Supporting Information

Asymmetric Cycloaddition of CO₂ and Epoxide using Recyclable Bi-functional Polymeric Co(III) Salen Complexes under Mild Condition

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General Procedure for HKR of epichlorohydrin using catalyst 1a:

A solution of freshly prepared bifunctional Co(III) polymeric salen complex 1a (0.01 mmol) in epichlorohydrin (100 mmol) was taken in an reaction vial and water (55 mmol) was added drop wise to it over a period of 30 min keeping under ice followed by stir at room temperature. After completion of the reaction the catalyst was precipitated out from the reaction mixture by addition of methanol and the unreacted epichlorohydrin was distilled out under reduced pressure. The catalyst which was precipitated out earlier was washed several times with methanol, dried overnight in a desiccator and used as such for next cycle. The catalyst was regenerated using acetic acid after 4 cycles.
Counter-ion source used for the synthesis of bifunctional polymeric Co(III) salen complex:

<table>
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<tr>
<th>Catalyst</th>
<th>Counter-ion source</th>
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<tr>
<td>1a</td>
<td>Acetic Acid (CH₃COOH) (a)</td>
</tr>
<tr>
<td>1b</td>
<td>2,6-dimethyl pyridinium tosylate (b)</td>
</tr>
<tr>
<td>1c</td>
<td>Para nitrobenzoic acid (NO₂C₆H₄COOH) (c)</td>
</tr>
<tr>
<td>1d</td>
<td>Trifluoroacetic acid (CF₃COOH) (d)</td>
</tr>
<tr>
<td>1e</td>
<td>Trichloroacetic acid (CCl₃COOH) (e)</td>
</tr>
<tr>
<td>1f</td>
<td>Ferrocenium tetrafluoroborate (f)</td>
</tr>
<tr>
<td>1g</td>
<td>Ferrocenium hexafluorophosphate (g)</td>
</tr>
</tbody>
</table>

Additive tested for asymmetric cycloadditon of CO₂ to propylene oxide using catalyst 1e:

TBAF

TBAC

TBAB

TBAI

Chiral imine

Cinchonine bromide salt
Characterization data of cyclic carbonate products:

(S)-4-methyl-1,3-dioxolan-2-one: The product was isolated as colourless liquid after distillation. $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$: 4.98-4.81 (m, 1H), 4.63-4.55 (t, 1H, $J$=8Hz), 4.09-4.01 (t, 1H, $J$=8Hz), 1.51-1.48 (d, 3H, $J$=6Hz); $^{13}$C NMR (50 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 155.2, 73.7, 70.7, 19.2; GC-MS: 102; GC analysis: Astec CHIRALDEX BTA column, 160 °C isothermal, $t_R$(minor) = 9.21 min, $t_R$(major) = 9.90 min. Area percentage ratio: 13.0:87.0.
**(R)-4-ethyl-1,3-dioxolan-2-one**: The product was isolated as colourless liquid after distillation (Catalyst 1e with opposite configuration was used). $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$: 4.76-4.63 (m, 1H), 4.59-4.51 (t, 1H, $J$=8Hz), 4.14-4.06 (t, 1H, $J$=8Hz), 1.84-1.75 (m, 2H$_2$), 1.07-1.00 (t, 3H, $J$=6Hz); $^{13}$C NMR (50 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 155.2, 78.0, 69.0, 26.9, 8.4; GC-MS: 116; GC analysis: Astec CHIRALDEX BTA column, 160 °C isothermal, $t_R$(major) = 10.33 min, $t_R$(minor) = 11.23 min. Area percentage ratio: 73.9:26.1.
(S)-4-buty1-1,3-dioxolane-2-one: The product was isolated as colourless liquid after distillation. $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$: 4.76-4.66 (m, 1H), 4.59-4.51 (t, 1H, $J$=8Hz), 4.12-4.04 (t, 1H, $J$=8Hz), 1.83-1.68 (m, 2H), 1.42-1.37 (m, 4H), 0.96-0.89 (t, 3H, $J$=6Hz); $^{13}$C NMR (50 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 155.2, 77.1, 69.4, 33.5, 26.4, 22.2, 13.8; GC-MS: 144; GC analysis: Astec CHIRALDEX BTA column, 160 °C isothermal, $t_R$(minor) = 10.46 min, $t_R$(major) = 10.96 min. Area percentage ratio: 85.5:14.5.
(S)-4-(chloromethyl)-1,3-dioxolan-2-one: The product was isolated as colourless liquid after distillation. \(^1\)H NMR (200 MHz, CDCl\(_3\), 25°C, TMS): \(\delta\): 5.10-4.99 (m, 1H), 4.66-4.58 (t, 1H, \(J=8\)Hz), 4.45-4.37(t, 1H, \(J=8\)Hz), 3.91-3.71 (qd, 2H, \(J=12, 4\)Hz); \(^1^3\)C NMR (50 MHz, CDCl\(_3\), 25°C, TMS) \(\delta\): 154.6, 74.5, 67.0, 44.2; GC-MS: 144; GC analysis: Astec CHIRALDEX BTA column, 160 °C isothermal, \(t_R\)(minor) = 14.44 min, \(t_R\)(major) = 14.79 min. Area percentage ratio: 76.4:23.6.

