Supporting Information (SI)

Intermolecular Cyclization between Carboranylphosphines and Electron-Deficient Alkynes

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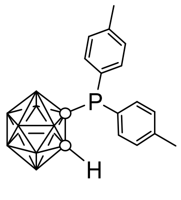
1. General methods and materials:

All reactions were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Dry THF and Toluene were obtained by distillation from Na/benzophenone. N-butyl lithium (1.6 M in hexane) were purchased from J&K Scientific Ltd. *o*-Carborane were purchased from United Boron (Zhengzhou) Energy Materials S&T LLC. Silica gel (200-300 mesh) was used for chromatographic separations. NMR spectra were obtained using Bruker AV300 spectrometer. Chemical shifts were expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. Element analytic data were obtained on a Thermo Electron Corporation flash EA 1112 element spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffract meter.

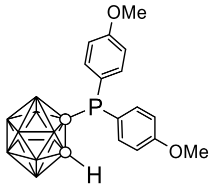
2. General procedure and spectral data of new compounds

Preparation of phosphino-*o*-carboranes (1).

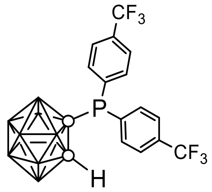
To a solution of *o*-Carborane (2.0 mmol) in 10 mL of dry THF, *n*-BuLi (1.1 equiv, 1.1 mmol) was added dropwise at -78 °C. The reaction mixture was stirred for 1h at this temperature, chlorophosphin (1.1 equiv, 1.1 mmol) was added to this mixture. The solution was slowly warmed to room temperature and stirred at this temperature for 2 h. The mixture was separated by silica gel column chromatography (CH_2Cl_2 / Petroleum ether = 1: 30) to obtain compound **1b-1e**.



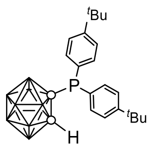
1b (584 mg, 82% yield). **Colorless crystal**. **m.p.** 135-136 ^{o}C. **^{31}P NMR (121 MHz, $CDCl_3$)**: δ 23.83. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.75-7.70 (m, 4H), 7.32 (d, *J* = 7.4 Hz, 4H), 3.52 (s, 1H, Cage C-H), 2.44 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 141.71 (s, 2C), 135.10 (d, *J* = 26.4 Hz, 4CH), 129.77 (d, *J* = 9.5 Hz, 4CH), 128.83 (d, *J* = 14.2 Hz, 2C), 73.44 (d, *J* = 76.5 Hz, C), 63.62 (d, *J* = 14.2 Hz, CH), 21.55 (s, $2CH_3$); **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -2.8 (d, J_{BH} = 145 Hz; 2B), -7.1 ~ -15.7 (m, 8B). **HRMS**: Calcd. For $C_{16}H_{26}B_{10}P$: $[M+H]^+$, 359.2697. Found: 359.2706.



1c (660 mg, 85% yield). **Colorless crystal**. **m.p.** 129-130 °C. **^{31}P NMR (121 MHz, CDCl$_3$)**: δ 22.62. **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 7.74-7.69 (m, 4H), 6.99 (d, J = 9.0 Hz, 4H), 3.86 (s, 6H, OMe), 3.46 (s, 1H, Cage C-H); **^{13}C NMR (75 MHz, CDCl$_3$)**: δ 161.92 (s, 2C), 136.71 (d, J = 27.0 Hz, 4CH), 123.31 (d, J =11.3 Hz, 2C), 114.50 (d, J = 10.5 Hz, 4CH), 74.03 (d, J = 75.0 Hz, C), 63.55 (d, J = 14.3 Hz, CH), 55.32 (s, 2OMe). **^{11}B NMR (96 MHz, CDCl$_3$)**: δ -2.0 (d, J_{BH} = 148 Hz; 2B), -6.8 ~ -13.3 (m, 8B). **HRMS**: Calcd. For $C_{16}H_{26}B_{10}O_2P$: $[M+H]^+$, 391.2595. Found: 391.2602.



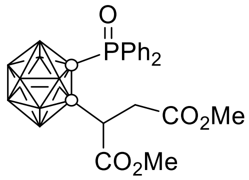
1d (678 mg, 73% yield). **Colorless crystal. m.p.** 145-146 °C. **^{31}P NMR (121 MHz, CDCl$_3$)**: δ 23.22. **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 7.96-7.90 (m, 4H), 7.78 (d, J = 7.6 Hz, 4H), 3.64 (s, 1H). **^{13}C NMR (75 MHz, CDCl$_3$)**: δ 136.07 (d, J = 18.4 Hz, 2C), 135.39 (d, J = 26.3 Hz, 4CH), 133.35 (q, J = 32.9 Hz, 2C), 125.75 (d, J = 3.7 Hz, 2CH), 125.87 (d, J = 3.7 Hz, 2CH), 123.54 (q, $J_{C\text{-}F}$ = 272.7 Hz, C), 71.19 (d, J = 69.8 Hz, C), 64.20 (d, J = 20.3 Hz, CH). **^{11}B NMR (96 MHz, CDCl$_3$)**: δ -0.7 ~ -3.1 (m, 2B), -6.5 ~ -15.6 (m, 8B). **HRMS**: Calcd. For $C_{16}H_{20}B_{10}F_6P$: $[M+H]^+$, 467.2132. Found: 467.2138.



1e (696 mg, 79% yield). **Colorless oil.** **^{31}P NMR (121 MHz, CDCl$_3$)**: δ 22.79. **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 7.76-7.71 (m, 4H), 7.49 (d, J = 9.0 Hz, 4H), 3.49 (s, 1H), 1.36 (s, 18H). **^{13}C NMR (75 MHz, CDCl$_3$)**: δ 154.62 (s, 2C), 134.95 (d, J = 26.4 Hz, 4CH), 128.84 (d, J = 13.5 Hz, 2C), 125.91 (d, J = 9.0 Hz, 4CH), 73.27 (d, J = 76.5 Hz, C), 63.50 (d, J = 14.2 Hz, CH), 34.93 (s, 2C), 31.14 (s, 9CH$_3$); **^{11}B NMR (96 MHz, CDCl$_3$)**: δ -2.1 (d, J_{BH} = 152 Hz; 2B), -6.9 ~ -13.2 (m, 8B). **HRMS**: Calcd. For $C_{22}H_{38}B_{10}P$: $[M+H]^+$, 443.3636. Found: 443.3629.

Preparation of compound 2a.

To a solution of phosphino-*o*-carboranes (1.0 mmol) in 10 mL of Aqueous THF, electron deficient alkynes (1.2 equiv, 1.2 mmol) were added dropwise at room temperature. The solution was stirred at this temperature for 24 h. After evaporation of the solvent, the crude product was chromatographed on silica gel (dichloromethane / petroleum ether = 1: 3) and we afforded **2a** as a colorless crystal.

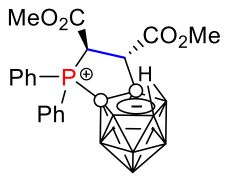


2a (244 mg, 50% yield). **Colorless crystal. m.p.** 169-170 °C. **^{31}P NMR (121 MHz, CDCl$_3$)**: δ 23.69. **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 8.19-8.02 (m, 4H), 7.70-7.52 (m, 6H), 4.34 (dd, $J_{C\text{-}P}$ = 9.0 Hz, J = 3.0 Hz, CH), 3.69 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 3.18-2.97 (m, 2H, CH_2). **^{13}C NMR (75 MHz, CDCl$_3$)**: δ 171.28 (s, C=O), 169.61 (s, C=O), 133.56 (d, $J_{C\text{-}P}$ = 3.0 Hz, CH), 133.52 (d, $J_{C\text{-}P}$ = 3.7 Hz, CH), 132.54 (d, $J_{C\text{-}P}$ = 9.0 Hz, 2CH), 132.20 (d, $J_{C\text{-}P}$ = 9.0 Hz, 2CH), 129.53 (d, $J_{C\text{-}P}$ = 94.5 Hz, C), 128.99 (d, $J_{C\text{-}P}$ = 12.8 Hz, 2CH), 128.77 (d, $J_{C\text{-}P}$ = 12.8 Hz, 2CH), 128.07 (d, $J_{C\text{-}P}$ = 91.5 Hz, C), 81.84 (s, C), 77.93 (d, $J_{C\text{-}P}$ = 51.5 Hz, C), 52.49 (s, OCH_3), 52.02 (s, OCH_3), 45.22 (s, CH), 37.59 (s, CH_2). **^{11}B NMR (96 MHz, CDCl$_3$)**: δ -0.8 ~ -2.9 (m, 2B), -8.9 ~ -11.7 (8B). **HRMS**: Calcd. For $C_{20}H_{30}B_{10}O_5P$: $[M+H]^+$, 491.2756. Found: 491.2778.

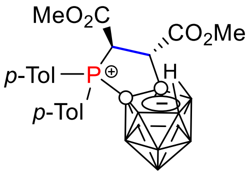
Preparation of *nido*-Carborane Fused Five-Membered Phosphacycles (3).

To a solution of phosphino-*o*-carboranes (1.0 mmol) in 5 mL of dry THF, electron deficient alkynes (1.2 equiv, 1.2 mmol) was added dropwise at 0 °C. The solution was slowly warmed to 50 °C and stirred at this temperature for 24 h. After evaporation of the solvent, the crude product was chromatographed on silica gel (dichloromethane / petroleum ether = 1: 3) and we afforded **3a-3l** as a colorless crystal.

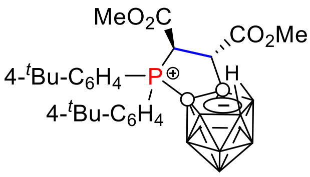
The yields are the overall yields for both diastereomers, while the characterization data and spectra are only for the separated major isomers (expect for 3e and 3e').



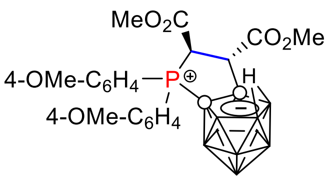
3a (350 mg, 76% yield). **Colorless crystal. m.p.** 181-182 °C. **^{31}P NMR (121 MHz, CDCl$_3$)**: δ 50.51, 48.02. **^{1}H NMR (300 MHz, CDCl$_3$)**: δ 7.89-7.79 (m, 4H), 7.74-7.64 (m, 4H), 7.59-7.52 (m, 2H), 4.68 (dd, $J_{C\text{-}P}$ = 18.0 Hz, J = 9.0 Hz, CH), 4.38 (d, J = 12.0 Hz, CH), 3.81 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3). **^{13}C NMR (75 MHz, CDCl$_3$)**: δ 169.35 (d, J = 15.8 Hz, C=O), 164.69 (s, C=O), 135.59 (d, $J_{C\text{-}P}$ = 3.0 Hz, CH), 135.46 (d, $J_{C\text{-}P}$ = 3.8 Hz, CH), 133.78 (d, $J_{C\text{-}P}$ = 10.5 Hz, 2CH), 133.20 (d, $J_{C\text{-}P}$ = 9.8 Hz, 2CH), 130.04 (d, $J_{C\text{-}P}$ = 9.0 Hz, 2CH), 129.87 (d, $J_{C\text{-}P}$ = 9.8 Hz, 2CH), 119.44 (d, $J_{C\text{-}P}$ = 87.8 Hz, C), 115.34 (d, $J_{C\text{-}P}$ = 87.0 Hz, C), 53.49 (s, OCH_3), 53.15 (s, OCH_3), 47.11 (d, J = 9.0 Hz, CH), 46.33 (d, J = 54 Hz, CH). **^{11}B NMR (96 MHz, CDCl$_3$)**: δ -7.6 ~ -19.3 (m, 7B), -28.1 (d, J_{BH} = 113 Hz; 1B), -34.5 (d, J_{BH} = 137 Hz; 1B). **HRMS**: Calcd. For $C_{20}H_{29}B_9O_4P$: $[M+H]^+$, 463.2635. Found: 463.2636.



3b (386 mg, 79% yield). **Colorless crystal. m.p.** 264-265 ºC. **^{31}P NMR (121 MHz, $CDCl_3$)**: 47.27 (s). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.72-7.65 (m, 2H, Ph), 7.51-7.42 (m, 6H, Ph), 4.62 (dd, J_{C-P} = 17.0 Hz, J = 10.8 Hz, CH), 4.35 (d, J = 10.8 Hz, CH), 3.79 (s, 3H, OCH_3), 3.42 (s, 3H, OCH_3), 2.52 (s, 3H, CH_3), 2.49 (s, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 169.48 (d, J = 15.8 Hz, C=O), 164.88 (d, J_{C-P} = 1.6 Hz, C=O), 147.08 (d, J_{C-P} = 3.0 Hz, CH), 146.87 (d, J_{C-P} = 3.0 Hz, CH), 133.74 (d, J_{C-P} = 10.9 Hz, 2CH), 133.11 (d, J_{C-P} = 10.9 Hz, 2CH), 130.79 (d, J_{C-P} = 11.3 Hz, 2CH), 130.61 (d, J_{C-P} = 12.9 Hz, 2CH), 115.78 (d, J = 91.6 Hz, C), 111.82 (d, J = 89.9 Hz, C), 53.42 (s, OCH_3), 53.07 (s, OCH_3), 47.08 (d, J = 8.8 Hz, CH), 46.27 (d, J = 51.7 Hz, CH), 21.99 (s, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -9.6 ~ -19.6 (m, 7B), -28.7 (d, J_{BH} = 105 Hz; 1B), -34.9 (d, J_{BH} = 146 Hz; 1B). **HRMS**: Calcd. For $C_{22}H_{33}B_9O_4P$: $[M+H]^+$, 491.2948. Found: 491.2963. **Anal.**: Calcd. For $C_{22}H_{32}B_9O_4P$: C 54.06; H 6.60; Found: C 53.89; H 6.48.

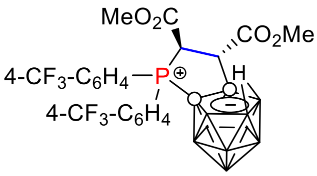


3c (452 mg, 79% yield). **Colorless crystal. m.p.** 161-162 ºC. **^{31}P NMR (121 MHz, $CDCl_3$)**: δ 46.21. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.78-7.65 (m, 6H), 7.54-7.47 (m, 2H), 4.63 (dd, J_{C-P} = 15.0 Hz, J = 9.0 Hz, CH), 4.35 (d, J = 12.0 Hz, CH), 3.81 (s, 3H, OCH_3), 3.40 (s, 3H, OCH_3), 1.40 (s, 9H, $3CH_3$), 1.37 (s, 9H, $3CH_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 169.50 (d, J = 15.8 Hz, C=O), 164.92 (s, C=O), 159.79 (d, J_{C-P} = 3.0 Hz, C), 159.53 (d, J_{C-P} = 3.0 Hz, C), 133.77 (d, J_{C-P} = 10.5 Hz, 2CH), 133.05 (d, J_{C-P} = 10.5 Hz, 2CH), 127.07 (d, J_{C-P} = 8.2 Hz, 2CH), 126.89 (d, J_{C-P} = 8.2 Hz, 2CH), 115.75 (d, J_{C-P} = 90.8 Hz, C), 111.87 (d, J = 88.5 Hz, C), 53.33 (s, OCH_3), 53.06 (s, OCH_3), 47.06 (d, J = 8.3 Hz, CH), 46.39 (d, J = 54.8 Hz, CH), 35.57 (s, C), 30.91 (s, 9H, CH_3), 30.88 (s, 9H, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -8.4 ~ -20.1 (m, 7B), -29.0 (1B), -35.4 (1B). **HRMS**: Calcd. For $C_{28}H_{44}B_9NaO_4P$: $[M+Na]^+$, 597.3707. Found: 597.3712.

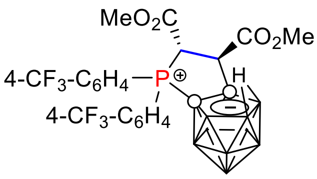


3d (427 mg, 82% yield). **Colorless crystal. m.p.** 244-245 ºC. **^{31}P NMR (121 MHz, $CDCl_3$)**: 46.53. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.76-7.69 (m, 2H, Ph), 7.53-7.46 (m, 2H, Ph), 7.17-7.11 (m, 4H, Ph), 4.57 (dd, J_{C-P} = 17.0 Hz, J = 10.8 Hz, CH), 4.33 (d, J = 10.8 Hz, CH), 3.95 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 3.44 (s, 3H, OCH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 169.52 (d, J = 15.9 Hz, C=O), 165.19 (d, J_{C-P} = 3.0 Hz, CH), 165.05 (s, C=O), 165.03 (d, J_{C-P} = 3.0 Hz, CH), 135.84 (d, J_{C-P} = 12.2 Hz, 2CH), 135.19 (d, J_{C-P} = 11.8 Hz, 2CH), 115.77 (d, J_{C-P} = 8.2 Hz, 2CH), 115.58 (d, J_{C-P} = 7.6 Hz, 2CH), 109.10 (d, J

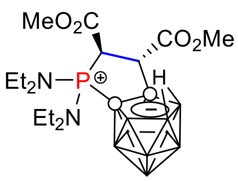
= 96.9 Hz, C), 105.59 (d, J = 95.9 Hz, C), 55.86 (s, OCH_3), 55.84 (s, OCH_3), 53.39 (s, OCH_3), 53.01 (s, OCH_3), 47.02 (d, J = 8.3 Hz, CH), 46.55 (d, J = 56.2 Hz, CH). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -9.3 ~ -19.6 (m, 7B), -28.2 (1B), -34.9 (d, J_{BH} = 134 Hz; 1B). **HRMS**: Calcd. For $C_{22}H_{33}B_9O_6P$: $[M+H]^+$, 523.2847. Found: 523.2851. **Anal**.: Calcd. For $C_{22}H_{32}B_9O_6P$: C 50.74; H 6.19; Found: C 51.03; H 6.31.



3e (305 mg, 51% yield). **Colorless crystal. m.p.** 269-270 °C. **^{31}P NMR (121 MHz, $CDCl_3$)**: δ 48.01. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.02-7.94 (m, 6H, Ph), 7.76-7.69 (m, 2H, Ph), 4.80 (dd, J_{C-P} = 18.0 Hz, J = 12.0 Hz, CH), 4.37 (d, J = 12.0 Hz, CH), 3.84 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 168.87 (d, J = 16.6 Hz, C=O), 164.19 (d, J_{C-P} = 1.1 Hz, C=O), 137.22 (q, J_{C-F} = 33.2 Hz, 2C), 134.54 (d, J_{C-P} = 11.1 Hz, 2CH), 133.87 (q, J_{C-P} = 10.6 Hz, 2CH), 127.03 (d, J_{C-P} = 3.5 Hz, 2CH), 126.86 (d, J_{C-P} = 3.5 Hz, 2CH), 124.54 (q, J_{C-F} = 272.7 Hz, C), 123.63 (d, J = 87.6 Hz, C), 119.61 (d, J = 86.6 Hz, C), 53.96 (s, OCH_3), 53.35 (s, OCH_3), 47.26 (d, J = 16.7 Hz, CH), 46.81 (d, J_{C-P} = 29.4 Hz, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -8.4 ~ -19.9 (m, 7B), -28.3(1B), -34.8 (d, J_{BH} = 121 Hz; 1B). **HRMS**: Calcd. For $C_{22}H_{27}B_9F_6O_4P$: $[M+H]^+$, 599.2383. Found: 599.2381.

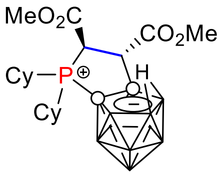


3e' (131 mg, 22% yield). **Colorless crystal. m.p.** 238-239 °C. **^{31}P NMR (242 MHz, $CDCl_3$)**: δ 50.76. **^{1}H NMR (600 MHz, $CDCl_3$)**: δ 8.11-8.07 (m, 2H, Ph), 7.90-7.85 (m, 4H, Ph), 7.77-7.74 (m, 2H, Ph), 4.59 (dd, J = 18.0 Hz, J = 6.0 Hz, CH), 3.79 (dd, J = 30.0 Hz, J = 6.0 Hz, CH), 3.77 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3). **^{13}C NMR (150 MHz, $CDCl_3$)**: δ 173.10 (s, C=O), 164.29 (s, C=O), 138.19 (d, J_{C-P} = 12.0 Hz, 2CH), 136.77 (dd, J = 12.0 Hz, J = 3.0 Hz, C), 136.55 (dd, J = 13.5 Hz, J = 3.0 Hz, C), 133.43 (d, J_{C-P} = 10.5 Hz, 2CH), 126.49 (dd, J_{C-P} = 13.5 Hz, J_{C-F} = 3.0 Hz, 2CH), 124.99 (dd, J_{C-P} = 13.5 Hz, J_{C-F} = 3.0 Hz, 2CH), 123.83 (d, J = 85.5 Hz, C), 122.05 (q, J_{C-F} = 271.5 Hz, C), 122.79 (d, J = 88.5 Hz, C), 122.73 (q, J_{C-F} = 271.5 Hz, C), 53.96 (s, OCH_3), 52.78 (s, OCH_3), 50.67 (d, J = 3.0 Hz, CH), 48.79 (d, J_{C-P} = 57.0 Hz, CH_3). **^{11}B NMR (192 MHz, $CDCl_3$)**: δ -6.9 ~ -21.9 (m, 7B), -27.5 (1B), -34.0 (d, J_{BH} = 129 Hz; 1B). **HRMS**: Calcd. For $C_{22}H_{26}B_9F_6O_4NaP$: $[M+Na]^+$, 621.2239. Found: 621.2239.

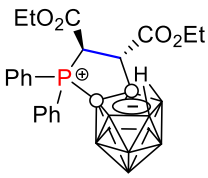


3f (338 mg, 75% yield). **Colorless crystal. m.p.** 213-214 °C. **^{31}P NMR ($CDCl_3$)**: δ 76.91. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 4.06 (dd, J_{C-P} = 12.0 Hz, J = 12.0 Hz, 1H, CH), 3.79 (d, J = 3.0 Hz, 1H, CH), 3.78 (s, OCH_3), 3.76 (s, OCH_3), 3.36-3.26 (m, 4H, $2CH_2$), 3.22-3.10

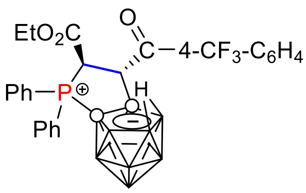
(m, 4H, $2CH_2$), 1.27 (d, J = 6.0 Hz, 6H, $2CH_3$), 1.20 (d, J = 6.0 Hz, 6H, $2CH_3$). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 169.59 (d, J = 17.3 Hz, C=O), 166.03 (d, J = 2.3 Hz, C=O), 53.64 (s, OCH_3), 52.83 (s, OCH_3), 46.52 (s, CH), 45.94 (d, J = 62.3 Hz, CH), 40.24 (d, J = 3.7 Hz, CH_2), 38.80 (d, J = 4.5 Hz, CH_2), 12.87 (d, J = 3.8 Hz, CH_3), 12.70 (d, J = 3.8 Hz, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -10.1 ~ -20.8 (m, 7B), -28.4 (d, J_{BH} = 129 Hz; 1B), -34.5 (d, J_{BH} = 145 Hz; 1B). **HRMS**: Calcd. For $C_{16}H_{39}B_9N_2O_4P^+$, $[M+H]^+$, 453.3479. Found: 453.3480.



3g (307 mg, 65% yield). **Colorless crystal. m.p.** 289-290 °C. **^{31}P NMR ($CDCl_3$)**: 53.43, 59.36. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 4.16 (d, J = 12 Hz, 1H, CH), 4.00 (dd, J = 18 Hz, J = 9 Hz, 1H, CH), 3.81 (s, 3H, OMe), 3.77 (s, 3H, OMe), 2.73-2.61 (m, 2H, CH), 2.48-2.35 (m, 2H, CH), 2.07-1.84 (m, 10H, CH_2, overlapped with BHs of *nido*-carborane), 1.34-1.27 (m, 8H, CH_2, overlapped with BHs of *nido*-carborane). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.62 (d, J = 12.9 Hz, CO,), 165.79 (s, CO), 53.68 (s, OMe), 52.93 (s, OMe), 48.70 (d, J = 6.9 Hz, CH), 41.48 (d, J = 39.5 Hz, CH), 35.88 (d, J = 46.7 Hz, CH), 32.82 (d, J = 36.8 Hz, CH), 27.76 (d, J = 2.2 Hz, CH_2), 26.72 (d, J = 5.3 Hz, CH_2), 26.58 (s, CH_2), 26.35 (d, J = 8.3 Hz, CH_2), 26.25 (d, J = 9.0 Hz, CH_2), 26.17 (d, J = 3.7 Hz, CH_2), 25.40 (s, CH_2), 25.03 (s, CH_2), 24.97 (s, $2CH_2$). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -7.9 ~ -20.8 (m, 7B), -28.5 (d, J_{BH} = 132 Hz; 1B), -34.5 (d, J_{BH} = 151 Hz; 1B). **HRMS**: Calcd. For $C_{20}H_{41}B_9O_4P^+$: $[M+H]^+$, 475.3574. Found: 475.3574.

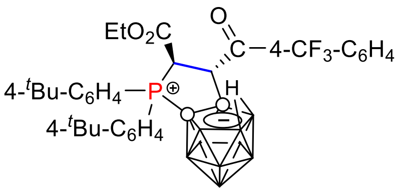


3h (342 mg, 70% yield). **Colorless crystal. m.p.** 162-163 °C. **^{31}P NMR (121 MHz, $CDCl_3$)**: 47.45. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.90-7.78 (m, 4H), 7.74-7.62 (m, 4H), 7.57-7.50 (m, 2H), 4.65 (dd, $J_{C\text{-}P}$ = 18.0 Hz, J = 12.0 Hz, 1H, CH), 4.37 (d, J = 9.0 Hz, 1H, CH), 4.29-4.22 (m, 2H, CH_2), 3.97-3.76 (m, 2H, CH_2), 1.35 (t, J = 9.0 Hz, 3H, CH_3), 0.94 (t, J = 9.0 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$):** δ 168.83 (d, J = 16.5 Hz, C=O), 164.21 (s, C=O), 135.49 (d, $J_{C\text{-}P}$ = 3.0 Hz, CH), 135.42 (d, $J_{C\text{-}P}$ = 3.0 Hz, CH), 133.85 (d, $J_{C\text{-}P}$ = 10.5 Hz, 2CH), 133.31 (d, $J_{C\text{-}P}$ = 10.5 Hz, 2CH), 129.95 (d, $J_{C\text{-}P}$ = 12.7 Hz, 2CH), 129.78 (d, $J_{C\text{-}P}$ = 12.7 Hz, 2CH), 119.71 (d, $J_{C\text{-}P}$ = 87.8 Hz, C), 115.38 (d, $J_{C\text{-}P}$ = 86.3 Hz, C), 63.12 (s, CH_2), 62.46 (s, CH_2), 47.10 (d, $J_{C\text{-}P}$ = 8.3 Hz, CH), 46.46 (d, $J_{C\text{-}P}$ = 54.0 Hz, CH), 14.05 (s, CH_3), 13.66 (s, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -8.8 ~ -19.3 (m, 7B), -28.0 (d, J_{BH} = 112 Hz; 1B), -34.5 (d, J_{BH} = 142 Hz; 1B). **HRMS**: Calcd. For $C_{22}H_{32}B_9NaO_4P$: $[M+Na]^+$, 513.2768. Found: 513.2772.

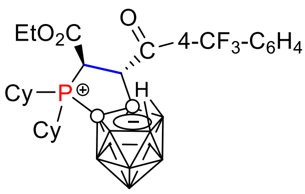


3i (400 mg, 68% yield). **Colorless crystal. m.p.** 256-257 °C. **^{31}P**

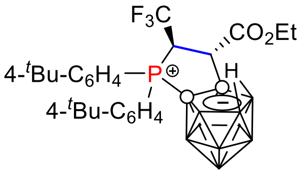
NMR (121 MHz, $CDCl_3$): 47.19. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.20 (d, J_{C-P} = 9.0 Hz, 2H, CH), 7.95-7.60 (m, 12H, CH), 5.40 (d, J = 9.0 Hz, 1H, CH), 5.10 (dd, J_{C-P} = 15.0 Hz, J = 9.0 Hz, 1H, CH), 3.94-3.69 (m, 2H, CH_2), 0.91 (t, J = 6.0 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 193.65 (d, J = 11.3 Hz, C=O), 164.41 (s, C=O), 138.99 (s, C), 135.64 (d, J_{C-P} = 3.8 Hz, CH), 135.34 (d, J_{C-P} = 11.3 Hz, CH), 135.06 (q, J_{C-F} = 32.3 Hz, C), 133.86 (d, J_{C-P} = 10.5 Hz, 2CH), 133.34 (d, J_{C-P} = 9.8 Hz, 2CH), 130.12 (d, J_{C-P} = 12.7 Hz, 2CH), 129.87 (d, J_{C-P} = 13.5 Hz, 2CH), 129.82 (s, 2CH), 125.65 (q, J_{C-F} = 3.8 Hz, 2CH), 123.50 (d, J_{C-F} = 271.5 Hz, C), 119.76 (d, J_{C-P} = 88.5 Hz, C), 115.38 (d, J_{C-P} = 86.3 Hz, C), 63.36 (s, CH_2), 47.53 (d, J_{C-P} = 8.3 Hz, CH), 46.68 (d, J_{C-P} = 54.8 Hz, CH), 13.64 (s, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -8.6 ~ -16.8 (m, 7B), -28.2 (1B), -34.2 (d, J_{BH} = 131 Hz; 1B). **HRMS**: Calcd. For $C_{27}H_{31}B_9F_3NaO_3P$: $[M+Na]^+$, 613.2693. Found: 613.2723.



3j (504 mg, 72% yield). **Colorless crystal. m.p.** 201-202 °C. **^{31}P NMR (121 MHz, $CDCl_3$)**: 47.09. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.23 (d, J_{C-P} = 9.0 Hz, 2H, CH), 7.87-7.69 (m, 8H, CH), 7.62-7.55 (m, 2H, CH), 5.41 (d, J = 12.0 Hz, 1H, CH), 5.06 (dd, J_{C-P} = 18.0 Hz, J = 9.0 Hz, 1H, CH), 3.90-3.73 (m, 2H, CH_2), 1.40 (s, 9H, CH_3), 1.36 (s, 9H, CH_3), 0.86 (t, J = 6.0 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 193.82 (d, J = 12.0 Hz, C=O), 164.65 (s, C=O), 159.86 (d, J_{C-P} = 3.0 Hz, C), 159.59 (d, J_{C-P} = 3.0 Hz, C), 139.09 (s, C), 134.93 (q, J_{C-F} = 32.3 Hz, C), 133.84 (d, J_{C-P} = 11.3 Hz, 2CH), 133.22 (d, J_{C-P} = 11.3 Hz, 2CH), 129.85 (s, 2CH), 127.18 (d, J_{C-P} = 13.5 Hz, 2CH), 126.89 (d, J_{C-P} = 13.5 Hz, 2CH), 125.62 (q, J_{C-F} = 3.8 Hz, 2CH), 125.54 (q, J_{C-F} = 271.5 Hz, C), 116.13 (d, J_{C-P} = 90.7 Hz, C), 111.88 (d, J_{C-P} = 89.3 Hz, C), 63.20 (s, CH_2), 47.52 (d, J_{C-P} = 7.5 Hz, CH), 46.80 (d, J_{C-P} = 54.8 Hz, CH), 35.58 (s, C), 30.92 (s, CH_3), 30.86 (s, CH_3), 13.63 (s, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -8.2 ~ -16.8 (m, 7B), -28.2 (1B), -33.9 (1B). **HRMS**: Calcd. For $C_{35}H_{47}B_9F_3NaO_3P$: $[M+Na]^+$, 725.3945. Found: 725.3948.



3k (350 mg, 69% yield). **Colorless crystal. m.p.** 282-283 °C. **^{31}P NMR (121 MHz, $CDCl_3$)**: 57.04, 53.07. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.16 (d, J_{C-P} = 9.0 Hz, 2H, CH), 7.76 (d, J_{C-P} = 9.0 Hz, 2H, CH), 5.13 (d, J = 9.0 Hz, 1H, CH), 4.41 (dd, J_{C-P} = 18.0 Hz, J = 9.0 Hz, 1H, CH), 4.29-4.08 (m, 2H, CH_2), 2.75 (m, 1H, CH), 2.47 (m, 1H, CH), 2.13 (s, 2H, overlapped with BHs of *nido*-carborane), 1.99-1.83 (m, 10H, CH_2), 1.58-1.34 (m, 8H, CH_2, overlapped with BHs of *nido*-carborane), 1.22 (t, J = 6.0 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 193.81 (d, J = 9.8 Hz, C=O), 165.38 (s, C=O), 138.82 (s, C), 135.03 (q, J_{C-F} = 32.3 Hz, C), 129.64 (s, 2CH), 125.62 (q, J_{C-F} = 3.7 Hz, 2CH), 123.50 (q, J_{C-F} = 271.5 Hz, C), 63.42 (s, CH_2), 48.81 (d, J_{C-P} = 5.3 Hz, CH), 42.11 (d, J_{C-P} = 43.5 Hz, CH), 36.06 (d, J_{C-P} = 43.5 Hz, CH), 33.24 (d, J_{C-P} = 36.8 Hz, CH), 27.00 (d, J_{C-P} = 4.5 Hz, CH_2), 26.76 (d, J_{C-P} = 14.3 Hz, CH_2), 26.66 (s, CH_2), 26.48 (s, CH_2), 26.38 (s, CH_2), 26.27 (d, J_{C-P} = 9.8 Hz, CH_2), 25.43 (d, J_{C-P} = 1.5 Hz, CH_2), 25.30 (d, $J_{C\text{-}P}$ = 3.0 Hz, CH_2), 25.18 (d, $J_{C\text{-}P}$ = 4.5 Hz, CH_2), 25.02 (d, $J_{C\text{-}P}$ = 1.5 Hz, CH_2), 13.87 (s, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -10.0 ~ -22.6 (m, 7B), -28.9 (1B), -34.0 (d, J_{BH} = 114 Hz; 1B). **HRMS**: Calcd. For $C_{27}H_{43}B_9F_3NaO_3P$: $[M+Na]^+$, 625.3632. Found: 625.3645.



