

Supporting Information

Phosphine-Iminoquinoline Iron Complexes for Ethylene Polymerization and Copolymerization

Dan Zhang[†], Yanlu Zhang[†], Wenjun Hou[†], Zhibin Guan^{*‡}, and Zheng Huang^{*†}

[†]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.

[‡]Department of Chemistry, University of California, 1102 Natural Sciences 2, Irvine, California 92697-2025, United States

Contents

1. General Information.	S3
2. Preparation of PNN Ligands and Iron complexes	S5
2.1. <i>General procedure for the synthesis of the ligands:</i>	S5
2.2. <i>General Procedure for Preparation of Iron Complexes:</i>	S11
2.3. <i>Crystallographic data for Fe complex 3a.</i>	S14
3. Procedure for Polymerization of Ethylene	S16
3.1. <i>General Procedure for Ethylene Polymerization at 1 atm:</i>	S16
3.2. <i>General Procedure for High-Pressure Ethylene Polymerizations:</i>	S16
3.3. <i>GPC traces of polyethylene</i>	S20
3.4. <i>DSC traces of polyethylene</i>	S28
3.5. <i>Attempted ethylene polymerization with phosphinite-imonopyridine Fe complexes..</i> S38	
3.6. <i>Time dependence of ethylene polymerization activity over complex 3a</i>	S39
4. Copolymerization of Ethylene and 1-Octene	S40
4.1. <i>General Procedure for Copolymerization of Ethylene and 1-Octene:</i>	S40
4.2. <i>GPC trace of poly(ethylene-co-1-octene)</i>	S43
4.3. <i>DSC trace of poly(ethylene-co-1-octene)</i>	S45
4.4. <i>¹³C NMR of poly(ethylene-co-1-octene)</i>	S47
5. References	S49
6. NMR Spectra	S50

1. General Information.

a. Materials

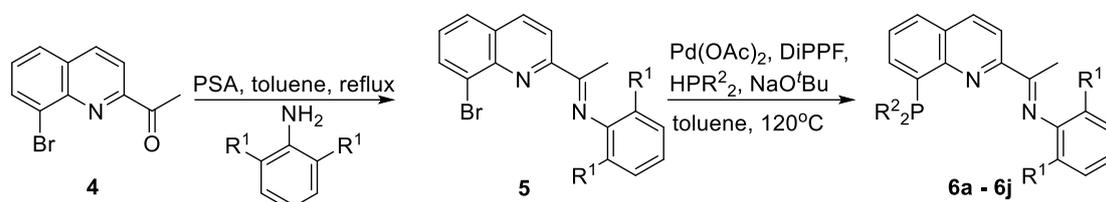
All air- or moisture-sensitive manipulations were carried out under an argon atmosphere either by using Schlenk techniques or in a glovebox. Toluene, THF and 1-octene were distilled over sodium benzophenone ketyl prior to use. Polymerization-grade ethylene was purified by passing through Et₃Al before use. Modified-methylaluminoxane (MMAO) was purchased from Akzo Chemical as a 1.88 M heptane solution. The following chemicals were purchased and used as received: FeCl₂ (Steam), NaHBEt₃ (1.0 M in toluene) (Aldrich). 2-acetyl-8-bromoquinoline (**4**) were prepared according to procedures previously reported¹. All other chemicals were purchased from TCI, Alfa Aesar, Aldrich or J&K, and used as received unless otherwise noted.

b. Analytical Methods

¹H NMR, ¹³C NMR, ³¹P NMR and ¹⁹F NMR spectra were recorded on a Agilent or Varian 400 MHz spectrometer with chemical shifts reported in ppm relative to the residual deuterated solvent, the internal standard tetramethylsilane, or external 85% H₃PO₄ for ³¹P. Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for ¹³C NMR are reported in terms of chemical shift (δ , ppm). GC-MS analysis was performed on Agilent 7890A gas chromatograph coupled to an Agilent 5975C inert mass selective detector. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). X-ray crystallographic data were collected using a Bruker AXSD8 X-ray diffractometer. Molecular weights (M_n , M_w , and M_w/M_n values) of polymers were determined using a Waters Alliance GPC 2000 series at 150 °C (using polystyrene calibration, 1,2,4-trichlorobenzene as the solvent at a flow rate of 1.0 mL/min). ¹H NMR and ¹³C NMR data for polymers were obtained using 1,1,2,2-tetrachloroethane-d₂ as the solvent at 110 °C.

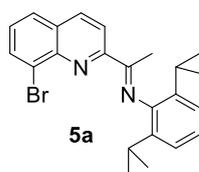
2. Preparation of PNN Ligands and Iron complexes

2.1. General procedure for the synthesis of the ligands:

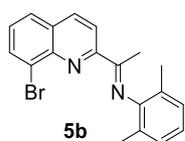


To a solution of 2-acetyl-8-bromoquinoline **4** (5.00 g, 20 mmol) in toluene (40 mL) was added arylamines (24 mmol). After the addition of *p*-toluenesulfonic acid (5 %), the solution was refluxed overnight with Dean-Stark head for the remove of water. Toluene was removed in vacuum and the residue was purified by flash column chromatography on silica gel to afford the product 8-bromo-2-iminoquinolines **5** as yellow solids.

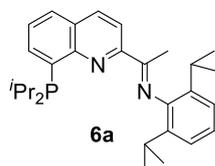
According to the literature², to an oven-dried re-sealable Schlenk tube was charged with Pd(OAc)₂ (16.8 mg, 0.075 mmol), DiPPF (37.6 mg, 0.090 mmol), NaO^tBu (173.0 mg, 1.8 mmol) and the 8-bromo-2-iminoquinolines **5** (1.5 mmol) The solution was stirred for 1 h at room temperature. Then the secondary phosphine (1.0 mmol) was added by syringe. The Schlenk tube was sealed with a Teflon valve, heated at 120 °C and stirred for 24 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the desired PNN ligands as yellow solids.



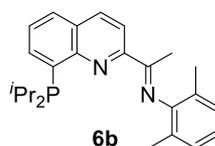
Yellow solid (0.81 g, 98%). ¹H NMR (400 MHz, CDCl₃) δ 8.60 (d, ³J_{H,H} = 8.4 Hz, 1H), 8.24 (d, ³J_{H,H} = 8.8 Hz, 1H), 8.10 (d, ³J_{H,H} = 7.2 Hz, 1H), 7.85 (d, ³J_{H,H} = 8.0 Hz, 1H), 7.45 (t, ³J_{H,H} = 8.0 Hz, 1H), 7.19 (d, ³J_{H,H} = 7.2 Hz, 2H), 7.15-7.09 (m, 1H), 2.77 (p, ³J_{H,H} = 6.8 Hz, 2H), 2.43 (s, 3H), 1.16 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 167.31, 156.50, 136.66, 135.52, 133.15, 130.02, 127.79, 127.38, 123.69, 122.99, 119.40, 28.30, 23.20, 22.84, 16.95. Anal. Calcd for C₂₃H₂₅BrN₂: C, 67.48; H, 6.16; N, 6.84. Found: C, 67.31; H, 6.15; N, 6.79.



Yellow solid (1.49 g, 92%). ^1H NMR (400 MHz, CDCl_3) δ 8.61 (d, $^3J_{\text{H,H}} = 8.8$ Hz, 1H), 8.23 (d, $^3J_{\text{H,H}} = 8.8$ Hz, 1H), 8.09 (m, 1H), 7.84 (m, 1H), 7.45 (t, $^3J_{\text{H,H}} = 8.0$ Hz, 1H), 7.10 (d, $^3J_{\text{H,H}} = 7.6$ Hz, 2H), 6.98 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 1H), 2.41 (s, 3H), 2.07 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.55, 156.48, 136.63, 133.15, 129.99, 127.89, 127.80, 127.37, 125.87, 125.15, 123.12, 119.37, 17.95, 16.29. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{BrN}_2$: C, 64.60; H, 4.85; N, 7.93. Found: C, 64.20; H, 5.05; N, 8.10.

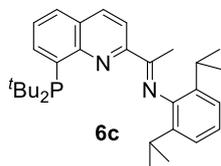


$i\text{PrPNN}^{i\text{Pr}}$ Ligand (**6a**). Yellow solid (225.0 mg, 85%). ^1H NMR (400 MHz, CDCl_3) δ 8.55 (d, $^3J_{\text{H,H}} = 8.4\text{Hz}$, 1H), 8.25 (d, $^3J_{\text{H,H}} = 8.8\text{Hz}$, 1H), 7.87 (m, 2H), 7.59 (t, $^3J_{\text{H,H}} = 8.0\text{Hz}$, 1H), 7.22-7.12 (m, 3H), 2.81 (m, CHMe_2 , 2H), 2.54 (m, PCHMe_2 , 2H), 2.43 (s, N=CMe , 3H), 1.22 (dd, $^3J_{\text{P,H}} = 13.2\text{Hz}$, $^3J_{\text{H,H}} = 6.8\text{Hz}$, PCHMe_2 , 6H), 1.19 (d, $^3J_{\text{H,H}} = 6.8\text{Hz}$, CHMe_2 , 12H), 1.08 (dd, $^3J_{\text{P,H}} = 13.2\text{Hz}$, $^3J_{\text{H,H}} = 6.8\text{Hz}$, PCHMe_2 , 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.86, 154.98, 146.74, 136.82, 135.73, 134.71, 134.63, 128.36, 126.88, 126.84, 123.69, 123.09, 118.63, 28.42, 23.41, 23.34, 23.27, 22.99, 20.55, 20.42, 20.24, 20.08, 17.68. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 4.94. Anal. Calcd for $\text{C}_{29}\text{H}_{39}\text{N}_2\text{P}$: C, 77.99; H, 8.80; N, 6.27. Found: C, 77.43; H, 8.79; N, 5.73.

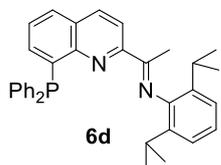


$i\text{PrPNN}^{\text{Me}}$ Ligand (**6b**). Yellow solid (450.0 mg, 74%). ^1H NMR (400 MHz, CDCl_3) δ 8.57 (d, $^3J_{\text{H,H}} = 8.4\text{Hz}$, 1H), 8.24 (d, $^3J_{\text{H,H}} = 8.8\text{Hz}$, 1H), 7.89-7.83 (m, 2H), 7.59 (t, $^3J_{\text{H,H}} = 7.6\text{Hz}$, 1H), 7.12 (d, $^3J_{\text{H,H}} = 7.6\text{Hz}$, 2H), 6.97 (t, $^3J_{\text{H,H}} = 7.6\text{Hz}$, 1H), 2.54 (m, PCHMe_2 , 2H), 2.40 (s, N=CMe , 3H), 2.08 (s, PhMe , 6H), 1.22 (dd, $^3J_{\text{P,H}} = 13.2\text{Hz}$, $^3J_{\text{H,H}} = 6.8\text{Hz}$, PCHMe_2 , 6H), 1.07 (dd, $^3J_{\text{P,H}} = 13.2\text{Hz}$, $^3J_{\text{H,H}} = 6.8\text{Hz}$, PCHMe_2 , 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.90, 154.79, 148.90, 136.70, 134.70, 134.62, 128.91, 128.90, 128.30, 127.90, 126.80, 126.76, 125.28, 123.04, 118.47, 23.32, 23.19,

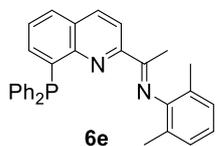
20.45, 20.32, 20.18, 20.02, 18.02, 16.90. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 5.13. Anal. Calcd for $\text{C}_{25}\text{H}_{31}\text{N}_2\text{P}$: C, 76.89; H, 8.00; N, 7.17. Found: C, 76.99; H, 8.11; N, 7.19.



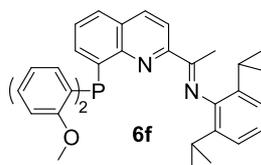
$t\text{BuPNN}^{i\text{Pr}}$ Ligand (**6c**). Yellow solid (240.0 mg, 84%). ^1H NMR (400 MHz, CDCl_3) δ 8.53 (d, $^3J_{\text{H,H}} = 8.4\text{Hz}$, 1H), 8.22 (m, 2H), 7.88 (d, $^3J_{\text{H,H}} = 8.0\text{Hz}$, 1H), 7.60 (t, $^3J_{\text{H,H}} = 7.6\text{Hz}$, 1H), 7.22-7.12 (m, 3H), 2.81 (m, CHMe_2 , 2H), 2.45 (s, $\text{N}=\text{CMe}$, 3H), 1.31 (d, $^3J_{\text{H,H}} = 11.2\text{Hz}$, PCMe_3 , 18H), 1.19 (d, $^3J_{\text{H,H}} = 6.8\text{Hz}$, CHMe_2 , 12H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.46, 155.00, 146.90, 139.86, 139.55, 136.60, 136.58, 136.55, 135.78, 128.89, 128.87, 128.60, 126.14, 123.59, 123.07, 118.33, 118.31, 32.86, 32.59, 31.16, 31.01, 28.40, 23.50, 23.39, 23.03, 17.71. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 16.90. Anal. Calcd for $\text{C}_{31}\text{H}_{43}\text{N}_2\text{P}$: C, 78.44; H, 9.13; N, 5.90. Found: C, 78.71; H, 9.36; N, 5.96.



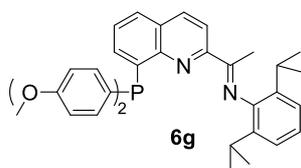
$\text{PhPNN}^{i\text{Pr}}$ Ligand (**6d**). Yellow solid (378.8 mg, 92%). ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, $^3J_{\text{H,H}} = 8.8\text{Hz}$, 1H), 8.24 (d, $^3J_{\text{H,H}} = 8.4\text{Hz}$, 1H), 7.86 (d, $^3J_{\text{H,H}} = 8.0\text{Hz}$, 1H), 7.47 (t, $^3J_{\text{H,H}} = 7.6\text{Hz}$, 1H), 7.40 (m, 4H), 7.32 (m, 6H), 7.13 (m, 3H), 7.10 (m, 1H), 2.64 (m, CHMe_2 , 2H), 1.86 (s, $\text{N}=\text{CMe}$, 3H), 1.12 (d, $^3J_{\text{H,H}} = 6.8\text{Hz}$, CHMe_2 , 6H), 1.06 (d, $^3J_{\text{H,H}} = 7.2\text{Hz}$, CHMe_2 , 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.65, 154.42, 146.49, 137.17, 137.08, 136.28, 136.26, 135.62, 134.43, 134.22, 133.65, 128.54, 128.33, 128.26, 128.06, 127.42, 123.48, 122.86, 118.71, 28.13, 23.15, 22.81, 16.74. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ -11.79. Anal. Calcd for $\text{C}_{35}\text{H}_{35}\text{N}_2\text{P}$: C, 81.68; H, 6.85; N, 5.44. Found: C, 81.19; H, 6.70; N, 5.65.



PhPNN^{Me} Ligand (**6e**). Yellow solid (510.0 mg, 84%). ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, ³J_{H,H} = 8.4 Hz, 1H), 8.14 (d, ³J_{H,H} = 8.4 Hz, 1H), 7.76 (d, ³J_{H,H} = 8.4 Hz, 1H), 7.38 (t, ³J_{H,H} = 7.6 Hz, 1H), 7.33-7.28 (m, 4H), 7.24 (m, 6H), 7.04 (m, 1H), 6.95 (d, ³J_{H,H} = 7.6 Hz, 2H), 6.83 (t, ³J_{H,H} = 7.6 Hz, 1H), 1.86 (s, 6H), 1.76 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 154.40, 137.17, 137.08, 136.34, 136.32, 134.43, 134.22, 133.75, 133.74, 128.58, 128.38, 128.30, 128.12, 127.77, 127.49, 125.38, 123.04, 118.74, 67.98, 25.61, 17.92, 16.08. ³¹P{¹H}NMR (CDCl₃, 162 MHz) δ -12.02. HRMS-ESI (*m/z*): Calcd for [(C₃₁H₂₇N₂P+H)⁺], 459.1985; found: 459.1985.

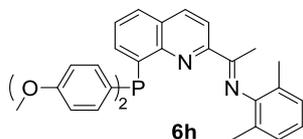


o-MeO-PhPNN^{*i*Pr} Ligand (**6f**). Yellow solid (480.0 mg, 74%). ¹H NMR (400 MHz, CDCl₃) δ 8.45 (d, ³J_{H,H} = 8.8Hz, 1H), 8.22 (d, ³J_{H,H} = 8.8Hz, 1H), 7.83 (d, ³J_{H,H} = 8.0Hz, 1H), 7.47 (t, ³J_{H,H} = 7.6Hz, 1H), 7.32 (m, 2H), 7.25 (m, 1H), 7.15 (m, 2H), 7.11 (m, 1H), 6.93 (m, 2H), 6.81 (m, 4H), 3.77 (s, PhOMe, 6H), 2.68 (m, CHMe₂, 2H), 1.90 (s, N=CMe, 3H), 1.15 (d, ³J_{H,H} = 6.8Hz, CHMe₂, 6H), 1.09 (d, ³J_{H,H} = 6.8Hz, CHMe₂, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 161.94, 161.77, 154.03, 136.21, 136.19, 135.85, 135.13, 133.54, 130.07, 128.38, 127.67, 127.47, 125.34, 125.22, 123.53, 122.95, 120.97, 118.31, 110.20, 110.18, 55.75, 28.26, 23.27, 22.98, 16.68. ³¹P{¹H}NMR (CDCl₃, 162 MHz) δ -34.86. Anal. Calcd for C₃₇H₃₉N₂O₂P: C, 77.33; H, 6.84; N, 4.87. Found: C, 77.30; H, 6.94; N, 4.80.

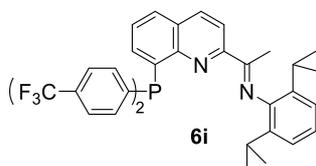


p-MeO-PhPNN^{*i*Pr} Ligand (**6g**). Yellow solid (560.0 mg, 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, ³J_{H,H} = 8.0Hz, 1H), 8.23 (d, ³J_{H,H} = 8.8Hz, 1H), 7.83 (d, ³J_{H,H} = 8.0Hz, 1H), 7.46 (t, ³J_{H,H} = 8.0Hz, 1H), 7.31 (m, 4H), 7.15-7.06 (m, 4H), 6.86 (d, 4H), 3.78 (s, PhOMe, 6H), 2.65 (m, CHMe₂, 2H), 1.91 (s, N=CMe, 3H), 1.12 (d, ³J_{H,H} = 6.8Hz, CHMe₂, 6H), 1.06 (d, ³J_{H,H} = 6.8Hz, CHMe₂, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 167.75, 160.02, 154.34, 146.53, 136.24, 135.75, 135.66, 135.53, 133.49, 128.39, 128.33, 127.84, 127.36, 123.47, 122.87, 118.58, 114.00, 113.92, 77.20, 55.10,

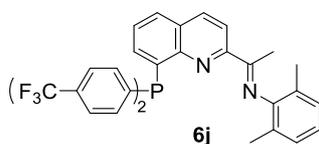
29.69, 28.14, 23.16, 22.76, 22.69, 16.85. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ -14.16. Anal. Calcd for $\text{C}_{37}\text{H}_{39}\text{N}_2\text{O}_2\text{P}$: C, 77.33; H, 6.84; N, 4.87. Found: C, 77.05; H, 6.88; N, 4.84.



p-MeO-PhPNN^{Me} Ligand (**6h**). Yellow solid (530.0 mg, 77%). ^1H NMR (400 MHz, CDCl_3) δ 8.46 (d, $^3J_{\text{H,H}} = 8.8$ Hz, 1H), 8.21 (d, $^3J_{\text{H,H}} = 8.8$ Hz, 1H), 7.82 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 1H), 7.46 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 1H), 7.33 (t, $^3J_{\text{H,H}} = 8.0$ Hz, 4H), 7.14 (m, 1H), 7.04 (d, $^3J_{\text{H,H}} = 7.6$ Hz, 2H), 6.92 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 1H), 6.86 (d, $^3J_{\text{H,H}} = 8.4$ Hz, 4H), 3.79 (s, 6H), 1.96 (s, 6H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.04, 154.39, 136.28, 135.76, 135.54, 133.58, 128.39, 128.33, 128.30, 127.91, 127.78, 127.41, 125.38, 123.00, 118.62, 114.04, 113.96, 55.15, 17.93, 16.19. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ -15.42. HRMS-ESI (m/z): Calcd for $[(\text{C}_{33}\text{H}_{31}\text{N}_2\text{O}_2\text{P}+\text{H})^+]$, 519.2196; found: 519.2196.



p-CF₃-PhPNN^{iPr} Ligand (**6i**). Yellow solid (690.0 mg, 77%). ^1H NMR (400 MHz, CDCl_3) δ 8.57 (d, $^3J_{\text{H,H}} = 8.8$ Hz, 1H), 8.30 (d, $^3J_{\text{H,H}} = 8.8$ Hz, 1H), 7.95 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 1H), 7.62 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 4H), 7.56-7.49 (m, 5H), 7.17-7.08 (m, 4H), 2.64 (m, CHMe₂, 2H), 1.87 (s, N=CMe, 3H), 1.14 (d, $^3J_{\text{H,H}} = 6.8$ Hz, CHMe₂, 6H), 1.06 (d, $^3J_{\text{H,H}} = 6.8$ Hz, CHMe₂, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.34, 146.45, 141.82, 141.69, 137.69, 137.58, 136.71, 136.69, 135.73, 134.78, 134.57, 133.88, 133.86, 131.29, 130.97, 129.08, 128.60, 127.76, 125.48, 125.40, 125.37, 125.33, 125.29, 125.26, 123.88, 123.12, 119.35, 28.39, 23.30, 22.83, 16.84. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ -11.39; ^{19}F NMR (CDCl_3 , 376 MHz): δ 77.02. Anal. Calcd for $\text{C}_{37}\text{H}_{33}\text{F}_6\text{N}_2\text{P}$: C, 68.30; H, 5.11; N, 4.31. Found: C, 68.09; H, 5.12; N, 4.55.

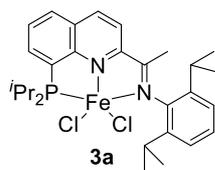


p-CF₃-PhPNN^{Me} Ligand (**6j**). Yellow solid (210.0 mg, 60%). ¹H NMR (400 MHz, CDCl₃) δ 8.51 (d, ³J_{H,H} = 8.8 Hz, 1H), 8.27 (d, ³J_{H,H} = 8.4 Hz, 1H), 7.92 (d, ³J_{H,H} = 8.0 Hz, 1H), 7.60 (d, ³J_{H,H} = 8.0 Hz, 4H), 7.55-7.46 (m, 5H), 7.12 (m, 1H), 7.05 (d, ³J_{H,H} = 7.2 Hz, 2H), 6.93 (t, ³J_{H,H} = 7.2 Hz, 1H), 1.94 (s, 6H), 1.83 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.33, 154.85, 148.51, 141.68, 141.56, 137.49, 137.39, 136.55, 136.53, 134.60, 134.39, 133.78, 133.77, 131.11, 130.79, 128.96, 128.44, 128.42, 127.84, 127.59, 125.32, 125.30, 125.26, 125.22, 125.19, 125.15, 125.11, 123.14, 119.19, 17.78, 15.98. ³¹P{¹H}NMR (CDCl₃, 162 MHz) δ -12.51; ¹⁹F NMR (CDCl₃, 376 MHz): δ -62.82. HRMS-ESI (*m/z*): Calcd for [(C₃₃H₂₅F₆N₂P+H)⁺], 595.1732; found: 595.1733.

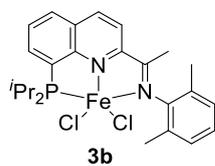
2.2. General Procedure for Preparation of Iron Complexes:

In an argon-filled glovebox, FeCl₂ (0.254 g, 2 mmol, 1 equiv) and THF (50 mL) were added to a 100 mL Schlenk tube. After stirring for 30 min, a solution of PNN ligands (2.2 mmol, 1.1 equiv) in THF (10 mL) was added. The orange solution turned to dark-blue immediately. Being stirred for 24 h, the resulting suspension was filtered. The solid was washed with 10 mL ether and dried under vacuum to afford the title compound as blue solids.

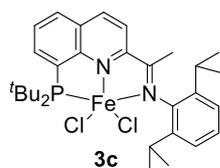
Magnetic Susceptibility of those iron complexes was studied using the Evans' method³, by preparing solutions of known concentration of the complexes (approximately 5×10^{-3} M) in d²-dichloromethane: cyclohexane (v: v = 1: 1) mixture in a NMR tube. A portion of d²-dichloromethane: cyclohexane mixture was sealed in a melting point capillary tube and dropped into the NMR tube. The chemical shift difference between the inner and the outer tubes was recorded and used to calculate the magnetic susceptibility.



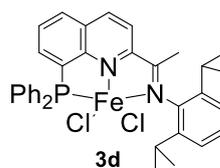
(ⁱPr₂PNNⁱPr)FeCl₂ Complex (**3a**). Blue solid (120.0 mg, 88%). Anal. Calcd for C₂₉H₃₉Cl₂FeN₂P: C, 60.75; H, 6.86; N, 4.89. Found: C, 61.20; H, 7.04; N, 4.61. μ_{eff} (Evans' method, CDCl₃, 25 °C) = 5.19 μ_{B} .



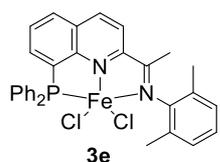
(ⁱPr₂PNN^{Me})FeCl₂ Complex (**3b**). Blue solid (107.1 mg, 83%). Anal. Calcd for C₂₅H₃₁Cl₂FeN₂P: C, 58.05; H, 6.04; N, 5.42. Found: C, 57.71; H, 6.03; N, 5.42. μ_{eff} (Evans' method, CDCl₃, 25 °C) = 5.21 μ_{B} .



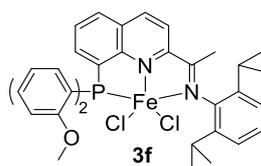
(*t*BuPNN^{*i*Pr})FeCl₂ Complex (**3c**). Blue solid (157.0 mg, 87%). Anal. Calcd for C₃₁H₄₃Cl₂FeN₂P: C, 61.91; H, 7.21; N, 4.66. Found: C, 62.31; H, 7.36; N, 4.78. μ_{eff} (Evans' method, CDCl₃, 25 °C) = 5.11 μ_{B} .



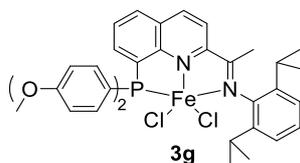
(PhPNN^{*i*Pr})FeCl₂ Complex (**3d**). Blue solid (240.0 mg, 92%). Anal. Calcd for C₃₅H₃₅Cl₂FeN₂P: C, 65.54; H, 5.50; N, 4.37. Found: C, 65.74; H, 5.71; N, 4.02. μ_{eff} (Evans' method, CD₂Cl₂, 25 °C) = 5.17 μ_{B} .



(PhPNN^{Me})FeCl₂ Complex (**3e**). Blue solid (156.2 mg, 83%). Anal. Calcd for C₃₁H₂₇Cl₂FeN₂P: C, 63.62; H, 4.65; N, 4.79. Found: C, 63.14; H, 5.03; N, 4.60. μ_{eff} (Evans' method, CD₂Cl₂, 25 °C) = 5.21 μ_{B} .

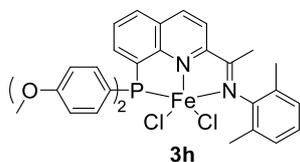


(*o*-MeO-PhPNN^{*i*Pr})FeCl₂ Complex (**3f**). Blue solid (160.0 mg, 93%). Anal. Calcd for C₃₇H₃₉Cl₂FeN₂O₂P: C, 63.35; H, 5.60; N, 3.99. Found: C, 63.63; H, 5.38; N, 3.82. μ_{eff} (Evans' method, CD₂Cl₂, 25 °C) = 5.06 μ_{B} .

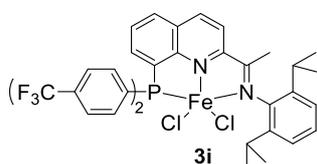


(*p*-MeO-PhPNN^{*i*Pr})FeCl₂ Complex (**3g**). Blue solid (109.7 mg, 85%). Anal. Calcd for

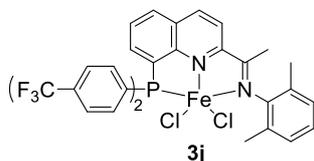
$C_{37}H_{39}Cl_2FeN_2O_2P$: C, 63.35; H, 5.60; N, 3.99. Found: C, 63.17; H, 5.66; N, 3.89. μ_{eff} (Evans' method, $CDCl_3$, 25 °C) = 5.23 μ_B .



(*p*-MeO-Ph) $PNN^{Me}FeCl_2$ Complex (**3h**). Blue solid (170.0 mg, 90%). Anal. Calcd for $C_{33}H_{31}Cl_2FeN_2O_2P$: C, 61.42; H, 4.84; N, 4.34. Found: C, 60.70; H, 5.27; N, 4.58. μ_{eff} (Evans' method, $CDCl_3$, 25 °C) = 5.40 μ_B .



(*p*-CF₃-Ph) $PNN^{iPr}FeCl_2$ Complex (**3i**). Blue solid (124.1 mg, 86%). Anal. Calcd for $C_{37}H_{33}Cl_2F_6FeN_2P$: C, 57.17; H, 4.28; N, 3.60. Found: C, 57.49; H, 4.64; N, 3.20. μ_{eff} (Evans' method, CD_2Cl_2 , 25 °C) = 5.36 μ_B .



(*p*-CF₃-Ph) $PNN^{Me}FeCl_2$ Complex (**3j**). Blue solid (94.3 mg, 96%). Anal. Calcd for $C_{33}H_{25}Cl_2F_6FeN_2P$: C, 54.95; H, 3.49; N, 3.88. Found: C, 54.63; H, 3.86; N, 4.06. μ_{eff} (Evans' method, CD_2Cl_2 , 25 °C) = 5.27 μ_B .

