

## Synthesis of Heteroarylferrocenes by Friedländer Reaction and Their Spectral Properties

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A series of mono- and 1,1'-bis(heteroaryl)-substituted ferrocenes were prepared by employing Friedländer reaction of acetyl- and 1,1'-diacetylferrocene with a series of *o*-aminoaldehydes. Reactions of 1,1'-diacetylferrocene with two equivalents of 1-aminonaphthalene-2-carbaldehyde and 8-aminoquinoline-7-carbaldehyde afforded a mixture of mono- and 1,1'-bis(heteroaryl)-substituted ferrocenes in a ratio of 1 : 3.1 - 3.8, while the reaction with 4-aminoacridine-3-carbaldehyde did not provide any characterizable product presumably due to the redox instability of the product induced by low reduction potential of benzo[*b*]-1,10-phenanthroline. Structural and optical properties of the compounds prepared were described.

**Key Words:** Ferrocene, Benzo[*h*]quinoline, 1,10-Phenanthroline, Benzo[*b*]-1,10-phenanthroline, Heteroarylferrocene

### Introduction

Ferrocene<sup>1</sup> is an aromatic compound in which two cyclopentadienyl (Cp) anions form covalent bonds to ferrous iron symmetrically<sup>2</sup> and possesses a low rotational barrier<sup>3</sup> which enables to interconvert *syn* and *anti* isomers of a 1,1'-disubstituted derivative (Figure 1) thus showing excellent mobility about the organometallic bond.



In the case that substituents A and B are planar aromatic species, however, rotation about the A/B-Cp bond becomes important. Although an *anti*-isomer is expected to be the major, proton resonances of 1,1'-diaryl-substituted ferrocenes<sup>4</sup> (aryl = phenyl, 1'-naphthyl, or 4-biphenyl) are upfield shifted compared to those of monoaryl-substituted ferrocenes to suggest that the 1,1'-diaryl-substituted ferrocenes retain a *syn* geometry. Similarly studies<sup>5</sup> on <sup>1</sup>H NMR spectra of a series of mono- and bis-heteroaryl ferrocenes support that two heteroaromatic rings are coplanar with their adjacent Cp ring. The single-crystal X-ray analysis of 1,1'-bis[2-(8-methoxyquinolyl)]ferrocene additionally confirms two quinoline rings are pointing in opposite direction, with their pyridine moieties partially overlapped.

However, the substituents at C3 position of the heteroaryls would impose an increase of dihedral angle between Cp and heteroaryl rings to lead inhibition against rotation about the organometallic bond. Musso and co-workers<sup>6</sup> have shown that when the Cp is perpendicular to the aryl substituent,  $\pi$ -stacking does not occur and the diarylferrocene adopts an *anti* conformation.

The ferrocene moiety not only plays a significant role as backbone or an ancillary substituent in ligands due to the unique structure<sup>7</sup> but also has potential application in material science especially in asymmetric catalysis<sup>8</sup> and molecular devices and

electronic sensors due to the redox-active properties of such ligands.<sup>9</sup> Even though interest in ferrocene chemistry is increasing, numbers of heteroarylferrocenes are somewhat limited.<sup>10</sup>

Our interest<sup>11</sup> in the preparation and properties of polydentates spurred to prepare a series of 1-heteroaryl- and 1,1'-di(heteroaryl)ferrocenes and to study their properties.

### Experimental Section

Melting points were determined using a Fischer-Jones melting points apparatus and are not corrected. IR spectra were obtained using a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained using a Bruker-250 spectrometer 300 MHz, 400 MHz or 600 MHz for <sup>1</sup>H NMR and 75 MHz, 100 MHz, and 150 MHz for <sup>13</sup>C NMR and are reported as parts per million (ppm) from the internal standard tetramethylsilane (TMS). The starting *o*-aminoaldehydes (2)<sup>12</sup> were prepared by employing previously reported methods. Chemicals and solvents were commercial reagent grade and used without further purification. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on a LCQ advantage-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). Elemental analyses were taken on a Hewlett-Packard Model 185B elemental analyzer. Abbreviations bq, phen, and bphen were introduced for benzo[*h*]quinoline, 1,10-phenanthroline, and benzo[*b*]-1,10-phenanthroline, respectively.