3l (352 mg, 59% yield). **Colorless crystal. m.p.** 180-181 °C. **^{31}P NMR (121 MHz, $CDCl_3$)**: 45.36 ppm. **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 7.74-7.52 (m, 8H, CH), 4.47-4.37 (m, 1H, CH), 4.32-4.25 (m, 2H, CH_2), 4.07 (d, J = 12.0 Hz, 1H, CH), 1.41 (s, 9H, CH_3), 1.40 (s, 9H, CH_3), 1.35 (t, J = 6.0 Hz, 3H, CH_3). **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 167.45 (d, J = 15.0 Hz, C=O), 160.59 (d, J = 3.7 Hz, C), 160.21 (d, $J_{C\text{-}P}$ = 3.7 Hz, C), 134.57 (d, $J_{C\text{-}P}$ = 11.3 Hz, 2CH), 132.77 (d, $J_{C\text{-}P}$ = 10.5 Hz, 2CH), 127.35 (d, $J_{C\text{-}P}$ = 9.0 Hz, 2CH), 127.17 (d, $J_{C\text{-}P}$ = 9.0 Hz, 2CH), 123.10 (q, $J_{C\text{-}F}$ = 277.5 Hz, C), 113.91 (d, $J_{C\text{-}P}$ = 90.0 Hz, C), 111.08 (d, $J_{C\text{-}P}$ = 90.0 Hz, C), 62.81 (s, CH_2), 46.12 (d, $J_{C\text{-}P}$ = 7.5 Hz, CH), 45.20 (dd, $J_{C\text{-}P}$ = 57.8 Hz, $J_{C\text{-}F}$ = 29.3 Hz, CH), 35.66 (s, C), 30.86 (s, CH_3), 14.00 (s, CH_3). **^{11}B NMR (96 MHz, $CDCl_3$)**: δ -4.7 ~ -20.5 (m, 7B), -24.9 (1B), -37.5 (d, J_{BH} = 149 Hz; 1B). **HRMS**: Calcd. $C_{28}H_{43}B_9F_3NaO_2P$: $[M+Na]^+$, 621.3682. Found: 621.3690.

3. Reaction with extra dry THF and deuterated substrate.

a) Following the general procedure, the reaction was set up in a N_2-filled glovebox with extra dry THF (99.5%, with molecular sieves and Enegryseal). The ^{31}P NMR of the reaction mixture after 24 h was shown in Fig. S1. Apart from the products (chemical shifts: 46.72, 49.61), the main remaining species were proposed to be the phosphonium salts (*trans* and *cis* mixtures, chemical shift:28.18, 31.51). The crude ^{1}H NMR of the mixture was also shown (see Fig. S2).

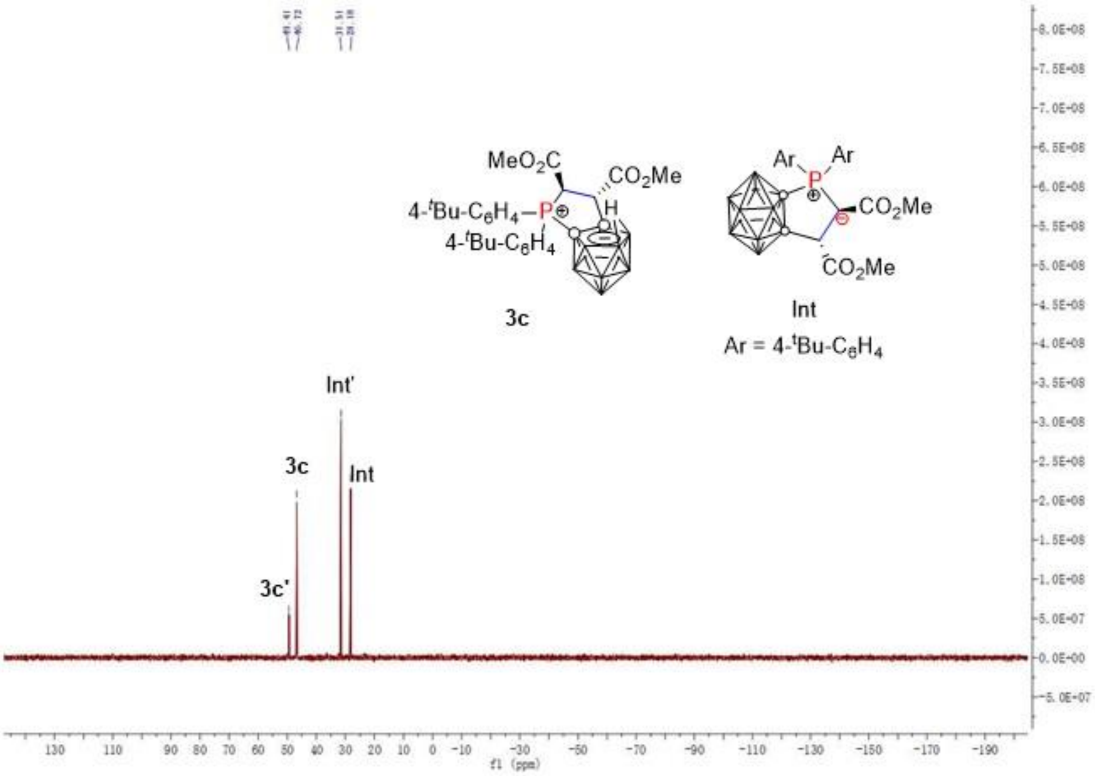


Figure S1. ^{31}P NMR spectrum of reaction mixture in C_6D_6

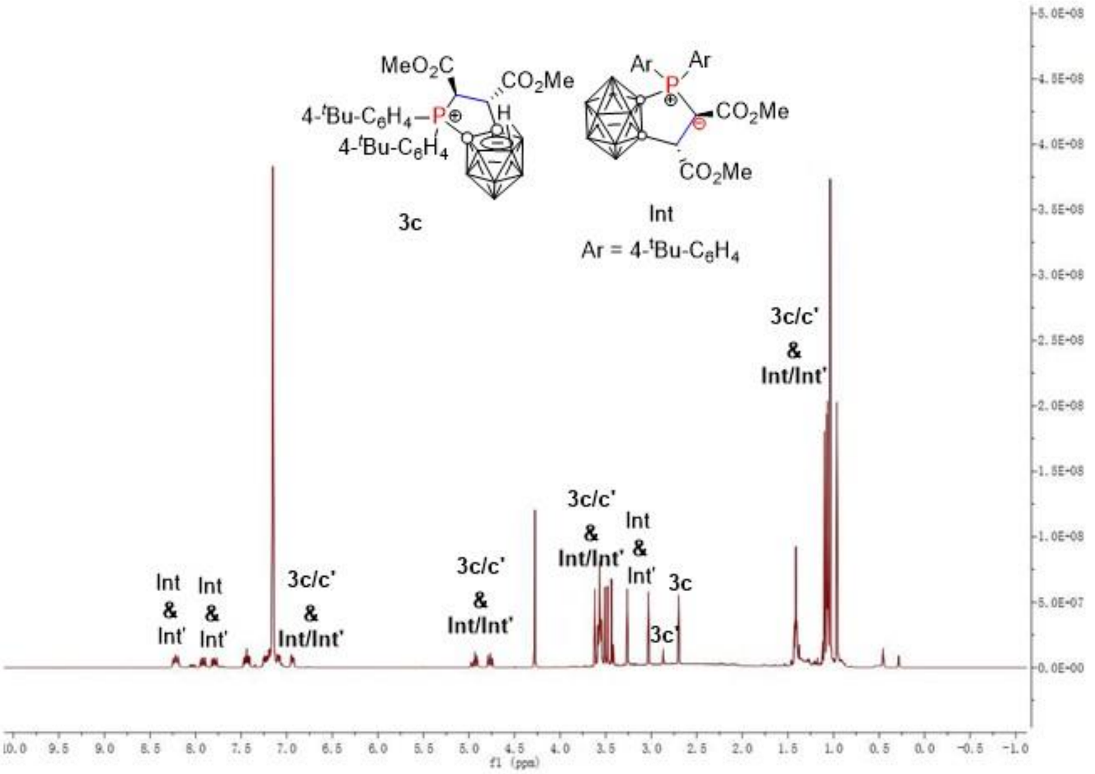
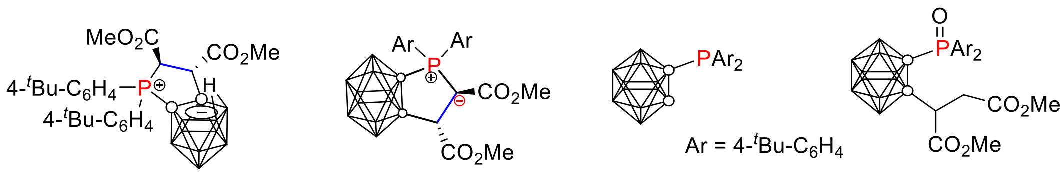


Figure S2. ^1H NMR spectrum of reaction mixture in C_6D_6

b) Following the general procedure, the reaction was set up with *d8*-THF in a NMR tube (0.1 mmol **1e**, 0.12 mmol DMAD, and 0.6 ml undried *d8*-THF at 60 °C). The reaction was monitored using ^{31}P NMR measurement at indicated time (see Fig. S3). As can be seen here, the starting material 1e was almost fully consumed after 8 hours, affording mainly the intermediates (**Int** & **Int'**). These intermediates gradually undergone deboronation or hydrolysis to give *nido*-*O*-carboranes (**3c** & **3c'**) or phosphorous oxide (**2b,** confirmed by comparison with **2a**).



3c Int **1e** 2b

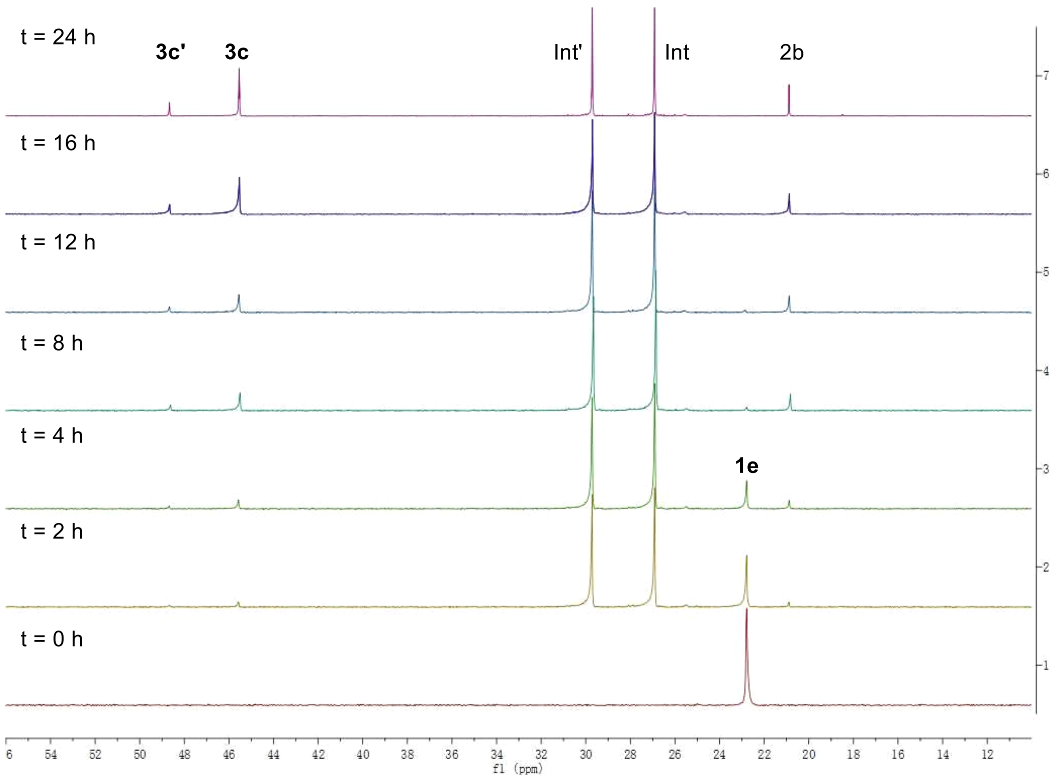


Figure S3. ^{1}H NMR progression of reaction with *d8*-THF in a NMR tube

c) Based on a modified procedure, we prepared deuterated substrate **1e'** (95% D) and run the reaction using the general procedure. In the product **3c'**, the peak of proton next to phosphorus changed from *dd* to *d* in ^{1}H NMR. The integration of the proton connected to the nido-carborane changed from 1.0 to 0.05 (95% D). This indicates that the vinyl proton is originated from cage CH.

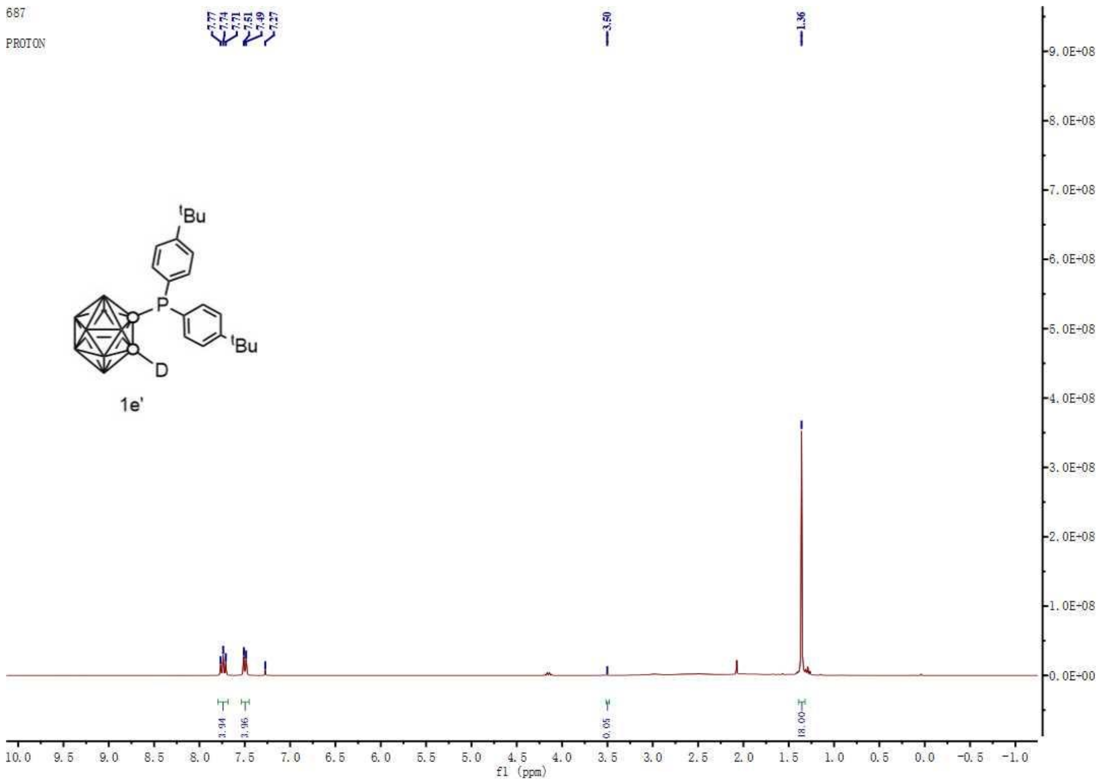


Figure S4. ^{1}H NMR spectrum of **1e'** in $CDCl_3$

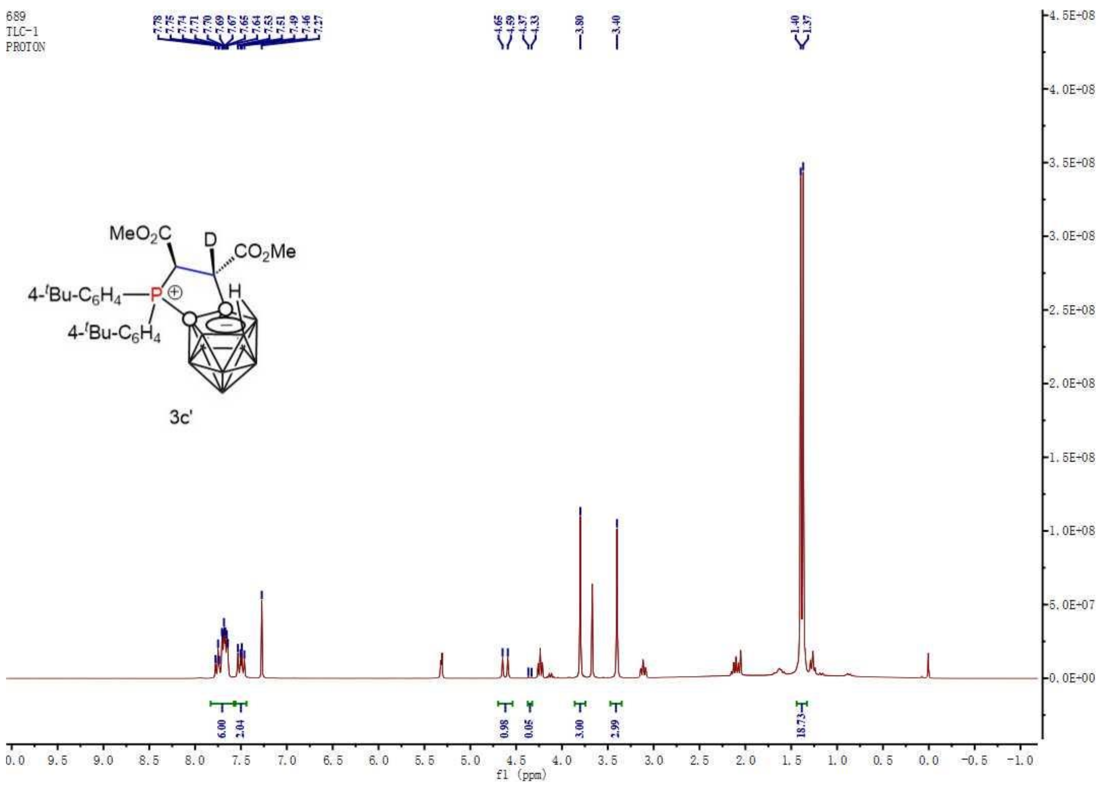


Figure S5. ^{1}H NMR spectrum of **3c'** in $CDCl_3$

4. X-ray crystal of 3a, 3d, 3k.

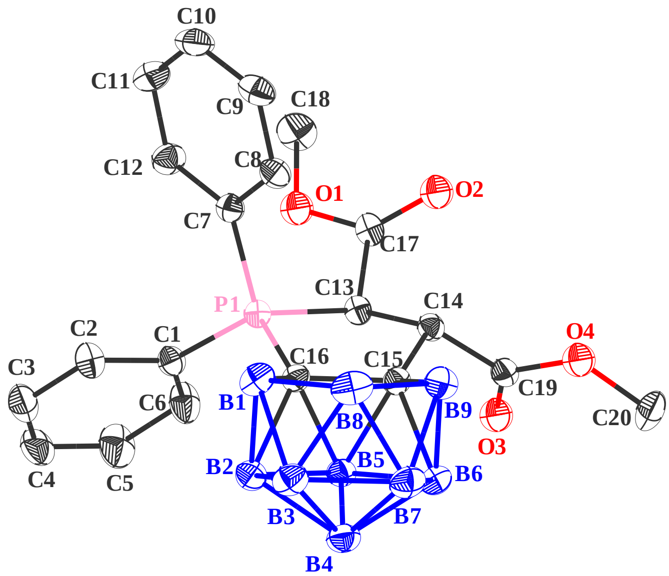


Figure S6. X-ray crystal structure of **3a**. The level set for thermal ellipsoids of all atoms is 30%. Except for the hydrogen atom on the carborane, it has been omitted for clarity. Main bond lengths (Å) and angles (deg): P1-C1 1.782(16), P1-C7 1.790(16), P1-C13 1.823(16), P1-C16 1.779(16), C13-C14 1.539(2), C15-C16 1.570(2), C1-P1-C7 111.07(8), C7-P1-C13 110.02 (7), C1-P1-C13 112.99(7), C16-P1-C7 110.72(7), C16-P1-C13 97.16(7), C16-P1-C1 114.14(8), C14-C13-P1 106.64(10), C17-C13-P1 114.31(11), C15-C16-P1 107.31(10), B5-C16-P1 110.77(10), B2-C16-P1 125.12(12), B1-C16-P1 125.96(12). CCDC reference number: 1949790.

Table S1 Crystal data and structure refinement for 3a

Identification code	3a
Empirical formula	$C_{20}H_{28}B_9O_4P$
Formula weight	460.68
Temperature/K	270.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	16.9930(2)
b/Å	15.3764(2)
c/Å	18.8864(3)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	4934.85(12)
Z	8
ρ_{calc}g/cm^3	1.240
μ/mm^{-1}	1.181
F(000)	1920.0
Crystal size/mm^3	0.05 × 0.05 × 0.04
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.366 to 146.634
Index ranges	-20 ≤ h ≤ 10, -18 ≤ k ≤ 18, -23 ≤ l ≤ 21
Reflections collected	12772
Independent reflections	4764 [R_{int} = 0.0255, R_{sigma} = 0.0303]
Data/restraints/parameters	4764/0/397
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.1104
Final R indexes [all data]	R_1 = 0.0480, wR_2 = 0.1147
Largest diff. peak/hole / e Å^{-3}	0.20/-0.31

Table S2 Bond Lengths for 3a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C7	1.7901(16)	C2	C3	1.382(3)
P1	C13	1.8233(16)	C12	C11	1.382(3)
P1	C1	1.7815(16)	C6	C5	1.385(3)
P1	C16	1.7788(16)	C10	C9	1.380(3)
O1	C17	1.321(2)	C10	C11	1.379(3)
O1	C18	1.446(2)	C4	C3	1.382(3)
O4	C19	1.329(2)	C4	C5	1.369(3)
O4	C20	1.446(2)	B5	B2	1.779(3)
O3	C19	1.198(2)	B5	B4	1.757(3)
O2	C17	1.197(2)	B5	B6	1.757(3)
C14	C13	1.539(2)	B2	B4	1.770(3)
C14	C19	1.518(2)	B2	B3	1.752(3)
C14	C15	1.543(2)	B2	B1	1.795(3)
C7	C8	1.393(2)	B4	B6	1.761(3)
C7	C12	1.389(2)	B4	B3	1.792(3)
C13	C17	1.510(2)	B4	B7	1.801(3)
C1	C2	1.392(2)	B6	B9	1.802(3)
C1	C6	1.383(2)	B6	B7	1.756(3)
C16	C15	1.570(2)	B9	B7	1.773(3)
C16	B5	1.732(2)	B9	B8	1.854(3)

C16	B2	1.736(2)	B3	B7	1.823(3)
C16	B1	1.624(2)	B3	B1	1.757(3)
C15	B5	1.731(2)	B3	B8	1.771(3)
C15	B6	1.721(2)	B7	B8	1.771(3)
C15	B9	1.614(2)	B1	B8	1.834(3)
C8	C9	1.381(3)			

Table S3 Bond Angles for 3a.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	P1	C13	110.02(7)	C16	B2	B4	102.13(14)
C1	P1	C7	111.07(8)	C16	B2	B3	99.61(14)
C1	P1	C13	112.99(7)	C16	B2	B1	54.74(10)
C16	P1	C7	110.72(7)	B5	B2	B1	106.50(14)
C16	P1	C13	97.16(7)	B4	B2	B5	59.36(11)
C16	P1	C1	114.14(8)	B4	B2	B1	107.97(15)
C17	O1	C18	117.23(14)	B3	B2	B5	107.65(15)
C19	O4	C20	115.63(15)	B3	B2	B4	61.18(12)
C13	C14	C15	109.67(12)	B3	B2	B1	59.37(12)
C19	C14	C13	109.25(13)	B5	B4	B2	60.58(11)
C19	C14	C15	111.48(13)	B5	B4	B6	59.94(11)
C8	C7	P1	118.86(13)	B5	B4	B3	106.85(14)
C12	C7	P1	121.02(13)	B5	B4	B7	106.51(14)
C12	C7	C8	120.00(16)	B2	B4	B3	58.94(12)
C14	C13	P1	106.64(10)	B2	B4	B7	108.07(15)
C17	C13	P1	114.31(11)	B6	B4	B2	109.10(14)
C17	C13	C14	114.20(13)	B6	B4	B3	108.22(15)
C2	C1	P1	117.86(13)	B6	B4	B7	59.06(12)
C6	C1	P1	121.85(13)	B3	B4	B7	60.97(13)
C6	C1	C2	120.10(16)	C15	B6	B5	59.68(10)
C15	C16	P1	107.31(10)	C15	B6	B4	104.06(14)
C15	C16	B5	63.00(10)	C15	B6	B9	54.47(10)
C15	C16	B2	113.20(13)	C15	B6	B7	101.08(14)
C15	C16	B1	115.59(14)	B5	B6	B4	59.93(12)
B5	C16	P1	110.77(10)	B5	B6	B9	106.27(14)
B5	C16	B2	61.71(10)	B4	B6	B9	108.49(15)
B2	C16	P1	125.12(12)	B7	B6	B5	108.51(15)
B1	C16	P1	125.96(12)	B7	B6	B4	61.62(13)
B1	C16	B5	117.08(13)	B7	B6	B9	59.78(12)
B1	C16	B2	64.48(12)	C15	B9	B6	60.21(11)
O4	C19	C14	111.38(14)	C15	B9	B7	104.75(15)

O3	C19	O4	124.58(16)	C15	B9	B8	106.44(15)
O3	C19	C14	124.02(15)	B6	B9	B8	107.17(15)
O1	C17	C13	110.43(13)	B7	B9	B6	58.82(12)
O2	C17	O1	125.72(16)	B7	B9	B8	58.40(12)
O2	C17	C13	123.84(16)	B2	B3	B4	59.89(12)
C14	C15	C16	112.43(13)	B2	B3	B7	107.86(15)
C14	C15	B5	113.94(13)	B2	B3	B1	61.52(12)
C14	C15	B6	124.95(13)	B2	B3	B8	112.98(14)
C14	C15	B9	123.54(14)	B4	B3	B7	59.75(12)
C16	C15	B5	63.08(10)	B1	B3	B4	108.64(14)
C16	C15	B6	111.16(13)	B1	B3	B7	107.22(15)
C16	C15	B9	111.54(13)	B1	B3	B8	62.66(13)
B6	C15	B5	61.20(11)	B8	B3	B4	109.71(16)
B9	C15	B5	116.67(14)	B8	B3	B7	59.04(13)
B9	C15	B6	65.32(12)	B4	B7	B3	59.28(12)
C9	C8	C7	119.71(17)	B6	B7	B4	59.32(12)
C3	C2	C1	119.46(18)	B6	B7	B9	61.40(12)
C11	C12	C7	119.47(18)	B6	B7	B3	107.07(15)
C1	C6	C5	119.57(19)	B6	B7	B8	113.06(14)
C11	C10	C9	120.09(18)	B9	B7	B4	107.96(14)
C10	C9	C8	120.17(18)	B9	B7	B3	107.08(15)
C5	C4	C3	120.10(19)	B8	B7	B4	109.29(15)
C10	C11	C12	120.5(2)	B8	B7	B9	63.07(13)
C2	C3	C4	120.24(19)	B8	B7	B3	59.01(13)
C16	B5	B2	59.25(10)	C16	B1	B2	60.79(11)
C16	B5	B4	102.81(13)	C16	B1	B3	103.94(14)
C16	B5	B6	102.23(13)	C16	B1	B8	104.37(15)
C15	B5	C16	53.92(9)	B2	B1	B8	108.07(14)
C15	B5	B2	103.77(13)	B3	B1	B2	59.11(12)
C15	B5	B4	103.80(14)	B3	B1	B8	59.03(13)
C15	B5	B6	59.12(10)	B3	B8	B9	105.86(15)
B4	B5	B2	60.06(12)	B3	B8	B7	61.95(13)
B4	B5	B6	60.14(12)	B3	B8	B1	58.31(12)
B6	B5	B2	108.84(14)	B7	B8	B9	58.52(12)
C4	C5	C6	120.5(2)	B7	B8	B1	106.13(15)
C16	B2	B5	59.04(10)	B1	B8	B9	101.88(13)

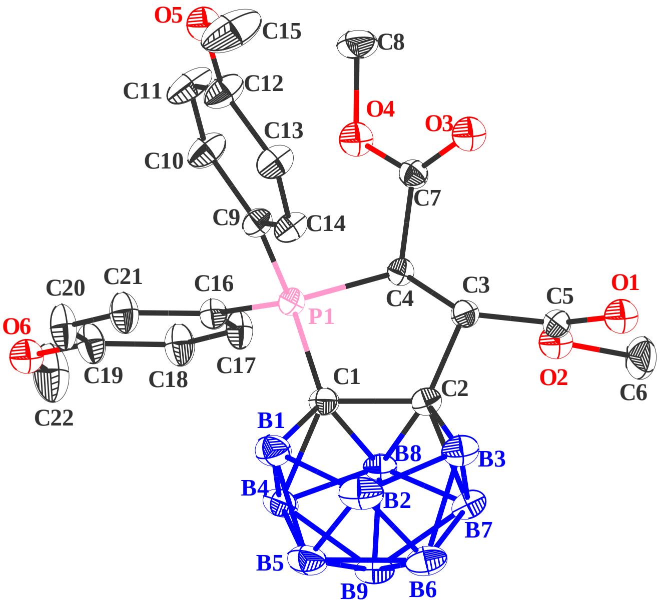


Figure S7. X-ray crystal structure of **3d**. The level set for thermal ellipsoids of all atoms is 30%. Except for the hydrogen atom on the carborane, it has been omitted for clarity. Main bond lengths (Å) and angles (deg): P1-C1 1.7816(18), P1-C4 1.8360(17), P1-C9 1.7825(18), P1-C16 1.7805(18), C1-C2 1.569(3), C3-C4 1.544(2), C1-P1-C4 96.22(8), C1-P1-C9 111.50(9), C9-P1-C4 108.70(8), C16-P1-C1 114.98(9), C16-P1-C4 112.69(8), C16-P1-C9 111.70(9), C2-C1-P1 107.68(12), C3-C4-P1 104.76(11), C7-C4-P1 113.22(12), B1-C1-P1 126.04(14), B4-C1-P1 123.97(14), B8-C1-P1 110.01(12). CCDC reference number: 2068612.

Table S4 Crystal data and structure refinement for 3d.

