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Design and synthesis of new functional compounds related to ferrocene bearing heterocyclic moieties A new approach towards electron donor organic materials

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Abstract

The synthesis of heterocyclic systems incorporating more than one ferrocene unit was shown to be a facile and convenient route for the synthesis of new ferrocene-heterocycles. Hydrazide **2** was prepared and cyclized to oxadiazole, triazole, and pyrazole using the procedures described in this context with good yields. A pyrazolone derivative could not be obtained and instead a hydrazone derivative **17** was isolated. Hydrazide **2** was condensed with aromatic aldehydes and ferrocene-1,1′-dicarbaldehyde derivatives to give the corresponding hydrazones **11a–c** and dihydrazones **12**, **14** and **18** in high yields. Cyclic voltammetry (CV) of the selected ferrocene-heterocycles **8** and **9** was studied comparing with the parent ferrocene and acetylferrocene. The CV of the compound **8** revealed an additional, quasireversible, one-electron oxidation wave at 849 mV, corresponding to the second ferrocene unit connected to the oxadiazole ring through the SCH_2CO spacer.

Keywords: Ferrocene-heterocycles; Hydrazide; Cyclic voltammetry

1. Introduction

Ferrocene has attracted the interest of many scientists and research groups worldwide because its applications in materials science [1] and asymmetric synthesis [2]. Ferrocene chemistry was revived during the last years because ferrocenyl derivatives have found numerous uses in various fields of science from biology to materials chemistry [1e]. Due to the inherent importance of ferrocene as a starting material in synthetic organometalic systems and industrial applications, ferrocene and its derivatives have become a great area of interest for many researchers and industrial chemists. It was reported that ferrocenyl alkenes and dienes are important substrates for co- and homopolymer synthesis, which are used as coating materials for aerospace to increase resistance toward photodegradiation [3]. Ferrocene-1,3-butadiene was used as fuel in solid propellants [3]. Polymers containing directly linked ferrocene centers have been prepared and many studies on linked ferrocene dimmers and oligomers have also been reviewed [4]. Several compounds bearing ferrocenyl moieties have been synthesized and used for chemotherapy of drug-resistant cancer and tropical diseases [5]. Recently, ferrocenyl-2-thiazolamine [6] and ferrocenyl-2-oxazolines [7] have been reported by several groups. It has been found that *N*-ferrocenylmethyl benzimidazolium iodide exhibited an excellent in vitro activity against the *P. falciparum* malarial parasite strain NF54 [8]. Spectrochemical and electrochemical behaviors of ferrocene-heteroaromatic analogues were also observed [9]. It is also known that ferrocene behaves in many aspects like an aromatic electron-rich phenol compound, and this has led to its use as precursors for synthesis of several crown-ethers, azacrown-ethers and thiacrown-ethers as well [10]. It has been reported that a wide variety of macrocycles, cryptands, and cavitands containing the ferrocene unit have been synthesized and

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characterized [1e] as well as some ferrocenes have been incorporated into a number of anion sensors [11].

Due to the structural and electrochemical properties of ferrocene-containing tetrathiafulvalene (TTF) derivatives, several ferrocene–TTFs were constructed as donors for conducting CT complexes. The first compound belongs to this class of heterocyclic donor conducting materials [12] and very similar type of donor heterocycles has been reported also in the literature [13]. Several CT complexes of metal bis(arene) compounds containing the familiar organic acceptor tetracyano-*p*-quinodimethane (TCNQ) have also been reported. Recently, 1,1′-disubstituted ferrocenes were synthesized as novel donors for the preparation of CT complexes, which are structurally and electronically related to the TTFs heterocycles conjugated with ferrocene moiety [14]. These findings prompted us to synthesize a number of new heterocyclic systems incorporating ferrocene moieties separated by aryl rings as conjugated spacers and to study the electrochemical redox behavior of these new types of heterocyclic donors comparing with the parent ferrocene and acetylferrocene.

2. Results and discussion

The first facile incorporation of heterocyclic ring system into ferrocene with a phenyl ring as a spacer was achieved by the use of *p*-(ferrocenyl)benzoyl hydrazide (**2**). The synthesis of ferrocene compounds bearing heterocyclic rings and the study of the biological and electrochemical behavior of these new ferrocenyl heterocycles seem to be of interest since marked biological activity appeared recently for the ferrocene derivatives. The ethyl-*p*-(ferrocenyl)benzoate (**1**) was prepared by direct coupling of the diazonium salt of the methyl *p*-aminobenzoate in the presence of acetic acid [15]. Refluxing of compound **1** with hydrazine hydrate in ethanol for 24 h afforded the expected hydrazide derivative **2** as orange crystals in 94% yield. The oxadiazole derivative **4** was obtained as follows. By refluxing **2** with CS_2 in methanol containing a slightly excess of KOH to give the intermediate xanthate derivative **3** was obtained, which on acidification with concentrated hydrochloric acid gave the oxadiazole **4** as yellow crystals in 92.5% over all yield (Scheme 1). The structure of hydrazide **2** and oxadiazole **4** was determined both chemically and using spectral analyses including IR, ^{1}H-, ^{13}C-NMR, FABMS spectra and elemental analysis. The analyses of **2** and **4** were found in satisfactory agreement with the suggested structures.

The reaction of oxadiazole **4** with hydrazine hydrate in refluxing ethanol afforded the *N*-aminotriazole **6** in 39.5% yield. On the other hand, the fusion of the oxadiazole **4** with ammonium acetate at 150 °C afforded the corresponding 1,2,4-*s*-triazole derivative **5** in 70% yield. An attempt to synthesize the thiazolo[3,2-*b*]triazole (**7**) using the acidified acetic acid method [16] was unsuccessful and an unknown black material was obtained. This might be attributed to the oxidation of ferrocene unit in the presence of concentrated sulfuric acid at high temperatures leading to the iron oxide formation as black material (Scheme 2).

The reaction of oxadiazole **4** with α-chloroacetylferrocene in the presence of sodium acetate afforded the oxadiazolyl-5-thiomethylcarbonyl ferrocene derivative **8** as dark red crystals in 73.5% yield. The α-chloroacetylferrocene was obtained via Friedel–Crafts acylation reaction in CH_2Cl_2 at 0 °C in moderate yield. Introduction of two-ferrocene units into oxadiazole molecule seems to be of interest for electrochemical studies, particularly when these two-ferrocene moieties are not symmetrical (Chart 1).

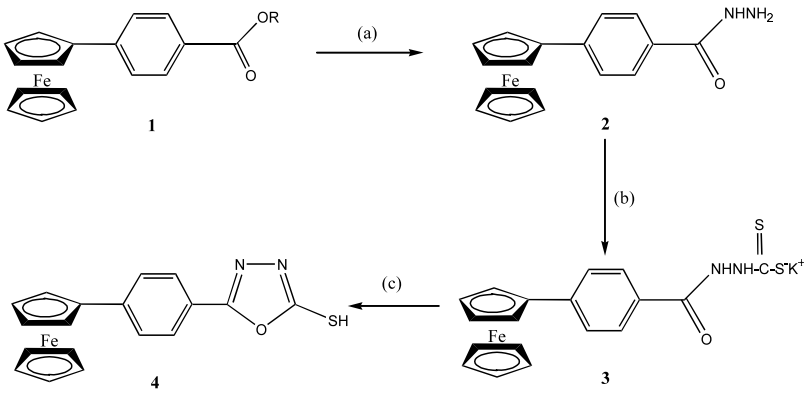
Condensation of the hydrazide derivative **2** with acetylacetone in refluxing ethanol containing a catalytic amount of acetic acid afforded the corresponding pyrazol derivative **9** in 69.5% yield. Condensation of the hydrazide **2** with *p*-(ferrocenyl)benzaldehyde or aromatic aldehydes such as benzaldehyde or *p*-anisaldehyde using the same reaction conditions afforded the hydrazones **11a–c** in excellent yields. Reaction of **2** with acetylferrocene in ethanol containing acetic acid (20:1) afforded the corresponding hydrazone **10a** in 4.5% yield.

