Supporting information

PCCP ligands with a semi-rigid backbone for the chromium-catalyzed selective ethylene tri-/tetramerization

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1. Experimental Section

1.1 General Information

Unless otherwise stated, all reactions and manipulations were carried out under an atmosphere of nitrogen using standard Schenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. MMAO-3A (modified methylaluminoxane) (7 wt % in heptane solution) was purchased from Akzo-Nobel. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^{1}H NMR $CDCl_3$: 7.26 ppm; ^{13}C NMR $CDCl_3$: 77.0 ppm). Elemental analysis were performed by microanalytical laboratory in house. Quantitative gas chromatographic analysis of the products of oligomerization was performed on an Agilent 6890 series GC instrument with a J&W DB-1HT column working at 38 ^{o}C for 10 min and then heating at 10 ^{o}C min^{-1} until 250 ^{o}C. *n*-Nonane was used as an internal standard. Mass spectra were recorded on the XEVO G2 TOF instrument by ESI methods. IR spectra were recorded on the Nicolet Magna-IR 550 spectrometer.

$CrCl_3(THF)_3$ was prepared by literature method [1] and its purity verified by elemental analysis. Known compounds **1a~3a** [2], **1b** [2a], (±)-cyclohexylphenylphosphine oxide [3], chloro(cyclohexyl)(phenyl)phosphane [4] were prepared according to the literature methods and the purity assessed by ^{1}H and ^{31}P NMR spectroscopy.

1.2 Preparation and characterization of L^1~L^5

Cyclohexyl(3-methylbuta-1,2-dien-1-yl)(phenyl)phosphine oxide (4a)

4a was prepared according to literature method [2a]. In a 50 mL Schlenk flask, 2-methylbut-3-yn-2-ol (0.84 g, 10.0 mmol) and Et_3N (2.10 mL, 15.1 mmol) were dissolved in 15 mL of tetrahydrofuran under argon atmosphere. Ph_2PCl (2.70 mL, 15 mmol) was added dropwise to the solution at -78 °C. After the addition, the reaction mixture was warmed to ambient temperature and stirred overnight. The resulting mixture was filtered and the filtrate was dried in vacuo to give the crude intermediate product. Then, the crude product was purified by flash chromatography on silica gel (PE/EA = 1/1) which give the pure product as white oil (2.29 g, 83.6%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80–7.60 (m, 2H), 7.52–7.40 (m, 3H), 5.44 (tt, *J* = 6.6, 3.3 Hz, 1H), 2.15–1.97 (m, 2H), 1.95–1.81 (m, 2H), 1.76–1.65 (m, 7H), 1.62–1.54 (m, 1H), 1.52–1.38 (m, 1H), 1.32–1.14 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.39, 134.68, 133.72, 133.47, 133.23, 132.55, 132.26, 131.73, 131.67, 131.58, 131.57, 131.17, 131.08, 130.94, 128.66, 128.55, 128.43, 128.32, 128.21, 117.73, 117.63, 116.73, 37.76, 37.05, 32.76, 32.65, 32.09, 31.97, 26.84, 26.70, 26.47, 26.34, 25.95, 25.71, 25.67, 25.40.
^{31}P NMR (162 MHz, $CDCl_3$) δ = 33.87 (s).

(1-cyclohexylideneethane-1,2-diyl)bis(diphenylphosphine oxide) (2b)

2b was prepared according to the literature method [2a]. **2a** (3.08 g, 10 mmol) and $Ph_2P(O)H$ (2.02 g, 10 mmol) were added to a 50 mL round-bottom flask and stirred for 1 h at 100 °C. The resulting mixture was purified by chromatography on silica gel (DCM/EtOH = 50/1) to give the pure product as white solid (4.95 g, 97%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88–7.65 (m, 4H), 7.64–7.45 (m, 4H), 7.44–7.21 (m, 12H), 3.77 (t, *J* = 13.7 Hz, 2H), 2.55–2.35 (m, 2H), 2.15–2.05 (m, 2H), 1.60–1.50 (m, 2H), 1.45–1.30 (m, 2H), 1.05–0.90 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.37, 163.28, 163.20, 134.38, 133.95, 133.37, 132.98, 131.81, 131.71, 131.55, 131.52, 131.19, 131.16, 131.10, 131.01, 128.63, 128.40, 128.33, 128.28, 128.21, 114.87, 114.77, 113.87, 113.77, 58.01, 36.10, 36.03, 36.01, 35.10, 34.99, 31.42, 31.29, 30.75, 30.62, 28.01, 26.65, 25.70, 18.43.
^{31}P NMR (162 MHz, $CDCl_3$) δ = 30.53 (d, *J* = 7.3 Hz), 27.59 (d, *J* = 7.1 Hz).

(E)-(3-phenylprop-2-ene-1,2-diyl)bis(diphenylphosphine oxide) (3b)

3b was prepared and purified by the same procedure and experimental conditions as those employed for **2b**, using **3a** (3.16 g, 10.0 mmol) and $Ph_2P(O)H$ (2.02 g, 10 mmol). **3b** was obtained as orange solid (5.02 g, 96.9%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84–7.61 (m, 6H), 7.59–7.41 (m, 6H), 7.40–7.21 (m, 13H), 6.90 (dd, *J* = 22.1, 4.1 Hz, 1H), 3.92 (t, *J* = 14.8 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 147.87, 147.78, 147.74, 147.65, 134.92, 134.89, 134.74, 134.71, 133.56, 132.58, 132.13, 132.04, 131.90, 131.81, 131.78, 131.67, 131.43, 131.40, 131.31, 131.22, 131.12, 131.03, 130.87, 129.35, 129.05, 128.88, 128.75, 128.63, 128.54, 128.50, 128.38, 128.32, 128.25, 128.20, 127.39, 127.01, 126.92, 126.04, 125.94, 31.17, 31.07, 30.51, 30.42.
^{31}P NMR (162 MHz, $CDCl_3$) δ = 34.26 (d, *J* = 5.4 Hz), 27.24 (d, *J* = 4.9 Hz).

Cyclohexyl(1-(diphenylphosphoryl)-3-methylbut-2-en-2-yl)(phenyl)phosphine oxide (4b)

4b was prepared and purified by the same procedure and experimental conditions as those employed for **2b**, using **1a** (2.68 g, 10.0 mmol) and CyPhP(O)H (2.08 g, 10 mmol). **4b** was obtained as white solid (4.32 g, 90.7%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94–7.72 (m, 4H), 7.58–7.43 (m, 5H), 7.42–7.32 (m, 4H), 7.31–7.23 (m, 2H), 3.89–3.31 (m, 2H), 2.49–2.23 (m, 1H), 2.06 (s, 1H), 1.93 (dd, *J* = 4.6, 2.1 Hz, 3H), 1.89–1.64 (m, 7H), 1.61–1.37 (m, 2H), 1.34–1.13 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 154.39, 134.68, 133.72, 133.47, 133.23, 132.55, 132.26, 131.73, 131.67, 131.58, 131.57, 131.17, 131.08, 130.94, 128.66, 128.55, 128.43, 128.32, 128.21, 117.73, 117.63, 116.73, 37.76, 37.05, 32.76, 32.65, 32.09, 31.97, 26.84, 26.70, 26.47, 26.34, 25.95, 25.71, 25.67, 25.40.

^{31}P NMR (162 MHz, $CDCl_3$) δ = 39.11 (d, *J* = 5.7 Hz), 28.52 (d, *J* = 5.5 Hz).

Cyclohexyl(2-(diphenylphosphoryl)-3-methylbut-2-en-1-yl)(phenyl)phosphine oxide (5b)

5b was prepared and purified by the same procedure and experimental conditions as those employed for **2b**, using **4a** (2.74 g, 10.0 mmol) and $Ph_2P(O)H$ (2.02 g, 10 mmol). **5b** was obtained as white solid (4.56 g, 95.8%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76–7.56 (m, 6H), 7.50–7.38 (m, 4H), 7.37–7.27 (m, 5H), 3.37 (t, *J* = 13.3 Hz, 2H), 2.12 (s, 1H), 1.82–1.66 (m, 5H), 1.64–1.54 (m, 5H), 1.52–1.40 (m, 1H), 1.18–0.95 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 155.86, 155.78, 134.79, 133.91, 133.77, 132.90, 132.08, 131.98, 131.77, 131.72, 131.67, 131.62, 131.54, 131.43, 131.40, 131.37, 131.26, 131.24, 130.84, 128.60, 128.49, 128.37, 128.20, 128.10, 118.40, 118.31, 117.39, 117.30, 58.09, 39.23, 38.56, 29.57, 29.45, 28.96, 28.84, 26.27, 26.22, 26.19, 26.14, 25.75, 25.40, 25.37, 25.25, 25.22, 25.12, 25.09, 24.51, 24.47, 18.49.

^{31}P NMR (162 MHz, $CDCl_3$) δ = 41.00 (d, *J* = 4.6 Hz), 30.46 (d, *J* = 5.5 Hz).

(3-methylbut-2-ene-1,2-diyl)bis(diphenylphosphane) (L^1)

In a 250 mL Schlenk flask, **1b** (0.94 g, 2.0 mmol), $Ti(O^iPr)_4$ (0.33 mL, 1.1 mmol) and $(EtO)_2MeSiH$ (1.92 mL, 12.0 mmol) were dissolved in 80 mL of toluene under argon atmosphere. The resulting solution was heated to reflux for 30 min and dried under reduced pressure. The crude product was purified by flash chromatography on silica gel (PE/EA = 50/1) under argon atmosphere to give the pure product as white solid (0.62 g, 70.6%). The product was highly reactive with oxygen, so an oxygen-free environment was needed for purification process.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40–7.30 (m, 4H), 7.24–7.09 (m, 13H), 7.07–7.01 (m, 3H), 2.90–2.81 (m, 2H), 1.81 (d, *J* = 4.8 Hz, 3H), 1.20 (d, *J* = 2.7 Hz, 3H).
^{31}P NMR (162 MHz, $CDCl_3$) δ = -5.17 (d, *J* = 5.1 Hz), -15.87 (d, *J* = 5.3 Hz).
HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $C_{29}H_{29}P_2^+$: 439.1744. Found: 439.1745.

(1-cyclohexylideneethane-1,2-dil)bis(diphenylphosphane) (L^2)

L^2 was prepared and purified by the same procedure and experimental conditions as those employed for **L^1**, using **2b** (1.02 g, 2.0 mmol), $Ti(O^iPr)_4$ (0.33 mL, 1.1 mmol) and $(EtO)_2MeSiH$ (1.92 mL, 12.0 mmol). **L^2** was obtained as white solid (0.67 g, 70.3%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58–7.47 (m, 4H), 7.35–7.31 (m, 6H), 7.30–7.23 (m, 6H), 7.21–7.14 (m, 4H), 3.03 (dd, *J* = 5.1, 3.2 Hz, 2H), 2.51 (s, 2H), 1.87 (s, 2H), 1.43 (s, 4H), 1.13 (s, 4H).
^{31}P NMR (162 MHz, $CDCl_3$) δ = 6.74 (d, *J* = 3.1 Hz), -15.19 (d, *J* = 3.5 Hz).
HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $C_{32}H_{33}P_2^+$: 479.2057. Found: 479.2056.

(E)-(3-phenylprop-2-ene-1,2-diyl)bis(diphenylphosphane) (L^3)

L^3 was prepared and purified by the same procedure and experimental conditions as those employed for **L^1**, using **3b** (1.04 g, 2.0 mmol), $Ti(O^iPr)_4$ (0.33 mL, 1.1 mmol) and $(EtO)_2MeSiH$ (1.92 mL, 12.0 mmol). **L^3** was obtained as white solid (0.58 g, 59.7%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57–7.47 (m, 4H), 7.45–7.37 (m, 5H), 7.37–7.15 (m, 14H), 7.06 (d, *J* = 7.0 Hz, 2H), 6.33 (d, *J* = 7.2 Hz, 1H), 3.39 (d, *J* = 13.7 Hz, 2H).
^{31}P NMR (162 MHz, $CDCl_3$) δ = -1.71 (d, *J* = 76.7 Hz), -14.36 (d, *J* = 76.7 Hz).
HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $C_{33}H_{29}P_2^+$: 487.1744. Found: 487.1743.

cyclohexyl(1-(diphenylphosphaneyl)-3-methylbut-2-en-2-yl)(phenyl)phosphane (L^4)

L^4 was prepared and purified by the same procedure and experimental conditions as those employed for **L^1**, using **4b** (0.95 g, 2.0 mmol), $Ti(O^iPr)_4$ (0.33 mL, 1.1 mmol) and $(EtO)_2MeSiH$ (1.92 mL, 12.0 mmol). **L^4** was obtained as white solid (0.59 g, 66.8%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59–7.46 (m, 2H), 7.44–7.40 (m, 2H), 7.37–7.28 (m, 8H), 7.26–7.17 (m, 3H), 3.03 (dt, *J* = 13.8, 4.3 Hz, 1H), 2.68 (d, *J* = 13.8 Hz, 1H), 2.62–2.48 (m, 1H), 2.16 (d, *J* = 4.4 Hz, 3H), 1.92–1.82 (m, 2H), 1.78–1.70 (m, 2H), 1.46–1.22 (m, 9H).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -9.82 (s), -13.95 (s).
HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $C_{29}H_{35}P_2^+$: 445.2214. Found: 445.2215.

cyclohexyl(2-(diphenylphosphaneyl)-3-methylbut-2-en-1-yl)(phenyl)phosphane (L^5)

L^5 was prepared and purified by the same procedure and experimental conditions as those employed for L^1, using **5b** (0.95 g, 2.0 mmol), $Ti(O^iPr)_4$ (0.33 mL, 1.1 mmol) and $(EtO)_2MeSiH$ (1.92 mL, 12.0 mmol). L^5 was obtained as white solid (0.62 g, 69.7%).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50–7.38 (m, 6H), 7.37–7.26 (m, 9H), 2.83 (s, 1H), 2.49 (d, *J* = 12.1 Hz, 1H), 1.90 (d, *J* = 4.1 Hz, 3H), 1.64–1.54 (m, 2H), 1.46 (s, 3H), 1.34–1.25 (m, 4H), 1.10–0.96 (m, 2H), 0.95–0.88 (m, 1H), 0.78–0.63 (m, 2H).
^{31}P NMR (162 MHz, $CDCl_3$) δ = -4.52 (s), -9.33 (s).
HRMS (ESI): *m/z* $[M+H]^+$ calcd. for $C_{29}H_{35}P_2^+$: 445.2214. Found: 445.2213.

1.3 Preparation and characterization of complex 1~8

[$L^1CrCl_2(\mu\text{-}Cl)_2$] (**1**)

To a solution of L^1 (0.44 g, 1.0 mmol) in toluene was added $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol), the solution was stirred overnight at 80 °C. The resulting mixture was filtered and the obtained solid was washed with n-hexane (3×20 mL) and vacuum dried to get complex **1** as blue powder (0.54 g, 90.2%). Anal. Calcd for $C_{29}H_{28}Cl_3CrP_2$ (%): C, 58.36; H, 4.73. Found: C, 58.77; H, 4.78.

