

Short Communication

# A convenient synthesis of *E*-alkenylferrocenes

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## Abstract

Alkenylferrocenes,  $\text{FcCHCHR}$  [ $\text{R} = (\text{CH}_2)_n\text{CH}_3$ ,  $n = 0-4$ ], and 1,1'-bisalkenylferrocenes,  $\text{Fc}(\text{CHCHR})_2$  ( $\text{R} = \text{CH}_3$ ,  $\text{CH}_2\text{CH}_3$ ) were synthesized by elimination reaction from the corresponding  $\alpha$ -hydroxyferrocenylalkanes using methanesulfonylchloride and triethylamine. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The reactivity and chemical properties of ferrocene derivatives have been widely explored [1]. The ongoing interest in ferrocene chemistry stems from their increasing use and application in the fields of organic synthesis, catalysis, and material science [2]. The ferrocenyl ligands represent one of the most important classes among the different types of chiral ligands used in asymmetric homogenous catalysis [3] and they find application in a variety of transition-metal catalyzed reactions.  $\alpha$ -Ferrocenylalkylamines are by far the most common chiral ferrocene starting materials [4]. The stereoselective formation of  $\alpha$ -chiral ferrocenyl carbocations without loss of chiral information offers the possibility to introduce a variety of hetero atom functionality at this stereogenic center [5]. With this in mind, we started to investigate methods for the synthesis of new, centrally chiral ferrocenyl diols, which can serve as precursors for new chiral ligands [6].

Application of Sharpless' asymmetric dihydroxylation reaction for this purpose requires isomerically pure

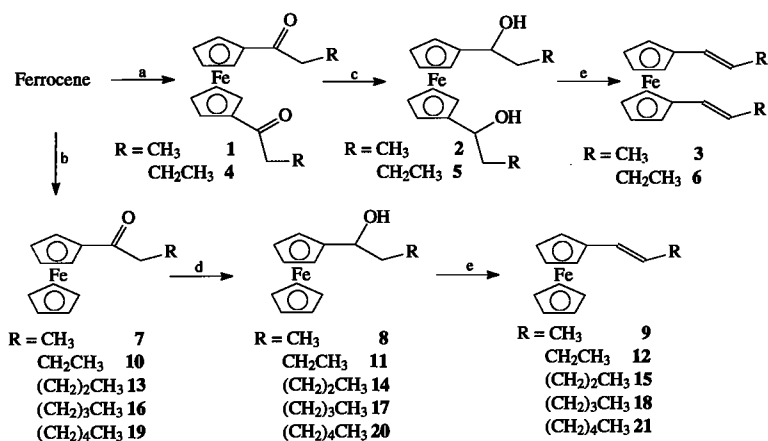
alkenylferrocenes as starting materials. However, although there are several methods known for the formation of vinyl- or propenylferrocene, derivatives with longer alkenyl chains are hardly known in literature. The same holds for their precursors, namely, the respective alkanoyl- and hydroxyferrocenes. For the few derivatives described in the literature so far, almost no NMR data have been reported.

## 2. Results and discussion

The Friedel–Crafts [7] acylation of ferrocene is one of the most important methods to prepare alkanoylferrocenes. The high reactivity of these carbonyl compounds towards electrophilic substitution [8] makes them the most often used prochiral starting materials in ferrocene chemistry. A standard procedure for this reaction is the use of acid chlorides and aluminum chloride [9]. Unfortunately, in our hands under these conditions, we obtained exclusively diacylation (**1**, **4**) instead of monoacylation. However, employment of the respective acid anhydride and boron trifluoride etherate in dichloromethane [10,11] produced the desired products (**7**, **10** [12]; **13** [13]; **16** [12], **19**) in good to excellent yields.