2.3. Crystallographic data for Fe complex **3a**.

Table S1-1. Selected bond length for **3a**

Selected bond length	Distance (Å)
Fe(1)-P(1)	2.4941(12)
Fe(1)-N(1)	2.206(3)
Fe(1)-N(2)	2.187(3)
Fe(1)-Cl(1)	2.2823(11)
Fe(1)-Cl(2)	2.3409(11)

Table S1-2. Selected bond angles for **3j**

Selected bond angles	(Deg)
N(1)-Fe(1)-P(1)	76.76(7)
N(1)-Fe(1)-N(2)	73.04(10)
P(1)-Fe(1)-N(2)	144.93(8)
N(1)-Fe(1)-Cl(1)	144.51(8)
N(1)-Fe(1)-Cl(2)	100.61(7)
Cl(1)-Fe(1)-Cl(2)	114.84(4)

Table S2. Crystal data and structure refinement for **3a**

Identification code	mo_dm15495_0m	
Empirical formula	C ₂₉ H ₃₉ Cl ₂ Fe N ₂ P	
Formula weight	573.34	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P 4 ₂ /n	
Unit cell dimensions	a = 26.507(3) Å	α = 90°.
	b = 26.507(3) Å	β = 90°.
	c = 8.7463(9) Å	γ = 90°.
Volume	6145.1(14) Å ³	
Z	8	
Density (calculated)	1.239 Mg/m ³	
Absorption coefficient	0.736 mm ⁻¹	
F(000)	2416	
Crystal size	0.25 x 0.22 x 0.18 mm ³	
Theta range for data collection	1.536 to 30.555°.	
Index ranges	-37 ≤ h ≤ 36, -36 ≤ k ≤ 37, -12 ≤ l ≤ 12	
Reflections collected	62641	
Independent reflections	9413 [R(int) = 0.0827]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6316	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9413 / 39 / 325	
Goodness-of-fit on F ²	1.052	
Final R indices [I > 2σ(I)]	R1 = 0.0734, wR2 = 0.1883	
R indices (all data)	R1 = 0.1422, wR2 = 0.2115	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.985 and -0.474 e.Å ⁻³	

3. Procedure for Polymerization of Ethylene

3.1. General Procedure for Ethylene Polymerization at 1 atm:

Freshly distilled toluene (100 mL) was added to a 200mL Schlenk flask and saturated with ethylene at polymerization temperature. Modified-methylaluminoxane (MMAO) was syringed into the flask in sequence, and the mixture was stirred for 10 min. Then the precatalyst solution in toluene was injected via a syringe. The polymerization was carried out for the desired time and then quenched with acidified ethanol and poured into a large amount of acidified ethanol (300 mL, 10% HCl (v/v) in ethanol). The precipitated polymer was collected, washed with ethanol, and then dried at 60 °C under reduced pressure until a constant weight.

3.2. General Procedure for High-Pressure Ethylene Polymerizations:

A 300 mL autoclave with a magnetic stirrer was heated under vacuum to 110 °C and then was cooled to the desired reaction temperature and back-filled with ethylene. The autoclave was charged with toluene (100 mL) and modified-methylaluminoxane (MMAO) and was stirred for 10 min. In an argon glovebox, the precatalyst was weighed and dissolved in 10 mL of toluene. Then the precatalyst solution in toluene was injected via a syringe. The autoclave was sealed and pressurized to the desired level. After the prescribed reaction time, the reactor was vented and the mixture was poured into a large amount of acidified ethanol (300 mL, 10% HCl (v/v) in ethanol). The precipitated polymer was collected, washed with ethanol, and then dried at 60 °C under reduced pressure until a constant weight.

NMR spectroscopy was used to analyze the polyethylene produced by the Fe catalyst systems. The polyethylene is similar to those produced by the 2,6-bis(imino)pyridyl Fe(II) catalysts. NMR studies show that the polyethylenes are highly linear and contain only ca. 3~11 branches per 1000 C, most of which are methyl ($1B_1 = 19.9$) branches. Trace amounts of ethyl ($1B_2 = 11.1$) and propyl ($2B_3 = 20.3$) branches were also detected by ^{13}C NMR.⁴

The total branching of polyethylene was determined by ^1H NMR spectroscopy, as shown in Table S3.

Table S3. Results of ethylene polymerization using iron complexes 3a-3j^a

Entry	Complex	Yield (g)	Activity ^b	$M_w (M_n)^c$	\bar{D}^c	M_p^c	T_m (°C)	Branches /1000 C ^g
1	(ⁱ PrPNN ⁱ Pr)FeCl ₂ , 3a	4.06	4.1×10 ⁶	1820 (840)	2.2	700	122 ^d	3
2	(ⁱ PrPNN ^{Me})FeCl ₂ , 3b	2.75	2.8×10 ⁶	970 (600)	1.6	560	119 ^d	7
3	(^t BuPNN ⁱ Pr)FeCl ₂ , 3c	2.15	2.2×10 ⁶	- (3530) ^e	-	-	127	4
4	(^{Ph} PNN ⁱ Pr)FeCl ₂ , 3d	1.80	1.8×10 ⁶	20600 (1090)	18.8	1100	126	9
5	(^{Ph} PNN ^{Me})FeCl ₂ , 3e	1.64	1.6×10 ⁶	3300 (810)	4.1	570	121 ^d	6
6	(^p -MeOC ₆ H ₄ PNN ⁱ Pr)FeCl ₂ , 3f	3.21	3.2×10 ⁶	- (2690) ^e	-	-	129	4
7	(^p -MeOC ₆ H ₄ PNN ^{Me})FeCl ₂ , 3g	1.68	1.7×10 ⁶	6070 (860)	7.1	570	123 ^d	11
8	(^p -CF ₃ C ₆ H ₄ PNN ⁱ Pr)FeCl ₂ , 3h	2.05	2.1×10 ⁶	- (2920) ^e	-	-	127	8
9	(^p -CF ₃ C ₆ H ₄ PNN ^{Me})FeCl ₂ , 3i	3.40	3.4×10 ⁶	5450 (830)	6.6	580	121 ^d	5
10	(^o -MeOC ₆ H ₄ PNN ⁱ Pr)FeCl ₂ , 3j	2.71	2.7×10 ⁶	5500 (940)	5.9 ^f	5000	128	5

^a Conditions: 2 μmol of a complex in 100 mL toluene, 1 atm ethylene, 2000 equiv. of MMAO, 20 °C, 0.5 h. Yields are average of two runs. ^b In units of g PE/mol Fe·h. ^c Molecular weight distribution (MWD, or \bar{D}) as determined by GPC analysis unless otherwise noted. ^d Very broad melting transition. ^e M_n was determined by end group analysis using ¹³C NMR spectroscopy because the sample was unsuitable to GPC analysis due to its limited solubility. ^f Bimodal MW distribution. ^g Total branching was determined by ¹H NMR spectroscopy

¹³C NMR end group analysis reveals unsaturated end group (vinyl end group) in addition to saturated end group. The ratio of vinyl end group/methyl end group depends on reaction conditions (such as MMAO concentration, reaction time, ethylene pressure) and precatalyst. For those reactions with low MMAO concentration, long reaction, or high ethylene, the ratio is higher (Figures S1, S2 and S3); and especially for the reaction under 500 psi, the ratio is approximately 1:1, consistent with one saturated chain end and one unsaturated chain end (Figure S3). For the most steric bulky complexes **3c**, the vinyl groups have completely gone, probably because it's impossible for β-H transfer to metal or monomer. The resonances at 39.6 ppm, 28.4 ppm, 27.8 ppm, and 22.9 ppm are attributed to the chain transfer to MMAO, probably ended with the isopropyl group.

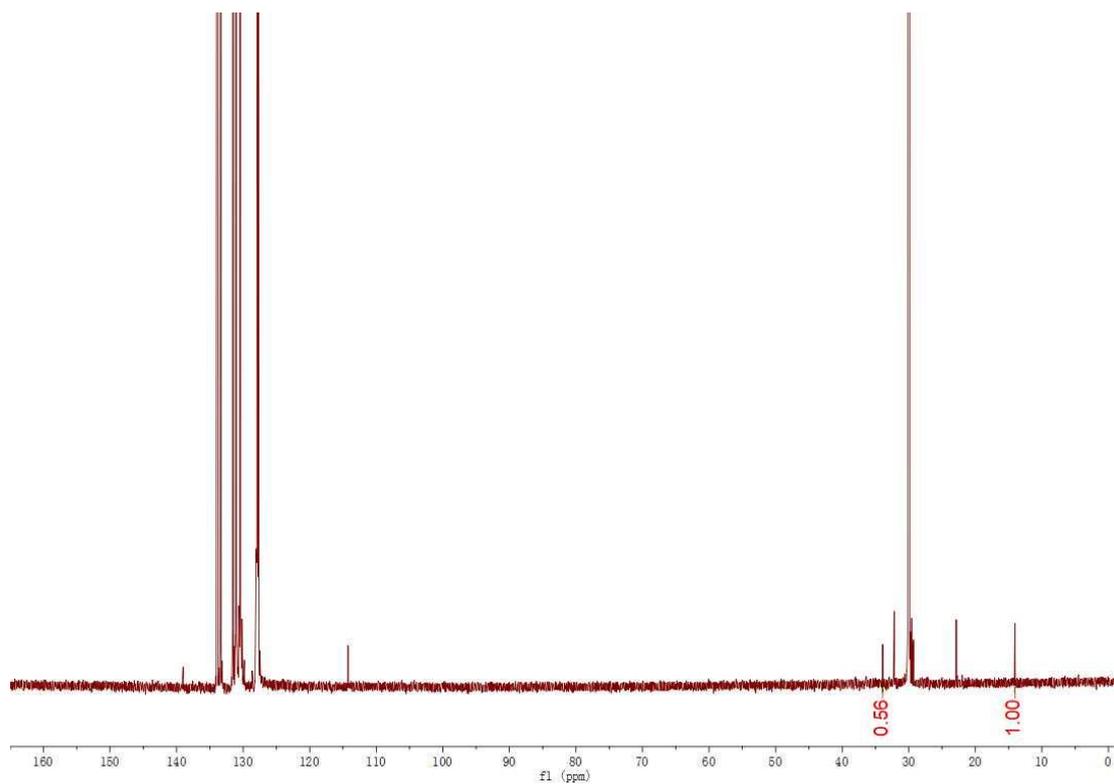


Figure S1. ^{13}C NMR (CD_2Cl_4 , $110\text{ }^\circ\text{C}$) of polyethylene obtained in entry 15, Table 1. At 200 equiv of MMAO, a broad unimodal molecular weight distribution is observed, centered at $12800(M_p)$, and the ratio of vinyl end group/methyl end group is 0.56:1.00.

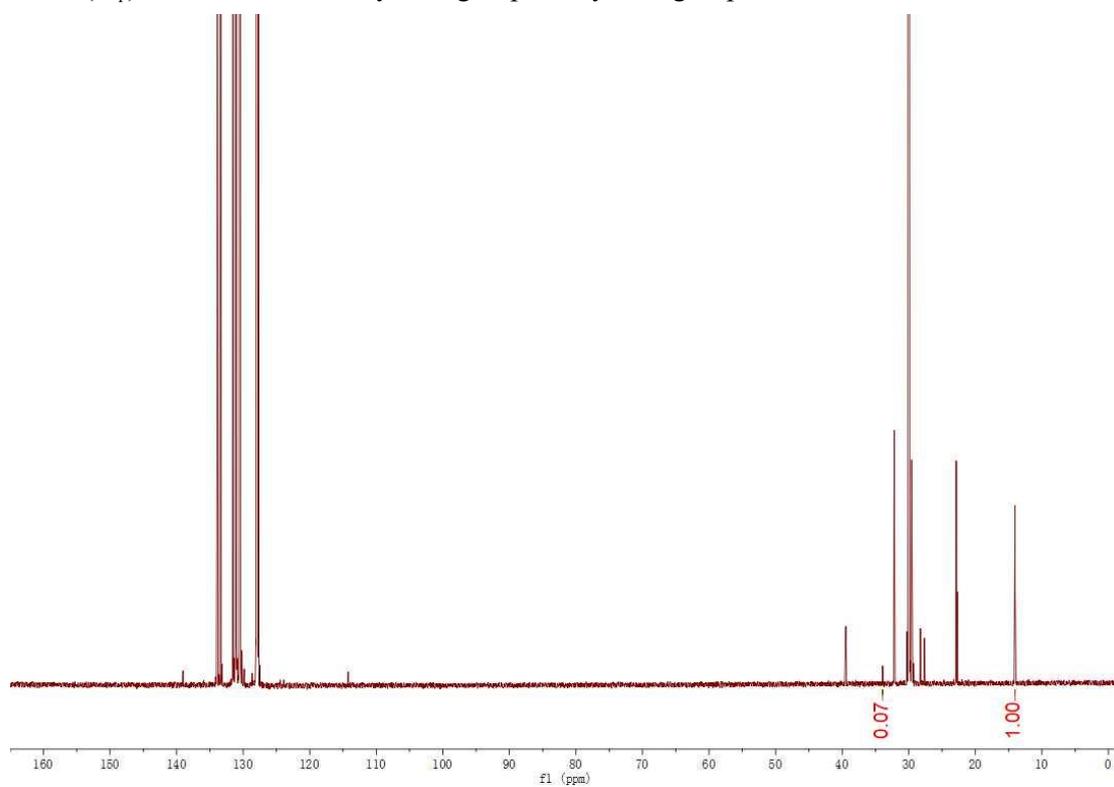


Figure S2. ^{13}C NMR (CD_2Cl_4 , $110\text{ }^\circ\text{C}$) of polyethylene obtained in entry 17, Table 1. At 4000 equiv of MMAO, unimodal molecular weight distributions appear again, with M_p at much lower 640, and the ratio of vinyl end group/methyl end group is 0.07:1.00.

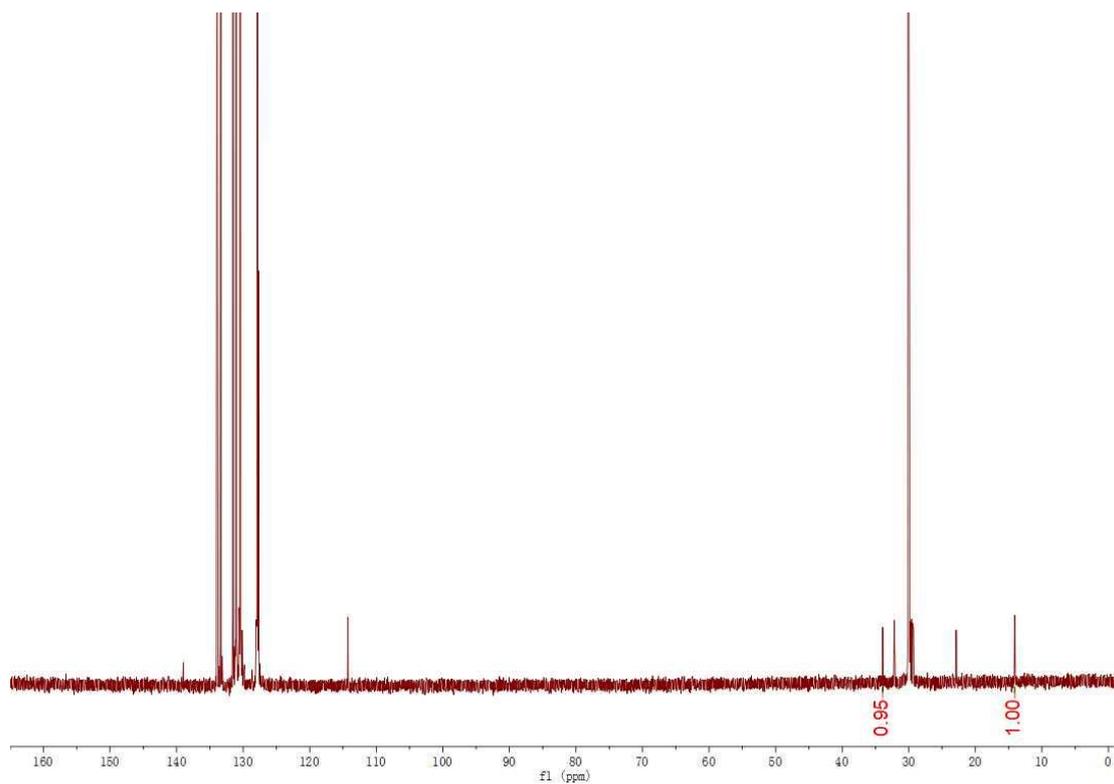


Figure S3. ^{13}C NMR (CD_2Cl_4 , $110\text{ }^\circ\text{C}$) of polyethylene obtained in entry 12, Table 1. Under 500 psi ethylene, the ratio of vinyl end group/methyl end group being approximately 1:1, consistent with one saturated chain end and one unsaturated chain end.

3.3. GPC traces of polyethylene

MW Averages

Mp: 698 Mn: 839 Mv: 1513 Mw: 1819
Mz: 8 278 Mz+1:2 1082 PD:2 .1681

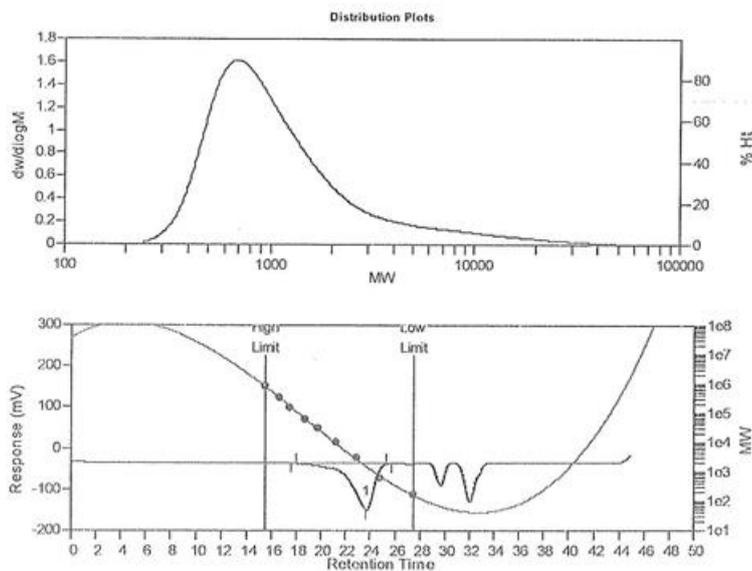


Figure S4. GPC trace of polyethylene obtained in entry 1, Table 1.

MW Averages

Mp: 564 Mn: 600 Mv: 865 Mw: 973
Mz:3 099 Mz+1:8 379 PD:1 .6217

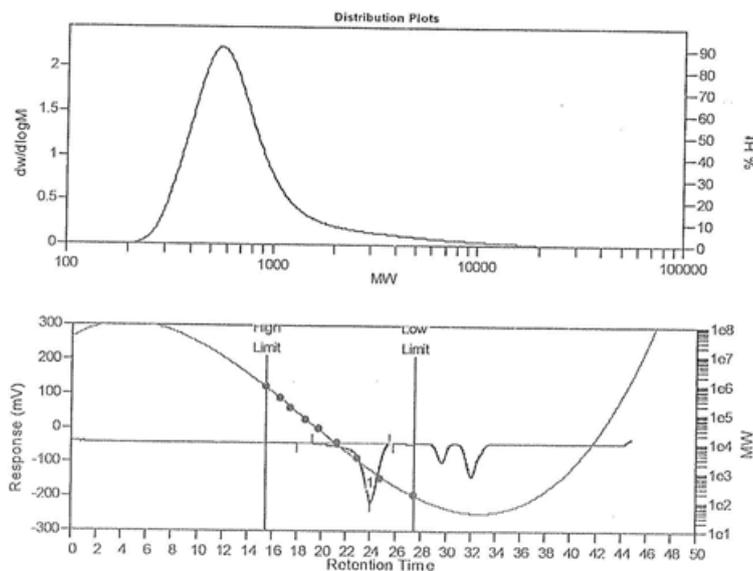


Figure S5. GPC trace of polyethylene obtained in entry 2, Table 1.

MW Averages

Mp:1 109

Mn:1 094

Mv: 12001

Mw: 20557

Mz:2 14486

Mz+1:3 65283

PD:1 8.7907

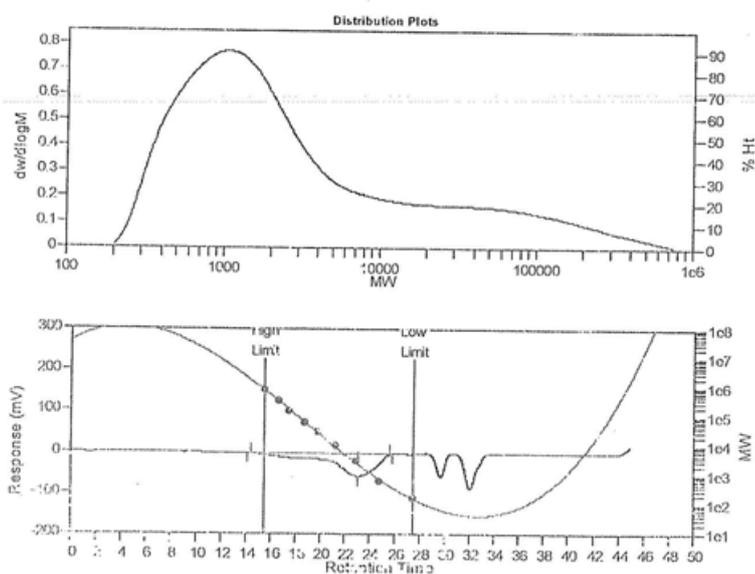


Figure S6. GPC trace of polyethylene obtained in entry 4, Table 1.

MW Averages

Mp: 572

Mn: 813

Mv: 2307

Mw: 3289

Mz: 37908

Mz+1: 102945

PD: 4.0455

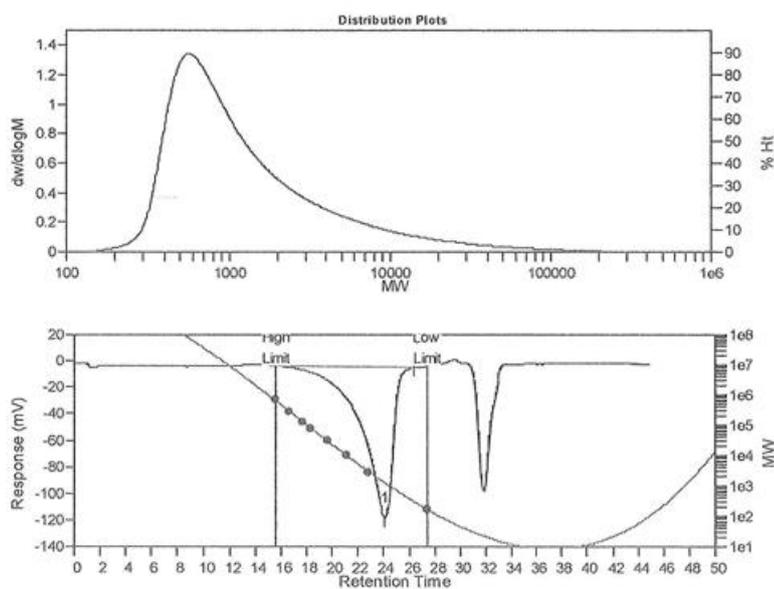


Figure S7. GPC trace of polyethylene obtained in entry 5, Table 1.

MW Averages

Mp: 572 Mn: 860 Mv: 3644 Mw: 6070
Mz: 115555 Mz+1: 265804 PD: 7.0581

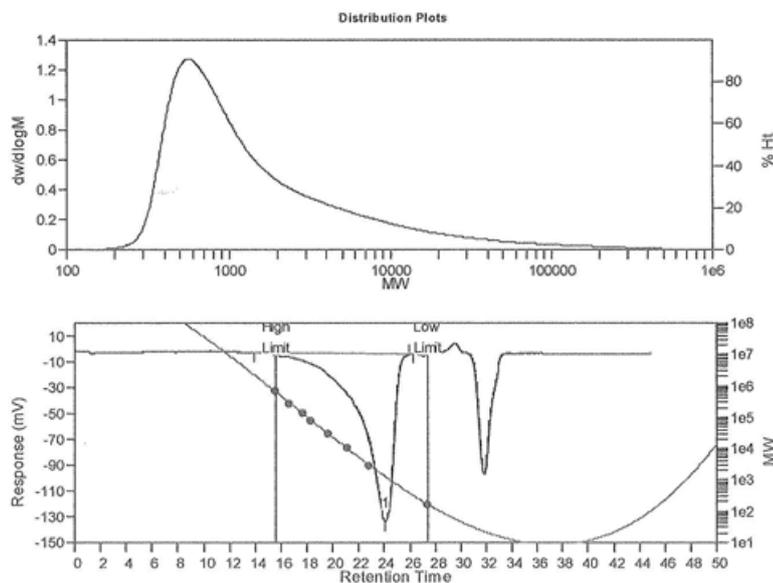


Figure S8. GPC trace of polyethylene obtained in entry 7, Table 1.

MW Averages

Mp: 584 Mn: 831 Mv: 3239 Mw: 5455
Mz: 120829 Mz+1: 281777 PD: 6.5644

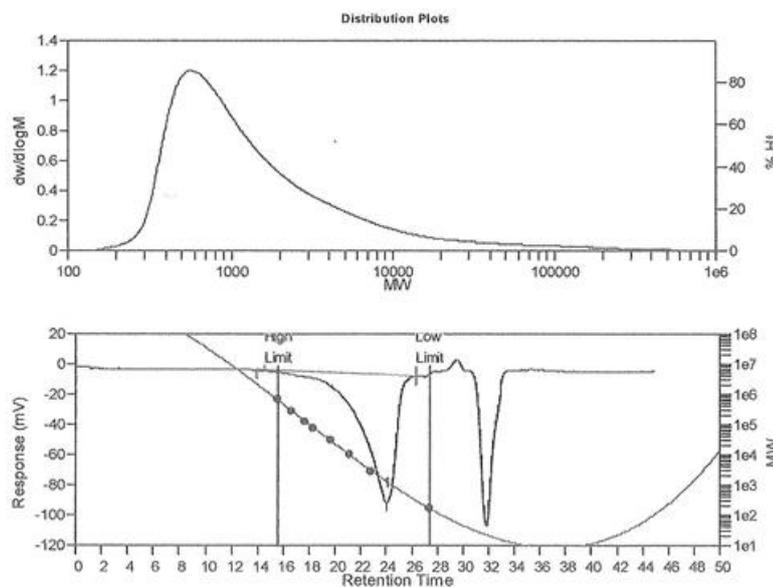


Figure S9. GPC trace of polyethylene obtained in entry 9, Table 1.

MW Averages

Mp: 5 020

Mn: 936

Mv: 4575

Mw: 5533

Mz: 1 9150

Mz+1: 4 6524

PD: 5.9113

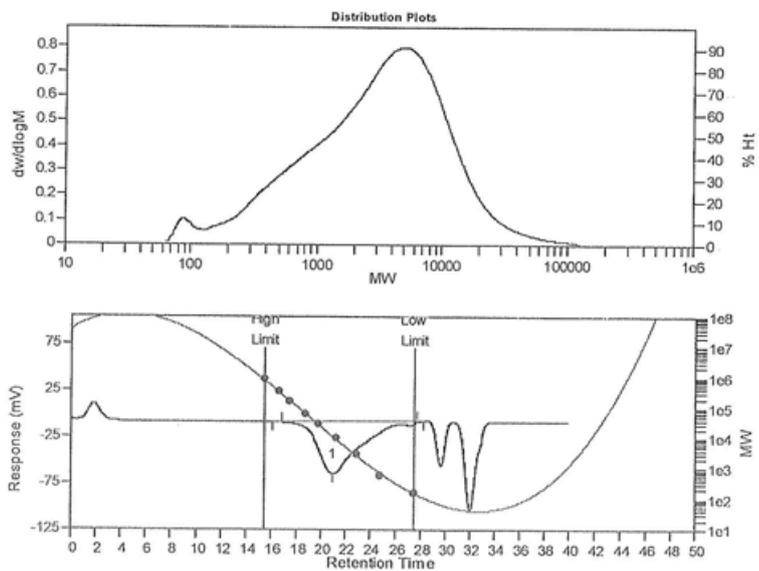


Figure S10. GPC trace of polyethylene obtained in entry 10, Table 1.

MW Averages

Mp: 765

Mn: 996

Mv: 2104

Mw: 2487

Mz: 7776

Mz+1: 15524

PD: 2.4970

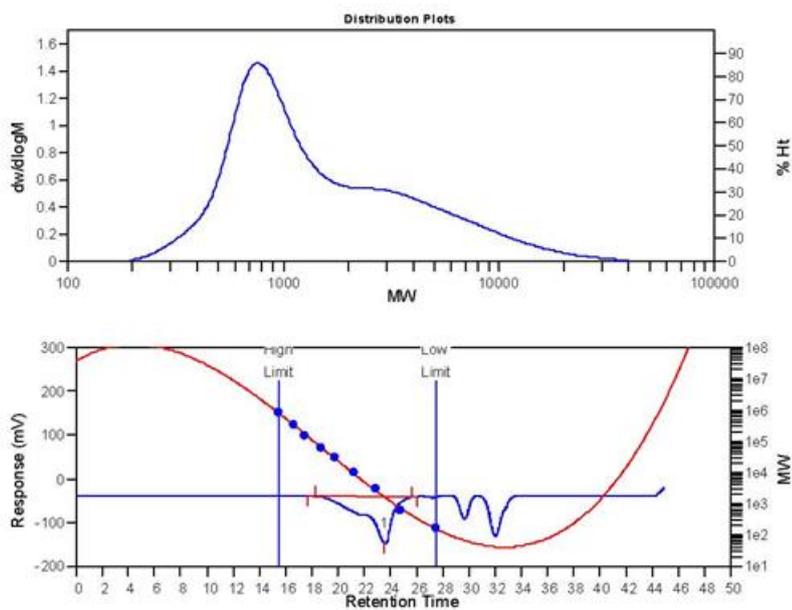


Figure S11. GPC trace of polyethylene obtained in entry 11, Table 1.

MW Averages

Mp: 675

Mn: 610

Mv: 823

Mw: 904

Mz: 2612

Mz+1: 8291

PD: 1.4820

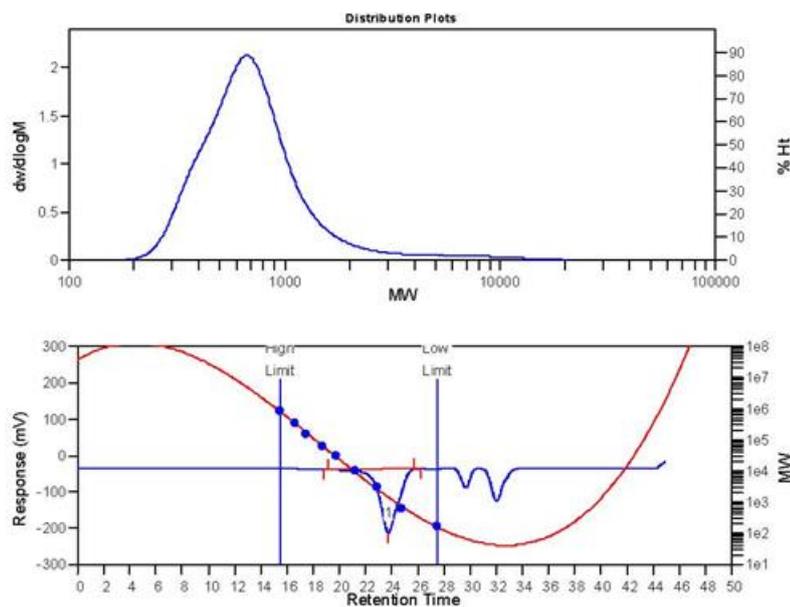


Figure S12. GPC trace of polyethylene obtained in entry 12, Table 1.

