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Synthesis of ferrocenyl monospirooxindolopyrrolidines—a facile [3+2]-cycloaddition of azomethine ylides

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ABSTRACT

One-pot synthesis of novel ferrocenylmonospirooxindolopyrrolidines has been accomplished in good yield via a facile [3+2]-cycloaddition reaction of several azomethine ylides, derived from isatin/5,7-dibromoisatin and sarcosine, with various ferrocene derivatives as the dipolarophile. The effect of solvent on the [3+2]-dipolar cycloaddition reaction is also studied.

Ferrocene, an organometallic compound, was discovered in the early 1950s[1] and since then, there has been enormous growth in ferrocene chemistry.[2] Ferrocene is employed as a component for redox-active chemical sensors for voltammetric detection of cations[3] as well as anions,[4] metal-containing signaling probes for the detection of estrogen receptors,[5] dinucleotides[6] and DNA hybridization events[7] thus opening the way to DNA and gene sensors.[8] Ferrocene materials are used as asymmetric catalysts,[9] liquid crystals,[10] conductive,[11] magnetic[12] and optical devices[13] and as electron transfer devices.[14] Ferrocene derivatives offer advantages over other organometallics due to their synthetic versatility and thermal and photochemical stability. Ferrocene-substituted organic molecules hold great potential due to their biological activity. Ferrocene derivatives have been used for the treatment of malaria and cancer.[15–18] Many ferrocene-based heterocycles are known to exhibit anti-bacterial and anti-fungal properties.[19–21] Hence, there has been renewed interest in the synthesis of ferrocene-based heterocycles.

The intermolecular [3+2]-cycloaddition reaction of azomethine ylides with olefinic and acetylenic dipolarophiles has resulted in a number of novel heterocyclic scaffolds, which are particularly useful for the creation of diverse chemical libraries of drug-like molecules for biological screening.[22,23] Functionalized pyrrolidines and oxindoles are the central skeleton for numerous alkaloids and constitute classes of compounds with significant biological activity.[24,25] Spirooxindoles are an important class of naturally occurring substances characterized by highly pronounced biological properties.[26] Recently, we reported on the bioactivity of several spiropyrrolidines.[27]

As part of ongoing program on the synthesis of complex novel spiropyrrolidines,[28,29] herein we report an expeditious and facile protocol for the synthesis of novel ferrocene-based monospirooxindolopyrrolidines. The reaction of various ferrocene derivatives[30] **1a–c**, **8a–b**, **13**, **16**, **19a–b** and **22** with various azomethine ylides generated from isatin **2a**/5,7-dibromoisatin **2b** and sarcosine **3** afforded a series of novel monospirooxindolopyrrolidines[31] **4a–c**, **5a–c**, **9a–b**, **10a–b**, **14a–b**, **17**, **20a–b** and **23**. The structures of the ferrocenyl monospiroheterocycles were confirmed through spectral and elemental analysis.[32] No traces of the other possible regioisomers **6a–c**, **7a–c**, **11a–b**, **12a–b**, **15a–b**, **21a–b** and **24** were formed. The reactions were carried out under two different sets of conditions, and the results are shown in Table 1.

Scheme 1 depicts the mechanism for the generation of azomethine ylide from isatin **2a** and sarcosine **3**. Schemes 2–6 show the one-pot, three component reactions involving isatin/5,7-dibromoisatin, sarcosine and various ferrocene derivatives for the synthesis of novel ferrocenyl monospirooxindolopyrrolidines. The reactions were found to be highly regioselective and proceed via *endo*-transition state. Control of the relative stereochemistry at the spiro centre is observed. Presumably, an *anti*-ylide is involved in the transition state, which adds to double bond of the ferrocene-derived dipoarophiles, to give the observed cycloadducts. Formation of *syn*-ylide is not observed due to the unfavourable steric repulsion between the carbonyl groups of oxindole and the dipolarophile.

