

**Effects of Dendritic Interface on Enantioselective Catalysis
by Polymer-Bound Prolines**

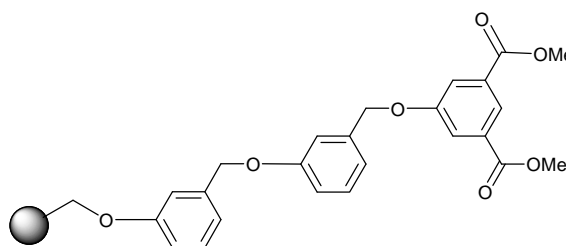
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Supporting Information

Synthesis of hydroxymethyl-terminated precursor for resin 7

Dimethyl 5-hydroxyisophthalate (5 equiv per chloromethyl unit), LiH (2.5 equiv per chloromethyl unit) and TBAI (1.5 equiv per chloromethyl unit) were added to a suspension of (3-(3-chloromethyl)phenoxy)methyl)phenoxy-Wang resin (1 equiv) in DMF. The suspension was heated to 60 °C overnight. The resin was washed with DMF/water, DMF, THF/water, THF, DCM and then dried under vacuum.

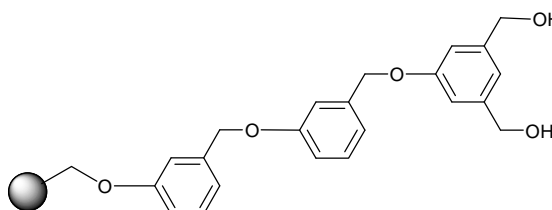


Conversion 100%, yield 94%, loading 0.34 mmol/g.

Following TFA-induced cleavage:

^1H NMR (200 MHz, CDCl_3/TFA 1:1): δ 8.34 (s, 1H); 7.85 (s, 2H); 6.80-7.25 (m, 8H); 5.29 (m, 4H); 4.06 (s, 6H). Partial ^{13}C NMR (100.8 MHz, CDCl_3/TFA 1:1): δ 169.5, 159.5, 158.5, 155.8, 131.9, 131.1, 130.9, 124.8, 122.9, 122.5, 117.0, 115.3, 70.4, 70.5, 54.0.

The product resin [(3-(3-(3,5-bis-carboxymethyl)phenoxy)methyl)phenoxy)methyl)phenoxy-Wang resin] (1 equiv) was suspended in THF (10 ml per 1 g resin) and LiBH_4 (10 equiv per ester unit, 2M solution in THF) and $\text{B}(\text{OMe})_3$ (0.5 equiv per ester unit) were added to the suspension. The mixture was refluxed overnight. The resin was washed with water, an aqueous solution of ammonium chloride/THF, 10% HCl/THF , THF, DCM and then dried under vacuum.



Conversion 100%, yield 100%, loading 0.35 mmol/g.

Following TFA-induced cleavage:

^1H NMR (400 MHz, CDCl_3/TFA 1:1): δ 6.75 -7.20 (m, 11H); 5.39 (s, 4H); 5.29 (s, 4H). Partial ^{13}C NMR (100.8 MHz, CDCl_3/TFA 1:1): δ 155.3, 136.5, 131.1, 130.9, 123.1, 122.9, 122.3, 116.9, 71.7, 70.6, 69.7.

General procedure for the Mannich reaction:

The catalytic resin (0.3 mmol, 0.3 equiv) was added to a mixture of DMSO:hydroxyacetone 4:1 (27 mmol, 27 equiv of the hydroxyacetone). The suspension was stirred for 5 min at room temperature and then the benzaldehyde (1 mmol, 1 equiv) and *p*-anisidine (1.1 mmol, 1.1 equiv) were added. The suspension was mixed at room temperature for 2 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 2:3 EtOAc:Hexanes) to yield the pure products as a yellow oil. The major product ee was determined by HPLC, using Chiralpak AD column.

The products were identified according to their ^1H NMR spectra.¹

¹ B. List, P. Pojarliev, W. T. Biller and H. J. Martin, *J. Am. Chem. Soc.*, 2002, **124**, 827.