Supporting Information

for

Access to highly active and thermally stable iron procatalyst using bulky 2-[1-(2,6-Dibenzhydryl-4-methylphenylimino) ethyl]-6-[1-(arylimino)ethyl]pyridine ligands

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Content

Experimental section

General Consideration. All manipulations of air- or/and moisture-sensitive compounds were performed in a nitrogen atmosphere using standard Schlenk techniques. All solvents were purified and distilled by common techniques prior to use unless otherwise stated. Methylaluminoxane (a 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 1.93 M in heptane, 3A) were purchased from Akzo Nobel Corp. Other reagents were purchased from Aldrich or Acros Chemicals or local suppliers and used as received. NMR spectra were recorded on Bruker DMX 400/600 MHz instrument at ambient temperature using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Molecular weights and molecular weight distribution (MWD) of polyethylenes were determined by a PL-GPC220 at 150 ºC, with 1,2,4-trichlorobenzene as the solvent. DSC trace and melting points of polyethylene were obtained from the second scanning run on Perkin-Elmer DSC-7 at a heating rate of 10 ºC/min.

Preparation of the bis(imino)pyridines.

Synthesis of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-acetylpyridine 2,6-bis[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]pyridine (**L'**). A mixture of 2,6-diphenylmethyl-4-methylaniline (8.80 g, 20 mmol), 2,6-diacetylpyridine (3.26 g, 20 mmol) and a catalytic amount of *p*-toluenesulfonic acid in toluene (150 mL) was refluxed for 6 h. After solvent evaporation at reduced pressure, the crude product was purified by alumina-based column chromatography ($V_{\text{petroleum ether}}$:$V_{\text{ethyl acetate}}$ = 20: 1) to afford yellow 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-acetylpyridine (6.63 g, 51.5% isolated yield), and further elution gave yellow 2,6-bis[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]pyridine (**L'**) in 2.1g (10.5%). **2-[1-(2,6-Dibenzhydryl-4-methyl phenylimino)ethyl]-6-acetylpyridine**: Mp: 134-136 ºC. FT-IR (KBr, cm^{-1}): 3024, 2919, 2160, 2030, 1977, 1702, 1642 ($\nu_{C=N}$), 1493, 1466, 1365, 1235, 1118, 1076, 1031, 819, 765, 739, 698. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.16 (d, *J* = 7.8 Hz, 1H, Py *H*); 8.07 (d, *J* = 7.6 Hz, 1H, Py *H*); 7.84 (t, *J* = 7.8 Hz, 1H, Py *H*); 7.24 (t, *J* = 7.3 Hz, 4H, Ar *H*); 7.16 (d, *J*

= 7.3 Hz, 8H, Ar *H*); 7.01 (t, J = 7.3 Hz, 8H, Ar *H*); 6.68 (s, 2H, Ar *H*); 5.25 (s, 2H, 2 × C*H*); 2.66 (s, 3H, CH_3); 2.18 (s, 3H, CH_3); 1.07 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 200.3, 169.5, 155.5, 152.3, 145.9, 143.7, 142.6, 137.1, 132.2, 131.8, 129.9, 129.5, 128.8, 128.4, 128.1, 126.2, 126.1, 124.7, 122.4, 52.2, 52.1, 25.7, 21.4, 16.9, 16.8. Anal. Calcd for $C_{42}H_{36}N_2O$ (585): C, 86.27, H, 6.21; N, 4.79. Found: C, 86.06, H, 6.11; N, 4.42.

2,6-Bis[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]pyridine (**L'**): Mp: decomposed about 240 °C. FT-IR (KBr, cm^{-1}): 3058, 3023, 2921, 2162, 2024, 1978, 1638 ($\nu_{C=N}$), 1599, 1493, 1446, 1368, 1237, 1123, 1077, 1032, 795, 767, 749, 698. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.10 (d, *J* = 7.7 Hz, 2H, Py *H*); 7.77 (t, *J* = 7.8 Hz, 1H, Py *H*); 7.24 (t, *J* = 7.4 Hz, 8H, Ar *H*); 7.12 (d, *J* = 7.2 Hz, 16H, Ar *H*); 7.03 (t, 16H, *J* = 8.6 Hz, 16H, Ar *H*); 6.70 (s, 4H, Ar *H*); 5.30 (s, 4H, 4 × C*H*); 2.18 (s, 6H, 2 × CH_3); 0.94 (s, 6H, 2 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.4, 155.0, 146.3, 144.0, 142.8, 136.6, 132.4, 131.7, 130.0, 129.6, 128.8, 128.4, 128.2, 126.2, 122.1, 52.2, 21.5, 17.0. Anal. Calcd for $C_{75}H_{63}N_3$ (1006): C, 89.51, H, 6.31; N, 4.18. Found: C, 89.27, H, 5.94; N, 4.47.

Synthesis of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]- 6-[1-(2,6-dimethyl phenylimino)ethyl]pyridines (**L1**). A solution of 2-[1-(2,6-dibenzhydryl-4-methyl phenylimino)ethyl]-6-acetylpyridine (1.17 g, 2.0 mmol), 2,6-dimethylaniline (0.24 g, 2.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid in toluene(50 mL) was mixed and refluxed for 3 h. The solution was evaporated at reduced pressure. The residual solids was further purified by alumina-based column chromatography ($V_{petroleum\ ether}$:$V_{ethyl\ acetate}$ = 50 :1) to afford **L1** in 0.72 g (yellow, 52% yield). Mp: 203-204 ºC. FT-IR (KBr, cm^{-1}): 3058, 3023, 2916, 2361, 2161, 2034, 1641($\nu_{C=N}$), 1493, 1447, 1364, 1239, 1120, 1076, 1030, 763, 698. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.40 (d, *J* = 7.7 Hz, 1H, Py *H*); 8.06 (d, *J* = 7.7 Hz, 1H, Py *H*); 7.82 (t, *J* = 7.8 Hz, 1H, Py *H*); 7.25 (t, *J* = 7.7 Hz, 4H, Ar *H*); 7.14 (d, *J* = 7.3 Hz, 8H, Ar *H*); 7.04 (m, 11H, Ar *H*); 6.69 (s, 2H, Ar *H*); 5.29 (s, 2H, 2 × C*H*); 2.18 (s, 3H, CH_3); 2.11 (s, 3H, CH_3); 2.06 (s, 6H, 2 × CH_3); 1.13 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.0, 167.4, 155.2, 155.0, 148.9, 146.2, 143.8, 142.8, 136.7, 132.3, 131.7, 130.0, 129.6, 128.8, 128.3, 126.2,126.1, 125.5, 123.1, 122.4, 122.0, 118.1, 52.2, 21.4, 18.1, 17.7, 17.0, 16.5. Anal. Calcd for $C_{50}H_{45}N_3$ (688): C, 87.30, H, 6.59; N, 6.11. Found: C, 86.96, H, 6.34; N, 5.92.

Synthesis of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diethyl phenylimino)ethyl]pyridines (**L2**). Using the same procedure as for the synthesis of **L1**, **L2** was obtained as a yellow powder in 0.69 g (48%). Mp: 203-204 °C. FT-IR (KBr, cm^{-1}): 3022, 2966, 2965, 2868, 2162, 2032, 1978, 1642($\nu_{C=N}$), 1494, 1453, 1363, 1238, 1120, 1074, 765, 699. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.38 (d, *J* = 7.7 Hz, 1H, Py *H*); 8.05 (d, *J* = 7.7 Hz, 1H, Py *H*); 7.82 (t, *J* = 7.7 Hz, 1H, Py *H*); 7.24 (t, *J* = 6.7 Hz, 4H, Ar *H*); 7.16 (m, 10H, Ar *H*); 7.04 (m, 9H, Ar *H*); 6.69 (s, 2H, Ar *H*); 5.29 (s, 2H, 2 × C*H*); 2.44 (m, 4H, 2 × CH_2); 2.18 (s, 3H, CH_3); 2.12 (s, 3H, CH_3); 1.14 (m, 9H, 3 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.1, 167.2, 155.3, 155.1, 148.0, 146.2, 143.8, 142.8, 136.8, 132.3, 131.7, 130.0, 129.6, 128.8, 138.4, 138.1, 126.2,126.1, 126.0, 123.4, 122.4, 122.0, 52.2, 24.7, 21.4, 17.0, 16.9, 13.9. Anal. Calcd for $C_{52}H_{49}N_3$ (715): C, 87.23, H, 6.90; N, 5.87. Found: C, 87.12, H, 6.61; N, 5.99.

