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Full Paper

Development of Novel Guanidine–Bisurea Bifunctional Organocatalysts and their Application to Asymmetric α-Hydroxylation of Tetralone-derived β-Keto Esters

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A series of guanidine–bisurea bifunctional organocatalysts **4**, with chiral centres located outside the urea groups, were synthesized. The novel catalyst **4** is conformationally more flexible than the original catalyst **1**. In α-hydroxylation of tetralone- derived β-keto esters, **4** afforded the corresponding alcohols in high yields with moderate enantioselectivity.

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Introduction

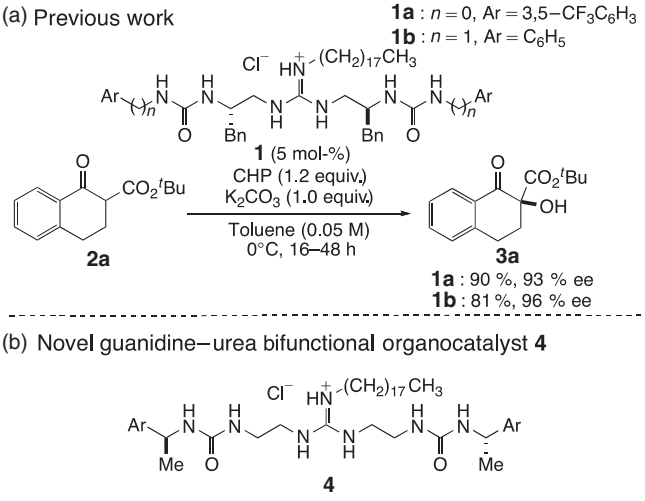
α-Hydroxy-β-dicarbonyl moieties are widely found in natural products, as well as pharmaceuticals,[1] and many synthetic approaches have been explored, especially from the viewpoint of enantioselectivity. A straightforward strategy used for the construction of α-hydroxy-β-dicarbonyl compounds is the enantioselective direct oxidation at the α-position of β-keto esters using metal catalysts in combination with chiral ligands and/or chiral organocatalysts.[2–4] In regards to organocatalytic approaches, cinchona alkaloid derivatives[4a,d–f,i] and chiral phosphoric acids[4b] have been reported as efficient catalysts for asymmetric α-hydroxylation of β-keto esters. In addition, lappaconitine[4c] and *S*-timolol analogues[4,g] are known to catalyze the reaction with moderate enantioselectivity. Recently, Qu et al. reported that TADDOL-derived guanidine effectively catalyzed asymmetric α-hydroxylation of β-keto esters derived from indanone.[4h]

We have recently reported asymmetric α-hydroxylation of tetralone-derived β-keto esters mediated by guanidine–bisurea bifunctional organocatalyst **1a** in the presence of cumene hydroperoxide (CHP), which is a safe and commercially available oxidant (Scheme 1a).[5o] In this reaction, α-hydroxylation products were obtained in high yields with high enantioselectivity.[5o,p] During structure–activity relationship studies of the catalyst **1** that focused on the acidity of the urea moiety, we found that catalyst **1b**, substituted with benzyl groups on the urea nitrogen atoms, was also effective, and α-hydroxylated **3a** was obtained in good yield with excellent enantioselectivity (96 % ee, Scheme 1a). This gave us the idea of shifting the chiral centre in catalyst **1** from the linker position to outside the urea groups, e.g. catalyst **4** (Scheme 1b). Catalyst **4** is conformationally more flexible than **1**, and control of the transition state of the reaction by **4** is therefore an interesting area.

