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Asymmetric α-Hydroxylation of Tetralone-Derived β-Ketoesters by Using a Guanidine–Urea Bifunctional Organocatalyst in the Presence of Cumene Hydroperoxide

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Abstract: Highly enantioselective catalytic oxidation of 1-tetralone-derived β-keto esters was achieved by using a guanidine–urea bifunctional organocatalyst in the presence of cumene hydroperoxide (CHP), a safe, commercially available oxidant. The α-hydroxylation products were obtained in 99% yield with up to 95% enantiomeric excess (*ee*). The present oxidation was successfully applied to synthesize a key intermediate of the anti-cancer agent daunorubicin (**2**).

Keywords: esters · enantioselectivity · hydroxylation · organocatalysis · oxidation · synthetic methods

Introduction

Intact or masked α-hydroxy-β-dicarbonyl structure is frequently found in natural products, as represented by hamigeran A (**1**) and daunorubicin (**2**; Figure 1), as well as various pharmaceuticals,[1–3] and great efforts have been made to achieve stereoselective synthesis of this structure.

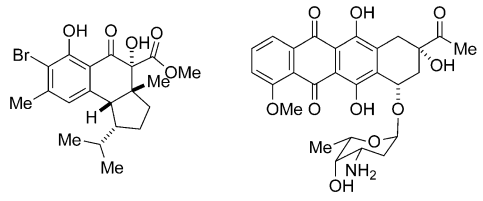

Figure 1. Representative natural products bearing an intact or masked α-hydroxy-β-keto ester moiety.

One of the most widely investigated approaches to the synthesis of this structure is oxidation of the α-position of β-keto esters, and many methods have been developed by using appropriate oxidants in the presence of metal catalysts.[4,5] On the other hand, there has been only limited study of organocatalyts.[6] The groups of Jørgensen and Meng independently reported the α-hydroxylation of β-keto esters by using cinchona alkaloid-derived organocatalysts in the presence of cumene hydroperoxide (CHP).[6a,c,e] In these cases, moderate to high enantioselectivities were obtained, although the substrate scope was limited to 1-indanone-derived β-keto esters.[5d,f,6b–e,7] Recently, Zhong et al. reported the selective oxidation of various β-keto esters, including 1-indanone-, cyclopentanone-, and cyclohexanone-derived β-keto esters, using nitrosobenzene as an oxidant with a chiral phosphoric acid-type organocatalyst.[6b]

Recently, we have developed a series of guanidine–(thio)-urea bifunctional organocatalysts **3** bearing a conformationally flexible chiral linker, and have applied them to several asymmetric carbon–carbon bond-forming reactions as well as oxidation reactions.[8] In the case of asymmetric nucleophilic epoxidation of chalcones, the guanidine–urea catalyst **3a** was very effective, and the corresponding epoxides were obtained in 99% yield with up to 99% enantiomeric excess (*ee*; Scheme 1a).[9,10] It was suggested that urea and guanidine in the catalyst interacted with hydrogen peroxide and a carbonyl group. Based upon this mechanism,[9] we envisaged that **3** would be effective for catalyzing the α-hydroxylation of β-keto esters with the aid of similar interactions between guanidine and the β-keto ester, and urea and the oxidant, respectively (Scheme 1b). These interactions were expected to promote the reaction and to enhance asymmetric induction through a synergistic proximity effect, with control of the transition state by the chirality of the catalyst. Herein, we describe catalytic enantioselective α-hydroxylation of β-keto esters derived from 1-tetralone, which is a challenging substrate for α-hydroxylation,[7] by using the guanidine–urea bifunctional organocatalyst **3**.

Results and Discussion

We commenced our investigation of α-hydroxylation with the 1-tetralone-derived β-keto methyl ester **4a** in the presence of **3a** and CHP in toluene (Table 1). First, several bases (1 equiv) were examined. In the case of organic bases

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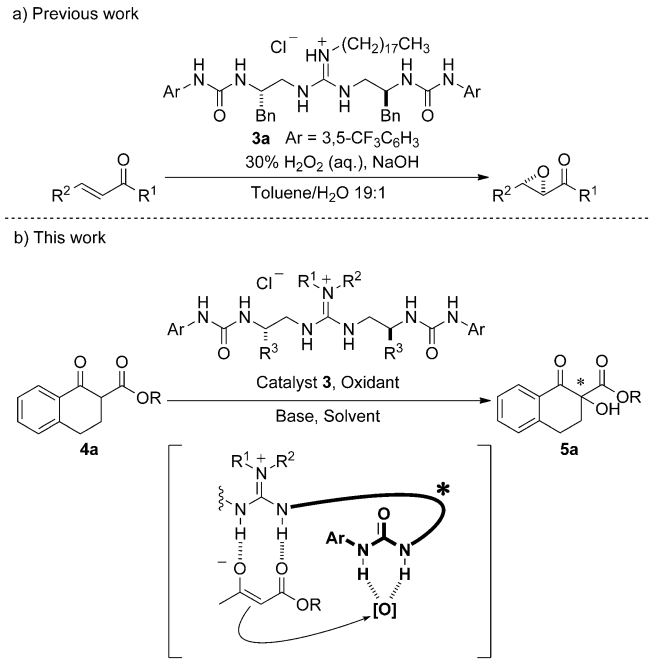
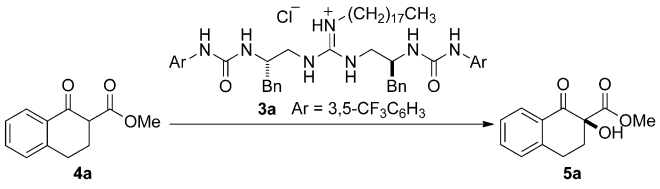


Scheme 1. Asymmetric epoxidation catalyzed by **3a**, and catalytic asymmetric α-hydroxylation of β-keto ester showing the proposed transition model.

