

## ELECTRONIC SUPPLEMENTARY INFORMATION

### Notes on Synthetic Chemistry

#### a. Preparation of starting Materials

##### **Racemic (1-hydroxyethyl)ferrocene 2.**

Acetylferrocene ( 2.880 g, 12 mmol) was dissolved in MeOH (40 mL) and brought to 0°C, then NaBH<sub>4</sub> (0.908 g, 24 mmol) was added as a solid in portion. The red solution was stirred for 20min at 0°C and warmed at room temperature for 12h until judged complete by TLC (R<sub>f</sub> 0.5, cyclohexane:diethylether 4:7), then the reaction was quenched with water-ice mixture. MeOH was evaporated under reduced pressure, and the resulting mixture was extracted with Et<sub>2</sub>O (2 x 5mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated under reduced pressure to give an orange solid. The solid was triturated with a solution of hexane: diethylether (20:1, 10mL) and filtered. The resulting yellow solid was utilized without further purification for successive reactions. Yield 76%.

mp = 80-82°C. Yellow solid.

##### **9-benzyl-9H-Carbazole 3.**

To a mixture of carbazole (0.87 g, 5 mmol) in dry THF (5mL), NaH (0.24 g, 10 mmol) was slowly added in portions. The mixture was stirred during 1 hour at room temperature, and then benzylbromide (0.89 mL, 7.5 mmol) was added dropwise. The resulting mixture was stirred for 5 hours at room temperature until judged complete by TLC (R<sub>f</sub> 0.44, cyclohexane:dichloromethane 4:1), then the reaction was quenched with water-ice mixture. THF was evaporated under reduced pressure, and the resulting mixture was extracted with Et<sub>2</sub>O (2 x 5mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated under reduced pressure to give a white solid. The solid was triturated with hexane (10mL) and the mixture was filtered and utilized without further purification for successive reactions. Yield 62%.

mp 139 °C, White solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.1 (d, J = 7.5Hz, 2H, ArH); 7.7-7.1 (m, 11H, ArH); 5.5 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, δ): 140.5 (2C), 137.0, 128.6 (2C), 127.2, 126.2 (2C), 125.7 (2C), 122.9 (2C), 120.3 (2C), 119.1 (2C), 108.8 (2C), 46.2. HRMS (m/z) calcd for C<sub>19</sub>H<sub>15</sub>N, 257.1204; found, 257.1198.

#### **9-(6-iodohexyl)-9H-carbazole 4.**

To a mixture of carbazole (0.5 g, 2.99 mmol) in dry THF (6 mL), NaH (0.25 g, 6 mmol) was slowly added in portions. The mixture was stirred during 1 hour at room temperature, then the resulting suspension was transferred to a dropping funnel. The sodium carbazole suspension was added in 10 min to a solution in dry THF (3mL) of 1,6-diodohexane (3 ml, 18 mmol). The mixture was stirred for further 2 hours at room temperature until judged complete by TLC ( $R_f = 0.55$ , cyclohexane :dichloromethane 3:1), then the reaction was quenched with water and ice. THF was evaporated under reduced pressure, and the resulting mixture was extracted with Et<sub>2</sub>O (2 x 5mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, evaporated under reduced pressure to give an oil purified by flash chromatography (hexane: dichloromethane 10:1). Yield 83%.

mp 65-69 °C, White solid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 8.0 (d, J = 7.8 Hz, 2H, ArH ); 7.4 (dt, J = 6.9,2, 1.2 Hz, ArH); 7.3 (d, J = 8,4 Hz, 2H, ArH); 7.1 (dt, J = 8.1, 1.2 Hz, 2H, ArH ); 4.1 (t, J = 6.9 Hz, 2H, CH<sub>2</sub>N); 3.0 (t, J = 6.9 Hz, 2H, CH<sub>2</sub>I); 2.9 (t, J = 6.9 Hz, 2H, CH<sub>2</sub>, Hz); 1.7-1.5 (m, 3H, CH<sub>2</sub>); 1.4-1.2 (m, 3H, CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) δ: 140.1 (2C), 125.4 (2C), 122.5 (2C), 120.1 (2C), 118.6 (2C), 108.4 (2C), 42.5, 33.0, 29.9, 28.5, 25.9, 7.0. ESI-MS: (m/z). rt: 16.03 min:[m + H]<sup>+</sup> 378.

HRMS (m/z) calcd for C<sub>18</sub>H<sub>20</sub>IN, 377.0640; found, 377.0632.

### **3. Optimized procedure for the addition of *N*-alkylated carbazole molecules to (*R*)-2.**

Into a mixture of carbazole nucleophile (0.5 mmol) and Bi(OTf)<sub>3</sub> (0.328 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was introduced dropwise, via a syringe pump, a solution of (*R*)-1-(hydroxyethyl)ferrocene **2** (0.253 g, 1.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at -15°C during of 2 hours. The resulting mixture was stirred at -15°C for 20h until judged complete by TLC, then the reaction was filtered and the solid was washed with CH<sub>2</sub>Cl<sub>2</sub> one time. Organic solution was quenched with water. The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 5 mL). The organic phases were reunited, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated at reduced pressure to give a crude product purified by chromatography.

#### **(*S,S*)-9-benzyl-3,6-bis(1-ethylferrocene)-9H-carbazole 7a,c.**

Prepared according to the optimized procedure from 9-benzyl-9H-carbazole **3** (0.129 g, 0.50 mmol), until judged complete by TLC ( $R_f = 0.3$ , cyclohexane: dichloromethane 4:1) and purified by gravimetric chromatography (before cyclohexane, then from cyclohexane:

dichloromethane 20:1 to cyclohexane: dichloromethane 9:2) or preparative TLC (3:1 hexane:dichloromethane). Yield 30% yellow solid;  $[\alpha]_D^{25} = -73$  (c = 0.7 in  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.9 (s, 2H, Ar), 7.3-7.2 (m, 5H, Ar), 7.2-7.1 (m, 4H, Ar), 5.4 (s, 2H,  $\text{CH}_2$ ), 4.3-4.0 (m, 20H, Cp + CH), 1.7 (d, J = 7.4 Hz, 6H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 139.6 (2C), 138.5 (2C), 137.4, 128.7 (2C), 127.3, 126.5 (2C), 125.1 (2C), 122.8 (2C), 118.4 (2C), 108.5 (2C), 95.2 (2C), 68.6 (10C), 68.0 (2C), 67.5 (2C), 66.8 (2C), 66.4 (2C), 46.7, 39.8 (2C), 23.1 (2C). ESI-MS: rt: 58.02 min; m/z:  $:[m + \text{H}]^+$  682,  $:[m]^+$  681. HRMS (m/z) calcd for  $\text{C}_{43}\text{H}_{39}\text{Fe}_2\text{N}$ , 681.1781; found, 681.1790.

**(S,S)-3,6-bis(1-ethylferrocen)-9-(6-iodohexyl)-9H-carbazole 8a,c.**

Prepared according to the optimized procedure from 9-(6-iodohexyl)-9H-carbazole **4** (0.038 g, 0.1 mmol), until judged complete by TLC ( $R_f = 0.3$ , cyclohexane: dichloromethane 3:1) and purified by gravimetric chromatography (before cyclohexane, then from cyclohexane: dichloromethane 20:1 to cyclohexane: dichloromethane 9:2) or preparative TLC (3:1 hexane: dichloromethane). Yield 30%, mp 65-69 °C,  $[\alpha]_D^{25} = -91$  (c 0.6 in  $\text{CHCl}_3$ ). yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.8 (m, 2H, Ar); 7.2 (s, 4H, Ar); 4.2 (brs, 2H, Cp); 4.21 (t, J = 7.2 Hz, 2H, Cp) 4.16 (s, 10H, Cp); 4.15-4.0 (m, 6H, Cp + CH); 3.1 (t, J = 6.8 Hz, 2H,  $\text{CH}_2\text{N}$ ); 1.9-1.76 (m, 6H,  $\text{CH}_2$ ); 1.68 (d, J = 7.2 Hz, 6H,  $\text{CH}_3$ ), 1.42-1.37 (m, 6H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 139.3 (2C), 138.0; (2C), 124.9 (2C), 122.6 (2C), 118.3 (2C), 108.1 (2C), 95.3 (2C), 68.5 (10C), 68.9 (2C), 67.5 (2C), 66.8 (2C). 66.4 (2C), 42.9, 39.8 (2C), 33.2, 30.2, 28.9, 26.2, 23.1 (2C), 6.9. IR (KBr):  $\nu = 3368, 3088, 2961, 2918, 1651, 1456, 1099, 809 \text{ cm}^{-1}$ .

