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Ionic-liquid-supported organocatalyst for the enantioselective Michael addition of ketones to nitroolefins

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Abstract—Ionic-liquid-supported triazole-pyrrolidine **2**, for the direct asymmetric Michael reaction was successfully synthesized. The supported catalyst demonstrated good activity and high enantioselectivity in the addition of cyclohexanone to nitroolefins. Furthermore, the supported catalyst can be readily recovered and reused four times without significant loss of catalytic activity.

1. Introduction

Since the discovery of the synthetic potential of chiral pyrrolidines and imidazolines as highly enantioselective organocatalysts by List et al. and MacMillan et al.,[1] amine catalysis using proline or related catalysts has been successfully applied to a long list of synthetic transformations.[2] Although excellent results were obtained, it is a protocol that in many cases, required a high loading of catalysts (normally in 10–20 mol %) to achieve an acceptable yield. It is therefore of interest to develop efficient approaches for the recovery and reuse of asymmetric organocatalysts, which will make the reactions economical and environmentally friendly. Undoubtedly, the immobilization of catalysts onto different platforms is one of the promising processes and displays some advantage since it can allow simple product separation while offering the possibility of catalyst recycling as an additional bonus.[3] Up to now, several papers have been reported describing how to immobilize the asymmetric organocatalysts on different supports.[4]

Room-temperature ionic liquids (RTILs), because of their special characteristics, have been not only accepted as excellent media[5] but also increasingly applied in other areas of organic synthesis.[6] One of the more recent developments is the use of RTILs as homogeneous supports for organic synthesis.[7] Impressive progress in ionic-liquid-supported (IL-supported) catalysis has been achieved, but a very few highly efficient anchored organocatalysts for asymmetric reactions have been reported. Luo et al. and Xu et al. independently reported ionic-liquid-type catalysts with highly efficient potential in the asymmetric Michael reaction.[8] The ionic-liquid moiety, in the proximity of the active site, not only kept its unique properties but also influenced shielding of the cyclic five-membered secondary amine, so authors called them functional ionic liquids but not IL-supported catalysts. Miao and Chan first reported an ionic-liquid-supported organocatalyst in asymmetric organic synthesis.[4f] They attached (2*S*,4*R*)-4-hydroxyproline to ionic liquids to successfully catalyze a direct aldol reaction. The supported catalyst can be easily recycled and reused with the same efficacy for four cycles.

The organocatalytic asymmetric Michael reaction is one of the most powerful and efficient methods for the formation of carbon–carbon bond to provide enantiomerically enriched nitroalkanes.[9] During the last year, our group[10] and Cheng's[11] independently developed a series of chiral pyrrolidine-triazoles **1** (Fig. 1) to successfully catalyze the direct Michael addition of ketones under different conditions. The research showed that the catalyst gave one of the best outcomes in terms of both activity and selectivity when R was phenyl. Our current interest in the application of RTILs in organic synthesis led us to explore IL-supported triazole-pyrrolidine **2** (Fig. 1) as a recyclable and

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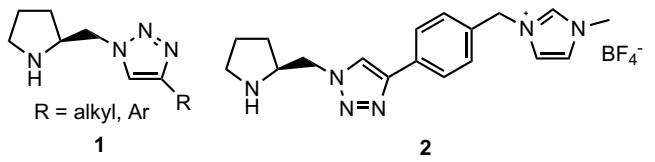


Figure 1.

reusable catalyst.[12] Herein, we wish to report the synthesis of IL-supported catalyst **2** and the application in the Michael reaction. Following research showed that this IL-supported catalyst remained good catalytic activity and enantioselectivity for the addition of ketones to nitroolefins, and after simple operations, the catalyst **2** can be recycled four times without a substantial loss in the enantioselectivity or yield.

