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Bidentate Iron(II) Dichloride Complexes Bearing Substituted 8-(Benzimidazol-2-yl)quinolines: Synthesis, Characterization, and Ethylene Polymerization Behavior

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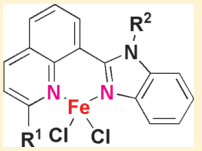
Supporting Information

ABSTRACT: The series of *N*-benzimidazolyl-substituted 2-alkyl-8-(benzimidazol-2-yl)quinolines (**L1**−**L10**) and 2-phenyl-8-(benzimidazol-2-yl)quinolines (**L11**−**L14**) and their respective bidentate iron(II) dichloride complexes (**C1**−**C14**) were synthesized and fully characterized. The molecular structures of a representative ligand (**L5**) and iron complexes (**C2**, **C7**) were determined by X-ray crystal structure analyses, and the distorted tetrahedral coordination geometry was observed around the iron center in both complexes **C2** and **C7**. After activation of the iron complexes with methylaluminoxane, the iron catalysts showed activities up to 10^6 g·mol^{-1}·h^{-1} in ethylene polymerization at elevated temperature (100 °C), yielding linear polyethylenes. The reaction parameters of the polymerization reactions were optimized, and the effect of the substituents of the different ligands on the catalytic activity and on the obtained polyethylene was discussed.



1. INTRODUCTION

The market for polyolefins is in the tens of billions of dollars, indicating both the importance and interest of academic and industrial views.[1] The demand for advanced polyolefins has resulted in new complex pro-catalysts,[2] and the progress of late transition metal catalysis has been witnessed in the past dozen years,[3] in which the pioneer works included diiminometal (Ni(II) or Pd(II)) complexes[4] and 2,6-bis(imino)pyridine metal (Fe(II) or Co(II)) complexes.[5] The iron-derived catalysts have drawn great attention due to economic and environmental views in industry and academic consideration of the formation of highly linear ethylene oligomers and polymers. Efforts have been devoted to modifying bis(imino)pyridyliron complexes[6] and designing iron complexes with alternative organic ligands.[7] In addition, the active species and the polymerization mechanism have been explored focusing on the iron complexes bearing bis(imino)-pyridine derivatives.[8] In general, these late transition metal catalysts maintained good catalytic activities in ethylene polymerization at relatively lower reaction temperature, but elevated reaction temperatures resulted either in catalyst deactivation or in producing low molecular weight polyethylenes or even oligomers. As ethylene polymerization is a highly exothermic reaction and industrial operating temperatures above 70 °C are preferable, more bulky substituents[9] and geometry-constrained ligands[10] were used in order to maintain good activity of their complex pro-catalysts in ethylene polymerization at elevated reaction temperatures. In addition, the iron pro-catalysts bearing new ligands such as 2-imino-1,10-phenanthrolines,[11] 2-(benzimidazol-2-yl)-1,10-phenanthrolines,[12] 2-benzimidazolyl-6-iminopyridines,[13] 2-benzoxazolyl-6-iminopyridines,[14] 2-quinoxalinyl-6-iminopyridines,[15] 2-methyl-2,4-bis(6- iminopyridin-2-yl)-1*H*-1,5-benzodiazepines,[16] iminoquinolines,[17] and 2,8-bis(imino)quinoline[18] have been investigated in our group in Beijing, resulting in high activities in ethylene oligomerization and/or polymerization. Interestingly the metal pro-catalysts bearing 2,8-bis(imino)quinolines preferred ethylene polymerization at high temperature (100 °C). Examining the molecular structures of 2,8-bis(imino)quinolyl metal dichloride complexes (Chart 1) revealed a distorted coordination geometry around the metal and indicated different bonding interactions between the metal and the nitrogen atoms.[18] As a consequence, the quinoline derivatives acting as bidentate ligands are promising for generating metal catalysts for ethylene polymerization. Regarding the literature, although bidentate iron pro-catalysts showed relatively lower activities toward ethylene oligomerization and polymerization,[13a,19] iron complexes bearing bidentate ligands were good activators in atom transfer radical polymerization.[6c,20] As a consequence a series of 2-alkyl/phenyl 8-(benzoimidazol-2-yl)quinoline derivatives were prepared and used to form their iron complexes. Their iron complexes (Chart 1) showed high catalytic activities toward ethylene polymerization when the reaction temperature was elevated above 60 °C. The syntheses and characterizations of 2-alkyl or 2-phenyl 8-(benzoimidazol-2-yl)quinoline derivatives and their iron complexes are reported along with the catalytic behaviors of iron complexes toward ethylene.

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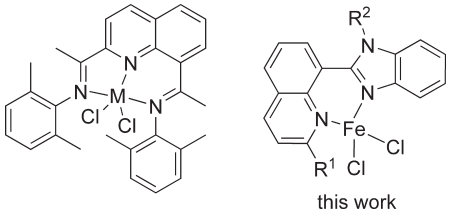
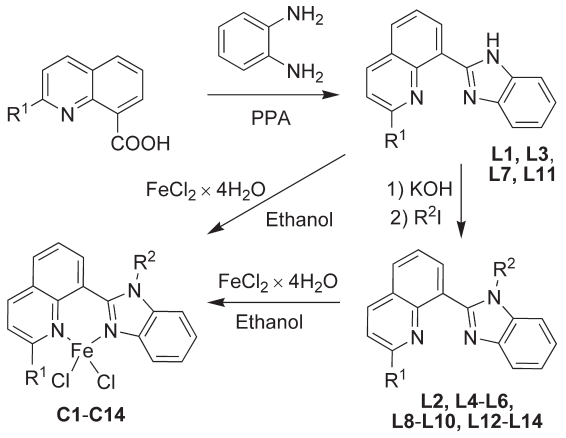
Chart 1



Scheme 1. Synthesis of the Ligands (Ln) and Their Iron Complexes (Cn)



Ln	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12	L13	L14
Cn	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14
R^1	Me	Me	Et	Et	Et	Et	Pr	Pr	Pr	Pr	Ph	Ph	Ph	Ph
R^2	H	Me	H	Me	Et	iPr	H	Me	Et	iPr	H	Me	Et	iPr

2. RESULTS AND DISCUSSION

2.1. Synthesis of 2-R^1-8-(1-R^2-Benzoimidazol-2-yl)quinoline Derivatives. As reported in the literature,[21] the condensation reactions of 1,2-phenylenediamine with either 2-alkylquinoline-8-carboxylic acid or 2-phenylquinoline-8-carboxylic acid in the presence of polyphosphoric acid (PPA) gave the 2-alkyl/phenyl 8-(1*H*-benzoimidazol-2-yl)quinoline derivatives (**L1**, **L3**, **L7**, and **L11**, Scheme 1). The N-alkylation of **L1**, **L3**, **L7**, and **L11**, respectively, was carried out using a straightforward procedure[13a,22] to obtain the respective ligands in yields of 23% to 96% (Scheme 1). All organic compounds **L1** to **L14** were characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. In addition, compound **L5** was confirmed by an X-ray crystal structure analysis.