**2-(Ferrocenyl)benzo[*h*]quinoline (3a) (General Procedure).** To a mixture of 8-aminoquinoline-7-carbaldehyde (133 mg, 1.10 mmol) and 1-acetylferrocene (358 mg, 1.00 mmol) in absolute EtOH (20 mL) was added saturated alcoholic KOH (1 mL). The resulting mixture was refluxed for 5 h. Upon cooling the reaction mixture, a yellow solid was formed which was collected (389 mg, 88%); mp 181 °C. IR (KBr)  $\nu$  3056, 1593, 1445, 1429, 824 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$  9.42 (d, *J* = 8.0 Hz, 1H, H10 of bq), 8.05 (d, *J* = 8.5 Hz, 1H, H4 of bq), 7.90 (d, *J* = 8.0 Hz, 1H, H7 of bq), 7.76 (d, *J* = 8.5 Hz, 1H, H5/H6 of bq), 7.73 (td, *J* = 8.0, 1.3 Hz, 1H, H9 of bq), 7.71 (td, *J* = 8.0, 1.3 Hz, 1H, H8 of bq), 7.64 (d, *J* = 8.5 Hz, 2H, H3

and H6/H5 of bq). 5.18 (d,  $J = 1.8$  Hz, 2H, H $\alpha$  and H $\alpha'$ ), 4.48 (t,  $J = 1.8$  Hz, 2H, H $\beta$  and H $\beta'$ ), 4.07 (br s, 5 Cp-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  158.02, 146.06, 135.41, 133.83, 131.45, 127.87, 127.63, 126.56, 126.30, 125.32, 124.66, 124.17, 119.18, 84.34, 70.19, 69.64, 67.85. MS (ESI) calcd for  $\text{C}_{23}\text{H}_{18}\text{FeN}$  [ $\text{M}+\text{H}$ ] $^+$ : 364. Found: 364. Elemental Analysis: Calcd for  $\text{C}_{23}\text{H}_{17}\text{FeN}$ : C, 76.05; H, 4.72; N, 3.86. Found: C, 76.17; H, 4.75; N, 3.76.

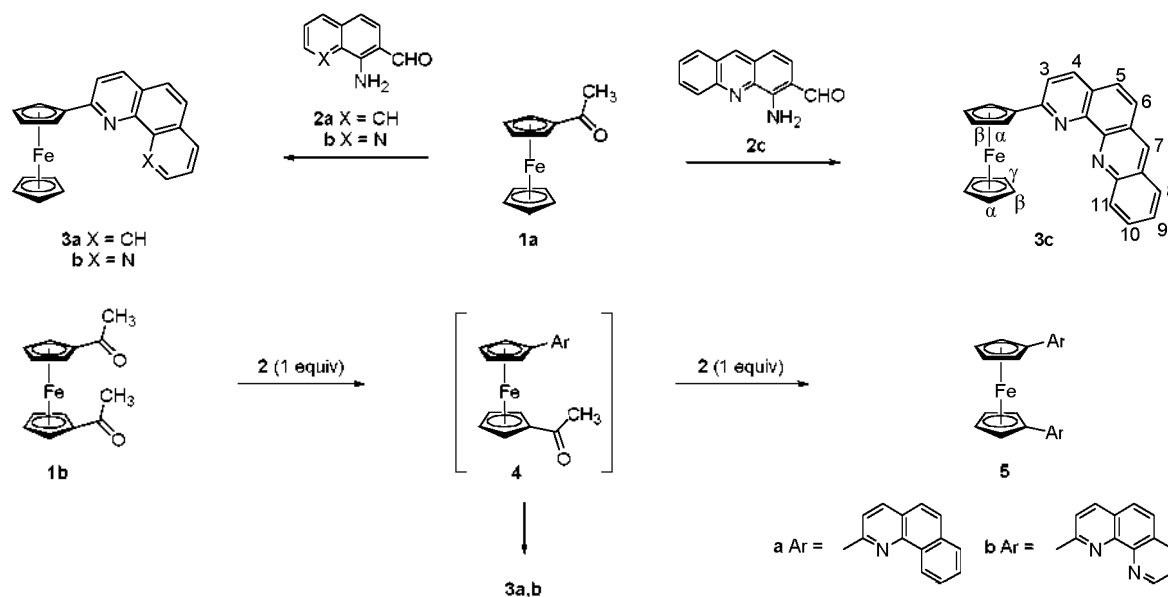
**2-(Ferrocenyl)-1,10-phenanthroline (3b).** Yellow needles (86%); mp 198 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  9.17 (d,  $J = 4.8$  Hz, 1H, H9 of bq), 8.19 (d,  $J = 7.8$  Hz, 1H, H4 of bq), 8.09 (d,  $J = 8.3$  Hz, 1H, H7 of bq), 7.81 (d,  $J = 8.5$  Hz, H3 of bq), 7.70 (2H, AB quartet, H5 and H6 of bq), 7.57 (dd,  $J = 8.0$ , 4.8 Hz, H8 of bq), 5.22 (br s, 2H, H $\alpha$  and H $\alpha'$ ), 4.46 (br s, 2H, H $\beta$  and H $\beta'$ ), 4.03 (br s, 5 Cp-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  160.53, 150.53, 146.40, 146.27, 136.42, 135.93, 129.47, 127.16, 126.97, 125.59, 123.00, 121.72, 84.62, 70.76, 70.09, 69.08. MS (ESI) calcd for  $\text{C}_{22}\text{H}_{17}\text{FeN}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 365. Found: 365.

