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Remote Sulfonamido Group Enhances Reactivity and Selectivity for Asymmetric Michael Addition of Nitroalkanes to α,β-Unsaturated Aldehydes

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Abstract: The pyrrolidine–camphorsulfonamide-based catalyst **1a** catalyzes the enantioselective conjugate addition of nitroalkanes to α,β -unsaturated aldehydes in the presence of five equivalents of water in *i*PrOH to give the corresponding chiral Michael adducts in good yields and high enantioselectivities (up to 99% *ee*) with a catalyst loading as low as 1 mol%.

Asymmetric organocatalysis is one of the most rapidly growing research areas in synthetic organic chemistry.^[1] The organocatalytic asymmetric conjugate addition of nitroalkanes to α , β -unsaturated carbonyl compounds to generate a new carbon–carbon bond with concomitant formation of a new stereogenic center is a powerful synthetic method.^[2] This methodology could be applied to the synthesis of biologically important pharmaceuticals and chiral precursors for the synthesis of biological active compounds such as Baclofen,^[3] Pregabalin,^[4] and Rolipram^[2e,5] (Figure 1). Thus,



Figure 1. Biologically active γ-amino acid derivatives.

the development of an efficient chiral organocatalytic system for this reaction has attracted great interest from organic chemists. Currently, a high catalyst loading of diarylprolinol silyl ether and its analogues is required to ensure the Michael adducts with high yields and enantioselectivi-

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ties.^[6] Therefore, there is room for improvement through the development of new and efficient organocatalysts.

As part of our endeavor to develop camphor-derived chiral ligands for the catalytic asymmetric reactions,^[7] we envisaged that the sulfonamido N–H moiety on catalyst **1a** might provide additional assistance in the Michael reaction of nitroalkanes with α , β -unsaturated aldehydes. Initially, the reaction of nitromethane and *trans*-cinnamaldehyde **2a**, with a mole ratio of 3:1 for nitromethane to **2a**, in the presence of catalyst **1a** (10 mol%) and PhCO₂H (10 mol%) in MeOH at 30 °C was examined. The Michael adduct **3a** was obtained in 69% yield and 76% *ee* (Table 1, entry 1). To examine the effect of the N–H moiety from the sulfonamido

Table 1. The examination of catalysts ${\bf 1a-f}$ for the asymmetric Michael reaction of nitromethane to trans-cinnamaldehyde. $^{[a]}$

	H + CHaNOa	catalyst (10 mol%)			
	Ph	MeOH	(0.5 м), 30 °С ⊂ _{Рh}	Ph NO ₂	
	2a (3 equiv) (0.2 mmol)			3a	
Entry	Catalyst	<i>t</i> [h]	Yield [%] ^[b]	ee [%] ^[c]	
1	1 a	24	69	76	
2	1 b	24	70	75	
3	1c	24	61	74	
4	1 d	48	50	7	
5	1e	24	65	62	
6	1f	24	39	1	
7	1 a	48	58	73	

[a] Reaction conditions: cinnamaldehyde (0.2 mmol), nitromethane (0.6 mmol), catalyst (10 mol %), and PhCO₂H (10 mol %) in MeOH (0.4 mL) at 30°C. [b] Yield of isolated product. [c] Determined by HPLC using a Chiracel AD-H column.



