Substitution and ring-opening reactions of an azasubstituted [5]ferrocenophane: preparation of 1,1'-unsymmetrically disubstituted ferrocenes

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Dedicated to Professor Joan Bosch on the occasion of her 60th birthday

Abstract
New synthetic routes to 1,1'-unsymmetrically disubstituted ferrocene ligands bearing a quinoline ring directly linked to the ferrocene unit, along with the synthesis of a new structural motif based on an azasubstituted [5]ferrocenophane which incorporates a dihydroquinoline subunit, are presented.

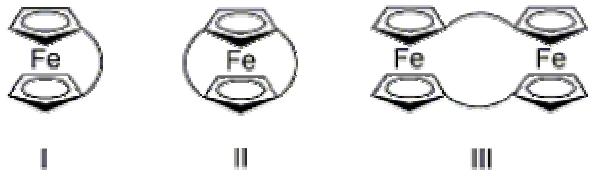
Keywords: Ferrocenophanes, 1,1'- disubstituted ferrocenes; ferrocenyl-quinolines; ferrocenyl carbenium ions

Introduction

New methods to obtain selectively ferrocenyl structures are of great interest because of the booming involvement of ferrocene derivatives in various fields such as catalysis, organic synthesis, new materials such as liquid crystals or polymers and supramolecular chemistry.[1] Then, in the last few decades the chemistry of ferrocenes has led to a wide variety of interesting compounds with valuable properties. In this context, much attention has been paid to the study of those ferrocenyl redox-active ligands in which a change in their electrochemical behaviour can be used to monitor complexation of guest species. For this reason, ferrocene derivatives containing atoms with good donor abilities have attracted additional interest, and then, the integration of one or more ferrocene units into a heterocyclic ring system has been recognized to constitute an increasingly important area of molecular recognition.

On the other hand, ferrocenophanes, in which the two cyclopentadienyl rings of ferrocene are joined by an atomic or molecular bridge, retain many of the characteristics of the parent ferrocene and are expected to show unique chemical properties owing to functionality of the side

arm. There have been many different classes of ferrocenophanes described, most of them possess exclusively carbon-based bridges with three modes of ring attachment[2]: mononuclear [m]ferrocenophanes (type I), mononuclear multiply-bridged $[m]^n$ ferrocenophanes (type II) and multinuclear $[m^n]$ferrocenophanes (type III).



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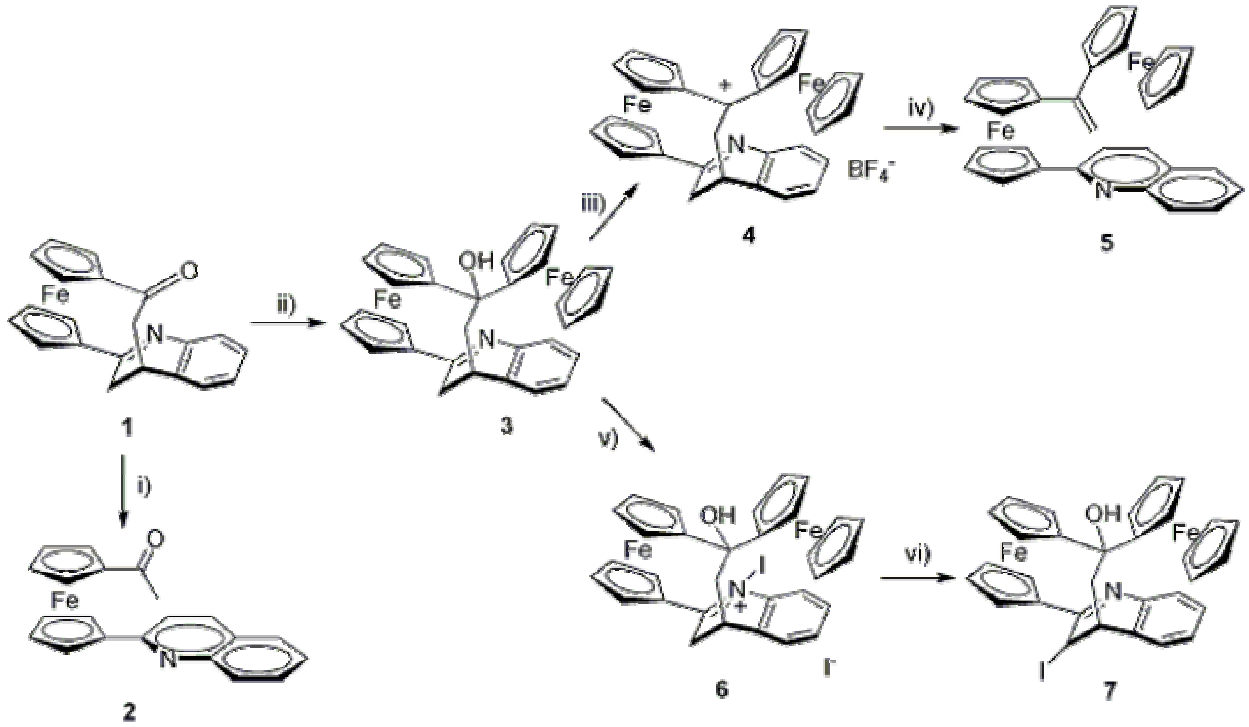
In the frame of our research program on the preparation of both azaheteroaryl substituted ferrocene derivatives[3] and nitrogen-rich $[m]^n$ ferrocenophanes[4] displaying not only redox-switchable character but also recognition properties for anions and metal cations, we now wish to report new aspects on the reactivity of the recently reported [5]ferrocenophane **1**[5] bearing a 2,4-bridged dihydroquinoline ring and efficient routes for its conversion into novel ferrocenyl-substituted quinolines.