2.2. Synthesis of Iron Complexes. The reaction of $FeCl_2 \cdot 4H_2O$ with one equivalent of the respective ligand (**L1**−**L14**) in ethanol yielded the corresponding iron complexes (**C1**−**C14**) in high yields (80% to 94%) as orange or yellow solids. All iron complexes were characterized by elemental analyses and IR spectroscopy. In addition, the structures of complexes **C2** and **C7** were confirmed by X-ray crystal structure analysis.

2.3. X-ray Single-Crystal Structure Study. Single crystals of compound **L5** suitable for an X-ray crystal structure analysis were obtained by slow evaporation of a solution of **L5** in ethyl acetate. The molecular structure of **L5** is shown in Figure 1 along with its selected bond lengths and angles. In the structure of **L5**, the dihedral angle between the quinolinyl plane and the benzimidazole plane is 57.7°. The N1−C10 bond [1.324(2) Å] is longer than the typical imino C═N bond [1.22−1.27 Å].[13,23] The ethyl group on the imidazole nitrogen atom N3 stretches to the inner side because of the flexibility of the single C8−C10 bond.

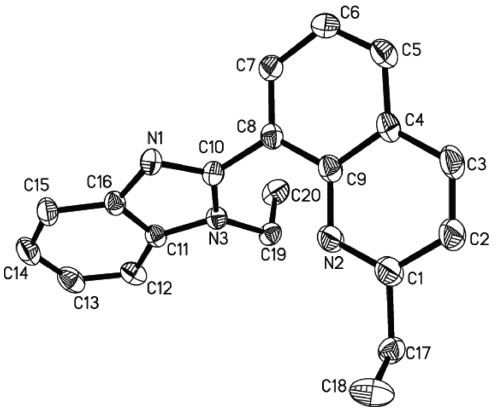


Figure 1. Molecular structure of **L5** with thermal ellipsoids at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): N1−C10 = 1.324(2), N1−C16 = 1.390(3), N3−C10 = 1.369(2), N3−C11 = 1.379(2); C10−N1−C16 = 104.42(16), C10−N3−C11 = 106.57(16).

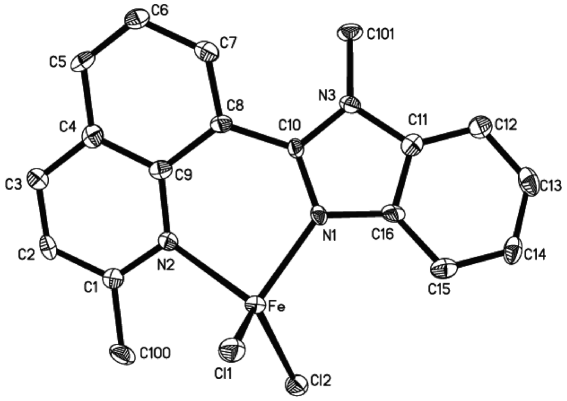


Figure 2. Molecular structure of **C2**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe−N1 = 2.027(7), Fe−N2 = 2.143(7), Fe−Cl1 = 2.255(3), Fe−Cl2 = 2.270(3), N1−C10 = 1.327(1), N3−C10 = 1.371(1); N1−Fe−N2 = 89.2(3), N1−Fe−Cl1 = 112.9(2), N1−Fe−Cl2 = 110.1(2), N2−Fe−Cl1 = 109.8(2), N2−Fe−Cl2 = 117.4(2), Cl1−M−Cl2 = 114.89(1).

Single crystals of the iron complexes **C2** and **C7** suitable for single-crystal X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a methanol solution of **C2** and **C7**, respectively, under a nitrogen atmosphere. The geometry at the iron center in both complexes is best described as distorted tetrahedral. The molecular structures of complexes **C2** and **C7** are shown in Figures 2 and 3 with their selected bond lengths and angles.

In the structure of complex **C2**, the dihedral angle formed by the planes Cl1−Fe−Cl2 and N1−Fe−N2 is 86.02°. The two Fe−Cl bond lengths are similar; however, the Fe−N1 distance is slightly shorter than the Fe−N2 length. The dihedral angle between the quinoline and benzimidazole rings is 28.94°.

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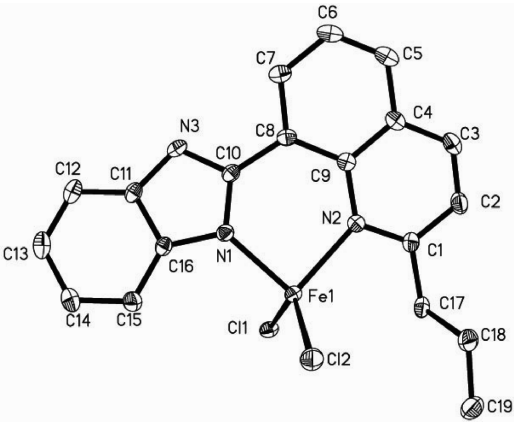

Figure 3. Molecular structure of **C7**. Thermal ellipsoids are shown at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Fe−N1 = 2.023(2), Fe−N2 = 2.112(2), Fe−Cl1 = 2.3006(9), Fe−Cl2 = 2.2306(9), N1−C10 = 1.331(3), N3−C10 = 1.357(3); N1−Fe−N2 = 91.11(8), N1−Fe−Cl1 = 100.91(7), N1−Fe−Cl2 = 113.48(7), N2−Fe−Cl1 = 110.35(6), N2−Fe−Cl2 = 114.05(6), Cl1−M−Cl2 = 121.90(3).

Table 1. Optimization of the Ethylene Polymerization Parameters with C1/MAO[a]

entry	Al/Fe	T/°C	activity[b]	M_w[c](10^4)	M_w/M_n[c]
1	3000	40	0.799	nd	nd
2	3000	60	1.35	98.1	25
3	3000	80	5.48	45.2	17
4	3000	100	6.11	16.4	3.9
5	1000	100	2.91	25.3	7.4
6	2000	100	4.43	23.5	4.7
7	2500	100	5.73	18.1	3.7
8	3500	100	5.93	14.5	3.9

[a] Conditions: 2 μmol of Fe; 30 atm of ethylene; 30 min; 40 mL of toluene. [b] 10^6 g·mol^{-1}(Fe)·h^{-1}. [c] Determined by GPC.

The atoms N2, C9, C8, C10, and N1 are almost coplanar, with the largest deviation of C10 at 0.157 Å, and the deviation of the iron atom from the plane is 0.578 Å.

As shown in Figure 3, the structure of **C7** is slightly different from that of **C2** due to the difference of substituents. The dihedral angle between the quinoline and benzimidazole rings is 20.41°. Around the iron atom, there is no significant difference in their bond lengths. However, a smaller deviation of the iron atom forming the plane defined by N2, C9, C8, C10, and N1 atoms is observed (0.092 Å).

2.4. Catalytic Behavior toward Ethylene Polymerization. Methylaluminoxane (MAO) was found to be the best co-catalyst, and a low activity was observed at ambient pressure and 10 atm of ethylene; however, a good activity was obtained at 30 atm of ethylene, attributable to the higher monomer concentration around the active iron centers at higher pressure.[5,6a] The catalytic system of **C1**/MAO was investigated with varying reaction conditions including the molar ratio of Al/Fe and reaction temperature. At room temperature, a low activity was observed. When the reaction temperature was increased (Table 1), the activities were significantly improved to the range of 10^6 g·mol^{-1}(Fe)·h^{-1}. Therefore we assume that the formation of the thermally stable active species requires relatively high temperature.

