Electronic Supplementary Information

Platinum Carbon Bond Formation via Cu(I) Catalyzed Stille-Type Transmetallation: Reaction Scope and Spectroscopic Study of Platinum-Arylene Complexes

Ali S. Gundogan, Xiangli Meng, Russell W. Winkel and Kirk S. Schanze*

Department of Chemistry, University of Florida, Gainesville, Florida 32611, United States

*Author to whom correspondence should be addressed. TEL: 352-392-9133, FAX: 352-392-2395, e-mail: kschanze@chem.ufl.edu

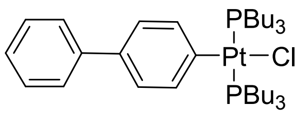
Content

1. Experimental Section

General Procedure for the formation of Monosubstituted Products

1 equivalent of *cis*-$(PBu_3)_2PtCl_2$ was dissolved in 10 mL of dry DMF and degassed for 30 minutes. 1.2 equivalents of a corresponding tin compound was then added to the system along with CuI (10 mol% with respect to tin). The system was heated to 70°C and stirred for 4 hours. The solvent was then removed in vacuo. Column chromatography, using silica gel as the adsorbent, was employed to purify the monosubstituted products.

***trans*-$(PBu_3)_2$Pt(BPh)Cl (2a)**



Yield: 63%**,** R_f = 0.45 (1:1 DCM/Hexane).

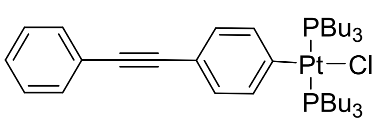
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 9Hz, 2H), 7.40 (m, 4H), 7.28 (m, 2H), 7.18 (d, J = 9Hz, 2H), 1.70-1.55 (m, 12H), 1.55-1.41 (m, 12H), 1.41-1.27 (m, 12H), 0.89 (t, J = 6Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.00, 137.66, 137.46(t, J = 2.3Hz), 134.35(t, J=6.5Hz), 128.60, 126.30, 126.12, 125.97, 25.85 ($J^{Pt\text{-}C}$=23Hz), 24.26 ($J^{Pt\text{-}C}$=13Hz), 21.18 ($J^{Pt\text{-}C}$=32Hz), 13.76.

^{31}P NMR (121 MHz, $CDCl_3$) δ 5.98 ($J^{Pt\text{-}P}$ = 2755 Hz).

Calculated for $C_{36}H_{63}P_2Pt$ 752.4051, found DART-MS (m/z) : 752.4039 $[M\text{-}Cl]^+$.

***trans*-$(PBu_3)_2$Pt(PEP)Cl (3a)**



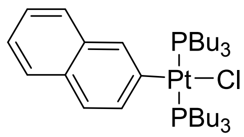
Yield: 60%, R_f = 0.51 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 9Hz, 2H), 7.36-7.28 (m, 5H), 7.09(d, J = 9Hz 2H), 1.68-1.52 (m, 12H), 1.51-1.42 (m, 12H), 1.40-1.31 (m, 12H), 0.90 (t, J = 6Hz, 18H).

^{13}C NMR (75 MHz, $CDCl_3$) 141.36 (t, J = 9Hz), 137.19(t, J=2.3), 131.31, 130.43(t, J=37Hz), 128.24, 127.60, 124.02, 115.79, 90.92, 87.34, 25.83($J^{Pt\text{-}C}$ =23Hz), 24.23($J^{Pt\text{-}C}$ =13Hz), 20.98 ($J^{Pt\text{-}C}$ = 33Hz), 13.78. ^{31}P NMR (121 MHz, $CDCl_3$) δ 5.80 ($J^{Pt\text{-}P}$ = 2733 Hz).

Calculated for $C_{38}H_{63}P_2Pt$ 776.4051, found DART-MS (m/z): 752.4020 $[M\text{-}Cl]^+$.

***trans*-(PBu$_3$)$_2$Pt(Naphto)Cl (4a)**

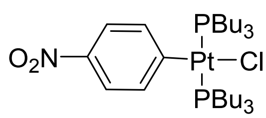


Yield: 65%, R_f = 0.56 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.74(s, 1H), 7.68(dd, J = 9Hz, J = 2.1,1H), 7.58(dd J=9Hz, J=2.1 2H), 7.42 (m, 1H), 7.36-7.24 (m, 2H), 1.68-1.42 (m, 24H), 1.33 (sextet, 12H), 0.87 (t, J=7.2Hz, 18H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 136.72, 136.16, 134.52, 134.20, 130.29, 127.34, 126.00, 125.59, 124.71, 123.03, 25.87 ($J^{Pt\text{-}C}$ =23Hz), 24.22 ($J^{Pt\text{-}C}$ =13Hz), 21.05 ($J^{Pt\text{-}C}$ = 33Hz), 13.72. ^{31}P NMR (121 MHz, CDCl$_3$) δ 6.00 ($J^{Pt\text{-}P}$ = 2740 Hz)

Calculated for $C_{34}H_{61}P_2Pt$ 726.3894, found MALDI-TOF-MS (m/z): 726.3878 $[M\text{-}Cl]^+$.

***trans*-(PBu$_3$)$_2$Pt(*p*-NO$_2$Ph)Cl (5a)**

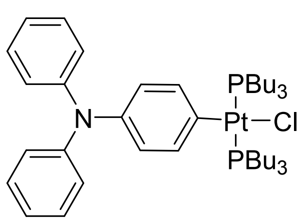


Yield: 45%, R_f =0.41 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.78 (d, J=6Hz), 7.56 (d, J=9Hz), 1.70 – 1.56 (m, 12Hz), 1.49-1.29 (m, 24H), 0.88 (t, J=9Hz). ^{13}C NMR (75 MHz, CDCl$_3$) δ 155.47 ($J^{Pt\text{-}C}$=15Hz), 143.33, 137.54($J^{Pt\text{-}C}$ =39Hz), 121.53($J^{Pt\text{-}C}$ =80Hz), 25.80($J^{Pt\text{-}C}$ =23Hz), 24.16($J^{Pt\text{-}C}$ =13Hz), 21.05($J^{Pt\text{-}C}$ =33Hz), 13.71. ^{31}P NMR (121 MHz, CDCl$_3$) δ 5.61 ($J^{Pt\text{-}P}$ =2666 Hz).

DIP-CI-MS (m/z): 756.3363 $[M]^+$

***trans*-(PBu$_3$)$_2$Pt(TPA)Cl (6a)**



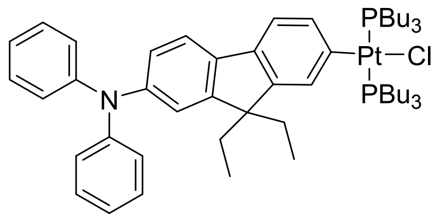
Yield: 53%, R_f = 0.6 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.28 (m, 2H), 7.17 (m, 4H), 7.04 (m, 4H), 6.91 (t, J = 7.5Hz, 2H), 6.77 (d J = 7.8Hz 2H), 1.79-1.75 (m, 12H), 1.50-1.34 (m, 24H), 0.92 (t, J = 7.2Hz, 18H).

^{13}C NMR (125 MHz, CDCl$_3$) δ 148.31, 141.39, 137.71, 133.95 ($J^{Pt\text{-}C}$ = 10Hz), 128.80, 126.58, 122.35, 121.17. ^{31}P NMR (121 MHz, CDCl$_3$) δ 6.31 ($J^{Pt\text{-}P}$ = 2756 Hz).

Calculated for $C_{42}H_{68}NP_2PtCl$ 879.4162, found MALDI-TOF-MS (m/z) : 879.4170 $[M]^+$.

***trans*-(PBu$_3$)$_2$Pt(DPAF)Cl (7a)**

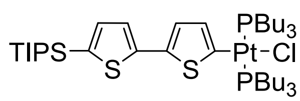


Yield: 30%, R_f=0.45 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J*=8Hz, 1H), 7.30-7.22 (m, 7H), 7.14-7.08(m, 5H), 7.03-6.96 (m, 3H), 1.89(q, *J*=7.2, 4H), 1.61(m, 12H), 1.53(m, 12H), 1.38(m, 12H), 0.82(t, *J*=7.2Hz, 18H), 0.36 (t, *J*=7.2Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.01, 148.98, 148.21, 145.75, 138.56, 137.36 ($J^{Pt\text{-}C}$ =10Hz), 135.52, 135.31, 130.86, 129.05, 124.22, 123.30, 121.97, 120.16, 119.18, 118.46, 32.87, 25.92 ($J^{Pt\text{-}C}$ =23Hz), 24.24 ($J^{Pt\text{-}C}$ =13Hz), 20.85 ($J^{Pt\text{-}C}$ =33Hz), 13.9, 8.69. ^{31}P NMR (121 MHz, $CDCl_3$) δ 6.09 ($J^{Pt\text{-}P}$ = 2775Hz).

Calculated for $C_{53}H_{80}NP_2PtCl$ 1023.5065, found MALDI-TOF-MS (m/z) : 1023.5065 $[M]^+$.

***trans*-(PBu$_3$)$_2$Pt(TIPSBTh)Cl (9a)**



Yield: 16%, R_f= 0.40 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 2H), 7.05 (d, *J*= 6Hz, 2H), 6.45(d, *J*=6Hz, $J^{Pt\text{-}H}$ =23Hz), 1.81-1.55(m, 12H), 1.50-1.45(m, 12H), 1.43-1.31(m, 15H), 1.12 (d, *J*=7.2, 18H, 2H), 0.91 (t, *J*=7Hz, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.92, 137.34, 136.25, 130.45, 129.85, 128.85, 124.80 ($J^{Pt\text{-}C}$ =40Hz), 122.33, 25.93 ($J^{Pt\text{-}C}$ =23Hz), 24.26 ($J^{Pt\text{-}C}$ =13Hz), 20.64 ($J^{Pt\text{-}C}$ =32Hz), 18.61, 13.79, 11.79. ^{31}P NMR (121 MHz, $CDCl_3$) δ 6.22 ($J^{Pt\text{-}P}$ = 2554 Hz).

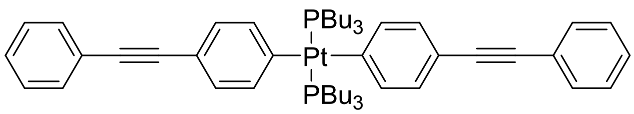
Calculated for $C_{41}H_{79}P_2S_2SiPtCl$ 956.4197, found MALDI-TOF-MS (m/z) : 956.4213$[M]^+$.

Disubstituted Symmetric and Asymmetric Products:

General Procedure for disubstituted products.

1 equivalent of *trans*-PtAr$(PBu_3)_2$Cl was dissolved in 5 mL of dry DMF and degassed for 30 minutes, then 1.2 equivalents of a corresponding tin compound was added to the system along with CuI (10 mol% with respect to tin). The system was stirred at room temperature overnight and the precipitated product was filtered off and dried under vacuum.

***trans*-$(PBu_3)_2$Pt$(PEP)_2$ (3b)**



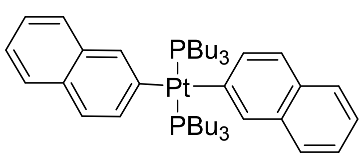
Yield: 45%, R_f = 0.80 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d. J=6Hz, 4H), 7.45(d, J=6Hz, 4H), 7.34-7.29 (m, 6H), 7.17 (d, J=6Hz, 4H), 1.46-1.37 (m, 12H), 1.34-1.25 (m, 24H), 0.89 (t, J = 6Hz)

^{13}C NMR (75 MHz, $CDCl_3$) δ 165.43 (J=21Hz), 139.82, 131.28, 129.48 (J=21Hz), 128.1, 127.22, 124.53, 115.13, 91.88, 86.80, 26.00 ($J^{Pt\text{-}C}$=23Hz), 24.14 ($J^{Pt\text{-}C}$=13Hz), 21.82 ($J^{Pt\text{-}C}$=33Hz), 13.58. ^{31}P NMR (121 MHz, $CDCl_3$) $\boldsymbol{\delta}$ 0.75 ($J^{Pt\text{-}P}$ =2775 Hz).

Calculated for $C_{52}H_{72}P_2$ PtH 954.4834, found MALDI-TOF-MS (m/z): 954.4898$[M+H]^+$.

***trans*-$(PBu_3)_2$Pt$(Naphto)_2$ (4b)**



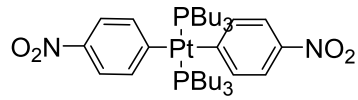
Yield: 52%, R_f = 0.85 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98(s, $J^{Pt\text{-}H}$=20Hz, 2H), 7.81(d, J=6Hz, 4H), 7.72(m, 2H), 7.60(dd, J=6Hz, =1.2Hz, 2H), 7.44(m, 2H), 7.35(m, 2H**).** ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.54, 139.85, 137.36, 134.43, 130.64, 127.46, 126.26, 124.49, 124.13, 122.36, 26.25($J^{Pt\text{-}C}$ = 23Hz), 24.39($J^{Pt\text{-}C}$=13Hz), 22.00($J^{Pt\text{-}C}$=32Hz), 13.90.

^{31}P NMR (121 MHz, $CDCl_3$) δ 1.65, 1.59 ($J^{Pt\text{-}P}$ = 2775 Hz).

Calculated for $(C_{44}H_{68}P_2$ Pt)H 854.4521, found DIP-CI-MS (m/z): 854.4507$[M+H]^+$.

trans-(PBu3)2Pt(p-NO2Ph)2 (5b)

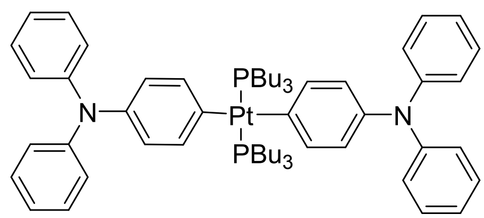


Yield: 60%, R_f = 0.82 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J=8Hz, 4H), 7.74 (d, J = 8Hz, $J^{Pt\text{-}H}$ =23Hz, 4H), 1.54-1.43 (m, 12H), 1.4-1.27 (m, 24H), 0.96 (t, J=9Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.03 ($J^{Pt\text{-}C}$ =40Hz), 143.92, 139.63, 120.63($J^{Pt\text{-}C}$=86Hz), 26.02 ($J^{Pt\text{-}C}$=23Hz), 24.28 ($J^{Pt\text{-}C}$=13Hz), 21.71 ($J^{Pt\text{-}C}$=33Hz), 13.85. ^{31}P NMR (121 MHz, $CDCl_3$) δ -0.12 ($J^{Pt\text{-}P}$ = 2687 Hz)

Calculated for ($C_{36}H_{62}N_2O_4P_2$ Pt)H 844.3909, found DIP-CI-MS (m/z): 844.3932 $[M+H]^+$.

trans-(PBu3)2Pt(TPA)2 (6b)

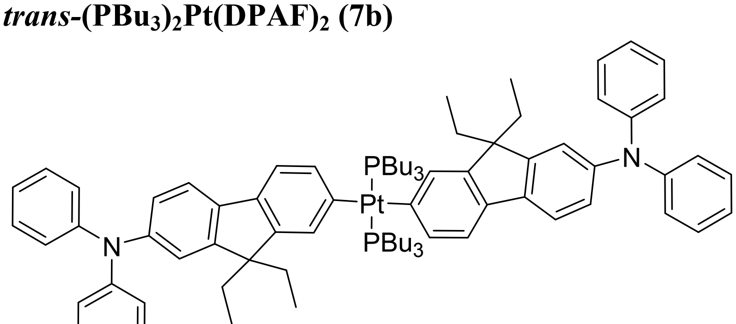


Yield:10%, R_f = 0.87 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J=7.5Hz, 2H), 7.20 - 7.14(m, 8H), 7.08-7.05 (m, 8H), 6.87 (m, 8H), 1.42–1.31(m, 36H), 0.89 (t, J=6Hz, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.79 ($J^{Pt\text{-}C}$=21Hz), 148.56, 140.81, 140.27, 128.66, 125.73, 122.19, 120.73, 25.94, 24.30($J^{Pt\text{-}C}$=13Hz), 21.86 ($J^{Pt\text{-}C}$=33Hz), 13.78. ^{31}P NMR (121 MHz, $CDCl_3$) δ 1.00 ($J^{Pt\text{-}P}$=2787 Hz).

Calculated for ($C_{60}H_{82}N_2P_2$ Pt) 1088.5616, found MALDI-TOF-MS (m/z): 1088.5634 $[M]^+$.

trans-(PBu3)2Pt(DPAF)2 (7b)

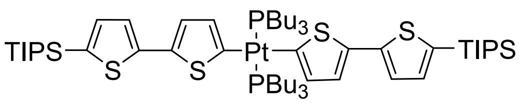


Yield: 5%, R_f = 0.75 (1:1 DCM/Hexane)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 2H), 7.42 -7.31 (m, 6H), 7.25 -7.22 (m, 8H), 7.13-7.08 (m, 10H), 7.01 -6.93 (m, 6H), 1.94-1.86 (m, 6H), 1.52-1.38(m, 12H), 1.32-1.27 (m, 24H), 0.88

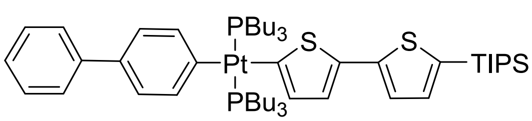
(t, J=7.8Hz, 18H), 0.36(t, J=14Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.21 ($J^{Pt\text{-}C}$=21Hz), 150.08, 148.31, 147.85, 145.11, 139.78, 138.08, 134.81, 133.67, 128.9, 124.4, 123.07, 121.71, 120.55, 118.83, 55.49, 53.41, 33.02, 26.17, 24.25, 13.99. ^{31}P NMR (121 MHz, $CDCl_3$) δ 1.08, 0.91 ($J^{Pt\text{-}P}$=2805 Hz).
Calculated for ($C_{82}H_{106}N_2P_2$ Pt)H 1375.7478, found MALDI-TOF-MS (m/z): 1375.7582$[M+H]^+$.

***trans*-$(PBu_3)_2$Pt$(TIPSBTh)_2$ (9b)**



Yield: 16%, R_f= 0.90 (1:1 DCM/Hexane)
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J=1.8Hz, 2H), 7.12 (d, J=1.8Hz), 7.11(d, J=1.8Hz, 2H), 6.55 (d, 1.8Hz), 1.50-1.40 (m, 24H), 1.37-1.31(m, 18H), 1.13 (d, J=6Hz, 36H), 0.90 (t, J=6Hz, 18H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.61, 145.78, 138.35, 136.40, 131.28, 129.74, 125.43, 122.09, 26.22, 24.41 ($J^{Pt\text{-}C\gamma}$=13Hz), 21.21 ($J^{Pt\text{-}C\alpha}$=33Hz), 18.75, 13.93, 11.93.
^{31}P NMR (121 MHz, $CDCl_3$) δ 2.33 ($J^{Pt\text{-}P}$=2556 Hz).
Calculated for ($C_{82}H_{106}N_2P_2$ Pt)H 1041.3921, found MALDI-TOF-MS (m/z): 1041.3940 $[M+H]^-$.

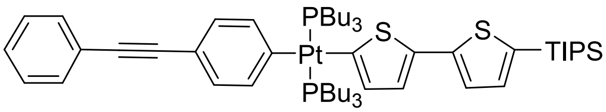
***trans*-$(PBu_3)_2$Pt(BPh)(TIPSBTh) (10)**



50 mg, 62 mmol of *trans*-$(PBu_3)_2$Pt(PEP)Cl was dissolved in 5 mL dry DMF and degassed for 30 min. then 52 mg, 74 mmol of triisopropyl(5'-(tributylstannyl)-[2,2'-bithiophen]-5-yl)silane was added to the system along with 2 mg of CuI. The system was stirred at room temperature overnight. The resulting precipitate was filtered off and dried under vacuum.
Yield: 60%, R_f= 0.80 (1:1 DCM/Hexane).
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 6.6Hz, 2H), 7.46- 7.38 (m, 5H), 7.28(m, 3H), 27.13 (m, 2H), 6.60 (s, $J^{Pt\text{-}H}$=23Hz, 2H), 1.53-1.38(m, 24H), 1.37-1.31(m, 15H), 1.14 (d, J = 7.2Hz, 18H), 0.88 (t, J =9Hz, 18Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.85 ($J^{Pt\text{-}C}$ =21Hz), 157.04 ($J^{Pt\text{-}C}$=23Hz), 145.93, 142.58, 139.62, 138.17, 136.31, 133.71, 131.46, 129.27, 128.51, 126.30, 125.79, 125.33 ($J^{Pt\text{-}C}$ = 45Hz), 121.80, 26.07($J^{Pt\text{-}C}$=23Hz), 24.28 ($J^{Pt\text{-}C}$=13Hz), 21.57($J^{Pt\text{-}C}$=33Hz), 18.54, 13.78, 11.82. ^{31}P NMR (121 MHz, $CDCl_3$) δ 1.00 ($J^{Pt\text{-}P}$ = 2770 Hz).

Calculated for ($C_{53}H_{88}S_2SiP_2$ Pt) 1074.5227, found MALDI-TOF-MS (m/z): 1047.5267 $[M]^+$.

***trans*-$(PBu_3)_2$Pt(PEP)(TIPSBTh) (11)**



50 mg, 62 mmol of ***trans*-$(PBu_3)_2$Pt(PEP)Cl**, (**3a**) was dissolved in 5 mL of dry DMF and degassed for 30 minutes. Then 52 mg, 74 mmol of triisopropyl(5'-(tributylstannyl)-[2,2'-bithiophen]-5-yl)silane was added to the system along with 2 mg of CuI. The system was stirred at room temperature overnight. The resulting precipitate was filtered off and dried under vacuum.

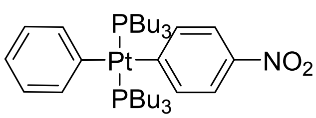
Yield: 65%, R_f=0.86 (1:1 DCM/Hexane).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.12 (m. 12H), 6.58 ($J^{Pt\text{-}H}$=46Hz, 1H). 1.5-1.23(m, 39H), 1.14 (d, *J*=7Hz, 18H), 0.89 (t, *J*=7.2, 18Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.4($J^{Pt\text{-}C}$ = 21Hz), 156.14($J^{Pt\text{-}C}$=12Hz), 145.83, 139.26, 138.28, 136.32, 131.49, 131.31, 129.76 ($J^{Pt\text{-}C}$=46Hz), 129.39, 128.21, 127.40, 125.33, 124.30, 121.87, 115.09, 91.67, 86.90, 26.06($J^{Pt\text{-}C}$=23Hz), 24.27 ($J^{Pt\text{-}C}$=13Hz), 21.39($J^{Pt\text{-}C}$=33Hz), 18.64, 13.83, 11.82.

^{31}P NMR (121 MHz) δ 1.45 ($J^{Pt\text{-}P}$ = 2675 Hz)

Calculated for ($C_{55}H_{88}S_2P_2$Si Pt) 1098.5227, found MALDI-TOF-MS (m/z): 1047.5223 $[M]^+$.

***trans*-$(PBu_3)_2$Pt(Ph)(*p*-NO_2Ph) (12)**



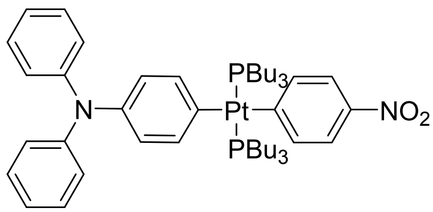
50 mg, 70 mmol of ***trans*-$(PBu_3)_2$Pt(Ph)Cl (1a**) was dissolved in dry DMF and degassed for 30 minutes. Then 43 mg, 68 mmol of tributyl(4-nitrophenyl)stannane was added to the system along with 2 mg of CuI. The system was stirred at room temperature overnight. The resulting precipitate was filtered off and dried under vacuum. Yield : 60%, R_f=0.5 (1:5 DCM/Hexane).

^{1}H NMR (300 MHz, $CDCl_3$) 7.82 (d, *J*=9Hz, 2H), 7.68 (d, *J* = 9Hz, $J^{Pt\text{-}H}$=41Hz, 2H), 7.35 (d, *J* = 7.2Hz, $J^{Pt\text{-}H}$ =42Hz, 2H), 6.98 (t, *J*=7.2Hz, 2H), 6.81 (t, *J*=7.2Hz, 1H), 1.51-1.35(m, 12H), 1.30 (m, 24H) 0.86 (t, *J*=7.2Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.82 ($J^{Pt\text{-}C}$=40Hz), 127.04, 121.43, 120.06 ($J^{Pt\text{-}C}$=46Hz), 25.93 ($J^{Pt\text{-}C}$=23Hz), 24.10($J^{Pt\text{-}C}$=13Hz), 21.62($J^{Pt\text{-}C}$=33Hz).

^{31}P NMR (121 MHz) δ 0.63 ($J^{Pt\text{-}P}$=2749 Hz).

Calculated for $(C_{36}H_{63}NO_2P_2\,Pt)H$ 799.4058, found DIP-CI-MS (m/z): 799.4029 $[M+H]^+$.

***trans*-(PBu$_3$)$_2$Pt(TPA)(*p*-NO$_2$Ph) (13)**



40 mg, 45 mmol of **(PBu$_3$)$_2$Pt(TPA)Cl** (**6a**) was dissolved in DMF and degassed for 30 minutes. Then 30 mg, 68 mmol of tributyl(4-nitrophenyl)stannane was added to the system along with 2 mg of CuI. The system was stirred at room temperature overnight. The solvent was evaporated and the product was isolated via preparative thin layer chromatography using silica gel as an adsorbent and 1:1 DCM/Hexane mixture as eluent. Yield : 45%, R_f=0.5 (1:5 DCM/Hexane). ^{1}H NMR (300 MHz, $CDCl_3$) 7.84 (d, J =9Hz, 2H), 7.69(d, J=9Hz, 2H J^{Pt-H}=23Hz), 7.34(d, J=9Hz, 2H J^{Pt-H}=23Hz), 7.17(m, 4H), 7.05(m, 4H), 6.89(m, 4H), 1.57-1.37(m, 12H), 1.37-1.27(m, 24H), 0.88(t, J=7.2Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.77(J^{Pt-C}=20Hz), 154.78(J^{Pt-C}=22Hz), 148.47, 143.42, 141.39, 140.05(J^{Pt-C}=20Hz), 139.70(J^{Pt-C}=23Hz), 128.70, 125.97(J^{Pt-C}=43Hz), 122.27, 120.91, 120.16, 25.90(J^{Pt-C}=23Hz), 24.22(J^{Pt-C}=13Hz), 21.69 (J^{Pt-C}=13Hz), 13.75. ^{31}P NMR (121 MHz) δ 0.47(J^{Pt-P}=2773Hz).

