

Supporting Information

**Synergistic Zinc Catalyst Mediated Oxa-Michael Kinetic Resolution
Reaction**

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CONTENTS:

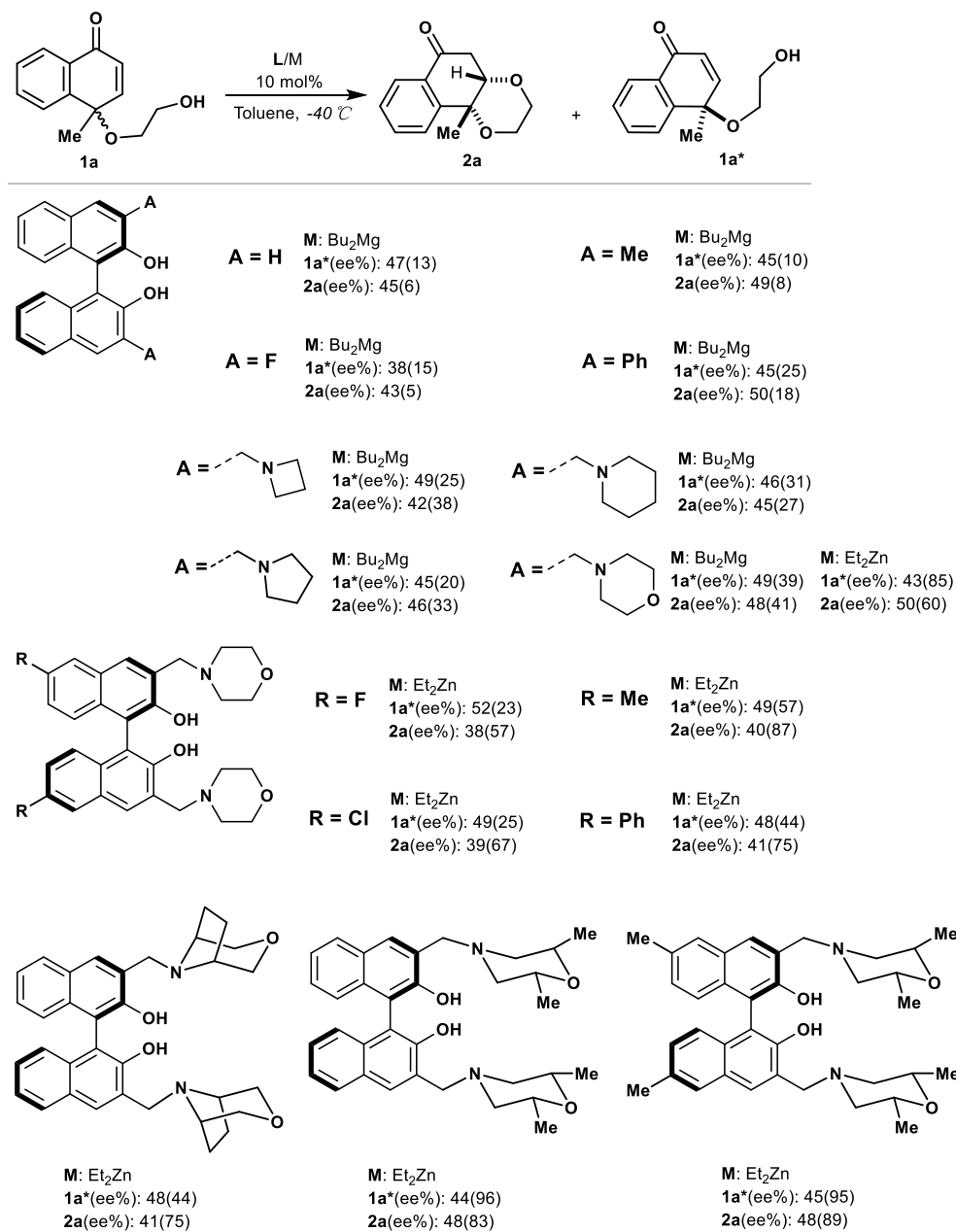
General Remarks	2
Screening Tables	3
General Synthesis Methods of the Initial Materials.....	5
Synthesis Procedure of L10	9
Experimental Procedures for the Oxa-Michael KR Reaction	11
Nonlinear effects studies	33
Control experiments	34
X-Ray Analysis of Product 2a	38
Gram Scale Trial of the Oxa-Michael KR Reaction and Transformation of the Resolution Products	39
HPLC Results	43
NMR Spectra.....	92

General Remarks

All reactions were performed under an argon atmosphere and solvents were dried according to established procedures. ^1H NMR (300 MHz), and ^{13}C NMR (75 MHz or 150 MHz) spectra were obtained in CDCl_3 or DMSO. The chemical shifts are reported in ppm relative to internal standard TMS (^1H NMR), to residual signals of the solvents (CHCl_3 , 7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR). IR spectra were recorded on a FT-IR spectrometer with KBr pellet and only major peaks were reported in cm^{-1} . High resolution massspectra (HRMS) were obtained by the ESI ionization sources. The er values determination were carried out using chiral HPLC on Waters with a 2996UV-detector. Et_2Zn (1.0 M in toluene) is commercially available at Energy-Chemical.

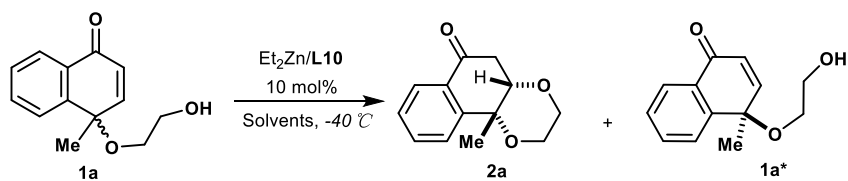
Screening Tables

a) Ligand Screening Table



Reactions were carried out with **1a** (0.1 mmol) with Et₂Zn (10 mol%) or Bu₂Mg (10 mol%) and ligands (10 mol%), in toluene at -40 °C for appropriate time, isolated yields were reported and ee values were analyzed by chiral HPLC.

b) Solvent Screening Table

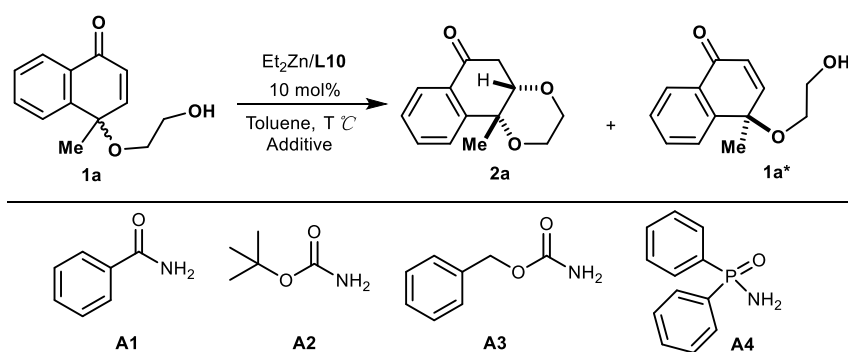


entry ^a	L	M	solvents	1* (ee%)	2 (ee%)	s ^b
1	L10	Et ₂ Zn	THF	43 (63)	48 (59)	7.2
2	L10	Et ₂ Zn	DCM	69 (15)	31 (45)	3.0
3	L10	Et ₂ Zn	PhCl	50 (53)	43 (81)	16.1
4	L10	Et ₂ Zn	Et ₂ O	78 (0)	21 (5)	0
5	L10	Et ₂ Zn	toluene	43 (95)	48 (89)	63.7
6	L10	Et ₂ Zn	<i>o</i> -xylene	45 (89)	43 (85)	36.6
7	L10	Et ₂ Zn	<i>m</i> -xylene	48 (86)	47 (86)	36.6
8	L10	Et ₂ Zn	<i>p</i> -xylene	47 (85)	48 (78)	21.6

DCM, dichloromethane; THF, tetrahydrofuran.

^aReactions were carried out with **1a** (0.1 mmol) with Et₂Zn (10 mol%) and **L10** (10 mol%), in different solvents at -40 °C for appropriate time, isolated yields were reported and ee values were analyzed by chiral HPLC. ^bs = ln[(1 - C)(1 - ee**1a***)]/ln[(1 - C)(1 + ee**1a***)], C is monitored by HPLC analysis and calculated according to C = ee**1a***/(ee**1a*** + ee**2a**).

c) Detail Condition Screening Table



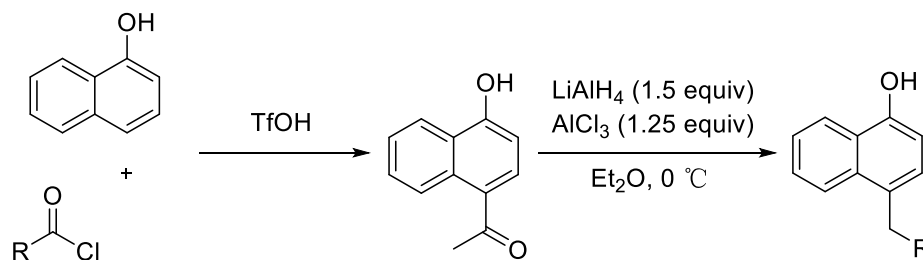
entry ^a	T (°C)	additive	1* (ee%)	2 (ee%)	s ^b
1	-78	-	-	-	0
2	-40	-	45 (92)	49 (88)	51.2

3	-20	-	47 (99)	50 (86)	68.9
4	RT	-	19 (99)	82 (5)	3.3
5	-20	A1	44 (79)	50 (40)	5.2
6	-20	A2	47 (99)	48 (90)	99.4
7	-20	A3	42 (92)	47 (82)	32.8
8	-20	A4	46 (85)	50 (64)	11.9

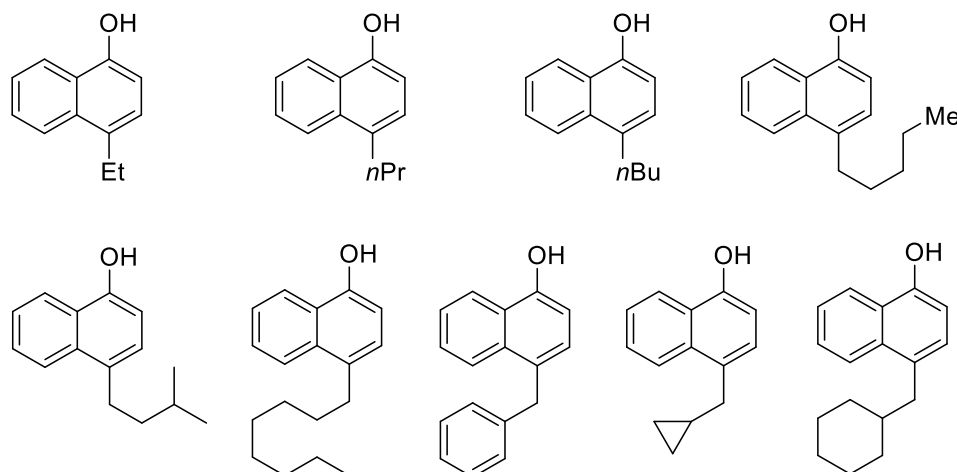
^aReactions were carried out with **1a** (0.1 mmol) with Et₂Zn (10 mol%) and **L10** (10 mol%), in toluene at different temperature or added different additives for appropriate time, isolated yields were reported and ee values were analyzed by chiral HPLC. ^b $s = \ln[(1 - C)(1 - ee1a^*)]/\ln[(1 - C)(1 + ee1a^*)]$, C is monitored by HPLC analysis and calculated according to $C = ee1a^*/(ee1a^* + ee2a)$.

General Synthesis Methods of the Initial Materials

General Procedure A:



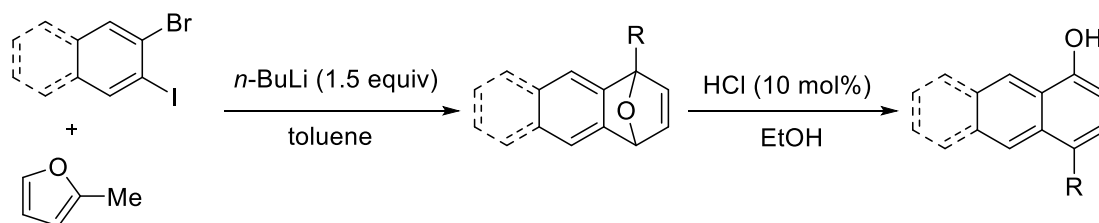
For the synthetic routes to:



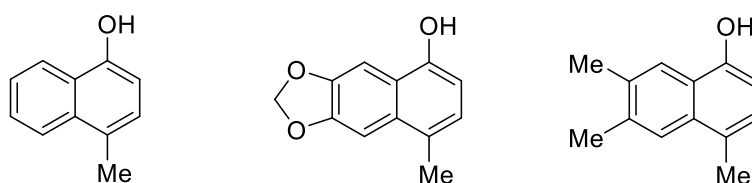
Methods: To a solution of 1-naphthol (1.0 equiv) in TfOH (10 mL) at 0°C was added chloride (1.0 equiv). The mixture was stirred at 0 °C for 0.5-1.0 hours. After completed, the mixture was quenched with H₂O, extracted with CH₂Cl₂, then the separated organic

phase was washed with saturated NaHCO_3 solution, dried with Na_2SO_4 , and purified via flash column chromatography to give pure products.

General Procedure B:



For the synthetic routes to:



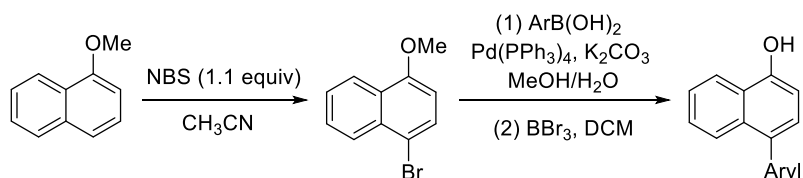
Methods: To a solution of halide (1.0 equiv) and 2-methylfuran (2.0 equiv) in dried toluene at $-20\text{ }^\circ\text{C}$ was added $n\text{-BuLi}$ (1.5 equiv, 2.5 M in hexane) under an argon atmosphere. The mixture was stirred at $-20\text{ }^\circ\text{C}$ for 2 hours. After completed, the reaction was quenched with saturated NH_4Cl and extracted with EA. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. Then the residue was purified by column chromatography to afford the products.

General Procedure C:

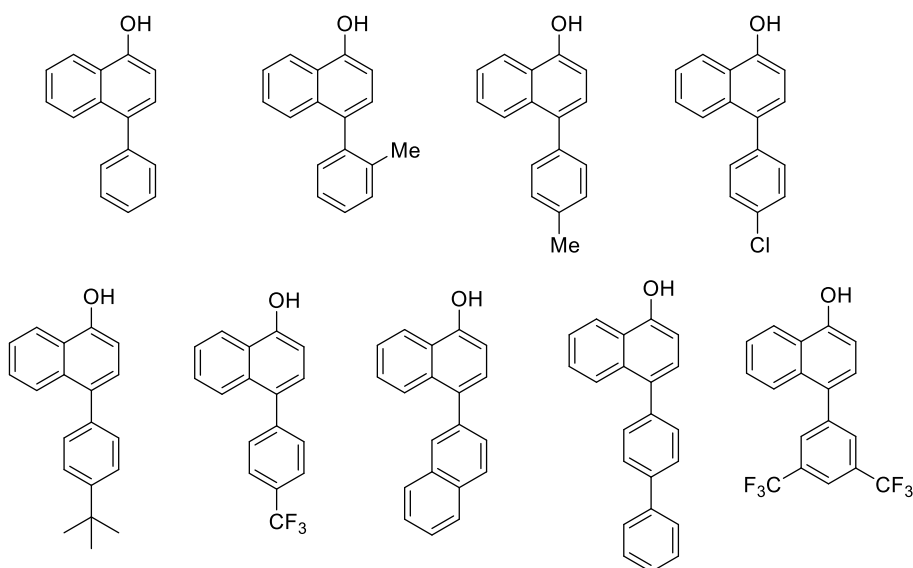
Method: To a solution of 1-Methoxynaphthalene (1.0 equiv) in CH_3CN at room temperature was added NBS (1.1 equiv). The mixture was stirred at room temperature overnight. After completed, the mixture was concentrated under vacuum. Then the residue was purified by column chromatography to afford the products.

The compound obtained above (1.0 equiv) in $\text{MeOH}/\text{H}_2\text{O}$ (v:v = 10/1) was successively added $\text{Pd}(\text{PPh}_3)_4$ (5 mol%), K_2CO_3 (2.0 equiv), and $\text{ArB}(\text{OH})_2$ (1.0 equiv) at room temperature, followed by refluxing for 24 hours under an argon atmosphere. The solution was cooled to room temperature and extracted with CH_2Cl_2 , washed with water and brine, dried over MgSO_4 , and concentrated to give a crude product. Then, it was

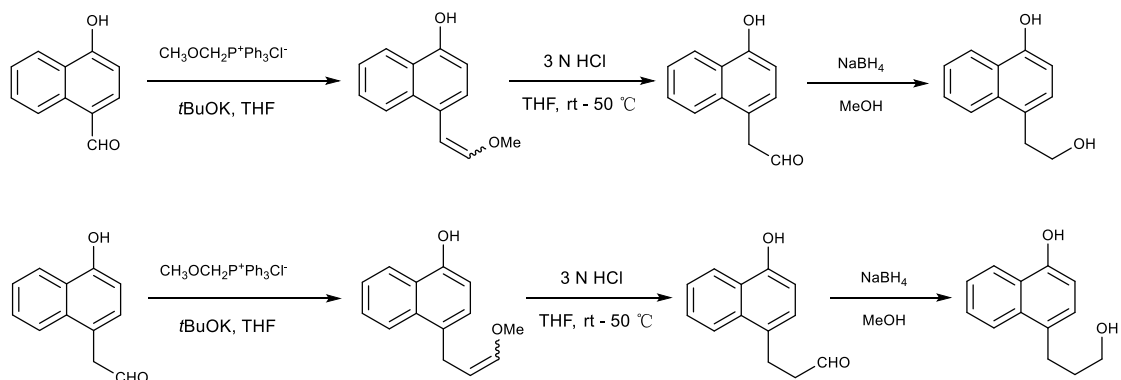
dissolved in DCM, and BBr_3 (1.2 equiv) was added at room temperature, after the reaction was completed, H_2O was added cautiously at $0\text{ }^\circ\text{C}$, extracted with CH_2Cl_2 , washed with water and brine, dried over MgSO_4 , then purified by column chromatography to afford the pure products.



For the synthetic routes to:



General Procedure D:



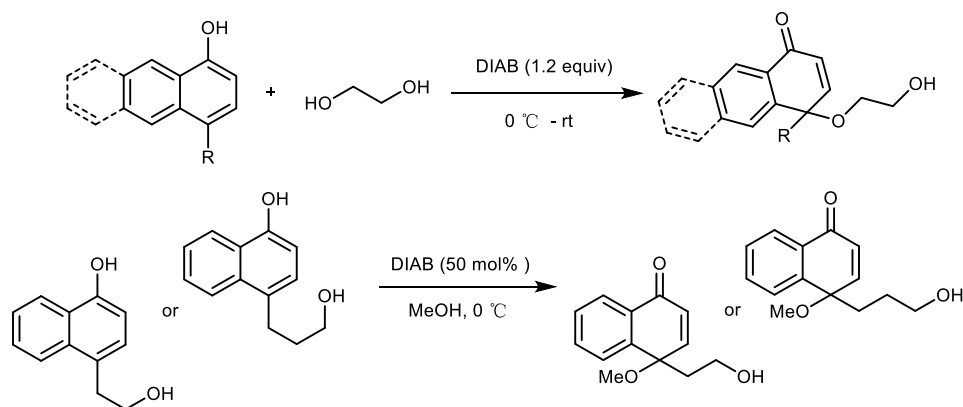
Method: To a solution of (methoxymethyl)triphenylphosphonium chloride (1.5 equiv) in THF, at $0\text{ }^\circ\text{C}$ under an argon atmosphere, was added *t*-BuOK (1.5 equiv). The mixture was stirred at $0\text{ }^\circ\text{C}$ for 30 min before the aldehyde (1.0 equiv) was added. The resulting

mixture was allowed to warm to room temperature and stirred for about 10 h. After completion (monitored by TLC), the reaction mixture was quenched with saturated NH_4Cl solution and THF was removed under reduced pressure. The mixture was diluted with H_2O and extracted with ethyl acetate. The combined ethyl acetate extract was washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography.

A round-bottomed flask was filled with argon. To this flask were added the above obtained olefin (1.0 equiv) and THF. To the mixture was added 3 N HCl solution (3.0 equiv). Then the resulting mixture was heated at 50°C for about 1 h. After completion (monitored by TLC), the reaction mixture was quenched with saturated NaHCO_3 . The mixture was extracted with ethyl acetate. The combined ethyl acetate extract was washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product aldehyde was obtained, which was used in the following reduction step without further purification.

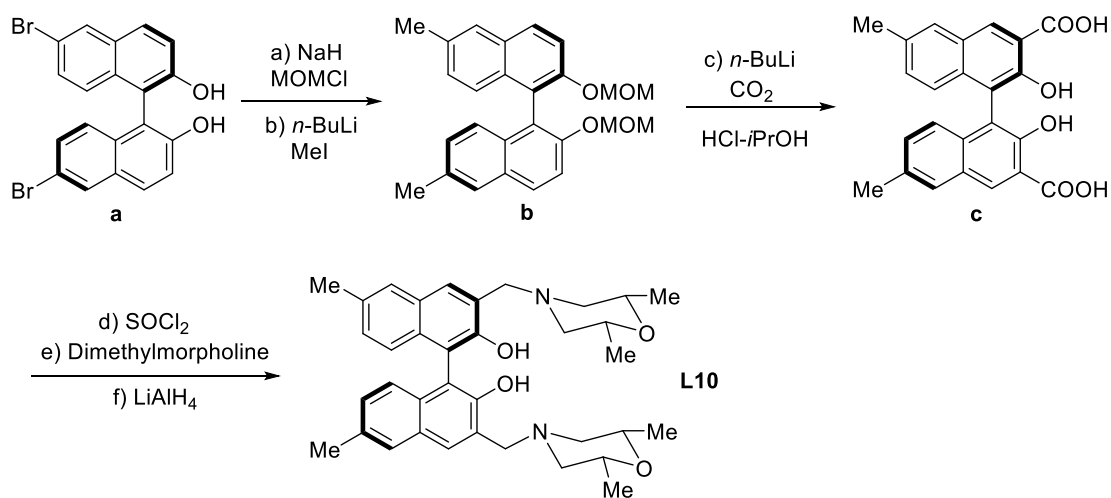
To a solution of the above aldehyde in MeOH was added NaBH_4 (1.0 equiv). Then the resulting mixture was stirred at room temperature for about 5 min. After completion (monitored by TLC), the reaction mixture was quenched with saturated NH_4Cl and MeOH was removed under reduced pressure. The mixture was diluted with H_2O and extracted with ethyl acetate. The combined ethyl acetate extract was washed with brine, dried over anhydrous Na_2SO_4 and filtrated. After the solvent was concentrated under reduced pressure, the crude product was purified by silica gel column chromatography to afford the desired product (30% yield for three steps).

General Procedure E:



Methods: To a solution of substituted-naphthol (1.0 equiv) in MeOH or glycol at 0°C was added DIAB (1.2 equiv or 50 mol%). The mixture was stirred for further 0.5 - 2 hours. After completed, the mixture was quenched with H₂O, extracted with ethyl acetate, and the separated organic phase was washed with saturated NaHCO₃ solution, dried with Na₂SO₄, then purified via flash column chromatography to give products **1**.

Synthesis Procedure of L10



Step 1: **a** (1.0 equiv) was dissolved in dried THF, after cooling to 0 °C, NaH (2.5 equiv) was added, then the mixture was stirred for further 0.5 hours, MOMCl (2.5 equiv) was added. After the reaction was completed, H₂O was carefully added, then the mixture was extracted with EA, dried with Na₂SO₄, filtration, and concentrated to give a crude product which was used directly in the next step without further purification. To the crude product in dried THF, *n*-BuLi (2.5 equiv) was added under an argon atmosphere at -78 °C, then MeI (3.0 equiv) in THF was added after 0.5 hours, the mixture was

stirred at room temperature for 12 hours. After completed, the reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 and concentrated to give a crude product which was purified via flash column chromatography to give **b** in 55% yield.

Step 2: **b** (1.0 equiv) was dissolved in dried Et_2O , *n*-BuLi (2.5 equiv) was added at room temperature, then the mixture was stirred for further 2 hours at the same temperature, CO_2 gas was pumped through a balloon at 0 °C for about 1 hours. After the reaction was completed, quenched with water and the aqueous was separated and acidified to $\text{pH} = 2$ with hydrochloric acid. The mixture was extracted with EA, dried with Na_2SO_4 , filtration, and concentrated. The crude product diluted with THF and added saturated HCl -*i*PrOH, then the mixture was stirred for further 4 hours at the room temperature. After completed, concentrated to give a crude product which was purified via flash column chromatography to give **c** in 80% yield.

Step 3: **c** obtained above was treated with SOCl_2 for 4 hours at reflux. Removal of the excess SOCl_2 in vacuo to afforded the crude acyl-chloride as a dark brown oil. A solution of Dimethylmorpholine (10 equiv) in THF was then added dropwise to the chloride in THF at 0 °C. The reaction mixture was stirred at room temperature for about 8 hours. After the reaction was completed, the mixture was poured into 1 N HCl. Extracted with CH_2Cl_2 , dried with Na_2SO_4 and concentrated to give a crude product which was purified via flash column chromatography to give amide in 60% yield.

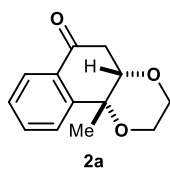
Step 4: To a solution of above amide (1.0 equiv) in dry THF at 0°C was added LiAlH_4 (4.0 equiv). The mixture was stirred at reflux for about 4 hours. After completed, the mixture was cooled to 0 °C, quenched with saturated KF solution, filtered through celite, and purified via flash column chromatography to give pure **L10** (85% yield).

Pale yellow solid, m.p. 228 – 229°C; $[\alpha]_{\text{D}}^{26.3} = 71.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 10.93 (s, 2H), 7.54 (s, 4H), 7.04 (dd, $J = 8.7, 4.9$ Hz, 4H), 4.03 (d, $J = 13.6$ Hz, 2H), 3.83 (d, $J = 13.7$ Hz, 2H), 3.69 – 3.50 (m, 4H), 2.86 (m, $J = 16.9, 11.4$ Hz, 4H), 2.42 (s, 6H), 1.91 (dd, $J = 23.9, 11.1$ Hz, 4H), 1.12 (m, $J = 6.1, 4.2$ Hz, 12H);

^{13}C NMR (75 MHz, CDCl_3): δ 152.52, 132.35, 131.88, 128.38, 128.28, 127.45, 126.71, 124.72, 123.35, 116.55, 77.47, 77.25, 77.05, 76.62, 71.48, 71.40, 62.01, 58.68, 58.25, 21.33, 19.01, 18.98; **IR** (neat): 3006, 2973, 2869, 1917, 1614, 1507, 1457, 1142, 755, 665, 555 cm^{-1} ; **HRMS** (ESI): $\text{C}_{36}\text{H}_{44}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ calcd: 569.3374, found: 569.3388.

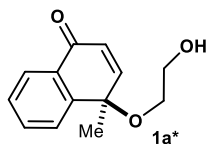
Experimental Procedures for the Oxa-Michael KR Reaction

To a stirred solution of **L10** (5.68 mg, 0.01 mmol) in toluene (0.5 mL) was added Et_2Zn (10 μL , 1.0 M in toluene, 0.01 mmol) under an argon atmosphere, the mixture was then stirred at room temperature for 30 min to generate the catalyst. The substrate **1** (0.1 mmol) and BocNH_2 (4.68 mg, 40 mol%) in toluene (0.5 mL) was quickly added to the flask containing the in situ generated zinc catalyst. After the addition, the reaction was stirred at $-20\text{ }^\circ\text{C}$ to room temperature and analyzed by TLC. After completion the reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 and concentrated under vacuum. Then the residue was purified by column chromatography to afford the product **1*** and **2**.

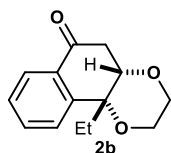


With 10 mol% catalyst at $-20\text{ }^\circ\text{C}$ for 3 h.

White solid, m.p. $135 - 136\text{ }^\circ\text{C}$; 48% yield; 90% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.42$ min, $t_{\text{minor}} = 7.46$ min); $[\alpha]_{\text{D}}^{28.0} = 27.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.09 – 7.88 (m, 1H), 7.57 (dd, $J = 8.0, 1.5$ Hz, 2H), 7.34 (s, 1H), 3.98 (s, 1H), 3.76 – 3.64 (m, 1H), 3.60 – 3.43 (m, 3H), 2.94 – 2.73 (m, 2H), 1.46 (s, 3H); **^{13}C NMR** (75 MHz, CDCl_3): δ 194.51, 144.52, 134.58, 131.85, 127.77, 126.85, 126.27, 79.21, 77.49, 77.07, 76.64, 73.00, 66.80, 61.35, 42.61, 28.32; **IR** (neat): 3368, 2923, 2853, 1691, 1496, 1454, 1287, 1111, 760, 701 cm^{-1} ; **HRMS** (ESI): $\text{C}_{13}\text{H}_{14}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 241.0835, found: 241.0839.

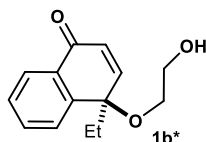


Purple liquid; 45% yield; 99% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 19.56$ min, $t_{\text{minor}} = 17.25$ min); $[\alpha]_{\text{D}}^{28.0} = -80.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.13 (d, $J = 7.7$ Hz, 1H), 7.65 (tt, $J = 7.9, 4.0$ Hz, 2H), 7.51 – 7.40 (m, 1H), 7.00 (d, $J = 10.3$ Hz, 1H), 6.50 (d, $J = 10.3$ Hz, 1H), 3.68 (d, $J = 4.1$ Hz, 2H), 3.33 (dt, $J = 14.1, 4.7$ Hz, 1H), 3.17 – 3.03 (m, 1H), 2.70 (s, 1H), 1.64 (s, 3H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 184.25, 152.59, 144.87, 133.37, 131.10, 130.06, 128.20, 126.76, 126.22, 77.58, 77.16, 76.73, 73.57, 66.31, 61.97, 30.47; **IR** (neat): 3421, 2923, 2854, 1716, 1456, 1364, 1298, 1077, 721, 529 cm^{-1} ; **HRMS** (ESI): $\text{C}_{13}\text{H}_{14}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 241.0835, found: 241.0833.



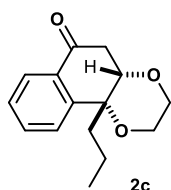
With 10 mol% catalyst at -20 °C for 3 h.

Yellow solid, m.p. $85 - 86$ °C; 49% yield; 90.5% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.14$ min, $t_{\text{minor}} = 7.72$ min); $[\alpha]_{\text{D}}^{27.3} = 43.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.05 (dd, $J = 7.8, 0.7$ Hz, 1H), 7.69 – 7.51 (m, 2H), 7.47 – 7.35 (m, 1H), 4.15 (t, $J = 3.1$ Hz, 1H), 3.84 – 3.70 (m, 1H), 3.68 – 3.51 (m, 3H), 2.90 (qd, $J = 17.9, 3.2$ Hz, 2H), 1.93 – 1.74 (m, 2H), 1.02 (t, $J = 7.5$ Hz, 3H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 194.56, 143.70, 133.96, 132.00, 127.64, 127.10, 127.08, 77.58, 77.47, 77.05, 76.62, 74.86, 66.89, 61.22, 42.15, 33.80, 7.53; **IR** (neat): 3349, 2961, 2855, 1600, 1455, 1286, 1112, 965, 763, 597 cm^{-1} ; **HRMS** (ESI): $\text{C}_{14}\text{H}_{16}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 255.0992, found: 255.0993.



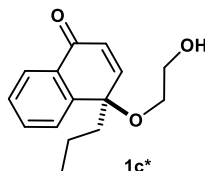
Purple liquid; 42% yield; 99% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, $t_{\text{major}} = 15.71$ min, $t_{\text{minor}} = 11.80$ min); $[\alpha]_{\text{D}}^{26.1} = -46.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.13 (d, $J = 7.7$ Hz,

1H), 7.70 – 7.57 (m, 2H), 7.49 – 7.39 (m, 1H), 6.89 (d, $J = 10.4$ Hz, 1H), 6.59 (d, $J = 10.4$ Hz, 1H), 3.68 (d, $J = 4.3$ Hz, 2H), 3.36 (dt, $J = 9.8, 5.0$ Hz, 1H), 3.22 – 3.07 (m, 1H), 2.34 (s, 1H), 2.03 (dt, $J = 14.7, 4.4$ Hz, 2H), 0.57 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 184.48, 151.40, 143.61, 133.33, 132.30, 131.70, 128.16, 126.60, 125.93, 77.66, 77.51, 77.08, 76.66, 66.07, 62.10, 35.69, 7.97; **IR** (neat): 3458, 2928, 2859, 1668, 1601, 1457, 1300, 1085, 892, 762 cm^{-1} ; **HRMS** (ESI): $\text{C}_{14}\text{H}_{16}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 255.0992, found: 255.1000.



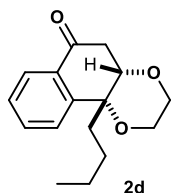
With 10 mol% catalyst at -20 °C for 1 h.

Colourless oil liquid; 48% yield; 90% ee determined by HPLC on Chiralpak IA-H column (n -hexane/ i -PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.98$ min, $t_{\text{minor}} = 7.47$ min); $[\alpha]_{\text{D}}^{28.3} = 36.0$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 8.05 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.80 – 7.51 (m, 2H), 7.48 – 7.33 (m, 1H), 4.15 (t, $J = 3.1$ Hz, 1H), 3.84 – 3.68 (m, 1H), 3.67 – 3.45 (m, 3H), 2.90 (qd, $J = 17.9, 3.2$ Hz, 2H), 1.83 – 1.65 (m, 2H), 1.58 – 1.39 (m, 2H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.54, 143.89, 133.97, 131.94, 127.60, 127.02, 77.71, 77.52, 77.10, 76.67, 75.01, 66.88, 61.22, 43.34, 42.17, 16.37, 14.46; **IR** (neat): 3380, 2924, 1698, 1601, 1463, 1373, 1278, 1175, 1142, 761 cm^{-1} ; **HRMS** (ESI): $\text{C}_{15}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 269.1148, found: 269.1151.



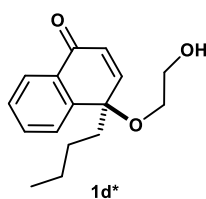
Purple liquid; 45% yield; 99% ee determined by HPLC on Chiralpak OD-H column (n -hexane/ i -PrOH = 9/1, flow rate = 1.0 mL/min, $t_{\text{major}} = 15.16$ min, $t_{\text{minor}} = 11.90$ min); $[\alpha]_{\text{D}}^{26.6} = -39.0$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 8.12 (d, $J = 7.7$ Hz, 1H), 7.63 (d, $J = 4.0$ Hz, 2H), 7.45 (m, $J = 8.2, 5.0, 3.5$ Hz, 1H), 6.93 (d, $J = 10.4$ Hz, 1H), 6.56 (d, $J = 10.3$ Hz, 1H), 3.68 (d, $J = 3.2$ Hz, 2H), 3.35 (m, $J = 9.8, 4.6$ Hz, 1H),

3.23 – 3.08 (m, 1H), 2.38 (s, 1H), 2.02 – 1.92 (m, 2H), 1.30 – 1.08 (m, 2H), 0.77 (d, $J = 4.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 184.46, 151.77, 144.01, 133.31, 132.07, 131.38, 128.13, 126.62, 125.98, 77.52, 77.10, 76.99, 76.67, 65.89, 62.09, 45.11, 16.94, 14.02; IR (neat): 3443, 2924, 1666, 1600, 1455, 1377, 1299, 1066, 788, 765 cm^{-1} ; HRMS (ESI): $\text{C}_{14}\text{H}_{16}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 269.1148, found: 269.1153.



