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Synthesis of unsymmetrical 1,1′-disubstituted ferrocenes. Formation of ferrocenophanes via intramolecular cycloaddition

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Abstract

Unsymmetrical 1,1′-disubstituted ferrocenes bearing appropriate substituents for intramolecular cycloadditions were synthesized conveniently starting from 1,1′-ferrocenedicarbaldehyde. Ferrocenenitrone derivatives reacted in an intramolecular regioselective manner affording ferrocenophanes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Unsymmetrical disubstituted ferrocenes; Ferrocenophanes; Intramolecular cycloadditions; Nitrones

1. Introduction

Since its discovery in the early 1950s [1], ferrocene has attracted the attention of scientists worldwide because of its numerous applications in chemical sensing, in asymmetric catalysis and in material science [2]. The integration of a ferrocene unit into macrocyclic architectures has been recognized as an attractive way to endow molecules with secondary functionalities. Ferrocenophanes comprise a class of ferrocene macrocycles, which besides their bifunctional character have also drawn interest as building blocks via ring opening polymerization [3].

Our interest on ferrocene [4] and 1,3-dipolar cycloaddition chemistry [5] prompted us to study the possible formation of ferrocenophanes using a dipolar cycloaddition methology. An appropriate way for this approach relies on the use of unsymmetrical 1,1′-disubstituted ferrocenes bearing two substituents suitable to give intramolecular 1,3-dipolar cycloaddition reaction. Ferrocene derivatives in which the two cyclopentadienyl rings bear different substituents receive considerable interest owing to their utility in the synthetic construction of large ferrocene based assemblies [6]. The methods of their preparation involve selective introduction of a second substituent in the 1′-position of a monosubstituted derivative or selective transformation of one substituent of symmetrical disubstituted compounds.

2. Results and discussion

For the purpose of this work compound **4** was considered an appropriate starting material since it incorporates both a typical dipolarophile moiety and the aldehyde group as the dipole precursor. Attempts at its synthesis from the readily available ester **2** by typical formylation [7a] as shown in Scheme 1 gave disappointingly low yield (15%). Compound **4** was finally synthesized in high yield (85%) by a partial Wittig olefination of the 1,1′-ferrocenedicarbaldehyde **3** which was prepared directly from ferrocene by the previously described procedure [7b,7c]. Minor amounts of the *cis*-isomer **5** (4% yield) and the bis-adduct **6** (7% yield) were also isolated.

Treatment of the aldehyde **4** with hydroxylamine gave the aldoxime **7** in good yield (90%). This compound may be considered as a potential 1,3-dipole either via an 1,2 proton transfer to form the corresponding NH nitrone or via an intramolecular 1,3-azaprotiocyclotransfer to form the ferrocenophane dipole **9**. It should be noted that several oximes have been used in a wide range of tandem nitrone-cycloaddition processes over the past few years [4b,9]. However, after prolonged reflux of **7** in

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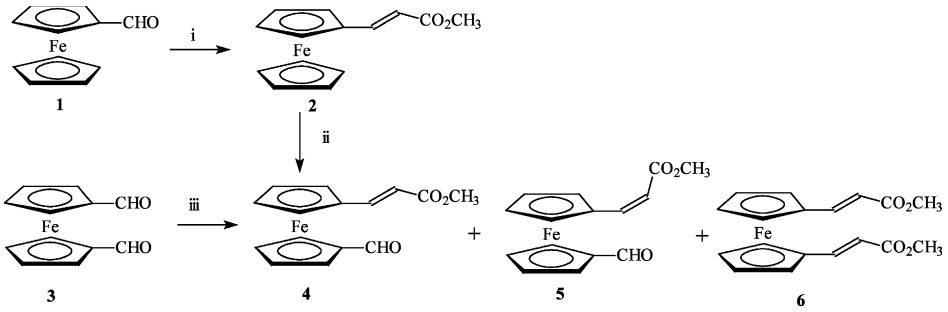
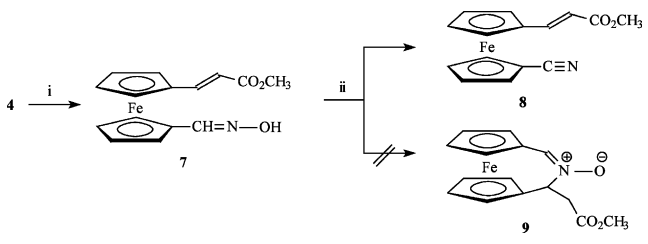