Table 1. Optimization of the reaction conditions with catalyst **3a**.[a]



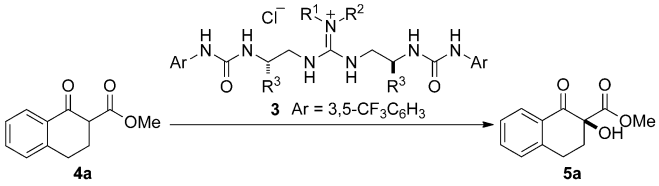
Entry	Solvent	Base	Oxidant	Product **5a** Yield [%][b]	*ee* [%][c]
1	Toluene	DBU	CHP	57	59
2	Toluene	TEA	CHP	58	60
3	Toluene	2 N NaOH (aq)	CHP	86	62
4	Toluene	K_2CO_3	CHP	88	72
5	Toluene	$CsCO_3$	CHP	80	36
6	Toluene	K_2CO_3	TBHP	47	50
7	Toluene	K_2CO_3	*m*CPBA	99	3
8	Toluene	K_2CO_3	Davis oxaziridine	99	18
9	Toluene	K_2CO_3	H_2O_2	trace	
10	Toluene	K_2CO_3	UHP	trace	

[a] These reactions were carried out with **4a** (0.1 mmol), oxidant (120 mol%), base (100 mol%), and **3a** (5 mol%) in solvent (0.1 M) at 0 °C for 24 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by chiral HPLC.

(1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and triethylamine (TEA)), moderate yields (57–58%) and enantioselectivities (59–60% *ee*) were obtained (Table 1, entries 1 and 2). Under biphasic conditions with NaOH (aq, 2 N), the chemical yield of **5a** increased to 86%, but the selectivity was still only moderate (Table 1, entry 3). Interestingly, liquid–solid biphasic conditions also gave high yields, and high selectivity (72% *ee*) was obtained in the case of potassium carbonate (Table 1, entry 4), though only low selectivity (36% *ee*) was observed with cesium carbonate as a base (Table 1, entry 5). Next, the oxidants were varied under the conditions of entry 4 (Table 1). *tert*-Butyl hydroperoxide (TBHP) is frequently used for this oxidation reaction, as well as CHP, but here the yield and enantioselectivity were decreased (Table 1, entry 6). *meta*-chloroperoxybenzoic acid (*m*CPBA) and 2-*p*-toluenesulfonyl-3-phenyl oxaziridine (Davis oxaziridine)[11] each gave 99% yield, but the selectivity was drastically decreased, and almost racemic **5a** was obtained with *m*CPBA (Table 1, entries 7 and 8). Hydrogen peroxide and urea hydrogen peroxide (UHP) were ineffective for the oxidation (Table 1, entries 9 and 10). Thus, we adopted the reaction conditions of entry 4 in Table 1 as the optimized conditions, with the catalyst **3a**.[12]

Next, we carried out structure–activity relationship studies of catalyst **3** focusing on the R^3 substituent on the chiral spacer (Table 2, entries 1–5). Changing the R^3 group to methyl, isopropyl, or isobutyl drastically reduced the selectivity to 13, 49, and 38% *ee*, respectively, although the yields were moderate to high (Table 2, entries 2–4). In the case of a phenyl group at R^3, selectivity was similar to that with **3a**, but the yield was decreased to 55% (Table 2, entry 5). The effects of the R^1 and R^2 groups in catalyst **3** were also exam-

Table 2. Structure–activity relationship studies of catalyst **3**.[a]



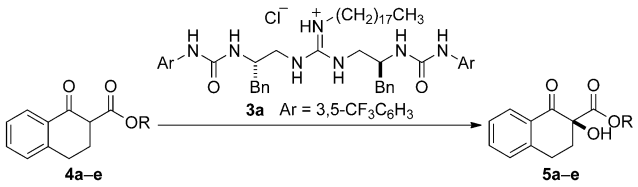
Entry	Catalyst **3**	R^1, R^2	R^3	**5a** Yield [%][b]	*ee* [%][c]
1	**3a**	H, $C_{18}H_{37}$	Bn	88	72
2	**3b**	H, $C_{18}H_{37}$	Me	66	13
3	**3c**	H, $C_{18}H_{37}$	*i*Pr	94	49
4	**3d**	H, $C_{18}H_{37}$	*i*Bu	80	38
5	**3e**	H, $C_{18}H_{37}$	Ph	55	69
6	**3f**	$-(CH_2)_4-$	Bn	70	-7
7	**3g**	$-(CH_2)_5-$	Bn	67	1
8	**3h**	Et, Et	Bn	57	0
9[d]	**3e**	H, $C_{18}H_{37}$	Bn	93	82
10[e]	–			65	
11[f]	–			13	