Calculated for $(C_{48}H_{72}N_2O_2P_2Pt)$ 966.4793, found MALDI-TOF-MS (m/z): 966.4849 $[M]^+$.

2. NMR Spectra

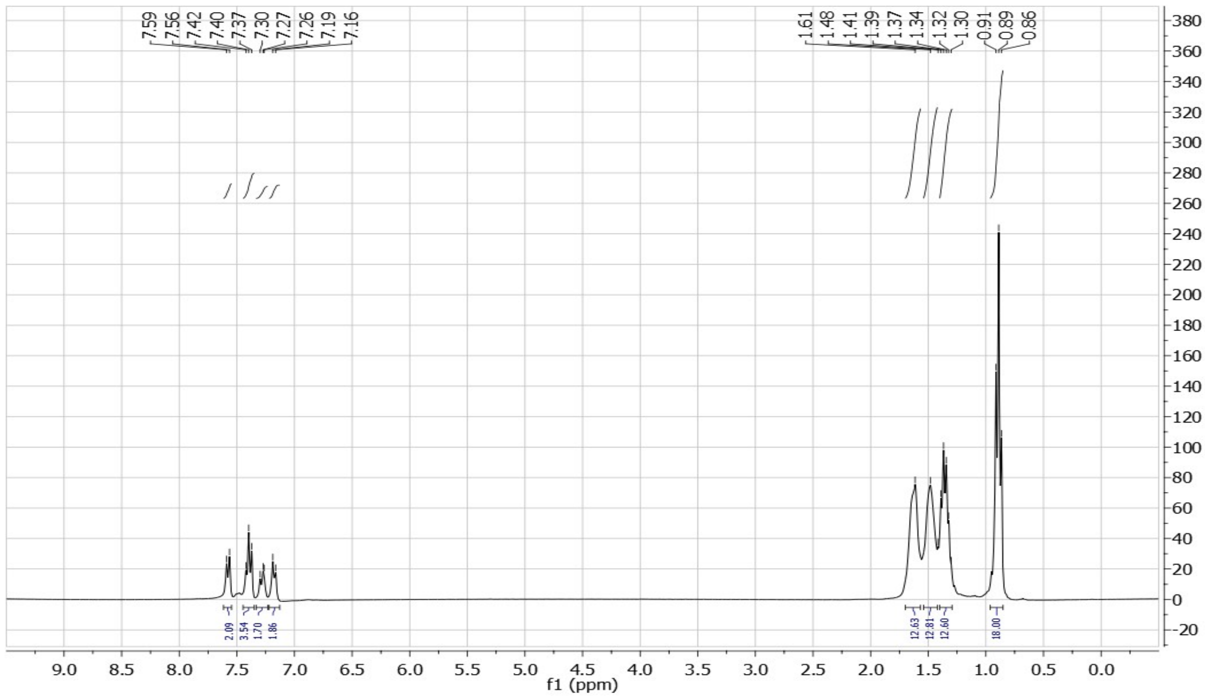


Figure S1. ^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(BPh)Cl (2a)**

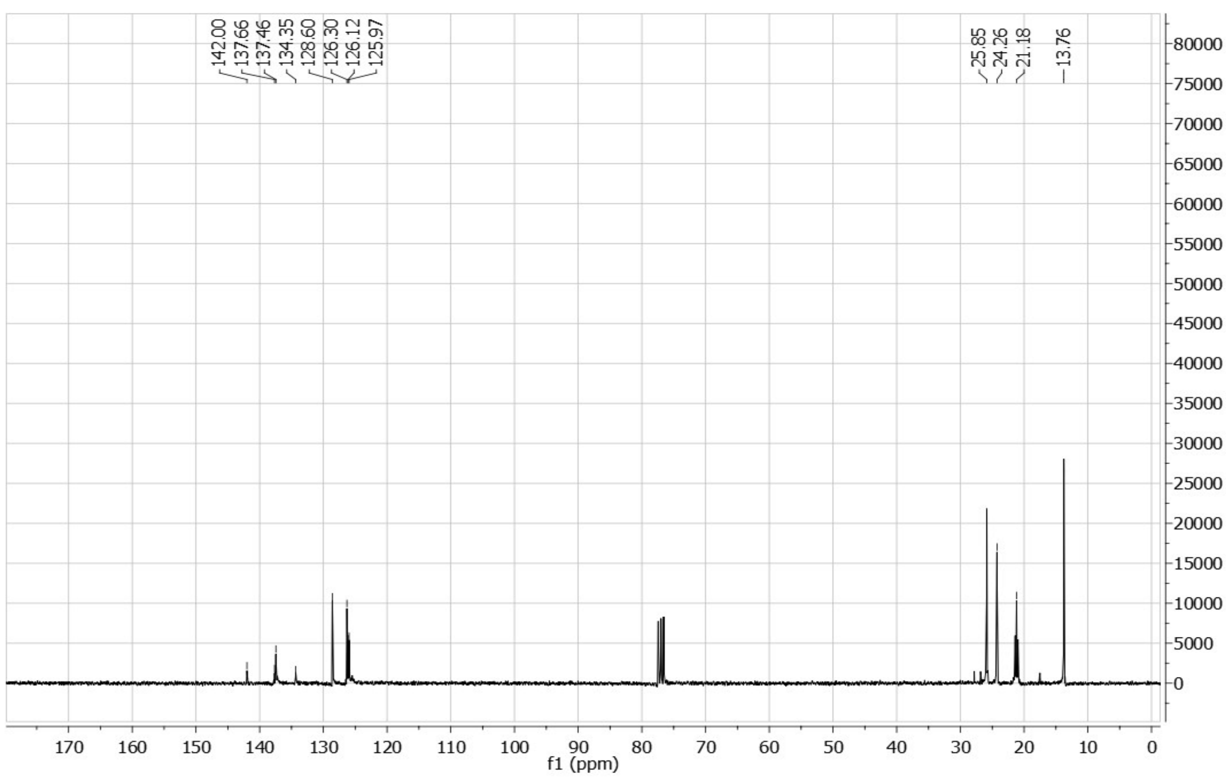


Figure S2. ^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(BPh)Cl (2a)**

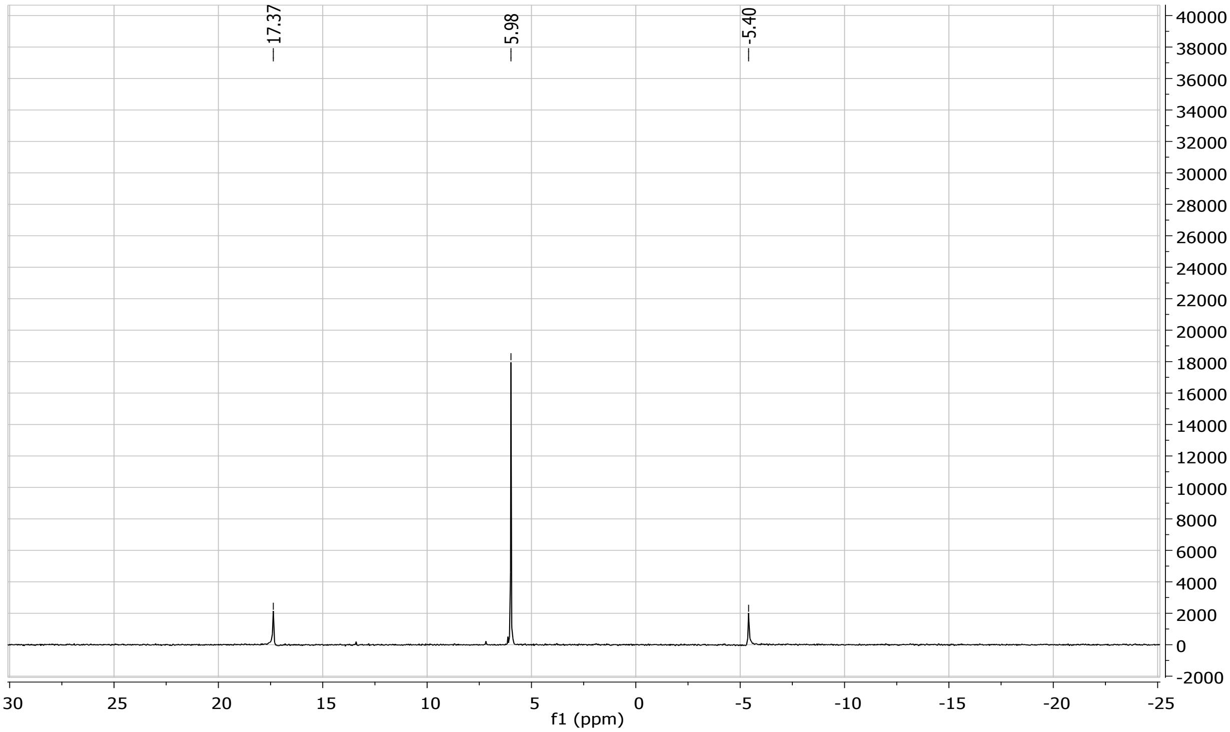


Figure S3. ^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(BPh)Cl (2a)**

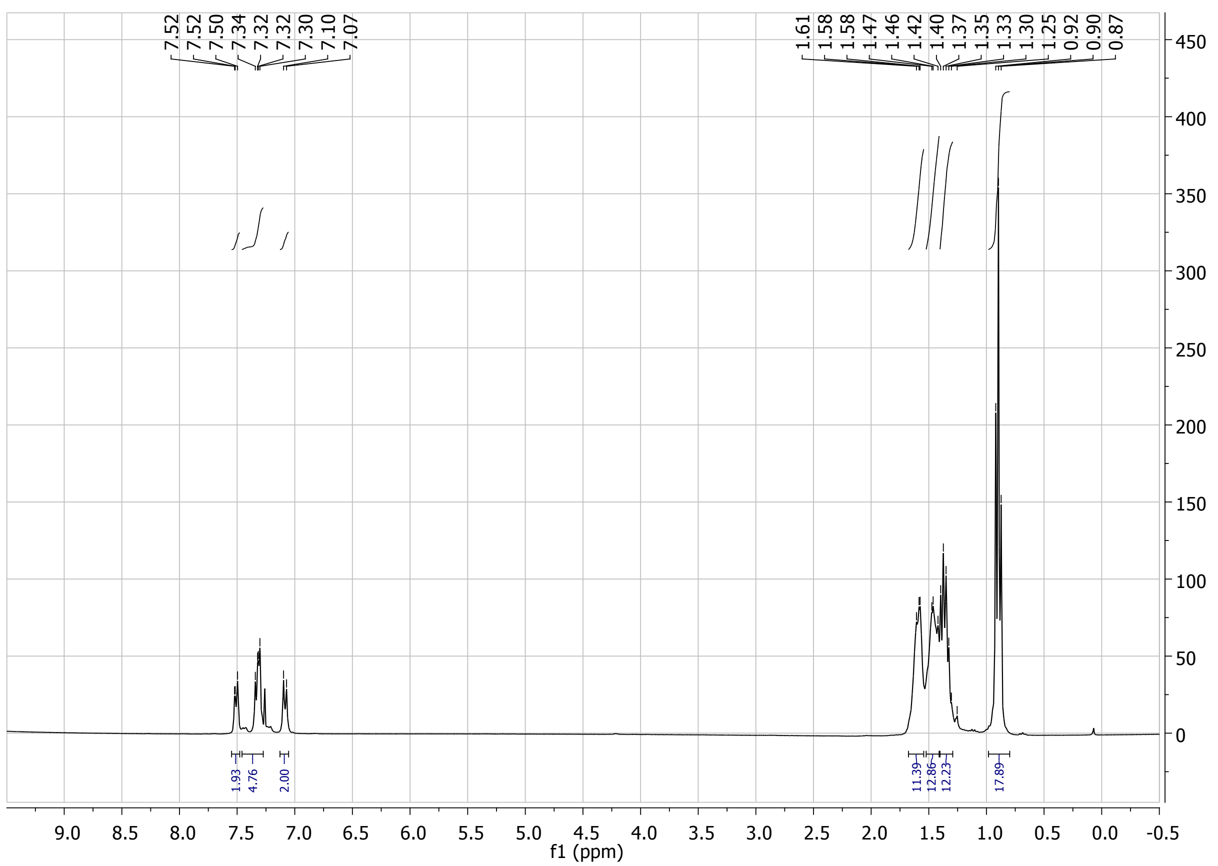


Figure S4. ^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)Cl (3a)**

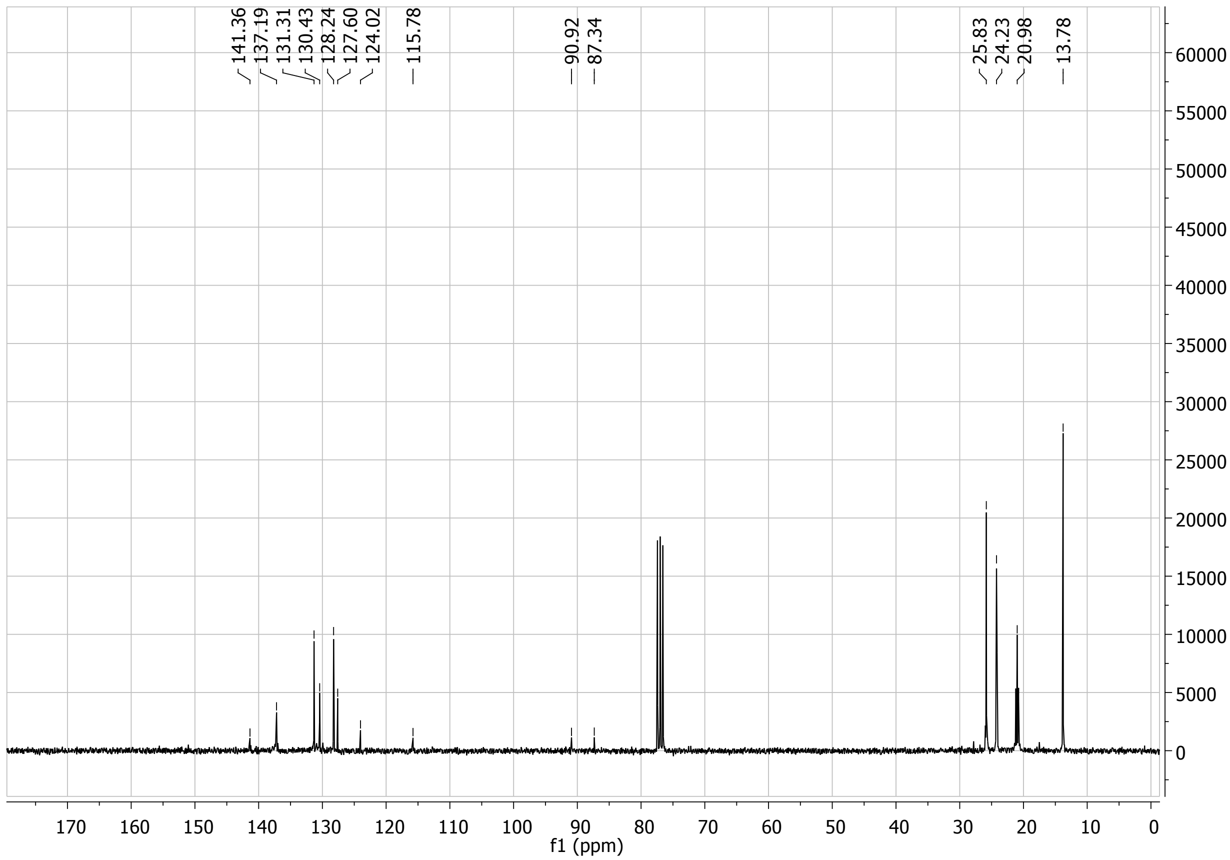


Figure S5. ^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)Cl (3a)**

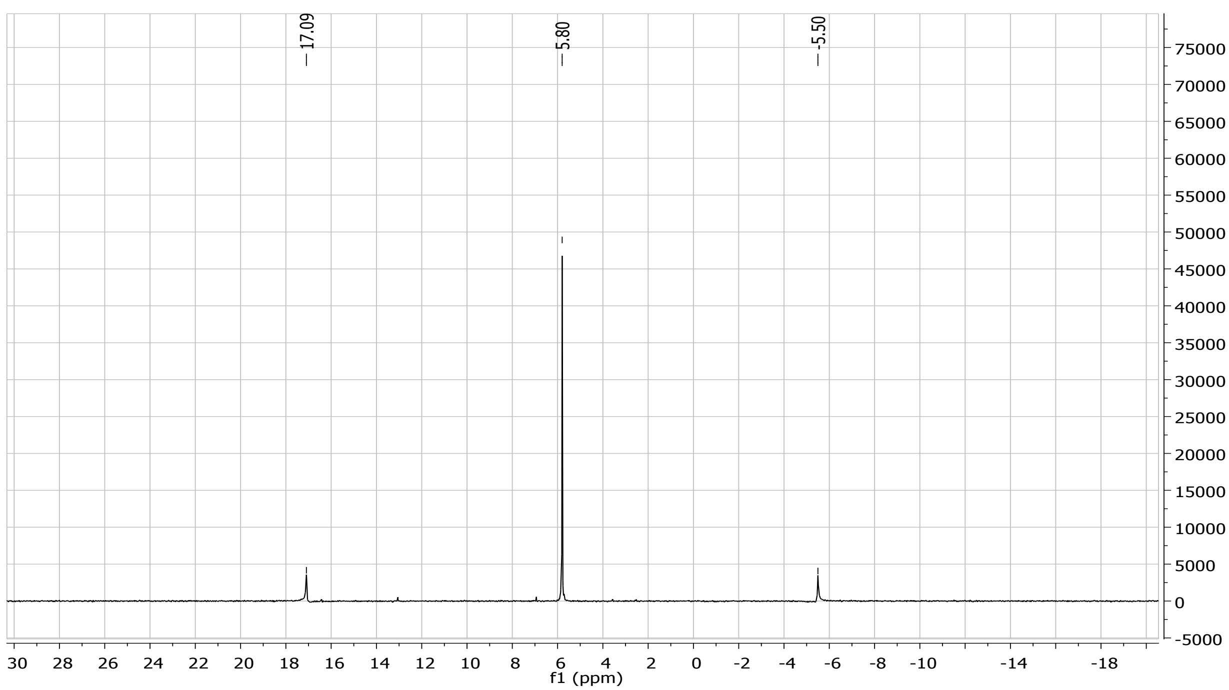


Figure S6. ^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)Cl (3a)**

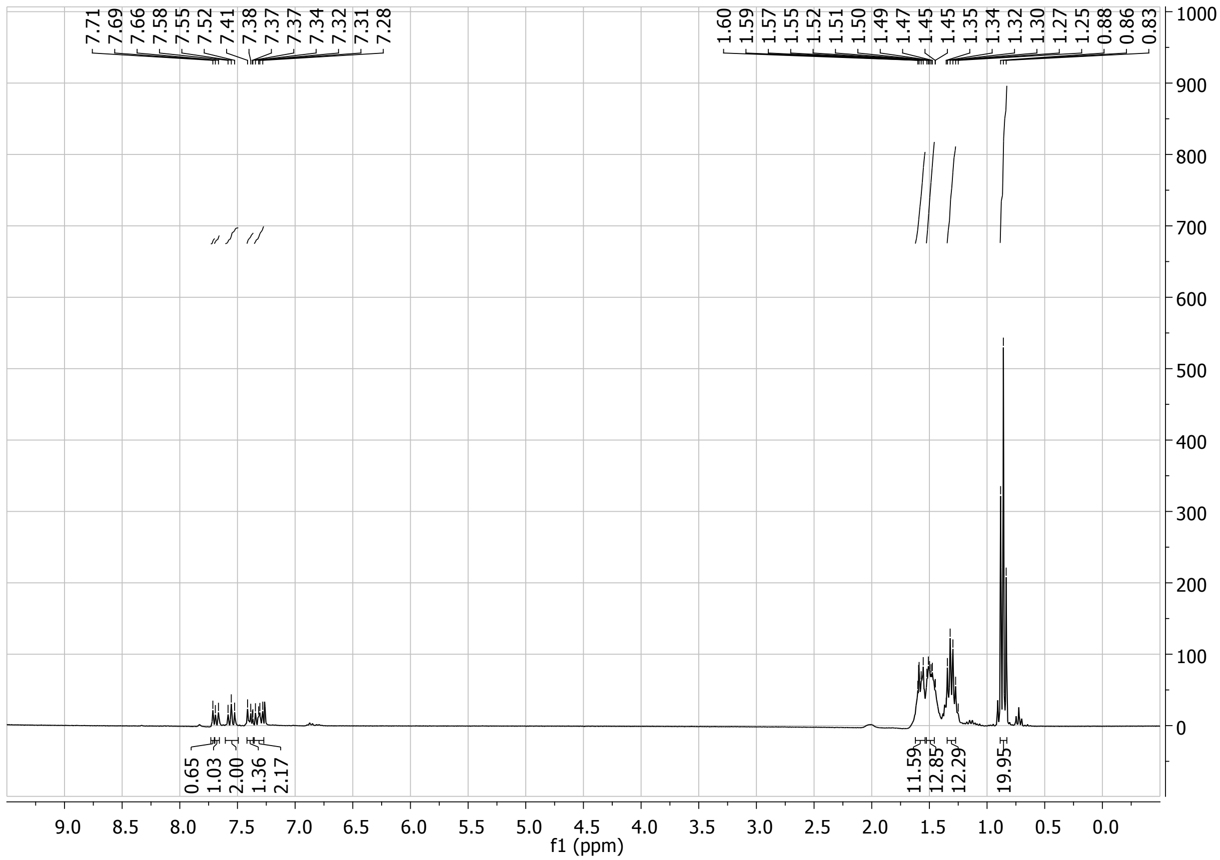


Figure S7. ^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Naphto)Cl (4a)**

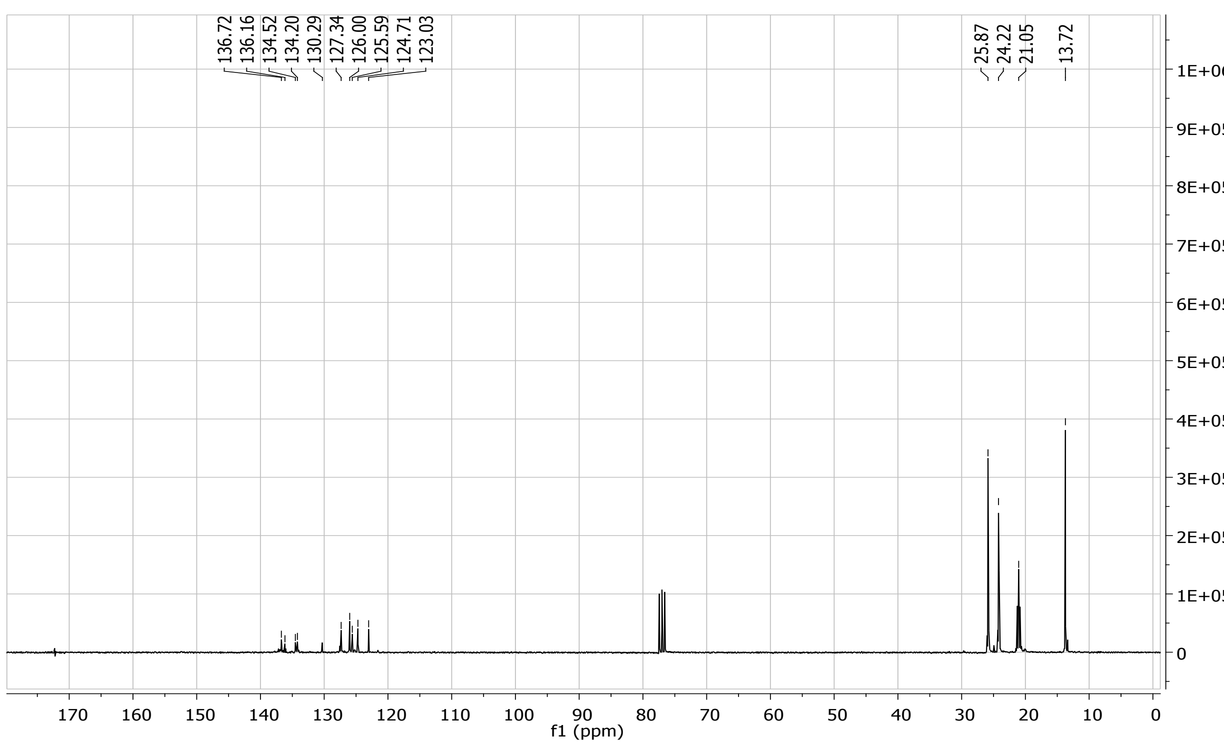


Figure S8. ^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Naphto)Cl (4a)**

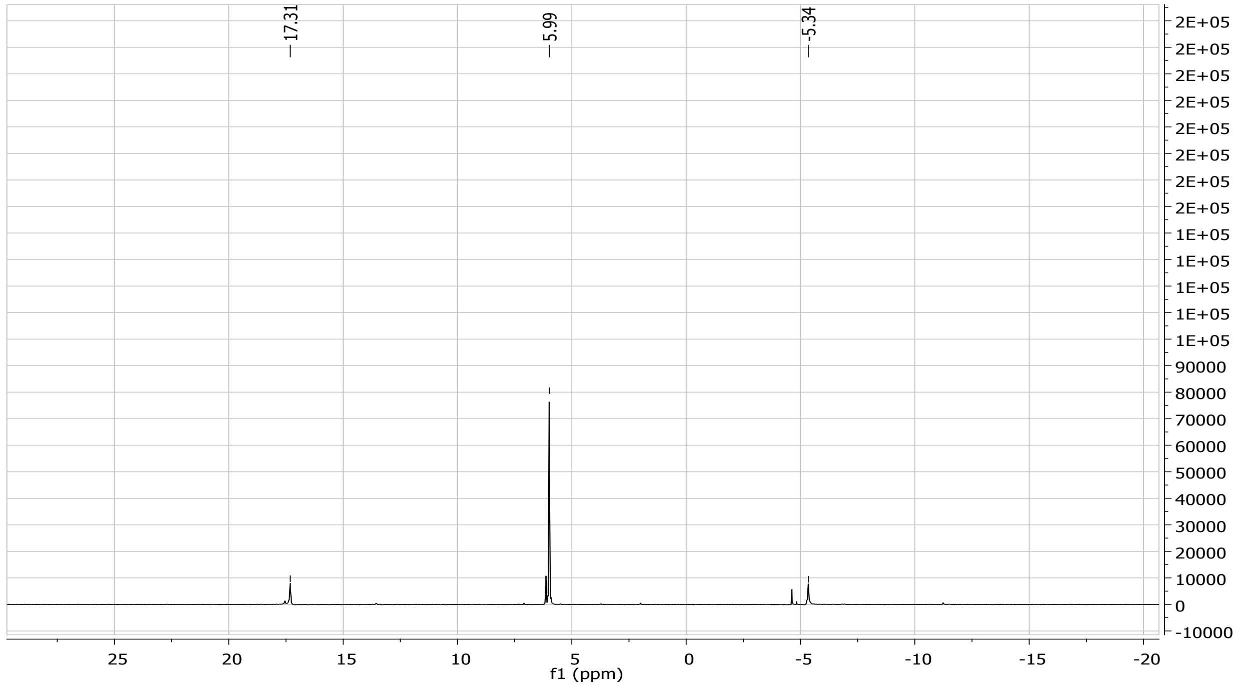


Figure S9.[31]P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Naphto)Cl (4a)**

