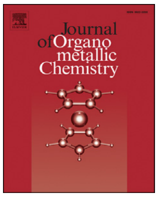
Journal of Organometallic Chemistry 758 (2014) 36–44

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem



Synthesis, characterization and electrochemical properties of novel trinuclear ferrocenyl based organosilane compounds

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ARTICLE INFO

Article history:
Received 4 December 2013
Received in revised form
21 January 2014
Accepted 1 February 2014

Keywords:
Ferrocene
Bisalkenylferrocene
Hydrosilylation reaction
Cyclic voltammetry

ABSTRACT

Some trinuclear ferrocenyl based organosilane compounds were synthesized by hydrosilylation reaction of [4-(ethylferrocenyl)butyl]dimethylsilane and (4-ferrocenylbutyl)dimethylsilane with bisalkenylferrocene derivatives, in the presence of the Karstedt catalyst at room temperature. In addition a simple method for the preparation of 1,1′-bis(3-butenyl)alkylferrocenes from 1,1′-bis(4-chlorobutyl)alkylferrocenes under mild conditions was developed. ^{1}H and ^{13}C NMR, FT-IR, GC–MS, CHN analysis, atomic absorbtion spectroscopy supported the predicted structure of the products. The electrochemical behavior of synthesized compounds was studied by cyclic voltammetry in CH_3CN/0.1 M $LiClO_4$ utilizing a glasse carbon working electrode. The relationship between the peak currents and the square root of the scan rate, showed that the redox process is diffusion limited.

1. Introduction

Ferrocene as a historically important molecule was first discovered in 1951, when Kealy and Pauson reacted cyclopentadienyl magnesium bromide Grignard reagent with ferric chloride [1,2], however its correct structure was only clarified soon afterward independently by Wilkinson et al. [3] and Fischer and Pfab [4]. The resemblance of its reactivity to that of benzene inspired Woodward et al. to coin the new iron compound with the name ferrocene [5]. The elucidation of its structure led to the birth of the modern organometallic chemistry. Soon the scientific and technical community got interested in ferrocene due to its fascinating chemistry [6,7]. Chemists started to develop synthetic strategies resulting ferrocene derivatives, and investigate their applications in a wide range of scientific areas [8].

Due to the favorable electronic properties of ferrocene and its easy functionalization, these compounds have found many applications in materials science, including electroactive materials [9–11], catalysts [12–14], aerospace materials [15,16], medicines [17–20], and sensors [21–23]. Recently ferrocene containing polymers and molecules with several ferrocene units have attracted attention with respect to their electrochemical, electronic and magnetic properties [24]. The stability of ferrocene in aerobic and aqueous media, the accessibility of a large variety of derivatives, and its favorable electrochemical properties have made ferrocenyl compounds very popular molecules for biological applications [25–28].

Since the synthesis of the first silyl metal complex (η^5-C_5H_5)$Fe(CO)_2SiMe_3$ by Wilkinson in 1956, research transition metal silyl compounds continues because these compounds are assumed to be key intermediates in a number of important stoichiometric and catalytic transformations [29,30]. Organosilicon reagents and compounds are also valuable in organic synthesis. A special feature of hydrosilanes is their ability to undergo hydrosilylation reaction with different types of unsaturated compounds, like substituted alkenes, leading to various organosilanes [31].

Friedel–Crafts acylation reactions are powerful tools for substituting larger and more complex functional groups in place of aromatic protons [32]. Similar to other aromatic compounds, ferrocene is also incorporated in these reactions. Indeed, a lewis acid e.g. aluminum chloride is needed as a catalyst. Alkylferrocenes are obtained by a two step process involving the Friedel–Crafts acylation of ferrocene continued by the reduction of the acylated ferrocene [33]. Other methods like Friedel–Crafts alkylation reactions are also able to obtain this product, however the yield of reaction would be reduced due to rearrangement in structure of the formed carbocation.

Ferrocene derivatives are a well-known class of one-electron donors which exhibit well established reversible redox couples. As a consequence, ferrocene derivatives, particularly those possessing functionalized tethers, have emerged as strong candidates

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http://dx.doi.org/10.1016/j.jorganchem.2014.02.001
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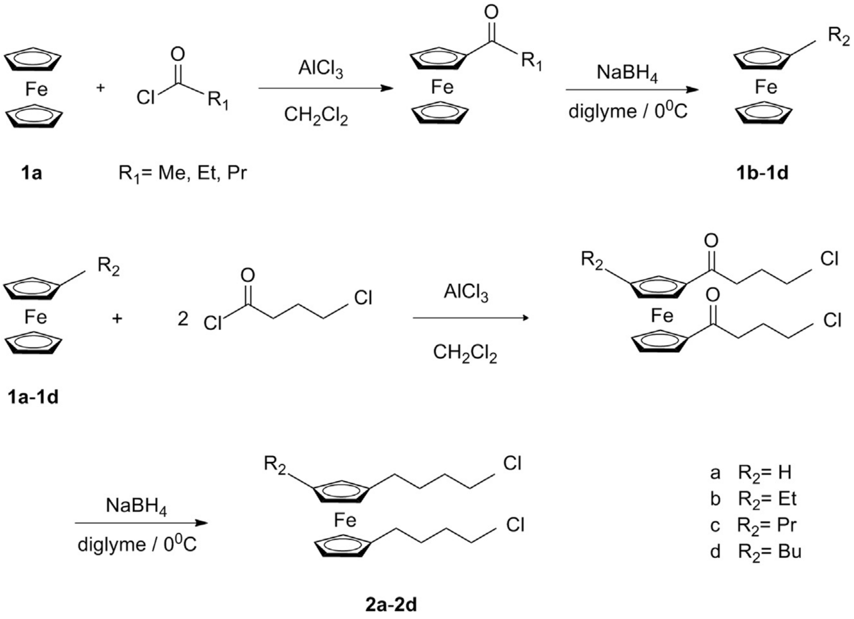


Scheme 1. Synthesis of 1,1′-bis(4-chlorobutyl) alkylferrocene.

for molecular electronic devices, electro-optical materials, multi-electron redox catalysts and electrode surface modifiers [34,35]. Although there are several methods known for the formation of vinyl or propenylferrocene, derivatives with longer alkenyl chains are hardly known in literature. Previous methods for the synthesis of alkenylferrocenes, were based on the dehydration and dehydrohalogenation reactions of corresponding ferrocenylalkanols and ferrocenylalkylhalides with a suitable reagent, respectively [36,37].

Cyclic voltammetry (CV) has been widely used in investigating the electrochemical properties of chemicals for its own advantages [38]: ease of its operation, low cost and low dosage. While the application of electrochemical methods in anion recognition requires the receptor containing an electrochemical signaling unit, the ferrocene group has been proven to be one of the most effective electrochemical signaling units not only for its stable redox characteristics, but also because it can significantly enhance its binding strength with anion by modulating its own redox state [39–42].

To the best of our knowledge, there is no report available for the synthesis of trinuclear ferrocenyl based organosilane derivatives with (4-ferrocenylbutyl)dimethylsilyl group installed on both alkyl groups of Cp rings of a center ferrocene matrix. In this article these compounds have been designed and synthesized through hydrosilylation reaction of 1,1′-dialkenylferrocene and [4-(alkylferrocenyl)butyl]dimethylsilane derivatives. The 1,1′-dialkenylalkylferrocene derivatives were synthesized from the elimination reaction of corresponding 1,1′-bis(4-chlolorobutyl) alkylferrocene derivatives under mild conditions using sodium tert-butoxide as strong base. Furthermore, the electrochemical properties of these novel compounds in solution were also studied.

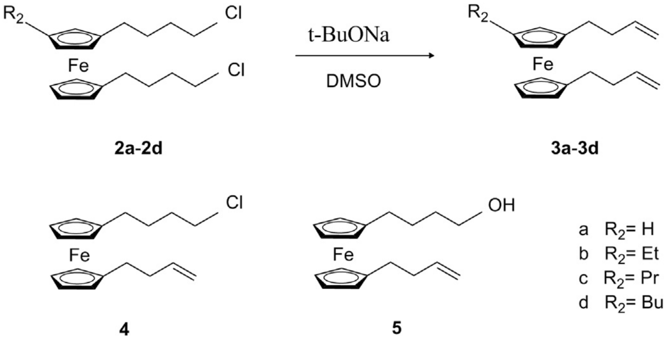
2. Results and discussion

We have recently reported the dehydrocoupling reaction of (4-ferrocenylbutyl)dimethylsilane with some alcohols derivatives in the presence of the Karstedt catalyst for synthesis of various ferrocenylsilyl ethers [43]. A few articles reporting the synthesis and electrochemistry of ferrocene derivatives are found in the literature [9–11,29–31]. Due to interesting properties of silane based ferrocene derivatives we decided to use hydrosilylation reaction of [4-(alkylferrocenyl)butyl]dimethylsilane and 1,1′-bis(3-butenyl) alkylferrocene derivatives for the synthesis of novel trinuclear ferrocenyl based organosilane compounds.

