Electronic Supplementary Information

Synthesis and Coordination Chemistry of New Asymmetric Donor/Acceptor Pincer Ligands, 2,6-$C_6H_4(CH_2P^tBu(R_f))_2$ (R_f = CF_3, C_2F_5)

Contribution from The Department of Chemistry at The University of Wyoming
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Contents:

NMR Spectra.

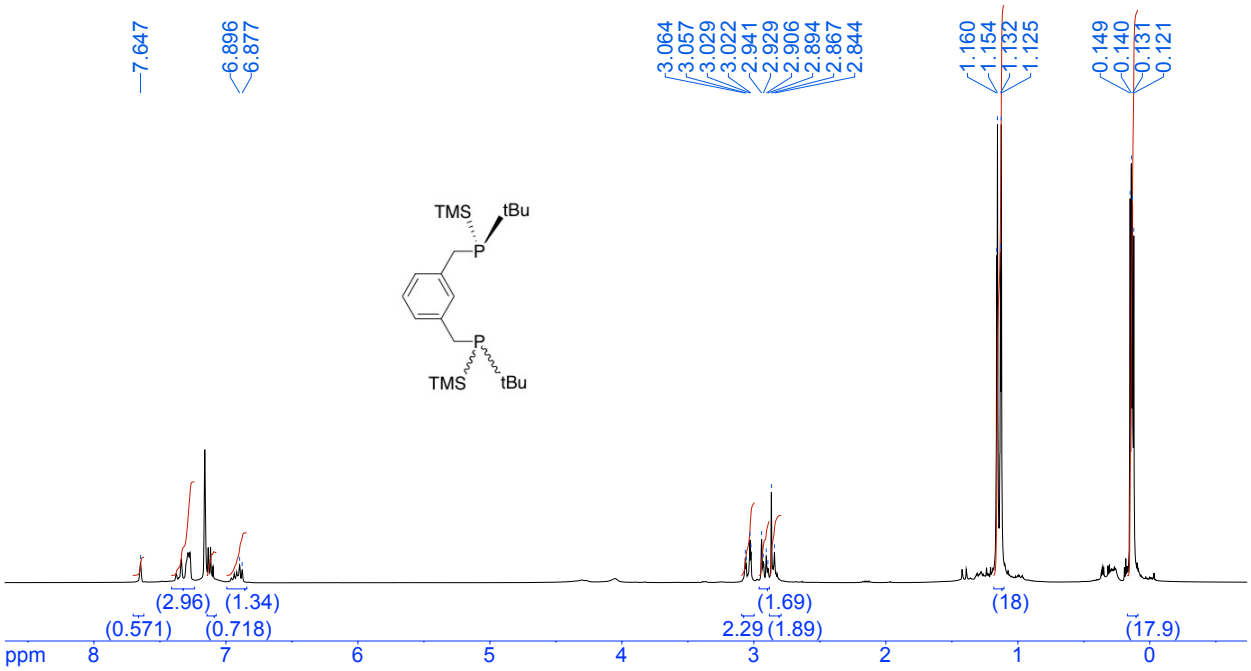

Figure S1a. ^{1}H (400.13 MHz) NMR spectrum for $^{t\text{Bu,TMS}}$PCPH in benzene-d_6 at 25 ºC. Solvent impurity at 2.87.

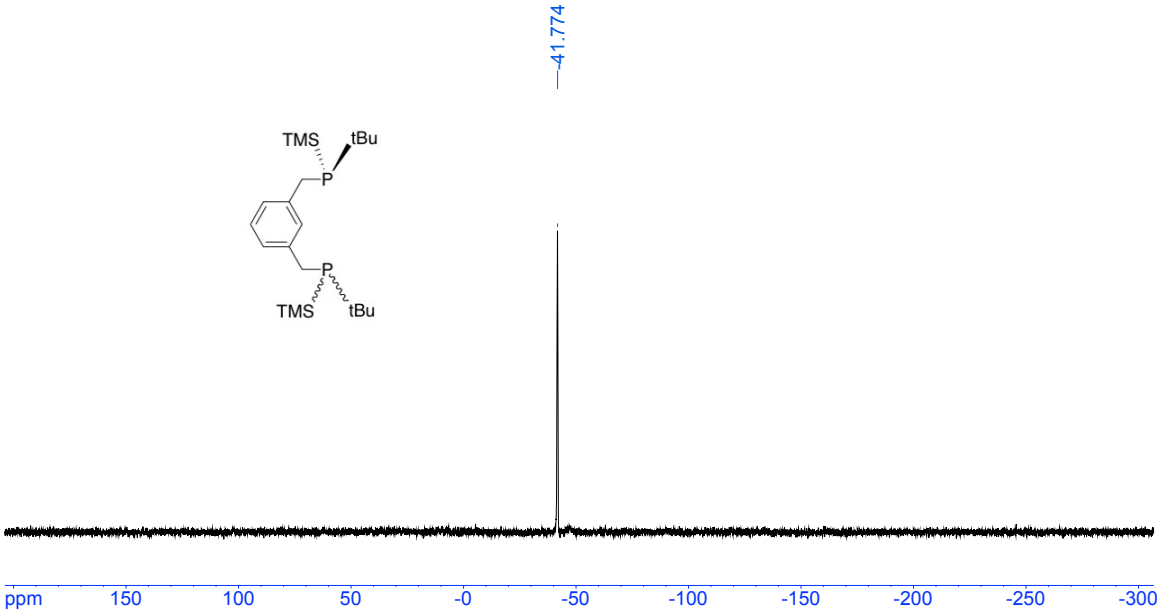

Figure S1b. ^{31}P (161.97 MHz) NMR spectrum for $^{t\text{Bu,TMS}}$PCPH in benzene-d_6 at 25 ºC.

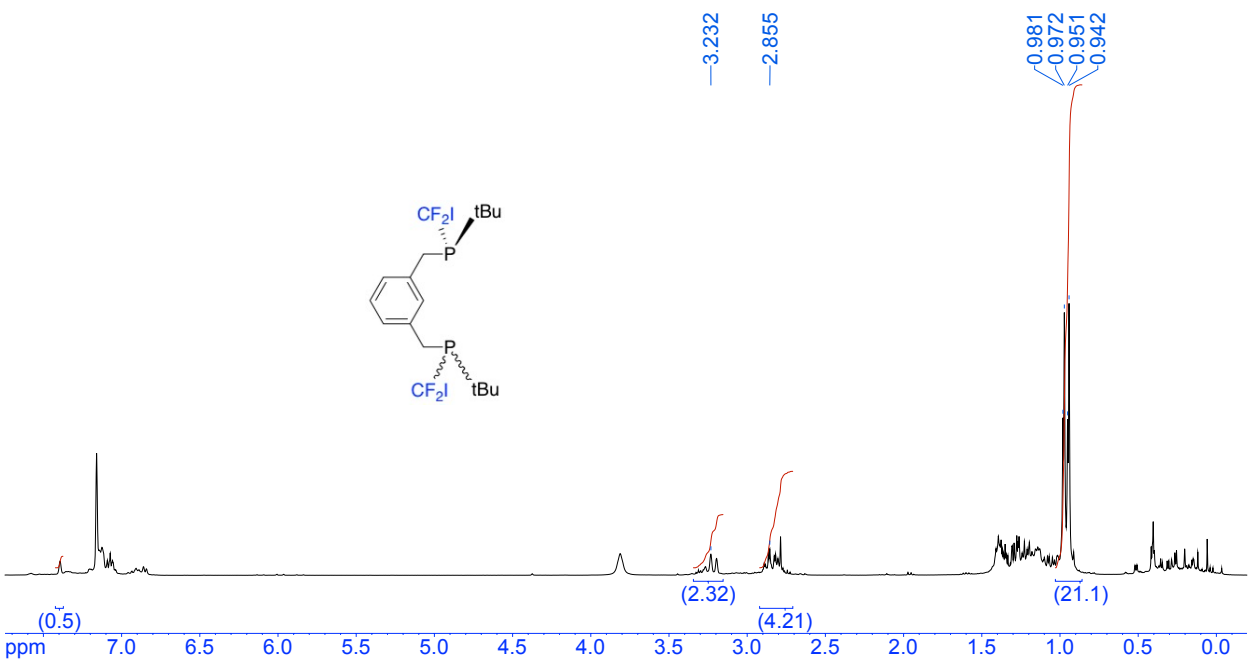

Figure S2a. ^{1}H (400.13 MHz) NMR spectrum for $^{t\text{Bu,CF2I}}$PCPH in benzene-d_6 at 25 ºC. Unidentified impurities appear at 2.85, 1.0 – 1.4, 0.0 – 0.5 ppm, and residual THF at 3.6 and 1.4.

