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Methylhydrazine-induced enantioselective α-hydroxylation of β-keto esters with molecular oxygen catalyzed by hydroquinine

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ABSTRACT

Methylhydrazine-induced α-hydroxylation of β-dicarbonyl compounds was achieved using O_2 as the oxygen source. This reaction provides an efficient approach to enantioenriched *α*-hydroxy β-dicarbonyl compounds, which are valuable substances and widely used in the chemical and pharmaceutical industry. A wide variety of β-keto esters could undergo this oxidation to give the corresponding products in excellent yields (up to 95%) and with good enantioselectivities (up to 85% *ee*). The mild reaction conditions and the use of molecular oxygen as oxidant make this protocol very environmentally friendly and practical.

1. Introduction

Chiral α-hydroxy β-dicarbonyl compounds represent a functional and common structural motif in a variety of natural products, pharmaceuticals, and agrochemicals.[1] Furthermore, they have been used as an important intermediate in the synthesis of the insecticide indoxacarb.[2] Therefore, the asymmetric α-hydroxylation of 1,3-dicarbonyl compounds is a significant transformation, which allows for direct formation of a carbon–oxygen bond. A large number of catalytic systems for asymmetric α-hydroxylation of β-dicarbonyl compounds have been developed over the past two decades and can be categorized into the following two classes based on the combination of catalysts and oxidants **a)** metal complex/active oxidant.[3] **b)** organocatalyst/active oxidant.[4] It is worth mentioning that molecular oxygen has been considered as an ideal oxidant and an atom-efficient reagent in synthetic chemistry.[5] In recent years, photooxygenation becomes an important oxidation method using molecular oxygen as oxidant. This oxidation reaction could be achieved by the activation of O_2 with light and photosensitizer. In 2004, Córdova and his co-workers first reported enantioselective photooxygenation of aldehydes and ketones catalyzed by amino-acids[6] and our group demonstrated an efficient enantioselective phase-transfer-catalyzed photooxygenation of β-keto esters under mild conditions.[7] Furthermore, $P(OEt)_3/O_2$ system has been reported as an efficient combination for enantioselective oxidation of aromatic ketones and oxindoles,[8] but the $P(OEt)_3/O_2$ system showed narrow substrate scope possibly because of the inherent low reactivity to activate O_2.

Despite tremendous efforts by many groups, the catalytic asymmetric α-hydroxylation of β-dicarbonyl compounds by molecular oxygen is still a challenge. Herein we disclose the first α-hydroxylation of β-dicarbonyl compounds, using O_2 as the oxygen source, through the catalysis by methylhydrazine (H_2NNHMe) and a cinchona alkaloid. Enantiomerically α-hydroxy-β-dicarbonyl compounds were obtained with excellent yields (up to 95%) and good enantioselectivities (up to 85% *ee*).

2. Results and discussions

Hydrazine compounds are useful building blocks in organic synthesis of pharmaceuticals and pesticides, such as the antituberculosis medication isoniazid and the antifungal fluconazole.[9] Furthermore, they are widely used as reducing agent[10] and rocket fuels.[11] Recently, methylhydrazine-induced aerobic epoxidation of β,β-disubstituted enones has been reported.[12] Inspired by these results, we attempted the reaction of 1-indanone-derived β-keto ester **1a** with commercially available CH_3NHNH_2 in combination with Cs_2CO_3 (Table 1, entry 1). To our delight, **2a** was obtained in 80% yield in 6 h. Then we investigated the influence of the base and hydrazine. The reaction did not take place in the absence of

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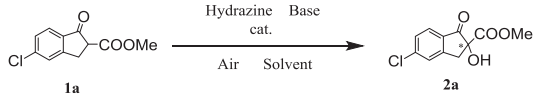
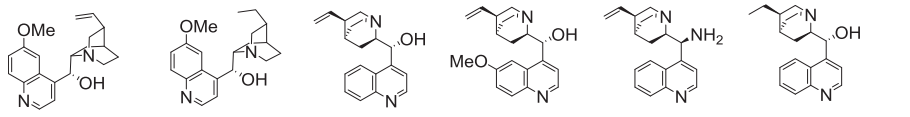
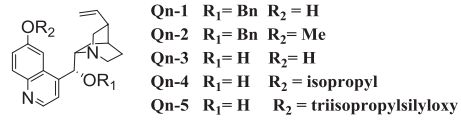
Table 1
Hydrazine-induced aerobic asymmetric α-hydroxylation of **1a**: Optimization of reaction conditions[a]