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(a) 3 equiv of AlCl<sub>3</sub> and acid chloride, CH<sub>2</sub>Cl<sub>2</sub>, 0°C→r.t.; (b) 2 equiv acid anhydride, boron trifluoride etherate 99%, CH<sub>2</sub>Cl<sub>2</sub>, 0°C→r.t.; (c) 2.4 equiv LAH, Et<sub>2</sub>O, 0°C→r.t.; (d) 1.2 equiv LAH, Et<sub>2</sub>O, 0°C→r.t.; (e) CH<sub>2</sub>Cl<sub>2</sub>: triethylamine 2:1, 1.5 equiv methylsulfonyl chloride, 0°C→r.t..

Recently, an electrochemical acylation of ferrocene was reported by the in situ generation of the acylating agent and the catalyst [14]. Under these conditions, compounds **7**, **10**, and **13** were obtained. The same authors also presented a Friedel–Crafts acylation procedure with PCl<sub>3</sub> and AlCl<sub>3</sub> for the formation of compounds **1**, **4**, **7**, **10**, and **16**, but unfortunately no spectral data were reported [15].

All diols (**2**, **5**, **8**, **11**, **14**, **17**, and **20**) were prepared by the reduction of the corresponding ketones with LAH in diethylether using a standard procedure [10,16].

The synthesis of propenylferrocene has been reported several times, but only once both isomers were obtained in pure state, employing modifications of the Wittig reaction [17]. Under the standard Wittig reaction conditions with alkyltriphenylphosphoranes [18], *E/Z* ratios of about 3:1 for the alkenylferrocenes **9**, **12**, and **15** were reported.

An alternative method for the synthesis of alkenylferrocenes, is the dehydration of the corresponding alcohols with neutral alumina yielding about 90% d.e. of the *E* isomer in the case of **9**, but the reported yields of about 50% are not convincing for the preparation of a starting material [9]. Changing to acidic alumina improves this yield to 60–80% [19]. Another attempt was reported using Fe<sub>2</sub>(CO)<sub>9</sub> as a dehydration reagent with a similar yield for **9** [20].

As we were interested in a method which is simple and produces reliably just the *E* isomer, we decided to attempt the elimination of the secondary alcohol via reaction with methanesulfonyl chloride and triethylamine [21]. By this reaction, we obtained exclusively the *E* isomers in good yields for the cases of **6**, **12**, **15**, **18**, and **21**. Only for the propenyl compounds **3** and **9**, both isomers were formed under these conditions as inseparable mixtures.

### 3. Experimental

The melting points were recorded on a Tottoli apparatus (Büchi) and are uncorrected. NMR spectra were recorded on Bruker MSL 300, or Varian Gemini 200 spectrometers. *J*-values are reported in Hz. All NMR spectra were recorded in CDCl<sub>3</sub>. Flash chromatography was performed on silica gel 60 (0.040–0.063 mm, Merck). Mixtures of cyclohexane and ethyl acetate were used as eluents. Reagents were obtained from commercial sources and used as received. Dichloromethane was distilled from P<sub>2</sub>O<sub>5</sub>, Et<sub>2</sub>O from CaH<sub>2</sub> and Et<sub>3</sub>N from KOH prior to use.

#### 3.1. Synthesis of bisalkanoylferrocenes **1** and **4**

Ferrocene (5.0 g, 27 mmol) and AlCl<sub>3</sub> 98% (11.0 g, 83 mmol) were suspended in 70 ml CH<sub>2</sub>Cl<sub>2</sub> and cooled to 0°C. The respective acid chloride (three equivalents) was added dropwise over 10 min and the reaction was stirred at room temperature (r.t.) for additional 2 h until complete conversion was achieved. The mixture was poured on ice water and the layers were separated. The organic layer was washed with a saturated NaHCO<sub>3</sub> solution and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo and the pure product was obtained after flash chromatography.

##### 3.1.1. 1,1'-Bis(hydroxypropanoyl)ferrocene (**1**)

A red–brown oil was obtained in 98% yield. <sup>1</sup>H-NMR (200 MHz, δ ppm): 1.16 (t, *J* = 7.3 Hz, 6H, 2CH<sub>3</sub>); 2.66 (q, *J* = 7.3 Hz, 4H, 2CH<sub>2</sub>); 4.45 (t, *J* = 1.9 Hz, 4H, Fc); 4.75 (t, *J* = 1.9 Hz, 4H, Fc). <sup>13</sup>C-NMR (50 MHz, δ ppm): 8.2, 33.1, 70.5, 73.3, 80.3, 204.1. HRMS; Found: 298.06561; Calc. for C<sub>16</sub>H<sub>18</sub>O<sub>2</sub>Fe [M<sup>+</sup>]: 298.06559.

