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Ferrocenyl Oligo(phenylene-vinylene) Thiols for the Construction of Self-Assembled Monolayers

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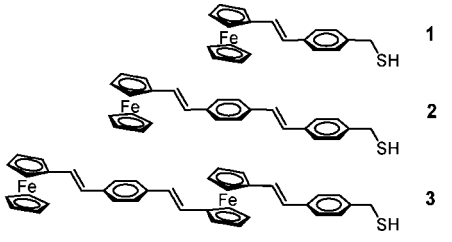
A short and efficient preparation of conjugated oligo(phenylene-ethylene) thiols bearing redox-active ferrocene moieties is described. While minimising the number of synthetic steps, the proposed strategy permits the development of sets of oligomers with varying chain length. The redox properties of the compounds in solution are determined. Preliminary studies of self-assembled monolayers (SAMs) on gold electrodes are discussed, and indicate that electron transfer through the SAMs is indeed rapid.

Introduction

There is growing interest in nanotechnologies for attaching and wiring conductive molecules onto surfaces for a wide series of applications. Electrochemical systems may be promising for developing, for example, molecular electronic devices,[1] efficient artificial photosynthetic systems,[2] organic liquid crystal light-emitting diodes[3] or biosensors. The use of self-assembly allows easy formation of monolayers of a redox-active species over an electrode by soaking an appropriate electrode surface in a nonaqueous solution of the suitably derivatised redox-active compound to enable it to tether to the surface. Typically, an electroactive moiety is located at one end of the molecule, whilst the grafting end is terminated by a Lewis base.[4] When using gold electrodes, such compounds often terminate with thiol moieties, owing to the exquisite affinity of sulfur groups for gold. This methodology is also highly attractive for electroanalytical sensors, as this method requires little preparative work, and furnishes a reagent-immobilised electrode relatively inexpensively. The attached compounds are able to carry electrons back and forth from the electrode to redox enzymes.

In this context, the investigation of electron transfer through molecular bridges has revealed that the rates usually decrease exponentially as the distance to the electrode decreases. The attenuation factor is typically 10 nm^{-1} (i.e., 1 $Å^{-1}$) for alkyl bridges, a value that may be too high for fast signal processing over long distances. Recent contributions by the groups of Chidsey,[5] Creager[6] and Finklea[7] illustrate the tendency to use conjugated bridges because π-delocalisation increases the coupling between the redox probe and the electrode. For this reason conjugated π-systems are potentially the most adapted and most promising molecular wires, assuring fast electron transfer kinetics over distances up to 20 Å and longer. Hitherto, oligo(*p*-phenylene-*trans*-vinylene) chains have exhibited the fastest electron transfer rates of all investigated systems.[5] Ferrocene has been used in various studies as a convenient electroactive centre showing fast and reversible one-electron oxidation. Furthermore, ferrocenes may act as a local molecular switch as their Cp/Cp conduction (Cp = cyclopentadienyl ligand) is poor in the reduced state and effective in the ferricinium cations. It is thus important to develop rapid and efficient access for sets of ferrocenyl oligo(phenylene-ethylene) thiols with varying chain length. Our synthetic strategy described herein also permits the insertion of additional ferrocenyl groups into the bridge itself and thus the building of more complex structures leading eventually to more sophisticated signal processing functions such as field-effect transistors. We wish to report here the rapid access to a set of three ferrocenyl oligo(*p*-phenylene-*trans*-vinylene) derivatives, **1**, **2** and **3**, bearing a mercaptomethyl group on the terminating phenyl ring. The peculiar electrochemical properties of **3** will also be described.



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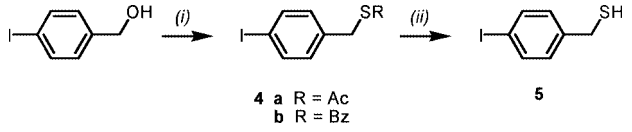
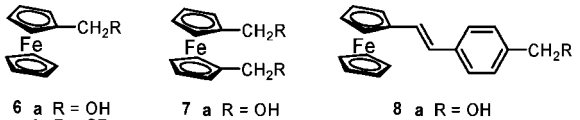
Results and Discussion

Two main approaches are commonly used in the synthesis of free thiol derivatives: either the use of a protective group or the late introduction of the thiol group as a final step so as to avoid interferences during the earlier synthetic steps. In the case of benzyl derivatives, a possible approach involves masking a hydroxy group by an aldehyde, which, after reduction to the corresponding primary alcohol, can be converted in several steps to the desired thiol. Compounds **1** and **2** have been prepared in this way.[8] As an alternative, we opted for the late introduction of a thioester group. We chose the *S*-protected 4-iodobenzylthiol **4**, as this useful building block significantly reduces the number of synthetic steps. In a more convergent approach, **4a** can be easily obtained by treatment of 4-iodobenzyl bromide with sodium thioacetate.[9] As an alternative route, we tried to exploit the 4-iodobenzyl alcohol as a starting material, thus favouring the direct conversion of the generally more stable and readily available alcohol into the corresponding thioester without any preceding halogenation. The Mitsunobu reaction of 4-iodobenzyl alcohol with thioacetic acid affords **4a** in only low yield (30%) (Scheme 1). Hughes and Reamer[10] showed evidence for improved yields in the Mitsunobu esterification of alcohols in the presence of acids stronger than acetic acid. Accordingly, we employed thiobenzoic acid instead of thioacetic acid so that, under the same conditions, the thiobenzoic acid ester **4b** is obtained in high yield (95%).

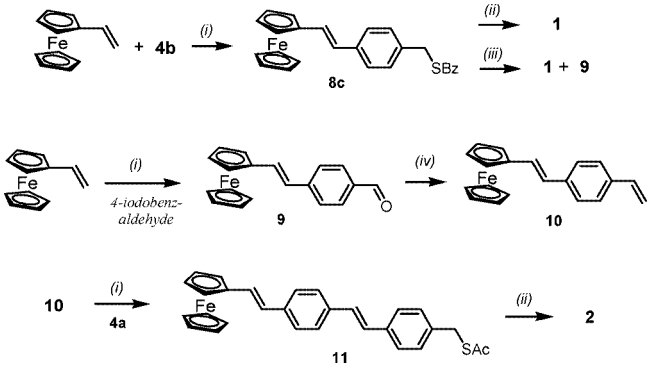


Scheme 1. Synthesis of the precursors **4a** and **4b**: (i) AcSH (for **4a**), BzSH (for **4b**), PPh_3, DEAD, THF, 0 °C; (ii) $LiAlH_4$, THF, 0 °C.