Interestingly, when hydrazide **2** was condensed with acetylferrocene in acetic acid under severe conditions (reflux for 36 h) the reaction underwent chemoselectively and the *N*-acetyl derivative **10b** was isolated after chromatography in 86% yield as red crystals rather than the formation of **10a** (Scheme 3).

On the other hand, ferrocene-1,1′-dihydrazone derivative **12** was synthesized in very high yield (98%) by a direct condensation of the ferrocene-1,1′-dicarbaldehyde which was prepared directly from ferrocene by a previously described procedure [17] with hydrazide **2** in refluxing ethanol in the presence of acetic acid as a catalyst (Chart 2).

Following the method reported in literature, the 1-(*p*-formylphenyl)-1′-(4-formyl-1-naphthyl)ferrocene (**13**) was synthesized in good yield [18] and subjected to be a starting for synthesis of dihydrazone **14**. The reaction of hydrazide **2** with asymmetric ferrocene-1,1′-diaromatic aldehydes using the same method described above afforded the dihydrazone derivative **14** in 84.6% yield (Scheme 4).

Using the same method the 1-(*m*-formylphenyl)-1′-(3-formyl-5-methoxyphenyl)ferrocene (**15**) was synthesized according to Gomberg's arylation of ferrocene with diazonium salt of the methyl 3-amino-4-methoxybenzoate to afford the corresponding 1-(3-methoxycarbonyl-2-methoxyphenyl)ferrocene which subjected to diazotization with diazonium salt derived from methyl 3-aminobenzoate to give the corresponding diester **16**,



Scheme 1. (a) NH_2NH_2/EtOH, reflux, 24 h, 94%. (b) CS_2/KOH, EtOH, reflux, 5 h. (c) Aq HCl, 92.5%.

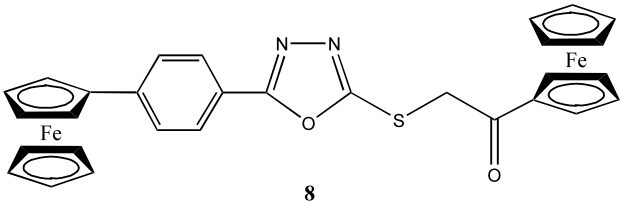


Chart 1.

followed by reduction with $LiAlH_4$ to **17** and oxidation with activated MnO_2 in dry $CHCl_3$. Using the same method described above condensation of hydrazide **2** with 1-(*m*-formylphenyl)-1′-(3-formyl-5-methoxyphenyl)ferrocene (**15**) in ethanol containing few drops of acetic acid afforded the dihydrazone derivative **18** as orange crystals in 92.8% yield (Scheme 5).

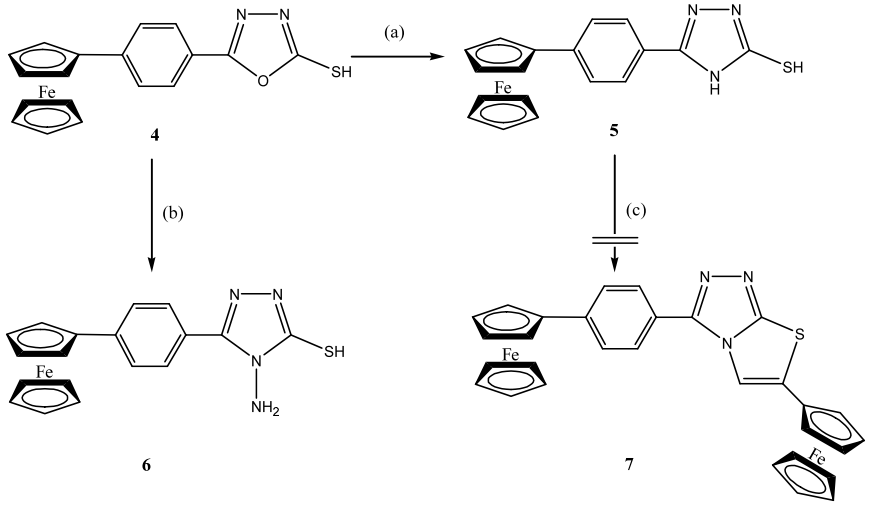
On reaction of **2** with ethyl acetoacetate under the same reaction conditions, the unpredictable hydrazone derivative **20** was isolated in 51.4% yield instead of the expected pyrazolone derivative **19** (Chart 3).

Formation of the hydrazone **20**, rather than the expected pyrazolone **19**, can be explained by the formation of the ester derivative **21** followed by hydrolysis to the corresponding acid **22** and elimination of CO_2 as shown in Scheme 6.

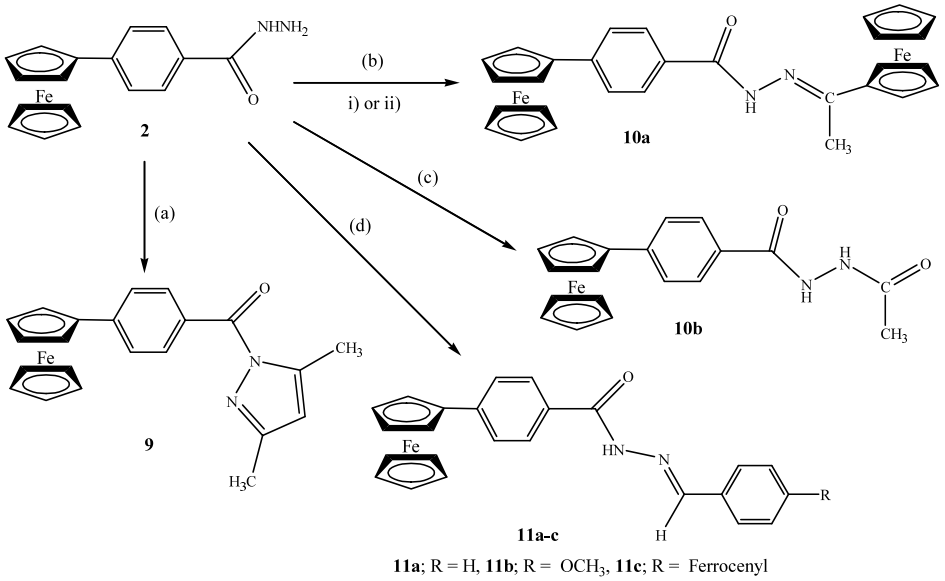
All new compounds were confirmed successfully by spectral analyses including IR, ^{1}H-, ^{13}C-NMR, FABMS spectroscopy and elemental analyses. The analytical and spectroscopic data clearly support the proposed structures. Details of the analytical spectra are summarized in the Section 5.

3. Electrochemistry

The electrochemical behaviors of ferrocene, acetylferrocene, Fc-oxadiazole **8** and Fc-pyrazole **9** were investigated by cyclic voltammetry (CV) (Fig. 1), which is sensitive electrochemical method and permit the collection of excellent data at low concentration of electroactive substance [19]. The electrochemical results of the investigated compounds were compared to that of ferrocene and acetylferrocene. Summaries of cyclic voltammetric results are given in Table 1. The cyclic



Scheme 2. (a) CH_3COONH_4, EtOH, reflux, 8 h. (b) NH_2NH_2, EtOH, reflux, 5 h. (c) Aceteylferrocene, H_2SO_4/AcOH, reflux, 5 h.



Scheme 3. (a) Acetylacetone, EtOH/AcOH, reflux, 5 h, 69.5%. (b) (i) Acetylferrocene, EtOH/AcOH, reflux, 8 h, 4.5%. (ii) neat, 19%. (c) Acetylferrocene, EtOH/AcOH, reflux, 36 h, 86%. (d) ArCHO, EtOH/AcOH, reflux, 5–7 h.

voltammetric behavior of these compounds showed one cathodic peak and the corresponding oxidation peak in the potential range of 450–900 mV at the Pt electrode. The separation of the anodic and the cathodic peak potentials, ΔE_p, were 95, 73, 119 and 130 mV at 20 mV s^{-1} for Fc, Fc-pyrazole **9**, Fc-$COCH_3$ and Fc-oxadiazole **8**, respectively. These values are larger than that expected for a reversible two-electron transfer reaction, which is given by $57/z$ mV, where z is the number of electrons transferred in the process [20], indicating that the irreversibility of the electron-transfer process was maintained under this condition. At higher scan rates, v ($v \geq 600$ mV s^{-1}) Fig. 2, broadening of ΔE_p was observed ($\Delta E_p > 150$ mV), possibly due to the onset of kinetic complications.

