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Microwave-assisted synthesis of 1,5-dioxo-3-substituted [5]ferrocenophanes

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Abstract

The Claisen–Schmidt reaction between 1,1′-diacetylferrocene and ferrocenecarboxaldehyde under microwave irradiation has been investigated in different conditions. The selective synthesis of 1,5-dioxo-3-ferrocenyl[5]ferrocenophane has been achieved and a simple protocol for its purification was established. The reaction was generally applicable to other non-enolizable aldehydes and the corresponding 1,5-dioxo-3-substituted [5]ferrocenophanes were obtained in high yield within 30 min.

Keywords: [5]Ferrocenophanes; Claisen–Schmidt condensation; Diacetylferrocene; Microwave-assisted synthesis

1. Introduction

Ferrocenophanes are cyclic organometallic compounds bearing one or more bridges between two cyclopentadienyl (Cp) rings on the same or different ferrocene unit [1]. Metal-bridged [1]-ferrocenophanes and derivatives with a short carbon chain in the bridge experience substantial strain between the Cp rings and easily undergo a ring-opening polymerization reaction giving rise to polymers with peculiar electronic properties [2–7]. Several aza-ferrocenophanes have been designed as selective electrochemical sensors for cations or anions [8–12] and more recently the potential of ferrocene-based macrocycles as molecular machines has been reported [13,14]. The synthesis of homochiral ferrocenophanes and their application as catalyst in asymmetric synthesis has been also described [15–20].

Among the carbon-bridged ferrocenophanes, [3]- and [4]-ferrocenophanes have been extensively investigated [21–25] but a relatively small number of [5]-ferrocenophane derivatives have been reported. Many of them are derived from [5]ferrocenophane-1,5-dione, **1** (R = H) (see Fig. 1), obtained by a sequence of Friedel–Crafts acylation of acetylferrocene with 3-chloropropionyl chloride followed by base-catalyzed cyclization [26]. The related 3-substituted [5]ferrocenophane-1,5-diones **2** (R = Ar, alkyl) can be prepared by means the reaction of 1,1′-diacetylferrocene, **3** and aldehydes in NaOH ethanolic solution [27–31], resulting in a mixture of α,β-unsaturated ferrocenylketones and ferrocenophanes, whose selective formation was obtained in some cases [30,31]. Improved methods for the synthesis of **2a** (R = Ph) starting from **5a** [26] or **6a** [32] independently prepared by Friedel–Craft acylations and treated with NaOH ethanolic solution for long time (up to 65 h), have been proposed.

In the course of a study on the synthesis of 1,3-diferrocenylpropane systems, we investigated the Claisen–Schmidt condensation of **3** with ferrocenecarboxaldehyde **4** and evidenced that such reaction, when carried out under microwave irradiation, can be easily driven toward the exclusive formation of the [5]ferrocenophane system. This one-pot procedure appeared highly effective also using other non-enolizable aldehydes giving high yields of 1,5-dioxo-3-substituted [5]ferrocenophanes and herein we describe the obtained results.

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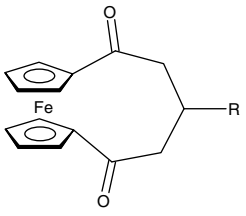


1 R = H
2 R = Ar, alkyl

Fig. 1. General structure of 1,5-dioxo-[5]ferrocenophanes.

2. Results and discussion

Microwave technology has become a popular and useful way to achieve consistent acceleration, in some instances coupled with enhancements in selectivity, for a wide range of organic reactions [33,34] and has been also applied to the synthesis of ferrocenylchalcones [35]. On the contrary, the effect of microwave activation in the Claisen–Schmidt condensation of 1,1′-diacetylferrocene with aldehydes has not been systematically evaluated [36].

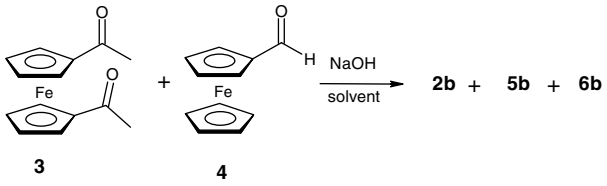
Since we were interested in the preparation of derivatives containing more than one ferrocene unit we performed different reactions under microwave irradiation using **4** as aldehydic component. Each reaction was carried out in a closed vessel using a microwave apparatus with a single-mode cavity and equipped with temperature and pressure control devices, which allowed us to achieve high reproducibility. A 50 W microwave power was chosen as a compromise between a sufficiently high speed of heating and control of the temperature, set at 80 °C.

