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Enantioselective Michael addition of anthrone to nitroalkenes catalyzed by bifunctional thiourea-tertiary amines

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ABSTRACT

A highly bifunctional thiourea-tertiary amine-catalyzed enantioselective Michael addition reaction of anthrone to a wide variety of nitroalkenes has been developed, and the corresponding adducts were obtained smoothly in high yields (up to 97%) and good enantioselectivities (up to 94% ee).

1. Introduction

The past several years have witnessed an advancement in organocatalysis.[1] With the development of organocatalysts, numerous reports on bifunctional thiourea-catalyzed asymmetric transformations have been published.[2] In this area, worthy great progress has been made in the Michael addition to highly reactive nitroalkenes promoted by bifunctional thiourea catalysts,[3] in particular, in the work pioneered by Jacobsen and Takemoto. It maybe concluded that the causes for this are attributed to the following three factors: (i) the Michael addition reaction belongs to one of the most important C–C bond-forming reactions;[4] (ii) the favorable double-hydrogen-bonding interactions between thiourea moieties and the nitro-group of nitroalkene substrates contribute to promoting the reactivity and selectivity; and (iii) the nitroalkene substrate is more attractive, since the nitro moiety can be easily transformed into a range of different functionalities(a range of functionalities),[5] which lead to important building blocks and products.[6]

It is well known that with the asymmetric Michael reaction version, various carbon nucleophiles have been employed in this reaction; however, the use of anthrone as a nucleophile in the analogous transformation is extremely rare. Moreover, a perusal of the literature indicates that only a few examples of organocatalyzed asymmetric reactions of anthrone have been reported.[7] We should note that the only excellent protocol of asymmetric Michael addition of anthrone to nitroalkenes was reported by Shi using cinchona-based organocatalysts.[7b] Based on the extensive application of bifunctional thiourea catalysts in organocatalyzed asymmetric reaction,[3] we envisioned that the Michael addition of anthrone to nitroalkenes could unquestionably be catalyzed by thiourea catalysts. Herein, we report the first example of a bifunctional thiourea-catalyzed enantioselective Michael addition of anthrone to a very wide range of nitroalkenes, providing the corresponding products in up to 94% ee and 97% yield.

2. Results and discussion

As a model reaction, we studied the reactivity of anthrone **2** with *trans*-β-nitrostyrene **3a** for determining the optimal reaction conditions; the results are summarized in Table 1. In the initial experiments, a variety of optically active thiourea molecules were evaluated as bifunctional catalysts for the above-mentioned model reactions (Fig. 1).[8] Compounds **1a**–**e** all catalyzed the asymmetric formation of the corresponding Michael adduct **4a** in good yields and enantioselectivities with dichloromethane as solvent; compound **1e** resulted in a higher selectivity than **1a**–**d** (Table 1, entries 5 vs 1–4). Next, we performed solvent screening using **1e** as the catalyst (Table 1, entries 6–13). Interestingly 5 mol % **1e** was able to catalyze the corresponding transformation in a variety of solvents;[9] when the reaction was carried out in toluene we obtained **4a** in the best yield and enantioselectivity (Table 1, entry 11). Unfortunately, when the catalyst loading was elevated from 5 mol % to 10 mol %, there was no significant improvement in the results (Table 1, entries 14 vs 11). In order to achieve higher levels of enantioselectivity, when we carried out the reaction at −10 °C, the ee value rose to 91% but the reaction became very inert at this temperature (Table 1, entry 15). With 10 mol % catalyst loading, the corresponding product was provided smoothly in 88% yield and 93% enantioselectivity at −10 °C within 36 h (Table 1, entry 16).

Once we optimized the reaction conditions for the Michael addition of anthrone **2** to *trans*-β-nitrostyrene **3a** (catalyst **1e** 10 mol % in toluene at −10 °C), the scope and the limitations of this Michael reaction with respect to different nitroalkenes[10] were examined. As shown in Table 2, in all the entries we achieved high levels of yield and enantioselectivity. It was found that the reactions worked well with various nitroalkenes bearing either electro-donating or electron-withdrawing substituents in the

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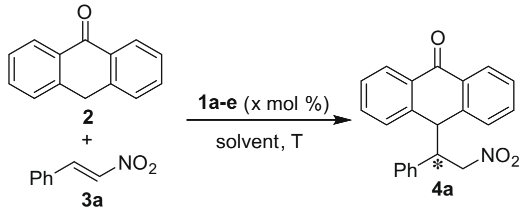
Table 1
Screening of various reaction conditions[a]



Entry	**1** (*x*)	Solvent	*T* (°C)	Time (h)	Yield[b] (%)	ee[c,d] (%)
1	**1a** (5)	CH_2Cl_2	0	24	77	(−)69
2	**1b** (5)	CH_2Cl_2	0	24	81	(+)71
3	**1c** (5)	CH_2Cl_2	0	24	83	(+)73
4	**1d** (5)	CH_2Cl_2	0	24	80	(−)71
5	**1e** (5)	CH_2Cl_2	0	24	79	(+)79
6	**1e** (5)	$CHCl_3$	0	24	71	(+)57
7	**1e** (5)	DCE	0	24	74	(+)72
8	**1e** (5)	THF	0	24	71	(+)66
9	**1e** (5)	Et_2O	0	24	64	(+)34
10	**1e** (5)	CH_3CN	0	24	77	(+)56
11	**1e** (5)	Toluene	0	24	84	(+)88
12	**1e** (5)	Xylene	0	24	77	(+)81
13	**1e** (5)	Mesitylene	0	24	80	(+)72
14	**1e** (10)	Toluene	0	24	84	(+)89
15	**1e** (5)	Toluene	−10	84	80	(+)91
16	**1e** (10)	Toluene	−10	36	88	(+)93

[a] Unless otherwise noted, reactions were performed with **2** (0.24 mmol), **3** (0.20 mmol) and catalysts **1** in the corresponding solvent (1.0 mL) for the specified time.

