

## Synthesis and study of electrochemical behavior of new 4-ferrocenylbutylamine derivatives

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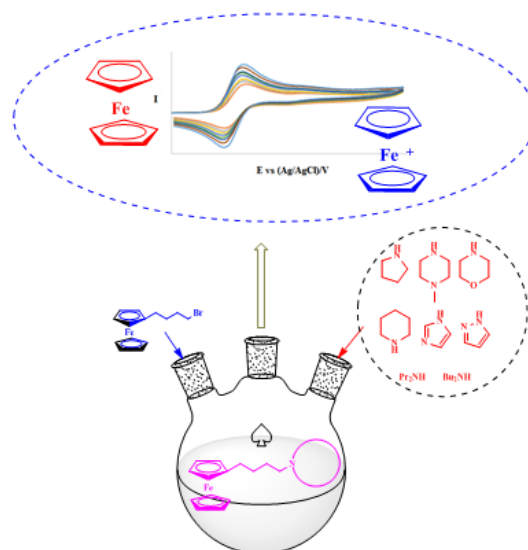
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### Abstract

Ferrocene derivatives play important roles in the fields of biological, material and synthetic chemistries. Some 4-ferrocenylbutylamine derivatives were synthesized by the nucleophilic-substitution reactions of 4-bromobutylferrocene with various aliphatic and aromatic secondary amines, and their electrochemical properties have been investigated. The electrochemical behavior of the synthesized compounds was studied by cyclic voltammetry. The relationship between the peak currents and the square root of the scan rate showed that the redox process is diffusion limited.



**Keywords:** 4-Ferrocenylalkylamine,  $S_N2$  reaction, ferrocene, cyclic voltammetry

## Introduction

Ferrocene or di ( $\eta^5$ -cyclopentadienyl) iron (II) was accidentally discovered by Peter L. Pauson and Tom Kealy in 1951 when they attempted the reductive coupling of the Grignard reagent cyclopentadienyl magnesium bromide in the presence of ferric chloride. The unique sandwich structure of ferrocene was first predicted by infrared and nuclear magnetic resonance spectroscopies, and later confirmed by X-ray crystallography in 1954.<sup>1</sup>

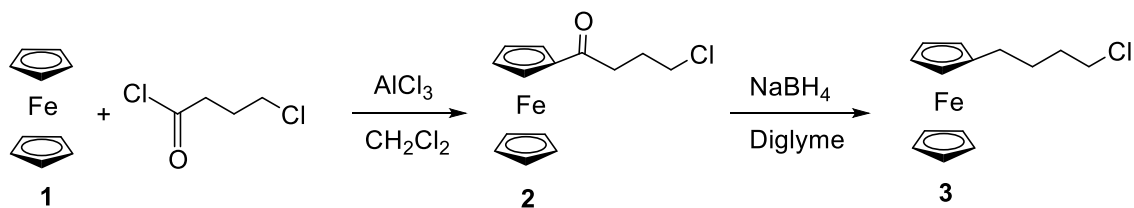
Ferrocene derivatives play important roles in the fields of synthetic, material and biological chemistries. Hence, chemists began to synthesize various ferrocene derivatives and investigated their applications in various scientific fields.<sup>2</sup> The ferrocenyl group plays an important role in electron-transfer reactions, which are involved in many living systems, and in synthetic chemistry as multi-redox nano systems, especially, in ferrocenyl polymers,<sup>3</sup> dendrimers,<sup>4</sup> nanoparticles,<sup>5</sup> vectors,<sup>6</sup> biosensors,<sup>7</sup> biological-redox processes,<sup>8</sup> molecular conductors and semiconductors,<sup>9</sup> mixed-valence stabilizers,<sup>10</sup> catalytic reactions,<sup>11</sup> redox recognition,<sup>12</sup> as redox reagents,<sup>13</sup> redox catalysts,<sup>14</sup> electron-transfer catalysts,<sup>15</sup> sensors,<sup>16</sup> and green catalysts.<sup>17</sup> Ferrocenyl compounds possess many cytotoxic properties including antitumour effects,<sup>18</sup> antimalarial<sup>19</sup> and anti-cancer effect in human lung cancer cells.<sup>20</sup> Many ferrocenyl derivatives display interesting cytotoxic, antifungal and DNA-cleaving activities.<sup>21</sup>

