Electronic Supplementary Information

# The stability of group 10 metal POCOP pincer complexes: decomposition/reconstruction pathways of the pincer backbone

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**Synthesis and characterization of [2,6-($^i$Pr$_2$PO)$_2$C$_6$H$_3$]PtI**

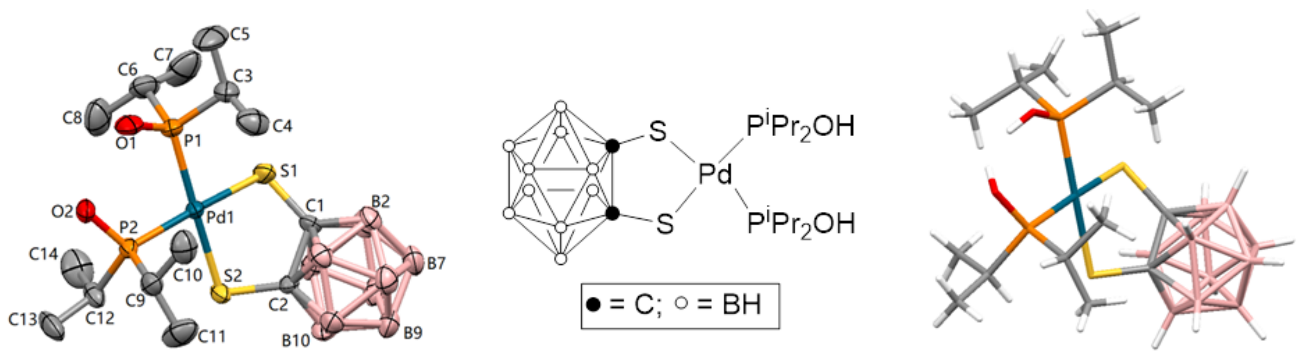
A mixture of [2,6-($^i$Pr$_2$PO)$_2$C$_6$H$_3$]PtCl (0.25 mmol), THF (5 mL), methanol (5 mL) and NaI (1 mmol) was stirred at room temperature in a flask for 6 h. Solvents in the reaction mixture were then removed under vacuum and the resulting residue was extracted with toluene. Removal of toluene from the combined extractions followed by washing with hexanes produced [2,6-($^i$Pr$_2$PO)$_2$C$_6$H$_3$]PtI as a light yellow solid (80%). $^1$H NMR (600 MHz, CDCl$_3$, $\delta$): 7.01 (t, 1H, Ar*H*, $J_{\text{H-H}}$ = 8.1 Hz), 6.58 (d, 2H, Ar*H*, $J_{\text{H-H}}$ = 8.1 Hz), 2.63–2.70 (m, 4H, C*H*(CH$_3$)$_2$), 1.12–1.40 (m, 24H, CH(C*H*$_3$)$_2$). $^{13}$C{$^1$H} NMR (151 MHz, CDCl$_3$, $\delta$): 164.4 (t, Ar*C*, $J_{\text{C-P}}$ = 6.2 Hz), 126.9 (s, Ar*C*), 122.7 (s, Ar*C*), 105.5 (t, Ar*C*, $J_{\text{C-P}}$ = 6.2 Hz), 29.5–29.9 (m, *C*H(CH$_3$)$_2$), 17.7–17.8 (m, CH(*C*H$_3$)$_2$), 16.7 (s, Pt satellites, CH(*C*H$_3$)$_2$, $J_{\text{C-Pt}}$ = 20.7 Hz). $^{31}$P{$^1$H} NMR (243 MHz, CDCl$_3$, $\delta$): 177.3 (s, Pt satellites, $J_{\text{P-Pt}}$ = 2977 Hz).

**Table S1.** Summary of crystal data and structure refinement for complexes **2a**, **2c** and **3b**

| Complex | **2a** | **2c** | **3b** |
|---|---|---|---|
| Empirical formula | $C_{24}H_{36}O_2P_2Ni$ | $C_{24}H_{36}O_2P_2Pt$ | $C_{20}H_{42}B_{10}O_2P_2Pd$ |
| Formula weight | 477.18 | 613.56 | 590.97 |
| Temp, K | 170 | 295 | 294 |
| Crystal system | Monoclinic | Monoclinic | Orthorhombic |
| Space group | P2$_1$/m | P2$_1$/m | Cmce |
| *a*, Å | 8.3415(1) | 8.4272(3) | 13.2661(2) |
| *b*, Å | 16.5817(3) | 16.7958(4) | 15.3835(2) |
| *c*, Å | 9.2895(1) | 9.4851(3) | 28.9916(3) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 112.390(2) | 112.887(4) | 90 |
| $\gamma$ (°) | 90 | 90 | 90 |
| Volume, Å$^3$ | 1188.02(3) | 1236.84(7) | 5916.58(13) |
| Z | 2 | 2 | 8 |
| $d_{calc}$, g cm$^{-3}$ | 1.334 | 1.647 | 1.327 |
| $\lambda$, Å | 1.54184 | 0.71073 | 1.54184 |
| $\mu$, mm$^{-1}$ | 2.577 | 5.819 | 6.194 |
| No. of data collected | 9944 | 11328 | 11829 |
| No. of unique data | 2379 | 3043 | 2976 |
| $R_{int}$ | 0.0355 | 0.0339 | 0.0432 |
| Goodness-of-fit on $F^2$ | 1.104 | 1.061 | 1.071 |
| $R_1$, w$R_2$ ($I > 2\sigma(I)$) | 0.0397, 0.1024 | 0.0292, 0.0539 | 0.0354, 0.0877 |
| $R_1$, w$R_2$ (all data) | 0.0408, 0.1037 | 0.0386, 0.0581 | 0.0377, 0.0889 |

**Table S2.** Summary of crystal data and structure refinement for complexes **3c**, **5a** and **6a**

| Complex | **3c** | **5a** | **6a** |
|---|---|---|---|
| Empirical formula | $C_{20}H_{42}B_{10}O_2P_2Pt$ | $C_{38}H_{72}B_{10}O_4P_4S_2Ni_2$ | $C_{16}H_{48}B_{20}P_2S_2Ni$ |
| Formula weight | 679.66 | 1006.47 | 641.51 |
| Temp, K | 170 | 295 | 150 |
| Crystal system | Orthorhombic | Orthorhombic | Monoclinic |
| Space group | Cmce | Pbcn | $P2_1/c$ |
| $a$, Å | 13.1407(2) | 18.7762(6) | 11.4737(2) |
| $b$, Å | 15.2729(2) | 15.5899(5) | 9.9192(2) |
| $c$, Å | 28.7118(3) | 17.6800(6) | 14.6100(3) |
| $\alpha$ (°) | 90 | 90 | 90 |
| $\beta$ (°) | 90 | 90 | 100.711(2) |
| $\gamma$ (°) | 90 | 90 | 90 |
| Volume, Å$^3$ | 5762.36(13) | 5175.3(3) | 1633.79(6) |
| Z | 8 | 4 | 2 |
| $d_{calc}$, g cm$^{-3}$ | 1.567 | 1.292 | 1.304 |
| $\lambda$, Å | 1.54184 | 1.54184 | 1.54184 |
| $\mu$, mm$^{-1}$ | 10.275 | 0.968 | 3.031 |
| No. of data collected | 12332 | 24457 | 9910 |
| No. of unique data | 2940 | 5072 | 3179 |
| $R_{int}$ | 0.0304 | 0.0408 | 0.0238 |
| Goodness-of-fit on $F^2$ | 1.042 | 1.133 | 1.043 |
| $R_1$, w$R_2$ ($I > 2\sigma(I)$) | 0.0230, 0.0531 | 0.0529, 0.1179 | 0.0257, 0.0631 |
| $R_1$, w$R_2$ (all data) | 0.0266, 0.0553 | 0.0770, 0.1318 | 0.0310, 0.0659 |




Selected bond lengths (Å) and angles (˚): Pd1-S1, 2.379(2); Pd1-S2, 2.3852(19); Pd1-P1, 2.276(2); Pd1-P2, 2.2863(19); P1-O1, 1.575(7); P2-O2, 1.553(6); C1-C2, 1.658(10); P1-Pd1-P2, 93.21(7); P1-Pd1-S1, 89.43(8); S1-Pd1-S2, 87.84(7); P2-Pd1-S2, 89.48(7); S1-Pd1-P2, 177.13(8); S2-Pd1-P1, 176.75(8).