2. Results and discussion

The synthetic procedure for making the IL-supported catalyst **2** is showed in Fig. 2. Compound **4** was prepared from Boc-*S*-proline in four simple steps.[11,13] Using (4-bromophenyl)-methanol as starting material, compound **5** was synthesized via a Sonogashira coupling reaction and decomposition with KOH. Then treating **5** with $SOCl_2$/pyridine gave **6**. Introduction of the imidazolium moiety with 1-methylimidazole to **6** was achieved to give the quaternary salt **7**. The desired compound **2** was provided smoothly via the 1,3-dipolar cycloaddition[14] of **4** and **7** and then anion-exchange.

The catalytic activity of the IL-supported organocatalyst **2** was evaluated in the Michael addition reaction of cyclohexanone to β-nitrostyrene at room temperature, and the results are summarized in Table 1. Our previous works demonstrated that catalyst **1** showed good catalytic activity and stereoselectivity without any additives.[10] Therefore, we initially attempted the Michael reaction in an aprotic polar solvent, DMSO. However, β-nitrostyrene could not be completely converted and a low yield was observed in this homogenous system (Table 1, entry 1). Then, changing the solvent to $CHCl_3$, H_2O, or testing under solvent-free condition, the reaction gave similar yields (entries 2–4). Interestingly, the addition of 5 mol % of TFA greatly enhanced the reaction rate, and good yields (90–97%) and high enantioselectivities (88–94%) were achieved (Table 1, entries 5–8). Under solvent-free conditions, a good yield and the best ee were observed. When decreased the loading of the catalyst to 10 mol % or reduced **8** to 10 equiv, a similar diastereoselectivity and enantioselectivity but lower yield was afforded (Table 1, entries 9 and 10). Other acids were also investigated, but the results showed some decrease compared to the TFA's (Table 1, entries 11 and 12), especially in the yields. Under solvent-free conditions, the system is homogenous.

With the optimal conditions in hand, the scope of the Michael reaction with cyclohexanone was briefly explored to several β-nitroolefins (Table 2). All reactions were performed at ambient temperature in the presence of 15 mol % of **2** and 5 mol % TFA within 48 h. As shown in Table 2, all β-nitroolefins are good acceptors to give the desired *syn* adducts in good yields with high diastereoselectivity and enantioselectivity. It should be noted that the reaction of 3,4-methylenedioxy-β-nitrostyrene only gave the desired product in moderate yield (56%) along with other unidentified compounds. We thought that the result was caused by the poor solubility of 3,4-methylenedioxy-β-nitrostyrene in cyclohexanone. When 0.5 mL of $CHCl_3$ was added, the yield was improved to 95% (entry 11).

Under the same conditions, the reactions of other Michael donors with β-nitrostyrene were evaluated as well and the results are shown in Table 3. The addition with cyclopentanone gave the corresponding product in moderate yield and enantioselectivity but low diastereoselectivity (Table 3, entry 1). Acetone and isovaleraldehyde were also suitable

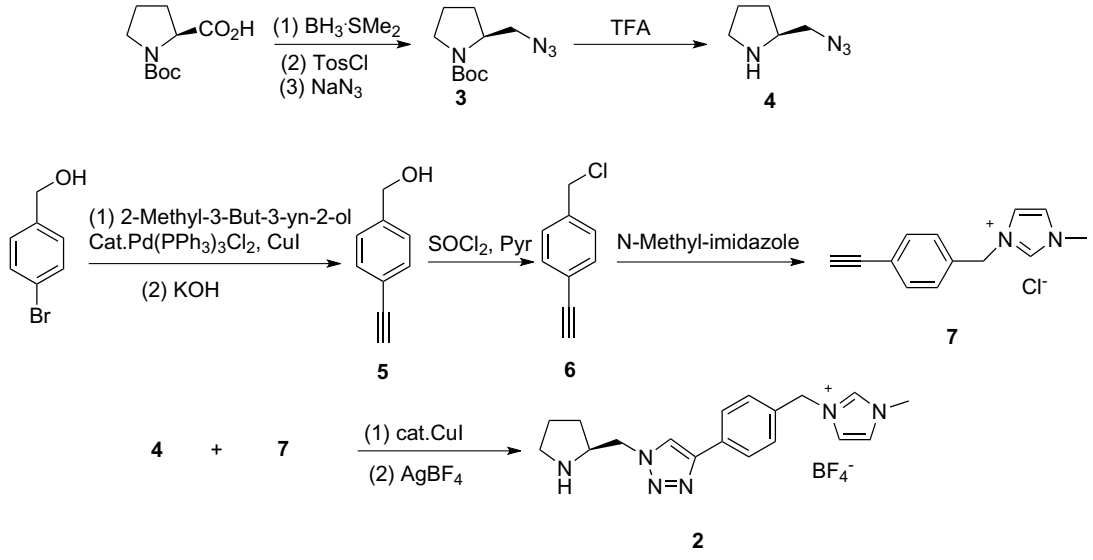
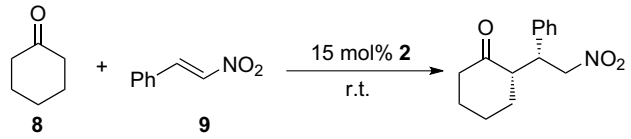