The thiobenzoates **6b** and **7b** are also formed in satisfactory yields (84 and 63%) from the respective hydroxymethyl derivatives **6a** and **7a**. The reaction of alcohol **8a** to the thioacetate **8b**[8] shows a low yield (20%) compared to the thiobenzoate **8c** (75%), confirming the observed tendency. All of the thiobenzoic acid esters discussed above were successfully converted into the respective free thiols **5**, **6c**, **7c** and **1** through reduction with sodium borohydride (Scheme 1). Both of the building blocks **4a** and **4b** were employed in the following syntheses leading to the target compounds **1**, **2** and **3**.



The preparation of the short ferrocenyl-vinylene-phenylene thiol **1** was achieved in only two steps. The Heck coupling of **4b** with vinylferrocene afforded thiobenzoate **8c** directly (Scheme 2). The subsequent reduction of the latter compound with sodium borohydride in a mixture of methanol and tetrahydrofuran afforded the desired free thiol (88%). The use of lithium aluminium hydride (LAH) as a reducing agent gave thiol **1** in only a 46% yield. Even with an excess of LAH, the aldehyde **9** was isolated as an unexpected sideproduct. Whilst the analytical characterisation data of **9** are consistent with previously published data for this compound,[11] it is important to note that in contrast to the earlier work, we also prepared compound **9** by Heck reaction of vinylferrocene with 4-iodobenzaldehyde, thus unambiguously identifying the structure of **9**.

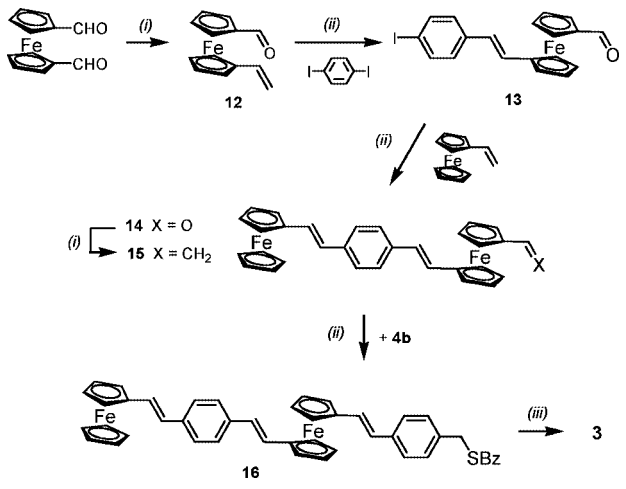


Scheme 2. Synthesis of compounds **1** and **2**: (i) $Pd(OAc)_2$, $P(Tol)_3$, tributylamine, dimethylacetamide; (ii) $NaBH_4$, THF, MeOH, 0 °C; (iii) $LiAlH_4$, THF, 0 °C.

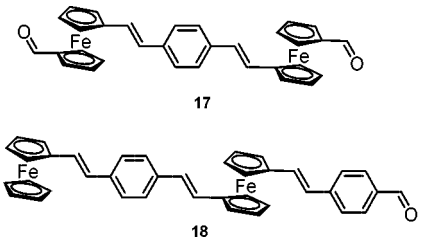
Access to the ferrocene thiol **2** is achieved in only 3 steps starting from aldehyde **9** (Scheme 2). The Heck coupling of the olefin **10** and **4a** leads directly to the thioacetate **11**, which was subsequently converted into the free thiol **2** through reduction with lithium aluminium hydride.

Taking into account our previous results, we performed the synthesis of the bis(ferrocenyl) thiol **3** in only 6 steps involving Heck coupling, standard methyl Wittig conversion and a final reduction (Scheme 3). Our synthetic strategy is based on the monofunctionalisation of 1,1′-ferrocenedicarbaldehyde leading, in two steps, to the key intermediate **13**. The methyl Wittig conversion of ferrocenedicarbaldehyde in dioxane allows for its selective monoolefination. Upon using the less polar tetrahydrofuran as a solvent, the reaction is faster (TLC analysis) but less selective, indicative of a strong kinetic control depending on the solvent polarity. In the following Heck reaction of **12** with a twofold excess of 1,4-diiodobenzene, the monoiodo derivative **13** was obtained as the major product. Only small amounts of the symmetric bis(ferrocenyl) derivative **17** (2%) are isolated. Inversion of the molar ratio of the starting compounds should afford this potential precursor of a tris(ferrocenyl) derivative in reasonable yields. An alternative, but longer and less efficient, synthesis of **13** involving a protective group is described in the literature.[12,13] A second Heck reaction of compound **13** with vinylferrocene affords the dissymmetric bis(ferrocenyl) monocarbaldehyde **14**. The

R_f values of starting material **13** and product **14** are very similar, and it is difficult to monitor the reaction by TLC. In order to obtain a complete conversion, a higher temperature has to be maintained during the reaction. The relatively low yield (53%) is probably due to a competitive degradation of either starting material or product under these conditions. A methyl Wittig conversion of **14** leads to the corresponding vinyl derivative **15**. This highly conjugated and relatively apolar compound displays low solubility in solvents such as diethyl ether or chloroform. The use of dichloromethane is necessary for the purification steps in the workup following the reaction. Unreacted starting compound **14** was recovered and the reaction repeated in order to improve the total yield to 60%. The thiobenzoate **16** was obtained by a third Heck reaction of **15** with **4b**. In the final step, **16** is reduced with sodium borohydride to the target compound **3**. The use of LAH as a reducing agent considerably lowers the yield and affords the aldehyde **18** as a side product, like in the reduction of **8c**.



Scheme 3. Synthesis of compound **3**: (i) methyltriphenylphosphonium bromide, *tert*-butoxide, dioxane/water; (ii) $Pd(OAc)_2$, $P(Tol)_3$, tributylamine, dimethylacetamide; (iii) $NaBH_4$, THF, MeOH, 0 °C.



