SUPPLEMENTARY INFORMATION FOR


Alfonso Latorre, Antonio Urbano,* M. Carmen Carreño*

Experimental Procedures

General. Melting points were obtained in open capillary tubes and are uncorrected. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 300 and 75 MHz, respectively. UV/Vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. The spectra were measured in CH₂Cl₂ in a quartz cuvette (1 cm) at 298 °K. Circular dichroism spectra were measured with a JASCO J-810 spectropolarimeter. All reactions were monitored by thin layer chromatography that was performed on pre-coated sheets of silica gel 60, and flash column chromatography was done with silica gel 60 (230-400 mesh) of Merck. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments was dried by flaming in a stream of dry argon. Ethyl ether, CH₂Cl₂, THF and CH₃CN were dried over 4Å molecular sieves. All other reagent quality solvents were used without further purification. For routine workup, hydrolysis was carried out with water, extractions with CH₂Cl₂, and solvent drying with MgSO₄.

(±)-3,4-Ferrocene-1-trifluoromethanesulphonyloxyacyclohexene (7).
To a solution of 3,4-ferrocenecyclohexanone (rac)-1 \(^1\) (15 mg, 0.06 mmol) and N-phenyl-bis(trifluoromethanesulfonimide) (23 g, 0.06 mmol) in dry THF (2.5 mL) was slowly added a solution of KHMDS 0.5M in THF (155 µL, 0.078 mmol) at –78 ºC, under argon. The mixture was stirred for 1 h and quenched with H₂O at –78 ºC. After warming to room temperature, workup and flash chromatography with silica deactivated with 10% of water (eluent CH₂Cl₂/hexane 1:4), enol triflate (rac)-7 was obtained as an orange oil, in 65% yield: \(^1\)H NMR \(\delta \) 2.47-2.93 (m, 4H), 4.17 (broad s, 8H), 6.30 (d, \(J = 2.8\) Hz, 1H); \(^13\)C NMR \(\delta \) 22.8, 27.8, 65.9, 66.7, 67.4, 69.8, 76.4, 82.4, 117.7, 146.5; MS (ESI): m/z (%) 253 (22), 282 (15), 386 (M\(^+\), 15); HRMS (ESI) calcd. for C\(_{15}\)H\(_{13}\)O\(_3\)F\(_3\)FeS (M\(^+\)) 386.1671, found 386.9881.

(±)-3,4-Ferrocene-1-vinylcyclohexene (2).

To a mixture of enol triflate (rac)-7 (55 mg, 0.142 mmol), LiCl (28 mg, 0.71 mmol) and Pd(PPh\(_3\))\(_4\) (9 mg, 5% mol) in THF (1.4 mL), vinyltributylstannane (44 µL, 0.142 mmol) was added, under argon. The reaction mixture was heated at 90 ºC for 45 min, filtered over celite and washed with water. After workup and flash chromatography (eluent CH₂Cl₂/hexane 2:1), diene (rac)-2 was obtained as a red oil, in 58% yield; \(^1\)H NMR \(\delta \) 2.31-2.49 (m, 2H), 2.61-2.74 (m, 2H), 4.09 (s, 5H), 4.13 (broad s, 3H), 5.02 (d, \(J = 10.8\) Hz, 1H), 5.25 (d, \(J = 17.4\) Hz, 1H), 6.25 (broad s, 1H), 6.42 (dd, \(J = 10.8\) and 17.4 Hz, 1H); \(^13\)C NMR \(\delta \) 22.3, 23.4, 64.6, 66.3, 66.4, 69.5, 79.9, 85.1, 109.9, 126.7, 134.9, 139.2; MS (ESI): m/z (%) 264 (M\(^+\), 55); HRMS (ESI) calcd. for C\(_{16}\)H\(_{16}\)Fe (M\(^+\)) 264.0601 found 264.0595.

