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Asymmetric Michael reactions of α,α-disubstituted aldehydes with maleimides using a primary amine thiourea organocatalyst

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ABSTRACT

Primary amine thiourea organocatalyst **8** was used to promote Michael additions of bulky α,α-disubstituted aldehydes, such as isobutyraldehyde with maleimides to afford the corresponding adducts in high to excellent yields and with up to 91% ee.

1. Introduction

Chiral α-substituted succinimides have attracted a great deal of attention because related compounds play an important role as building blocks in synthetic and medicinal chemistry.[1] The asymmetric Michael reaction of maleimides using an organocatalyst is one of the most practical synthetic procedures for effectively obtaining chiral α-substituted succinimides. Many asymmetric Michael additions of maleimides with a variety of nucleophiles promoted by organocatalysts have been reported.[2] However, reports with aldehydes as nucleophiles are rare.[3–5] Although Córdova et al. have reported asymmetric Michael reactions of maleimides with aldehydes using diphenylprolinol silyl ether **1** as a catalyst, only moderate enantioselectivity and chemical yield were obtained when bulky α,α-disubstituted aldehydes such as isobutyraldehyde were employed as nucleophiles (Fig. 1).[3] In recent years, three research groups have reported efficient asymmetric Michael additions of α,α-disubstituted aldehydes to maleimides using thiourea organocatalysts **2** and **3** derived from 1,2-cyclohexanediamine as the chiral source.[4] We recently reported recyclable organocatalyst **4** which introduced a fluorous tag into a thiourea organocatalyst.[5] Only thiourea organocatalysts **2**–**4** derived from 1,2-cyclohexanediamine as the chiral source can successfully promote Michael reactions of maleimides with bulky α,α-disubstituted aldehydes, despite the utility of the resulting products as synthetic building blocks.[1] Therefore, the development of a novel organocatalyst for Michael reactions of maleimides with α,α-disubstituted aldehydes remains a challenging research theme in organic chemistry.

We recently reported direct aldol reactions in brine, catalyzed by chiral β-aminosulfonamides **5** and **6** derived from L-phenylalanine, which is a commercially available and inexpensive natural amino acid.[6] Moreover, we had also developed recyclable organocatalyst **7** with a fluorous tag which promoted direct aldol reactions in brine.[7] We found that the simple skeleton of phenylalanine with only one stereogenic center is suitable for organocatalyzed asymmetric reactions. To further demonstrate the usefulness of the phenylalanine structure as an organocatalyst, we attempted to develop a novel organocatalyst, which introduced a 3,5-bis(trifluoromethyl)phenylthiourea group instead of a trifluoromethanesulfonamide group of **6**, because it was reported that primary amine thiourea organocatalysts are preferable to primary amine sulfonamide organocatalysts for Michael reactions of maleimides with aldehydes.[4a,b] Herein, we describe the asymmetric Michael reactions of maleimides with α,α-disubstituted aldehydes using a simple organocatalyst thiourea **8** prepared from L-phenylalanine.

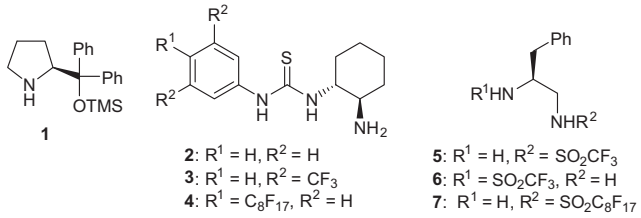

Figure 1. Structure of organocatalysts.

2. Results and discussion

Thiourea **8**, an organocatalyst for the Michael reactions, was prepared as shown in Scheme 1. Treatment of compound **9**, which is an intermediate for the preparation of organocatalyst **6**,[6b] with 3,5-bis(trifluoromethyl)phenyl isothiocyanate in THF afforded thiourea **10**. The azide group of **10** was then reduced with triphenylphosphine in THF–H_2O to give the desired organocatalyst thiourea **8** in 75% yield (two steps).