The formal potential, $E^{0\prime}$, taken as the average of E_{pc} and E_{pa}, were 518, 582, 584 and 788 mV for Fc, Fc-pyrazole **9**, Fc-oxadiazole **8** and Fc-$COCH_3$, respectively. $E^{0\prime}$ shifted to more positive potentials by ca. 200 mV for Fc-$COCH_3$ and E_{p2} of Fc-oxadiazole **8** in compared to Fc and Fc-pyrazole **9**, this revealed that the reduction of carbonyl compounds Fc-$COCH_3$ and **8** become more easily at the Pt electrode. The significant differences between the $E^{0\prime}$ values of Fc-$COCH_3$ and Fc-oxadiazole **8** and other compounds are highly interesting considering the structural difference between these compounds, namely a single surplus carbonyl group of compounds Fc-$COCH_3$ and Fc-oxadiazole **8** in compared with ferrocene and Fc-pyrazole **9**.

In all compounds like Fc, acetylferrocene, Fc-Oxadiazole **8** and Fc-Pyrazole **9**, where the ferrocene is connected to an oxadiazole or pyrazole ring system through a conjugated spacer, showed one reversible electron transfer oxidation within the range ca. 0.5–0.9 V in case of ferrocene, acetylferrocene and Fc-pyrazole **9** and two reversible electron transfer oxidations as Fc-oxadiazole **8**. These correspond to $Fc \rightarrow Fc^+$ ion and to the second ferrocene unit in compound **8**. As shown in Fig. 1, the first oxidation in compound **8** belongs to $Fc \rightarrow Fc^{+\bullet}$, whereas the second oxidation potential is related also to the second ferrocene unit ($Fc \rightarrow Fc^{+\bullet}$) connected to the oxadiazole ring through SCH_2CO spacer.

The low solubility of the hydrazones and triazoles in non-polar organic solvent (CH_2Cl_2, THF) and even in CH_3CN could not allow us to study the electrochemical properties of those compounds. The biological screenings of these compounds will be in consideration and will be investigate separately.

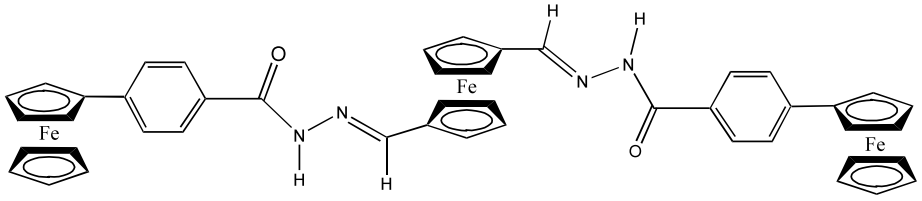


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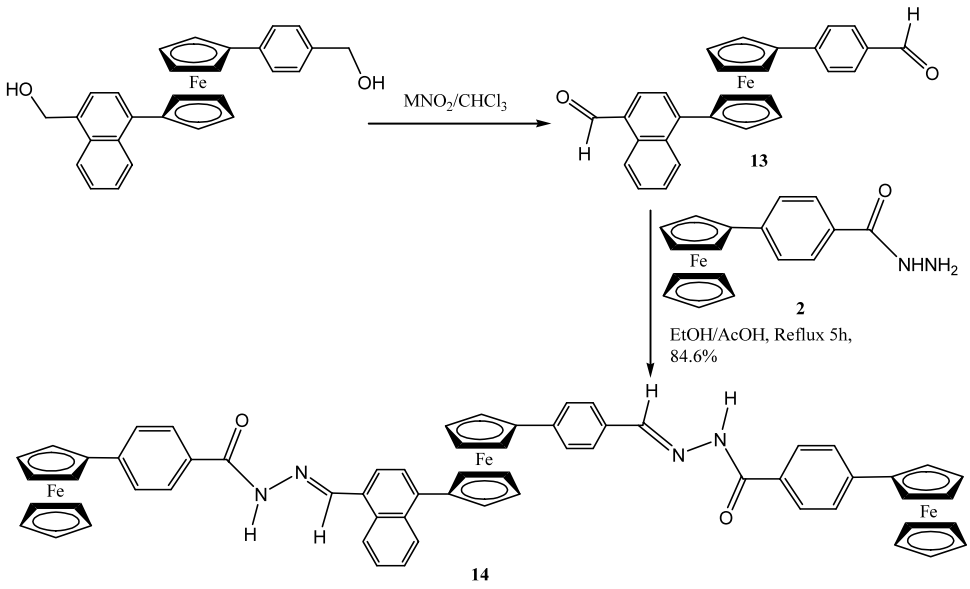
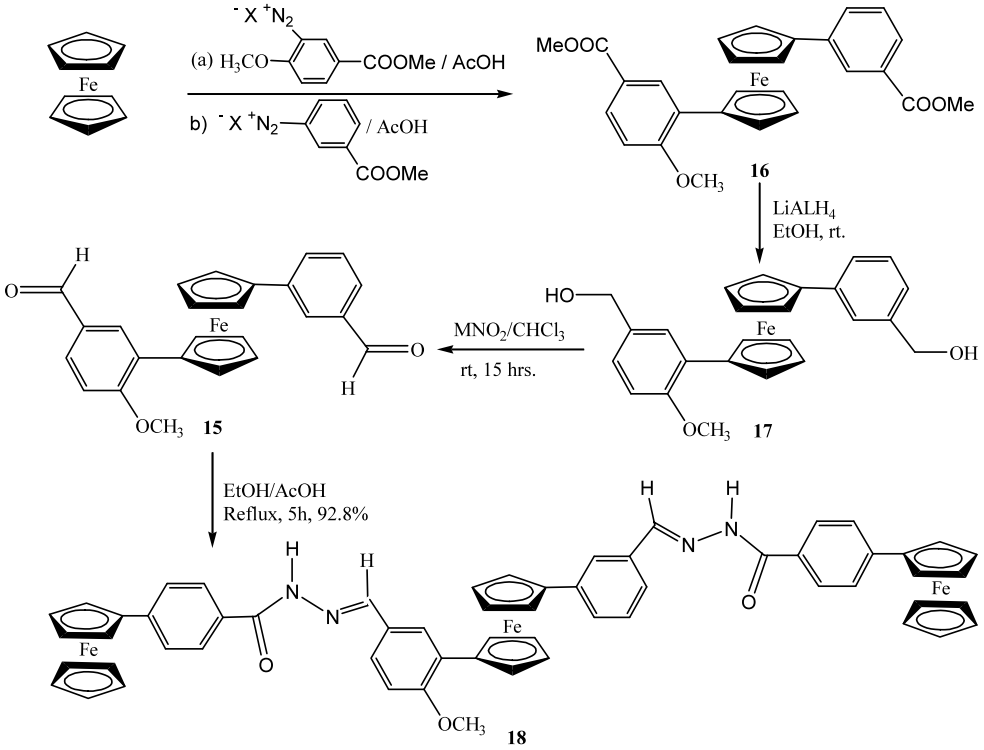
Chart 2.



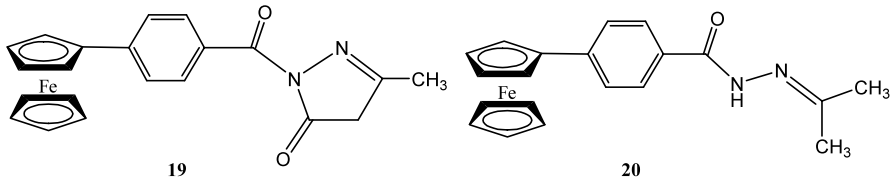
Scheme 4.