Figure 2. Synthetic procedure of the IL-supported catalyst.

Table 1. Effect of IL-supported catalyst in the asymmetric Michael addition reaction of cyclohexanone and *trans*-β-nitrostyrene[b]

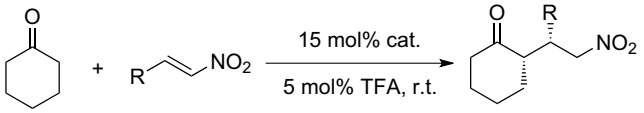


8 **9**

Entry	Solvent	Additive	Time (h)	Yield[c] (%)	dr[d] (*syn*/*anti*)	ee[e] (%)
1	DMSO	—	72	41	n.d.[a]	n.d.
2	$CHCl_3$	—	72	34	n.d.	n.d.
3	H_2O	—	72	29	n.d.	n.d.
4	—	—	72	47	n.d.	n.d.
5	DMSO	TFA[a]	48	90	94:6	88
6	$CHCl_3$	TFA	48	95	96:4	92
7	H_2O	TFA	48	94	93:7	90
8	—	TFA	48	97	97:3	94
9[f]	—	TFA	48	89	96:4	94
10[g]	—	TFA	72	90	96:4	93
11	—	TosOH	72	73	94:6	93
12	—	AcOH	72	60	95:5	83

[a] TFA = trifluoroacetic acid, n.d. = not determined.
[b] Unless otherwise noted, reaction conducted in solvent (1 mL) using **8** (10 mmol), **9** (0.5 mmol) and 15 mmol % catalyst **2**.
[c] Isolated yield.
[d] Determined by ^1H NMR of crude mixture.
[e] Determined by chiral HPLC analysis (Chiralpak AD-H, hexane:2-propanol = 90:10).
[f] 10 mmol % catalyst was used.
[g] 5 mmol **8** was used.

Table 2. Screening of different nitroolefins with cyclohexanone[a]



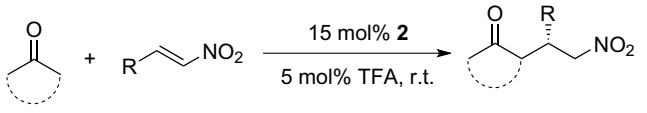
Entry	R	Yield[b] (%)	dr[c] (*syn*/*anti*)	ee[d] (%) (*syn*)
1	Ph	97	97:3	94
2	4-MeO–C_6H_4	98	49:1	92
3	4-Me–C_6H_4	99	97:3	94
4	4-Cl–C_6H_4	99	49:1	94
5	2-Cl–C_6H_4	97	49:1	93
6	2-Br–C_6H_4	96	49:1	95
7	4-Br–C_6H_4	94	49:1	97
8	2,4-Cl_2–C_6H_3	97	97:3	94
9	3-NO_2–C_6H_4	97	92:8	94
10	2-Naphthyl	96	49:1	93
11[e]	3,4-Methylenedioxy-C_6H_3	95	97:3	94
12	2-Furyl	94	92:8	85

[a] Experiments were performed on a 0.5-mmol scale using 10 mmol ketone and 15 mol % of catalyst.
[b] Yield of isolated product.
[c] Determined by ^1H NMR of crude mixture.
[d] Determined by chiral HPLC analysis (Chiralpak AD-H column).
[e] 0.5 mL $CHCl_3$ was added.