Entry	Hydrazine	Cat.	Base	Solvent	T [h]	T [°C]	Yield [%][b]	*ee* [%][c]
1	CH_3NHNH_2	—	Cs_2CO_3	MTBE	6	20	80	
2	None	—	Cs_2CO_3	MTBE	24	20	Nr	
3	CH_3NHNH_2	—	none	MTBE	12	20	Nr	/
4[f]	CH_3NHNH_2	**PTC-1**	Cs_2CO_3	MTBE	12	20	85	5 (*R*)[e]
5	CH_3NHNH_2	**Qn**	Cs_2CO_3	$CHCl_3$	12	20	89	23 (*R*)
6	CH_3NHNH_2	**Qn**	Et_3N	$CHCl_3$	12	20	75	35 (*R*)
7	CH_3NHNH_2	**Qn**	TMG[d]	$CHCl_3$	6	20	87	7 (*R*)
8	CH_3NHNH_2	**Qn**	imidazole	$CHCl_3$	12	20	73	41 (*R*)
9	CH_3NHNH_2	**Qn**	—	$CHCl_3$	24	20	67	49 (*R*)
10	$NH_2NH_2{\cdot}H_2O$	**Qn**	—	$CHCl_3$	24	20	Trace	n.d.
11	$NH_2NHCH_2CH_2OH$	**Qn**	—	$CHCl_3$	24	20	73	45 (*R*)
12	NH_2NHAc	**Qn**	—	$CHCl_3$	24	20	Trace	n.d.
13	NH_2NHPh	**Qn**	—	$CHCl_3$	24	20	70	35 (*R*)
14	NH_2NHCH_2Ph	**Qn**	—	$CHCl_3$	24	20	71	40 (*R*)
15	$C_6H_5NHNHCON{=}NC_6H_5$	**Qn**	—	$CHCl_3$	24	20	50	48 (*R*)
16	CH_3NHNH_2	**Cn**	—	$CHCl_3$	24	20	63	43 (*S*)
17	CH3NHNH$_2$	**Cn1**	—	$CHCl_3$	24	20	30	5 (*S*)
18	CH_3NHNH_2	**Qd**	—	$CHCl_3$	24	20	51	37 (*S*)
19	CH_3NHNH_2	**HCn**		$CHCl_3$	24	20	70	45 (*S*)
20	CH_3NHNH_2	**Qn1**	—	$CHCl_3$	24	20	43	17 (*S*)
21	CH_3NHNH_2	**Qn2**	—	$CHCl_3$	24	20	Trace	n.d.
22	CH_3NHNH_2	**Qn3**	—	$CHCl_3$	24	20	38	7 (*R*)
23	CH_3NHNH_2	**Qn4**	—	$CHCl_3$	24	20	65	41 (*R*)
24	CH_3NHNH_2	**Qn5**	—	$CHCl_3$	24	20	53	36 (*R*)
25	CH_3NHNH_2	**HQn**	—	$CHCl_3$	24	20	71	50 (*R*)
26[g]	CH_3NHNH_2	**HQn**	—	$CHCl_3$	24	15	85	67 (*R*)

[a] The reaction of **1a** with hydrazine (3.0 equiv) was carried out in the presence of cat (20 mol %) and base (3.0 equiv) in solvent (2 mL) under air atmosphere at room temperature.
[b] Isolated yields.
[c] The enantiomeric excess was determined by HPLC analysis of the product **2a** using a chiral column (DAICEL Chiralcel OD-H) with hexane/2-propanol (90:10) as the eluent.
[d] TMG=Tetramethylguanidine.
[e] The absolute configuration of the products were determined by comparison of the optical rotation and the HPLC retention time of the corresponding ester with literature values.[4b]
[f] 5 mol % of catalyst.
[g] Reaction condition: 1equiv. of β-keto ester, 1.3 equiv of H_2NNHMe and 40 mol % of hydroquinine in $CHCl_3$ at 15 °C.

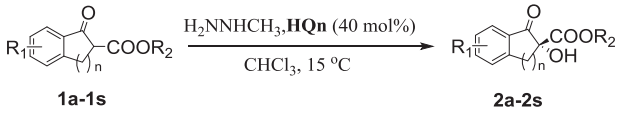
methylhydrazine or Cs_2CO_3 (Table 1, entries 2, 3). Next, we explored the use of cinchona alkaloid phase-transfer catalyst **PTC-1** for enantioselective α-hydroxylation, but the enantioselectivity was quite poor (Table 1, entry 4). To our delight, when we use natural cinchona alkaloid **Qn** as catalyst, the *ee* value of **2a** was increased to 23% (Table 1, entry 5). Prompted by this result, we investigated the influence of different bases. Tetramethylguanidine promoted the reaction but afforded almost racemic product (Table 1, entry 7). Triethylamine, imidazole were also tested but the desired product was obtained with moderate *ee* values (Table 1, entries 6 and 8). These results indicated that the choice of base was crucial to achieve good yields and *ee* values. We were surprised to find that the α-hydroxylation also took place efficiently with only a catalytic amount of **Qn**, through reaction time was extended to 24 h (Table 1, entry 9). Shibata reported that methylhydrazine is indispensable for aerobic epoxidation and this phenomenon would not have been discovered using other hydrazine derivatives.[12] We attempted to use different hydrazines to promote this reaction. Nearly no products were obtained when $NH_2NH_2{\cdot}H_2O$ and H_2NNHAc were used to replace H_2NNHMe (Table 1, entries 10 and 12). However, when $NH_2NHCH_2CH_2OH$, NH_2NHPh, and NH_2NHCH_2Ph were applied to this asymmetric α-hydroxylation, the oxidation product **2a** was obtained in good yields (70%–83%) with moderate *ee* values (35%–45%) (Table 1, entries 11, 13, and 14). $C_6H_5NHNHCON{=}NC_6H_5$ could lead to the formation of **2a** with good enantioselectivity (48%) but in poor yield (Table 1, entry 15). These results showed that the reactivity of the hydrazines is possibly related to electron density of the nitrogen atom. H_2NNHMe, $NH_2NHCH_2CH_2OH$, and NH_2NHCH_2Ph bearing electron donating groups ($-CH_3$, $-CH_2CH_2OH$, and $-CH_2Ph$) provided better results than other hydrazines. In consideration of atom economy, yield and enantioselectivity of the product, H_2NNHMe was selected as the oxygen activation substance for this α-hydroxylation. After that, we screened different cinchona alkaloids as organocatalysts under

