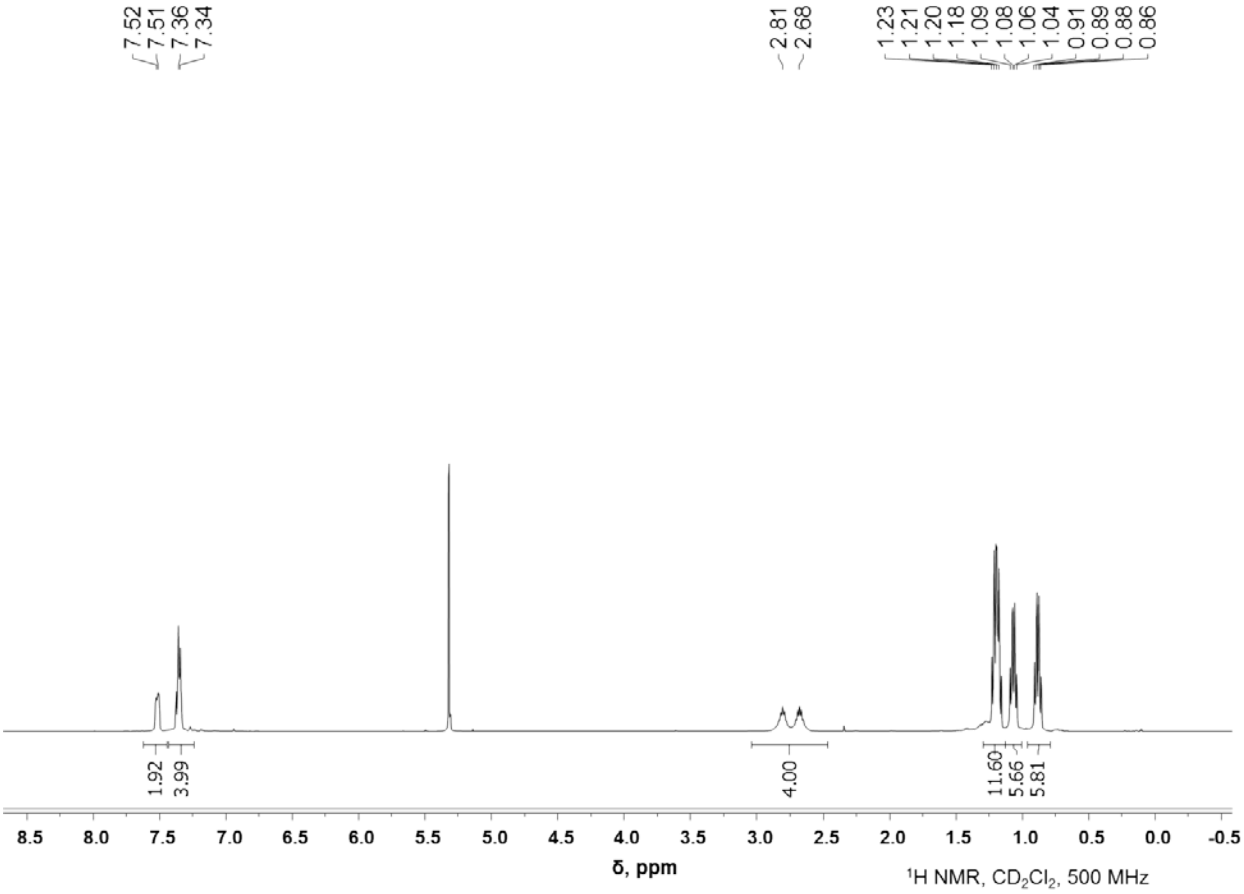


Figure S23. ^{1}H NMR spectrum of **3a-D** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

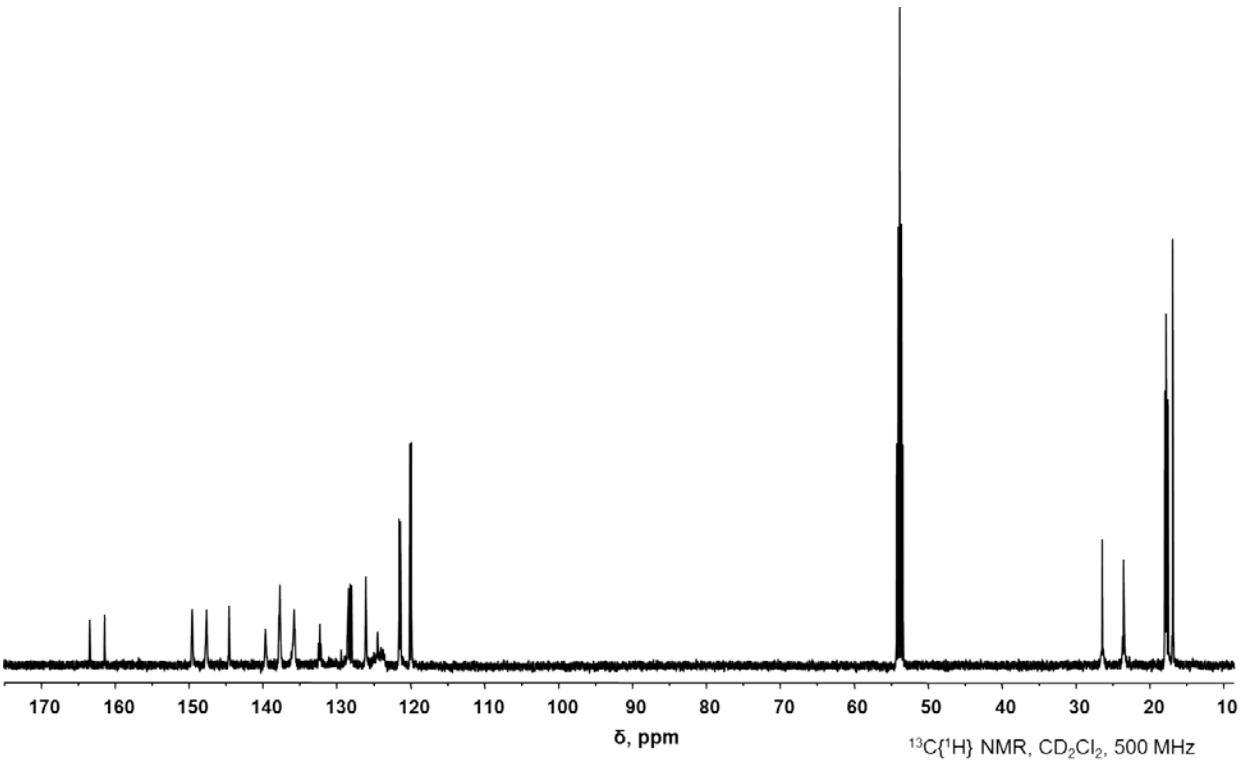


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **3a-D** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

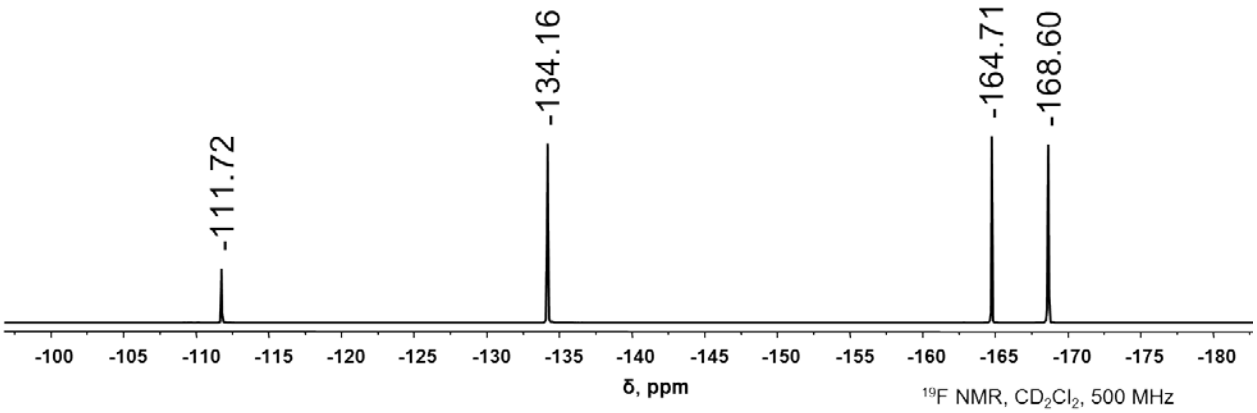


Figure S25. ^{19}F NMR spectrum of **3a-D** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

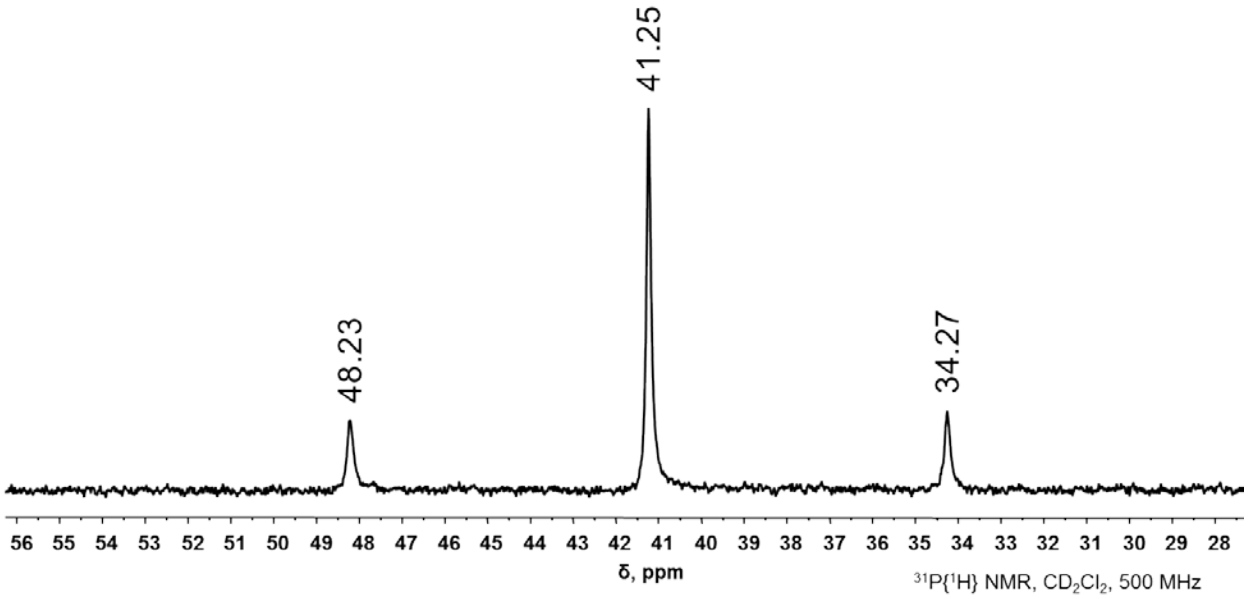


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum of **3a-D** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

[(^{F}PN(H)P)PtC$_6$H$_4$Me][BARF] (3b-d). 1 (107 mg, 0.137 mmol) and K-BARF (98 mg, 0.14 mmol) were added to a 10 mL round-bottomed Teflon screw-capped flask. Approximately 5 mL of C_6H_5Me was added, forming a yellow solution containing some undissolved K-BARF. The flask was then placed in an oil bath at 80°C. After 2 h, the solution had become cloudy brown, and after 16 h, the solution had become cloudy blue. The solution was then filtered over a pad of Celite and washed through with CH_2Cl_2. The volatiles were removed under vacuum, yielding an oily blue residue. A minimal amount of CH_2Cl_2 was used to redissolve the solids, and the solution was layered with pentane. After recrystallization at -35°C, the resulting pale blue solid was washed with pentane and dried under vacuum. Isolated yield: 165 mg, 84%. The ratio of **3b**:(**3c** plus **3d**) in the product mixture was approximately 8%:92% (**3c** and **3d** signals overlap). Characterization was achieved by comparing the ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of the product mixture to those of the independently synthesized isomers (see below). ^{19}F NMR (CD_2Cl_2): δ -111.7. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 41.1 (br, $J_{195Pt-P}$ = 2,840 Hz). Elemental analysis,

found (calculated) for $C_{55}H_{41}BF_{22}NP_2Pt$: C, 47.07 (47.13); H, 3.02 (2.95). IR (solid): 3240 cm^{-1} (N-H).

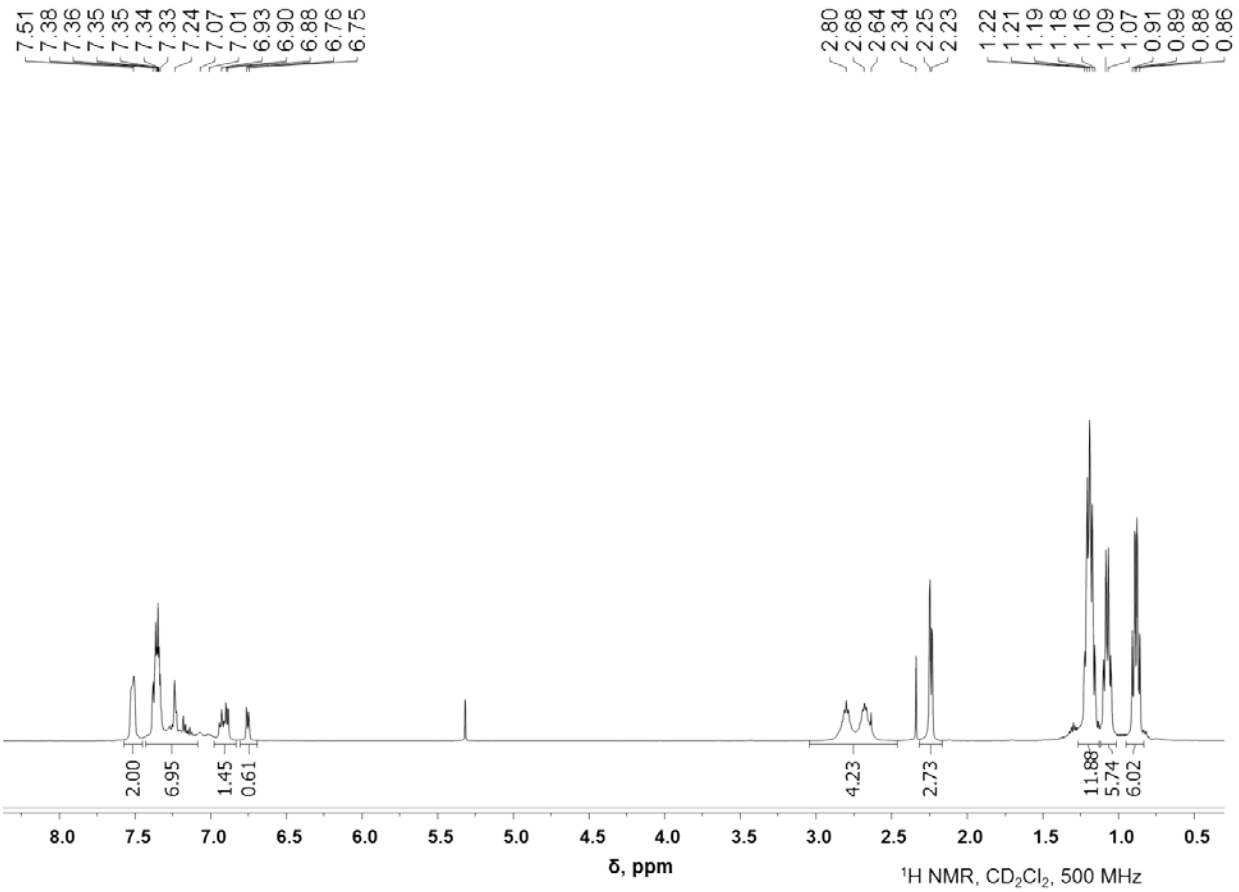


Figure S27. ^{1}H NMR spectrum of the **3b-d** product mixture in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

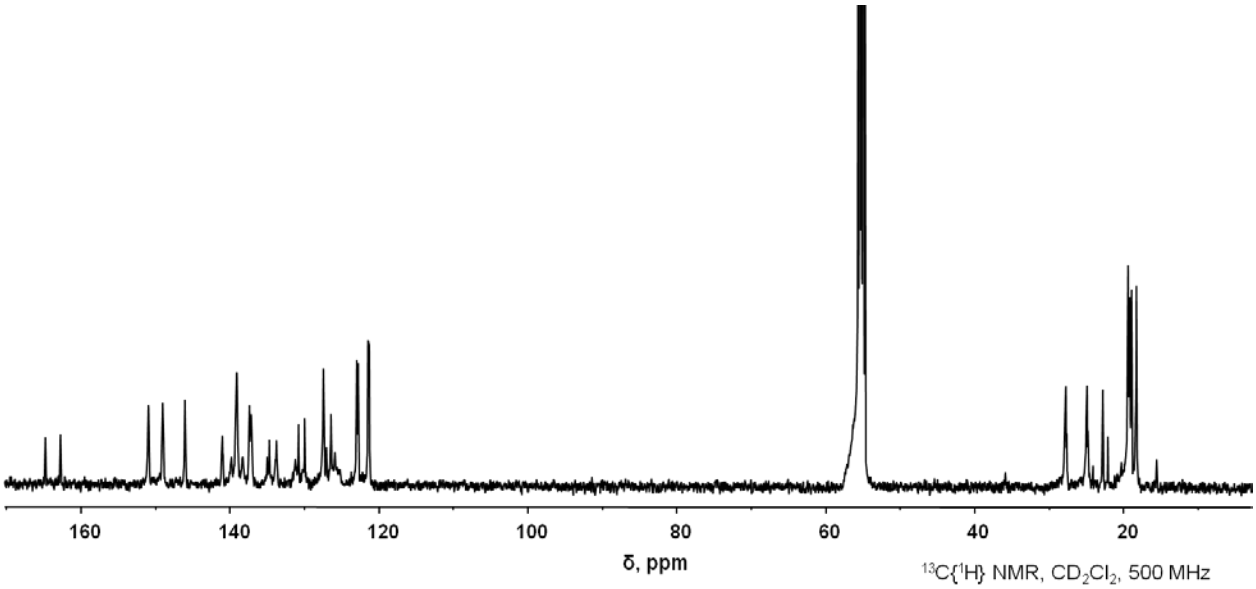


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of the **3b-d** product mixture in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

