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Synthesis and Diels-Alder Reactions of 3-methylene-2-ferrocenylmethylenequinuclidine

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Abstract: The synthesis and chemical reactivity in Diels-Alder reactions of the title compound **6** is described. When **6** was reacted with N-phenylmaleimide, a 3:1 mixture of isomers *exo* **14a** and *endo* **14b** was found, while with triazolinedione **13**, a novel ferrocenyl heterocycle **15** was formed. The structures for **14b** and **15** were confirmed by X-ray diffraction analysis. © 1997 Elsevier Science Ltd.

Introduction

In the last years, new methodologies have been developed for the synthesis of 1,3 dienes bearing the ferrocenyl moiety.[1-4] These compounds are key intermediates for dimerization,[5] cyclodimerization,[6,7] cycloaddition reactions and the preparation of new polyheterocycles.[3,8]

Recently the synthesis of 2-methylene-3-ferrocenylmethylenecamphene (**1**), and 1-methylene-3-ferrocenylmethylenetetralin (**2**), two 1,3-dienes with fixed conformation, obtained by a dehydration process from the corresponding alcohols, has been described.[4,7] Compound **2** was shown to be unstable, dimerization occurring spontaneously to afford the spiro adduct **3**. In contrast, diene **1** is a stable compound which could also be obtained from the salt **4** by treatment with N,N-dimethylaniline in pyridine. Several ferrocenyl compounds have shown various antiphlogistic activities[9-11] among other biological properties.[10,11] Some substances structurally related to CP-96345 (**5**)[12] having the quinuclidine moiety have also shown biological activity.[13]

In the present work we describe the synthesis of **6** a new 1,3 diene which combines both quinuclidinyl and ferrocenyl moieties in its structure and report on the chemical reactivity of this diene in ($4\pi+2\pi$)-cycloaddition reactions.

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Results and Discussion

The synthesis of diene **6** was carried out as outlined in Scheme 1. Quinuclidinone hydrochloride **7** was reacted with sodium hydroxide and ferrocencarboxaldehyde **(8)** to give the corresponding aldol-condensation product **9**. Treatment of **9** with methyllithium afforded alcohol **10**, which in turn was dehydrated with phosphorus oxychloride and converted to diene **6** in 46% overall yield. An alternative route to **6** from carbinol **10** involved the formation of the corresponding tetrafluoroborate cation[14] and subsequent deprotonation with N,N-dimethylaniline. The structures of compounds **9**, **10** and **6** have been confirmed by spectroscopic methods.

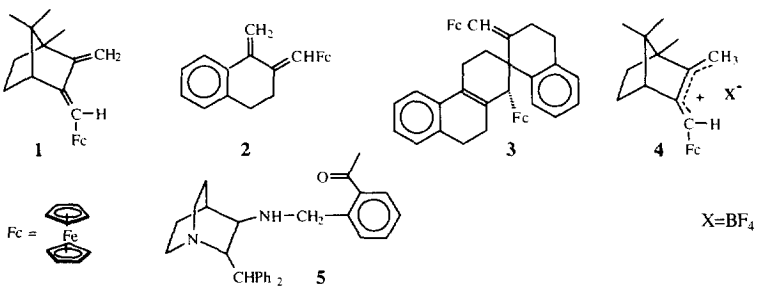
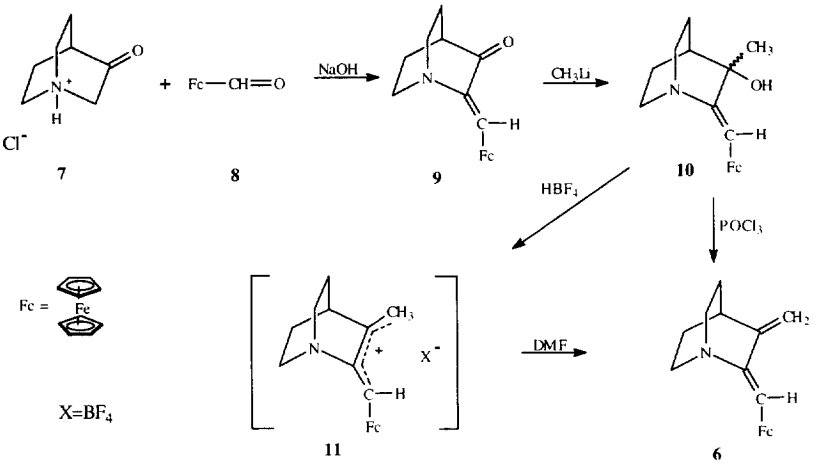