certain reaction conditions. Cinchonine (**Cn**) provided the oxidation product **2b** in 63% yield and with 43% *ee* (*S*) (Table 1, entry 16). Quinidine (**Qd**) was also tested and **2a** was obtained in 51% yield and with 37% *ee* (*S*) (Table 1, entry 18). **Cn-1**(*epi*-9-amino-(9-deoxy)-cinchonine) gave the α-hydroxylation product with poor yield and *ee* value (Table 1, entry 17). Hydrocinchonine (**HCn**) was then introduced, providing a slightly higher *ee* value and yield compared with cinchonine (**Cn**) (Table 1, entry 19). Several **Qn** derivatives with modification at C-6′ and C-9 were investigated. **Qn-1**, bearing a benzyl ether group at C-9 position, provided **2a** in 43% yield and with 17% *ee* (Table 1, entry 20). The di-ether derivative **Qn-2** could not promote this reaction (Table 1, entry 21). The di-hydroxyl derivative **Qn-3** was not an effective catalyst for this reaction, either (Table 1, entry 22). We also investigated the impact of C-6′ substituent group on this α-hydroxylation. Neither an isopropyl (**Qn-4**) nor a more bulky triisopropylsilyloxy substituent at this position (**Qn-5**) could enhance the enantioselectivity and yield (Table 1, entries 23 and 24). To our delight, *ee* value was improved to 50% when hydroquinine (**HQn**) was used as the catalyst (Table 1 entry 25). After selecting **HQn** as the catalyst for this transformation, we optimized the reaction conditions such as the solvent, temperature, substrate concentration, catalyst loading and methylhydrazine dosage and others (See Supplementary data for details). The optimal reaction conditions required the use of 40 mol % hydroquinine (**HQn**), 1.3 equiv of H_2NNHMe in $CHCl_3$ at 15 °C in air, 24 h (Table 1, entry 26).

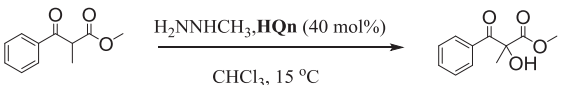
Under the optimized reaction conditions (1 equiv of β-keto ester, 1.3 equiv of H_2NNHMe and 40 mol % of hydroquinine in $CHCl_3$ at 15 °C, in air, 24 h), a range of β-keto esters were further investigated, and the results were outlined in Table 2. A series of indone methyl esters (**1a**–**1h**) bearing different substituents, such as methyl, methoxy, chloro, bromo groups at the phenyl ring could be converted into the corresponding products **2a**–**2h** in good yields (71–85%) and with 64–78% *ee* (Table 2, entries 1–8). Interestingly, 5,6-dimethoxy β-keto ester **1i** did not give the oxidation product, possibly due to the inherently low reactivity of **1i**. The effect of the ester group of indanone derivatives on this asymmetric process was also investigated.

The yield and enantioselectivity from ethyl ester (**1j**) was slightly lower than the methyl ester (Table 2, entry 10). When the methyl group was replaced by 3-ethyl amyl, the *ee* value was improved to 75% with a little sacrifice of yield (Table 2, entry 11). The isopropyl, *tert*-butyl, 1-Ad, and benzyl groups were also investigated. The α-hydroxylation of these substrates gave the corresponding **21**-**2o** in good yields (71–78%) and with high *ee* values (55–61%) (Table 2, entries 12–15). Interestingly, when R_2 was changed to $-C(Ph)_2CH_3$, the *ee* value was significantly improved to 85% and the yield of **2p** was excellent (Table 2, entry 16). We then tested some substrates with steric hindrance group. **1q** bearing a 9-anthracenylmethyl afforded the corresponding product **2r** in 81% yield and with 72% *ee* (Table 2, entry 18). Similarly, **2q** was obtained in 82% yield and with 73% *ee* (Table 2, entry 17). Overall, this method showed good substrate suitability. The scope of the reaction was further probed for six-membered cyclic substrate **1s**, as well as acyclic substrate **1t**. Under the optimized reaction conditions, tetralone β-keto esters (**1s**) did not give the oxidation product, nor did the simple acyclic β-keto ester **1t** (Table 2, entries 19, 20). The inherently lower reactivity of the two substrates led to no oxidation under this method. In addition, the activity of α-hydrogen atom is so weak that our catalyst is not alkaline enough to activate the α-hydrogen atom. To test the generality of our asymmetric oxidation, a 1.12 g sample of indanone carboxylate **1a** was treated with H_2NNHMe (1.3 equiv) in 200 mL $CHCl_3$ under the above optimized conditions of catalyst Hydroquinine (**HQn**) loading of 40 mol % on a gram-quantity scale. After stirring 24 h at 15 °C, the α-hydroxylation product **3b** was obtained by flash chromatography in