Representative Procedure for Kinetic Resolutions

To a solution of diene (rac)-2 (33 mg, 0.12 mmol) in CH₂Cl₂ (7.6 mL) at –78 ºC, a solution of (SS)-5-methyl-2-(p-tolylsulfinyl)-1,4-benzoquinone (3)\(^2\) (see Table for conditions) in CH₂Cl₂ (7.6 mL)


was rapidly added under argon. The reaction was slowly warmed up to room temperature and the solvent eliminated. After flash chromatography (eluent CH$_2$Cl$_2$), unreacted optically active diene (p$_R$)-2 (see Table for yields and optical purities) and tetracyclic ferrocene (p$_S,S,P$)-4 (see Table for yields and optical purities), were respectively obtained.

<table>
<thead>
<tr>
<th>entry</th>
<th>T</th>
<th>(SS)-3 (equiv)</th>
<th>(p$_R$)-2 (% yield / % ee)</th>
<th>(p$_S,S,P$)-4 (% yield / % ee)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–78 to rt</td>
<td>2.0</td>
<td>(56 / 55)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>–78 to rt</td>
<td>0.5</td>
<td>(50 / 63)</td>
<td>(34 / 93)</td>
</tr>
<tr>
<td>3</td>
<td>–78 to rt</td>
<td>0.9</td>
<td>(28 / 99)</td>
<td>(46 / 73)</td>
</tr>
<tr>
<td>4</td>
<td>–10</td>
<td>0.5</td>
<td>(32 / 47)</td>
<td>(45 / 97)</td>
</tr>
</tbody>
</table>

(p$_R$)-3,4-Ferrocene-1-vinylcyclohexene (2).

Compound (p$_R$)-2 (99% ee)$^3$ was obtained from kinetic resolution of diene (rac)-2 with 0.9 equiv of (SS)-4 (entry 3), as a red oil, in 28% yield: $[\alpha]_D^{20} = -1455$ (c 0.022, CHCl$_3$).

---

$^3$ The enantiomeric excess of optically active diene (p$_R$)-2 was determined from optical purity of tricyclic ferrocenyl diester (p$_R$)-5 (see below).
(pS,10aS,P)-9,10-Ferrocene-3-methyl-5,7,8,10a-tetrahydrophenanthrene-1,4-quinone (4)

Compound (pS,10aS,P)-4 (97% ee)\(^4\) was obtained from kinetic resolution of diene (rac)-2 with 0.5 equiv of (SS)-3 at –10 ºC for 3 h, as a dark blue solid, in 45% yield: m.p. 270 ºC; \(^1\)H NMR \(\delta\) 2.04 (d, \(J = 1.5\) Hz, 3H), 2.37-2.54 (m, 2H), 2.68-2.89 (m, 2H), 2.94-3.15 (m, 2H), 3.68 (broad s, 1H), 3.91 (dd, \(J = 2.4\) and 2.5 Hz, 1H), 3.95 (m, 1H), 4.22 (s, 5H), 4.9 (t, \(J = 6.7\) Hz, 1H), 5.49 (broad s, 1H), 6.66 (d, \(J = 1.5\) Hz, 1H); \(^{13}\)C NMR \(\delta\) 15.7, 25.2, 28.4, 32.5, 36.0, 65.2, 66.0, 66.8, 70.3, 84.4, 88.0, 114.6, 133.3, 136.1, 136.5, 138.7, 140.6, 145.1, 188.0 (2C).

(pR)-Dimethyl 7,8-ferrocene-5,6-dihydronaphthalene-1,2-dicarboxylate (5).

To a solution of diene (pR)-2 (99% ee, 15 mg, 0.056 mmol) in toluene (1.5 mL), dimethyl acetylenedicarboxylate (40 \(\mu\)L, 6 mmol) was added. The reaction mixture was heated to 110 ºC for 3 h and the solvent evaporated. The residue was solved in CH\(_2\)Cl\(_2\) (7.5 mL) and DDQ (10 mg, 0.045 mmol) was added. The reaction mixture was stirred for 15 min and washed with a saturated aqueous solution of sodium bicarbonate. After workup and flash chromatography (eluent hexane/EtOAc 1:1), pure tricyclic ferrocenyl diester (pR)-5 was obtained as a yellow solid, in 63% yield: mp 134-135 ºC; [\(\alpha\)]\(_D\)\(^{20}\) = +283 (c 0.012, CHCl\(_3\)), 99% ee;\(^5\) \(^1\)H NMR \(\delta\) 2.34 (ddd, \(J = 5.4, 14.1\) and 14.5 Hz, 1H), 2.59 (ddd, \(J = 2.0, 14.1\) and 15.6 Hz, 1H), 3.03 (ddd, \(J = 2.0, 5.4\) and 15.6 Hz, 1H), 3.32 (ddd, \(J = 6.5, 14.1\) and 15.6 Hz, 1H), 3.88 (s, 3H), 4.00 (s, 3H), 4.06 (s, 5H), 4.30-4.31 (m, 2H), 4.51 (broad s, 1H), 7.25 (d, \(J = 7.8\) Hz, 1H), 7.80 (d, \(J = 7.8\) Hz, 1H); \(^{13}\)C NMR \(\delta\) 22.3, 31.8, 52.3, 52.6, 63.1, 67.7, 68.0,

