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SUPPORTING INFORMATION

Title: Polymer-Immobilized Pyrrolidine-Based Chiral Ionic Liquids as Recyclable Organocatalysts for Asymmetric Michael Additions to Nitrostyrenes under Solvent-Free Reaction Conditions
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Ref. No.: O200701037

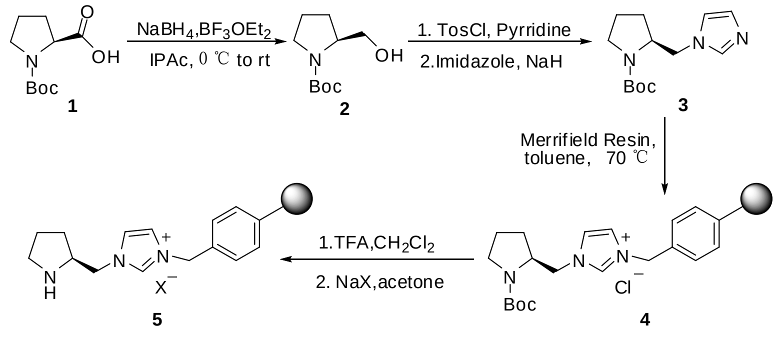
Experimental Section

General Remarks

Melting points were recorded on a WRS-2B melting point apparatus and were uncorrected. All ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 300 MHz FT-NMR spectrometer (300 and 75 MHz, for ^{1}H and ^{13}C NMR, respectively). Chemical shifts were given as δ value with reference to tetramethylsilane (TMS) as the internal standard. HPLC analysis was performed on Agilent 1100 using a ChiralPak AD-H or AS-H column purchased from Daicel Chemical Industries, Ltd. Products were purified by flash column chromatography on 230–400 mesh silica gel, SiO_2.

The chemicals were purchased from commercial suppliers (Aldrich, USA and Shanghai Chemical Company, China) and were used without purification prior to use. All reactions unless otherwise noted were carried out directly under air. Nitroolefins were prepared according to literature procedures.[1, 2] (*S*)-*N*-(*tert*-butoxycarbonyl)prolinol (**2**) and (*S*)-*N*-(*tert*-butoxycarbonyl)prolinol *p*-toluenesulfonate were prepared according to the literature.[3]

Preparation of polymer immobilized pyrrolidine-based chiral ionic liquids



5a: X = Cl; **5b:** X = BF_4; **5c**: X = PF_6

Preparation of 3: Imidazole (680 mg, 10 mmol) and NaH (480 mg, 60% of purity, 12 mmol) were added in 30 mL of anhydrous acetonitrile and stirred at room temperature for 0.5 h, then **2** (1.78 g, 5 mmol) was added to the solution. The mixture was heated to reflux for 5 h under nitrogen atmosphere and then cooled to room temperature. Solvent was removed under *vacuo* and the residue was diluted with 10 mL of water. The resulted mixture was extracted with chloroform (20 mL×3). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatograph on silica gel (eluant, EtOAc:EtOH = 5:1, V/V) to give the desired product **3** as colorless crystal solid (1.08 g, 86% yield).

Preparation of 5: Under nitrogen atmosphere, **3** (0.5 g, 2 mmol) and Merrifield Resin (1.5 g, 2% DBV, loading 2.5 mmol/g active Cl from Aldrich Company) were mixed in toluene (15 mL). The solution was kept at 70 ^oC and stirred for 24 h, then the solution was filtered and the solid was washed with chloroform, methanol and ethyl ether, respectively, and dried under *vacuo* at 60 ^oC, 1.46 g of **4** as pale yellow solid was obtained. The *Boc* protective group in obtained pale yellow solid (**4**) was deprotected by using CF_3COOH/CH_2Cl_2 solution (10 mL, V/V = 1:1) with shaking at room temperature for 3 h, and the solution was filtered and subsequently neutralized with NEt_3 (5 mL). The solution was filtered and the solid was washed with dichloromethane, methanol and ethyl ether, respectively, and dried under *vacuo* at room temperature, 1.32 g of **5a** as yellow solid was obtained. The loading of the polymer immobilized pyrrolidine-based chiral ionic liquid (**5a**) was readily quantified *via* CHN microanalysis and found to be 1.02 mmol•g^{-1} of pyrrolidine-based imidazole. The **5b** and **5c** were prepared by the exchange of Br^- for BF_4^- and PF_6^- by using $NaBF_4$ and KPF_6, respectively in co-solvent of acetonitrile and acetone (V/V = 9:1).