**Fig. S1** Molecular image of Pd(II)($^i$Pr$_2$POH)$_2$(1,2-S$_2$-*o*-carborane)

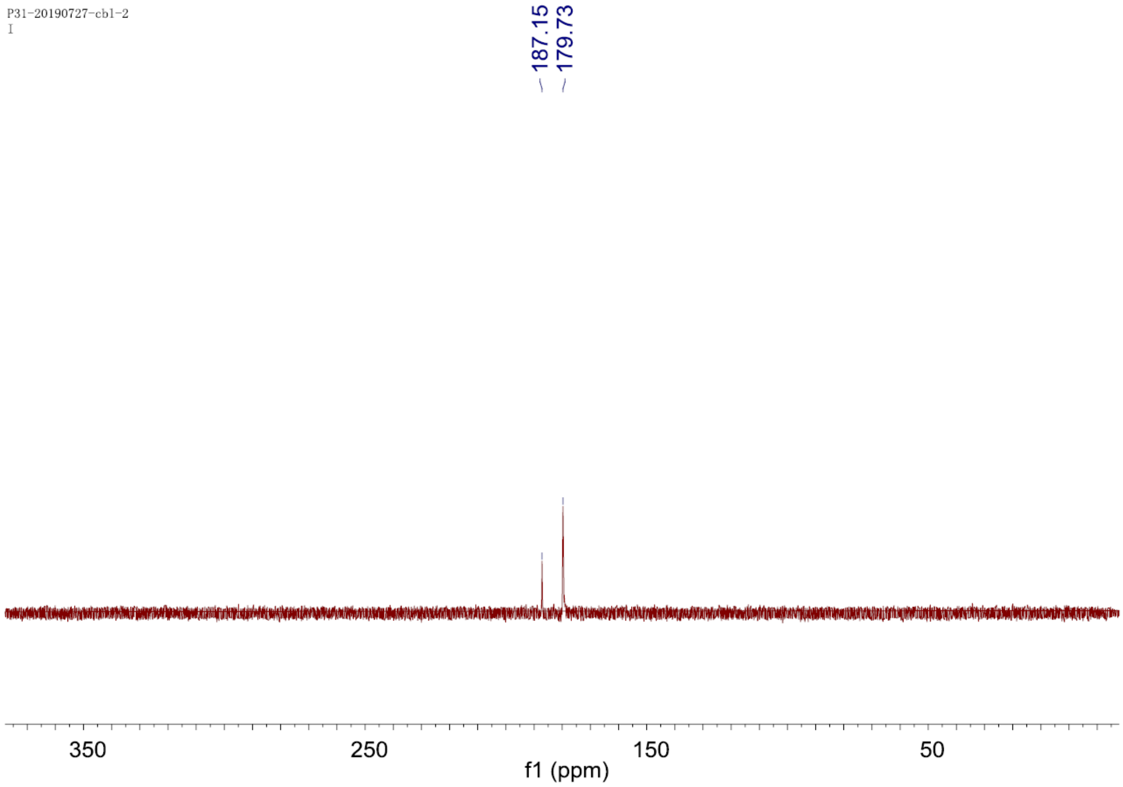



**Fig. S2** $^{31}P\{^1H\}$ NMR spectra of the reaction of **4a** with 1 equiv of $^nBuLi$ in toluene-$d_8$.

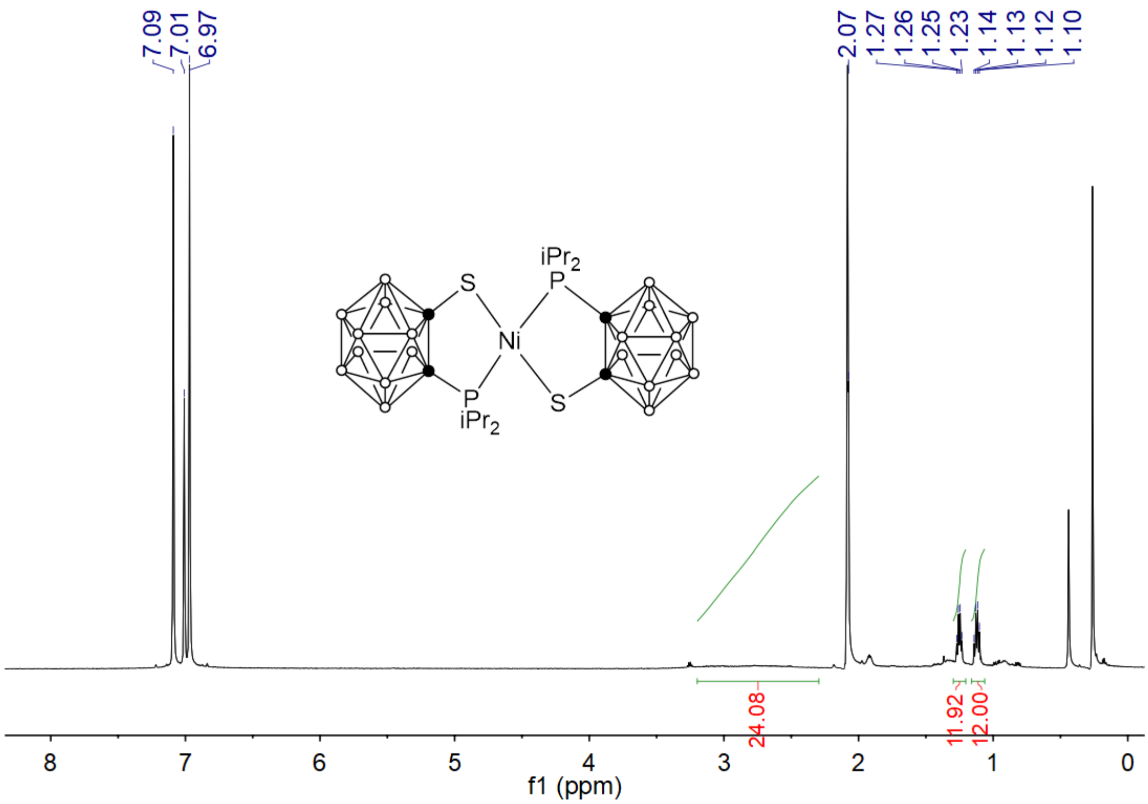



