

# Synthesis of novel bis[(tris(dimethylsilyl)methyl)alkyl]ferrocene derivatives as new ferrocenyl multi-functional silyl ether compounds

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## Abstract

Some new branched polysilyl ethers with a ferrocene core were synthesized through treatment of 1,1'-bis[tris(dimethylsilyl)methyl]alkylferrocenes with various alcohols by Karstedt catalyst. Bis(chloroalkyl)ferrocenes are synthesized by acylation of ferrocene with 3-chloropropanoyl chloride and 4-chlorobutanoyl chloride. The obtained 1,1'-bis(3-chloropropanoyl)ferrocene and 1,1'-bis(4-chlorobutanoyl)ferrocene underwent a reduction and chlorides were replaced by bromides, and then they were treated with  $(\text{Me}_3\text{Si})_3\text{CLi}$  and  $(\text{HMe}_2\text{Si})_3\text{CLi}$  give silane compounds **6a-b** and **7a-b**.

**Keywords:** Ferrocene, silane, silyl ether, alcoholysis, dehydrocoupling

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## Introduction

Dendrimers with refined inner and outer structural conformations give access to macromolecular materials having special properties such as nanoscale catalysts, drug delivery, chemical sensors and so on.<sup>1-4</sup> There are many publications which are concerned with the synthesis and identification of the dendritic compounds.<sup>5-6</sup> The first dendrimers studied were those with an organic skeleton, and there were followed by transition metal-containing dendritic molecules. More recently, examples of dendrimers with silicon-included, such as carbosilane and siloxane, that have come to the fore.<sup>7,8</sup> The dendrimers including silicon can be classified into three main categories, having siloxane (Si-O),<sup>9</sup> carbosilane (Si-C)<sup>10-15</sup> or polysilane (Si-Si)<sup>16</sup> backbones. Synthetic methods for the preparation of silicon-containing dendrimers were reported by many researchers who used the simple repeating procedures such as hydrosilylation, dehydrocoupling, alkenylation as well as alcoholysis.<sup>17-22</sup>

The chemistry of ferrocene-based structures has attracted much attention because of its importance in the fields of redox electrochemistry, materials science, novel materials, organic

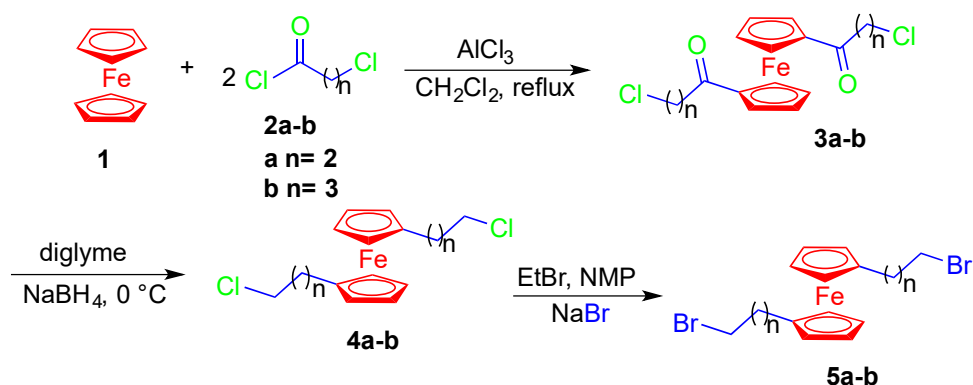
synthesis,<sup>23-26</sup> catalysis for asymmetric synthesis,<sup>27-30</sup> biology<sup>31-33</sup> and non-linear optical materials.<sup>34-36</sup> Recent discoveries of a broad range of applications in the biomedical and aerospace industries such as coating and catalysts greatly increased the interest in the incorporation of transition metals into organic monomers and polymers.<sup>37-41</sup>

Since the synthesis of the first silyl metal complex ( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)<sub>2</sub>SiMe<sub>3</sub> by Wilkinson in 1956, research on transition metal silyl compounds has continued because these compounds are assumed to be the key intermediates in a number of important stoichiometric and catalytic transformations.<sup>42-43</sup> Herein we report the first simple silyl etheric dendrimer generated with a ferrocene core and six branched silyl ethers by the dehydrocoupling reaction using the Karstedt catalyst.

## Results and Discussion

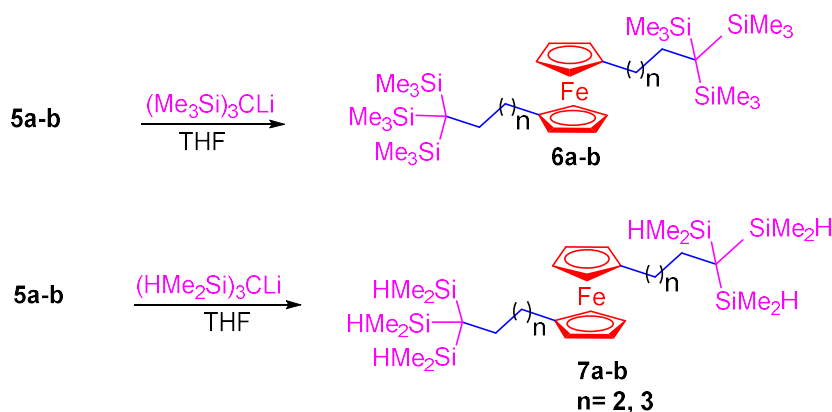
We have recently used dehydrocoupling reactions for the preparation of tris(alkoxydimethylsilyl)methanes,<sup>44</sup> calix[4]arenes bearing silylether groups<sup>45</sup> and functionalized poly(methylalkoxy)siloxanes<sup>46</sup> under mild conditions using Karstedt catalysis. We also applied this methodology in the synthesis of ferrocenyl silyl ethers for the attachment of ferrocenyl groups to the cellulose acetate butyrate backbone.<sup>47</sup> In continuation of our work on ferrocene and silane compounds, we designed and synthesized some six new branched Si-H groups cored with a metallocene group. By applying our experiences from these methodologies, we aimed to introduce a completely new branched polysilyl ether with a ferrocene core.