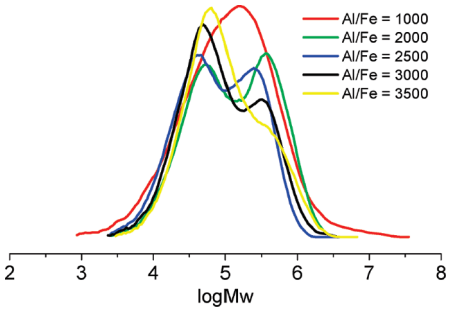

Figure 4. GPC curves of PEs by **C1** with various Al/Fe molar ratios at 100 °C (entries 4−8 in Table 1).

Table 2. Ethylene Polymerization by C1−C14/MAO at 100 °C[a]

entry	complex	R^1	R^2	activity[b]	M_w[c](10^4)	M_w/M_n[c]
1	**C1**	Me	H	6.11	16.4	3.9
2	**C2**	Me	Me	6.81	21.0	6.1
3	**C3**	Et	H	1.73	15.4	5.3
4	**C4**	Et	Me	1.83	26.1	17
5	**C5**	Et	Et	1.64	28.1	20
6	**C6**	Et	*i*Pr	1.31	35.5	13
7	**C7**	Pr	H	2.41	30.4	10
8	**C8**	Pr	Me	2.46	31.7	24
9	**C9**	Pr	Et	1.92	35.2	25
10	**C10**	Pr	*i*Pr	1.85	51.1	28
11	**C11**	Ph	H	2.56	32.0	5.6
12	**C12**	Ph	Me	3.63	32.7	13
13	**C13**	Ph	Et	2.16	37.7	23
14	**C14**	Ph	*i*Pr	1.94	64.6	28

[a] Conditions: 2 μmol of Fe; 3000 equiv of MAO; 30 atm of ethylene; 30 min; 40 mL of toluene. [b] 10^6 g·mol^{-1}(Fe)·h^{-1}. [c] Determined by GPC.

With variation of the Al/Fe molar ratios between 1000 and 3500 at 100 °C reaction temperature (entries 4−8 in Table 1), the GPC measurements of the respective polyethylenes showed wide or bimodal distributions (Figure 4). In addition, more portions of polyethylenes with low molecular weights were observed when the Al/Fe molar ratios were increased. In the catalytic system, multiple active species were formed and transformed into the active species producing polyethylenes with low molecular weights, indicating the increase of chain transfer and termination at higher Al/Fe molar ratios. The best activity was obtained with the Al/Fe molar ratios of 3000.

In the following, all iron pro-catalysts were investigated for ethylene polymerization by using the reaction conditions optimized for the activity of C1 (30 atm ethylene, Al/Fe = 3000, 100 °C) (Table 2). Their differences in catalytic activities were considered as a function of the nature of the ligands with different substituents R^1 and R^2.

The influence of the substituents R^1 and R^2 would be interesting with fine-tuning ligands for adapting catalytic activities and properties of resultant polyethylenes. In the series of pro-catalysts with R^1 = Et (entries 3−6, Table 2), with the exception of **C3** with R^2 = H, the activity order **C4** > **C5** > **C6**

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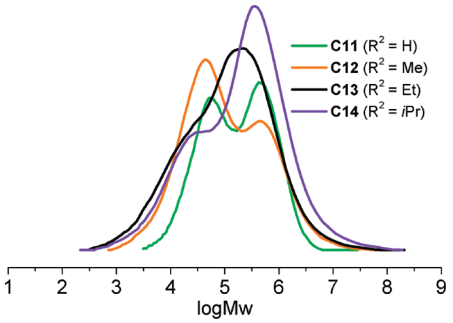

Figure 5. GPC curves of PEs obtained by **C11**−**C14** (R1 = Ph).

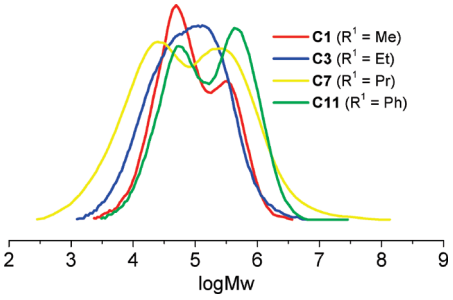

Figure 6. GPC curves of PEs by iron pro-catalysts with R^2 = H.

seems to be governed by the electronic influences of the ligands with electron-donating features of alkyl substituents listed as R^2 = Me (**C4**) < Et (**C5**) < *i*Pr (**C6**). This is consistent with the slow insertion of ethylene on the electron-rich active species in late transition metal catalytic systems.[14a] The same trend of catalytic activities was also observed in the series of iron pro-catalysts with R^1 = Me, Pr, or Ph, respectively. Therefore the electronic effect was a major issue caused by the substituent R^2 because R^2 is too far removed from the active iron center. Broad molecular weight distributions were obtained due to multimodal polymers observed in the GPC traces,[5] and multiactive species of iron pro-catalysts were imaged along with the chain transfer to excessive amounts of Al centers.[8,24] Checking the influences of the ligand environment on the properties of polyethylenes obtained with fixing R^1 = Ph (Figure 5), the molecular weights of the resultant polyethylenes gradually increased with broader molecular weight distributions, along with changing the R^2 substituent from hydrogen to isopropyl, M_w (**C11**, R^2 = H) < M_w (**C12**, R^2 = Me) < M_w (**C13**, R^2 = Et) < M_w (**C14**, R^2 = *i*Pr).

Considering the influence of R^1 substituents (closer to the active iron center) on the catalytic performance of the iron pro-catalysts, shown in the series of iron pro-catalysts with R^2 = Me (entries 2, 4, 8, and 12, Table 2), their catalytic activities were ordered as R^1 = Me (**C2**) > Ph (**C12**) > Pr (**C8**) > Et (**C4**). Beyond the electronic influence on explaining the better activities of **C2** (Me) and **C12** (Ph),[14a] more bulky substituents could protect the active species as Ph (**C12**) > Pr (**C8**) > Et (**C4**).[5,6] Other series of iron pro-catalysts with R^2 = H, Et, or *i*Pr also exhibited the same trend in their catalytic activities.

Considering polyethylenes obtained by iron procatalysts with R^2 = H (entries 1, 3, 7, and 11, Table 2), their molecular weights and molecular weight distributions were generally increased with varying the R^1 group with bulky alkyl and phenyl groups (Figure 6), although similar molecular weights for polyethylenes by **C1** (R^1 = Me) and **C3** (R^1 = Et) were observed. Therefore synergic steric and electronic influences were considered with the substituent R^1 due to it being closer to the active iron center. This fine-tuning of ligands could induce catalytic behaviors of their iron pro-catalysts and new properties of resultant polyethylenes.