[b] Yield of isolated product by column chromatography.

[c] The ee values were determined by HPLC using a Chiralpak AS-H column.

[d] The symbols in parentheses are the signs of the specific rotation of the chiral products. DCE = 1,2-dichloroethane.

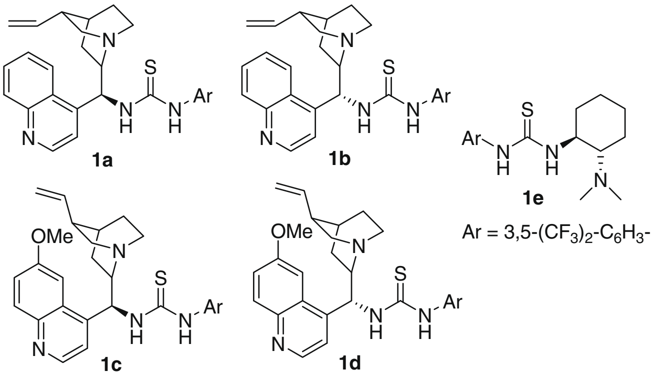
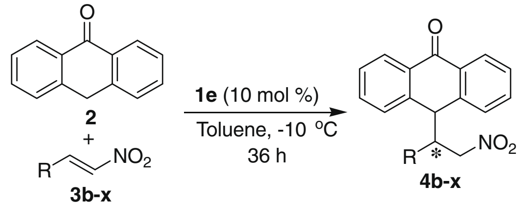


Figure 1. Catalysts tested in the Michael addition reaction.

aromatic ring, regardless of the substituents at the *ortho*- (Table 2, entries 8–11), *meta*- (Table 2, entries 12–16) or *para*-position (Table 2, entries 1–7). Significantly, when 2,4-dichloro-nitrostyrene **3r** was used in the transformation under the optimal reaction conditions, the reaction smoothly afforded the corresponding product **4r** in good results (Table 2, entry 17). Extending the investigation further to heteroaromatic nitroalkenes, the reaction also took place in both cases in good yields and enantioselectivities (Table 2, entries 18 and 19). When 1-(1-naphthyl)-nitroethene **3u** was used, we obtained the corresponding adduct **4u** in 90% yield but in only 60% ee (Table 2, entry 20). Extending the investigation further to aliphatic nitroalkenes, although good enantioselectivities were also obtained, the yields significantly decreased for adducts **4v** and **4x** (Table 2, entries 21 and 23), while the yield of **4w** was 80% (Table 2, entry 22). All the above showed the broad range of applicability of this methodology.

Table 2
Scope of the Michael addition with anthrone **2** and nitroalkenes **3b–x**[a]



Entry	R-**3**	Product	Yield[b] (%)	ee[c] (%)
1	4-ClC_6H_4-**3b**	**4b**	93	(+)93
2	4-$CH_3OC_6H_4$-**3c**	**4c**	94	(+)86
3	4-$CH_3C_6H_4$-**3d**	**4d**	97	(+)85
4	4-$NO_2C_6H_4$-**3e**	**4e**	77	(+)80
5	4-BrC_6H_4-**3f**	**4f**	83	(+)91[d]
6	4-FC_6H_4-**3g**	**4g**	90	(+)94
7	4-CNC_6H_4-**3h**	**4h**	82	(+)91
8	2-BrC_6H_4-**3i**	**4i**	95	(+)83
9	2-$CH_3OC_6H_4$-**3j**	**4j**	89	(−)89
10	2-$NO_2C_6H_4$-**3k**	**4k**	91	(−)90
11	2-ClC_6H_4-**3l**	**4l**	96	(−)84
12	3-$CH_3C_6H_4$-**3m**	**4m**	87	(+)91
13	3-$NO_2C_6H_4$-**3n**	**4n**	60	(+)90
14	3-BrC_6H_4-**3o**	**4o**	65	(+)90
15	3-$CF_3C_6H_4$-**3p**	**4p**	65	(+)91
16	3-FC_6H_4-**3q**	**4q**	80	(+)90
17	2,4-$Cl_2C_6H_3$-**3r**	**4r**	92	(−)81
18	2-Furyl-**3s**	**4s**	97	(−)90
19	2-Thienyl-**3t**	**4t**	84	(+)91
20	1-Naphthyl-**3u**	**4u**	90	(−)60
21	$(CH_3)_2CH$-**3v**	**4v**	49	(+)84
22	$(CH_3)_2CHCH_2$-**3w**	**4w**	80	(+)86
23	*c*-C_6H_{11}-**3x**	**4x**	57	(+)85

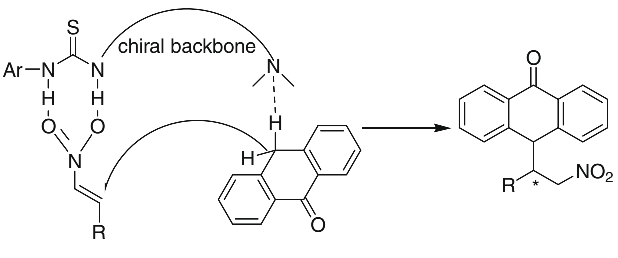
[a] Unless otherwise noted, reactions were performed with **2** (0.24 mmol), **3** (0.2 mmol) and catalyst **1e** (10 mol %) in toluene (1.0 mL) at −10 °C for 36 h.

