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Synthesis and electrochemical study of novel oxazolo-ferrocene derivatives displaying redox-switchable character

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Abstract—A synthetic procedure has been developed to prepare new oxazolo-ferrocene ligands. The method, which allows the formation of homobimetallics oxazole–ferrocenes **4–7** containing two oxazole rings in the conjugation chain, is based on the aza-Wittig reaction of α-azidoacetyl ferrocene **1** with diacyl chlorides and triphenylphosphine. This route has the characteristic of tuning the size and shape of the spacer which could have aliphatic, aromatic, and heteroaromatic nature. Likewise, the reaction of 1,1′-bis(α-azidoacetyl) ferrocene **3** with aroyl chlorides in the presence of triphenylphosphine affords ferrocene ligands **11** linked to two oxazole rings. The stable solids were thoroughly characterized by spectroscopic means and electrochemical methods. Ligands **4–7** showed chemically reversible oxidations with two one-electron processes, indicating that the iron centres do not electronically communicate with each other. Electrochemical investigations reveal the respective ferrocene–ferrocenium redox couples of the ligands **11** and **14** are perturbed to a more positive potentials upon protonation and co-ordination of Zn(II) guest cation. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

The reason for the widespread interest in the study of molecular systems containing more than one metallocene is that, with certain π-conjugated bridges, the metal centres are no longer independent of each other. Homobimetallic complexes in which two ferrocene units are coupled intimately through suitable bridging units serve as important benchmarks for the optimization of synthetic methods and for the investigation of intramolecular (intrachain) communication among the convalently linked ferrocene units. The shortest bridge is just one bond and the biferrocene itself and some methylated derivatives have been studied intensively[1–8] as well as biferrocenes bridged by π-unsaturated units[9–12] or heteroaromatic rings[13–15] (thiophene and furan).

Although biferrocenes linked by alkene bridges present high electron transmission efficiency, their thermal and photochemical instability posses several drawbacks. On the other hand, the efficiency of the more stable aromatic systems appear limited by excessive charge confinement. The very stable oxazole ring possesses a sextet of π-electrons, however, the ease with which the oxazole ring undergoes Diels–Alder reactions with dienophiles and autooxidation with singlet oxygen indicates that the delocalization is quite incomplete; hence it has but little aromatic character. Due to this, bisferrocene systems with oxazole conjugation may be considered a good tradeoff between the efficiency of ethylenic systems and the stability of the aromatic ones. On the other hand, in this kind of molecules the nitrogen atom in the oxazole ring adds another dimension. Thus, the reversibility of the ferrocene/ferroccenium redox couple and the ability of the oxazole ring to act as ligand towards metal ions can cooperate within the molecule. This synergetic relation creates a switch on a molecular level, which allows the complexing ability to be turned off of the oxazole subcomponent, once a positive charge within the ferrocene moiety is generated. Upon reduction the ability for complexation is restored; consequently the combination of ferrocene and oxazole could be of interest for the construction of hetero-bimetallic systems, which can behave as redox-switched receptors with the capability of selectively sensing ionic-guest species via electrochemical and/or optical methodologies.[16–22]

In continuation of our studies on the synthesis of ferrocenyl-substituted azaheterocycles,[23–28] we wish to present here the synthesis of bis(ferrocene) ligands type **I** bearing two oxazole rings, and ferrocene ligands linked to two oxazole rings type **II**, using the iminophosphorane methodology.[29] The persistent advantage of this approach is flexibility with respect to the tethering groups between the metal centres. In this context, electronic structure and/or length of the spacer have been systematically varied to gain insight into the redox behaviour of the unreported oxazolo-ferrocene ligands prepared.

Keywords: ferrocenes; oxazoles; palladium complexes; aza-Wittig reaction; electrochemistry.

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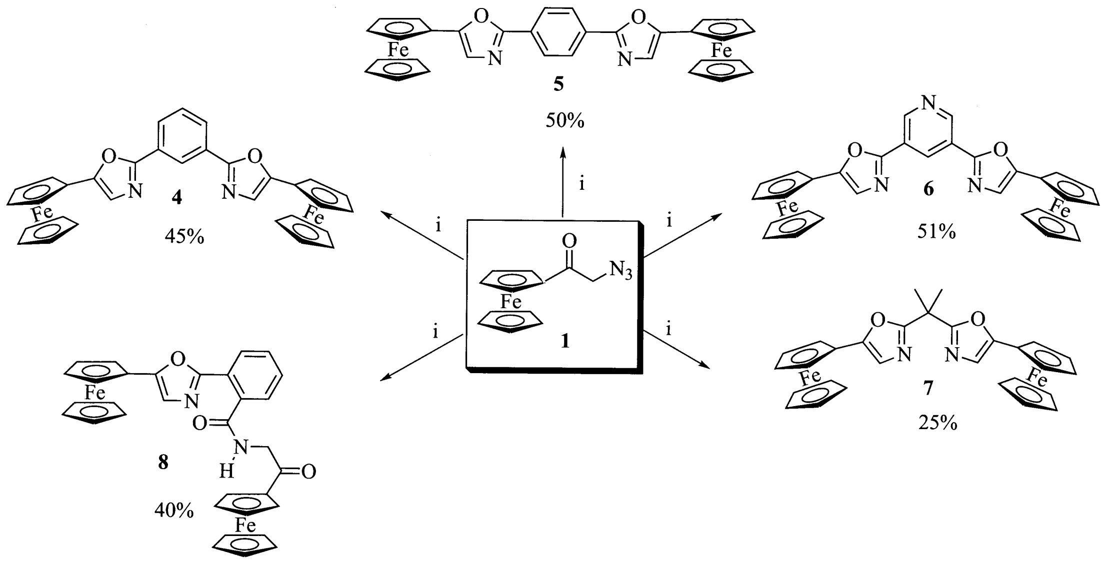
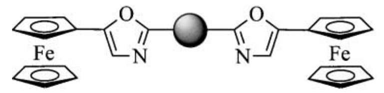


Scheme 1. *Reagents:* Ph_3P, polymer supported BEMP, the appropriate dicarbonyl chloride, Et_2O, rt.



