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Investigation of the Acid Catalysed Diels-Alder Reaction of Furan Derivatives with β-Ferrocenyl-α-enones

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Abstract: Attempts have been made on trifluoroacetic acid catalysed Diels-Alder reaction of furan, 2,5-dimethylfuran and 2,5-diphenylfuran with β-ferrocenyl-α-enones. No Diels-Alder products were isolated or detected but products from the Friedel-Crafts β-alkylation of furan ring were prepared in some cases. Reaction with 1,3-diphenylbenzo[*c*]furan under the same conditions resulted in the formation of a formal [4+3] cycloaddition product containing 1,2-disubstituted ferrocene.

The high reactivity of furan and its derivatives in Diels-Alder reactions is well documented.[1,2] Friedel-Crafts reactions of furan are also well known and it is proved that the α-position of the furan ring is, in the acetylation process, at least 10^4 times more reactive than its β-position.[3,4] Especially Diels-Alder reactions of furan and of its derivatives are frequently used for the synthesis of natural products.[5]

In our previous paper[6] we reported the attempts of Diels-Alder reactions of 1,3-diphenylbenzo[*c*]furan (**1**) with ferrocenyl derivatives of the structure Fc-CO-CH=CH-X, where X = H, Ph and with Fc-CH=CH-Y, where Y = COMe, COPh, NO_2. It has been observed that non-catalysed Diels-Alder reactions are rather sluggish with these dienophiles and just traces of the products were isolated. The reactions are going well as solid

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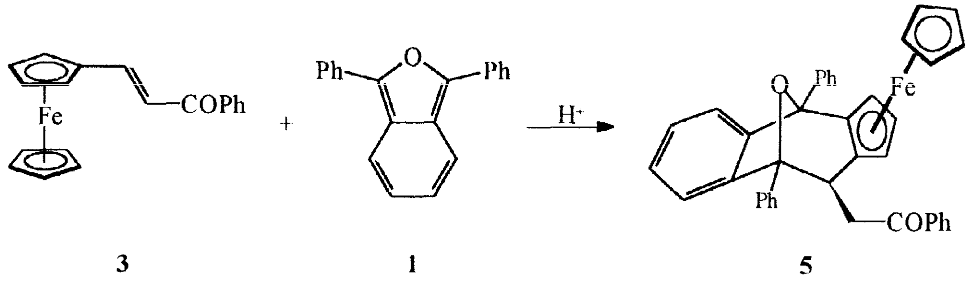
supported processes either on silica gel or on acidic clay KSF. On our attempts at $AlCl_3$-catalysis on the reaction of diene **1** with 4-ferrocenyl-3-butene-2-one (**2**), 3-ferrocenyl-1-phenyl-2-propenone (**3**) and 2-nitrovinylferrocene (**4**) we found that the isolated products are not Diels-Alder products but formally [4+3] cycloadducts with a 1,2-disubstituted ferrocene in the molecule.

The main goal of this work was to examine trifluoroacetic acid catalysis of the Diels-Alder reaction of 1,3-diphenylbenzo[*c*]furan, furan, 2,5-dimethylfuran and 2,5-diphenylfuran with β-ferrocenyl-α-enones Fc-CH=CH-CO-R (R = CH_3, Ph) and with Fc-CH=CH-NO_2.

RESULTS AND DISCUSSION

Trifluoroacetic acid and KSF as the catalysts in the reaction of diene **1** with **3** afforded to obtain the same [4+3] adduct **5** as with $AlCl_3$ catalysis. (Scheme 1, Table 1). H^+-montmorillonit KSF operated as a donor of protons only after the irradiation of the mixture of reactants by microwaves. The normal Diels-Alder product was formed without the microwave irradiation. Full characterisation of 10-*endo*-benzoylmethyl-4,9-diphenyl-9,10-dihydro-4,9-epoxy-4H-benzo[*a*]-*exo*-ferroceno[*d*]-cycloheptene (**5**) including X-ray analysis has been already been published.[6]



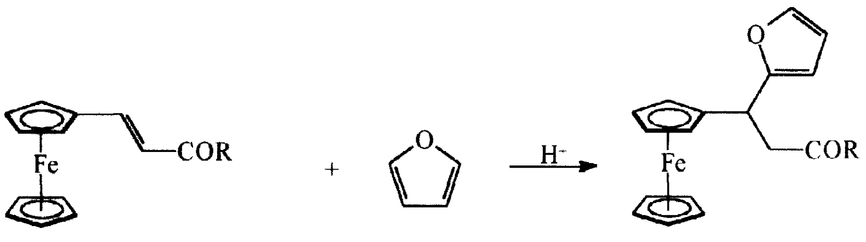
Scheme 1.

