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Preparation and heterocyclization reactions of ferrocenylazido ketones. Useful building blocks for the synthesis of ferrocenyl-substituted azaheterocycles

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Abstract

Several kinds of ferrocenylaryl ketones bearing an azido functionality at the *ortho*-position of the aryl ring have been prepared and they have proven to be useful building blocks for the synthesis of azaheterocycles. Thus, thermally induced azide decomposition of these compounds allows the formation of ferrocene-substituted 2,1-benzisoxazoles and indoles. Moreover, the Staudinger reaction with triphenylphosphine followed by aza-Wittig reaction of the resulting iminophosphorane with isocyanates provides access to ferrocene-substituted quinolines and quinazolinones. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocene-substituted azaheterocycles; Azide decomposition; Iminophosphorane; aza-Wittig reaction; Microwave irradiation

1. Introduction

Incorporation of a ferrocene moiety into an organic molecule imparts the chemical and physicochemical properties that are absent or little manifested in the parent substance. Ferrocene-containing compounds often possess unexpected biological activity which is rationalized as being due to their different membrane-permeation properties an anomalous metabolism, e.g. a ferrocenyl derivative of hydroxytamoxifen has been prepared as an estradiol receptor site-directed cytotoxic agent and tested against a human breast cancer cell line [1]. On the other hand, considerable attention has been paid in the last few years to systems containing a ferrocene unit and a heterocyclic fragment able to act as a ligand, with a well-defined geometry because of its fixed intramolecular spacing, toward transition-metal ions. These kind of ligands are of valuable interest for the construction of heterobimetallic systems, which can behave either as chemical sensors [2] or as redox-active and photoactive molecular devices [3]. In this context we have recently reported the preparation and structural characterization of several ferrocene-containing imidazoles bearing one, two or three ferrocene subunits. They were prepared from β-ferrocenylvinyl heterocumulenes, which in turn were available by aza-Wittig reactions of the [β-(ferrocenylvinyl)amino]phosphorane with carbon dioxide, carbon disulfide or isocyanates [4,5].

The present work is undertaken for the synthesis of several ferrocenyl-substituted azaheterocycles such as indole, quinoline, 2,1-benzisoxazole (anthranil) and quinazoline by using the iminophosphorane methodology [6]. We chose the use of the arylferrocenylketone **1**, 1-aryl-3-ferrocenylpropenone **2** and the isomeric 3-aryl-1-ferrocenylpropenone **3** as building blocks for the synthesis of the new ferrocene derivatives. The closely related ferrocenyl derivatives Fec–CO–CH=CH–X (X = H, Ph) and Fec–CH=CH–Y (Y=COMe, COPh, NO_2) have been previously prepared and tested as dienophiles in Diels–Alder reactions under strong acidic conditions [7,8].

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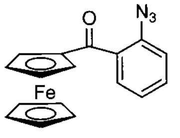

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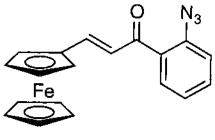

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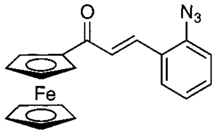

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2. Results and discussion

Acylation of ferrocene with *o*-azidobenzoyl chloride [9] in the presence of aluminum trichloride in dry dichloromethane at room temperature (r.t.) afforded a deep blue solution from which three compounds were isolated by column chromatography. The major product was found to be the expected *o*-azidobenzoylferrocene **1** (36%), the 2-(*o*-azidophenyl)carbamoylbenzoylferrocene **4** was isolated in 12% yield and the *o*-aminobenzoylferrocene **5** was isolated in 2% yield as the minor product (Scheme 1).

Formation of compound **4** arises by acylation of the *o*-aminobenzoylferrocene **5**, which in turn is probably formed by decomposition of the initially formed azide **1** by participation of the metal in the formation of the nitrene, either via the nonbonding pair of electrons on the iron atom or by a $\sigma - \pi$ carbon metal hyperconjugation. This type of mechanism has been suggested for the conversion of ferrocenylazide into ferrocenylamine [10] or for metal participation in metallocenylphenylcarbinyl azides [11,12].

The Staudinger reaction of azides **1** and **4** with triphenylphosphine in dry dichloromethane at r.t. provided the corresponding iminophosphoranes **6** and **7** in 60 and 85% yield, respectively. Azide **1** also reacted with diphosphines such as 1,3-bis(diphenylphosphino)propane and 1,1′-bis(diphenylphosphino)ferrocene in a 2:1 molar ratio under the same conditions to give the corresponding bis-iminophosphoranes **8** (82%) and **9** (94%) bearing 2 and 3 ferrocene subunits, respectively (see Section 3 for structures **6**–**9**).

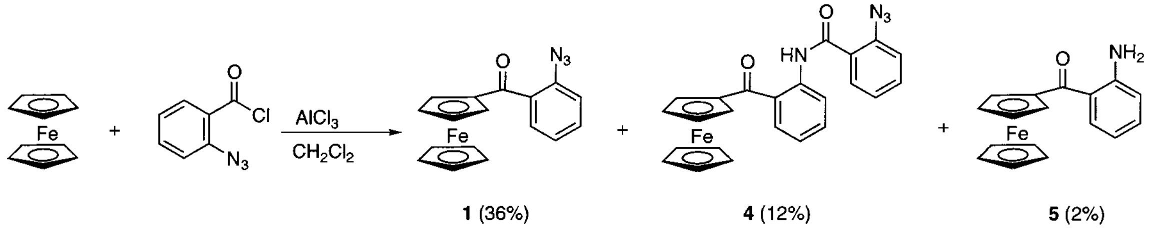
All spectroscopic data (IR, ^{1}H-, ^{13}C- and ^{31}P-NMR and MS) of iminophosphoranes **6**–**9** are in good agreement with the proposed structures. In particular, the ^{1}H- and ^{13}C-NMR spectra of the bis(iminophosphorane) **9** clearly reveal that the two-end ferrocene subunits are equivalent, whereas the central ferrocene moiety shows the characteristic pattern for a symmetrically 1,1′-disubstituted ferrocene (see Section 3).

The aza-Wittig reaction of iminophosphorane **6** with aryl isocyanates in dry dichloromethane at r.t. yielded the corresponding carbodiimides **10**, which were used without further purification for the next step. All attempts to promote the thermal intramolecular cyclization of carbodiimides **10** to give the annelated ferrocene derivatives **11** failed and only the unaltered starting material or the urea derivative were isolated. By contrast, the aza-Wittig reaction of iminophosphorane **7** with benzyl and aryl isocyanates in dichloromethane at r.t. directly gave 2-arylamino-3-(*o*-ferrocenecarbonyl)phenyl-3H-quinazolin-4-ones **13** in 40 to 49% yields. Conversion **7** → **13** can be understood by initial formation of the carbodiimide **12** which, under reaction conditions, underwent cyclization by nucleophilic attack of the NH group of the amido function on the central sp-hybridized carbon atom of the carbodiimide moiety (Scheme 2).

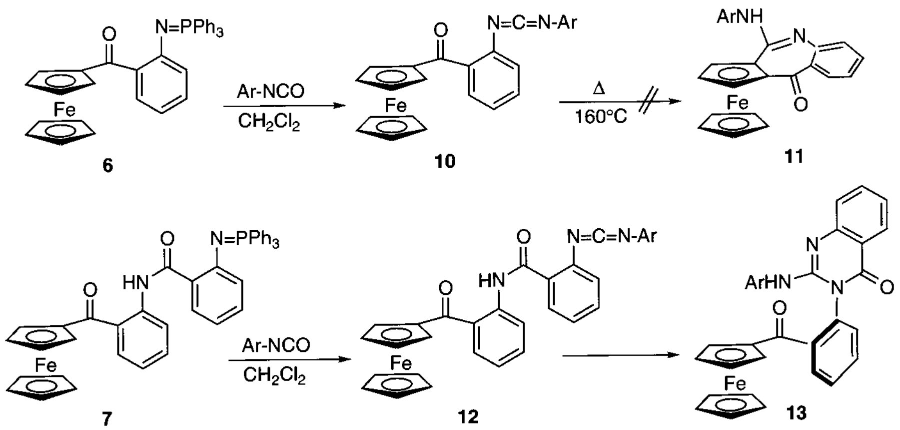
This behavior is slightly different from that previously observed for the aza-Wittig reaction of iminophosphoranes, derived from *N*-substituted *o*-azidobenzamides with isocyanates. In this case, the intermediate carbodiimide underwent, under the same reaction conditions, cyclization across the hard end of the carboxamide group (oxygen atom) to give 3H-3,1-benzoxazine-4-imines [13].

The ^{1}H-NMR spectra of **13** are characteristic: the ferrocenyl substituent gives rise to a five-proton singlet in the range 4.03–4.16 ppm for the unsubstituted cyclopentadienyl ring and two apparent triplets at 4.56–4.64 and 4.82–4.90 ppm, respectively corresponding to the AA′MM′ pattern for the monosubstituted ring. Similar behavior was observed in the ^{13}C-NMR spectra.

Condensation of ferrocenecarboxaldehyde with *o*-azidoacetophenone **14a** [14] in basic medium at 0°C yielded 1-(*o*-azidophenyl)-3-ferrocenylpropenone **2a** in 55% yield. Similarly, reaction with the previously unreported *o*-azidophenones **14b** and **14c** provided the 3-ferrocenylpropenones **2b** and **2c** in 60 and 61% yield,



Scheme 1.



