Electronic Supplementary Information

Stereoselective synthesis of enantiomerically pure bowl-shaped hydroxytribenzotriquinacenes

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Parameter optimisation of the enzymatic ester hydrolysis

\[
\begin{align*}
\text{rac-11} & \xrightarrow{\text{different lipases}} \text{buffer (50 mM, pH 7.0-9.0)} \\
& \text{toluene or MTBE} \\
& 25-80 \degree C, 24 \text{ h}
\end{align*}
\]

![Diagram of chemical structures](image)

<table>
<thead>
<tr>
<th>lipase</th>
<th>amount enzyme [mg]</th>
<th>amount rac-11 [mg]</th>
<th>solvent</th>
<th>buffer(^{[e]}) (pH/amount [mL])</th>
<th>temp. [° C]</th>
<th>conv. to 12 [%]</th>
<th>ee [%]</th>
<th>E-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAL-B(^{[a]})</td>
<td>25</td>
<td>50</td>
<td>MTBE (7)</td>
<td>KP(_1) (7.0, 7)</td>
<td>50</td>
<td>3</td>
<td>88</td>
<td>17</td>
</tr>
<tr>
<td>CAL-B(^{[a]})</td>
<td>50</td>
<td>9</td>
<td>toluene (0.05)</td>
<td>AMP (9.0, 0.5)</td>
<td>25</td>
<td>16</td>
<td>84</td>
<td>15</td>
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<tr>
<td>CAL-B(^{[a]})</td>
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<td>52</td>
<td>toluene (7)</td>
<td>KP(_1) (7.0, 7)</td>
<td>80</td>
<td>6</td>
<td>94</td>
<td>36</td>
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<tr>
<td>CAL-B(^{[a]})</td>
<td>50</td>
<td>9</td>
<td>toluene (0.05)</td>
<td>KP(_1) (7.4, 0.5)</td>
<td>25</td>
<td>9</td>
<td>74</td>
<td>8</td>
</tr>
<tr>
<td>CAL-B(^{[b]})</td>
<td>5</td>
<td>9</td>
<td>toluene (0.05)</td>
<td>KP(_1) (7.4, 0.5)</td>
<td>25</td>
<td>20</td>
<td>38</td>
<td>2</td>
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<tr>
<td>D 20(^{[c]})</td>
<td>5</td>
<td>9</td>
<td>toluene (0.05)</td>
<td>KP(_1) (7.4, 0.5)</td>
<td>25</td>
<td>7</td>
<td>38</td>
<td>2</td>
</tr>
<tr>
<td>CAL-B(^{[d]})</td>
<td>49</td>
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<td>toluene (0.05)</td>
<td>KP(_1) (7.0, 0.5)</td>
<td>25</td>
<td>23</td>
<td>88</td>
<td>25</td>
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<tr>
<td>CAL-B(^{[d]})</td>
<td>51</td>
<td>9</td>
<td>toluene (0.05)</td>
<td>AMP (9.0, 0.5)</td>
<td>25</td>
<td>25</td>
<td>92</td>
<td>40</td>
</tr>
<tr>
<td>CAL-A(^{[d]})</td>
<td>52</td>
<td>9</td>
<td>toluene (0.05)</td>
<td>KP(_1) (7.0, 0.5)</td>
<td>25</td>
<td>52</td>
<td>48</td>
<td>5</td>
</tr>
<tr>
<td>CAL-A(^{[d]})</td>
<td>30</td>
<td>30</td>
<td>toluene (10)</td>
<td>KP(_1) (7.0, 10)</td>
<td>25</td>
<td>40</td>
<td>92</td>
<td>45</td>
</tr>
</tbody>
</table>

\(^{[a]}\): C-Lecta (immobilised); \(^{[b]}\): C-Lecta (lyophilised); \(^{[c]}\): Amano; \(^{[d]}\): Sigma Aldrich (immobilised); \(^{[e]}\): KP: phosphate buffer; AMP: 2-amino-2-methyl-1-propanol buffer.
HPLC chromatograms

HPLC chromatogram of compound (\textit{M})-12 (>99% ee)

HPLC chromatogram of compound (\textit{P})-12 (>99% ee)
$^1$H and $^{13}$C NMR spectra

$^1$H NMR spectrum of compound 15 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 15 (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 16a (all-cis-isomer) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 16a (all-cis-isomer) (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 16b (cis,trans-isomer, ~1:1 mixture of two diastereomers) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 16b (cis,trans-isomer, ~1:1 mixture of two diastereomers) (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 17 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 17 (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 12 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound 12 (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound 11 (500 MHz, CDCl$_3$); residual solvent signals: 5.30 ppm (dichloromethane), 1.55 ppm (water), 1.44 ppm (cyclohexane).

$^{13}$C NMR spectrum of compound 11 (126 MHz, CDCl$_3$); residual solvent signals: solvent residuals: 27.07 ppm (cyclohexane).
$^1$H NMR spectrum of compound (P)-11 (64% ee) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound (P)-11 (64% ee) (126 MHz, CDCl$_3$)
$^1$H NMR spectrum of compound (M)-12 (>99% ee) (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound (M)-12 (>99% ee) (126 MHz, CDCl$_3$)
\(^1\)H NMR spectrum of compound (M)-11 (500 MHz, CDCl\(_3\))

\(^{13}\)C NMR spectrum of compound (M)-11 (126 MHz, CDCl\(_3\))
$^1$H NMR spectrum of compound (P)-13 (500 MHz, CDCl$_3$)

$^{13}$C NMR spectrum of compound (P)-13 (126 MHz, CDCl$_3$)
$^{1}H$ NMR spectrum of compound (P)-11 (500 MHz, CDCl$_3$)

$^{13}C$ NMR spectrum of compound (P)-11 (126 MHz, CDCl$_3$)