[$L^2CrCl_2(\mu\text{-}Cl)_2$] (**2**)

2 was prepared and purified by the same procedure and experimental conditions as those employed for **1**, using L^2 (0.48 g, 1.0 mmol) and $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol). **2** was obtained as blue powder (0.55 g, 86.7%). Anal. Calcd for $C_{32}H_{32}Cl_3CrP_2 \cdot 0.5H_2O$ (%): C, 59.51; H, 5.15. Found: C, 58.92; H, 4.67.

[$L^3CrCl_2(\mu\text{-}Cl)_2$] (**3**)

3 was prepared and purified by the same procedure and experimental conditions as those employed for **1**, using L^3 (0.49 g, 1.0 mmol) and $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol). **3** was obtained as blue powder (0.59 g, 91.0%). Anal. Calcd for $C_{32}H_{32}Cl_3CrP_2 \cdot 0.5$Toluene (%): C, 63.45; H, 4.67. Found: C, 63.77; H, 5.04.

[$L^4CrCl_2(\mu\text{-}Cl)_2$] (**4**)

4 was prepared and purified by the same procedure and experimental conditions as those employed for **1**, using **L**^{4} (0.44 g, 1.0 mmol) and $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol). **4** was obtained as blue powder (0.48 g, 80.6%). Anal. Calcd for $C_{29}H_{34}Cl_3CrP_2$ (%): C, 57.78; H, 5.68. Found: C, 57.43; H, 5.76.

[**L**^{5}$CrCl_2(\mu\text{-}Cl)_2$] (**5**)

5 was prepared and purified by the same procedure and experimental conditions as those employed for **1**, using **L**^{5} (0.44 g, 1.0 mmol) and $CrCl_3(THF)_3$ (0.37 g, 1.0 mmol). **5** was obtained as blue powder (0.47 g, 77.9%). Anal. Calcd for $C_{29}H_{34}Cl_3CrP_2 \cdot 0.25$Toluene (%): C, 59.01; H, 5.80. Found: C, 58.71; H, 5.70.

[L^{3}$Cr(CO)_4$] (**6**)

To a solution of **L**^{3} (0.49 g, 1.0 mmol) in dry diglyme (40 mL) was added $Cr(CO)_6$ (0.33 g, 1.5 mmol), and the resulting mixture was stirred at 170 °C for 2 h. The solvent was evaporated, and the crude product was purified by chromatography on silica gel to yield **6** as yellow solid (0.33 g, 50.8 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.57–7.50 (m, 4H), 7.48–7.41 (m, 8H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.38–7.30 (m, 8H), 7.29–7.25 (m, 4H), 6.69 (d, *J* = 12.7 Hz, 1H), 3.46 (dd, *J* = 19.3, 10.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 227.75, 227.72, 227.67, 227.60, 227.57, 227.51, 227.46, 219.54, 219.45, 138.32, 138.22, 136.25, 136.02, 135.66, 133.64, 133.39, 131.75, 131.67, 130.38, 130.33, 130.25, 129.04, 128.65, 128.02, 127.66, 127.60, 127.50, 127.43, 33.40, 33.25, 33.17, 33.02, 30.91, 30.42, 29.29, 29.17, 28.68, 28.34, 21.68, 13.11.

^{31}P NMR (243 MHz, $CDCl_3$) δ = 84.07 (s), 70.91 (d, *J* = 8.5 Hz).

Anal. Calcd for $C_{37}H_{28}CrO_4P_2$ (%): C, 68.31; H, 4.34. Found: C, 67.91; H, 4.30.

[L^{1}$Cr(CO)_4$] (**7**)

To a solution of **L**^{1} (0.44 g, 1.0 mmol) in dry diglyme (40 mL) was added $Cr(CO)_6$ (0.33 g, 1.5 mmol), and the resulting mixture was stirred at 170 °C for 2 h. The solvent was evaporated, and the crude product was purified by chromatography on silica gel to yield **7** as yellow solid (0.34 g, 56.3 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.63–7.48 (m, 8H), 7.42–7.30 (m, 12H), 3.37 (dd, *J* = 18.7, 10.1 Hz, 2H), 2.23 (s, 3H), 1.36 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 228.57, 228.51, 227.75, 227.64, 219.23, 219.14, 219.06, 146.43, 146.34, 136.85, 136.62, 134.69, 134.68, 134.47, 134.45, 130.58,

130.50, 129.72, 129.65, 128.73, 128.00, 127.55, 127.49, 127.41, 127.34, 123.43, 123.32, 123.23, 123.12, 39.87, 39.69, 39.59, 39.41, 25.51, 25.48, 25.34, 25.30.

^{31}P NMR (243 MHz, $CDCl_3$) δ = 77.33 (s), 70.32 (s).

Anal. Calcd for $C_{33}H_{28}CrO_4P_2 \cdot H_2O$(%): C, 63.87; H, 4.87. Found: C, 63.89; H, 4.88.

[L^{4}Cr(CO)$_4$] (8)

To a solution of **L^4** (0.44 g, 1.0 mmol) in dry diglyme (40 mL) was added $Cr(CO)_6$ (0.33 g, 1.5 mmol), and the resulting mixture was stirred at 170 °C for 2 h. The solvent was evaporated, and the crude product was purified by chromatography on silica gel to yield **7** as yellow solid (0.26 g, 42.6 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68–7.58 (m, 2H), 7.50–7.44 (m, 2H), 7.43–7.35 (m, 6H), 7.30–7.18 (m, 5H), 3.86–3.63 (m, 1H), 2.78–2.67 (m, 1H), 2.66–2.59 (m, 1H), 2.47–2.40 (m, 1H), 2.16 (s, 3H), 2.03–1.93 (m, 2H), 1.86–1.69 (m, 2H), 1.67–1.53 (m, 5H), 1.47–1.40 (m, 1H), 1.34–1.29 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ = 228.33, 227.45, 222.54, 217.58, 143.98, 143.88, 139.95, 139.75, 137.88, 137.66, 136.09, 135.86, 131.37, 131.30, 130.42, 129.85, 129.79, 129.15, 128.89, 128.44, 127.96, 127.90, 127.62, 127.51, 127.46, 127.45, 127.24, 127.18, 127.11, 123.93, 123.82, 123.76, 123.65, 41.20, 41.01, 40.94, 40.75, 40.36, 40.25, 31.54, 31.50, 30.41, 28.68, 26.90, 26.86, 26.83, 26.18, 26.09, 25.42, 25.38, 24.93, 24.34, 24.31, 19.09, 13.10.

^{31}P NMR (243 MHz, $CDCl_3$) δ = 80.11 (s), 69.26 (s).

Anal. Calcd for $C_{33}H_{34}CrO_4P_2$ (%): C, 65.13; H, 5.63. Found: C, 64.78; H, 5.57.

2. Ethylene Oligomerization

A 120 mL stainless steel reactor was dried at 120°C for 3 h under vacuum, and then cooled down to the desired reaction temperature. Precatalysts were weighed into a Schlenk vessel under nitrogen, Methylcyclohexane was added before MMAO was transferred into the Schlenk vessel. The resulting mixture was stirred for 0.5 min and immediately transferred to the reactor. Then the reactor was immediately pressurized. After the specified reaction time, the reaction was stopped by shutting in the ethylene feed, cooling the system at 0°C, depressurizing, and quenching by the addition of 30 mL of 10% aq. HCl. A small sample of the upper-layer solution was filtered through a layer of Celite and analysed by GC using nonane as the internal standard. The individual oligomerization products were identified by GC-MS. The remaining upper-layer solution was filtered to isolate the solid polymeric products. The solid products were

suspended in 10% aq. HCl and stirred for 24 h, dried under reduced pressure and weighed.