Table 2
Substrate scope in the asymmetric α-hydroxylation of β-keto esters[a]



1a-1s 2a-2s



1t 2t

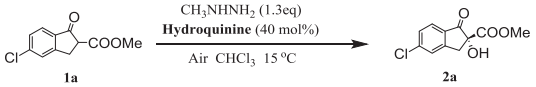
Entry	Sub	*n*	R_1	R_2	Yield [%][b]	*ee* [%][c]
1	1a	1	Cl	Me	85	67
2	1b	1	6-Me	Me	78	65
3	1c	1	6-MeO	Me	69	78
4	1d	1	6-F	Me	81	67
5	1e	1	6-Br	Me	85	64
6	1f	1		Me	82	68
7	1g	1	5-Br	Me	75	66
8	1h	1	4-MeO	Me	71	67
9[d]	1i	1	5,6-diMeO	Me	Trace	Nd
10	1j	1	H	Et	72	66
11	1k	1	H	$C(Et)_3$	67	75
12	1l	1	H	$CH(CH_3)_2$	73	61
13	1m	1	H	t-Bu	78	58
14	1n	1	H	Bn	75	60
15	1o	1	H	^{1}Ad	71	55
16	1p	1	H	$C(Ph)_2CH_3$	95	85
17	1q	1	H		82	73
18	1r	1	H		81	72
19[d]	1s	2	H	CH_3	Trace	Nd
20[d]	1t	—	—	—	Trace	Nd

[a] Unless otherwise noted, the reaction was carried out with 1equiv. of β-keto ester, 1.3 equiv of H_2NNHMe and 40 mol % of hydroquinine in $CHCl_3$ at 15 °C.
[b] Isolated yield.
[c] Determined by HPLC.
[d] Monitored by TLC.

78% yield with high enantioselectivity (65% *ee*). It is worth mentioning that the catalyst hydroquinine (**HQn**) was recovered in 86% yield by flash chromatography and the recovered catalyst could be reused in the model reaction (Table 2, entry 1), giving identical yield and enantioselectivity.

In order to understand the reaction mechanism, we designed some control experiments. The yield and enatioselectivity of **2a** were slightly better under an O_2 atmosphere than under air, and reaction time could be shortened (Table 3, entry 1). The α-hydroxylation did not occur under a nitrogen atmosphere(Table 3, entry 2). Furthermore, the addition of water to the reaction system could not promote this transformation (Table 3, entry 3). These results clearly indicate that the oxygen atom in the hydroxylation product originates from molecular oxygen in air. It was reported that in the presence of hydrazine and O_2 and base, hydrogen peroxide could be formed through a single-electron transfer process.[13–15] When 30% H_2O_2 was used instead of the H_2NNHMe/air system, lower *ee* value and chemical yield were observed (Table 3, entry 4). We then tested the H_2NNHMe/air system with additional H_2O. Interestingly, the reaction could provide **2a** with similar enantioselectivity and yield compared with 30% H_2O_2 system (Table 3, entry 5). The reaction proceeded well in the presence of the singlet oxygen inhibitor 1,4-diazabicyclo[2,2,2] octane (DABCO) (Table 3, entry 6). Furthermore, the reaction also worked well in the dark (Table 3, entry 8). These results suggest singlet molecular oxygen was not involved in this transformation. However, when 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was added, nearly

Table 3
Some control experiments[a]



Entry	Conditions	Yield [%][b]	*ee* [%][c]
1[d]	O_2	87	68
2[e]	Nitrogen	Nr	—
3[e]	Nitrogen+5equiv of H_2O	Nr	—
4[f]	30% H_2O_2 (1.3 equiv)	50	53
5	H_2O (0.7 equiv)	58	51
6	DABCO (0.5 equiv)	84	54
7	TEMPO (1.0 equiv)	<5	nd
8	Without light	82	67

[a] Unless otherwise noted, the reaction was carried out with 1 equiv of β-keto ester, 1.3 equiv of H_2NNHMe and 40 mol % of hydroquinine in $CHCl_3$ at 15 °C.
[b] Isolated yield.
[c] Determined by HPLC.
[d] Reaction time:12 h.
[e] Monitored by TLC.
[f] The reaction was carried out in the absence of H_2NNHMe under nitrogen atmosphere (Fig. 1).

no oxidation product was obtained, indicating a possible radical mechanism (Table 3, entry 7).