Table 1. [4+3] Cycloaddition Reactions of 3-ferrocenyl-1-phenyl-2-propenone (**3**) with 1,3-diphenylbenzo[c]furan (**1**).

Conditions	Yield of **5** (%)
$AlCl_3/CH_2Cl_2$, 29 h, rt	32
KSF/MWO, 3x10 min (360 Watt)	20
CF_3-CO_2H/CH_2Cl_2, 6.5 h, rt	46

Later 1,3-diphenylbenzo[*c*]furan was transformed to furan (**6**) and 2,5-diphenylfuran (**7**). Different products than expected were prepared when 4-ferrocenyl-3-buten-2-one (**2**) and 3-ferrocenyl-1-phenyl-2-

propenone (**3**) were stirred with 50-fold excess of furan in the presence of CF_3-CO_2H (Scheme 2). Isolated materials had correct C, H microanalyses but their ^1H NMR spectra measured at 80 MHz, did not agree with the expected structures of [4+3] adducts at all. Better-resolved ^1H and ^{13}C NMR and $^1H^1H$ COSY and $^1H^{13}C$ COSY spectra recorded at higher frequency, revealed the fact that furan was substituted in α-position with C-electrophile Fc-CH$^+$-CH=C(R)-OH (or Fc-CH$^+$-CH_2-CO-R), R = Me, Ph. The X-ray analysis assured us of the correct structure of the product **9** (Table 2 and Figure 1), (see also Table 3 in Experimental).



2: R = CH_3
3: R = Ph

6

8: R = CH_3
9: R = Ph

Scheme 2.

Table 2. Comparison of Fe-C and C-C Bond Lengths in Ferrocene Unit in Compound **9** and for Unsubstituted Ferrocene

Compound	Fe-C Bond Length (Å)		C-C Bond Length (Å)	
9	Fe(1)-C(14)	2.067(4)	C(14)-C(15)	1.421(6)
	Fe(1)-C(15)	2.042(4)	C(15)-C(16)	1.429(6)
	Fe(1)-C(16)	2.033(4)	C(16)-C(17)	1.416(8)
	Fe(1)-C(17)	2.045(4)	C(17)-C(18)	1.425(7)
	Fe(1)-C(18)	2.055(4)	C(14)-C(18)	1.427(6)
	Fe(1)-C(19)	2.087(6)	C(19)-C(20)	1.456(9)
	Fe(1)-C(20)	2.109(6)	C(20)-C(21)	1.420(8)
	Fe(1)-C(21)	2.039(8)	C(21)-C(22)	1.37(1)
	Fe(1)-C(22)	2.029(7)	C(22)-C(23)	1.39(1)
	Fe(1)-C(23)	2.033(7)	C(19)-C(20)	1.418(10)
Ferrocene[7]	Fe-C	2.045	C-C	1.403

The lengths of Fe-C and C-C bonds are summarised in Table 2 and show that the substituent Ph-CO-CH_2-CH(C_4H_3O)- brings some irregularity into the whole ferrocene unit. Both parts of compound **9** (ferrocenyl and Ph-CO-CH_2-CH(C_4H_3O)-) are placed in two almost parallel planes.