3. Copies of the NMR spectra

Figure S1. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***4a***

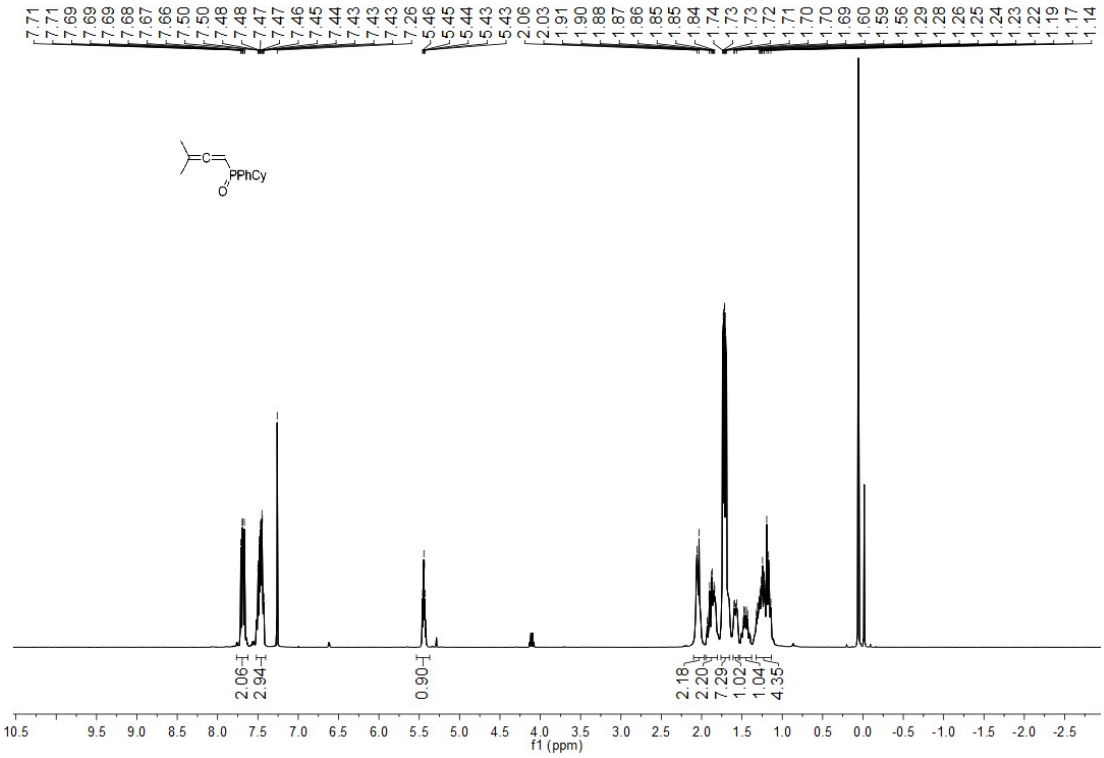


Figure S2. *^{13}C NMR spectrum (101 MHz, $CDCl_3$) of* ***4a***

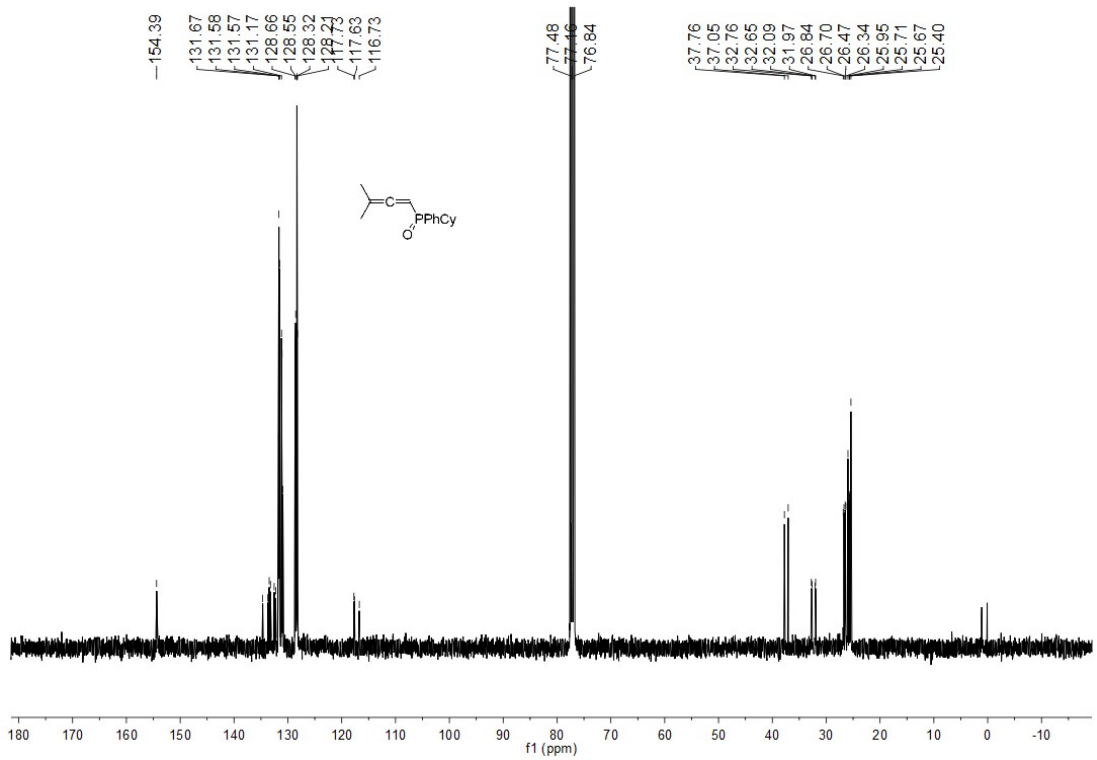


Figure S3. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***4a***

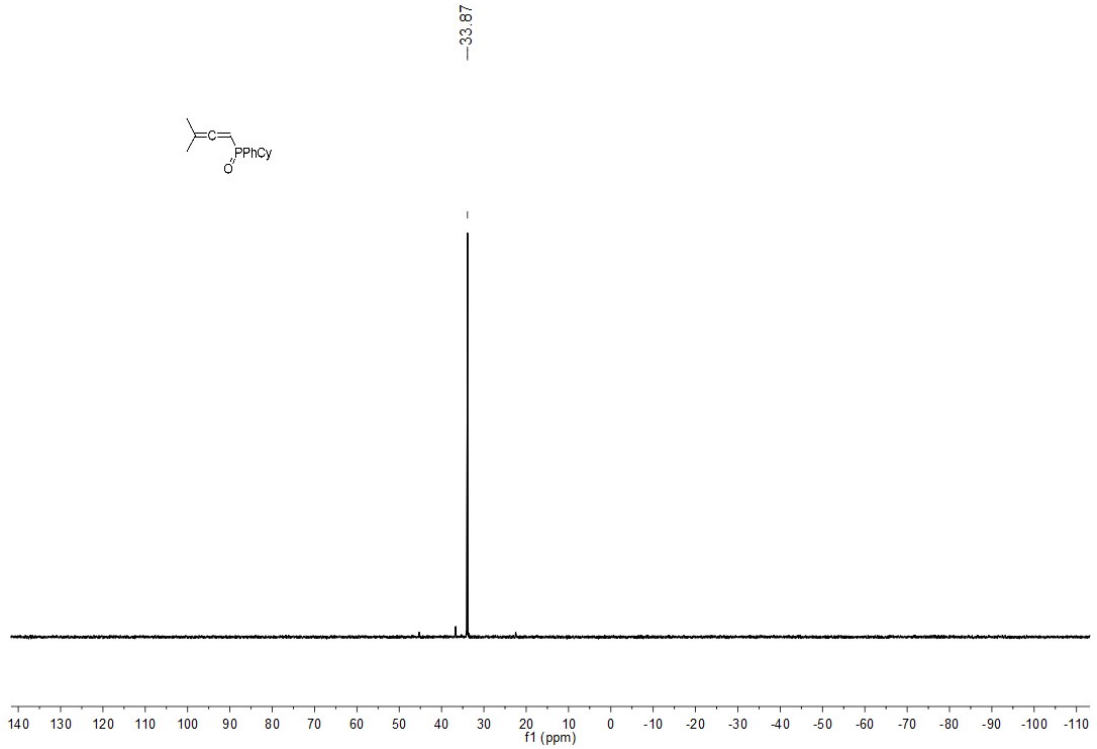


Figure S4. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***2b***

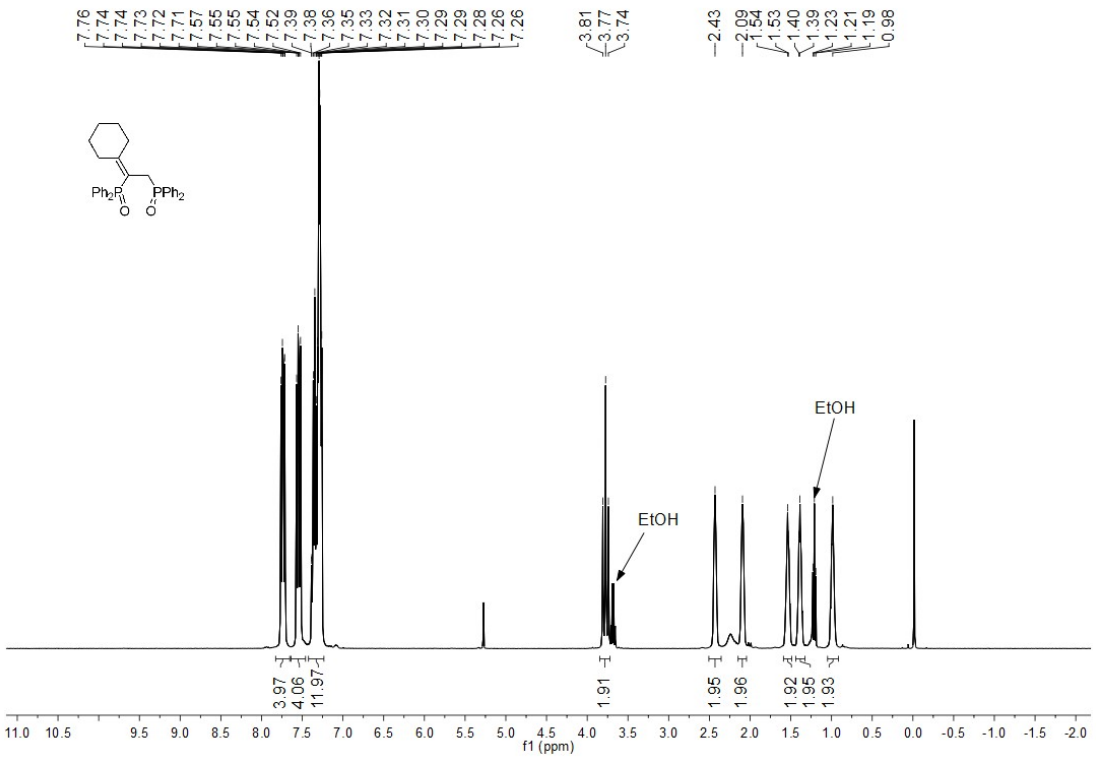


Figure S5. *^{13}C NMR spectrum (101 MHz, $CDCl_3$) of* ***2b***

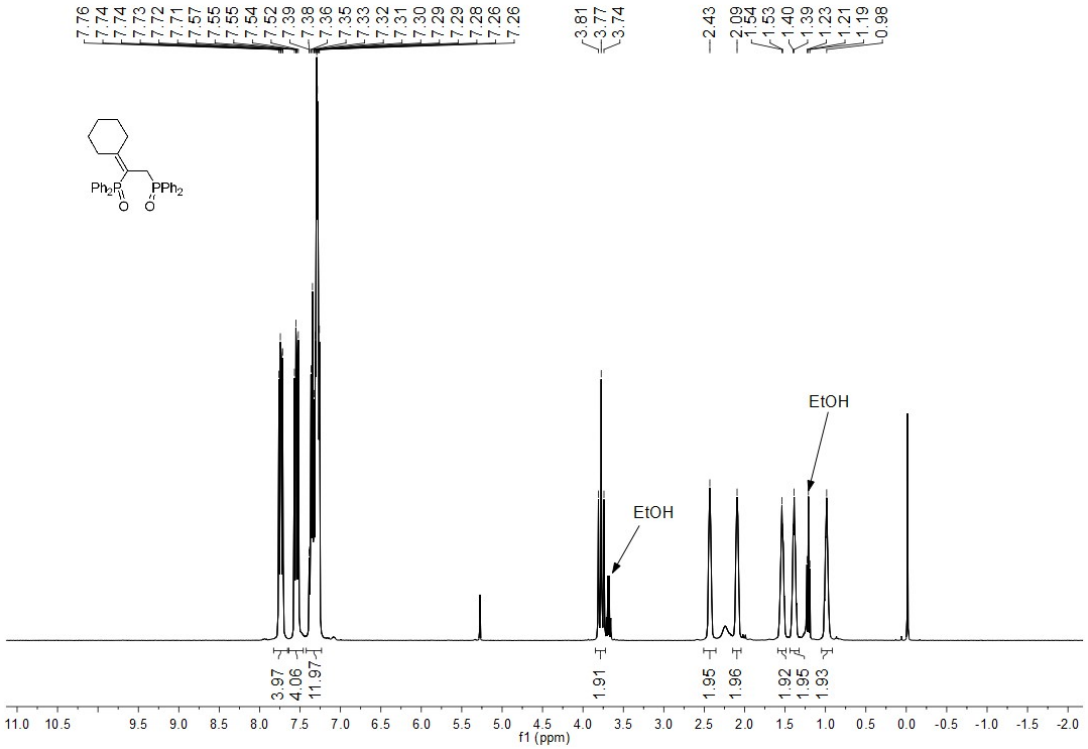


Figure S6. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***2b***