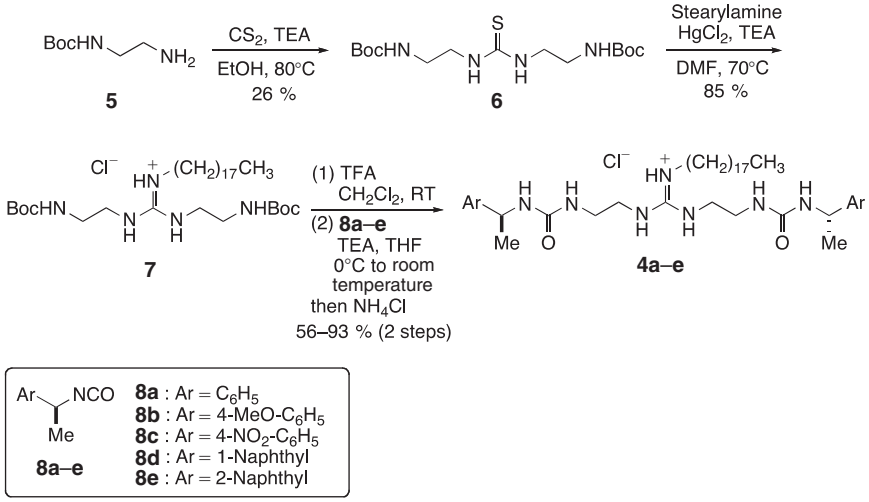
Results and Discussion

The synthesis of the novel guanidine–bisurea compounds **4** is illustrated in Scheme 2. Reaction between amine **5** and carbon disulfide gave thiourea **6**, which was coupled with stearylamine in the presence of mercury chloride and triethylamine (TEA) to give guanidine **7**. The *tert*-butoxycarbonyl (Boc) groups in **7** were deprotected with trifluoroacetic acid (TFA), and the resulting amine was reacted with optically active isocyanates **8a**–**e** derived from the corresponding amines in the presence of triethylamine to give **4a**–**e** in 56–93 % yield (2 steps).

Initially, we examined α-hydroxylation of β-keto *tert*-butyl ester **2a** with **4a** in the presence of cumene hydroperoxide (CHP, 1.2 equiv.) and potassium carbonate (1 equiv.) in toluene at 0°C; these conditions were previously developed for catalyst **1a** (Table 1). The α-hydroxylation product **3a** was obtained in 80 % yield with 37 % ee (entry 1). (Note, the absolute

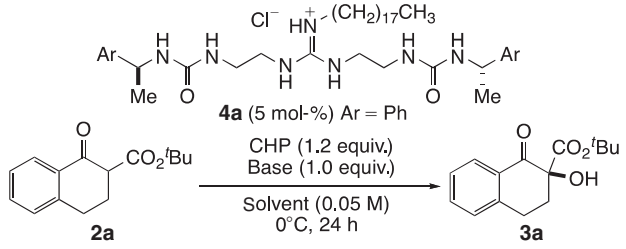


Scheme 1. α–Hydroxylation of tetralone-derived β-keto ester **2a** in the presence of guanidine–bisurea bifunctional organocatalysts **1a** and **1b** (previous work[5o]), and catalysts **4** bearing chiral centres outside the urea groups (current work).



Scheme 2. Synthesis of guanidine–bisurea compounds **4a**–**e**. Boc, *tert*-butoxycarbonyl; TEA, triethylamine; DMF, *N*,*N*–dimethylformamide; TFA, trifluoroacetic acid; THF, tetrahydrofuran.

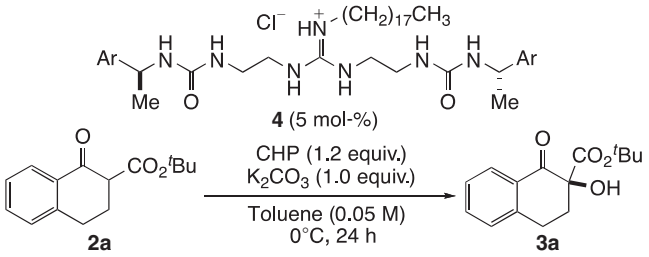
Table 1. Optimization of reaction conditions with catalyst 4a[A]



Entry	Base	Solvent	Product **3a**	
			Yield [%][B]	ee [%][C]
1	K_2CO_3	Toluene	80	37
2	DBU	Toluene	79	25
3	TEA	Toluene	7	10
4	2 N NaOH(aq)	Toluene	82	27
5	K_2CO_3	CH_2Cl_2	29	31
6	K_2CO_3	MeCN	16	0
7	K_2CO_3	Ethyl acetate	16	13

[A]Reaction conditions: **2a** (0.1 mmol), CHP (0.12 mmol), base (0.1 mmol), and **4a** (0.005 mmol) in solvent (2 mL) at 0°C for 24 h.
[B]Determined by ^{1}H NMR spectroscopy.
[C]Determined by chiral HPLC.

Table 2. Optimization of structure of catalyst 4[A]



Entry	Catalyst **4**	Product **3a**		
		Ar	Yield [%][B]	ee [%][C]
1	**4b**	4-MeO-C_6H_4	81	33
2	**4c**	4-NO_2-C_6H_4	82	22
3	**4d**	1-Naphthyl	99	50
4	**4e**	2-Naphthyl	80	47