Chart 1

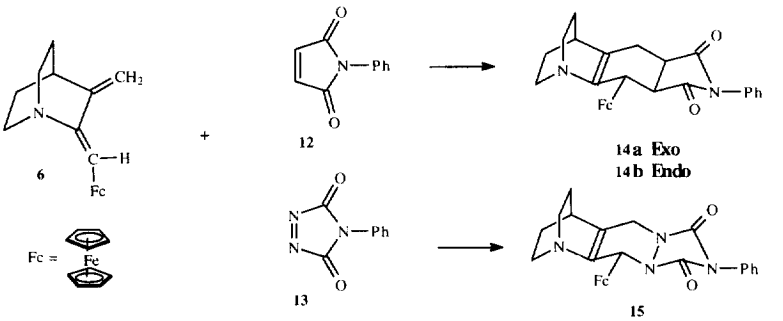
The ferrocenyl moiety has been considered as electron-donating substitutent[15] and its location on the diene is important in terms of its reactivity. When a 1,3-diene contains a ferrocenyl moiety in position 2, the (4π+2π)-cycloaddition reaction with an appropiate dienophile carrying an electron attracting group readily occurs at ambient temperature. However, when the ferrocenyl moiety is on position 1, the reaction takes place only in benzene at reflux temperature.[14] Along with the expected adducts, dimerization products are often isolated.[14,16] In order to provide knowledge on the chemical reactivity of diene **6**, several (4π+2π)-cycloaddition reactions were performed using N-phenylmaleimide **(12)** and 4-phenyl-3H-1,2,4-triazole-3,5(4H)-dione **(13)** as dienophiles. In the first case, the adducts **14** were obtained in 80% yield as a 3:1 mixture of the *exo* **14a** and *endo* **14b** stereoisomers. The adducts were separated by crystallization, purified by column chromatography and characterized by spectroscopic methods and X-ray crystallography for **14b**. The bulky ferrocenyl moiety tends to have the major influence on the regioselectivity of the cycloaddition affording the *exo*-stereoisomer **14a** as the main product. In the second case, adduct **15** was obtained in 85% as the only product and its structure was confirmed by X-ray analysis. The reactivity of the diene **6** towards dienophiles was that expected for a diene with a ferrocenyl substituent in position 1. Indeed, attempts to react **6** with N-phenylmaleimide **(12)** at room temperature proved futile. Therfore the cycloaddition reaction was

carried out in toluene at reflux for 8 h. In contrast, **6** reacted smoothly under non-forcing conditions with the highly-reactive heterodienophile **13**.



Scheme 1

The ORTEP views of **14b** and **15** are shown in Figure 1. The quinuclidine nucleus consists of three six-membered rings, all of them approaching an ideal boat conformation, despite the fact that two rings share two sp^2 hybridized C-atoms; C(9) and C(10), that show trigonal arrangement. The sum for the three angles is



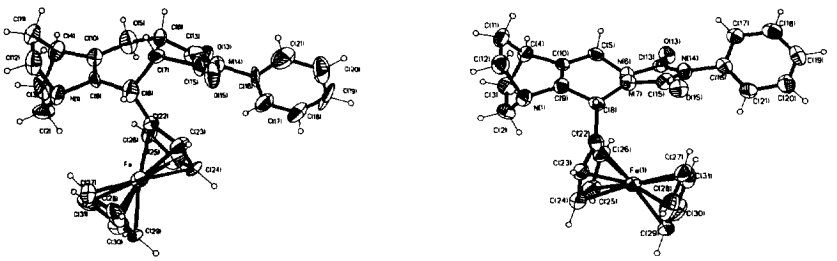
Scheme 2

360 (2)° for compound **14b** and **15**. In both compounds, the cyclopentadienyl group is covalently bounded to a sp^3 hybridized C(8)-atom in a pseudo-axial orientation. The bond lengths are 1.541(48) and 1.537(10) for **14b** and **15**, respectively. The cyclopentadienes themselves are slightly eclipsed and the distances are normal and comparable with those found in ferrocene.