ESI-MS: rt: 88.87 min; m/z:  $:[m + \text{H}]^+$  802.1,  $:[m]^+$  801.2,

HRMS (m/z) calcd for  $\text{C}_{42}\text{H}_{44}\text{Fe}_2\text{IN}$ , 801.1217; found, 801.1228.

#### 4. Cleavage of benzyl group

##### 3,6-bis(1-ethylferrocen)-9H-carbazole 10a,c.

9-Benzyl-3,6-bis(1-ethylferrocene)-9H-carbazole mixture of diastereoisomers **7a-c** (0,068 g, 0.1 mmol) synthesized by the optimized procedure were dissolved in a mixture of DMSO (1.0 mL), THF (1.0 mL) and *t*BuOK solid (0.224 g, 2,0 mmol) at room temperature. After the reaction, the mixture was bubbled dried O<sub>2</sub> (over P<sub>2</sub>O<sub>5</sub>) until judged complete by TLC (R<sub>f</sub> = 0.2, hexane: dichloromethane 2:1). The reaction was quenched with water and THF was removed at reduced pressure, then the resulting crude was extracted with Et<sub>2</sub>O (3 x 5 mL) and the organic phases were collected. The resulting organic phase was washed with a water solution of HCl 0.1M (2 x 5 mL) to remove DMSO, then the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure to give a crude product purified by flash chromatography (cyclohexane: dichloromethane 2:1) or preparative TLC (hexane: dichloromethane 3:1). Yield 83%, 99% ee (*S,S*), 85:15 d.r.

mp 77-85 °C, yellow solid; RF = 0.23 (hexane/dichloromethane 2/1); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.9-7.2 (m, 7H, Ar); 4.3 (br, 2H, CH<sub>2</sub>); 4.2-4.0 (m, 20H, Cp + CH); 1.7 (d, J = 7.2Hz, 6H, CH<sub>3</sub>). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz) δ: 138.6 (2C), 138.3 (2C), 125,1 (2C), 123.1 (2C), 118.2 (2C), 110.2 (2C), 95.2 (2C), 68.5 (10C), 68.0 (2C), 67.5 (2C), 66.8 (2C), 66.4 (2C), 39.8 (2C), 23.1 (2C). IR (KBr): ν = 3400, 2858, 2916, 2847, 1633, 1468, 1242, 1100, 743 cm<sup>-1</sup>.

ESI-MS: rt, m/z:27.55 min; m/z: [m + H]<sup>+</sup> 592.1, [m]<sup>+</sup> 591.0.

HRMS (m/z) calcd for C<sub>36</sub>H<sub>33</sub>Fe<sub>2</sub>N, 591.1312; found, 591.1329.

HPLC analysis IC: gradient from 99:1 (hexane: *i*-PrOH) to 90:10, flow 0.5mL/min, 30 °C. TM (*S,S*): 35.79 min; *meso* 42.55 min; tm (*R,R*): 48.71 min. (*S,S*): *meso*, 85:15 d.r. Ee (*S,S*) 99%.

#### 5. Preparation of the thiol bisferrocene compounds.

##### (*S,S*)-6-[3,6-bis(1-ethylferrocen)-9H-carbazol-9-yl]-6-hexylethanethioate 11a,c.

Compound (3,6-bis(1-ethylferrocene)-9-(6-iodohexyl)-9H-carbazole) **8a,c** (0.42 g, 0.56 mmol) was dissolved in DMF (2 mL) and KSCOCH<sub>3</sub> (0.072 g, 0.62 mmol) was added. The mixture was stirred at room temperature overnight and checked by TLC (R<sub>f</sub> = 0.3 cyclohexane: dichloromethane 3:1). The reaction was quenched by adding HCl 1M (10mL),

then it was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10mL). The mixture was extracted with HCl 0.1 M (2 x 5 mL) and the organic phase was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated at reduced pressure to give a crude product used without any further purification for successive reaction. Quantitative yield.

Yellow oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.9 (s, 2H, Ar); 7.2-(m, 4H, Ar); 4.3 (brs, 2H, Cp); 4.22-4.16 (m, 2H, Cp) 4.17 (s, 10H, Cp); 4.16-4.0 (m, 6H, Cp + CH ); 2.8 (t, J = 7.2 Hz, 2H, CH<sub>2</sub>N); 2,32 (s, 3H, CH<sub>3</sub>CO); 1.9-1.8 (m, 2H, CH<sub>2</sub>); 1,70 (d, J = 6.8Hz, 6H, CH<sub>3</sub>); 1.6-1.5 (m, 2H, CH<sub>2</sub>); 1.4-1.3 (m, 4H, CH<sub>2</sub>); 0.92 (m, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>,δ): 197.7, 139.1 (2C), 137.8 (2C), 124.7 (2C), 122.4 (2C), 118.2 (2C), 108.0 (2C), 95.2 (2C), 68.4 (10C), 67.9 (2C), 67.3 (2C), 66.7 (2C), 66.3 (2C), 42.8, 39.6 (2C), 30.5 (2C), 29.2, 28.8, 28.3, 26.6, 23.0 (2C). IR (KBr): ν = 3357, 3092, 2922, 1683, 1492, 1350, 1258, 1106, 1017, 809 cm<sup>-1</sup>.

HRMS (m/z) calcd for C<sub>43</sub>H<sub>45</sub>Fe<sub>2</sub>NOS, 735.5785; found, 735.5770.

#### **(*S,S*)-6-[3,6-bis(1-ethylferrocen)-9H-carbazol-9-yl]-6-hexan-1-thiol 1a,c.**

The (*S,S*)-S-6-[3,6-bis(1-ethylferrocen)-9H-carbazol-9-yl]-6-hexylethanethioate (**11a,c**) compound (0.040 g, 0.053 mmol) was dissolved in a carefully degassed (freezing pump) mixture constituted by iPrOH:THF:H<sub>2</sub>O (5:12:3). Solid KOH (0.218 g, 3.89 mmol) was added, and the mixture was stirred at 60 °C for 3 h until judged complete by TLC (R<sub>f</sub> = 0.3, cyclohexane: dichloromethane 3:2), then the reaction was quenched with HCl 1 M added until pH = 7. The mixture was extracted with Et<sub>2</sub>O (3 x 5 mL), the organic phases were reunited, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure to give a crude product oil purified by flash chromatography (cyclohexane: dichloromethane 3:1).

Yield 60%.

mp 65-87 °C, yellow solid; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ): 7.8 (s, 2H, Ar); 7.3-7.2 (m, 4H, Ar); 4.3-4.0 (m, 20H, Cp + CH); 2.55 (t, J = 7.2Hz, 2H, CH<sub>2</sub>N ); 2.32 (s, 1H, SH); 1.89-0.8 (m, 10H); 1.68 (d, J = 7Hz, 6H,CH<sub>3</sub> ). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, δ): 139.3 (2C), 137.9 (2C), 124.9 (2C), 122.6 (2C), 118.3 (2C), 108.2 (2C), 95.3 (2C), 68.5. (10C), 68.0 (2C), 67.5 (2C), 66.8 (2C), 66.4 (2C), 43.0, 39.7 (2C), 30.5, 28.9, 28.8, 28.6, 26.9, 23.1 (2C).

HRMS (m/z) calcd for C<sub>41</sub>H<sub>43</sub>Fe<sub>2</sub>NS, 693.1815; found, 683.1785.