Scheme 2.

respectively. An interesting feature of compounds **2** is its thermal behavior. When a solution of compound **2a** was heated in *o*-xylene at reflux temperature, the 2-ferrocenylmethylideneindoxyl **15a** was isolated in 30% yield. However, when the heating was performed in benzene at reflux temperature the anthranil **16a** was formed in 35% yield. Similarly, heating of azidoketones **2b** and **2c** in benzene at reflux temperature provided the corresponding anthranils **16b** and **16c** in 52 and 50% yield, respectively. Nevertheless, while compound **16a** was converted into **15a**, in 70% yield, by heating in *o*-xylene at reflux temperature, unexpectedly the analogs **16b** and **16c** remained unaltered. However, microwave-promoted heating of compound **16a** as well as compounds **16b** and **16c** for a short period of time allowed the isolation of the corresponding 2-ferrocenylmethylideneindoxyls **15a**, **15b** and **15c** in 75, 65 and 60% yields, respectively as the only reaction products (Scheme 3). At first, there is no obvious reason which explains the different thermal conditions required for compounds **16b** and **16c** to undergo the rearrangement, anthranil to indoxyl.

Taking into account that the thermal ring-closure of azidoketones to give anthranils, involves either a 1,3-dipolar cycloaddition process [15] or a 6π-electrocyclization [16] with concomitant loss of nitrogen rather than a nitrene insertion reaction, and the fact that 3-β-styrylanthranils undergo rearrangement at high temperature (245°C) to give 3-arylquinolin-4-ones, albeit in low yields, whereas at lower temperatures (about 160°C) 2-arylideneindoxyls are formed [17,18], the formation of compounds **15** and **16** from **2** could be explained by an initial intramolecular 1,3-cycloaddition of the azido functionality either on the ethylenic carbon–carbon double bond, to give the triazoline **17** as intermediate [19], or on the adjacent carbonyl group, followed by loss of nitrogen from the cycloadduct, to give the nitrenoketone **18**, which undergoes electrocyclization to the anthranil **16**. It is worth noting that nitrogen extrusion from the intermediate triazoline **17** would also explain the formation of the nitroketone **18**. Nitrogen evolution from the triazoline intermediate **17** followed by proton migration would lead to the indoxyl **15**. However, the formation of indoxyl **15** from anthranil **16** probably involves ring-opening of the 2,1-benzisoxazole ring, followed by cyclization of the resulting nitrenoketone **18** to give an intermediate type **19** which, by proton migration, leads to the thermodynamic product, 2-ferrocenylmethylidenindoxyl **15**. The fact that anthranils **16** rearrange to indoxyls **15** more cleanly, in good yields and in milder conditions than those reported for the aromatic series could be due to the high stability exhibited by α-ferrocenylalkyl carbocations [20], as in the proposed intermediate **19** (Scheme 4).

The structure of compounds **15** has been well established on the basis of spectroscopic data; the chemical shift values observed in their ^{13}C-NMR spectra being of particular interest. For this analysis we have selected, for simplicity, compound **15b** as representative of compounds **15**; the most interesting feature of its ^{13}C-NMR spectrum being the presence of two quaternary carbon atoms at δ 134.1 and 141.9 ppm due to a C2 and C7a of the indole ring and a CH group at δ 111.7 ppm corresponding to the methylidene moiety. These data are in agreement with those observed in related systems [21] and are totally different from those reported in the literature for 3-substituted-quinolin-4-ones [22] which could also be obtained through such rearrangement.

On the other hand, preparation of 1-ferrocenylpropenone **3** was achieved in 74% yield by condensation of acetylferrocene with *o*-azidobenzaldehye [23] under standard conditions. Compound **3** has proven to be a useful starting material for the preparation of ferrocene-containing azaheterocycles. Thus, it was converted in 67% yield into the 2-ferrocenecarbonyl indole **20** by heating in *o*-xylene at reflux temperature. Staudinger reaction of **3** with triphenylphosphine in dry dichloromethane at r.t. afforded the iminophosphorane **21** in 85% yield. Attempts to promote thermally the intramolecular aza-Wittig reaction in compound **21** to give 2-ferrocenylquinoline **22** fails, probably due to the unfavorable disposition of the carbonyl and iminophosphorane groups in the molecule. However, iminophosphorane **21** does react with isocyanates at r.t. to give the expected carbodiimides **23** which were used without further purification for the next step. Carbodiimides **23** underwent electrocyclization by heating to give 2-arylamino-3-ferrocene-carbonylquinolines **24**, isolated as crystalline solids in yields ranging from 32 to 38%, after chromatographic purification (Scheme 5).

The spectroscopic data and elemental analysis for compounds **24** are in agreement with the proposed structures, with particular interest for the signals corresponding to the monosubstituted ferrocene moiety not only in their ^{1}H-NMR but also in their ^{13}C-NMR spectra.

In conclusion, the results reported here clearly show that ferrocenylarylketones bearing an azido group at the *ortho*-position of the aryl ring are useful building blocks for the preparation of several kinds of ferrocenyl azaheterocycles. In particular, the aza-Wittig reaction of iminophosphorane derivatives appears to be a simple but very effective new way to prepare ferrocene-substituted quinolines and quinazolinones, whereas the thermally-induced azide decomposition provides access to ferrocene-substituted 2,1-benzisoxazoles and indoles.

3. Experimental

3.1. General

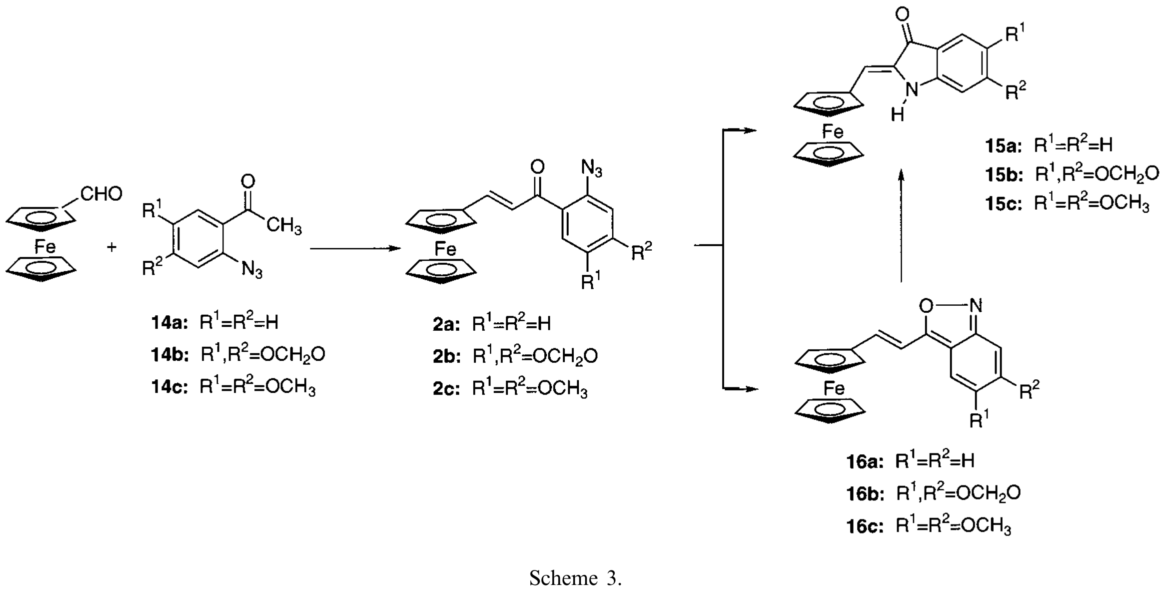
All melting points were determined on a Kofler hotplate melting point apparatus and are uncorrected. IR spectra were obtained on nujol emulsions on a Nicolet Impact 400 spectrophotometer. ^{1}H-NMR, ^{13}C-NMR and ^{31}P-NMR spectra were recorded at 299.95 MHz, 74.43 MHz and 121.42 MHz, respectively on a Varian UNITY-300 spectrometer. Chemical shifts refer to signals of TMS in the case of ^{1}H and ^{13}C spectra and to 85% aqueous phosphoric acid in the case of ^{31}P spectra. The EI and FAB mass spectra were carried out on a VG-Autospec spectrometer. Reactions under microwave irradiation were performed in a Synthewave 402 (Prolabo Fr) microwave reactor with a single mode focused system.

3.2. Reaction of ferrocene with *o*-azidobenzoyl chloride

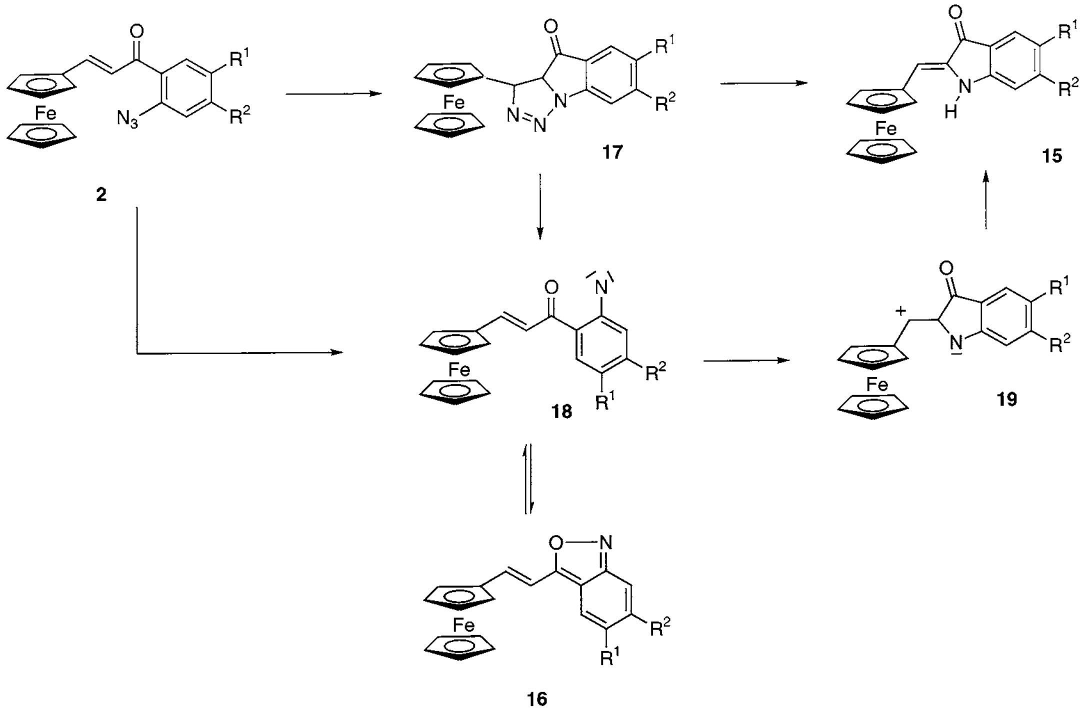
To a cooled (0°C) solution of *o*-azidobenzoyl chloride (6.0 g, 0.033 mol) in anhydrous dichloromethane (30 ml), $AlCl_3$ (4.40 g, 0.033 mol) and a solution of ferrocene (5.28 g, 0.028 mol) in anhydrous dichloromethane (30 ml) were added under nitrogen. The resulting deep blue solution was stirred at 0°C for 30 min and then allowed to warm to r.t. and stirred for 2 h. The solution was recooled at 0°C and water (60 ml) was added. The organic layer was separated and washed with water (2 × 50 ml), 10% NaOH solution (2 × 50 ml) and dried (Na_2SO_4). After filtration, the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using ethyl acetate:*n*-hexane (1:7) as eluent to give the following compounds.