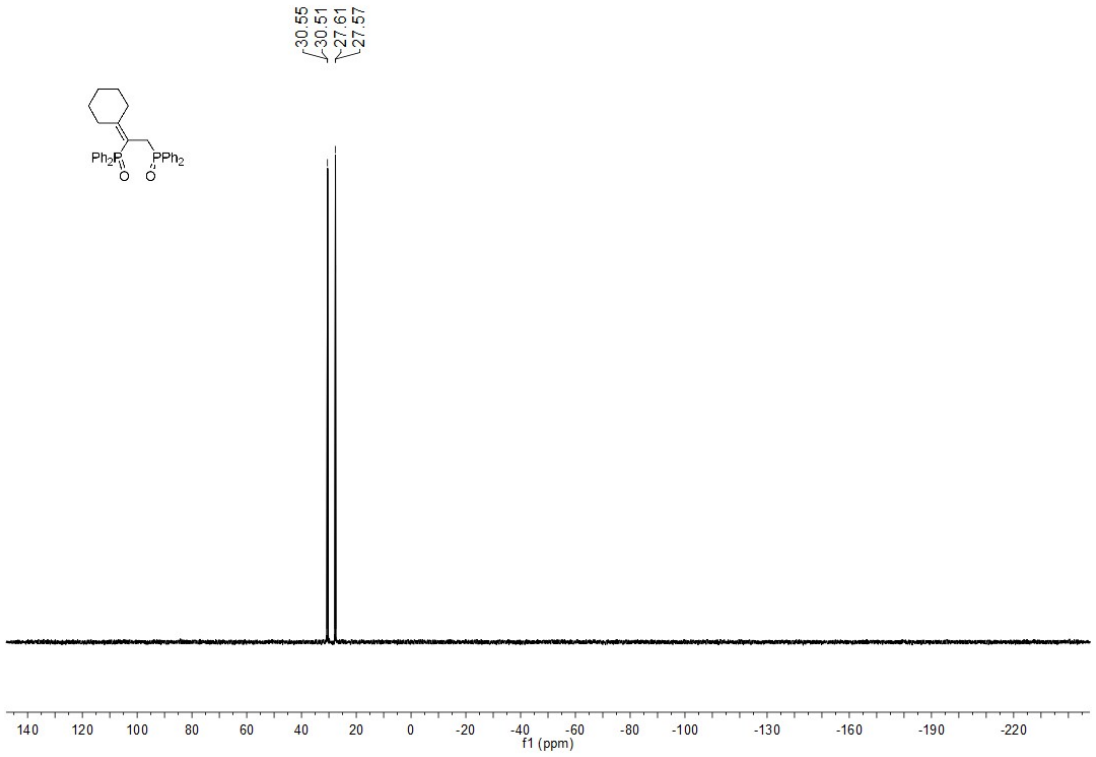


Figure S7. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***3b***

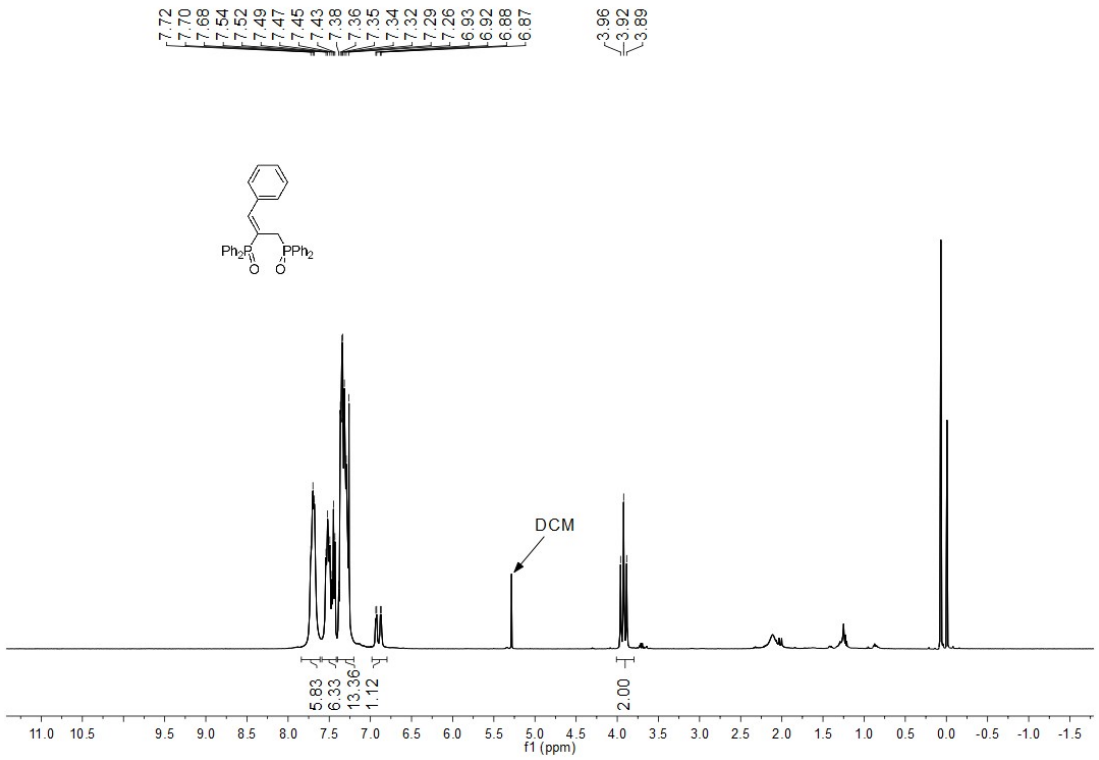


Figure S8. *^{13}C NMR spectrum (101 MHz, $CDCl_3$) of* ***3b***

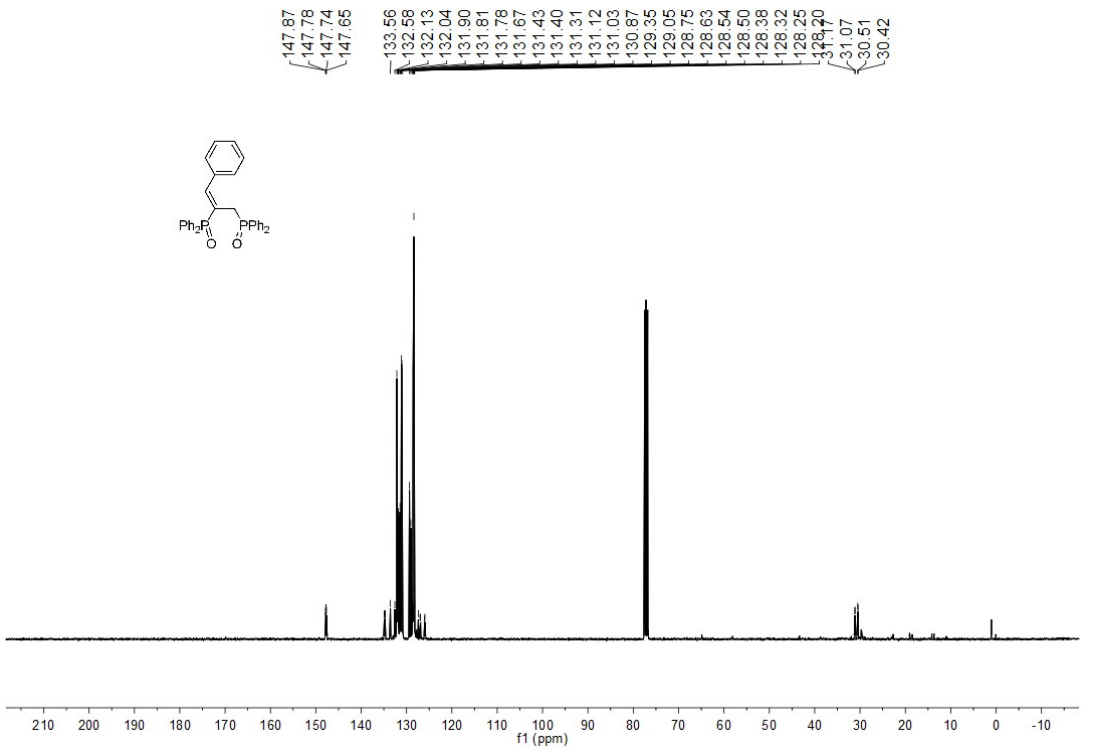


Figure S9. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***3b***

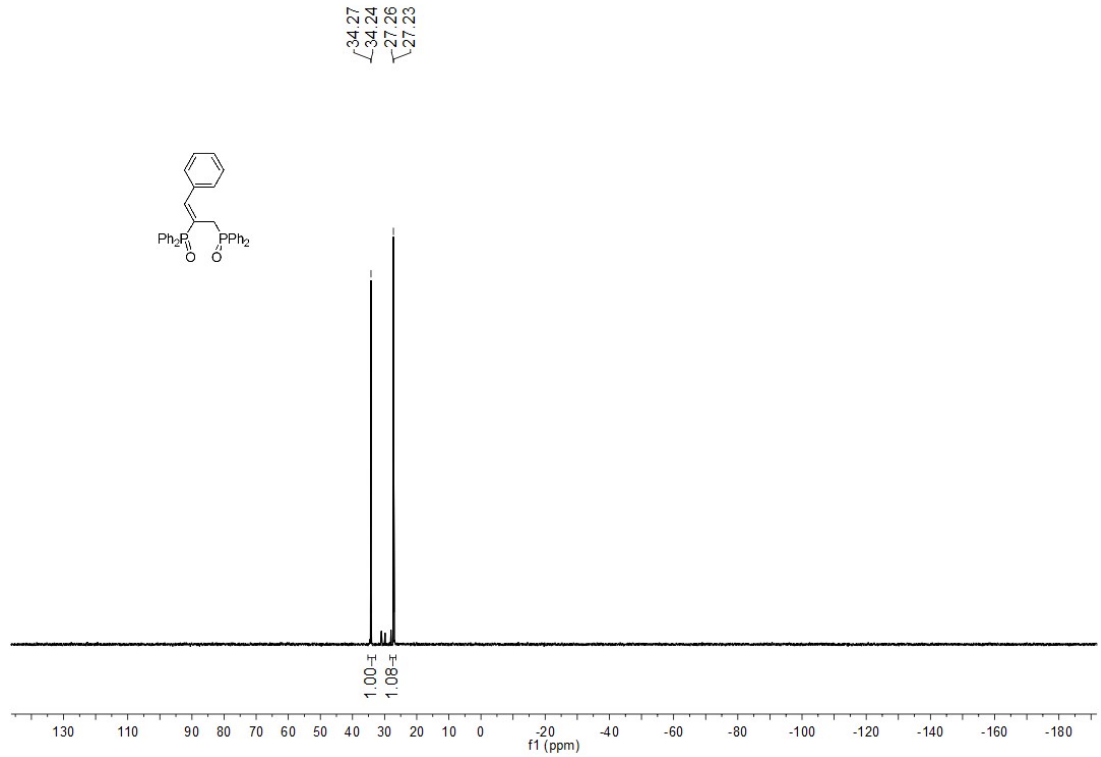


Figure S10. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***4b***

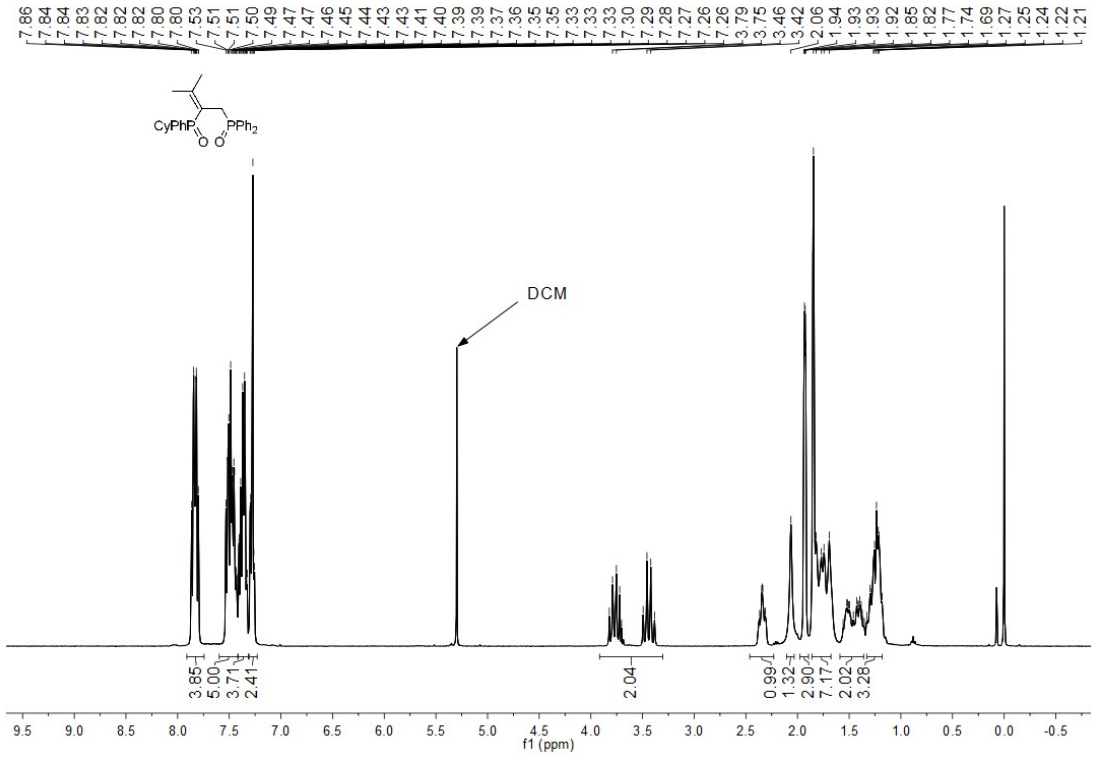


Figure S11. *^{13}C NMR spectrum (101 MHz, $CDCl_3$) of* ***4b***

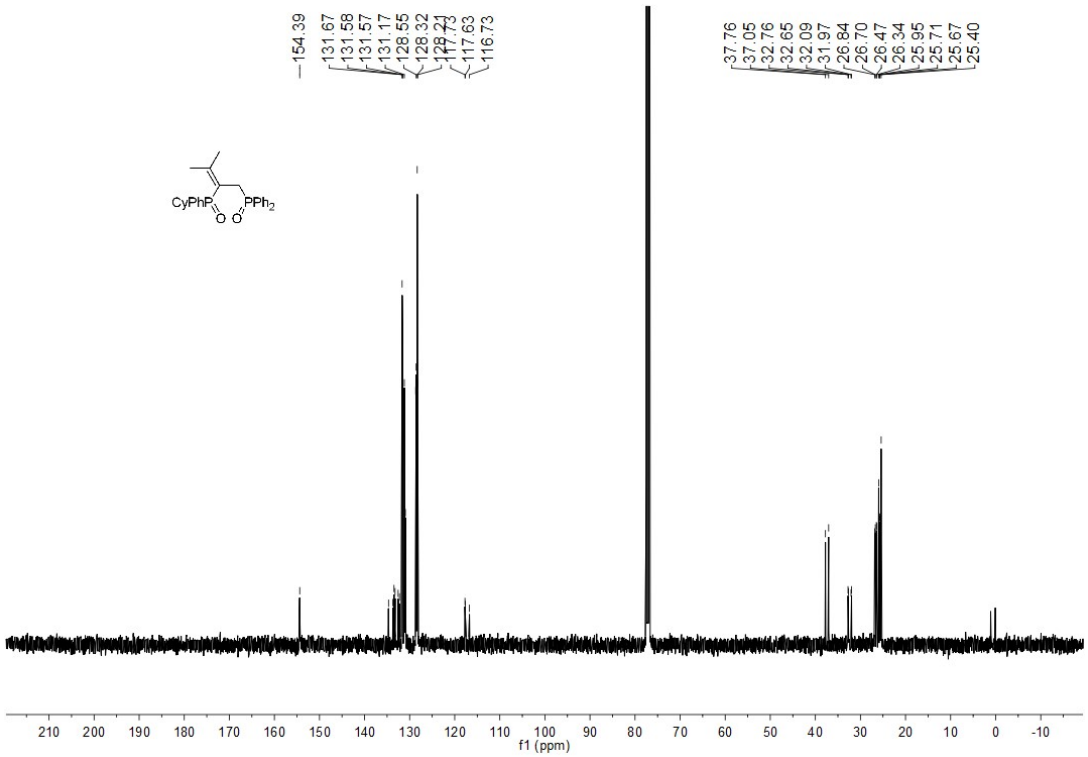


Figure S12. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***4b***

