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Highly efficient and enantioselective Michael addition of acetylacetone to nitroolefins catalyzed by chiral bifunctional organocatalyst bearing multiple hydrogen-bonding donors

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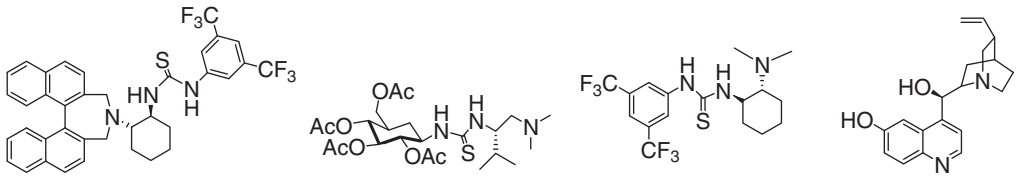
ABSTRACT

A new efficient catalyst system for the asymmetric addition of acetylacetone to nitroolefins using a chiral bifunctional organocatalyst bearing multiple hydrogen-bonding donors was developed. When using the organocatalyst **2c** derived from natural *cinchona* alkaloid in optimal conditions, up to 98% chemical yield and 98% ee were observed with a variety of aromatic nitroolefins.

Asymmetric Michael addition of ketones/aldehydes to nitroalkenes is one of the most powerful carbon–carbon bond-forming reactions, since the resulting γ-nitrocarbonyl compounds are versatile synthetic building blocks, which can be readily converted into valuable chiral structural scaffolds.[1] In the past decades, remarkable progress has been made in developing efficient asymmetric Michael addition by using chiral metal complexes[2] and transition metal-free organocatalysts.[3] Of the development of organocatalysts, small chiral molecules bearing hydrogen bonding donors have emerged as an important and popular approach in enantioselective catalysis.[4] Chiral bifunctional organocatalysts (Fig. 1) are among the most successful organocatalysts in asymmetric Michael addition reactions,[5] since they would facilely activate the electrophile and the nucleophile simultaneously by the hydrogen bond. In many cases, catalyst loading of 15–30 mol % is usually required to achieve good isolated yields and high enantioselectivities.[6,1f,3h] Therefore, the development of highly efficient and enantioselective chiral catalysts for a broad scope of substrates at low catalyst loading is still in great demand.

As a part of our ongoing program to develop facile and effective chiral catalysts for asymmetric transformations,[7] we were interested in investigating chiral bifunctional amine–thioureas with multiple hydrogen bonding donors[8] based on the 'privilege' skeleton, *cinchona* alkaloids, which use sp^3 nitrogen of the *cinchona* alkaloids as the tertiary amine moiety to activate acetylacetone, while both the thiourea moiety and the hydroxyl group in β-amino



1a 1b 1c 1d

Figure 1. Examples of chiral bifunctional organocatalysts used for Michael addition.

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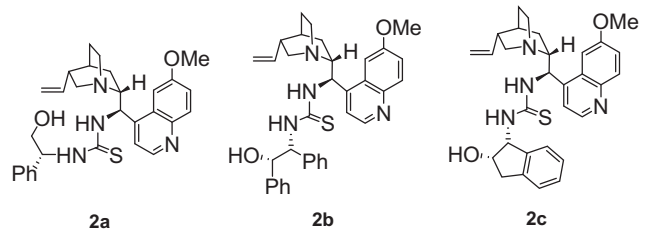
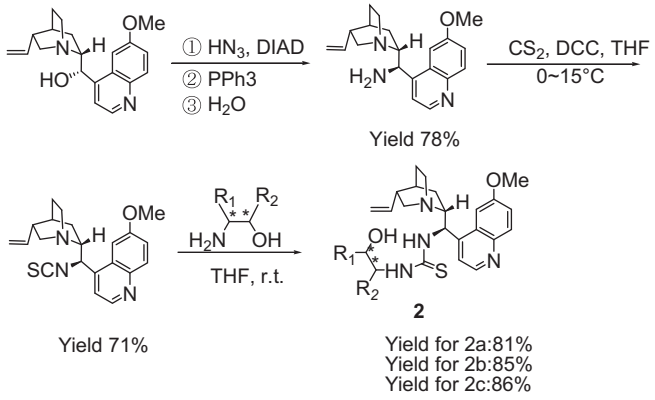


Figure 2. Chiral organocatalysts **2a–c** derived from natural *cinchona* alkaloid.



Scheme 1. General synthetic route for organocatalysts **2a–c**.

