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A Triazole Organocatalyst with Spiropyrrolidine Framework and its Application to the Catalytic Asymmetric Addition of Nitromethane to α,β-Unsaturated Aldehydes

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Abstract: A series of new water-compatible "spiropyrrolidine triazole" catalysts was designed and synthesized. The asymmetric Michael addition of nitromethane and α,β-unsaturated aldehydes in an aqueous system was investigated to evaluate these new catalysts, and the resulting adducts were obtained with excellent enantioselectivity (up to 95.5% *ee*) and moderate to good yield (63–88%).

Keywords: azaspiro skeleton; Michael addition; nitromethane; organic catalysis; 1,2,3-triazoles; α,β-unsaturated aldehydes

Asymmetric organocatalysis has become an important method for constructing valuable chiral building blocks in both industrial and fundamental research in organic synthesis.[1] In recent decades, a broad array of organocatalytic asymmetric reactions has been extensively investigated,[2] one class of which is particularly important because they are water-compatible transformations[3] that can benefit humans and the environment. These transformations require effective water-compatible organocatalysts that contain appropriate hydrophobic and hydrophilic moieties in their structures.[3h] Considering the unique characteristics of triazole as a privileged framework,[4] and encouraged by the excellent results of our newly developed "spiropyrrolidine silyl ether" organocatalyst **1** (Figure 1) for the asymmetric construction of quaternary carbon centers,[5] we imagined that 1-azaspiro[4.4]nonane could be further derived to other organocatalysts, such as a water-compatible triazole-type (**2**, Figure 1). Here we report the design and synthesis of a series of new spiropyrrolidine organocatalysts bearing a triazole unit and their application to the asymmetric Michael addition of nitromethane to α,β-unsaturated aldehydes under water-compatible conditions.[6]

Catalysts **2a**–**2g** were synthesized as shown in Scheme 1. Starting from the known chiral 1-azaspiro[4.4]nonane-6-one (**3**),[5,7] the ketone group in **3** was oximated and stereoselectively reduced with $NaBH_4$/$NiCl_2$ in MeOH to give the primary amine intermediate, which was stereospecifically converted to azide **4** *via* a diazo transfer reaction.[8] The azide **4** then underwent a "click reaction"[9] with alkynes substituted with various functional groups, affording the precursors **5a**–**5f**. Next, removal of the protecting group of **5a**–**5f** gave the desired "spiropyrrolidine triazole" catalysts **2a**–**2f** (Scheme 1). For synthesis of catalyst **2g**, the last two steps of the reaction sequence were reversed. The absolute configuration of these catalysts

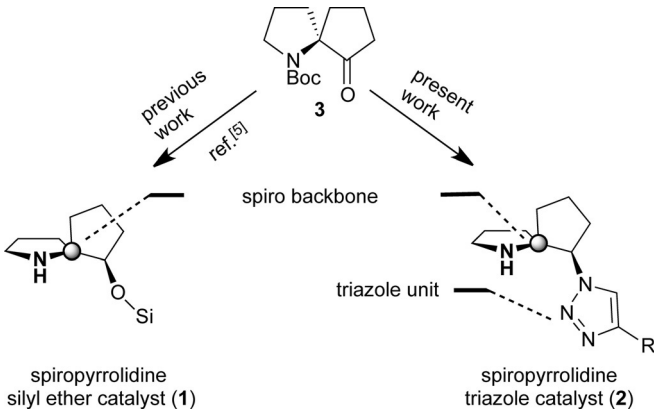

Figure 1. The design of new "spiropyrrolidine triazole" catalysts.