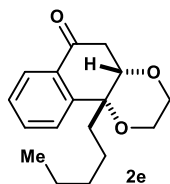
With 10 mol% catalyst at -15 °C for 3 h.

Yellow liquid; 46% yield; 92% ee determined by HPLC on Chiralpak IA-H column (n -hexane/ i -PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.91$ min, $t_{\text{minor}} = 7.77$ min); $[\alpha]_{\text{D}}^{28.4} = 28.0$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.97 (d, $J = 7.8$ Hz, 1H), 7.63 – 7.44 (m, 2H), 7.33 (t, $J = 7.4$ Hz, 1H), 4.08 (t, $J = 3.1$ Hz, 1H), 3.68 (dt, $J = 13.4, 5.2$ Hz, 1H), 3.60 – 3.41 (m, 3H), 2.83 (qd, $J = 17.9, 3.1$ Hz, 2H), 1.68 (dddd, $J = 21.9, 17.6, 8.8, 4.5$ Hz, 2H), 1.48 – 1.34 (m, 2H), 1.20 (dt, $J = 14.7, 7.2$ Hz, 2H), 0.81 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 194.55, 143.99, 134.01, 131.93, 127.60, 127.03, 126.99, 77.66, 77.50, 77.08, 76.65, 74.97, 66.89, 61.25, 42.17, 41.02, 25.18, 23.17, 14.00; IR (neat): 3368, 2923, 2855, 1694, 1601, 1452, 1288, 1110, 760, 565 cm^{-1} ; HRMS (ESI): $\text{C}_{16}\text{H}_{20}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 283.1305, found: 283.1308.



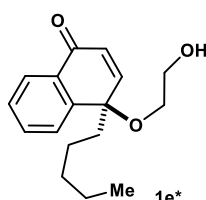
Purple liquid; 43% yield; 99% ee determined by HPLC on Chiralpak OD-H column (n -hexane/ i -PrOH = 9/1, flow rate = 1.0 mL/min, $t_{\text{major}} = 10.89$ min, $t_{\text{minor}} = 9.63$ min); $[\alpha]_{\text{D}}^{25.7} = -29.0$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 8.13 (d, $J = 7.7$ Hz, 1H), 7.71 – 7.56 (m, 2H), 7.52 – 7.39 (m, 1H), 6.91 (d, $J = 10.3$ Hz, 1H), 6.57 (d, $J = 10.3$ Hz, 1H), 3.67 (s, 2H), 3.34 (dt, $J = 9.7, 4.7$ Hz, 1H), 3.22 – 3.04 (m, 1H), 2.19 (s, 1H), 1.98 (dt, $J = 12.8, 5.6$ Hz, 2H), 1.29 – 1.07 (m, 4H), 0.76 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 184.48, 151.70, 143.96, 133.33, 132.11, 131.44, 128.15,

126.64, 125.95, 77.49, 77.07, 77.00, 76.64, 65.86, 62.13, 42.68, 25.61, 22.63, 13.77;
IR (neat): 3457, 2925, 2855, 1728, 1669, 1601, 1457, 1299, 1085, 766 cm^{-1} ; **HRMS**
(ESI): $\text{C}_{16}\text{H}_{20}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 283.1305, found: 283.1308.



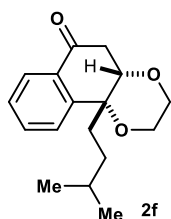
With 10 mol% catalyst at $-20\text{ }^\circ\text{C}$ for 2 h.

Yellow liquid; 50% yield; 92% ee determined by HPLC on Chiralpak IA-H column (n -hexane/ i -PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.79$ min, $t_{\text{minor}} = 6.84$ min); $[\alpha]_{\text{D}}^{27.6} = 46.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.05 (d, $J = 7.7$ Hz, 1H), 7.61 (dt, $J = 18.2, 7.0$ Hz, 2H), 7.45 – 7.35 (m, 1H), 4.16 (t, $J = 3.0$ Hz, 1H), 3.76 (dt, $J = 13.3, 5.3$ Hz, 1H), 3.69 – 3.48 (m, 3H), 2.90 (qd, $J = 17.9, 3.1$ Hz, 2H), 1.75 (dtdd, $J = 17.7, 13.3, 9.0, 4.6$ Hz, 2H), 1.55 – 1.39 (m, 2H), 1.33 – 1.21 (m, 4H), 0.86 (t, $J = 7.0$ Hz, 3H); **^{13}C NMR** (75 MHz, CDCl_3): δ 194.57, 144.01, 134.01, 131.93, 127.60, 127.03, 126.98, 77.64, 77.50, 77.08, 76.65, 75.00, 66.89, 61.24, 42.17, 41.24, 32.23, 22.71, 22.55, 14.04; **IR** (neat): 3368, 2924, 2854, 1693, 1601, 1454, 1287, 1112, 767, 562 cm^{-1} ; **HRMS** (ESI): $\text{C}_{17}\text{H}_{22}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 297.1461, found: 297.1471.



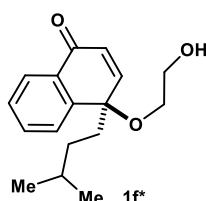
Yellow liquid; 48% yield; 95% ee determined by HPLC on Chiralpak OD-H column (n -hexane/ i -PrOH = 9/1, flow rate = 1.0 mL/min, $t_{\text{major}} = 11.55$ min, $t_{\text{minor}} = 10.23$ min); $[\alpha]_{\text{D}}^{26.3} = -25.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.13 (d, $J = 7.8$ Hz, 1H), 7.65 (t, $J = 6.0$ Hz, 2H), 7.52 – 7.40 (m, 1H), 6.93 (d, $J = 10.3$ Hz, 1H), 6.57 (d, $J = 10.3$ Hz, 1H), 3.68 (s, 2H), 3.42 – 3.28 (m, 1H), 3.21 – 3.08 (m, 1H), 2.55 (s, 1H), 2.07 – 1.88 (m, 2H), 1.13 (s, 6H), 0.76 (t, $J = 6.5$ Hz, 3H); **^{13}C NMR** (75 MHz, CDCl_3): δ 184.50, 151.81, 144.00, 133.32, 132.08, 131.38, 128.12, 126.60, 125.96, 77.55, 77.13, 77.03, 76.70, 65.94, 62.05, 42.82, 31.64, 23.11, 22.24, 13.86; **IR** (neat): 3456, 2925, 2853, 1744, 1671, 1457, 1371, 1279, 1141, 761 cm^{-1} ; **HRMS** (ESI): $\text{C}_{17}\text{H}_{22}\text{O}_3$ $[\text{M} +$

$\text{Na}]^+$ calcd: 297.1461, found: 297.1474.



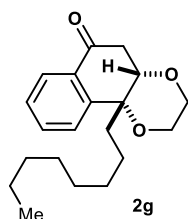
With 10 mol% catalyst at $-20\text{ }^\circ\text{C}$ for 2 h.

Yellow liquid; 53% yield; 91% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.72$ min, $t_{\text{minor}} = 7.27$ min); $[\alpha]_{\text{D}}^{27.3} = 34.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.97 (d, $J = 7.8$ Hz, 1H), 7.62 – 7.44 (m, 2H), 7.36 – 7.26 (m, 1H), 4.08 (t, $J = 3.1$ Hz, 1H), 3.68 (dt, $J = 13.6, 5.2$ Hz, 1H), 3.60 – 3.39 (m, 3H), 2.82 (qd, $J = 17.9, 3.1$ Hz, 2H), 1.78 – 1.60 (m, 2H), 1.43 – 1.26 (m, 3H), 0.78 (dd, $J = 6.2, 2.4$ Hz, 6H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 193.52, 143.14, 133.01, 130.91, 126.57, 126.00, 125.91, 76.50, 76.46, 76.04, 75.62, 73.96, 65.85, 60.22, 41.11, 38.25, 30.83, 27.46, 21.58, 21.39; **IR** (neat): 3368, 2924, 2855, 1693, 1601, 1452, 1287, 1108, 759, 479 cm^{-1} ; **HRMS** (ESI): $\text{C}_{17}\text{H}_{22}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 297.1461, found: 297.1459.



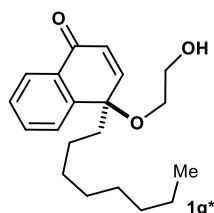
Yellow liquid; 45% yield; 98% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, $t_{\text{major}} = 11.41$ min, $t_{\text{minor}} = 9.63$ min); $[\alpha]_{\text{D}}^{26.5} = -22.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.13 (d, $J = 7.7$ Hz, 1H), 7.69 – 7.58 (m, 2H), 7.46 (ddd, $J = 8.2, 6.3, 2.3$ Hz, 1H), 6.89 (d, $J = 10.3$ Hz, 1H), 6.57 (d, $J = 10.3$ Hz, 1H), 3.67 (s, 2H), 3.39 – 3.28 (m, 1H), 3.20 – 3.05 (m, 1H), 2.17 (s, 1H), 2.05 – 1.92 (m, 2H), 1.37 (dd, $J = 13.3, 6.6$ Hz, 1H), 1.07 – 0.96 (m, 1H), 0.75 (dd, $J = 13.8, 6.6$ Hz, 6H), 0.60 – 0.48 (m, 1H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 184.50, 151.63, 143.89, 133.36, 132.15, 131.51, 128.17, 126.64, 125.90, 77.49, 77.06, 76.64, 65.86, 62.13, 40.79, 32.22, 29.70, 28.02, 22.40, 22.26; **IR** (neat): 3457, 2925, 2856, 1668, 1601, 1457, 1379, 1299, 1085, 766 cm^{-1} ; **HRMS** (ESI): $\text{C}_{17}\text{H}_{22}\text{O}_3$ $[\text{M} + \text{Na}]^+$

calcd: 297.1461, found: 297.1469.



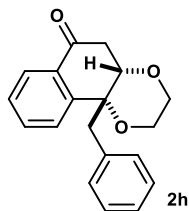
With 10 mol% catalyst at -20 °C for 2 h.

Yellow liquid; 48% yield; 91% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.84$ min, $t_{\text{minor}} = 7.04$ min); $[\alpha]_{\text{D}}^{27.2} = 39.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.05 (d, $J = 7.8$ Hz, 1H), 7.72 – 7.50 (m, 2H), 7.46 – 7.36 (t, 1H), 4.16 (t, $J = 3.1$ Hz, 1H), 3.85 – 3.72 (m, 1H), 3.67 – 3.50 (m, 3H), 2.90 (qd, $J = 17.9, 3.1$ Hz, 2H), 1.89 – 1.62 (m, 2H), 1.48 (m, $J = 14.1, 9.8$ Hz, 2H), 1.24 (m, 10H), 0.86 (t, $J = 6.6$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 194.57, 144.02, 134.01, 131.93, 127.60, 127.04, 126.98, 77.65, 77.49, 77.07, 76.64, 75.01, 66.89, 61.25, 42.18, 41.29, 31.82, 30.08, 29.48, 29.25, 23.06, 22.63, 14.11; **IR** (neat): 3368, 2957, 1692, 1601, 1455, 1287, 1130, 1112, 760, 665 cm^{-1} ; **HRMS** (ESI): $\text{C}_{20}\text{H}_{28}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 339.1931, found: 339.1928.



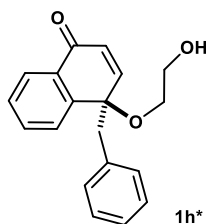
Purple liquid; 46% yield; 93% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, $t_{\text{major}} = 10.79$ min, $t_{\text{minor}} = 8.64$ min); $[\alpha]_{\text{D}}^{26.0} = -24.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.13 (d, $J = 7.7$ Hz, 1H), 7.71 – 7.59 (m, 2H), 7.45 (m, $J = 8.1, 5.6, 2.9$ Hz, 1H), 6.91 (d, $J = 10.3$ Hz, 1H), 6.57 (d, $J = 10.3$ Hz, 1H), 3.69 (dd, $J = 15.9, 5.7$ Hz, 2H), 3.42 – 3.28 (m, 1H), 3.23 – 3.09 (m, 1H), 2.33 (s, 1H), 1.98 (dd, $J = 8.0, 5.9$ Hz, 2H), 1.31 – 1.08 (m, 12H), 0.83 (t, $J = 6.9$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 184.47, 151.73, 143.98, 133.31, 132.10, 131.42, 128.13, 126.63, 125.95, 77.51, 77.08, 77.03, 76.66, 65.89, 62.10, 42.88, 31.72,

29.50, 29.16, 29.08, 23.45, 22.56, 14.06; **IR** (neat): 3456, 2925, 1727, 1668, 1600, 1457, 1378, 1301, 1084, 766 cm^{-1} ; **HRMS** (ESI): $\text{C}_{16}\text{H}_{20}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 339.1931, found: 339.1937.



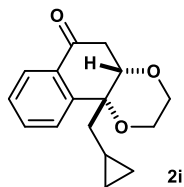
With 10 mol% catalyst at $-10\text{ }^\circ\text{C}$ for 1 h.

Yellow solid, m.p. $85 - 86\text{ }^\circ\text{C}$; 47% yield; 94% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 6.49$ min, $t_{\text{minor}} = 9.65$ min); $[\alpha]_{\text{D}}^{27.5} = 69.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 7.98 (d, $J = 7.8$, 1.1 Hz, 1H), 7.48 (td, $J = 7.6$, 1.3 Hz, 1H), 7.39 – 7.24 (m, 2H), 7.20 – 7.12 (m, 3H), 7.03 (m, $J = 6.0$, 3.3 Hz, 2H), 3.91 (t, $J = 3.1$ Hz, 1H), 3.62 – 3.44 (m, 4H), 3.11 – 2.82 (m, 3H), 2.72 (dd, $J = 17.8$, 3.1 Hz, 1H); **^{13}C NMR** (75 MHz, CDCl_3): δ 194.56, 143.34, 135.56, 134.04, 132.16, 130.77, 128.00, 127.89, 127.27, 126.90, 126.87, 77.51, 77.08, 76.66, 75.24, 66.67, 61.27, 47.43, 42.25; **IR** (neat): 3368, 2923, 1730, 1693, 1601, 1455, 1286, 1112, 766, 665 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 317.1148, found: 317.1155.



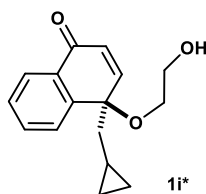
Yellow solid, m.p. $68 - 69\text{ }^\circ\text{C}$; 48% yield; 91% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 7.15$ min, $t_{\text{minor}} = 6.44$ min); $[\alpha]_{\text{D}}^{27.8} = 28.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.01 (d, $J = 7.8$, 0.7 Hz, 1H), 7.68 (m, $J = 9.2$, 7.8, 1.2 Hz, 2H), 7.45 (m, $J = 14.7$, 1.5 Hz, 1H), 7.18 – 7.02 (m, 3H), 6.88 (d, 1H), 6.84 – 6.73 (m, 2H), 6.42 (d, $J = 10.4$ Hz, 1H), 3.79 – 3.64 (m, 2H), 3.47 – 3.19 (m, 3H), 3.14 (d, $J = 13.1$ Hz, 1H), 2.12 (s, 1H); **^{13}C NMR** (75 MHz, CDCl_3): δ 183.81, 150.97, 143.55, 134.65, 133.03, 132.08, 131.40,

130.58, 128.34, 127.80, 127.00, 126.64, 126.37, 77.51, 77.27, 77.09, 76.66, 66.21, 62.14, 50.11; **IR** (neat): 3455, 2927, 1712, 1700, 1600, 1456, 1377, 1299, 764, 479 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 317.1148, found: 317.1151.



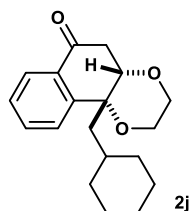
With 10 mol% catalyst at $-20\text{ }^\circ\text{C}$ for 4 h.

Yellow liquid; 49% yield; 92% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.27$ min, $t_{\text{minor}} = 7.63$ min); $[\alpha]_{\text{D}}^{28.3} = 36.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.00 (d, $J = 7.8$ Hz, 1H), 7.68 – 7.52 (m, 2H), 7.42 – 7.31 (m, 1H), 4.34 (t, $J = 3.1$ Hz, 1H), 3.76 (td, $J = 11.8, 3.6$ Hz, 1H), 3.65 – 3.49 (m, 3H), 2.89 (qd, $J = 17.8, 3.2$ Hz, 2H), 1.82 (dd, $J = 14.6, 5.8$ Hz, 1H), 1.54 (dd, $J = 14.7, 7.6$ Hz, 1H), 0.96 (tdd, $J = 7.9, 5.5, 2.8$ Hz, 1H), 0.56 – 0.36 (m, 2H), 0.01 (dt, $J = 9.1, 5.0$ Hz, 1H), -0.11 (td, $J = 9.1, 5.0$ Hz, 1H); **^{13}C NMR** (75 MHz, CDCl_3): δ 194.74, 144.02, 134.09, 132.04, 127.66, 127.07, 126.80, 77.48, 77.20, 77.06, 76.63, 75.66, 66.82, 61.21, 46.40, 42.47, 5.85, 5.49, 4.93; **IR** (neat): 3346, 2923, 2853, 1739, 1683, 1598, 1456, 1290, 1102, 779 cm^{-1} ; **HRMS** (ESI): $\text{C}_{16}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 281.1148, found: 281.1150.



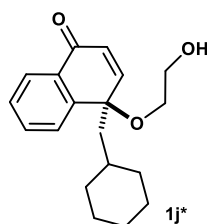
Purple liquid; 46% yield; 99% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, $t_{\text{major}} = 18.24$ min, $t_{\text{minor}} = 13.04$ min); $[\alpha]_{\text{D}}^{26.7} = -20.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.19 (d, $J = 7.8$ Hz, 1H), 7.78 – 7.61 (m, 2H), 7.58 – 7.45 (m, 1H), 7.09 (d, $J = 10.4$ Hz, 1H), 6.64 (d, $J = 10.3$ Hz, 1H), 3.74 (dd, $J = 9.4, 4.9$ Hz, 2H), 3.42 (dt, $J = 9.8, 4.6$ Hz, 1H), 3.31 – 3.11 (m, 1H), 2.29 (t, $J = 5.8$ Hz, 1H), 2.13 (dd, $J = 13.5, 5.8$ Hz, 1H), 1.82 (dd, $J = 13.4, 7.2$ Hz, 1H), 0.53 – 0.30 (m, 2H), 0.26 – 0.10 (m, 1H), 0.07 – -0.06 (m, 1H), -0.33 (td, $J = 9.8, 5.0$ Hz, 1H); **^{13}C NMR** (75 MHz, CDCl_3): δ 184.52, 152.08, 144.31, 133.05,

132.20, 131.24, 128.12, 126.62, 126.11, 77.50, 77.46, 77.08, 76.65, 65.84, 62.13, 48.34, 5.78, 4.73, 4.53; **IR** (neat): 3445, 2923, 2853, 1667, 1599, 1456, 1377, 1299, 1084, 760 cm^{-1} ; **HRMS** (ESI): $\text{C}_{16}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 281.1148, found: 281.1159.



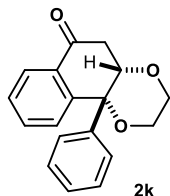
With 10 mol% catalyst at $-20\text{ }^\circ\text{C}$ for 2 h.

White solid, m.p. $70 - 71\text{ }^\circ\text{C}$; 50% yield; 91% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 7.15\text{min}$, $t_{\text{minor}} = 10.48\text{min}$); $[\alpha]_{\text{D}}^{25.4} = 60.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.96 (d, $J = 7.6$ Hz, 1H), 7.63 – 7.49 (m, 2H), 7.37 – 7.26 (m, 1H), 4.14 (t, $J = 3.1$ Hz, 1H), 3.71 (td, $J = 11.8, 3.5$ Hz, 1H), 3.60 – 3.44 (m, 3H), 2.83 (qd, $J = 17.9, 3.1$ Hz, 2H), 1.72 – 1.47 (m, 9H), 1.14 – 0.98 (m, 2H), 0.94 – 0.79 (m, 2H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 194.67, 144.69, 134.16, 131.83, 127.56, 126.97, 126.75, 77.45, 77.03, 76.61, 75.87, 66.91, 61.14, 48.77, 42.38, 35.34, 35.17, 33.11, 29.71, 26.42, 26.31, 26.15; **IR** (neat): 3372, 2923, 2852, 1693, 1601, 1450, 1287, 1111, 765, 592 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{24}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 323.1618, found: 323.1623.



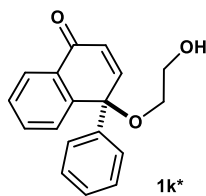
Yellow liquid; 49% yield; 92% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 7/3, flow rate = 1.0 mL/min, $t_{\text{major}} = 23.10$ min, $t_{\text{minor}} = 21.18$ min); $[\alpha]_{\text{D}}^{28.2} = -30.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.13 (d, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 3.8$ Hz, 2H), 7.46 (dq, $J = 8.3, 4.2$ Hz, 1H), 6.93 (d, $J = 10.3$ Hz, 1H), 6.57 (d, $J = 10.3$ Hz, 1H), 3.65 (d, $J = 4.5$ Hz, 2H), 3.30 (dt, $J = 9.7, 4.8$ Hz, 1H), 3.17 – 2.97 (m, 1H), 2.16 (t, $J = 5.2$ Hz, 1H), 1.94 (d, $J = 4.9$ Hz, 2H), 1.70 – 1.54 (m, 2H), 1.45 (dd, $J = 19.3, 9.9$ Hz, 2H), 1.13 – 0.89 (m, 6H), 0.65 (dd, $J = 22.0, 11.2$ Hz, 1H);

^{13}C NMR (75 MHz, CDCl_3): δ 184.48, 151.74, 144.15, 133.14, 131.96, 131.19, 128.20, 126.66, 126.47, 77.49, 77.07, 76.74, 76.64, 65.46, 62.11, 50.47, 35.01, 34.37, 33.25, 26.05, 25.94; **IR** (neat): 3431, 2926, 2854, 1735, 1668, 1457, 1378, 1216, 1083, 758 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{24}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 323.1618, found: 323.1629.



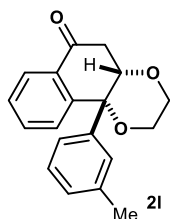
With 10 mol% catalyst at $-20\text{ }^\circ\text{C}$ for 5 h.

White solid, m.p. $69 - 70\text{ }^\circ\text{C}$; 51% yield; 90% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 7.57$ min, $t_{\text{minor}} = 10.44$ min); $[\alpha]_{\text{D}}^{27.4} = 74.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.24 – 8.08 (d, 1H), 7.78 – 7.64 (m, 1H), 7.60 – 7.48 (m, 2H), 7.37 – 7.27 (m, 3H), 7.19 (dd, $J = 6.8, 3.0$ Hz, 2H), 4.21 (t, $J = 3.1$ Hz, 1H), 3.99 (ddd, $J = 12.1, 10.2, 5.4$ Hz, 1H), 3.84 – 3.67 (m, 3H), 2.67 (qd, $J = 17.3, 3.1$ Hz, 2H); **^{13}C NMR** (75 MHz, CDCl_3): δ 193.94, 141.42, 140.88, 133.74, 132.70, 127.36, 127.31, 127.25, 127.16, 126.51, 125.47, 79.20, 77.32, 76.43, 76.21, 76.00, 75.58, 65.95, 60.17, 40.83, 28.67; **IR** (neat): 3368, 2922, 2855, 1693, 1560, 1447, 1288, 1108, 759, 565 cm^{-1} ; **HRMS** (ESI): $\text{C}_{18}\text{H}_{16}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 303.0992, found: 303.0999.



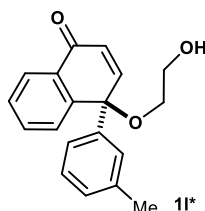
Yellow solid, m.p. $109 - 110\text{ }^\circ\text{C}$; 46% yield; 99% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 15.22$ min, $t_{\text{minor}} = 16.02$ min); $[\alpha]_{\text{D}}^{28.5} = 41.1$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.18 (d, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 6.9$ Hz, 1H), 7.45 (t, $J = 7.1$ Hz, 1H), 7.40 – 7.21 (m, 6H), 6.89 (d, $J = 10.2$ Hz, 1H), 6.53 (d, $J = 10.2$ Hz, 1H), 3.79 (d, $J = 4.5$ Hz, 2H), 3.57 (dt, $J = 9.5, 4.7$ Hz, 1H), 3.35 – 3.21 (m, 1H), 2.06 (s, 1H); **^{13}C NMR** (75 MHz, CDCl_3): δ 184.64, 151.06, 144.14, 141.83, 133.58, 131.76, 129.36, 128.56, 128.46, 128.36, 127.81, 126.51, 125.98, 77.52, 77.34, 77.10, 76.67, 65.78, 62.15; **IR** (neat): 3448, 2924,

2854, 1667, 1600, 1456, 1299, 1084, 768, 561 cm^{-1} ; **HRMS** (ESI): $\text{C}_{18}\text{H}_{16}\text{O}_3$ $[\text{M} + \text{Na}]^+$
calcd: 303.0992, found: 303.0991.



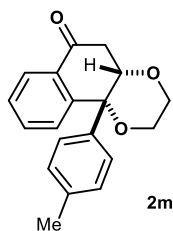
With 10 mol% catalyst at $-10\text{ }^\circ\text{C}$ for 2 h.

Pale yellow solid, m.p. $118 - 120\text{ }^\circ\text{C}$; 48% yield; 95% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.29$ min, $t_{\text{minor}} = 7.09$ min); $[\alpha]_{\text{D}}^{28.2} = 66.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.16 (d, $J = 7.6$ Hz, 1H), 7.69 (t, $J = 7.1$ Hz, 1H), 7.53 (dd, $J = 14.6, 7.3$ Hz, 2H), 7.21 – 7.05 (m, 3H), 6.86 (d, $J = 7.4$ Hz, 1H), 4.21 (t, $J = 2.9$ Hz, 1H), 3.98 (m, $J = 11.8, 10.0, 5.7$ Hz, 1H), 3.84 – 3.66 (m, 3H), 2.81 – 2.55 (m, 2H), 2.30 (s, 3H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 195.13, 142.40, 142.00, 138.04, 134.78, 133.67, 129.16, 128.36, 128.20, 128.11, 128.02, 126.46, 124.80, 80.23, 78.36, 77.51, 77.09, 76.66, 66.96, 61.19, 41.92, 29.71, 21.58; **IR** (neat): 3369, 2923, 1733, 1697, 1601, 1454, 1286, 1110, 764, 568 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 317.1148, found: 317.1157.



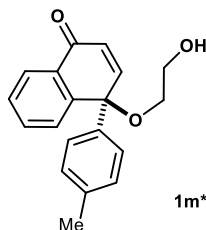
Green liquid; 49% yield; 95% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 14.63$ min, $t_{\text{minor}} = 13.63$ min); $[\alpha]_{\text{D}}^{28.1} = 67.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.17 (d, $J = 7.7, 0.9$ Hz, 1H), 7.61 – 7.33 (m, 3H), 7.21 – 7.09 (m, 3H), 7.09 – 7.01 (m, 1H), 6.88 (d, $J = 10.2$ Hz, 1H), 6.52 (d, $J = 10.2$ Hz, 1H), 3.79 (t, $J = 4.5$ Hz, 2H), 3.55 (m, 1H), 3.33 – 3.16 (m, 1H), 2.40 (s, 1H), 2.28 (s, 3H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 184.76, 151.22, 144.25, 141.69, 138.28, 133.58, 131.72, 129.27, 128.62, 128.47, 128.42, 128.35, 126.51, 126.49, 123.08, 77.56, 77.33, 77.13, 76.71, 65.78, 62.14, 21.59; **IR** (neat): 3452,

2929, 1726, 1668, 1601, 1458, 1300, 1077, 843, 762 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{18}\text{O}_3$ [$\text{M} + \text{Na}$] $^+$ calcd: 317.1148, found: 317.1156.



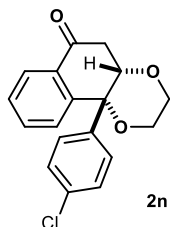
With 10 mol% catalyst at $-20\text{ }^\circ\text{C}$ for 4 h.

Pale yellow solid, m.p. $58 - 59\text{ }^\circ\text{C}$; 52% yield; 88% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.81$ min, $t_{\text{minor}} = 7.92$ min); $[\alpha]_{\text{D}}^{28.1} = 76.7$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.16 – 7.98 (d, 1H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.43 (dd, $J = 16.1, 7.8$ Hz, 2H), 7.06 – 6.92 (m, 4H), 4.10 (t, $J = 3.1$ Hz, 1H), 3.94 – 3.78 (m, 1H), 3.70 – 3.54 (m, 3H), 2.68 – 2.46 (m, 2H), 2.22 (s, 3H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 195.11, 142.14, 139.57, 138.17, 134.77, 133.65, 128.96, 128.33, 128.20, 127.45, 126.44, 80.27, 78.19, 77.55, 77.33, 77.13, 76.70, 66.98, 61.21, 41.93, 21.06; **IR** (neat): 3370, 2924, 2854, 1732, 1689, 1611, 1457, 1294, 1115, 759 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{18}\text{O}_3$ [$\text{M} + \text{Na}$] $^+$ calcd: 317.1148, found: 317.1152.



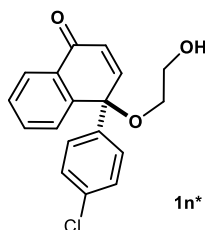
Yellow liquid; 46% yield; 99% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 93.20$ min, $t_{\text{minor}} = 97.73$ min); $[\alpha]_{\text{D}}^{26.2} = 93.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.17 (d, $J = 7.8, 1.0$ Hz, 1H), 7.53 (t, $J = 7.5, 1.4$ Hz, 1H), 7.42 (m, $J = 16.9, 11.7, 4.5$ Hz, 2H), 7.28 – 7.17 (d, 2H), 7.09 (d, $J = 8.1$ Hz, 2H), 6.88 (d, $J = 10.2$ Hz, 1H), 6.50 (d, $J = 10.2$ Hz, 1H), 3.78 (d, $J = 2.6$ Hz, 2H), 3.55 (m, $J = 9.6, 4.7$ Hz, 1H), 3.34 – 3.17 (m, 1H), 2.29 (s, 3H), 2.23 (s, 1H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 184.66, 151.22, 144.25, 138.88, 137.64, 133.51, 131.74, 129.23, 129.12, 128.37, 128.27, 126.46, 125.87, 77.48, 77.27,

77.05, 76.63, 65.71, 62.15, 21.02; **IR** (neat): 3449, 2927, 2855, 1668, 1601, 1457, 1380, 1297, 1068, 761 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 317.1148, found: 317.1152.



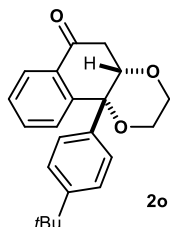
With 10 mol% catalyst at $-20\text{ }^\circ\text{C}$ for 3 h.

White solid, m.p. $53 - 54\text{ }^\circ\text{C}$; 52% yield; 89% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.66$ min, $t_{\text{minor}} = 7.76$ min); $[\alpha]_{\text{D}}^{28.4} = 75.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.15 – 7.95 (d, 1H), 7.67 – 7.55 (t, 1H), 7.43 (dd, $J = 7.5, 5.7$ Hz, 2H), 7.16 (d, $J = 8.7$ Hz, 2H), 7.05 (d, $J = 8.7$ Hz, 2H), 4.05 (t, $J = 3.1$ Hz, 1H), 3.86 (dt, $J = 12.1, 8.3$ Hz, 1H), 3.64 (t, $J = 9.0$ Hz, 3H), 2.57 (qd, $J = 20.0, 17.3, 3.1$ Hz, 2H); **^{13}C NMR** (75 MHz, CDCl_3): δ 193.54, 140.35, 139.99, 133.87, 133.19, 132.52, 127.95, 127.56, 127.35, 126.98, 125.53, 78.96, 76.80, 76.50, 76.27, 76.07, 75.65, 65.83, 60.10, 40.65; **IR** (neat): 3378, 2925, 2854, 1740, 1695, 1602, 1457, 1215, 1109, 759 cm^{-1} ; **HRMS** (ESI): $\text{C}_{18}\text{H}_{15}\text{ClO}_3$ $[\text{M} + \text{Na}]^+$ calcd: 337.0602, found: 337.0600.



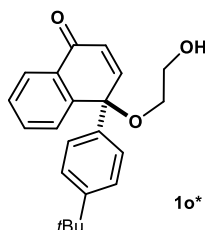
White solid, m.p. $59 - 60\text{ }^\circ\text{C}$; 46% yield; 99% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 11.44$ min, $t_{\text{minor}} = 12.42$ min); $[\alpha]_{\text{D}}^{25.8} = 61.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.08 (d, $J = 7.7$ Hz, 1H), 7.45 (t, $J = 7.3$ Hz, 1H), 7.36 (t, $J = 7.3$ Hz, 1H), 7.20 (dt, $J = 19.5, 8.3$ Hz, 5H), 6.77 (d, $J = 10.2$ Hz, 1H), 6.44 (d, $J = 10.2$ Hz, 1H), 3.69 (d, $J = 3.9$ Hz, 2H), 3.46 (dt, $J = 9.5, 4.7$ Hz, 1H), 3.25 – 3.07 (m, 1H), 2.38 (s, 1H); **^{13}C NMR** (75 MHz, CDCl_3): δ 183.37, 149.52, 142.62, 139.40, 132.66, 130.59, 128.55, 127.63, 127.18,

126.41, 125.57, 76.50, 76.07, 75.89, 75.65, 64.86, 60.99; **IR** (neat): 3458, 2924, 2853, 1742, 1668, 1601, 1457, 1215, 1083, 759 cm^{-1} ; **HRMS** (ESI): $\text{C}_{18}\text{H}_{15}\text{ClO}_3$ $[\text{M} + \text{Na}]^+$ calcd: 337.0602, found: 337.0608.



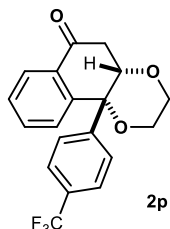
With 10 mol% catalyst at $-15\text{ }^\circ\text{C}$ for 6 h.