The development of new methods for the formation of carbon–nitrogen bonds is an interesting challenge in organic synthesis.<sup>22</sup> A variety of powerful approaches have been devised, including venerable processes such as reductive amination<sup>23</sup> and Ullmann coupling,<sup>24</sup> as well as the more recently developed Buchwald–Hartwig reaction.<sup>25</sup> Despite the utility of such processes, the discovery of novel methods for the formation of carbon–nitrogen bonds remains an important objective.<sup>26,27</sup> Perhaps the most classic reported approach in the literature for carbon–nitrogen bond formation is the reaction of an amine with an alkyl halide,<sup>28,29</sup> a transformation that continues to play an important role in amine-derivatives synthesis.<sup>30</sup> Because this process generally follows a  $S_N2$  pathway, elevated reaction temperatures are typically employed for hindered primary and secondary electrophiles that are inactivated.<sup>22</sup> Due to the interesting electrochemical properties of the ferrocene moiety, research and investigations of chemical and electrochemical properties of ferrocenyl organic molecules are important. Cyclic voltammetry (CV) is a very useful electroanalytical technique for the characterization of the electroactive species. This method provides valuable information regarding the stabilities of the oxidation states and the rate of electron transfer between the electrode and the analyte. Applications of cyclic voltammetry have been extended to almost every aspect of chemistry, e.g., the investigation of biosynthetic reaction pathways, the examination of the ligand effect on the metal complex potential, and enzymatic catalysis.<sup>31, 32</sup>

We report, herein, the synthesis and electrochemical properties of some 4-ferrocenylbutylamine derivatives and obtain information about substituent effects on the electrochemical properties of the ferrocene moiety using cyclic voltammetry.

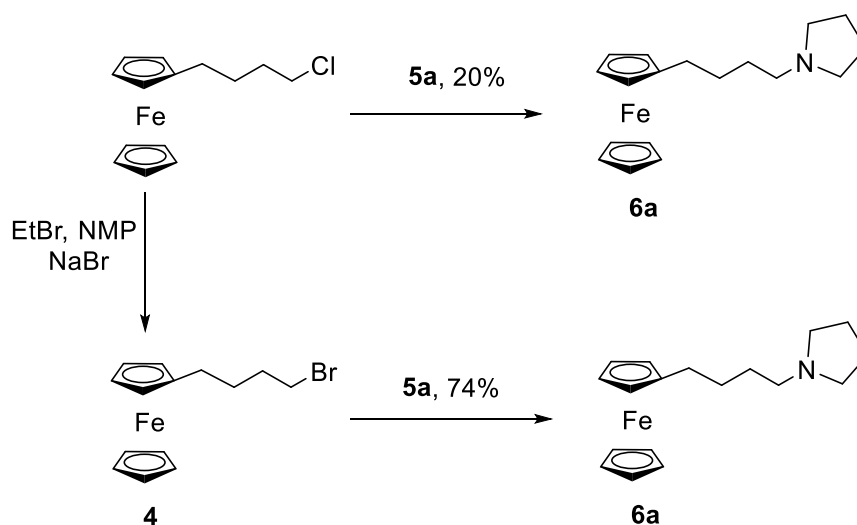
## Results and Discussion

Due to interesting electronic properties of ferrocene and its derivatives,<sup>33-37</sup> we decided to synthesize a series of novel 4-ferrocenylbutylamine derivatives. Initially, 4-chlorobutylferrocene (**2**) was synthesized from ferrocene (**1**) as shown in Scheme 1.<sup>33</sup> Subsequent reduction with  $\text{NaBH}_4$  solution in diglyme provided the corresponding 4-chlorobutylferrocene (**3**).



**Scheme 1.** Synthesis of 4-chlorobutylferrocene (**3**).

Compound **3** was subsequently treated with pyrrolidine in acetonitrile as solvent in reflux conditions. After 24 h, the reaction was not complete; the desired compound was obtained in only 20% yield (Table 1, Entry 6). To increase the efficiency and improve the reaction conditions, the 4-bromobutylferrocene (**4**) was synthesized (Scheme 2).



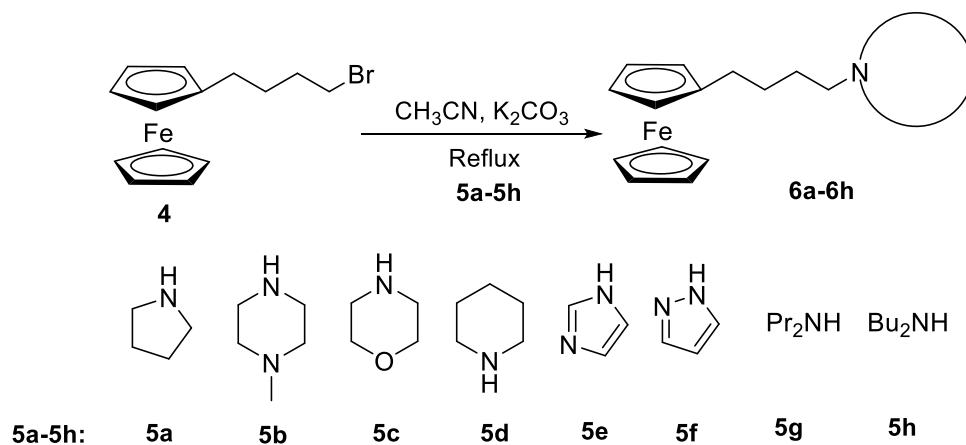
**Scheme 2.** Synthesis of 1-(4-butylferrocene)pyrrolidine (**6a**).