4. Conclusions

The title compounds were synthesized as new donors and their structures were confirmed successfully by spectral analyses. The electrochemical properties of Fc-oxadiazole **8** and Fc-pyrazole **9** were studied in comparison with the parent ferrocene and acetylferrocene by CV. A two-electron redox behavior was observed as two waves in **8**, while a one-electron redox behavior was observed as a one wave in **9**. The advantage of introducing ferrocene into these types of heterocycles is that ferrocene has only a single one-electron redox process. The cyclic voltammetric behavior of these compounds showed one cathodic peak and the corresponding oxidation peak in the potential rang of 450–900 mV at the Pt electrode. At higher scan rate, v ($v \geq 600$ mV s^{-1}), broadening of ΔE_p was observed ($\Delta E_p > 150$ mV), possibly due to the onset of kinetic



Scheme 5.



19 20

Chart 3.

complications. The significant differences between the $E^{0/}$ values of Fc-$COCH_3$ and **9** and other compounds are highly interesting considering the structural difference between these compounds, namely a single surplus carbonyl group of compounds Fc-$COCH_3$ and Fc-oxadiazole **8** in compared with compounds like Fc and Fc-pyrazole **9**.

5. Experimental

5.1. General

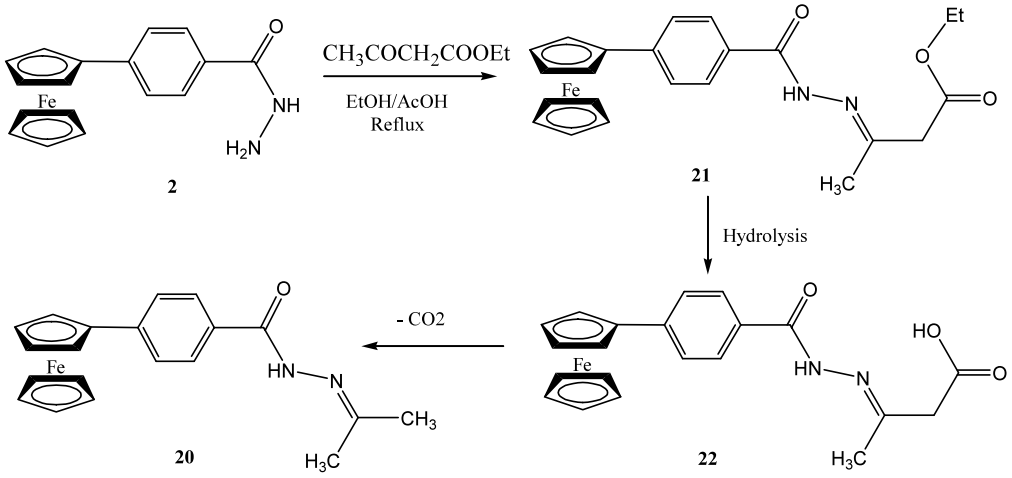
Melting points (m.p.) were recorded on a Gallencamp melting point apparatus and are uncorrected. Infrared spectra (IR) were measured on a Hitachi 260-10 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded at room temperature (r.t.) on Varian Spectrometer 500 MHz. Chemical shifts are denoted in δ units (ppm) relative to Me_4Si as internal standard; J values are given in Hz. $CDCl_3$ and Me_2SO-d_6 were used unless otherwise stated. Mass spectra were obtained using a JEOL JMS-AX505HA. CV was measured on a cyclic voltammeter (Model CS-1090/Model CS-1087). Column chromatography was performed on silica gel 60 (230–400 Mesh ASTM). Solvents were distilled before use. Acetylferrocene, and α-chloroacetylferrocene were prepared following the previously reported methods [21].

5.2. p-(Ferrecenyl)benzoic acid hydrazide (2)

A mixture of the ester **1** (10 g, 29.9 mmol) and hydrazine hydrate (30 ml) was refluxed in EtOH (100 ml) for 24 h. The reaction mixture was cooled and the crystals thus formed were collected by filtration and crystallized from EtOH to give dark yellow crystals of the corresponding hydrazide **2**: 9.0 g, yield 94%, m.p. 189–192 °C; IR (KBr) ν 3320s, 3305s, 3099m, 3095m, 1623s, 1621s, 1558s, 1506s, 1328s, 1282s, 1105s, 950s, 856s, 771s cm^{-1}. ^{1}H-NMR (Me_2SO-d_6, 500 MHz): δ = 9.73 (bs, 1H, NH), 7.78–7.76 (d, J = 8 Hz, 2H, aromatic-H), 7.55 (d, J = 8 Hz, 2H, aromatic-H), 4.85 (s, 2H, ferrocene-H), 4.49 (s, 2H, NH_2), 4.38 (s, 2H, ferrocene-H), 4.00 (s, 5H, ferrocene-H); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): δ = 165.82 (CO), 142.52 (aromatic-C), 127.16, 125.49 (aromatic-CH), 83.40 (ferrocene-C), 69.54, 66.64 (ferrocene-CH); FABMS m/z (%) [M^+, 320 (100)]. Anal. Calc. for $C_{17}H_{16}FeN_2O$: C, 63.77; H, 5.03; N, 8.74. Found: C, 63.69; H, 5.00; N, 8.56%.

5.3. 2-[(Ferrocenyl)-p-phenyl]oxadiazol-5-thiol (4)

A mixture of the hydrazide **2** (3.2 g, 10 mmol) and carbon disulfide (10 ml) was refluxed in MeOH (25 ml) in the presence of KOH (0.84 g, 15 mmol) for 5 h. The reaction mixture was cooled and the solvents removed under vacuum to give a dark yellow-red precipitate of the salt **3**, which was used without further purification.



2 21 20 22

Scheme 6.

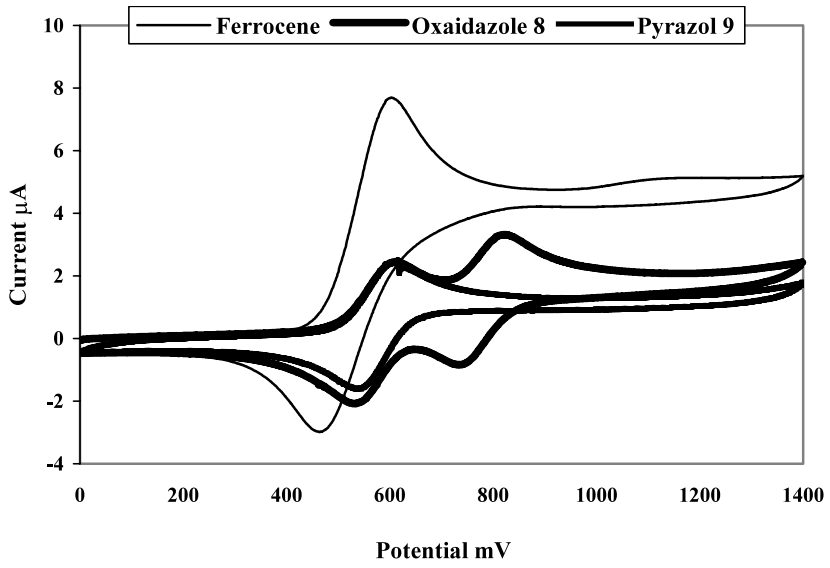


Fig. 1. Cyclic voltammetry (CV) of ferrocene, Fc-oxadiazole **8** and Fc-pyrazole **9** in CH_2Cl_2 at scan rate 20 mV s^{-1} using TBAP as the supporting electrolyte in 0.1 mol concentration on a Pt working electrode, a Pt gauze counter electrode and a Ag/AgCl reference electrode at ambient temperature.

Table 1
Cyclic voltammetric parameters of ferrocene, Fc-$COCH_3$, Fc-pyrazole **9** and Fc-oxadiazole **8**

Compound	E_{pc} (mV)	E_{pa} (mV)	$E^{0/}$ (mV)	ΔE_p (mV)
Ferrocene	481	554	518	73
Fc-$COCH_3$	847	728	788	119
Fc-pyrazole **9**	631	536	584	95
Fc-oxadiazole **8**	647	517	582	130 [a]

[a] $\Delta E_{p2} = E^{Ox\,2} - E^{Red\,2} = 849 - 712 = 137$ mV, $E^{0/} = 781$ mV.

