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Synthesis of epoxyferrocenes by the oxidation of acyl- and allyl-substituted ferrocenes with dimethyldioxirane

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Abstract

The oxidation of acyl- and allylferrocenes **1** and **2** with dimethyldioxirane as the oxygen transfer agent affords the corresponding epoxides **5** and **6** in fair to good yields. Large excesses of oxidant, high temperatures, and an inert atmosphere (argon) minimize side reactions due to electron transfer processes, through which the ferrocene functionality is oxidized. In general, the allylferrocenes **2** are more reactive than the corresponding acyl derivatives **1**. For the phenyl-substituted substrate **2a** some C–H insertion (5%) to the acyl derivative **1a** is also observed.

Keywords: Acyl; Allyl; Epoxidation; Ferrocene; Iron; Dioxirane

1. Introduction

Selective oxidations for the oxyfunctionalization of ferrocenes are quite limited due to the easy generation of ferricenium cations [1] by electron transfer. Besides the ozonation [2] of vinylferrocene, only the oxidation [3] of alkylferrocenes at the α position by air, activated manganese dioxide or during chromatography on alumina have been reported. Attempts to epoxidize alkenylferrocenes by peracids [5] failed because of the sensitivity of the ferrocene moiety towards oxidation. Epoxyferrocenes have therefore been prepared from chlorohydrins [4] or by methylation of carbonyl-substituted ferrocenes by sulfur ylides [5] without the use of oxidation reactions.

Dimethyldioxirane has been established as a selective oxygen transfer agent for the oxyfunctionalization of organometallic substrates [6] and should be advantageous for the direct epoxidation of unsaturated ferrocenes. Indeed, we demonstrate herein that the acyl- and allyl-substituted ferrocenes **1** and **2** are converted to the corresponding epoxides **5** and **6** by dimethyldioxirane.

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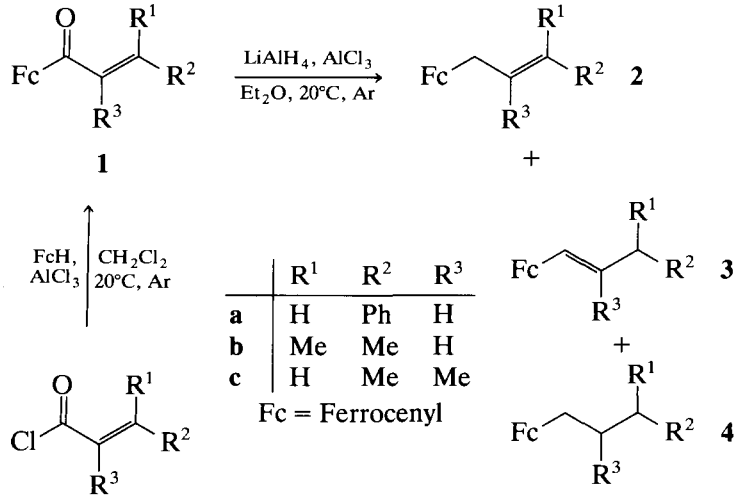
2. Results and discussion

The acyl ferrocenes **1a** and **1b** were synthesized according to the literature procedure [7] by Friedel-Crafts acylation of ferrocene. The synthesis of the hitherto unknown derivative **1c** was carried out in analogy (Scheme 1). Reduction of the keto functionality in **1a–c** with lithium aluminium hydride [8] afforded the corresponding allyl ferrocenes **2a–c**, of which **2b** and **2c** were accompanied by minor amounts of the vinyl isomers **3b** and **3c** and the saturated products **4b** and **4c** (Scheme 1).

The olefinic ferrocenes **1** and **2** were oxidized by dimethyldioxirane to the respective epoxides **5** and **6** in yields up to 84% (Table 1). The progress of the oxyfunctionalization was monitored by TLC and complete dioxirane consumption was determined by the peroxide test (KI/HOAc). Paramagnetic impurities prevented the acquisition of NMR spectra directly on the crude product mixture, which was therefore first submitted to column chromatography. Considerable amounts of iron-derived oxidation products remained on the column and were not accessible for mass balance.