To optimize the reaction conditions for synthesis of 4-ferrocenylbutylamine derivatives, a variety of solvents and bases were tested, as shown in Table 1. Among the various solvents and bases screened at  $80\text{ }^\circ\text{C}$ , the best results were obtained when acetonitrile was used as a solvent and  $\text{K}_2\text{CO}_3$  was employed as the base (Table 1, Entries 2 and 9).

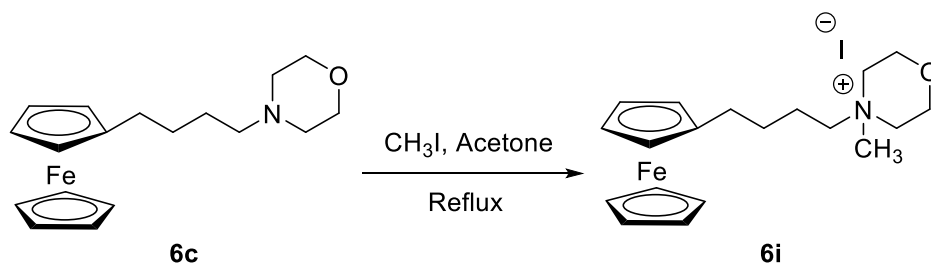
After optimization of the reaction conditions, to explore the scope and generality of the optimal method, we investigated the synthesis of the corresponding 4-ferrocenylbutylamine derivatives (**6a-h**) via the  $\text{S}_{\text{N}}2$  alkylation of compound **4** with a variety of aliphatic and aromatic amines (**5a-h**) (Scheme 3). Saturated secondary amines such as dipropylamine, dibutylamine, pyrrolidine, morpholine, piperidine and *N*-methyl piperazine show good reactivity in  $\text{S}_{\text{N}}2$  reactions with compound **4**; morpholine showed the best reactivity (Table 2, Entry 3). Aromatic amines undergo the same reaction with compound **4**, and the results showed that aromatic amines such as imidazole and pyrazole afforded the 4-ferrocenylbutylamines in good yield.

**Table 1.** Optimization of nucleophilic substitution ( $S_N2$ ) reaction conditions for synthesis of **6a**

Entry	X	Solvent	Base	Temp. (°C)	Yield (%)
1	Br	CH <sub>3</sub> CN	Na <sub>2</sub> CO <sub>3</sub>	80	43
2	Br	CH <sub>3</sub> CN	K <sub>2</sub> CO <sub>3</sub>	80	74
3	Br	CH <sub>3</sub> CN	Et <sub>3</sub> N	80	37
4	Br	CH <sub>3</sub> CN	NaHCO <sub>3</sub>	80	29
5	Br	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	40
6	Br	EtOH	K <sub>2</sub> CO <sub>3</sub>	reflux	35
7	Br	Toluene	K <sub>2</sub> CO <sub>3</sub>	80	38
8	Cl	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	5
9	Cl	CH <sub>3</sub> CN	K <sub>2</sub> CO <sub>3</sub>	80	20
10	Cl	EtOH	K <sub>2</sub> CO <sub>3</sub>	reflux	15
11	Cl	Toluene	K <sub>2</sub> CO <sub>3</sub>	80	10

**Scheme 3.** Synthesis of 4-ferrocenylbutylamine derivatives (**6a-6h**).

Subsequently, we synthesized the corresponding ferrocenyl-based ammonium salts from the morpholine derivative (**6c**) by treating **6c** with MeI to produce the ferrocenyl-based morpholinium iodide salt (**6i**) in very good yield (Table 2, Entry 9).