White solid, m.p. $68 - 69\text{ }^\circ\text{C}$; 45% yield; 92% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.02$ min, $t_{\text{minor}} = 6.16$ min); $[\alpha]_{\text{D}}^{27.7} = 72.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.15 (d, $J = 7.8$ Hz, 1H), 7.68 (t, $J = 10.9, 4.1$ Hz, 1H), 7.58 – 7.46 (m, 2H), 7.29 (t, $J = 7.8$ Hz, 2H), 7.10 (d, $J = 8.4$ Hz, 2H), 4.22 (t, $J = 3.0$ Hz, 1H), 3.98 (td, $J = 11.4, 4.7$ Hz, 1H), 3.85 – 3.64 (m, 3H), 2.78 – 2.56 (m, 2H), 1.27 (s, 9H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 195.12, 151.32, 142.11, 139.39, 134.70, 133.64, 128.29, 128.22, 127.19, 126.45, 125.20, 80.22, 78.18, 77.46, 77.03, 76.61, 67.01, 61.21, 42.00, 34.51, 31.24, 29.72; **IR** (neat): 3380, 2923, 1746, 1695, 1601, 1457, 1286, 1110, 815, 765 cm^{-1} ; **HRMS** (ESI): $\text{C}_{22}\text{H}_{24}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 359.1618, found: 359.1620.



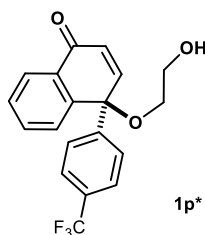
Green solid, m.p. $59 - 60\text{ }^\circ\text{C}$; 48% yield; 98% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 18.66$ min, $t_{\text{minor}} = 17.43$ min); $[\alpha]_{\text{D}}^{25.0} = 79.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.18 (d, $J = 7.8$ Hz, 1H), 7.54 (td, $J = 7.6, 1.3$ Hz, 1H), 7.43 (dd, $J = 17.7, 8.0$ Hz, 2H), 7.27 (q, $J = 8.7$ Hz, 4H), 6.90 (d, $J = 10.2$ Hz, 1H), 6.50 (d, $J = 10.2$ Hz, 1H), 3.78 (m, 2H), 3.56 (m, 1H), 3.27 (m, 1H), 2.12 (s, 1H), 1.27 (s, 9H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 184.66, 151.27, 150.85, 144.17, 138.77, 133.47, 131.82, 129.11, 128.39, 128.37, 126.48,

125.68, 125.49, 77.47, 77.32, 77.05, 76.63, 65.69, 62.19, 34.49, 31.26; **IR** (neat): 3455, 2928, 1726, 1668, 1601, 1456, 1380, 1300, 1084, 767 cm^{-1} ; **HRMS** (ESI): $\text{C}_{22}\text{H}_{24}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 359.1618, found: 359.1623.



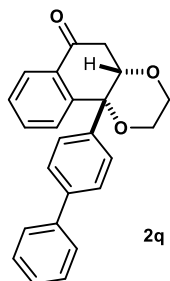
With 10 mol% catalyst at $-10\text{ }^\circ\text{C}$ for 2 h.

Yellow liquid; 49% yield; 89% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.45$ min, $t_{\text{minor}} = 7.03$ min); $[\alpha]_{\text{D}}^{24.5} = 64.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.10 (dd, $J = 7.8, 0.9$ Hz, 1H), 7.63 (td, $J = 7.6, 1.3$ Hz, 1H), 7.55 – 7.41 (m, 4H), 7.27 (d, $J = 8.3$ Hz, 2H), 4.08 (t, $J = 3.1$ Hz, 1H), 3.97 – 3.82 (m, 1H), 3.69 (t, $J = 9.0$ Hz, 3H), 2.82 – 2.42 (m, 2H); **^{13}C NMR** (75 MHz, CDCl_3): δ 193.42, 145.33, 140.13, 133.99, 132.59, 129.46 (q, $J_{\text{C-F}} = 32.25$), 127.75, 127.03, 126.97, 125.69, 124.62, 124.18 (q, $J_{\text{C-F}} = 3.75$), 123.27, 121.02, 78.83, 76.98, 76.44, 76.02, 75.60, 65.87, 60.08, 40.62; **IR** (neat): 3376, 2924, 1742, 1697, 1601, 1455, 1326, 1111, 839, 761 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{15}\text{F}_3\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 371.0866, found: 371.0869.



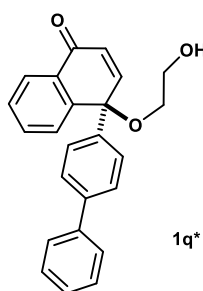
Yellow liquid; 45% yield; 99% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, $t_{\text{major}} = 21.38$ min, $t_{\text{minor}} = 19.53$ min); $[\alpha]_{\text{D}}^{27.9} = 27.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.20 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.66 – 7.43 (m, 6H), 7.33 (dd, $J = 7.7, 0.8$ Hz, 1H), 6.87 (d, $J = 10.2$ Hz, 1H), 6.58 (d, $J = 10.2$ Hz, 1H), 3.82 (s, 2H), 3.59 (m, 1H), 3.38 – 3.20 (m, 1H), 2.36 (s, 1H); **^{13}C NMR** (75 MHz, CDCl_3): δ 184.23, 149.92, 145.87, 143.30, 133.81, 131.68, 130.23, 130.08, 129.80, 128.85, 128.21, 126.74, 126.43, 126.36, 125.70, 125.53 (q, $J_{\text{C-}}$

$F = 3.75$), 124.63 (t, $J_{C-F} = 4.88$), 77.47, 77.25, 77.04, 76.62, 65.90, 62.08; **IR** (neat): 3372, 2924, 1733, 1698, 1601, 1454, 1326, 1169, 839, 765 cm^{-1} ; **HRMS** (ESI): $\text{C}_{19}\text{H}_{15}\text{F}_3\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 371.0866, found: 371.0884.



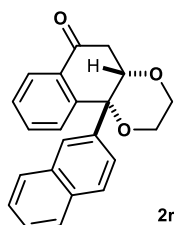
With 10 mol% catalyst at $-10\text{ }^\circ\text{C}$ for 12 h.

White solid, m.p. $208 - 209\text{ }^\circ\text{C}$; 50% yield; 92% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 6.98$ min, $t_{\text{minor}} = 8.70$ min); $[\alpha]_{\text{D}}^{28.5} = 82.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.18 (d, $J = 7.4$ Hz, 1H), 7.71 (t, $J = 7.0$ Hz, 1H), 7.64 – 7.49 (m, 6H), 7.41 (t, $J = 16.5, 8.8$ Hz, 2H), 7.33(d, 1H), 7.27 (d, $J = 7.5$ Hz, 2H), 4.25 (t, $J = 3.0$ Hz, 1H), 4.08 – 3.94 (m, 1H), 3.89 – 3.71 (m, 3H), 2.87 – 2.58 (m, 2H); **^{13}C NMR** (75 MHz, CDCl_3): δ 195.01, 141.90, 141.43, 141.25, 140.36, 134.87, 133.68, 128.84, 128.48, 128.20, 127.99, 127.57, 127.12, 127.00, 126.57, 80.20, 78.23, 77.47, 77.05, 76.63, 67.00, 61.23, 41.95; **IR** (neat): 3367, 2923, 1692, 1601, 1453, 1351, 1288, 1111, 1018, 762 cm^{-1} ; **HRMS** (ESI): $\text{C}_{24}\text{H}_{20}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 379.1305, found: 379.1307.



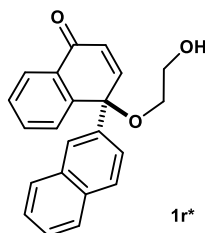
White solid, m.p. $64 - 65\text{ }^\circ\text{C}$; 46% yield; 99% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 17.33$ min, $t_{\text{minor}} = 22.58$ min); $[\alpha]_{\text{D}}^{26.2} = 85.0$ ($c = 1.0$ in CHCl_3); **^1H NMR** (300 MHz, CDCl_3): δ 8.20 (d, $J = 7.8$ Hz, 1H), 7.69 – 7.30 (m, 12H), 6.92 (d, $J = 10.2$ Hz, 1H), 6.55 (d, $J = 10.2$ Hz, 1H), 3.81 (t, $J = 4.4$ Hz, 2H), 3.59 (m, 1H), 3.40 – 3.12 (m, 1H), 2.11 (s, 1H); **^{13}C**

NMR (75 MHz, CDCl₃): δ 184.60, 150.91, 144.02, 140.79, 140.78, 140.37, 133.64, 131.80, 129.44, 128.82, 128.56, 128.36, 127.52, 127.30, 127.08, 126.59, 126.45, 77.49, 77.31, 77.07, 76.64, 65.80, 62.20; **IR** (neat): 3458, 2925, 1725, 1601, 1455, 1381, 1298, 1076, 761, 701 cm⁻¹; **HRMS** (ESI): C₂₄H₂₀O₃ [M + Na]⁺ calcd: 379.1305, found: 379.1322.



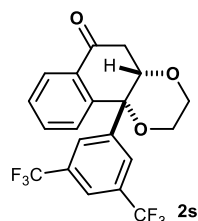
With 10 mol% catalyst at -20 °C for 5 h.

White solid, m.p. 114 – 115 °C; 47% yield; 91% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, t_{major} = 6.39 min, t_{minor} = 8.47 min); $[\alpha]_{\text{D}}^{27.4}$ = 90.0 (c = 1.0 in CHCl₃); **¹H NMR** (300 MHz, CDCl₃): δ 8.22 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 8.7 Hz, 2H), 7.75 – 7.64 (m, 2H), 7.64 – 7.55 (m, 2H), 7.55 – 7.42 (m, 4H), 4.32 (t, J = 3.0 Hz, 1H), 4.13 – 3.96 (m, 1H), 3.86 – 3.69 (m, 3H), 2.84 – 2.56 (m, 2H); **¹³C NMR** (75 MHz, CDCl₃): δ 195.11, 141.94, 139.87, 134.92, 133.76, 133.02, 132.72, 128.55, 128.37, 128.31, 128.11, 127.51, 127.25, 126.62, 126.58, 126.38, 124.92, 80.03, 78.49, 77.48, 77.06, 76.64, 67.02, 61.28, 41.93; **IR** (neat): 3367, 2924, 2855, 1691, 1601, 1454, 1287, 1112, 759, 665 cm⁻¹; **HRMS** (ESI): C₂₂H₁₈O₃ [M + Na]⁺ calcd: 353.1148, found: 353.1152.



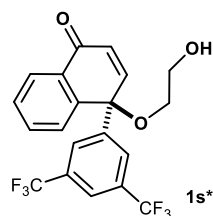
White solid, m.p. 65 – 66 °C; 51% yield; 88% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, t_{major} = 11.67 min, t_{minor} = 12.56 min); $[\alpha]_{\text{D}}^{25.2}$ = 64.0 (c = 1.0 in CHCl₃); **¹H NMR** (300 MHz, CDCl₃): δ 8.22 (d, J = 7.6, 1.3 Hz, 1H), 8.02 (s, 1H), 7.88 – 7.72 (m, 2H), 7.70 (d, J = 8.7 Hz, 1H), 7.55 – 7.41 (m, 4H), 7.38 (dd, J = 7.6, 1.1 Hz, 1H), 7.22 (dd, J = 8.7, 1.8 Hz, 1H), 6.93 (d, J =

10.2 Hz, 1H), 6.58 (d, $J = 10.2$ Hz, 1H), 3.84 (t, $J = 4.6$ Hz, 2H), 3.62 (dt, $J = 9.6, 4.7$ Hz, 1H), 3.42 – 3.24 (m, 1H), 2.28 (s, 1H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 184.69, 150.80, 144.05, 138.93, 133.65, 133.20, 132.70, 132.72, 131.82, 129.68, 128.57, 128.46, 128.33, 128.23, 127.62, 126.59, 126.45, 124.69, 123.96, 77.51, 77.46, 77.09, 76.66, 65.90, 62.21; **IR** (neat): 3444, 2925, 2856, 1667, 1600, 1456, 1300, 1067, 763, 539 cm^{-1} ; **HRMS** (ESI): $\text{C}_{22}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 353.1148, found: 353.1154.



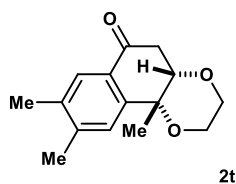
With 10 mol% catalyst at -10 °C for 2 h.

White solid, m.p. $84 - 85$ °C; 51% yield; 89% ee determined by HPLC on Chiralpak IA-H column (n -hexane/ i -PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 4.64$ min, $t_{\text{minor}} = 5.80$ min); $[\alpha]_{\text{D}}^{26.6} = 37.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.13 (d, $J = 7.8$ Hz, 1H), 7.76 (s, 1H), 7.66 (t, $J = 7.6, 1.2$ Hz, 1H), 7.59 (s, 2H), 7.51 (t, $J = 10.9, 4.2$ Hz, 1H), 7.42 (d, $J = 7.8$ Hz, 1H), 4.06 (t, $J = 3.0$ Hz, 1H), 3.94 (td, $J = 11.1, 4.2$ Hz, 1H), 3.78 – 3.60 (m, 3H), 2.72 (dd, $J = 17.3, 3.6$ Hz, 1H), 2.48 (dd, $J = 17.3, 2.6$ Hz, 1H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 193.89, 145.40, 140.11, 135.36, 133.57, 131.74 (q, $J_{\text{C-F}} = 33.25$), 129.34, 128.48, 127.88, 127.80, 127.76, 127.05, 124.87, 122.47 (t, $J_{\text{C-F}} = 3.75$), 121.25, 79.69, 77.70, 77.47, 77.25, 77.04, 76.62, 66.83, 61.14, 41.48; **IR** (neat): 3367, 2925, 2854, 1742, 1693, 1601, 1454, 1287, 1113, 760 cm^{-1} ; **HRMS** (ESI): $\text{C}_{20}\text{H}_{14}\text{F}_6\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 439.0739, found: 439.0753.



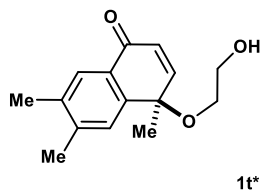
Green solid, m.p. $105 - 106$ °C; 48% yield; 99% ee determined by HPLC on Chiralpak OD-H column (n -hexane/ i -PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 6.42$ min, $t_{\text{minor}} = 5.61$ min); $[\alpha]_{\text{D}}^{26.9} = 6.0$ ($c = 1.0$ in CHCl_3); $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.23 (d,

$J = 7.7, 1.2$ Hz, 1H), 7.80 (d, $J = 5.2$ Hz, 3H), 7.64 – 7.50 (m, 2H), 7.34 – 7.27 (s, 1H), 6.84 (d, $J = 10.2$ Hz, 1H), 6.65 (d, $J = 10.2$ Hz, 1H), 3.83 (t, $J = 4.5$ Hz, 2H), 3.60 (dt, $J = 9.6, 4.7$ Hz, 1H), 3.43 – 3.20 (m, 1H), 2.02 (s, $J = 18.3$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 183.86, 148.88, 145.03, 142.33, 134.13, 132.22(t, $J_{\text{C-F}} = 33.38$), 131.64, 131.33, 130.85, 129.33, 128.50, 128.17, 127.07, 126.30(d, $J_{\text{C-F}} = 2.25$), 124.89, 122.02(q, $J_{\text{C-F}} = 3.75$), 121.27, 77.49, 77.07, 76.64, 66.17, 61.91; **IR** (neat): 3445, 2924, 2855, 1667, 1600, 1456, 1299, 1090, 763, 538 cm^{-1} ; **HRMS** (ESI): $\text{C}_{20}\text{H}_{14}\text{F}_6\text{O}_3$ [$\text{M} + \text{Na}$] $^+$ calcd: 439.0739, found: 439.0744.



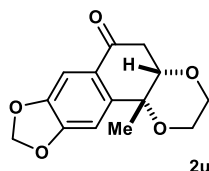
With 10 mol% catalyst at -10 °C for 10 h.

Purple liquid; 53% yield; 87% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.55$ min, $t_{\text{minor}} = 7.86$ min); $[\alpha]_{\text{D}}^{27.6} = 2.9$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.80 (s, 1H), 7.36 (s, 1H), 4.02 (t, $J = 3.1$ Hz, 1H), 3.77 (td, $J = 11.5, 3.2$ Hz, 1H), 3.70 – 3.46 (m, 3H), 3.03 – 2.71 (m, 2H), 2.36 (s, 3H), 2.31 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.49, 144.51, 141.98, 136.51, 129.77, 127.65, 127.07, 79.36, 77.47, 77.04, 76.62, 72.91, 66.79, 61.38, 42.62, 28.33, 20.48, 19.39; **IR** (neat): 3326, 2916, 2860, 1677, 1450, 1381, 1271, 1122, 1022, 757 cm^{-1} ; **HRMS** (ESI): $\text{C}_{15}\text{H}_{18}\text{O}_3$ [$\text{M} + \text{Na}$] $^+$ calcd: 269.1148, found: 269.1150.



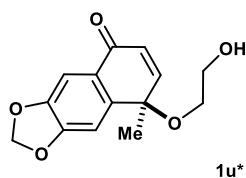
Purple solid, m.p. $135 - 136$ °C; 47% yield; 95% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 7.67$ min, $t_{\text{minor}} = 6.85$ min); $[\alpha]_{\text{D}}^{28.0} = -79.0$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.88 (s, 1H), 7.39 (s, 1H), 6.90 (d, $J = 10.3$ Hz, 1H), 6.45 (d, $J = 10.3$ Hz, 1H), 3.81 – 3.54 (t, 2H), 3.29 (m, $J = 9.8, 4.7$ Hz, 1H), 3.19 – 3.05 (m, 1H), 2.37 (s, 3H), 2.33 (s, 3H),

2.28 (s, 1H), 1.61 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 184.41, 152.06, 143.22, 142.36, 137.11, 130.26, 129.13, 127.42, 127.10, 77.51, 77.09, 76.66, 73.37, 66.06, 62.12, 30.34, 20.42, 19.49; IR (neat): 3459, 2924, 2854, 1733, 1670, 1601, 1457, 1299, 1085, 765 cm^{-1} ; HRMS (ESI): $\text{C}_{15}\text{H}_{18}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 269.1148, found: 269.1154.

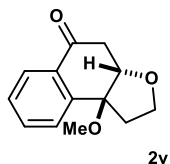


With 10 mol% catalyst at room temperature for 0.5 h.

Yellow solid, m.p. 119 – 120 $^{\circ}\text{C}$; 52% yield; 86.5% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 7.97$ min, $t_{\text{minor}} = 13.35$ min); $[\alpha]_{\text{D}}^{28.4} = 54.0$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.45 (s, 1H), 7.03 (s, 1H), 6.05 (dd, $J = 4.0, 1.1$ Hz, 2H), 4.00 (t, $J = 3.1$ Hz, 1H), 3.77 (td, $J = 11.3, 3.5$ Hz, 1H), 3.69 – 3.50 (m, 3H), 2.96 – 2.75 (m, 2H), 1.49 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 192.58, 153.25, 147.70, 141.60, 126.98, 106.02, 105.53, 101.84, 79.01, 77.49, 77.07, 76.64, 73.13, 66.66, 61.40, 42.24, 28.21; IR (neat): 3405, 2924, 2854, 1733, 1678, 1617, 1478, 1288, 1119, 760 cm^{-1} ; HRMS (ESI): $\text{C}_{14}\text{H}_{14}\text{O}_5$ $[\text{M} + \text{Na}]^+$ calcd: 285.0733, found: 285.0747.

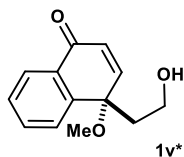


Pink solid, m.p. 134 – 135 $^{\circ}\text{C}$; 48% yield; 93% ee determined by HPLC on Chiralpak OD-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, $t_{\text{major}} = 12.58$ min, $t_{\text{minor}} = 11.06$ min); $[\alpha]_{\text{D}}^{25.6} = -73.0$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.51 (s, 1H), 7.08 (s, 1H), 6.92 (d, $J = 10.2$ Hz, 1H), 6.44 (d, $J = 10.2$ Hz, 1H), 6.07 (s, 2H), 3.69 (d, $J = 3.6$ Hz, 2H), 3.32 (dt, $J = 9.7, 4.7$ Hz, 1H), 3.21 – 3.07 (m, 1H), 2.62 (s, 1H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 182.97, 152.39, 151.81, 148.06, 141.97, 129.83, 126.49, 105.61, 105.56, 101.89, 77.56, 77.14, 76.71, 73.82, 66.23, 61.98, 30.38; IR (neat): 3455, 2926, 1726, 1669, 1600, 1456, 1326, 1127, 1069, 763 cm^{-1} ; HRMS (ESI): $\text{C}_{14}\text{H}_{14}\text{O}_5$ $[\text{M} + \text{Na}]^+$ calcd: 285.0733, found: 285.0739.

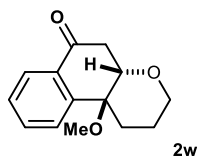


With 10 mol% catalyst at room temperature for 2 h.

Yellow oil liquid; 50% yield; 75% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 4/6, flow rate = 1.0 mL/min, $t_{\text{major}} = 6.88$ min, $t_{\text{minor}} = 7.39$ min); $[\alpha]_{\text{D}}^{26.3} = 47.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 7.88 (d, $J = 7.6$ Hz, 1H), 7.69 – 7.52 (m, 2H), 7.43 – 7.33 (m, 1H), 4.55 (m, 1H), 4.02 (dd, $J = 16.0, 8.2$ Hz, 1H), 3.89 (td, $J = 8.4, 4.3$ Hz, 1H), 3.03 (s, 3H), 2.97 – 2.84 (dd, 1H), 2.74 (dd, $J = 16.1, 7.9$ Hz, 1H), 2.42 (m, 1H), 2.33 – 2.17 (m, 1H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 195.74, 141.54, 134.60, 132.55, 128.34, 127.88, 126.41, 83.70, 77.52, 77.25, 77.10, 76.67, 66.60, 51.94, 43.69, 41.31; **IR** (neat): 3369, 2931, 1695, 1600, 1453, 1293, 1077, 768, 609, 568 cm^{-1} ; **HRMS** (ESI): $\text{C}_{13}\text{H}_{14}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 241.0835, found: 241.0843.



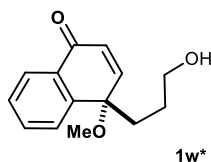
Purple oil liquid; 48% yield; 91% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 7/3, flow rate = 1.0 mL/min, $t_{\text{major}} = 11.70$ min, $t_{\text{minor}} = 14.85$ min); $[\alpha]_{\text{D}}^{26.3} = 50.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.14 (d, $J = 7.9$ Hz, 1H), 7.75 – 7.64 (m, 2H), 7.48 (m, 1H), 7.11 (d, $J = 10.4$ Hz, 1H), 6.57 (d, $J = 10.4$ Hz, 1H), 3.79 – 3.65 (m, 1H), 3.58 (m, 1H), 3.05 (s, 3H), 2.59 (s, 1H), 2.29 (m, 1H), 2.13 – 2.04 (m, 1H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 184.07, 151.07, 143.48, 133.34, 131.65, 131.37, 128.43, 126.91, 126.31, 77.50, 77.27, 77.07, 76.87, 76.65, 58.95, 52.54, 45.77; **IR** (neat): 3444, 2931, 1667, 1660, 1456, 1381, 1300, 1084, 843, 766 cm^{-1} ; **HRMS** (ESI): $\text{C}_{13}\text{H}_{14}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 241.0835, found: 241.0842.



With 10 mol% catalyst at room temperature for 24 h.

White solid, m.p. 64 – 66 °C; 47% yield; 92% ee determined by HPLC on Chiralpak IA-

H column (*n*-hexane/*i*-PrOH = 6/4, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.24$ min, $t_{\text{minor}} = 6.31$ min); $[\alpha]_{\text{D}}^{26.3} = 6.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.15 (d, $J = 8.0$, 1.3 Hz, 1H), 7.68 – 7.58 (m, 1H), 7.47 (m, 2H), 4.01 (t, $J = 3.6$ Hz, 1H), 3.84 (ddd, $J = 6.7$, 3.8, 2.5 Hz, 1H), 3.54 (td, $J = 11.5$, 2.7 Hz, 1H), 3.29 (dd, $J = 17.4$, 3.6 Hz, 1H), 3.10 (s, 3H), 2.90 (dd, $J = 13.6$, 4.2 Hz, 1H), 2.77 (dd, $J = 17.4$, 3.6 Hz, 1H), 1.83 – 1.62 (m, 2H), 1.51 (m, 1H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): δ 196.14, 138.81, 133.14, 132.76, 128.59, 128.00, 127.44, 79.37, 77.46, 77.04, 76.62, 72.58, 67.64, 49.58, 40.23, 30.04, 23.33; **IR** (neat): 3362, 2952, 1693, 1599, 1453, 1364, 1282, 1084, 943, 767 cm^{-1} ; **HRMS** (ESI): $\text{C}_{14}\text{H}_{16}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 255.0992, found: 255.1000.



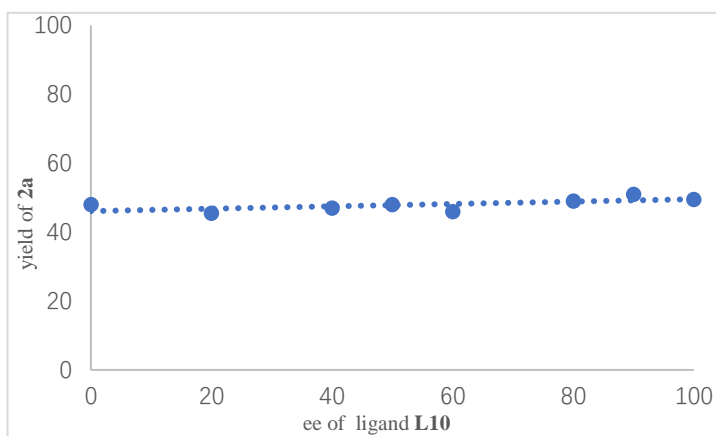
Purple oil liquid; 49% yield; 91% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 7/3, flow rate = 1.0 mL/min, $t_{\text{major}} = 10.99$ min, $t_{\text{minor}} = 14.49$ min); $[\alpha]_{\text{D}}^{26.3} = 28.0$ ($c = 1.0$ in CHCl_3); **$^1\text{H NMR}$** (300 MHz, CDCl_3): δ 8.13 (d, $J = 7.7$ Hz, 1H), 7.71 – 7.59 (m, 2H), 7.52 – 7.42 (m, 1H), 6.92 (d, $J = 10.4$ Hz, 1H), 6.59 (d, $J = 10.4$ Hz, 1H), 3.51 (t, $J = 6.3$ Hz, 2H), 3.05 (s, 3H), 2.11 – 1.95 (m, 2H), 1.69 (s, 1H), 1.54 – 1.37 (m, 1H), 1.19 – 1.00 (m, 1H); **$^{13}\text{C NMR}$** (75 MHz, CDCl_3): $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 184.39, 151.53, 143.65, 133.31, 132.26, 131.89, 128.22, 126.75, 126.04, 77.46, 77.24, 77.04, 76.61, 62.44, 52.63, 39.63, 27.09; **IR** (neat): 3424, 2929, 1667, 1600, 1456, 1379, 1299, 1086, 842, 767 cm^{-1} ; **HRMS** (ESI): $\text{C}_{14}\text{H}_{16}\text{O}_3$ $[\text{M} + \text{Na}]^+$ calcd: 255.0992, found: 255.1002.

Nonlinear effects studies

Methods: To a stirred solution of **L10** (11.36 mg, 0.02 mmol) with different *ee* value from different ratio of (*R*)-**L10** and (*S*)-**L10** in toluene (0.5 mL), was added Et_2Zn (20 μL , 1.0 M in toluene, 0.02 mmol) under an argon atmosphere. The mixture was then stirred at room temperature for 30 min to generate the catalyst. **1a** (0.2 mmol) in toluene (0.5 mL) was quickly added to the flask containing the in situ generated zinc catalyst.

After the addition, the reaction was stirred at $-20\text{ }^{\circ}\text{C}$ for 2 hours. The reaction was quenched with saturated NH_4Cl and extracted with CH_2Cl_2 . The organic layer was dried over Na_2SO_4 and concentrated under vacuum. Then the residue was purified by column chromatography to afford the resolution product **1a*** and **2a**. The ee value determination was carried out using chiral HPLC on Waters with a 2996UV-detector.

ee (L10)	yield (2a)
0	48
20	45.5
40	47
50	48
60	46
80	49
90	51
100	49.5



ee (L10)	ee (2a)
0	0
20	17.5
40	39
50	48.9
60	61.5
80	80.8
90	91.5
100	95

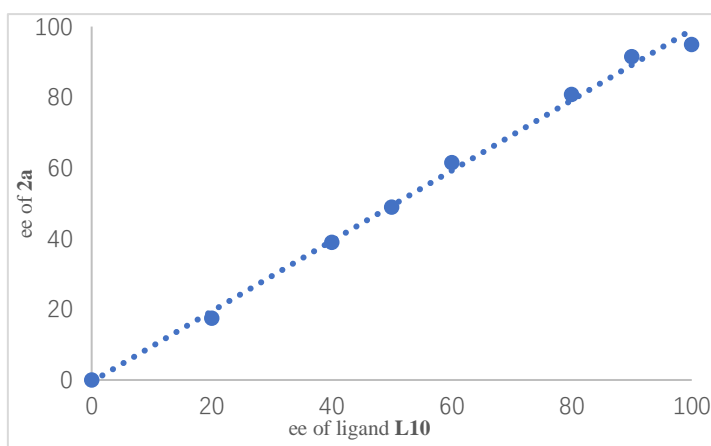


Figure S1. Nonlinear effects studies of the kinetic resolution reaction

Control experiments

i) Methods: To a stirred solution of **L11** (4.66 mg, 0.01 mmol) in toluene (0.5 mL) was added Et_2Zn (10 μL , 1.0 M in toluene, 0.01 mmol) under an argon atmosphere, the mixture was then stirred at room temperature for 30 min to generate the catalyst. **1a**

(0.1 mmol) in toluene (0.5 mL) was quickly added to the flask containing the in situ generated catalyst. After the addition, the reaction was stirred at -20 °C for each identified time. The reaction was quenched with saturated NH₄Cl and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄ and concentrated under vacuum for ¹H NMR studies to confirm the conversions.

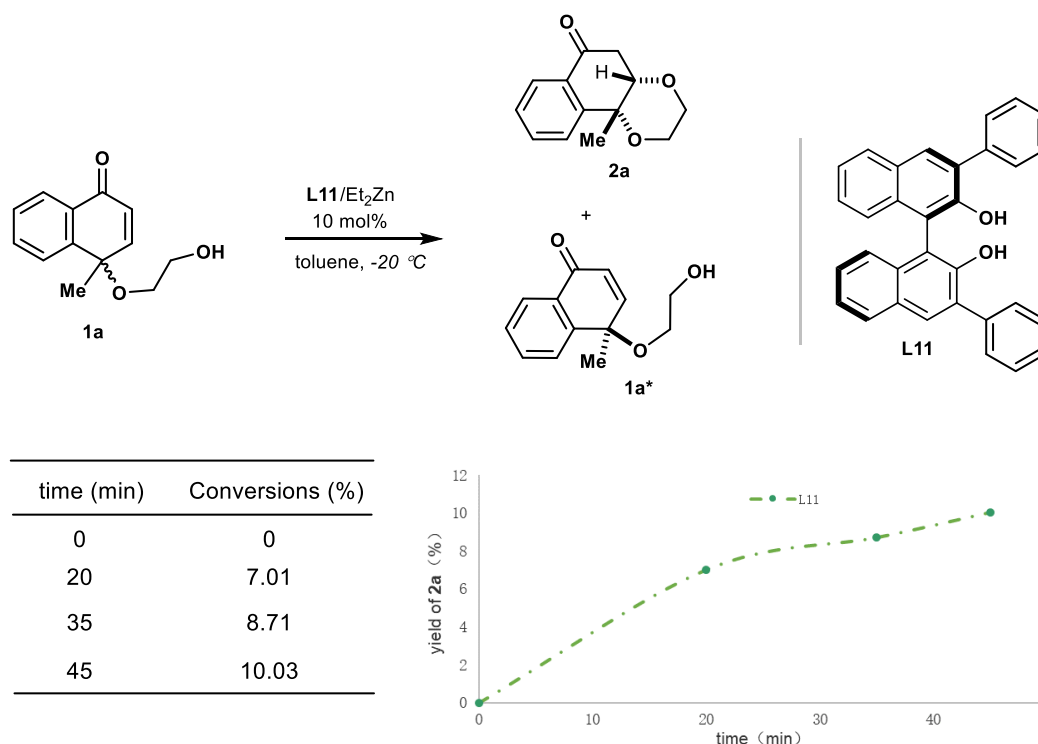


Figure S2. Control experiment using **L11** as catalyst

Methods: To a stirred solution of **L10** (5.68 mg, 0.01 mmol) in toluene (0.5 mL) was added Et₂Zn (10 μL, 1.0 M in toluene, 0.01 mmol) under an argon atmosphere, the mixture was then stirred at room temperature for 30 min to generate the catalyst. **1a** (0.1 mmol) in toluene (0.5 mL) was quickly added to the flask containing the in situ generated catalyst. After the addition, the reaction was stirred at -20 °C for each identified time. The mixture was quenched with saturated NH₄Cl and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄ and concentrated under vacuum for ¹H NMR studies to confirm the conversions.

