Electronic Supplementary Material (ESI) for Chemical Communications.

Asymmetric iminium ion-catalyzed conjugate addition of 2-hydroxycinnamaldehydes and 2-oxocarboxylic esters: synthesis of chiral polysubstituted bridged bicyclic ketals

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Supporting Information

Contents

A. General information

The ^{1}H and ^{13}C NMR spectra were recorded at600 MHz, 500 MHz or 400 MHz for ^{1}H and at 150 MHz, 125 MHz or 100 MHz for ^{13}C. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CDCl_3$ at 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR. d_6-DMSO at 2.50 ppm ^{1}H NMR, 39.52 ppm ^{13}C NMR). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra (HRMS) were obtained from the Waters Q-Tof Ultima Global. X-ray data were obtained from Zhongke chemical technology service center. Optical rotations are reported as follows: $[\alpha]_D^{20}$ (c in g per 100 mL, solvent: $CHCl_3$, MeOH).

Note: NMR signals containing common solvent contaminants were list. H_2O in $CDCl_3$ at 1.56 ppm ^{1}H NMR, and in d_6-DMSO at 3.33 ppm ^{1}H NMR; Ethyl acetate in $CDCl_3$ at 2.05 (s), 4.12 (q), 1.26 (t) ppm ^{1}H NMR; CH_2Cl_2 in $CDCl_3$ at 5.30 (s) ppm ^{1}H NMR; Grease in $CDCl_3$ at 0.86 (m), 1.26 (br, s) ppm 1H NMR.

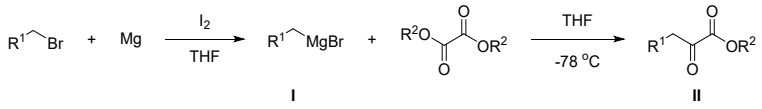
All the reactions were set up under air and using commercial solvents, without any precautions to exclude moisture, unless otherwise noted open air chemistry on the bench-top. Chromatographic purification of products was accomplished using force-flow chromatography (FC) on silica gel (300-400 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF254, 0.25 mm) were used, using UV light as the visualizing agent and a phosphomolybdic acid or basic aqueous potassium permanganate ($KMnO_4$) as stain developing solutions. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

HPLC analyses on chiral stationary phase were performed on a Hitachi Chromaster. Daicel Chiralpak IA, IB, IC, ID, OD-H or AD-H columns with *n*-hexane/*i*-PrOH as the eluent were used. HPLC traces were compared to racemic samples which prepared by mixture of two enantiomeric final products obtained using (*S*) and (*R*) catalyst.

Commercial reagents and solvents were purchased from Sigma Aldrich, Fluka, and Alfa Aesar used as received, without further purification. The 2-hydroxyinnamaldehyde **1** were prepared according to literature procedures. [1]

B. General procedure for the synthesis of α-Ketoesters 2

The synthesis of α-Ketoesters 2b-2s：



The α-Ketoesters **2** were prepared according to literature procedures. [2]

Step 1: To a stirred suspension of magnesium turnings (2.2 mmol, 1.1 equiv.) in anhydrous THF (2 mL) was added a crystal of I_2 as an activator. Then bromide (2.4 mmol, 1.2 equiv.) in anhydrous THF (2 mL) was added dropwise. The suspension was stirred until magnesium was disappeared at room temperature, and the resulting Grignard reagent was used directly for the next step.

Step 2: To a solution of diethyl oxalate (2 mmol, 1.0 equiv.) in anhydrous THF (4 mL) at −78 °C was added dropwise the Grignard reagents (commercially available or prepared as shown above). After stirring for 1 h at −78 °C, the mixture was warmed to room temperature, quenched with a saturated solution of NH_4Cl (5 mL), and extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in a rotary evaporator under vacuum. The residue was purified by silica gel column chromatography.

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[1] Chen, Y.-H.; Sun, X.-L.; Guan, H.-S.; Liu, Y.-K., *J. Org. Chem.* **2017**, *82*, 4774.

[2] Zhu, J.; Yuan, Y.; Wang, S.; Yao, Z.-J., *ACS Omega* **2017**, *2*(8), 4665.

C. Optimization of the reaction conditions

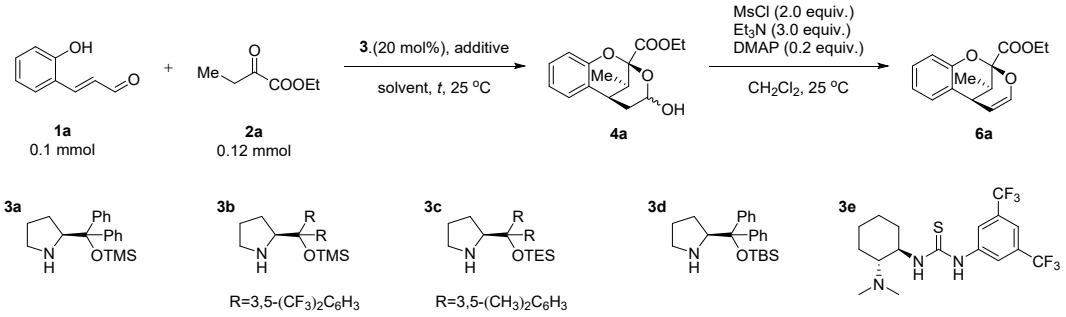
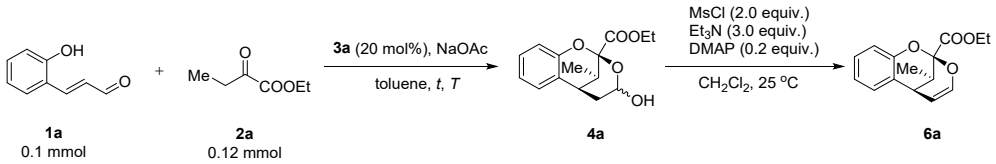


Table S1: Optimization of the Reaction Catalyst, Solvent and Additive

entry[*a*]	catalyst	solvent	additive	*t*(h)[*b*]	yield (%)[*c*]	ee (%)[*d*]	*dr* (%)[*e*]
1	**3a**	DCE	NaOAc	3	69	99	7:1
2	**3b**	DCE	NaOAc	48	47	99	4:1
3	**3c**	DCE	NaOAc	4	58	99	9:1
4	**3d**	DCE	NaOAc	5	47	99	7:1
5	**3a**	DCE	BA	4.5	76	99	9:1
7	**3a**	DCE	DABCO	3	62	99	7:1
8	**3a**	DCE	DBU	2	47	99	4:1
9	**3a**	toluene	NaOAc	3	76	99	11:1
10	**3a**	THF	NaOAc	>5.5	62	99	7:1
11	**3a**	$CHCl_3$	NaOAc	3	54	99	11:1
12	**3a**	EA	NaOAc	5.5	58	99	9:1
13	**3a**	Et_2O	NaOAc	>5.5	47	99	4:1

[*a*] Unless otherwise specified, all reactions were carried out in solvent (0.2 mL) with cat. (20 mol %), additive (20 mol%) at 25 °C. After workup, the mixture was purified by flash chromatography on silica gel to afford **4a**. Compound **4a** was respectively dissolved in CH_2Cl_2 (0.1 mmol in 0.5 mL) at 0 °C. TEA (3.0 equiv.), MsCl (2.0 equiv.) and DMAP (0.2 equiv.) were added in order, then transferred to 25 °C. After full conversion of the second step, the residue was purified by flash chromatography on gel to give product **6a**. [*b*] For the first step. [*c*] Isolated yield of **6a** over two steps. [*d*] Determined by HPLC analyses of isolated compound **6a** on chiral stationary phases. [*e*] Determined by ^1H NMR analyses of isolated compound **6a**.



1a 0.1 mmol + **2a** 0.12 mmol → **4a** → **6a**

Table S2: Optimization of the Reaction Temperature

entry[a]	catalyst	additive	*T* (℃)	*t* (h) [b]	yield (%) [c]	ee (%) [d]	*dr* (%) [e]
1	**3a**	NaOAc	0	40	43	99	10:1
2[f]	**3a**	NaOAc	0	6	62	99	5:1
3[f]	**3a**	NaOAc	25	2.5	51	99	4:1
4	**3a**	NaOAc	40	2.5	53	99	5:1

[*a*] Unless otherwise specified, all reactions were carried out in solvent (0.2 mL) with cat. (20 mol %), additive (20 mol%) at 25 °C. After workup, the mixture was purified by flash chromatography on silica gel to afford **4a**. Compound **4a** was dissolved in CH_2Cl_2 (0.1 mmol in 0.5 mL) at 0 °C. TEA (3.0 equiv.), MsCl (2.0 equiv.) and DMAP (0.2 equiv.) were added in order, then transferred to 25 °C. After full conversion of the second step, the residue was purified by flash chromatography on silica gel to give product **6a**. [*b*] For the first step. [*c*] Isolated yield of **6a** over two steps. [*d*] Determined by HPLC analyses of isolated compound **6a** on chiral stationary phases. [*e*] Determined by ^{1}H NMR analyses of isolated compound **6a**. [*f*] The reaction was carried out with **3e** (20 mol%).

