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Asymmetric organocatalytic Michael addition of anthrone to enone†

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Catalyzed by the bifunctional tertiary amino–thiourea organocatalyst derived from epicinchona alkaloid, the asymmetric Michael addition of anthrone to enone was achieved in high yield with excellent enantioselectivity.

Introduction

As one of the most important approaches to carbon–carbon bond forming, the Michael addition has drawn significant attention in organic chemistry,[1] as well as asymmetric organocatalysis.[2] The past decade has witnessed explosive growth in the field of asymmetric organocatalysis with a catalytic amount of a small organic molecule.[3] Bifunctional organocatalysts bearing tertiary amine and thiourea, which are able to simultaneously bind and activate two reactants, have exhibited enormous potential in a broad range of enantioselective reactions.[4] Up to now, a variety of bifunctional catalysts have been developed for the asymmetric Michael addition of nitroolefins[5] and enones.[6]

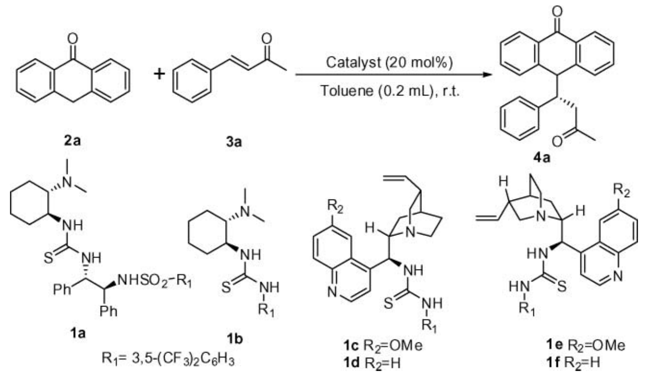
As a reactive diene, anthrone has been successfully applied in the Diels–Alder reaction, which makes it a promising synthetic tool for the formation of cyclic compounds.[7] Effective catalytic asymmetric Diels–Alder reactions of phenylmaleimide activated olefin with anthrone have been reported in the presence of chiral Brønsted base.[7i] However, the Michael addition of anthrone with α,β-unsaturated ketone is still a great challenge due to the Diels–Alder reaction byproducts.[8] So we envisioned the corresponding Michael addition could be exclusively produced in good yield and excellent enantioselectivity in the presence of bifunctional organocatalyst.

Herein we presented a catalytic asymmetric Michael addition of anthrone to α,β-unsaturated ketones for the first time with bifunctional catalyst **1c** developed from cinchona alkaloid.[9]

Results and discussion

In the initial investigation of screening organocatalysts, the Michael addition of anthrone **2a** to α,β-unsaturated ketone **3a** (2.0 equiv) was carried out in toluene (0.5 M) in the presence of tertiary amine–thiourea organocatalysts (**1a–1f**) at room temperature. As illustrated in Table 1, the **1a**-catalyzed reaction afforded 78% conversion with only 39% ee (Entry 1). To our delight, the conversion increased to 91% with 78% ee when **1b** was employed (Entry 2). In order to obtain excellent conversion and enantioselectivity, we next promoted the Michael reaction in the presence of cinchona alkaloid derived tertiary amino–thiourea organocatalysts **1c–1f**, which have exhibited high catalytic activity in the Michael addition of enone. Gratifyingly, the Michael addition of **2a** with **3a** proceeded to 97% conversion with 86% ee with **1c** as the organocatalyst (Entry 3). The same result was observed when the methoxyl group on the quinoline was removed, using **1d** instead of **1c** (Entry 4). However, when the stereo-configuration of organocatalysts (**1c–1d**) was reversed, replacing **1c** and **1d** with **1e** and **1f**, the enantioselectivity decreased to 71% and 78% (Entries 5–6). It also indicated that 9-amino(9-deoxy)epiquinine would be more helpful to control the enantioselectivity. After screening the catalysts, the conclusion was arrived at that the Michael addition of **2a** and **3a** could be efficiently catalyzed by tertiary amino–thiourea organocatalysts **1c** and **1d**. Therefore, we next conducted the Michael addition using **1c** as the bifunctional organocatalyst.

Table 1 Screening of catalysts



Entry [a]	Catalyst	Time/h	Conv. [b](%)	ee [b](%)
1	**1a**	24 h	78	−39
2	**1b**	24 h	91	−78
3	**1c**	24 h	97	86
4	**1d**	24 h	97	86
5	**1e**	24 h	94	−71
6	**1f**	24 h	99	−78

[a] In each case, the reaction was carried out with **2a** (0.1 mmol), **3a** (0.2 mmol) and catalyst (0.02 mmol) in toluene (0.2 mL). [b] Detected by HPLC analysis on chiral column.

