Supporting information

Highly active chromium-based selective ethylene tri-/tetramerization catalysts supported by alkenylphosphanyl PNP ligands

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1. Experimental Section

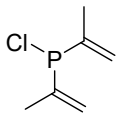
1.1 General Information

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; $CDCl_3$ (δ = 7.26 ppm) and $CDCl_3$ (δ = 77.0 ppm) served as internal standards for ^1H and ^{13}C NMR, respectively; *J* values are reported in Hz. 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 ^oC for 10 min and then heating at 10 ^oC min^{-1} until 250 ^oC. *n*-Nonane was used as an internal standard. Mass spectra were recorded on the HP-5989 instrument by EI methods. $Ph_2PN(^iPr)H$, Ph_2PN(cyclopentyl)H, Ph_2PN(cyclohexyl)H and Ph_2PN(1-cyclohexylethyl)H are known compounds, and were prepared according to modified literature methods, respectively.[1] Their spectra were consistent with that of the published data.

1.2 Preparation of chlorophosphine

Chlorodi(prop-1-en-2-yl)phosphane, chloro(phenyl)(prop-1-en-2-yl)phosphane, chloro(ethyl)(prop-1-en-2-yl)phosphane and (*E*)-chloro(ethyl)(prop-1-en-1-yl) phosphane were prepared according to modified literature methods[2] and were directly used in next step without purification.

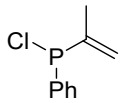
Chlorodiisopropenylphosphane



In a 100 mL Schlenk flask, PCl_3 (0.87 mL, 10 mmol) was dissolved in 30 mL of Et_2O and stirred at -78 °C for 5 min under argon atmosphere. Isopropenyl magnesium bromide (20 mL, 1.0 M in hexane, 20 mmol) was added dropwise to the solution and the mixture was warmed to ambient temperature and stirred for 12 h. After filteration, the filtrate was collected and concentrateted in vacuo to give the crude chlorodiisopropenylphosphane. It can be used directly in the next step without

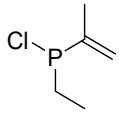
purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73–5.62 (m, 4H), 1.90-1.88 (m, 6H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 86.26 (s).

Chloro(phenyl)(prop-1-en-2-yl)phosphane



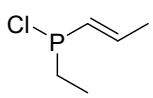
In a 100 mL Schlenk flask, $PhPCl_2$ (1.36 mL, 10 mmol) was dissolved in 20 mL of THF and stirred at -78 °C for 5 min under argon atmosphere. Isopropenyl magnesium bromide (10 mL, 1.0 M in hexane, 10 mmol) was added dropwise to the solution and the mixture was warmed to ambient temperature and stirred for 12 h. After filteration, the filtrate was collected and concentrateted in vacuo to give the crude chloro(phenyl)(prop-1-en-2-yl)phosphane. It was used directly in the next step without purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.39 (m, 5H), 5.81-5.67 (m, 2H), 1.85 (d, J = 4.0 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 87.95 (s).

Chloro(ethyl)(prop-1-en-2-yl)phosphane



In a 100 mL Schlenk flask, $(Et)_2NPCl_2$ (2.18 mL, 15 mmol) was dissolved in 60 mL of THF and stirred at -78 °C for 5 min under argon atmosphere. Ethyl magnesium bromide (15 mL, 1.0 M in hexane, 15 mmol) was added dropwise to the solution and the mixture was warmed to ambient temperature and stirred for 12 h. After cooling to -78 °C again and stirred for 10 min, isopropenyl magnesium bromide (10 mL, 1.0 M in hexane, 10 mmol) was added dropwise to the solution and the mixture was warmed to ambient temperature and stirred for 12 h. After the reaction mixture was concentrated to 45 mL and then stirred at 0 °C for 10 min, HCl (7.5 mL, 4 M in 1,4-dioxane, 30 mmol) was added dropwise to the solution and the mixture was warmed to ambient temperature and stirred for 2 h. After filteration, the filtrate was collected and concentrateted in vacuo to give the crude chloro(ethyl)(prop-1-en-2-yl)phosphane. It was used directly in the next step without purification.

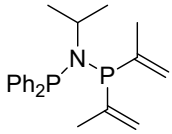
(*E*)-chloro(ethyl)(prop-1-en-1-yl)phosphane



(*E*)-chloro(ethyl)(prop-1-en-1-yl)phosphane was prepared by the same procedure and experimental conditions as those employed for chloro(ethyl)(prop-1-en-2-yl)phosphane. Using propenyl magnesium bromide instead of isopropenyl magnesium bromide led to the formation of crude (*E*)-chloro(ethyl)(prop-1-en-1-yl)phosphane. It was used directly in the next step without purification.

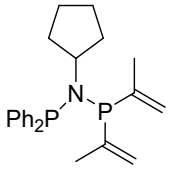
1.3 Preparation and characterization of ligands 1-7

N-(di(prop-1-en-2-yl)phosphaneyl)-N-isopropyl-1,1-diphenylphosphanamine (1)



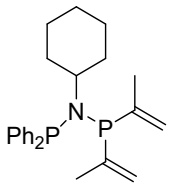
In a 100 mL Schlenk flask, $Ph_2PN(^iPr)H$ (1.28 g, 5.04 mmol) was dissolved in 15 mL of hexane and stirred at -35 °C for 5 min under argon atmosphere. ^{n}BuLi (3.15 mL, 1.6 M in hexane, 5.04 mmol) was added dropwise to the solution and the mixture was warmed to ambient temperature and stirred for 0.5 h. After cooling to -35 °C again and crude chlorodiisopropenylphosphane (6.05 mmol calculated from crude reaction mixture) was then added dropwise, the mixture was warmed to ambient temperature and stirred for 12 h. After the volatiles were removed in vacuo, the residue was purified by silica gel chromatography (PE:EA = 20:1 as eluent) to give ligand **1** as colorless oil (0.72 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.47 (m, 4H), 7.36–7.31 (m, 6H), 5.55 (dt, J = 24.8, 2.0 Hz, 2H), 5.34 (d, J = 9.6 Hz, 2H), 3.78–3.69 (m, 1H), 1.82 (s, 3H), 1.80 (s, 3H), 1.22 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.67, 144.64, 144.44, 144.42, 140.56, 140.53, 140.39, 140.36, 133.01, 132.98, 132.93, 132.78, 132.71, 128.44, 128.40, 127.91, 127.87, 123.99, 123.77, 54.52, 51.41, 51.31, 24.49, 24.47, 21.78, 21.71, 21.70, 21.60, 21.54, 21.49. ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.76 (br. s), 49.93 (br. s). HRMS (EI): m/z $[M]^+$ calcd. for $C_{21}H_{27}NP_2^+$: 355.1619. Found: 355.1622.

N-cyclopentyl-N-(di(prop-1-en-2-yl)phosphaneyl)-1,1-diphenylphosphanamine (2)



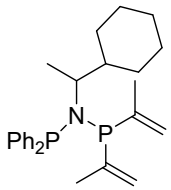
2 was prepared and purified by the same procedure and experimental conditions as those employed for **1**. Using Ph_2PN(cyclopentyl)H and (1.36 g, 5.04 mmol) and chlorodiisopropenylphosphane (6.05 mol, calculated from crude reaction mixture) led to the formation of **2** as colorless oil (0.83 g, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.47 (m, 4H), 7.35–7.31 (m, 6H), 5.53 (dt, J = 24.4, 2.0 Hz, 2H), 5.33 (d, J = 10.0 Hz, 2H), 3.87–3.77 (m, 1H), 1.89–1.83 (m, 1H), 1.83 (s, 3H), 1.80 (s, 3H), 1.71–1.68 (m, 4H), 1.41–1.38 (m, 2H), 0.89–0.84 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.77, 144.74, 144.55, 144.52, 140.63, 140.59, 140.46, 140.43, 132.96, 132.89, 132.77, 132.70, 128.45, 128.39, 127.92, 127.89, 123.77, 123.58, 62.34, 34.11, 24.19, 21.85, 21.82. ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.58 (br. s), 51.24 (br. s). HRMS (EI): m/z $[M]^+$ calcd. for $C_{23}H_{29}NP_2^+$: 381.1775. Found: 381.1772.

N-cyclohexyl-N-(di(prop-1-en-2-yl)phosphaneyl)-1,1-diphenylphosphanamine (3)



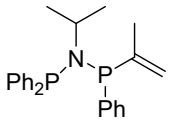
3 was prepared and purified by the same procedure and experimental conditions as those employed for **1**. Using Ph_2PN(cyclohexyl)H and (1.43 g, 5.04 mmol) and chlorodiisopropenylphosphane (6.05 mol, calculated from crude reaction mixture) led to the formation of **3** as colorless oil (1.30 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.48 (m, 4H), 7.34–7.30 (m, 6H), 5.53 (d, J = 24.8 Hz, 2H), 5.32 (d, J = 10.0 Hz, 2H), 3.25–3.18 (m, 1H), 1.86–1.79 (m, 2H), 1.82 (s, 3H), 1.79 (s, 3H), 1.69–1.52 (m, 5H), 1.15–1.10 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.80, 144.58, 140.77, 140.73, 140.60, 140.56, 132.98, 132.89, 132.69, 132.66, 128.40, 128.38, 127.88, 127.85, 123.94, 123.72, 60.13, 60.05, 59.97, 35.16, 35.12, 35.06, 26.23, 25.51, 21.69, 21.55, 21.48. ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.54 (br. s), 51.21 (br. s). HRMS (EI): m/z $[M]^+$ calcd. for $C_{24}H_{31}NP_2^+$: 395.1932. Found: 395.1936.

N-(1-cyclohexylethyl)-N-(di(prop-1-en-2-yl)phosphaneyl)-1,1-diphenylphosphanamine (4)



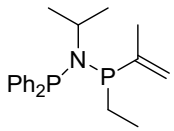
4 was prepared and purified by the same procedure and experimental conditions as those employed for **1**, Using Ph_2PN(1-cyclohexylethyl)H and (1.57 g, 5.04 mmol) and chlorodiisopropenylphosphane (6.05 mol, calculated from crude reaction mixture) led to the formation of **4** as colorless oil (1.15 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.53 (m, 2H), 7.44 (br., s, 2H), 7.35–7.30 (m, 6H), 5.63 (dt, J = 22.8, 2.0 Hz, 1H), 5.54–5.42 (m, 3H), 3.39–3.31 (m, 1H), 2.05–2.03 (m, 1H), 1.92–1.78 (m, 5H), 1.65–1.51 (m, 4H), 1.33–1.23 (m, 4H), 0.98–0.75 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.90 (m), 140.85, 140.67, 140.39, 140.25, 133.79 (m), 132.22 (m), 128.80 (m), 128.02, 127.87, 127.81, 127.79, 127.73, 60.56, 60.45, 45.33, 31.86, 27.60, 26.79, 26.51, 26.48, 21.69, 21.50 (m), 18.08 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 57.27. HRMS (EI): m/z $[M]^+$ calcd. for $C_{26}H_{35}NP_2^+$: 423.2245. Found: 423.2247.

N-(diphenylphosphaneyl)-N-isopropyl-1-phenyl-1-(prop-1-en-2-yl)phosphanamine (5)



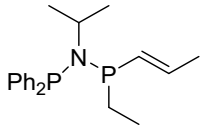
5 was prepared and purified by the same procedure and experimental conditions as those employed for **1**. Using Ph_2PN(*i*-Pr)H (1.23 g, 5.04 mmol) and chloro(phenyl)(prop-1-en-2-yl)phosphane (6.05 mol, calculated from crude reaction mixture) led to the formation of **5** as colorless oil (1.32 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.46 (m, 2H), 7.33–7.27 (m, 9H), 7.24–7.09 (m, 4H), 5.56 (dt, *J* = 18.8, 2.0 Hz, 1H), 5.39 (d, *J* = 7.2 Hz, 1H), 3.70–3.58 (m, 1H), 1.69 (d, *J* = 10.4 Hz, 3H), 1.29 (d, *J* = 7.2 Hz, 3H), 0.74 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.05, 145.03, 144.86, 144.84, 140.26, 140.09, 139.91, 139.89, 139.76, 139.74, 137.23, 137.01, 134.32, 134.09, 133.63, 133.42, 132.05, 131.83, 129.06, 128.63, 128.13, 128.03, 128.01, 127.96, 127.84, 127.78, 121.80, 121.67, 51.41, 51.32, 51.22, 24.52, 24.44, 24.37, 24.16, 24.10, 24.04, 21.34, 21.07. ^{31}P NMR (243 MHz, $CDCl_3$) δ 48.58 46.416. HRMS (EI): m/z $[M]^+$ calcd. for $C_{24}H_{27}NP_2^+$: 391.1619. Found: 391.1617.