Synthesis of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diisopropylphenylimino)ethyl]pyridines (**L3**). Using the same procedure as for the synthesis of **L1**, **L3** was obtained as a yellow powder in 0.82 g (55%). Mp: 165-167 ºC. FT-IR (KBr, cm^{-1}): 3060, 3025, 2958, 2927, 2867, 2161, 2035, 1978, 1635($\nu_{C=N}$), 1494, 1451, 1367, 1237, 1124, 828, 767, 698. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.38 (d, *J* = 7.7 Hz, 1H, Py *H*); 8.06 (d, *J* = 7.7 Hz, 1H, Py *H*); 7.83 (t, *J* = 7.7 Hz, 1H, Py *H*); 7.23 (t, *J* = 6.7 Hz, 4H, Ar *H*); 7.17 (m, 11H, Ar *H*); 7.04 (t, 8H, *J* = 6.7 Hz, Ar *H*); 6.69 (s, 2H, Ar *H*); 5.29 (s, 2H, 2 × C*H*); 2.78 (m, 2H, 2 × C*H*); 2.18 (s, 3H, CH_3); 2.14 (s, 3H, CH_3); 1.17 (d, *J* = 6.7 Hz, 12H, 4 × CH_3); 1.14 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.1, 167.3, 155.3, 155.1, 146.6, 146.2, 143.8, 142.8, 136.8, 135.9, 132.3, 131.7, 130.0, 129.6, 128.8, 128.1, 126.2, 126.1, 123.7, 123.1, 122.3, 122.0, 52.2, 28.4, 23.4, 23.1, 21.4, 17.3, 17.0. Anal. Calcd for $C_{54}H_{53}N_3$ (744): C, 87.17, H, 7.18; N, 5.65. Found: C, 86.88, H, 7.11; N, 5.70.

Synthesis of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,4,6-trimethylphenylimino)ethyl]pyridines (**L4**). Using the same procedure as for the synthesis of **L1**, **L4** was obtained as a yellow powder in 0.65 g (46%). Mp: 213-215 °C. FT-IR (KBr, cm^{-1}): 3055, 3025, 2912, 2164, 2029, 1978, 1635($\nu_{C=N}$), 1490, 1449, 1360, 1211, 1119, 760, 696. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.38 (d, *J* = 7.3 Hz, 1H, Py *H*);

8.05 (d, *J* = 7.2 Hz, 1H, Py *H*); 7.81 (t, *J* = 7.7 Hz, 1H, Py *H*); 7.24 (t, *J* = 7.4 Hz, 4H, Ar *H*); 7.16 (d, *J* = 7.2 Hz, 8H, Ar *H*); 7.03 (t, 8H, *J* = 7.2 Hz, Ar *H*); 6.89 (s, 2H, Ar *H*); 6.69 (s, 2H, Ar *H*); 5.29 (s, 2H, 2 × C*H*); 2.29 (s, 3H, CH_3); 2.23 (s, 3H, CH_3); 2.18 (s, 3H, CH_3), 2.02 (s, 6H, 2 × CH_3); 1.13 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.1, 167.7, 155.2, 146.4, 143.8, 142.8, 136.7, 132.3, 131.7, 130.0, 129.6, 128.8, 128.7, 128.4, 128.1, 126.2, 126.1, 125.4, 122.3, 122.0, 52.2, 21.5, 20.9, 18.0, 17.0, 16.5. Anal. Calcd for $C_{51}H_{47}N_3$ (701): C, 87.26, H, 6.75; N, 5.99. Found: C, 87.21, H, 6.38; N, 6.15.

Synthesis of 2-[1-(2,6-dibenzhydryl-4-methylphenylimino)ethyl]-6-[1-(2,6-diethyl-4-methylphenylimino)ethyl]pyridines (**L5**). Using the same procedure as for the synthesis of **L1**, **L5** was obtained as a yellow powder in 0.60 g (41%). Mp: 200-202 °C. FT-IR (KBr, cm^{-1}): 3061, 3025, 2963, 2929, 2870, 2162, 2030, 1979, 1637($\nu_{C=N}$), 1494, 1447, 1363, 1209, 1119, 1075, 1031, 860, 743, 695. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.37 (d, *J* = 7.7 Hz, 1H, Py *H*); 8.05 (d, *J* = 7.7 Hz, 1H, Py *H*); 7.81 (t, *J* = 7.7 Hz, 1H, Py *H*); 7.24 (t, *J* = 7.4 Hz, 4H, Ar *H*); 7.17 (d, *J* = 7.2 Hz, 8H, Ar *H*); 7.04 (t, 8H, *J* = 7.2 Hz, Ar *H*); 6.93 (s, 2H, Ar *H*); 6.69 (s, 2H, Ar *H*); 5.29 (s, 2H, 2 × C*H*); 2.41 (m, 4H, 2 × CH_2); 2.34 (s, 3H, CH_3); 2.18 (s, 3H, CH_3); 2.12 (s, 3H, CH_3); 1.14 (m, 9H, 3 × CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 170.1, 167.4, 155.2, 146.2, 143.8, 142.8, 136.7, 132.5, 132.3, 131.7, 130.0, 129.6, 128.8, 128.3, 128.1, 126.8, 126.2, 126.1, 122.3, 121.9, 52.2, 24.7, 21.4, 21.1, 17.0, 16.8, 14.0. Anal. Calcd for $C_{53}H_{51}N_3$ (730): C, 87.20, H, 7.04; N, 5.76. Found: C, 87.02, H, 6.83; N, 5.91.

Preparation of the iron complexes.

The complexes **Fe1**-**Fe5** and **Fe'** were synthesized by the reaction of $FeCl_2{\cdot}4H_2O$ with the corresponding ligands in ethanol. A typical synthetic procedure for **Fe1** can be described as follows: The ligand **L1** (151 mg, 0.22 mmol) and $FeCl_2{\cdot}4H_2O$ (79.5 mg, 0.20 mmol) were added to a Schlenk tube, followed by the addition of freshly distilled ethanol (5 mL) with rapid stirring at room temperature. The solution turned blue immediately, and a blue precipitate was formed. The reaction mixture was stirred for 8 h, and then the precipitate was washed with diethyl ether (3 × 5 mL) and dried to give the pure product as a blue powder in 145 mg (88.7%). ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 79.20 (s, 1H, Py

H$_m$); 77.89 (s, 1H, Py *H*$_m$); 70.50 (s, 1H, Py *H*$_p$); 23.51 (s, 3H, C*H*$_3$); 14.42 (s, 2H, Ar *H*$_m$); 14.34 (s, 2H, Ar *H*$_m$); 7.07 (s, 6H, aryl *H*); 6.78 (s, 4H, aryl *H*); 4.74 (s, 10H, aryl *H*); 1.27 (s, 2H, 2 × C*H*); -3.67 (s, 6H, 2 × C*H*$_3$); -14.29 (s, 1H, Ar *H*$_p$); -26.00 (s, 3H, N=CC*H*$_3$); -43.16 (s, 3H, N=CC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 191.6, 154.2, 143.8, 143.7, 127.8, 127.2, 126.2, 124.4, 124.1, 54.8, 40.9, 40.8. FT-IR (KBr; cm^{-1}): 3058, 3024, 2913, 2161, 2016, 1978, 1581($\nu_{C=N}$), 1493, 1469, 1444, 1371, 1266, 1216, 1097, 1035, 813, 782, 766, 749, 699. Anal. Calcd for $C_{50}H_{45}Cl_2FeN_3$ (815): C, 73.72; H, 5.57; N, 5.16. Found: C, 73.42; H, 5.34; N, 5.44.