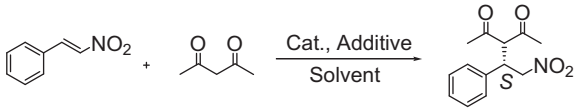
alcohol serve as the hydrogen bonding donors to activate the nitro group. We anticipate that the organocatalysts with multiple hydrogen bonding donors would show high regioselectivity and enantioselectivity in Michael addition. In this Letter, we wish to communicate our investigation on the asymmetric addition of nitroolefins to acetylacetone using bifunctional organocatalyst **2a–c** (Fig. 2) derived from natural *cinchona* alkaloid.

Chiral organocatalysts **2a–c** were synthesized from natural *cinchona* alkaloid quinine as shown in Scheme 1. 9-Amino-(9-deoxy)-epiquinine was synthesized according to the known procedure.[9] Then it was reacted with carbon disulfide and DCC in THF to obtain the isothiocyanate intermediate. The synthesis of thiourea organocatalysts **2** can be conducted by treatment of isothiocyanate with the corresponding chiral β-amino alcohol.[10,11]

When these organocatalysts **2a–c** were examined in the asymmetric Michael addition reactions between acetylacetone and a-nitrostyrene (**3a**) in CH_2Cl_2 at −30 °C for 24 h, high yields, and moderate enantioselectivities were achieved and **2c** gave the best enantioselectivities (Table 1, entries 1–3).

After selecting **2c** as the most efficient catalyst, we proceeded to investigate the influence of different experimental parameters including additive, temperature, solvent, and catalyst loading in the asymmetric Michael addition reaction. The results were also summarized in Tables 1. It has been reported that the presence of additive has a significant influence on the asymmetric reaction.[12] When using KI, KF, and NaCl as additives, both yields and ee value were inferior (Table 1, entries 4–6 vs 3). When TFA was used, the reaction became sluggish and no enantioselectivity was observed (Table 1, entry 7). As the literature reported,[13] the

Table 1
Optimization of reaction conditions for asymmetric Michael addition reactions between 1,3-carbonyl compounds (**4**) and a-nitrostyrene (**3a**)[a]

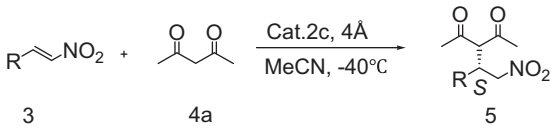


3a 4a 5a

Entry	Catalyst	Catalyst loading (mol %)	Michael donors	Additive	Solvent	Time (h)	Temperature (°C)	Yield[c] (%)	ee[d] (%)	Product config.[e]
1	2a	10	**4a**	—	CH_2Cl_2	24	−30	71	25	S
2	2b	10	**4a**	—	CH_2Cl_2	24	−30	80	15	S
3	2c	10	**4a**	—	CH_2Cl_2	24	−30	91	56	S
4	2c	10	**4a**	KI	CH_2Cl_2	24	−30	30	35	S
5	2c	10	**4a**	KF	CH_2Cl_2	24	−30	44	46	S
6	2c	10	**4a**	NaCl	CH_2Cl_2	24	−30	56	26	S
7	2c	10	**4a**	TFA	CH_2Cl_2	24	−30	10	rac	S
8	2c	10	**4a**	MS4Å[b]	CH_2Cl_2	24	−30	94	60	S
9	2c	10	**4a**	MS4Å[b]	CH_2Cl_2	15	−20	95	57	S
10	2c	10	**4a**	MS4Å[b]	CH_2Cl_2	10	0	96	51	S
11	2c	10	**4a**	MS4Å[b]	CH_2Cl_2	24	−40	90	66	S
12	2c	10	**4a**	MS4Å[b]	$CHCl_3$	24	−40	97	21	S
13	2c	10	**4a**	MS4Å[b]	Et_2O	24	−40	93	41	S
14	2c	10	**4a**	MS4Å[b]	EtOH	24	−40	75	71	S
15	2c	10	**4a**	MS4Å[b]	THF	24	−40	90	79	S
16	**2c**	**10**	**4a**	**MS4Å[b]**	**MeCN**	**24**	**−40**	**93**	**98**	**S**
17	2c	10	**4a**	MS4Å[b]	toluene	24	−40	78	31	S
18	2c	10	**4a**	MS4Å[b]	DMF	24	−40	26	9	S
19	2c	20	**4a**	MS4Å[b]	MeCN	24	−40	96	91	S
20	2c	5	**4a**	MS4Å[b]	MeCN	24	−40	91	90	S
21	2c	2	**4a**	MS4Å[b]	MeCN	24	−40	90	90	S
22	2c	1	**4a**	MS4Å[b]	MeCN	24	−40	83	85	S
23	2c	10	**4b**[f]	MS4Å[b]	MeCN	24	−40	20	10	S
24	2c	10	**4c**[g]	MS4Å[b]	MeCN	24	−40	95	75	S

[a] The Unless otherwise specified, reaction was carried out with 2 equiv of 1,3-carbonyl compounds **4** and 1 equiv of a-nitrostyrene **3a** in the presence of catalyst and additive on a scale of 0.1 mmol of **3a** in 1 mL solvent.
[b] 20 mg MS4Å.
[c] Isolated yields.
[d] Enantiomeric excess (ee) was determined by chiral HPLC analysis (Chiralpak AD–H).
[e] Absolute configuration was determined by comparison with available literature HPLC data.[14,15]
[f] **4b** is diethyl malonate.
[g] **4c** is ethyl acetoacetate.