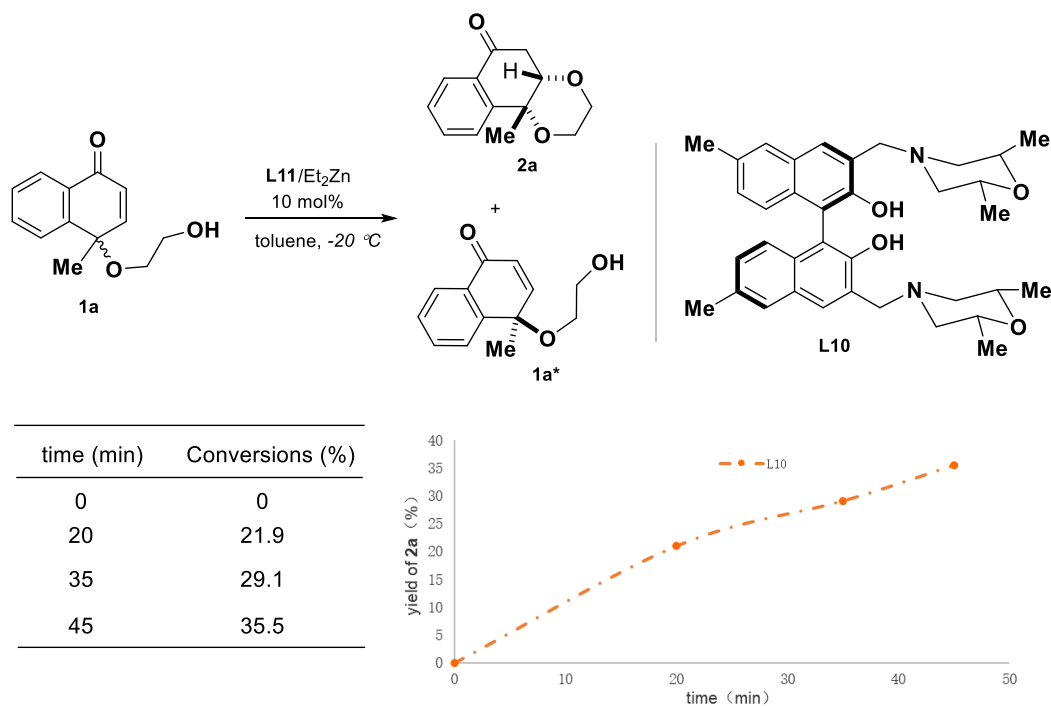
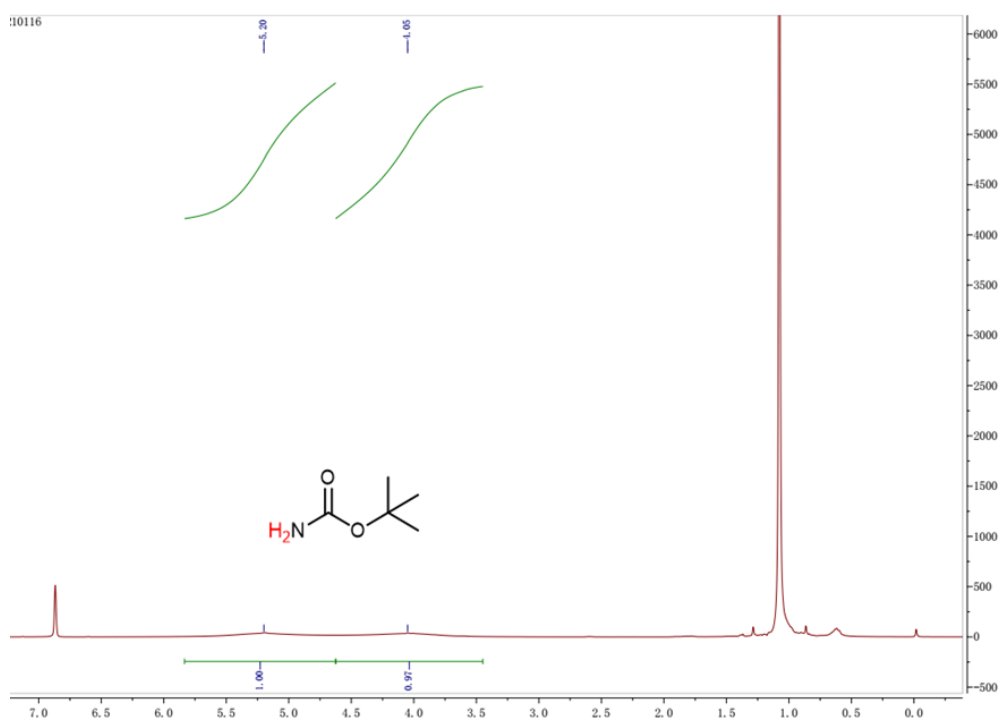


Figure S3. Control experiment using **L10** as catalyst

NMR investigation of the additive's effects

As the introduction of Boc-NH₂ into the KR reaction could slightly improve the enantioselectivities of products, control experiment of NMR analysis was carried out to study the role of this additive. In the dried flask, chiral ligand **L10** (10 mol%, 0.1 mmol) in deuterated benzene (0.5 mL) was added Et₂Zn (100 μL, 1.0 M in toluene, 0.1 mmol) under an argon atmosphere, respectively. The mixtures were stirred at room temperature for 30 min. Then was added 0.4 mmol Boc-NH₂ before the NMR analysis. As show in Figure S4, the introduction of the Boc-NH₂ additive to the **L10**-Zn complex results in an obvious shift of the ¹H NMR peaks. It was observed that the ¹H NMR signals of the amide hydrogens in Boc-NH₂ became to two distinct peaks after introduction to the zinc catalyst, we proposed that Boc-NH₂ might play a stabilizing effect to the catalyst via hydrogen bonding with the amine group in the chiral ligand, as well as the coordination of amide group to the zinc centre (Figure S4), thus made the amide bond fixed to show distinct ¹H NMR signals.

a) ^1H NMR of Boc-NH $_2$



b) ^1H NMR of (L10 + Et $_2$ Zn + Boc-NH $_2$)

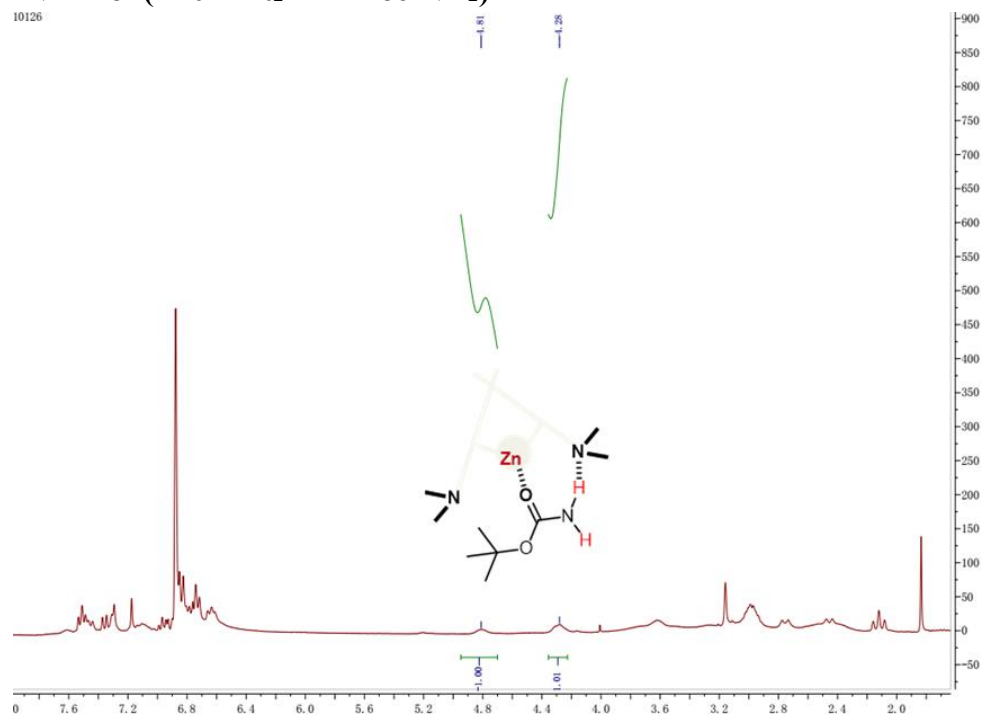
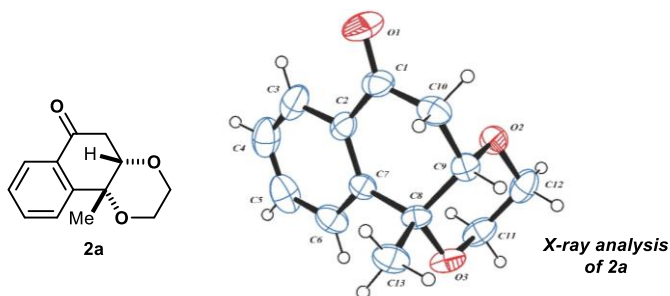


Figure S4. NMR experiment of additive influence

X-Ray Analysis of Product 2a



Bond precision:	C-C = 0.0035 Å	Wavelength=1.54184	
Cell:	a=8.20676(18)	b=11.3756(2)	c=12.0915(3)
	alpha=90	beta=90	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	1128.82(4)	1128.82(4)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C13 H14 O3	C13 H14 O3	
Sum formula	C13 H14 O3	C13 H14 O3	
Mr	218.24	218.24	
Dx,g cm-3	1.284	1.284	
Z	4	4	
Mu (mm-1)	0.741	0.741	
F000	464.0	464.0	
F000'	465.48		
h,k,lmax	9,13,14	9,13,14	
Nref	2134[1248]	2111	
Tmin,Tmax	0.882,0.901	0.015,1.000	
Tmin'	0.882		

Correction method= # Reported T Limits: Tmin=0.015 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.69/0.99

Theta(max)= 69.839

R(reflections)= 0.0425(1997)

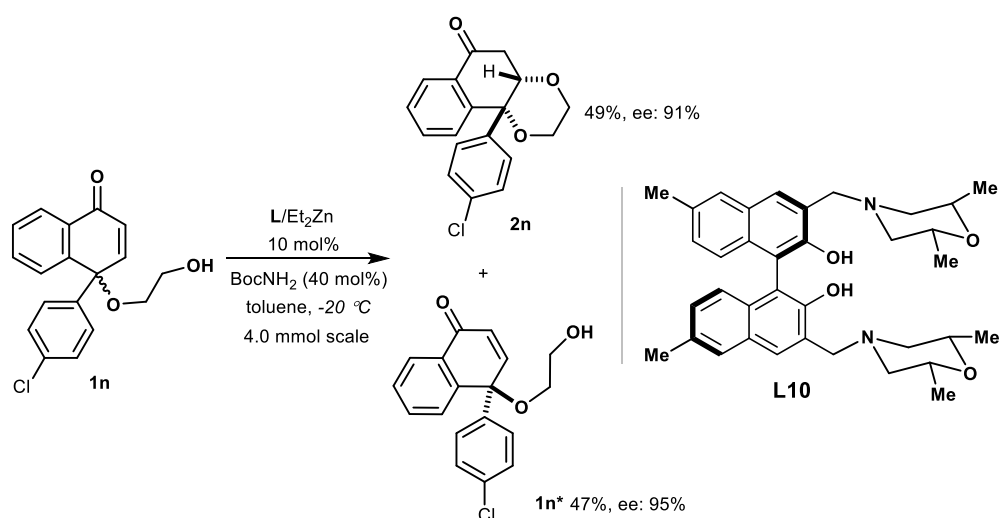
wR2(reflections)= 0.1081(2111)

S = 1.112

Npar= 146

Gram Scale Trial of the Oxa-Michael KR Reaction and Transformation of the Resolution Products

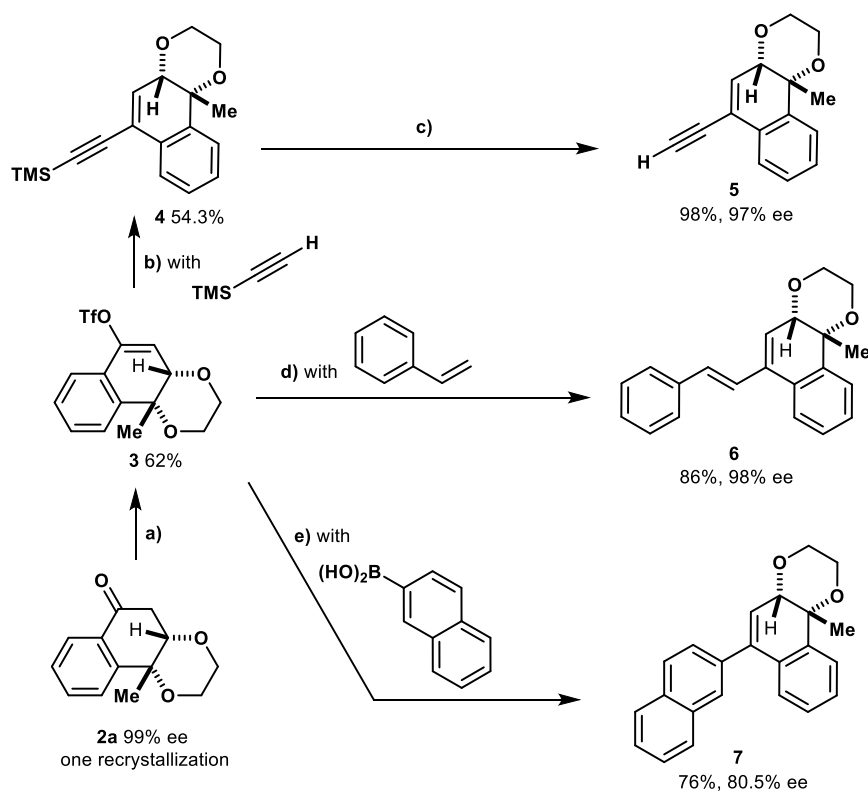
I) Gram scale experiments of the KR process



To a stirred solution of **L10** (227.33 mg, 0.40 mmol) in toluene (10.0 mL) was added Et_2Zn (400 μL , 1.0 M in toluene, 0.40 mmol) under an argon atmosphere, the mixture was then stirred at room temperature for 30 min to generate the catalyst. **1n** (4.0 mmol) and BocNH_2 (187.20 mg, 40 mol%) in toluene (10.0 mL) was quickly added to the flask containing the in situ generated zinc catalyst. After the addition, the reaction was stirred at -20°C for about 2 h. The reaction was quenched with saturated NH_4Cl and extracted with DCM. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. Then the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1 - 4:1) to afford the product **1n*** (0.59 g, 47% yield) and **2n** (0.62 g, 49% yield).

II) Transformation of the Resolution Products

(a) The separated product **2a** through recrystallization (1.0 equiv) was dissolved in THF, then LiHMDS (1.2 equiv) was added under an argon atmosphere at -40 °C. The mixture was stirred for further 0.5 hours, followed by cooling to -70 °C and bistrifluoromethylsulfonylaminochloropyridine (1.1 equiv) was added. The reaction was slowly warmed to room temperature and stirred for further 12 hours. After completed, the mixture was quenched with saturated NH₄Cl solution and extracted with EA. The organic layer was dried over Na₂SO₄ and concentrated under vacuum. Then the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the product **3** (62% yield).



(b) Compound **3** (119mg, 0.34 mmol), Pd(PPh₃)₄ (2.5 mol%), Et₃N (2.0 equiv) and CuI (2.5 mol%) was stirred in DMF, then trimethylsilylacetylene (5.0 equiv) was added under an argon atmosphere at rt. After completed, the mixture was quenched with H₂O, extracted with EA, dried with Na₂SO₄, then purified via flash column chromatography (petroleum ether/ethyl acetate = 20:1) to give the product **4** (55 mg, 54.3 % yield).

¹H NMR (300 MHz, CDCl₃): δ 7.68 (dd, J = 7.4, 1.4 Hz, 1H), 7.53 (dd, J = 7.4, 1.4 Hz,

1H), 7.42 – 7.28 (m, 2H), 6.43 (d, J = 6.4 Hz, 1H), 3.90 (d, J = 6.4 Hz, 1H), 3.75 (m, 2H), 3.66 – 3.48 (m, 2H), 1.30 (s, 3H), 0.26 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): δ 138.48, 130.94, 130.19, 129.44, 127.54, 127.04, 125.21, 124.47, 101.81, 98.81, 77.58, 77.36, 77.16, 76.73, 74.45, 66.36, 61.68, 27.31, 0.00.

(c) A solution of K₂CO₃ (11 mg, 40 mmol%) in 5 ml MeOH was added the compound **4** (55 mg, 0.19 mmol), the mixture was stirred at room temperature. After completed, the mixture was quenched with H₂O and concentrated under vacuum, extracted with EA, dried with Na₂SO₄, then purified via flash column chromatography to obtain the product **5** (40 mg, 98 % yield).

Yellow solid, m.p. 84 – 86°C; 97% ee determined by HPLC on Chiralpak IC-H column (*n*-hexane/*i*-PrOH = 9/1, flow rate = 1.0 mL/min, *t*_{major} = 6.841 min, *t*_{minor} = 7.287 min); [α]_D^{26.3} = 305.0 (c = 1.0 in CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.70 (dd, J = 7.5, 1.3 Hz, 1H), 7.54 (dd, J = 7.5, 1.2 Hz, 1H), 7.35 (m, J = 19.8, 7.4, 1.4 Hz, 2H), 6.48 (d, J = 6.4 Hz, 1H), 3.92 (d, J = 6.4 Hz, 1H), 3.72 (m, J = 23.5, 14.9, 11.7, 9.4 Hz, 4H), 3.21 (s, 1H), 1.31 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 138.38, 130.96, 130.69, 129.51, 127.52, 126.89, 124.46, 124.40, 81.05, 80.46, 77.51, 77.09, 76.67, 74.38, 74.25, 66.30, 61.60, 27.23; IR (neat): 3454, 3295, 2960, 2925, 2862, 1617, 1448, 1246, 1100, 756 cm⁻¹; HRMS (ESI): C₁₅H₁₄O₂ [M + Na]⁺ calcd: 249.0886, found: 249.0900.

(d) Compound **3** (0.43 mmol), Pd(OAc)₂ (10 mol%), Et₃N (5.0 equiv) and PPh₃ (20 mol%) was stirred in THF/CH₃CN (3/1), then styrene (2.0 equiv) was added under an argon atmosphere at room temperature. After completed, the mixture was quenched with H₂O, extracted with EA, dried with Na₂SO₄, then purified via flash column chromatography (petroleum ether/ethyl acetate = 10:1) to give the product **6** (112.5 mg, 86% yield).

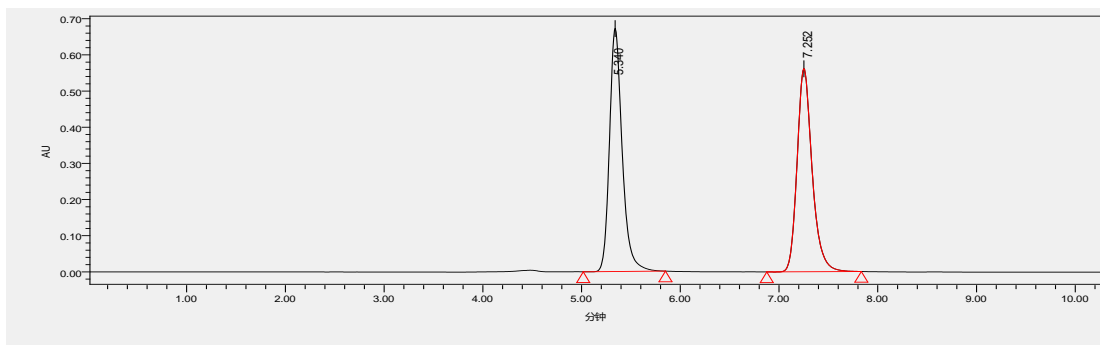
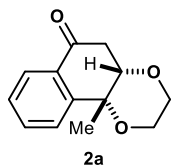
Yellow oil liquid, 98% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 8/2, flow rate = 1.0 mL/min, *t*_{major} = 8.163 min, *t*_{minor} = 9.086 min); [α]_D^{26.3} = 67.0 (c = 1.0 in CHCl₃); ¹H NMR (300 MHz, CDCl₃): δ 7.59 (dd, J = 7.5, 1.0 Hz, 1H), 7.47 (d, J = 7.7 Hz, 3H), 7.30 (m, J = 19.7, 14.3, 6.7 Hz, 5H), 7.10 – 6.89 (m, 2H), 6.27

(d, $J = 6.6$ Hz, 1H), 3.96 (d, $J = 6.6$ Hz, 1H), 3.87 – 3.54 (m, 4H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 139.28, 139.12, 137.03, 132.76, 132.71, 129.53, 128.98, 128.76, 128.08, 127.37, 126.78, 125.87, 125.74, 124.92, 123.73, 120.45, 77.55, 77.32, 77.12, 76.70, 75.01, 74.92, 66.44, 61.58, 27.15; IR (neat): 3424, 2958, 2925, 2859, 1448, 1213, 1105, 752, 693, 633 cm^{-1} ; HRMS (ESI): $\text{C}_{21}\text{H}_{20}\text{O}_2$ $[\text{M} + \text{Na}]^+$ calcd: 327.1356, found: 327.1368.

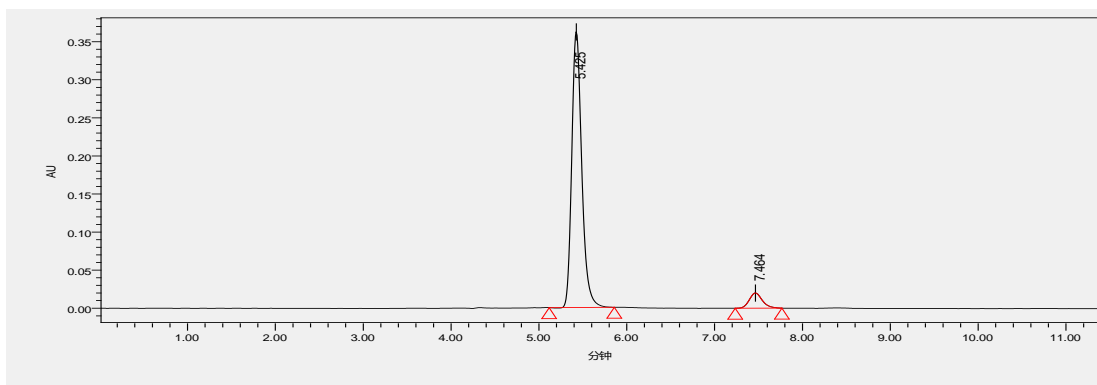
(e) Compound **3** (146mg, 0.42 mmol), 2-Naphthaleneboronic acid(108.4mg, 1.5 equiv) $\text{Pd}(\text{PPh}_3)_4$ (2.5 mol%), K_2CO_3 (232mg, 4.0 equiv) in toluene/EtOH/ H_2O (5/2/1) under an argon atmosphere was stirred at reflux conditions for 15 h. After completed analyzed by TLC, the mixture was quenched with NH_4Cl , extracted with DCM, dried with Na_2SO_4 , then purified via flash column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product **7** (105 mg, 76% yield).

White solid, m.p. 182 – 184°C; 80.5% ee determined by HPLC on Chiralpak IA-H column (*n*-hexane/*i*-PrOH = 7/3, flow rate = 1.0 mL/min, $t_{\text{major}} = 5.462$ min, $t_{\text{minor}} = 6.054$ min); $[\alpha]_{\text{D}}^{26.3} = 62.0$ ($c = 1.0$ in CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ 7.84 (dd, $J = 15.2, 7.0$ Hz, 4H), 7.64 (d, $J = 7.3$ Hz, 1H), 7.55 – 7.42 (m, 3H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.24 – 7.06 (m, 2H), 6.16 (d, $J = 6.5$ Hz, 1H), 4.01 (d, $J = 6.5$ Hz, 1H), 3.94 – 3.59 (m, 4H), 1.48 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.19, 139.59, 137.02, 133.39, 133.28, 132.98, 128.92, 128.12, 127.79, 127.75, 127.20, 126.91, 126.36, 126.25, 124.81, 123.51, 77.57, 77.15, 76.73, 75.07, 74.99, 66.67, 61.69, 27.42; IR (neat): 3340, 2957, 2925, 2854, 1629, 1600, 1451, 1096, 816, 756 cm^{-1} ; HRMS (ESI): $\text{C}_{23}\text{H}_{20}\text{O}_2$ $[\text{M} + \text{Na}]^+$ calcd: 351.1356, found: 351.1364.

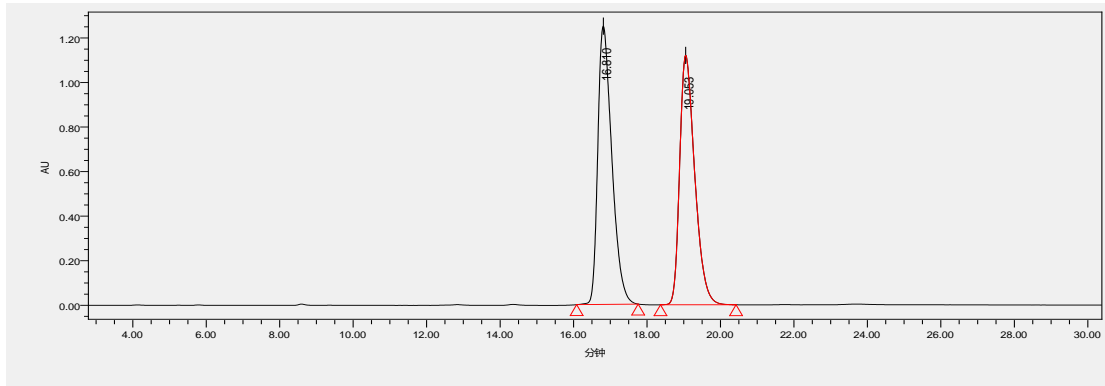
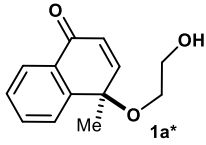
HPLC Results



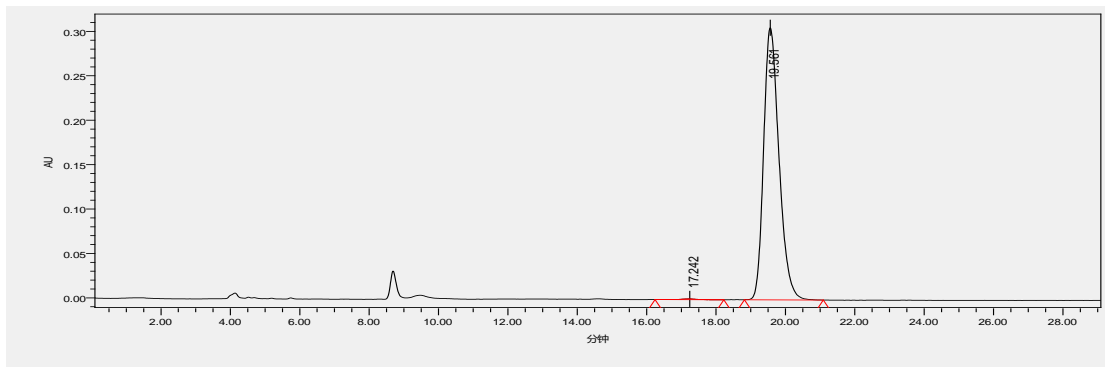
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1	5.340	6010215	50.24	672388
2	7.252	5953149	49.76	562143



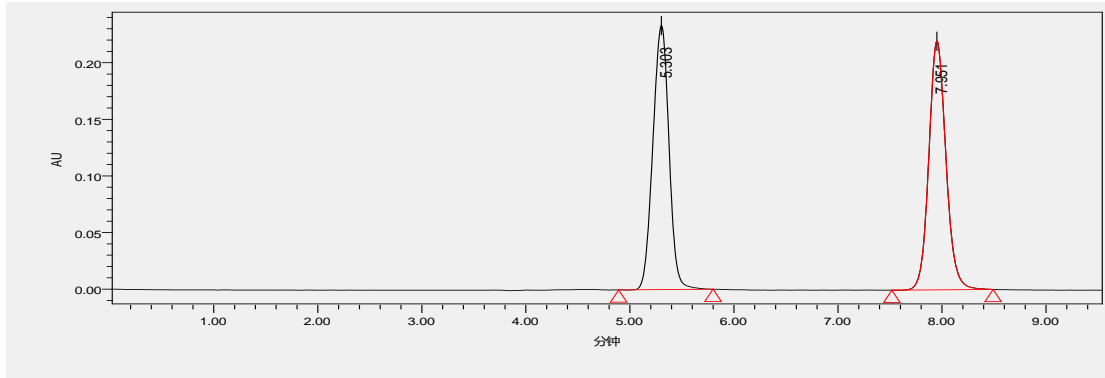
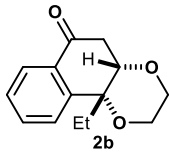
	Retention Time	Area	% Area	Height
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2	7.464	142479	4.78	16815



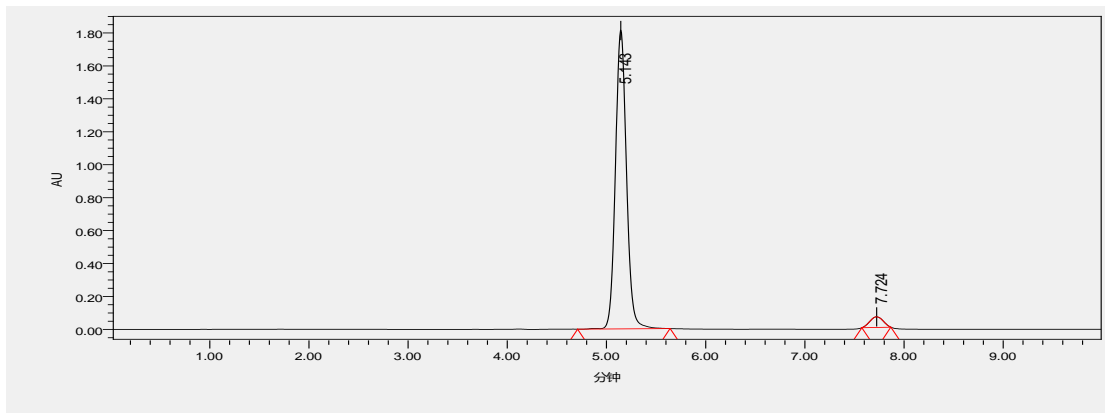
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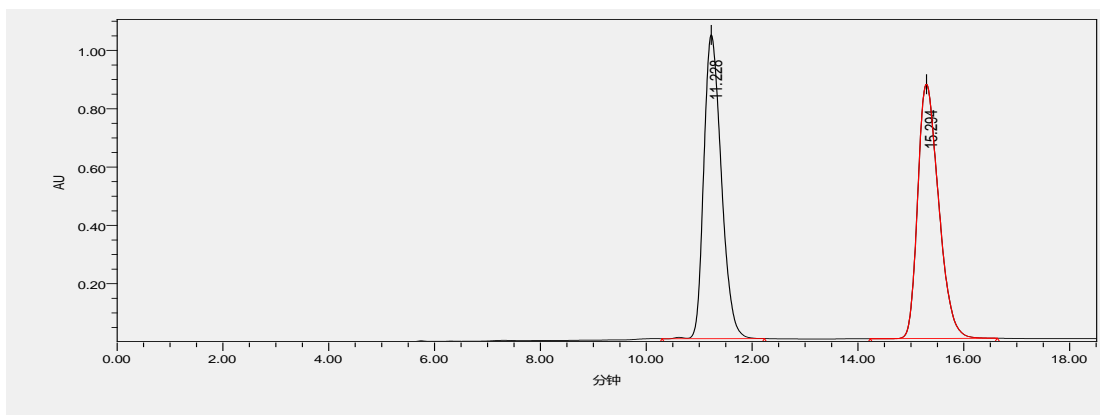
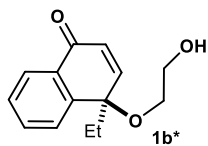
	Retention Time	Area	% Area	Height
1	17.258	3301	0.06	147
2	19.561	5386741	99.94	175077



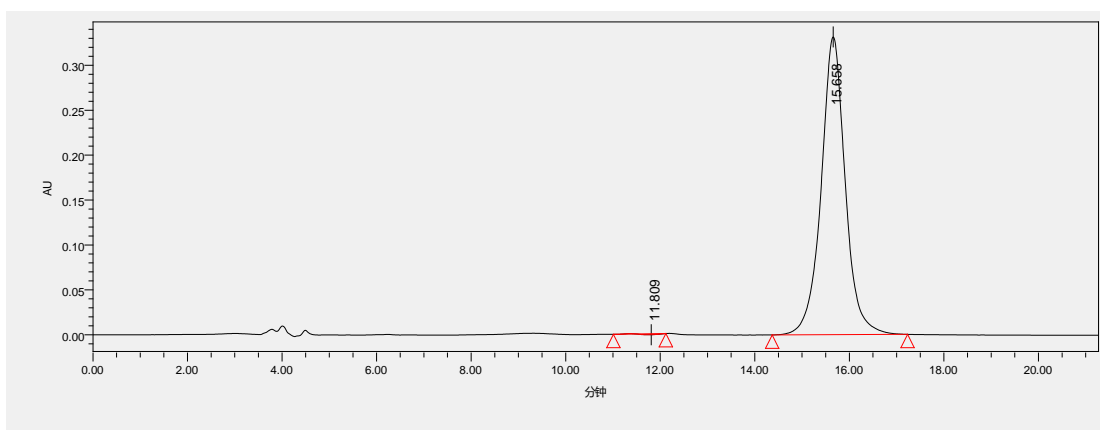
	Retention Time	Area	% Area	Height
1	5.303	2514365	49.99	233393
2	7.951	2515458	50.01	219827



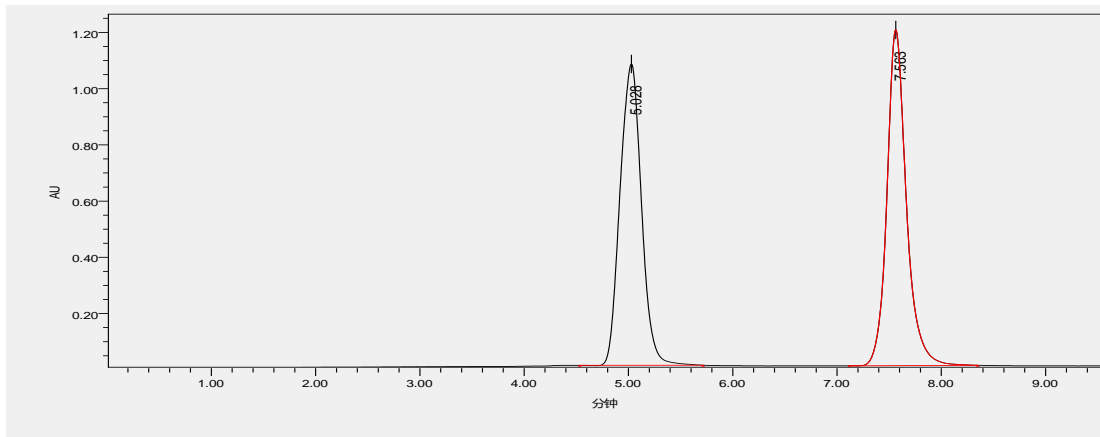
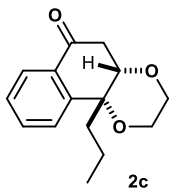
	Retention Time	Area	% Area	Height
1	5.143	13955384	95.91	1815276
2	7.724	595340	4.09	64880



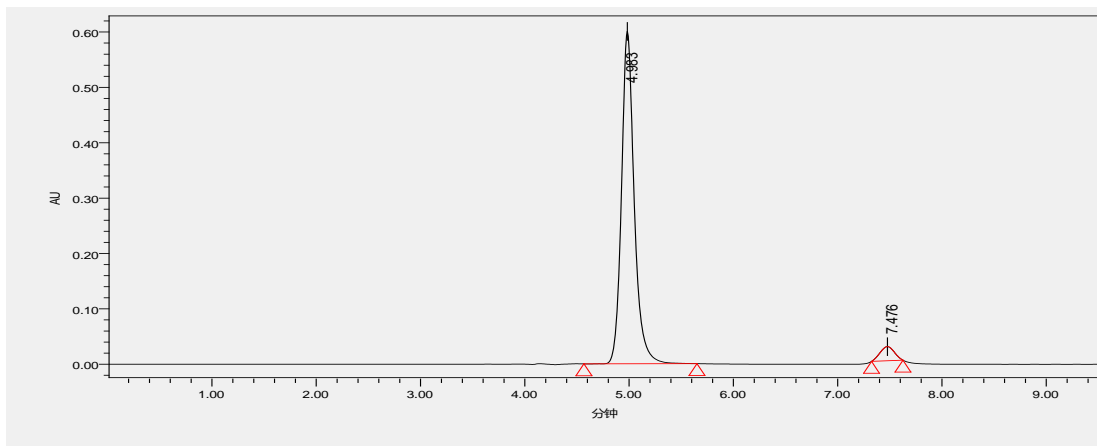
	Retention Time	Area	% Area	Height
1	11.228	23974400	50.03	1041852
2	15.294	23949394	49.97	871949