Based on the above observations, we propose the reaction mechanism as shown in Fig. 2. First, H_2NNHMe reacted with molecular oxygen through a single-electron transfer to generate hydrogen peroxide. Different from Shibata's work,[15] in which stoichiometric Cs_2CO_3 was used to promote the epoxidation, **HQn** was used not only as an organocatalyst, but also as a base in our case. Moreover, several other hydrazines including $NH_2NHCH_2CH_2OH$, NH_2NHPh, NH_2NHCH_2Ph, and $C_6H_5NHNHCON{=}NC_6H_5$ could promote this α-hydroxylation (Table 1, entries 11, 13–15), which extended the application of this method At the second step, the generated H_2O_2 reacted with the substrates, affording α-hydroxylation products along with 1 equiv of water. The lower chemical yield of **3a** when using 30% H_2O_2 instead of the H_2NNHMe/air system (entry 5, Table 3) might be explained by the purity of H_2O_2, since our H_2NNHMe/air system generates highly reactive and pure H_2O_2.

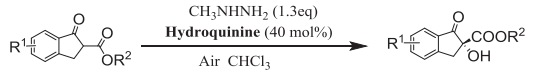


Fig. 1. Asymmetric α-hydroxylation of β-keto esters by a methylhydrazine/cinchona alkaloid/air/system.

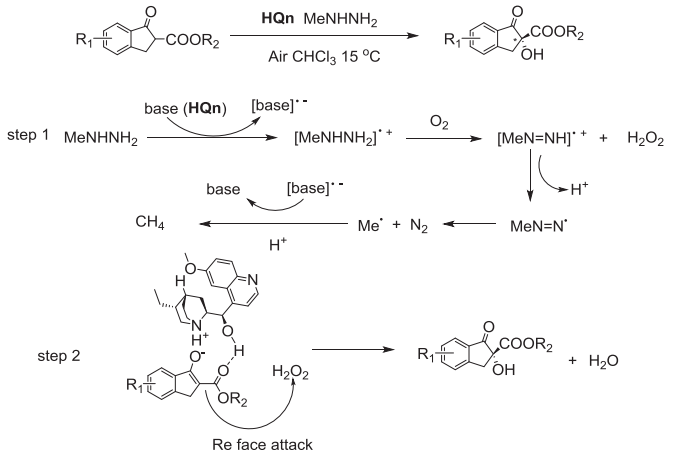


Fig. 2. Mechanism for methylhydrazine-induced enantioselective α-hydroxylation of β-keto esters.

3. Conclusion

In summary, an efficient and enantioselective methylhydrazine-induced α-hydroxylation of β-keto esters has been developed under mild conditions. This transformation is applicable to a range of β-keto esters, providing the desired products in high yields and with good enantioselectivities. The α-hydroxydicarbonyl compounds are highly valued chemicals and widely used in the chemical and pharmaceutical industry. Molecular oxygen in air, the most environmentally friendly oxidant, was employed at room temperature and many kinds of hydrazines could promote this reaction. Further work on the application of this methylhydrazine-induced asymmetric oxidation reaction is currently underway.

4. Experimental

4.1. General

Unless otherwise stated, all commercial reagents and solvents were used without further additional purification. Analytical TLC was visualized with UV light at 254 nm. Thin layer chromatography was carried out on TLC aluminum sheets with silica gel 60 F_{254}. Purification of reaction products was carried out with chromatography on silica gel 60 (200–400 mesh). Melting points were determined with a hot plate apparatus. Optical rotations were measured on a digital polarimeter with a sodium lamp at room temperature. ^1H NMR (400 MHz) or (500 MHz) spectra were obtained at 25 °C; ^{13}C NMR (101 MHz) were recorded on a VARIAN INOVA-400M and AVANCE II 400 spectrometer at 25 °C. Chemical shifts are reported as δ (ppm) values relative to TMS as internal standard and coupling constants (J) in Hz. The enantiomeric excesses (*ee*) were determined by chiral HPLC. HPLC analyses were performed with Diacel Chiralpak AD-H, OD-H and AS-H chiral column (0.46 cm×25 cm), using mixtures of n-hexane/isopropyl alcohol as mobile phase at 25 °C.

4.2. General procedure for α-hydroxylation of β-keto esters

To a solution of β-keto ester **1** (0.1 mmol) and catalyst **HQn** (1.3 mg, 0.04 mmol, 40 mol %) in chloroform (2 mL) was added H_2NNHMe (0.13 M in chloroform solution, 1.3 equiv, 2 mL). The resulting mixture was stirred at 15 °C for 24 h. The reaction was monitored by TLC, and the solvent was removed under reduced pressure upon the completion of the reaction. The residue was purified by flash chromatography (silica gel; petroleum ether/ethyl acetate=13:1–5:1) to afford products.