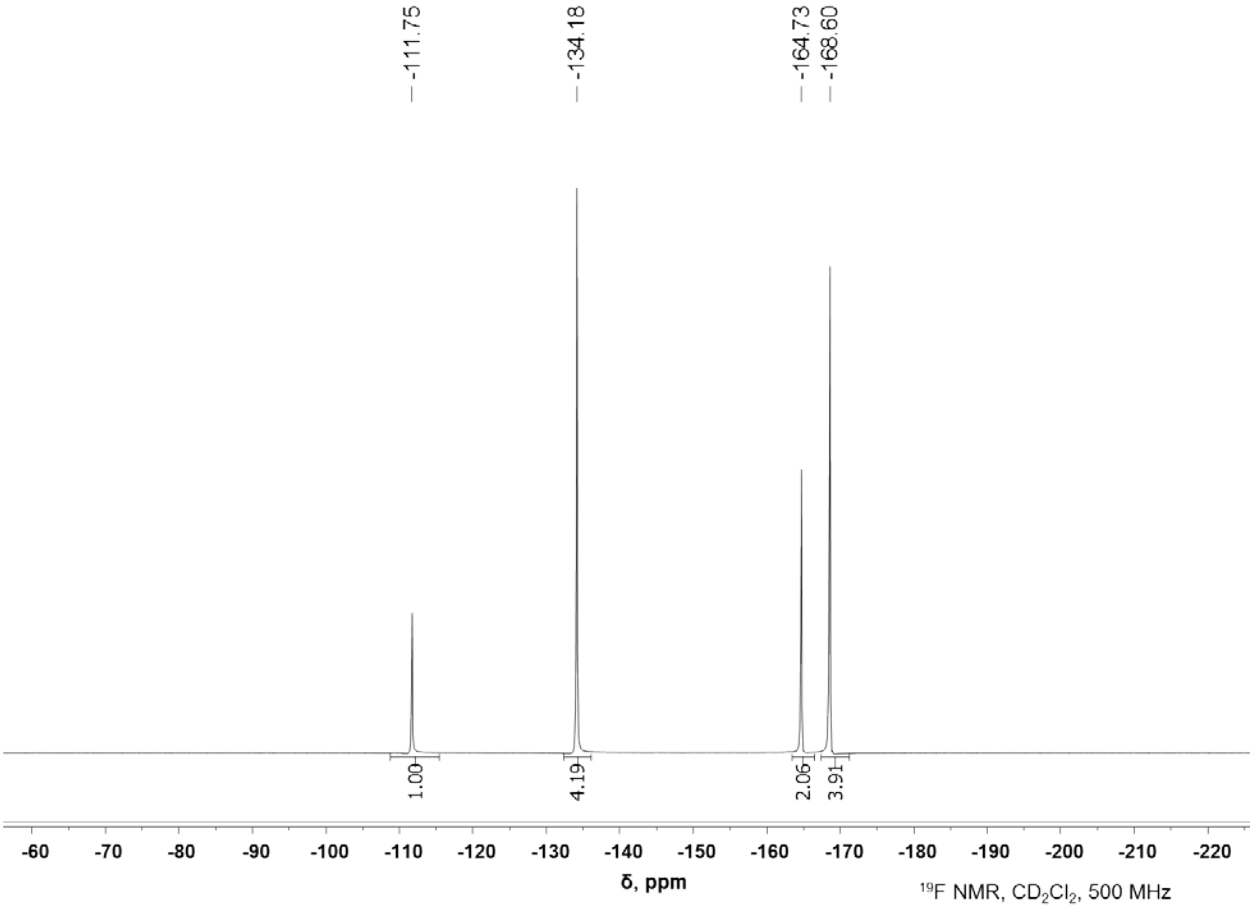


Figure S29. ^{19}F NMR spectrum of the **3b-d** product mixture in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

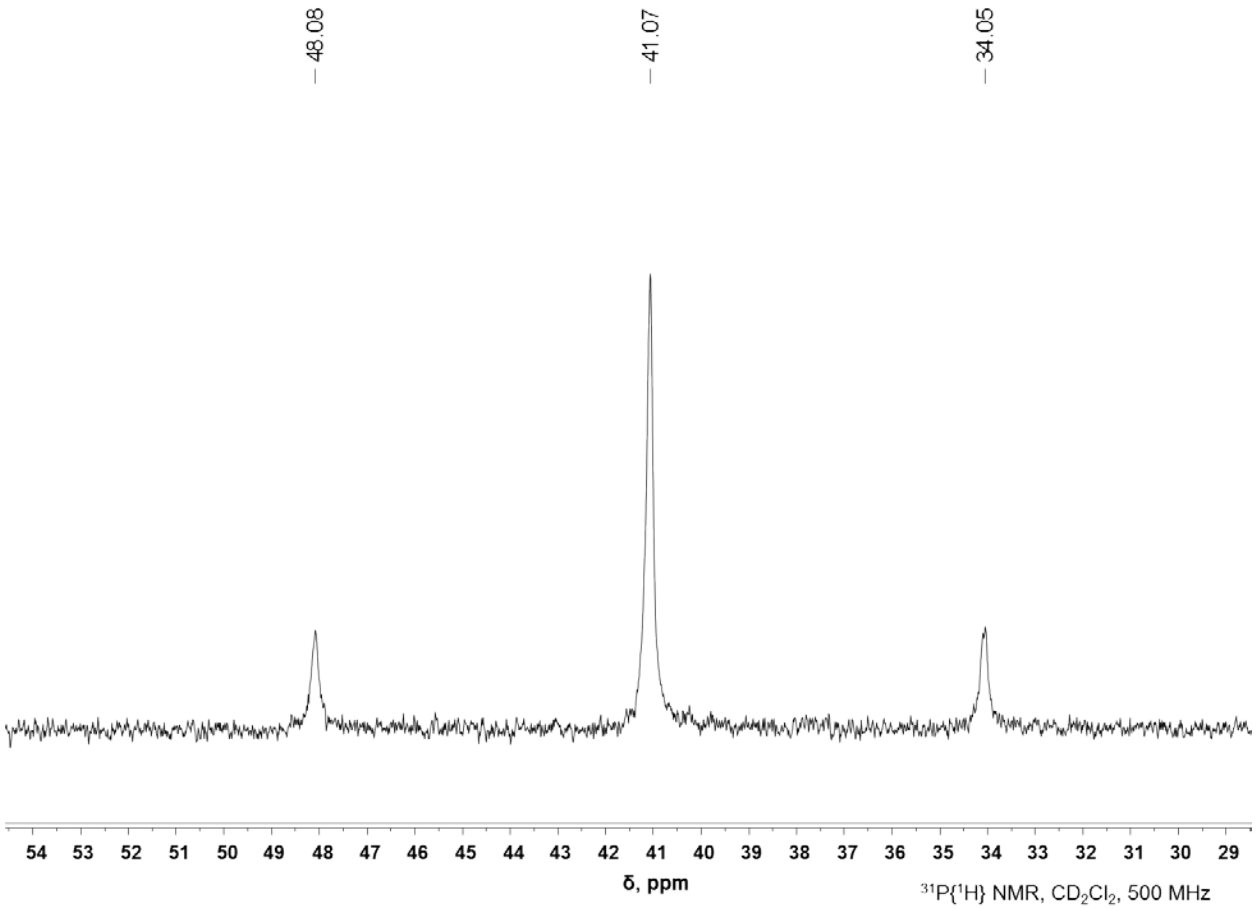


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of the **3b-d** product mixture in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

[(^{F}PN(H)P)PtC$_6$H$_4$F][BARF] (3e). 1 (99 mg, 0.13 mmol) and K-BARF (91 mg, 0.13 mmol) were added to a round-bottomed Teflon screw-capped flask. C_6H_5F was added, forming a yellow solution containing some undissolved K-BARF. The flask was then placed in an oil bath at 80°C. After 2 h, the solution had a pale green appearance. The solution was filtered over a pad of Celite and eluted with CH_2Cl_2 and C_6H_5F. The volatiles were removed under vacuum, yielding an oily blue residue along with a white solid. A minimal amount of CH_2Cl_2 was used to redissolve the solids, and the solution was layered with pentane. The resulting blue crystals were collected and washed with cold pentane. After drying under vacuum, a pale blue solid was collected. Isolated

yield: 120 mg, 71%. ^{1}H NMR (CD_2Cl_2): δ 7.52 (m, Ar-*H* overlapping with N-*H* signal and *o*-*H* of minor rotamer), 7.47 (br s, $J_{195Pt-H}$ = 40 Hz, N-*H*, major rotamer), 7.37 (m, Ar-*H*), 7.26 (ddd, J = 7.4 Hz, 4.5 Hz, 1.1 Hz, $J_{195Pt-H}$ = 74 Hz, *o*-aryl-*H*, major rotamer), 7.06 (app q, J = 7.3 Hz, *m*-aryl-*H*, major rotamer), 7.02 (app q, J = 7.0 Hz, *m*-aryl-*H*, minor rotamer), 6.94 (t, J = 7.4 Hz, *m*-aryl-*H*, major rotamer), 6.92 (t, J = 7.4 Hz, *m*-aryl-*H*, minor rotamer), 6.87 (td, J = 8.2 Hz, 1.3 Hz, *p*-aryl-*H*, major rotamer), 6.86 (td, J = 8.2 Hz, 1.3 Hz, *p*-aryl-*H*, minor rotamer), 2.83 (m, 2H, C*H*Me$_2$), 2.71 (m, 2H, C*H*Me$_2$), 1.18 (m, CH*Me*$_2$), 1.17 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, CH*Me*$_2$), 1.10 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, 12H, CH*Me*$_2$), 0.89 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, CH*Me*$_2$), 0.84 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.3 (dvt, J_{F-C} = 254 Hz, J_{P-C} = 5 Hz, C_{Ar}-F), 144.7 (vtd, J_{P-C} = 8 Hz, J_{F-C} = 2.5 Hz, C_{Ar}-N, major rotamer), 144.4 (vt, J_{P-C} = 8 Hz, C_{Ar}-N, minor rotamer), 137.4, 131.8 (vtd, J_{P-C} = 18 Hz, J_{F-C} = 6 Hz, C_{Ar}-P), 126.3 (d, J_{F-C} = 8 Hz), 126.1 (d, J_{F-C} = 8 Hz), 125.9 (m), 125.2, 124.9, 121.6 (d, J_{F-C} = 24 Hz, C_{Ar}-H), 121.2, 120.2 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 115.4 (d, J_{F-C} = 27 Hz, C_{Ar}-H), 114.7 (d, J_{F-C} = 27 Hz, C_{Ar}-H), 26.7 (vt, J_{P-C} = 15 Hz, *C*HMe$_2$), 26.0 (vt, J_{P-C} = 14 Hz, *C*HMe$_2$), 24.9 (vt, J_{P-C} = 14 Hz, *C*HMe$_2$), 23.3 (vt, J_{P-C} = 15 Hz, *C*HMe$_2$), 18.1 (CH*Me*$_2$, major rotamer), 17.9 (CH*Me*$_2$, minor rotamer), 17.7 (CH*Me*$_2$, major rotamer), 17.7 (CH*Me*$_2$, minor rotamer), 17.5 (CH*Me*$_2$, minor rotamer), 17.3 (CH*Me*$_2$, major rotamer), 17.1 (CH*Me*$_2$, minor rotamer), 16.8 (CH*Me*$_2$, major rotamer). ^{19}F NMR (CD_2Cl_2): δ -92.7 ($J_{195Pt-F}$ = 390 Hz, major rotamer), -94.7 ($J_{195Pt-F}$ = 317 Hz, minor rotamer), -111.3 (major rotamer), -111.4 (minor rotamer). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 43.4 ($J_{195Pt-P}$ = 2,716 Hz, minor rotamer), 43.0 ($J_{195Pt-P}$ = 2,700 Hz, major rotamer). Elemental analysis, found (calculated) for $C_{54}H_{39}BF_{23}NP_2Pt$: C, 46.04 (46.11); H, 2.71 (2.79). IR (solid): 3233 cm^{-1} (N-H).

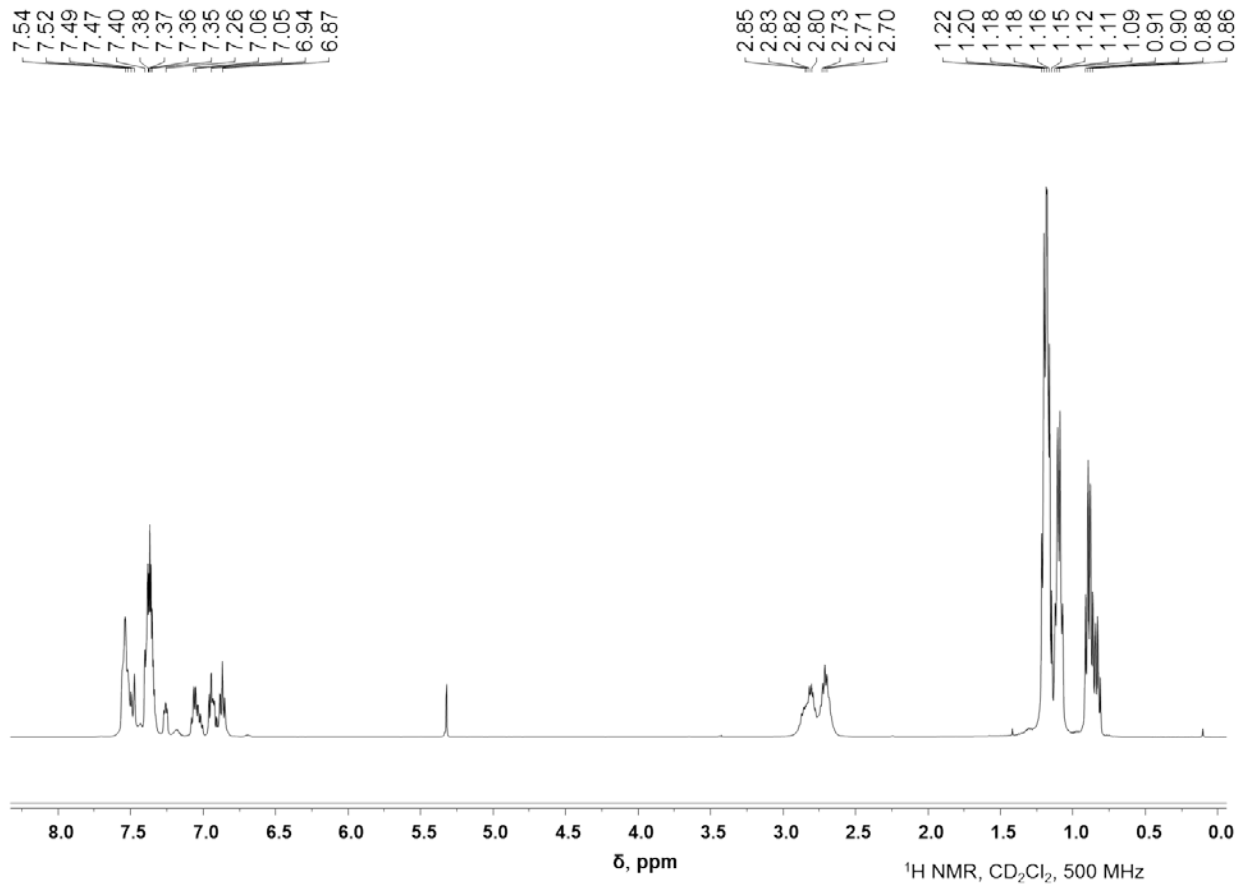


Figure S31. ^{1}H NMR spectrum of **3e** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

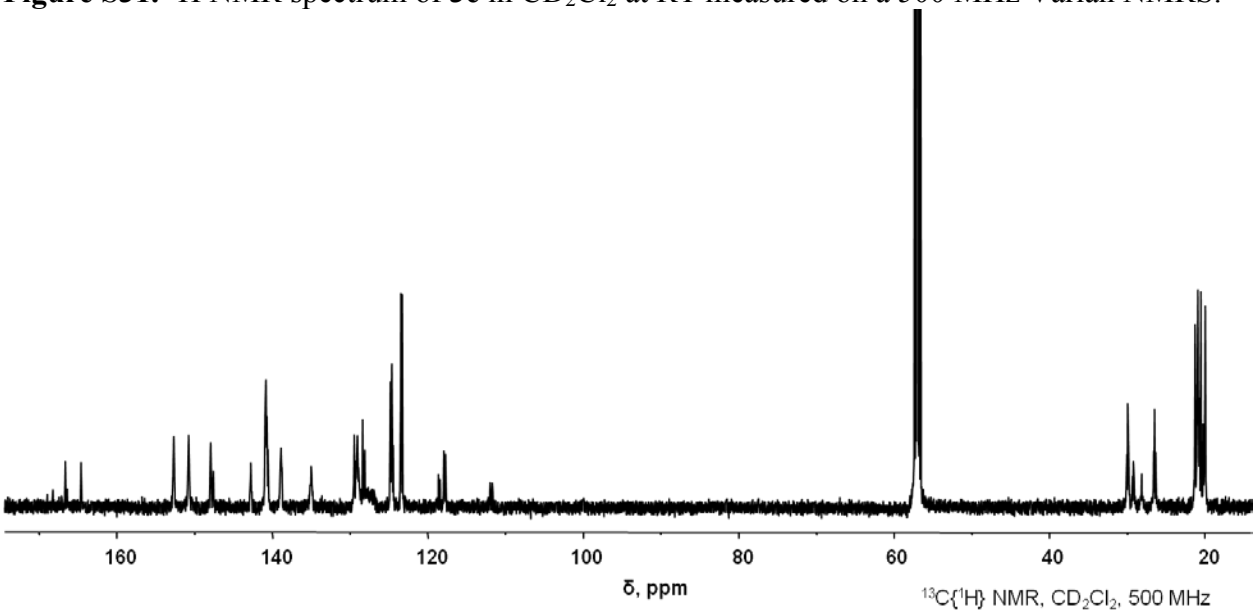


Figure S32. ^{13}C{^{1}H} NMR spectrum of **3e** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

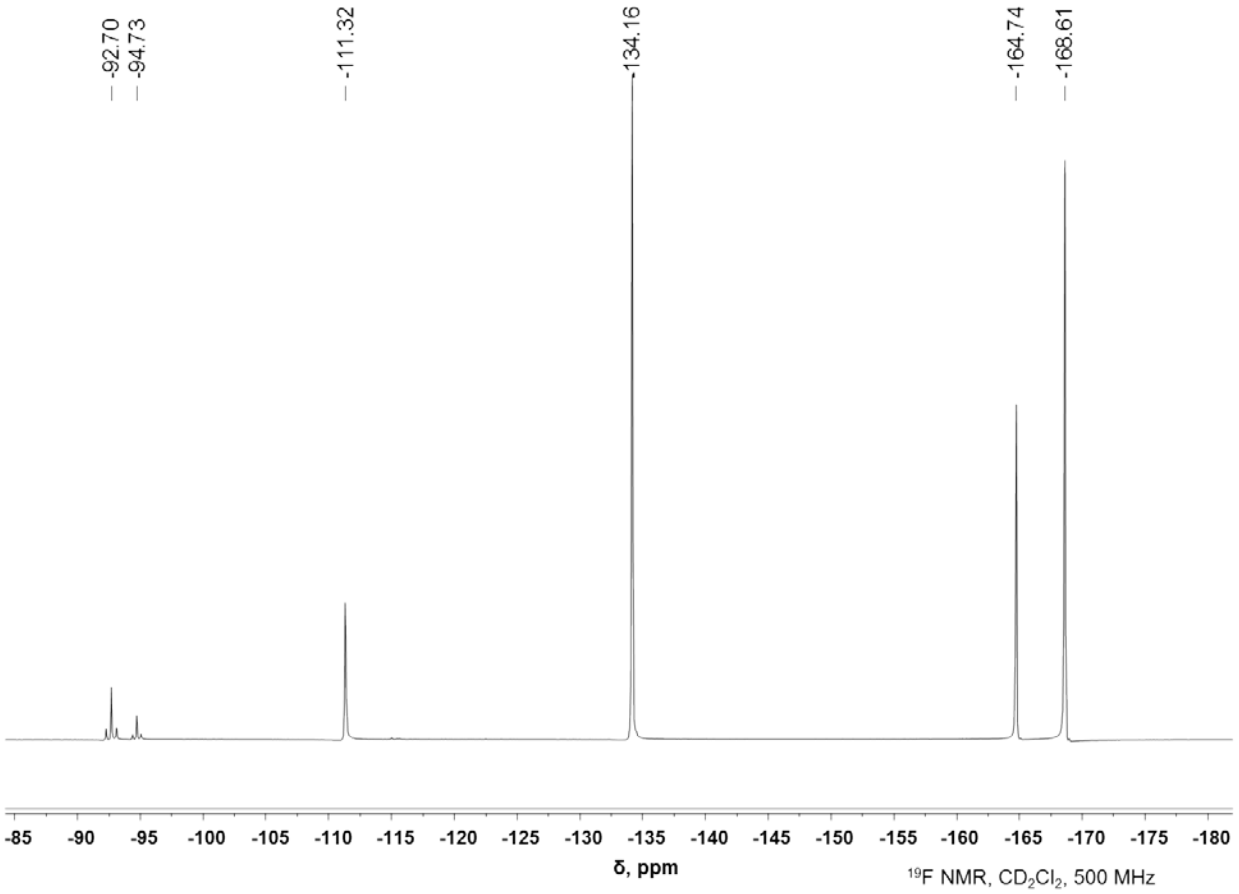


Figure S33. ^{19}F NMR spectrum of **3e** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