MW Averages

Mp: 6 644

Mn: 2 775

Mv: 7 051

Mw: 8 005

Mz: 1 8706

Mz+1: 3 5775

PD: 2 .8847

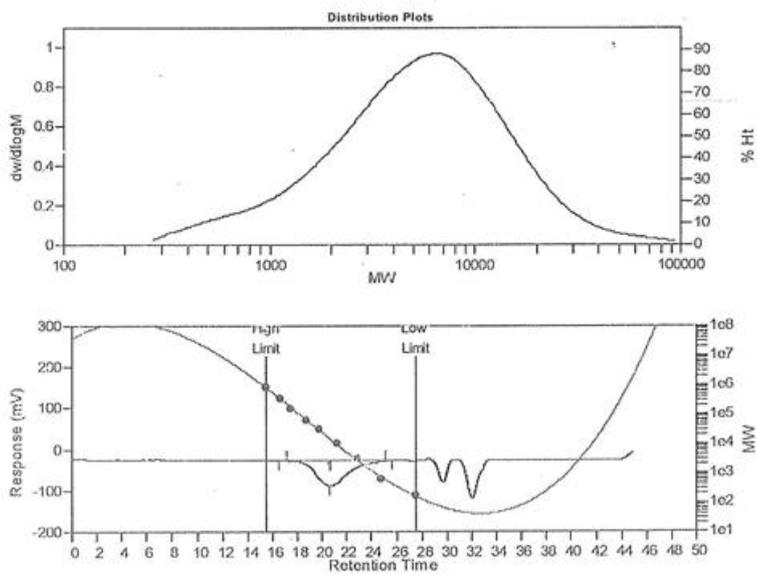


Figure S13. GPC trace of polyethylene obtained in entry 13, Table 1.

MW Averages

Mp: 7 174

Mn: 2 793

Mv: 7 584

Mw: 8 653

Mz: 2 2563

Mz+1: 5 7570

PD: 3 .0981

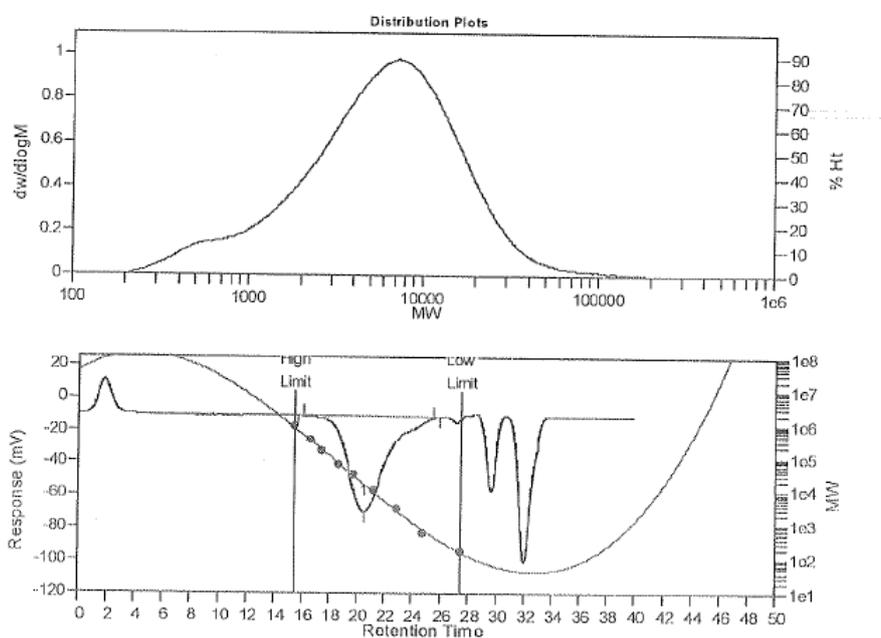


Figure S14. GPC trace of polyethylene obtained in entry 14, Table 1.

MW Averages

Mp: 12815

Mn: 4451

Mv: 15053

Mw: 17797

Mz: 54657

Mz+1: 120769

PD: 3.9984

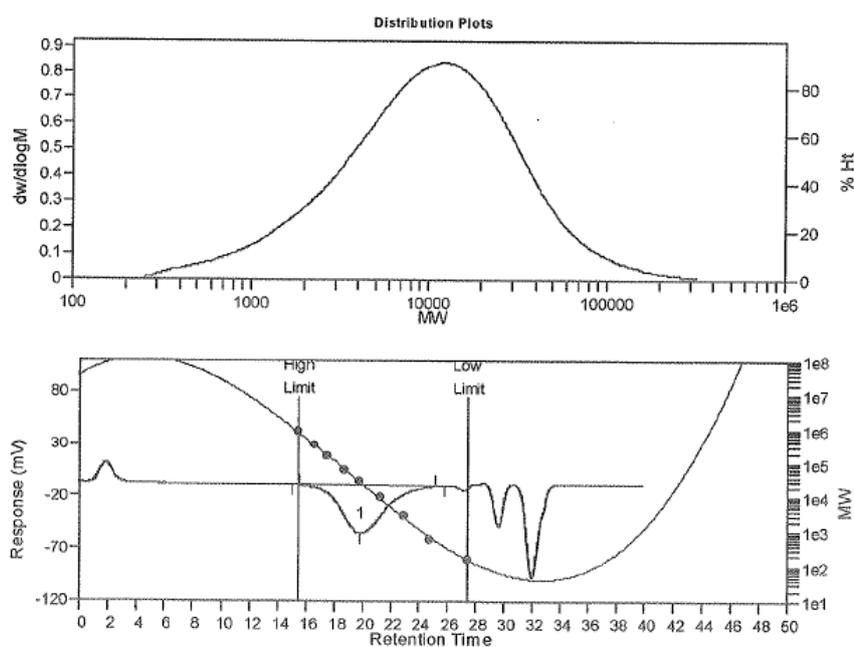


Figure S15. GPC trace of polyethylene obtained in entry 15, Table 1.

MW Averages

Mp:1 309

Mn:1 386

Mv: 5303

Mw: 6785

Mz:2 9018

Mz+1:6 3473

PD:4 .8954

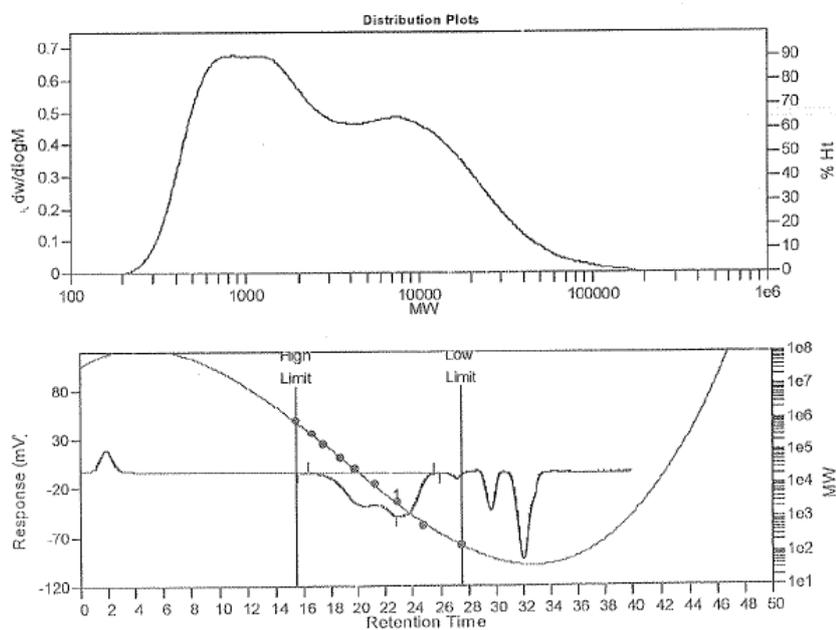


Figure S16. GPC trace of polyethylene obtained in entry 16, Table 1.

MW Averages

Mp: 645

Mn: 774

Mv: 1498

Mw: 1905

Mz:1 3468

Mz+1:3 7464

PD:2 .4612

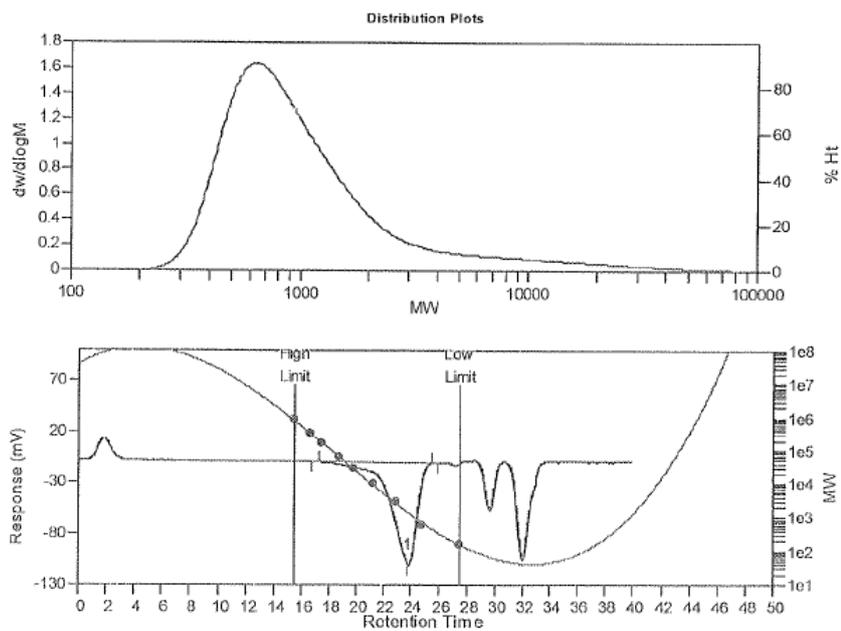


Figure S17. GPC trace of polyethylene obtained in entry 17, Table 1.

MW Averages

Mp: 714

Mn: 772

Mv: 1167

Mw: 1318

Mz: 4491

Mz+1: 13808

PD: 1.7073

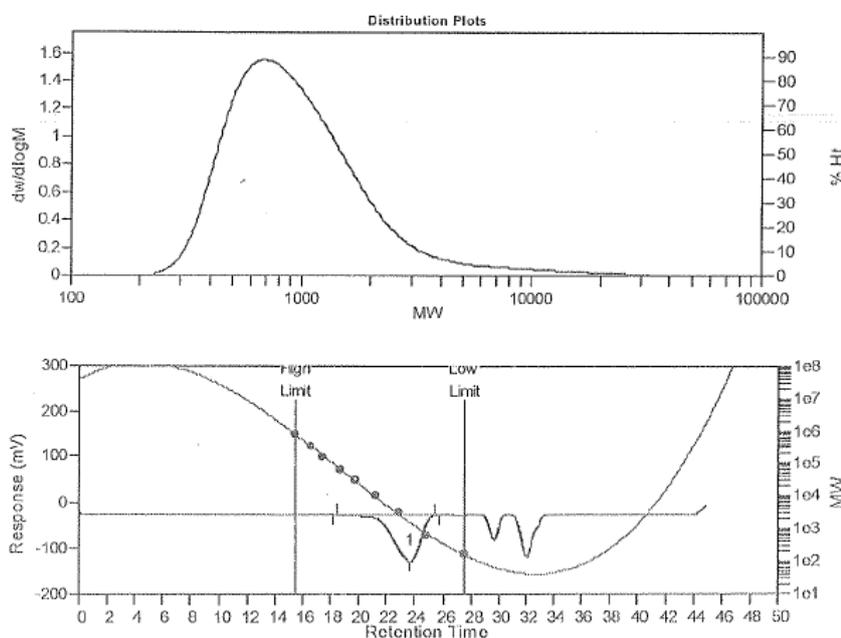


Figure S18. GPC trace of polyethylene obtained in entry 18, Table 1.

MW Averages

Mp: 722

Mn: 1392

Mv: 8553

Mw: 12482

Mz: 106119

Mz+1: 249025

PD: 8.9670

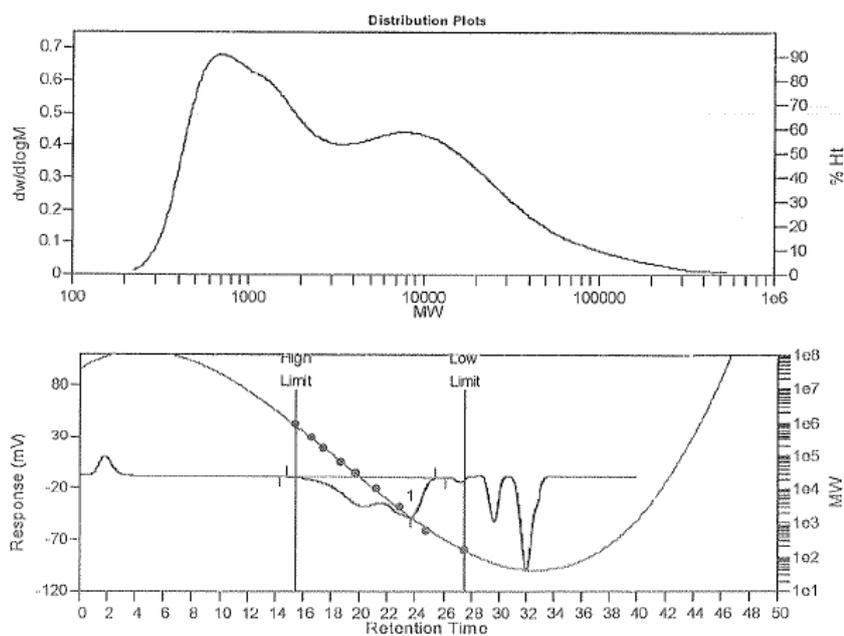


Figure S19. GPC trace of polyethylene obtained in entry 19, Table 1.

3.4. DSC traces of polyethylene

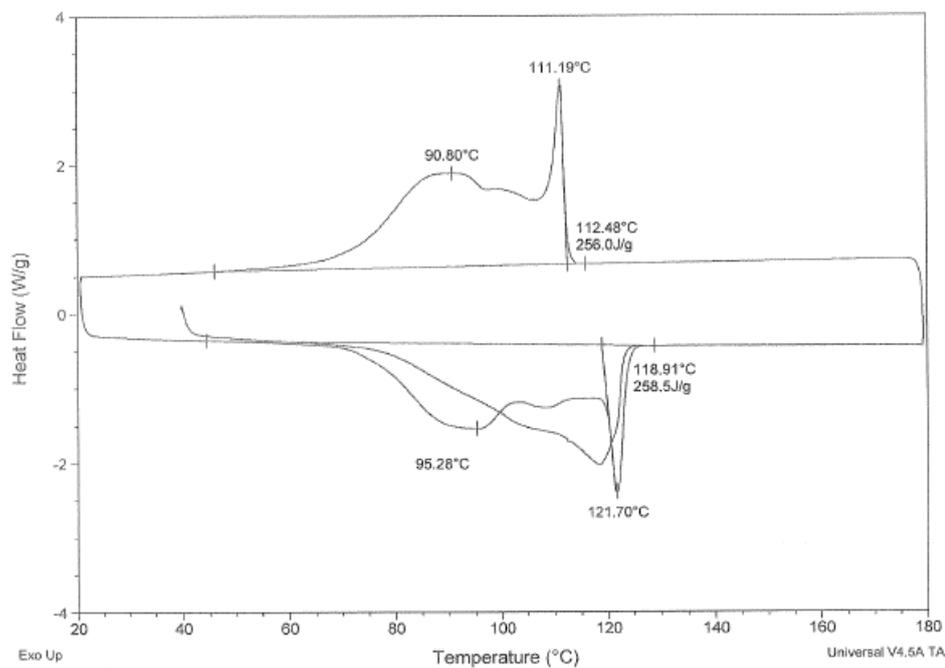


Figure S20. DSC trace of polyethylene obtained in entry 1, Table 1.

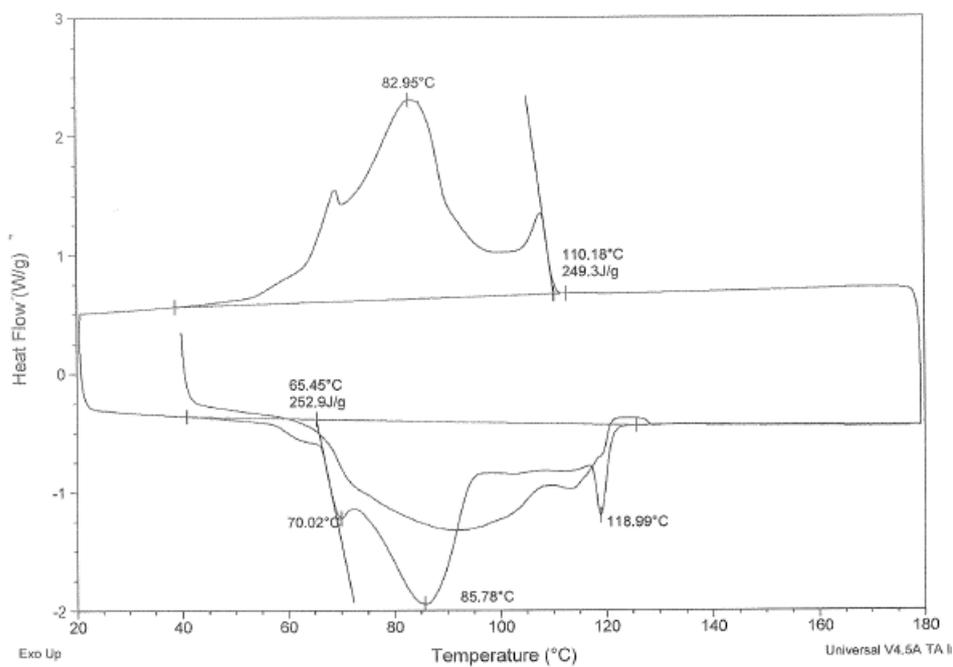


Figure S21. DSC trace of polyethylene obtained in entry 2, Table 1.

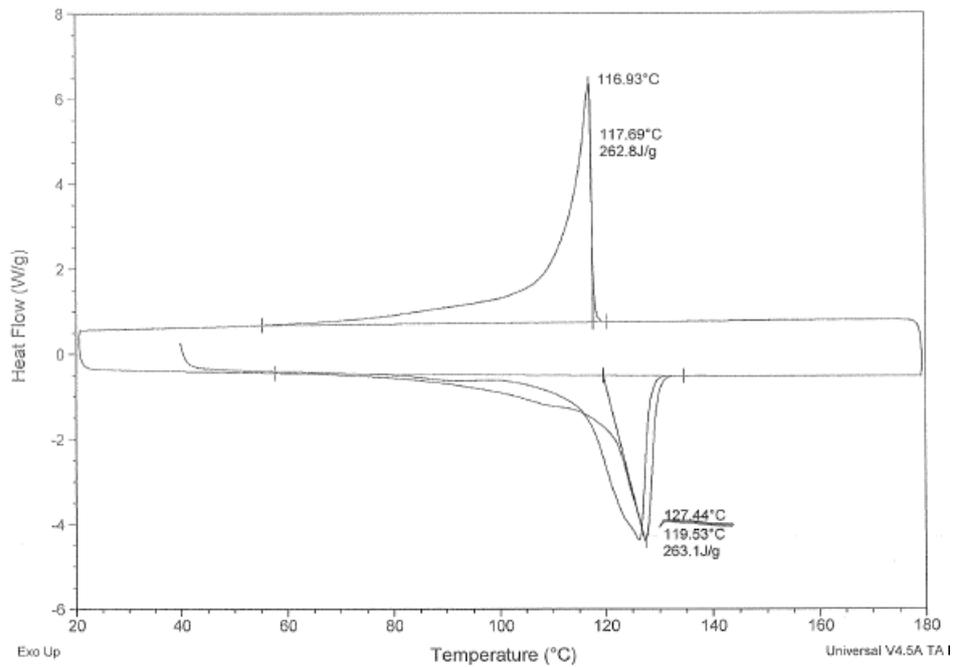


Figure S22. DSC trace of polyethylene obtained in entry 3, Table 1.

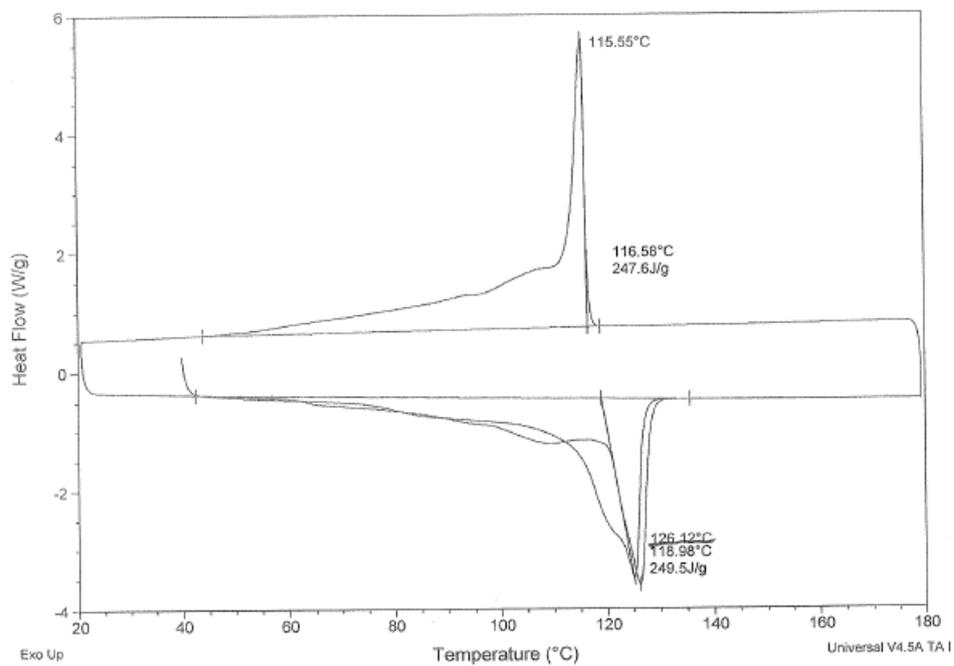


Figure S23. DSC trace of polyethylene obtained in entry 4, Table 1.

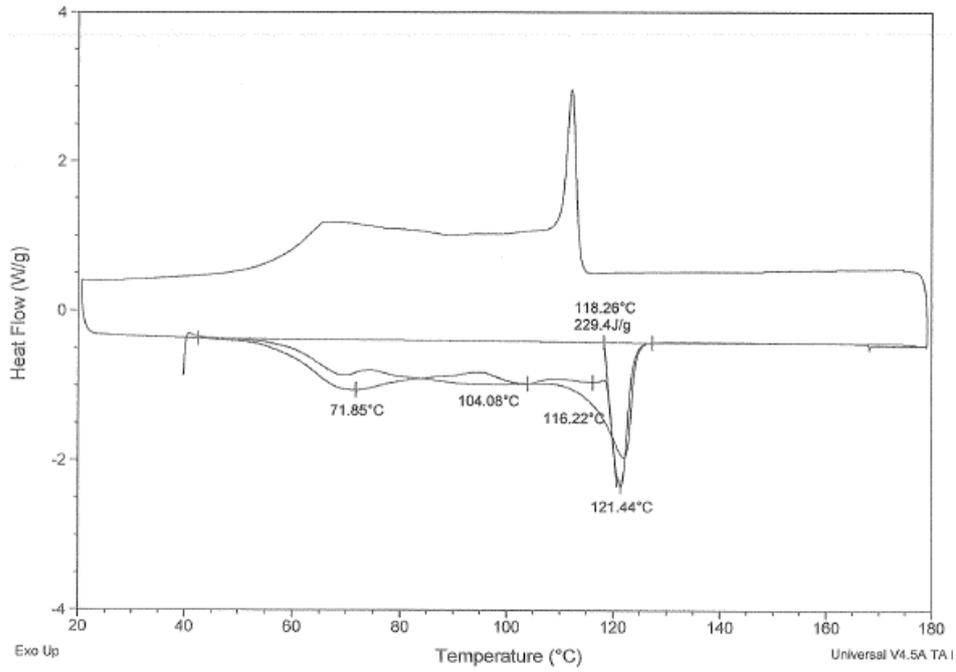


Figure S24. DSC trace of polyethylene obtained in entry 5, Table 1.

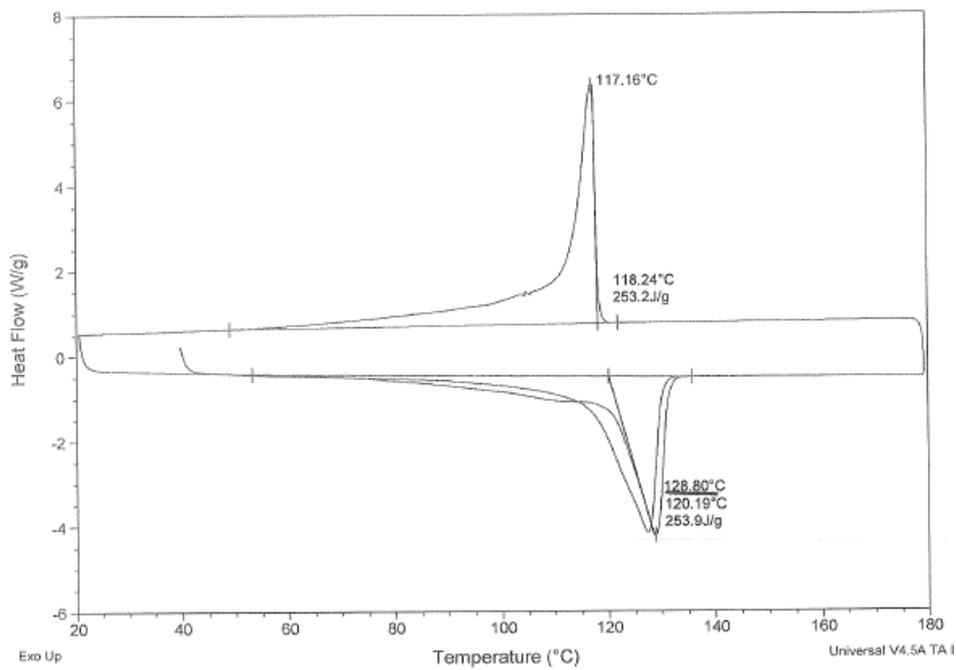


Figure S25. DSC trace of polyethylene obtained in entry 6, Table 1.

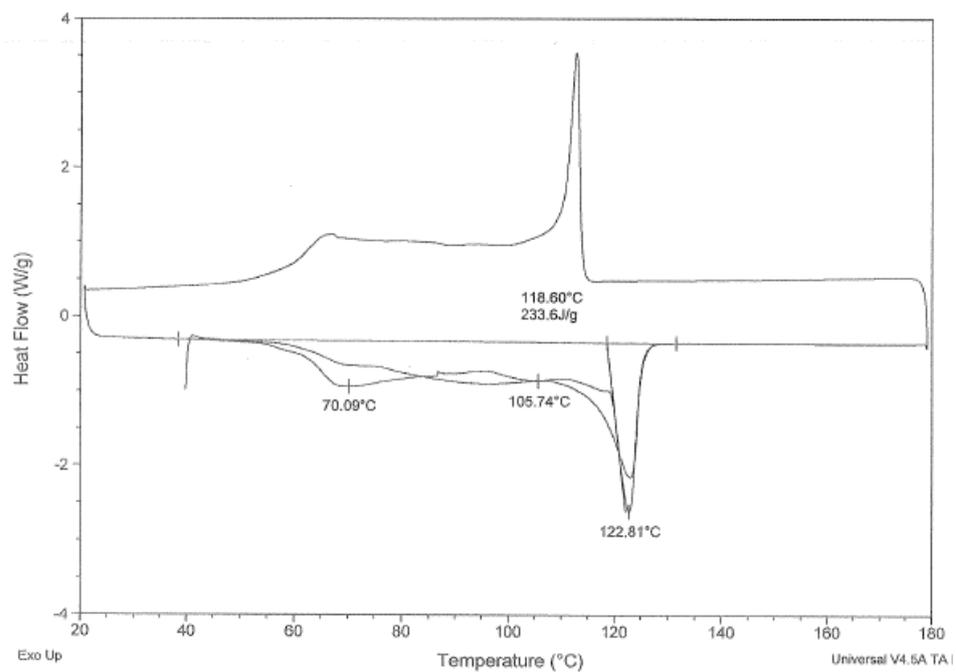


Figure S26. DSC trace of polyethylene obtained in entry 7, Table 1.

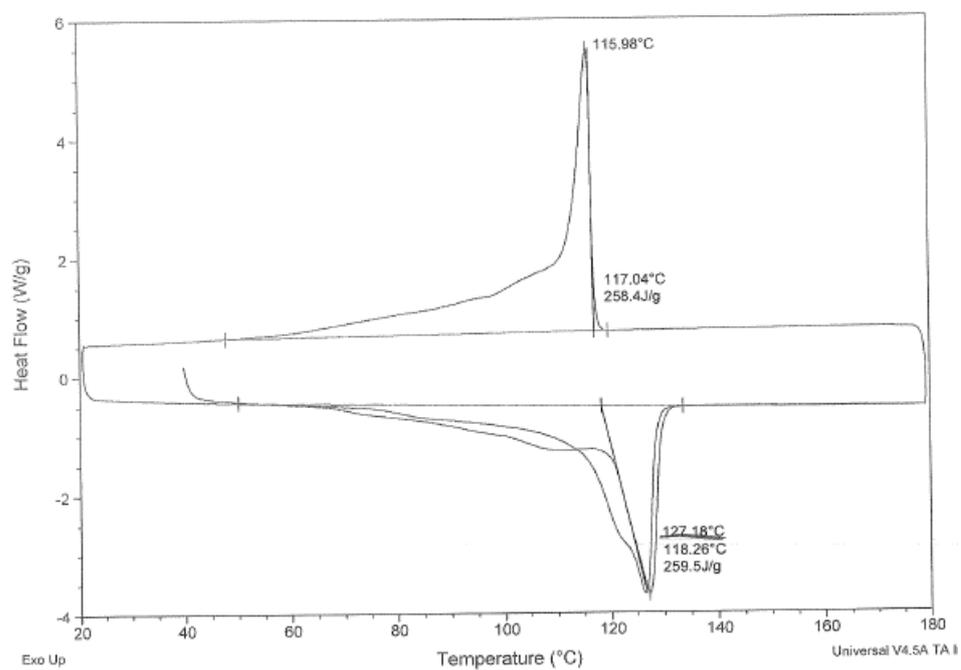


Figure S27. DSC trace of polyethylene obtained in entry 8, Table 1.