1,1'-Bis(3-chloropropanoyl)ferrocene **3a** and 1,1'-bis(4-chlorobutanoyl)ferrocene **3b** were prepared by Friedel-Crafts acylation of ferrocene **1** with 3-chloropropanoyl chloride **2a** and 4-chlorobutanoyl chloride **2b**, respectively, in dry CH<sub>2</sub>Cl<sub>2</sub> in the presence of AlCl<sub>3</sub> as catalyst under reflux conditions. After reduction of the carbonyl groups in **3a-b** by NaBH<sub>4</sub> in diglyme, bis(chloroalkyl)ferrocene derivatives (**4a-b**) were obtained in high yields.<sup>48</sup> The chlorine atoms in compounds **4a-b** were replaced by bromine using ethyl bromide and sodium bromide in NMP (*N*-methyl-2-pyrrolidone) as solvent at 60 °C for five days to give bis(bromoalkyl)ferrocene derivatives (**5a-b**) (Scheme 1).<sup>49</sup>



**Scheme 1.** Synthesis of **5a** and **5b**.

Tris(trimethylsilyl)methane was prepared by the reaction of chlorotrimethylsilane, chloroform and Li in THF. Tris(trimethylsilyl)methane reacted with MeLi under reflux conditions in THF to produce  $(\text{Me}_3\text{Si})_3\text{CLi}$  (Scheme 2).<sup>50</sup> The precursor  $(\text{HMe}_2\text{Si})_3\text{CH}$  was made by the reaction of  $\text{CHBr}_3$  and Mg with  $\text{HMe}_2\text{SiCl}$  in THF,<sup>45,51</sup> which resulted in  $(\text{HMe}_2\text{Si})_3\text{CLi}$  after treatment with LDA (lithium diisopropylamide) at room temperature.



**Scheme 2.** Synthesis of **6a-b** and **7a-b**.

1,1'-Bis(bromoalkyl)ferrocenes **5a-b** were converted into 1,1'-bis[tris(trimethylsilyl)methyl]alkylferrocenes (**6a-b**) and 1,1'-bis[tris(dimethylsilyl)methyl]alkylferrocenes (**7a-b**) by treatment with  $(\text{Me}_3\text{Si})_3\text{CLi}$  and  $(\text{HMe}_2\text{Si})_3\text{CLi}$ , respectively, in THF at 0 °C in good to high yields (Table 1).

**Table 1.** Synthesis of compounds **6a-b** and **7a-b**

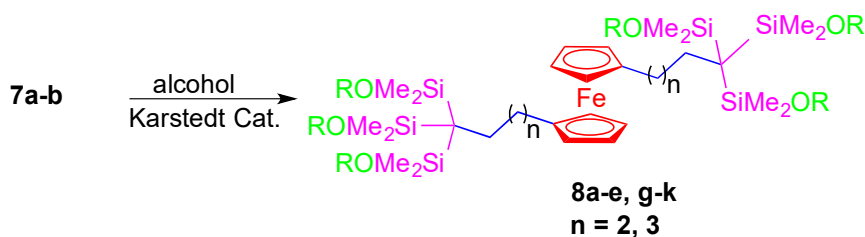
Entry	compounds	Reagent	products	Time(h)	Yields(%) <sup>a</sup>
1	<b>5a</b>	(Me <sub>3</sub> Si) <sub>3</sub> CLi	<b>6a</b>	6	90
2	<b>5b</b>	(Me <sub>3</sub> Si) <sub>3</sub> CLi	<b>6b</b>	6	92
3	<b>5a</b>	(HMe <sub>2</sub> Si) <sub>3</sub> CLi	<b>7a</b>	8	87
4	<b>5b</b>	(HMe <sub>2</sub> Si) <sub>3</sub> CLi	<b>7b</b>	8	90

<sup>a</sup> Isolated yields.

As shown by the results in Table 2, for the synthesis of the target molecule **8a**, the conversion was tested in various solvents such as THF and acetone<sup>52</sup> in the presence of Karstedt catalyst, but was not complete at room temperature or under reflux condition after 12 hours. Methanol was tried as both the solvent and the reagent in this reaction, but at room temperature, no desired product was obtained after 12 hours. However, under reflux conditions the desired polysilyl ether **8a** was produced after 6 hours in excellent yield (Entry 1, Table 3). Therefore, this reaction was performed with other alcohols as reagent and solvent with heating at 60-80 °C to give the desired polysilyl ethers in good to excellent yields (Table 3).

**Table 2.** Optimization of reaction conditions for synthesis of **8a**

Entry	Solvent	Condition	Time/h	Yield/%
1	THF	rt	12	-
2	THF	reflux	12	-
3	acetone	rt	12	-
4	methanol	rt	12	-
5	methanol	reflux	6	92

**Table 3.** Synthesis of 1,1'-bis[tris(alkoxydimethylsilyl)methyl]alkylferrocenes<sup>a</sup>

Entry	Compounds	Alcohol	Products	Yield (%) <sup>b</sup>
1	<b>7a</b>	CH <sub>3</sub> OH	<b>8a</b>	90
2	<b>7a</b>	CH <sub>3</sub> CH <sub>2</sub> OH	<b>8b</b>	85
3	<b>7a</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	<b>8c</b>	82
4	<b>7a</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	<b>8d</b>	80

