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A chiral pyrrolidine-pyrazole catalyst for the enantioselective Michael addition of carbonyls to nitroolefins

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ABSTRACT

An enantioselective Michael reaction of carbonyl compounds to nitroolefins has been accomplished using a novel chiral pyrrolidine-pyrazole catalyst. This newly prepared catalyst was found to be very effective in providing good yields as well as good diastereo- and enantio-selectivities. The mechanism of the reaction has also been substantiated by mass spectral studies.

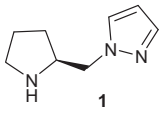
1. Introduction

Asymmetric organocatalysis of L-proline has taken strides toward better selectivities, diversity of substrates, and lower concentration of catalysts.[1] The original catalyst concentration of over 30% L-proline being used by Barbas/List for an aldol reaction[2] to afford moderate enantiomeric excess has undergone modifications in the pyrrolidine ring and also in the appended carboxylic acid. Examples include triflamides,[3] diphenylprolinol,[4] proline-triazole,[5] prolinamides,[6] amino acid derived compounds,[7] and others.[8,9] These modifications have allowed organic chemists to expand the diversity of C–C bond forming reactions, such as aldol reaction,[10] asymmetric Michael reactions,[11] domino processes, and so on.[12] In this progressive strategy, new mechanistic insights have been reported for a better understanding of the reaction path, which helps in designing more efficient catalysts.[13]

Our interest in this field prompted us to contribute new catalysts for the asymmetric Michael and aldol reactions as well as for domino processes toward novel scaffolds, which are now easily available.[14] In continuation, we have synthesized a new pyrrolidine-pyrazole catalyst **1** (Fig. 1), which showed a very efficient catalytic cycle for the Michael addition of carbonyl compounds to nitroolefins with excellent diastereo- and enantio-selectivities.

2. Results and discussion

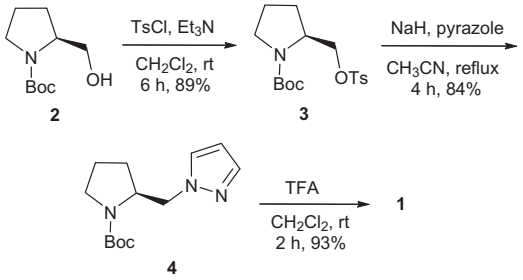
The chiral pyrrolidine-pyrazole **1** employed for this work was easily obtained in three steps from commercially available Boc-protected prolinol **2** (Scheme 1).



1

Figure 1. Structure of pyrrolidine-pyrazole catalyst.

Initial experiments were performed with a reaction between cyclohexanone **5a** and β-nitrostyrene **6a** to test the efficiency of pyrrolidine-pyrazole catalyst **1** in different solvents; the results are summarized in Table 1. At first, the reaction was carried out in CH_2Cl_2 at room temperature using 10 mol % of catalyst. The reaction proceeded well to give the corresponding Michael adduct **7a** in 80% yield with 94:6 (*syn*/*anti*) diastereoselectivity and 89% enantiomeric excess (Table 1, entry 1). With the aim of improving the yield and selectivity, a variety of solvents were screened for the same reaction. The best yield with high selectivity was observed



Scheme 1. Synthesis of pyrrolidine-pyrazole **1**.

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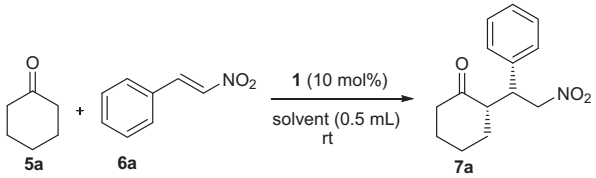
under solvent-free reaction conditions (Table 1, entry 5). Among the solvents screened, THF gave a better yield (92%) as well as selectivity (Table 1, entry 7). Other solvents such as H_2O, DMF, CH_3CN, toluene, and MeOH, provided moderate to good yields of the product (50–85%, Table 1, entries 2–4, 6 and 8). On the other hand, hexane and Alliquat® 336 gave low yields of the product (Table 1, entries 9 and 10).