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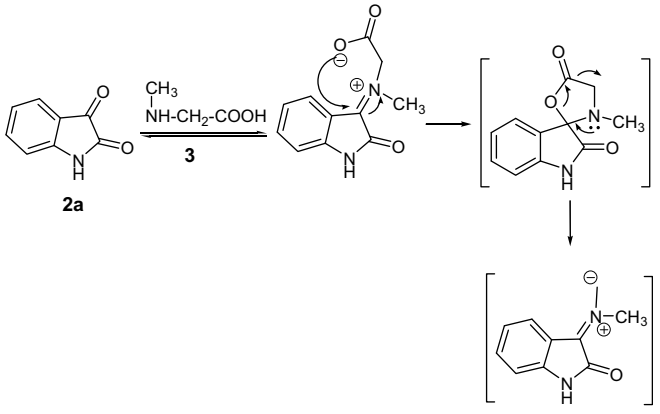
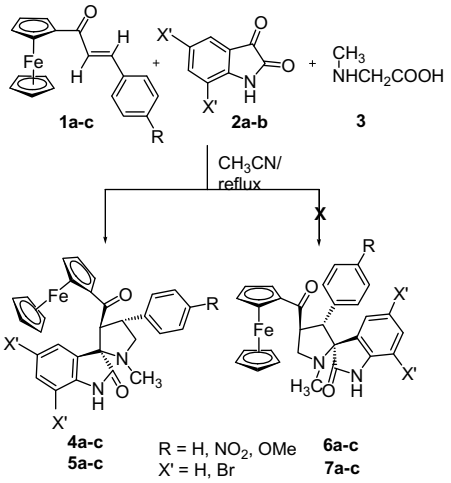
Table 1
[3+2]-cycloaddition reaction of ferrocene-derived dipolarophiles **1a–c/8a–b/13/16/19a–b/22** with isatin **2a**/5,7-dibromoisatin **2b** and sarcosine (**3**)

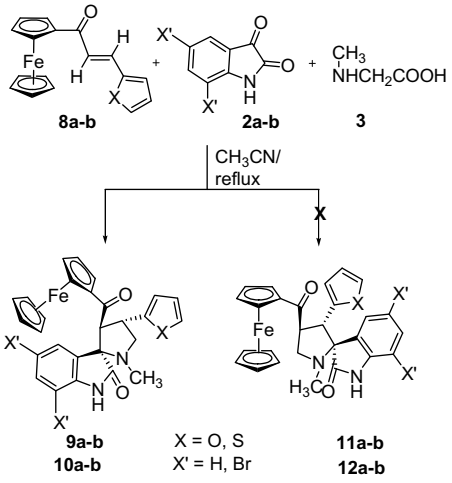
Product	R	X	X′	Toluene/reflux		Acetonitrile/reflux		Melting point
				T (h)	*Y* (%)	*T* (h)	*Y* (%)	(°C)
4a	H	—	H	12	58	5.0	72	158–159
4b	NO_2	—	H	10	60	3.0	83	170–172
4c	OMe	—	H	—	—	6.0	62	133–135
5a	H		Br	—	—	4.8	68	122–124
5b	NO_2	—	Br	—	—	3.4	75	134–136
5c	OMe	—	Br	—	—	4.3	70	154–155
9a	—	0	H	10	62	3.5	78	167–169
9b	—	**s**	H	—	—	4.5	65	124–126
10a	—	0	Br	—	—	3.3	72	134–136
10b	—	**s**	Br	—	—	4.0	70	112–114
14a	—	—	H	—	—	3.0	80	172–174
14b	—	—	Br	7	55	3.3	74	130–132
17	—	—	H	—	—	4.0	70	155–157
20a	H	—	H	—	—	4.8	68	141–143
20b	OMe	—	H	—	—	6.0	60	160–162
23	—	—	H	10	48	5.0	72	230–231



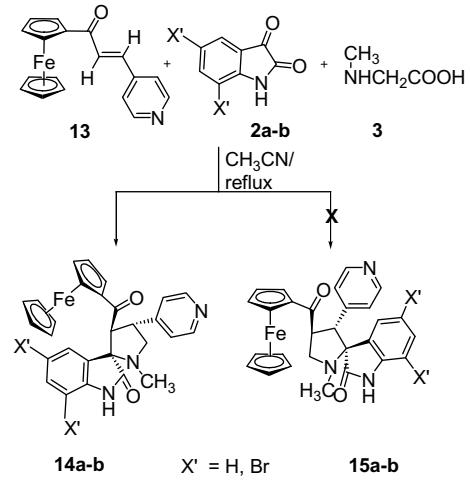
Scheme 1.