*4.2.1. Methyl 2-hydroxy-5-chloro-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2a**).* White solid (18.6 mg, 85% yield); $[\alpha]_D^{25}$ −61.5 (*c* 0.07, $CHCl_3$, 67% *ee*); mp 134–136 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J*=8.2 Hz, 1H), 7.50 (d, *J*=0.7 Hz, 1H), 7.43 (dd, *J*=8.2, 0.8 Hz, 1H), 3.75 (s, 3H), 3.71 (d, *J*=17.4 Hz, 1H), 3.24 (d, *J*=17.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.36, 171.53, 153.53, 142.89, 131.99, 129.09, 126.77, 126.40, 80.43, 53.62, 38.95. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=10.4 min, τ_R (minor)=8.8 min.

*4.2.2. Methyl 2-hydroxy-6-methyl-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2b**).* White solid (15.9 mg, 78% yield); $[\alpha]_D^{25}$ −46.2 (*c* 0.04, $CHCl_3$, 65% *ee*); mp132–134 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.50 (d, *J*=7.8 Hz, 1H), 7.38 (d, *J*=7.8 Hz, 1H), 3.74 (s, 3H), 3.68 (d, *J*=17.1 Hz, 1H), 3.21 (d, *J*=17.1 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.03, 172.21, 149.79, 138.44, 137.68, 133.84, 126.31, 125.38, 80.89, 53.64, 39.11, 21.28. HPLC conditions:

Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=12.4 min, τ_R (minor)=10.7 min.

*4.2.3. Methyl 2-hydroxy-6-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2c**).* Yellow solid (15.2 mg, 69% yield); $[\alpha]_D^{25}$ −38.6 (*c* 0.06, $CHCl_3$, 78% *ee*); mp 118–120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J*=8.3 Hz, 1H), 7.28 (m, 1H), 7.21 (d, *J*=8.6 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 3.65 (d, *J*=16.9 Hz, 1H), 3.18 (d, *J*=16.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.85, 172.04, 159.85, 145.22, 134.66, 127.23, 125.77, 106.19, 81.04, 55.69, 53.57, 38.67. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=15.6 min, τ_R (minor)=13.8 min.

*4.2.4. Methyl 2-hydroxy-6-fluorine-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2d**).* White solid (16.8 mg, 81% yield); $[\alpha]_D^{25}$ −46.5 (*c* 0.09, $CHCl_3$, 67% *ee*); mp 130–132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56–7.35 (m, 3H), 3.76 (s, 3H), 3.69 (d, *J*=17.1 Hz, 1H), 3.22 (d, *J*=17.1 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ=200.10, 200.07, 171.57, 163.75, 161.27, 147.68, 147.66, 135.26, 135.18, 127.99, 127.92, 124.05, 123.81, 111.12, 110.90, 81.04, 53.57, 38.79. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=13.0 min, τ_R (minor)=10.9 min.

*4.2.5. Methyl 2-hydroxy-6-bromine-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2e**).* Yellow solid (22.9 mg, 85% yield); $[\alpha]_D^{25}$ −28.3 (*c* 0.10, $CHCl_3$, 64% *ee*); mp 119–121 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J*=1.8 Hz, 1H), 7.78 (dd, *J*=8.2, 1.9 Hz, 1H), 7.39 (d, *J*=8.2 Hz, 1H), 3.75 (s, 3H), 3.67 (d, *J*=17.4 Hz, 1H), 3.20 (d, *J*=17.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 199.52, 171.49, 150.67, 138.94, 135.35, 128.13, 128.03, 122.30, 80.61, 53.67, 38.92. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=14.1 min, τ_R (minor)=11.8 min.

*4.2.6. Methyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2f**).* Colorless solid (15.5 mg, 82% yield); $[\alpha]_D^{25}$ −56.1 (*c* 0.08, $CHCl_3$, 68% *ee*); mp 134–136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J*=7.7 Hz, 1H), 7.68 (t, *J*=7.5 Hz, 1H), 7.50 (d, *J*=7.7 Hz, 1H), 7.44 (t, *J*=7.5 Hz, 1H), 3.78–3.69 (m, 4H), 3.26 (d, *J*=17.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.82, 171.93, 152.21, 136.21, 133.54, 128.19, 126.49, 125.36, 80.38, 53.50, 39.26. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=80/20, 1 mL/min, 254 nm, τ_R (major)=9.2 min, τ_R (minor)=8.0 min.

*4.2.7. Methyl 2-hydroxy-5-bromine-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2g**).* White solid (20.2 mg, 75% yield); $[\alpha]_D^{25}$ −63.1 (*c* 0.08, $CHCl_3$, 66% *ee*); mp 126–128 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74–7.63 (m, 2H), 7.58 (dd, *J*=8.2, 0.6 Hz, 1H), 3.75 (s, 3H), 3.70 (d, *J*=17.4 Hz, 1H), 3.24 (d, *J*=17.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl3) δ 199.52, 171.49, 150.67, 138.94, 135.35, 128.13, 128.03, 122.30, 80.61, 53.67, 38.92. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=15.8 min, τ_R (minor)=13.4 min.