Data for **Fe2** are as follows. Yield: 144 mg (85.2%). ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): δ 79.96 (s, 1H, Py *H*$_m$); 77.34 (s, 1H, Py *H*$_m$); 75.26 (s, 1H, Py *H*$_p$); 24.05 (s, 3H, C*H*$_3$); 14.68 (s, 2H, Ar *H*$_m$); 14.16 (s, 2H, Ar *H*$_m$); 7.17 (s, 6H, aryl *H*); 6.78 (s, 4H, aryl *H*); 4.67 (s, 4H, aryl *H*); 4.59 (s, 6H, Ar *H*$_m$); 1.27 (s, 2H, 2 × C*H*); -4.58 (s, 4H, 2 × C*H*$_2$); -4.81 (s, 6H, 2 × C*H*$_3$); -13.59 (s, 1H, Ar *H*$_p$); -32.05 (s, 3H, N=CC*H*$_3$); -40.38 (s, 3H, N=CC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$, TMS): δ 191.7, 154.5, 143.1, 129.8, 129.4, 127.9, 126.9, 126.2, 124.4, 124.0, 54.5, 43.1, 39.8, 18.63. FT-IR (KBr, cm^{-1}): 3058, 3026, 2968, 2915, 2876, 2162, 2030, 1979, 1962, 1580 ($\nu_{C=N}$), 1494, 1444, 1371, 1266, 1214, 1077, 1032, 808, 770, 746, 701. Anal. Calcd for $C_{52}H_{49}Cl_2FeN_3$ (843): C, 74.11; H, 5.86; N, 4.99. Found: C, 74.01; H, 5.69; N, 5.12.

Data for **Fe3** are as follows. Yield: 164 mg (94.3%). ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): δ 82.10 (s, 1H, Py *H*$_m$); 81.10 (s, 1H, Py *H*$_m$); 76.22 (s, 1H, Py *H*$_p$); 24.29 (s, 3H, C*H*$_3$); 14.78 (s, 2H, Ar *H*$_m$); 13.49 (s, 2H, Ar *H*$_m$); 7.31 (s, 6H, aryl *H*); 6.87 (s, 4H, aryl *H*); 4.44 (s, 4H, aryl *H*); 4.30 (s, 6H, Ar *H*$_m$); 1.28 (s, 2H, 2 × C*H*); -4.54 (s, 6H, 2 × C*H*$_3$); -5.69 (s, 2H, 2 × C*H*); -6.25 (s, 6H, 2 × C*H*$_3$); -13.19 (s, 1H, Ar *H*$_p$); -36.89 (s, 3H, N=CC*H*$_3$); -39.80 (s, 3H, N=CC*H*$_3$). FT-IR (KBr, cm^{-1}): 3061, 3023, 2917, 2865, 2161, 2030, 2012, 1978, 1962, 1582 ($\nu_{C=N}$), 1494, 1444, 1371, 1268, 1214, 1200, 1100, 1077, 1031, 795, 770, 745, 701. Anal. Calcd for $C_{54}H_{53}Cl_2FeN_3$ (871): C, 74.48; H, 6.13; N, 4.83. Found: C, 74.21; H, 6.03; N, 4.99.

Data for **Fe4** are as follows. Yield: 142 mg (85.9%). ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): δ 79.03 (s, 1H, Py *H*$_m$); 77.20 (s, 1H, Py *H*$_m$); 72.85 (s, 1H, Py *H*$_p$); 23.67 (s, 3H, C*H*$_3$); 23.35 (s, 3H, C*H*$_3$); 14.62 (s, 2H, Ar *H*$_m$); 13.66 (s, 2H, Ar *H*$_m$); 7.13 (s, 6H, aryl *H*); 6.84

(s, 4H, aryl *H*); 4.63 (s, 10H, aryl *H*); 1.26 (s, 2H, 2 × C*H*); -3.81 (s, 6H, 2 × CH_3); -28.23 (s, 3H, N=CCH_3); -42.00 (s, 3H, N=CCH_3). FT-IR (KBr, cm^{-1}): 3436, 3056, 3041, 3026, 2969, 2917, 2162, 2022, 1978, 1963, 1582 ($\nu_{C=N}$), 1494, 1444, 1365, 1365, 1220, 1078, 1051, 1032, 769, 701. Anal. Calcd for $C_{51}H_{47}Cl_2FeN_3$ (829): C, 73.92; H, 5.72; N, 5.07. Found: C, 73.66; H, 5.41; N, 5.01.

Data for **Fe5** are as follows. Yield: 156 mg (91.1%). ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): δ 79.61 (s, 1H, Py H_m); 76.51 (s, 1H, Py H_m); 76.22 (s, 1H, Py H_p); 24.13 (s, 3H, CH_3); 23.14 (s, 3H, CH_3); 14.99 (s, 2H, Ar H_m); 13.37 (s, 2H, Ar H_m); 7.24 (s, 6H, aryl *H*); 6.84 (s, 4H, aryl *H*); 4.56 (s, 4H, aryl *H*); 4.56 (s, 6H, aryl *H*); 1.27 (s, 2H, 2 × C*H*); -4.71 (s, 4H, 2 × CH_2); -4.99 (s, 6H, 2 × CH_3); -34.04 (s, 3H, N=CCH_3); -33.38 (s, 3H, N=CCH_3). FT-IR (KBr, cm^{-1}): 3062, 3028, 2959, 2867, 2161, 2030, 2012, 1978, 1963, 1582 ($\nu_{C=N}$), 1495, 1446, 1372, 1267, 1216, 1079, 1034, 867, 808, 767, 705. Anal. Calcd for $C_{53}H_{51}Cl_2FeN_3$ (829): C, 74.30; H, 6.00; N, 4.90. Found: C, 73.98; H, 5.83; N, 5.12.

Data for **Fe'** are as follows. Yield: 128 mg (56.5%). ^{1}H-NMR (600 MHz, $CDCl_3$, TMS): δ 80.01 (s, 2H, Py H_m);, 78.81 (s, 1H, Py H_p); 23.98 (s, 3H, CH_3); 12.98 (s, 4H, Ar H_m); 6.31 (s, 20H, aryl *H*); 4.83 (s, 8H, aryl *H*); 4.56 (s, 12H, aryl *H*); 1.27 (s, 4H, 4 × C*H*); -4.80 (s, 3H, CH_3); -32.59 (s, 6H, 2 × N=CCH_3). FT-IR (KBr, cm^{-1}): 3025, 2161, 2030, 2012, 1978, 1600, 1580 ($\nu_{C=N}$), 1494, 1445, 1271, 1214, 1077, 1033, 807, 768, 699. Anal. Calcd for $C_{75}H_{63}Cl_2FeN_3$ (1133): C, 79.50; H, 5.60; N, 3.71. Found: C, 79.23; H, 5.33; N, 3.96.

Complex **FeR** was prepared according to a published procedure.[1-2]

X-ray Crystallographic Studies.

Single-crystal X-ray diffraction studies for **Fe1, Fe3** and **Fe5** were carried out on a Rigaku RAXIS Rapid IP diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[3] Crystal data and processing

parameters for **Fe1**, **Fe3** and **Fe5** are summarized in Table S1. For complex **Fe3**, it is more difficult to get crystals due to its bulkier substituent. The obtained crystals were always slice and not so good that led to the high value of Rint, however, the data are still useful and indicative.

Table S1 Crystal data and structure refinement for **Fe1**, **Fe3** and **Fe5**

	Fe1	**Fe3**	2**Fe5**
empirical formula	$C_{50}H_{45}Cl_2N_3Fe$	$C_{54}H_{53}Cl_2FeN_3$	$C_{106}H_{102}Cl_4N_6Fe_2$
Fw	814.64	870.74	1713.44
T (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Cryst syst	triclinic	monoclinic	triclinic
space group	P-1	P2(1)/C	P-1
a (Å)	9.851(2)	16.461(3)	13.245(3)
b (Å)	11.505(2)	14.946(3)	16.820(3)
c (Å)	20.416(4)	18.995(4)	24.704(5)
α (°)	75.61(3)	90	82.54(3)
β (°)	77.34(3)	90.10(3)	80.94(3)
γ (°)	72.54(3)	90	88.01(3)
V (Å^3)	2111.7(7)	4673.3(16)	5388.5(19)
Z	2	4	2
*D*calcd. (g cm^{-3})	1.281	1.238	1.056
μ (mm^{-1})	0.522	0.476	0.412
F(000)	852	1832	1800
Cryst size (mm)	0.24 × 0.18 × 0.15	0.23 × 0.17 × 0.04	0.12 × 0.07 × 0.04
θ range (°)	1.04-27.48	1.24–25.31	0.84–25.94
Limiting indices	-8 ≤ h ≤ 12 -14 ≤ k ≤ 14 -19 ≤ l ≤ 26	-19 ≤ h ≤ 16 -17 ≤ k ≤ 17 -22 ≤ l ≤ 22	-15 ≤ h ≤ 16 -20 ≤ k ≤ 20 -30 ≤ l ≤ 30
No. of rflns collected	26053	31868	51617
No. unique rflns [R(int)]	9299 (0.0410)	8450(0.1228)	20799 (0.0764)
Completeness to θ (%)	96.1	99.3	98.8
Abs corr.	None	None	None
data/ restranints/ params	9299 / 0 / 505	8450/ 0/ 541	20799 / 19 / 1085
Goodness of fit on F^2	1.214	1.409	1.028
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0682 wR2 = 0.1623	R1 = 0.1568 wR2 = 0.3231	R1 = 0.0970 wR2 = 0.2426
R indices (all data)	R1 = 0.0787 wR2 = 0.1775	R1 = 0.1802 wR2 = 0.3416	R1 = 0.1310 wR2 = 0.2627
Largest diff peak and hole (e Å^{-3})	0.617 and -0.635	0.602 and -0.857	0.428 and -0.467

Single crystals of complexes **Fe1** and **Fe3** and **Fe5** suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a dichloromethane solution under a nitrogen atmosphere. The molecular structures of **Fe1**, **Fe3** and **Fe5** drawn by ORTEP are showed in Figures S1, S2 and S3, and bond lengths and angles for them are listed in Tables S2, S3 and S4, respectively.