Results and Discussion

The required ferrocene precursor for the synthesis of the new ferrocenyl substituted quinoline derivatives **2, 5**, **6** and **7** is the ferrocenophane **1,** which can be viewed either as a [5]ferrocenophane bearing a 2,4-bridged dihydroquinoline ring or [4](2,4)dihydroquinolinophane containing a 1,1'-disubstituted ferrocene bridge. Compound **1** has been prepared by Staudinger reaction of 3-(*o*-azidophenyl)[5]ferrocenophane-1,5-dione with tri-*n*-butylphosphine followed by an intramolecular aza-Wittig reaction.[5] Treatment a methanolic solution of 1,1'-[(3,4-dihydro-2,4-quinolinediyl)(2-oxo-1,2-ethanediyl)]-ferrocene **1** (1 equiv), containing an excess of KOH, under reflux temperature, afforded the quinoline-ferrocene derivative **2,** in 90% yield (Scheme 1), which was fully characterized using ^{1}H and ^{13}C NMR and mass spectrometry. ^{1}H NMR spectrum shows, as the most characteristic features, the presence of four signals corresponding to the Cp protons of the ferrocene moiety at δ 4.38, 4.49, 4.62 and 5.10 ppm, in addition to the signals corresponding to the heteroaromatic ring. On the other hand, ^{13}C NMR is also in agreement with the proposed 1,1'-unsymmetrically substituted structure, showing two sets of three signals each, corresponding to the CH and quaternary carbon atoms present within the two differently substituted Cp rings of the ferrocene unit. Formation of **2** probably involves an initial proton abstraction on the methylene group at position 4 of the bridge, followed by the cleavage of the cyclophane ring with simultaneous formation of the corresponding enolate, which tautomerizes to the acetyl substituent present at the 1 position of the ferrocene unit. It is worth

mentioning that 1,1'-unsymmetrically disubstituted ferrocenyl ligands are not very common due to the difficulty in preventing either 1,2-substitution or symmetrical substitution in both cyclopentadienyl (Cp) rings. This unprecedent synthetic methodology constitutes an elegant approach which allows the easy access to a 1,1'-unsymmetrical disubstituted ferrocene in which a quinoline ring is directly linked to one of the Cp rings of the ferrocene moiety.