The dark yellow-red product was dissolved in water and neutralized by HCl solution to give yellow red crystals of the oxadiazole **4**: yield 3.35 g, 92.5%, m.p. 216–218 °C; IR (KBr) *v* 3079s, 2946s, 2767s, 1612s, 1515s, 1504s, 1423s, 1348s, 1284s, 1178s, 1070s, 966s, 885s, 742s, 696s cm^{-1}; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta =$ 7.91 (s, 1H, NH), 7.78 (d, $J = 8$ Hz, 2H, aromatic-H), 7.71 (d, $J = 8$ Hz, 2H, aromatic-H), 4.89 (s, 2H, ferrocene-H), 4.44 (s, 2H, ferrocene-H), 4.03 (s, 5H, ferrocene-H); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): $\delta =$ 177.35 (C-5), 160.77 (C-2), 144.22, 126.43 (aromatic-C), 126.16, 119.45 (aromatic-CH), 82.67 (ferrocene-C), 69.91, 69.66, 66.84, 66.77 (ferrocene-CH); FABMS *m/z* (%) [M^+, 362 (100)]. Anal. Calc. for $C_{18}H_{14}FeN_2OS$: C, 59.68; H, 3.89; N, 7.73. Found: C, 59.51; H, 3.81; N, 7.68%.

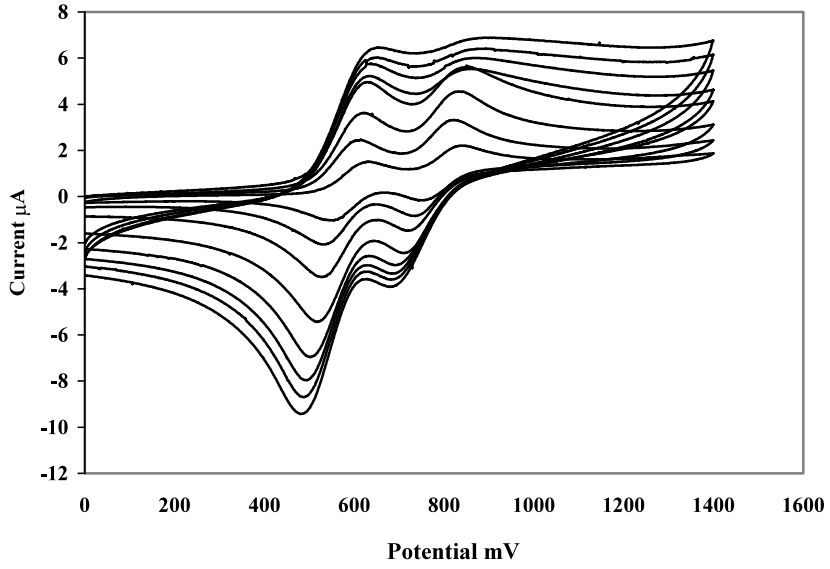


Fig. 2. Cyclic voltammetry (CV) of Fc-oxadiazole **8** in CH_2Cl_2 at scan rate 20–600 mV s^{-1}.

5.4. 2-[p-(Ferrocenyl)phenyl]-5-[(ferrocenyl)carbonylmethylthio]oxadiazole (**8**)

A mixture of oxadiazole **4** (0.362 g, 1.0 mmol) and α-chloroacetylferrocene (0.269 g, 1.02 mmol) was heated gently in EtOH containing excess amount of AcONa for 2 h. The EtOH was removed under reduced pressure and the solid residue was washed with water to remove the excess AcONa. The brown precipitate was filtered off and dried on air suction. The crude product was chromatographed on silica gel using $CHCl_3$ to give the corresponding oxadiazole-5-thioacetylferrocene derivative **8** as dark red crystals: yield 0.432 g, 73.5%, m.p. 181–183 °C; IR (KBr) *v* 3220w, 3091s, 2960s, 1656s, 1608s, 1583s, 1513s, 1477s, 1454s, 1378s, 1340s, 1301s, 1218s, 1182s, 1086s, 1031s, 1000s, 887s, 821s, 742s, 701s cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): $\delta = 7.92$ (dd, $J = 7$, $J = 2$ Hz, 2H, aromatic-H), 7.56 (dd, $J = 7$, $J = 2$ Hz, 2H, aromatic-H), 4.91 (t, $J = 2$ Hz, 2H, ferrocene-H), 4.71 (t, $J = 2$ Hz, 2H, ferrocene-H), 4.70 (s, 2H, SCH_2), 4.62 (t, $J = 2$ Hz, 2H, ferrocene-H), 4.39 (t, $J = 2$ Hz, 2H, ferrocene-H), 4.29 (s, 5H, ferrocene-H), 4.05 (s, 5H, ferrocene-H); ^{13}C-NMR ($CDCl_3$, 125 MHz): $\delta =$ 196.014 (C=O), 166.16 (C-5), 163.58 (C-2), 143.98, 126.80 (aromatic-C), 126.77, 126.30, 126.23, 120.59 (aromatic-CH), 83.25, 76.54 (ferrocene-C), 70.33, 70.30, 70.27, 69.85, 69.82, 69.69, 69.62, 66.75 (ferrocene-CH), 41.45 (SCH_2); MS *m/z* (%) [M^+, 588 (10)]. Anal. Calc. for $C_{30}H_{24}Fe_2N_2O_2S$: C, 61.23; H, 4.10; N, 4.76. Found: C, 60.94; H, 3.92; N, 4.61%.

5.5. 3-[p-(Ferrocenyl)phenyl]-1,2,4-s-triazol-5-thiol (**5**)

A mixture of **4** (1.0 g, 2.76 mmol) and ammonium acetate (5 g) is heated gently without solvent for 2 h. The reaction mixture was cooled and refluxed in dry EtOH for further 16 h. The resulting precipitate thus formed after cooling was dissolved in water to remove the excess ammonium acetate. The residue was collected by filtration and chromtographed on silica gel using hexane–acetone (1:2) to give in the last fraction a yellow crystal of triazole **5**: yield 0.7 g, 70%, m.p. 199 °C (dec.); IR (KBr) *v* 3315s, 3099m, 1623s, 1610s, 1558s, 1506s, 1409w, 1328s, 1282s, 1105s, 1002m, 950s, 771s cm^{-1}; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta = 10.22$ (s, 1H, NH), 9.86 (s, 1H, NH), 7.81–7.79 (d, $J = 8.5$ Hz, 2H, aromatic-H), 7.64–7.62 (d, $J = 8.5$ Hz, 2H, aromatic-H), 4.88 (t, $J = 2$ Hz, 2H, ferrocene-H), 4.41 (t, $J = 1.5$ Hz, 2H, ferrocene-H), 4.02 (s, 5H, ferrocene-H); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): $\delta = 168.46$, 165.22 (C-3, C-5), 143.21, 129.40 (aromatic-C), 127.49, 125.33 (aromatic-CH), 82.95 (ferrocene-C), 69.43, 69.43, 66.54 (ferrocene-CH); FABMS *m/z* (%) [M^{+1} 362 (22)]. Anal. Calc. for $C_{18}H_{15}FeN_3S$: C, 59.84; H, 4.18; N, 11.63. Found: C, 59.67; H, 4.01; N, 11.51%.

5.6. 3-[p-(Ferrecenyl)phenyl]-N-amino-1,2,4-s-triazol-5-thiol (**6**)

A mixture of **4** (1.0 g, 2.76 mmol) and hydrazine hydrate (5 ml) is refluxed in dry EtOH for 5 h. The resulting precipitate thus formed after cooling was collected by filtration and crystallized from EtOH to give a dark yellow crystal of the corresponding *N*-amino triazole derivative **6**: yield 0.41 g, 39.5%, m.p. 171–173 °C; IR (KBr) *v* 3313s, 3089m, 2942w, 1608s, 1508s, 1409m, 1322s, 1280s, 1191w, 1105s, 948s, 887s, 846s, 813s, 771m, 696m cm^{-1}; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta = 7.97$ (d, $J = 8$ Hz, 1H, aromatic-H), 7.75 (s, 1H, NH), 7.65 (m, 3H, aromatic-H), 5.81 (s, 1H, NH), 4.88 (d, $J = 7$ Hz, 2H, ferrocene-H), 4.41 (d, $J = 7$ Hz, 2H, ferrocene-H), 4.02 (t, $J = 4$ Hz, 5H, ferrocene-H); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): $\delta = 166.76$ (C-5), 149.46 (C-2), 141.913, 127.96, (aromatic-C), 125.68, 122.91 (aromatic-CH), 83.35 (ferrocene-C), 69.53, 69.01, 66.65 (ferrocene-CH); FABMS *m/z* (%) [M^+, 376 (10)]. Anal. Calc. for $C_{18}H_{16}FeN_4S$: C, 57.46; H, 4.28; N, 14.89. Found: C, 57.61; H, 4.21; N, 14.59%.