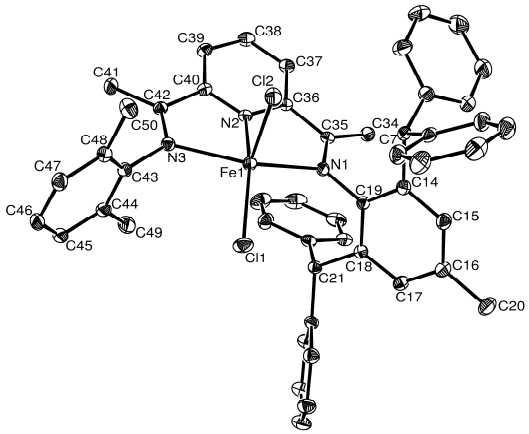

Figure S1 ORTEP drawing of complex **Fe1** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

Table S2. Bond Lengths and Angles for complexes **Fe1**

Bond lengths (Å)							
Fe(1)-N(1)	2.269(3)	C(14)-C(7)	1.534(4)	C(1)-C(6)	1.394(5)	C(25)-C(24)	1.369(5)
Fe(1)-N(2)	2.094(3)	C(35)-C(34)	1.490(4)	C(42)-C(41)	1.493(4)	C(25)-C(26)	1.388(5)
Fe(1)-N(3)	2.236(3)	C(35)-C(36)	1.494(4)	C(8)-C(9)	1.381(5)	C(23)-C(24)	1.390(5)
Fe(1)-Cl(1)	2.2649(10)	C(37)-C(38)	1.382(5)	C(8)-C(13)	1.394(5)	C(27)-C(26)	1.380(5)
Fe(1)-Cl(2)	2.3344(11)	C(37)-C(36)	1.384(4)	C(18)-C(17)	1.388(4)	C(13)-C(12)	1.378(5)
N(1)-C(35)	1.286(4)	C(7)-C(1)	1.522(5)	C(18)-C(21)	1.537(4)	C(29)-C(30)	1.398(5)
N(1)-C(19)	1.441(4)	C(7)-C(8)	1.523(4)	C(33)-C(32)	1.380(5)	C(2)-C(3)	1.391(6)
N(2)-C(40)	1.339(4)	C(40)-C(39)	1.390(4)	C(48)-C(47)	1.393(5)	C(9)-C(10)	1.391(5)
N(2)-C(36)	1.345(4)	C(40)-C(42)	1.479(4)	C(38)-C(39)	1.380(5)	C(10)-C(11)	1.373(6)
N(3)-C(42)	1.290(4)	C(19)-C(18)	1.412(4)	C(17)-C(16)	1.390(5)	C(31)-C(30)	1.369(7)
N(3)-C(43)	1.437(4)	C(28)-C(33)	1.387(5)	C(15)-C(16)	1.391(5)	C(31)-C(32)	1.374(6)
C(22)-C(23)	1.384(5)	C(28)-C(29)	1.388(5)	C(47)-C(46)	1.383(5)	C(12)-C(11)	1.379(6)
C(22)-C(27)	1.404(5)	C(28)-C(21)	1.519(4)	C(44)-C(45)	1.391(5)	C(5)-C(4)	1.386(6)
C(22)-C(21)	1.534(4)	C(43)-C(44)	1.395(4)	C(44)-C(49)	1.507(5)	C(4)-C(3)	1.370(7)
C(14)-C(19)	1.391(4)	C(43)-C(48)	1.397(5)	C(16)-C(20)	1.512(5)	C(48)-C(50)	1.499(5)
C(14)-C(15)	1.398(4)	C(1)-C(2)	1.387(5)	C(46)-C(45)	1.386(5)		
Bond angles (°)							
N(2)-Fe(1)-N(3)	73.14(10)	C(22)-C(21)-C(18)	113.4(2)	N(2)-C(40)-C(42)	113.8(3)		
N(2)-Fe(1)-Cl(1)	149.85(8)	C(16)-C(15)-C(14)	121.5(3)	C(39)-C(40)-C(42)	125.1(3)		
N(3)-Fe(1)-Cl(1)	100.45(8)	C(46)-C(47)-C(48)	120.8(3)	C(14)-C(19)-C(18)	121.5(3)		
N(2)-Fe(1)-N(1)	73.08(10)	C(5)-C(6)-C(1)	121.0(4)	C(14)-C(19)-N(1)	118.7(3)		
N(3)-Fe(1)-N(1)	142.93(9)	C(45)-C(44)-C(43)	118.2(3)	C(18)-C(19)-N(1)	119.7(3)		
Cl(1)-Fe(1)-N(1)	101.05(7)	C(45)-C(44)-C(49)	121.2(3)	C(33)-C(28)-C(29)	118.9(3)		
N(2)-Fe(1)-Cl(2)	93.06(8)	C(43)-C(44)-C(49)	120.6(3)	C(33)-C(28)-C(21)	121.0(3)		
N(3)-Fe(1)-Cl(2)	98.99(7)	C(17)-C(16)-C(15)	118.7(3)	C(29)-C(28)-C(21)	119.9(3)		
Cl(1)-Fe(1)-Cl(2)	117.09(5)	C(17)-C(16)-C(20)	121.1(3)	C(44)-C(43)-C(48)	122.1(3)		
N(1)-Fe(1)-Cl(2)	97.59(7)	C(15)-C(16)-C(20)	120.2(3)	C(44)-C(43)-N(3)	118.2(3)		
C(35)-N(1)-C(19)	118.8(3)	C(47)-C(46)-C(45)	120.3(3)	C(48)-C(43)-N(3)	119.7(3)		
C(35)-N(1)-Fe(1)	115.7(2)	C(24)-C(25)-C(26)	119.5(3)	C(2)-C(1)-C(6)	118.0(4)		
C(40)-N(2)-C(36)	120.1(3)	C(22)-C(23)-C(24)	121.4(3)	C(2)-C(1)-C(7)	119.1(3)		
C(40)-N(2)-Fe(1)	118.7(2)	C(26)-C(27)-C(22)	120.2(3)	C(6)-C(1)-C(7)	122.9(3)		
C(36)-N(2)-Fe(1)	119.6(2)	C(12)-C(13)-C(8)	120.7(3)	N(2)-C(36)-C(37)	121.6(3)		
C(42)-N(3)-C(43)	118.8(3)	C(46)-C(45)-C(44)	120.6(3)	N(2)-C(36)-C(35)	113.9(3)		

