

## 一些二茂铁苯基亚胺化合物的合成与表征

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**摘要:** 通过回流对应的二茂铁苯胺和芳香醛的混合物的同样路径合成了一系列新颖的二茂铁苯基亚胺化合物(**5~12**)。当暴露于空气时化合物 **5~12** 稳定, 不发生任何分解。所有化合物均用  $^1\text{H}$ 、 $^{13}\text{C}$  NMR, MS, IR, UV-Vis 和元素分析表征。还报导了化合物 *N*-(3-bromo-2-hydroxybenzylidene)-4-ferrocenylimine (**10**) 的单晶结构, 其结晶属单斜晶系  $P2_1/c$  空间群。

**关键词:** 二茂铁; 合成; 表征; 亚胺; X-射线衍射

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## Synthesis and Characterization of Some Ferrocenylphenylimine Compounds

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**Abstract:** A novel series of ferrocenylimine compounds (**5~12**) were synthesized via the same route by refluxing a mixture of corresponding ferrocenylaniline with aromatic aldehyde. Compounds **5~12** were air stable without any decomposition when exposed to air. The compounds were all characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, mass spectrometry, IR, UV-Visible and elemental analysis. The single crystal structure of compound **10** was also reported, which revealed that compound **10** crystallized in monoclinic system with  $P2_1/c$  space group. CCDC: 1010246, **10**.

**Key words:** ferrocene; synthesis; characterization; imine; X-ray diffraction

## 0 Introduction

The synthesis of ferrocene based compounds has become an active research because of the rich chemistry and properties of ferrocene<sup>[1]</sup>. Over the last few years, ferrocene and its derivatives have found wide application in homogeneous catalysis<sup>[2-6]</sup>, materials science<sup>[7]</sup>, sensors<sup>[8-9]</sup>, electroactive materials<sup>[10-12]</sup> and in medicine<sup>[13-14]</sup>. In addition the easy functionalization of ferrocene and their stability in aqueous, aerobic media

and their unique electronic properties is advantageous to their wide applications<sup>[15-17]</sup>. Ornelas C.<sup>[18]</sup> had reviewed on the use of ferrocene-based compounds for medicinal applications as an active research, especially in anticancer activity.

Recently, some ferrocene derived compounds reported by Mathiyalagan et al.<sup>[19]</sup> have greater antibacterial and antifungal activity than the respective standards. Various examples of enhanced activity of some drugs are reported when ferrocene fragment is

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incorporated into an organic compound<sup>[17,20-22]</sup>. A common example is tamoxifen well-known anticancer drug, when ferrocene fragment is incorporated by replacing the phenyl group of tamoxifen with ferrocene to produce a compound (Ferrocifen) that exhibits a stronger effect against breast cancer cells that are resistant to tamoxifen<sup>[18,23]</sup>. Ikhile et al.<sup>[2]</sup> had also reported the synthesis and catalytic activity of some ferrocenyl based imidazolium salts. As a result of the enhanced and increased activity when ferrocene is incorporated into an organic compound, it is therefore important to design, synthesize novel ferrocene derived compounds and evaluate their activity.

Imine also known as Schiff bases, are structurally nitrogen analogue of an aldehyde or ketone in which the Carbonyl group has been replaced by an imine or azomethine group<sup>[24]</sup>. Schiff bases have found applications in most branches of chemistry especially in biological, inorganic and analytical chemistry<sup>[25]</sup>. The biological application of Schiff bases has been recently reviewed<sup>[25]</sup>. Schiff bases derived from various heterocyclic compounds have showed different ranges of biological application especially as antitumor<sup>[26-27]</sup>, antimicrobial<sup>[28]</sup>, anti-depressant<sup>[29]</sup>, anti-inflammatory<sup>[30]</sup>, anti-viral<sup>[31]</sup>, angiotension-II receptor antagonist<sup>[32]</sup>, antioxidant<sup>[33]</sup>, anti-bacterial<sup>[34]</sup>, anti-glycation<sup>[35]</sup>, anticonvulsant<sup>[36]</sup> and anti-tuberculosis<sup>[37]</sup>. Therefore modifying the Schiff bases by incorporation of ferrocene into their molecules will improve their wide applications.

Recently, Zaheer et al.<sup>[38]</sup> synthesized some ferrocenyl Schiff bases with some low cytotoxicity and appreciable antifungal, antioxidant and DNA protection activities. Also, Chen et al.<sup>[39]</sup> synthesized three new hydroxyl substituted ferrocenyl Schiff bases from a mixture of aminoferrocene and corresponding aldehyde in dry methanol. The three compounds synthesized by Chen et al.<sup>[39]</sup> exhibit antioxidant and anti cancer activities. The synthesis and spectroscopic characterization of Schiff base ligands containing pyridine moiety and their nickel, copper and zinc complexes have been reported<sup>[40]</sup>. Therefore; it is paramount to synthesize new Schiff bases with ferrocene moiety due to the wide application of these

effective compounds. Herein, we report the synthesis and characterization of some ferrocenyl imine compounds, starting with either 3-ferrocenylaniline or 4-ferrocenylaniline.