[b] Yield of isolated product by column chromatography.

[c] The ee values were determined by chiral stationary phase HPLC.

[d] The absolute configuration of the product **4f** was determined to be (*S*)- by comparison of the sign of the specific rotation and the X-ray diffraction of the same compound with the reported data.[7b]

On the basis of the observed reactivity and experimental results of the aforementioned reactions, we proposed that the reaction proceeded via a dual activation model. As shown in Scheme 1, the nitroalkene was activated through double-hydrogen-bonding interactions between thiourea moieties and the nitro-group. Simultaneously, the anthrone was activated by the tertiary amine moiety of catalyst.



Scheme 1. Proposed dual activation in the Michael addition reaction.

3. Conclusion

In conclusion, we have reported an organocatalyzed Michael addition of anthrone to a wide variety of nitroalkenes. The reaction was catalyzed by bifunctional thiourea-tertiary amine catalysts and afforded the corresponding adducts in high yields of up to 97% and high enantioselectivities of up to 94%. The studies carried out in this report demonstrated that thiourea-tertiary amines are powerful bifunctional organocatalysts in catalytic asymmetric reaction and that anthrone is a highly reactive carbon nucleophile towards nitroalkene-type Michael acceptors.

4. Experimental

4.1. General

Unless otherwise indicated, chemicals and solvents were purchased from commercial suppliers or purified by standard techniques. Flash column chromatography was performed using silica gel. For thin-layer chromatography (TLC), silica gel plates (HSGF-254) were used and compounds were visualized by irradiation with UV light. All reactions were conducted in a closed system with an atmosphere of air and were monitored by TLC. Racemic products were obtained from the corresponding substrates catalyzed by DABCO at room temperature. ^{1}H and ^{13}C NMR spectra were performed on a Brucker-300 MHz spectrometer for products dissolved by CDCl$_3$ or DMSO-d_6 with tetramethylsilane (TMS) as an internal standard. Optical rotations were measured on a Perkin–Elmer 241 Polarimeter. Melting points were recorded on a Buchi Melting Point B-545 without correction.

4.2. General procedures for the asymmetric Michael addition of anthrone to nitroalkenes

A solution of nitroalkenes **3** (0.2 mmol) and bifunctional thiourea catalyst **1e** (0.02 mmol) in toluene (1 mL) was cooled to −10 °C, and then anthrone **2** was added. After being stirred for 36 h at this temperature, the reaction mixture was subjected directly to flash column chromatography on silica gel (petroleum ether/CH$_2$Cl$_2$ = 2:1–1:1) to furnish the corresponding products **4**.

4.2.1. 9-(2-Nitro-1-phenylethyl)anthracen-10(9H)-one 4a[7b]

White solid, yield 88%; 93% ee, $[\alpha]_D^{20} = +25.4$ (c 0.48, CHCl$_3$); Mp 146.8–149.0 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.02–4.08 (m, 1H), 4.55 (d, J = 3.6 Hz, 1H), 4.59 (dd, J = 13.2, 6.9 Hz, 1H), 4.86–4.90 (dd, J = 13.2, 9.0 Hz, 1H), 6.05 (d, J = 7.5 Hz, 2H), 6.95 (t, J = 7.8 Hz, 2H), 7.13–7.15 (m, 1H), 7.41–7.46 (m, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.58–7.66 (m, 2H), 7.98 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 7.9 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 46.0, 53.1, 76.6, 126.6, 127.1, 127.6, 127.9, 128.0, 128.1, 128.3, 128.5, 132.2, 132.4, 133.0, 133.2, 134.2, 139.2, 141.8, 183.4. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 10:90, flow rate 0.7 mL/min, UV detection at 254 nm, t_{major} = 24.58 min, t_{minor} = 27.80 min.

4.2.2. 9-(1-(4-Chlorophenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4b[7b]

White solid, yield 93%; 93% ee, $[\alpha]_D^{20} = +21.7$ (c 0.40, CHCl$_3$); Mp 168.7–171.2 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.03–4.06 (m, 1H), 4.52 (d, J = 3.3 Hz, 1H), 4.59 (dd, J = 13.2, 7.5 Hz, 1H), 4.86 (dd, J = 13.2, 8.4 Hz, 1H), 6.03 (d, J = 8.4 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 7.39–7.54 (m, 4H), 7.60–7.66 (m, 2H), 8.02 (d, J = 7.8 Hz, 1H), 8.10 (d, J = 7.5 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 46.0, 52.7, 76.5, 127.0, 127.2, 127.4, 127.9, 128.1, 128.2 128.3, 128.4, 129.8, 131.8, 132.4, 132.8, 133.2, 134.1, 134.3, 139.0, 141.5, 183.0. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 10:90, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 21.34 min, t_{minor} = 24.88 min.