Exploring the Electron Transfer Properties of the Ferrocene-Based Compounds in Homogeneous Solution

We resorted to cyclic voltammetry to explore the electrochemical properties of **1**, **2**, **3**, **14**, **16** and **17**. Owing to the low solubility of some of the compounds in conventional electrochemical solvents, investigations were undertaken in dichloromethane with tetrabutylammonium tetrafluoroborate ($TBABF_4$) at 0.1 M concentration as the supporting electrolyte. In a preliminary study, we checked that **1** and **2**, bearing a single redox centre, behave similarly to ferrocene. Each gave a monoelectronic reversible wave whose current intensity was proportional to $v^{1/2}$, where v is the scan rate. This is typical of a diffusive behaviour. The average of the forward and backward peak currents allows evaluation of a standard potential of (0.55 ± 0.01) V versus SCE for **1** and (0.54 ± 0.01) V versus SCE for **2**. Figure 1a depicts a cyclic voltammogram at a scan rate of 200 $mV\,s^{-1}$ of a 0.38 mM solution of **14** at a glassy carbon electrode. This bis(ferrocenyl) monocarbonyl species gives rise to two apparently reversible waves centred at $E°_1 = (0.54 \pm 0.01)$ V versus SCE and (0.81 ± 0.01) V versus SCE, both waves being of the same height. Given that the first wave occurs at the same potential as that of the nonderivatised ferrocene, we infer that this wave represents the one-electron oxidation of the ferrocene moiety within the conjugated chain to yield the corresponding ferricinium cation. The second wave is related to oxidation of the terminal ferrocenyl group bearing an electron-withdrawing substituent.

Conversely, the voltammetry of the thiobenzoate **16** (cf. Figure 1b) reveals a single oxidation wave, despite the presence of two redox centres. Complex **16** is a larger molecule

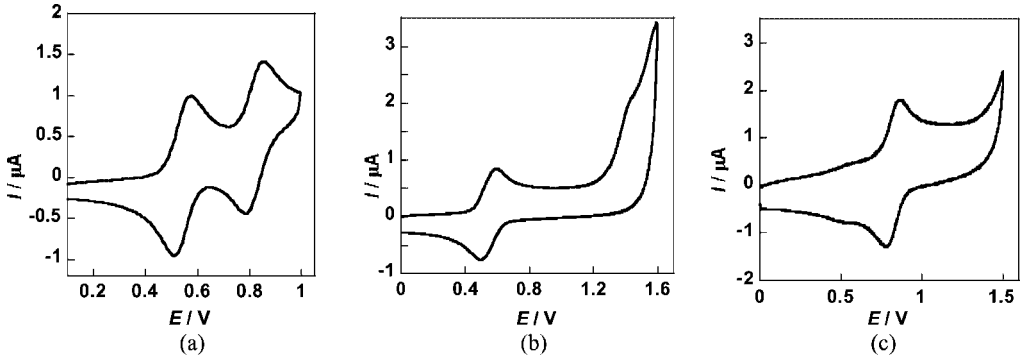


Figure 1. Cyclic voltammogram of (a) **14** (3.8×10^{-4} M), (b) **16** (2.5×10^{-4} M), (c) **17** (2.7×10^{-4} M) in dichloromethane containing 0.1 M $TBABF_4$ at a scan rate of 0.2 $V\,s^{-1}$.

than **14**, so that its diffusion coefficient is necessarily smaller. Hence, we infer from the peak current intensities that two electrons are involved in the oxidation. Unfortunately, free thiol **3** adsorbs slightly even onto a carbon electrode, which prevents its full characterisation in solution. However, a single wave was also observed. This unusual behaviour may seem counterintuitive as the electrostatic repulsion should destabilise the dication and thus raise the potential of the second oxidation. In fact, such behaviour has already been observed by Launay et al. for polyvinylferrocenes,[14] and by Saveant et al. for carotenoids.[15] These authors proposed a rationalisation of this effect. As the monocationic species are in a mixed-valence state, the charge is delocalised inside the large volume defined between both redox centres, so that the solvation is necessarily weak. Conversely, in the dication, because of coulombic repulsion, the charges are localised onto the two redox centres, thus minimising the electrostatic repulsion and also allowing a much stronger stabilisation by the solvent. In some cases, this effect may balance the electrostatic repulsion and may result in a potential inversion. A single two-electron process then occurs, being thermodynamically and kinetically controlled by the first electron transfer. This effect corresponds with previous observations by Amatore and Kochi, revealing that for common aromatic compounds, there is a linear correlation between the standard potential $E°_1$ and the ionisation potential IP [Equation (1)],[16] where $0 < \mu < 1$ and C^{te} is a constant depending on the reference electrode:

$$E° \approx \mu IP + C^{te} \quad (1)$$

Here, μ reflects how the variations in IP are transmitted to $E°$; $\mu = 1$ would mean that any variation in IP is fully reflected in the condensed phase. In this study, the electroactive moieties were normally solvated and $\mu = 0.71$ was obtained; $(1 - \mu)$ reflects the effects of solvation. For the monocation, the charge is only poorly solvated, so that μ should be close to 1 so that [Equation (2)]:

$$E°_1 \approx IP + C^{te} \quad (2)$$

Conversely, in the dication, the charges are normally solvated, so that in a very approximate model [Equation (3)], where ΔE_{coul} is the electrostatic contribution, we can evaluate that:

$$E°_2 - E°_1 \approx -2(1 - \mu)IP + \Delta E_{coul} \quad (3)$$

This formulation leads to [Equation (4)]:

$$E°_2 \approx (2\mu - 1)IP + \Delta E_{coul} + C^{te} \quad (4)$$

We can then predict that there is a potential inversion when [Equation (5)]:

$$IP > \Delta E_{coul}/(2 - 2\mu) \quad (5)$$

If the compound is dissymmetrical (for example **14**), another term, ΔE_{chim}, should be added to Equation (2), taking into account the different chemical nature of both electroactive moieties. Agreeing with this analysis, the voltammetry of **17**, which is totally symmetrical, also reveals a single peak (cf. Figure 1c). The weak signal around 0.55 V may be attributed to an impurity in the crude product **17**.

In Figure 1b a second wave is observed as a shoulder on the medium discharge, reflecting an oxidative degradation of compound **16**, probably due to the irreversible thiobenzoate oxidation.

The electrochemical behaviour of **3** while attached to a gold electrode will be described elsewhere.[17] As a preliminary result, Figure 2 illustrates typical cyclic voltammograms for **3**, coadsorbed with diphenyl disulfide or pentanethiol diluents. A single two-electron wave is still observed as anticipated. Although the scan rate is high (cf. Figure 2b), the relatively low peak-to-peak potential difference confirms that electron transfer inside this molecule is indeed very fast.