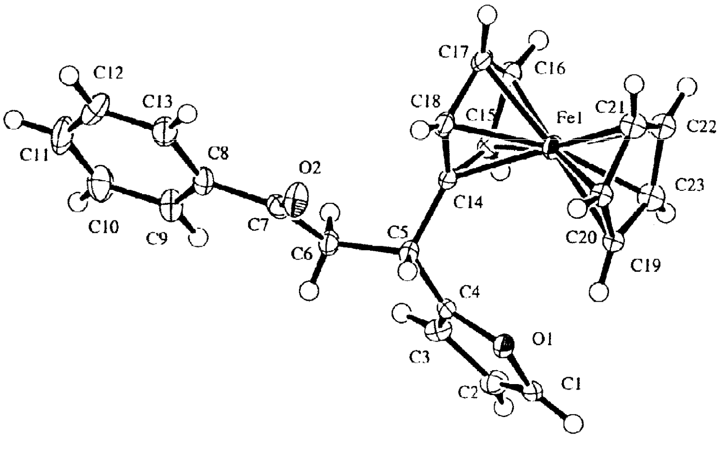
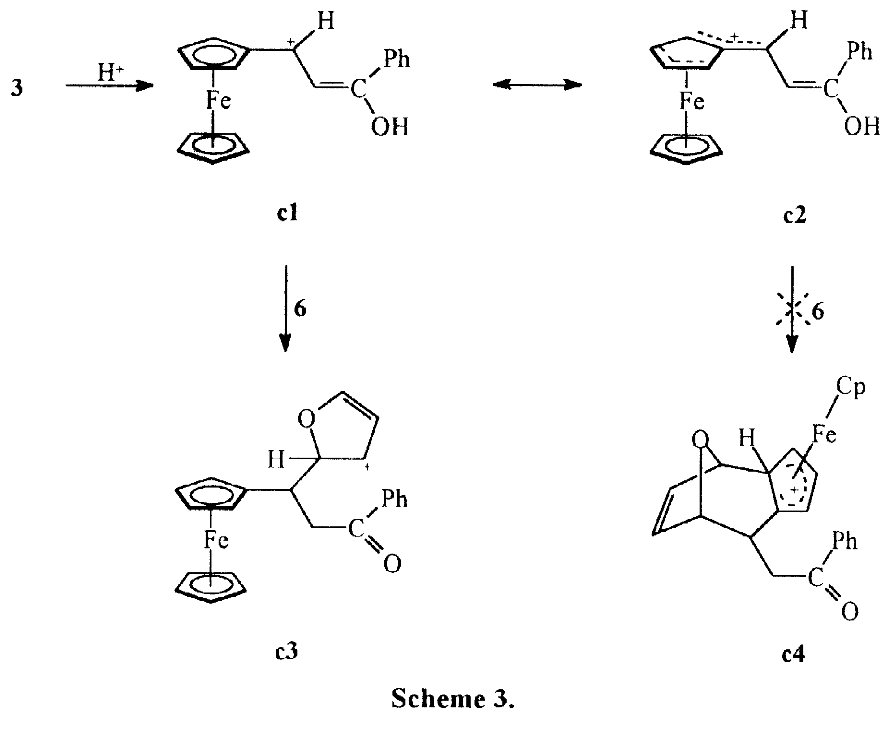


Figure 1. Molecular structure of the compound **9** with 20 % probability ellipsoids for each atom and with atom numbering

Although furan is the most reactive diene among the five-membered heterocyclic compounds the expected Diels-Alder adduct was not even isolated in traces. There are two possibile routes for the reaction of furan with protonated enones (Scheme 3).

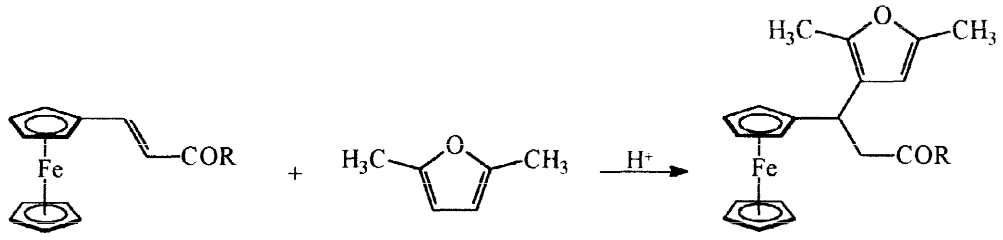


Scheme 3.

If carbocation (**c1↔c2**) reacts with the substrate in such a way that the possibility of the cleavage of H^+ exists (e. g. with furan) then electrophilic substitution proceeds. In cation **c3'** (analogous cation formed by reaction of 1,3-diphenylbenzo[*c*]furan with enone **3**) phenyl cation should be cleaved off. This is less probable than formation of [4+3] cycloadduct **5**.

