Electronic Supporting Information for:

Regioselective addition of DDQ on a quinoid ring: an entry into chiral zwitterionic bridging ligands

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Table S1: Structural analysis and refinement of 11a

<table>
<thead>
<tr>
<th>Compound</th>
<th>11a</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCDC</td>
<td>1572929</td>
</tr>
<tr>
<td>Formula</td>
<td>C_{22}H_{22}N_{4}O_{4}</td>
</tr>
<tr>
<td>M_{w}</td>
<td>473.33</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Measurement temperature (K)</td>
<td>293</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2_{1/c}</td>
</tr>
<tr>
<td>a (Å)</td>
<td>13.4139(16)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>19.1246(19)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>9.4516(9)</td>
</tr>
<tr>
<td>β/°</td>
<td>103.255(10)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2360.1(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Dc (g.cm⁻³)</td>
<td>1.343</td>
</tr>
<tr>
<td>Crystal colour</td>
<td>red</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.01×0.05×0.05</td>
</tr>
<tr>
<td>μ(Mo-Kα) (cm⁻¹)</td>
<td>2.776</td>
</tr>
<tr>
<td>N° of unique refl.</td>
<td>6451</td>
</tr>
<tr>
<td>N° of observed refl.[F² &gt; 4σF²]</td>
<td>3612</td>
</tr>
<tr>
<td>N° parameters refined/restraints</td>
<td>321/27</td>
</tr>
<tr>
<td>R₁ [F²&gt;4σF²]</td>
<td>0.0820</td>
</tr>
<tr>
<td>wR₁ [F²&gt;4σF²]</td>
<td>0.2048</td>
</tr>
<tr>
<td>R₂ [all refl.]</td>
<td>0.1383</td>
</tr>
<tr>
<td>wR₂ [all refl.]</td>
<td>0.2342</td>
</tr>
<tr>
<td>Goodness of fit [all refl.]</td>
<td>1.032</td>
</tr>
<tr>
<td>Largest diff. peak/hole /e. Å³</td>
<td>+0.445; -0.417</td>
</tr>
</tbody>
</table>
Determination of the enantiomerization barrier of 11a

A solution of about 0.5 mg of the second eluted enantiomer in 1 mL of the mixture hexane / ethanol + trifluoroacetic acid (0.1% v/v) / dichloromethane (10/80/10 v/v/v) was thermostated at 25 °C and 10 µL of this solution were injected on (S,S)-Whelk-O1 every 12 minutes. The decreasing percentage of the second eluted enantiomer was monitored and transferred to a kinetic analysis giving the following values, $k_{\text{enantiomerization}} = 8.88 \times 10^{-5}$ s$^{-1}$, $t_{1/2} = 65$ minutes and $\Delta G^\neq = 96.2$ kJ.mol$^{-1}$.

Table S2: time decreasing percentage of the second enantiomer of 11a in the acidic mobile phase

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>% enantiomer</th>
<th>$\ln \left(\frac{% (t=0)-50%}{% (t=0)-50%}\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>87.59</td>
<td>0.0000</td>
</tr>
<tr>
<td>12</td>
<td>83.35</td>
<td>-0.1197</td>
</tr>
<tr>
<td>24</td>
<td>79.42</td>
<td>-0.2451</td>
</tr>
<tr>
<td>36</td>
<td>75.62</td>
<td>-0.3834</td>
</tr>
<tr>
<td>48</td>
<td>72.69</td>
<td>-0.5048</td>
</tr>
</tbody>
</table>

**Fig S1:** Determination of the enantiomerization barrier of 11a
Preparative chiral HPLC separation and optical purity analysis of 11a enantiomers

- Sample preparation: About 70 mg of the racemic 11a are dissolved in 15 mL of a mixture ethanol / dichloromethane (2/1).
- Chromatographic conditions: stationary phase: (S,S)-Whelk-O1; mobile phase: hexane / ethanol + trifluoroacetic acid (0,1%) / dichloromethane (10/80/10); flow-rate = 5 mL/min; UV detection at 254 nm.
- Injections (stacked): 60 times 250 µL, every 8 minutes.
- Collection: each enantiomer was collected in a flask containing sodium carbonate in ethanol, because racemization occurs in acidic media.
- First fraction: 25 mg of the first eluted with ee > 99%; Second fraction: 25 mg of the second eluted with ee > 96

- Chromatograms and HPLC data of the collected fractions:

  - first eluted enantiomer:

<table>
<thead>
<tr>
<th>RT [min]</th>
<th>Area</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.48</td>
<td>2782</td>
<td>99.62</td>
</tr>
<tr>
<td>8.10</td>
<td>11</td>
<td>0.38</td>
</tr>
<tr>
<td>Sum</td>
<td>2793</td>
<td>100.00</td>
</tr>
</tbody>
</table>

UV 254nm

CD 254nm
- second eluted enantiomer:

<table>
<thead>
<tr>
<th>RT [min]</th>
<th>Area</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.65</td>
<td>226</td>
<td>1.69</td>
</tr>
<tr>
<td>7.61</td>
<td>13134</td>
<td>98.31</td>
</tr>
<tr>
<td>Sum</td>
<td>13361</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Fig S2: Partial views of the $^1$H NMR spectra (in DMSO-$d_6$) of 4a, 4c, 11a, 11c and of an equimolar mixture of 4c and 11a after 20 minutes and 18 hours.
$^{1}H$ and $^{13}C$ NMR spectra of 11a-c

Fig. S3: $^{1}H$ NMR spectrum of 11a in DMSO-d$_6$ (400 MHz, 294 K).
Fig. S4: $^1$H NMR spectrum of 11a in MeOD-d$_4$ (400 MHz, 294 K).

Fig. S5: $^{13}$C NMR spectrum of 11a in DMSO-d$_6$ (100 MHz, 294 K).

Fig. S6: $^1$H NMR spectrum of 11b in DMSO-d$_6$ (400 MHz, 294 K)
Fig. S7: $^{13}$C NMR spectrum of 11b in DMSO-d$_6$ (100 MHz, 294 K).

Fig. S8: $^1$H NMR spectrum of 11c in DMSO-d$_6$ (400 MHz, 294 K).
Fig. S9: $^{13}$C NMR spectrum of 7c in DMSO-$d_6$ (100 MHz, 294 K).