C(42)-N(3)-Fe(1)	115.5(2)	C(28)-C(29)-C(30)	119.9(4)	C(37)-C(36)-C(35)	124.5(3)
C(43)-N(3)-Fe(1)	125.72(19)	C(27)-C(26)-C(25)	120.7(3)	N(3)-C(42)-C(40)	115.6(3)
C(23)-C(22)-C(27)	118.0(3)	C(1)-C(2)-C(3)	121.1(4)	N(3)-C(42)-C(41)	125.5(3)
C(40)-N(2)-Fe(1)	118.7(2)	C(8)-C(9)-C(10)	120.3(4)	C(40)-C(42)-C(41)	118.8(3)
C(36)-N(2)-Fe(1)	119.6(2)	C(11)-C(10)-C(9)	120.3(4)	C(9)-C(8)-C(13)	118.7(3)
C(42)-N(3)-C(43)	118.8(3)	C(25)-C(24)-C(23)	120.1(3)	C(9)-C(8)-C(7)	123.5(3)
C(42)-N(3)-Fe(1)	115.5(2)	C(30)-C(31)-C(32)	119.5(4)	C(13)-C(8)-C(7)	117.7(3)
C(43)-N(3)-Fe(1)	125.72(19)	C(13)-C(12)-C(11)	120.1(4)	C(17)-C(18)-C(19)	117.8(3)
C(23)-C(22)-C(27)	118.0(3)	C(31)-C(32)-C(33)	120.9(4)	C(17)-C(18)-C(21)	122.8(3)
C(23)-C(22)-C(21)	122.5(3)	C(31)-C(30)-C(29)	120.5(4)	C(19)-C(18)-C(21)	119.3(3)
C(27)-C(22)-C(21)	119.4(3)	C(10)-C(11)-C(12)	119.8(4)	C(32)-C(33)-C(28)	120.3(3)
C(19)-C(14)-C(15)	118.3(3)	C(6)-C(5)-C(4)	120.0(4)	C(47)-C(48)-C(43)	117.9(3)
C(19)-C(14)-C(7)	121.1(3)	C(3)-C(4)-C(5)	119.8(4)	C(47)-C(48)-C(52)	120.5(3)
C(15)-C(14)-C(7)	120.5(3)	C(4)-C(3)-C(2)	120.1(4)	C(43)-C(48)-C(52)	121.6(3)
N(1)-C(35)-C(34)	127.5(3)	C(1)-C(7)-C(8)	115.0(3)	C(39)-C(38)-C(37)	120.0(3)
C(38)-C(39)-C(40)	118.8(3)	C(1)-C(7)-C(14)	113.1(3)	C(18)-C(17)-C(16)	122.0(3)
C(28)-C(21)-C(22)	111.2(2)	C(8)-C(7)-C(14)	109.9(3)	N(2)-C(40)-C(39)	121.1(3)
C(28)-C(21)-C(18)	113.6(3)				

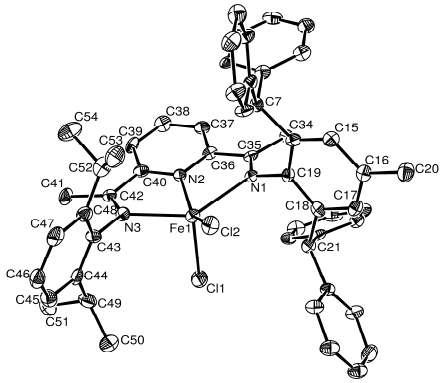

Figure S2 ORTEP drawing of complex **Fe3** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

Table S3. Bond Lengths and Angles for complexes **Fe3**

Bond lengths (Å)

Fe(1)-N(1)	2.256(7)	C(35)-C(34)	1.497(11)	C(8)-C(9)	1.389(13)	C(27)-C(26)	1.388(12)
Fe(1)-N(2)	2.099(7)	C(35)-C(36)	1.484(12)	C(8)-C(13)	1.414(13)	C(13)-C(12)	1.386(13)
Fe(1)-N(3)	2.204(7)	C(37)-C(38)	1.387(13)	C(18)-C(17)	1.417(12)	C(29)-C(30)	1.371(13)
Fe(1)-Cl(1)	2.303(3)	C(37)-C(36)	1.391(11)	C(18)-C(21)	1.520(12)	C(2)-C(3)	1.375(12)
Fe(1)-Cl(2)	2.282(3)	C(7)-C(1)	1.540(12)	C(33)-C(32)	1.412(14)	C(9)-C(10)	1.383(13)
N(1)-C(35)	1.299(10)	C(7)-C(8)	1.521(12)	C(48)-C(47)	1.397(13)	C(10)-C(11)	1.363(14)
N(1)-C(19)	1.419(10)	C(40)-C(39)	1.377(12)	C(38)-C(39)	1.384(13)	C(31)-C(30)	1.375(15)
N(2)-C(40)	1.342(11)	C(40)-C(42)	1.501(12)	C(17)-C(16)	1.381(13)	C(31)-C(32)	1.381(15)
N(2)-C(36)	1.484(12)	C(19)-C(18)	1.402(12)	C(15)-C(16)	1.405(12)	C(12)-C(11)	1.393(15)
N(3)-C(42)	1.272(11)	C(28)-C(33)	1.392(13)	C(47)-C(46)	1.387(15)	C(5)-C(4)	1.375(14)
N(3)-C(43)	1.443(11)	C(28)-C(29)	1.402(12)	C(44)-C(45)	1.415(13)	C(4)-C(3)	1.393(14)
C(22)-C(23)	1.393(12)	C(28)-C(21)	1.544(11)	C(44)-C(49)	1.525(14)	C(49)-C(50)	1.525(15)
C(22)-C(27)	1.392(12)	C(43)-C(44)	1.398(13)	C(16)-C(20)	1.492(13)	C(49)-C(51)	1.546(15)
C(22)-C(21)	1.518(12)	C(43)-C(48)	1.418(13)	C(46)-C(45)	1.369(15)	C(48)-C(52)	1.517(14)
C(14)-C(19)	1.416(12)	C(1)-C(2)	1.410(12)	C(25)-C(24)	1.384(15)	C(52)-C(54)	1.523(14)
C(14)-C(15)	1.385(12)	C(1)-C(6)	1.366(13)	C(25)-C(26)	1.375(15)	C(52)-C(53)	1.541(14)
C(14)-C(7)	1.544(12)	C(42)-C(41)	1.506(12)	C(23)-C(24)	1.389(13)		

Bond angles (º)

N(2)-Fe(1)-N(3)	73.3(3)	C(8)-C(7)-C(14)	111.6(7)	C(22)-C(21)-C(18)	112.6(7)
N(2)-Fe(1)-Cl(1)	148.5(2)	N(2)-C(40)-C(39)	122.1(9)	C(16)-C(15)-C(14)	122.5(8)
N(3)-Fe(1)-Cl(1)	108.9(2)	N(2)-C(40)-C(42)	112.7(8)	C(46)-C(47)-C(48)	121.6(10)
N(2)-Fe(1)-N(1)	72.2(3)	C(39)-C(40)-C(42)	125.0(9)	C(5)-C(6)-C(1)	120.9(9)
N(3)-Fe(1)-N(1)	141.6(3)	C(14)-C(19)-C(18)	120.8(8)	C(45)-C(44)-C(43)	116.6(10)
Cl(1)-Fe(1)-N(1)	92.42(19)	C(14)-C(19)-N(1)	119.1(7)	C(45)-C(44)-C(49)	118.3(9)
N(2)-Fe(1)-Cl(2)	109.33(19)	C(18)-C(19)-N(1)	119.9(8)	C(43)-C(44)-C(49)	125.1(8)
N(3)-Fe(1)-Cl(2)	94.0(2)	C(33)-C(28)-C(29)	119.5(8)	C(17)-C(16)-C(15)	117.4(8)
Cl(1)-Fe(1)-Cl(2)	108.64(11)	C(33)-C(28)-C(21)	123.4(8)	C(17)-C(16)-C(20)	121.8(9)
N(1)-Fe(1)-Cl(2)	109.33(19)	C(29)-C(28)-C(21)	117.1(8)	C(15)-C(16)-C(20)	120.7(8)
C(35)-N(1)-C(19)	121.0(7)	C(44)-C(43)-C(48)	123.3(8)	C(47)-C(46)-C(45)	120.4(10)
C(35)-N(1)-Fe(1)	116.4(6)	C(44)-C(43)-N(3)	121.7(9)	C(24)-C(25)-C(26)	119.4(9)
C(40)-N(2)-C(36)	118.7(7)	C(48)-C(43)-N(3)	114.9(8)	C(22)-C(23)-C(24)	119.8(9)
C(40)-N(2)-Fe(1)	120.2(6)	C(2)-C(1)-C(6)	118.2(9)	C(26)-C(27)-C(22)	122.2(9)
C(36)-N(2)-Fe(1)	121.2(6)	C(2)-C(1)-C(7)	119.5(8)	C(12)-C(13)-C(8)	119.9(9)