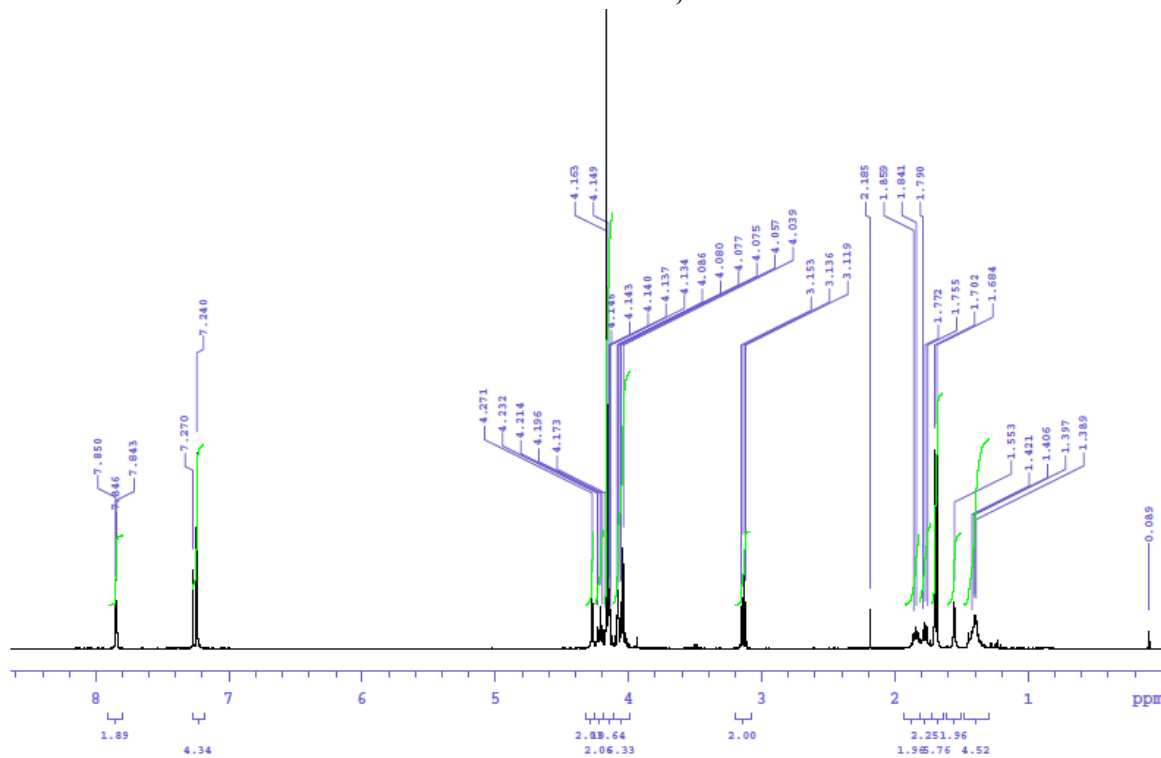
#### **Optically active bisferrocene. Optimization and analysis.**

After tuning the FC reaction for the racemic compound **1**, entiopure **2** (99 % ee) was employed to maximize the enantiomeric and diastereoisomer excess in the reaction with

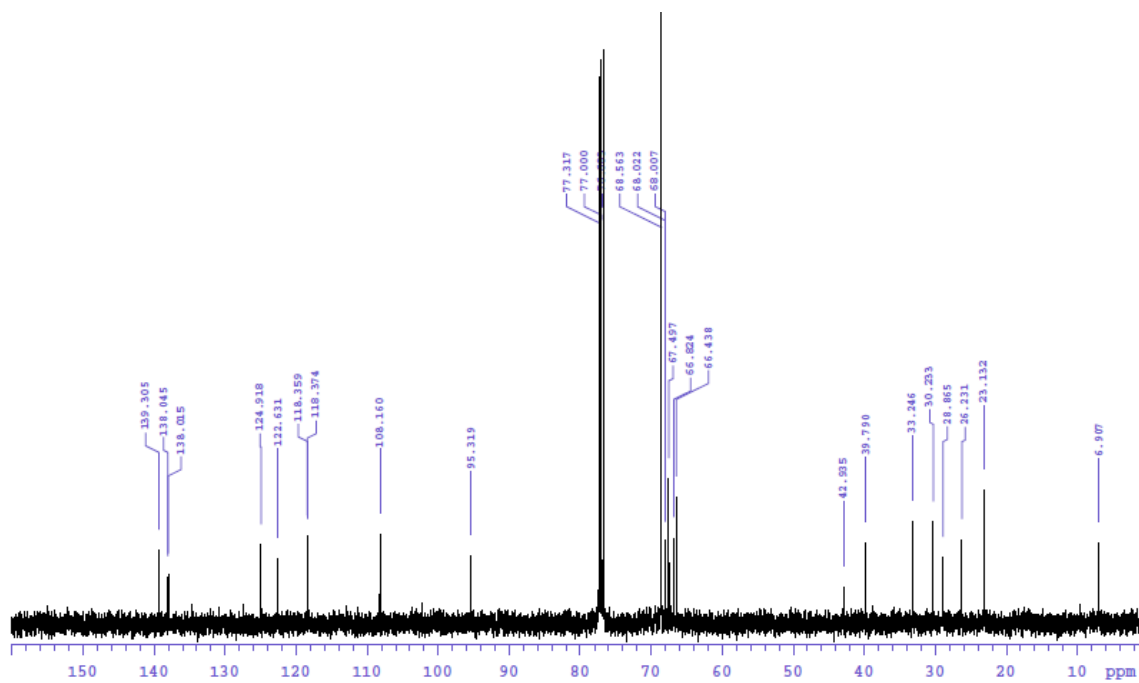
carbazole derivatives **3**. Careful optimization yielded a diastereoisomeric ratio of 85:15 for **7a** and **7c**, (chiral bisferrocene against meso diastereoisomer) with an ee of 99% for the chiral **7a** derivatives. It was not possible to improve the yield of bis-adducts **7-8** even in strong excess of **2**. All attempts to improve the diastereoisomeric ratio changing the reaction temperature and mode of addition failed (see Table ST2). The presence of inseparable meso compound **7c** in 15 %, derives from slight racemisation of ferrocenylethanol **2** occurring during the reaction. To make bisferrocenes suitable for immobilization on a gold surface, the optimized reaction conditions were used with the carbazole derivatives **4**, and the corresponding products **8, 8c** were isolated in an unseparable diastereoisomeric mixture of the chiral (*S,S*) **8a** and meso **8c** derivative, similarly to the reaction of benzylcarbazole **3**. Unfortunately, chiral HPLC analysis performed with several chiral columns was unable to quantify the stereoselectivity obtained in the reaction. However, it was indirectly proved that the addition of (*R*)-**2** to carbazole **4** gave the same results in term of diastereoisomeric and enantiomeric excess to those obtained with the carbazole **3**. In fact, the de-benzylated derivatives **10a** obtained in 99% ee, as an unseparable mixture of diastereoisomer **10a** and **10c** in a ratio 85 : 15, were alkylated with diiodohexane to afford the mixture of products **8a** and **8c**, identical by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR to those of the reaction performed with (*R*)-**2** on the carbazole derivative **4**. The measured optical rotation of the mixtures of **8a,c** products was identical for the two synthesis methodologies, whereby we can conclude that identical enantiomeric and diastereoisomeric ratios were obtained with carbazoles **3** and **4**, in both the reactions. The inseparable mixture of the iododerivatives (*S,S*) **8a** of 99% ee and *meso* **8c** was transformed into the corresponding thiols (*S,S*) **1a** and *meso* **1c** by addition of potassium thioacetate followed by alkaline hydrolysis.