4.2.3. 9-(1-(4-Methoxyphenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4c[7b]

White solid, yield 94%; 86% ee, $[\alpha]_D^{20} = +18.7$ (c 0.74, CHCl$_3$); Mp 119.8–122.7 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 3.68 (s, 3H), 4.00–4.02 (m, 1H), 4.50 (d, J = 3.9 Hz, 1H), 4.55 (dd, J = 13.2, 7.2 Hz, 1H), 4.84 (dd, J = 13.2, 9.0 Hz, 1H), 5.97 (d, J = 8.7 Hz, 2H), 6.48 (d, J = 8.7 Hz, 2H), 7.38–7.52 (m, 4H), 7.58–7.64 (m, 2H), 8.00 (d, J = 7.8 Hz, 1H), 8.08 (d, J = 7.2 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 46.2, 52.6, 55.1, 77.0, 113.4, 124.8, 126.7, 127.2, 127.6, 128.0, 128.1, 128.3, 129.6, 132.2, 132.6, 133.2, 134.2, 139.4, 142.0, 159.4, 183.0. HPLC conditions: Chiralcel OD-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 24.70 min, t_{minor} = 17.20 min.

4.2.4. 9-(2-Nitro-1-*p*-tolylethyl)anthracen-10(9*H*)-one 4d[7b]

White solid, yield 97%; 85% ee, $[\alpha]_D^{20} = +25.4$ (c 0.62, CHCl$_3$); Mp 156.0–158.1 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 2.12 (s, 3H), 4.02–4.05 (m, 1H), 4.51 (d, J = 3.6 Hz, 1H), 4.56 (dd, J = 13.2, 7.2 Hz, 1H), 4.85 (dd, J = 13.2, 9.0 Hz, 1H), 5.97 (d, J = 8.1 Hz, 2H), 6.76 (d, J = 7.8 Hz, 2H), 7.37–7.47 (m, 2H), 7.51 (d, J = 7.5 Hz, 2H), 7.57–7.64 (m, 2H), 8.00 (d, J = 7.8 Hz, 1H), 8.08 (d, J = 7.2 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 21.0, 46.1, 52.9, 76.7, 126.7, 127.2, 127.6, 128.0, 128.1, 128.3, 128.6, 130.0, 132.2, 132.6, 133.2, 134.1, 137.9, 139.4, 141.9, 183.2. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 10:90, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 13.50 min, t_{minor} = 15.10 min.

4.2.5. 9-(2-Nitro-1-(4-nitrophenyl)ethyl)anthracen-10(9*H*)-one 4e[7b]

White solid, yield 77%; 80% ee, $[\alpha]_D^{20} = +21.2$ (c 0.42, CHCl$_3$); Mp 194.5–196.1 °C. ^{1}H NMR ((CD$_3$)$_2$SO, 300 MHz) δ 4.11–4.16 (m, 1H), 4.94 (d, J = 4.2 Hz, 1H), 5.05 (dd, J = 14.1, 10.5 Hz, 1H), 5.46 (dd, J = 14.1, 4.8 Hz, 1H), 6.44 (d, J = 8.7 Hz, 2H), 7.48–7.59 (m, 3H), 7.68–7.83 (m, 6H), 7.89 (d, J = 7.2 Hz, 1H); ^{13}C NMR ((CD$_3$)$_2$SO, 75 MHz) δ 45.1, 52.4, 77.1, 122.4, 125.9, 126.3, 128.0, 128.2, 128.8, 129.1, 129.8, 132.4, 132.8, 133.2, 133.3, 139.2, 142.1, 142.7, 146.6, 182.8. HPLC conditions: Chiralcel AD-H column, *i*-PrOH/hexane 30:70, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 12.95 min, t_{minor} = 10.90 min.

4.2.6. 9-(1-(4-Bromophenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4f[7b]

White solid, yield 83%; 91% ee, $[\alpha]_D^{20} = +15.4$ (c 0.54, CHCl$_3$); Mp 182.5–184.8 °C. ^{1}H NMR ((CD$_3$)$_2$SO, 300 MHz) δ 3.92–3.97 (m, 1H), 4.85–4.89 (m, 2H), 5.39 (dd, J = 13.8, 5.4 Hz, 1H), 6.03 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.45–7.56 (m, 3H), 7.66–7.74 (m, 3H), 7.83 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 7.8 Hz, 1H); ^{13}C NMR ((CD$_3$)$_2$SO, 75 MHz) δ 45.0, 52.3, 77.5, 120.8, 125.9, 126.3, 127.7, 128.0, 128.6, 128.9, 130.3, 130.4, 132.4, 132.5, 133.1, 133.3, 133.5, 139.4, 142.5, 182.6. HPLC conditions: Chiralcel OD-H column, *i*-PrOH/hexane 30:70, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 22.64 min, t_{minor} = 16.94 min.

4.2.7. 9-(1-(4-Fluorophenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4g[7b]

White solid, yield 90%; 94% ee, $[\alpha]_D^{20} = +31.0$ (c 0.46, CHCl$_3$); Mp 170.1–172.0 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.02–4.07 (m, 1H), 4.53 (d, J = 3.6 Hz, 1H), 4.58 (dd, J = 13.2, 7.2 Hz, 1H), 4.89 (dd, J = 13.2, 9.0 Hz, 1H), 6.01 (dd, J = 8.7, 5.1 Hz, 2H), 6.65 (t, J = 8.7 Hz, 2H), 7.43–7.55 (m, 4H), 7.63–7.67 (m, 2H), 8.00 (d, J = 7.2 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 46.1, 52.6, 76.8, 115.0 (d, J = 21.4 Hz), 126.9, 127.4, 127.9, 128.0, 128.3, 128.3, 128.8 (d, J = 3.2 Hz), 130.2 (d, J = 8.3 Hz), 132.4, 132.9, 133.3, 134.2, 139.0, 141.8, 162.4 (d, J = 247.0 Hz), 183.1. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 30:70, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 9.62 min, t_{minor} = 11.44 min.