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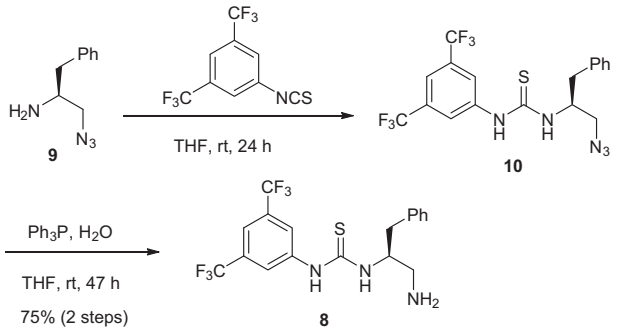
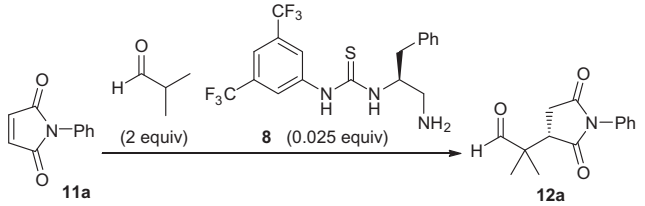


Scheme 1. Preparation of organocatalyst.

The reaction conditions were optimized for the enantioselective Michael reactions using **8** as shown in Table 1. Michael reactions were performed using *N*-phenylmaleimide **11a** and isobutyraldehyde (2 equiv) as test reactants in the presence of catalytic amounts of **8**. The representative solvents were examined at room temperature (entries 1–3). Dichloromethane was found to be the most suitable solvent and high enantioselectivity (90% ee) was obtained (entry 3). Adding H_2O (0.15 equiv) and conducting the reaction at 0 °C under similar conditions resulted in a decrease of stereoselectivities (entries 4–6). The addition of benzoic acid (0.025 equiv) also resulted in a reduction of enantioselectivity (entry 7). Increasing the catalyst loading to 0.05 equiv shortened the reaction time while retaining the high enantioselectivity (entry 8). Therefore, by considering the reaction time, the optimal conditions were determined to be 0.05 equiv of **8** in dichloromethane at room temperature. As expected, both sulfonamide catalysts **5** and **6** are poor catalysts for the Michael reaction of maleimides with aldehydes under similar reaction conditions (entries 9 and 10).

Table 1
Optimization of reaction conditions

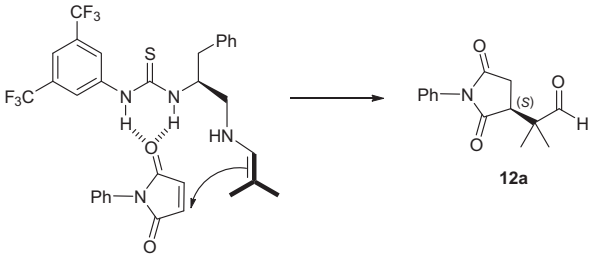


Entry	Solvent	H_2O (equiv)	Temp	Time (h)	Yield[a]	% ee[b]
1	THF	—	rt	48	45	69
2	Toluene	—	rt	48	42	76
3	CH_2Cl_2	—	rt	48	71	90
4	CH_2Cl_2	0.15	rt	48	96	83
5	CH_2Cl_2	—	0 °C	67	36	84
6	CH_2Cl_2	0.15	0 °C	67	68	84
7[c]	CH_2Cl_2	—	rt	48	83	70
8[d]	CH_2Cl_2	—	rt	24	96	88
9[e]	CH_2Cl_2	—	rt	48	15	65
10[f]	CH_2Cl_2	—	rt	48	40	30

[a] Isolated yields.
[b] Determined by HPLC analysis.
[c] Benzoic acid (0.025 equiv) was added.
[d] 0.05 equiv of **8** was used.
[e] Organocatalyst **5** (0.025 equiv) was used instead of **8**.
[f] Organocatalyst **6** (0.025 equiv) was used instead of **8**.