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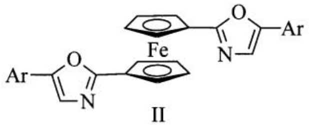


II

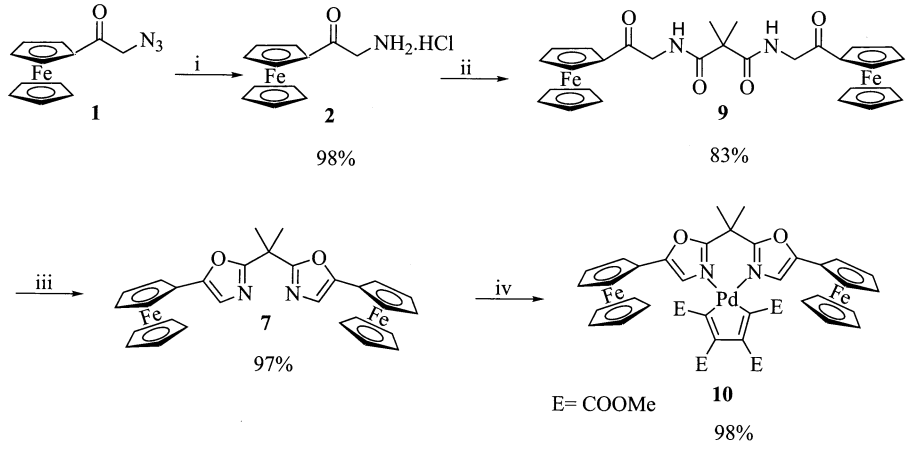
2. Results and discussion

The synthesis of the ferrocenyloxazole derivatives is based on the aza-Wittig reaction of acyl chlorides with iminophosphoranes derived from the appropriate α-azido carbonyl compound. Although this methodology has successfully applied to the synthesis of oxazole derivatives,[30–32] no reaction of dicarbonyl chlorides with iminophosphoranes derived from α-azidocarbonyl compounds has been reported to the best of our knowledge. In this context, it has been found that aza-Wittig reactions of several kinds of dicarbonyl chlorides with *N*-aryliminophosphoranes are very substrate-dependent.[33,34]

The required aza-substituted ferrocene precursors have been prepared as follow. The α-azidocarbonylferrocene **1** has been prepared in 78% overall yield from acetylferrocene trimethylsilylenol ether by bromination followed by halogen–azido substitution.[27]

The bis(azide) **3** has been prepared in an overall yield of 80% from 1,1′-diacetylferrocene by the two-step sequence: (a) metallation with LDA at −78°C followed by sequential treatment with chlorotrimethylsilane and NBS and (b) reaction with sodium azide or polymeric quaternary ammonium azide.[35]

At first, formation of homobimetallic complexes bearing two ferrocenyloxazole units linked by an aromatic, heteroaromatic or aliphatic spacer was attempted by using the triazaphosphadiene pathway,[36] in view of the excellent results obtained from the reaction of azides with tertiary phosphines and acyl chlorides to give five-membered rings.[37] In this way, the reaction is carried out with the acyl chloride present before addition of the phosphine. Thus, addition of triphenylphosphine to a mixture of α-azidoacetylferrocene **1**, the appropriate dicarbonyl chloride and triethylamine produced the expected **4**–**7** albeit in very disappointing yields (no more than 10%). These frustrating results are probably due to the fact that the HCl liberated from the aza-Wittig reaction adds to the very basic iminophosphorane or triazaphosphadiene, leading to diminished yields or preventing the cyclization step. For this reason, the polymer-supported BEMP (2-*tert*-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-diazaphosphorine) was used as a base, which has been used in diverse alkylation and acylation reactions as a scavenger of HCl.[38–41] Remarkably, the aza-Wittig reaction followed by intramolecular cyclization of the resulting bis(imidoyl chloride) proceeded with up to fourfold increase in the isolated yields of the desired cyclized products **4**–**7**. In spite of the moderate yields and considering that this conversion concatenates three transformations: Staudinger reaction, aza-Wittig reaction across the triazaphosphadiene to give the intermediates bis(imidoyl chlorides) and finally cyclization, the yields may be considered as good. Only in one case, when the phthaloyl chloride was used, the monocyclised product **8** was obtained in 40% yield. All attempts to promote the formation of the second oxazole ring in compound **8**, using conventional dehydrating agents[42] and even the powerful dehydrating agent Appel system[43,44] ($Ph_3P/I_2/Et_3N$ or $Ph_3P/CCl_3{-}CCl_3/Et_3N$) or the Burgess[45,46] reagent [methyl *N*-(triethylammoniumsulfonyl)-carbamate] failed. This fact could be ascribed to steric factors. The reaction did not work at all when oxalyl chloride and 2,6-bis(chlorocarbonyl)pyridine were used (Scheme 1). The synthesis of **7** was best accomplished by using a different strategy which starts with the α-aminoacetyl ferrocene hydrochloride **2** easily prepared in 98% yield from **1** by catalytic hydrogenation. As expected, compound **9** formed



Scheme 2. *Reagents:* (i) H_2, Pd/C, AcOH, rt, then dry HCl; (ii) Et_3N, THF, N_2, rt 5 min., then $(CH_3)_2C(COCl)_2$, rt; (iii) $(COCl)_2$, CH_2Cl_2, N_2, rt; (iv) $Pd_2(dba)_3$, dmad, acetone, rt.

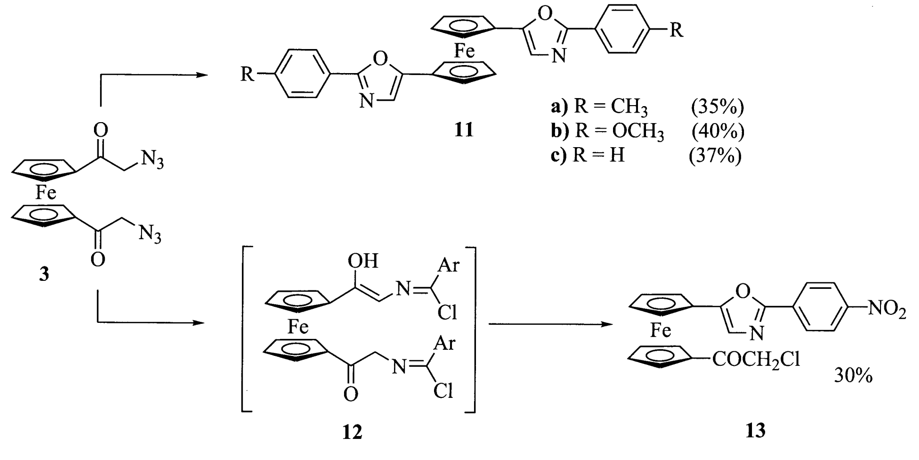
in 83% yield by treatment of the free amine **2** with dimethylmalonyl chloride, underwent cyclization to give the bis-(ferrocene)-oxazole **7** in 97% yield, when it was treated with oxalyl chloride at room temperature for 6 h. The conversion of **9** to **7** should involve initial formation of the corresponding bis(imidoyl)chloride which under the reaction conditions give rise to the oxazole rings.