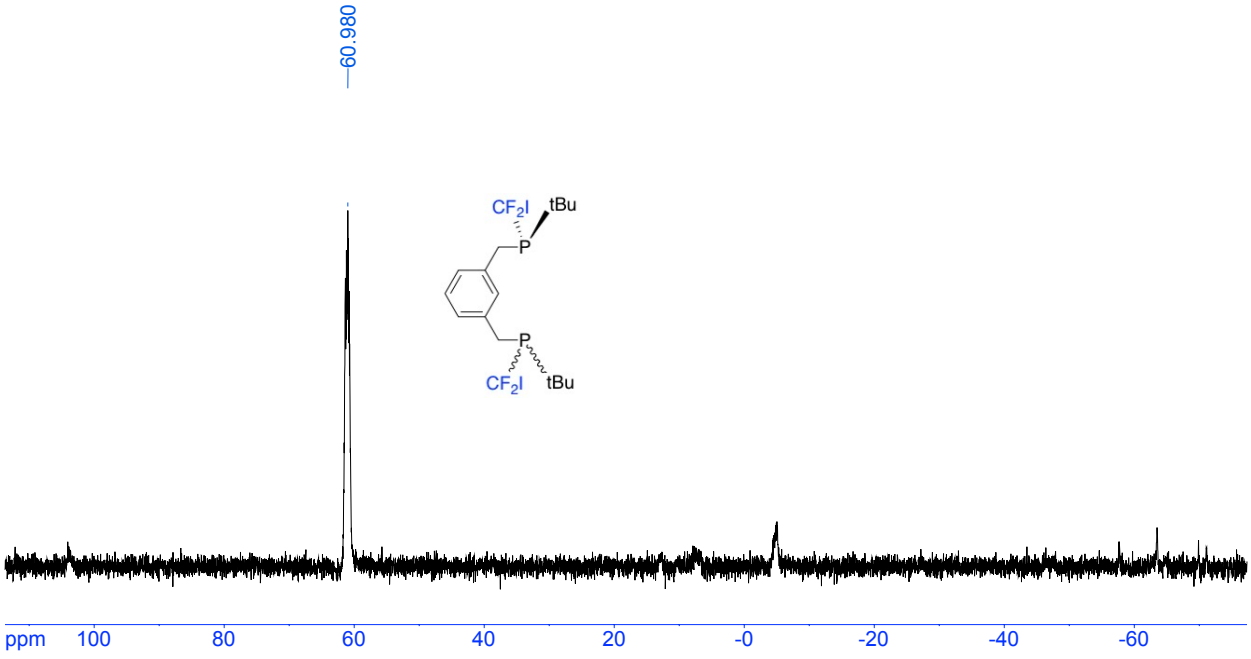

Figure S2b. ^{31}P (161.97 MHz) NMR spectrum for $^{t\text{Bu,CF2I}}$PCPH in benzene-d_6 at 25 ºC.

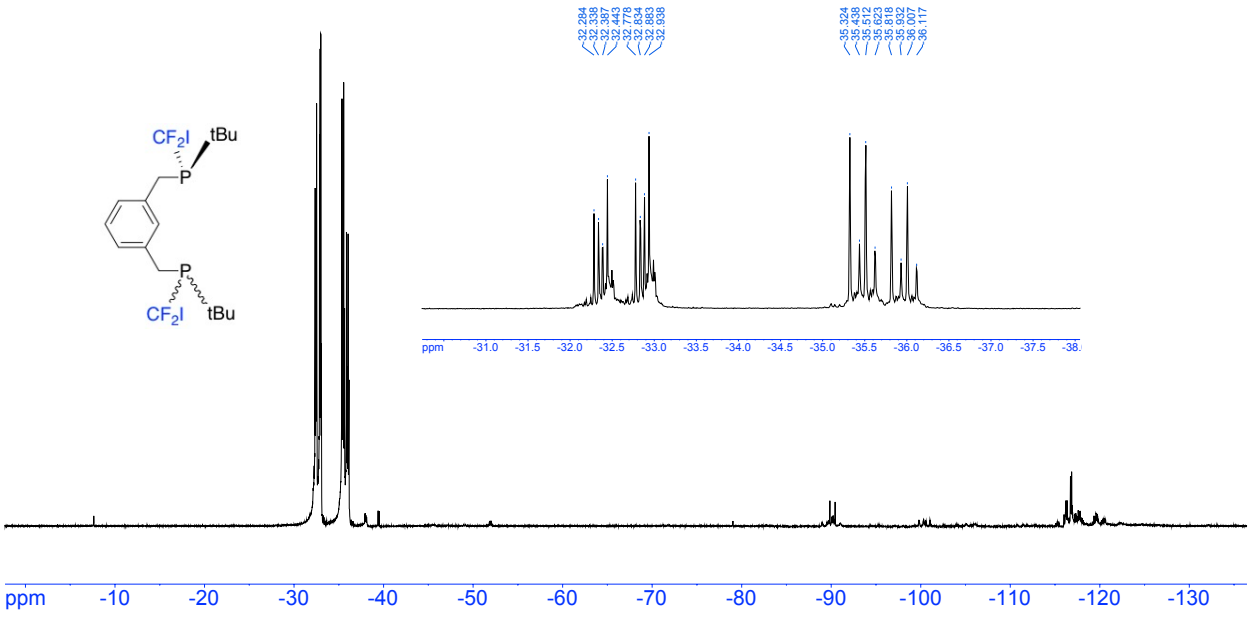

Figure S2c. ^{19}F (376.50 MHz) NMR spectrum for $^{t\text{Bu,CF2I}}$PCPH in benzene-d_6 at 25 ºC, with P-CF_2I expanded region inset.

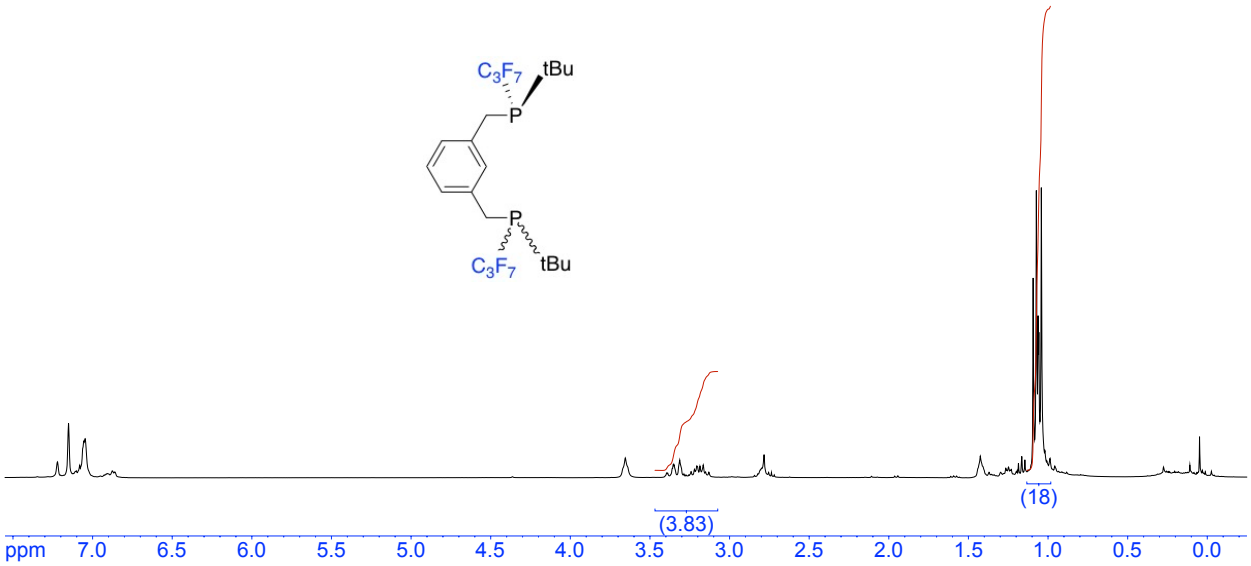

Figure S3a. ^{1}H (400.13 MHz) NMR spectrum for $^{t\text{Bu,C3F7}}$PCPH in benzene-d_6 at 25 ºC. Residual THF solvent at 3.63 and 1.4 ppm, solvent impurities at 2.8, 0.0 – 0.5 ppm

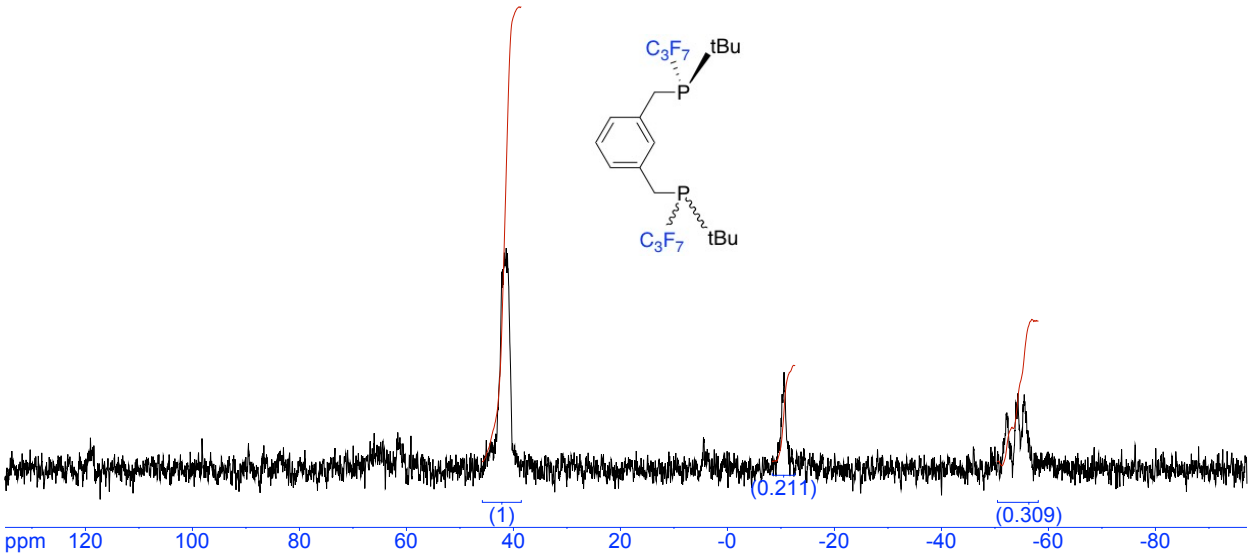

Figure S3b. ^{31}P (161.97 MHz) NMR spectrum for $^{t\text{Bu,C}_3\text{F}_7}$PCPH in benzene-$d_6$ at 25 ºC.

