Ferrocene Studies. IV. Some Furan Containing Derivatives of Ferrocene (1)

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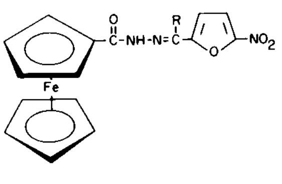
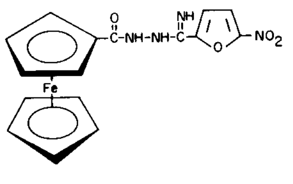
The condensation of ferrocenecarboxyhydrazide, ferrocenecarboxaldehyde and acetylferrocene with a number of furan derivatives is reported. The reaction of chalcones containing both the furan and the ferrocene nucleus with phenylhydrazine and hydrazine proceeds to yield pyrazolines.

The antibacterial activity of various 2-substituted-5-nitrofurans is well known (2) while the application of the ferrocene system to medicinal chemistry has not been investigated to any extent (3). We with to report on work aimed at the synthesis of compounds containing both of these groups.

Condensation of ferrocenecarboxyhydrazide with 5-nitro-2-furaldehyde or with 5-nitro-2-acetylfuran gave Ia and Ib, respectively. Using the procedure of Burch and Smith (4) ferrocenecarboxyhydrazide was condensed with ethyl 5-nitro-2-furimidate hydrochloride to give *N*-ferrocenecarboxamido-5-nitro-2-furamidine (II). Attempts to cyclize II to a triazole derivative failed under a variety of conditions (4).



Ia, R = H
b, R = CH$_3$



II

The infrared, nuclear magnetic resonance, and mass spectra of Ia, Ib, and II are consistent with the structures assigned and are shown in the Experimental Section. It is of interest to note that contrary to the general pattern with metallocenes the molecular ion is not the base peak in these three compounds. The major distinguishable path, however, seems to be one typical of ferrocene giving rise to fragments such as A - G (Fc = $C_{10}H_9Fe$). Peaks with m/e of 137 and 230 are also present in all three compounds.

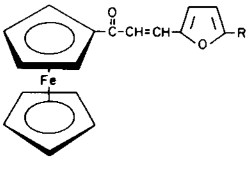
$FcCO^+$	$C_5H_5Fe^+$	$C_5H_5FeC_5H_4^+$
213	121	185
A	B	C

$C_5H_5C_5H_4^+$	$C_5H_4C_5H_4^+$	$C_5H_5^+$
129	128	65
D	E	F

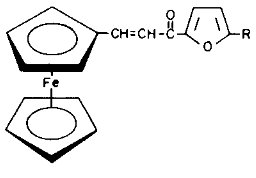
Fe^+	$FcCH{=}CHCO^+$	$FcCH{=}CH^+$
56	239	211
G	H	I

It was found that although acetylferrocene condenses readily with 2-furaldehyde (5) and with 5-methyl-2-furaldehyde to give IIIa and IIIb, this reaction failed under a wide variety of conditions when applied to 5-nitro-2-furaldehyde in attempts to prepare IIIc.

Although the condensation to lead to IIIc failed, it was found that ferrocenecarboxaldehyde could be condensed with both 2-acetylfuran and with 2-acetyl-5-nitrofuran to give IVa and b, the isomers of IIIa and c.



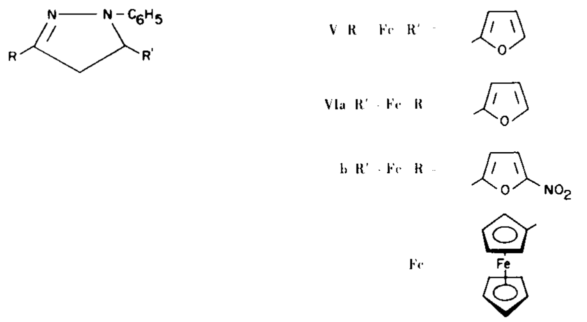
IIIa, R = H
b, R = CH$_3$
c, R = NO$_2$



IVa, R = H
b, R = NO$_2$

The infrared, nuclear magnetic resonance and mass spectra of III and IV are consistent with the structures assigned and are shown in the Experimental Section. As is typical of metallocenes, but in contrast to I and II, III and IV exhibited a molecular ion peak that was also the base peak. In contrast to I and II, III exhibited only a very weak peak at m/e = 213 (A). A fairly strong M-65 (C_5H_5) peak was observed in IIIa, IIIb, and IVa, while IVb exhibited strong peaks at m/e = 239 and 211 (H and I) which were only weak in IVa. Peaks assigned to B, D, E, and G played a major role in these four chalcones.