## NMR Spectra

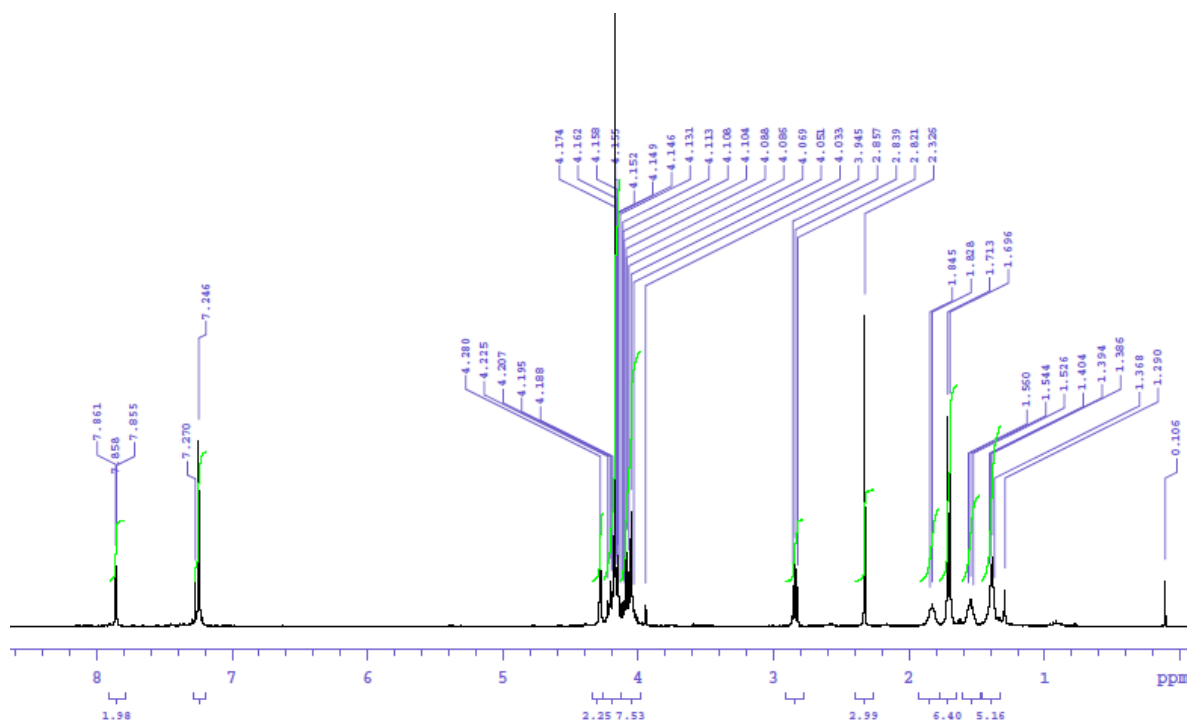
### <sup>1</sup>H NMR of 8a,c



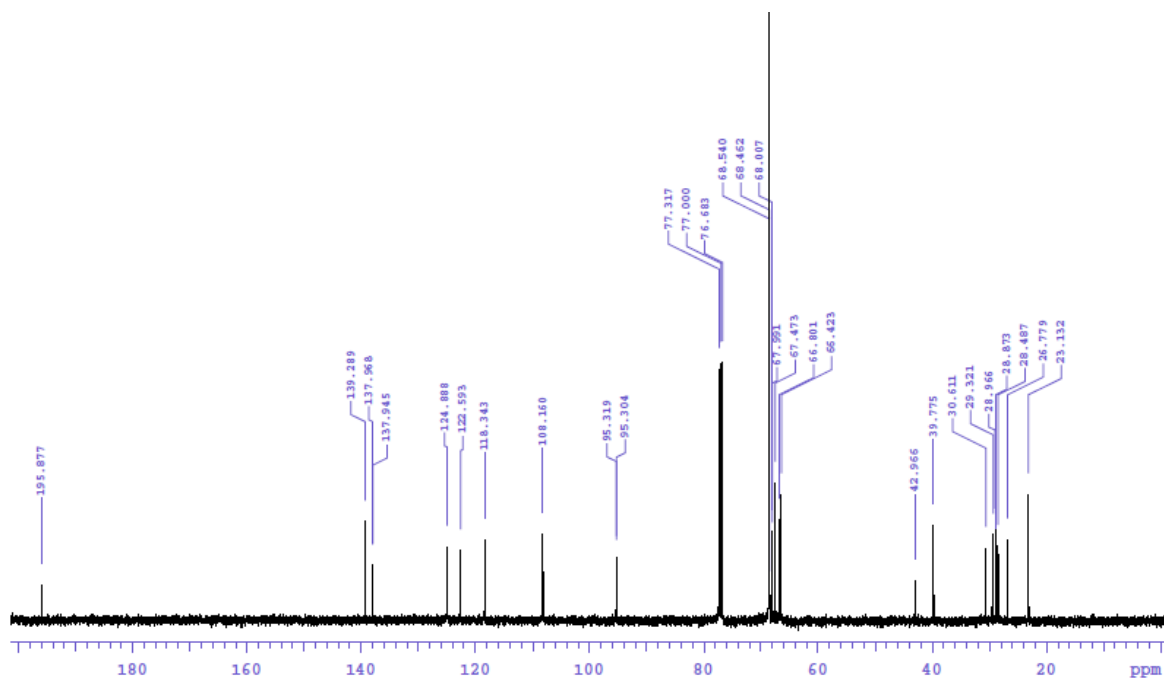
### <sup>13</sup>C NMR of 8a,c



### <sup>1</sup>H NMR of 11a,c



### <sup>13</sup>C NMR of 11a,c





## Instrumentation and Measurements

**Electrochemistry.** In the voltammetric experiments, a one-compartment, airtight design electrochemical cell was used, with high-vacuum glass stopcocks fitted with Viton (DuPont) O-rings to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenk flask containing the solvent were made by spherical joints fitted with the Viton O-rings. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically  $1.0\text{--}2.0 \times 10^{-5}$  mbar. The working electrode consisted of platinum disk ultramicroelectrodes (with radii from 5 to 62.5  $\mu\text{m}$ ) also sealed in glass. The counter electrode consisted of a platinum spiral, and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and reference electrodes were separated from the working electrode by  $\sim 0.5$  cm. Potentials were measured with the ferrocene or decamethylferrocene standards and are always referred to saturated calomel electrode (SCE).  $E_{1/2}$  values correspond to  $(E_{\text{pc}} + E_{\text{pa}})/2$  from CV. Ferrocene (or decamethylferrocene) was also used as an internal standard for checking the electrochemical reversibility of a redox couple. The temperature dependence of the relevant internal standard redox couple potential was measured with respect to SCE by a nonisothermal arrangement<sup>SR1</sup>. Voltammograms were recorded with an AMEL Model 552 potentiostat controlled by an AMEL Model 568 function generator. Data acquisition was performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 °C with a Lauda thermostat. Minimization of the ohmic drop was achieved through the positive feedback circuit implemented in the potentiostat.

EIS and CA experiments were performed using a two-compartment electrochemical cell also fitted with a saturated calomel electrode (SCE) and a platinum spiral as counter electrode with an Autolab Model PGSTAT 30 (ECO CHEMIE).

## Additional notes on the electrochemical results

**Cyclic voltammetry.** Various scan rates and temperatures were tested, in addition to those indicated. At variance with **7**, the oxidation of the carbazole unit in both **3** and **4** turned out to be irreversible. This is associated to the reported oxidative electrochemically-induced polymerization of carbazoles that was prevented in the case of **7** and **8** (data not shown) by the

substitutions in the positions 3 and 6 of the carbazole core. By contrast, the oxidation at ~1.2 V of **3** brought about the progressive growth of a polymer film onto the electrode surface; in the case of singly-substituted carbazole, where polymerization cannot occur due to the presence of the ferrocenyl substituent, the observed irreversible oxidation behavior is likely associated to the fast dimerization of the oxidized species. Interestingly, the separation between the two consecutive oxidation peaks around 0.35 V became more visible at lower temperature where a shoulder was distinctly observed in the overall two-electron peak.

**Capacitance measurement.** Various molar concentrations were tried for the starting solution. In spite of the observed voltage-independence of capacitance, the typical potential-dependent semicircle associated with relatively slow electron transfer (ET) processes was observed in the EIS spectra (Figure S6), that was attributed to the Fc moieties. Simulation and fitting of the EIS spectra obtained at various potentials allowed calculation of the relevant parameters associated with the electric response of the interface:  $C_{dl}$  was 5.8 and 11.0  $\mu\text{Fcm}^{-2}$  in the case of 50:50 and 25:75 SAMs respectively, while the corresponding values for  $R_{ct}$  were 41 and 55 k $\Omega$  respectively. As expected, as the content of **1** in the SAM increased,  $R_{ct}$  decreased, which corresponds to faster electron transfer kinetics. This is, in fact, in line with the inverse dependence of  $R_{ct}$  on the surface coverage  $\Gamma$ :

$$R_{ct} = \left( \frac{RT}{n^2 F^2 A \Gamma} \right) \times \left( \frac{1}{k^0} \right)$$