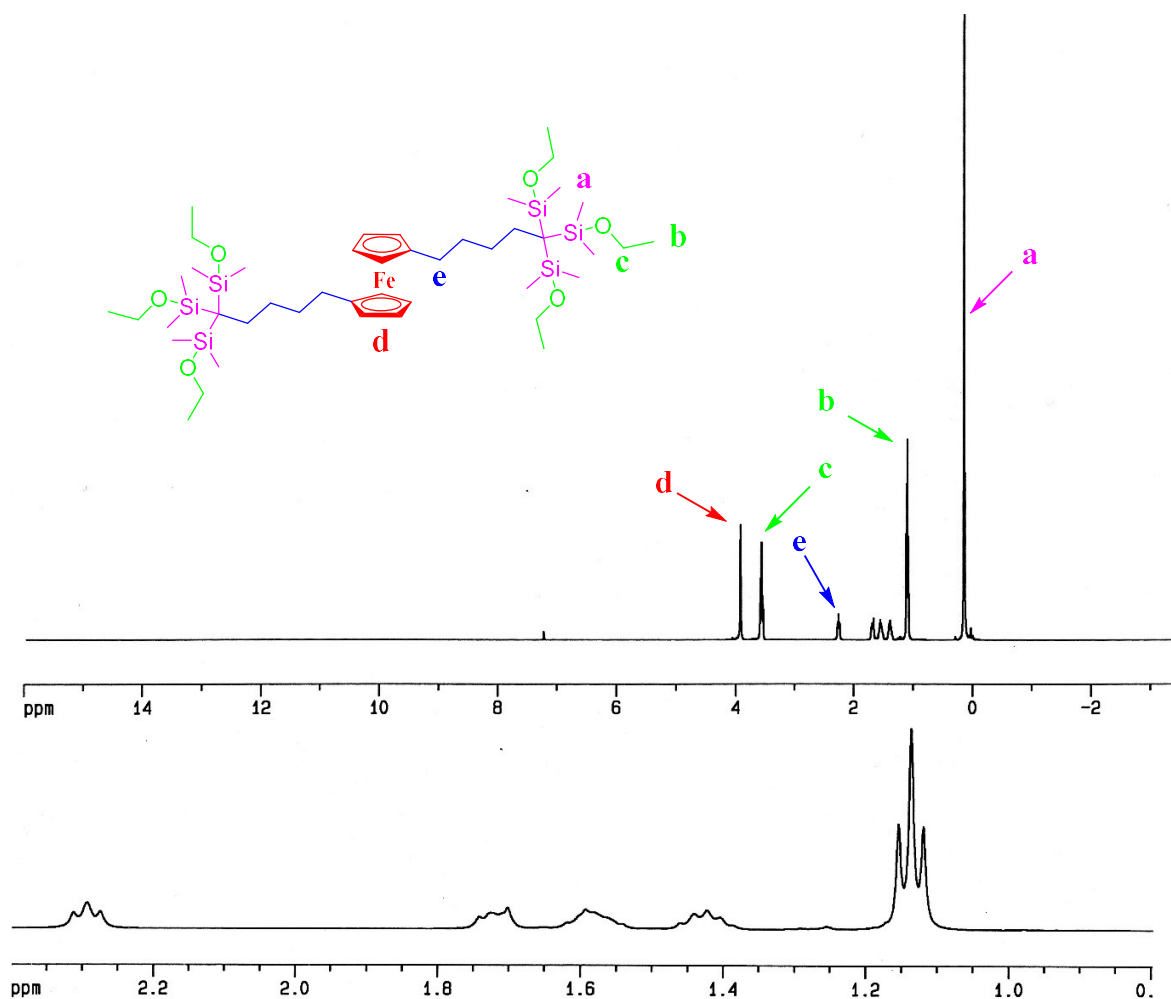
**Table 3 (continued)**

Entry	Compounds	Alcohol	Products	Yield (%) <sup>b</sup>
5	<b>7a</b>	PhCH <sub>2</sub> OH	<b>8e</b>	89
6	<b>7a</b>	PhOH	<b>8f</b>	-
7	<b>7b</b>	CH <sub>3</sub> OH	<b>8g</b>	92
8	<b>7b</b>	CH <sub>3</sub> CH <sub>2</sub> OH	<b>8h</b>	89
9	<b>7b</b>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	<b>8i</b>	86
10	<b>7b</b>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH	<b>8j</b>	83
11	<b>7b</b>	PhCH <sub>2</sub> OH	<b>8k</b>	92

<sup>a</sup> reaction conditions: **7a-b** (0.20g) and ROH (20 mL), Karstedt catalyst ([Pt]/[Si-H]= 7.2×10<sup>-3</sup>) under dry argon at 60-80 °C. <sup>b</sup> Isolated yields

Primary aliphatic alcohols with long alkyl chains were less effective than those with short chains (Table 3). Alcohols with an aromatic ring such as benzyl alcohol gave the corresponding silyl ethers in high yields (Entry 5, Table 3, 92%), but phenols failed to give the desired phenolic compound (Entry 6 Table 3). We also used secondary alcohols in this reaction but the reaction did not go to completion, and our attempt at the synthesis of branched polysilyl ether with secondary alcohols failed and one or two alcohols react with Si-H bond in each side. Tertiary alcohols such as *tert*-butanol did not react with the silane. Also, attempted use of kojic acid as a biological alcohol, was unsuccessful in this reaction.

The <sup>1</sup>H NMR spectrum of compound **8b** (Figure 1) shows the signal for the ferrocenyl protons at 3.95 ppm, the singlet ascribed to SiMe<sub>2</sub> at 0.18 ppm, CH<sub>2</sub>O protons at 3.57-3.62, and CH<sub>3</sub> protons at 1.12-1.15 ppm.



**Figure 1.** <sup>1</sup>H NMR spectra of 1,1'-bis[4-(tris(ethoxydimethylsilyl)methyl)butyl]ferrocene.

## Conclusions

In summary, we report the synthesis of 1,1'-bis[tris(trimethylsilyl)methyl]alkylferrocenes and 1,1'-bis[tris(dimethylsilyl)methyl]alkylferrocenes from treatment of (Me<sub>3</sub>Si)<sub>3</sub>CLi and (HMe<sub>2</sub>Si)<sub>3</sub>CLi with 1,1'-bis(bromoalkyl)ferrocene derivatives (**5a-b**).

1,1'-[Tris(alkoxydimethylsilyl)methyl]alkylferrocenes were prepared by dehydrocoupling reactions of hydrosilane derivatives with various aliphatic and benzylic alcohols in the presence of the Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene). These products are potentially capable of various applications such as dendrimer cores, nano materials, macromolecules and intermediates in organic synthesis.

## Experimental Section

**General.** Chemicals were either prepared in our laboratory or purchased from Merck, Fluka and Aldrich. Commercial products were used without purification.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature and with  $\text{CDCl}_3$  as solvent. The FTIR spectra were recorded on a Bruker-Tensor 270 spectrometer. The mass spectra were obtained with a GC-Mass Agilent quadrupole mode 5973N instrument, operating at 70 eV. Elemental analyses were carried out with an Elementar vario EL III instrument.