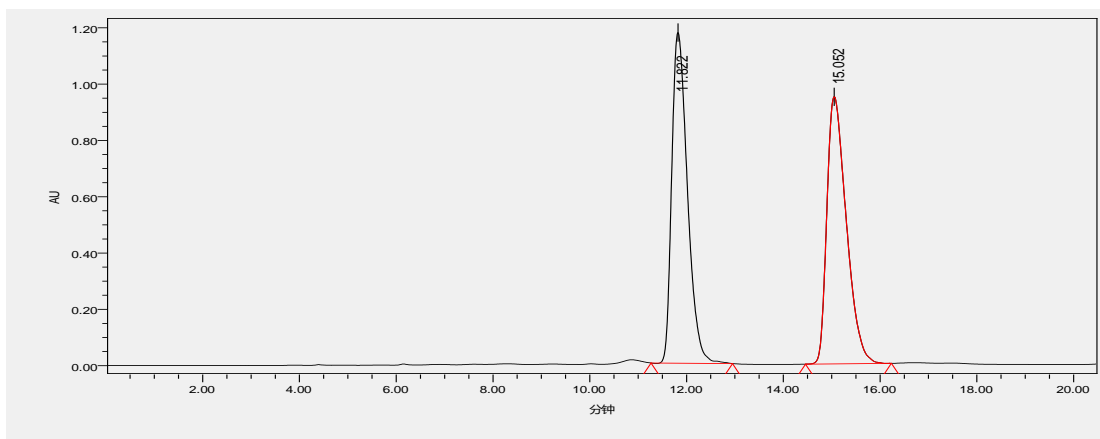
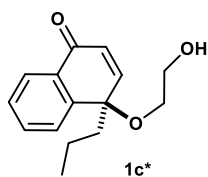
	Retention Time	Area	% Area	Height
1	11.809	31896	0.27	-1034
2	15.658	11737673	99.73	331324



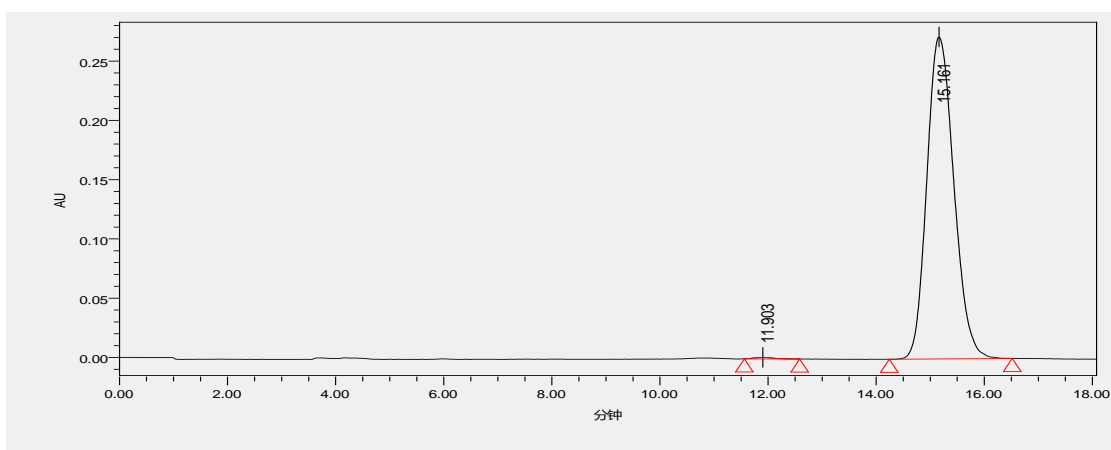
	Retention Time	Area	% Area	Height
1	5.028	15281053	49.71	1072444
2	7.563	15457556	50.29	1195365



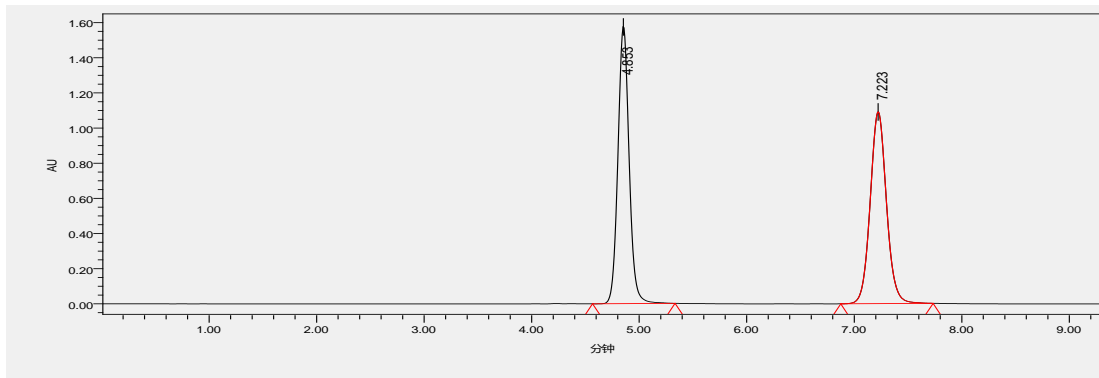
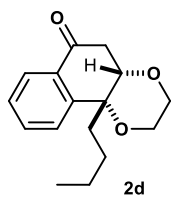
	Retention Time	Area	% Area	Height
1	4.983	5120395	95.46	600339
2	7.476	243488	4.54	25646



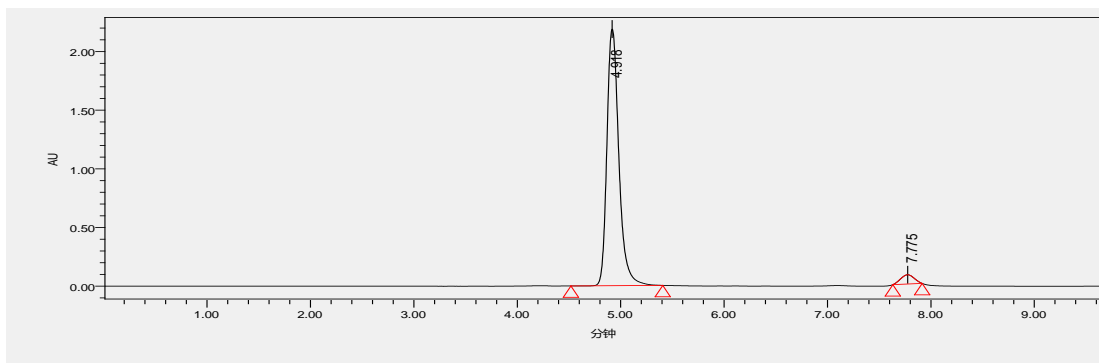
	Retention Time	Area	% Area	Height
1	11.822	26490656	50.04	1174615
2	15.052	26448098	49.96	949054



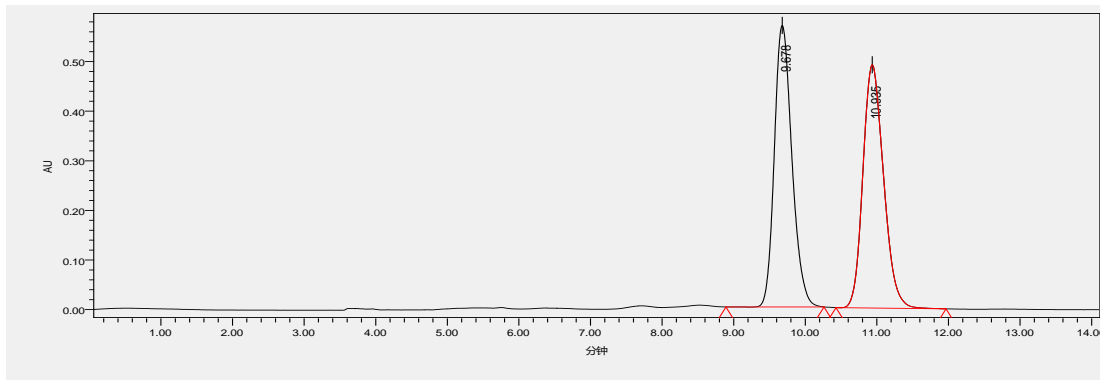
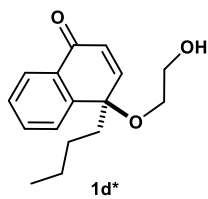
	Retention Time	Area	% Area	Height
1	11.903	30599	0.32	1287
2	15.161	9433301	99.68	271592



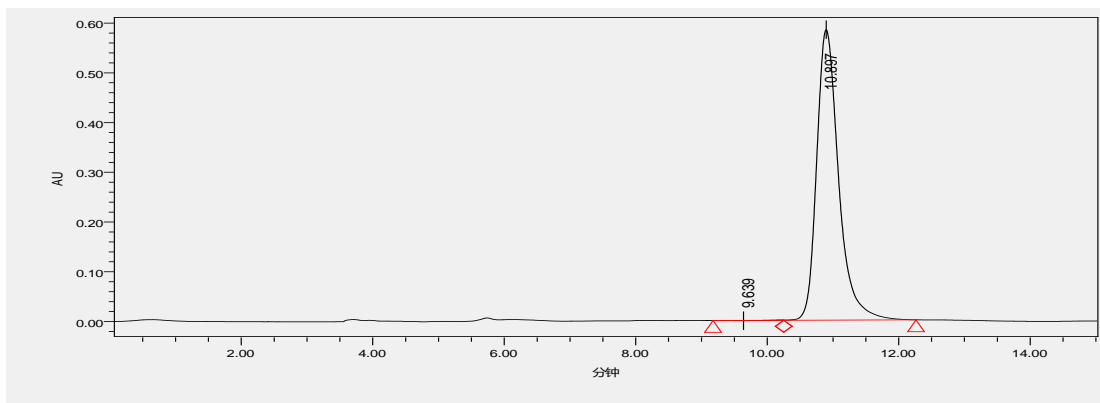
	Retention Time	Area	% Area	Height
1	4.853	12079523	49.84	1663309
2	7.223	12155057	50.16	1153175



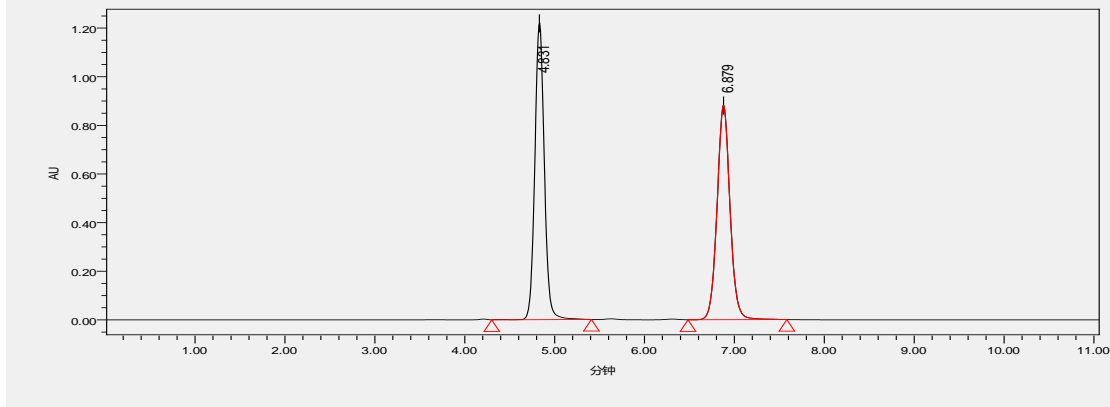
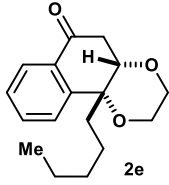
	Retention Time	Area	% Area	Height
1	4.918	17572865	96.58	2187766
2	7.775	622715	3.42	73080



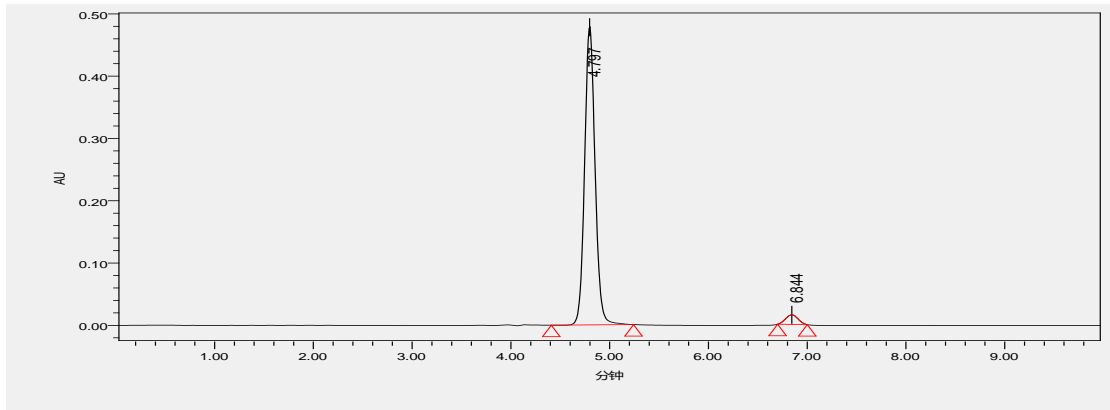
	Retention Time	Area	% Area	Height
1	9.678	9691352	49.70	567421
2	10.935	9810010	50.30	490106



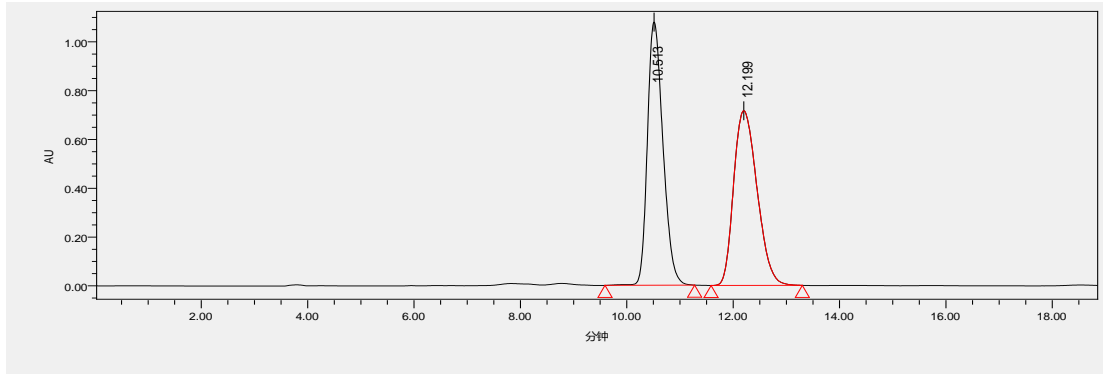
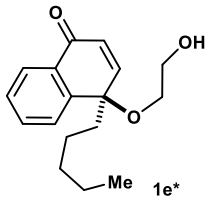
	Retention Time	Area	% Area	Height
1	9.639	16954	0.13	-642
2	10.897	13516904	99.87	583981



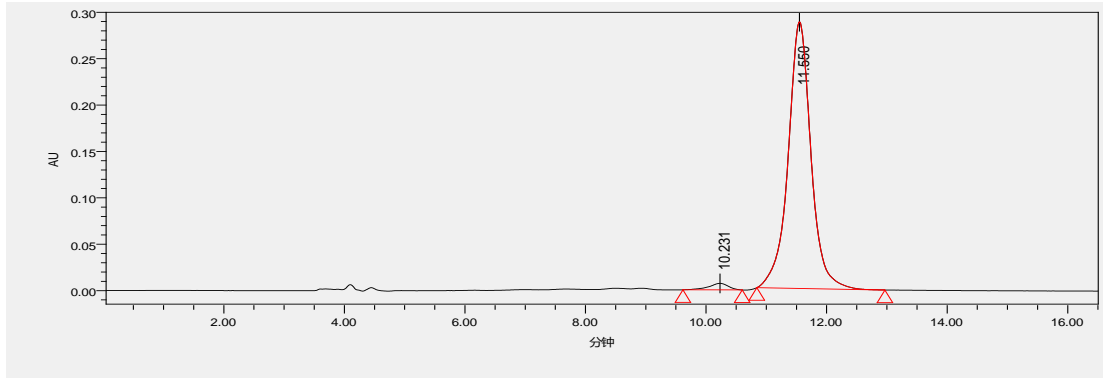
	Retention Time	Area	% Area	Height
1	4.831	8949611	50.28	1221229
2	6.879	8848598	49.72	882224



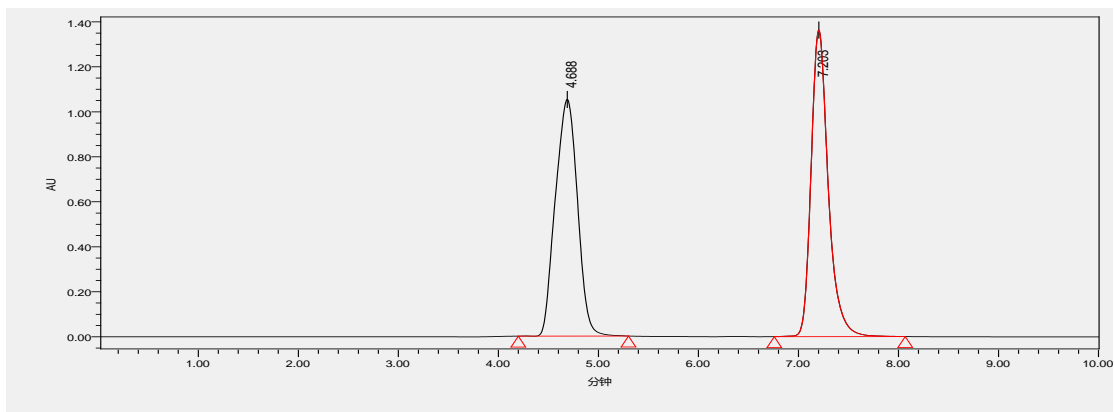
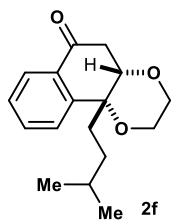
	Retention Time	Area	% Area	Height
1	4.797	3525176	96.30	479245
2	6.844	135597	3.70	15428



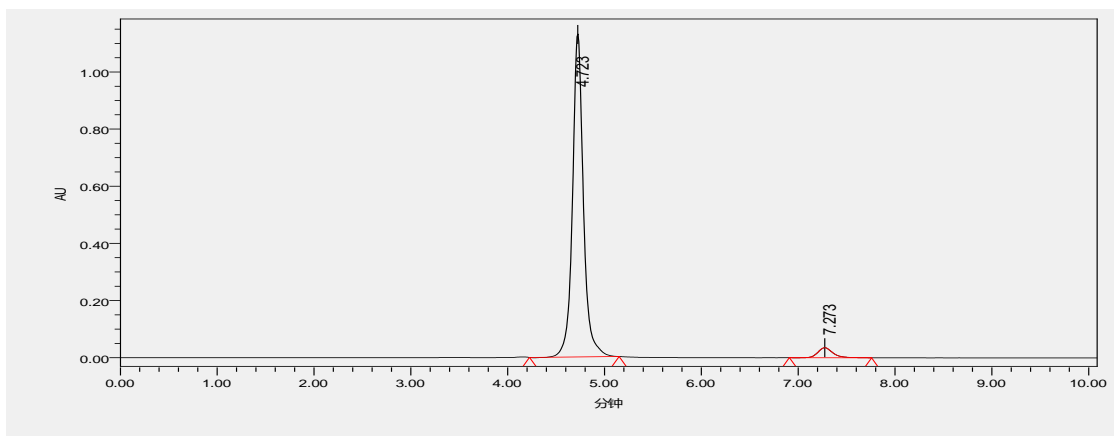
	Retention Time	Area	% Area	Height
1	10.513	21937582	50.04	1078748
2	12.199	21905058	49.96	716261



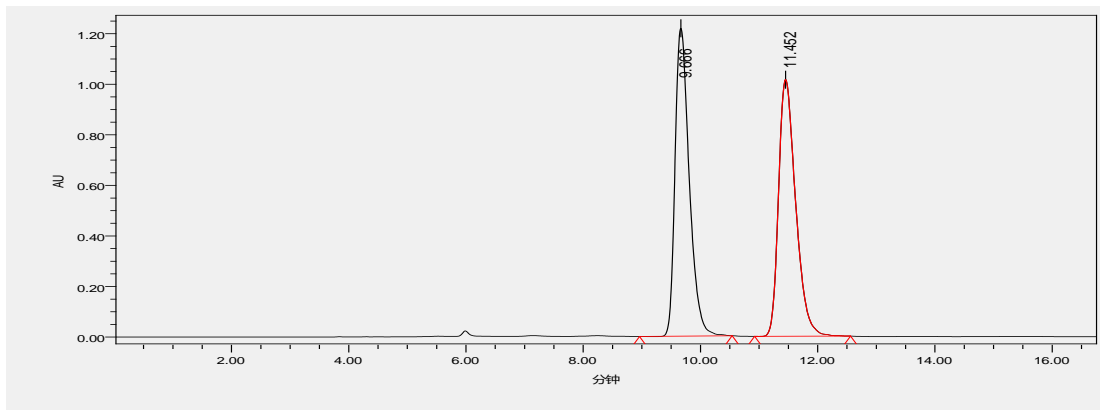
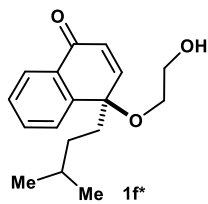
	Retention Time	Area	% Area	Height
1	10.231	159500	2.06	7062
2	11.550	7574959	97.94	287408



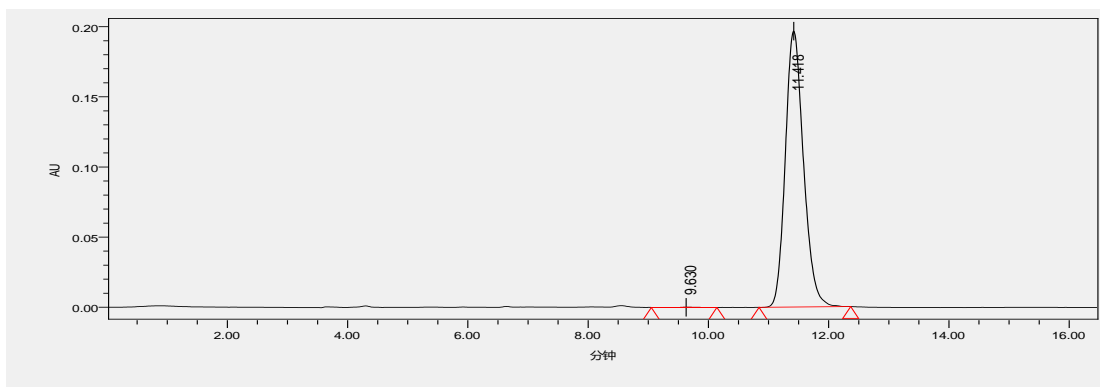
	Retention Time	Area	% Area	Height
1	4.688	16184616	49.92	1052936
2	7.203	16236894	50.08	1364264



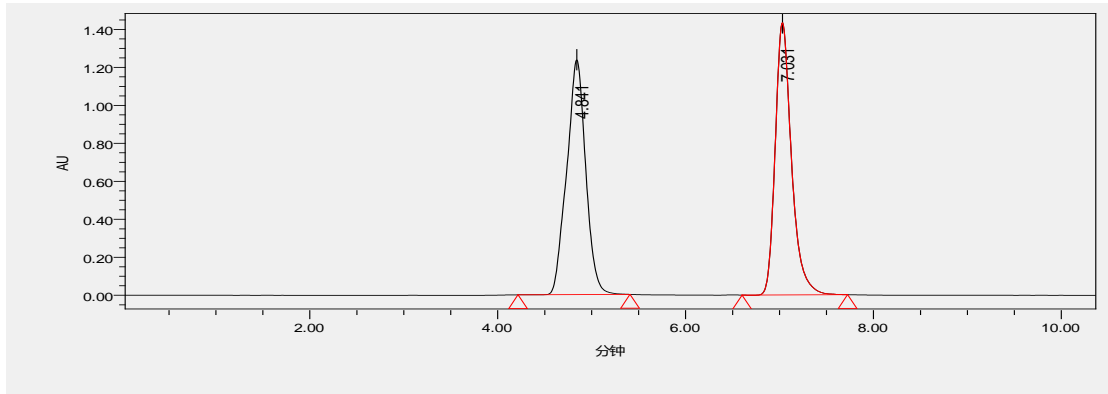
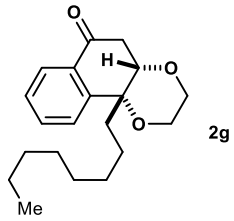
	Retention Time	Area	% Area	Height
1	4.723	8877551	95.91	1131099
2	7.273	378661	4.09	35136



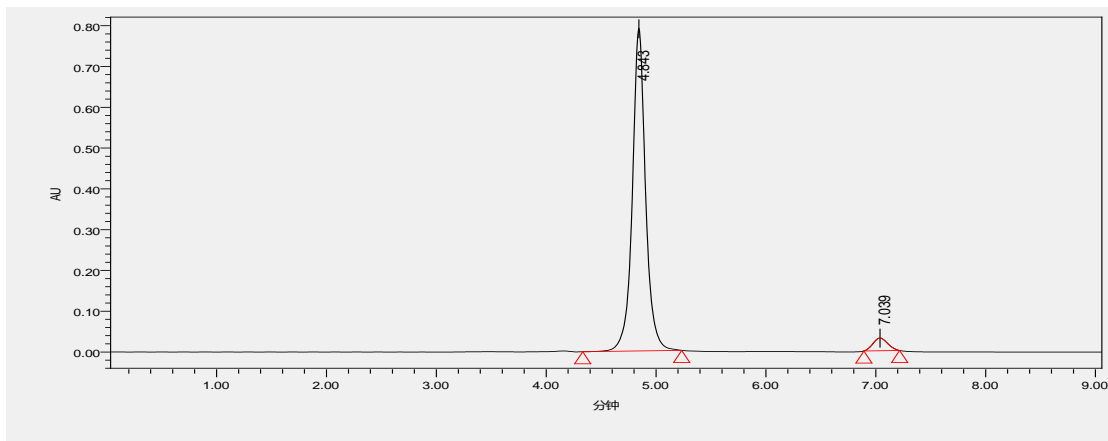
	Retention Time	Area	% Area	Height
1	9.666	20520323	49.93	1217850
2	11.452	20579182	50.07	1015679



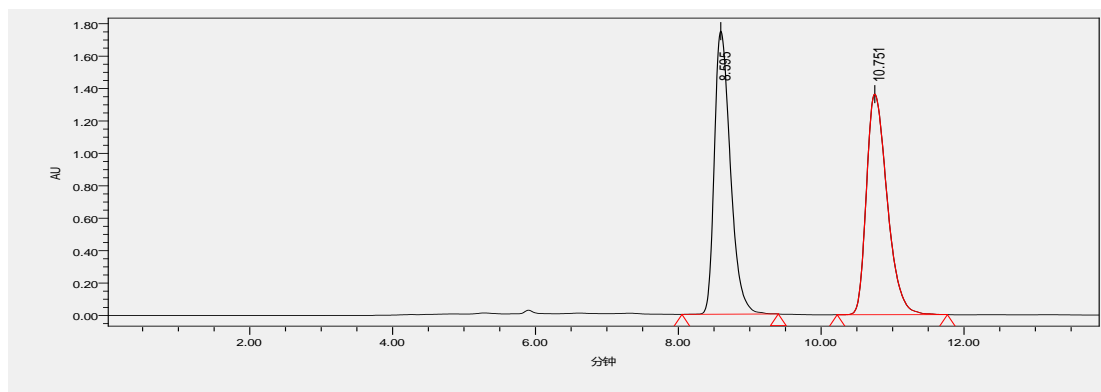
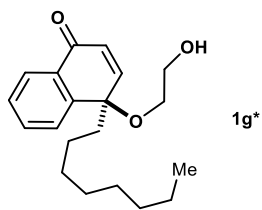
	Retention Time	Area	% Area	Height
1	9.630	3089	0.07	170
2	11.418	4133992	99.93	196736



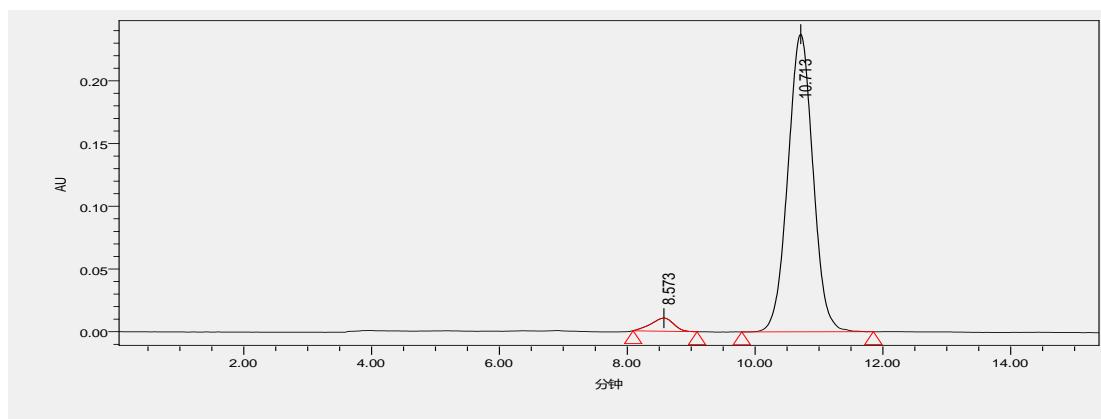
	Retention Time	Area	% Area	Height
1	4.841	17404737	50.12	1236614
2	7.031	17318250	49.88	1434269



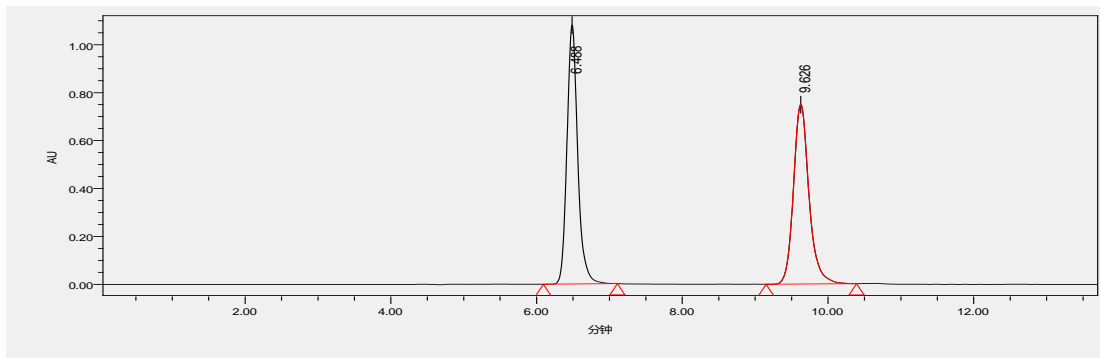
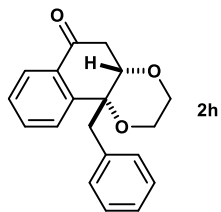
	Retention Time	Area	% Area	Height
1	4.843	6644318	95.85	791674
2	7.039	287849	4.15	31179



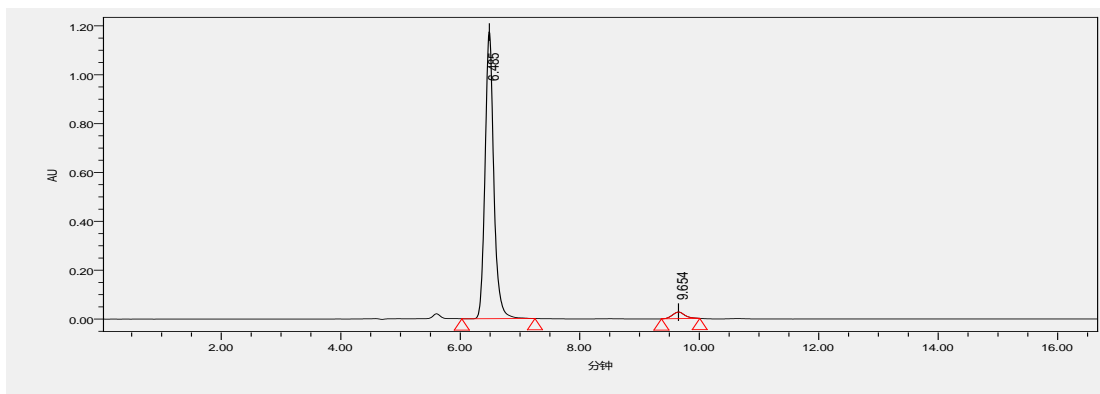
	Retention Time	Area	% Area	Height
1	8.595	27200101	49.72	1747560
2	10.751	27502587	50.28	1361162



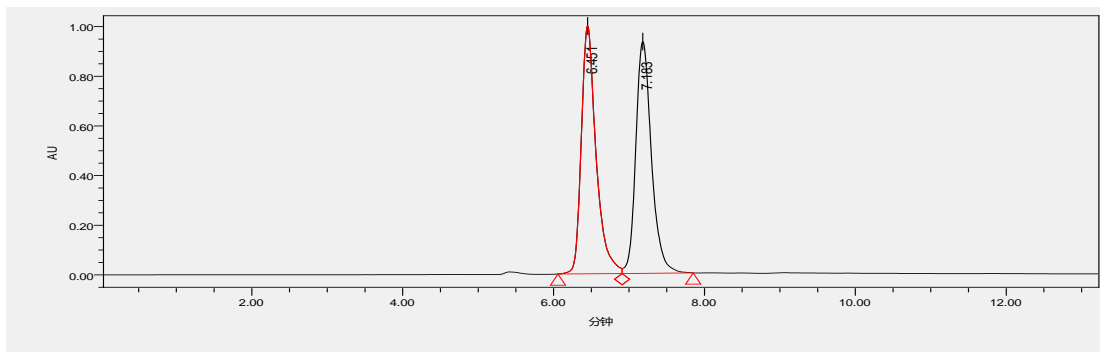
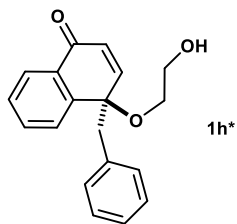
	Retention Time	Area	% Area	Height
1	8.636	360386	3.08	15556
2	10.792	11349510	96.92	402316



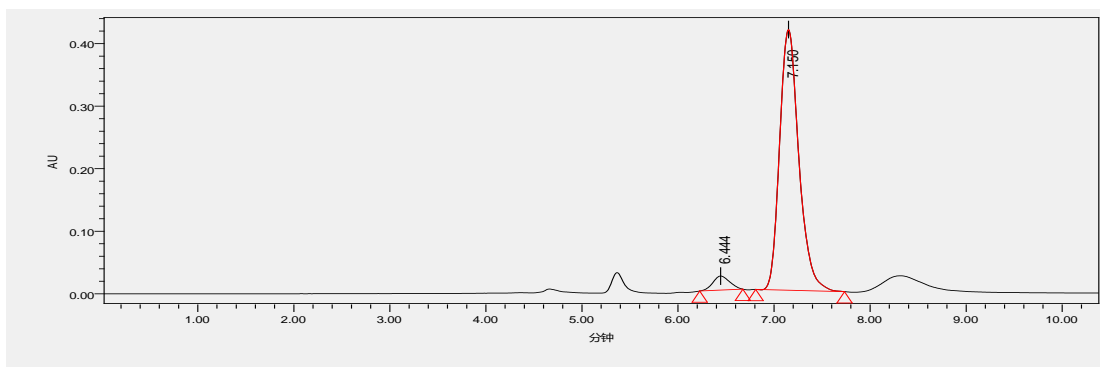
	Retention Time	Area	% Area	Height
1	6.488	1111638	49.97	1081927
2	9.626	11128445	50.03	749280