To examine the scope and limitations of the reaction substrates, we next investigated the Michael reaction of various maleimides and aldehydes under the optimal conditions (Table 2). We selected methoxy and methyl substituents as the representative electron-donating group, and nitro and halogen substituents as the electron-withdrawing groups on the benzene ring of the maleimide. The reactions of maleimides **11b–e** with isobutyraldehyde smoothly gave the corresponding adducts **12b–e** in high to excellent yields with 75%–83% ee (entries 2–5). *N*-Benzylmaleimide **11f** successfully coupled with isobutyraldehyde, to afford adduct **12f** in 96% yield with the highest enantioselectivity (91% ee) (entry 6). Next, we examined the Michael reaction of *N*-phenylmaleimide **11a** with various types of aldehydes. The reactions of cyclohexanecarboxaldehyde and cyclopentanecarboxaldehyde, which are aldehydes with a cyclic structure, were performed in the presence of 0.1 equiv of **8** to afford the corresponding adducts **12g** and **12h** in high yields with 65% and 79% ee, respectively (entries 7 and 8). Organocatalyst **8** catalyzed the reactions of the linear aldehyde decanal with **11a** to afford the corresponding adduct **12j** in high yield with moderate enantioselectivity and low diastereoselectivity (entry 10). The stereochemistries of the Michael reaction products obtained using **8** were determined by comparison with the literature chiral-phase HPLC retention times and the specific rotation data.[4]

We can infer that the Michael reactions of aldehydes with maleimides using organocatalyst **8** proceed via a transition state similar to that proposed by Xu et al.,[4c] which is based on the stereochemistry of products **12**. A plausible reaction mechanism for Michael reaction is proposed in Scheme 2. From this hypothesis, the primary amino group of **8** condenses with the aldehyde to generate the enamine intermediate. Then, the two acidic protons of the thiourea group of **8** coordinate to the carbonyl oxygen of the maleimide to control the direction of approach of the maleimides to the enamine intermediate, affording the corresponding addition products **12** with an (*S*)-configuration.



Scheme 2. Proposed transition state model of Michael reaction.

3. Conclusion

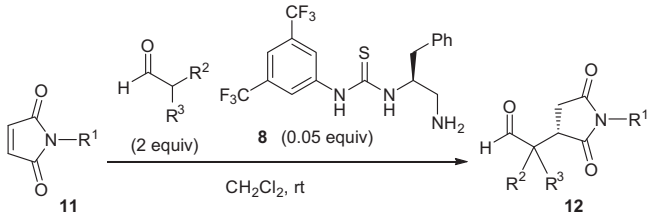
In conclusion, novel organocatalyst thiourea **8** bearing a primary amino group can be easily prepared from L-phenylalanine, a commercially available, inexpensive natural amino acid. The simple primary amine thiourea **8**, which has only one stereogenic center, functions as an efficient catalyst for the Michael reactions of various aldehydes with maleimides in dichloromethane to give the corresponding adducts **12** in high to excellent yields and with high enantioselectivities. Further applications of this process to the synthesis of bioactive compounds and to novel reactions are currently in progress in our laboratory.