Table 1
Screening of solvents[a]



Entry	Solvent	Time (h)	Yield[b] (%)	*syn*/*anti*[c]	ee[d] (%)
1	CH_2Cl_2	24	80	94:6	89
2	H_2O	24	52	7:3	80
3	DMF	20	65	92:8	85
4	CH_3CN	20	85	8:2	79
5	—	24	96	98:2	94
6	Toluene	24	60	9:1	82
7	THF	24	92	96:4	91
8	MeOH	20	78	92:8	82
9	Hexane	36	35	8:2	72
10	Alliquat-336	36	42	9:1	76

[a] Reaction conditions: Nitrostyrene (1 mmol), cyclohexanone (5 mmol), catalyst (10 mol %).
[b] Isolated yields.
[c] Determined by the ^{1}H NMR of the crude product.
[d] Determined by chiral HPLC.

To further optimize the reaction conditions, the effect of an acid additive was tested. It has already been well documented that the presence of an acid additive increases the catalyst efficiency toward the acceleration of enamine formation.[15] Therefore, the effect of various additives on the Michael reaction of cyclohexanone **5a** with β-nitrostyrene **6a** under solvent-free conditions was tested and the results are summarized in Table 2. The addition of AcOH (2 mol %) in the reaction produced 84% yield of the desired product with 89% ee (Table 2, entry 1) in 20 h. The other additives screened were TFA, HCOOH, PhCOOH, *p*TSA, and CSA and we found that TFA (2 mol %) affected the reaction by giving the product in 98% yield with 95% ee in 15 h reaction time (Table 2, entry 4). The use of the TFA salt of catalyst **1** has resulted the product in 80% yield after 24 h.

Table 2
Screening of additives[a]

Entry	Additive (2 mol %)	Time (h)	Yield[b] (%)	*syn*/*anti*[c]	ee[d] (%)
1	AcOH	20	84	94:6	89
2	HCOOH	24	82	92:8	85
3	PhCOOH	18	92	95:5	92
4	TFA	15	98	98:2	95
5	*p*TSA	24	76	93:7	82
6	CSA	24	68	9:1	78

[a] Reaction conditions: Nitrostyrene (1 mmol), cyclohexanone (5 mmol), catalyst (10 mol %).
[b] Isolated yields.
[c] Determined by ^{1}H NMR of the crude product.
[d] Determined by chiral HPLC.

Next, we turned our attention to test the effect of catalyst loading in the Michael addition reaction of **5a** with **6a**; the results are shown in Table 3. A decrease in catalyst loading resulted in a longer reaction time, without affecting the yield or the selectivity (Table 3, entries 1–4).

Table 3
Effect of catalyst loading[a]

Entry	Catalyst (mol %)	Time (h)	Yield[b] (%)	*syn*/*anti*[c]	ee[d] (%)
1	20	15	98	98:2	95
2	10	15	98	98:2	95
3	5	50	95	97:3	93
4	2	72	92	94:6	94

[a] Reaction conditions: Nitrostyrene (1 mmol), cyclohexanone (5 mmol), TFA (2 mol %).
[b] Isolated yields.
[c] Determined by ^{1}H NMR of the crude product.
[d] Determined by chiral HPLC.

Having established the optimal conditions, we then explored the generality of this reaction with a variety of nitroolefins using cyclohexanone **5a** as the Michael donor (Table 4). The present catalytic system is tolerant to a broad range of nitroolefins derived from aromatic aldehydes bearing electron-donating as well as electron-withdrawing groups (Table 4, entries 2–6) and heteroaromatic aldehydes providing a series of γ-nitro carbonyl compounds in high yields and with good to high selectivities (Table 4, entries 7–9).