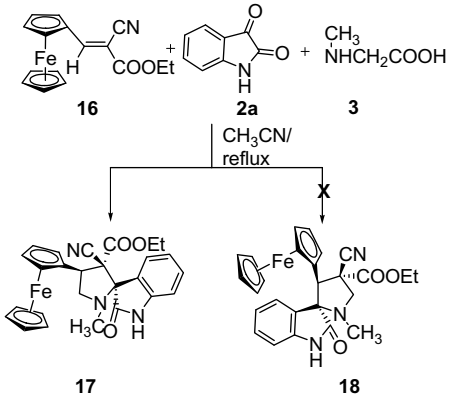
Scheme 2.



Scheme 3.

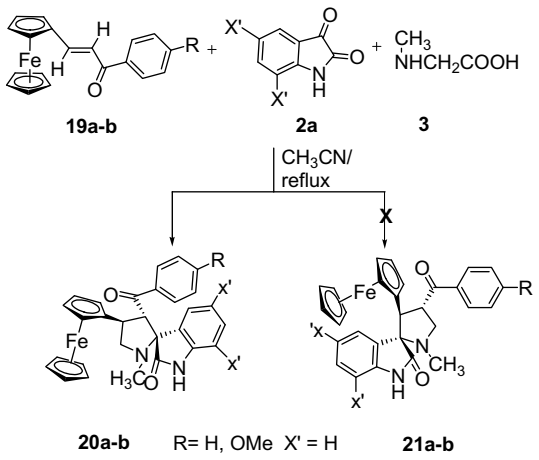


Scheme 4.



Scheme 5.

The formations of the cycloadducts were confirmed through spectral and elemental analysis. Thus, the IR spectrum of the monospirooxindolopyrrolidine **4a** showed peaks at 1668 and 1706 cm^{-1} due to the ferrocenyl and oxindole carbonyl groups. The ^1H NMR spectrum of **4a** exhibited a singlet at δ 2.22 due to the $-NCH_3$ protons of the pyrrolidine moiety. The benzylic proton and $-NCH_2$ protons of the pyrrolidine ring occurred as multiplets in the region δ 3.42–3.43 and δ 4.50–4.53. The pyrrolidine proton adjacent to the ferrocenyl moiety appeared as a doublet at δ 4.04 (J = 9.3 Hz). The protons of the ferrocene moiety occurred as singlets at δ 3.63, δ 3.94, δ 4.13, δ 4.20 and δ 4.27. The aromatic protons



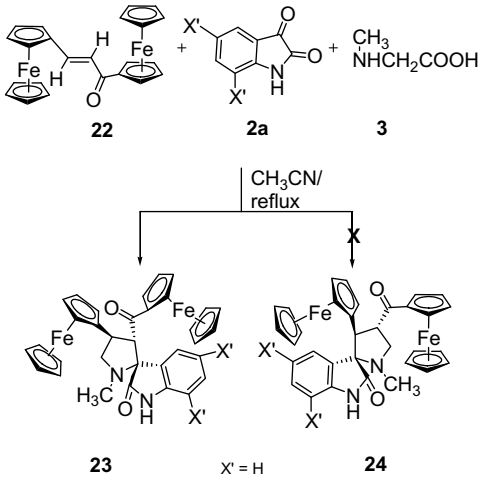
Scheme 6.

resonated as multiplets in the region δ 6.66–8.00. The –NH proton of the oxindole moiety appeared as a singlet at δ 8.38. The off-resonance proton decoupled ^{13}C spectrum of **4a** exhibited peaks at δ 34.86 and δ 47.74 due to the pyrrolidine $-NCH_3$ and $-NCH_2$ carbons. The spiro carbon resonated at δ 79.19. The oxindole and the ferrocenyl carbonyl carbons resonated at δ 180.13 and δ 199.62, respectively. The structure of the product **4a** was further confirmed through mass spectroscopy, which showed a molecular ion peak at 490.5 (M^+) (Scheme 2). Similar results were obtained with ferrocene derivatives **1b–c** affording the cycloadducts **4b–c** and **5a–c**.

Schemes 3 and 4 depict the formation of cycloadducts **9a–b**/**10a–b**/**14a–b**, where the ferrocene dipolarophiles **8a–b** and **13** were trapped with the azomethine ylides generated from **2a–b** and **3**. The formation of the cycloadducts was confirmed by spectroscopic techniques.