The influence of the amount of oxidant, temperature, and atmosphere on the epoxidation was assessed as a function of substitution at the double bond of the ferrocene substrates (Table 1). As expected from the



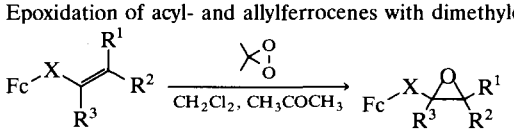
	R¹	R²	R³
a	H	Ph	H
b	Me	Me	H
c	H	Me	Me

Scheme 1. Synthesis of acyl- and allylferrocenes.

deactivation by the electron-accepting carbonyl group towards the electrophilic dioxirane oxidant, the allylferrocenes **2** (entries 7–14) react much faster and with less decomposition compared to the acylferrocenes **1** (entries 1–6). While three equivalents of dimethyldioxirane are sufficient to epoxidize the allyl substrates **2** completely, six or more equivalents are necessary for the acyl derivatives **1**. The need for such high amounts of dioxirane for complete conversion points to a destruction of the oxidant through induced decomposition by paramagnetic iron-containing products derived from oxidation of the ferrocene moiety. We therefore tried to inhibit such suspected redox-induced radical chain processes [9] by employing dioxygen as scavenger. However, under an O_2 atmosphere the dimethyldioxirane persisted longer, but the yield of epoxides actually dropped (entries 6, 12, 14). In view of the low oxidation potential of the ferrocenyl unit ($E_0 = -0.56$ V [10]), its oxidation by electron transfer is unavoidable and competes with the desired epoxidation process. A control experiment confirmed that ferrocene itself effectively promotes the decomposition of the dimethyldioxirane.

The temperature effect observed in the attempt to optimize the reaction conditions for epoxidation was

Table 1
Epoxidation of acyl- and allylferrocenes with dimethyldioxirane



Entry	Substrate	X	R¹	R²	R³	Dioxirane (equiv.)	t	T [°C]	gas	conv. [%]	m.b. [%] [a]	Product	Yield [%] [b]
1	**1a**	CO	H	Ph	H	6.0	8 h	20	Ar	100	30	**5a**	30
2	**1b**	CO	Me	Me	H	6.0	5 h	20	Ar	47	73	**5b**	50
3	**1b**	CO	Me	Me	H	9.0	9 h	20	Ar	73	71	**5b**	60
4	**1b**	CO	Me	Me	H	12.0	14 h	20	Ar	80	77	**5b**	72
5	**1c**	CO	H	Me	Me	6.0	6 h	20	Ar	100	59	**5c**	59
6	**1c**	CO	H	Me	Me	6.0	24 h	20	O_2	100	38	**5c**	38
7	**2a**	CH_2	H	Ph	H	6.0	45 min	20	Ar	100	43	**6a** [c]	38
8	**2b**	CH_2	Me	Me	H	3.0	40 min	0	Ar	100	66	**6b**	66
9	**2b**	CH_2	Me	Me	H	3.0	10 min	20	Ar	100	75	**6b**	75
10	**2b**	CH_2	Me	Me	H	3.0 [d]	1 min	56	Ar	75	87	**6b**	83
11	**2b**	CH_2	Me	Me	H	4.0 [d]	1 min	56	Ar	90	86	**6b**	84
12	**2b**	CH_2	Me	Me	H	3.0	25 min	20	O_2	100	28	**6b**	28
13	**2c** [e]	CH_2	H	Me	Me	3.0	15 min	20	Ar	100	76	**6c**	67
14	**2c** [e]	CH_2	H	Me	Me	3.0	30 min	20	O_2	100	66	**6c**	53

[a] After column chromatography.
[b] Yield of isolated material after column chromatography corrected for conversion.
[c] Contains 5% of **1a**.
[d] Only acetone as solvent.
[e] Contains 24% of **3c**.

informative. As shown for the reduced allylferrocene **2b** (entries 8–11), at room temperature or even in boiling acetone (56°C) higher yields of the epoxide were obtained than at 0°C; however, a higher amount of dimethyldioxirane had to be used at 56°C for full conversion. Consequently, higher temperatures favor the epoxidation process in the case of the allyl derivatives **2**; but that this is not general is manifested by the less readily epoxidized acylferrocenes **1**, of which **1a** was completely destroyed in boiling acetone (56°C) with no evidence for the formation of epoxide **5a** (data not shown in Table 1).