A survey of solvents revealed that the reaction medium played an important role in the Michael addition. The results are

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† Electronic supplementary information (ESI) available: General procedure for the synthesis of substrate and chiral catalyst; HPLC analysis of Michael addition products; ^1H and ^{13}C NMR spectra of Michael addition products. CCDC reference number 764606. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b927421a

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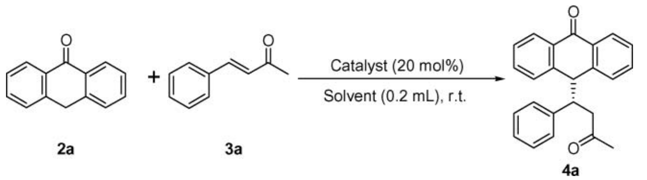
Table 2 Optimization of Michael addition conditions



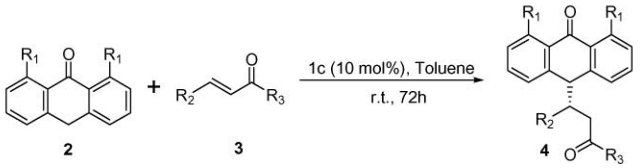
Entry[a]	Catalyst	Solvent	Time/h	Conv. [b](%)	ee [b](%)
1	**1c**	Toluene	24 h	97	86
2	**1c**	MTBE[h]	24 h	97	84
3	**1c**	CH_2Cl_2	24 h	97	76
4	**1c**	THF	24 h	72	78
5	**1c**	Acetone	24 h	97	56
6[c]	**1c**	Toluene	72 h	17	59
7[d]	**1c**	Toluene	24 h	96	89
8[e]	**1c**	Toluene	48 h	94	91
9[f]	**1c**	Toluene	60 h	89	91
10[g]	**1c**	Toluene	120 h	98	89

[a] In each case, the reaction was carried out with **2a** (0.1 mmol), **3a** (0.2 mmol) and catalyst **1c** (0.02 mmol) in solvent (0.2 mL) under room temperature. [b] Detected by HPLC analysis on chiral column. [c] Reaction was carried out at −30 °C. [d] Reaction was carried out with 0.5 ml solvent. [e] Reaction was carried out with 1 mL solvent. [f] Reaction was carried out with 10 mol% catalyst in 1 mL solvent. [g] Reaction was carried out with 5 mol% catalyst in 1 mL solvent. [h] MTBE means methyl *tert*-butyl ether.

summarized in Table 2. Full conversions and excellent ee values were observed in nonpolar solvents, such as toluene and MTBE (Entries 1–2). In contrast, use of dichloromethane, THF or acetone led to a significant decrease in enantioselectivity (Entries 3–5). For THF and acetone, this might be attributed to the hydrogen bonding interaction between catalyst **1c** and the solvents. Screening solvents revealed that toluene was the best medium in terms of conversion and enantioselectivity. Nevertheless, the reaction became sluggish with lower enantioselectivity if the temperature was reduced to −30 °C (Entry 6). Further investigations revealed that improvement of enantioselectivity was observed when the reactions were carried out in 0.2 M and 0.1 M solutions of the substrate. For example, up to 89% ee value was obtained when the reaction took place in 0.5 mL toluene (Entry 7) and the same level of ee value was observed in 1.0 mL toluene with a slight decrease in conversion (Entry 8). Besides, studies demonstrated that as low as 10 mol% **1c** in 0.1 M solution of the substrate afforded the Michael adduct in 89% conversion with 91% ee in prolonged reaction time (Entry 9). Even when the catalyst loading was reduced to 5 mol%, up to 98% of conversion with 89% ee was obtained after 120 h (Entry 10).

After establishing the optimal reaction conditions, the generality of this Michael addition was explored. The representative results are displayed in Table 3. We first carried out the Michael additions of anthrone **2a** to various aryl enones (**3a–3p**). To our great delight, aryl enones bearing electron-withdrawing and donating groups in the *o*-, *m*-, *p*-positions of the aromatic ring all afforded the desired adducts in high yields (74–98%) with excellent enantioselectivities (84–93%) (Entries 1–16). It appeared that the position and the electronic property of the substituent group on the aromatic ring played a limited role in the yields and the enantioselectivities. If a highly sterically hindered substrate such as 1-phenylpent-1-en-3-one (**3q**) was used, up to 81% yield with 70% ee could still be obtained (Entry 17). Further investigations revealed that the Michael addition of 1,8-dichloroanthracen-9-one (**2b**) to 4-phenylbut-3-en-2-one (**3a**) also proceeded in 92% yield and 90% ee value (Entry 18). However, only 57% ee value was obtained when using 1,8-dihydroxyanthracen-9-one (**2c**) as the nucleophile (Entry 19). This might be attributed to the competitive activation with **3i** of catalyst **1c** and anthrone derivate **2c**. However, less than 30% enantioselectivities were obtained in the Michael addition of anthrone to alkyl enones (not shown in Table 3).

