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# Samarium diiodide-promoted sequential coupling-aldol-reduction reactions of ferrocene-substituted enones

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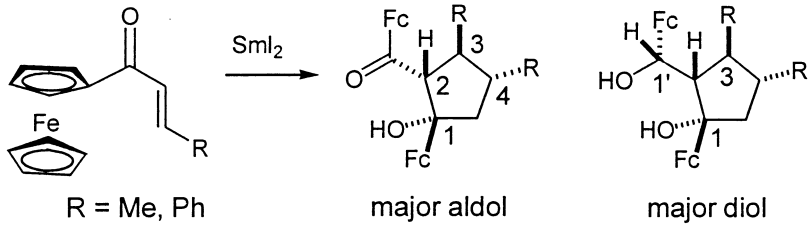
**Abstract –** On treatment with $SmI_2$ in THF, 1-ferrocenyl-3-phenyl-2-propen-1-one and its related ferrocene-substituted enones underwent cyclodimerizations to give aldols (**2a–g**) with 3,4-*trans* configuration. Further reduction by using increased amounts of $SmI_2$ produced the corresponding diols. The stereoselectivity in this study was comparable with that in the $SmI_2$-promoted cyclodimerization of chalcones, but in contrast to that in the $SmI_2$-promoted cyclization-aldol reaction of 1,1'-dicinnamoylferrocenes. The thienyl- and furyl-substituted enones **5a** and **5b** could be visualized as an extended system of conjugated ketones, so that the $SmI_2$-mediated coupling reactions occurred preferably by linkages of β-carbons with thiophene or furan rings, giving compounds **8a**,**b** and **9a**,**b**. © 2001 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS




**samarium diiodide / ferrocene / α,β-unsaturated ketones / coupling reaction**

**Résumé –** Le traitement du 1-ferrocényl-3-phényl-2-propèn-1-one et autres cétones substituées par un groupe ferrocényle par le $SmI_2$ dans le THF induit une cyclodimérisation, conduisant aux composés aldol **2a–g**, possédant une configuration 3,4-trans. Une réduction plus poussée, par l'ajout de quantités supplémentaires de $SmI_2$, fournit les diols correspondants. La stéréosélectivité obtenue est comparable à celle observée dans la cyclodimérisation des chalcones induites par la $SmI_2$, mais contraste avec la cyclisation-aldol des 1,1'-dicinnamoylferrocènes. Les cétones **5a** et **5b**, substituées par un groupe thiényle ou furyl, peuvent être considérées comme des cétones conjuguées étendues, puisque les réactions de couplage induites par $SmI_2$ relient préférentiellement les carbones en β- avec les noyaux thiophène ou furanne, pour donner les composés **8a**,**b** et **9a**,**b** respectivement. © 2001 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

**diiodure de samarium / ferrocène / cétones α,β-insaturées / réaction de couplage**



## 1. Introduction

An α,β-unsaturated ketone can react with metal or low-valent metallic salts to give hydrodimeric coupling products by linkage of two β-carbons. Although the coupling product may exist as a mixture of *dl* and *meso* isomers, stereoselective reactions have been found in certain cases. For

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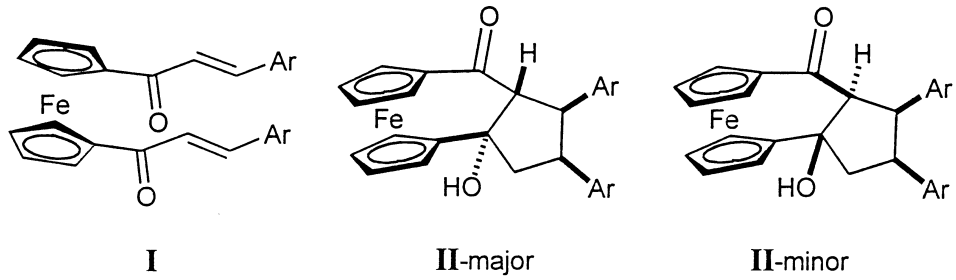



**I** **II**-major **II**-minor

**Scheme 1.**

example, the reductive coupling reaction of (*E*)-1,3-diphenyl-2-propenone (chalcone) by Zn/HOAc/EtOH gives 1,3,4,6-tetraphenylhexane-1,6-dione as a single *dl*-isomer [1]. In the conditions of $SmI_2$/THF/HMPA [2–4], the reductive coupling reaction of chalcone also occurs with *dl*-selectivity, and the subsequent aldol reaction proceeds intramolecularly to afford the cyclodimerization product, 2-benzoyl-1,3,4-triphenylcyclopentanol, with 3,4-*trans* configuration [2, 3]. In the absence of HMPA, chalcone is simply reduced by $SmI_2$/THF to give 1,3-diphenylpropanone [2, 3]. The cyclodimerization of chalcone is also achieved by using Yb/THF/HMPA [5], Zn/$LnCl_3$/THF [6] or Zn/$TiCl_4$ [7] to give mainly the 3,4-*trans* isomer. However, treatment of chalcone with Nd/DME [8] or $Bu_3SnH$/AIBN/PhH [9] gives a mixture of cyclodimerization products with unidentified stereochemistry. Nevertheless, unexpected stereoselectivity is observed in an electrochemical reaction of chalcone in DMF, giving the cyclodimerization products with 3,4-*cis* configuration [10, 11].

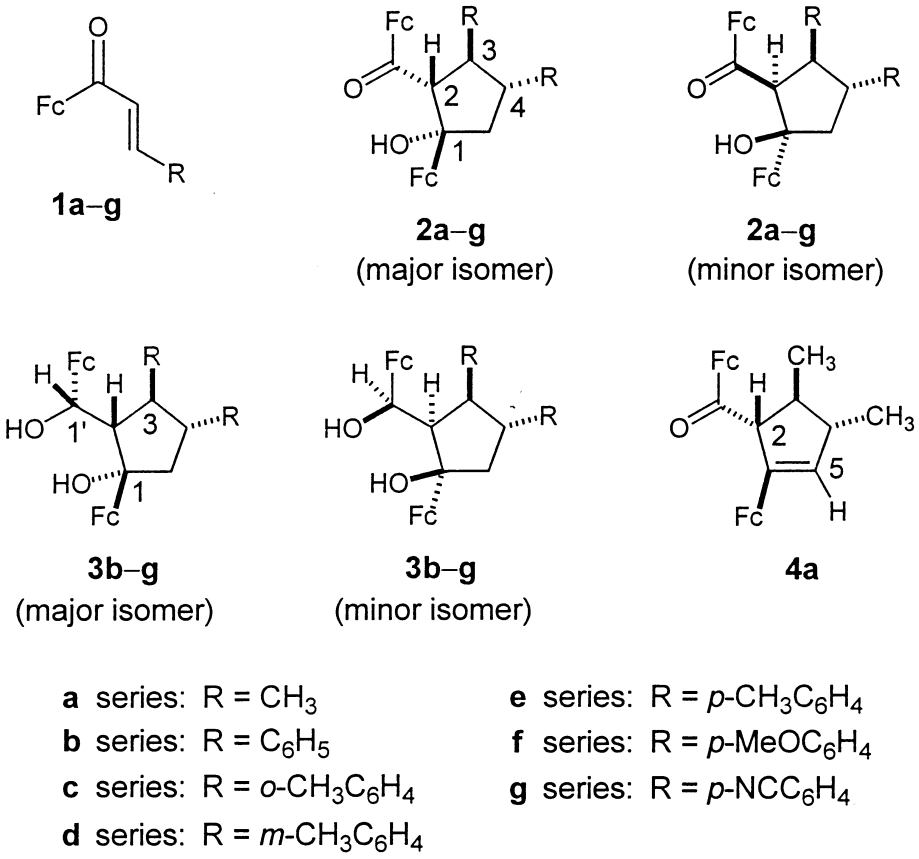
It has been reported that 1-ferrocenyl-3-phenyl-2-propen-1-one (**1b**) is reduced by the electrochemical method to give 1-ferrocenyl-3-phenylpropanone [12]. A previous study also indicated that the $Fe(CO)_3$-coordinated chalcone (in $\eta_4$ form) undergoes mainly 1,4-reduction on treatment with $SmI_2$/THF/HMPA [3]. However, we recently demonstrated that $SmI_2$ is an effective one-electron transfer reagent for the intramolecular coupling reactions of 1,1'-dicinnamoylferrocenes (**I**) [13] (*scheme 1*). The coupling reaction with a linkage of the β- and β'-carbons occurs in a highly stereoselective manner to form a *meso* intermediate, which proceeds with an intramolecular aldol reaction to give [3]ferrocenophanes (**II**-major and **II**-minor) with two phenyl groups on the same face (*scheme 1*). Such *cis* selectivity is opposite to the *trans* selectivity in the cyclodimerization of chalcones [3]. As the ferrocenyl group is known to exhibit the reaction aptitude similar to the phenyl group in many aspects of organic reactions, we thus investigated the $SmI_2$-promoted reactions of ferrocene-substituted enones **1a–g** in order to compare and contrast the reactions of chalcones and 1,1'-dicinnamoylferrocenes.