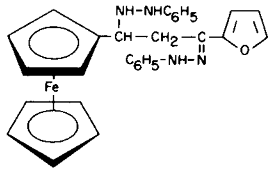
The only ferrocenylpyrazoline derivative found in the literature is 1-phenyl-3-ferrocenyl-2-pyrazoline synthesized by Hauser and coworkers (6) through reaction of phenylhydrazine with the appropriate Mannich base. Reaction of IIIa and IVa with phenylhydrazine gave the pyrazolines V and VIa respectively.



The infrared, nuclear magnetic resonance and mass spectra of these compounds is included in the Experimental Section and is consistent with the pyrazoline structure rather than an unsaturated hydrazone. For example, in V the deshielding effect of the C=N causes the protons of the substituted cyclopentadienyl ring to be shifted downfield, the $H_{2,5}$ protons occurring at 5.99δ, and the $H_{3,4}$ protons at 4.66 δ relative to the unshifted C_5H_5 protons at 4.45 δ, whereas in VIa all nine ferrocene protons occur at 4.45 δ indicating the absence of such deshielding. The chalcone (IVa) precursor of VIa exhibits this shielding with the $H_{2,5}$ protons at 4.88 δ and the $H_{3,4}$ protons at 4.77 δ. In addition a two proton absorption for the newly formed methylene group is found at 3.62 δ and 3.98 δ for V and VIa, respectively, and the absence of vinyl protons is noted. The mass spectra indicate a major fragmentation path through m/e = 238, 211, and on to A - D and G to be common for both pyrazolines. In VIa the fragment m/e 238 is apparently formed by stepwise loss of 92 and 66 while in V it occurs directly.

When the chalcone IVa was reacted with phenylhydrazine at room temperature rather than reflux, a compound believed to be VII was obtained rather than the pyrazoline VIa. In addition to the ferrocene and the aromatic protons the nuclear magnetic resonance spectrum of this product had peaks at 3.47 δ (CH_2) and 4.27 δ (CH). The mass spectrum indicates fragmentation with a loss of phenylhydrazine followed by a loss of C_6H_5NH.

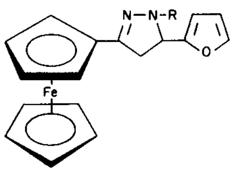
Several attempts to prepare VIb from IVb failed. Only 2-acetyl-1-phenylhydrazine was obtained using the procedure that led to V and VIa while use of benzene or ethanol as solvent with small amounts of acetic acid present led only to decomposition. Addition of an aqueous acetic acid solution of phenylhydrazine to IVb in ethanol gave a product which did not contain the nitro group. Data on this unidentified product is included in the Experimental Section.



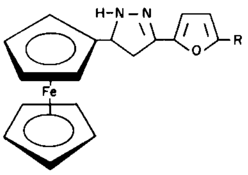
VII

Reaction of hydrazine with IIIa in an attempt to prepare VIIIa led to the formation of 1,2-diacetylhydrazine and the pyrazoline VIIIb. The nuclear magnetic resonance spectrum of this compound shows typical splitting of the $H_{2,5}$ and $H_{3,4}$ protons by the C=N. Other features of the nuclear magnetic resonance spectrum and the infrared and mass spectra are included in the Experimental Section and are consistent with the cyclic structure.

Reaction of the isomeric chalcone IVa with hydrazine led to the pyrazoline IXa and, in contrast to the case of phenylhydrazine, reaction of IVb with hydrazine led to pyrazoline IXb. The spectral data for these pyrazolines are presented in the Experimental Section and are consistent with the structures assigned and with the other pyrazolines. The absence of deshielding of the ferrocene protons is again evidence that a C=N or C=C is not attached directly to the ferrocene.



VIIIa, R = H
b, R = -COCH$_3$



IXa, R = H
b, R = NO_2

Chemotherapeutic evaluations of the compounds were conducted by The Norwich Pharmacal Company. No significant antibacterial, antifungal, or antiparasitic activity was uncovered in this series of compounds.

EXPERIMENTAL (7)

Reaction of 5-Nitro-2-furaldehyde with Ferrocenecarboxyhydrazide.