**2-(Ferrocenyl)benzo[*b*]-1,10-phenanthroline (3c).** Pale yellow needles (83%); mp 215 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  9.76 (s, 1H, H7 of bq), 8.60 (d,  $J = 8.5$  Hz, 1H, H11 of bq), 8.12 (d,  $J = 8.3$  Hz, 1H, H4 of bq), 8.05 (dd,  $J = 8.3$ , 1.0 Hz, 1H, H8 of bq), 7.87 (td,  $J = 8.0$ , 1.0 Hz, H9 of bq), 7.83 (d,  $J = 9.0$  Hz, H5/H6 of bq), 7.66 (d,  $J = 9.0$  Hz, H6/H5 of bq), 7.63 (td,  $J = 8.0$ , 1.0 Hz, H10 of bq), 7.55 (d,  $J = 8.0$  Hz, H3 of bq), 5.18 (d,  $J = 1.8$  Hz, 2H, H $\alpha$  and H $\alpha'$ ), 4.48 (t,  $J = 1.8$  Hz, 2H, H $\beta$  and H $\beta'$ ), 4.07 (br s, 5 Cp-H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  157.08, 148.10, 146.67, 146.04, 136.11, 135.67, 130.96, 129.70, 127.42, 127.17, 127.08, 126.75, 126.52, 125.92, 125.75, 124.03, 79.05, 72.24, 69.73, 69.46. MS (ESI) calcd for  $\text{C}_{26}\text{H}_{20}\text{FeN}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 425. Found: 425. Elemental Analysis: Calcd for  $\text{C}_{26}\text{H}_{20}\text{FeN}_2$ : C, 73.59; H, 6.65; N, 6.60. Found: C, 73.72; H, 6.58; N, 6.59.

**1,1'-Bis(benzo[*h*]quinolin-2-yl)ferrocene (5a).** To a solution of 1,1'-diacetylferrocene (100 mg, 0.37 mmol) and 8-aminoquinoline-7-carbaldehyde (140 mg, 0.81 mmol) in EtOH (10 mL) was added saturated alcoholic KOH (0.1 mL). Resulting mixture was refluxed for 8 h. Evaporation of the solvent gave a solid material which was chromatographed on silica gel eluting with  $\text{CH}_2\text{Cl}_2$ : hexane (1 : 1). The early fractions ( $R_f = 0.85$ )