DCE= dichloroethane

EA = ethyl acetate

THF = tetrahydrofuran

BA = benzoic acid

TEA = triethylamine

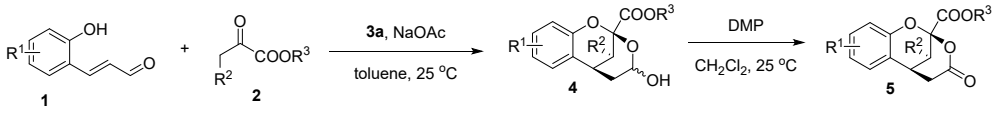
MsCl = methylsufonyl chloride

DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene

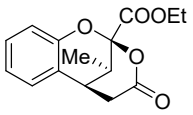
DMAP = 4-dimethylaminopyridine

DABCO = triethylenediamine

D. Scope of the reaction

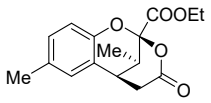


General procedure of oxidation: A glass vial equipped with a magnetic stirring bar was charged with catalyst **3a** (0.02 mmol, 6.5 mg, 20 mol%) in toluene (0.2 mL), then 2-hydroxycinnamaldehyde **1** (0.1 mmol, 1.0 equiv.), NaOAc (0.02 mmol, 1.6 mg, 20 mol%) and 2-oxocarboxylic ester **2** (0.12 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at 25 °C for 3 h until the material **1** disappeared. After completion of the reaction, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **4**. Then the product **4** (1.0 equiv.) was dissolved in CH_2Cl_2 (0.2 mmol in 1 mL). Dess-Martin Periodinane (DMP, 1.5 equiv.) was added to the reaction mixture. After full conversion of the reaction, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give product **5a, 5b** and **5i** for NMR and HPLC analysis.



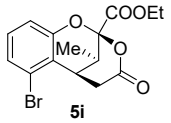
5a

5a was obtained as a white solid 21 mg in 76% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.3 (dd, J = 6.9, 1.5 Hz, 1H), 7.1 (dd, J = 7.6, 1.8 Hz, 1H), 7.1 (td, J = 8.0, 7.4, 1.2 Hz, 3H), 4.4 (ddd, J = 10.5, 7.1, 3.5 Hz, 2H), 3.1 – 3.0 (m, 2H), 2.9 – 2.8 (m, 1H), 2.8 (qd, J = 6.9, 1.7 Hz, 1H), 1.4 (t, J = 7.1 Hz, 4H), 1.0 (d, J = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ δ 166.9, 164.6, 148.5, 129.5, 129.5, 123.5, 121.9, 117.9, 100.7, 63.0, 40.5, 34.7, 31.7, 14.1, 13.5 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{15}H_{17}O_5^+$ 277.1071, found 277.1072. **$[\alpha]_D^{20}$** -52.13 (c = 0.5 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [n-hexane/i-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 14.15 min, t_{minor} = 10.85 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 11:1**.



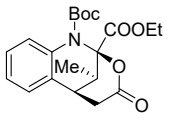
5b

5b was obtained as a yellow solid 14 mg in 48% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.0 (dd, J = 8.4, 2.2 Hz, 1H), 7.0 (d, J = 8.4 Hz, 1H), 6.9 (d, J = 2.2 Hz, 1H), 4.4 (dtt, J = 14.3, 7.1, 3.6 Hz, 2H), 3.0 – 2.9 (m, 2H), 2.9 (dd, J = 19.4, 3.7 Hz, 1H), 2.8 – 2.7 (m, 1H), 2.3 (s, 3H), 1.4 (t, J = 7.2 Hz, 4H), 1.0 (d, J = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 164.7, 146.2, 133.0, 130.1, 129.7, 121.5, 117.6, 100.8, 63.0, 40.6, 34.7, 31.8, 20.6, 14.1, 13.5 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{16}H_{19}O_5^+$ 291.1227, found 291.1222. **$[\alpha]_D^{20}$** -86 (c = 0.8 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [n-hexane/i-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 24.31 min, t_{minor} = 9.96 min, **ee = 97%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



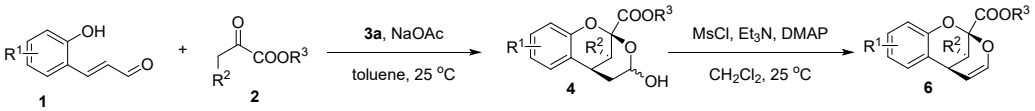
5i

5i was obtained as a white solid 15 mg in 39% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 (d, J = 1.1 Hz, 1H), 7.1 (t, J = 8.1 Hz, 1H), 6.9 (dd, J = 8.3, 1.1 Hz, 1H), 4.4 (qd, J = 7.2, 2.6 Hz, 2H), 3.4 (ddd, J = 5.6, 3.6, 1.6 Hz, 1H), 3.0 (dd, J = 18.7, 5.8 Hz, 1H), 2.8 (dt, J = 19.0, 1.4 Hz, 1H), 2.7 (qd, J = 7.0, 3.6 Hz, 1H), 1.4 (t, J = 7.1 Hz, 3H), 1.3 (d, J = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 164.8, 150.1, 130.2, 126.7, 124.7, 123.2, 116.9, 101.2, 63.1, 33.4, 31.2, 30.6, 14.1, 12.5 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{15}H_{16}{}^{79}BrO_5^+$ 355.0176, found 355.0179; *calcd.* for $C_{15}H_{16}{}^{81}BrO_5^+$ 357.0155, found 357.0157. **$[\alpha]_D^{20}$** -71.62 (c = 0.7 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak ID column [n-hexane/i-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 21.61 min, t_{minor} = 23.84 min, **ee = 91%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 7:1**.

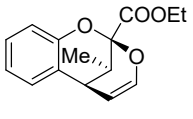


5'

5' was obtained as a colorless oil 15 mg in 41% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 (td, J = 7.8, 1.6 Hz, 1H), 7.1 (dd, J = 7.6, 1.6 Hz, 1H), 7.0 (td, J = 7.5, 1.2 Hz, 1H), 6.9 (dd, J = 8.1, 1.1 Hz, 1H), 4.2 (q, J = 7.2 Hz, 2H), 3.7 (dq, J = 8.6, 7.0 Hz, 1H), 3.3 (ddd, J = 8.8, 5.5, 3.5 Hz, 1H), 2.8 (dd, J = 5.8, 4.5 Hz, 2H), 1.6 (s, 9H), 1.2 (t, J = 7.1 Hz, 3H) 1.2 (d, J = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.4, 167.7, 160.4, 151.4, 136.9, 128.7, 128.1, 126.7, 124.4, 117.6, 85.2, 62.5, 44.2, 38.0, 34.5, 27.7, 13.9, 12.6 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{20}H_{26}NO_6^+$ 376.1755, found 376.1756. **$[\alpha]_D^{20}$** +24.72 (c = 1.0 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 35.62 min, t_{minor} = 23.18 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



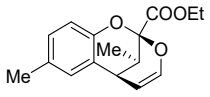
General procedure of dehydration: The method for obtaining product **4** has been described above. Then the product **4** (1.0 equiv.) was dissolved in CH_2Cl_2 (0.2 mmol in 1 mL) at 0 °C in the ice bath. TEA (3.0 equiv.), MsCl (2.0 equiv.), DMAP (0.2 equiv.) were added to the reaction mixtures in order. After full conversion of the reaction, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100/1 to 10/1) to give product **6** for NMR and HPLC analysis.



6a

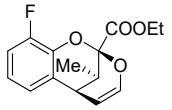
6a was obtained as a white solid 19 mg in 76% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.2 (ddd, *J* = 8.1, 7.2, 1.7 Hz, 1H), 7.1 (ddd, *J* = 11.4, 7.8, 1.5 Hz, 2H), 6.9 (td, *J* = 7.3, 1.3 Hz, 1H), 6.4 (d, *J* = 5.8 Hz, 1H), 5.3 (dd, *J* = 7.1, 5.8 Hz, 1H), 4.4 – 4.3 (m, 2H), 3.2 (dd, *J* = 7.1, 2.9 Hz, 1H), 2.6 (qd, *J* = 6.9, 2.9 Hz, 1H), 1.4 (t, *J* = 7.2 Hz, 3H), 0.9 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 166.6, 150.9, 140.6, 128.0, 127.7, 124.3, 121.9, 116.6, 108.0, 98.3, 62.4, 33.6, 30.5, 14.1, 13.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{15}H_{17}O_4^+$ 261.1121, found 261.1125. **$[\alpha]_D^{20}$** -228.93 (*c* = 0.50 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak OD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], *λ* = 210 nm, t_{major} = 8.47 min, t_{minor} = 6.05 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 11:1**.



6b

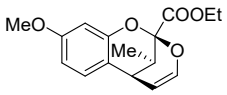
6b was obtained as a yellow solid 17 mg in 62% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.0 – 6.9 (m, 2H), 6.8 (d, *J* = 1.9 Hz, 1H), 6.4 (d, *J* = 5.7 Hz, 1H), 5.3 (dd, *J* = 7.2, 5.8 Hz, 1H), 4.4 – 4.3 (m, 2H), 3.1 (dd, *J* = 7.1, 2.9 Hz, 1H), 2.6 (qd, *J* = 7.0, 2.9 Hz, 1H), 2.3 (s, 3H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.9 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 166.7, 148.6, 140.7, 131.2, 128.4, 128.2, 124.0, 116.3, 108.0, 98.3, 62.4, 33.6, 30.5, 20.6, 14.1, 13.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{16}H_{19}O_4^+$ 275.1278, found 275.1273. **$[\alpha]_D^{20}$** -67.64 (*c* = 0.75 in $CHCl_3$). The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 9:1**.