4.2.8. 4-(2-Nitro-1-(9-oxo-9,10-dihydroanthracen-10-yl)ethyl)-benzonitrile 4h

White solid, yield 82%; 91% ee, $[\alpha]_D^{20} = +22.0$ (c 0.62, CHCl$_3$); Mp 159.4–162.5 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.09–4.16 (m, 1H), 4.58 (d, J = 2.7 Hz, 1H), 4.62 (dd, J = 13.2, 7.8 Hz, 1H), 4.94 (dd, *J* = 13.2, 8.4 Hz, 1H), 6.20 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 2H), 7.44–7.58 (m, 4H), 7.63–7.72 (m, 2H), 8.01 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 46.0, 53.2, 76.2, 112.3, 118.0, 127.1, 127.6, 128.0, 128.2, 128.3, 128.6, 129.3, 131.7, 132.6, 133.1, 134.1, 138.4, 138.7, 141.1, 182.9. IR (KBr) ν 1662, 1601, 1551, 1317, 933 cm^{-1}. HRMS (ESI) Calcd for $C_{23}H_{16}N_2NaO_3$ $(M+Na)^+$: 391.1053; Found: 391.1047. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 30:70, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 26.01 min, t_{minor} = 32.03 min.

4.2.9. 9-(1-(2-Bromophenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4i

White solid, yield 95%; 83% ee, $[\alpha]_D^{20} = +7.1$ (*c* 0.74, $CHCl_3$); Mp 62.8–65.6 °C. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 4.02–4.45 (m, 1H), 4.78 (d, *J* = 5.3 Hz, 1H), 4.92–5.03 (m, 1H), 5.09 (dd, *J* = 13.8, 5.4 Hz, 1H), 6.59–6.60 (m, 1H), 7.08–7.11 (m, 2H), 7.30–7.38 (m, 2H), 7.49–7.63 (m, 5H), 7.93 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR ($(CD_3)_2SO$, 75 MHz) δ 45.5, 50.4, 77.5, 126.4, 126.4, 127.1, 128.0, 128.6, 129.2, 129.4, 129.9, 132.4, 132.6, 132.7, 133.5, 134.7, 140.3, 141.2, 183.2. IR (KBr) ν 1662, 1599, 1552, 1317, 932 cm^{-1}. HRMS (ESI) Calcd for $C_{22}H_{16}BrNNaO_3$ $(M+Na)^+$: 444.0206; Found: 444.0187. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 10.85 min, t_{minor} = 13.54 min.

4.2.10. 9-(1-(2-Methoxyphenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4j

White solid, yield 89%; 89% ee, $[\alpha]_D^{20} = -8.6$ (*c* 0.88, $CHCl_3$); Mp 128.5–131.4 °C. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 3.21 (s, 1H), 4.42–4.46 (m, 1H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.82 (dd, *J* = 13.2, 10.2 Hz, 1H), 5.12 (dd, *J* = 13.5, 6.0 Hz, 1H), 6.06 (d, *J* = 6.6 Hz, 1H), 6.54 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.43–7.54 (m, 4H), 7.62–7.67 (t, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.91 (m, *J* = 7.8 Hz, 1H); ^{13}C NMR ($(CD_3)_2SO$, 75 MHz) δ 45.2, 45.5, 55.0, 76.9, 110.5, 119.4, 122.5, 125.7, 126.1, 127.4, 127.7, 128.2, 128.8, 128.9, 129.3, 132.3, 133.3, 140.7, 142.3, 157.1, 182.8. IR (KBr) ν 1658, 1602, 1553, 1510, 1317, 932 cm^{-1}. HRMS (ESI) Calcd for $C_{23}H_{19}NNaO_4$ $(M+Na)^+$: 396.1206; Found: 396.1192. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 9.75 min, t_{minor} = 11.08 min.

4.2.11. 9-(2-Nitro-1-(2-nitrophenyl)ethyl)anthracen-10(9*H*)-one 4k

White solid, yield 91%; 90% ee, $[\alpha]_D^{20} = -4.0$ (*c* 0.20, $CHCl_3$); Mp 68.1–71.7 °C. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 4.71–4.76 (m, 1H) 4.86(d, *J* = 5.1 Hz, 1H), 5.11 (dd, *J* = 13.5, 10.2 Hz, 1H), 5.28 (dd, *J* = 13.8, 5.4 Hz, 1H), 6.70–6.73 (m, 1H), 7.32–7.40 (m, 3H), 7.50–7.64 (m, 6H), 7.89 (dd, *J* = 13.8, 7.5 Hz, 2H); ^{13}C NMR ($(CD_3)_2SO$, 75 MHz) δ 45.4, 45.7, 77.4, 124.3, 126.4, 126.5, 128.1, 128.2, 128,6, 129.0, 129.1, 129.3, 129.4, 132.1, 132.2, 132.5, 133.0, 133.5, 139.7, 141.0, 149.9, 182.9. IR (KBr) ν 1666, 1600, 1553, 1526, 1315, 932 cm^{-1}. HRMS (ESI) Calcd for $C_{22}H_{16}N_2NaO_5$ $(M+Na)^+$: 411.0951; Found: 411.0944. HPLC conditions: Chiralcel OD-H column, *i*-PrOH/hexane 30:70, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 13.05 min, t_{minor} = 16.93 min.