N-(diphenylphosphaneyl)-1-ethyl-N-isopropyl-1-(prop-1-en-2-yl)phosphanamine (6)



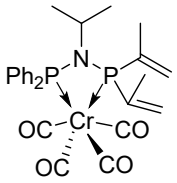
6 was prepared and purified by the same procedure and experimental conditions as those employed for **1**. Using $Ph_2PN(i\text{-}Pr)H$ (1.23 g, 5.04 mmol) and chloro(ethyl)(prop-1-en-2-yl)phosphane (6.05 mol, calculated from crude reaction mixture) led to the formation of **6** as colorless oil (0.71 g, 41%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.48 (m, 4H), 7.37–7.31 (m, 6H), 5.46 (dt, J = 14.8, 1.2 Hz, 1H), 5.32 (d, J = 6.4 Hz, 1H), 3.64–3.59 (m, 1H), 1.94–1.87 (m, 2H), 1.91 (d, J = 4.8 Hz, 3H), 1.17 (d, J = 4.4 Hz, 3H), 1.04-0.99 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.93, 146.88, 146.71, 146.68, 140.52, 140.35, 140.03, 139.87, 132.95 (m), 132.52 (m), 128.54 (m), 128.31 (m), 127.99 (m), 121.24, 121.05, 50.95, 50.80, 50.65, 24.40 (m), 22.14 (m), 21.06 (m), 9.63 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.32 (s), 46.45 (s). HRMS (EI): m/z $[M]^+$ calcd. for $C_{20}H_{27}NP_2^+$: 343.1619. Found: 343.1622.

(E)-N-(diphenylphosphaneyl)-1-ethyl-N-isopropyl-1-(prop-1-en-1-yl)phosphanamine (7)

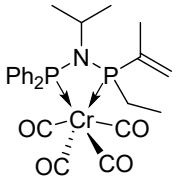


7 was prepared and purified by the same procedure and experimental conditions as those employed for **1**. Using $Ph_2PN(i\text{-}Pr)H$ (1.23 g, 5.04 mmol) and (*E*)-chloro(ethyl)(prop-1-en-1-yl)phosphane (6.05 mol, calculated from crude reaction mixture) led to the formation of **7** as colorless oil (0.73 g, 42%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57–7.52 (m, 2H), 7.45–7.41 (m, 2H), 7.37–7.28 (m, 6H), 6.29–6.19 (m, 2H), 3.59–3.50 (m, 1H), 1.89 (d, J = 5.2 Hz, 3H), 1.84–1.61 (m, 2H), 1.09 (d, J = 6.4 Hz, 3H), 1.04 (d, J = 6.4 Hz, 3H), 0.89 (dt, J = 18.0, 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.23, 140.13, 140.08, 139.96, 139.55, 139.26, 132.97 (m), 132.14 (m), 128.56 (m), 127.95 (m), 50.42 (m), 24.50 (m), 24.09 (m), 17.09 (m), 9.00 (m). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.87 (d, J = 19.4 Hz), 19.34 (br s). HRMS (EI): m/z $[M]^+$ calcd. for $C_{20}H_{27}NP_2^+$: 343.1619. Found: 343.1621.

1.4 Preparation and characterization of complex $Cr(CO)_4$(1) and $Cr(CO)_4$(6)



To a solution of **1** (0.10 g, 0.28 mmol) in dry toluene (2.0 mL) was added $Cr(CO)_6$ (92.0 mg, 0.42 mmol), and the resulting mixture was stirred under reflux for 48 h. The solvent was evaporated, and the crude product was purified by chromatography on short silica gel to yield $Cr(CO)_4$(**1**) as yellow solid (84.0 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78–7.74 (m, 4H), 7.47–7.46 (m, 6H), 5.85–5.78 (m, 4H), 3.56–3.54 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 0.89 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.93, 131.83, 130.43, 130.42, 128.29, 128.22, 125.61, 125.56, 23.52, 21.32, 21.19; ^{31}P NMR (243 MHz, $CDCl_3$) δ 116.20–115.53 (m), 109.72–109.32 (m). MS (MALDI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{25}H_{28}CrNO_4P_2^+$: 520.1. Found: 520.1.



$Cr(CO)_4$(**6**) was prepared and purified by the same procedure and experimental conditions as those employed for $Cr(CO)_4$(**1**). Using ligand **6** (100 mg, 0.29 mmol) led to the formation of $Cr(CO)_4$(**6**) as yellow solid (80 mg, 54%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69–7.65 (m, 2H), 7.59–7.56 (m, 2H), 7.48–7.45 (m, 6H), 5.69 (d, J = 31.2 Hz, 1H), 5.59 (d, J = 14.4 Hz, 1H), 3.50–3.45 (m, 1H), 2.78–2.72 (m, 1H), 2.17 (d, J = 8.0 Hz, 3H), 2.18–2.13 (m, 1H), 1.31–1.28 (m, 3H), 1.04 (d, J = 4.8 Hz, 3H), 0.83 (d, J = 4.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.28, 141.18, 132.13, 131.99, 131.26, 131.13, 130.63 (m), 130.26 (m), 128.52, 128.49, 128.45, 128.44, 128.39, 128.36, 50.46 (t, J = 6.4 Hz), 30.27 (dd, J = 7.6, 6.4 Hz), 24.34 (d, J = 24.1 Hz), 17.03 (d, J = 10.2 Hz), 8.24 (d, J = 7.0 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 113.46 (pent, J = 17.0 Hz), 108.31 (dd, J = 51.0, 12.2 Hz). MS (MALDI-TOF): *m/z* $[M+H]^+$ calcd. for $C_{24}H_{28}CrNO_4P_2^+$: 508.1. Found: 508.1.

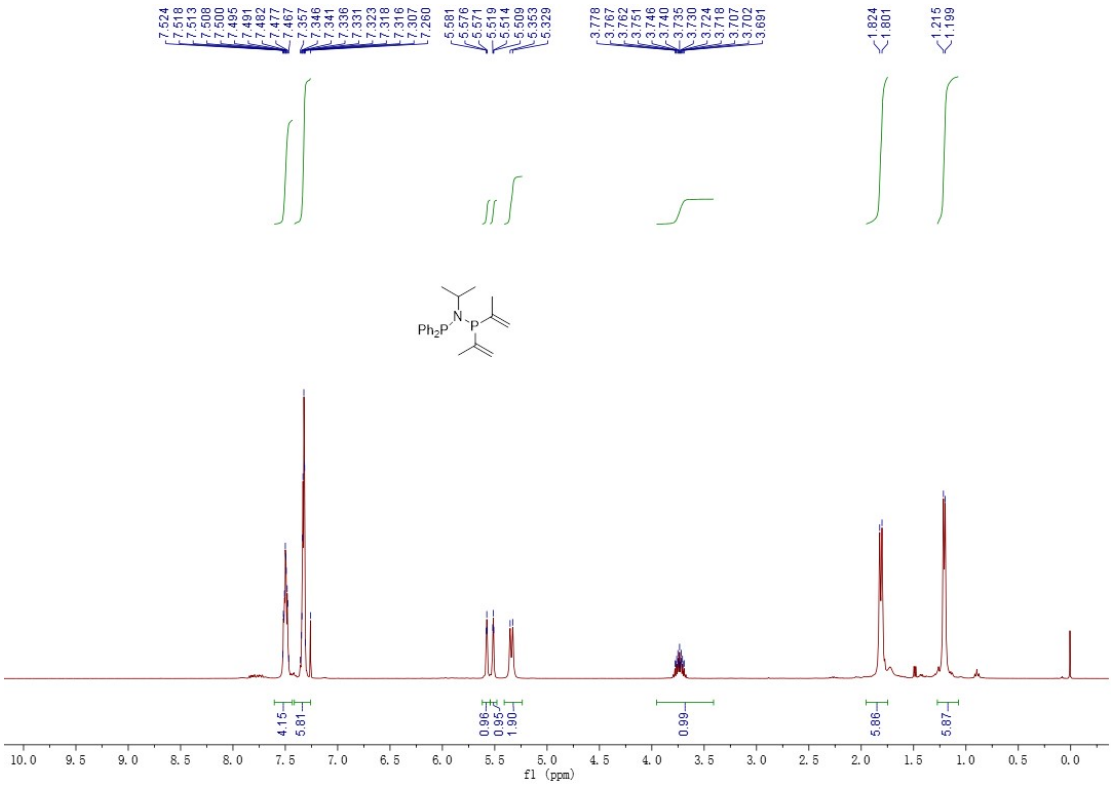
Reference:

1. Carter, A.; Cohen, S. A.; Cooley, N. A.; Murphy, A.; Scutt, J.; Wass, D. F. *Chem. Commun.* **2002**, 858.

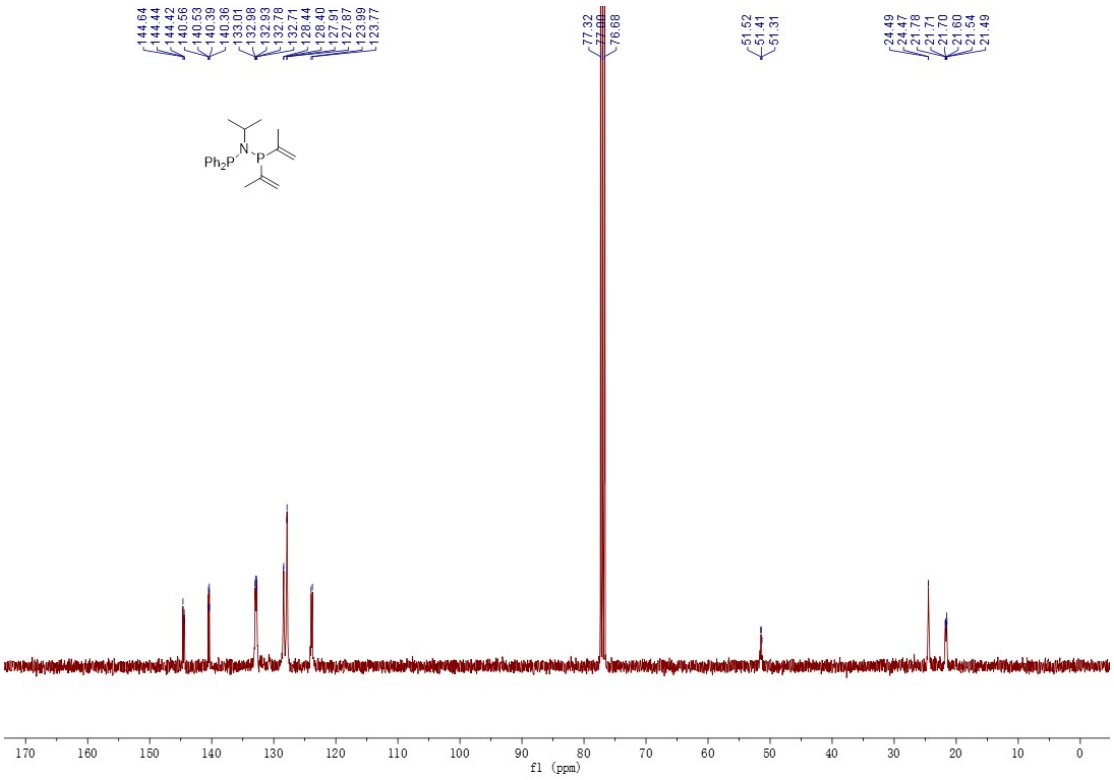
2. Kong, W.; Ma, X.; Zuo, J.; Zhao, X.; Zhang, J. *Organometallics* **2023**, *42*, 651.

2. NMR Spectra of Ligands 1-7, Complex $Cr(CO)_4$(1) and Complex $Cr(CO)_4$(6), Chlorodiisopropenylphosphane, Chloro(phenyl)(prop-1-en-2-yl)phosphane

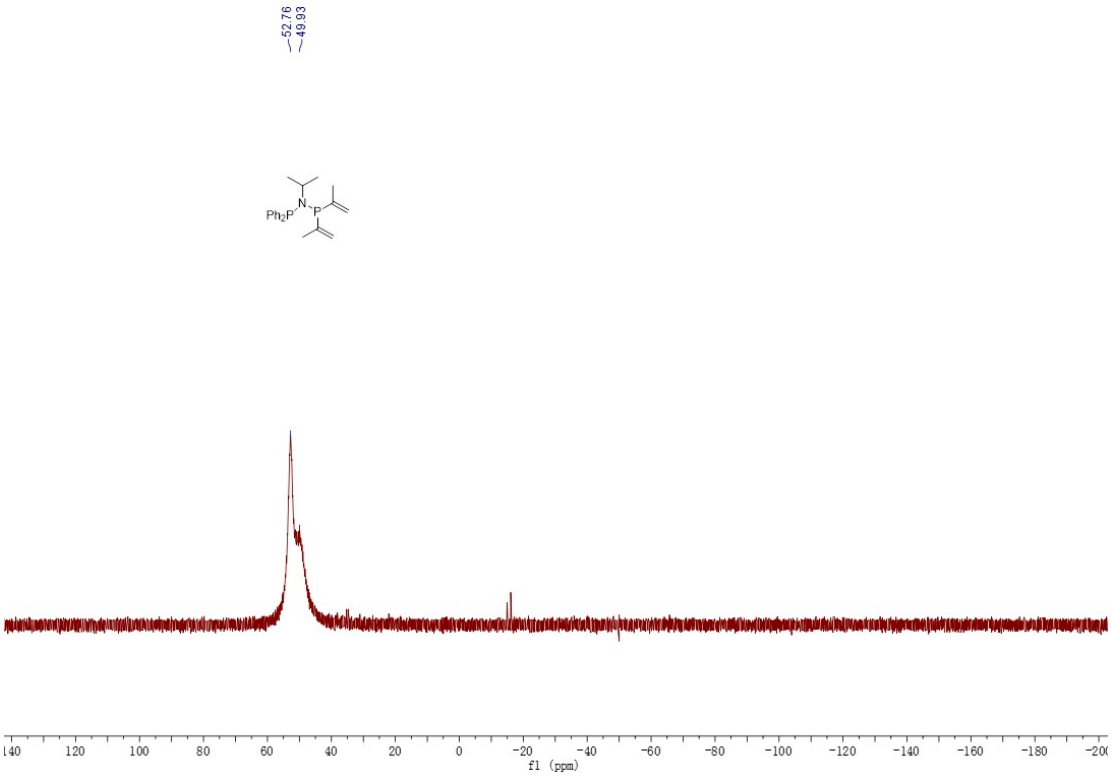
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **1**