The reaction of substrate **2a** with dimethyldioxirane (entry 7) afforded the acylferrocene **1a** as byproduct (5% yield), which clearly indicates that the α position of **2a** is susceptible towards allylic oxidation by C–H insertion. In view of the electron-donating nature of the ferrocenyl moiety [11], the proximate C–H bond is activated towards oxygen atom insertion with dimethyldioxirane to produce the alcohol, which is subsequently oxidized to the final acyl derivative. Such C–H insertions are well-known for activated alkanes [12], but for allylic substrates competition with C=C epoxidation is quite rare [13]. In fact, for the alkyl-substituted allylferrocenes **2b,c** only epoxidation to **6b,c** prevailed, since the corresponding acyl derivatives **1b,c** (insertion products) were not observed.

In summary, the present results demonstrate that dimethyldioxirane is the oxygen transfer agent of choice for the epoxidation of olefinic ferrocenes. The redox-type oxidation of the ferrocene functionality can be sufficiently suppressed, so that the present methodology constitutes a convenient and novel entry to sidechain oxyfunctionalized ferrocene derivatives.

3. Experimental section

3.1. General

Melting points: Reichert Thermovar Kofler apparatus. IR: Perkin Elmer 1420. ^{1}H and ^{13}C NMR: Bruker AC 200 (200 MHz) or WM 250 (250 MHz); chemical shifts refer to TMS. All solvents were purified by standard literature methods. Silica gel (63-200 mesh; Woelm) was used for column chromatography, silica gel (32–64 mesh; Woelm) for flash chromatography. Ferrocene was purchased from Merck-Schuchardt. The ferrocenyl compounds **1a** [7a], **1b** [7b] and **2a** [8] were synthesized according to literature procedures. Dimethyldioxirane was prepared as acetone solution by the published procedure [14] and dried over molecular sieves (4 Å) at −20°C before use. All reactions were run under an argon gas atmosphere, if not stated otherwise. Petroleum ether of b.p. 30–50°C was used throughout.

3.2. (2-Methyl-1-oxo-2-butenyl)ferrocene (1c)

Analogous to the literature procedure [7c], from 3.56 g (30.0 mmol) 2-methyl-2-butenoic acid chloride, 5.58 g (30.0 mmol) ferrocene and 4.00 g (30.0 mmol) aluminium chloride 7.37 g (92%) of a reddish brown oil was isolated after a reaction time of 2.5 d. Although the product was obtained analytically pure, it resisted crystallization on treatment with pentane or vacuum destillation (150°C/0.01 Torr). (Found: C, 67.20; H, 6.09. $C_{15}H_{16}FeO$ Calc.: C, 67.19; H, 6.01%). IR (neat): 3120, 2980, 2940, 2880, 1740 (C=O), 1635 (C=C), 1450, 1380, 1285, 1110, 1070, 1035, 1010, 830, 755, 670 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.77 (dd, J = 6.9 Hz, J = 1.0 Hz, 3 H, 4-H), 1.87 (t, J = 1.2 Hz, 3 H, 5-H), 4.10 (s, 5 H, C_5H_5), 4.40 (t, J = 1.9 Hz, 2 H, C_5H_4), 4.72 (t, J = 1.9 Hz, 2 H, C_5H_4), 6.48 (qq, J = 6.9 Hz, J = 1.4 Hz, 1 H, 3-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 12.9 (q, C-4), 14.2 (q, C-5), 69.9 (d, C_5H_5), 71.1 (d, C_5H_4), 78.6 (d, C_5H_4), 78.6 (s, C_5H_4), 133.5 (d, C-3), 138.3 (s, C-2), 200.6 (s, C-1).