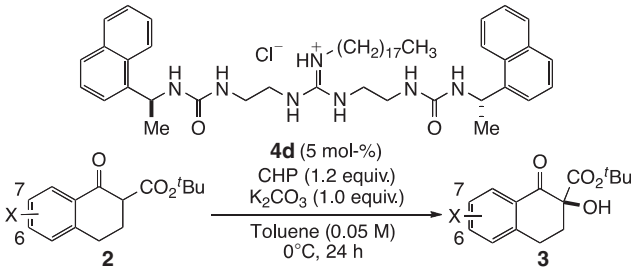
[A]Reaction conditions: **2a** (0.1 mmol), CHP (0.12 mmol), K_2CO_3 (0.1 mmol), and catalyst **4** (0.005 mmol) in toluene (2 mL) at 0°C for 24 h.
[B]Determined by ^{1}H NMR spectroscopy.
[C]Determined by chiral HPLC.

stereochemistry of **3a** was assigned by comparison with previous reported data.[3b]) Although the enantioselectivity was only 37 % ee as compared with 95 % ee in the case of **1a**, it is noteworthy that the outer chiral centres in **4a** were at least partially effective in controlling the transition state of the reaction. Thus, the reaction conditions were further investigated to improve the selectivity for **3a** in the reaction mediated by **4a**. First, the effects of base on the reaction were investigated (Table 1, entries 2–4). In the case of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU), **3a** was obtained in 79 % yield, but the enantioselectivity decreased to 25 % ee (entry 2). When the base was switched to triethylamine, the yield and enantioselectivity decreased to 7 % and 10 % ee, respectively (entry 3). Biphasic conditions were then examined with 2 N NaOH in toluene, but the selectivity was still poor (27 % ee, entry 4). The solvent was then changed to dichloromethane, acetonitrile, and ethyl acetate in the presence of catalyst **4a** and potassium carbonate. However, no improvement in the selectivity was observed. Moreover, the yield of **3a** declined drastically (Table 1, entries 5–7).

Next, the structure of catalyst **4** was explored, focusing on the Ar group under the conditions listed in entry 1 of Table 1 (Table 2, entries 1–4). The phenyl group in **4a** was changed to 4-methoxyphenyl **4b**, 4-nitrophenyl **4c**, 1-naphthyl **4d**, and 2-naphthyl **4e**. Among these compounds, **4d** was the most effective for the reaction, affording **3a** in 99 % yield with 50 % ee. This was the best result achieved so far with **4**.

Based on the conditions developed in Table 2 (entry 3), we investigated the performance of organocatalyst **4d** towards the α-hydroxylation of β-keto esters **2b**–**g** (Table 3). Compounds **2b** and **2c,** which have a benzyloxy group at the 6-position and a methoxy group at the 7-position on the aromatic ring, respectively, afforded the corresponding α-hydroxylation products **3b** and **3c** in high yields (93 % and 98 %, entries 1 and 2) with moderate enantioselectivity (48 % ee and 44 % ee, respectively). Bis-methoxy β-keto ester **2d** afforded a low yield (11 %, entry 3) and low enantioselectivity (20 % ee). Halogenated substrates

Table 3. Substrate performance in α-hydroxylation of 2[A]



Entry	Substrate **2**		Product **3**		
		X		Yield [%][B]	ee [%][C]
1	**2b**	6-OBn	**3b**	93	48
2	**2c**	7-OMe	**3c**	98	44
3	**2d**	5,8-OMe	**3d**	11	20
4	**2e**	6-Cl	**3e**	73	45
5	**2f**	6-Br	**3f**	70	42
6	**2g**	7-F	**3g**	90	51

[A]Reaction conditions: **2** (0.1 mmol), CHP (0.12 mmol), K_2CO_3 (0.1 mmol), and **4d** (0.005 mmol) in toluene (2 mL) at 0°C for 24 h.
[B]Determined by ^{1}H NMR spectroscopy.
[C]Determined by chiral HPLC.

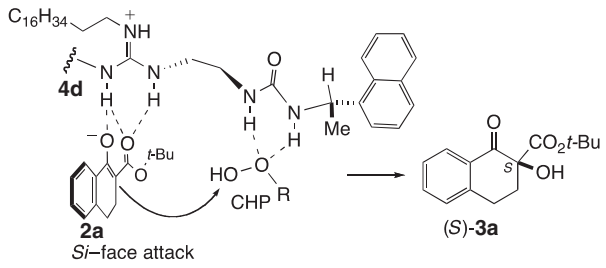


Fig. 1. Plausible transition state model of α-hydroxylation of **2a** catalyzed by **4d**.

2e–**g** gave **3e**–**g** in high yields (70–90 % yield) with moderate enantioselectivity (42–51 % ee, entries 4–6).