Table 2
Asymmetric Michael addition of acetylacetone with different nitroolefins catalyzed by organocatalyst **2c**[a]



3 4a 5

Entry	R	Time (h)	Yield[b] (%)	ee[c] (%)
1	Ph (**3a**)	24	93 (91[d])	98 (90 [d])
2	4-F–C_6H_4 (**3b**)	24	85 (80[d])	95 (94 [d])
3	4-Cl–C_6H_4 (**3c**)	24	91 (84[d])	94 (92 [d])
4	3-Cl–C_6H_4 (**3d**)	24	93 (90[d])	97 (96 [d])
5	2-Cl–C_6H_4 (**3e**)	24	95 (93[d])	99 (95 [d])
6	4-Br–C_6H_4(**3f**)	24	80 (75[d])	89 (87 [d])
7	4-Me–C_6H_4(**3g**)	24	75 (67[d])	90 (90 [d])
8	4-MeO–C_6H_4 (**3h**)	24	98 (95[d])	92 (89 [d])
9	2-MeO–C_6H_4(**3i**)	24	83 (77[d])	96 (95 [d])
10	4-NO_2–C_6H_4 (**3j**)	24	89 (66[d])	88 (87 [d])
11	4-CF_3–C_6H_4 (**3k**)	72	76	89
12	2-Furyl (**3l**)	36	87 (79[d])	87 (90 [d])
13	1-Naphthyl (**3m**)	36	94 (87[d])	96 (96 [d])
14	PhCH=CH– (**3n**)	72	46	82
15	$PhCH_2CH_2$– (**3o**)	72	28	74

[a] The reaction was carried out with 2 equiv of acetylacetone and 1 equiv of **3** in the presence of 10 mol % of **2c** at −40 °C on a scale of 1 mmol of **3a**.
[b] Isolated yields.
[c] Enantiomeric excess (ee) was determined by chiral HPLC analysis (Chiralpak AD–H).
[d] 5 mol % catalyst **2c** was used.

addition of 4 Å molecular sieves improved the yield and enantiomeric excess (Table 1, entry 8 vs 3). The reaction temperature also plays a very important role in the chiral induction (Table 1, entries 8–11). Apparently, decreasing the temperature to −40 °C led to a higher ee value (Table 1, entry 11).

Different solvents also led to different enantio excess value. When using acetonitrile as solvent, the enantioselectivity increased dramatically and up to 98% ee was obtained (Table 1, entry 16). Acetonitrile was also superior to other tested solvents, such as $CHCl_3$, Et_2O, EtOH, THF, toluene, and DMF(Table 1, entries 11–18), resulting in both excellent yield and enantioselectivity.

In order to evaluate the efficiency of chiral bifunctional organocatalyst **2c** in the Michael addition of acetylacetone to nitroolefins, different catalyst loadings (1, 2, 5, 10, 20 mol %) were also tested. Increasing of catalyst loading from 10% to 20% led to an obvious loss of stereocontrol[15] (Table 1, entry 19 vs 16). When using the lower catalyst loading 2% and 5%, good enantioselectivities were also obtained (90% ee) as expected (Table 1, entries 19–21). We also examined diethyl malonate and ethyl acetoacetate as Michael donors, but lower enantioselectivities were observed (Table 1, entries 23 and 24).

Through extensive screening, the optimized reaction conditions of the Michael addition of acetylacetone to nitroolefins were set up (catalyst **2c**, acetonitrile as solvent, 4 Å molecular sieves as additive, −40 °C). We then examined the scope and limitations of the enantioselective Michael addition. A variety of nitroolefins were examined and two different catalyst loadings (5 mol %, 10 mol %) were tested for most substrates. In general, good to excellent chemical yields and enantioselectivity were achieved with both the electron-donating group (Table 2, entries 7–9) and electron-withdrawing group (Table 2, entries 2–6 and 10) on the phenyl ring. Moreover, nitroolefins with furyl and naphthyl moiety (Table 2, entries 12 and 13) also gave high yields and ee's. It is also worth mentioning that, **3k** with trifluoromethyl group on the phenyl ring (Table 2, entry 11) needed longer reaction time, the result was still good. However, the aliphatic nitroolefins **3n** and **3o** (Table 2, entries 14 and 15) gave poor chemical yields and moderate enantioselectivities. Table 2 also indicated that, for most substrates, lower catalyst loading (5 mol %) still showed excellent enantioselectivity.