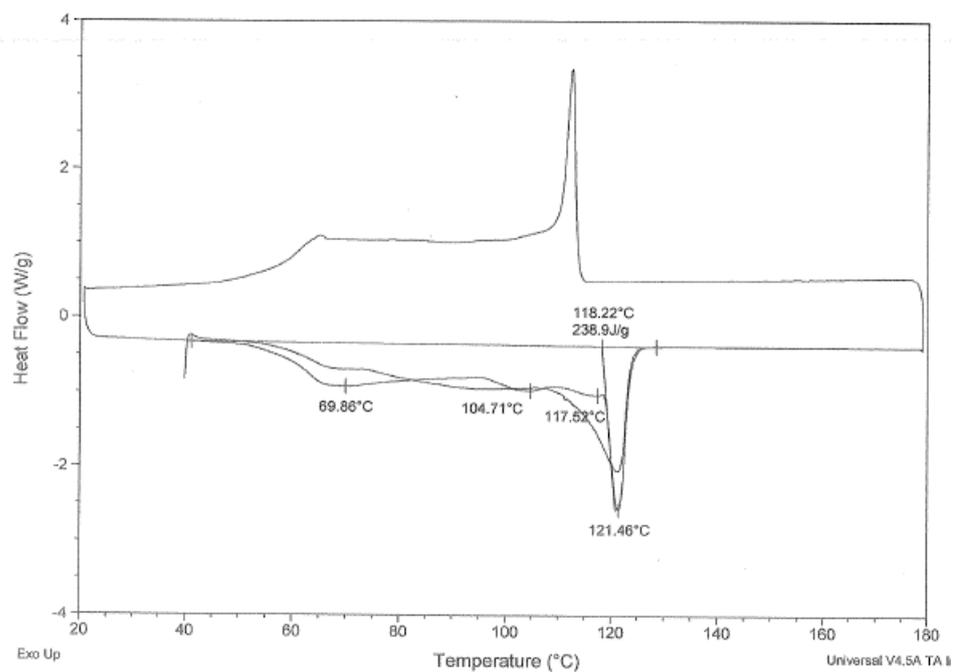


Figure S28. DSC trace of polyethylene obtained in entry 9, Table 1.

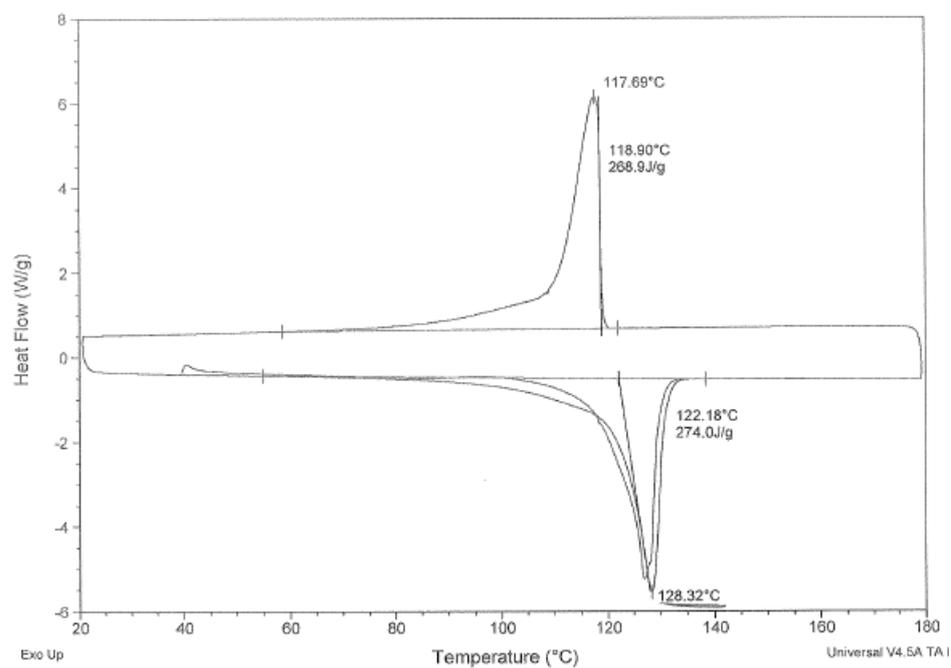


Figure S29. DSC trace of polyethylene obtained in entry 10, Table 1.

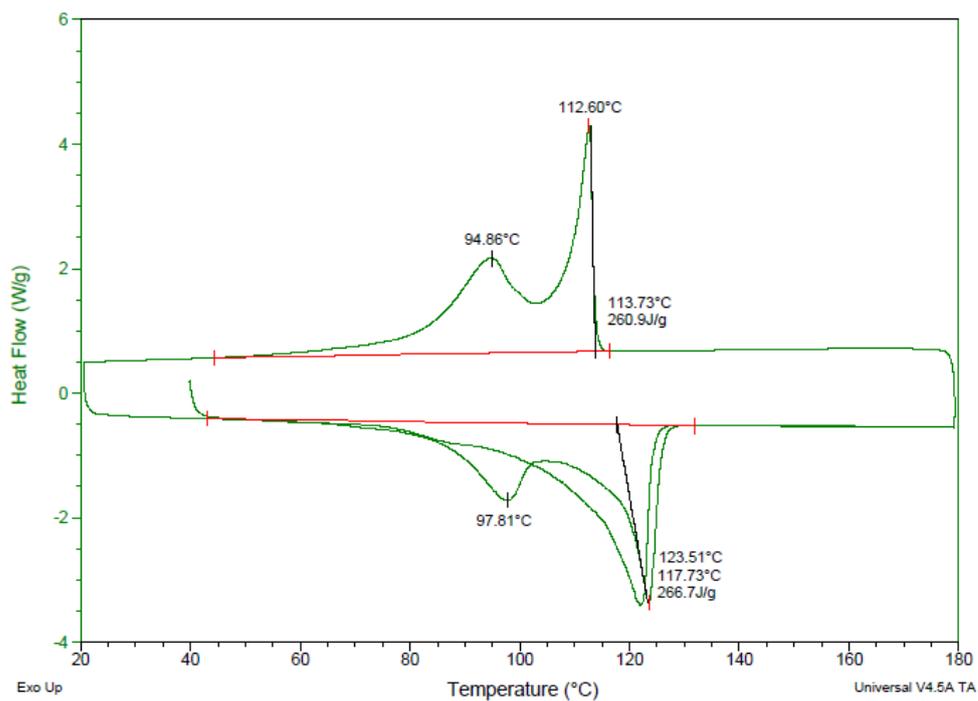


Figure S30. DSC trace of polyethylene obtained in entry 11, Table 1.

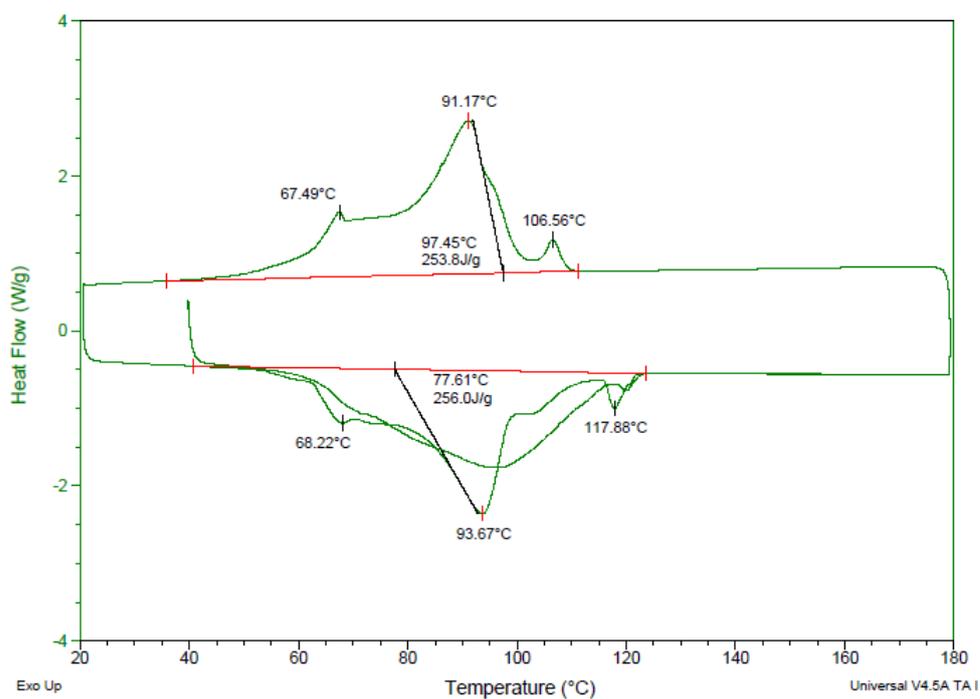


Figure S31. DSC trace of polyethylene obtained in entry 12, Table 1.

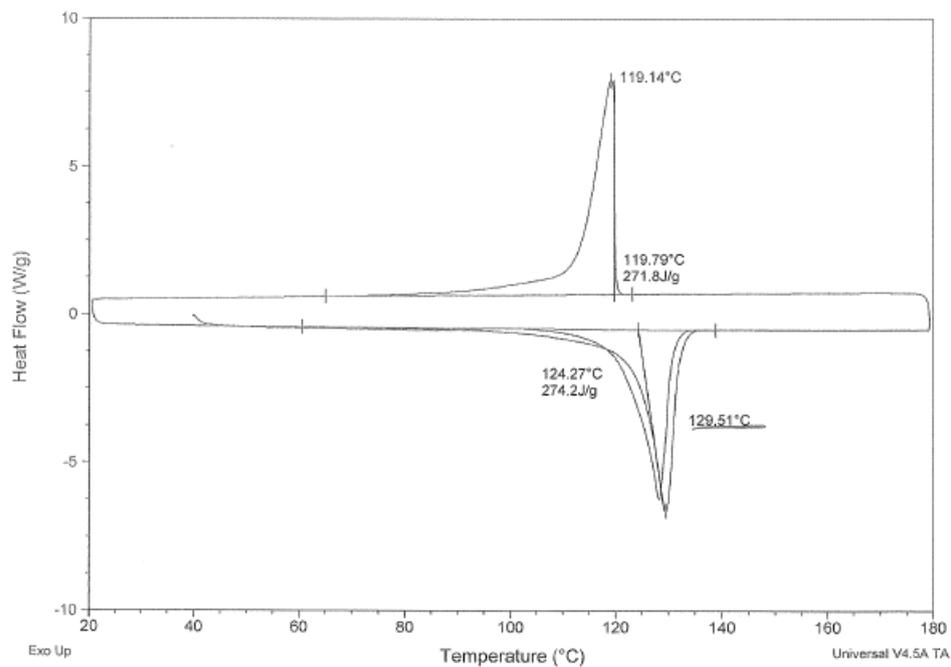


Figure S32. DSC trace of polyethylene obtained in entry 13, Table 1

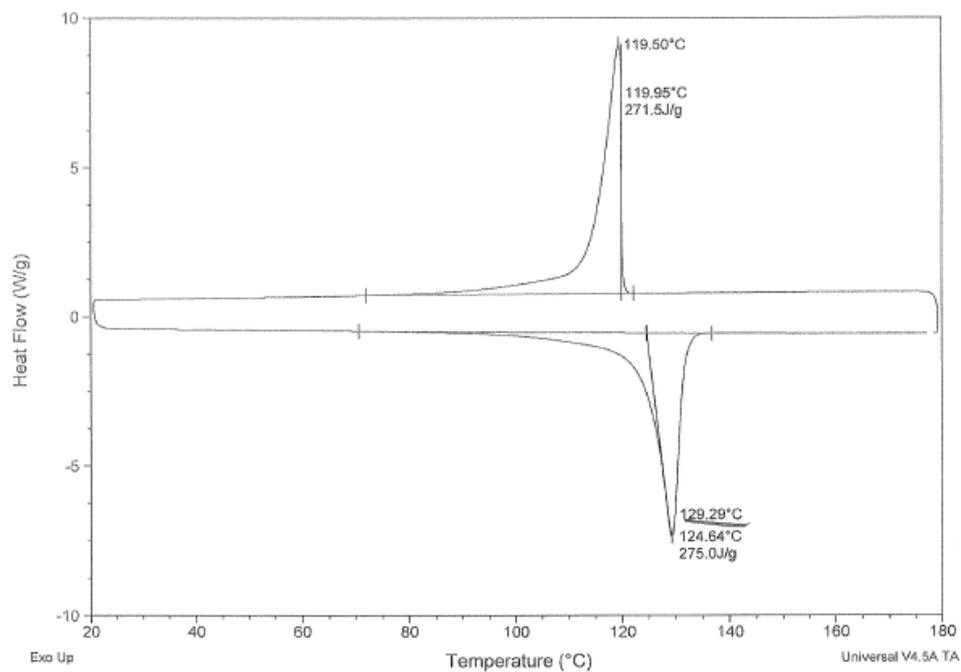


Figure S33. DSC trace of polyethylene obtained in entry 14, Table 1.

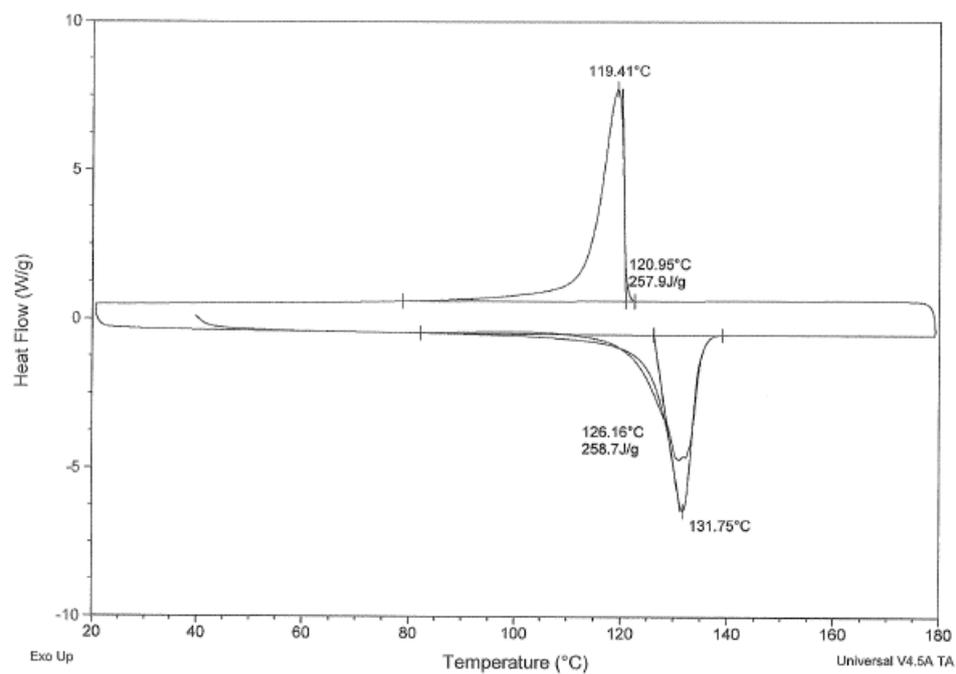


Figure S34. DSC trace of polyethylene obtained in entry 15, Table 1.

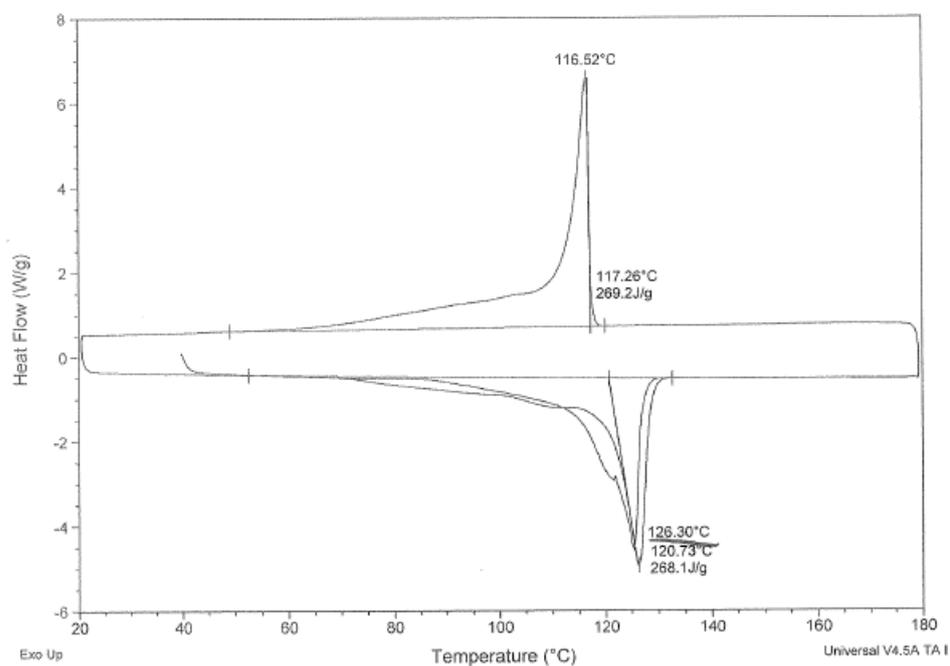


Figure S35. DSC trace of polyethylene obtained in entry 16, Table 1.

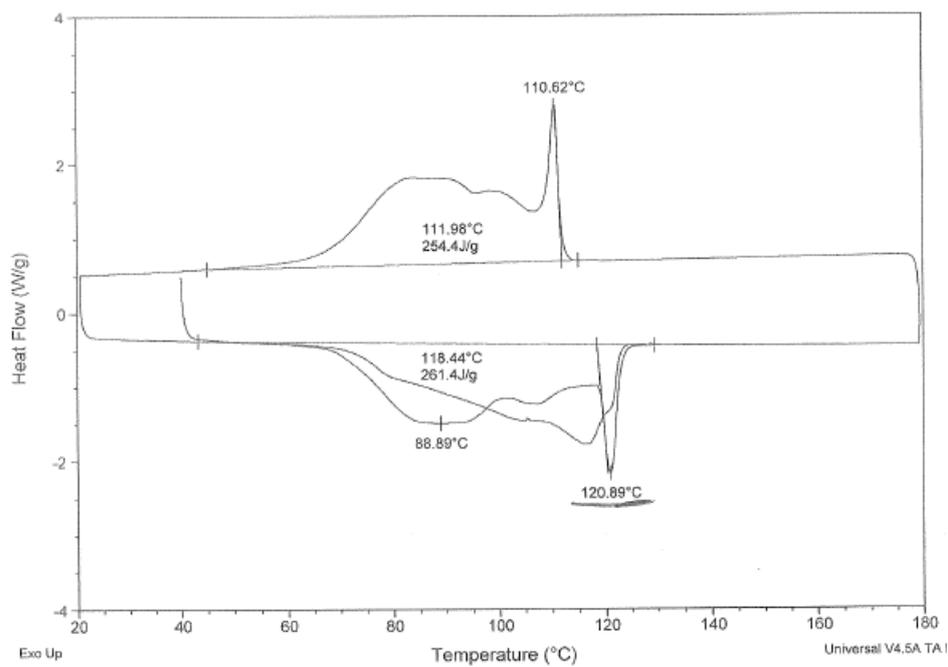


Figure S36. DSC trace of polyethylene obtained in entry 17, Table 1.

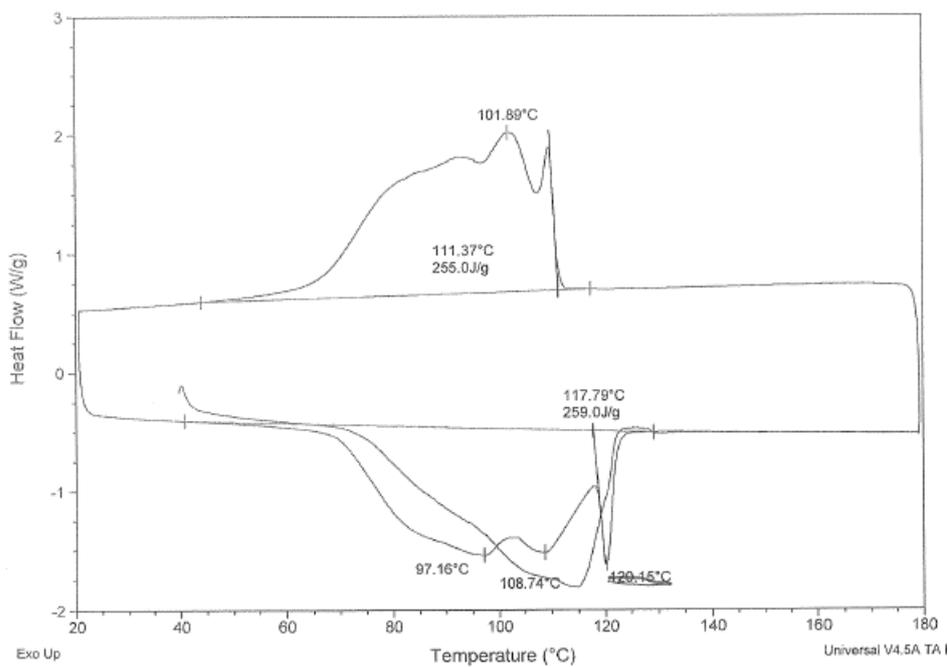


Figure S37. DSC trace of polyethylene obtained in entry 18, Table 1.

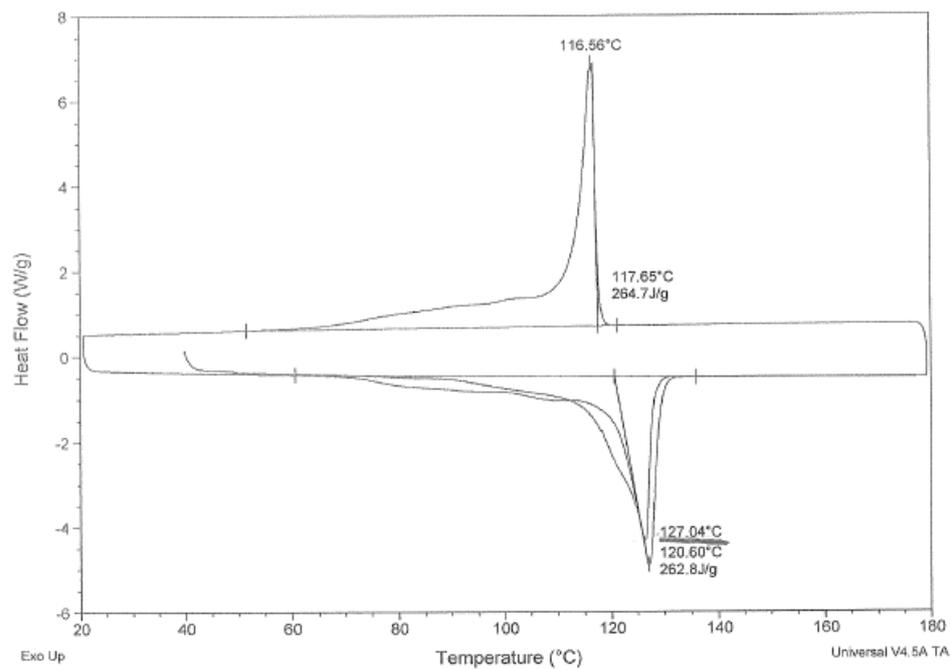
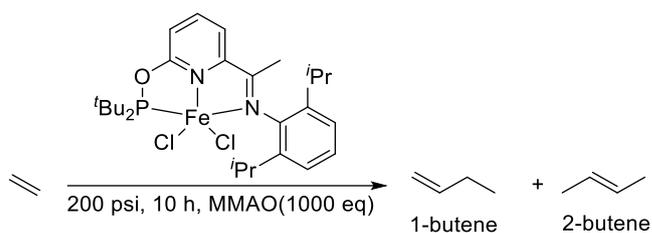


Figure S38. DSC trace of polyethylene obtained in entry 19, Table 1.

3.5. Attempted ethylene polymerization with phosphinite-imonopyridine

Fe complexes

Attempted ethylene polymerization/oligomerization using the phosphinite-imonopyridine Fe complex **1** has also been carried out. The reaction under 200 psi ethylene pressure activated by 1000 equiv. of MMAO produced 1-butene as the major product (62% selectivity) and 2-butene as the minor product (27% selectivity), with activity of $0.9 \times 10^3 \text{ g (mol Fe)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$.



3.6. Time dependence of ethylene polymerization activity over complex **3a**

Time dependence is studied as well. We perform the ethylene polymerization for prolonged time, say, 12 h and 24 h.

Previously, Artem A. Barabanov and Nina V. Semikolenova reported that the bis(imino)pyridine iron catalysts had short lifetime (about 30 min).⁵

The yields are observed to increase, albeit slowly at longer time, partly due to the limited diffusion of ethylene. Those phosphine-iminoquinoline iron complexes have lifetime of 12 h and even larger, which is longer than bis(imino)pyridine iron catalysts.

Table S4 Ethylene polymerization using iron complex **3a** for prolonged time

Entry	Time	Yield (g)	Activity ^b
1	10 min	2.63	7.9×10^6
2	0.5 h	4.06	4.1×10^6
3	1.0 h	6.04	3.0×10^6
4	2.0 h	7.84	2.0×10^6
5	4.0 h	8.90	1.1×10^6
6	6.0 h	9.71	0.8×10^6
7	12.0 h	11.49	0.5×10^6
8	24.0 h	13.42	0.3×10^6

^a Conditions: 2 μ mol of complex **3a** in 100 mL toluene, 1 atm ethylene, 2000 equiv. of MMAO, 20 °C. ^b In units of g PE/mol Fe·h.

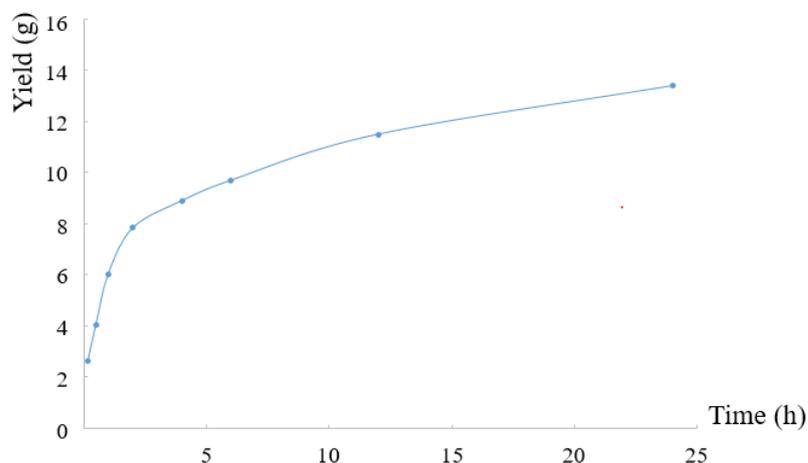


Figure 38. Plot of polymer yield as a function of reaction time for ethylene polymerization.

4. Copolymerization of Ethylene and 1-Octene

4.1. General Procedure for Copolymerization of Ethylene and 1-Octene:

Freshly distilled toluene (30 mL) and 1-octene (30 mL) were added into a 200mL Schlenk flask and saturated with ethylene at polymerization temperature. Modified-methylaluminoxane (MMAO) was syringed into the flask in sequence, and the mixture was stirred for 10 min. Then the precatalyst solution in toluene was injected via a syringe. The polymerization was carried out for the desired time and then quenched with ethanol and then poured into a large amount of acidified ethanol (300 mL, 10% HCl (v/v) in ethanol). The precipitated polymer was collected, washed with ethanol, and then dried at 40 °C under reduced pressure until a constant weight.

NMR analysis of the copolymer produced above reveals that it has similar backbone structures to polyethylene, having highly linear structure with less than 10 branch per 1000 C. In addition to the signals of the methyl, methylene and methane groups originating from ethylene, the ^1H and ^{13}C NMR spectra of the copolymers exhibit characteristic resonances due to the comonomer.

For poly(ethylene-*co*-1-octene), a general structure for copolymers from ethylene and 1-octene is shown in Figure S39. The carbons in this structure are labeled based on nomenclature first defined by Carman and modified by Dorman and Randall.⁶

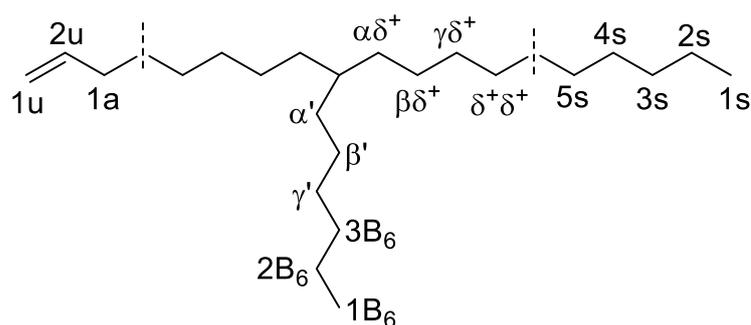


Figure S39. General structure and nomenclature for poly(ethylene-*co*-1-octene)

The ^{13}C NMR spectrum of poly(ethylene-*co*-1-octene) is dominated by the resonance from main-chain $\delta^+\delta^+$ (ca. 30 ppm) repeat units. Resonance at 38.153 ppm is attributed to the methine group CH_{EOE} ⁵.

The resonances of the main-chain methylene groups such as $\beta\delta^+$ (27.3 ppm), and

$\gamma\delta^+$ (30.5 ppm) are resolved from the resonances of side-chain methylene groups $\beta'(5B_6)$ (27.2 ppm), and $\gamma'(4B_6)$ (30.1 ppm) of the branch points, except for the $\alpha\delta^+$ and $\alpha'(6B_6)$ resonances (34.5 ppm), which are completely overlapped. The peak attributed to the $\gamma'(4B_6)$ (30.1 ppm) resonance is well resolved and appears as a shoulder on the $\delta^+\delta^+$ resonance. The resonance labeled $\gamma\delta^+$ (30.5 ppm) is separated from the large $\delta^+\delta^+$ resonance region by a significant region of baseline.

In the ^{13}C NMR spectra, the signals at 14.2 ppm, 22.9 ppm, and 32.2 ppm are attributed to the 1s/1B₆, 2s/2B₆, and 3s/3B₆, respectively.

A single methylene resonance 1u at 114.4 ppm and a single methine resonance 2u at 139.4 ppm indicate that the vinyl end group is present. The resonance at 34.0 ppm is attributed to the 1a methylene group adjacent to the vinyl end group. The peak at 29.6 ppm that is separated by baseline from the others is attributed to the 4s methylene group at the methyl end group according to the literature data. The ratio of those two is approximately 1:1 (Figure S41), consistent with one saturated chain end and one unsaturated chain end, which indicates that β -H transfer predominates under those conditions.