Alkylferrocene derivatives like ethylferrocene (**1b**), propylferrocene (**1c**) and butylferrocene (**1d**) were synthesized according to the modified procedure described by Graindorge and coworkers in 89, 85 and 84% yields, respectively (Scheme 1) [33].

1,1′-Bis(4-chlorobutyroyl)alkylferrocene derivatives were prepared by Friedel–Crafts acylation of ferrocene and some alkylferrocene derivatives (**1a**–**1d**) with two equivalent of 4-chlorobutyroyl chloride in dichloromethane in the presence of $AlCl_3$ as catalyst (Scheme 1). 1,1′-Bis(4-chlorobutyroyl) alkylferrocenes were reduced to the corresponding 1,1′-bis(4-chlorobutyl) alkylferrocenes (**2a**–**2d**) by $NaBH_4$ in diglyme at 0 °C in total yields of 83–90% (Scheme 1).

The dehydrohalogenation of 1,1′-bis(4-chlorobutyl) alkylferrocenes (**2a**–**2d**) in the presence of sodium tert-butoxide as a strong base in DMSO as solvent at 50 °C results in the corresponding 1,1′-bis(3-butenyl) alkylferrocenes (**3a**–**3d**) in 76–82% yields (Scheme 2). 1-(3-Butenyl)- 1′-(4-chlorobutyl) ferrocene (**4**) was isolated from reaction mixture before completion of the reaction and the dehydrohalogenation reaction was consecutively carried out on this product and compound **3a** was obtained (Scheme 2).



Scheme 2. Synthesis of 1,1′-bis(3-butenyl) alkylferrocene.

We also achieved this conversion using potassium hydroxide as a simple base in the dehydrohalogenation reaction of 1,1′-bis(4-chlorobutyl) ferrocene (**2a**), but in this case the yield of **3a** as the desired product was decreased to 58% and 1-(4-hydroxybutyl)-1′-(3-butenyl) ferrocene (**5**) was formed as byproduct in 15% yield (Scheme 2).

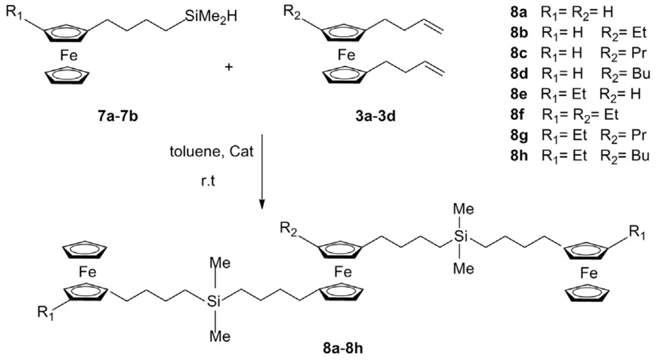
A few articles reporting the synthesis of (4-ferrocenylbutyl) dimethylsilane (**7a**) are found in the literature [44–46]. [4-(ethylferrocenyl)butyl]dimethylsilane (**7b**) was synthesized from (4-chlorobutyl) ethylferrocene (**6b**) via a Grignard reaction in THF in 91% yield [44–46]. (4-Chlorobutyroyl) ethylferrocene was prepared by Friedel–Crafts acylation of ethylferrocene with 4-chlorobutyroyl chloride in dichloromethane in the presence of $AlCl_3$ as catalyst (Scheme 3) [33,47]. (4-Chlorobutyroyl) ethylferrocene was reduced to (4-chlorobutyl) ethylferrocene (**6b**) by sodium borohydride in diglyme in 96% total yield (Scheme 3) [33].

The hydrosilylation reaction of 1,1′-bis(3-butenyl) alkylferrocenes (**3a**–**3d**) with (4-ferrocenyl butyl)dimethylsilane (**7a**) and [4-(ethylferrocenyl)butyl]dimethylsilane (**7b**) in the presence of catalytic amount of the Karstedt catalyst was carried out in toluene at room temperature (Scheme 4). FT-IR spectroscopy was utilized to follow the progress of the reaction, by monitoring the loss of the Si–H absorption at 2110 cm^{-1} (Fig 1), the reaction was completed in 24 h. The novel trinuclear ferrocenyl based organosilanes (**8a**–**8h**) (Table 1) were isolated as air stable, dark orange viscous oils. In the ^{1}H NMR spectra of (**6a**–**6h**), appearance of a triplet around 0.5 ppm corresponding to $\mathbf{CH_2}SiMe_2$ and complete disappearance of $-\mathbf{CH}{=}\mathbf{CH_2}$ peaks were confirmed showing the end of hydrosilylation reaction (Fig 2).

Data obtained from the mass spectra, IR, ^{1}H and ^{13}C NMR spectra and elemental analyses are fully consistent with the proposed structures.

In order to compare the influence of the substituents on the redox ability of Fe (II), we carried out electrochemical studies on the synthesized ferrocene derivatives. CV experiments performed in dry CH_3CN/0.100 M $LiClO_4$ exhibited reversible voltammetric behavior for the ferrocenyl group in this compounds with $\Delta E_p = E_{pa} - E_{pc} \leq 0.08$ V at scan rates up to 0.25 V s^{-1} (Table 2). Cathodic and anodic peak current ratios measured for the derivatives were in the range $0.99 < i_{pc}/i_{pa} < 1.07$, and E_p values were independent of the scan rate.

All of the compounds exhibit only one pair of well-defined redox peak in CH_3CN indicating the existence of only one kind of electroactive center in this compounds which is corresponding to its ferrocenyl group. Fig 3 shows an example of typical voltammograms of the ferrocene compounds in CH_3CN/0.100 M $LiClO_4$. The influences of the scan rate was studied on the voltammetric response of the ferrocenyl compounds in the range of 0.025–0.25 V s^{-1}. As seen, the anodic and cathodic peak currents increased with increasing the scan rate. The plots of the anodic and cathodic currents versus the square root of scan rates ($v^{1/2}$) show a linear relationship (Fig 4). This behavior suggests that the redox process is diffusion limited.

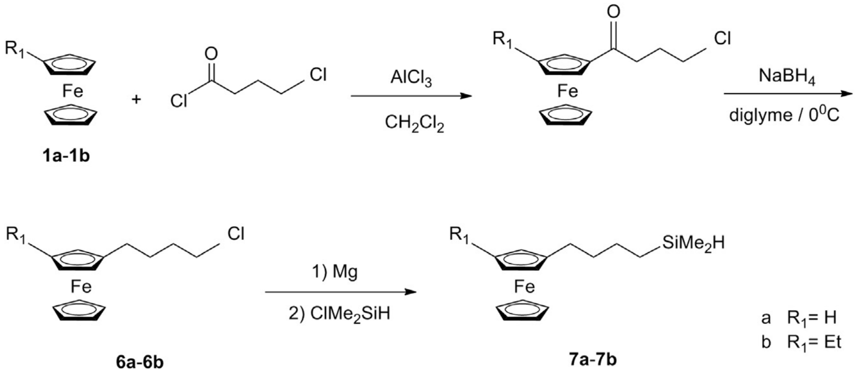


Scheme 4. Synthesis of trinuclear ferrocenyl based organosilanes.

Both reduction and oxidative peak currents increase obviously as Fc unit increases in the structure of compounds (Fig 5). The elevation of the Fc unit is responsible for the increase of electroactive substance and the charge generated in the reaction became more and more leading to the increasing of the peak currents. These compounds can be potentially used as new electroactive materials for sensors and other electrochemical systems due to their well reversible redox behavior and the ability to tailor functional groups without affecting the electrochemical aspects.

3. Conclusion

In summary, we report the design and synthesis of some trinuclear ferrocenyl based organosilane compounds through the reaction of [4-(ethylferrocenyl)butyl]dimethylsilane and (4-ferrocenylbutyl)dimethylsilane with dialkenylferrocene derivatives, in the presence of the Karstedt catalyst at room temperature. In addition a simple method for the preparation of 1,1′-bis(3-butenyl)alkylferrocenes from 1,1′-bis(4-chlorobutyl)alkylferrocenes under mild conditions was developed. Electrochemical behavior of synthesized compounds with the increase of scan rate was investigated. The relationship between the peak currents and the square root of the scan rate, showed that the electrode processes were diffusion controlled.



Scheme 3. Synthesis of [4-(alkylferrocenyl)butyl]dimethylsilane derivatives.