[a] Unless otherwise noted, reactions were carried out with **4a** (0.1 mmol), cumene hydroperoxide (120 mol%), K_2CO_3 (100 mol%), and catalyst **3** (5 mol%) in solvent (0.1 M) at 0 °C for 24 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by chiral HPLC. [d] Reactions were carried out with **4a** (0.1 mmol), cumene hydroperoxide (120 mol%), K_2CO_3 (20 mol%), and catalyst (5 mol%) in toluene (0.05 M) at 0 °C for 24 h. [e] Reaction was carried out with **4a** (0.1 mmol), cumene hydroperoxide (120 mol%), and K_2CO_3 (100 mol%) in toluene (0.1 M) at 0 °C for 24 h without catalyst. [f] Reactions were carried out with **4a** (0.1 mmol), cumene hydroperoxide (120 mol%) and K_2CO_3 (20 mol%) in toluene (0.05 M) at 0 °C for 24 h without catalyst.

ined.[8f,h] Interestingly, selectivity was drastically reduced with **3f–3h** bearing disubstituted guanidines, even though R^3 was a benzyl group, and almost racemic **5a** was obtained (Table 2, entries 6–8). Thus, the catalyst **3a** appeared to be optimal for the present oxidation reaction. With the catalyst **3a** in hand, we fine-tuned the reaction conditions based upon entry 1 in Table 1, and finally found that the selectivity could be improved to 82% *ee* without affecting the yield by decreasing the amount of base (K_2CO_3) to 20 mol% (Table 2, entry 9). This condition was effective for suppressing the background oxidation reaction of **4a** (Table 2, entries 10 and 11).

Using the optimized conditions together with catalyst **3a**, we next focused on the ester group of the substrates (Table 3).[6a,d] Changing the methyl ester group to an isopropyl or *tert*-butyl group improved the selectivity, and the corresponding alcohol **5d** or **5e** was obtained with 90 and 94% *ee* in 94 and 60% yield, respectively (Table 3, entries 4 and 5). Interestingly, the yield of *tert*-butyl ester **5e** was improved to 90% without loss of enantioselectivity simply by employing one equivalent of potassium carbonate (Table 3, entry 6).[13]

Table 3. Optimization of ester group of **4**.[a]



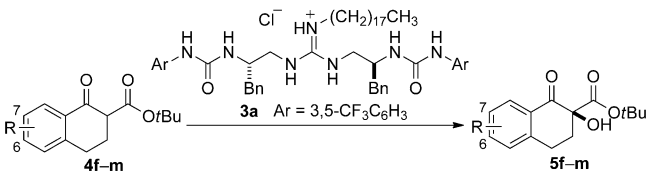
Entry	β-Keto ester **4**	R		Product **5** Yield [%][b]	*ee* [%][c]
1	**4a**	Me	**5a**	93	81
2	**4b**	Et	**5b**	95	81
3	**4c**	Bn	**5c**	87	78
4	**4d**	*i*Pr	**5d**	94	90
5	**4e**	*t*Bu	**5e**	60	94
6[d]	**4e**	*t*Bu	**5e**	90	93

[a] Unless otherwise noted, reactions were run with **4a** (0.1 mmol), cumene hydroperoxide (120 mol%), K_2CO_3 (20 mol%), and **3a** (5 mol%) in toluene (0.05 M) at 0°C for 24 h. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by chiral HPLC. [d] The reaction was run with **4a** (0.1 mmol), cumene hydroperoxide (120 mol%), K_2CO_3 (100 mol%), and **3a** (5 mol%) in toluene (0.05 M) at 0°C for 24 h.

As either an isopropyl or a *tert*-butyl group was suitable as the ester, the scope of the reaction was investigated for α-hydroxylation using 1-tetralone-derived β-keto *tert*-butyl esters. As depicted in Table 4, substituents on the aromatic ring of **4** did not affect the yield or selectivity, and derivatives with both electron-donating and electron-withdrawing groups **4f–4m** gave the corresponding **5f–5m** in high yields (82–99%) with high enantioselectivities (87–95% *ee*).[14]

Daunorubicin (**2**; Figure 1) is an anthracycline antibiotic isolated from *Streptomyces peucetius*. It shows potent antitumor activity by inhibiting topoisomerase II through intercalating the target DNA. Because of its remarkable antitumor activity, compound **2** has attracted much synthetic interest, and various derivatives of **2** have been developed for anticancer chemotherapy. α-Hydroxy-ketone **6** (Scheme 2) is a key intermediate in a Friedel–Crafts reaction-based synthesis of **2**,[15] and therefore the present α-hydroxylation of the β-keto ester was applied to the synthesis of *ent*-**6**.