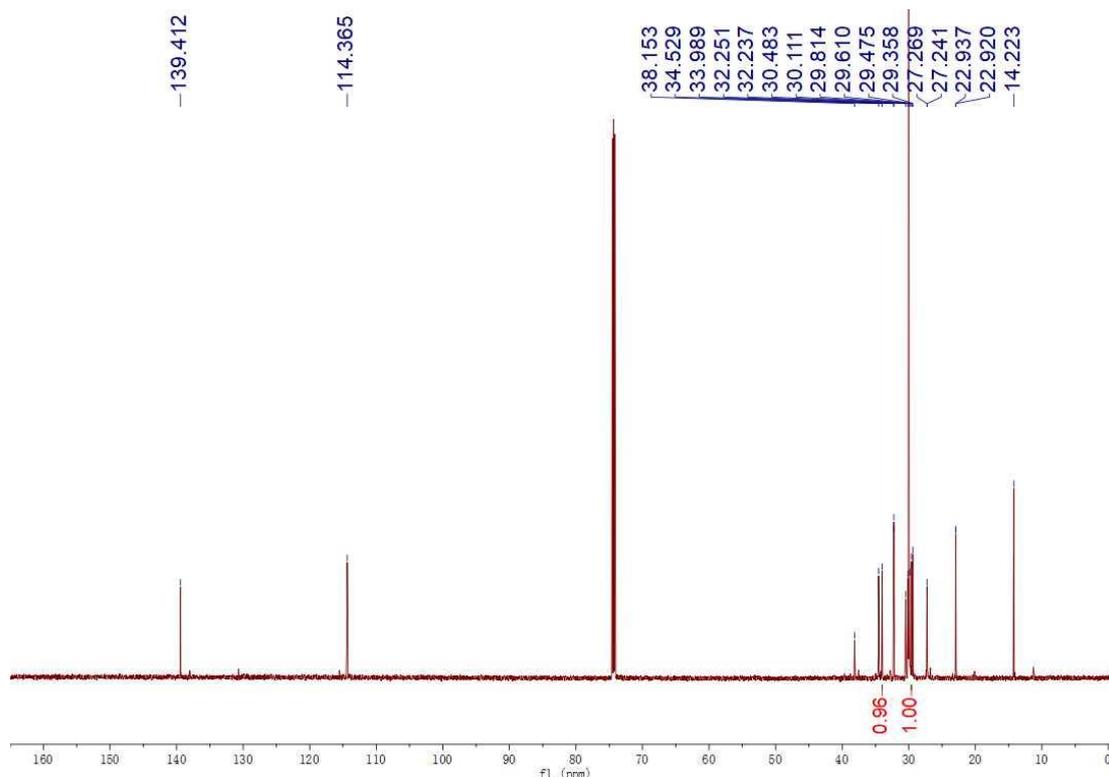


Figure S40. ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C) of poly(ethylene-*co*-1-octene) (0 – 160 ppm)

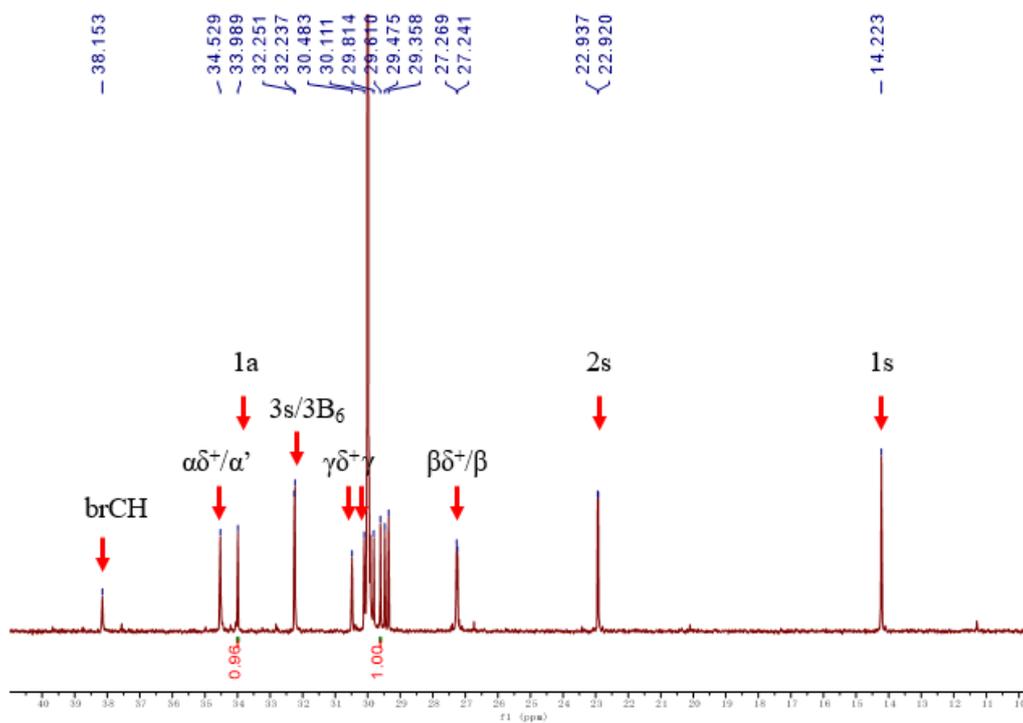


Figure S41. ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C) of poly(ethylene-*co*-1-octene) (10 – 40 ppm)

4.2. GPC trace of poly(ethylene-co-1-octene)

MW Averages

Mp: 450

Mn: 399

Mv: 650

Mw: 722

Mz: 1697

Mz+1: 3612

PD: 1.8095

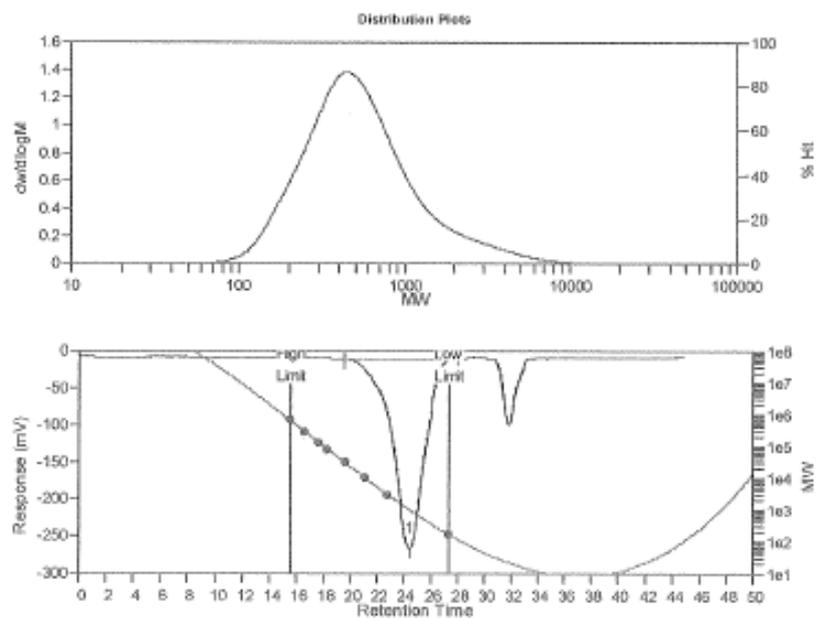


Figure S42. GPC trace of poly(ethylene-co-1-octene) obtained in entry 4, Table 2.

MW Averages

Mp: 578

Mn: 583

Mv: 1085

Mw: 1249

Mz: 3822

Mz+1: 9515

PD: 2.1424

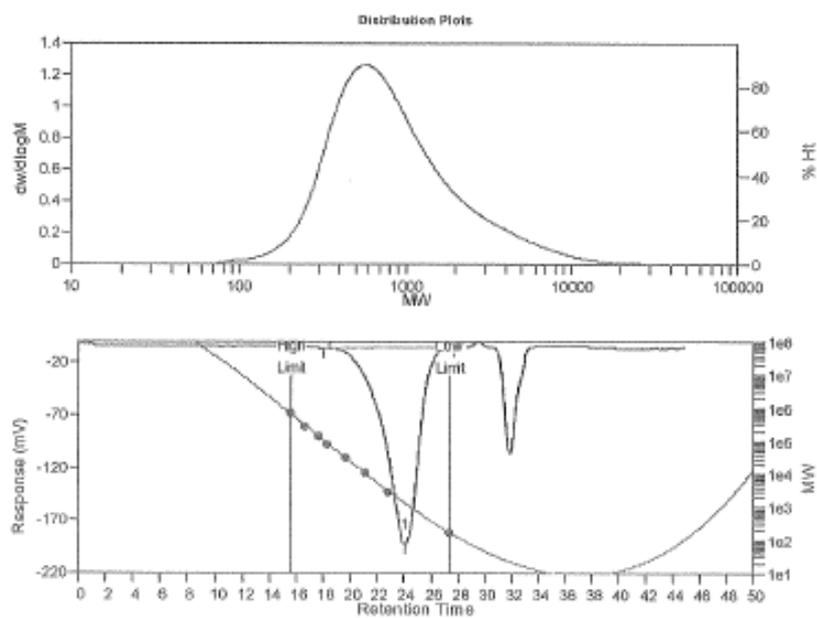


Figure S43. GPC trace of poly(ethylene-co-1-octene) obtained in entry 5, Table 2.

MW Averages

Mp: 460

Mn: 388

Mv: 627

Mw: 702

Mz: 1901

Mz+1: 4894

PD: 1.8093

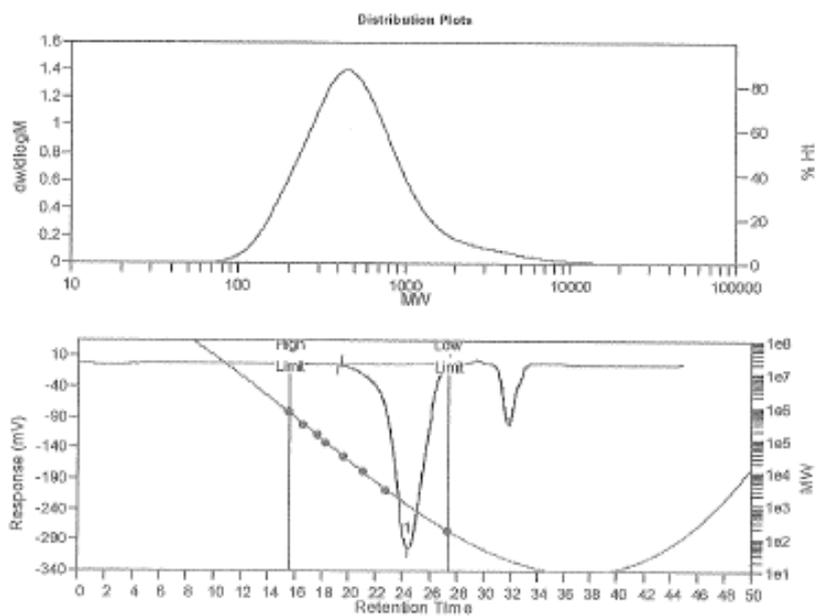


Figure S44. GPC trace of poly(ethylene-*co*-1-octene) obtained in entry 6, Table 2.

4.3. DSC trace of poly(ethylene-co-1-octene)

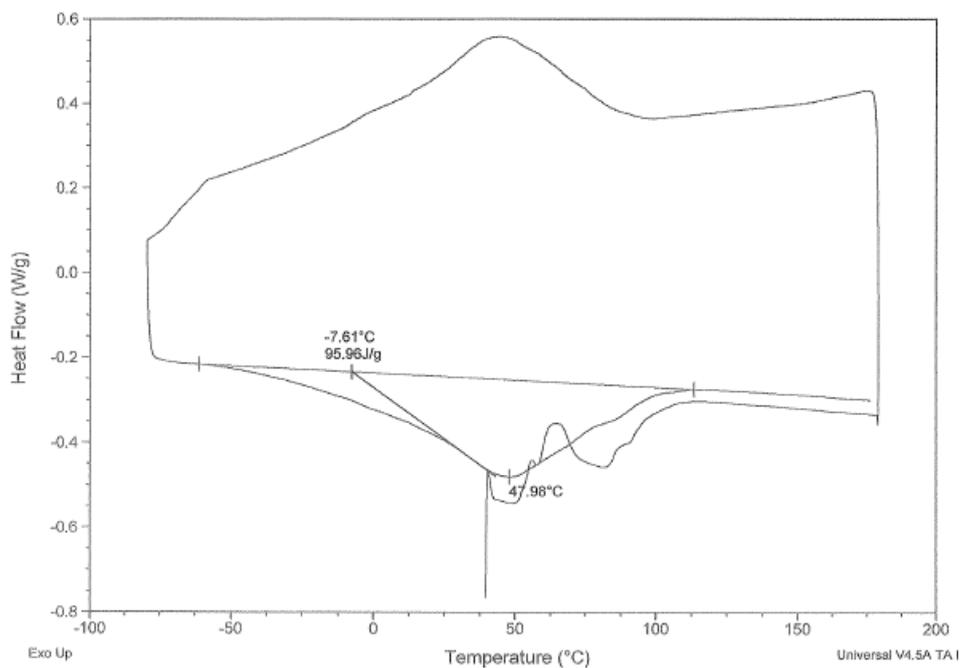


Figure S45. GPC trace of poly(ethylene-co-1-octene) obtained in entry 4, Table 2.

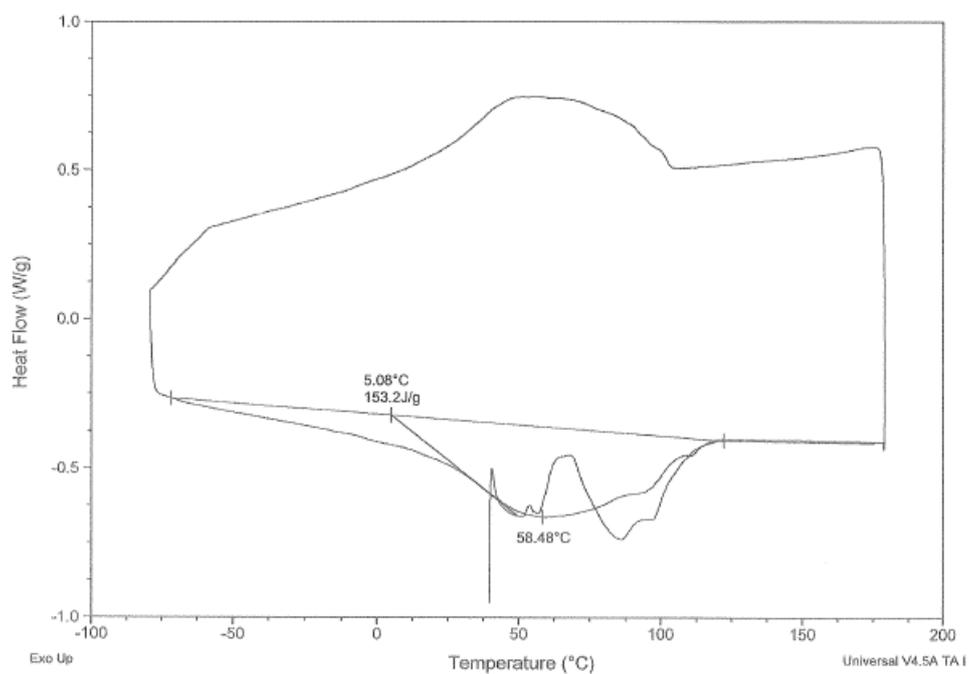


Figure S46. GPC trace of poly(ethylene-co-1-octene) obtained in entry 5, Table 2.

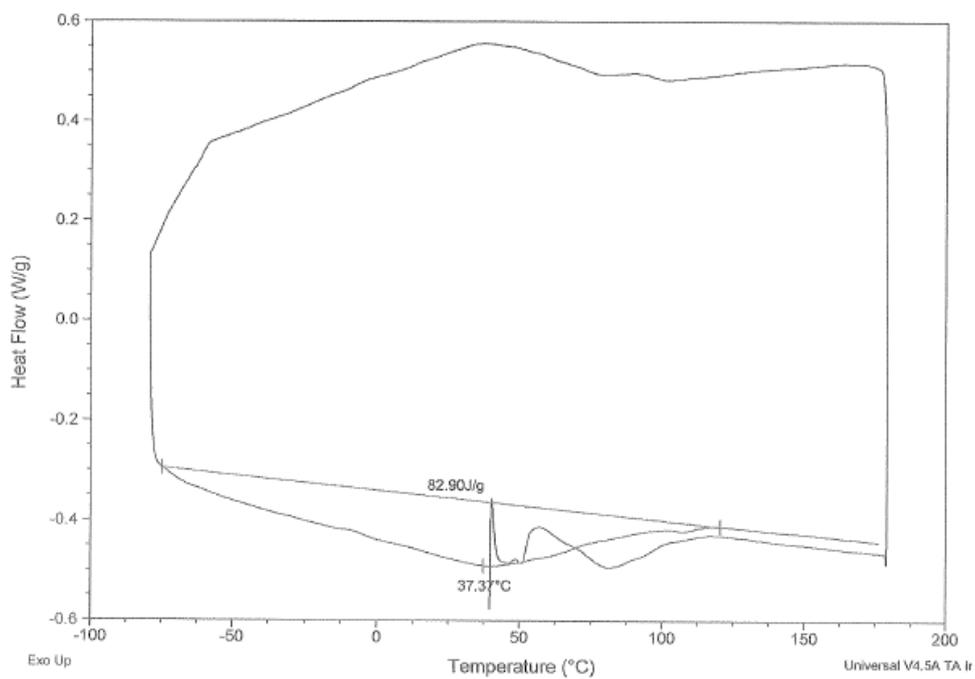


Figure S47. GPC trace of poly(ethylene-*co*-1-octene) obtained in entry 6, Table 2.

4.4. ^{13}C NMR of poly(ethylene-co-1-octene)

ZD-9-54-C-110

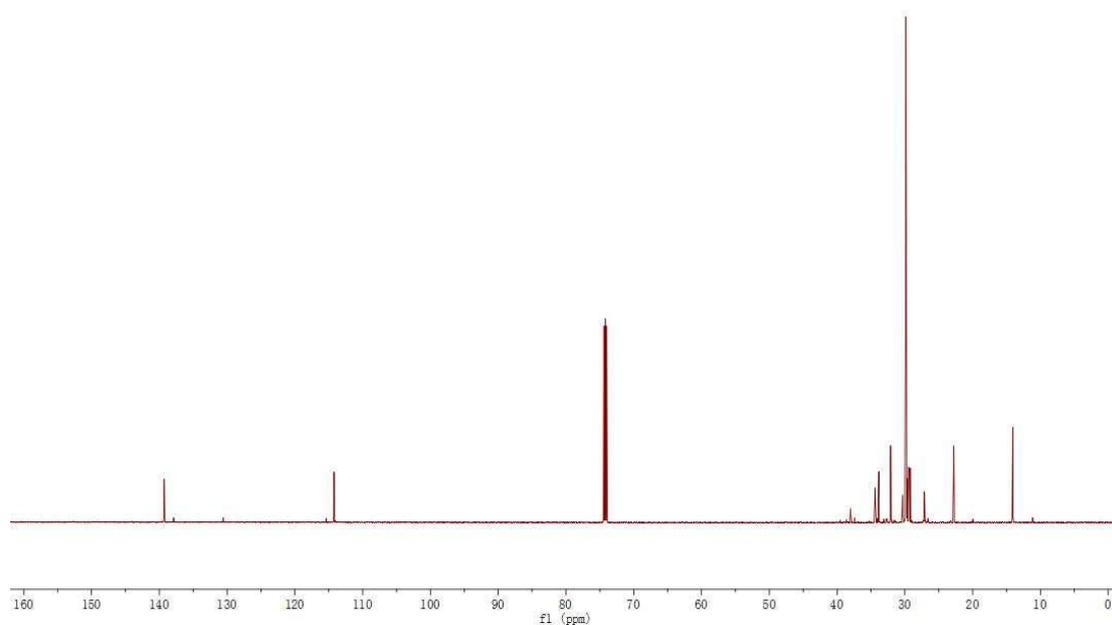


Figure S48. ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C) of poly(ethylene-co-1-octene) obtained in entry 4, Table 2.

ZD-9-55-C-110

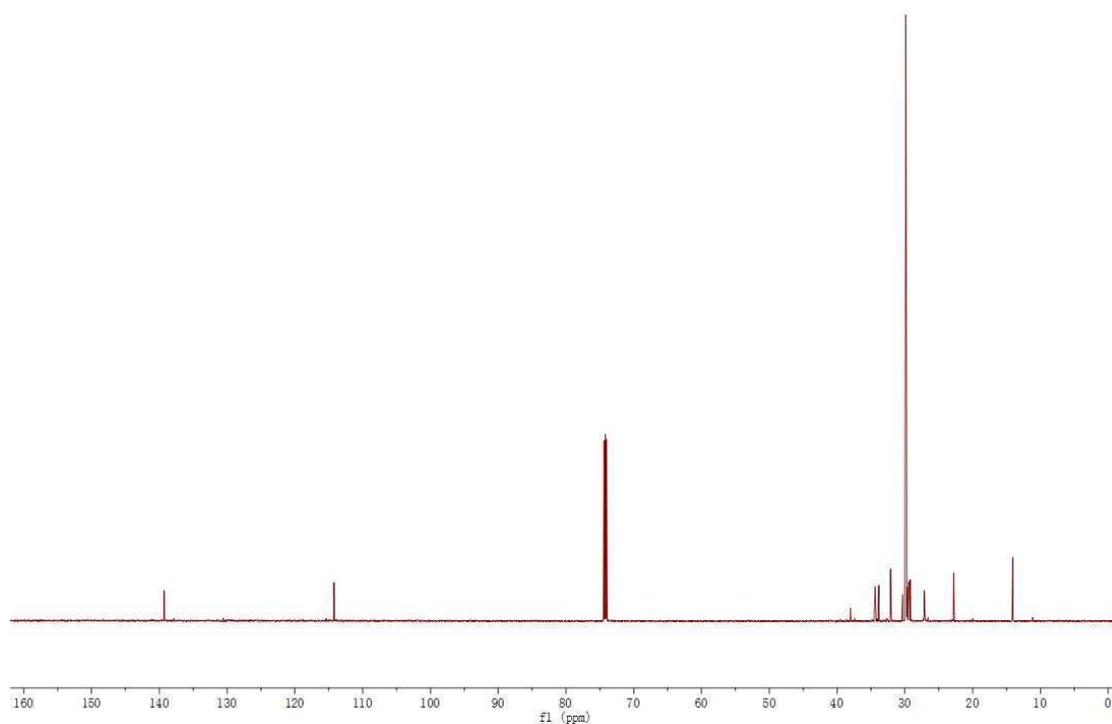


Figure S49. ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C) of poly(ethylene-co-1-octene) obtained in entry 5,

Table 2

ZD-9-56-C-110

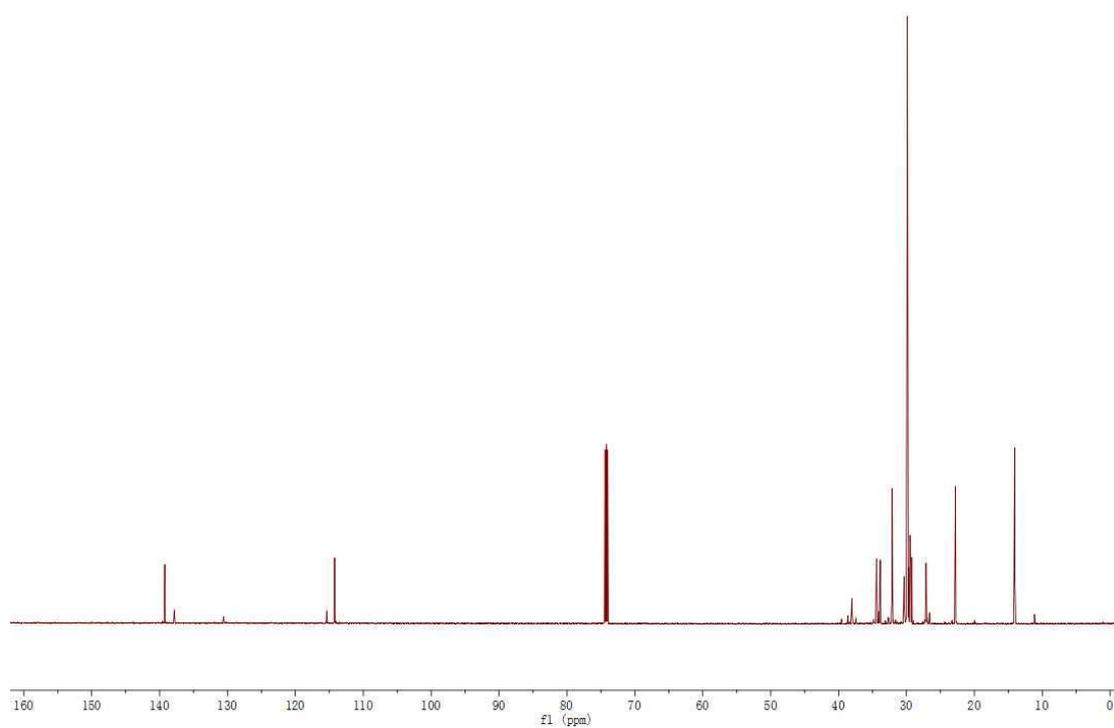
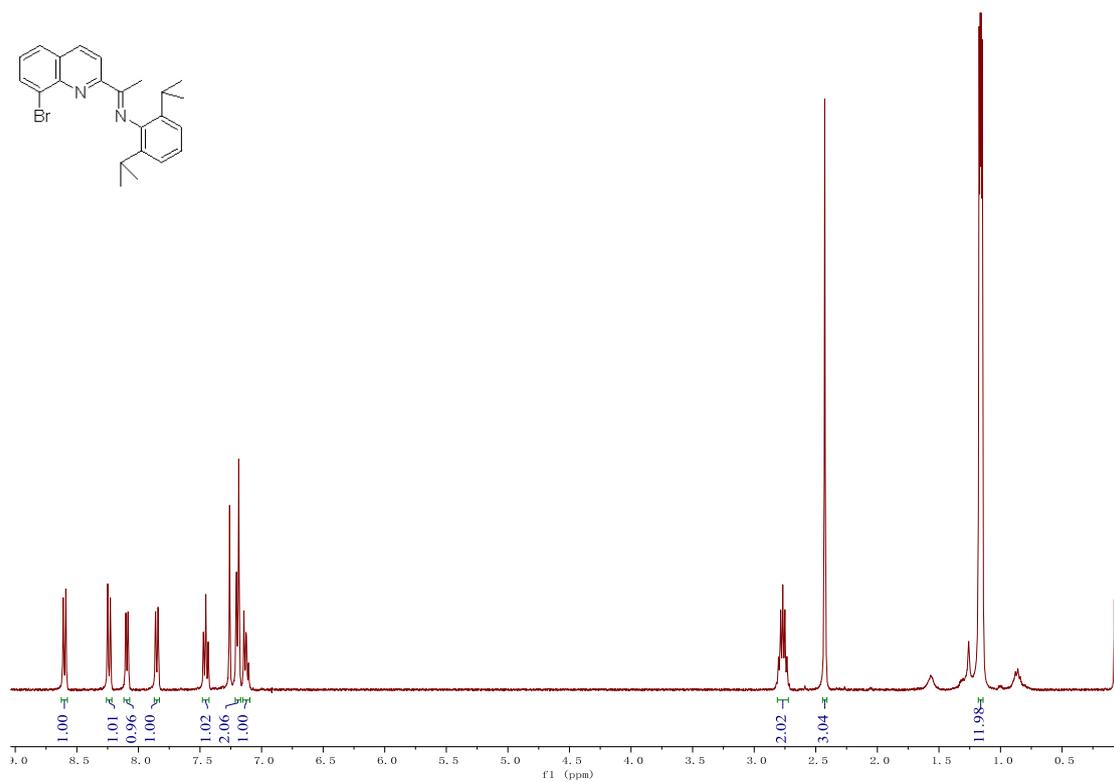


Figure S50. ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C) of poly(ethylene-*co*-1-octene) obtained in entry 6, Table 2.

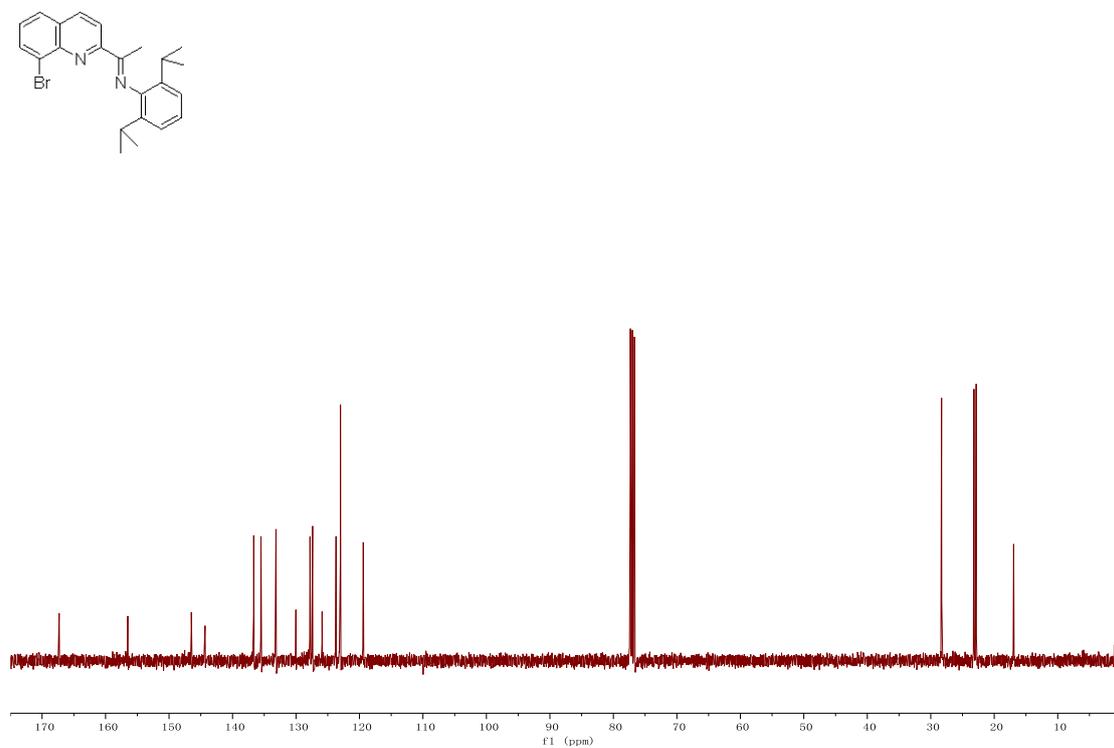
5. References

- 1) Nagy, S.; Winslow, L. N.; Mihan, S.; Lukesova, L.; Nifant'ev, E.; Ivchenko, P. V.; Bagrov, V. US Patent 2012/0016092 **2012**.
- 2) Murata, M.; Buchwald, S. L. *Tetrahedron* **2004**, *60*, 7397.
- 3) Evans, D. F. *J. Chem. Soc. (Resumed)* **1959**, 2003.
- 4) Galland, G. B.; de Souza, R. F.; Mauler, R. S.; Nunes, F. F. *Macromolecules* **1999**, *32*, 1620.
- 5) (a) Souane, R.; Isel, F.; Peruch, F.; Lutz, P. J. *C. R. Chimie* **2002**, *5*, 43; (b) Ivancheva, N. I.; Badaev, V. K.; Oleinik, I. I.; Ivanchev, S. S.; Tolstikov, G. A. *Dokl. Phys. Chem.*, **2000**, *374*, 203.
- 6) (a) Liu, W.; Ray, D. G.; Rinaldi, P. L. *Macromolecules* **1999**, *32*, 3817; (b) Randall, J. C. *J. Macromol. Sci., Polym. Rev.* **1989**, *C29*, 201; (c) Kimura, K.; Yuasa, S.; Maru, Y. *Polymer* **1984**, *25*, 441.