## 2. Results and discussion

Friedel–Crafts acylation of ferrocene with (*E*)-crotonyl chloride gave 1-ferrocenyl-2-buten-1-one (**1a**) [14], whereas aldol condensations of acetylferrocene with appropriate benzaldehydes in alkaline conditions afforded the ferrocene-substituted enones **1b–g** [15] (*scheme 2*). All of these enones had (*E*)-configurations, as their vinyl protons showed large coupling constants (15–16 Hz) in the $^1H$ NMR spectra.

The results for the $SmI_2$-mediated coupling reactions of **1a–g** are listed in *table I*. The ferrocene-substituted enones **1a–g** underwent cyclodimerizations at 0 °C to afford aldols **2a–g** on treatment with 1.1 molar proportions of $SmI_2$ in THF. Further reduction occurred, giving diols **3b–g**, by using increased amounts of $SmI_2$ (2.2 molar proportions). The reactions were completed in less than 1 h without the assistance of HMPA or other additives. A side product **4a** (11 % yield) was also obtained as a consequence of dehydration of **2a**-major. The nonconjugated enone **4a**, showing a vinyl proton at $\delta$ 5.87 (br s), was selectively formed, presumably by the catalysis of samarium ions. The conjugated isomer of **4a** was not produced because it would cause severe steric effect between the adjacent ferrocenyl and ferrocenoyl groups.

When an individual $SmI_2$-mediated reaction gave an isomeric mixture of products, the isomers were successfully separated by silica gel chromatography with elution of gradients of EtOAc and hexane. The structures of **2a**-major, **3b**-major and **3c**-major were established by X-ray diffraction analyses. Aldol **2a**-major had (1*S**,2*R**,3*S**,4*R**) configuration with 1-OH, 2-ferrocenoyl and 4-Ph substituents on the same face, but the 3-Ph group on the opposite




**a** series: R = $CH_3$
**b** series: R = $C_6H_5$
**c** series: R = *o*-$CH_3C_6H_4$
**d** series: R = *m*-$CH_3C_6H_4$
**e** series: R = *p*-$CH_3C_6H_4$
**f** series: R = *p*-$MeOC_6H_4$
**g** series: R = *p*-$NCC_6H_4$

**Scheme 2.**

face. Diols **3b**,**c**-major had (1*S**,1'*S**,2*S**,3*S**,4*R**) configurations presumably derived from the stereoselective reductions of the corresponding aldols **2b**,**c**-major. The structures of **2e**-minor (R = *p*-$CH_3C_6H_4$) and **3g**-minor (R = *p*-$NCC_6H_4$) were also deduced to have (1*R**,2*S**,3*S**,4*R**) and (1*R**,1'*R**,2*R**,3*S**,4*R**) configurations, respectively, on the basis of their NOESY spectra (500 MHz). The H-4 (at $\delta$ 4.06, m) in **2e**-minor aldol was assigned to the β-orientation because it had an NOE correlation with H-5β (at $\delta$ 2.64, dd, $J$ = 13.0, 6.6 Hz). The NOE correlations of H-5α (at $\delta$ 2.38, dd, $J$ = 13.0, 12.7 Hz) with H-2 and H-3 (at $\delta$ 3.62-3.73, m) indicated that they were on the same α-face. In a similar fashion, H-4 (at $\delta$ 4.17, m) in **3g**-minor diol had an NOE correlation with H-5β (at δ 2.24, dd, $J$ = 13.0, 5.3 Hz). Two $D_2O$-exchangeable signals at $\delta$ 3.38 (s) and 3.39 (s) were attributed to the two hydroxyl groups, which likely formed intramolecular hydrogen bonding.

**Table I.** The $SmI_2$-mediated coupling reactions of ferrocenyl enones **1a–g** (THF, 0 °C).

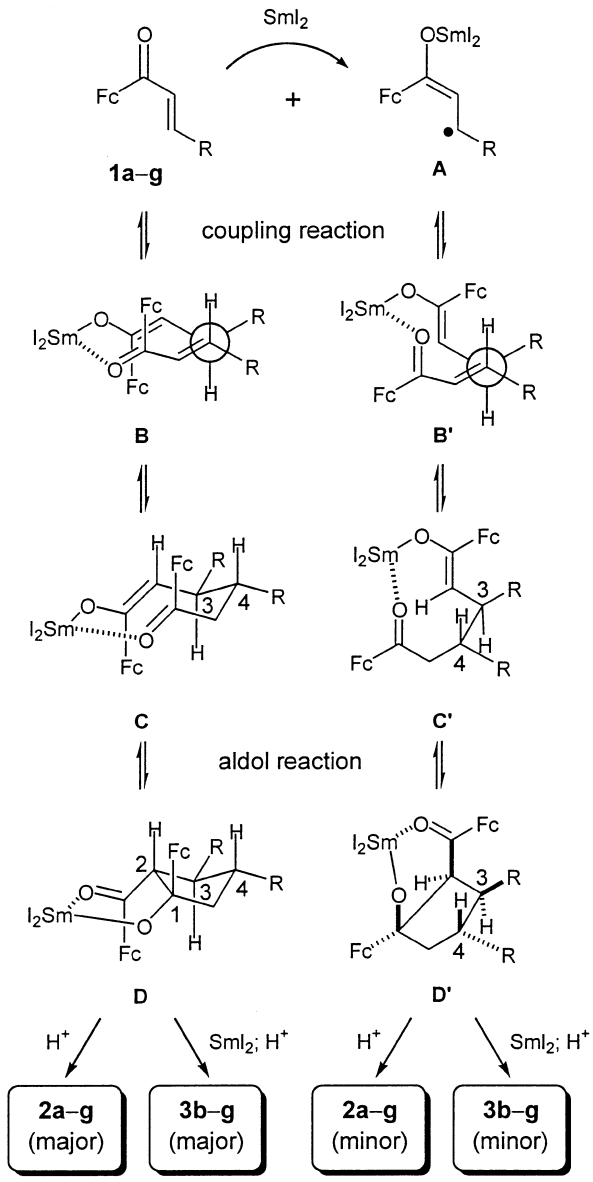
| Entry | Substrate | R = | $SmI_2$ (molar proportions) | Products (yields, %; ratio of isomers) |
|---|---|---|---|---|
| 1 | **1a** | $CH_3$ | 1.1 | **2a** (46)[a] + **4a** (11)[a] |
| 2 | **1b** | $C_6H_5$ | 1.1 | **2b** (59)[a] |
| 3 | **1b** | $C_6H_5$ | 2.2 | **3b** (92; 86:14) |
| 4 | **1c** | *o*-$CH_3C_6H_4$ | 1.1 | **2c** (97; 81:19) |
| 5 | **1c** | *o*-$CH_3C_6H_4$ | 2.2 | **3c** (85; 85:15) |
| 6 | **1d** | *m*-$CH_3C_6H_4$ | 1.1 | **2d** (75; 91:9) |
| 8 | **1e** | *p*-$CH_3C_6H_4$ | 1.1 | **2e** (72; 79:21) |
| 9 | **1e** | *p*-$CH_3C_6H_4$ | 2.2 | **3e** (84; 73:27) |
| 10 | **1f** | *p*-$MeOC_6H_4$ | 1.1 | **2f** (55)[a] |
| 12 | **1g** | *p*-$NCC_6H_4$ | 1.1 | **2g** (33)[a] |
| 13 | **1g** | *p*-$NCC_6H_4$ | 2.2 | **3g** (86; 64:36) |

[a] Other possible isomers were not observed.