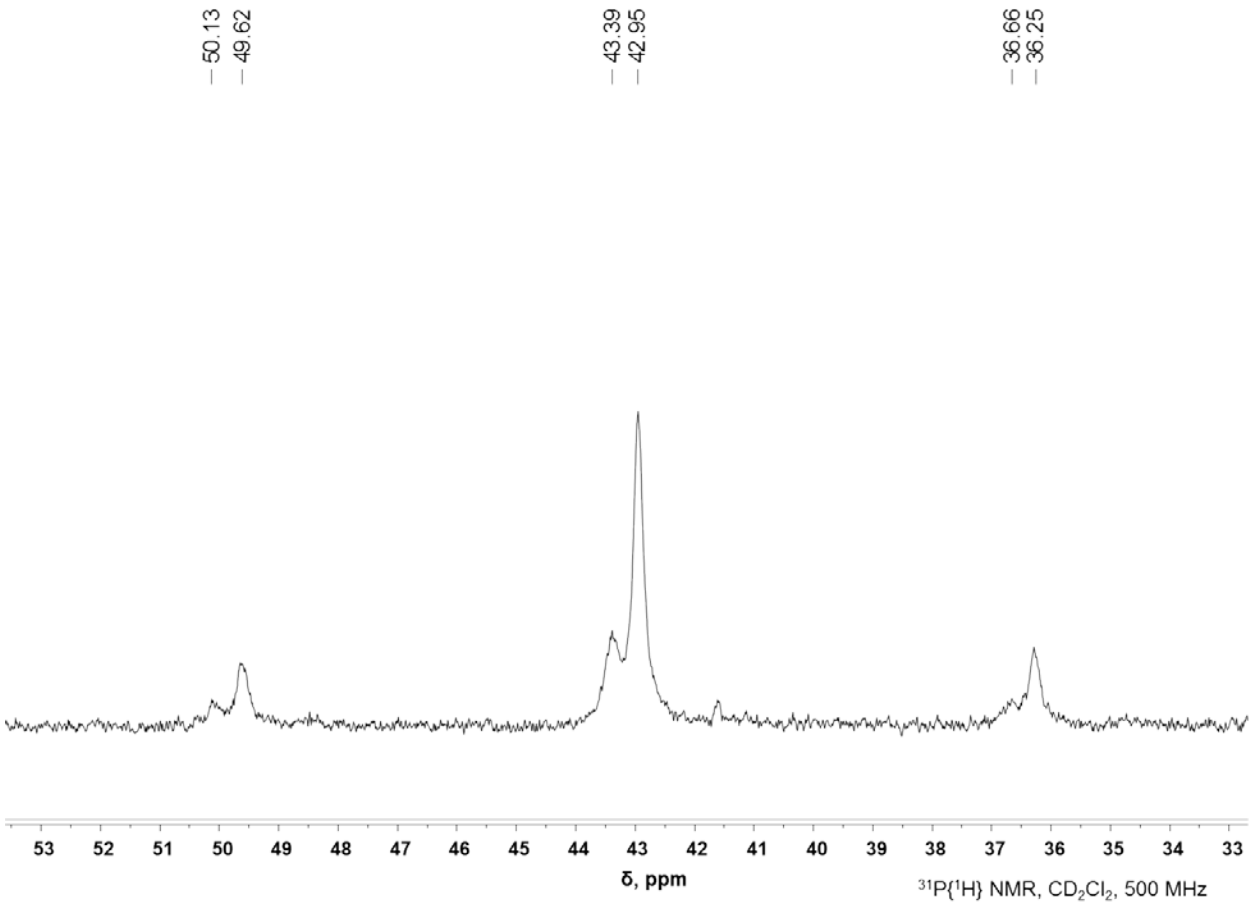
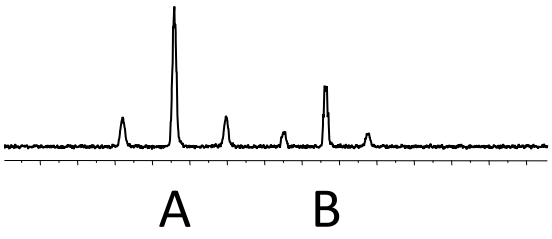


Figure S34. $^{31}P\{^{1}H\}$ NMR spectrum of **3e** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

Table S1. ^{19}F NMR VT study monitoring the *ortho* fluorine resonances of rotamer A and rotamer B for **3e** in C_6D_5Br from -20°C to 120°C.

T, (°C)	Integration A	Integration B
-20	1	0.49
RT	1	0.51
40	1	0.52
60	1	0.54
80	1	0.56
100	1	0.58
120	1	0.59



[(^{F}PN(H)P)PtC$_6$H$_4$Cl][BARF] (3f). 1 (21.8 mg, 0.0279 mmol) and K-BARF (19 mg, 0.026 mmol) were added to a 10 mL round-bottomed Teflon screw-capped flask. About 5 mL of C_6H_5Cl was added, forming a yellow solution. An aliquot was taken after 15 min, and 2 new signals were observed by ^{19}F NMR. The signal at -110.8 ppm corresponded to a C-H activation product, and the signal at -122.8 ppm is believed to be indicative of a Pt-chlorobenzene adduct (**4**). After 1 h at RT, the signal at -122.8 ppm was the major peak. After 48 h at RT, this signal was no longer visible by ^{19}F NMR, and full conversion to the C-H activation product was observed. The formation of (^{F}PNP)PtCl was not observed upon addition of decamethyl ferrocene (6 mg, 0.02 mmol). Conversion to the C-H activation product could also be achieved by heating the sample overnight at 80°C. **[(^{F}PNP)Pt-ClC$_6$H$_5$][BARF] (4).** ^{19}F NMR (C_6H_5Cl): δ -122.8. ^{31}P{^{1}H} NMR (C_6H_5Cl): δ 48.6 ($J_{195Pt-P}$ = 2,515 Hz). **[(^{F}PN(H)P)PtC$_6$H$_4$Cl][BARF] (3f).** ^{1}H NMR (CD_2Cl_2): δ 7.51 (m, 2H, Ar-*H*), 7.45 (br s, 1H, N-*H*, ^{195}Pt coupling buried), 7.36 (m, 4H, Ar-*H*), 7.23 (dd, J = 6.7 Hz, 2.5 Hz, 1H, ortho C-*H* of C_6H_4Cl, ^{195}Pt coupling buried), 7.19 (dd, J = 6.8 Hz, 2.5 Hz, 1H, meta C-*H* of C_6H_4Cl), 7.01 (m, 2H, meta and para C-*H* of C_6H_4Cl), 2.80 (m, 4H, C*H*Me$_2$), 1.19 (app q (dvt), J = 8 Hz, 12H, CH*Me*$_2$), 1.10 (app q (dvt), J = 8.5 Hz, 6H, CH*Me*$_2$), 0.87 (vtd, J_{P-H} = 9.5 Hz, J_{H-H} = 7.7 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.4 (d, J_{F-C} = 233 Hz, C_{Ar}-F), 144.7, 140.3 (t, J_{P-C} = 3 Hz), 138.3 ($J_{195Pt-C}$ = 38 Hz), 131.5 (m), 128.9 ($J_{195Pt-C}$ = 33 Hz), 127.2 ($J_{195Pt-C}$ = 69 Hz), 126.1, 123.9 (t, J_{P-C} = 9 Hz), 122.5, 121.5 (d, J_{F-C} = 24 Hz, C_{Ar}-H), 120.2 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 26.9 (vt, J_{P-C} = 14.3 Hz, *C*HMe$_2$), 23.1 (vt, J_{P-C} = 15 Hz, *C*HMe$_2$), 18.0 (CH*Me*$_2$), 17.4 (CH*Me*$_2$), 17.2 (CH*Me*$_2$), 16.6 (CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -111.3. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.5 ($J_{195Pt-P}$ = 2,775 Hz). IR (solid): 3235 cm^{-1} (N-H).

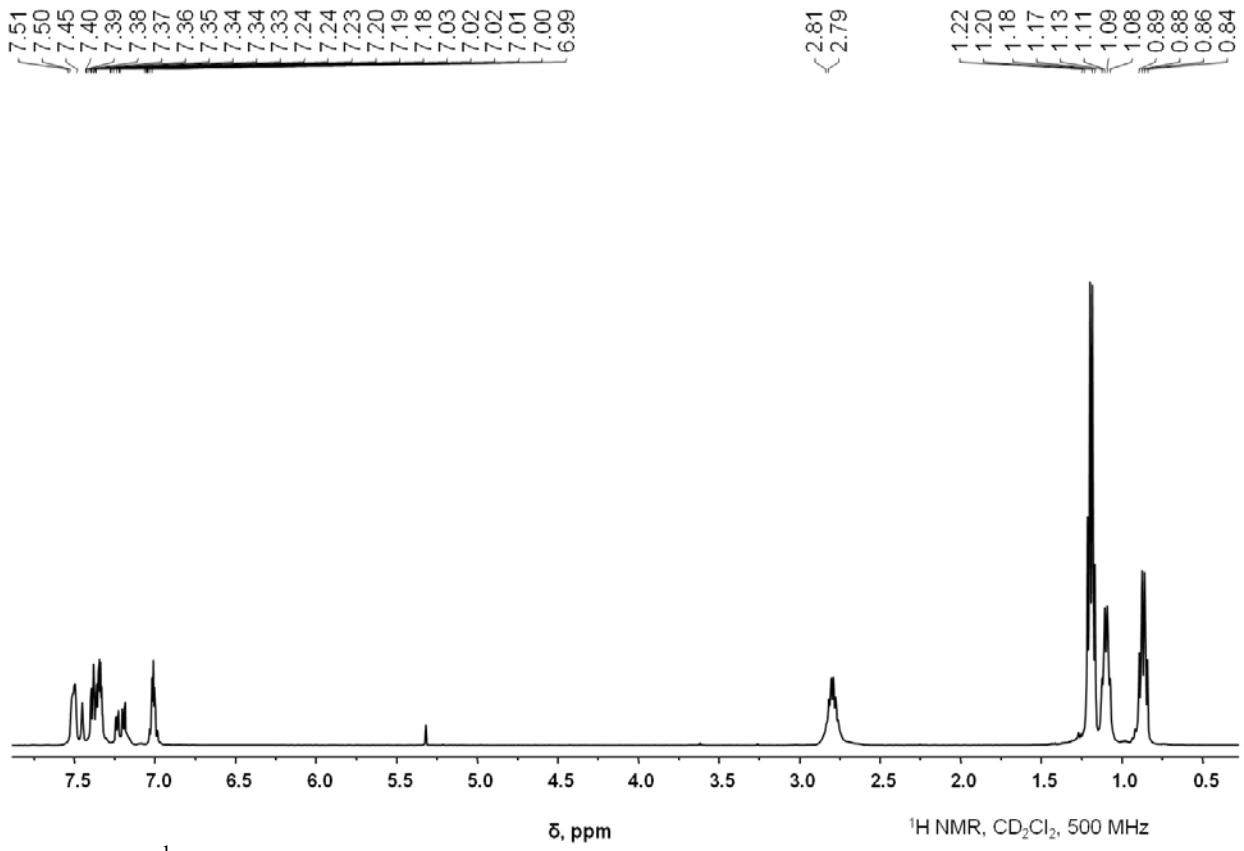


Figure S35. ^{1}H NMR spectrum of **3f** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

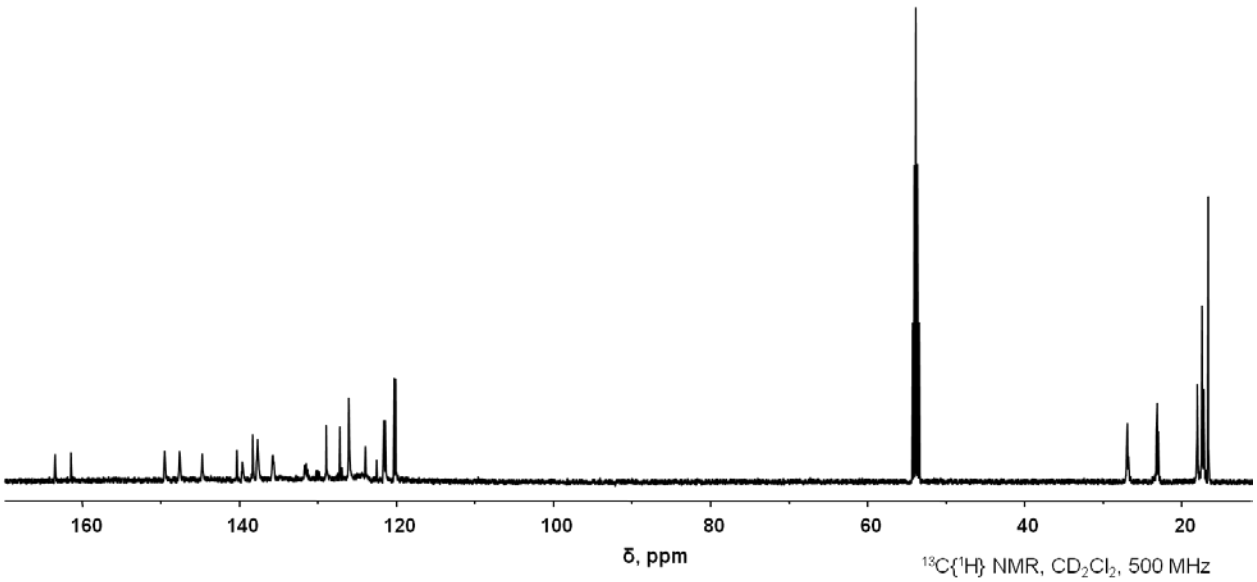


Figure S36. ^{13}C{^{1}H} NMR spectrum of **3f** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

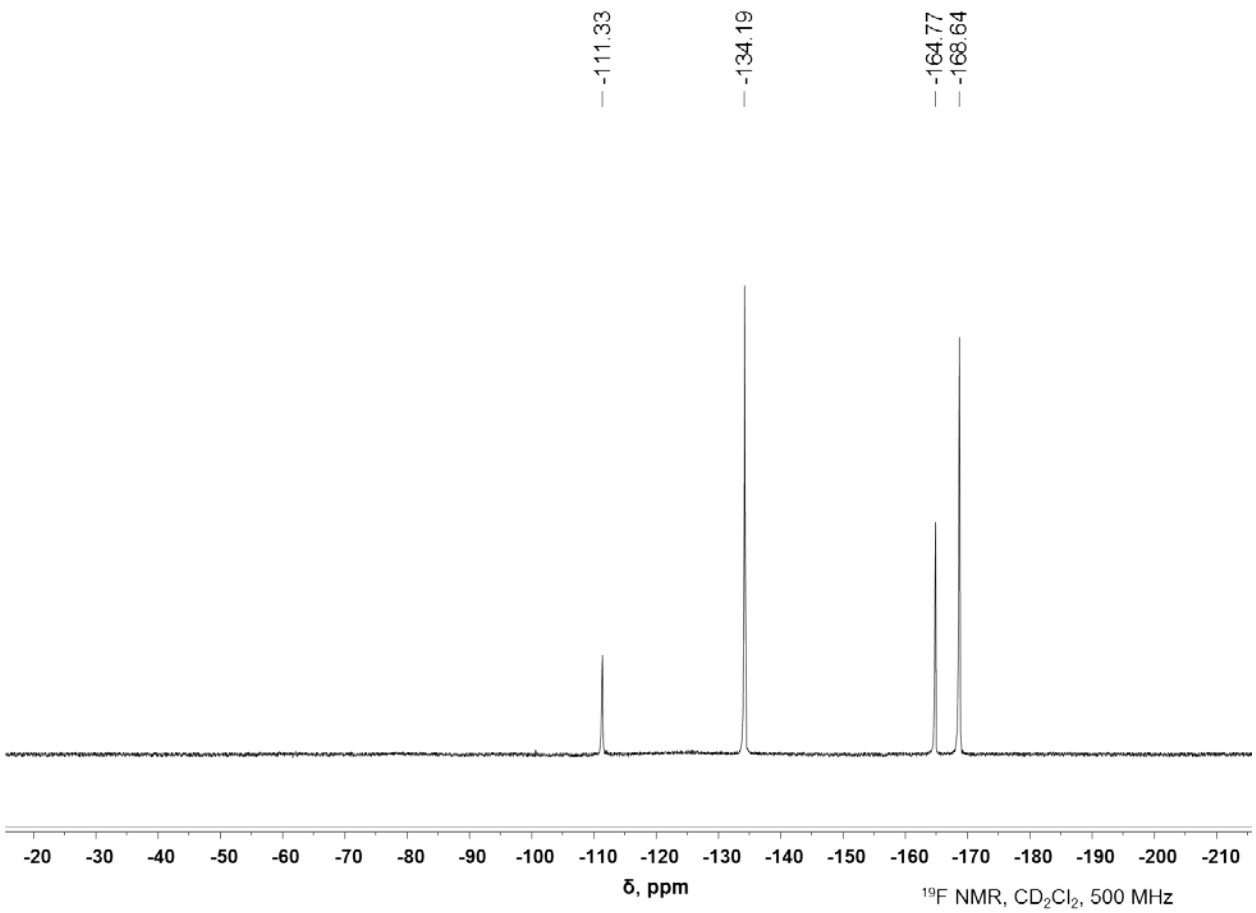


Figure S37. ^{19}F NMR spectrum of **3f** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