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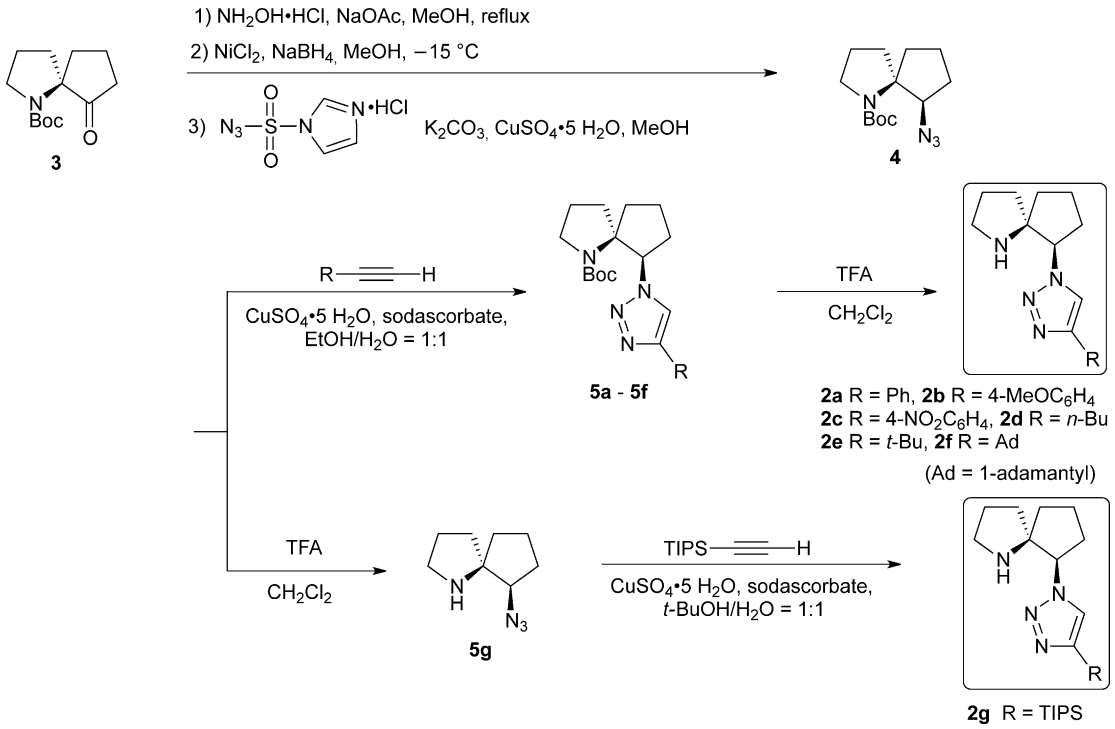

Scheme 1. Synthesis of "spiropyrrolidine triazole" catalysts.

was further confirmed based on the X-ray analysis of catalyst **2a**.[10] It is noteworthy that all catalysts could be smoothly prepared from **3** in approximately 65% overall yields (for details, see the Supporting Information).

With the desired organocatalysts in hand, we then evaluated the ability of these organocatalysts to efficiently promote the Michael addition of nitromethane (1 mmol) to cinnamaldehyde (**6a**, 0.1 mmol). To our delight, all catalysts could promote the reaction in the presence of benzoic acid (BA) in methanol as solvent. Substituents on the triazole ring obviously affected the enantioselectivity of this reaction (Table 1, entries 1–8). Aryl-substituted catalysts **2a**–**2c** gave adduct **7a** with 40–49% *ee* and 77–84% yield (entries 1–3), indicating that the electronic property of substituent in the phenyl ring slightly affected the reaction results. Alkyl-substituted catalysts **2d**–**2f** gave higher enantioselectivity with similar yield (entries 4–6). The TIPS-substituted catalyst **2g** led to slightly lower selectivity than catalyst **2f** (entry 7). Using the enantiomer of catalyst **2f** completely reversed the enantioselectivity of the current reaction (entry 8). Therefore, catalyst **2f** was selected for further investigation of the reaction conditions.

Extensive solvent screening[11] showed polar alcohol solvents to be more suitable than others, although yield and enantioselectivity significantly decreased in the sequence MeOH < EtOH < *i*-PrOH (entries 7–10). Replacing methanol with trifluoroethanol (TFE) slightly improved the enantioselectivity, but it required longer reaction times and still gave a low yield (entry 11). Conducting the reaction in water gave complex mixtures, and the use of brine also gave unsatisfactory results (entries 12 and 13). Use of the mixed solvent of MeOH/H_2O ($v/v = 4/1$) led to a significantly higher yield (94%) and *ee* (90%) (entry 14). Encouraged by this result, the ratio of the solvent mixture was fine-tuned, and it was found that modifying the proportion of H_2O strongly influenced both reactivity and stereoselectivity (entries 14--16).[11] In contrast, various additives (entries 17–20) and lower temperature (entry 21) failed to improve the reaction performance. Pleasingly, replacing MeOH in the mixed solvent by TFE gave the product **7a** in 88% yield and 95% *ee* (entry 22), albeit with a longer reaction time. Finally, further increasing the loading of catalyst **2f** and $PhCO_2H$ to 20 mol% and 35 mol%, respectively, could both shorten the reaction time to 36 h and slightly increase the *ee* value to 95.5% (Table 1, entry 23).