Representative experimental procedure for Michael addition reaction

The polymer immobilized pyrrolidine-based chiral ionic liquid **5a** (50 mg, contains pyrrolidine-based organocatalyst 0.05 mmol of active units), *trans*-β-nitrostyrene (75 mg, 0.5 mmol), cyclohexanone (2.0 mmol) were added to a round-bottom flask, the mixture was stirred at room temperature for 24 h. After completed the reaction, the reaction mixture was vacuum filtered using a sintered glass funnel and washed with ethyl acetate

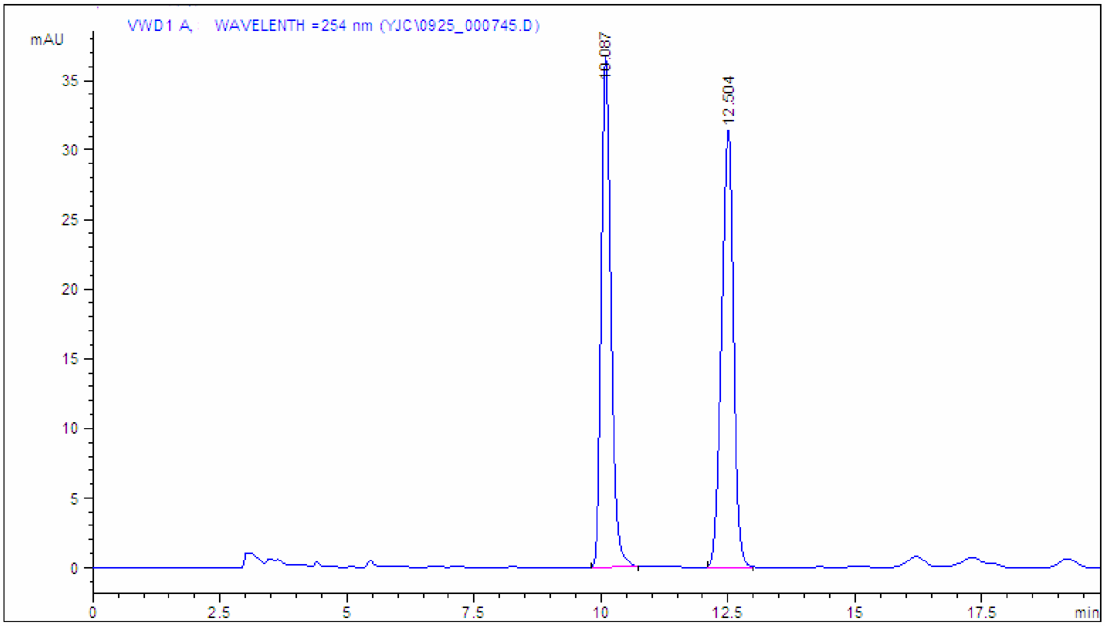
(3 mL×3). The combined organics were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by flash chromatography on silica gel by using hexane/ethyl acetate = 3:1 (V/V) as eluent to give the corresponding asymmetric Michael addition product γ-nitroketone (119.8 mg) as a colorless crystal solid (97% yield) with >99:1 dr (*syn/anti*) and 98% ee (determined by HPLC on a chiralpak AD-H column, $\lambda = 254$ nm, *i*-PrOH/hexane (10:90) as eluent, flow rate = 1.0 mL·min^{-1}, $t_{minor} = 10.1$ min, $t_{major} = 13.8$ min). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.34–7.26 (m, 3H), 7.17 (d, *J* = 6.8 Hz, 2H), 4.96 (dd, *J* = 4.6, 12.5 Hz, 1H), 4.63 (dd, *J* = 9.6, 12.4 Hz, 1H), 3.76 (dt, *J* = 4.5, 9.8 Hz, 1H), 2.68 (ddd, *J* = 8.2, 8.5, 11.8 Hz, 1H), 2.52–2.33 (m, 2H), 2.09–2.04 (m, 1H), 1.79–1.53 (m, 4H), 1.28–1.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 211.9, 137.7, 128.8, 128.1, 127.7, 78.8, 52.4, 43.8, 42.7, 33.2, 28.5, 25.0.