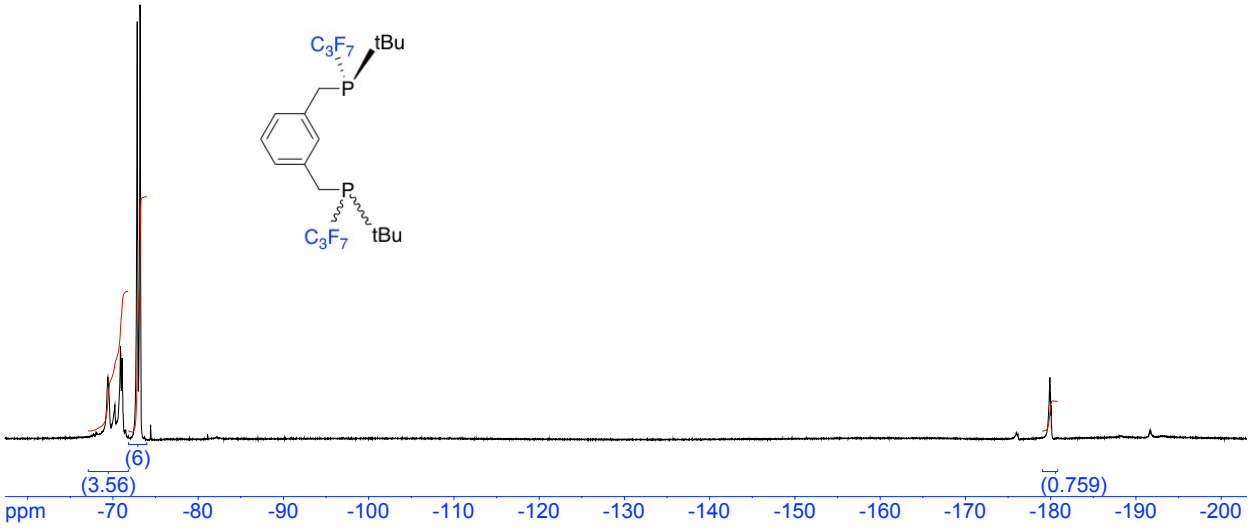

Figure S3c. ^{19}F (376.50 MHz) NMR spectrum for $^{t\text{Bu,C}_3\text{F}_7}$PCPH in benzene-$d_6$ at 25 ºC.

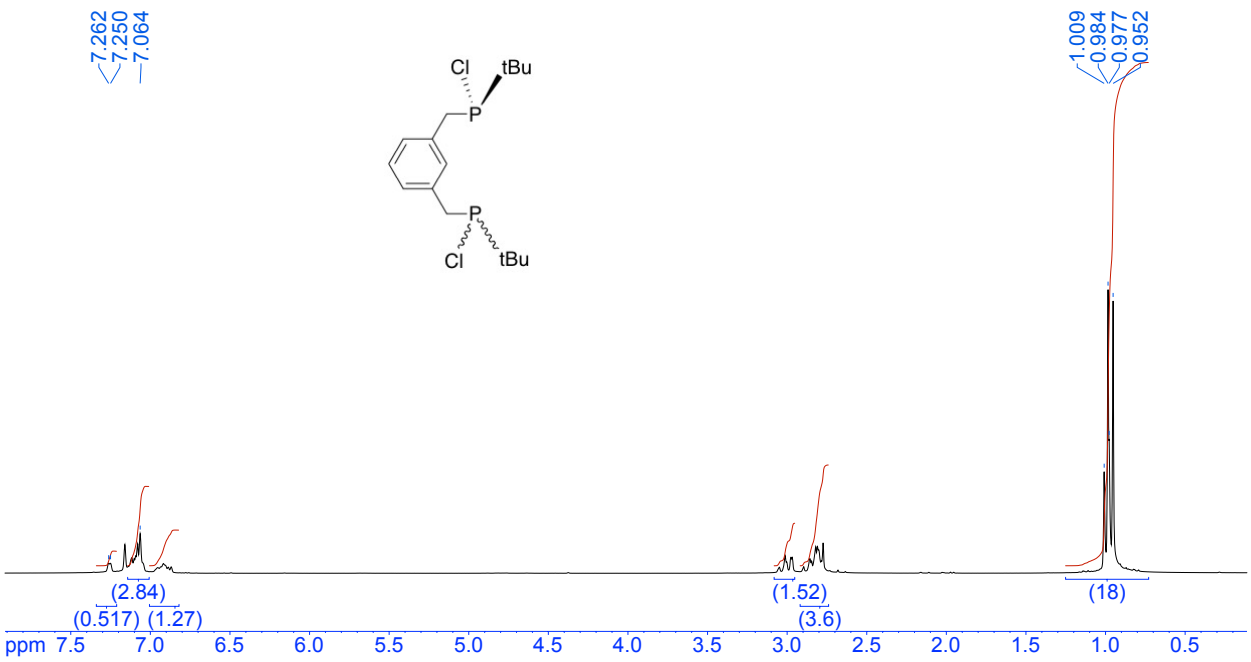

Figure S4a. ^{1}H (400.13 MHz) NMR spectrum for $^{t\mathrm{Bu,Cl}}$PCPH in benzene-d_6 at 25 ºC. A solvent impurity overlaps the upfield PCH_2 multiplet.

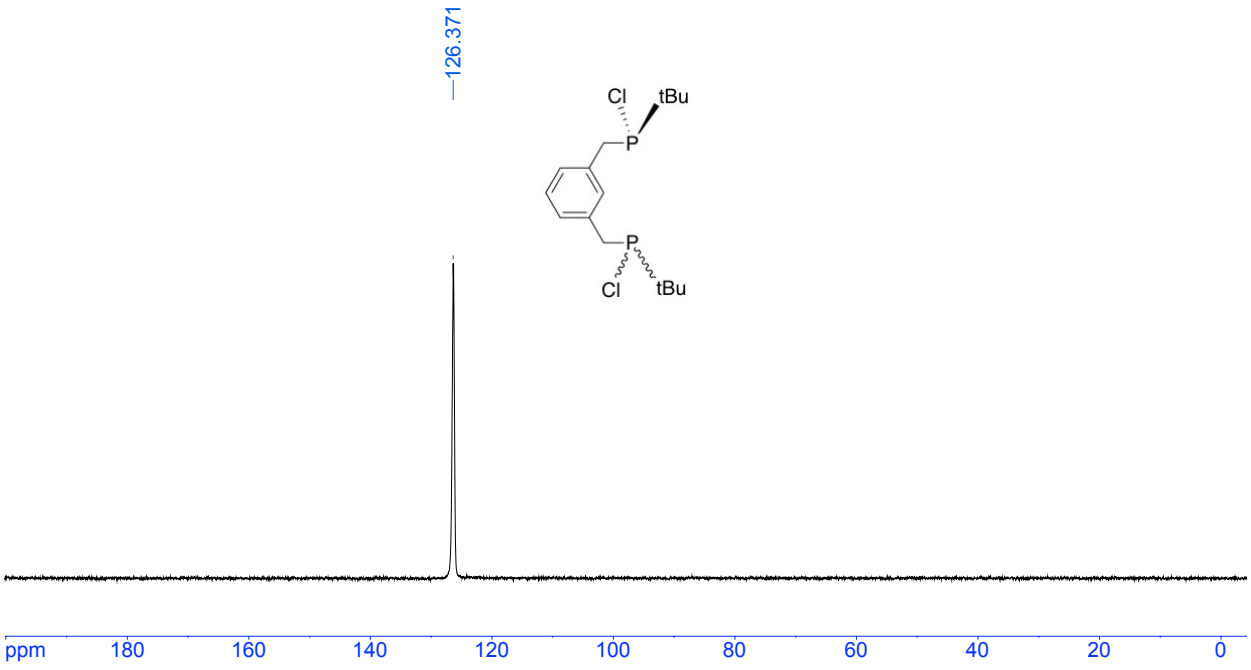

Figure S4b. ^{31}P (161.97 MHz) NMR spectrum for $^{t\mathrm{Bu,Cl}}$PCPH in benzene-d_6 at 25 ºC.

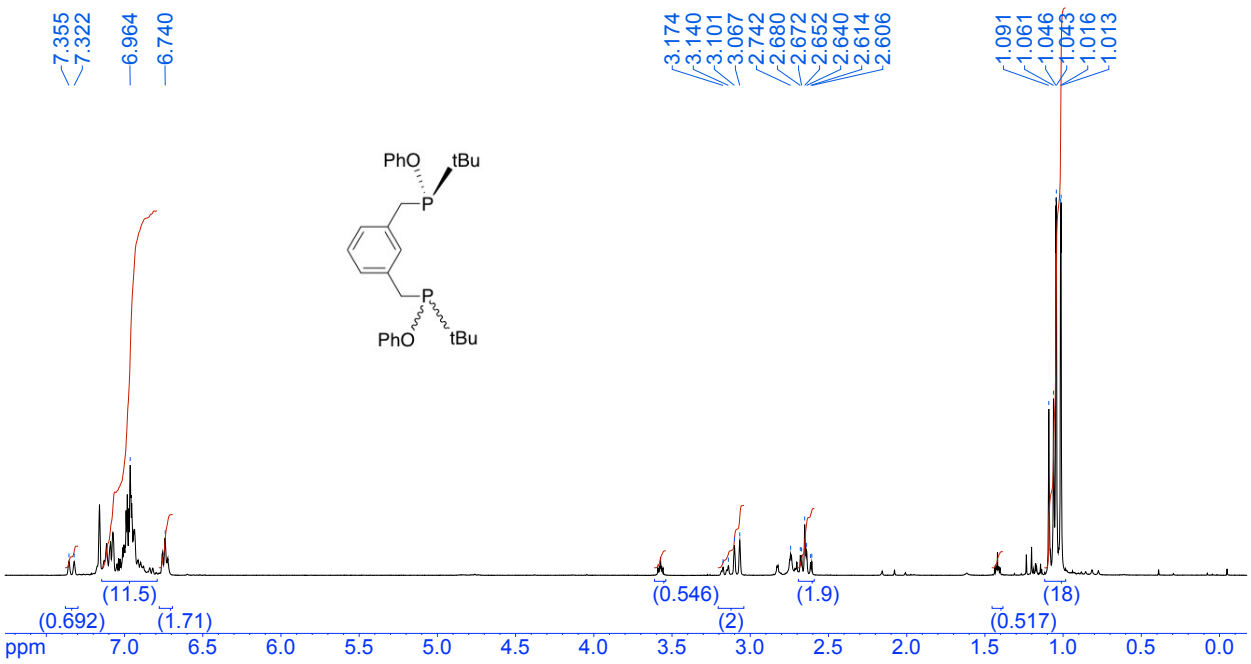

Figure S5a. ^{1}H (400.13 MHz) NMR spectrum for $^{t\text{Bu,OPh}}$PCPH in benzene-d_6 at 25 ºC. A solvent impurity underlies the 2.65 multiplet, and residual THF appears at 3.6 and 1.4.