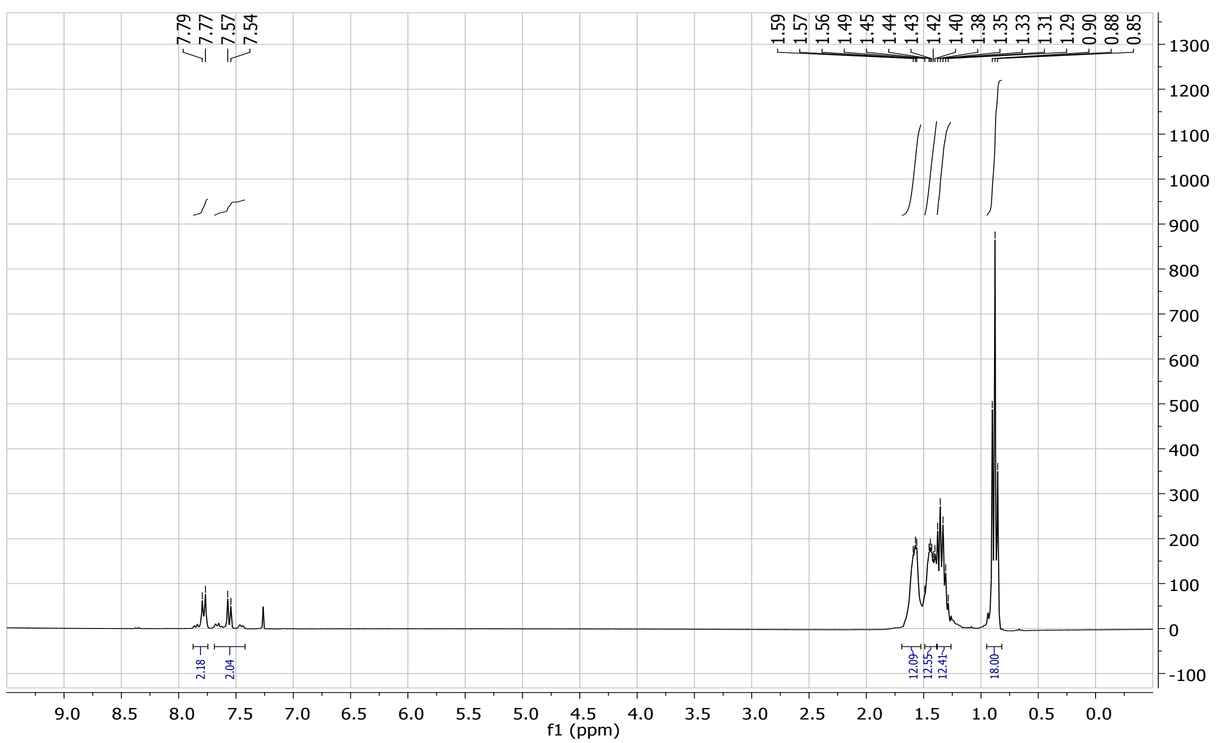


Figure S10. ^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(*p*-NO$_2$Ph)Cl (5a)**

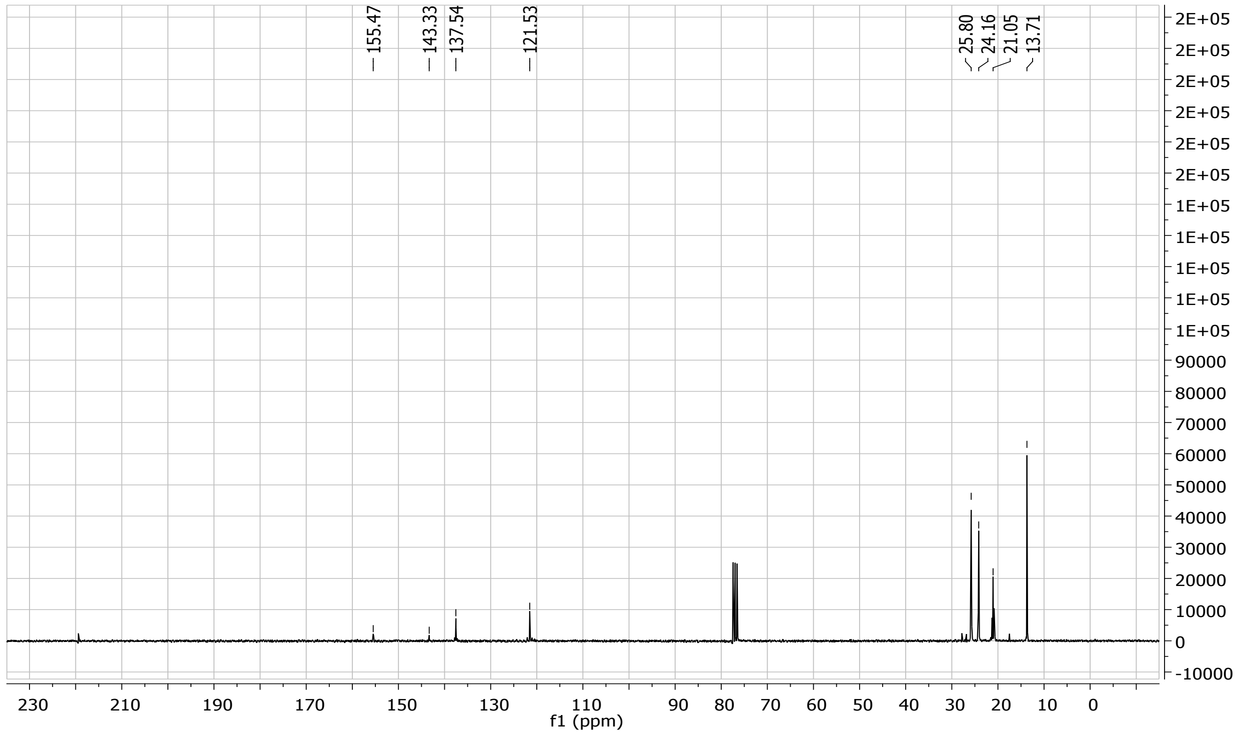


Figure S11. ^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(*p*-NO$_2$Ph)Cl (5a)**

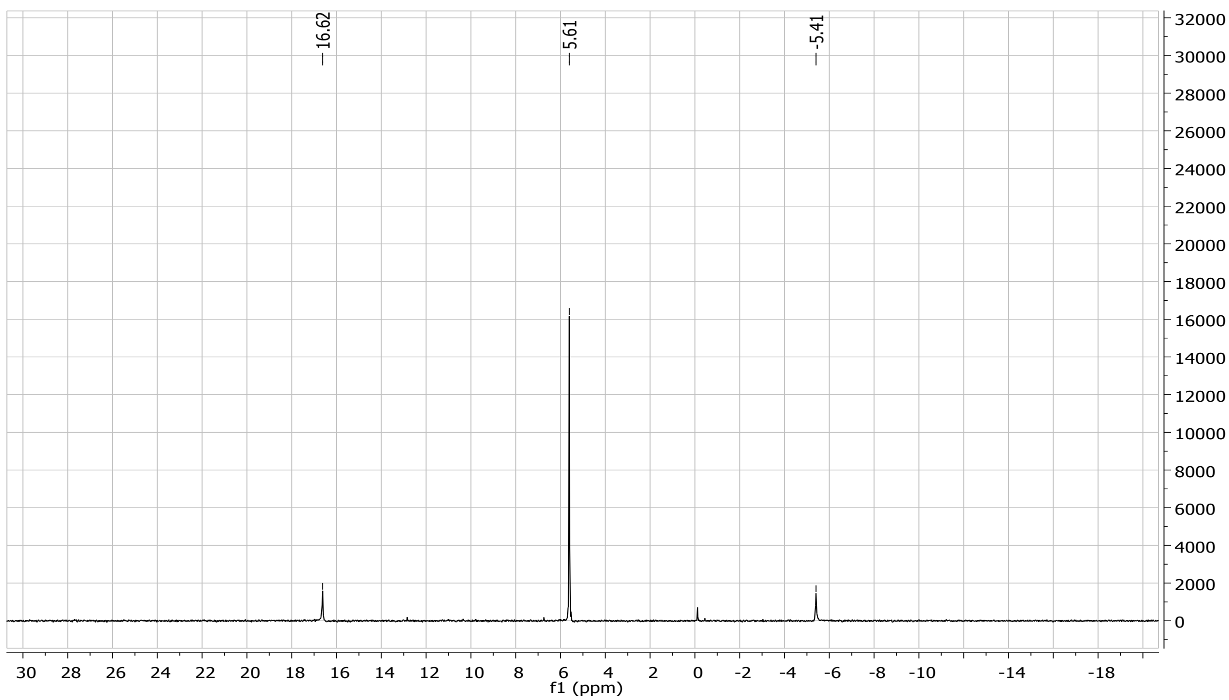


Figure S12. ^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(*p*-NO$_2$Ph)Cl (5a)**

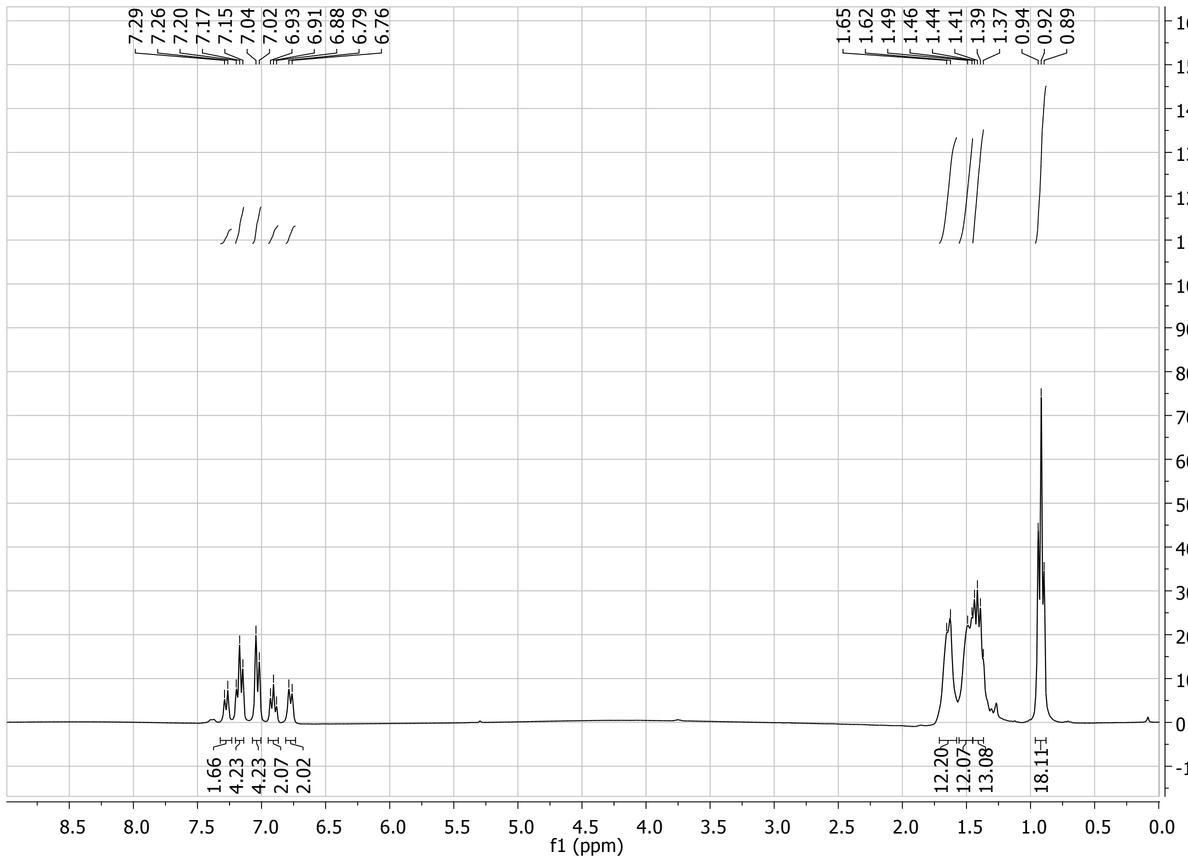


Figure S13. ^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TPA)Cl (6a)**

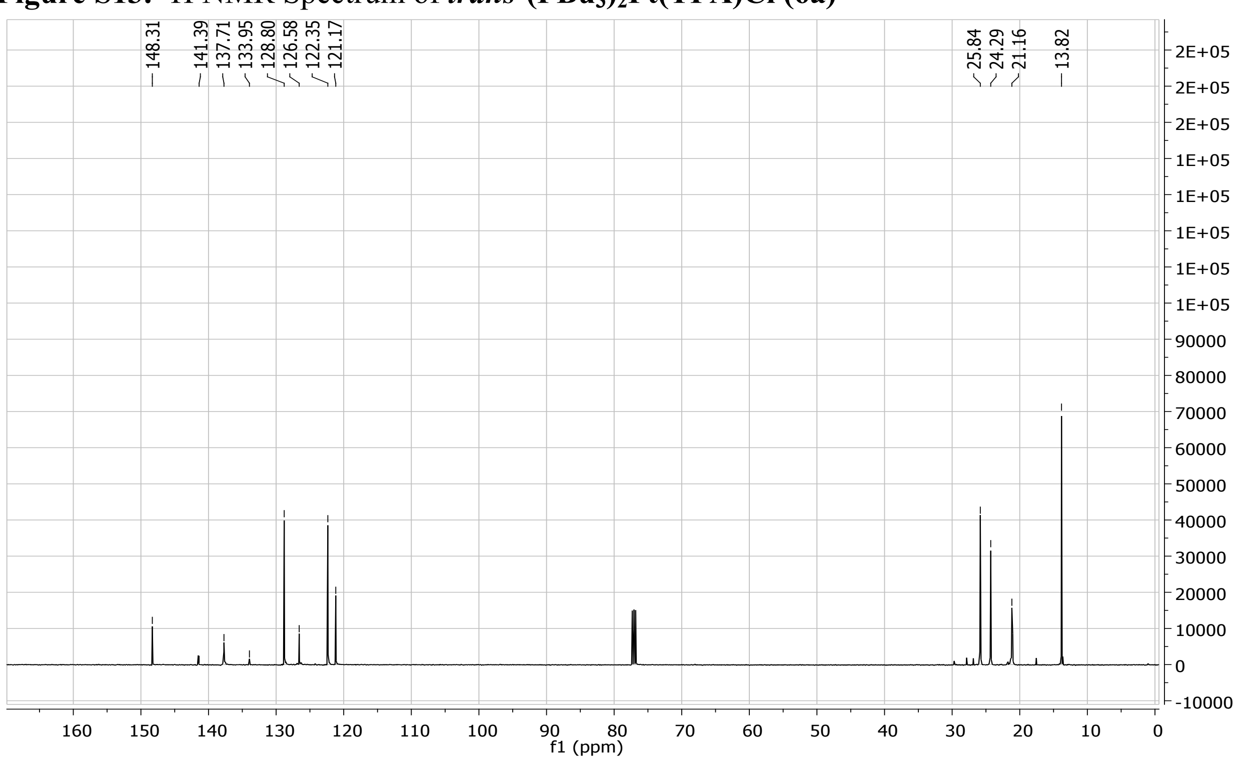


Figure S14. ^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TPA)Cl (6a)**

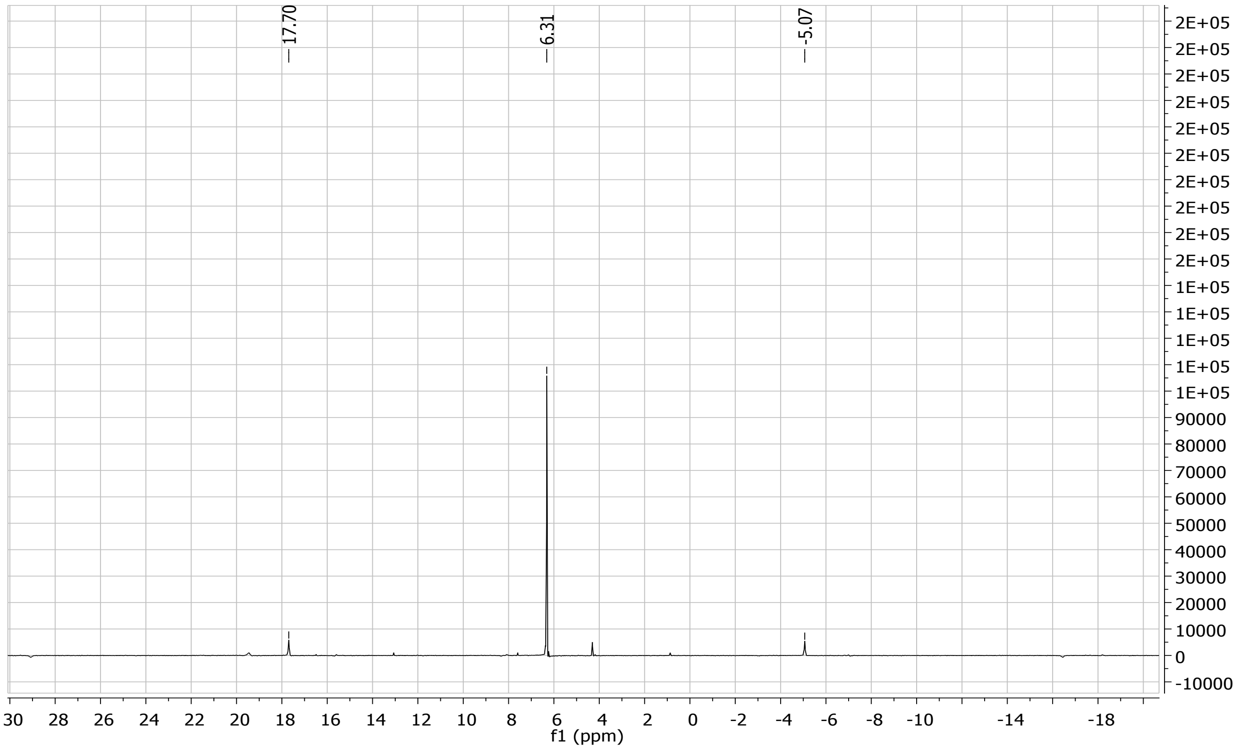


Figure S15. ^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TPA)Cl (6a)**

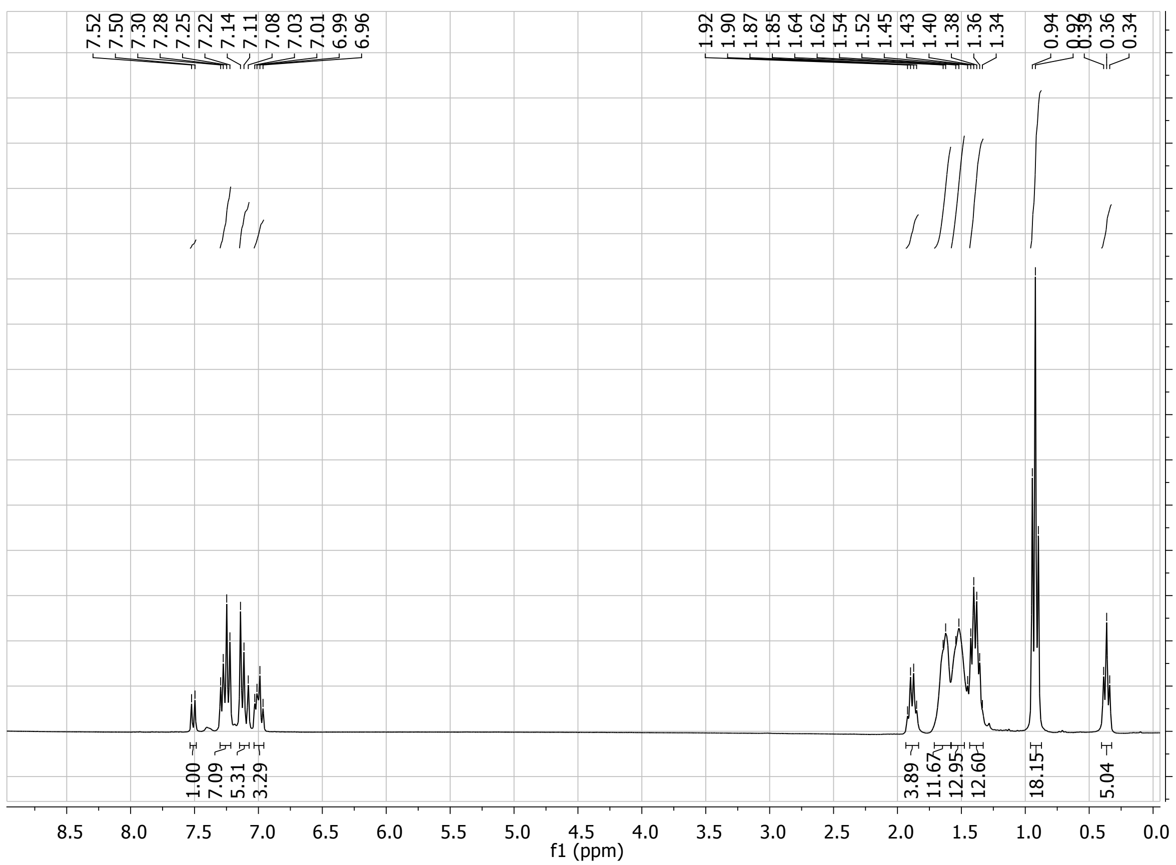


Figure S16. ^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(DPAF)Cl (7a)**

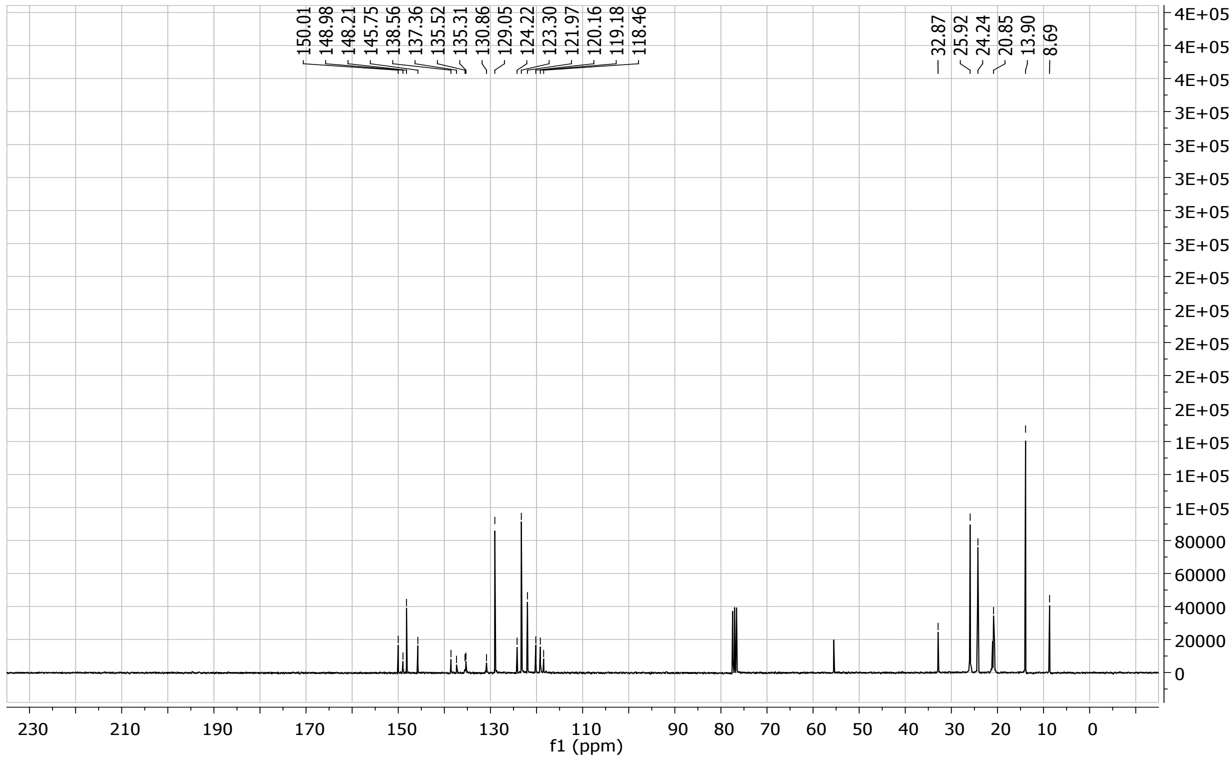


Figure S17. ^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(DPAF)Cl (7a)**

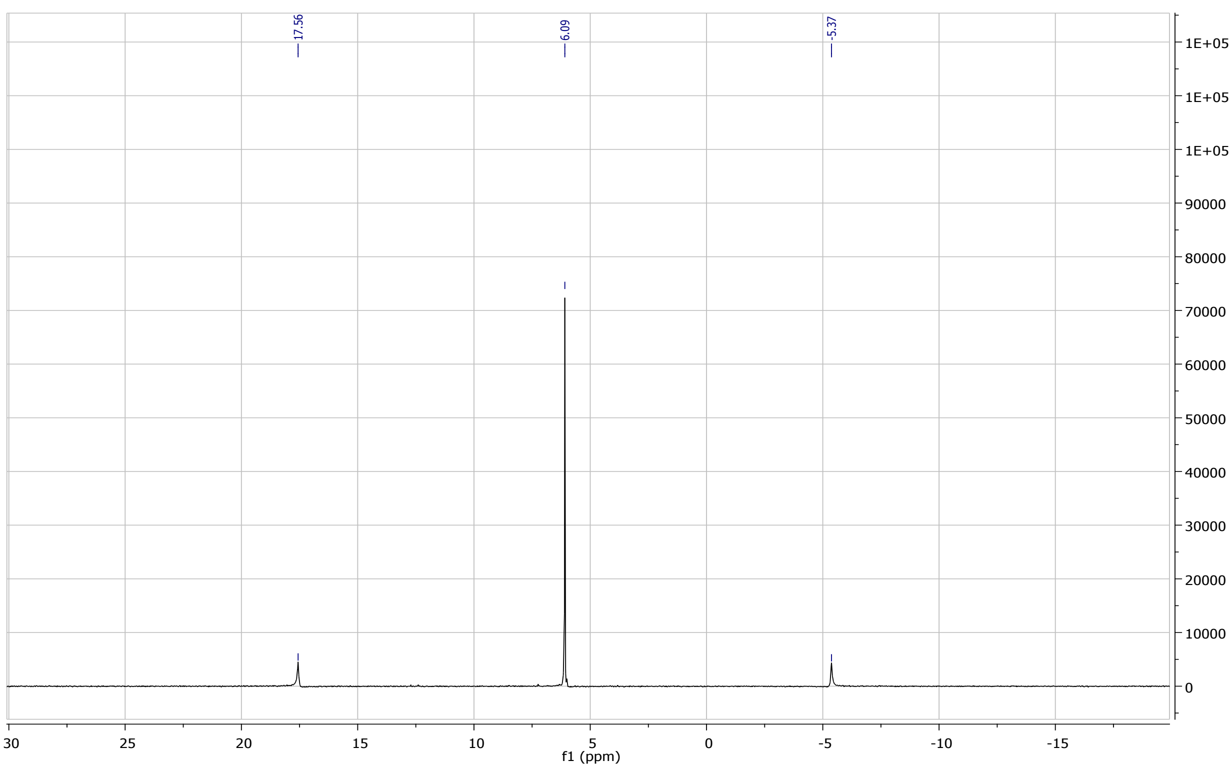


Figure S18. ^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(DPAF)Cl (7a)**