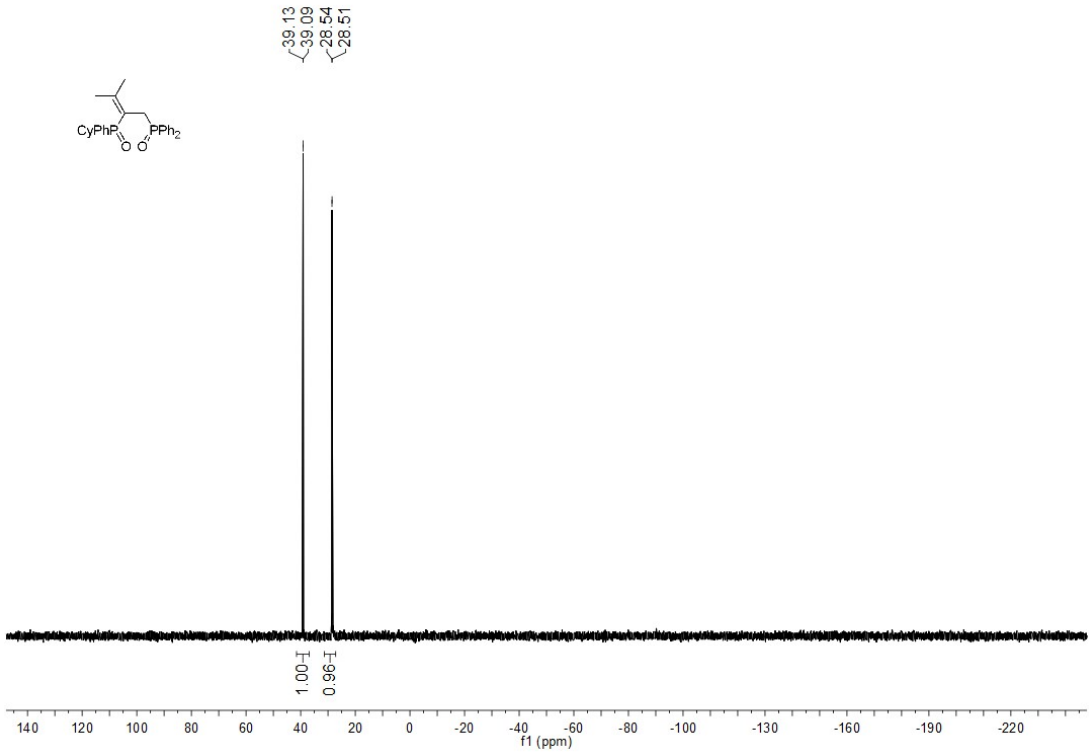


Figure S13. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***5b***

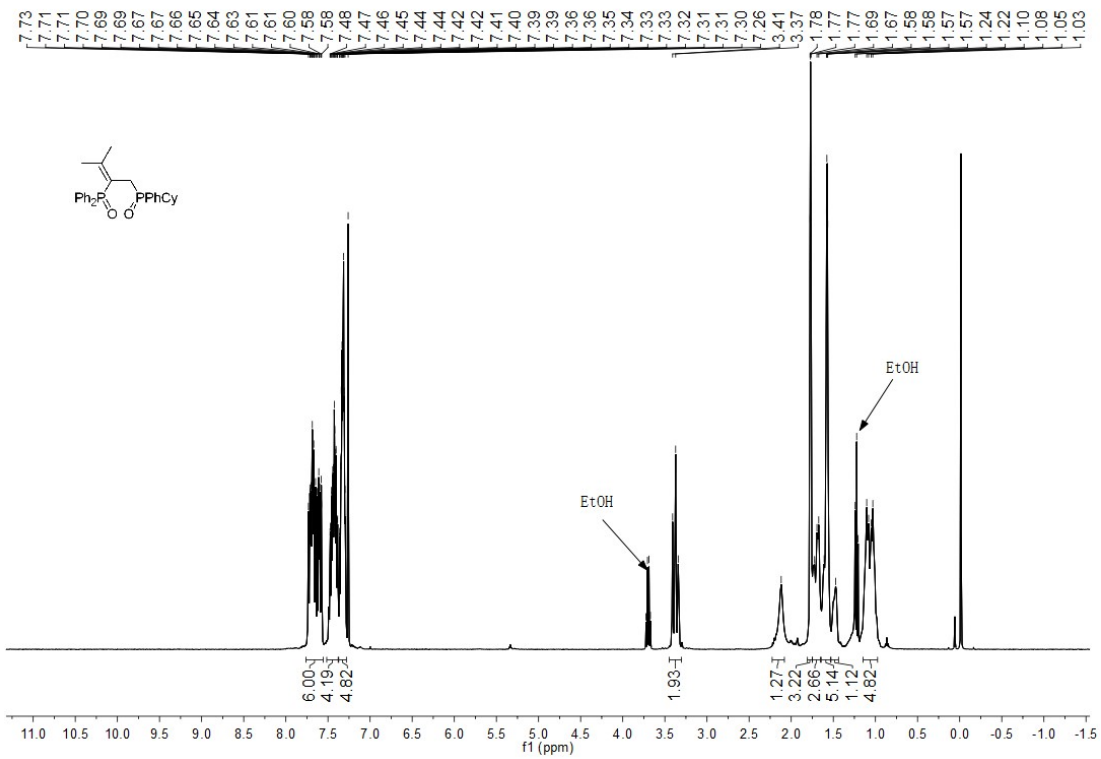


Figure S14. *^{13}C NMR spectrum (151 MHz, $CDCl_3$) of* ***5b***

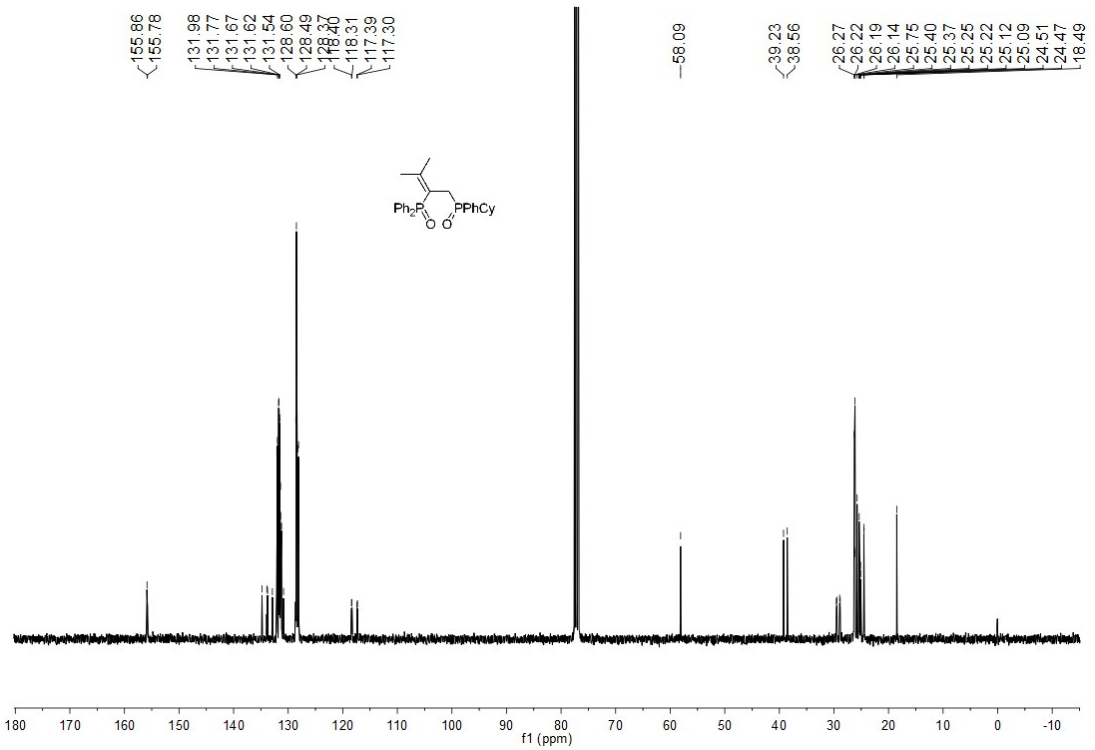


Figure S15. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***5b***

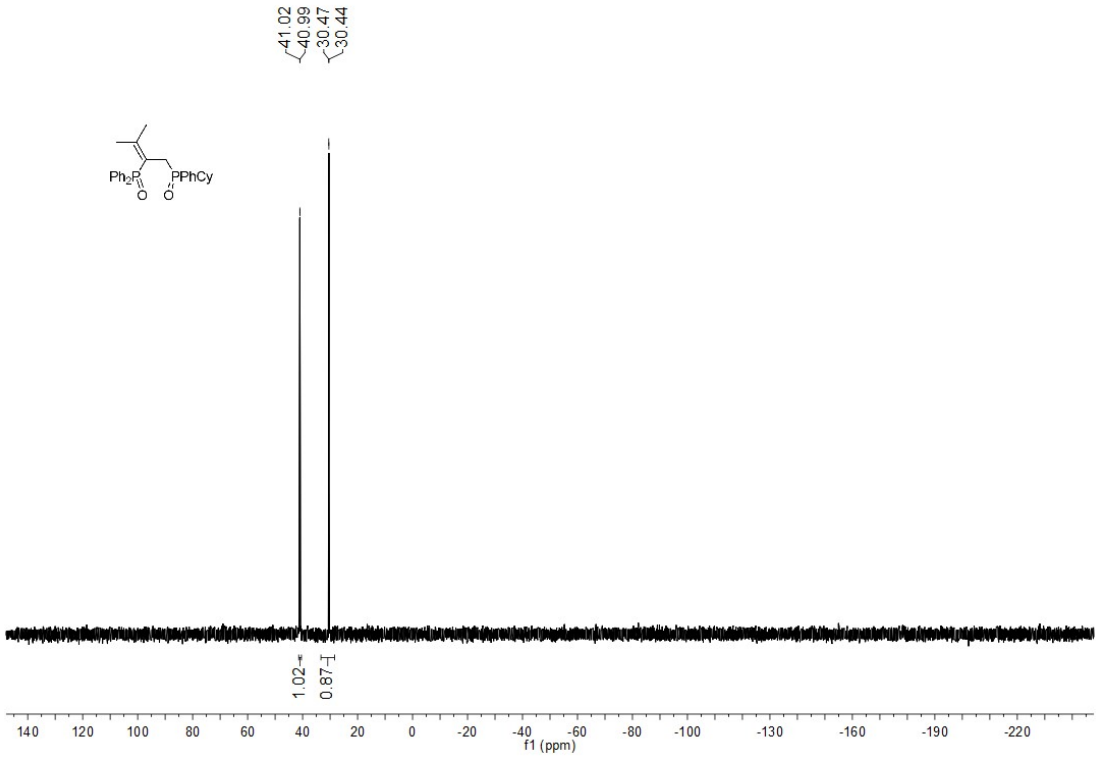


Figure S16. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***L^{1}***

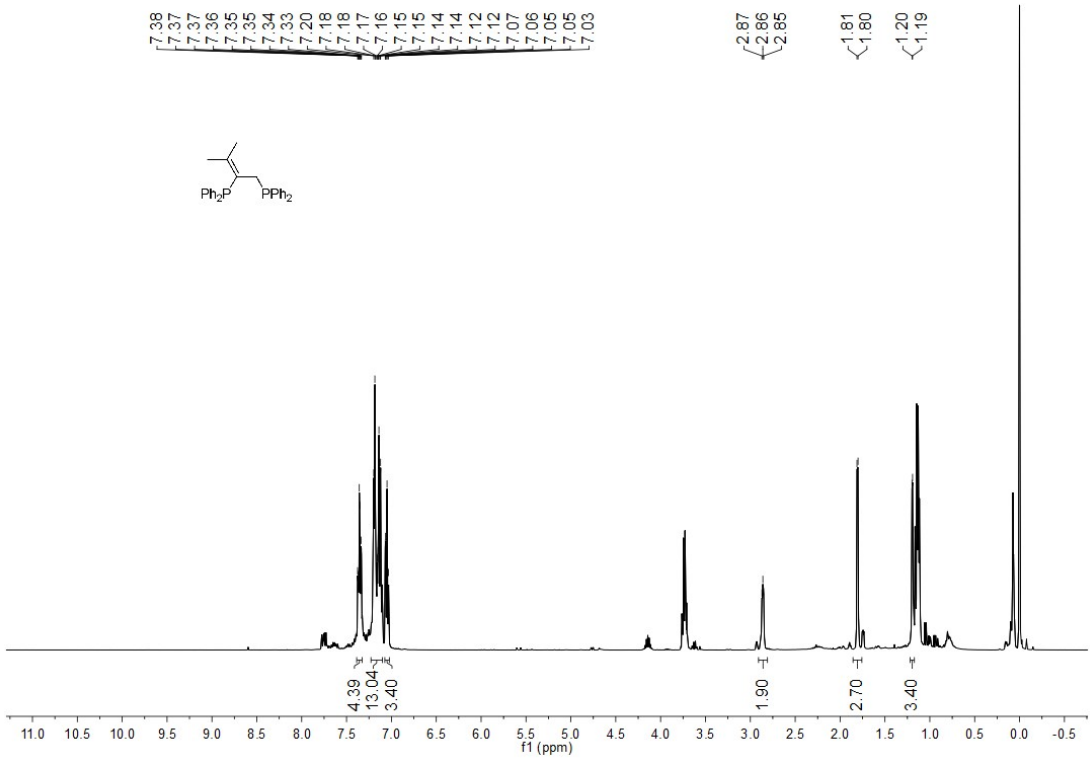


Figure S17. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***L^{1}***

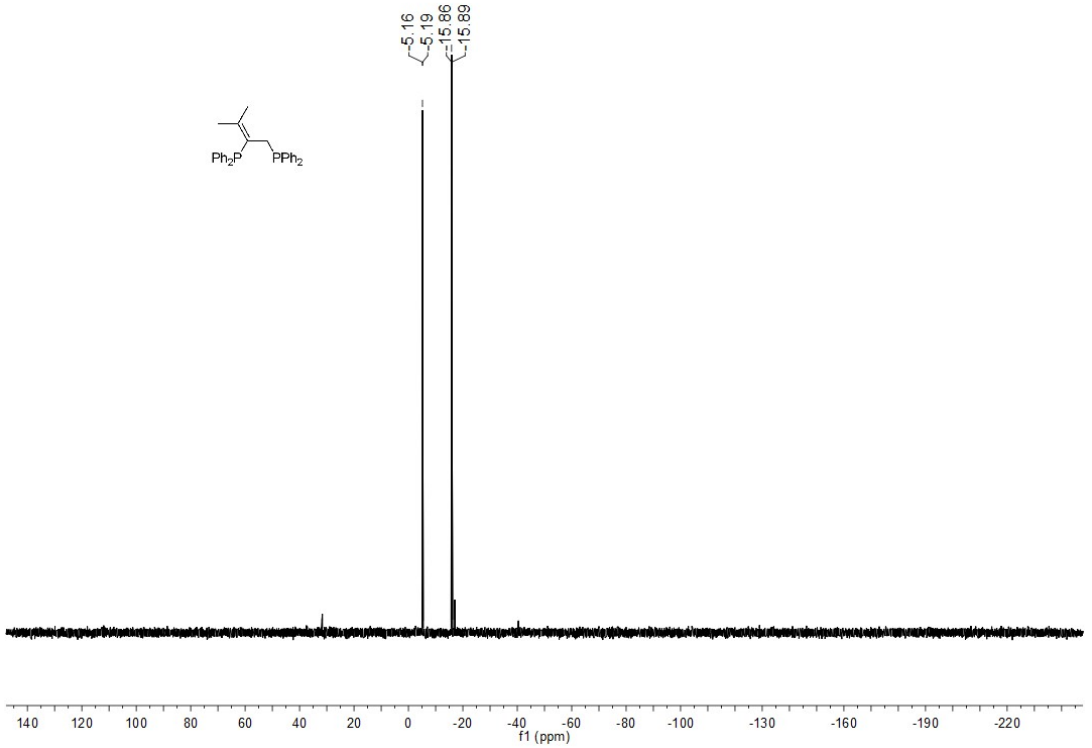