In structure **14b**, the succinimide ring is in an envelope conformation with C(6) out of the plane, and the N atom bearing the phenyl substituent shows a slightly pyramidal geometry with a sum of the bond angles

around of 370(2)°. C(6) And C(7) show tetrahedral geometry (the sum of the three bond angles is 332(2)° and 328(2)° respectively) with a *cis* relationship between the H atoms; H(6)-C(6)-C(7)-H and a torsion angle of 28.8 (8)°. The cyclohexene ring exists in the half-boat conformation with C(5) and C(8) displaced by 0.367 Å and 0.255 Å, respectively, in the same direction and opposite to C(7) by 0.399 Å from the least-square plane. The torsion angle between C(5)-C(6)-C(7)-C(8) is 28 (4)°.

The triazolinedione ring in **15** is planar to within 0.026 Å. The nitrogen atom bearing the phenyl substituent is trigonal, the sum of the three bond angles is 359.9 (6)°. The nitrogen atoms N(6) and N(7) are slightly pyramidal and the sum of the bond angles is 340.6(5)° and 354.6(5)°, respectively. Carbons C(5) and C(8), which are included in the six-membered ring are *trans* and twisted out of the triazole plane by an average of 23.2°. The cyclohexene ring exhibits a half-chair conformation with N(6) and N(7) displaced by 0.254 Å and 0.397 Å in the opposite direction from the least-square plane and shows a torsion angle C(5)-N(6)-N(7)-C(8) of 63.1 (7)°.



14b **15**

Figure 1. The molecular structure of compounds **14b** and **15.**

Finally, a remarkable difference between molecules **14b** and **15** is the orientation of the ferrocenyl moiety. In the first case, it is located under the quinuclidine ring while in the second structure it is found beneath the quinuclidine ring under the triazolinedione unit, probably because **15** exhibits a more planar conformation than **14b**, and consequently there is less interaction between the ferrocenyl moiety and the quinuclidine ring.

Preliminary biological tests have shown anti-inflammatory activity for compounds **6**, **9**, **10** and **15**. A complete study is in progress and the results will be reported elsewhere.

Experimental Section

General Remarks.

Melting points were determined with a Fisher-Johns melting point apparatus and are

uncorrected. Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer. ^{1}H NMR spectra were measured on a Varian Gemini 200 (200 MHz) and a Varian VX-300 (300 MHz) spectrometers. The chemical shifts are expressed in ppm downfield from tetramethylsilane (δ=0) as an internal standard. Mass spectra were taken with a JEOL JMS AX505HA mass spectrometer. Elemental analyses were performed at Galbraith Laboratories, INC. Knoxville, TN. HRMS were recorded with a JEOL JMS-SX102A mass spectrometer. X-ray crystallographic data were collected at room temperature on a Siemens P4 and Siemens P3/F diffractometers for **14b** and **15** respectively.

2-Ferrocenylmethylenequinuclidinone (9). To a well stirred mixture of 1g (6.18 mmoles) of quinuclidinone, 20 ml of ethanol and 1.32 g (6.18 mmoles) of ferrocenylcarboxaldehyde was added 2 ml of a 30% aquous solution of sodium hydroxide and stirring continued at room temperature for 4 h. Benzene (50 ml) and water (20 ml) were added to the mixture and the organic layer separated. The aqueous layer was extracted (2 x 20 ml) with benzene. The organic extracts were combined, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was crystallized from hexane to give 1.68 g (85%) of compound **9** as dark-red crystals. mp 122-123 °C. IR ($CHCl_3$): 3030, 2961, 2930, 2871, 1716, 1608, 1460, 1381, 1277, 1123, 1098, 1041, 925 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.95 (m, 4H, -CH_2-), 2.55 (m, 1H, CH-CO), 2.88 (m, 2H, CH_2-N), 3.05 (m, 2H, CH_2-N), 4.09 (s, 5H, Fc), 4.39 (m, 2H, Fc), 4.89 (m, 2H, Fc), 6.94 (s, 1H, =CH). ^{13}C NMR 26.12 (-CH_2-), 40.37 (CH-), 47.61 (CH_2-N), 69.46 (Fc), 71.02 (Fc), 71.8 (Fc), 127.61 (CHFc), 142.0 (C=), 205.25 (C=O). MS m/z, %: 321 (M^+, 48), 279 (27), 261 (21), 167 (55), 149 (100), 112 (39), 70 (40). HRMS Calcd for $C_{18}H_{19}NOFe$ 321.0816. Found 321.0829. Anal. calcd for $C_{18}H_{19}NOFe$: C, 67.28; H, 5.96; N, 4.36. Found: C, 67.30; H, 5.94; N, 4.25.