3.3. Reduction of the acylferrocenes 1b,c

3.3.1. (3-Methyl-2-butenyl)ferrocene (2b)

Analogous to the literature procedure [8], from 670 mg (2.50 mmol) **1b**, 115 mg (3.00 mmol) lithium aluminium hydride and 800 mg (6.00 mmol) aluminium chloride 669 mg of an orange oil were isolated after a reaction time of 1.5 h. Purification by column chromatography on silica gel with petroleum ether/diethylether (9:1) as eluent yielded 547 mg (86%) of a 70:19:11 mixture of (3-methyl-2-butenyl)ferrocene (**2b**) [8], (3-methylbutyl)ferrocene (**4b**) and (3-methyl-1-butenyl)ferrocene (**3b**), which were separated by flash chromatography with petroleum ether as eluent.

2b: R_f (petroleum ether) = 0.20. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.60 (s, 3 H, 5-H), 1.67 (s, 3 H, 4-H), 2.93 (d, J = 7.0 Hz, 2 H, 1-H), 3.69 (s, 4 H, C_5H_4), 4.03 (s, 5 H, C_5H_5), 5.27 (t, J = 7.0 Hz, 1 H, 2-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 17.9 (q, C-5), 25.7 (q, C-4), 27.8 (t, C-1), 67.0 (d, C_5H_4), 67.9 (d, C_5H_4), 68.4 (d, C_5H_5), 88.8 (s, C_5H_4), 123.5 (d, C-2), 131.4 (s, C-3).

4b: R_f (petroleum ether) = 0.28. (Found: C, 70.14; H, 7.53. $C_{15}H_{20}Fe$ Calc.: C, 70.33; H, 7.87%). IR (neat): 3080, 2950, 2920, 2860, 1465, 1450, 1410, 1380, 1365, 1100, 1040, 1020, 100, 920, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 0.85 (d, J = 6.8 Hz, 6 H, 4-H), 1.34 (m, 1 H, 2-H), 1.49 (m, J = 6.6 Hz, 2 H, 3-H), 2.24 (t, J = 7.9 Hz, 2 H, 1-H), 4.01 (s, 4 H, C_5H_4), 4.08 (s, 5 H, C_5H_5). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 22.6 (q, C-4), 27.2 (t, C-2), 27.9 (d, C-3), 40.2 (t, C-1), 68.9 (d, C_5H_4), 69.0 (d, C_5H_5), 89.6 (s, C_5H_4).

3b: R_f (petroleum ether) = 0.24. (Found: C, 70.83; H, 7.19. $C_{15}H_{18}Fe$ Calc.: C, 70.89; H, 7.14%). IR (CCl_4): 3080, 2940, 2900, 2850, 1450, 1370, 1350, 1100,

1040, 1020, 1000, 955 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.04 (d, $J = 6.7$ Hz, 6 H, 4-H), 2.31 (md, $J = 6.7$ Hz, $J = 1.0$ Hz, 1 H, 3-H), 4.07 (s, 5 H, C_5H_5), 4.19 (t, $J = 1.9$ Hz, 2 H, C_5H_4), 4.28 (t, $J = 1.9$ Hz, 2 H, C_5H_4), 5.78 (dd, $J = 15.8$ Hz, $J = 6.6$ Hz, 1 H, 2-H), 6.03 (dd, $J = 15.8$ Hz, $J = 0.9$ Hz, 1 H, 1-H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 22.6 (q, C-4), 31.4 (d, C-3), 66.3 (d, C_5H_4), 68.1 (d, C_5H_4), 69.0 (d, C_5H_5), 81.0 (s, C_5H_4), 123.5 (d, C-1), 135.5 (d, C-2).

3.3.2. (2-Methyl-2-butenyl)ferrocene (2c)

Analogous to the literature procedure [8], from 4.56 g (17.0 mmol) **1c**, 797 mg (21.0 mmol) lithium aluminium hydride and 5.60 g (42.0 mmol) aluminium chloride 3.60 g of an orange oil were isolated after a reaction time of 3.5 d. Purification by column chromatography on silica gel with petroleum ether/diethyl-ether (9:1) as eluent yielded 600 mg (13%) starting material **1c** and 2.90 g (78%) of a 65:19:16 mixture of (2-methyl-2-butenyl)ferrocene (**2c**), (2-methyl-1-butenyl)ferrocene (**3c**) and (2-methylbutyl)ferrocene (**4c**), from which the unsaturated product **4c** could be removed by flash chromatography with petroleum ether as eluent.