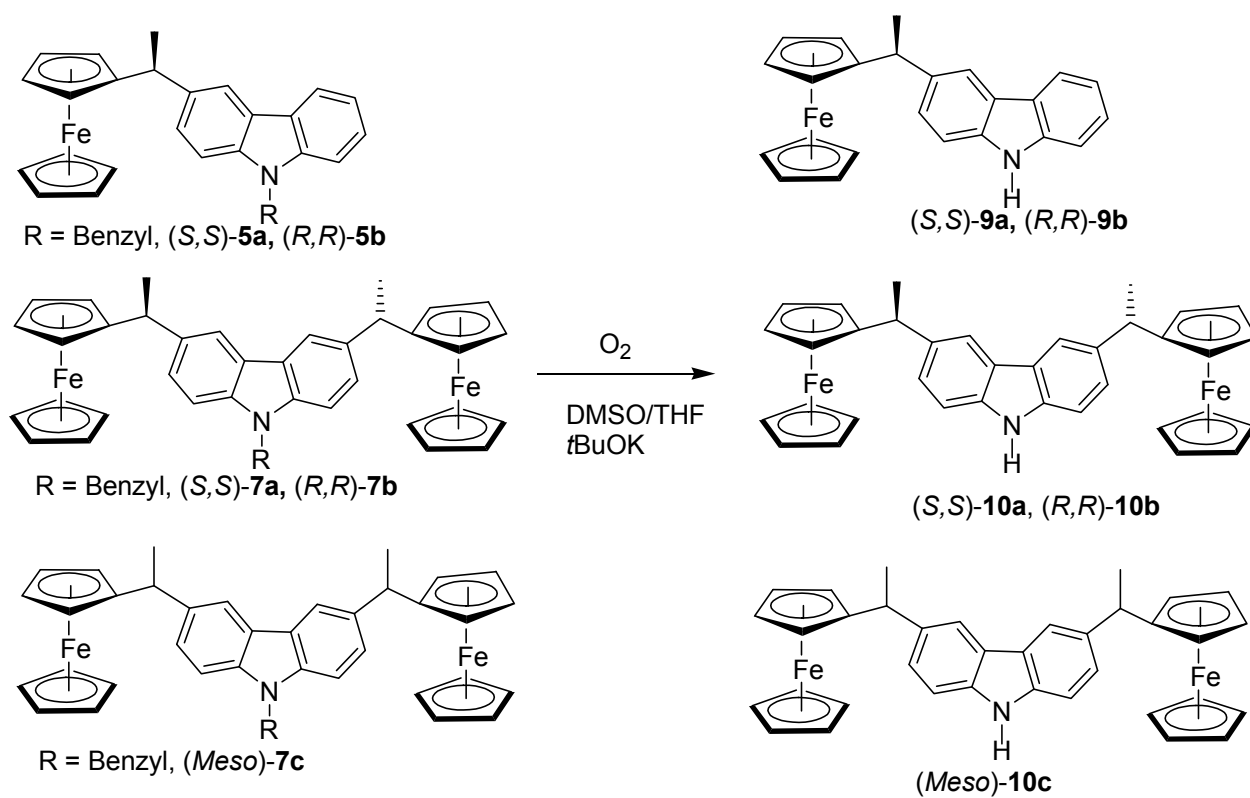
Rather unexpectedly, more blocking properties (i.e., lower capacitance) were also associated to higher **1** content, thus showing that the length of the C6 chain anchoring the bis-ferrocenyl carbazole moiety to the gold surface is adequate to accommodate the bulky head group over the mixed **1** : MEO SAM.

A value of  $k^0 \sim 10^2 \text{ s}^{-1}$  was finally obtained for the heterogeneous ET rate constant by the abovementioned relationship with the experimental values of  $R_{ct}$ . Such a low value, together with the rather small time constant of the electrode (~ 0.3 ms, also obtained by fitting of the EIS data), permitted an independent investigation of the heterogeneous ET kinetics to and from immobilized **1** by potential step chronoamperometry (CA)<sup>SR2,35</sup>. In such experiments (Figure S7), the electrode potential is stepped between two limiting values while the current is monitored continuously during the experiment over a timescale that fits in that of the relevant electrochemical process. At very short times, double-layer charging dominates the current decay while, at relatively longer timescales, faradic currents involving oxidation of the redox centres on the surface are observed.

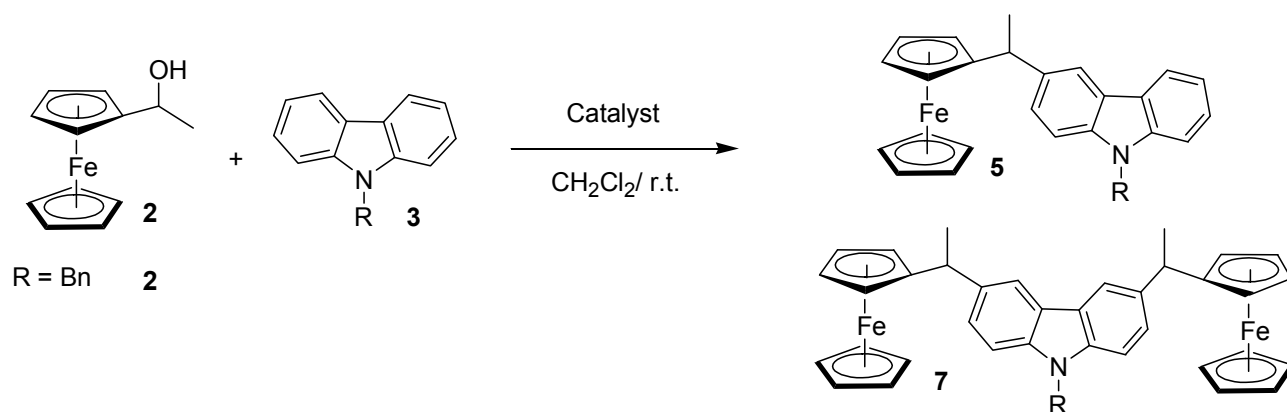
All transients, recorded during either the forward or the backward steps, displayed a short-lived ( $\sim 0.6$  ms) component associated with double-layer charging, in agreement with the very small time constant of the electrode as given by EIS. A relatively slower component (with  $\tau \sim 6$  ms) was finally observed in both transients, associated to the oxidation (in the forward step) and re-reduction (in the backward one) of the ferrocenyl moieties in **1**, in agreement with the EIS experimental findings.

### Additional Figures and Tables

**Scheme SS1.** Debenzylation of benzyl-ferrocene carbazole by oxygen.



**Table ST1.** Synthesis of mono-ferrocenyl protected carbazole: optimization of the reaction conditions.



Entry <sup>[a]</sup>	Catalyst	Ratio 7/5 <sup>[b]</sup>	Yield (%) <sup>[c]</sup>	Yield (%) <sup>[c]</sup>
1	InBr <sub>3</sub> <sup>[d]</sup>	1/1	23%	40
2	PTSA	1/-	15%	-
3	Bi(OTf) <sub>3</sub>	9/2	36%	15
4	AuCl	-	-	-

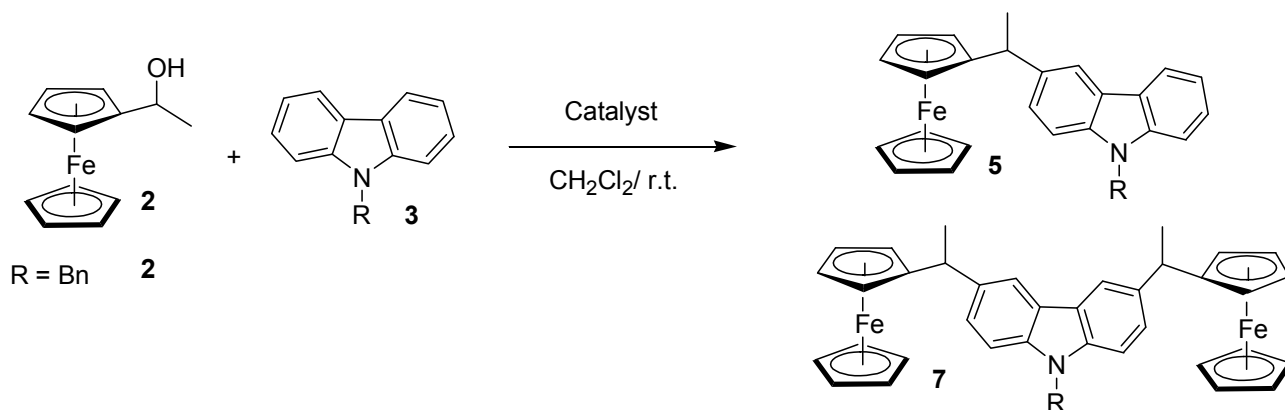
[a] All the reactions were carried out under inert atmosphere, with 0.1 mmol of alcohol **2**, 0.25 mmol of nucleophile **3** and 10 mol% of catalyst in 1.0 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 2-5 hours;

[b] The ratio was determined by the <sup>1</sup>H-NMR signals of benzylic hydrogen of the ferrocenyl compounds **7** and **5** in crude reaction mixture;

[c] Yields of purified products after chromatography;

[d] InBr<sub>3</sub> was added as solution in CH<sub>3</sub>CN (0.33M).