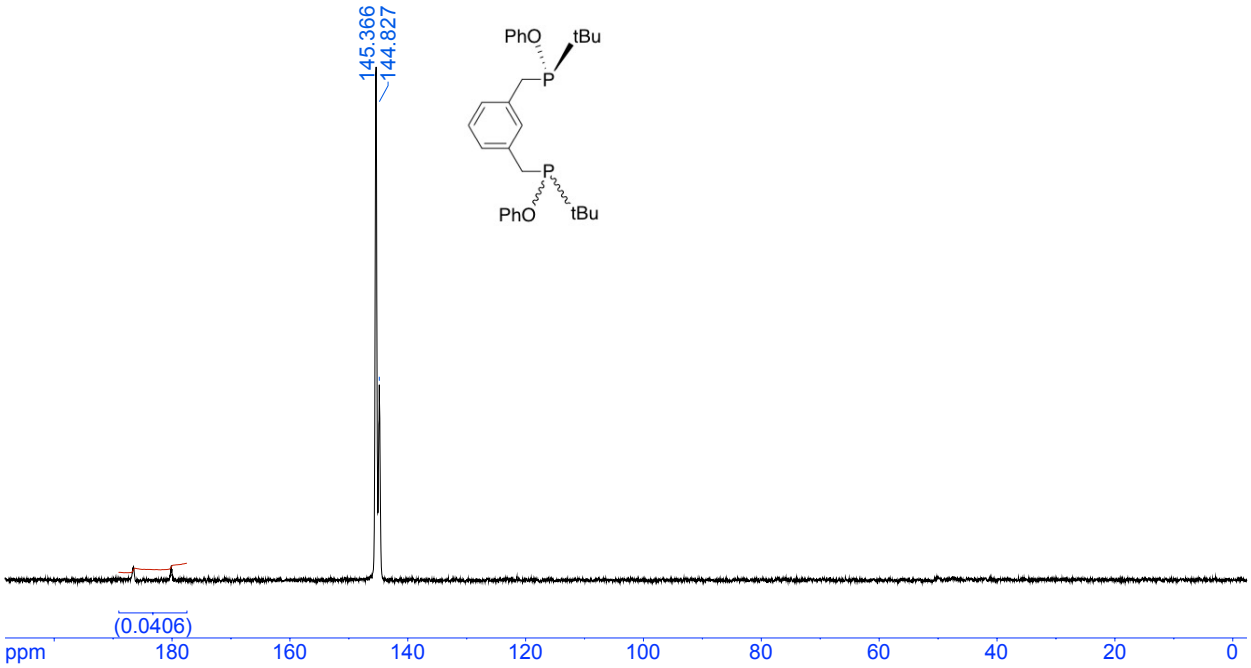

Figure S5b. ^{31}P (161.97 MHz) NMR spectrum for $^{t\text{Bu,OPh}}$PCPH in benzene-d_6 at 25 ºC.

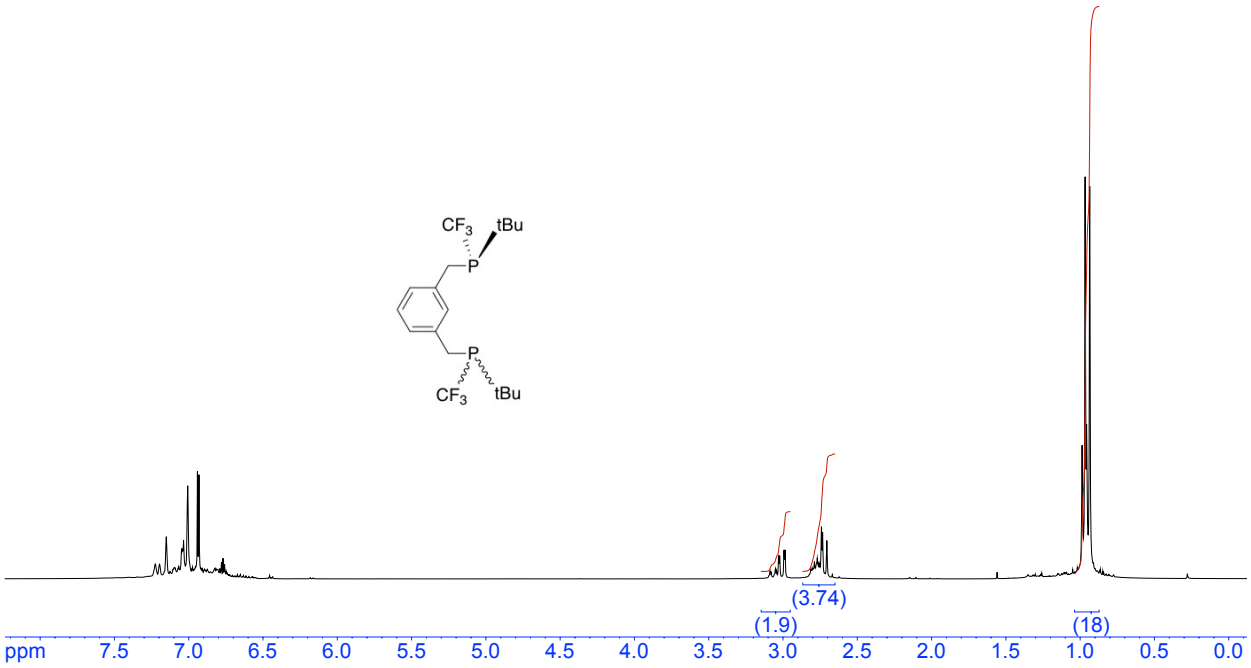

Figure S6a. ^{1}H (400.13 MHz) NMR spectrum for $^{t\text{Bu,CF}_3}$PCPH in benzene-d_6 at 25 ºC. A solvent impurity underlies the 2.73 multiplet.

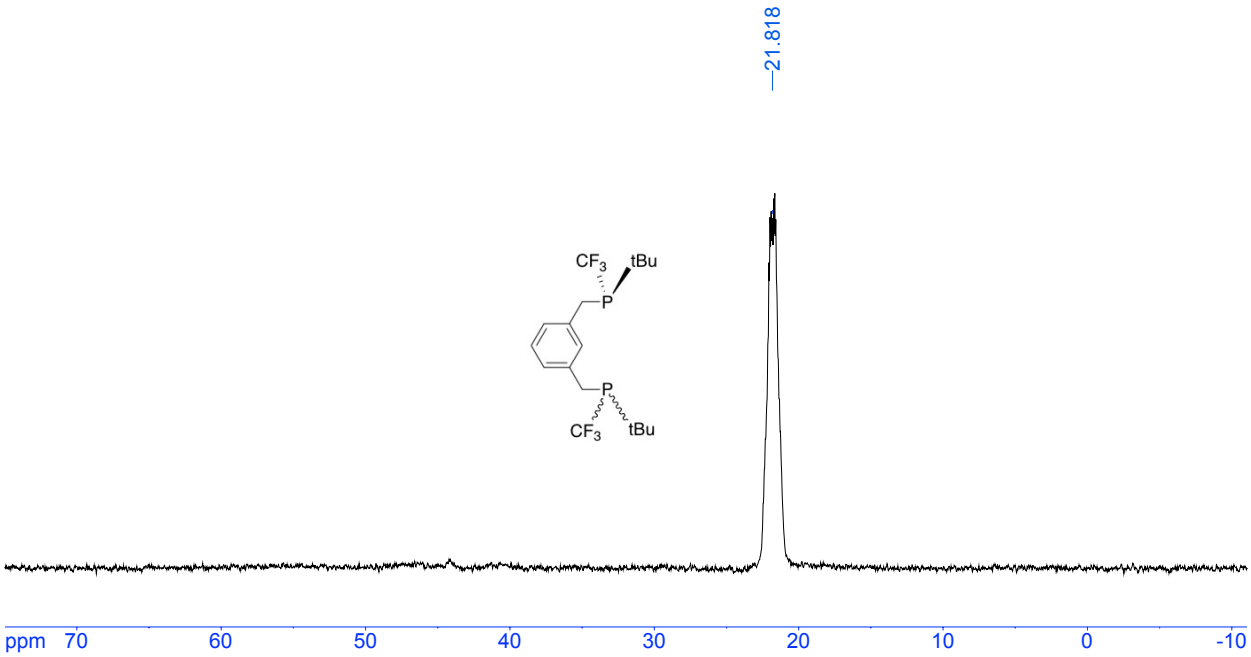

Figure S6b. ^{31}P (161.97 MHz) NMR spectrum for $^{t\text{Bu,CF}_3}$PCPH in benzene-d_6 at 25 ºC.