3-Hydroxy-3-methyl-2-ferrocenylmethylenequinuclidine (10). To a suspension of 5.12 g (10 mmol) of methyllithium in dry ether was added dropwise under argon atmosphere a solution of 3.1 g (9.65 mmoles) of **9** in benzene and the mixture stirred at room temperature for 2 h. The reaction was quenched with a 5% aquous solution of sodium hydroxide. The organic layer was separated, washed with water (2x15 ml) and dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was cyrstallized from ethanol to afford 2.6 g (77%) of compound **10** as orange crystals. mp: 161-162 °C. IR ($CHCl_3$): 3689, 3606, 3025, 2954, 2873, 1521, 1476, 1195, 1105, 1041, 925 cm^{-1}. ^{1}H NMR ($CHCl_3$); δ 1.50 (s, 3H, CH_3-), 1.62 (m, 2H, -CH_2-), 1.69 (m, 3H, -CH_2-, OH), 2.05 (m, 1H, CH), 2.76 (m, 1H, CH_2-N), 2.97 (m, 2H, CH_2-N), 4.05 (s, 5H, Fc), 4.17 (m, 2H, Fc), 4.67 (m, 1H, Fc), 4.72 (m, 1H, Fc), 6.05 (s, H, =CH-Fc). ^{13}C NMR ($CDCl_3$): 21.98 (CH_2-), 24.79 (-CH_2-), 27.68 (CH_3-), 36.06 (CH-), 46.57 (CH_2-N), 47.50 (CH_2-N), 68.45 (Fc), 68.89 (Fc), 69.51 (Fc), 69.62 (Fc), 72.03 (C-OH), 80.20 (Fc-ipso), 117.64 (CHFc), 153.19 (-C=). MS m/z, %: 337

(M^+, 100), 338 (M^++1, 44), 319 (M^+-H_2O, 11), 272 (25), 254 (13), 171 (10), 121 (12). HRMS Calcd for $C_{19}H_{23}NOFe$ 337.1129. Found 337.1123. Anal. calcd for $C_{19}H_{23}NOFe$: C, 67.63; H, 6.88; N, 4.15. Found: C, 67.06; H, 6.95; N, 3.98.

3-Methylene-2-ferrocenylmethylenequinuclidine (6).

Procedure A. A solution of 1.12 g (3.32 mmol) of carbinol **10** in 50 ml of pyridine was cooled at -10°C and were 2 ml of $POCl_3$ added dropwise. After stirring for 3 h, the reaction was quenched with water (100 ml), the organic layer separated, washed with water (20 ml) and the solvent removed under reduced pressure. The residue was purified by flash chromatography (silica gel) to afford 0.75 g (70%) of compound **6** as orange crystals, mp. 92-93 °C.

Procedure B. In a round bottom flask fitted with a magnetic stirrer and nitrogen atmosphere a solution of 2.0 g (5.93 mmoles) of carbinol **10** in 100 ml of anhydrous ether was placed and the system swept with nitrogen. Tetrafluroboric acid etherate (54 Wt%) (2ml) was added dropwise via a hypodermic syringe at room temperature while the mixture turned orange. After stirring for 30 min a yellow solid was formed and removed by filtration under nitrogen atmosphere. The crude product was placed in a round bottom flask fitted with a septum and immediately covered with 20 ml of methylene chloride and swept with nitrogen. Next, 2.0 ml of N,N-dimethylaniline were added dropwise via syringe. After 20 min of stirring at room temperature, 50 ml of benzene were added to the red-colored reaction mixture and stirring continued for 30 min. Next, 50 ml of water were added, the organic layer separated, washed with a 1% v/v solution of hydrochloric acid, water, dried over sodium sulfate and the solvent removed under reduced pressure. The residue was chromatographied on neutral alumine using hexane as eluent to afford 1.23 g (65%) of diene **6**. IR ($CHCl_3$): 3043, 2947, 2871, 1604, 1521, 1476, 1423, 1027, 929 cm^{-1}. ^1H NMR ($CDCl_3$): 1.67 (td, J=7.7 J=2.6, 4H, -CH_2-), 2.50 (q, 1H, CH-C=), 2.95 (m, 4H, CH_2-N), 4.07 (s, 5H, Fc), 4.19 (m, 2H, Fc), 4.70 (s, 1H, CH=C), 4.76 (m, 2H, Fc), 5.16 (s, CH=C), 6.20 (s, 1H, CHFc=C). ^{13}C NMR ($CDCl_3$): δ 28.08 (-CH_2-), 34.36 (CH), 47.83 (CH_2-N), 68.67 (Fc), 68.88 (Fc), 69.74 (Fc), 80.70 (Fc), 101.14 (CH_2=), 114.95 (C=), 144.87 (C-Fc), 150.80 (N-C=). MS *m/z*, %: 319 (M^+, 22), 319 (18), 256 (28), 213 (15), 171 (20), 149 (43), 83 (60), 69 (95), 57 (100). HRMS Calcd for $C_{19}H_{21}NFe$ 319.1023. Found 319.1027. Anal. calcd for $C_{19}H_{21}NFe{\cdot}H_2O$ C, 67.63; H, 6.82; N, 4.15. Found: C, 67.24; H, 6.59; N, 3.99.