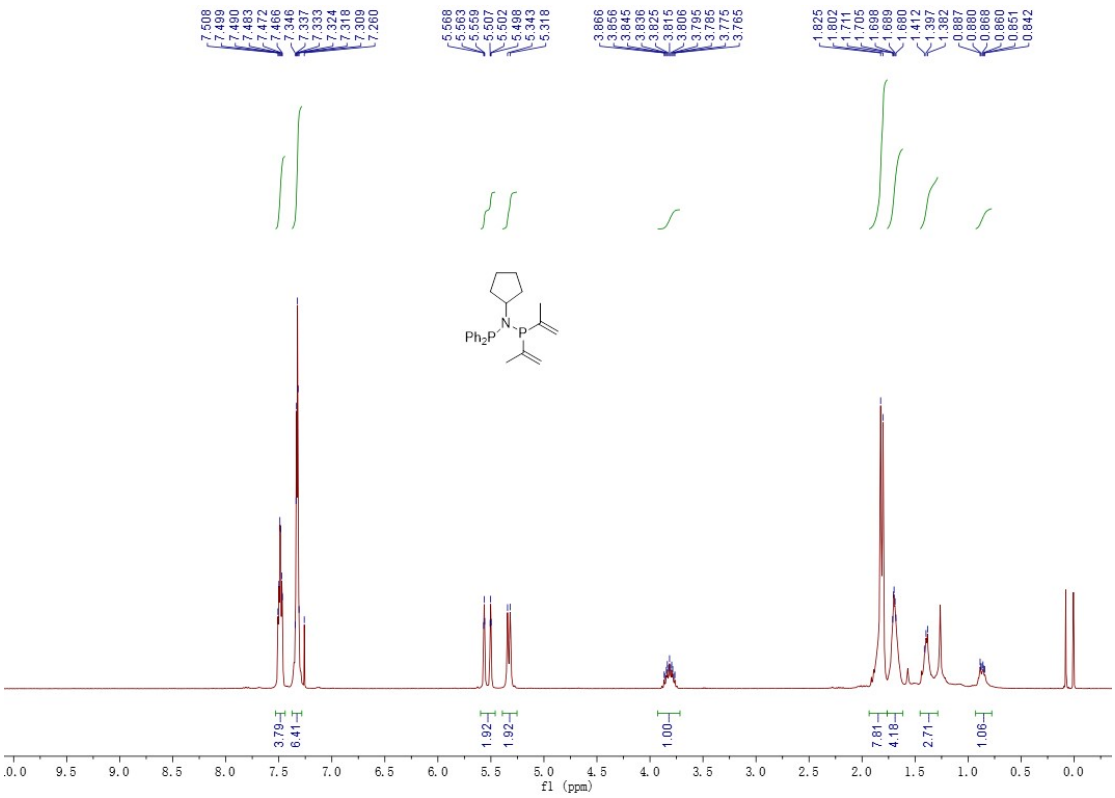
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **1**



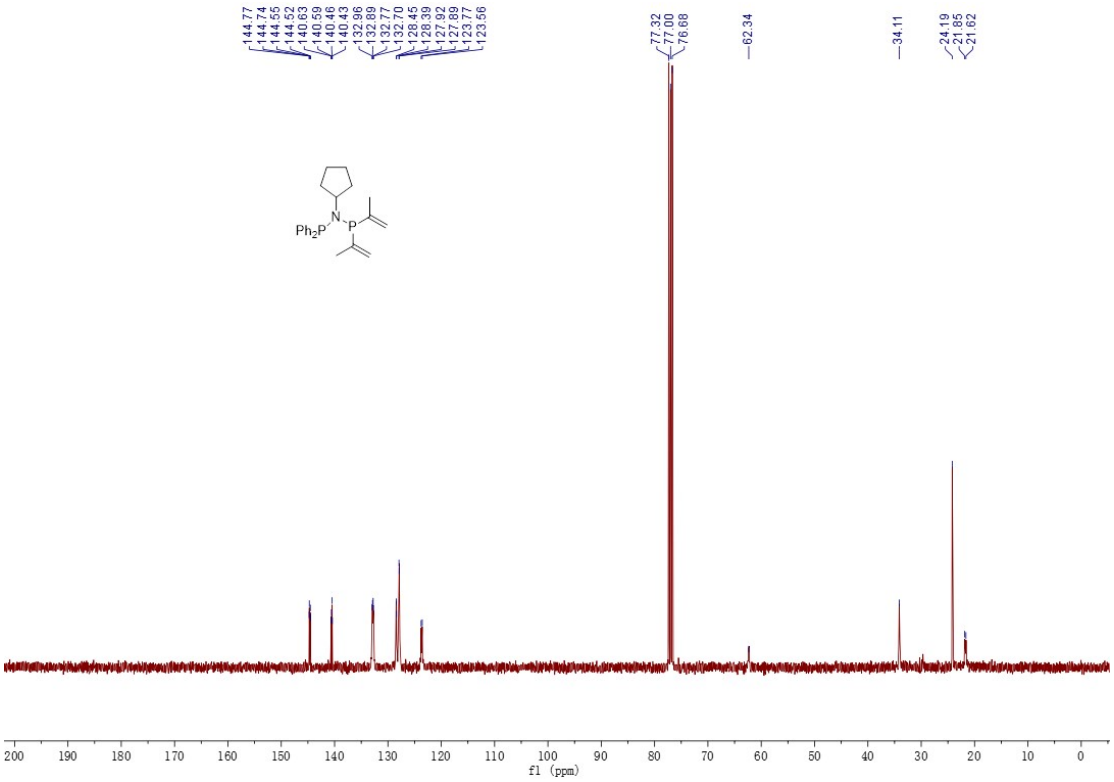
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **1**



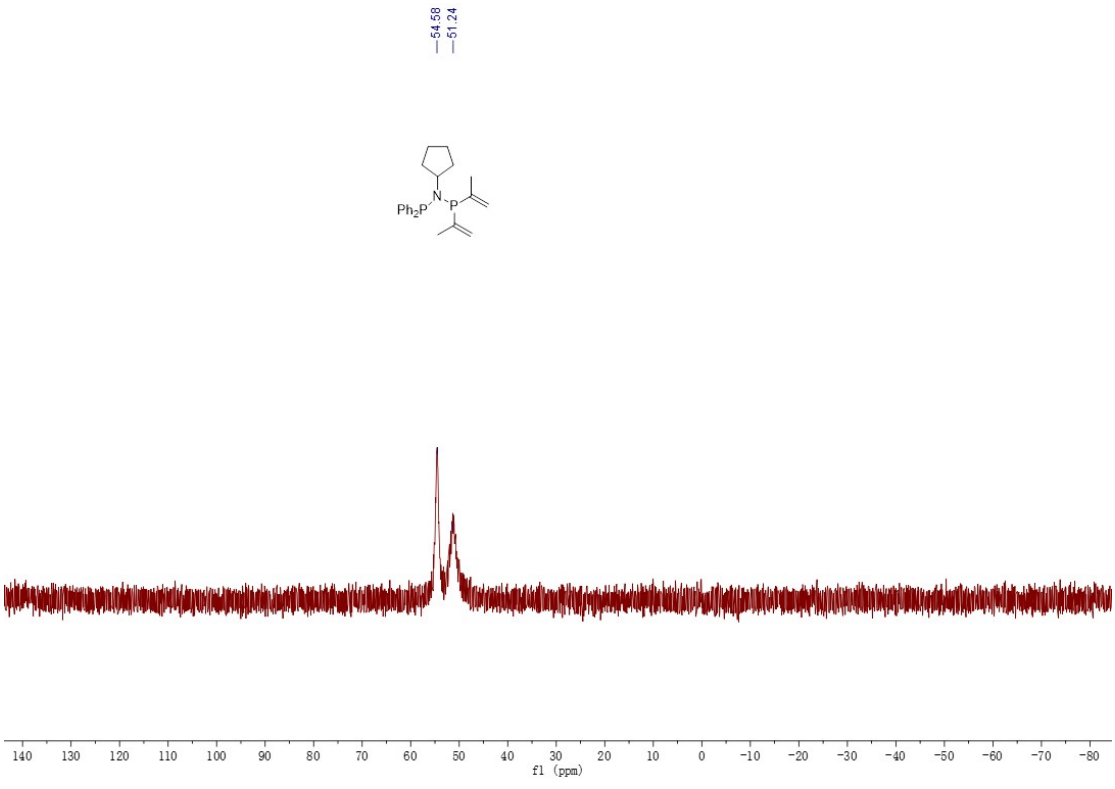
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2**



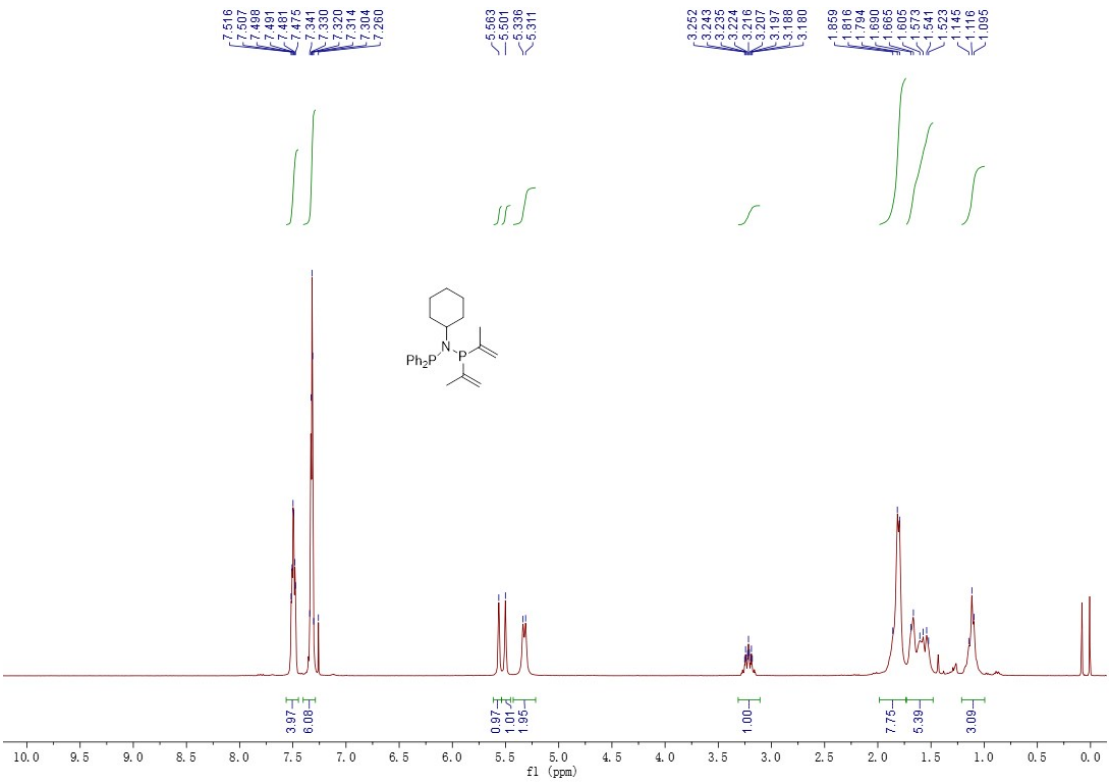
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **2**



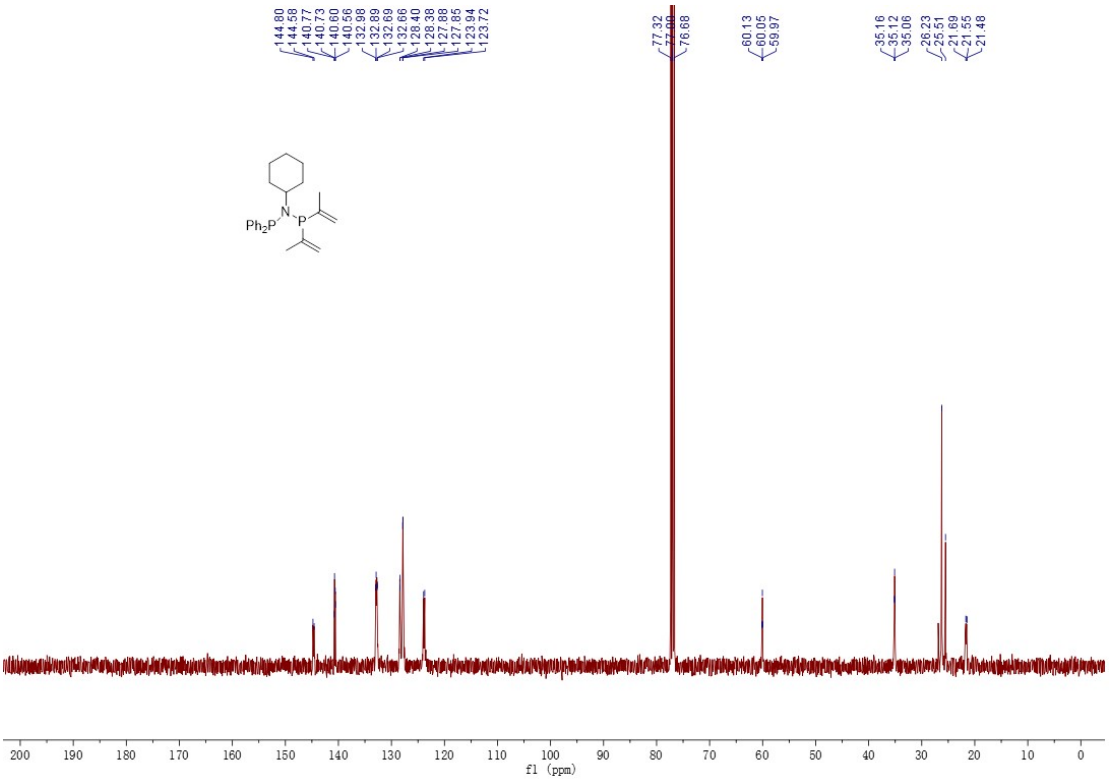
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **2**