**Fig. S3** $^1H$ NMR spectrum of complex **6a** (600 MHz, toluene-$d_8$)

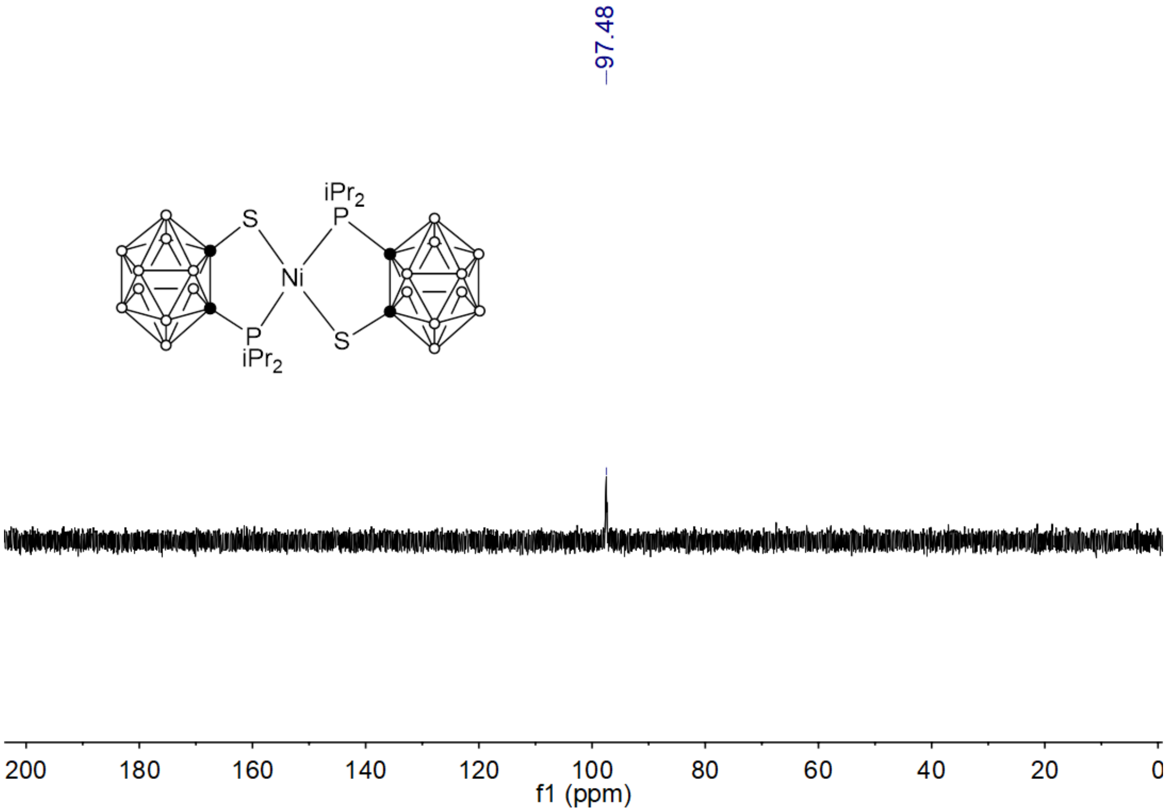



**Fig. S4** $^{31}P\{^1H\}$ NMR spectrum of complex **6a** (243 MHz, toluene-$d_8$)

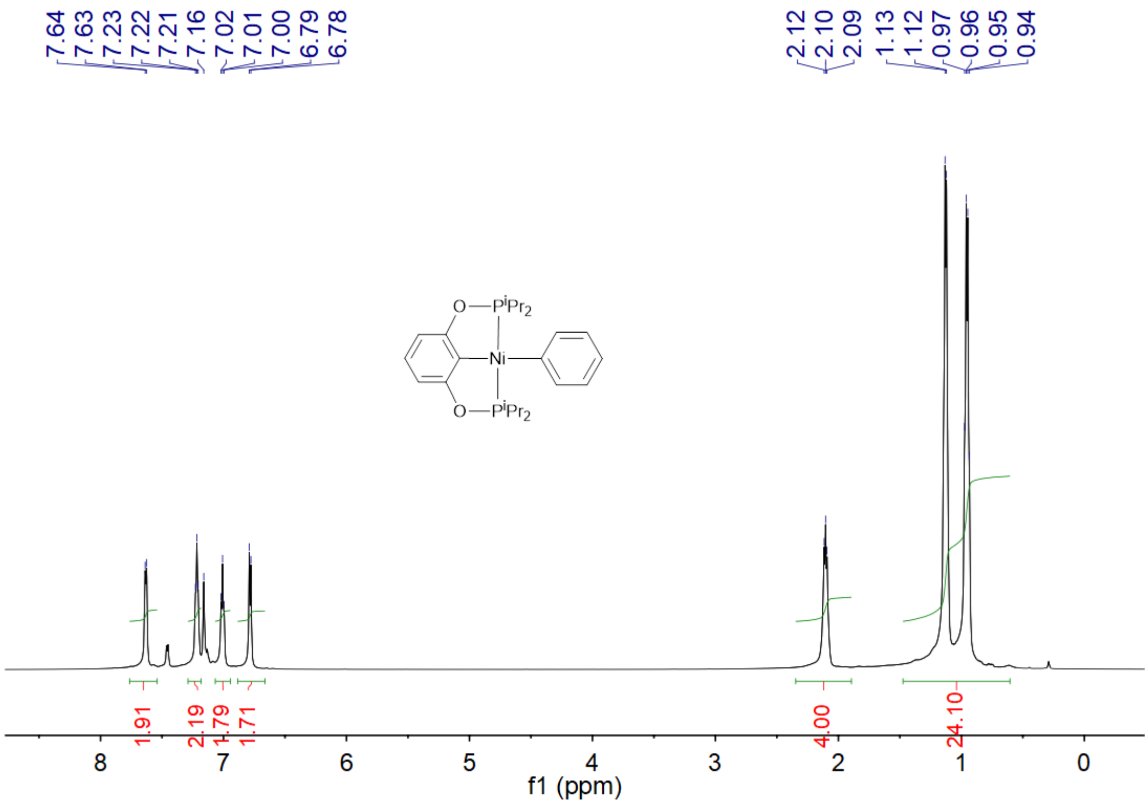



**Fig. S5** $^1H$ NMR spectrum of complex **2a** (600 MHz, benzene-$d_6$)

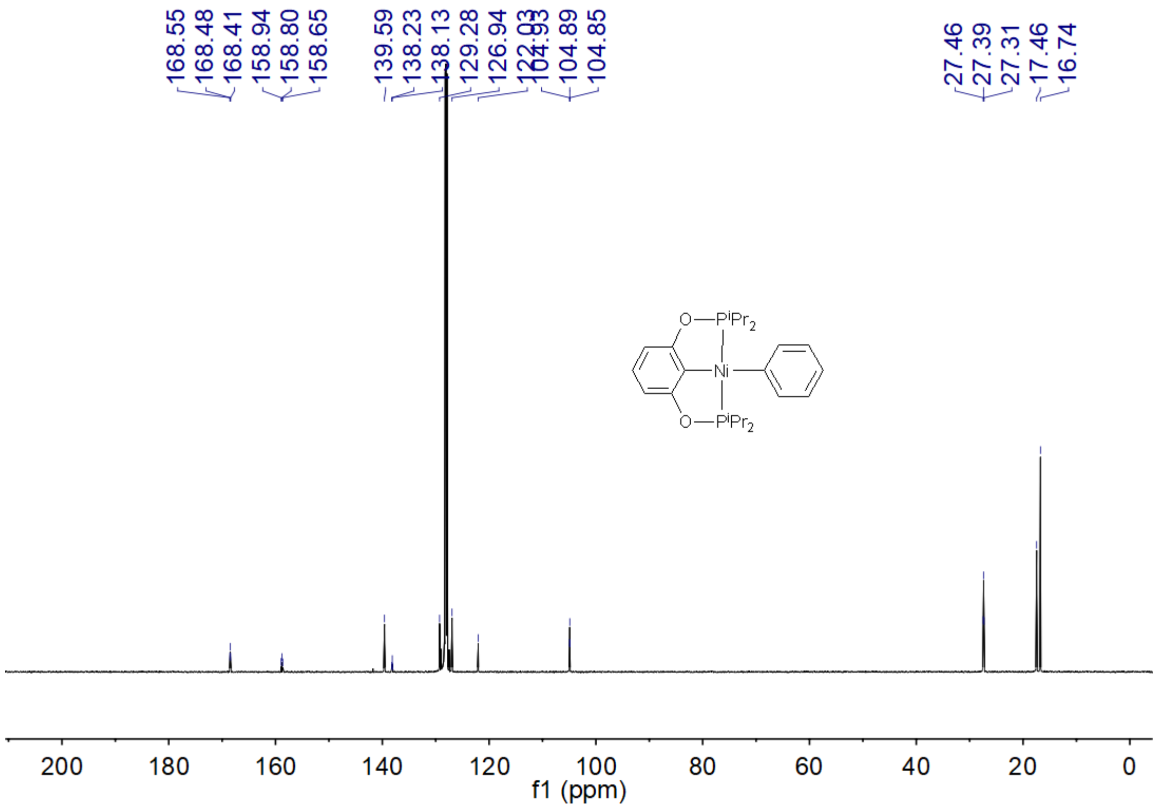