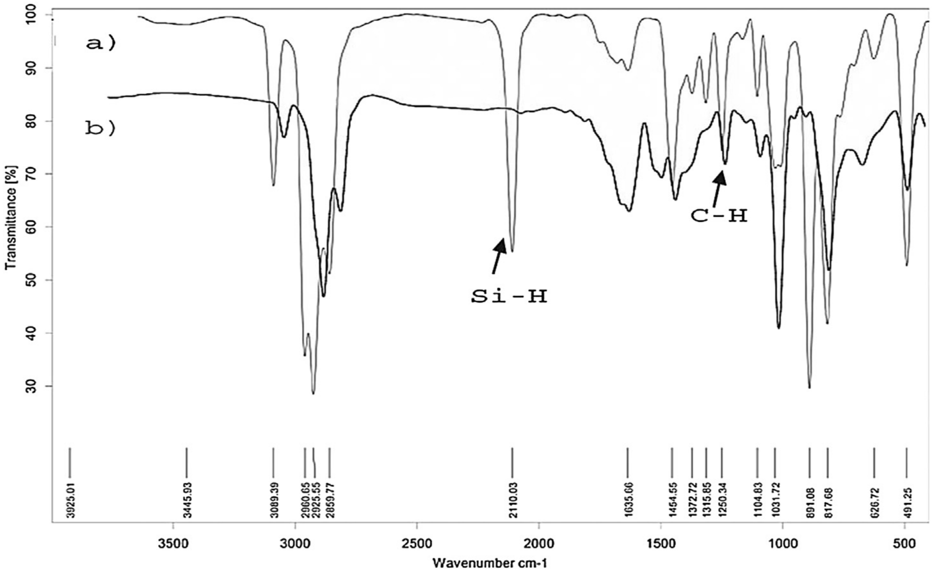


Fig. 1. Comparing the FT-IR spectra of a) (4-ferrocenylbutyl)dimethylsilane (**7a**) b) 1,1′-bis [4-[[4-(dimethylsilyl)butyl]ferrocenyl]butyl]ferrocene (**8a**).

4. Experimental

4.1. Solvents and reagents

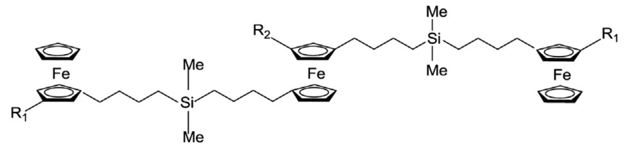
Chemicals were either prepared in our laboratory or purchased from Merck, Fluka, Sigma, Aldrich and Yantai Suny Chem. International Co., Ltd. Commerical solid reagents were used without further purification. Liquid reactants were distilled prior to use. Solvents were dried and distilled prior to use according to standard laboratory practices; water was doubly distilled. THF and diglyme were dried by refluxing under argon over sodium wire and distilled directly before use. Column chromatography was performed on silicagel 60 (Merck, grain size 0.063–0.2 mm) with *n*-hexane as eluant. All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring.

4.2. Instrumentation

The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker FT-400 MHz spectrometer at room temperature and with $CDCl_3$ as solvent while chemical shifts are presented delta-values expressed in ppm referenced to $CHCl_3$ residue at 7.25 and 78 ppm, respectively. The FT-IR spectra were recorded on a Bruker-Tensor 270 spectrophotometer as KBr disks or smears between salt plates. The mass spectra obtained with a GC-Mass Agilent quadrupole mode 5973N instrument, operating at 70 eV. Elemental analyses were carried out with an Elementor Vario EL. III instrument. Iron analysis was performed by Analytikjene (novaa 400) atomic absorption spectrophotometer.

Cyclic voltammetry measurements were performed on 1 mM solutions of ferrocene derivatives in dry CH_3CN/0.1 M $LiClO_4$ using potentiostat/galvanostat Autolab (PGASTAT 30) equipped with a standard three-electrode cell. A 2-mm-diameter GC was used as the working electrode. A silver/silver chloride (Ag/AgCl) electrode and a platinum electrode were used as the reference and the counter electrodes, respectively. All potentials in this study are reported with respect to the Ag/AgCl.

Table 1
Synthesis of trinuclear ferrocenyl based organosilanes.



Entry	R_1	R_2	Product	Yield
1	H	H	**8a**	68%
2	H	Et	**8b**	63%
3	H	Pr	**8c**	59%
4	H	Bu	**8d**	57%
5	Et	H	**8e**	64%
6	Et	Et	**8f**	62%
7	Et	Pr	**8g**	56%
8	Et	Bu	**8h**	65%

4.3. General procedure for the synthesis of alkylferrocene

A solution of acid chloride (63 mmol) in 30 ml dry dichloromethane was added to a suspension of anhydrous aluminum chloride (8.41 g, 63 mmol) in 30 ml dry dichloromethane and the mixture was stirred at 5 °C for 1 h under Argon. The solution of aluminum chloride: acid chloride complex was added dropwise over 30 min to a solution of ferrocene (11.16 g, 60 mmol) in 100 ml dry dichloromethane at 0 °C. The reaction mixture was warmed to room temperature and stirred for 16 h. A solution of $NaBH_4$ (2.38 g, 63 mmol) in 25 ml diglyme was added dropwise to the purple reaction mixture at −5 °C. An orange solution was formed and stirred at 0 °C for 1 h. The mixture was then hydrolyzed with addition of 20 ml water while maintaining its temperature at less than or equal to 10 °C. The mixture was allowed to separate by settling and the organic phase was then withdrawn. The aqueous phase was extracted with 3 times 30 ml of dichloromethane and then all the organic phases are combined. Combined organic layer was washed with 50 ml of brine and then dichloromethane was distilled under atmospheric pressure. The diglyme and the residual ferrocene which was found to be entrained by the diglyme were then distilled at reduced pressure approximately 20 mm Hg and a column head temperature of 85°–95 °C. The alkylferrocene derivatives were distilled at a more reduced pressure, less than 5 mm Hg.

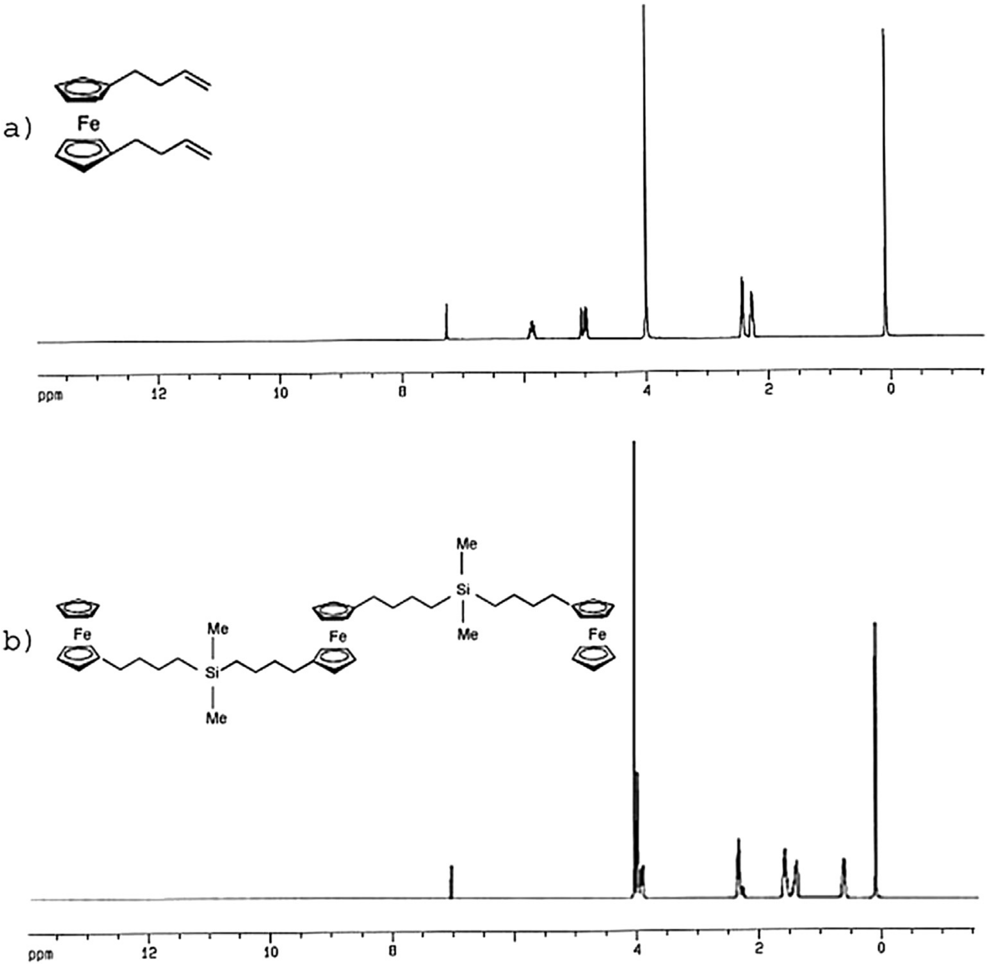


Fig. 2. NMR spectra of a) 1,1′-bis(3-butenyl)ferrocene (**3a**) b) 1,1′-bis [4-[[4-(dimethylsilyl)butyl]ferrocenyl]butyl]ferrocene (**8a**).

4.3.1. *Ethylferrocene (**1b**)*

From 4.95 g acetylchloride, 11.43 g of light brown liquid was obtained in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.16–1.19 (t, 3H, C**H**$_3$), 2.32–2.37 (q, 2H, FcC**H**$_2$), 3.99–4.16 (m, 9H, Fc); *m*/*z* (EI): 214 (100%[M]$^+$).

