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

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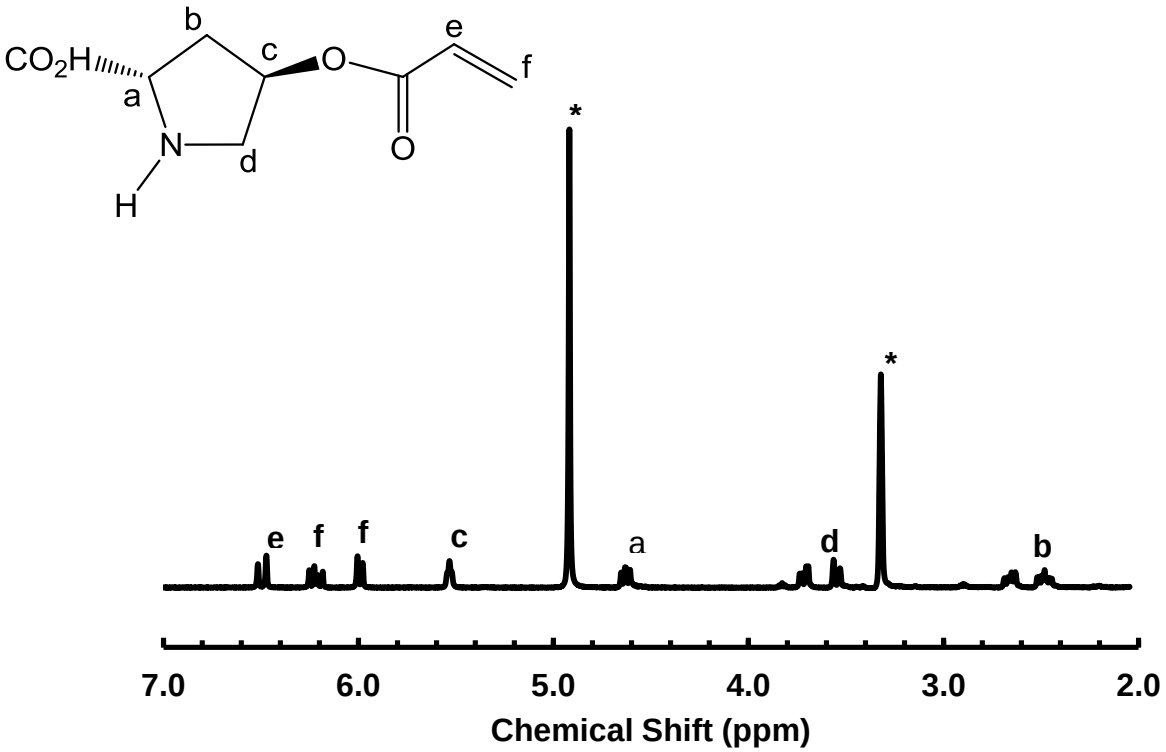

Figure S1 ^{1}H NMR (400 MHz, CD_3OD) spectrum of O-acryloyl-trans-4-hydroxy-L-proline hydrochloride (**2**) : δ = 2.44-2.68 ppm (m, 2H, b), 3.52-3.73 ppm (m, 2H, d), 4.60-4.64 (m, 1H, a), 5.52 (br s, 1H, c), 5.96-5.99 (m, 1H, f), 6.17/6.20/6.21/6.24 (s, 1H, f), 6.46/6.50 (s, 1H, e), * represents the peak of the solvent.

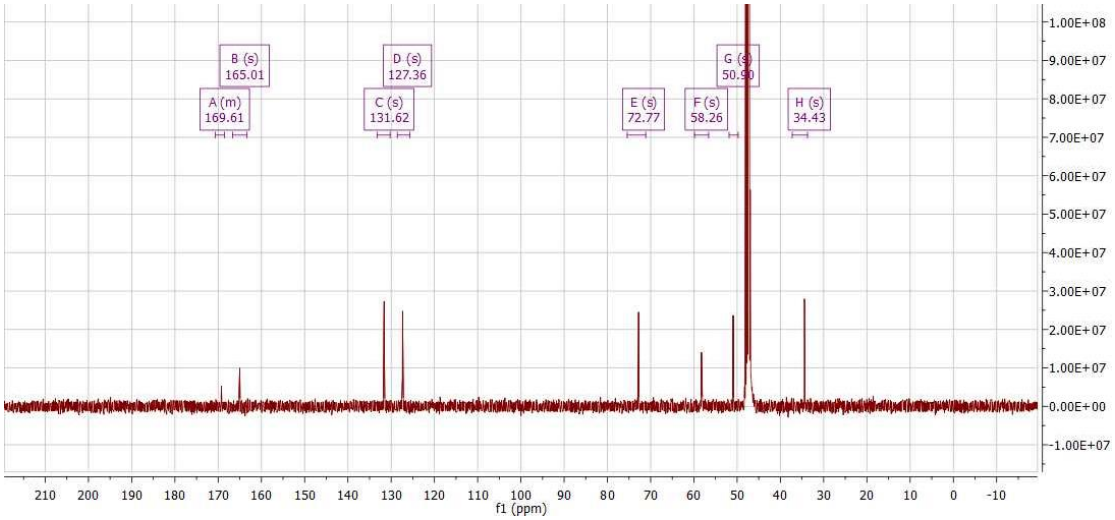

Figure S2 ^{13}C NMR (100 MHz, CD_3OD) spectrum of O-acryloyl-trans-4-hydroxy-L-proline hydrochloride (**2**)

ESI-MS: calculated for $C_8H_{13}NO_4^+$ [M+H^+]: 186.1 , found: 185.9 .