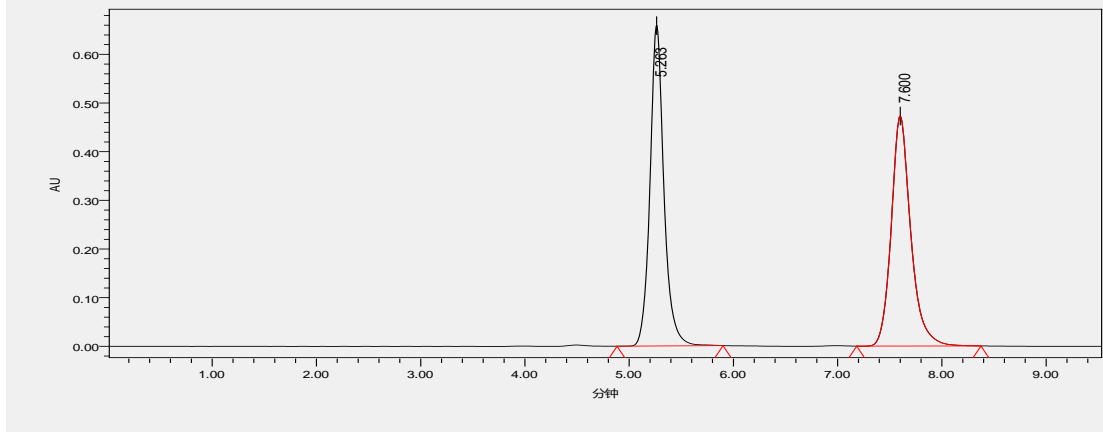
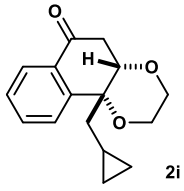
	Retention Time	Area	% Area	Height
1	6.485	11928798	97.06	1174598
2	9.654	361599	2.94	26378



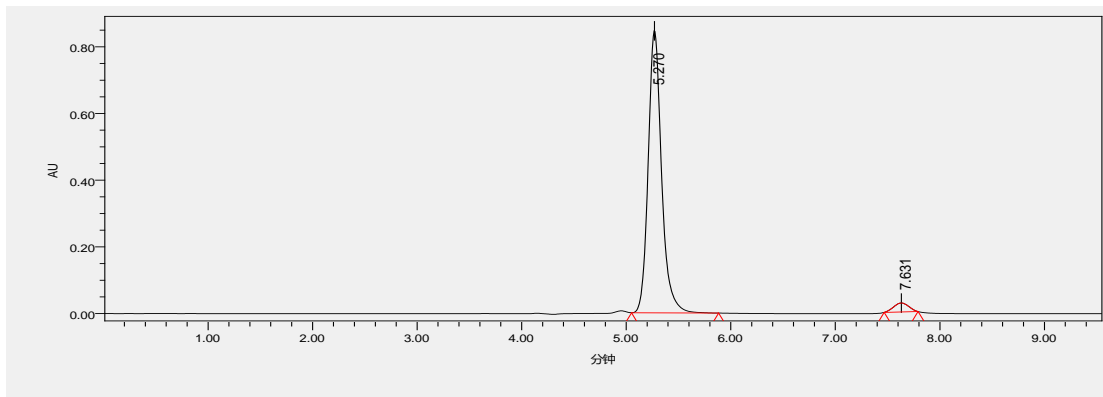
	Retention Time	Area	% Area	Height
1	6.451	13553636	50.14	998570
2	7.183	13479227	49.86	933193



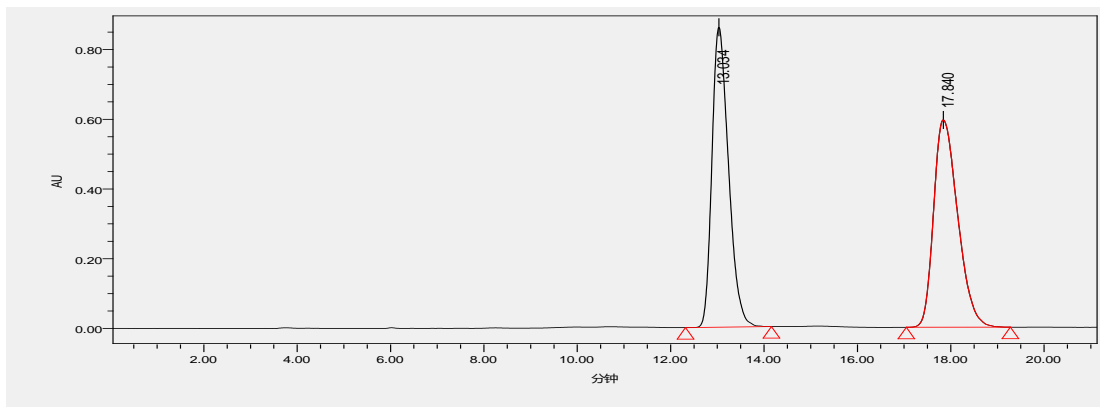
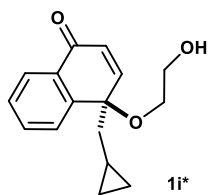
	Retention Time	Area	% Area	Height
1	6.444	262712	4.34	22187
2	7.150	5794216	95.66	416656



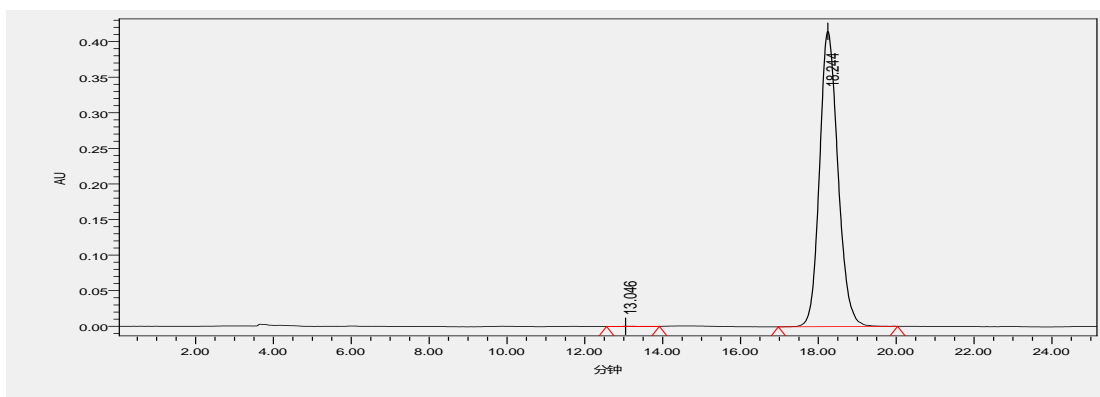
	Retention Time	Area	% Area	Height
1	5.263	6131941	49.92	659711
2	7.600	6152334	50.08	472893



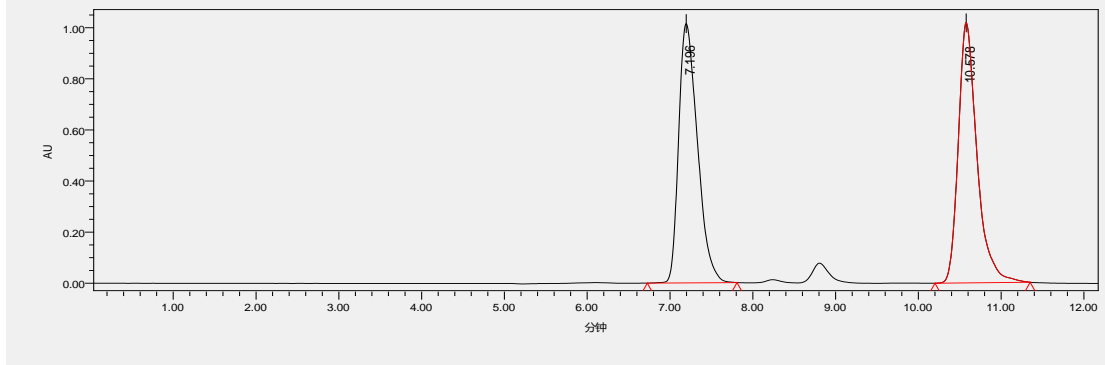
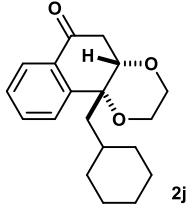
	Retention Time	Area	% Area	Height
1	5.270	7520701	96.52	847501
2	7.631	270768	3.48	26939



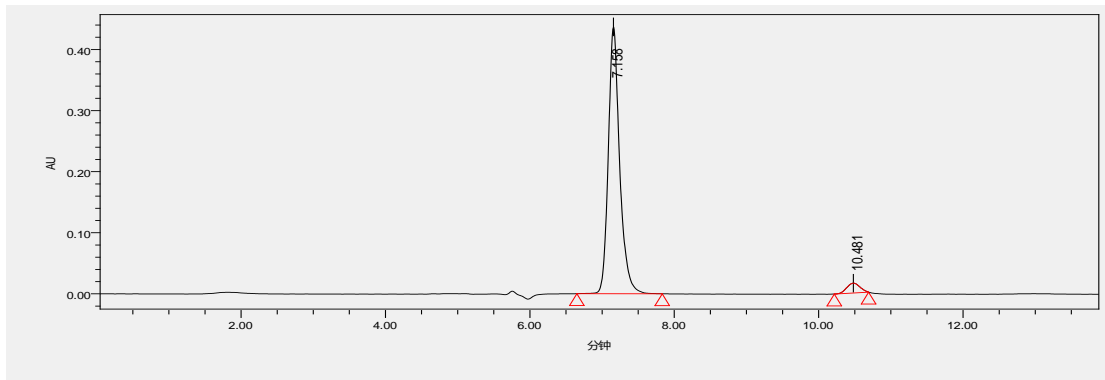
	Retention Time	Area	% Area	Height
1	13.034	21249933	49.89	860359
2	17.840	21345516	50.11	594864



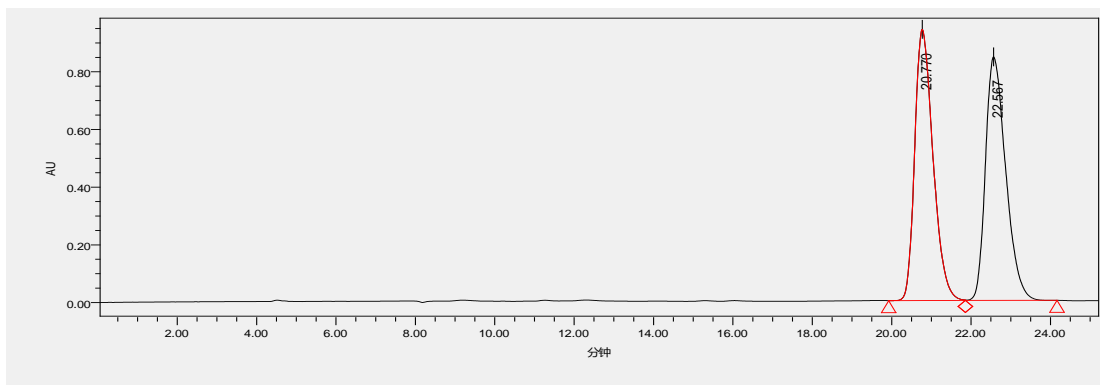
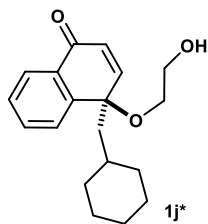
	Retention Time	Area	% Area	Height
1	13.046	6591	0.05	158
2	18.244	13624774	99.95	414863



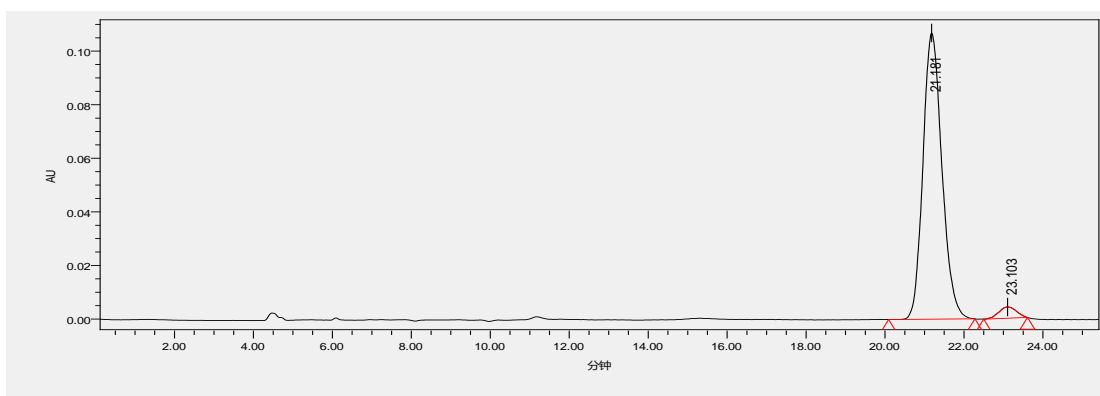
	Retention Time	Area	% Area	Height
1	7.196	15992183	49.99	1015372
2	10.578	15996229	50.01	1018930



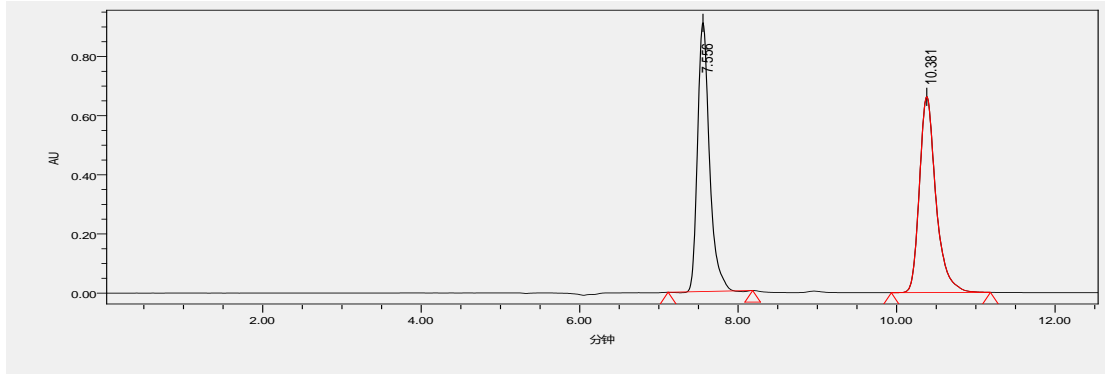
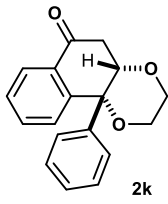
	Retention Time	Area	% Area	Height
1	7.158	4777573	95.94	436654
2	10.481	202084	4.06	16044



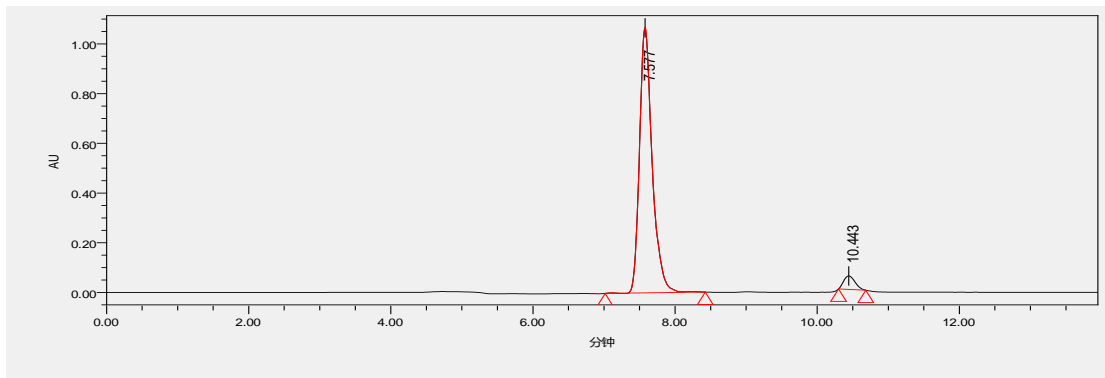
	Retention Time	Area	% Area	Height
1	20.770	30069105	50.12	940258
2	22.567	29929343	49.88	844192



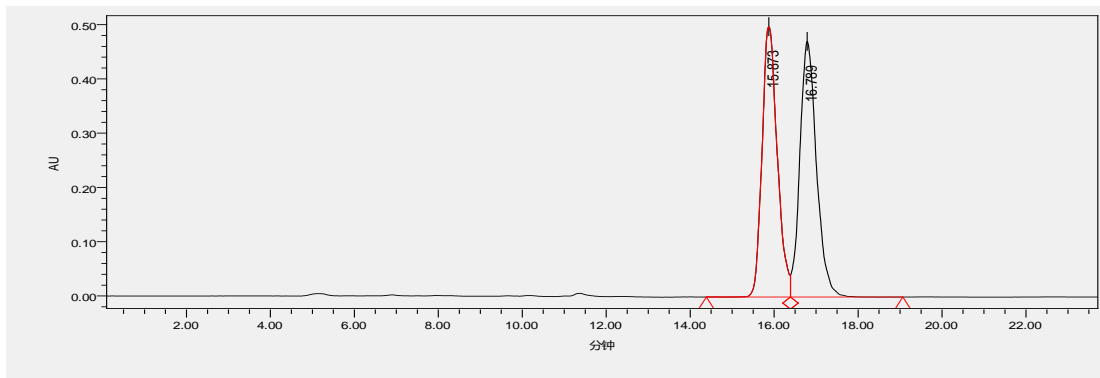
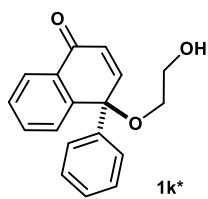
	Retention Time	Area	% Area	Height
1	21.181	3567847	96.47	106853
2	23.103	130648	3.53	4192



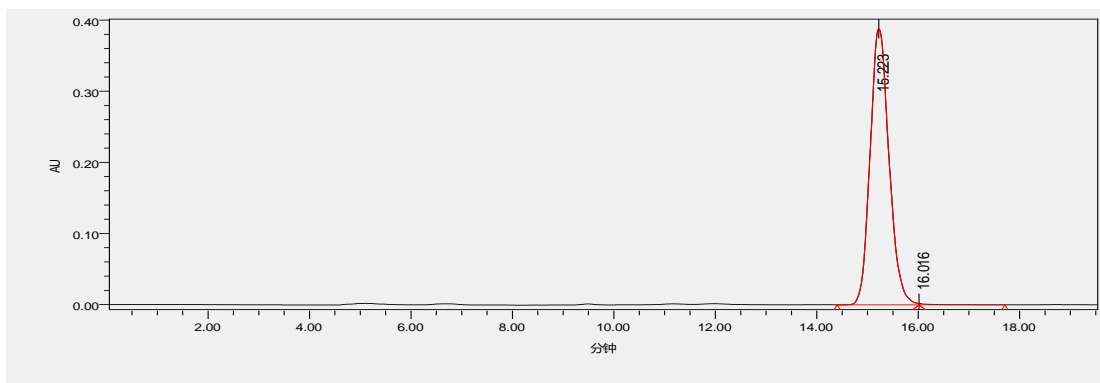
	Retention Time	Area	% Area	Height
1	7.556	9580714	49.97	909576
2	10.381	9591793	50.03	662246



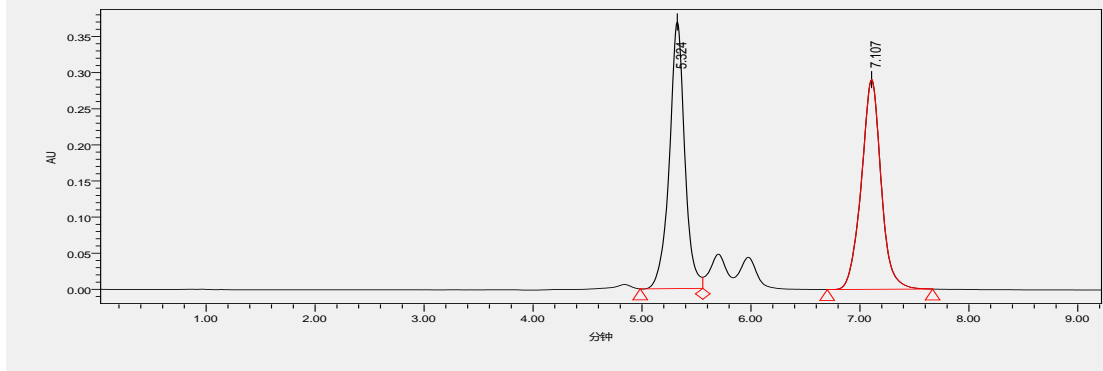
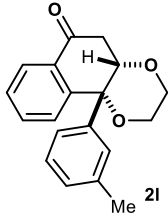
	Retention Time	Area	% Area	Height
1	7.577	13284446	95.64	1067383
2	10.443	605202	4.36	54488



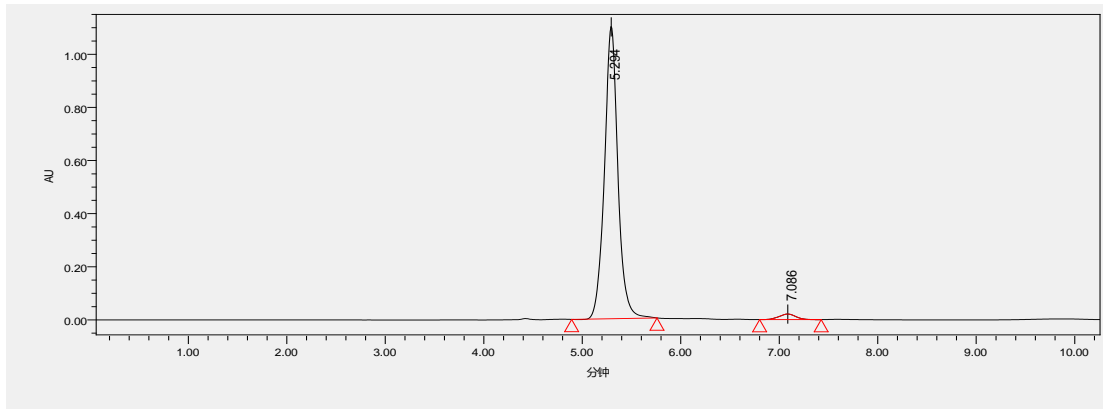
	Retention Time	Area	% Area	Height
1	15.873	12524059	49.16	498032
2	16.789	12952282	50.84	471055



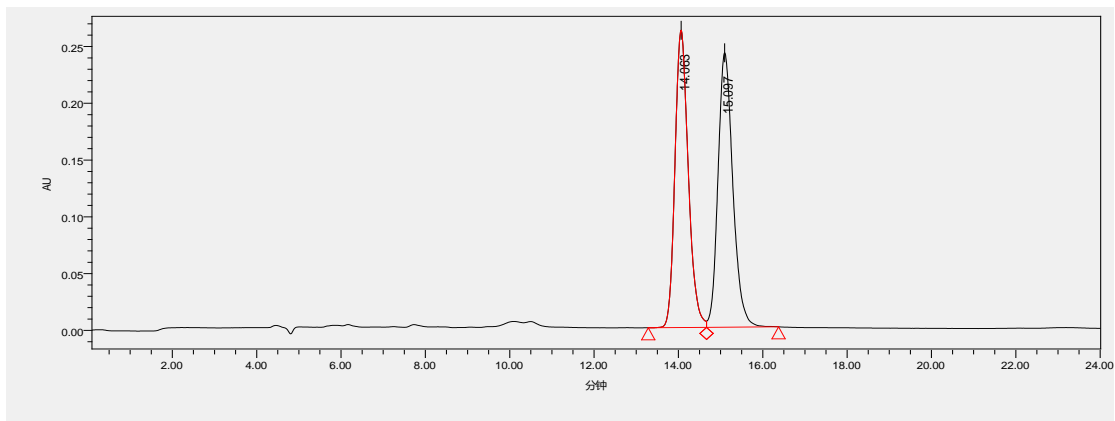
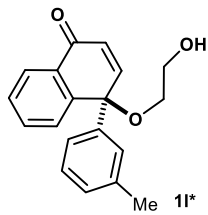
	Retention Time	Area	% Area	Height
1	15.223	10066663	99.72	388252
2	16.016	28268	0.28	2008



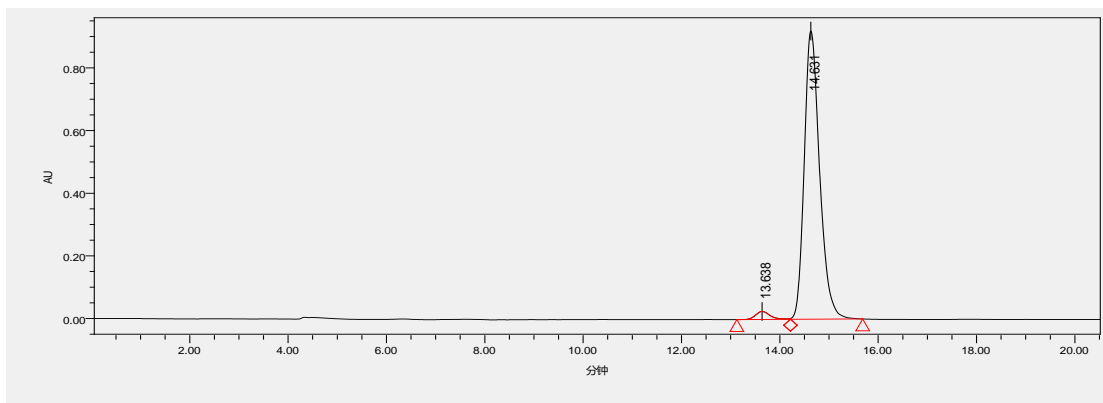
	Retention Time	Area	% Area	Height
1	5.324	3612923	49.73	369369
2	7.107	3651713	50.27	290457



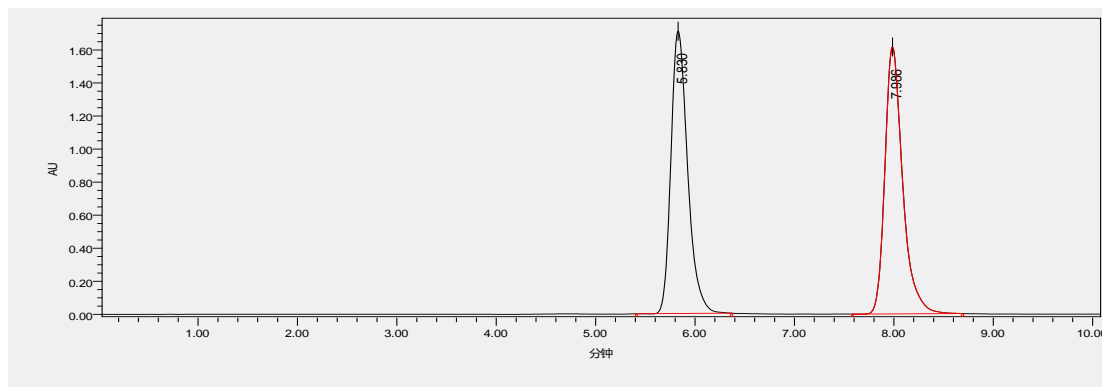
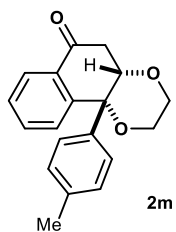
	Retention Time	Area	% Area	Height
1	5.294	10457631	97.67	1100575
2	7.086	249725	2.33	21077



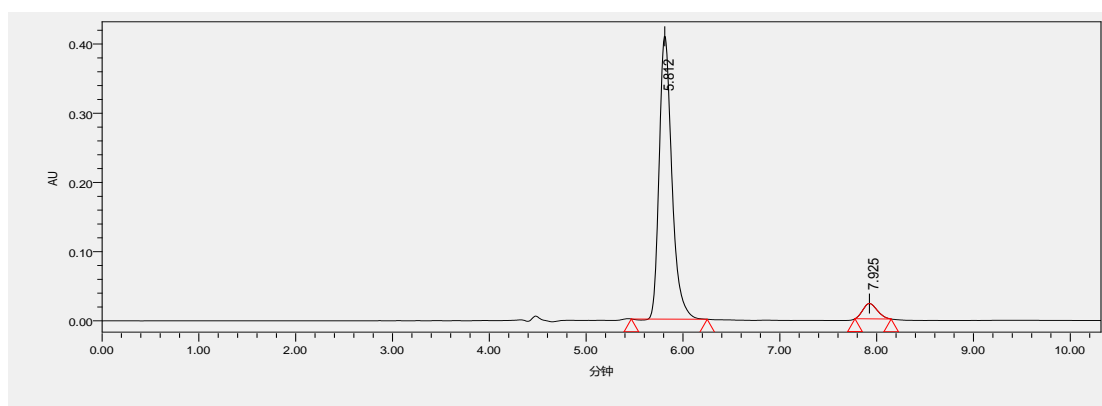
	Retention Time	Area	% Area	Height
1	14.063	5753138	49.31	261870
2	15.097	5913461	50.69	241715



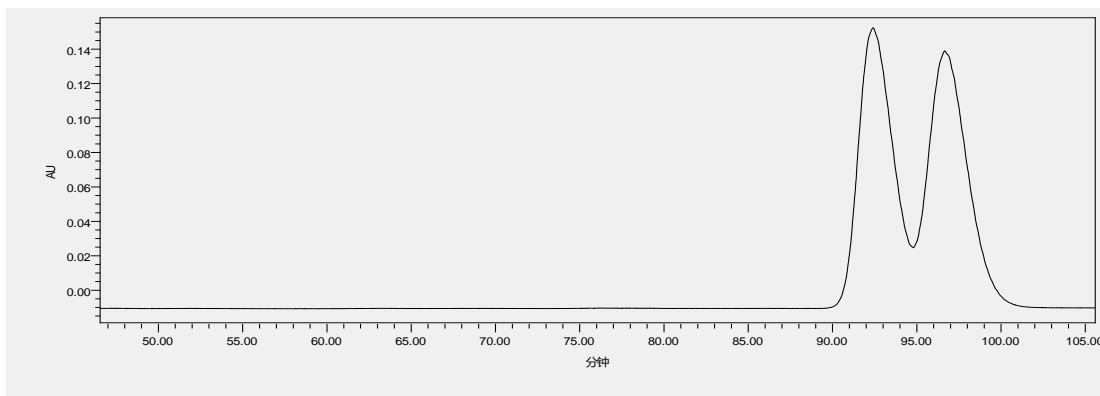
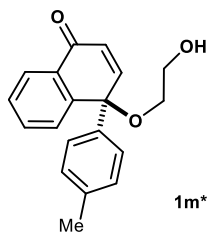
	Retention Time	Area	% Area	Height
1	13.638	504893	2.46	25605
2	14.631	20045598	97.54	919988



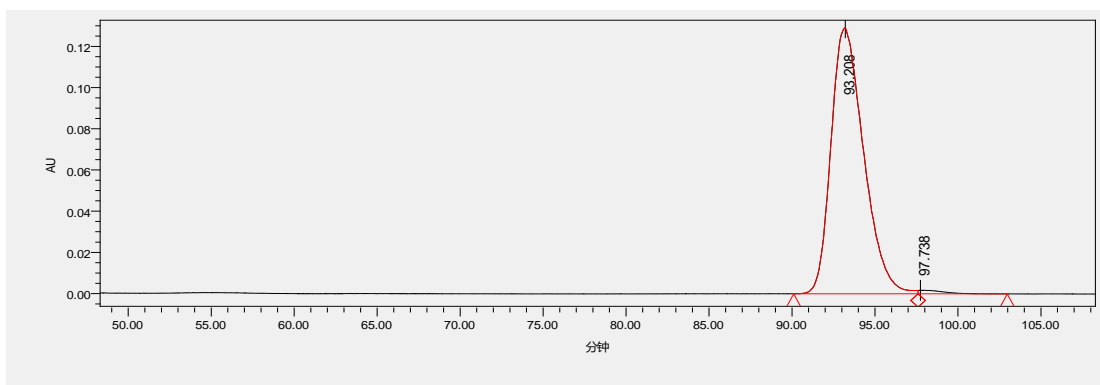
	Retention Time	Area	% Area	Height
1	5.830	19946734	49.85	1710062
2	7.986	20062821	50.15	1616793



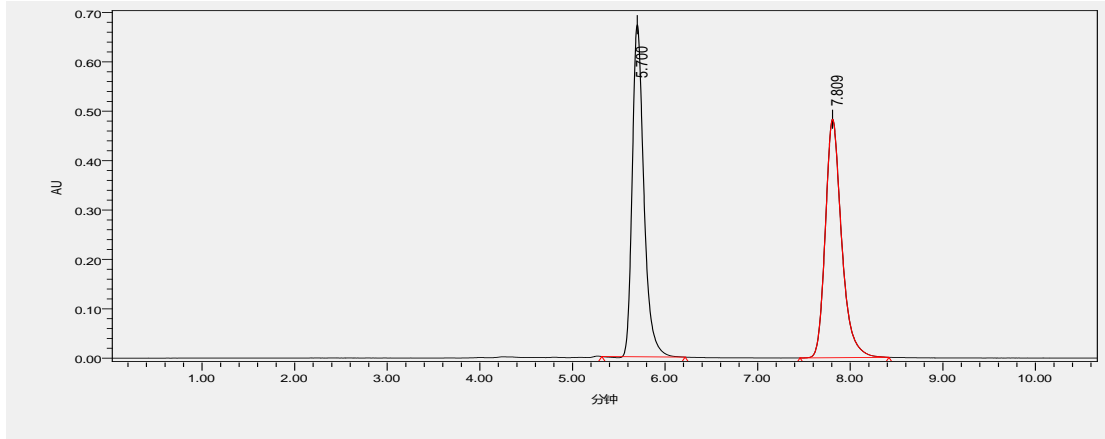
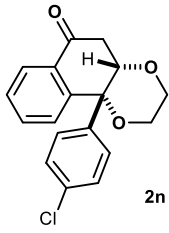
	Retention Time	Area	% Area	Height
1	5.812	3742225	94.21	409634
2	7.925	229896	5.79	22253



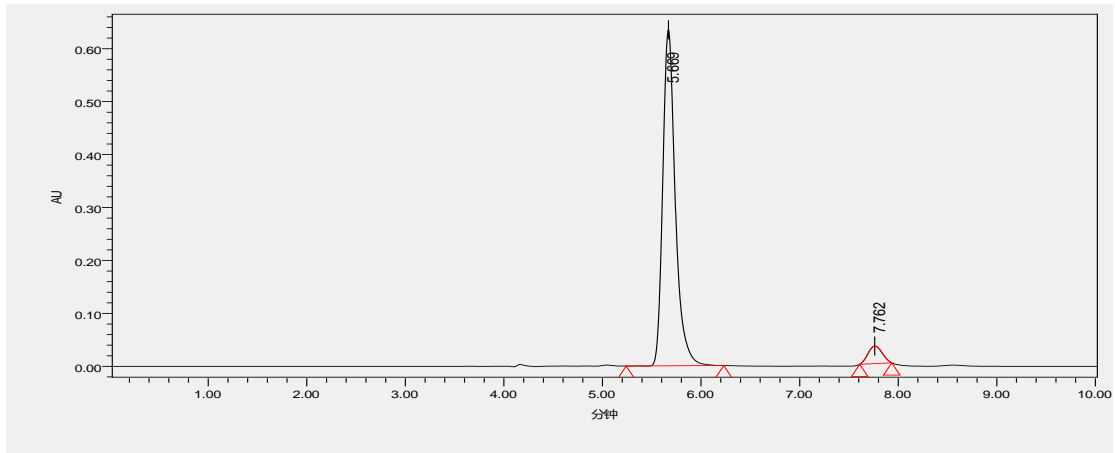
	Retention Time	Area	% Area	Height
1	92.420	23545711	49.20	162865
2	96.659	24308521	50.80	149305