C(42)-N(3)-C(43)	121.7(8)	C(6)-C(1)-C(7)	122.3(9)	C(46)-C(45)-C(44)	121.6(10)
C(42)-N(3)-Fe(1)	117.3(6)	N(2)-C(36)-C(37)	122.5(8)	C(28)-C(29)-C(30)	121.0(9)
C(43)-N(3)-Fe(1)	120.9(6)	N(2)-C(36)-C(35)	113.5(7)	C(27)-C(26)-C(25)	119.3(10)
C(23)-C(22)-C(27)	117.8(8)	C(37)-C(36)-C(35)	123.6(8)	C(1)-C(2)-C(3)	121.2(8)
C(40)-N(2)-Fe(1)	120.2(6)	N(3)-C(42)-C(40)	115.5(8)	C(8)-C(9)-C(10)	121.4(10)
C(36)-N(2)-Fe(1)	121.2(6)	N(3)-C(42)-C(41)	126.5(8)	C(11)-C(10)-C(9)	120.3(10)
C(42)-N(3)-C(43)	121.7(8)	C(40)-C(42)-C(41)	118.0(8)	C(25)-C(24)-C(23)	121.4(10)
C(42)-N(3)-Fe(1)	117.3(6)	C(9)-C(8)-C(13)	118.0(9)	C(30)-C(31)-C(32)	120.7(10)
C(43)-N(3)-Fe(1)	120.9(6)	C(9)-C(8)-C(7)	122.3(8)	C(13)-C(12)-C(11)	120.4(10)
C(23)-C(22)-C(27)	117.8(8)	C(13)-C(8)-C(7)	119.7(8)	C(31)-C(32)-C(33)	120.1(10)
C(23)-C(22)-C(21)	121.8(8)	C(17)-C(18)-C(19)	117.7(8)	C(31)-C(30)-C(29)	119.8(10)
C(27)-C(22)-C(21)	120.4(8)	C(17)-C(18)-C(21)	123.1(8)	C(10)-C(11)-C(12)	119.9(10)
C(19)-C(14)-C(15)	118.6(8)	C(19)-C(18)-C(21)	119.1(8)	C(6)-C(5)-C(4)	120.5(10)
C(19)-C(14)-C(7)	118.5(8)	C(32)-C(33)-C(28)	118.8(9)	C(3)-C(4)-C(5)	119.3(9)
C(15)-C(14)-C(7)	122.9(8)	C(47)-C(48)-C(52)	122.2(9)	C(4)-C(3)-C(2)	120.0(9)
N(1)-C(35)-C(34)	126.0(8)	C(43)-C(48)-C(52)	121.2(8)	C(44)-C(49)-C(50)	112.0(10)
N(1)-C(35)-C(36)	114.6(7)	C(39)-C(38)-C(37)	119.8(9)	C(44)-C(49)-C(51)	111.3(9)
C(34)-C(35)-C(36)	119.3(7)	C(18)-C(17)-C(16)	122.8(9)	C(48)-C(52)-C(53)	112.8(8)
C(38)-C(37)-C(36)	117.7(9)	C(38)-C(39)-C(40)	119.1(9)	C(54)-C(52)-C(53)	110.0(9)
C(1)-C(7)-C(8)	113.0(7)	C(28)-C(21)-C(22)	113.6(7)	C(28)-C(21)-C(18)	113.6(7)
C(1)-C(7)-C(14)	113.4(7)				

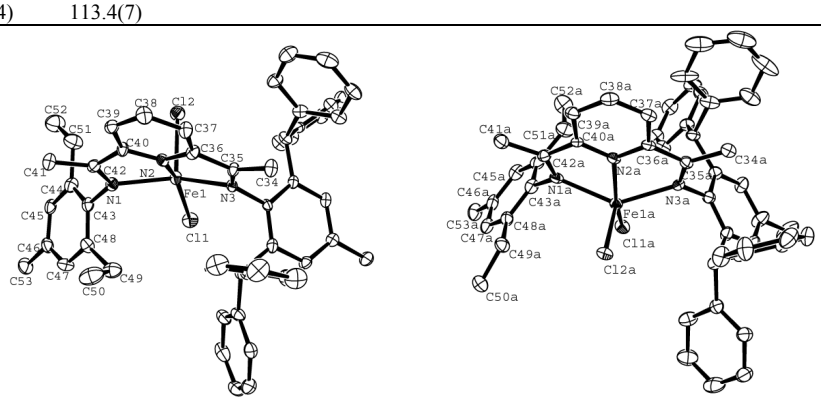

Figure S3 ORTEP drawing of complex **Fe5** with thermal ellipsoids at 30% probability level. Hydrogen atoms have been omitted for clarity.

Table S4. Bond Lengths and Angles for complexes **Fe5**

Bond lengths (Å)					
Fe(1)-N(1)	2.227(5)	C(35)-C(34)	1.490(4)	C(8)-C(9)	1.381(5)
Fe(1)-N(2)	2.085(4)	C(35)-C(36)	1.494(4)	C(8)-C(13)	1.394(5)
Fe(1)-N(3)	2.179(5)	C(37)-C(38)	1.382(5)	C(18)-C(17)	1.388(4)
Fe(1)-Cl(1)	2.2690(17)	C(37)-C(36)	1.384(4)	C(18)-C(21)	1.537(4)
Fe(1)-Cl(2)	2.3379(19)	C(7)-C(1)	1.522(5)	C(33)-C(32)	1.380(5)
N(1)-C(35)	1.301(7)	C(7)-C(8)	1.523(4)	C(48)-C(47)	1.393(5)
N(1)-C(19)	1.458(6)	C(40)-C(39)	1.390(4)	C(38)-C(39)	1.380(5)
N(2)-C(40)	1.360(7)	C(40)-C(42)	1.479(4)	C(17)-C(16)	1.390(5)
N(2)-C(36)	1.322(7)	C(19)-C(18)	1.412(4)	C(15)-C(16)	1.391(5)
N(3)-C(42)	1.303(7)	C(28)-C(33)	1.387(5)	C(47)-C(46)	1.383(5)
N(3)-C(43)	1.450(7)	C(28)-C(29)	1.388(5)	C(44)-C(45)	1.391(5)
C(22)-C(23)	1.384(5)	C(28)-C(21)	1.519(4)	C(16)-C(20)	1.512(5)
C(22)-C(27)	1.404(5)	C(43)-C(44)	1.395(4)	C(46)-C(45)	1.386(5)
C(22)-C(21)	1.534(4)	C(43)-C(48)	1.397(5)	C(25)-C(24)	1.369(5)
C(14)-C(19)	1.391(4)	C(1)-C(2)	1.387(5)	C(25)-C(26)	1.388(5)
C(14)-C(15)	1.398(4)	C(1)-C(6)	1.394(5)	C(23)-C(24)	1.390(5)
C(14)-C(7)	1.534(4)	C(42)-C(41)	1.493(4)	C(27)-C(26)	1.380(5)
Fe(1A)-N(2A)	2.058(4)	C(7A)-C(1A)	1.519(8)	C(51A)-C(44A)	1.526(9)
Fe(1A)-N(1A)	2.182(5)	C(7A)-C(14A)	1.536(8)	C(45A)-C(46A)	1.384(10)
Fe(1A)-N(3A)	2.202(5)	C(7A)-C(8A)	1.540(8)	C(45A)-C(44A)	1.399(9)
Fe(1A)-Cl(1A)	2.2607(17)	C(34)-C(35)	1.497(8)	C(15A)-C(16A)	1.387(9)
Fe(1A)-Cl(2A)	2.3567(17)	C(34A)-C(35A)	1.487(8)	C(47A)-C(46A)	1.396(10)
N(2A)-C(40A)	1.343(7)	C(8A)-C(9A)	1.358(8)	C(47A)-C(48A)	1.418(8)
N(2A)-C(36A)	1.343(7)	C(8A)-C(13A)	1.407(9)	C(48A)-C(49A)	1.509(9)
N(3A)-C(35A)	1.294(7)	C(40A)-C(39A)	1.374(8)	C(10A)-C(11A)	1.384(10)
N(3A)-C(19A)	1.438(7)	C(38A)-C(37A)	1.379(9)	C(10A)-C(9A)	1.385(9)
N(1A)-C(42A)	1.281(7)	C(38A)-C(39A)	1.404(9)	C(11A)-C(12A)	1.362(10)
N(1A)-C(43A)	1.448(7)	C(14A)-C(15A)	1.394(8)	C(27A)-C(26A)	1.392(9)