## 1 Experimental

### 1.1 General procedure

All manipulations involving air and moisture sensitive compounds were performed through the use of standard Schlenk techniques under an atmosphere of dry argon. All NMR experiments were conducted on a 400 MHz Bruker Ultrashield spectrometer and samples were dissolved in deuterated chloroform. Infrared spectra were recorded with a PerkinElmer Universal ATR Spectrum 100 FTIR spectrometer. All low resolution mass data were run on the Waters Alliance 3100 Empower 2154 HPLC-mass spectrometer using Electrospray Ionisation in positive/negative mode. Elemental analyses were performed in a Flash2000 organic elemental analyzer. UV-Visible spectra were recorded on Agilent Technologies Cary 60 UV-Visible spectrophotometer. Reagents were purchased from Sigma-Aldrich and were used as received. The 3-ferrocenyl phenyl and 4-ferrocenyl phenyl aniline were synthesized by a modified literature procedures<sup>[41]</sup>. Melting points were recorded on an Electrothermal, model IA8103 digital melting point apparatus and were uncorrected.

### 1.2 Synthesis of 3-nitrophenylferrocene and 4-nitrophenylferrocene (1 and 2)

In a two round-bottomed flasks, 3-nitroaniline or 4-nitroaniline, 30 mL of water and 30 mL of concentrated hydrochloric acid were mixed together and cooled to 0~5 °C. A solution of sodium nitrite in water was added dropwise with stirring. After the addition was complete, the solution was stirred for 30 min and kept below 5 °C during this period. Ferrocene and 1 g hexadecyltrimethylammonium bromide were added to 100 mL ethyl ether and cooled to 0~5 °C. The above prepared diazonium salt solution was added dropwise with stirring. After the addition was complete, the reaction mixture was stirred for an additional 5 h at room temperature. The reaction

mixture was evaporated and the crude product was extracted with dichloromethane.

### 1.2.1 Synthesis of 3-nitrophenylferrocene (**1**)

Starting materials used were 3-nitroaniline (13.4 g, 96.8 mmol), ferrocene (9.0 g, 48.3 mmol) and the other starting materials as stated above (see Section 1.2). The yield was an orange powder: 12.6 g, 85%, m.p. 112.4 °C, IR (ATR,  $\text{cm}^{-1}$ ): 2 922, 2 853, 1 522, 1 343, 1 285, 1 268, 1 104, 1 036, 1 017, 999, 911, 894, 828, 807, 772, 742, 723, 673, 652, 615;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.26 (1H, s,  $\text{C}_6\text{H}_4$ ), 8.00 (1H, d,  $J$  7.6 Hz,  $\text{C}_6\text{H}_4$ ), 7.74 (1H, d,  $J$  7.7 Hz,  $\text{C}_6\text{H}_4$ ), 7.42 (1H, t,  $J$  7.9 Hz,  $\text{C}_6\text{H}_4$ ), 4.71 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.40 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.05 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 148.62, 142.15, 131.60, 129.28, 120.48, 120.38, 82.63, 69.98, 66.89;  $m/z$  (ESI): 307.2 ( $\text{M}^+$ , 100%); Anal. Calcd. for  $\text{C}_{16}\text{H}_{13}\text{NFeO}_2$  (%): C, 62.57; H, 4.27; N, 4.56; Found (%): C, 62.60; H, 4.28; N, 4.54.

### 1.2.2 Synthesis of 4-nitrophenylferrocene (**2**)

Starting materials used were 4-nitroaniline (14.0 g, 100 mmol), ferrocene (9.0 g, 48.3 mmol) and the other starting materials as stated above (see Section 1.2). The product was a violet solid: 13.0 g, yield 88%, m.p. 164.5 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 104, 2 924, 2 850, 2 365, 1 700, 1 594, 1 518, 1 338, 1 108, 1 009, 849, 753, 690;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.12 (2H, d,  $J$  7.6 Hz,  $\text{C}_6\text{H}_4$ ), 7.55 (2H, d,  $J$  7.7 Hz,  $\text{C}_6\text{H}_4$ ), 4.73 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.46 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.04 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 148.49, 145.83, 126.22, 124.12, 82.03, 70.88, 70.33, 67.51;  $m/z$  (ESI): 306.9 ( $\text{M}^+$ , 100%); Anal. Calcd. for  $\text{C}_{16}\text{H}_{13}\text{NFeO}_2$  (%): C, 62.57; H, 4.27; N, 4.56; Found (%): C, 62.60; H, 4.24; N, 4.57.

## 1.3 Synthesis of 3-ferrocenylaniline and 4-ferrocenylaniline (**3** and **4**)

To a stirred mixture of 3-nitrophenylferrocene, **1**, or 4-nitrophenylferrocene, **2**, in 35 mL of concentrated HCl and 50 mL ethanol was added granulated tin and the reaction mixture was heated under reflux at 50 °C for 5 h. After the mixture was cooled, 300 mL water was added and aqueous NaOH was added to adjust the pH value to 14 before filtration. The filtrate was extracted with DCM and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent

was removed by rotary evaporation. It was then subjected to column chromatography using hexane/diethylether (7:3, V/V) as the eluent to give a pure compound.