To further expand the scope of the newly prepared catalyst, the reaction of β-nitrostyrene **6a** with different carbonyl compounds was examined (Table 5). Thus, the Michael reaction of cyclopentanone **5b** with β-nitrostyrene **6a** under the present conditions provided the desired product **7k** in 97% yield in 20 h with 90% ee and 97:3 diastereoselectivity (Table 5, entry 1). Tetrahydropyranone **5c** and *N*-methyl piperidone **5d** are also well suited to obtain the corresponding γ-nitro carbonyls **7l** and **7m** in good yields (94% and 95%), albeit with low selectivities (Table 5, entries 2 and 3). However, the acyclic ketones, acetophenone **5e,** and acetone **5f** provided Michael addition products in lower yields with poor selectivities (Table 5, entries 4 and 5) and took longer for completion of the reaction. Additionally, we were able to use two aldehyde substrates, propionaldehyde **5g** and isobutyraldehyde **5h** as Michael donors under the present chiral pyrrolidine-pyrazole **1** catalysis and the reaction was completed in 18 h to give **7p** in 82% yield with 78% ee and 93:7 diastereoselectivity (Table 5, entry 6) and **7q** in 85% yield with 82% ee (Table 5, entry 7).

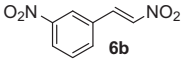
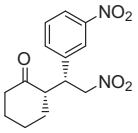
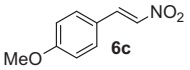
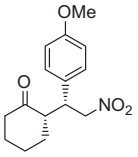
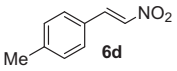
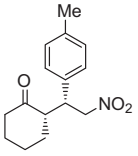
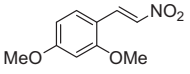
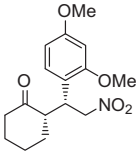
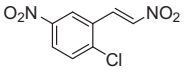
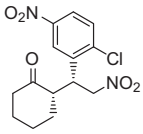
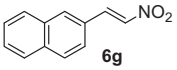
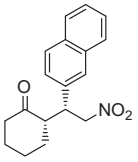
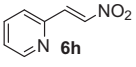
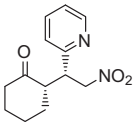
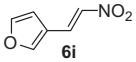
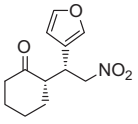
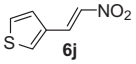
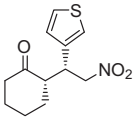
These successful experiments directed us to study the mechanistic pathway and the transition state involved in the reaction. On the basis of our experimental findings, we propose a possible mechanism for the asymmetric Michael reaction catalyzed by the pyrrolidine-pyrazole catalyst **1** (Fig. 2). Initially, catalyst **1** forms a chiral enamine **A** (predominantly *anti*) with cyclohexanone **5a** and then a Michael reaction between the enamine-activated **A** and the nitroolefin **6a** (in *anti-Re* addition fashion) leads to the formation of corresponding Michael product **7a** via transition state **TS-I** (an acyclic synclinal transition state). After hydrolysis, catalyst **1** is regenerated for use in the subsequent catalytic cycle.

This mechanism was further supported by the ESI-MS of the reaction mixture at regular intervals. The ESI-MS (Fig. 3) showed the mass of the reaction intermediates (**A** and **B**), which supports the proposed reaction mechanism.

3. Conclusions

In conclusion, an efficient and stereoselective organocatalyst, a chiral pyrrolidine-pyrazole for the asymmetric Michael addition of carbonyls to nitroolefins has been developed. The new catalyst has a pyrazole moiety attached to chiral pyrrolidine and gives high enantio- and diastereoselectivities in the case of cyclohexanone reactions. In the present protocol, good yields of the products, high stereoselectivities, and solvent-free reaction conditions are noteworthy features.