Figure S18. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***L²***

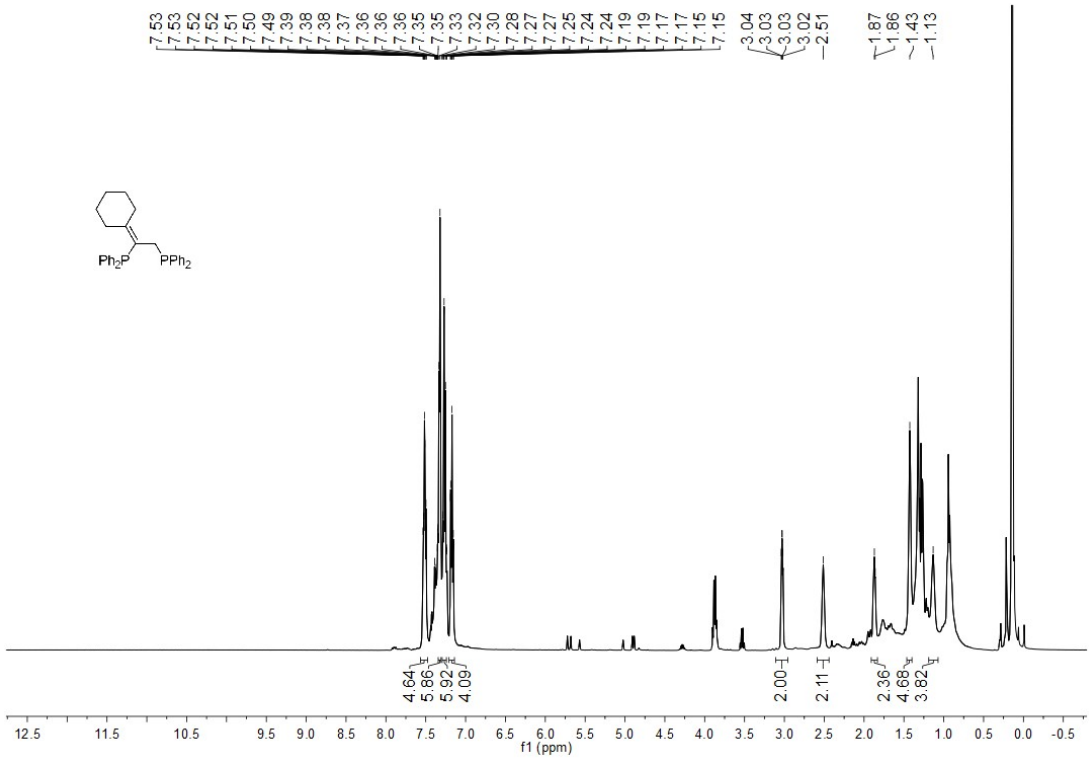


Figure S19. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***L²***

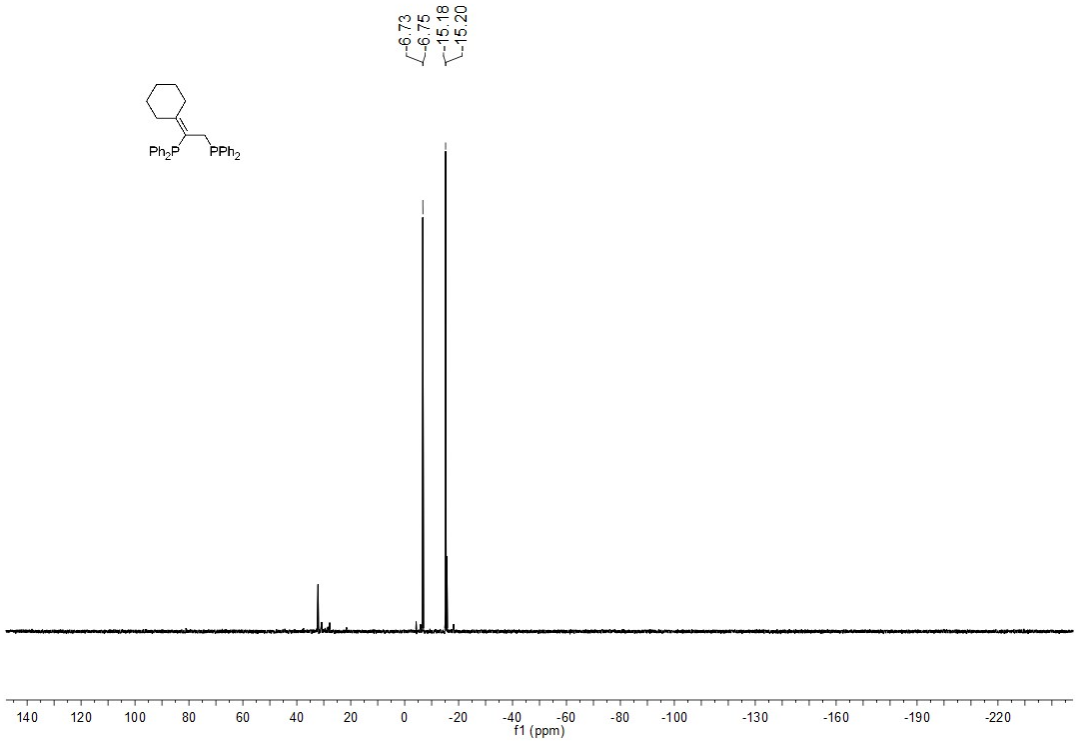


Figure S20. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***L^3***

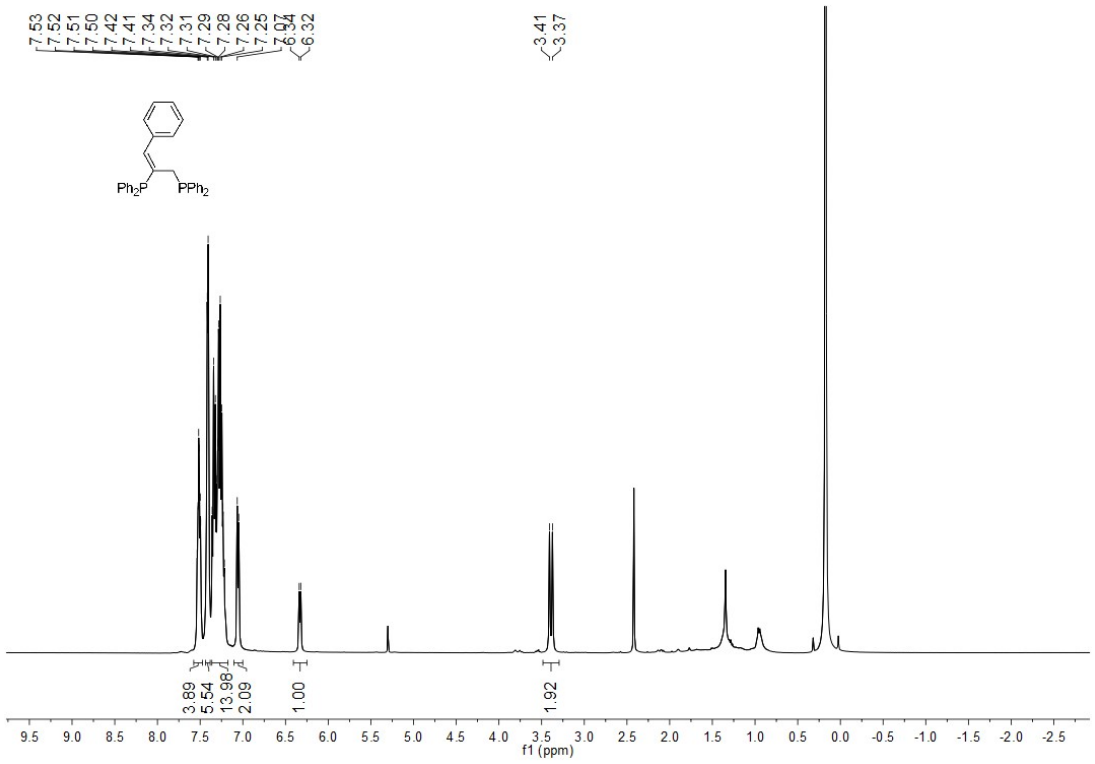


Figure S21. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***L^3***

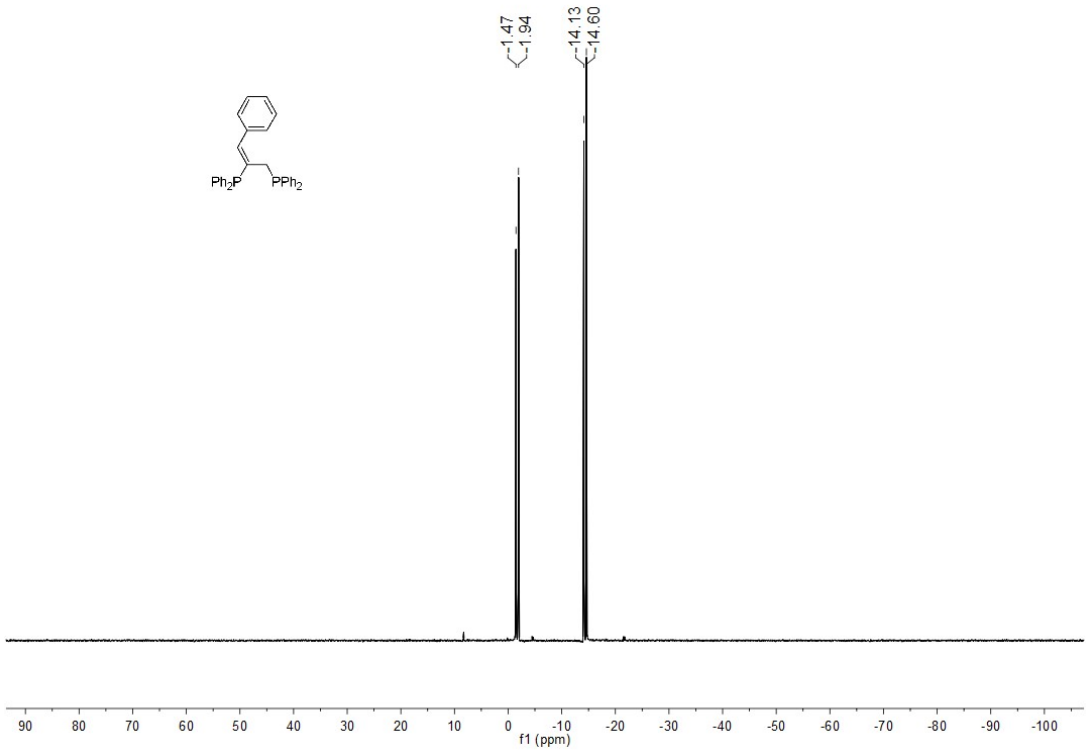


Figure S22. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***L*^{4}**

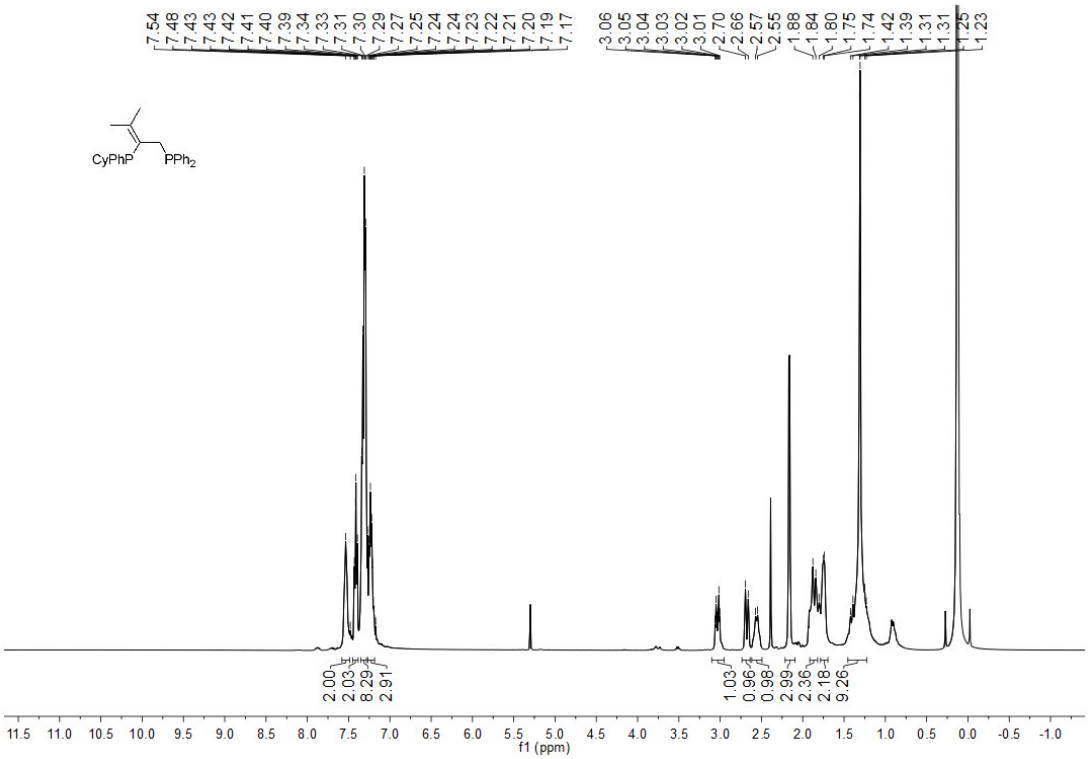


Figure S23. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***L*^{4}**.