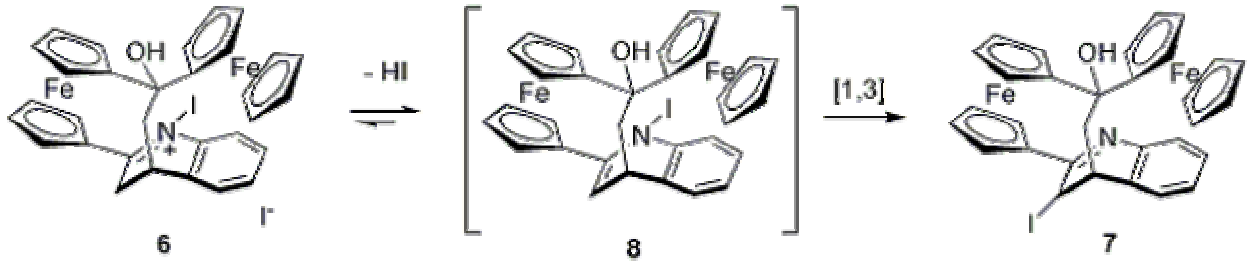


Scheme 1. i) KOH/MeOH, Δ, 18 h.; ii) FcLi/THF, N_2, rt, 10 min.; iii) HBF_4 (0.1 M in CH_2Cl_2)/CH_2Cl_2, r.t., 30 min.; iv) K_2CO_3 (0.1 M in anhydrous MeOH), CH_2Cl_2, r.t., 30 min.; v) I_2/dry toluene, N_2, r.t., 1 h.; vi) anhydrous $CHCl_3$, r.t., 72 h.

Likewise, 1,1'-[(3,4-dihydro-2,4-quinolinediyl)(2-ferrocenyl-2-hydroxy-1,2-ethanediyl)]-ferrocene **3**, obtained from **1** by reaction with ferrocenyllithium[6], was converted in 30% yield into 1-(α-ferrocenyl)vinyl-1'-(2-quinolyl)ferrocene **5** by a two step synthetic sequence. The first step, outlined in Scheme 1, involves the formation of a tertiary diferrocenylcarbenium ion **4,** by treatment of **3** with two equivalents of HBF_4 in dichloromethane at room temperature. It is worth mentioning that the stepwise addition of HBF_4 to a solution of **3** resulted in a clear evolution of the color from orange to deep purple, when the carbenium ion was fully formed. The second step involves the reaction of **4** with a methanolic solution of potassium carbonate, which should promote a proton abstraction on the methylene group at position 4 of the bridge with concomitant aromatization of the dihydroquinoline ring. It is important to emphasize that in spite of the high reactivity shown by the related (diferrocenyl)methyl carbocations towards methanol[7] the reaction of **4** with methanol in the presence of potassium carbonate provided the

diferrocenlmethylene derivative 5 instead of the expected methoxy derivative. The structure of the ferrocenylquinoline derivative **5** has been fully elucidated from its spectroscopic data. In the ^{1}H NMR spectrum of compound **5**, the ferrocenyl groups show clearly two sets of well-separated signals in addition to those corresponding to both the vinyl and heterocyclic moieties. This non-equivalence of the two ferrocenyl groups is also showed in its ^{13}C NMR spectrum. The ability of this methodology to provide the homobimetallic complex **5,** in which the two ferrocene units are coupled intimately, is of major importance due to the interest of this kind of molecular systems, containing more than one metallocene unit, which constitute key targets for the study of intramolecular communication between the covalently linked ferrocene units.[8]

In this context, attempts to promote the formation of a mixed-valence cation derived from compound **3**, bearing two metallocene centers, were carried out by partial chemical oxidation. Nevertheles, on treatment with iodine, compound **3** did not yield the corresponding mixed-valence derivative but, instead, it was directly converted into the 1-hydroxy-4-iodo-ferrocenophane **7**. Presumably, the reaction involves the initial formation of the intermediate N-iododihydroquinolinium salt **6**, isolated from the reaction medium which, on standing at room temperature, was transformed into **7** through a mechanism which should involve a previous intramolecular dehydrohalogenation followed by a [1,3]-halogen migration process, which is a very well established phenomenon in the azole derivatives[9] (Scheme 2).



Scheme 2

Compounds **6** and **7** were both fully characterised using ^{1}H and ^{13}C-NMR and FAB mass spectrometry. In addition, it is worth mentioning that a complete analogy exists between the NMR data of compound **6** and those corresponding to the monoprotonated species obtained upon addition of 1 equivalent of HBF_4 to **3.** This observation constitutes additional evidence which demonstrates that in this reaction a quaternization of the dihydroquinoline N atom takes place and consequently compound **6** is then formed. In general, the relative positions and multiplicity of the signals in ^{1}H-NMR of compound **7** constitutes a useful dataset to demonstrate the substitution at the 4 position of the cyclophane ring by the iodine atom. In fact, together with the characteristic pattern for the signals corresponding to the methylene and methine groups at 2 and 3 positions of the cyclophane bridge, appearing as double doublets at δ = 1.88 and 2.38 ppm and as a multiplet at δ = 3.56-3.58 ppm, respectively, a new deshielded methine proton appears, as a doublet, at δ = 6.24 ppm.