4.2.12. 9-(1-(2-Chlorophenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4l[7b]

White solid, yield 96%; 84% ee, $[\alpha]_D^{20} = -14.8$ (*c* 0.54, $CHCl_3$); Mp 163.4–165.8 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.41–4.43 (m, 2H), 4.71–4.75 (m, 2H), 6.26 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 7.21–7.27 (m, 1H), 7.38–7.58 (m, 4H), 7.70–7.73 (m, 2H), 8.20 (t, *J* = 8.3 Hz, 2H); ^{13}C NMR ($(CD_3)_2SO$, 75 MHz) δ 45.3, 47.8, 77.4, 126.3, 126.4, 127.9, 128.0, 128.6, 129.0, 129.1, 129.7, 132.3, 132.4, 132.6, 132.7, 133.5, 135.0, 140.1, 141.5, 183.0. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 10.42 min, t_{minor} = 12.69 min.

4.2.13. 9-(2-Nitro-1-*m*-tolylethyl)anthracen-10(9*H*)-one 4m

White solid, yield 87%; 91% ee, $[\alpha]_D^{20} = +33.2$ (*c* 0.60, $CHCl_3$); Mp 111.5–113.9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.01 (s, 3H), 3.96–4.02 (m, 1H), 4.51 (d, *J* = 3.3 Hz, 1H), 4.57 (dd, *J* = 13.2, 7.2 Hz, 1H), 4.86 (dd, *J* = 13.2, 9.0 Hz, 1H), 5.77 (s, 1H), 5.86 (d, *J* = 7.5 Hz, 1H), 6.82–6.84 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 7.37–7.44 (m, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.57–7.64 (m, 2H), 7.97 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.0, 46.1, 53.1, 76.6, 125.4, 126.6, 127.0, 127.6, 127.8, 128.0, 128.1, 128.3, 128.7, 129.5, 132.2, 132.6, 132.8, 133.3, 134.3, 137.5, 139.3, 141.9, 183.0. IR (KBr) ν 1657, 1601, 1547, 1314, 931 cm^{-1}. HRMS (ESI) Calcd for $C_{23}H_{19}NNaO_3$ $(M+Na)^+$: 380.1257; Found: 380.1250. HPLC conditions: Chiralcel OD-H column, *i*-PrOH/hexane 30:70, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 12.21 min, t_{minor} = 9.50 min.

4.2.14. 9-(2-Nitro-1-(3-nitrophenyl)ethyl)anthracen-10(9*H*)-one 4n[7b]

White solid, yield 60%; 90% ee, $[\alpha]_D^{20} = +38.1$ (*c* 0.40, $CHCl_3$); Mp 163.0–166.4 °C. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 4.12–4.17 (m, 1H), 4.96 (d, *J* = 3.9 Hz, 1H), 5.06 (dd, *J* = 13.8, 10.8 Hz, 1H), 5.51 (dd, *J* = 14.1, 5.1 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.88 (s, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.48–7.62 (m, 3H), 7.70–7.87 (m, 5H), 7.96 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($(CD_3)_2SO$, 75 MHz) δ 45.0, 52.2, 77.1, 122.4, 123.0, 125.7, 126.2, 127.9, 128.2, 128.8, 129.0, 129.1, 132.4, 132.8, 133.3, 133.4, 135.1, 136.5, 139.0, 142.3, 146.6, 182.5. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 35.48 min, t_{minor} = 42.52 min.

4.2.15. 9-(1-(3-Bromophenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4o

White solid, yield 65%; 90% ee, $[\alpha]_D^{20} = +31.0$ (*c* 0.58, $CHCl_3$); Mp 114.7–117.1 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.97–4.03 (m, 1H), 4.52–4.59 (m, 2H), 4.85 (dd, *J* = 13.2, 8.7 Hz, 1H), 6.00 (d, *J* = 7.2 Hz, 1H), 6.14 (s, 1H), 6.82 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 9.0 Hz, 1H), 7.39–7.55 (m, 4H), 7.60–7.67 (m, 2H), 8.01 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 46.1, 52.9, 76.3, 122.0, 126.9, 127.0, 127.4, 128.0, 128.0, 128.3, 128.4, 129.4, 131.3, 131.7, 132.5, 132.9, 133.3, 134.2, 135.4, 138.8, 141.4, 182.9. IR (KBr) ν 1656, 1599, 1550, 1315, 931 cm^{-1}. HRMS (ESI) Calcd for $C_{22}H_{16}BrNNaO_3$ $(M+Na)^+$: 444.0206; Found: 444.0199. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 12.67 min, t_{minor} = 14.98 min.

4.2.16. 9-(2-Nitro-1-(3-(trifluoromethyl)phenyl)ethyl) anthracen-10(9*H*)-one 4p

White solid, yield 65%; 91% ee, $[\alpha]_D^{20} = +26.2$ (*c* 0.44, $CHCl_3$); Mp 147.5–150.4 °C. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 4.06–4.11 (m, 1H), 4.93 (d, *J* = 3.7 Hz, 1H), 5.02 (dd, *J* = 13.8, 10.5 Hz, 1H), 5.51 (dd, *J* = 13.8, 5.1 Hz, 1H), 6.24 (s, 1H), 6.36 (d, *J* = 7.5 Hz, 1H), 7.11–7.14 (t, *J* = 7.8 Hz, 1H) 7.41–7.60 (m, 4H), 7.69–7.79 (m, 4H), 7.87 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($(CD_3)_2SO$, 75 MHz) δ 45.0, 52.5, 77.2, 116.6, 121.9, 122.5, 123.6, 124.2, 124.3, 124.9, 125.0, 125.4, 125.5, 125.7, 126.2, 126.6, 127.5, 127.7, 127.9, 128.0, 128.4, 128.7, 129.0, 132.3, 132.4, 132.6, 133.0, 133.2, 133.3, 135.3, 139.1, 142.5, 182.2. IR (KBr) ν 1665, 1602, 1551, 1324, 932 cm^{-1}. HRMS (ESI) Calcd for $C_{23}H_{16}F_3NNaO_3$ $(M+Na)^+$: 434.0974; Found: 434.0967. HPLC conditions: Chiralcel AD-H column, *i*-PrOH/hexane 10:90, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 11.05 min, t_{minor} = 11.82 min.