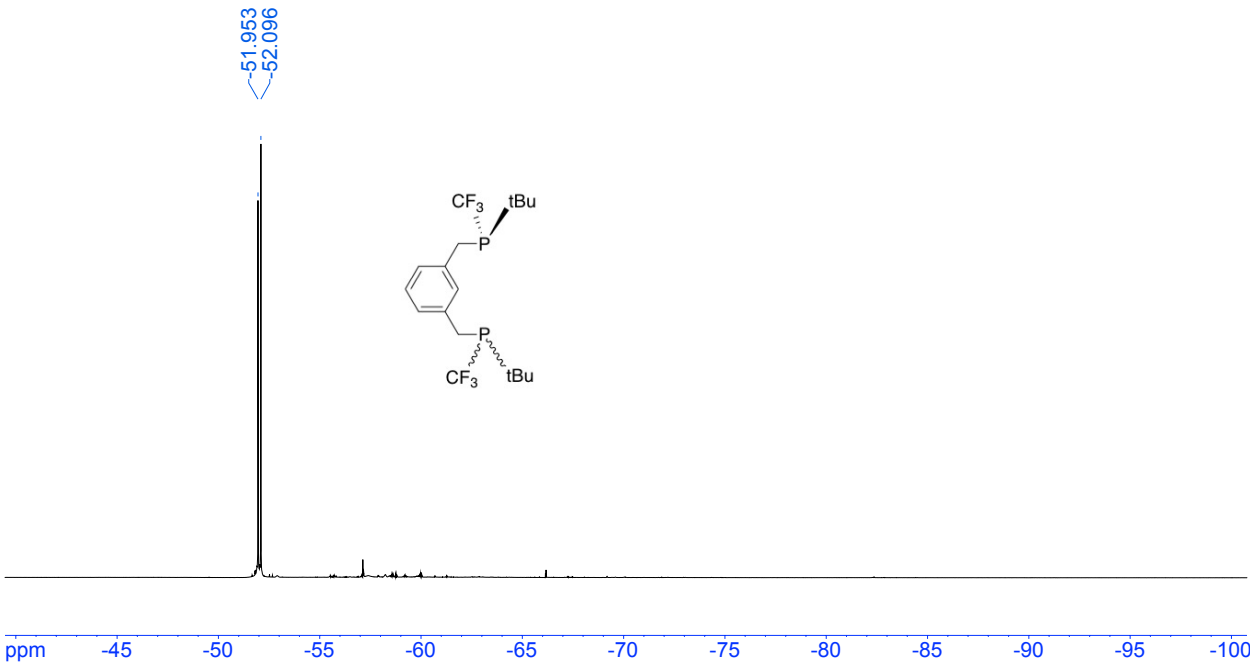

Figure S6c. ^{19}F (376.50 MHz) NMR spectrum for $^{t\text{Bu,CF}_3}$PCPH in benzene-d_6 at 25 ºC.

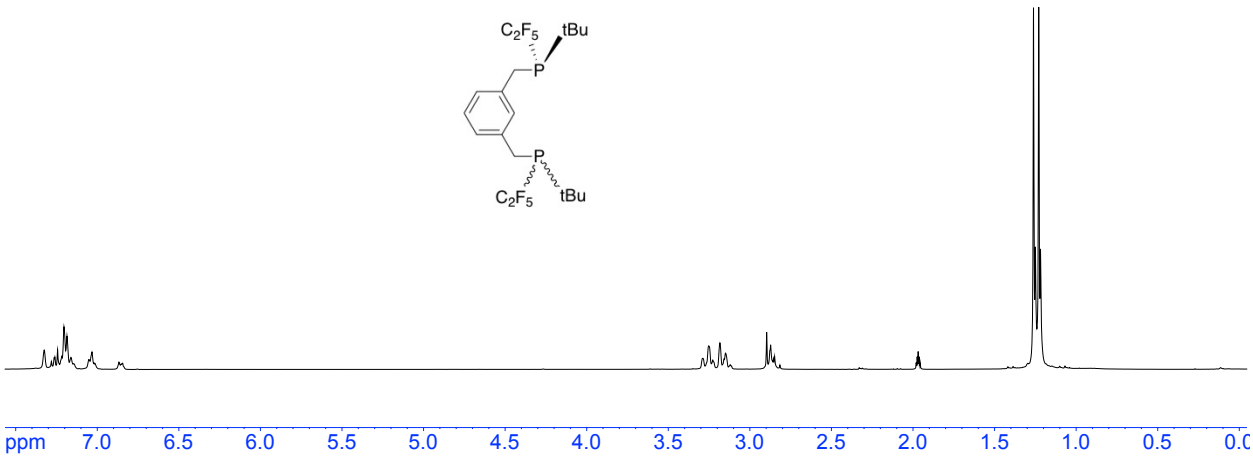

Figure S7a. ^{1}H (400.13 MHz) NMR spectrum for $^{t\text{Bu,CF}_2\text{F}_5}$PCPH in benzene-$d_6$ at 25 ºC.

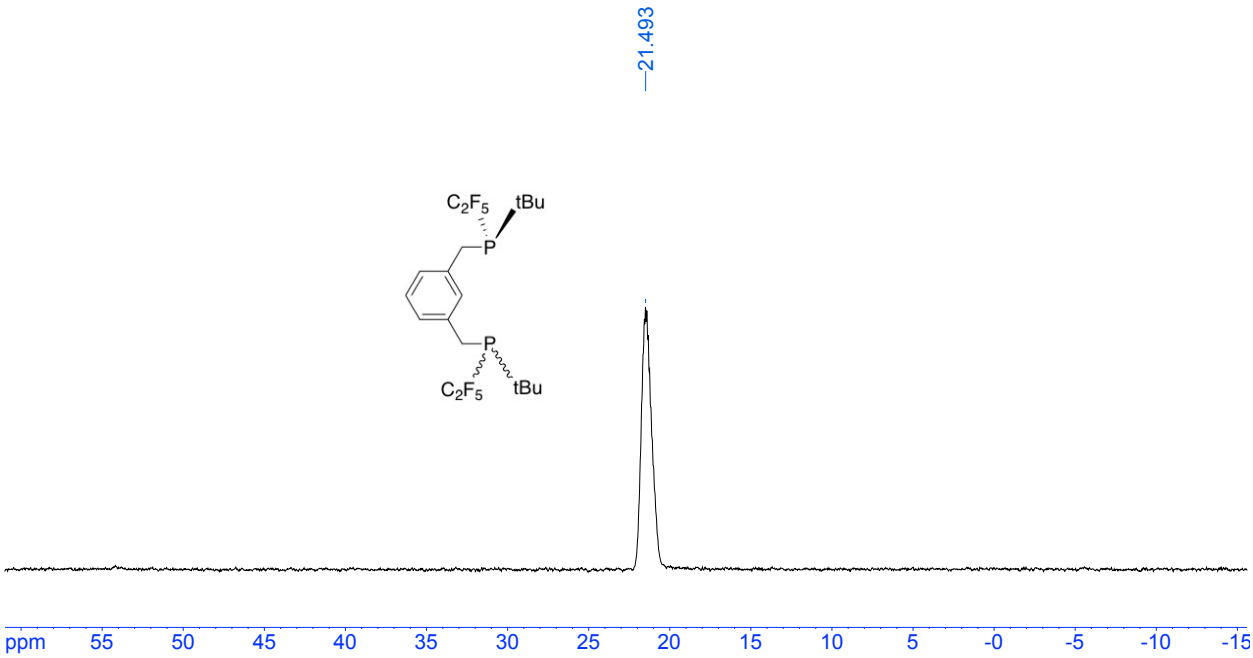

Figure S7b. ^{31}P (161.97 MHz) NMR spectrum for $^{t\text{Bu,CF}_2\text{F}_5}$PCPH in benzene-$d_6$ at 25 ºC.

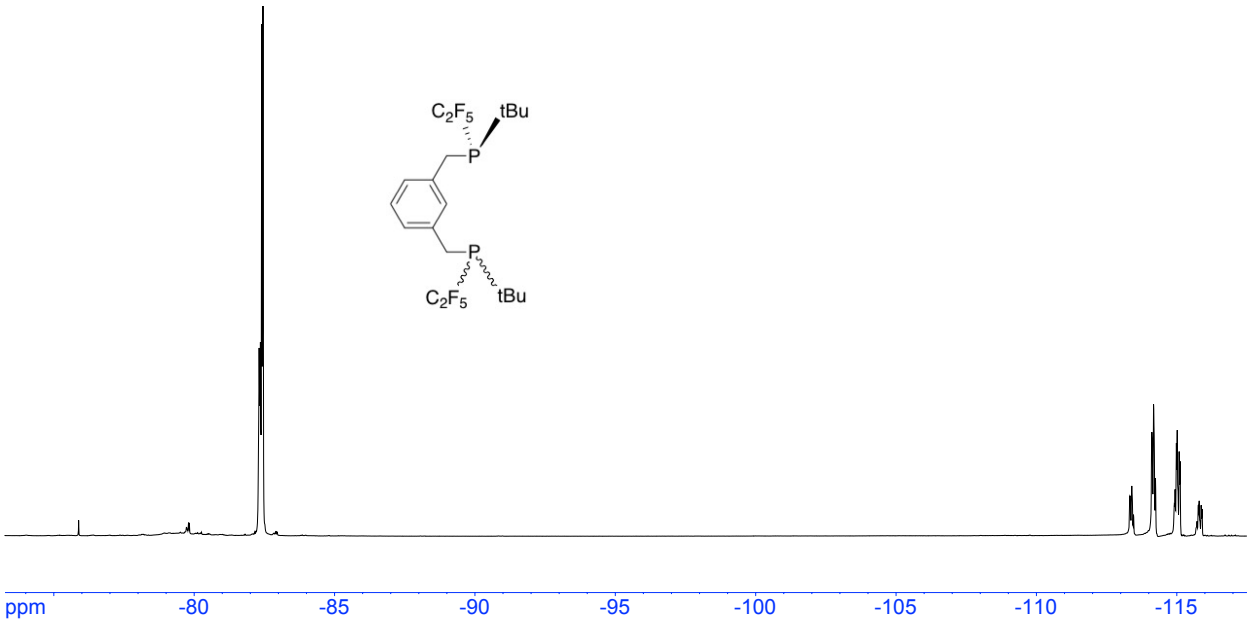

Figure S7c. ^{19}F (376.50 MHz) NMR spectrum for $^{t\text{Bu,CF}_2\text{F}_5}$PCPH in benzene-$d_6$ at 25 ºC.