It is worth noting that this transformation proceeded very cleanly, without any traces of side products and, to the best of our knowledge, it constitutes the first example of the preparation of an 1,1,4-unsymmetrically trisubstituted [5]ferrocenophane.

Experimental Section

General Procedures. 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 a column of dimensions 60x4.5 cm and of silica gel (60 A C.C. 70-200µm, sds) as the stationary phase. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were determined as Nujol emulsions on a Nicolet Impact 400 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 400 MHz on a Bruker AC300 and 400. Chemical shifts refer to signals of tetramethylsilane in the case of ^{1}H and ^{13}C spectra. The EI and FAB$^+$ mass spectra were recorded on a Fisons AUTOSPEC 500 VG spectrometer, using 3-nitrobenzylalcohol as a matrix. Microanalyses were performed on a Carlo Erba 1108 instrument.

Preparation of 1-(acetyl)-1'-(2-quinolyl)ferrocene (2). To a solution of 1,1'-[3,4-dihydro-2,4-quinolinediyl)(2-oxo-1,2-ethanediyl)]ferrocene[5] **1** (0.1 g, 0.22 mmol) in freshly distilled MeOH (15 ml) KOH (0.145 g, 2.2 mmol) was added and the reaction mixture was heated under reflux temperature for 18 h. After cooling to room temperature, water (15 ml) was added and the product was extracted with CH_2Cl_2 (3×50 ml). The organic layer was dried over anhydrous $MgSO_4$ and then the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel using ethyl acetate/*n*-hexane (9/1) as eluent affording the pure compound **2** in 90% yield. IR (Nujol; cm^{-1}): 1684, 1606, 1512, 1283, 1124, 914, 832, 762, 628. ^{1}H-NMR ($CDCl_3$): δ 2.23 (s, 3H), 4.38 (t, 2H, ^{3}J = 1.8 Hz, Cp), 4.49 (t, 2H, ^{3}J = 1.8 Hz, Cp), 4.62 (t, 2H, ^{3}J = 1.8 Hz, Cp), 5.1 (t, 2H, ^{3}J = 1.8 Hz, Cp), 7.47 (t, 1H, J = 7.8 Hz), 7.5 (t, 1H, J = 8.5 Hz) 7.67 (td, 1H, J = 8.4 Hz, J = 1.3 Hz), 7.76 (d, 1H, J = 7.8 Hz), 8,03 (d, 1H, J = 8.5 Hz), 8.07 (d, 1H, J = (8.5 Hz). ^{13}C-NMR ($CDCl_3$): δ 27.50 (CH_3), 69.35 (2xCH, Cp), 71.02 (2xCH, Cp), 71.91 (2xCH, Cp), 73.63 (2xCH, Cp), 80.38 (q, Cp), 85.74 (q, Cp), 119.16 (CH), 125.84 (CH), 126.91 (q), 127.67 (q), 129.05 (CH), 129.66 (CH), 135.97 (CH), 148.27 (q), 157.46 (q), 201.96 (C=O). FAB MS (m/z (relative intensity):356 (M^++1, 100). Anal. Calcd for $C_{21}H_{17}FeNO$: C, 71.01; H, 4.82; N, 3.94. Found: C, 69.79; H, 4.61; N, 4.22.