Identification code	3d
Empirical formula	$C_{22}H_{32}B_9O_6P$
Formula weight	520.73
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.4554(3)
b/Å	19.4040(3)
c/Å	12.6188(3)
α/°	90
β/°	113.557(2)
γ/°	90
Volume/Å^3	2795.62(10)
Z	4
ρ_{calc}g/cm^3	1.237

μ/mm^{-1}	1.156
F(000)	1088.0
Crystal size/mm^3	0.17 × 0.13 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.432 to 134.15
Index ranges	-13 ≤ h ≤ 14, -23 ≤ k ≤ 23, -15 ≤ l ≤ 15
Reflections collected	22006
Independent reflections	4989 [R_{int} = 0.0406, R_{sigma} = 0.0304]
Data/restraints/parameters	4989/0/363
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0467, wR_2 = 0.1229
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1324
Largest diff. peak/hole / e Å^{-3}	0.29/-0.32

Table S5 Bond Lengths for 3d.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.7816(18)	C11	C12	1.391(3)
P1	C4	1.8360(17)	C12	C13	1.382(3)
P1	C9	1.7825(18)	C13	C14	1.378(3)
P1	C16	1.7805(18)	C16	C17	1.384(3)
O1	C5	1.193(2)	C16	C21	1.395(3)
O2	C5	1.333(2)	C17	C18	1.378(3)
O2	C6	1.450(2)	C18	C19	1.385(3)
O3	C7	1.185(2)	C19	C20	1.388(3)
O4	C7	1.325(2)	C20	C21	1.376(3)
O4	C8	1.453(2)	B1	B2	1.831(4)
O5	C12	1.355(2)	B1	B4	1.798(3)
O5	C15	1.430(3)	B1	B5	1.758(3)
O6	C19	1.350(3)	B2	B3	1.850(4)
O6	C22	1.426(3)	B2	B5	1.774(4)
C1	C2	1.569(3)	B2	B6	1.774(4)
C1	B1	1.628(3)	B3	B6	1.773(3)
C1	B4	1.728(3)	B3	B7	1.805(3)
C1	B8	1.737(3)	B4	B5	1.758(3)
C2	C3	1.540(2)	B4	B8	1.785(3)
C2	B3	1.622(3)	B4	B9	1.770(4)
C2	B7	1.725(3)	B5	B6	1.824(4)
C2	B8	1.730(3)	B5	B9	1.794(4)
C3	C4	1.544(2)	B6	B7	1.755(3)
C3	C5	1.514(3)	B6	B9	1.800(3)

C4	C7	1.513(2)	B7	B8	1.762(3)
C9	C10	1.393(3)	B7	B9	1.768(4)
C9	C14	1.388(3)	B8	B9	1.754(3)
C10	C11	1.372(3)			

Table S6 Bond Angles for 3d.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	C4	96.22(8)	B5	B2	B3	106.10(16)
C1	P1	C9	111.50(9)	B5	B2	B6	61.87(15)
C9	P1	C4	108.70(8)	B6	B2	B1	106.15(17)
C16	P1	C1	114.98(9)	B6	B2	B3	58.54(14)
C16	P1	C4	112.69(8)	C2	B3	B2	106.16(18)
C16	P1	C9	111.70(9)	C2	B3	B6	104.36(16)
C5	O2	C6	115.82(17)	C2	B3	B7	60.16(12)
C7	O4	C8	115.95(16)	B6	B3	B2	58.60(14)
C12	O5	C15	117.80(19)	B6	B3	B7	58.74(13)
C19	O6	C22	118.44(19)	B7	B3	B2	107.37(17)
C2	C1	P1	107.68(12)	C1	B4	B1	54.97(12)
C2	C1	B1	115.66(16)	C1	B4	B5	99.66(17)
C2	C1	B4	113.46(15)	C1	B4	B8	59.23(11)
C2	C1	B8	62.86(11)	C1	B4	B9	102.06(16)
B1	C1	P1	126.04(14)	B5	B4	B1	59.24(14)
B1	C1	B4	64.69(14)	B5	B4	B8	107.58(18)
B1	C1	B8	117.45(15)	B5	B4	B9	61.15(14)
B4	C1	P1	123.97(14)	B8	B4	B1	106.81(16)
B4	C1	B8	62.02(12)	B9	B4	B1	107.88(18)
B8	C1	P1	110.01(12)	B9	B4	B8	59.13(13)
C1	C2	B3	111.50(16)	B1	B5	B2	62.46(16)
C1	C2	B7	111.39(14)	B1	B5	B4	61.51(14)
C1	C2	B8	63.33(12)	B1	B5	B6	107.15(18)
C3	C2	C1	111.21(14)	B1	B5	B9	108.55(16)
C3	C2	B3	122.85(16)	B2	B5	B6	59.06(15)
C3	C2	B7	127.26(15)	B2	B5	B9	109.50(19)
C3	C2	B8	115.55(14)	B4	B5	B2	112.61(17)
B3	C2	B7	65.19(13)	B4	B5	B6	107.59(17)
B3	C2	B8	116.72(15)	B4	B5	B9	59.75(14)
B7	C2	B8	61.32(12)	B9	B5	B6	59.64(14)
C2	C3	C4	109.03(14)	B2	B6	B5	59.07(16)
C5	C3	C2	112.50(14)	B2	B6	B9	109.26(19)
C5	C3	C4	113.17(14)	B3	B6	B2	62.86(14)
C3	C4	P1	104.76(11)	B3	B6	B5	107.25(17)
C7	C4	P1	113.22(12)	B3	B6	B9	108.19(15)
C7	C4	C3	112.45(14)	B7	B6	B2	113.12(16)

O1	C5	O2	124.83(19)	B7	B6	B3	61.53(13)
O1	C5	C3	123.49(19)	B7	B6	B5	107.61(17)
O2	C5	C3	111.67(15)	B7	B6	B9	59.65(13)
O3	C7	O4	124.84(17)	B9	B6	B5	59.36(15)
O3	C7	C4	124.09(17)	C2	B7	B3	54.64(11)
O4	C7	C4	111.05(15)	C2	B7	B6	100.91(15)
C10	C9	P1	121.61(15)	C2	B7	B8	59.48(11)
C14	C9	P1	118.67(14)	C2	B7	B9	103.41(16)
C14	C9	C10	119.26(17)	B6	B7	B3	59.73(13)
C11	C10	C9	120.03(19)	B6	B7	B8	108.22(17)
C10	C11	C12	120.20(19)	B6	B7	B9	61.43(14)
O5	C12	C11	116.04(19)	B8	B7	B3	106.29(15)
O5	C12	C13	123.7(2)	B8	B7	B9	59.60(13)
C13	C12	C11	120.21(19)	B9	B7	B3	108.18(17)
C14	C13	C12	119.38(19)	C1	B8	B4	58.75(11)
C13	C14	C9	120.91(17)	C1	B8	B7	102.16(14)
C17	C16	P1	121.20(14)	C1	B8	B9	102.35(14)
C17	C16	C21	118.74(17)	C2	B8	C1	53.81(10)
C21	C16	P1	119.92(14)	C2	B8	B4	103.36(14)
C18	C17	C16	121.62(18)	C2	B8	B7	59.20(11)
C17	C18	C19	119.14(19)	C2	B8	B9	103.80(15)
O6	C19	C18	124.1(2)	B7	B8	B4	108.94(16)
O6	C19	C20	115.86(19)	B9	B8	B4	59.99(13)
C18	C19	C20	120.05(19)	B9	B8	B7	60.39(13)
C21	C20	C19	120.35(19)	B4	B9	B5	59.10(14)
C20	C21	C16	120.10(19)	B4	B9	B6	108.16(17)
C1	B1	B2	104.12(17)	B5	B9	B6	61.00(15)
C1	B1	B4	60.35(12)	B7	B9	B4	109.34(15)
C1	B1	B5	103.69(17)	B7	B9	B5	108.35(17)
B4	B1	B2	108.15(17)	B7	B9	B6	58.92(14)
B5	B1	B2	59.21(15)	B8	B9	B4	60.88(12)
B5	B1	B4	59.25(14)	B8	B9	B5	107.35(16)
B1	B2	B3	102.38(15)	B8	B9	B6	106.57(16)
B5	B2	B1	58.33(15)	B8	B9	B7	60.01(12)

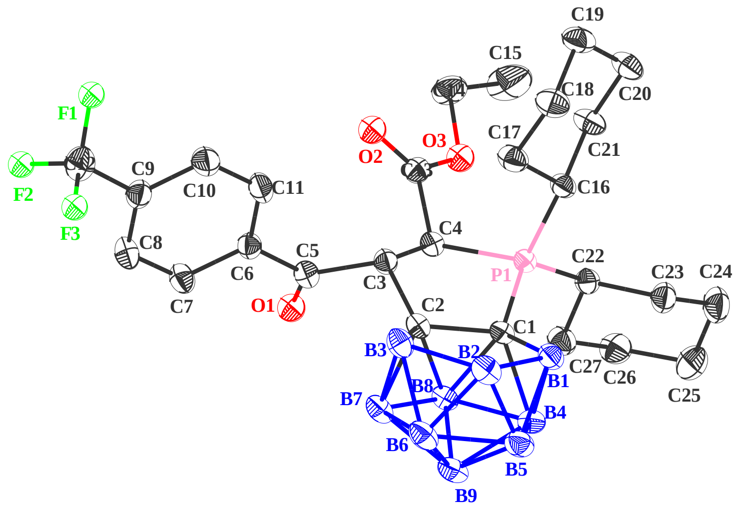


Figure S8. X-ray crystal structure of **3k**. The level set for thermal ellipsoids of all atoms is 30%. Except for the hydrogen atom on the carborane, it has been omitted for clarity. Main bond lengths (Å) and angles (deg): P1-C1 1.7860(18), P1-C4 1.8331(19), P1-C16 1.8318(18), P1-C22 1.8188(18), C1-C2 1.580(2), C2-C3 1.537(3), C1-P1-C4 96.06(8), C1-P1-C16 108.69(9), C1-P1-C22 117.71(9), C16-P1-C4 113.43(9), C22-P1-C16 107.65(9), C2-C1-P1 106.53(13), B1-C1-P1 124.37(13), B4-C1-P1 128.35(13), B8-C1-P1 113.60(13), C3-C4-P1 103.84(13), C13-C4-P1 116.86(13). CCDC reference number: 2081457.

Table S7 Crystal data and structure refinement for 3k.

Identification code	3k
Empirical formula	$C_{27}H_{43}B_9F_3O_3P$
Formula weight	600.87
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21/n
a/Å	14.8215(3)
b/Å	14.2119(3)
c/Å	15.2758(3)
α /°	90
β /°	95.2953(16)
γ /°	90
Volume/Å3	3203.97(11)
Z	4
ρ calcg/cm3	1.246

μ /mm-1	1.138
F(000)	1264.0
Crystal size/mm3	0.13 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.952 to 134.156
Index ranges	-17 ≤ h ≤ 16, -16 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	27852
Independent reflections	5723 [Rint = 0.0409, Rsigma = 0.0291]
Data/restraints/parameters	5723/16/415
Goodness-of-fit on F2	1.039
Final R indexes [I>=2σ (I)]	R1 = 0.0492, wR2 = 0.1351
Final R indexes [all data]	R1 = 0.0602, wR2 = 0.1460
Largest diff. peak/hole / e Å-3	0.36/-0.24

Table S8 Bond Lengths for 3k.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.7860(18)	C10	C11	1.375(3)
P1	C4	1.8331(19)	C14	C15	1.469(4)
P1	C16	1.8318(18)	C16	C17	1.533(3)
P1	C22	1.8188(18)	C16	C21	1.537(3)
F1	C12	1.346(4)	C17	C18	1.528(3)
F2	C12	1.326(3)	C18	C19	1.518(3)
F3	C12	1.332(4)	C19	C20	1.516(3)
F1A	C12	1.300(15)	C20	C21	1.524(3)
F2A	C12	1.333(14)	C22	C23	1.537(3)
F3A	C12	1.293(15)	C22	C27	1.532(3)
O1	C5	1.209(2)	C23	C24	1.535(3)
O2	C13	1.190(3)	C24	C25	1.511(3)
O3	C13	1.324(2)	C25	C26	1.518(4)
O3	C14	1.458(3)	C26	C27	1.526(3)
C1	C2	1.580(2)	B1	B2	1.835(3)
C1	B1	1.617(3)	B1	B4	1.799(3)
C1	B4	1.727(3)	B1	B5	1.761(3)
C1	B8	1.749(3)	B2	B3	1.851(4)
C2	C3	1.537(3)	B2	B5	1.777(4)
C2	B3	1.624(3)	B2	B6	1.780(3)
C2	B7	1.721(3)	B3	B6	1.769(4)
C2	B8	1.727(3)	B3	B7	1.809(3)
C3	C4	1.535(2)	B4	B5	1.758(3)
C3	C5	1.525(2)	B4	B8	1.789(3)

C4	C13	1.514(3)	B4	B9	1.772(3)
C5	C6	1.499(3)	B5	B6	1.818(4)
C6	C7	1.387(3)	B5	B9	1.802(3)
C6	C11	1.389(3)	B6	B7	1.761(3)
C7	C8	1.380(3)	B6	B9	1.805(4)
C8	C9	1.372(3)	B7	B8	1.763(3)
C9	C10	1.378(3)	B7	B9	1.765(4)
C9	C12	1.494(3)	B8	B9	1.758(3)

Table S9 Bond Angles for 3k.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	C4	96.06(8)	C1	B1	B2	105.12(16)
C1	P1	C16	108.69(9)	C1	B1	B4	60.45(12)
C1	P1	C22	117.71(9)	C1	B1	B5	104.03(15)
C16	P1	C4	113.43(9)	B4	B1	B2	108.38(15)
C22	P1	C4	113.12(9)	B5	B1	B2	59.19(14)
C22	P1	C16	107.65(9)	B5	B1	B4	59.16(13)
C13	O3	C14	116.92(16)	B1	B2	B3	101.55(15)
C2	C1	P1	106.53(13)	B5	B2	B1	58.35(13)
C2	C1	B1	115.32(15)	B5	B2	B3	105.34(17)
C2	C1	B4	112.69(14)	B5	B2	B6	61.49(15)
C2	C1	B8	62.25(12)	B6	B2	B1	105.60(16)
B1	C1	P1	124.37(13)	B6	B2	B3	58.26(14)
B1	C1	B4	64.99(13)	C2	B3	B2	106.78(16)
B1	C1	B8	117.55(15)	C2	B3	B6	104.45(17)
B4	C1	P1	128.35(13)	C2	B3	B7	59.90(12)
B4	C1	B8	61.93(12)	B6	B3	B2	58.86(13)
B8	C1	P1	113.60(13)	B6	B3	B7	58.95(14)
C1	C2	B3	111.04(16)	B7	B3	B2	107.96(18)
C1	C2	B7	111.70(16)	C1	B4	B1	54.56(12)
C1	C2	B8	63.69(12)	C1	B4	B5	99.75(16)
C3	C2	C1	111.16(14)	C1	B4	B8	59.64(12)
C3	C2	B3	123.00(17)	C1	B4	B9	102.56(16)
C3	C2	B7	127.16(15)	B5	B4	B1	59.36(13)
C3	C2	B8	115.31(15)	B5	B4	B8	107.81(17)
B3	C2	B7	65.38(13)	B5	B4	B9	61.39(14)
B3	C2	B8	116.94(16)	B8	B4	B1	106.77(16)
B7	C2	B8	61.50(12)	B9	B4	B1	108.12(17)
C4	C3	C2	109.45(15)	B9	B4	B8	59.18(13)
C5	C3	C2	112.31(14)	B1	B5	B2	62.46(14)
C5	C3	C4	112.01(15)	B1	B5	B6	107.07(18)
C3	C4	P1	103.84(13)	B1	B5	B9	108.45(17)

C13	C4	P1	116.86(13)	B2	B5	B6	59.33(14)
C13	C4	C3	113.24(16)	B2	B5	B9	110.03(19)
O1	C5	C3	120.93(18)	B4	B5	B1	61.48(13)
O1	C5	C6	121.25(18)	B4	B5	B2	112.94(17)
C6	C5	C3	117.81(16)	B4	B5	B6	107.68(18)
C7	C6	C5	118.45(17)	B4	B5	B9	59.69(13)
C7	C6	C11	118.58(19)	B9	B5	B6	59.81(14)
C11	C6	C5	122.97(17)	B2	B6	B5	59.18(14)
C8	C7	C6	120.70(19)	B2	B6	B9	109.76(17)
C9	C8	C7	119.74(19)	B3	B6	B2	62.88(14)
C8	C9	C10	120.4(2)	B3	B6	B5	107.09(15)
C8	C9	C12	121.4(2)	B3	B6	B9	108.07(16)
C10	C9	C12	118.2(2)	B7	B6	B2	113.45(16)
C11	C10	C9	119.8(2)	B7	B6	B3	61.66(14)
C10	C11	C6	120.71(19)	B7	B6	B5	107.53(17)
F1	C12	C9	112.4(2)	B7	B6	B9	59.32(14)
F2	C12	F1	106.0(2)	B9	B6	B5	59.64(14)
F2	C12	F3	107.4(3)	C2	B7	B3	54.72(11)
F2	C12	C9	113.8(2)	C2	B7	B6	100.83(15)
F3	C12	F1	104.1(3)	C2	B7	B8	59.40(11)
F3	C12	C9	112.4(3)	C2	B7	B9	103.54(15)
F1A	C12	F2A	112.9(14)	B6	B7	B3	59.39(14)
F1A	C12	C9	105.8(12)	B6	B7	B8	108.39(18)
F2A	C12	C9	105.0(11)	B6	B7	B9	61.59(15)
F3A	C12	F1A	121(3)	B8	B7	B3	106.23(15)
F3A	C12	F2A	102(2)	B8	B7	B9	59.79(14)
F3A	C12	C9	109(2)	B9	B7	B3	108.07(17)
O2	C13	O3	125.80(19)	C1	B8	B4	58.43(12)
O2	C13	C4	123.90(18)	C1	B8	B7	102.19(15)
O3	C13	C4	110.30(16)	C1	B8	B9	102.23(15)
O3	C14	C15	107.6(2)	C2	B8	C1	54.06(10)
C17	C16	P1	113.45(13)	C2	B8	B4	103.11(15)
C17	C16	C21	110.51(17)	C2	B8	B7	59.10(12)
C21	C16	P1	114.29(14)	C2	B8	B9	103.60(16)
C18	C17	C16	109.96(17)	B7	B8	B4	108.53(17)
C19	C18	C17	110.62(19)	B9	B8	B4	59.93(13)
C20	C19	C18	110.79(19)	B9	B8	B7	60.16(14)
C19	C20	C21	111.59(18)	B4	B9	B5	58.92(13)
C20	C21	C16	110.23(18)	B4	B9	B6	107.67(16)
C23	C22	P1	111.24(14)	B5	B9	B6	60.56(14)
C27	C22	P1	114.62(13)	B7	B9	B4	109.20(16)
C27	C22	C23	111.31(17)	B7	B9	B5	108.08(18)
C24	C23	C22	109.39(19)	B7	B9	B6	59.09(14)
C25	C24	C23	111.38(19)	B8	B9	B4	60.88(13)

C24	C25	C26	111.5(2)	B8	B9	B5	107.21(15)
C25	C26	C27	112.1(2)	B8	B9	B6	106.63(17)
C26	C27	C22	109.51(17)	B8	B9	B7	60.05(13)

5. DFT calculation

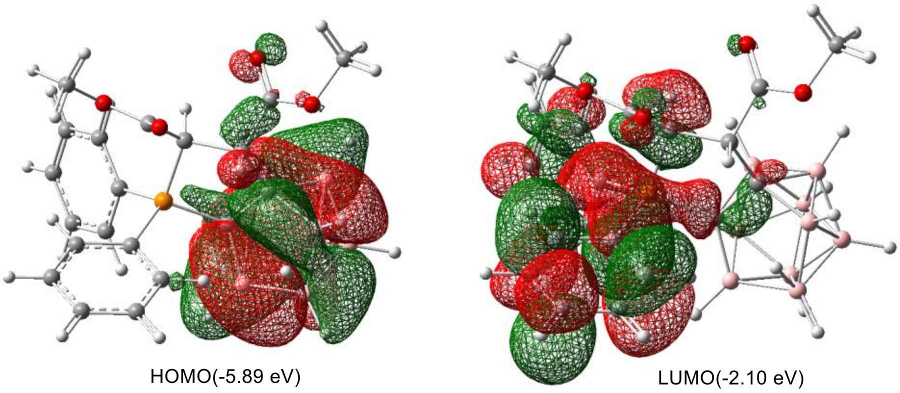


Figure S9. Calculated HOMO (left) and LUMO (right) of 3a.

Density functional theory calculations (DFT) was performed with compound **3a** on the B3LYP/6-31+G (d, p) level.

6. NMR spectra

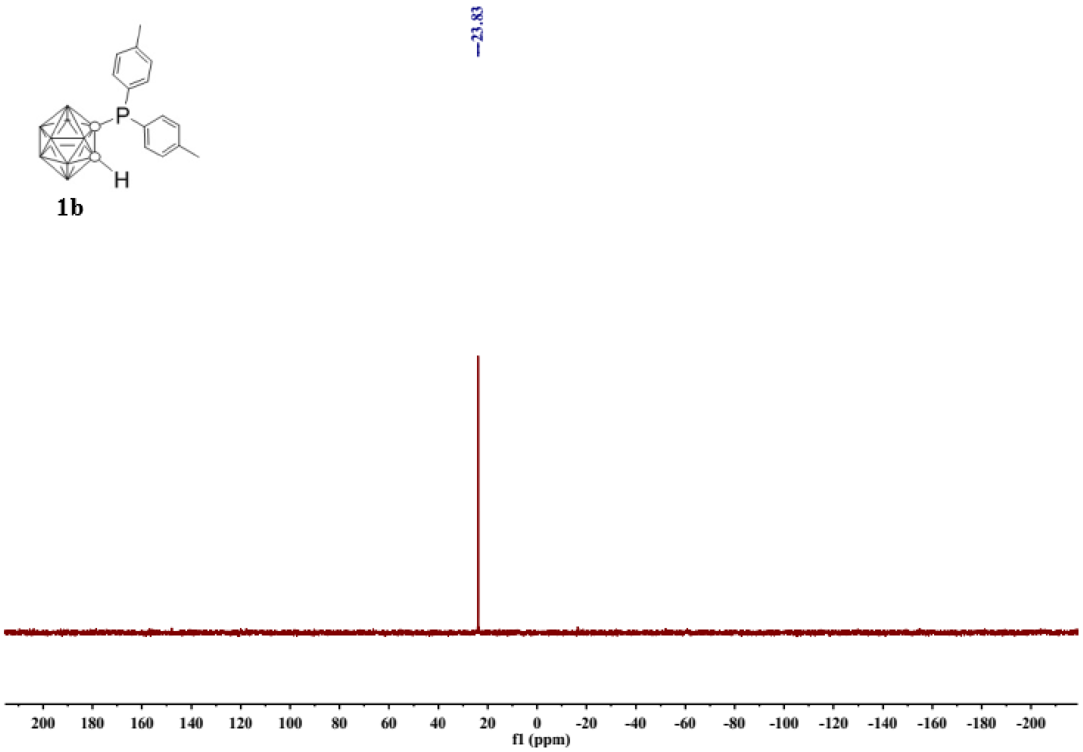


Figure S10. ^{31}P NMR spectrum of **1b** in $CDCl_3$.

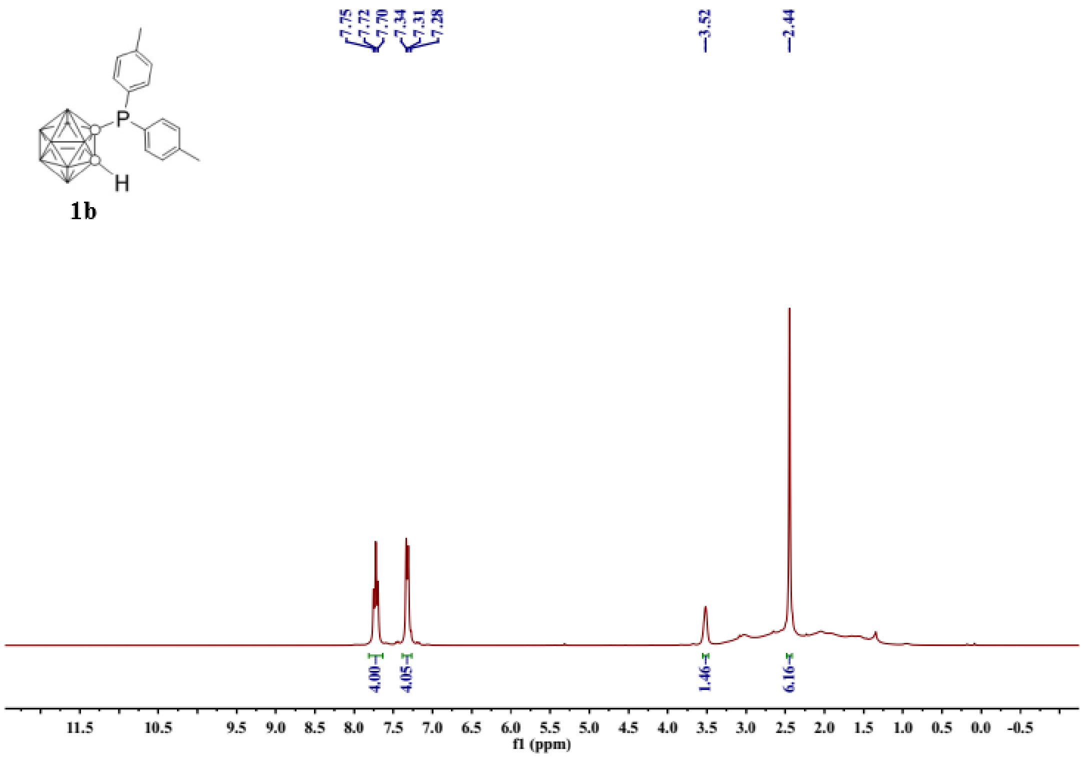


Figure S11. ^{1}H NMR spectrum of **1b** in $CDCl_3$.

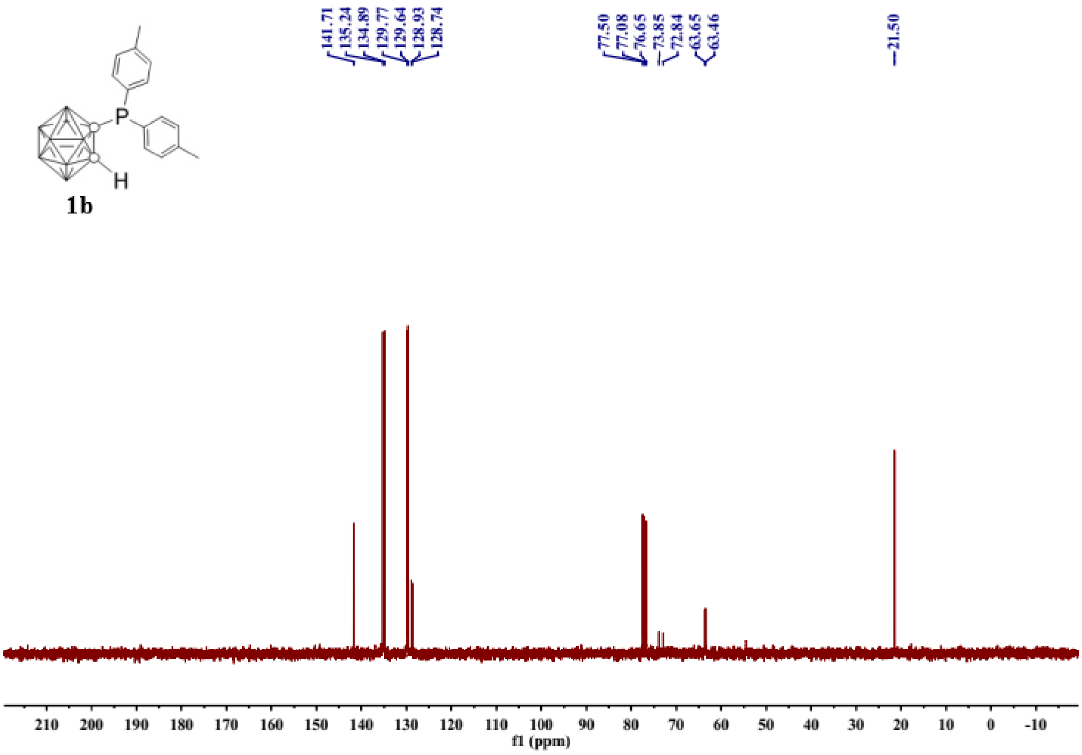


Figure S12. ^{13}C NMR spectrum of **1b** in $CDCl_3$.

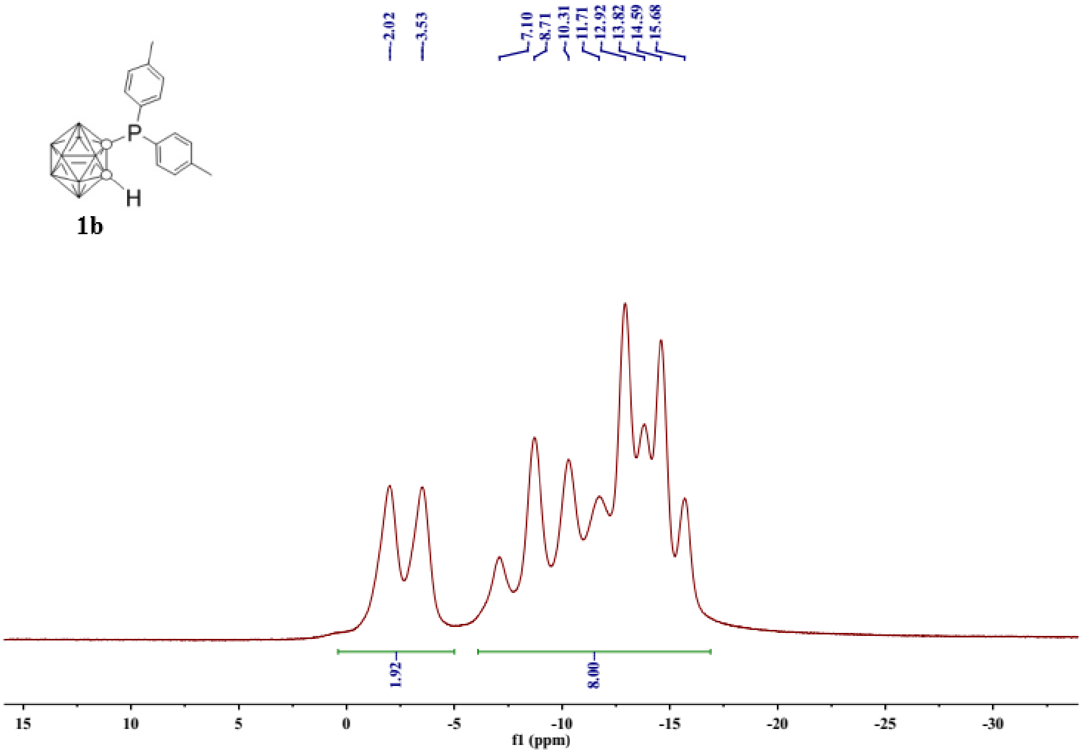


Figure S13. ^{11}B NMR spectrum of **1b** in $CDCl_3$.

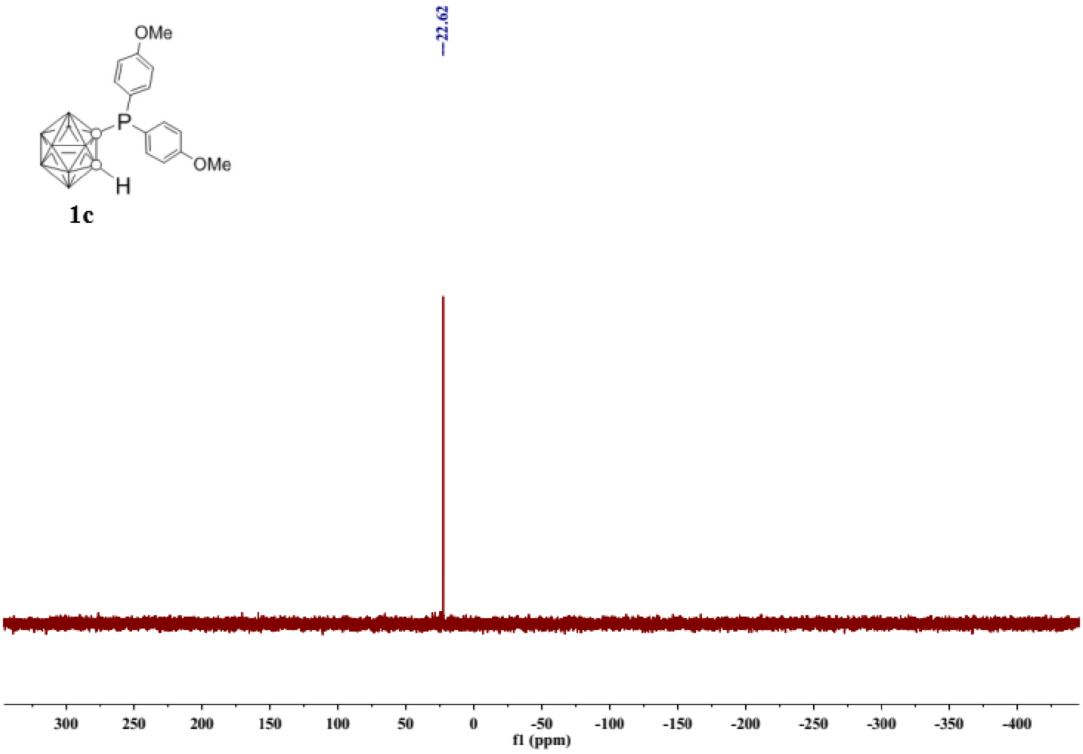


Figure S14. ^{31}P NMR spectrum of **1c** in $CDCl_3$.

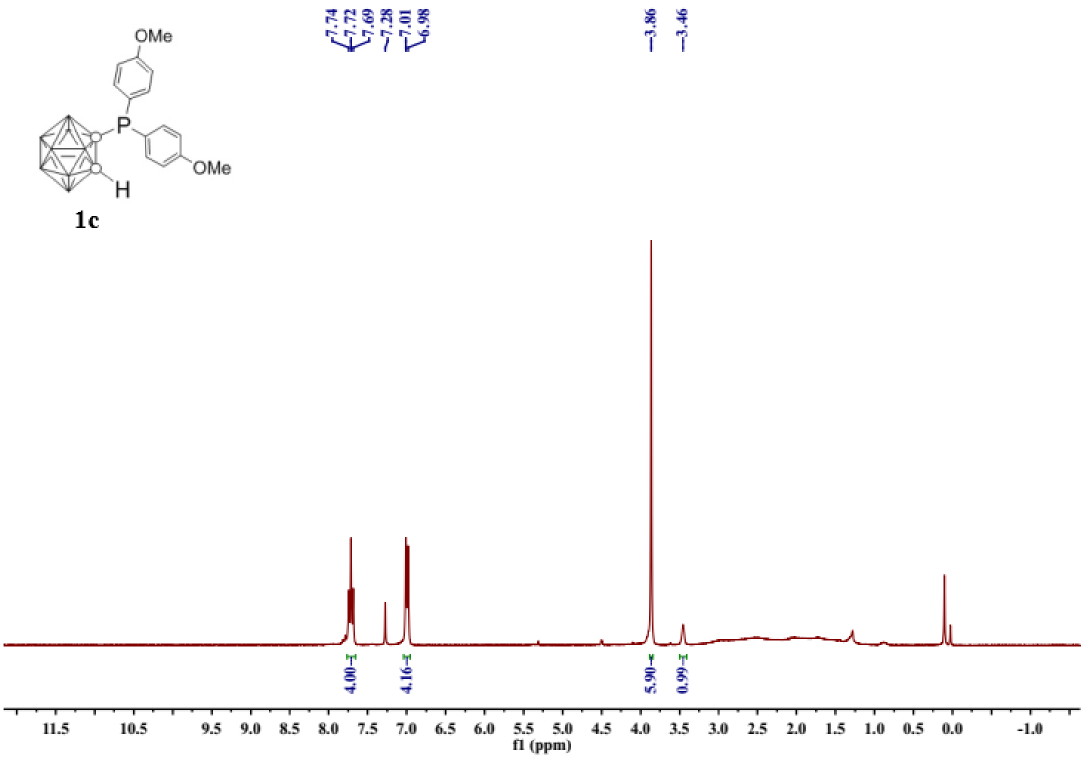


Figure S15. ^{1}H NMR spectrum of **1c** in $CDCl_3$.

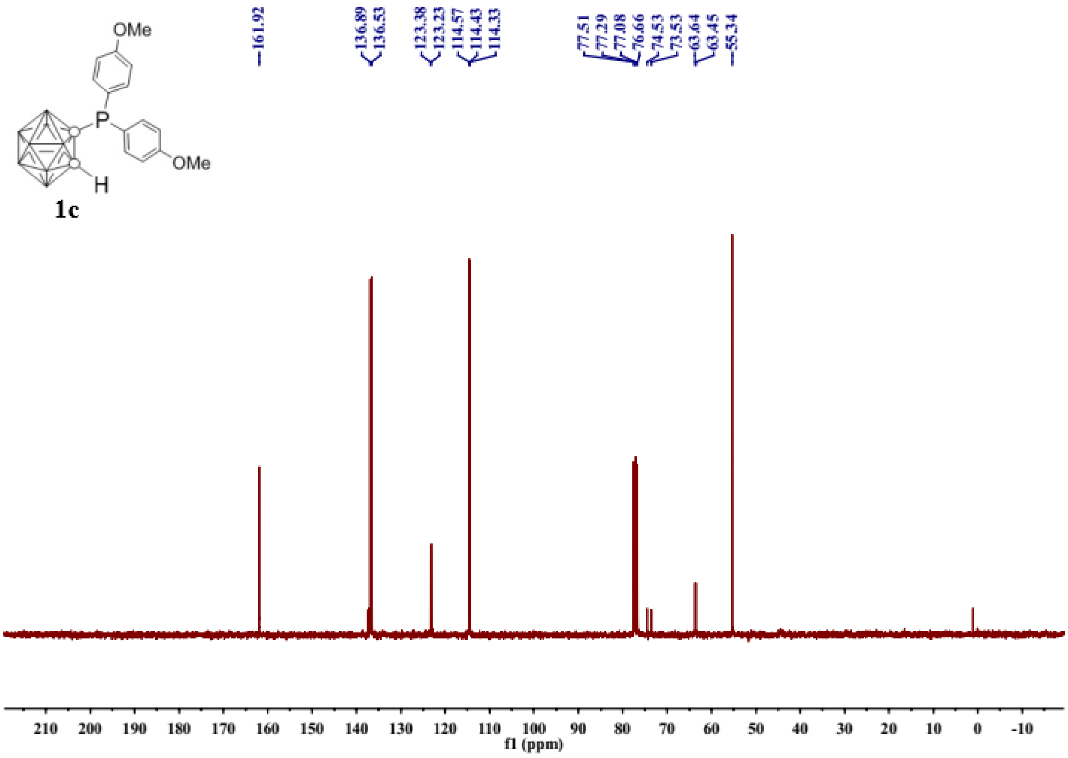


Figure S16. ^{13}C NMR spectrum of **1c** in $CDCl_3$.