Table 3 The Michael addition of **2** to **3** in the presence of **1c**

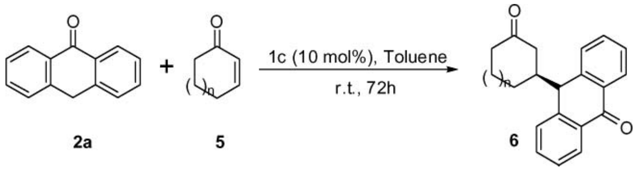


Entry[a]	R_1	R_2	R_3	adduct	Yield[b](%)	ee[c](%)
1	H (**2a**)	C_6H_5 (**3a**)	Me	**4aa**	95	86
2	H (**2a**)	2-ClC_6H_4 (**3b**)	Me	**4ab**	98	91
3	H (**2a**)	3-ClC_6H_4 (**3c**)	Me	**4ac**	97	91
4	H (**2a**)	4-ClC_6H_4 (**3d**)	Me	**4ad**	97	91
5	H (**2a**)	2-FC_6H_4 (**3e**)	Me	**4ae**	97	90
6	H (**2a**)	3-FC_6H_4 (**3f**)	Me	**4af**	97	86
7	H (**2a**)	4-FC_6H_4 (**3g**)	Me	**4ag**	74	87
8	H (**2a**)	2-BrC_6H_4 (**3h**)	Me	**4ah**	97	91
9	H (**2a**)	3-BrC_6H_4 (**3i**)	Me	**4ai**	98	91
10	H (**2a**)	4-BrC_6H_4 (**3j**)	Me	**4aj**	88	90
11	H (**2a**)	2-$OMeC_6H_4$ (**3k**)	Me	**4ak**	90	90
12	H (**2a**)	3-$OMeC_6H_4$ (**3l**)	Me	**4al**	80	91
13	H (**2a**)	4-$OMeC_6H_4$ (**3m**)	Me	**4am**	85	90
14	H (**2a**)	2-MeC_6H_4 (**3n**)	Me	**4an**	83	93
15	H (**2a**)	3-MeC_6H_4 (**3o**)	Me	**4ao**	97	90
16	H (**2a**)	4-MeC_6H_4 (**3p**)	Me	**4ap**	83	84
17	H (**2a**)	C_6H_5 (**3q**)	Et	**4aq**	81	70
18	Cl (**2b**)	C_6H_5 (**3a**)	Me	**4ba**	92	90
19	OH (**2c**)	3-BrC_6H_4 (**3i**)	Me	**4ci**	83	57

[a] In each case, the reaction was carried out with **2** (0.5 mmol), **3** (1.0 mmol) and **1c** (10 mol%) in toluene (2.5 mL) under room temperature for 72 h. [b] Isolated yield. [c] Detected by chiral HPLC analysis on chiral column.

The asymmetric Michael additions of anthrone **2a** to cyclic enones **5** catalyzed by **1c** were also investigated. The results are shown in Table 4. To our delight, the Michael reaction of cyclohex-2-enone (**5a**) with anthrone **2a** afforded the desired adduct **6aa** with 85% yield and 78% ee (Entry 1). However, the Michael addition of

Table 4 The Michael addition of **2a** to **5** in the presence of **1c**



Entry[a]	n(**5**)	adduct	yield[b](%)	ee (%)[c]
1	1 (**5a**)	**6aa**	85	78
2	2 (**5b**)	**6ab**	91	44

[a] In each case, the reaction was carried out with **2** (0.5 mmol), **5** (1.0 mmol) and **1c** (10 mol%) in toluene (2.5 mL) under room temperature for 72 h. [b] Isolated yield. [c] Detected by chiral HPLC analysis on chiral column

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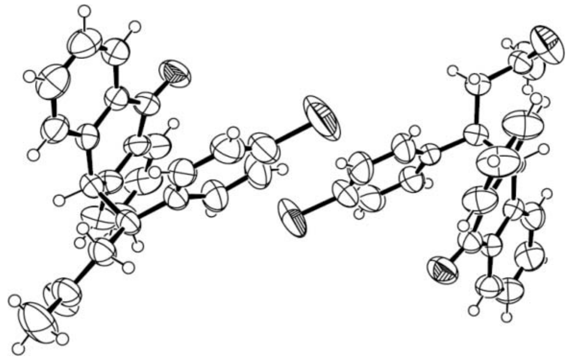
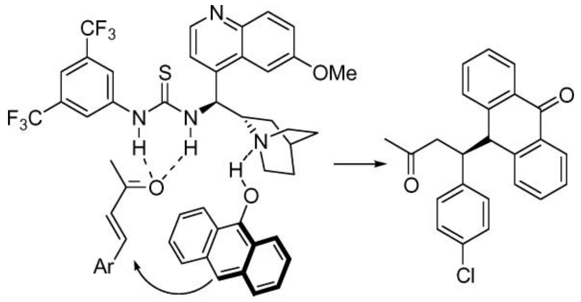
anthrone **2a** to other cyclic enones produced low enantioselectivity. For example, only 44% ee with 91% yield was obtained when cyclohept-2-enone (**5b**) reacted with anthrone **2a** (Entry 2). The absolute configuration of **4ad** was determined to be *S* by X-ray crystal structural analysis (Scheme 1),† and a working model of the reaction transition state was proposed based on the stereo-outcome (Scheme 2).



Scheme 1 X-Ray structure of enantiopure **4ad**. Thermal ellipsoids are shown with 50% ellipsoids.



Scheme 2 Proposed working model of the reaction transition state.

Conclusions

In conclusion, a new organocatalytic methodology has been developed for the asymmetric Michael addition of anthrone to enone. This methodology could afford the required Michael adducts in high yields and excellent enantioselectivities with 10 mol% catalyst loading. It is noteworthy that the Michael addition of anthrone to enone has not been reported yet. Further investigations on anthrone chemistry are underway and results from these studies will be presented in the future.

Experimental

General methods

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). Mass spectra (ESI) were measured on a Waters Micromass LCT spectrometer. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using a Daicel Chirapak AS-H column (0.46 cm x 25 cm), Chiralpak IA-H, IC–H column (0.46 cm x 25 cm), and Regis (R, R)-Whelk O1 column (0.46 cm x 25 cm) as noted.