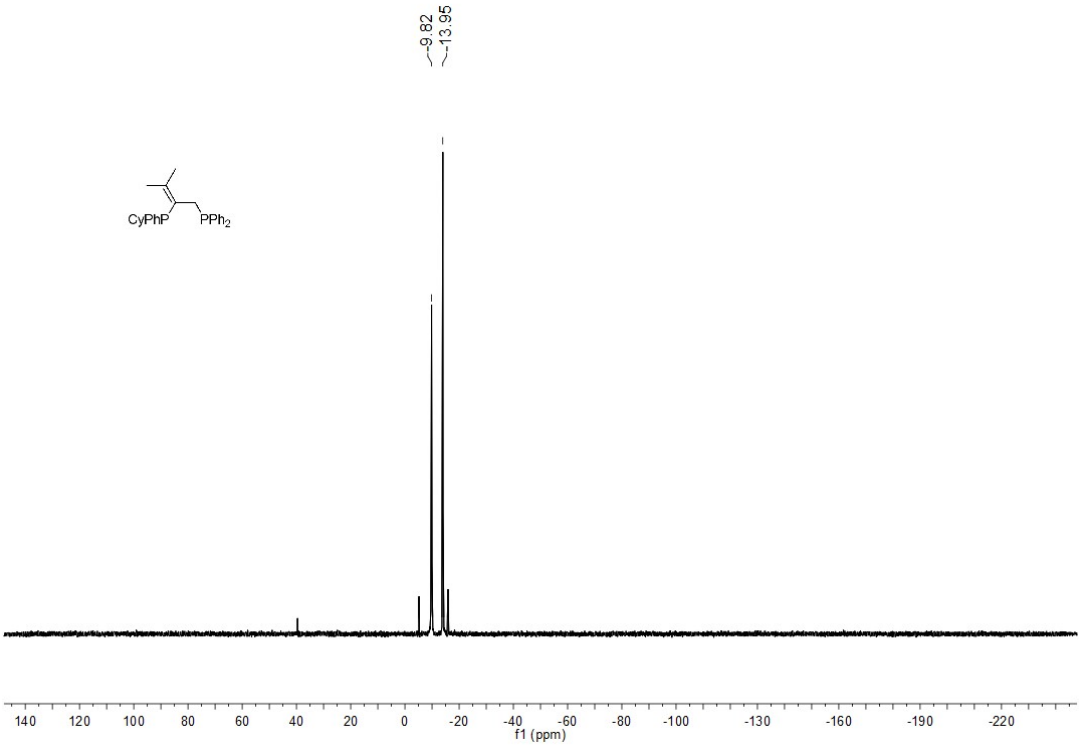


Figure S24. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of* ***L^5***

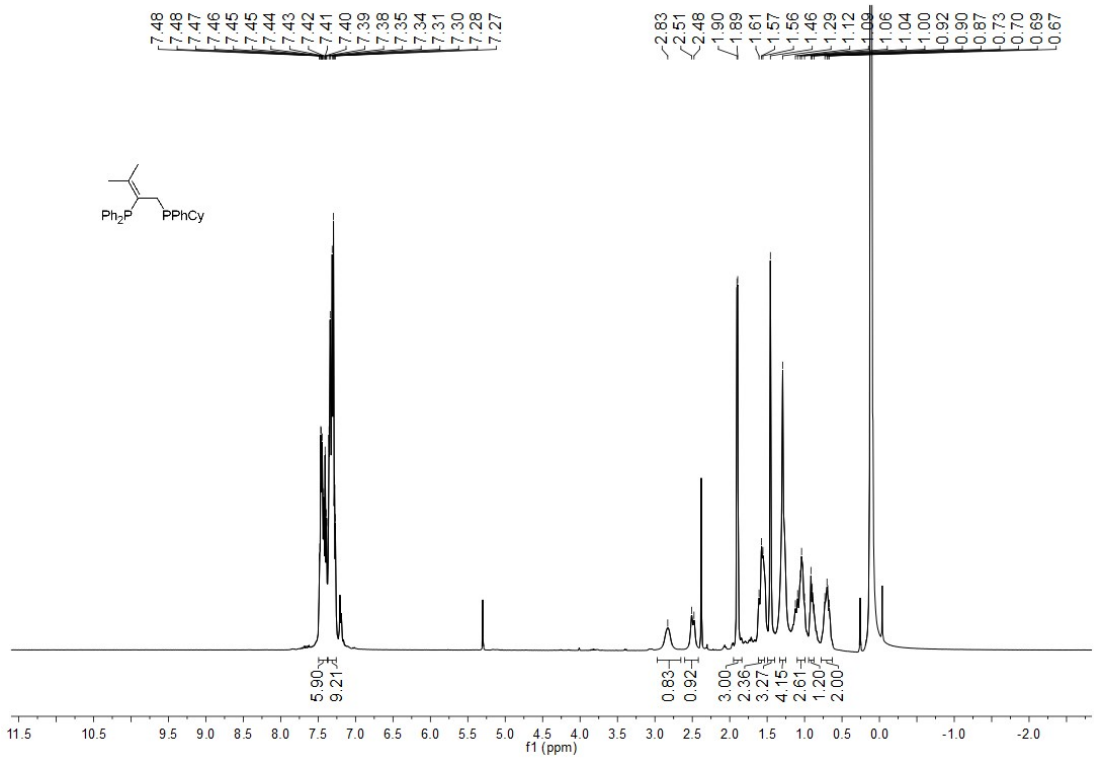


Figure S25. *^{31}P NMR spectrum (162 MHz, $CDCl_3$) of* ***L^5***

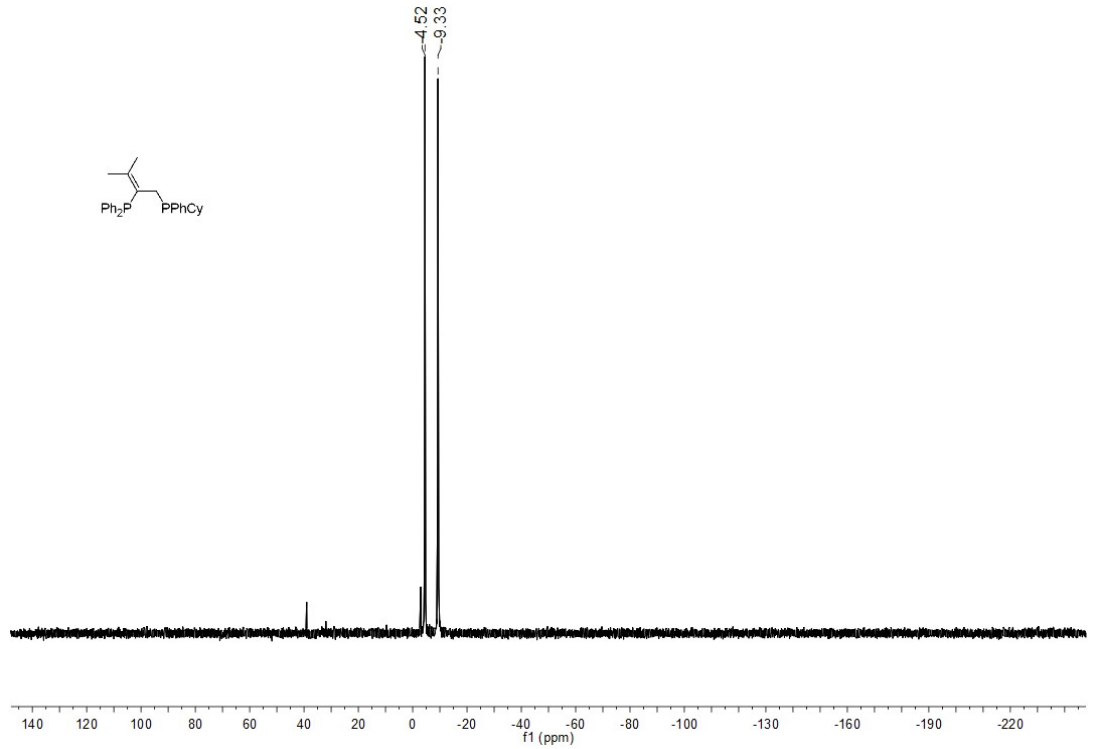


Figure S26. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex* ***6***

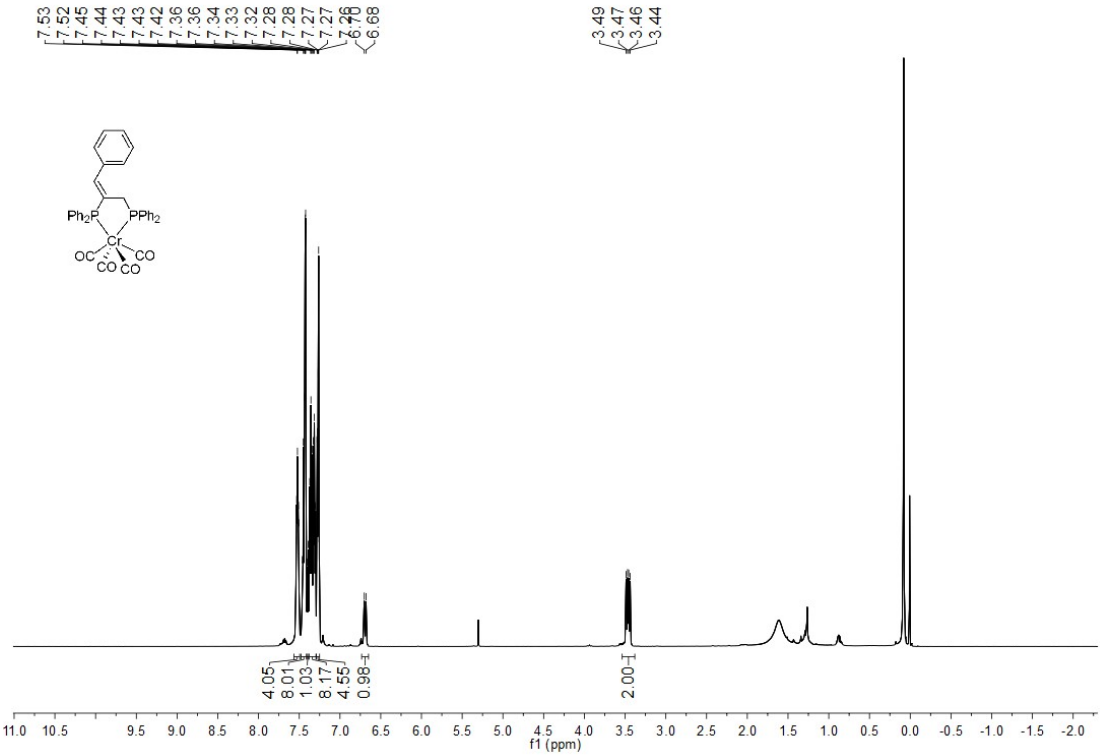


Figure S27. *^{13}C NMR spectrum (151 MHz, $CDCl_3$) of complex* ***6***

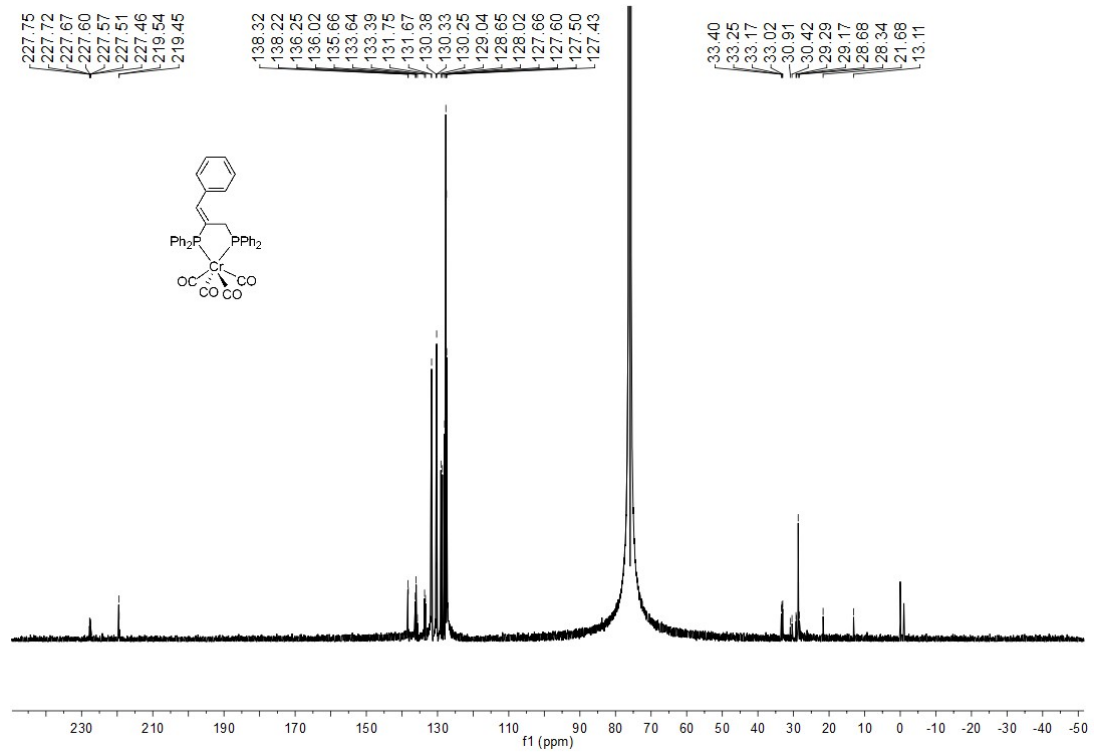


Figure S28. *^{31}P NMR spectrum (243 MHz, $CDCl_3$) of complex* ***6***

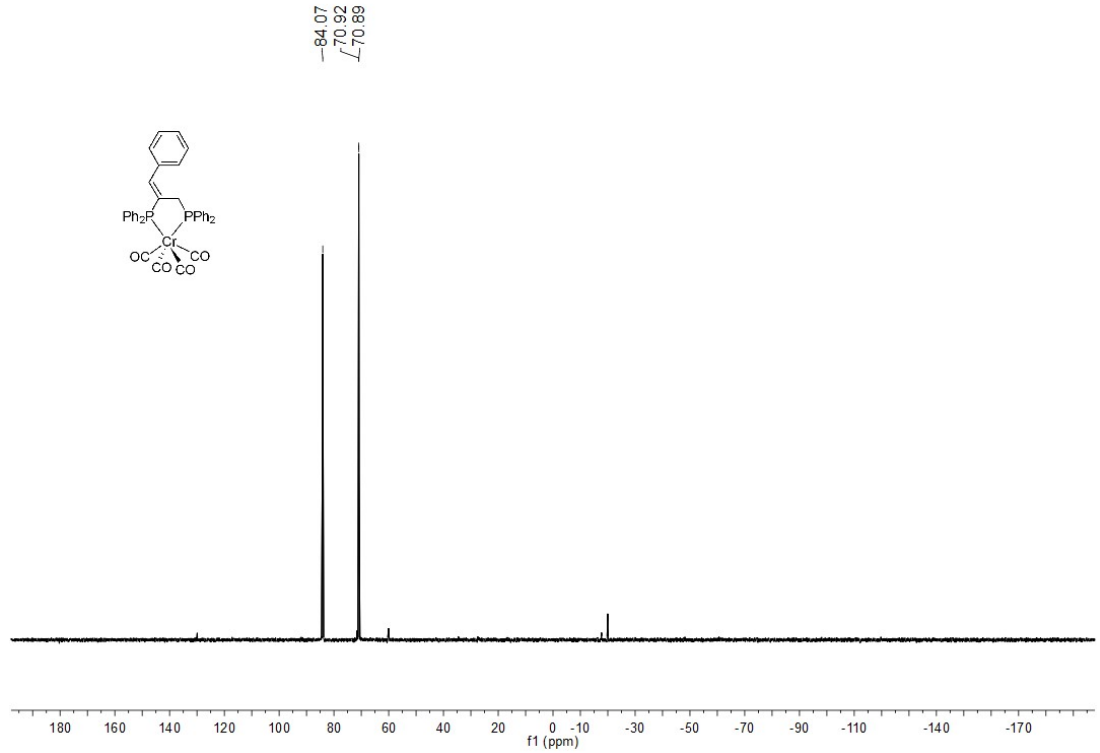


Figure S29. *2D-NOESY spectrum (600 MHz, $CDCl_3$) of complex* ***6***

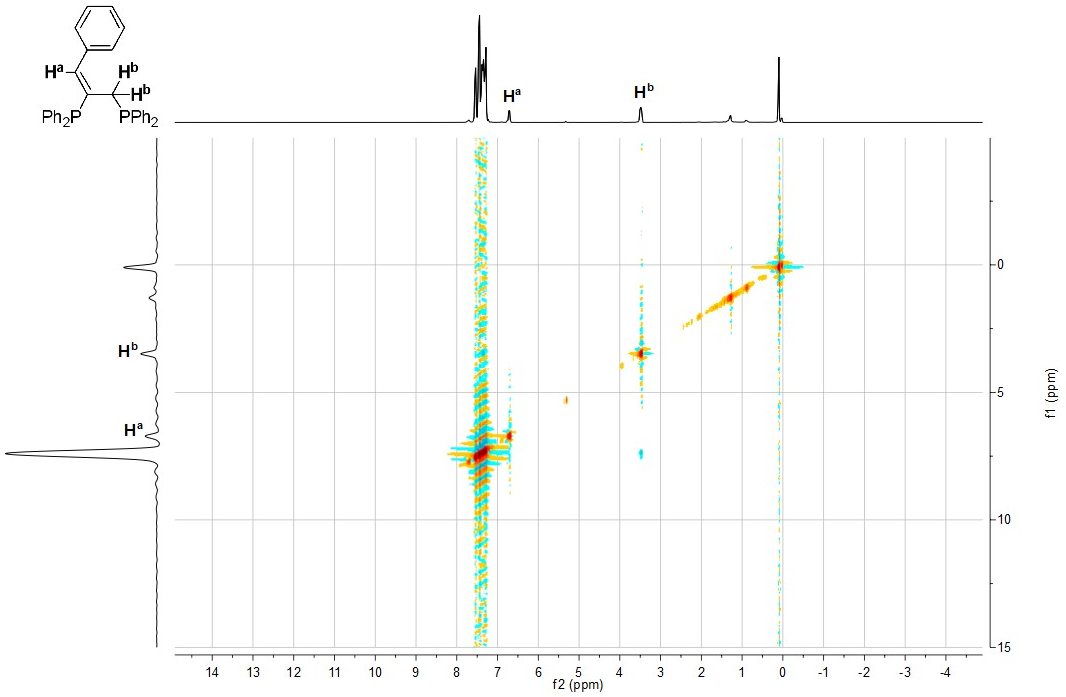


Figure S30. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex 7*

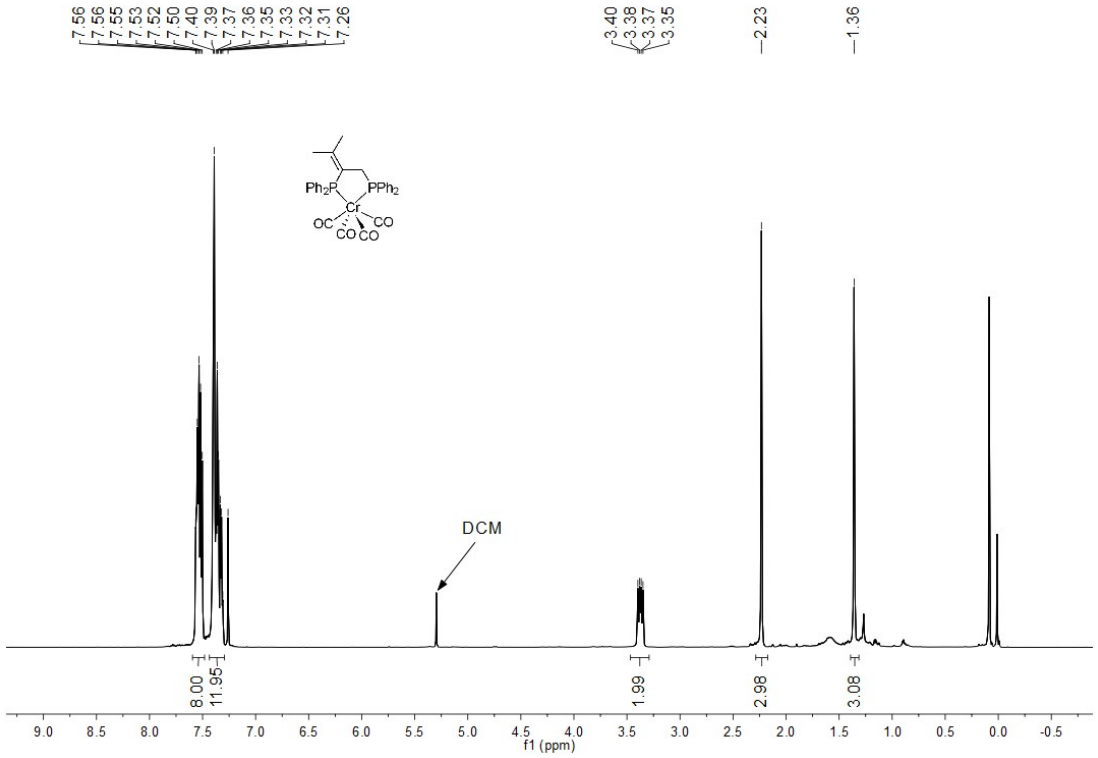


Figure S31. *^{13}C NMR spectrum (151 MHz, $CDCl_3$) of complex 7*

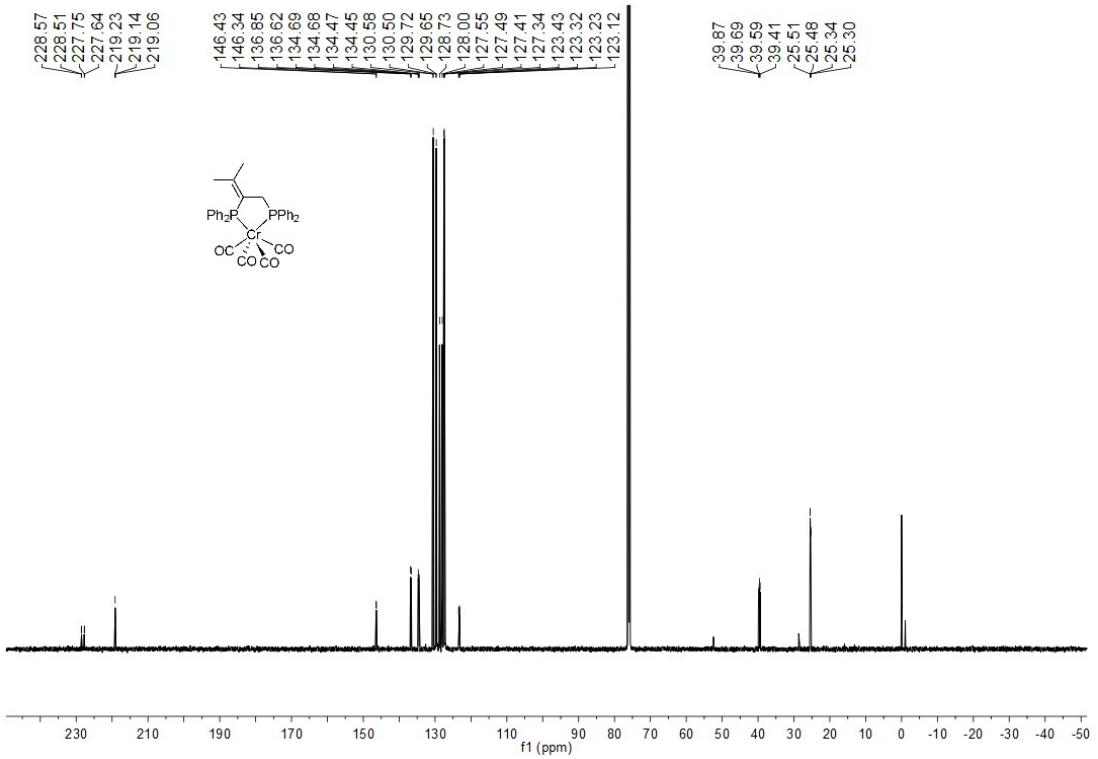


Figure S32. *^{31}P NMR spectrum (243 MHz, $CDCl_3$) of complex 7*

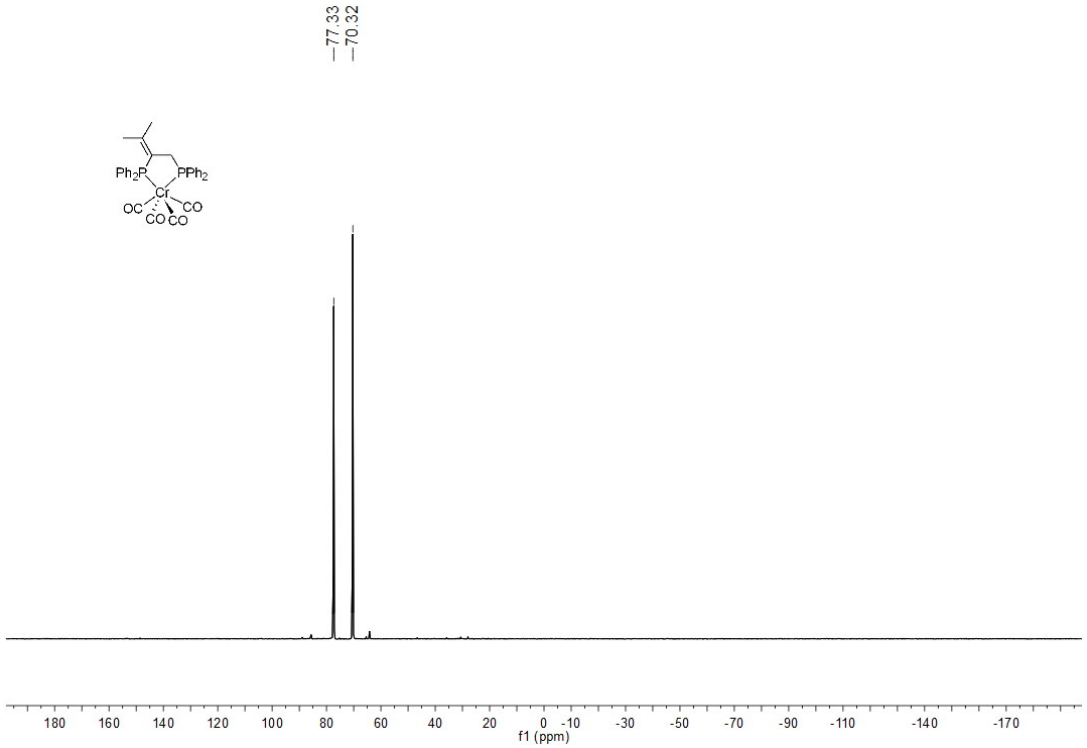


Figure S33. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of complex **8***

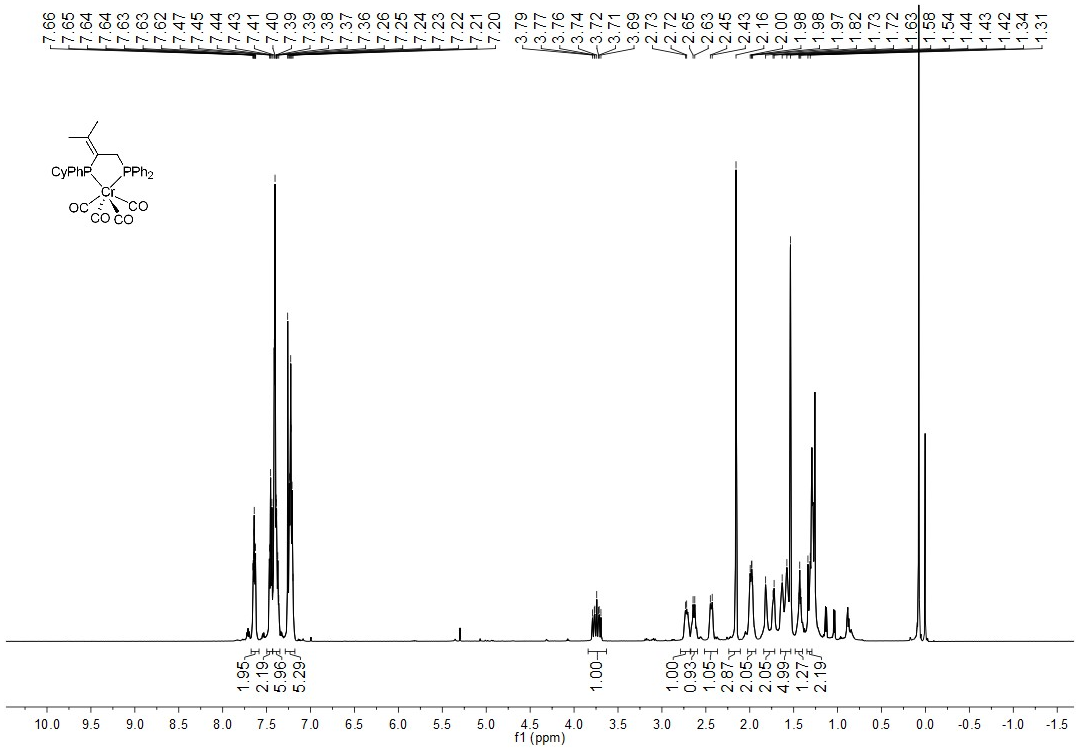


Figure S34. *^{13}C NMR spectrum (151 MHz, $CDCl_3$) of complex* ***8***

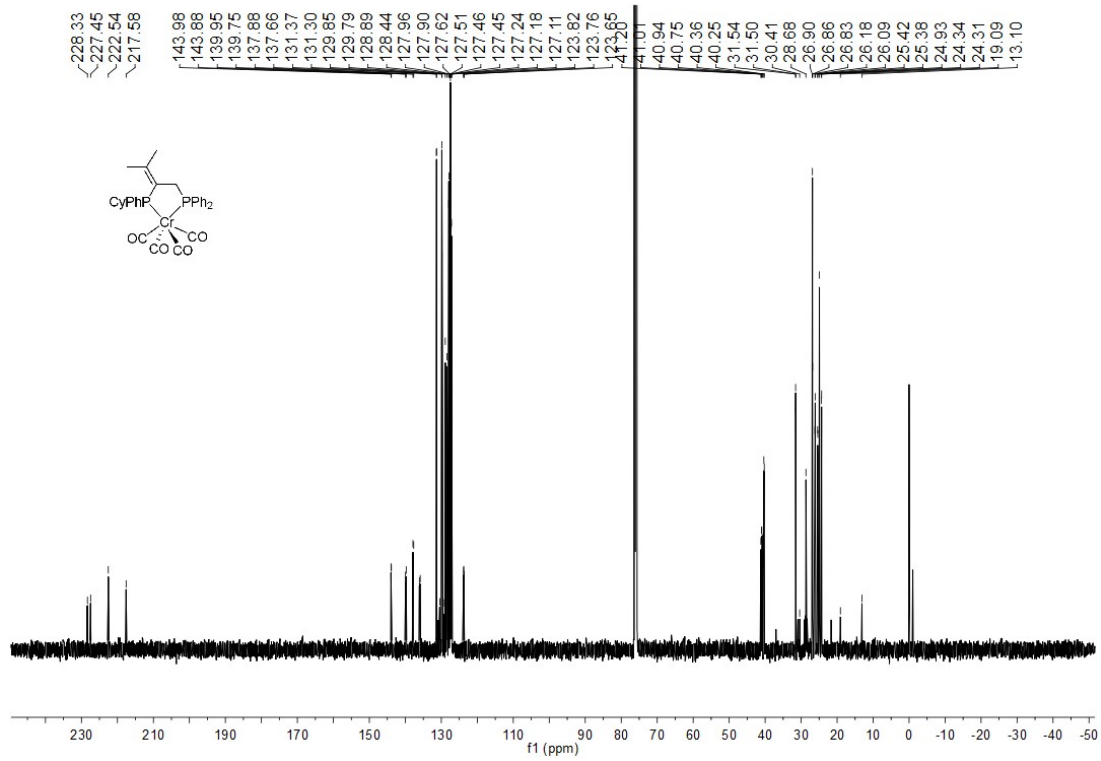
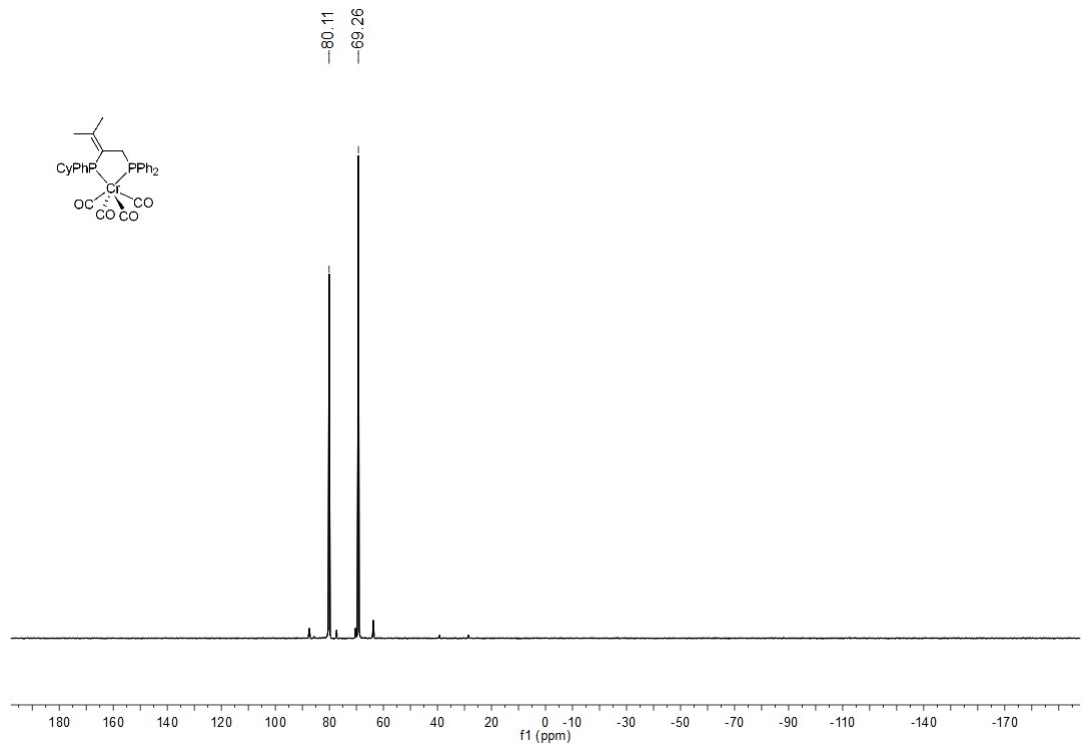


Figure S35. *^{31}P NMR spectrum (243 MHz, $CDCl_3$) of complex* ***8***



4. X-Ray Crystallography for complexes 7 and 8

Single crystals of X-ray quality were grown by slow diffusion of hexane into a concentrated CH_2Cl_2 solution of **7** and **8**, respectively. The crystals were mounted on a glass fiber. Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-Kαradiation ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å). The structures were solved by directed methods (SHELXS-2018) and refined on F^2 by full-matrix least squares (SHELXL-2018) using all unique data. All the calculations were carried out with the SHELXTL18 program.

Key details of the crystal and structure refinement data are summarized in Table S1 and Table S2. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK.