Initial experiments were carried out under 30 min microwave irradiation using **3** and **4** in a 1:2 molar ratio and 10 molar amount of NaOH, in order to evaluate the relative ratios of all the possible products. In solvent-free conditions the reaction was fast but not very selective affording **5b** as main product; prolonging the reaction time increased amounts of both **6b** and **2b** were observed (Table 1, entry 1).

In the presence of a polar solvent, ethanol/water 4:1 mixture or dioxane, compound **3** completely reacted giving a 1:1 mixture of **2b** and unreacted **4** (entries 2 and 3); the use of an excess of aldehyde (entry 4), reported to enhance the formation of the dienonylferrocene derivative [31,36], resulted in a comparable composition of the final reaction mixture.

According the mechanism previously proposed [26], the first product of Claisen–Schmidt condensation between **3** and **4** is the 1-acetyl-1′-(β-ferrocenylacryloyl)ferrocene **5b**, which can further react to afford the 1,1′-diacryloylderivative **6b** (path a) or undergo an intramolecular Michael addition leading to the formation of the interannular bridge of **2b** (path b). Also compound **6b** could contribute to the formation of the ferrocenophane system via an alkali-catalyzed retro-aldol reaction and subsequent intramolecular Michael addition [32] (Scheme 1).

Table 1
Claisen–Schmidt condensation of **3** and **4**[a]



3 **4**

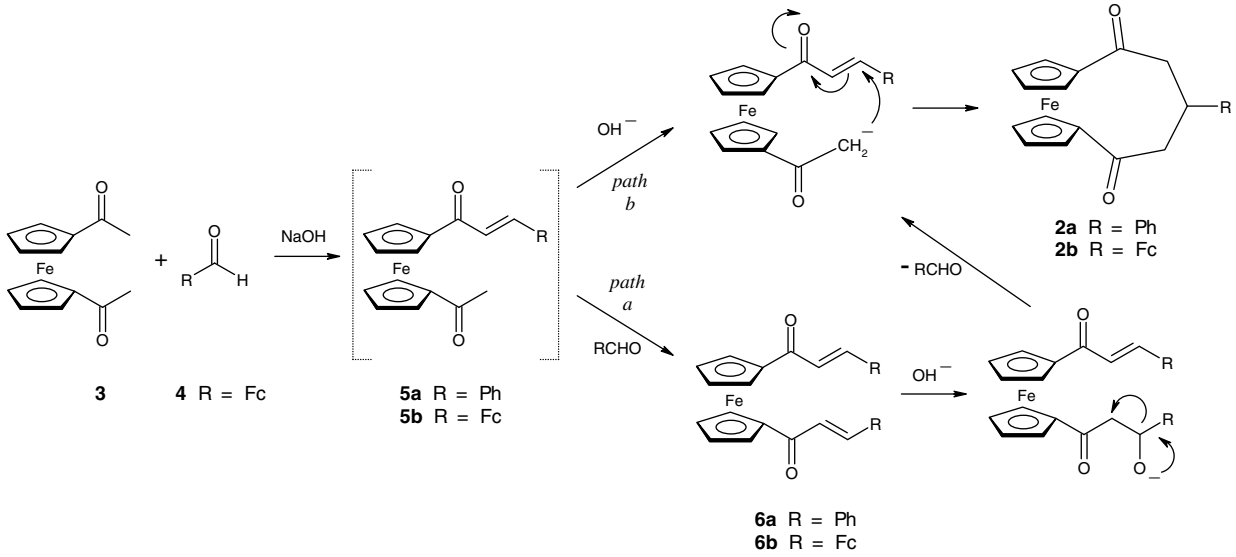
Entry	Solvent	**3**:**4** mol. ratio	Reaction mixture composition[b]			
			3 (%)	**2b** (%)	**5b** (%)	**6b** (%)
1	–	1:2	24	24	38	14
			5[c]	44	25	26
2	Dioxane	1:2	4	84	nd[d]	12
3	EtOH/water	1:2	2	88	5	5
4	EtOH/water	1:4	8	78	7	7
5	–	1:1	51	15	30	4
6	Dioxane	1:1	15	79	3	3
7	EtOH/water	1:1	6	88	nd	6
8	EtOH/water	1:1[e]	64[c]	30	6	nd
			5[f]	95	nd	nd
9	EtOH/water	1:1[g]	13	76	7	4
10	EtOH/water	1:1[h]	68	16	14	2

[a] Conditions: compound **3** (0.2 mmol), NaOH (2 mmol), solvent (2 mL), 80 °C, 50 W Mw power, 30 min reaction time.
[b] Determined by ^{1}H NMR analysis of the crude reaction mixture.
[c] One hour of reaction time.
[d] Not detected.
[e] Conventional heating 80 °C.
[f] Twenty four hours of reaction time.
[g] Compound **3**:NaOH 1:4 molar ratio.
[h] K_2CO_3 was used as base.