4.3.2. *Propylferrocene (**1c**)*

From 5.83 g propionylchloride, 11.63 g of light brown liquid was obtained in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.93–0.96 (t, 3H, C**H**$_3$), 1.49–1.58 (m, 2H, C**H**$_2$CH$_3$), 2.31–2.35 (t, 2H, FcC**H**$_2$), 4.05–4.15 (m, 9H, Fc); *m*/*z* (EI): 228 (100%[M]$^+$).

4.3.3. *Butylferrocene (**1d**)*

From 6.71 g butyrylchloride, 12.20 g of light brown liquid was obtained in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.89–0.92 (t, 3H, C**H**$_3$), 1.31–1.36 (m, 2H, C**H**$_2$CH$_3$), 1.42–1.45 (m, 2H, C**H**$_2$CH$_2$CH$_3$), 2.29–2.36 (t, 2H, CpC**H**$_2$), 4.02–4.13 (m, 9H, Fc); *m*/*z* (EI): 242 (100%[M]$^+$).

4.4. *General procedure for the synthesis of 1,1′-bis(4-chlorobutyl) alkylferrocene*

A solution of 4-chlorobutyroyl chloride (15.28 g, 108 mmol) in 50 ml dry dichloromethane was added dropwise at room temperature to a suspension of anhydrous aluminum chloride (15.89 g, 119 mmol) in 50 ml of dry dichloromethane. The mixture was stirred at room temperature for 1 h under Argon. The homogeneous yellow solution was added dropwise to a solution of ferrocene or alkylferrocene derivatives (54 mmol) in 130 ml dry dichloromethane at 0 °C. The dark purple solution was then slowly allowed to warm to room temperature. After 24 h stirring at room temperature, a solution of $NaBH_4$ (4.09 g, 108 mmol) in 50 ml diglyme was added, while maintaining the temperature at less than or equal to 0 °C to the reaction mixture. A dark orange solution was formed and stirred at 0 °C for 1 h. The mixture was then hydrolyzed with the addition of 120 ml water while maintaining its temperature at less than or equal to 5 °C. The mixture was allowed to separate by settling and the organic phase was then withdrawn. The aqueous phase was extracted with 3 times 50 ml of dichloromethane and then all the organic phases were combined. Combined organic layer was washed with 100 ml of brine and then dichloromethane was distilled under atmospheric pressure. The diglyme were evaporated under reduced pressure. The residue was purified by column chromatography on silicagel with *n*-hexane as eluant. Specific details are given for each compound.

4.4.1. *1,1′-Bis(4-chlorobutyl)ferrocene (**2a**)*

From 10.04 g ferrocene, 17.63 g of orange liquid was obtained in 89% yield. FT-IR (KBr, cm^{-1}): 3084 (Cp–H), 2938 (C–H), 1648, 1455 (C=C), 1312 (CH$_2$–Cl), 1025 (Cp), 815 (C–Cl), 496 (Cp–Fe); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 1.62–1.66 (m, 4H, CpCH$_2$C**H**$_2$), 1.76–1.82 (m, 4H, C**H**$_2$CH$_2$Cl), 2.33–2.37 (t, 4H, Cp–C**H**$_2$), 3.53–3.56 (t, 4H,

Table 2
Selected potentials (V) and current (μA) data for 1.0 mM solutions of the ferrocenyl containing compounds in CH_3CN/0.100 M $LiClO_4$ at 25.0 °C.

Compound	ΔE_p	i_{pc}/i_{pa}	Compound	ΔE_p	i_{pc}/i_{pa}
2a	0.078	1.02	**5a**	0.073	0.99
2b	0.079	1.04	**5b**	0.080	1.05
2c	0.073	1.03	**5c**	0.079	1.03
2d	0.076	0.99	**5d**	0.074	0.99
3a	0.073	1.03	**5e**	0.060	1.04
3b	0.079	1.03	**5f**	0.078	1.07
3c	0.080	1.02	**5g**	0.080	0.99
3d	0.075	0.99	**5h**	0.080	1.02

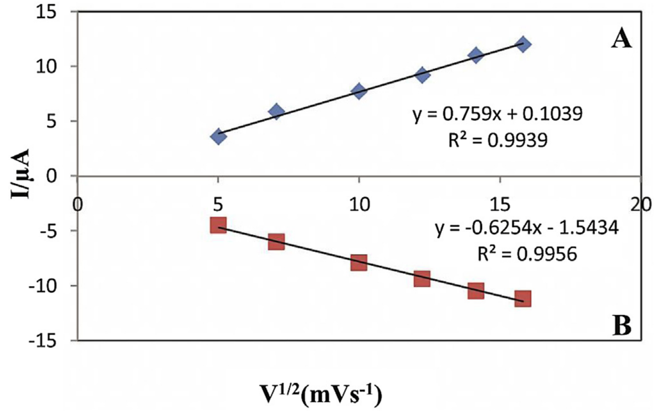


Fig. 4. Linear relationship between the A) cathodic peak current, B) anodic peak current and the square root of scan rates.

C**H**$_2$Cl), 3.98 (d, 4H, J = 1.4 Hz, CH_2C_5**H**$_4$), 4.00 (d, 4H, J = 1.4 Hz, CH_2C_5**H**$_4$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 27.38 ($CpCH_2$**C**H_2), 27.61 (**C**H_2CH_2Cl), 31.28 (Cp**C**H_2), 43.97 (**C**H_2Cl), 67.59, 66.83 (**Cp**), 87.42 ($CpCH_2$); m/z (EI): 368 (64.26%[M]$^+$), 366 (100%[M]$^+$), 91 (14.82% [$CH_2CH_2CH_2CH_2Cl$]$^+$); Anal. Calc. for: $C_{18}H_{24}Cl_2Fe$ (367.141): C, 58.89; H, 6.59; Fe, 15.21. Found: C, 58.86; H, 6.55; Fe, 15.11%.

4.4.2. *1,1′-Bis(4-chlorobutyl) ethylferrocene (**2b**)*

From 11.56 g ethylferrocene, 18.34 g of orange liquid was obtained in 86% yield. FT-IR (KBr, cm^{-1}): 3082 (Cp–H), 2935 (C–H), 1675, 1449 (C=C), 1309 (CH_2–Cl), 1032 (Cp), 820 (C–Cl), 496 (Cp–Fe); ^1H NMR (400 MHz, $CDCl_3$, ppm): 1.12–1.16 (t, 3H, C**H**$_3$), 1.57–1.67 (m, 4H, $CpCH_2C$**H**$_2$), 1.76–1.81 (m, 4H, C**H**$_2CH_2Cl$), 2.26–2.36 (m, 6H, CpC**H**$_2$), 3.52–3.54 (t, 4H, C**H**$_2$Cl), 3.86–3.99 (m, 7H, **Cp**); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 12.56 (**C**H_3), 27.38 (Cp–CH_2**C**H_2), 27.59 (**C**H_2CH_2Cl), 31.49, 31.39, 31.30 (Cp**C**H_2), 43.94 (**C**H_2Cl), 68.28, 67.38, 67.31, 67.13, 66.58 (**Cp**), 88.28, 86.14, 85.48 ($CpCH_2$); m/z (EI): 396 (64.93%[M]$^+$), 394 (100%[M]$^+$), 91 (14.74% [$CH_2CH_2CH_2CH_2Cl$]$^+$); Anal. Calc. for: $C_{20}H_{28}Cl_2Fe$ (395.195): C, 60.78; H, 7.14; Fe, 14.13. Found: C, 60.45; H, 7.10; Fe, 14.05%.

4.4.3. *1,1′-Bis(4-chlorobutyl) propylferrocene (**2c**)*

From 12.31 g propylferrocene, 19.88 g of orange liquid was obtained in 90% yield. FT-IR (KBr, cm^{-1}): 3099 (Cp–H), 2935 (C–H), 1675, 1449 (C=C), 1319 (CH_2–Cl), 1039 (Cp), 820 (C–Cl), 497 (Cp–Fe); ^1H NMR (400 MHz, $CDCl_3$, ppm): 0.90–0.93 (t, 3H, C**H**$_3$), 1.44–1.49 (m, 2H, C**H**$_2CH_3$), 1.59–1.66 (m, 4H, $CpCH_2C$**H**$_2$), 1.76–1.82 (m, 4H, C**H**$_2CH_2Cl$), 2.23–2.33 (m, 6H, CpC**H**$_2$), 3.52–3.54 (t, 4H, C**H**$_2$Cl), 3.85–3.93 (m, 7H, **Cp**); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 12.59 (**C**H_3), 27.71, 27.60, 23.81 (–CH_2–), 31.49, 31.38, 31.29 ($CpCH_2$), 43.98 (**C**H_2Cl), 68.48, 67.58, 67.34, 67.15, 66.68 (**Cp**), 88.26, 87.13, 86.37 ($CpCH_2$); m/z (EI): 410 (64.19%[M]$^+$), 408 (100%[M]$^+$), 91 (17.45% [$CH_2CH_2CH_2CH_2Cl$]$^+$); Anal. Calc. for: $C_{21}H_{30}Cl_2Fe$ (409.22): C, 61.63; H, 7.38; Fe, 13.64. Found: C, 61.89; H, 7.34; Fe, 13.56%.