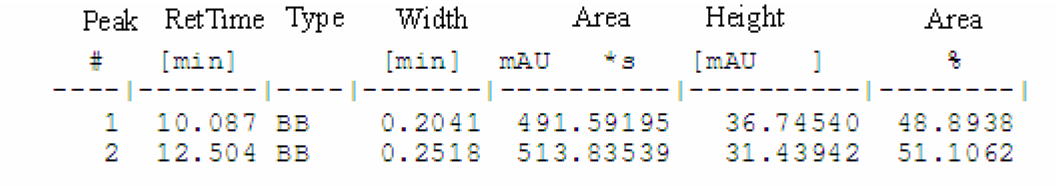
[1] For the preparation of aryl nitroolefins: Jang, Y.-J.; Shih, Y.-K.; Liu, J.-Y.; Kuo, W.-Y.; Yao, C.-F. *Chem. Eur. J.* **2003**, *9*, 2123–2128.

[2] For the preparation of alkyl nitroolefines: Kumaran, G.; Kulkarni, G. H. *Synthesis* **1995**, 1545–1548.

[3] (a) D. Zhao, J. T. Kuethe, M. Journet, Z. Peng, G. R. Humphrey, *J. Org. Chem.* **2006**, *71*, 9111–9114; (b) G. Bartoli, M. Bosco, A. Giuliani, T. Mecozzi, L. Sambri, E. Torregiani, E. Marcantoni, *J. Org. Chem.* **2002**, *67*, 4336–4338.

HPLC Diagram of Racemic Standard Samples:





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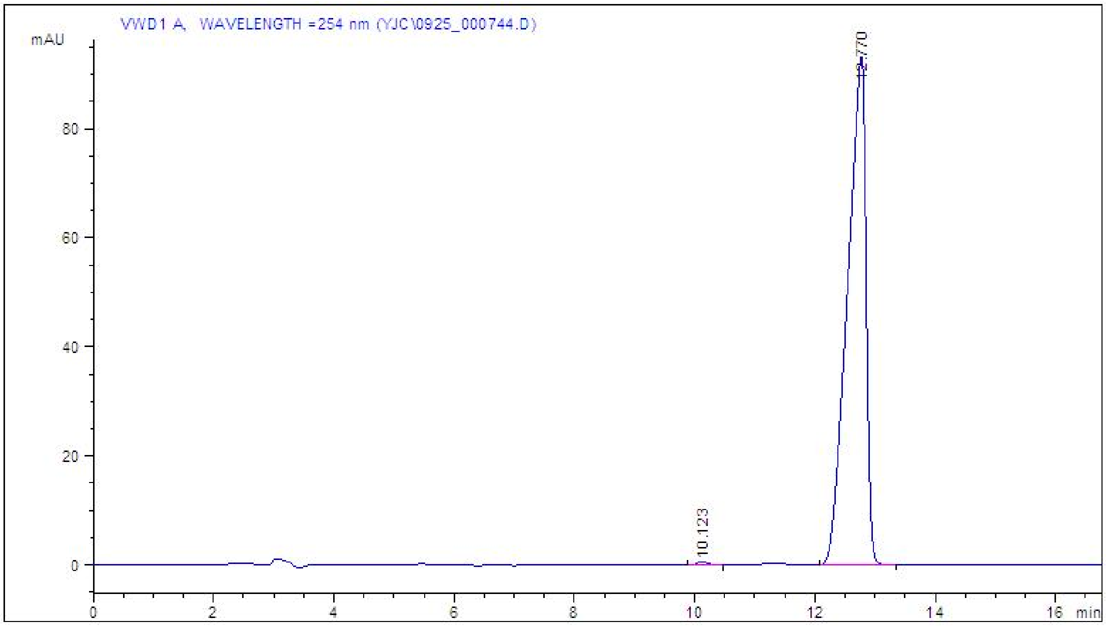