2,5-Diphenylfuran (**7**) being selected as a diene for its resemblance to 1,3-diphenylbenzo[*c*]furan did not react with alkenones **2** and **3** at all. We examined CF_3-CO_2H and KSF in microwave oven and also silica gel as solid support but no traces of any product were detected. The donor character of two phenyl substituents increases the reactivity of the "mother diene" toward an electrophilic attack but also sterically hinders the access of cationic dienophile to the molecule **7**. This disadvantage acts also in 1,3-diphenylbenzo[*c*]furan but it is counterbalanced by aromatization of the six-membered ring in the adduct **5** that is the driving force leading to [4+3] cycloaddition product. We decided to check the reactivity of 2,5-diphenylfuran with more reactive maleic anhydride as a dienophile but we were not successful (reflux in toluene, 17.5 h; silica gel (100/160 mesh), 17.5 h; $AlCl_3/CH_2Cl_2$, overnight, rt), in all cases no new compound was detected on TLC.

After these negative experiments with 2,5-diphenylfuran we turned to 2,5-dimethylfuran (**10**). The methyl groups in **10** are smaller substituents and hence we expected its higher reactivity in cycloaddition reactions. Surprisingly, 2,5-dimethylfuran did not react as a diene. Both 4-ferrocenyl-1-phenyl-3-butenone and 3-ferrocenyl-1-phenyl-2-propenone gave 57 % and 75 % yields of products of β-substitution on the furan ring, respectively, after 18.5 h stirring in the presence of trifluoroacetic acid (Scheme 4).



2: R = CH_3
3: R = Ph

10

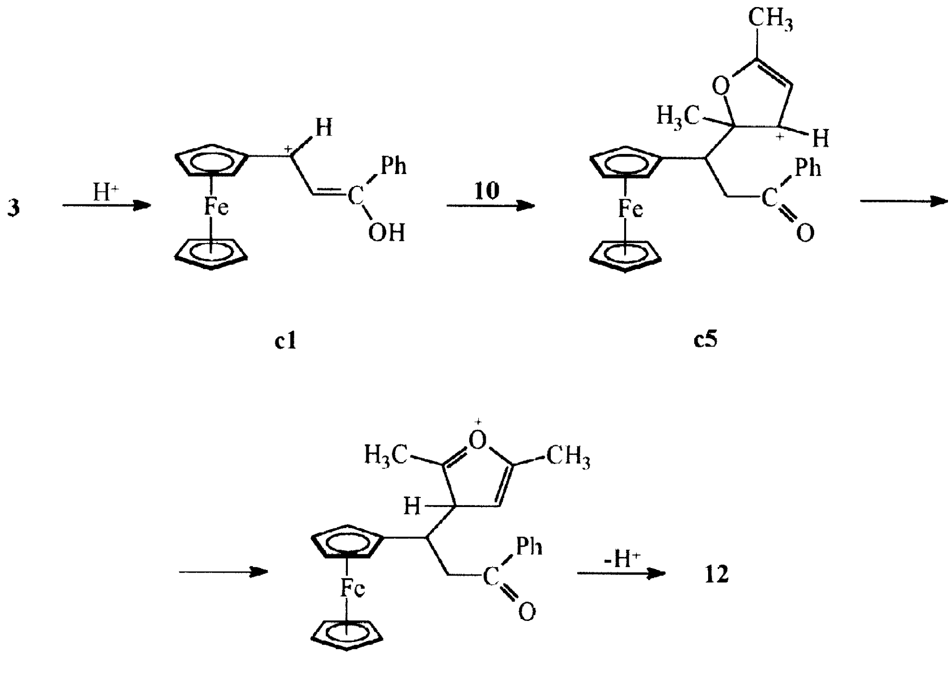
11: R = CH_3
12: R = Ph

Scheme 4.

The attack of the β-position of the furan ring is but seldom described. Alkylation of furan with isobutene over Kieselguhr in an autoclave in the presence of H_3PO_4 yielded a mixture of 2- and 3-*terc*-butylfurans.[8] Extension of reaction time and increased amount of the catalyst positively influenced the amount of 3-*terc*-butylfuran. Electrophilic substitution of 2,5-dimethylfuran can proceed by three different pathways. Terrier et al.[9] described the electrophilic substitution of one methyl group in 2,5-dimethylfuran as the only observed process in the reaction with 2,4-dinitrobenzofuroxan. The electrophilic character of this molecule is comparable with 2,4-