Under the optimal reaction conditions (Table 1, entry 23), we next studied the generality of this catalytic asymmetric conjugate addition reaction of nitromethane with a variety of α,β-unsaturated aldehydes, which showed that the reaction could be achieved with excellent enantioselectivity (83–95.5% *ee*) and 63–88% yield (Table 2). Notably, cinnamaldehyde derivatives with electron-withdrawing or electron-donating groups at the 2- or 4-position of the phenyl ring produced the corresponding products in 63–88% yield and with 93–95.5% *ee* (entries 1–7). However, sub-

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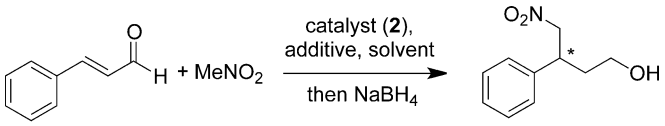
Table 1. Screening of the reaction conditions[a]



6a 7a

Entry	Catalyst	Solvent	Additive	Time [h]	Yield[b]	*ee*[c]
1	**2a**	MeOH	BA[d]	24	84%	44%
2	**2b**	MeOH	BA	34	79%	49%
3	**2c**	MeOH	BA	34	77%	40%
4	**2d**	MeOH	BA	29	87%	71%
5	**2e**	MeOH	BA	24	82%	73%
6	**2f**	MeOH	BA	24	87%	83%
7	**2g**	MeOH	BA	24	88%	80%
8[e]	*ent*-**2f**	MeOH	BA	24	85%	−83%
9	**2f**	EtOH	BA	36	75%	72%
10	**2f**	*i*-PrOH	BA	60	19%	68%
11	**2f**	TFE	BA	120	38%	84%
12	**2f**	H_2O	BA	7	N.D.[f]	N.D.
13	**2f**	brine	BA	6	38%	82%
14	**2f**	MeOH/H_2O 4:1	BA	40	94%	90%
15	**2f**	MeOH/H_2O 1:4	BA	36	47%	84%
16	**2f**	MeOH/H_2O 1:1	BA	36	95%	93%
17	**2f**	MeOH/H_2O 1:1	HOAc	36	95%	93%
18	**2f**	MeOH/H_2O 1:1	Et_3N	8	trace	N.D.
19	**2f**	MeOH/H_2O 1:1	TsOH	120	trace	N.D.
20	**2f**	MeOH/H_2O 1:1	–	21	45%	77%
21[g]	**2f**	MeOH/H_2O 1:1	BA	48	85%	94%
22	**2f**	TFE/H_2O 1:1	BA	72	88%	95%
23[h]	**2f**	**TFE/H_2O 1:1**	**BA**	**36**	**88%**	**95.5%**

[a] Unless otherwise stated, the reaction was performed employing cinnamaldehyde (0.1 mmol), nitromethane (1 mmol), catalyst **2** (0.01 mmol), additive (0.02 mmol) and solvent (1.0 mL) at room temperature.
[b] Isolated yield after reduction to the corresponding alcohol.
[c] Determined by chiral HPLC analysis on a Chiralpak OD-H column.
[d] BA = $PhCO_2H$.
[e] The enantiomer of catalyst **2f** was used, for the synthetic details of *ent*-**2 f** see the Supporting Information.
[f] N.D. = not determined.
[g] The reaction was performed at 4 °C with catalyst **2f** (20 mol%) and BA (20 mol%).
[h] Catalyst **2f** (20 mol%) and BA (35 mol%) were used.

stituents at the 3-position slightly decreased the *ee* value of the products (entries 8 and 9). In addition, acrolein substituted at the 1-position with naphthyl or a heteroaromatic group such as a furyl moiety led to the expected products **7j** and **7k** in excellent *ee* (entries 10 and 11). Aliphatic enals also worked well, giving the desired adducts in moderate yield and good enantioselectivity (Table 2, entries 12–14). An optical rotation analysis of the **7a** showed it to have the *R* absolute configuration as reported in the literature.[12] Furthermore, we have tried to use nitroethane as substrate to check the corresponding diastereoselectivity of the current process under the optimal reaction conditions. However, it was frustrating that only moderate diastereoselectivity and enantioselectivity (*dr* = 1:1.2, 76% *ee* for *syn*-**8**) were obtained (Scheme 2).