5.7. p-(Ferrocenyl)phenyl-(3,5-dimethylpyrazolyl)-methanone (**9**)

A mixture of hydrazide **2** (0.36 g, 1.13 mmol) and acetylacetone (1 ml) was refluxed in MeOH (25 ml) containing AcOH (1 ml) for 5 h. The reaction mixture was cooled and the yellow precipitate was collected by filtration and washed with water several times. The crude product was crystallized from MeOH to give 310 mg of golden yellow crystals of pyrazole derivative **9**: yield 69.5%, m.p. 104–105 °C; IR (KBr) *v* 2958w, 2923m, 1693s, 1606s, 1523m, 1479m, 1457m, 1411s, 1344s, 1276s, 1189s, 1116s, 1029s, 921s, 759s, 698s cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 7.96$–7.94 (d, $J = 7$ Hz, 2H, aromatic-H), 7.47–7.46 (d, $J = 7$ Hz, 2H, aromatic-H), 6.06 (s, 1H, pyrazole-H), 4.82 (s, 2H, ferrocene-H), 4.5 (s, 2H, ferrocene-H), 4.16 (s, 5H, ferrocene-H), 2.62 (s, 3H, CH_3), 2.27 (s, 3H, CH_3); ^{13}C-NMR ($CDCl_3$): $\delta = 168.63$ (CO), 152.60, 145.76 (C-3, C-5, pyrazole), 145.69, 132.54, (aromatic-C), 130.94, 126.12, 111.60 (aromatic-CH), 109.79 (pyrazole-CH), 71.43, 68.41, 58.96 (ferrocene-C), 15.04, 14.63 (2 CH_3); FABMS *m/z* (%) [M^+ 384 (100)]. Anal. Calc. for $C_{22}H_{20}FeN_2O$: C, 68.76; H, 5.24; N, 7.29. Found: C, 68.96; H, 5.29; N, 7.22%.

5.8. 1-[p-(Ferrocenyl)benzoylhydrazono]-1-(ferrocenyl)ethane (**10a**)

5.8.1. Method A

A mixture of hydrazide **2** (0.5 g, 1.56 mmol) and acetylferrocene (0.4 g, 1.75 mmol) was refluxed in EtOH (20 ml) containing AcOH (1 ml) for 8 h. The reaction

mixture was cooled and the yellow precipitate was collected by filtration and washed with water several times. The crude product was chromatographed on silica using acetone–hexane (1:3) to give yellow powder in the second fraction, which on crystallization from EtOH gave 37 mg, 4.5% of hydrazone **10a** as orange crystals, m.p. 140–143 °C.

5.8.2. Method B

A sample of hydrazide **2** (0.32 g, 1 mmol) was condensed with acetylferrocene (0.228 g, 1 mmol) under neat conditions for 30 min. The reaction mixture was further refluxed in EtOH for further 3 h. The precipitate thus formed was collected by filtration and chromtographed on silica and worked up as described in method A to give 0.102 g, 19% of **10a**. IR (KBr) ν 3210w, 3091m, 1648s, 1606s, 1540s, 1511s, 1411m, 1389m, 1299s, 1270s, 1181s, 1105s, 887s, 850s, 819s, 765s, 700s cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 10.53$ (s, 1H, CONH), 7.81 (m, 2H, aromatic-H), 7.65 (m, 2H, aromatic-H), 4.89 (s, 2H, ferrocene-H), 4.71 (s, 2H, ferrocene-H), 4.42 (s, 4H, ferrocene-H), 4.23 (s, 5H, ferrocene-H), 4.04 (s, 5H, ferrocene-H), 2.25 (s, 3H, CH_3); ^{13}C-NMR (Me_2SO-d_6): $\delta = 167.17$ (CO), 144.49, 129.32 (aromatic-C), 127.65, 127.52, 125.50, 108.39 (aromatic-CH), 82.80, 82.79 (ferrocene-C), 72.00, 69.59, 69.52, 69.46, 69.08, 66.66, 66.55 (ferrocene-CH), 30.84 (CH_3); FABMS m/z (%) [M^+ 530 (15)].

*5.9. 1-[p-(N-Acetylhydrazinoylphenyl)]ferrocene (**10b**)*

A mixture of hydrazide **2** (0.32 g, 1 mmol) and acetylferrocene (0.228 g, 1 mmol) was refluxed in AcOH (20 ml) for 36 h. The excess AcOH was removed under vacuum and the residue was chromatographed on silica gel using $CHCl_3$–acetone mixture (5:1) to afford the unexpected *N*-acetyl derivative **10b** (0.32 g in 86%) as red crystals, m.p. 245 °C (dec.). ^{1}H-NMR (Me_2SO-d_6): $\delta = 10.21$ (s, 1H, CONH), 9.85 (s, 1H, CONH), 7.80–7.79 (d, $J = 8.5$ Hz, 2H, aromatic-H), 7.64–7.63 (d, $J = 8.5$ Hz, 2H, aromatic-H), 4.89 (t, $J = 1.5$ Hz, 2H, ferrocene-H), 4.41 (t, $J = 1.5$ Hz, 2H, ferrocene-H), 4.02 (s, 5H, ferrocene-H), 1.92 (s, 3H, CH_3); ^{13}C-NMR (Me_2SO-d_6) $\delta = 168.45$ (CO), 165.21 (CO), 143.21, 129.40, (aromatic-C), 127.47, 125.34, (aromatic-CH), 82.93 (ferrocene-C), 69.42, 66.54 (ferrocene-CH), 20.52 (CH_3); FABMS m/z (%) [M^+, 362 (20)]. Anal. Calc. for $C_{19}H_{18}FeN_2O_2$: C, 63.00; H, 5.00; N, 7.73. Found: C, 62.86; H, 4.89; N, 7.47%.

*5.10. Synthesis of p-(ferrocenyl)benzoylhydrazono-p-substituted arylidenes (**11a–c**)*

A mixture of hydrazide **2** (0.5 g, 1.56 mmol) and aromatic aldehydes or *p*-ferrocenylbenzaldehyde (1.7 mmol) was refluxed in EtOH (50 ml) containing AcOH (1 ml) for 5–7 h. The reaction mixture was cooled and the yellow precipitate was collected by filtration and washed with water several times. The crude products were crystallized from EtOH to give the corresponding hydrazones **11a–c** as yellow crystals in very good yield.

*5.10.1. p-(Ferrocenyl)benzoylhydrazono-benzylidene (**11a**)*

R = H: yield 95.6%, m.p. 241–243 °C; IR (KBr) ν 3266s, 3100m, 3065s, 3010m, 1650s, 1604s, 1552s, 1519s, 1488s, 1448s, 1365s, 1295s, 1274s, 1195s, 1139s, 1058s, 1000s, 954s, 916s, 819s, 759s, 694s cm^{-1}; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta = 8.48$ (s, 1H, N=CH), 7.85–7.84 (d, $J = 6$ Hz, 2H, aromatic-H), 7.74 (s, 2H, aromatic-H), 7.68 (s, 2H, aromatic-H), 7.45 (s, 3H, aromatic-H), 4.90 (s, 2H, ferrocene-H), 4.42 (s, 2H, ferrocene-H), 4.03 (s, 5H, ferrocene-H); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): $\delta = 162.91$ (CONH), 147.44, 143.44, 134.41 (aromatic-C), 130.03, 128.86, 127.81, 127.06, 125.54 (aromatic-CH), 83.08 (ferrocene-C), 69.61, 69.55, 66.72 (ferrocene-CH); FABMS m/z (%) [M^+, 408 (30)]. Anal. Calc. for $C_{24}H_{20}FeN_2O$: C, 70.60; H, 4.93; N, 6.86. Found: C, 70.49; H, 5.10; N, 6.65%.