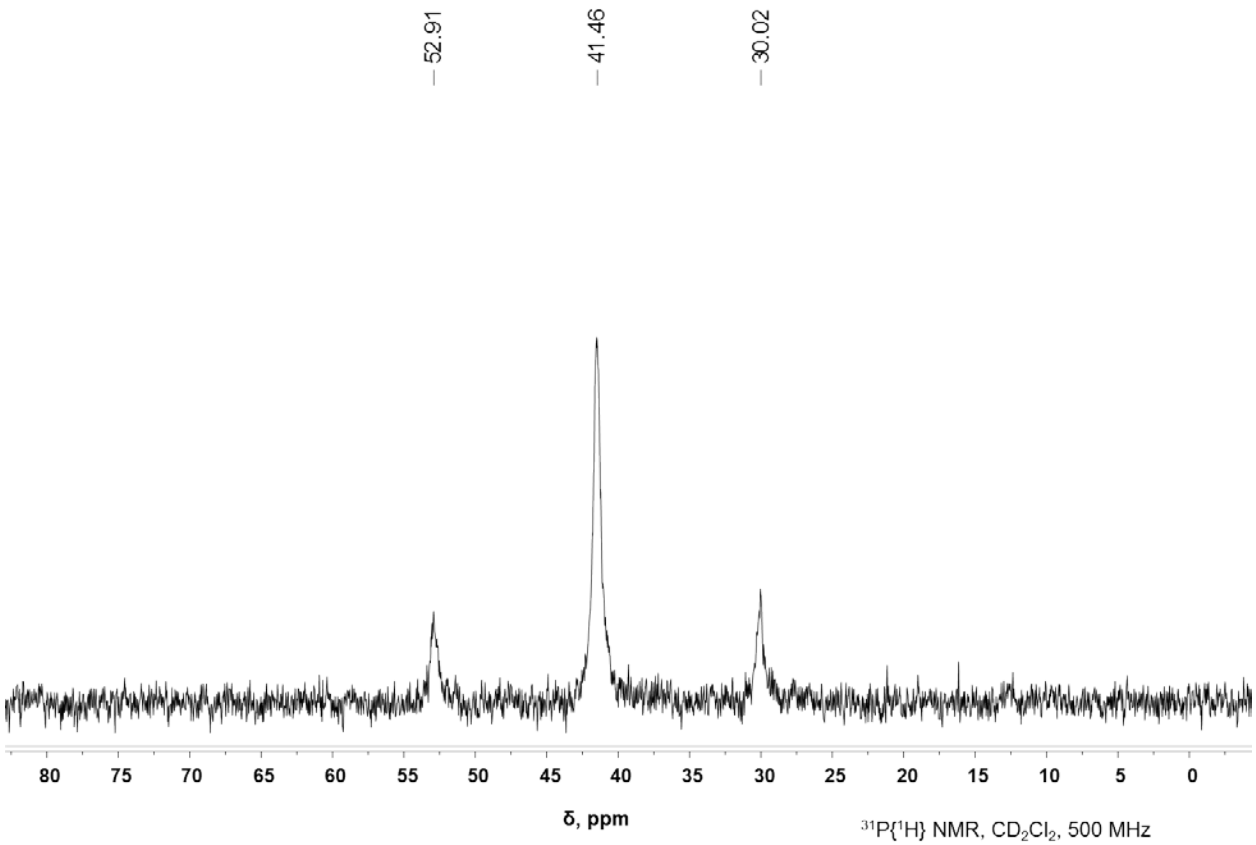


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum of **3f** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

Activation of bromobenzene and observation of [(^{F}PNP)Pt-BrC_6D_5][BARF] (10). 1 (21.4 mg, 0.0274 mmol) and K-BARF (19 mg, 0.026 mmol) were transferred to a J. Young NMR tube. C_6D_5Br was added, forming a yellow-orange solution. A capillary containing 1-fluorooctane in C_6D_6 was used to track the conversion of (^{F}PNP)PtOTf to the products. After 2 h, a new signal was observed in the ^{19}F NMR spectrum at -122.9 ppm, corresponding to what is believed to be [(^{F}PNP)Pt-BrC_6D_5][BARF] (**10**). After a total of 12 h, **1** was no longer observed by NMR. Continued monitoring of the reaction mixture showed no C-H activation products, even after 2 weeks at RT. The addition of MeCN led to the formation of **6**. A decrease in the BARF signals relative to the ^{19}F NMR signals of the ligand was noted after 2 weeks. Reduction of the reaction

mixture with decamethyl ferrocene led to the formation of (^{F}PNP)PtBr (**12**) (20% conversion). **[(^{F}PNP)Pt-BrC$_6$D$_5$][BARF] (10).** ^{1}H NMR (C$_6$D$_5$Br): δ 7.24 (br s, 2H, Ar-*H*), , 6.75 (t, J = 8 Hz, 2H, Ar-*H*), 6.67 (m, 2H, Ar-*H*), 2.05 (m, 4H, C*H*Me$_2$), 0.99 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 8 Hz, 12H, CH*Me*$_2$), 0.89 (app q (dvt), J = 7 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C$_6$D$_5$Br): δ 158.3 (vt, J_{P-C} = 10 Hz, C_{Ar}-N), 156.0 (d, J_{F-C} = 244 Hz, C_{Ar}-F), 119.6 (d, J_{F-C} = 22.5 Hz, C_{Ar}-H), 117.2 (d, J_{F-C} = 21.5 Hz, C_{Ar}-H), 116.4 (m, C_{Ar}-P), 116.3 (m, C_{Ar}-H), 25.3 (vt, J_{P-C} = 29 Hz, *C*HMe$_2$), 17.5 (CH*Me*$_2$), 16.9 (CH*Me*$_2$). ^{19}F NMR (C$_6$D$_5$Br): δ -122.9. ^{31}P{^{1}H} NMR (C$_6$D$_5$Br): δ 46.9 ($J_{195Pt-P}$ = 2,490 Hz). **(^{F}PNP)PtBr (12).** ^{19}F NMR (C$_6$D$_5$Br): -128.5. ^{31}P{^{1}H} NMR (C$_6$D$_5$Br): δ 40.8 ($J_{195Pt-P}$ = 2,623 Hz).

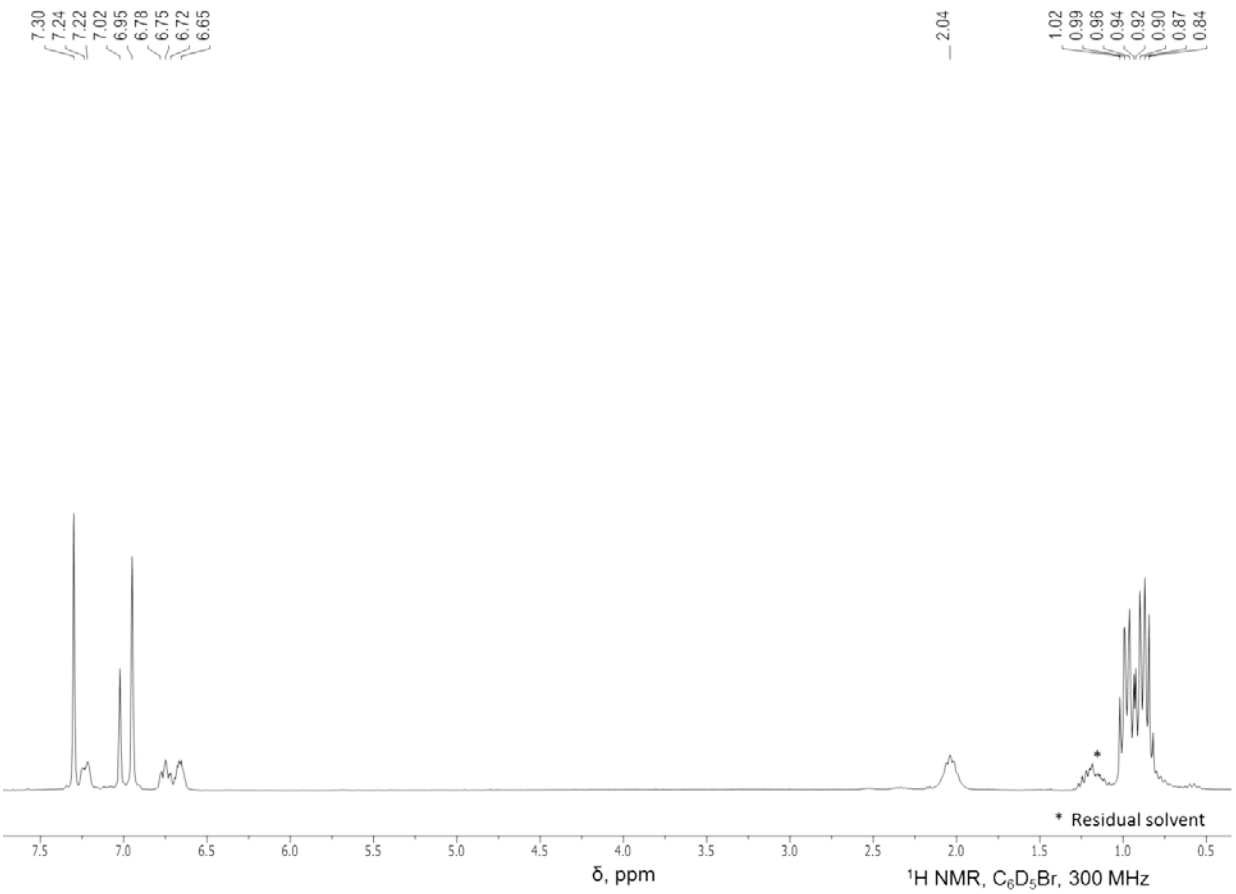


Figure S39. ^{1}H NMR spectrum of **10** in C$_6$D$_5$Br at RT measured on a 300 MHz Varian iNova.

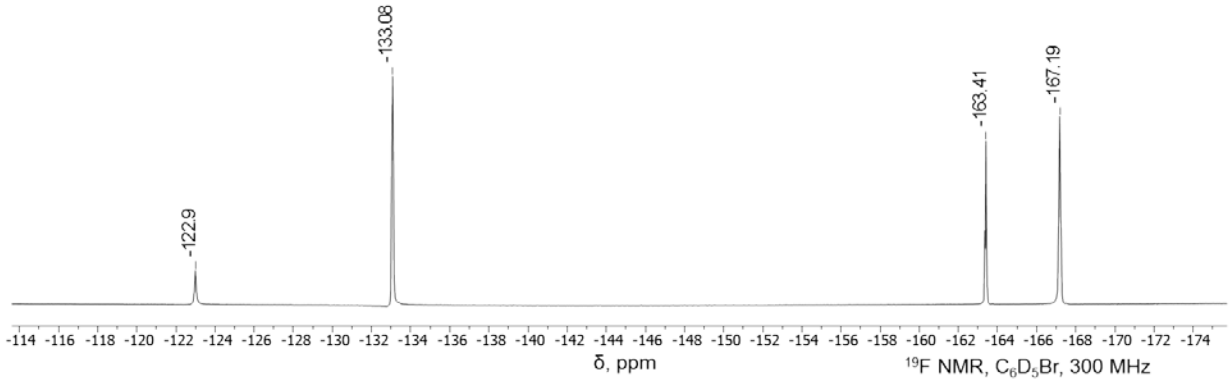


Figure S40. ^{19}F NMR spectrum of **10** in C_6D_5Br at RT measured on a 300 MHz Varian iNova.

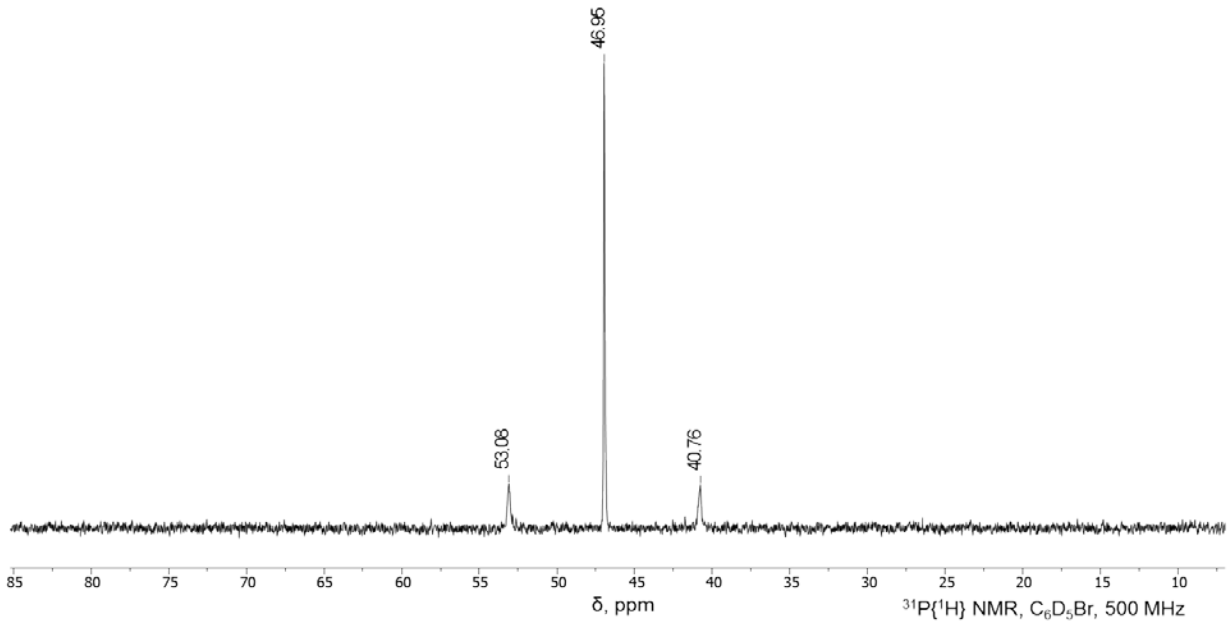


Figure S41. $^{31}P\{^1H\}$ NMR spectrum of **10** in C_6D_5Br at RT measured on a 500 MHz Varian NMRS.

II-E. Syntheses of [(PN(H)P)Pt-R]$^+$ by protonation of (PNP)Pt-R.

[(PN(H)P)Pt-C_6H_5][BARF] (3a). 2a (21 mg, 0.030 mmol) was dissolved in about 3 mL of pentane in a small vial, forming a clear yellow solution. HOTf (15.4 µL, 1.88 M solution in Et_2O, 0.0290 mmol) was added, and a white precipitate immediately crashed out of the solution. The solvent was decanted off, and the solid was washed with 3x 3 mL of pentane, dried under vacuum and then dissolved in 3 mL of CH_2Cl_2. K-BARF (21 mg, 0.029 mmol) was added, and the solution was stirred overnight at RT. The solution was filtered over Celite, the volatiles were removed and the residual oily blue solid was redissolved in CD_2Cl_2 for characterization. The NMR spectra matched those of the compound synthesized via the C-H activation experiment described above.

Protonation of (^{F}PNP)PtC_6H_4Me isomers. The protonated tolyl isomers were independently synthesized to help confirm the characterization of the products from the toluene C-H activation reactions. The neutral (^{F}PNP)PtC_6H_4Me species were reacted with a substoichiometric amount of [H(OEt_2)$_2$][BARF] (0.9 eq). The mixtures were dissolved in approximately 5 mL of a 3:1 mixture of pentane and diethyl ether and stirred for 30 min. The resulting solids were loaded onto a bed of Celite, rinsed with pentane and diethyl ether and then washed through with CH_2Cl_2. The volatiles were removed and the isolated solids were redissolved in CD_2Cl_2 for characterization.

[(^{F}PN(H)P)Pt-*o*-C_6H_4Me][BARF] (3b). Isolated yield: 36 mg, 59%. ^{1}H NMR (CD_2Cl_2): δ 7.49 (m, 2H, Ar-*H*), 7.37 (m, 2H, Ar-*H*), 7.32 (m, 2H, Ar-*H*), 7.27 (br s, $J_{195Pt-H}$ = 32.6 Hz, 1H, N-*H*), 7.21 (d, J = 7.4 Hz, $J_{195Pt-H}$ = 66.8 Hz, 1H, *o*-tolyl-*H*), 6.99 (d, J = 7.4 Hz, 1H, *m*-tolyl-*H*), 6.92 (t, J = 7.2 Hz, 1H, tolyl-*H*), 6.87 (td, J = 7.4 Hz, 1.3 Hz, 1H, tolyl-*H*), 2.82 (m, 2H, C*H*Me_2), 2.68 (m, 2H, C*H*Me_2), 2.63 (s, 3H, C_6H_4*Me*), 1.20 (app q (dvt), J = 8 Hz, 6H, CH*Me*$_2$), 1.14 (app

q (dvt), J = 8 Hz, 6H, CH*Me*$_2$), 1.05 (app q (dvt), J = 8 Hz, 6H, CH*Me*$_2$), 0.83 (app q (dvt), J = 8 Hz, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.3 (d, J_{F-C} = 257 Hz, C_{Ar}-F), 144.5, 141.2 (t, J_{P-C} = 2.3 Hz), 136.1 (t, J_{P-C} = 2.4 Hz, $J_{195Pt-C}$ = 42 Hz), 131.7 (m), 129.5 ($J_{195Pt-C}$ = 40 Hz), 126.2 (br s), 126.1 ($J_{195Pt-C}$ = 66 Hz), 124.5, 124.4, 121.5 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 120.1 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 27.4 ($C_6H_4CH_3$), 26.7 (vt, J_{P-C} = 14.3 Hz, *C*HMe$_2$), 23.1 (vt, J_{P-C} = 15.2 Hz, *C*HMe$_2$), 18.0 (CH*Me*$_2$), 17.6 (CH*Me*$_2$), 17.2 (CH*Me*$_2$), 16.5 (CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -111.6. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 40.3 ($J_{195Pt-P}$ = 2,848 Hz).

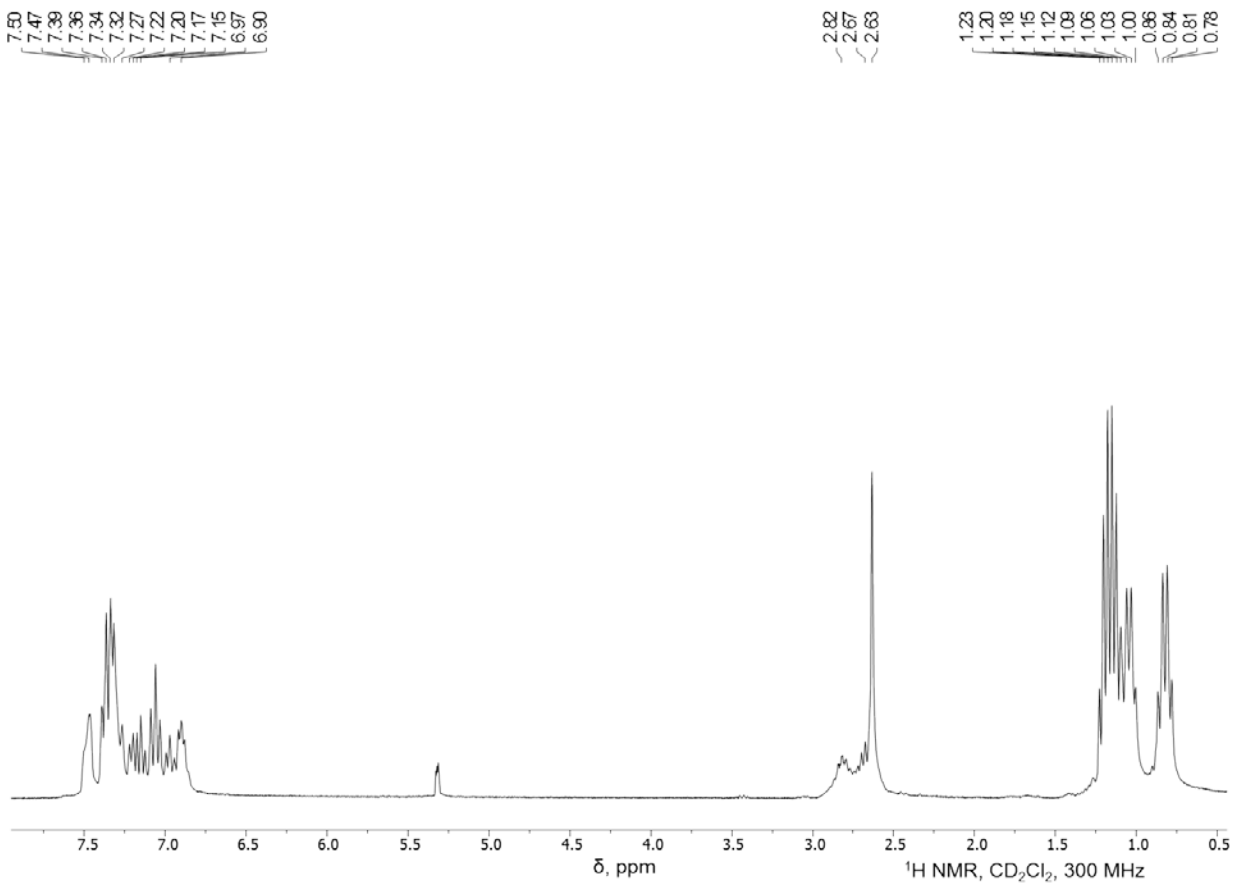


Figure S42. ^{1}H NMR spectrum of **3b** in CD_2Cl_2 at RT measured on a 300 MHz Varian iNova.