**Preparation of 1,1'-bis(chloroalkyl)ferrocenes (4a-4b).** A solution of 4-chlorobutanoyl chloride (15.28 g, 108 mmol) or 3-chloropropionyl chloride (13.60 g, 108 mmol) in 50 mL dry  $\text{CH}_2\text{Cl}_2$  was added drop wise to a suspension of anhydrous  $\text{AlCl}_3$  (15.89 g, 119 mmol) in 100 mL dry  $\text{CH}_2\text{Cl}_2$  at rt. The mixture was stirred at rt for 1 h under argon. The obtained homogeneous yellow solution was added dropwise to a solution of ferrocene (54 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (130 mL) at 0 °C. The solution turned to dark purple, and was refluxed for 8 h, and then a solution of  $\text{NaBH}_4$  (4.09 g, 108 mmol) in diglyme (50 mL) was added to the mixture while maintaining the solution temperature at less than or equal to 0 °C. A dark orange solution was formed and stirred at 0 °C for 1 h. The mixture was hydrolyzed by the addition of  $\text{H}_2\text{O}$  (120 mL) while keeping its temperature at 0 to 5 °C. The mixture was allowed to separate by settling and the organic phase, was withdrawn. The aqueous phase was extracted by  $\text{CH}_2\text{Cl}_2$ , (50 mL) which was repeated 3 times and then all the organic phases were combined and washed with brine (100 mL). The  $\text{CH}_2\text{Cl}_2$  was distilled off under atmospheric pressure and the diglyme was distilled off under reduced pressure. The residue was purified by column chromatography on silica gel with *n*-hexane as eluant.

**1,1'-Bis(3-chloropropyl)ferrocene (4a).** Brown oil (90%); FTIR ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3084 (Cp-H), 2932, 2853 (C-H), 1650, 1441 (C=C), 1039, 495 (Cp), 815 ( $\text{CH}_2\text{-Cl}$ );  $^1\text{HNMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.91-1.98 (m, 4H, *J* 6.5 Hz, Cp- $\text{CH}_2\text{-CH}_2$ ), 2.47-2.51 (t, 4H, *J* 7.6 Hz, Cp- $\text{CH}_2$ ), 3.52-3.55 (t, 4H, *J* 6.5 Hz,  $\text{CH}_2\text{-Cl}$ ), 4.01-4.04 (d, 8H, *J* 8.1 Hz, Cp);  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 26.6, 32.7, ( $-\text{CH}_2-$ ), 32.9 ( $\text{CH}_2\text{-Cl}$ ), 67.7, 67.1 (Cp), 86.1 ( $\text{C}_1$  Cp); *m/z* (EI) 338 [ $\text{M}$ ] $^+$ , 340 [ $\text{M}+2$ ] $^+$ . Calc. for  $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{Fe}$ : C, 56.68; H 5.95. Found: C, 56.53; H, 5.91%.

**1,1'-Bis(4-chlorobutyl)ferrocene (4b).** Brown oil (92% yield). FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  = 3085 (Cp-H), 2936, 2857 (C-H), 1640, 1445 (C=C), 1105, 492 (Cp), 819 (C-Cl);  $^1\text{HNMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  = 1.62-1.66 (m, 4H, *J* 8 Hz, Cp- $\text{CH}_2\text{-CH}_2$ ), 1.76-1.82 (m, 4H, *J* 6.5 Hz,  $\text{CH}_2\text{-CH}_2\text{-Cl}$ ), 2.33-2.37 (t, *J* 7.6 Hz, 4H, Cp- $\text{CH}_2$ ), 3.53-3.56 (t, 4H, *J* 6.6 Hz  $\text{CH}_2\text{-Cl}$ ), 3.98-4.01 (d, 8H, Cp);  $^{13}\text{CNMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  = 27.3, 27.6, 31.28 ( $-\text{CH}_2-$ ), 43.9 ( $\text{CH}_2\text{-Cl}$ ), 66.8, 67.5 (Cp), 87.4 ( $\text{C}_1$  Cp); *m/z* (EI) 366 [ $\text{M}$ ] $^+$ , 368 [ $\text{M}+2$ ] $^+$ . Calc. for  $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{Fe}$ : C, 58.89; H 6.59. Found: C, 58.75; H, 6.53%.

**Preparation of 1,1'-bis(bromoalkyl)ferrocene (5a-5b).** A mixture of 0.01 mol of 1,1'-bis(bromoalkyl)ferrocene derivatives, EtBr (20 mL), and NaBr (0.24 g, 0.004 mol) in NMP (30 mL) was heated at 65 °C for 5 days. The mixture was allowed to cool and then was poured into a

mixture of ice-water, and brine, in a separatory funnel. The lower layer was removed and the organic layer washed with brine and distilled water. The solvent was removed and the product was purified by column chromatography on silica. A brown band was eluted with a hexane/EtOAc (6:2) mixture to give the product.

**1,1'-Bis(3-bromopropyl)ferrocene (5a).** From 1,1'-bis(3-chloropropyl)ferrocene (4 g), a brown oil was obtained (4.63 g, 92%). FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3085$  (Cp-H), 2931, 2848 (C-H), 1638, 1437 (C=C), 1029, 497, (Cp), 820 (C-Br);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 1.99$ -2.06 (m, 4H,  $J$  6.6 Hz, CpCH<sub>2</sub>-CH<sub>2</sub>), 2.47-2.51 (t, 4H,  $J$  7.5 Hz, Cp-CH<sub>2</sub>), 3.39-3.42 (t, 4H,  $J$  6.5 Hz, CH<sub>2</sub>-Br), 4.01-4.04 (d, 8H, Cp);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 26.6$ , 32.7, 32.9 (-CH<sub>2</sub>-), 67.0, 67.7 (Cp), 86.1 (C<sub>1</sub> Cp);  $m/z$  (EI) 426 [M]<sup>+</sup>, 428 [M+2]<sup>+</sup>. Calc. for C<sub>16</sub>H<sub>20</sub>Br<sub>2</sub>Fe: C, 44.90; H 4.71. Found: C, 44.79; H, 4.65%.