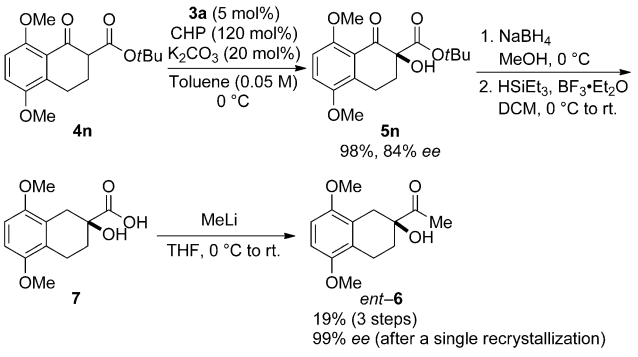
Table 4. Substrate scope of the α-hydroxylation of **4**.[a]



Entry	β-Keto ester **4**	R	*t* [h]	Product **5**	Yield [%][b]	*ee* [%][c]
1	**4f**	6-OMe	24	**5f**	91	87
2	**4g**	6-OBn	16	**5g**	99	92
3[d]	**4h**	6-NMe_2	48	**5h**	92	95
4	**4i**	6-Cl	36	**5i**	88	95
5[d]	**4j**	6-Br	20	**5j**	83	85
6	**4k**	7-OMe	16	**5k**	94	93
7	**4l**	7-Br	20	**5l**	82	89
8	**4m**	7-F	23	**5m**	90	90

[a] Unless otherwise noted, reactions were carried out with **4** (0.1 mmol), cumene hydroperoxide (120 mol%), K_2CO_3 (100 mol%), and **3a** (5 mol%) in toluene (0.05 M) at 0°C. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by chiral HPLC. [d] Reactions were carried out with **4** (0.1 mmol), cumene hydroperoxide (120 mol%), K_2CO_3 (20 mol%), and catalyst (5 mol%) in toluene (0.05 M) at 0°.

Oxidation of **4n** with CHP in the presence of **3a** (5 mol%) gave **5n** in 92% yield with 84% *ee*. Reduction of the ketone moiety of **5n** with $NaBH_4$ afforded the benzylic alcohol, which was selectively reduced with triethylsilyl hydride in the presence of BF_3•Et_2O. The *tert*-butyl group was simultaneously removed to generate carboxylic acid **7**. This was treated with methyllithium to furnish *ent*-**6** in 19% yield from **5n**. The optical purity of the product was improved to 99% *ee* by a single recrystallization from hexane/ether (Scheme 2).



Scheme 2. Synthesis of key intermediate *ent*-**6** for synthesis of *ent*-daunorubicin (**2**).

Conclusion

We have developed a catalytic enantioselective α-hydroxylation reaction of β-keto esters of 1-tetralone derivatives by using a guanidine–urea bifunctional organocatalyst **3a** and cumene hydroperoxide (CHP), a safe, commercially available oxidant. The corresponding α-hydroxy-β-keto esters were obtained in 82–99% yield with high enantioselectivity (84–95% *ee*). The usefulness of this reaction was confirmed by applying it to the synthesis of *ent*-**6**, a key intermediate for *ent*-daunorubicin (**4**).

Experimental Section

General remarks: 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 polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on AL300, ECX400 (JEOL) and AVANCE 400 (Bruker) instruments. Chemical shifts in [D]chloroform and [D$_4$]MeOH were reported on the scale relative to [D]chloroform (δ=7.26 ppm), [D$_4$]MeOH (δ=3.30 ppm) and [D$_6$]dimethylsulfoxide (δ=2.50 ppm) for ^{1}H NMR spectroscopy, respectively. For ^{13}C NMR spectroscopy, chemical shifts were reported on the scale relative to [D]chloroform (δ=77.0 ppm), [D$_4$]MeOH (δ=49.0 ppm), and [D$_6$]dimethylsulfoxide (δ=39.5 ppm) as internal references, respectively. Mass spectra were recorded on JMS-T100 LC (JEOL) spectrometer.

Synthesis of β-keto *tert*-butyl esters (4a–4f, 4j-4m): β-Keto esters **4a**, **4b**, and **4d**,[16] **4c**,[17] **4e**,[5b] **4f**,[18] **4j**,[19] **4k–4m**[20] were prepared according to the literature.

Synthesis of β-keto *tert*-butyl esters (4g–4i, 4n): β-Keto esters **4g–4i** and **4n** were prepared by the following procedure reported by Jørgensen,[21] and **4g** was synthesized as follows. Lithium hexamethyldisilazide (LHMDS; 3 mL, 4 mmol, 1.3 M in THF) at −78 °C was added to a solution of 6-benzyloxy-1-tetralones (250 mg, 1 mmol) in THF (3 mL) and hexamethylphosphoramide (720 μL, 4 mmol), and the mixture was stirred for 90 min. 1-(*tert*-butoxycarbonyl)-imidazole (670 mg, 4 mmol) was added to the resulting mixture, then the mixture was allowed to warm to RT and stirred for additional 24 h. A saturated NH_4Cl solution was then added to the reaction mixture, and the organic layer was extracted with ethyl acetate (three times). The combined extracts were dried over $MgSO_4$, and the filtrates were concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to give *tert*-butyl 6-benzyloxy-1-tetralone-2-carboxylate **4g** (256 mg, 72% yield). The ratio of enol form to keto form is 5:1. ^{1}H NMR (400 MHz, $CDCl_3$): δ=12.64 (dr, 1H), 8.02 (d, J=8.8 Hz, 0.2H), 7.72 (d, J=8.3 Hz, 1H), 7.45–7.31 (m, 5H), 6.92–6.89 (m, 0.2H), 6.87–6.85 (m, 1H), 6.78–6.77 (m, 1.2H), 5.51 (s, 0.4H), 5.09 (s, 2H), 3.45 (dd, J=9.86, 4.67, 0.2H), 3.02–2.93 (m, 0.4H), 2.76 (t, J=7.3 Hz, 2H), 2.52–2.48 (t, J=8.3 Hz, 2H), 2.45–2.39 (m, 0.2H), 2.34–2.27 (m, 0.2H), 1.54 (s, 9H), 1.48 ppm (s, 2.5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=192.3, 169.6, 164.7, 162.8, 160.3, 146.0, 141.5, 136.5, 136.0, 130.0, 128.6, 128.5, 1281, 127.9, 127.3, 125.8, 125.6, 123.3, 113.9, 113.4, 112.2, 96.3, 81.5, 80.8, 70.0, 69.8, 55.0, 28.2, 28.1, 27.9, 27.8, 26.4, 20.9 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{24}NaO_4$ 375.1572: [M+Na]; found: 375.1569.