At this point it seemed interesting to us to test the complexation properties of this kind of oxazolo-ferrocene ligands with transition metals, as these compounds possess two oxazole rings which has demonstrated its versatility toward forming M–N σ bonds to metals transition.[47] Taking into account the structural features of this type of compounds, the ligand of choice was **7**, since the '*gem*-dimethyl effect', which increases the population of the more reactive rotamer,[48] could improve the complexation capability as *N,N*-ligand. The new heterotrimetallic system **10**, bearing a palladacyclopentadiene moiety, was prepared in almost quantitative yield (98%) by the simultaneous addition of the ligand **7** and dimethylacetylene dicarboxylate (dmad) to a suspension of $Pd_2(dba)_3$ in acetone under nitrogen (Scheme 2).

The complex thus obtained, air-stable solid which was very soluble in common organic solvents, was analysed by mass spectrometry, FT-IR, and ^{1}H- and ^{13}C NMR in solution. The FT-IR spectrum displays two strong absorptions bands at 1719 and 1701 cm^{-1} due to the two different methoxycarbonyl groups. In the ^{1}H NMR spectrum two singlets due to the methoxycarbonyl groups are observed at 3.58 and 3.64 ppm, whereas the characteristic signals due to the ferrocene moieties and the oxazole ring proton are slightly downfield shifted (0.15–0.25 ppm). Another feature of this tris(heterometallic) system concerns the chemical shift of the alkene fragment in the ^{13}C NMR spectrum at approximately 164 and 145 ppm, of which the latter is assigned to the α-carbon attached to palladium.

Formation of palladacyclopentadiene complexes with *cis*-fused 1,4-bidentate nitrogen ligands such as bipyridine, and bipyrimidine has been described.[49–52] In particular, palladium complexes with ancillary rigid 1,2-diimines have proved to be good catalysts in several kind of C–C coupling reactions.[53,54] To the best of our knowledge, compound **10** represents the first example of a palladacyclopentadiene complex bearing 1,5-bidentate nitrogen ligand in the guise of a bis(oxazole).

With the aim of preparing ligands type II we turned our



Scheme 3. *Reagents:* Ph_3P, ArCOCl, THF, rt.

Table 1. Electrochemical data for ligands **4**–**7** and complex **10**

Compound	$E^{0'}$ [1][a]	$E^{0'}$ [2][a]	$\Delta E^{0'}$ [K_c][b]	Half-peak width
Ferrocene	0.405			90
4	0.482	0.524	42 (5.13)	92
5	0.489	0.534	45 (5.76)	100
6	0.503	0.545	42 (5.13)	92
7	0.485	0.530	45 (5.76)	100
10	0.485	0.530	45 (5.76)	92

[a] From differential pulse voltammetry. All the potential values are in V vs SCE for a scan rate of 0.004 V s^{-1}.

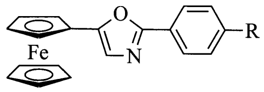
[b] Determined from Richardson and Taube method[58], $\Delta E^{0'}$ in mV.

attention to the aza-Wittig reaction between the bis(azide) **3** and acyl chlorides. In a model study we have found that the three component reaction bis(azide) **3**/triphenylphosphine/aroyl chloride allows the preparation of novel 1,1′-bis(oxazolyl)ferrocenes. Thus, when triphenylphosphine was added to a mixture of bis(azide) **3** and 4-methyl-, 4-methoxy- or benzoyl chloride in tetrahydrofuran at room temperature the 1,1′-bis(oxazolyl)ferrocenes **11a–c** were obtained in 35–40% yields, after chromatographic purification. The only exception to this behaviour was observed when the 4-nitrobenzoyl chloride was used. In this case, the reaction product was found to be the unsymmetrical 1,1′-disubstituted ferrocene **13** isolated in 30% yield This conversion deserves special mention, since to our knowledge it is so far the only exception to the customarily retentive course of the reaction of this kind of azides with acyl chlorides. The unexpected formation of this compound probably involves initial formation of the 1,1′-bis(imidoyl chloride)ferrocene **12**, in which one of the imidoyl chloride moiety undergoes cyclization to give the oxazole ring followed by nucleophilic counterattack of the leaving chloride on the other side chain with concomitant elimination of 4-nitrobenzonitrile (Scheme 3).

In view of the interest in assessing the existence of electronic interactions among linked ferrocene subunits in oligoferrocene molecules, we have examined the electrochemical behaviour of the homobimetallic ligands **4**–**7** by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). When the biferrocene ligands **4**–**7** were subjected to CV measurement only one characteristic superimposed single-step oxidation process[55,56] was observed, with a peak-to-peak separation (ΔE_p=60–76 mV) notably higher than that expected for a two-electron process (ΔE_p=28.5 mV).[57] An estimate for the extent of the ferrocene–ferrocene interactions is obtained from the value of the comproportionation constant K_c, which is related to the separation between the two consecutive redox potentials by the expression $\ln K_c = \Delta E^{0'} nF/RT$.The values of $E^{0'}$ (1) and $E^{0'}$ (2) for all bis(ferrocenes) were estimated by using the method outlined by Richardson and Taube[58] from DPV data (Table 1). The relatively low resolution of electrochemical techniques means that accurate determination of K_c values smaller than about 33 (corresponding to a $\Delta E^{0'}$ of ca. 90 mV) are difficult. However, one could say that K_c is near to the statistical limit (K_c=4).[58] This fact is of relevance as it implies that the aliphatic, aromatic or heteroaromatic spacer does not allow the relevant peripheral ferrocenyl subunits to communicate electronically with each other and they are oxidized independently. Analogous phenylene and biphenylene-linked diferrocene species also showed no voltammetry splitting.[59–62]

We have also carried out electrochemical studies of complex **10** to evaluate the effect that the presence of the Pd centre could have on the peripheral redox-active groups. The complex **10** exhibits an uncomplicated electron-transfer. A peak separation of 62 mV in the CV response and a 92 mV half-peak width of the DPV profile corresponding to a two one-electron transfer which is shifted to a more positive potentials with respect to the free ligand. That means that the mixed-valence species $[\mathbf{10}]^+$ is not stabilized by any kind of electron delocalisation.