Preparation of 1-(α-ferrocenyl)vinyl-1'-(2-quinolyl)ferrocene (5). To a solution of diferrocenyl carbenium tetrafluoroborate **4** (0.1 g, 0.16 mmol) in CH_2Cl_2 (5 ml) a solution of 0.1 M K_2CO_3 in dry MeOH (8 ml) was added and the solution was stirred for 30 min at room temperature. During this time, a change of the color in the solution, from green to brown, was observed. The solvent was removed under vacuum and the residue was chromatographed on a silica gel column using a mixture of ethyl acetate/*n*-hexane (3/7) as eluent. Crystallisation from Et_2O/*n*-hexane (1:1) gave the pure product in 30% yield. Mp 117-120 ºC. IR (Nujol; cm^{-1}) 1604,

1526, 1294, 1111, 1050, 853, 774, 741. ^{1}H-NMR ($CDCl_3$): δ 4.1 (s, 5H), 4.13 (t, 2H, ^{3}J = 1.8 Hz, Cp), 4.20 (t, 2H, ^{3}J = 1.8 Hz, Cp), 4.44-4.46 (m, 4H, Cp), 4.54 (t, 2H, ^{3}J = 2.1 Hz, Cp), 5.02 (t, 2H, ^{3}J = 2.1 Hz, Cp), 5.31 (d, 1H, ^{2}J = 1.2 Hz), 5.36 (d, 1H, ^{2}J = 1.2 Hz), 7.42-7.48 (m, 2H), 7.60 (td, 1H, J = 7.2 Hz, J = 1.6 Hz), 7.67 (d, 1H, J = 7. 8 Hz), 8.00 (d, 1H, J = 8.4 Hz), 8.03 (d, 1H, J = 7.8 Hz). ^{13}C-NMR ($CDCl_3$): δ 69.68 (2xCH, Cp), 69.99 (5xCH, Cp), 70.44 (2xCH, Cp), 71.56 (2xCH, Cp), 71.99 (2xCH, Cp), 72.43 (2xCH, Cp), 72.85 (2xCH, Cp), 84.97 (q, Cp), 87.20 (q, Cp), 88.13 (q, Cp), 110.42 (=CH_2), 119.77 (CH), 122.54 (q), 124.63 (CH), 125.23 (CH), 126.23 (q), 128.09 (CH), 129.62 (CH), 130.06 (CH), 148.20 (q), 154.00 (q). FAB MS (m/z (relative intensity):524 (M^++1, 77). Anal. Calcd for $C_{31}H_{25}Fe_2N$: C, 71.16; H, 4.82; N, 2.68. Found: C, 69.89; H, 4.82; N, 2.55.

Preparation of the *N*-iodo dihydroquinolinium iodide (6). To a solution of 1,1'-[3,4-dihydro-2,4-quinolinediyl)(2-ferrocenyl-2-hydroxy-1,2-ethanediyl)]ferrocene **3**[6] (0.1 g, 0.37 mmol) in freshly distilled toluene, a solution of I_2 (0.140 mg, 0.55 mmol) in the same solvent (10 ml) was added. The reaction mixture was stirred at room temperature and under N_2 atmosphere for 1 h. Then, Et_2O (25 ml) was added and the resulting deep purple precipitated was filtered , washed with dry toluene (3x5 ml) and crystallized from CH_2Cl_2/toluene (1/1), to give **6** in 60% yield. Mp 220-222 ºC (d). IR (Nujol; cm^{-1}) 3565, 1631, 1606, 1572, 1238, 1204, 1160, 1096, 836, 762. ^{1}H-NMR ($CDCl_3$): δ 1.92 (t, 1H, ^{3}J = 14.4 Hz), 2.48 (dd, 1H, J_{gem} = 14.4 Hz, ^{3}J = 4.8 Hz), 2.60 (s, 1H, OH), 2.61 (dd, 1 H, J_{gem} = 15.4 Hz, ^{3}J = 5.6 Hz), 3.45 (m, 1 H), 3.74 (d, 1H, J_{gem} = 15.4 Hz), 3.89 (m, 1 H, Cp), 4.04-4.07 (m, 3 H, Cp), 4.15-4.16 (m, 1 H, Cp), 4.17-4.18 (m, 1 H, Cp), 4.18-4.19 (m, 1 H, Cp), 4.20 (s, 5H, Cp), 4.45-4.47 (m, 1H, Cp), 4.80.4.84 (m, 1H, Cp), 4.95-4.97 (m, 2H, Cp), 5.35-5.37 (m, 1H, Cp), 7.13-7.42 (m, 3H), 7.66 (d, 1H, J = 7.0 Hz). ^{13}C-NMR ($CDCl_3$): δ 31.30 (CH_2), 32.41 (CH), 42.82 (CH_2), 65.60 (CH, Cp), 65.80 (CH, Cp), 67.31 CH, Cp), 67.81 (q), 68.09 (CH, Cp), 68.50 (CH, Cp), 68.59 (5xCH, Cp), 68.80 (CH, Cp), 69.79 (CH, Cp), 71.70 (CH, Cp), 73.08 (CH, Cp), 75.31 (CH, Cp), 76.52 (CH, Cp), 77.71 (CH, Cp), 99.50 (q, Cp), 104.39 (q, Cp), 122.90 (CH), 126.91 (CH), 127.57 (CH), 128.43 (CH), 131.78 (q), 139.80 (q), 173.11 (C=N). FAB MS (m/z (relative intensity): 669 (M^++1-I, 42), 542 (M^++1-2I, 100). Anal. Calcd for $C_{31}H_{27}Fe_2I_2NO$: C, 46.83; H, 3.42; N, 1.76. Found: C, 46.58; H, 3.17; N, 1.50.