3.2.1. *o*-Azidobenzoyl ferrocene (**1**)

$R_f = 0.50$; yield 36%; m.p. (dec.) 96–98°C (from diethyl ether); IR (Nujol): ν 2128, 1648, 1455, 1378, 1295, 832 and 771 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.43 (2H, m), 7.17 (2H, m), 4.67 (2H, t, $J = 1.98$ Hz), 4.51 (2H, t,



Scheme 3.



Scheme 4.

$J = 1.98$ Hz), 4.19 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 198.6 (C=O), 137.3 (q), 132.6 (q), 131.1 (CH), 128.7 (CH), 124.2 (CH), 119.0 (CH), 78.6 (*ipso*-Fec), 72.9 (2 × CH, C_5H_4), 71.1 (2 × CH, C_5H_4), 70.1 (5 × CH, C_5H_5); EI MS: *m*/*z* (%) 331 (M^+, 8), 303 (25), 275 (11), 237 (25), 209 (15), 182 (20), 154 (19), 128 (23), 121 (58) and 56 (100). Anal. Calc. for $C_{17}H_{13}FeN_3O$: C, 61.66; H, 3.96; N 12.69. Found: C, 61.50; H, 4.10; N, 12.45%.

3.2.2. 2-(*o*-Azidophenyl)carbamoylbenzoyl ferrocene (**4**)

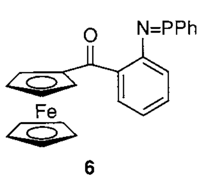
$R_f = 0.30$; yield 12%; m.p. (dec.) 133–135°C (from diethyl ether); IR (Nujol): ν 3315, 2133, 1669, 1624, 1605, 1516, 1465, 1383, 1307, 836, 779 and 766 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 11.21 (s, 1H), 8.61 (d, 1H, $J = 8.4$ Hz), 8.06 (dd, 1H, $J = 7.8$, $J = 1.2$ Hz), 7.85 (dd, 1H, $J = 7.8$, $J = 1.2$ Hz), 7.50–7.48 (m, 2H), 7.27–7.14 (m, 3H), 4.88 (t, 2H, $J = 1.8$ Hz), 4.60 (t, 2H, $J = 1.8$ Hz), 4.18 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 200.4 (C=O), 163.6 (C=O), 137.2 (q), 137.2 (q), 132.5 (CH), 132.2 (CH), 131.7 (CH), 129.5 (CH), 128.2 (q), 126.2 (q), 125.1 (CH), 122.8 (CH), 122.7 (CH), 118.9 (CH), 78.7 (*ipso*-Fec), 73.0 (2 × CH, C_5H_4), 71.7 (2 × CH, C_5H_4), 70.1 (5 × CH, C_5H_5); EI MS: *m*/*z* (%) 450 (M^+, 5), 331 (52), 329 (8), 265 (28), 238 (99), 213 (33), 184 (22), 182 (46), 146 (47), 139 (50), 121 (100), 120 (48), 119 (13) and 56 (74). Anal. Calc. for $C_{24}H_{18}FeN_4O_2$: C, 64.02; H, 4.03; N 12.44. Found: C, 63.85; H, 4.18; N, 12.60%.

3.2.3. *o*-Aminobenzoyl ferrocene (**5**)

$R_f = 0.84$; yield 2%; m.p. (dec.) 78–80°C (from diethyl ether); IR (Nujol): ν 3471, 3352, 1628, 1591, 1448, 1379, 1304, 1255, 1174, 1111, 1049, 837, 769 and 676 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.83 (dd, 1H, $J = 7.8$, $J = 1.4$ Hz), 7.22 (td, 1H, $J = 7.2$, $J = 1.5$ Hz), 6.68 (d, 1H, $J = 8.2$ Hz), 6.62 (t, 1H, $J = 7.5$ Hz), 5.62 (s, 2H), 4.86 (t, 2H, $J = 1.9$ Hz), 4.50 (t, 2H, $J = 1.9$ Hz), 4.21 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 200.1 (C=O), 148.6 (q), 132.8 (CH), 131.2 (CH), 121.2 (q), 116.9 (CH), 115.7 (CH), 80.1 (*ipso*-Fec), 72.1 (2 × CH, C_5H_4), 71.7 (2 × CH, C_5H_4), 70.1 (5 × CH, C_5H_5); EI MS: *m*/*z* (%) 305 (M^+, 96), 288 (38), 277 (14), 240 (89), 212 (62), 184 (100), 167 (44), 148 (75), 121 (82), 92 (47), 65 (56), and 56 (62). Anal. Calc. for $C_{17}H_{15}FeNO$: C, 66.91; H, 4.95; N, 4.59. Found: C, 66.70; H, 4.75; N, 4.40%.

3.3. Preparation of iminophosphoranes **6** and **7**

To a solution of triphenylphosphine (0.739 g, 2.20 mmol) in anhydrous dichloromethane (20 ml) a solution of the azide **1** or **4** (2.20 mmol) in the same solvent (20 ml) was added, under nitrogen. The resultant mixture was stirred at r.t. for 4 h and the solvent was then removed under reduced pressure and the residue was



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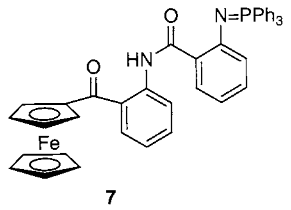

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slurried with dry diethyl ether. The solid formed was separated by filtration and recrystallized from dry ethanol to give **6** or **7**.

3.3.1. *Iminophosphorane* **6**

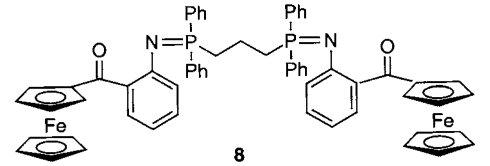
Yield 60%; m.p. 216–218°C (yellow prisms); IR (Nujol): ν 1648, 1585, 1473, 1451, 1435, 1331, 1288, 1108, 1018, 750, 723 and 701 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.61–7.35 (m, 16H), 6.96 (t, 1H, $J = 7.3$ Hz), 6.71 (t, 1H, $J = 7.1$ Hz), 6.46 (d, 1H, $J = 7.8$ Hz), 4.81 (t, 2H, $J = 1.8$ Hz), 4.38 (t, 2H, $J = 1.8$ Hz), 4.17 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 204.1 (C=O), 148.8 (q), 136.6 (CH), 132.5 (CH, $^{2}J_{\mathrm{P-C}} = 9.8$ Hz), 131.5 (CH, $^{4}J_{\mathrm{P-C}} = 2.8$ Hz), 130.6 (q, $^{1}J_{\mathrm{P-C}} = 99.3$ Hz), 129.7 (q, $^{3}J_{\mathrm{P-C}} = 10.0$ Hz), 128.3 (CH, $^{3}J_{\mathrm{P-C}} = 12.1$ Hz), 127.8 (CH, $^{4}J_{\mathrm{P-C}} = 2.8$ Hz), 121.7 (CH, $^{3}J_{\mathrm{P-C}} = 10.3$ Hz), 116.6 (CH), 80.7 (*ipso*-Fec), 71.4 (2 × CH, C_5H_4), 71.3 (2 × CH, C_5H_4), 69.7 (5 × CH, C_5H_5); EI MS: *m*/*z* (%) 565 (M^+, 73), 500 (100), 472 (8), 303 (4), 262 (7), 183 (66), 182 (4), 152 (13), 121 (41), 77 (12), 65 (7) and 56 (62). Anal. Calc. for $C_{35}H_{28}FeNOP$: C, 74.35; H, 4.99; N, 2.48. Found: C, 74.50; H, 4.80; N, 2.30%.