One of the most interesting attributes of 1,1′-bis(oxazolo)-ferrocenes **11** is the presence of two proton binding oxazole sites in proximity of the ferrocene redox-active moiety. Due to this structural feature, it was of interest the preparation of oxazolo-ferrocenes **14**, bearing only one proton binding oxazole ring. So, the electrochemical behaviour of the free ligands **11** and **14** as well as in the presence of variable concentrations of HBF_4 was investigated. The CV of **11** and **14**, which display a single anodic process with features of chemical and electrochemical reversibility, showed that 5-ferrocenyloxazoles **14** ($E^{0'}$=0.488–0.502 V vs SCE) are easier oxidized than 1,1′-bis(oxazolyl)ferrocenes **11** ($E^{0'}$=0.526–0.560 V vs SCE), indicating that the introduction of a second oxazole ring in the unsubstituted cyclopentadienyl ring of **14** does give rise to addition effects.



14

a) R = H
b) R = CH_3
c) R = OCH_3
d) R = Cl
e) R = NO_2

Upon protonation by addition of stoichiometric quantities of HBF_4 in CH_3CN to a solution of ligands **11** and **14** in CH_3CN/CH_2Cl_2 (3:2), the redox potential of the ferrocene nucleus was shifted anodically in each case, oxazole protonation builds up positive charge close to the ferrocene nucleus and this electrostatically repels the ferrocenium cation, thermodynamically hindering its formation.

The protonation-induced redox shift is higher for compounds **11** ($\Delta E^{0'}$=144–248 mV) than for compounds **14** ($\Delta E^{0'}$=74–114 mV). These values are in good agreement with the fact that for molecules containing the same number of redox groups, and protonation sites with similar distances Fe–N, the larger $\Delta E^{0'}$ shift is found for compounds containing more protonation sites.[63] Thus, although **11** and **14** contain the same number of ferrocene units, **11** has two protonation sites and therefore ΔE^0 is higher than those observed for **14**. In addition, the protonation-induced redox shift found for compounds **11** also reflect the electron-donating ability of the substituents on the aromatic ring to increase the basicity of the nitrogen atom of the oxazole ring: $\Delta E^{0'}$ **11b**($R{=}OCH_3$)>**11a**($R{=}CH_3$)>**11c** ($R{=}H$).

Table 2. Electrochemical data for compounds **11** and **14**

Compound	$E^{0'}$ $[\Delta E_p]^a$	$\Delta E^{0'}$ [mV]	K_{ox}/K_{red} (BEF)^b
Ferrocene	0.409 (70)		
11a	0.542 (60)		
11a+Zn^{2+}	0.702 (88)	160	1.97×10^{-3}
11a+H^+	0.744 (88)	202	3.85×10^{-4}
11b	0.526 (60)		
11b+Zn^{2+}	0.690 (88)	164	1.68×10^{-3}
11b+H^+	0.774 (84)	248	6.43×10^{-5}
11c	0.560 (64)		
11c+Zn^{2+}	0.664 (96)	104	1.7×10^{-2}
11c+H^+	0.704 (96)	144	3.68×10^{-3}
14a	0.502 (68)		
14a+Zn^2	0.564 (88)	62	8.9×10^{-2}
14a+H^+	0.576 (76)	74	5.6×10^{-1}
14b	0.490 (67)		
14b+Zn^2	0.579 (88)	89	3.1×10^{-2}
14b+H^+	0.594 (76)	104	1.75×10^{-2}
14c	0.488 (64)		
14c+Zn^{+2}	0.585 (88)	97	2.29×10^{-2}
14c+H^+	0.602 (68)	114	$1.18.\ 10^{-2}$
14d	0.494 (76)		
14d+Zn^2	n.i.		
14d+H^+	0.550 (86)	56	1.13×10^{-1}
14e	0.532 (64)		
14e+Zn^2	n.i.		
14e+H^+	0.548 (72)	16	5.36×10^{-1}

[a] Potential formal is in V vs SCE; ΔE_p is in mV. Data from cyclic voltammetry in CH_3CN/CH_2Cl_2 (3:2) at scan rate of 0.200 V s^{-1}.

[b] The equilibrium constants K_{ox} and K_{red} correspond to the complexation proccesses by the oxidized and reduced form of the ligand. The ratio K_{ox}/K_{red} has been calculated using the equation $\Delta E^{0'}nF/RT = \ln(K_{ox}/K_{red})$.

The magnitude of the electrochemical shift on protonation provides important thermodynamic information. The shift in redox potential on protonation is related to the ratio of protonation constant for the oxidized and reduced forms of the ligand. For compound **11b** the potential shift on protonation was 248 mV and consequently the binding enhancement factor (BEF) is 6.43×10^{-5} and the reaction coupling efficiency [64,65] (RCE) is 15560. This means that it is 15560 times more difficult to protonate the oxidized form of the ligand than the reduced form (Table 2).

The effect of several metal ions (Li, Na, K, Ca, Ni, Zn) on receptor redox chemistry was then investigated. For ligands studied only a new redox wave evolved on stepwise addition of zinc (II) perchlorate in acetonitrile solutions. The addition of zinc (II) perchlorate elicited different shifts from each of the receptors, being highly shifted from ligand **11b** (164 mV) (Table 2).

It is noteworthy that the evolving peaks in the electrochemical study of ligands **14** directly correspond to the redox wave of the protonated ligands, with addition of HBF_4 to the final solution causing no further change in the redox behaviour (Fig. 1). In the case of ligands **11**, however the redox wave resulting from the addition of zinc(II) perchlorate has decisively different potential from those assigned to the protonated species (Fig. 2). Recently, it has been reported[66] that the electrochemical response of a number of ferrocene-based receptors to a range of metal cations in non-aqueous solution fell into two types: co-ordination and protonation effects, the later is due to the use of hydrated metal perchlorate salts with ionizable protons. The redox shifts corresponding to protonation are larger than that for co-ordination. It can therefore be concluded that metal-ion co-ordination is observed for ligands **11**, in which the *syn* spatial arrangement may be induced by the cation in an optimal manner by the ball bearing motion[67] of the two cyclopentadienyl rings of the ferrocene unit to give rise to a more effectively organised donor set and consequently the strength of the co-ordination is enhanced. For ligands **14**, co-ordination type behaviour is not observed electrochemically, and that protonation- type behaviour is dominant.