Scheme 1. Reagents and conditions: (i) $Ph_3P{=}CHCO_2CH_3$ (one equivalevts), CH_2Cl_2, 20 °C, 24 h; (ii) Cl_2CHOCH_3, $TiCl_4$, CH_2Cl_2, reflux, 6 h; (iii) $Ph_3P{=}CHCO_2CH_3$ (1/2 equivalent), CH_2Cl_2, 20 °C, 24 h.

toluene and in xylene solution only the nitrile **8**, the dehydration product of **7**, was isolated. Another possibility which was also examined is the transformation of the aldoxime **7** to the corresponding nitrile oxide and its subsequent cyclization to an isoxazoline ferrocenophane. Although a variety of several well known conventional procedures for the generation of the nitrile oxide were employed [8], all attempts to obtain any ferrocenophane cycloadduct failed (Scheme 2).

Then we turned our attention to the synthesis of nitrones **10** in which the α,β-unsaturated ester and the nitrone functionalities are appropriate candidates for the desired intramolecular process. Reaction of the aldehyde **4** with methylhydroxylamine afforded the nitrone **10a** in satisfactory yield (74%). Only one stereoisomer was formed which was assumed to be the *Z*-isomer since aldonitrones generally exist as the stable *Z*-isomers [4b,10]. Furthermore the *Z*-structure of **10a** is supported by the significant enhancement of the ^{1}H-NMR C*H*N(O)CH_3 signal at δ 6.95 observed upon saturation of the NCH_3 signal at δ 3.65. Nitrone **10a** was transformed in the ferrocenophane **11a** after reflux in toluene in high dilution conditions for 3 days. The yield of the transformation was moderate (32% based on the starting nitrone, 54% based on the consumed) and it was not improved with longer reflux time. On the contrary, compound **11a** was not detected in the reaction mixture after reflux for 6 days (Scheme 3).

The structure assignment of **11a** was made on the basis of its spectral data. The yellow color of compound **11a** compared with the red–brown of **10a** is indicative of the lack of conjugation due to cycloaddition, whereas



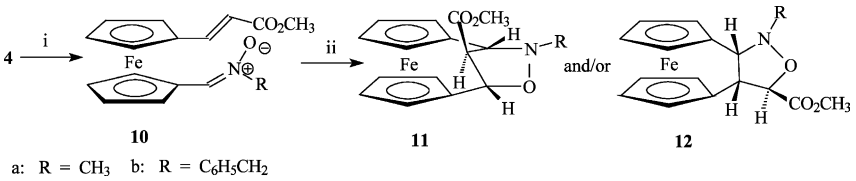
Scheme 2. Reagents and conditions: (i) $NH_2OH{\cdot}HCl$, Na_2CO_3, H_2O–EtOH, 20 °C, 24 h; (ii) xylene, reflux, 1 day.

the molecular ion peak at 327 shows an intramolecular cycloaddition. For an intramolecular cycloaddition, there are two possible reaction pathways via the transition states TS_A and TS_B (Fig. 1) leading to the regioisomeres **11** and **12**, respectively. Due to the steric demand for a *cis* orientation of the two α-cyclopentadienyl hydrogens the formation of other stereoisomers is not possible.

The structure discrimination between the two possible isomers **11** and **12** was mainly based on the ^{1}H-NMR spectrum. The obtained cycloadduct exhibits three single peaks at δ 3.61, 4.46 and 5.64 corresponding to the 4H, 3H and 5H protons. The absence of any essential coupling between them is indicative of their *trans* orientation with orthogonal dihedral angles, consistent with structure **11**. On the contrary in the alternative structure **12** the 3H and 4H protons have a *cis* orientation and are expected to show a noticeable coupling. The structure **11** is further supported by NOE measurements. As depicted in Fig. 2 the mutual observed NOE enhancements between 3H, 4H and 4H, 5H are small in agreement with their *trans* geometry, whereas the observed significant enhancement of 4H upon saturation of the two cyclopendadienyl hydrogens shows a close proximity between them, evident in molecular models for structure **11**.