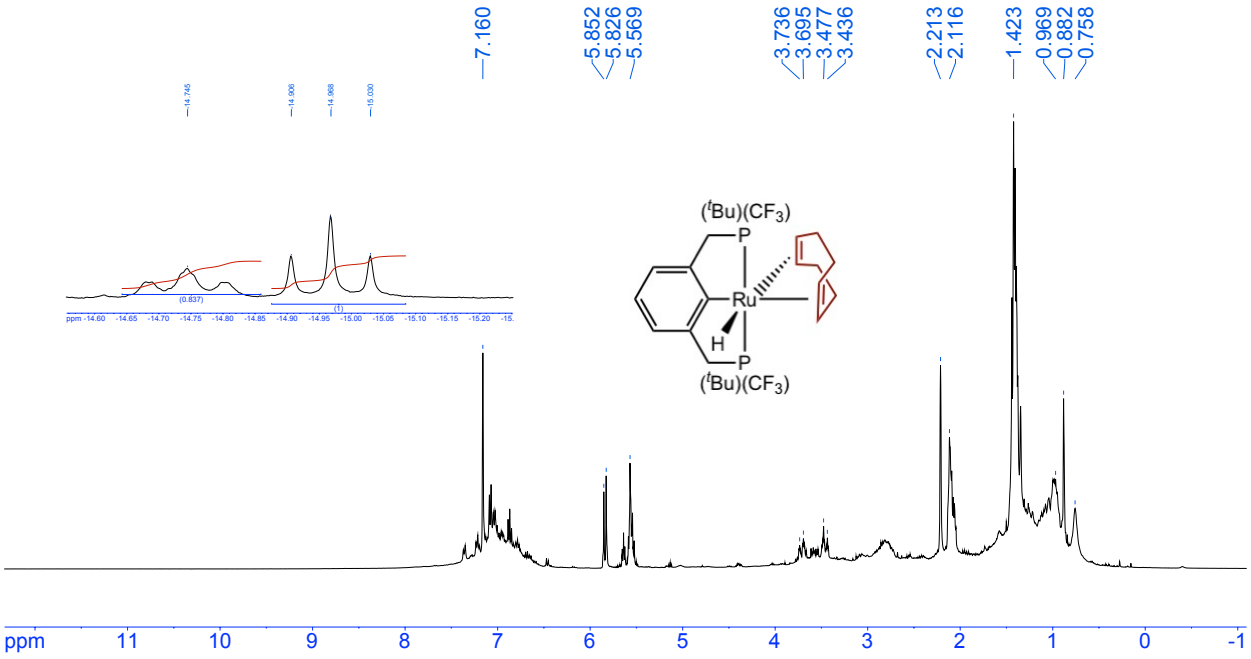

Figure S8a. ^{1}H (400.13 MHz) NMR spectrum for ($^{t\text{Bu,CF}_3}$PCP)Ru(cod)(H) (**1**) in benzene-d_6 at 25 ºC, with hydride region inset.

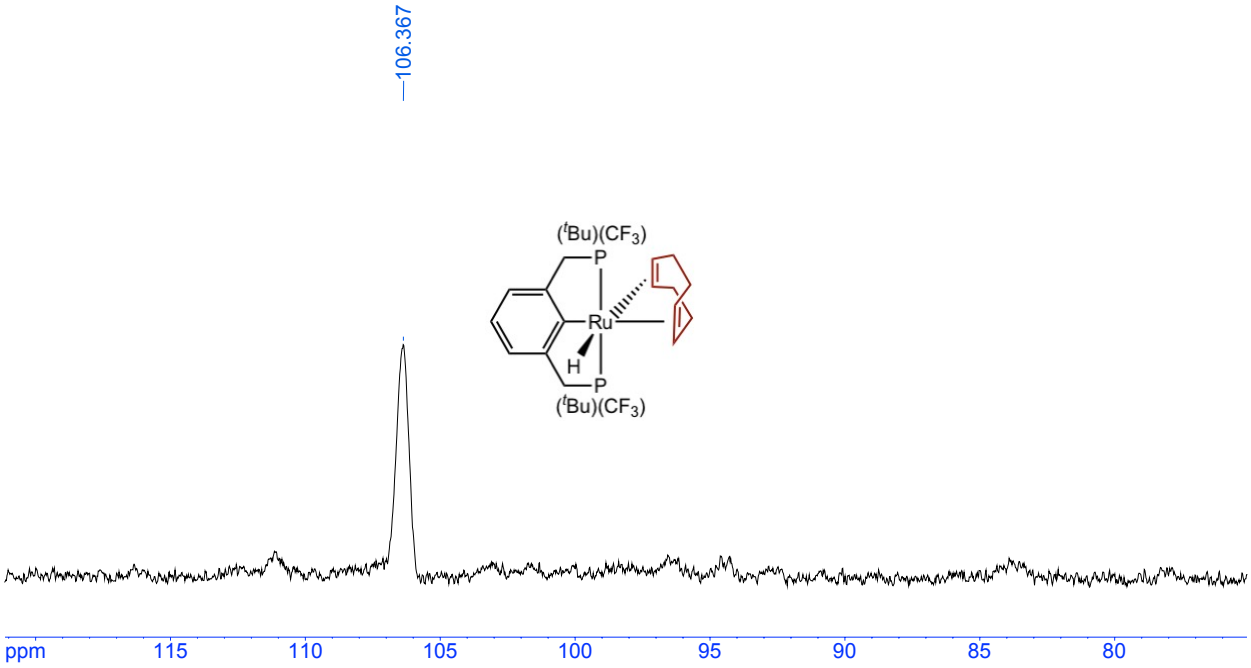

Figure S8b. ^{31}P (161.97 MHz) NMR spectrum for ($^{t\text{Bu,CF}_3}$PCP)Ru(cod)(H) (**1**) in benzene-d_6 at 25 ºC.

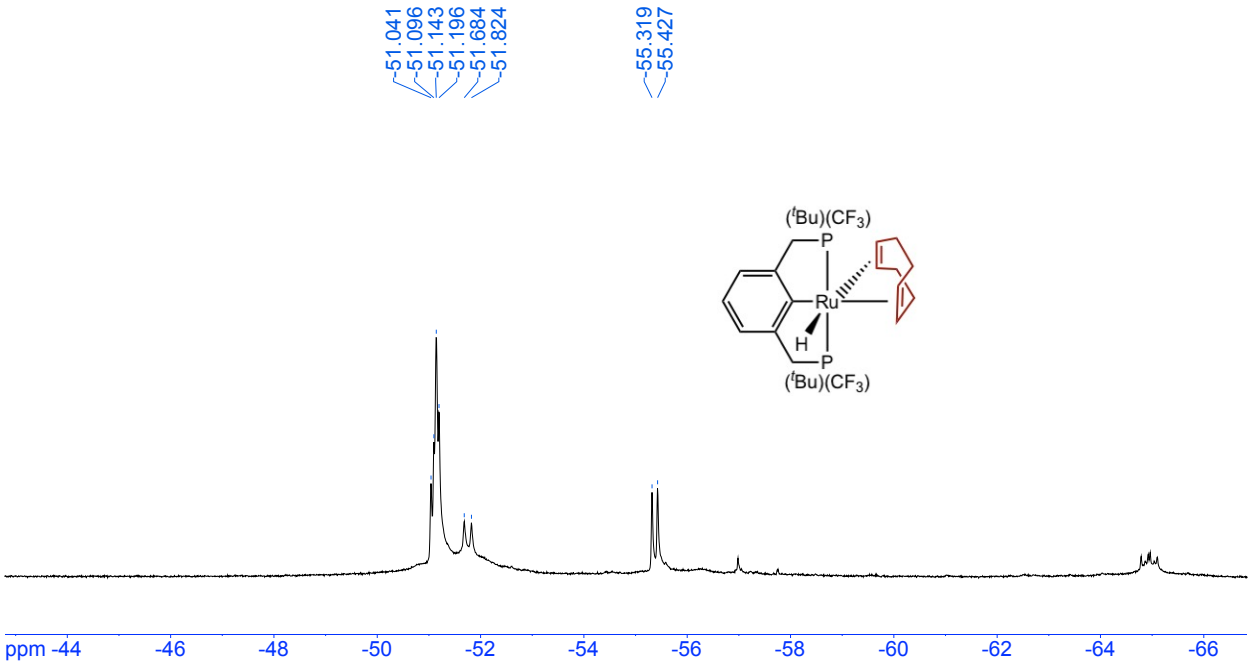

Figure S8c. ^{19}F (376.50 MHz) NMR spectrum for ($^{t\text{Bu,CF}_3}$PCP)Ru(cod)(H) (**1**) in benzene-d_6 at 25 ºC.