afforded 30 mg (20%) of 2-(2-ferrocenyl)benzo[*h*]quinoline (3a); mp 181 °C, of which the spectral data were identical to those described above for 3a. The latter fractions ( $R_f = 0.80$ ) afforded 150 mg (75%) yellow solid as 1,1'-bis(benzo[*h*]quinolin-2-yl)ferrocene: mp 219 °C (EtOH).  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.01 (dd,  $J = 8.8$ , 2.0 Hz, 2H, H10 of bq), 7.77 (dd,  $J = 8.0$ , 1.8 Hz, 2H, H7 of bq), 7.60 (td, 2H,  $J = 7.0$ , 2.5 Hz, H9), 7.53 (td, 2H,  $J = 7.0$ , 2.5 Hz, H9), 7.47 (d,  $J = 8.8$  Hz, 2H, H4 of bq), 7.09 (AB quartet, 4H, H5 and H6 of bq), 7.00 (d,  $J = 8.8$  Hz, 2H, H3 of bq), 5.13 (d,  $J = 1.8$  Hz, 2H, H $\alpha$  and H $\alpha'$ ), 4.47 (t,  $J = 1.8$  Hz, 2H, H $\beta$  and H $\beta'$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  154.97, 145.52, 134.70, 133.53, 131.02, 127.51, 127.37, 126.06, 125.77, 124.98, 124.57, 123.62, 118.66, 85.94, 70.82, 68.81. MS (ESI) calcd for  $\text{C}_{36}\text{H}_{25}\text{FeN}_2$  [ $\text{M}+\text{H}$ ] $^+$ : 541. Found: 541. Elemental Analysis: Calcd for  $\text{C}_{36}\text{H}_{24}\text{FeN}_2$ : C, 80.01; H, 4.48; N, 5.18. Found: C, 79.87; H, 4.55; N, 5.22.

**1,1'-Bis(1,10-phenanthrolin-2-yl)ferrocene (5b).** Reaction mixture obtained was chromatographed on alumina eluting with  $\text{CH}_2\text{Cl}_2$ . The early fractions ( $R_f = 0.5$ ) afforded 20 mg (21%) of orange needles: mp 198 °C, of which the spectral data were identical to those described above for 3b. The latter fractions ( $R_f = 0.3$ ) afforded 5b as pale orange needles (65%): 230 °C.  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ )  $\delta$  9.14 (dd, 2H,  $J = 4.3$ , 1.8 Hz, H9 of phen), 8.16 (dd, 2H,  $J = 7.8$ , 1.2 Hz, H7 of phen), 7.56 (dd, 2H,  $J = 7.5$ , 4.2 Hz, H8 of phen), 7.54 (d, 2H,  $J = 8.4$  Hz, H4 of phen), 7.30 (d, 2H,  $J = 8.4$  Hz, H5 of phen), 7.21 (d, 2H,  $J = 8.4$  Hz, H6 of phen), 7.15 (d, 2H,  $J = 8.4$  Hz, H3), 5.28 (t, 4H,  $J = 1.8$  Hz, H $\alpha$  of Cp), 4.48 (t, 4H,  $J = 1.8$  Hz, H $\beta$  of Cp).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ , with 5 mg of isoascorbic acid)  $\delta$  9.11 (dd, 2H,  $J = 4.2$ , 1.2 Hz, H9 of phen), 8.17 (dd, 2H,  $J = 8.0$ , 1.8 Hz, H7 of phen), 7.55 (dd, 2H,  $J = 7.5$ , 4.8 Hz, H8 of phen), 7.54 (d, 2H,  $J = 8.4$  Hz, H4 of phen), 7.30 (d, 2H,  $J = 9.0$  Hz, H6 of phen), 7.20 (d, 2H,  $J = 9.0$  Hz, H3 of phen), 7.16 (d, 2H,  $J = 8.4$  Hz, H5 of phen), 5.24 (t, 4H,  $J = 1.8$  Hz, H $\alpha$  of Cp), 4.48 (t, 4H,  $J = 1.8$  Hz, H $\beta$  of Cp).  $^{13}\text{C}$  NMR (62.5 MHz,  $\text{CDCl}_3$ )  $\delta$  157.73, 149.86, 146.13, 145.72, 135.68, 135.00, 128.80, 126.37, 126.32, 124.66, 122.36, 121.02, 85.99, 71.16, 69.81. MS (ESI) calcd for  $\text{C}_{34}\text{H}_{23}\text{FeN}_4$  [ $\text{M}+\text{H}$ ] $^+$ : 543. Found: 543.