Taking into account this mechanism, in the presence of polar solvent and microwave irradiation the path a leading to the formation of **6b** appeared quite limited, independently from the stoichiometry of the reacting aldehyde, so that **5b** selectively evolved to **2b**. A fast conversion of **6b** into **2b** was ruled out, since parallel runs carried out by treatment of separate **5b** and **6b** with ethanolic NaOH without aldehyde for 30 min under Mw irradiation afforded **2b** in 60% and 25% yield, respectively.

The use of equimolar mixture of **3** and **4** resulted in lower substrate conversion in the solvent-free reaction (entry 5), while almost quantitative formation of **2b** was observed in polar solvents (entries 6–7). For the sake of comparison, a parallel run was carried out using conventional heating at 80 °C and a consistent reduction in the reaction rate was observed (entry 8). Satisfactory values of conversion and yield of **2b** were also obtained using a decreased amount of NaOH (entry 9), but not in the presence of K_2CO_3 as base (entry 10).

Ferrocenophane **2b** was found highly insoluble in common organic solvents and sparingly soluble in CH_2Cl_2 (about 2 mg/mL) and attempts to purify it by chromatography led to severe decrease in the final yields. As a simple protocol for the isolation of **2b**, the reaction mixture was



Scheme 1. Mechanism of formation of [5]ferrocenophane system by Claisen–Schmidt condensation of 1,1′-diacetylferrocene with aldehydes.

partitioned between water and a sufficient volume of CH_2Cl_2, the organic phase taken to dryness and the residue twice washed with hexane:AcOEt 1:1 (v/v) affording **2b** as gold-yellow solid. A preparative run on 2 mmol scale, performed in open vessel applying conditions of entry 7 and the above purification method, gave **2b** in 75% isolated yield (Table 2, entry 2) and 95% purity, the impurity mainly due to **6b** which showed similar solubility property.

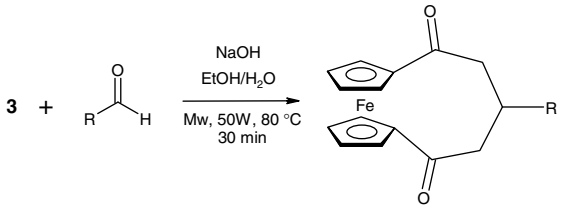
This purification procedure gave a good compromise between the isolated yield and chemical purity of **2b**, which could be used in this form as a substrate for further modification; pure **2b** samples for its characterization were obtained repeating the washing procedure more times or by crystallization from CH_2Cl_2.

The ^{1}H NMR spectrum of **2b** displayed four separate resonances, each accounting for two protons on the bridged Cp rings, two partially overlapped double doublets for H_a and H_b in the methylene groups and a broad triplet for the methinic proton on the bridge so that an asymmetric conformation of the molecule could be inferred [31]. The ferrocenyl substituent at the 3-position appeared conformationally unfixed giving rise to two singlets in a 4:5 ratio.

Our standard conditions were then applied to the Claisen–Schmidt condensation between **3** and different non-enolizable aldehydes as reported in Table 2. The reaction works well with aromatic and heteroaromatic aldehydes giving high yields of 1,5-dioxo-3-substituted [5]ferrocenophanes as sole products (the α,β-ferrocenylenone derivatives not being detected in the reaction mixture) and no obvious relationship between the electronic and/or steric properties of aldehydes and their reactivity was evidenced. Although *p*-NMe_2-benzaldehyde resulted to be less reactive, the obtained 40% isolated yield of **2d** is comparable with the results obtained in the synthesis of the *N*-diethyl analogue using a fourfold excess of aldehyde and 18 h reaction time [30].