A solution of 0.705 g. (0.005 mole) of the aldehyde and 1.355 g. (0.0055 mole) of the hydrazide in 80 ml. of absolute ethanol was refluxed for 15 minutes. After 24 hours at room temperature the solution was cooled and filtered to give a quantitative yield of

Ia, m.p. 233-234° (from ethanol); IR (potassium bromide), 3425 (NH), 1590 (C=N), 1665 (C=O), 1110 and 1005 (Fc), 1360 and 1530 cm^{-1} (NO$_2$); NMR (DMSO-d$_6$): 4.58(5Fc), 4.85 (2Fc), 5.42 (2Fc), 7.78 (1Fu), 8.38 (1Fu), 9.05 (CH), 12.47 δ (NH). Mass Spec.: 367 (54%), 335 (9), 333 (10), 270 (8), 230 (28), 229 (16), 213 (100), 211 (43), 186 (12), 185 (70), 138 (41), 137 (18), 129 (93), 128 (22), 121 (89), 95 (11), 65 (16), 56 (62).

Anal. Calcd. for $C_{16}H_{13}N_3O_4Fe$: C, 52.34; H, 3.57; N, 11.44. Found: C, 51.99; H, 3.74; N, 11.28.

Reaction of Ferrocenecarboxyhydrazide with Methyl 5-Nitro-2-furyl Ketone.

A mixture of 10.0 g. of ferrocenecarboxyhydrazide and 6.36 g. of methyl 5-nitro-2-furyl ketone, 8 drops of glacial acetic acid, and 100 ml. of absolute ethanol were refluxed for 15 minutes and cooled to give 11.86 g. (76%) of Ib, m.p. 207-208° (from DMF). IR (potassium bromide), 3450 (NH), 1640 (C=O), 1600 (C=N), 1110, 1005 (Fc), 1355, 1530 cm^{-1} (NO$_2$); NMR (DMSO-d$_6$): 4.58 (5Fc), 4.88 (2Fc), 5.52 (2Fc), 7.83 (1Fu), 8.43 (1Fu), 11.27 (NH), 2.52 δ (CH$_3$). Mass Spec., 381 (42%), 349 (13), 347 (12), 230 (25), 229 (28), 213 (100), 211 (43), 186 (12), 185 (64), 138 (31), 137 (25), 129 (67), 128 (18), 121 (84), 95 (11), 73 (37), 65 (17), 56 (73).

Anal. Calcd. for $C_{17}H_{15}N_3O_4Fe$: C, 53.56; H, 3.97; N, 11.02. Found: C, 53.73; H, 4.09; N, 11.21.

N-Ferrocenecarboxamido-5-nitro-2-furamidine (II).

Anhydrous hydrogen chloride was bubbled through a solution of 6.9 g. (0.05 mole) of 5-nitro-2-furonitrile and 3.2 ml. (0.055 mole) of absolute ethanol in 50 ml. of anhydrous ether. After 2 hours, ethyl 5-nitro-2-furimidate hydrochloride was collected and washed with ether to give 8.01 g. A mixture of 4.53 g. (0.0205 mole) of this hydrochloride and 5.0 g. (0.0205 mole) of ferrocenecarboxyhydrazide was added to a stirred solution of 75 ml. of anhydrous methanol and 2.42 g. of sodium methoxide. After refluxing for 3 hours, cooling, and filtration gave, after washing with methanol 5.94 g. (76%) of product, m.p. 225-226° from ethanol-water; IR (potassium bromide), 3450, 3360 (NH), 1640 (C=O), 1600 (C=N), 1112, 1000 (Fc), 1350, 1530 cm^{-1} (NO$_2$). Mass Spec., 382 (26%), 365 (15), 364 (9), 333 (17), 230 (36), 229 (39), 227 (15), 213 (88), 212 (13), 211 (82), 186 (14), 185 (58), 184 (10), 138 (40), 137 (31), 129 (54), 128 (18), 121 (100), 120 (9), 95 (12), 80 (22), 65 (17), 56 (64).

Anal. Calcd. for $C_{16}H_{14}N_4O_4Fe$: C, 50.28; H, 3.69; N, 14.66. Found: C, 50.18; H, 3.92; N, 14.84.

Reaction of 2-Furaldehyde and Acetylferrocene.