Crystal structure determination of compound of **4ad**: $C_{24}H_{19}ClO_2$, $M = 374.84$; a block crystal (0.20 ×0.15 × 0.10 mm), $T = 298(2)$, λ(Mo-Kα) = 0.71073 Å, Orthorhombic, space group: $P2_12_12_1$, $a = 12.5855(10)$ Å, $b = 14.0795(11)$ Å, $c = 21.9701(17)$ Å, $V = 3893.0(5)$ Å^3, 16570 total reflections, 5543 unique, $R_{int} = 0.0315$, , $R_1 = 0.0535$ [$I > 2\sigma(I)$], w$R_2 = 0.1440$, min/max residual electron density –0.298/+0.464 e Å^{-3}, Flack parameter: 0.04(14).

General procedure for asymmetric Michael addition

To a solution of α,β-unsaturated ketone **3** (1.0 mmol) and catalyst **1c** (0.05 mmol) in toluene (2.5 mL) was added anthrone **2a** (0.5 mmol). The reaction mixture was stirred at room temperature for 72 h and then the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel to yield the desired addition product.

(*S*)-9-(3-Oxo-1-phenylbutyl)anthracen-10(9*H*)-one (4aa). White solid, Mp: 110–112 °C, 95% yield. $[\alpha]_D^{23}$ +2.88 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.07 (d, *J* = 7.6 Hz, 1H), 8.01(d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 6.8 Hz, 1H), 7.53-7.49 (m, 1H), 7.47–7.37 (m, 3H), 7.26–7.25 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 2H), 6.24 (d, *J* = 7.6 Hz, 1H), 4.56–4.55 (m, 1H), 3.81–3.77 (m, 1H), 2.83 (dd, *J* = 7.2, 17.2 Hz, 1H), 2.69 (dd, *J* = 7.6, 17.2 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.67, 183.97, 143.04, 141.42, 138.07, 134.09, 133.31, 132.21, 131.93, 128.69, 128.62, 128.56, 127.71, 127.47, 127.22, 127.13, 126.89, 126.48, 60.41, 48.34, 44.84, 30.60. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{20}O_2$) require *m/z* 358.1807, found *m/z* 358.1801. 86% ee, determined by Chiral HPLC. [Regis (R, R)-Whelk O1 column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 36.0 min (major), 40.3 min (minor).

(*S*)-9-(1-(2-Chlorophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4ab). White solid, Mp: 147–149 °C, 98% yield. $[\alpha]_D^{24}$ +19.58 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.22–8.20 (m, 2H), 7.77–7.75 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.44–7.41 (m, 2H), 7.32–7.29 (m, 1H), 7.21–7.18 (m, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 6.26 (d, *J* = 7.6 Hz, 1H), 4.66–4.65 (m, 1H), 4.42–4.38 (m, 1H), 2.41 (dd, *J* = 9.6, 17.2 Hz, 1H), 2.32 (dd, *J* = 5.6, 17.2 Hz, 1H), 1.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.53, 184.72, 143.02, 140.29, 137.41, 134.82, 133.45, 133.41, 133.02, 131.51, 129.98, 129.92, 129.20, 128.40, 128.37, 127.63, 127.55, 126.98, 126.90, 126.16, 46.17, 45.86, 41.89, 30.06. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}ClO_2$) require *m/z* 392.1417, found *m/z* 392.1399. 91% ee, determined by Chiral HPLC. [Daicel Chiralpak IC–H column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 28.0 min (major), 30.9 min (minor).

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(*S*)-9-(1-(3-Chlorophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4ac). White solid, Mp: 129–131 °C, 97% yield. $[\alpha]_D^{23}$ +11.58 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12–8.10 (m, 1H), 8.05–8.03 (m, 1H), 7.63–7.60 (m, 1H), 7.55–7.52 (m, 1H), 7.49–7.46 (m, 1H), 7.43–7.40 (m, 2H), 7.27–7.25 (m, 1H), 7.10–7.09 (m, 1H), 6.91 (t, J = 8.0 Hz, 1H), 6.18 (s, 1H), 6.12 (d, J = 8.0 Hz, 1H), 4.53– 4.52 (m, 1H), 3.78–3.74 (m, 1H), 2.82 (dd, J = 7.2, 17.6 Hz, 1H), 2.65 (dd, J = 7.6, 17.6 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.10, 183.71, 142.64, 140.95, 140.32, 133.98, 133.49, 133.21, 132.38, 132.08, 128.88, 128.83, 128.53, 128.48, 127.60, 127.43, 127.18, 126.97, 126.78, 126.57, 50.01, 48.03, 44.60, 30.60. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}ClO_2$) require *m/z* 392.1417, found *m/z* 392.1402. 91% ee, determined by Chiral HPLC. [Regis (R, R)-Whelk O1 column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 40.3 min (major), 46.4 min (minor).

