Supporting Information
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Supporting Information for

Organocatalytic Allylic Amination of Morita-Baylis-Hillman Carbonates

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Table S1. Catalyst screening (GP4).

- Entry 1: Catalyst: none, Time [d]: 10, Yield [%]: n.r., e.e. [%]: n.d.
- Entry 2: Catalyst: β-ICD, Time [d]: 2, Yield [%]: 96, e.e. [%]: 52
- Entry 3: Catalyst: β-ICD+BNDHP, Time [d]: 10, Yield [%]: n.r., e.e. [%]: n.d.
- Entry 4: Catalyst: quinine, Time [d]: 10, Yield [%]: 17, e.e. [%]: 21
- Entry 5: Catalyst: Takemoto, Time [d]: 10, Yield [%]: n.r., e.e. [%]: n.d.
- Entry 6: Catalyst: phosphine-(thio)urea, Time [d]: 10, Yield [%]: n.r., e.e. [%]: n.r.
- Entry 7: Catalyst: (DHQD)$_2$PHAL, Time [d]: 7, Yield [%]: 53, e.e. [%]: 10
- Entry 8: Catalyst: (DHQD)$_2$AQN, Time [d]: 10, Yield [%]: 63, e.e. [%]: 66
- Entry 9: Catalyst: (DHQD)$_2$AQN, Time [d]: 6, Yield [%]: 48, e.e. [%]: 55
- Entry 10: Catalyst: (DHQD)$_2$AQN, Time [d]: 7, Yield [%]: 89, e.e. [%]: 57

**Notes:**
- β-ICD (10 mol%) and BNDHP (10 mol%) was used.
- Performed at 40 °C.
- An increased concentration (0.5M).

Table S2. Catalyst loading (GP4).

- Entry 1: Catalyst loading [%]: 2, Time [d]: 3, Yield [%]: 58, e.e. [%]: 52
- Entry 2: Catalyst loading [%]: 5, Time [d]: 3, Yield [%]: 90, e.e. [%]: 52
- Entry 3: Catalyst loading [%]: 10, Time [d]: 2, Yield [%]: 96, e.e. [%]: 52
Table S3. Reagents ratio (GP4).

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<th>Ratio 1a:9a</th>
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<th>e.e. [%]</th>
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<td>2</td>
<td>40</td>
<td>50</td>
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<tr>
<td>2</td>
<td>1 : 1.2</td>
<td>2</td>
<td>60</td>
<td>52</td>
</tr>
<tr>
<td>3</td>
<td>1 : 1.5</td>
<td>2</td>
<td>96</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>1 : 2</td>
<td>2</td>
<td>96</td>
<td>52</td>
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Table S4. Solvent screening (GP4).

<table>
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<tr>
<th>Entry</th>
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<th>Time [d]</th>
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<td>2</td>
<td>96</td>
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</tr>
<tr>
<td>2</td>
<td>p-xylene</td>
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<td>95</td>
<td>52</td>
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<tr>
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<td>o-xylene</td>
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<td>78</td>
<td>51</td>
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<tr>
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<td>96</td>
<td>25</td>
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<tr>
<td>7</td>
<td>DCE</td>
<td>2</td>
<td>78</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
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<td>2</td>
<td>96</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>CHCl₃</td>
<td>2</td>
<td>88</td>
<td>34</td>
</tr>
<tr>
<td>10</td>
<td>Et₂O</td>
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<td>49</td>
</tr>
<tr>
<td>11</td>
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</tr>
<tr>
<td>13</td>
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<td>n.d.</td>
</tr>
<tr>
<td>14</td>
<td>DMSO</td>
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</tr>
<tr>
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</tr>
<tr>
<td>16</td>
<td>H₂O</td>
<td>10</td>
<td>n.r.</td>
<td>n.d.</td>
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</table>
Table S5. Screening of ester group (GP4).

Table S6. Evaluation of reagents in cyclization reaction of 17a.

a Performed at 0 °C.
Table S7. Evaluation of reagents in cyclization reaction of 18a.