3.3.2. *Iminophosphorane* **7**

Yield 85%; m.p. 276–278°C (orange prisms); IR (Nujol): ν 3225, 1655, 1622, 1587, 1578, 1520, 1469, 1448, 1437, 1377, 1337, 1275, 1106, 828, 756, 728 and 693 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 12.97 (s, 1H), 8.14 (d, 1H, $J = 7.8$ Hz), 8.05 (d, 1H, $J = 8.1$ Hz), 7.81–7.75 (m, 6H), 7.61–7.35 (m, 11H), 7.21 (t, 1H, $J = 7.1$ Hz), 6.85 (t, 1H, $J = 7.2$ Hz), 6.67 (t, 1H, $J = 7.3$ Hz), 6.41 (d, 1H, $J = 8.1$ Hz), 4.59 (t, 2H, $J = 1.7$ Hz), 4.37 (t, 2H, $J = 1.7$ Hz), 3.98 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 198.2 (C=O), 166.9 (C=O), 150.1 (q), 136.2 (q), 132.6 (CH, $^{2}J_{\mathrm{P-C}} = 9.9$ Hz), 131.9 (CH, $^{4}J_{\mathrm{P-C}} = 2.6$ Hz), 131.5 (q, $^{4}J_{\mathrm{P-C}} = 3.0$ Hz), 131.2 (CH), 130.6 (CH), 129.4 (q, $^{1}J_{\mathrm{P-C}} = 99.5$ Hz), 128.6 (CH, $^{4}J_{\mathrm{P-C}} = 8.6$ Hz), 128.3 (CH), 126.1 (CH), 125.3 (CH, $^{3}J_{\mathrm{P-C}} = 20$ Hz), 123.3 (CH), 122.3 (CH, $^{1}J_{\mathrm{P-C}} = 2.1$ Hz), 117.3 (CH), 79.0 (*ipso*-Fec), 72.2 (2 × CH, C_5H_4), 71.1 (2 × CH, C_5H_4), 70.3 (5 × CH, C_5H_5); EI MS: *m*/*z* (%) 684 (M^+, 2), 619 (8), 380 (10), 304 (3), 228 (14), 210 (4), 201 (48), 186 (69), 185 (13), 183 (100), 121 (59), 120 (12), 65 (22) and 56 (50). Anal. Calc. for $C_{42}H_{33}FeN_2O_2P$: C, 73.69; H, 4.86; N, 4.09. Found: C, 73.80; H, 4.68; N, 4.15%.

3.4. *Preparation of bis(iminophosphoranes)* **8** *and* **9**

Bis(iminophosphoranes) **8** and **9** were obtained analogously from *o*-azidobenzoyl ferrocene (0.24 g, 0.72 mmol) and 1,3-bis(diphenylphosphino)propane (0.15 g, 0.36 mmol) or 1,1′-bis(diphenylphosphino)ferrocene (0.20 g, 0.36 mmol), respectively.



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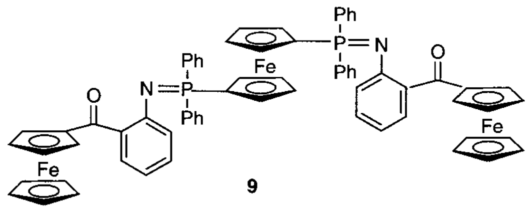

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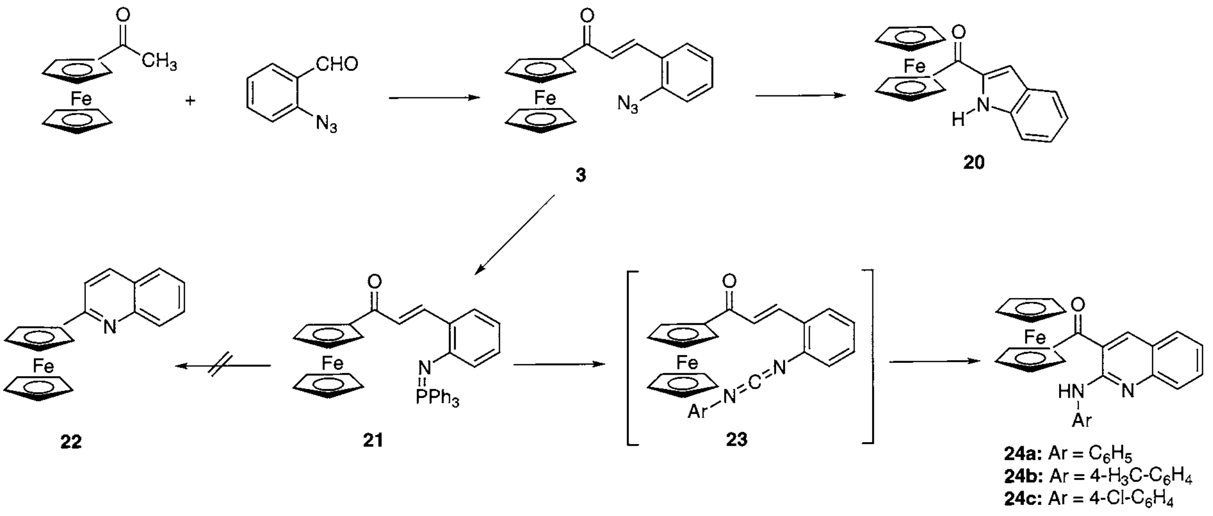
3.4.1. *Bis(iminophosphorane)* **8**

Yield 82%; m.p. 110–112°C (orange prisms, from dichloromethane:ethyl ether); IR (Nujol): ν 1640, 1586, 1469, 1456, 1435, 1337, 1290, 1111, 1054, 1038, 1021, 863, 824, 750, 717 and 694 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 7.47–7.24 (m, 22H), 6.93 (t, 2H, $J = 7.6$ Hz), 6.66 (t, 2H, $J = 7.1$ Hz), 6.22 (d, 2H, $J = 8.1$ Hz), 4.78 (t, 4H,



24a: Ar = C_6H_5
24b: Ar = 4-H_3C-C_6H_4
24c: Ar = 4-Cl-C_6H_4

Scheme 5.

$J = 1.8$ Hz), 4.37 (t, 4H, $J = 1.8$ Hz), 4.19 (s, 10H, 2.34 (m, 4H), 1.41 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ 204.0 (C=O), 149.6 (q), 136.5 (q, $^3J_{P-C} = 24.3$ Hz), 131.5 (CH, $^2J_{P-C} = 9.4$ Hz), 131.3 (CH, $^4J_{P-C} = 2.8$ Hz), 130.6 (q, $^1J_{P-C} = 96.0$ Hz), 139.9 (CH), 128.5 (CH, $^3J_{P-C} = 11.6$ Hz), 127.8 (CH, $^4J_{P-C} = 2.9$ Hz), 121.5 (CH, $^3J_{P-C} = 11.6$ Hz), 116.1 (CH), 80.8 (*ipso*-Fec), 71.4 (2 × CH, C_5H_4), 71.2 (2 × CH, C_5H_4), 69.8 (5 × CH, C_5H_5), 26.5 (2 × CH_2, $^1J_{P-C} = 65.2$ Hz), 15.28 (CH_2, $^2J_{P-C} = 16.4$ Hz); ^{31}P-NMR ($CDCl_3$): δ 4.57 ppm; MS FAB$^+$ 1019 ($M^+ + 1$, 100). Anal. Calc. for $C_{61}H_{52}Fe_2N_2O_2P_2$: C, 71.92; H, 5.14; N, 2.75. Found: C, 71.70; H, 5.26; N, 2.60%.

3.4.2. Bis(iminophosphorane) **9**

Yield 94%; m.p. > 320°C (orange prisms, from dichloromethane:ethyl ether); IR (Nujol): ν 1643, 1590, 1474, 1455, 1439, 1350, 1300, 1115, 1056, 1034, 1024, 748, 721, 696 and 657 cm^{-1}; ^{1}H-NMR (CD_2Cl_2): δ 7.48–7.26 (m, 22H), 6.88 (t, 2H, $J = 7.6$ Hz), 6.66 (t, 2H, $J = 7.3$ Hz), 6.19 (d, 2H, $J = 7.9$ Hz), 5.31 (t, 4H, $J = 1.6$ Hz), 4.81 (t, 4H, $J = 1.8$ Hz), 4.47 (t, 4H, $J = 1.8$ Hz), 4.23 (t, 4H, $J = 1.6$ Hz), 4.21 (s, 10H); ^{13}C-NMR (CD_2Cl_2): δ 181.8 (C=O), 149.4 (q), 132.3 (CH, $^2J_{P-C} = 10.1$ Hz), 132.1 (q, $^1J_{P-C} = 102.2$ Hz), 131.8 (CH, $^4J_{P-C} = 2.5$ Hz), 129.9 (CH), 128.7 (CH, $^3J_{P-C} = 12.1$ Hz), 127.9 (CH, $^4J_{P-C} = 2.5$ Hz), 121.7 (CH, $^3J_{P-C} = 11.0$ Hz), 116.4 (CH), 81.4 (*ipso*-Fec), 74.7 (CH, C_5H_4, $^2J_{P-C} = 9.9$ Hz), 74.2 (*ipso*-Fec, $^1J_{P-C} = 115.9$ Hz), 74.0 (CH, C_5H_4, $^3J_{P-C} = 12.2$ Hz), 72.1 (2 × CH, C_5H_4), 71.5 (2 × CH, C_5H_4), 70.2 (5 × CH, C_5H_5); ^{31}P-NMR ($CDCl_3$): δ 2.48 ppm; MS FAB$^+$ 1161 ($M^+ + 1$, 100). Anal. Calc. for $C_{68}H_{54}Fe_3N_2O_2P_2$: C, 70.37;H, 4.69; N, 2.41. Found: C, 70.54; H, 4.46; N, 2.30%.

3.5. General procedure for the preparation of 2-arylamino-3-(o-ferrocenecarbonyl)phenyl-3H-quinazolin-4-ones **13**

To a solution of iminophosphorane **7** (0.4 g, 0.58 mmol) in anhydrous dichloromethane (20 ml) the appropriate isocyanate (0.58 mmol) was added. The resultant mixture was stirred at r.t. under nitrogen for 96 h. The solution was concentrated to dryness and the residue was chromatographed on a silica gel column using ethyl acetate:*n*-hexane (3:2) as eluent. The following products were isolated after recrystallization from dichloromethane:diethyl ether (1:1).