2c: ^1H NMR ($CDCl_3$, 250 MHz): δ 1.46 (d, $J = 6.4$ Hz, 3 H, 4-H), 1.48 (s, 3 H, 5-H), 2.94 (s, 2 H, 1-H), 4.05 (s, 4 H, C_5H_4), 4.09 (s, 5 H, C_5H_5), 5.08 (q, $J = 6.4$ Hz, 1 H, 3-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.3 (q, C-4), 15.8 (q, C-5), 40.2 (t, C-1), 67.2 (d, C_5H_4), 68.5 (d, C_5H_5), 68.9 (d, C_5H_4), 87.2 (s, C_5H_4), 118.7 (d, C-3), 136.0 (s, C-2).

3c: ^1H NMR ($CDCl_3$, 250 MHz): δ 1.06 (t, $J = 7.5$ Hz, 3 H, 4-H), 1.81 (s, 3 H, 5-H), 2.07 (q, $J = 7.5$ Hz, 2 H, 3-H), 4.08 (s, 5 H, C_5H_5), 4.14 (s, 2 H, C_5H_4), 4.27 (s, 2 H, C_5H_4), 5.81 (s, 1 H, 1-H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 10.9 (q, C-4), 17.9 (q, C-5), 33.5 (t, C-3), 67.7 (d, C_5H_4), 68.7 (d, C_5H_4), 68.8 (d, C_5H_5), 83.8 (s, C_5H_4), 119.7 (d, C-1), 137.9 (s, C-2).

2c and **3c** as mixture: R_f (petroleum ether) = 0.22. (Found: C, 70.61; H, 6.88. $C_{15}H_{18}Fe$ Calc.: C, 70.89; H, 7.14%). IR (neat): 3100, 2970, 2920, 2880, 1460, 1440, 1410, 1380, 1220, 1105, 1040, 1025, 1000, 925, 820 cm^{-1}.

4c: R_f (petroleum ether) = 0.32. (Found: C, 70.81; H, 7.82. $C_{15}H_{20}Fe$ Calc.: C, 70.33; H, 7.87%). IR (CCl_4): 3080, 2940, 2900, 2850, 1450, 1370, 1100, 1035, 1015, 995 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 0.60–0.80 (m, 6 H, 4, 5-H), 0.84–1.30 (m, 3 H, 2, 3-H), 2.03 (dd, $J = 13.7$ Hz, $J = 7.0$ Hz, 1 H, 1-H), 2.22 (dd, $J = 13.7$ Hz, $J = 5.3$ Hz, 1 H, 1-H), 3.90 (s, 4 H, C_5H_4), 3.94 (s, 5 H, C_5H_5). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 11.5 (q, C-4), 19.1 (q, C-5), 29.1 (t, C-3), 37.0 (d, C-2), 37.4 (t, C-1), 67.0 (d, C_5H_4), 67.1 (d, C_5H_4), 68.5 (d, C_5H_5), 69.0 (d, C_5H_4), 69.3 (d, C_5H_4), 87.6 (s, C_5H_4).

3.4. General procedure for the epoxidation of alkenylferrocenes by dimethyldioxirane

The particular alkenylferrocene (0.200–0.600 mmol), freshly purified by column chromatography, was dissolved in 2–10 ml of dry dichloromethane in a Schlenk-tube and kept at the stated temperature. A solution of dimethyldioxirane (3–12 equivalents) in acetone (0.08–0.10 *M*) was added at once and stirred at this temperature until the dioxirane was consumed (negative peroxide test with KI). The solvent was removed under vacuum (20°C/20 Torr) until 1–2 ml final volume and the residue chromatographed on silica gel with dichloromethane or mixtures of petroleum ether and diethyl ether as eluent. The appropriate reaction conditions, conversions, mass balances and yields in the epoxidation of **1** and **2** are summarized in Table 1.