Conclusions

A particularly short and efficient preparation of conjugated oligo(phenylene-ethylene) thiols bearing redox-active ferrocene moieties is described. The proposed strategy to introduce the sulfur group by Heck reaction of a vinyl group with the key synthone **4** readily yields a set of oligomers with varying chain length in only 2 (compound **1**) or 4

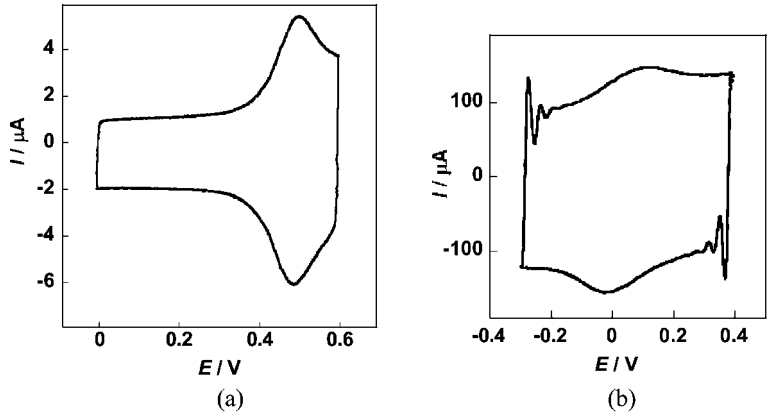


Figure 2. Cyclic voltammogram in 1 M perchloric acid of **3** coadsorbed (a) with pentanethiol onto a 111 gold single-crystal electrode, scan rate: 12 $V s^{-1}$; (b) with diphenyl disulfide onto a gold ball ultramicroelectrode, scan rate: 220000 $V s^{-1}$.

synthetic steps (compound **2**). The preparation of the thioesters by Mitsunobu reaction of benzyl alcohol was improved by replacing thioacedic acid with thiobenzoic acid. The additional insertion of ferrocenyl units into the conjugated bridge can be easily achieved by the use of 1′-vinylferrocene-1-carbaldehyde (**12**), a key intermediate in the synthesis of the bis(ferrocenyl) derivative **3**. For the bis(ferrocenyl) derivatives, the nature of the second side chain attached to the second ferrocene species may have a significant effect on the redox thermodynamics, leading to an inverted series of electrode potentials, causing a single two-electron wave to occur. The ultrafast cyclic voltammetry of **1**, **2** and **3** when they are adsorbed onto gold electrodes confirms that these compounds are indeed very efficient molecular wires. A full kinetic analysis of electrochemical results for monolayers of these compounds will be published elsewhere.[17]

Experimental Section

General: All reactions were performed with previously dried solvents under argon, if not stated otherwise. The compounds ferrocene, ferrocenemonocarbaldehyde, ferrocenylmethanol (**6a**) and ferrocene-1,1′-diyldimethanol (**7a**) were bought from Sigma/Aldrich (France). The commercially available vinylferrocene was obtained in larger quantities from ferrocenemonocarbaldehyde in a Wittig reaction with methyltriphenylphosphonium bromide. Ferrocene-1,1′-dicarbaldehyde was prepared from freshly sublimed ferrocene.[18] Thin layer chromatography (TLC) was performed on aluminium sheets precoated with 60 F_{254} silica gel. Preparative flash column chromatography was performed on silica gel 60 (0.040–0.063 mm, Merck). ^1H and ^{13}C NMR spectra were recorded with a Bruker AC 250 or a Bruker DRX 400 spectrometer. Chemical shifts are reported using the deuterated (^{13}C NMR) or the residual monoprotonated (^1H NMR) solvent signals as reference, based on the values published by Gottlieb and Nudelman.[19] Mass spectra were recorded with a Jeol JMS-700 spectrometer and UV/Vis spectra with a Beckman DU 7400 spectrophotometer. Elemental analyses were conducted at the University of Pierre and Marie Curie (Paris, Jussieu, France) or the Centre Nationale de Recherche Scientifique (Gif-sur-Yvette, France).

Electrochemistry: The electrochemical experiments in dichloromethane were conducted in an air-tight, three-electrode glass cell, controlled by a commercially available computer-controlled potentiostat (AUTOLAB PGSTAT 30, Eco Chemie, the Netherlands). A platinum wire and an aqueous saturated calomel electrode (SCE) were used as a counter and a reference electrode, respectively. The reference electrode was kept in a side arm separated from the electrochemical cell by a porous frit. The side arm was filled with the solvent/supporting electrolyte solution. A glassy carbon disk electrode, having a disk radius of 0.5 mm, was used as the working electrode. The working electrode was polished prior to each experiment on successively finer grades of carborundum paper (P1200 down to P4000), and then using a 0.3 μM aqueous alumina slurry on a wetted, napped polishing cloth. The supporting electrolyte employed was a 0.1 M solution of tetrabutylammonium tetrafluoroborate ($TBAF_4$) in dichloromethane (distilled from barium oxide). $TBABF_4$ had been recrystallised and dried at 70 °C for at least 24 h before use. Prior to experimentation, argon gas was bubbled into the electrolyte solution to remove oxygen, and was flushed over the cell solution during the electrochemical measurements. Cyclic voltammograms (CV) were recorded at room temperature [(22 ± 1) °C] and at a potential sweep rate of 0.2 $V s^{-1}$. To form self-assembled monolayers, we left gold electrodes to bathe for one night in a mixture of **1** and pentanethiol or **1** and diphenyl disulfide in chloroform. Either a 111 Au single crystal or a gold ball ultramicroelectrode (made by melting a 10 μm diameter wire in a blue flame)[17] were used. Cyclic voltammograms were then recorded in H_2O + 1 M $HClO_4$. For Figure 2b, a home-built potentiostat allowing scan rates up to 2.5 $MV s^{-1}$ was used.[20,21] A full analysis of the electrochemical behaviour of self-assembled monolayers will be described elsewhere.