**Scheme 4.** Synthesis of 4-(4-ferrocenylbutyl)-4-methyl morpholinium iodide (**6i**) from compound **6c**.

**Table 2.** Yields of compound (**6a-i**) under optimal conditions<sup>a</sup>

Entry	Product	Yield (%) <sup>b</sup>
1	<b>6a</b>	74
2	<b>6b</b>	82
3	<b>6c</b>	87
4	<b>6d</b>	71
5	<b>6e</b>	73
6	<b>6f</b>	57
7	<b>6g</b>	69
8	<b>6h</b>	78
9	<b>6i</b>	91

<sup>a</sup> K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CN, reflux<sup>b</sup> Isolated yield**Cyclic voltammetry**

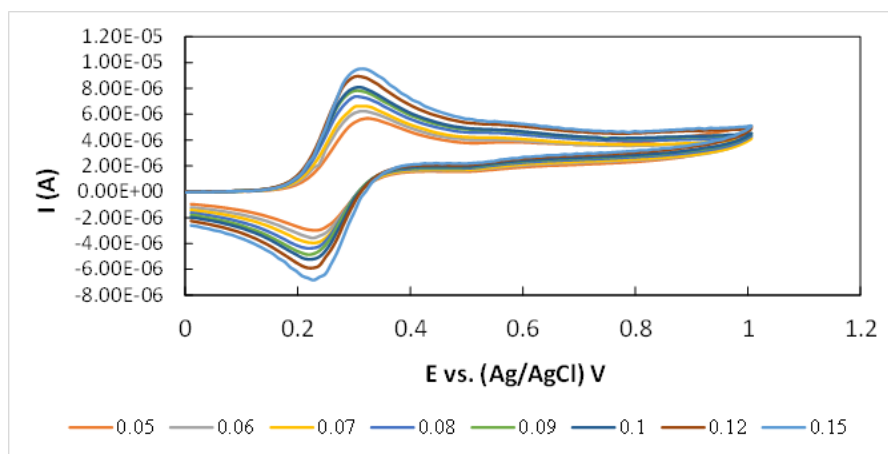
To compare the influence of the substituents on the redox ability of Fe (II), electrochemical studies on the synthesized ferrocene derivatives (**6a-i**) were carried out. Cyclic voltammetry (CV) experiments performed in dry CH<sub>3</sub>CN/0.01 M LiClO<sub>4</sub> solution exhibited quasi-reversible voltammetric behavior for the ferrocenyl group in these compounds, with  $\Delta E_p = E_{pa} - E_{pc} < 0.07$  V at scan rates up to 0.15 V s<sup>-1</sup> (Table 3). Cathodic and anodic peak current ratios measured for the derivatives were in the range 1.07 <  $i_{pc}/i_{pa}$  < 1.13, and  $E_p$  values were independent of the scan rate.

**Table 3.** Selected potentials (V) and current (mA) data for 1.0 mM solutions of the 4-ferrocenylbutylamines (**6a-i**) in CH<sub>3</sub>CN/0.1M LiClO<sub>4</sub>

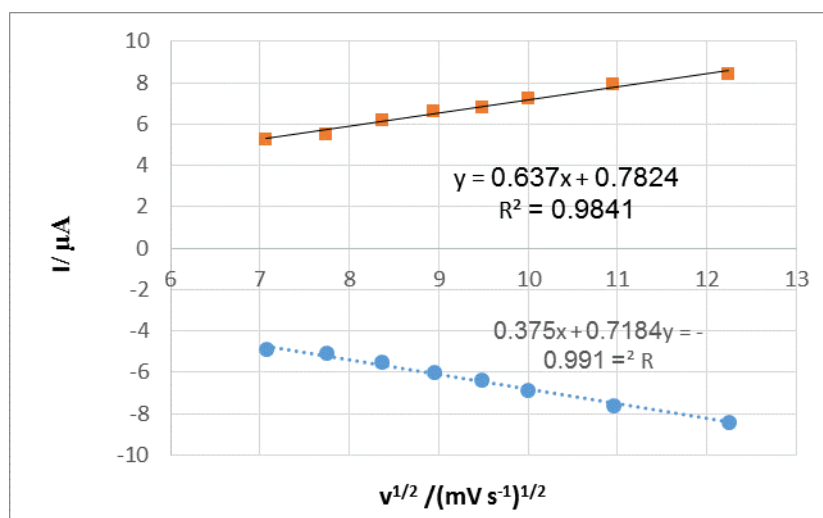
Entry	Compound	$\Delta E_p$	$i_{pc}/i_{pa}$
1	<b>6a</b>	0.065	1.13
2	<b>6b</b>	0.069	1.08
3	<b>6c</b>	0.067	1.11
4	<b>6d</b>	0.071	1.07
5	<b>6e</b>	0.062	1.12
6	<b>6f</b>	0.069	1.08
7	<b>6g</b>	0.068	1.07
8	<b>6h</b>	0.071	1.12
9	<b>6i</b>	0.062	1.10