Preparation of 1,1'-[3-iodo-(3,4-dihydro-2,4-quinolinediyl)(2-ferrocenyl-2-hydroxy-1,2-ethanediyl]ferrocene (7). A solution of *N*-iodo dihidroquinolinium yodide **6** (0.1 g, 0.126 mmol) in anhydrous $CHCl_3$ was stirred at room temperature and under N_2 atmosphere for 72 h. The solution was filtered over a deactivated silica gel pad which was washed with CH_2Cl_2 (3x25 ml). The solution was evaporated to dryness and the resulting residue was triturated with Et_2O/*n*-pentane to give an orange solid which was chromatographed on a silica gel column using ethyl acetate/*n*-hexane (1/1) as eluent to yield **7,** in 70%, as an analytically solid pure sample. Mp 225-228 ºC (d). IR (Nujol; cm^{-1}) 3510, 1592, 1562, 1248, 110, 1066, 1302, 880, 831, 757, 723. ^{1}H-NMR ($CDCl_3$): δ 1.88 (dd, 1H, J_{gem} = 14.4 Hz, ^{3}J = 12.3 Hz), 2.38 (dd, 1H, J_{gem} = 14.4 Hz, J = 5.4 Hz), 2.68 (s, OH), 3.56-3.58 (m, 1H), 3.81-3.82 (m, 1H, Cp), 3.84-3.85 (m, 1H, Cp), 3.94-3.95 (m, 1H, Cp), 4.00-4.01 (m, 1H, Cp), 4.07-4.10 (m, 1H, Cp), 4.16 (t, 2 H, Cp, ^{3}J = 1.8 Hz),

4.17, s, 5H, Cp), 4.45-4.50 (m, 2H, Cp), 4.59-4.61 (m, 1H, Cp), 4.92-4.93 (m, 1H, Cp), 5.02-5.03 (m, 1H, Cp), 6.24 (d, 1H, ^{3}J = 3.0 Hz), 7.20 (dd, 1H, J = 7.5 Hz, J = 1.5 Hz), 7.29 (dd, 1H, J = 7.5 Hz, J = 1.2 Hz), 7.37 (td, 1H, J = 7.8 Hz, J = 1.5 Hz), 7.47 (d, 1H, J = 7.2 Hz). ^{13}C-NMR ($CDCl_3$): δ 22.05 (CH), 43.27 (CH), 43.68 (CH_2), 65.18 (CH, Cp), 65.26 (CH, Cp), 65.91 (CH, Cp), 66.11 (CH, Cp), 67.51 (q), 67.97 (CH, Cp), 67.86 (CH, Cp), 67.89 (CH, Cp), 68.47 (5xCH, Cp), 68.62 (CH, Cp), 69.31 (CH, Cp), 69.68 (CH, Cp), 71.36 (CH, Cp), 73.35 (CH, Cp), 83.21 (q, Cp), 97.87 (q, Cp), 104.6 (q, Cp), 126.47 (CH), 126.70 (CH), 126.83 (CH), 128.48 (CH), 129.70 (q), 143.94 (q), 165.42 (C=N). FAB MS (m/z (relative intensity): 668 (M^{+}+1, 96). Anal. Calcd for $C_{31}H_{26}Fe_2INO$: C, 55.81; H, 3.93; N, 2.10. Found: C, 55.51; H, 4.21; N, 2.05.

Acknowledgements

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