Synthesis

4-[(*E*)-2-Ferrocenylvinyl]benzylthiol (1). (a) A solution of **8b** (45 mg, 0.12 mmol) in tetrahydrofuran (THF) (2 mL) was chilled with a water/ice bath. A 1 M solution of lithium aluminium hydride (LAH) in diethyl ether (0.24 mL, 0.24 mmol) was added slowly. The reaction mixture was stirred at room temperature for 30–60 min, and the reaction progress was monitored by thin layer chromatography (TLC). The mixture was neutralised with 1 M hydrochloric acid, and extracted with dichloromethane. The organic phase was washed with water, brine and then dried with magnesium sulfate. Purification by chromatography (silica gel, dichloromethane/petroleum ether using a solvent gradient of 20:80 to 50:50) yielded **1** as a red solid (39 mg, 97%). **(b) 8c** (45 mg, 0.10 mmol) was dissolved in a mixture of methanol (2 mL) and tetrahydrofuran (1 mL). Sodium borohydride (8 mg, 0.21 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, and the reaction progress was monitored by TLC. The mixture was neutralised with 1 M hydrochloric acid, and extracted with dichloromethane. The organic phase was washed with water, brine and then dried with magnesium sulfate. Purification by chromatography (silica gel, dichloromethane/petroleum ether using a solvent gradient of 20:80 to 50:50) yielded **1** as a red solid (32 mg, 93%). **(c)** Compound **1** (10 mg, yield 47%) was prepared from **8c** (28 mg, 0.064 mmol) and lithium aluminium hydride as described. Compound **9** was found to be a sideproduct (7.4 mg, yield 36%).

Compound 1: ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.39 (d, J = 8.2 Hz, 2 H, aromatic), 7.28 (d, J = 8.2 Hz, 2 H, aromatic), 6.86 (d, J = 16 Hz, 1 H, vinyl), 6.67 (d, J = 16 Hz, 1 H, vinyl), 4.46 (t, J = 1.7 Hz, 2 H, Cp), 4.28 (t, J = 1.7 Hz, 2 H, Cp), 4.13 (s, 5 H, unsubstituted Cp), 3.74 (d, J = 7.4 Hz, 2 H, CH_2), 1.76 (t, J = 7.4 Hz, 1 H, SH) ppm. ^{13}C NMR ($CDCl_3$, 400 MHz): δ = 139.6, 136.8, 128.3, 127.0, 126.0, 125.5, 69.2, 69.1, 66.8, 28.8 ppm. MS (CI^+, NH_3): m/z (%) = 335 (95) [M + 1], 303 (100). HRMS (CI^+, CH_4): calcd. for $[C_{19}H_{19}FeS]^+$ 335.0551; found 335.0546. UV (CH_3Cl): λ (ε) = 456 (908) nm (br.).

4-[(*E*)-2-{4-[(*E*)-2-Ferrocenylvinyl]phenyl}vinyl]benzylthiol (2): Compound **2** (74 mg, yield 71%) was prepared from **11** (114 mg, 0.24 mmol) and lithium aluminium hydride as described for the preparation of **1** (procedure a). ^1H NMR ($CDCl_3$, 250 MHz): δ = 7.45–7.19 (m, 10 H, aromatic, vinyl), 6.83 (d, J = 16 Hz, 1 H, vinyl), 6.62 (d, J = 16 Hz, 1 H, vinyl), 4.42 (d, J = 2.7 Hz, 2 H, Cp), 4.23 (d, J = 2.7 Hz, 2 H, Cp), 4.08 (s, 5 H, unsubstituted Cp), 3.68 (d, J = 7.5 Hz, 2 H, CH_2), 1.60 (t, J = 7.5 Hz, 1 H, SH) ppm. MS (CI^+, CH_4): m/z (%) = 437 (50) [M + 1], 405 (100). HRMS (CI^+, CH_4): calcd. for $[C_{27}H_{25}FeS]^+$ 437.1021; found 437.1024.

4-[(*E*)-2-{1′-[(*E*)-2-{4-[(*E*)-2-Ferrocenylvinyl]phenyl}vinyl]ferrocen-1-yl}vinyl]benzylthiol (3). (a) Compound **3** (14 mg, yield 81%) was prepared from **16** (20 mg, 0.026 mmol) and sodium borohydride as described for the preparation of **1** (procedure b). Compound **16** is soluble in dichloromethane, whereas its solubility is very low in diethyl ether. Chromatography (silica gel; dichloromethane/petro-

leum ether gradient of 20:80 to 40:60) to yield pure compound **3**. **(b)** Compound **3** (7 mg, yield 46%) was prepared from **16** (18 mg, 0.023 mmol) and lithium aluminium hydride as described for the preparation of **1** (procedure a). Aldehyde **18** was isolated as a side-product {MS (CI; NH_3): *m*/*z* (%) = 648 (37) [M + 1], 631 (33), 613 (100)}.

Compound 3: ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.25 (m, 6 H, aromatic), 7.14 (m, 2 H, aromatic), 6.88 (d, *J* = 16Hz, 1 H, vinyl), 6.76 (d, *J* = 16 Hz, 1 H, vinyl), 6.73 (d, *J* = 16 Hz, 1 H, vinyl), 6.68 (d, *J* = 16 Hz, 1 H, vinyl), 6.61 (d, *J* = 16 Hz, 1 H, vinyl), 6.59 (d, *J* = 16 Hz, 1 H, vinyl), 4.48 (t, *J* = 1.8 Hz, 2 H, Cp), 4.42 (m, 4 H, Cp), 4.28 (t, *J* = 1.8 Hz, 2 H, Cp), 4.25 (m, 4 H, Cp), 4.13 (s, 5 H, unsubst. Cp), 3.68 (m, 2 H, CH_2), 0.88 (t, *J* = 7.6 Hz, 1 H, SH) ppm. MS (CI^+, NH_3): *m*/*z* (%) = 647 (100) [M + 1], 615 (65). HRMS (FAB^+, NH_3): calcd. for $[C_{39}H_{35}FeS]^+$ 647.1153; found 647.1157. UV (CH_3Cl): λ (ε) = 463 (4311) nm (br.).

***S*-(4-Iodobenzyl) Thioacetate (4a):** A solution of 4-iodobenzyl alcohol (200 mg, 0.85 mmol), triphenylphosphane (448 mg, 1.71 mmol) and thioacetic acid (122 μL, 1.71 mmol) in tetrahydrofuran (3.5 mL) was cooled to 0 °C, and diethyl diazodicarboxylate (298 mg, 1.71 mmol, 40% mixture in toluene) was added dropwise. The reaction mixture was stirred for 12 h. Diethyl ether was added and the organic phase was washed with aqueous sodium hydrogen carbonate solution, water and brine and then dried with magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel; 40% dichloromethane in petroleum ether) to yield **4a** as a colourless oil (72 mg, 29%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.62 (d, *J* = 8.3 Hz, 2 H, aromatic) 7.03 (d, *J* = 8.3 Hz, 2 H, aromatic), 4.04 (s, 2 H, CH_2), 2.35 (s, 3 H, CH_3) ppm.