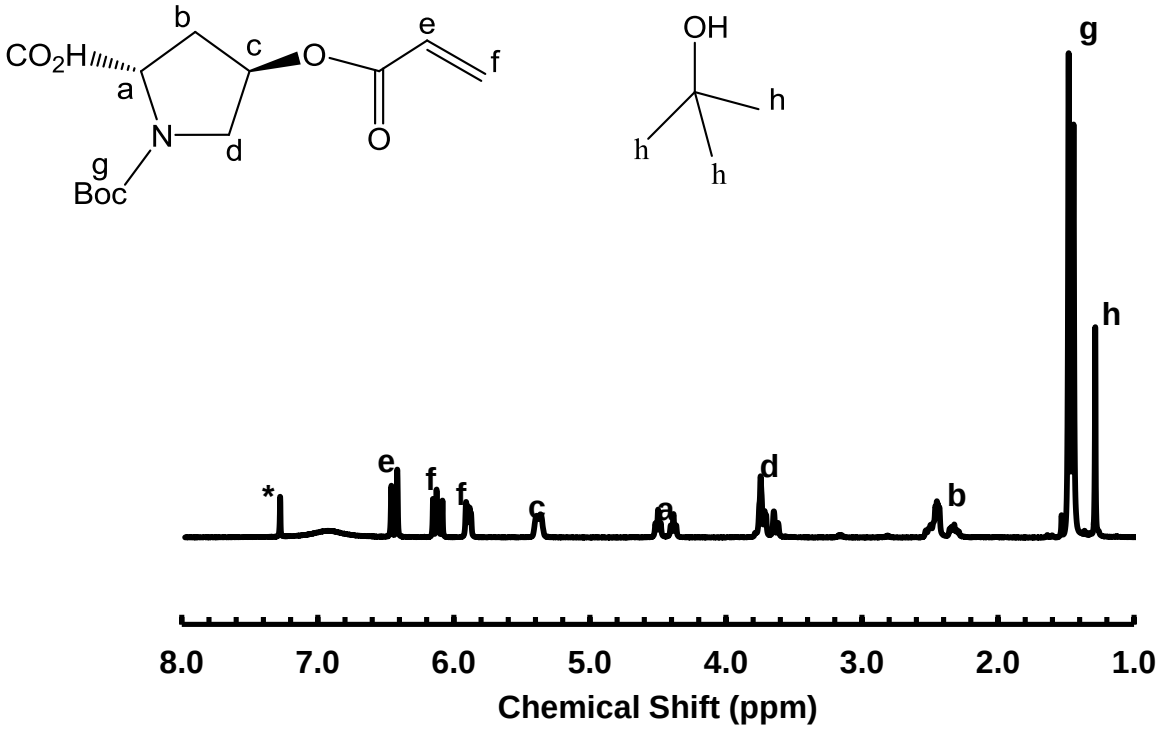

Figure S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of N-tert-butyloxycarbonyl- O-acryloyl-trans-4-hydroxy-L-proline (**3**): δ = 1.43/1.46 (s, 9H, h), 2.27-2.51 (m, 2H, b), 3.60-3.73 (m, 2H, d), 4.37/4.48 (t, 1H, a), 5.35 (br s, 1H, c), 5.86-5.89 (m, 1H, f), 6.07/6.09/6.11/6.14 (s, 1H, f), 6.40/6.44 (s, 1H, e), * represents the peak of the solvent.

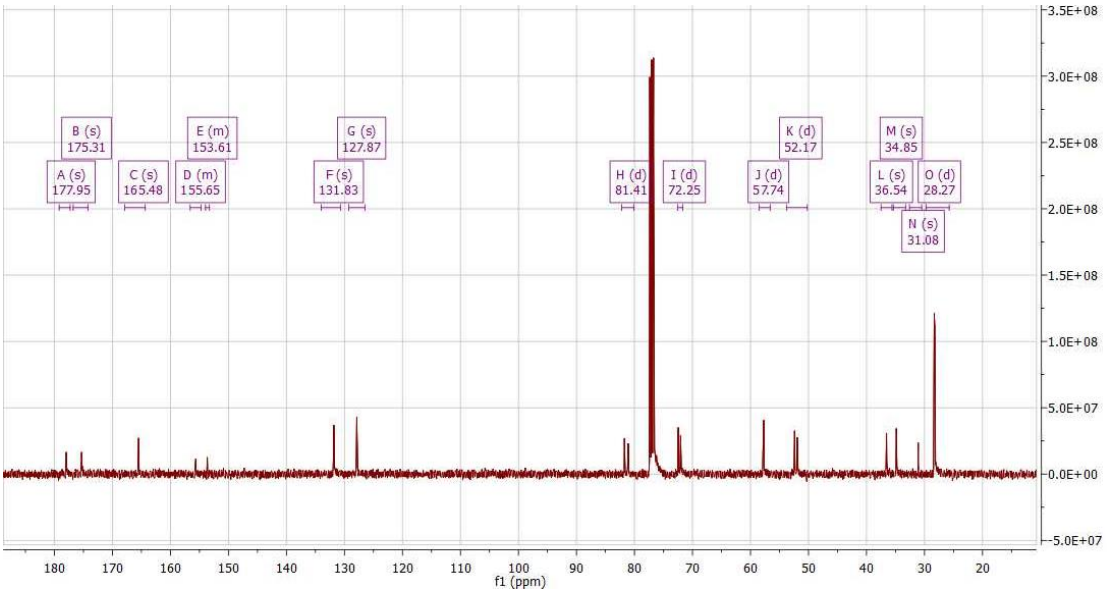

Figure S4 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of N-tert-butyloxycarbonyl- O-acryloyl-trans-4-hydroxy-L-proline (**3**) and tertiary butanol.