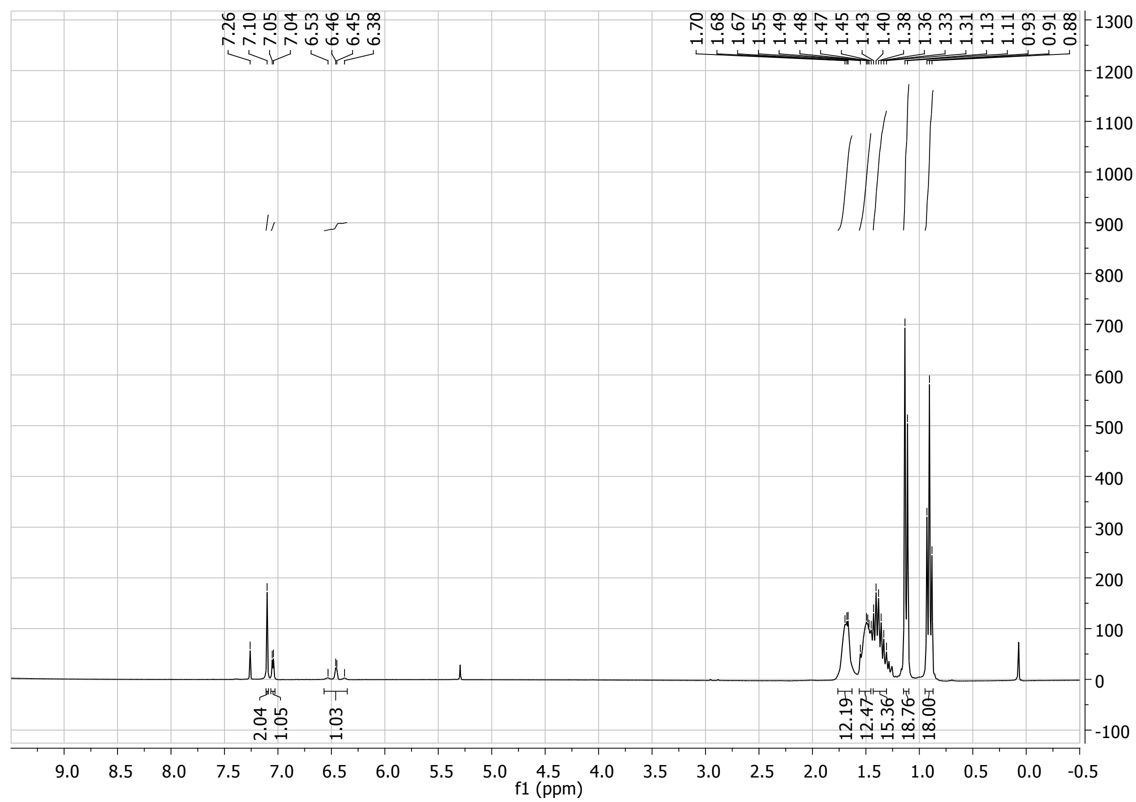


Figure S19. [1]H NMR Spectrum of ***trans*-$(PBu_3)_2$Pt(TIPSBTh)Cl (9a)**

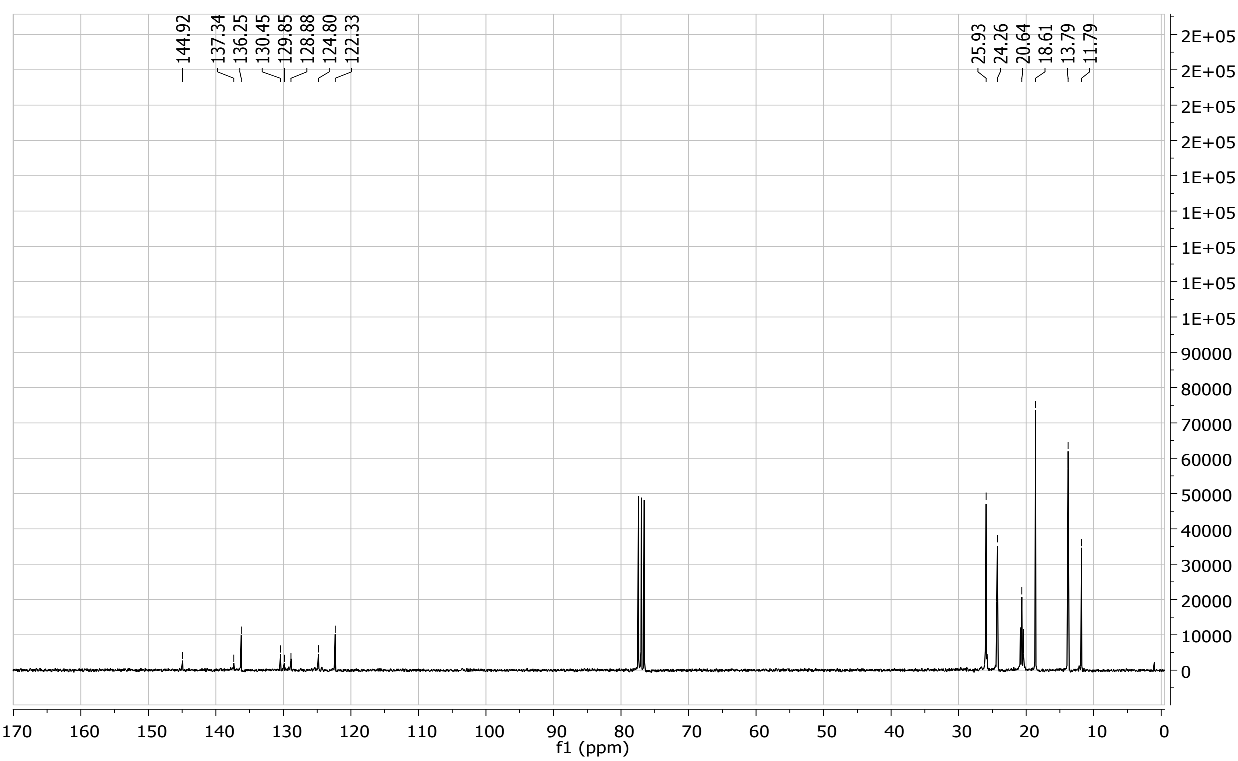


Figure S20.[13]C NMR Spectrum of ***trans*-$(PBu_3)_2$Pt(TIPSBTh)Cl (9a)**

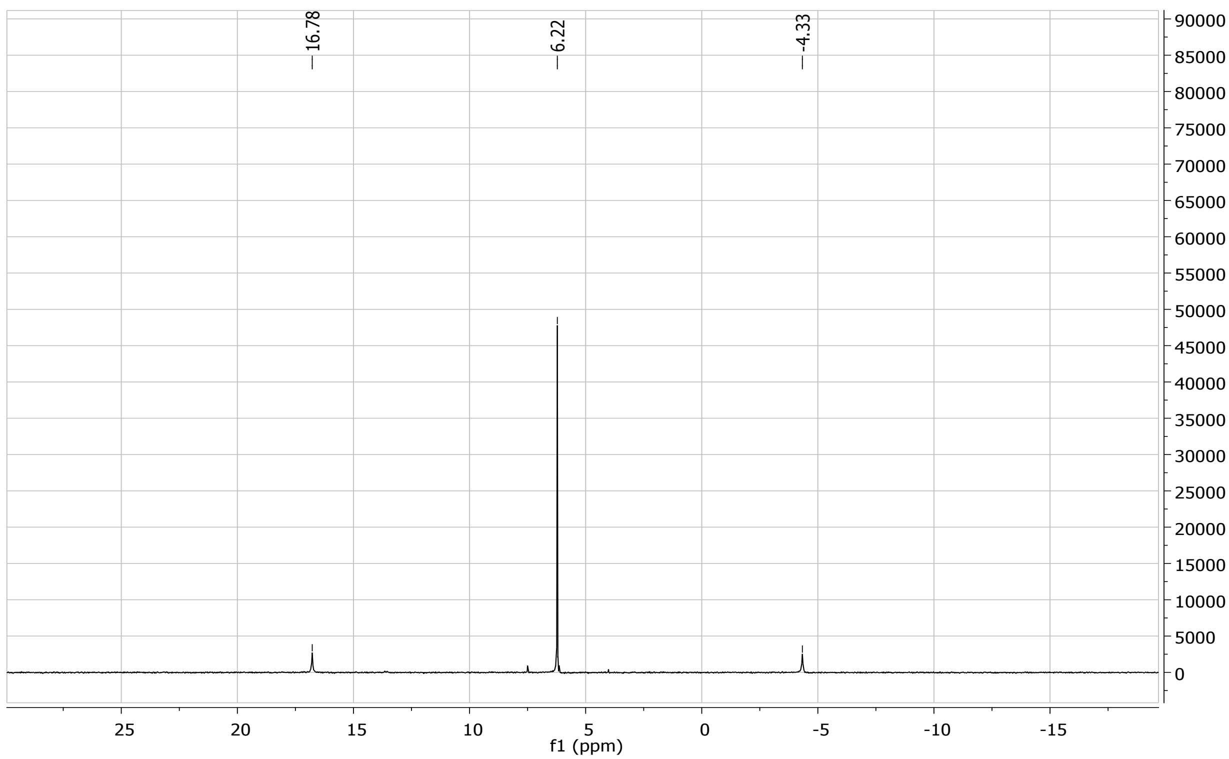


Figure S21.[31]P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TIPSBTh)Cl (9a)**

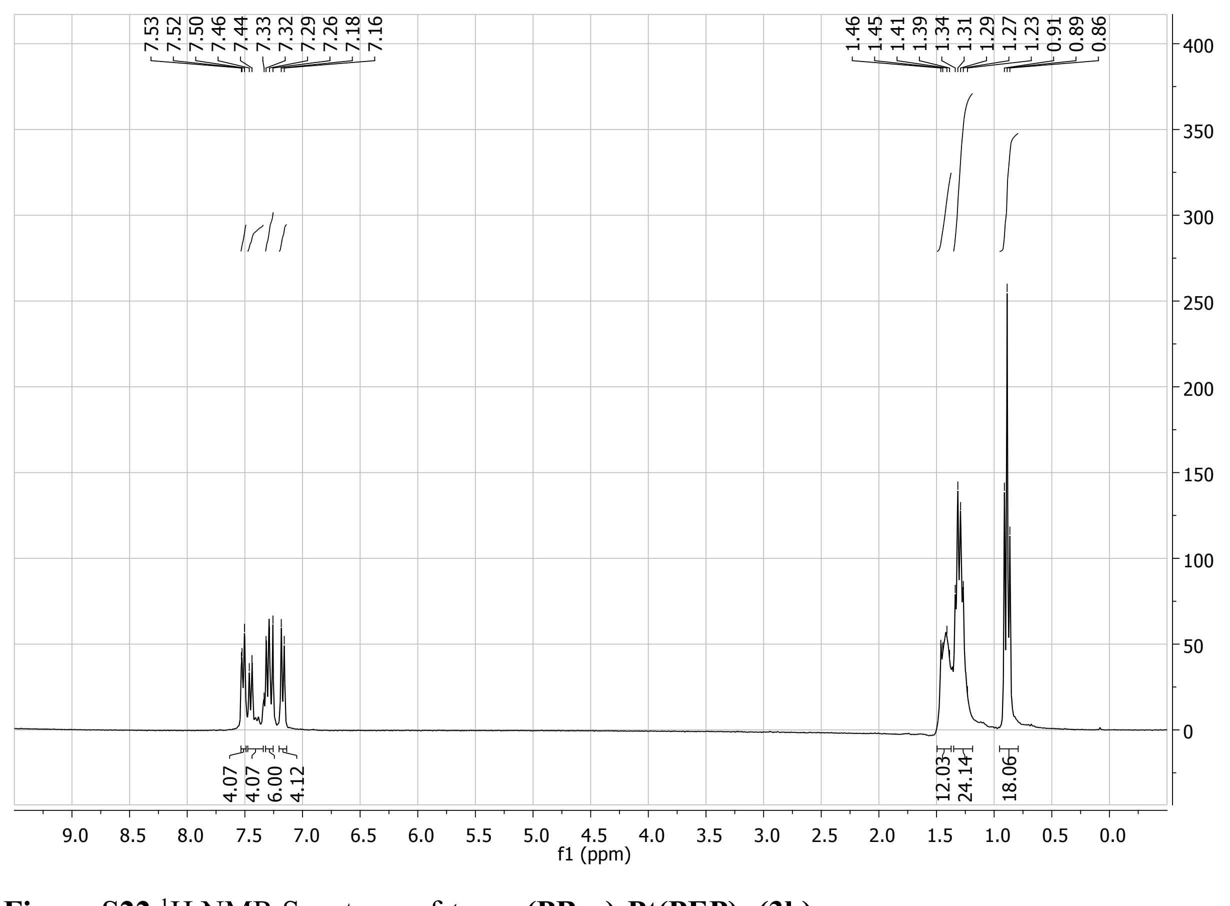


Figure S22.[1]H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)$_2$ (3b)**

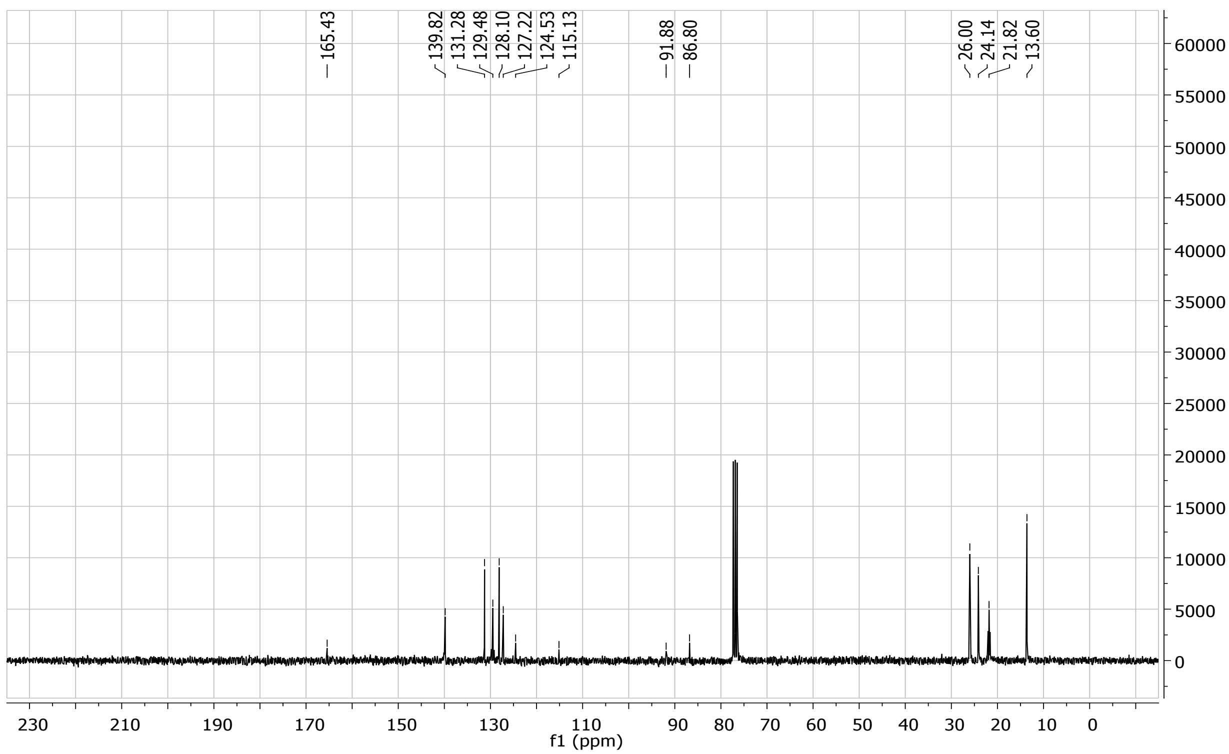


Figure S23.^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)$_2$ (3b)**

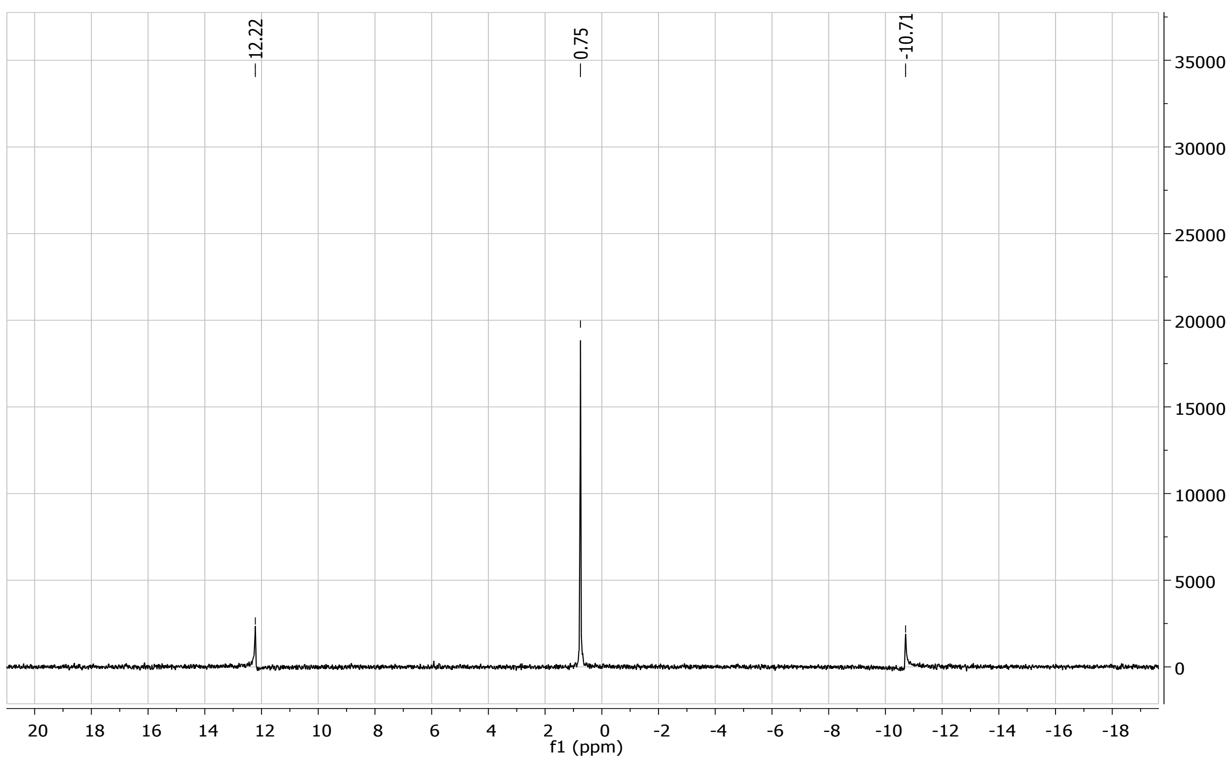


Figure S24.^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)$_2$ (3b)**

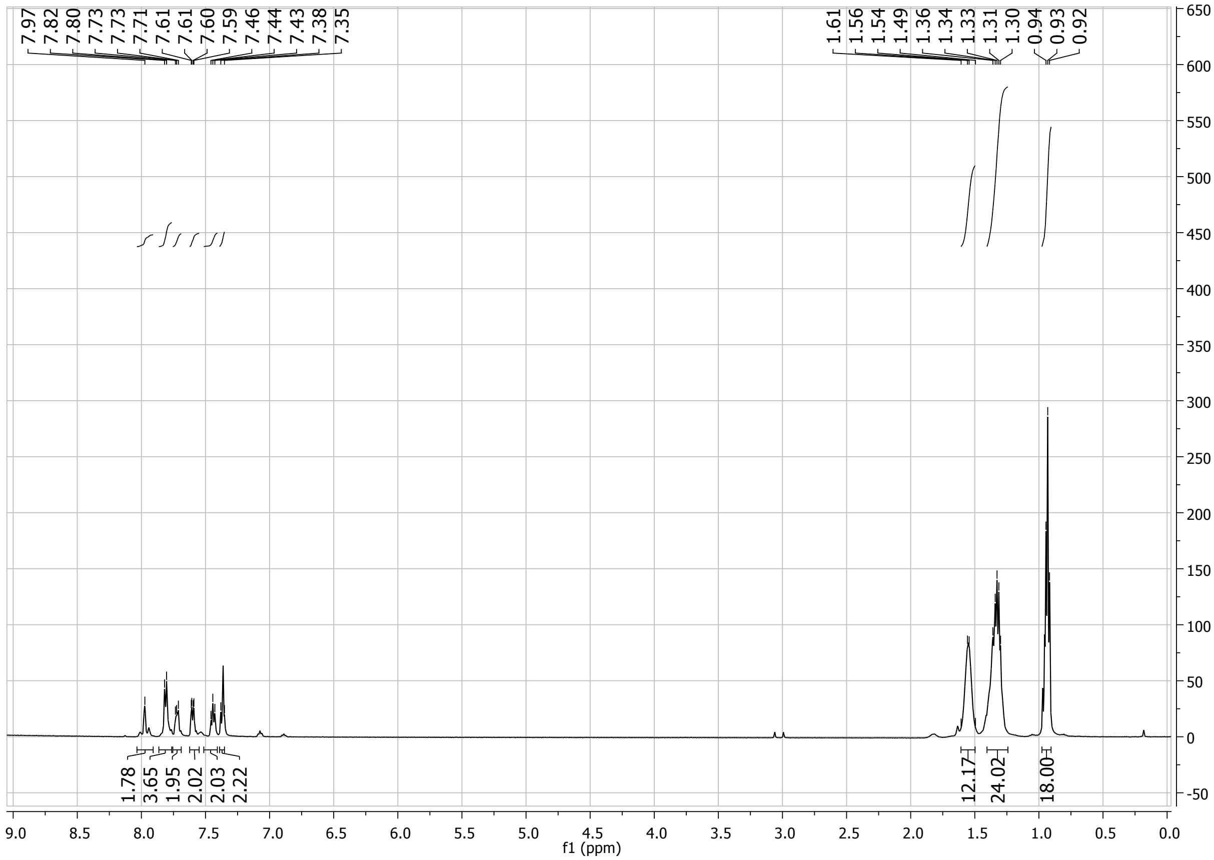


Figure S25.[1]H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Naphto)$_2$ (4b)**

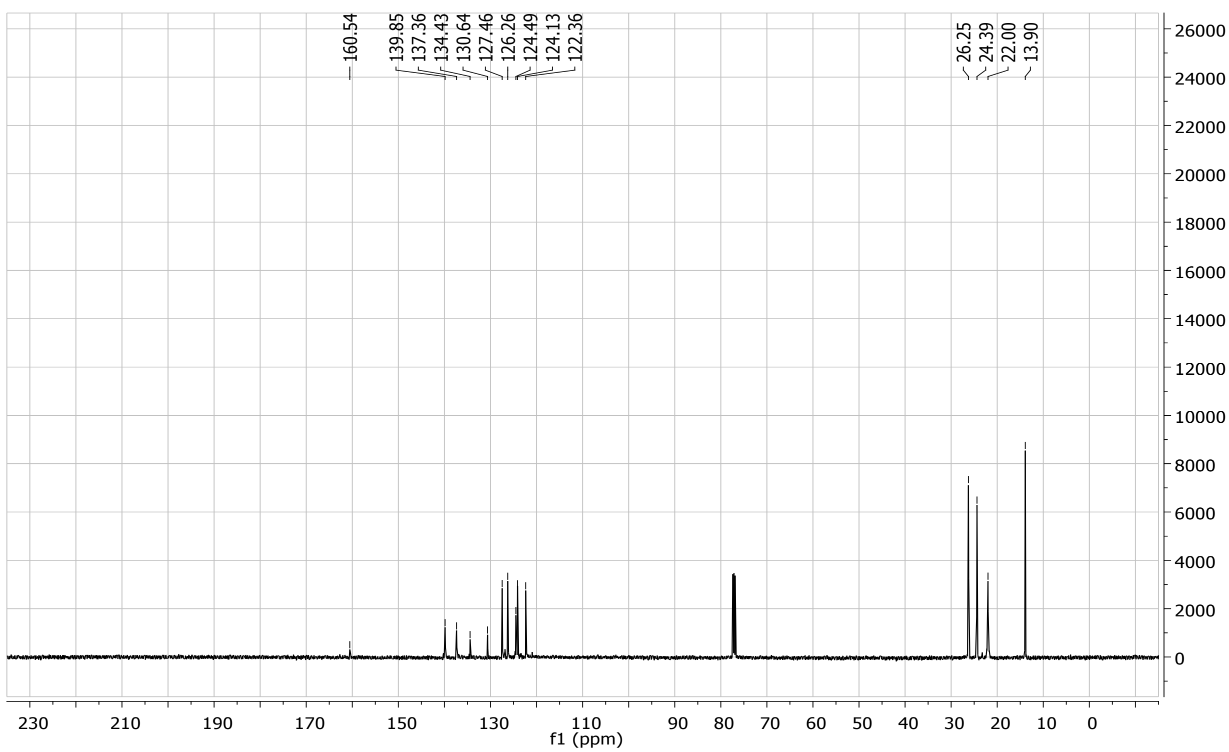


Figure S26.[13]C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Naphto)$_2$ (4b)**

