Supplementary Material (ESI) for Chemical Communications

Polymer-Supported Proline-Decorated Dendrons: Dendritic Effect in Asymmetric Aldol Reaction

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Supporting Information

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware in dry solvents. ^{1}H NMR (200, 400 MHz) and ^{13}C NMR (50.4, 100.8 MHz) spectra were recorded on Bruker AVANCE-200 and AVANCE-400 spectrometers, in $CDCl_3$ or $CDCl_3$/TFA 1:1, using residual $CHCl_3$ (^{1}H, 7.26 ppm), or $CDCl_3$ (^{13}C, 77.0 ppm) as an internal standard. Gel-phase ^{13}C NMR (100.8 MHz) spectra were recorded in benzene-d_6 on Bruker AVANCE-400, using the solvent as an internal standard (126.0 ppm). All HPLC experiments were carried out using Chiralpak-AD or OJ columns on a Jasco instrument, equipped with a UV/VIS detector, with hexanes and ^{i}PrOH as the eluting solvents.

For solid-phase synthesis, yields were determined using the ^{1}H NMR spectra of TFA: $CDCl_3$ (1:1) cleavage solutions with 11mM C_6H_6 (7.36 ppm) as an internal standard. Alcohols were fully or partially converted to TFA esters under these conditions.

Synthesis of (2S,4R)-O-propargyl-N-trityl-4-hydroxyproline methyl ester (**3**)

Sodium hydride (0.14 g, 3.6 mmol, 2 equiv, 60% in oil) and **2** (0.7 g, 1.8 mmol, 1 equiv) were dissolved in THF. The solution was mixed for 0.5 h and propargyl bromide (0.24 ml, 2.2 mmol, 1.2 equiv, 80% in toluene) was added. The mixture was refluxed for 4 h and the reaction completion confirmed by TLC analysis. The solvent was evaporated and the crude residue was extracted with ethyl acetate (30ml) and washed with water (20 ml x 3) and saturated aqueous NH_4Cl solution (20 ml x 2). The organic phase was dried on $MgSO_4$ and the crude material was chromatographed on a silica gel column (1% Et_2NH in 5:95 EtOAc:Hexanes) to give the pure product (0.3 g, 40%) as a white solid, which was dried under vacuum.

^{1}H NMR (200 MHz, $CDCl_3$/TFA 1:1): δ 7.48 (dd, J = 8.6 Hz, J = 1.5 Hz, 6H); 7.20 (m, 9H); 4.34 (m, 1H); 3.89 (d, J = 2.4 Hz, 2H); 3.86 (d, J = 2.0 Hz, 1H); 3.62 (dd, J = 6.6 Hz, J = 10.3 Hz, 1H); 3.54 (s, 3H); 2.63 (dd, J = 6.2 Hz, J = 10.3 Hz, 1H); 2.32 (t, J = 2.4 Hz, 1H); 1.86 (ddd, J = 1.9 Hz, J = 6.5 Hz, J = 12.4 Hz, 1H); 1.12 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$/TFA 1:1): δ 176.2, 143.5, 129.4, 127.9, 126.3, 80.0, 77.0, 75.2, 74.2, 60.7, 57.0, 53.1, 51.6, 36.5.

MS (FAB): Calcd. for $C_{28}H_{28}NO_3$ (MH^+) 426.1, found 426.1.

Proline loading of the catalytic resins (mmol/g):

G0(Pro)	0.23
G1(Pro)	0.64
G2(Pro)	0.20
G3(Pro)	0.48
G1(mono-Pro)	0.27
G2(mono-Pro)	0.16

General procedure for the aldol reaction:

The catalytic resin (0.3 mmol of proline units, 0.3 equiv) was added to a mixture of DMSO:Acetone 4:1 (8 mL : 2 mL). The suspension was stirred for 5 min at room temperature and then the aldehyde (1 mmol, 1 equiv) was added. The suspension was mixed at room temperature for 9 days. Progress of the reaction was followed by TLC analysis. The resin was separated from the solution by filtration and washed with ethyl acetate. Water (10 mL) and saturated aqueous NH_4Cl solution (10 mL) were added to the combined filtrate. The mixture was extracted with ethyl acetate (3 x 10 mL). The organic phase was dried on $MgSO_4$. The solvent was evaporated, and the crude material was analyzed to determine conversion and yield, and then chromatographed on a silica gel column (1:9 EtOAc: Hexanes up to 3:7 EtOAc:Hexanes) to yield the pure product as yellow oil. The product ee was determined by HPLC, using Chiralpak AD (benzaldehyde product) or OJ (4-nitrobenzaldehyde product) columns.