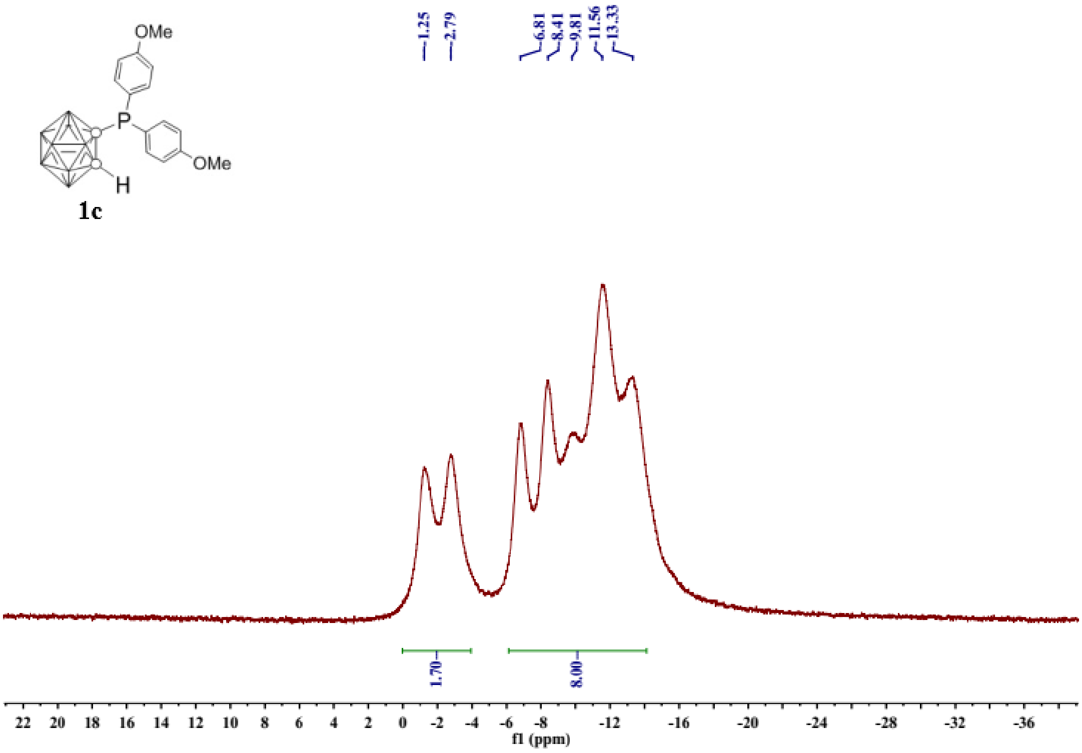


Figure S17. ^{11}B NMR spectrum of **1c** in $CDCl_3$.

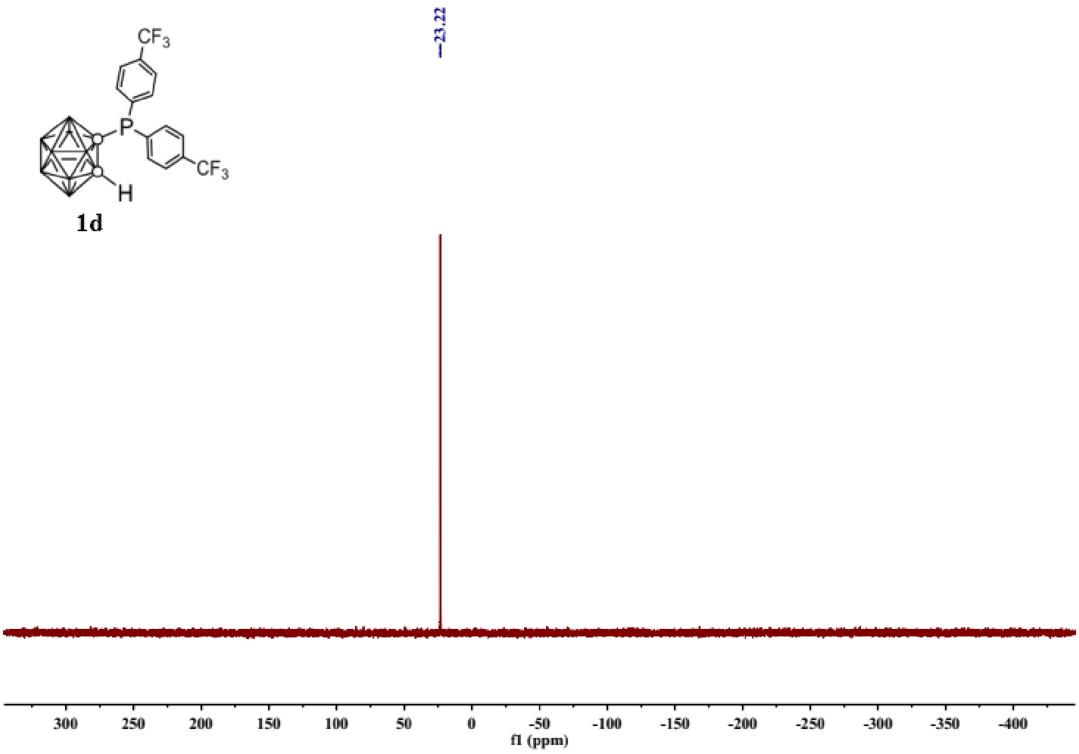


Figure S18. ^{31}P NMR spectrum of **1d** in $CDCl_3$.

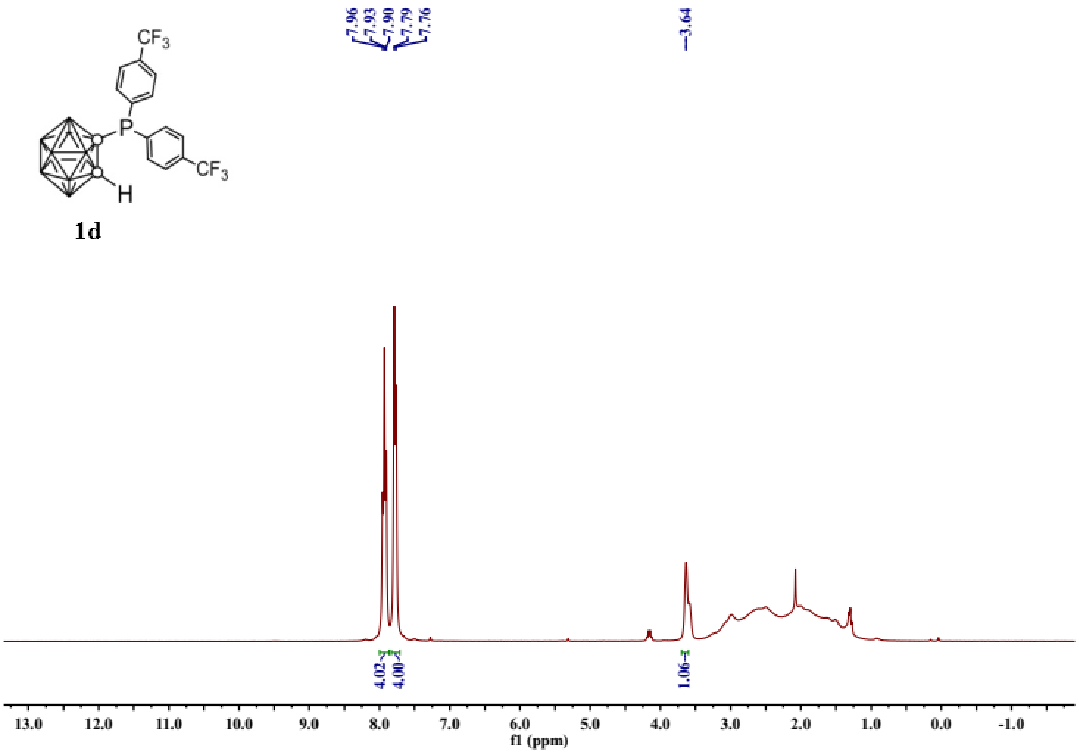


Figure S19. ^{1}H NMR spectrum of **1d** in $CDCl_3$.

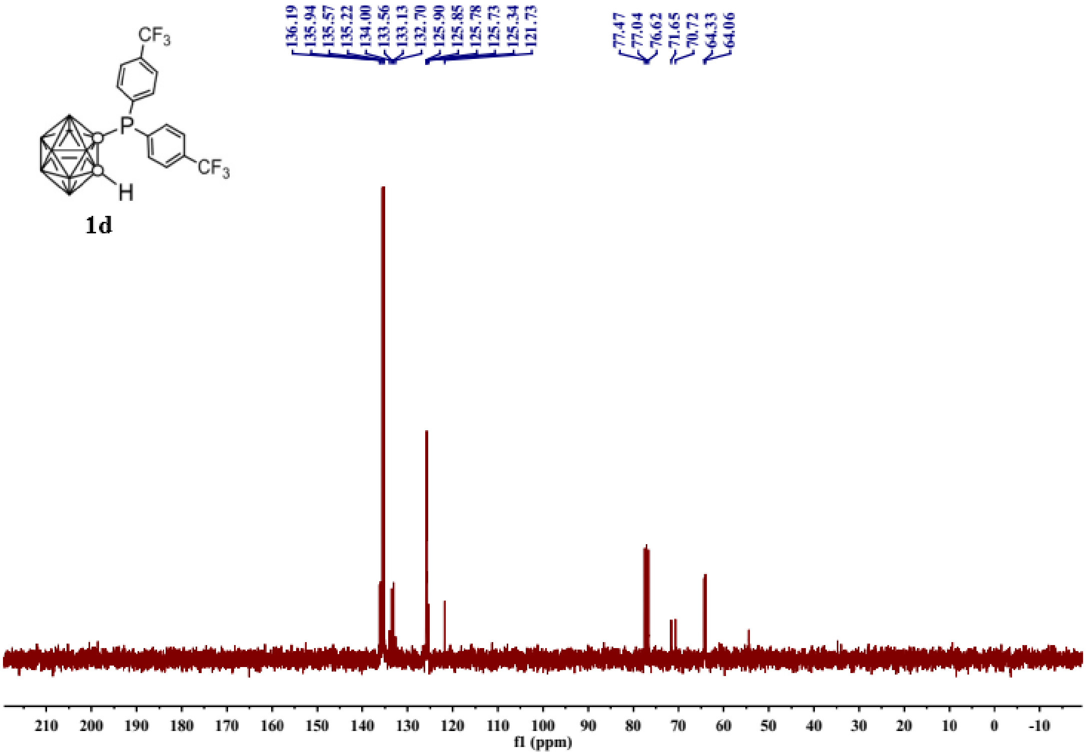


Figure S20. ^{13}C NMR spectrum of **1d** in $CDCl_3$.

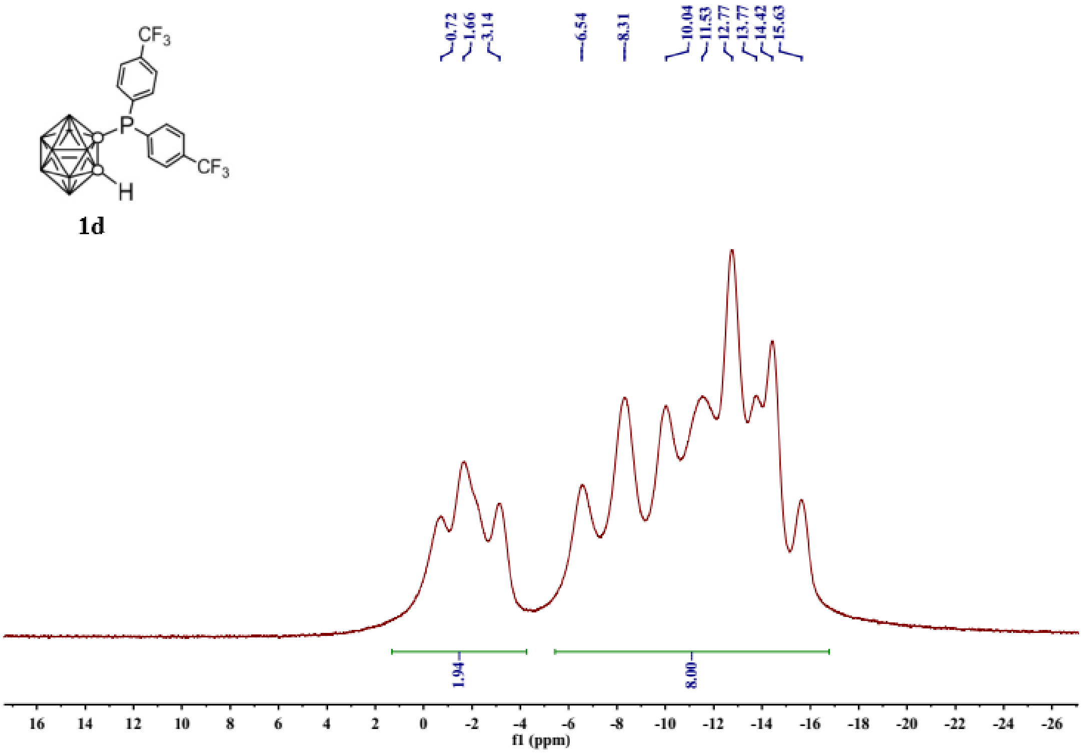


Figure S21. ^{11}B NMR spectrum of **1d** in $CDCl_3$.

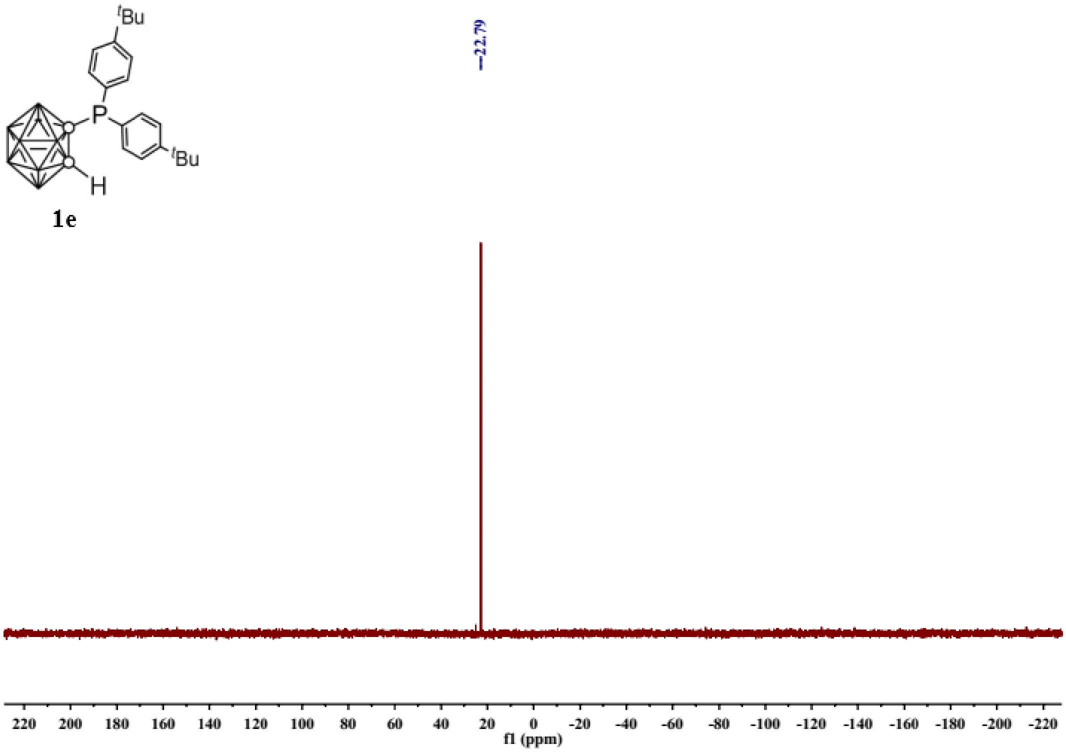


Figure S22. ^{31}P NMR spectrum of **1e** in $CDCl_3$.

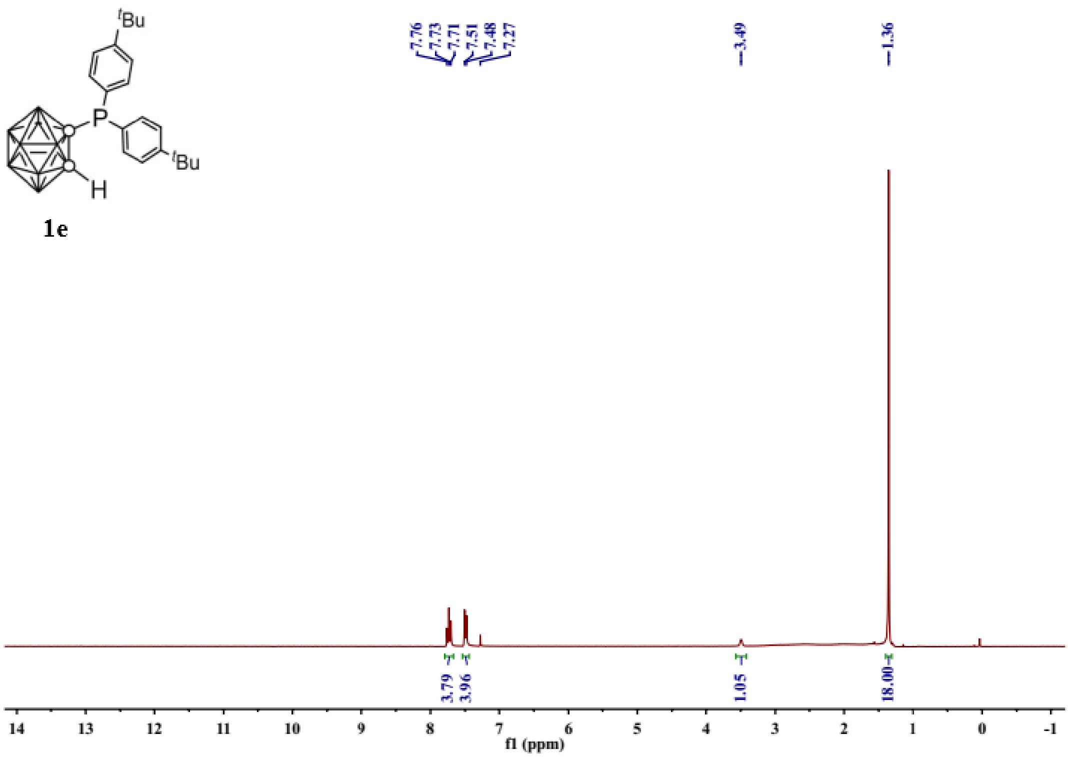


Figure S23. ^{1}H NMR spectrum of **1e** in $CDCl_3$.

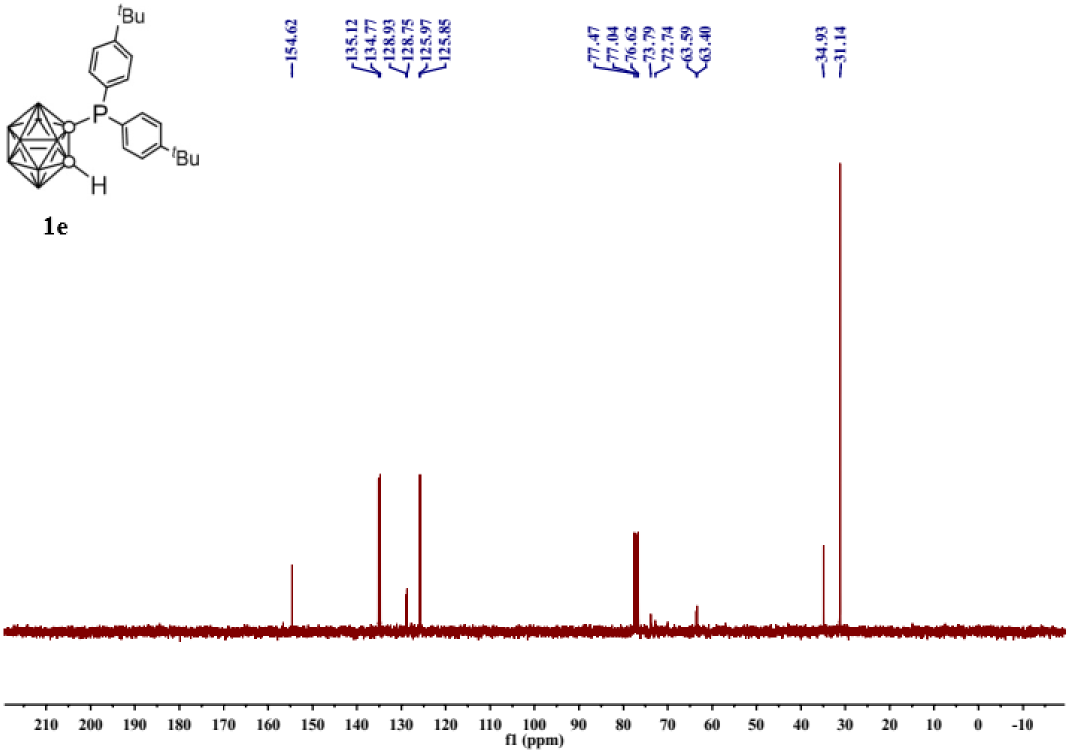


Figure S24. ^{13}C NMR spectrum of **1e** in $CDCl_3$.

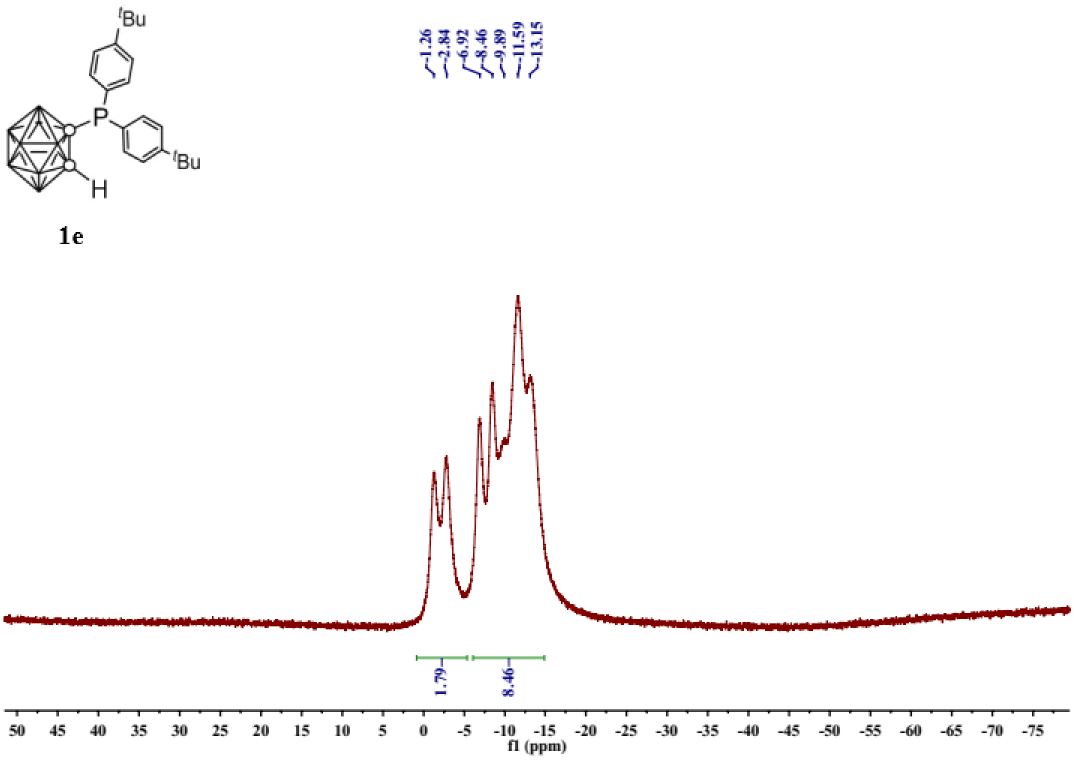


Figure S25. ^{11}B NMR spectrum of **1e** in $CDCl_3$.

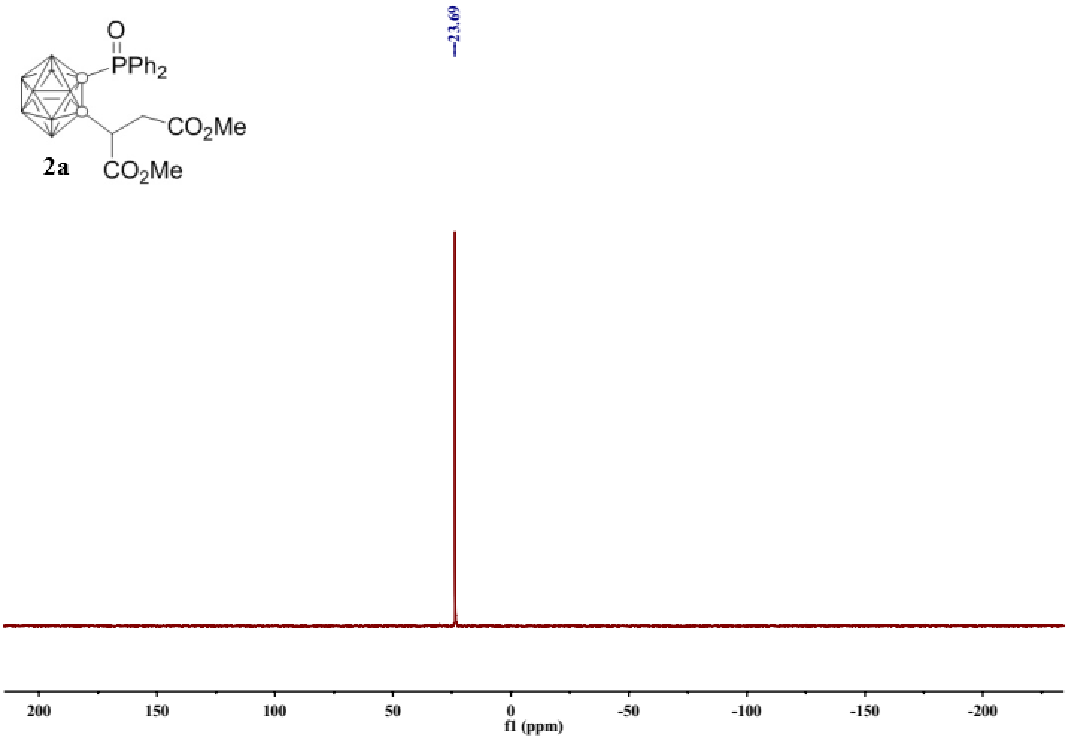


Figure S26. ^{31}P NMR spectrum of **2a** in $CDCl_3$.

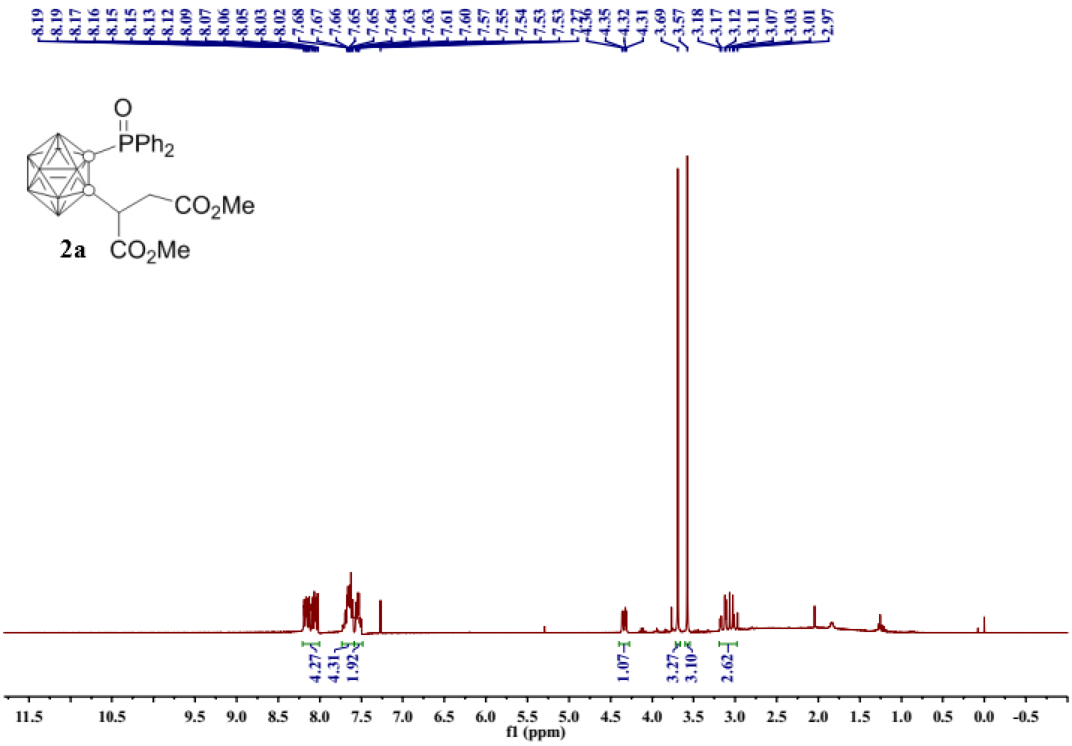


Figure S27. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

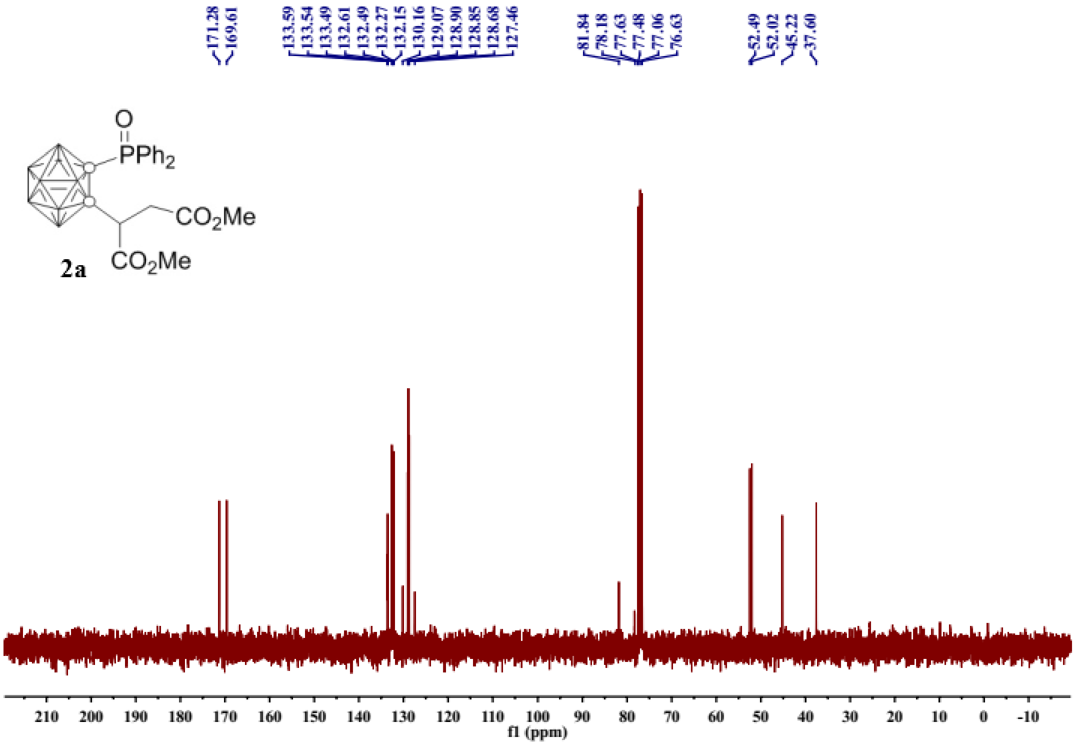


Figure S28. ^{13}C NMR spectrum of **2a** in $CDCl_3$.

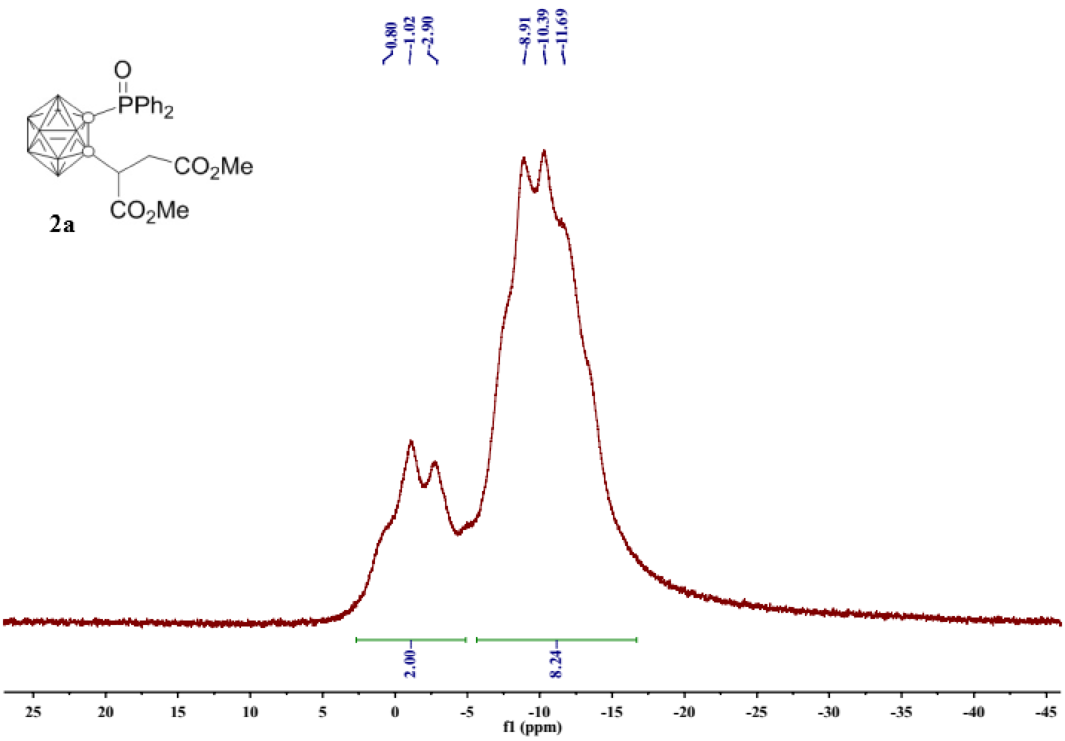


Figure S29. ^{11}B NMR spectrum of **2a** in $CDCl_3$.

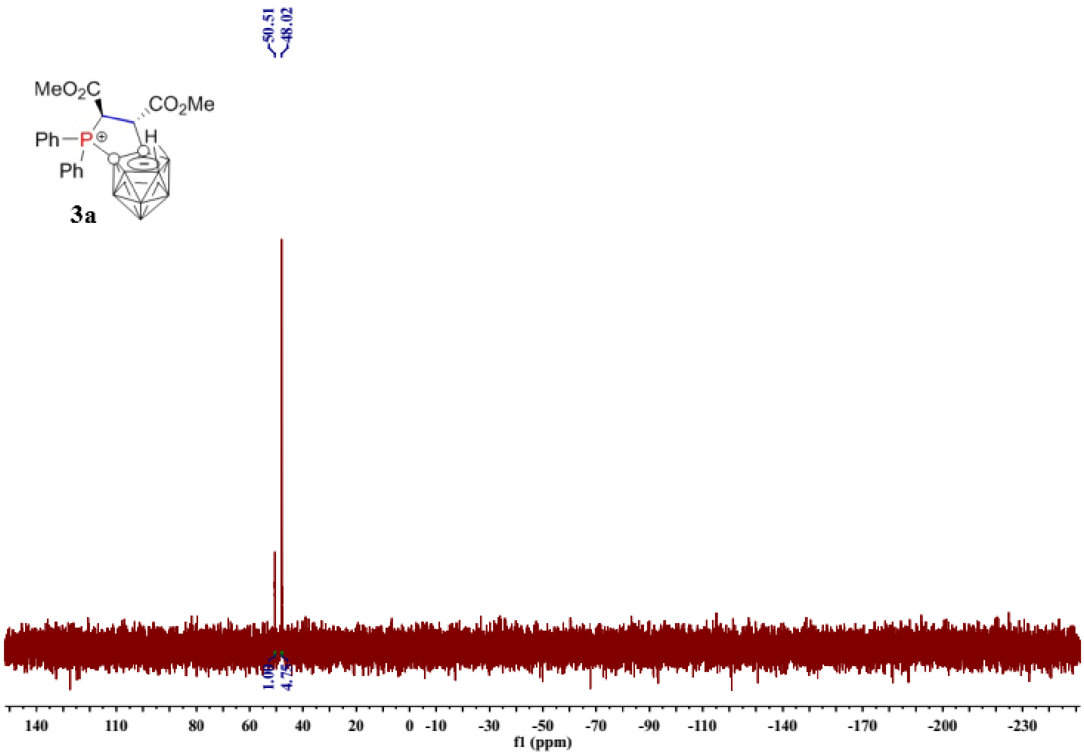


Figure S30. ^{31}P NMR spectrum of **3a** in $CDCl_3$.

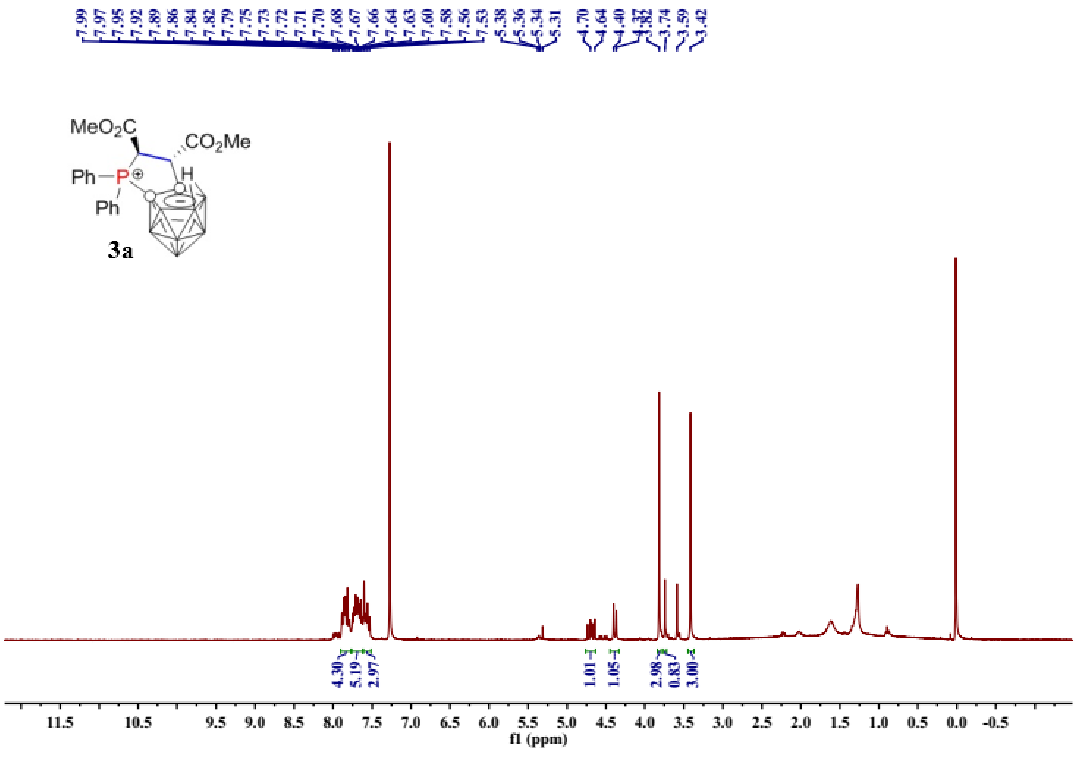


Figure S31. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

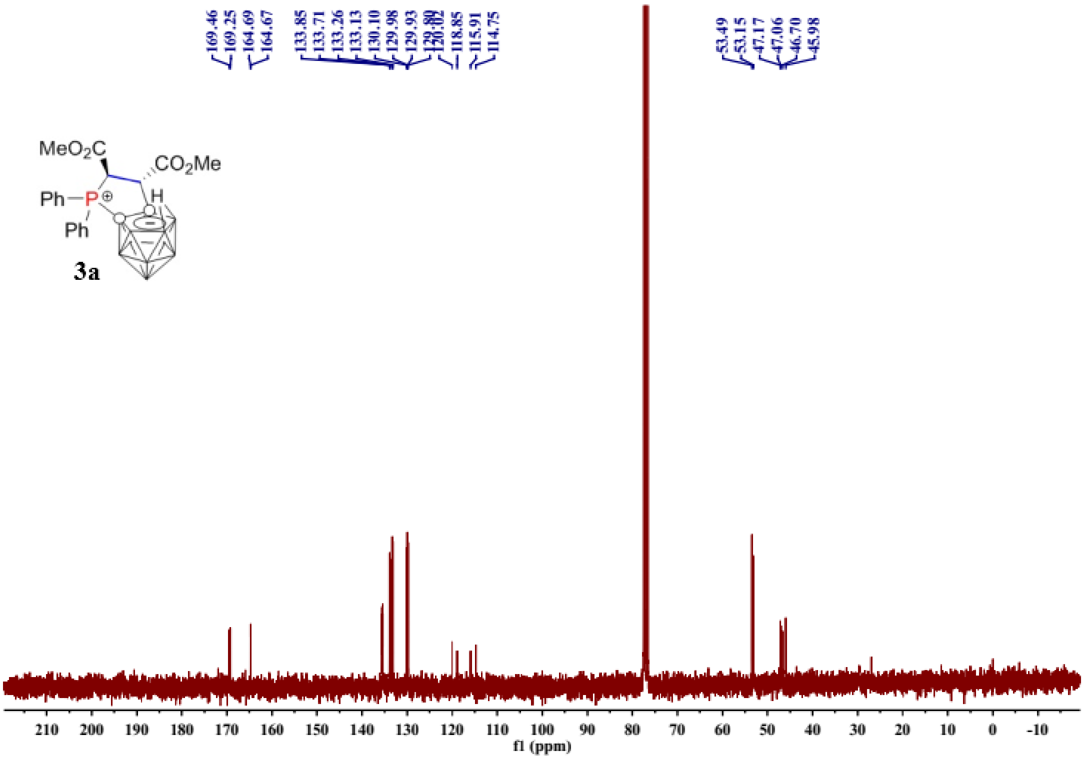


Figure S32. [13]C NMR spectrum of **3a** in $CDCl_3$.

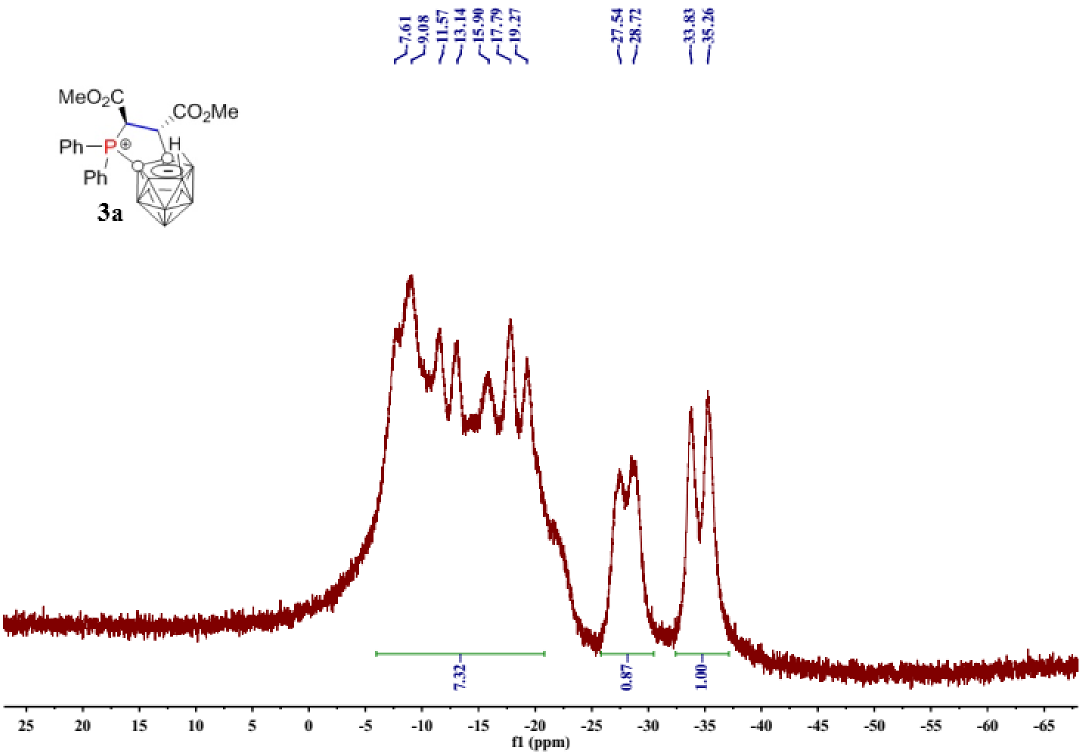


Figure S33. [11]B NMR spectrum of **3a** in $CDCl_3$.

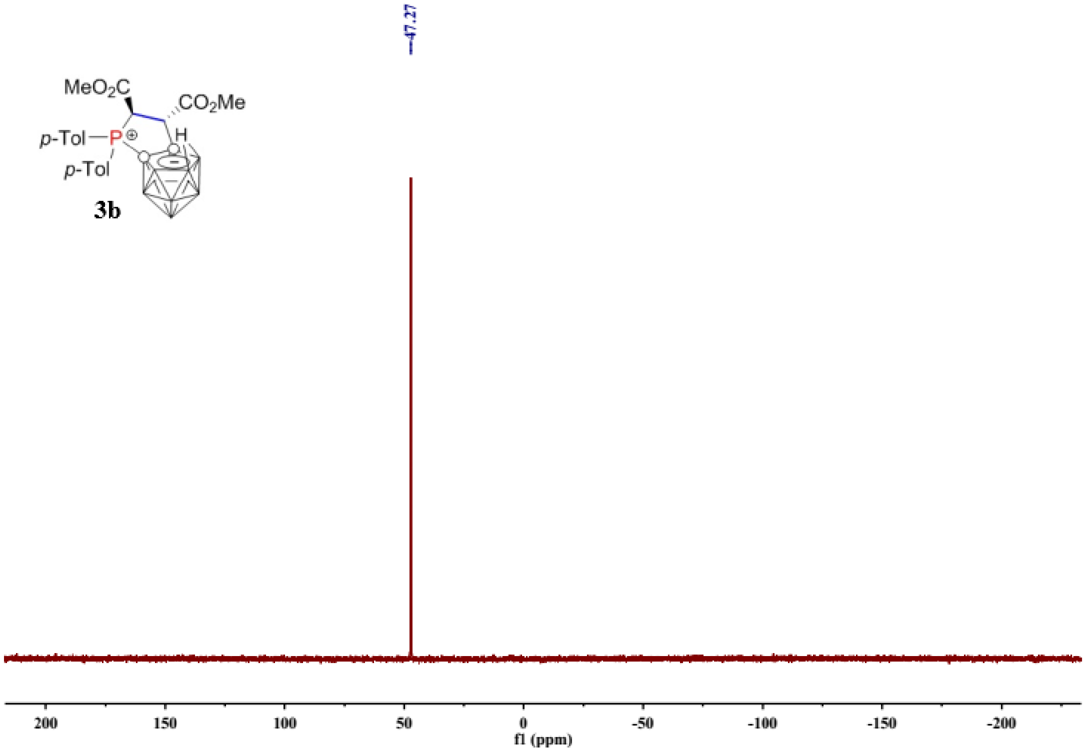


Figure S34. ^{31}P NMR spectrum of **3b** in $CDCl_3$.

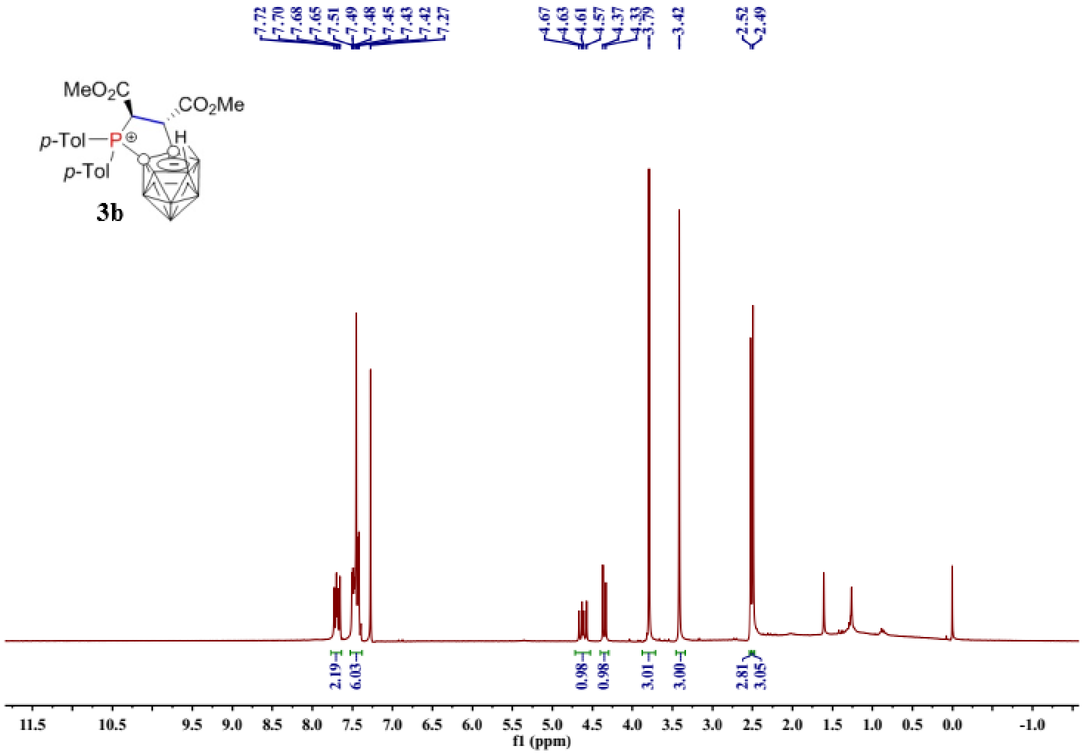


Figure S35. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

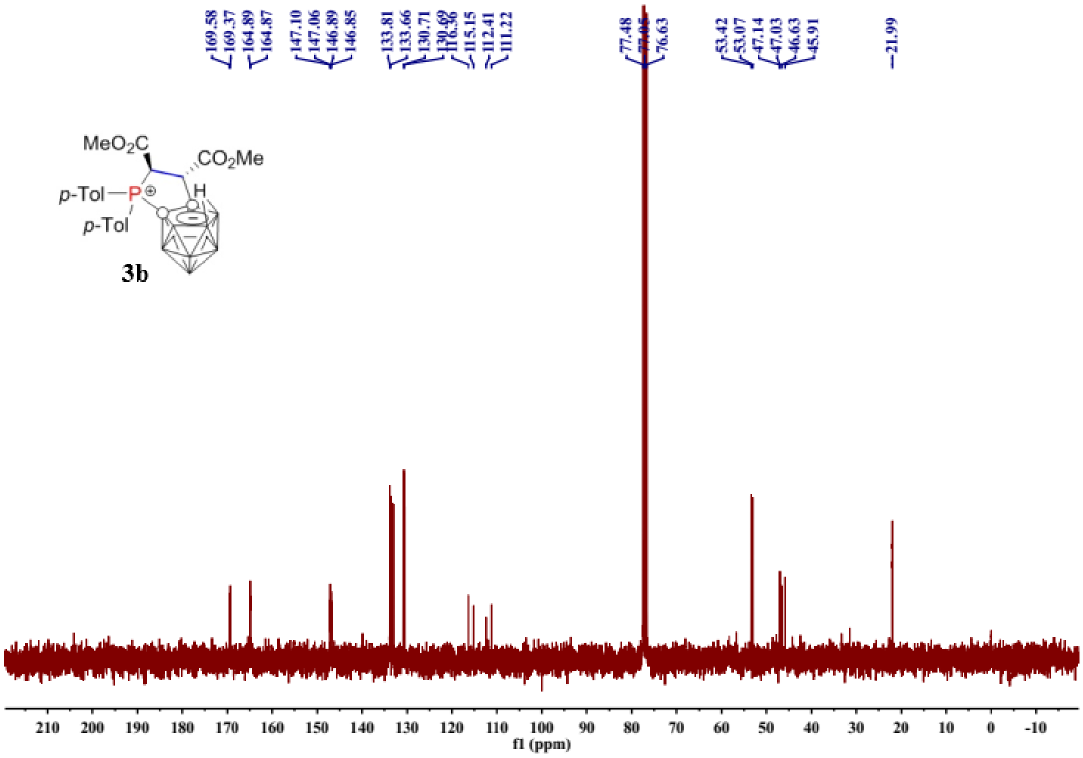


Figure S36. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

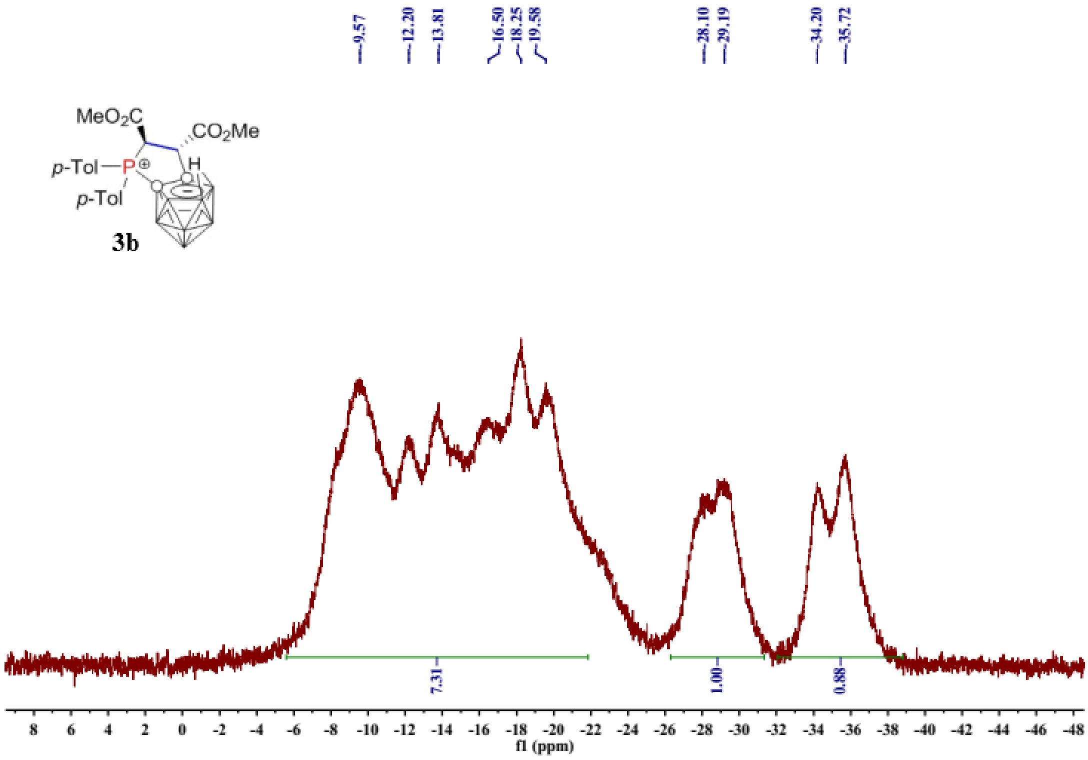


Figure S37. ^{11}B NMR spectrum of **3b** in $CDCl_3$.

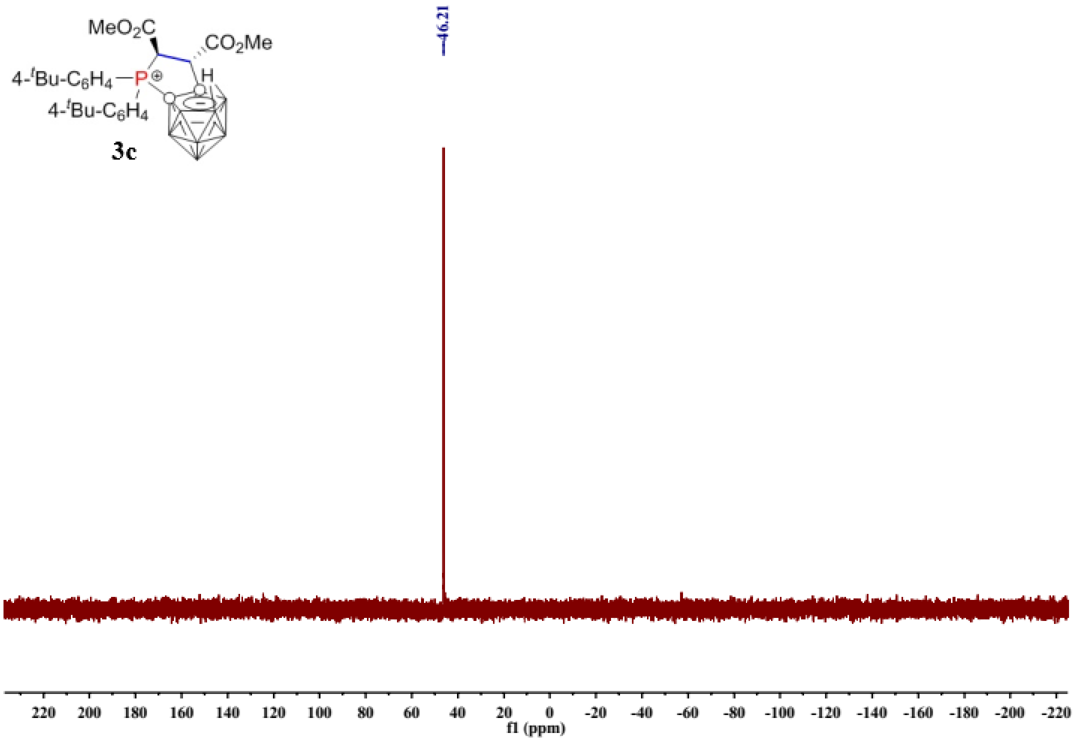


Figure S38. ^{31}P NMR spectrum of **3c** in $CDCl_3$.

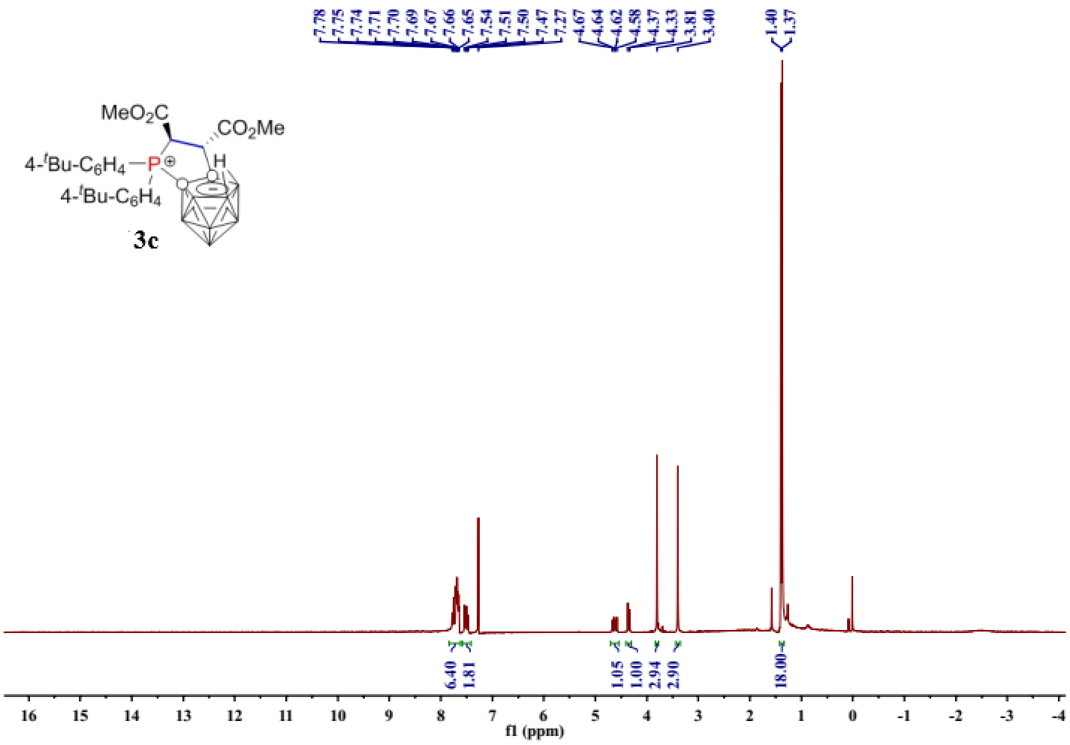


Figure S39. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

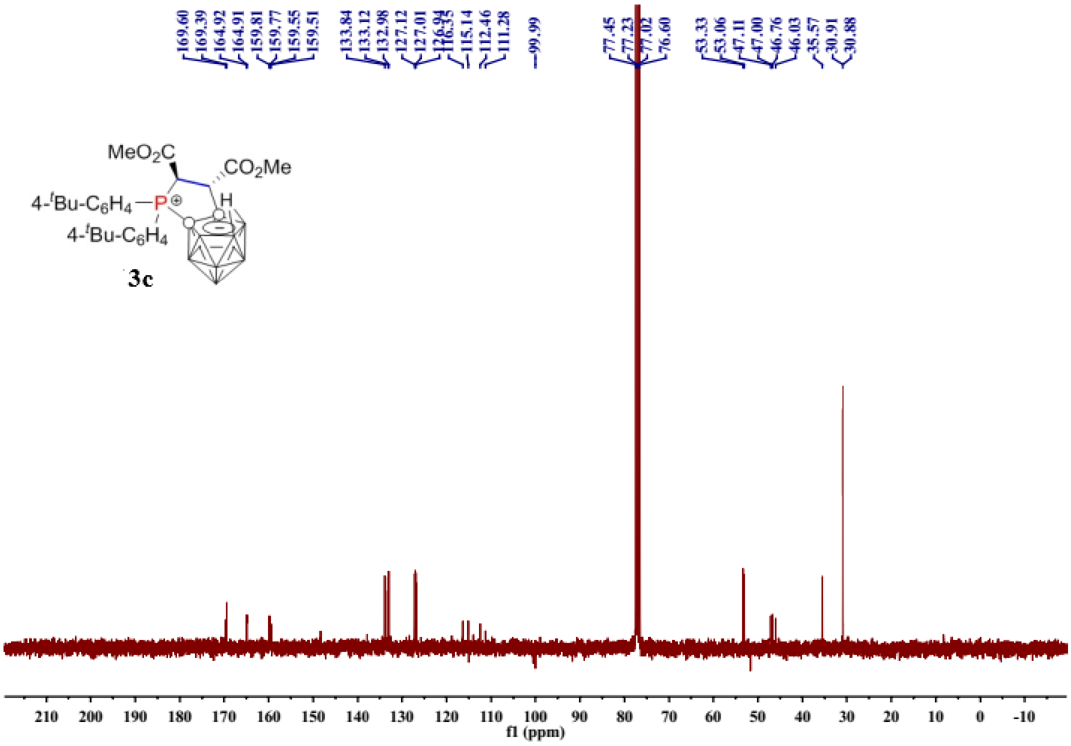


Figure S40. ^{13}C NMR spectrum of **3c** in $CDCl_3$.

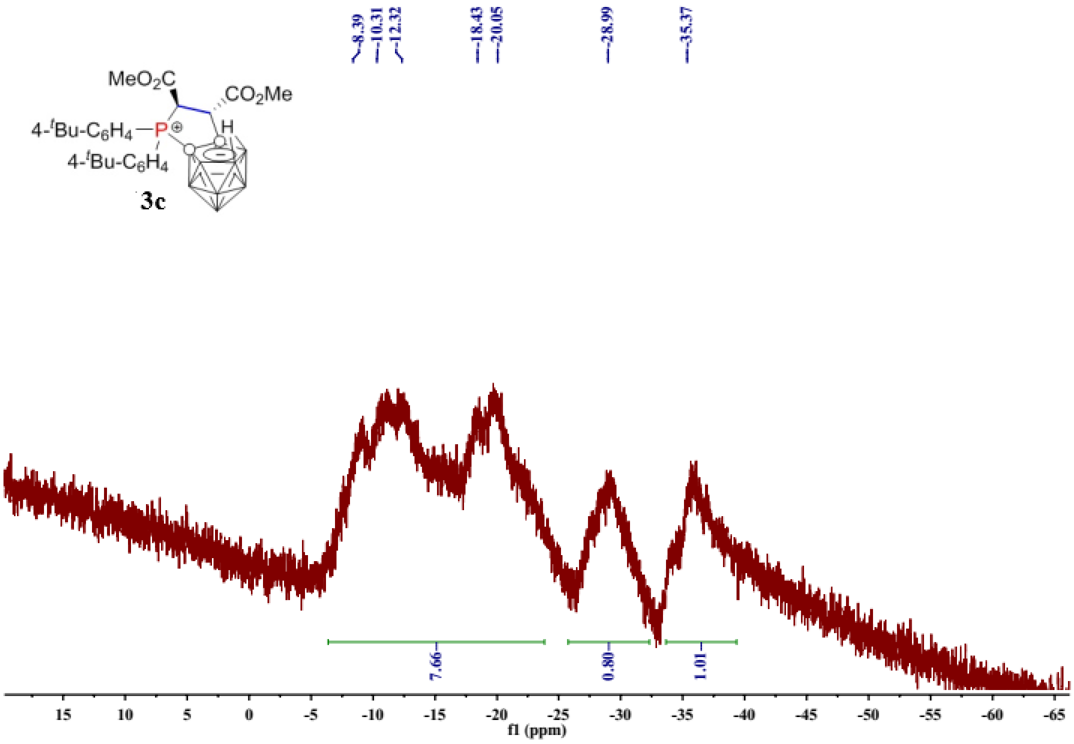


Figure S41. ^{11}B NMR spectrum of **3c** in $CDCl_3$.

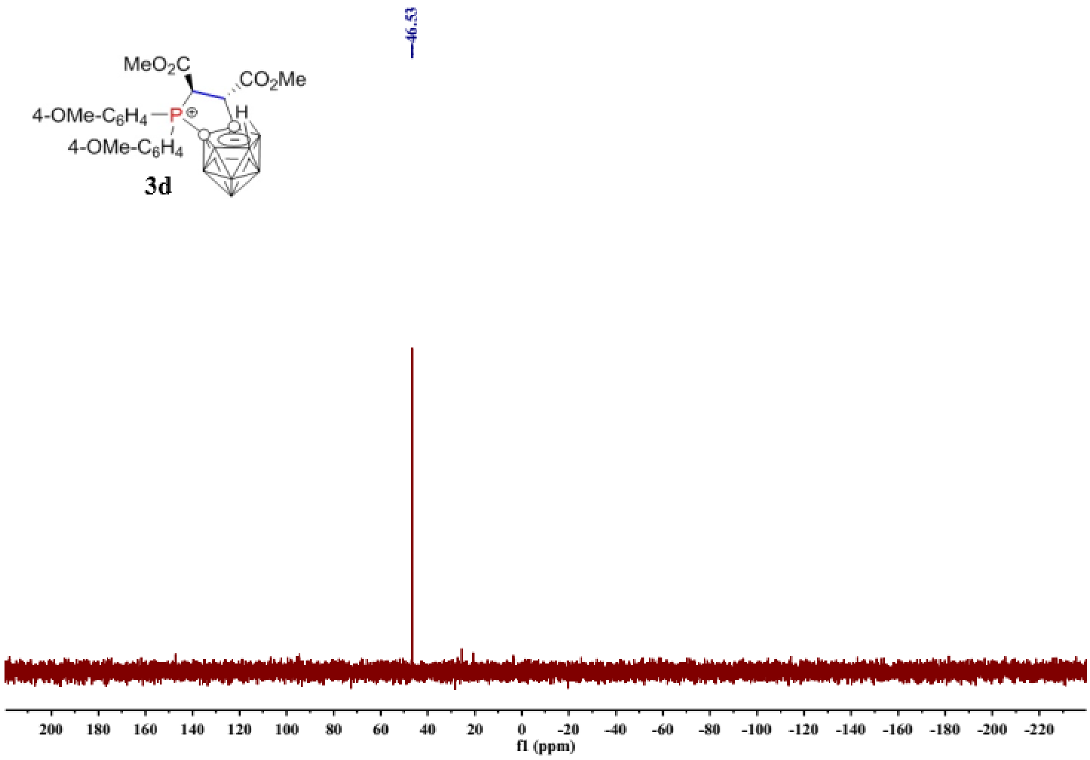


Figure S42. ^{31}P NMR spectrum of **3d** in $CDCl_3$.