<table>
<thead>
<tr>
<th>Entry</th>
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<th>Conditions</th>
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<tr>
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<td>THF, RT</td>
<td>traces</td>
</tr>
<tr>
<td>2</td>
<td>BOP</td>
<td>Et3N, MeCN, RT</td>
<td>traces</td>
</tr>
<tr>
<td>3</td>
<td>Cl[MeN]</td>
<td>Et3N, DCM, RT</td>
<td>60%</td>
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**X-Ray section**

Crystallographic data for 14c were collected on Bruker D8 VENTURE Kappa Duo PHOTON100 by IµS micro-focus sealed tube MoKα (λ= 0.71073) at a temperature of 150(2) K. The structure was solved by direct methods (XT)\(^1\) and refined by full matrix least squares based on \(F^2\) (SHELXL2014).\(^2\) The hydrogen atoms on carbon were fixed into idealized positions (riding model) and assigned temperature factors either \(H_{iso}(H) = 1.2 \text{U}_{eq}(\text{pivot atom})\) or \(H_{iso}(H) = 1.5 \text{U}_{eq}(\text{pivot atom})\) for methyl moiety. The absolute structure determination was based on anomalous dispersion.

Crystal data for 14c: C\(_{23}\)H\(_{19}\)BrN\(_2\)O\(_4\)S, \(M_r = 499.37\); Orthorhombic, \(P 2_1 \ 2_1 \ 2_1\) (No 4), \(a = 9.7197\) (4) Å, \(b = 11.6764\) (5) Å, \(c = 19.8573\) (7) Å, \(\beta = 103.581\) (1)°, \(V = 2190.61\) (15) Å\(^3\), \(Z = 4\), \(D_x = 1.514 \text{Mg m}^{-3}\), yellow plate of dimensions \(0.30 \times 0.17 \times 0.07\) mm, numerical absorption correction (\(\mu = 2.00 \text{mm}^{-1}\)) \(T_{\text{min}} = 0.61\), \(T_{\text{max}} = 0.87\); a total of 58313 measured reflections (\(\theta_{\text{max}} = 27.5^\circ\)), from which 10064 were unique (\(R_{\text{int}} = 0.028\)) and 9578 observed according to the \(I > 2\sigma(I)\) criterion. The refinement converged (\(\Delta/\sigma_{\text{max}} = 0.002\)) to \(R = 0.030\) for observed reflections and \(wR(F^2) = 0.074\), \(GOF = 1.09\) for 566 parameters and all 10064 reflections.

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\(^1\) Sheldrick, G.M. Acta Cryst. 2015, A71, 3.

The final difference map displayed no peaks of chemical significance ($\Delta \rho_{\text{max}} = 0.47$, $\Delta \rho_{\text{min}} = 1.21$ e Å$^{-3}$). Absolute structure parameter (Flack) is -0.0057(13).

X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition number 1812260 for 14c, respectively and can be obtained free of charge from the Centre via its website (www.ccdc.cam.ac.uk/getstructures).

Figure 1. View on one of symmetrically independent molecule of 14c, the displacement ellipsoids at 30% probability level.

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Copies of $^1$H and $^{13}$C NMR spectra
7a
SI-45
13a
SI-80
F

NH

CO$_2$Me

TBSO

17q


$\delta$ (ppm)

$\delta$ (ppm)

SI-90
8. HPLC analysis

Column IC, n-heptane/iPrOH 90:10, \( V = 1 \) mL/min, \( T_{\text{oven}} = 25^\circ\text{C} \), 207 nm

\( t_R = 16.3, 21.4 \text{ min}, \text{ee} = 52\% \)
11a

Column IC, n-heptane:iPrOH 95:5, V = 1 mL/min, T_oven = 25°C, 220 nm

$\text{t}_R = 10.0, 13.2 \text{ min}, \text{ ee } = 58\%$
12a

Column IC, n-heptane:iPrOH 90:10, V =1 mL/min, T_{oven} = 25°C, 206 nm

$\text{t}_R = 14.6, 21.2 \text{ min}, \text{ ee} = 50\%$
13a

Column AD, n-heptane:iPrOH 90:10, V = 1 mL/min, T<sub>oven</sub> = 25°C, 206 nm
t<sub>R</sub> = 18.1, 22.1 min, ee = 31%
14a