***S*-(4-Iodobenzyl) Thiobenzoate (4b):** A solution of 4-iodobenzyl alcohol (200 mg, 0.85 mmol), triphenylphosphane (448 mg, 1.71 mmol) and thiobenzoic acid (222 μL) in tetrahydrofuran (3.5 mL) was cooled to 0 °C, and diethyl diazodicarboxylate (298 mg, 1.71 mmol, 40% mixture in toluene) was added dropwise. The reaction mixture was stirred for 4–12 h (TLC control). Diethyl ether was added and the organic phase was washed with aqueous sodium hydrogen carbonate solution, water and brine and then dried with magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel; 40% dichloromethane in petroleum ether) to yield **4b** as a colourless oil (287 mg, 95%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.95 (d, 2 H, *J* = 7.4 Hz, aromatic), 7.63 (d, 2 H, *J* = 8.2 Hz, aromatic), 7.58 (t, 1 H, *J* = 7.4 Hz, aromatic), 7.44 (t, 2 H, *J* = 7.4 Hz, aromatic), 7.12 (d, 2 H, *J* = 8.2 Hz, aromatic), 4.24 (s, 2 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 250 MHz): δ = 191.0, 137.7, 137.4, 136.7, 133.6, 130.9, 128.7, 127.3, 32.8 ppm. MS (CI^+, NH_3): *m*/*z* (%) = 372 (100) [M + NH_4], 355 (8) [M + 1], 246 (33) [M – I + NH_4]. $C_{14}H_{11}IOS$ (354.21): calcd. C 47.47, H 3.13; found C 47.40, H 3.13.

(4-Iodophenyl)methanethiol (5): Compound **5** (32 mg, yield 91%) was prepared from **4b** (50 mg, 0.14 mmol) and sodium borohydride as described for the preparation of **1** (procedure b). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.64 (d, *J* = 8.2 Hz, 2 H, aromatic), 6.96 (d, *J* = 8.2 Hz, 2 H), 3.54 (s, 2 H, CH_2), 1.85 (s, 1 H, SH) ppm.

***S*-(Ferrocenylmethyl) Thiobenzoate (6b):** Compound **6b** (208 mg, yield 84%) was prepared from ferrocenylmethanol **6a** (159 mg, 0.74 mmol) and thiobenzoic acid as described for the preparation of **4b**. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.93 (d, *J* = 7.4 Hz, 2 H, aromatic), 7.54 (t, *J* = 7.4 Hz, 1 H, aromatic), 7.41 (t, *J* = 7.4 Hz, 2 H, aromatic), 4.33 (m, 2 H, Cp), 4.26 (m, 2 H, Cp), 4.22 (s, 5 H, Cp), 4.13 (s, 2 H, CH_2) ppm.

Compound 7b: Compound **7b** (194 mg, yield 63%) was prepared from **7a** (156 mg, 0.63 mmol) and thiobenzoic acid as described for the preparation of **4b**. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.96 (d, *J* = 7.4 Hz, 4 H, aromatic), 7.56 (m, 2 H, aromatic), 7.44 (m, 4 H, aromatic), 4.27 (s, 4 H, Cp), 4.18 (s, 4 H, Cp), 4.15 (s, 4 H, CH_2) ppm. MS (CI^+, NH_3): *m*/*z* (%) = 504 (62) [M + NH_4], 349 (96), 213 (100).

{4-[(*E*)-2-Ferrocenevinyl]phenyl}methanol (8a): Compound **8a** (436 mg, yield 85%) was prepared from **9** (510 mg, 1.61 mmol) and sodium borohydride as described for the preparation of **1** (procedure b). Chromatography (silica gel; dichloromethane) yielded a red-orange solid. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.44 (d, *J* = 8.1 Hz, 2 H, aromatic), 7.33 (d, *J* = 8.1 Hz, 2 H, aromatic), 6.89 (d, *J* = 16.1 Hz, 1 H, vinyl), 6.69 (d, *J* = 16.1 Hz, 1 H, vinyl), 4.68 (d, *J* = 5 Hz, 2 H, CH_2), 4.47 (s, 2 H, Cp), 4.29 (s, 2 H, Cp), 4.14 (s, 5 H, unsubstituted Cp), 1.61 (t, *J* = 5 Hz, 1 H, OH) ppm.

S-{4-[(*E*)-2-Ferrocenylvinyl]benzyl} Thioacetate (8b): Compound **8b** (78 mg, yield 22%), a red solid, was prepared from **8a** (300 mg, 0.94 mmol) and thioacetic acid as described for the preparation of **4a**. Chromatography: silica gel; dichloromethane/petroleum ether, 40:60 v/v. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.36 (d, *J* = 8.2 Hz, 2 H, aromatic), 7.24 (d, *J* = 8.2 Hz, 2 H, aromatic), 6.85 (d, *J* = 16.1 Hz, 1 H, vinyl), 6.66 (d, *J* = 16.1 Hz, 1 H, vinyl), 4.45 (t, *J* = 1.6 Hz, 2 H, Cp), 4.29 (t, *J* = 1.6 Hz, 2 H, Cp), 4.13 (s, 5 H, unsubstituted Cp), 4.11 (s, 2 H, CH_2), 2.35 (s, 3 H, CH_3) ppm. The ^{1}H NMR data described in the literature[8] confirms the above data.