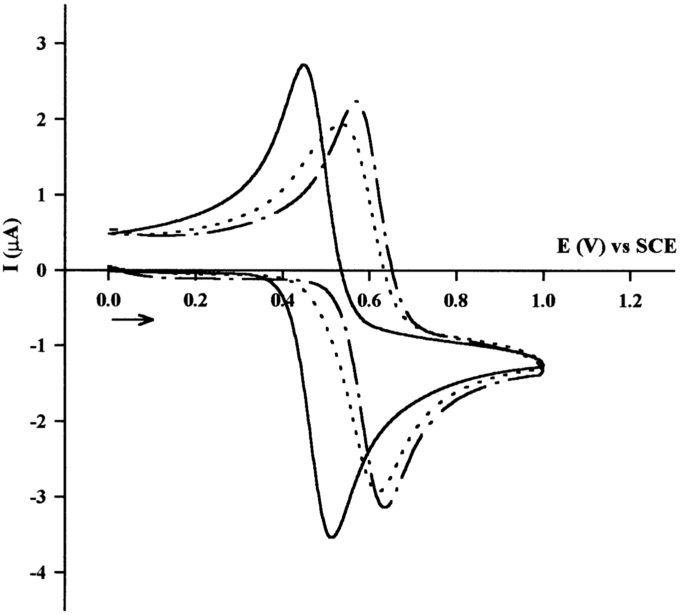


Figure 1. Cyclic voltammogram of a 10^{-3} mol dm^{-3} solution of **14c** in CH_3-CN/CH_2Cl_2 (3:2), 0.1 mol dm^{-3} TBAP; (—) free ligand; (···) ligand with 12 equiv. of zinc (II) perchlorate salt; (-–-) ligand with 2 equiv. of HBF_4. Scan rate: 0.200 V s^{-1}.

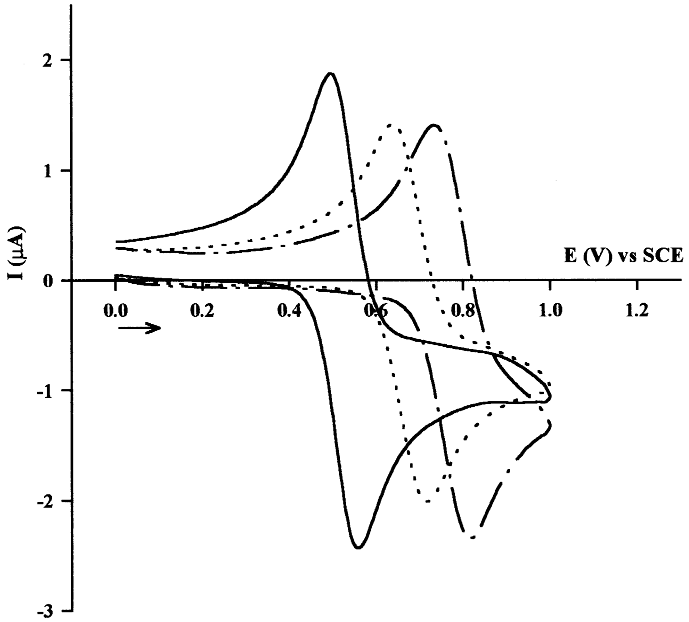


Figure 2. Cyclic voltammogram of a 10^{-3} mol dm^{-3} solution of **11b** in CH_3CN/CH_2Cl_2 (3:2), 0.1 mol dm^{-3} TBAP; (—) free ligand; (···) ligand with 20 equiv. of zinc (II) perchlorate salt; (---) ligand with 4 equiv. of HBF_4. Scan rate: 0.200 V s^{-1}.

3. Conclusions

In the present investigation a number of bis(oxazolo-ferrocenes) **4–7**, bis(oxazolo)-ferrocenes **11** and oxazolo-ferrocenes **14** have been prepared starting from mono or diazido ferrocenyl derivatives and mono or dicarboxylic acid chlorides using the aza-Wittig methodology. This route has the characteristic of tuning the size and shape of the spacer, which could have aliphatic, aromatic and hetero-aromatic nature. In some of the described compounds, a reversible switching can be induced by chemical input (protonation or co-ordination with Zn(II)) and where the output is electrochemical (CV or DPV). In this way, these compounds represent a novel prototype amperometric sensors for the electrochemical recognition of zinc-containing species and may also afford a method for electrochemically modifying reactions in which zinc co-ordination plays a pivotal role. A new heterotrimetallic complex incorporating two ferrocene moieties and palladium has been successfully obtained in excellent yield. It shows reversible redox behaviour and may be useful as catalyst in C–C coupling reactions. Efforts in this direction and in extending this protocol to prepare complexes incorporating others transition-metals are underway.

4. Experimental

4.1. General

All reactions were carried out under N_2 and using solvents which were dried by routine procedures. Column chromatography was performed with the use of silica gel (60 A.C.C. 70–200 μm, sds) as the stationary phase. Compounds **14d**, and **14e** were prepared as described in the literature.[27] All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. FT-IR spectra were determined as Nujol emulsions or films on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker AC200 (200 MHz) or a Varian Unity 300 (300 MHz). The EI and FAB mass spectra were recorded on a Fisons AUTOSPEC 500 VG spectrometer. Microanalyses were performed on a Perkin–Elmer 240C instrument. The cyclic voltammetric measurements were performed on a QUICELTRON potentiostat/galvanostat controlled by a personal computer and driven by dedicated software. Cyclic voltammetry was performed with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a SCE reference electrode. The experiments were carried out with a 10^{-3} M solution of sample in dry CH_2Cl_2/CH_3CN (2:3) containing 0.1 M $(n\text{-}C_4H_9)_4ClO_4$ as supporting electrolyte. All the potential values reported are relative to a SCE electrode at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min and the working electrode was cleaned after each run. The cyclic voltammograms were recorded with a scan rate increasing from 0.05 to 1.00 V s^{-1}. Differential pulse voltammetry was done with a pulse amplitude of 10 mV, a sweep rate of 4 mV s^{-1} and a pulse width of 0.5 s. Typically, receptor (1×10^{-3} mol) was dissolved in solvent (5 mL) and TBAP (base electrolyte) (0.170 g) added. The guest under investigation was then added as a 0.1 M solution in acetonitrile using a microsyringe whilst the cyclic voltammetric properties of the solution were monitored. A minimum equiv, of metal perchlorate salt was required to produce a detectable second redox peak, but more equiv. of metal salt was required to complete disappearance of original ligand redox peak and addition of guest causing no further change in the redox behaviour.

4.1.1. α-Aminoacetylferrocene hydrochloride (2). To a suspension of Pd/C (10%) (0.2 g) in acetic acid (5 mL) a solution of α-azidoacetylferrocene (0.6 g, 2.23 mmol) in the same solvent (25 mL) was added dropwise and the reaction mixture was stirred at room temperature for 3 h, while a stream of H_2 was bubbled over the solution. The solution was filtered over a zelite pad which was washed with acetic acid (3×15 mL). To the combined filtrates a stream of dry HCl was bubbled for 2 h and then the solvent was evaporated under reduced pressure. The resulting oil was triturated with diethyl ether (20 mL) to give the hydrochloride (**2**) in 98% yield; mp 138–140°C. IR (Nujol) cm^{-1}: 1672, 1270, 1113, 1035, 889, 833. ^1H NMR (D_2O): δ 4.42 (bs, 2H), 4.53 (bs, 2H), 4.75 (bs (7H). ^{13}C NMR (D_2O): δ 47.23, 71.65, 73.03, 75.92, 77.01, 201.02. EIMS *m/z*: (rel intensity): 243 (M^+, 82), 185 (99), 129 (100), 121 (65), 94 (34), 81 (39), 56 (46).

