

Short communication

POSS supported C₂-symmetric bisprolinamide as a recyclable chiral catalyst for asymmetric Aldol reaction



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ABSTRACT

POSS supported prolinamide-type catalysts were synthesized and used to catalyze asymmetric Aldol reactions between unmodified ketones and aldehydes. Immobilization of the prolinamide-type catalysts onto POSS resulted in good yields and improved diastereoselectivity as well as enantioselectivity. The POSS-supported catalysts were recycled simply by precipitation and filtration, and could be reused in five consecutive cycles without losing its effectiveness.

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1. Introduction

The asymmetric Aldol reaction is one of the most commonly used C–C bond forming reactions. Up to now, a number of outstanding organocatalysts have been developed for this reaction [1–3]. Most organocatalysts are used in homogeneous form, which often makes them difficult to recycle and reused after a reaction. A more facile method is to anchor the homogeneous organocatalysts onto soluble supports, which allows the reaction to be operated under homogeneous catalysis conditions, and the simple recovery and recycle of the catalyst from the product [4–10].

Polyhedral oligomeric silsesquioxanes (POSS) is a new class of organic–inorganic hybrid materials with the advantages of thermally robust cage structure, nanoscale dimension and multi-functionality [11]. Furthermore, it has good solubility in conventional solvents. Thus, POSS, as a new type support, can immobilize small molecular catalysts for homogeneous reactions [12–16].

The C₂-symmetric bisprolinamide is one of the most popular and efficient catalysts for asymmetric Aldol reaction [17–20], which has two prolinamide moieties and was found to be an excellent catalyst with more than doubled reactivity and better asymmetric induction than its monoprolinamide counterpart. However, immobilization of the C₂-symmetric bisprolinamide onto supports for asymmetric Aldol reaction is still absent.

Recently, our group has successfully synthesized POSS supported (S)- α,α -diphenylprolinol trimethylsilyl ether and used it for the

catalysis of the asymmetric Michael reaction [21]. Based on this endeavor, in an effort to provide an efficient, operationally simple and recyclable catalyst, we designed and synthesized POSS supported C₂-symmetric bisprolinamide chiral catalysts for asymmetric Aldol reactions (Scheme 1).