In conclusion, we have developed a new series of "spiropyrrolidine triazole" catalysts and demonstrated their high catalytic activity and stereoselectivity for iminium-type activation of α,β-unsaturated aldehydes. The present results provide the basis for generating novel organocatalysts based on the 1-azaspiro[4.4]nonane backbone and applying them to synthetic challenges. Such work is already underway in our laboratory.

Experimental Section

General Procedure for Catalyst 2f-Promoted Michael Addition of Nitromethane to α,β-Unsaturated Aldehydes

To a solution of α,β-unsaturated aldehyde (0.1 mmol) and catalyst **2f** (0.2 equiv.) in TFE/H_2O (1 mL, *v/v* 1:1) was added BA (0.35 equiv.) and CH_3NO_2 (10 equiv.) at room

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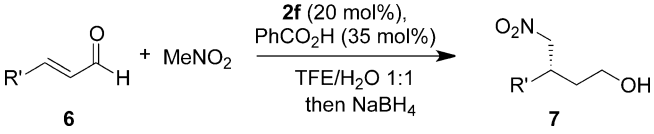
Table 2. Catalyst **2f**-promoted Michael addition of nitromethane to α,β-unsaturated aldehydes.[a]



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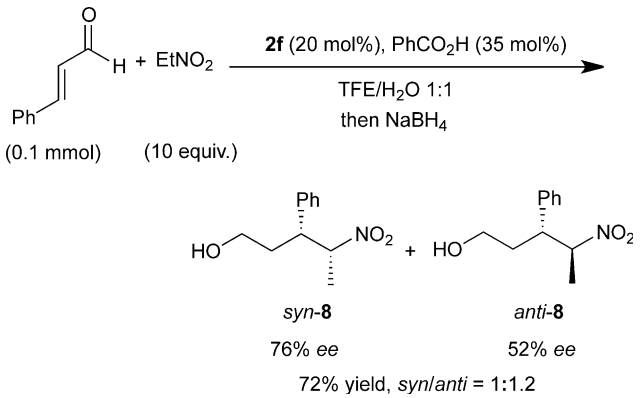
Entry	R′	Product	Time [h]	Yield[b]	*ee*[c]
1	Ph	**7a**	36	88%	95.5%
2	4-$MeOC_6H_4$	**7b**	58	75%	93%
3	4-$NO_2C_6H_4$	**7c**	24	75%	95%
4	4-ClC_6H_4	**7d**	24	82%	95%
5	4-BrC_6H_4	**7e**	24	66%	94%
6	2-$MeOC_6H_4$	**7f**	30	80%	95%
7	2-$NO_2C_6H_4$	**7g**	16	63%	95%
8	3-$MeOC_6H_4$	**7h**	28	80%	87%
9	3-FC_6H_4	**7i**	36	79%	87%
10	1-naphthyl	**7j**	20	65%	94%
11[d]	2-furanyl	**7k**	20	66%	90%
12[d]	Me	**7l**	24	73%	83%
13[d]	Pr	**7m**	18	73%	88%
14[d]	*i*-Bu	**7n**	18	74%	85%

[a] Unless otherwise stated, the reaction was performed employing cinnamaldehyde (0.1 mmol), nitromethane (1 mmol), catalyst **2f** (20 mol%), BA (35 mol%) and TFE/H_2O (1.0 mL, *v*/*v* 1:1) at room temperature.
[b] Isolated yield after reduction to the corresponding alcohol.
[c] Determined by chiral HPLC analysis.
[d] 0.2 mmol substrate was employed.



Scheme 2. Catalyst **2f**-promoted Michael addition of nitroethane to cinnamaldehyde.

temperature. The mixture was stirred until the substrate had disappeared *via* TLC detection. Then 0.5 mL MeOH and $NaBH_4$ (3 equiv.) were added sequentially at 0 °C. After the reaction was completed (about 5 min), a small spoonful of silica gel (about 0.5 g) was added into the system. The resulting mixture was concentrated under vacuum to remove water, MeOH and TFE, and the residue (mainly product on silica gel) was purified through column chromatography on silica gel (petroleum ether:EtOAc = 3:1 to 1.5:1) to yield the desired product **7**.

Acknowledgements

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[10] CCDC 1059289 (compound **2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[11] For the detailed screening works, see the Supporting Information.

[12] The absolute configuration of products was determined by the comparison with **7a** and **7l** in ref.[6l]

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