4.1.2. 1,3-Bis(5-ferrocenyloxazol-2-yl)benzene (4). To a mixture of α-azidoacetylferrocene **1** (0.4 g, 1.48 mmol), isophthaloyl dichloride (0.16 g, 0.81 mmol) and the polymer supported BEMP (0.97 g) in dry Et_2O (20 mL), a solution of triphenylphosphine (0.44 g, 1.7 mmol) in the same solvent (10 mL) was slowly dropped, at room temperature and under nitrogen atmosphere. The mixture was stirred for 24 h and the resin was then removed by filtration. The solution was evaporated to dryness under reduced pressure and the residue was chromatographed on a silica gel column, using EtOAc/*n*-hexane 1:3, as eluent. After evaporating to dryness the residue was triturated in Et_2O to give (**4**), in 45% yield, as an analytically solid pure sample; mp 187–189°C. IR (Nujol) cm^{-1}: 1613, 1468, 1287, 1108, 826. ^1H NMR ($CDCl_3$): δ 4.16 (s, 10H), 4.38 (t, 4H, J=1.7 Hz), 4.71 (t, 4H, J=1.7 Hz), 7.12 (s, 2H), 7.60 (t, 1H, J=7.8 Hz), 8.16 (dd, 2H, J=7.8 Hz, J=1.3 Hz, 2H), 8.74 (bs, 1H). ^{13}C NMR ($CDCl_3$): δ 66.06, 69.23, 69.67, 72.32, 122.12, 123.28, 127.28, 128.40, 129.38, 152.03, 159.51. EIMS *m/z*: (rel intensity): 580 (M^+, 100), 354 (47), 328 (33), 290 (94), 241 (32), (186 (56), 152 (47), 128 (48), 121 (90), 103 (54). Anal. Calcd for $C_{32}H_{24}Fe_2N_2O_2$: C, 66.24; H, 4.17; N, 4.83. Found: C, 66.36; H, 3.88; N, 4.70.

4.1.3. 1,4-Bis(5-ferrocenyloxazol-2-yl)benzene (5). It was prepared in 50% yield as described above for (**4**), using terephthaloyl dichloride (0.35 g, 1.30 mmol); mp 250–252°C. IR (Nujol) cm^{-1}: 1614, 1108, 1075, 1029, 963, 852, 831. ^1H NMR ($CDCl_3$): δ 4.16 (s, 10H), 4.38 (t, 4H, J=1.8 Hz), 4.70 (t, 4H, J=1.8 Hz), 7.11 (s, 2H), 8.18 (s, 4H) ^{13}C NMR ($CDCl_3$): δ 66.07, 69.27, 69.71, 72.35, 122.37, 126.35, 128.65, 152.10, 159.61. EIMS *m/z*: (rel intensity): 580 (M^+, 100), 354 (10), 328 (11), 290 (49), 186 (11), 121 (31), 77 (10), 56 (17).). Anal. Calcd for $C_{32}H_{24}Fe_2N_2O_2$: C, 66.24; H, 4.17; N, 4.83. Found: C, 66.40; H, 4.09; N, 4.67.

4.1.4. 3,5-Bis(5-ferrocenyloxazol-2-yl)pyridine (6). It was prepared in 51% yield as described above for (**4**), using 3,5-pyridinedicarbonyl dichloride (0.08 g, 0.41 mmol); mp 186–188°C. IR (Nujol) cm^{-1}: 1660, 1597, 1446, 1416, 1280, 1245, 1124, 1109, 1029. ^1H NMR ($CDCl_3$): δ 4.17 (s, 10), 4.41 (bs, 4H), 4.73 (bs, 4H), 7.16 (s, 2H), 8.91 (bs, 1H), 9.35 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ 66.14, 69.48, 69.75, 71.73, 122.29, 123.96, 129.61, 147.73, 153.07, 157.13. EIMS *m/z*: (rel intensity): 581 (M^+, 85), 355 (17), 329 (12), 291 (99), 186 (29), 141 (29), 121 (100), 556 (43).). Anal. Calcd for $C_{31}H_{23}Fe_2N_3O_2$: C, 64.06; H, 3.99; N, 7.23. Found: C, 64.25; H, 3.77; N, 6.95.

4.1.5. 2,2-Bis(5-ferrocenyloxazol-2-yl)propane (7). *Method A*: following the procedure described above for the preparation of (**4**), using dimethylmalonyl chloride (25% yield).

Method B: to a solution of *N,N′*-(ferrocenecarbonylmethyl)-2,2-dimethyl-propanediamide (**9**) (0.2 g, 0.34 mmol) in dry CH_2Cl_2 (5 mL), oxalyl chloride (5 mL) was added and the reaction mixture was stirred at room temperature and under nitrogen for 3 h. Afterwards, dry toluene (15 mL) was added and the solution was concentrated to dryness under vaccum and this operation was repeated four times. Finally, the product was isolated in 97% yield following the procedure described above; mp 164–166°C. IR (Nujol) cm^{-1}: 1619, 1559, 1467, 1447, 1388, 1023. ^1H NMR ($CDCl_3$): δ 1.95 (s, 6H), 4.08 (s, 10H), 4.27 (t, 4H, J=1.8 Hz), 4.55 (t, 4H, J=1.8 Hz), 6.90 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 25.31, 39.32, 66.11, 69.00, 69.50, 72.48, 120.42, 151.56, 164.42. EIMS *m/z*: (rel intensity): 546 (M^+, 88), 294 (36), 185 (58), 121 (100), 56 (37). Anal. Calcd for $C_{29}H_{26}Fe_2N_2O_2$: C, 63.77; H, 4.80; N, 5.13. Found: C, 63.56; H, 4.67; N, 5.25.