(*S*)-9-(1-(4-Chlorophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4ad). White solid, Mp: 113–115 °C, 97% yield. $[\alpha]_D^{23}$ −2.72 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.6 Hz, 1H), 7.62–7.59 (m, 1H), 7.54–7.50 (m, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.26–7.24 (m, 1H), 6.98 (m, 1H), 6.96 (m, 1H), 6.20 (m, 1H), 6.18 (m, 1H), 4.52–4.51 (m, 1H), 3.79–3.75 (m, 1H), 2.80 (dd, J = 7.2, 17.6 Hz, 1H), 2.64 (dd, J = 8.0, 17.6 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.23, 183.85, 142.72, 141.12, 136.86, 133.93, 133.17, 132.96, 132.34, 132.07, 129.90, 128.57, 128.53, 127.86, 127.63, 127.39, 127.07, 126.68, 49.815, 48.10, 44.85, 30.59. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}ClO_2$) require *m/z* 392.1417, found *m/z* 392.1410. 91% ee, determined by Chiral HPLC. [Regis (R, R)-Whelk O1 column, λ = 254 nm, n-Hexane: EtOH = 30 : 1, flow rate = 0.8 mL min^{-1}]: 55.2 min (major), 66.5 min (minor).

(*S*)-9-(1-(2-Fluorophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4ae). white solid, Mp: 94–95 °C, 97% yield. $[\alpha]_D^{24}$ +1.28 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16–8.11 (m, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.55–7.53 (m, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.43–7.41 (m, 2H), 7.21–7.16 (m, 1H), 6.98–6.90 (m, 2H), 6.83 (t, J = 7.6 Hz, 1H), 6.19 (t, J = 7.2 Hz, 1H), 4.58–4.57 (m, 1H), 4.17–4.13 (m, 1H), 2.63–2.51 (m, 2H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, CDCl3): δ (ppm) 205.98, 184.35, 162.27, 159.82, 142.19, 141.74, 133.59, 133.14, 132.48, 132.01, 129.43, 129.39, 129.10, 128.91, 128.83, 128.66, 127.60, 127.44, 126.93, 126.78, 126.53, 126.40, 123.47, 123.42, 115.50, 115.27, 47.29, 43.33, 42.80, 30.27. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}FO_2$) require *m/z* 376.1713 found *m/z* 376.1706. 90% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 8 : 1, flow rate = 0.8 mL min^{-1}]: 10.3 min (major), 14.2 min (minor).

(*S*)-9-(1-(3-Fluorophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4af). White solid, Mp: 112–114 °C, 97% yield. $[\alpha]_D^{23}$ +5.16 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.43–7.40 (m, 2H), 7.27–7.25 (m, 1H), 6.98–6.93 (m, 1H), 6.84–6.79 (m, 1H), 6.05 (d, J = 7.6 Hz, 1H), 5.95–5.92 (m, 1H), 4.55–4.54 (m, 1H), 3.81–3.77 (m, 1H), 2.82 (dd, J = 7.2, 17.6 Hz, 1H), 2.66 (dd, J = 8.0, 17.6 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.192, 183.89, 163.31; 160.86, 142.69, 141.06, 140.92; 140.86, 134.00, 133.24, 132.37, 132.07, 129.20; 129.11, 128.49, 128.50, 127.67, 127.43, 127.01, 126.60, 124.38; 124.36, 115.68; 115.46, 114.08; 113.87, 49.99, 48.09, 44.70, 30.59. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}FO_2$) require *m/z* 376.1713, found *m/z* 376.1697. 86% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 8 : 1, flow rate = 0.8 mL min^{-1}]: 11.1 min (major), 14.0 min (minor).

(*S*)-9-(1-(4-Fluorophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4ag). White solid, Mp: 142–144 °C, 74% yield. $[\alpha]_D^{23}$ +7.18 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J = 7.6 Hz, 1H), 6.02 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.2 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.42–7.39 (m, 2H), 7.32–7.30 (m, 1H), 6.69–6.64 (m, 2H), 6.17–6.14 (m, 2H), 4.53–4.52 (m, 1H), 3.80–3.75 (m, 1H), 3.50–3.49 (m, 1H), 5.70 (dd, J = 7.2, 17.2 Hz, 1H), 2.67 (dd, J = 7.6, 17.6 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.43, 183.82, 163.06; 160.61, 143.05, 141.06, 134.07, 133.74; 133.70, 133.23, 132.36, 131.95, 130.15, 130.07, 128.49, 128.50, 127.58, 127.31, 127.01, 126.57, 114.67, 114.46, 49.69, 48.16, 45.28, 30.60. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}FO_2$) require *m/z* 376.1713, found *m/z* 376.1695. 87% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 8 : 1, flow rate = 0.8 mL min^{-1}]: 12.2 min (major), 18.9 min (minor).

(*S*)-9-(1-(2-Bromophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4ah). White solid, Mp: 159–161 °C, 97% yield. $[\alpha]_D^{23}$ +33.22 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.24–8.21 (m, 2H), 7.85–7.83 (m, 1H), 7.67–7.63 (m, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.30–7.28 (m, 1H), 7.14–7.10 (m, 1H), 7.08–7.04 (m, 1H), 6.42 (d, J = 7.6 Hz, 1H), 6.25–6.23 (m, 1H), 4.68 (m, 1H), 4.39–4.37 (m, 1H), 2.39 (dd, J = 10.0, 17.2 Hz, 1H), 2.28 (dd, J = 4.2, 17.2 Hz, 1H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205,48, 184.85, 143.10, 139.95, 138.99, 133.54, 133.47, 133.42, 133.10, 131.40, 130.15, 129.47, 128.74, 128.33, 127.66, 127.60, 127.02, 126.94, 126.76, 125.87, 48.37, 46.10, 41.91, 30.03. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}BrO_2$) require *m/z* 436.0912, found *m/z* 436.0888. 91% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 8 : 1, flow rate = 0.8 mL min^{-1}]: 9.0 min (major), 10.5 min (minor).