6c

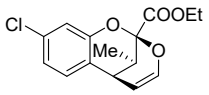
6c was obtained as a white solid 15 mg in 54% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.0 – 6.9 (m, 1H), 6.9 – 6.8 (m, 2H), 6.4 (d, *J* = 5.7 Hz, 1H), 5.3 (dd, *J* = 7.1, 5.8 Hz, 1H), 4.5 – 4.3 (m, 2H), 3.2 (ddd, *J* = 7.2, 3.0, 1.3 Hz, 1H), 2.6 (qd, *J* = 6.9, 2.9 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.9 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 166.1, 152.1, 149.6,

140.9, 127.1, 122.9 (d, *J* = 3.6 Hz), 121.8 (d, *J* = 6.7 Hz), 114.8 (d, *J* = 17.9 Hz), 107.5, 98.1, 62.6, 33.3 (d, *J* = 2.7 Hz), 30.4, 14.1, 13.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{15}H_{16}FO_4^+$ 279.1027, found 279.1025. **$[\alpha]_D^{20}$** -52.27 (*c* = 0.75 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 5.16 min, t_{minor} = 5.51 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6d

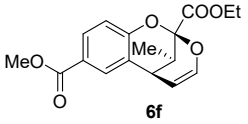
6d was obtained as a yellow solid 17 mg in 48% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.9 (d, *J* = 8.3 Hz, 1H), 6.7 (d, *J* = 2.5 Hz, 1H), 6.5 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.4 (d, *J* = 5.8 Hz, 1H), 5.3 (dd, *J* = 7.1, 5.8 Hz, 1H), 4.5 – 4.3 (m, 2H), 3.8 (s, 3H), 3.1 (dd, *J* = 7.1, 3.0 Hz, 1H), 2.6 (qd, *J* = 6.9, 2.9 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.9 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 159.3, 151.6, 140.3, 128.3, 116.5, 108.5, 108.4, 101.9, 98.3, 62.4, 55.4, 32.8, 30.7, 14.1, 13.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{16}H_{19}O_5^+$ 291.1227, found 291.1224 **$[\alpha]_D^{20}$** -101.80 (*c* = 0.85 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 15.90 min, t_{minor} = 32.61 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6e

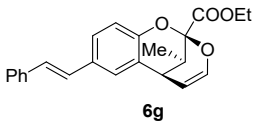
6e was obtained as a white solid 16 mg in 54% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate =40/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.1 (d, *J* = 2.0 Hz, 1H), 7.0 (d, *J* = 8.0 Hz, 1H), 6.9 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.4 (d, *J* = 5.8 Hz, 1H), 5.3 (dd, *J* = 7.1, 5.8 Hz, 1H), 4.4 (qq, *J* = 10.8, 7.1 Hz, 2H), 3.1 (dd, *J* = 7.1, 3.0 Hz, 1H), 2.6 (qd, *J* = 7.0, 3.0 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.9 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 151.6, 140.7, 132.8, 128.7, 123.0, 122.0, 117.0, 107.7, 98.3,

62.5, 33.1, 30.3, 14.1, 13.0 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{15}H_{16}{}^{35}ClO_4{}^+$ 295.0732, found 295.0730; *calcd.* for $C_{15}H_{16}{}^{37}ClO_4{}^+$ 297.0301, found 297.0303. **$[\alpha]_D^{20}$** -167.90 (*c* = 0.70 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak Id column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 7.15 min, t_{minor} = 6.51 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6f

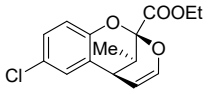
6f was obtained as a white solid 17 mg in 53% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.8 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.7 (d, *J* = 2.1 Hz, 1H), 7.0 (d, *J* = 8.5 Hz, 1H), 6.3 (d, *J* = 5.8 Hz, 1H), 5.3 (dd, *J* = 7.1, 5.8 Hz, 1H), 4.4 – 4.2 (m, 2H), 3.8 (s, 3H), 3.2 (dd, *J* = 7.1, 3.0 Hz, 1H), 2.6 (qd, *J* = 6.9, 2.9 Hz, 1H), 1.3 (t, *J* = 7.1 Hz, 3H), 0.8 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 166.1, 155.0, 140.6, 129.9, 129.7, 124.5, 123.8, 116.5, 107.7, 98.5, 62.6, 52.0, 33.4, 30.3, 14.1, 13.0 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{17}H_{19}O_6{}^+$ 319.1176, found 319.1176. **$[\alpha]_D^{20}$** -121.18 (*c* = 0.85 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak ID column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 12.22 min, t_{minor} = 11.21 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6g

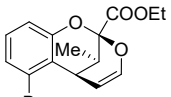
6g was obtained as a white solid 17 mg in 47% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate =50/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.5 – 7.5 (m, 2H), 7.3 (t, *J* = 7.7 Hz, 3H), 7.3 – 7.2 (m, 2H), 7.1 (d, *J* = 8.5 Hz, 1H), 7.0 (d, *J* = 5.1 Hz, 2H), 6.4 (d, *J* = 5.8 Hz, 1H), 5.3 (dd, *J* = 7.2, 5.7 Hz, 1H), 4.5 – 4.3 (m, 2H), 3.2 (dd, *J* = 7.1, 2.9 Hz, 1H), 2.6 (qd, *J* = 6.9, 2.9 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.9 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 150.6, 140.7, 137.5, 131.4, 128.7, 127.9, 127.4, 127.3, 126.3, 126.1, 126.0, 124.6, 116.9, 107.9, 62.5, 33.7, 30.5, 14.2, 13.1 ppm.

HRMS: $[M+H]^+$ *calcd.* for $C_{23}H_{23}O_4^+$ 363.1591, found 363.1591. **$[\alpha]_D^{20}$** -206.12 (*c* = 0.85 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 13.05 min, t_{minor} = 9.30 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 14:1**.



6h

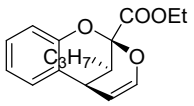
6h was obtained as a white solid 16 mg in 54% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.1 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.1 – 7.0 (m, 2H), 6.4 (d, *J* = 5.8 Hz, 1H), 5.3 (dd, *J* = 7.2, 5.7 Hz, 1H), 4.5 – 4.3 (m, 2H), 3.1 (dd, *J* = 7.1, 2.9 Hz, 1H), 2.6 (qd, *J* = 7.0, 2.9 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.9 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 149.6, 141.0, 127.7, 127.6, 126.5, 126.0, 117.9, 107.4, 98.3, 62.5, 33.5, 30.2, 14.1, 13.0 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{15}H_{16}{}^{35}ClO_4^+$ 295.0732, found 295.0733; *calcd*. $C_{15}H_{16}{}^{37}ClO_4^+$ 297.0703, found 297.0702. **$[\alpha]_D^{20}$** -148.36 (*c* = 0.75 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IB column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 19.75 min, t_{minor} = 11.13 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6i

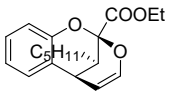
6i was obtained as a white solid 15 mg in 34% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 40/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.1 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.0 (t, *J* = 8.0 Hz, 1H), 6.9 (dt, *J* = 8.1, 1.0 Hz, 1H), 6.5 (d, *J* = 5.8 Hz, 1H), 5.1 (td, *J* = 6.2, 1.6 Hz, 1H), 4.4 (qq, *J* = 10.8, 7.2 Hz, 2H), 3.6 (dd, *J* = 6.6, 2.2 Hz, 1H), 2.4 (qt, *J* = 6.8, 1.9 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 1.1 (d, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 152.7, 140.9, 128.7, 128.2, 125.1, 121.1, 115.6, 101.9, 98.1, 62.5, 33.3, 30.2, 14.1, 12.6 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{15}H_{16}{}^{79}BrO_4^+$ 339.0227,

found 339.0225; *calcd.* for $C_{15}H_{16}{}^{81}BrO_4{}^+$ 341.0207, found 341.0209. **$[\alpha]_D{}^{20}$** -106.86 (*c* = 0.35 in $CHCl_3$). The diastereomeric ratio was determined by ^1H NMR, ***dr* = 5:1**.



6j

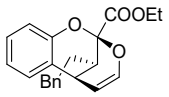
6j was obtained as a yellow oil 12 mg in 42% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 75/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 (td, *J* = 7.8, 1.7 Hz, 1H), 7.1 – 7.0 (m, 2H), 6.9 (td, *J* = 7.3, 1.3 Hz, 1H), 6.4 (d, *J* = 5.7 Hz, 1H), 5.3 (dd, *J* = 7.2, 5.7 Hz, 1H), 4.5 – 4.3 (m, 3H), 3.3 (dd, *J* = 7.3, 2.9 Hz, 1H), 2.5 (dt, *J* = 10.6, 3.1 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 1.3 – 1.3 (m, 1H), 1.2 (ddt, *J* = 15.7, 9.5, 2.8 Hz, 2H), 1.1 – 1.0 (m, 1H), 0.8 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 151.1, 140.8, 127.9, 127.7, 124.2, 121.8, 116.6, 107.7, 98.4, 62.4, 35.2, 30.3, 28.4, 19.8, 14.1, 13.8 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{17}H_{21}O_4{}^+$ 289.1434, found 289.1431. **$[\alpha]_D{}^{20}$** -56.00 (*c* = 0.60 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak ID column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 21.63 min, t_{minor} = 48.50 min, **ee = 99%**. The diastereomeric ratio was determined by ^1H NMR, ***dr* = 8:1**.



6k

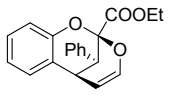
6k was obtained as a colorless oil 14 mg in 44% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 75/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.1 (td, *J* = 7.8, 7.3, 1.7 Hz, 1H), 7.1 – 7.0 (m, 2H), 6.9 (td, *J* = 7.3, 1.2 Hz, 1H), 6.4 (d, *J* = 5.7 Hz, 1H), 5.3 (dd, *J* = 7.2, 5.7 Hz, 1H), 4.4 – 4.3 (m, 2H), 3.3 (dd, *J* = 7.3, 2.9 Hz, 1H), 2.4 (dt, *J* = 10.5, 2.9 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 1.3 – 1.1 (m, 8H), 0.8 (t, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR** (150 MHz, $CDCl_3$) δ 166.8, 151.2, 140.9, 127.9, 127.7, 124.3, 121.9, 116.7, 107.7, 98.5, 62.4, 35.5, 31.4, 30.4, 26.3, 26.2, 22.4, 14.2, 14.0 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{19}H_{25}O_4{}^+$ 317.1747, found 317.1747. **$[\alpha]_D{}^{20}$** -53.68 (*c* = 1.00 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column

[*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 4.67 min, t_{minor} = 6.6 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6l

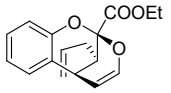
6l was obtained as a colorless oil 12 mg in 34% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 7.5 Hz, 2H), 7.2 – 7.1 (m, 2H), 7.1 – 7.0 (m, 4H), 7.0 – 6.9 (m, 1H), 6.4 (d, *J* = 5.7 Hz, 1H), 5.3 (dd, *J* = 7.2, 5.7 Hz, 1H), 4.3 (dddd, *J* = 14.9, 10.7, 7.1, 3.6 Hz, 2H), 3.3 (dd, *J* = 7.3, 2.9 Hz, 1H), 2.6 (ddd, *J* = 14.7, 9.4, 5.6 Hz, 1H), 2.6 – 2.5 (m, 1H), 2.5 (dd, *J* = 10.5, 3.1 Hz, 1H), 1.6 (ddt, *J* = 13.3, 6.3, 3.2 Hz, 1H), 1.3 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 151.2, 140.9, 140.8, 128.5, 128.3, 128.2, 127.9, 127.8, 126.1, 124.0, 122.0, 116.7, 107.5, 98.2, 62.5, 35.0, 32.9, 30.4, 27.9, 14.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{22}H_{23}O_4^+$ 351.1591, found 351.1588. **$[\alpha]_D^{20}$** -118.00 (*c* = 0.60 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak OD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 6.02 min, t_{minor} = 8.79 min, **ee = 97%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 8:1**.