Table 4
Asymmetric Michael addition of **5a** with various nitroolefins using organocatalyst **1**[a]

Entry	Nitroolefins	Time (h)	Product	Yield[b] (%)	*syn*/*anti*[c]	ee[d] (%)
1	 **6b**	15	 **7b**	96	95:5	92
2	 **6c**	15	 **7c**	97	96:4	98
3	 **6d**	15	 **7d**	93	97:3	99
4	 **6e**	15	 **7e**	95	98:2	95
5	 **6f**	18	 **7f**	98	96:4	97
6	 **6g**	18	 **7g**	92	94:6	92
7	 **6h**	20	 **7h**	90	92:8	89
8	 **6i**	18	 **7i**	94	95:5	90
9	 **6j**	18	 **7j**	93	94:6	86

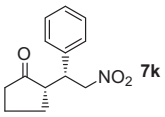
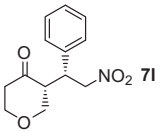
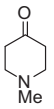
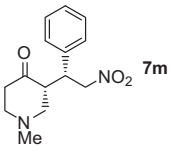
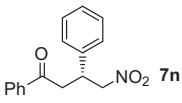
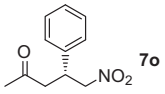
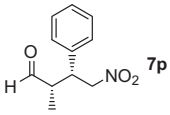
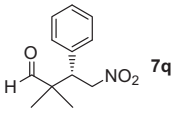
[a] Reaction conditions: Nitrostyrene (1 mmol), cyclohexanone (5 mmol), catalyst (10 mol %), TFA (2 mol %), solvent free, rt.
[b] Isolated yields.
[c] Determined by ^{1}H NMR and HPLC analysis.
[d] Determined by chiral HPLC using chiral pak-IA, IC or OD_H columns.

4. Experimental

4.1. General

^{1}H NMR and ^{13}C NMR spectra were recorded in a $CDCl_3$ solvent on a 300, 500, or 75 MHz spectrometer at ambient temperature. The chemical shifts (δ) are reported in ppm on a scale downfield from TMS as the internal standard and signal patterns are as follows: s, singlet; d, doublet; dd, doublet of doublet; td, triplet of doublet; t, triplet; m, multiplet; br s, broad singlet. Coupling constants *J* are in Hertz. FTIR spectra were recorded as KBr thin films or neat. For low (MS) and high (HRMS) resolution, *m*/*z* ratios are reported as values in atomic mass units. All the reagents and solvents were reagent grade and used without further purification unless specified otherwise. Technical grade ethyl acetate and petroleum ether were used for column chromatography and were distilled prior to use. Column chromatography was carried out using silica gel (60–120 mesh) packed in glass columns. All the reactions were performed under an atmosphere of nitrogen in flame-dried or oven-dried glassware with magnetic stirring.

Table 5
Asymmetric Michael addition of different carbonyls with **6a** using organocatalyst **1**[a]

Entry	Carbonyls	Time (h)	Product	Yield[b] (%)	*syn*/*anti*[c]	ee[d] (%)
1	 **5b**	20	 **7k**	97	97:3	96
2	 **5c**	15	 **7l**	94	98:2	91
3	 **5d**	15	 **7m**	95	95:5	86
4	 **5e**	24	 **7n**	72	—	48
5	 **5f**	24	 **7o**	67	—	39
6	 **5g**	18	 **7p**	82	93:7	78
7	 **5h**	18	 **7q**	85	—	82

[a] Reaction conditions: Nitrostyrene (1 mmol), cyclohexanone (5 mmol), catalyst (10 mol %), TFA (2 mol %), solvent free, rt.
[b] Isolated yields.
[c] Determined by ^{1}H NMR and HPLC analysis.
[d] Determined by chiral HPLC using chiral pak-IA, IC or OD_H columns.