The dipolarophile **16** derived from ferrocene-1-carboxaldehyde and cyanoethyl acetate underwent a smooth reaction with the azomethine ylide generated from isatin **2a** and sarcosine **3** affording the cycloadduct **17** in good yield. The formation of the cycloadduct **17** was confirmed from the spectroscopic data. No trace of the other possible regioisomer **18** was observed. The pyrrolidine ring proton adjacent to the ferrocene moiety appeared as a triplet at δ 4.45 (J = 8.7 Hz), which clearly proved the regiochemistry of the cycloaddition reaction. If the other regioisomer **18** had been formed, the pyrrolidine ring proton adjacent to the ferrocene moiety would have appeared as a singlet in the ^{1}H NMR spectrum. The $-CH_3$protons of the ester moiety and the $-NCH_3$ protons of the pyrrolidine ring occurred as a triplet and a singlet at δ 0.74 and δ 2.15, whereas the –NH proton of the oxindole moiety appeared as a singlet at δ 9.00. The off-resonance proton decoupled ^{13}C spectrum of **17** exhibited peaks at δ 14.60 and δ 36.82 due to the methyl carbon of the ester group and the $-NCH_3$ carbon of the pyrrolidine ring. The spiro carbon resonated at δ 84.08. The cyano carbon resonated at δ 131.88, whereas the ester and oxindole carbonyl carbons resonated at δ 166.29 and δ 176.44, respectively. The structure of the product **17**was further confirmed through mass spectroscopy, which showed a molecular ion peak at 483 (M^+) (Scheme 5). Similarly, the reaction of the dipolarophiles **19a–b** with the azomethine ylide generated from **2a** and **3** afforded the ferrocenyl oxindolopyrrolidines **20a–b** in good yields (Scheme 6). The formation of the cycloadduct was confirmed by spectral and elemental analysis. Finally, the regiochemical outcome of the cycloaddition reaction was unambiguously determined by single crystal X-ray analysis of **20b** (Fig. 1).[33]

It was interesting to note that the cycloadduct **23** has two ferrocene moieties on the pyrrolidine ring and was synthesized easily by trapping the azomethine ylide generated from isatin **2a** and sarcosine **3** with the unusual dipolarophile **22** (Scheme 7). Thus, the IR



Scheme 7.

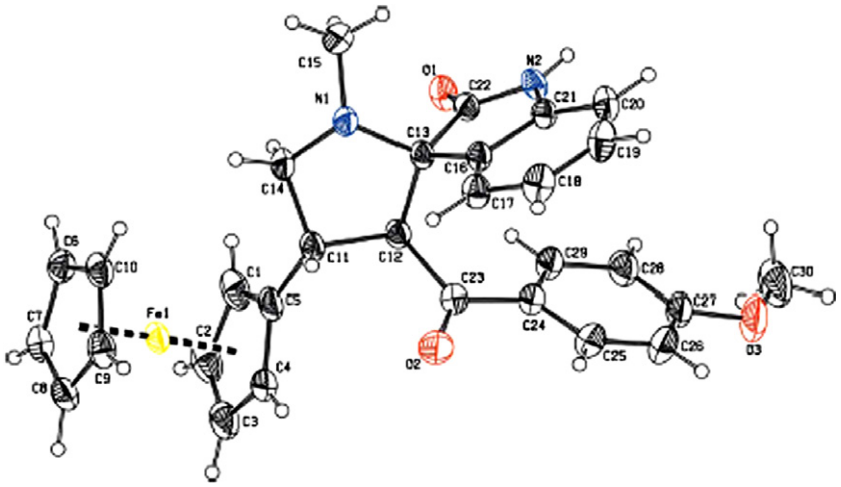


Figure 1. ORTEP diagram of **20b**.

spectrum of the monospirooxindolopyrrolidine **23** showed peaks at 1668 and 1706 cm^{-1} due to the ferrocenyl and oxindole carbonyl groups. The ^1H NMR spectrum of **23** exhibited a singlet at δ 2.22 due to the $-NCH_3$ protons of the pyrrolidine moiety. The pyrrolidine ring protons occurred as multiplets at δ 3.47–3.54, δ 3.66–3.69, δ 3.72–3.74 and δ 4.17–4.26. The protons of the ferrocene moiety appeared as singlets at δ 3.82, δ 4.09, δ 4.16, δ 4.22, δ 4.44 and δ 4.53. The –NH proton of the oxindole moiety occurred as a singlet at δ 8.54. The structure of the product **23** was further confirmed through mass spectroscopy, which showed a molecular ion peak at 598 (M^+) (Scheme 6). The cycloadduct **23** gave satisfactory elemental analysis. From the Table 1, it is evident that the rate of the reactions and the yields of the products were good in acetonitrile (60–83%).