All compounds **2a** and **2c–l** could be purified exploiting their low solubility in hexane:AcOEt as above described for **2b** and fully characterized. As a common feature in their

Table 2
Microwave-assisted synthesis of 1,5-dioxo-3-substituted[5]ferrocenophanes[a]



Entry	R	Compound	Conversion (%)[b]	% Isolated yield of **2**[c] (% purity[d])
1	Ph	**2a**	74	63 (94)
2	Fc	**2b**	93[e]	75 (95)
3	*p*-Cl–Ph	**2c**	87	78 (95)
4	*p*-NMe_2–Ph	**2d**	50[f]	40 (93)
5	*p*-Me–Ph	**2e**	94	80 (95)
6	*o*-Me–Ph	**2f**	92	78 (95)
7	β-Naphtyl	**2g**	77	69 (94)
8	$C(CH_3)_3$	**2h**	64	52 (92)
9	4-Pyr	**2i**	73	61 (93)
10	2-Quinoline	**2l**	94	82 (95)

[a] Compound **3** (2 mmol), aldehyde (2 mmol), NaOH (10 mmol), EtOH/H_2O 4:1 (20 mL), 80 °C, 50 W Mw power, 30 min.
[b] Determined by ^{1}H NMR analysis of an aliquot of the crude reaction mixture.
[c] Referred to the starting diketone **3**.
[d] After two washing cycles with *n*-hexane:AcOEt (see Section 3).
[e] The α,β-unsaturated ferrocenylketone **6b** was present in the reaction mixture (7%).
[f] One hour of reaction time.

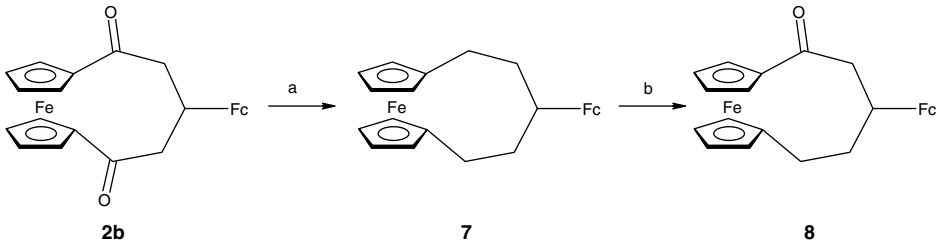


Fig. 2. Chemical modification of the keto-group of ferrocenophane.

^{1}H NMR spectrum the methylenic protons were observed as a well separated (about 0.4 ppm) triplet and broad doublet, substantially unchanged upon heating up to 80 °C.

The keto-group modification of 1,5-dioxo-[5]ferrocenophanes and the peculiar chemistry of ferrocenes (e.g. the nucleophilic substitution of an α-acetoxy group and the diastereoselective ring metalation/electrophilic quenching sequence, both occurring with stereochemical control [37]) could give access to a large number of derivatives with [5]ferrocenophane skeleton, many of them with defined chirality.

A simple deoxygenation–oxygenation sequence can be applied to convert 1,5-dioxo-[5]ferrocenophanes into the related derivatives possessing only one carbonyl group; indeed, the treatment of **2b** with BH_3/Me_2S in CH_2Cl_2 [38] gave the alkane derivative **7**, which was in turn reacted with MnO_2 to afford monoketone **8** (Fig. 2).

Due to the asymmetry of the molecule, the ^{1}H NMR spectrum of **8** showed a separate resonance for each proton on the bridge and the analysis of the coupling constants evidenced a *trans*-diaxial relationship between the methinic proton and two adjacent protons on C-2 and C-4 positions of the bridge ($J_{H3–H2a} = 12.5$ Hz and $J_{H3–H4a} = 9.8$ Hz), so that an equatorial disposition of the 3-substituent can be deduced.

3. Experimental

3.1. General

All the aldehydes and 1,1′-diacetylferrocene were commercially available and used as received. Microprills sodium hydroxide was purchased from Riedel–de-Haën. Microwave irradiation was performed in a CEM Discover Benchmate equipped with a pressure control device. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise stated, at 400.13 and 100.62 MHz, respectively. Chemical shifts (δ) are given as ppm relative to the residual solvent peak and coupling constants (J) are in Hz. In the assignment of the NMR signals, CpH refers to cyclopentadienyl protons or carbons whereas Cp refers to the quaternary carbon on the metallocene ring. ESI-MS spectra were acquired on a Waters Micromass ZQ2000 instrument using 3.75 kV capillary voltage and 50 V cone voltage. Melting points are uncorrected.

3.1.1. Optimizazion of the reaction conditions for the synthesis of *2b*

To a solution of **3** (54 mg, 0.2 mmol) in EtOH/H_2O (4:1 v/v 2 mL), aldehyde **4** in appropriate amount (see Table 1) and NaOH (80 mg, 2 mmol) were added. The reaction was carried out in a closed vessel using 50 W microwave power and temperature set at 80°C. After 30 min the reaction mixture was diluted with satd. NH_4Cl (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was washed with brine, dried over Na_2SO_4 and an aliquot analyzed by ^{1}H NMR to determine the composition of the whole crude reaction mixture.

