Electronic Supplementary Information for

Zwitterionic indenylammonium with carbon-centred reactivity toward reversible CO$_2$ binding and catalytic reduction

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**Figure S2.** $^{13}$C NMR spectrum of 1 in CDCl$_3$.
Figure S3. $^1$H NMR spectrum of 2 in CDCl$_3$

Figure S4. $^{13}$C NMR spectrum of 2 in CDCl$_3$
Figure S5. $^1$H NMR spectrum of 3 in CDCl$_3$.

Figure S6. $^{13}$C NMR spectrum of 3 in CDCl$_3$. 

\[
\text{CH}_3\text{N(CH}_2\text{CH}_3)_2\text{BF}_4^-
\]
Figure S7. $^1$H NMR spectrum of 4 in CDCl$_3$.

Figure S8. $^{13}$C NMR spectrum of 4 in CDCl$_3$. 

\[ \text{CH}_3\text{N(CH}_2\text{CH}_3)_2 \]
Figure S9. $^1$H NMR spectrum of 4 in DMSO-d$_6$
Figure S10. $^1$H NMR spectrum of 5 in DMSO-d$_6$. The peak at 9.98 ppm in the $^1$H NMR spectrum corresponds to a carboxylic acid.

Figure S11. $^{13}$C NMR spectrum of 5 in DMSO-d$_6$. The $^{13}$C NMR spectrum confirms the formation of a carboxylic acid species with a new peak at 166.63 ppm.
Figure S12. IR spectrum of 5 in nujol.

Figure S13. The hydrogen bonded pair in the crystal lattice of 5. The intermolecular O1–O2 distance is ~2.6 Å.

Table S1. Selected crystallographic data of 5:

<table>
<thead>
<tr>
<th></th>
<th>5</th>
</tr>
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<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>C_{15}H_{19}NO_{2}·0.5CH_{2}Cl_{2}</td>
</tr>
<tr>
<td><strong>FW</strong></td>
<td>287.77</td>
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<tr>
<td><strong>T (K)</strong></td>
<td>150(2)</td>
</tr>
<tr>
<td><strong>space group</strong></td>
<td>P2_{1}/n</td>
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<tr>
<td><strong>a (Å)</strong></td>
<td>7.8390(9)</td>
</tr>
<tr>
<td><strong>b (Å)</strong></td>
<td>10.837(1)</td>
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<tr>
<td><strong>c (Å)</strong></td>
<td>17.382(2)</td>
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<tr>
<td><strong>α (deg)</strong></td>
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<tr>
<td><strong>β (deg)</strong></td>
<td>94.666(5)</td>
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<tr>
<td><strong>γ (deg)</strong></td>
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<tr>
<td><strong>V (Å³)</strong></td>
<td>1471.7(3)</td>
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<tr>
<td><strong>Z</strong></td>
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</tr>
<tr>
<td><strong>D_{0} (g·cm⁻³)</strong></td>
<td>1.299</td>
</tr>
<tr>
<td><strong>μ (mm⁻¹)</strong></td>
<td>0.259</td>
</tr>
<tr>
<td><strong>no. of refln collected</strong></td>
<td>12831</td>
</tr>
<tr>
<td><strong>no. of indept refln</strong></td>
<td>3347</td>
</tr>
<tr>
<td><strong>GOF on F²</strong></td>
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</tr>
<tr>
<td><strong>R (I &gt; 2σ(I))</strong></td>
<td>R₁ = 0.0664</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.1285</td>
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<tr>
<td><strong>R (all data)</strong></td>
<td>R₁ = 0.1588</td>
</tr>
<tr>
<td></td>
<td>wR₂ = 0.1635</td>
</tr>
</tbody>
</table>
\[ \text{CO}_2 + \text{CH}_3(\text{OBBN})_2 + \text{CH}_3\text{OBNN} + \text{O(BBN)}_2 \]

\[ \text{TON} = 32 \quad 39.5 \]

**Figure S14.** $^1$H NMR spectrum of the final reaction mixture above.

**Figure S15.** $^1$B NMR spectrum of the final reaction mixture above.
**Figure S16.** $^1$H NMR spectrum of the final reaction mixture above

**Figure S17.** $^{11}$B NMR spectrum of the final reaction mixture above
\[ 4 + 100 \text{BH}_2\text{SMe}_2 \xrightarrow{\text{CO}_2} \text{CDCl}_3 \rightarrow (\text{CH}_2\text{OBO})_3 \]

25 °C, 12 h

TON = 109

Figure S18. $^1$H NMR spectrum of the final reaction mixture above

Figure S19. $^{11}$B NMR spectrum of the final reaction mixture above
4 + 100 BH₂·SMe₂ → \( \text{CO}_2 \text{CDCl}_3 \) \( \text{70 °C, 12 h} \) (CH₃OBO)₃ TON = 72.7

**Figure S20.** \( ^1\text{H} \) NMR spectrum of the final reaction mixture above

**Figure S21.** \( ^{11}\text{B} \) NMR spectrum of the final reaction mixture above
4 + 100 BH₃·SMe₂ → 2.5 atm CO₂
CDC₃ → (CH₂OBO)₃
25 °C, 10 h

Figure S22. ¹H NMR spectrum of the final reaction mixture above

Figure S23. ¹B NMR spectrum of the final reaction mixture above
4 + 100 BH₃·SMe₂ → (CH₃OBO)₃
CDCl₃
5 atm CO₂
25 °C, 10 h
TON = 269

Figure S24. ¹H NMR spectrum of the final reaction mixture above

Figure S25. ¹¹B NMR spectrum of the final reaction mixture above
Figure S26. $^1$H NMR spectrum of the final reaction mixture above

Figure S27. $^{11}$B NMR spectrum of the final reaction mixture above