*4.2.8. Methyl 2-hydroxy-4-methoxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2h**).* White solid (15.6 mg, 71% yield); $[\alpha]_D^{25}$ −45.7 (*c* 0.07, $CHCl_3$, 67% *ee*); mp 141–143 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.35 (m, 2H), 7.12 (d, *J*=7.1 Hz, 1H), 3.92 (s, 3H), 3.74 (s, 3H), 3.66 (d, *J*=17.7 Hz, 1H), 3.12 (d, *J*=17.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.05, 172.08, 156.71, 141.21, 134.86, 129.71, 116.64, 116.32, 80.23, 55.58, 53.47, 36.17. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=14.2 min, τ_R (minor)=16.0 min.

*4.2.9. Ethyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2j**).* Colorless oil (14.7 mg, 72% yield); $[\alpha]_D^{25}$ −41.5 (*c* 0.14, $CHCl_3$, 66% *ee*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J*=7.7 Hz, 1H), 7.68 (td, *J*=7.6, 1.1 Hz, 1H), 7.50 (d, *J*=7.7 Hz, 1H), 7.47–7.41 (m, 1H), 4.30–4.13 (m, 2H), 3.73 (d, *J*=17.2 Hz, 1H), 3.26 (d, *J*=17.2 Hz, 1H), 1.19 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.97, 171.47, 152.30, 136.12, 133.61, 128.12, 126.46, 125.29, 80.32, 62.79, 39.30, 13.97. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=11.0 min, τ_R (minor)=9.6 min.

*4.2.10. 3-Ethyl amyl 2-hydroxy-1-oxo-2,3-dihydro-1H-ind-ene-2-carboxylate (**2k**).* Colorless oil (18.4 mg, 67% yield); $[\alpha]_D^{25}$ −23.5 (*c* 0.05, $CHCl_3$, 75% *ee*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J*=7.7 Hz, 1H), 7.65 (td, *J*=7.6, 1.1 Hz, 1H), 7.48 (d, *J*=7.7 Hz, 1H), 7.42 (t, *J*=7.5 Hz, 1H), 4.04 (s, 1H), 3.64 (d, *J*=17.0 Hz, 1H), 3.26 (d, *J*=17.0 Hz, 1H), 1.70 (q, *J*=7.5 Hz, 6H), 0.65 (t, *J*=7.5 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.47, 170.12, 152.16, 135.80, 134.20, 127.98, 126.21, 124.97, 92.17, 80.76, 39.66, 26.87, 7.40. HPLC conditions: Chiralcel AS-H column (250×4.6 mm), hexane/*i*-PrOH=80/20, 1 mL/min, 254 nm, τ_R (major)=9.1 min, τ_R (minor)=10.9 min.

*4.2.11. Isopropyl 2-hydroxy-1-oxo-2,3-dihydro-1H-ind-ene-2-carboxylate (**2l**).* White solid (15.9 mg, 73% yield); $[\alpha]_D^{25}$ −30.9 (*c* 0.06, $CHCl_3$, 61% *ee*); mp 68–74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J*=7.7 Hz, 1H), 7.67 (td, *J*=7.6, 1.0 Hz, 1H), 7.49 (d, *J*=7.7 Hz, 1H), 7.43 (dd, *J*=11.1, 3.9 Hz, 1H), 5.19–4.94 (m, 1H), 3.70 (d, *J*=17.2 Hz, 1H), 3.24 (d, *J*=17.2 Hz, 1H), 1.20 (d, *J*=6.3 Hz, 3H), 1.13 (d, *J*=6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.02, 171.02, 152.35, 136.03, 133.67, 128.07, 126.41, 125.23, 80.30, 70.91, 39.27, 21.54, 21.34. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=8.7 min, τ_R (minor)=7.8 min.

*4.2.12. tert-Butyl 2-hydroxy-1-oxo-2,3-dihydro-1H-ind-ene-2-carboxylate (**2m**).* White solid (18.0 mg, 78% yield); $[\alpha]_D^{25}$−29.5 (*c* 0.06, $CHCl_3$, 58% *ee*); mp 128–129 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J*=7.7 Hz, 1H), 7.64 (d, *J*=7.5 Hz, 1H), 7.48 (d, *J*=7.7 Hz, 1H), 7.42 (t, *J*=7.5 Hz, 1H), 3.65 (d, *J*=17.1 Hz, 1H), 3.22 (d, *J*=17.1 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.37, 170.55, 152.33, 135.86, 133.93, 127.95, 126.28, 125.08, 83.95, 83.51, 80.54, 80.11, 39.44, 27.70. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=6.8 min, τ_R (minor)=6.3 min.

*4.2.13. Benzyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate (**2n**).* Colorless solid (20.0 mg, 75% yield); $[\alpha]_D^{26}$ −47.6 (*c* 0.04, $CHCl_3$, 60% *ee*); mp 94–97 °C; ^{1}H NMR (500 MHz, CDCl3) δ 7.80 (d, *J*=7.7 Hz, 1H), 7.65 (t, *J*=7.2 Hz, 1H), 7.50–7.39 (m, 2H), 7.33–7.26 (m, 3H), 7.14 (dd, *J*=6.5, 2.8 Hz, 2H), 5.22 (d, *J*=12.4 Hz, 1H), 5.12 (d, *J*=12.4 Hz, 1H), 3.72 (d, *J*=17.2 Hz, 1H), 3.25 (d, *J*=17.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.77, 171.28, 152.21, 136.19, 134.77, 133.60, 128.59, 128.47, 128.18, 127.76, 126.49, 125.35, 80.62, 68.01, 39.27; HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=19.1 min, τ_R (minor)=15.9 min.