Column IC, n-heptane:iPrOH 95:5, V = 1 mL/min, T\textsubscript{oven} = 25°C, 242 nm

\( t_R = 7.4, 8.3 \text{ min}, ee = 62\%, 82\% \)
Column IC, n-heptane:iPrOH 99:1, V = 1 mL/min, T_{oven} = 25°C, 210 nm

\[ t_R = 10.5, \ 12.5 \text{ min, } ee = 62\%, \ 92\% \]
14c

Column IC, n-heptane/iPrOH 98:2, V = 1 mL/min, $T_{oven}$ = 25°C, 236 nm

$t_R = 9.0, 11.6$ min, $ee = 78\%, 99\%$
Column IC, n-heptane:iPrOH 80:20, V = 1 mL/min, T\textsubscript{oven} = 25°C, 242 nm
t\(_R = 14.9, 20.9\) min, ee = 78%, 98%
14e

Column IC, n-heptane:iPrOH 80:20, V = 1 mL/min, T_{oven} = 25°C, 242 nm

$t_R = 12.9, 16.7$ min, $ee = 62\%$
Column IC, n-heptane/iPrOH 99:1, V = 1 mL/min, \( T_{\text{oven}} = 25^\circ\text{C}, \) 242 nm

\[ t_R = 11.6, \ 13.9 \text{ min, } ee = 30\% \]

![Graph showing chromatogram results]

**Peak Table**

<table>
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<th>Height</th>
<th>Similarity Index</th>
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<td>13.104</td>
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</table>
Column IC, n-heptane/iPrOH 99:1, $V = 1 \text{ mL/min}$, $T_{oven} = 25^\circ\text{C}$, 240 nm

$t_R = 10.9, 12.4 \text{ min, } ee = 63\%$
14h

Column IA, n-heptane:iPrOH 80:20, V = 1 mL/min, T\textsubscript{oven} = 25°C, 242 nm

\[ t_R = 8.5, \ 16.5 \text{ min}, \ ee = 52\% \]
Column IA, n-heptane: iPrOH 80:20, V = 1 mL/min, T\textsubscript{oven} = 25°C, 205 nm
\[ t_R = 7.9, 10.6 \text{ min}, ee = 52\% \]
Column IA, n-heptane:iPrOH 70:30, V = 1 mL/min, $T_{\text{oven}} = 25^\circ$C, 242 nm

$t_R = 10.6, 21.3$ min, $ee = 53\%$
Column IA, n-heptane:iPrOH 98:2, V = 1 mL/min, T\textsubscript{oven} = 25°C, 242 nm

t\textsubscript{R} = 13.6, 15.0 min, ee = 56\%
Column IB, n-heptane:iPrOH 90:10, V = 1 mL/min, T_{oven} = 25°C, 210 nm

\( t_R = 6.5, 7.2 \text{ min, } ee = 16\% \)
14m

Column IB, n-heptane:iPrOH 95:5, $V = 1 \text{ mL/min}$, $T_{oven} = 25^\circ\text{C}$, 210 nm

$t_R = 7.8, 8.5 \text{ min}$, $ee = 52\%$
14n

Column AD, n-heptane:iPrOH 99:1, V = 1 mL/min, \( T_{\text{oven}} = 25^\circ\text{C} \), 205 nm

\( t_R = 10.2, 12.4 \text{ min, } ee = 32\% \)
Column AD, n-heptane:iPrOH 99:1, V = 1 mL/min, T_{oven} = 25°C, 204 nm

$t_R = 17.8, 23.5$ min, $ee = 59\%$
Column AD, n-heptane:iPrOH 99:1, V = 1 mL/min, T_{oven} = 25°C, 242 nm