In conclusion, we have synthesized a series of hitherto unknown ferrocene-based monospirooxindolopyrrolidine heterocycles through the [3+2]-cycloaddition of azomethine ylides with unusual ferrocene dipolarophiles.

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31. *Representative procedure for the synthesis of spiropyrrolidines derivatives* **4a**: *Method A:* A solution of the ferrocene-derived dipolarophile **1a** (1 mmol), isatin **2a**/5,7-dibromoisatin **2b** (1 mmol) and sarcosine **3** (1 mmol) was refluxed in toluene (10 mL). After the completion of the reaction as evidenced by TLC, the solvent was removed under reduced pressure, and the crude product was subjected to column chromatography using petroleum ether: ethyl acetate (4:1) as eluent. The product **4a** was then recrystallized from methanol. *Method B*: A solution of the ferrocene-derived dipolarophile **1a** (1 mmol), isatin **2a**/5,7-dibromoisatin **2b** (1 mmol) and sarcosine **3** (1 mmol) was refluxed in acetonitrile (10 mL) until completion of the reaction as evidenced by TLC. The solvent was removed under reduced pressure, and the crude product was subjected to column chromatography using petroleum ether/ethyl acetate (4:1) as eluent. The product **4a** was then recrystallized from methanol.
32. *Physical properties and spectroscopic data 1-N-methyl-spiro-[2.3′]-oxindole-3-ferrocenoyl-4-phenyl-pyrrolidine* **4a**: Orange solid; IR (KBr): 1668, 1706 cm^{-1}; ^1H NMR ($CDCl_3$/400 MHz): δ 2.22 (s, 3H), 3.42–3.43 (m, 1H), 3.63 (s, 5H), 3.94 (s, 1H), 4.04 (d, J = 9.3 Hz, 1H), 4.13 (s, 1H), 4.20 (s, 1H), 4.27 (s, 1H), 4.50–4.53 (m, 2H), 6.66–8.00 (m, 9H), 8.38 (s, 1H); ^{13}C NMR ($CDCl_3$/100 MHz): δ 34.86, 47.74, 60.55, 64.41, 68.40, 68.59, 69.26, 72.10, 72.55, 73.54, 79.19, 109.30, 123.03, 123.88, 125.74, 127.11, 127.26, 128.75, 129.02, 138.59, 141.89, 180.13, 199.62 ppm; EIMS m/z: 490.5 (M^+); CHN Anal. Calcd for $C_{29}H_{26}N_2O_2Fe$: C, 71.03; H, 5.34; N, 5.71. Found: C, 71.24; H, 5.49; N, 5.53.
1-N-Methyl-spiro-[2.3′]-5′,7′-dibromooxindole-3-ferrocenoyl-4-furyl-pyrrolidine **10a**: Orange solid; IR (KBr): 1668, 1708 cm^{-1}; ^1H NMR ($CDCl_3$/300 MHz): δ 2.20 (s, 3H), 3.36 (t, 1H), 3.65 (t, 1H), 3.89 (s, 5H), 4.16 (d, J = 9.3 Hz, 1H), 4.27 (s, 2H), 4.39 (s, 1H), 4.58–4.64 (m, 1H), 4.66 (s, 1H), 5.30 (s, 1H), 6.33 (s, 1H), 7.16 (s,1H), 7.34 (s, 1H), 7.41 (s, 1H), 8.01 (br s, 1H); EIMS m/z: 638 (M^+); CHN Anal. Calcd for $C_{27}H_{22}N_2O_3Br_2Fe$: C, 50.81; H, 3.47; N, 4.38. Found: C, 51.01; H, 3.61; N, 4.21.