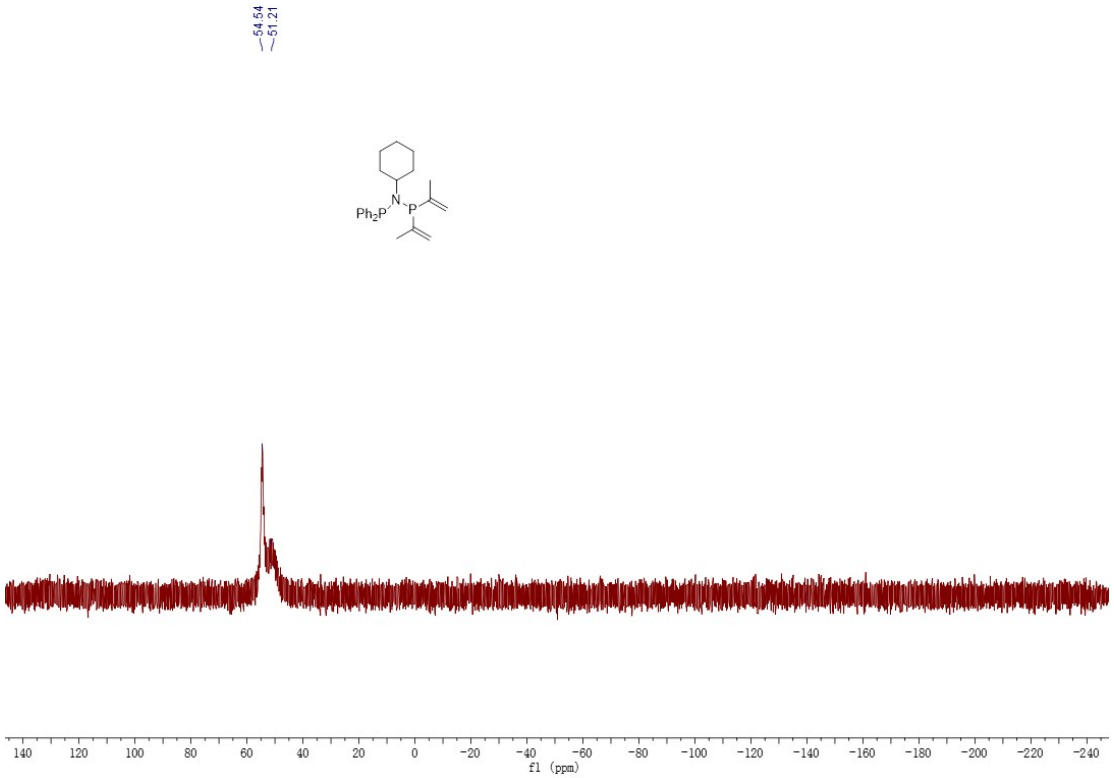
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3**



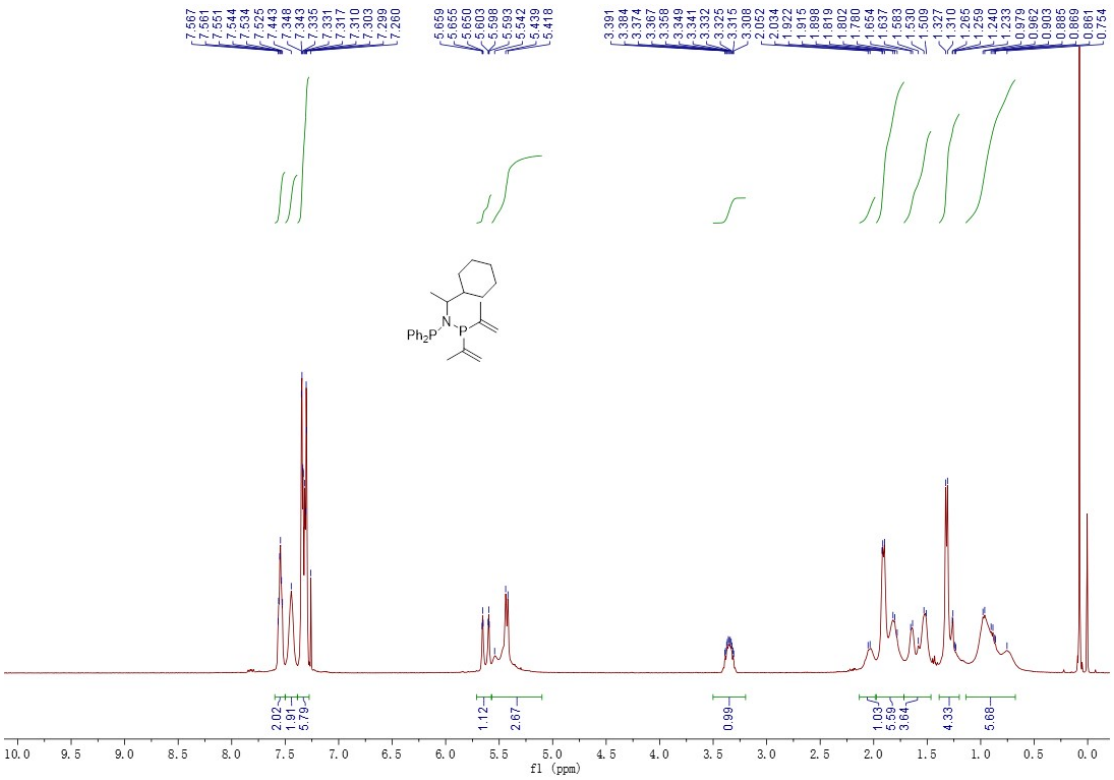
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **3**



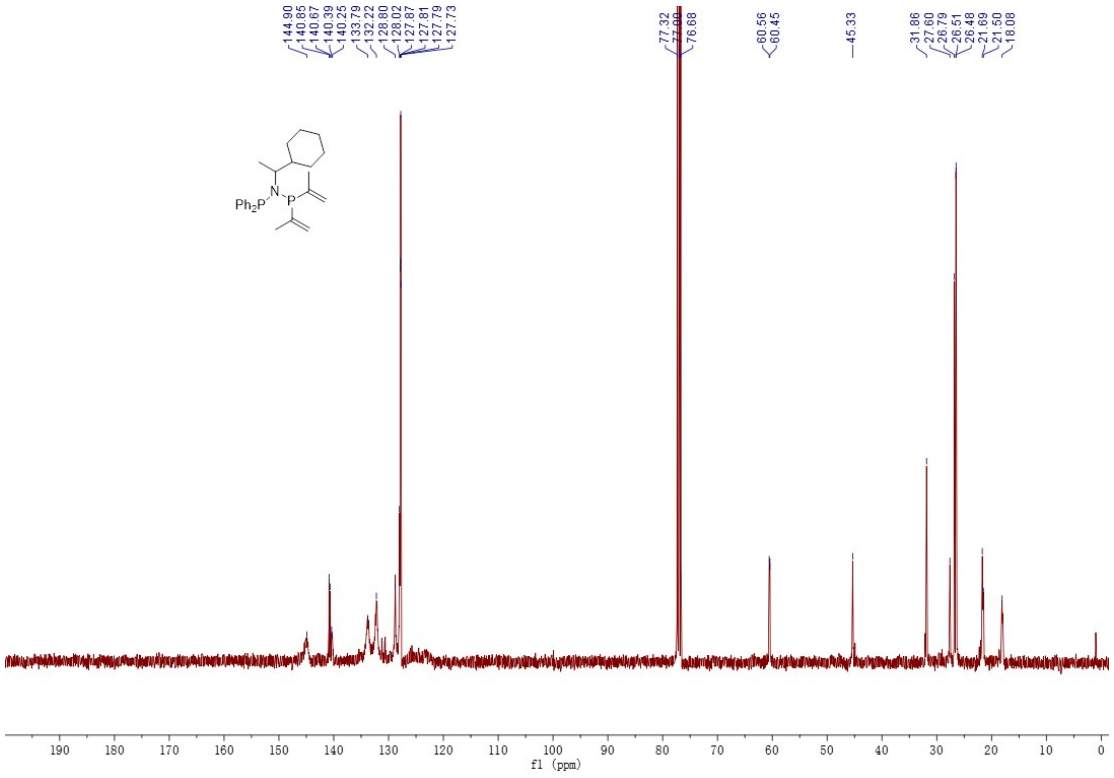
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **3**



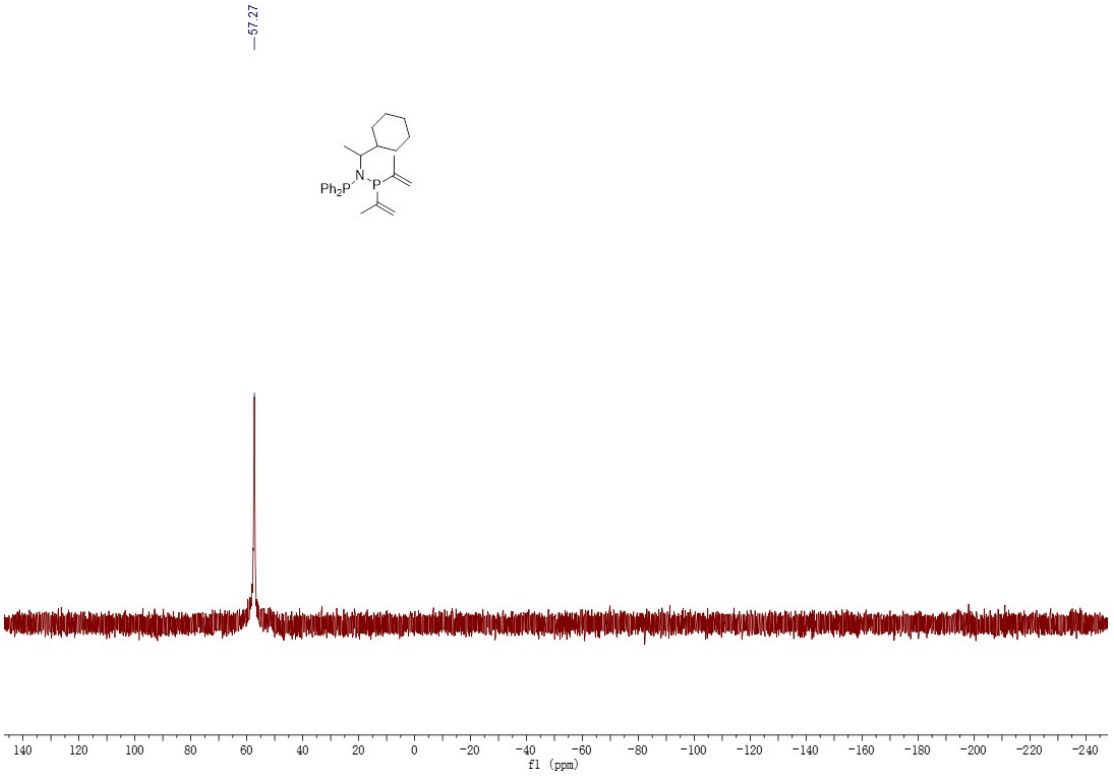
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **4**