**Fig. S6** $^{13}C\{^{1}H\}$ NMR spectrum of complex **2a** (151 MHz, benzene-$d_6$)

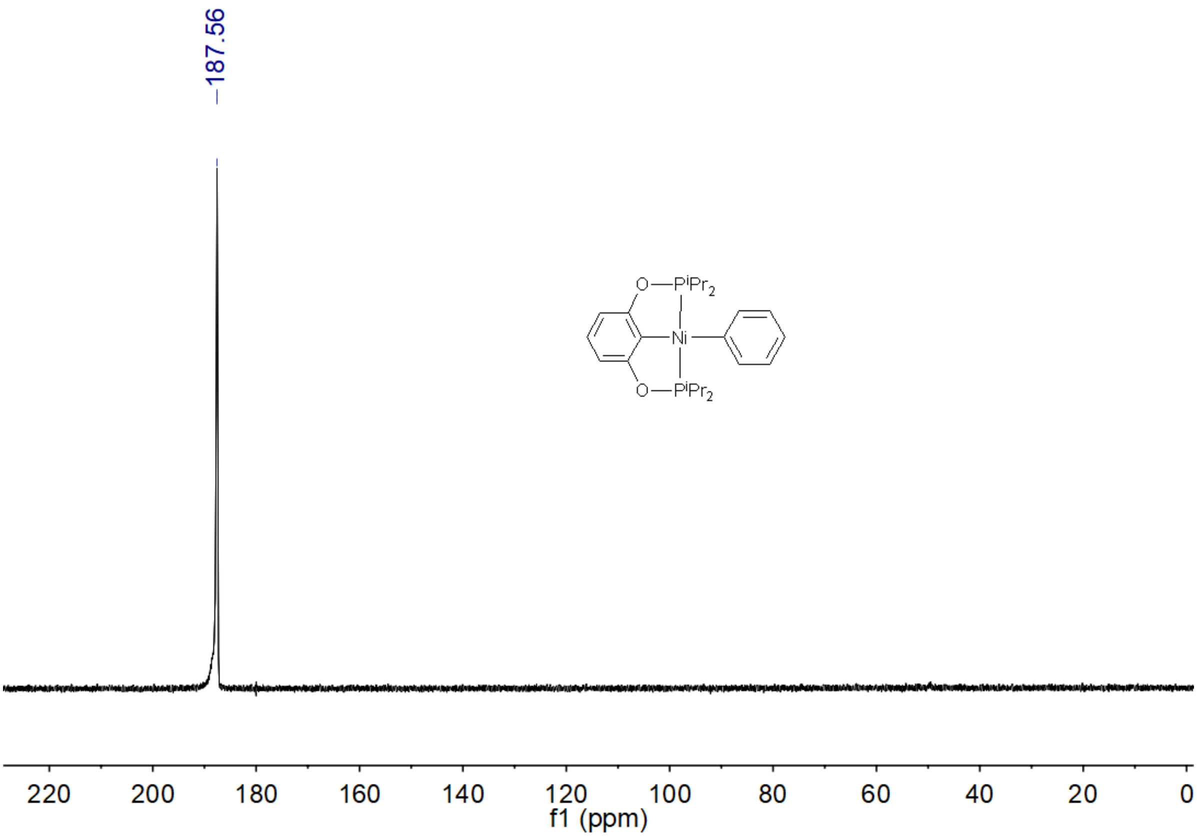



**Fig. S7** $^{31}P\{^{1}H\}$ NMR spectrum of complex **2a** (243 MHz, benzene-$d_6$)

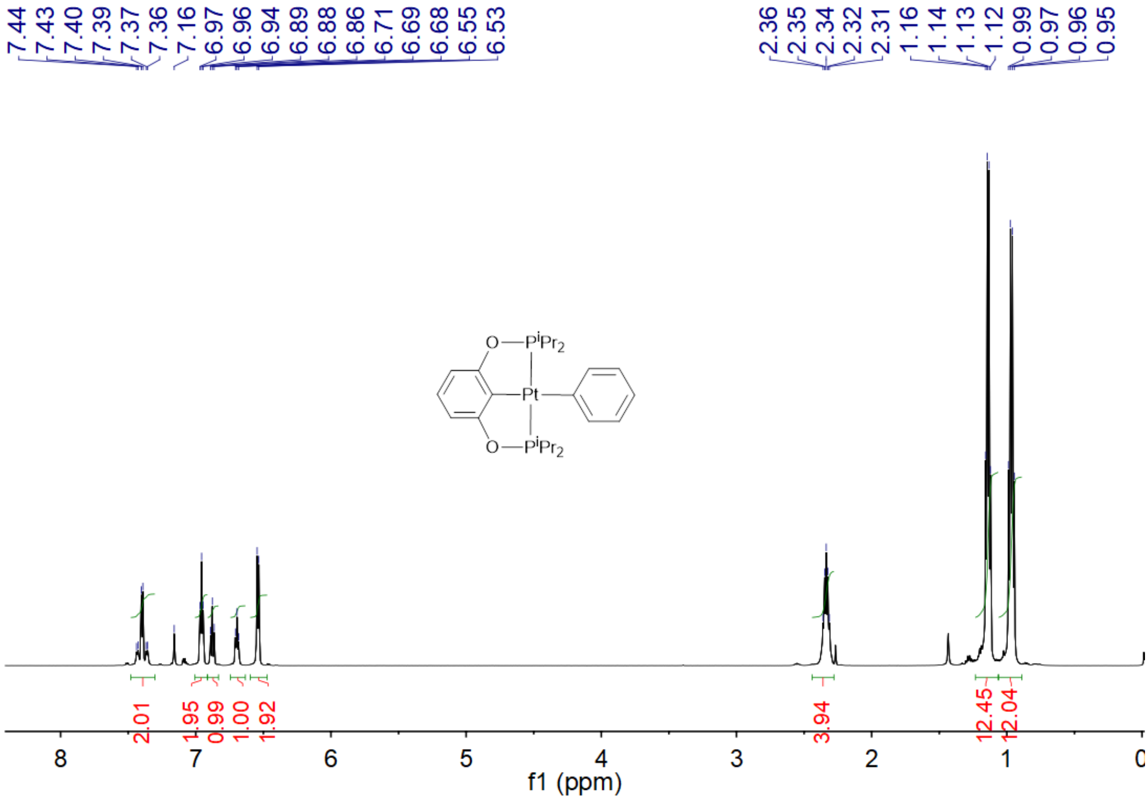


**Fig. S8** $^{1}H$ NMR spectrum of complex **2c** (600 