A plausible transition model for the **4d**-catalyzed α-hydroxylation of **2a** is shown in Fig. 1. A guanidine and a urea group in **4d** interact with β-keto ester **2a** and CHP, respectively, so that the enolate **2** approaches the oxidant from the *Si* face to avoid the bulky 1-naphthyl group of **4d**, predominantly affording (*S*)-**3a**.

Conclusion

We have developed a series of novel guanidine–bisurea bifunctional organocatalysts **4**, bearing chiral centres outside the urea moieties. Asymmetric α-hydroxylation of tetralone-derived β-keto esters in the presence of cumene hydroperoxide as oxidant generated the corresponding α-hydroxy-β-keto esters in excellent yields (up to 99 %) with moderate enantioselectivity (up to 51 % ee).

Experimental

Flash chromatography was performed using silica gel 60 (spherical, particle size 0.040–0.100 mm; Kanto Co., Inc., Japan). Optical rotations were measured on a JASCO P–2200 polarimetre. ^{1}H and ^{13}C NMR spectra were recorded on AL300, ECX400 (JEOL), and AVANCE 400 (Bruker) instruments. For ^{1}H NMR spectroscopy, chemical shifts in [D]chloroform and [D4]methanol (MeOH) were reported on the scale relative to [D]chloroform (δ 7.26 ppm) and [D4]MeOH (δ 3.30 ppm), respectively. For ^{13}C NMR spectroscopy, chemical shifts were reported on the scale relative to [D]chloroform (δ 77.0 ppm), [D4]MeOH (δ 49.0 ppm), and as internal references. Mass spectra were recorded on a JMS–T100 LC (JEOL) spectrometer.

*Catalyst Synthesis (**4a**–**e**)*

*Compound **6***

To a solution of *N*-(*tert*-butoxycarbonyl)-1,2-ethylenediamine (**5**) (3.75 g, 23.25 mmol) in ethanol (EtOH) (150 mL) was added CS_2 (780 μL, 12.79 mmol) at room temperature, and the resulting mixture was heated at 70°C for 12 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography to give **6** (2.47 g, 29 %). The spectroscopic data correspond to previously reported data.[6]

*Compound **7***

To a mixture of **6** (807 mg, 2.23 mmol), stearylamine (900 mg, 3.34 mmol), and triethylamine (940 μL, 6.68 mmol) in DMF (11 mL) was added $HgCl_2$ (906 mg, 3.34 mmol) at room temperature, and the resulting mixture was stirred for 12 h at 80°C. The resulting mixture was diluted with ethyl acetate, and filtered though a pad of Celite. The filtrates were washed with saturated NH_4Cl(aq), and then dried over $MgSO_4$. After removing the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel to give **7** (1.19 g, 85 %). δ_H (CD_3OD, 400 MHz) 3.40–3.17 (10H, m), 1.75–1.60 (2H, m), 1.48 (18H, s), 1.43–1.27 (30H, m), 0.92 (3H, t, *J* 6.9 Hz). δ_C (CD_3OD, 75 MHz) 160.0, 156.9, 81.35, 44.0, 43.8, 41.0, 33.9, 31.7, 31.5, 31.3, 31.3, 30.7, 29.7, 28.8, 24.6, 15.4, 15.3. *m*/*z* 598.5296. HRMS (ESI, M–Cl) Anal. Calc. for $C_{33}H_{68}N_5O_4$ 598.5271.

*Typical Procedure for Preparation of Compound **4***

To a solution of **7** (100 mg, 0.16 mmol) in CH_2Cl_2 (1.6 mL) was added TFA (600 μL) at 0°C. The reaction mixture was stirred at room temperature for 1 h, and the resulting mixture was concentrated under reduced pressure to give diamine. To a solution of diamine and triethylamine (190 μL, 1.33 mmol) in THF (1.6 mL) was added (*S*)-(−)-1-phenylethyl isocyanate (140 μL, 1.00 mmol), and the mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel to give bisurea. The counter anion of the catalyst was exchanged to chloride by treatment with saturated NH_4Cl(aq) in ethyl acetate to give **4a** (208 g, 86 % in 2 steps). $[\alpha]_D$ 25° −33.2 (*c* 1.0 in $CHCl_3$). δ_H (CD_3OD, 400 MHz) 7.34–7.27 (8H, m), 7.27–7.19 (2H, m), 4.82 (2H, q, *J* 6.9), 3.37–3.06 (8H, m), 3.01 (2H, t, *J* 7.3), 1.59–1.48 (2H, m), 1.42 (6H, d, *J* 6.9), 1.38–1.23 (30H, m), 0.92 (3H, t, *J* 6.6). δ_C (CD_3OD, 75 MHz) 161.8, 156.7, 147.3, 130.3, 128.7, 127.6, 51.8, 50.9, 44.9, 43.6, 40.4, 33.9, 31.7, 31.3, 31.3, 30.6, 28.7, 24.6, 15.4. *m*/*z* 692.5560. HRMS (ESI, M–Cl) Anal. Calc. for $C_{41}H_{70}N_7O_2$ 692.5591.