[(^{F}PN(H)P)Pt-*m*-C_6H_4Me][BARF] (3c). Isolated yield: 51 mg, 73%. ^{1}H NMR (CD_2Cl_2): δ 7.52 (m, 2H, Ar-*H*), 7.36 (m, 5H, Ar-*H* and *o*-C*H* of tolyl), 7.24 (br s, $J_{195Pt-H}$ = 34.9 Hz, 1H, N-*H*), 7.05 (br m, 1H, *o*-C*H*), 6.93 (t, J = 7.5 Hz, 1H, *m*-C*H*), 6.76 (d, J = 7.5 Hz, 1H, *p*-C*H*), 2.80 (m, 2H, C*H*Me_2), 2.68 (m, 2H, C*H*Me_2), 2.25 (s, 3H, C_6H_4*Me*), 1.20 (m, 12H, CH*Me*$_2$), 1.08 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, CH*Me*$_2$), 0.89 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.3 (dvt, J_{F-C} = 256 Hz, J_{P-C} = 4 Hz, C_{Ar}-F), 144.6 (vtd, J_{P-C} = 7 Hz, J_{F-C} = 3 Hz, C_{Ar}-N), 138.6, 136.9, 133.3, 132.3 (vtd, J_{P-C} = 17 Hz, J_{F-C} = 6 Hz, C_{Ar}-P), 128.7, 126.0, 125.0, 124.5, 121.5 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 120.0 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 26.4 (vt, J_{P-C} = 13 Hz, *C*HMe_2), 23.5 (vt, J_{P-C} = 15 Hz, *C*HMe_2), 21.5 (C_6H_4*C*H_3), 18.0 (CH*Me*$_2$), 17.9 (CH*Me*$_2$), 17.6 (CH*Me*$_2$), 17.0 (CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -111.8. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.0 ($J_{195Pt-P}$ = 2,838 Hz).

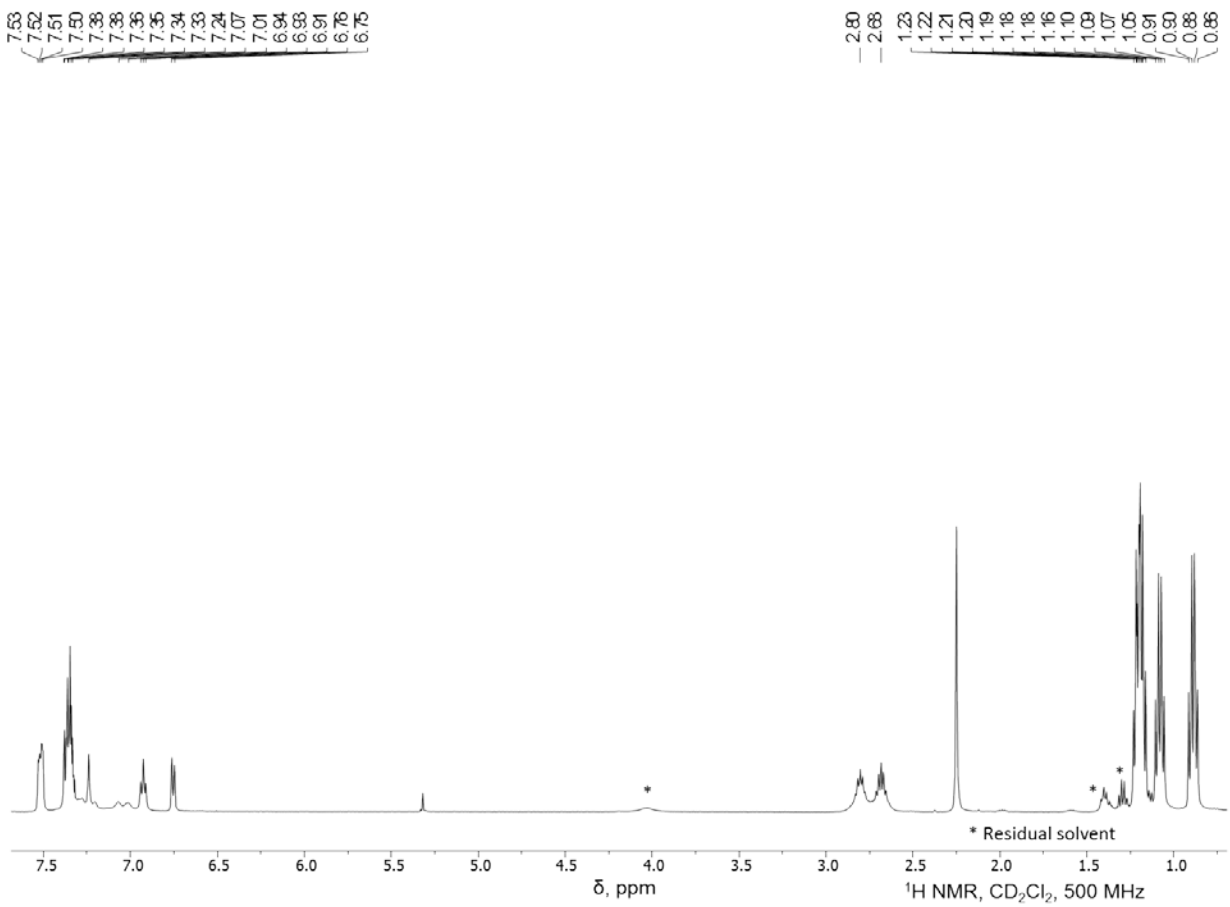


Figure S43. ^{1}H NMR spectrum of **3c** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

[(^{F}PN(H)P)Pt-*p*-C$_6$H$_4$Me][BARF] (3d). Isolated yield: 49 mg, 80%. ^{1}H NMR (CD_2Cl_2): δ 7.51 (m, 2H, Ar-*H*), 7.44-7.0 (very broad signal, 2H, *o*-C*H*), 7.36 (m, 4H, Ar-*H*), 7.22 (br s, $J_{195Pt-H}$ = 37.6 Hz, 1H, N-*H*), 6.89 (d, J = 7.7 Hz, 2H, *m*-C*H*), 2.80 (m, 2H, C*H*Me$_2$), 2.67 (m, 2H, C*H*Me$_2$), 2.23 (s, 3H, C$_6$H$_4$*Me*), 1.19 (m, 12H, CH*Me*$_2$), 1.07 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 8 Hz, CH*Me*$_2$), 0.88 (dvt, J_{H-H} = 9 Hz, J_{P-H} = 8 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 162.3 (dvt, J_{F-C} = 256 Hz, J_{P-C} = 5 Hz, C_{Ar}-F), 144.6 (vtd, J_{P-C} = 8 Hz, J_{F-C} = 3 Hz, C_{Ar}-N), 135.9 (t, J_{P-C} = 2.4 Hz, overlapping with BARF signal, $J_{195Pt-C}$ = 42 Hz), 133.6, 132.4 (vtd, J_{P-C} = 17 Hz, J_{F-C} = 6 Hz, C_{Ar}-P), 129.9, 126.1, 121.5 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 120.0 (d, J_{F-C} = 23 Hz, C_{Ar}-H), 26.4 (vt, J_{P-C} = 14.7 Hz, *C*HMe$_2$), 23.6 (vt, J_{P-C} = 15.2 Hz, *C*HMe$_2$), 20.8 (C$_6$H$_4$*C*H$_3$), 18.1 (CH*Me*$_2$), 17.9

(CH*Me*$_2$), 17.6 (CH*Me*$_2$), 17.0 (CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -111.4. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.1 ($J_{195Pt-P}$ = 2,830 Hz).

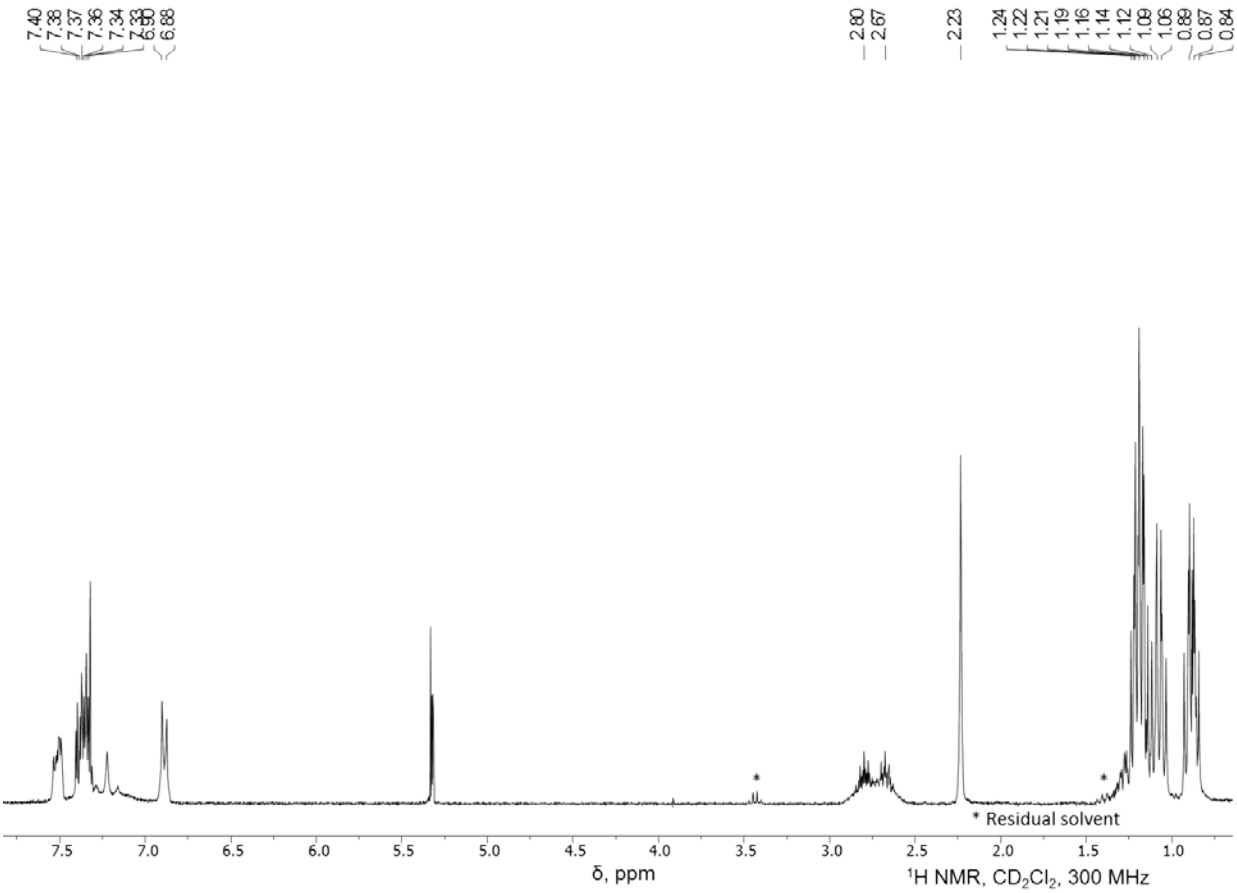


Figure S44. ^{1}H NMR spectrum of **3d** in CD_2Cl_2 at RT measured on a 300 MHz Varian iNova.

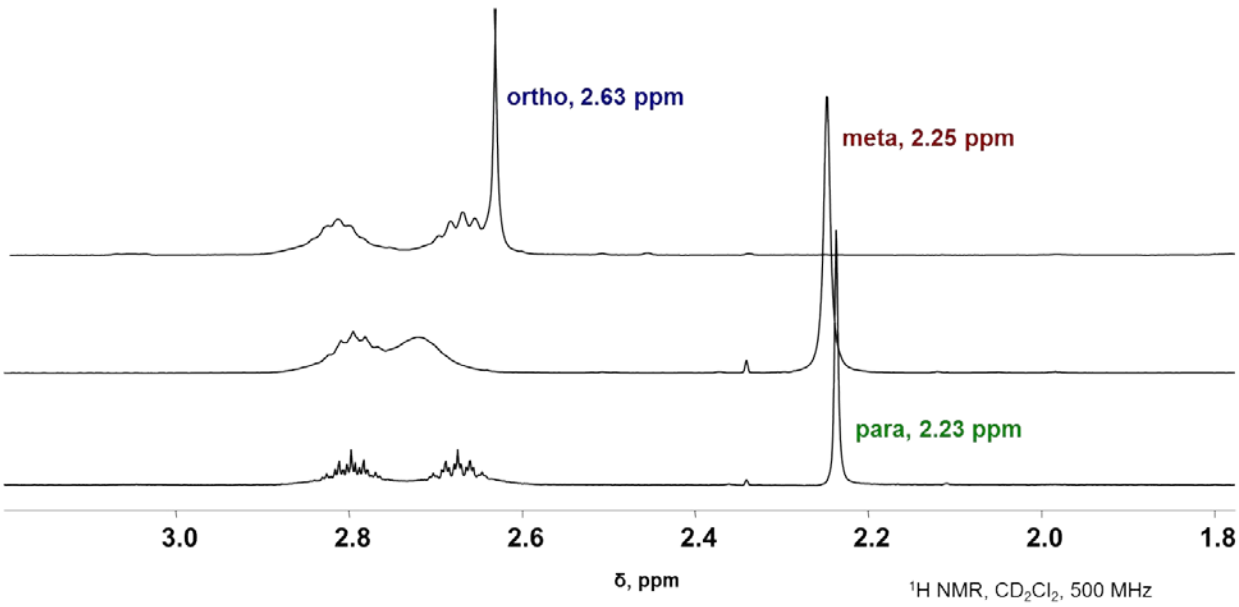


Figure S45. ^{1}H NMR spectra of the tolyl methyl resonances for **3b, 3c** and **3d** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

[(^{F}PN(H)P)PtCH$_2$C$_6$H$_5$][BARF] (3g). In a 25 mL Schlenk flask covered with Al foil, **2g** (18.6 mg, 0.0257 mmol) was dissolved in approximately 5 mL of a 1:1 Et_2O/pentane solution. [H(OEt$_2$)$_2$][BARF] (19.4 mg, 0.0234 mmol, 0.9 eq) was added, and the formation of a white precipitate was noted after 30 min. The solution was stirred overnight, and the formation of additional precipitate was observed after 12 h. The volatiles were removed, and the resulting solid was resuspended in pentane, loaded on a bed of Celite, rinsed with pentane and then washed through with CH_2Cl_2. The volatiles were removed, and the solid was redissolved in CD_2Cl_2 for characterization. ^{1}H NMR (CD_2Cl_2): δ 7.42-7.38 (m, 2H, Ar-*H*), 7.38-7.32 (m, 6H, Ar-*H* overlapping with o-C*H* of benzyl), 7.23 (t, J = 7.5 Hz, 2H, *m*-C*H* of benzyl), 7.12 (t, J = 8 Hz, 1H, *p*-C*H* of benzyl), 7.09 (br s, $J_{195Pt-H}$ = 35 Hz, 1H, N-*H*), 3.46 (t, J = 6.3 Hz, $J_{195Pt-H}$ = 95 Hz, 2H, C*H*$_2$C$_6$H$_5$), 2.85 (m, 2H, C*H*Me$_2$), 2.41 (m, 2H, C*H*Me$_2$), 1.32 (app q (dvt), J = 8 Hz, 6H, CH*Me*$_2$), 1.28 (app q (dvt), J = 7.5 Hz, 6H, CH*Me*$_2$), 1.15 (app q (dvt), J = 8 Hz, 6H,

CH*Me*$_2$), 1.10 (vtd, J_{P-H} = 9 Hz, J_{H-H} = 7 Hz, 6H, CH*Me*$_2$). ^{19}F NMR (CD_2Cl_2): δ -111.5. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.1 ($J_{195Pt-P}$ = 2,954 Hz).

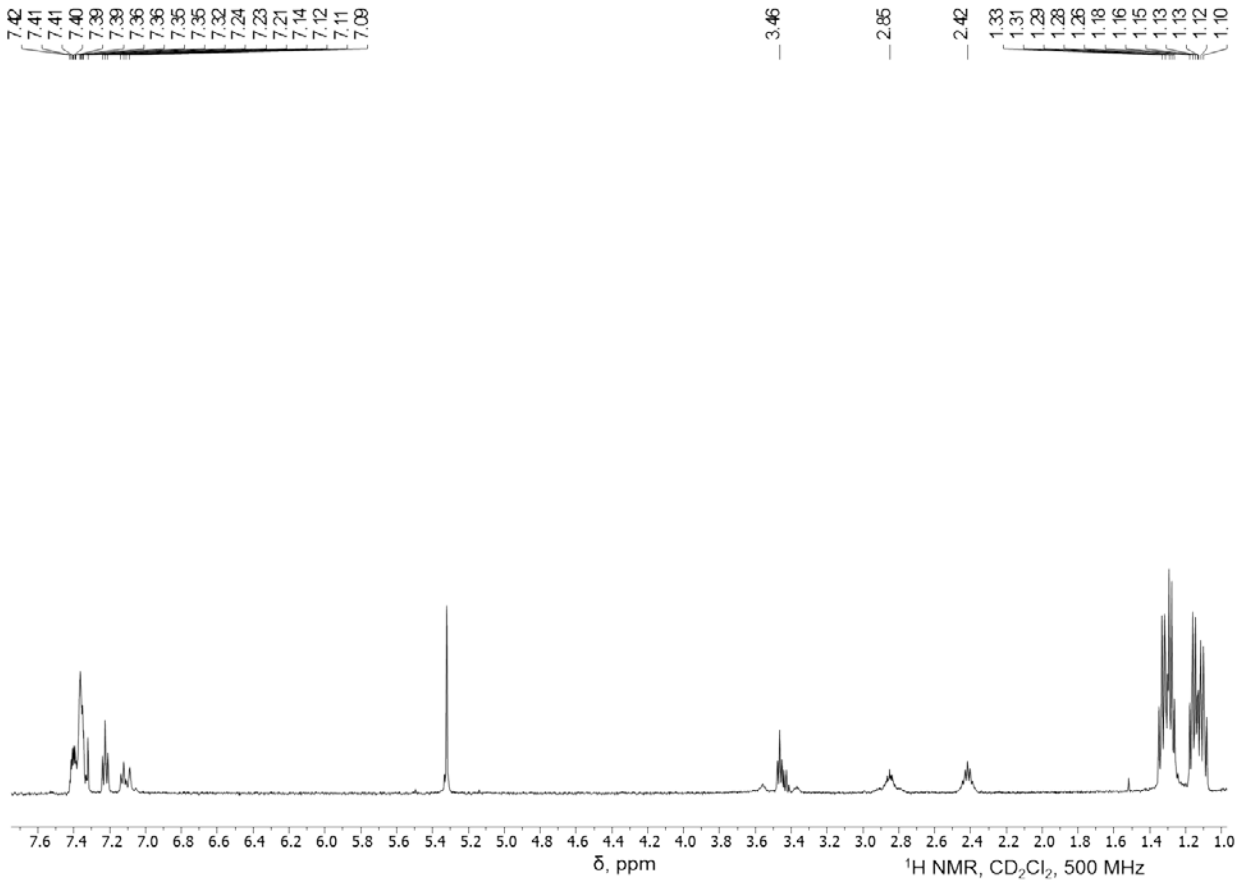


Figure S46. ^{1}H NMR spectrum of **3g** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

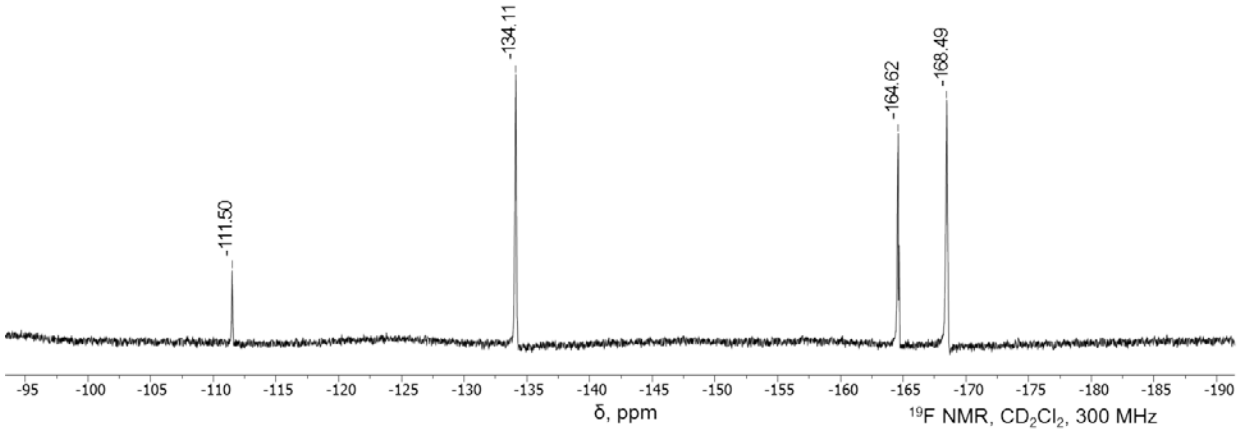


Figure S47. ^{19}F NMR spectrum of **3g** in CD_2Cl_2 at RT measured on a 300 MHz Varian iNova.