In addition, the representative polyethylenes (entries 3, 7, and 12, Table 2) were characterized by $^{13}C\{^1H\}$ NMR at 90 °C in bromobenzene-d_5 and approved as highly linear polyethylenes. The NMR spectra are available in the Supporting Information.

3. CONCLUSIONS

The series of bidentate iron(II) complexes bearing 2-R^1-8-(1-R^2-benzimidazol-2-yl)quinolines give highly active catalysts for ethylene polymerizations upon activation with MAO at 100 °C. The catalytic activities were achieved only at elevated reaction temperature. Two substituents of R^1 and R^2 showed different influences on the activities of the iron complexes; therefore fine-tuning the ligands would potentially control the catalytic activities of iron pro-catalysts and resultant polyethylenes.

4. EXPERIMENTAL SECTION

4.1. General Considerations. All manipulations of air- and moisture-sensitive compounds were performed in a nitrogen atmosphere using standard Schlenk techniques. Toluene was refluxed over sodium-benzophenone and distilled under argon prior to use. Methylaluminoxane (a 1.46 M solution in toluene) was purchased from Akzo Nobel Corp. Other reagents were purchased from Aldrich or Acros Chemicals. ^1H and ^{13}C NMR spectra were recorded on a Bruker DMX 300 MHz or a Bruker DMX 400 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 an HPMOD 1106 microanalyzer. A Midea PJ21B-A microwave oven (800 W, 21 L) was used for microwave-assisted condensation reactions. $^{13}C\{^1H\}$ NMR spectra of the PE samples were recorded on a Bruker DMX 200 MHz instrument at 90 °C in bromobenzene-d_5.

4.2. Preparation of the Ligands. *Synthesis of 8-(1H-benzimidazol-2-yl)-2-methylquinoline (**L1**).* 2-Methylquinoline-8-carboxylic acid (1.87 g, 10 mmol), *o*-phenylenediamine (1.08 g, 10 mmol), and polyphosphoric acid (8 g) were mixed together and irradiated in the microwave oven (450 W) three times for 1 min. The dark green solution of the reactants was poured into an ice−water mixture, and a yellow solid precipitated. A NH_3 solution was added to adjust the mixture pH value to 8−9, and the precipitate was filtrated. After drying, it was eluted with petroleum ether/ethyl acetate (v/v = 1:1) on a silica column, and a white powder (1.756 g, 6.77 mmol) was obtained. Yield: 68%. Mp: 172−173 °C. IR (KBr; cm^{-1}): 3188, 3053, 1613, 1598, 1572, 1501, 1422, 1402, 1319, 1278, 1128, 839, 797, 764, 729, 698. ^1H NMR (300 MHz, $CDCl_3$): δ 13.55 (s, 1H, NH); 9.00 (d, J = 7.5 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.87 (br, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.64−7.48 (m, 2H), 7.34−7.16 (m, 3H), 2.74 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 158.9 (C), 151.9 (C), 144.8 (C), 143.3 (C), 137.6 (CH), 134.1 (C), 130.2 (CH), 129.7 (CH), 127.0 (C), 125.9 (CH), 125.0 (C), 122.8 (CH), 122.3 (CH), 122.1 (CH), 119.4 (CH), 111.4 (CH), 25.8 (Me). Anal. Calcd for $C_{17}H_{13}N_3$ (259.31): C, 78.74; H, 5.05; N, 16.20. Found: C, 79.02; H, 5.27; N, 15.83.

*Synthesis of 2-Methyl-8-(1-methyl-benz[d]imidazol-2-yl)quinoline (**L2**).* Powdered potassium hydroxide (0.504 g, 9 mmol) was added to a stirred solution of **L1** (1.554 g, 6 mmol) in acetone. After 3 h, methyl iodide (1.022 g, 7.2 mmol) was added to the reaction mixture with vigorous stirring. After 6 h, the solvent was removed, the resulting solid was eluted with petroleum ether/ethyl acetate (v/v = 1:1) on a silica

column, and white crystals (1.1983 g, 4.39 mmol) were obtained in a yield of 73%. Mp: 145−146 °C. IR (KBr; cm^{-1}): 3060, 1615, 1600, 1498, 1464, 1440, 1425, 1389, 1320, 1281, 1240, 841, 761, 734. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 7.2 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H); 7.87 (d, J = 8.4 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.2 Hz, 1H), 7.37−7.30 (m, 3H), 3.64 (s, 3H, ^{N}Me), 2.63 (s, 3H, ^{C}Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 159.9 (C), 153.7 (C), 146.1 (C), 143.3 (C), 136.5 (C), 136.4 (CH), 133.1 (CH), 130.1 (CH), 129.5 (C), 126.5 (C), 125.5 (CH), 122.5 (CH), 122.4 (CH), 122.0 (CH), 119.9 (CH), 109.6 (CH), 31.9 (^{N}Me), 25.6 (^{C}Me). Anal. Calcd for $C_{18}H_{15}N_3$ (273.33): C, 79.10; H, 5.53; N, 15.37. Found: C, 78.83; H, 5.51; N, 14.99.

*Synthesis of 8-(1H-Benzimidazol-2-yl)-2-ethylquinoline (**L3**).* 2-Ethylquinoline-8-carboxylic acid (2.4 g, 12 mmol), *o*-phenylenediamine (1.56 g, 14.4 mmol), and phosphoric acid (15 mL) were mixed together and reacted at 170−180 °C for 6 h. The dark green solution of the reactants was poured into an ice−water mixture after cooling, and a green solid precipitated. Aqueous ammonia was added to adjust the pH of the mixture to 8−9, and the precipitate was filtrated and washed with water. After drying, it was eluted with petroleum ether/ethyl acetate (v/v = 4:1) on a silica column, and a white powder (1.91 g, 6.99 mmol) was obtained. Yield: 58.3%. Mp: 174−176 °C. IR (KBr; cm^{-1}): 3045, 3013, 1633, 1614, 1524, 1499, 1435, 1278, 1186, 1143, 962, 851, 788, 672. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.89 (s, 1H, NH); 9.11 (d, J = 7.4 Hz, 1H); 8.18 (d, J = 8.5 Hz, 1H); 7.89−7.85 (m, 2H); 7.66 (t, J = 7.7 Hz, 1H); 7.59 (br, 1H); 7.42 (d, J = 8.5 Hz, 1H); 7.31−7.28 (m, 2H); 3.21 (q, J = 7.5 Hz, 2H, Et); 1.60 (t, J = 7.5 Hz, 3H, Et). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.4 (C), 152.0 (C), 144.8 (C), 143.4 (C), 137.7 (CH), 134.2 (C), 130.2 (CH), 129.7 (CH), 127.4 (C),126.1 (CH), 125.3 (C), 122.8 (CH), 122.3 (CH), 121.4 (CH), 119.5 (CH), 111.3 (CH), 32.0 (Et), 12.9 (Et). Anal. Calcd for $C_{18}H_{15}N_3$ (273.33): C, 79.10; H, 5.53; N, 15.37. Found: C, 79.21; H, 5.32; N, 15.21.

