Hyperbranched Polyethylene-Supported L-Proline: A Highly Selective and Recyclable Organocatalyst for Asymmetric Aldol Reactions

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Figure S1 $^1$H NMR (400 MHz, CD$_3$OD) spectrum of O-acryloyl-trans-4-hydroxy-L-proline hydrochloride (2): $\delta$ = 2.44-2.68 ppm (m, 2H, b), 3.52-3.73 ppm (m, 2H, d), 4.60-4.64 (m, 1H, a), 5.52 (br s, 1H, c), 5.96-5.99 (m, 1H, f), 6.17/6.20/6.21/6.24 (s, 1H, f), 6.46/6.50 (s, 1H, e), * represents the peak of the solvent.

Figure S2 $^{13}$C NMR (100 MHz, CD$_3$OD) spectrum of O-acryloyl-trans-4-hydroxy-L-proline hydrochloride (2)

ESI-MS: calculated for C$_8$H$_{13}$NO$_4^+$ [M+H$^+$]: 186.1, found: 185.9.
Figure S3 \(^1\)H NMR (400 MHz, CDCl\(_3\)) spectrum of N-tert-butoxycarbonyl- O-acryloyl-trans-4-hydroxy-L-proline (3): \(\delta = 1.43/1.46\) (s, 9H, h), 2.27-2.51 (m, 2H, b), 3.60-3.73 (m, 2H, d), 4.37/4.48 (t, 1H, a), 5.35 (br s, 1H, c), 5.86-5.89 (m, 1H, f), 6.07/6.09/6.11/6.14 (s, 1H, f), 6.40/6.44 (s, 1H, e). * represents the peak of the solvent.

Figure S4 \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) spectrum of N-tert-butoxycarbonyl- O-acryloyl-trans-4-hydroxy-L-proline (3) and tertiary butanol.

ESI-MS: calculated for C\(_{13}\)H\(_{20}\)NO\(_6\) [\(M+H^+\)]: 286.1, found: 285.9.
**Figure S5** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of tert-butyl-N-tert-Butyloxycarbonyl-O-acryloyl-trans-4-hydroxy-L-proline ester (4): $\delta = 1.43$ (t, 18H, g), 2.13-2.44 (m, 2H, b), 3.51-3.73 (m, 2H, d), 4.20-4.30 (m, 1H, a), 5.31 (br s, 1H, c), 5.82-5.86 (m, 1H, f), 6.04/6.07/6.08/6.11 (s, 1H, f), 6.36/6.41 (s, 1H, e).

**Figure S6** $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of tert-butyl-N-tert-Butyloxycarbonyl-O-acryloyl-trans-4-hydroxy-L-proline ester (4)

ESI-MS: calculated for C$_{17}$H$_{28}$NO$_6$ [M+H$^+$]: 342.2, found: 342.0.
Figure S7 ¹H NMR (400 MHz, CDCl₃) data of the products from the aldol reaction of cyclohexanone and p-nitrobenzaldehyde (p-NBA) in Run 9 with de-protected P3 (DP3) as catalyst, DP3 (60 mg, 0.03 mmol L-proline), p-NBA (0.1 mmol, 15 mg) cyclohexanone (0.5 mmol, 47 mg), and THF (0.5 mL, containing 5.4 μL water). Figure S7 (a) was used to calculate the conversion of p-NBA (conversion of p-NBA = ½S₂/(S₁ + ½S₂), S₁ and S₂ are integral area of peak 1 and 2, respectively; Figure S7 (b) was used to calculate the anti/syn value of the product mixture.
**Figure S8** Chiral HPLC results of the products from the aldol reaction of p-NBA and cyclohexanone in Run 9 with DP3 as catalyst. The value of ee was calculated based on the integrations of the two peaks from the anti-products.
Table S1 Determination of element contents in run P3 sample

<table>
<thead>
<tr>
<th>Element</th>
<th>N (%)</th>
<th>C (%)</th>
<th>H (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element analysis a</td>
<td>0.87</td>
<td>81.39</td>
<td>13.42</td>
</tr>
<tr>
<td>¹H NMR b</td>
<td>0.66</td>
<td>81.45</td>
<td>13.34</td>
</tr>
</tbody>
</table>

a determined by an elemental analyzer; b estimated from ¹H NMR spectrum using the following equations:

\[ C(\%) = \frac{2 \times 100 + 17 \times F_4}{m_{w_E} \times 100 + m_{w_4} \times F_4} \times a_C \times 100; \]
\[ H(\%) = \frac{4 \times 100 + 27 \times F_4}{m_{w_E} \times 100 + m_{w_4} \times F_4} \times a_H \times 100; \]
\[ N(\%) = \frac{F_4}{m_{w_E} \times 100 + m_{w_4} \times F_4} \times a_N \times 100, \]

where \( F_4 \) (mol%) is mole ratio of incorporated comonomer 4 in run P3 sample; \( m_{w_E} \) and \( m_{w_4} \) are molecular weights of ethylene and comonomer 4, respectively; and \( a_C, a_H, \) and \( a_N \) are atomic weights for carbon, hydrogen, and nitrogen, respectively.
Figure S9 IR spectra of run P3 sample before and after de-protection treatment (DP3)
Figure S10 $^1$H NMR (400 MHz, CDCl$_3$) data of the products from the Aldol reaction in Run 16 (Table 4) with de-protected P4 (DP4) as catalyst.
Figure S11 $^1$H NMR (400 MHz, CDCl$_3$) data of the products from the Aldol reaction in Run 17 (Table 4) with de-protected P4 (DP4) as catalyst.
Figure S12 $^1$H NMR (400 MHz, CDCl$_3$) data of the products from the Aldol reaction in Run 18 (Table 4) with de-protected P4 (DP4) as catalyst.
Figure S13 $^1$H NMR (400 MHz, CDCl$_3$) data of the products from the Aldol reaction in Run 19 (Table 4) with de-protected P4 (DP4) as catalyst.
Figure S14: $^1$H NMR (400 MHz, CDCl$_3$) data of the products from the Aldol reaction in Run 20 (Table 4) with de-protected P4 (DP4) as catalyst.