3.2. General procedure for the synthesis of 1,5-dioxo-3-substituted [5]ferrocenophanes

To a solution of **3** (540 mg, 2.0 mmol) in EtOH/H_2O (4:1 v/v 20 mL), aldehyde (2.0 mmol) and NaOH (800 mg, 20.0 mmol) were added. The reaction was carried out in a 100 mL open vessel equipped with a reflux condenser using 50 W microwave power and temperature set at 80 °C. After 30 min the reaction mixture was diluted with satd. NH_4Cl (50 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was washed with brine, dried over Na_2SO_4 and, after have determined the composition of the reaction mixture as above, it was taken to dryness. The residue was suspended in *n*-hexane:EtOAc 1:1 (15 mL) and the insoluble solid separated by filtration and the solution discarded. The solid was dissolved in CH_2Cl_2, the solution taken to dryness and the residue washed again with *n*-hexane:EtOAc 1:1 (15 mL) leaving ferrocenophanes as insoluble yellow solids with 92–95% chemical purity, the main impurity being the starting **3**, and 80–90% recovery yield.

The above washing procedure was repeated on samples of **2a**–**2l** until satisfactory purity (>98%) for their NMR characterization and elemental analyses was reached.

3.2.1. 1,5-Dioxo-3-phenyl[5]ferrocenophane (*2a*)

Obtained from the reaction of **3** and benzaldehyde, compound **2a** was known [26,32] but its NMR spectra were not reported. ^{1}H NMR δ 2.51 (2H, br d, CH_{2a}), 2.95 (2H, br t, CH_{2b}), 4.35 (1H, tt, $J = 2.5$ and 11.5, CH), 4.58 (2H, m, CpH), 4.62 (2H, m, CpH), 4.89 (4H, m, CpH), 7.28 (2H,

m, Ar-H), 7.37 (3H, m, Ar-H); ^{13}C NMR δ 45.6 (CH), 47.3 (CH_2), 69.8 (CpH), 72.2 (CpH), 73.9 (CpH), 74.7 (CpH), 83.3 (Cp), 126.8 (Ar-CH), 127.0 (Ar-CH), 128.9 (Ar-CH), 145.1 (Ar-C), 202.4 (CO).

*3.2.2. 1,5-Dioxo-3-ferrocenyl[5]ferrocenophane (**2b**)*

From the reaction of **3** and ferrocenylcarboxaldehyde, m.p. 302–303 (dec), ^{1}H NMR δ 2.72 (4H, two overlapped AB systems, CH_2), 4.08 (1H, m, CH), 4.15 (4H, br s, CpH), 4.21 (5H, s, unsubstd. CpH), 4.55 (2H, br s, CpH), 4.60 (2H, br s, CpH), 4.83 (2H, br s, CpH), 4.87 (2H, br s, CpH), ^{13}C NMR δ 41.0 (CH), 46.7 (CH_2), 66.6 (CpH), 67.5 (CpH), 68.8 (unsubstd. CpH), 71.7 (CpH), 73.5 (CpH), 74.3 (CpH), 77.2 (CpH), 81.8 (Cp), 93.8 (Cp), 198.7 (CO); ESI-MS: 489 $(M \cdot Na)^+$. Anal Calc. for $C_{25}H_{22}Fe_2O_2$: C, 64.42; H, 4.76. Found: C, 64.38; H, 4.73%.

*3.2.3. 1,5-Dioxo-3-(p-chlorophenyl)[5]ferrocenophane (**2c**)*

From **3** and *p*-chlorobenzaldehyde, m.p. 311–312 (dec) ^{1}H NMR δ 2.48 (2H, br d, CH_{2a}), 2.90 (2H, br t, CH_{2b}), 4.32 (1H, br t, CH), 4.59 (2H, s, CpH), 4.62 (2H, s, CpH), 4.88 (4H, s, CpH), 7.33 (4H, m, Ar-H); ^{13}C NMR (CD_2Cl_2) δ 45.6 (CH), 46.5 (CH_2), 69.4 (CpH), 72.2 (CpH), 74.1 (CpH), 74.8 (CpH), 82.2 (Cp), 128.6 (Ar-CH), 129.1 (Ar-CH), 132.6 (Ar-C), 144.2 (Ar-C), 198.1 (CO). ESI-MS: 414.8 $(M \cdot Na)^+$ and 416.8 $(M \cdot Na)^+$. Anal Calc. for $C_{21}H_{17}ClFeO_2$: C, 64.24; H, 4.36. Found: C, 64.18; H, 4.34%.