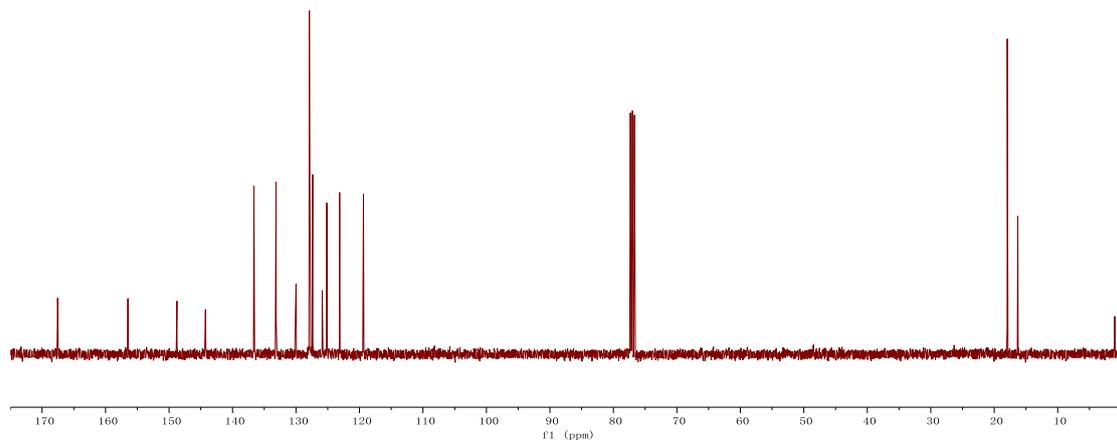
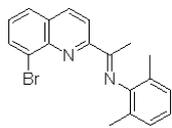
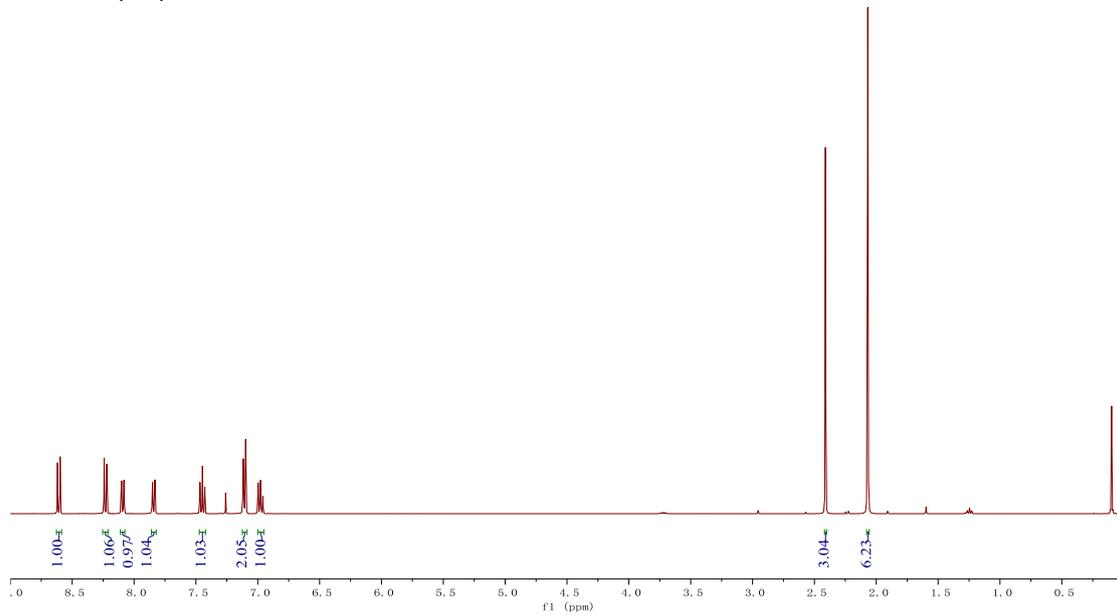
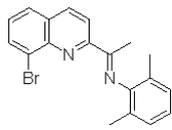
6. NMR Spectra

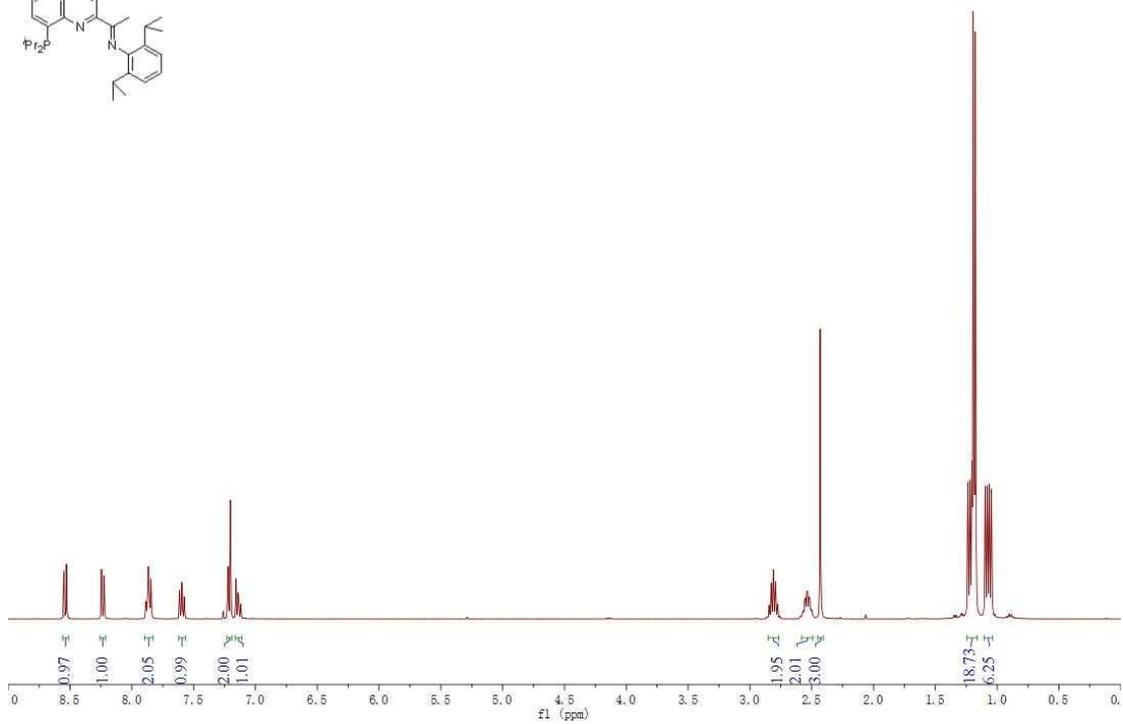
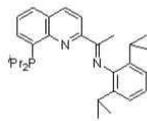


¹H NMR (400 MHz, CDCl₃) of **5a**

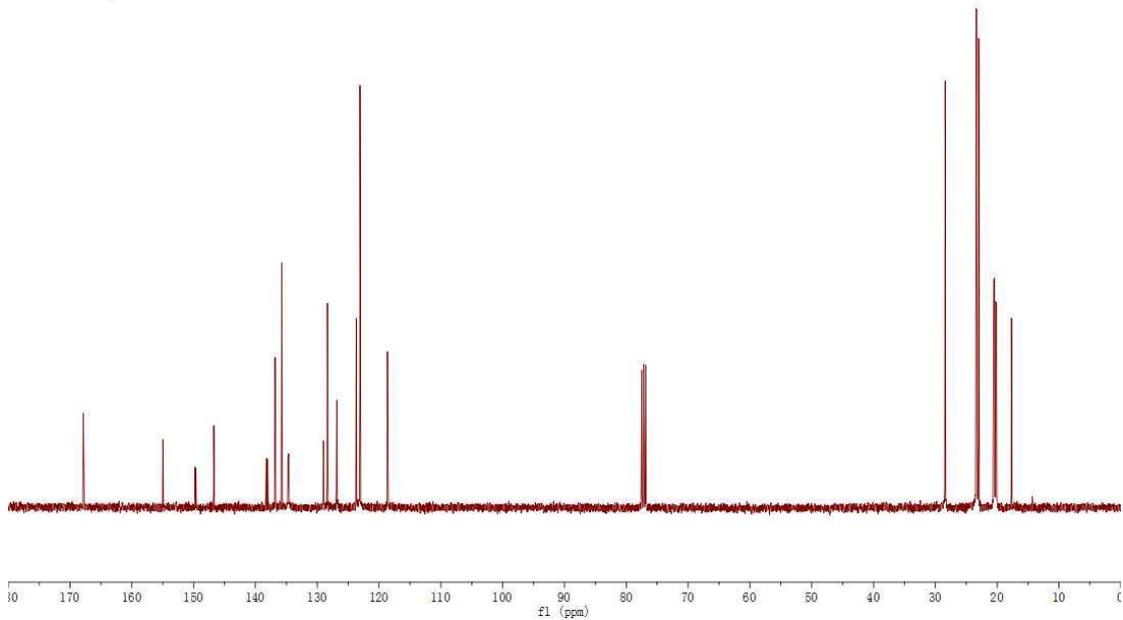
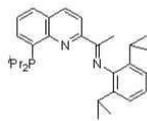


¹³C NMR (101 MHz, CDCl₃) of **5a**

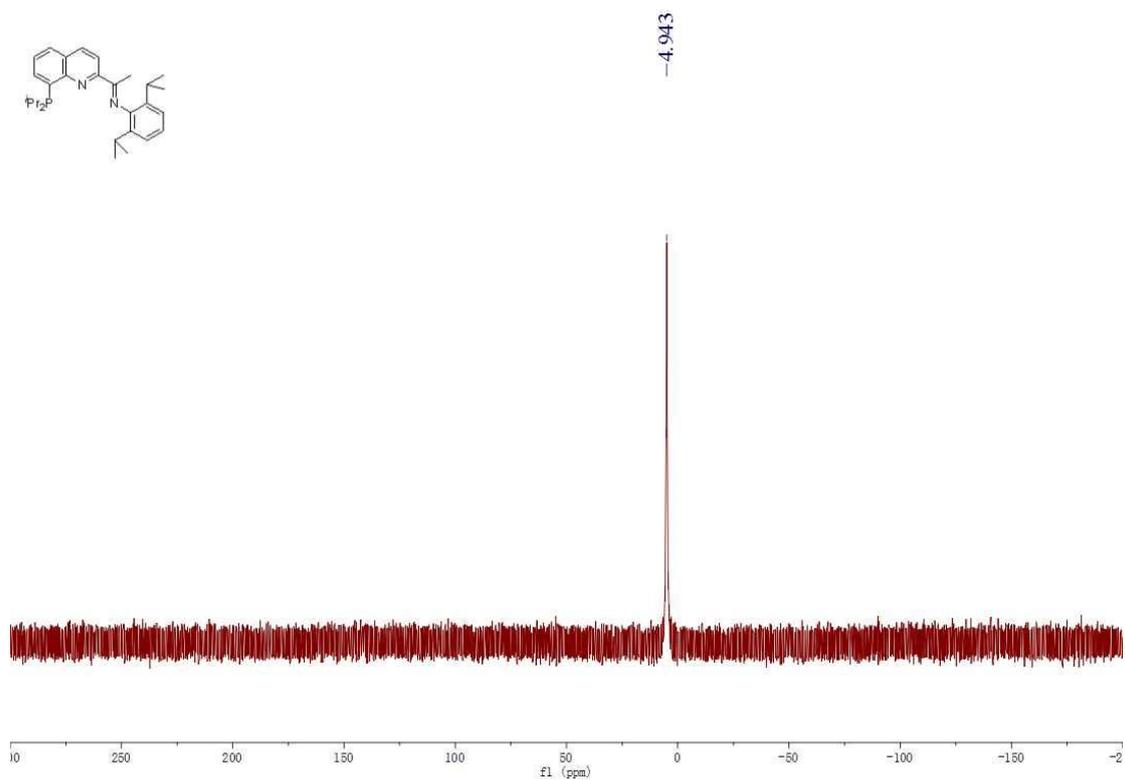




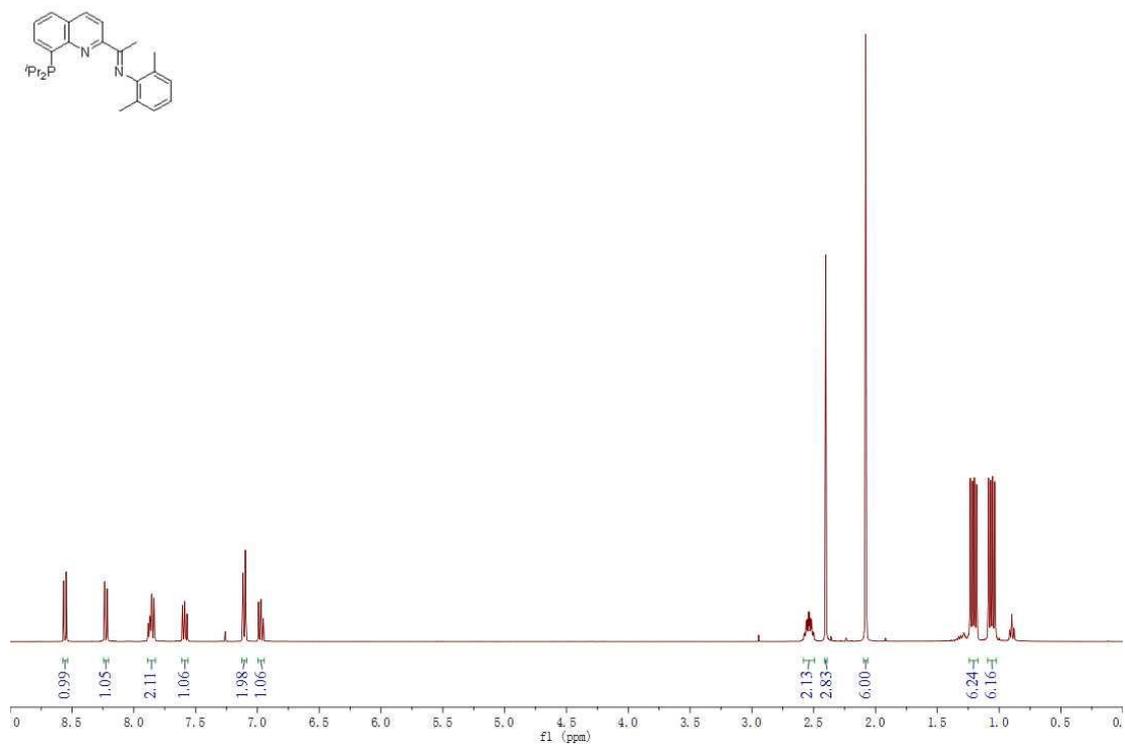
^1H NMR (400 MHz, CDCl_3) of **6a**



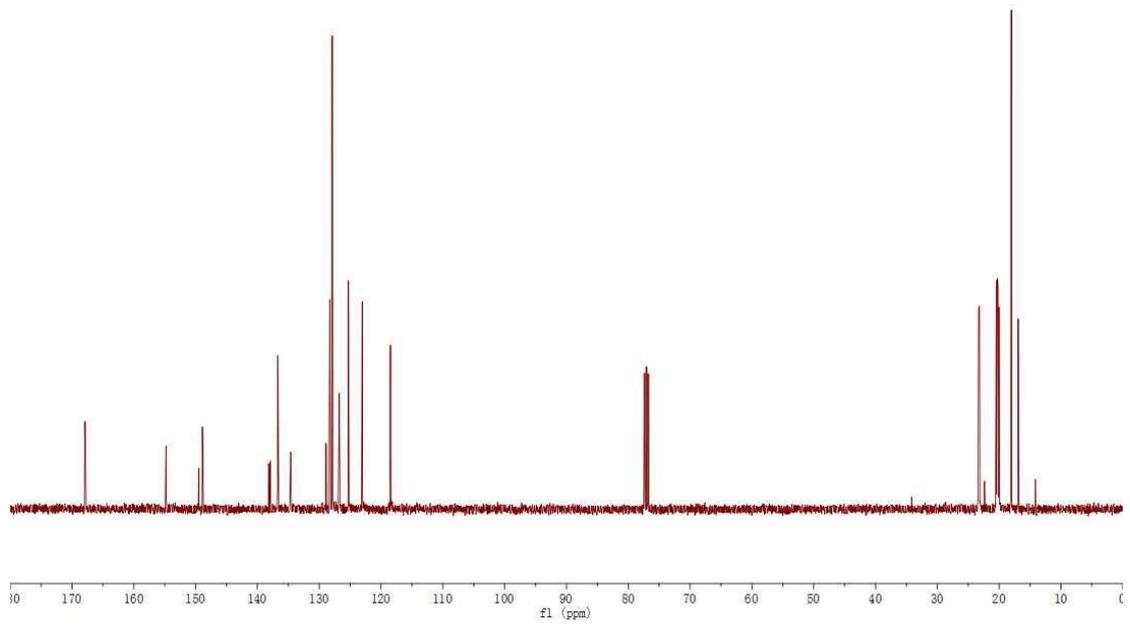
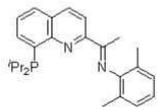
^{13}C NMR (101 MHz, CDCl_3) of **6a**



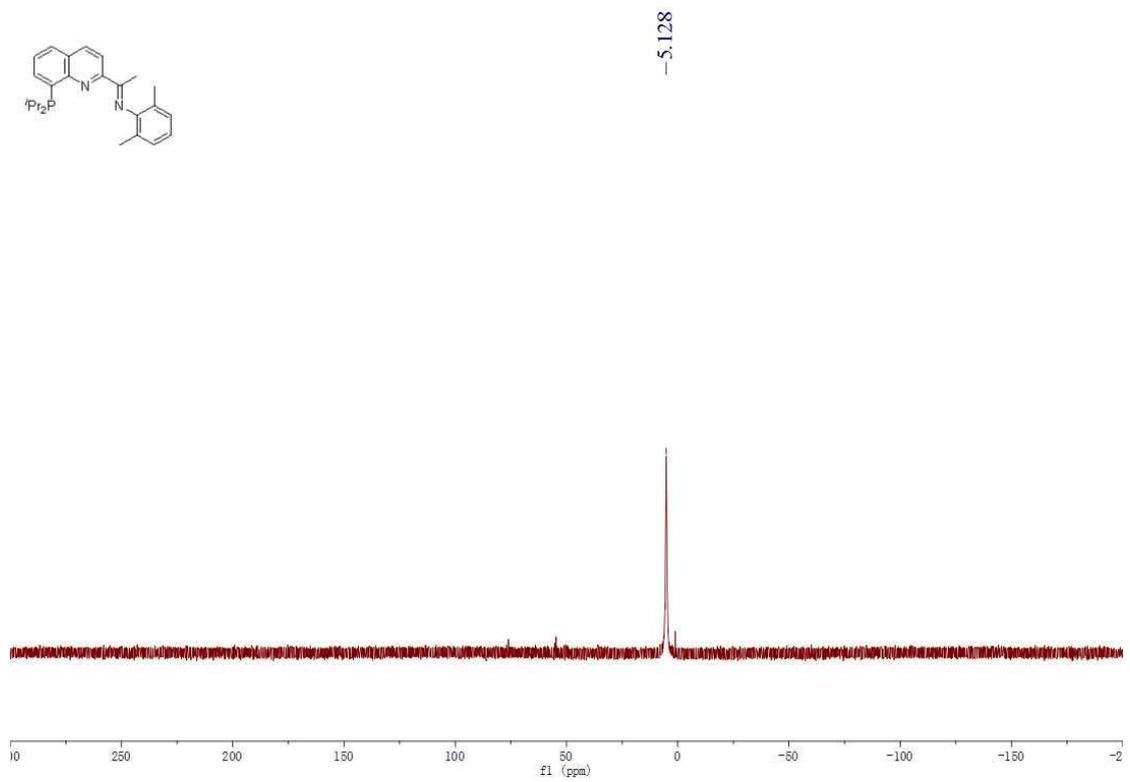
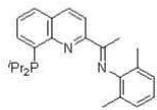
^{31}P NMR (162 MHz, CDCl_3) of **6a**



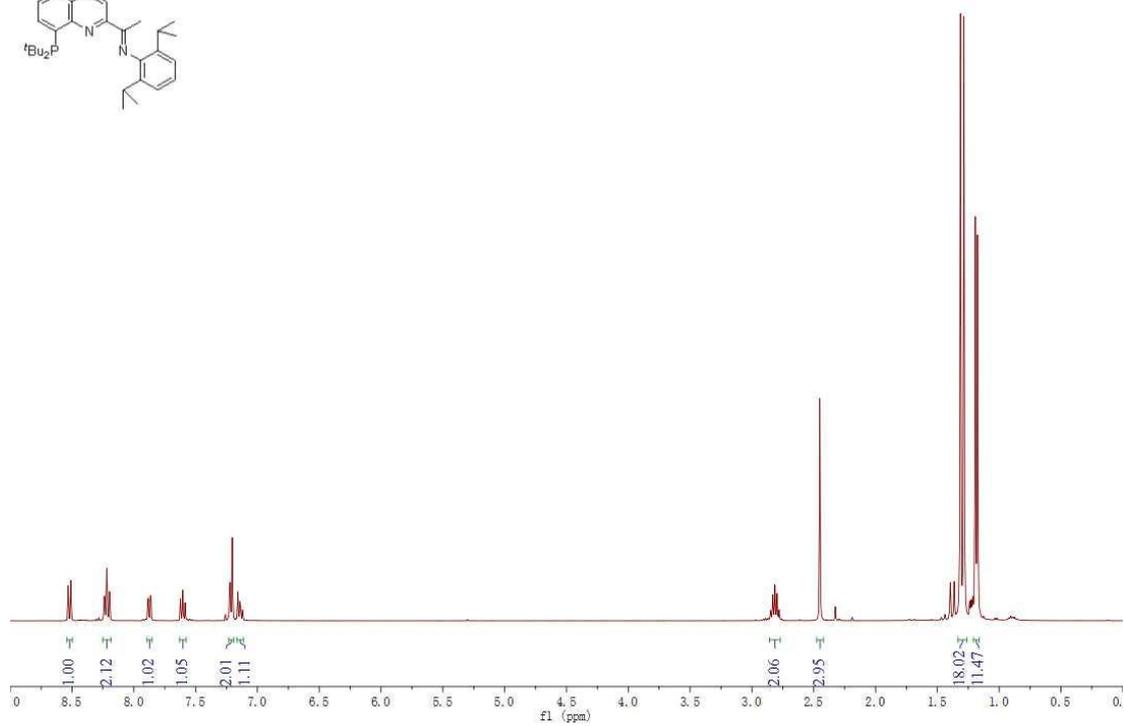
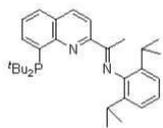
^1H NMR (400 MHz, CDCl_3) of **6b**



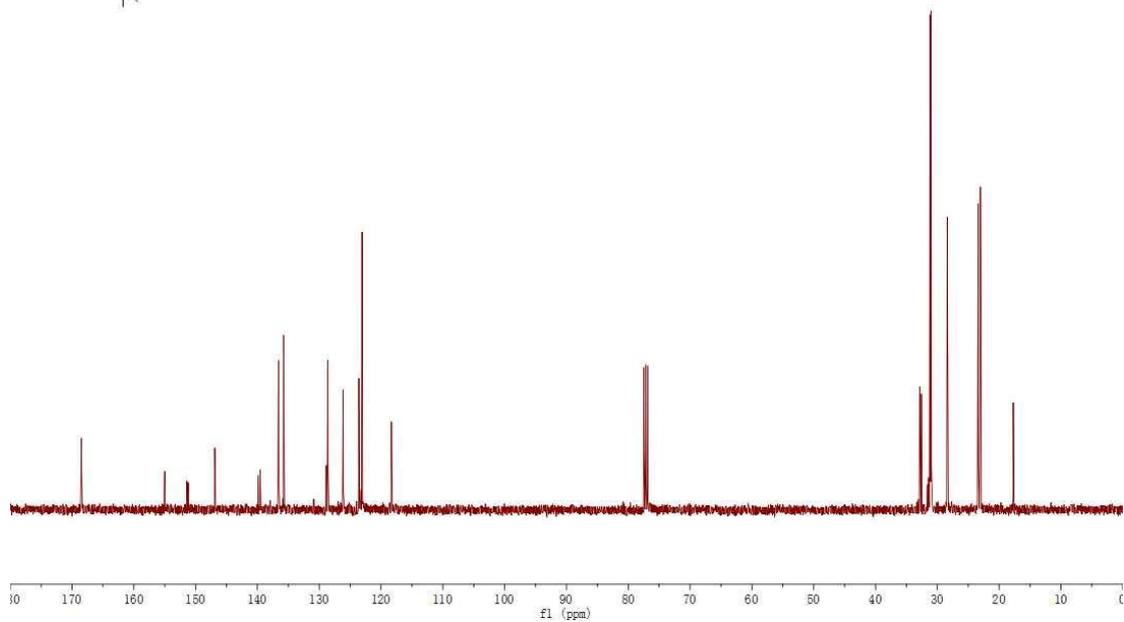
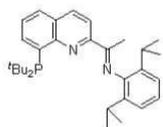
^{13}C NMR (101 MHz, CDCl_3) of **6b**