### 1.3.1 Synthesis of 3-ferrocenylaniline (**3**)

Starting materials used were 3-nitrophenylferrocene (5.0 g, 16.3 mmol), granulated tin (10.0 g, 84.0 mmol) and the other starting materials as stated above (see Section 1.3). The product was an orange solid: 3.5 g, yield 78%, m.p. 129.5 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 712, 2 806, 2 579, 1 960, 1 734, 1 598, 1 582, 1 509, 1 468, 1 442, 1 408, 1 388, 1 235, 1 168, 1 079, 1 018, 998, 779, 693, 648;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 7.07 (1H, s,  $\text{C}_6\text{H}_4$ ), 6.90 (1H, d,  $J$  7.6 Hz,  $\text{C}_6\text{H}_4$ ), 6.53 (1H, t,  $J$  7.8 Hz,  $\text{C}_6\text{H}_4$ ), 6.51 (1H, d,  $J$  7.6 Hz,  $\text{C}_6\text{H}_4$ ), 4.58 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.39 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.04 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 146.25, 140.32, 130.25, 115.17, 113.12, 112.95, 85.66, 69.63, 68.75, 66.56;  $m/z$  (ESI): 260.1 ( $\text{M}^+ - \text{NH}_2$ , 5%), 278.2 ( $\text{M}^+$ , 100%), 278.3 ( $\text{M}^+$ , 70%); Anal. Calcd. for  $\text{C}_{16}\text{H}_{15}\text{NFe}$ : C, 69.34; H, 5.46; N, 5.05; Found: C, 69.29; H, 5.52; N, 5.02.

### 1.3.2 Synthesis of 4-ferrocenylaniline (**4**)

Starting materials used were 4-nitrophenylferrocene (6.0 g, 21.0 mmol), granulated tin (13.5 g, 120.0 mmol) and the other starting materials as stated above (see Section 1.3). The product was an orange solid: 4.5 g, yield 77%, m.p. 160.5 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 372, 3 651, 2 922, 2 852, 1 878, 1 684, 1 539, 1 452, 1 387, 1 280, 1 182, 1 085, 1032, 998, 818, 727, 668, 634;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 7.27 (2H, d,  $J$  7.6 Hz,  $\text{C}_6\text{H}_4$ ), 6.76 (2H, d,  $J$  7.6 Hz,  $\text{C}_6\text{H}_4$ ), 4.54 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.24 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.02 (5H, s,  $\text{C}_5\text{H}_5$ ), 2.15 (s, 2H,  $\text{NH}_2$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 144.89, 127.12, 116.19, 115.17, 86.76, 69.44, 68.24, 65.78;  $m/z$  (ESI): 278.1 ( $\text{M}^+$ , 100%), 278.9 ( $\text{M}^+$ , 48%); Anal. Calcd. for  $\text{C}_{16}\text{H}_{15}\text{NFe}$  (%): C, 69.34; H, 5.46; N, 5.05; Found (%): C, 69.33; H, 5.49; N, 5.07.

## 1.4 Synthesis of ferrocenylphenylimine (**5**~**12**)

In a pre-packed two-necked flask supplied with a magnetic stirrer was added 3-ferrocenylaniline or 4-ferrocenylaniline in 15 mL of dried ethanol, was mixed with an equimolar amount of aromatic

aldehydes in 15 mL of dried ethanol. The mixture was heated under reflux and the progress of the reaction was monitored by TLC. The required product was formed in 5~6 h. The solvent was removed under vacuum to give the crude product.

#### 1.4.1 Synthesis of *N*-(3-nitro-2-hydroxybenzylidene)-3-ferrocenylimine (**5**)

Starting materials used were 3-ferrocenylaniline (0.05 g, 0.19 mmol) and 2-hydroxy-3-nitrobenzaldehyde (0.03 g, 0.19 mmol). The product was a brick red powder: 0.075 g, yield 95%, m.p. 187.9 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 348, 2 922, 2 851, 2 365, 1 718, 1 684, 1 577, 1 440, 1 221, 1 105, 1 019, 1 000, 907, 806, 773, 727, 668;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.75 (1H, s, HC=N), 8.10 (1H, d,  $J$  7.6 Hz,  $\text{C}_6\text{H}_3$ ), 7.99 (1H, d,  $J$  7.8 Hz,  $\text{C}_6\text{H}_3$ ), 7.85 (1H, t,  $J$  7.9 Hz,  $\text{C}_6\text{H}_3$ ), 7.82 (1H, d,  $J$  7.6 Hz,  $\text{C}_6\text{H}_4$ ), 7.14 (1H, t,  $J$  7.9 Hz,  $\text{C}_6\text{H}_4$ ), 7.09 (2H, m,  $\text{C}_6\text{H}_4$ ), 4.66 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.35 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.03 (5H, s,  $\text{C}_5\text{H}_5$ ), 3.90 (1H, s, OH);  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 160.00, 130.18, 126.21, 126.06, 120.34, 119.45, 117.66, 84.40, 72.24, 69.20;  $m/z$  (ESI): 425.5 ( $\text{M}^+$ , 100%); Anal. Calcd. for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_3\text{Fe}$  (%): C, 64.81; H, 4.26; N, 6.57; Found(%): C, 64.79; H, 4.24; N, 6.54.

