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An efficient preparation of novel ferrocenylimidazole and ferrocenyloxazolinone derivatives from β-ferrocenylvinylheterocumulenes

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Abstract

A rapid and efficient synthetic procedure has been developed to prepare new ferrocenylimidazole derivatives bearing an oxygen or sulfur atom at the 2-position in the imidazole ring. The method is based on the thermal heterocyclization of β-ferrocenylvinylcarbodiimides or related compounds such as β-ferrocenylvinylureas or β-ferrocenylvinylthioureas. A slight modification using TBAF as cyclizing agent allows the preparation of ferrocenyloxazolidinones.

Keywords: Ferrocene, Imidazoles, Oxazolinones, Aza-Wittitg reaction, X-Ray crystal structures.

In the last few years, considerable attention has been paid to molecular systems containing a ferrocene unit and a fragment able to act as a ligand, with a well-defined geometry because of its fixed intramolecular spacing, towards transition-metal ions; these systems can behave either as chemical sensors [1-4] or redox-active and photoactive molecular devices [5-7].

The present work was undertaken to synthesize and characterize a range of ferrocene-containing species, in which the electron-releasing ferrocene moiety is attached to an imidazole ring by an ethylenic linkage. It is important to note that the imidazole ring possesses a high complex-forming capacity with a wide variety of transition metal compounds [8-10]. So, these kind of ligands could be of valuable interest for the construction of heterobimetallic systems in which the two metals remain sufficiently close to allow a multisite activation of organic substrate or give rise to a long metal-metal interaction.

In spite of much work devoted towards the preparation of ferrocene-substituted azoles, i.e. pyrazole [11-12] and oxazoline [13-18], methods for the preparation of ferrocenylimidazole derivatives are somewhat rare [19-20].

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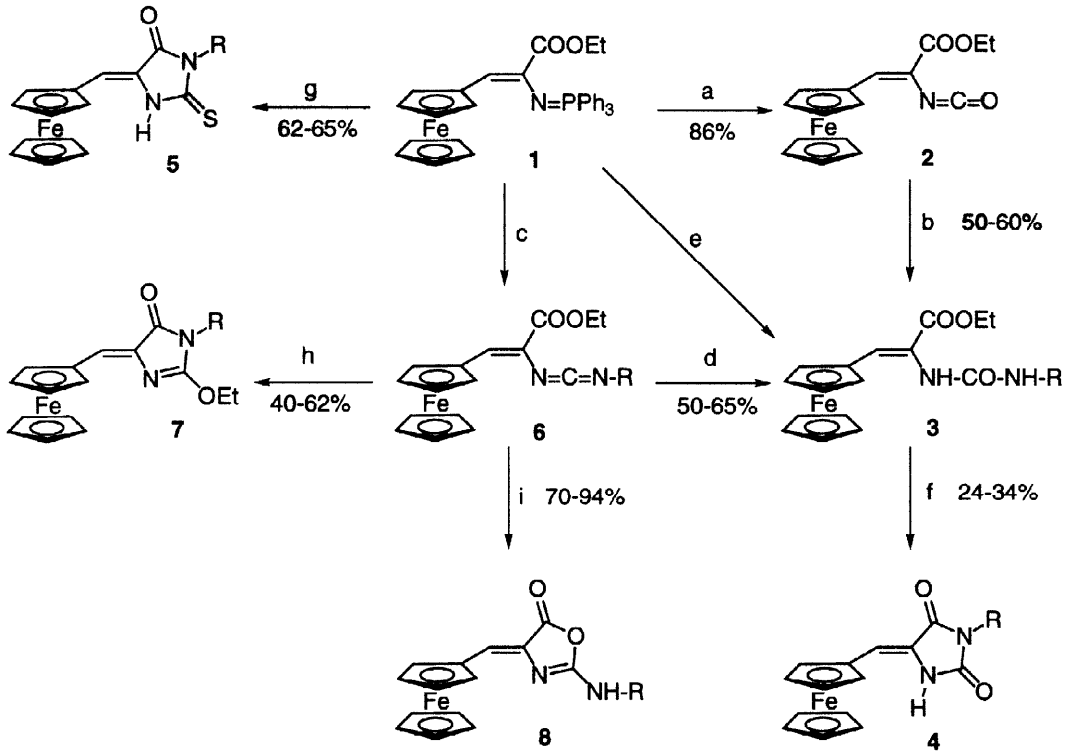
Following our work on the preparation of new ferrocene derivatives using iminophosphorane methodology [21], we now wish to report a general and efficient synthesis of a wide variety of imidazolylferrocenes. Our approach is based on the formation of β-ferrocenylvinylheterocumulenes, readily available by aza-Wittig reactions of iminophosphorane derived from β-ferrocenylvinylazides with isocyanates, carbon dioxide or carbon disulfide, and further heterocyclization.