*Synthesis of 2-Ethyl-8-(1-methylbenzimidazol-2-yl)quinoline (**L4**).* A 1.5 equiv amount of powdered potassium hydroxide (0.2461 g, 4.4 mmol) was added to a solution of **L3** (0.8 g, 2.93 mmol) in acetone. After 3 h, methyl iodide (0.4993 g, 3.52 mmol) was added to the reaction mixture with vigorous stirring. After the mixture was stirred for 6 h, aqueous ammonia was added to adjust the pH of the mixture to 7, and the mixture was extracted with CH_2Cl_2. The desired ligand **L4** (0.7649 g, 3.97 mmol) was obtained as a white solid in 90.3% yield after purification by column chromatography (silica gel, petroleum ether/ethyl acetate, 4:1). Mp: 130−132 °C. IR (KBr; cm^{-1}): 3051, 2928, 1594, 1496, 1443, 1423, 1387, 1319, 1282, 848, 770, 739, 659. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 7.0 Hz, 1H), 7.94 (d, J = 7.1 Hz, 1H), 7.87 (d, J = 7.4 Hz, 1H), 7.61 (t, J = 7.5 Hz, 1H), 7.46 (d, J = 7.4 Hz, 1H), 7.37−7.31 (m, 3H), 3.64 (s, 3H, Me), 2.89 (q, J = 7.5 Hz, 2H, Et), 1.26 (t, J = 7.5 Hz, 3H, Et). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.5 (C), 153.9 (C), 146.1 (C), 143.4 (C), 136.6 (C), 136.5 (CH), 133.0 (CH), 130.1 (CH), 129.8 (C), 126.8 (C), 125.5 (CH), 122.5 (CH), 121.9 (CH), 121.5 (CH), 120.0 (CH), 109.5 (CH), 32.2 (Me), 31.8 (Et), 13.5 (Et). Anal. Calcd for $C_{19}H_{17}N_3$ (287.36): C, 79.41; H, 5.96; N, 14.62. Found: C, 79.66; H, 5.93; N, 14.55.

*Synthesis of 2-Ethyl-8-(1-ethylbenzimidazol-2-yl)quinoline (**L5**).* A solution of **L3** (0.8 g, 2.93 mmol) in 20 mL of acetone was refluxed with 1.5 equiv of KOH (0.2461 g, 4.4 mmol) for 3 h. After the mixture was cooled to room temperature, iodoethane (0.5475 g, 3.51 mmol) was added to the reaction mixture, which was stirred for 24 h at 40 °C. The solvent was evaporated at reduced pressure before water (20 mL) was added, and aqueous ammonia was added to adjust the pH of the mixture to 7. Then the aqueous phase was extracted with CH_2Cl_2 (4 × 15 mL). The combined extract was dried over anhydrous Na_2SO_4 and filtered, and the solvent was finally evaporated at reduced pressure. The desired compound **L5** (0.6271 g, 2.08 mmol) was obtained as a white solid in 71.1% yield after purification by column chromatography (silica gel, petroleum ether/ethyl acetate, 2:1). Mp: 104−106 °C. IR (KBr; cm^{-1}): 3054, 2971, 1606, 1451, 1397, 1270, 1004, 847. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J = 8.5 Hz, 1H), 7.99 (d, J = 7.1 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 7.1 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.36−7.30 (m, 3H), 4.12 (q, J = 7.2 Hz, 2H, ^{N}Et), 2.88 (q, 2H, J = 7.6 Hz, ^{C}Et), 1.26 (t, J = 7.2 Hz, ^{N}Et), 1.24 (t, J = 7.6 Hz, ^{C}Et). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.6 (C), 153.1 (C), 146.2 (C), 143.7 (C), 136.4 (CH), 135.3 (C), 132.8 (CH), 130.2 (C), 129.9 (CH), 126.8 (C), 125.5 (CH), 122.3 (CH), 121.8 (CH), 121.5 (CH), 120.1 (CH), 110.0 (CH), 39.9 (^{N}Et), 32.1 (^{C}Et), 15.0 (^{N}Et), 13.5 (^{C}Et). Anal. Calcd for $C_{20}H_{19}N_3$ (301.38): C, 79.70; H, 6.35; N, 13.94. Found: C, 79.69; H, 6.53; N, 13.78.

*Synthesis of 2-Ethyl-8-(1-isopropylbenzimidazol-2-yl)quinoline (**L6**).* A solution of **L3** (0.8 mg, 2.93 mmol) in 20 mL of acetone was refluxed with 1.5 equiv of KOH (0.2461 mg, 4.4 mmol) for 3 h. After the mixture was cooled to room temperature, 2-iodopropane (0.5967 g, 3.51 mmol) was added to the reaction mixture, which was stirred for 24 h at refluxing temperature. The solvent was evaporated at reduced pressure before water (20 mL) was added, and aqueous ammonia was added to adjust the pH of the mixture to 7. Then the aqueous phase was extracted with CH_2Cl_2 (4 × 15 mL). The combined extract was dried over anhydrous Na_2SO_4 and filtered; the solvent was finally evaporated at reduced pressure. The desired compound **L6** (0.2331 g, 0.74 mmol) was obtained as a white solid in 25.1% yield after purification by column chromatography (silica gel, petroleum ether/ethyl acetate, 2:1). Mp: 114 − 116 °C. IR (KBr; cm^{-1}): 2971, 2931, 1606, 1577, 1436, 1377, 1280, 1156, 841. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.5 Hz, 1H), 7.94−7.90 (m, 2H), 7.87 (br, 1H), 7.69 (br, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.34−7.28 (m, 3H), 4.34 (sept, J = 6.8 Hz, 1H, *i*Pr), 2.87 (q, J = 7.7 Hz, 2H, Et), 1.75 (br, 3H, *i*Pr), 1.58 (br, 3H, *i*Pr), 1.23 (t, J = 7.7 Hz, 3H, Et). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 164.8 (C), 153.0 (C), 146.5 (C), 144.4 (C), 136.4 (CH), 133.5 (C), 132.7 (CH), 130.7 (C), 129.9 (CH) 126.7 (C), 125.4 (CH), 121.9 (CH), 121.5 (CH), 121.3 (CH), 120.4 (CH), 112.1 (CH), 49.4 (*i*Pr), 32.2 (Et), 21.2 (br, *i*Pr), 13.8 (Et). Anal. Calcd for $C_{21}H_{21}N_3$ (315.97): C, 79.97; H, 6.71; N, 13.32. Found: C, 80.03; H, 6.64; N, 13.33.

*Synthesis of 8-(1H-Benzimidazol-2-yl)-2-propylquinoline (**L7**).* Using the same procedure as for the synthesis of **L3**, **L7** was obtained as a white powder in a yield of 42.6%. Mp: 174 − 176 °C. IR (KBr; cm^{-1}): 3048, 2953, 1614, 1524, 1499, 1435, 1396, 1306, 1278, 1186, 1131, 850, 787, 727, 656. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.84 (br, 1H, NH); 9.10 (d, J = 7.4 Hz, 1H); 8.17 (d, J = 8.0 Hz, 1H); 7.90−7.84 (m, 2H); 7.65 (t, J = 7.6 Hz, 1H); 7.60 (br, 1H); 7.39 (d, J = 8.4 Hz, 1H); 7.30−7.29 (m, 2H); 3.14 (t, J = 7.5 Hz, 2H, Pr); 2.05 (sext, 2H, Pr), 1.15 (t, J = 7.3 Hz, 3H, Pr). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.6 (C), 152.0 (C), 144.9 (C), 143.4 (C), 137.7 (CH), 134.2 (C), 130.4 (CH), 129.7 (CH), 127.4 (C), 126.2 (CH), 125.3 (C), 122.8 (CH), 122.3 (CH), 121.8 (CH), 119.5 (CH), 111.3 (CH), 41.1 (Pr), 22.3 (Pr), 14.0 (Pr). Anal. Calcd for $C_{19}H_{17}N_3$ (287.36): C, 79.41; H, 5.96; N, 14.62. Found: C, 79.21; H, 5.92; N, 14.61.