3.4.1. Epoxidation of 1a: (2,3-oxiranyl-1-oxo-3-phenylpropyl)ferrocene (5a)

Red, amorphous solid, m.p. 120°C, R_f (dichloromethane) = 0.37. (Found: C, 68.51; H; 4.83. $C_{19}H_{16}FeO_2$ Calc.: C, 68.70; H, 4.85%). IR (KBr): 3080, 2910, 1645 (C=O), 1585, 1450, 1400, 1370, 1250, 1070, 995, 880, 820, 810, 750, 690 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 3.81 (d, $J = 1.7$ Hz, 1 H, 3-H), 4.10 (d, $J = 1.6$ Hz, 1 H, 2-H), 4.20 (s, 5 H, C_5H_5), 4.54 (t, $J = 1.9$ Hz, 2 H, C_5H_4), 4.81 (m, 1 H, C_5H_4), 4.88 (m, 1 H, C_5H_4), 7.32 (m, 5 H, arom. H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 59.2 (d, C-2), 61.2 (d, C-3), 69.4 (d, C_5H_4), 70.0 (d, C_5H_5), 73.2 (d, C_5H_4), 78.5 (s, C_5H_4), 125.6 (d, arom. *meta*-C), 128.7 (d, arom. *ortho*-C), 128.8 (d, arom. *para*-C), 135.8 (d, arom. *ipso*-C), 197.2 (s, C-1).

3.4.2. Epoxidation of 1b: (3-methyl-2,3-oxiranyl-1-oxobutyl)ferrocene (5b)

Orange, amorphous solid, m.p. 120–121°C, R_f (petroleum ether/diethyl ether 1:1) = 0.32. (Found: C, 63.50; H, 5.56. $C_{15}H_{16}FeO_2$ Calc.: C, 63.41; H, 5.68%). IR (KBr): 3120, 2980, 2960, 1665 (C=O), 1465, 1395, 1380, 1260, 1100, 1090, 1330, 1000, 905, 845, 815, 800 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.24 (s, 3 H, 5-H), 1.45 (s, 3 H, 4-H), 3.73 (s, 1 H, 2-H), 4.21 (s, 5 H, C_5H_5), 4.53 (m, 2 H, C_5H_4), 4.75 (m, 1 H, C_5H_4), 4.92 (m, 1 H, C_5H_4). ^{13}C NMR ([D_6]acetone, 50 MHz): δ 18.4 (q, C-5), 24.5 (q, C-4), 61.2 (s, C-3), 64.2 (d, C-2), 69.8 (d, C_5H_4), 70.1 (d, C_5H_4), 70.5 (d, C_5H_5), 73.1 (d, C_5H_4), 73.4 (d, C_5H_4), 79.4 (s, C_5H_4), 198.2 (s, C-1).

3.4.3. Epoxidation of 1c: (2-methyl-2,3-oxiranyl-1-oxobutyl)ferrocene (5c)

Red, amorphous solid, m.p. 49°C, R_f (dichloromethane) = 0.35. (Found: C, 63.81; H, 5.99. $C_{15}H_{16}FeO_2$ Calc.: C, 63.41; H, 5.68%). IR (KBr): 2960, 2920, 1630 (C=O), 1430, 1370, 1290, 1250, 1100, 1050, 1020,

810, 800 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.33 (d, $J = 5.4$ Hz, 3 H, 4-H), 1.54 (s, 3 H, 5-H), 3.17 (q, $J = 5.4$ Hz, 1 H, 3-H), 4.16 (s, 5 H, C_5H_5), 4.43 (m, 1 H, C_5H_4), 4.48 (m, 1 H, C_5H_4), 4.91 (m, 1 H, C_5H_4), 4.98 (m, 1 H, C_5H_4). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 13.8 (q, C-4), 14.6 (q, C-5), 58.0 (d, C-3), 64.8 (s, C-2), 69.8 (d, C_5H_5), 70.5 (d, C_5H_4), 70.8 (d, C_5H_4), 72.3 (d, C_5H_4), 72.6 (d, C_5H_4), 75.1 (s, C_5H_4), 204.0 (s, C-1).