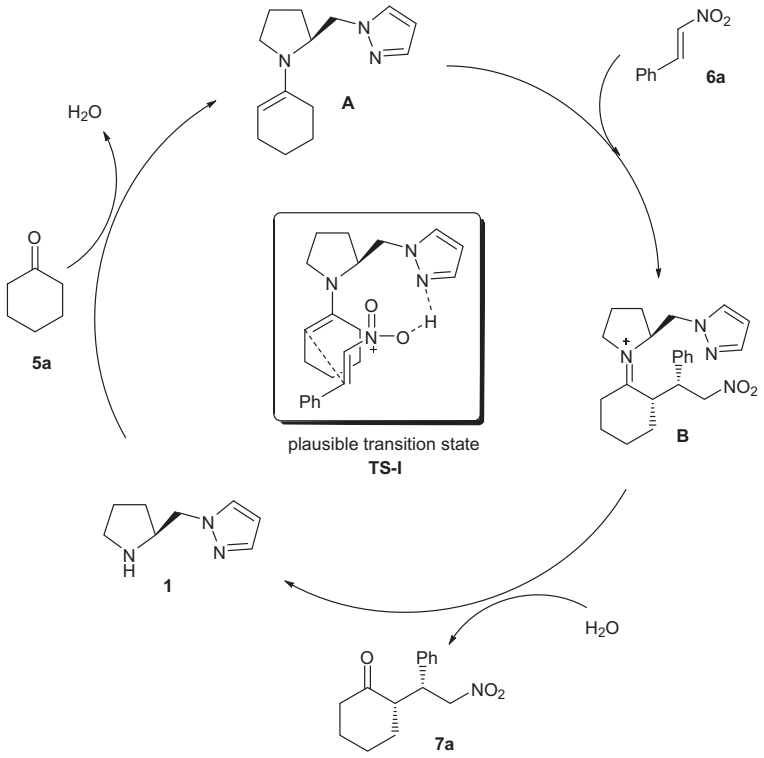


Figure 2. Proposed mechanism of the asymmetric Michael reaction catalyzed by **1**.

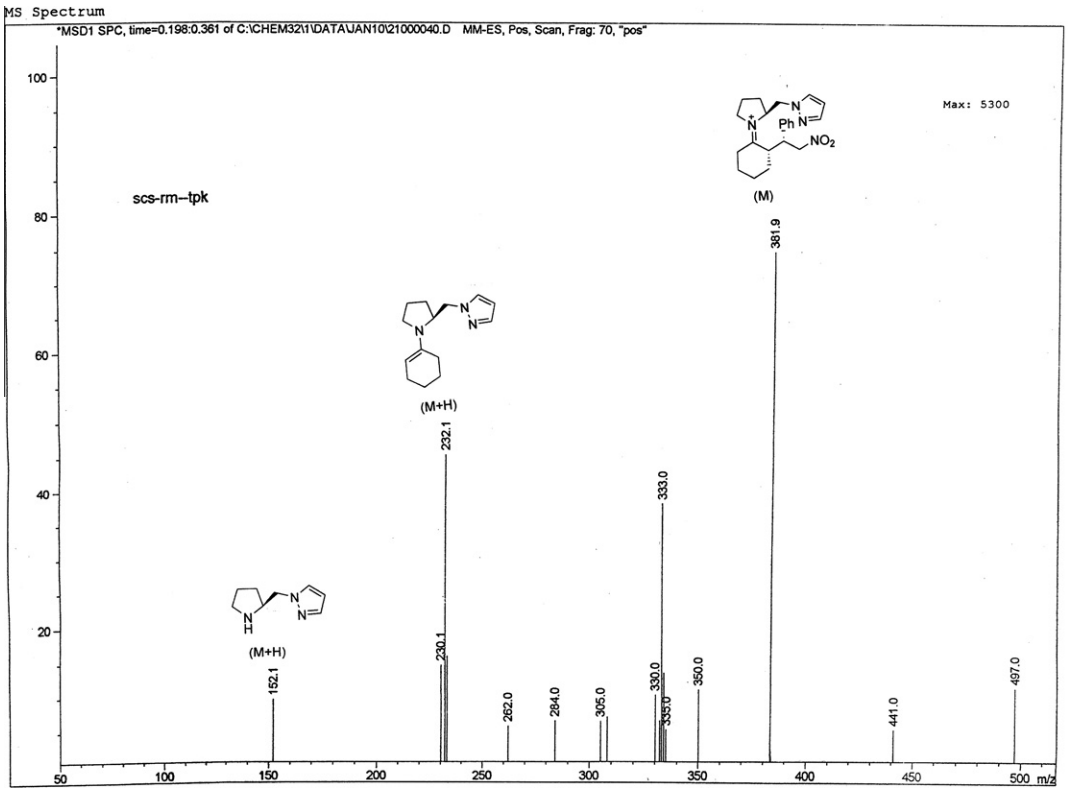


Figure 3. ESI-MS of the reaction mixture.