ESI-MS: calculated for $C_{13}H_{20}NO_6$ [M+H^+]: 286.1, found: 285.9.

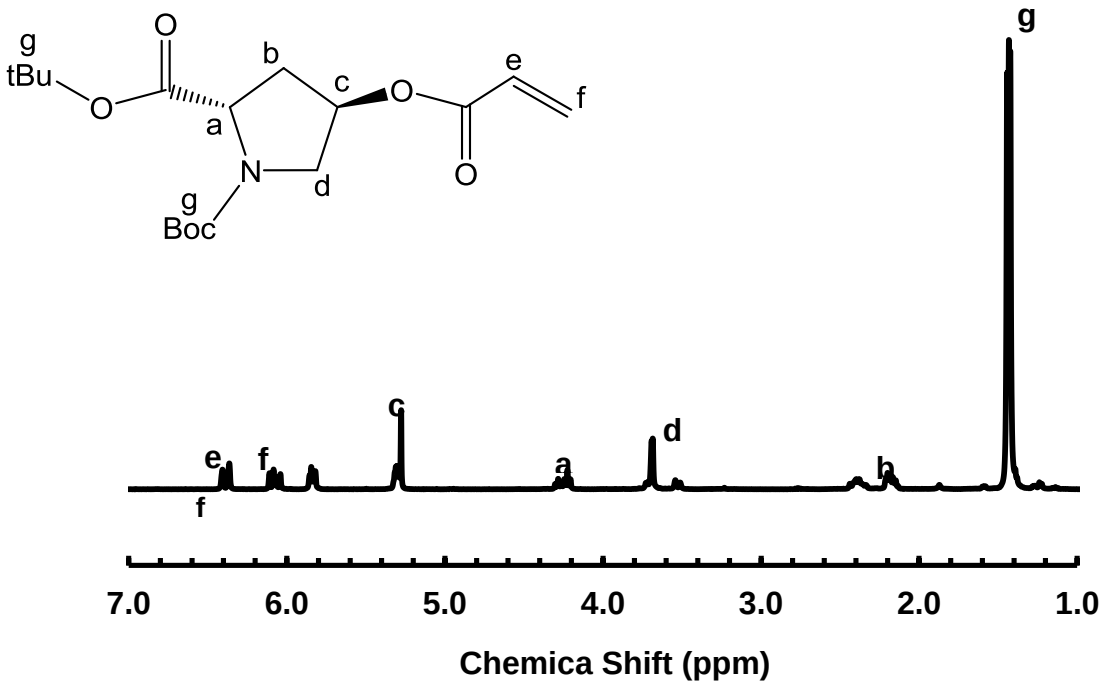

Figure S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of tert-butyl-N-tert-Butyloxycarbonyl-O-acryloyl-trans-4-hydroxy-L-proline ester (**4**): δ = 1.43 (t, 18H, g), 2.13-2.44 (m, 2H, b), 3.51-3.73 (m, 2H, d), 4.20-4.30 (m, 1H, a), 5.31 (br s, 1H, c), 5.82-5.86 (m, 1H, f), 6.04/6.07/6.08/6.11 (s, 1H, f), 6.36/6.41 (s, 1H, e).

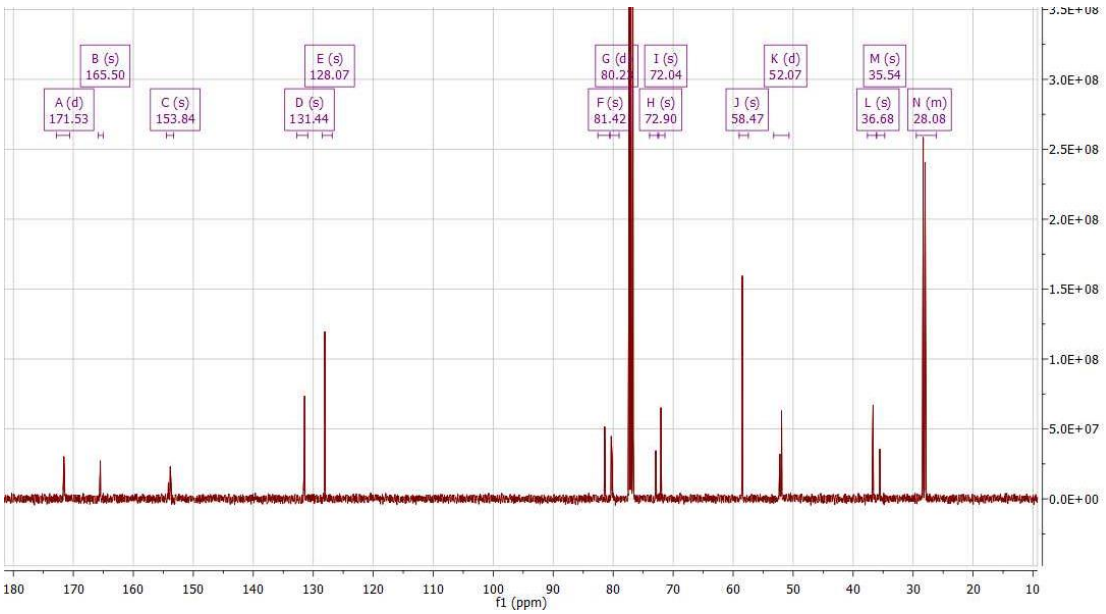

Figure S6 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of tert-butyl-N-tert-Butyloxycarbonyl-O-acryloyl-trans-4-hydroxy-L-proline ester (**4**)

ESI-MS: calculated for $C_{17}H_{28}NO_6$ [M+H^+]: 342.2, found: 342.0.