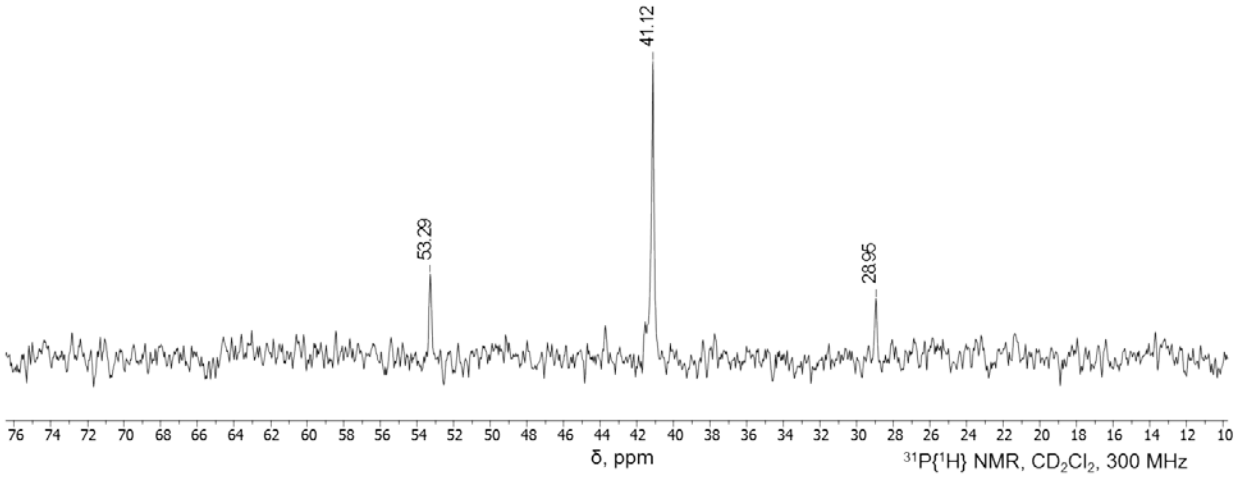


Figure S48. $^{31}P\{^1H\}$ NMR spectrum of **3g** in CD_2Cl_2 at RT measured on a 300 MHz Varian iNova.

II-F. Syntheses of (PNP)Pt-R by deprotonation of [(PN(H)P)Pt-R]$^+$.

(^{F}PNP)PtC$_6$D$_5$ (2a-D). 3a-D (29 mg, 0.023 mmol) was transferred to a J. Young NMR tube and dissolved in C_6D_6. KO^{t}Bu (3 mg, 0.03 mmol) was added, and the NMR tube was shaken, yielding a yellow solution with a colorless precipitate. Full conversion to **2a-D** was confirmed by ^{19}F NMR, using fluorobenzene as an internal standard. The solution was filtered into a 10 mL Schlenk flask, the volatiles were removed and the resulting yellow solid was redissolved in C_6D_6 for characterization. ^{1}H NMR (C_6D_6): δ 7.55 (m, 2H, Ar-*H*), 6.75 (m, 4H, Ar-*H*), 2.08 (m, 4H, C*H*Me$_2$), 0.90-0.83 (m, 24H, CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -130.6. ^{31}P{^{1}H} NMR (C_6D_6): δ 40.1 ($J_{195Pt-P}$ = 2,848 Hz).

Deprotonation of 3b-d with KO^{t}Bu. [(^{F}PN(H)P)PtC$_6$H$_4$Me][BARF] (65 mg, 0.047 mmol) was transferred to a J. Young NMR tube and dissolved in C_6D_6. KO^{t}Bu (6 mg, 0.05 mmol) was added, and the NMR tube was shaken, yielding a yellow solution with a colorless precipitate. The ^{19}F NMR spectrum showed full conversion to **2b-d**, and the ^{1}H NMR spectrum showed a **2b**:(**2c** plus **2d**) ratio of 8%:92% (**2c** and **2d** signals overlap).

(^{F}PNP)PtC$_6$H$_4$F (2e). 3e (19.8 mg, 0.0141 mmol) was transferred to a J. Young NMR tube and dissolved in C_6D_6. KO^{t}Bu (2 mg, 0.02 mmol) was added, and the NMR tube was shaken, yielding a yellow solution with a colorless precipitate. The ^{19}F NMR spectrum showed full conversion to **2e**. ^{1}H NMR (C_6D_6): δ 7.61 (m, $J_{195Pt-H}$ = 65 Hz, 1H, ortho C-*H* of C$_6$H$_4$F), 7.52 (m, 2H, Ar-*H*), 6.95-6.91 (m, 3H, meta and para C-*H* of C$_6$H$_4$F), 6.77-6.71 (m, 4H, Ar-*H*), 2.17 (m, 2H, C*H*Me$_2$), 2.04 (m, 2H, C*H*Me$_2$), 0.96-0.79 (m, 24H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 166.8 (d, J_{F-C} = 227 Hz, C_{Ar}-F), 160.6 (br s, C_{Ar}-N), 154.2 (d, J_{F-C} = 237 Hz, C_{Ar}-F), 140.5 (dvt, J_{F-C} = 18 Hz, J_{P-C} = 2 Hz, C_{Ar}-H), 124.0 (J_{Pt-C} = 58 Hz, C_{Ar}-Pt), 123.5 (dvt, J_{F-C} = 7.5 Hz, J_{P-C} = 1.4 Hz, C_{Ar}-H), 121.3 (vt, J_{P-C} = 18 Hz, C_{Ar}-P), 120.7 (m), 118.5 (d, J_{F-C} = 21.5 Hz, C_{Ar}-H), 117.9

(d, J_{F-C} = 22.5 Hz, C_{Ar}-H), 115.0 (br s, C_{Ar}-H), 113.5 (d, J_{F-C} = 29 Hz, C_{Ar}-H), 25.3 (vt, J_{P-C} = 15 Hz, *C*HMe$_2$), 23.8 (vt, J_{P-C} = 15 Hz, *C*HMe$_2$), 17.6 (br, CH*Me*$_2$), 17.3 (CH*Me*$_2$), 17.0 (CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -92.3 ($J_{195Pt-F}$ = 338 Hz), -131.3. ^{31}P{^{1}H} NMR (C_6D_6): δ 42.1 ($J_{195Pt-P}$ = 2,770 Hz).

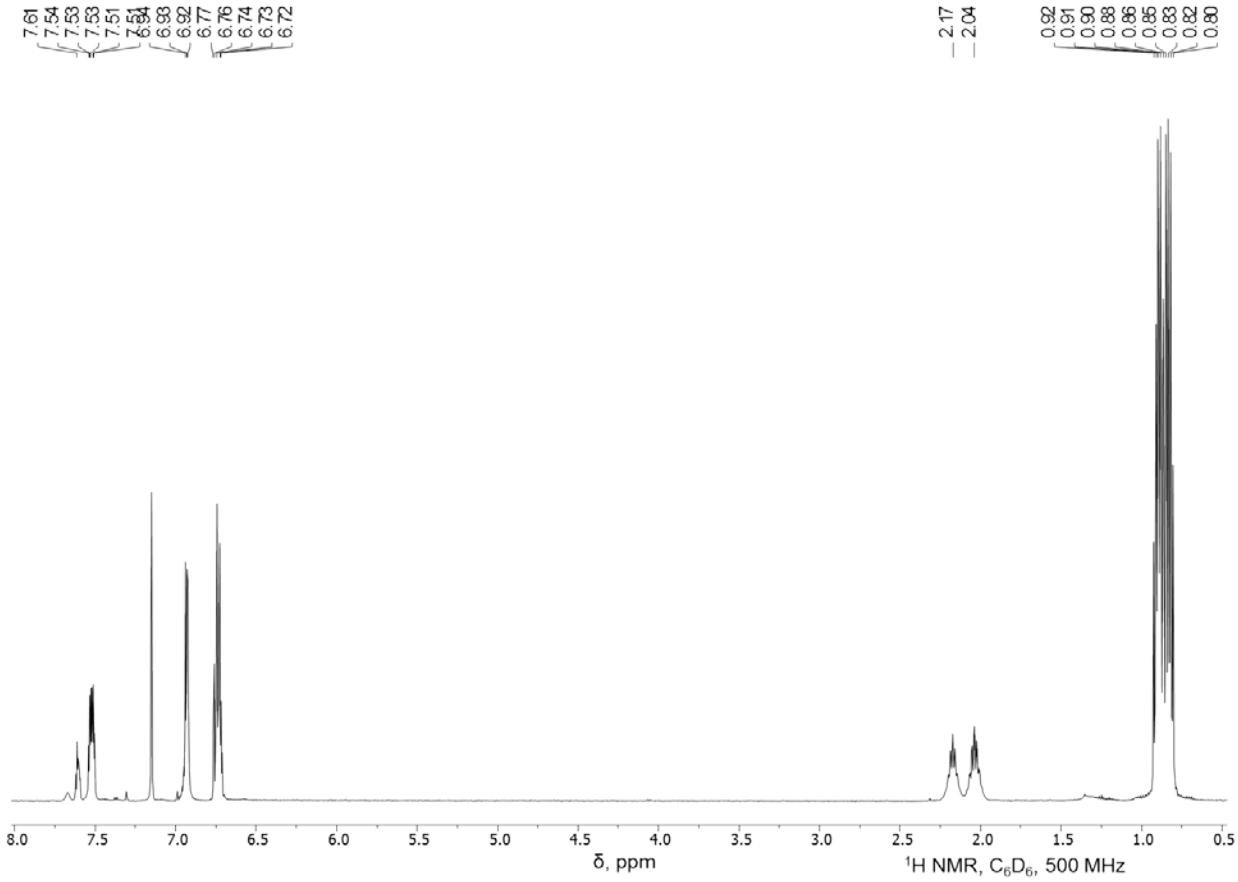


Figure S49. ^{1}H NMR spectrum of **2e** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

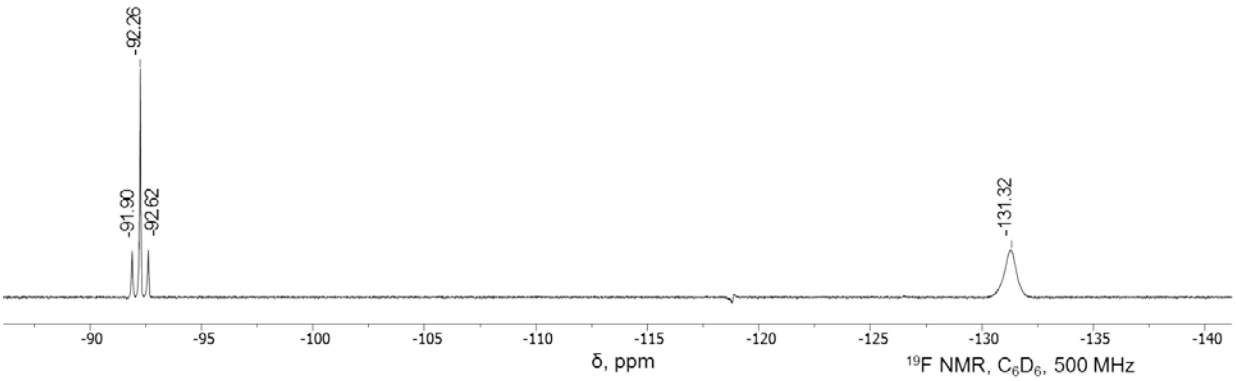


Figure S50. ^{19}F NMR spectrum of **2e** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

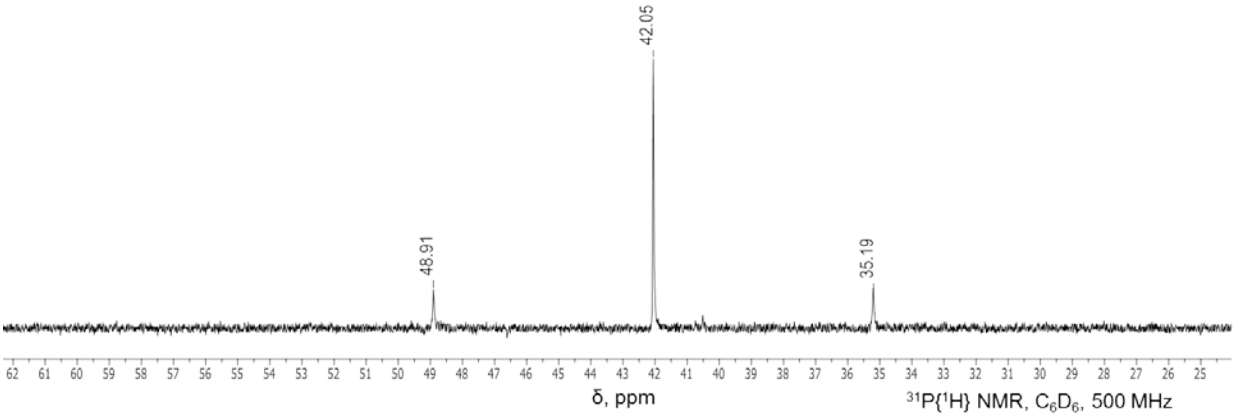


Figure S51. ^{31}P{^{1}H}NMR spectrum of **2e** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

(^{F}PNP)PtC_6H_4Cl (2f). 3f (24.2 mg, 0.0170 mmol) was transferred to a J. Young NMR tube and dissolved in C_6D_6. KO^{t}Bu (2 mg, 0.02 mmol) was added, and the NMR tube was shaken, yielding a yellow solution and a colorless precipitate. The solution was filtered over Celite and silica gel, and the resulting clear yellow solution was used for characterization. ^{1}H NMR (C_6D_6):

δ 7.59 (dd, J = 7.5 Hz, 1.9 Hz, $J_{195Pt-H}$ = 60.6 Hz, 1H, ortho C-*H* of C_6H_4Cl), 7.47 (br s, 2H, Ar-*H*), 7.31 (d, J = 7.6 Hz, 1H, meta C-*H* of C_6H_4Cl), 6.90 (td, J = 7.6 Hz, 1.8 Hz, 1H, meta C-*H* of C_6H_4Cl), 6.79 (td, J = 7.6 Hz, 1.9 Hz, 1H, para C-*H* of C_6H_4Cl), 6.72 (m, 4H, Ar-*H*), 2.29 (m, 2H, C*H*Me_2), 2.04 (m, 2H, C*H*Me_2), 0.98-0.77 (m, 24H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 160.3 (vt, J_{P-C} = 10 Hz, C_{Ar}-N), 154.2 (d, J_{F-C} = 233 Hz, C_{Ar}-F), 143.5 (t, J_{P-C} = 3 Hz), 141.1 (t, J_{P-C} = 2 Hz), 137.3 (t, J_{P-C} = 9 Hz), 127.9, 125.6 ($J_{195Pt-C}$ = 56 Hz, C_{Ar}-Pt), 123.5, 121.4 (m, C_{Ar}-P), 118.4 (d, J_{F-C} = 21 Hz, C_{Ar}-H), 117.9 (d, J_{F-C} = 22 Hz, C_{Ar}-H), 115.1 (app q, J = 6 Hz, C_{Ar}-H), 25.5 (vt, J_{P-C} = 15.6 Hz, *C*HMe_2), 23.6 (vt, J_{P-C} = 15.3 Hz, *C*HMe_2), 17.5 (CH*Me*$_2$), 17.4 (CH*Me*$_2$), 17.2 (CH*Me*$_2$), 16.8 (CH*Me*$_2$). ^{19}F NMR (C_6D_6): δ -130.2. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 41.6 ($J_{195Pt-P}$ = 2,809 Hz).