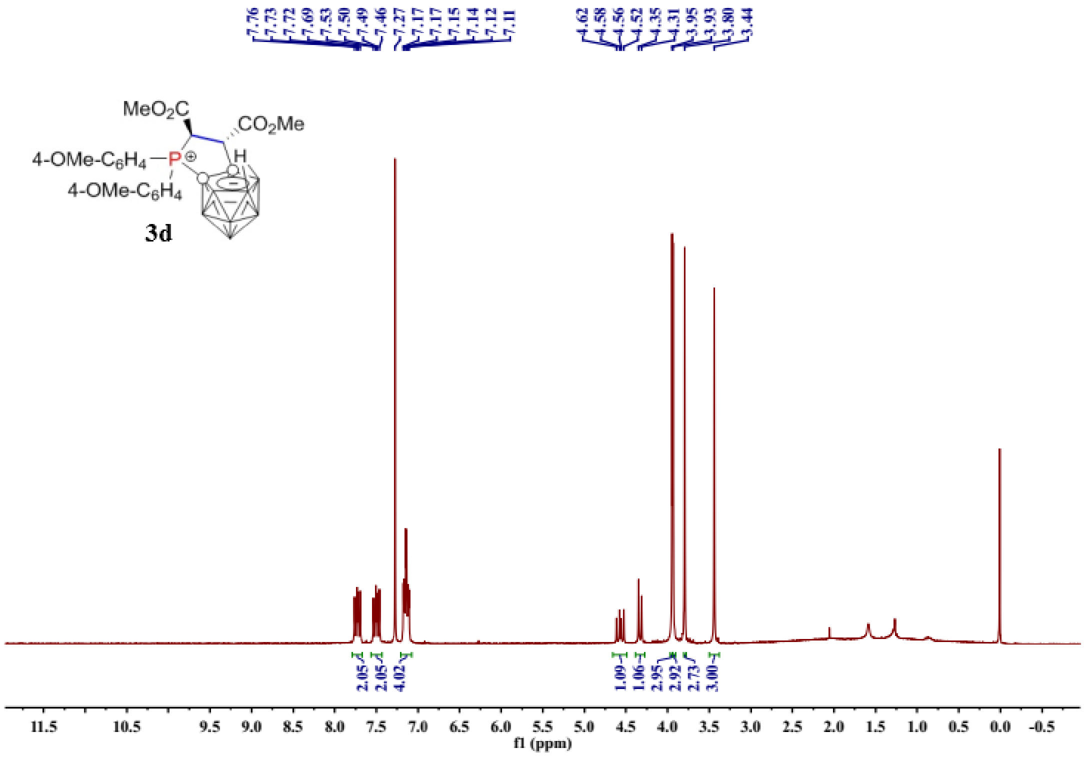


Figure S43. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

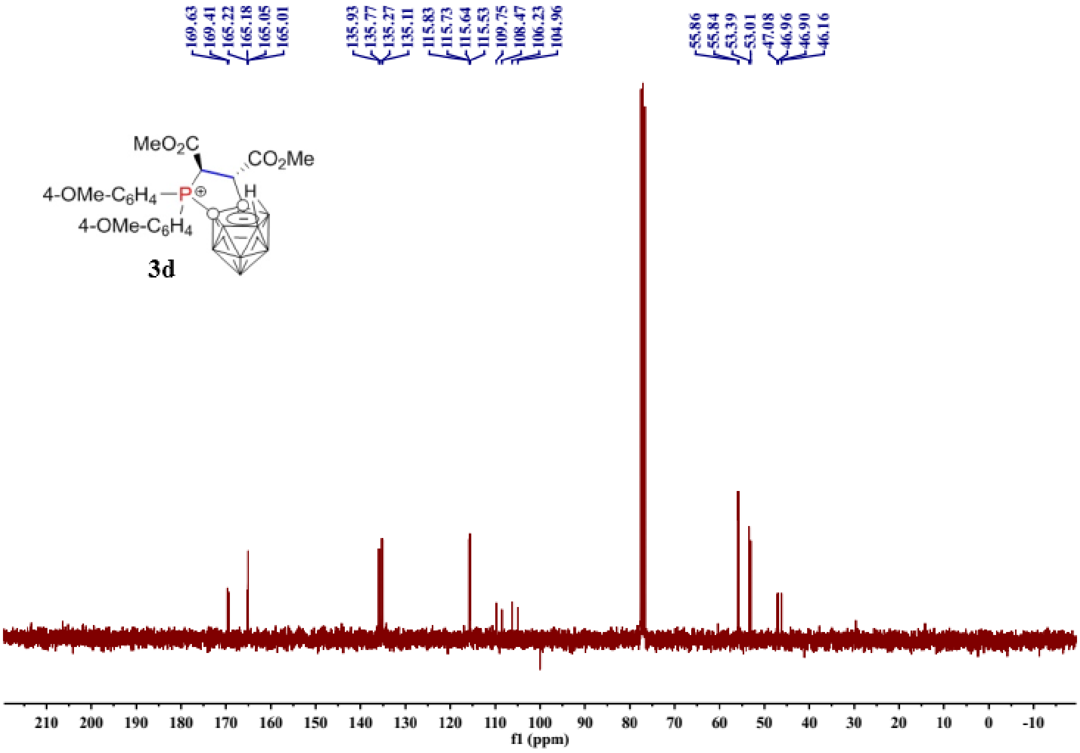


Figure S44. ^{13}C NMR spectrum of **3d** in $CDCl_3$.

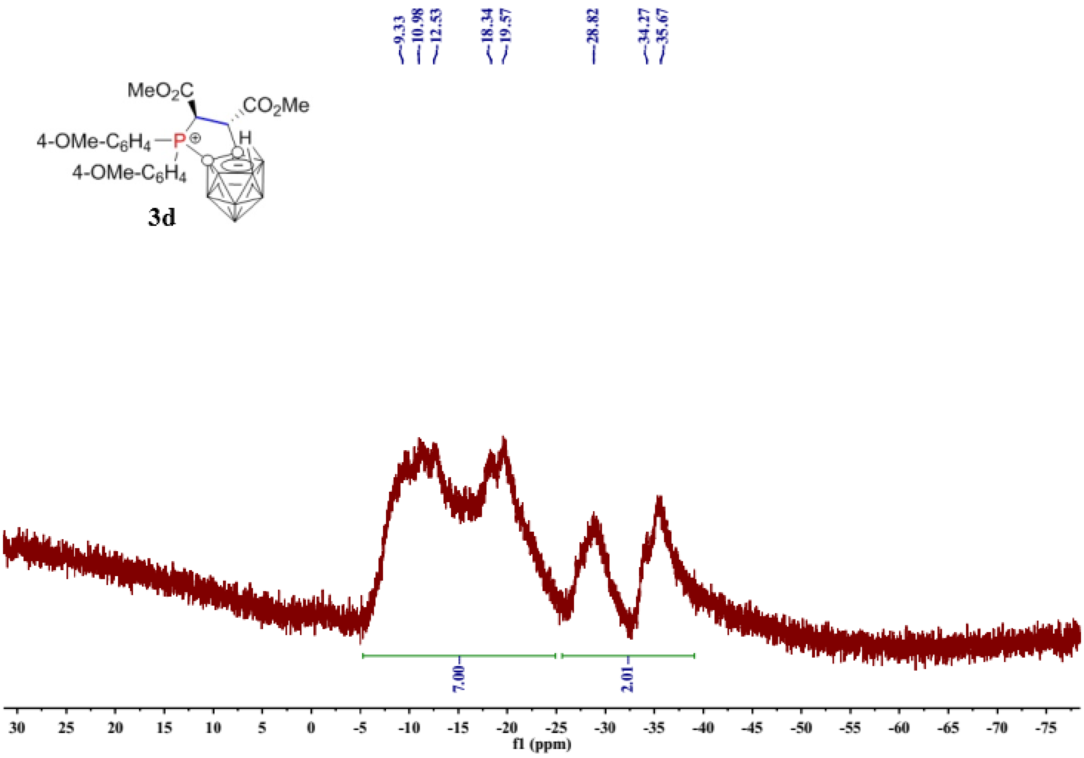


Figure S45. ^{11}B NMR spectrum of **3d** in $CDCl_3$.

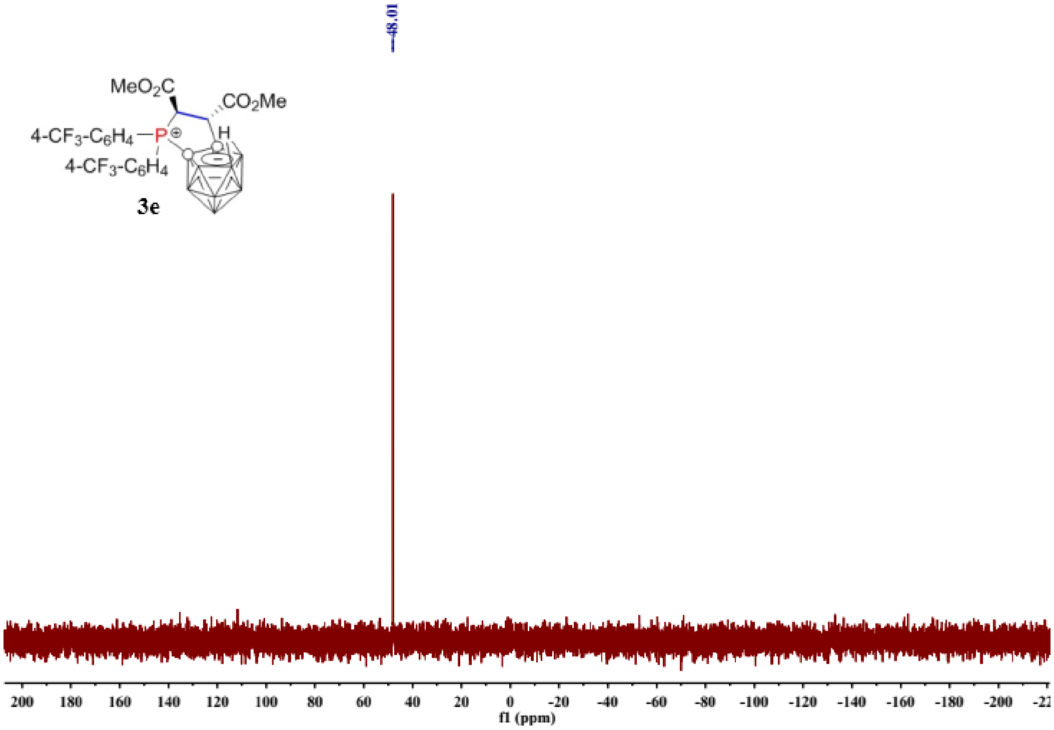


Figure S46. ^{31}P NMR spectrum of **3e** in $CDCl_3$.

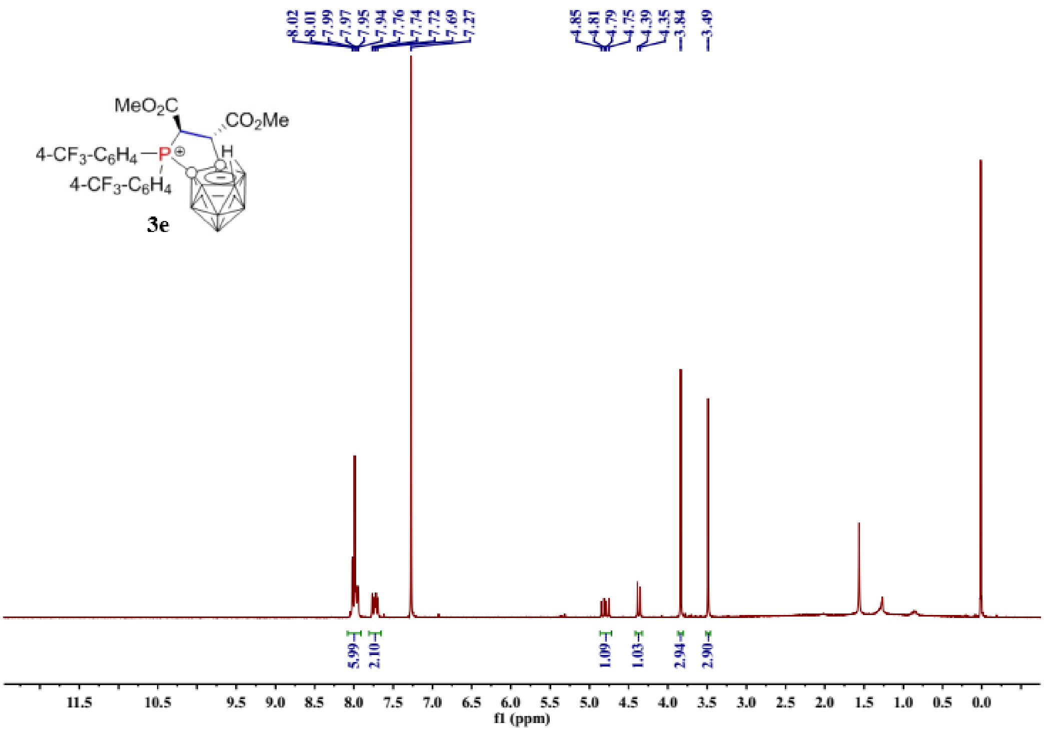


Figure S47. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

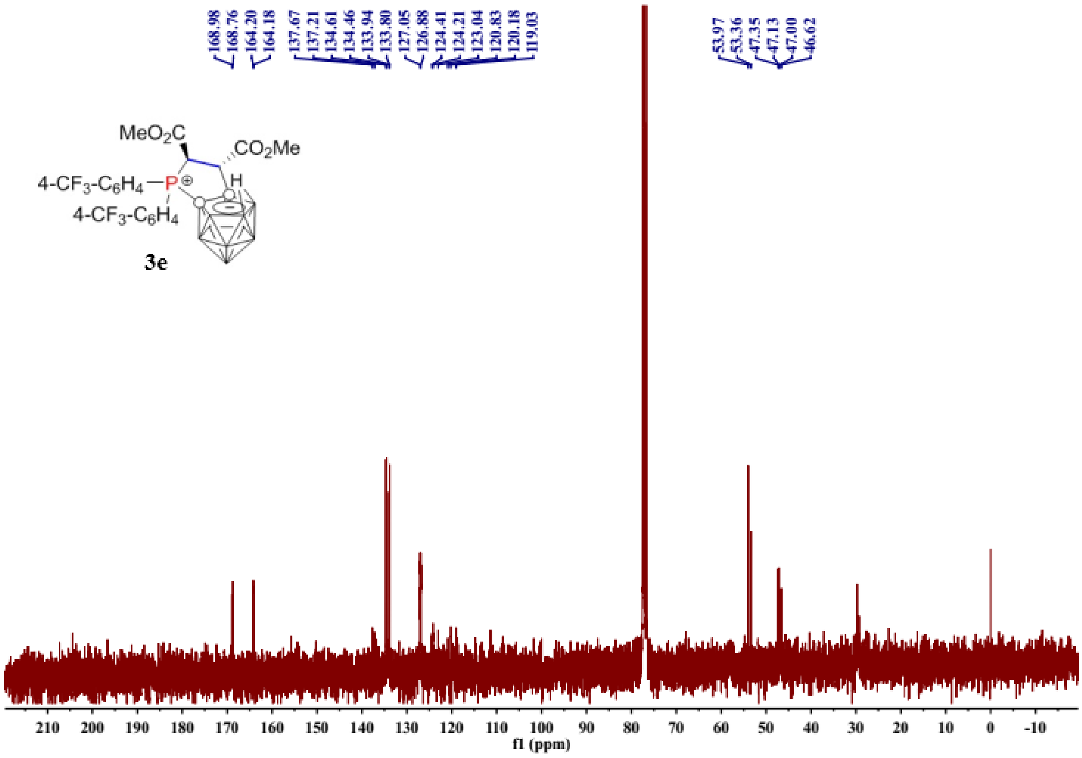


Figure S48. ^{13}C NMR spectrum of **3e** in $CDCl_3$.

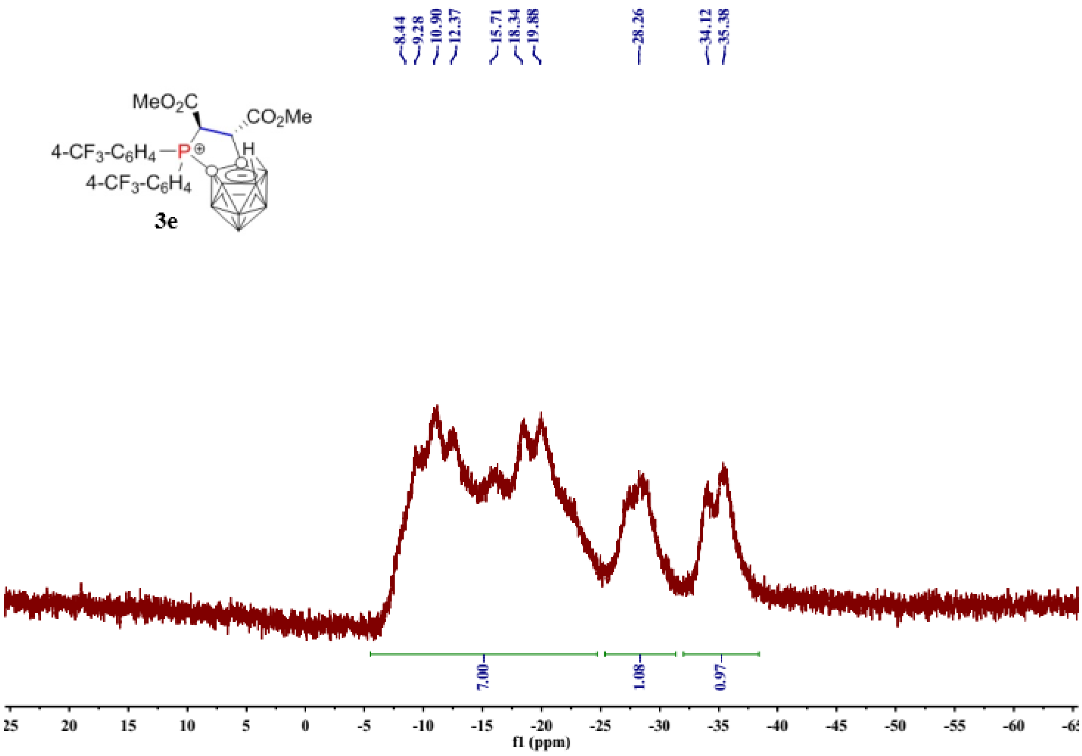


Figure S49. ^{11}B NMR spectrum of **3e** in $CDCl_3$.

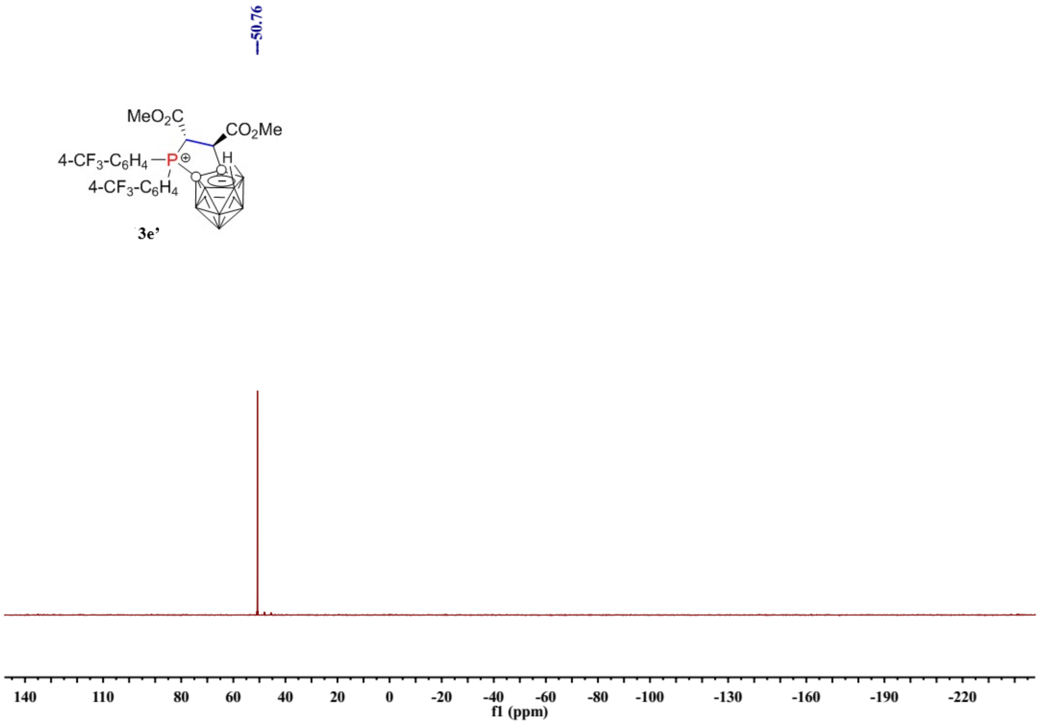


Figure S50. ^{31}P NMR spectrum of **3e'** in $CDCl_3$.

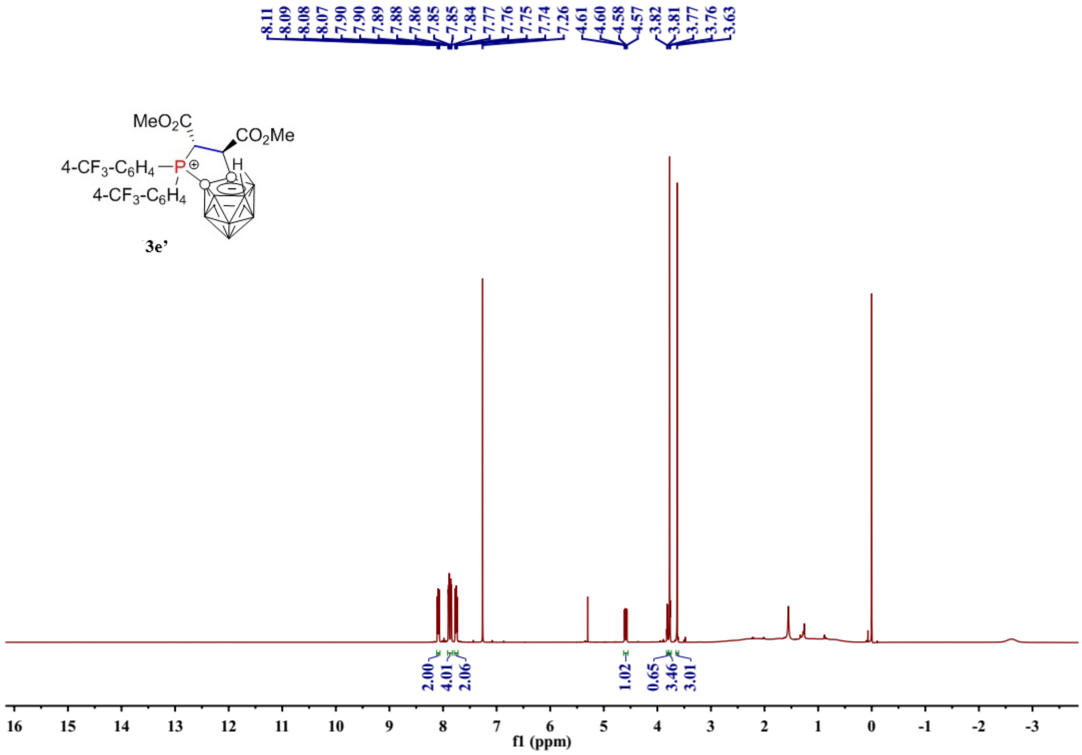


Figure S51. ^{1}H NMR spectrum of **3e'** in $CDCl_3$.

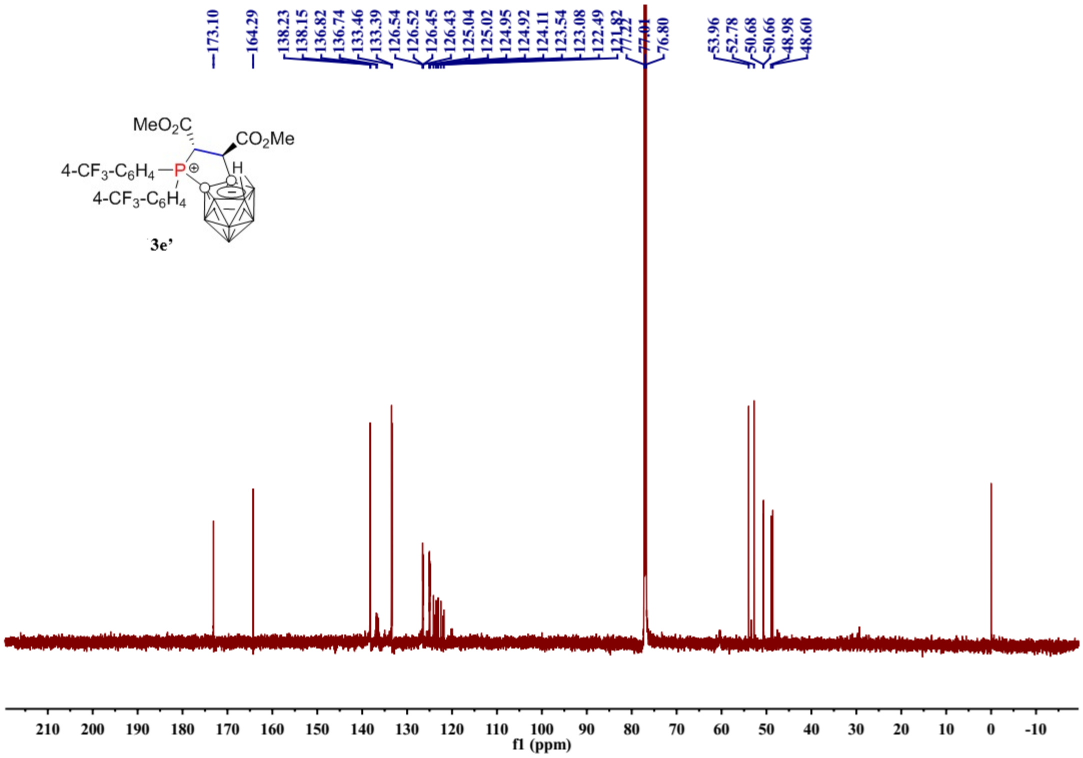


Figure S52. ^{13}C NMR spectrum of **3e'** in $CDCl_3$.

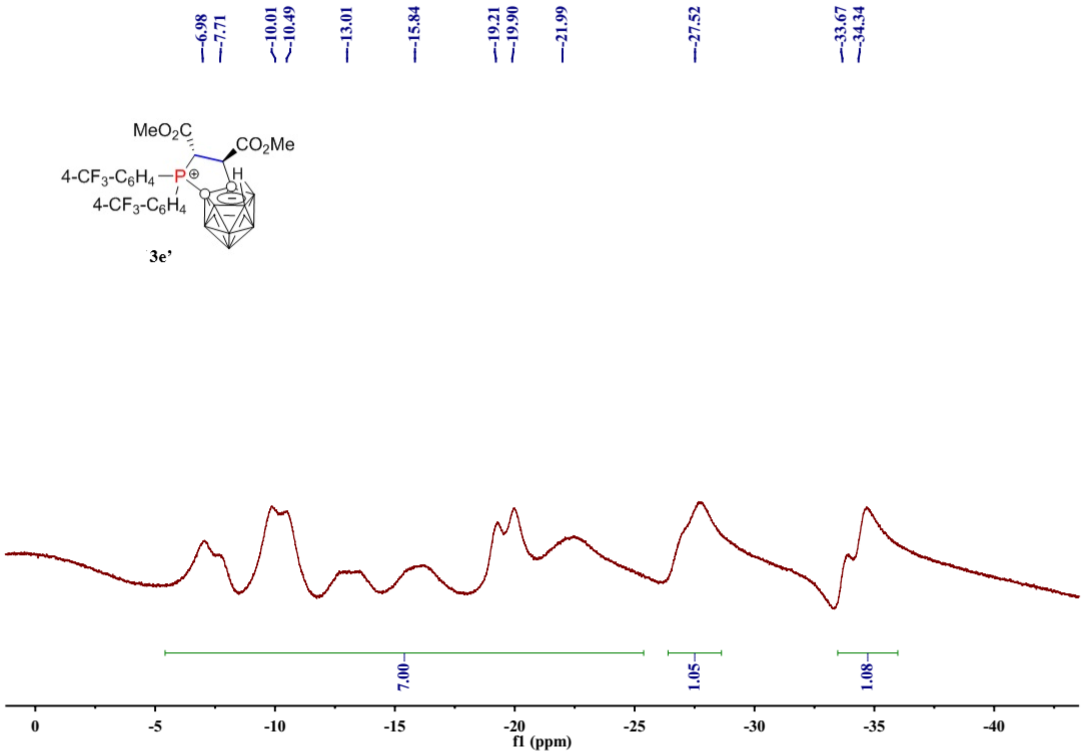


Figure S53. ^{11}B NMR spectrum of **3e'** in $CDCl_3$.

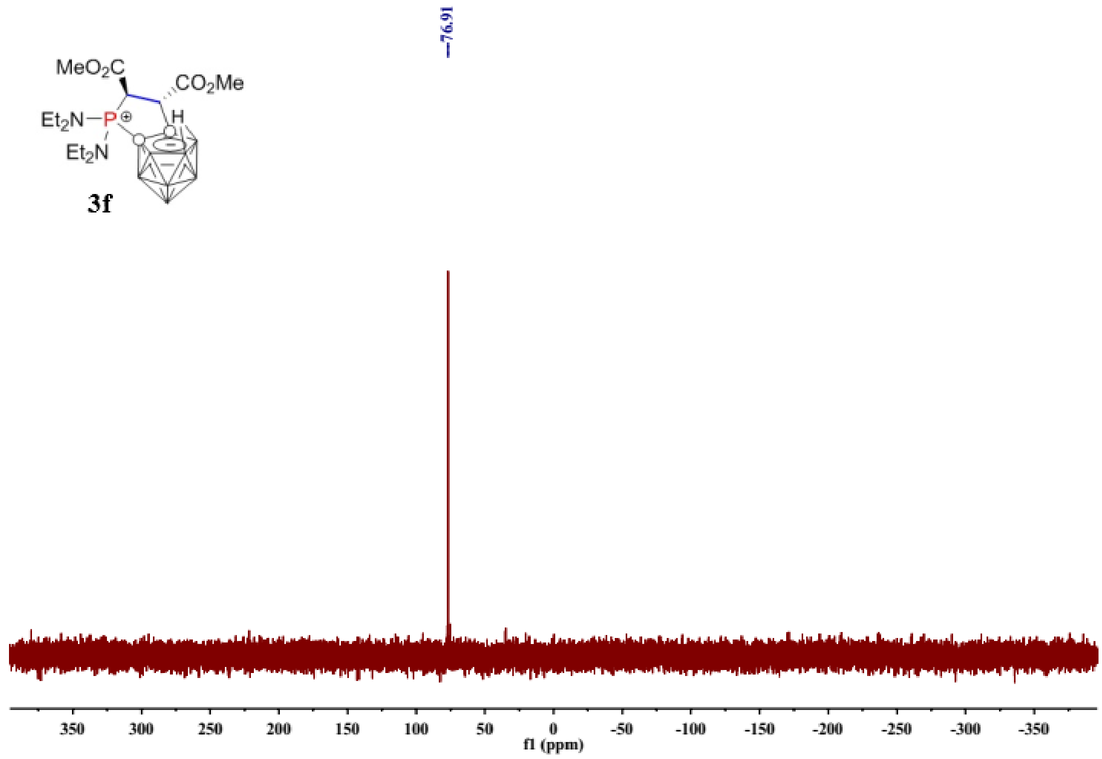


Figure S54. ^{31}P NMR spectrum of **3f** in $CDCl_3$.