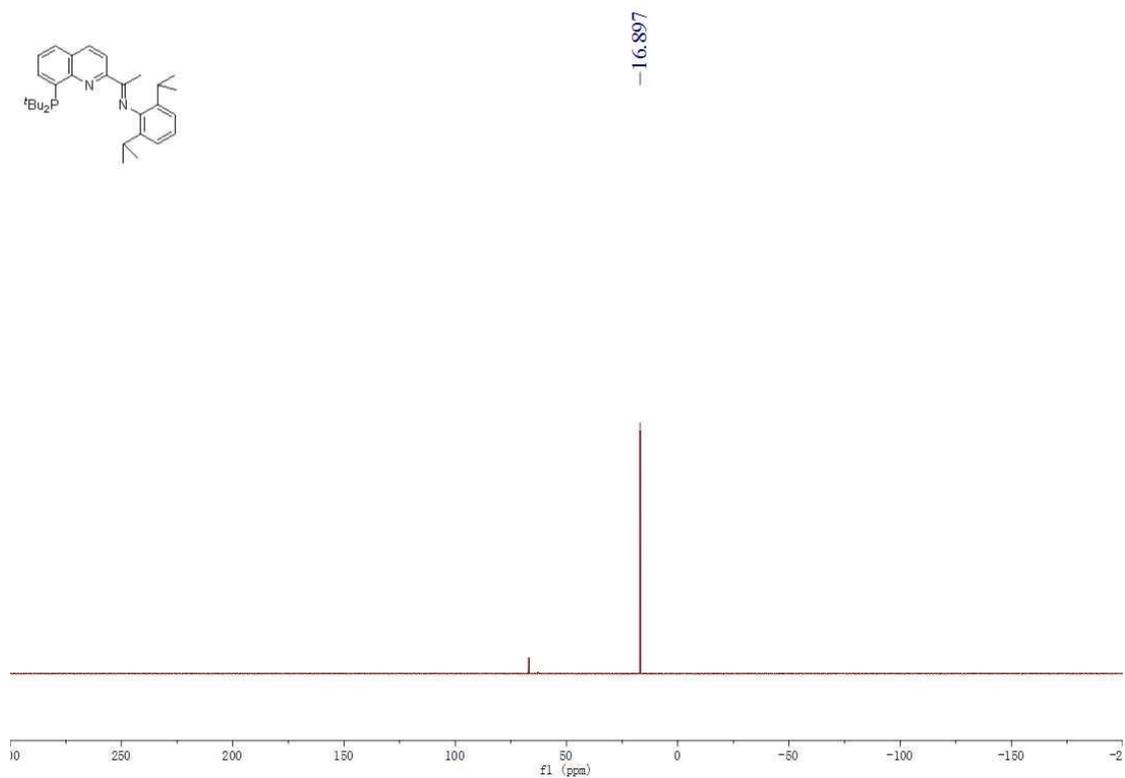
^{31}P NMR (162 MHz, CDCl_3) of **6b**



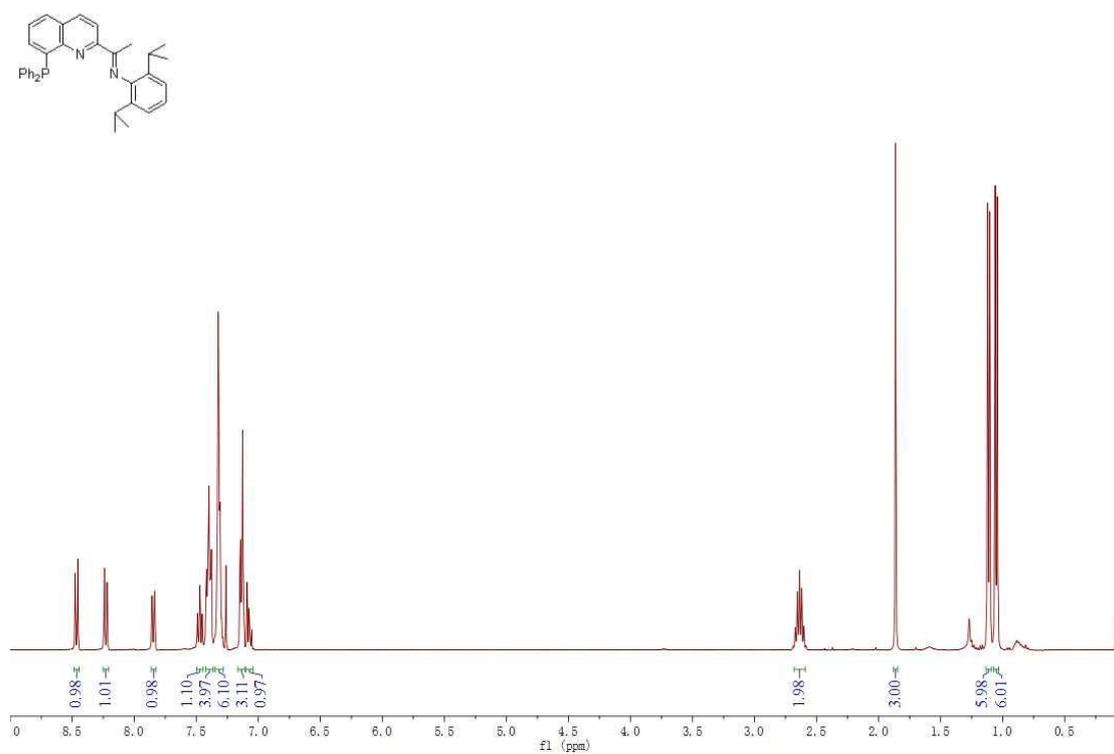
^1H NMR (400 MHz, CDCl_3) of **6c**



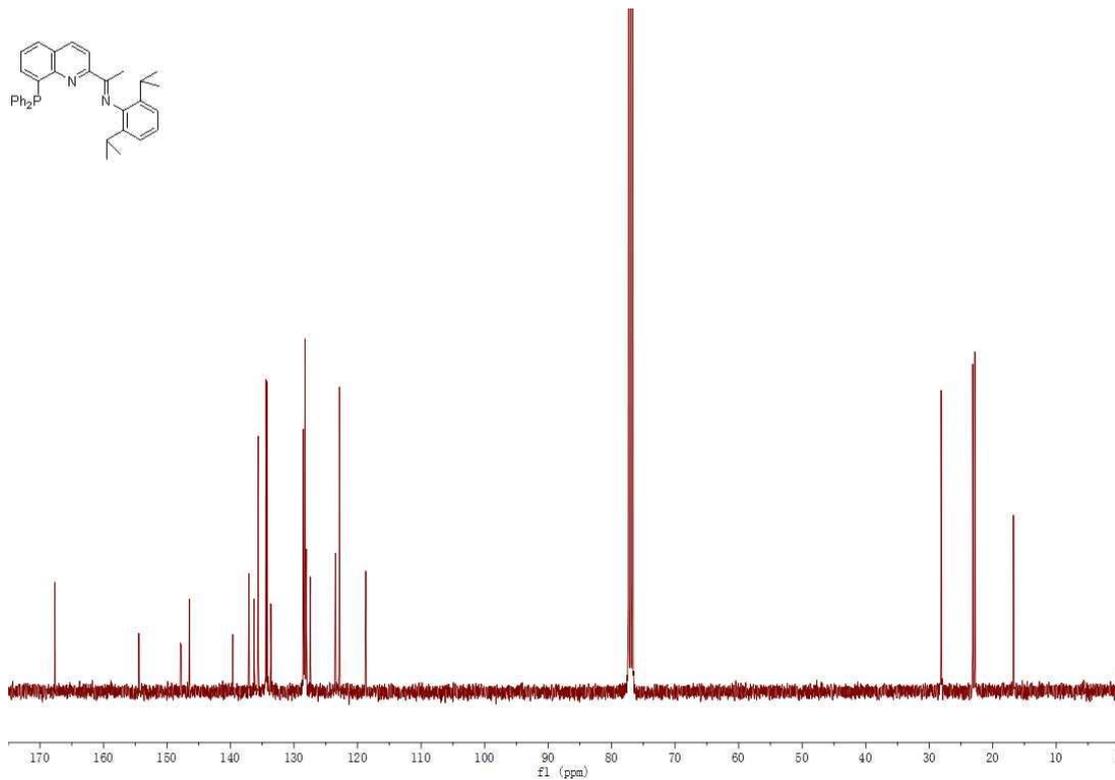
^{13}C NMR (101 MHz, CDCl_3) of **6c**



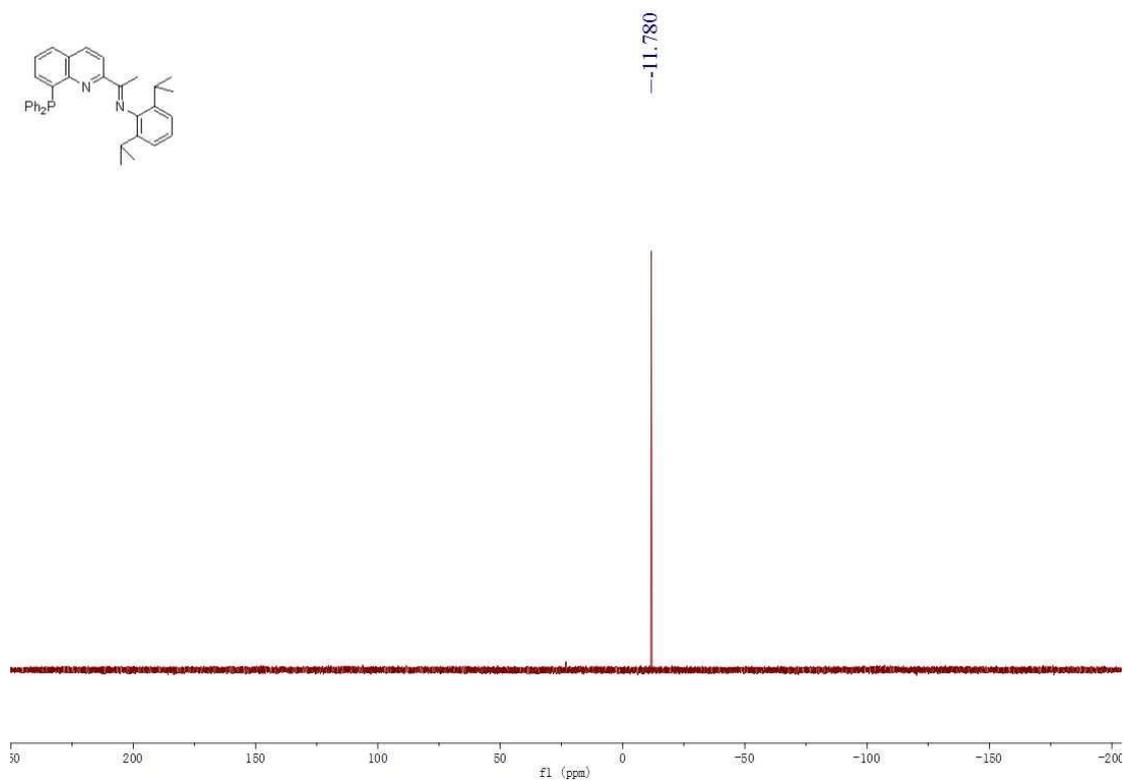
^{31}P NMR (162 MHz, CDCl_3) of **6c**



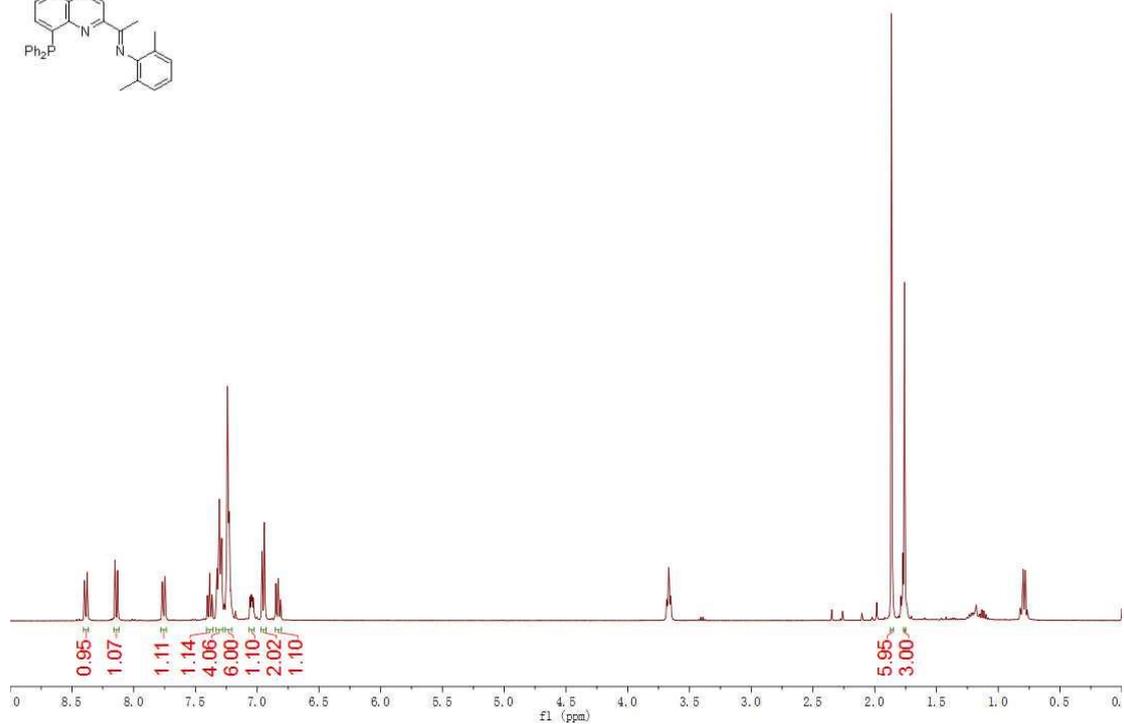
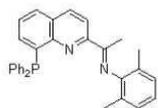
^1H NMR (400 MHz, CDCl_3) of **6d**



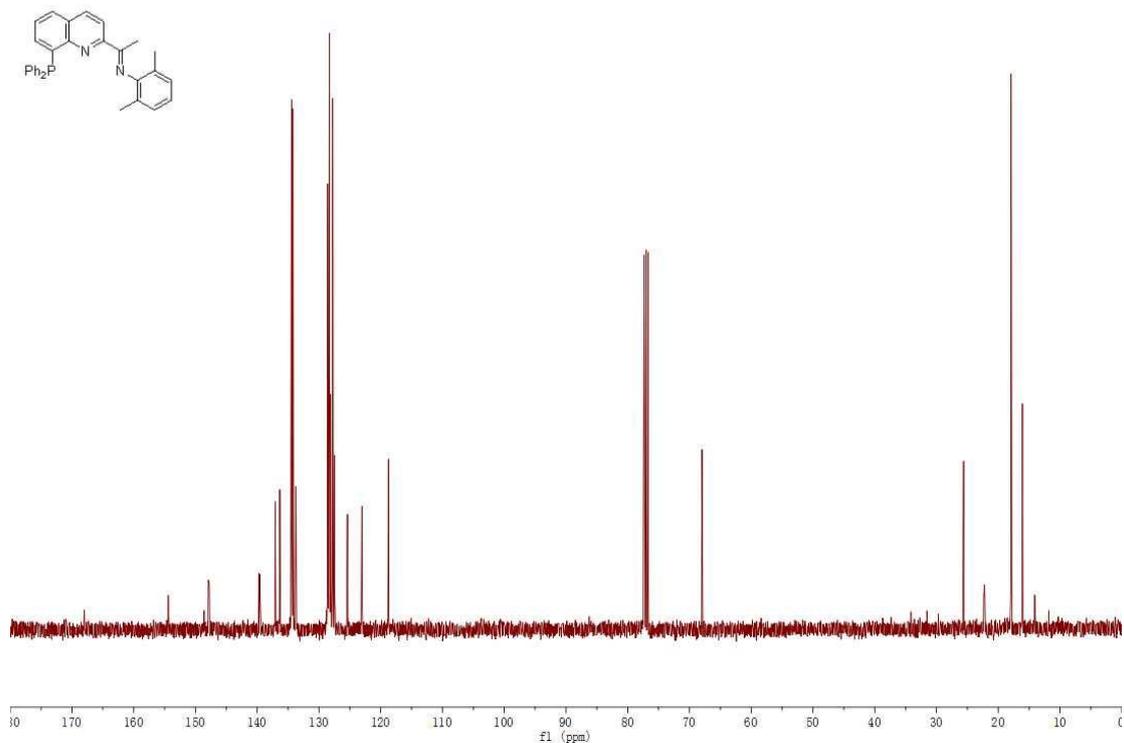
¹³C NMR (101 MHz, CDCl₃) of **6d**



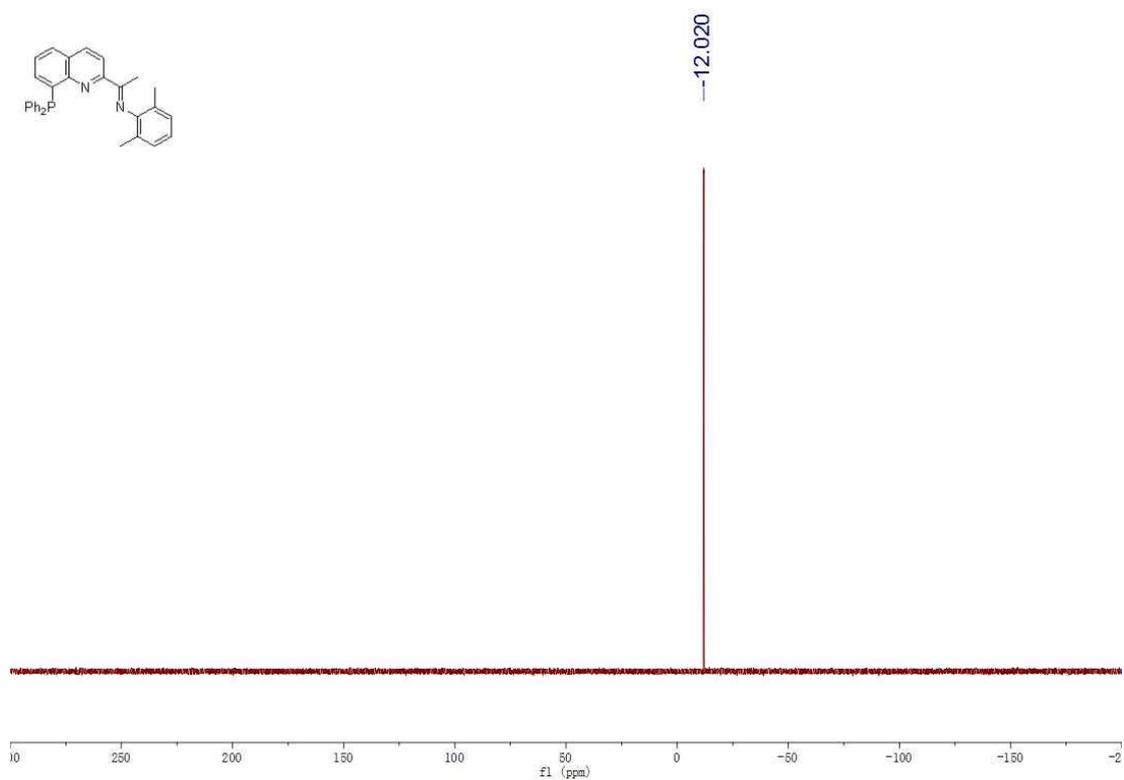
³¹P NMR (162 MHz, CDCl₃) of **6d**



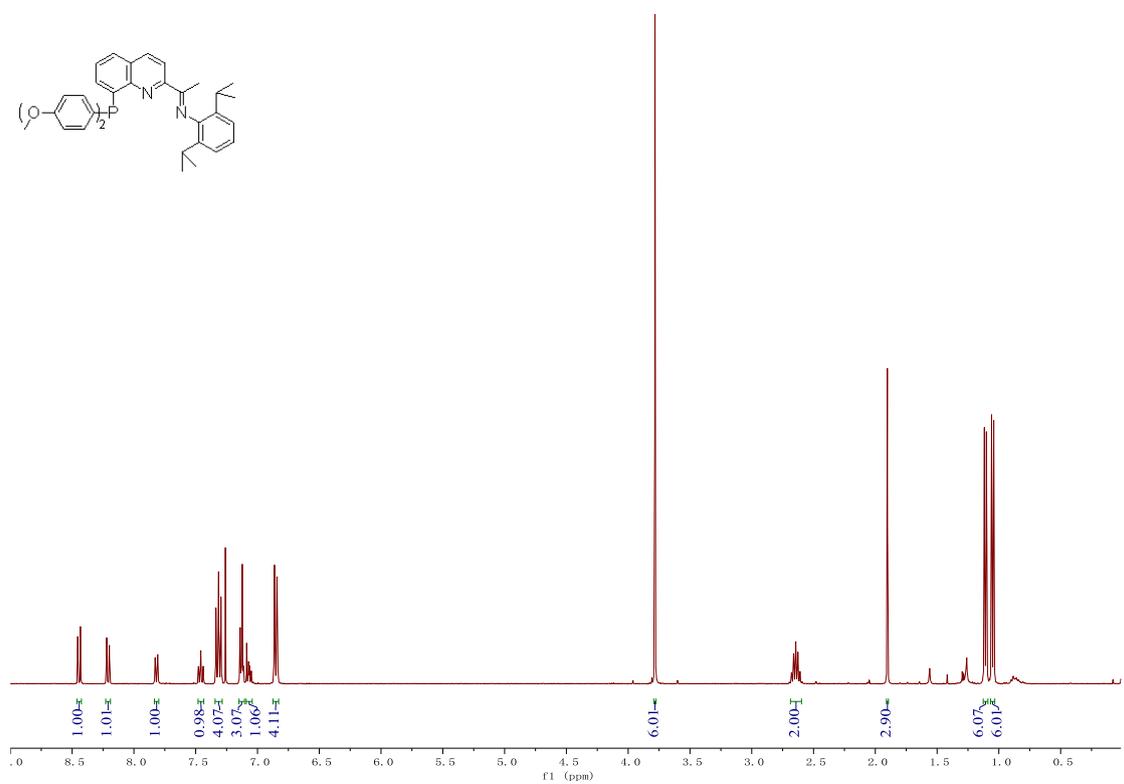
^1H NMR (400 MHz, CDCl_3) of **6e**



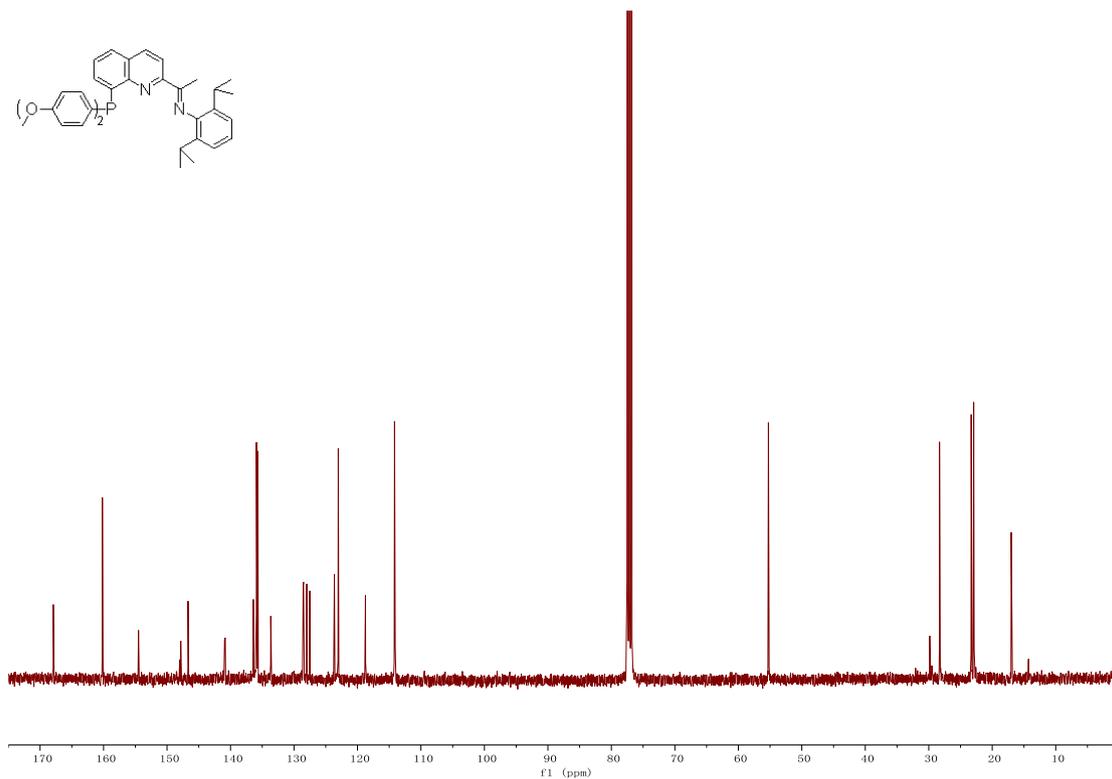
^{13}C NMR (101 MHz, CDCl_3) of **6e**



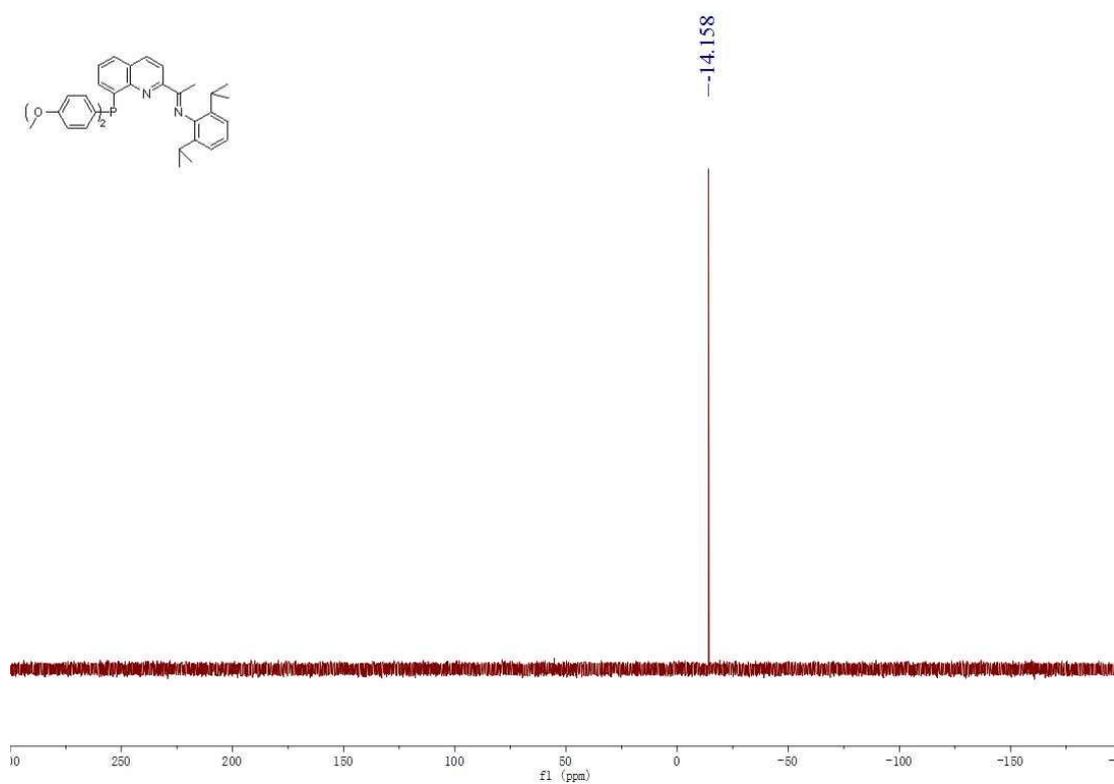
^{31}P NMR (162 MHz, CDCl_3) of **6e**



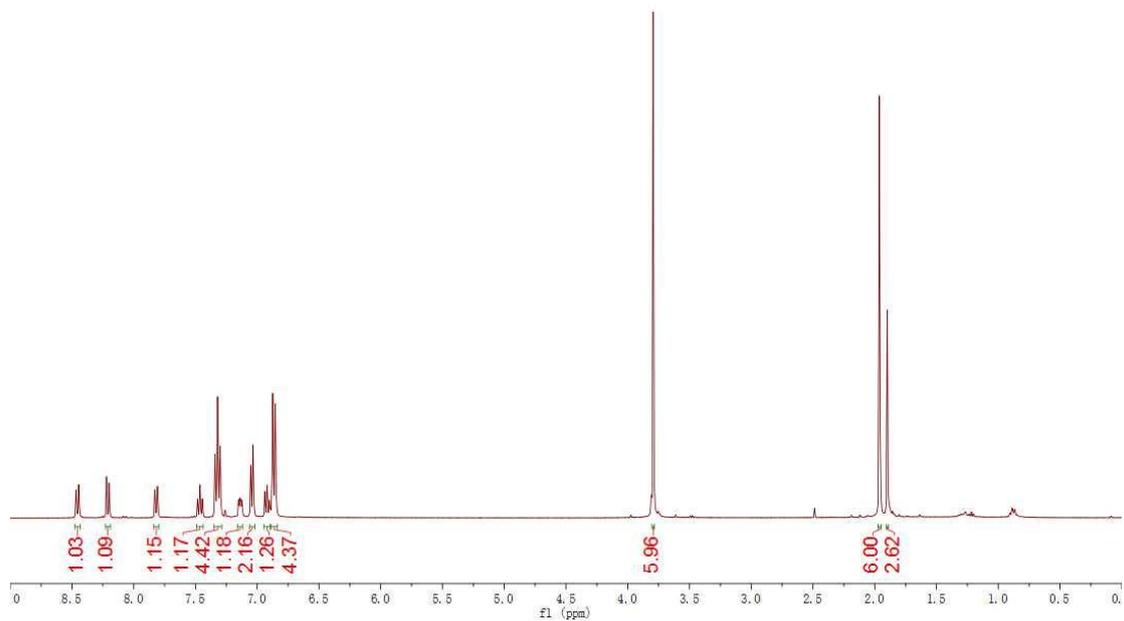
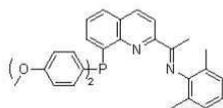
^1H NMR (400 MHz, CDCl_3) of **6f**



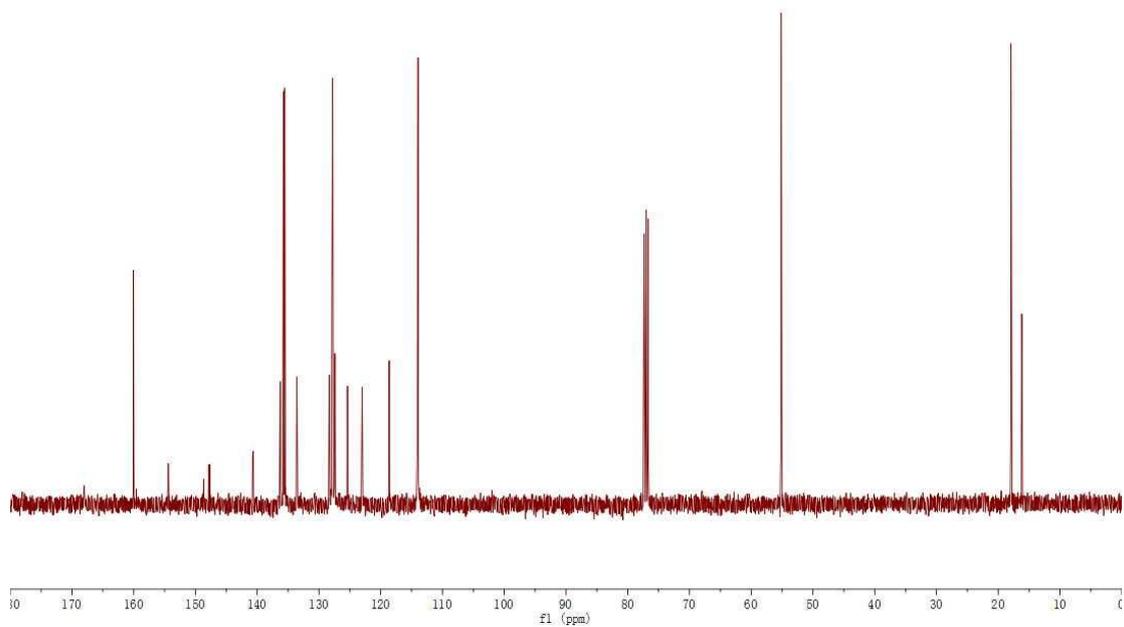
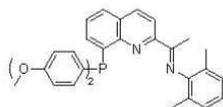
^{13}C NMR (101 MHz, CDCl_3) of **6f**