All of the newly synthesized compounds (**6a-6i**) exhibited only one pair of well-defined redox peaks in CH<sub>3</sub>CN indicating the existence of only one kind of electroactive center in these compounds which correspond to its ferrocenyl group. A series of voltammograms of the ferrocene compounds in CH<sub>3</sub>CN/0.100 M LiClO<sub>4</sub>, at various scan rates, such as 50, 60, 70, 80, 90, 100, 120 and 150 mVs<sup>-1</sup>, were also recorded, as shown in Figure 1. It was found that both cathodic- and anodic-peak currents linearly increase with the increasing of scan rate. The position of the cathodic peak slightly shifted towards the negative potential, and the anodic peak shifted a little towards the positive direction with increase of scan rate. The plots of the anodic and cathodic currents

versus the square root of scan rates ( $v^{1/2}$ ) show a linear relationship. This behavior suggests that the redox process is diffusion limited (Figure 2).



**Figure 1.** CV curves of the 1-(4-ferrocenylbutyl)pyrrolidine (**6a**) in different scan rates.



**Figure 2.** Linear relationship between the A) cathodic peak current, B) anodic peak current and the square root of the scan rates.

As indicated in Table 3, electrochemical parameters, such as the position of redox potentials and degree of reversibility of the electrochemical behavior, are negligibly affected by the presence and type of the amine functional groups attached to the central ferrocene rings. Therefore, it can be said that nature of the appending groups does not significantly affect the electrochemical properties of the ferrocene rings.

## Conclusions

In summary, we report the synthesis of some 4-ferrocenylbutylamine derivatives in good yields through the substitution reactions of 4-bromobutylferrocene with various secondary aliphatic and aromatic amines. The

electrochemical behavior of the synthesized compounds with the increase of scan rate was investigated. Based on the results, the synthesized 4-ferrocenylbutylamine derivatives showed quasi-reversible single-electron electroactivity. The relationship between the peak currents and the square root of the scan rate showed that the electrode processes were diffusion controlled.

## Experimental Section

**General.** Chemicals were either prepared in our laboratory or purchased from Merck, Sigma-Aldrich and Yantai Suny Chem. International Co., Ltd. Commercial solid reagents were used without further purification. Liquid reactants were distilled prior to use. Solvents were dried and distilled prior to use according to standard laboratory practices; water was doubly distilled. THF and diglyme were dried by refluxing under argon over sodium wire and distilled directly before use.

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at room temperature using a Bruker FT- 400 MHz and 100 MHz spectrometer, respectively.  $\text{CDCl}_3$  was used as solvent and internal standard, and chemical shifts are presented with delta-values expressed in ppm referenced to  $\text{CDCl}_3$  peaks at 7.25 ( $^1\text{H}$  NMR) and 78 ppm ( $^{13}\text{C}$  NMR), respectively. The FT-IR spectra were recorded on a Bruker-Tensor 270 spectrophotometer as KBr disks or smears between salt plates. Elemental analyses were carried out with an Elementor Vario EL. III instrument. Iron analysis was performed using an Analytikjene (novaa 400) Atomic Absorption Spectrophotometer. Cyclic voltammetry measurements were performed on 1 mM solutions of ferrocene derivatives in dry  $\text{CH}_3\text{CN}/0.1\text{ M LiClO}_4$  using potentiostat/galvanostat Autolab (PGASTAT 30) equipped with a standard three-electrode cell. A 2-mm-diameter GC was used as the working electrode. A silver/silver chloride (Ag/AgCl) electrode and a platinum electrode were used as the reference and counter electrodes, respectively. All potentials in this study are reported with respect to the Ag/AgCl electrode.

**Synthesis of 4-chlorobutylferrocene (3).** The procedure for synthesis of 4-chlorobutylferrocene was carried out according to the reported method.<sup>33</sup>

**Synthesis of 4-bromobutylferrocene (4).** The procedure for synthesis of 4-bromobutylferrocene was carried out according to the reported method.<sup>34</sup>

**General procedure for the synthesis of 4-ferrocenylbutylamine derivatives (6a-6h).** 4-bromobutylferrocene (**4**) (0.4g, 1.2 mmol), the appropriate amine derivatives (4.7 mmol) and potassium carbonate (0.63g, 5.94 mmol) were dissolved in acetonitrile (25 ml). The mixture was refluxed for 48 hours. After the completion of the reaction, acetonitrile was evaporated under vacuum, and the cooled residue mixture was diluted with 25 ml of  $\text{CH}_2\text{Cl}_2$  and washed with water (3×10 ml). The organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvent was removed under atmospheric pressure. The crude products were purified by preparative thin layer chromatography on silica gel with EtOAc/MeOH (9:1) as eluent. Specific details are described for each of the compounds.