***tert*-Butyl 6-(dimethylamino)-1-tetralone-2-carboxylate (4h)**: 51% yield (mixture of enol and keto form (1:99)). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.95 (d, J=8.7 Hz, 1H), 6.60 (dd, J=8.7, 2.3 Hz, 1H), 6.36 (d, J=2.3 Hz, 1H), 3.41 (dd, J=10.7, 5.0 Hz, 1H), 3.05 (s, 6H), 2.99–2.84 (m, 2H), 2.44–2.35 (m, 1H), 2.30–2.23 (m, 1H), 1.48 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=191.8, 170.2, 153.5, 145.6, 129.7, 120.7, 110.3, 109.1, 81.1, 55.1, 40.0, 39.9, 28.3, 27.9, 26.7 ppm; HRMS (ESI): *m/z* calcd for $C_{17}H_{23}NNaO_3$: 312.1575 [M+Na]; found: 375.1538.

***tert*-Butyl 6-chloro-1-tetralone-2-carboxylate (4i)**: 89% yield; mixtures of enol and keto form (2.5:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.98 (d, J= 8.3 Hz, 1H), 7.70 (d, J=8.3 Hz, 0.4H), 7.31–7.23 (m, 1.4H), 3.49 (dd, J= 9.3, 4.7 Hz, 1H), 3.07–2,91 (m, 2H), 2.77 (t, J=7.3 Hz, 0.8H), 2.53–2.42 (m, 1.4H), 2.37–2.29 (m, 1H), 1.47 ppm (s, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=192.3, 192.2, 172.2, 168.9, 163.3, 151.9, 144.9, 140.8, 139.7, 135.7, 130.2, 129.0, 128.6, 128.4, 127.2, 126.4, 125.3, 98.2, 81.7, 81.5, 81.2, 80.7, 80.5, 7 77.2, 54.8, 28.1, 27.8, 27.6, 27.4, 27.1, 26.0, 20.6 ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{17}ClNaO_3$: 303.0763 [M+Na]; found: 303.0752.

***tert*-Butyl 5,8-dimethoxy-1-tetralone-2-carboxylate (4n)**: 60% yield; (mixtures of enol and keto form (1:99)): ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.08 (s, 1H), 7.37 (br, 1H), 7.04 (br, 1H), 6.97 (d, J=8.7 Hz, 1H), 6.80 (d, J=8.7 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.45 (dd, 10.0, 4.6 Hz, 1H), 3.08–3.00 (m, 1H), 2.81–2.67 (m, 1H), 2.41–2.23 (m, 1H), 1.62 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=193.2, 172.5, 169.5, 166.0, 154.1, 152.4, 150.0, 149.8, 134.0, 130.9, 122.3, 120.3, 115.4, 113.5, 111.3, 110.0, 99.3, 81.3, 81.0, 77.2, 57.0, 56.4, 56.3, 56.0, 55.8, 31.0, 28.2, 27.9, 25.2, 21.8, 21.3, 20.4 ppm; HRMS (ESI): *m/z* calcd for $C_{17}H_{22}NaO_5$: 329.1364 [M+ Na]; found: 329.1343.

General procedure: *The catalytic asymmetric α-hydroxylation of 1-tetralone derivatives **4** using guanidine–urea bifunctional organocatalyst* **3a**: A mixture of **3a** (5.6 mg, 0.005 mmol), **4a** (20.4 mg, 0.1 mmol), and K_2CO_3 (2.7 mg, 0.02 mmol) in toluene (2.0 mL) was cooled to 0 °C, and cumene hydroperoxide (22 μL, 0.12 mmol, contains ca. 20% aromatic hydrocarbon) was added to the solution. After stirring for 24 h at 0 °C, the reaction was quenched by addition of 10% $Na_2S_2O_3$ solution (2 mL), and the mixture was vigorously stirred for 1 h. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (three times). The combined extracts were dried over $MgSO_4$, and the filtrates were concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate 10:1 to 5:1) to give **5a**[7] with inseparable 2-phenyl-2-propanol derived from CHP (the yield of **3a** (93%) was determined by using ^{1}H NMR spectroscopy).[22] $[\alpha]_D^{25}$=−13.2 (c=0.8, $CHCl_3$); the enantiomeric excess of **5a** was determined to be 81% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250× 4.6 mm), *n*-hexane/2-propanol=90:10, flow rate 1 mL min^{-1}, τ_1(major)= 9.5, τ_2 (minor)=10.9.

Ethyl 2-hydroxy-1-tetralone-2-carboxylate (5b):[7] $[\alpha]_D^{25}$=−12.1 (c=0.9, $CHCl_3$); the enantiomeric excess of **5b** was determined to be 81% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250× 4.6 mm), *n*-hexane/2-propanol=90:10, flow rate 1 mL min^{-1}, τ_1(major)= 8.7, τ_2 (minor)=9.7.