A mixture of 2 g. (0.0088 mole) of acetylferrocene and 0.845 g. (0.0088 mole) of 2-furaldehyde in 15 ml. of 95% ethanol was added to a cooled solution of 0.5 g. of sodium hydroxide in 4.1 ml. of water and 2.0 ml. of ethanol. Stirring was continued for 1 hour and the solution was filtered to give a quantitative yield of IIIa, m.p. 157-158° (reported (5) m.p. 158°); IR (potassium bromide), 1655 (C=O), 1600 (C=C), 1110, 1010 cm^{-1} (Fc); NMR (deuteriochloroform), 4.53 (5Fc), 4.92 (2Fc), 5.30 (2Fc), 7.02-8.13 δ (3Fu, CH=CH); Mass Spec., 306 (100%), 241 (19), 214 (10), 213 (4), 212 (5), 186 (7), 185 (8), 184 (8), 159 (4), 158 (6), 157 (4), 149 (6), 129 (20), 128 (15), 121 (31), 95 (7), 94 (4), 56 (25).

Reaction of 5-Methyl-2-furaldehyde with Acetylferrocene.

Reaction of the aldehyde and the methylketone as described above gave after stirring for 3 hours a 78% yield of IIIb, m.p. 110-111° from Skellysolve B; IR (potassium bromide), 1650 (C=O), 1605 (C=C), 1110, 1010 cm^{-1} (Fc); NMR (deuteriochloroform) 4.55 (5Fc), 4.93 (2Fc), 5.32 (2Fc), 2.60 (CH$_3$) 6.62-8.02 δ (2Fu, CH=CH). Mass Spec., 320 (100%), 255 (31), 213 (5), 186 (6), 185 (8), 184 (7), 129 (20), 128 (15), 121 (31), 56 (25).

Anal. Calcd. for $C_{18}H_{16}O_2Fe$: C, 67.52; H, 5.04. Found: C, 67.30; H, 5.16.

Reaction of 2-Acetylfuran with Ferrocenecarboxaldehyde.

A mixture of the aldehyde and methyl ketone were reacted as described above to give a 92% yield of IVa, m.p. 137-138° from ethanol; IR (potassium bromide), 1650 (C=O), 1590 (C=C), 1115, 1005 cm^{-1} (Fc); NMR (deuteriochloroform), 4.45 (5Fc), 4.77 (2Fc), 4.88 (2Fc), 7.05 (Fu), 7.40-7.83 (Fu, CH), 8.15-8.57 δ (Fu, CH); Mass Spec., 306 (100%), 241 (92), 239 (8), 213 (14), 211 (15), 187 (5), 185 (8), 183 (6), 171 (4), 169 (7), 157 (7), 145 (9), 139 (6), 129 (22), 128 (12), 121 (21), 115 (5), 104 (4), 95 (12), 89 (9), 81 (5), 56 (24).

Anal. Calcd. for $C_{17}H_{14}O_4Fe$: C, 66.69; H, 4.61. Found: C, 66.55; H, 4.60.

Reaction of Ferrocenecarboxaldehyde with Methyl 5-Nitro-2-furyl Ketone.

A mixture of 5.0 g. (0.0234 mole) of ferrocenecarboxaldehyde and 3.64 g. (0.0234 mole) of methyl 5-nitro-2-furyl ketone with 60 drops of piperidine and 120 ml. of absolute ethanol were heated at 100° for 30 minutes and cooled to give 6.83 g. (83.4%) of IVb, m.p. 236-237° from chloroform; IR (potassium bromide), 1650(C=O), 1590(C=C), 1110, 1000(Fc), 1530, 1355 cm^{-1} (NO$_2$); Mass Spec., 351 (100%), 319 (14), 286 (8), 239 (23), 211 (26), 210 (18), 156 (10), 155 (9), 153 (12), 146 (10), 145 (8), 133 (14), 129 (7), 128 (11), 121 (58), 89 (14), 56 (37).

Anal. Calcd. for $C_{17}H_{13}NO_4Fe$: C, 58.16; H, 3.73; N, 3.99. Found: C, 58.16; H, 3.70; N, 3.92.

Reactions of IIIa with Phenylhydrazine.