*Synthesis of 2-Propyl-8-(1-methylbenzimidazol-2-yl)quinoline (**L8**).* Using the same procedure as for the synthesis of **L4**, **L8** was obtained as a white powder in a yield of 87.6%. Mp: 131−133 °C. IR (KBr; cm^{-1}): 3045, 2961, 2854, 1605, 1441, 1419, 1384, 1325, 1279, 848, 768, 737, 659. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 7.0 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.87 (d, J = 7.4 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.37−7.30 (m, 3H), 3.63 (s, 3H, Me), 2.83 (t, J = 7.5 Hz, 2H, Pr), 1.73 (sext, 2H, Pr), 0.92 (t, J = 7.3 Hz, 3H, Pr). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.6 (C), 153.9 (C), 146.2 (C), 143.4 (C), 136.6 (C), 136.3 (CH), 133.1 (CH), 130.1 (CH), 129.8 (C), 126.8 (C), 125.5 (CH), 122.4 (CH), 121.9 (2 × CH), 120.0 (CH), 109.6 (CH), 41.2 (Pr), 31.8 (Me), 22.7 (Pr), 14.1 (Pr). Anal. Calcd for $C_{20}H_{19}N_3$ (301.38): C, 79.70; H, 6.35; N, 13.94. Found: C, 79.66; H, 6.53; N, 14.14.

*Synthesis of 2-Propyl-8-(1-ethylbenzimidazol-2-yl)quinoline (**L9**).* Using the same procedure as for the synthesis of **L5**, **L9** was obtained as a white powder in a yield of 41.1%. Mp: 106−108 °C. IR (KBr; cm^{-1}): 2958, 1606, 1449, 1426, 1389, 1271, 848, 768, 737, 659. ^1H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 7.1 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 7.2 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.50 (d, J = 7.4 Hz, 1H), 7.36−7.30 (m, 3H), 4.10 (q, J = 7.3 Hz, 2H, Et), 2.82 (t, J = 7.6 Hz, 2H, Pr), 1.71 (sext, 2H, Pr), 1.25 (t, J = 7.3 Hz, 3H, Et), 0.90 (t, J = 7.1 Hz, 3H, Pr). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.7 (C), 153.2 (C), 146.3 (C), 143.8 (C), 136.3 (CH), 135.3 (C), 132.8 (CH), 130.3 (C), 130.0 (CH), 126.8 (C), 125.4 (CH), 122.3 (CH), 122.0 (CH), 121.8 (CH), 120.1 (CH), 110.0 (CH), 41.1 (Pr), 39.9 (Et), 22.7 (Pr), 15.0 (Et), 14.1 (Pr). Anal. Calcd for $C_{21}H_{21}N_3$ (315.41): C, 79.97; H, 6.71; N, 13.32. Found: C, 79.99; H, 6.73; N, 13.28.

*Synthesis of 2-Propyl-8-(1-isopropylbenzimidazol-2-yl)quinoline (**L10**).* Using the same procedure as for the synthesis of **L6**, **L10** was obtained as a white powder in a yield of 23.3%. Mp: 118−120 °C. IR (KBr; cm^{-1}): 2958, 2926, 1607, 1576, 1497, 1436, 1379, 1281, 848, 768, 737, 659. ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.4 Hz, 1H), 7.95−7.90 (m, 2H), 7.86 (br, 1H), 7.70 (br, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.34−7.29 (m, 3H), 4.34 (sept, 1H, J = 8.4 Hz, *i*Pr), 2.82 (t, J = 7.7 Hz, 2H, Pr), 1.81 (br, 3H, *i*Pr) 1.69 (sext, 2H, Pr), 1.44 (br, 3H, *i*Pr), 0.91 (t, J = 7.3 Hz, 3H, Pr). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.8 (C), 153.1 (C), 146.7 (C), 144.4 (C), 136.3 (CH), 133.6 (C), 132.8 (CH), 130.7 (C), 129.9 (CH), 126.7 (C), 125.4 (CH), 122.0 (CH), 121.8 (CH), 121.6 (CH), 120.4 (CH), 112.1 (CH), 49.4 (*i*Pr), 41.3 (Pr), 23.0 (Pr), 21.4 (br, *i*Pr), 14.2 (Pr). Anal. Calcd for $C_{22}H_{23}N_3$ (329.44): C, 80.21; H, 7.04; N, 12.76. Found: C, 80.23; H, 7.36; N, 12.42.

*Synthesis of 8-(1H-Benzimidazol-2-yl)-2-phenylquinoline (**L11**).* Using the same procedure as for the synthesis of **L3**, **L11** was obtained as a white powder in a yield of 32.0%. Mp: 173−174 °C. IR (KBr; cm^{-1}): 3059, 2923, 1600, 1563, 1489, 1446, 1420, 1399, 1324, 1278, 1132, 843, 768, 739, 727, 665. ^1H NMR (400 MHz, $CDCl_3$): δ 13.72 (br, 1H, NH); 9.15 (d, J = 7.4 Hz, 1H); 8.36 (d, J = 8.5 Hz, 1H); 8.12 (d, J = 7.8 Hz, 2H); 7.98−7.91 (m, 2H); 7.90 (d, J = 7.4 Hz, 1H); 7.72 (t, J = 7.6 Hz, 1H); 7.66 (t, J = 7.5 Hz, 2H); 7.61 (d, J = 6.9 Hz, 1H); 7.56 (d, J = 7.3 Hz, 1H); 7.35−7.25 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.7 (C), 151.7 (C), 145.2 (C), 143.4 (C), 139.8 (C), 138.5 (CH), 134.2 (C), 130.8 (CH), 130.0 (CH), 129.7 (CH), 129.4 (2 × CH), 127.8 (2 × CH), 127.7 (C), 126.8 (CH), 125.9 (C), 122.9 (CH), 122.4 (CH), 119.6 (CH), 119.5 (CH), 111.3 (CH). Anal. Calcd for $C_{22}H_{15}N_3$ (321.37): C, 82.22; H, 4.70; N, 13.08. Found: C, 82.09; H, 4.93; N, 12.65.