Analogous behavior to the nitrone **10a** showed the benzyl derivative **10b**. Although nitrone **10b** was unstable and was not isolated in pure form, used as an intermediate gave the analogous cycloadduct **11b** in 35% yield. Cycloadduct **11b** exhibits the same characteristics with **11a**. This is a yellow solid, in the mass spectrum it gives the expected molecular ion at *m*/*z* 403, whereas in the ^{1}H-NMR spectrum has three singlets at δ 3.64, 4.62 and 5.68 corresponding to the 4H, 3H and 5H isoxazolidine protons.

The observed regioselectivity of the reaction is attributed besides electronic factors to the stability of the possible regioisomeric products. From a FMO point of view both transition states are *Z-endo* and are favored by secondary interactions. Despite transition state TS_B appears to be sterically favored, the corresponding adduct **12** with a two carbon bridge is expected to



Scheme 3. Reagents and conditions: (i) $CH_3NHOH{\cdot}HCl$ or $C_6H_5CH_2NHOH.HCl$, Na_2CO_3, H_2O–EtOH, 20 °C, 24 h) (ii) toluene, reflux, 3 days.

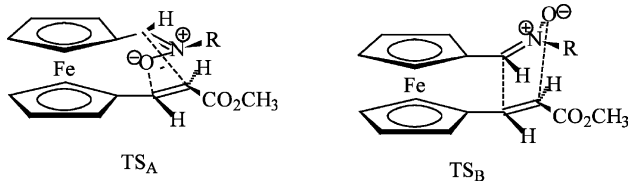


Fig. 1.

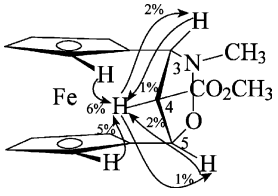


Fig. 2.

experience more strain than **11** with a three carbon bridge which predominates. The inability to obtain analogous to **11** isoxazoline derivatives from nitrile oxide cycloaddition as well as compounds of structure **9** may be also attributed to a higher strain introduced by a sp^2 carbon on the ferrocenophane bridge.

In conclusion, new 1,1′- unsymmetrical substituted ferrocenes with dipolarophile and dipole substituents have been synthesized applying simple procedures. Nitrone derivatives were transformed by an intramolecular regioselective dipolar cycloaddition to new ferrocenophanes, in which the carbon bridge is annulated with a heterocyclic ring. To the best of our knowledge ferrocenophanes of this type are referred for the first time. Studies on the synthesis of analogous ferrocene derivatives with other appropriate dipole and dipolarophile substituents are currently under way in our laboratory.

3. Experimental

3.1. General

M.p.s. were determined on a Kofler hot-stage apparatus and are uncorrected. The IR spectra were obtained with a Perkin–Elmer Model 297 spectrometer. ^{1}H-NMR spectra were recorded on a Bruker 300 AM spectrometer at 300 MHz and ^{13}C-NMR spectra on the same spectrometer at 75.7 MHz, in deuteriochloroform solutions and are quoted relative to Me_4Si as internal standard. Mass spectra were determined on a VG-250 spectrometer with ionization energy maintained at 70 eV. Microanalyses were performed on a Perkin–Ermer Model 2400-II analyser. Column chromatography was carried out on Merck Kieselgel (particle size 0.063–0.200).