3.5.1. Compound **13a** (Ar = C_6H_5)

Yield 40%; m.p. 98–100°C; IR (Nujol): ν 3332, 1709, 1669, 1599, 1517, 1502, 1450, 1298, 1243 and 761 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 10.72 (s, 1H), 8.45 (dd, 1H, $J = 8.4$, $J = 0.8$ Hz), 8.38 (dd, 1H, $J = 8.4$, $J = 0.8$ Hz), 7.95 (dd, 1H, $J = 7.9$, $J = 1.5$ Hz), 7.68 (dd, 1H, $J = 8.0$, $J = 1.0$ Hz), 7.47–7.02 (m, 9H), 4.83 (t, 2H, $J = 1.9$ Hz), 4.57 (t, 2H, $J = 1.9$ Hz), 4.09 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 201.5 (C=O), 168.0 (C=O), 152.5 (q), 141, 7 (q), 138.3 (q), 137.6 (q), 133.2 (CH), 132.7 (CH), 130.5 (CH), 129.0 (CH), 127.0 (CH), 126.9 (q), 123.5 (CH), 123.1 (CH), 122.1 (CH), 121.9 (CH), 121.1 (CH), 120.2 (CH), 119.1 (q), 78.6 (*ipso*-Fec), 73.3 (2 × CH, C_5H_4), 72.0 (2 × CH, C_5H_4), 70.3 (5 × CH, C_5H_5); EI MS: *m*/*z* (%) 525 (M^+, 53), 450 (100), 389 (54), 340 (58), 248 (16), 237 (32), 145 (28), 92 (85), 65 (35), and 55 (17). Anal. Calc. for $C_{31}H_{23}FeN_3O_2$: C, 70.87; H, 4.41; N 8.00. Found: C, 70.74; H, 4.20; N, 7.96%.

3.5.2. Compound **13b** (Ar = 4-H_3CO–C_6H_5)

Yield 49%; m.p. 99–100°C; IR (Nujol): ν 3313, 1707, 1656, 1585, 1515, 1438, 1297, 1246, 1175, 1041, 836 and 747 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 10.59 (s, 1H), 8.45 (d, 1H, $J = 8.4$ Hz), 8.35 (d, 1H, $J = 8.4$ Hz), 7.93 (d, 1H, $J = 7.8$ Hz), 7.68 (d, 1H, $J = 8.1$ Hz), 7.43 (t, 1H, $J = 7.0$ Hz), 7.40 (t, 1H, $J = 7.0$ Hz), 7.22 (d, 2H, $J = 8.7$ Hz), 7.10 (t, 1H, $J = 7.5$ Hz), 7.04 (t, 1H, $J = 7.5$ Hz), 6.77 (d, 2H, $J = 8.7$ Hz), 4.82 (t, 2H, $J = 1.8$ Hz), 4.56 (t, 2H, $J = 1.8$ Hz), 4.03 (s, 5H), 3.71 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 201.5 (C=O), 167.8 (C=O), 156.5 (q), 153.4 (q), 141.7 (q), 137.7 (q), 133.1 (CH), 132.7 (CH), 131.0 (q), 130.4 (CH), 126.9 (CH), 126.8 (q), 123.5 (CH), 122.9 (CH), 122.0 (CH), 121.8 (CH), 121.1 (CH), 119.2 (q), 78.6 (*ipso*-Fec), 73.3 (2 × CH, C_5H_4), 72.0 (2 × CH, C_5H_4), 70.4 (5 × CH, C_5H_5), 55.5 (CH_3O); EI MS: *m*/*z* (%) 555 (M^+, 8), 450 (100), 424 (12), 385 (47), 371 (23), 342 (12), 268 (60), 146 (20), 123 (74) and 108 (85). Anal. Calc. for $C_{32}H_{25}FeN_3O_3$: C, 69.20; H, 4.54; N 7.57. Found: C, 69.35; H, 4.40; N, 7.24%.

3.5.3. Compound **13c** (Ar = 4-H_3C–C_6H_5)

Yield 45%; m.p. 110–112°C; IR (Nujol): ν 3303, 1717, 1667, 1584, 1506, 1456, 1378, 1295, 1245, 1118, 1057, 835 and 757 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 10.72 (s, 1H), 8.52 (d, 1H, $J = 8.3$ Hz), 8.43 (d, 1H, $J = 8.3$ Hz), 8.02 (dd, 1H, $J = 7.8$, $J = 1.3$ Hz), 7.77 (dd, 1H, $J = 7.9$, $J = 1.1$ Hz), 7.52 (t, 1H, $J = 7.0$ Hz), 7.48 (t, 1H, $J = 7.1$ Hz), 7.28 (d, 2H, $J = 8.3$ Hz), 7.11–7.06 (m, 4H), 4.90 (t, 2H, $J = 1.8$ Hz), 4.64 (t, 2H, $J = 1.8$ Hz), 4.16 (s, 5H), 2.16 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 201.6 (C=O), 168.0 (C=O), 152.9 (q), 141.7 (q), 137.6 (q), 133.3 (q), 133.2 (CH), 132.7 (CH), 130.5 (CH), 129.5 (CH), 127.0 (CH), 126.9 (q), 123.0 (CH), 122.1 (CH), 121.8 (CH), 121.1 (CH), 120.9 (CH), 119.4 (q), 78.6 (*ipso*-Fec), 73.3 (2 × CH, C_5H_4), 72.0 (2 × CH, C_5H_4), 70.3 (5 × CH, C_5H_5), 20.1 (CH_3); EI MS: *m*/*z* (%) 539 (M^+, 6), 450 (100), 424 (78), 385 (36), 359 (85), 341 (52), 293 (33), 252 (12), 146 (13), 133 (36), 121 (24) and 107 (51). Anal. Calc. for $C_{32}H_{25}FeN_3O_2$: C, 71.25; H, 4.67; N 7.79. Found: C, 71.12; H, 4.70; N, 7.58%.

3.5.4. Compound **13d** (Ar = 4-Cl–C_6H_5)

Yield 40%; m.p. 96–98°C; IR (Nujol): ν 3290, 1719, 1666, 1579, 1526, 1453, 1288, 1248, 837, 836 and 757 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 10.71 (s, 1H), 8.42 (d, 1H, $J = 8.6$ Hz), 8.36 (d, 1H, $J = 8.6$ Hz), 7.98 (d, 1H, $J = 7.8$ Hz), 7.72 (d, 1H, $J = 7.5$ Hz), 7.47 (t, 1H, $J = 7.0$ Hz), 7.44 (t, 1H, $J = 7.0$ Hz), 7.28 (d, 2H, $J = 8.8$ Hz), 7.19–7.08 (m, 4H), 4.84 (t, 2H, $J = 1.8$ Hz), 4.59 (t, 2H, $J = 1.8$ Hz), 4.10 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 201.6 (C=O), 168.0 (C=O), 152.4 (q), 141.4 (q), 137.5 (q), 137.1 (q), 133.3 (CH), 132.7 (CH), 130.5 (CH), 128.9 (CH), 128.3 (q), 127.0 (CH), 123.2 (CH), 122.1 (CH), 121.3 (CH), 121.1 (CH), 119.2 (q), 77.7 (*ipso*-Fec), 73.4 (2 × CH, C_5H_4), 72.1 (2 × CH, C_5H_4), 70.3 (5 × CH, C_5H_5); EI MS: *m*/*z* (%) 561 ($M^+ + 2$, 9), 559 (M^+, 27), 450 (100), 449 (25), 447 (69), 385 (92), 341 (69), 292 (79), 274 (34), 272 (90), 146 (65), 129 (86), 128 (14), 127 (57), 126 (51), 121 (85), 113 (6), and 111 (13). Anal. Calc. for $C_{31}H_{22}ClFeN_3O_2$: C, 66.51; H, 3.96; N 7.51. Found: C, 66.30; H, 3.80; N, 7.65%.

3.5.5. Compound **13e** (Ar = C_6H_5–CH_2)

Yield 43%; m.p. 95–97°C; IR (Nujol): ν 3317, 1707, 1667, 1588, 1522, 1455, 1280, 827, 778, 742 and 700 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 10.68 (bs, 1H), 8.53 (d, 1H, $J = 8.4$ Hz), 8.45 (d, 1H, $J = 8.4$ Hz), 8.01 (d, 1H, $J = 7.8$ Hz), 7.77 (d, 1H, $J = 7.0$ Hz), 7.54 (t, 1H, $J = 7.0$ Hz), 7.47 (t, 1H, $J = 7.0$ Hz), 7.29–7.10 (m, 7H), 4.90 (t, 2H, $J = 1.9$ Hz), 4.64 (t, 2H, $J = 1.9$ Hz), 4.42 (d, 2H, $J = 5.6$ Hz), 4.16 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 201.5 (C=O), 168.1 (C=O), 154.9 (q), 142.2 (q), 137.7 (q), 133.3 (CH), 132.7 (CH), 130.4 (CH), 128.6 (CH), 127.7 (CH), 127.3 (CH), 127.0 (CH), 123.0 (CH), 122.1 (CH), 121.5 (CH), 120.7 (CH), 118.9 (q), 78.6 (*ipso*-Fec), 73.3 (2 × CH, C_5H_4), 72.0 (2 × CH, C_5H_4), 70.3 (5 × CH, C_5H_5), 44.4 (CH_2); EI MS: *m*/*z* (%) 539 (M^+, 10), 450 (100), 424 (41), 385 (31), 359 (21), 341 (15), 293 (28), 252 (13), 146 (13), 121 (16), 107 (22) and 91 (18). Anal. Calc. for $C_{32}H_{25}FeN_3O_2$: C, 71.25; H, 4.67; N 7.79. Found: C, 71.33; H, 4.58; N, 7.60%.

