General Procedures.

All manipulations of air- and/or water-sensitive compounds were carried out under Ar using standard Schlenk techniques or dry glove box. Solvents were dried by refluxing with appropriate drying agents and distilled under nitrogen prior to use. Methylaluminoxane (MAO) was purchased from Aldrich as 10% weight of a toluene solution and used without further purification. AlEt₃ was purchased from Aldrich. n-BuLi (1.6 M) were obtained from Acros Chem. Co. NMR spectra were recorded with a Varian Unity-500 pectrometer. The $^{13}$C NMR spectra of the PE were obtained at 140° C. Sample solutions of the polymer were prepared in 1,2,4-trichlorobenzene and benzene-d$_6$ (9/1, v/v) in a 5 mm sample tube. The deuterated solvent was used to provide the internal lock signal. Elemental analyses were performed on an Elementarvario EL III Analyzer. FT-IR analyses were detected with a Nicolet-FT-IR-50X spectrometer. X-ray Data collection for complexes were performed at 293K on a Bruker Smart APEX CCD diffractometer equipped with a graphite-monochromatized Mo K- radiation($\lambda = 0.71073$ Å ). Lorentz-Polarization corrections and empirical absorption correction were applied to the data. The structures was solved by direct methods with SHELXS-97 and refined on $F^2$ using full-matrix least-squares calculations with SHELXL-97. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. The thermal characteristics of the PE were examined using a DSC Perkin-Elmer
Instrument with a heating rate of 10 °C/min, in the range from 50 to 160 °C. The viscosity–average molar masses ($M_v$) of the polyethylene were calculated using the Mark – Houwink equation: $[\eta] = 6.77 \times 10^{-4} M_v^{0.67}$. The β-ketoiminato and β-diketiminate ligands were obtained according to literature methods or using analogous methods reported.¹

**Synthesis of complex 1a:**

A solution of n-BuLi (1.6M, 0.28 mL, 0.36 mmol) in hexane was added dropwise to a stirred solution of ligand $L_{1a}$ (0.35 mmol) in THF (10 mL) at -78 °C. The mixture was slowly warmed to room temperature and stirred for 6 h, then was channeled at -78 °C to a solution of CpCr(THF)Cl₂ which was prepared by the reaction of CrCl₃(THF)₃ (0.14 g, 0.36 mmol) and CpNa(THF)$_{0.38}$ (0.041 g, 0.36 mmol) in THF (15 mL) at 0 °C. The mixture was slowly warmed to room temperature and continuously stirred overnight at room temperature. A blue-green solution was obtained and the solvent was removed under vacuum. After the residual solid was solved in CH₂Cl₂ and filtered to remove inorganic salts, the filtrate was concentrated to about 5 mL, and mixed with hexane (25 mL). Cooling to -30 °C to give blue-green solid 1a (0.058 g, 49%). Anal. Calcd for C₁₆H₁₇ClCrNO (326.76): C, 58.81; H, 5.24; N, 4.29. Found: C, 58.85; H, 5.21; N, 4.26. IR: 3025, 2960, 2863, 1580, 1512, 1485, 1449, 1397, 1264, 1196, 1163, 1096, 1023, 942, 849, 804 (m), 762, 700, 527.

**Synthesis of complex 1b:**

Complex 1b was synthesized as the same way for synthesis of complex 1a. Cooling to -30 °C to give blue-green solid 1b (0.068 g, 51%). Anal. Calcd for C₁₉H₂₃ClCrNO (368.84): C, 61.87; H, 6.29; N, 3.80. Found: C, 61.92; H, 6.34; N, 3.78. IR: 3050, 2963,
2919, 1577, 1509, 1391, 1316, 1262, 1206, 1094, 1026, 932, 866, 806 (m), 765, 494.

**Synthesis of complex 1c:**

Complex 1c was synthesized as the same way for synthesis of complex 1a. Cooling to -30 °C to give blue-green crystal 1c (0.071g, 48%). Anal. Calcd for C_{22}H_{29}ClCrNO (410.91): C, 64.30; H, 7.11; N, 3.41. Found: C, 64.34; H, 7.15; N, 3.37. IR: 3058, 2964, 2925, 2863, 1578, 1511, 1439, 1401, 1317, 1272, 1178, 1101, 1050, 1019, 934, 800 (m), 753, 520.

**Synthesis of complex 1d:**

Complex 1d was synthesized as the same way for synthesis of complex 1a. Cooling to -30 °C to give green solid 1d (0.073g, 53%). Anal. Calcd for C_{16}H_{14}ClF_{3}CrNO (380.73): C, 50.47; H, 3.71; N, 3.68. Found: C, 50.49; H, 3.68; N, 3.65. IR: 3031, 2962, 2865, 1579, 1513, 1489, 1453, 1399, 1266, 1199, 1161, 1094, 1021, 943, 850, 802 (m), 761, 705, 537.

**Synthesis of complex 1e:**

Complex 1e was synthesized as the same way for synthesis of complex 1a. Cooling to -30 °C to give green solid 1e (0.084g, 50%). Anal. Calcd for C_{22}H_{26}ClF_{3}CrNO (464.89): C, 56.84; H, 5.64; N, 3.01. Found: C, 56.81; H, 5.61; N, 3.05. IR: 3056, 2961, 2926, 2865, 1577, 1516, 1435, 1405, 1319, 1274, 1179, 1105, 1048, 1021, 935, 806 (m), 756, 526.

**Synthesis of complex 2:**

Complex 2 was synthesized as the same way for synthesis of complex 1a. Cooling to -30 °C to give green solid 2 (0.084g, 50%). Anal. Calcd for C_{22}H_{22}ClCrN_{2} (401.87): C, 65.75; H, 5.52; N, 6.97. Found: C, 65.71; H, 5.54; N, 6.99. IR: 3063, 2965, 1540, 1580, 1440, 1381, 1264, 1188, 1088, 1022, 924, 810 (m), 756, 701, 516.
Ethylene polymerization

A flame dried 100 ml Schlenk flask with a magnetic stirrer was charged with 50 ml of toluene, and saturated with ethylene (1.0 bar). The polymerization reaction was started by injection of a mixture of AlEt₃ and a precatalyst in toluene (10 ml). and the contents were magnetically stirred and maintained under ethylene (1 bar) for 0.5 h. The polymerization was quenched by injecting 10% acidified ethanol and the polymer was collected by filtration, washed with water, ethanol, and dried at 70 °C in vacuo to a constant weight.

¹³C NMR spectrum of PE obtained by chromium complex 1d (run 4, Table 1)
References