3.2. Preparation of (E)-1′-formyl-1-[β-(methoxycarbonyl)ethenyl]ferrocene (4)

3.2.1. Formylation of β-(methoxycarbonyl)ethenylferrocene (2)

To a solution of **2** (200 mg, 0.74 mmol) prepared as previously described [4a] in 20 ml dry CH_2Cl_2 at 0 °C under argon there were subsequently added dropwise titanium(IV) chloride (570 mg, 3 mmol) and dichloromethyl methyl ether (259 mg, 2.25 mmol). After the addition the reaction mixture was stirred at room temperature (r.t.) for 1 h and then it was held at reflux for 6 h. The reaction was stopped with 10 ml of water. The organic phase was washed with water (2 × 20 ml) dried over Na_2SO_4 and evaporated. The residue was chromatographed on a silica gel column using C_6H_{14}–EtOAc 5:1 as eluent to give compound **4** (36 mg, 15%)

3.2.2. Wittig olefination of 1,1′-ferrocenedicarbaldehyde (3)

A solution of aldehyde **4** (968 mg, 4 mmol) prepared according to the literature [7] and methyl-(triphenylphosphoranylidene)acetate (668 mg, 2 mmol) in dry CH_2Cl_2 (10 ml) was allowed to stay at r.t. under argon for 2 days. The solvent was evaporated under reduced pressure and the residue was chromatographed on a silica gel column using C_6H_{14}–EtOAc 3:1 as eluent to give in order of elution compound **6** (10 mg), a mixture of compounds **5** and **6** (40 mg, in a ratio 1:2 as determined by NMR integration, yield of **5** 4% and total yield of **6** 7%) compound **4** (507 mg, 85%) and unreacted **3** (390 mg).

3.2.2.1. (E)-1′-formyl-1-[β-(methoxycarbonyl)-ethenyl]ferrocene (4). This compound was obtained as a red–brown solid, m.p. 70–72 °C; IR (Nujol): *ν* 1700, 1670 (C=O), 1625 (C=C) cm^{-1}; ^{1}H-NMR: *δ* 3.78 (s, 3H, OCH_3), 4.49 (br s, 2H, Cp–H), 4.57 (br s, 4H, Cp–H), 4.77 (br s, 2H, Cp–H), 6.06 (d, $J = 15.9$ Hz, 1H, $CHCO_2CH_3$), 7.46 (d, $J = 15.9$ Hz, 1H, CHC_5H_4), 9.89

(s, 1H, C*H*O); ^{13}C-NMR: δ 51.5 (CO_2CH_3), 69.7, 70.8, 72.0, and 74.5 (CH in Cp), 80.1 and 80.4 (quaternary C in Cp), 116.7 ($CHCO_2CH_3$), 143.3 (CHC_5H_4), 167.0 (CO_2CH_3), 193.0 (CHO); MS (RI): *m/z* 298 [100, M^+]. Anal. Found: C, 60.02; H, 4.51. Calc. for $C_{15}H_{14}FeO_3$: C, 60.43; H, 4.73%.

*3.2.2.2. (Z)-1′-formyl-1-[β-(methoxycarbonyl)-ethenyl]ferrocene (**5**).* This compound was assigned only from its NMR spectra of its mixture with **6**; ^{1}H-NMR: δ 3.74 (s, 3H, OCH_3), 4.46 (br s, 2H, Cp–H), 4.57 (br s, 2H, Cp–H), 4.75 (br s, 2H, Cp–H), 4.95 (br s, 2H, Cp–H), 5.84 (d, $J = 12.6$ Hz, 1H, $CHCO_2CH_3$), 6.56 (d, $J = 12.6$ Hz, 1H, CHC_5H_4), 9.89 (s, 1H, C*H*O); ^{13}C-NMR: δ 51.1 (CO_2CH_3), 70.9, 71.8, 73.2, and 74.4 (CH in Cp), 79.2 and 80.0 (quaternary C in Cp), 116.2 ($CHCO_2CH_3$), 141.7 (CHC_5H_4), 166.5 (CO_2CH_3), 193.2 (CHO).