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group of 1a, catalysts 1b and 1c were prepared and tested for the reaction. Catalyst 1b, with a CF₃ group at the paraposition of the benzene ring, catalyzed the reaction and gave a similar enantioselectivity and yield (Table 1, entry 2). However, catalyst 1c, with a OMe group at the para-position of the benzene ring, gave a similar enantioselectivity but lower yield. This result might be due to the electron-donating behavior of the OMe group, which could have decreased the assistance of the sulfonamido N-H moiety (Table 1, entry 3). To further examine the influence of the sulfonamido N-H group, catalysts 1d-f were synthesized. When the reaction was catalyzed with N,N-disubstituted sulfonamide catalyst 1d, it gave poor enantioselectivity (Table 1, entry 4). When the reaction was catalyzed with catalyst 1e, in which the hydroxy group at the C4 position of the pyrrolidine ring was removed, it resulted in slightly lower enantioselectivity (62% ee; Table 1, entry 5) as compared with catalyst 1a. The hydroxy group on the catalyst played a minor role in the enantioselective Michael addition. When the reaction was catalyzed by 1 f, in which the sulfonamido group was removed, it resulted in the racemic Michael adduct and a significantly lower yield after 24 h (Table 1, entry 6). This result suggested that the enhancement in the reactivity and enantioselectivity might be due to the hydrogen-bond interactions between the nitroalkane and the sulfonamido N-H moiety of catalyst 1a. To improve the reaction yield of the Michael reaction, the reaction time was prolonged from 24 h to 48 h in the presence of catalyst 1a, however, the yield decreased unexpectedly (Table 1, entry 7). This is presumably due to the formation of side products from the Henry reaction of 2a, 3a and/or iminium intermediates with nitromethane over the prolonged reaction period.

Next, we studied the effect of the solvents and the results are summarized in Table 2. When the reaction was conducted in N,N-dimethylformamide (DMF) at 30°C for 24 h, it afforded **3a** in a poor yield with lower enantioselectivity

Table 2. The effect of solvent on the asymmetric conjugate addition reaction. $\ensuremath{^{[a]}}$

	$\begin{array}{c} O \\ H \\ Ph \end{array} + CH_3NO_2 \\ \hline 2a \\ (0.2 \text{ mmol}) \end{array} (3 \text{ equiv})$	1a (10 mol%) PhCO ₂ H (10 mol%) solvent (0.5 m), 30 °C 24 h	Ph H NO ₂ 3a
Entry	Solvent	Yield [%] ^[b]	<i>ee</i> [%] ^{[c}
1	DMF	33	68
2	CH_2Cl_2	24	92
3	THF	31	94
4	Toluene	41	96
5	MeOH	69	76
6	EtOH	59	95
7	iPrOH	62	97
8	tBuOH	39	<u>> 00</u>

[a] Reaction conditions: cinnamaldehyde (0.2 mmol), nitromethane (0.6 mmol), **1a** (10 mol%), and PhCO₂H (10 mol%) in solvent (0.4 mL) at 30 °C. [b] Yield of isolated product. [c] Determined by HPLC using a Chiracel AD-H column.

(Table 2, entry 1). When the reaction was conducted in solvents such as CH_2Cl_2 , THF, or toluene at 30 °C for 24 h, it gave higher enantioselectivities (92~96% *ee*), but the yields remained low (Table 2, entries 2–4). The reaction was faster in polar protic solvents such as MeOH, EtOH, or *i*PrOH and gave higher yields and enantioselectivities (Table 2, entries 5–7). However, despite achieving >99% enantioselectivity when the reaction was conducted in *t*BuOH, the yield was low. This could be due to the low solubility of the catalyst and substrate in *t*BuOH. The reaction in *i*PrOH was selected for further studies as judged from the yield and enantioselectivity (Table 2, entry 7).

To improve the reaction yield, we turned our attention to study the effect of the acid additive, and the results are summarized in Table 3. When benzoic acid was replaced with acetic acid, the reaction gave a similar yield with the same enantioselectivity. When acid additives such as 4-fluorobenzoic acid, 4-nitrobenzoic acid, and 2,4-dinitrophenol were employed, this resulted in similar enantioselectivity, but lower yields (Table 3, entries 3–5). Interestingly, when the reaction was run in the absence of the acid additive it gave almost the same yield and enantioselectivity (Table 3, entry 6 vs entry 1). Therefore, the reaction without an acid additive was further investigated.

Table 3. The effect of acid additive on the asymmetric conjugate addition reaction.



Entry	Additive	Yield [%] ^[a]	ee [%] ^[b]
1	PhCO ₂ H	62	97
2	AcOH	61	97
3	$4-F-C_6H_4CO_2H$	42	96
4	$4-NO_2-C_6H_4CO_2H$	50	96
5	2,4-dinitrophenol	54	97
6	-	57	97

[[]a] Yield of isolated product. [b] Determined by HPLC using a Chiracel AD-H column.

