Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary information:

Efficient synthesis of supported proline catalysts for asymmetric aldol reaction

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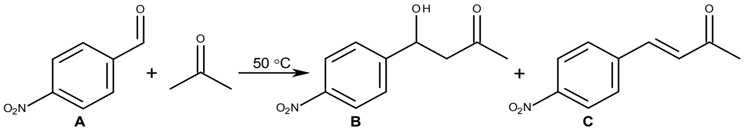
Test reaction:



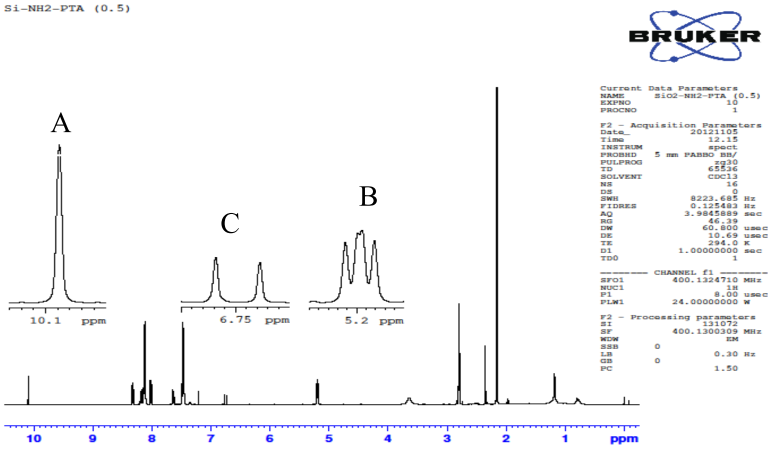


Figure 1. NMR spectrum of aldol condensation reactants and products.

A: 4-nitrobenzaldehyde: 1H-NMR (400 MHz, CDC13)= 8.01 (2H, d, J=8.56, Ar-H-$_{\text{ortho}}$), 8.32 (2H, d, J=8.56 Ar-H-$_{\text{meta}}$), **10.09 (1H, s).**

B: 4-hydroxy-4-(p-nitrophenyl)butan-2-one: 1H-NMR (400 MHz, CDC13)= 8.11 (2H, d, J=8.64, Ar-H-$_{\text{ortho}}$), 7.47 (2H, d, J=8.56, Ar-H-$_{\text{meta}}$), **5.20 (1H, q, J=4.05, -CH-),** 3.66 (1H, d, J=12.04, -OH), 2.80 (2H, d, J=3.12, -CH_2-), 2.16 (3H, s, -CH_3).

C: 4-(4-nitrophenyl)but-3-en-2-one: 1H-NMR (400 MHz, CDC13)= 8.17 (2H, d, J=8.64, Ar-H-ortho), 7.64 (2H, d, J=8.64, Ar-H-$_{\text{meta}}$), 7.47 (1H, d, J=8.56, C(4)H-), **6.75 (1H, d, J=16.37, C(3)H-),** 2.35 (3H, s, CH_3).

$$\mathbf{B}(\%) = \frac{H(B)}{H(A) + H(B) + H(C)}$$

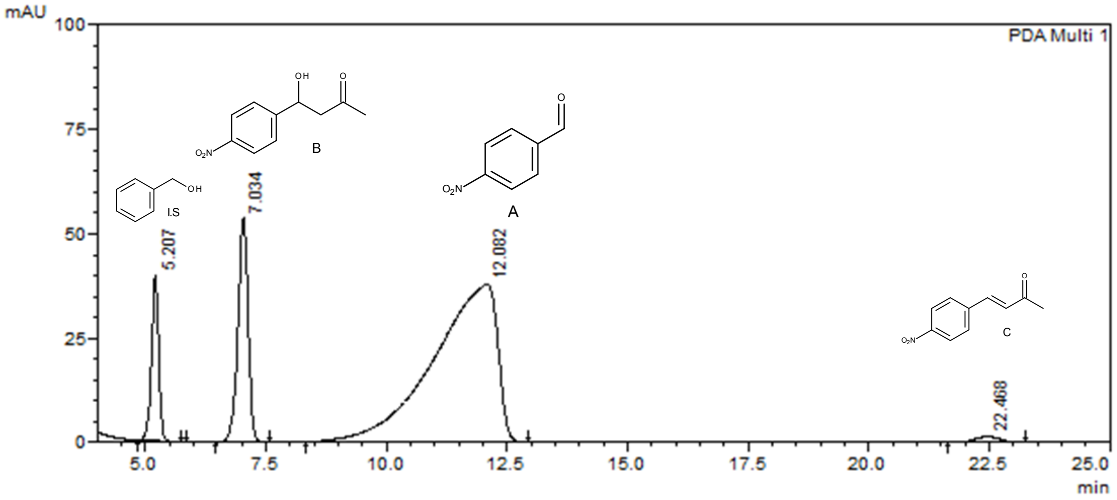


Figure 2. Standard HPLC chromatogram of reactants and products of cross-aldol reaction between 4-nitrobenzaldehyde and acetone plus the internal standard (I.S).