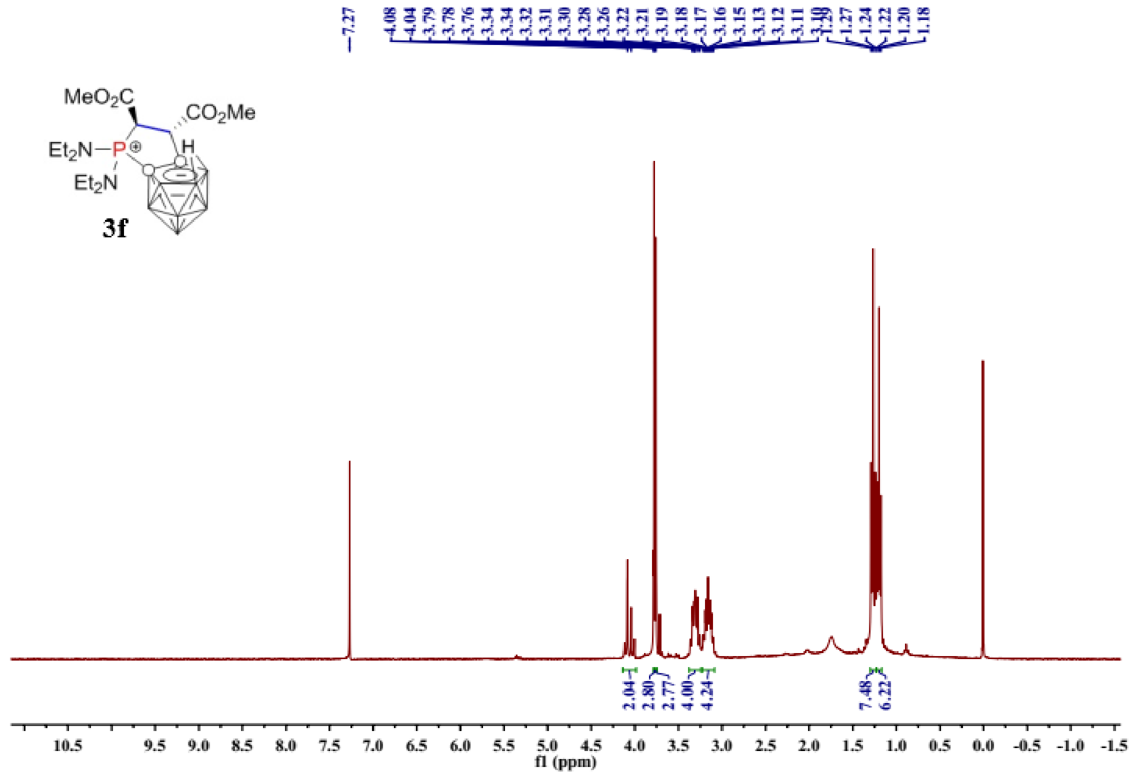


Figure S55. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

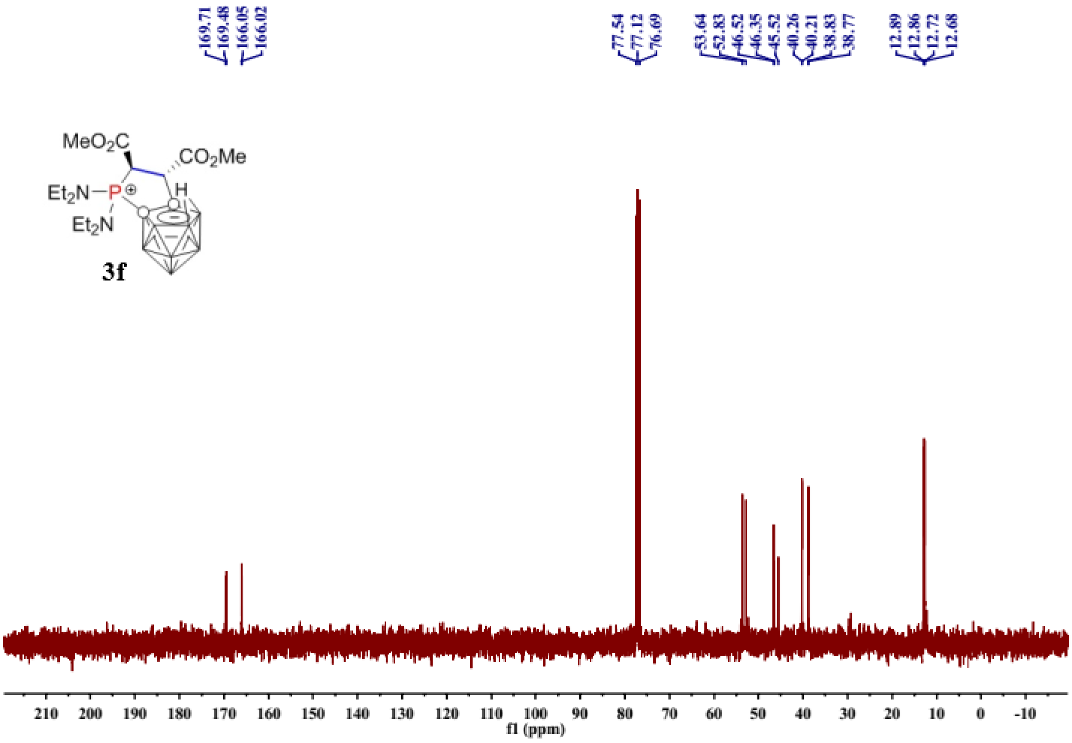


Figure S56. ^{13}C NMR spectrum of **3f** in $CDCl_3$.

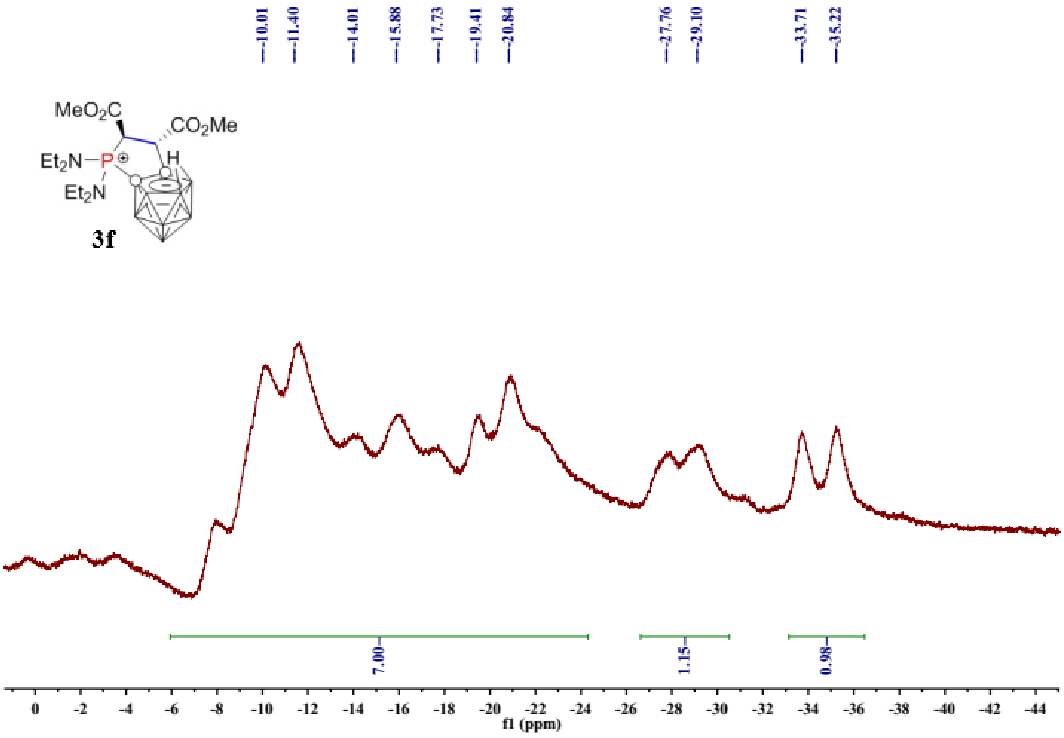


Figure S57. ^{11}B NMR spectrum of **3f** in $CDCl_3$.

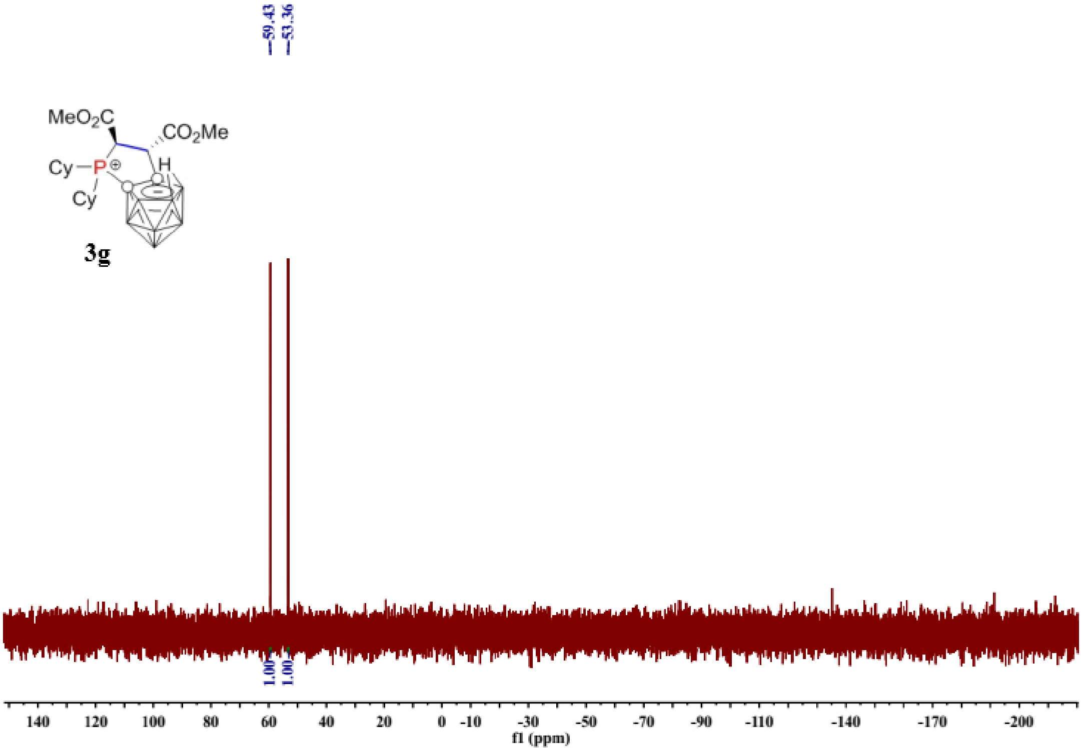


Figure S58. ^{31}P NMR spectrum of **3g** in $CDCl_3$.

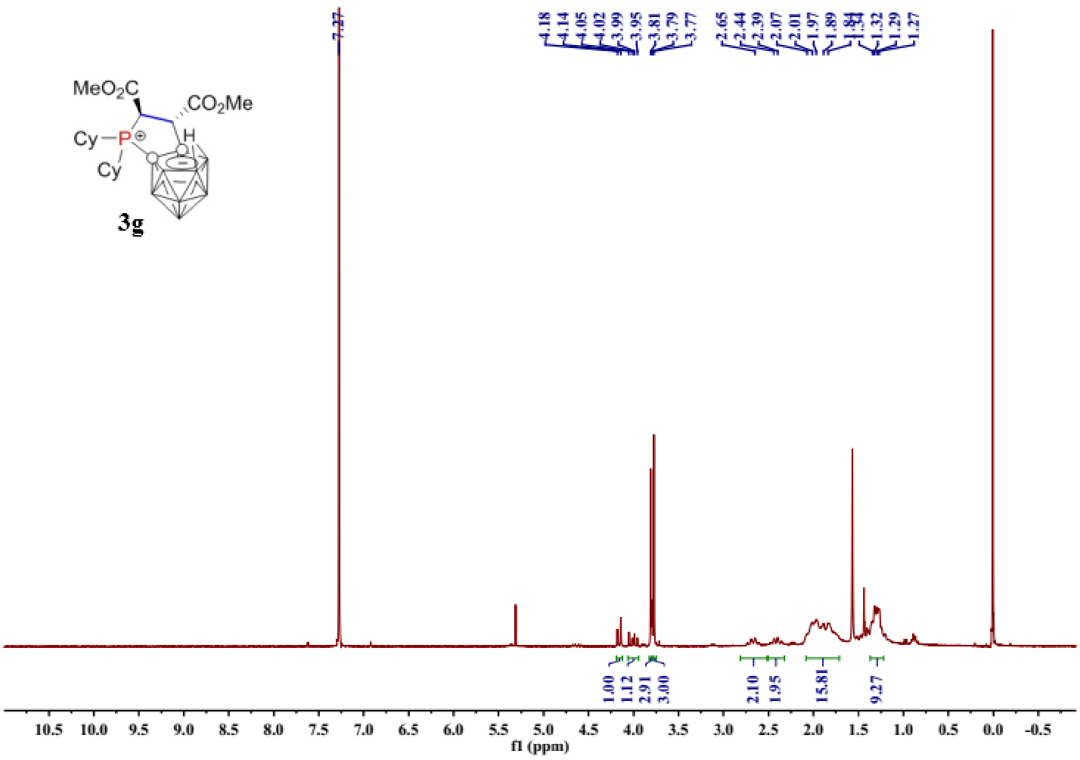


Figure S59. ^{1}H NMR spectrum of **3g** in $CDCl_3$.

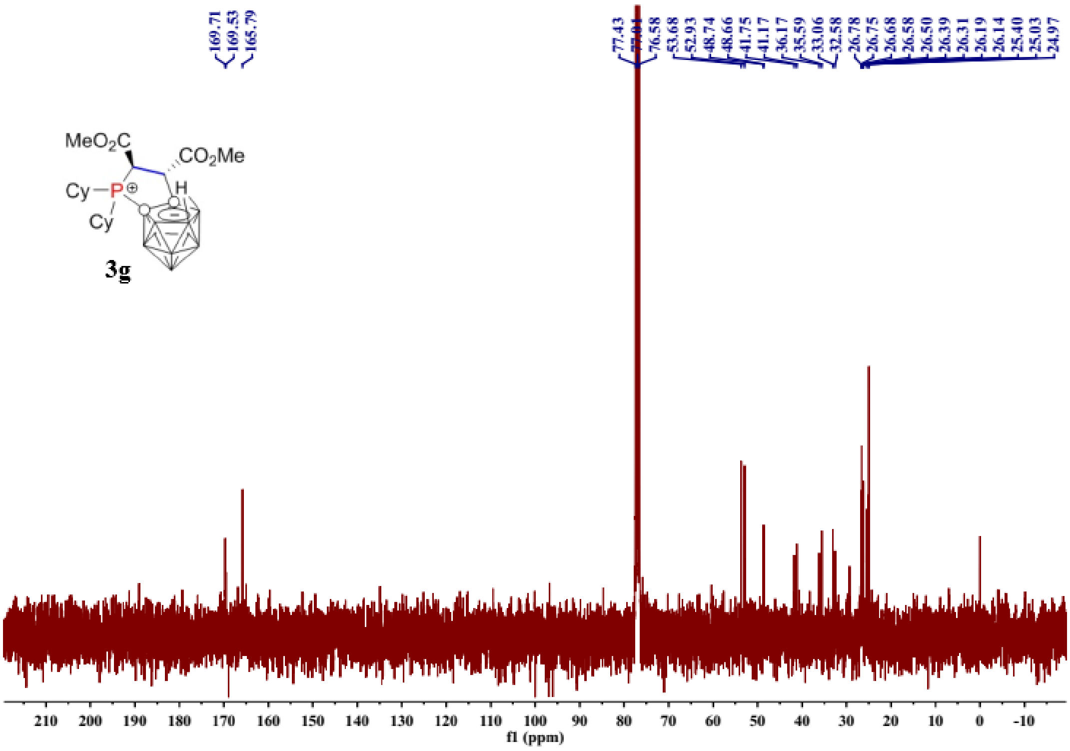


Figure S60. ^{13}C NMR spectrum of **3g** in $CDCl_3$.

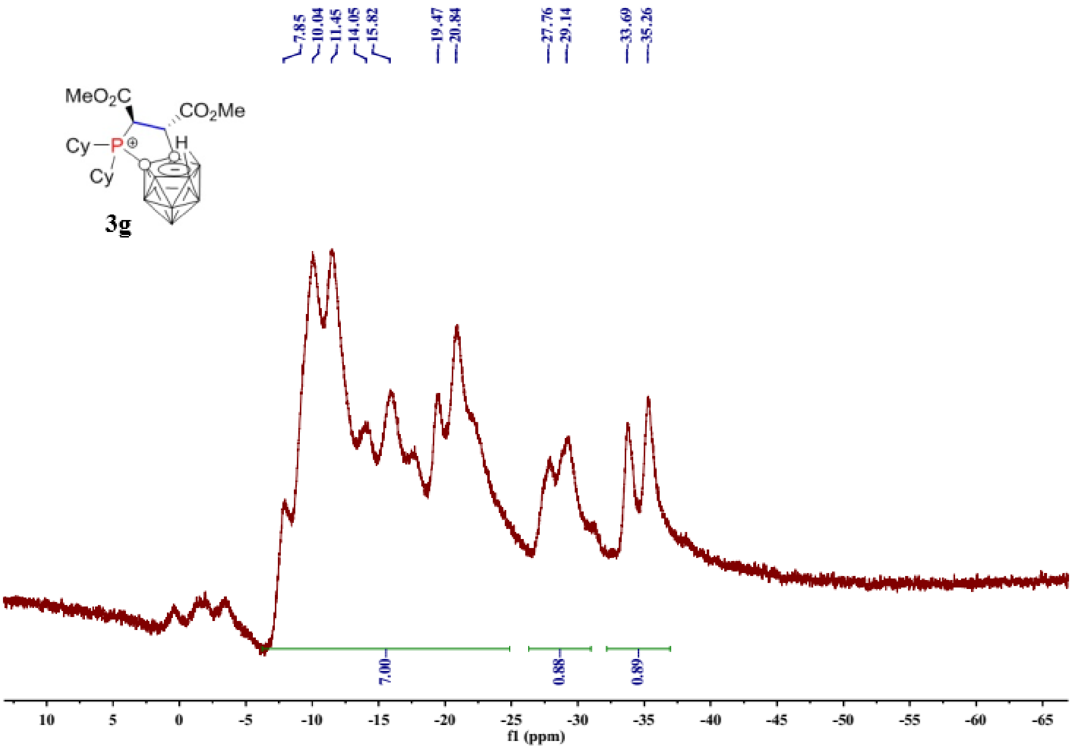


Figure S61. ^{11}B NMR spectrum of **3g** in $CDCl_3$.

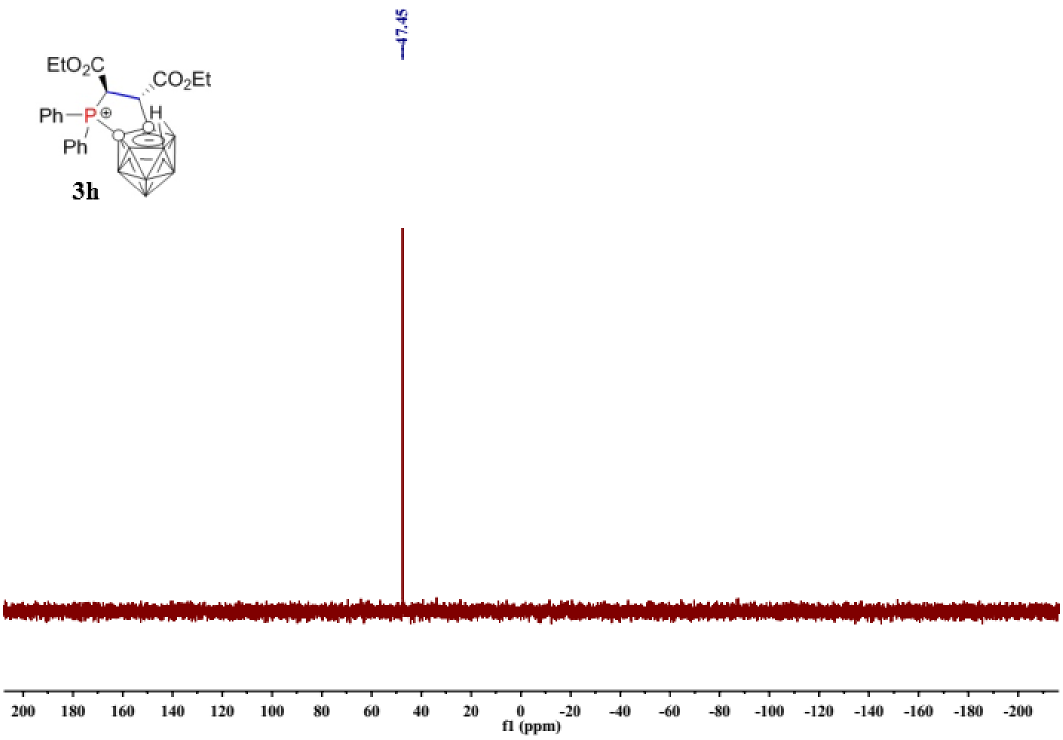


Figure S62. ^{31}P NMR spectrum of **3h** in $CDCl_3$.

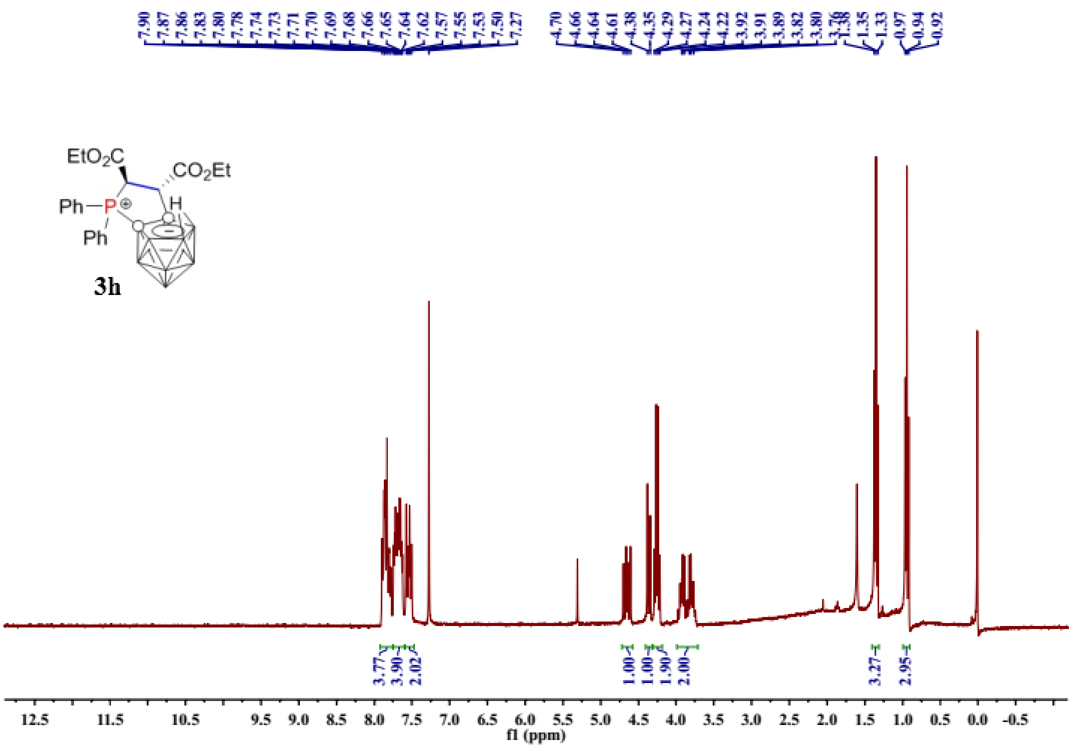


Figure S63. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

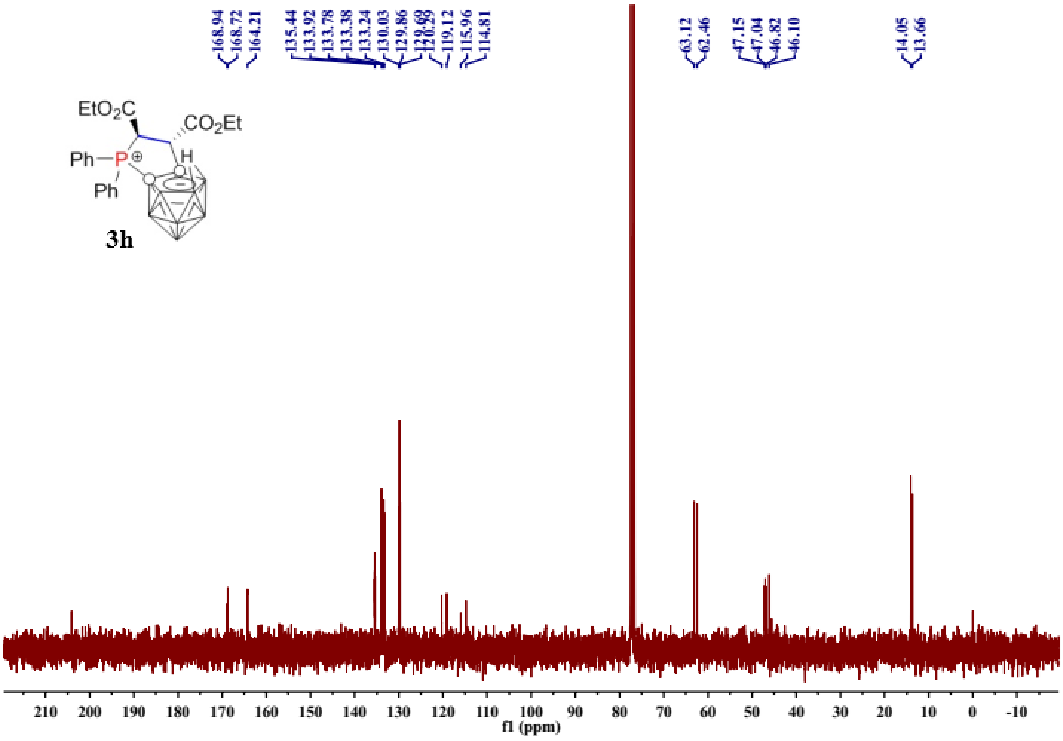


Figure S64. ^{13}C NMR spectrum of **3h** in $CDCl_3$.

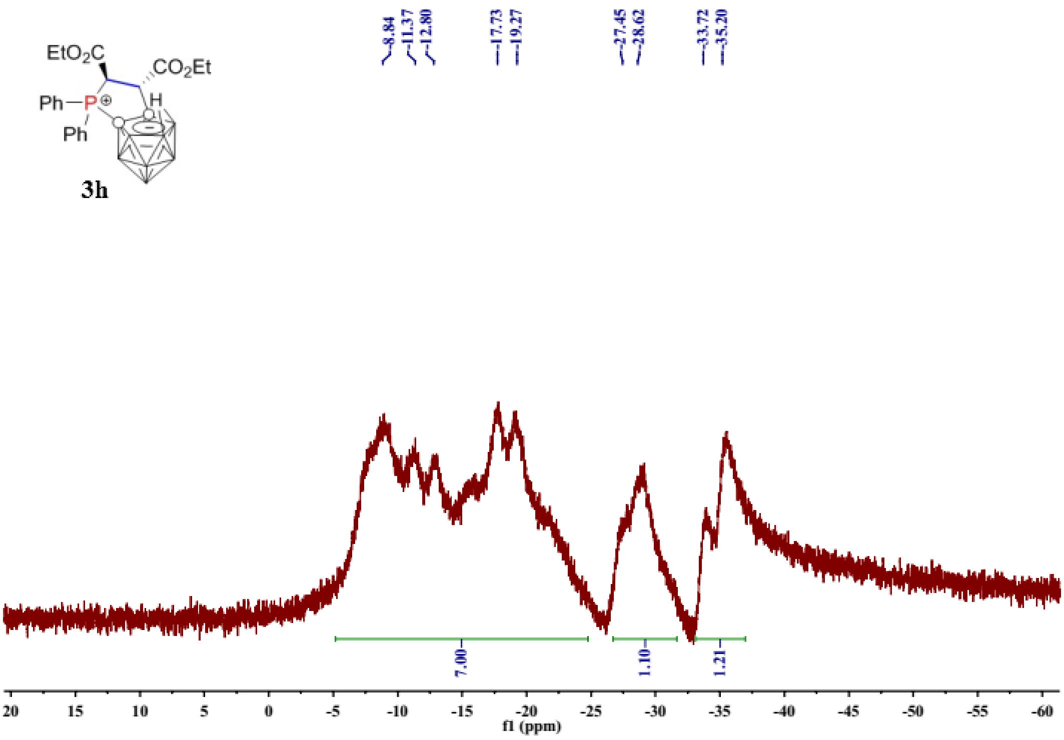


Figure S65. ^{11}B NMR spectrum of **3h** in $CDCl_3$.

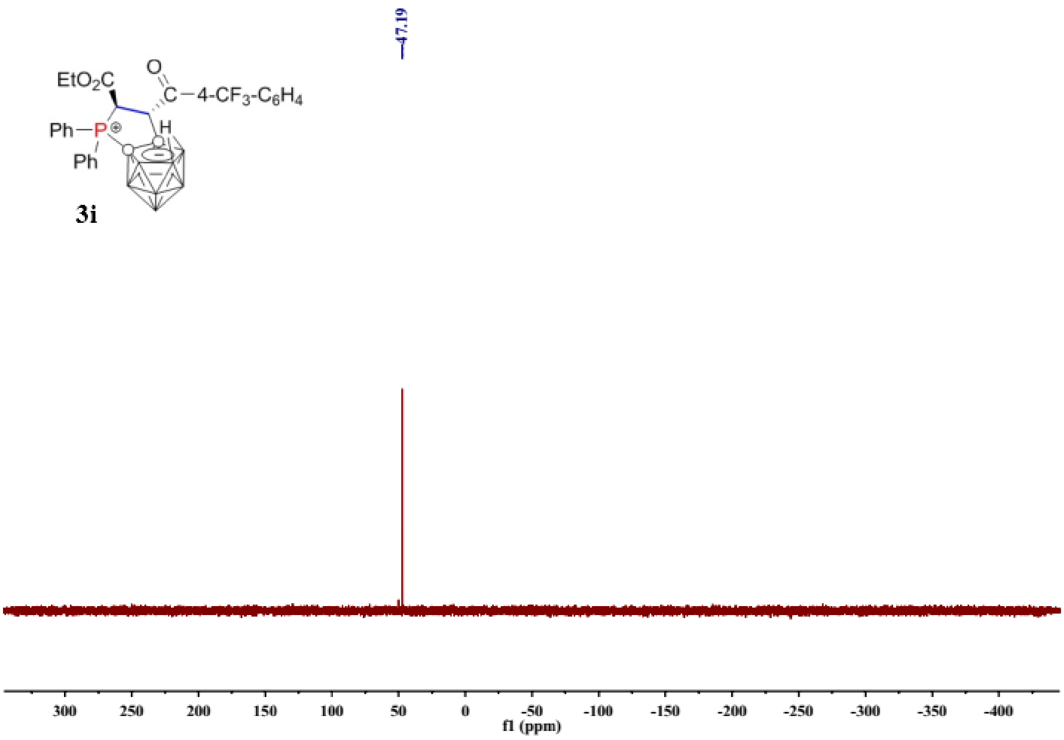


Figure S66. ^{31}P NMR spectrum of **3i** in $CDCl_3$.

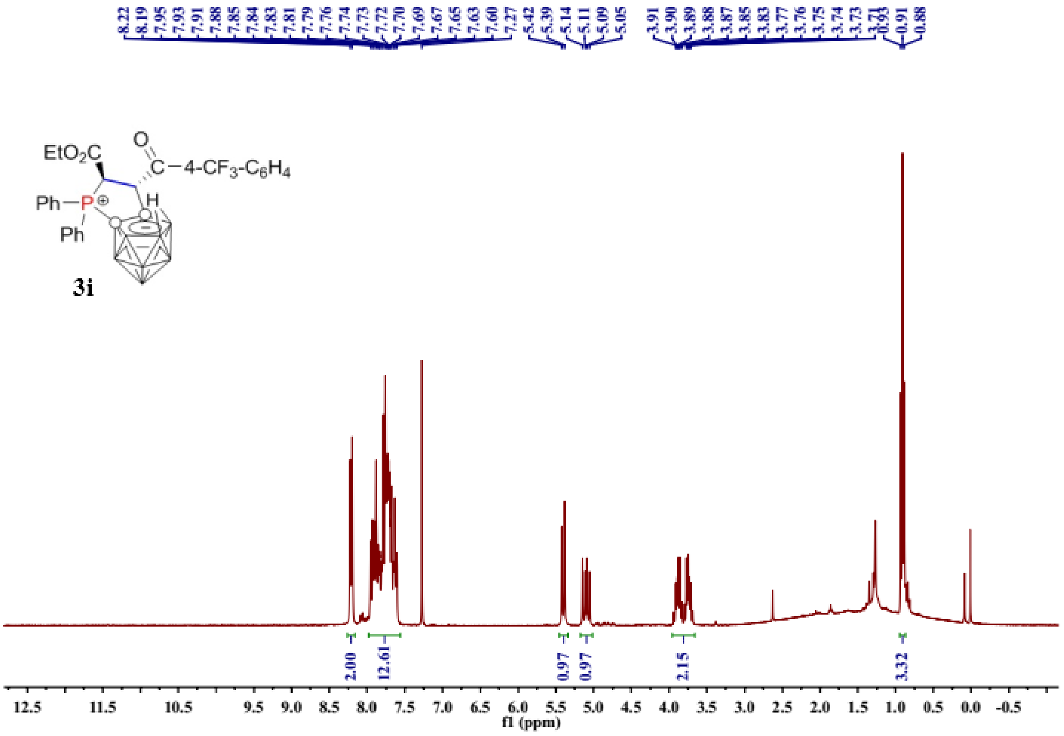


Figure S67. ^{1}H NMR spectrum of **3i** in $CDCl_3$.

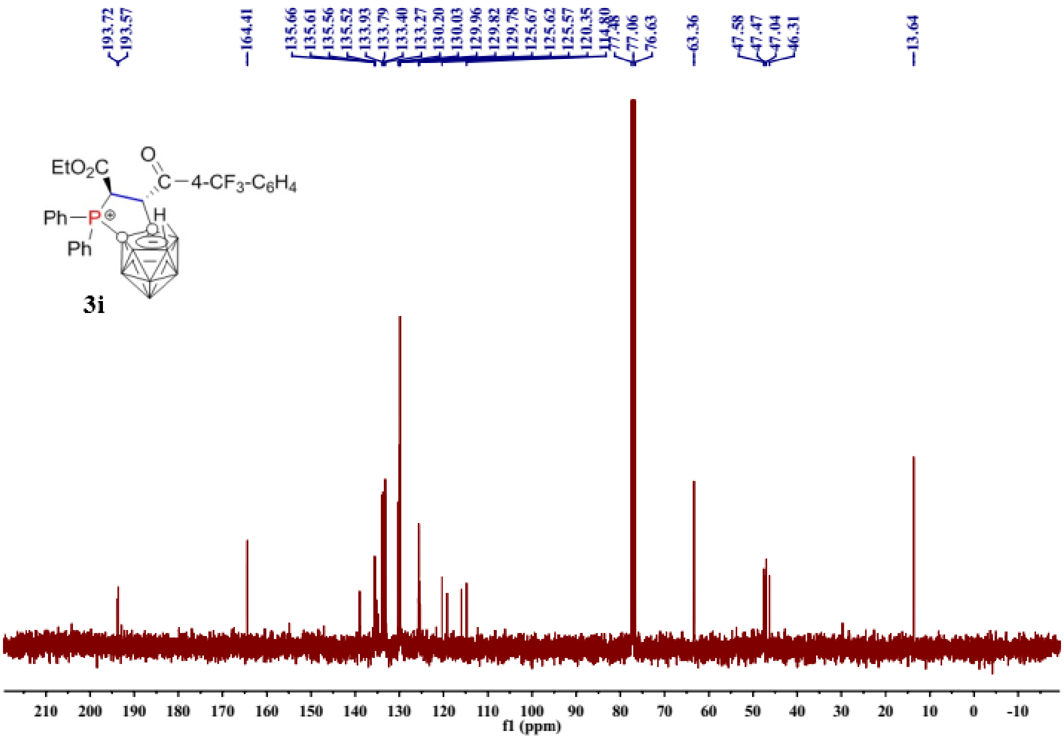


Figure S68. ^{13}C NMR spectrum of **3i** in $CDCl_3$.