C(36A)-C(37A)	1.395(8)	C(43A)-C(48A)	1.400(9)	C(12A)-C(13A)	1.412(9)
C(36A)-C(35A)	1.521(8)	C(43A)-C(44A)	1.413(9)	C(33A)-C(32A)	1.401(9)
C(22A)-C(23A)	1.404(9)	C(23A)-C(24A)	1.381(9)	C(17A)-C(16A)	1.371(9)
C(22A)-C(27A)	1.414(9)	C(18A)-C(17A)	1.366(8)	C(26A)-C(25A)	1.369(11)
C(22A)-C(21A)	1.512(8)	C(18A)-C(21A)	1.543(8)	C(29A)-C(30A)	1.384(10)
C(42A)-C(41A)	1.488(8)	C(28A)-C(33A)	1.386(9)	C(46A)-C(53A)	1.516(9)
C(42A)-C(40A)	1.496(8)	C(28A)-C(29A)	1.404(10)	C(49A)-C(50A)	1.517(9)
C(19A)-C(18A)	1.380(8)	C(28A)-C(21A)	1.521(8)	C(2A)-C(1A)	1.393(11)
C(19A)-C(14A)	1.399(8)	C(51A)-C(52A)	1.520(10)	C(2A)-C(3A)	1.414(11)
C(13)-C(12)	1.378(5)	C(4)-C(3)	1.370(7)	C(1A)-C(6A)	1.381(11)
C(29)-C(30)	1.398(5)	C(49)-C(50)	1.489(10)	C(16A)-C(20A)	1.555(10)
C(2)-C(3)	1.391(6)	C(44)-C(51)	1.534(10)	C(30A)-C(31A)	1.384(12)
C(9)-C(10)	1.391(5)	C(51)-C(52)	1.472(13)	C(6A)-C(5A)	1.427(11)
C(10)-C(11)	1.373(6)	C(46)-C(53)	1.527(8)	C(32A)-C(31A)	1.399(12)
C(31)-C(30)	1.369(7)	C(51)-C(52')	1.478(14)	C(3A)-C(4A)	1.400(15)
C(31)-C(32)	1.374(6)	C(51)-C(52)	1.472(13)	C(5A)-C(4A)	1.313(15)
C(12)-C(11)	1.379(6)	C(51)-C(52')	1.478(14)	C(25A)-C(24A)	1.427(11)
C(5)-C(4)	1.386(6)				

Bond angles (º)

N(2)-Fe(1)-N(3)	73.93(17)	N(2)-C(40)-C(39)	121.1(3)
N(2)-Fe(1)-Cl(1)	155.08(14)	N(2)-C(40)-C(42)	113.8(3)
N(3)-Fe(1)-Cl(1)	103.20(14)	C(39)-C(40)-C(42)	125.1(3)
N(2)-Fe(1)-N(1)	72.42(16)	C(14)-C(19)-C(18)	121.5(3)
N(3)-Fe(1)-N(1)	139.11(17)	C(14)-C(19)-N(1)	118.7(3)
Cl(1)-Fe(1)-N(1)	97.72(12)	C(18)-C(19)-N(1)	119.7(3)
N(2)-Fe(1)-Cl(2)	92.34(13)	C(33)-C(28)-C(29)	118.9(3)
N(3)-Fe(1)-Cl(2)	98.60(14)	C(33)-C(28)-C(21)	121.0(3)
Cl(1)-Fe(1)-Cl(2)	112.48(7)	C(29)-C(28)-C(21)	119.9(3)
N(1)-Fe(1)-Cl(2)	105.27(13)	C(44)-C(43)-C(48)	122.1(3)
C(35)-N(1)-C(19)	118.8(3)	C(44)-C(43)-N(3)	118.2(3)
C(35)-N(1)-Fe(1)	115.7(2)	C(48)-C(43)-N(3)	119.7(3)
C(40)-N(2)-C(36)	120.1(3)	C(2)-C(1)-C(6)	118.0(4)
C(40)-N(2)-Fe(1)	118.7(2)	C(2)-C(1)-C(7)	119.1(3)
C(36)-N(2)-Fe(1)	119.6(2)	C(6)-C(1)-C(7)	122.9(3)
C(42)-N(3)-C(43)	118.8(3)	N(2)-C(36)-C(37)	121.6(3)
C(42)-N(3)-Fe(1)	115.5(2)	N(2)-C(36)-C(35)	113.9(3)
C(43)-N(3)-Fe(1)	125.72(19)	C(37)-C(36)-C(35)	124.5(3)
C(23)-C(22)-C(27)	118.0(3)	N(3)-C(42)-C(40)	115.6(3)
C(40)-N(2)-Fe(1)	118.7(2)	N(3)-C(42)-C(41)	125.5(3)
C(36)-N(2)-Fe(1)	119.6(2)	C(40)-C(42)-C(41)	118.8(3)
C(42)-N(3)-C(43)	118.8(3)	C(9)-C(8)-C(13)	118.7(3)
C(42)-N(3)-Fe(1)	115.5(2)	C(9)-C(8)-C(7)	123.5(3)
C(43)-N(3)-Fe(1)	125.72(19)	C(13)-C(8)-C(7)	117.7(3)
C(23)-C(22)-C(27)	118.0(3)	C(17)-C(18)-C(19)	117.8(3)
C(23)-C(22)-C(21)	122.5(3)	C(17)-C(18)-C(21)	122.8(3)
C(27)-C(22)-C(21)	119.4(3)	C(19)-C(18)-C(21)	119.3(3)
C(19)-C(14)-C(15)	118.3(3)	C(32)-C(33)-C(28)	120.3(3)
C(19)-C(14)-C(7)	121.1(3)	C(47)-C(48)-C(43)	117.9(3)
C(15)-C(14)-C(7)	120.5(3)	C(47)-C(48)-C(52)	120.5(3)
N(1)-C(35)-C(34)	127.5(3)	C(43)-C(48)-C(52)	121.6(3)
N(1)-C(35)-C(36)	115.5(3)	C(39)-C(38)-C(37)	120.0(3)
C(34)-C(35)-C(36)	116.9(3)	C(18)-C(17)-C(16)	122.0(3)
C(38)-C(37)-C(36)	118.4(3)	C(38)-C(39)-C(40)	118.8(3)
C(1)-C(7)-C(8)	115.0(3)	C(28)-C(21)-C(22)	111.2(2)
C(1)-C(7)-C(14)	113.1(3)	C(28)-C(21)-C(18)	113.6(3)
C(8)-C(7)-C(14)	109.9(3)	C(22)-C(21)-C(18)	113.4(2)
N(2A)-Fe(1A)-N(1A)	73.83(18)	C(9A)-C(8A)-C(13A)	117.5(6)
N(2A)-Fe(1A)-N(3A)	74.13(17)	C(9A)-C(8A)-C(7A)	124.5(6)
N(1A)-Fe(1A)-N(3A)	139.81(16)	C(13A)-C(8A)-C(7A)	117.8(5)
N(2A)-Fe(1A)-Cl(1A)	154.78(14)	N(2A)-C(40A)-C(39A)	121.5(5)
N(1A)-Fe(1A)-Cl(1A)	100.17(13)	N(2A)-C(40A)-C(42A)	112.3(5)
N(3A)-Fe(1A)-Cl(1A)	98.54(13)	C(39A)-C(40A)-C(42A)	126.1(5)
N(2A)-Fe(1A)-Cl(2A)	89.92(13)	C(40)-C(39)-C(38)	118.8(5)
N(1A)-Fe(1A)-Cl(2A)	99.79(13)	C(37A)-C(38A)-C(39A)	120.1(6)
N(3A)-Fe(1A)-Cl(2A)	103.78(13)	C(38A)-C(37A)-C(36A)	117.4(5)
Cl(1A)-Fe(1A)-Cl(2A)	115.30(7)	C(15A)-C(14A)-C(19A)	118.1(5)
C(40A)-N(2A)-C(36A)	119.5(5)	C(15A)-C(14A)-C(7A)	122.0(5)
C(40A)-N(2A)-Fe(1A)	119.7(3)	C(19A)-C(14A)-C(7A)	119.8(5)
C(36A)-N(2A)-Fe(1A)	120.6(4)	C(48A)-C(43A)-C(44A)	122.7(5)
C(35A)-N(3A)-C(19A)	122.2(5)	C(48A)-C(43A)-N(1A)	120.5(5)
C(35A)-N(3A)-Fe(1A)	115.7(4)	C(44A)-C(43A)-N(1A)	116.4(5)
C(19A)-N(3A)-Fe(1A)	122.0(3)	C(24A)-C(23A)-C(22A)	121.7(6)
C(42A)-N(1A)-C(43A)	121.3(5)	C(17A)-C(18A)-C(19A)	118.6(6)
C(42A)-N(1A)-Fe(1A)	116.1(4)	C(17A)-C(18A)-C(21A)	122.8(6)
C(43A)-N(1A)-Fe(1A)	122.5(4)	C(19A)-C(18A)-C(21A)	118.6(5)