6m

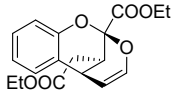
6m was obtained as a yellow solid 14 mg in 42% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 – 7.2 (m, 2H), 7.1 – 7.1 (m, 3H), 7.1 (dd, *J* = 6.9, 3.0 Hz, 2H), 6.9 – 6.8 (m, 2H), 6.5 (d, *J* = 5.8 Hz, 1H), 5.4 (dd, *J* = 7.0, 5.8 Hz, 1H), 4.3 – 4.1 (m, 2H), 3.9 (d, *J* = 2.8 Hz, 1H), 3.5 (dd, *J* = 7.1, 2.8 Hz, 1H), 1.0 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 151.9, 140.6, 136.5, 128.4, 127.9, 127.8, 127.3, 123.9, 122.2, 116.5, 108.8, 97.4, 62.3, 42.3, 35.5, 13.7 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{20}H_{19}O_4^+$ 323.1278, found 323.1277. **$[\alpha]_D^{20}$** -23.67 (*c* = 0.69 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} =

7.88 min, t_{minor} = 7.38 min, **ee = 92%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6n

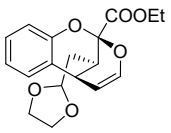
6n was obtained as a white solid 13 mg in 45% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 100/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 (ddd, J = 8.7, 7.2, 1.7 Hz, 1H), 7.1 (dd, J = 8.2, 1.3 Hz, 1H), 7.0 (dd, J = 7.5, 1.7 Hz, 1H), 6.9 (td, J = 7.3, 1.3 Hz, 1H), 6.4 (d, J = 5.7 Hz, 1H), 5.7 (dddd, J = 17.0, 10.1, 8.3, 5.8 Hz, 1H), 5.3 – 5.3 (m, 1H), 5.0 (d, J = 10.1 Hz, 1H), 4.8 (dq, J = 17.0, 1.6 Hz, 1H), 4.4 – 4.3 (m, 2H), 3.3 (dd, J = 7.3, 2.9 Hz, 1H), 2.5 – 2.5 (m, 1H), 2.2 – 2.1 (m, 1H), 1.7 – 1.7 (m, 1H), 1.4 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 151.1, 140.8, 134.3, 128.0, 127.8, 123.9, 122.0, 117.8, 116.6, 107.7, 97.9, 62.5, 35.1, 31.1, 30.1, 14.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{17}H_{19}O_4^+$ 287.1278, found 287.1274. **$[\alpha]_D^{20}$** -126.46 (c = 0.65 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [n-hexane/i-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 4.98 min, t_{minor} = 5.99 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 8:1**.



6o

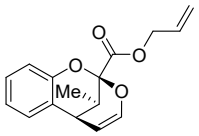
6o was obtained as a colorless oil 12 mg in 34% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 – 7.1 (m, 1H), 7.1 – 7.0 (m, 2H), 6.9 (td, J = 7.4, 1.2 Hz, 1H), 6.4 (d, J = 5.8 Hz, 1H), 5.3 (dd, J = 7.3, 5.7 Hz, 1H), 4.4 – 4.3 (m, 2H), 4.1 (q, J = 7.1 Hz, 2H), 3.4 (dd, J = 7.3, 2.9 Hz, 1H), 3.0 (ddd, J = 9.5, 3.9, 2.9 Hz, 1H), 2.4 (dd, J = 17.0, 3.9 Hz, 1H), 2.0 (dd, J = 16.9, 9.5 Hz, 1H), 1.4 (t, J = 7.1 Hz, 3H), 1.2 (t, J = 7.2 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 166.3, 150.8, 140.7, 128.2, 128.0, 123.8, 122.2, 116.8, 107.6, 97.2, 62.7, 60.8, 32.3, 32.2, 31.4, 14.1, 14.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{18}H_{21}O_6^+$ 333.1333, found 333.1333. **$[\alpha]_D^{20}$** -118.22 (c = 0.60 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [n-hexane/i-PrOH = 90/10, 1 mL/min], λ = 220

nm, t_{major} = 7.24 min, t_{minor} = 14.75 min, **ee >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 7:1**.



6p

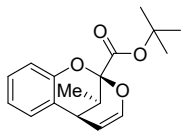
6p was obtained as a yellow oil 7.5 mg in 23% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 60/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.1 (ddd, *J* = 8.2, 7.2, 1.7 Hz, 1H), 7.1 – 7.0 (m, 2H), 6.9 – 6.9 (m, 1H), 6.4 (d, *J* = 5.7 Hz, 1H), 5.3 (dd, *J* = 7.3, 5.7 Hz, 1H), 4.9 (t, *J* = 4.7 Hz, 1H), 4.4 – 4.3 (m, 2H), 3.9 – 3.9 (m, 2H), 3.8 – 3.8 (m, 2H), 3.5 (dd, *J* = 7.3, 3.0 Hz, 1H), 2.7 (dt, *J* = 9.8, 3.0 Hz, 1H), 1.6 (ddd, *J* = 14.5, 4.7, 3.0 Hz, 1H), 1.4 – 1.4 (m, 1H), 1.4 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 151.0, 140.7, 128.2, 127.7, 124.3, 122.0, 116.7, 107.6, 102.9, 97.9, 64.9, 64.7, 62.5, 31.7, 31.3, 30.8, 14.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{18}H_{21}O_6^+$ 333.1333, found 333.1335. **$[\alpha]_D^{20}$** +23.96 (*c* = 0.37 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IB column [*n*-hexane/*i*-PrOH = 80/20, 1 mL/min], λ = 205 nm, t_{major} = 6.56 min, t_{minor} = 7.71 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6q

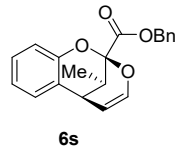
6q was obtained as a colorless oil 15 mg in 44% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 60/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 (ddd, *J* = 8.8, 7.3, 1.7 Hz, 1H), 7.1 – 7.0 (m, 2H), 6.9 (td, *J* = 7.3, 1.3 Hz, 1H), 6.4 (d, *J* = 5.8 Hz, 1H), 6.0 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.4 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.4 – 5.3 (m, 2H), 4.8 – 4.7 (m, 2H), 3.2 (dd, *J* = 7.1, 2.9 Hz, 1H), 2.6 (qd, *J* = 6.9, 2.9 Hz, 1H), 0.9 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 150.8, 140.6, 131.2, 128.0, 127.7, 124.2, 121.9, 119.4, 116.6, 108.0, 98.4, 66.7, 33.5, 30.5, 13.1ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{16}H_{17}O_4^+$ 273.1121, found 273.1120. **$[\alpha]_D^{20}$** -154.58 (*c* = 0.75 in $CHCl_3$). The

enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column [*n*-hexane/*i*-PrOH = 95/5, 1 mL/min], λ = 205 nm, t_{major} = 8.23 min, t_{minor} = 12.45 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**



6r

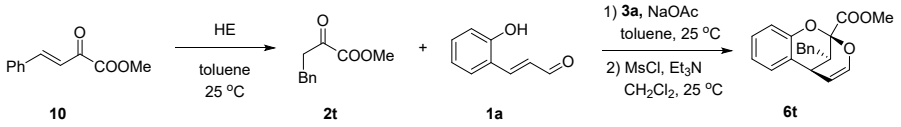
6r was obtained as a white solid 18 mg in 62% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 50/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.1 (td, *J* = 7.7, 7.2, 1.7 Hz, 1H), 7.0 (ddd, *J* = 12.5, 7.8, 1.5 Hz, 2H), 6.9 (td, *J* = 7.3, 1.3 Hz, 1H), 6.4 (d, *J* = 5.8 Hz, 1H), 5.3 (dd, *J* = 7.1, 5.8 Hz, 1H), 3.1 (dd, *J* = 7.1, 2.9 Hz, 1H), 2.6 (qd, *J* = 6.9, 2.9 Hz, 1H), 1.6 (s, 9H), 0.9 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.6, 151.1, 140.8, 127.9, 127.6, 124.4, 121.7, 116.6, 107.8, 98.1, 83.2, 33.7, 30.5, 27.9, 13.0 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{17}H_{21}O_4^+$ 289.1434, found 289.1430. **$[\alpha]_D^{20}$** -171.73 (*c* = 0.50 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak OD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 8.82 min, t_{minor} = 4.49 min, **ee = 97%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6s