Benzyl 2-hydroxy-1-tetralone-2-carboxylate (5c):[7] $[\alpha]_D^{25}$=−8.3 (c=0.7, $CHCl_3$); the enantiomeric excess of **5c** was determined to be 78% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250× 4.6 mm), *n*-hexane/2-propanol=90:10, flow rate 1 mL min^{-1}, τ_1(major)= 14.8, τ_2 (minor)=17.3.

Isopropyl 2-hydroxy-1-tetralone-2-carboxylate (5d):[5d] $[\alpha]_D^{25}$=−11.6 (c= 1.0, $CHCl_3$); the enantiomeric excess of **5d** was determined to be 90% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250× 4.6 mm), *n*-hexane/2-propanol=95:5, flow rate 1 mL min^{-1}, τ_1(major)= 7.7, τ_2 (minor)=8.5.

***tert*-Butyl 2-hydroxy-1-tetralone-2-carboxylate (5e)**:[5b] $[\alpha]_D^{25}$=−7.6 (c= 0.7, $CHCl_3$); the enantiomeric excess of **5e** was determined to be 93% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250× 4.6 mm), *n*-hexane/2-propanol=95:5, flow rate 1 mL min^{-1}, τ_1(major)= 6.7, τ_2 (minor)=7.3.

***tert*-Butyl 6-methoxy-2-hydroxy-1-tetralone-2-carboxylate (5f)**: $[\alpha]_D^{25}$=+ 11.1 (c=1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.01 (d, J= 8.7 Hz, 1H), 6.86 (d, J=8.7 Hz, 1H), 6.70 (s, 1H), 4.25 (br s, 1H), 3.87 (s, 3H), 3.08 (t, J=6.9 Hz, 2H), 2.19 (dt, J=13.3, 5.5 Hz, 1H), 2.63 (dt, J= 13.7, 7.3 Hz, 1H), 1.40 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 193.5, 170.4, 164.3, 146.6, 130.6, 124.1, 113.8, 112.7, 83.3, 77.7, 55.6, 32.9, 27.9, 26.1 ppm; HRMS (ESI): *m/z* calcd for $C_{16}H_{20}NaO_5$: 315.1208 [M+ Na]; found: 315.1257; enantiomeric excess of **5f** was determined to be 87% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250×4.6 mm), *n*-hexane/2-propanol=95:5, flow rate 1 mL min^{-1}, τ_1-(major)=10.2, τ_2 (minor)=12.6.

***tert*-Butyl 6-benzyloxy-2-hydroxy-1-tetralone-2-carboxylate (5g)**: $[\alpha]_D^{25} = +9.7$ ($c = 2.7$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.02$ (d, $J = 8.7$ Hz, 1H), 7.43–7.34 (m, 5H), 6.93 (d, $J = 8.7$ Hz, 1H), 6.79 (s, 1H), 5.13 (s, 2H), 4.27 (br s, 1H), 3.07 (t, $J = 6.4$ Hz, 2H), 2.62 (dt, $J = 13.3$, 5.5 Hz, 1H), 2.19 (dt, $J = 13.7$, 7.3 Hz, 1H), 1.40 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.5$, 170.4, 163.5, 146.6, 136.1, 130.7, 128.9, 128.4, 127.9, 127.6, 127.4, 126.8, 124.3, 114.4, 13.7, 83.4, 77.7, 77.5, 55.6, 32.8, 27.9, 26.1 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{24}NaO_5$: 391.1521 [*M*+Na], found: 391.1551; enantiomeric excess of **5g** was determined to be 92% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250×4.6 mm), *n*-hexane/2-propanol = 90:10, flow rate 1 mL min^{-1}, τ_1(major) = 13.4, τ_2 (minor) = 16.2.

***tert*-Butyl 6-(dimethylamino)-2-hydroxy-1-tetralone-2-carboxylate (5h)**: $[\alpha]_D^{25} = +60.2$ ($c = 1.1$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$ (d, $J = 8.7$ Hz, 1H), 6.61 (d, $J = 8.9$ Hz, 1H), 6.63–6.60(m, 1H), 6.37–6.36 (m, 1H), 4.31 (s, 1H), 3.10–2.96 (m, 8H), 2.63–2.57 (m, 1H), 2.19–2.11 (m, 1H), 1.41 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 192.5$, 170.6, 153.9, 145.9, 130.2, 118.9, 110.5, 109.1, 82.6, 77.4, 39.9, 32.9, 27.7, 26.3 ppm; HRMS (ESI): *m/z* calcd for $C_{17}H_{23}NNaO_4$: 328.1525 [*M*+Na], found 328.1543; enantiomeric excess of **5h** was determined to be 95% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250×4.6 mm), *n*-hexane/2-propanol = 90:10, flow rate 1 mL min^{-1}, τ_1 (major) = 12.07, τ_2 (minor) = 16.9.