**Table ST2.** Synthesis of bis-ferrocenyl protected carbazole: optimization of the conditions.



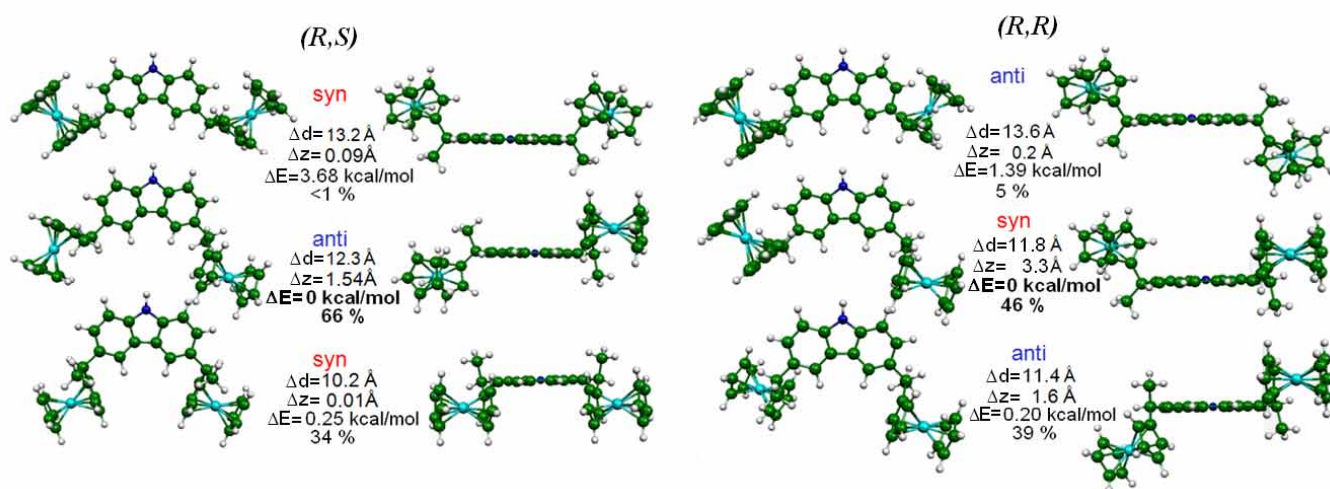
Entry <sup>[a]</sup>	Catalyst	(equiv.)	Ratio 3/7/5 <sup>[b]</sup>	Yield 7(%) <sup>[c]</sup>	Yield 5(%) <sup>[c]</sup>
1	BF <sub>3</sub> -OEt <sub>2</sub> <sup>[d]</sup>	3	2/1/1	23	24
2	InBr <sub>3</sub> <sup>[e]</sup>	0.15	4/4/3	35	24
3	Bi(OTf) <sub>3</sub>	0.15	6/3/1	33	10
4	Bi(OTf) <sub>3</sub>	0.5	1/2/2	40	40
5	Bi(OTf) <sub>3</sub>	1	2/4/5	36	46
6	Al(OTf) <sub>3</sub>	1	9/4/2	40	19
7	Zn(OTf) <sub>2</sub>	1	3/4/3	39	32
8	PTSA <sup>[f]</sup>	1	-	-	-

[a] All the reactions were carried out under inert atmosphere, with 0.22 mmol of alcohol **2**, 0.1 mmol of nucleophile **3** and the suitable catalyst in 1.0 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature for 2-5 hours; [b] The ratio was determined by the <sup>1</sup>H-NMR signals of benzylic hydrogen of **3**, **7**, and **5** in the crude reaction mixture; [c] Yields of purified products after chromatography; [d] by-product **F** was observed in traces; [e] InBr<sub>3</sub> is added as solution in CH<sub>3</sub>CN (0.33M) [f] Undesired products were isolated from the reaction mixture.

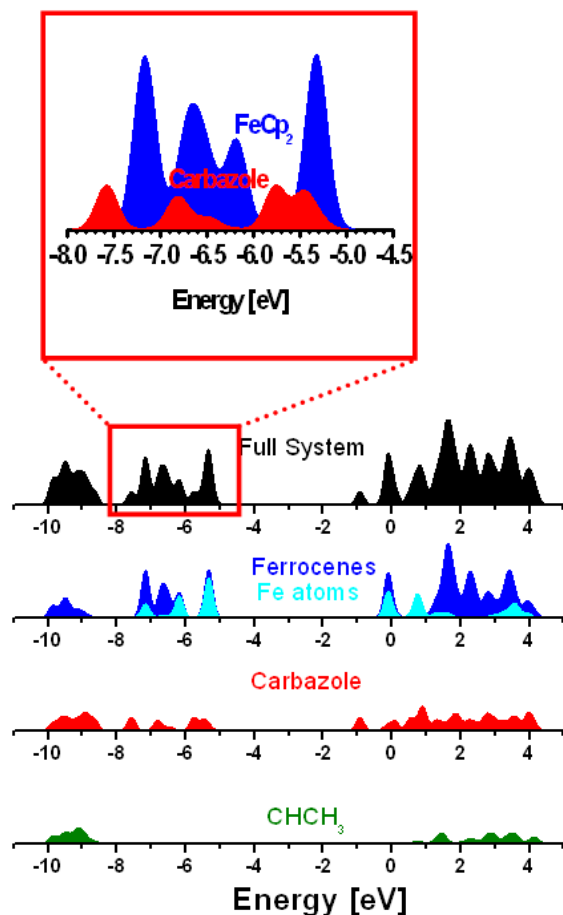
**Table ST3** - Energy differences among different isomers (relative to the ground-state one) at the SCS-MP2 level of theory<sup>SR3</sup> and associated Boltzmann distribution at room temperature.

	Energy [kcal/mol]	Distribution at 300K
RS1	<i>3.09</i>	<i>&lt;1%</i>
RS2	<i>0.03</i>	<i>49%</i>
RS3 (ground-state)	<i>0.00</i>	<i>51%</i>
RR1	<i>0.95</i>	<i>10%</i>
RR2 (ground-state)	<i>0.00</i>	<i>50%</i>
RR3	<i>0.13</i>	<i>40%</i>

**Figure SF1.** Optimized rotational isomers of free bisferrocene in (*R,S*) and (*R,R*) configurations in side- and top-view (left and right, respectively), along with  $\Delta d$ ,  $\Delta z$ ,  $\Delta E$ , and relative abundance, as already reported in Table 1.