3.6. General procedure for the preparation of *o*-azidoacetophenones **14b** and **14c**

To a solution, cooled at 0°C, of the appropriate *o*-aminoacetophenone (50 mmol) in HCl (50 ml) and water (50 ml) a solution of $NaNO_2$ (3.8 g, 55 mmol) in water (30 ml) was added and the mixture was stirred at that temperature for 30 min. Then, a solution of sodium azide (6.5 g, 100 mmol) in water (30 ml) was added and the resulting suspension was stirred at 0°C for 30 min and later at r.t. for 1 h. The precipitated formed was filtered, washed with water (100 ml), dried and crystallized from *n*-hexane.

3.6.1. Compound **14b**

Yield 83%; m.p. 112–113°C; IR (Nujol): ν 2117, 1673, 1620, 1524, 1385, 1294, 1262, 1150, 1037, 926 and 829 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.26 (s, 1H), 6.68 (s, 1H), 6.04 (s, 2H), 2.61 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 196.6 (C=O), 151.9 (q), 145.2 (q), 134.9 (q), 124.3 (q), 109.4 (CH), 102.4 (CH_2), 99.4 (CH), 31.3 (CH_3); EI MS: *m*/*z* (%) 205 (M^+, 10), 177 (85), 148 (100), 131 (40), 121 (11), 119 (18), 105 (14), 91 (29) and 66 (10). Anal. Calc. for $C_9H_7N_3O_3$: C, 52.69; H, 3.44; N 20.48. Found: C, 52.50; H, 3.22; N, 20.62%.

3.6.2. Compound **14c**

Yield 86%; m.p. 114–115°C; IR (Nujol): ν 2104, 1657, 1597, 1466, 1373, 1226, 1046, and 838 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.37 (s, 1H), 6.63 (s, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 2.64 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ 196.6 (C=O), 153.3 (q), 146.2 (q), 133.1 (q), 122.5 (q), 112.4 (CH), 101.55 (CH), 56.1 (OCH_3), 56.0 (OCH_3), 31.4 (CH_3); EI MS: *m*/*z* (%) 221 (M^+, 8), 193 (100), 164 (12), 162 (8), 150 (43), 121 (17) and 66 (12). Anal. Calc. for $C_{10}H_{11}N_3O_3$: C, 54.30; H, 5.01; N 18.99. Found: C, 54.46; H, 4.89; N, 18.78%.

3.7. General procedure for the preparation of α,β-unsaturated ketones **2** and **3**

To a cooled (0°C) ethanolic solution of KOH (0.35 g, 6.22 mmol) the appropriate *o*-azidoacetophenone (3.11 mmol) was added and the reaction mixture was stirred at 0°C for 15 min. Then, the adequate aldehyde (3.11 mmol) was added and the reaction was stirred at r.t. for 8 h. Compounds **2** were isolated on a silica gel column using ethyl acetate:*n*-hexane (1:3) as eluent while compound **3** was separated by filtration from the reaction mixture.

3.7.1. Compound **2a**

Yield 55%; m.p. 87–88°C (from *n*-hexane); IR (Nujol): ν 2118, 1664, 1600, 1585, 1289, 1010, 798 and 699 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.55–7.46 (m, 2H), 7.42 (d, 1H, $J = 15.6$ Hz), 7.25 (d, 1H, $J = 8.8$ Hz), 7.23 (td, 1H, $J = 6.8$, $J = 0.9$ Hz), 6.76 (d, 1H, $J = 15.6$ Hz), 4.55 (t, 2H, $J = 1.8$ Hz), 4.48 (t, 2H, $J = 1.8$ Hz), 4.18 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 192.4 (C=O), 147.7 (CH), 137.6 (q), 132.4 (q), 131.6 (CH), 129.8 (CH), 124.7 (CH), 123.6 (CH), 119.6 (CH), 78.6 (*ipso*-Fec), 71.6 (2 × CH, C_5H_4), 69.8 (5 × CH, C_5H_5), 69.1 (2 × CH, C_5H_4); EI MS: *m*/*z* (%) 357 (M^+, 9), 329 (100), 264 (95), 208 (11), 180 (15), 153 (15), 121 (19) and 56 (9). Anal. Calc. for $C_{19}H_{15}FeN_3O$: C, 63.89; H, 4.23; N 11.76. Found: C, 63.70; H, 4.38; N, 11.50%.

3.7.2. Compound **2b**

Yield 60%; m.p. 133–134°C (from *n*-hexane); IR (Nujol): ν 2125, 1653, 1615, 1578, 1460, 1374, 1266, 1046 and 837 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.51 (d, 1H, $J=15.4$ Hz), 7.07 (s, 1H), 6.86 (d, 1H, $J=15.4$ Hz), 6.71 (s, 1H), 6.04 (s, 2H), 4.55 (t, 2H, $J=1.8$ Hz), 4.47 (t, 2H, $J=1.8$ Hz), 4.18 (s, 5H); ^{13}C-NMR (CDCl$_3$): δ 190.0 (C=O), 150.5 (q), 146.5 (CH), 145.1 (q), 133.1 (q), 125.8 (q), 123.5 (CH), 109.4 (CH), 102.2 (CH$_2$), 99.7 (CH), 78.9 (*ipso*-Fec), 71.4 ($2\times$CH, C$_5$H$_4$), 69.8 ($5\times$CH, C$_5$H$_5$), 69.1 ($2\times$CH, C$_5$H$_4$); EI MS: *m/z* (%) 401 (M$^+$, 5), 373 (94), 308 (100), 252 (8), 185 (10), 149 (12), 121 (39 and 56 (20). Anal. Calc. for $C_{20}H_{15}FeN_3O_3$: C, 59.87; H, 3.77; N 10.47. Found: C, 59.90; H, 3.60; N, 10.24%.

3.7.3. Compound **2c**

Yield 61%; m.p. 125–126°C (from *n*-hexane); IR (Nujol): ν 2118, 1657, 1582, 1466, 972 and 857 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.55 (d, 1H, $J=15.3$ Hz), 7.20 (s, 1H), 6.99 (d, 1H), $J=15.3$ Hz), 6.67 (s, 1H), 4.57 (t, 2H, $J=1.8$ Hz), 4.47 (t, 2H, $J=1.8$ Hz), 4.18 (s, 5H), 3.97 (s, 3H), 3.90 (s, 3H); ^{13}C-NMR (CDCl$_3$): δ 189.8 (C=O), 152.4 (q), 146.4 (q), 145.9 (CH), 131.6 (q), 124.4 (q), 123.6 (CH), 112.8 (CH), 102.1 (CH), 79.1 (*ipso*-Fec), 71.3 ($2\times$CH, C$_5$H$_4$), 69.7 ($5\times$CH, C$_5$H$_5$), 69.1 ($2\times$CH, C$_5$H$_4$), 56.3 (OCH$_3$), 56.2 (OCH$_3$); EI MS: *m/z* (%) 389 (M$^+ -$ N$_2$, 98), 324 (100), 293 (12), 280 (15), 237 (45), 228 (56), 186 (14), 131 (18), 121 (13) and 56 (6). Anal. Calc. for $C_{21}H_{19}FeN_3O_3$: C, 60.45; H, 4.59; N 10.07. Found: C, 60.21; H, 4.35; N, 10.20%.

3.7.4. Compound **3**

Yield 74%; m.p. 122–123°C (from *n*-hexane); IR (Nujol): ν 2134, 1655, 1598, 1444, 1376, 1296, 1233, 1074, 977, 829 and 755 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.99 (d, 1H, $J=15.7$ Hz), 7.67 (d, 1H, $J=7$, 1 Hz), 7.42 (t, 1H, $J=7.1$ Hz), 7.19–7.12 (m, 3H), 4.90 (t, 2H, $J=1.8$ Hz), 4.58 (t, 2H, $J=1.8$ Hz), 4.21 (s, 5H); ^{13}C-NMR (CDCl$_3$): δ 193.0 (C=O), 139.4 (q), 135.2 (CH), 131.0 (CH), 128.4 (CH), 126.9 (q), 125.0 (CH), 124.9 (CH), 118.9 (CH), 80.5 (*ipso*-Fec), 72.8 ($2\times$CH, C$_5$H$_4$), 70.1 ($5\times$CH, C$_5$H$_5$), 69.8 ($2\times$CH, C$_5$H$_4$). EI MS: *m/z* (%) 357 (M$^+$, 17), 329 (100), 313 (27), 264 (13), 237 (33), 213 (12), 180 (33), 152 (15) and 121 (27). Anal. Calc. for $C_{19}H_{15}FeN_3O$, C, 63.89; H, 4.23; N 11.76. Found: C, 63.70; H, 4.12; N, 11.90%.

3.8. Preparation of 2-ferrocenylmethyliden-1,2-dihydro-3H-indol-3-one (**15a**)

A solution of the α,β-unsaturated ketone **2a** (0.55 g, 1.4 mmol) in *o*-xylene (15 ml) was stirred at reflux temperature for 3 h. The solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column, using ethyl acetate:*n*-hexane (2:5) as eluent, to give the following compound.

3.8.1. Compound **15a**

$R_f=0.53$; yield 30%; m.p. >320°C; IR (Nujol): ν 3342, 1679, 1625, 1588, 1465, 1380, 1129 and 750 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 9.17 (s, 1H), 7.50 (m, 2H), 7.15 (d, 1H, $J=8.0$ Hz), 6.87 (t, 1H, $J=7.3$ Hz), 6.56 (s, 1H), 4.87 (t, 2H, $J=1.8$ Hz), 4.55 (t, 2H, $J=1.8$ Hz), 4.17 (s, 5H); ^{13}C-NMR (DMSO-d_6): δ 184.2 (C=O), 153.0 (q), 135.4 (CH), 132.9 (q), 123.7 (CH), 120.5 (q), 119.0 (CH), 112.4 (CH), 77.6 (*ipso*-Fec), 70.7 ($2\times$CH, C$_5$H$_4$), 70.0 ($2\times$CH, C$_5$H$_4$), 69.4 ($5\times$CH, C$_5$H$_5$); EI MS: *m/z* (%) 329 (M$^+$, 73), 264 (100), 208 (17), 180 (18), 152 (17), 121 (23) and 77 (10). Anal. Calc. for $C_{19}H_{15}FeNO$: C, 69.33; H, 4.59; N 4.25. Found: C, 69.12; H, 4.60; N, 4.05%.