dinitrobenzenediazonium cation. If 2,5-dimethylfuran is allowed to react with $(CF_3\text{-}CO)_2O$ in benzene the electrophilic substitution occurs at α-position and on the methyl group on the second α-C atom of 2,5-dimethylfuran.[10] Several articles give information about Friedel-Crafts acylations of β-position in **10**. Levine et al. obtained 3-acetyl-, 3-propionyl- and 3-butyryl-2,5-dimethylfuran in 65 %, 63 % and 60 % yields, respectivelly[11] by acylation of **10** with anhydrides in the presence of $BF_3.CH_3CO_2H$. 3-Acetyl-2,5-dimethylfuran is formed in 77 % yield at 150°C with $SnCl_4$ as the catalyst.[12] Methylselenoheptanoate allowed production of 3-hexanoyl-2,5-dimethylfuran 91 % yield within 10 min.[13] This process was catalysed with Cu_2O and Et_3N.

The Scheme 5 describes the possible route to compounds **11** and **12**. The easy formation of α-ferrocenylmethyl cation **c1** by protonization of carbonyl group[14] can be explained by its very high stability. The cation **c1** may attack the α-position of the furan ring and then rearrange to β-position. We suppose this process is more probable than direct attack of β-C atom of **10**, because of higher electron density at α-C atoms of furan. Though rearrangement of methyl group should be theoretically possible no such migration was observed. The ferrocenylmethyl cation migrates much more easily because of its much higher stability. The very high stability of ferrocenylmethyl cation was thoroughly studied.[15-17]



c6

Scheme 5.

Since 2-nitrovinylferrocene (**4**) has formed a [4+3] adduct with 1,3-diphenylbenzo[*c*]furan in the presence of $AlCl_3$[6], we also tried the effect of $CF_3\text{-}CO_2H$ on the reaction of **4** with furan and 2,5-dimethylfuran.

Our attempts to isolate any product have failed. This can be explained by the fact that 2-nitrovinylfuran is not protonated at the reaction conditions and no α-ferrocenylmethyl cation is formed.

EXPERIMENTAL

General. 1,3-Diphenylbenzo[*c*]furan and 2,5-dimethylfuran were purchased from Aldrich. 2,5-Diphenylfuran was synthesised according to reference 18. CH_2Cl_2 was dried in the usual manner. All products have been purified from unreacted starting materials and minor by-products by flash-chromatography on silica gel (35/70 mesh) with isohexane and isohexane/ethylacetate mixtures as eluents. Melting points were measured on a Kofler hot plate and are uncorrected. If not stated otherwise, ^1H and ^{13}C NMR spectra were recorded on Bruker DRX as $CDCl_3$ solutions at 400 MHz and 100 MHz, respectively, using tetramethylsilane as internal standard. IR spectra were measured on Specord 75 IR as $CHCl_3$ solutions or in nujol and mass spectra were measured on AET-MS 902 spectrometer at 70 eV.

A general procedure for the cycloaddition reaction of 1,3-diphenylbenzo[*c*]furan with 3-ferrocenyl-1-phenyl-2-propenone upon acidic catalysis.

0.100 g (0.36 mmol) of 1,3-diphenylbenzo[*c*]furan and 0.114 g (0.36 mmol) of enone **3** were dissolved in 20 ml of dry CH_2Cl_2. The appropriate catalyst was added and the reaction mixture was stirred at rt and controlled by TLC. Then the contents of flask were poured onto iced water and extracted into CH_2Cl_2. The extracts were washed with water and dried over Na_2SO_4. The excess solvent was evaporated *in vaccuo* and the obtained residue was purified by flash-chromatography to give 10-*endo*-benzoylmethyl-4,9-diphenyl-9,10-dihydro-4,9-epoxy-4H-benzo[*a*]-*exo*-ferroceno[*d*]-cycloheptene (**5**) as a yellow crystalline compound, m.p. 253-256 °C. Calcd. for $C_{39}H_{30}FeO_2$: C, 79.87; H, 5.16; Found: C, 79.63; H, 5.21.

The cycloaddition reaction proceeded in the presence of $AlCl_3$ (48 mg, 0.36 mmol) affording 0.067 g (32 %) of **5**.

In the presence of CF_3-CO_2H (0.1 ml, 1.30 mmol) 0.097 g (46 %) of **5** were prepared.