Based on some previous reports^[8] and our experience, the addition of an appropriate amount of water could accelerate the reaction, and furnish the product in promising yield and stereoselectivity. To explore this effect, five equivalents of water were added to the reaction mixture. It was found that the reaction gave a better yield in a shorter reaction time with excellent enantioselectivity (Table 4, entry 2). Next, we examined the effect of catalyst loading and when the reaction was conducted in the presence of 10 mol%, 5 mol%, 2.5 mol%, or 1 mol% catalyst, it resulted in almost the same enantioselectivity (Table 4, entries 2, and 4–6), and the yield was improved slightly at the expense of the reaction time. When 1 mol% of **1a** was used, the Michael adduct was afforded in 74% yield and 96% *ee* (Table 4, entry 6).

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Table 4. The effect of water and catalyst loading on the asymmetric conjugate addition reaction.



Entry	X [mol %]	<i>t</i> [h]	Yield [%] ^[a]	ee [%] ^[b]
1 ^[c]	10	24	57	97
2	10	12	69	94
3 ^[c]	5	48	69 (75) ^[d]	97
4	5	24	80	95
5	2.5	42	76	94
6	1	48	74 (76) ^[d]	96

[a] Yield of isolated product. [b] Determined by HPLC using a Chiracel AD-H column. [c] No water was added. [d] Yields in parenthesis are based on recovered starting material.

In light of the above observations, we investigated the substrate scope for the asymmetric catalytic conjugate addition reaction of nitromethane with α , β -unsaturated aldehydes **2a–I** using the reaction conditions reported in Table 4 (entry 6). The results showed that the reaction of β -aryl acrylaldehyde with nitromethane gave moderate-to-good yields with high *ee*, except for 4-nitro cinnamaldehyde (Table 5, entries 1–10). The decrease in reaction rate and lower enantioselectivity for 4-nitro cinnamaldehyde is presumably due to its poor solubility in *i*PrOH (Table 5, entry 5). Cinnamaldehyde derivatives with a OMe group at a president of the 2 - and the context of the 2 - and the context of the

either the 2-, 3-, or 4-position of the phenyl ring gave moderate reaction yields (60–64%) and high enantioselectivities (95– 99%) when 2 mol% of **1a** was used as the catalyst (Table 5, entries 7–9). The addition of nitromethane to β -substituted α , β -unsaturated aliphatic aldehydes such as crotonaldehyde,

2-pentenal, 4-methyl-2-pentenal also gave high enantioselectivities (91–97%) when 5 mol% of **1a** was used, albeit the yields were lower (Table 5, entry 11–13).

Previously, it has been reported that the diastereoselectivities are poor in the reaction of nitroethane and nitropropane with cinnamaldehyde.^[6a,b,d,e,g] In light of our previous results, we investigated the reaction of nitroethane and nitropropane with cinnamaldehyde using **1a** as the catalyst. The reaction gave the desired products **3m** in 40% yield with high enantioselectivities for both *syn* and *anti* diastereomers in the presence of 1 mol% of **1a**. The reaction yield could be improved to 60% for nitroethane with high enantioselectivities (96% for *syn*, and 90% for *anti*), and for nitropropane in 62% yield with good enantioselectivities (88% for *syn*, and 84% for *anti*) when using 2 mol% of **1a** in the catalytic system. Although the enantioselectivities in our system were good, the diastereoselectivities remained similar to the previous reports [Eq. (1)]. This may be beTable 5. Catalyst ${\bf 1a}\mbox{-}promoted conjugate addition of nitromethane to <math display="inline">\alpha,\beta\mbox{-}unsaturated aldehydes.}^{[a]}$