**1,1'-Bis(4-bromobutyl)ferrocene (5b).** From 1,1'-bis(4-chlorobutyl)ferrocene (4.0 g), a brown oil (4.51 g, 91%) was obtained. FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3085$  (Cp-H), 2933, 2854 (C-H), 1643, 1439 (C=C), 1105, 1028, 491 (Cp), 818 (C-Br);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 1.60$ -1.68 (m, 4H,  $J$  7.2 Hz, Cp-CH<sub>2</sub>-CH<sub>2</sub>), 1.84-1.91 (m, 4H,  $J$  6.8 Hz, CH<sub>2</sub>-CH<sub>2</sub>-Br), 2.32-2.36 (t, 4H,  $J$  7.7 Hz, Cp-CH<sub>2</sub>), 3.39-3.43 (t, 4H,  $J$  6.7 Hz, CH<sub>2</sub>-Br), 3.97-3.99 (d, 8H, Cp);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 27.5$ , 28.6, 31.4, 32.8 (-CH<sub>2</sub>-), 66.8, 67.6 (Cp), 87.4 (C<sub>1</sub> Cp);  $m/z$  (EI) 454 [M]<sup>+</sup>, 456 [M+2]<sup>+</sup>, 199 [FcCH<sub>2</sub>]<sup>+</sup>, 121 [CpFe]<sup>+</sup>. Anal. Calc. for C<sub>18</sub>H<sub>24</sub>Br<sub>2</sub>Fe: C, 47.41; H, 5.30. Found: C, 47.35; H, 5.24%.

**Preparation of tris(trimethylsilyl)methyl lithium, (Me<sub>3</sub>Si)<sub>3</sub>CLi.** The reagent was prepared as described by Gröbel and co-workers.<sup>47</sup>

**Preparation of tris(dimethylsilyl)methyl lithium, (HSiMe<sub>2</sub>)<sub>3</sub>CLi.** A 50 mL round-bottom flask equipped with a stirrer, septum, and a gas-inlet needle was charged with *i*-Pr<sub>2</sub>NH (1.06 g, 10.6 mmol) and THF (20 mL). The flask was placed in a water ice bath and then *n*-BuLi (7.6 mL, 1.5 M solution in hexane) was added dropwise to the stirring mixture to form a clear yellow solution. The solution was stirred for an additional 30 min. The lithium diisopropylamide (LDA) solution was transferred into a dropping funnel then added dropwise to a 50 mL round-bottom flask containing tris(dimethylsilyl)methane, (HSiMe<sub>2</sub>)<sub>3</sub>CH, (2.0 g, 10.6 mmol), in THF (20 mL) under argon at rt. Finally the orange-red solution was stirred at ambient temperature for 10 h.

**Preparation of compounds (6a-b) and (7a-b).** To a stirred solution of (Me<sub>3</sub>Si)<sub>3</sub>CLi or (HSiMe<sub>2</sub>)<sub>3</sub>CLi (5.3 mmol) in THF at 0 °C was added 1,1'-bis(3-bromopropyl)ferrocene **5a** or 1,1'-bis(4-bromobutyl)ferrocene **5b** (5.0 mmol) in THF (10 mL), and the mixture was stirred for 6-8 h at rt. It was then poured into aq NH<sub>4</sub>Cl (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL). The organic phase was washed with H<sub>2</sub>O (100 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent was removed to leave a viscous oil.

**1,1'-Bis[3-(tris(trimethylsilyl)methyl)propyl]ferrocene (6a).** From 1,1'-bis(3-bromopropyl)ferrocene (3.0 g), a yellowish oil (4.62 g, 90%) of was obtained. FTIR (KBr,  $\text{cm}^{-1}$ ):



$\nu = 3085$  (Cp-H), 2952, 2844 (C-H), 1645, 1454 (C=C), 1254, 838 (Si-C), 1025, 956, 496 (Fc);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.1$  (s, 54H,  $\text{SiMe}_3$ ), 1.65-1.69 (m, 8H,  $J$  7 Hz,  $-\text{CH}_2-$ ), 2.24-2.27 (t, 4H,  $J$  7.2 Hz, Cp- $\text{CH}_2$ ), 3.94-3.97 (d, 8H, Cp);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 2.0$  ( $\text{SiMe}_3$ ), 4.8 ( $\text{C}(\text{SiMe}_3)_3$ ), 29.7, 29.9, 30.3 ( $-\text{CH}_2-$ ), 66.6, 67.4 (Cp), 87.6 ( $\text{C}_1$  Cp);  $m/z$  (EI) 730  $[\text{M}]^+$ . Anal. Calc. for  $\text{C}_{36}\text{H}_{74}\text{FeSi}_6$ : C, 59.12; H 10.20. Found: C, 59.02; H, 10.11%.

**1,1'-Bis[4-(tris(trimethylsilyl)methyl)butyl]ferrocene (6b).** From 1,1'-bis(4-bromobutyl)ferrocene (3.0 g), a yellowish oil (4.6 g, 92%) was obtained. FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3086$  (Cp-H), 2952, 2848 (C-H), 1626, 1441 (C=C), 1255, 842 (Si-C), 1039, 495 (Cp), 484 (Fc);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.1$  (s, 54H,  $\text{SiMe}_3$ ), 1.42-1.54 (m, 8H,  $J$  7.2 Hz,  $-\text{CH}_2-$ ), 1.54-1.61 (t, 4H,  $-\text{CH}_2\text{C}(\text{SiMe}_3)_3$ ), 2.29-2.32, (t, 4H,  $J$  7 Hz, Cp- $\text{CH}_2$ ), 3.95-3.96 (d, 8H, Cp);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = 1.8$  ( $\text{SiMe}_3$ ), 5.1 ( $\text{C}(\text{SiMe}_3)_3$ ), 28.4, 29.1, 30.0, 31.9 ( $-\text{CH}_2-$ ), 66.7, 67.5 (Cp), 88.0 ( $\text{C}_1$  Cp);  $m/z$  (EI) 758  $[\text{M}]^+$ . Anal. Calc. for  $\text{C}_{38}\text{H}_{78}\text{FeSi}_6$ : C, 60.10; H 10.35. Found: C, 60.01; H, 10.29%.