Results

We chose to use the [(β-ferrocenylvinyl)imino]phosphorane (**1**) as a building block for the synthesis of the new imidazolylferrocenes. Compound (**1**) was obtained in 76% overall yield by Knoevenagel condensation of ferrocenecarboxaldehyde with ethylazidoacetate and further Staudinger reaction of the resulting β-ferrocenylvinylazide with triphenylphosphine [20].



Reagents and conditions: **a)** solid CO_2, 110°C, sealed tube; **b)** R-NH_2, toluene, r.t.; **c)** R-NCO, CH_2Cl_2, r.t.; **d)** 0.2M HCl, r.t.; **e)** CO_2, R-NH_2, toluene, 80°C; **f)** toluene reflux; **g)** I, CS_2, r.t.; II, R-NH_2, C_6H_6, reflux; **h)** toluene, reflux; **i)** TBAF, THF, r.t.

Scheme 1

(Vinylimino)phosphorane (**1**), reacted with solid carbon dioxide at 110°C in a sealed tube to afford the β-ferrocenylvinylisocyanate (**2**) as a crystalline solid in 86% yield [20]. Compound (**2**) was converted in good yield (50-60%) into the corresponding ureas (**3**) by reaction with aromatic primary amines in toluene at room temperature. Ureas (**3**) can also be prepared in a similar yield (50-65%) either by reaction of (vinylimino)phosphorane (**1**) with arylisocyanates and subsequent hydrolysis of the carbodiimides (**6**) formed or by passing a carbon dioxide stream through a heated at 80°C mixture of (vinylimino)phosphorane (**1**) and

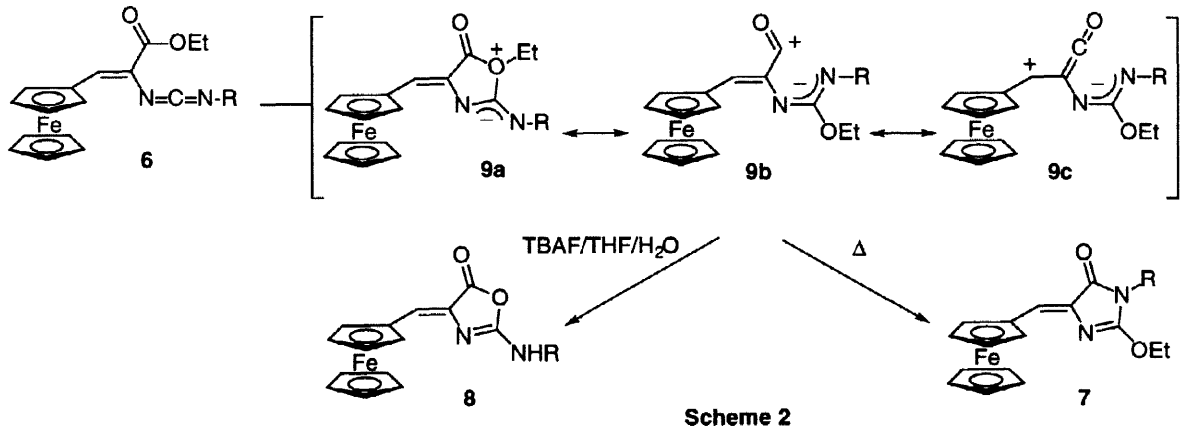
the corresponding amine. Compounds (**3**) underwent cyclization by thermal treatment to give ferrocenylmethylideneimidazolindiones (**4**) in modest yields (24-34%).

In a similar way, (vinylimino)phosphorane (**1**) provided the corresponding thioanalog (**5**) in 62% and 65% yields, by sequential treatment with carbon disulfide, primary amines and further reaction of the resulting thiourea. Whereas the ^{1}H NMR spectra of (**4**) are characteristic, that is, the ferrocenyl substituent gives rise to a five-proton singlet for the unsubstituted cycopentadienyl ring and two apparent triplets for the monosubstituted ring, the ^{1}H NMR spectra of (**5**) show a four-proton sharp singlet for the monosubstituted cyclopentadienyl ring.

(Vinylimino)phosphorane (**1**) also reacted with aromatic isocyanates in dry dichloromethane at room temperature to give the corresponding β-ferrocenylvinylcarbodiimides (**6**) which were used in the next step without further purification. When toluene solutions of (**6**) were heated in a sealed tube at 110°C for 72 h, the corresponding ferrocenylimidazoles (**7**) were obtained in yields ranging from 40% to 62% after chromatographic purification.

On the other hand, when carbodiimides (**6**) were treated with a solution of tetrabutylammonium fluoride (TBAF) in THF (1:4 molar ratio) at room temperature, the ferrocenyl 1,3-oxazolin-5-ones (**8**) were obtained after chromatographic separation, in 70% and 94% yield. When a 1:1 molar ratio was used, the corresponding urea (**3**) was found to be the major product, and when the reaction was carried out without TBAF under the same conditions, the carbodiimide (**6**) remained unchanged (Scheme 1).