Thus, the stereochemistry at C-1' of **3g**-minor diol could be inferred from the NOE correlations of H-1' (at $\delta$ 5.11, br s) with H-2 (at $\delta$ 2.57, d, $J$ = 6.2 Hz) and H-3 (at $\delta$ 4.07, m).

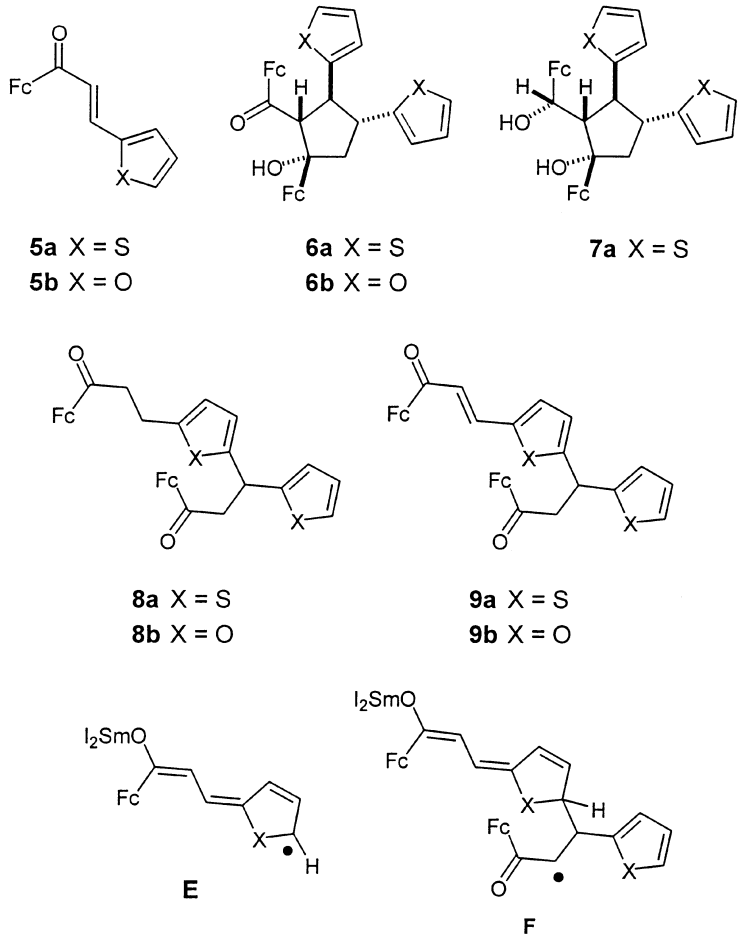
The stereoselectivity in the formation of aldols **2a**-**g** with 3,4-*trans* configuration was comparable with that in the $SmI_2$-promoted cyclodimerization of chalcones, but in contrast to that in the $SmI_2$-promoted cyclization-aldol reaction of 1,1'-dicinnamoylferrocenes. According to the present study, we propose the reaction mechanisms (*scheme 3*) for the stereochemical outcomes. An electron-transfer process from $SmI_2$ to the ferrocene-substituted enone (**1a**-**g**) would generate a β-carbon radical intermediate **A**. The coupling reaction of the enone and β-carbon radical would provide dimers **C** and **C'**, via the transition states **B** and **B'** respectively. Both **B** and **B'** were considered to hold the chelate modes with the *dl*-dispositions. The alternative *meso*-dispositions (not shown) might be thermodynamically disfavored. The distribution of **B** and **B'** would determine the ratio between the major and minor products. According to the results of this study, the transition state **B** with an *s*-trans enone moiety was considered to be more stable than **B'** with an *s-cis* enone moiety. The intramolecular aldol reactions of **C** and **C'** with appropriate orientations could be facilitated by samarium ions to give the major and minor aldols **2a**-**g**, respectively. In the presence of excess of $SmI_2$, the ferrocenoyl groups in aldolates **D** and **D'** were further reduced to the ketyl radicals (or the corresponding carbinyl anions), which could abstract a hydrogen atom (or proton) to yield diols **3b**-**g**. This process occurred apparently from the less hindered *exo* face.

We also prepared the thienyl- and furyl-substituted enones **5a** and **5b** by condensation of acetylferrocene with 2-thiophenecarbaldehyde or 2-furancarbaldehyde (*scheme 4*). The reaction of **5a** with $SmI_2$ (1.0 molar proportion) in THF at 0 °C for 2 h gave aldol **6a** (13 %), diol **7a** (6 %), ketone **8a** (41 %) and enone **9a** (9 %). The structure of **7a** was confirmed by an X-ray diffraction to have the (1*S**,1'*S**,2*S**,3*S**,4*R**) configuration. The stereochemistry was in agreement with that operated in the $SmI_2$-mediated cyclodimerizations of **1a**-**g**. The substrate **5a** could be visualized as an extended system of conjugated ketone [16], so that the $SmI_2$-initiated electron-transfer could lead preferably to the radical **E** (or the corresponding organo-samarium species) with a stabilization by the sulfur atom [16–19]. The Michael-type addition of **E** to the second molecule of enone **5a** would afford the intermediate **F**. Ketone **8a** could be obtained by consecutive processes including abstraction of hydrogen atom, protonation and rearomatization. Oxidation of the enolate **F** by trapping molecular dioxygen during workup might derive the enone **9a**. In addition to the cyclodimerization product **6b** (16 %), the reaction of **5b** also proceeded at the furan ring to give ketone **8b** (19 %) and enone **9b** (33 %).




**Scheme 3.**

In summary, the coupling reaction of 1-ferrocene-substituted enones **1a-g**, **5a** and **5b**, proceeded with *dl*-selectivity via transition states **B** or **B'**. If two enone moieties were confined in one ferrocene unit such as 1,1'-dicinnamoylferrocene (**I**), the transition state analogous to **B** (or **B'**) would be highly distorted and disfavored. In such a case, the intramolecular coupling reaction would occur with




**Scheme 4.**

*meso*-selectivity [8]. Chalcones also undergo coupling reactions with *dl*-selectivity by the promotion of $SmI_2$ and HMPA, giving 3,4-*trans* cyclodimerization products after in situ aldol reactions [3]. Our study showed that both cyclodimerization products (aldols **2**) and further reduction products (diols **3**) could be obtained in stereoselective manners by treatment of 1-ferrocene-substituted enones with appropriate amounts of $SmI_2$ in THF without the assistance of HMPA (*table I*).

Crystal data of compounds **2a**-major, **3b**-major and **7a** are given in *table II*.

## 3. Experimental section

Melting points are uncorrected. Chemical shifts are reported relative to $CHCl_3$ ($\delta_H$ 7.26) and $CDCl_3$ [$\delta_C$ (central line of t) 77.0]. All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of nitrogen. Syringes and needles for the transfer of reagents were dried at 120 °C and allowed to cool in a desiccator over $P_2O_5$ before use. THF was distilled from sodium benzophenone ketyl, and HMPA from $CaH_2$. Column chromatography was carried out on Kieselgel 60 (40-63 μm). Merck silica gel 60F sheets were used for analytical thin-layer chromatography.

***Caution***

HMPA should be handled with precaution because it is considered as a potential carcinogen.