### Results and Discussion

Preparation of the ferrocene-derived ligands is straight forward as shown in Scheme 1. The Friedländer condensation of acetylferrocene (**1a**)<sup>13</sup> with a series of *o*-aminoaldehydes (**2**) afforded the corresponding monoheteroarylferrocenes (**3**) in 83 ~ 88% yields. On the other hand, reaction of 1,1'-diacetylferrocene (**1b**)<sup>14</sup> with 2.2 equivalents of **2** afforded a mixture of 1,1'-bis(heteroaryl)ferrocenes (**5**) and mono-condensed 2-(ferrocenyl)heteroaromatics (**3**), which were readily separable by column chromatography. Surprisingly, reaction of **1b** with **2** afforded 1,1'-bis(2-heteroaryl)ferrocene (**5**) and unexpected 2-(ferrocenyl)heteroaromatics (**3**) instead of expected 1-acetyl-1'-(2-heteroaryl)ferrocenes (**4**) in a ratio of 3.1 : 1. Formation of **3** from **1b** and **2** could be explained by base-catalyzed deacetylation of acetylferrocenes (**4**). An initial equimolar condensation of **1b** and **2** would afford **4**, which were then undergone either Friedländer condensation with additional **2** to lead the desired compounds **5** or base-catalyzed deacetylation to afford **3** as had been reported previously.<sup>15</sup> Attempts for the condensation of **1b** with **2c** were failed to afford either bis-condensed one or mono-condensed **3c**, but instead as yet unidentifiable black solid. Although we can not explain clearly, reduction potentials of the heteroaromatics may affect the stability of the compounds. We reasoned that the half-way reduction potential (-1.52 V vs SCE) of benzo[*b*]-1,10-phenanthroline is much lower than those of benzo[*h*]quinoline (-2.23 V)<sup>16</sup> and 1,10-phenanthroline (-2.12 V),<sup>16</sup> which implies that benzo[*b*]-1,10-phenanthroline nucleus is the better electron acceptor and thus more readily reduced than 1,10-phenanthroline and benzo[*h*]quinoline. Such a potential would affect the stability of Fe(II) ion in ferrocene moiety to oxidize Fe(II) to Fe(III). Similar redox-instability of Fe(II) ion was also observed in **5b**. Reduction potentials of the two 1,10-phenanthrolines are enough to lead at least partial oxidation of Fe(II) yielding paramagnetic Fe(III) species, thus fail to provide a good <sup>1</sup>H NMR spectrum of **5b** at either room temperature or even lower temperature (-43 °C). The addition of isoascorbic acid (~3 mg) as a reducing agent in <sup>1</sup>H NMR sample tube<sup>17</sup> stabilizes Fe(II) species to result a well-resolved spectrum (Supporting Information).

It should be noted that (1,10-phenanthrolin-2-yl)ferrocene (**3b**) and 1,1'-bis(1,10-phenanthrolin-2-yl)-ferrocene (**5b**) were prepared in 20 ~ 35% and 14% yield, respectively, by the direct reactions of monolithio- and dilithioferrocenes with 1,10-phenanthroline.<sup>18a</sup> Above reaction was modified by subsequent oxidation of addition adducts with strong oxidizing agent such as DDQ to improve the corresponding yields to 80% and 65%, respectively.<sup>18b</sup> Attempts to prepare 1,1'-bis(benzo[*b*]-1,10-phenanthrolin-2-yl)ferrocene from dilithioferrocene and benzo[*b*]-1,10-phenanthroline<sup>19</sup> were also failed.