**1,1'-Bis[3-(tris(dimethylsilyl)methyl)propyl]ferrocene (7a).** From 1,1'-bis(3-bromopropyl)ferrocene (3.0 g), a yellowish oil (3.95 g, 87%) was obtained. FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3085$  (Cp-H), 2955, 2903 (C-H), 2106 (Si-H), 1589 (Cp), 1253, 849 (Si-C), 1054, 438;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.16$ -0.17 (d, 36H,  $J$  3.7 Hz,  $\text{SiMe}_2$ ), 1.65-1.75 (m, 8H,  $-\text{CH}_2-$ ), 2.25-2.29 (t, 4H,  $J$  7.5 Hz, Cp- $\text{CH}_2$ ), 3.94-3.98 (dd,  $J$  1.5, 8H, Cp), 4.00-4.05 (m,  $J$  3.7 Hz, 6H, Si-H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = -4.1$  ( $\text{SiMe}_2$ ), 0.36 ( $\text{C}(\text{SiMe}_2)_3$ ), 29.0, 29.4, 29.5 ( $-\text{CH}_2-$ ), 66.6, 67.5 (Cp), 87.7 ( $\text{C}_1$  Cp);  $m/z$  (EI): 646  $[\text{M}]^+$ . Anal. Calc. for  $\text{C}_{30}\text{H}_{62}\text{FeSi}_6$ : C, 55.68; H 9.66. Found: C, 55.55; H, 9.59%.

**1,1'-Bis[4-(tris(dimethylsilyl)methyl)butyl]ferrocene (7b).** From 1,1'-[4-bromobutyl]ferrocene (3.0 g), a yellowish oil (4 g, 90%) was obtained. FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3087$  (Cp), 2933, 2851 (C-H), 2107 (Si-H), 1642, 1425 (Cp), 1253, 839 (Si-C), 1028, 889, 493 (Cp);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.15$ -0.16 (d,  $J$  3.1 Hz, 36H,  $\text{SiMe}_2$ ), 1.43-1.48 (m, 8H,  $-\text{CH}_2-$ ), 1.54-1.63 (t, 4H,  $\text{CH}_2\text{C}(\text{SiMe}_2\text{H})_3$ ), 2.29-2.33, (t, 4H,  $J$  7.6 Hz, Cp- $\text{CH}_2$ ), 3.95-3.96, (d, 8H Cp), 4.00-4.03 (m,  $J$  3.5 Hz, 6H, Si-H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = -4.1$  ( $\text{SiMe}_2$ ), 0.40 ( $\text{C}(\text{SiMe}_2)_3$ ), 28.2, 28.3, 29.0, 31.4 ( $-\text{CH}_2-$ ), 68.2, 67.5 (Cp), 87.4 ( $\text{C}_1$  Cp);  $m/z$  (EI): 674  $[\text{M}]^+$ . Anal. Calc. for  $\text{C}_{32}\text{H}_{66}\text{FeSi}_6$ : C, 56.92; H 9.58. Found: C, 56.83; H, 9.43%.

**General procedure for the synthesis of 1,1'-bis[(tris(methoxydimethylsilyl)methyl)alkyl]ferrocene.** A 50 mL round-bottom two-neck flask with magnetic stirrer was charged with **7a** or **7b** (0.20 g, 0.29 mmol **7a** and 0.3 mmol **7b**) and ROH (20 mL) under dry argon. Karstedt catalyst ( $[\text{Pt}]/[\text{Si-H}] = 7.2 \times 10^{-3}$ ) was added and the reaction progress was monitored. Several samples were taken over reaction time and were analyzed by FTIR spectroscopy. The mixture was stirred at 60-80 °C until complete disappearance of the Si-H peak in the FTIR spectra. After completion of the reaction, the mixture was allowed to cool to rt., then the alcohol was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, 10:1 *n*-hexane:EtOAc) to give a highly viscous oily product.

**1,1'-Bis[3-(tris(methoxydimethylsilyl)methyl)propyl]ferrocene (8a).** Yellowish oil, FTIR

(KBr,  $\text{cm}^{-1}$ ):  $\nu = 3096$  (Cp-H), 2925 (C-H), 1638, 1463 (C=C), 1252, 833 (C-Si), 1093, 488 (Cp), 1002 (Si-O);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.21$  (s, 18H, SiMe<sub>2</sub>), 1.76-1.79 (m, 8H, -CH<sub>2</sub>-), 2.22-2.24 (t, 4H,  $J$  7.2 Hz, Cp-CH<sub>2</sub>), 3.37 (s, 18H, OCH<sub>3</sub>), 3.95-3.96 (d, 8H, Cp);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = -0.92$  (SiMe<sub>2</sub>), 16.0, 27.5, 29.7, 30.4 (-CH<sub>2</sub>-), 48.9 (OCH<sub>3</sub>), 65.5, 67.4 (Cp), 88.1 (C<sub>1</sub> Cp); Anal. Calc. for C<sub>36</sub>H<sub>74</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 52.26; H 9.02. Found: C, 52.13; H, 8.89%.

**1,1'-Bis[3-(tris(ethoxydimethylsilyl)methyl)propyl]ferrocene (8b)**. Yellowish oil, FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3092$  (Cp-H), 2930, 2859 (C-H), 1633, 1458 (C=C), 1252, 853 (Si-C), 1096, 1030, 485 (Cp), 954 (Si-O);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.2$  (s, 36H, SiMe<sub>2</sub>), 1.12-1.15 (t, 18H,  $J = 6.9$ , -CH<sub>3</sub>), 1.76-1.86 (m, 8H, -CH<sub>2</sub>-), 2.22-2.26 (t, 4H,  $J$  7.9 Hz, Cp-CH<sub>2</sub>), 3.58-3.63 (q, 12H,  $J$  6.9 Hz, OCH<sub>2</sub>), 3.95-3.96 (d, 8H, Cp), 4.1;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = -0.31$  (SiMe<sub>2</sub>), 15.4, 17.6 (-CH<sub>3</sub>), 27.5, 29.7, 29.8 (-CH<sub>2</sub>-), 63.3 (OCH<sub>2</sub>), 66.8, 67.4 (Cp), 88.3 (C<sub>1</sub> Cp); Anal. Calc. for C<sub>42</sub>H<sub>86</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 55.34; H 9.51. Found: C, 55.42; H, 9.60%.