*5.10.2. p-(Ferrocenyl)benzoylhydrazono-p-methoxybenzylidene (**11b**)*

R = *p*-OCH_3: Yield 98%, m.p. 228–230 °C; IR (KBr) ν 3220s, 3060s, 2900s, 2830s, 1643s, 1610s, 1562s, 1511s, 1421s, 1386s, 1299s, 1253s, 1170s, 1147s, 1105s, 1060s, 1029s, 964s, 916s, 887s, 854s, 831s, 769s, 669s cm^{-1}; ^{1}H-NMR ($CDCl_3$ + Me_2SO-d_6, 500 MHz): $\delta = 8.40$ (s, 1H, N=CH), 7.87 (s, 2H, aromatic-H), 7.72 (s, 2H, aromatic-H), 7.56 (d, $J = 6.5$ Hz, 2H, aromatic-H), 6.92 (s, 2H, aromatic-H), 4.74 (s, 2H, ferrocene-H), 4.39 (s, 2H, ferrocene-H), 4.03 (s, 5H, ferrocene-H), 3.85 (s, 3H, OCH_3); ^{13}C-NMR ($CDCl_3$ + Me_2SO-d_6, 125 MHz): $\delta =$ 161.17 (CONH), 148.15, 130.91 (aromatic-C), 129.09, 128.02, 125.54, 114.09 (aromatic-CH), 83.40 (ferrocene-C), 69.74, 66.72 (ferrocene-CH), 55.35 (OCH_3); FABMS m/z (%) [M^+, 438 (48)]. Anal. Calc. for $C_{25}H_{22}FeN_2O_2$: C, 68.50; H, 5.05; N, 6.39. Found: C, 68.48; H, 4.89; N, 6.23%.

*5.10.3. p-(Ferrocen-1-yl)benzoylhydrazono-p-(ferrocen-1-yl)benzylidene (**11c**)*

R = *p*-ferrocenyl: yield 100%, m.p. 209–211 °C; IR (KBr) ν 3089m, 1650s, 1604s, 1546s, 1517s, 1417m, 1353s, 1270s, 1182m, 1139s, 1105s, 998s, 887s, 825s, 765s, 696m cm^{-1}; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta = 11.77$ (s, 1H, CONH), 8.45 (s, 1H, N=CH), 7.87 (d, $J = 8$ Hz, 2H, aromatic-H), 7.65 (m, 6H, aromatic-H), 4.90 (s, 2H, ferrocene-H), 4.85 (s, 2H, ferrocene-H), 4.42 (s, 2H, ferrocene-H), 4.40 (s, 2H, ferrocene-H), 4.04 (s, 10H, ferrocene-H); ^{13}C-NMR ($CDCl_3$ + Me_2SO-d_6, 125 MHz): $\delta = 162.89$ (CONH), 147.53, 143.27, 141.34, 131.73 (aromatic-C), 127.73, 127.14, 125.84, 125.36

(aromatic-CH), 83.62, 82.90 (ferrocene-C), 69.45, 69.41, 66.55, 66.33 (ferrocene-CH), FABMS *m/z* (%) [M^+, 592 (8)]. Anal. Calc. for $C_{34}H_{28}Fe_2N_2O$: C, 68.95; H, 4.76; N, 4.73. Found: C, 68.60; H, 5.18; N, 5.15%.

5.11. Synthesis of 1-(*p*-formylphenyl)-1′-(4-formyl-1-naphthyl)ferrocene (**13**) and 1-(*m*-formylphenyl)-1′-(3-formyl-5-methoxyphenyl)ferrocene (**15**)

A mixture of ferrocene-dialcohols (3 g, 6.7 mmol) and MnO_2 (30 g) was stirred at r.t. in $CHCl_3$ (300 ml) for 15 h. The reaction mixture was filtered off through glass wool and the filtrate was distilled under reduced pressure at 30 °C. The residue was chromatographed on silica gel using $CHCl_3$–hexane (3:1) to give the corresponding 1-(*p*-formylphenyl)-1′-(4-formyl-1-naphthyl)ferrocene (**13**) and 1-(*m*-formylphenyl)-1′-(3-formyl-5-methoxyphenyl)ferrocene (**15**), respectively.

5.11.1. 1-(*p*-Formylphenyl)-1′-(4-formyl-1-naphthyl)ferrocene (**13**)

Dark red crystals, m.p. 106–107 °C, yield 2.2 g, 73%, literature (64%) [18]; IR (KBr) *ν* 3089m, 2973m, 1691s, 1602s, 1567s, 1513s, 1216s, 1168s, 1058s, 829s, 765s cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 10.35$ (s, 1H, CHO), 9.92 (s, 1H, CHO), 9.30 [dd, $J = 8.5$, $J = 0.5$ Hz, 1H, CH=CH (naphthalene-H)], 8.54 [dd, $J = 8.5$, $J = 0.5$ Hz, 1H, CH=CH (naphthalene-H)], 7.82 (d, $J = 1$ Hz, 2H, naphthalene-H), 7.66 (m, 3H, aromatic-H), 7.63 (m, 1H, aromatic-H), 7.45 (d, $J = 8$ Hz, 2H, aromatic-H), 4.72 (t, $J = 1.5$ Hz, 2H, ferrocene-H), 4.64 (t, $J = 1.5$ Hz, 2H, ferrocene-H), 4.45 (t, $J = 1.5$ Hz, 2H, ferrocene-H), 4.37 (t, $J = 1.5$ Hz, 2H, ferrocene-H). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 192.92$, 191.57 (2 CHO), 145.56, 143.53 (aromatic-C), 135.55, 134.23 (aromatic-C), 131.85, 131.13 (aromatic-C), 129.81, 129.57, 128.64, 126.85, 126.44, 126.36, 126.32, 125.14 (aromatic-CH), 86.47, 84.30 (ferrocene-C), 72.49, 72.27, 71.40, 68.85 (ferrocene-CH). FABMS *m/e* [M^+, 444 (92)].

5.11.2. 1-(*m*-Formylphenyl)-1′-(3-formyl-5-methoxyphenyl)ferrocene (**15**)

Orange red crystals, m.p. 87–88 °C, yield 71%; IR (KBr) *ν* 3095s, 2975w, 2840m, 2800s, 2721s, 1702s, 1677s, 1590s, 1504s, 1461s, 1438s, 1388s, 1272s, 1249s, 1186s, 1147s, 1079s, 1018s, 935s, 815s, 790s, 688s cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 9.8$ (s, 1H, CHO), 9.7 (s, 1H, CHO), 7.62–7.18 (m, 6H, aromatic-CH), 6.67 (m, 1H, aromatic-CH), 4.82 (s, 2H, ferrocene-CH), 4.61 (s, 2H, ferrocene-H), 4.36 (s, 2H, ferrocene-H), 4.32 (s, 2H, ferrocene-H), 3.81 (s, 3H, OCH_3). ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 193.24$, 191.76 (2 CHO), 162.10 (aromatic-C), 139.18, 137.19, 132.63, 130.56 (aromatic-C), 130.45, 129.55, 128.15, 127.09, 126.81, 111.72 (aromatic-CH), 86.00, 83.79 (ferrocene-C), 71.57, 71.24, 70.89, 68.68 (ferrocene-CH), 56.43 (OCH_3). FABMS *m/e* (%) [M^+, 424 (45)]. Anal. Calc. for $C_{25}H_{20}FeO_3$: C, 70.77; H, 4.75. Found: C, 71.01; H, 4.51%.

5.12. Synthesis of the ferrocene-1,1′-dihydrazones **12**, **14** and **18**

According to the method described above, a mixture of hydrazide **2** (0.64 g, 2 mmol) and 1,1′-ferrocene-dialdehyde derivatives (1 mmol) was refluxed in EtOH (50 ml) in the presence of AcOH (1 ml) for 5 h to give the corresponding di-hydrazones **12**, **14** and **18** in very good yield.