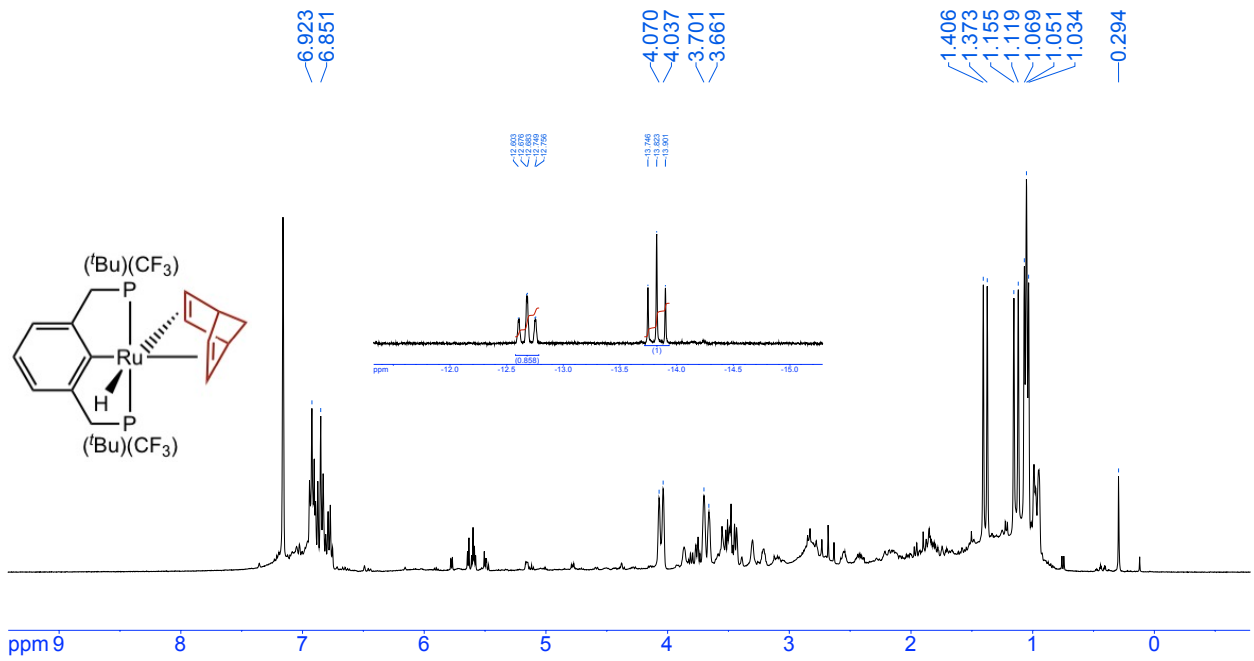

Figure S9a. ^{1}H (400.13 MHz) NMR spectrum for ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)(H) (**2**) in benzene-d_6 at 25 ºC.

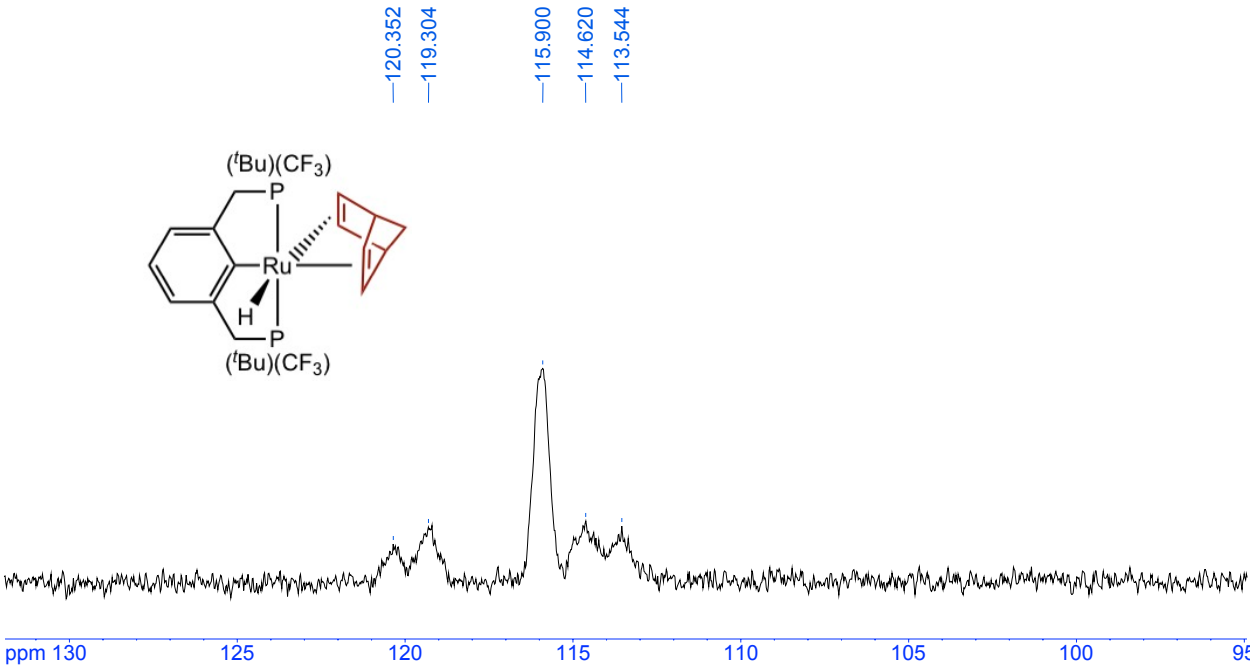

Figure S9b. ^{31}P (161.97 MHz) NMR spectrum for ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)(H) (**2**) in benzene-d_6 at 25 ºC.

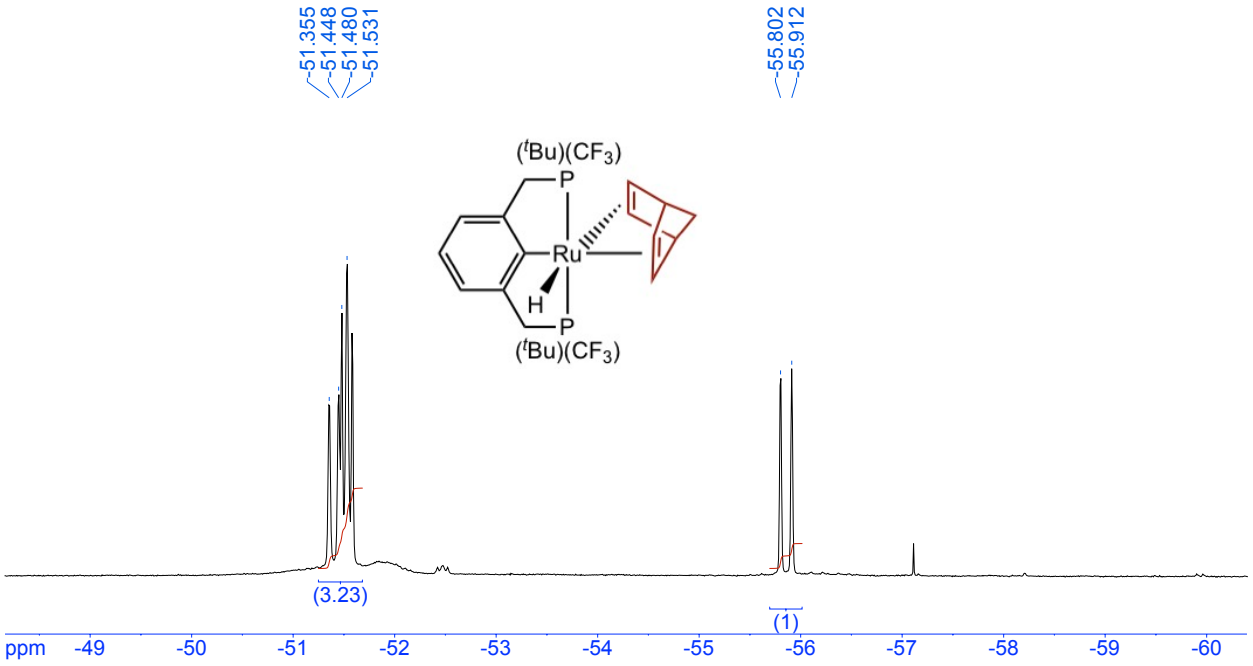

Figure S9c. ^{19}F (376.50 MHz) NMR spectrum for ($^{t\text{Bu,CF}_3}$PCP)Ru(nbd)(H) (**2**) in benzene-d_6 at 25 ºC.

Synthesis of $^{tBu,Cl,(BH_3)}$PCPH:

1,3-C_6H_4{$CH_2P(^tBu,Cl,(BH_3))$}$_2$ ($^{tBu,Cl,(BH_3)}$PCPH). 1.0M BH_3(THF) (6.4 mL, 6.4 mmol)) was added to a solution of ^{tBu,Cl}PCPH (1.08g, 3.1 mmol) in THF (30 mL) and the resulting colorless solution was stirred at ambient temperature for 2 h. Removal of the volatiles under vacuum yielded a white solid (0.73 g, 62%). Crystals suitable for X-ray diffraction were grown from a saturated THF solution (recrystallized yield: 0.28 g, 38%). ^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C): δ 7.3 – 6.8 (m, 4H; ArH), 2.99 (m, 2H; C$\underline{H}_a$H$_b$P), 2.81 (m, 2H; CH$_a\underline{H}_b$P), 0.97 (d, $^3J_{HP}$ = 13 Hz, 18H; C(CH$_3$)$_3$) 0.96 (br. m, 6H; BH_3). ^{31}P NMR (C_6D_6, 161.97 MHz, 25 °C): δ 133.8 (s)