\(^4\) Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min\(^{-1}\), 254 nm, \(R_I = 7.3\) min, \(T = 25\) ºC.

\(^5\) Chiral HPLC: Daicel Chiralpak AS-H, hexane/2-propanol 90:10; 0.8 mL min\(^{-1}\), 254 nm, \(R_I = 13.3\) min, \(T = 25\) ºC.
69.9, 77.2, 88.2, 125.9, 127.2, 129.1, 131.3, 133.7, 142.4, 166.1, 170.9; MS (ESI): m/z (%) 404 (M+, 100), 405 (M+ + 1, 18); HRMS (ESI) calcd. for C_{22}H_{20}O_{4}Fe (M+) 404.0712, found 404.0711.

(pS,M)-9,10-Ferrocene-3-methyl-7,8-dihydrophenantrene-1,4-quinone (6).

To a solution of tetrahydroaromatic ferrocene (pS,10aS,P)-(4) (97% ee, 12 mg, 0.031 mmol) in CH_{2}Cl_{2} (1.2 mL) at room temperature, DDQ (7 mg, 0.031 mmol) was added. The reaction mixture was stirred for 15 min and washed with a saturated aqueous solution of sodium bicarbonate. After workup and flash chromatography, pure dihydroaromatic helical ferrocene (pS,M)-6 was obtained as a dark green solid, in 72% yield: mp 270 ºC; [α]_{D}^{20} = +1704 (c = 0.001 in CHCl_{3}), 97% ee;^6 ¹H NMR δ 2.14 (d, J = 1.4 Hz, 3H), 2.41 (dt, J = 5.4 and 14.0 Hz, 1H), 2.60 (ddd, J = 1.9, 6.6 and 14.0 Hz, 1H), 3.03 (ddd, J = 1.9, 5.4 and 16.1 Hz, 1H), 4.67 (d, J = 2.2 Hz, 1H), 6.80 (d, J = 1.4 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H); ¹³C NMR δ 15.7, 22.0, 32.5, 67.6, 67.8, 67.9, 70.2, 77.7, 90.7, 124.4, 130.0, 132.3, 133.0, 138.0, 138.7, 145.1, 145.2, 185.4, 186.5; MS (ESI): m/z (%) 382 (M+, 24), 383 (M+ + 1, 39); HRMS (ESI) calcd. for C_{23}H_{18}FeO_{2} (M+) 382.2328, found 382.0650.

Bis(--)-camphanate (pS,M)-8.