1-N-Methyl-spiro-[2.3′]-oxindole-3-ferrocenoyl-4-pyridyl-pyrrolidine **14a**: Pale orange solid; IR (KBr): 1670, 1706 cm^{-1}; ^1H NMR ($CDCl_3$/300 MHz): δ 2.20 (s, 3H), 3.40 (t, 1H), 3.60 (t, 1H), 3.72 (s, 5H), 3.99 (d, J = 9.3 Hz, 1H), 4.16 (s, 1H), 4.22 (s, 1H), 4.34 (s, 1H), 4.42–4.45 (m, 1H), 4.60 (s, 1H), 6.58–8.40 (m, 8H), 8.44 (s, 1H); ^{13}C NMR ($CDCl_3$/75 MHz): δ 34.77, 43.83, 59.89, 63.76, 68.62, 69.30, 72.26, 72.77, 73.64, 78.73, 109.42, 122.98, 124.03, 126.95, 129.23, 140.85, 140.93, 180.42, 199.90 ppm; EIMS m/z: 491 (M^+); CHN Anal. Calcd for $C_{28}H_{25}N_3O_2Fe$: C, 68.30; H, 5.12; N, 8.53. Found: C, 68.45; H, 5.29; N, 8.34.
1-N-Methyl-spiro-[2.3′]-oxindole-3-cyanoethoxycarbonyl-4-ferrocenyl-pyrrolidine **17**: Yellow solid; IR (KBr): 1708, 1725 cm^{-1}; ^1H NMR ($CDCl_3$/400 MHz): δ 0.74 (t, 3H), 2.15 (s, 3H), 3.46 (t, J = 9.2 Hz, 1H), 3.71–3.76 (q, J = 7.1, 2H), 3.82 (t, 1H), 4.13 (s, 6H), 4.18 (s, 2H), 4.45 (t, J = 8.7 Hz, 1H), 4.53 (s, 1H), 6.88–7.24 (m, 4H), 9.00 (s, 1H); ^{13}C NMR ($CDCl_3$/100 MHz): δ14.60, 36.82, 45.86, 58.61, 63.40, 64.47, 69.30, 70.05, 71.04, 84.08, 112.15, 116.49, 123.90, 125.26, 127.28, 131.88, 142.91, 166.29, 176.44 ppm; EIMS m/z: 483 (M^+); CHN Anal. Calcd for $C_{26}H_{25}N_3O_3Fe$: C, 64.61; H, 5.21; N, 8.69. Found: C, 64.83; H, 5.38; N, 8.50.
1-N-methyl-spiro-[2.3′]-oxindole-3-(p-methoxybenzoyl)-4-ferrocenyl-pyrrolidine **20b**: Red crystalline solid; IR (KBr): 1665, 1704 cm^{-1}; ^1H NMR ($CDCl_3$/400 MHz): δ 2.19 (s, 3H), 3.47 (t, 1H), 3.57 (t, J = 8.9 Hz, 1H), 3.66 (s, 3H), 4.06 (s, 2H), 4.10 (s, 1H), 4.15 (s. 1H), 4.17 (s, 5H), 4.24–4.26 (m, 1H), 4.44 (d, J = 9.3 Hz, 1H), 6.54–7.52 (m, 8H), 8.72 (s, 1H); ^{13}C NMR ($CDCl_3$/100 MHz): δ 35.12, 38.75, 55.28, 59.57, 61.50, 66.48, 67.41, 67.47, 67.73, 68.51, 74.24, 89.45, 109.38, 113.42, 122.80, 127.04, 127.16, 128.94, 130.04, 130.38, 140.47, 163.23, 180.38, 196.03 ppm; EIMS m/z: 520 (M^+); CHN Anal. Calcd for $C_{30}H_{28}N_2O_3Fe$: C, 69.24; H, 5.42; N, 5.38. Found: C, 69.09; H, 5.59; N, 5.58.
1-N-Methyl-spiro-[2.3′]-oxindole-3-ferrocenoyl-4-ferrocenyl-pyrrolidine **23**: Orange solid; IR (KBr): 1668, 1706 cm^{-1}; ^1H NMR ($CDCl_3$/300 MHz): δ 2.22 (s, 3H), 3.47–3.54 (m, 1H), 3.66–3.69 (m, 1H), 3.72–3.74 (m, 1H), 3.82 (s, 4H), 4.09 (s, 1H), 4.16 (s, 3H), 4.17–4.26 (m, 1H), 4.22 (s, 8H), 4.44 (s, 1H), 4.53 (s, 1H), 6.59–7.63 (m, 4H), 8.54 (br s, 1H); EIMS m/z: 598 (M^+); CHN Anal. Calcd for $C_{33}H_{30}N_2O_2Fe_2$: C, 66.24; H, 5.05; N, 4.68. Found: C, 66.41; H, 5.22; N, 4.49.
33. Satis Kumar, B. K.; Gayathri, D.; Velmurugan, D.; Ravikumar, K.; Suresh Babu, A. R. *Acta Crystallogr.* **2007**, *E63*, m1287.