**1-(4-Ferrocenylbutyl)pyrrolidine (6a).** From 0.4 g of 4-bromobutylferrocene, 0.25 g of light brown oil viscous oil (**6a**) was obtained in 67% yield. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3085, 2926, 2855, 1669, 1457, 1360, 1094, 1021, 488.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.52-1.56 (4H, m,  $-\text{CH}_2-$ ), 1.84 (4H, m,  $-\text{CH}_2-$ ), 2.32-2.36 (2H, t,  $J$  7 Hz  $\text{CpCH}_2$ ), 2.52-2.54 (2H, m,  $\text{NCH}_2$ ), 2.64 (4H, br,  $\text{NCH}_2$ ), 4.02-4.04 (4H, d,  $J$  6.2 Hz, Cp), 4.08 (5H, s, Cp).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  22.3, 27.2, 28.0, 28.4, ( $-\text{CH}_2-$ ), 55.2, 53.0 ( $\text{NCH}_2$ ), 66.0, 67.0, 67.4 (Cp), 88.8 ( $\text{C}_{\text{ipso}}$  Cp). Anal. Calc. for:  $\text{C}_{18}\text{H}_{25}\text{FeN}$  (311.25): C, 69.46; H, 8.10; Fe, 17.94; N, 4.50. Found: C, 69.78; H, 7.99; Fe, 17.82; N, 4.41%.

**1-Methyl-4-(ferrocenylbutyl)piperazine (6b).** From 0.4 g of 4-bromobutylferrocene, 0.35 g of light brown oil viscous oil (**6b**) was obtained in 87% yield. FT-IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 3090, 2933, 2796, 1683, 1455, 1363, 1011, 486;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.48-1.50 (4H, m,  $-\text{CH}_2-$ ), 2.27 (2H, s,  $-\text{CH}_3$ ), 2.31-2.35 (4H, q,  $J$  7 Hz,  $\text{CpCH}_2$ ), 2.44-2.49 (8H, br,  $\text{NCH}_2$ ) 4.01-4.02 (4H, d,  $J$  1.35 Hz, Cp), 4.06 (5H, s, Cp).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  25.6, 27.9, 28.3, 57.3 ( $-\text{CH}_2-$ ), 44.8 ( $-\text{CH}_3$ ), 51.1, 53.8 ( $\text{CH}_2\text{N}$ ), 65.9, 66.9, 67.3 (Cp), 87.9 ( $\text{C}_{\text{ipso}}$  Cp). Anal. Calc. for:  $\text{C}_{19}\text{H}_{28}\text{FeN}_2$  (340.29): C, 67.06; H, 8.29; Fe, 16.41; N, 8.23. Found: C, 66.83; H, 8.34; Fe, 16.51; N, 8.32%.

**1-(4-Ferrocenylbutyl)morpholine (6c).** From 0.4 g of 4-bromobutylferrocene, 0.34 g of light brown oil viscous oil (**6c**) was obtained in 87% yield. FT-IR (KBr,  $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 2923, 2854, 1665, 1469, 1362, 1057, 490;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.49-1.53 (4H, m,  $-\text{CH}_2-$ ), 2.31-2.35 (4H, t,  $J$  6.4 Hz,  $\text{CpCH}_2$ ), 2.43 (4H, br,  $\text{NCH}_2$ ) 3.70-3.72 (4H, m,  $\text{OCH}_2$ ), 4.02-4.04 (4H, d,  $J$  4.96 Hz, Cp), 4.08 (5H, s, Cp);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  25.3, 27.8, 28.4 ( $-\text{CH}_2-$ ), 57.8, 52.6 ( $\text{NCH}_2$ ), 65.1 ( $\text{OCH}_2$ ), 65.8, 66.9, 67.3 (Cp), 87.9 ( $\text{C}_{\text{ipso}}$  Cp); Anal. Calc. for:  $\text{C}_{18}\text{H}_{25}\text{FeNO}$  (327.25): C, 66.07; H, 7.70; Fe, 17.06; N, 4.28. Found: C, 65.92; H, 7.75; Fe, 17.11; N, 4.30%.