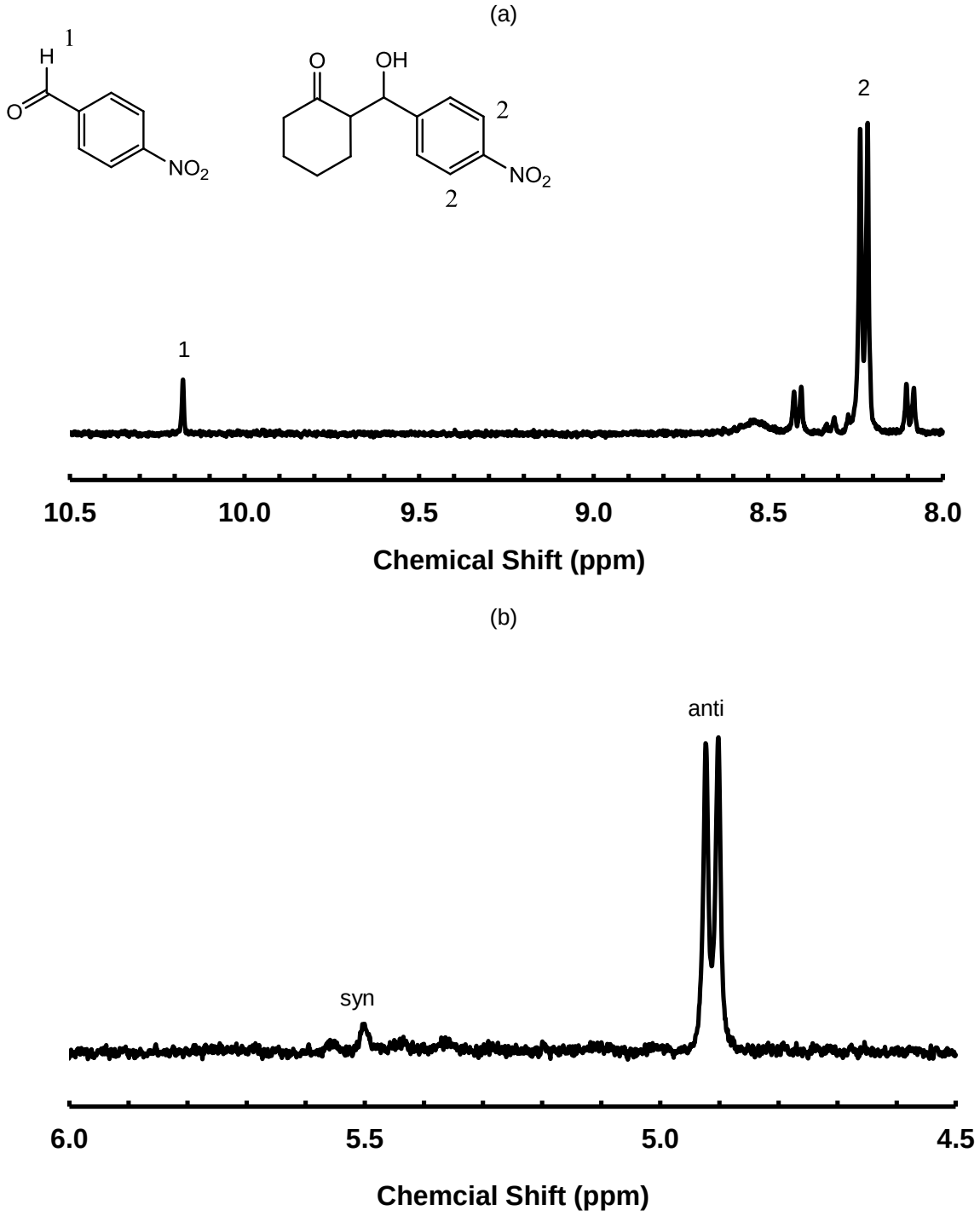

Figure S7 ^{1}H NMR (400 MHz, $CDCl_3$) data of the products from the aldol reaction of cyclohexanone and p-nitrobenzaldehyde (p-NBA) in Run 9 with de-protected P3 (DP3) as catalyst, DP3 (60 mg, 0.03 mmol L-proline), p-NBA (0.1 mmol, 15 mg) cyclohexanone (0.5 mmol, 47 mg), and THF (0.5 mL, containing 5.4 μL water). Figure S7 (a) was used to calculate the conversion of p-NBA (conversion of p-NBA = $½S_2/(S_1 + ½S_2)$, 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.