Keeping in mind that β-arylvinylcarbodiimides under thermal conditions undergo pyrido annelation to give isoquinoline derivatives [22], the thermal behaviour of the closely related β -ferrocenylvinylcarbodiimides (**6**) to give (**7**) could be considered unexpected. At first, there is no reason that can explain the completely different thermal behaviour, going from the β-aryl to the β-ferrocenyl substituent, because the ferrocene undergoes electrophilic substitution under non-oxidixing conditions like an aromatic compound activated for this kind of reaction.



Scheme 2

A tentative mechanism for the conversions (**6**) → (**7**) and (**6**) → (**8**) could involve initial formation of the intermediate (**9**) promoted either thermally or by the action of the TBAF. Under thermal conditions the intermediate (**9**), in which both the negative and the positive charges are highly delocalized, could undergo ring closure across the nitrogen atom of the isourea moiety to provide (**7**). As regards the cyclization promoted by TBAF, the

intermediate (**9**) by the action of the water present in the TBAF/THF solution could afford (**8**) (Scheme 2). Two aspects could support these assumptions: first, the extraordinary stability exhibited by α-ferrocenylalkyl carbocations [23] may promote the formation of the intermediate (**9**); second, it has been reported [24, 25] that TBAF strongly increases the electrophilic character of the central carbon atom of the carbodiimide function.

The structure of compound (**4**) was further corroborated by a single-crystal X-ray difraction study. In the crystal structure of compound (**4a**) (Figure 1) (Table 1) an intermolecular NH...O interaction is observed. The pattern of the interaction contains an eight atom planar ring with two donor and two acceptors [$R_{2,2}(8)$], showing a dimeric crystal packing.

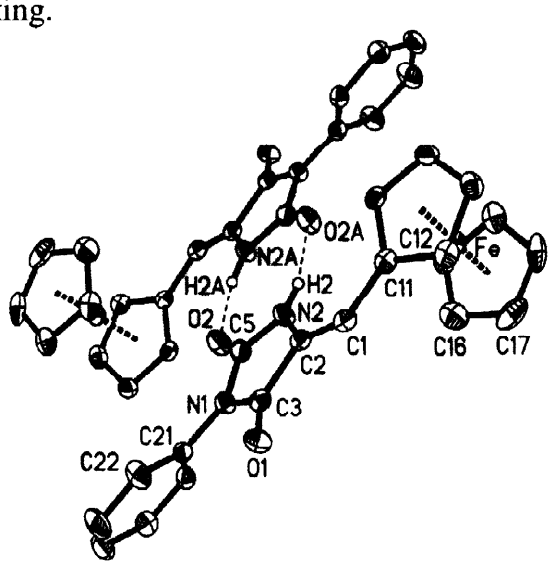


Figure 1. Diagram showing the hydrogen interaction and the labelling scheme for **4a**. Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

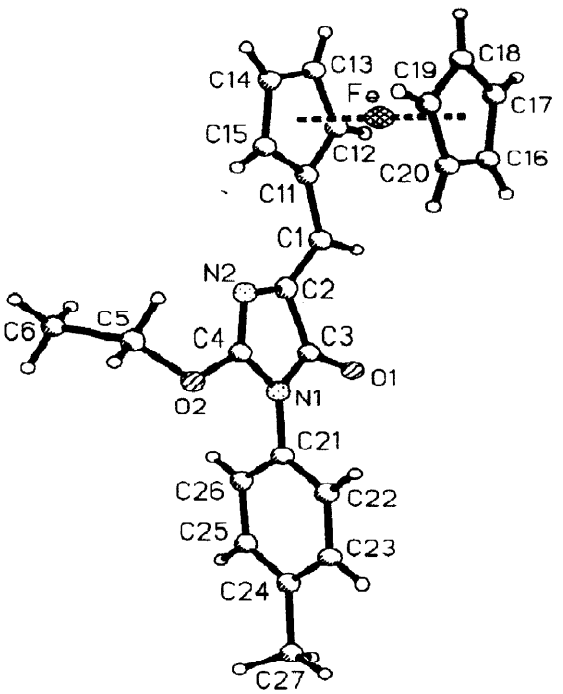


Figure 2. Labelling scheme for **7c**.

Table 1. Selected bond lengths (Å) and angles (°) for **4a**.

lengths (Å)			
N(1)-C(3)	1.395(2)	N(1)-C(5)	1.405(2)
N(2)-C(5)	1.363(3)	N(2)-C(2)	1.397(2)
O(1)-C(3)	1.207(2)	O(2)-C(5)	1.212(2)
C(1)-C(2)	1.331(3)	C(2)-C(3)	1.478(3)
angles (°)			
C(3)-N(1)-C(5)	110.6(2)	C(5)-N(2)-C(2)	111.6(2)
C(2)-C(1)-C(11)	130.3(2)	C(1)-C(2)-N(2)	131.4(2)
C(1)-C(2)-C(3)	122.9(2)	N(2)-C(2)-C(3)	105.7(2)
N(1)-C(3)-C(2)	105.3(2)	N(2)-C(5)-N(1)	106.9(2)

hydrogen bond (#: -x+1, -y-1, -z)

N(2)...O(2)#	2.824(2)	H(2)...O(2)#	2.013(19)	N(2)-H(2)...O(2)	158.1(2.0)

The highly disordered (**7c**) X ray structure makes it difficult to determine the bonding scheme in the heteronuclear ring. The bond lengths and angles (Figure 2) (Table 2) for the disordered fragment have been averaged.