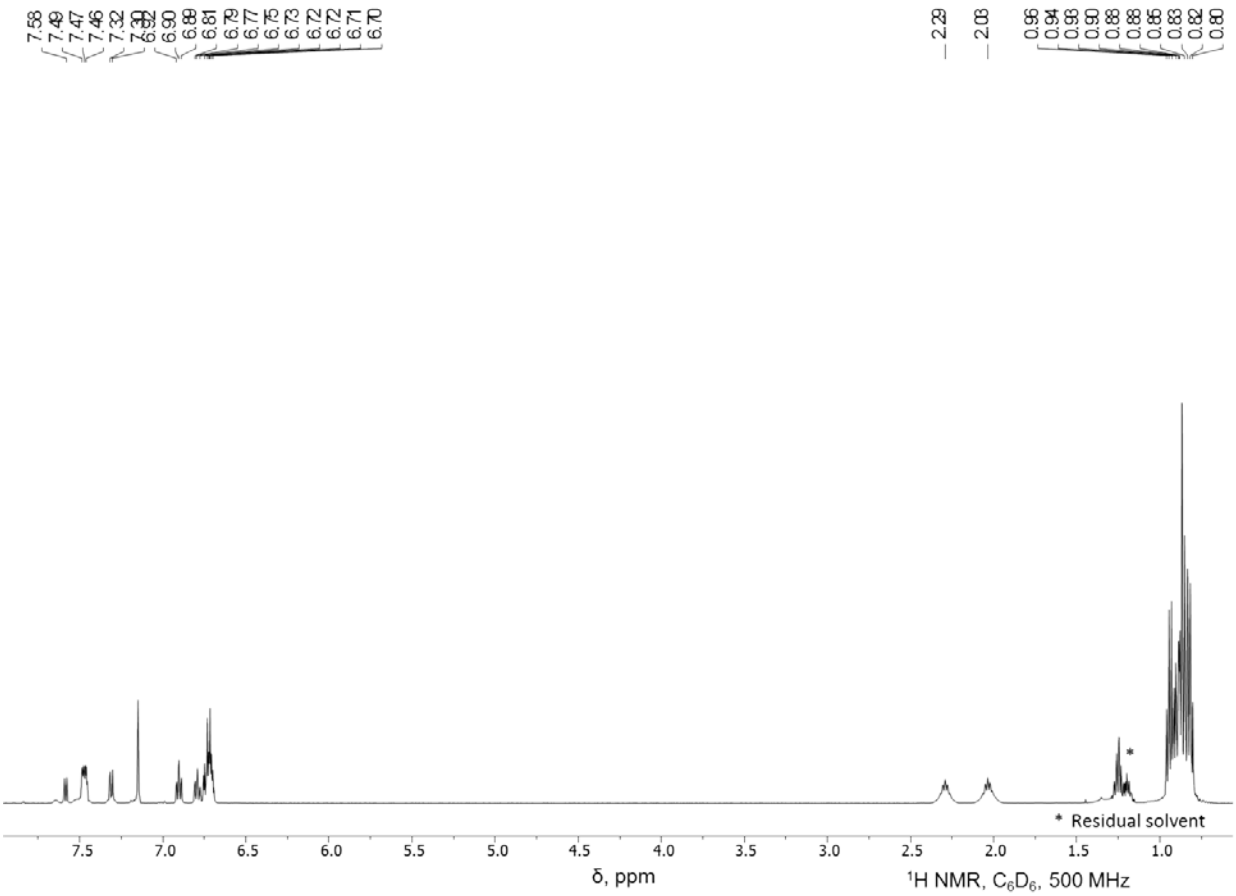


Figure S52. ^{1}HNMR spectrum of **2f** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

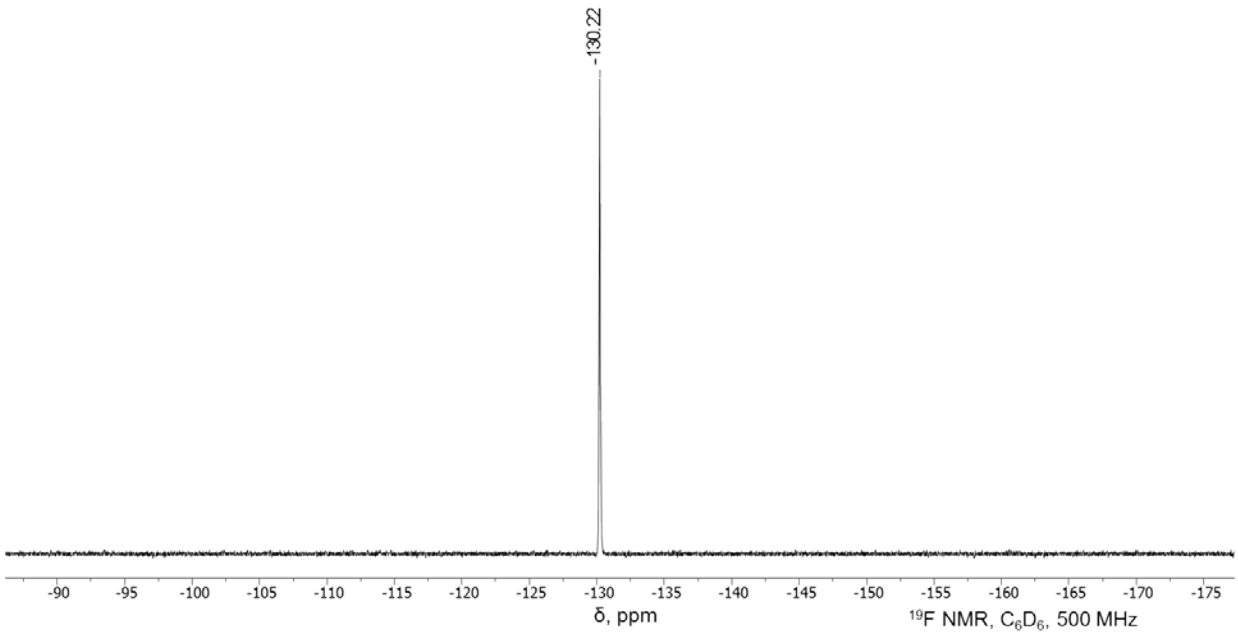


Figure S53. ^{19}F NMR spectrum of **2f** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

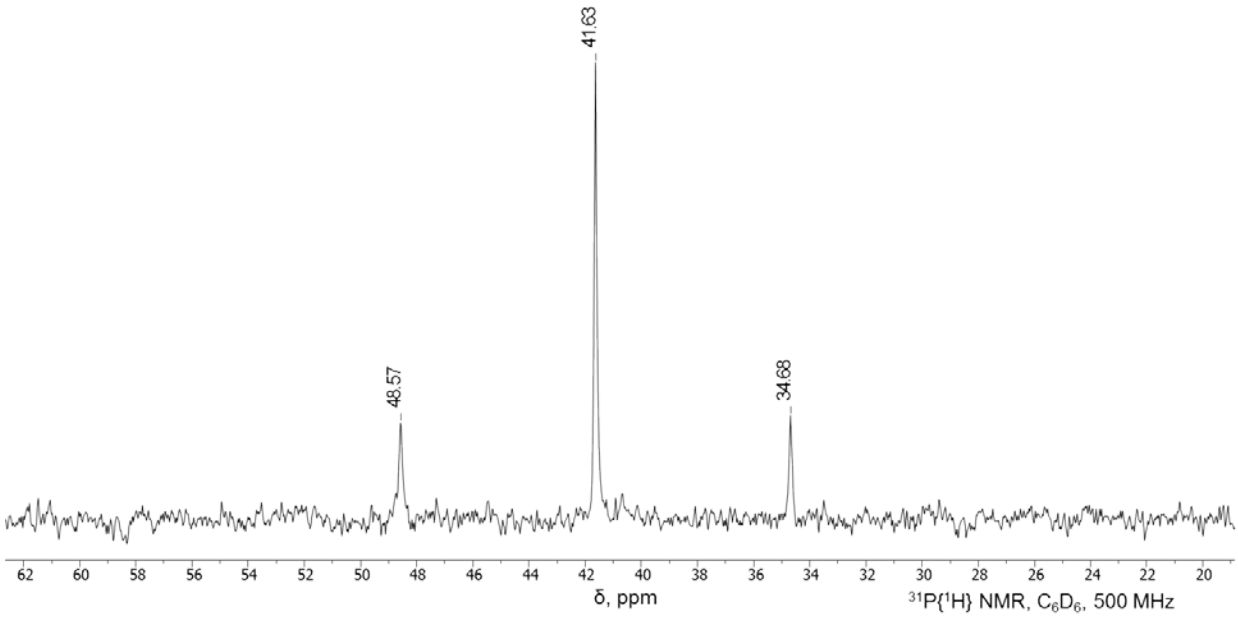


Figure S54. ^{31}P{^{1}H}NMR spectrum of **2f** in C_6D_6 at RT measured on a 500 MHz Varian NMRS.

II-G. Activation of dichloromethane.

[(^{F}PNP)PtCl][BARF] (9a). 1 (20.8 mg, 0.0266 mmol) and K-BARF (21 mg, 0.029 mmol) were transferred to a J. Young NMR tube. CD_2Cl_2 was added, and the solution immediately went from a bright yellow color to a darker brown/green, followed by a more gradual change to a blue solution. NMR spectra provided evidence for a paramagnetic species. Upon the addition of decamethyl ferrocene (10 mg, 0.031 mmol), the solution changed from dark blue to orange/brown. After filtering the solution over Celite, (^{F}PNP)PtCl (50% conversion) was observed by ^{19}F NMR.

[(^{F}PNP)PtCl][$HCB_{11}Cl_{11}$] (9b). The paramagnetic [(^{F}PNP)PtCl]$^{+}$ species was independently generated by reacting (^{F}PNP)PtCl (54.3 mg, 0.0814 mmol) with Ag[$HCB_{11}Cl_{11}$] (51.3 mg, 0.0815 mmol) in CD_2Cl_2. The solution was stirred for 5 min in a 10 mL Schlenk flask covered with Al foil and then filtered over Celite through a glass microfiber into a J. Young NMR tube. No product signals were observed by ^{31}P{^{1}H} or ^{19}F NMR. Broad signals were observed in the ^{1}H NMR spectrum along with the C-H signal of the carborane anion. Crystals were obtained from a CH_2Cl_2 solution that was layered with pentane and cooled to -35°C. One of the crystals was used for X-ray diffraction studies. The remaining crystals were washed with cold pentane and dried under vacuum. Isolated yield of the remaining fraction: 42 mg, 44%. Elemental analysis, found (calculated) for $C_{25}H_{35}B_{11}Cl_{11}F_2NP_2Pt$: C, 25.18 (25.26); H, 2.98 (2.97).

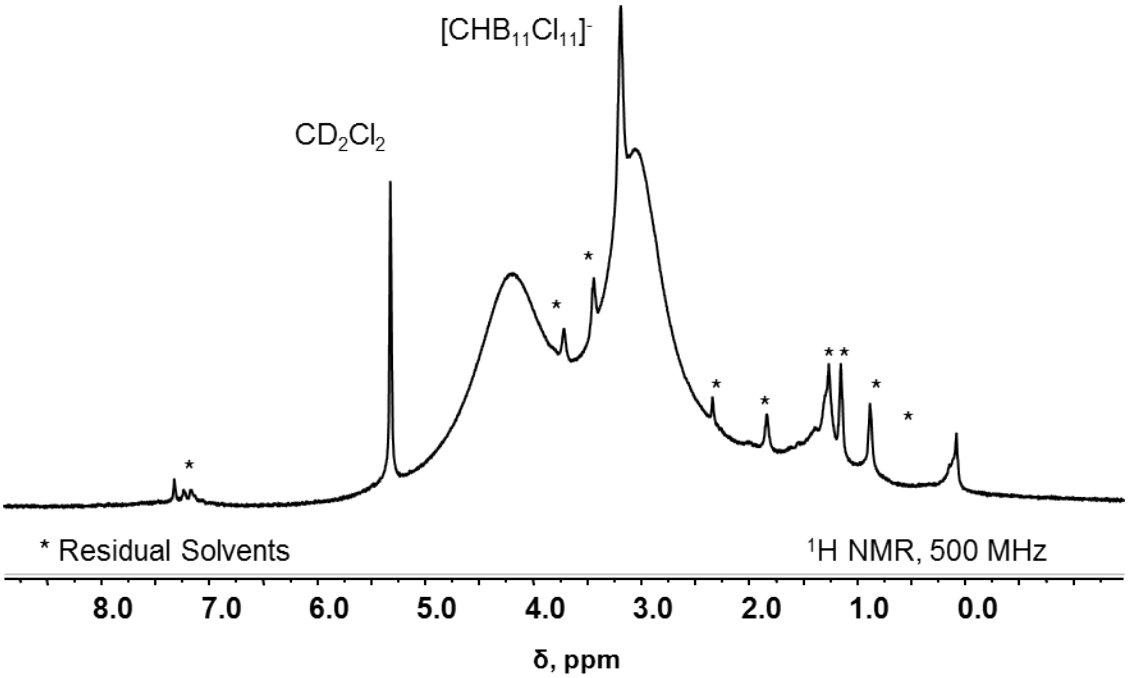


Figure S55. ^{1}H NMR spectrum of **9b** in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

II-H. Crossover and competition studies.

Crossover studies. A solid sample of **3b-d** yielded no crossover products when dissolved or suspended in C_6D_6 (minimally soluble) or fluorobenzene in a J. Young NMR tube. The solutions were monitored at RT for up to 48 h, and no changes were observed by ^{19}F, ^{31}P or ^{1}H NMR. Additionally, no changes were observed after heating at 80°C for up to 48 h. Similar observations were made for **3e** in C_6D_6 (minimally soluble) or toluene (minimally soluble) and **3a-D** in toluene (minimally soluble) or fluorobenzene.

Thermolysis of 3a-D in the presence of MeCN. 3a-D (26.8 mg, 0.0192 mmol) was transferred to a J. Young NMR tube and dissolved in CD_2Cl_2, forming a pale blue solution. Fluorobenzene (5.0 µL) was added as an internal standard, followed by 300 µL of MeCN. The solution was monitored at RT for 5 days, and no changes were observed by NMR. The volatiles were removed, and the resulting solid was dissolved in neat MeCN. After heating at 80°C for 24 h, the solution had become clear green, and the formation of **6** (approximately 26%) was observed by ^{19}F and ^{31}P NMR.

Competition studies:

Table S2. Arene solvent molar ratios, observed C-H activation product ratios and adjusted molar-weighted ratios for competition studies.

Solvent Mixture	Molar Ratio	Observed Ratio of Products		Molar-Weighted Product Ratio
C_6D_6:PhF	1.06	**3e**:**3a-D**	16:1	17:1
C_6H_6:PhF	1.05	**3e**:**3a**	5.3:1	5.5:1
C_6H_6:C_6D_6	0.994	**3a**:**3a-D**	3.2:1	3.2:1
C_6H_6:toluene	1.19	**3a**:**3b-d**	2.3:1	2.0:1

C_6D_6 vs PhF. 1 (20.3 mg, 0.0260 mmol) was combined with K-BARF (20.2 mg, 0.0281 mmol) in a J. Young NMR tube, and a 1:1 (by volume) C_6D_6:C_6H_5F solution (prepared by combining 1.00 mL of C_6D_6 and 1.00 mL of C_6H_5F) was added, forming a cloudy orange

solution. After combining the reagents at RT, the ^{19}F NMR spectrum showed only starting material. After heating the NMR tube for 30 min at 80°C, **3e** was observed to be the major product by ^{19}F NMR. After 24 h at 80°C, a pale blue solution containing a white precipitate had formed. The ^{19}F and ^{1}H NMR spectra showed a **3e**:**3a-D** ratio of approximately 16:1.

C_6H_6 vs PhF. A 1:1 (by volume) solution of C_6H_6:C_6H_5F was prepared by combining 1.00 mL of C_6H_6 and 1.00 mL of C_6H_5F in a small vial. **1** (25.0 mg, 0.0320 mmol) and K-BARF (23.3 mg, 0.0325 mmol) were transferred as solids into a Teflon-stoppered round-bottomed flask. The C_6H_6:C_6H_5F solution was added, and the reaction flask was placed in an oil bath at 80°C. After 3 h, the solution had become a pale blue with a grey precipitate. The volatiles were removed, and the products were extracted with CD_2Cl_2 and passed through a layer of Celite into a J. Young NMR tube. The ^{19}F NMR and ^{1}H NMR spectra showed a **3e**:**3a** ratio of approximately 5:1.

C_6H_6 vs C_6D_6. A 1:1 (by volume) solution of C_6H_6:C_6D_6 was prepared by combining 1.00 mL of C_6H_6 and 1.00 mL of C_6D_6 in a small vial. **1** (22.4 mg, 0.0287 mmol) and K-BARF (21.2 mg, 0.0295 mmol) were transferred as solids into a Teflon-stoppered round-bottomed flask. The C_6H_6:C_6D_6 solution was added, and the reaction flask was placed in an oil bath at 80°C. After 3 h, the solution had become a pale blue with a grey precipitate. The volatiles were removed, and the products were extracted with CD_2Cl_2 and passed through a layer of Celite into a J. Young NMR tube. The ^{1}H NMR spectrum showed a **3a**:**3a-D** ratio of approximately 3:1.

C_6H_6 vs C_6H_5Me. A 1:1 (by volume) solution of C_6H_6:C_6H_5Me was prepared by combining 1.00 mL of C_6H_6 and 1.00 mL of C_6H_5Me in a small vial. **1** (21.7 mg, 0.0278 mmol) and K-BARF (20.9 mg, 0.0279 mmol) were transferred as solids into a Teflon-stoppered round-bottomed flask. The C_6H_6:C_6H_5Me solution was added, and the reaction flask was placed in an oil bath at 80°C. After 3 h, the solution had become a pale blue with a grey precipitate. The

volatiles were removed, and the products were extracted with CD_2Cl_2 and passed through a layer of Celite into a J. Young NMR tube. The ^{1}H NMR spectrum showed a **3a**:**3b-d** ratio of approximately 2.3:1.

II-I. Probing the interconversion of isomers of tolyl isomers 3b-d.

Monitoring the isomerization of 3b in CD_2Cl_2. 3b (36 mg, 0.026 mmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a pale blue solution. The solution was monitored at RT by ^1H, ^{19}F and ^{31}P NMR spectroscopy for up to 2 weeks. No changes were observed. Addition of neat HOTf (9.0 μL, 0.10 mmol, 4 eq) resulted in the formation of **8** as the major product and a **3b**:**3c**:**3d**:free toluene ratio of approximately 9%:35%:16%:40%.

Monitoring the isomerization of 3c in CD_2Cl_2. 3c (51 mg, 0.036 mmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a pale blue solution. The solution was monitored at RT by ^1H, ^{19}F and ^{31}P NMR spectroscopy for up to 2 weeks, but no changes were observed. A 0.11 M solution of HOTf was prepared in fluorobenzene. 20 min after the addition of the HOTf solution (33 μL, 0.0036 mmol, 0.1 eq), some **3d** was observed along with the appearance of free toluene. After 16 h at RT, the **3b**:**3c**:**3d**:free toluene ratio was 3%:70%:26%:1%. An additional portion of the HOTf solution (163 μL, 0.0179 mmol, 0.5 eq) was added, and after another 16 h at RT, the **3b**:**3c**:**3d**:free toluene ratio was 11%:56%:18%:15%. Finally, 19.0 μL of neat HOTf (0.233 mmol total, 6.46 eq) was added to the NMR tube, and the **3b**:**3c**:**3d**:free toluene ratio became 6%:25%:10%:59%. The major product was identified as **8**.

Monitoring the isomerization of 3d in CD_2Cl_2. 3d (49 mg, 0.035 mmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a pale blue solution. The solution was monitored at RT by ^1H, ^{19}F and ^{31}P NMR spectroscopy for up to 2 weeks, but no changes were observed. A 0.11 M solution of HOTf was prepared in fluorobenzene. 20 min after the addition of the HOTf solution (90.0 μL, 0.0099 mmol, 0.28 eq), some formation of **3c** was observed along with the appearance of free toluene. After 16 h, the **3b**:**3c**:**3d**:free toluene ratio was approximately 2%:9%:80%:9%. An additional portion of the HOTf solution (286 μL, 0.0315 mmol, 0.9 eq) was

added, and after another 16 h at RT, the **3b**:**3c**:**3d**:free toluene ratio was approximately 3%:24%:59%:14%. Finally, 18.0 µL of neat HOTf (0.235 mmol total, 6.7 eq) was added to the NMR tube, and the **3b**:**3c**:**3d**:free toluene ratio became approximately 3%:22%:35%:39%. The major product was identified as **8**.