**1-(4-Ferrocenylbutyl)piperidine (6d).** From 0.4 g of 4-bromobutylferrocene, 0.27 g of light brown oil viscous oil (**6d**) was obtained in 71% yield. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2933, 2859, 1649, 1402, 1366, 1077, 486;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.50-1.51 (2H, m,  $-\text{CH}_2-$ ), 1.52-1.57 (4H, m,  $-\text{CH}_2-$ ), 1.57-1.62 (4H, m,  $-\text{CH}_2-$ ), 2.28-2.31 (4H, m,  $\text{CH}_2\text{N}$ ,  $\text{CpCH}_2$ ), 2.38 (4H, br,  $\text{CH}_2\text{N}$ ), 4.00-4.03 (4H, d,  $J$  1.6 Hz, Cp), 4.06 (5H, s, Cp);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  23.0, 23.6, 24.6, 27.9, 28.3, ( $-\text{CH}_2-$ ), 50.9, 58.1 ( $\text{NCH}_2$ ), 65.8, 66.8, 67.2 (Cp), 87.9 ( $\text{C}_{\text{ipso}}$  Cp); Anal. Calc. for:  $\text{C}_{19}\text{H}_{27}\text{FeN}$  (325.28): C, 70.16; H, 8.37; Fe, 17.17; N, 4.31. Found: C, 69.89; H, 8.47; Fe, 17.27; N, 4.37%.

**1-(4-Ferrocenylbutyl)imidazole (6e).** From 0.4 g of 4-bromobutylferrocene, 0.27 g (73%) of light brown oil viscous oil (**6e**) was obtained. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2933, 2859, 1506, 1453, 1228, 1105, 1000, 650, 486;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  1.42-1.50 (2H, m,  $-\text{CH}_2-$ ), 1.75-1.79 (2H, m,  $-\text{CH}_2-$ ), 2.32-2.36 (2H, t,  $J$  7.5 Hz,  $\text{CpCH}_2$ ), 3.89-3.92 (2H, t,  $J$  6.5 Hz,  $\text{NCH}_2$ ), 4.01-4.03 (4H, d,  $J$  9.66 Hz, Cp), 4.06 (5H, s, Cp), 6.98-7.14 (2H, m, Im), 7.49 (1H, s, Im);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  27.0, 28.0, 29.7 ( $-\text{CH}_2-$ ), 45.9 ( $\text{NCH}_2$ ), 66.1, 66.9, 67.3 (Cp), 87.9 ( $\text{C}_{\text{ipso}}$  Cp), 118.23, 128.78, 136.64 (C-Im); Anal. Calc. for:  $\text{C}_{17}\text{H}_{20}\text{FeN}_2$  (308.21): C, 66.25; H, 6.54; Fe, 18.12; N, 9.09. Found: C, 65.98; H, 6.57; Fe, 18.27; N, 9.18%.

**1-(4-Ferrocenylbutyl)pyrazole (6f).** From 0.4 g of 4-bromobutylferrocene, 0.21 g (57%) of light brown oil viscous oil (**6f**) was obtained. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3094, 2935, 2857, 1610, 1440, 1390, 1000, 486;  $^1\text{H}$  NMR (400 MHz):  $\delta_{\text{H}}$  1.44-1.52 (2H, m,  $-\text{CH}_2-$ ), 1.86-1.93 (2H, m,  $-\text{CH}_2-$ ), 2.32-2.36 (2H, t,  $J$  7.6 Hz,  $\text{CpCH}_2$ ), 4.03-4.07 (9H, m, Cp), 4.11-4.15 (2H, t,  $\text{NCH}_2$ ), 6.23, 7.36, 7.56 (3H, br, py).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  26.9, 27.9, 29.1, 50.8 ( $-\text{CH}_2-$ ), 66.0, 66.9, 67.3 (Cp), 87.5 ( $\text{C}_{\text{ipso}}$  Cp), 104.1, 127.7, 137.9 (C-py). Anal. Calc. for:  $\text{C}_{17}\text{H}_{20}\text{FeN}_2$  (308.21): C, 66.25; H, 6.54; Fe, 18.12; N, 9.09. Found: C, 66.79; H, 6.41; Fe, 17.89; N, 8.91%.