Michael donors to produce the desired adducts with good yields but low enantioselectivities (Table 3, entries 2 and 3).

Finally, the recyclability and reusability of IL-supported catalyst **2** was investigated (Table 4). The reaction of cyclohexanone and β-nitrostyrene was chosen as a model study. When the first run of the reaction was complete, diethyl ether was added. The adduct and cyclohexanone was dissolved in the ether, and the catalyst was precipitated. After removing the ether phase, the catalyst was dried under vacuum for 20 min and then reused for the next cycle of the reaction without additional TFA. As can be seen from Table 4, the supported catalyst showed good catalytic activity with high diastereo- and enantioselectivity up to the fourth cycle.

Table 3. The reactions of other Michael donors with nitrostryene catalyzed by **2**



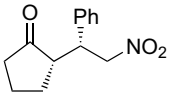
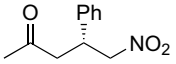
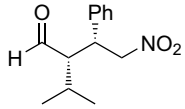
Entry	Product	Time (h)	Yield (%)	*syn*/*anti*	ee (%) (*syn*/*anti*)
1		60	63	5:3	81:77
2		36	95	—	40
3		60	82	98:2	58

Table 4. Recycling studies of ionic-liquid-supported catalyst **2** in the Michael reaction of cyclohexanone to β-nitrostyrene

Cycle	1	2	3	4
Yield (%)	96	94	97	95
dr (*syn*/*anti*)	97:3	96:4	95:5	97:3
ee (%)	94	95	93	94

3. Conclusions

In conclusion, we have successfully immobilized an organocatalyst for asymmetric direct Michael reaction of ketones and nitroolefins onto the ionic liquid. The research demonstrated that the IL-supported catalyst retained good activity and high selectivity.[11] Furthermore, the catalyst can be easily recycled and reused for four times without a significant decrease in yields and enantioselectivities.

4. Experimental

4.1. General

Unless specified, all reactions were performed under an aerobic atmosphere. Commercial solvents and reagents were used without further purification unless otherwise noted. TLC plates with F254 indicator were used for monitoring

the reactions. Column chromatography was performed with silica gel (200–300 mesh). All yields given refer to isolated yields. ^{1}H NMR spectra were recorded at 300 or 400 MHz, and ^{13}C NMR spectra at 75 MHz or 100 MHz. Mass spectra were recorded by the EI method or HRMS method. HPLC analysis was performed on Varian-ProStar using a ChiralPak AD-H column with 2-propanol in hexanes as the eluent.

4.2. Typical experimental procedure for the asymmetric Michael addition of cyclohexanone to nitroolefins

To a mixture of nitroolefins (0.5 mmol), the catalyst (0.075 mmol) and TFA (0.025 mmol) was added ketone (10 mmol). The mixture was stirred vigorously at ambient temperature and monitored by TLC. The homogeneous reaction mixture was diluted with 5 mL diethyl ether to precipitate the catalyst. The organic layer was separated and rotary evaporated. The resulting residue was then purified by silica gel chromatography (ethyl acetate/petroleum ether = 1:20 to 2:1) and fractions were collected and concentrated in vacuum.

The relative configurations of the products (*syn* and *anti*) were determined by the comparison of ^{1}H NMR spectral data with those reported in the literature. The absolute configurations of the products were determined by comparison of specific rotation values with those reported in the literature. All compounds in Tables 2 and 3 are known.[9]