**1,1'-Bis[3-(tris(propoxydimethylsilyl)methyl)propyl]ferrocene (8c)**. Yellowish oil, FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3095$  (Cp-H), 2928, 2862 (C-H), 1632, 1465 (C=C), 1252, 837 (Si-C), 1094, 487 (Cp), 1007 (Si-O);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.21$  (s, 36H, SiMe<sub>2</sub>), 0.88-0.92 (t, 18H,  $J$  7.3 Hz, -CH<sub>3</sub>), 1.50-1.57 (m, 12H, -CH<sub>2</sub>-), 1.74-1.85 (m, 8H), 2.24-2.28 (t, 4H,  $J$  7.5 Hz, Cp-CH<sub>2</sub>), 3.48-3.51 (t, 12H,  $J$  6.5 Hz, OCH<sub>2</sub>), 3.95-3.96 (d, 8H, Cp);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = -0.32$  (SiMe<sub>2</sub>), 9.6 (-CH<sub>3</sub>), 16.0, 24.8, 27.9, 29.8, 30.7 (-CH<sub>2</sub>), 63.4 (OCH<sub>2</sub>), 66.5, 67.3 (Cp), 88.3 (C<sub>1</sub> Cp); Anal. Calc. for C<sub>48</sub>H<sub>98</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 57.90; H 9.92. Found: C, 57.78; H, 9.86%.

**1,1'-Bis[3-(tris(butoxydimethylsilyl)methyl)propyl]ferrocene (8d)**. Yellowish oil, FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3092$  (Cp-H), 2934, 2859 (C-H), 1675, 1452 (C=C), 1254, 835 (Si-C), 1109, 1009, 488 (Cp), 948 (Si-O);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.21$  (s, 36H, SiMe<sub>2</sub>), 0.88-0.92 (t, 18H,  $J$  7.2 Hz, -CH<sub>3</sub>), 1.32-1.41 (m, 12H, -CH<sub>2</sub>-), 1.45-1.50 (m, 12H, -CH<sub>2</sub>-), 1.78-1.84 (m, 8H, -CH<sub>2</sub>-), 2.22-2.24 (t,  $J$  6.5 Hz, 4H, Cp-CH<sub>2</sub>), 3.50-3.54 (t,  $J$  6.3 Hz, 12H, OCH<sub>2</sub>), 3.96-3.97 (d, 8H, Cp);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = -0.41$  (SiMe<sub>2</sub>), 12.8 (-CH<sub>3</sub>), 15.1, 18.1, 27.6, 29.9, 30.2, 33.8 (CH<sub>2</sub>), 60.8 (OCH<sub>2</sub>), 66.7, 67.8 (Cp), 88.3 (C<sub>1</sub> Cp); Anal. Calc. for C<sub>54</sub>H<sub>110</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 60.06; H 10.27. Found: C, 59.85; H, 10.21%.

**1,1'-Bis[3-(tris(benzyloxydimethylsilyl)methyl)propyl]ferrocene (8e)**. Yellowish oil, FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3093$ , 3030 (Ar-H), 2929, 2857 (C-H), 1643, 1496 (C=C), 1253, 838 (Si-C), 1099, 1027, 489 (Cp) 905 (Si-O);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.31$  (s, 36H, SiMe<sub>2</sub>), 1.25-1.28 (m, 8H,  $J$  6 Hz, -CH<sub>2</sub>-), 2.22-2.26 (t, 4H,  $J$  7.2 Hz, Cp-CH<sub>2</sub>), 3.96-3.97 (d, 8H, Cp), 4.68 (s, 12H, OCH<sub>2</sub>), 7.25-7.35 (m, 8H, Ar-H), 7.33-7.34 (m, 24H, Ar-H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = -0.1$  (SiMe<sub>2</sub>), 15.8, 27.5, 29.7, 29.9, 63.5 (OCH<sub>2</sub>), 66.6, 67.7 (Cp), 88.3 (C<sub>1</sub> Cp), 125.5, 127.5, 127.0, 140.2 (Ar); Anal. Calc. for C<sub>66</sub>H<sub>98</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 67.75; H 7.84. Found: C, 67.62; H, 7.79%.

**1,1'-Bis[4-(tris(methoxydimethylsilyl)methyl)butyl]ferrocene (8g)**. Yellowish oil, FTIR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3085$  (Cp-H), 2934, 2829 (C-H), 1649, 1462 (C=C), 1252, 854, (Si-C), 1088, 497 (Cp) 982 (Si-O);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta = 0.18$  (s, 36H, SiMe<sub>2</sub>), 1.41-1.46 (m, 4H, -CH<sub>2</sub>-), 1.50-1.58 (m, 4H, -CH<sub>2</sub>-), 1.68-1.72 (t, 4H, -CH<sub>2</sub>-), 2.28-2.32 (t, 4H,  $J$  7.6 Hz, Cp-CH<sub>2</sub>), 3.36 (s, 18H, OCH<sub>3</sub>), 3.94-3.95 (d, 8H, Cp);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta = -0.9$  (SiMe<sub>2</sub>), 16.0 [-

C(SiMe<sub>2</sub>OCH<sub>3</sub>), 27.3, 28.5, 29.4, 31.7 (-CH<sub>2</sub>-), 48.9 (OCH<sub>3</sub>), 66.7, 67.6 (Cp), 87.5 (C<sub>1</sub> Cp); Anal. Calc. for C<sub>38</sub>H<sub>78</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 53.36; H 9.19. Found: C, 53.25; H, 9.12%.