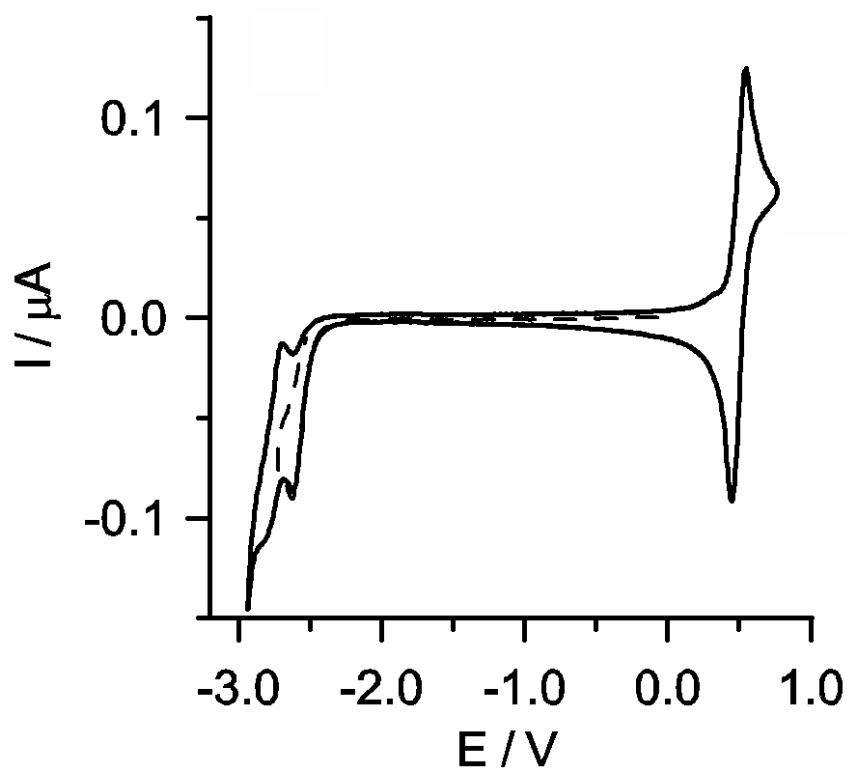


**Figure SF2.** Projected Density of States (pDoS) of the most stable (*R,S*) isomer.

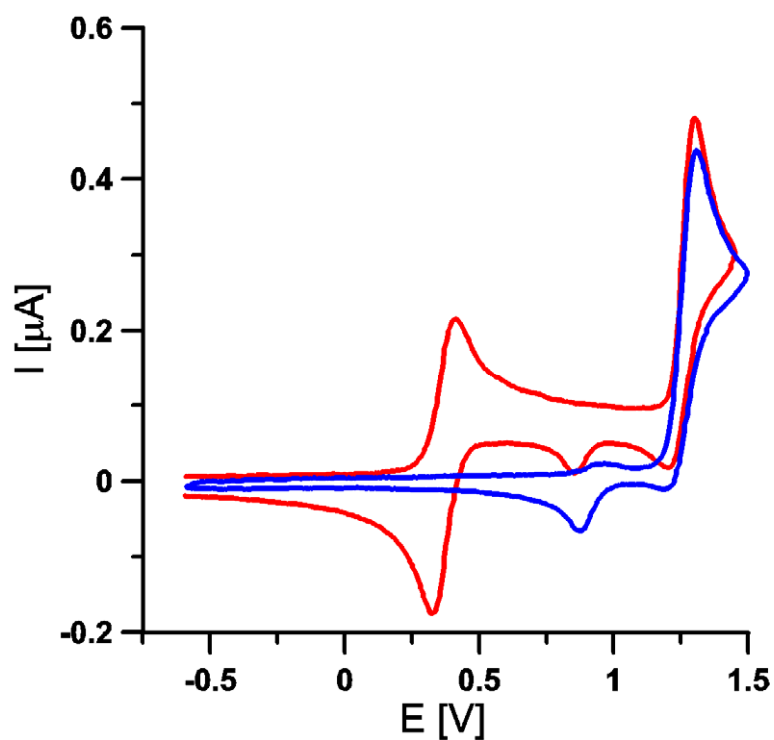




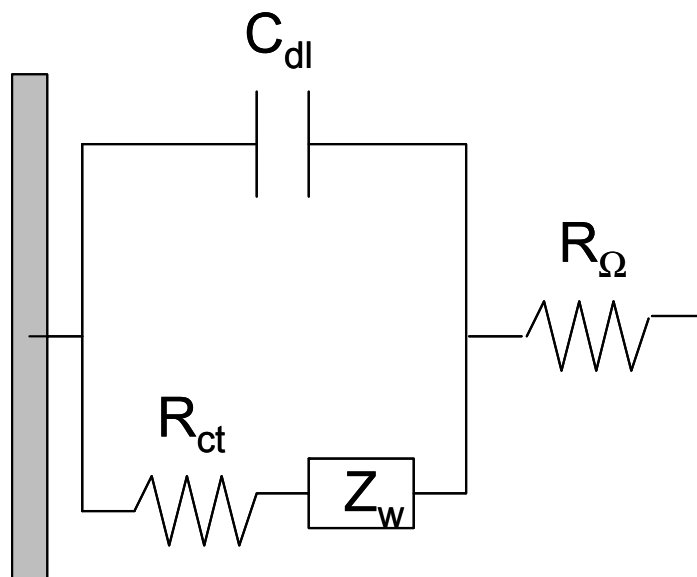
**Figure SF3.** CV curves of a 0.5 mM solution of **1a-c** in THF (supporting electrolyte: 0.05 M TBAH). First scan in the negative direction, reverse scan potential: -2.95 V (full line) -2.70 V (dashed line).



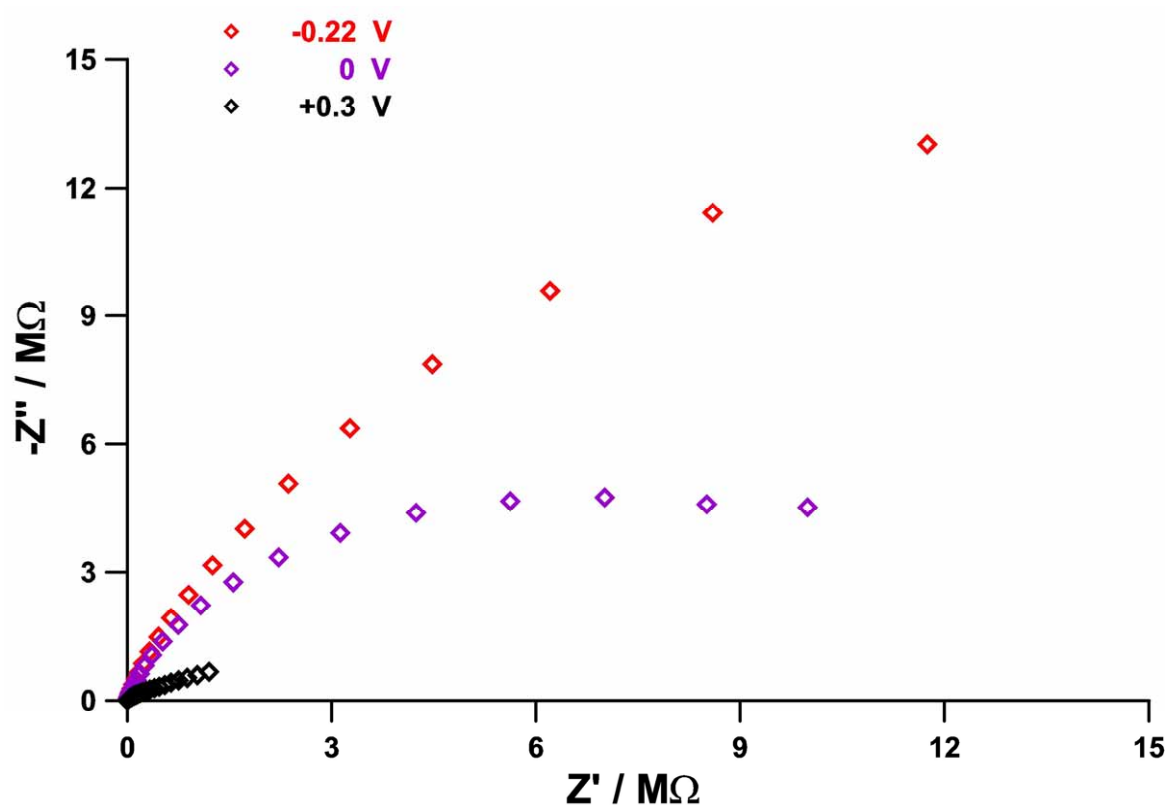
**Figure SF4.** CV curves of a 0.5 mM solution of **3** and **5a-b** in DCM (supporting electrolyte: 0.05 M TBAH).



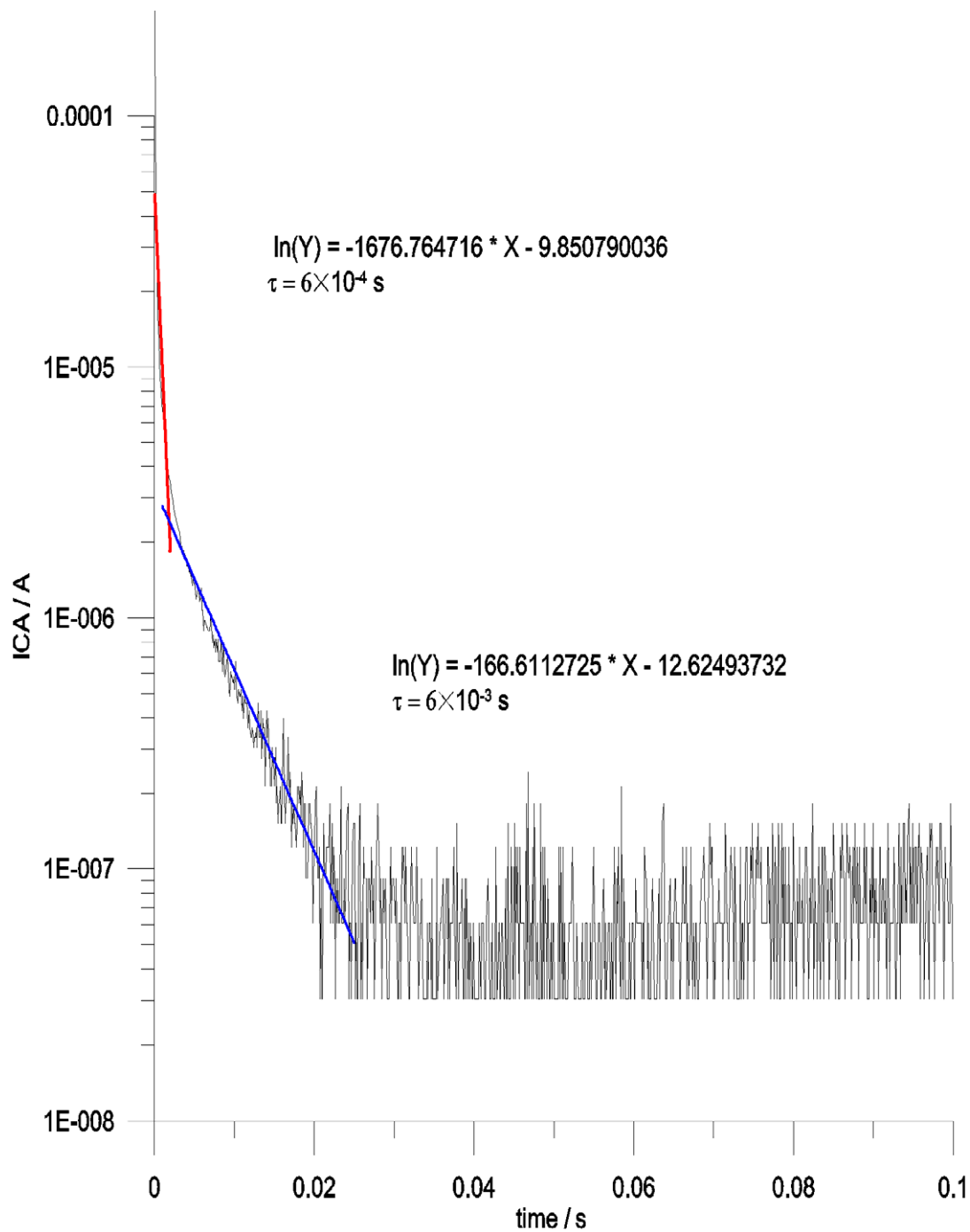
**Figure SF5.** Randles equivalent circuit describing the electrical response of the electrochemical interface. In the circuit,  $R_{\Omega}$  represents the solution resistance,  $C_{dl}$  the double layer capacitance,  $R_{ct}$  the charge transfer resistance (related to the exchange current  $i_0$  and standard rate constant) and  $Z_w$  the Warburg element, describing the time (frequency) dependence of mass transport.