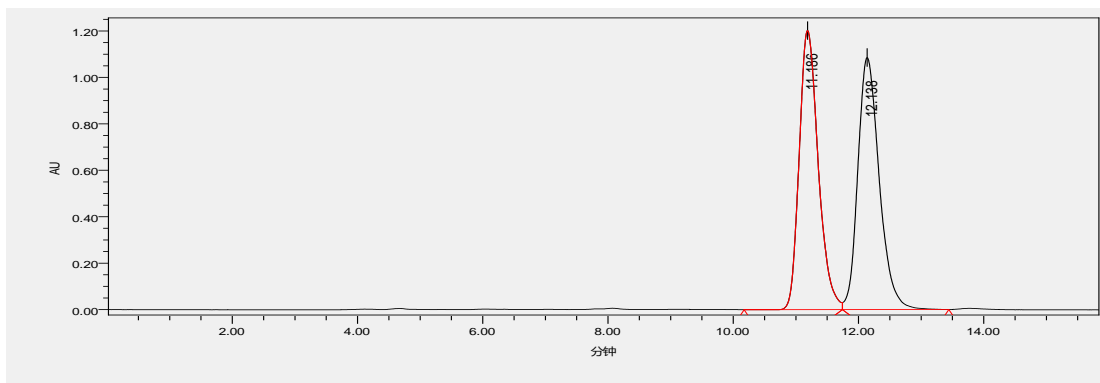
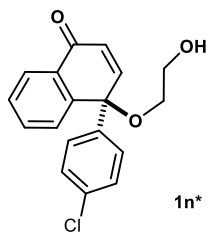
	Retention Time	Area	% Area	Height
1	93.208	17676157	99.01	129082
2	97.738	176903	0.99	1741



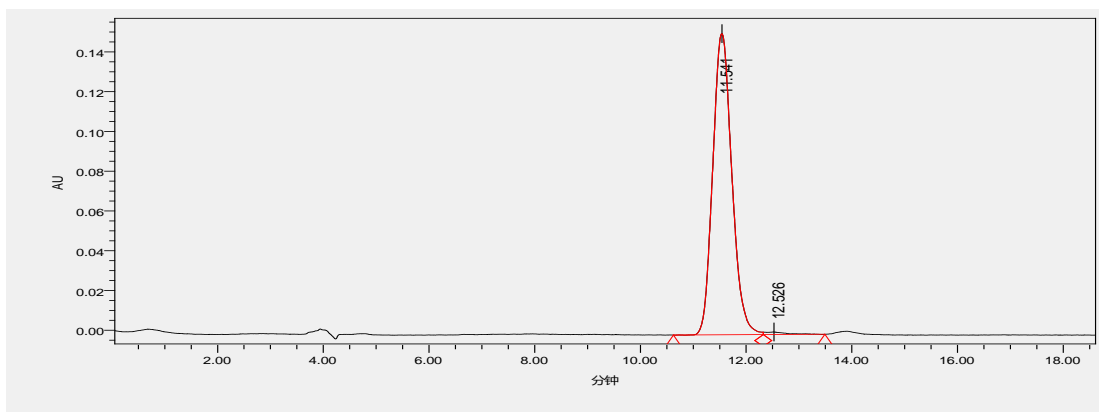
	Retention Time	Area	% Area	Height
1	5.700	5887485	49.96	672319
2	7.809	5896554	50.04	482959



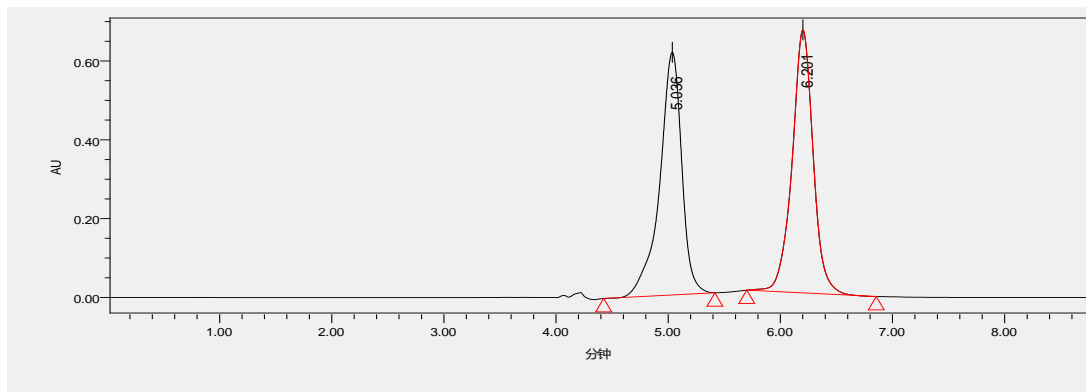
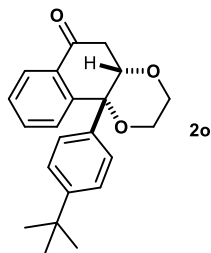
	Retention Time	Area	% Area	Height
1	5.669	5621019	94.46	634566
2	7.762	329456	5.54	33158



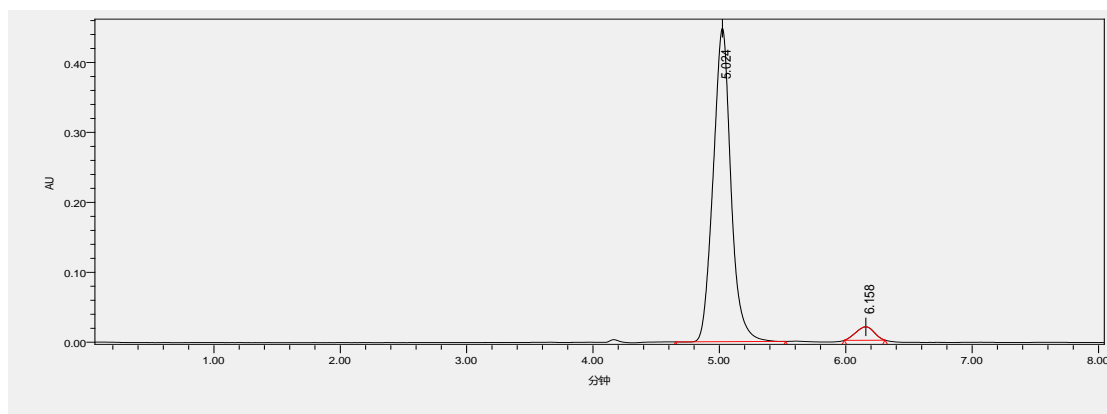
	Retention Time	Area	% Area	Height
1	11.186	25419153	49.63	1201796
2	12.138	25798144	50.37	1085309



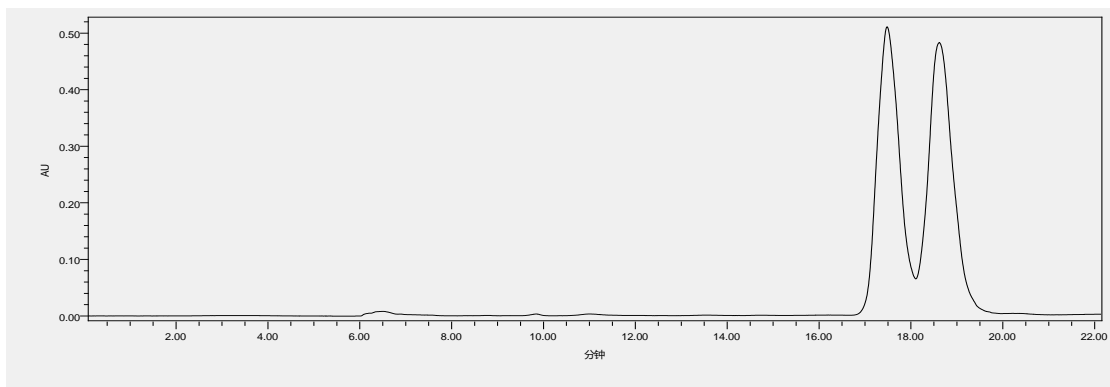
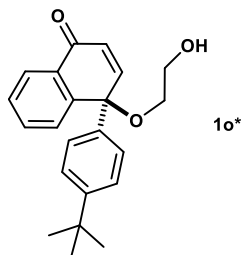
	Retention Time	Area	% Area	Height
1	11.441	3802391	99.07	151472
2	12.426	35609	0.93	1263



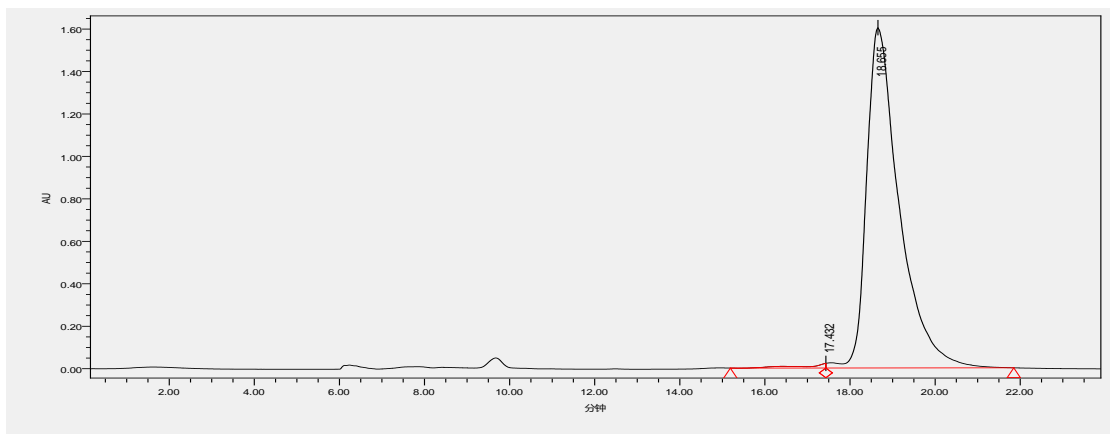
	Retention Time	Area	% Area	Height
1	5.036	7888890	49.69	576812
2	6.201	7986780	50.31	621520



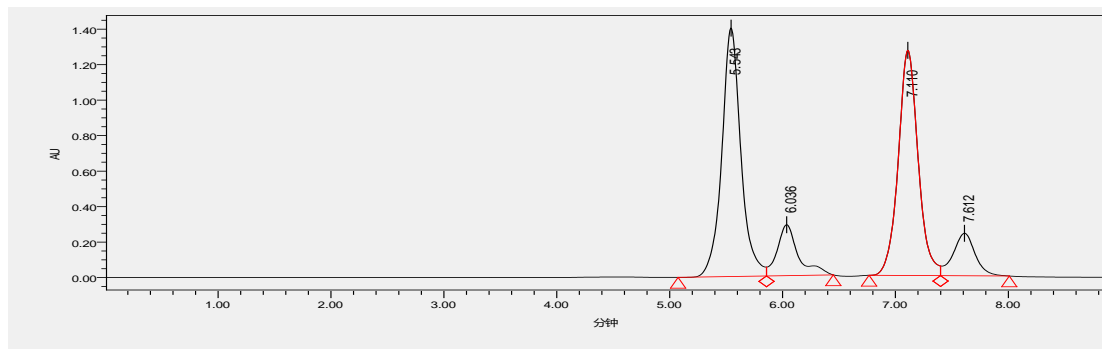
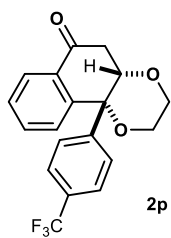
	Retention Time	Area	% Area	Height
1	5.024	4216150	96.59	432394
2	6.158	148729	3.41	16480



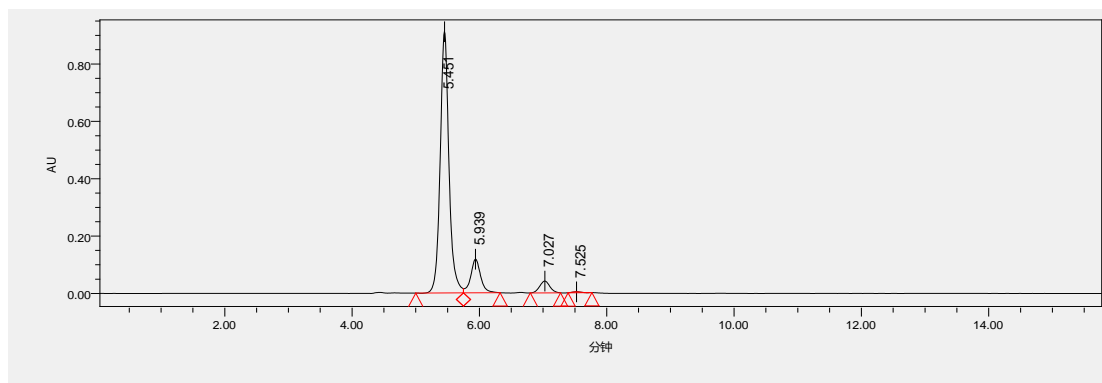
	Retention Time	Area	% Area	Height
1	17.481	17312401	49.09	509022
2	18.618	17953478	50.91	480141



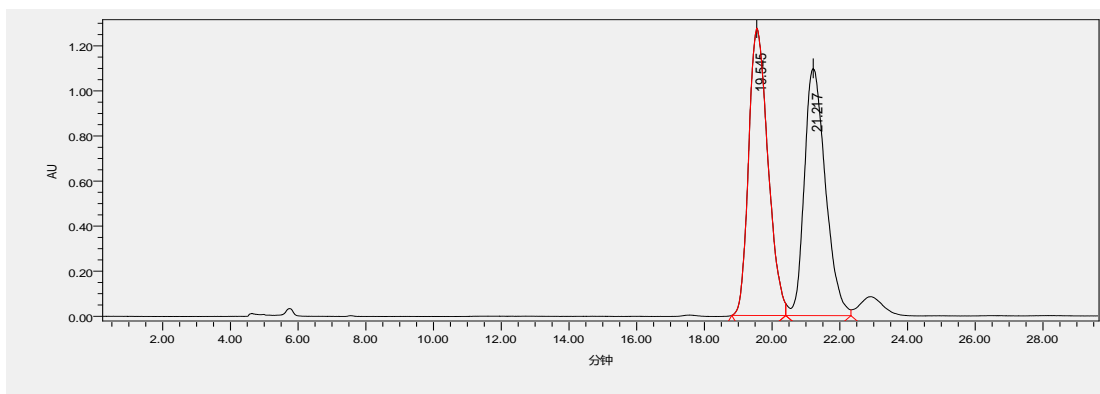
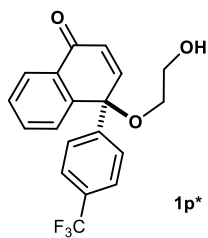
	Retention Time	Area	% Area	Height
1	17.432	766127	0.89	21821
2	18.655	85647064	99.11	1602580



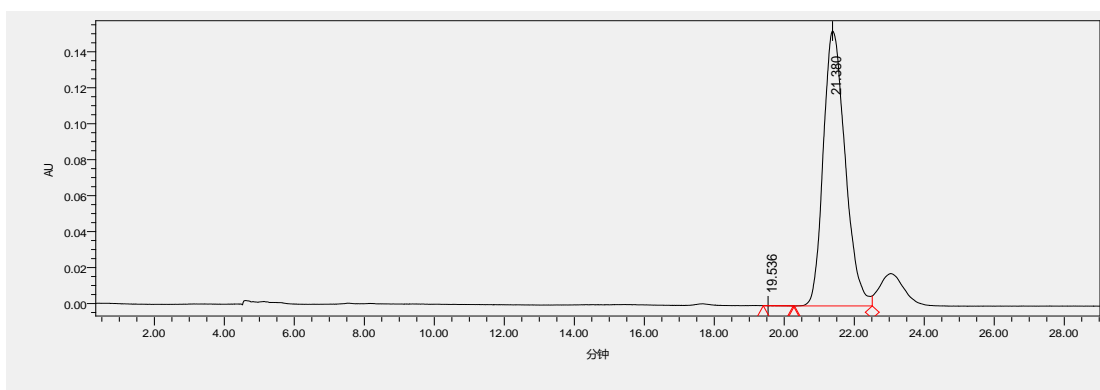
	Retention Time	Area	% Area	Height
1	5.545	18311023	43.49	1573987
2	6.038	2883061	6.85	261312
3	7.111	17780099	42.23	1439731
4	7.613	3130791	7.44	238026



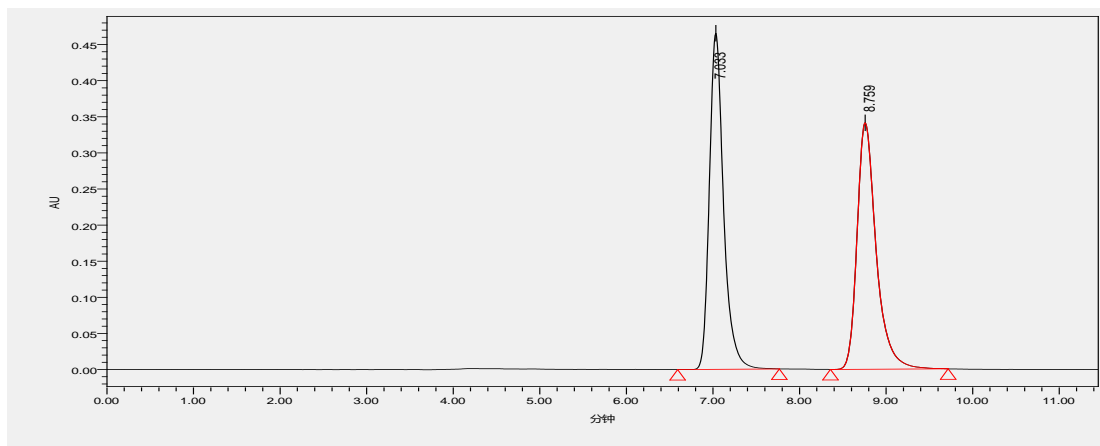
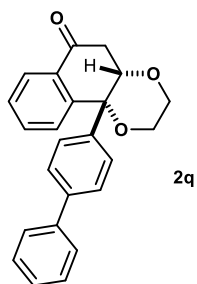
	Retention Time	Area	% Area	Height
1	5.451	8359377	87.20	897518
2	5.939	853282	8.90	98643
3	7.027	344601	3.59	35782
4	7.525	29602	0.31	3269



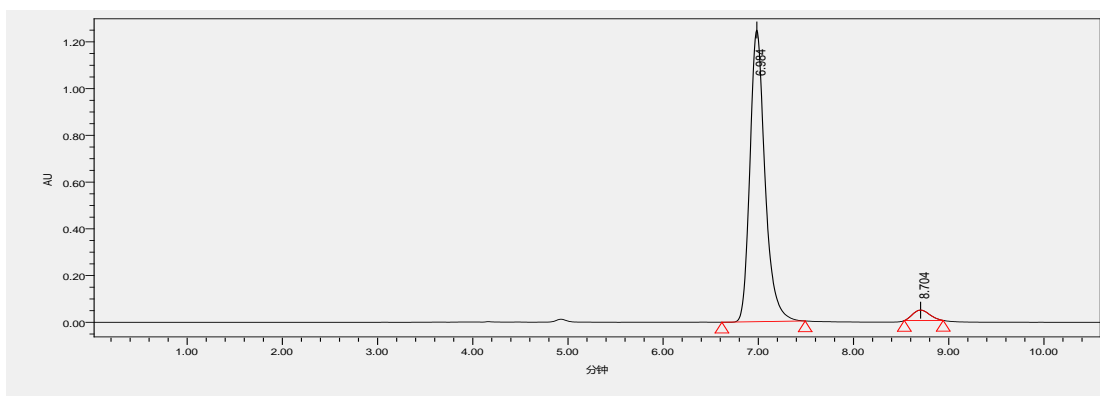
	Retention Time	Area	% Area	Height
1	19.545	50375957	51.35	1275910
2	21.217	47733121	48.65	1097567



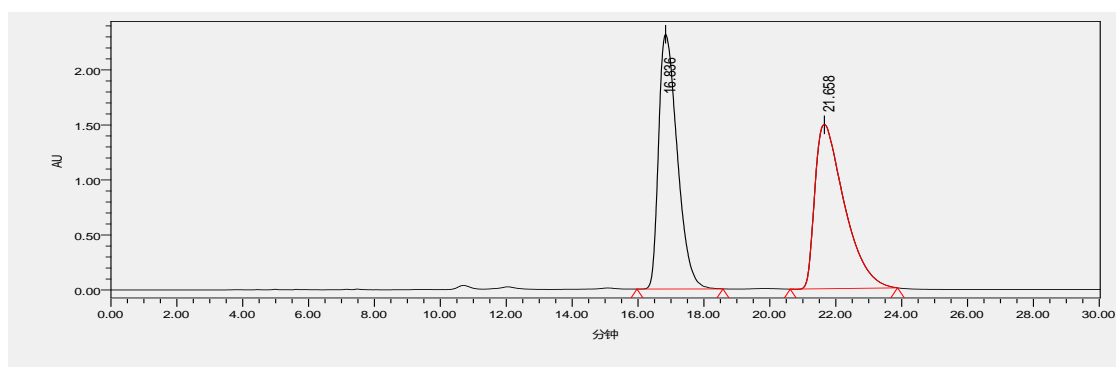
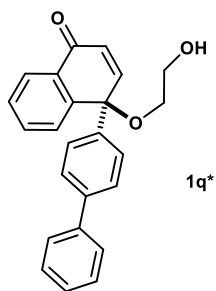
	Retention Time	Area	% Area	Height
1	19.536	25148	0.36	307
2	21.380	6953705	99.64	142758



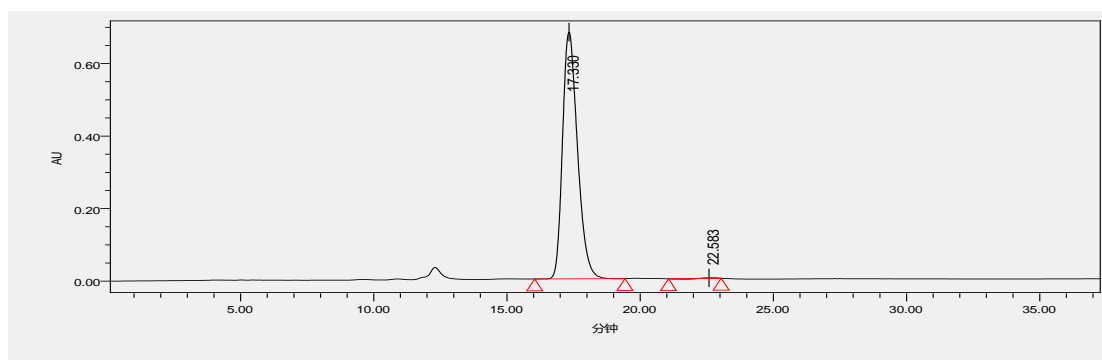
	Retention Time	Area	% Area	Height
1	7.033	5301981	50.30	465316
2	8.759	5238657	49.70	341384



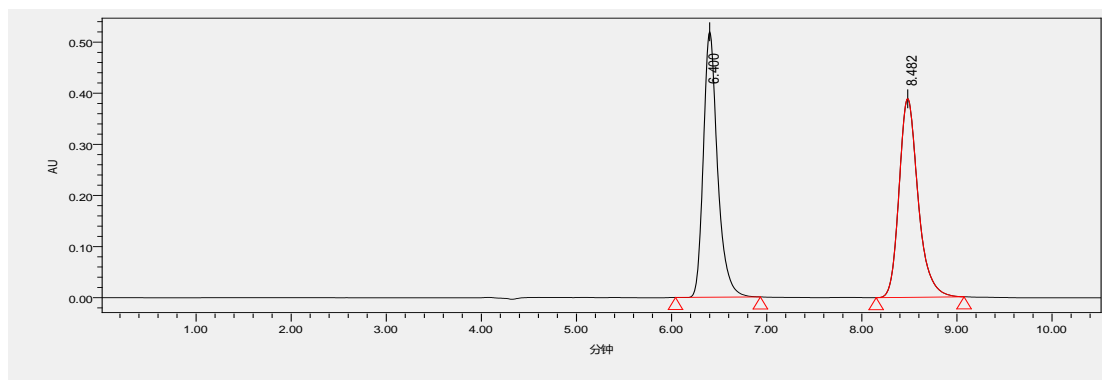
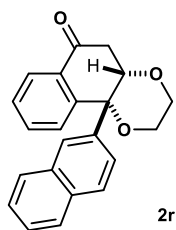
	Retention Time	Area	% Area	Height
1	6.984	13727764	96.16	1248112
2	8.704	548800	3.84	44542



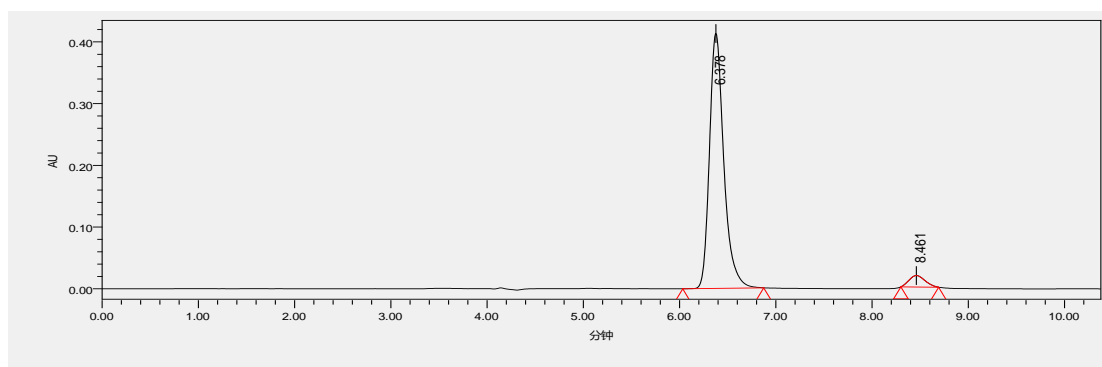
	Retention Time	Area	% Area	Height
1	16.836	91153126	49.60	2313954
2	21.658	92606661	50.40	1490444



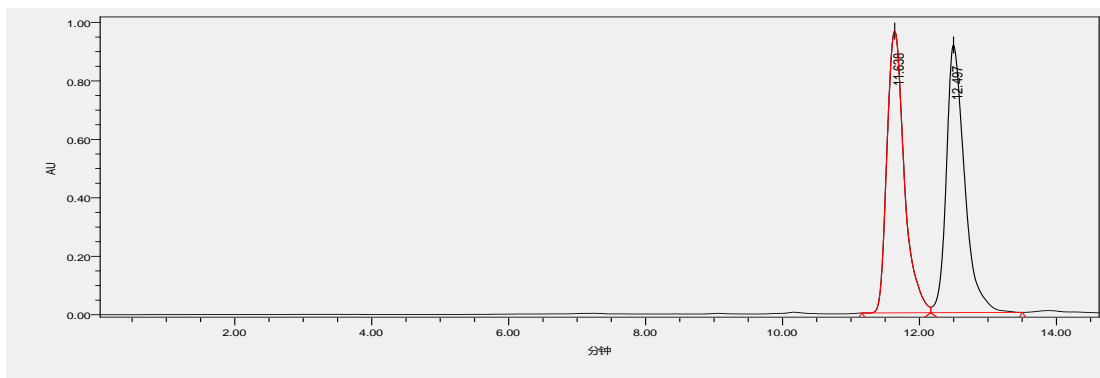
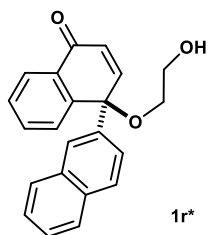
	Retention Time	Area	% Area	Height
1	17.330	26577006	99.62	680463
2	22.583	102385	0.38	1431



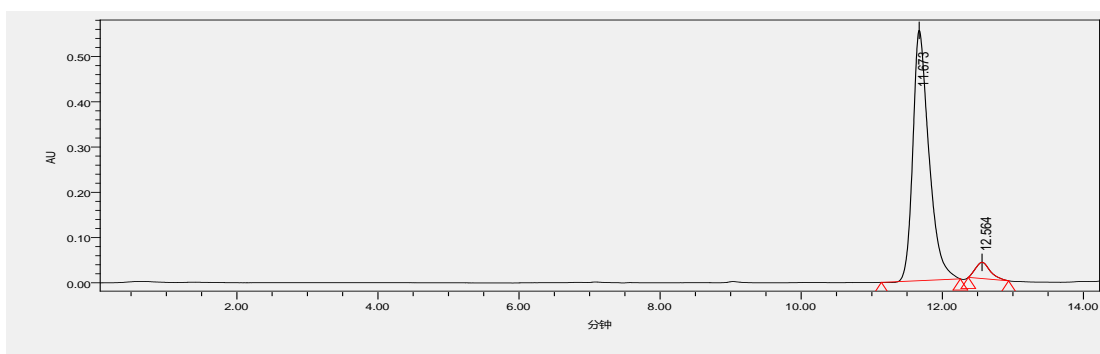
	Retention Time	Area	% Area	Height
1	6.400	5377990	49.86	519633
2	8.482	5407709	50.14	388874



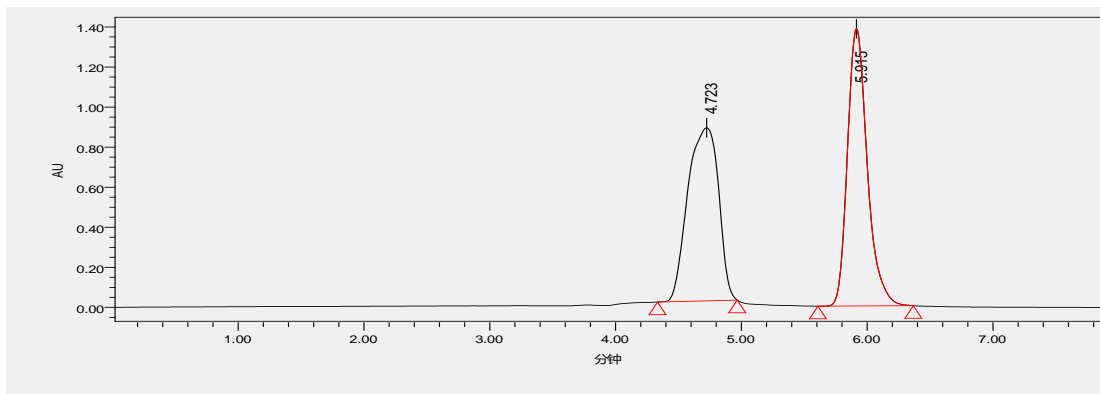
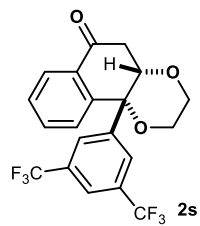
	Retention Time	Area	% Area	Height
1	6.385	9409661	95.58	912545
2	8.465	435487	4.42	38559



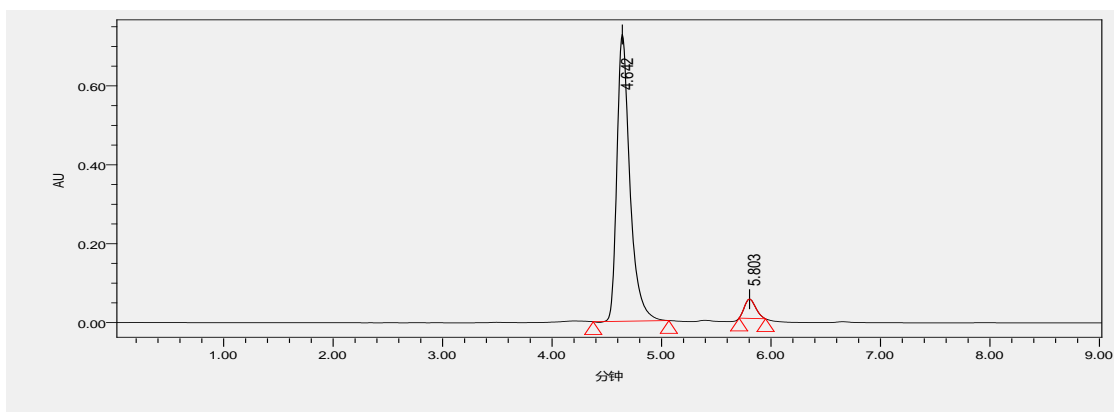
	Retention Time	Area	% Area	Height
1	11.638	16970801	50.03	963592
2	12.497	16949367	49.97	915480



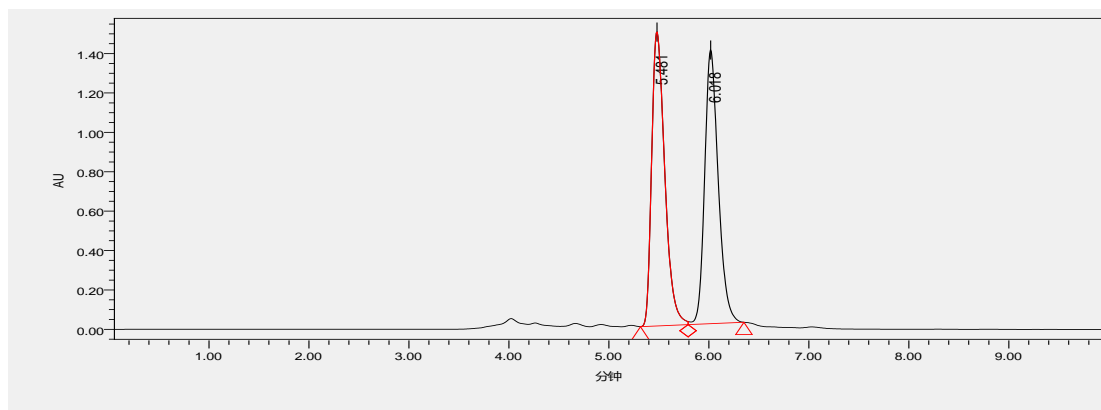
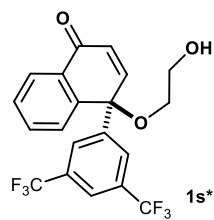
	Retention Time	Area	% Area	Height
1	11.673	8781843	94.40	553104
2	12.564	520485	5.60	35916



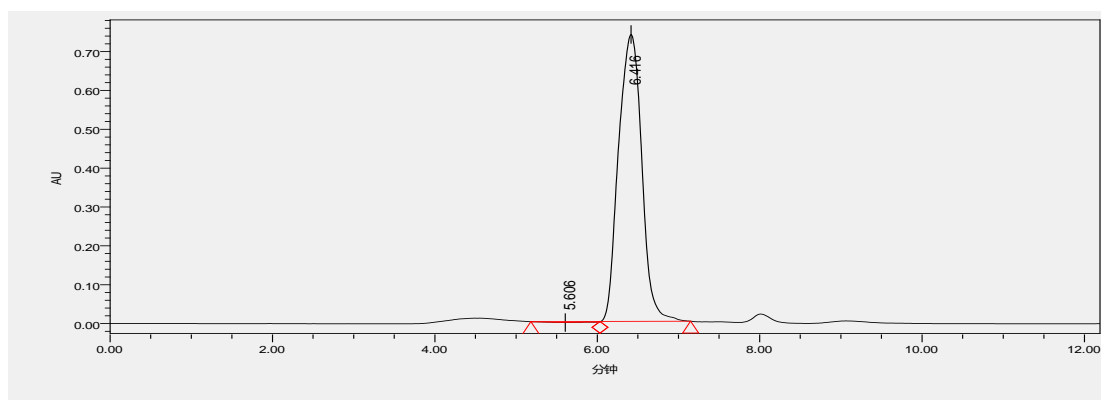
	Retention Time	Area	% Area	Height
1	4.723	14690496	49.20	864573
2	5.915	15169531	50.80	1385062