6s was obtained as a yellow oil 19 mg in 59% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 30/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.5 – 7.3 (m, 5H), 7.1 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.1 (ddd, *J* = 13.9, 7.8, 1.5 Hz, 2H), 6.9 (td, *J* = 7.3, 1.3 Hz, 1H), 6.4 (d, *J* = 5.8 Hz, 1H), 5.4 (d, *J* = 12.3 Hz, 1H), 5.3 – 5.3 (m, 2H), 3.1 (dd, *J* = 7.1, 2.9 Hz, 1H), 2.6 (qd, *J* = 7.0, 2.9 Hz, 1H), 0.8 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 150.9, 140.6, 135.1, 128.7, 128.6, 128.4, 128.0, 127.7, 124.2, 121.9, 116.6, 108.0, 98.4, 67.8, 33.5, 30.5, 13.0 ppm. **HRMS**: $[M+H]^+$ *calcd.* for

$C_{20}H_{19}O_4^+$ 323.1278, found 323.1276. **$[\alpha]_D^{20}$** -149.16 (*c* = 0.75 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak OD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 10.03 min, t_{minor} = 8.74 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

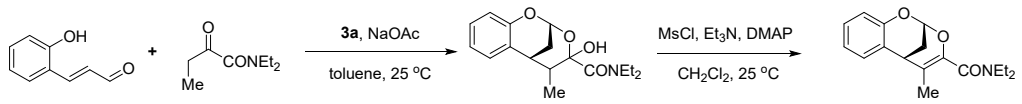


Detailed method: A glass vial equipped with a magnetic stirring bar was charged with methyl (*E*)-2-oxo-4-phenylbut-3-enoate **10** (0.13 mmol, 25 mg, 1.3 equiv.) in toluene (0.2 mL), then Hantzsch ester (HE) (0.14 mmol, 35 mg, 1.4 equiv.) was added and the resulting solution was stirred for about 12 h at 25 °C until the material **10** disappeared. After completion of the reaction, the crude product was directly put into the next step without column chromatography separation. Then the catalyst **3a** (0.02 mmol, 6.5 mg, 20 mol%), 2-hydroxycinnamaldehyde **1a** (0.1 mmol, 14.8 mg, 1.0 equiv.) and NaOAc (0.02 mmol, 1.6 mg, 20 mol%) was added in one portion and the resulting solution was stirred for about 3 h at 25 °C until the material **1a** disappeared. The reaction mixtures were diluted by 0.5 mL dichloromethane. Then TEA (0.3 mmol, 30.3 mg, 3.0 equiv.), MsCl (0.2 mmol, 22.9 mg, 2.0 equiv.), DMAP (0.02 mmol, 2.4 mg, 0.2 equiv.) were added to the reaction mixtures at 0 °C in the ice bath. After full conversion of the reaction about 8 h at 25 °C, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) to give product **6t** as a yellow oil 15 mg in 47% yield for two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.3 – 7.3 (m, 1H), 7.3 (s, 1H), 7.2 (dt, *J* = 5.4, 1.2 Hz, 1H), 7.2 – 7.2 (m, 2H), 7.1 (d, *J* = 8.1 Hz, 1H), 7.0 – 7.0 (m, 4H), 6.4 (d, *J* = 5.7 Hz, 1H), 5.2 (dd, *J* = 7.3, 5.7 Hz, 1H), 3.9 (s, 3H), 3.0 (dd, *J* = 7.3, 2.6 Hz, 1H), 2.8 – 2.7 (m, 2H), 2.2 (dd, *J* = 14.6, 12.3 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.1, 151.0, 140.7, 138.1, 129.1, 128.5, 128.2, 127.9, 126.6, 124.0, 122.2, 116.8, 107.8, 98.1, 53.3, 37.5, 32.9, 29.7 ppm. **HRMS**: $[M+Na]^+$ *calcd.* for $C_{20}H_{18}O_4Na^+$ 345.1097, found 345.1100. **$[\alpha]_D^{20}$** -107.17 (*c* = 0.40 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IB column [*n*-

hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 220 nm, t_{major} = 6.21 min, t_{minor} = 8.08 min, **ee = 94%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 7:1**.

E. Other reactions

E1. Synthesis of 8

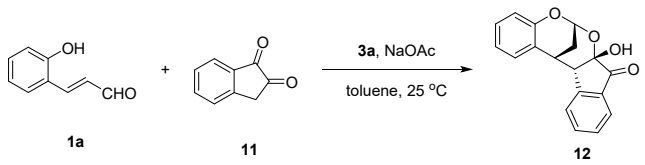


1a **7** **4'a** **8**

Detailed method: A glass vial equipped with a magnetic stirring bar was charged with catalyst **3a** (0.02 mmol, 6.5 mg, 20 mol%) in toluene (0.2 mL), then 2-hydroxycinnamaldehyde **1a** (0.1 mmol, 14.8 mg, 1.0 equiv.), NaOAc (0.02 mmol, 1.6 mg, 20 mol%) and the 2-oxocarboxylic amide **7** (0.12 mmol, 18.9 mg, 1.2 equiv.) was added. The reaction mixture was stirred at 25 °C for 8 h. until the material **1a** disappeared. After completion of the reaction, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **4'a**. Then the product **4'a** (0.1 mmol, 30.5 mg, 1.0 equiv.) was respectively dissolved in CH_2Cl_2 (0.2 mmol in 1 mL) at 0 °C in the ice bath. TEA (0.3 mmol, 30.3 mg, 3.0 equiv.), MsCl (0.2 mmol, 22.8 mg, 2.0 equiv.), DMAP (0.02 mmol, 2.4 mg, 0.2 equiv.) were added to the reaction mixtures in order. After full conversion of the reaction, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give product **8** as a yellow solid 13 mg in 43% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 – 7.0 (m, 2H), 7.0 – 6.8 (m, 2H), 6.0 (q, *J* = 2.0 Hz, 1H), 3.4 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.3 (dq, *J* = 14.2, 7.2 Hz, 1H), 3.1 – 3.1 (m, 2H), 3.0 (dq, *J* = 14.3, 7.1 Hz, 1H), 2.3 (ddd, *J* = 12.9, 3.4, 2.0 Hz, 1H), 2.0 (dt, *J* = 13.0, 2.6 Hz, 1H), 1.7 (s, 3H), 1.1 (t, *J* = 7.1 Hz, 3H), 0.9 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 152.1, 140.1, 127.8, 126.9, 126.2, 120.8, 115.8, 112.0, 91.7, 42.6, 39.2, 31.6, 25.4, 16.0, 13.9, 12.8 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{17}H_{22}NO_3^+$ 288.1594, found 288.1594. **$[\alpha]_D^{20}$** +83.28 (*c* = 0.65 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 7.17 min, t_{minor} = 9.01 min, **ee = 98%**.

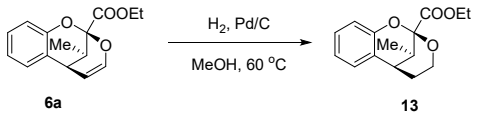
.

E2. Synthesis of 12



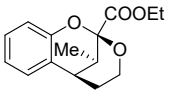
Detailed method: A glass vial equipped with a magnetic stirring bar was charged with catalyst **3a** (0.02 mmol, 6.5 mg, 20 mol%) in toluene (0.2 mL), then 2-hydroxycinnamaldehyde **1a** (0.1 mmol, 14.8 mg, 1.0 equiv.), NaOAc (0.02 mmol, 1.6 mg, 20 mol%) and the indan-1,2-dione **11** (0.12 mmol, 17.5mg, 1.2 equiv.) was added. The reaction mixture was stirred at 25 °C for 1 h until the material **1a** disappeared. After completion of the reaction, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 7/1) to afford **12** as a yellow solid 22 mg in 78% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.9 (d, J = 7.6 Hz, 1H), 7.8 – 7.7 (m, 1H), 7.7 – 7.7 (m, 1H), 7.5 (t, J = 7.5 Hz, 1H), 7.3 – 7.3 (m, 2H), 7.0 – 7.0 (m, 1H), 7.0 (d, J = 8.1 Hz, 1H), 5.6 (s, 1H), 3.7 (s, 1H), 3.7 – 3.6 (m, 1H), 3.6 (s, 1H), 1.8 (q, J = 2.6 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.1, 152.2, 150.4, 136.2, 133.3, 129.0, 129.0, 128.1, 125.9, 124.9, 124.2, 121.4, 116.6, 94.9, 91.8, 49.7, 28.5, 22.5 ppm. **HRMS**: $[M+NH_4]^+$ *calcd.* for $C_{18}H_{18}O_4N^+$ 312.1230, found 312.1231. **$[\alpha]_D^{20}$** -90.27 (c = 0.65 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak OD-H column [n-hexane/i-PrOH = 80/20, 1 mL/min], λ = 205 nm, t_{major} = 24.69 min, t_{minor} = 18.95 min, **ee = 95%**.