MHz, benzene-$d_6$)

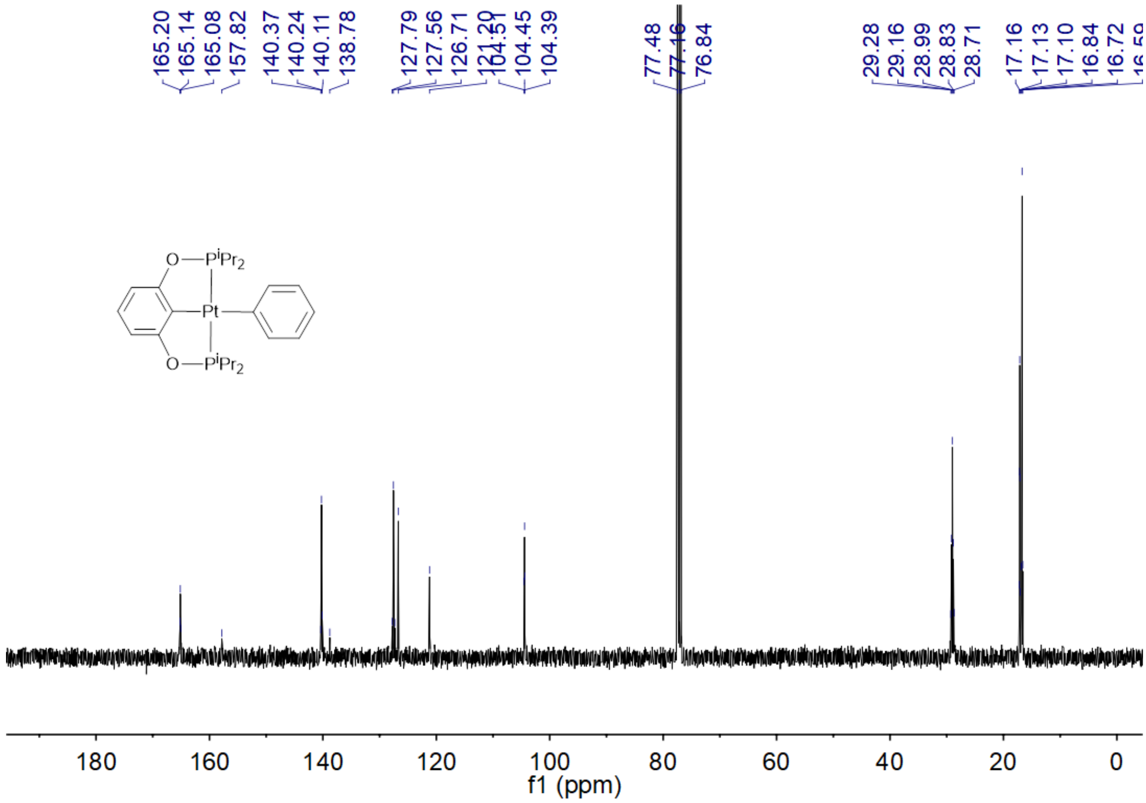


**Fig. S9** $^{13}C\{^{1}H\}$ NMR spectrum of complex **2c** (101 MHz, $CDCl_3$)

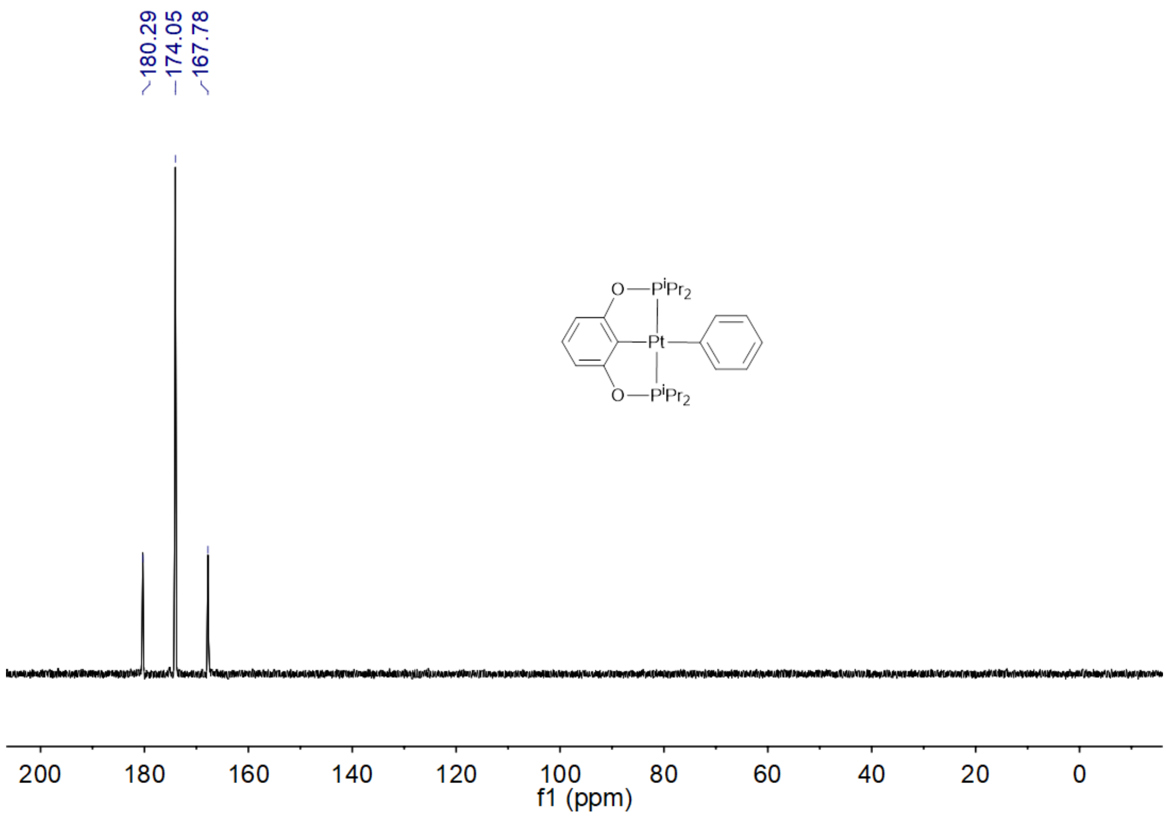



**Fig. S10** $^{31}P\{^1H\}$ NMR spectrum of complex **2c** (243 MHz, benzene-$d_6$)

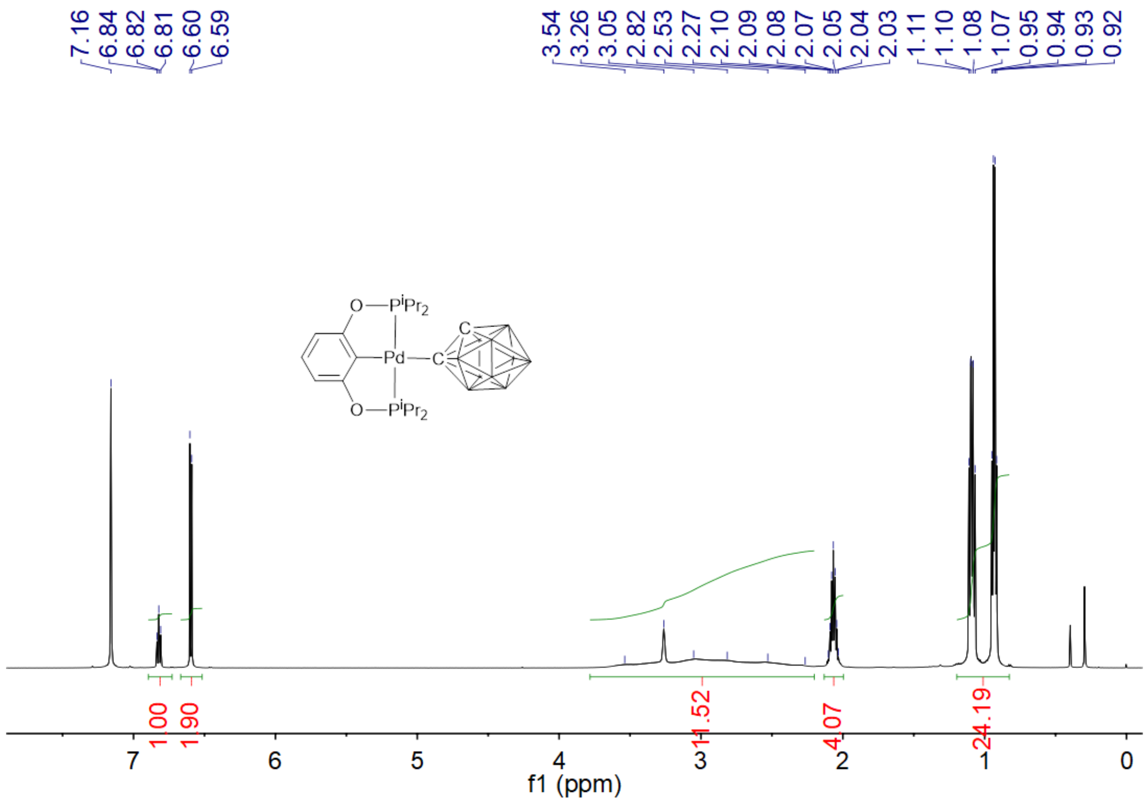