3.9. Preparation of 3-(2-ferrocenyl)vinyl-2,1-benzisoxazoles **16**

A solution of the appropriate α,β-unsaturated ketone **2** (0.55 g, 1.4 mmol) in dry benzene (30 ml) was stirred at reflux temperature, under nitrogen, for 24 h. The solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column, using ethyl acetate:*n*-hexane (2:5) as eluent, to give compounds **16**, which were crystallized from the adequate solvent.

3.9.1. Compound **16a**

$R_f=0.69$; yield 35%; m.p. 166–167°C (from *n*-hexane); IR (Nujol): ν 1640, 1619, 1530, 1460, 1378, 820 and 750 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.62–7.52 (m, 2H), 7.45 (d, 1H, $J=16.1$ Hz), 7.28 (qd, 1H, $J=9.0$, $J=6.3$, $J=0.9$ Hz), 7.00 (dd, $J=8.6$, $J=0.8$ Hz), 6.91 (d, 1H, $J=16.1$ Hz), 4.58 (t, 2H, $J=1.8$ Hz), 4.44 (t, 2H, $J=1.8$ Hz), 4.19 (s, 5H); ^{13}C-NMR (CDCl$_3$): δ 164.2 (q), 153.5 (q), 135.8 (CH), 130.9 (CH), 123.2 (CH), 120.1 (CH), 114.9 (CH), 114.5 (q), 109.3 (CH), 80.9 (*ipso*-Fec), 70.57 ($2\times$CH, C$_5$H$_4$), 69.6 ($5\times$CH, C$_5$H$_5$), 67.8 ($2\times$CH, C$_5$H$_4$); EI MS: *m/z* (%) 329 (M$^+$, 45), 264 (100), 208 (10), 180 (9), 152 (9), 121 (12) and 56 (8). Anal. Calc. for $C_{19}H_{15}FeNO$,%C, 69.33; H, 4.59; N 4.25. Found: C, 69.21; H, 4.62; N, 4.33%.

3.9.2. Compound **16b**

$R_f=0.60$; yield 52%; m.p. 188–189°C (from dry benzene); IR (Nujol): ν 1634, 1602, 1523, 1467, 1375, 1106 and 972 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 7.25 (d, 1H, $J=16.2$ Hz), 6.75 (d, 1H, $J=16.2$ Hz), 6.74 (s, 1H), 6.71 (s, 1H), 5.98 (s, 2H), 4.53 (t, 2H, $J=1.8$ Hz), 4.40 (t, 2H, $J=1.8$ Hz), 4.18 (s, 5H); ^{13}C-NMR (CDCl$_3$): δ 161.7 (q), 156.7 (q), 152.8 (q), 147.0 (q), 133.9 (CH), 111.3 (q), 109.2 (CH), 101.8 (CH$_2$), 93.2 (CH), 89.8 (CH), 81.2 (*ipso*-Fec), 70.8 ($2\times$CH, C$_5$H$_4$), 69.5 ($5\times$CH, C$_5$H$_5$), 67.5 ($2\times$CH, C$_5$H$_4$); EI MS: *m/z* (%) 373 (M$^+$, 100), 308 (94), 252 (5), 182 (2), 186 (6), 121 (10) and 56 (7). Anal. Calc. for $C_{20}H_{15}FeNO_3$: C, 64.37; H, 4.05; N 3.75. Found: C, 64.22; H, 4.15; N, 3.90%.

3.9.3. Compound **16c**

$R_f = 0.50$; yield 50%; m.p. 160–161°C (from dry benzene); IR (Nujol): ν 1638, 1525, 1453, 1373, 1280, 963, 827 and 754 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.28 (d, 1H, $J = 16.2$ Hz), 6.78 (d, 1H, $J = 16.2$ Hz), 6.72 (s, 1H), 6.65 (s, 1H), 4.55 (t, 2H, $J = 1.8$ Hz), 4.40 (t, 2H, $J = 1.8$ Hz), 4.17 (s, 5H), 3.94 (s, 6H); ^{13}C-NMR ($CDCl_3$): δ 161.3 (q), 155.5 (q), 155.0 (q), 149.2 (q), 133.6 (CH), 110.0 (q), 109.2 (CH), 94.9 (CH), 91.3 (CH), 81.3 (*ipso*-Fec), 70.2 ($2 \times$ CH, C_5H_4), 69.5 ($5 \times$ CH, C_5H_5), 67.5 ($2 \times$ CH, C_5H_4) 56.1(OCH_3), 55.9 (OCH_3); EI MS: *m*/*z* (%) 389 (M^+, 100), 324 (77), 308 (18), 280 (13), 186 (3), 121 (6) and 56 (4). Anal. Calc. for $C_{21}H_{19}FeNO_3$: C, 64.80; H, 4.92; N 3.60. Found: C, 64.91; H, 4.80; N, 3.39%.

3.10. Rearrangement of anthranils **16** to indoxyls **15**

3.10.1. Method A

A solution of the anthranil **16a** (0.33 g, 1 mmol) in *o*-xylene (20 ml) was heated at reflux temperature for 3 h. After cooling, the solvent was removed under reduced pressure and the residual material was chromatographed on a silica gel column using ethyl acetate:*n*-hexane (2:5) as eluent to give **15a** in 70% yield.

3.10.2. Method B

A solution of the appropriate anthranil **16a**, **16b** or **16c** (1 mmol) in *N*,*N*-dimethylformamide (6 ml) was placed in a cylindrical quartz tube. Then the tube was introduced in the microwave reactor fitted with a rotational system and a IR detector of temperature. Microwave irradiation was carried out at 140°C for 6 min (the microwave oven is monitored by a computer which allows the temperature of the reaction mixture to be adjusted). After cooling, the mixture was concentrated to dryness and the residue was chromatographed on a silica gel column using ethyl acetate:*n*-hexane (2:5) as eluent. The following products were isolated after recrystallization from chloroform.

3.10.3. Compound **15a**

75% yield, which was identified as above.

3.10.4. Compound **15b**

$R_f = 0.20$; yield 65%; m.p. > 320°C; IR (Nujol): ν 3270, 1673, 1625, 1567, 1513, 1465, 1284, 1129, 1033, 947 and 750 cm^{-1}; ^1H-NMR (DMSO-d_6): δ 8.94 (s, 1H), 6.95 (s, 1H), 6.64 (s, 1H), 6.45 (s, 1H), 6.06 (s, 2H), 4.81 (t, 2H, $J = 1.8$ Hz), 4.52 (t, 2H, $J = 1.8$ Hz), 4.17 (s, 5H); ^{13}C-NMR (DMSO-d_6): δ 182.1 (C=O), 154.4 (q), 151.9 (q), 141.9 (q), 134.1 (q), 113.1 (q), 111.7 (CH), 101.7 (CH_2), 101.3 (CH), 93.2 (CH), 77.6 (*ipso*-Fec), 70.4 ($2 \times$ CH, C_5H_4), 69.7 ($2 \times$ CH, C_5H_4), 69.3 ($5 \times$ CH, C_5H_5); EI MS: *m*/*z* (%) 373 (M^+, 68), 264 (100), 308 (17), 186 (3), 149 (4), 121 (4) and 56 (3). Anal. Calc. for $C_{20}H_{15}FeNO_3$: C, 64.37; H, 4.05; N 3.75. Found: C, 64.12; H, 3.85; N, 3.90%.

3.10.5. Compound **15c**

$R_f = 0.17$; yield 60%; m.p. > 320°C; IR (Nujol): ν 3300, 1666, 1625, 1576, 1506, 1469, 1135, 1034 and 950 cm^{-1}; ^1H-NMR (DMSO-d_6): δ 8.85 (s, 1H), 7.00 (s, 1H), 6.68 (s, 1H), 6.44 (s, 1H), 4.81 (t, 2H, $J = 1.8$ Hz), 4.51 (t, 2H, $J = 1.8$ Hz), 4.16 (s, 5H), 3.88 (s, 3H), 3.73 (s, 3H); ^{13}C-NMR (DMSO-d_6): δ 179.4 (C=O), 155.2 (q), 154.3 (q), 142.4 (q), 133.2 (q), 113.4 (CH), 112.1 (q), 104.3 (CH), 92.2 (CH), 77.5 (*ipso*-Fec), 70.3 ($2 \times$ CH, C_5H_4), 69.5 ($2 \times$ CH, C_5H_4), 69.0 ($5 \times$ CH, C_5H_5), 55.8 (OCH_3), 55.2 (OCH_3); EI MS: *m*/*z* (%) 389 (M^+, 89), 324 (100), 149 (21), 121 (9) and 55 (22). Anal. Calc. for $C_{21}H_{19}FeNO_3$: C, 64.80; H, 4.92; N 3.60. Found: C, 64.65; H, 4.71; N, 3.79%.

3.11. Preparation of 2-ferrocenecarbonyl indole (**20**)

A solution of the α,β-unsaturated ketone **3** (0.55 g, 1.4 mmol) in *o*-xylene (15 ml) was stirred at reflux temperature for 3 h. The solvent was removed under reduced pressure and the crude product was chromatographed on a silica gel column, using ethyl acetate:*n*-hexane (1:10) as eluent, to give the following compound.