3.4.4. Epoxidation of ***2a****: (2,3-oxiranyl-3-phenylpropyl)ferrocene (****6a****)*

Yellow needles, m.p. 87–88°C, R_f (petroleum ether/diethyl ether 9:1) = 0.40. (Found: C, 72.07; H, 6.18. $C_{19}H_{18}FeO$ Calc.: C, 71.72; H, 5.70%). IR (KBr): 3080, 3040, 2980, 2920, 1490, 1450, 1280, 1100, 1020, 990, 880, 820, 760, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 2.39 (dd, $J = 15.0$ Hz, $J = 5.2$ Hz, 1 H, 1-H), 2.49 (dd, $J = 14.9$ Hz, $J = 5.6$ Hz, 1 H, 1-H), 3.03 (dt, $J = 5.4$ Hz, $J = 1.9$ Hz, 1 H, 2-H), 3.46 (d, $J = 1.9$ Hz, 1 H, 3-H), 3.94 (m, 2 H, C_5H_4), 3.96 (s, 5 H, C_5H_5), 3.99 (m, 1 H, C_5H_4), 4.04 (m, 1 H, C_5H_4), 7.03–7.23 (m, 5 H, arom. H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 31.4 (t, C-1), 57.0 (d, C-2), 61.4 (d, C-3), 66.5 (d, C_5H_4), 66.6 (d, C_5H_4), 67.3 (d, C_5H_4), 67.5 (d, C_5H_4), 65.5 (d, C_5H_5), 82.6 (s, C_5H_4), 124.5 (d, arom. *ortho*-C), 126.6 (d, arom. *para*-C), 127.3 (d, arom. *meta*-C), 137.1 (s, arom. *ipso*-C).

3.4.5. Epoxidation of ***2b****: (3-methyl-2,3-oxiranylbutyl)ferrocene (****6b****)*

Yellow oil, R_f (petroleum ether/diethyl ether 4:1) = 0.37. (Found: C, 66.97; H, 6.93. $C_{15}H_{18}FeO$ Calc.: C, 66.69; H, 6.72%). IR (CCl_4): 3090, 2960, 2920, 2020, 1970, 1455, 1380, 1260, 1125, 1105, 1040, 1025, 1000 cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 1.26 (s, 3 H, 5-H), 1.27 (s, 3 H, 4-H), 2.45 (dd, $J = 15.1$ Hz, $J = 6.1$ Hz, 1 H, 1-H), 2.62 (dd, $J = 15.1$ Hz, $J = 6.2$ Hz, 1 H, 1-H), 2.98 (t, $J = 6.2$ Hz, 1 H, 2-H), 4.09 (m, 2 H, 2, C_5H_4), 4.13 (m, 2 H, C_5H_4), 4.13 (s, 5 H, C_5H_5). ^{13}C NMR (C_6D_6, 50 MHz): δ 18.9 (q, C-4 or 5), 24.8 (q, C-4 or 5), 29.5 (t, C-1), 57.4 (s, C-3), 63.7 (d, C-2), 67.9 (2 × d, C_5H_4), 68.4 (d, C_5H_4), 68.7 (d, C_5H_4), 68.9 (d, C_5H_5), 84.9 (s, C_5H_4).

3.4.6. Epoxidation of ***2c****: (2-methyl-2,3-oxiranylbutyl)ferrocene (****6c****)*

Yellow oil, R_f (petroleum ether/diethyl ether 9:1) = 0.20. (Found: C, 66.21; H, 6.88. $C_{15}H_{18}FeO$ Calc.: C, 66.69; H, 6.72%). IR (neat): 3100, 3000, 2980, 2960, 1390, 1260, 1140, 1050, 1030, 1020, 870, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.10 (s, 3 H, 5-H), 1.16 (d, $J = 5.5$ Hz, 3 H, 4-H), 2.45 (d, $J = 14.3$ Hz, 1 H, 1-H), 2.61 (d, $J = 14.3$ Hz, 1 H, 1-H), 2.76 (q, $J = 5.5$ Hz, 1 H, 3-H), 4.02 (s, 9 H, C_5H_4, C_5H_5). ^{13}C NMR ($CDCl_3$, 63 MHz): δ 14.0 (q, C-4), 16.3 (q, C-5), 39.4 (t, C-1), 58.3 (d, C-3), 61.0 (s, C-2), 67.6 (d, C_5H_4), 67.7 (d, C_5H_4), 68.6 (d, C_5H_5), 69.2 (d, C_5H_4), 69.4 (d, C_5H_4), 83.1 (s, C_5H_4).

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