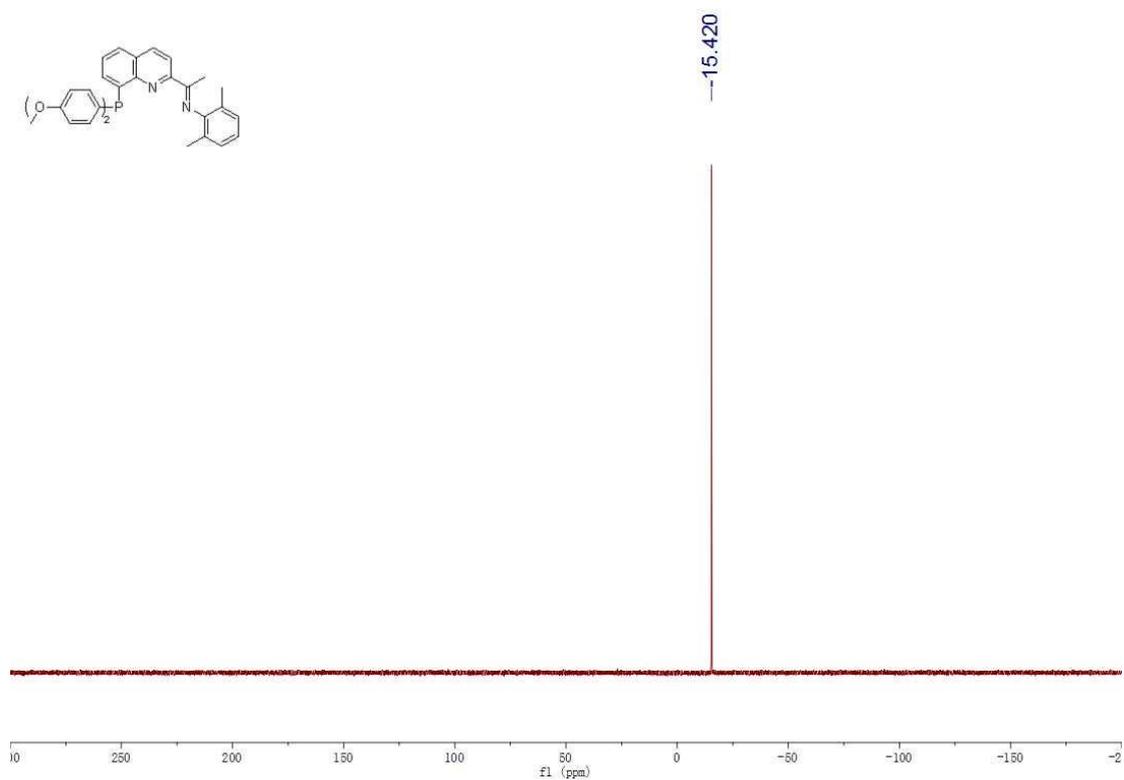
^{31}P NMR (162 MHz, CDCl_3) of **6f**



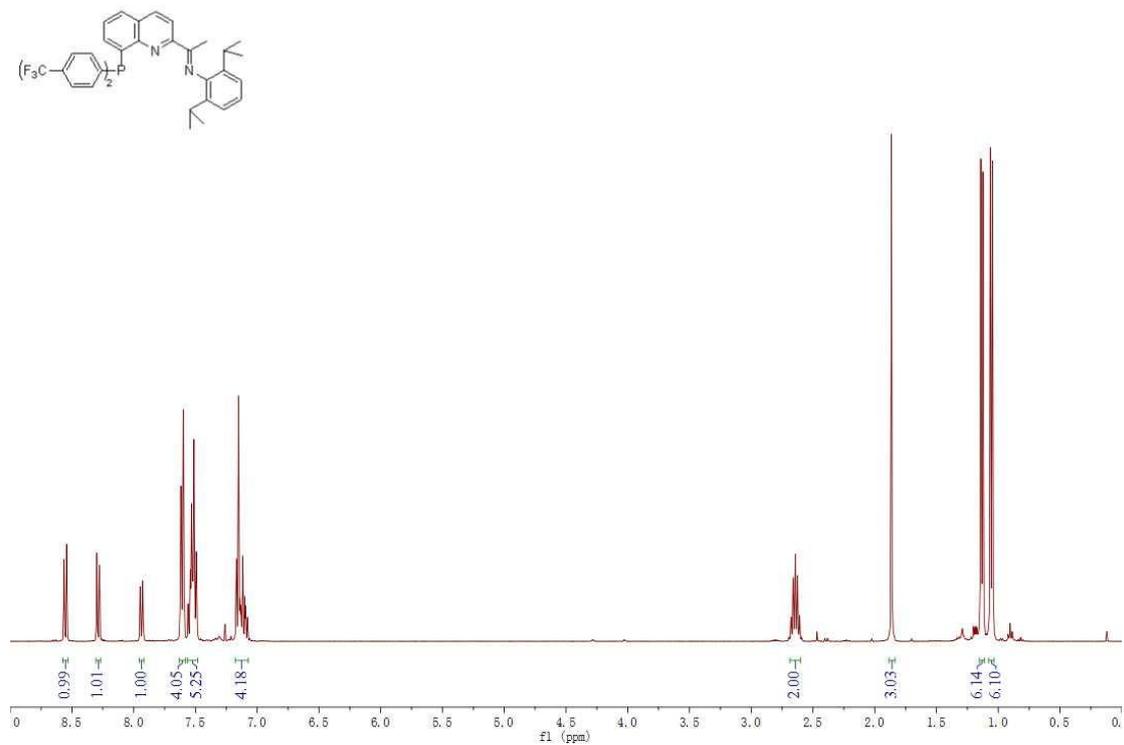
¹H NMR (400 MHz, CDCl₃) of **6g**



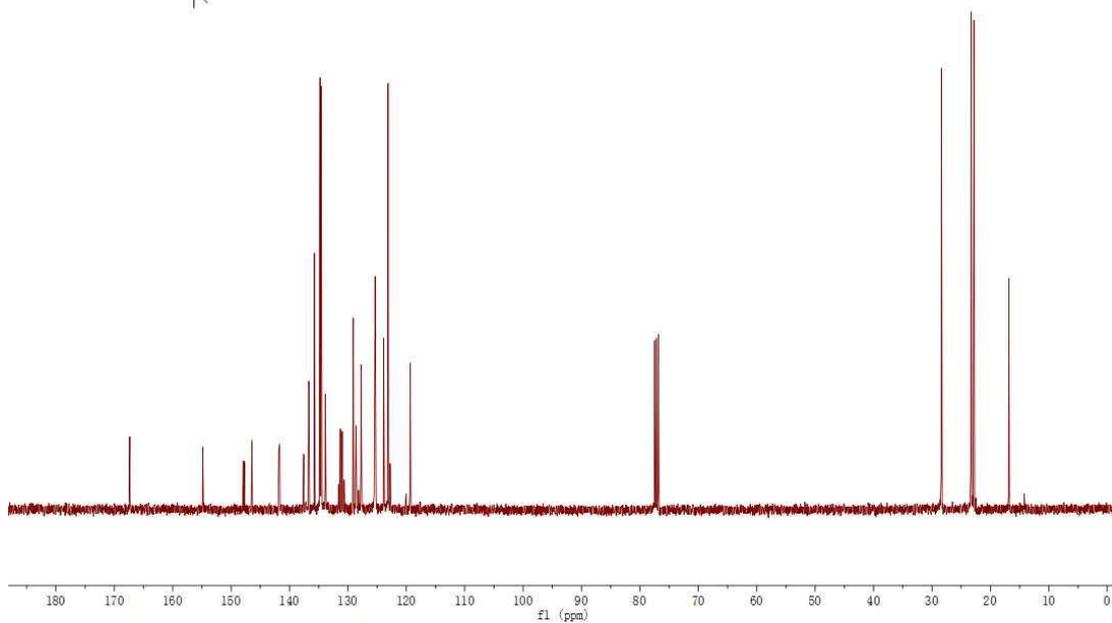
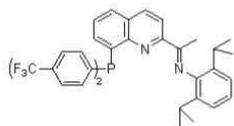
¹³C NMR (101 MHz, CDCl₃) of **6g**



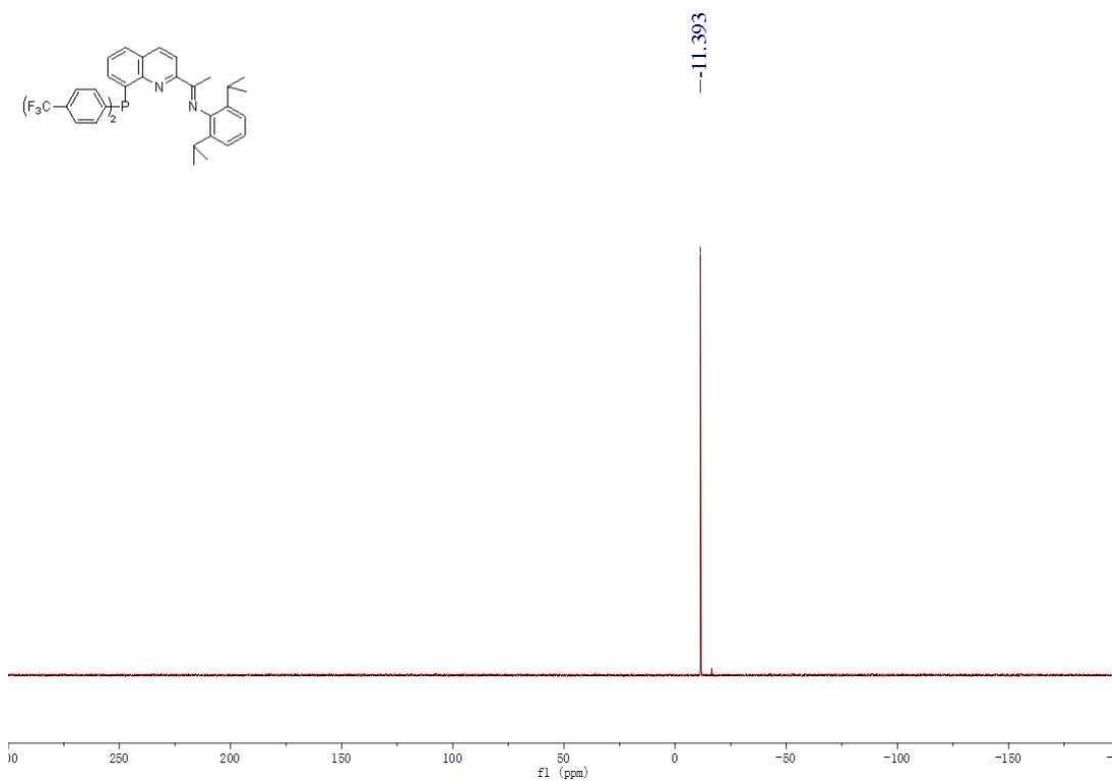
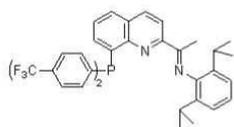
^{31}P NMR (162 MHz, CDCl_3) of **6g**



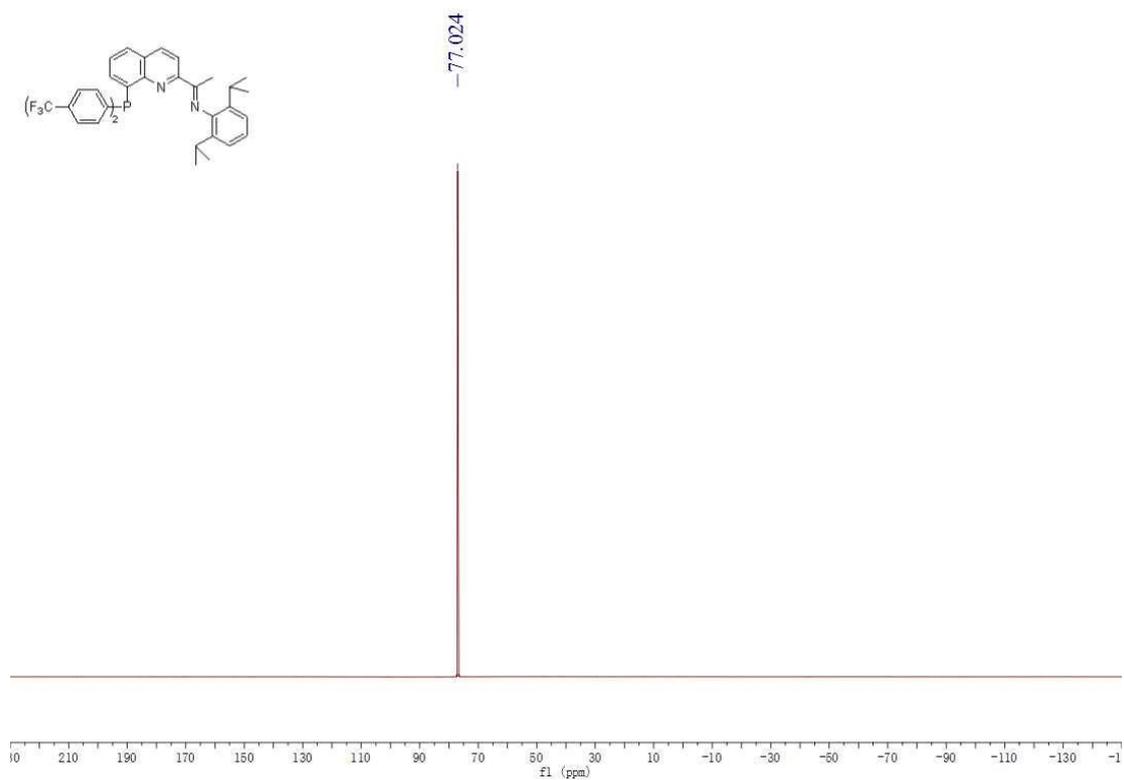
^1H NMR (400 MHz, CDCl_3) of **6h**



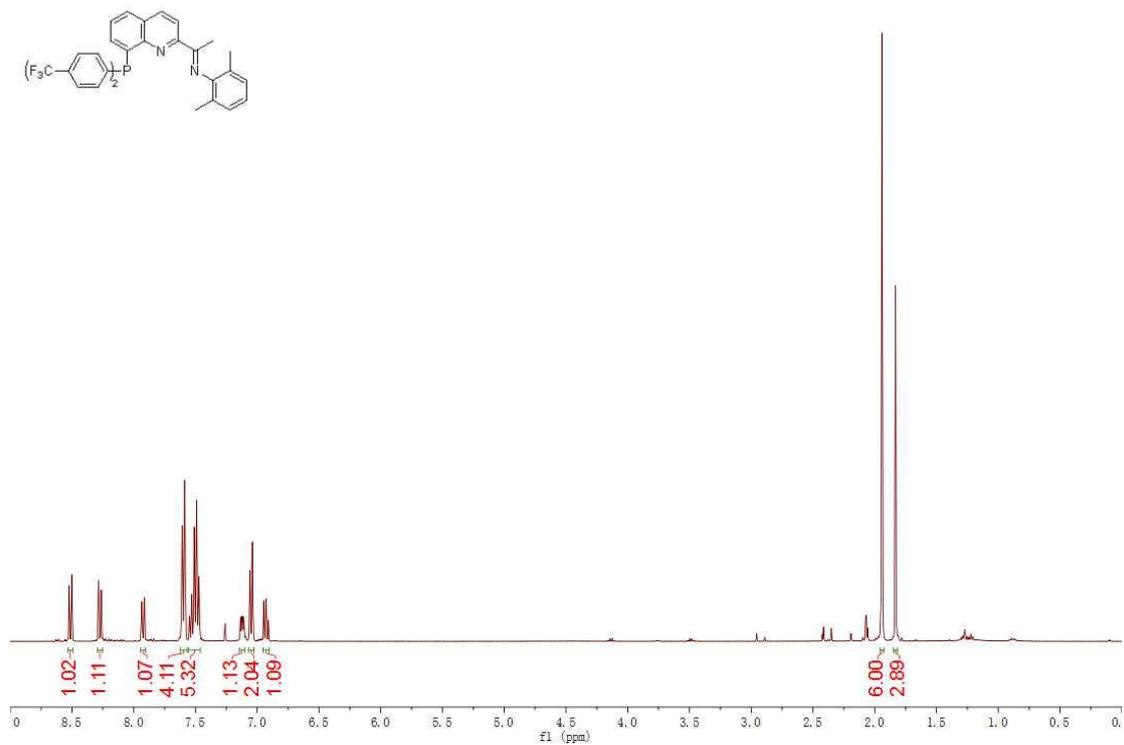
¹³C NMR (101 MHz, CDCl₃) of **6h**



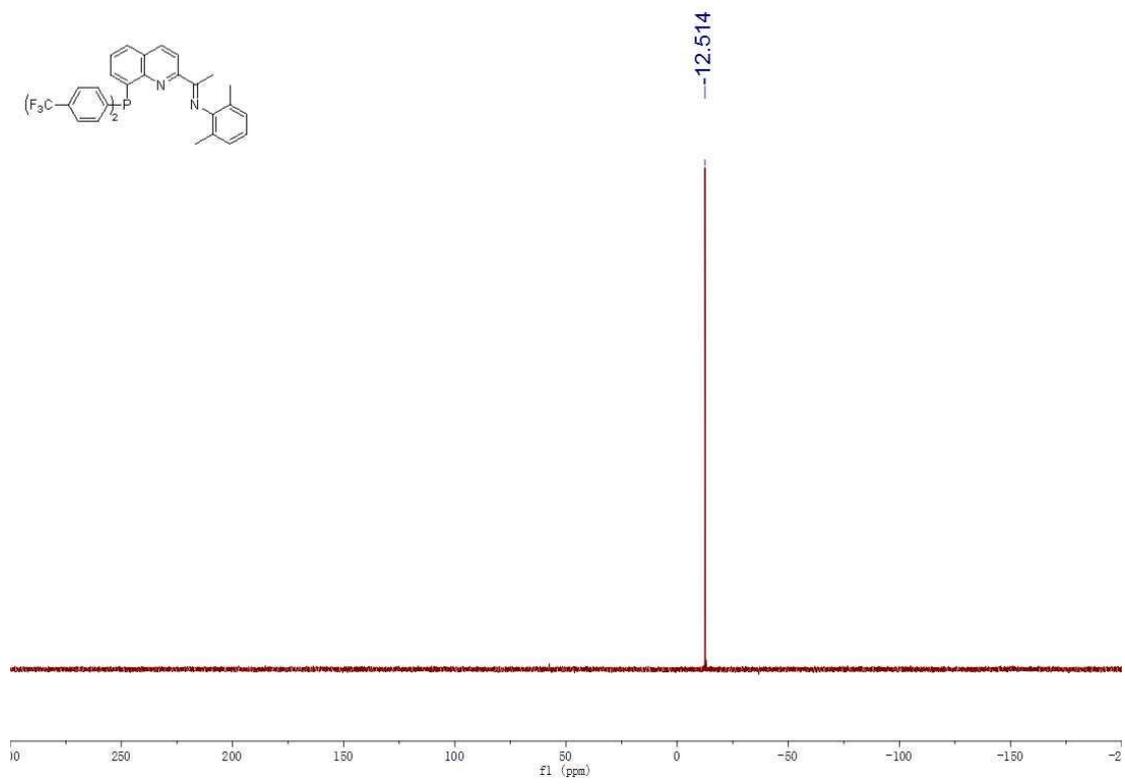
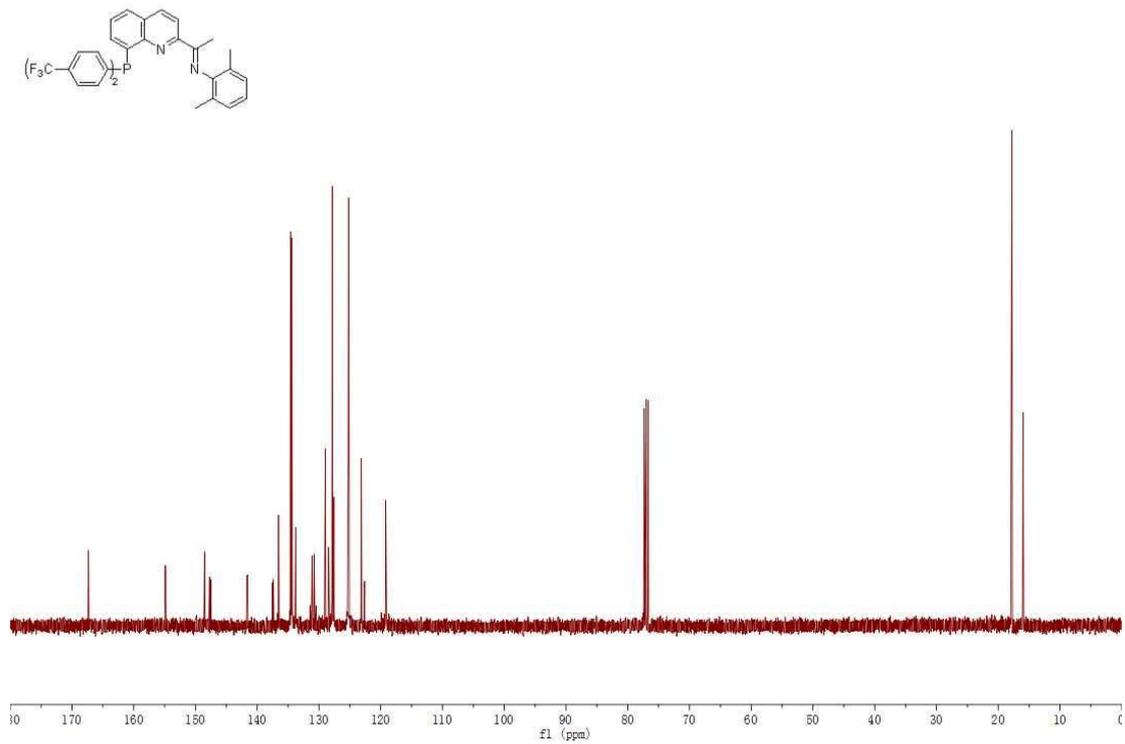
³¹P NMR (162 MHz, CDCl₃) of **6h**

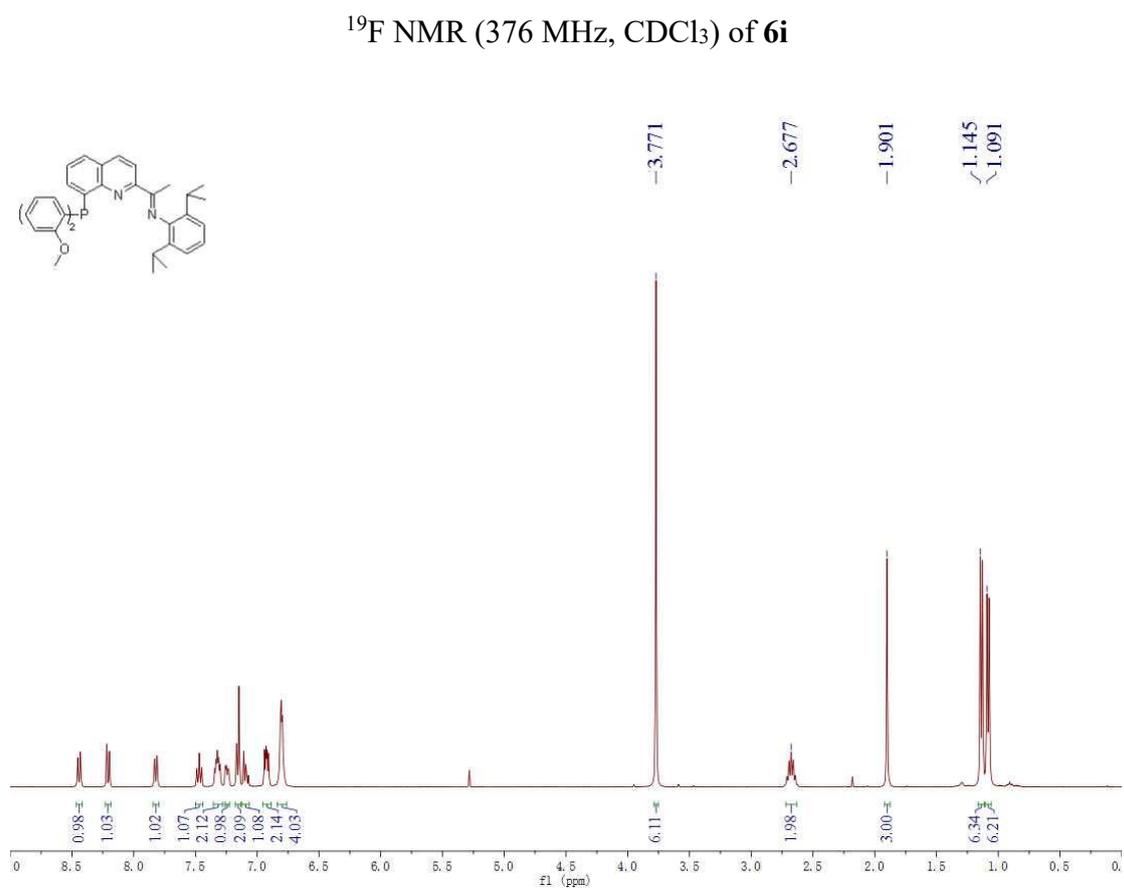
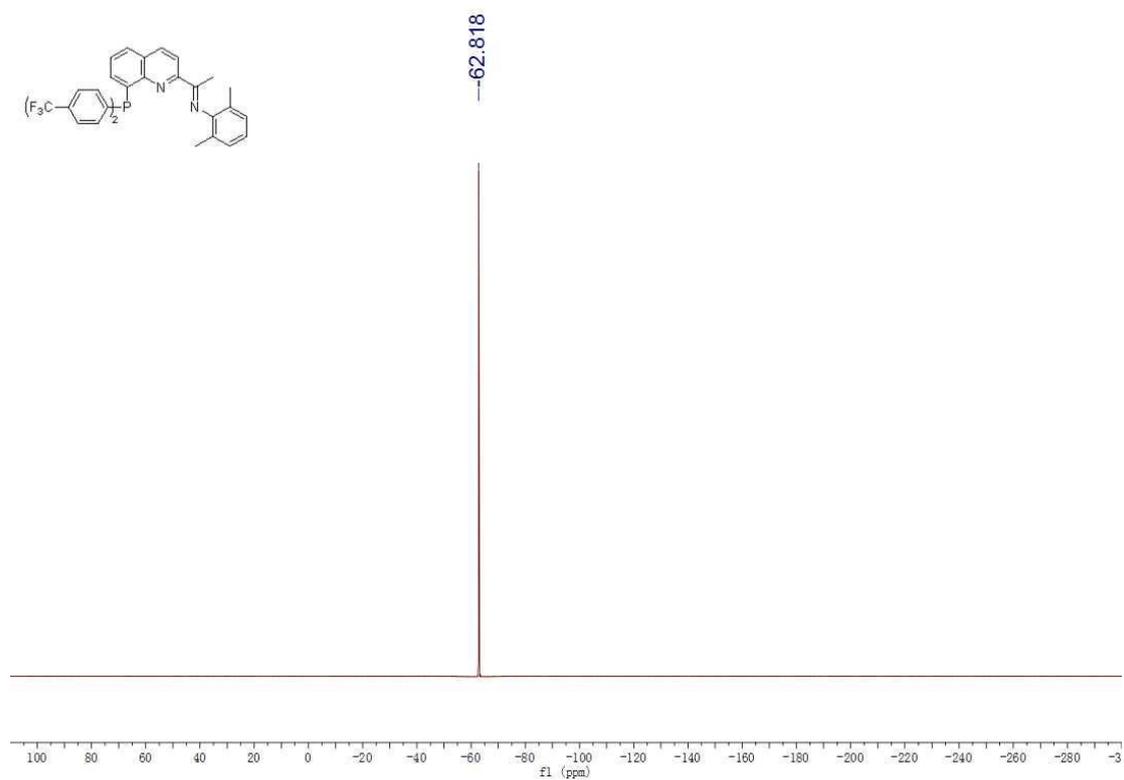


^{19}F NMR (376 MHz, CDCl_3) of **6h**

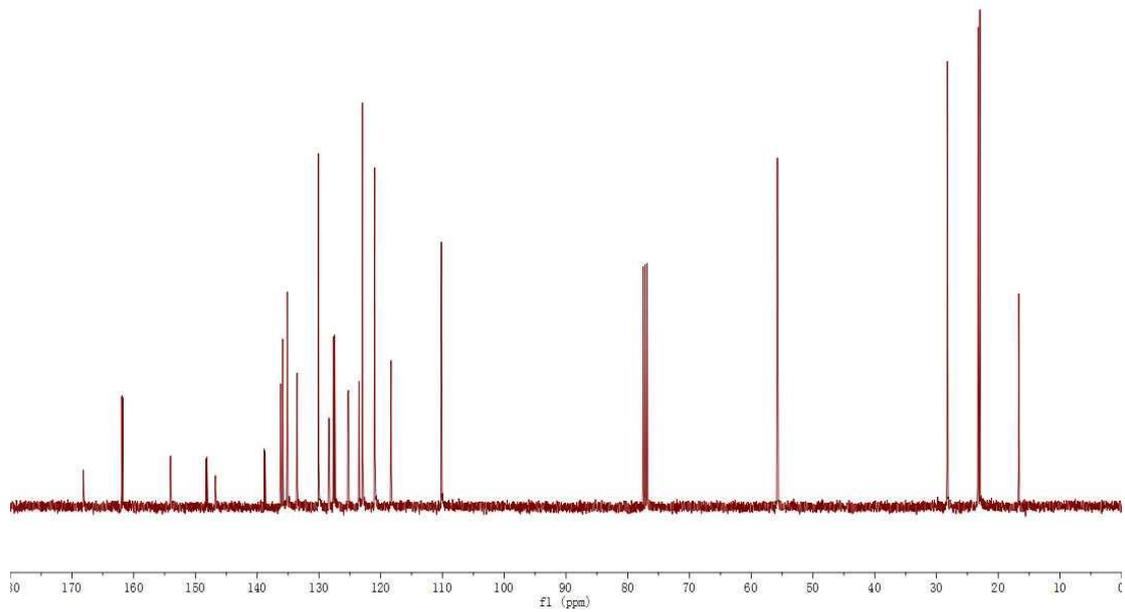
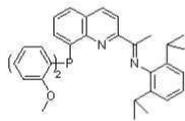


^1H NMR (400 MHz, CDCl_3) of **6i**

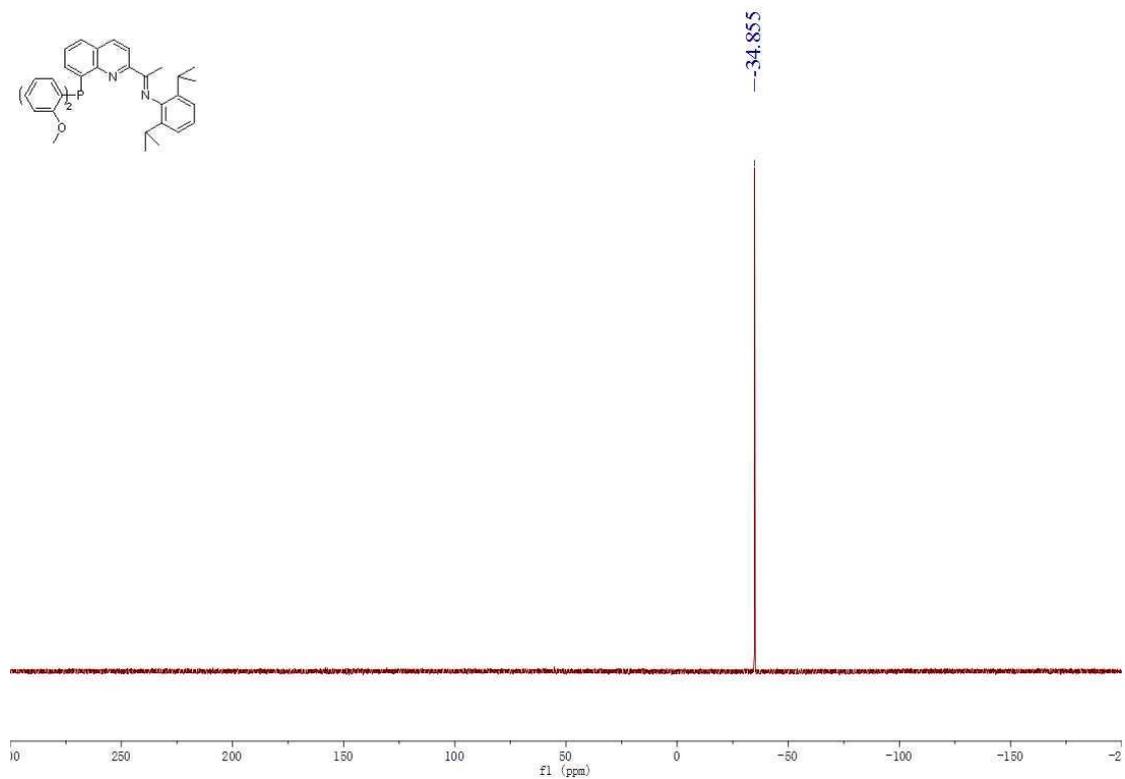
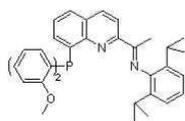




^1H NMR (400 MHz, CDCl_3) of **6j**



¹³C NMR (101 MHz, CDCl₃) of **6j**



³¹P NMR (162 MHz, CDCl₃) of **6j**