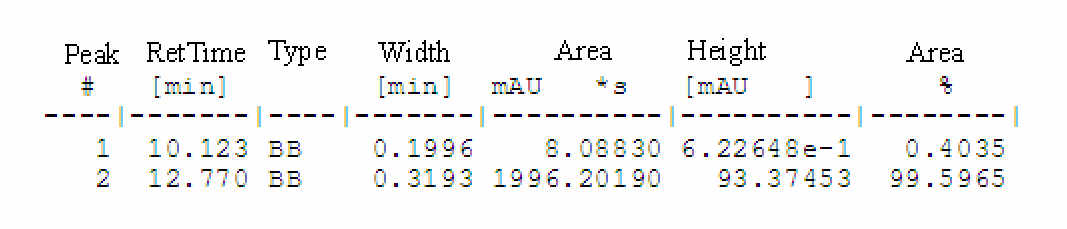

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Peak  RetTime  Type   Width        Area       Height        Area
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   2  12.770 BB      0.3193 1996.20190   93.37453  99.5965
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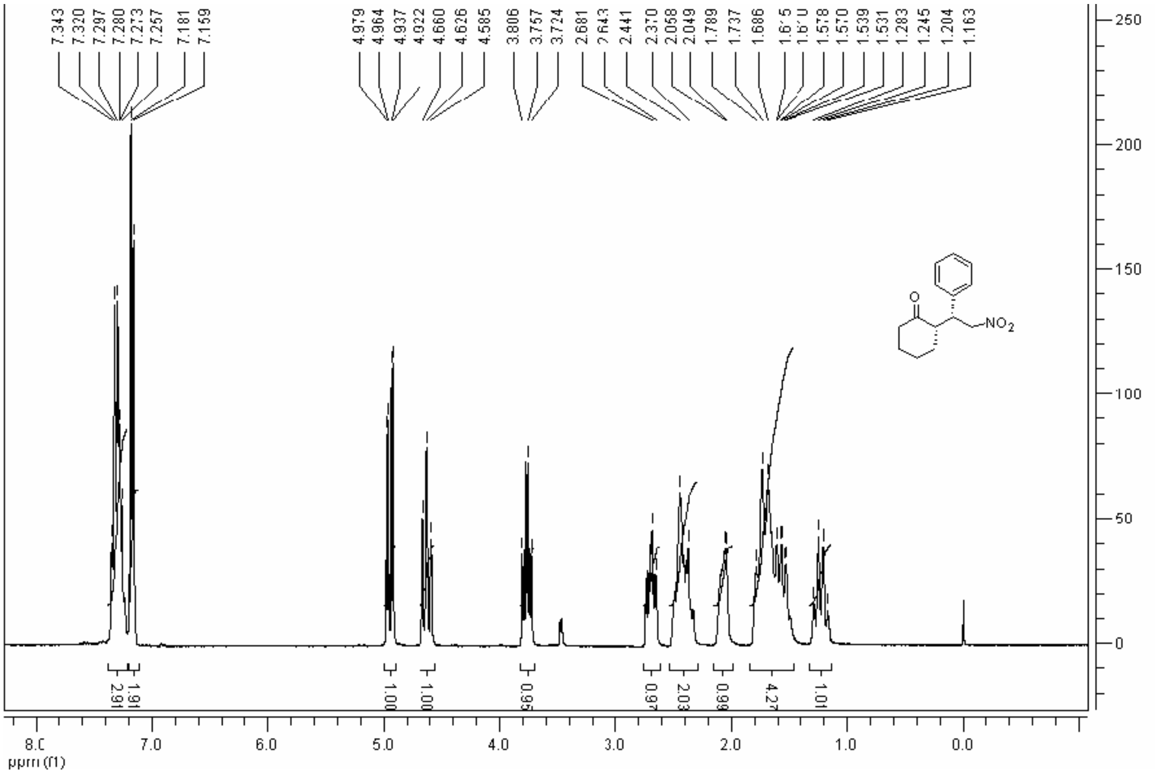
^{1}H NMR



^{13}C NMR