Reaction in a microwave oven: 7.0 g of acidic clay KSF was added to a solution of both reactants and the solvent was evaporated to dryness. The prepared red powder was irradiated three times during 10 minutes at

360 Watt in a commercially available microwave oven. Dark grey powder was then extracted into CH_2Cl_2. After the above-described work-up 0.042 g (20 %) of the adduct **5** was obtained.

4-Ferrocenyl-4-(2-furyl)-2-butanone (8): 0.100 g (0.39 mmol) of **2** were dissolved in 10 ml of dry CH_2Cl_2 and 1.43 ml of furan (19.7 mmol, 50 equiv.) and 0.11 ml (1.4 mmol) of $F_3C\text{-}CO_2H$ were added. The solution was stirred for 18.5 h at rt and the composition of reaction mixture was controlled by TLC. The resulting dark liquid was then poured onto iced water, extracted into CH_2Cl_2 and dried with Na_2SO_4. The excess of the solvent was evaporated and the residue purified by flash-chromatography on a short silica gel column that gave 0.095 g of **8** as an orange-red oil (76 %). ^{1}H NMR: δ (ppm) 2.09 (s, 3H, CH_3CO), 2.93 (dd, J_{gem} = 16.3, J(H$_A$-C(3), H-C(4)) = 5.3, 1H, H$_A$-C(3)), 3.09 (dd, J_{gem} = 16.3, J(H$_{A'}$-C(3), H-C(4)) = 8.9, 1H, H$_{A'}$-C(3)), 4.08 (s, 5H, C_5H_5Fe), 4.11 (br s, 4H, C_5H_4Fe), 4.34 (dd, J(H$_A$-C(3), H-C(4)) = 5.3, J(H$_{A'}$-C(3), H-C(4)) = 8.9, 1H, H-C(4)), 6.08 (dm, J(H-C(2'), H-C(3')) = 3.2, $w_{1/2} \approx 2.0$, 1H, H-C(2')), 6.31 (dd, J(H-C(2'), H-C(3')) = 3.2, J(H-C(3'), H-C(4')) = 1.8, 1H, H-C(3')), 7.35 (dd, J(H-C(3'), H-C(4')) = 1.8, J(H-C(2'), H-C(4')) = 0.7, 1H, H-C(4')). ^{13}C NMR and APT: δ (ppm) 30.69 (q, C(1)), 34.64 (d, C(4)), 49.68 (t, C(3)), 67.54, 67.65, 67.70, 67.93 (4d, 2C$_\alpha$, 2C$_\beta$, C_5H_4Fe), 69.05 (5d, 5C, C_5H_5Fe); 91.01 (s, C$_i$, C_5H_4Fe), 105.40 (d, C(2')), 110.27 (d, C(3')), 140.96 (d, C(4')), 156.87 (s, C(1')), 206.85 (s, C(2)). IR ($CHCl_3$): ν (cm^{-1}) 3105, 3015, 1715, 1502, 1358, 1260, 1160, 1145, 1102, 1010, 820, 595.