### 3.1.2. 1,1'-Bis(butanoyl)ferrocene (**4**)

Orange crystals (m.p.: 73–74°C, identical with Lit. [22]) were obtained in 93% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 1.00 (t,  $J = 7.5$  Hz, 6H, 2CH<sub>3</sub>); 1.72 (m, 4H, 2CH<sub>2</sub>); 2.63 (t,  $J = 7.4$  Hz, 4H, 2CH<sub>2</sub>); 4.48 (t,  $J = 1.5$  Hz, 4H, Fc); 4.77 (t,  $J = 1.9$  Hz, 4H, Fc). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.1, 17.7, 41.9, 70.6, 73.4, 80.5, 203.7. HRMS; Found: 326.0977; Calc. for C<sub>18</sub>H<sub>22</sub>O<sub>2</sub>Fe [M<sup>+</sup>]: 326.0969.

## 3.2. Synthesis of alkanoylferrocenes **7**, **10**, **13**, **16**, and **19**

Ferrocene (5.0 g, 27 mmol) and the respective acid anhydride (two equivalents) were suspended in 40 ml CH<sub>2</sub>Cl<sub>2</sub> and cooled to 0°C. Boron trifluoride etherate 99% (30 ml) was added via a syringe over 10 min and the reaction was stirred at r.t. for additional 3 h until the reaction was complete. The following work-up procedure was analogous to the one described for the bisalkanylferrocenes.

### 3.2.1. 1-Propionylferrocene (**7**)

Dark-red crystals (m.p.: 67–68°C, Lit. [9]: 30–31°C) were obtained in 98% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 1.14 (t,  $J = 7.3$  Hz, 3H, CH<sub>3</sub>); 2.68 (q,  $J = 7.5$  Hz, 2H, CH<sub>2</sub>); 4.12 (s, 5H, Fc); 4.42 (s, 2H, Fc); 4.72 (s, 2H, Fc). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 8.6, 32.8, 69.3, 69.8, 72.1, 78.9, 204.9. HRMS; Found: 242.03943; Calc. for C<sub>13</sub>H<sub>14</sub>OFe [M<sup>+</sup>]: 242.03936.

### 3.2.2. 1-Butanoylferrocene (**10**)

A dark-red oil was obtained in 98% yield. <sup>1</sup>H-NMR (300 MHz,  $\delta$  ppm): 0.96 (t,  $J = 7.4$  Hz, 3H, CH<sub>3</sub>); 1.70 (m, 2H, CH<sub>2</sub>); 2.63 (t,  $J = 7.3$  Hz, 2H, CH<sub>2</sub>); 4.14 (s, 5H, Fc); 4.43 (t,  $J = 1.8$  Hz, 2H, Fc); 4.73 (t,  $J = 1.6$  Hz, 2H, Fc). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.2, 18.0, 41.6, 69.3, 69.7, 72.1, 79.3, 204.3. HRMS; Found: 256.05511; Calc. for C<sub>14</sub>H<sub>16</sub>OFe [M<sup>+</sup>]: 256.05503.

### 3.2.3. 1-Pentanoylferrocene (**13**)

A red oil was obtained in 98% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.93 (t,  $J = 7.3$  Hz, 3H, CH<sub>3</sub>); 1.37 (m, 2H, CH<sub>2</sub>); 1.64 (m, 2H, CH<sub>2</sub>); 2.66 (t,  $J = 7.7$  Hz, 2H, CH<sub>2</sub>); 4.15 (s, 5H, Fc); 4.44 (t,  $J = 1.9$  Hz, 2H, Fc); 4.74 (t,  $J = 2.0$  Hz, 2H, Fc). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.1, 22.7, 26.8, 39.5, 69.4, 69.8, 72.1, 79.2, 204.7. HRMS; Found: 270.07071; Calc. for C<sub>15</sub>H<sub>18</sub>OFe [M<sup>+</sup>]: 270.07067.