N-phenylimide-3-ferrocenyl-4,5-(piperidine-1,4diyl) Δ^4-tetra hydrophtalic acid 14a and 14b.

A mixture of 1.06 g (3.32 mmol) of diene **6**, 0.6 g (3.46 mmol) of N-phenylmaleimide and 50 ml of toluene was heated under reflux. The reaction was monitored by tlc until dissappearance of starting material, 8h. After this time, the solvent was removed by rotatory evaporation under reduced pressure and the residue chromatographed on silica gel using a mixture of hexane-benzene 10:1 as eluent to afford 1.3 g (81.5%) of a

3:1 mixture of the exo and endo isomers. The endo isomer **14b** could be separated by fractional crystallization from benzene to give 0.26g (16%). The mother liquor was evaporated to dryness and the residue chromatographed on a silica gel column to afford the exo isomer **14a** 0.78 g (49%).

Exo isomer **14a**: red crystals, mp 181-182 °C. IR ($CHCl_3$): 3099, 3040, 2946, 2912, 2874, 1710, 1501, 1457, 1386, 1184, 1105, 1028, 966 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.35 (m, 2H, -CH_2-), 1.55 (m, 2H, -CH_2-), 2.43 (m, 3H, CH_2-N, C=C-C$\underline{H}_2$), 2.72 (m, 2H, C=C-CH, C=C-C$\underline{H}_2$), 2.89 (m, 2H, CH_2-N), 3.40 (m, 1H, CH-CO), 3.76 (dd, J=8.9 Hz, J=1.3 Hz), 3.99 (m, 2H, Fc), 4.12 (m, 2H, Fc), 4.26 (s, 5H, Fc), 4.30 (m, 1H, CH-Fc), 7.27 (m, 2H, Ar), 7.43 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$) δ: 26.80 (-CH_2-C=C), 28.51 (-CH_2-), 29.07 (-CH_2-), 32.19 (CH-Fc), 40.10 (CH-C=O), 40.29 (CH-C=O), 47.23 (CH-C=), 49.05 (CH_2-N), 50.27 (CH_2-N), 65.54 (Fc), 67.70 (Fc), 67.90 (Fc), 68.93 (Fc). 90.24 (Fc ipso), 126.11 (Ar), 128.64 (Ar), 129 (Ar), 132.06 (Ar ipso), 136.42 (-C=), 146.93 (N-C=), 178.49 (C=0), 179.49 (C=0). MS m/z %: 492 (M^+, 56), 491 (100), 463 (22), 425 (27), 398 (14). HRMS Calcd for $C_{29}H_{28}N_2O_2Fe$ 492.1500. Found 492.1511. Anal. calcd for $C_{29}H_{28}N_2O_2Fe$: C, 70.71; H, 5.73; N, 5.69. Found: C, 70.46; H, 5.83; N, 5.34.