***S*-{4-[(*E*)-2-Ferrocenylvinyl]benzyl} Thiobenzoate (8c):** A solution of vinylferrocene (106 mg, 0.50 mmol), **4b** (176 mg, 0.50 mmol), palladium acetate (11 mg, 0.014 mmol) and tributylamine (180 μL, 0.75 mmol) in *N*,*N*-dimethylacetamide (10 mL) was stirred at room temperature for 1 h. Tri(*ortho*-tolyl)phosphane (3 mg, 0.01 mmol) was added. After 3 h of stirring at room temperature, the reaction mixture was heated at 100 °C for 12 h. After extraction with diethyl ether, the organic phase was washed with 1 M hydrochloric acid, water, brine and then dried with magnesium sulfate. After evaporation of the solvent, the residue was purified by column chromatography (silica gel; 50% dichloromethane in petroleum ether) to yield **8c** (138 mg, 63%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.97 (d, *J* = 7.2 Hz, 2 H, aromatic), 7.31–7.57 (m, 7 H, aromatic), 6.85 (d, *J* = 16 Hz, 1 H, vinyl), 6.66 (d, *J* = 16 Hz, 1 H, vinyl), 4.46 (m, 2 H, Cp), 4.31 (s, 2 H, CH_2), 4.28 (m, 2 H, Cp), 4.12 (s, 5 H, unsubstituted Cp) ppm. ^{13}C NMR ($CDCl_3$, 250 MHz): δ = 185.0, 133.4, 129.3, 128.6, 127.3, 127.1, 126.0, 125.5, 69.2, 69.1, 66.9, 33.3 ppm. MS (CI^+, NH_3): *m*/*z* (%) = 456 (12) [M + NH_4], 439 [17] [M + 1], 303 (100).

{4-[(*E*)-2-Ferrocenevinyl]phenyl}carbaldehyde (9): Compound **9** (406 mg, yield 56%) was prepared from vinylferrocene (486 mg, 2.30 mmol) and 4-iodobenzaldehyde (532 mg, 2.29 mmol) as described for the preparation of **8c**. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 9.98 (s, 1 H, CHO), 7.84 (d, *J* = 8.2 Hz, 2 H, aromatic), 7.56 (d, *J* = 8.2 Hz, 2 H, aromatic), 7.08 (d, *J* = 16.1 Hz, 1 H, vinyl), 6.72 (d, *J* = 16.1 Hz, 1 H, vinyl), 4.52 (s, 2 H, Cp), 4.36 (s, 2 H, Cp), 4.16 (s, 5 H, unsubstituted Cp) ppm. ^{13}C NMR ($CDCl_3$, 250 MHz): δ = 191.6, 131.5, 130.3, 126.0, 124.6, 69.8, 69.5, 69.4, 67.4 ppm. MS (CI^+, NH_3): *m*/*z* (%) = 317 (100) [M + 1].

4-[(*E*)-2-Ferrocenylvinyl]styrene (10): Compound **10** (301 mg, yield 86%) was prepared from aldehyde **9** (352 mg, 1.11 mmol) as described for the preparation of **12**. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.40 (s, 4 H, aromatic), 6.88 (d, *J* = 16.2 Hz, 1 H, vinyl), 6.70 (dd, *J* = 16.2, 10.7 Hz, 1 H, vinyl), 6.67 (d, *J* = 16.2 Hz, 1 H, vinyl), 5.75 (d, *J* = 17.5 Hz, 1 H, vinyl), 5.22 (d, *J* = 10.7 Hz, 1 H, vinyl),

4.46 (t, *J* = 1.6 Hz, 2 H, Cp), 4.3 (m, 2 H, Cp), 4.15 (s, 5 H, Cp) ppm.

***S*-{4-[(*E*)-2-{1′-[(*E*)-2-{4-[(*E*)-2-Ferrocenylvinyl]phenyl}vinyl]-ferrocen-1-yl}vinyl]benzyl} Thioacetate (11):** Compound **11** (152 mg, yield 83%) was prepared from **10** (120 mg, 0.38 mmol) and **4a** (233 mg, 0.80 mmol) as described for the preparation of **8c**. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.45 (m, 8 H, aromatic), 7.20 (2d, *J* = 17 Hz, 2 H, vinyl), 6.85 (2d, *J* = 16.1 Hz, 2 H, vinyl), 4.65 (s, 2 H, CH_2) 4.45 (d, *J* = 2.67 Hz, 2 H, Cp), 4.30 (d, *J* = 1.6 Hz, 2 H, Cp), 4.15 (s, 5 H, unsubstituted Cp), 3.95 (s, 3 H, CH_3) ppm. The ^{1}H NMR data described in the literature[8] confirms the above data. MS (CI^+, NH_3): *m*/*z* (%) = 479 (20) [M + 1], 295 (100). MS (FAB^+): *m*/*z* (%) = 478 (10) [M], 295 (100).

1′-Vinylferrocene-1-carbaldehyde (12): A solution of ferrocene-1,1′-dicarbaldehyde (0.849 g, 3.51 mmol) and methyltriphenylphosphonium bromide (1.25 g, 3.51 mmol) in dioxane (20 mL) was treated with potassium *tert*-butoxide (0.39 g, 3.5 mmol) and water (100 μL). After stirring at room temperature for 3 h, the reaction mixture was extracted with diethyl ether. The organic phase was washed with water and dried with magnesium sulfate. Purification by chromatography (silica gel; dichloromethane) yielded **12** as a brown oil (0.37 g, 44%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 9.88 (s, 1 H, CHO), 6.37 (dd, *J* = 17.5, 10.7 Hz, 1 H, vinyl), 5.40 (d, *J* = 17.5 Hz, 1 H, vinyl), 5.14 (d, *J* = 10.7 Hz, 1 H), 4.72 (s, 2 H, Cp), 4.54 (s, 2 H, Cp), 4.51 (s, 2 H, Cp), 4.31 (s, 2 H, Cp) ppm. MS (CI^+, NH_3): *m*/*z* (%) = 241 (100) [M + 1], 215 (12), 124 (7).