![Chromatogram](attachment:chromatogram.png)
**(S)-4-phenyl-1,3-dioxolan-2-one:** The product was isolated as colourless liquid after purification by column chromatography. $^1$H NMR (200 MHz, CDCl$_3$, 25°C, TMS): $\delta$: 7.44-7.38 (m, 5H), 5.71-5.63 (t, 1H, $J$=8Hz), 4.84-4.76(t, 1H, $J$=8Hz), 4.37-4.29 (t, 1H, $J$=8Hz); $^{13}$C NMR (50 MHz, CDCl$_3$, 25°C, TMS) $\delta$: 154.9, 135.8, 129.7, 129.2, 125.9, 71.2; GC-MS: 164; HPLC analysis: Chiralcel OD column, 1.0 ml/min, Hexane:IPA 90:10, $t_R$(minor) = 14.45 min, $t_R$(major) = 16.52 min. Area percentage ratio: 56.7:43.3. (220 nm)
**GC profile of (S)-epichlorohydrin obtained by HKR of racemic epichlorohydrin using catalyst 1a:**

GC analysis: Astec CHIRALDEX BTA column, 70 °C isothermal, $t_R$(minor) = 7.31 min, $t_R$(major) = 7.54 min. Area percentage ratio: 99.54:0.45.
NMR spectra:

$^1$H NMR of compound A:

$^{13}$C NMR of compound A:
$^1H$ NMR of compound B:

$^{13}C$ NMR of compound B:
$^1$H NMR of compound C:

$^{13}$C NMR of compound C:
$^{1}H$ NMR of compound $I'$:

$^{13}C$ NMR of compound $I'$:
$^1$H NMR of chiral 4-methyl-1,3-dioxolan-2-one:

$^{13}$C NMR of chiral 4-methyl-1,3-dioxolan-2-one:
$^1$H NMR of chiral 4-ethyl-1,3-dioxolan-2-one:

$^{13}$C NMR of chiral 4-ethyl-1,3-dioxolan-2-one:
$^1$H NMR of chiral 4-butyl-1,3-dioxolan-2-one:

$^{13}$C NMR of chiral 4-butyl-1,3-dioxolan-2-one:
$^1$H NMR of chiral 4-(chloromethyl)-1,3-dioxolan-2-one:

$^{13}$C NMR of chiral 4-(chloromethyl)-1,3-dioxolan-2-one:
$^1$H NMR of chiral 4-phenyl-1,3-dioxolan-2-one:

$^{13}$C NMR of chiral 4-phenyl-1,3-dioxolan-2-one:
D2O exchange- $^1$H NMR of compound $1'$: