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Thiazolidine-based organocatalysts for a highly enantioselective direct aldol reaction

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ABSTRACT

A set of enantiopure thiazolidine-based organocatalysts have been synthesized from L-cysteine, in a straightforward manner allowing numerous structural variations. In particular, organocatalyst **3a** exhibits the highest catalytic performance working in an aqueous medium. It catalyzed the direct catalytic asymmetric intermolecular aldol reaction between unmodified ketones and an aldehyde with excellent stereocontrol and furnished the corresponding aldol products in up to 99% ee. Compound **3a** also showed excellent asymmetric catalytic activity in the asymmetric Michael reaction (up to 99% ee).

1. Introduction

The first asymmetric reaction in which low molecular weight organic molecules were used as catalysts was an intramolecular asymmetric aldol reaction of a triketone catalyzed by L-proline and was reported by two industrial research groups in 1971.[1,2] Although this chemical transformation using organocatalysts has been documented sporadically since then, it was only in the late 1990s that this research area has experienced an exponential growth. More precisely since the prior work of List,[3] Barbas[4] et al. it was found that L-proline could catalyze a direct intermolecular asymmetric aldol reaction. In addition some mechanistic aspects were also investigated. They suggested that this catalyst could act as a '*micro aldolase*',[5] activating the nucleophile through enamine formation.[2a] With regards to this activation mode, two aspects should be noted: first it avoids the use of transition metals in the reaction and second, the reaction can be performed directly by using aldol donors and acceptors.[6] Since then, the amino acid L-proline has been studied intensively, and has been described to catalyze more than 10 different reactions, which would render to it the status of a privileged catalyst.[7] With proline is the most promising catalyst, various amino acids and small peptides were also used in order to promote the direct aldol reaction and in some cases furnished the desired product with excellent enantioselectivities.[8]

On the other hand, further studies of Barbas et al.[3a] showed that thiazolidine-4-carboxylic acids could also promote the aldol reaction in high ee. Despite these results, there are only a few examples where this kind of heterocycle has been employed as chiral modifiers in organocatalysts.[3,9] In addition, these thiazolidines have been successfully used as chiral ligands in several organometallic reactions. For example Braga et al. have reported their use as highly efficient ligands for the enantioselective addition of diethylzinc[10] or alkynylzinc[11] to aldehydes, as well as in the asymmetric palladium-catalyzed allylic alkylation.[12] In general the products were obtained with excellent enantiomeric excesses.

As part of our broader program to explore the preparation and use of chiral catalysts in asymmetric synthesis, we herein report the synthesis of a class of chiral thiazolidine-derived organocatalysts (Scheme 1) and their application in the organocatalytic asymmetric aldol reaction. The first evaluation of their catalytic activity on the asymmetric Michael reaction is also reported.

2. Results and discussion

Organocatalysts **3a**–**d** were synthesized in a short, high yielding sequence. By using the described synthetic route, a high structural diversity can be readily generated, which is important for the systematic optimization of a catalyst structure. Thus, (*R*)-cysteine was first converted into thiazolidine carboxylic acids **1** by treatment with formaldehyde, and a subsequent reaction with Boc_2O. A double Grignard addition or reduction of the corresponding aminoesters afforded the desired aminoalcohols, which were reacted with thiazolidine **1** in the presence of stoichiometric amounts of ClCOOEt and NMM to give the corresponding amides **2**. Removal of the Boc group gave the desired organocatalysts **3** in good overall yields (Scheme 1).

With the target ligands in hand, we focused our attention toward the optimization of the aldol reactions. Organocatalyst **3a** was chosen for the optimization studies and several parameters such as temperature, solvent, and catalyst loading were screened in the aldol reaction between acetone and benzaldehyde. The results are shown in Table 1.

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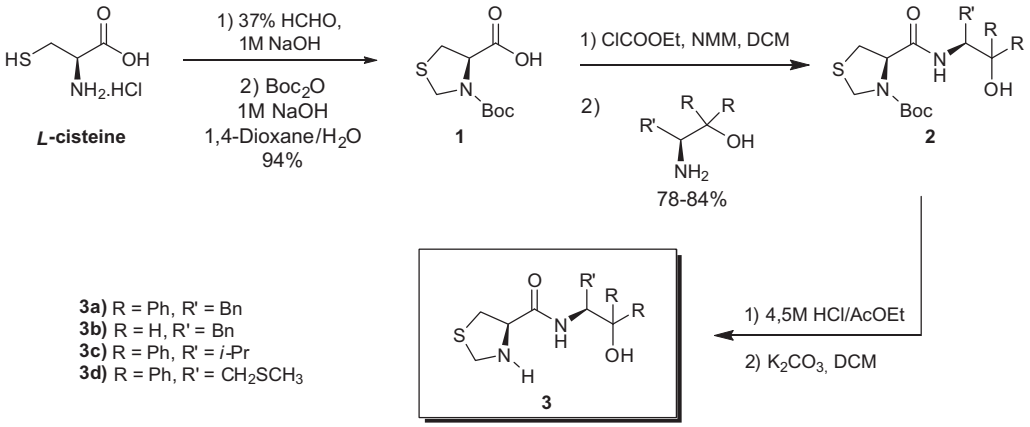
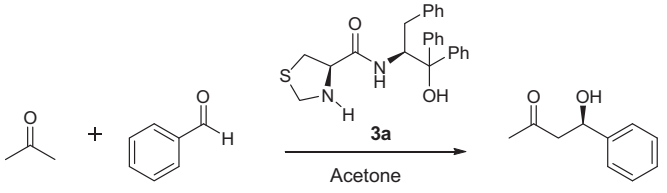


Scheme 1. Synthesis of the organocatalysts.

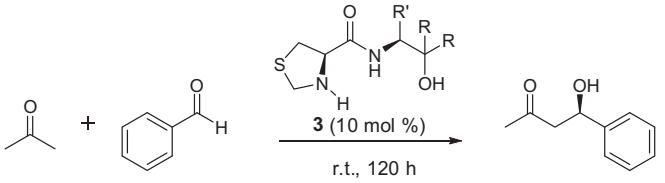
Table 1
Optimization of the reaction conditions



Entry	**3a** (mol %)	Time (h)	*T* (°C)	Yield[a] (%)	ee (%)[b]
1	5	120	rt	75	83
2	10	120	rt	91	82
3	20	120	rt	94	80
4	10	48	rt	62	76
5	10	72	rt	76	74
6	10	120	0	76	84
7	10	120	−20	71	88

[a] Isolated yields.
[b] Determined by HPLC using Chiralpak AD-H column and the absolute configurations were determined by comparison with the literature data.[13]

Table 2
Solvent effect and organocatalyst evaluation



Entry	Catalyst	Solvent	Yield[a] (%)	ee[b] (%)
1	**3a**	Brine	95	99
2	**3a**	H_2O	92	86
3	**3b**	Brine	55	99
4	**3c**	Brine	70	88
5	**3d**	Brine	85	88

[a] Isolated yields.
[b] Determined by HPLC using Chiralpak AD-H column and the absolute configurations were determined by comparison with the literature data.[13]

In this way, the effect of catalyst loading and temperature was first investigated in some detail for ligand **3a**. Running a test experiment in the presence of 5 mol % of catalyst **3a**, at room temperature and using acetone as the solvent, the aldol product was obtained in good yield and satisfactory enantiomeric excess (Table 1, entry 1; 75% yield, 83% ee). When increasing the amount of organocatalyst to 10 mol %, no increase in the ee was observed, despite the chemical yield being improved. We also observed that reaction mixtures containing 10 mol % of **3a** were equally enantioselective as reactions containing 20 mol % (Table 1, entries 2 and 3). Carrying out the reaction in shorter reaction times, with 10 mol % of ligand, caused a dramatic decrease in the chemical yields (Table 1, entries 4 and 5). No changes in the ee values were observed when the temperature of the reaction was decreased from room temperature to 0 °C or to −20 °C (entries 6 and 7).

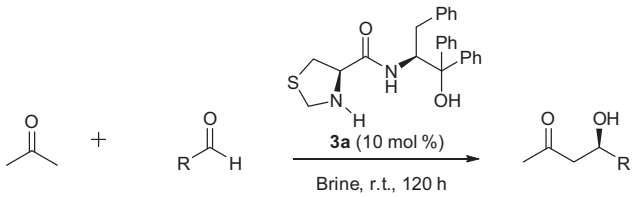
According to previous studies,[9,14] organocatalysts with hydrophobic groups show a remarkable difference in stereoselectivity for the direct aldol reaction in aqueous medium or in brine. Hence we performed the same reaction, with the optimized conditions using organocatalyst **3a**, and found that the enantioselectivity was increased up to 99% using brine (Table 2, entry 1). In fact brine seems to be more effective than water, furnishing the desired product with higher yield and ee (Table 2, compare entries 1 and 2).

Having established the optimal reaction conditions, the activity of catalysts **3a**–**d** was then evaluated in the direct aldol reaction consisting of 10 mol % organocatalyst with benzaldehyde and acetone at room temperature in brine. Catalyst **3a** was the most effective in the asymmetric reaction, furnishing the product in excellent yields and enantiomeric excesses up to 99% (Table 2, entry 1). By examining the results obtained with catalyst **3b**, we can conclude that the presence of a *gem*-diphenyl group at the β-carbon is crucial for a high chemical yield. When the *gem*-diphenyl was replaced by hydrogen a dramatic decrease in the yield was observed, despite no changes on the ee being observed (Table 2; compare entries 1 and 3). Catalysts **3c** and **3d** were also screened and revealed to be less efficient in the asymmetric aldol reaction, furnishing the desired products in moderate yields and ee (Table 2, entries 4 and 5).

The scope and limitations of the direct aldol reaction catalyzed by **3a** were also examined. Thus, the optimal conditions were applied to the organocatalytic reaction and a wide range of aldehydes including both aromatic and aliphatic reacted smoothly with acetone to give the aldol adducts with good to excellent enantioselectivities ranging from 67% to up to 99% ee (Table 3).

In general, high enantioselectivies were obtained by reacting acetone with aromatic aldehydes bearing electron-withdrawing or electron-donating groups, with the exception of *para*-bromobenzaldehyde and *meta*-nitrobenzaldehyde, which furnished the desired product in 67% and 73% ee, respectively. Remarkably, benzaldehyde and 1-naphthaldehyde reacted with acetone to generate

Table 3
Organocatalytic asymmetric aldol reaction of acetone with different aldehydes

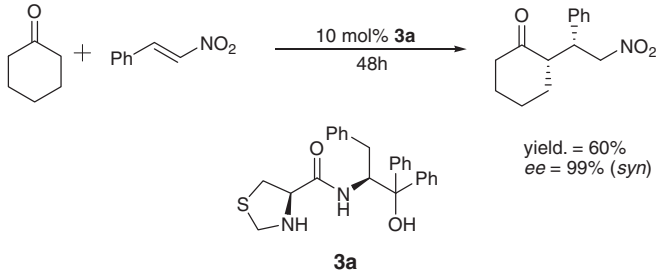


Entry	R	Yield[a] (%)	ee[b] (%)
1	Ph	95	99
2	1-Naphthyl	96	99
3	*p*-F–C_6H_4	88	81
4	*p*-Cl–C_6H_4	61	83
5	*p*-Br–C_6H_4	58	67
6	*o*-NO_2–C_6H_4	97	90
7	*m*-NO_2–C_6H_4	55	73
8	*p*-OMe–C_6H_4	92	95
9	*p*-Me–C_6H_4	88	80
10	*tert*-Bu	63	89

[a] Isolated yields.
[b] Determined by HPLC using Chiralpak AD-H column and the absolute configurations were determined by comparison with the literature data.[13]

the aldol product with extremely high enantioselectivities (Table 3, entries 1 and 2; ee up to 99% in both cases). It is worth noting that this methodology can also be applied to aliphatic aldehydes. When butyraldehyde was used, the corresponding aldol product was obtained in moderate yield and 89% ee (Table 3, entry 10).

The nature of the substrate also plays a critical role in the efficacy of the catalyst. Therefore, we decided to extend the application of catalyst **3a**, which exhibited the best performance in the asymmetric aldol reaction and the asymmetric Michael reaction. The model reaction chosen was the Michael addition between cyclohexanone and *trans*-β-nitrostyrene, with 10 mol % of ligand **3a**; a high yield and enantiomeric excess up to 99% were obtained for the *syn*-diastereoisomer (Scheme 2).



Scheme 2. Asymmetric Michael reaction using chiral organocatalyst **3a**.

3. Conclusions

In conclusion, a collection of thiazolidine amides derived from different β-amino alcohols were synthesized in a straightforward manner, which allowed us to explore the influence of electronic and steric characteristics of our organocatalyst in order to find an efficient catalytic system. The organocatalysts were evaluated for their ability to catalyze the direct aldol reactions of aromatic and aliphatic aldehydes with acetone. These results demonstrate that the organocatalysts **3a** and **3b** furnished the aldol adducts in enantiomeric excesses of up to 99%. Furthermore, catalyst **3a** was also applied in the asymmetric Michael addition between cyclohexanone and *trans*-β-nitrostyrene gave the product in good yield and excellent ee (up to 99%). Further studies on the scope of this organocatalyst in asymmetric transformations are currently underway.

4. Experimental

4.1. General methods

^{1}H NMR, ^{13}C NMR, 2D-COSY NMR, and 2D-HMQC NMR spectra were recorded on 300 MHz spectrometers Varian Inova 300 and Varian VNMRS 300. Chemical shifts (δ) are expressed in ppm downfield from TMS as the internal standard in spectra made in $CDCl_3$. Coupling constants are reported in Hertz. All enantiomeric excesses were obtained from HPLC using a chiral stationary phase (Chiracel AD-H or OD-H columns) on a Shimadzu LC-20AT chromatograph. Optical rotations were carried out on a Perkin Elmer Polarimeter 341. Infrared spectra were obtained on a Varian 640-IR spectrometer. All the column chromatography separations were done by using silica gel Fluka, 100–200 Mesh. Solvents were purified by usual methods.[15] Other reagents were obtained from a commercial source and used without further purification. The organic extracts were dried over anhydrous sodium sulfate. Evaporation of the solvent was performed under reduced pressure. Brine refers to saturated solution of NaCl in water at 25 °C.

4.2. General procedure for the synthesis of catalysts 3a–d

In a 150 mL two-necked round-bottomed flask, the N-protected thiazolidine **1** (3.5 g, 15 mmol), anhydrous dichloromethane (30 mL), and *N*-methylmorpholine (1.62 mL, 15 mmol) were added under an argon atmosphere at 0 °C. The solution was stirred for 30 min, then ethyl chloroformate (1.43 mL, 15 mmol) was added. After 30 min, the aminoalcohol (15 mmol) was added and the mixture was stirred for 24 h at rt. Then, the mixture was diluted in dichloromethane (20 mL) and washed with 1 M NaOH and an aqueous solution of NaCl. The organic layer was dried over Na_2SO_4 and evaporated. The residue was dissolved in ethyl acetate (60 mL) and a solution of 4.5 M HCl in ethyl acetate (54 mL) was added dropwise at 0 °C. The suspension was stirred for 15 min and the solvent was then evaporated. The residue was dissolved in dichloromethane and evaporated again. This procedure was repeated three times. The residue was dissolved in a solution of DCM (1:1) H_2O, at 0 °C and neutralized with K_2CO_3. The organic layer was separated and the aqueous layer was washed with DCM (3 × 50 mL). The combined organic extracts were dried over Na_2SO_4 and evaporated. The residue was recrystallized to furnish the product.

4.2.1. Compound 3a

Recrystallization from ethyl ether furnished a white solid. Yield 80%. Mp 171–173 °C. $[\alpha]_D^{20} = -44$ (*c* 1, DCM). IR (FT-IR/ATR, cm^{-1}) 1519, 1652, 3318. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.08 (m, 15H), 4.88–4.01 (m, 1H), 3.85–3.73 (m, 2H), 3.12–3.04 (m, 2H), 2.90–2.78 (m, 3H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 171.9, 164.7, 145.9, 144.7, 138.9, 129.0, 128.5, 128.4, 128.1, 126.9, 126.8, 126.4, 125.5, 125.5, 80.8, 65.4, 60.1, 52.9, 34.9, 34.6.

4.2.2. Compound 3b

Recrystallization from DCM furnished a white solid. Yield 65%. Mp 136 °C. $[\alpha]_D^{20} = -20$ (*c* 1, DCM). IR (FT-IR/ATR, cm^{-1}) 1517, 1633, 3309, 3374. ^{1}H NMR (300 MHz, $CDCl_3$/DMSO-d_6) δ 7.40–7.15 (m, 6H), 4.17–4.11 (m, 2H), 4.04 (d, 1H, *J* = 9.9 Hz), 3.73 (dd, 1H, *J* = 3.6 Hz, *J* = 10.8 Hz), 3.62 (dd, 1H, *J* = 5.7 Hz, *J* = 11.1 Hz), 3.40 (d, 1H, *J* = 10.2 Hz), 3.31 (dd, 1H, *J* = 4.2 Hz, *J* = 11.1 Hz), 3.05 (dd, 1H, *J* = 7.8 Hz, *J* = 11.1 Hz), 2.97 (dd, 1H, *J* = 6.6 Hz, *J* = 13.8 Hz), 2.77 (dd, 1H, *J* = 8.7 Hz, *J* = 14.1 Hz). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 169.8, 137.4, 128.4, 127.4, 125.4, 76.6, 65.3, 61.8, 52.6, 51.4, 35.9, 34.5.

4.2.3. Compound 3c

Recrystallization from DCM furnished a white solid. Yield 70%. Mp 203–205 °C. $[\alpha]_D^{20} = -73$ (*c* 1, DCM). IR (FT-IR/ATR, cm^{-1}) 1521, 1652, 3334. ^1H NMR (300 MHz, $CDCl_3$) δ 7.61–7.13 (m, 11H), 4.86 (dd, 1H, *J* = 2.4 Hz, *J* = 10.2 Hz), 4.15 (d, 1H, *J* = 9.9 Hz), 3.94 (d, 1H, *J* = 9.9 Hz), 3.80 (dd, 1H, *J* = 4.8 Hz, *J* = 7.5 Hz), 3.29 (br, –NH), 3.07 (dd, 1H, *J* = 4.9 Hz, *J* = 10.9 Hz), 2.87 (dd, 1H, *J* = 7.5 Hz, *J* = 10.8 Hz), 2.34 (br, –OH), 1.95–1.87 (m, 1H), 0.94–0.86 (m, 6H). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 170.8, 146.2, 145.3, 128.4, 128.3, 127.0, 126.9, 125.4, 125.3, 82.1, 66.1, 58.4, 53.6, 35.5, 28.9, 22.8, 17.9.

4.2.4. Compound 3d

Recrystallization from DCM furnished a white solid. Yield 75%. Mp 164–167 °C. $[\alpha]_D^{20} = -67$ (*c* 1, DCM). IR (FT-IR/ATR, cm^{-1}) 1515, 1654, 3331. ^1H NMR (300 MHz, $CDCl_3$) δ 7.63–7.60 (d, 1H, *J* = 9.0 Hz), 7.54–7.35 (m, 4H), 7.33–7.18 (m, 6H), 4.94–4.87 (td, 1H, *J* = 3.6 Hz, *J* = 8.7 Hz, *J* = 8.7 Hz), 4.84 (br, –NH), 4.06 (d, 1H, *J* = 10.2 Hz), 3.93 (dd, 1H, *J* = 4.5 Hz, *J* = 7.8 Hz), 3.63 (d, 1H, *J* = 10.2 Hz), 3.18 (dd, 1H, *J* = 4.5 Hz, *J* = 10.8 Hz), 2.96 (dd, 1H, *J* = 7.8 Hz, *J* = 11.1 Hz), 2.83 (dd, 1H, *J* = 8.4 Hz, *J* = 13.8 Hz), 2.74 (dd, 1H, *J* = 3.6 Hz, *J* = 13.8 Hz), 2.03 (s, 3H), 1.97 (br, –OH). ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 171.7, 145.2, 144.3, 128.5, 127.1, 126.9, 125.3, 125.2, 80.8, 65.7, 55.8, 53.3, 35.0, 34.8, 16.1.

4.3. General procedure for the asymmetric direct aldol addition

A solution of a catalyst **3a**–**d** in dry acetone (2 mL) was stirred at the temperature indicated in the tables, for 2 h. The aldehyde (1 mmol) was slowly added followed by the addition of brine (0.5 mL). The resulting mixture was stirred for the indicated time in Table 1. After that, the reaction mixture was treated with saturated aqueous ammonium chloride solution and the whole mixture was extracted with dichloromethane (3×20 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by column chromatography on silica gel with hexane/ethyl acetate (80:20) as the eluant. The enantiomeric excess (ee) was determined by HPLC analysis using Chiracel AD-H or OD-H columns.

4.4. Typical procedure for the Michael addition reaction

To a solution of cyclohexanone (0.26 mL, 2.5 mmol) and the catalyst **3a**, 1-((*E*)-2-nitrovinyl)benzene (74.5 mg, 0.5 mmol) was added. The solution was stirred at room temperature for 48 h. Then, ethyl acetate was added and the solution was washed with water and aqueous 0.5 M HCl. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give the crude product, which was purified by flash chromatography on silica gel with hexane/ethyl acetate (80:20) as the eluant. The enantiomeric purity was determined by HPLC on chiralpak AD-H column (hexane/2-propanol 90:10.

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