(*S*)-9-(1-(3-Bromophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4ai). White solid, Mp: 120–121 °C, 98% yield. $[\alpha]_D^{23}$ +14.22 (*c* 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.56–7.52 (m, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.44–7.40 (m, 2H), 7.27–7.24 (m, 2H), 6.86–6.83 (m, 1H), 6.32 (m, 1H), 6.17–6.15 (d, J = 7.6 Hz, 1H), 4.53–4.52 (m, 1H), 3.77–3.73 (m, 1H), 2.82 (dd, J = 7.6, 17.6 Hz, 1H), 2.65 (dd, J = 7.6, 17.6 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.08, 183.68, 142.61, 140.92, 140.59, 134.00, 133.22, 132.38, 132.07, 131.75, 130.10, 129.16, 128.53, 128.47, 127.69, 127.45, 127.21, 126.99, 126.69, 121.78, 50.03, 48.04, 44.58, 30.62. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}BrO_2$) require *m/z* 436.0912, found *m/z* 436.0906. 91% ee, determined by Chiral HPLC. [Regis (R, R)-Whelk O1 column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 43.0 min (major), 49.8 min (minor).

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(*S*)-9-(1-(4-Bromophenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4aj). White solid, Mp: 132–134 °C, 88% yield. $[\alpha]_D^{23}$ −4.04 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.11 (d, J = 6.8 Hz, 1H), 8.05 (d, J = 6.8 Hz, 1H), 7.62–7.58 (m, 1H), 7.54–7.50 (m, 1H), 7.49–7.45 (m, 1H), 7.43–7.39 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 7.13–7.11 (m, 2H), 6.16–6.14 (m, 2H), 4.51 (d, J = 3.6 Hz, 1H), 3.78–3.73 (m, 1H), 2.78 (dd, J = 7.2, 17.6 Hz, 1H), 2.63 (dd, J = 8.0, 17.2 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.18, 183.83, 142.64, 141.14, 137.46, 133.88, 133.14, 132.33, 132.10, 130.81, 130.26, 128.59, 128.53, 127.63, 127.39, 127.07, 126.69, 121.09, 49.87, 48.03, 44.73, 30.59. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}BrO_2$) require *m/z* 436.0912, found *m/z* 436.0897. 90% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 8 : 1, flow rate = 0.8 mL min^{-1}]: 13.0 min (major), 16.6 min (minor).

(*S*)-9-(1-(2-Methoxyphenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4ak). White foamy solid, 90% yield. $[\alpha]_D^{23}$ −26.46 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.18–8.14(m, 2H), 7.65–7.60 (m, 2H), 7.48–7.44 (m, 1H), 7.41–7.35 (m, 2H), 7.23–7.20 (m, 1H), 6.83 (d, J = 8.4 Hz, 1H), 6.75 (d, J = 7.2 Hz, 1H), 6.70 (t, J = 7.6 Hz, 1H), 6.21–6.20 (m, 1H), 4.61–4.60 (m, 1H), 4.33–4.29 (m, 1H), 3.74 (s, 3H), 2.47–2.34 (m, 2H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.70, 184.69, 157.11, 143.50, 141.99, 133.46, 133.21, 132.52, 131.47, 129.54, 128.63, 128.37, 128.23, 127.87, 127.27, 127.09, 126.67, 126.61, 119.81, 110.27, 55.30, 46.69, 43.08, 42.37, 30.15. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{25}H_{22}O_3$) require *m/z* 388.1913, found *m/z* 388.1895. 90% ee, determined by Chiral HPLC. [Daicel Chiralpak IA-H column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, 0.8 mL min^{-1}]: 16.4 min (major), 18.5 min (minor).

(*S*)-9-(1-(3-Methoxyphenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4al). White solid, 108–110 °C, 80% yield. $[\alpha]_D^{23}$ +1.88 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10 (d, J = 7.6 Hz, 1H), 8.06 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.48–7.38 (m, 3H), 7.27–7.26 (m, 1H), 6.90 (t, J = 7.6 Hz, 1H), 6.6–6.65 (m, 1H), 5.87 (d, J = 7.2 Hz, 1H), 5.78 (m, 1H), 4.55–4.54 (m, 1H), 3.78–3.71 (m, 1H), 3.53 (s, 3H), 2.79 (dd, J = 7.2, 10.4 Hz, 1H), 2.67 (dd, J = 7.6, 9.6 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.60, 183.93, 158.86, 143.00, 141.44, 139.67, 134.06, 133.31, 132.17, 131.92, 128.66, 128.64, 128.53, 127.43, 127.19, 126.88, 126.48, 120.99, 114.30, 113.00, 55.00, 50.34, 48.25, 44.79, 30.58. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{25}H_{22}O_3$) require *m/z* 388.1913, found *m/z* 388.1895. 91% ee, determined by Chiral HPLC. [Regis (R, R)-Whelk O1 column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 51.5 min (major), 58.9 min (minor).