2. Experimental

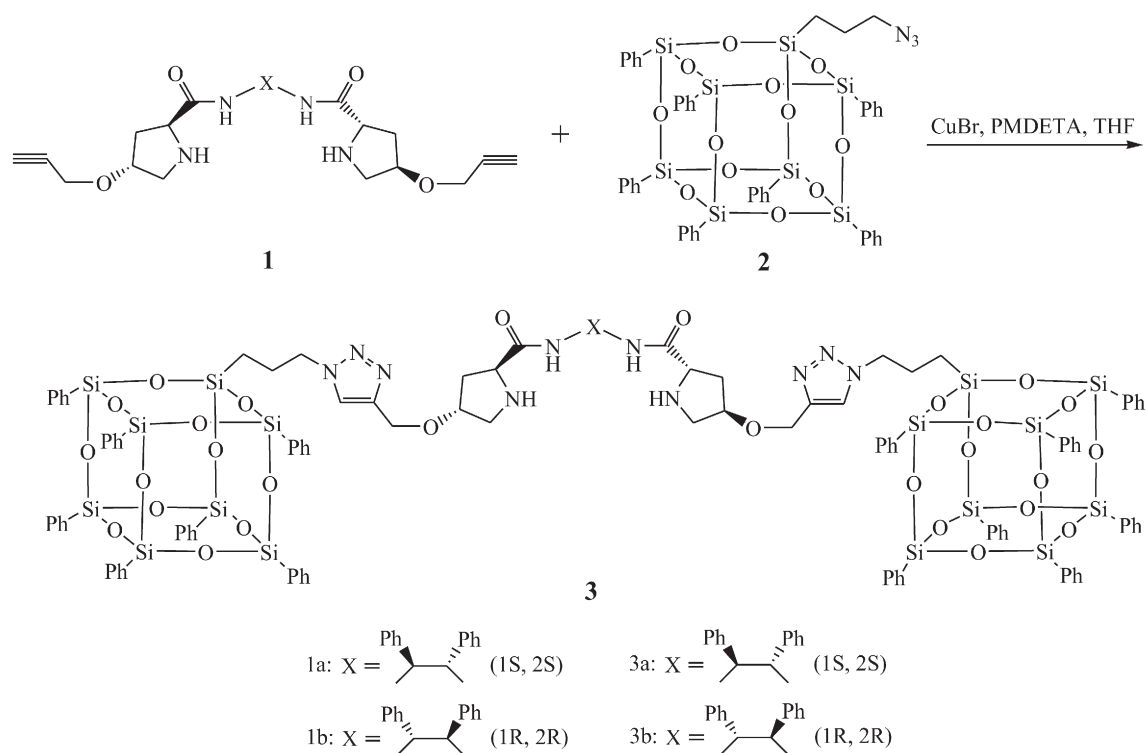
2.1. General

NMR spectra were recorded on a WIPM 400 spectrometer (¹H at 400 MHz, ¹³C at 100 MHz) and a Varian Unity Inova 600 spectrometer (¹³C at 150 MHz, ²⁹Si NMR at 79.5 MHz). IR spectra were recorded on an IR-spectrum one (PE) spectrometer. Optical rotations were measured using an Autopol IV-T Automatic Polarimeter. HPLC were performed with a Dionex UltiMate 3000 equipped with a chiral column (chiralpak AD-H and AS-H) using *i*-PrOH/*n*-hexane as an eluent. A UV detector (UVD-3000) was used for peak detection. Elemental analyses were operated on a Vario MICRO cube Elemental analyzer.

2.2. Synthesis of POSS-supported chiral catalysts

3-azidopropylheptaphenyl POSS **2** (3.12 g, 3.0 mmol), C₂-symmetric bisprolinamide **1** (0.64 g, 1.25 mmol) and dry THF (40 mL) were charged to a three-neck round-bottomed flask. Then CuBr (71 mg, 0.5 mmol) and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (104 μ L, 0.5 mmol) were added under N₂. The reaction was performed at room temperature for 24 h and dropped into dilute HCl solution (1 wt.%, 30 mL). The resultant mixture was extracted with CH₂Cl₂ (25 mL \times 3)

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Scheme 1. Synthesis of POSS supported the C_2 -symmetric bisprolinamide chiral catalyst.

and dried with anhydrous MgSO_4 . Then the solvent was removed and the residue was purified by flash chromatography with 1:20 methanol: dichloromethane mixture to give the desired product as a white solid (2.76 g, 85%).

3a: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.83 (t, $J = 8.0$ Hz, 4 H), 1.82 (m, 2 H), 2.08 (m, 4 H), 2.33 (m, 4 H), 2.65 (m, 2 H), 3.10 (m, 1 H), 3.89 (m, 2 H), 4.0 (m, 2 H), 4.25 (t, $J = 8.0$ Hz, 4 H), 4.45 (s, 4 H), 5.21 (s, 2 H), 7.07–7.21 (m, 12 H), 7.33–7.44 (m, 47 H), 7.74 (m, 30 H), 8.51 (2 H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3): δ 9.10, 24.45, 36.57, 52.35, 52.60, 58.77, 60.18, 62.27, 80.66, 122.77, 127.73, 128.37, 128.75, 130.26, 131.25, 134.49, 135.79, 139.13, 144.98, 174.92; $^{29}\text{Si NMR}$ (79.5 MHz, CDCl_3): δ -64.06, -76.24, -76.56; IR (KBr): ν 3302, 3073, 1667, 1594, 1514, 1431, 1134, 1029, 998, 774, 697, 501 cm^{-1} ; elemental analyses ($\text{C}_{120}\text{H}_{116}\text{N}_{10}\text{O}_{28}\text{Si}_{16}$): calcd. C 55.53, H 4.50, N 5.39; found C 55.70, H 4.73, N 5.22; $[\alpha]_D^{21} = -3.5$ (c 0.1, CH_2Cl_2).