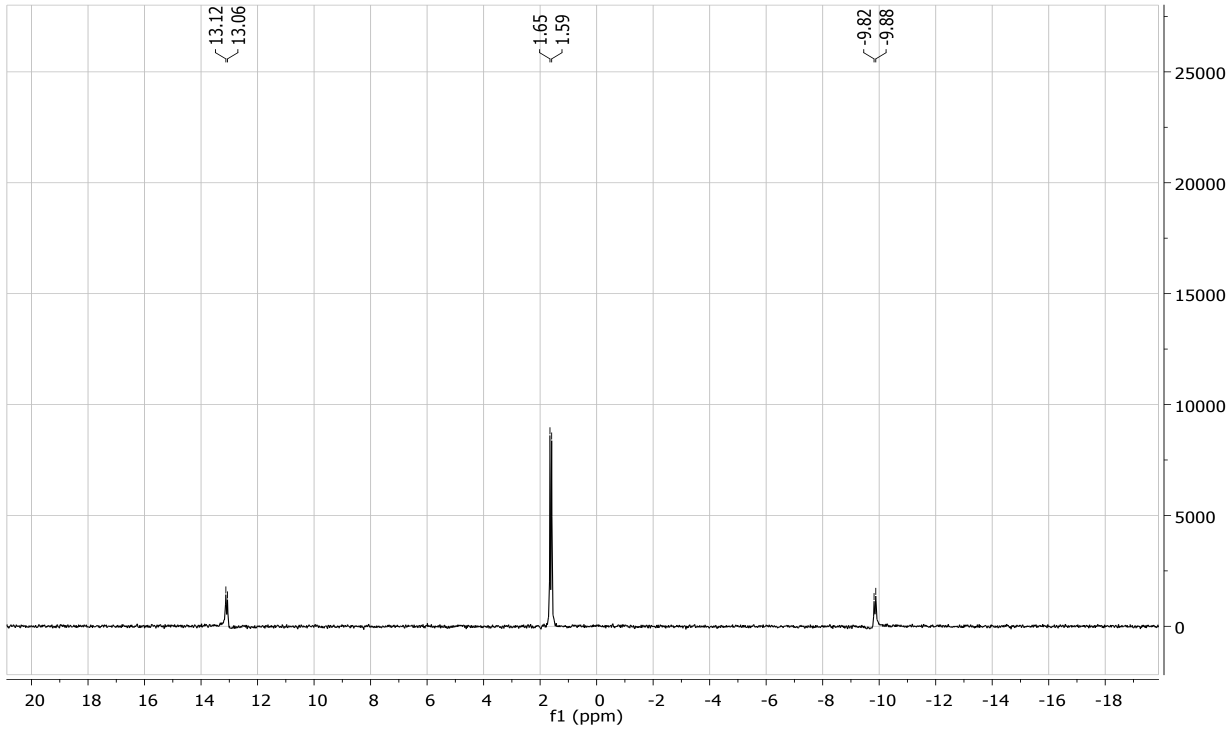


Figure S27.^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Naphto)$_2$ (4b)**

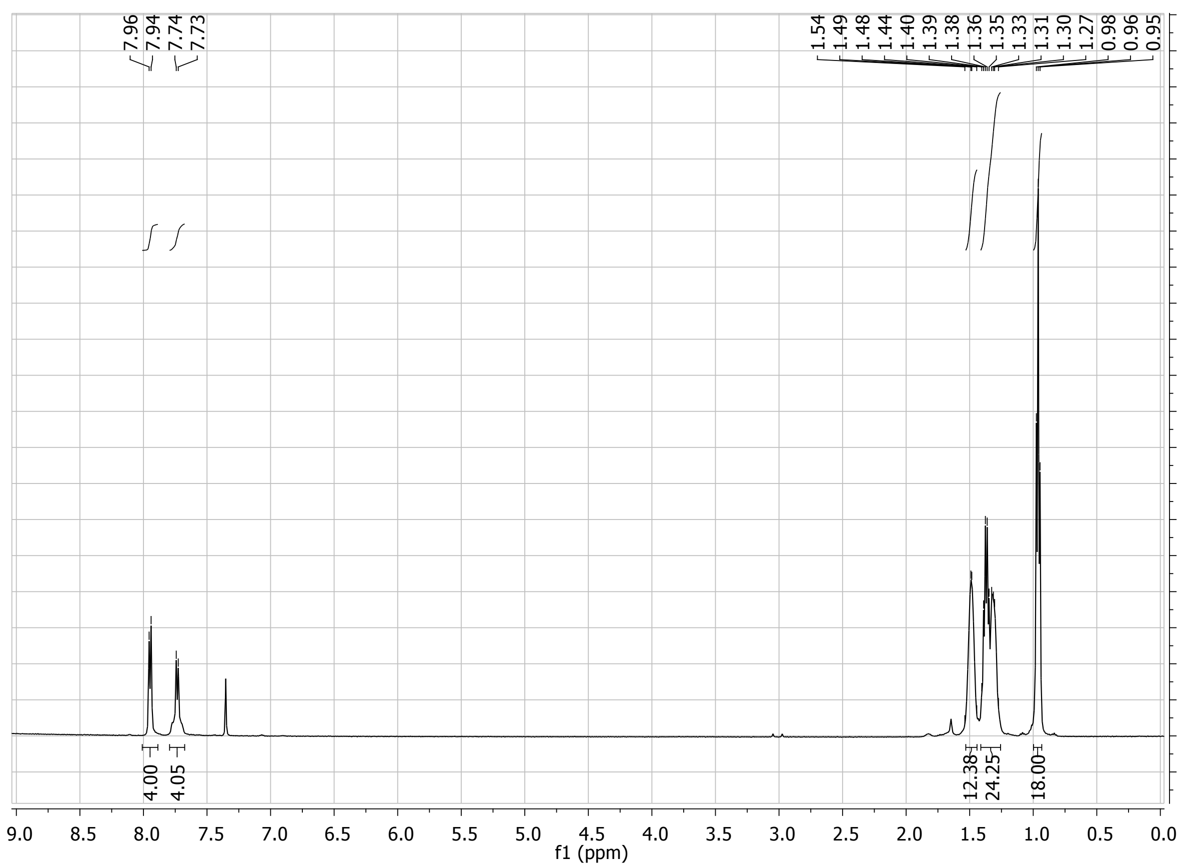


Figure S28.^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(*p*-NO$_2$Ph)$_2$ (5b)**

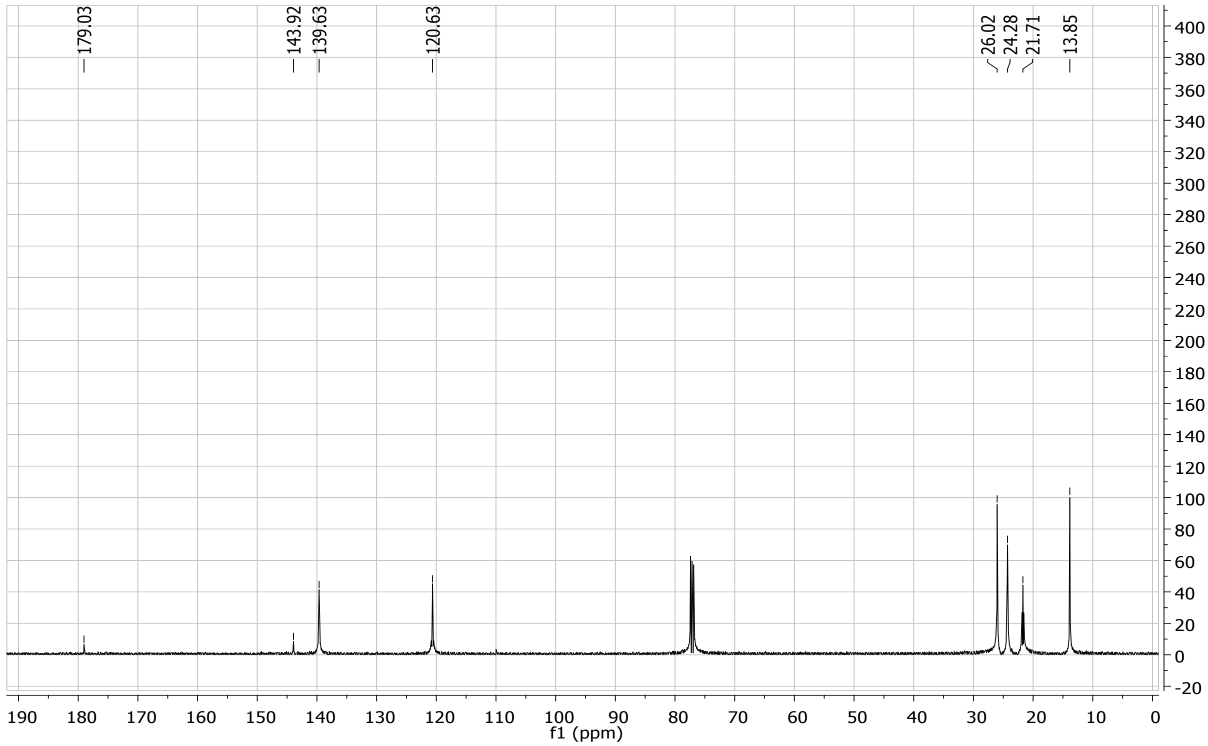


Figure S29.[13]C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(*p*-NO$_2$Ph)$_2$ (5b)**

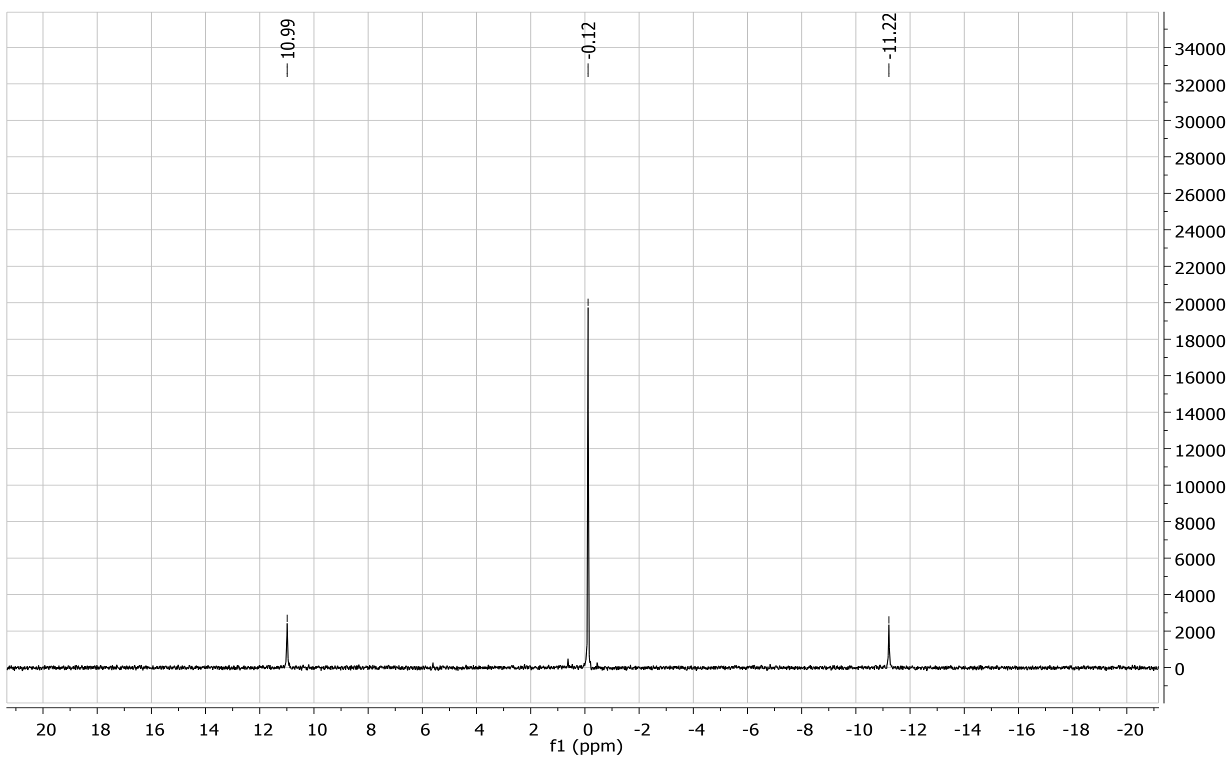


Figure S30.[31]P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(*p*-NO$_2$Ph)$_2$ (5b)**

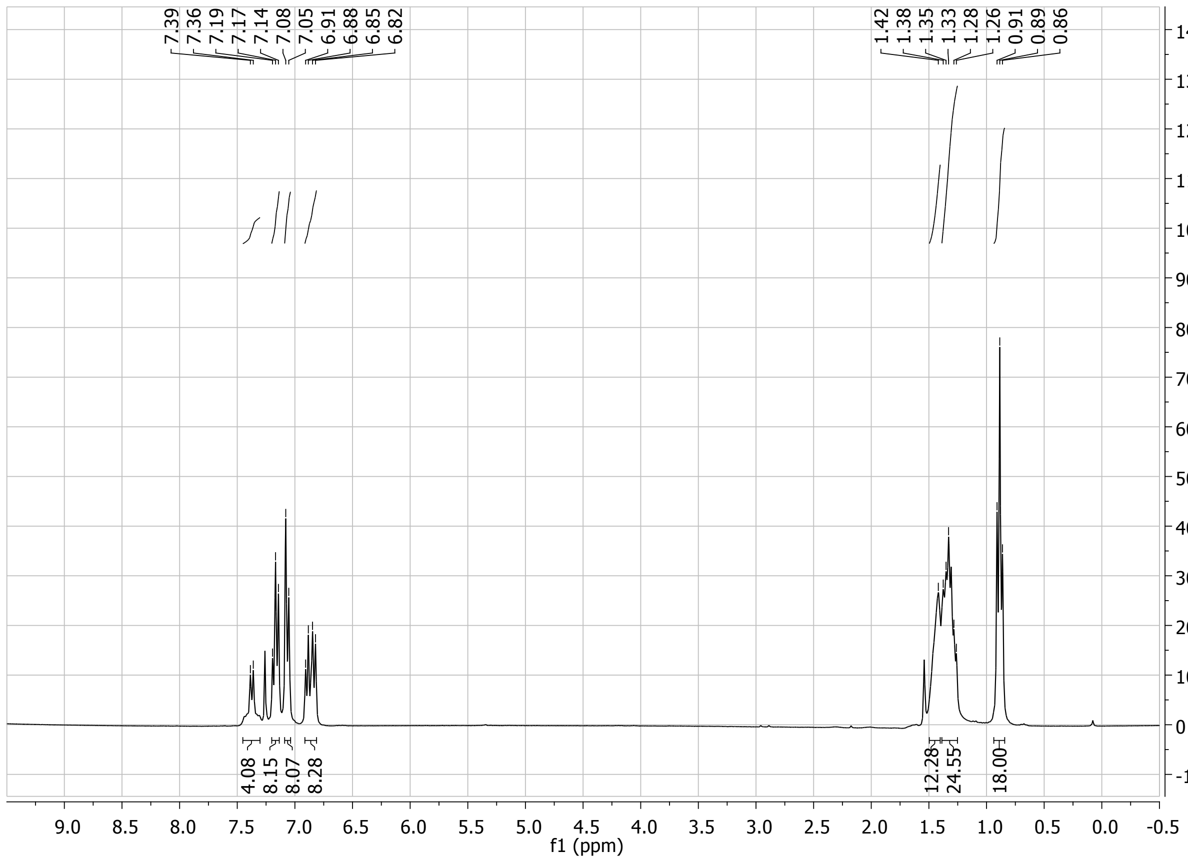


Figure S31.[1]H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TPA)$_2$ (6b)**

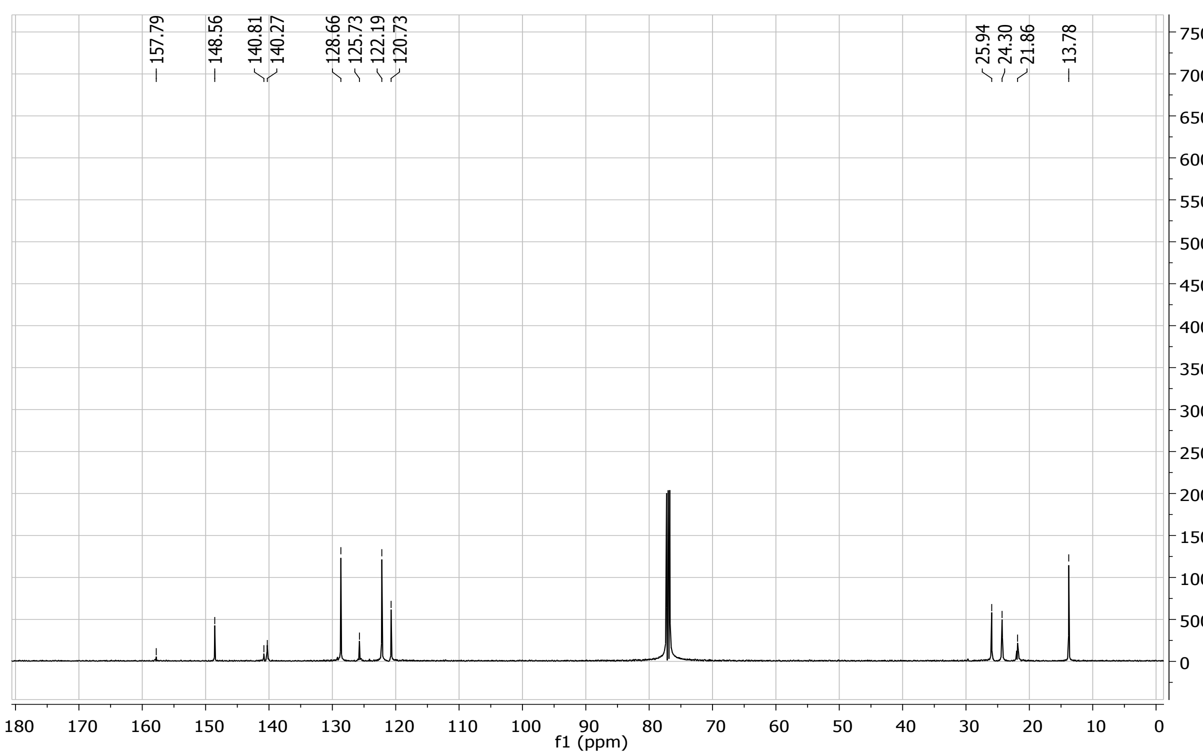


Figure S32.[13]C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TPA)$_2$ (6b)**

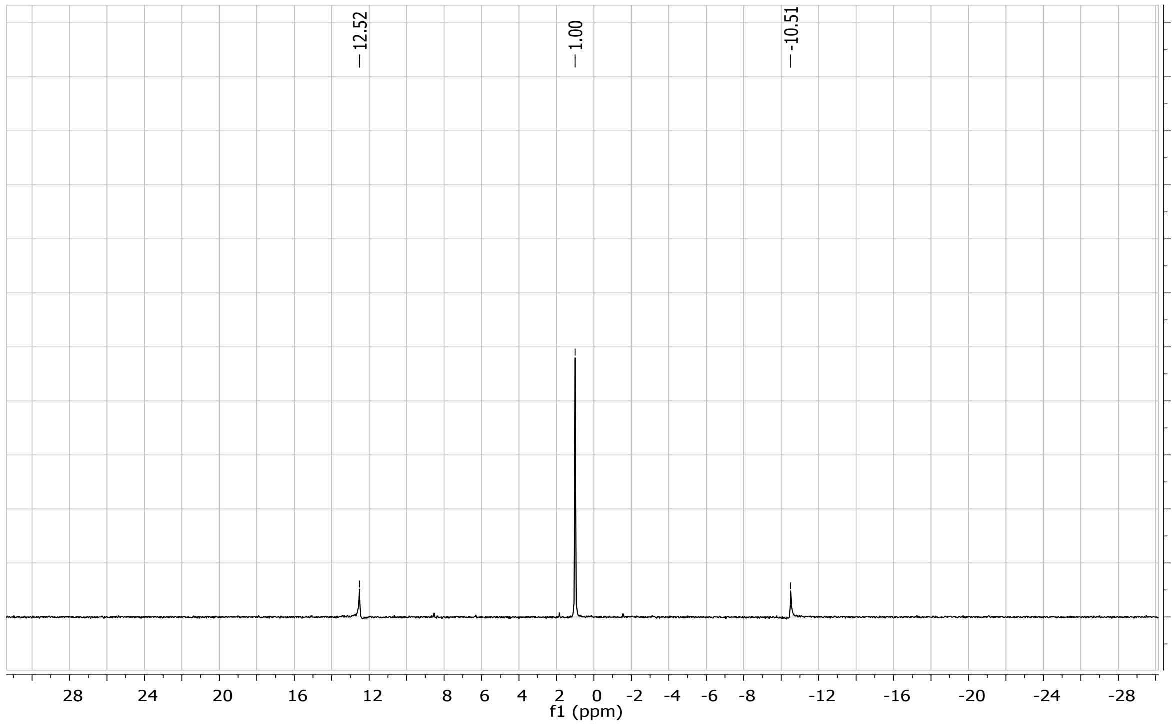


Figure S33.[31]P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TPA)$_2$ (6b)**

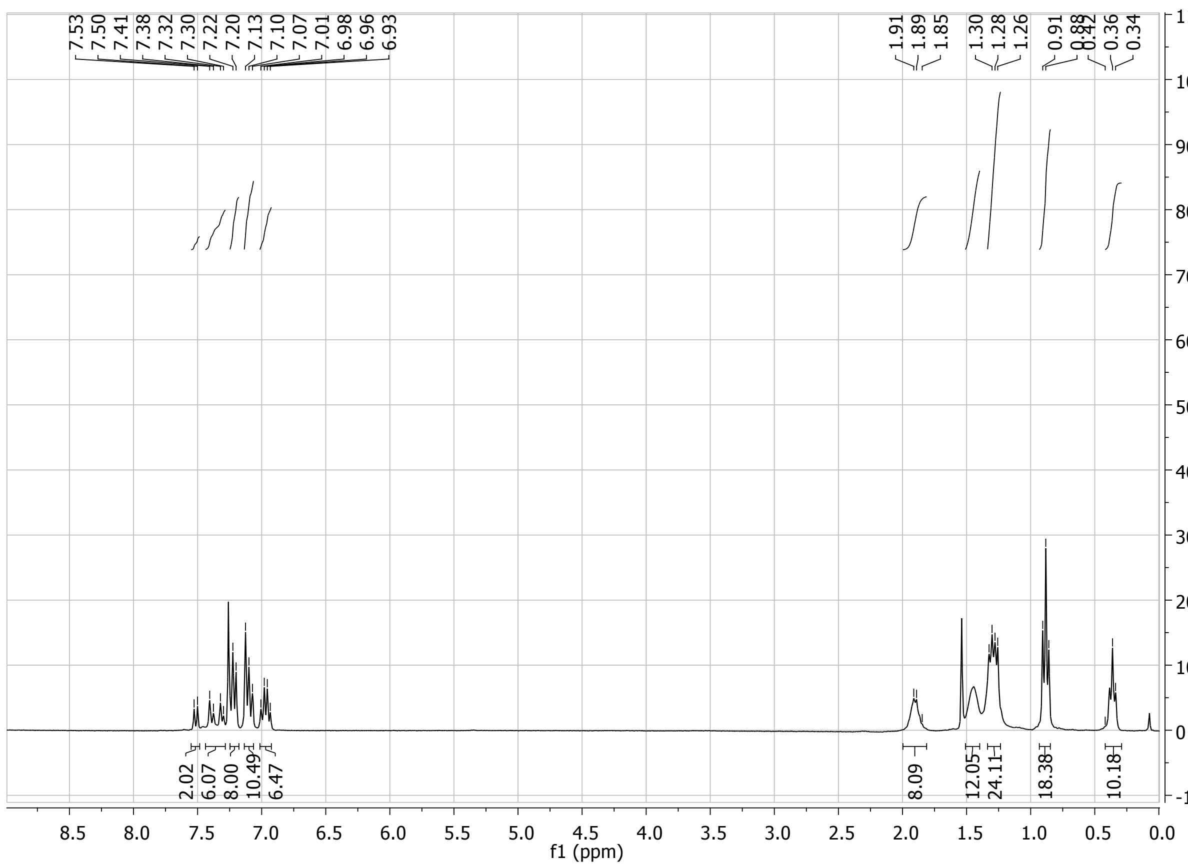


Figure S34.[1]H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(DPAF)$_2$ (7b)**

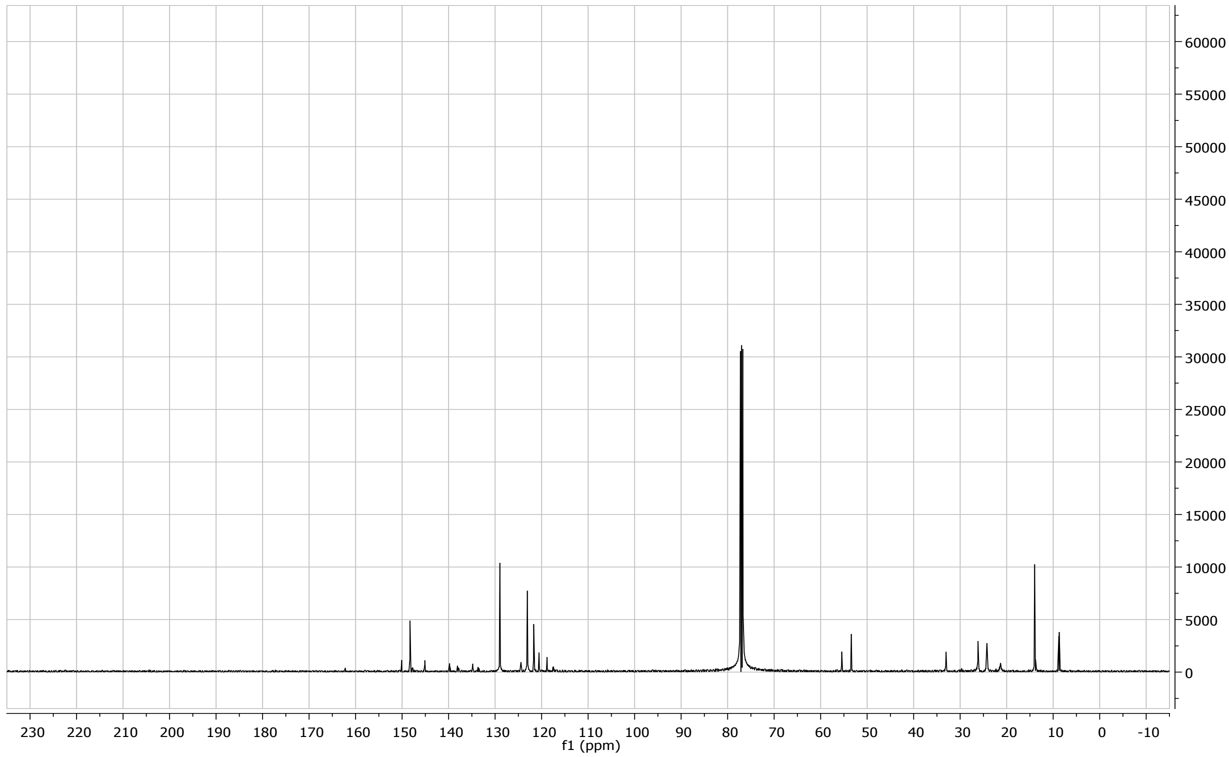


Figure S35.^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(DPAF)$_2$ (7b)**