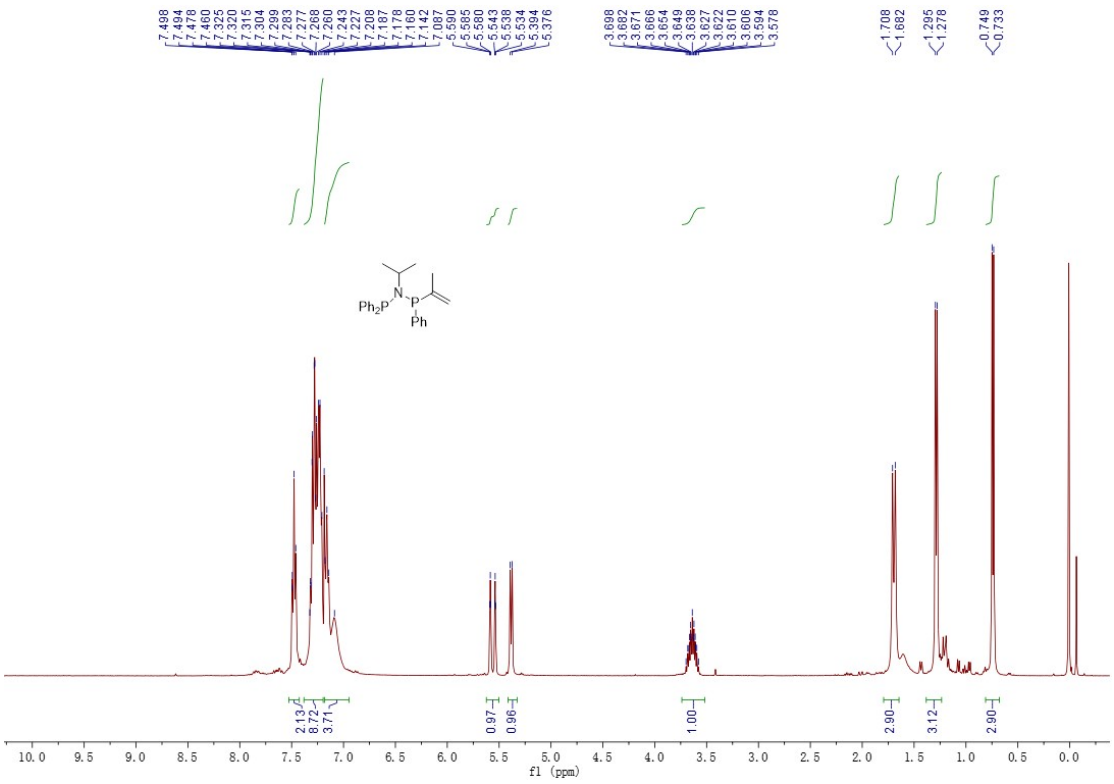
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **4**



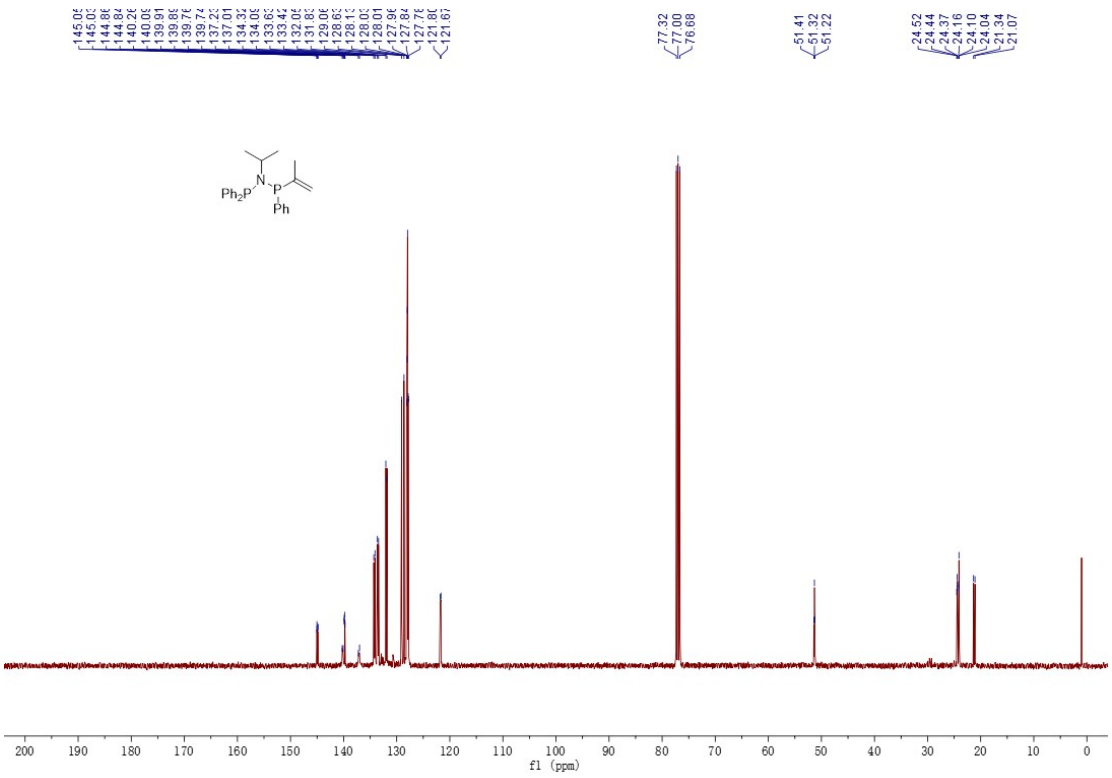
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **4**



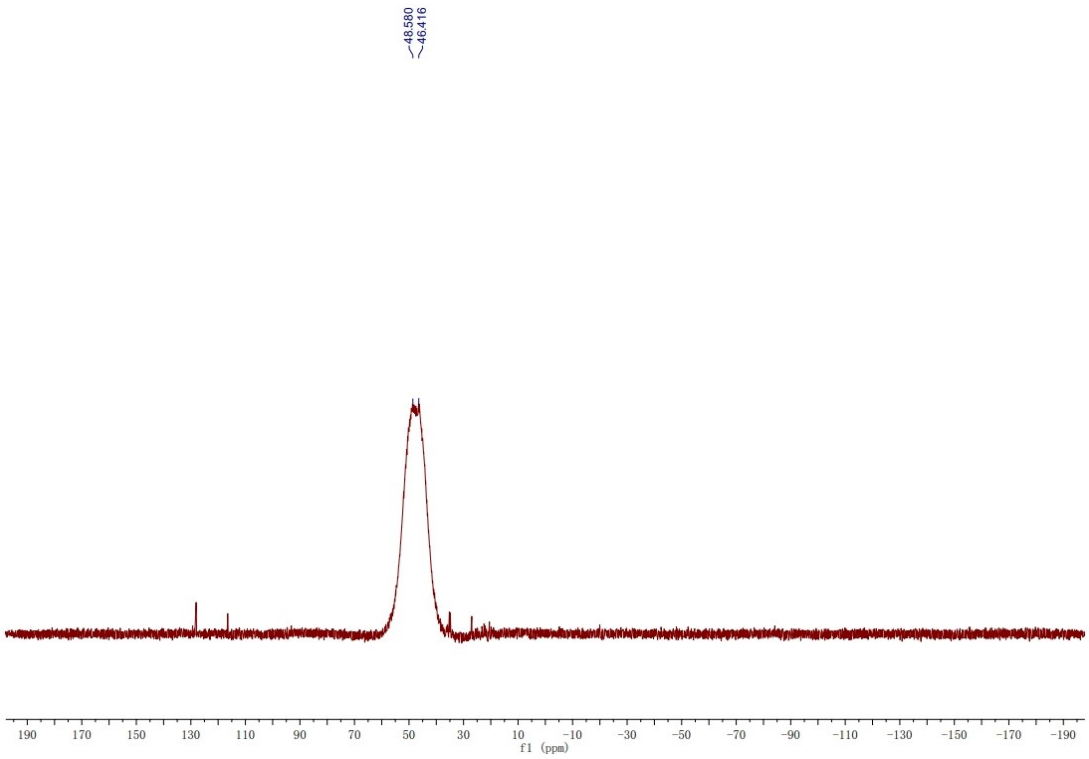
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5**



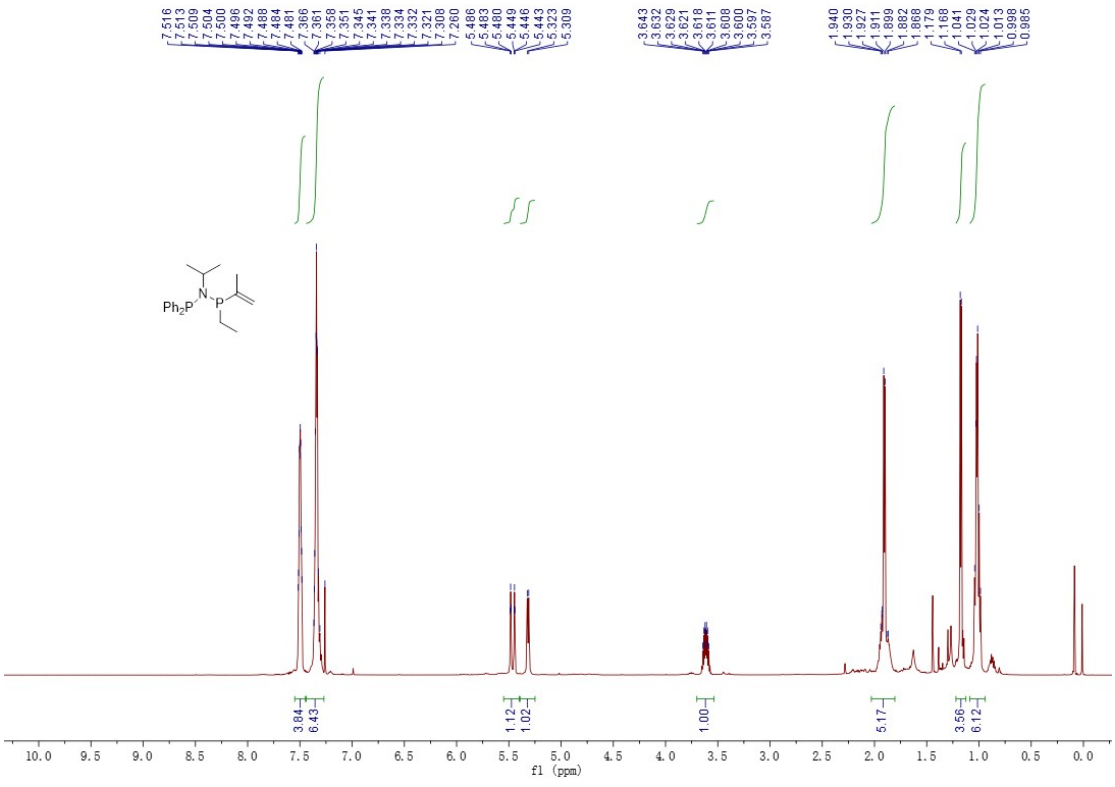
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **5**



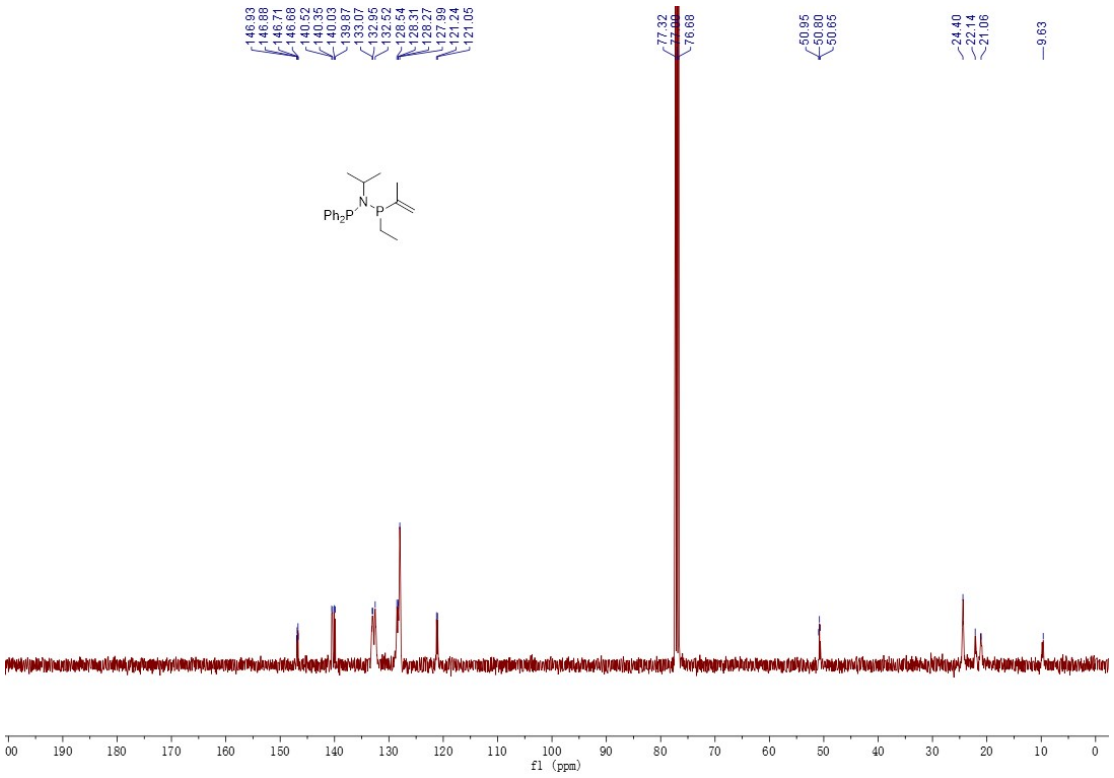
^{31}P NMR spectrum (243 MHz, $CDCl_3$) of **5**