4.4.4. *1,1′-Bis(4-chlorobutyl) butylferrocene (**2d**)*

From 13.07 g butylferrocene, 18.96 g of orange liquid was obtained in 83% yield. FT-IR (KBr, cm^{-1}): 3082 (Cp–H), 2933 (C–H), 1707, 1451 (C=C), 1305 (CH_2–Cl), 1034 (Cp), 819 (C–Cl), 496 (Cp-Fe); ^1H NMR (400 MHz, $CDCl_3$, ppm): 0.90–0.94 (t, 3H, C**H**$_3$), 1.31–1.37 (m, 2H, C**H**$_2CH_2CH_3$), 1.43–1.48 (m, 2H, C**H**$_2CH_3$), 1.60–1.67 (m, 4H, $CpCH_2C$**H**$_2$), 1.78–1.82 (m, 4H, C**H**$_2CH_2Cl$), 2.25–2.36 (m, 6H, CpC**H**$_2$), 3.52–3.54 (t, 4H, C**H**$_2$Cl), 3.86–3.94 (m, 7H, **Cp**); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 12.97(**C**H_3), 21.62 (**C**H_2CH_3), 27.61, 27.38, 26.89 (CH_2), 31.50, 31.36, 31.28 (Cp**C**H_2), 43.96 (**C**H_2Cl), 68.45, 67.52, 67.36, 67.21, 66.48 (**Cp**), 88.24, 87.15, 86.39 ($CpCH_2$); m/z (EI): 424 (65.09%[M]$^+$), 422 (100%[M]$^+$), 91 (13.10% [$CH_2CH_2CH_2CH_2Cl$]$^+$); Anal. Calc. for: $C_{22}H_{32}Cl_2Fe$ (423.243): C, 62.43; H, 7.62; Fe, 13.19. Found: C, 62.10; H, 7.58; Fe, 13.11%.

4.5. *General procedure for the synthesis of 1,1′-bis(3-butenyl) alkylferrocene*

A 50 ml round-bottom flask was charged with 1,1′-bis(4-chlorobutyl) alkylferrocene (2.7 mmol), sodium tert-butoxide (8.1 mmol) and 16 ml DMSO as solvent under argon. Mixture was

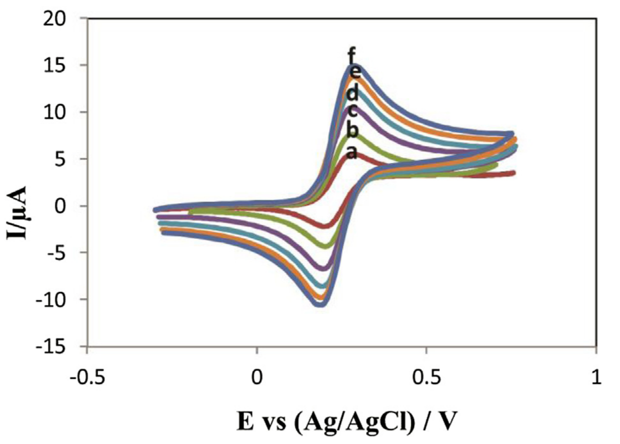


Fig. 3. CV curves of the 1,1′-bis(4-chlorobutyl)ferrocene in different scan rates. (a) 0.025 (b) 0.05 (c) 0.1 (d) 0.15 (e) 0.2 (f) 0.25 V s^{-1}.

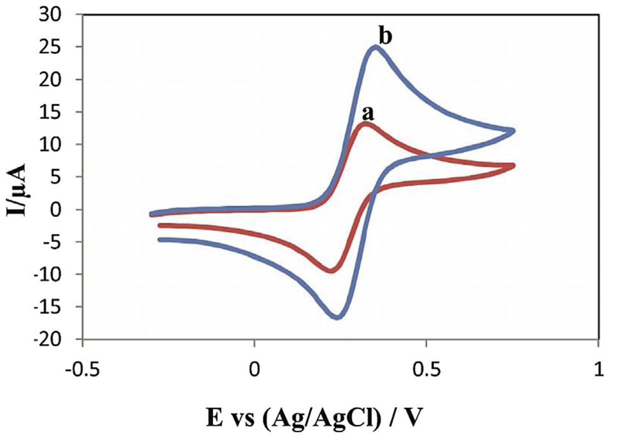


Fig. 5. CV curves for 1.0 mM of a) 1,1′-bis(4-chlorobutyl)ferrocene b) 1,1′-bis [4-[[4-(dimethylsilyl) butyl]ferrocene]butyl]ferrocene in CH_3CN/0.100 M $LiClO_4$ at 250 mV s^{-1}.

stirred at 50 °C and reaction progress was monitored with thin layer chromatography (TLC) until complete disappearance of 1,1′-bis(4-chlorobutyl) alkylferrocene. The mixture was allowed to cool to room temperature and extracted with 4 times 25 ml of *n*-hexane and then all the *n*-hexane phases were combined. The combined *n*-hexane extracts were washed with 3 times 10 ml water and dried over Na$_2$SO$_4$ before removal of the solvent. The solvent was evaporated and the residue purified by column chromatography with *n*-hexane as eluant to give the corresponding products. Specific details are given for each compound.

*4.5.1. 1,1′-Bis(3-butenyl)ferrocene (**3a**)*

From 0.99 g 1,1′-bis(4-chlorobutyl)ferrocene, 0.63 g of orange oil was obtained in 79% yield. FT-IR (KBr, cm^{-1}): 3083 (Cp–H), 2930 (C–H), 1647, 1629, 1460 (C=C), 1025 (Cp), 503 (Cp–Fe); ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 2.23–2.28 (m, 4H, CpCH$_2$C**H**$_2$), 2.39–2.43 (t, 4H, CpC**H**$_2$), 3.99–4.01 (m, 8H, Cp), 4.97 (d, *J* = 10.1 Hz, 2H, =C**H**$_2$), 5.03 (d, *J* = 17.1 Hz, 2H, =C**H**$_2$), 5.82–5.89 (m, 2H, –C**H**=); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 27.95 (CpCH$_2$**C**H$_2$), 34.43 (Cp**C**H$_2$), 66.76, 67.60 (Cp), 87.56 (CpCH$_2$), 113.50 (=**C**H$_2$), 137.58 (–**C**H=); *m*/*z* (EI): 294 (100%[M]$^+$), 199 (28.04% [Fc–CH$_2$]$^+$); Anal. Calc. for: C$_{18}$H$_{22}$Fe (294.219): C, 73.48; H, 7.54; Fe, 18.98. Found: C, 73.05; H, 7.58; Fe, 18.87%.

*4.5.2. 1,1′-Bis(3-butenyl)ethylferrocene (**3b**)*

From 1.07 g 1,1′-bis(4-chlorobutyl) ethylferrocene, 0.71 g of orange oil was obtained in 82% yield. FT-IR (KBr, cm^{-1}): 3076 (Cp–H), 2923 (C–H), 1643, 1625, 1444 (C=C), 1056 (Cp), 494 (Cp–Fe); ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 1.12–1.16 (t, 3H, C**H**$_3$), 2.23–2.32 (m, 4H, CpCH$_2$C**H**$_2$), 2.35–2.43 (m, 6H, CpC**H**$_2$), 3.88–3.99 (m, 7H, Cp), 4.96 (d, *J* = 10.0 Hz, 2H, =C**H**$_2$), 5.03 (d, *J* = 17.1 Hz, 2H, =C**H**$_2$), 5.82–5.87 (m, 2H, –C**H**=); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 13.73 (**C**H$_3$), 26.44, 27.88 (CpCH$_2$**C**H$_2$), 34.21, 34.39, 34.65 (Cp**C**H$_2$), 66.57, 67.23, 67.56, 67.84, 68.29 (Cp), 86.78, 87.42, 89.35 (CpCH$_2$), 113.38 (=**C**H$_2$), 137.60 (–**C**H=); *m*/*z* (EI): 322 (100%[M]$^+$); Anal. Calc. for: C$_{20}$H$_{26}$Fe (322.26): C, 74.54; H, 8.13; Fe, 17.33. Found: C, 74.18; H, 8.08; Fe, 17.23%.

*4.5.3. 1,1′-Bis(3-butenyl)propylferrocene (**3c**)*

From 1.1 g 1,1′-bis(4-chlorobutyl) propylferrocene, 0.69 g of orange oil was obtained in 76% yield. FT-IR (KBr, cm^{-1}): 3076 (Cp–H), 2923 (C–H), 1641, 1620, 1449 (C=C), 1048 (Cp), 496 (Cp–Fe); ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 0.91–0.94 (t, 3H, C**H**$_3$), 1.48–1.51 (m, 2H, C**H**$_2$CH$_3$), 2.23–2.27 (m, 6H, CpCH$_2$C**H**$_2$, CpC**H**$_2$CH$_2$CH$_3$), 2.36–2.39 (t, 4H, CpC**H**$_2$), 3.87–4.00 (m, 7H, Cp), 4.97 (d, *J* = 9.7 Hz, 2H, =C**H**$_2$), 5.03 (d, *J* = 17.0 Hz, 2H, =C**H**$_2$), 5.86–5.87 (m, 2H, –C**H**=); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 13.21 (**C**H$_3$), 22.05 (**C**H$_2$CH$_3$), 26.86, 28.01 (–**C**H$_2$–), 30.65, 33.48, 34.64 (Cp**C**H$_2$), 66.57, 66.75, 66.86, 67.61, 68.33 (Cp), 85.66, 86.40, 87.40, (CpCH$_2$), 113.37 (=**C**H$_2$), 137.63 (–**C**H=); *m*/*z* (EI): 336 (100%[M]$^+$); Anal. Calc. for: C$_{21}$H$_{28}$Fe (336.29): C, 75.00; H, 8.39; Fe, 16.61. Found: C, 74.60; H, 8.34; Fe, 16.52%.