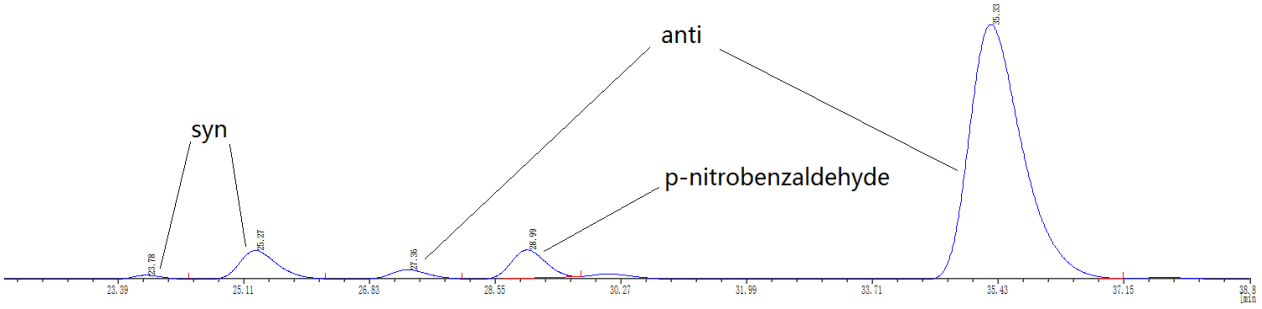

Figure S8 Chiral HPLC results of the products from the aldol reaction of p-NBA and cyclohexanone in Run 9 with DP3 as catalyst. The value of ee was calculated based on the integrations of the two peaks from the anti-products.

Table S1 Determination of element contents in run P3 sample

Element	N (%)	C(%)	H(%)
Element analysis [a]	0.87	81.39	13.42
^{1}H NMR[b]	0.66	81.45	13.34

[a] determined by an elemental analyzer; [b] estimated from ^{1}H NMR spectrum using the following equations: $C(\%) = \frac{2\times100 + 17\times F_4}{mw_E\times100 + mw_4\times F_4}\times a_{rC}\times100$; $H(\%) = \frac{4\times100 + 27\times F_4}{mw_E\times100 + mw_4\times F_4}\times a_{rH}\times100$; and $N(\%) = \frac{F_4}{mw_E\times100 + mw_4\times F_4}\times a_{rN}\times100$, where F_4 (mol%) is mole ratio of incorporated comonomer **4** in run P3 sample; mw_E and mw_4 are molecular weights of ethylene and comonomer **4**, respectively; and a_{rC}, a_{rH}, and a_{rN} are atomic weights for carbon, hydrogen, and nitrogen, respectively.

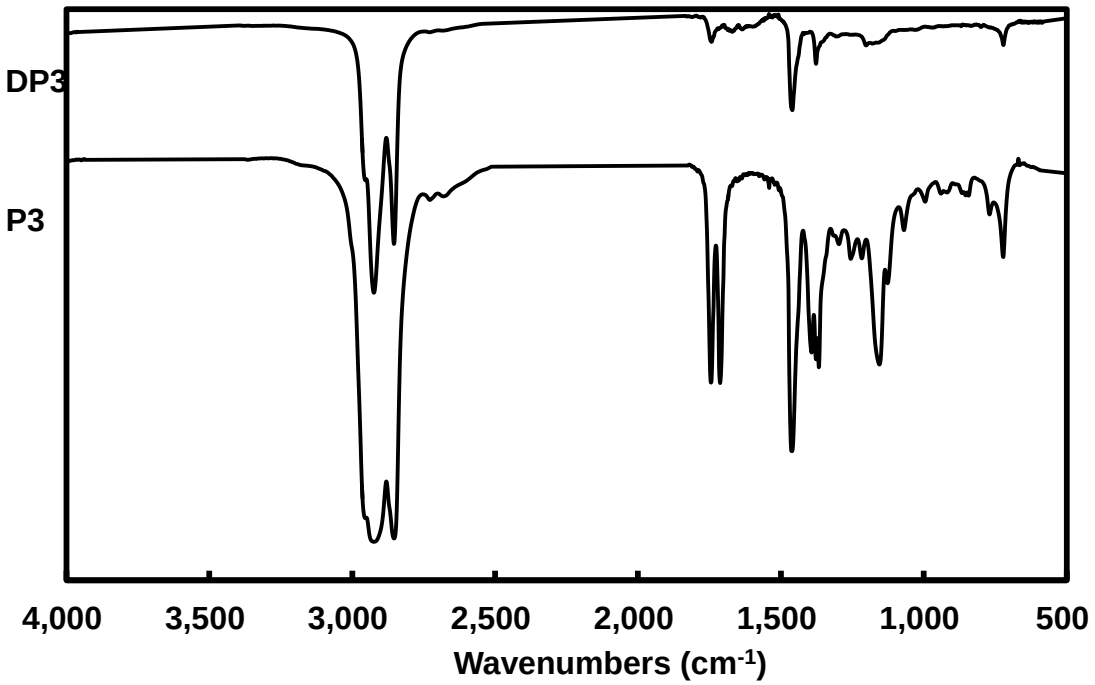

Figure S9 IR spectra of run P3 sample before and after de-protection treatment (DP3)