**Fig. S11** $^1H$ NMR spectrum of complex **3b** (600 MHz, benzene-$d_6$)

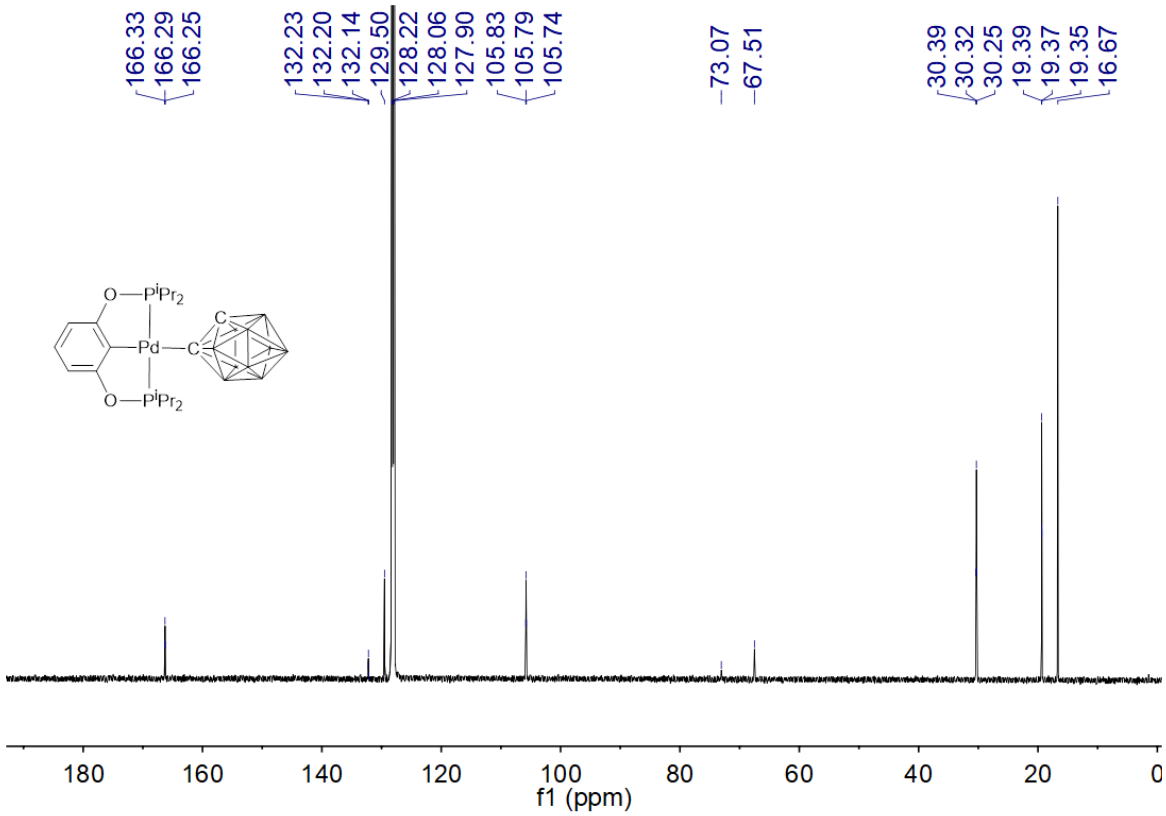



**Fig. S12** $^{13}C\{^{1}H\}$ NMR spectrum of complex **3b** (151 MHz, benzene-$d_6$)

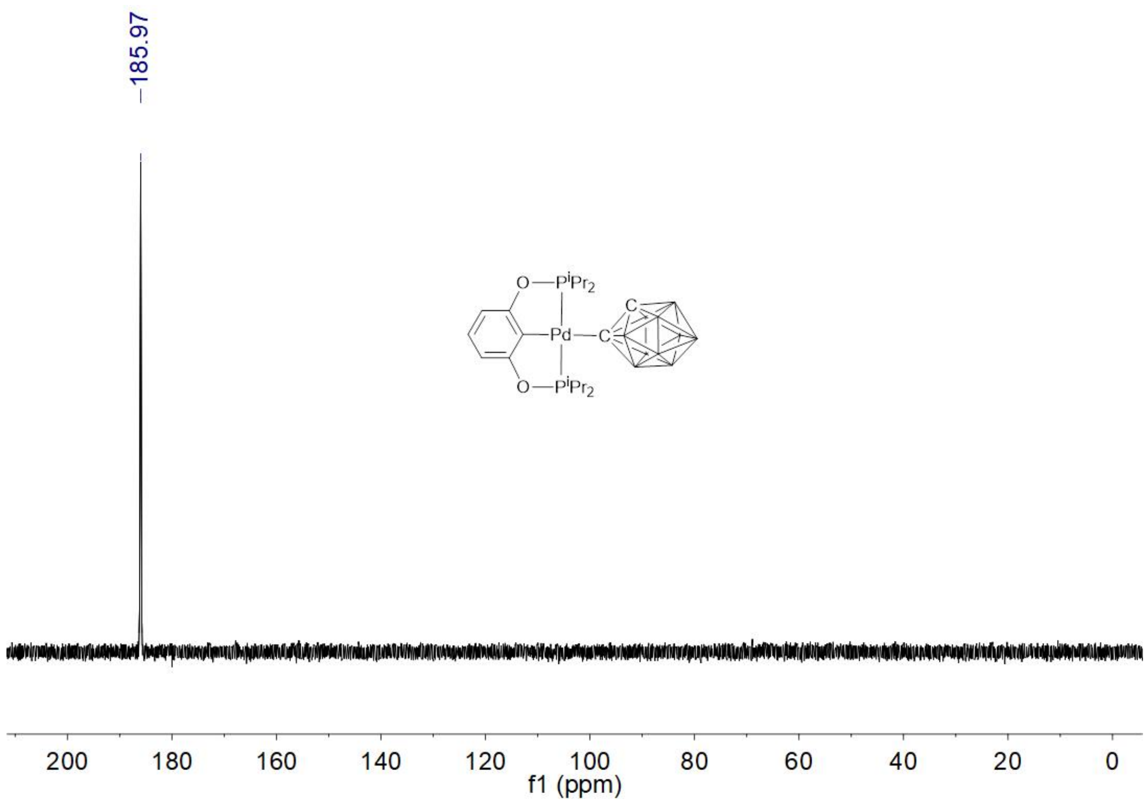



**Fig. S13** $^{31}P\{^{1}H\}$ NMR spectrum of complex **3b** (243 