### 3.2.4. 1-Hexanoylferrocene (**16**)

A dark-red oil was obtained in 73% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.92 (t,  $J = 6.2$  Hz, 3H, CH<sub>3</sub>); 1.35 (m, 4H, 2CH<sub>2</sub>); 1.70 (m, 2H, CH<sub>2</sub>); 2.69 (t,  $J = 7.6$  Hz, 2H, CH<sub>2</sub>); 4.18 (s, 5H, Fc); 4.33 (t,  $J = 1.9$  Hz, 2H, Fc); 4.77 (t,  $J = 2.0$  Hz, 2H, Fc). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.1, 22.6, 24.4, 31.8, 39.8, 69.4, 69.8, 72.1, 79.2,

204.8. HRMS; Found: 284.08631; Calc. for C<sub>16</sub>H<sub>20</sub>OFe [M<sup>+</sup>]: 284.08633.

### 3.2.5. 1-Heptanoylferrocene (**19**)

A brown oil was obtained in 63% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.89 (t,  $J = 6.4$  Hz, 3H, CH<sub>3</sub>); 1.32 (m, 6H, 3CH<sub>2</sub>); 1.68 (m, 2H, CH<sub>2</sub>); 2.67 (t,  $J = 7.6$  Hz, 2H, CH<sub>2</sub>); 4.17 (s, 5H, Fc); 4.46 (t,  $J = 1.8$  Hz, 2H, Fc); 4.76 (t,  $J = 1.9$  Hz, 2H, Fc). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.2, 22.6, 24.6, 29.3, 31.8, 39.8, 69.4, 69.8, 72.1, 79.2, 204.7. HRMS; Found: 298.10151; Calc. for C<sub>17</sub>H<sub>22</sub>OFe [M<sup>+</sup>]: 298.10198.

## 3.3. Synthesis of bishydroxyferrocenes **2**, **5** and hydroxyferrocenes **8**, **11**, **14**, **17**, and **20**

To an ice-cooled solution of the alkanoylferrocene in Et<sub>2</sub>O, LAH (1.2 equivalents and 2.4 equivalents for the bisalkanylferrocenes) was added in several portions. After stirring for 3 h, the reaction was complete and a saturated MgSO<sub>4</sub> solution (4 ml for each gram of LAH) was added dropwise. After filtration over Celite®, the solvent was removed in vacuo and the product was purified by flash chromatography.

### 3.3.1. 1,1'-Bis(hydroxypropyl)ferrocene (**2**)

An orange oil was obtained in a yield of 66%. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.94 (m, 6H, 2CH<sub>3</sub>); 1.10 (m, 4H, 2CH<sub>2</sub>); 1.85 (bs, 1H, OH); 2.05 (bs, H, OH); 4.11–4.43 (m, 10H, Fc, 2CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 10.0, 10.2, 32.1, 32.8, 65.5, 66.3, 66.5, 67.0, 67.4, 67.5, 67.6, 70.8, 70.5, 93.9, 94.0. HRMS; Found: 302.0971; Calc. for C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>Fe [M<sup>+</sup>]: 302.0969.

### 3.3.2. 1,1'-Bis(hydroxybutyl)ferrocene (**5**)

A brown oil was obtained in 94% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.94 (m, 6H, 2CH<sub>3</sub>); 1.29–1.70 (m, 8H, 4CH<sub>2</sub>); 1.88 (bs, 1H, OH); 2.28 (bs, H, OH); 4.12–4.27 (m, 8H, Fc); 4.45 (m, 2H, 2CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.0, 14.1, 18.9, 19.0, 41.5, 42.3, 65.4, 66.2, 66.5, 66.9, 67.5, 67.6, 69.2, 70.0, 94.0, 94.4. HRMS; Found: 330.1285; Calc. for C<sub>18</sub>H<sub>26</sub>O<sub>2</sub>Fe [M<sup>+</sup>]: 330.1282.