To a solution of 10.0 g. (0.0326 mole) of IIIa in 150 ml. of absolute ethanol was added 16.0 g. (0.0148 mole) of phenylhydrazine in 150 ml. of glacial acetic acid. The mixture was heated for 24 hours at reflux, filtered and cooled. Filtration gave 8.07 g. (62.5%) of V, m.p. 144-145° from heptane; IR (potassium bromide), 1600, 1110, 1000 cm^{-1}; NMR (deuteriochloroform), 4.45 (5Fc), 4.66 (2Fc), 5.99 (2Fc), 5.60 (CH), 3.62 (CH$_2$), 6.8 (2Fu), 7.7-8.0 δ (1Fu, 5Ph); Mass Spec., 396 (100%), 331 (2), 304 (4), 276 (8), 239 (4), 238 (20), 225 (3), 213 (6), 212 (10), 211 (40), 210 (9), 198 (6), 186 (6), 185 (20), 146 (4), 129 (18), 128 (4), 121 (52), 77 (8), 56 (16).

Anal. Calcd. for $C_{23}H_{20}N_2OFe$: C, 69.71; H, 5.09; N, 7.07. Found: C, 69.65; H, 5.11; N, 7.17.

Reaction of IVa with Phenylhydrazine.

As described above 10 g. of IVa and 10 g. of phenylhydrazine in 100 ml. of glacial acetic acid and 100 ml. of absolute ethanol gave, after recrystallization from cyclohexane, 1.90 g. (15%) of VIa, m.p. 165-167°; IR (potassium bromide), 1600, 1105, 1005 cm^{-1}; NMR (deuteriochloroform), 4.45 (9Fc), 5.38 (CH), 3.98 (CH$_2$), 7.02 (1Fu), 7.23 (1Fu), 7.4-8.1 δ (1Fu, 5Ph); Mass Spec., 396 (100%), 331 (6), 329 (3), 304 (27), 303 (5), 275 (4), 238 (35), 213 (20), 212 (60), 211 (15), 210 (12), 198 (14), 186 (62), 185 (3), 147 (10), 129 (5), 128 (3), 121 (72), 56 (20).

Anal. Calcd. for $C_{23}H_{20}N_2OFe$: C, 69.71; H, 5.09; N, 7.07. Found: C, 69.84; H, 4.99; N, 7.06.

Reaction of 1 g. of IVa and 1 g. of phenylhydrazine in 15 ml. of absolute ethanol containing 15 drops of glacial acetic acid at room temperature for 48 hours gave 1.05 g. (82%) of VII, m.p.

150-152° from benzene; IR (potassium bromide), 3320, 3250, 1610, 1560, 1115, 1010 cm^{-1}; NMR (deuteriochloroform), 4.51 (9Fc), 4.27 (CH), 3.47 (CH_2), 6.80-8.15 δ (10Ph, 3Fu); Mass Spec., 504 (10%), 472 (5), 470 (5), 397 (12), 396 (22), 395 (33), 394 (100), 329 (8), 305 (10), 304 (22), 238 (5), 213 (15), 212 (11), 211 (21), 200 (14), 186 (9), 185 (15), 129 (6), 128 (3), 121 (21), 108 (17), 92 (12), 91 (10), 78 (31), 77 (26), 65 (12), 56 (12).

Anal. Calcd. for $C_{29}H_{28}N_4OFe$: C, 69.05; H, 5.59; N, 11.11; Fe, 11.07. Found: C, 69.35; H, 5.46; N, 11.19; Fe, 11.78.

Reaction of IVb with Phenylhydrazine.

To 1.0 g. of IVb in 25 ml. of ethanol was added 2.0 g. of phenylhydrazine in 10 ml. of water containing sufficient acetic acid to dissolve the phenylhydrazine. The mixture was refluxed for 12 hours, filtered hot and cooled. Removal of the solvent *in vacuo* gave a residue which was dissolved in benzene and chromatographed on alumina. Elution with benzene-chloroform gave 0.9 g. of solid, m.p. 215-217° from benzene; IR (potassium bromide), 3400, 3050, 1675, 1600, 1560, 1115, 1005 cm^{-1}; NMR (deuteriochloroform), 4.45 (5Fc), 4.60 (4Fc), 7.70-9.05 δ; Mass Spec., 500 (16%), 499 (54), 498 (100), 497 (8), 496 (12), 433 (5), 431 (8), 365 (4), 288 (4), 287 (4), 249 (9), 248 (8), 235 (8), 222 (5), 212 (5), 180 (4), 121 (20), 78 (8), 77 (13), 56 (7).