Some proton resonances of heteroaryl moieties were characteristic enough to afford a probe for the structure suggested. The H10 of 2-substituted benzo[*h*]quinoline (**3a** and **5a**) is experiencing deshielding effect of N1 and thus the most downfield shifted resonance in the system, while H9 of 1,10-phenanthroline (**3b** and **5c**) is the one of characteristic chemical shifts with relatively small <sup>3</sup>J coupling constants (<sup>3</sup>J = 4 - 5 Hz).<sup>20</sup> Similarly H11 of benzo[*b*]-1,10-phenanthroline (**3c**) is parallel to the lone pairs of electrons of nitrogen at the *peri*-position to show characteristic chemical shifts in the region of δ 8.60 - 8.60.<sup>11,18</sup> In addition, the resonances of α-protons at the substituted Cp moiety generally appeared in the region of δ 5.18 - 5.24 due to the deshielding effect of nitrogen as two triplets with a characteristically small coupling constant (<sup>3</sup>J = 1.8 - 2.3 Hz) while β-protons δ 4.44 - 4.48. Protons of unsubstituted Cp ring are generally resonanced in the range of δ 4.03 - 4.07.

The 1,1'-bis(heteroaryl)ferrocenes may have three possible conformations as shown in Figure 2. The proton resonances of mono- and bis-heteroarylferrocenes may afford information for the conformation. All the proton resonances of bis(heteroaryl)ferrocenes are upfield shifted as compared to the analogous resonances of the mono-substituted ferrocenes **3** as has been reported previously for 1,1'-bis(aryl)ferrocenes, which excludes the possible anti-isomer (C in Figure 1). The magnitudes of the shift are highly dependent on the protons (Table 1). Protons of H3, H4, H5, and H6 of the 1,1'-bis(2-heteroaryl)ferrocenes are the most upfield-shifted ones by 0.42 - 0.64 ppm due to the anisotropic effect of the neighboring heteroaryl groups while the rest were upfield-shifted only by 0.02 - 0.14 ppm except H10 which was shifted by 0.41 ppm. Such

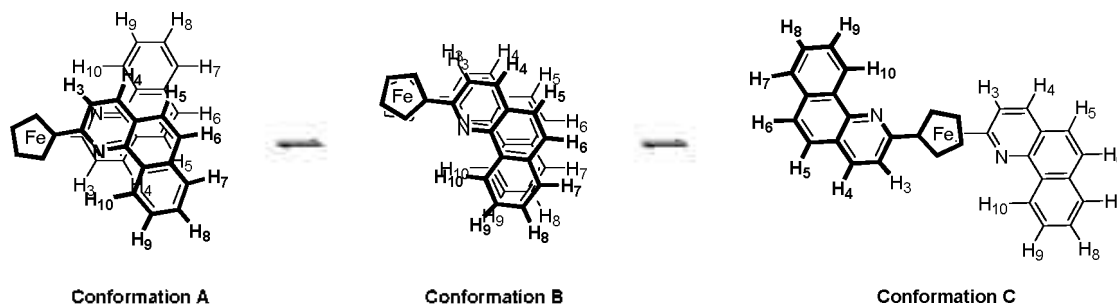
**Table 1.** <sup>1</sup>H NMR Chemical Shift Data for Heteroaryl-Substituted Ferrocenes

Comd	heteroaryl protons									ferrocene protons		
	H3	H4	H5	H6	H7	H8	H9	H10	H11	Hα	Hβ	Hγ
<b>3a</b>	7.64	8.05	7.76 <sup>a</sup>	7.64 <sup>a</sup>	7.90	7.71	7.73	9.42	-	5.18	4.48	4.07
<b>5a</b>	7.03	7.50	7.12	7.12	7.78	7.57	7.61	9.01	-	5.13	4.47	-
<b>Δδ</b>	(0.61)	(0.55)	(0.64)	(0.52)	(0.12)	(0.14)	(0.12)	(0.41)	-	(0.05)	(0.01)	-
<b>3b</b>	7.81	8.09	7.70	7.70	8.19	7.57	9.18	-	-	5.22	4.46	4.03
<b>5b</b>	7.20	7.54	7.11	7.28	8.17	7.55	9.11	-	-	5.24	4.44	-
<b>Δδ</b>	(0.61)	(0.45)	(0.59)	(0.42)	(0.02)	(0.02)	(0.07)	-	-	-	-	-
<b>3c</b>	7.55	8.12	7.83	7.66	9.76	8.05	7.87	7.63	8.60	5.18	4.48	4.07
<b>QF<sup>b</sup></b>	7.56	8.03	7.74	7.45	7.66	8.04	-	-	-	5.07	4.47	4.06
<b>BQF<sup>b</sup></b>	6.98	7.19	7.40	7.38	7.58	7.86	-	-	-	5.05	4.43	-
<b>Δδ</b>	(0.58)	(0.84)	(0.34)	(0.07)	(0.08)	(0.18)	-	-	-	(0.02)	(0.04)	-