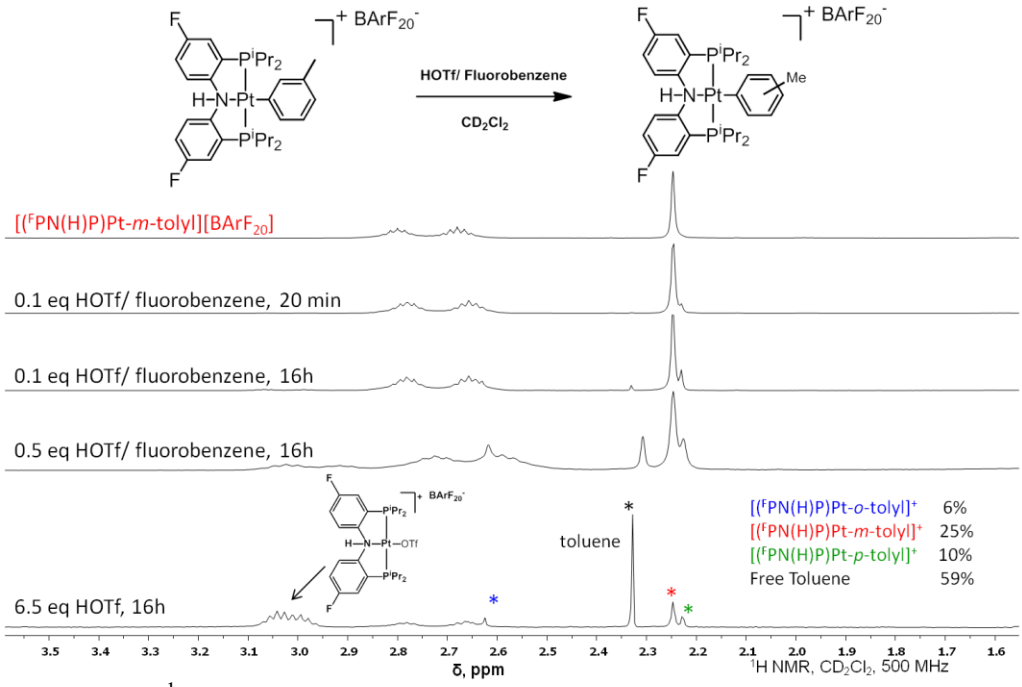


Figure S56. ^{1}H NMR spectra showing the isomerization of **3c** upon addition of HOTf in CD_2Cl_2 at RT measured on a 500 MHz Varian NMRS.

Monitoring the isomerization of 3g in CD_2Cl_2. 3g (19.8 mg, 0.0141 mmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a pale blue solution. The solution was monitored at RT by ^{1}H, ^{19}F and ^{31}P NMR spectroscopy for up to 2 weeks, but no changes were observed. Then, 5.0 µL of neat HOTf (0.057 mmol, 4 eq) was added to the NMR tube. After 16 h at RT, the starting material had been completely consumed, and the **3b**:**3c**:**3d**:free toluene ratio was approximately 2%:39%:9%:50%. The major product was identified as **8**.

Attempted isomerization of 3c in the presence of 2c. 3c (12.8 mg, 9.13 μmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a pale blue solution. A 5.33 mM solution of **2c** was prepared in CD_2Cl_2, and 84 μL of this solution (0.45 μmol) was added to the NMR tube. No changes were observed after 12 h at RT. Up to one equivalent of **2c** (6.6 mg, 9.1 μmol) was added, but no changes were observed after 24 h.

Attempted isomerization of 3c in the presence of BF_3. 3c (9.0 mg, 6.4 μmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a pale blue solution. A 47.5 mM solution of $BF_3{\cdot}SMe_2$ was prepared in CD_2Cl_2, and 7.0 μL of this solution (0.33 μmol) was added to the NMR tube. No changes were observed after 12 h at RT. Up to one equivalent of $BF_3{\cdot}SMe_2$ (135 μL, 6.41 μmol) was added, but no changes were observed after 24 h.

Attempted isomerization of 3c in the presence of $[H(OEt_2)_2][BARF]$. 3c (9.0 mg, 6.4 μmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a pale blue solution. A 0.0128 M solution of $[H(OEt_2)_2][BARF]$ was prepared in Et_2O, and 25 μL of this solution (0.33 μmol) was added to the NMR tube. No changes were observed after 12 h at RT. Up to one equivalent of $[H(OEt_2)_2][BARF]$ (0.50 mL, 6.4 μmol) was added, but no changes were observed after 24 h.

Attempted isomerization of 3c in the presence of $B(C_6F_5)_3$. 3d (25.8 mg, 0.0184 mmol) was added to a CD_2Cl_2 solution of $B(C_6F_5)_3$ (4.88 μmol, 0.265 eq) in a J. Young NMR tube. The solution was monitored for 3 days, but no changes were observed by NMR.

Attempted isomerization of 3c in the presence of $[H(OEt_2)_2][OTf]$. 3c (32.1 mg, 0.0228 mmol) was dissolved in CD_2Cl_2 in a J. Young NMR tube, forming a pale blue solution. A 1.88 M solution of HOTf was prepared in Et_2O, and 12.0 μL of this solution (0.0226 mmol) was added to the NMR tube. After 16h, no changes were observed by ^1H, ^{19}F, and ^{31}P NMR. A total of 3.4

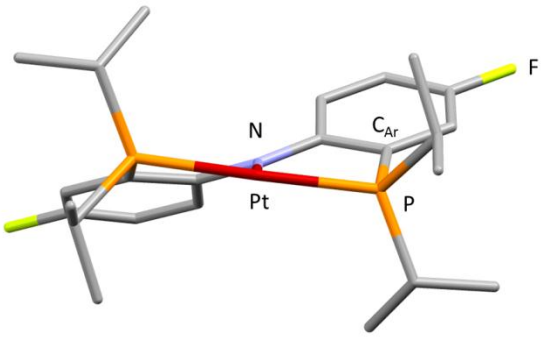
equivalents of $[H(OEt_2)_2][OTf]$ (0.0775 mmol) was added with no isomerization observed after 5 days at RT.

III. DFT Studies.

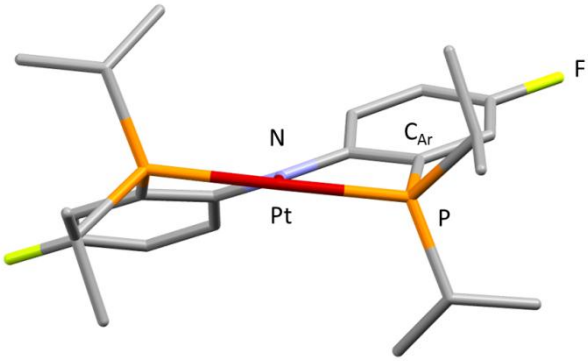
Computational details. All calculations were carried out in Gaussian 09[3] using the PBE1PBE (also known as PBE0)[4] and M06-L[5] functionals, tight optimizations, and the ultrafine integration grid (a pruned (99,590) grid). The basis sets[6] included Def2-QZVPP (with the corresponding ECP) for Pt,[7] 6-311+G(2df) for the N, F, and P atoms, and 6-31+G(d,p) for all other atoms. The default PCM method (solvent = tetrahydrofurane) was used for all calculations of this work with the UFF radii scaled by 1.1 (explicit hydrogens). The optimized geometries were verified to have no negative harmonic frequencies by frequency calculations which also provided the enthalpies and free energies reported here. The free energies were calculated under P = 302 atm in THF.[68]

	$[(^{F}PNP)Pt]^{+}$ Singlet PBE1PBE	$[(^{F}PNP)Pt]^{+}$ Triplet PBE1PBE
Pt-P	2.327	2.298
Pt-N	1.964	2.090
N-C_{Ar}	1.393	1.381
P-Pt-P	166.59	167.02
P-Pt-N	83.29	83.51
C_{Ar}-N-C_{Ar}	122.94	124.15
C_{Ar}-N-Pt	118.53	117.93

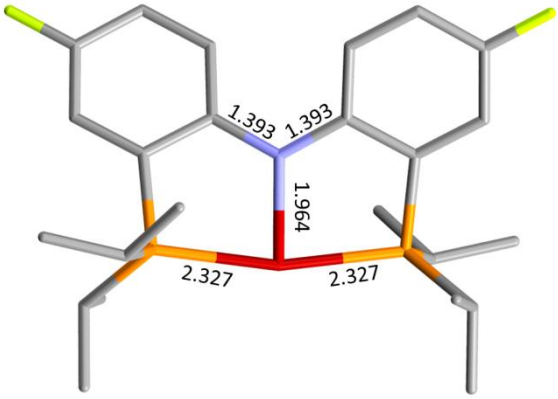
Table S3. Calculated bond distance data (in Å) and angles (deg) using PBE1PBE functional for $[(^{F}PNP)Pt]^{+}$.



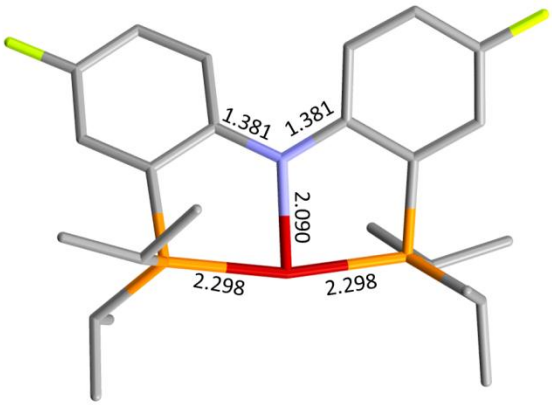
$[(^{F}PNP)Pt]^{+}$ Singlet PBE1PBE



$[(^{F}PNP)Pt]^{+}$ Triplet PBE1PBE



$[(^{F}PNP)Pt]^{+}$ Singlet PBE1PBE

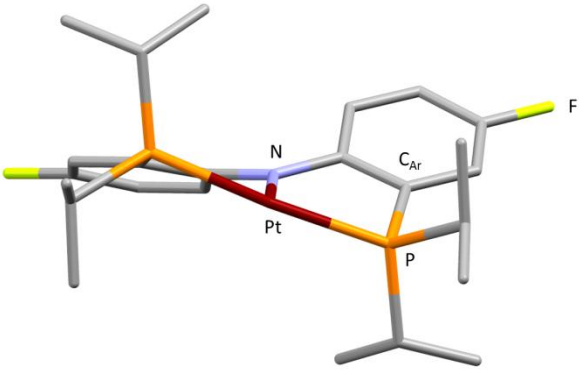


$[(^{F}PNP)Pt]^{+}$ Triplet PBE1PBE

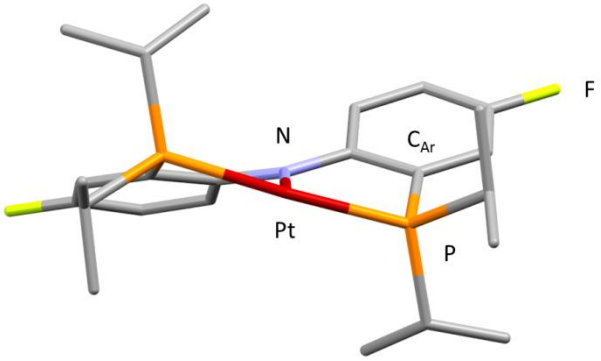
Figure S57. PBE1PBE optimized geometries for singlet and triplet states of $[(^{F}PNP)Pt]^{+}$.

	$[(^{F}PNP)Pt]^{+}$ Singlet M06-L	$[(^{F}PNP)Pt]^{+}$ Triplet M06-L
Pt-P	2.342	2.314
Pt-N	1.994	2.142
N-C_{Ar}	1.391	1.377
P-Pt-P	164.11	163.51
P-Pt-N	82.05	81.75
C_{Ar}-N-C_{Ar}	123.69	125.02
C_{Ar}-N-Pt	118.16	117.49

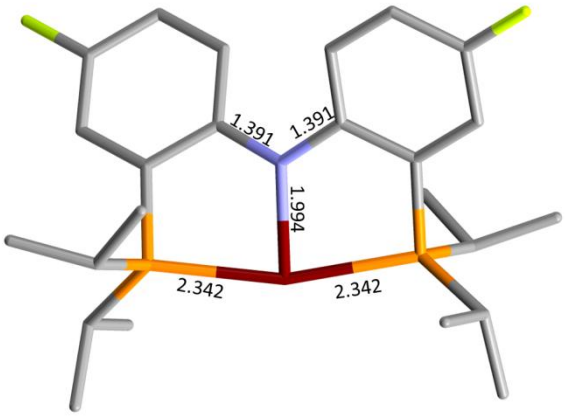
Table S4. Calculated bond distance data (in Å) and angles (deg) using M06-L functional for $[(^{F}PNP)Pt]^{+}$.



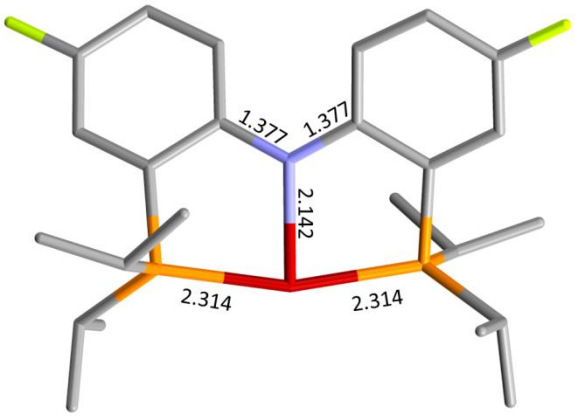
$[(^{F}PNP)Pt]^{+}$ Singlet M06-L



$[(^{F}PNP)Pt]^{+}$ Triplet M06-L



$[(^{F}PNP)Pt]^{+}$ Singlet M06-L



$[(^{F}PNP)Pt]^{+}$ Triplet M06-L

Figure S58. M06-L optimized geometries for singlet and triplet states of $[(^{F}PNP)Pt]^{+}$.

IV. Details of X-Ray diffractometry studies.

X-Ray data collection, solution, and refinement for 3e. A pale blue, multi-faceted block of suitable size (0.20 x 0.11 x 0.06 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a nylon loop. Low temperature (110 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[9] An absorption correction was applied using SADABS.[10] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the monoclinic $P2_1/c$ space group using XS[11] (incorporated in SHELXTL). No missed symmetry was reported by PLATON.[12] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and refined using riding model. Deuterium atoms of the solvent molecules were not placed due to solvent disorder. The structure was refined (weighted least squares refinement on F^2) and the final least-squares refinement converged to R_1 = 0.0285 ($I > 2\sigma(I)$, 10152 data) and wR_2 = 0.0670 (F^2, 11953 data, 757 parameters, 1 restraints). The fluorine atom on the metallated fluorobenzene residue was found to reside with partial occupancy on C(43) and C(45) and was refined as such.

X-Ray data collection, solution, and refinement for 3c/d. A Leica MZ 75 microscope was used to identify a suitable pale blue blocks with very well defined faces with dimensions (max, intermediate, and min) 0.15 mm x 0.13 mm x 0.10 mm from a representative sample of crystals of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER APEX 2 X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0.[9] The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube (K_α= 0.70173Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes).

Sixty data frames were taken at widths of 0.5°. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the h k l overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, a standard data collection procedure was initiated using omega scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[9] The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects and were finally merged and scaled to produce a suitable data set. The absorption correction program SADABS[10] was employed to correct the data for absorption effects (as well as systematic errors).

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/n$. A solution was obtained readily using SHELXTL (XS).[11] The tolyl group attached to the

Pt was disordered with para and meta isomers, which was modeled successfully, with a ratio of 53:47 respectively. The hydrogen atoms were placed in idealized positions geometrically and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined (weighted least squares refinement on F^2) to convergence.[11,13]

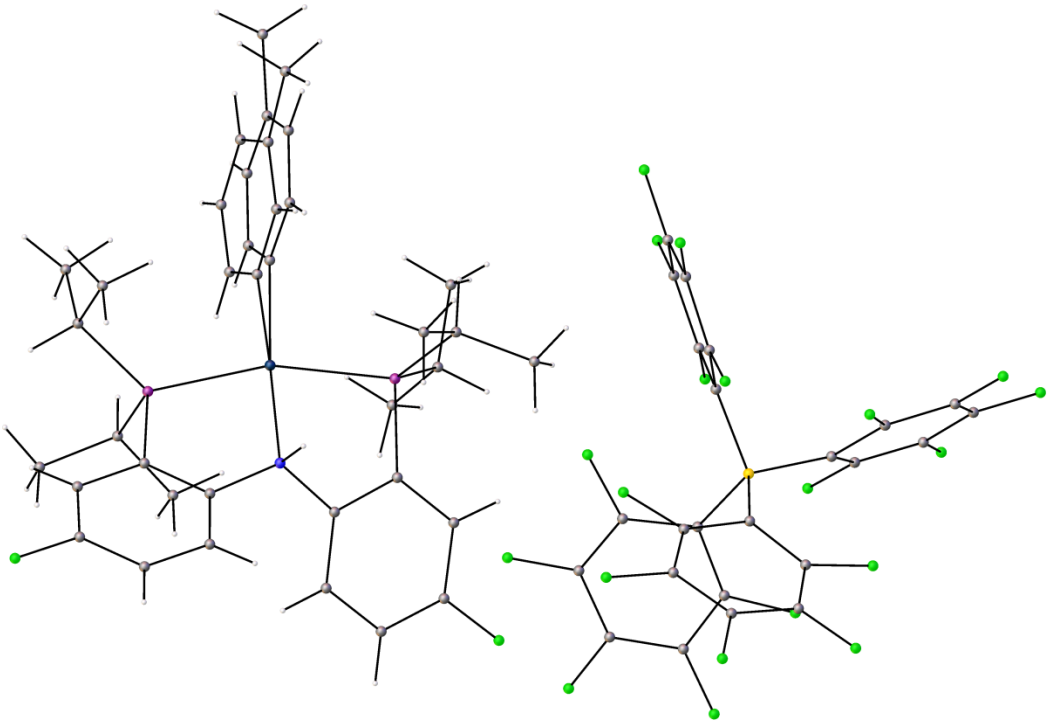


Figure S59. Olex2[13]structure plot of **3c-d** showing tolyl group attached to Pt as disordered with para and meta isomers modeled successfully in a ratio of 53:47, respectively.

X-Ray data collection, solution, and refinement for 9b. A Leica MZ 75 microscope was used to identify a suitable blue blocks with very well defined faces with dimensions (max, intermediate, and min) 0.60 mm x 0.08 mm x 0.04 mm from a representative sample of crystals

of the same habit. The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 110 K.

A BRUKER APEX 2 X-ray (three-circle) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX2 software suite, v2008-6.0.[9] The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 6.0 cm from the crystal sample (APEX2, 512x512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube (K_α = 0.70173Å with a potential of 40 kV and a current of 40 mA) fitted with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes).

Sixty data frames were taken at widths of 0.5°. These reflections were used in the auto-indexing procedure to determine the unit cell using CELL_NOW.* Two components were identified and refined by nonlinear least squares and Bravais lattice procedures. The orientation matrices were verified by examination of the h k l overlays on several frames of data. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, a standard data collection procedure was initiated using omega scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[9] The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects and were finally merged and scaled to produce a suitable data set. The absorption correction program TWINABS[10] was employed to correct the data for absorption

effects (as well as systematic errors) and also to separate the twin components. Only the major component was used for structure solution as well as least squares refinement.

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/c$. A solution was obtained readily using SHELXTL (XS).[11] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined (weighted least squares refinement on F^2) to convergence.[11,13]

V. Supporting Information References.

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