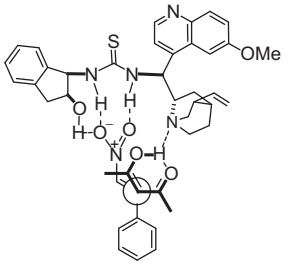


Figure 3. Proposed transition state model through multiple hydrogen bonding activations.

A plausible catalytic mode representing the Michael addition of acetylacetone to nitroolefins in the presence of **2c** as a catalyst is shown in Figure 3, in which a thiourea moiety of the catalyst **2c** interacts through hydrogen bonding with a nitro group of the nitroolefins, meanwhile the hydroxyl group of the indanol and the nitro group may form another hydrogen bond, which enhances the electrophilicity of the nitroolefins. On the other hand, the tertiary amine of azabicyclo in the quinine deprotonates an acidic proton of acetylacetone, generating a ternary complex. The synergistic steric hindrance from both moieties (*cinchona* alkaloid moiety and the amino alcohol moiety) of the chiral bifunctional catalyst **2c** might be helpful for the increased stereocontrol of the Michael addition reaction. The multiple hydrogen bonding interactions may be responsible for the high catalytic activity and low catalyst loading of this organocatalyst. Nevertheless, the real catalytic mechanism still needs further investigation.

In summary, we have developed an efficient catalyst system for the asymmetric addition of acetylacetone to nitroolefins using bifunctional organocatalyst bearing multiple hydrogen-bonding donors. In optimal conditions, organocatalyst **2c** showed high efficiency and excellent enantioselectivity, affording the desired products with levels of enantioselectivity of up to 98% ee. Further detailed catalytic mechanism and catalytic performance in other asymmetric reactions using this type of *cinchona* alkaloid organocatalysts are currently being investigated.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.04.043.

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10. *Spectrum data of* **2a**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.69 (d, 1H), 7.98 (d, 1H), 7.66 (s, 1H), 7.33–7.38 (m, 5H), 7.15 (s, 2H), 5.60-5.63 (q, 1H), 5.16 (s, 1H), 4.91–4.95 (t, 2H), 3.93–3.97 (s, 3H), 3.78–3.80 (d, 1H), 3.86–3.70 (d, 1H), 2.91–2.94 (m, 3H), 2.54 (s, 3H), 2.22 (s, 3H), 1.53–1.61 (d, 4H), 1.32 (ddd, 1H), 0.90 (d, 1H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 181.87, 156.88, 147.46, 146.05, 144.08, 142.88, 141.91, 141.33, 131.11, 127.98, 127.84, 126.94, 126.81, 126.79, 126.49, 121.11, 114.17, 103.02, 67.24, 64.60, 59.47, 58.94, 57.18, 55.59, 55.17, 40.76, 27.36, 27.07, 25.47 ppm. IR (CH_2Cl_2): 3246, 3061, 3030, 2866, 1663, 1622, 1589, 1545, 1473, 1454, 1433, 1362, 1263, 1229, 1062, 1029, 920, 854, 829, 735, 702 cm^{-1}.HRMS (*m*/*z*, ESI$^+$) (free base) calcd for $C_{29}H_{34}N_4O_2S$ $(M+H)^+$503.2475, found 503.2484. Spectrum data of **2c**: ^{1}H NMR ($CDCl_3$,400 MHz): δ = 8.75 (d, 1H), 8.03 (dd, 2H), 7.80 (s, 1H), 7.38 (s, 1H), 7.13 (dd, 2H), 6.89 (s, 2H), 6.38 (s, 1H), 5.73 (dd, 2H), 5.03 (dd, 2H), 4.63 (s, 1H), 4.00 (s, 5H), 3.78 (s, 1H), 3.41(d, 1H), 3.06 (d, 1H), 2.85 (d, 2H), 2.71 (d, 2H), 2.29 (s,1H), 1.68 (s, 3H),1.44 (s, 1H),1.25 (s, 1H),0.78 (s, 1H) ppm. ^{13}C NMR (100 MHz, MeOD): δ = 184.46, 159.84, 148.35, 145.28, 142.25, 142.06, 141.80, 131.17, 130.15, 128.81, 127.67 (2C), 126.17 (2C), 124.87, 124.12, 115.35, 104.41, 73.90, 64.18, 61.70, 56.86, 56.73, 43.39, 49.02, 40.47, 39.80, 28.66, 28.13, 27.22 ppm. HRMS (*m*/*z* −ES) (free base) calcd for $C_{30}H_{34}N_4O_2S$ $(M+H)^+$ 515.2475, found 515.2485.
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