<sup>a</sup>Assignment can be reversed. <sup>b</sup>QF and BQF are the abbreviations of (2-quinolyl)ferrocene and 1,1'-bis(2-quinolyl)ferrocene, respectively.

**Table 2.** Absorption and Emission Spectral Data of Heteroaryl-Substituted Ferrocenes

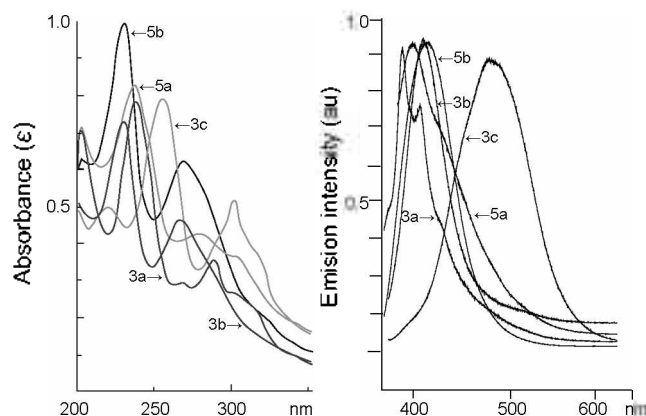
Compound	$\lambda_{\text{max}}$ , (95% EtOH) ( $\epsilon$ M <sup>-1</sup> cm <sup>-1</sup> )							$\lambda_{\text{emission}}$
<b>Ferrocene</b>	240 (3,500)	265 (1,600)	325 (50)	440 (100)				
<b>3a</b>	238 (12,500)	268 (4,700)	290 (5,700)	305 (4,000)	315 (3,500)	447 (320)		396, 417, 440 (sh)
<b>3b</b>	231 (11,700)	267 (7,400)	370 (1,100)	447 (320)				420
<b>3c</b>	223 (8,000)	257 (12,600)	290 (6,600, sh)	302 (8,300)	316 (6,000)	380 (50)	460 (80)	510
<b>5a</b>	237 (13,100)	278 (69,000)	305 (5,900)	370 (160)				408, 440 (sh)
<b>5b</b>	232 (15,900)	269 (10,000)	307 (4,100)	326 (70)				425

**Figure 1.** Conformational pictures of **5a** derived from <sup>1</sup>H NMR data.

anisotropic effect would not affect very much for H7, H8 and H9, which excluded the possible conformation B in Figure 1. Such a difference in the magnitude of shift suggests that two heteroaryl rings are pointing in opposite direction, with their pyridine moieties partially overlapped as shown in Figure 1 (conformation A).