*3.2.4. 1,5-Dioxo-3-(p-dimethylaminophenyl)[5]ferrocenophane (**2d**)*

From **3** and *p*-dimethylaminobenzaldehyde, m.p. 254–255 (dec) ^{1}H NMR δ 2.50 (2H, br d, CH_{2a}), 2.91 (2H, br t, CH_{2b}), 2.95 (6H, s, N-CH_3), 4.26 (1H, br t, CH), 4.56 (2H, br s, CpH), 4.60 (2H, br s, CpH), 4.87 (2H, br s, CpH), 4.89 (2H, br s, CpH), 6.74 (2H, d, $J = 8.6$, Ar-H), 7.24 (2H, d, $J = 8.6$, Ar-H); ^{13}C NMR δ 40.7 (N-CH_3), 45.0 (CH), 46.9 (CH_2), 69.5 (CpH), 71.6 (CpH), 73.9 (CpH), 74.3 (CpH), 81.9 (Cp), 112.9 (Ar-CH), 127.3 (Ar-CH), 133.1 (Ar-C), 149.5 (Ar-C), 198.6 (CO). ESI-MS: 423.9 $(M \cdot Na)^+$. Anal Calc. for $C_{23}H_{23}FeNO_2$: C, 68.84; H, 5.78; N, 3.49. Found: C, 68.80; H, 5.77; N, 3.47%.

*3.2.5. 1,5-Dioxo-3-(p-methylphenyl)[5]ferrocenophane (**2e**)*

From **3** and *p*-tolualdehyde, m.p. 284–285 (dec), ^{1}H NMR δ 2.35 (3H, s, CH_3), 2.48 (2H, br d, CH_{2a}), 2.93 (2H, t, $J = 12.3$, CH_{2b}), 4.32 (1H, br t, CH), 4.57 (2H, m, CpH), 4.62 (2H, m, CpH), 4.87 (2H, s, CpH), 4.89 (2H, s, CpH), 7.17 (2H, d, $J = 7.7$, Ar-H), 7.26 (2H, d, $J = 7.7$, Ar-H); ^{13}C NMR δ 21.0 (CH_3), 45.5 (CH), 46.5 (CH_2), 69.4 (CpH), 71.6 (CpH), 73.5 (CpH), 74.4 (CpH), 81.8 (Cp), 126.6 (Ar-CH), 129.4 (Ar-CH), 136.4 (Ar-C), 142.1 (Ar-C), 198.4 (CO). ESI-MS: 394.9 $(M \cdot Na)^+$. Anal Calc. for $C_{22}H_{20}FeO_2$: C, 70.99; H, 5.42. Found: C, 70.89; H, 5.39%.

*3.2.6. 1,5-Dioxo-3-(o-methylphenyl)[5]ferrocenophane (**2f**)*

From **3** and *o*-tolualdehyde, m.p. 275–276 (dec), ^{1}H NMR δ 2.41 (2H, br d, CH_{2a}), 2.56 (3H, s, CH_3), 2.93 (2H, br t, CH_{2b}), 4.56 (3H, m, CH and CpH), 4.62 (2H, m, CpH), 4.90 (4H, br s, CpH), 7.22 (5H, m, Ar-H); ^{13}C NMR δ 19.3 (CH_3), 41.8 (CH), 45.8 (CH_2), 69.2 (CpH), 71.8 (CpH), 73.5 (CpH), 74.3 (CpH), 82.1 (Cp), 125.2 (Ar-CH), 126.2 (Ar-CH), 126.6 (Ar-CH), 131.0 (Ar-CH), 135.3 (Ar-C), 143.2 (Ar-C), 198.5 (CO). ESI-MS: 394.8 $(M \cdot Na)^+$. Anal Calc. for $C_{22}H_{20}FeO_2$: C, 70.99; H, 5.42. Found: C, 70.91; H, 5.41%.