F. Synthetic transformation



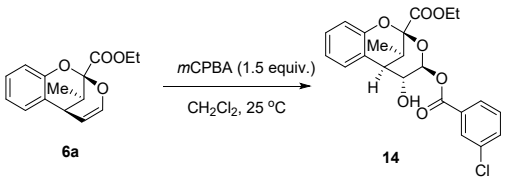
6a 13

A solution of **6a** (18.2 mg, 0.07 mmol) and 20% Pd/C (3.6 mg) in absolute MeOH (1 mL) was placed under an atmosphere of hydrogen. After stirring for 18 h at 60 °C, the reaction mixture was filtered through a short pad of silica gel and concentrated in vacuo. The product was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate = 20/1) to afford the desired product **13** as a colorless oil (19 mg, 99%).

ethyl (2*S*,6*R*,11*R*)-11-methyl-5,6-dihydro-4*H*-2,6-methanobenzo[*d*][1,3]dioxocine-2-carboxylate (13) : 

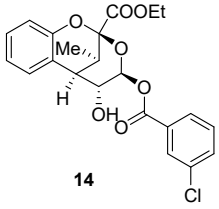
13

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (ddd, *J* = 8.2, 7.3, 1.8 Hz, 1H), 7.1 (ddd, *J* = 9.3, 7.8, 1.5 Hz, 2H), 7.0 (td, *J* = 7.4, 1.2 Hz, 1H), 4.4 – 4.3 (m, 2H), 3.9 (dd, *J* = 12.0, 5.5 Hz, 1H), 3.6 (td, *J* = 12.5, 3.2 Hz, 1H), 3.0 (q, *J* = 3.2 Hz, 1H), 2.5 (qd, *J* = 6.9, 2.4 Hz, 1H), 2.3 (ddd, *J* = 13.0, 5.8, 3.5 Hz, 1H), 1.7 (td, *J* = 3.4, 1.1 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.8 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 154.2, 129.1, 128.2, 122.5, 121.7, 115.3, 98.9, 62.2, 59.8, 36.2, 33.8, 33.1, 14.3, 14.2 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{15}H_{19}O_4^+$ 263.1278, found 263.1280. **$[\alpha]_D^{20}$** -59.78 (*c* = 0.90 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak OD-H column [*n*-hexane/*i*-PrOH = 95/5, 1 mL/min], λ = 220 nm, t_{major} = 14.14 min, t_{minor} = 7.67 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



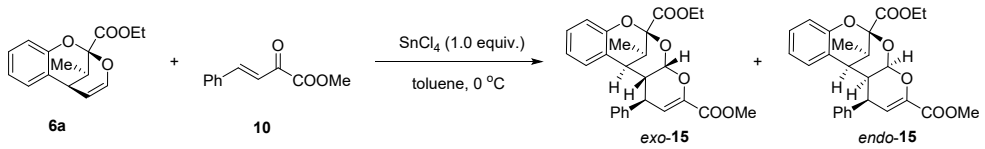
6a 14

To a solution of **6a** (26 mg, 0.1 mmol) in CH_2Cl_2 (0.5mL) was added a solution of 3-chloroperbenzoic acid (26 mg, 0.15 mmol) at 25 °C. The reaction mixture was stirred at room temperature for 0.5 h. After completion of the reaction, the product was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate = 4/1) to afford the desired product **14** as a white solid (36 mg, 83%)



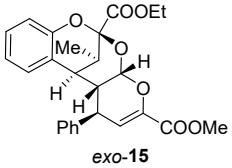
14

ethyl (2*R*,4*S*,5*S*,6*R*,11*R*)-5-((3-chlorobenzoyl)oxy)-4-hydroxy-11-methyl-5,6-dihydro-4*H*-2,6-methanobenzo[*d*][1,3]dioxocine-2-carboxylate (14) : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (ddd, *J* = 7.9, 2.1, 1.2 Hz, 1H), 7.4 – 7.3 (m, 1H), 7.3 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.2 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.2 (t, *J* = 7.9 Hz, 2H), 7.1 (ddt, *J* = 7.5, 3.8, 1.9 Hz, 2H), 7.0 (t, *J* = 1.9 Hz, 1H), 6.3 (d, *J* = 0.9 Hz, 1H), 4.4 – 4.3 (m, 2H), 4.1 (d, *J* = 3.3 Hz, 1H), 3.1 – 3.1 (m, 2H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.9 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 163.4, 152.0, 134.2, 133.4, 130.6, 129.6, 129.5, 129.4, 129.3, 128.1, 122.2, 119.8, 116.6, 98.2, 93.6, 71.7, 62.7, 40.4, 25.7, 14.1, 13.5 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{22}H_{22}ClO_7^+$ 433.1049, found 433.1048. **$[\alpha]_D^{20}$** -78.29 (*c* = 1.75 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 210 nm, t_{major} = 11.31 min, t_{minor} = 13.00 min, **ee >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6a 10 *exo*-15 *endo*-15

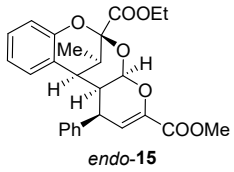
6a (26 mg, 0.1 mmol) and methyl (*E*)-2-oxo-4-phenylbut-3-enoate **10** (28.6 mg, 0.15 mmol) was dissolved in 1.0 mL toluene under argon atmosphere, and the resulting mixture was cooled to 0 °C. $SnCl_4$ (26 mg, 0.1 mmol) was then added and the reaction mixture was stirred vigorously at 0 °C. When substrate **6a** was disappeared on TLC, the crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1 to 4/1) to afford pure product *exo*-**15** (10 mg, 22% yield) as a white solid and *endo*-**15** (15 mg, 33% yield) as a white solid.



exo-15

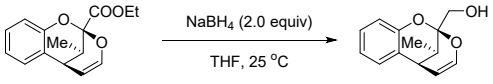
***exo*-6-ethyl 3-methyl (1*R*,6*R*,12*R*,13*R*)-13-methyl-1-phenyl-4a,12a-dihydro-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,2-*g*][1,3]dioxocine-3,6-dicarboxylate (*exo*-15) : ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.5 – 7.4 (m, 2H), 7.4 – 7.4 (m, 1H), 7.4 – 7.3 (m, 2H), 7.1 (ddd, *J* = 8.8, 7.4, 1.7 Hz, 1H), 7.0 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.7 (td, *J* = 7.4, 1.2 Hz, 1H), 6.4 (d,

J = 2.6 Hz, 1H), 5.8 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.7 (d, *J* = 4.9 Hz, 1H), 4.4 – 4.3 (m, 2H), 4.2 (dd, *J* = 6.8, 3.1 Hz, 1H), 3.9 (s, 3H), 2.6 (t, *J* = 2.7 Hz, 1H), 2.6 (td, *J* = 6.7, 2.9 Hz, 1H), 2.5 – 2.4 (m, 1H), 1.4 (t, *J* = 7.1 Hz, 4H), 0.6 (d, *J* = 6.7 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.2, 162.4, 150.2, 143.9, 139.0, 129.0, 129.0, 128.1, 127.7, 125.6, 122.1, 116.8, 110.5, 98.6, 92.7, 62.2, 52.5, 44.6, 39.7, 33.8, 27.2, 14.1, 13.6 ppm. **HRMS**: $[M+NH_4]^+$ *calcd.* for $C_{26}H_{30}NO_7^+$ 468.2017, found 468.2014. **$[\alpha]_D^{20}$** -33.73 (*c* = 0.50 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 33.95 min, t_{minor} = 23.15 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



endo-**15**

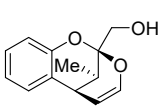
***endo*-6-ethyl 3-methyl (1*R*,6*R*,12*R*,13*R*)-13-methyl-1-phenyl-4a,12a-dihydro-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,2-*g*][1,3]dioxocine-3,6-dicarboxylate (*endo*-15): ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.4 (dd, *J* = 8.1, 6.4 Hz, 2H), 7.4 – 7.4 (m, 1H), 7.2 (d, *J* = 1.3 Hz, 2H), 7.2 (ddd, *J* = 8.3, 7.3, 1.7 Hz, 1H), 7.0 (dd, *J* = 8.3, 1.3 Hz, 1H), 6.9 (td, *J* = 7.4, 1.2 Hz, 1H), 6.8 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.2 (d, *J* = 2.5 Hz, 1H), 5.5 (d, *J* = 3.1 Hz, 1H), 4.5 – 4.3 (m, 2H), 3.9 (dd, *J* = 11.3, 2.6 Hz, 1H), 3.8 (s, 3H), 3.1 (qd, *J* = 6.9, 2.5 Hz, 1H), 2.8 (t, *J* = 2.9 Hz, 1H), 2.1 (dt, *J* = 11.4, 3.1 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 0.8 (d, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ165.5, 162.5, 153.7, 141.5, 140.6, 129.2, 128.9, 128.8, 128.2, 127.7, 122.3, 122.2, 115.4, 114.3, 100.7, 92.6, 62.5, 52.3, 44.3, 38.1, 36.2, 28.1, 14.2, 12.9 ppm. **HRMS**: $[M+NH_4]^+$ *calcd.* for $C_{26}H_{30}NO_7^+$ 468.2017, found 468.2014. **$[\alpha]_D^{20}$** -57.78 (*c* = 0.30 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 25.90 min, t_{minor} = 6.59 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6a **16**

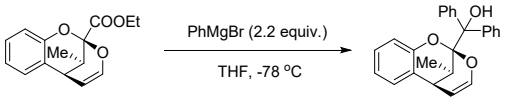
6a (27.8 mg, 0.11 mmol) was dissolved in THF (0.2 mL), and sodium borohydride (8.3 mg, 0.22 mmol) was added portionwise to maintain a gentle evolution of gas. Then, the mixture was stirred for 6 h at room temperature. The reaction mixture was quenched

with saturated aqueous NH_4Cl and diluted with water. The aqueous portion was extracted with ethyl acetate. The organic parts were combined, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatograph on a silica gel (petroleum ether/ethyl acetate = 10/1) to get compound alcohol **16** (24 mg, 99%) as a white solid.



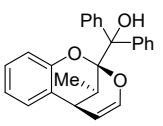
16

((2*S*,6*R*,11*R*)-11-methyl-6*H*-2,6-methanobenzo[*d*][1,3]dioxocin-2-yl)methanol (16) : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 – 7.1 (m, 1H), 7.0 (dd, J = 7.6, 1.7 Hz, 1H), 6.9 – 6.9 (m, 2H), 6.4 (d, J = 5.8 Hz, 1H), 5.2 (dd, J = 6.9, 5.8 Hz, 1H), 3.9 – 3.8 (m, 2H), 3.1 (dd, J = 6.9, 3.0 Hz, 1H), 2.4 (qd, J = 7.0, 3.0 Hz, 1H), 2.0 (s, 1H), 0.9 (d, J = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 140.9, 128.1, 127.5, 125.1, 121.4, 115.8, 108.2, 100.7, 65.0, 34.3, 29.2, 13.2 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{13}H_{15}O_3^+$ 219.1016, found 219.1015. **$[\alpha]_D^{20}$** -156.22 (c = 1.20 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 7.61 min, t_{minor} = 9.97 min, **ee >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



6a **17**

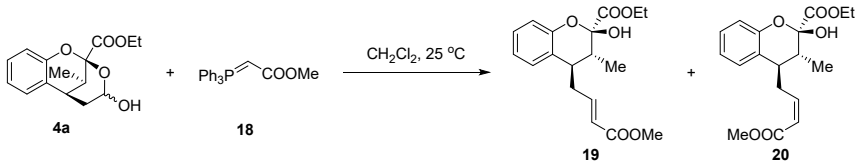
To a solution of **6a** (26 mg, 0.1 mmol) in anhydrous THF (1 mL) at −78 °C was added dropwise the Grignard reagents (75 μL, 2.9 M). After stirring for 1 h at −78 °C, the mixture was quenched with a saturated solution of NH_4Cl (1 mL), and extracted with ethyl acetate. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated in a rotary evaporator under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to get compound alcohol **17** (40 mg, 99%) as a white solid.