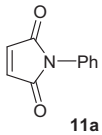
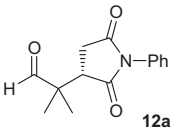
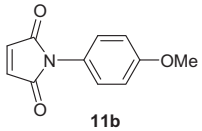
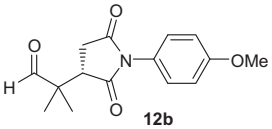
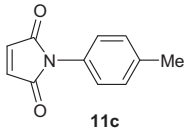
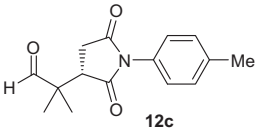
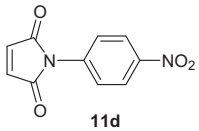
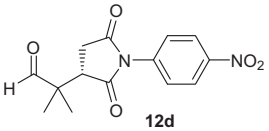
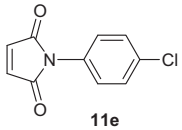
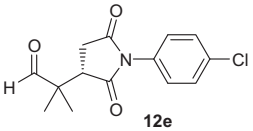
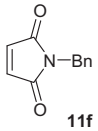
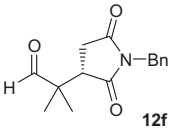
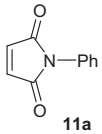
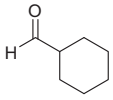
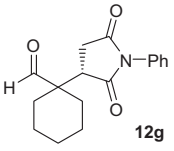
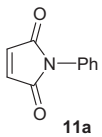
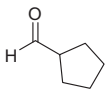
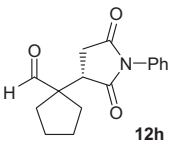
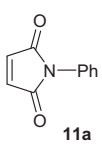
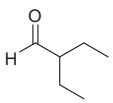
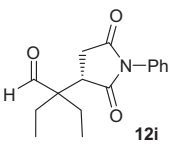
4. Experimental

4.1. General

^{1}H NMR and ^{13}C NMR spectra were measured with a JEOL AL 400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR), or JEOL ECA-500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). The chemical shifts are expressed in ppm downfield from tetramethylsilane ($\delta = 0.00$) as an internal standard. The high-resolution mass spectra (HRMS) of the compounds

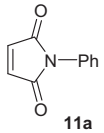
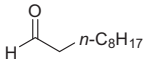
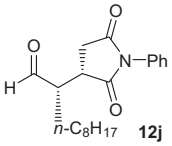
Table 2
Michael reactions of various maleimides with aldehyde in the presence of **8**



Entry	Maleimide	Aldehyde	Product	Time (h)	Yield[a] (%)	% ee[b]
1	 **11a**		 **12a**	24	96	88
2	 **11b**		 **12b**	48	96	83
3	 **11c**		 **12c**	48	85	75
4	 **11d**		 **12d**	48	87	77
5	 **11e**		 **12e**	46	81	82
6	 **11f**		 **12f**	48	96	91
7[c]	 **11a**		 **12g**	168	90	65
8[c]	 **11a**		 **12h**	25	98	79
9[c]	 **11a**		 **12i**	144	79	60

(*continued on next page*)

Table 2 (*continued*)

Entry	Maleimide	Aldehyde	Product	Time (h)	Yield[a] (%)	% ee[b]
10[c]	 **11a**		 **12j**	168	87[d]	42 (28)[e]

[a] Isolated yields.
[b] Determined by HPLC analysis.
[c] 0.1 equiv of **8** was used.
[d] The ratio of *syn* and *anti* isomers was 56:44.
[e] Enantio excess of *syn* isomer. Enantio excess of *anti* isomer in parentheses.

were recorded using a LEOL JMS-T100TD (ESI-TOF-MS) spectrometer. For thin layer chromatographic (TLC) analyses, Merck precoated TLC plates (Silica Gel 60 F_{254}, Art 5715) were used. The products were isolated by flash column chromatography on silica gel (Kanto Chemical, silica gel 60N, spherical, neutral, 40–50 μm).