### 3.1. General procedure for preparation of ferrocene-substituted enones 1a–g and 5a–b

**Method A** [9]. 1-Ferrocenyl-2-buten-1-one (**1a**) (860 mg, 3.4 mmol) was prepared in 34 % yield by acylation of ferrocene (1.86 g, 10 mmol) with (*E*)-crotonyl chloride (1.04 g, 10 mmol) and $AlCl_3$ (1.33 g, 10 mmol) in $CH_2Cl_2$ (10 mL) according to the known procedure.[9]

**Table II.** Crystal data of compounds **2a**-major, **3b**-major, **3c**-major and **7a**.

| Compound | **2a**-major | **3b**-major | **3c**-major | **7a** |
|---|---|---|---|---|
| Formula | $C_{28}H_{30}O_2Fe_2$ | $C_{38}H_{36}O_2Fe_2$ | $C_{40}H_{40}O_2Fe_2.H_2O$ | $C_{40}H_{32}O_2Fe_2S_2$ |
| Diffractometer | CAD-4 | CAD-4 | SMART CCD | CAD-4 |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 5.837(1) | 11.360(2) | 10.131(1) | 9.775(1) |
| $b$ (Å) | 12.925(3) | 12.200(2) | 11.999(1) | 9.863(1) |
| $c$ (Å) | 16.360(4) | 12.341(2) | 15.091(1) | 18.150(2) |
| $\alpha$ (deg.) | 72.21(2) | 111.41(1) | 76.12(1) | 79.80(1) |
| $\beta$ (deg.) | 88.92(2) | 103.07(1) | 86.51(1) | 74.35(1) |
| $\gamma$ (deg.) | 78.20(2) | 96.67(1) | 68.26(1) | 66.86(1) |
| $V$ (Å$^3$) | 1 149.0(5) | 1 513.5(4) | 1 653.44(2) | 1 544.5(3) |
| $Z$ | 2 | 2 | 2 | 2 |
| $D_{(calc)}$, g·cm$^{-3}$ | 1.475 | 1.396 | 1.371 | 1.549 |
| $\lambda$(Mo, K$_\alpha$), Å | 0.710 7 | 0.710 7 | 0.710 7 | 0.710 7 |
| $F$(000) | 533 | 665 | 716 | 746 |
| Unit cell detn: #; 2$\theta$ range | 25; 17-25 | 25; 20-30 | — | 25; 19-26 |
| Scan type | $\theta$/2 $\theta$ | $\theta$/2 $\theta$ | — | $\theta$/2 $\theta$ |
| Scan width (deg) | 2 (0.65 + 0.35 tan$\theta$) | 2 (0.70 + 0.35 tan$\theta$) | — | 2 (0.60 + 0.35 tan$\theta$) |
| 2$\theta$ max (deg) | 55.0 | 50.0 | 50.0 | 50.0 |
| $\mu$(Mo K$_\alpha$) (cm$^{-1}$) | 12.84 | 9.90 | 9.15 | 10.962 |
| Crystal size (mm) | 0.15 × 0.25 × 0.40 | 0.55 × 0.50 × 0.20 | 0.40 × 0.25 × 0.20 | 0.15 × 0.20 × 0.35 |
| Temperature (K) | 298 | 298 | 295(2) | 298 |
| No. of measured reflections | 5 797 | 5 332 | 13 160 | 5 790 |
| No. of unique reflections, $R_{int}$ | 5 272 | 5 319 | 5 797, 0.033 | 5 441 |
| No.of obs. reflections ($I > 2(\sigma)I$) | 3 423 | 4 256 | 5 192 | 3 988 |
| No. of refined params. | 289 | 380 | 399 | 289 |
| $R_f$, $R_w$ | 0.039, 0.039 | 0.038, 0.044 | 0.059, 0.122 * | 0.069, 0.076 |
| $GoF$ | 1.87 | 2.43 | 1.20 | 1.80 |
| Minimized function | $\Sigma w \lvert F_o - F_c \rvert^2$ | $\Sigma w \lvert F_o - F_c \rvert^2$ | $\Sigma w \lvert F_o - F_c \rvert^2$ | $\Sigma w \lvert F_o - F_c \rvert^2$ |
| Weighing scheme | $1/[\sigma^2(F_o) + 0.6\cdot10^{-4}\ F_o^2]$ | $1/[\sigma^2(F_o) + 0.6\cdot10^{-4}\ F_o^2]$ | $a = 0.035$, $b = 2.40$ # | $1/\sigma^2(F_o)$ |
| $g$ (second ext. coeff.) × 10$^4$ | — | 0.35(2) | 0.17 | 0.43(2) |
| $(\Delta/\sigma)_{mas}$ | 0.001 9 | 0.035 6 | 0.002 | 0.12 |
| Residual in final $D$-map (e·Å$^{-3}$) | -0.30, 0.46 | -0.26, 0.39 | –0.52, 0.66 | –0.79, 0.99 |

$R_{int} = \Sigma \lvert I_f - I \rvert / \Sigma I$

$R_f = [\Sigma \lvert F_o - F_c \rvert / \Sigma F_o]$; $R_w = [\Sigma w \lvert F_o - F_c \rvert^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$

$GoF = [\Sigma w \lvert F_o - F_c \rvert^2 /$ No. of unique reflections – No. of refined parameters$]^{1/2}$

* $R_w(F^2) = [\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$

\# $w = 1/[\sigma^2(F_o^2) + (a P)^2 + b P]$; $P = (F_o^2 + 2 F_c^2)/3$; weight coefficients $a$, $b$

**Method B** [10]. 1-Ferrocenyl-3-phenyl-2-propen-1-one (**1b**) (2.56 g, 8 mmol) was prepared in 80 % yield by condensation of acetylferrocene (2.28 g, 10 mmol) with benzaldehyde (1.38 g, 13 mmol) and NaOH (200 mg) in MeOH (20 mL) according to the known procedure [10].

According to method B, condensation of acetylferrocene (2.28 g, 10 mmol) with appropriate benzaldehydes (13 mmol) gave respectively 1-ferrocenyl-3-(2-methylphenyl)-2-propen-1-one (**1c**, 94 % yield), 1-ferrocenyl-3-(3-methylphenyl)-2-propen-1-one (**1d**, 97 % yield), 1-ferrocenyl-3-(4-methylphenyl)-2-propen-1-one (**1e**, 87 % yield), 1-ferrocenyl-3-(4-methoxyphenyl)-2-propen-1-one (**1f**, 72 % yield) and 1-ferrocenyl-3-(4-cyanophenyl)-2-propen-1-one (**1g**, 59 % yield). The similar reactions by condensation of acetylferrocene with 2-thiophenecarbaldehyde or 2-furancarbaldehyde gave, respectively, 1-ferrocenyl-3-(2-thienyl)-2-propen-1-one (**5a**, 80 % yield) and 1-ferrocenyl-3-(2-furyl)-2-propen-1-one (**5b**, 91 % yield).

### 3.2. General procedure for $SmI_2$-mediated coupling reactions of ferrocene-substituted enones

A deep blue $SmI_2$ solution (0.1 M, 0.9 mmol) was prepared by treatment of Sm (165.4 mg, 1.1 mmol) with 1,2-diiodoethane (253.6 mg, 0.9 mmol) in anhydrous THF (10 mL) for 1.5 h at room temperature. The $SmI_2$ solution was cooled in an ice bath, a solution of **1a–g** (0.8 mmol) in THF (5 mL) was added dropwise over a period of 5 min. The mixture was stirred for additional 40 min, and filtered through a pad of silica gel. The filtrate was concentrated, and chromatographed on a silica gel column by elution with gradients of EtOAc/hexane to give the aldols **2a–g**. The reaction of 1-ferrocenyl-2-buten-1-one (**1a**) also gave the enone **4a**. The reactions of **1b–g** (0.8 mmol) with larger amounts of $SmI_2$ (1.8 mmol) gave the diols **3b–g** (*table I*).