#### 1.4.2 Synthesis of *N*-(3-bromo-2-hydroxybenzylidene)-3-ferrocenylimine (**6**)

Starting materials used were 3-ferrocenylaniline (0.05 g, 0.19 mmol) and 3-bromo-2-hydroxybenzaldehyde (0.04 g, 0.19 mmol). The product was a dark-brown powder: 0.085 g, yield 99%, m.p. 391.3 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 432, 3 062, 2 951, 2 920, 2 851, 1 774, 1 688, 1 523, 1 431, 1 381, 1 293, 1 175, 1 020, 1 105, 999, 905, 843, 790, 735, 691, 669;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.63 (1H, s, HC=N), 7.77 (1H, s,  $\text{C}_6\text{H}_3$ ), 7.63-7.37 (4H, m,  $\text{C}_6\text{H}_4$ ), 6.84 (2H, s,  $\text{C}_6\text{H}_3$ ), 4.65 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.34 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.04 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 163.24, 159.14, 158.99, 140.59, 138.22, 129.97, 129.34, 128.21, 121.59, 121.22, 119.27, 117.67, 111.04, 81.54, 69.65, 66.51;  $m/z$  (ESI): 457.3 ( $\text{M}^+$ , 100%), 458.1 ( $\text{M}^+$ , 50%); Anal. Calcd. for  $\text{C}_{23}\text{H}_{18}\text{NOBrFe}$  (%): C, 60.03; H, 3.94; N, 3.04; Found (%): C, 60.04; H, 3.95; N, 3.02.

#### 1.4.3 Synthesis of *N*-(3-bromo-5-chlorosalicylidene)-

#### 3-ferrocenylimine (**7**)

Starting materials used were 3-ferrocenylaniline (0.05 g, 0.19 mmol) and 3-bromo-5-chlorosalicylaldehyde (0.04 g, 0.19 mmol). The product was a reddish paste: 0.07 g, yield 76%, m.p. 108.6 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 340, 2 916, 2 849, 2 551, 2 157, 1 733, 1 662, 1 597, 1 557, 1 445, 1 352, 1 288, 1241, 1 162, 1 105, 1 019, 973, 951, 927, 861, 788, 739, 711, 689, 606, 587;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.55 (1H, s, HC=N), 7.74 (1H, s,  $\text{C}_6\text{H}_2$ ), 7.61 (1H, s,  $\text{C}_6\text{H}_2$ ), 7.43 (1H, d,  $J$  7.4 Hz,  $\text{C}_6\text{H}_4$ ), 7.33 (2H, s,  $\text{C}_6\text{H}_4$ ), 7.09 (1H, d,  $J$  7.5 Hz,  $\text{C}_6\text{H}_4$ ), 4.66 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.35 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.05 (5H, s,  $\text{C}_5\text{H}_5$ ), 2.03 (1H, s, OH);  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 159.93, 157.19, 141.43, 139.38, 135.55, 131.84, 129.55, 129.55, 125.61, 123.69, 119.97, 119.27, 117.78, 111.95, 84.20, 69.81, 69.45, 66.66;  $m/z$  (ESI): 186.7 ( $\text{M}^+ - \text{C}_{13}\text{H}_8\text{NOBrCl}$ , 91%), 493.4 ( $\text{M}^+$ , 21%); Anal. Calcd. for  $\text{C}_{23}\text{H}_{17}\text{NOBrClFe}$  (%): C, 55.85; H, 3.46; N, 2.83; Found (%): C, 55.87; H, 3.48; N, 2.85.

#### 1.4.4 Synthesis of *N*-(ferrocenylformidene)-3-ferrocenylimine (**8**)

Starting materials used were 3-ferrocenylaniline (0.03 g, 0.11 mmol) and ferrocene carboxaldehyde (0.02 g, 0.11 mmol). The product was a brown solid: 0.04 g, yield 77%, m.p. 329.4 °C, IR (ATR,  $\text{cm}^{-1}$ ): 2 920, 1 648, 1 597, 1 451, 1 306, 1 105, 1 025, 1 000, 817, 760, 692, 625, 580;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.36 (1H, s, HC=N), 7.17 (1H, d,  $J$  7.3 Hz,  $\text{C}_6\text{H}_4$ ), 7.13 (1H, t,  $J$  7.2 Hz,  $\text{C}_6\text{H}_4$ ), 6.93 (1H, s,  $\text{C}_6\text{H}_4$ ), 6.70 (1H, d,  $J$  7.2 Hz,  $\text{C}_6\text{H}_4$ ), 4.78 (2H, d,  $J$  1.8 Hz,  $\text{C}_5\text{H}_4$ ), 4.66 (2H, d,  $J$  1.8 Hz,  $\text{C}_5\text{H}_4$ ), 4.59 (2H, d,  $J$  1.7 Hz,  $\text{C}_5\text{H}_4$ ), 4.30 (2H, d,  $J$  1.8 Hz,  $\text{C}_5\text{H}_4$ ), 4.26 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.04 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 159.50, 149.44, 140.44, 125.69, 119.71, 115.39, 86.95, 82.95, 70.11, 69.98, 69.69, 69.01, 67.43, 66.57;  $m/z$  (ESI): 472.1 ( $\text{M}^+$ , 50%), 472.8 ( $\text{M}^+$ , 30%); Anal. Calcd. for  $\text{C}_{27}\text{H}_{23}\text{NFe}_2$  (%): C, 68.54; H, 4.90; N, 2.96; Found (%): C, 68.53; H, 4.93; N, 2.98.