Table S1. Crystal data and structure refinement of complex **7.**

Complex	**7**	
CCDC NO	2333951	
Empirical formula	$C_{33}H_{28}CrO_4P_2$	
Formula weight	602.49	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 11.6589(3) Å	α= 90°.
	b = 9.9032(2) Å	
	β=112.8800(10)°.	
	c = 14.3096(3) Å	γ = 90°.
Volume	1522.20(6) $Å^3$	
Z	2	
Density (calculated)	1.314 Mg/m^3	
Absorption coefficient	4.370 mm^{-1}	
F(000)	624	
Crystal size	0.170 x 0.110 x 0.080 mm^3	
Theta range for data collection	3.352 to 70.297°.	
Index ranges	-12<=h<=14, -11<=k<=11, -17<=l<=17	
Reflections collected	15680	
Independent reflections	4945 [R(int) = 0.0609]	
Completeness to theta = 67.679°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.570	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4945 / 1 / 331	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1228	
R indices (all data)	R1 = 0.0560, wR2 = 0.1293	
Absolute structure parameter	0.058(11)	
Extinction coefficient	n/a	

Largest diff. peak and hole	0.294 and -0.440 e.Å^{-3}

Table S2. Crystal data and structure refinement of complex **8.**

Complex	**8**	
CCDC NO	2299615	
Empirical formula	$C_{33}H_{34}CrO_4P_2$	
Formula weight	608.54	
Temperature	213(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 20.1424(8) Å	α= 90°.
	b = 10.9490(3) Å	β= 90°.
	c = 13.4777(4) Å	γ = 90°.
Volume	2972.36(17) Å^3	
Z	4	
Density (calculated)	1.360 Mg/m^3	
Absorption coefficient	0.529 mm^{-1}	
F(000)	1272	
Crystal size	0.150 x 0.120 x 0.090 mm^3	
Theta range for data collection	2.022 to 25.998°.	
Index ranges	-24<=h<=24, -13<=k<=13, -16<=l<=16	
Reflections collected	25531	
Independent reflections	5840 [R(int) = 0.0396]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6465	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5840 / 1 / 363	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R1 = 0.0308, wR2 = 0.0647	
R indices (all data)	R1 = 0.0372, wR2 = 0.0682	
Absolute structure parameter	0.016(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.199 and -0.246 e.Å^{-3}	

5. Reference

[1] W. Herwig, H. Zeiss, Notes: Chromium Trichloride Tetrahydrofuranate. J. Org. Chem. 23 (1958) 1404.

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