4.1.6. {*o*-[*N*-(Ferrocenecarbonylmethyl)carbamoyl]-phenyl}-5-ferrocenyloxazole (8). It was prepared in 40% yield as described above for (**4**), using phthaloyl dichloride (0.12 g, 0.61 mmol); mp 181–183°C. IR (Nujol) cm^{-1}: 1679, 1659, 1461, 1116. ^1H NMR ($CDCl_3$): δ 4.14 (s, 5H), 4.25 (s, 5H), 4.31 (s, 2H), 4.60 (bs, 4H), 4.74 (d, J= 4.2 Hz, 2H), 4.88 (s, 2H), 7.04 (s, 1H), 7.16 (t, J=4.2 Hz, 1H), 7.51, 7.67 (m, 3H), 8.03, 8.07 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 47.45, 65.89, 69.00, 69.13, 69.67, 70.21, 72.28, 72.90, 75.35, 122.12, 124.95, 128.39, 128.45, 129.77, 129.94, 135.42, 151.89, 158.47, 169.58, 198.10. EIMS *m/z*: (rel intensity): 598 (M^+, 38), 580 (40), 533 (25), 467 (39), 394 (45), 367 (51), 213 (90), 186 (58), 129 (64), 121 (100), 65 (36), 56 (78).). Anal. Calcd for $C_{32}H_{26}Fe_2N_2O_3$: C, 64.24; H, 4.38; N, 4.68. Found: C, 64.46; H, 4.19; N, 4.50.

4.1.7. *N,N′*-(Ferrocenecarbonylmethyl)-2,2-dimethyl-propanediamide (9). To a suspension of α-aminoacethyl-ferrocene hydrochloride (0.418 g, 1.5 mmol) in dry THF (15 mL) dry triethyl amine (0.353 g, 3.5 mmol) was added and the mixture was stirred at room temperature and under nitrogen for 5 min. Then, a solution of dimethylmalonyl chloride (0.127 g, 0.75 mmol) in the same solvent (5 mL) was added dropwise and the reaction mixture was stirred at room temperature for 6 h. Afterwards, the solution was concentrated under vacuum and the residue was chromatographed on a silica gel column with EtOAc/CH_2Cl_2, 7/3, as eluent to give (**9**) in 83% yield; mp 183–185°C. IR (CH_2Cl_2) cm^{-1}: 3384, 3324, 1659, 1531, 1457, 1381, 1258, 1110.^1H NMR ($CDCl_3$): δ 1.60 (s, 6H), 4.28 (s, 10H), 4.52–4.57 (m, 8H), 4.83 (s, 4H), 7.68 (bs, 2H). ^{13}C NMR ($CDCl_3$): δ 24.15, 47.13, 50.08, 68.91, 70.22, 72.77, 75.66, 174.45, 198.99. EIMS *m/z*: (rel intensity): 582 (M^+, 100), 517 (82), 455 (32), 213 (52), 185 (40), 129 (39), 121 (41). Anal. Calcd for $C_{29}H_{30}Fe_2N_2O_4$: C, 59.82; H, 5.19; N, 4.81. Found: C, 59.61; H, 5.30; N, 4.98.

4.1.8. Reaction of $Pd_2(dba)_3$ with dimethyl acetylenedicarboxylate (dmad) in the presence of ligand (7). Into an acetone solution (5 mL) of $Pd_2(dba)_3$ (0.13 g, 0.146 mmol) and ligand (**7**) (0.08 g, 0.146 mmol), dimethyl acetylenedicarboxylate (dmad) (0.054 g, 0.38 mmol) was added. After 6 h stirring at room temperature crystals of palladacyclopendiene complex (**10**) precipitated. This complex was purified by column chromatography on a silica gel column, using acetone/*n*-hexane, 4/6, as eluent and crystallized in acetone/ethyl ether (1/2); mp 168–170°C. IR (Nujol) cm^{-1}: 1719, 1701, 1627, 1346, 1213, 1167. ^1H NMR (acetone-d_6): δ 2.25 (s, 6H). 3.58 (s, 6H), 3.64 (s, 6H), 4.20 (s, 10H), 4.44 (s, 4H), 4.75 (s, 4H), 7.15 (s, 2H). ^{13}C NMR (acetone-d_6): δ 26.45, 41.56, 51.86, 51.91, 67.96, 71.27, 71.34, 72.27, 121.46, 145.18, 154.10, 164.40, 165.25, 165.68, 174.89. FABMS *m/z*: (rel intensity): 937 (M^++1, 46), 546 (86). Anal. Calcd for $C_{41}H_{38}Fe_2N_2O_{10}Pd$: C, 52.56; H, 4.09; N, 2.99. Found: C, 52.48; H, 3.88; N, 3.05.

4.1.9. General procedure for the preparation of 1,1′-bis(2-aryloxazol-5-yl)ferrocenes (11). To a solution of 1,1′-bis(α-azidoacetyl)ferrocene **3** (0.3 g, 0.85 mmol) and the appropriate aroyl chloride (2.2 mmol) in dry THF (20 mL), a solution of triphenylphospine (0.49 g, 1.87 mmol) in the same solvent (10 mL) was slowly dropped, at room temperature and under nitrogen. The mixture was stirred for 24 h and then, evaporated to dryness under reduced pressure. The crude product was chromatographed on a silica gel column, using EtOAc/*n*-hexane, 2/1, as eluent. After evaporating to dryness, the product was triturated in Et_2O to give (**11**).

Compound (11a). (R=CH_3). Yield: 35%; mp 179–181°C. IR (Nujol) cm^{-1}: 1612, 1498, 1447, 1423, 1131, 1117, 1103, 1022, 898, 827. ^1H NMR ($CDCl_3$): δ 2.38 (s, 6H), 4.34 (t, 4H, *J*=2.1 Hz), 4.62 (t, 4H, *J*=2.1 Hz, 4H), 6.98 (s, 2H), 7.13 (d, 4H, *J*=7.8 Hz), 7.75 (d, 4H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$): δ 21.48, 66.95, 70.21, 74.69, 122.31, 124.72, 125.94, 129.27, 149.12, 167.90. EIMS *m/z*: (rel intensity): 500 (M^+,100), 250 (4), 191 (4), 133 (4). Anal. Calcd for $C_{30}H_{24}FeN_2O_2$: C, 72.01; H, 4.83; N, 5.60. Found: C, 71.82; H, 4.70; N, 5.85.

Compound (11b). (R=OCH_3). Yield: 40%; mp 147–149°C. IR (Nujol) cm^{-1}: 1615, 1500, 1425, 1309, 1256, 1175, 1106, 1031. ^1H NMR ($CDCl_3$): δ 3.84 (s, 6H), 4.33 (s, 4H), 4.60 (s, 4H), 6.82 (d, 4H, *J*=8.8 Hz), 6.92 (s, 2H), 7.77 (d, 4H, *J*=8.8 Hz). ^{13}C NMR ($CDCl_3$): δ 55.23, 66.81, 70.03, 74.86, 113.95, 120.31, 122.36, 127.51, 148.65, 160.41, 160.84. EIMS *m/z*: (rel intensity): 532 (M^+,100), 516 (10), 266 (10), 135 (9), 77 (9), 69 (13). Anal. Calcd for $C_{30}H_{24}FeN_2O_4$: C, 67.68; H, 4.54; N, 5.26. Found: C, 67.49; H, 4.30; N, 5.36.