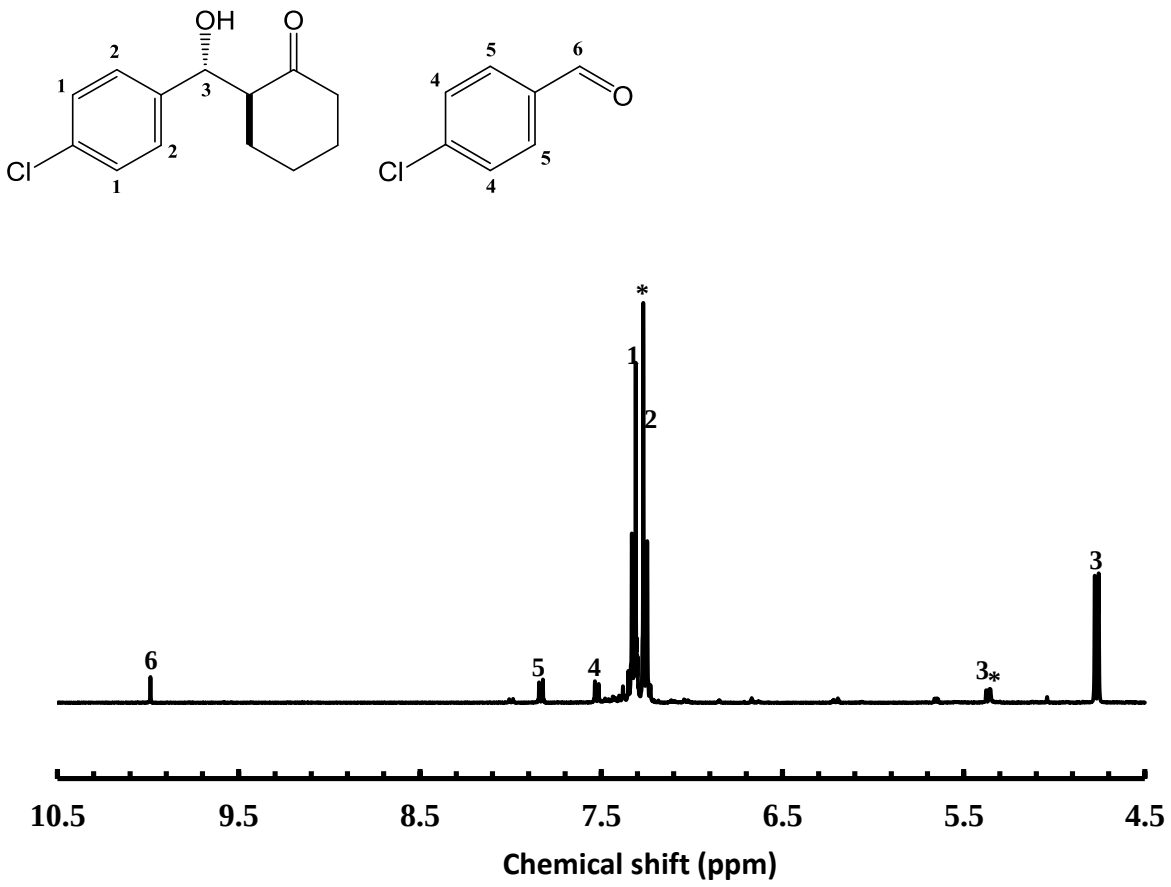

Figure S10 ^{1}H NMR (400 MHz, $CDCl_3$) data of the products from the Aldol reaction in Run 16 (Table 4) with de-protected P4 (DP4) as catalyst

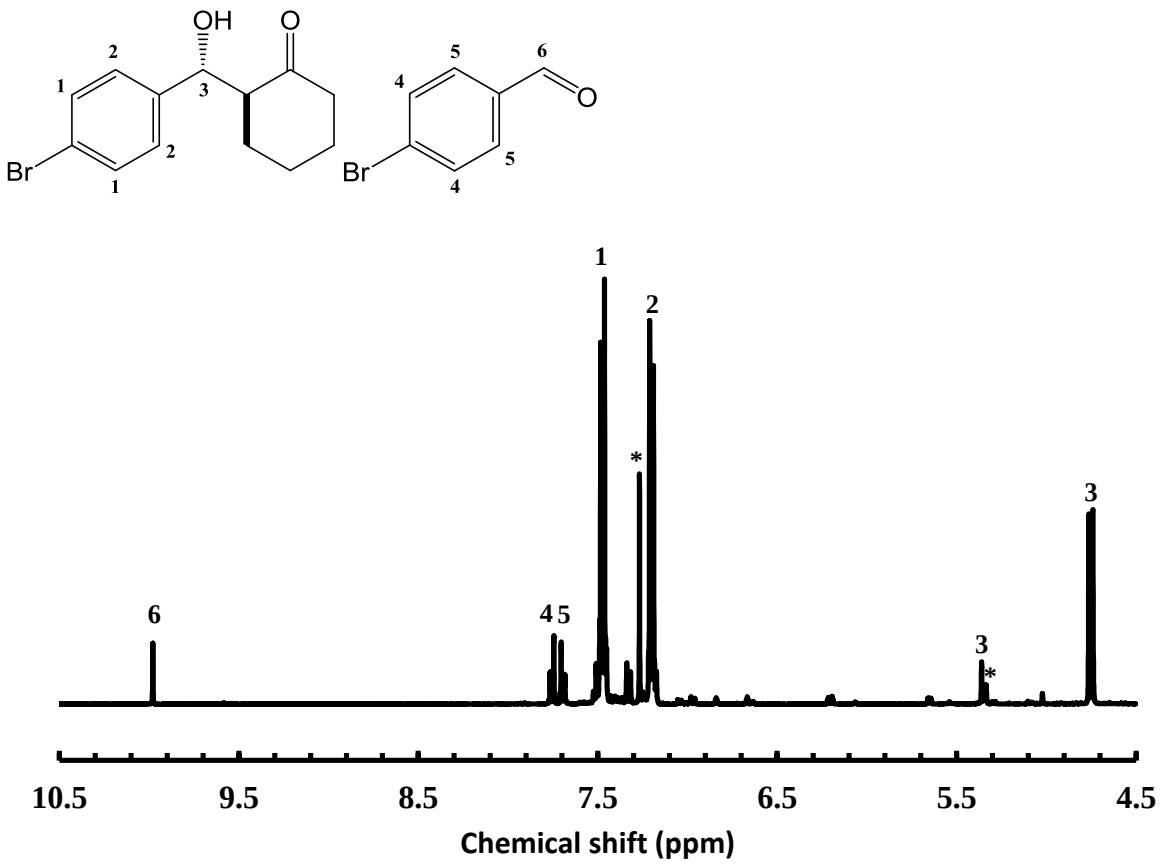

Figure S11 ^{1}H NMR (400 MHz, $CDCl_3$) data of the products from the Aldol reaction in Run 17 (Table 4) with de-protected P4 (DP4) as catalyst.