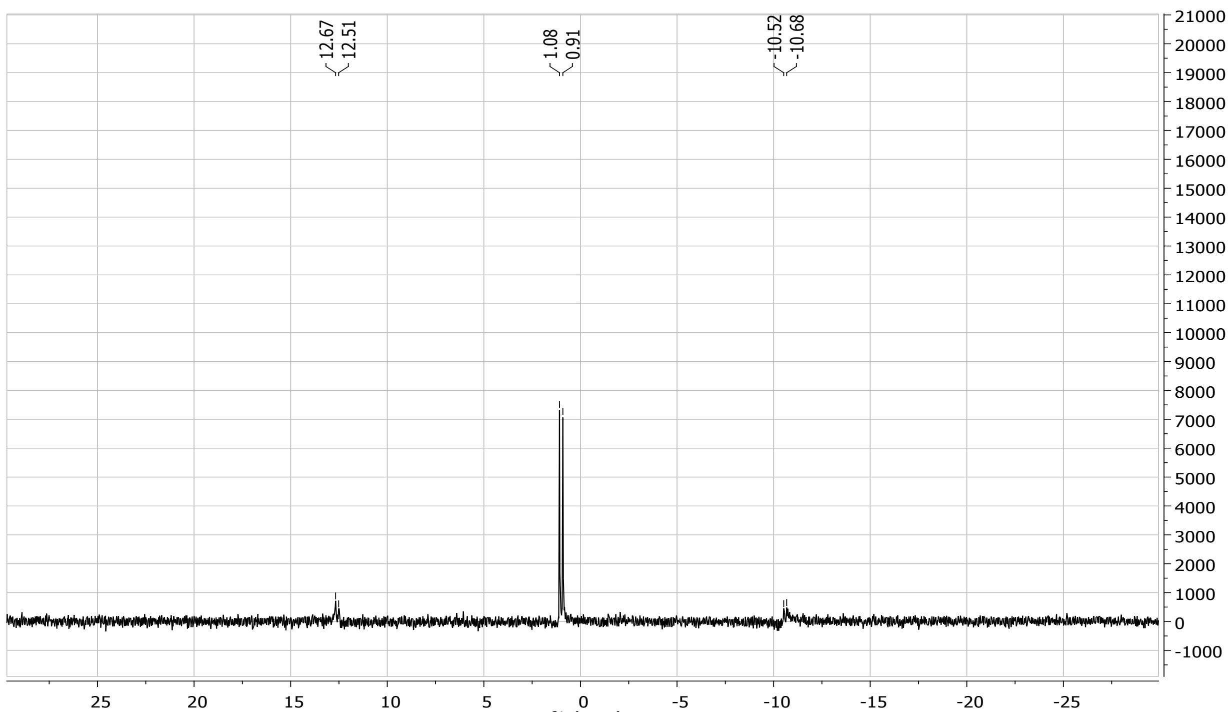


Figure S36. ^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(DPAF)$_2$ (7b)**

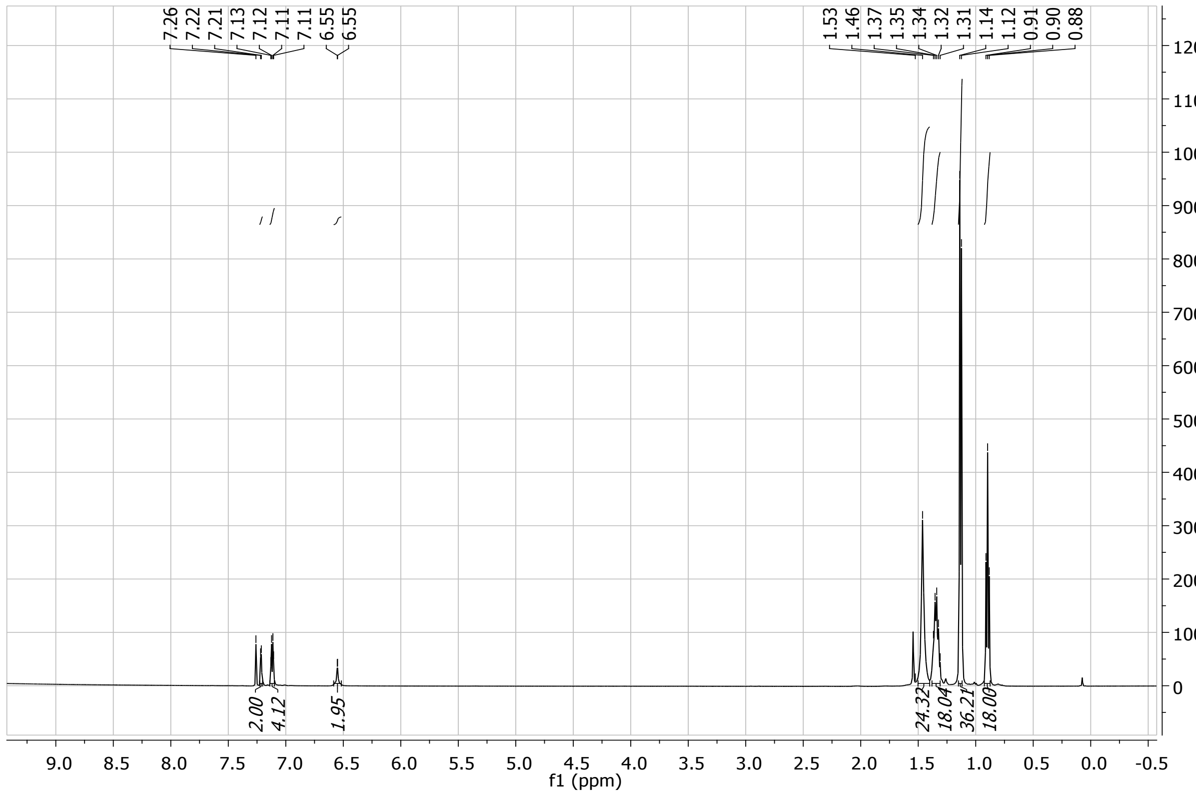


Figure S37.^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TIPSBTh)$_2$ (9b)**

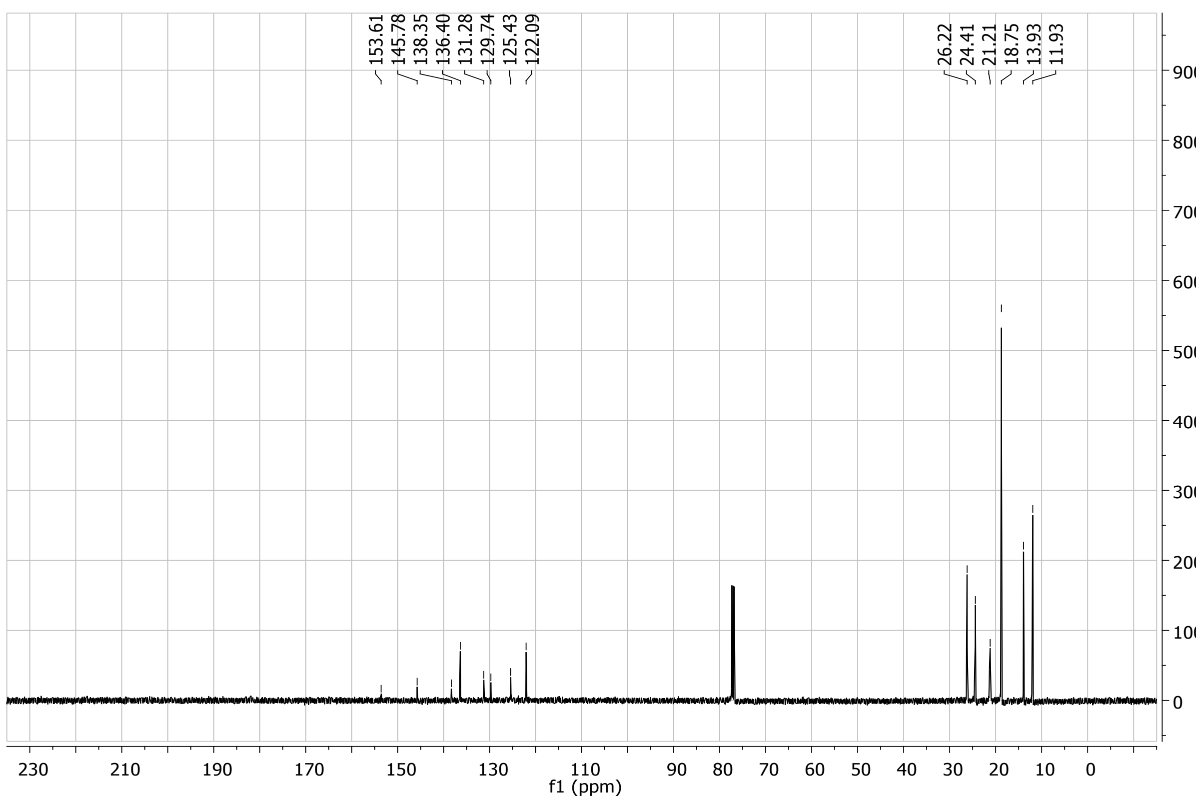


Figure S38.^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TIPSBTh)$_2$ (9b)**

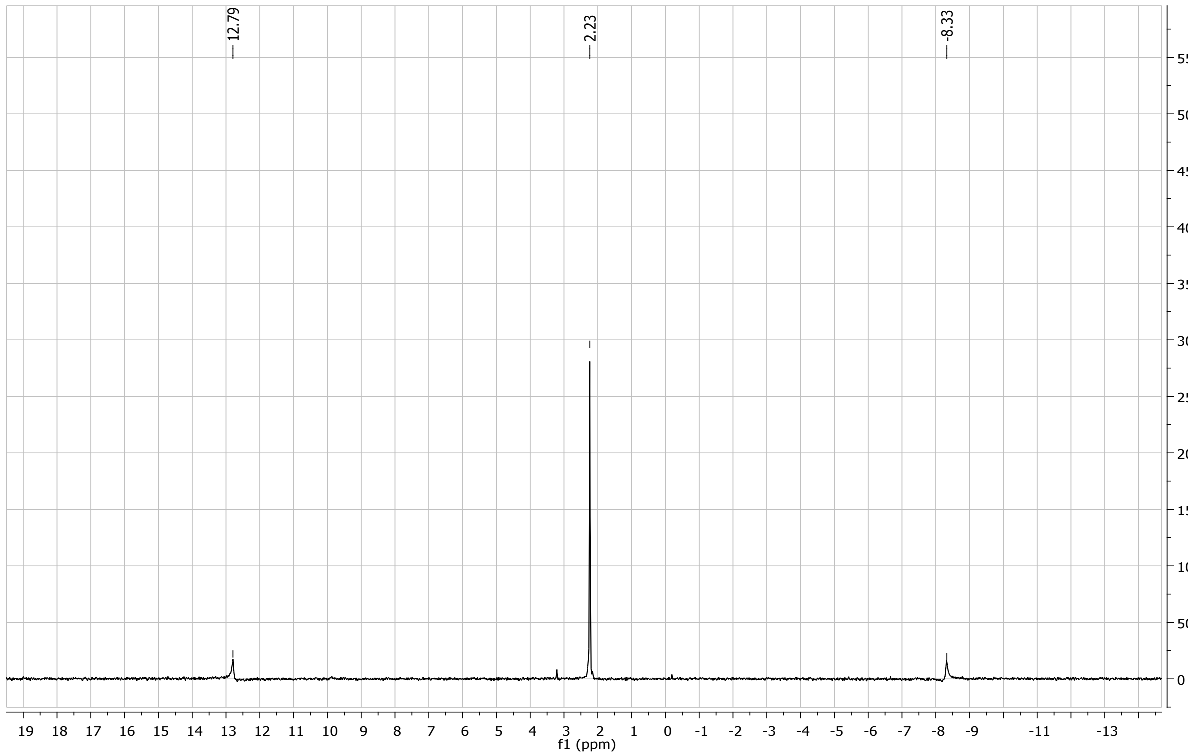


Figure S39.^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TIPSBTh)$_2$ (9b)**

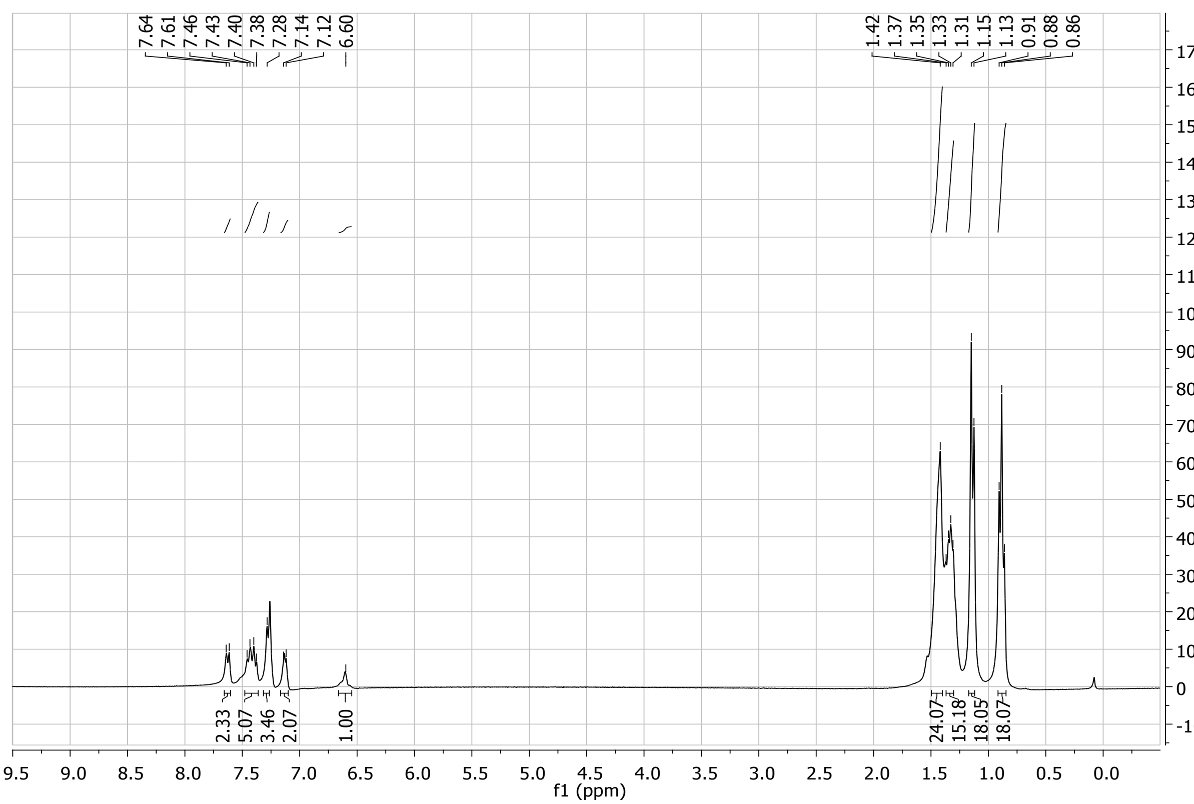


Figure S40.^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(BPh)(TIPSBTh) (10)**

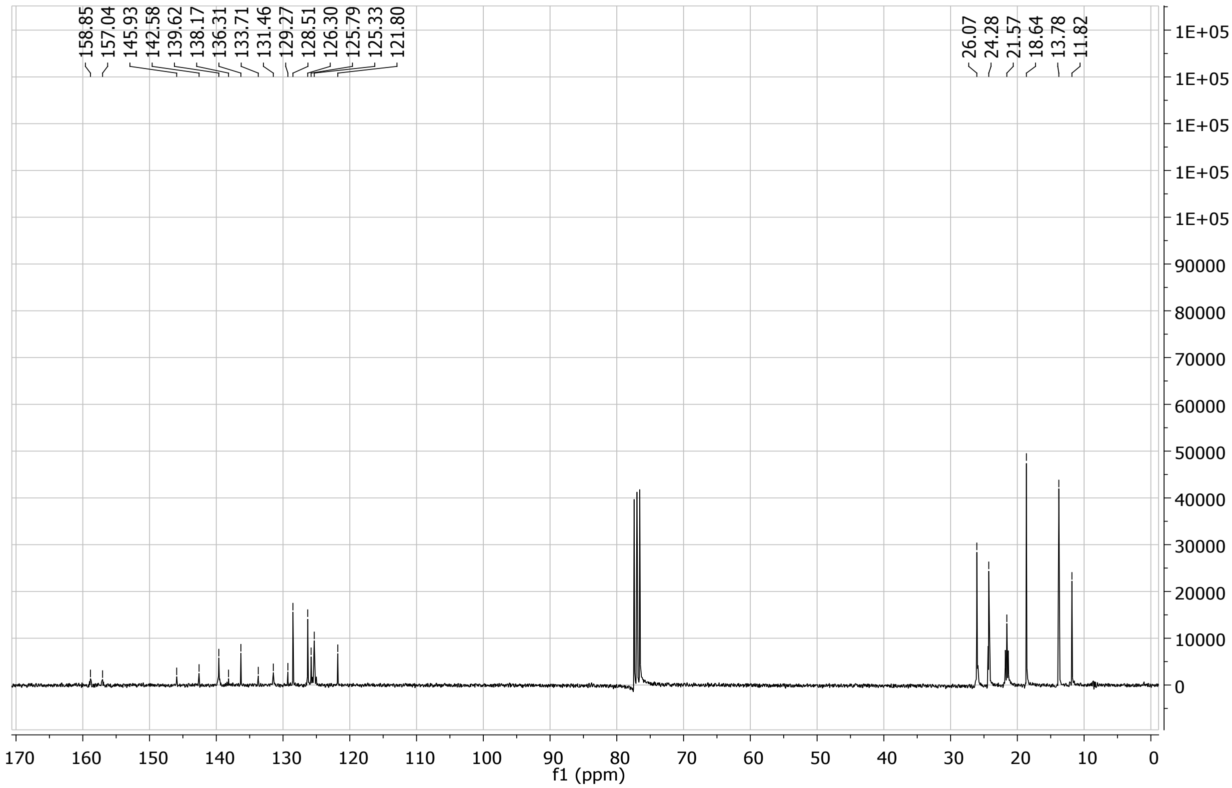


Figure S41. ^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(BPh)(TIPSBTh) (10)**

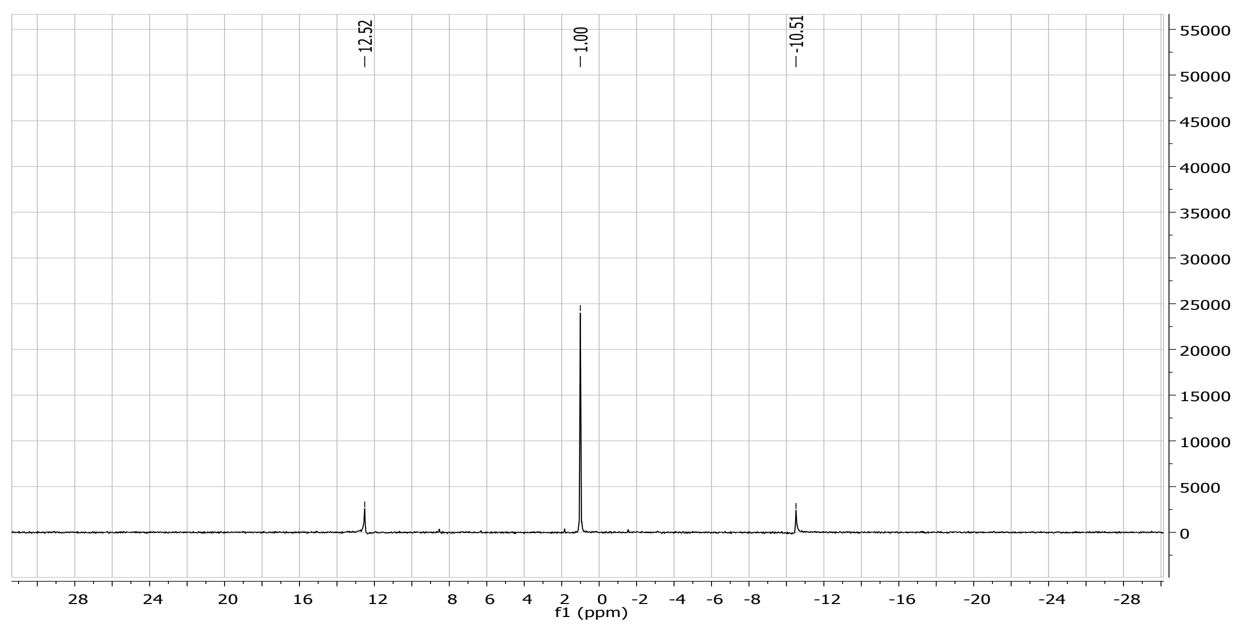


Figure S42. ^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(BPh)(TIPSBTh) (10)**

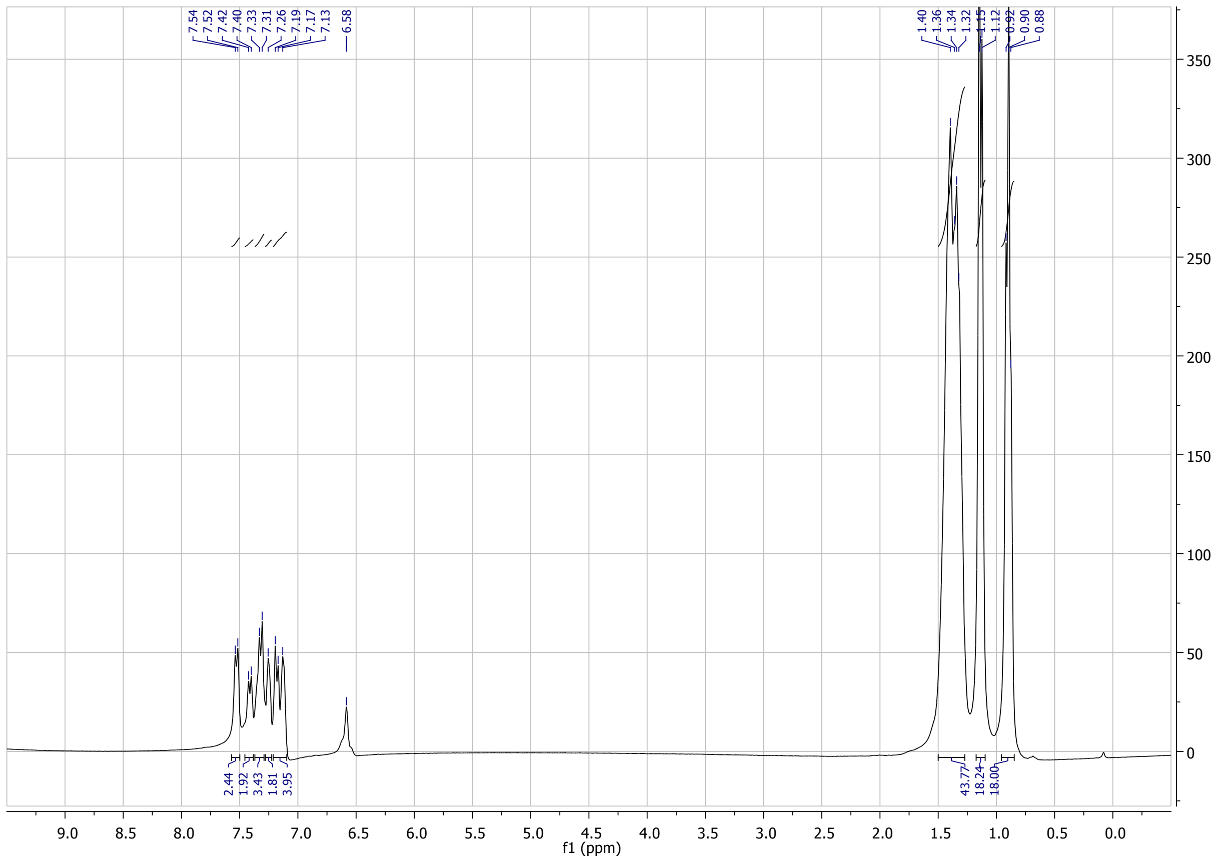


Figure S43. ^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)(TIPSBTh) (11)**

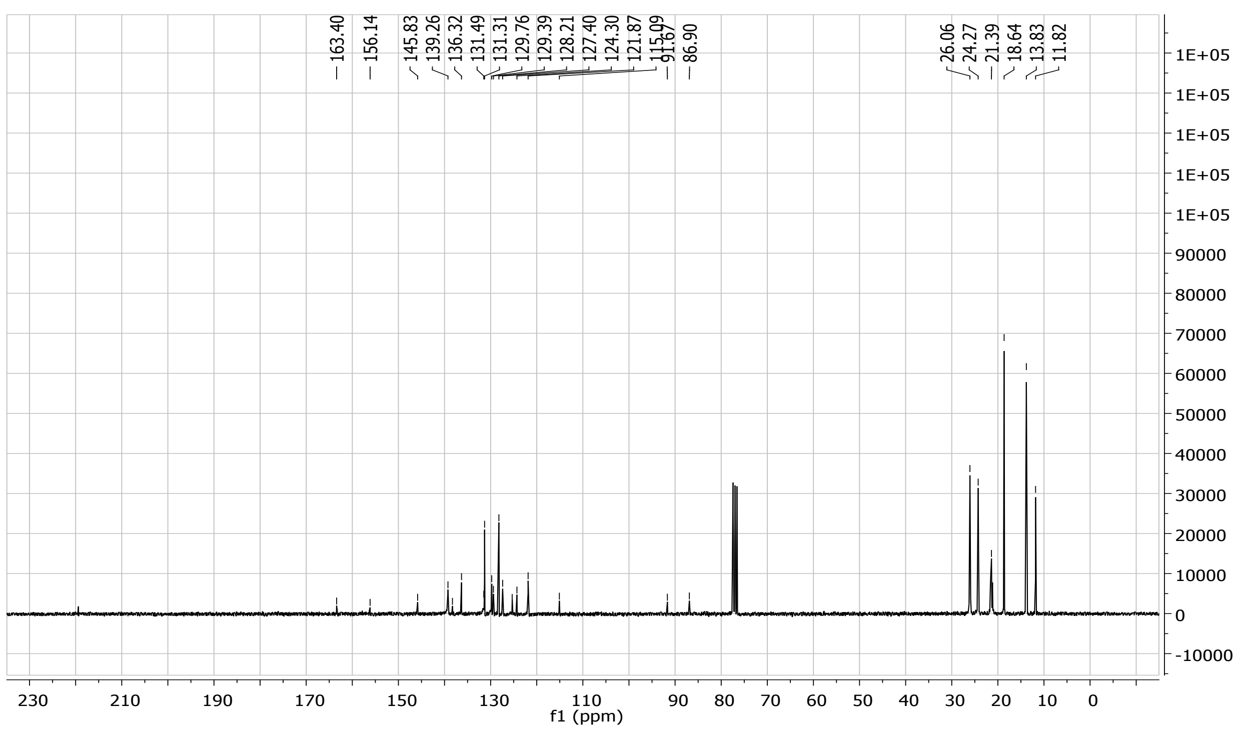


Figure S44.^{13}C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)(TIPSBTh) (11)**