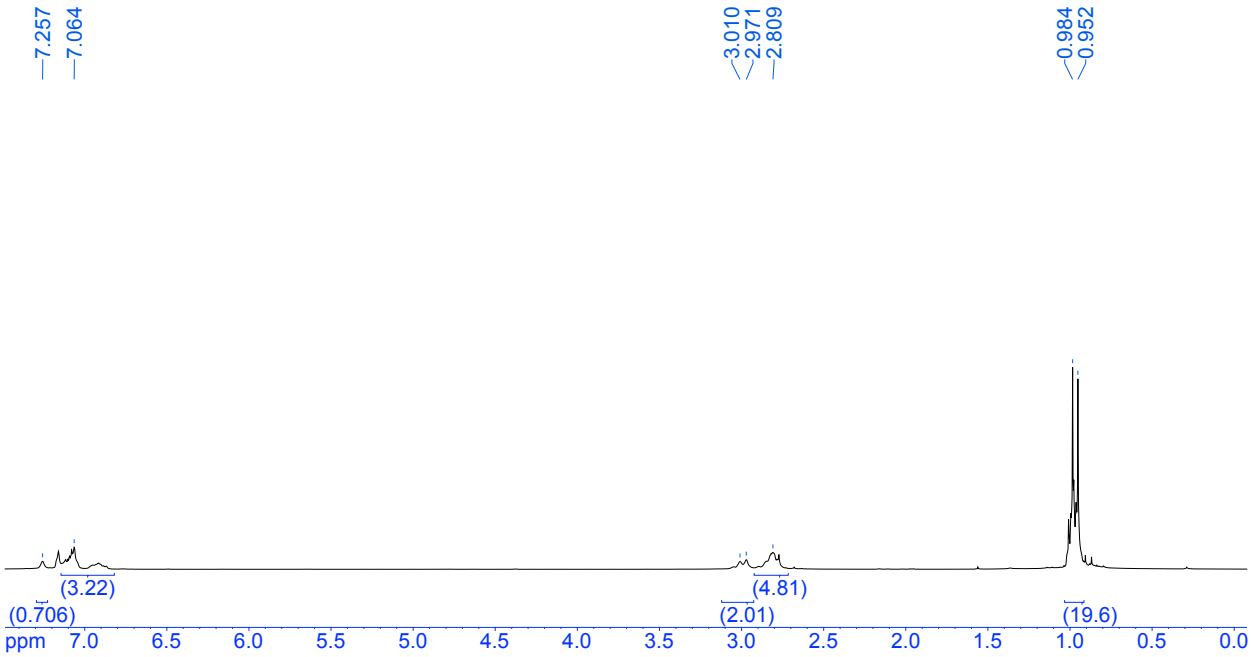

Figure S10a. ^{1}H (400.13 MHz) NMR spectrum for ^{tBu,Cl}PCPH$(BH_3)_2$ in benzene-d_6 at 25 ºC. Solvent impurity overlapping 2.81 ppm CH_2P resonance.

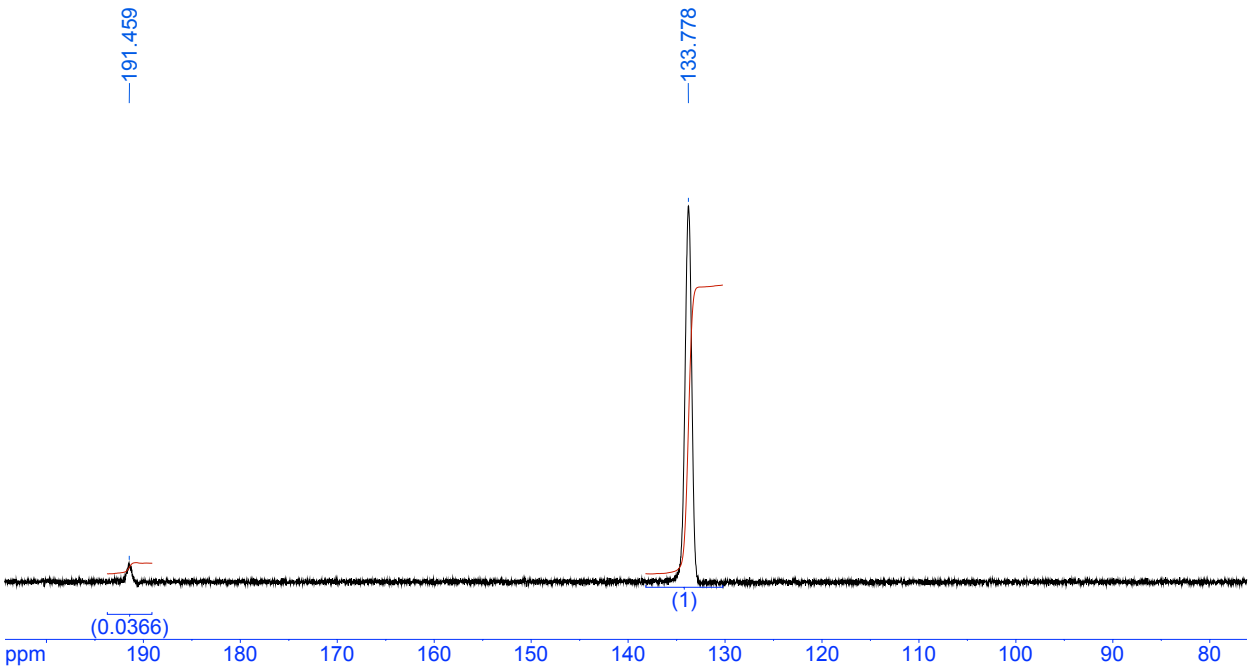

Figure S10b. ^{31}P (161.97 MHz) NMR spectrum for $^{t\text{Bu,Cl}}$PCPH$(BH_3)_2$ in benzene-d_6 at 25 ºC.

X-Ray Data for $^{t\text{Bu,Cl}}$PCPH$(BH_3)_2$. X-ray diffraction data were measured at 150 K on a Bruker SMART APEX II CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.5 kW power (50 kV, 30 mA). A colorless rectangular plate of PCPH(PCl(Bu^t)$_2$)of approximate dimensions 0.46 × 0.44 × 0.18 mm^3 was glued to a glass fiber using Paratone N oil. The detector was placed at a distance of 5.13 cm from the crystal during the data collection.

A series of narrow frames of data were collected with a scan width of 0.5˚ in ω or ϕ and an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT Software package[1] using a narrow-frame integration algorithm. The integration of the data using a triclinic unit cell yielded a total of 26414 reflections in the θ range of 1.78 to 33.73° of which 8626 were independent with $I \geq 2\sigma(I)$ (R_{int} = 0.0263). The data were corrected for absorption effects by the multi-scan method (SADABS). The structure was solved by the direct methods using the Bruker SHELXTL Software Package.[1] All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The asymmetric unit consists of a well ordered PCPH(PCl(Bu^t)$_2$) molecule. All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The H atoms of the centrZl phenylene ring and the two

methylene groups were also located in the Fourier maps and refined isotropically. The rest of the H atoms were placed in calculated positions and refined by a riding model with fixed thermal parameters. A view of the PCPH(PCl(Bu^t)$_2$) molecule is shown in Figure S11. The final refinement parameters are R_1 = 0.0639 and wR_2 = 0.1734 for data with $F > 4\sigma(F)$ giving the data to parameter ratio of 30.7. The refinement data for all data are R_1 = 0.0814 and wR_2 = 0.1886.

Acknowledgment. Financial support by the NSF (CHE 0619920) for the purchase of the Bruker Apex II Diffractometer is gratefully acknowledged.

References

APEX2 Software Suite V. 2.2, Bruker AXS Inc.: Madison, WI, 2008.

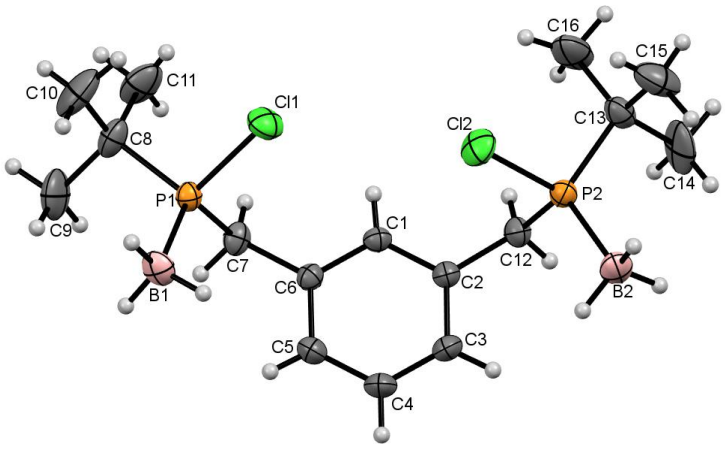

Figure S11. Molecular plot of *meso*-$^{t\text{Bu,Cl}}$PCPH(BH$_3$)$_2$ showing 50% probability thermal ellipsoids and the labeling scheme for unique atoms. Crystal data has been deposited with the CCDC, # 1853106

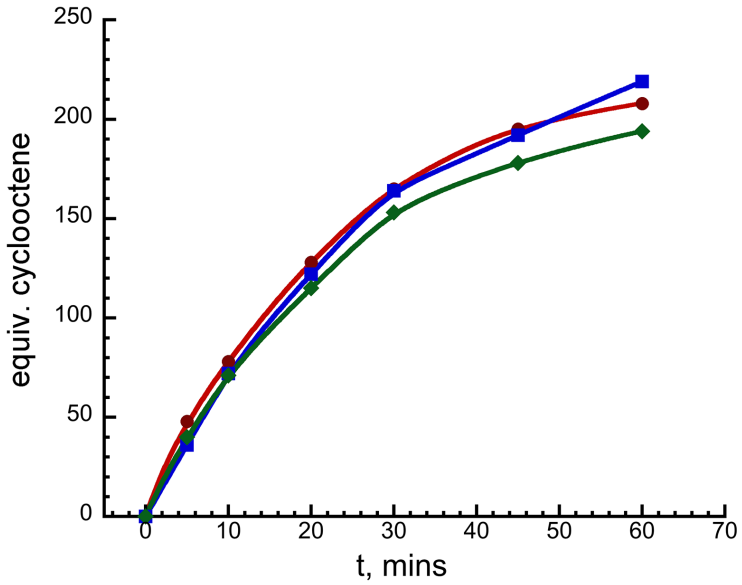

Figure S12. Comparative catalyst activity plot for ($^{t\text{Bu,CF3}}$PCP)Ru(nbd)H under 590 Torr of N_2 (■), under vacuum (●), and with 100 equiv of added H_2O (◆) in 1:1 cyclooctane/*tert*-butylethylene at 200 °C (0.033 mol % catalyst loading).