Table 2 Selected bond lengths (Å) and angles (°) for **7c**

lengths (Å)			
C(1)-C(2)	1.340(10)	C(1)-C(11)	1.447(9)
C(2)-N(2)	1.400(13)	C(2)-C(3)	1.499(10)
C(3)-O(1)	1.180(12)	C(3)-N(1)	1.435(17)
N(1)-C(4)	1.365(20)	C(4)-N(2)	1.300(20)
angles (°)			
C(2)-C(1)-C(11)	126.9(7)	N(2)-C(2)-C(1)	127.2(8)
N(2)-C(2)-C(3)	109.1(8)	C(1)-C(2)-C(3)	121.9(8)
N(1)-C(3)-C(2)	102.4(9)	C(3)-N(1)-C(4)	106.5(10)
N(2)-C(4)-N(1)	116.3(13)	C(4)-N(2)-C(2)	105.5(10)

Conclusions

The results reported here clearly show that β-ferrocenylvinyl heterocumulenes (carbodiimides, isocyanates and isothiocyanates), easily prepared by aza-Wittig reactions of the iminophosphorane derived from β-ferrocenylvinylazide, are useful building blocks for the preparation of a variety of novel ferrocenylimidazole derivatives bearing an oxygen or sulfur atom at the 2-position, in the imidazole ring. β-Ferrocenylvinylcarbodiimides are also efficient precursors for the preparation of ferrocenyloxazolinone derivatives.

Experimental

General Methods

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. 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). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer or a Fisson AUTOSPEC 500 VG. Microanalyses were performed on a Perkin-Elmer 240C instrument.

X-ray Analysis

Crystals of (**4a**) and (**7c**) were mounted in inert oil on a glass fibre and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment). The structures were solved by the heavy atom method (**4a**) or by direct methods (**7c**) and refined anisotropically on F^2 [program SHELXL-93] [26].

For compound (**4a**) unit cell parameters were determined from a least-squares fit of 75 accurately centred reflections ($9.8 < 2\theta < 24.6$). The hydrogen atom of the NH group was located in a difference Fourier synthesis and refined with a restrained N-H bond length.

Other hydrogen atoms were included using a riding model. Maximun $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 0.23$ eÅ^3.

Unit cell parameters of (**7c**) were determined from a least-squares fit of 43 accurately centred reflections ($8.8 < 2\theta < 24.5$). The N2-C4(OEt)-N1(p-tol) fragment is disordered over two sites (50% occupancy). The hydrogen atoms were included using a riding model. Maximun $\Delta/\sigma = 0.001$, maximum $\Delta\rho = 0.92$ eÅ^3.

The program use the neutral atom scattering factors, Δf' and Δf" and absorption coefficients from International Tables for Crystallography [27].

General procedure for the preparation of ethyl 3-ferrocenyl-2-(N'-arylureido)acrylate, **3**.

Method A: To a solution of iminophosphorane (**1**) (0.35 g, 0.626 mmol) in anhydrous THF (10 ml) a solution of the appropriate arylisocyanate was added dropwise under nitrogen and the mixture was stirred at room temperature until the corresponding carbodiimide was completely formed. Then, 0.2M HCl (4 ml) was added and stirring continued for 5 h. The solvent was removed under reduced pressure and the residual product was chromatographed on a silica gel column with ethyl acetate/n-hexane (1:2) as eluent, to give the corresponding ureas as red solids which were crystallized from ethanol.

Method B: To a solution of the appropriate amine (5.4 mmol) in dry toluene (15 ml), with a continuous stream of CO_2, a solution of the iminophosphorane (**1**) (0.3 g, 0.54 mmol), in the same solvent (10 ml), was added. The reaction mixture was heated at 80°C for 5 h yielding the corresponding urea (**3**), which was isolated as above.

Method C: To a solution of isocyanate (**2**) (0.3 g, 0.9 mmol) in dry toluene (15 ml) an equimolar amount of the appropriate amine was added. The reaction mixture was stirred at room temperature for 12 h to give the corresponding urea (**3**), which was isolated as above.