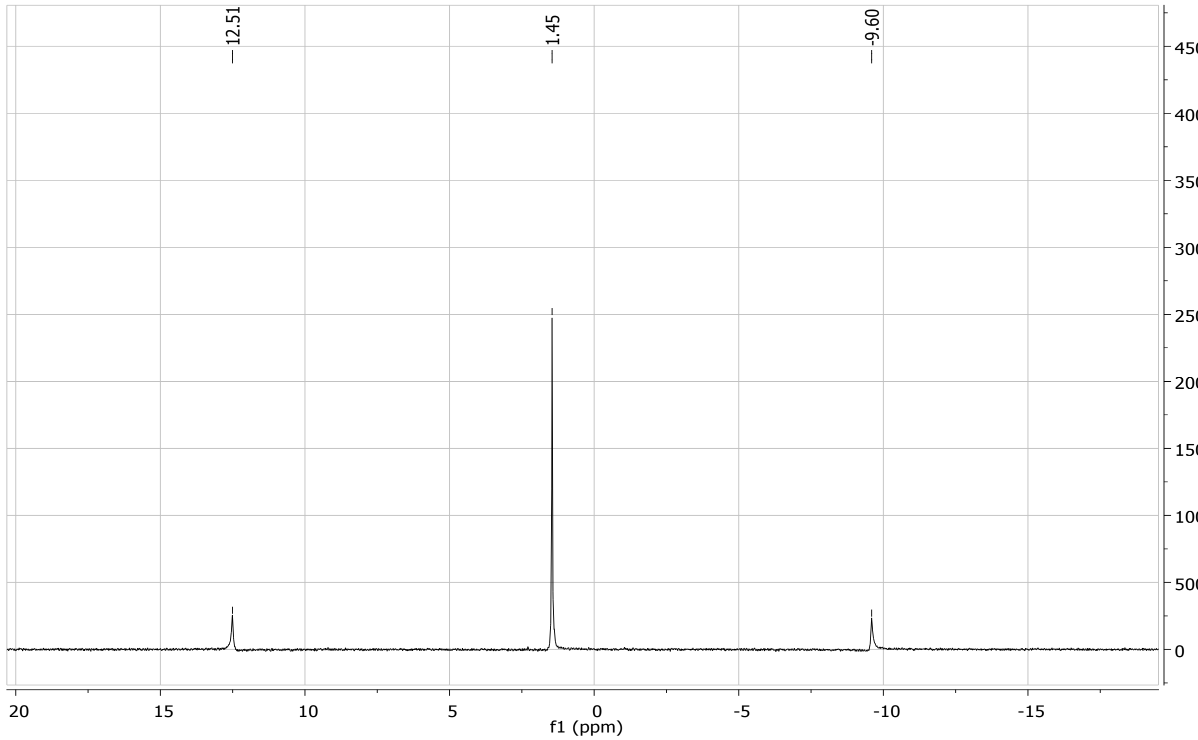


Figure S45.^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(PEP)(TIPSBTh) (11)**

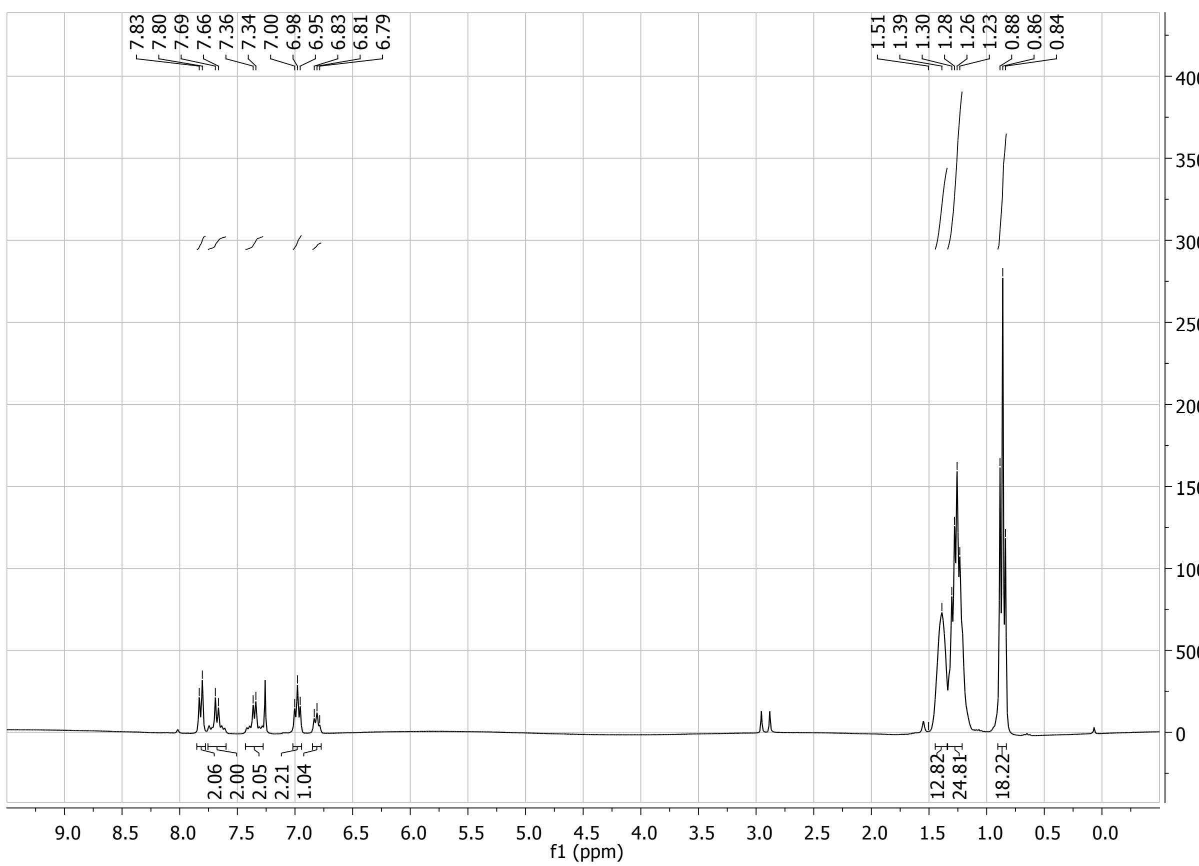


Figure S46.^{1}H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Ph)(p-NO$_2$Ph) (12)**

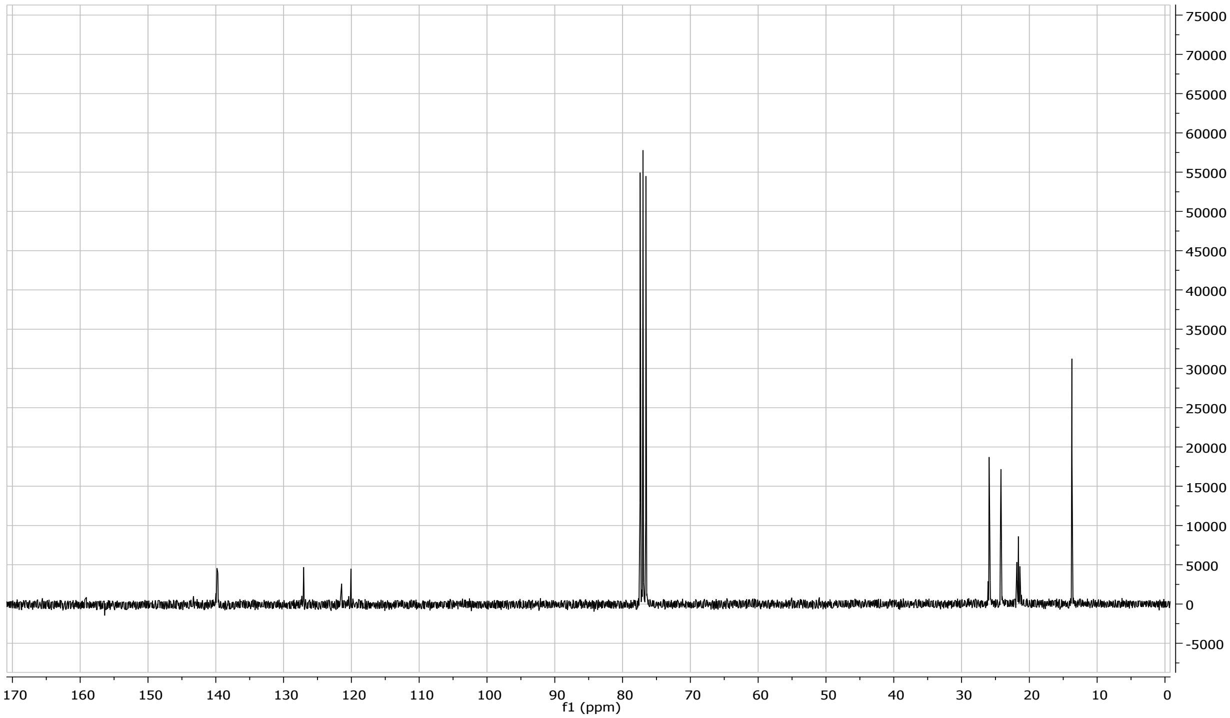


Figure S47.[13]C NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Ph)(p-NO$_2$Ph) (12)**

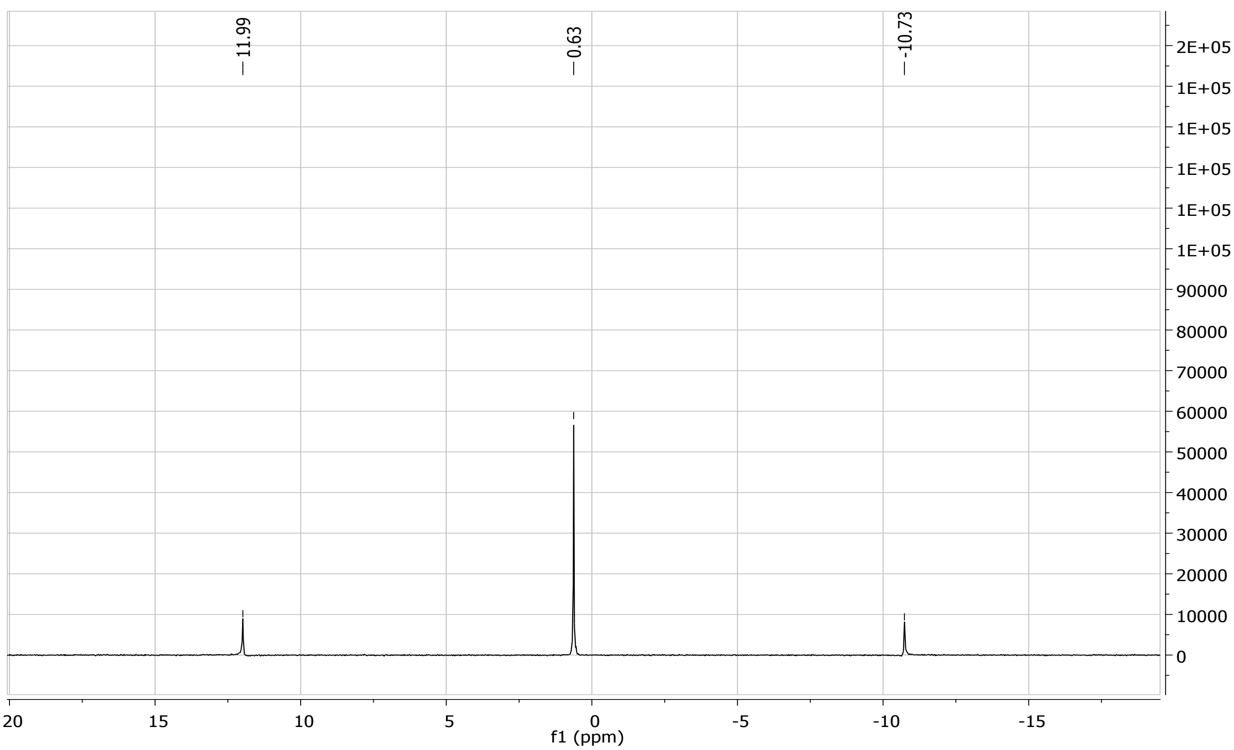


Figure S48.[31]P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(Ph)(p-NO$_2$Ph) (12)**

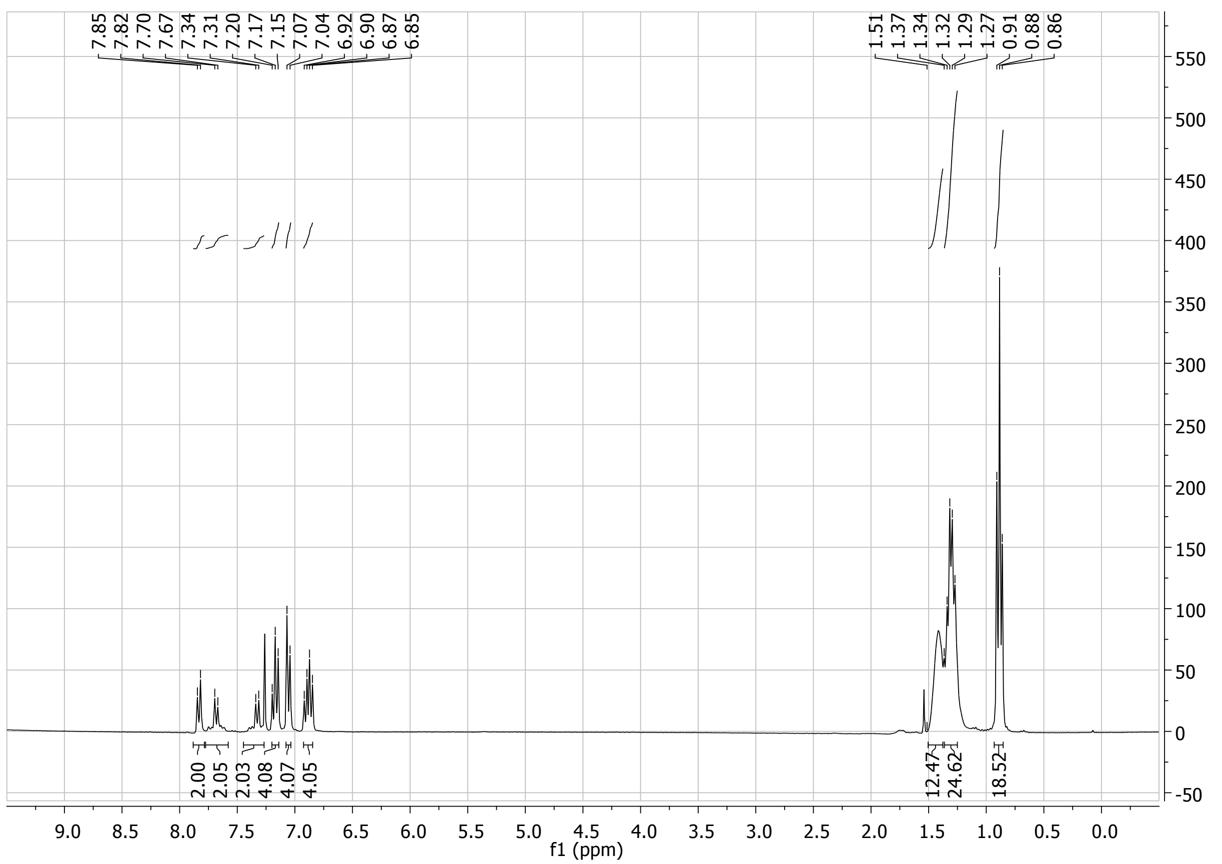


Figure S49. ^{1}H NMR Spectrum of ***trans*-Pt(PBu$_3$)$_2$(TPA)(*p*-NO$_2$Ph) (13)**

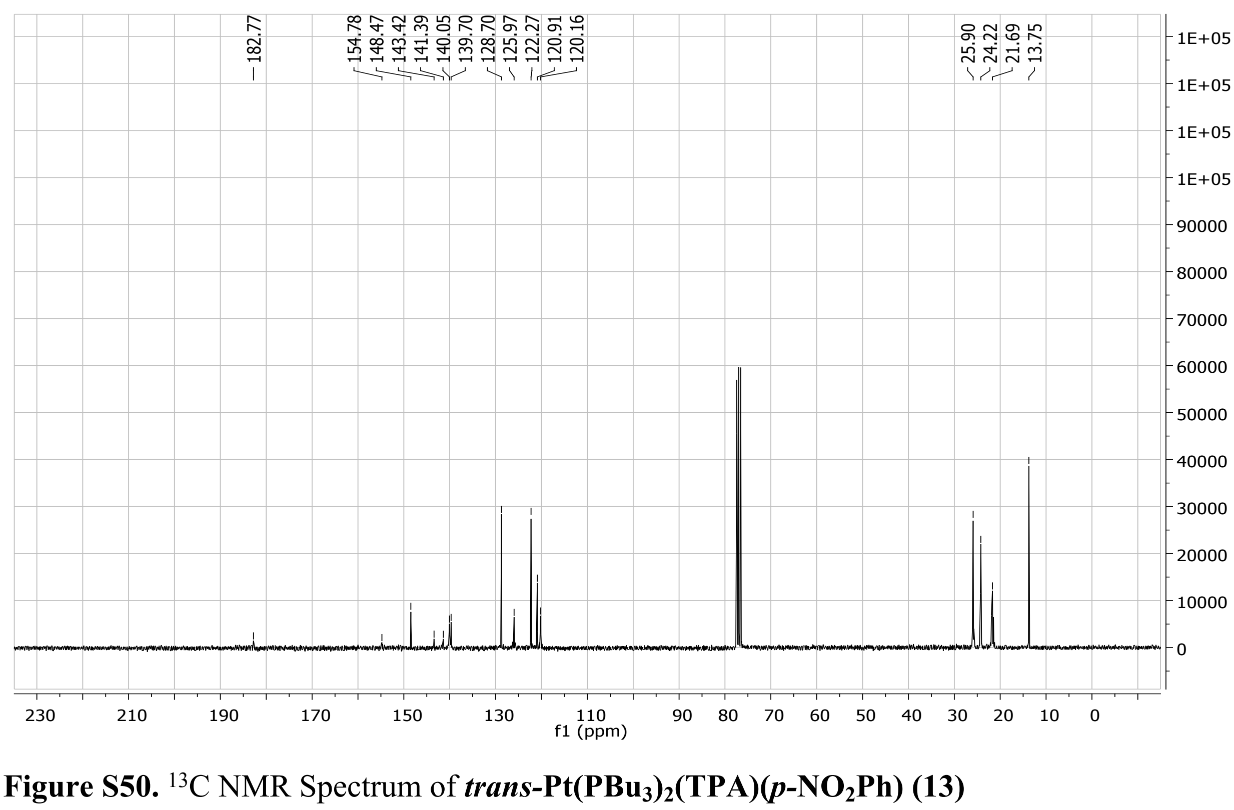


Figure S50. ^{13}C NMR Spectrum of ***trans*-Pt(PBu$_3$)$_2$(TPA)(*p*-NO$_2$Ph) (13)**

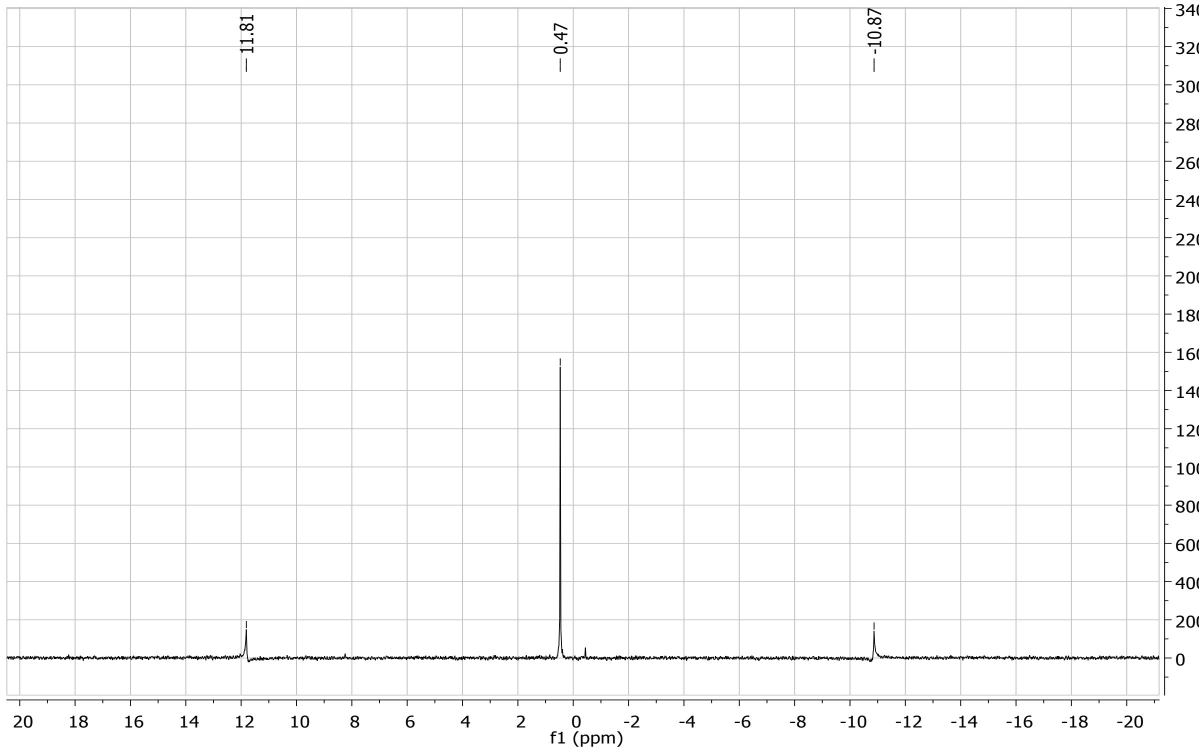


Figure S51. ^{31}P NMR Spectrum of ***trans*-Pt(PBu$_3$)$_2$(TPA)(*p*-NO$_2$Ph) (13)**

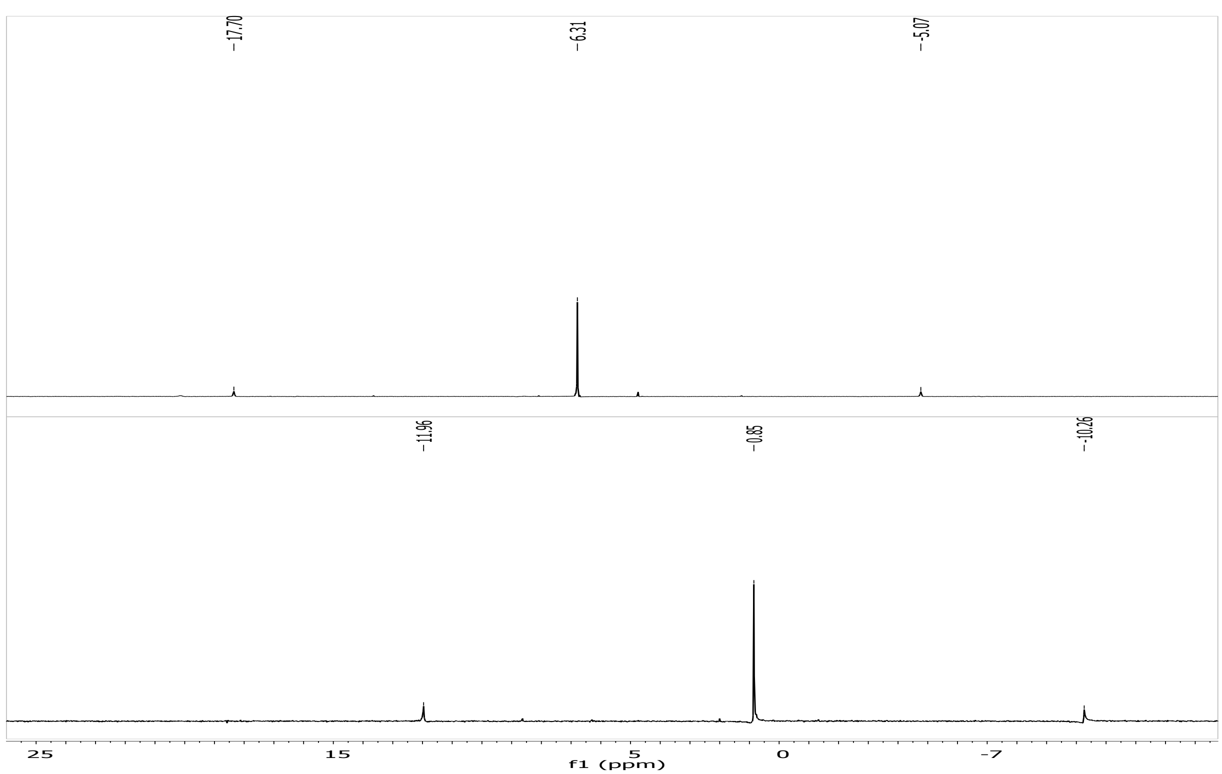


Figure S52. ^{31}P NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TPA)Cl (6a)** (top) and ***trans*-(PBu$_3$)$_2$Pt(TPA)I** (bottom)