(*S*)-9-(1-(4-Methoxyphenyl)-3-oxobutyl)anthracen-10(9*H*)-one (4am). White solid, 78–80 °C, 85% yield. $[\alpha]_D^{23}$ −3.2 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.10 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.590 (t, J = 7.6 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.47–7.42 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 6.54–6.52 (m, 2H), 6.18–6.16 (m, 2H), 4.52–4.51 (m, 1H), 3.76–3.73 (m, 1H), 3.71 (s, 3H), 2.76 (dd, J = 6.8, 16.8 Hz, 1H), 2.63 (dd, J = 8.0, 17.2 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.93, 183.89, 158.64, 143.11, 141.58, 134.00, 133.25, 132.14, 131.90, 130.05, 129.62, 128.65, 128.55, 127.39, 127.14, 126.90, 126.51, 113.15, 55.12, 49.81, 48.55, 45.12, 30.56. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{25}H_{22}O_3$) require *m/z* 388.1913, found *m/z* 388.1893. 90% ee, determined by Chiral HPLC. [Regis (R, R)-Whelk O1 column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 48.2 min (major), 54.9 min (minor).

(*S*)-9-(3-Oxo-1-*o*-tolylbutyl)anthracen-10(9*H*)-one (4an). White solid, Mp: 123–125 °C, 83% yield. $[\alpha]_D^{24}$ −21.28 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12–8.09 (m, 2H), 7.57–7.53 (m, 1H), 7.47–7.40 (m, 3H), 7.37 (d, J = 7.6 Hz, 1H), 7.08–7.04 (m, 2H), 7.01–6.99 (m, 1H), 6.86 (t, J = 7.2 Hz, 1H), 6.08 (d, J = 7.6 Hz, 1H), 4.43–4.42 (m, 1H), 4.05–4.00 (m, 1H), 2.70–2.58 (m, 2H), 1.94 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.46, 184.41, 142.40, 142.23, 137.33, 137.25, 134.10, 133.36, 132.13, 131.73, 130.41, 129.67, 128.25, 127.69, 127.46, 127.41, 126.93, 126.88, 126.85, 126.17, 48.10, 45.32, 45.27, 30.57, 19.14. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{25}H_{22}O_2$) require *m/z* 372.1964, found *m/z* 372.1946. 93% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 8 : 1, flow rate = 0.8 mL min^{-1}]: 8.4 min (major), 9.6 min (minor).

(*S*)-9-(3-Oxo-1-*m*-tolylbutyl)anthracen-10(9*H*)-one (4ao). White solid, Mp: 96–98 °C, 97% yield. $[\alpha]_D^{23}$ +8.54 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.08 (d, J = 7.6 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.52–7.48 (m, 1H), 7.47–7.43 (m, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 6.94–6.92 (m, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.04 (d, J = 7.2 Hz, 1H), 6.00 (m, 1H), 4.54–4.53 (m, 1H), 3.77–3.72(m, 1H), 2.78 (dd, J = 7.2, 17.2 Hz, 1H), 2.66 (dd, J = 7.6 Hz, 17.2 Hz, 1H), 2.07 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.76, 183.86, 143.05, 141.55, 137.91, 137.16, 134.13, 133.36, 132.11, 131.89, 129.68, 128.68, 128.55, 127.73, 127.55, 127.39, 127.15, 126.76, 126.38, 125.55, 50.34, 48.41, 44.74, 30.60, 21.18. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{25}H_{22}O_2$) require *m/z* 372.1964, found *m/z* 372.1956. 90% ee, determined by HPLC. [Regis (R, R)-Whelk O1 column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 30.8 min (major), 34.2 min (minor).

(*S*)-9-(3-Oxo-1-*p*-tolylbutyl)anthracen-10(9*H*)-one (4ap). White foamy solid, 83% yield. $[\alpha]_D^{23}$ −2.00 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J = 7.6 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.51–7.43 (m, 3H), 7.41–7.37 (m, 1H), 7.22–7.20 (m, 1H), 6.81–6.79 (m, 2H), 6.18–6.16 (m, 2H), 4.53–4.52 (m, 1H), 3.78–3.73 (m, 1H), 2.75 (dd, J = 6.8, 17.2 Hz, 1H), 2.64 (dd, J = 8.0, 17.2 Hz, 1H), 2.23 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.827, 184.101, 142.987, 141.725, 136.713, 135.156, 133.986, 133.271, 132.121, 131.967, 128.718, 128.572, 128.494, 128.457, 127.410, 127.170, 126.933, 126.551, 50.135, 48.490, 44.805, 30.581, 21.037. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{25}H_{22}O_2$) require *m/z* 372.1964, found *m/z* 372.1953. 84% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 12.0 min (major), 13.2 min (minor).

(*S*)-10-(3-Oxo-1-phenylpentyl)anthracen-9(10*H*)-one (4aq). Colourless oil, 81% yield. $[\alpha]_D^{22}$ −17.12 (*c* 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.09 (d, J = 6.0 Hz, 1H), 8.03

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(d, J = 8.0 Hz, 1H), 7.62–7.60 (m, 1H), 7.56–7.41 (m, 4H), 7.31 (d, J = 7.6 Hz, 1H), 7.15–7.12 (m, 1H), 6.99 (t, J = 7.6 Hz, 2H), 6.24 (d, J = 7.2 Hz, 2H), 4.59–4.58 (m, 1H), 3.87–3.82 (m, 1H), 2.85 (dd, J = 10.0, 17.2 Hz, 1H), 2.70 (dd, J = 10.0, 17.2 Hz, 1H), 2.41–2.35 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.43, 184.04, 143.17, 141.48, 138.16, 134.14, 133.33, 132.23, 131.89, 128.72, 128.63, 128.56, 127.70, 127.46, 127.20, 127.11, 126.92, 126.48, 50.33, 48.34, 43.70, 36.60, 7.64. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{25}H_{26}NO_2$) require m/z 372.1964, found m/z 372.1954. 70% ee, determined by Chiral HPLC. [Regis (R, R)-Whelk O1 column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 21.2 min (major), 23.4 min (minor).