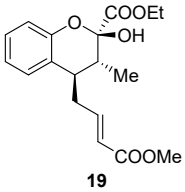
17

((2*S*,6*R*,11*R*)-11-methyl-6*H*-2,6-methanobenzo[*d*][1,3]dioxocin-2-yl)diphenylmethanol (17) : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8 – 7.8 (m, 2H), 7.7 (dd, J = 8.5, 1.5 Hz, 2H), 7.4 (dd, J = 8.3, 6.3 Hz, 2H), 7.3 – 7.3 (m, 2H), 7.3 (d, J = 1.7 Hz, 1H), 7.2 (ddd, J = 8.2, 7.3, 1.7 Hz, 1H), 7.1 (ddd, J = 9.3, 7.7, 1.4 Hz, 2H), 6.9

(td, *J* = 7.4, 1.2 Hz, 1H), 6.4 (d, *J* = 5.7 Hz, 1H), 5.3 (dd, *J* = 7.0, 5.7 Hz, 1H), 3.3 (s, 1H), 2.9 (dd, *J* = 7.0, 2.9 Hz, 1H), 2.1 (d, *J* = 7.7 Hz, 1H), 0.9 (d, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 144.8, 140.5, 129.1, 128.2, 127.7, 127.6, 127.5, 127.4, 127.2, 126.9, 125.3, 121.7, 115.9, 108.5, 104.2, 81.9, 36.0, 31.0, 15.0 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{25}H_{23}O_3^+$ 371.1642, found 371.1640. **$[\alpha]_D^{20}$** -107.00 (*c* = 2.00 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 220 nm, t_{major} = 7.52 min, t_{minor} = 5.97 min, **ee >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

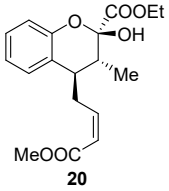


4a (27.8 mg, 0.1 mmol) and a stabilized ylide **18** (50.1 mg, 0.15 mmol) were dissolved in CH_2Cl_2 (0.5 mL), and the solution was stirring at room temperature for overnight. The crude product was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate =15/1) to get product **19** as white solid (25 mg, 75%) and product **20** as white solid (7 mg, 21%).



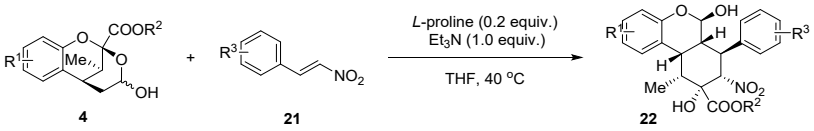
19

ethyl (2*S*,3*R*,4*R*)-2-hydroxy-4-((*E*)-4-methoxy-4-oxobut-2-en-1-yl)-3-methylchromane-2-carboxylate (19) : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.2 (d, *J* = 7.9 Hz, 1H), 7.1 (t, *J* = 7.6 Hz, 1H), 7.0 (t, *J* = 7.5 Hz, 1H), 6.8 (d, *J* = 8.1 Hz, 1H), 6.8 – 6.7 (m, 1H), 5.9 (d, *J* = 15.3 Hz, 1H), 4.5 (s, 1H), 4.4 – 4.3 (m, 2H), 3.7 (s, 3H), 3.1 – 3.0 (m, 2H), 2.8 – 2.7 (m, 1H), 2.2 (dq, *J* = 13.0, 6.6 Hz, 1H), 1.4 (t, *J* = 7.1 Hz, 3H), 1.0 (d, *J* = 6.5 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.1, 166.6, 151.6, 145.2, 127.8, 126.7, 123.7, 123.6, 121.8, 117.6, 96.8, 63.2, 51.5, 35.4, 34.5, 32.1, 14.1, 13.6 ppm. **HRMS**: $[M+NH_4]^+$ *calcd.* for $C_{18}H_{26}O_6N^+$ 352.1755, found 352.1754. **$[\alpha]_D^{20}$** +16.94 (*c* = 1.20 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak OD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 7.59 min, t_{minor} = 6.29 min, **ee >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

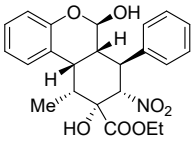


20

ethyl (2*S*,3*R*,4*R*)-2-hydroxy-4-((*Z*)-4-methoxy-4-oxobut-2-en-1-yl)-3-methylchromane-2-carboxylate (20) : ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.4 (dd, J = 8.1, 6.4 Hz, 2H), 7.2 (d, J = 7.9 Hz, 1H), 7.1 (t, J = 7.5 Hz, 1H), 7.0 (td, J = 7.6, 1.2 Hz, 1H), 6.8 (dd, J = 8.1, 1.0 Hz, 1H), 6.0 (ddd, J = 11.7, 8.5, 5.3 Hz, 1H), 5.8 (dt, J = 11.6, 1.8 Hz, 1H), 4.4 – 4.3 (m, 2H), 3.7 (s, 3H), 3.6 (dd, J = 15.3, 8.5 Hz, 1H), 3.3 – 3.2 (m, 1H), 3.1 (d, J = 11.8 Hz, 1H), 2.2 (dt, J = 12.6, 6.4 Hz, 1H), 1.4 (t, J = 7.1 Hz, 3H), 1.0 (d, J = 6.6 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 166.9, 151.9, 146.6, 127.7, 127.1, 124.0, 121.8, 121.4, 117.5, 96.9, 63.2, 51.2, 35.6, 34.8, 28.3, 14.1, 13.7 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{18}H_{23}O_6^+$ 335.1489, found 335.1487. **$[\alpha]_D^{20}$** +32.67 (c = 0.30 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 95/5, 1 mL/min], λ = 205 nm, t_{major} = 17.76 min, t_{minor} = 14.59 min, **ee >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



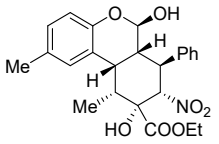
L-proline (0.02 mmol, 2.3 mg.) was added to a mixture of Et_3N (0.1 mmol, 10.1 mg), 4 (0.1 mmol, 27.8 mg), and nitroolefin **21** (0.12 mmol, 17.8 mg) in THF (0.2 mL) and stirred at room temperature. After completion of the reaction (as monitored by TLC), the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **22.**



22a

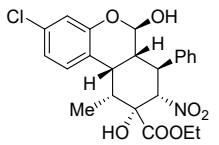
22a was obtained as a white solid 15 mg in 35% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.6 (d, J = 7.9 Hz, 1H), 7.3 (s, 4H), 7.3 (dd, J = 5.5, 2.7 Hz, 1H), 7.2 (t, J = 7.6 Hz, 1H), 6.9 – 6.9 (m, 2H), 5.3 (d, J = 12.1 Hz, 1H), 4.9 (d, J = 1.9 Hz, 1H), 4.4 (q, J = 7.1 Hz, 2H), 3.6 (d, J = 5.8 Hz, 1H), 3.6 (d, J = 12.3 Hz, 1H), 3.4 (s, 1H), 2.7 (dd, J = 7.3, 4.5 Hz, 1H), 2.3 (ddd,

J = 12.3, 4.8, 2.0 Hz, 1H), 1.6 (d, *J* = 7.3 Hz, 3H), 1.4 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 150.3, 137.4, 129.3, 129.0, 127.9, 127.7, 123.0, 120.9, 117.9, 93.6, 90.9, 79.0, 63.6, 44.2, 41.3, 39.9, 33.1, 16.6, 14.2 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{23}H_{29}N_2O_7^+$ 445.1969, found 445.1964. **$[\alpha]_D^{20}$** +72.17 (*c* = 0.40 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], *λ* = 205 nm, t_{major} = 37.59 min, t_{minor} = 50.40 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



22b

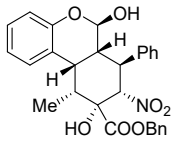
22b was obtained as a white solid 17 mg in 37% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.4 (s, 1H), 7.3 (d, *J* = 2.6 Hz, 4H), 7.3 (d, *J* = 8.4 Hz, 1H), 7.0 (dd, *J* = 8.1, 2.2 Hz, 1H), 6.8 (d, *J* = 8.2 Hz, 1H), 5.3 (d, *J* = 12.1 Hz, 1H), 4.8 (d, *J* = 2.3 Hz, 1H), 4.4 (q, *J* = 7.1 Hz, 2H), 3.6 – 3.6 (m, 2H), 3.4 (s, 1H), 2.8 (d, *J* = 3.1 Hz, 1H), 2.7 (qd, *J* = 7.2, 4.4 Hz, 1H), 2.3 (dd, *J* = 4.8, 2.1 Hz, 1H), 2.3 (s, 3H), 1.6 (d, *J* = 7.4 Hz, 3H), 1.4 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 172.7, 148.0, 137.4, 130.0, 129.6, 129.0, 128.4, 127.9, 122.5, 117.7, 93.6, 90.8, 63.6, 44.2, 41.4, 39.9, 33.1, 21.2, 16.7, 14.2 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{24}H_{27}NO_7^+$ 442.1861, found 442.1860. **$[\alpha]_D^{20}$** +16.94 (*c* = 1.15 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], *λ* = 205 nm, t_{major} = 32.95 min, t_{minor} = 43.15 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