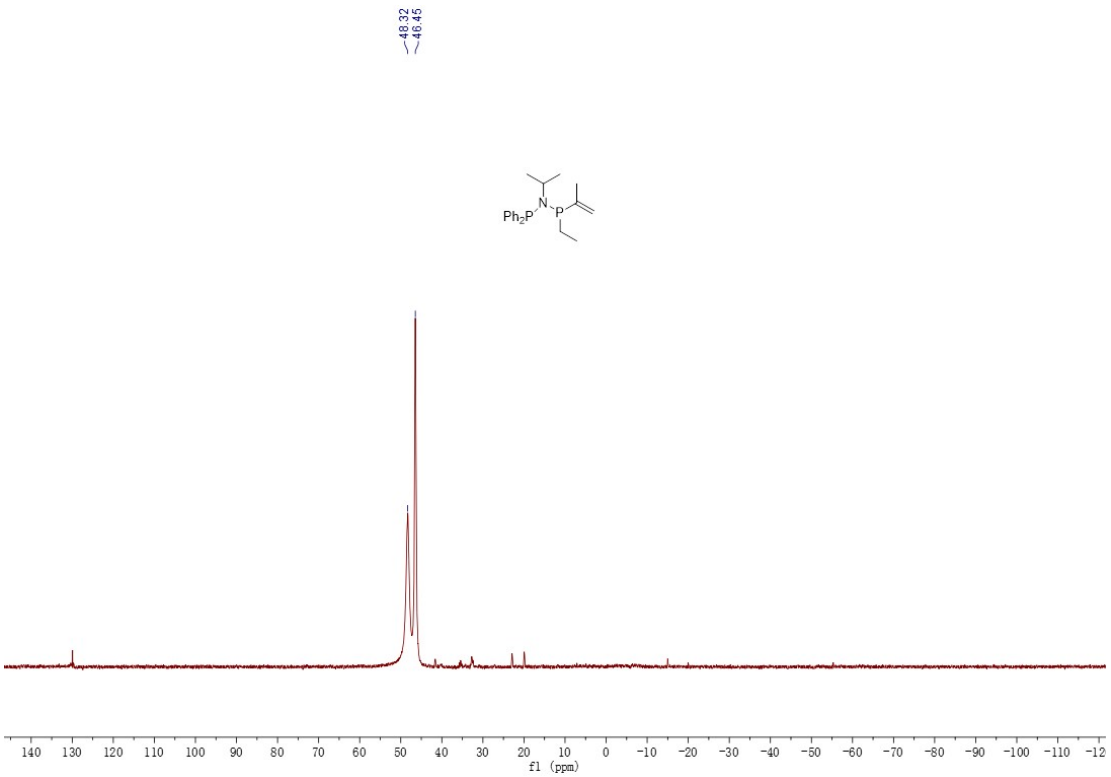
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **6**



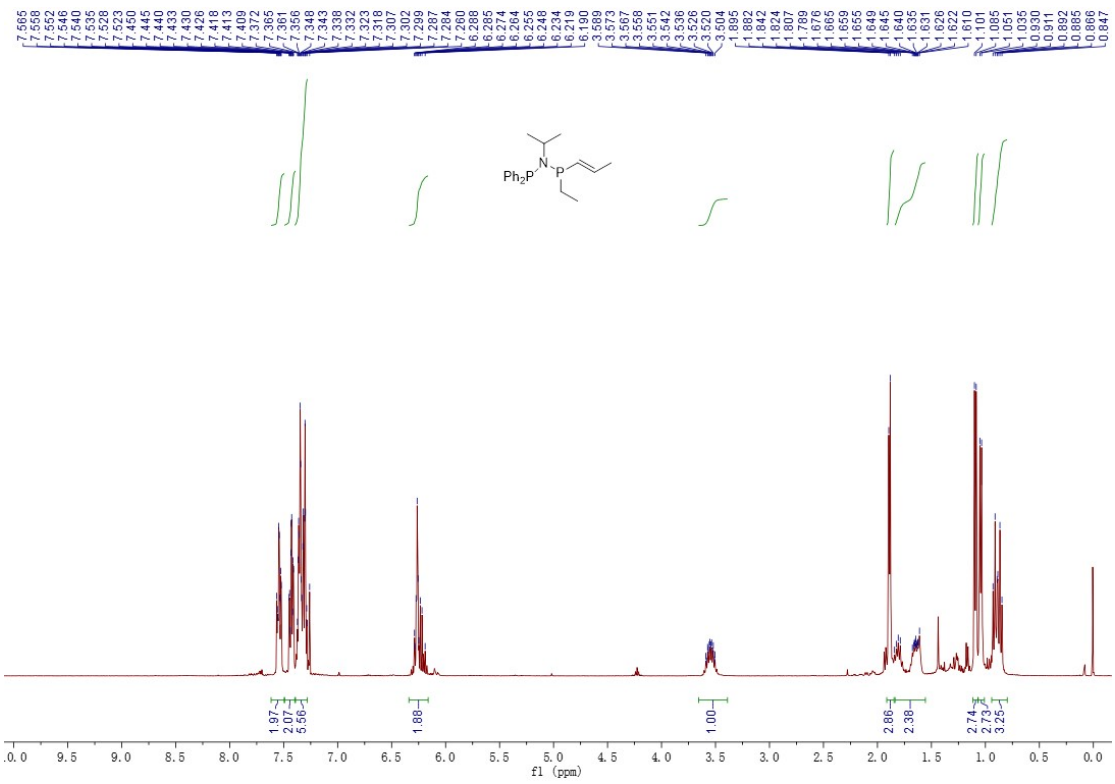
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **6**



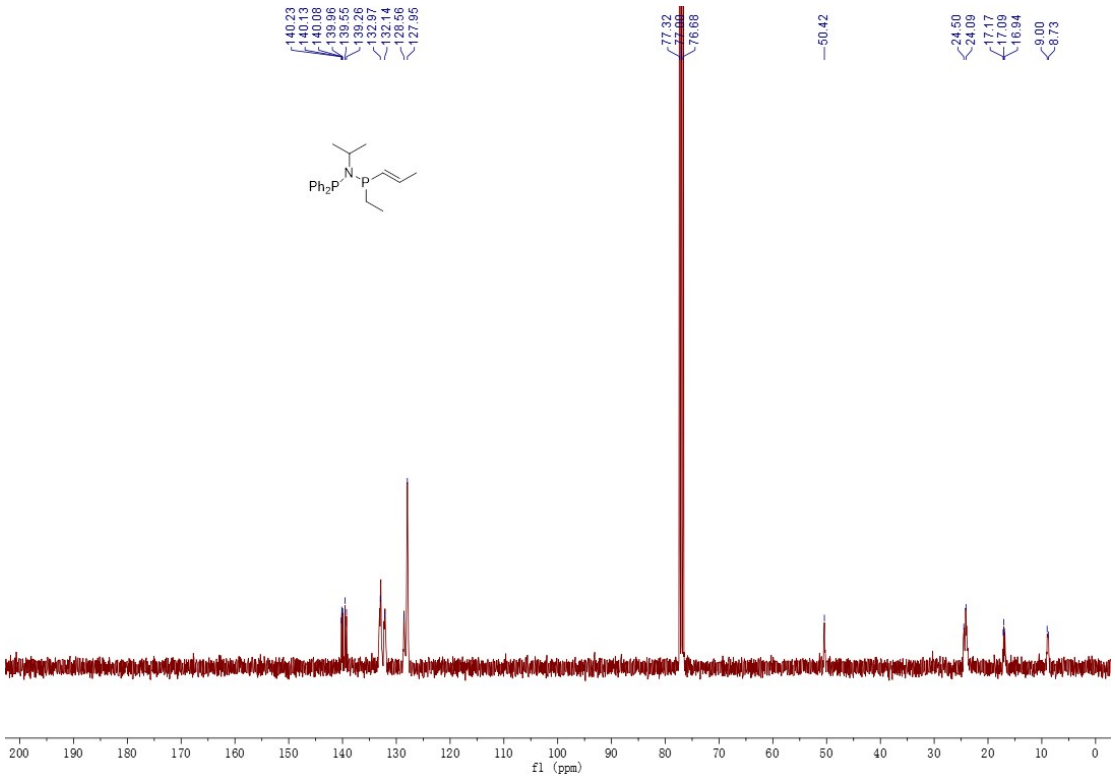
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **6**



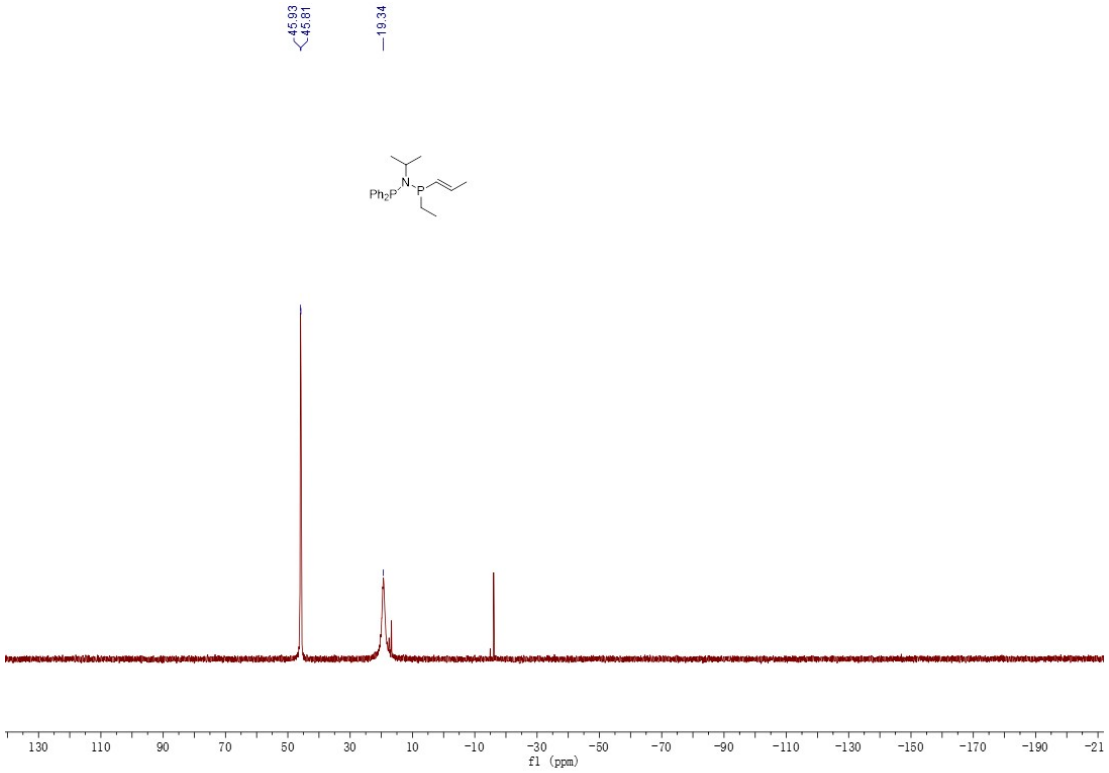
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **7**



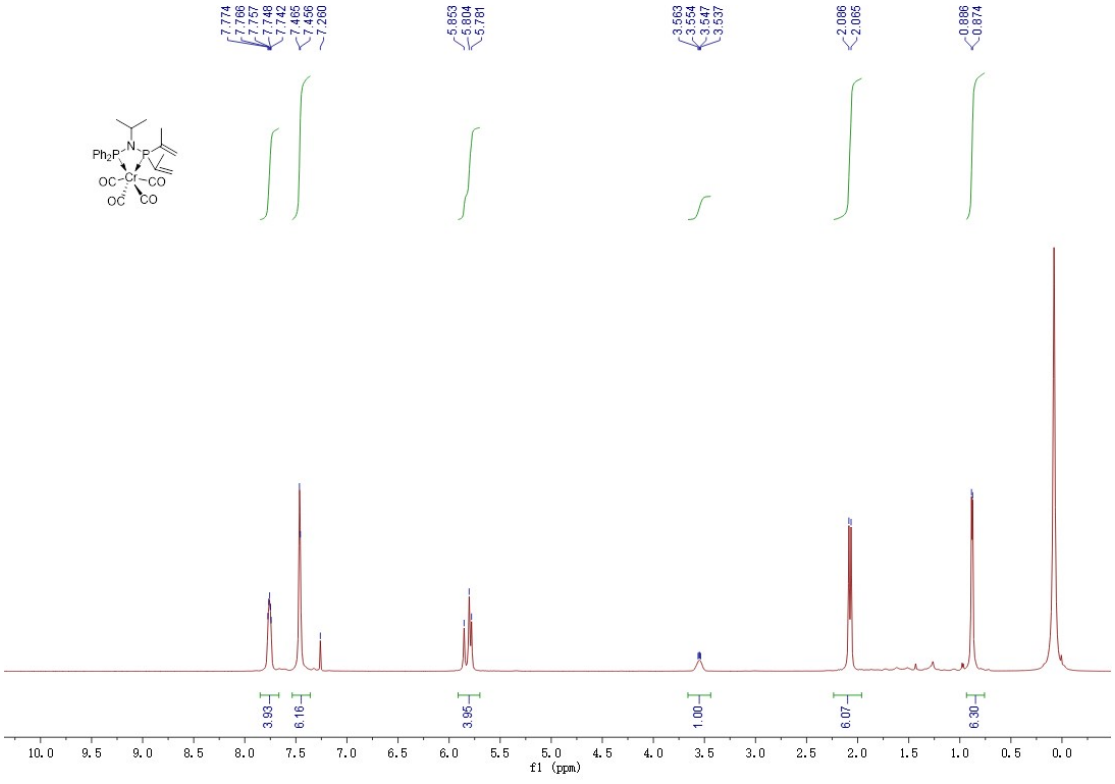
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **7**