The reaction of **5a** (258 mg, 0.8 mmol) with $SmI_2$ (0.8 mmol) in THF (10 mL) at 0 °C for 2 h gave aldol **6a** (33 mg, 13 %), diol **7a** (15 mg, 6 %), ketone **8a** (106 mg, 41 %) and enone **9a** (24 mg, 9 %). The similar reaction of **5b** (245 mg, 0.8 mmol) with $SmI_2$ (0.8 mmol) gave aldol **6b** (40 mg, 16 %), ketone **8b** (45.2 mg, 19 %) and enone **9b** (80 mg, 33 %).

#### 3.2.1. 3,4-Dimethyl-2-ferrocenoyl-1-ferrocenylcyclopentanol, 2a

Orange solid, mp 176-178 °C; TLC (EtOAc/hexane (1:9)) $R_f$ 0.23; IR (KBr) 3 407, 1 625 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 0.94 (3 H, d, $J$ = 6.6 Hz), 1.16 (3 H, d, $J$ = 6.6 Hz), 1.72 (1 H, m), 1.90 (1 H, dd, $J$ = 6.3, 13.6 Hz), 2.28 (1 H, m), 2.56 (1 H, dd, $J$ = 9.9, 13.6 Hz), 2.67 (1 H, d, $J$ = 11.6 Hz), 3.87 (5 H, s), 4.02 (2 H, m), 4.19 (5 H, s), 4.25 (1 H, m), 4.41 (2 H, m), 4.52 (1 H, m), 4.58 (1 H, m), 5.23 (1 H, br s, OH); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 18.1, 20.0, 40.1, 47.3, 50.5, 65.3, 66.5, 67.1, 67.3, 68.2, 68.6 (5 ×), 69.7 (5 ×), 69.8, 72.3, 72.5, 80.4, 81.7, 96.6, 210.1. FAB-MS $m/z$ 510 ($M^+$). Anal. Calcd for $C_{28}H_{30}Fe_2O_2$: C, 65.91; H, 5.93. Found: C, 65.69; H, 5.84. The structure of **2a** (crystallized from $CHCl_3$/hexane) was confirmed by an X-ray diffraction.

#### 3.2.2. 3,4-Diphenyl-2-ferrocenoyl-1-ferrocenylcyclopentanol, 2b

Orange solid, mp 137–139 °C; IR (KBr) 3 407, 1 625 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.52 (1 H, dd, $J$ = 7.6, 14.0 Hz), 3.04 (1 H, dd, $J$ = 10.2, 14.0 Hz), 3.44 (1 H, d, $J$ = 11.7 Hz), 3.50–4.86 (21 H, m), 7.02–7.48 (10 H, m); FAB-MS $m/z$ 634 ($M^+$). Anal. Calcd for $C_{38}H_{34}Fe_2O_2$: C, 71.72; H, 5.70. Found: C, 72.04; H, 5.53.

#### 3.2.3. 3,4-Bis(2-methylphenyl)-2-ferrocenoyl-1-ferrocenylcyclopentanol, 2c

Major isomer: orange solid, mp 193–194 °C; IR (KBr) 3 449, 1 639 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.92 (3 H, s), 1.96 (3 H, s), 2.42 (1 H, dd, $J$ = 7.2, 14.1 Hz), 3.03 (1 H, dd, $J$ = 10.4, 14.1 Hz), 3.56–4.57 (22 H, m), 6.85–7.98 (8 H, m); FAB-MS $m/z$ 662 ($M^+$). HRMS Calcd for $C_{40}H_{38}Fe_2O_2$: 662.157 1. Found: 662.156 3.

Minor isomer: orange solid, mp 181–182 °C; IR (KBr) 3 386, 1 636 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 1.73 (3 H, s), 1.86 (3 H, s), 2.46 (1 H, dd, $J$ = 12.9, 12.9 Hz), 2.61 (1 H, dd, $J$ = 12.9, 6.5 Hz), 3.80–4.52 (21 H, m), 6.47 (1 H, s, OH), 6.65–7.60 (8 H, m); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 19.6, 19.7, 29.7, 48.5, 49.3, 52.3, 62.1, 65.1, 67.0, 67.7, 68.0, 68.7 (5 ×), 69.7 (5 ×), 71.9, 72.5, 79.3, 81.7, 95.8, 125.7, 125.9, 126.0, 126.1, 126.2, 129.0, 129.4, 130.4, 135.3, 137.0, 139.1, 141.3, 208.1; FAB-MS $m/z$ 662 ($M^+$). Anal. Calcd for $C_{40}H_{38}Fe_2O_2$: C, 72.53; H, 5.78. Found: C, 72.48; H, 6.08.

#### 3.2.4. 3,4-Bis(3-methylphenyl)-2-ferrocenoyl-1-ferrocenylcyclopentanol, 2d

Major isomer: orange solid, mp 172–174 °C; IR (KBr) 3 421, 1 625 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.20 (3 H, s), 2.30 (3 H, s), 2.45 (1 H, dd, $J$ = 7.7, 14.1 Hz), 3.03 (1 H, dd, $J$ = 10.4, 14.1 Hz), 3.40 (1 H, d, $J$ = 11.7 Hz), 3.54 (1 H, m), 3.61-4.46 (20 H, m), 6.86-7.19 (8 H, m); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 21.4. 21.5. 50.9, 51.4, 57.3, 65.5, 66.9, 67.4, 67.9, 68.4, 68.6 (5 ×), 69.1, 69.2 (5 ×), 69.6, 69.7, 70.2, 71.7, 72.1, 78.0, 81.0, 95.9, 124.9, 127.0, 127.7, 128.2, 128.3, 128.5, 128.9, 137.8, 140.9, 143.8, 206.3. FAB-MS $m/z$ 662 ($M^+$). Anal. Calcd for $C_{40}H_{38}Fe_2O_2$: C, 72.53; H, 5.78. Found: C, 72.13; H, 5.68.

Minor isomer: orange solid, mp 175–177 °C; TLC (EtOAc/hexane (1:20)) $R_f$ 0.17; IR (KBr) 3 380, 1 628 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.10 (3 H, s), 2.32 (3 H, s), 2.42 (1 H, dd, $J$ = 13.0, 13.0 Hz), 2.66 (1 H, dd, $J$ = 6.7, 13.0 Hz), 3.60–4.48 (21 H, m), 6.08 (1 H, s), 6.57–7.24 (8 H, m); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 21.3, 21.5, 48.5, 52.4, 57.9, 62.4, 65.0, 67.3, 68.0, 68.2, 68.6, 68.8 (5 ×), 69.7 (5 ×), 69.8, 72.1, 72.4, 77.2, 79.3, 81.7, 95.3, 124.4, 126.8, 127.1, 127.2, 127.5, 128.0, 128.3, 130.4, 137.1, 137.9, 140.3, 208.4. FAB-MS $m/z$ 662 ($M^+$). HRMS Calcd for $C_{40}H_{38}Fe_2O_2$: 662.157 1. Found: 662.154 4.

#### 3.2.5. 3,4-Bis(4-methylphenyl)-2-ferrocenoyl-1-ferrocenylcyclopentanol, 2e

Major isomer: orange solid, mp 230 °C (decomposed); TLC (EtOAc/hexane (1:9)) $R_f$ 0.2; IR (KBr) 3 416, 1 625 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.16 (3 H, s), 2.19 (3 H, s), 2.45 (1 H, dd, $J$ = 14.1, 7.4 Hz), 3.01 (1 H, dd, $J$ = 14.1, 10.4 Hz), 3.39 (1 H, d, $J$ = 11.7 Hz), 3.42-3.73 (6 H, m), 3.96–4.44 (15 H, m), 6.93–7.24 (8 H, m); FAB-MS $m/z$ 662 ($M^+$). HRMS Calcd for $C_{40}H_{38}Fe_2O_2$: 662.157 1. Found: 662.156 0.