3a: (R= C_6H_5), m.p. 168-171°C (red prisms); (65%, A; 60%, B; 62%, C) (Found: C, 62.95; H, 5.44; N, 6.58. $C_{22}H_{22}FeN_2O_3$ requires; C, 63.17; H, 5.30; N, 6.70). i.r (Nujol): 3312, 1725, 1648, 1603, 1496, 1262, 1191 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 1.34 (t, 3H, J=6.9 Hz), 4.17 (s, 5H), 4.25 (q, 2H, J= 6.9 Hz), 4.43 (bs, 2H), 4.66 (bs, 2H), 7.03 (m, 2H), 7.16-7.32 (m, 4H), 7.40 (s, 1H), 8.80 (bs, 1H); ^{13}C n.m.r. δ (DMSO d_6): 14.30, 61.62, 69.88, 70.95, 71.53, 76.67, 120.36, 123.64, 128.98, 129.02, 136.37, 138.24, 153.55 (C=O), 165.72 (C=O); m/z(%): 418 (M$^+$, 56), 372 (100), 307 (84), 121 (57), 77 (31).

3b: (R= *m*-CH_3-C_6H_4), m.p. 176-178°C (red prisms); (50%, A; 55%, B; 51% C) (Found: C, 63.76; H, 5.49; N, 6.60. $C_{22}H_{24}FeN_2O_3$ requires; C, 63.90; H, 5.60; N, 6.48). i.r. (Nujol): 3340, 1725, 1650, 1613, 1562, 1259, 1190 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 1.24 (t, 3H, J=7.0 Hz), 2.26 (s, 3H), 4.14-4.21 (m, 7H), 4.44 (bs, 2H), 4.69 (bs, 2H), 6.77 (d, 1H, J=7.0 Hz), 7.09 (s, 1H), 7.13-7.30 (m, 3H), 7.43 (s, 1H), 8.77 (s, 1H); ^{13}C n.m.r. δ (DMSO d_6): 14.16, 21.14, 60.29, 69.32, 70.23, 70.31, 76.45, 115.00, 118.32, 122.27, 123.00, 128.53, 132.62, 137.83, 139.82, 152.90 (C=O), 165.12 (C=O); m/z(%):432 (M$^+$, 5), 387 (61), 325 (58), 321 (43), 299 (43), 225 (18), 152 (18), 133 (100), 121 (57), 106 (78), 104 (48), 91 (30), 77 (43).

3c: (R= *p*-Cl-C_6H_4) m.p. 89-92°C (red prisms); (57%, A; 60%, B; 50% C) (Found: C, 58.57; H, 4.48; N, 6.22. $C_{22}H_{21}FeClN_2O_3$ requires; C, 58.37; H, 4.68; N, 6.19). i.r. (Nujol): 3333, 1708, 1656, 1555, 1486, 1270, 1192 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 1.24 (t, 3H, J=7.2 Hz), 4.13-4.20 (m, 7H), 4.44 (bs, 2H), 4.70 (bs, 2H), 7.14 (s, 1H), 7.31 (d, 2H, J=9.0 Hz), 7.50 (d,

2H, J=9.0 Hz), 7.52 (s, 1H), 8.99 (bs, 1H); ^{13}C n.m.r. δ (DMSO d_6): 14.22, 60.39, 69.41, 70.37, 70.46, 76.42, 119.50, 122.80, 125.13, 128.57, 133.47, 139.03, 153.01 (C=O), 165.15 (C=O); m/z(%):454 (M^++ 2, 10), 452 (M^+, 32), 406 (100), 341 (83), 325 (31), 299 (68), 225 (25), 153 (40), 127 (23), 121 (61), 104 (22), 77 (17).

General procedure for the preparation of 3-aryl-5-ferrocenylmethylidenimidazolin-2,4-diones, **4**.

A solution of the appropriate urea **3** (1 mmol) in dry toluene (40 ml) was heated at reflux temperature for 24 h. Once the mixture had reached room temperature, the solvent was evaporated under reduced pressure and the crude product was cromatographed on a silica gel column with ethyl acetate/n-hexane (1:2) as eluent to give **4**, which was crystallized from EtOH.

4a: (R= C_6H_5), m.p. 231-234°C (d) (red prisms); (34%); (Found: C, 64.48; H, 4.20; N, 7.60. $C_{20}H_{16}FeN_2O_2$ requires; C, 64.54; H, 4.33; N, 7.53). i.r. (Nujol): 3254, 1759, 1712, 1671, 1401, 1243 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$): 4.22 (s, 5H), 4.47 (t, 2H, J=1.8 Hz), 4.52 (t, 2H, J=1.8 Hz), 6.72 (s, 1H), 7.27-7.52 (m, 5H), 8.57 (bs, 1H) ; ^{13}C n.m.r. δ ($CDCl_3$): 69.27, 69.74, 71.01, 76.36, 114.02, 123.13, 126.07, 128.18, 129.09, 132.43, 156.85 (C=O), 162.25 (C=O); m/z(%): 372 (M^+, 100), 307 (64), 213 (42), 121 (35), 93 (88).