Entry	R	Product	<i>t</i> [h]	Yield [%] ^[b]	ee [%] ^[c]
1	Ph	3a	48	75 (80) ^[f]	96
2	4-F-Ph	3b	48	60 (86) ^[f]	94
3	4-Cl-Ph	3c	48	77 (84) ^[f]	94
4	4-Br-Ph	3 d	48	64 (83) ^[f]	97
5	4-NO ₂ -Ph	3e	72	61 (65) ^[f]	80
6	4-MeO-Ph	3 f	48	46 (68) ^[f]	98
7 ^[d]	4-MeO-Ph	3 f	48	62 (76) ^[f]	97
8 ^[d]	3-MeO-Ph	3g	48	$64 \ (82)^{[f]}$	99
9 ^[d]	2-MeO-Ph	3h	48	60 (76) ^[f]	95
10	2-furanyl	3i	48	48 (75) ^[f]	94
11 ^[e]	Ме	3 j	72	48	94
12 ^[e]	Et	3k	72	53	91
13 ^[e]	<i>i</i> -Pr	31	72	56	97

[a] Reaction conditions: α,β -unsaturated aldehyde (0.4 mmol), nitromethane (1.2 mmol), **1a** (1 mol%), and H₂O (5 equiv) in *i*PrOH (0.8 mL) under 30°C. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis (see the Supporting Information). [d] Catalyst **1a** (2 mol%) was used. [e] Catalyst **1a** (5 mol%) was used. [f] Yields in parenthesis are based on recovered starting material.

cause the conformational energies of both faces of the substituted nitronate toward the iminium ion in the transition states are comparable.



3m: R= Me, X=1, 40% (90% brsm), syn/anti= 52:48, 94% ee (syn), 89% ee (anti) 3m: R= Me, X=2, 60% (93% brsm), syn/anti= 57:43, 96% ee (syn), 90% ee (anti) 3ln: R= Et, X=2, 62% (96% brsm), syn/anti= 52:48, 88% ee (syn), 84% ee (anti)

A plausible mechanism for the asymmetric Michael addition of nitroalkane to α,β -unsaturated aldehydes is shown in Scheme 1. At the outset, catalyst **1a** and α,β -unsaturated aldehydes formed the iminium ion, which then reacted with the nitronate. Hydrogen-bond interactions existed between the nitronate and the hydroxy group of catalyst **1a**, nitronate and the sulfonamido group of catalyst **1a** at the transition state. The addition of nitronate to α,β -unsaturated aldehydes was favored from the *Si*-face. Finally, the Michael adduct **3** was obtained after work up.

In conclusion, we have demonstrated that the remote sulfonamido group is able to enhance the asymmetric catalytic Michael addition reaction of nitroalkanes to α , β -unsaturated aldehydes. This catalytic system could be conducted in the absence of acid additive to produce the desired product with up to 99% *ee* and good yields unlike other catalytic systems that required acid additive.^[6a-c,f-i,k] In addition, the advantage of this catalytic system is that it gives high yields and



Scheme 1. A plausible mechanism for the asymmetric Michael reaction.

enantioselectivity with low catalyst loading (1–2 mol %).^[1i] Although the mechanism remains to be understood for the catalytic efficiency in alcoholic solvents, this catalytic system may provide some information for the development of new organocatalysts.

Experimental Section

General procedure for the asymmetric conjugate addition of nitroalkanes to α , β -unsaturated aldehydes (Table 5)

 α ,β-Unsaturated aldehyde (0.4 mmol), nitroalkane (1.2 mmol), catalyst **1a** (0.004 mmol), and H₂O (2.0 mmol) were added to a solution of *i*PrOH (0.8 mL). The reaction mixture was stirred at 30 °C for the time indicated in Table 5, and was then quenched by the addition of saturated NH₄Cl(aq). The mixture was extracted with ethyl acetate (3×10 mL), and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated to give the crude product, which was purified by column chromatography (ethyl acetate/hexanes=1:3) to yield the corresponding adduct.

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Keywords: asymmetric synthesis \cdot michael addition \cdot nitroalkane \cdot organocatalysis $\cdot \alpha, \beta$ -unsaturated aldehyde

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