*Compound **4b***

$[\alpha]_D$ 25° −38.4 (*c* 1.0 in $CHCl_3$). δ_H (CD_3OD, 400 MHz) 7.18 (4H, d, *J* 8.7), 6.82 (4H, d, *J* 8.7), 4.74 (2H, q, *J* 6.9), 3.73 (6H, s), 3.33–3.05 (8H, m), 3.00 (2H, t, *J* 7.3), 1.57–1.45 (2H, m), 1.36 (6H, d, *J* 6.9), 1.28–1.19 (30H, m), 0.88 (3H, t, *J* 6.9).

δ_C (CD_3OD, 75 MHz) 161.8, 160.8, 156.7, 139.2, 128.8, 115.6, 56.5, 51.2, 44.8, 43.6, 40.4, 33.9, 31.6, 31.3, 31.3, 30.7, 28.7, 24.6, 24.5, 15.4. *m/z* 752.5848. HRMS (ESI, M–Cl) Anal. Calc. for $C_{43}H_{74}N_7O_4$ 752.5802.

Compound ***4c***

$[\alpha]_D$ 25° −45.1 (*c* 1.0 in $CHCl_3$). δ_H (CD_3OD, 400 MHz) 8.20 (4H, d, *J* 8.7), 7.57 (4H, d, *J* 8.7), 4.93 (2H, q, *J* 7.1), 3.38–3.14 (8H, m), 3.03–2.96 (2H, m), 1.54–1.42 (8H, m), 1.36–1.21 (30H, m), 0.92 (3H, t, *J* 6.9). δ_C (CD_3OD, 75 MHz) 161.6, 156.8, 155.5, 149.0, 128.8, 125.5, 51.7, 50.7, 44.6, 43.7, 43.6, 40.5, 33.9, 31.6, 31.3, 31.2, 30.6, 28.7, 24.6, 24.1, 15.3. *m/z* 782.5244. HRMS (ESI, M–Cl) Anal. Calc. for $C_{41}H_{68}N_9O_6$ 782.5293.

Compound ***4d***

$[\alpha]_D$ 25° −33.2 (*c* 1.0 in $CHCl_3$). δ_H (CD_3OD, 400 MHz) 8.13 (2H, d, *J* 7.8), 7.92–7.83 (2H, m), 7.70 (2H, d, *J* 8.2), 7.56–7.40 (8H, m), 5.65 (2H, q, *J* 6.4), 3.37–2.95 (8H, m), 2.89–2.79 (2H, m), 1.55 (6H, d, *J* 6.4), 1.42–1.03 (32H, m), 0.91 (3H, t, *J* 6.9). δ_C (CD_3OD, 75 MHz) 161.7, 156.6, 142.8, 136.1, 132.7, 130.7, 129.4, 127.9, 127.3, 124.9, 123.8, 50.7, 47.8, 44.9, 43.5, 40.4, 33.9, 31.6, 31.5, 31.3, 31.1, 30.5, 28.5, 24.6, 23.7, 15.4. *m/z* 792.5854. HRMS (ESI, M–Cl) Anal. Calc. for $C_{49}H_{74}N_7O_2$ 792.5904.

Compound ***4e***

$[\alpha]_D$ 25° +23.7 (*c* 1.0 in $CHCl_3$). δ_H (CD_3OD, 400 MHz) 7.34–7.27 (8H, m), 7.47–7.19 (6H, m), 4.82 (2H, q, *J* 6.9), 3.37–3.06 (8H, m), 3.01 (2H, t, *J* 7.3), 1.59–1.48 (2H, m), 1.42 (6H, d, *J* 6.9), 1.38–1.23 (30H, m), 0.92 (3H, t, *J* 6.6). δ_C (CD_3OD, 75 MHz) 161.9, 156.7, 147.3, 130.3, 128.7, 127.6, 51.8, 50.9, 44.9, 43.6, 40.4, 33.9, 31.7, 31.3, 31.3, 30.6, 28.7, 24.6, 15.4. *m/z* 792.5871. HRMS (ESI, M–Cl) Anal. Calc. for $C_{49}H_{74}N_7O_2$ 792.5904.

Supplementary Material

^1H and ^{13}C NMR spectra of catalysts **4a**–**e** and HPLC charts of **3a**–**g** are available on the Journal's website.

Acknowledgements

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