5.12.1. Bis-[*p*-(ferrocenyl)benzoylhydrazono]ferrocen-1,1′-ylidene (**12**)

Yield 98%, m.p. 206–208 °C; IR (KBr) *ν* 3220s, 3090s, 1658s, 1639s, 1604s, 1554s, 1521s, 1465s, 1365s, 1326s, 1295s, 1274s, 1191s, 1143s, 1105s, 1056s, 1000s, 944s, 885s, 850s, 821s, 765s cm^{-1}; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta = 11.51$ (s, 2H, 2 CONH), 8.23 (s, 2H, 2 N=CH), 7.77 (s, 4H, aromatic-H), 7.57 (s, 4H, aromatic-H), 4.85 (s, 4H, ferrocene-H), 4.75 (s, 4H, ferrocene-H), 4.49 (s, 4H, ferrocene-H), 4.41 (s, 4H, ferrocene-H), 4.01 (s, 10H, ferrocene-H); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): $\delta = 162.28$ (2 CONH), 147.79, 143.00, 130.60 (aromatic-C), 127.76, 125.35 (aromatic-CH), 83.09, 80.40 (ferrocene-C), 71.14, 69.52, 68.49, 66.68 (ferrocene-CH); FABMS *m/z* (%) [$M^{+1}+H$, 847 (35)]. Anal. Calc. for $C_{46}H_{38}Fe_3N_4O_2$: C, 65.25; H, 4.52; N, 6.61. Found: C, 64.86; H, 4.37; N, 6.40%.

5.12.2. 1-[*p*-(Ferrocenyl)benzoylhydrazono-4-benz-1-ylidene]-1′-[*p*-(ferrocen-1-yl)benzoylhydrazono-4-naphth-1-ylidene]ferrocene (**14**)

Yield 84.6%, m.p. 197–199 °C; IR (KBr) *ν* 3215ms, 3087s, 3030m, 1648s, 1606s, 1544s, 1517s, 1417m, 1363m, 1294s, 1272s, 1187s, 1141s, 1105s, 1056m, 1002m, 958w, 887s, 848s, 827s, 763s, 698s cm^{-1}; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta = 11.88$ (s, 1H, CONH), 11.77 (s, 1H, CONH), 8.42 (s, 1H, N=CH), 8.31 (s, 1H, N=CH), 7.91–7.84 (m, 6H, aromatic-H), 7.70–7.65 (m, 6H, aromatic-H), 7.59–7.51 (m, 6H, aromatic-H), 4.91 (m, 6H, ferrocene-H), 4.65 (s, 2H, ferrocene-H), 4.44 (m, 6H, ferrocene-H), 4.36 (s, 2H, ferrocene-H), 4.05–4.01 (m, 10H, ferrocene-H); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): $\delta = 164.66$ (2 CONH), 144.13, 139.14, 131.07, 130.27, 130.18 (complex aromatic-C), 128.15, 127.18, 125.90, 125.13, 123.83 (complex aromatic-CH), 83.42 (ferrocene-C), 71.76, 69.82, 69.71, 68.18, 66.86, 66.77 (complex ferrocene-CH); FABMS *m/z* (%) [M^{+1}, 1049 (30)]. Anal. Calc. for $C_{62}H_{48}Fe_3N_4O_2$: C, 71.01; H, 4.61; N, 5.34. Found: C, 70.87; H, 4.48; N, 5.24%.

*5.12.3. 1-[p-(Ferrocenyl)benzoylhydrazono-3-benz-1-ylidene]-1′-[p-(ferrocen-1-yl)benzoylhydrazono-4-methoxy-3-benz-1-ylidene]ferrocene (**18**)*

Yield 92.8%, m.p. 192–193 °C; IR (KBr) *v* 3210m, 3085s, 2820s, 1650s, 1606s, 1550s, 1504s, 1463s, 1411s, 1357s, 1295s, 1268s, 1182s, 1141s, 1105s, 1029s, 948s, 885s, 850s, 817s, 765s, 694s cm^{-1}; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta = 11.80$ (s, 1H, CONH), 11.70 (s, 1H, CONH), 8.37 (s, 1H, N=CH), 8.31 (s, 1H, N=CH), 7.86–7.84 (d, $J = 7.5$ Hz, 4H, aromatic-H), 7.65–7.47 (m, 8H, aromatic-H), 7.32–7.19 (m, 2H, aromatic-H), 6.87 (d, $J = 8.5$ Hz, aromatic-H), 4.88 (m, 4H, ferrocene-H), 4.77 (s, 2H, ferrocene-H), 4.68 (s, 2H, ferrocene-H), 4.42 (s, 4H, ferrocene-H), 4.31 (s, 2H, ferrocene-H), 4.26 (s, 2H, ferrocene-H), 4.03 (s, 10H, ferrocene-H), 3.81 (s, 3H, OCH_3); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): $\delta =$ 162.94, 162.75 (2 CONH), 157.52, 147.70, 143.20, 143.08, 137.50, 134.13, 130.53, 130.38 (complex aromatic-C), 128.36, 127.76, 127.69, 127.23, 126.49, 125.78, 125.37, 124.83, 124.24, 123.95, 111.49 (complex aromatic-CH), 84.90, 83.04, 82.99, 82.83 (ferrocene-C), 79.07, 70.13, 69.76, 69.43, 69.72, 67.26, 67.17, 66.50 (complex ferrocene-CH), 55.25 (OCH_3); FABMS *m/z* (%) [M^{+1}, 1029 (25)]. Anal. Calc. for $C_{59}H_{48}Fe_3N_4O_3$: C, 68.89; H, 4.70; N, 5.44. Found: C, 68.67; H, 4.59; N, 5.26%.

*5.13. Reaction of hydrazide **2** with ethyl acetoacetate*

A mixture of hydrazide **2** (0.5 g, 1.56 mmol) and ethyl acetoacetate (1 ml) was refluxed in EtOH (25 ml) containing AcOH (1 ml) for 5 h. The reaction mixture was cooled and the yellow precipitate was collected by filtration and washed with water several times. The crude product was chromatographed on silica gel using hexane–acetone (1:2) to give in the second fraction 0.31 g of the unexpected product **20** as orange crystals.

*5.13.1. Analytical data of p-(ferrocen-1-yl)benzoylhydrazono-2-propylidene (**20**)*

Yield 51.4%, m.p. 203–205 °C; IR (KBr) *v* 3200s, 3080s, 3020m, 2900m, 1639s, 1608s, 1540s, 1515s, 1419s, 1371s, 1297s, 1263s, 1187s, 1147s, 1105s, 1031s, 1000s, 887s, 852s, 821s, 767s cm^{-1}; ^{1}H-NMR ($CDCl_3$, 500 MHz): $\delta = 7.73$ (s, 2H, aromatic-H), 7.53 (d, $J = 6.5$ Hz, 2H, aromatic-H), 4.69 (s, 2H, ferrocene-H), 4.38 (s, 2H, ferrocene-H), 4.03 (s, 5H, ferrocene-H), 2.16 (s, 3H, CH_3), 1.99 (s, 3H, CH_3); FABMS *m/z* (%) [M^{+1}, 360 (50)]. Anal. Calc. for $C_{20}H_{20}FeN_2O$: C, 66.68; H, 5.59; N, 7.78. Found: C, 66.51; H, 5.42; N, 7.64%; ^{1}H-NMR (Me_2SO-d_6, 500 MHz): $\delta = 10.39$ (s, 1H, CONH), 7.76–7.75 (d, $J = 8.5$ Hz, 2H, aromatic-H), 7.62–7.6 (d, $J =$ 8.5 Hz, 2H, aromatic-H), 4.86 (t, $J = 1.5$ Hz, 2H, ferrocene-H), 4.40 (t, $J = 1.5$ Hz, 2H, ferrocene-H), 4.02 (s, 5H, ferrocene-H), 2.01 (s, 3H, CH_3), 1.96 (s, 3H, CH_3); ^{13}C-NMR (Me_2SO-d_6, 125 MHz): $\delta =$ 162.96, (CON), 159.71 (N=C), 142.63, 131.03, 127.74, 125.24 (aromatic-C and CH), 83.21 (ferrocene-C), 69.39, 69.36, 66.52 (ferrocene-CH), 25.05 (2 CH_3).

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