#### 1.4.5 Synthesis of *N*-(2-hydroxy-3-nitrobenzylidene)-4-ferrocenylimine (**9**)

Starting materials used were 4-ferrocenylaniline (0.057 g, 0.21 mmol) and 2-hydroxy-3-nitrobenzaldehyde (0.034 g, 0.21 mmol). The product was a brick

red crystal: 0.07 g, yield 80%, m.p. 234.8 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 427, 3 080, 2 918, 2 850, 2 108, 1 730, 1 619, 1 526, 1 453, 1 349, 1 242, 1 083, 955, 834, 813, 742, 692.21;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.76 (1H, s, HC=N), 8.10 (1H, d,  $J$  7.4 Hz  $\text{C}_6\text{H}_3$ ), 7.84 (1H,  $J$  8.2 Hz  $\text{C}_6\text{H}_3$ ), 7.54 (1H, d,  $J$  7.3 Hz,  $\text{C}_6\text{H}_3$ ), 7.30 (2H, d,  $J$  7.7 Hz,  $\text{C}_6\text{H}_4$ ), 6.64 (2H, d,  $J$  7.8 Hz,  $\text{C}_6\text{H}_4$ ), 4.52 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.29 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.04 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 158.96, 152.34, 149.26, 142.56, 138.46, 134.36, 133.64, 128.56, 127.12, 125.12, 115.49, 84.15, 69.37, 68.19, 65.80;  $m/z$  (ESI): 425.5 ( $\text{M}^+$ , 100%); Anal. Calcd. for  $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_3\text{Fe}$  (%): C, 64.81; H, 4.26; N, 6.57; Found (%): C, 64.78; H, 4.30; N, 6.53.

#### 1.4.6 Synthesis of *N*-(3-bromo-2-hydroxybenzylidene)-4-ferrocenylimine (**10**)

Starting materials used were 4-ferrocenylaniline (0.047 g, 0.17 mmol) and 3-bromo-2-hydroxybenzaldehyde (0.034 g, 0.17 mmol). The product was a brown crystal: 0.058 g, yield 73%, m.p. 241.6 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 425, 3 093, 2 917, 2 850, 1 733, 1 675, 1 589, 1 521, 1408, 1 281, 1 183, 1 183, 1105, 888, 819, 771, 729, 691, 655;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.64 (1H, s, HC=N), 7.62 (2H, d,  $J$  7.5 Hz  $\text{C}_6\text{H}_4$ ), 7.51 (2H, d,  $J$  7.8 Hz,  $\text{C}_6\text{H}_4$ ), 7.37 (1H, d,  $J$  7.5 Hz,  $\text{C}_6\text{H}_3$ ), 7.34 (1H, d,  $J$  7.4 Hz  $\text{C}_6\text{H}_4$ ), 6.83 (1H, d,  $J$  7.2 Hz,  $\text{C}_6\text{H}_3$ ), 4.65 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.34 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.05 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 162.31, 159.92, 146.51, 136.06, 131.24, 129.72, 126.99, 122.49, 121.30, 119.71, 118.98, 111.23, 84.50, 69.74, 69.34, 66.56;  $m/z$  (ESI): 326.0 ( $\text{M}^+ - \text{C}_4\text{H}_3\text{Br}$ , 100%), 456.4 ( $\text{M}^+ - 1$ , 67%), 458.0 ( $\text{M}^+$ , 54%), 458.1 ( $\text{M}^+$ , 54%); Anal. Calcd. for  $\text{C}_{23}\text{H}_{18}\text{NOBrFe}$  (%): C, 60.03; H, 3.94; N, 3.04; Found (%): C, 59.99; H, 3.91; N, 3.07.

#### 1.4.7 Synthesis of *N*-(3-bromo-5-chlorosalicyl)-4-ferrocenylimine (**11**)

Starting materials used were 4-ferrocenylaniline (0.044 g, 0.16 mmol) and 3-bromo-5-chlorosalicylaldehyde (0.037 g, 0.16 mmol). The product was a dark brown powder: 0.06 g, yield 77%, m.p. 60.1 °C, IR (ATR,  $\text{cm}^{-1}$ ): 3 424, 3 086, 2 923, 2 452, 1 982, 1 736, 1 616, 1 523, 1 441, 1 286, 1 135, 1 004, 815, 758, 752;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.56 (1H, s, HC=N), 7.61

(2H, d,  $J$  7.2 Hz,  $\text{C}_6\text{H}_4$ ), 7.51 (2H, d,  $J$  7.6 Hz  $\text{C}_6\text{H}_4$ ), 7.41 (1H, s,  $\text{C}_6\text{H}_2$ ), 7.33 (1H, s,  $\text{C}_6\text{H}_2$ ), 4.65 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.37 (2H, s,  $\text{C}_5\text{H}_4$ ), 4.07 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 160.36, 158.17, 156.74, 135.00, 130.30, 129.99, 129.52, 126.72, 122.23, 121.06, 111.57, 83.73, 69.46, 69.16, 66.28;  $m/z$  (ESI): 273.1 ( $\text{M}^+ - \text{C}_7\text{H}_4\text{BrClO}$ , 100%), 495.2 ( $\text{M}^+$ , 12%), 494.6 ( $\text{M}^+$ , 1%); Anal. Calcd. for  $\text{C}_{23}\text{H}_{17}\text{NOBrClFe}$  (%): C, 55.85; H, 3.46; N, 2.83; Found (%): C, 55.83; H, 3.43; N, 2.80.