4.2. Preparation of the organocatalyst

4.2.1. (*S*)-1-(1-Azido-3-phenylpropan-2-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea 10

To a solution of (*S*)-1-azido-3-phenylpropan-2-amine **9**[6b] (570 mg, 3.23 mmol) in dry THF (9 mL) was added 3,5-bis (trifluoromethyl)phenyl isothiocyanate (590 μL, 3.23 mmol) at rt under an argon atmosphere. After stirring for 24 h, the reaction mixture was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with a 4:1 mixture of hexane and AcOEt to afford pure **10** (1.44 g, 100%) as a colorless powder. Mp = 97–99 °C; $[\alpha]_D^{22} = +4.8$ (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.85 (dd, *J* = 8.0, 13.7 Hz, 1H), 3.03 (dd, *J* = 6.3, 13.7 Hz, 1H), 3.44 (d, *J* = 12.0 Hz, 1H), 3.68 (dd, *J* = 4.0, 12.0 Hz, 1H), 4.87 (br s, 1H), 6.39 (br s, 1H), 7.20–7.32 (m, 5H), 7.69 (s, 2H), 7.72 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 37.3, 52.3, 55.3, 119.7, 122.6 (q, $^1J_{C\text{-}F}$ = 274 Hz), 124.0, 127.1, 128.9, 129.0, 133.1 (q, $^2J_{C\text{-}F}$ = 33.6 Hz), 136.2, 138.3, 179.8; HRMS (ESI-TOF): calcd for $C_{18}H_{16}F_6N_5S$ $(M+H)^+$: 448.1025, found: 448.1007.

4.2.2. (*S*)-1-(1-Amino-3-phenylpropan-2-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea 8

To a solution of **10** (1.44 g, 3.23 mmol) in dry THF (36 mL) were added PPh_3 (1.05 g, 4.01 mmol) and H_2O (197 μL, 10.9 mmol) at rt. After stirring for 47 h at rt, the reaction mixture was evaporated. The residue was purified by flash column chromatography on silica gel with a 9:1:0.08 mixture of $CHCl_3$, MeOH and H_2O to give pure **8** (1.02 g, 75%) as a colorless powder. Mp = 41–43 °C; $[\alpha]_D^{20} = -57.6$ (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, CD_3OD): δ = 2.75 (dd, *J* = 13.2, 7.5 Hz, 1H), 2.85–2.91 (m, 3H), 2.95 (br s, 1H), 7.20 (m, 1H), 7.30 (m, 6H), 7.26 (s, 1H); ^{13}C NMR (125 MHz, CD_3OD): δ = 39.0, 45.2, 58.5, 117.9, 123.8, 124.7 (q, $^1J_{C\text{-}F}$ = 272 Hz), 127.5, 129.5, 130.3, 132.6 (q, $^2J_{C\text{-}F}$ = 33.6 Hz), 139.3, 143.1, 183.1; HRMS (ESI-TOF): calcd for $C_{18}H_{18}F_6N_3S$ $(M+H)^+$: 422.1120, found: 422.1097.

4.3. Typical procedure for a Michael reaction using organocatalyst 8 (Table 2)

A typical procedure for a Michael reaction using **8** and **11a** is as follows: to a solution of thiourea organocatalyst **8** (16.8 mg, 40.0 μmol) in 1 mL of CH_2Cl_2 were added isobutyraldehyde (147 μL, 1.60 mmol) and **11a** (139 mg, 0.80 mmol) at room temperature. After stirring at room temperature for 24 h, the reaction mixture was evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel with a 2:1 mixture of hexane and AcOEt to afford the pure **12a** (188 mg, 96%) as a colorless powder.

All the Michael addition products in the paper are known compounds that exhibited spectroscopic data identical to those reported in the literature.

4.3.1. (*S*)-2-(2,5-Dioxo-1-phenylpyrrolidin-3-yl)-2-methylpropanal 12a[4]

$[\alpha]_D^{27} = -4.8$ (*c* 1.02, $CHCl_3$). 88% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 75:25), flow rate = 0.9 mL/min; λ = 240 nm; t_{major} = 25.4 min, t_{minor} = 34.7 min.