### 3.3.3. 1-Hydroxypropylferrocene (**8**)

Orange crystals (m.p.: 40–41°C) were obtained in 94% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.95 (t,  $J = 7.3$  Hz, 3H, CH<sub>3</sub>); 1.68 (q,  $J = 7.1$  Hz, 2H, CH<sub>2</sub>); 2.00 (bs, 1H, OH); 4.21 (m, 10H, Fc, CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 10.5, 31.0, 65.3, 67.3, 67.8, 67.9, 71.1, 94.3. HRMS; Found: 244.05508; Calc. for C<sub>13</sub>H<sub>16</sub>OFe [M<sup>+</sup>]: 244.05501.

### 3.3.4. 1-Hydroxybutylferrocene (**11**)

A brown oil was obtained in 98% yield. <sup>1</sup>H-NMR (300 MHz,  $\delta$  ppm): 0.95 (t,  $J = 7.1$  Hz, 3H, CH<sub>3</sub>); 1.45

(m, 2H, CH<sub>2</sub>); 1.64 (m, 2H, CH<sub>2</sub>); 2.13 (bs, 1H, OH); 4.18 (m, 9H, Fc); 4.34 (q, *J* = 5.0, 7.4 Hz, 1H, CH). <sup>13</sup>C-NMR (75 MHz,  $\delta$  ppm): 14.2, 19.3, 40.4, 65.4, 67.2, 67.7, 67.9, 68.4, 69.4, 94.6. HRMS; Found: 258.07066; Calc. for C<sub>14</sub>H<sub>18</sub>OFe [M<sup>+</sup>]: 258.07068.

### 3.3.5. 1-Hydroxypentylferrocene (14)

A red oil was obtained in 98% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.90 (m, 3H, CH<sub>3</sub>); 1.35 (m, 4H, 2CH<sub>2</sub>); 1.67 (m, 2H, CH<sub>2</sub>); 1.97 (bs, 1H, OH); 4.21 (m, 9H, Fc); 4.31 (m, 1H, CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.1, 22.7, 28.2, 38.0, 65.2, 67.3, 67.8, 67.9, 68.3, 69.7, 94.7. HRMS; Found: 272.08630; Calc. for C<sub>15</sub>H<sub>20</sub>OFe [M<sup>+</sup>]: 272.08632.

### 3.3.6. 1-Hydroxyhexylferrocene (17)

A brown solid (m.p.: 92–93°C) was obtained in 85% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.89 (m, 3H, CH<sub>3</sub>); 1.31 (m, 6H, 3CH<sub>2</sub>); 1.64 (m, 2H, CH<sub>2</sub>); 1.96 (d, *J* = 3.4 Hz, 1H, OH); 4.22 (m, 9H, Fc); 4.32 (m, 1H, CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.1, 22.7, 25.8, 31.9, 38.2, 65.2, 67.3, 67.8, 67.9, 68.3, 69.7, 94.7. HRMS; Found: 286.10198; Calc. for C<sub>16</sub>H<sub>22</sub>OFe [M<sup>+</sup>]: 286.10198.

### 3.3.7. 1-Hydroxyheptylferrocene (20)

A brown oil was obtained in 80% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.88 (m, 3H, CH<sub>3</sub>); 1.28 (m, 8H, 4CH<sub>2</sub>); 1.64 (m, 2H, CH<sub>2</sub>); 1.94 (d, *J* = 2.3 Hz, 1H, OH); 4.21 (m, 9H, Fc); 4.29 (m, 1H, CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.2, 22.7, 26.0, 29.3, 31.9, 38.3, 65.2, 67.3, 67.7, 68.3, 94.7. HRMS; Found: 300.11727; Calc. for C<sub>17</sub>H<sub>24</sub>OFe [M<sup>+</sup>]: 300.11763.