#### 1.4.8 Synthesis of *N*-(ferrocenylformidene)-4-ferrocenylimine (**12**)

Starting materials used were 4-ferrocenylaniline (0.049 g, 0.18 mmol) and ferrocene carboxaldehyde (0.038 g, 0.18 mmol). The product was a reddish brown powder: 0.059 g, yield 70%, m.p. 159.1 °C. IR (ATR,  $\text{cm}^{-1}$ ): 3 067, 2 919, 2 854, 2 161, 1 733, 1 632, 1 589, 1 521, 1 439, 1 359, 1 244, 1 133, 1 033, 970, 846, 770, 727, 690, 655;  $\delta$  H (400 MHz,  $\text{CDCl}_3$ ): 8.38 (1H, s, HC=N), 7.47 (2H, d,  $J$  8.4 Hz,  $\text{C}_6\text{H}_4$ ), 7.30 (2H, d,  $J$  8.6 Hz,  $\text{C}_6\text{H}_4$ ), 4.79 (2H, d,  $J$  1.8 Hz,  $\text{C}_5\text{H}_4$ ), 4.63 (2H, d,  $J$  1.8 Hz,  $\text{C}_5\text{H}_4$ ), 4.61 (2H, d,  $J$  1.7 Hz,  $\text{C}_5\text{H}_4$ ), 4.30 (2H, d,  $J$  1.8 Hz,  $\text{C}_5\text{H}_4$ ), 4.24 (5H, s,  $\text{C}_5\text{H}_5$ ), 4.04 (5H, s,  $\text{C}_5\text{H}_5$ );  $\delta$  C (100 MHz,  $\text{CDCl}_3$ ): 160.44, 136.47, 130.54, 129.21, 121.96, 85.26, 82.71, 69.69, 69.64, 69.44, 69.36, 69.17, 68.93;  $m/z$  (ESI): 278.3 ( $\text{M}^+ - \text{C}_{11}\text{H}_{10}\text{Fe}$ , 100%), 475.3 ( $\text{M}^+$ , 40%); Anal. Calcd. for  $\text{C}_{27}\text{H}_{23}\text{NFe}_2$  (%): C, 68.54; H, 4.90; N, 2.96; Found (%): C, 68.57; H, 4.88; N, 2.94.

#### 1.5 X-ray crystal Determination of Compound (**10**)

A suitable crystal was selected and mounted on Mitegen 100 micrometer loop in NVH oil on a Bruker APEX-II CCD' diffractometer. The crystal was kept at 99.98 K during data collection. Using Olex2<sup>[42]</sup>, the structure was solved with the ShelXS<sup>[43]</sup> structure solution program using direct methods and refined with the ShelXL<sup>[43]</sup> refinement package using least squares minimization.

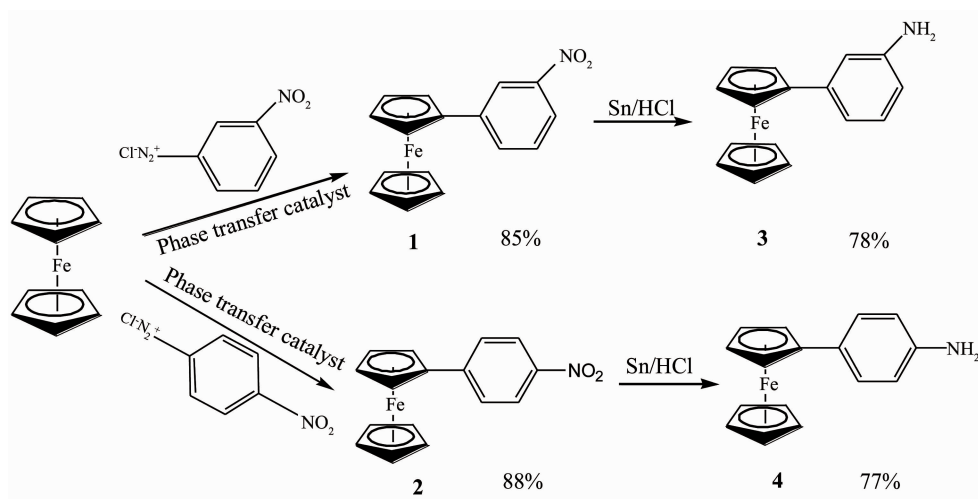
CCDC: 1010246, **10**.

## 2 Results and discussion

### 2.1 Synthesis and Characterization

This study involves the synthesis of a series of 3-ferrocenylimine (**5~8**) and 4-ferrocenylimine (**9~12**)