$t_R = 10.2, 11.7$ min, $ee = 57\%$
Column IC, n-heptane:iPrOH 99:1, \( V = 1 \text{ mL/min} \), \( T_{\text{oven}} = 25^\circ\text{C} \), 238 nm

\( t_R = 7.5, 8.8 \text{ min}, ee = 57\% \)
14r

Column AD, n-heptane:iPrOH 90:10, V = 1 mL/min, T_{oven} = 25°C, 241 nm

t_R = 9.7, 10.9 min, ee = 57 %
14s
Column AD, n-heptane:iPrOH 99:1, V = 1 mL/min, T<sub>oven</sub> = 25°C, 242 nm.

<chemicalformula>NO₂</chemicalformula>
<chemicalformula>CO₂t-Bu</chemicalformula>

<chemicalformula>\text{t}_R = 8.9, 10.6 \text{ min}, ee = 60\%

---

**Peak Table**

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<th>Peak</th>
<th>Ref</th>
<th>Name</th>
<th>Ref. Time</th>
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**Peak Table**

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<td>79.9565</td>
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</tbody>
</table>
17a

Column IB, n-heptane:iPrOH 98:2, V = 1 mL/min, T_{oven} = 25°C, 242 nm

{\text{t}}_R = 6.7, 7.1 \text{ min, } ee = 43\%
17b

Column IA, n-heptane:iPrOH 98:2, V = 1 mL/min, T_{oven} = 25°C, 242 nm

$t_R = 8.6, 9.4$ min, $ee = 62\%, 92\%$
17c

Column IA, n-heptane:iPrOH 98:2, V = 1 mL/min, T\textsubscript{oven} = 25°C, 242 nm
t\textsubscript{R} = 10.5, 11.3 min, ee = 78%, 99%
**17d**

Column OD-H, n-heptane:iPrOH 98:2, V = 1 mL/min, $T_{oven} = 25^\circ C$, 242 nm

t$_R$ = 31.9, 37.7 min, ee = 77%, 98%
Column IA, n-heptane:iPrOH 95:5, $V = 1$ mL/min, $T_{oven} = 25^\circ$C, 242 nm
$t_R = 17.4, 18.3$ min, $ee = 61\%$
Column IB, n-heptane:iPrOH 98:2, V = 1 mL/min, T_{oven} = 25°C, 242 nm
\( t_R = 7.0, 7.8 \text{ min}, ee = 55\%. \)
Column AD, n-heptane:iPrOH 99:1, V = 1 mL/min, $T_{oven} = 25^\circ$C, 242 nm

t_R = 6.7, 7.8 min, ee = 57\%
19a

Column ODH, n-heptane:iPrOH 95:5, V = 1 mL/min, T\textsubscript{oven} = 25°C, 210 nm

\( t_R = 6.7, 8.3 \text{ min}, ee = 43\% \)
19b

Column IC, n-heptane/iPrOH 99:1, V = 1 mL/min, T<sub>oven</sub> = 25°C, 210 nm

*<span><span>t<sub>R</sub> = 29.8, 32.4 min, ee = 62%, 93%<br></span></span>
19c

Column IC, n-heptane/iPrOH 98:2, $V = 1 \text{ mL/min}$, $T_{\text{oven}} = 25^\circ \text{C}$, 210 nm

t_R = 16.9, 18.0 min, ee = 78%, 99%
19d

Column IB, n-heptane:iPrOH 80:20, V = 1 mL/min, T_{oven} = 25°C, 210 nm

$$t_R = 8.5, 9.4 \text{ min, } ee = 78\%, 98\%$$
19k

Column IC, n-heptane:iPrOH 99:1, V = 1 mL/min, T_{oven} = 25°C, 210 nm

t_{R} = 19.2, 22.3 min, ee = 55%
19q

Column IC, n-heptane:iPrOH 99:1, V = 1 mL/min, T\textsubscript{oven} = 25°C, 242 nm

$t_R = 14.1, 15.3$ min, $ee = 58\%$