MHz, benzene-$d_6$)

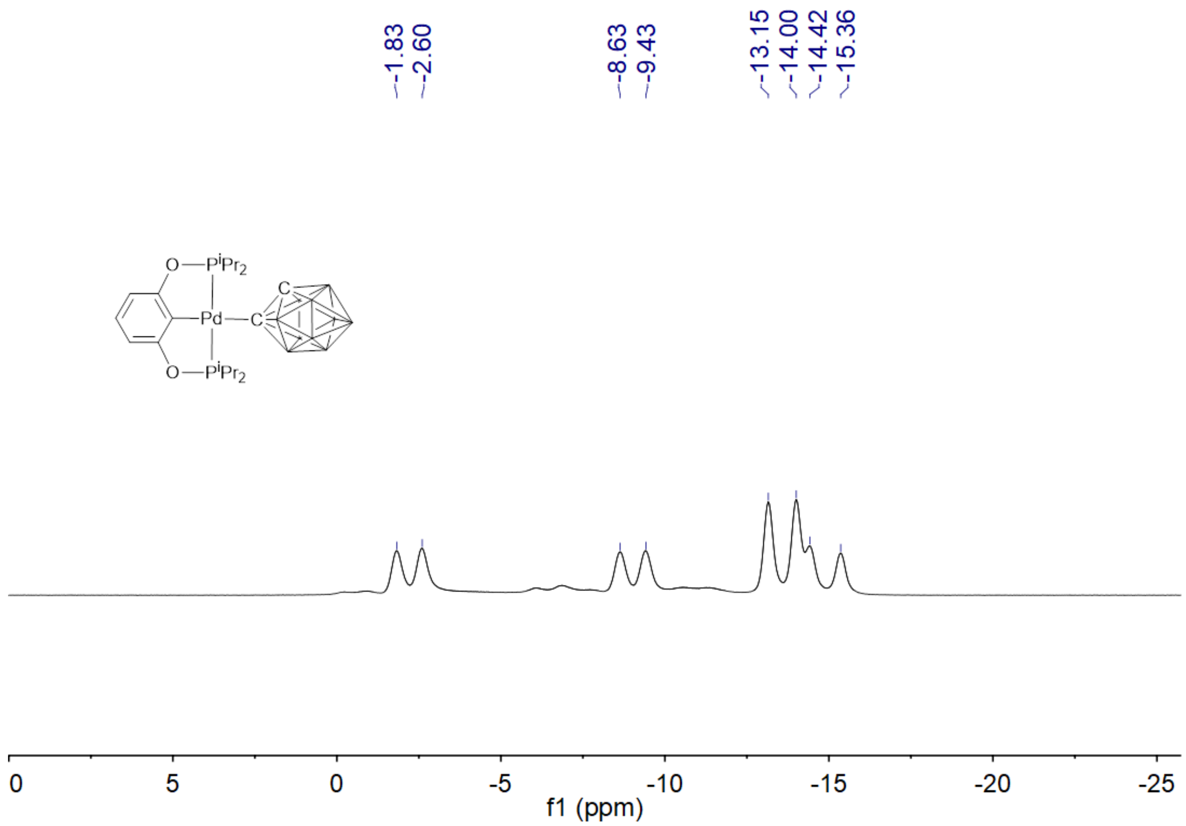



**Fig. S14** $^{11}$B NMR spectrum of complex **3b** (193 MHz, benzene-$d_6$)

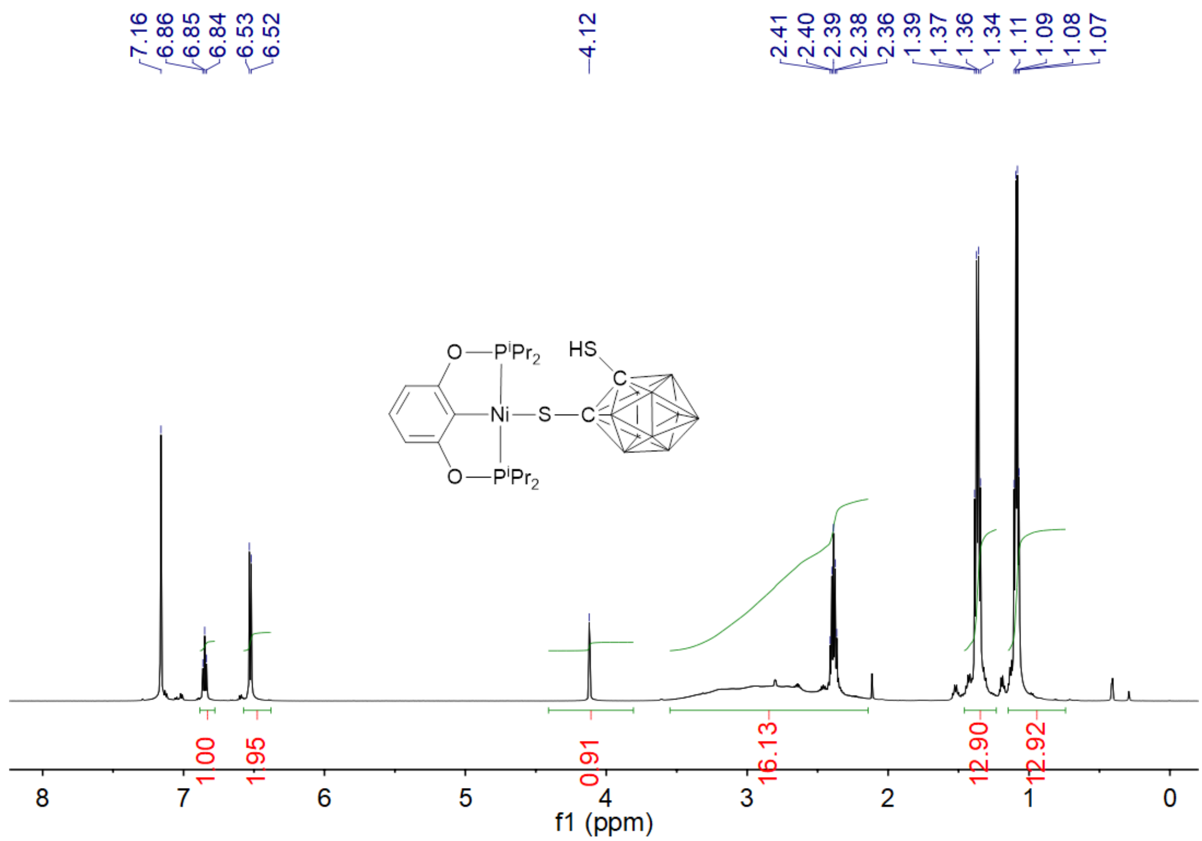



**Fig. S15** $^1$H NMR spectrum of complex **4a** (600 MHz, benzene-$d_6$)

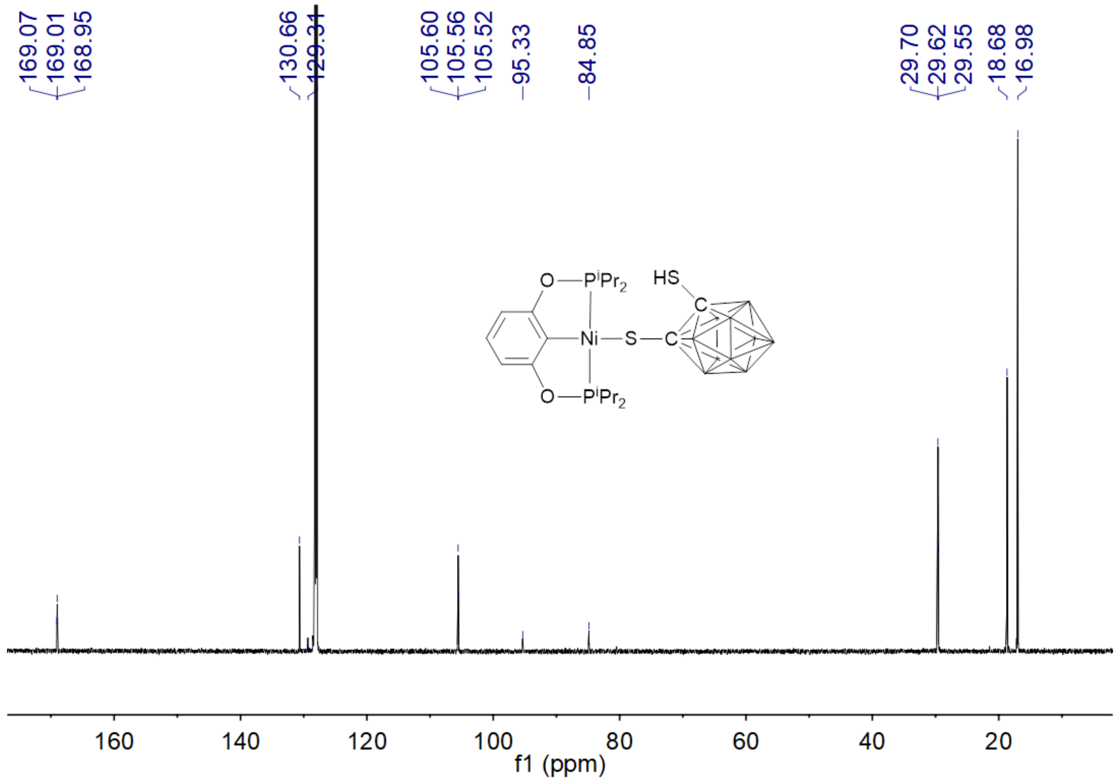