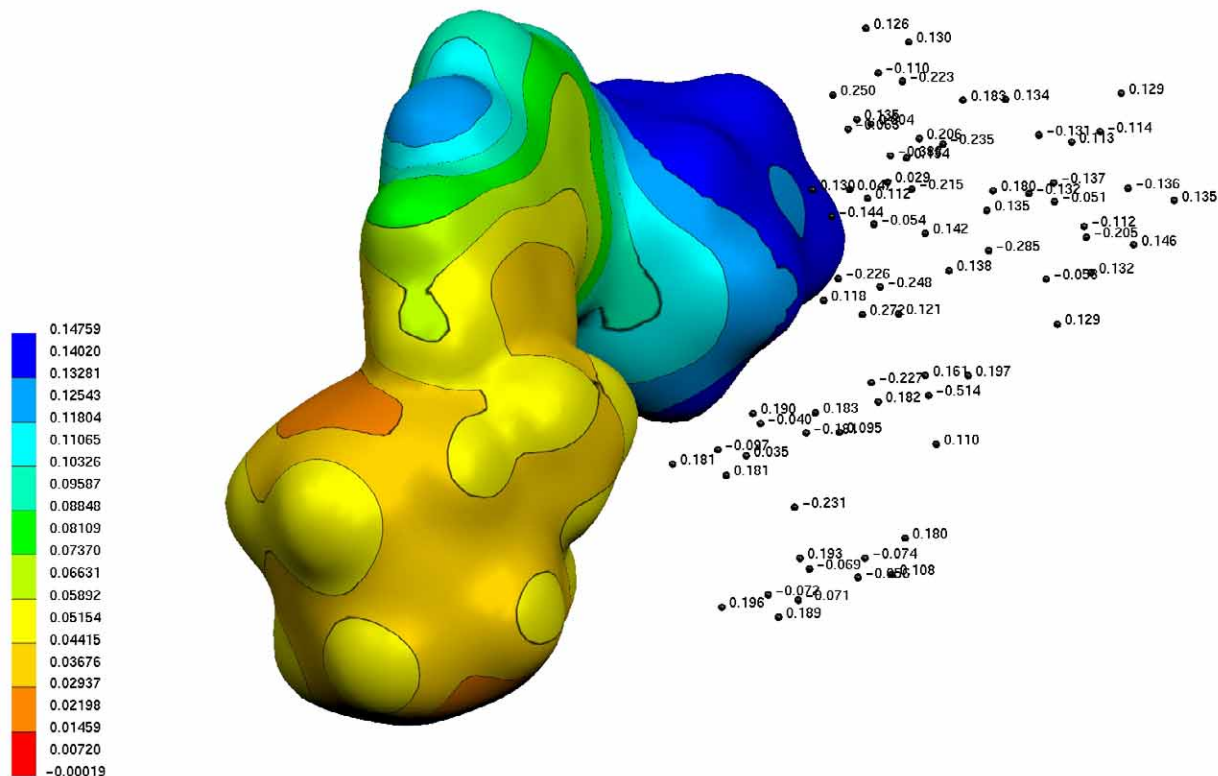
**Figure SF6.** EIS spectra of **1a-c**/MEO-SAM on Au at different potentials. Solution: aqueous 0.1 M KCl.  $T = 25\text{ }^{\circ}\text{C}$ . The out-of-phase component of the impedance,  $-Z''$ , is plotted vs. the in-phase one,  $Z'$  –  $Z''$  and  $Z'$  being parametric functions of the frequency (Nyquist plot). The spectra were taken at three potentials value: -0.22(OCP), 0 V and 0.3 V vs. SCE, i.e., in the same potential region where the two oxidations of **1a-c** may take place. The electrical response of the interface was described in terms of the equivalent circuit shown in Figure S5. The electrical parameters were evaluated by fitting procedures, using the CNLS method described by Boukamp<sup>SR4</sup>.



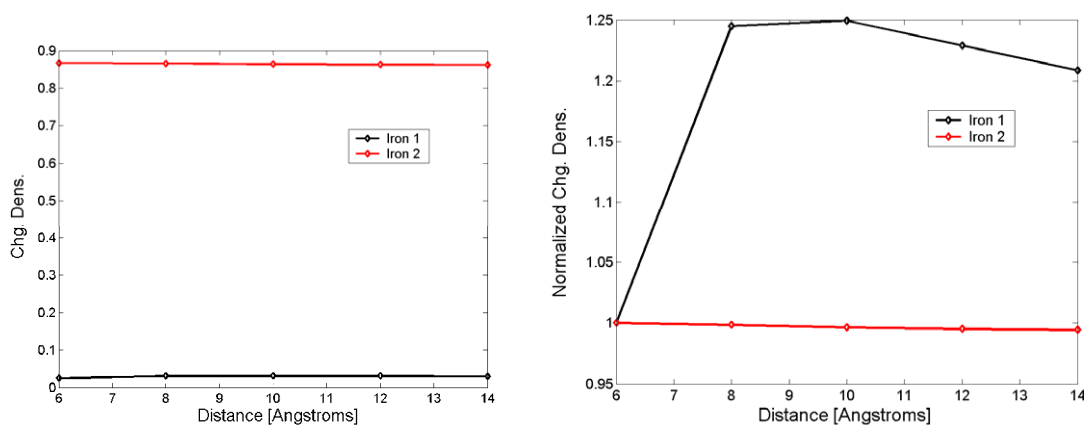
**Figure SF7.** CA transient recorded for the mixed SAM **1a-c/MEO on gold**.  $E = 0.4$  V; step duration: 0.1 s. Solution: aqueous 0.1 M KCl,  $T = 25$  °C.



**Figure SF8** – Plot of the electrostatic potential surface of a bisferrocene monomer interacting with a point-charge model.



**Figure SF9** – Charge densities on the two Fe atoms of the driven molecules (in the two-bisferrocene cell) vs. distance  $d$ , raw (left) and normalized to the value for  $d=6$  Å (right). In the second, the increase from 6 to 8 Å is attributable to a remainder of near-field effects at  $d=6$  Å. At larger distance, the flatness of the curves indicate a sharp response (i.e. close to complete charge localization and to some extent independent of distance) of the driven molecule to the driver.



### Supporting Information References

- [SR1] Yee, E. L., Cave, R. J., Guyer, K. L., Tyma, P. D., Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131-1137.
- [SR2] Chidsey, C.E.D. *Science* **1991**, *251*, 919-922.
- [SR3] Grimme, S. *J. Chem. Phys.* **2003**, *118*, 9095-9102.
- [SR4] Boukamp, B.A. *Solid State Ionics* **1986**, *20*, 31-44 (1986).