1′-[(*E*)-2-(4-Iodophenyl)vinyl]ferrocene-1-carbaldehyde (13): Compound **13** (276 mg, 57%) was prepared from **12** (271 mg, 1.1 mmol) and 1,4-diiodobenzene (0.74 g, 2.3 mmol), as described for the preparation of **8c**. However, the reaction mixture was not heated but stirred at room temperature for 3 d (chromatography: silica gel; dichloromethane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.90 (s, 1 H, CHO), 7.65 (d, *J* = 8.4 Hz, 2 H, aromatic), 7.17 (d, *J* = 8.4 Hz, 2 H, aromatic), 6.76 (d, *J* = 16.2 Hz, 1 H, vinyl), 6.63 (d, *J* = 16.2 Hz, 1 H, vinyl), 4.76 (t, *J* = 1.9 Hz, 2 H, Cp), 4.55 (multiplet, *J* = 1.9 Hz, 4 H, Cp), 4.38 (t, *J* = 1.9 Hz, 2 H, Cp) ppm. MS (CI^+, NH_3): *m*/*z* (%) = 443 (100) [M + 1], 317 (33). Only a small amount of the symmetrical bis(ferrocene) dicarbaldehyde **17** was isolated (12 mg, 2%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 9.90 (s, 2 H, CHO), 7.42 (s, 4 H, aromatic), 6.67 (s, 2 H, vinyl), 6.66 (s, 2 H, vinyl), 4.77 (t, *J* = 1.8 Hz, 4 H, Cp), 4.57 (m, 8 H, Cp), 4.39 (t, *J* = 1.8 Hz, 4 H, Cp) ppm. ^{13}C NMR ($CDCl_3$, 250 MHz): δ = 193.8, 136.4, 127.8, 126.4, 124.8, 85.5, 79.9, 74.4, 70.7, 70.5, 68.2 ppm. MS (CI^+, CH_4): *m*/*z* (%) = 455 (15) [M + 1], 241 (100).

1′-[(*E*)-2-{4-[(*E*)-2-Ferrocenylvinyl]phenyl}vinyl]ferrocene-1-carbaldehyde (14): Compound **14** (180 mg, 55%) was prepared from **13** (276 mg, 0.63 mmol) and vinylferrocene (265 mg, 1.25 mmol) as described for the preparation of **8c** (chromatography: silica gel; dichloromethane/petroleum ether, 40:60 v/v). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 9.91 (s, 1 H, CHO), 7.40 (s, 4 H, aromatic), 6.90 (d, *J* = 16 Hz, 1 H, vinyl), 6.72 (s, 2 H, vinyl), 6.66 (d, *J* = 16 Hz, 1 H, vinyl), 4.76 (t, *J* = 1.8 Hz, 2 H, Cp), 4.57 (t, *J* = 1.6 Hz, 4 H, Cp), 4.47 (t, *J* = 1.5 Hz, 2 H, Cp), 4.38 (t, *J* = 1.7 Hz, 2 H, Cp), 4.29 (t, *J* = 1.5 Hz, 2 H, Cp), 4.14 (s, 5 H, unsubstituted Cp) ppm. MS (CI^+, CH_4): *m*/*z* (%) = 527 (100) [M + 1], 391 (12), 345 (12), 317 (30), 279 (27). $C_{31}H_{26}Fe_2O$ (526.32): calcd. C 70.75, H 4.98; found C 69.78, H 4.87.

1′-[(*E*)-2-{4-[(*E*)-2-Ferrocenylvinyl]phenyl}vinyl]-1-vinylferrocene (15): A solution of **14** (127 mg, 0.20 mmol) and methyltriphenylphosphonium bromide (90 mg, 0.25 mmol) in dioxane (3 mL) was treated with potassium *tert*-butoxide (28 mg, 0.25 mmol) and the mixture stirred at room temperature for 12 h (TLC control). The reaction mixture was extracted with dichloromethane. The organic phase was washed with water and dried with magnesium sulfate. After evaporation of the solvent, the brown solid residue was purified by column chromatography (silica gel; dichloromethane/petroleum ether, 35:65 v/v) to yield **15** (56 mg, 44%). Repetition of the experiment with the recovered starting material afforded another 37 mg of **15**, increasing the total yield to 64%. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.4 (s, 4 H, aromatic), 6.9 (d, *J* = 16 Hz, 1 H, vinyl), 6.81 (d, *J* = 16 Hz, 1 H, vinyl), 6.68 (d, *J* = 16 Hz, 1 H, vinyl), 6.64 (d, *J* = 16 Hz, 1 H, vinyl), 6.38 (dd, *J* = 17.5, 10.7 Hz, 1 H, C*H*=CH_2), 5.24 (d, *J* = 17.5 Hz, 1 H, CH=CH_2), 5.0 (d, *J* = 10.7 Hz, 1 H, CH=CH_2), 4.47 (t, *J* = 1.3 Hz, 2 H, Cp), 4.39 (t, *J* = 1.6 Hz, 2 H, Cp), 4.30 (t, *J* = 2.3 Hz, 4 H, Cp), 4.23 (t, *J* = 1.7 Hz, 2 H, Cp), 4.19 (t, *J* = 1.6 Hz, 2 H, Cp), 4.14 (s, 5 H, Cp) ppm. MS (CI^+, NH_3): *m*/*z* (%) = 525 (100) [M + 1], 391 (5), 315 (7).

***S*-{4-[(*E*)-2-{1′-[(*E*)-2-{4-[(*E*)-2-Ferrocenylvinyl]phenyl}vinyl]-ferrocen-1-yl}vinyl]benzyl} Thiobenzoate (16):** Compound **16** (24 mg, 91%) was prepared from **15** (22 mg, 0.035 mmol) and **4b** (30 mg, 0.084 mmol) as described for the preparation of **8c** (chromatography: silica gel; 50% dichloromethane in petroleum ether). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 7.99 (dd, *J* = 7.1, 1.4 Hz, 2 H, aromatic), 7.58 (tt, *J* = 7.4, 1.4 Hz, 1 H, aromatic), 7.45 (m, 2 H, aromatic), 7.29 (aromatic, *J* = 8.3 Hz, 2 H, d), 7.23 (s, 4 H, aromatic), 7.21 (aromatic, *J* = 8.3 Hz, 2 H, d), 6.9 (d, *J* = 16 Hz, 1 H, vinyl), 6.75 (d, *J* = 16 Hz, 2 H, vinyl), 6.68 (d, *J* = 16 Hz, 1 H, vinyl), 6.60 (d, *J* = 16 Hz, 2 H, vinyl), 4.47 (t, *J* = 1.8 Hz, 2 H, Cp), 4.41 (t, *J* = 1.8 Hz, 4 H Cp), 4.29 (s, 2 H, CH_2), 4.27 (t, *J* = 1.8 Hz, 2 H, Cp), 4.25 (t, *J* = 1.8 Hz, 4 H, Cp), 4.12 (s, 5 H, Cp) ppm. MS (CI+, CH_4): *m*/*z* (%) = 751 (62) [M + 1], 242 (100), 186 (40). HRMS (CI^+, NH_3): calcd. for $[C_{46}H_{39}Fe_2OS]^+$ 751.1415; found 751.1412.

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