*4.5.4. 1,1′-Bis(3-butenyl) butylferrocene (**3d**)*

From 1.14 g 1,1′-bis(4-chlorobutyl) butylferrocene, 0.74 g of orange oil was obtained in 78% yield. FT-IR (KBr, cm^{-1}): 3076 (Cp–H), 2924 (C–H), 1639, 1628, 1452 (C=C), 1045 (Cp), 495 (Cp–Fe); ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 0.88–0.92 (t, 3H, C**H**$_3$), 1.30–1.35 (m, 2H, C**H**$_2$CH$_3$), 1.43–1.45 (m, 2H, C**H**$_2$CH$_2$CH$_3$), 2.22–2.26 (m, 6H, CpCH$_2$C**H**$_2$,CpC**H**$_2$), 2.34–2.39 (t, 4H, CpC**H**$_2$), 3.85–4.06 (m, 7H, Cp), 4.96 (d, *J* = 9.8 Hz, 2H, =C**H**$_2$), 5.03 (d, *J* = 17.2 Hz, 2H, =CH$_2$), 5.83–5.89 (m, 2H, –CH=); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 13.02 (CH$_3$), 21.69 (–**C**H$_2$CH$_3$), 26.39, 27.85, 28.10 (CpCH$_2$**C**H$_2$), 30.37, 34.34, 34.64 (Cp**C**H$_2$), 66.55, 66.68, 67.60, 67.94, 68.31 (Cp), 86.80, 87.39, 87.74 (CpCH$_2$), 113.45 (=CH$_2$), 137.71 (–CH=); *m*/*z* (EI): 350 (100%[M]$^+$); Anal. Calc. for: C$_{22}$H$_{30}$Fe (350.32): C, 75.43; H, 8.63; Fe, 15.94. Found: C, 74.17; H, 8.58; Fe 15.85%.

*4.5.5. 1-(3-Butenyl)-1′-(4-chlorobutyl) ferrocene (**4**)*

Orange oil. FT-IR (KBr, cm^{-1}): 3082 (Cp–H), 2925 (C–H), 1640, 1620, 1452 (C=C), 1311 (CH$_2$–Cl), 1032 (Cp), 814 (C–Cl), 494 (Cp–Fe); ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 1.63–1.69 (m, 2H, C**H**$_2$CH$_2$CH$_2$Cl), 1.77–1.82 (m, 2H, C**H**$_2$CH$_2$Cl), 2.23–2.31 (m, 2H, CpCH$_2$C**H**$_2$CH=), 2.35–2.38 (t, 2H, CpC**H**$_2$CH$_2$CH$_2$CH$_2$Cl), 2.40–2.44 (t, 2H, CpCH$_2$C**H**$_2$CH=), 3.53–3.56 (t, 2H, C**H**$_2$Cl), 3.99–4.01 (m, 8H, Cp), 4.98 (d, *J* = 10.1 Hz, 1H, =C**H**$_2$), 5.05 (d, *J* = 17.1 Hz, 1H, =C**H**$_2$), 5.82–5.92 (m, 1H, –C**H**=); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 27.38 (CpCH$_2$**C**H$_2$CH$_2$), 27.61 (**C**H$_2$CH$_2$Cl), 27.95 (**C**H$_2$CH=), 31.28 (Cp**C**H$_2$CH$_2$CH$_2$), 34.43 (Cp**C**H$_2$CH$_2$CH=), 43.90 (**C**H$_2$Cl), 66.76, 66.81, 67.33, 67.39 (**Cp**), 87.37 (**C**$_{1'}$ Cp), 87.53 (**C**$_1$ Cp), 113.49 (=**C**H$_2$), 137.50 (–**C**H=); *m*/*z* (EI): 332.5 (63.28%[M]$^+$), 330.5 (100%[M]$^+$); Anal. Calc. for: C$_{18}$H$_{23}$ClFe (330.68): C, 65.38; H, 7.01; Fe, 16.89. Found: C, 65.61; H, 6.97; Fe, 16.8%.

*4.5.6. 1-(4-Hydroxybutyl)-1′-(3-butenyl) ferrocene (**5**)*

Orange oil. FT-IR (KBr, cm^{-1}): 3480 (O–H), 3084 (Cp–H), 2923 (C–H), 1642, 1622, 1451 (C=C), 1030 (Cp), 496 (Cp–Fe); ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 1.34–1.36 (br, 1H, O**H**), 1.52–1.62 (m, 4H, CpCH$_2$C**H**$_2$C**H**$_2$CH$_2$OH), 2.23–2.29 (m, 2H, CpCH$_2$C**H**$_2$CH=), 2.33–2.36 (t, 2H, CpC**H**$_2$CH$_2$CH$_2$CH$_2$OH), 2.39–2.43 (t, 2H, CpCH$_2$C**H**$_2$CH=), 3.62–3.65 (t, 2H, C**H**$_2$OH), 3.98–4.01 (m, 8H, Cp), 4.97 (d, *J* = 10.1 Hz, 1H, =C**H**$_2$), 5.03 (d, *J* = 17.1 Hz, 1H, =C**H**$_2$), 5.81–5.91 (m, 1H, –C**H**=); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 26.43 (CpCH$_2$**C**H$_2$CH$_2$), 27.91 (**C**H$_2$CH$_2$OH), 28.19 (**C**H$_2$CH=), 31.56 (Cp**C**H$_2$CH$_2$CH$_2$), 34.41 (Cp**C**H$_2$CH$_2$CH=), 61.83 (**C**H$_2$OH), 66.75, 66.79, 67.58, 67.62 (**Cp**), 87.51 (**C**$_1$ Cp), 87.80 (**C**$_{1'}$ Cp), 113.49 (=**C**H$_2$), 137.58 (–**C**H=); *m*/*z* (EI): 312 (100%[M]$^+$); Anal. Calc. for: C$_{18}$H$_{24}$OFe (312.235): C, 69.24; H, 7.75; Fe, 17.88. Found: C, 68.81; H, 7.8; Fe, 17.76%.

4.6. Preparation of (4-chlorobutyl)alkylferrocene

*4.6.1. 4-Chlorobutylferrocene (**6a**)*

6a was prepared according to procedure described by J.C. Gautier and J.C. Mondet [47].

*4.6.2. 1-(4-Chlorobutyl)ethylferrocene (**6b**)*

6b was prepared according to similar procedure as section 4.6.1. as yellowish oil in 96% yield: FT-IR (KBr, cm^{-1}): 3088 (Cp–H), 2931, 2860 (C–H), 1667, 1450 (C=C), 1311, 1227 (CH$_2$–Cl), 1104, 1038 (Cp), 824 (C–Cl), 492 (Cp–Fe); ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 1.12–1.15 (t, 3H C**H**$_3$), 1.54–1.67 (m, 2H, CpCH$_2$C**H**$_2$), 1.75–1.81 (m, 2H, C**H**$_2$CH$_2$Cl), 2.25–2.39 (m, 4H, CpC**H**$_2$), 3.55–3.56 (t, 2H, C**H**$_2$Cl), 3.96–4.12 (m, 8H, Cp); ^{13}C NMR (100 MHz, CDCl$_3$, ppm): 12.54 (**C**H$_3$), 27.38 (CpCH$_2$**C**H$_2$), 27.59 (**C**H$_2$CH$_2$Cl), 31.49, 31.36 (Cp**C**H$_2$), 43.96 (**C**H$_2$Cl), 67.38, 67.31, 67.13, 66.58 (**Cp**), 88.28, 86.14 (CpCH$_2$); Anal. Calc. For: C$_{16}$H$_{21}$ClFe (304.64): C, 63.08; H, 6.95; Fe, 18.33. Found: C, 63.32; H, 6.91; Fe, 18.22%.

4.7. Preparation of [4-(alkylferrocenyl)butyl]dimethylsilane

*4.7.1. (4-Ferrocenylbutyl)dimethylsilane (**7a**)*

7a was prepared according to procedure described by M. Immelman, J.C. Swarts, G.J. Lamprecht and S.E. Greyling [44].