Minor isomer: orange solid, mp 228 °C (decomposed); IR (KBr) 3 430, 1 661 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.12 (3 H, s), 2.30 (3 H, s), 2.38 (1 H, dd, $J$ = 13.0, 12.7 Hz, H-5α), 2.65 (1 H, dd, $J$ = 13.0, 6.6 Hz, H-5β), 3.62–3.73 (2 H, m, H-2, 3), 3.82 (5 H, s), 4.06 (1 H, m, H-4), 4.15 (1 H, br s), 4.17 (2 H, br s), 4.26 (5 H, s), 4.31 (1 H, br s), 4.32 (1 H, br s), 4.39 (1 H, br s), 4.41 (1 H, br s), 4.48 (1 H, br s), 6.56 (1 H, s, OH), 6.80 (2 H, d, $J$ = 7.8 Hz), 7.03 (2 H, d, $J$ = 7.8 Hz), 7.07 (2 H, d, $J$ = 7.8 Hz), 7.12 (2 H, d, $J$ = 7.8 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 20.9, 21.0, 48.3, 52.4, 57.9, 62.3, 65.0, 67.3, 67.7, 68.0, 68.1, 68.8 (5 ×), 69.7 (5 ×), 69.9, 72.2, 72.4, 79.3, 81.7, 95.3, 127.1 (2 ×), 128.5 (2 ×), 129.1 (2 ×),

129.4 (2 ×), 135.7, 135.8, 137.4, 140.7, 207.9. FAB-MS *m/z* 662 ($M^+$). HRMS Calcd for $C_{40}H_{38}Fe_2O_2$: 662.157 1. Found: 662.155 9.

#### 3.2.6. 3,4-Bis(4-methoxyphenyl)-2-ferrocenoyl-1-ferrocenylcyclopentanol, 2f

Orange solid, mp 186–188 °C; IR (KBr) 3 429, 1 606 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.50 (1 H, dd, $J$ = 7.6, 14.2 Hz), 3.01 (1 H, dd, $J$ = 10.3, 14.2 Hz), 3.41 (1 H, d, $J$ = 11.0 Hz), 3.42-4.45 (27 H, m), 6.59-7.18 (8 H, m); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 50.8, 51.2, 55.1, 57.5, 65.5, 66.8, 67.5, 68.6, 68.9 (5 ×), 69.1, 69.2 (5 ×), 69.6, 69.7, 69.8, 70.1, 71.8, 72.2, 79.9, 81.0, 98.5, 111.6, 111.7, 113.5, 114.3, 120.2, 120.6, 129.2, 129.4, 142.7, 145.4, 159.5, 206.2. FAB-MS *m/z* 694 ($M^+$). HRMS. Calcd for $C_{40}H_{38}Fe_2O_4$: 694.146 9. Found: 694.148 1.

#### 3.2.7. 3,4-Bis(4-cyanophenyl)-2-ferrocenoyl-1-ferrocenylcyclopentanol, 2g

Orange solid, mp 178–180 °C; TLC (EtOAc/hexane (1:4)) $R_f$ 0.07; IR (KBr) 3 446, 1 647 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.47 (1 H, dd, $J$ = 6.6, 14.6 Hz), 3.03 (1 H, dd, $J$ = 10.4, 14.6 Hz), 3.37 (1 H, d, $J$ = 11.7 Hz), 3.52–4.45 (21 H, m), 7.09–7.60 (8 H, m); FAB-MS *m/z* 684 ($M^+$). HRMS Calcd for $C_{40}H_{32}Fe_2N_2O_2$: 684.384 4. Found: 684.114 8.

#### 3.2.8. 3,4-Diphenyl-1-ferrocenyl-2-(1-ferrocenyl-1-hydroxymethyl)cyclopentanol, 3b

Major isomer: orange solid, mp 187–189 °C; IR (KBr) 3 490 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.39 (2 H, m), 2.80 (1 H, dd, $J$ = 9.5, 13.8 Hz), 3.01 (1 H, m), 3.10 (1 H, s, OH), 3.51 (1 H, s, OH), 3.52-3.80 (7 H, m), 4.00-4.50 (12 H, m), 4.98 (1 H, m), 6.64-7.32 (10 H, m); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 50.7, 52.9, 53.2, 63.0, 65.8 (2 ×), 65.9 (2 ×), 66.2, 66.5, 67.0, 68.0, 68.2 (5 ×), 68.5 (5 ×), 68.6, 81.0, 91.0, 97.2, 125.4, 126.0, 127.5 (2 ×), 127.8 (2 ×), 127.9 (2 ×), 128.1 (2 ×), 142.5, 143.9. FAB-MS *m/z* 636 ($M^+$). Anal. Calcd for $C_{38}H_{36}Fe_2O_2$: C, 71.72; H, 5.70. Found: C, 71.43; H, 5.67. The structure of **3b**-major (crystallized from $CHCl_3$/hexane) was confirmed by an X-ray diffraction.

Minor isomer: orange solid, mp 89–91 °C; IR (KBr) 3 460 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.15 (1 H, dd, $J$ = 4.8, 12.8 Hz), 2.74 (1 H, dd, $J$ = 12.8, 12.8 Hz), 2.88 (1 H, d, $J$ = 4.6 Hz) 3.12 (1 H, s), 3.45-5.15 (22 H, m), 6.73-7.05 (10 H, m); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 29.6, 44.7, 48.4, 49.6, 60.7, 65.1, 65.5, 66.5, 67.4, 68.0 (5 ×), 68.2 (5 ×), 68.4, 68.7, 81.5, 90.1, 96.1, 125.3, 125.6, 127.3 (4 ×), 128.2 (2 ×), 128.8 (2 ×), 140.5, 142.8. FAB-MS *m/z* 636 ($M^+$). Anal. Calcd for $C_{38}H_{36}Fe_2O_2$: C, 71.72; H, 5.70. Found: C, 71.62; H, 5.99.

#### 3.2.9. 3,4-Bis(2-methylphenyl)-1-ferrocenyl-2-(1-ferrocenyl-1-hydroxymethyl)cyclopentanol, 3c

Major isomer: orange solid, mp 168–170 °C; IR (KBr) 3 491 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.67 (3 H, s), 1.80 (3 H, s), 2.35 (1 H, brs), 2.39 (1 H, brs), 2.85 (1 H, dd, $J$ = 10.4, 14.3 Hz), 3.12–4.97 (23 H, m), 6.76-7.89 (8 H, m); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 19.4, 19.5, 47.5, 48.3, 50.6, 63.6, 65.3, 65.6, 65.8 (2 ×), 66.3, 66.9, 67.8, 68.1 (5 ×), 68.5 (5 ×), 68.6 (2 ×), 81.7, 91.2, 96.5, 124.9, 125.3, 125.5, 126.2, 126.3, 127.4, 129.4, 129.5, 135.8, 136.2, 140.9, 143.2. FAB-MS *m/z* 664 ($M^+$). HRMS. Calcd for $C_{40}H_{40}Fe_2O_2$: 664.172 7. Found: 664.172 0. The structure of **3c**-major (crystallized from $CHCl_3$/hexane) was confirmed by an X-ray diffraction.

Minor isomer: orange solid, mp 118–120 °C; IR (KBr) 3 447 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.71 (3 H, s), 2.05 (1 H, dd, $J$ = 4.1, 11.5 Hz), 2.48 (3 H, s), 2.84 (1 H, m), 3.00 (1 H, d, $J$ = 2.7 Hz), 3.05 (1 H, s), 3.75-5.20 (22 H, m), 6.33–7.16 (8 H, m); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 19.6, 19.9, 43.0, 43.5, 46.0, 60.9, 65.0, 65.8 (2 ×), 66.2, 67.7, 68.3, 68.5 (5 ×), 68.6 (5 ×), 68.9(2 ×), 69.6, 81.3, 90.1, 96.3, 124.6, 125.1, 125.6, 125.7, 127.2, 127.6, 129.5, 129.9, 136.6, 137.4, 138.3, 141.4. FAB-MS *m/z* 664 ($M^+$). HRMS. Calcd for $C_{40}H_{40}Fe_2O_2$: 664.172 7. Found: 664.173 0.