*3.2.7. 1,5-Dioxo-3-(β-naphthyl)[5]ferrocenophane (**2g**)*

From **3** and β-naphthylaldehyde, m.p. 290–291 (dec), ^{1}H NMR δ 2.61 (2H, br d, CH_{2a}), 3.05 (2H, br t, CH_{2b}), 4.51 (1H, br t, CH), 4.59 (2H, s, CpH), 4.63 (2H, s, CpH), 4.91 (2H, s, CpH), 4.94 (2H, s, CpH), 7.49 (3H, m, Ar-H), 7.79 (1H, s, Ar-H), 7.85 (3H, m, Ar-H); ^{13}C NMR (CD_2Cl_2) δ 46.3 (CH), 46.8 (CH_2), 69.4 (CpH), 72.1 (CpH), 74.0 (CpH), 74.7 (CpH), 82.3 (Cp), 125.0 (Ar-CH), 126.0 (Ar-CH), 126.5 (Ar-CH), 127.9 (Ar-CH), 128.7 (Ar-CH), 132.8 (Ar-C), 134.0 (Ar-C), 143.2 (Ar-C), 198.4 (CO). ESI-MS: 430.8 $(M \cdot Na)^+$. Anal Calc. for $C_{25}H_{20}FeNO_2$: C, 73.55; H, 4.94. Found: C, 73.39; H, 4.91%.

*3.2.8. 1,5-Dioxo-3-(tert-butyl)[5]ferrocenophane (**2h**)*

From **3** and pivalaldehyde, m.p. 309–310 (dec), ^{1}H NMR δ 1.03 (9H, s, CH_3), 2.44 (4H, br d, CH_2), 2.85 (1H, br t, CH), 4.52 (2H, s, CpH), 4.56 (2H, s, CpH), 4.80 (4H, s, CpH); ^{13}C NMR δ 28.0 (CH_3), 33.5 (C), 41.7 (CH_2), 50.0 (CH), 69.9 (CpH), 71.9 (CpH), 73.6 (CpH), 74.4 (CpH), 82.5 (Cp), 200.0 (CO). ESI-MS: 360.6 $(M \cdot Na)^+$. Anal Calc. for $C_{19}H_{22}FeO_2$: C, 67.47; H, 6.56. Found: C, 67.38; H, 6.52%.

*3.2.9. 1,5-Dioxo-3-(4-pyridyl)[5]ferrocenophane (**2i**)*

From **3** and 4-pyridinecarboxaldehyde, m.p. 265–266 (dec), ^{1}H NMR δ 2.51 (2H, br d, CH_{2a}), 2.91 (2H, br t, CH^{2b}), 4.32 (1H, br t, CH), 4.60 (2H, s; CpH), 4.64 (2H, s, CpH), 4.89 (4H, s, CpH), 7.31 (2H, d, $J = 4.0$, Ar-H), 8.60 (2H, d, $J = 4.0$, Ar-H); ^{13}C NMR ($CDCl_3$/CD3OD) δ 44.7 (CH), 45.1 (CH_2), 69.1 (CpH), 72.0 (CpH), 74.1 (CpH), 74.9 (CpH), 81.3 (Cp), 122.5 (Ar-CH), 149.4 (Ar-CH), 154.2 (Ar-C), 198.3 (CO). ESI-MS: 381.8 $(M \cdot Na)^+$. Anal Calc. for $C_{20}H_{17}FeNO_2$: C, 66.87; H, 4.77; N, 3.90. Found: C, 66.80; H, 4.74; N, 3.88%.

*3.2.10. 1,5-Dioxo-3-(2-quinolyl)[5]ferrocenophane (**2l**)*

From **3** and 2-quinolylcarboxaldehyde, m.p. 282–283 (dec), ^{1}H NMR δ 2.65 (2H, br d, CH_{2a}), 3.25 (2H, t, $J = 12.5$, CH_{2b}), 4.61 (5H, m, CH and CpH) 4.91 (2H, s, CpH), 5.04 (2H, s, CpH), 7.53 (2H, m, Ar-H), 7.25 (1H, m, Ar-H), 7.82 (1H, d, $J = 8.2$, Ar-H), 8.08 (1H, d, $J = 8.4$, Ar-H), 8.15 (1H, d, $J = 8.4$, Ar-H); ^{13}C NMR δ 44.7 (CH), 48.3 (CH_2), 69.1 (CpH), 72.2 (CpH), 73.5 (CpH), 74.3 (CpH), 82.1 (Cp), 120.8 (Ar-CH), 126.1 (Ar-CH), 127.1

(Ar-C), 127.6 (Ar-CH), 129.0 (Ar-CH), 129.4 (Ar-CH), 136.8 (Ar-CH), 147.8 (Ar-C), 153.6 (Ar-C), 199.0 (CO). ESI-MS: 431.8 $(M \cdot Na)^+$. Anal Calc. for $C_{24}H_{19}FeNO_2$: C, 70.43; H, 4.68; N, 3.42. Found: C, 70.35; H, 4.65; N, 3.40%.