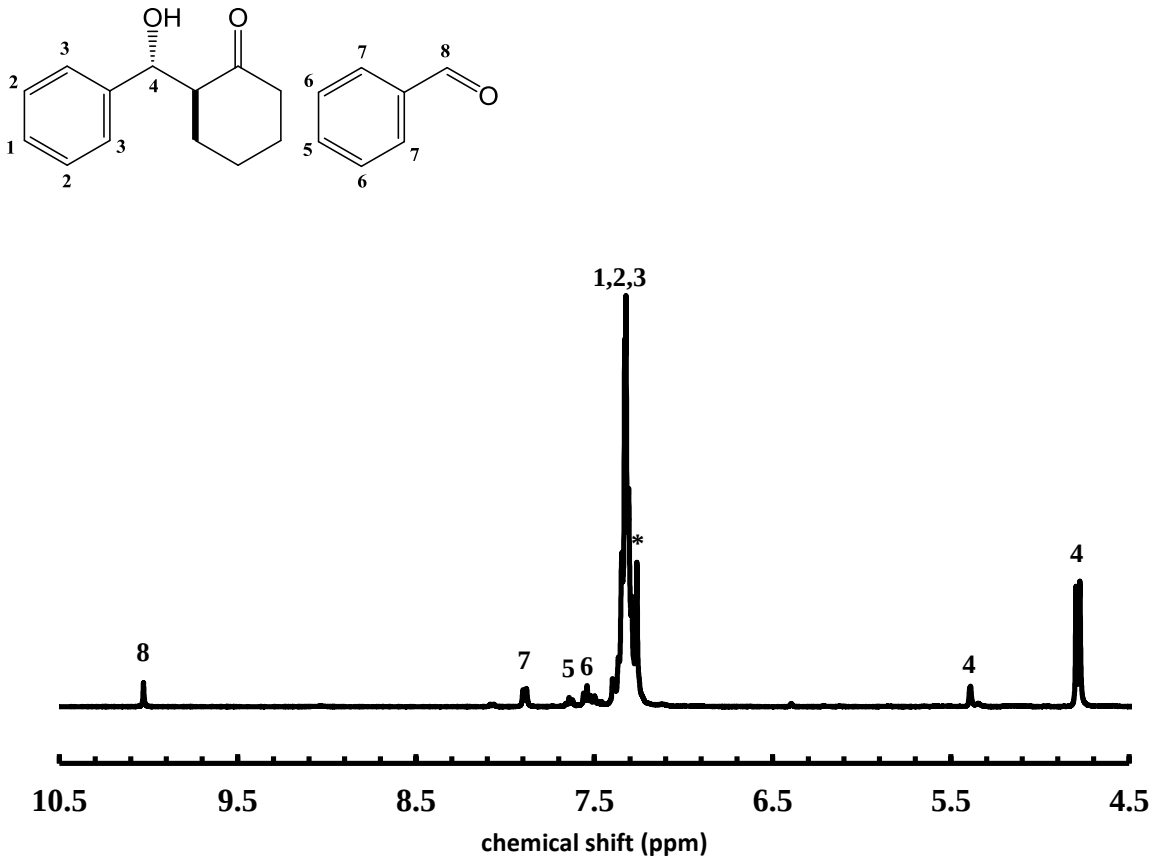

Figure S12 ^{1}H NMR (400 MHz, $CDCl_3$) data of the products from the Aldol reaction in Run 18 (Table 4) with de-protected P4 (DP4) as catalyst.