4.3. Synthesis of IL-supported catalyst 2

4.3.1. *p*-Ethynylbenzyl chloride 6.[16] At 0 °C, a mixture of (4-ethynylphenyl)methanol **5**[15] (1.98 g, 15 mmol) and pyridine (3.16 g, 40 mmol) in 20 mL CH_2Cl_2 was added to $SOCl_2$ (2.94 g, 25 mmol) in 10 min. After stirring overnight at ambient temperature, the mixture was diluted with 30 mL $CHCl_3$ and washed with 2 N HCl (15 mL × 2), saturated $NaHCO_3$ (20 mL × 2) and brine (20 mL × 1). The organic phase was dried over Na_2SO_4, concentrated under reduced pressure, and purified by column chromatography (silica gel, ethyl acetate/hexane = 1:10). Compound **6** was obtained as a colourless oil (1.69 g, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.10 (s, 1H), 4.55 (s, 2H), 7.32 (dt, J = 1.5, 3.3 Hz, 2H), 7.47 (dt, J = 1.5, 3.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.6, 77.9, 83.0, 122.1, 128.5, 132.4, 138.0; EI-MS *m*/*z* (EI) 150 (M^+), 115, 89.

4.3.2. 1-(4-Ethynyl-benzyl)-3-methyl-3*H*-imidazol-1-ium chloride 7. A mixture of *p*-ethynylbenzyl chloride **6** (1.50 g, 10 mmol) and *N*-methyl imidazole (1.64 g, 20 mmol) in 10 mL CH_3CN was refluxed 8 h under argon. After cooling, 60 mL ether was added to the mixture and the standing crystallization to afford a white solid (2.09 g, 90%), mp 183–185 °C. IR (cm^{-1}): 3381, 2959, 2102, 1573, 1162. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.16 (s, 1H), 3.68 (s, 3H), 5.17 (s, 2H), 7.46 (s, 2H), 7.52 (m, 2H), 7.68 (s, 2H), 10.58 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.1, 52.0, 77.4, 78.6, 121.8, 122.6, 123.4, 128.5, 132.3, 133.7, 137.0. HRMS for $C_{13}H_{13}N_2^+$ (M^+), calcd 197.1073, found 197.1077.

4.3.3. (*S*)-1-Methyl-3-(4-(1-(pyrrolidin-2-ylmethyl)-1,2,3-triazol-4-yl)benzyl)-imidazolium tetrafluoroborate 2. To a solvent of (2*S*)-2-azidomethyl-pyrrolidine **4** (1.00 g, 8 mmol) and **7** (1.74 g, 7.5 mmol) in 20 mL THF/H_2O (1:1) was added CuI (10 mol %, 0.75 mmol). The mixture was stirred for 24 h at ambient temperature. After removal of the solvent under vacuum, the residue was dissolved in 10 mL methanol and was added to $AgBF_4$ (1.95 g, 10 mmol) with vigorous stirring. After 10 min, the black precipitate was moved by filtration. The $Na_2S{\cdot}9H_2O$ (1.0 g, 4 mmol) was added and stirred for 10 min. The reaction was filtered again and concentrated. The residue was diluted with CH_3CN/CH_2Cl_2 (2:1) and the insolubles removed by filtration. The clear filtrate was concentrated to dryness under vacuum to afford a pale yellow viscous liquid **2** (2.95 g, 90%). $[\alpha]_D^{20} = +6$ (*c* 1.0, H_2O). IR (cm^{-1}): 3422, 2962, 1686, 1571, 1061. ^{1}H NMR (300 MHz, D_2O): 1.77 (dd, J = 3.6, 3.0 Hz, 1H), 1.97–2.08 (m, 2H), 2.20 (dd, J = 3.0, 5.1 Hz, 1H), 3.30–3.41 (m, 2H), 3.73 (s, 3H), 4.07 (m, 1H), 4.67–4.74 (m, 3H), 5.22 (s, 2H), 7.27–7.34 (m, 4H), 7.58 (d, J = 5.4 Hz, 2H), 8.18 (s, 1H), 8.34 (s, 1H). ^{13}C NMR (75 MHz, D_2O): δ 22.9, 27.6, 35.9, 46.1, 50.4, 52.4, 59.4, 122.2, 123.0, 124.1, 126.3, 129.3, 129.5, 130.1, 134.1, 136.2. HRMS for $C_{18}H_{23}N_6^+$ (M^+), calcd 323.1979, found 323.1983.

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