*4.7.2. [4-(Ethylferrocenyl)butyl]dimethylsilane (**7b**)*

7b was prepared according to similar procedure as Section 4.7.1. as dark brown oil in 91% yield: FT-IR (KBr, cm^{-1}): 3089 (Cp–H), 2960 (C–H), 2110 (Si–H), 1635, 1454 (Cp), 1250 (C–Si), 1031 (Cp), 491 (Cp–Fe); ^{1}H NMR (400 MHz, CDCl$_3$, ppm): 0.09–0.14 (d, 6H,

$Si(C\mathbf{H}_3)_2$), 0.61–0.65 (t, 2H, $C\mathbf{H}_2Si(CH_3)_2$), 0.91–0.96 (m, 2H, $C\mathbf{H}_2CH_2Si(CH_3)_2$), 1.16–1.21 (t, 3H, $C\mathbf{H}_3$), 1.43–1.56 (m, 2H, Cp–CH_2–$C\mathbf{H}_2$), 2.31–2.37 (m, 4H, Cp–$C\mathbf{H}_2$), 3.97–4.05 (m, 9H, Cp, Si–**H**); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −3.59 ($Si(\mathbf{C}H_3)_2$), 13.26 ($CH_2\mathbf{C}H_3$), 25.36 ($\mathbf{C}H_2Si(CH_3)_2$), 27.88, 28.49 (−$\mathbf{C}H_2$−), 31.56, 34.65 (Cp$\mathbf{C}H_2$), 66.58, 67.13, 67.31, 67.38 (Cp), 86.14, 88.28 ($CpCH_2$); Anal. Calc. for: $C_{18}H_{28}FeSi$ (328.347): C, 65.84; H, 8.59; Fe, 17.01. Found: C, 65.52; H, 8.55%; Fe, 17.12%.

4.8. General procedure for the synthesis of trinuclear ferrocenyl based organosilane

A 25 ml round-bottom flask with magnetic stirrer was charged with 1,1′-bis(3-butenyl) alkylferrocene (1 mmol), [4-(alkylferrocenyl)butyl]dimethylsilane (2 mmol) and 15 ml dry toluene as solvent. 30 μl of the Karstedt catalyst ($[Pt]/[Si–H] = 3.1 \times 10^{-6}$) was added. The FT-IR spectroscopy was utilized to follow the progress of the reaction, by monitoring the loss of the Si–H absorption. The reaction mixture was stirred at room temperature until the complete disappearance of Si–H bond in FT-IR spectra. The solvent was evaporated under reduced pressure and the residue purified by column chromatography with *n*-hexane as eluant to give the corresponding products. Specific details are given for each compound.

*4.8.1. 1,1′-bis[4-[[4-(dimethylsilyl)butyl]ferrocenyl]butyl]ferrocene (**8a**)*

From 0.29 g **3a** and 0.60 g **6a**, 0.61 g of dark orange oil was obtained in 68% yield. FT-IR (KBr, cm^{-1}): 3084 (Cp–H), 2918 (C–H), 1694, 1462 (C=C), 1253, 815 (C–Si), 1099 (Cp), 506 (Cp–Fe); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): −0.03 (S, 12H, $Si(C\mathbf{H}_3)_2$), 0.48–0.54 (t, 8H, −$C\mathbf{H}_2SiMe_2$), 1.29–1.40 (m, 8H, −$C\mathbf{H}_2CH_2SiMe_2$), 1.48–1.58 (m, 8H, $CpCH_2C\mathbf{H}_2$−), 2.29–2.33 (t, 8H, $CpC\mathbf{H}_2$), 4.03 (d, 8H, *J* = 1.3 Hz, $C_5\mathbf{H}_4$), 4.05 (d, 8H, *J* = 1.3 Hz, −$CH_2C_5\mathbf{H}_4$), 4.09 (s, 10H, $C_5\mathbf{H}_5$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −4.30 (−$Si(\mathbf{C}H_3)_2$), 21.11, 21.64 ($\mathbf{C}H_2SiMe_2$), 28.21, 28.33 (−$\mathbf{C}H_2$−), 34.09, 34.43 ($Cp\mathbf{C}H_2$), 66.43, 66.76, 66.83, 67.58, 67.60 (Cp), 87.42, 87.56 ($CpCH_2$); Anal. Calc. for: $C_{50}H_{70}Fe_3Si_2$ (894.82): C, 67.11; H, 7.88; Fe, 18.72. Found: C, 66.77; H, 7.83; Fe, 18.84%.

*4.8.2. 1,1′-bis[4-[[4-(dimethylsilyl)butyl]ferrocenyl]butyl] ethylferrocene (**8b**)*

From 0.32 g **3b** and 0.60 g **6a**, 0.58 g of dark orange oil was obtained in 63% yield. FT-IR (KBr, cm^{-1}): 3089 (Cp–H), 2924 (C–H), 1650, 1457 (C=C), 1250, 817 (C–Si), 1026 (Cp), 506 (Cp–Fe); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): −0.03 (S, 12H, $Si(C\mathbf{H}_3)_2$), 0.49–0.53 (t, 8H, $C\mathbf{H}_2SiMe_2$), 1.12–1.16 (t, 3H, $C\mathbf{H}_3$), 1.30–1.35 (m, 8H, $C\mathbf{H}_2CH_2SiMe_2$), 1.48–1.54 (m, 8H, $CpCH_2C\mathbf{H}_2$), 2.29–2.35 (m, 10H, $CpC\mathbf{H}_2$), 3.87–4.00 (m, 7H, $C_5\mathbf{H}_4$, $C_5\mathbf{H}_3$), 4.04–4.05 (d, 8H, $C_5\mathbf{H}_4$), 4.10 (s, 10H, $C_5\mathbf{H}_5$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −4.29 (-$Si(\mathbf{C}H_3)_2$), 13.74 ($\mathbf{C}H_3$), 21.17, 21.64 ($\mathbf{C}H_2SiMe_2$), 27.98, 28.35 (−$\mathbf{C}H_2$−), 30.38, 33.99, 34.21, 34.35 ($Cp\mathbf{C}H_2$), 65.32, 65.83, 66.58, 66.76, 67.14, 67.32, 67.38, 67.60 (Cp), 86.14, 87.38, 87.56, 88.28 ($CpCH_2$); Anal. Calc. for: $C_{52}H_{74}Fe_3Si_2$ (922.87): C, 67.68; H, 8.08; Fe, 18.15. Found: C, 67.36; H, 8.12; Fe, 18.07%.

*4.8.3. 1,1′-bis[4-[[4-(dimethylsilyl)butyl]ferrocenyl]butyl] propylferrocene (**8c**)*

From 0.34 g **3c** and 0.60 g **6a**, 0.55 g of dark orange oil was obtained in 59% yield. FT-IR (KBr, cm^{-1}): 3088 (Cp–H), 2923 (C–H), 1681, 1455 (C=C), 1251, 817 (C–Si), 1102 (Cp), 490 (Cp–Fe); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): −0.03 (s, 12H, $Si(C\mathbf{H}_3)_2$), 0.48–0.51 (t, 8H, $C\mathbf{H}_2SiMe_2$), 0.90–0.93 (t, 3H, $C\mathbf{H}_3$), 1.31–1.34 (m, 8H, $C\mathbf{H}_2CH_2SiMe_2$), 1.44–1.55 (m, 10H, $CpCH_2C\mathbf{H}_2$), 2.30–2.34 (t, 10H, $CpC\mathbf{H}_2$), 3.85–4.00 (m, 7H, $C_5\mathbf{H}_4$, $C_5\mathbf{H}_3$), 4.03–4.05 (d, 8H, $C_5\mathbf{H}_4$), 4.08 (s, 10H, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −4.28 (−$Si(\mathbf{C}H_3)_2$), 13.23 ($\mathbf{C}H_3$), 21.26, 21.53 ($\mathbf{C}H_2SiMe_2$), 23.89 ($\mathbf{C}H_2$–CH_3), 27.60, 28.02 (−$\mathbf{C}H_2$−), 31.29, 32.49, 34.27, 34.64 ($Cp\mathbf{C}H_2$), 65.57, 65.84, 66.43, 66.76, 67.13, 67.58, 67.61, 67.85 (Cp), 86.18, 87.42, 87.50, 88.26($CpCH_2$); Anal. Calc. for: $C_{53}H_{76}Fe_3Si_2$ (936.90): C, 67.95; H, 8.18; Fe, 17.88. Found: C, 67.62; H, 8.14; Fe, 17.79%.