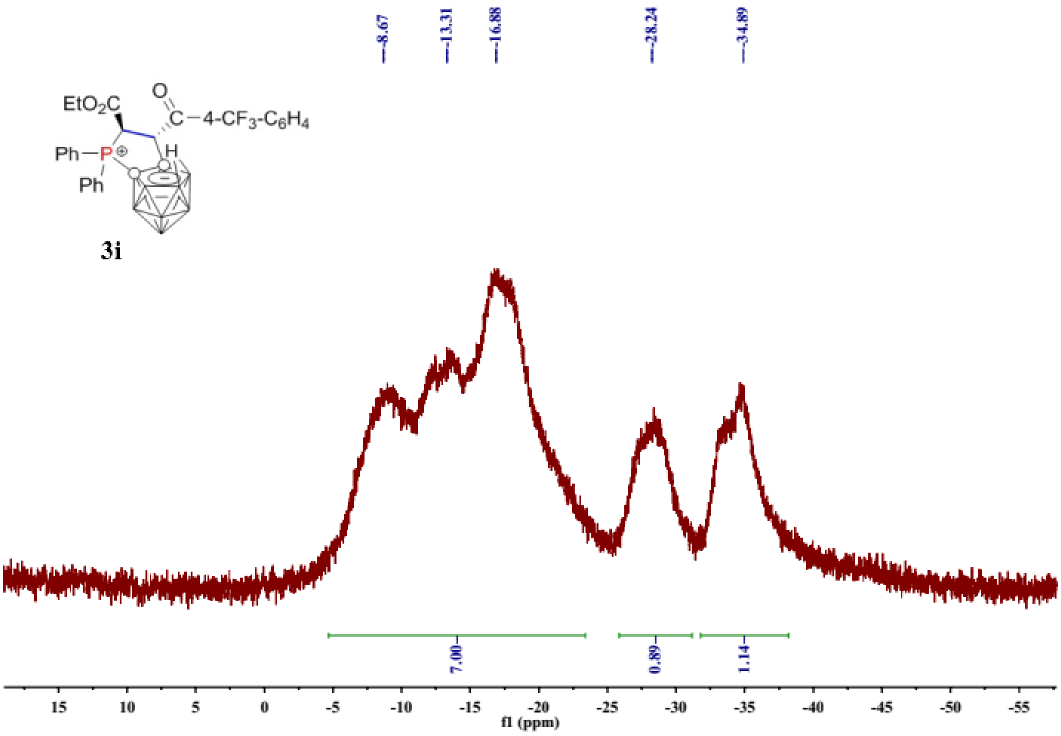


Figure S69. ^{11}B NMR spectrum of **3i** in $CDCl_3$.

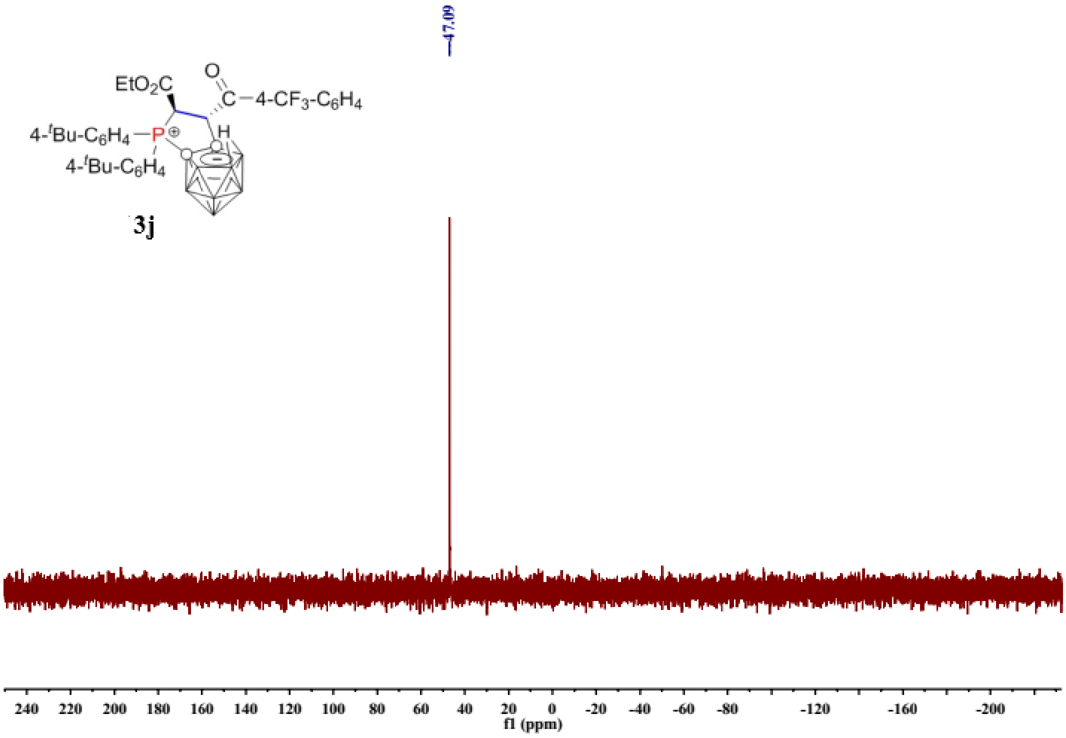


Figure S70. ^{31}P NMR spectrum of **3j** in $CDCl_3$.

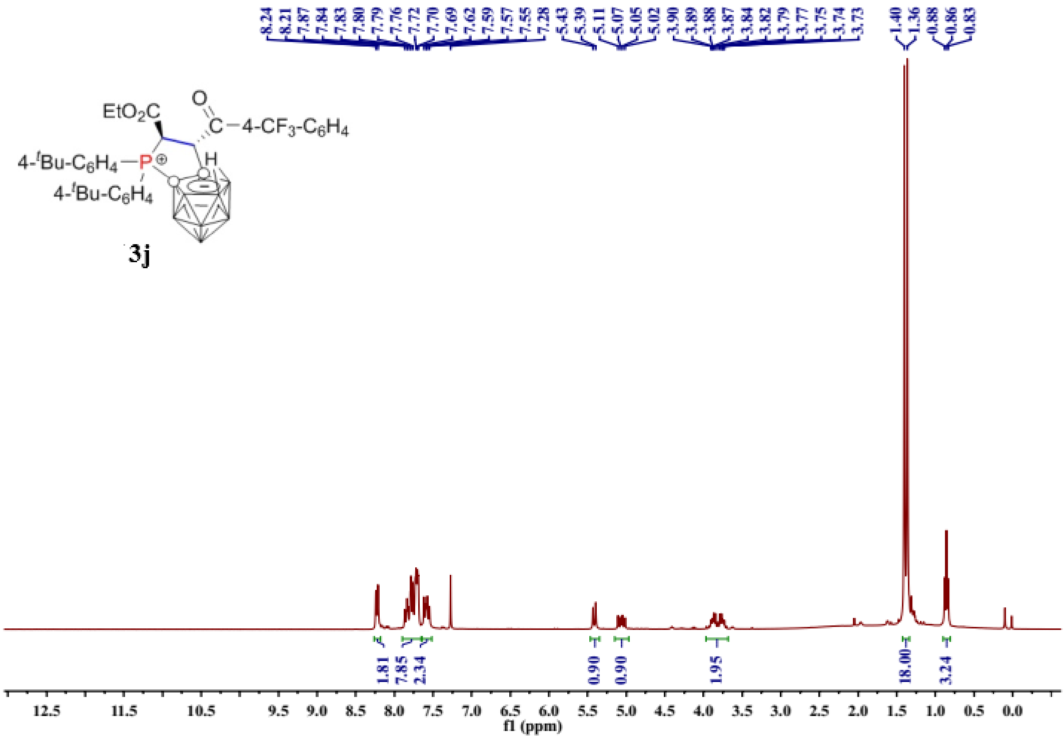


Figure S71. ^{1}H NMR spectrum of **3j** in $CDCl_3$.

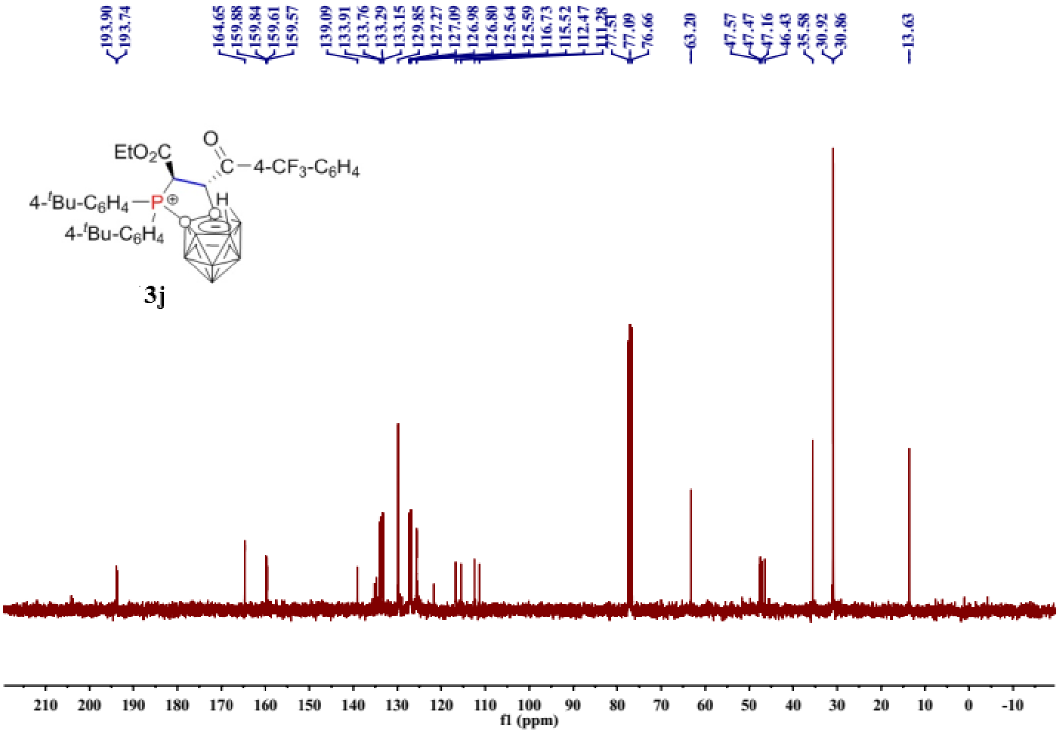


Figure S72. ^{13}C NMR spectrum of **3j** in $CDCl_3$.

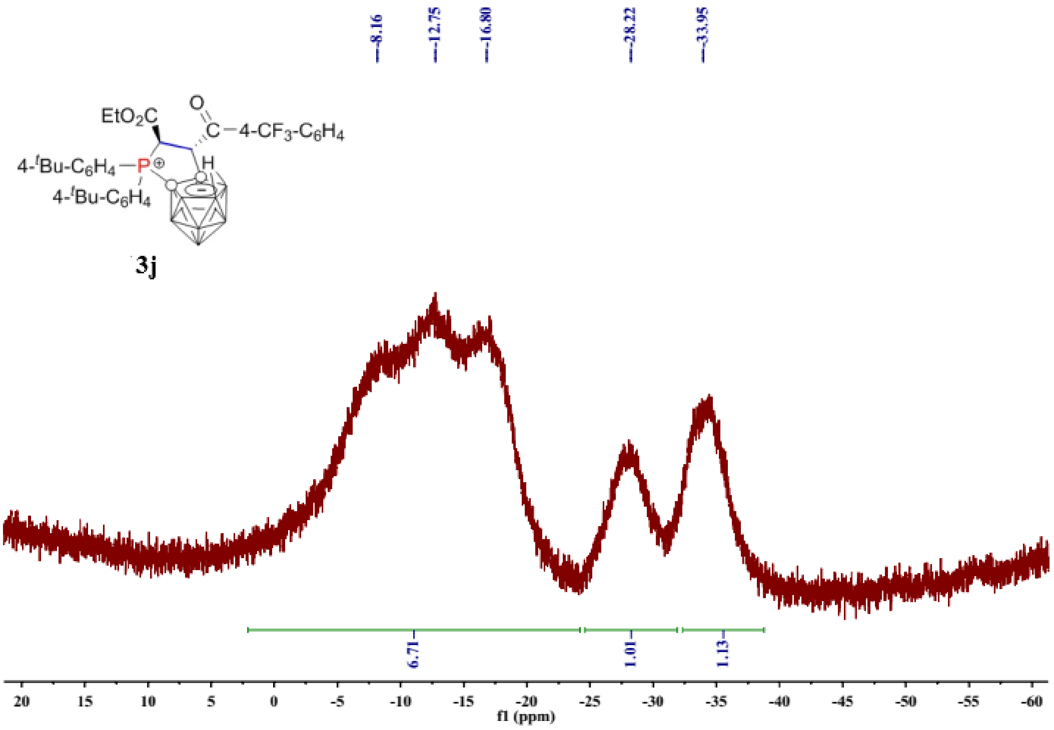


Figure S73. ^{11}B NMR spectrum of **3j** in $CDCl_3$.

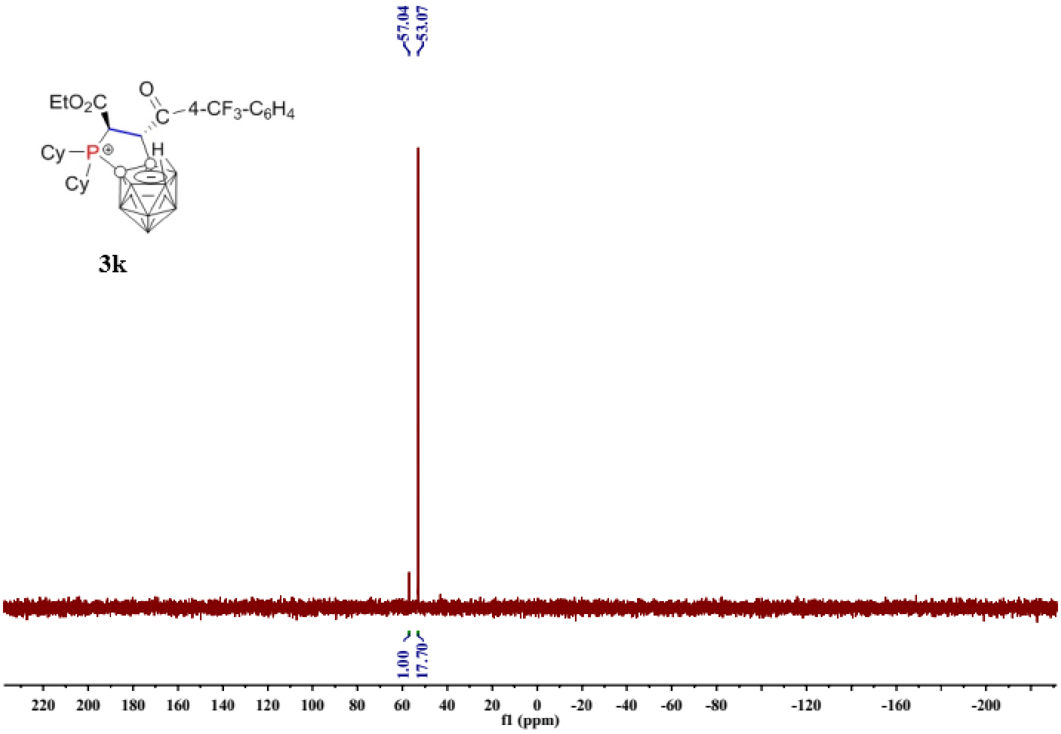


Figure S74. ^{31}P NMR spectrum of **3k** in $CDCl_3$.

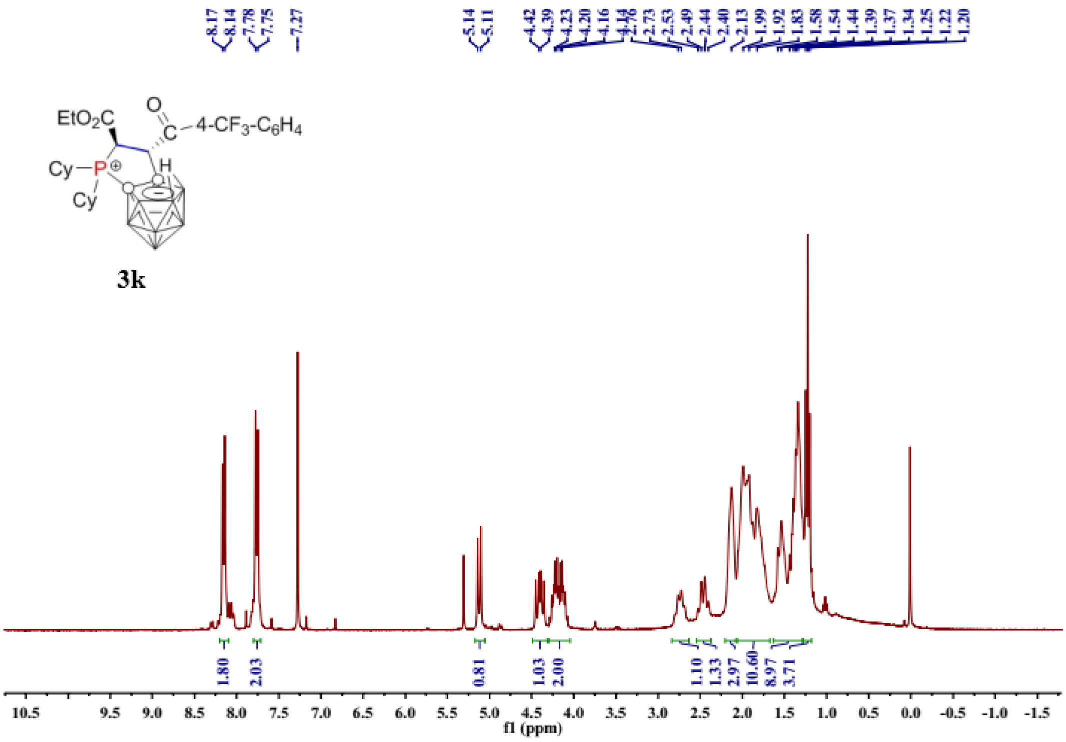


Figure S75. ^{1}H NMR spectrum of **3k** in $CDCl_3$.

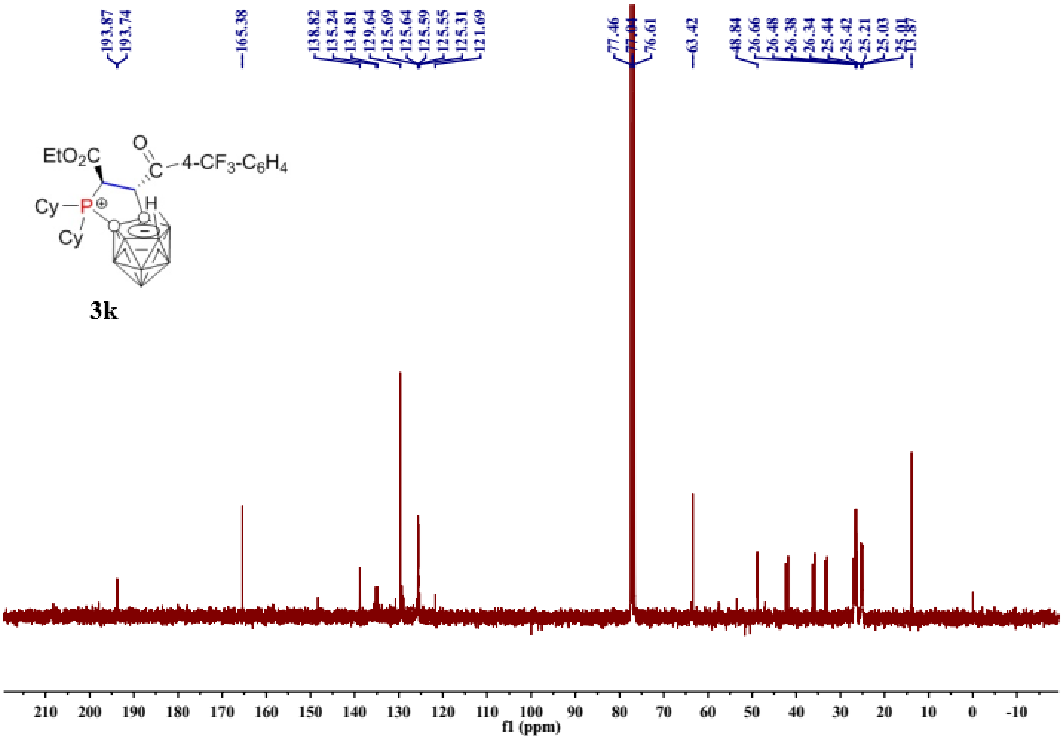


Figure S76. ^{13}C NMR spectrum of **3k** in $CDCl_3$.

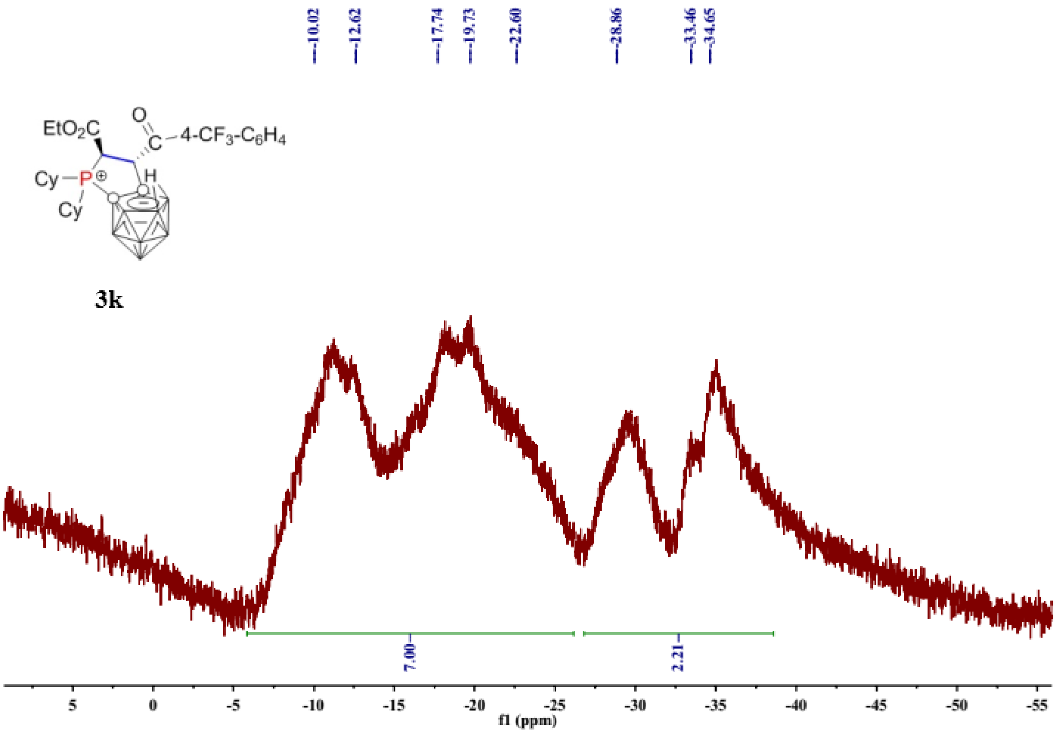


Figure S77. ^{11}B NMR spectrum of **3k** in $CDCl_3$.

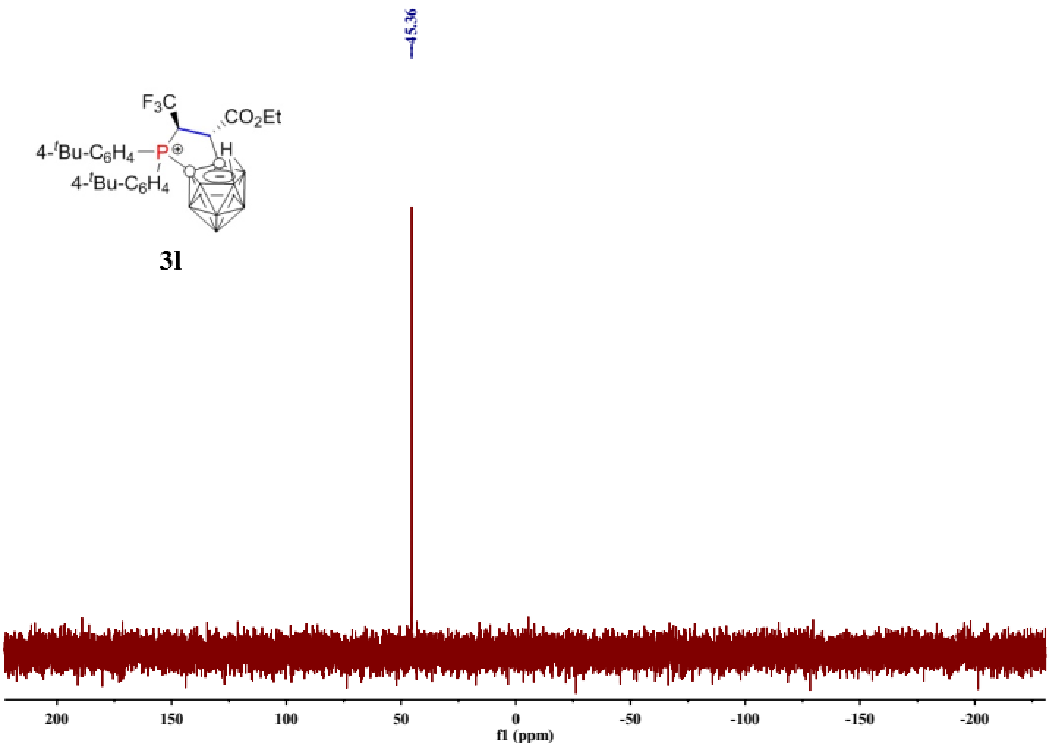


Figure S78. ^{31}P NMR spectrum of **3l** in $CDCl_3$.

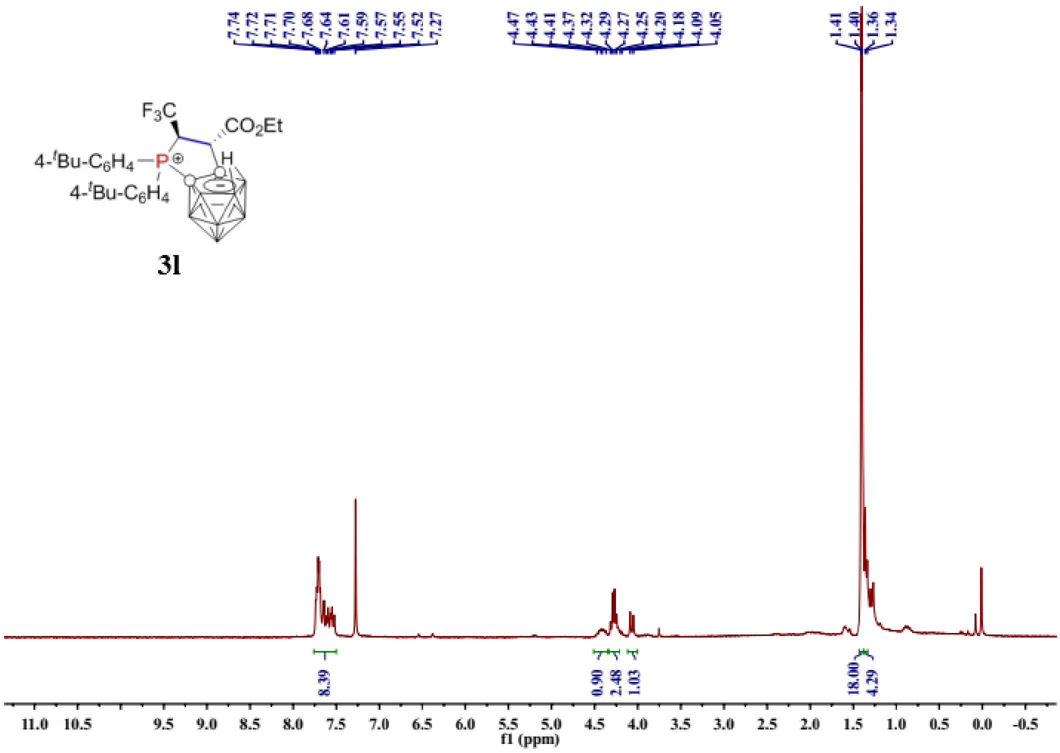


Figure S79. ^{1}H NMR spectrum of **3l** in $CDCl_3$.

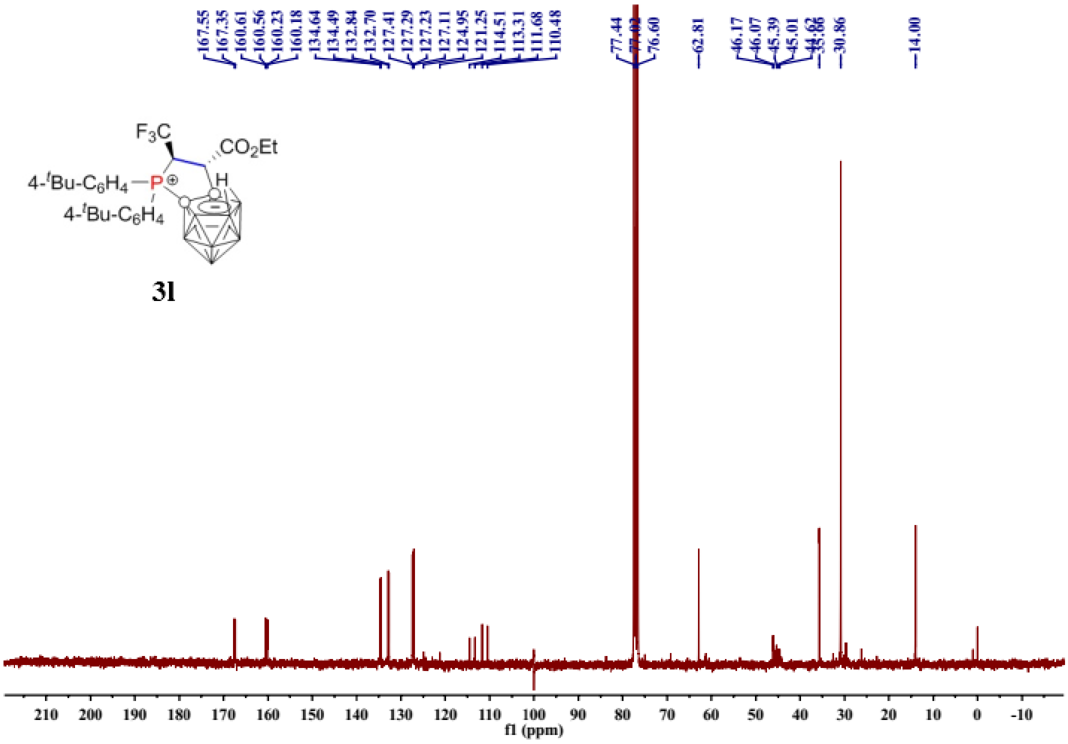


Figure S80. ^{13}C NMR spectrum of **3l** in $CDCl_3$.

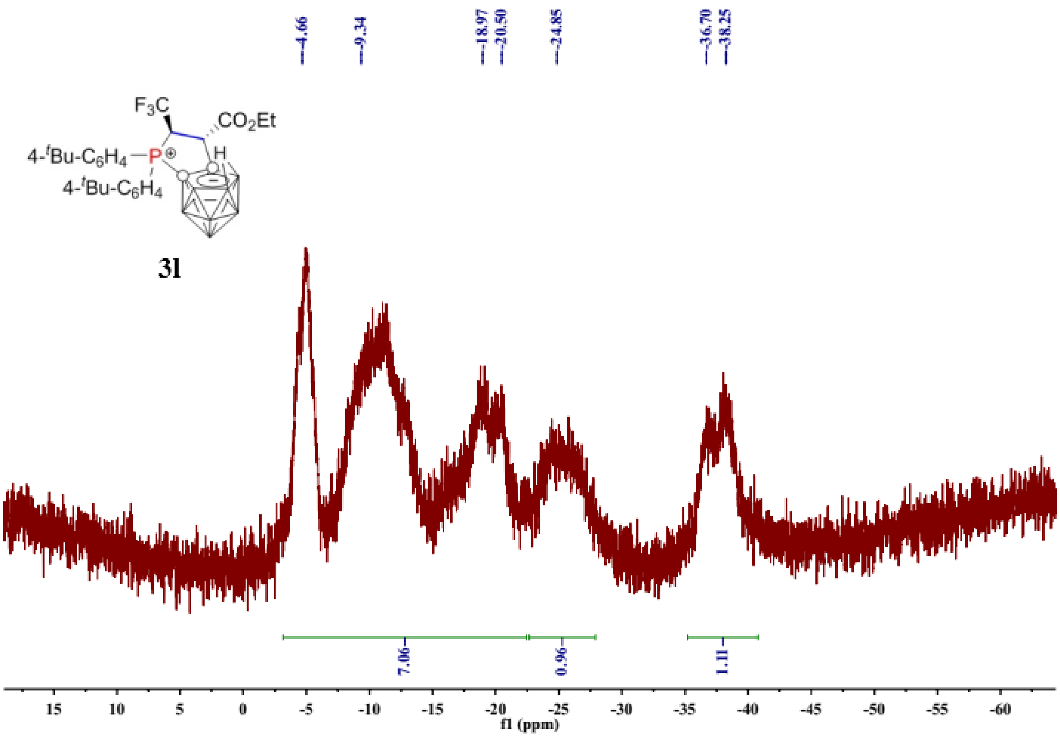


Figure S81. ^{11}B NMR spectrum of **3l** in $CDCl_3$.