*3.2.2.3. (E,E)-1,1′-bis-[β-(methoxycarbonyl)-ethenyl]ferrocene (**6**).* This compound was obtained as a red solid, m.p. 129–131 °C; IR (Nujol): *v* 1700 (C=O), 1620 (C=C) cm^{-1}; ^{1}H-NMR: δ 3.77 (s, 3H, OCH_3), 4.38 (t, $J = 1.6$ Hz, 2H, Cp–H), 4.45 (t, $J = 1.6$ Hz, 2H, Cp–H), 5.95 (d, $J = 16.0$ Hz, 1H, $CHCO_2CH_3$), 7.37 (d, $J = 16.0$ Hz, 1H, CHC_5H_4); ^{13}C-NMR: δ 51.4 (CO_2CH_3), 69.8, and 72.2 (CH in Cp), 80.0 (quaternary C in Cp), 115.9 ($CHCO_2CH_3$), 143.9 (CHC_5H_4), 167.3 (CO_2CH_3); MS (RI): *m/z* 354 [100, M^+]. Anal. Found: C, 61.30; H, 4.99. Calc. for $C_{18}H_{18}FeO_4$: C, 61.04; H, 5.12%.

3.3. Preparation of 1′-[β-(methoxycarbonyl)-ethenyl]ferrocen-1-yl oxime (7)

A solution of hydroxylamine hydrochloride (125 mg, 1.8 mmol) and Na_2CO_3 (127 mg, 1.2 mmol) in water (1 ml) was added to a solution of **4** (238 mg, 0.8 mmol) in EtOH (4 ml) and the reaction mixture was stirred under argon at r.t. for 24 h. The EtOH was evaporated under *vacuum* and the residue was extracted with CH_2Cl_2 (3 × 10 ml). The organic layer was dried with Na_2SO_4 and evaporated. Trituation of the residue with Et_2O gave oxime **7** (225 mg, 90%) as one stereoisomer as determined by ^{1}H- and ^{13}C-NMR spectra although TLC control showed two spots due probably to a partial conversion to the other isomer on the TLC plate. Oxime **7** was obtained as an orange–brown solid m.p. 104–107 °C; IR (Nujol): *v* 3220 (OH), 1695, (C=O), 1620 (C=N, C=C) cm^{-1}; ^{1}H NMR: δ 3.77 (s, 3H, OCH_3), 4.31 (t, $J = 1.7$ Hz, 2H, Cp–H), 4.43 (t, 2H, $J = 1.7$ Hz, 2H, Cp–H), 4.53 (t, $J = 1.7$ Hz, 4H, Cp–H), 6.05 (d, $J = 15.9$ Hz, 1H, $CHCO_2CH_3$), 7.48 (d, $J = 15.9$ Hz, 1H, CHC_5H_4), 7.85 (s, 1H, C*H*=NOH), 8.53 (br s, 1H, OH); ^{13}C-NMR: δ 51.5 (CO_2CH_3), 68.9, 69.6, 71.4 and 71.9 (CH in Cp), 77.7 and 79.8 (quaternary C in Cp), 115.9 ($CHCO_2CH_3$), 144.7 (CHC_5H_4), 148.8 (CH=NOH), 167.6 (CO_2CH_3); MS (RI): *m/z* 313 [26, M^+]. Anal. Found: C, 57.69; H, 4.77; N, 4.54. Calc. for $C_{15}H_{15}FeNO_3$: C, 57.54; H, 4.83; N, 4.47%.

3.4. Thermal decomposition of oxime 7

A solution of the oxime **7** (63 mg, 0.2 mmol) in dry $C_6H_5CH_3$ (50 ml) was heated to reflux under argon and the reaction was monitored by TLC. After reflux for 60 h the most of **7** remained unreacted. So the solvent was evaporated, dry xylene (50 ml) was added and the solution was heated again to reflux until the disappearance of the oxime spot (about 24 h). The xylene was evaporated under reduced pressure and the residue was chromatographed on a silica gel column using C_6H_{14}–EtOAc 3:1 as eluent to give **8** (42 mg, 71%).