*4.8.4. 1,1′-Bis[4-[[4-(dimethylsilyl)butyl]ferrocenyl]butyl] butylferrocene (**8d**)*

From 0.35 g **3d** and 0.60 g **6a**, 0.52 g of dark orange oil was obtained in 57% yield. FT-IR (KBr, cm^{-1}): 3088 (Cp–H), 2925 (C–H), 1648, 1458 (C=C), 1254, 812 (C–Si), 1100 (Cp), 490 (Cp–Fe);^{1}H NMR (400 MHz, $CDCl_3$, ppm): −0.03 (s, 12H, $Si(C\mathbf{H}_3)_2$), 0.49–0.53 (t, 8H, $C\mathbf{H}_2SiMe_2$), 0.89–0.93 (t, 3H, CH_3), 1.30–1.35 (m, 10H, $CpCH_2CH_2C\mathbf{H}_2$), 1.45–1.55 (m, 10H, $CpCH_2C\mathbf{H}_2$), 2.30–2.35 (t, 10H, Cp–CH_2), 3.85–3.99 (m, 7H, $C_5\mathbf{H}_4$, $C_5\mathbf{H}_3$), 4.04–4.05 (d, 8H, $C_5\mathbf{H}_4$), 4.09 (s, 10H, C_5H_5); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −4.35 ($Si(\mathbf{C}H_3)_2$), 13.05 ($\mathbf{C}H_3$), 21.36, 21.64 ($\mathbf{C}H_2SiMe_2$), 22.85 ($\mathbf{C}H_2$–CH_3), 25.38, 27.85, 28.10 (−$\mathbf{C}H_2$−), 31.21, 33.27, 34.35, 34.71 ($Cp\mathbf{C}H_2$), 66.35, 66.47, 66.73, 67.21, 67.35, 67.62, 67.86, 68.49 (Cp), 86.25, 87.16, 87.73, 88.28($CpCH_2$); Anal. Calc. for: $C_{54}H_{78}Fe_3Si_2$ (950.93): C, 68.21; H, 8.27; Fe, 17.62. Found: C, 67.82; H, 8.22; Fe, 17.53%.

*4.8.5. 1,1′-Bis [4-[[4-(dimethylsilyl)butyl]ethylferrocenyl]butyl] ferrocene (**8e**)*

From 0.29 g **3a** and 0.66 g **6b**, 0.61 g of dark orange oil was obtained in 64% yield. FT-IR (KBr, cm^{-1}): 3088 (Cp–H), 2925 (C–H), 1645, 1459 (C=C), 1250, 813 (C–Si), 1025 (Cp), 491 (Cp–Fe); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): −0.04 (s, 12H, $Si(C\mathbf{H}_3)_2$), 0.48–0.53 (t, 8H, −$C\mathbf{H}_2SiMe_2$), 1.14–1.16 (t, 6H, $C\mathbf{H}_3$), 1.28–1.38 (m, 8H, −$C\mathbf{H}_2CH_2SiMe_2$), 1.47–1.54 (m, 8H, $CpCH_2C\mathbf{H}_2$−), 2.27–2.33 (t, 12H, $CpC\mathbf{H}_2$), 3.94–4.03 (m, 24H, Cp); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −4.26 ($Si(\mathbf{C}H_3)_2$), 13.24 (−$CH_2\mathbf{C}H_3$), 21.34, 21.57 ($\mathbf{C}H_2SiMe_2$), 27.57, 27.88 (−$\mathbf{C}H_2$−), 31.39, 34.24, 34.46 ($Cp\mathbf{C}H_2$), 66.35, 66.57, 67.23, 67.56, 67.74, 68.27 (Cp), 86.31, 87.71, 87.43 ($CpCH_2$); Anal. Calc. for: $C_{54}H_{78}Fe_3Si_2$ (950.93): C, 68.20; H, 8.27; Fe, 17.62. Found: C, 68.56; H, 8.23; Fe, 17.53%.

*4.8.6. 1,1′-Bis[4-[[4-(dimethylsilyl)butyl]ethylferrocenyl]butyl] ethylferrocene (**8f**)*

From 0.32 g **3b** and 0.66 g **6b**, 0.61 g of dark orange oil was obtained in 62% yield. FT-IR (KBr, cm^{-1}): 3099 (Cp–H), 2958 (C–H), 1696, 1466 (C=C), 1256, 813 (C–Si), 1080 (Cp), 492 (Cp–Fe); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): −0.03 (s, 12H, $Si(C\mathbf{H}_3)_2$), 0.49–0.53 (t, 8H, −$C\mathbf{H}_2SiMe_2$), 1.13–1.18 (t, 9H, $C\mathbf{H}_3$), 1.30–1.36 (m, 8H, −$C\mathbf{H}_2CH_2SiMe_2$), 1.46–1.53 (m, 8H, $CpCH_2C\mathbf{H}_2$), 2.25–2.37 (m, 14H, $CpC\mathbf{H}_2$), 3.95–4.04 (m, 23H, Cp); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −4.31 ($Si(\mathbf{C}H_3)_2$), 13.13, 13.53 (−$CH_2\mathbf{C}H_3$), 21.10, 21.65 ($\mathbf{C}H_2$–$SiMe_2$), 28.10, 28.24 (−$\mathbf{C}H_2$−), 30.58, 34.01, 34.25 (Cp–$\mathbf{C}H_2$), 65.21, 65.75, 66.17, 66.55, 66.83, 66.96, 67.51, 67.83, 67.92 (Cp), 86.37, 86.44, 87.26, 87.49, 88.14 (Cp–CH_2); Anal. Calc. for: $C_{56}H_{82}Fe_3Si_2$ (978.98): C, 68.71; H, 8.44; Fe, 17.11. Found: C, 68.38; H, 8.39; Fe, 17.01%.

*4.8.7. 1,1′-Bis[4-[[4-(dimethylsilyl)butyl]ethylferrocenyl]butyl] propylferrocene (**8g**)*

From 0.34 g **3c** and 0.66 g **6b**, 0.56 g of dark orange oil was obtained in 56% yield. FT-IR (KBr, cm^{-1}): 3084 (Cp–H), 2923 (C–H), 1639, 1452 (C=C), 1251, 819 (C–Si), 1101 (Cp), 493 (Cp–Fe); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): −0.03 (S, 12H, $Si(C\mathbf{H}_3)_2$), 0.51–0.53 (t, 8H, $C\mathbf{H}_2SiMe_2$), 0.91–0.93 (t, 3H, $CpCH_2CH_2C\mathbf{H}_3$), 1.15–1.18 (t, 6H, −$CpCH_2C\mathbf{H}_3$), 1.31–1.35 (m, 8H, $C\mathbf{H}_2CH_2SiMe_2$), 1.47–1.53 (m, 10H, $CpCH_2C\mathbf{H}_2$), 2.25–2.36 (m, 14H, $CpC\mathbf{H}_2$), 3.94–4.04 (m, 23H, Cp); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −4.31 ($Si(\mathbf{C}H_3)_2$), 13.24, 13.67 (−$CH_2\mathbf{C}H_3$), 21.13, 21.28 ($\mathbf{C}H_2SiMe_2$), 22.05, 26.78, 28.03 (−$\mathbf{C}H_2$−), 31.38, 31.52, 34.28, 34.36 ($Cp\mathbf{C}H_2$), 65.59, 66.46, 66.58, 67.15, 67.34, 67.49, 67.58, 67.78, 68.32 (Cp), 86.31, 86.42, 87.15, 87.41, 88.25 ($CpCH_2$); Anal. Calc. for: $C_{57}H_{84}Fe_3Si_2$ (993.00): C, 68.94; H, 8.53; Fe, 16.87. Found: C, 68.57; H, 8.48; Fe, 16.79%.

4.8.8. *1,1′-Bis[4-[[4-(dimethylsilyl)butyl]ethylferrocenyl]butyl] butylferrocene (**8h**)*

From 0.35 g **3d** and 0.66 g **6b**, 0.65 g of dark orange oil was obtained in 65% yield. FT-IR (KBr, cm^{-1}): 3084 (Cp–H), 2924 (C–H), 1644, 1452 (C=C), 1256, 810 (C–Si), 1096 (Cp), 492 (Cp–Fe); ^1H NMR (400 MHz, $CDCl_3$, ppm): −0.03 (s, 12H, Si($\mathbf{CH_3}$)$_2$), 0.50–0.53 (t, 8H, $C\mathbf{H_2}SiMe_2$), 0.90–0.94 (t, 3H, $CpCH_2CH_2CH_2C\mathbf{H_3}$), 1.15–1.19 (m, 6H, $CpCH_2C\mathbf{H_3}$), 1.30–1.36 (m, 10H, $CpCH_2CH_2C\mathbf{H_2}$), 1.48–1.55 (m, 10H, $CpCH_2C\mathbf{H_2}$), 2.28–2.35 (m, 14H, $CpC\mathbf{H_2}$), 3.84–4.04 (m, 23H, Cp); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): −4.33 (Si($\mathbf{C}H_3$)$_2$), 13.18, 13.66 ($CH_2\mathbf{C}H_3$), 21.14, 21.32 ($\mathbf{C}H_2SiMe_2$), 21.64, 26.39, 27.84, 28.15 (–$\mathbf{C}H_2$–), 31.25, 31.38, 34.36, 34.65 ($Cp\mathbf{C}H_2$), 65.48, 65.68, 67.26, 67.35, 67.53, 67.65, 67.94, 68.31, 68.44 (Cp), 86.28, 87.11, 87.36, 87.73, 88.21($CpCH_2$); Anal. Calc. for: $C_{58}H_{86}Fe_3Si_2$ (1007.03): C, 69.18; H, 8.61; Fe, 16.64. Found: C, 68.79; H, 8.56, Fe, 16.55%.

Acknowledgment

We gratefully acknowledge the financial support for this work by the Research Council of University of Tabriz. The authors deeply thank Miss Sana Farhoudian for her careful review and with special thanks to Dr. K. Asadpour for his helpfull suggestion in electrochemical field of this work.

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