3.11.1. Compound **20**

$R_f = 0.13$; yield 67%; m.p. 191–192°C (from dichloromethane: *n*-hexane 1:1); IR (Nujol): ν 3329, 1600, 1519, 1456, 1370, 1342, 1273, 1136, 1108, and 748 cm^{-1}; ^1H-NMR ($CDCl_3$): δ 9.60 (bs, 1H), 7.76 (d, 1H, $J = 8.1$ Hz), 7.49 (d, 1H, $J = 8.5$ Hz), 7.39–7.33 (m, 2H), 7.17 (qd, 1H, $J = 8.5$ Hz, $J = 6.9$ Hz, $J = 1.0$ Hz), 5.15 (t, 2H, $J = 1.8$ Hz), 4.63 (t, t, 2H, $J = 1.8$ Hz), 4.21 (s, 5H); ^{13}C-NMR ($CDCl_3$): δ 188.8 (C=O), 136.5 (q), 135.3 (q), 127.9 (q), 125.7 (CH), 122.8 (CH), 120.8 (CH), 112.1 (CH), 108.4 (CH), 78.7 (*ipso*-Fec), 72.31 ($2 \times$ CH, C_5H_4), 70.8 ($2 \times$ CH, C_5H_4), 70.4 ($5 \times$ CH, C_5H_5); EI MS: *m*/*z* (%) 329 (M^+, 100), 264 (10), 237 (24), 212 (6), 208 (6), 185 (15), 179 (31), 152 (16), 144 (5), 121 (30), 116 (5) and 65 (11). Anal. Calc. for $C_{19}H_{15}FeNO$: C, 69.33; H, 4.59; N 4.25. Found: C, 69.28; H, 4.38; N, 4.15%.

3.12. Preparation of 1-ferrocenyl-3-(2-triphenylphosphoranylideneamino)phenyl propenone (**21**)

To a solution of triphenylphosphine (0.37 g, 1.4 mmol) in dry dichloromethane (20 ml) a solution of an equimolecular amount of the azide **3** was added dropwise, under nitrogen. The reaction mixture was stirred at r.t. for 12 h. The solvent was removed to dryness and the resulting orange solid was crystallized from *n*-hexane to give the following compound.

*3.12.1. Compound **21***

Yield 85%; m.p. 236–237°C; IR (Nujol): ν 1648, 1583, 1467, 1336, 1119, 748, 719, and 696 cm^{-1}; ^{1}H-NMR (DMSO-d_6): δ 8.65 (d, 1H, $J = 15.9$ Hz), 7.82–7.76 (m, 6H), 7.65–7.58 (m, 10H), 7.33 (d, 1H, $J = 15.9$ Hz), 6.85 (t, 1H, $J = 7.2$ Hz), 6.63 (t, 1H, $J = 7.8$ Hz), 6.39 (d, 1H, $J = 7.8$ Hz), 4.90 (s, 2H), 4.57 (s, 2H), 4.17 (s, 5H); ^{13}C-NMR (DMSO-d_6): δ 194.0 (C=O), 152.3 (q), 141.2 (CH), 132.5 (q, $^{2}J_{P-C} = 9.7$ Hz), 131.7 (q, $^{4}J_{P-C} = 2.8$ Hz), 130.2 (CH), 129.6 (q, $^{1}J_{P-C} = 92.0$ Hz), 129.3 (q, $^{3}J_{P-C} = 15$ Hz), 128.6 (CH, $^{3}J_{P-C} = 12.1$ Hz), 128.0 (CH, $^{4}J_{P-C} = 2.8$ Hz), 122.4 (CH, $^{3}J_{P-C} = 10.7$ Hz), 121.0 (CH), 117.2 (CH), 81.4 (*ipso*-Fec), 71.9 (2 × CH, C_5H_4), 69.9 (5 × CH, C_5H_5), 69.7 (2 × CH, C_5H_4); EI MS: *m/z* (%) 591 (M^{+}, 12), 378 (80), 329 (18), 313 (100), 278 (52), 248 (52), 201 (28), 183 (44), 121 (12), and 77 (22). Anal. Calc. for $C_{37}H_{30}FeNOP$: C, 75.14; H, 5.11; N 2.37. Found: C, 75.31; H, 4.99; N, 2.34%.

*3.13. General procedure for the preparation of 2-arylamino-3-ferrocenecarbonyl quinolines **24***

To a solution of the iminophosphorane **21** (0.55 g, 0.93 mmol) in a mixture of dry dichloromethane (15 ml) and dry toluene (15 ml) cooled at 0°C and under nitrogen, a solution of an equimolecular amount of the appropriate isocyanate was added. The reaction mixture was stirred at r.t. under nitrogen until the corresponding carbodiimide was completely formed. The dichloromethane was then removed using a stream of dry nitrogen, and the resulting solution was refluxed for 48 h. On cooling, the solvent was evaporated under reduced pressure and the residual product was chromatographed on a silica gel column with ethyl acetate:*n*-hexane (1:1) as eluent to give **24**. The following products were isolated after recrystallization from dichloromethane: *n*-hexane (1:1).

*3.13.1. Compound **24a** (Ar = C_6H_5)*

Yield 32%; m.p. 143–144°C; IR (Nujol): ν 3307, 1627, 1600, 1545, 1501, 1448, 1354, 1291, 1149, 1118, 798, 760 and 738 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 9.90 (s, 1H), 8.65 (s, 1H), 7.97 (d, 1H, $J = 7.5$ Hz), 7.70 (d, 1H, $J = 7.6$ Hz), 7.39 (t, 1H, $J = 7.6$ Hz), 7.35–7.26 (m, 5H), 7.06 (t, 1H, $J = 7.5$ Hz), 4.96 (t, 2H, $J = 1.8$ Hz), 4.68 (t, 2H, $J = 1.8$ Hz), 4.25 (s, 5H); ^{13}C-NMR (CDCl$_3$): δ 199.8 (C=O), 153.6 (q), 151.5 (q), 148.6 (q), 140.8 (CH), 138.8 (q), 132.2 (CH), 128.7 (CH), 128.6 (CH), 126.9 (CH), 123.7 (CH), 122.2 (CH), 121.2 (CH), 119.6 (q), 79.0 (*ipso*-Fec), 73.2 (2 × CH, C_5H_4), 71.8 (2 × CH, C_5H_4), 70.5 (5 × CH, C_5H_5); EI MS: *m/z* (%) 432 (M^{+}, 100), 367 (46), 272 (14), 219 (20), 215 (9), 185 (2), 121 (11), and 56 (4). Anal. Calc. for $C_{26}H_{20}FeN_2O$: C, 72.24; H, 4.66; N 6.48. Found: C, 72.09; H, 4.52; N, 6.39%.

*3.13.2. Compound **24b** (Ar = 4-H_3C–C_6H_4)*

Yield 35%; m.p. 124–125°C; IR (Nujol): ν 3302, 1634, 1604, 1542, 1511, 1440, 1109 and 754 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 9.90 (s, 1H), 8.42 (s, 1H), 8.05 (d, 1H, $J = 7.7$ Hz), 7.64 (d, 1H, $J = 7.7$ Hz), 7.40 (t, 1H, $J = 7.7$ Hz), 7.26 (d, 2H, $J = 8.0$ Hz), 7.12 (t, 1H, $J = 7.7$ Hz), 7.01 (d, 2H, $J = 8.0$ Hz), 4.84 (t, 2H, $J = 1.8$ Hz), 4.57 (t, 2H, $J = 1.8$ Hz), 4.09 (s, 5H), 2.23 (s, 3H); ^{13}C-NMR (CDCl$_3$): δ 195.0 (C=O), 153.5 (q), 138.4 (q), 137.1 (q), 136.7 (q), 132.6 (CH), 131.1 (CH), 129.4 (CH), 126.7 (q), 126.5 (CH), 124.1 (CH), 123.8 (CH), 119.9 (CH + q), 79.9 (*ipso*-Fec), 73.3 (2 × CH, C_5H_4), 69.9 (5 × CH, C_5H_5), 69.6 (2 × CH, C_5H_4), 20.4 (CH$_3$); EI MS: *m/z* (%) 446 (M^{+}, 100), 381 (38), 233 (15), 214 (12), 185 (6), 121 (13), 107 (9) and 55 6 (7). Anal. Calc. for $C_{27}H_{22}FeN_2O$: C, 72.66; H, 4.97; N 6.28. Found: C, 72.77; H, 4.81; N, 6.30%.

*3.13.3. Compound **24c** (Ar = 4-Cl–C_6H_4)*

Yield 38%; m.p. 143–144°C; IR (Nujol): ν 3304, 1626, 1596, 1537, 1489, 1445, 1291, 915 and 733 cm^{-1}; ^{1}H-NMR (CDCl$_3$): δ 9.90 (s, 1H), 8.62 (s, 1H), 7.85 (d, 1H, $J = (.5$ Hz), 7.74 (t, 1H, $J = 8.5$ Hz), 7.64 (d, 1H, $J = 7.5$ Hz), 7.28–7.24 (m, 5H), 4.88 (t, 2H, $J = 1.8$ Hz), 4.62 (t, 2H, $J = 1.8$ Hz), 4.18 (s, 5H); ^{13}C-NMR (CDCl$_3$): δ 199.1 (C=O), 151.6 (2q), 148.8 (q), 140.9 (CH), 138.9 (q), 132.2 (CH), 128.8 (CH), 128.7 (CH), 127.1 (CH), 123.8 (CH), 122.3 (q), 121.3 (CH), 119.7 (q), 79.2 (*ipso*-Fec), 73.3 (2 × CH, C_5H_4), 71.9 (2 × CH, C_5H_4), 70.6 (5 × CH, C_5H_5); EI MS: *m/z* (%) 468 (M^{+} + 2, 27), 466 (M^{+}, 100), 403 (19), 401 (50), 255 (8), 253 (20), 213 (9), 185 (7), 128 (2), 126 (9), 121 (12) and 56 (7). Anal. Calc. for $C_{26}H_{19}ClFeN_2O$: C, 66.91; H, 4.10; N 6.00. Found: C, 66.70; H, 4.22; N, 5.88%.

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