***tert*-Butyl 6-chloro-2-hydroxy-1-tetralone-2-carboxylate (5i)**: $[\alpha]_D^{25} = +8.8$ ($c = 0.9$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.97$ (d, $J = 8.2$ Hz, 1H), 7.33–7.23 (m, 2H), 4.18 (br s, 1H), 3.16–2.99 (m, 2H), 2.66–2.58 (m, 1H), 2.26–2.16 (m, 1H), 1.40 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.8$, 170.0, 145.5, 140.7, 129.7, 129.2, 128.8, 127.6, 83.8, 77.7, 32.6, 27.9, 25.6 ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{17}ClO_4$: 319.0713 [*M*+Na]; found: 319.0706; the enantiomeric excess of **5i** was determined to be 95% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250×4.6 mm), *n*-hexane/ethanol = 99:1, flow rate 1 mL min^{-1}, τ_1 (major) = 11.6, τ_2 (minor) = 12.3.

***tert*-Butyl 6-bromo-2-hydroxy-1-tetralone-2-carboxylate (5j)**: $[\alpha]_D^{25} = +15.2$ ($c = 0.5$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (d, $J = 8.2$ Hz, 1H), 7.51 (d, $J = 8.7$ Hz, 1H), 7.47 (s, 1H), 4.22 (br s, 1H), 3.13–3.09 (m, 2H), 2.68–2.62 (m, 1H), 2.27–2.20 (m, 1H), 1.43 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.0$, 170.0, 145.6, 140.7, 131.9, 130.6, 129.7, 129.6, 83.8, 77.7, 32.6, 27.9, 25.5 ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{17}BrNaO_4$: 363.0208 [*M*+Na]; found: 363.0161; the enantiomeric excess of **5j** was determined to be 85% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OJ-H column (250×4.6 mm), *n*-hexane/2-propanol = 99:1, flow rate 1 mL min^{-1}, τ_1 (major) = 23.6, τ_2 (minor) = 27.5.

***tert*-Butyl 7-methoxy-2-hydroxy-1-tetralone-2-carboxylate (5k)**: $[\alpha]_D^{25} = -18.5$ ($c = 0.3$, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$ (s, 1H), 7.17 (d, $J = 8.7$ Hz, 1H), 7.10 (d, $J = 8.5$ Hz, 1H), 4.21 (s, 1H), 3.84 (s, 3H), 3.01–2.94 (m, 2H), 2.63 (dt, $J = 13.7$, 5.5, 1H), 2.20 (dt, $J = 13.3$, 7.6, 1H), 1.40 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 195.0$, 170.2, 158.6, 136.6, 131.5, 130.2, 122.9, 109.7, 83.5, 77.9, 55.7, 33.1, 27.9, 25.0 ppm; HRMS (ESI): *m/z* calcd for $C_{16}H_{20}NaO_5$: 315.1208 [*M*+Na]; found: 315.1227; the enantiomeric excess of **5k** was determined to be 93% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250×4.6 mm), *n*-hexane/2-propanol = 95:5, flow rate 1 mL min^{-1}, τ_1 (major) = 8.0, τ_2 (minor) = 9.0.

***tert*-Butyl 7-bromo-2-hydroxy-1-tetralone-2-carboxylate (5l)**: $[\alpha]_D^{25} = -16.8$ ($c = 0.9$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.15$ (d, $J = 1.8$ Hz, 1H), 7.62 (dd, $J = 2.2$, 8.2 Hz, 1H), 7.15 (d, $J = 8.2$ Hz, 1H), 4.15 (s, 1H), 3.12–2.97 (m, 2H), 2.64–2.58 (m, 1H), 2.25–2.16 (m, 1H), 1.40 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.6$, 170.0, 142.7, 137.0, 132.3, 130.8, 121.0, 83.9, 77.6, 32.6, 27.9, 25.3 ppm; HRMS (ESI): *m/z* calcd for $C_{15}H_{17}BrNaO_4$: 363.0208 [*M*+Na]; found: 363.0196; the enantiomeric excess of **5l** was determined to be 89% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OD-H column (250×4.6 mm), *n*-hexane/2-propanol = 95:5, flow rate 1 mL min^{-1}, τ_1(major) = 16.1, τ_2 (minor) = 21.9.

***tert*-Butyl 7-fluoro-2-hydroxy-1-tetralone-2-carboxylate (5m)**: $[\alpha]_D^{25} = -3.4$ ($c = 0.9$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.68$ (d, $J = 8.7$ Hz, 1H), 7.26–7.20 (m, 2H), 7.26 (s, 1H), 4.18 (s, 1H), 3.14–2.99 (m, 2H) 2.65–2.59 (m, 1H), 2.25–2.18 (m, 1H), 1.39 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.0$, 170.0, 162.9, 160.4, 139.7, 132.3, 130.8, 121.8, 121.6, 113.9, 113.7, 83.8, 77.6, 32.9, 27.9, 25.1 ppm; HRMS (ESI): *m/z* calcd for $C_{16}H_{20}FNaO_5$: 303.1009 [*M*+Na]; found: 303.0993; the enantiomeric excess of **5m** was determined to be 90% *ee* by means of chiral HPLC analysis. DAICEL CHIRALPAK AD-H column (250×4.6 mm), *n*-hexane/2-propanol = 95:5, flow rate 1 mL min^{-1}, τ_1 (major) = 15.7, τ_2 (minor) = 21.2.