4.2.17. 9-(1-(3-Fluorophenyl)-2-nitroethyl)anthracen-10(9*H*)-one 4q[7b]

White solid, yield 80%; 90% ee, $[\alpha]_D^{20} = +26.3$ (*c* 0.58, CHCl$_3$); Mp 123.8–126.9 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.01–4.07 (m, 1H), 4.53 (d, *J* = 3.0 Hz, 1H), 4.57 (dd, *J* = 13.2, 7.5 Hz, 1H), 4.86 (dd, *J* = 13.2, 8.7 Hz, 1H), 5.78 (d, *J* = 9.6 Hz, 1H), 5.87 (d, *J* = 7.5 Hz, 1H), 6.86–6.94 (m, 2H), 7.39–7.54 (m, 4H), 7.59–7.65 (m, 2H), 8.01 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 46.1, 52.8 (d, *J* = 1.5 Hz), 76.4, 115.2 (d, *J* = 20.9 Hz), 115.7 (d, *J* = 22.1 Hz), 124.2 (d, *J* = 2.9 Hz), 126.9, 127.4, 128.0, 128.1, 128.3, 128.4, 129.5 (d, *J* = 8.3 Hz), 132.5, 132.9, 133.3, 134.2, 138.9, 141.5, 162.0 (d, *J* = 245.8 Hz), 183.1. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 10:90, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 18.83 min, t_{minor} = 22.81 min.

4.2.18. 9-(1-(2,4-Dichlorophenyl)-2-nitroethyl) anthracen-10(9*H*)-one 4r[7b]

White solid, yield 92%; 81% ee, $[\alpha]_D^{20} = -16.0$ (*c* 0.22, CHCl$_3$); Mp 63.1–66.9 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.29–4.45 (m, 2H), 4.61–4.72 (m, 2H), 6.17 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 6.6 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 7.37–7.59 (m, 4H), 7.65 (s, 2H), 8.17 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 44.9, 47.9, 74.3, 126.7, 127.5, 127.5, 128.1, 128.3, 128.4, 128.6, 129.5, 130.0, 131.5, 132.2, 132.9, 133.2, 133.5, 134.7, 135.8, 139.0, 140.4, 183.6. HPLC conditions: Chiralcel OD-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 11.34 min, t_{minor} = 15.29 min.

4.2.19. 9-(1-(Furan-2-yl)-2-nitroethyl)anthracen-10(9*H*)-one 4s[7b]

White solid, yield 97%; 90% ee, $[\alpha]_D^{20} = -2.3$ (*c* 0.74, CHCl$_3$); Mp 140.5–144.7 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.17–4.23 (m, 1H), 4.35 (dd, *J* = 13.2, 8.4 Hz, 1H), 4.49 (dd, *J* = 13.5, 6.9 Hz, 1H), 4.66 (d, *J* = 3.5 Hz, 1H), 5.55 (d, *J* = 3.2 Hz, 1H), 6.19–6.20 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 1.1 Hz, 1H), 7.47–7.56 (m, 4H), 7.63–7.65 (m, 1H), 8.18 (t, *J* = 6.0 Hz, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 45.0, 47.0, 74.2, 109.4, 110.5, 127.2, 127.6, 128.0, 128.1, 128.2, 128.3, 132.8, 132.9, 133.0, 133.2, 140.0, 140.5, 142.5, 148.6, 183.6. HPLC conditions: Chiralcel OD-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 8.85 min, t_{minor} = 10.06 min.

4.2.20. 9-(2-Nitro-1-(thiophen-2-yl)ethyl)anthracen-10(9*H*)-one 4t

White solid, yield 84%; 91% ee, $[\alpha]_D^{20} = +17.3$ (*c* 0.50, CHCl$_3$); Mp 151.2–153.9 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.34–4.40 (m, 1H), 4.54 (dd, *J* = 13.5, 6.9 Hz, 1H), 4.57 (d, *J* = 3.9 Hz, 1H), 4.83 (dd, *J* = 13.5, 9.0 Hz, 1H), 6.67–6.70 (m, 1H), 7.06 (d, *J* = 5.1 Hz, 1H), 7.40–7.54 (m, 4H), 7.60–7.67 (m, 2H), 8.06 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 46.2, 48.5, 77.1, 125.8, 126.6, 126.9, 127.1, 127.4, 127.9, 128.0, 128.3, 128.5, 132.5, 133.0, 133.4, 134.3, 134.9, 138.8, 141.6, 183.3. IR (KBr) *v* 1667, 1602, 1555, 1317, 931 cm^{-1}. HRMS (ESI) Calcd for C$_{20}$H$_{15}$NNaO$_3$S (M+Na)$^+$: 372.0665; Found: 372.0661. HPLC conditions: Chiralcel AD-H column, *i*-PrOH/hexane 10:90, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 15.49 min, t_{minor} = 16.57 min.