**1-(4-Ferrocenylbutyl)dipropylamine (6g).** From 0.4 g of 4-bromobutylferrocene, 0.28 g (69%) of light brown oil viscous oil (**6g**) was obtained. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2926, 2854, 1602, 1410, 1384, 1003;  $^1\text{H}$  NMR (400 MHz):  $\delta_{\text{H}}$  0.86-0.89 (3H, t,  $J$  7.3 Hz,  $\text{CH}_3$ ), 1.40-1.50 (8H, m,  $-\text{CH}_2-$ ), 2.31-2.43 (8H, m,  $\text{CpCH}_2$ ,  $\text{NCH}_2$ ), 4.02-4.05 (4H, m, Cp), 4.09 (5H, s, Cp).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  10.9 ( $\text{CH}_3$ ), 19.1, 26.1, 28.0, 28.5 ( $-\text{CH}_2-$ ) 55.2, 53.0 ( $\text{NCH}_2$ ), 65.9, 66.9, 67.3 (Cp), 88.3 ( $\text{C}_{\text{ipso}}$  Cp). Anal. Calc. for:  $\text{C}_{20}\text{H}_{31}\text{FeN}$  (341.32): C, 70.38; H, 9.16; Fe, 16.36; N, 4.10. Found: C, 70.03; H, 9.29; Fe, 16.51; N, 4.17%.

**1-(4-Ferrocenylbutyl)dibutylamine (6h).** From 0.4 g of 4-bromobutylferrocene, 0.34 g (78%) of light brown oil viscous oil (**6h**) was obtained. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3092, 2948, 2863, 1729, 1460, 1372, 1004, 490;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  0.89-0.93 (6H, t,  $J$  7.3  $\text{CH}_3$ ), 1.25-1.34 (4H, m,  $-\text{CH}_2-$ ), 1.38-1.44 (4H, m,  $-\text{CH}_2-$ ), 1.45-1.49 (4H, m,  $-\text{CH}_2-$ ), 2.31-2.34 (2H, t,  $J$  7.5  $\text{CpCH}_2$ ), 2.38-2.41 (6H, m,  $\text{NCH}_2$ ), 4.02-4.03 (2H, m, Cp), 4.04-4.05 (2H, d,  $J$  1.59 Hz, Cp), 4.09 (5H, s, Cp).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  13.1 ( $\text{CH}_3$ ), 19.7, 26.0, 28.0, 28.1, 28.4 ( $-\text{CH}_2-$ ), 52.8, 52.9 ( $\text{NCH}_2$ ), 65.9, 66.9, 67.3 (Cp), 88.2 ( $\text{C}_{\text{ipso}}$  Cp). Anal. Calc. for:  $\text{C}_{22}\text{H}_{35}\text{FeN}$  (369.37): C, 71.54; H, 9.55; Fe, 15.12; N, 3.79. Found: C, 71.74; H, 9.47; Fe, 15.02; N, 3.77%.



**Synthesis of 4-(4-ferrocenylbutyl)-4-methyl morpholinium iodide (6i).** 4-(4-ferrocenylbutyl)morpholine (**6c**) (0.1 g, 0.31 mmol) and methyl iodide (0.13g, 0.94 mmol) were dissolved in acetone (20 ml) and the mixture was refluxed for 72 hours. After the completion of the reaction, the cooled mixture was diluted with ethyl acetate and washed with water. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under atmospheric pressure. The crude product was purified by preparative thin layer chromatography on silica gel with n-hexane/acetone (1:1) as eluent to give 0.09 g (91%) of a light brown viscous oil (**6i**). FT-IR (KBr, cm<sup>-1</sup>): 2923, 2853, 1602, 1412, 1384, 1035, 487. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ<sub>H</sub> 1.47-1.54 (2H, m, -CH<sub>2</sub>-), 1.67-1.75 (2H, m, -CH<sub>2</sub>-), 2.33-2.37 (2H, t, J 7.6 Hz, CpCH<sub>2</sub>), 3.11 (3H, s, CH<sub>3</sub>), 3.138-3.41 (4H, m, OCH<sub>2</sub>), 3.45-3.48 (2H, m, NCH<sub>2</sub>), 3.91 (4H, m, NCH<sub>2</sub>) 4.06-4.12 (9H, m, Cp). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ<sub>C</sub> 20.7 (CH<sub>3</sub>), 27.1, 28.3, 46.0 (-CH<sub>2</sub>-), 58.9, 59.8 (NCH<sub>2</sub>), 63.5 (OCH<sub>2</sub>), 66.9, 67.7, 68.3 (Cp), 88.1 (C<sub>ipso</sub> Cp). Anal. Calc. for: C<sub>20</sub>H<sub>30</sub>FeIN (467.22): C, 51.42; H, 6.47; Fe, 11.95; I, 27.16; N, 3.00. Found: C, 50.99; H, 6.54; Fe, 12.12; I, 27.32; N, 3.03%.

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## Supplementary Material

Supplementary material related to this article, including Nuclear Magnetic Resonance (<sup>1</sup>H, <sup>13</sup>C NMR and FT-IR) figures for compounds **6a–i** are available in the online version of the text.

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