(6) Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min⁻¹, 254 nm, R_{i} = 11.6 min, T = 25 ºC.
Et$_3$N (60 µL) and CH$_2$Cl$_2$ (1 mL) were added to a mixture of dihydroaromatic helical ferrocene (p$S$,M)-6 (7.7 mg, 0.02 mmol), activated Zn (17 mg, 0.25 mmol), (−)-camphanoyl chloride (22 mg, 0.1 mmol) and DMAP (1.15 mg, 0.01 mmol), under argon. The mixture was refluxed 1.5 h and filtrated through celite, aided by several ethyl acetate washes, to remove remaining Zn. The organic solution was washed with saturated aqueous NaHCO$_3$, 2% HCl and water. After workup and flash chromatography (hexane/EtOAc 2:1), the corresponding pure bis-(−)-camphanate (p$S$,M)-8 was obtained as a red solid, in 48% yield; m.p. decomposes over 220 ºC; $[\alpha]_D^{20} = -400$ (c = 0.028 in CHCl$_3$); $^{1}$H NMR δ 0.84 (s, 3H), 1.02 (s, 3H), 1.08 (s, 3H), 1.21 (s, 3H), 1.24 (s, 3H), 1.25 (s, 3H), 1.46-1.60 (m, 2H), 1.72-1.91 (m, 3H), 2.01-2.10 (m, 1H), 2.34 (s, 3H), 2.34-2.42 (m, 2H), 2.56-2.73 (m, 2H), 3.07 (dd, $J = 4.8$ and 16.2 Hz, 1H), 3.43-3.57 (m, 1H), 3.87 (s, 5H), 4.28 (s, 1H), 4.32 (broad s, 1H), 5.00 (broad s, 1H), 6.96 (s, 1H), 7.31 and 7.59 (AB System, $J = 8.5$ Hz, 2H); $^{13}$C NMR (125 MHz) δ 9.7, 9.8, 16.4, 16.6, 16.7, 17.0, 17.2, 20.2, 20.8, 24.5, 29.0, 29.1, 30.4, 31.5, 33.5, 43.7, 53.8, 54.4, 54.5, 55.0, 55.1, 55.2, 90.6, 91.1, 118.4, 121.2, 123.3, 125.3, 128.1, 128.5, 130.9, 142.3, 143.8, 170.0, 172.7, 178.0, 178.5. MS (ESI): m/z (%) 744 (M$^+$, 61), 745 (M$^+$+1, 100); HRMS (ESI) calcd. for C$_{43}$H$_{44}$O$_8$Fe (M$^+$) 744.6497, found 744.2380.

(p$R$P)-9,10-Ferrocene-3-methyl-7,8-dihydrophenantrene-1,4-quinone (6).

To a solution of diene (p$R$)-2 (95% ee, 8.5 mg, 0.032 mmol) in CH$_2$Cl$_2$, a solution of (±)-5-methyl-2-(p-tolylsulfinyl)-1,4-benzoquinone (rac)-3 (17 mg, 0.062 mmol) in CH$_2$Cl$_2$ (1 mL) was rapidly added, under argon. After stirring for 2 h, DDQ (7.2 mg, 0.032 mmol) was added and the resulting solution was stirred for 15 min and washed with a saturated solution of sodium bicarbonate. After workup and flash chromatography (eluent CH$_2$Cl$_2$), helical ferrocene (p$R$P)-6 was obtained as a dark green solid, in 68% yield: $[\alpha]_D^{20} = -1660$ (c = 0.001 in CHCl$_3$), 95% ee.$^{7}$

---

$^{7}$ Chiral HPLC: Daicel Chiralpak IA, hexane/2-propanol 90:10; 0.8 mL min$^{-1}$, 254 nm, $R_t = 10.5$ min, $T = 25$ ºC
**CHIRAL HPLC**

**Analysis Method**: C:\CHEM32\DATA\DEF_LC 2009-12-16 13-52-07\IA-O,6-10-15.M
**Last changed**: 10/9/2008 4:59:22 PM by Alfonso

---

**Signal 1: DAD1 A, Sig=254, Ret=360,100**

<table>
<thead>
<tr>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.691</td>
<td>0.2725</td>
<td>23.99025</td>
<td>1.46137</td>
<td>1.3402</td>
</tr>
<tr>
<td>11.621</td>
<td>0.3655</td>
<td>1756.75159</td>
<td>109.97760</td>
<td>98.6596</td>
</tr>
</tbody>
</table>

**Totals**: 1782.64184 111.43897

---

**Signal 2: DAD1 A, Sig=254 Ref=360,100**

<table>
<thead>
<tr>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.561</td>
<td>0.2383</td>
<td>9435.99194</td>
<td>240.27887</td>
<td>97.3762</td>
</tr>
<tr>
<td>11.725</td>
<td>0.2549</td>
<td>92.50223</td>
<td>6.05382</td>
<td>2.6230</td>
</tr>
</tbody>
</table>

**Totals**: 3528.57417 246.33163
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2011
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2011

S-20

(P)-Helix: 2 NOEs
(M)-Helix: 1 NOE


(pS,M)-8

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2011