3.3. Synthesis of 3-ferrocenyl[5]ferrocenophane (7)

To a solution of **2b** (50 mg, 0.11 mmol) in CH_2Cl_2 (25 mL) was added BH_3/Me_2S (2 M in THF, 0.15 mL) and the reaction was stirred at room temperature for 5 h. As soon as the quantitative conversion of the substrate was observed by TLC analysis (CH_2Cl_2/AcOEt 9:1), the reaction was quenched by addition of MeOH, diluted with satd. NH_4Cl (30 mL) and extracted with CH_2Cl_2 (3×10 mL). The organic layer was washed with brine, dried over Na_2SO_4 and taken to dryness under vacuum to give a residue which was applied to Si gel column (*n*-hexane:AcOEt). Pure **7** (42 mg, 89% yield) was obtained as a yellow solid, m.p. 140–141, ^{1}H NMR δ 1.93 (2H, m), 2.17 (2H, dddd, $J = 3.8$, 3.8, 10.1 and 14.3), 2.29 (2H, ddd, $J = 3.8$, 6.5 and 15.8) 2.49 (2H, ddd, $J = 3.8$, 10.1 and 15.8), 3.55 (1H, m), 4.02 (2H, m), 4.05 (2H, m), 4.07 (2H, m), 4.13 (2H, d, $J = 1.6$), 4.15 (2H, d, $J = 1.6$), 4.18 (2H, m), 4.20 (5H, s); ^{13}C NMR δ 24.2 (CH_2), 31.9 (CH_2), 34.55 (CH), 66.5 (CH), 66.6 (CH), 66.9 (CH), 67.2 (CH), 67.9 (CH), 68.4 (CH, Cp′), 68.8 (CH), 89.8 (C), 96.5 (C). ESI-MS: 474.7 $(M \cdot Na)^+$. Anal. Calc. for $C_{25}H_{26}Fe_2$: C, 68.53; H, 5.98. Found: C, 68.48; H, 5.96%.

3.4. Synthesis of 1-oxo-3-ferrocenyl[5]ferrocenophane (8)

Compound **7** (40 mg, 0.09 mmol) was dissolved in CH_2Cl_2 (5 mL) and 100 mg of MnO_2 were added. The suspension was maintained under stirring at room temperature overnight. After removal of the black powder by filtration on Celite, the solution was taken to dryness and the residue purified by column chromatography (Si gel, *n*-hexane:AcOEt 9:1) to give **8** as orange solid (35 mg, 85% yield), R_f 0.2 (*n*-hexane:AcOEt 9:1), m.p. 195–196, ^{1}H NMR δ 1.82 (1H, dddd, $J = 3.0$, 5.8, 9.8 and 14.3), 2.19 (1H, dddd, $J = 3.4$, 3.4, 11.5 and 14.3), 2.38 (1H, ddd, $J = 3.5$, 5.8 and 17.1) 2.59 (1H, ddd, $J = 3.0$, 11.5 and 17.1), 2.80 (1H, dd, $J = 12.5$ and 13.3), 2.96 (1H, dd, $J = 2.0$ and 13.3), 3.78 (1H, m), 4.10 (1H, br s), 4.11(1H, br s), 4.15 (4H, br s), 4.18 (1H, br s), 4.20 (6H, s), 4.53 (1H, br s), 4.63 (1H, br s), 4.76 (1H, br s), 4.82 (1H, br s); ^{13}C NMR δ 22.3 (CH_2), 33.5 (CH_2), 35.9 (CH), 48.1 (CH_2), 66.0 (CH), 66.6 (CH), 67.2 (CH), 67.3 (CH), 68.0 (CH), 68.5 (CH, Cp′), 68.8 (CH), 68.9 (CH), 69.5 (CH), 70.0 (CH), 70.7 (CH), 72.4 (CH), 73.5 (CH), 79.9 (C), 88.5 (C), 95.5 (C), 203.1 (CO). ESI-MS: 437.8 $(M)^+$. Anal Calc. for $C_{25}H_{24}Fe_2O$: C, 66.41; H, 5.35. Found: C, 66.34; H, 5.34%.

4. Conclusion

We have shown that under microwave irradiation the one-pot Claisen–Schmidt reaction between 1,1′-diacetylferrocene and aldehydes is faster and more selective with respect to other reported methods in producing 1,5-dioxo-3-substituted[5]ferrocenophanes. The availability of functionalized aldehydes and the subsequent modifications of the keto-groups of the products can give access to a large variety of [5]ferrocenophanes, some of which have been here synthesized and characterized for the first time. Further study on the related chiral ferrocenophanes and their potential application in homogeneous catalysis field are in progress.

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