4b: (R= *m*-CH_3-C_6H_4), m.p. 236-240°C (d) (red prisms); (24%); (Found: C, 65.54; H, 4.90; N, 6.97. $C_{21}H_{18}FeN_2O_2$ requires; C, 65.31; H, 4.70; N, 7.25). i.r. (Nujol): 3255, 1761, 1715, 1663, 1408, 1246 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 2.25 (s, 3H), 4.10 (s, 5H), 4.36 (t, 2H, J=1.8 Hz), 4.77 (t, 2H, J=1.8 Hz), 6.38 (s, 1H), 7.20-7.40 (m, 4H), 8.67 (bs, 1H); ^{13}C n.m.r. δ (DMSO-d_6): 20.54, 69.06, 69.43, 70.16, 76.00, 115.00, 123.22, 123.65, 126.98, 128.16, 128.27, 131.57, 137.59, 153.35 (C=O), 162.19 (C=O); m/z(%): 386 (M^+, 100), 321 (95), 254 (6), 225 (6), 160 (14), 121 (42), 91 (14).

4c: (R= *p*-Cl-C_6H_4), m.p. 90-92°C (red prisms); (34%); (Found: C, 59.24; H, 3.60; N, 6.71. $C_{20}H_{15}FeClN_2O_2$ requires; C, 59.07; H, 3.72; N, 6.89). i.r.(Nujol): 3220, 1760, 1722, 1666, 1504, 1462, 1410, 1248, 1170 cm^{-1}; ^{1}H n.m.r. δ (DMSO-d_6): 4.21 (s, 5H), 4.48 (bs, 2H), 4.88 (bs, 2H), 6.51 (s, 1H), 7.51 (d, 2H, J=8.8 Hz), 7.58 (d, 2H, J=8.8 Hz), 10.50 (bs, 1H); ^{13}C n.m.r. δ (DMSO-d_6): 69.32, 69.69, 70.45, 76.12, 112.71, 123.27, 128.27, 128.67, 130.84, 132.06, 153.02 (C=O), 162.20 (C=O); m/z(%); 408 (M^++2, 63), 406 (100), 343 (46), 341 (82), 153 (5), 121 (39).

General procedure for the preparation of 3-aryl-5-ferrocenylmethyliden-2-thioxoimidazolin-4-one, **5**.

A solution of iminophosphorane **1** (0.30 g, 0.54 mmol) in CS_2 (3ml) was stirred for 12 h at room temperature. Afterwards the solvent was removed under vacuum and the crude product was solved in anhydrous benzene (20 ml). Then, the apropriate aniline (0.54 mmol) was added to the solution, which was heated at reflux temperature for 16 h. After cooling the solvent was evaporated under reduced pressure, and the resulting crude was cromatographed on a silica gel column using athylacetate/n-hexane (1:2) as eluent to give **5** which was crystallized from dichloromethane/ethyl ether (1:3).

5a: (R=*p*-CH_3O-C_6H_4) m.p. 204-206°C (red prisms); (62%); (Found: C, 60.17; H, 4.29; N, 6.82. $C_{21}H_{18}FeN_2O_2S$ requires; C, 60.30; H, 4.34; N, 6.70). i.r. (Nujol) 3200, 1718, 1650, 1516, 1460, 1256, 1170 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$):3.84 (s, 3H), 4.25 (s, 5H), 4.56 (s, 4H), 6.73 (s, 1H), 7.01 (d, 2H, J=8.9 Hz), 7.29 (d, 2H, J=8.9 Hz), 8.83 (bs, 1H).); ^{13}C-n.m.r. δ ($CDCl_3$): 55.43, 69.75, 70.01, 71.88, 75.86, 114.44, 116.60, 123.76, 125.27, 129.28, 159.88, 162.78 (C=O), 176.76 (C=S); m/z(%):418 (M^+, 100), 386 (18), 353 (36), 321 (14), 225 (22), 121 (24), 77 (16).

5b: (R=*p*-CH_3-C_6H_4) m.p. 188-191°C (red prisms); (65%); (Found: C, 62.71; H, 4.30; N, 6.77. $C_{21}H_{17}FeN_2OS$ requires; C, 62.86; H, 4.27; N, 6.98). i.r.(Nujol) 3400, 1720, 1660, 1520, 1484, 1249, 1173 cm^{-1}; ^1H-n.m.r. δ ($CDCl_3$): 2.41 (s, 3H), 4.24 (s, 5H), 4.55 (s, 4H), 6.72 (s, 1H), 7.27 (d, 2H, J=8.0 Hz), 7.30 (d, 2H, J=8.0 Hz), 8.88 (bs, 1H); ^{13}C-n.m.r. δ ($CDCl_3$): 21.27, 69.84, 70.10, 71.85, 75.88, 116.50, 123.80, 127.97, 129.90, 130.12, 139.25, 162.70 (C=O), 176.57 (C=S); m/z(%):401 (M^+, 100), 337 (64), 225 (14). 121 (35), 91 (14).

General procedure for the preparation of 3-aryl-2-ethoxy-5-ferrocenylmethylidenimidazolin-4-one, **7**.