(*E*)-1′-cyano-1-[β-(methoxycarbonyl)ethenyl]ferrocene (**8**) was obtained as an orange solid, m.p. 104–106 °C (from Et_2O); IR (Nujol): *v* 2220 (C≡N), 1710, (C=O), 1630 (C=C) cm^{-1}; ^{1}H-NMR: δ 3.78 (s, 3H, OCH_3), 4.38 (t, $J = 1.7$ Hz, 2H, Cp–H), 4.56 (t, 2H, $J = 1.7$ Hz, 2H, Cp–H), 4.62 (t, $J = 1.7$ Hz, 4H, Cp–H), 6.13 (d, $J = 15.7$ Hz, 1H, $CHCO_2CH_3$), 7.49 (d, $J = 15.7$ Hz, 1H, CHC_5H_4); ^{13}C-NMR: δ 51.6 (CO_2CH_3), 70.5, 72.3, 73.0 and 73.1 (CH in Cp), 80.9 (quaternary C in Cp), 117.2 ($CHCO_2CH_3$), 119.3 (CN), 142.7 (CHC_5H_4), 167.1 (CO_2CH_3); MS (RI): *m/z* 295 [55, M^+]. Anal. Found: C, 60.81; H, 4.21; N 5.07. Calc. for $C_{15}H_{13}FeNO_2$: C, 61.05; H, 4.44; N, 4.75%.

*3.5. Preparation of N-methyl-C-[1′-[β-(methoxycarbonyl)ethenyl]ferrocen-1-yl] nitrone (**10a**)*

A solution of *N*-methylhydroxylamine hydrochloride (115 mg, 1.4 mmol) and Na_2CO_3 (95 mg, 0.9 mmol) in water (1 ml) was added to a solution of **4** (179 mg, 0.6 mmol) in EtOH (3 ml) and the reaction mixture was stirred under argon at r.t. for 24 h. The EtOH was evaporated under reduced pressure and the residue was exctracted with CH_2Cl_2 (3 × 10 ml). The organic layer was dried with Na_2SO_4 and after the removal of the solvent the residue was chromatographed on a silica gel column using MeOH–EtOAc 1:10 as eluent to give **10a** (145 mg, 74%).

Compound **10a** was obtained as a red–brown solid, m.p. 68–70 °C; IR (Nujol): *v* 1700, 1625 (C=N, C=C) cm^{-1}; ^{1}H-NMR: δ 3.65 (s, 3H, NCH_3), 3.77 (s, 3H, OCH_3), 4.36 (br s, 2H, Cp–H), 4.42 (br s, 2H, Cp–H), 4.58 (br s, 2H, Cp–H), 5.07 (br s, 2H, Cp–H), 6.04 (d, $J = 15.4$ Hz, 1H, $CHCO_2CH_3$), 6.95 (s, 1H, C*H*=N(O)CH_3),7.47 (d, $J = 15.4$ Hz, 1H, CHC_5H_4); ^{13}C-NMR: δ 51.3 (CO_2CH_3), 53.0 (NCH_3), 69.3, 70.7, 71.3 and 71.5 (CH in Cp), 75.5 and 79.8 (quaternary C in Cp), 115.4 ($CHCO_2CH_3$), 134.4 (CH=N(O)CH_3), 144.5 (CHC_5H_4), 167.3 (CO_2CH_3); MS (RI): *m/z* 327 [15, M^+].

Anal. Found: C, 58.80; H, 5.19; N, 3.94. Calc. for $C_{16}H_{17}FeNO_3$: C, 58.74; H, 5.24; N, 4.28%.

3.6. Thermal transformation of nitrone **10a** to the 3S*,4R*,5R*-3,5-(1,1′-ferrocenediyl)-4-methoxycarbonyl-2-methylisoxazolidine (**11a**)

A solution of the nitrone **10a** (65 mg, 0.2 mmol) in dry $C_6H_5CH_3$ (50 ml) was heated to reflux under argon and the reaction was monitored by TLC. After reflux for 3 days the solvent was evaporated and the residue was subjected to column chromatography using successively C_6H_{14}–EtOAc 10:1 and EtOAc–MeOH 10:1 as eluent to give besides unreacted nitrone **10a** (26 mg), the ferrocenophane **11a** (21 mg, 32% on the starting nitrone, 54% on the consumed). Repeat of the reaction using longer reaction time (6 days) or higher temperature (reflux in xylene) lead to the full consumption of the nitrone and the formation of unidentified decomposition mixtures.