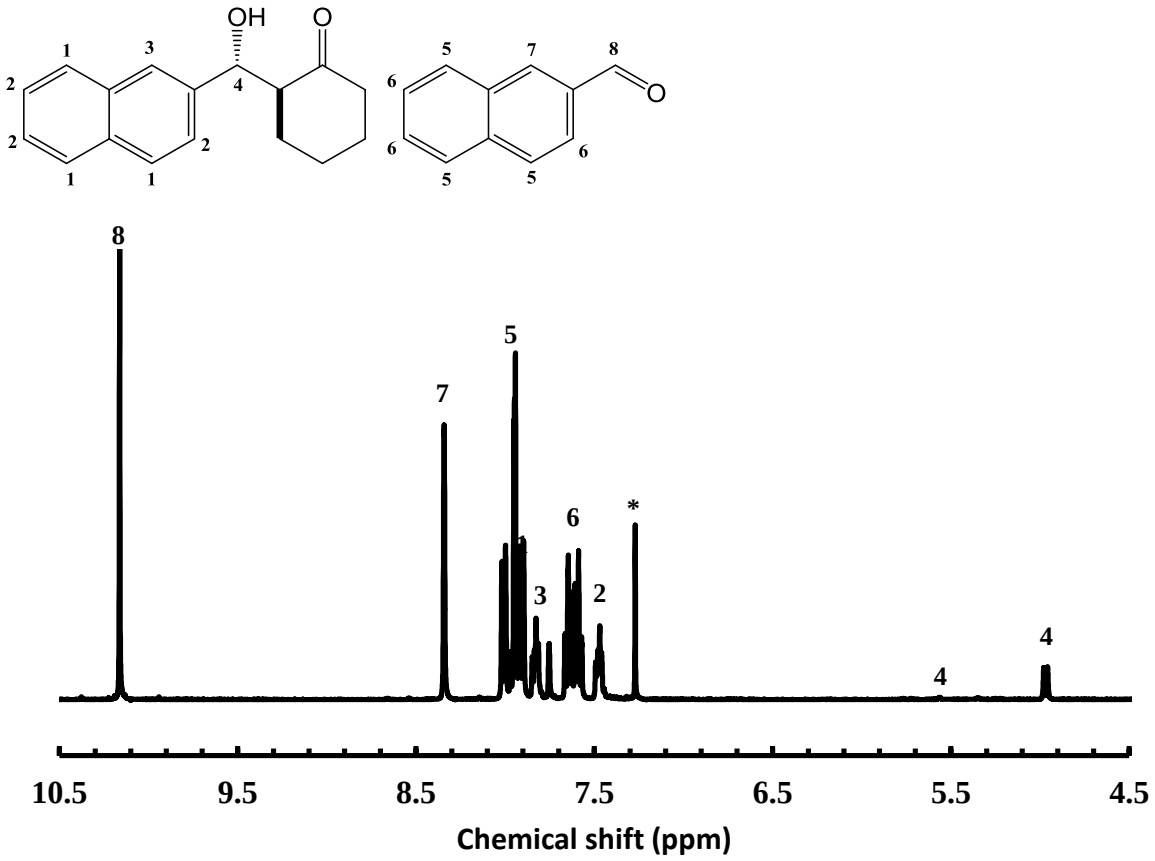

Figure S13 ^{1}H NMR (400 MHz, $CDCl_3$) data of the products from the Aldol reaction in Run 19 (Table 4) with de-protected P4 (DP4) as catalyst.

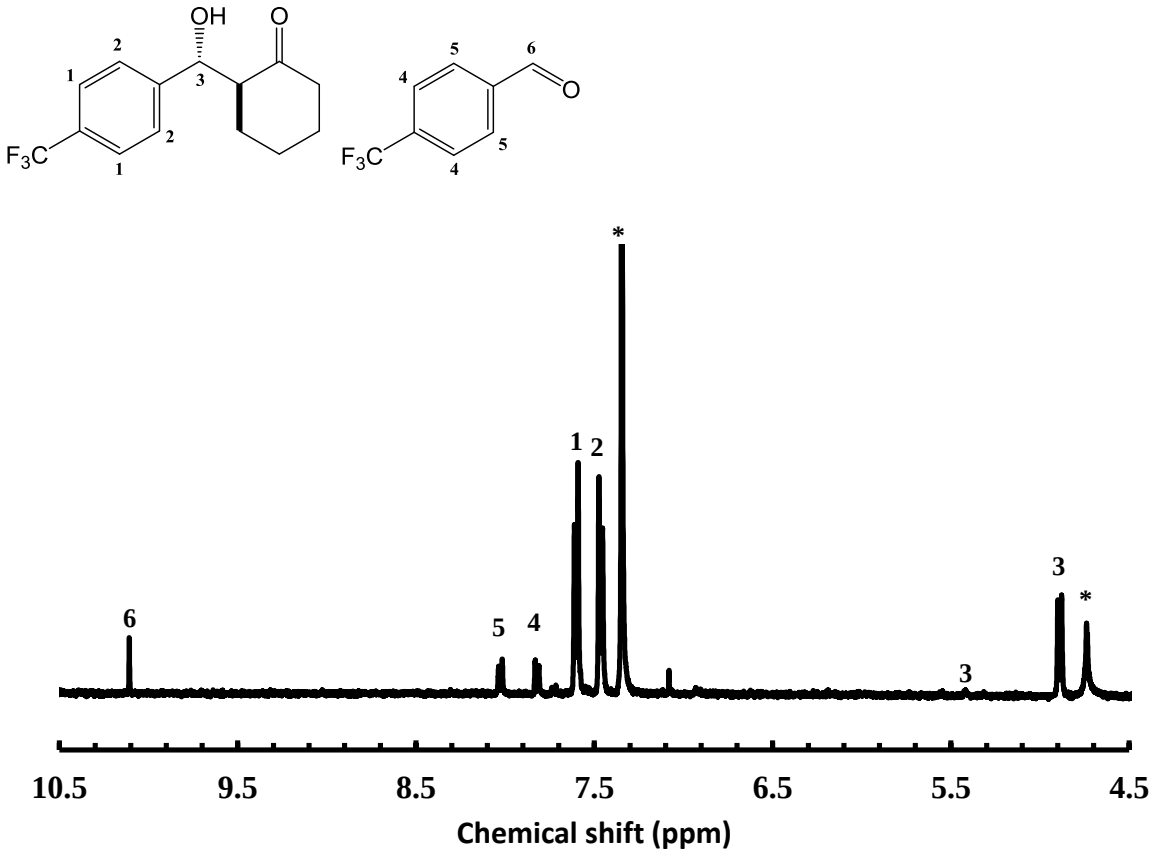

Figure S14 ^{1}H NMR (400 MHz, $CDCl_3$) data of the products from the Aldol reaction in Run 20 (Table 4) with de-protected P4 (DP4) as catalyst.