Supporting Information for:

Into the second dimension with ferrocene *bis*-amidinium salts

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**Figure S1** Definition of \( E \)- and \( Z \)- with respect to distribution of substituents about a tri-substituted amidinium cation (for 1 and 2, \( R = \) ferrocenyl, \( R' = \) Cy)

\[
\begin{align*}
R' & \quad N - H \quad \Rightarrow \\
R & \quad N - H \quad \Rightarrow \\
R' & \quad N - H \quad \Rightarrow \\
\{E,E\} & \quad \{E,Z\} & \quad \{Z,Z\}
\end{align*}
\]

**Figure S2** Definition of \( \alpha \) (dihedral angle between the amidinium and \( C_5 \)-ring, with +ve and –ve values defined relative to the \( E \)- and \( Z \)-nitrogen groups)

\[
\begin{align*}
\text{C}_5\text{-plane} & \quad +ve \\
\text{C}_5\text{-plane} & \quad -ve
\end{align*}
\]
Figure S3  Definition of $l$ (the C$_5$–CN$_2$ bond length)

![Diagram of Fe with distances](image)

Figure S4  Definition of $\phi_{\text{O}}$ and $\phi_{\text{N}}$ (the bond angle at oxygen and nitrogen subtending the amidinium:carboxylate bridge)

![Diagram of bond angles](image)

Figure S5  Definition of $d_{\text{O}}$ and $d_{\text{N}}$ (the distance of the oxygen and nitrogen atoms from the C–CN$_2$ and C–CO$_2$ planes, respectively)

![Diagram of distances](image)
**Figure S6** Definition ss-$S_P$ and ss-$R_P$ chirality, prioritizing the $(E)$-nitrogen group.
Table S1 Summary of geometric data for [1]_∞ and [2]_∞

<table>
<thead>
<tr>
<th></th>
<th>α, deg</th>
<th>l, Å</th>
<th>φO deg</th>
<th>dO, Å</th>
<th>φN, deg</th>
<th>dN, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+26.3(2)</td>
<td>1.480(3)</td>
<td>O1 116.41(15)</td>
<td>−0.343(5)</td>
<td>N1 130.34(16)</td>
<td>−0.293(5)</td>
</tr>
<tr>
<td></td>
<td>+153.7(2)</td>
<td></td>
<td>O2 140.26(18)</td>
<td>−0.367(5)</td>
<td>N2 129.69(15)</td>
<td>2.590(4)</td>
</tr>
<tr>
<td>2</td>
<td>+39.8(1)</td>
<td>1.477(2)</td>
<td>O1 ~135&lt;sup&gt;a&lt;/sup&gt;</td>
<td>~0.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>N1 ~101&lt;sup&gt;a&lt;/sup&gt;</td>
<td>~1.9&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>+39.8(1)</td>
<td></td>
<td>O2 ~110&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>N2 ~133&lt;sup&gt;a&lt;/sup&gt;</td>
<td>~1.0&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O3 ~109&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O4 ~147&lt;sup&gt;a&lt;/sup&gt;</td>
<td>~0.1&lt;sup&gt;a&lt;/sup&gt;</td>
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</tr>
</tbody>
</table>

<sup>a</sup> disorder in the [<sup>t</sup>BuCO₂····H···O₂<sup>t</sup>C<sup>t</sup>Bu]<sup>−</sup> anion precludes accurate determination of these distances and angle. The values provided are meant simply as an indication and should not be used for meaningful comparisons.
Figure S7  Representation of the disorder in the \([\text{tBuCO}_2 \cdots \text{H} \cdots \text{O}_2\text{tBu}]^-\) anion
**Figure S8** Contour map showing residual electron density corresponding to hydrogen H3x between the two pivalate anions.