Compound **11a** was obtained as a yellow solid, m.p. 156–158 °C; IR (Nujol): ν 1720 cm^{-1}, (C=O); ^{1}H-NMR: δ 2.79 (s, 3H, NCH_3), 3.61 (s, 1H, 4H), 3.84 (s, 3H, OCH_3), 3.95 (t, $J = 1$ Hz, 1H, Cp–H), 3.99 (t, $J = 1$ Hz, 1H, Cp–H), 4.12 (m, 4H, Cp–H), 4.46 (s, 1H, 3H), 4.51 (t, $J = 1$ Hz, 1H, Cp–H), 4.62 (t, $J = 1$ Hz, 1H, Cp–H), 5.64 (s, 1H, 5H); ^{13}C-NMR: δ 29.7 (C4), 47.6 (NCH_3), 52.5 (CO_2CH_3), 63.4, 64.2, 66.6, 66.7, 69.3 and 70.6 (CH in Cp and C3), 75.7 (C5) 85.3 and 85.4 (quaternary C in Cp), 171.4 (CO_2CH_3); MS (RI): m/z 327 [100, M^+]. Anal. Found: C, 58.73; H, 5.22; N, 3.88. Calc. for $C_{16}H_{17}FeNO_3$: C, 58.74; H, 5.24; N, 4.28%.

3.7. Formation and thermal transformation of nitrone **10b** to the 3S*,4R*,5R*-3,5-(1,1′-ferrocenediyl)-4-methoxycarbonyl-2-benzylisoxazolidine (**11b**)

A solution of *N*-benzylhydroxylamine hydrochloride (115 mg, 1.4 mmol) and Na_2CO_3 (95 mg, 0.9 mmol) in water (1 ml) was added to a solution of **4** (179 mg, 0.6 mmol) in EtOH (3 ml) and the reaction mixture was stirred under argon at r.t. for 24 h. The EtOH was evaporated under vacuum and the residue was extracted with CH_2Cl_2 (3×20 ml). After evaporation of the solvent the crude nitrone **10b** was obtained as a brown oil (230 mg, 91%). Attempts to purify nitrone **10b** by crystallization from several solvents were unsuccessful, whereas on column chromatography it was partially decomposed. So it was used for the next step without further purification. A solution of the nitrone **10b** (81 mg, 0.2 mmol) in dry $C_6H_5CH_3$ (50 ml) was heated to reflux under argon for 3 days. Then the solvent was evaporated and the residue was subjected to column chromatography using C_6H_{14}–EtOAc 10:1 as eluent to give the ferrocenophane **11b** (28 mg, 35%).

Compound **11b** was obtained as a yellow solid, m.p. 94–98 °C; IR (Nujol): ν 1725 cm^{-1}, (C=O); ^{1}H-NMR: δ 3.64 (s, 1H, 4H), 3.89 (s, 3H, OCH_3), 3.94 (br s, 2H, Cp–H), 3.97 (br s, 1H, Cp–H), 4.06 (m, 4H, Cp–H and one of $CH_2C_6H_5$), 4.31 (d, $J = 13.2$ Hz, 1H, one of $CH_2C_6H_5$), 4.57 (br s, 1H, Cp–H), 4.62 (s, 1H, 3H), 4.68 (br s, 1H, Cp–H), 5.68 (s, 1H, 5H), 7.33 (m, 3H, C_6H_5), 7.44 (m, 2H, C_6H_5); ^{13}C-NMR: δ 29.7 (C4), 52.6 (CO_2CH_3), 60.7 ($CH_2C_6H_5$), 63.3, 63.4, 66.4, 66.6, 69.2, 69.3, 69.9, 70.0 and 70.9 (CH in Cp and C3), 76.0 (C5), 85.3 and 85.4 (quaternary C in Cp), 127.4, 128.4, 128.8 and 137,6 (C_6H_5), 171.5 (CO_2CH_3). MS (RI): m/z 403 [20, M^+]. Anal Found: C, 65.88; H, 5.18; N, 3.78. Calc. for $C_{22}H_{21}FeNO_3$: C, 65.53; H, 5.25; N, 3.47%.

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