*4.2.14. 1-Adamantyl 2-hydroxy-1-oxo-2,3-dihydro-1H-inde-ne-2-carboxylate (**2o**).* Colorless oil (22.0 mg, 71% yield); $[\alpha]_D^{25}$ −25.0 (*c* 0.05, $CHCl_3$, 55% *ee*); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J*=7.7 Hz, 1H), 7.65 (td, *J*=7.6, 1.1 Hz, 1H), 7.48 (d, *J*=7.7 Hz, 1H), 7.42 (t, *J*=7.5 Hz, 1H), 3.66 (d, *J*=17.1 Hz, 1H), 3.22 (d, *J*=17.1 Hz, 1H), 2.12 (s, 3H), 1.96 (d, *J*=3.1 Hz, 6H), 1.60 (d, *J*=2.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.44, 170.22, 152.36, 135.80, 134.01, 127.91, 126.26, 125.06, 83.94, 80.54, 40.93, 39.55, 35.87, 30.82. HPLC conditions: Chiralcel AD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=18.2 min, τ_R (minor)=11.3 min.

*4.2.15. α-Methyl-α-phenyl-benzyl 2-hydroxy-1-indanone-carboxylate(**2p**).* White solid (31.7 mg, 89% yield); $[\alpha]_D^{25}$ −4.3 (*c* 0.12, $CHCl_3$, 85% *ee*); mp 90–92 °C; ^{1}H NMR (400 MHz, DMSO)

δ 7.90–7.78 (m, 2H), 7.70 (d, *J*=7.7 Hz, 1H), 7.57 (t, *J*=7.4 Hz, 1H), 7.23–7.07 (m, 6H), 7.02–6.85 (m, 4H), 6.69 (br s, 1H), 3.76 (d, *J*=17.4 Hz, 1H), 3.20 (d, *J*=17.4 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 202.11, 169.26, 152.41, 145.36, 145.27, 136.58, 134.74, 128.72, 128.53, 128.51, 127.54, 127.49, 127.45, 125.35, 125.32, 124.85, 85.71, 81.09, 41.24, 26.25. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=19.9 min, τ_R (minor)=15.4 min.

*4.2.16. 2,7-Dibromo-9H-fluoren-9-yl 2-hydroxyl-1-indanone-2-carboxylate (**2q**).* White solid (42.0 mg, 82% yield); $[\alpha]_D^{25}$ −18.8 (*c* 0.05, $CHCl_3$, 73% *ee*); mp 168–172 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J*=7.7 Hz, 1H), 7.64 (dd, *J*=13.0, 5.1 Hz, 2H), 7.56–7.52 (m, 1H), 7.49 (dd, *J*=8.1, 1.5 Hz, 1H), 7.43 (m, 5H), 6.66 (s, 1H), 3.76 (d, *J*=17.2 Hz, 1H), 3.31 (d, *J*=17.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.36, 172.07, 152.16, 142.55, 142.36, 139.08, 138.76, 136.37, 133.17, 133.09, 129.26, 129.03, 128.35, 126.56, 125.44, 122.10, 122.06, 121.48, 121.36, 80.85, 76.05, 39.05. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=21.9 min, τ_R (minor)=18.6 min.

*4.2.17. 9-Anthracenemethyl 2-hydroxy-1-indanone-2-carboxylate (**2r**).* Yellow solid (29.6 mg, 81% yield); $[\alpha]_D^{25}$ −20.0 (*c* 0.16, $CHCl_3$, 72% *ee*); mp 111–113 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.12 (d, *J*=8.1 Hz, 2H), 8.05–7.93 (m, 2H), 7.70 (d, *J*=7.6 Hz, 1H), 7.53 (t, *J*=7.5 Hz, 1H), 7.50–7.42 (m, 4H), 7.33 (t, *J*=7.5 Hz, 1H), 7.29–7.23 (m, 1H), 6.36 (d, *J*=12.6 Hz, 1H), 6.00 (d, *J*=12.6 Hz, 1H), 3.49 (d, *J*=17.1 Hz, 1H), 3.11 (d, *J*=17.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.73, 171.56, 152.15, 135.97, 133.47, 131.23, 130.95, 129.66, 129.08, 128.00, 126.81, 126.37, 125.24, 125.11, 124.83, 123.58, 80.77, 61.27, 39.17. HPLC conditions: Chiralcel OD-H column (250×4.6 mm), hexane/*i*-PrOH=90/10, 1 mL/min, 254 nm, τ_R (major)=31.7 min, τ_R (minor)=25.3 min.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.11.029. These data include MOL files and InChiKeys of the most important compounds described in this article.

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