Endo isomer **14b**. Yellow crystals. mp 203-204 °C. IR ($CHCl_3$): 3069, 3028, 2945, 2870, 1712, 1601, 1501, 1385, 1194, 1105, 1004, 928. ^1H NMR ($CDCl_3$) δ: 1.48 (m, 2H, -CH_2-), 1.58 (m, 2H, -CH_2-), 2.56 (m, 4H, CH_2-N, C=C-C$\underline{H}_2$), 2.91 (m, 1H, C=C-CH, C=C-C$\underline{H}_2$), 3.07 (m, 4H, CH_2-N), 3.22 (m, 2H, CH-CO), 3.75 (m,1H), 3.92(m, 1H, Fc), 4.08 (m, 2H, Fc), 4.12 (m,2H,Fc), 4.21(s, 5H, Fc), 6.96 (dd, 2H, Ar), 7.32 (m, 3H, Ar). ^{13}C NMR ($CDCl_3$) δ: 23.35 (-CH_2-C=C), 28.35 (-CH_2-), 29.48 (-CH_2-), 32.46 (CH-Fc), 39.18 (CH-C=O), 40.40 (CH-C=O), 49.61 (CH-C=), 49.95 (CH_2-N), 50.13 (CH_2-N), 66.87 (Fc), 67.67 (Fc), 68.06 (Fc), 69.13 (Fc), 84.35 (Fc ipso), 126.54 (Ar), 128.16 (Ar), 128.62 (Ar), 131.51 (Ar ipso), 138.76 (-C=), 145.77 (N-C=), 176.79 (C=0), 178.43 (C=0).MS m/z %: 492 (M+, 36), 491 (100), 463 (15), 425 (10), 398 (11). HRMS Calcd. for $C_{29}H_{28}N_2O_2Fe$ 492.1000. Found 492.1517. Anal. calcd for $C_{29}H_{28}N_2O_2Fe$: C, 70.73; H, 5.69; N, 5.69. Found: C, 70.32; H, 5.84; N, 5.40. Crystal data $C_{29}H_{28}N_2O_2Fe$, M=492.4. Rhombohedral, a=30.085(4), c= 14.630(7) Å, v=11470(7) $Å^3$, space group R-3. The structure was solved by the direct method[17,18] and refined by full-matrix least-squares with anisotropic temperature factor for the non-hydrogen atoms.

N-phenylimide-3-ferrocenyl-4,5-(piperidine-1,4diyl)-1,2 diaza Δ^4-tetrahydrophtalic acid 15.

To a well stirred solution of 1.06 g (3.32 mmol) of diene **6** in 70 ml of benzene was cooled to 0-5°C and added in small portions 0.6 g (3.43 mmoles) of triazolone **13** over 5 min. After stirred for 1 h the mixture reaction was allowed to warm at room temperature and stirred for 30 min. Solvent was removed under reduced pressure and the residue crystallized from benzene to afford 1.4 g (85%) of pure adduct **15** as yellow crystals mp 227-228 °C. IR ($CHCl_3$); 3069, 2948, 2871, 1769, 1710, 1604, 1504, 1421, 1290, 1141, 1027,

929. ^{1}H NMR ($CDCl_3$): 1.63 (m, 2H, -CH_2-), 1.84 (m, 2H, -CH_2-), 2.72 (m, 2H, CH_2-N), 2.95 (m, 1H, CH), 3.26 (m, 2H, -CH_2-N), 4.14 (m, 2H, Fc), 4.16 (d, J=16.8 Hz, 1H, =C-CH_2-N), 4.23 (m, 2H, Fc), 4.25 (s, 5H, Fc), 4.46 (d, J=16.8 Hz, 1H, =C-CH_2-N), 5.63 (s, 1H, CH-Fc), 7.48 (m, 5H, Ar). ^{13}C NMR ($CDCl_3$): δ 29.16 (-CH_2-), 29.27 (-CH_2-), 45.04 (CH), 49.39 (CH_2-N), 50.37 (CH_2-N), 55.58 (=C-CH_2-N), 67.20 (=C-CH-Fc), 67.56 (Fc), 68.54 (Fc), 69.35 (Fc), 84.46 (Fc ipso), 125.44 (Ar), 128.03 (Ar), 129.08 (Ar), 131.28 (C=), 133.91 (Ar-ipso), 142.56 (N-C=), 150.97 (C=0), 153.67 C=0). MS m/z, %: 494 (M^+, 34), 493 (M^+-1, 100), 319 (43), 254 (13). Anal. calcd for $C_{27}H_{26}N_4O_2Fe$: C, 65.57; H, 5.26; N, 11.33. Found: C, 64.92; H, 5.33; N, 11.48.

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