*Synthesis of 2-Phenyl-8-(1-methylbenzimidazol-2-yl)quinoline (**L12**).* Using the same procedure as for the synthesis of **L4**, **L12** was obtained as a white powder in a yield of 96.1%. Mp: 221−223 °C. IR (KBr; cm^{-1}): 3048, 2930, 1612, 1588, 1570, 1482, 1455, 1423, 1387, 1324, 1280, 844, 766, 737, 661. ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 8.6 Hz, 1H); 8.13 (d, J = 7.0 Hz, 1H); 8.08−7.98 (m, 4H); 7.91 (d, J = 7.2 Hz, 1H); 7.67 (t, J = 7.6 Hz, 1H); 7.49 (d, J = 7.4 Hz, 1H); 7.43−7.32 (m, 5H); 3.67 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.0 (C), 153.7 (C), 146.3 (C), 143.6 (C), 138.8 (C), 137.3 (CH), 136.7 (C), 133.7 (CH), 130.5 (C), 130.1 (CH), 129.8 (CH), 129.0 (2 × CH), 127.3 (2 × CH), 127.1 (C), 126.3 (CH), 122.6 (CH), 122.1 (CH), 120.1 (CH), 118.8 (CH), 109.7 (CH), 32.0 (Me). Anal. Calcd for $C_{23}H_{17}N_3$ (335.40): C, 82.36; H, 5.11; N, 12.53. Found: C, 82.18; H, 5.23; N, 12.39.

*Synthesis of 2-Phenyl-8-(1-ethylbenzimidazol-2-yl)quinoline (**L13**).* Using the same procedure as for the synthesis of **L5**, **L13** was obtained as a white powder in a yield of 88.3%. Mp: 131−133 °C. IR (KBr; cm^{-1}): 3053, 2927, 1598, 1566, 1451, 1397, 1273, 1011, 842, 768, 741, 697. ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.7 Hz, 1H); 8.06−7.94 (m, 5H); 7.91 (br, 1H); 7.66 (t, J = 7.6 Hz, 1H); 7.53 (d, J = 8.0 Hz, 1H); 7.40−7.30 (m, 5H); 4.17 (q, J = 7.2 Hz, 2H, Et); 1.18 (t, J = 7.2 Hz, 3H, Et). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.1 (C), 153.0 (C), 146.4 (C), 143.9 (C), 138.7 (C), 137.2 (CH), 135.4 (C), 133.4 (CH), 131.0 (C), 130.0 (CH), 129.8 (CH), 128.9 (2 × CH), 127.5 (2 × CH), 127.3 (C), 126.2 (CH), 122.4 (CH), 121.9 (CH), 120.2 (CH), 119.0 (CH), 110.1 (CH), 40.0 (Et), 15.0 (Et). Anal. Calcd for $C_{24}H_{19}N_3$ (349.43): C, 82.49; H, 5.48; N, 12.03. Found: C, 82.21; H, 5.65; N, 11.84.

*Synthesis of 2-Phenyl-8-(1-isopropylbenzimidazol-2-yl)quinoline (**L14**).* Using the same procedure as for the synthesis of **L6**, **L14** was obtained as a white powder in a yield of 55.3%. Mp: 161−163 °C. IR (KBr; cm^{-1}): 2927, 1611, 1568, 1452, 1376, 1281, 1157, 837, 768, 743, 696. ^1H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.7 Hz, 1H); 8.02−7.96 (m, 5H); 7.93−7.88 (m, 1H); 7.71−7.66 (m, 1H); 7.65 (t, J = 7.7 Hz, 1H); 7.38−7.31 (m, 5H); 4.34 (sept, 1H, J = 6.9 Hz, *i*Pr); 1.53 (br, 3H, *i*Pr), 1.41 (br, 3H, *i*Pr). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.3 (C), 153.0 (C), 146.9 (C), 144.5 (C), 138.7 (C), 137.1 (CH), 133.6 (C), 133.2 (CH), 131.4 (C), 129.9 (CH), 129.7 (CH), 128.8 (2 × CH), 127.7 (2 × CH), 127.2 (C), 126.1 (CH), 122.0, (CH), 121.6 (CH), 120.5 (CH), 119.2 (CH), 112.3 (CH), 49,5 (*i*Pr), 20.9 (br, *i*Pr). Anal. Calcd for $C_{25}H_{21}N_3$ (363.45): C, 82.61; H, 5.82; N, 11.56. Found: C, 82.63; H, 5.94; N, 11.41.

4.3. Synthesis of Iron Complexes C1−C14. The iron complexes **C1**−**C14** were synthesized by the reaction of $FeCl_2 \cdot 4H_2O$ with the corresponding ligands in ethanol. A typical synthetic procedure for **C1** can be described as follows. To a mixture of ligand **L1** (77.7 mg, 0.3 mmol) and $FeCl_2 \cdot 4H_2O$ (60.1 mg, 0.3 mmol) was added ethanol (4 mL) at room temperature. The solution turned orange immediately. The reaction mixture was stirred for 6 h, and absolute diethyl ether was added. The resulting precipitate was filtered, washed with diethyl ether, and dried in a vacuum to furnish the pure product as an orange powder (108.3 mg, 0.281 mmol) in 94.3% yield. IR (KBr; cm^{-1}): 3483, 3057, 1613, 1569, 1513, 1432, 1409, 843, 773, 741. Anal. Calcd for $C_{17}H_{13}Cl_2FeN_3$ (386.06): C, 52.89; H, 3.39; N, 10.88. Found: C, 52.95; H, 3.17; N, 10.66.

Complex **C2** was obtained as an orange powder in 89.1% yield. IR (KBr; cm^{-1}): 3059, 1613, 1531, 1569, 1514, 1454, 1404, 850, 773, 749. Anal. Calcd for $C_{18}H_{15}Cl_2FeN_3$ (400.08): C, 54.04; H, 3.78; N, 10.50. Found: C, 54.33; H, 3.59; N, 10.36.

Complex **C3** was obtained as an orange powder in 89.9% yield. IR (KBr; cm^{-1}): 3195, 2984, 1607, 1568, 1513, 1459, 1411, 1325, 1202, 1149, 846, 768, 741, 681. Anal. Calcd for $C_{18}H_{15}Cl_2FeN_3$ (400.08): C, 54.04; H, 3.78; N, 10.50. Found: C, 53.67; H, 3.71; N, 10.28.

Complex **C4** was obtained as an orange powder in 83.6% yield. IR (KBr; cm^{-1}): 2969, 1607, 1579, 1477, 1445, 1398, 1331, 1208, 1049, 848, 755. Anal. Calcd for $C_{19}H_{17}Cl_2FeN_3$ (414.11): C, 55.11; H, 4.14; N, 10.15. Found: C, 55.01; H, 4.04; N, 9.98.

Complex **C5** was obtained as an orange powder in 81.2% yield. IR (KBr; cm^{-1}): 2973, 1583, 1498, 1448, 1421, 1334, 1230, 1203, 1052, 842, 750. Anal. Calcd for $C_{20}H_{19}Cl_2FeN_3$ (428.14): C, 56.11; H, 4.47; N, 9.81. Found: C, 56.17; H, 4.41; N, 9.65.

Complex **C6** was obtained as an orange powder in 80.9% yield. IR (KBr; cm^{-1}): 2969, 1607, 1579, 1477, 1445, 1398, 1331, 1208, 1149, 846, 768, 741, 681. Anal. Calcd for $C_{21}H_{21}Cl_2FeN_3$ (442.16): C, 57.04; H, 4.79; N, 9.50. Found: C, 57.40; H, 4.61; N, 9.12.