4.2.21. 9-(1-(Naphthalen-1-yl)-2-nitroethyl)anthracen-10(9*H*)-one 4u[7b]

White solid, yield 90%; 60% ee, $[\alpha]_D^{20} = -36.0$ (*c* 0.60, CHCl$_3$); Mp 171.3–173.9 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 4.58 (dd, *J* = 12.6, 8.1 Hz, 1H), 4.71 (d, *J* = 3.9 Hz, 2H), 4.75 (dd, *J* = 13.2, 7.5 Hz, 1H), 5.01–5.09 (m, 1H), 6.20 (d, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.31–7.35 (m, 2H), 7.39–7.42 (m, 2H), 7.66–7.69 (m, 1H), 7.66–7.84 (m, 6H), 8.12 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 46.1, 46.4, 76.0, 121.7, 124.3, 125.6, 126.5, 127.0, 127.3, 127.9, 128.1, 128.2, 129.0, 129.1, 129.2, 131.7, 132.1, 132.7, 133.1, 133.7, 140.4, 183.3. HPLC conditions: Chiralcel AS-H column, *i*-PrOH/hexane 10:90, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 17.31 min, t_{minor} = 23.54 min.

4.2.22. 9-(3-Methyl-1-nitrobutan-2-yl)anthracen-10(9*H*)-one 4v

White solid, yield 49%; 84% ee, $[\alpha]_D^{20} = +34.1$ (*c* 0.45, CHCl$_3$); Mp 85.1–88.8 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.09 (d, *J* = 6.9 Hz, 3H), 0.82 (d, *J* = 6.9 Hz, 3H), 1.54–1.60 (m, 1H), 2.71–2.76 (m, 1H), 4.27 (dd, *J* = 13.2, 4.8 Hz, 1H), 4.36 (d, *J* = 2.7 Hz, 1H), 4.51 (dd, *J* = 13.2, 9.9 Hz, 1H), 7.26–7.57 (m, 3H), 7.59–7.67 (m, 3H), 8.30 (dd, *J* = 12.9, 7.8 Hz, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 17.4, 23.2, 25.6, 43.0, 52.7, 75.0, 127.2, 127.7, 128.0, 128.1, 128.3, 128.9, 132.8, 133.2, 133.3, 133.5, 140.9, 142.7, 184.6. IR (KBr) *v* 1659, 1602, 1559, 1315, 931 cm^{-1}. HRMS (ESI) Calcd for C$_{19}$H$_{19}$NNaO$_3$ (M+Na)$^+$: 332.1257; Found: 332.1256. HPLC conditions: Chiralcel AD-H column, *i*-PrOH/hexane 10:90, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 7.51 min, t_{minor} = 7.15 min.

4.2.23. 9-(4-Methyl-1-nitropentan-2-yl)anthracen-10(9*H*)-one 4w

White solid, yield 80%; 86% ee, $[\alpha]_D^{20} = +24.3$ (*c* 0.64, CHCl$_3$); Mp 110.8–114.1 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.51–0.56 (m, 1H), 0.59 (d, *J* = 6.6 Hz, 3H), 0.73 (d, *J* = 5.7 Hz, 3H), 0.74–0.88 (m, 1H), 2.82–2.87 (m, 1H), 4.13 (dd, *J* = 12.9, 6.0 Hz, 1H), 4.32–4.40 (m, 2H), 7.44–7.53 (m, 4H), 7.61–7.67 (m, 2H), 8.27 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 21.3, 22.8, 25.1, 35.2, 42.8, 45.0, 77.1, 127.2, 127.7, 127.8, 127.9, 128.4, 128.6, 132.9, 133.1, 133.5, 140.5, 142.1, 184.6. IR (KBr) *v* 1670, 1602, 1545, 1316, 932 cm^{-1}. HRMS (ESI) Calcd for C$_{20}$H$_{21}$NNaO$_3$ (M+Na)$^+$: 332.1414; Found: 332.1416. HPLC conditions: Chiralcel AD-H column, *i*-PrOH/hexane 1:99, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 15.32 min, t_{minor} = 14.08 min.

4.2.24. 9-(1-Cyclohexyl-2-nitroethyl)anthracen-10(9*H*)-one 4x

White solid, yield 57%; 85% ee, $[\alpha]_D^{20} = +61.0$ (*c* 0.24, CHCl$_3$); Mp 127.3–130.8 °C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 0.25–0.44 (m, 2H), 0.74–0.96 (m, 2H), 1.01–1.19 (m, 3H), 1.34–1.43 (m, 2H), 1.47–1.60 (m, 2H), 2.66–2.72 (m, 1H), 4.28 (dd, *J* = 13.2, 5.1 Hz, 1H), 4.35 (d, *J* = 2.4 Hz, 1H), 4.44 (dd, *J* = 13.2, 9.9 Hz, 1H), 7.42–7.56 (m, 4H), 7.59–7.65 (m, 2H), 8.29 (t, *J* = 8.7 Hz, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 25.9, 26.2, 26.4, 28.7, 33.3, 36.0, 42.7, 52.6, 75.5, 127.2, 127.7, 127.8, 127.9, 128.3, 128.8, 132.8, 133.1, 133.3, 133.4, 141.2, 142.6, 184.6. IR (KBr) *v* 1660, 1602, 1560, 1315, 930 cm^{-1}. HRMS (ESI) Calcd for C$_{22}$H$_{23}$NNaO$_3$ (M+Na)$^+$: 372.1570; Found: 372.1566. HPLC conditions: Chiralcel AD-H column, *i*-PrOH/hexane 20:80, flow rate 1.0 mL/min, UV detection at 254 nm, t_{major} = 5.73 min, t_{minor} = 6.17 min.

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