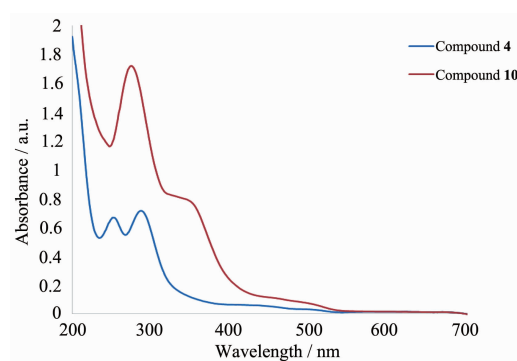


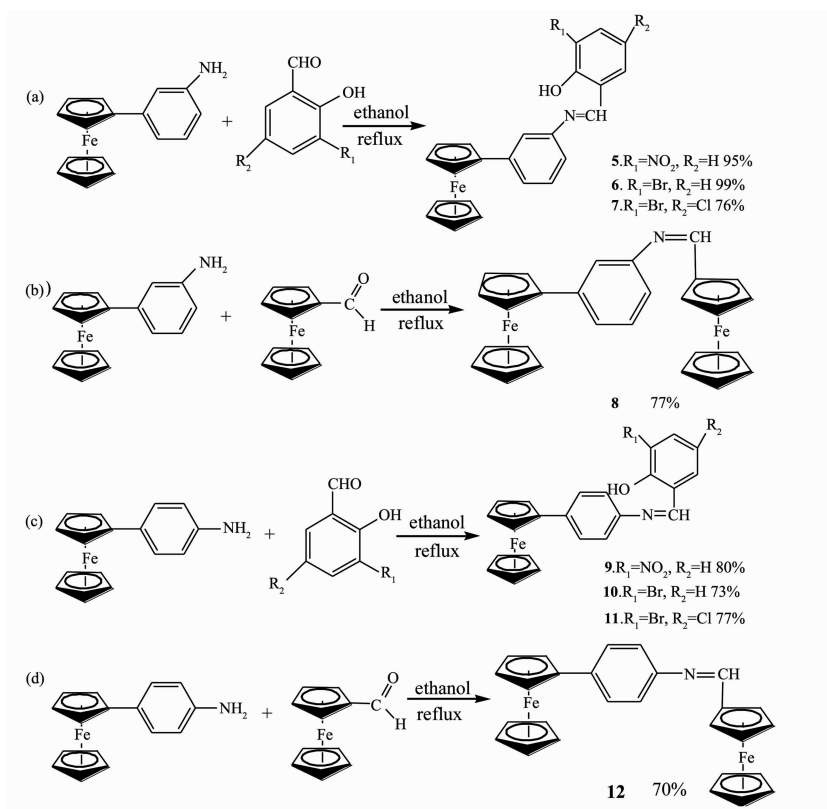
Scheme 1 Synthesis of 3-ferrocenyl and 4-ferrocenyl aniline

which were conducted via the same route. The ferrocenylphenylimine compounds were synthesized following a modified reported method<sup>[38]</sup>. Ferrocenylaniline (**3** and **4**) as precursors to ferrocenylimine were prepared as shown in Scheme 1 by reduction of 3-nitrophenylferrocene (**1**) or 4-nitrophenylferrocene (**2**) with tin in an acidic condition<sup>[41]</sup>. Compounds **1** and **2** were synthesized by arylation of ferrocene by a diazonium salt, method adapted from a modified procedure<sup>[44]</sup>.

The target compounds (**5~12**) were synthesized as shown in Scheme 2 by refluxing a mixture of 3-ferrocenylaniline (**3**) or 4-ferrocenylaniline (**4**) with corresponding aromatic aldehyde. The Compounds (**5~12**) were obtained as air stable and in relatively high yields (70%~99%). They also showed good stability in solution without decomposition when exposed to air. The compounds were all characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, mass spectrometry, IR, UV-Vis spectral and elemental analysis. The imine formation for compounds **5~12** was indicated by the appearance of a strong absorption band between 1 616 and 1 688 cm<sup>-1</sup> in the IR Spectra. The C-H stretching frequencies were observed around 2 806~3 093 cm<sup>-1</sup>, also the bands that are characteristics of the presence of ferrocene in a molecule were observed around 807 and 1 183 cm<sup>-1</sup>. The NMR spectra further confirmed the formation of the ferrocenylphenylimine (compounds **5~12**) by the appearance of a resonance

peak at around 8.36~8.76 in <sup>1</sup>H NMR spectra attributed to the imine proton (HC=N) as compared to ferrocenylaniline (compounds **3** and **4**). As expected the ferrocenyl protons were observed at around 4.02~4.71, which agree with the literature for reported related compounds<sup>[19,41,44-45]</sup>. In <sup>13</sup>C NMR spectra, the imine carbon (HC=N) appeared as the most deshielded around 158.96~163.24 and the ferrocenyl moiety carbon atoms appeared at around 65.80~86.76 ppm which is in agreement with the literature<sup>[2-39]</sup>. Further evidence for the formation of the compounds **1~12** was provided by the positive mode ESI-MS spectra which showed intense molecular ions corresponding to M<sup>+</sup>. The elemental analysis results are in agreement with the molecular formula of the synthesized compounds. The UV-Visible analysis was carried out in acetonitrile which are presented in Table 1. The compounds showed two absorption bands at about 247 and 364 nm. The absorption spectra of the