Complex **C7** was obtained as an orange powder in 81.6% yield. IR (KBr; cm^{-1}): 2960, 1607, 1570, 1512, 1458, 1408, 1327, 1148, 839, 808, 750, 680. Anal. Calcd for $C_{19}H_{17}Cl_2FeN_3$ (414.11): C, 55.11; H, 4.14; N, 10.15. Found: C, 54.96; H, 4.15; N, 9.87.

Complex **C8** was obtained as a pink powder in 80.3% yield. IR (KBr; cm^{-1}): 2952, 1601, 1569, 1501, 1461, 1391, 1329, 1103, 855, 781, 752, 680. Anal. Calcd for $C_{20}H_{19}Cl_2FeN_3 \cdot 1/3H_2O$: C, 55.33; H, 4.57; N, 9.68. Found: C, 55.57; H, 4.41; N, 9.64.

Complex **C9** was obtained as a yellow powder in 88.7% yield. IR (KBr; cm^{-1}): 2960, 1604, 1574, 1500, 1416, 1336, 1088, 844, 781, 749, 661. Anal. Calcd for $C_{21}H_{21}Cl_2FeN_3$ (442.16): C, 57.04; H, 4.79; N, 9.50. Found: C, 57.43; H, 4.61; N, 9.33.

Table 3. Crystal Data and Structure Refinement for L5, C2, and C7

	L5	C2	C7
empirical formula	$C_{20}H_{19}N_3$	$C_{18}H_{15}Cl_2FeN_3$	$C_{19}H_{17}Cl_2FeN_3$
fw	301.38	400.08	414.11
cryst color	colorless	orange	yellow
temperature (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2(1)2(1)2(1)$	$P2_1/n$	$C2/c$
a (Å)	6.8148(14)	7.2193(1)	14.916(3)
b (Å)	11.667(2)	17.200(3)	15.255(3)
c (Å)	20.822(4)	13.681(3)	15.909(3)
β (deg)	90	101.78(3)	94.98(3)
volume (Å^3)	1655.5(6)	1663.0(6)	3606.5(13)
Z	4	4	8
D_{calc} (Mg m^{-3})	1.209	1.598	1.525
μ (mm^{-1})	0.073	1.232	1.139
$F(000)$	640	816	1696
cryst size (mm)	0.80 × 0.80 × 30	0.30 × 0.25 × 0.20	0.18 × 0.0.08 × 0.07
θ range (deg)	2.62−27.48	2.81−25.01	1.91−30.03
limiting indices	$-8 \le h \le 8$,	$-8 \le h \le 8$,	$-17 \le h \le 20$,
	$-12 \le k \le 15$,	$-20 \le k \le 20$,	$-21 \le k \le 21$,
	$-26 \le l \le 27$	$-16 \le l \le 16$	$-22 \le l \le 21$
completeness to θ (%)	99.6 (θ = 27.48)	96.9 (θ = 25.01)	99.0 (θ = 30.03)
R(int)	0.0373	0.0651	0.0449
absorp corr	empirical	empirical	empirical
data/restraints/params	3786/32/227	2850/0/217	5211/0/230
goodness-of-fit on F^2	1.131	1.277	1.156
final R indices [$I > 2\sigma(I)$]	R1 = 0.0560, wR2 = 0.1376	R1 = 0.1143, wR2 = 0.1937	R1 = 0.0568, wR2 = 0.1102
R indices (all data)	R1 = 0.0590, wR2 = 0.1400	R1 = 0.1579, wR2 = 0.2096	R1 = 0.0643, wR2 = 0.1142
largest diff peak and hole (e Å^{-3})	0.165 and −0.225	0.543 and −0.446	0.476 and −0.401

Complex **C10** was obtained as a yellow powder in 79.9% yield. IR (KBr; cm^{-1}): 2961, 1607, 1512, 1408, 1327, 1148, 1079, 841, 748, 681. Anal. Calcd for $C_{22}H_{23}Cl_2FeN_3$ (456.19): C, 57.92; H, 5.08; N, 9.21. Found: C, 57.93; H, 5.01; N,9.09 .

Complex **C11** was obtained as a yellow powder in 92.3% yield. IR (KBr; cm^{-1}): 3060, 1590, 1449, 1405, 1283, 1180, 1052, 850, 767, 748, 689. Anal. Calcd for $C_{22}H_{15}Cl_2FeN_3$ (448.13): C, 58.96; H, 3.37; N, 9.38. Found: C, 58.76; H, 3.71; N, 9.58.

Complex **C12** was obtained as a yellow powder in 92.1% yield. IR (KBr; cm^{-1}): 3060, 1595, 1475, 1451, 1401, 1292, 843, 749, 696, 665. Anal. Calcd for $C_{23}H_{17}Cl_2FeN_3$ (462.15): C, 59.77; H, 3.71; N, 9.09. Found: C, 59.61; H, 3.90; N, 9.23.

Complex **C13** was obtained as a yellow powder in 90.2% yield. IR (KBr; cm^{-1}): 3057, 2980, 2932, 1599, 1472, 1451, 1415, 1280, 1245 1017, 847, 769, 736, 695, 665. Anal. Calcd for $C_{24}H_{19}Cl_2FeN_3$ (476.18): C, 60.54; H, 4.02; N, 8.82. Found: C, 60.76; H, 4.31; N, 9.05.

Complex **C14** was obtained as a yellow powder in 86.3% yield. IR (KBr; cm^{-1}): 3052, 2964, 1603, 1490, 1421, 1326, 952, 842, 759, 729, 692, 657. Anal. Calcd for $C_{25}H_{21}Cl_2FeN_3$ (490.21): C, 61.25; H, 4.32; N, 8.57. Found: C, 61.21; H, 4.01; N, 8.92.

4.4. Procedure for Ethylene Polymerization. Ethylene polymerization was performed in a stainless steel autoclave (100 mL scale). A typical reaction procedure was as follows. Catalyst (2 μmol), toluene (40 mL), and the required amount of MAO (1.46 mol/L solution in toluene) were added into the autoclave in the drybox. The reactor was sealed and moved out of the drybox. At the reaction temperature, the reaction apparatus was then immediately pressurized to 30 atm. The mixture was magnetically stirred for 30 min, the ethylene remaining was purged after the reaction, and the mixture was cooled to room temperature. Then the residual reaction solution was quenched with 5% hydrochloric acid ethanol. The precipitated polymer was collected by filtration, adequately washed with ethanol and water, and then dried in a vacuum until constant weight.

4.5. X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for **L5**, **C2**, and **C7** 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 H atom on the N atom of benzoimidazole in **C7** was calculated from a difference Fourier diagram. Other hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.[25] Crystal data and processing parameters for **L5**, **C2**, and **C7** are summarized in Table 3.

■ ASSOCIATED CONTENT

Supporting Information. Crystal data and processing parameters for compound **L5** and complexes **C2** and **C7**, a CIF file giving X-ray crystal structural data, and NMR sprectra of three representative polyethylenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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