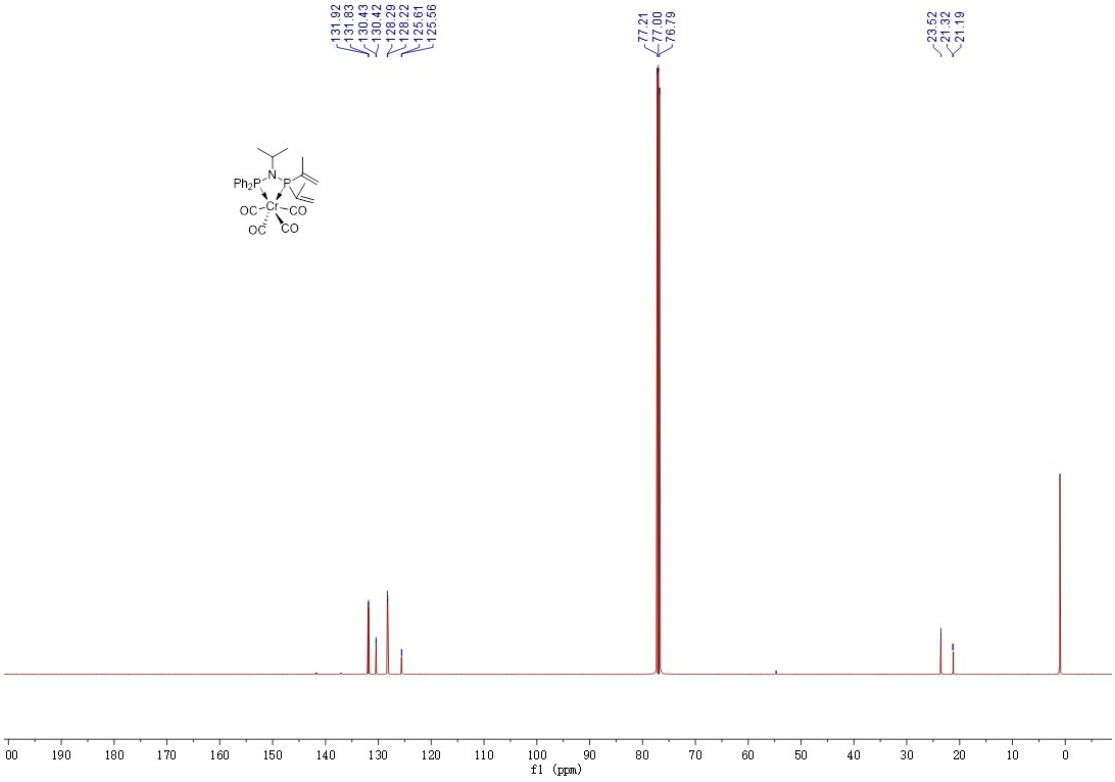
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **7**



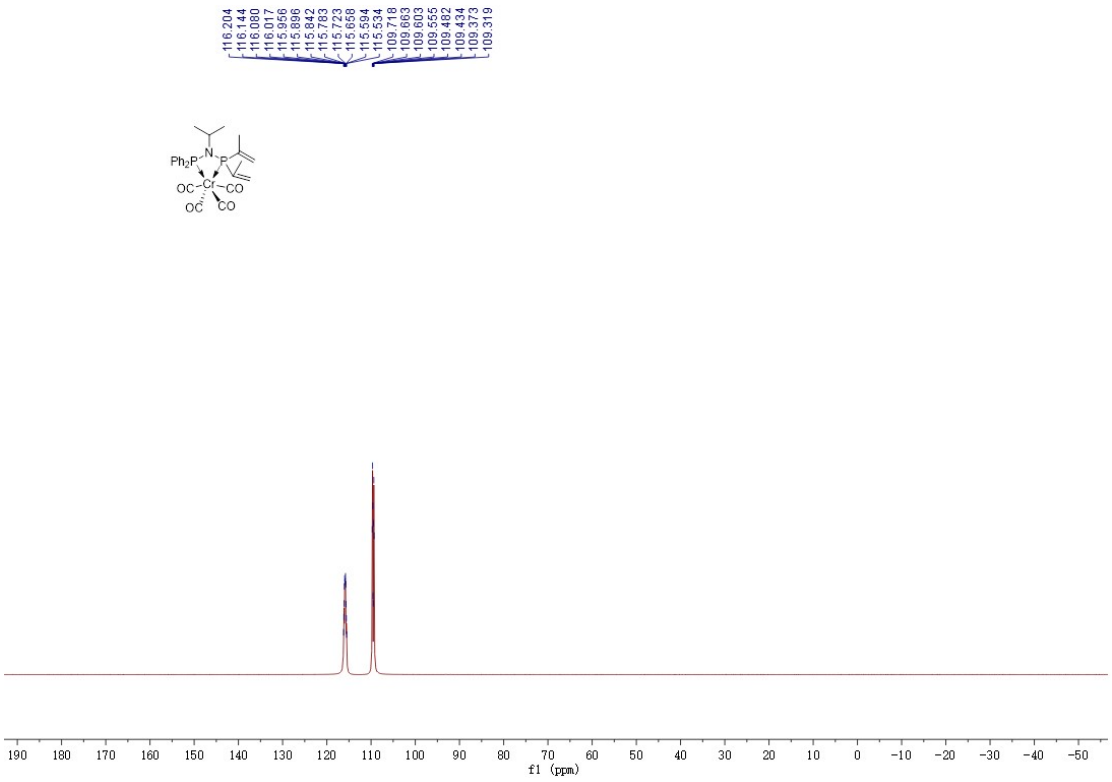
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **Cr(CO)$_4$(1)**



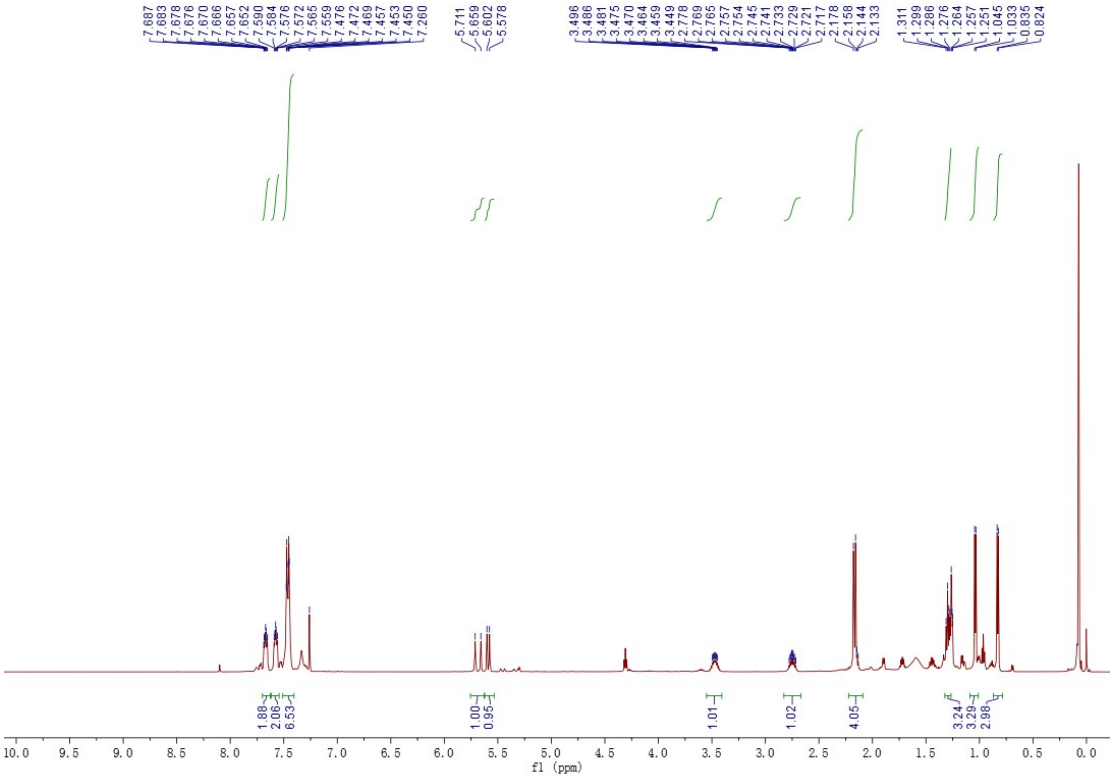
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **$Cr(CO)_4$(1)**



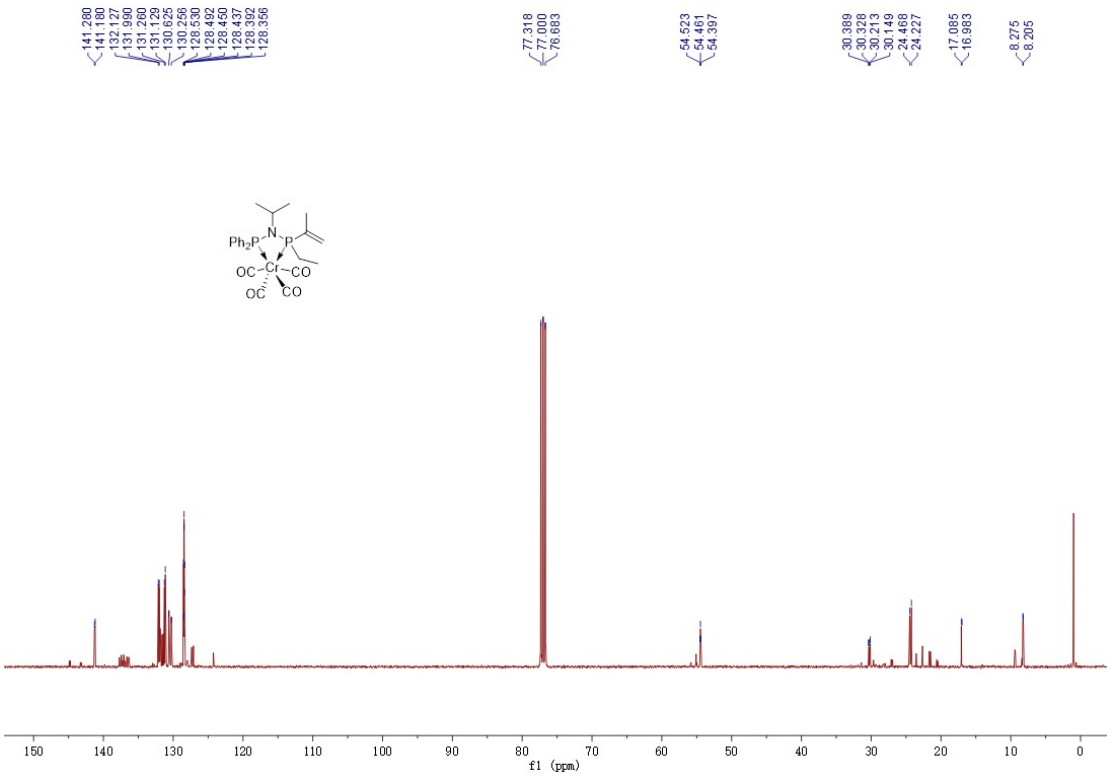
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **$Cr(CO)_4$(1)**



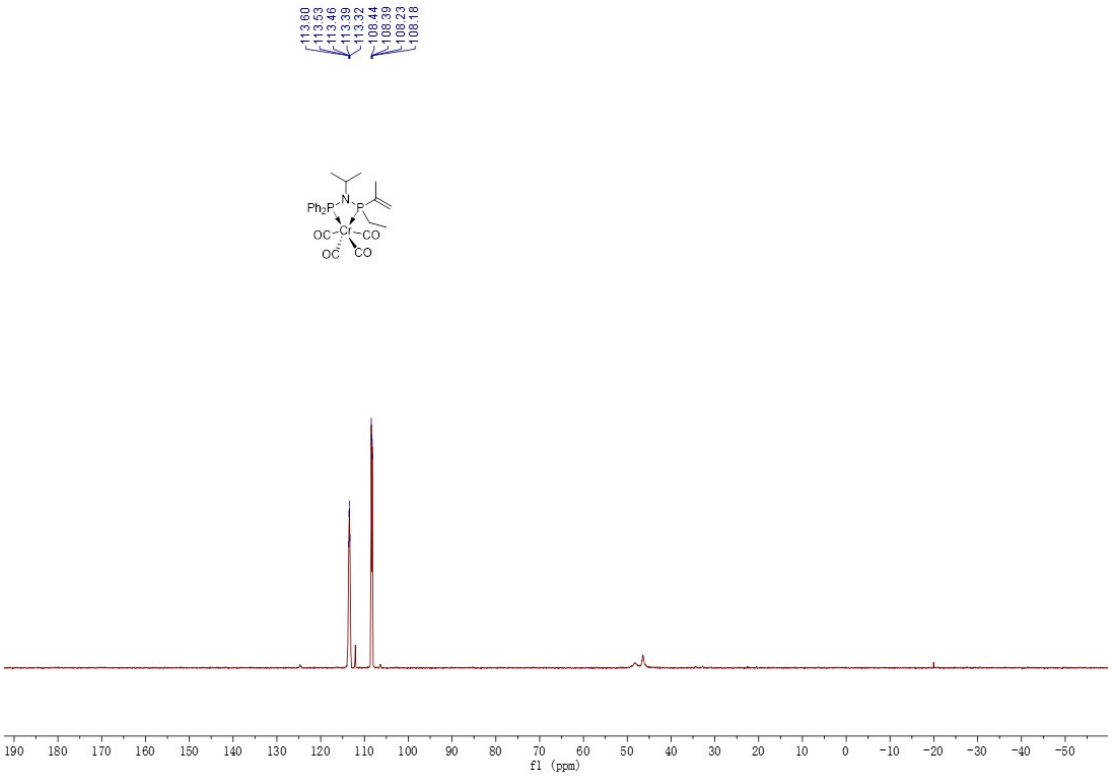
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of **$Cr(CO)_4$(6)**