***tert*-Butyl 5,8-dimethoxy-2-hydroxy-1-tetralone-2-carboxylate (5n)**: $[\alpha]_D^{25} = -48.5$ ($c = 1.0$, $CHCl_3$); Spectral data for **3n**: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.99$ (d, $J = 8.7$ Hz, 1H), 6.80 (d, $J = 9.2$ Hz, 1H), 4.54 (br s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.08–3.01 (m, 1H), 2.92–2.83 (m, 1H), 2.69–2.63 (m, 1H), 2.08–2.00 (m, 1H), 1.33 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 194.4$, 169.4, 154.2, 150.3, 134.1, 121.0, 116.1, 110.1, 82.8, 78,4, 56.5, 56.1, 31.6, 27.8, 20.5 ppm; HRMS (ESI): *m/z* calcd for $C_{17}H_{22}NaO_6$: 345.1314 [*M*+Na]; found: 345.1266; the enantiomeric excess of **5n** was determined to be 84% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OJ-H column (250×4.6 mm), *n*-hexane/2-propanol = 95:5, flow rate 1 mL min^{-1}, τ_1 (major) = 24.8, τ_2 (minor) = 33.0.

Synthesis of *ent*-6: Cumene hydroperoxide (670 μL, 3.66 mmol) was added to a mixture of **4n** (936 mg, 3.05 mmol), **3a** (171 mg, 0.15 mmol), and K_2CO_3 (84 mg, 0.61 mmol) in toluene (60 mL) at 0°C, and the mixture was stirred for 18 h. A solution of 10% $Na_2S_2O_3$ was added to the reaction mixture, and the resultant was stirred for 1 h vigorously. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined extracts were dried over $MgSO_4$, and the filtrates were concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10:1 to 5:1) to give **5n** (968 mg, 98% yield, 84% *ee*). $NaBH_4$ (29 mg, 0.8 mmol) was added to a solution of **5n** (500 mg, 1.5 mmol) in MeOH (15 mL) at 0°C. After stirring for 30 min at the same temperature, H_2O was added to the reaction mixture, and the organic layer was extracted with ethyl acetate. The extracts were dried over $MgSO_4$, and the filtrates were concentrated in vacuo to give diol, which was directly used in the next step. $BF_3{\cdot}Et_2O$ (195 μL, 1.5 mmol) was then added dropwise at 0°C to the solution of diol and triethylsilane (2.5 mL, 15.5 mmol) in dichloromethane (15 mL), and the resultant solution was allowed to RT. After stirring for 30 min, to the reaction mixture was added H_2O, and organic layer was extracted with dichloromethane. The combined extracts were dried over $MgSO_4$, and the filtrates were concentrated in vacuo to give α-hydroxy carboxylic acid **7**. Methyllithium (3.3 mL, 4.5 mmol, 1.36 M in 2-Me THF) was then added dropwise at 0°C to a solution of α-hydroxy carboxylic acid **7** in THF (10 mL), and the resulting mixture was allowed to RT. After stirring for 2 h, to the reaction mixture was added saturated NH_4Cl solution, and the organic layer was extracted with ethyl acetate. The extracts were dried over $MgSO_4$, and the filtrates were concentrated in vacuo. The residue was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate = 20:1 to 2:1) to give α-hydroxy ketone *ent*-**6** as a colorless solid (80 mg, 19%, 3 steps), whose optical purity was increased to 99% *ee* by a single recrystallization from *n*-hexane/ethyl acetate. $[\alpha]_D^{25} = +46.2$ ($c = 1.1$, $CHCl_3$) (lit. $[\alpha]_D^{25} = -22$ ($c = 0.8$, $CHCl_3$), 66% *ee*);[23] ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.67$ (d, $J = 9.1$ Hz, 1H), 6.64 (d, $J = 8.7$ Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 2.99–2.92 (m, 2H), 2.81–2.73 (m, 2H), 2.32 (s, 3H), 1.99–1.92 (m, 1H), 1.87–1.82 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 212.2$, 151.5, 151.0, 125.4, 122.6, 107.3, 106.9, 76.4, 55.6, 55.4, 32.3, 29.6, 23.9, 19.1 ppm; HRMS (ESI): *m/z* calcd for $C_{14}H_{18}NaO_4$: 273.11028 [*M*+Na]; found: 273.10863; the enantiomeric excess of *ent*-**5** was determined to be 99% *ee* by chiral HPLC analysis. DAICEL CHIRALPAK OJ-H column (250×4.6 mm), *n*-hexane/2-propanol = 95:5, flow rate 1 mL min^{-1}, τ_1 (major) = 26.1, τ_2 (minor) = 28.8.

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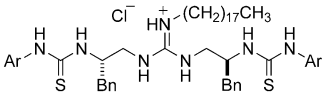
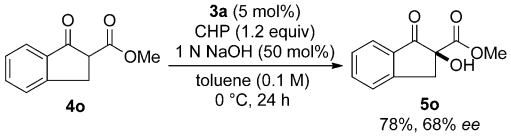


3i Ar = 3,5-$CF_3C_6H_3$

[13] In the case of the *tert*-butyl ester of **4e**, the background reaction was quite slow, and the amount of K_2CO_3 did not affect the enantioselectivity.
[14] Oxidation of the 1-indanone-derived substrate of **4o** was examined. In this case, oxidation took place to generate **5o** in 78% yield with 68% *ee* under NaOH/toluene (aqueous) biphasic conditions in the presence of catalyst **3a**. Further optimization of the reaction for 1-indanone-derived β-keto esters is in progress.



4o → **5o**
78%, 68% *ee*

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