Compound (11c). (R=H). Yield: 37%; mp 206–208°C. IR (Nujol) cm^{-1}: 1602, 1578, 1514, 1445, 1409, 1020, 946, 827, 737. ^1H NMR ($CDCl_3$): δ 4.35 (t, 4H, *J*=1.8 Hz), 4.63 (t, 4H, *J*=1.8 Hz), 6.97 (s, 2H), 7.34–7.36 (m, 6H), 7.87–7.88 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 67.33, 70.62, 74.81, 122.88, 126.22, 127.71, 128.89, 130.10, 149.85, 160.70. EIMS *m/z*: (rel intensity): 472 (M^+,82), 213(96), 185(100), 129(81), 121(45), 77(53), 56(50). Anal. Calcd for $C_{28}H_{20}FeN_2O_2$: C, 71.20; H, 4.27; N, 5.93. Found: C, 71.31; H, 4.19; N, 5.77.

4.1.10. 1-Chloroacetyl-1′-(2-*p*-nitrophenyloxazol-5-yl)-ferrocene (13). It was prepared in 30% yield as described above for (**11**), using *p*-nitrobenzoyl chloride (0.54 g, 2.94 mmol); mp 164–166°C. IR (Nujol) cm^{-1}: 1683, 1595, 1547, 1516, 1457, 1338, 1239, 1112, 1069. ^1H NMR ($CDCl_3$): δ 4.28 (s, 2H), 4.50 (s, 2H), 4.58 (s, 2H), 4.77 (s, 2H), 4.81 (s, 2H), 7.22 (s, 1H), 8.25 (d, *J*=7.5 Hz, 2H), 8.36 (d, *J*=7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 45.82, 67.38, 70.72, 71.02, 73.92, 74.51, 76.96, 123.91, 124.04, 126.63, 132.40, 148.20, 150.74, 158.63, 194.00. EIMS *m/z*: (rel intensity): 452 (M^++2, 38), 450 (M^+,84), 344 (51), 253 (39), 237 (95), 207 (100), 169 (48), 152 (60), 91 (75), 77 (97), 56 (84). Anal. Calcd for $C_{21}H_{15}ClFeN_2O_4$: C, 55.97; H, 3.35; N, 6.22. Found: C, 55.85; H, 3.50; N, 6.12.

4.2. General procedure for the preparation of 2-Aryl-5-ferrocenyl oxazoles (14)

To a solution of α-azidoacetyl ferrocene **1** (0.35 g, 1.3 mmol) and the appropriate aroyl chloride (1.5 mmol) in anhydrous diethyl ether (15 mL) a solution of triphenylphosphine (0.43 g, 1.63 mmol) in the same solvent (10 mL) was added dropwise at room temperature and under nitrogen. The reaction mixture was stirred for 24 h and the ethereal solution was concentrated under reduced pressure and chromatographed on a silica gel column with CH_2Cl_2/EtOAc, 20/1, as eluent to give the corresponding ferrocenyl–oxazoles **14** which were recrystallized from diethyl ether.

4.2.1. Compound (14a). (R=H): yield: 35%; mp 92–94°C. IR (Nujol) cm^{-1}: 1615, 1604, 1549, 1490, 1450, 1125, 1109, 1024, 963, 872, 775. ^1H NMR ($CDCl_3$): δ 4.14 (s, 5H), 4.35 (s, 2H), 4.66 (s, 2H), 7.06 (s, 1H), 7.45–7.49 (m, 3H), 8.05–8.10 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 65.95, 69.10, 69.62, 72.58, 121.99, 125.98, 127.72, 128.78, 129.90, 151.42, 160.20. EIMS *m/z*: (rel intensity): 329 (M^+, 100), 273 (39), 208 (33), 121 (75), 77 (64), 56 (50). Anal. Calcd for $C_{19}H_{15}FeNO$: C, 69.33; H, 4.59; N, 4.25. Found: C, 69.52; H, 4.40; N, 4.18.

4.2.2. Compound (14b). (R=CH_3): yield: 45%; mp 109–112°C. IR (Nujol) cm^{-1}: 1616, 1498, 1447, 1412, 1109, 1026, 871. ^1H NMR ($CDCl_3$): δ 2.41 (s, 3H), 4.14 (s, 5H), 4.34 (t, 2H, *J*=1.7 Hz), 4.65 (t, 2H, *J*=1.7 Hz), 7.04 (s, 1H), 7.28 (d, 2H, *J*=8.1 Hz), 7.96 (d, 2H, *J*=8.1 Hz). ^{13}C NMR ($CDCl_3$): δ 21.47, 65.90, 69.02, 69.60, 72.74, 121.86, 125.04, 125.95, 129.47, 140.14, 151.00, 160.43. EIMS *m/z*: (rel intensity): 343 (M^+, 100), 287 (55), 222 (67), 121 (82), 91 (62), 77 (78), 56 (70). Anal. Calcd for $C_{20}H_{17}FeNO$: C, 69.99; H, 4.99; N, 4.08. Found: C, 69.80; H, 4.74; N, 4.19.

4.2.3. Compound (14c). (R=OCH_3): yield: 31%; mp 88–91°C. IR (Nujol) cm^{-1}: 1616, 1498, 1456, 1439, 1426, 1310, 1262, 1170, 1107, 1031, 846, 812. ^1H NMR ($CDCl_3$): δ 3.88 (s, 3H), 4.14 (s, 5H), 4.34 (t, 2H, *J*=1.8 Hz), 4.65 (t, 2H, *J*=1.8 Hz), 7.00 (d, 2H, *J*=9.0 Hz), 7.02 (s, 1H), 8.00 (d, 2H, *J*=9.0 Hz). ^{13}C NMR ($CDCl_3$): δ 55.38, 65.84, 68.99, 69.60, 72.83, 114.22, 120.55, 121.74, 127.64, 150.72, 160.31, 161.06. EIMS *m/z*: (rel intensity): 359 (M^+, 100), 344 (29), 121 (25), 77 (14), 56 (10). Anal. Calcd for $C_{20}H_{17}FeNO_2$: C, 66.88; H, 4.77; N, 3.90. Found: C, 66.70; H, 4.56; N, 3.78.

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