## 3.4. Synthesis of bisalkenylferrocenes 3, 4 and alkenylferrocenes 9, 12, 15, 18, and 21

The hydroxyalkylferrocenes were dissolved in a 2:1 mixture of CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>3</sub>N and cooled to 0°C. After dropwise addition of methylsulfonyl chloride (1.5 equivalents), the solution was refluxed. The reaction was complete within 3 h and cooled to r.t. The solution was poured on ice cold 5% HCl and the layers were separated. The organic layer was washed with saturated NaHCO<sub>3</sub> and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuo and the pure product was obtained after flash chromatography.

### 3.4.1. (E,E')-1,1'-Diprop-1-enylferrocene (3)

An inseparable mixture (dark-brown oil) of the (E,E), (Z,Z), and (E,Z) isomers in a ratio of 3:1:1 (determined by <sup>1</sup>H-NMR from the crude product) was obtained in 66% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.97 (t, *J* = 7.3 Hz, 6H, 2CH<sub>3</sub>); 1.77 (m, 4H, 2CH<sub>2</sub>); 4.13 (m, 4H, Fc); 4.17 (m, 4H, Fc); 5.84 (dt, *J* = 6.3,

15.7 Hz, 1H, CH); 6.03 (dd, *J* = 1.3, 15.6 Hz, H, Fc-CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 18.6, 67.3, 69.1, 85.0, 122.9, 127.4. HRMS; Found: 266.07598; Calc. for C<sub>16</sub>H<sub>18</sub>Fe [M<sup>+</sup>]: 266.07576.

### 3.4.2. (E,E')-1,1'-Dibut-1-enylferrocene (6)

A brown oil was obtained in 67% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 1.07 (t, *J* = 7.5 Hz, 6H, 2CH<sub>3</sub>); 2.11 (dq, *J* = 1.2, 7.5 Hz, 4H, 2CH<sub>2</sub>); 4.11 (t, *J* = 1.9 Hz, 4H, Fc); 4.19 (t, *J* = 1.7 Hz, 4H, Fc); 5.84 (dt, *J* = 6.2, 15.7 Hz, 1H, CH); 6.03 (d, *J* = 15.8 Hz, H, Fc-CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 14.0, 30.4, 67.5, 69.2, 84.9, 125.3, 130.1. HRMS; Found: 294.10701; Calc. for C<sub>18</sub>H<sub>22</sub>Fe [M<sup>+</sup>]: 294.10706.

### 3.4.3. (E)-1-Prop-1-enylferrocene (9) and (Z)-1-Prop-1-enylferrocene (9a)

An inseparable mixture (orange oil) of **9** and **9a** in a ratio of *E/Z* = 4:1 (determined by <sup>1</sup>H-NMR from the crude product) was obtained in 74% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 1.79 (dd, *J* = 1.6, 6.5 Hz, 3H, (E)-CH<sub>3</sub>); 1.87 (dd, *J* = 1.6, 7.0 Hz, 3H, (Z)-CH<sub>3</sub>); 4.16 (m, 5H, Fc); 4.19 (t, *J* = 1.8 Hz, 2H, (E)-Fc); 4.24 (t, *J* = 1.9 Hz, 2H, (Z)-Fc); 4.32 (t, *J* = 1.8 Hz, 2H, (E)-Fc); 4.38 (t, *J* = 1.9 Hz, 2H, (Z)-Fc); 5.62 (dq, *J* = 7.0, 10.6 Hz, 1H, (Z)-CH); 5.85 (dq, *J* = 6.5, 15.6 Hz, 1H, (E)-CH); 6.15 (dd, *J* = 1.5, 15.5 Hz, 1H, (E)-Fc-CH). <sup>13</sup>C-NMR (200 MHz,  $\delta$  ppm): 15.3 (Z), 18.9 (E), 66.6, 68.6, 69.4, 84.8, 123.3 (E), 123.9 (Z), 127.3 (Z), 128.1 (E).