To a solution of iminophosphorane **1** (0.55 g, 0.98 mmol) in anhydrous dichloromethane (20 ml) a solution, in the same solvent, of an equimolar amount of the apropriate arylisocyanate was added. The reaction mixture was stirred at room temperature under nitrogen until the corresponding carbodiimide was completely formed. The solvent was then evaporated using a stream of dry nitrogen, and the crude was then solved in anhydrous toluene (10 ml) and transfered into a sealed tube where it was heated at 115°C for 72 h. On cooling the solvent was evaporated under reduced pressure and the residual product was cromatographed on a silica gel column with ethyl acetate/n-hexane (1:3) as eluent to give **7** which was crystallized from ethanol.

7a: (R=C_6H_5) m.p. 130-133°C (red prisms); (39%); (Found: C, 65.89; H, 5.15; N, 6.79. $C_{21}H_{20}FeN_2O_2$ requires; C, 66.02; H, 5.04; N, 7.00). i.r.(Nujol): 1735, 1651, 1593, 1504, 1431, 1292, 1223 cm^{-1}; ^1H-n.m.r.δ ($CDCl_3$): 1.45 (t, 3H, J=7.2 Hz), 4.18 (s, 5H), 4.47 (t, 2H, J=1.8 Hz), 4.58 (q, 2H, J=7.2 Hz), 4.97 (t, 2H, J=1.8 Hz), 6.98 (s, 1H), 7.30-7.46 (m, 5H); ^{13}C n.m.r. δ ($CDCl_3$): 14.28, 65.75, 69.59, 71.02, 71.22, 77.64, 125.29, 125.86, 127.59, 128.94, 132.39, 135.05, 158.82, 167.17(C=O); m/z(%): 400 (M^+, 100), 372 (33), 335 (17), 307 (54), 121 (76), 119 (26).

7b: (R=*p*-CH_3O-C_6H_4) m.p. 227-229°C (red prisms); (60%) (Found: C, 64.36; H, 5.20; N, 6.38. $C_{23}H_{22}FeN_2O_3$ requires; C, 64.20; H, 5.15; N, 6.51). i.r.(Nujol): 1729, 1655, 1587, 1519, 1464, 1260 cm^{-1}; ^1H-n.m.r. δ ($CDCl_3$):1.45 (t, 3H, J=7.2 Hz), 3.83 (s, 3H), 4.18 (s, 5H), 4.46 (t, 2H, J=1.8 Hz), 4.60 (q, 2H, J=7.2 Hz), 4.97 (t, 2H, J=1.8 Hz), 6.96 (s, 1H), 6.97 (d, 2H, J=9 Hz), 7.27 (d, 2H, J=9 Hz); ^{13}C-n.m.r. δ ($CDCl_3$): 14.32, 55.45, 65.70, 69.70, 70.98, 71.15, 77.69, 114.19, 125.10, 127.34, 127.47, 135.21, 158.91, 159.10, 167.52 (C=O); m/z(%): 430 (M^+, 14), 402 (6), 365 (3), 337 (17), 270 (10), 224 (8), 121 (100), 107 (5).

7c: (R=*p*-CH_3-C_6H_4) m.p. 206-208°C (red prisms); (62%): (Found: C, 66.45; H, 5.29; N, 6.90. $C_{23}H_{22}FeN_2O_2$ requires; C, 66.68; H, 5.35; N, 6.76). i.r.(Nujol): 1727, 1664, 1590, 1520, 1298; ^1H-n.m.r. δ ($CDCl_3$):1.35 (t, 3H, J=6.9 Hz), 2.30 (s, 3H), 4.09 (s, 5H), 4.38 (t, 2H, J=1.8 Hz), 4.53 (q, 2H, J=6.9 Hz), 4.88 (t, 2H, J=1.8 Hz), 6.80 (s, 1H), 7.15 (d, 2H, J=9

Hz), 7.19 (d, 2H, J=9 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 14.50, 21.24, 66.23, 70.10, 71.52, 71.62, 78.18, 124.65, 126.28, 129.85, 130.32, 135.82, 138.21, 159.56, 167.55 (C=O); m/z(%): 414 (M^+, 100), 386 (18), 349 (11), 321 (32), 254 (8), 224 (9), 121 (20), 91 (14).

7d: (R=*p*-Cl-C_6H_4) m.p. 128-131°C (red prisms); (40%); (Found: C, 60.54; H, 4.36; N, 6.29. $C_{22}H_{19}FeClN_2O_2$ requires; C, 60.79; H, 4.41; N, 6.44). i.r.(Nujol): 1728, 1647, 1597, 1491, 1435, 1329, 1298, 1155 cm^{-1}; ^{1}H n.m.r.δ ($CDCl_3$): 1.46 (t, 3H, J=7.2 Hz), 4.19 (s, 5H), 4.48 (t, 2H, J=1.8 Hz), 4.62(q, 2H, J=7.2 Hz), 4.97 (t, 2H, J=1.8 Hz), 6.98 (s, 1H), 7.35 (d, 2H, J=8.7 Hz), 7.41 (d, 2H, J=8.7 Hz); ^{13}C n.m.r. δ ($CDCl_3$): 14.30, 65.90, 69.70, 71.20, 71.30, 77.50, 125.91, 127.01, 128.83, 129.18, 131.01, 133.27, 158.23, 166.90(C=O); m/z(%): 436 (M^++2, 37), 434 (M^+, 100), 408 (10), 406 (30), 369 (11), 343 (12), 341 (40), 121 (82).