**1,1'-Bis[4-(tris(ethoxydimethylsilyl)methyl)butyl]ferrocene (8h).** Yellowish oil, FTIR (KBr, cm<sup>-1</sup>):  $\nu$  = 3085 (Cp-H), 2969, 2898 (C-H), 1648, 1442 (C=C), 1251, 849 (Si-C), 1108, 1078, 498 (Cp), 943 (Si-O); <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.18 (s, 36H, SiMe<sub>2</sub>), 1.12-1.15 (t, 18H,  $J$  = 6.9, -CH<sub>3</sub>), 1.40-1.44 (t,  $J$  7.1 Hz, 4H, -CH<sub>2</sub>-), 1.56-1.59 (m, 4H, -CH<sub>2</sub>-), 1.70-1.74 (t,  $J$  6.2 Hz, 4H, -CH<sub>2</sub>-), 2.27-2.31 (t,  $J$  7.2 Hz, 4H, Cp-CH<sub>2</sub>), 3.57-3.62 (q, 12H,  $J$  6.9 Hz, OCH<sub>2</sub>), 3.95 (s, 8H, Cp); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -0.35 (SiMe<sub>2</sub>), 15.4 (-CH<sub>3</sub>), 17.5, 27.5, 28.3, 29.1, 31.9 (-CH<sub>2</sub>-), 56.6 (OCH<sub>2</sub>), 66.6, 67.5 (Cp), 88.3 (C<sub>1</sub> Cp); Anal. Calc. for C<sub>44</sub>H<sub>90</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 56.25; H 9.66. Found: C, 56.12; H, 9.59%.

**1,1'-Bis[4-(tris(propoxydimethylsilyl)methyl)butyl]ferrocene (8i).** Yellowish oil, FTIR (KBr, cm<sup>-1</sup>):  $\nu$  = 3094 (Cp-H), 2929 (C-H), 1632, 1461 (C=C), 1252, 833 (Si-C), 1096, 1027, 488 (Si-C) 924 (Si-O); <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.19 (s, 36H, SiMe<sub>2</sub>), 0.87-0.90 (t, 18H,  $J$  7.3 Hz, -CH<sub>3</sub>), 1.40-1.44, (t, 4H,  $J$  7.2 Hz, -CH<sub>2</sub>-), 1.51-1.52 (m, 12H, -CH<sub>2</sub>-), 1.53-1.55 (m, 4H, -CH<sub>2</sub>-), 1.70-1.74 (t, 4H,  $J$  7.2 Hz, -CH<sub>2</sub>-) 2.28-2.30 (t, 4H,  $J$  7.6 Hz, Cp-CH<sub>2</sub>), 3.45-3.48, (t, 12H,  $J$  6.5 Hz, OCH<sub>2</sub>), 3.96 (s, 8H, p); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -0.4 (SiMe<sub>2</sub>), 9.5 (-CH<sub>3</sub>), 15.3, 24.7, 27.5, 28.7, 29.3, 31.8, 62.8 (OCH<sub>2</sub>), 66.6, 67.7 (Cp), 87.7, (C<sub>1</sub> Cp); Anal. Calc. for C<sub>50</sub>H<sub>102</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 58.66; H 10.04 Found: C, 58.52; H, 9.91%.

**1,1'- Bis[4-(tris(butoxydimethylsilyl)methyl)butyl]ferrocene (8j).** Yellowish oil, FTIR (KBr, cm<sup>-1</sup>):  $\nu$  = 3096 (Ar-H), 2925, 2870 (C-H), 1648, 1463 (C=C), 1252, 830 (Si-C), 1095, 1034, 484 (Cp) 889 (Si-O); 488; <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.19 (s, 36H, SiMe<sub>2</sub>), 0.88-0.91 (t, 18H,  $J$  = 7.2, -CH<sub>3</sub>), 1.30-1.39 (m, 12H,  $J$  7 Hz, -CH<sub>2</sub>-), 1.42-1.50 (m, 16H,  $J$  7.5 Hz, -CH<sub>2</sub>-), 1.56-1.60 (t, 4H,  $J$  7.2 Hz, -CH<sub>2</sub>-), 1.70-1.74 (t, 4H,  $J$  7.4 Hz, -CH<sub>2</sub>-), 2.29-2.33 (t, 4H,  $J$  7.6 Hz, CpCH<sub>2</sub>), 3.48-3.52 (t, 12H,  $J$  6.4 Hz, OCH<sub>2</sub>), 3.95 (d, 8H); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -0.4 (SiMe<sub>2</sub>), 12.8, 15.1, 18.1, 27.6, 28.5, 28.7, 29.4, 31.7, 33.8, 60.9 (OCH<sub>2</sub>), 66.7, 67.5 (Cp), 88.4 (C<sub>1</sub> Cp); Anal. Calc. for C<sub>56</sub>H<sub>114</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 60.71; H, 10.37, Found: C, 60.59; H, 10.25%.

**1,1'-Bis[4-(tris(benzyloxydimethylsilyl)methyl)butyl]ferrocene (8k).** Yellowish oil, FTIR (KBr, cm<sup>-1</sup>):  $\nu$  = 3091, 3035 (Ar-H), 2929, 2854 (C-H), 1645, 1489 (C=C), 1254, 858 (Si-C), 1065, 1024, 484 (Cp) 945 (Si-O); <sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 0.31 (s, 36H, SiMe<sub>2</sub>), 1.44-1.52 (m, 4H,  $J$  7.2 Hz, -CH<sub>2</sub>-), 1.68-1.75 (m, 4H, -CH<sub>2</sub>-), 1.86-1.90 (t, 4H,  $J$  6.8 Hz, -CH<sub>2</sub>-), 2.28-2.32 (t, 2H,  $J$  7.6 Hz, CpCH<sub>2</sub>), 3.96-3.97 (d, 8H, Cp), 4.68 (s, 12H, OCH<sub>2</sub>), 7.26-7.35 (m, 30H, Ar-H); <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = -0.1 (SiMe<sub>2</sub>), 15.9, 27.6, 28.7, 29.4, 31.9, 63.5 (OCH<sub>2</sub>), 66.5, 67.7 (Cp), 88.4 (C<sub>1</sub> Cp), 125.5, 125.7, 127.0, 140.2 (Ar); Anal. Calc. for C<sub>68</sub>H<sub>102</sub>FeO<sub>6</sub>Si<sub>6</sub>: C, 67.75; H 7.84, Found: C, 67.62; H, 7.79%.

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