### 3.4.4. (E)-1-But-1-enylferrocene (12)

A brown oil was obtained in 74% yield. <sup>1</sup>H-NMR (300 MHz,  $\delta$  ppm): 1.11 (t, *J* = 7.4 Hz, 3H, CH<sub>3</sub>); 2.15 (q, *J* = 6.9 Hz, 2H, CH<sub>2</sub>); 4.15 (s, 5H, Fc); 4.21 (s, 2H, Fc); 4.34 (s, 2H, Fc); 5.91 (dt, *J* = 12.9, 15.7 Hz, 1H, CH); 6.16 (d, *J* = 15.7 Hz, 1H, Fc-CH). <sup>13</sup>C-NMR (75 MHz,  $\delta$  ppm): 14.1, 26.3, 66.5, 68.3, 69.2, 84.5, 125.7, 130.2. HRMS; Found: 240.06000; Calc. for C<sub>14</sub>H<sub>16</sub>Fe [M<sup>+</sup>]: 240.06010.

### 3.4.5. (E)-1-Pent-1-enylferrocene (15)

A red oil was obtained in 84% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.97 (t, *J* = 7.3 Hz, 3H, CH<sub>3</sub>); 1.48 (m, 4H, 2CH<sub>2</sub>); 2.08 (dq, *J* = 1.2, 7.0 Hz, 2H, CH<sub>2</sub>); 4.11 (s, 5H, Fc); 4.17 (t, *J* = 1.8 Hz, 2H, Fc); 4.31 (t, *J* = 1.8 Hz, 2H, Fc); 5.82 (dt, *J* = 13.6, 15.7 Hz, 1H, CH); 6.10 (d, *J* = 15.7 Hz, 1H, Fc-CH). <sup>13</sup>C-NMR (50 MHz,  $\delta$  ppm): 13.8, 22.7, 27.0, 35.2, 66.3, 68.2, 69.1, 84.4, 126.8, 128.3. HRMS; Found: 2.07570; Calc. for C<sub>15</sub>H<sub>18</sub>Fe [M<sup>+</sup>]: 254.07576.

### 3.4.6. (E)-1-Hex-1-enylferrocene (18)

A brown oil was obtained in 86% yield. <sup>1</sup>H-NMR (200 MHz,  $\delta$  ppm): 0.94 (m, 3H, CH<sub>3</sub>); 1.40 (m, 6H, 3CH<sub>2</sub>); 2.09 (q, *J* = 6.8 Hz, 2H, CH<sub>2</sub>); 4.10 (s, 5H, Fc);

4.16 (t,  $J = 1.9$  Hz, 2H, Fc); 4.30 (t,  $J = 1.8$  Hz, 2H, Fc); 5.81 (dt,  $J = 6.9, 15.7$  Hz, 1H, CH); 6.09 (d,  $J = 15.6$  Hz, 1H, Fc-CH).  $^{13}\text{C-NMR}$  (50 MHz,  $\delta$  ppm): 14.1, 22.3, 31.7, 32.8, 66.3, 68.2, 69.1, 84.4, 126.5, 128.6. HRMS; Found: 268.09178; Calc. for  $\text{C}_{16}\text{H}_{20}\text{Fe} [\text{M}^+]$ : 268.09141.

### 3.4.7. (*E*)-1-Hept-1-enylferrocene (**21**)

A brown oil was obtained in 76% yield.  $^1\text{H-NMR}$  (200 MHz,  $\delta$  ppm): 0.93 (t,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ ); 1.37 (m, 8H, 4 $\text{CH}_2$ ); 2.08 (q,  $J = 6.1$  Hz, 2H,  $\text{CH}_2$ ); 4.10 (s, 5H, Fc); 4.16 (s, 2H, Fc); 4.30 (s, 2H, Fc); 5.81 (dt,  $J = 13.6, 15.5$  Hz, 1H, CH); 6.09 (d,  $J = 15.8$  Hz, 1H, Fc-CH).  $^{13}\text{C-NMR}$  (50 MHz,  $\delta$  ppm): 14.2, 22.7, 29.3, 31.5, 33.1, 66.4, 68.2, 69.1, 84.5, 126.6, 128.6. HRMS; Found: 282.10740; Calc. for  $\text{C}_{17}\text{H}_{22}\text{Fe} [\text{M}^+]$ : 282.10706.

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