#### 3.2.10. 3,4-Bis(4-methylphenyl)-1-ferrocenyl-2-(1-ferrocenyl-1-hydroxymethyl)cyclopentanol, 3e

Major isomer: orange solid, mp 153–155 °C; IR (KBr) 3 462 $cm^{-1}$; TLC (EtOAc/hexane (1:9)) $R_f$ 0.38; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.13 (3 H, s), 2.26 (3 H, s), 2.32 (2 H, m), 2.72 (1 H, dd, $J$ = 13.6, 9.8 Hz), 2.95 (1 H, t, $J$ = 9.6 Hz), 3.02 (1 H, s), 3.41 (1 H, s), 3.50–4.38 (19 H, m), 4.93 (1 H, s), 6.58 (2 H, d, $J$ = 8.0 Hz), 6.69 (2 H, d, $J$ = 8.0 Hz), 7.00 (2 H, d, $J$ = 8.2 Hz), 7.06 (2 H, d, $J$ = 8.2 Hz); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 20.9, 21.0, 30.9, 51.1, 52.2, 52.6, 63.2, 65.8, 65.9, 66.0, 66.3, 66.6, 66.9, 67.9, 68.2 (5 ×), 68.4, 68.5 (5 ×), 80.9, 91.2, 97.3, 127.6 (2 ×), 127.8 (2 ×), 128.2 (2 ×), 128.9 (2 ×), 134.6, 135.4, 139.5, 141.0. FAB-MS *m/z* 664 ($M^+$). HRMS. Calcd for $C_{40}H_{40}Fe_2O_2$: 664.172 7. Found: 664.172 9.

Minor isomer: orange solid, mp 105-107 °C; IR (KBr) 3 475 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.07 (1 H, dd, $J$ = 13.0, 4.8 Hz), 2.17 (3 H, s), 2.19 (3 H, s), 2.76 (1 H, dd, $J$ = 13.3, 13.0 Hz), 2.09 (1 H, d, $J$ = 4.1 Hz), 3.04 (1 H, s, OH), 3.42-4.64 (21 H, m), 3.72 (1 H, s, OH), 5.15 (1 H, s), 6.68-6.90 (8 H, m); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 20.9 (2 ×), 45.2, 48.3 (2 ×), 49.4, 60.8 (2 ×), 65.1, 65.6, 66.8, 67.6 (2 ×), 68.3 (5 ×), 68.5 (5 ×), 68.7 (2 ×), 68.8, 81.5, 90.2, 96.3, 128.2 (4 ×), 128.3 (2 ×), 128.8 (2 ×), 134.7, 135.0, 137.6, 139.9. FAB-MS *m/z* 664 ($M^+$). HRMS. Calcd for $C_{40}H_{40}Fe_2O_2$: 664.172 7. Found: 664.170 8.

#### 3.2.11. 3,4-Bis(4-cyanophenyl)-1-ferrocenyl-2-(1-ferrocenyl-1-hydroxymethyl)cyclopentanol, 3g

Major isomer: orange solid, mp 172–174 °C; IR (KBr) 3 436, 2 226, 1 607 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz) $\delta$ 2.32 (2 H, m), 2.76 (1 H, m), 3.02 (2 H, m), 3.49-4.93 (20 H, m), 4.94 (1 H, brs), 6.68-7.51 (8 H, m); FAB-MS $m/z$ 686 ($M^+$). Anal. Calcd for $C_{40}H_{34}Fe_2N_2O_2$: C 69.99, H 4.99. Found: C 69.73, H 5.34.

Minor isomer: orange solid, mp 185–187 °C; IR (KBr) 3 434, 2 226, 1 606 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz) $\delta$ 2.24 (1 H, dd, $J$ = 5.3, 13.0 Hz, H-5β), 2.57 (1 H, d, $J$ = 6.2 Hz, H-2), 2.59 (1 H, t, $J$ = 13.0 Hz, H-5α), 3.38 (1 H, s, OH), 3.39 (1 H, s, OH), 3.68 (1 H, br s), 3.78 (2 H, br s), 3.95 (5 H, s), 4.07 (1 H, m, H-3), 4.10 (1 H, br s), 4.17 (1 H, m, H-4), 4.29 (5 H, s), 4.35 (3 H, br s), 4.53 (1 H, br s), 5.11 (1 H, br s, H-1'), 6.68 (2 H, d, $J$ = 7.8 Hz), 6.94 (2 H, d, $J$ = 7.8 Hz), 7.21 (2 H, d, $J$ = 7.8 Hz), 7.29 (2 H, d, $J$ = 7.8 Hz); $^{13}C$ NMR ($CDCl_3$, 75 MHz) $\delta$ 45.0, 47.7, 48.9, 62.1, 65.3, 65.4, 65.8, 66.8, 67.3, 67.7, 68.2, 68.5 (5 ×), 68.7 (5 ×), 69.0, 69.6, 81.4, 90.1, 94.9, 118.7 (2 ×), 128.9 (2 ×), 129.3 (2 ×), 131.3 (2 ×), 131.5 (2 ×), 132.2 (2 ×), 145.9, 148.2. FAB-MS $m/z$ 686 ($M^+$). HRMS. Calcd for $C_{40}H_{34}Fe_2N_2O_2$: 686.131 9. Found: 686.132 4.

#### 3.2.12. 3,4-Dimethyl-1-ferrocenoyl-5-ferrocenyl-1-cyclopentene, 4a

Orange solid, mp 110–112 °C; TLC (EtOAc/hexane (1:19)) $R_f$ 0.23; IR (KBr) 1 660 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) δ 1.16 (3 H, d, $J$ = 7.0 Hz), 1.31 (3 H, d, $J$ = 7.0 Hz), 2.25 (1 H, m), 2.35 (1 H, m), 3.75 (1 H, m), 4.00–4.94 (18 H, m), 5.87 (1 H, br s); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 20.3, 21.7, 47.2, 48.8, 65.7, 66.6, 67.0, 67.2, 68.2, 68.8 (5 ×), 69.3 (5 ×), 69.7, 69.9, 71.6, 72.2, 80.1, 81.3, 131.7, 137.8, 207.1. FAB-MS $m/z$ 492 ($M^+$). Anal. Calcd for $C_{28}H_{27}Fe_2O$: C, 68.32; H, 5.73. Found: C, 68.21; H, 5.78.

#### 3.2.13. 3,4-Bis(2-thienyl)-2-ferrocenoyl-1-ferrocenylcyclopentanol, 6a

Orange solid, mp 212–214 °C; IR (KBr) 3 441, 1 613 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.55 (1 H, dd, $J$ = 14.1, 7.6 Hz), 3.08 (1 H, dd, $J$ = 14.1, 10.1 Hz), 3.36 (1 H, d, $J$ = 11.5 Hz), 3.72-4.48 (21 H, m), 6.77-7.12 (6 H, m); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 47.8, 51.3, 53.3, 65.6, 67.0, 67.6, 68.3, 68.5, 68.7 (5 ×), 69.2, 69.4 (5 ×), 69.8, 70.1, 72.0, 72.4, 79.9, 80.7, 95.4, 123.5, 123.7, 124.1, 126.1, 126.0, 145.0, 147.0, 205.4. FAB-MS $m/z$ 646 ($M^+$). Anal. Calcd for $C_{34}H_{30}Fe_2O_2S_2$: C, 63.17; H, 4.68. Found: C, 62.81; H, 4.86.