(*S*)-4,5-Dichloro-9-(3-oxo-1-phenylbutyl)anthracen-10(9*H*)-one (4ba). White solid, Mp: 139–140 °C, 92% yield. $[\alpha]_D^{24}$ 23.66 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40–7.38 (m, 2H), 7.35–7.32 (m, 1H), 7.31–7.28 (m, 1H), 7.20 (t, J = 7.6 Hz, 1H), 7.10 (s, J = 7.6 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.48–6.46(m, 2H), 4.36 (d, J = 5.2 Hz, 1H), 3.63–3.58 (m, 1H), 2.77–2.76 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.27, 181.74, 143.30, 142.31, 138.08, 132.82, 132.67, 132.49, 131.55, 131.27, 131.45, 130.41, 128.23, 127.65, 127.07, 126.93, 50.65, 50.09, 45.21, 30.54. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{18}Cl_2O_2$) require m/z 426.1028, found m/z 426.1010. 90% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 8 : 1, flow rate = 0.8 mL min^{-1}]: 12.2 min (major), 17.1 min (minor).

(*S*)-10-(1-(3-Bromophenyl)-3-oxobutyl)-1,8-dihydroxyanthracen-9(10*H*)-one (4ci). Yellow solid, 152 °C decomposed, 83% yield. $[\alpha]_D^{23}$ +5.52 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 11.82 (s, 1H), 11.68 (s, 1H), 7.52–7.47 (m, 2H), 7.27–7.26 (m, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.90–6.85 (m, 3H), 6.78 (d, J = 7.2 Hz, 1H), 6.30 (m, 1H), 6.14 (d, J = 7.6 Hz, 1H), 4.46–4.45 (m, 1H), 3.64–3.59 (m, 1H), 2.95 (dd, J = 8.0, 17.6 Hz, 1H), 2.69 (dd, J = 6.8, 18.0 Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 206.08, 192.57, 162.38, 161.96, 144.84, 142.18, 140.15, 136.10, 135.33, 131.72, 130.29, 128.99, 127.27, 121.67, 119.39, 119.20, 117.12, 116.80, 116.49, 116.29, 51.12, 48.28, 44.74, 30.64. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{24}H_{19}BrO_4$) require m/z 468.0810, found m/z 468.0807. 57% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 8 : 1, flow rate = 0.8 mL min^{-1}]: 10.7 min (major), 13.4 min (minor).

(*S*)-9-(3-Oxocyclohexyl)anthracen-10(9*H*)-one (6aa). White solid. Mp: 118–120 °C, 85% yield. $[\alpha]_D^{23}$ +4.90 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.27–8.24 (m, 2H), 7.62–7.56 (m, 2H), 7.50–7.44 (m, 3H), 7.38–7.36 (m, 1H), 4.20–4.19 (m, 1H), 2.27–2.20 (m, 3H), 2.02–1.97 (m, 1H), 1.94–1.89 (m, 2H), 1.67–1.64 (m, 1H), 1.48–1.36 (m, 1H), 1.11–1.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 210.39, 184.97, 142.17, 141.82, 133.38, 133.34, 132.52, 132.49, 128.70, 128.53, 127.51, 127.49, 127.23, 127.07, 48.58, 48.28, 45.08, 40.86, 27.65, 24.75. HRMS: exact mass calculated for $[M+NH_4]^+$($C_{20}H_{18}O_2$) require m/z 308.1651, found m/z 308.1644. 78% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 33.3 min (major), 36.7 min (minor).

(*S*)-10-(3-Oxocycloheptyl)anthracen-9(10*H*)-one (6ab). White solid, Mp: 227–228 °C, 91% yield. $[\alpha]_D^{23}$ −32.88 (c 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.30–8.26 (m, 2H), 7.60–7.58 (m, 2H), 7.52–7.44 (m, 4H), 4.32–4.31 (m, 1H), 2.59–2.56 (m, 1H), 2.45–2.30 (m, 3H), 2.21–2.15 (m, 1H), 1.84–1.75 (m, 2H), 1.68–1.64 (m, 1H), 1.37–1.32 (m, 1H), 1.14–1.07 (m, 1H), 0.90–0.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.94, 185.74, 143.78, 142.41, 134.16, 133.89, 133.37, 133.09, 129.11, 128.99, 128.21, 128.10, 127.98, 127.70, 50.38, 49.12, 46.78, 44.27, 32.96, 29.01, 24.28. HRMS: exact mass calculated for $[M+NH_4]^+$ ($C_{21}H_{24}NO_2$) require m/z 322.1807, found m/z 322.1804. 44% ee, determined by Chiral HPLC. [Daicel Chiralpak AS-H column, λ = 254 nm, n-Hexane: EtOH = 15 : 1, flow rate = 0.8 mL min^{-1}]: 32.5 min (major), 36.9 min (minor).

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