N(2A)-C(36A)-C(37A)	122.6(5)	N(3A)-C(35A)-C(34A)	125.7(5)
N(2A)-C(36A)-C(35A)	111.9(5)	N(3A)-C(35A)-C(36A)	115.0(5)
C(37A)-C(36A)-C(35A)	125.3(5)	C(34A)-C(35A)-C(36A)	119.3(5)
C(23A)-C(22A)-C(27A)	117.6(6)	C(33A)-C(28A)-C(29A)	118.3(6)
C(23A)-C(22A)-C(21A)	122.8(5)	C(33A)-C(28A)-C(21A)	123.1(6)
C(27A)-C(22A)-C(21A)	119.6(6)	C(29A)-C(28A)-C(21A)	118.6(6)
N(1A)-C(42A)-C(41A)	125.3(5)	C(22A)-C(21A)-C(28A)	112.9(5)
N(1A)-C(42A)-C(40A)	114.9(5)	C(22A)-C(21A)-C(18A)	111.3(5)
C(41A)-C(42A)-C(40A)	119.8(5)	C(28A)-C(21A)-C(18A)	113.3(5)
C(18A)-C(19A)-C(14A)	121.2(5)	C(52A)-C(51A)-C(44A)	115.8(6)
C(18A)-C(19A)-N(3A)	121.7(5)	C(46A)-C(45A)-C(44A)	122.9(6)
C(14A)-C(19A)-N(3A)	116.6(5)	C(16A)-C(15A)-C(14A)	120.6(6)
C(1A)-C(7A)-C(14A)	112.2(5)	C(46A)-C(47A)-C(48A)	121.0(6)
C(1A)-C(7A)-C(8A)	113.0(5)	C(43A)-C(48A)-C(47A)	117.6(6)
C(14A)-C(7A)-C(8A)	113.6(5)	C(43A)-C(48A)-C(49A)	119.8(5)
C(16)-C(15)-C(14)	121.5(3)	C(52)-C(51)-C(52')	40.2(10)
C(46)-C(47)-C(48)	120.8(3)	C(52')-C(51)-C(44)	111.4(11)
C(5)-C(6)-C(1)	121.0(4)	C(47A)-C(48A)-C(49A)	122.6(6)
C(45)-C(44)-C(43)	118.2(3)	C(11A)-C(10A)-C(9A)	119.4(6)
C(17)-C(16)-C(15)	118.7(3)	C(45A)-C(44A)-C(43A)	116.6(6)
C(17)-C(16)-C(20)	121.1(3)	C(45A)-C(44A)-C(51A)	123.3(6)
C(15)-C(16)-C(20)	120.2(3)	C(43A)-C(44A)-C(51A)	120.1(6)
C(47)-C(46)-C(45)	120.3(3)	C(12A)-C(11A)-C(10A)	120.6(6)
C(24)-C(25)-C(26)	119.5(3)	C(26A)-C(27A)-C(22A)	120.2(7)
C(22)-C(23)-C(24)	121.4(3)	C(11A)-C(12A)-C(13A)	119.1(7)
C(26)-C(27)-C(22)	120.2(3)	C(28A)-C(33A)-C(32A)	122.0(7)
C(12)-C(13)-C(8)	120.7(3)	C(18A)-C(17A)-C(16A)	122.3(6)
C(46)-C(45)-C(44)	120.6(3)	C(40A)-C(39A)-C(38A)	118.8(6)
C(28)-C(29)-C(30)	119.9(4)	C(25A)-C(26A)-C(27A)	122.2(7)
C(27)-C(26)-C(25)	120.7(3)	C(30A)-C(29A)-C(28A)	120.9(7)
C(1)-C(2)-C(3)	121.1(4)	C(45A)-C(46A)-C(47A)	119.0(6)
C(8)-C(9)-C(10)	120.3(4)	C(45A)-C(46A)-C(53A)	119.9(7)
C(11)-C(10)-C(9)	120.3(4)	C(47A)-C(46A)-C(53A)	121.0(6)
C(25)-C(24)-C(23)	120.1(3)	C(48A)-C(49A)-C(50A)	115.1(5)
C(30)-C(31)-C(32)	119.5(4)	C(26A)-C(25A)-C(24A)	118.1(7)
C(13)-C(12)-C(11)	120.1(4)	C(8A)-C(13A)-C(12A)	120.8(6)
C(31)-C(32)-C(33)	120.9(4)	C(23A)-C(24A)-C(25A)	120.1(7)
C(31)-C(30)-C(29)	120.5(4)	C(6A)-C(1A)-C(2A)	119.5(7)
C(10)-C(11)-C(12)	119.8(4)	C(6A)-C(1A)-C(7A)	121.0(7)
C(6)-C(5)-C(4)	120.0(4)	C(2A)-C(1A)-C(7A)	119.5(7)
C(3)-C(4)-C(5)	119.8(4)	C(17A)-C(16A)-C(15A)	119.0(6)
C(4)-C(3)-C(2)	120.1(4)	C(17A)-C(16A)-C(20A)	121.2(6)
C(47)-C(48)-C(49)	118.9(6)	C(15A)-C(16A)-C(20A)	119.8(6)
C(43)-C(48)-C(49)	122.5(6)	C(29A)-C(30A)-C(31A)	119.9(8)
C(50)-C(49)-C(48)	112.8(7)	C(1A)-C(6A)-C(5A)	118.1(10)
C(43)-C(44)-C(51)	121.9(6)	C(31A)-C(32A)-C(33A)	118.1(7)
C(45)-C(44)-C(51)	121.0(6)	C(30A)-C(31A)-C(32A)	120.9(7)
C(52)-C(51)-C(44)	119.6(9)	C(4A)-C(3A)-C(2A)	117.9(10)
C(45)-C(46)-C(53)	121.2(6)	C(4A)-C(5A)-C(6A)	122.5(11)
C(47)-C(46)-C(53)	120.9(6)	C(5A)-C(4A)-C(3A)	121.0(9)

General Procedure for Ethylene Polymerization.

Ethylene Polymerization under 1 atm ethylene. The procatalyst was dissolved in toluene using standard Schlenk techniques, and the reaction solution was stirred with a magnetic stir bar under ambient ethylene atmosphere. The require amount of cocatalyst (MAO, MMAO) was added by a syringe. After the reaction was carried out for the required period, the reaction solution was quenched with 10% hydrochloric acid ethanol. The precipitated polymer was collected by filtration, washed with ethanol and water, and dried in a vacuum at 60 °C until constant weight. All iron procatalysts were investigated using MMAO/MAO

with an Al/Fe molar ratio 2000 at ambient pressure (Table S5). In addition, 2,6-bis[1-(2,6-diisopropylphenylimino)-ethyl]pyridyliron(II) chloride (**FeR**) was used as a reference.

Table S5. Ethylene polymerization at ambient pressure [a]

entry	cocat.	procat.	Activity 10^6g·mol^{-1}(Fe)·h^{-1}	M_w [b] kg·mol^{-1}	M_w/M_n [b]	T_m [c] ºC
1	MMAO	**Fe1**	2.47	11.8	11.3	121.3
2	MMAO	**Fe2**	2.36	22.5	19.6	123.7
3	MMAO	**Fe4**	3.51	63.4	45.7	126.3
4	MMAO	**Fe5**	2.48	41.4	34.4	124.7
5	MMAO	**Fe'**	Trace	-	-	-
6	MMAO	**FeR**	2.36	38.5	34.5	124.0
7	MAO	**Fe3**	0.26	93.2	70.2	127.0
8	MAO	**FeR**	1.32	138.2	71.9	128.5

[a]General conditions:1.5 μmol Fe; 30 mL toluene; 20 °C; 30 min; 1 atm ethylene pressure. [b]Determined by GPC. [c]Determined by DSC.

Ethylene polymerization under 10 atm ethylene. A 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. Firstly, 50 mL toluene (freshly distilled) was injected to the clave which is full of ethylene. When the temperature rooted as we wanted, another 30 mL toluene which dissolved the complex (1.5 μmol), the require amount of cocatalyst (MAO, MMAO), the residual toluene were added by syringe successively. The reaction mixture was intensively stirred for the desired time under corresponding pressure of ethylene through the entire experiment. The reaction was terminated and analyzed using the same method as above for ethylene polymerization at ambient pressure.

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