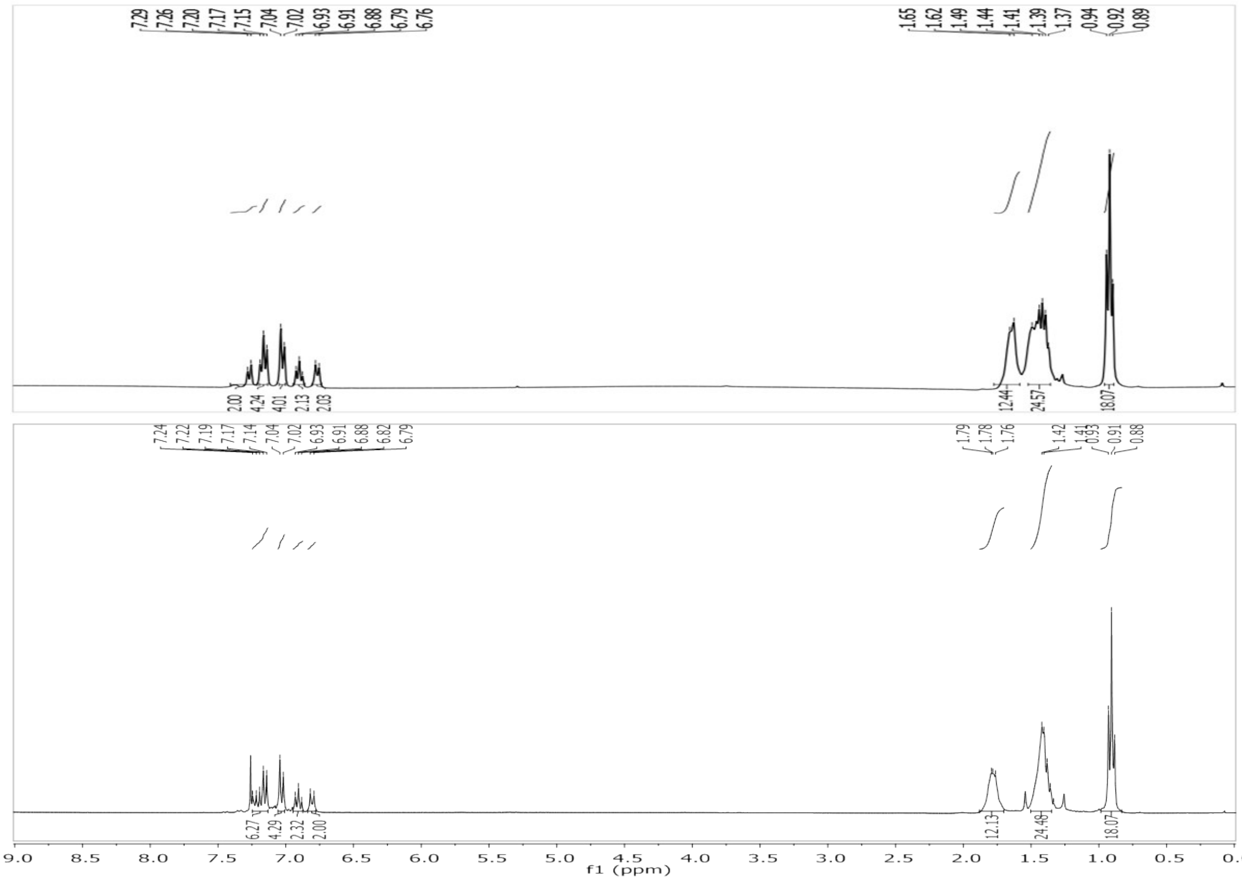


Figure S53. [1]H NMR Spectrum of ***trans*-(PBu$_3$)$_2$Pt(TPA)Cl (6a)** (top) and ***trans*-(PBu$_3$)$_2$Pt(TPA)I** (bottom)

3. Spectra

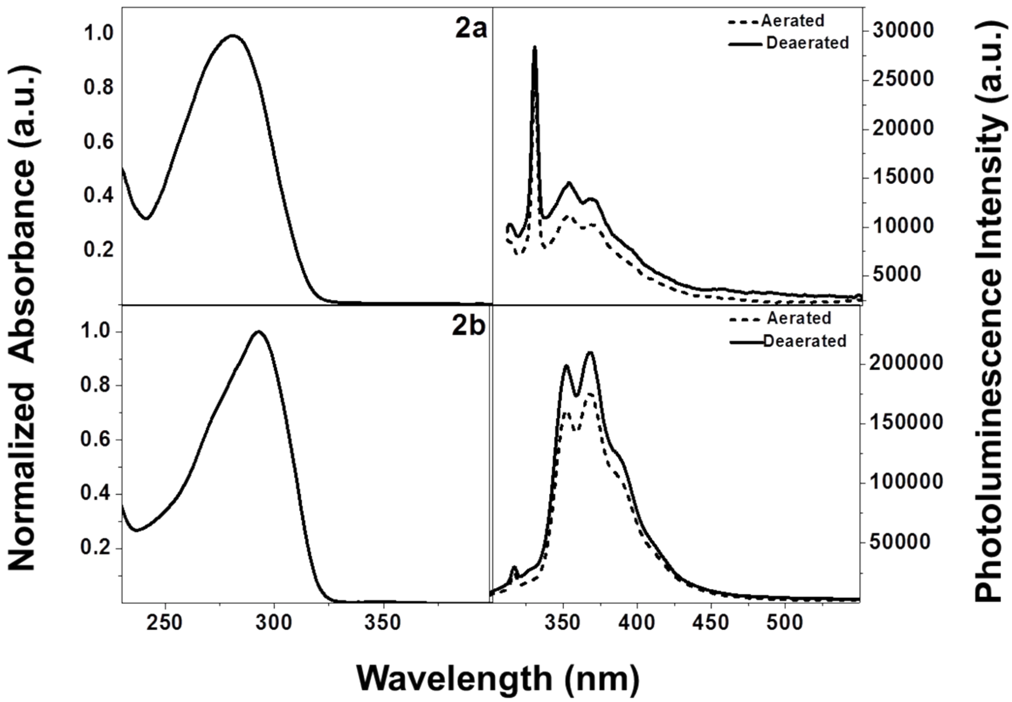


Figure S54. Absorption and Photoluminescence Spectra of **2a** and **2b**

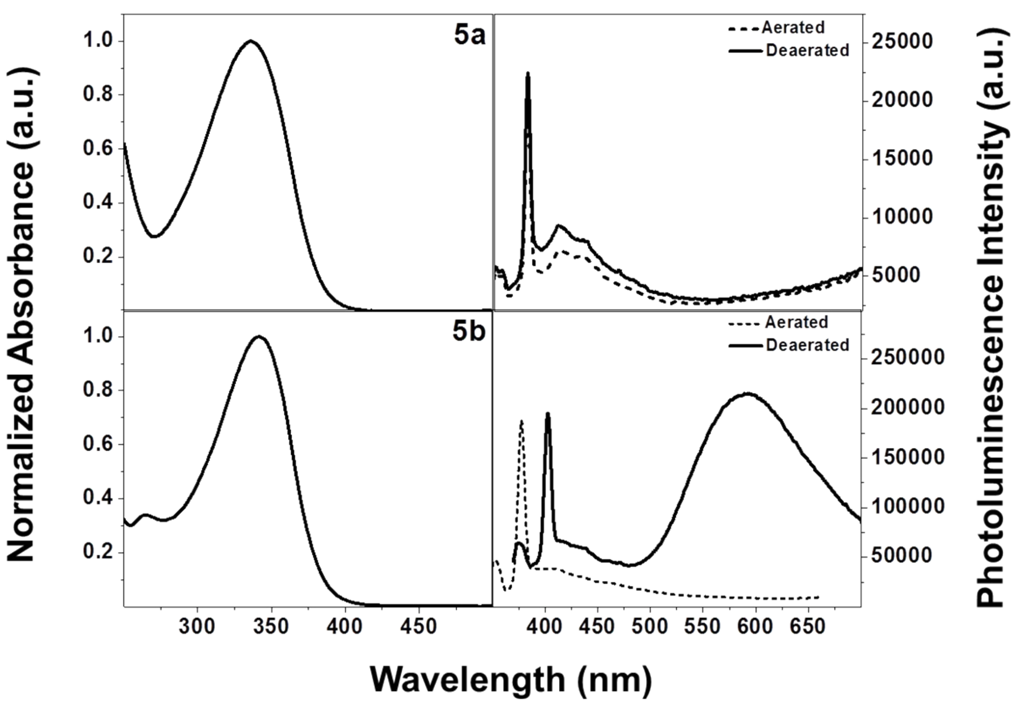


Figure S55. Absorption and Photoluminescence Spectra of **5a** and **5b**

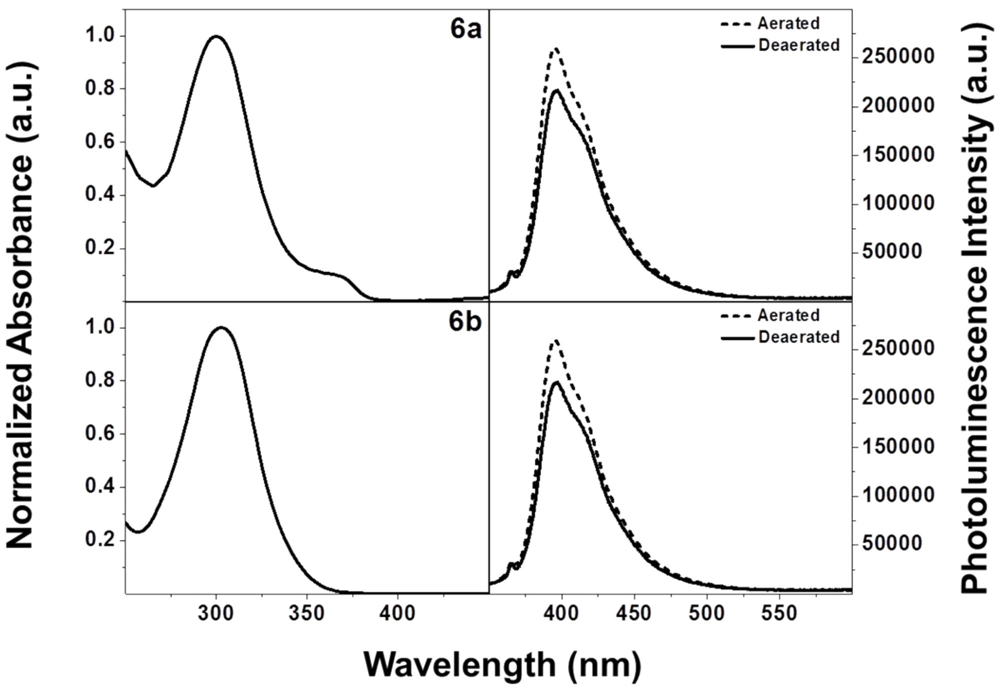


Figure S56. Absorption and Photoluminescence Spectra of **6a** and **6b**

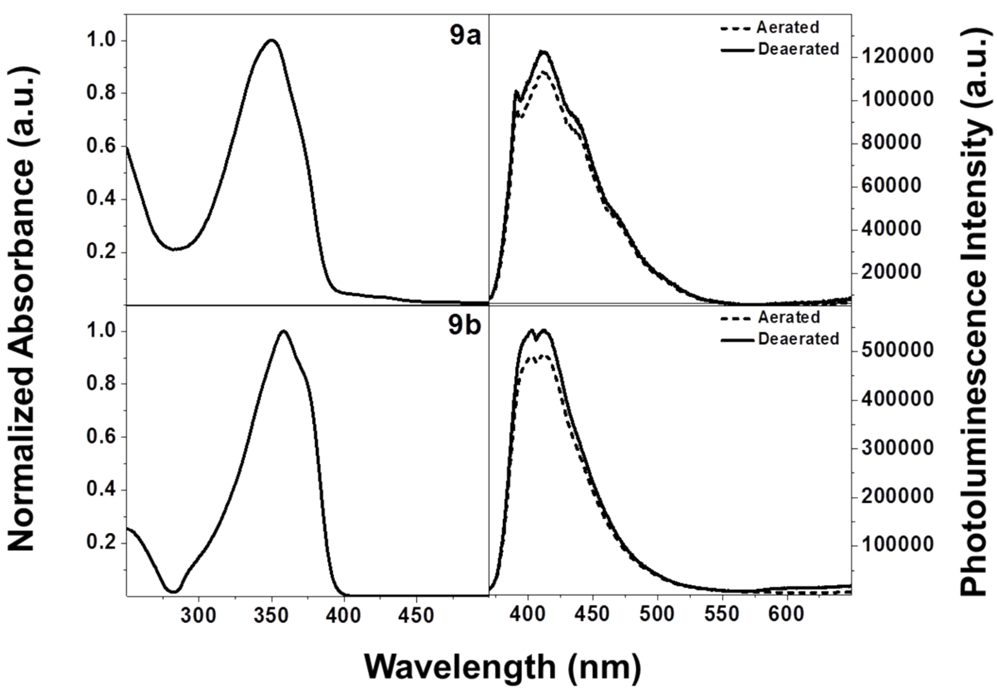


Figure S57. Absorption and Photoluminescence Spectra of **9a** and **9b**

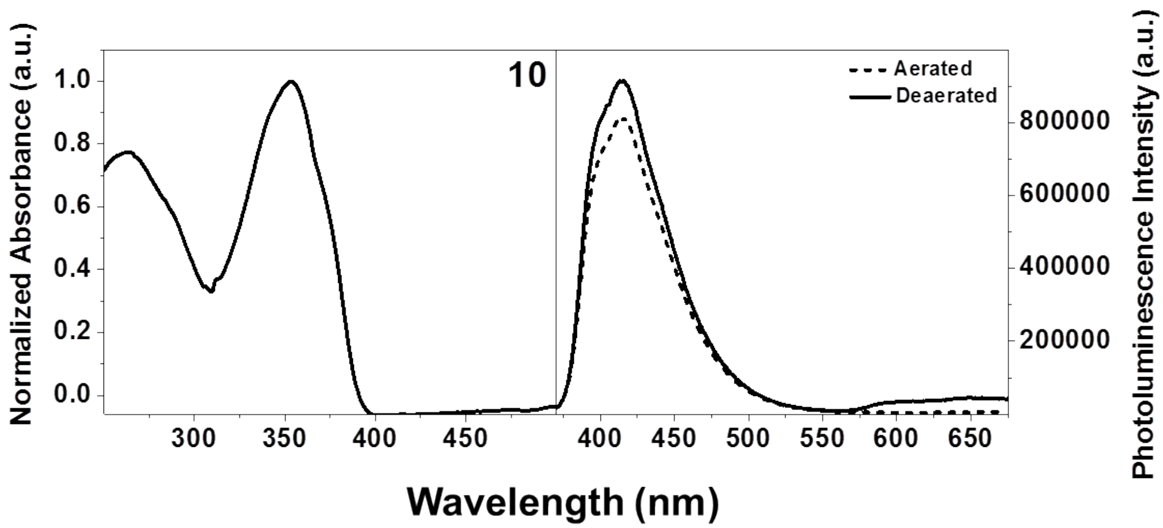


Figure S58. Absorption and Photoluminescence Spectra of **10**

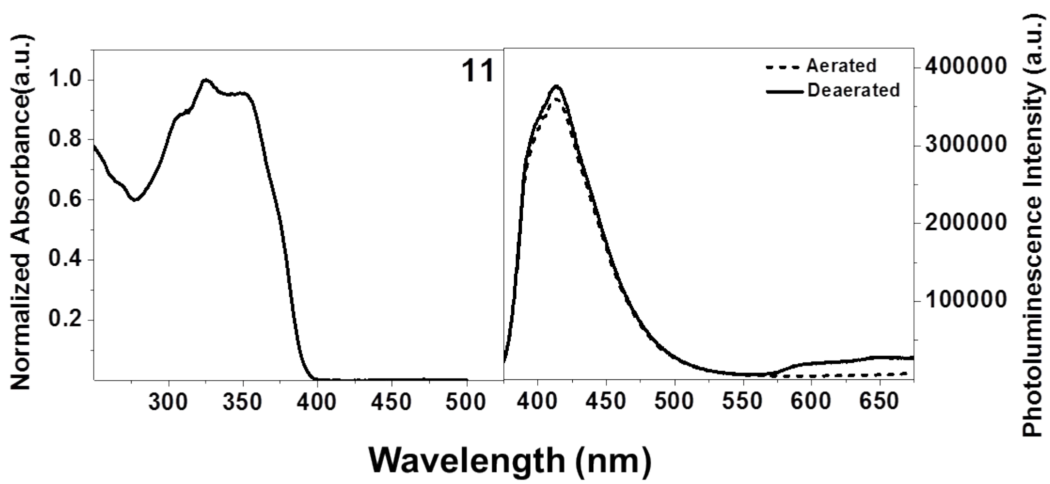


Figure S59. Absorption and Photoluminescence Spectra of **11**

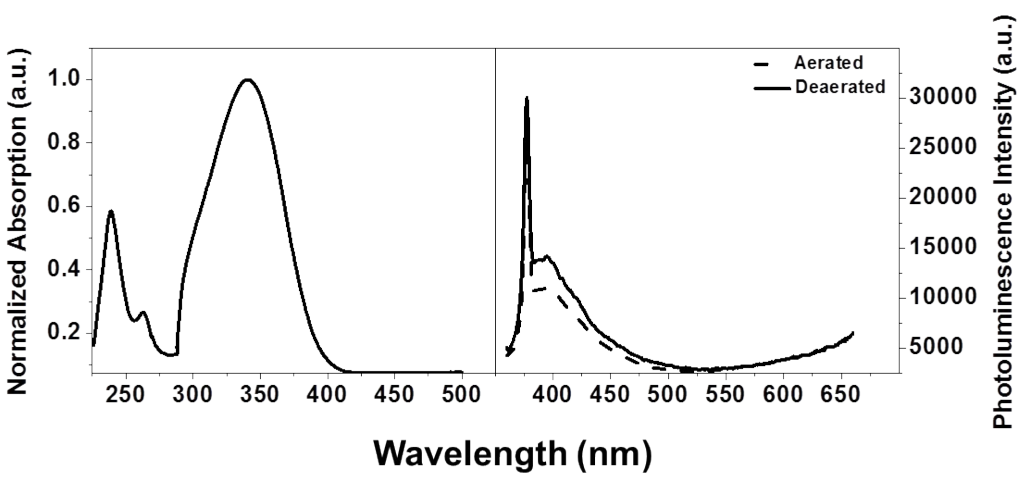


Figure S60. Absorption and Photoluminescence Specta of **12**

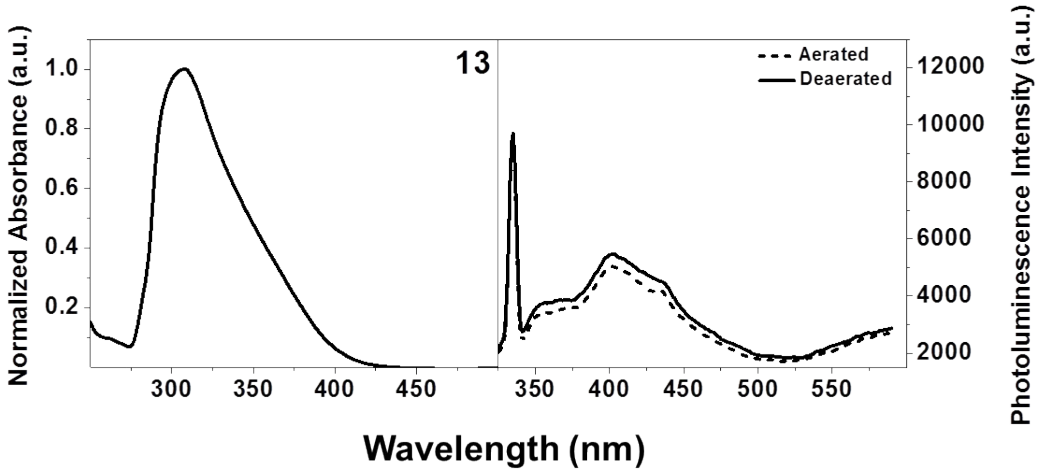


Figure S61. Absorption and Photoluminescence Spectra of **13**

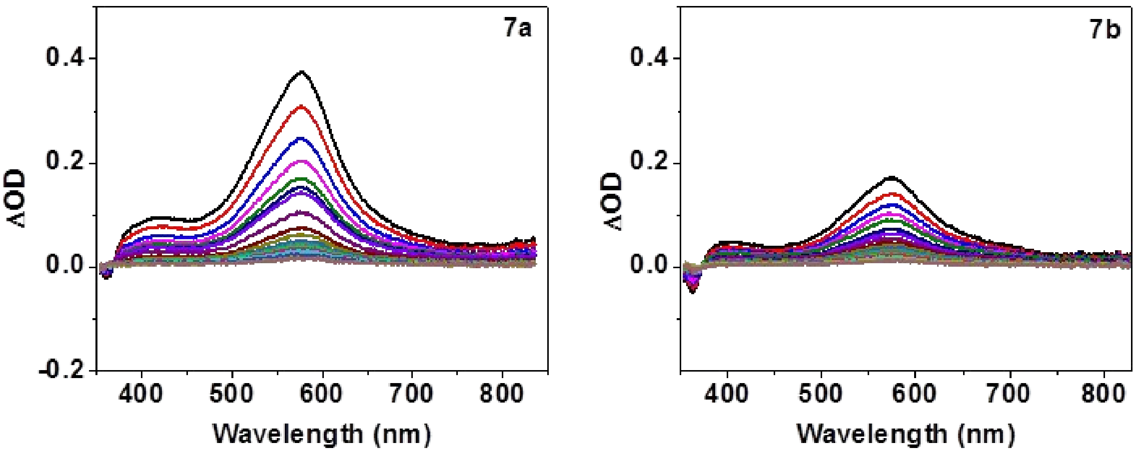


Figure S62. Transient Absorption Spectra of ***trans*-$(PBu_3)_2$Pt(DPAF)Cl (7a)** and ***trans*-$(PBu_3)_2$Pt$(DPAF)_2$ (7b)**.

Experimental Conditions:
7a: O.D = 0.7, Q-Switch:340 μs, Camera Delay: 50 ns, Camera Delay Increment: 250 ns.
7b: O.D. = 0.7, Q-Switch:340 μs, Camera Delay: 50 ns, Camera Delay Increment: 100 ns.

Table S1. Photophysical Data for 7a and 7b

Complex	UV-Vis λ^{max}	ε ($M^{-1}cm^{-1}$)	Fl λ^{max}	Φ^{Fl}(%)	τ^{Fl} (ns)	λ^{max} T^1-T^n (nm)	τ T^1-T^n (μs)
7a	337	20000	380	1.3	2.66	576	1.28
7b	355	95000	378	5	1.34	576	0.58

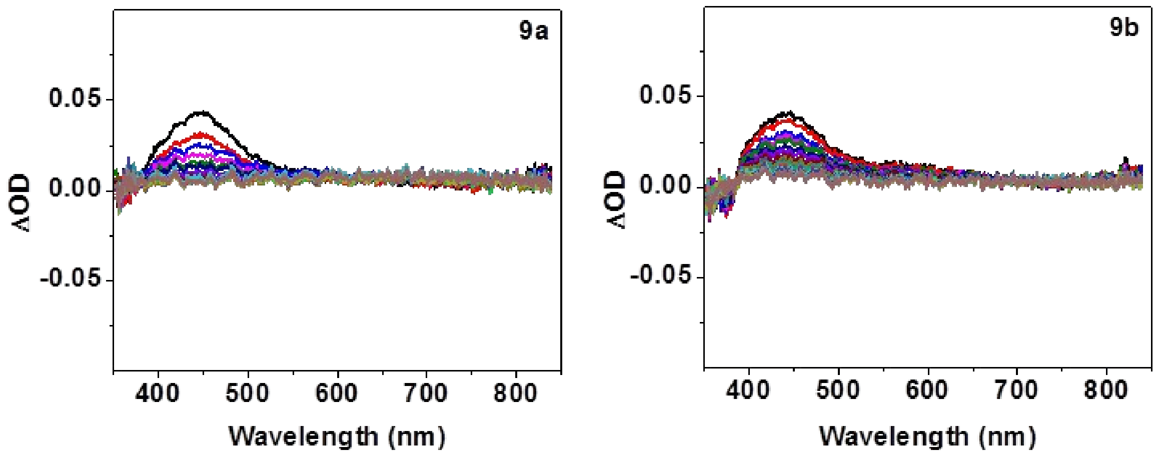


Figure S63. Transient Absorption Spectra of ***trans*-$(PBu_3)_2$Pt(TIPSBTh)Cl (9a)** and ***trans*-$(PBu_3)_2$Pt$(TIPSBTh)_2$ (9b)**.

Experimental Conditions:
9a: O.D. = 0.7, Q-Switch:360 μs, Camera Delay: 50 ns, Camera Delay Increment: 750 ns.
9b: O.D. = 0.7, Q-Switch:360 μs, Camera Delay: 50 ns, Camera Delay Increment: 500 ns.

Table S2. Photophysical Data for 9a and 9b

Complex	UV-Vis λ^{max}	ε ($M^{-1}cm^{-1}$)	Fl λ^{max}	Φ^{Fl}(%)	τ^{Fl}(ns)	λ^{max} T^1-T^n (nm)	τ T^1-T^n (μs)
9a	350	11800	412	0.9	0.32 (86%) 5.53 (14%)	445	2.33
9b	358	77700	407	3.6	0.25 (90%) 4.37 (10%)	445	3.40

4. References

1. Morris, J. V.; Mahaney, M. A.; Huber, J. R., Fluorescence Quantum Yield Determinations - 9,10-Diphenylanthracene as a Reference-Standard in Different Solvents. *J Phys Chem* **1976,** *80* (9), 969-974.
2. Kauffman, G. B.; Teter, L. A., Cis- and Trans-Dichlorobis(Tri-Normal-Butylphosphine)Platinum(II). *Inorg Syn* **1963,** *7*, 245-249.
3. Huang, C. H.; Liang, T.; Harada, S.; Lee, E.; Ritter, T., Silver-Mediated Trifluoromethoxylation of Aryl Stannanes and Arylboronic Acids. *J Am Chem Soc* **2011,** *133* (34), 13308-13310.
4. Maya, F.; Tour, J. M., Synthesis of terphenyl oligomers as molecular electronic device candidates. *Tetrahedron* **2004,** *60* (1), 81-92.
5. Weisemann, C.; Schmidtberg, G.; Brune, H. A., Synthesis of Substituted Trimethyl(Naphthyl)Stannanes and Tri(N-Butyl)(Naphthyl)Stannanes. *J Organomet Chem* **1989,** *361* (3), 299-307.
6. Mee, S. P. H.; Lee, V.; Baldwin, J. E., Significant enhancement of the Stille reaction with a new combination of reagents-copper(I) iodide with cesium fluoride. *Chem-Eur J* **2005,** *11* (11), 3294-3308.
7. Yang, M.; Chen, X. W.; Zou, Y. P.; Pan, C. Y.; Liu, B.; Zhong, H., A solution-processable D-A-D small molecule based on isoindigo for organic solar cells. *J Mater Sci* **2013,** *48* (3), 1014-1020.
8. Reinhardt, B. A.; Brott, L. L.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L. X.; He, G. S.; Prasad, P. N., Highly active two-photon dyes: Design, synthesis, and characterization toward application. *Chem Mater* **1998,** *10* (7), 1863-1874.
9. Henssler, J. T.; Zhang, X. N.; Matzger, A. J., Thiophene/Thieno[3,2-b]thiophene Co-oligomers: Fused-Ring Analogues of Sexithiophene. *J Org Chem* **2009,** *74* (23), 9112-9119.