4.1.1. (*S*)-*tert*-Butyl-2-((1*H*-pyrazol-1-yl)methyl)pyrrolidine-1-carboxylate 4

To a suspension of NaH (270 mg, 60% of purity, 6.7 mmol) in 20 mL of anhydrous acetonitrile was added pyrazole (384 mg, 5.6 mmol) and stirred at room temperature for 0.5 h. Then, the tosylated-*N*-Boc-prolinol **3** (1.0 g, 2.8 mmol) was added to the resulting mixture and heated at reflux under a nitrogen atmosphere for 4 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The solvent was removed in vacuo and the residue was diluted with 10 mL of water. The resulting mixture was extracted with chloroform (3×20 mL). The residue was purified by column chromatography to furnish the desired product **4** (588 mg, 84% yield) as a thick oil. $[\alpha]_D^{25} = -119$ (*c* 1.1, $CHCl_3$); IR (Neat): *v* 2973, 2880, 1691, 1512, 1449, 1396, 1170, 1117, 1048, 968, 753 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.40 (s, 1H), 7.28 (s, 1H), 6.19 (t, 1H, $J = 2.26$ Hz), 4.43–4.14 (m, 2H), 4.06–3.96 (m, 1H), 3.37–3.02 (m, 2H), 2.11–1.60 (m, 3H), 1.48 (s, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.4 and 154.1(rotamers), 139.0 and 138.8 (rotamers), 129.5 and 129.3 (rotamers), 105.7 and 105.6 (rotamers), 79.6 and 79.3 (rotamers), 57.4, 54.1 and 53.0 (rotamers), 46.8 and 46.3 (rotamers), 28.6, 28.3, 23.0 and 22.4 (rotamers); ESI(MS): *m*/*z* 252 $[M+H]^+$; HRMS calcd for $C_{13}H_{22}N_3O_2$: 252.1707, found: 252.1718.

4.1.2. (*S*)-1-(Pyrrolidine-2-ylmethyl)-1*H*-pyrazole 1

To a solution of **4** (580 mg, 2.3 mmol) in CH_2Cl_2 (5 mL) was added TFA (5 mL) at 0 °C and the reaction mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), saturated $NaHCO_3$ solution was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography to furnish the desired product **4** (323 mg, 93% yield) as a yellow liquid. $[\alpha]_D^{25} = -98$ (*c* 0.9, $CHCl_3$); IR (Neat): *v* 3407, 2980, 2361, 1677, 1175, 837 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.73 (d, 1H, $J = 2.45$ Hz), 7.69 (d, 1H, $J = 2.26$ Hz), 6.43 (t, 1H, $J = 2.26$ Hz), 4.81–4.52 (m, 2H), 4.21 (s, 1H), 3.41 (s, 2H), 2.34–1.79 (m, 3H), 1.80–1.63 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.4, 132.8, 107.2, 60.2, 50.3, 46.0, 27.1, 23.3; ESI(MS): *m*/*z* 152 $[M+H]^+$; HRMS calcd for $C_8H_{14}N_3$: 152.1182, found: 152.1188.

4.1.3. General procedure: Michael reaction of 5a with 6a–j to give 7a to 7q

Catalyst **1** (10 mol %) was added to a mixture of cyclohexanone **5a** (5 mmol) and TFA (2 mol %) at room temperature and stirred for 10 min, then nitroolefin **6a–j** (1 mmol) was added and stirred at the same temperature. After completion of the reaction (monitored by TLC), the crude product was purified by silica-gel column chromatography to give the corresponding Michael adducts. Relative and absolute configurations of the products were determined by comparison of ^1H NMR, ^{13}C NMR, and specific rotation values with those reported in the literature. Enantiomeric excess was determined by chiral HPLC.

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