3-Ferrocenyl-3-(2-furyl)-1-phenyl-1-propanone (9): 0.114 g (0.36 mmol) of **3**, 1.32 ml (18.0 mmol) of furan and 0.1 ml (1.3 mmol) of $CF_3\text{-}CO_2H$ were dissolved in 10 ml of CH_2Cl_2 and then stirred 16 h at rt. Analogical work-up as for **8** gave, after crystallization from isohexane/ethylacetate, 0.099 g (72 %) of **9**, m.p. = 104.5-105.5 °C. Anal. calctd. for $C_{23}H_{20}O_2Fe$ (384.26): C 71.89; H 5.25; Fe 14.53; Found: C 71.84; H 5.33; Fe 15.11. ^{1}H NMR: δ (ppm) 3.43 (dd, J_{gem} = 16.8, J(H$_A$-C(2), H-C(3)) = 5.3, 1H, H$_A$-C(2)), 3.70 (dd, J_{gem} = 16.8, J(H$_{A'}$-C(2), H-C(3)) = 8.6, 1H, H$_{A'}$-C(2)), 4.08 (s, 5H, C_5H_5Fe), 4.11 (m, 2H, C_5H_4Fe), 4.15 (dd, J(H-C$_\alpha$, H-C$_\beta$) = 1.7, 2H, C_5H_4Fe), 4.60 (dd, J(H$_A$-C(2), H-C(3)) = 5.3, J(H$_{A'}$-C(2), H-C(3)) = 8.6, 1H, H-C(3)), 6.12 (dm, J(H-C(2'), H-C(3')) = 3.2, $w_{1/2} \approx 16.0$, 1H, H-C(2')), 6.30 (dd, J(H-C(2'), H-C(3')) = 3.2, J(H-C(3'), H-C(4')) = 1.9, 1H, H-C(3')), 7.34 (dd, J(H-C(3'), H-C(4')) = 1.9, J(H-C(2'), H-C(4')) = 0.9, 1H, H-C(4')), 7.45 (dddd, J(H$_o$, H$_m$) = 8.4, J(H$_m$, H$_p$) = 7.4, J(H$_m$, H$_m$) = 1.4, 2H$_m$, C_6H_5) 7.56 (dddd, J(H$_m$, H$_p$) = 7.4, J(H$_o$, H$_p$) = 1.3, 1H$_p$, C_6H_5), 7.94 (dm, among others J(H$_o$, H$_m$) = 8.4, J(H$_o$, H$_p$) = 1.3, 2H$_o$, C_6H_5). ^{13}C NMR and APT: δ (ppm) 34.75 (d, C(3)), 45.02 (t, C(2)), 67.56, 67.63, 67.77, 67.83 (4d, 2C$_\alpha$, 2C$_\beta$, C_5H_4Fe); 68.96 (5d, 5C, C_5H_5Fe), 91.19 (s, C$_i$, C_5H_4Fe), 105.49 (d, C(2'), 110.29 (d, C(3')), 128.30 (2d, 2C$_o$, C_6H_5), 128.76 (2d, 2C$_m$, C_6H_5), 133.26 (d, C$_p$. C_6H_5), 140.94 (d, C(4')), 157.13 (s, C(1')), 198.14 (s, C(1)). IR (nujol): ν (cm^{-1}) 1675, 1585, 1490, 1400, 1355, 1270, 1210, 1015, 810, 755, 745, 735, 702, 680, 480. MS: m/z (%) 384 (100, M+), 290 (47), 265 (100), 240 (9), 198 (21), 120 (28), 86 (100), 84 (100), 77 (28). HRMS calctd. for $C_{23}H_{20}O_2Fe$ 384.0807, found 384.0822.

Table 3. X-ray Data and Structure Determination of **9**.

A. Crystal data	
Empirical formula	$C_{23}H_{20}O_2Fe$
Formula weight	384.26
Crystal color, Habit	yellow, needle
Crystal dimensions	0.85 x 0.35 x 0.05 mm
Crystal system	orthorhombic
Lattice type	primitive
No. of reflexions used for unit cell determination (2θ range)	25 (23.4 - 38.6°)
Omega scan peak width at half-height	0.39°
Lattice parameters	a = 37.717(9) Å b = 5.942(3) Å c = 7.845(2) Å V = 1758.2(8) $Å^3$
Space group	$Pna2_1$ (#33)
Z value	4
D_{calc}	1.452 g/cm^3
F_{000}	800.00
$\mu(MoK\alpha)$	8.71 cm^{-1}
B Intensity measurements	
Diffractometer	Rigaku AFC7S
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Attenuator	Zr foil (factors = 1.00, 8.91, 8.91, 8.91)
Take-off angle	6.0°
Detector aperture	3.0 mm horizontal 3.0 mm vertical
Crystal to detector distance	235 mm
Temperature	123 K
Scan type	ω

Scan rate	12.0°/min (in ω) (up to 6 scans)
Scan width	$(1.05 + 0.35 \tan \theta)°$
$2\theta_{max}$	54.1°
No. of reflexions measured	Total: 4606
	Unique: 4294 (R_{int} = 0.031)
Corrections	Lorentz-polarization
	Absorption
	(trans. Factors: 0.6907 - 1.0000)
	Decay (1.06 % decline)
C. Structure solution and refinement	
Structure solution	Direct methods (SIR92)[19]
Refinement	Full-matrix least-squares
Function minimized	$\Sigma \varpi(\lvert Fo \rvert - \lvert Fc \rvert)^2$
Least squares weights	$1/[\sigma^2(Fo)] = 4\, Fo^2/[\sigma^2(Fo^2)]$
p-factor	0.040
Anomalous dispersion	All non-hydrogen atoms
No. Observations (I>2.00σ(I))	3190
No. variables	225
Reflection/parameter ratio	14.18
Residuals; R; Rw	0.048; 0.061
Goodness of fit indicator	1.90
Max shift/error in final cycle	0.00
Maximum peak in final diff. map	0.69 e^-/Å
Minimum peak in final diff. map	-0.58 e^-/Å