Fig.1 UV-Visible spectra for compounds **4** and **10**



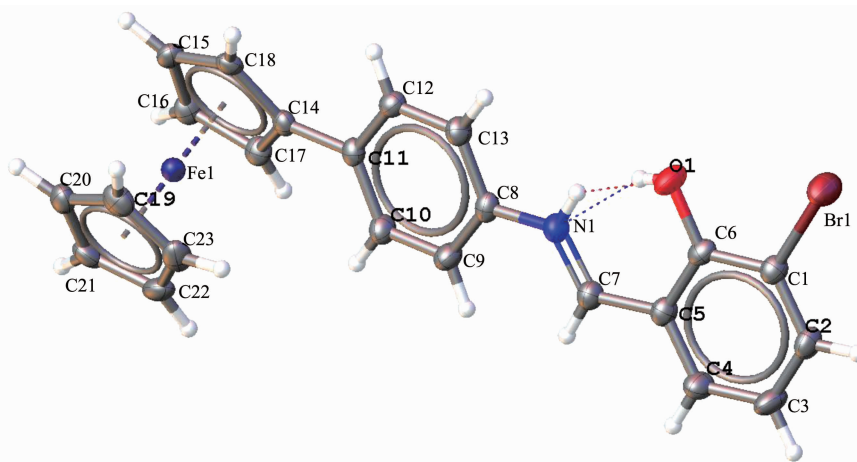
Scheme 2 Synthesis of 3-ferrocenylimine and 4-ferrocenylimine

Table 1 UV-Vis Data of compounds 1~12

Compound	1	2	3	4	5	6	7	8	9	10	11	12
$\lambda_{\text{max}} / \text{nm}$	247	248	255	256	287	287	281	280	281	293	280	281
	279	282	291	292	349	361	360	359	360	364	363	360

ferrocenylimines compounds **5**~**12** showed maximum wavelength shift as compared to the ferrocenyl anilines, compounds **3** and **4**. The two absorption bands in compound **4** (256 and 292 nm) considerably

shifted about 37 and 72 nm respectively to 293 and 364 nm as compared with compound **10** (Fig.1). This can be attributed as an indication of extended conjugated in the ferrocenylimines compounds.

Fig.2 ORTEP diagram of compound **10** shown at 50% probability thermal ellipsoids

## 2.2 Molecular structure of Compound 10

Crystals suitable for X-ray analysis for compound **10** was obtained by slow diffusion of hexane into saturated solution of dichloromethane at room temperature. Compound **10** crystallized in monoclinic system with  $P2_1/c$  space group. The diagram is shown in Fig.2. Selected bond lengths and angles are presented in Table 2, while crystal data and structure

refinement are summarized in Table 3. Compound **10** crystallized with one molecule in the asymmetric unit. The bond length of N1-C7 (0.127 9(4) nm) is shorter than the bond length of N1-C8 which is 0.141 4(3) nm. This can be attributed to the covalent imine bond in N1-C7, thus affording a shorter bond length for it. The imine bond length N1-C7 in compound **10** also fits well with imine bond with similar structure

Table 2 Selected bond length (nm) and angles (°) for compound 10

Compound 10					
N(1)-C(8)	0.141 4(3)	Fe(1)-C(16)	0.205 9(3)	N(1)-C(7)	0.127 9(4)
Fe(1)-C(20)	0.206 4(3)	C(8)-C(9)	0.140 2(4)	Fe(1)-C(21)	0.205 9(3)
C(5)-C(7)	0.145 5(4)	Fe(1)-C(15)	0.205 7(3)	C(5)-C(6)	0.141 8(4)
O(1)-C(6)	0.134 7(3)	Br(1)-C(1)	0.190 4(3)	Fe(1)-C(14)	0.205 0(3)
C(6)-C(1)-Br(1)	118.1(2)	N(1)-C(7)-C(5)	121.6(3)	C(7)-N(1)-C(8)	124.0(2)
C(23)-Fe(1)-C(15)	155.39(12)	C(14)-Fe-C(17)	41.00(10)	O(1)-C(6)-C(1)	119.2(3)

Table 3 Crystal data and structure refinement for compound 10

Compound 10	
Empirical formula	C <sub>23</sub> H <sub>18</sub> BrFeNO
Formula weight	461.15
Temperature / K	99.98
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i> / nm	1.769 1(16)
<i>b</i> / nm	0.731 1(7)
<i>c</i> / nm	1.550 9(14)
$\beta$ / (°)	113.91(2)
Volume / nm <sup>3</sup>	1.834(3)
<i>Z</i>	4
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.670
$\mu$ / mm <sup>-1</sup>	3.014
<i>F</i> (000)	932.0
Crystal size / mm	0.32×0.158×0.105
Radiation	Mo <i>K</i> α ( $\lambda$ =0.710 73 nm)
2 $\theta$ range for data collection / (°)	5.038~57.368
Index ranges	-23 ≤ <i>h</i> ≤ 23, -9 ≤ <i>k</i> ≤ 9, -20 ≤ <i>l</i> ≤ 20
Reflections collected	29 059
Independent reflections	4 603 ( <i>R</i> <sub>int</sub> =0.080 4, <i>R</i> <sub>sigma</sub> =0.054 4)
Data/restraints/parameters	4 603/0/247
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.028
Final <i>R</i> indexes [ <i>I</i> ≥ 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> =0.038 8, <i>wR</i> <sub>2</sub> =0.082 9
Final <i>R</i> indexes (all data)	<i>R</i> <sub>1</sub> =0.064 9, <i>wR</i> <sub>2</sub> =0.091 9
Largest diff. peak and hole / (e·nm <sup>-3</sup> )	690 and -760



reported<sup>[39]</sup>.

### 3 Conclusions

A new series and air stable ferrocenylimine compounds were synthesized. The molecular structure of one of the compounds was reported. The ferrocenylimine (**5~12**) compounds were synthesized from starting materials that are readily available, especially the ferrocenylaniline (**1~4**) in which their synthesis was also reported herein.

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