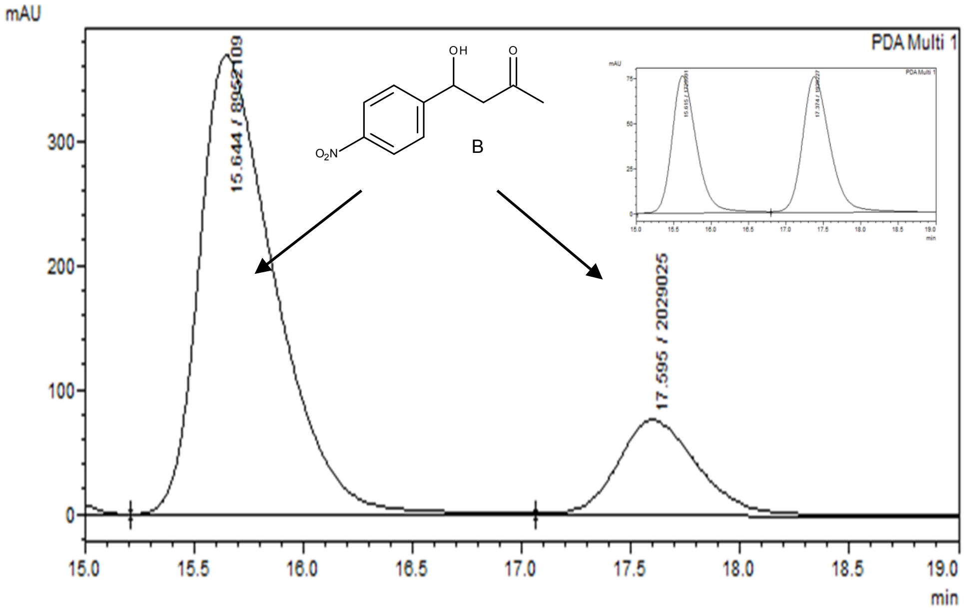


Figure 3. Chiral HPLC chromatogram of hydroxyl aldol product (B) from a cross-aldol reaction between 4-nitrobenzaldehyde and acetone in presence of SiO_2-Pr(H). In the top right is a standard HPLC chromatogram of B as racemic mixture.

Enantiomeric excess (ee%) was calculated from the chromatographic data by the following equation:

$$(ee\%) = \left[\frac{Peak\ area\ 1 - \ Peak\ area\ 2}{Peak\ area\ 1\ \ +\ \ Peak\ area\ 2}\right] x\ 100$$

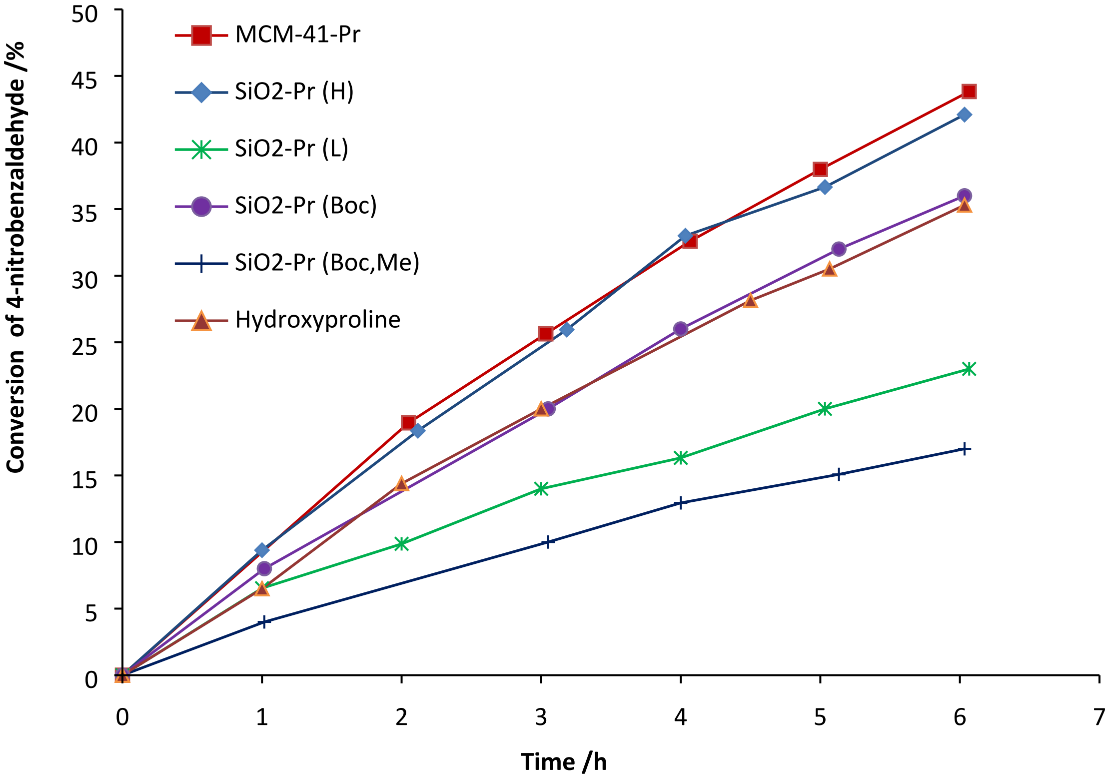


Figure 4. Conversion of 4-nitrobenzaldehyde in aldol reaction with time. Reaction conditions: 4-nitrobenzaldehyde (76 mg, 1 mmol), acetone (10 mL), benzyl alcohol (0.1 mL) as internal standard, solid catalyst (0.05 g), 50 °C. Where hydroxyproline has been used in homogeneous solution 0.019 mmol was added, which corresponds to between three and five times as much proline as was present on the supported proline catalysts.