4-(2,5-Dimethyl-3-furyl)-4-ferrocenyl-2-butanone (11): 0.150 g (0.59 mmol) of **2** were dissolved in 15 ml of dry CH_2Cl_2. 3.14 ml (29.5 mmol, 50 equiv.) of 2,5-dimethylfuran and 0.18 ml (2.36 mmol, 4 equiv.) of CF_3-CO_2H were added. The mixture was stirred for 18.5 h at rt. The above-described work-up gave 0.118 g (57 %) of **11** in the form of an orange oil. ^1H NMR (Tesla BS 487 A, 80 MHz): δ (ppm) 2.04 (s, 3H, CH_3-CO), 2.18 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.90 (m, 2H, CH_2-CO), 4.05-4.09 (m, 10H, CH-Fc and $C_5H_4FeC_5H_5$), 5.74 (s, 1H, H-C(4')). IR ($CHCl_3$): ν (cm^{-1}) 3107, 3040, 3015, 2965, 2930, 1710, 1580, 1358, 1260, 1160, 1105, 1010, 1000, 923, 820.

3-(2,5-dimethyl-3-furyl)-3-ferrocenyl-1-phenyl-1-propanone (12): 0.100 g (0.32 mmol) of **3** were stirred for 18.5 h with 50 equiv. of 2,5-dimethylfuran (1.68 ml, 15.8 mmol) and 4 equiv. of $F_3C\text{-}CO_2H$ (0.10 ml, 1.3 mmol) in 10 ml of dry CH_2Cl_2. Work-up of the reaction mixture gave 0.098 g (75 %) of an orange-red oil **12**. ^{1}H NMR: δ (ppm) 2.17 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 3.44 (dd, J_{gem} = 16.2, J(H_A-C(2), H-C(3)) = 4.1, 1H, H_A-C(2)), 3.52 (dd, J_{gem} = 16.2, J(H_A-C(2), H-C(3)) = 9.1, 1H, $H_{A'}$-C(2)), 4.15 (s, 5H, C_5H_5Fe), 4.10-4.19 (m, 4H, C_5H_4Fe), 4.31 (dd, J(H_A-C(2), H-C(3)) = 4.1, J($H_{A'}$-C(2), H-C(3)) = 9.1, 1H, H-C(3)), 5.80 (s, 1H, H-C(4')), 7.46 (dd, J(H_o, H_m) = 7.5, J(H_p, H_m) = 7.2, 2H_m, C_6H_5), 7.56 (dd, 2 J(H_p, H_m) = 7.2, H_p, C_6H_5), 7.92 (d, J(H_o, H_m) = 7.5, 2H_o, C_6H_5). ^{13}C NMR and APT: δ (ppm) 11.82 (q, CH_3), 13.72 (q, CH_3), 31.66 (d, C(3)), 46.13 (t, C(2)), 67.26, 67.54, 67.95, 68.97 (4d, 2C_α, 2C_β, C_5H_4Fe), 69.07 (5d, 5C, C_5H_5Fe), 94.24 (s, C_i, C_5H_4Fe), 105.79 (d, C(4')), 122.42 (s, C(3')), 128.23 (2d, 2 C_o, C_6H_5), 128.67 (2d, 2C_m, C_6H_5), 133.05 (d, C_p, C_6H_5), 137.46 (s, C_i, C_6H_5), 145.16, 149.37 (2*s*, C(3'), C(5')), 198.83 (s, C(1)). IR ($CHCl_3$): ν (cm^{-1}) 3100, 3075, 3015, 2970, 2930, 1683, 1600, 1580, 1450, 1403, 1358, 1262, 1105, 1023, 1005, 925, 820, 695. MS: m/z (%) 412 (100, M+,), 293 (100), 240 (15), 227 (15), 198 (17), 149 (32), 121 (26), 95 (100),84 (52). HRMS calctd. for $C_{25}H_{24}O_2Fe$ 412.1119, found 412.1083.

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