UV absorption spectra of mono- (**3**) and 1,1'-disubstituted ferrocenes (**5**) were taken from CH<sub>3</sub>CN ( $6.25 \times 10^{-5}$  M) and are summarized in Table 2. UV spectrum of ferrocene showed four absorptions at 240 ( $\epsilon$  3,500), 265 ( $\epsilon$  1,600), 325 ( $\epsilon$  50) and 440 ( $\epsilon$  102) nm, which are well matched to those in the literature.<sup>21</sup> Two major absorption maxima presumably originated from the  $\pi$ - $\pi^*$  transition were observed in the regions of 223 - 257 and 267 - 310 nm and two minor absorptions from ferrocene moiety in the regions of 325 - 370 and 440 - 460 nm. The absorption maximum is highly dependent on the nature of the heterocycles attached to ferrocene. Absorptions at 238 nm for **3a** and 231 nm of **3b** as well as absorptions at 268 nm for **3a** and 267 nm for **3b** were shifted bathochromatically (20 nm and 33 nm, respectively) in **3c**, in which the conjugation was extended by benzo-annulation. Such an extension of the conjugation additionally was also resolved absorptions at 223 and 252 nm of **3c** and absorptions in the region of 290 - 416 nm. UV absorption spectrum of ferrocene is characteristic to show two weak absorption maxima at 325 and 440 nm<sup>21</sup> and are, thus, tentatively assigned as an intramolecular charge transfer absorption involving promotion of iron *d* orbitals to ring  $\pi$  orbitals of ferrocene moiety.<sup>22</sup> Although both the position and the intensity of the 440 nm band are claimed to be particularly sensitive to ferrocene ring-tilt distortion,<sup>23</sup> UV spectra of the present system did not afford any clear evidence for the geometry.

Emission spectra of the compounds prepared were measured in EtOH ( $6.25 \times 10^{-5}$  M) and the data were summarized in Table 2. All the ligands could be well excited to show good

**Figure 2.** UV absorption and emission spectra of heteroarylferrocenes in 95% EtOH. UV spectrum of ferrocene was omitted for clarity.

emissions. The system with a benzo[*h*]quinoline ring showed three emission wavelengths of 396, 420, and 440 (sh) nm while with two benzo[*h*]quinoline rings 408 and 440 (sh) nm, respectively. The compounds with mono- and di-1,10-phenanthrolines showed only one emission at 420 and 425 nm, respectively and a system with benzo[*b*]-1,10-phenanthroline gave a green light emission at 510 nm with 100 nm of a full width at half max. The observed emission wavelength is highly dependent on the nature of the heterocycles. Each of the emission maxima is bathochromatically shifted from benzo[*h*]quinoline ring to benzo[*b*]-1,10-phenanthroline ring indicating that more planar ligand emits the lower energy.

## Conclusions

A series of mono- and 1,1'-bis(heteroaryl)-substituted ferro-

enes were prepared by employing Friedländer reaction of acetyl- and 1,1'-diacetylferrocene with a series of *o*-aminoaldehydes. Reactions of 1,1'-diacetylferrocene with two equivalents of 1-aminonaphthalene-2-carbaldehyde and 8-aminoquinoline-7-carbaldehyde afforded a mixture of mono- and 1,1'-bis(heteroaryl)-substituted ferrocenes in a ratio of 1 : 3.1 - 3.8, while the reaction with 4-aminoacridine-3-carbaldehyde did not provide any characterizable product presumably due to the redox instability of the product induced by low reduction potential of benzo[*b*]-1,10-phenanthroline. Structures of the compounds could be deduced from <sup>1</sup>H NMR data to show that two heteroaromatics are not only in coplanarity of heteroaryl ring(s) with cyclopentadienyl ring but also are in *syn* geometry around ferrocene moiety and pointing in opposite direction with their pyridine moieties partially overlapped. Two major absorption maxima presumably originated from the  $\pi$ - $\pi^*$  transition were observed in the regions of 223 - 257 and 267 - 310 nm and two minor absorptions from ferrocene moiety in the regions of 325 - 370 and 447 nm. All the ligands showed good emissions to give three emission wavelengths of 396, 420, and 440 (sh) nm for mono benzo[*h*]quinoline ring system comparable to those (408 and 440 nm) of two benzo[*h*]quinoline rings. The compounds with mono- and di-1,10-phenanthrolines showed only one emission at 420 and 425 nm, respectively and a system with benzo[*b*]-1,10-phenanthroline gave green light emission at 510 nm.

**Supporting Information.** <sup>1</sup>H NMR spectra (600 MHz) of 1,1'-bis(1,10-phenanthroline-2'-yl)ferrocene (**5b**) are available on request from the correspondence author.

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