4.3.2. (*S*)-2-(1-(4-Methoxyphenyl)-2,5-dioxopyrrolidin-3-yl)-2-methylpropanal 12b[4]

$[\alpha]_D^{25} = -11.0$ (*c* 0.63, $CHCl_3$); 83% ee; Enantiomeric excess was determined by HPLC with Chiralpak AS-H column (hexane/ethanol = 80:20), flow rate = 0.6 mL/min; λ = 240 nm; t_{minor} = 43.6 -min, t_{major} = 46.7 min.

4.3.3. (*S*)-2-(2,5-Dioxo-1-p-tolylpyrrolidin-3-yl)-2-methylpropanal 12c[4]

$[\alpha]_D^{24} = -4.4$ (*c* 0.74, $CHCl_3$); 75% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 75:25), flow rate = 0.9 mL/min; λ = 240 nm; t_{major} = 18.6 min, t_{minor} = 23.0 min.

4.3.4. (*S*)-2-Methyl-2-(1-(4-nitrophenyl)-2,5-dioxopyrrolidin-3-yl)propanal 12d[4a]

$[\alpha]_D^{25} = -6.8$ (*c* 0.63, $CHCl_3$); 77% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 80:20), flow rate = 1.0 mL/min; λ = 240 nm; t_{major} = 47.1 min, t_{minor} = 64.8 min.

4.3.5. (*S*)-2-(1-(4-Chlorophenyl)-2,5-dioxopyrrolidin-3-yl)-2-methylpropanal 12e[4b,c]

$[\alpha]_D^{27} = -5.0$ (*c* 0.35, $CHCl_3$); 82% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 75:25), flow rate = 0.9 mL/min; λ = 240 nm; t_{major} = 19.0 min, t_{minor} = 36.3 min.

4.3.6. (*S*)-2-(1-Benzyl-2,5-dioxopyrrolidin-3-yl)-2-methylpropanal 12f[4]

$[\alpha]_D^{26} = -8.6$ (*c* 0.88, $CHCl_3$); 91% ee; Enantiomeric excess was determined by HPLC with Chiralpak AD-H column (hexane/2-propanol = 80:20), flow rate = 1.0 mL/min; λ = 240 nm; t_{major} = 9.8 min, t_{minor} = 22.7 min.

4.3.7. (*S*)-1-(2,5-Dioxo-1-phenylpyrrolidin-3-yl)cyclohexanecarbaldehyde 12g[4]

$[\alpha]_D^{27} = -2.2$ (*c* 0.71, $CHCl_3$); 65% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 75:25), flow rate = 0.9 mL/min; λ = 240 nm; t_{major} = 21.5 min, t_{minor} = 28.2 min.

4.3.8. (*S*)-1-(2,5-Dioxo-1-phenylpyrrolidin-3-yl)cyclopentanecarbaldehyde 12h[4a]

$[\alpha]_D^{26} = +13.0$ (*c* 1.00, $CHCl_3$); 79% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 75:25), flow rate = 0.5 mL/min; λ = 240 nm; t_{major} = 36.1 min, t_{minor} = 51.1 min.

4.3.9. (*S*)-2-(2,5-Dioxo-1-phenylpyrrolidin-3-yl)-2-ethylbutanal 12i[4b]

$[\alpha]_D^{26} = -5.0$ (*c* 0.53, CH_2Cl_2); 60% ee; Enantiomeric excess was determined by HPLC with Chiralpak AS-H column (hexane/ethanol = 70:30), flow rate = 0.8 mL/min; λ = 240 nm; t_{minor} = 11.3 min, t_{major} = 14.1 min.

4.3.10. (*S*)-2-((*S*)-2,5-Dioxo-1-phenylpyrrolidin-3-yl)decanal 12j[4a]

Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexane/2-propanol = 90:10), flow rate = 0.5 mL/min; λ = 240 nm; major diastereomer: t_{minor} = 36.8 min, t_{major} = 38.8 min; minor diastereomer: t_{major} = 32.8 min, t_{minor} = 61.4 min.

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