7e: (R=C_6H_5-CH_2) m.p. 163-164°C (red prisms); (43%); (Found: C, 66.53; H, 5.20; N, 6.51. $C_{23}H_{22}FeN_2O_2$ requires; C, 66.68; H, 5.35; N, 6.76). i.r.(Nujol): 1725, 1654, 1594, 1501, 1327, 1295, 1228 cm^{-1}; ^{1}H n.m.r.δ ($CDCl_3$): 1.42 (t, 3H, J=7.2 Hz), 4.14 (s, 5H), 4.42 (t, 2H, J=1.8 Hz), 4.54 (q, 2H, J=7.2 Hz), 4.69 (s, 2H), 4.91 (t, 2H, J=1.8 Hz), 6.88 (s, 1H), 7.27-7.37 (m, 5H); ^{13}C n.m.r. δ ($CDCl_3$): 14.30, 42.86, 65.39, 69.53, 70.85, 71.10, 77.64, 124.62, 127.63, 128.09, 128.53, 135.66, 136.45, 159.93, 168.04 (C=O); m/z(%): 414 (M^+, 100), 386 (39), 349 (24), 321 (42), 253 (12), 225 (7), 121 (40), 91(64).

General procedure for the preparation of 2-arylamino-4-ferrocenylmethyliden-1,3-oxazolin-5-ones **8**.

To a mixture of the iminophosphorane **1** (0.35 g, 0.626 mmol), anhydrous THF (20 ml), anhydrous $MgSO_4$ (1 g) and anhydrous Na_2SO_4 (1 g), a solution of an equimolar amount of the appropriate isocyanate, in the same solvent (5 ml), was added under nitrogen. The resultant mixture was stirred at room temperature for 1 h. 1M TBAF in THF (2.5 ml, 2.5 mmol) was added and stirring was continued until the carbodiimide band had completely disappeared from the IR spectra. Then, the solvent was removed under reduced pressure and the crude was poured into Na_2HPO_4 buffer (pH 7, 15 ml), extracted with ethyl acetate (3x25 ml) and the organic layers were dried over anhydrous $MgSO_4$. After filtration the solution was concentrated to dryness and the crude product was cromatographed on a silica gel column, using ethyl acetate/n-hexane (1/2) as eluent to give **8** which was recrystallized from ethyl ether/n-hexane (1/3).

8a: (R= C_6H_5) m.p. 125-128°C (red prisms); (94%); (Found: C, 64.46; H, 4.22; N, 7.39. $C_{20}H_{16}FeN_2O_2$ requires; C, 64.54; H, 4.33; N, 7.53). i.r.(Nujol): 3242, 1765, 1725, 1670, 1411, 1243, 1125 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 4.21 (s, 5H), 4.47 (t, 2H, J=1.8 Hz), 4.88 (t, 2H, J=1.8 Hz), 6.50 (s, 1H), 7.44-7.51 (m, 5H), 10.47 (s, 1H); ^{13}C n.m.r. δ (DMSO d_6): 69.51, 69.87, 70.61, 76.43, 112.08, 123.65, 126.92, 127.96, 128.89, 132.12, 153.71, 162.62 (C=O); m/z(%): 372 (M^+, 100), 307 (78), 251 (9), 240 (7), 224 (8), 160 (16), 148 (16), 134 (14), 122 (46), 104 (15), 91 (7), 77 (21).

8b: (R= *p*-CH_3-C_6H_4) m.p. 224-226°C (red prisms); (70%); (Found: C, 65.43; H, 4.59; N, 7.41. $C_{21}H_{18}FeN_2O_2$ requires; C, 645.31; H, 4.70; N, 7.25). i.r.(Nujol): 3240, 1755, 1712, 1664, 1518, 1411, 1244 cm^{-1}; ^{1}H n.m.r.δ (DMSO d_6): 2.36 (s, 3H), 4.20 (s, 5H), 4.46 (t, 2H, J=1.8 Hz), 4.87 (t, 2H, J=1.8 Hz), 6.48 (s, 1H), 7.31 (s, 4H), 10.41 (s, 1H); ^{13}C n.m.r. δ (DMSO d_6): 21.10, 69.26, 69.61, 70.34, 76.22, 111.65, 123.44, 126.48, 129.10, 129.27,

137.18, 153.54, 162.41 (C=O); m/z(%):386 (M^+, 100), 322 (40), 254 (7), 225 (7), 193 (7), 160 (18), 133 (13), 121 (43), 104 (18), 91 (19), 77 (17).

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