**Fig. S16** $^{13}C\{^1H\}$ NMR spectrum of complex **4a** (151 MHz, benzene-$d_6$)

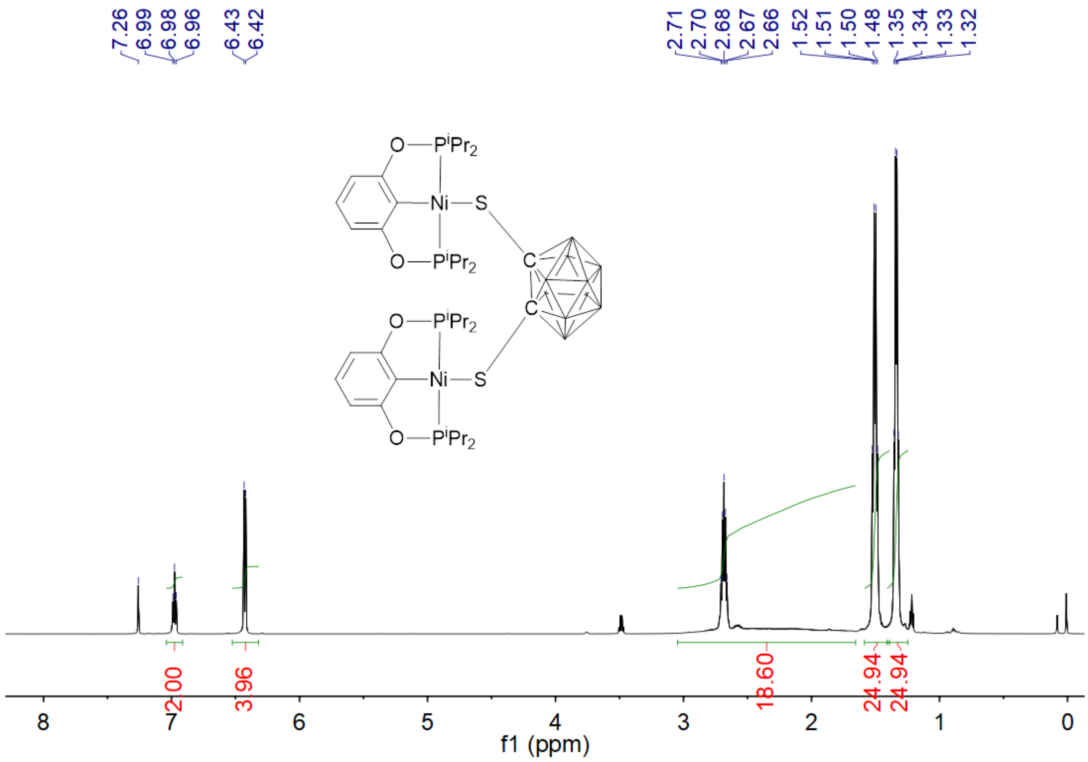



**Fig. S17** $^1H$ NMR spectrum of complex **5a** (600 MHz, $CDCl_3$)

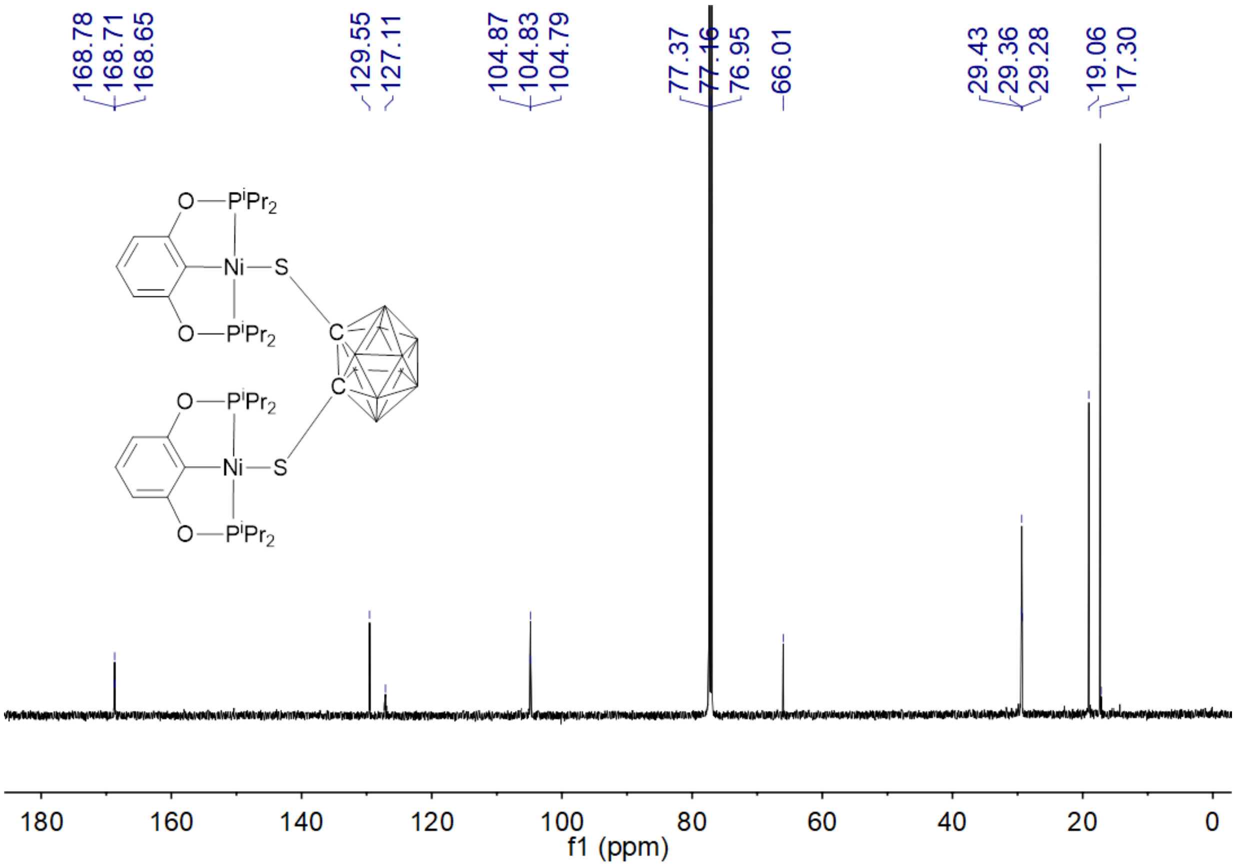



**Fig. S18** $^{13}C\{^{1}H\}$ NMR spectrum of complex **5a** (151 MHz, $CDCl_3$)