3b: $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 0.84 (t, $J = 8.0$ Hz, 4 H), 1.80 (m, 2 H), 2.09 (m, 4 H), 2.37 (m, 2 H), 2.76 (m, 3 H), 3.16 (m, 2 H), 3.85 (m, 2 H), 4.12 (m, 3 H), 4.25 (t, $J = 8.0$ Hz, 4 H), 4.49 (s, 4 H), 5.27 (s, 2 H), 7.11–7.17 (m, 16 H), 7.34–7.39 (m, 44 H), 7.75 (m, 28 H), 8.45 (2 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 8.84, 23.99, 36.42, 52.13, 52.42, 57.93, 59.87, 62.08, 80.69, 122.56, 127.45, 127.66, 128.00, 130.01, 130.11, 130.96, 134.21, 138.87, 144.64, 174.24; $^{29}\text{Si NMR}$ (79.5 MHz, CDCl_3): δ -64.17, -76.35, -76.67; IR (KBr): ν 3290, 3043, 1667, 1590, 1514, 1430, 1134, 1029, 998, 744, 697, 496 cm^{-1} ; elemental analyses ($\text{C}_{120}\text{H}_{116}\text{N}_{10}\text{O}_{28}\text{Si}_{16}$): calcd. C 55.53, H 4.50, N 5.39; found C 55.74, H 4.81, N 5.46; $[\alpha]_D^{21} = -9.8$ (c 0.1, CH_2Cl_2).

2.3. General procedure for asymmetric Aldol reactions

To a mixture of aldehyde (0.5 mmol) and acetone (2.5 mmol) in DMF/water (9/1, 1 mL), $\text{Sn}(\text{OTf})_2$ (0.025 mmol) and the POSS-supported catalyst (0.025 mmol) were added. The mixture was stirred at room temperature for 20 h. After precipitation from methyl *tert*-butyl ether (MTBE) (10 mL), the suspension was filtered and washed with MTBE to obtain recovered POSS supported catalyst. TLC ($\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2 = 1:20$) analysis showed that the catalyst was free from any

reactants and by-products. The filtrate was concentrated and purified by flash column chromatography to give the product. The enantiomeric excess values (*ee*) were determined by HPLC on a chiral phase. Diastereoselectivity (*anti/syn*) was determined by HPLC and $^1\text{H NMR}$ analysis of the isolated diastereomers.

3. Results and discussion

3.1. Preparation of POSS-supported catalyst

The synthetic routine of POSS supported chiral catalyst was described in Scheme 1. The intermediate 3-azidopropylheptaphenyl POSS **2** [22] and C_2 -symmetric bisprolinamide **1** [23–24] were prepared according to the established procedure. The CuAAC reaction between **2** and **1a** or **1b** was performed to give supported catalyst **3a** or **3b**. The supported catalyst is soluble in common organic solvents, such as DMF, CHCl_3 , CH_2Cl_2 , THF, but insoluble in Et_2O , MTBE and H_2O . This solubility allowed a simple recovery of the catalyst when precipitated with a poor solvent.

3.2. Optimizing of the reaction conditions

The asymmetric Aldol reactions between aldehyde and acetone is used to evaluate the catalytic reactivity of the catalyst. For comparison purpose, the reactions between 4-nitrobenzaldehyde and acetone catalyzed by **3a** or **3b** under the same condition were carried out and the results indicated that **3a** showed a higher enantioselectivity than **3b** (Table 1, entries 1–2). Therefore, **3a** was chosen as the catalyst to further optimize the reaction conditions.

Initially, a screening of the solvents was investigated (entries 1, 3–5). The results showed that DMF was the best solvent for this reaction to give the products with high *ee* values and good yields. The effect of different organic or Lewis acid co-catalyst on reactivity and selectivity was also examined (entries 1, 6–11). Tin(II) trifluoromethanesulfonate turned out to be the best cocatalyst, which provided good yields with excellent enantioselectivity. The co-catalyst acts as a Lewis acid in

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