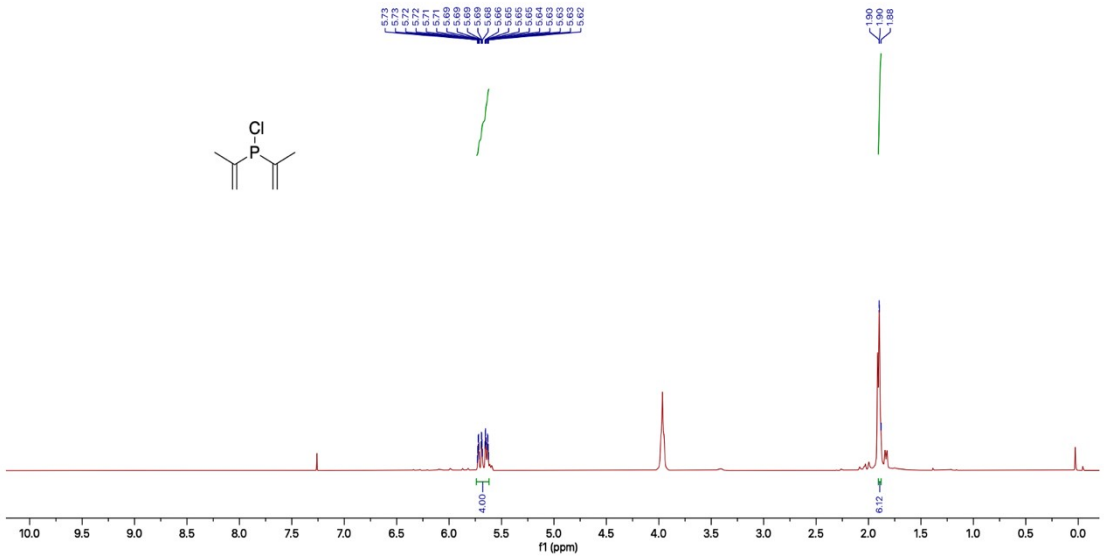
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of **$Cr(CO)_4$(6)**



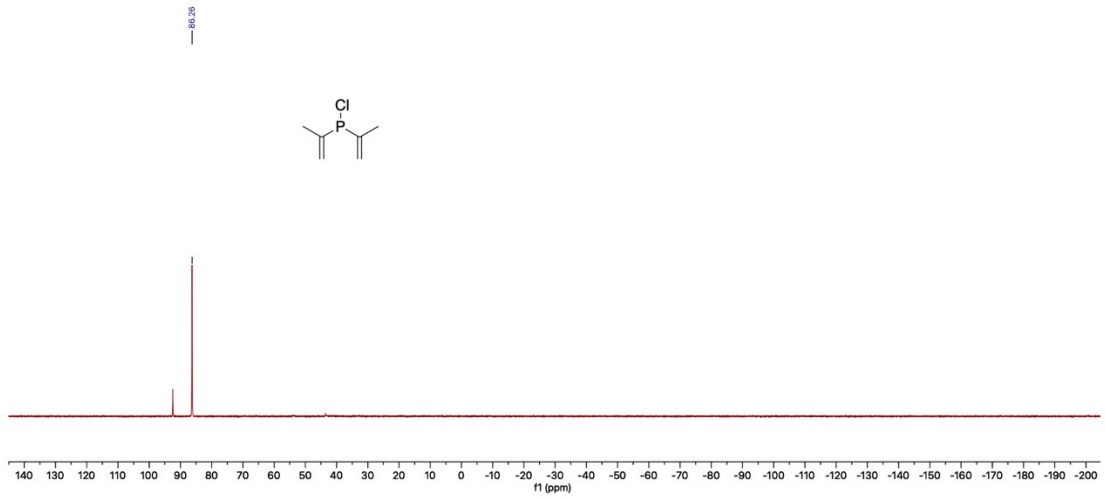
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of **$Cr(CO)_4$(6)**



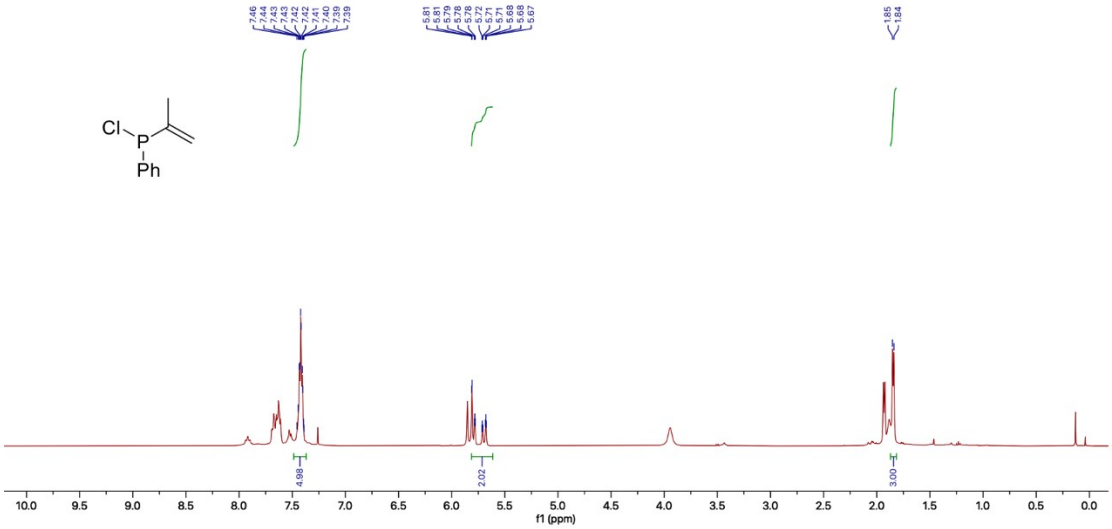
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude chlorodiisopropenylphosphane



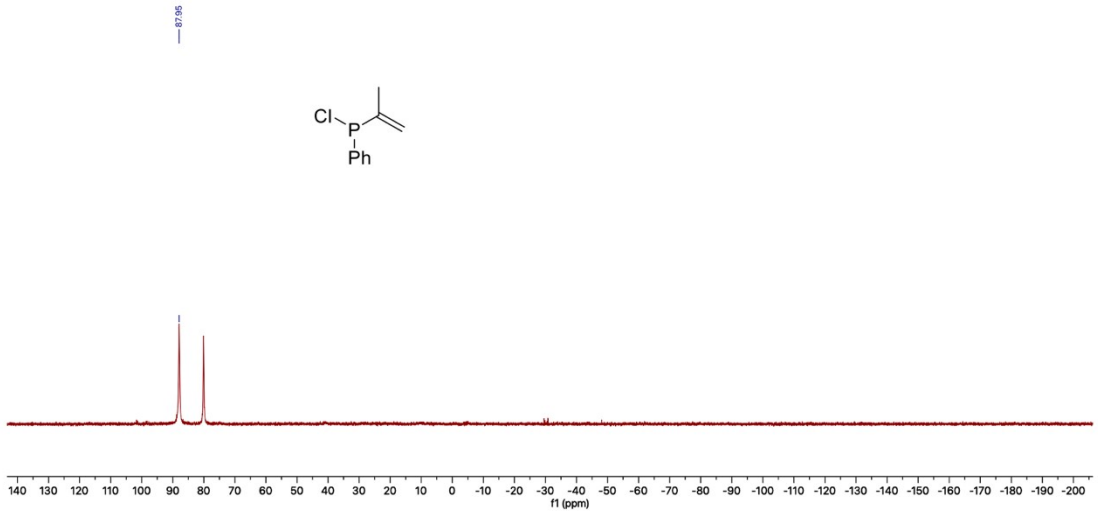
^{31}P NMR spectrum (162 MHz, $CDCl_3$) of crude chlorodiisopropenylphosphane



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of crude chloro(phenyl)(isopropenyl)phosphane



^{31}P NMR spectrum (162 MHz, $CDCl_3$) of crude chloro(phenyl)(isopropenyl)phosphane



3. X-Ray Crystallography for $Cr(CO)_4$(6)

Single crystals of X-ray quality were grown by slow diffusion of hexane into a concentrated toluene solution of **$Cr(CO)_4$(6)**. 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-97) and refined on F^2 by full-matrix least squares (SHELX-97) 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. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK (CCDC 2347064).

Table S1. Crystal data and structure refinement for **$Cr(CO)_4$(6)** (CCDC 2347064)

Empirical formula	$2(C_{24}H_{29}CrNO_4P_2)$
Formula weight	1018.84
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P 21/n
Unit cell dimensions	a = 9.4047(3) Å; α = 90°
	b = 30.1693(10) Å; β = 97.2300(10)°
	c = 18.1546(7) Å; γ = 90°
Volume	5110.1(3) $Å^3$
Z	4
Density (calculated)	1.324 Mg/m^3
Absorption coefficient	0.602 mm^{-1}
F(000)	2128
Crystal size	0.16 x 0.13 x 0.07 mm^3
Theta range for data collection	2.320 to 25.000°
Index ranges	-11≤ h ≤11, -35≤ k ≤35 -21≤ l ≤18
Reflections collected	43789
Independent reflections	8975 [R(int) = 0.0739]

Completeness to theta = 25.242°	97.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6909
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8975 / 1011 / 869
Goodness-of-fit on F^2	1.058
Final R indices [I > 2sigma(I)]	R1 = 0.0759, wR2 = 0.1562
R indices (all data)	R1 = 0.1260, wR2 = 0.1846
Largest diff. peak and hole	0.36 and -0.37 e.Å^{-3}

4. GC-FID spectrum of the typical oligomerization products

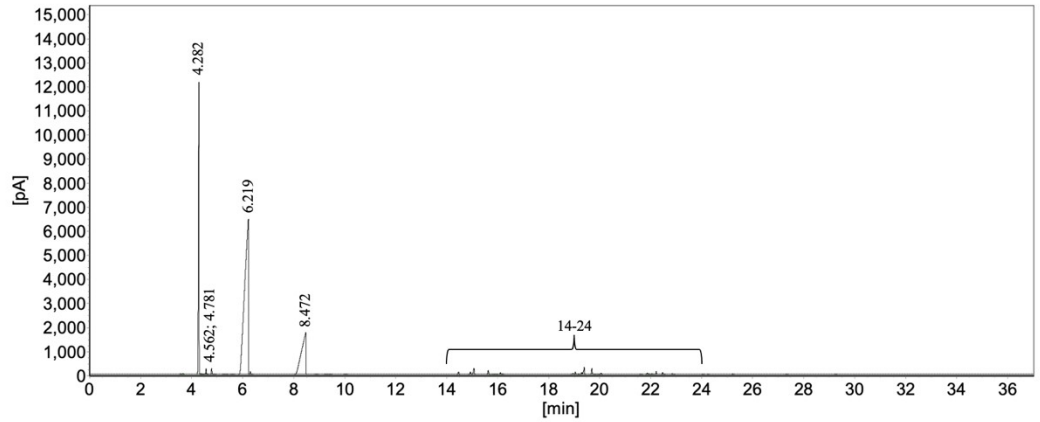


Figure S1 GC-FID spectrum of the oligomerization product obtained from Table 1 (Ligand **1**, entry 1).

Table S2. Corresponding residence time of chromatographic peak to the product.

Residence time	compound	%
4.282	1-Hexene	18.400
4.562; 4.781	cyclic C_6	0.724
6.219	Methylcyclohexane (Solvent)	58.183
8.472	1-Octene	18.566

14-24	C_{10}^{+}	3.636

Selectivity (1-C_6; 1-C_8; C_{10+}) calculation method:

$$Selectivity\ (\ 1-Hexene\ wt\ \%) = \left(\frac{18.4}{100-58.2}\right)\% = 44.0\ \%$$

$$Selectivity\ (\ 1-Octene\ wt\ \%) = \left(\frac{18.6}{100-58.2}\right)\% = \ 44.4\ \%$$

$$Selectivity\ (\ C10+\ wt\ \%) = \left(\frac{3.6}{100-58.2}\right)\% = 8.6\ \%$$

Polymer (PE) content：

$$PE\ (\ wt\ \%) = \left(\frac{g\ PE}{total\ g\ product}\right) \times 100\%$$

$$PE\ (\ wt\ \%) = \left(\frac{0.046\ g}{10.6\ g}\right) \times 100\% = 0.44\%$$