#### 3.2.14. 3,4-Bis(2-thienyl)-1-ferrocenyl-2-(1-ferrocenyl-1-hydroxymethyl)-1-cyclopentanol, 7a

Orange solid, mp 162–164 °C; TLC (EtOAc/hexane (1:9)) $R_f$ 0.14; IR (KBr) 3 473 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.38 (1 H, dd, $J$ = 10.0, 1.8 Hz), 2.40 (2 H, dd, $J$ = 13.2, 10.1 Hz), 2.66 (1 H, dd, $J$ = 13.2, 8.2 Hz), 3.08 (1 H, s), 3.34 (2 H, m), 3.80–4.37 (19 H, m), 5.06 (1 H, br s), 6.38–7.10 (6 H, m); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 47.5, 48.5, 51.4 ($CH_2$), 63.8, 65.6, 66.4 (2 ×), 67.0, 67.3, 68.1 (5 ×), 68.3 (5 ×), 68.4, 68.6, 68.7, 80.2, 91.0, 95.4, 97.3, 122.6, 123.2, 124.0, 125.0, 126.0, 126.5, 126.5, 147.2, 153.3. FAB-MS $m/z$ 648 ($M^+$). Anal. Calcd for $C_{34}H_{32}Fe_2O_2S_2$: C, 62.98; H, 4.97; Found: C, 63.33; H, 5.25. The structure of **7a** was confirmed by an X-ray diffraction.

#### 3.2.15. 1-Ferrocenyl-3-[(5-(2-ferrocenoylethyl))-2-thienyl]-3-(2-thienyl)-1-propanone, 8a

Orange solid, mp 155–157 °C; TLC (EtOAc/hexane (1:4)) $R_f$ 0.20; IR (KBr) 1 659 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.99 (2 H, t, $J$ = 6.6 Hz), 3.15 (2 H, t, $J$ = 6.6 Hz), 3.42 (2 H, d, $J$ = 7.0 Hz), 4.00 (5 H, s), 4.07 (5 H, s), 4.46 (4 H, m), 4.73 (4 H, m), 5.28 (1 H, t, $J$ = 7.0 Hz), 6.07–7.14 (5 H, m); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 24.4, 36.5, 41.5, 48.5, 68.6, 69.2 (2 ×), 69.3, 69.7 (10 ×), 70.0, 72.2 (2 ×), 72.3, 78.7, 78.8, 123.8, 124.3, 124.6, 126.6, 143.0, 145.9 (2 ×), 147.8, 200.5, 202.5. Anal. Calcd for $C_{34}H_{30}Fe_2O_2S_2$: C, 63.17; H, 4.68. Found: C, 62.97; H, 4.95.

#### 3.2.16. 1-Ferrocenyl-3-[(5-(2-ferrocenoylethen-1-yl))-2-thienyl]-3-(2-thienyl)-1-propanone, 9a

Orange solid, mp 156–158 °C; TLC (EtOAc/hexane (1:4)) $R_f$ 0.21; IR (KBr) 1 658, 1 645 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 3.49 (2 H, d, $J$ = 7.0 Hz), 4.01 (5 H, s), 4.16 (5 H, s), 4.51 (4 H, m), 4.81 (4 H, m), 5.36 (1 H, t, $J$ = 7.0 Hz), 6.77 (1 H, d, $J$ = 15.3 Hz), 6.94–7.24 (5 H, m), 7.78 (1 H, d, $J$ = 15.3 Hz); $^{13}C$ NMR ($CDCl_3$, 50 MHz) $\delta$ 36.8, 48.1, 69.2 (2 ×), 69.5, 69.6, 69.7 (5 ×), 70.0 (5 ×), 72.4 (2 ×), 72.6 (2 ×), 78.6, 80.5, 121.3, 124.3, 125.0, 126.0, 126.8, 131.8, 133.5, 139.4, 146.7, 151.0, 192.4, 200.3. FAB-MS $m/z$ 644 ($M^+$). HRMS. Calcd for $C_{34}H_{28}Fe_2O_2S_2$: 664.022 9. Found: 664.021 3.

#### 3.2.17. 3,4-Bis(2-furyl)-2-ferrocenoyl-1-ferrocenylcyclopentanol, 6b

Orange solid, mp 182–184 °C; TLC (EtOAc/hexane (1:4)) $R_f$ 0.48; IR (KBr) 3 455, 1 622 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 2.50 (2 H, dd, $J$ = 14.0, 6.5 Hz), 2.87 (1 H, dd, $J$ = 14.0, 11 Hz), 3.45 (1 H, d,

$J$ = 11.7 Hz), 3.75–4.63 (20 H, m), 5.96–6.28 (4 H, m) 7.28–7.32 (2 H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz) $\delta$ 40.9, 46.9, 48.5, 63.6, 65.5, 67.2, 67.6, 68.5, 68.7 (5 ×), 69.0, 69.5 (5 ×), 69.7, 69.9, 72.3, 72.5, 79.6, 81.3, 95.0, 104.9, 107.7, 110.2, 110.6, 141.3, 153.4, 156.9, 205.6. FAB-MS $m/z$ 614 ($M^+$). HRMS. Calcd for $C_{34}H_{30}Fe_2O_4$: 614.084 3. Found: 614.080 6.

#### 3.2.18. 1-Ferrocenyl-3-[(5-(2-ferrocenoylethyl))-2-furyl]-3-(2-furyl)-1-propanone, 8b

Orange solid, mp 135–137 °C; TLC (EtOAc/hexane (1:4)) $R_f$ 0.33; IR (KBr) 1 669 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 2.99 (4 H, s), 3.37 (2 H, dd, $J$ = 7.1, 2.2 Hz), 4.05 (5 H, s), 4.10 (5 H, s), 4.46 (4 H, m), 4.76 (4 H, m), 4.90 (1 H, t, $J$ = 7.1 Hz), 5.97 (1 H, d, $J$ = 3.2 Hz), 6.01 (1 H, d, $J$ = 3.2 Hz), 6.13 (1 H, d, $J$ = 3.2 Hz), 6.28 (1 H, dd, $J$ = 3.2, 1.9 Hz), 7.32 (1 H, m); $^{13}$C NMR ($CDCl_3$, 50 MHz) $\delta$ 22.7, 33.8, 37.9, 42.3, 69.1 (3 ×), 69.2 (3 ×), 69.7 (10 ×), 72.2 (2 ×), 72.3 (2 ×), 78.8, 106.2, 106.4, 106.9, 110.4, 141.3, 152.9, 153.9, 154.3, 200.7, 202.7. FAB-MS $m/z$ 614 ($M^+$). Anal. Calcd for $C_{34}H_{30}Fe_2O_4$: C, 66.48; H, 4.92. Found: C, 66.27; H, 4.91.

#### 3.2.19. 1-Ferrocenyl-3-[(5-(2-ferrocenoylethen-1-yl))-2-furyl]-3-(2-furyl)-1-propanone], 9b

Orange solid, mp 161–163 °C; TLC (EtOAc/hexane (1:4)) $R_f$ 0.21; IR (KBr) 1 664, 1 647, 1 584 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 3.41 (2 H, d, $J$ = 7.0 Hz), 3.98–4.81 (18 H, m), 4.98 (1 H, t, $J$ = 7.0 Hz), 6.15–6.55 (4 H, m), 6.82 (1 H, d, $J$ = 15.3 Hz), 7.30 (1 H, m), 7.40 (1 H, d, $J$ = 15.3); $^{13}$C NMR ($CDCl_3$, 50 MHz) $\delta$ 34.1, 42.3, 68.6, 69.2, 69.3, 69.4, 69.7, 69.8, 70.0 (5 ×), 70.1 (5 ×), 72.5, 72.6, 78.6, 80.7, 106.9, 109.7, 110.6, 116.7, 119.8, 127.1, 141.7, 150.9, 153.2, 157.2, 192.7, 200.4. FAB-MS $m/z$ 612 ($M^+$). Anal. Calcd for $C_{34}H_{28}Fe_2O_4$: C, 66.70; H, 4.61. Found: C, 66.48; H, 4.66.

### . Supplementary material available

For compounds **2a**-major, **3b**-major, **3c**-major, **6a** and **12**, ORTEP drawings and tables of X-ray crystallographic data including atomic coordinates, complete list of bond lengths and angles, thermal parameters and calculated and observed structure factors have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK under No. CCDC 158013-158016.

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