Anal. Calcd. for $C_{29}H_{22}N_4OFe$: C, 69.89; H, 4.45; N, 11.24; Fe; 11.21. Calcd. for $C_{29}H_{24}N_4OFe$: C, 69.60; H, 4.83; N, 11.19; Fe, 11.16. Found: C, 69.66; H, 4.53; N, 11.34; Fe, 11.40, 11.19.

Reaction of IIIa with Hydrazine.

A mixture of 1.0 g. of IIIa, 20 ml. of glacial acetic acid, 20 ml. of absolute ethanol, and 2.0 g. of hydrazine hydrate was refluxed for 8 hours, cooled, and concentrated *in vacuo*. The residue was washed with benzene and ether and recrystallized from tetrahydrofuran to give 1,2-diacetylhydrazine, m.p. 129-131°, reported (8) m.p. 130-131°. The IR was identical to that reported (9) in the literature. The organic washings from above and the mother liquors from the recrystallization were combined and the solvents removed *in vacuo*. The residue was chromatographed on alumina with chloroform to give VIIIb, m.p. 152-153° from Skellysolve B; IR (potassium bromide), 1660 (C=O), 1600, 1110, 1010 cm^{-1}; NMR (deuteriochloroform), 4.66 (5Fc), 4.89 (2Fc), 5.0-5.27 (2Fc), 2.58 (CH_3), 3.63, 3.79 (CH_2), 6.23 (1), 7.03 (2), 8.13 δ (1); Mass Spec., 362 (100%), 321 (9), 320 (40), 318 (7), 284 (6), 262 (6), 255 (10), 253 (4), 238 (4), 227 (7), 225 (10), 211 (9), 199 (8), 185 (9), 184 (7), 178 (6), 171 (7), 146 (10), 141 (12), 134 (7), 133 (6), 129 (8), 128 (6), 121 (54), 115 (14), 95 (7), 81 (7), 65 (6), 56 (30), 43 (44).

Anal. Calcd. for $C_{19}H_{18}N_2O_2Fe$: C, 63.00; H, 5.01; N, 7.78. Found: C, 63.49; H, 5.01; N, 7.78.

Reaction of IVa with Hydrazine.

A mixture of 2.0 g. of IVa, 50 ml. of absolute ethanol, 4.0 g. of hydrazine hydrate, and 8 drops of glacial acetic acid were refluxed for 12 hours, cooled, filtered, washed with ether, and recrystallized from methanol-water (containing a few drops of hydrazine) to give 1.75 g. (83%) of IXa, m.p. 114-117°; IR (potassium bromide), 3300, 1600, 1115, 1005 cm^{-1}; NMR (deuteriochloroform), 4.30 (9Fc), 3.25 (CH_2), 4.80 (CH), 6.0 (NH), 6.72 (2Fu), 7.71 δ (1Fu); Mass Spec., 320 (100%), 318 (18), 306 (4), 304 (4), 255 (10), 253 (4), 238 (8), 227 (18), 226 (6), 212 (24), 211 (3), 199 (7), 198 (3), 186 (37), 185 (3), 161 (11), 141 (7), 134 (8), 129 (4), 128 (4), 121 (45), 115 (10), 95 (6), 65 (3), 56 (31).

Anal. Calcd. for $C_{17}H_{16}N_2OFe$: C, 63.77; H, 5.04; N, 8.75. Found: C, 63.86; H, 5.01; N, 8.60.

Reaction of IVb with Hydrazine

A mixture of 14.25 g. (0.0406 mole) of IVb, 28.5 g. of hydrazine hydrate, 100 ml. of ethanol, and 100 ml. of glacial acetic acid was refluxed for 2 hours and filtered hot. After cooling, 8.25 g. (56%) of IXb, m.p. 177° (from glacial acetic acid) was obtained; IR (potassium bromide), 3400, 1600, 1110, 1005, 1365, 1550 cm^{-1}; NMR (DMSO-d_6), 4.68 (9Fc), 3.4-3.8 (CH_2, NH), 5.33 (CH), 7.7-7.9 δ (Fu); Mass Spec., 365 (100%), 333 (6), 331 (7), 300 (2), 227 (4), 213 (7), 212 (24), 211 (5), 186 (38), 185 (7), 147 (8), 141 (9), 129 (6), 128 (5), 121 (43), 115 (16), 95 (4), 81 (7), 65 (4), 56 (29).

Anal. Calcd. for $C_{17}H_{15}N_3O_3Fe$: C, 55.91; H, 4.14; N, 11.50. Found: C, 55.77; H, 4.16; N, 11.43.

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