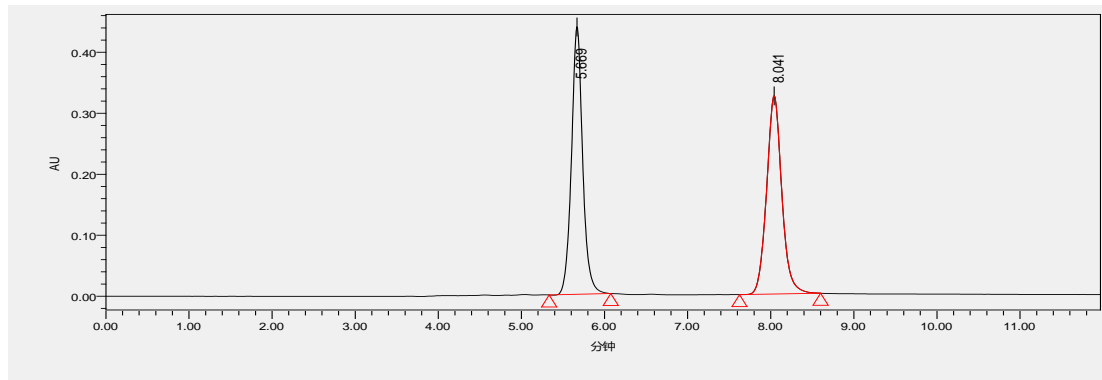
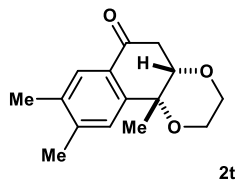
	Retention Time	Area	% Area	Height
1	4.642	6006953	94.51	727130
2	5.803	348976	5.49	49029



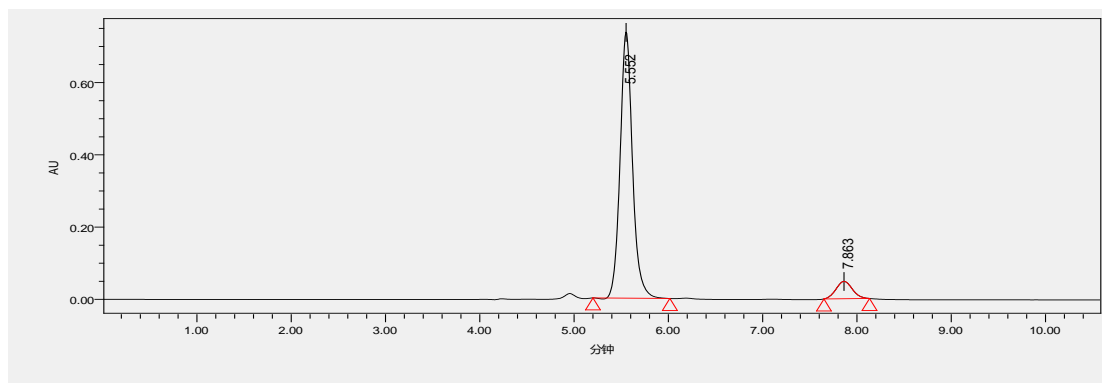
	Retention Time	Area	% Area	Height
1	5.481	13630022	50.87	1493901
2	6.018	13162433	49.13	1391559



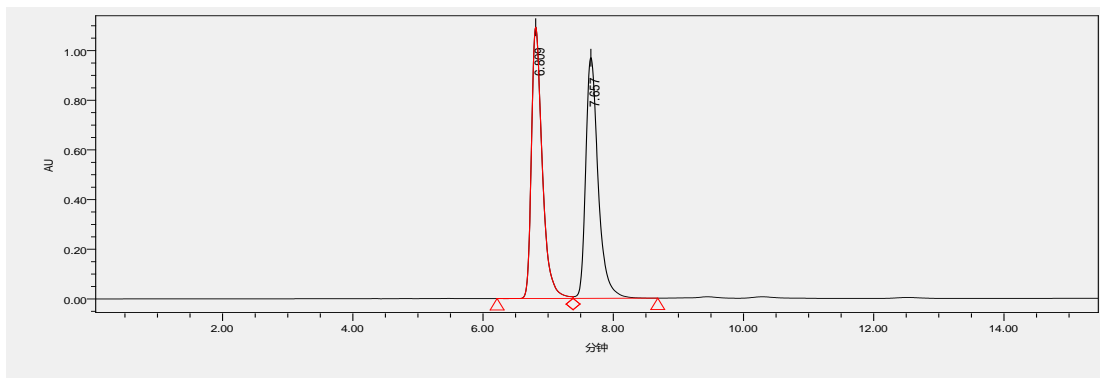
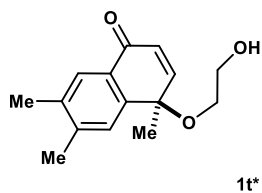
	Retention Time	Area	% Area	Height
1	5.406	78809	0.54	-2261
2	6.116	14648247	99.46	738413



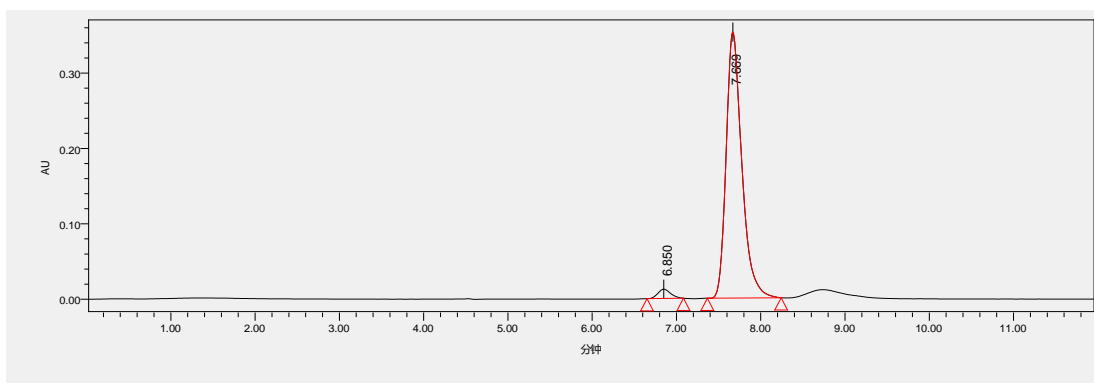
	Retention Time	Area	% Area	Height
1	5.669	4106523	49.85	439171
2	8.041	4130925	50.15	324988



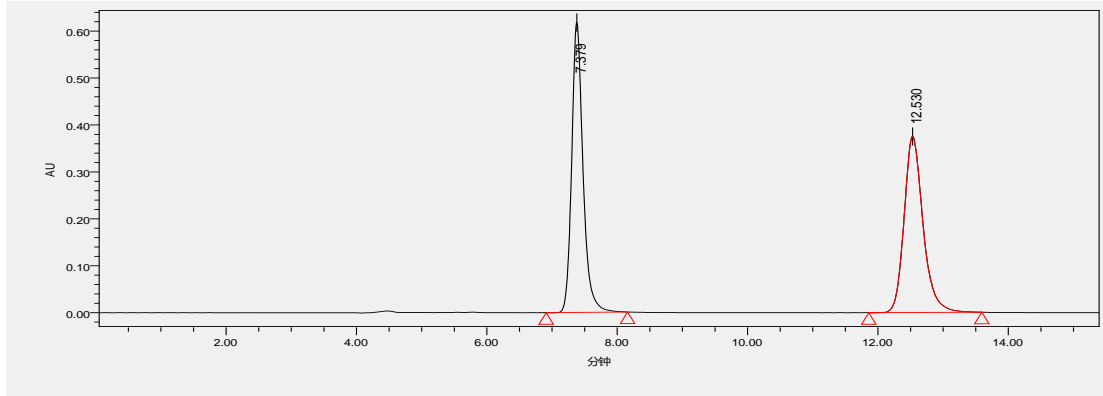
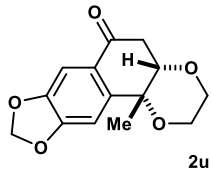
	Retention Time	Area	% Area	Height
1	5.552	6757231	93.51	737092
2	7.863	468771	6.49	43497



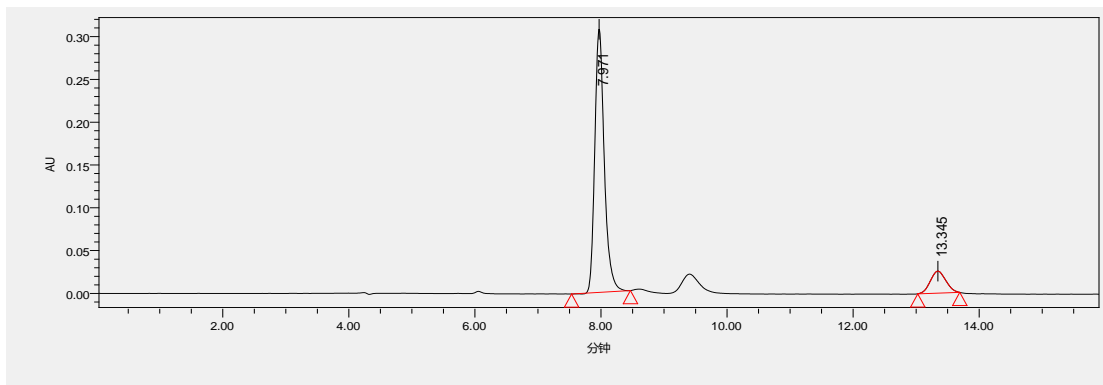
	Retention Time	Area	% Area	Height
1	6.809	12610145	49.46	1093088
2	7.657	12884301	50.54	969198



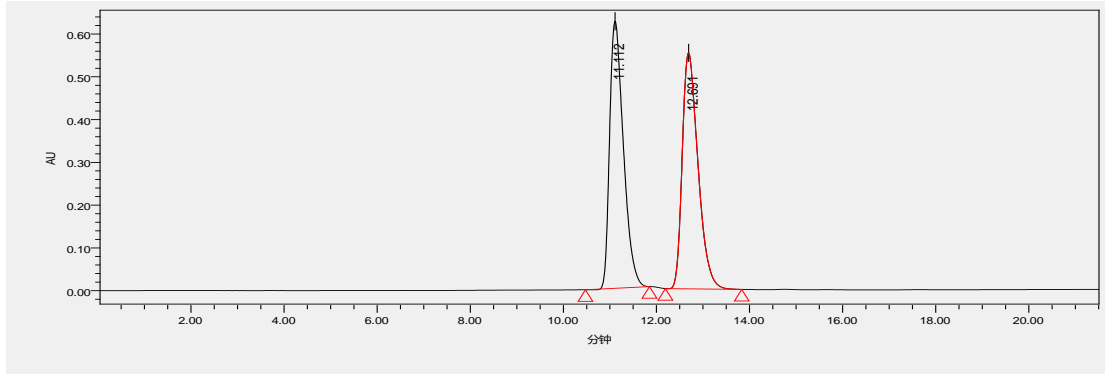
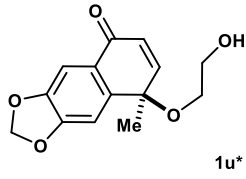
	Retention Time	Area	% Area	Height
1	6.850	113427	2.43	11705
2	7.669	4556574	97.57	353028



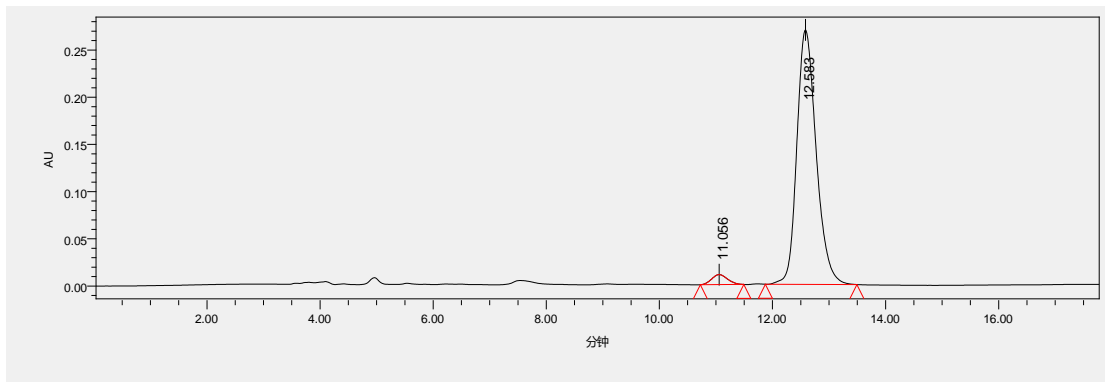
	Retention Time	Area	% Area	Height
1	7.379	7457765	49.62	618631
2	12.530	7571443	50.38	375490



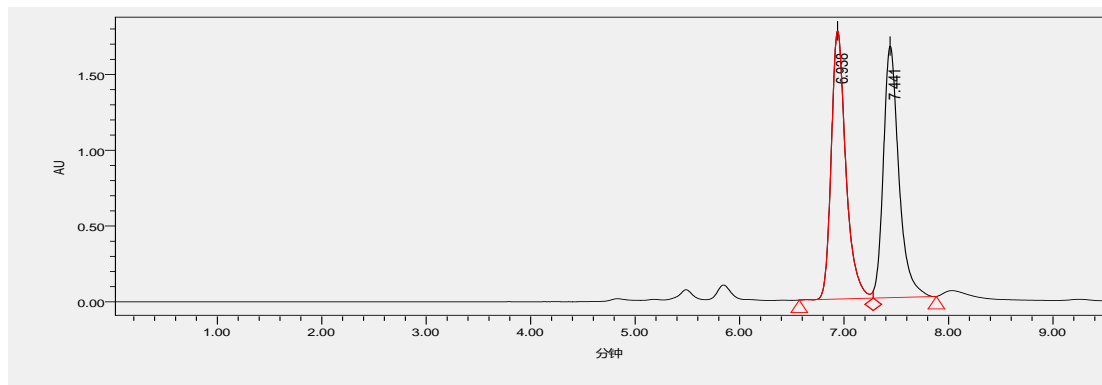
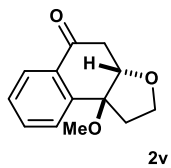
	Retention Time	Area	% Area	Height
1	7.971	3231115	93.39	307684
2	13.345	228668	6.61	17978



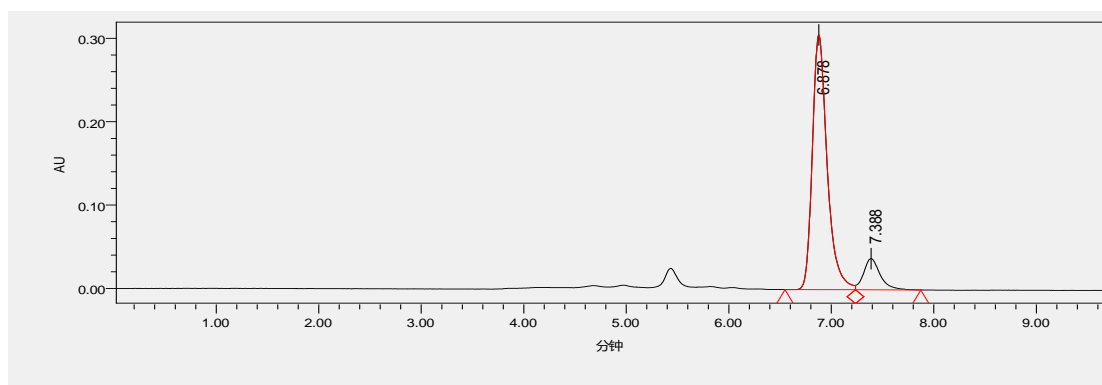
	Retention Time	Area	% Area	Height
1	11.112	12830963	49.74	624506
2	12.691	12963842	50.26	551671



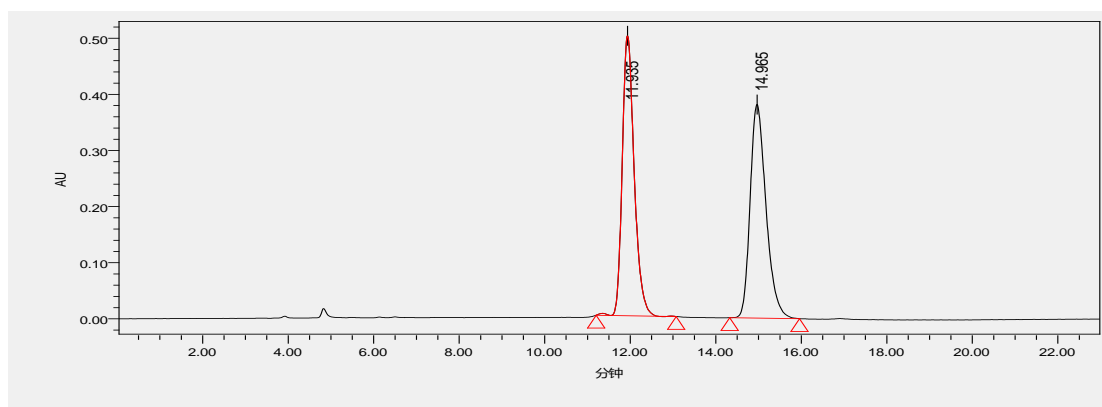
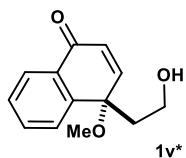
	Retention Time	Area	% Area	Height
1	11.056	206758	3.13	10619
2	12.583	6406629	96.87	269520



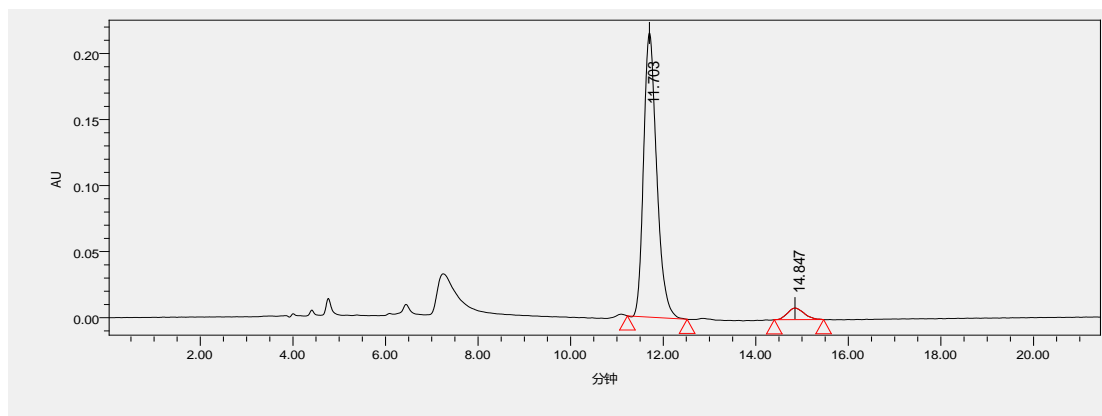
	Retention Time	Area	% Area	Height
1	6.938	17228996	50.22	1769761
2	7.441	17079322	49.78	1660004



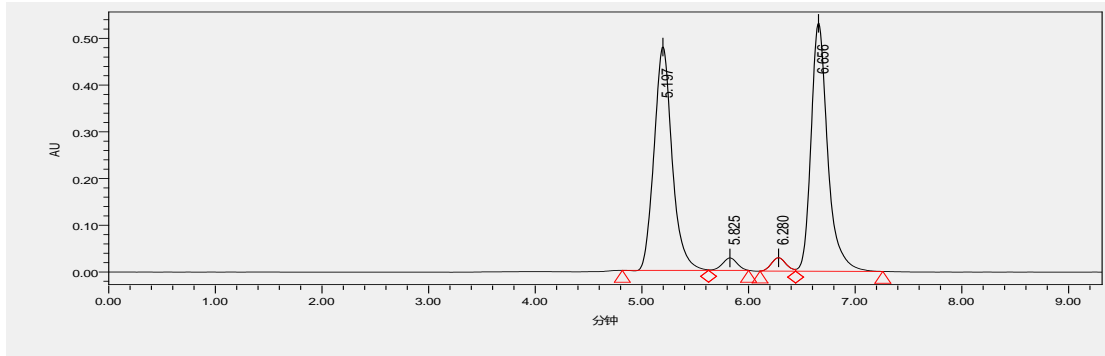
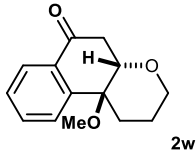
	Retention Time	Area	% Area	Height
1	6.878	3068324	87.96	305374
2	6.878	420041	12.04	37427



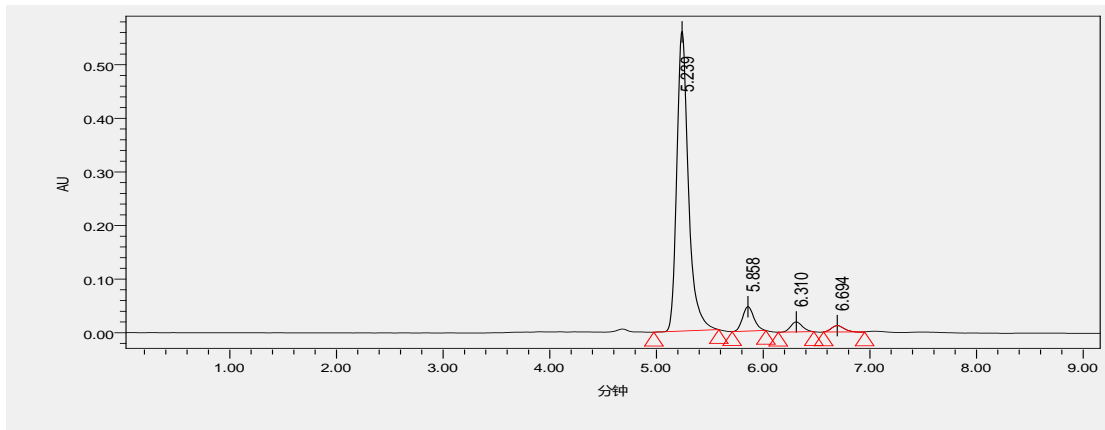
	Retention Time	Area	% Area	Height
1	11.935	9649870	49.81	498448
2	14.965	9722745	50.19	379512



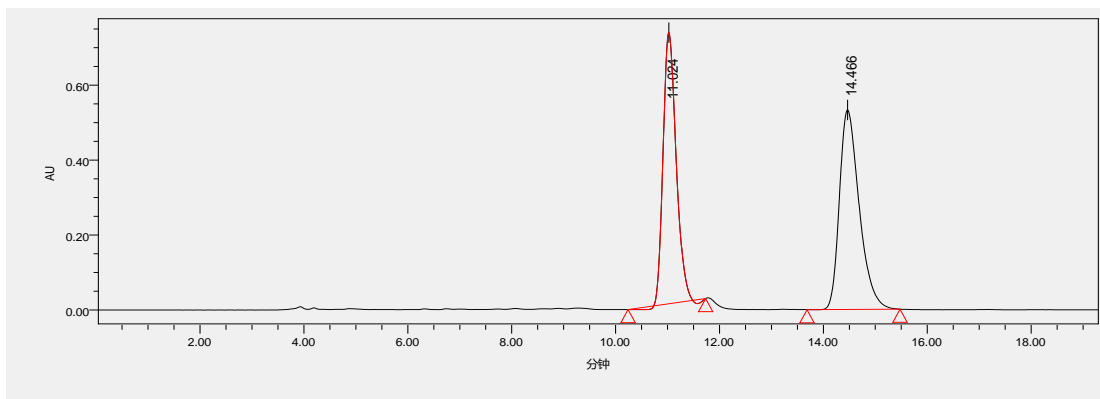
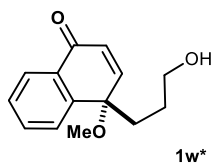
	Retention Time	Area	% Area	Height
1	11.703	4336177	95.93	223768
2	14.846	184106	4.07	9017



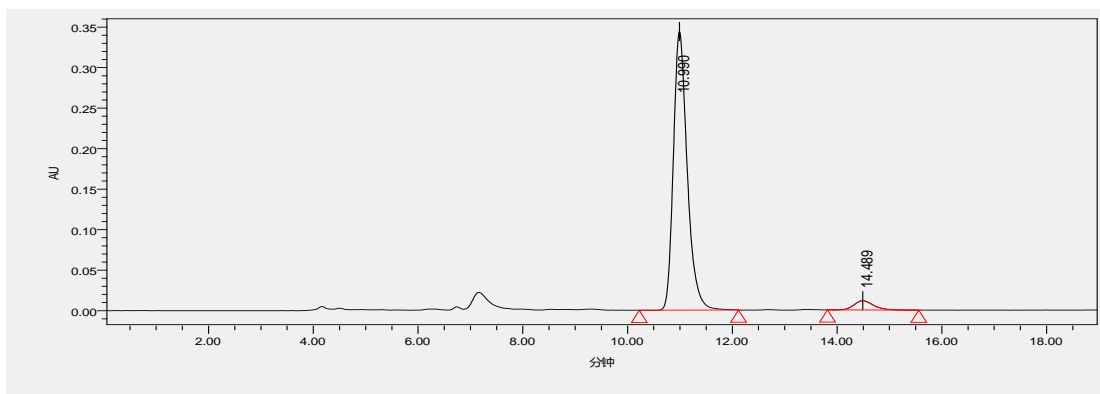
	Retention Time	Area	% Area	Height
1	5.197	5624645	47.31	478471
2	5.825	251144	2.11	26492
3	6.280	273045	2.30	28787
4	6.656	5739292	48.28	531257



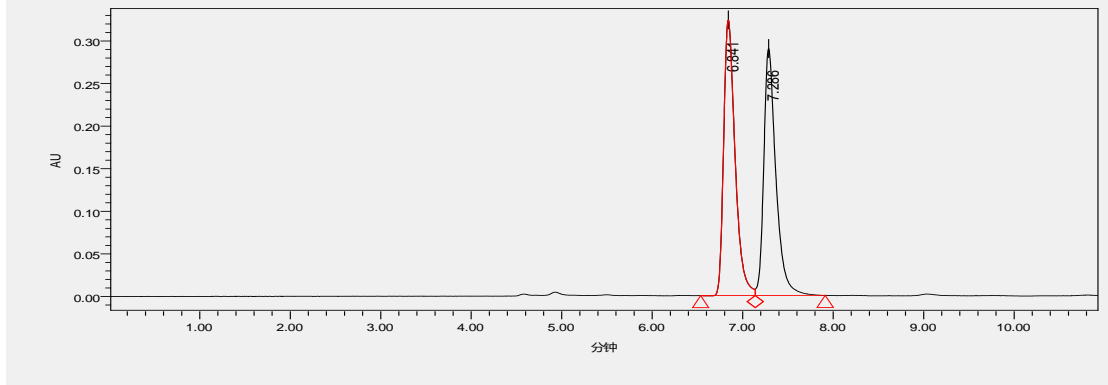
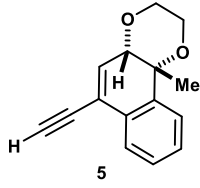
	Retention Time	Area	% Area	Height
1	5.239	4231981	87.96	559794
2	5.858	337935	7.02	45765
3	6.310	144260	3.00	18768
4	6.694	96946	2.02	11869



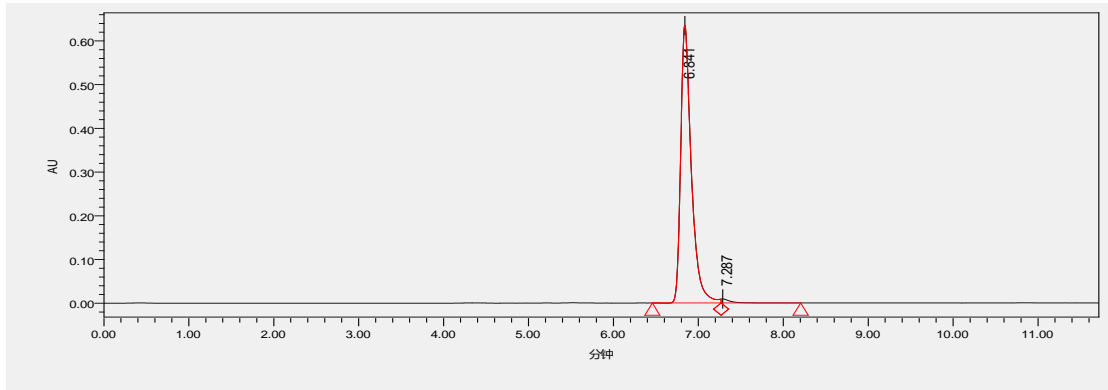
	Retention Time	Area	% Area	Height
1	11.024	13633418	49.14	734467
2	14.466	14112046	50.86	532734



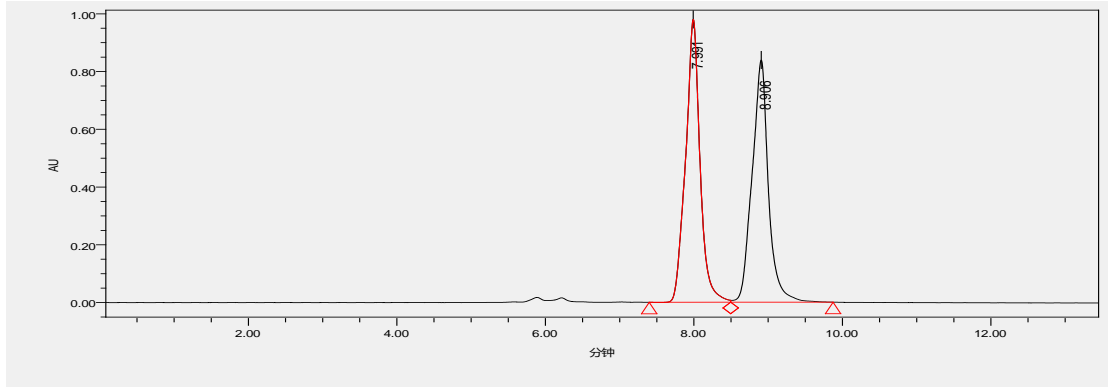
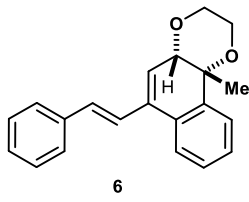
	Retention Time	Area	% Area	Height
1	10.990	6309947	95.54	343953
2	14.489	294791	4.46	11421



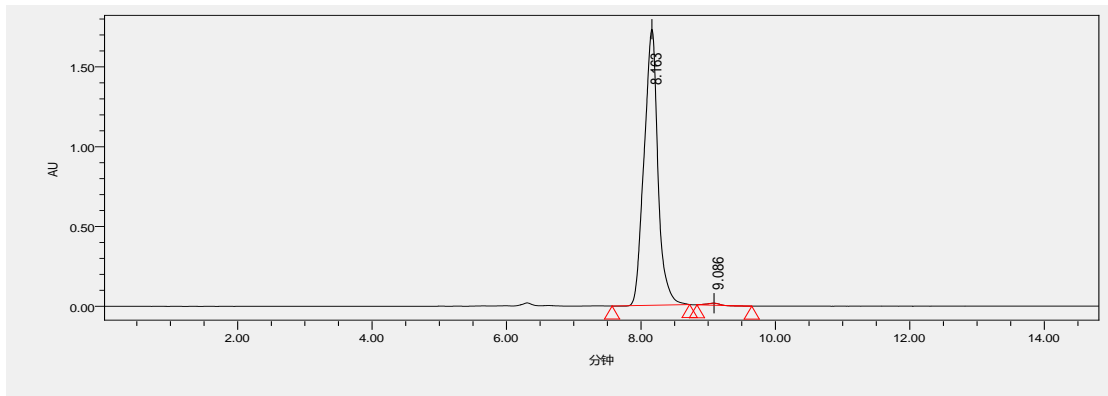
	Retention Time	Area	% Area	Height
1	6.841	2843513	51.33	323598
2	7.286	2696349	48.67	289795



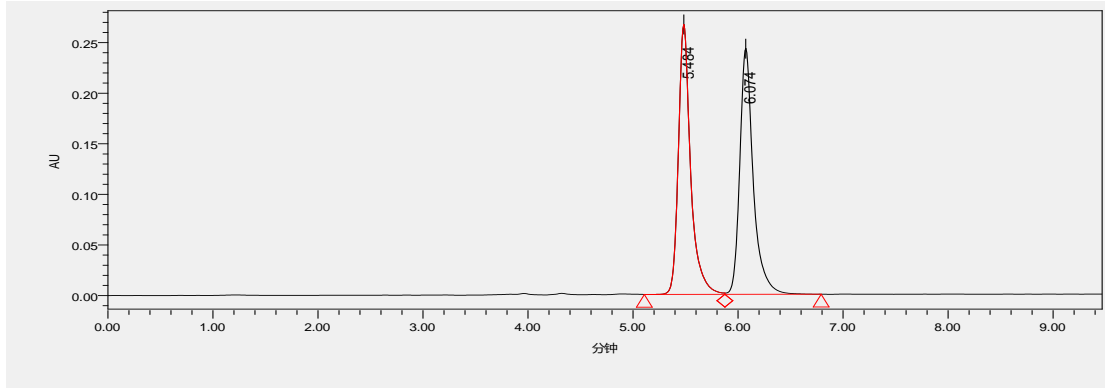
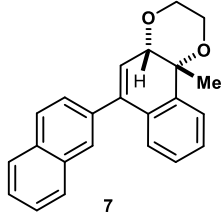
	Retention Time	Area	% Area	Height
1	6.841	5536692	98.80	634879
2	7.287	67431	1.20	9216



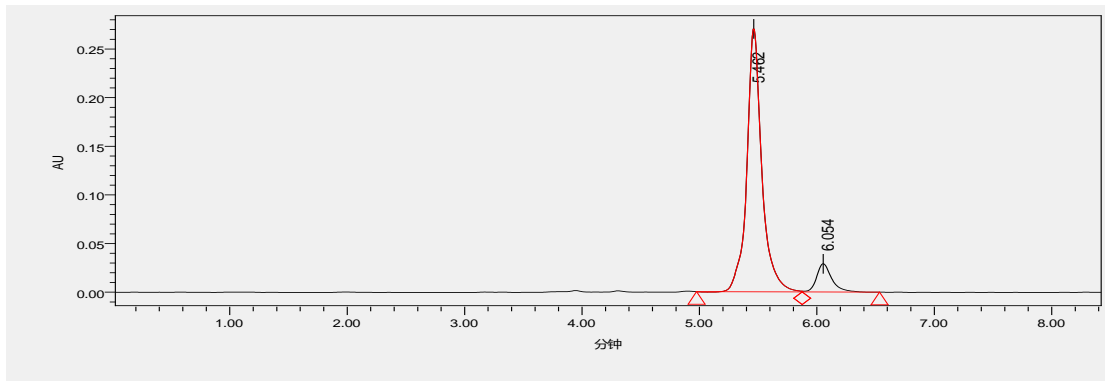
	Retention Time	Area	% Area	Height
1	7.991	13265788	50.89	979185
2	8.906	12800071	49.11	838523



	Retention Time	Area	% Area	Height
1	8.163	24740370	99.26	1729693
2	9.086	185567	0.74	12764



	Retention Time	Area	% Area	Height
1	5.484	2163121	49.98	266753
2	6.074	2164874	50.02	242984



	Retention Time	Area	% Area	Height
1	5.462	2411406	90.26	271127
2	6.054	260307	9.74	29130

NMR Spectra