22c

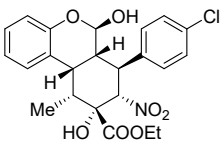
22c was obtained as a white solid 15 mg in 32% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.6 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.4 – 7.3 (m, 5H), 6.9 (d, *J* = 2.3 Hz, 1H), 6.9 (dd, *J* = 8.5, 2.4 Hz, 1H), 5.2 (d, *J* = 12.1 Hz, 1H), 4.8 (s, 1H), 4.4 (q, *J* = 7.1 Hz, 2H), 3.6 – 3.5 (m, 2H),

3.4 (d, *J* = 0.9 Hz, 1H), 3.0 (s, 1H), 2.7 (qd, *J* = 7.3, 3.8 Hz, 1H), 2.3 (ddd, *J* = 12.4, 4.8, 2.1 Hz, 1H), 1.6 (d, *J* = 7.3 Hz, 3H), 1.4 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ172.6, 151.1, 137.1, 132.6, 130.4, 129.1, 128.0, 121.6, 121.1, 118.0, 93.4, 91.0, 78.9, 63.7, 43.9, 41.1, 39.8, 32.8, 16.5, 14.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{23}H_{25}{}^{35}ClNO_7{}^+$ 462.1315, found 462.1318; *calcd.* for $C_{23}H_{25}{}^{37}ClNO_7{}^+$ 464.1285, found 464.1286. **$[\alpha]_D^{20}$** +34.79 (*c* = 0.80 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak ID column [*n*-hexane/*i*-PrOH = 80/20, 1 mL/min], λ = 205 nm, t_{major} = 18.78 min, t_{minor} = 22.76 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



22d

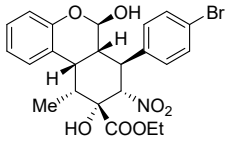
22d was obtained as a white solid 25 mg in 51% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.6 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.4 (dtd, *J* = 5.6, 3.6, 3.1, 2.0 Hz, 5H), 7.3 – 7.3 (m, 4H), 7.2 (ddt, *J* = 8.6, 7.7, 1.3 Hz, 1H), 6.9 (t, *J* = 7.5 Hz, 2H), 5.4 (d, *J* = 11.9 Hz, 1H), 5.3 (dd, *J* = 12.0, 1.6 Hz, 2H), 4.8 (t, J = 2.5 Hz, 1H), 3.6 – 3.6 (m, 2H), 3.4 (d, J = 0.9 Hz, 1H), 2.8 (d, J = 4.0 Hz, 1H), 2.7 (td, *J* = 7.4, 4.6 Hz, 1H), 2.3 (ddd, *J* = 12.4, 4.8, 2.1 Hz, 1H), 1.5 (d, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 150.3, 137.4, 129.3, 129.1, 129.1, 129.0, 128.9, 127.9, 127.7, 127.0, 122.9, 120.9, 117.9, 93.5, 90.8, 79.2, 69.3, 44.1, 41.3, 39.9, 33.1, 16.5 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{28}H_{28}NO_7{}^+$ 490.1861, found 490.1860. **$[\alpha]_D^{20}$** +17.87 (*c* = 0.96 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak OD-H column [*n*-hexane/*i*-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 30.93 min, t_{minor} = 26.17 min, **ee = 95%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



22e

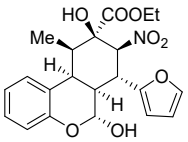
22e was obtained as a white solid 20 mg in 44% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 7.6 (d, J = 8.0 Hz, 1H), 7.4 – 7.3 (m, 4H), 7.2 (t, J = 7.7 Hz, 1H), 6.9 – 6.9 (m, 2H), 5.2 (d, J = 12.0 Hz, 1H), 4.9 (dd, J = 3.3, 2.0 Hz, 1H), 4.4 (q, J = 7.1 Hz, 2H), 3.7 – 3.5 (m, 2H), 3.4 (d, J = 0.8 Hz, 1H), 2.8 (d, J = 3.3 Hz, 1H), 2.7 – 2.6 (m, 1H), 2.3 (ddd, J = 12.3, 4.8, 2.1 Hz, 1H), 1.6 (d, J = 7.3 Hz, 3H), 1.4 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 13C NMR (100 MHz, $CDCl_3$) δ 172.7, 150.2, 136.1, 133.8, 129.4, 129.3, 127.8, 122.9, 121.1, 118.0, 93.4, 90.8, 79.0, 63.8, 44.1, 41.4, 39.5, 33.1, 16.6, 14.2 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{23}H_{25}{}^{35}ClNO_7{}^+$ 462.1315, found 462.1318; *calcd.* for $C_{23}H_{25}{}^{37}ClNO_7{}^+$ 464.1285, found 464.1286. **$[\alpha]_D^{20}$** +15.84 (c = 0.80 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [n-hexane/i-PrOH = 70/30, 1 mL/min], λ = 205 nm, t_{major} = 11.02 min, t_{minor} = 8.89 min, **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



22f

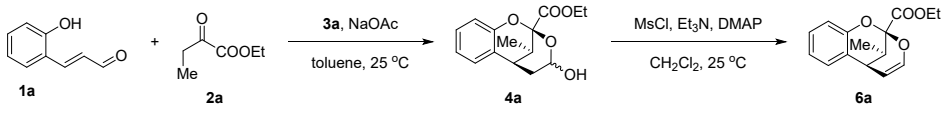
22f was obtained as a white solid 20 mg in 39% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.6 (dt, J = 7.9, 1.5 Hz, 1H), 7.5 (d, J = 8.7 Hz, 2H), 7.2 (d, J = 8.7 Hz, 3H), 7.2 (ddt, J = 8.2, 7.1, 1.2 Hz, 1H), 6.9 (ddd, J = 15.0, 7.8, 1.4 Hz, 2H), 5.2 (d, J = 12.1 Hz, 1H), 4.8 (s, 1H), 4.4 (q, J = 7.1 Hz, 2H), 3.6 (t, J = 4.6 Hz, 1H), 3.6 (t, J = 12.2 Hz, 1H), 3.4 (d, J = 0.8 Hz, 1H), 2.9 (s, 1H), 2.7 – 2.6 (m, 1H), 2.3 (ddd, J = 12.3, 4.8, 2.1 Hz, 1H), 1.6 (d, J = 7.3 Hz, 3H), 1.4 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 150.2, 136.6, 132.2, 129.3, 127.7, 122.8, 121.9, 121.0, 117.9, 93.3, 90.7, 79.0, 63.7, 44.1, 41.3, 39.5, 33.0, 16.5, 14.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{23}H_{25}{}^{79}BrNO_7{}^+$ 506.0809, found 506.0811; *calcd.* for $C_{23}H_{25}{}^{81}BrNO_7{}^+$ 508.0789, found 508.0790. **$[\alpha]_D^{20}$** +62.22 (c = 1.10 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column [n-hexane/i-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 29.65 min, t_{minor} = 12.23 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.



22g

22g was obtained as a white solid 20 mg in 48% yield for two steps after column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.6 (dt, J = 8.0, 1.4 Hz, 1H), 7.4 – 7.4 (m, 1H), 7.2 (t, J = 7.6 Hz, 1H), 6.9 – 6.9 (m, 2H), 6.3 (qd, J = 3.2, 1.3 Hz, 2H), 5.3 (d, J = 11.9 Hz, 1H), 5.0 (t, J = 2.6 Hz, 1H), 4.4 (qd, J = 7.1, 3.1 Hz, 2H), 3.7 (t, J = 12.1 Hz, 1H), 3.6 (t, J = 4.7 Hz, 1H), 3.4 (d, J = 0.9 Hz, 1H), 2.9 (d, J = 3.3 Hz, 1H), 2.7 – 2.6 (m, 1H), 2.5 (ddd, J = 12.3, 4.9, 2.1 Hz, 1H), 1.6 (d, J = 7.2 Hz, 3H), 1.4 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 150.3, 150.1, 142.4, 129.3, 127.7, 122.8, 120.9, 118.0, 110.6, 110.1, 91.2, 91.1, 78.8, 63.6, 41.8, 41.1, 34.3, 32.7, 16.5, 14.1 ppm. **HRMS**: $[M+H]^+$ *calcd.* for $C_{21}H_{24}NO_8^+$ 418.1497, found 418.1496. **$[\alpha]_D^{20}$** -20.45 (c = 1.50 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak AD-H column [n-hexane/i-PrOH = 90/10, 1 mL/min], λ = 205 nm, t_{major} = 48.07 min, t_{minor} = 40.93 min, **ee = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

G. 1 mmol scale reaction



Detailed method: A glass vial equipped with a magnetic stirring bar was charged with catalyst **3a** (0.2 mmol, 65 mg, 20 mol%) in toluene (2 mL); then 2-hydroxycinnamaldehyde **1a** (1 mmol, 148 mg, 1.0 equiv.), NaOAc (0.2 mmol, 16 mg, 20 mol%) and the **2a** (1.2 mmol, 156 mg, 1.2 equiv.) was added in one portion and the resulting solution was stirred for about 6 h at 25 °C until the material **1a** disappeared. After completion of the reaction, the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to afford **4a**. Then the product **4a** (1 mmol, 278 mg, 1.0 equiv.) was respectively dissolved in CH_2Cl_2 (5 mL) at 0 °C in the ice

bath. Then Et_3N (3.0 equiv.), MsCl (2.0 equiv.), DMAP (0.2 equiv.) were added to the reaction mixtures in order. After full conversion of the reaction, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) to give product **6a** as white solid 171 mg in 66% yield and **ee = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* = 11:1**.

H. DFT calculation

H1. Computational methods

The DFT calculations were performed with Gaussian 09[1]. All geometry optimizations were carried out at the M062X level[2] of theory with the 6-31G(d) basis set. Vibrational frequencies were computed at the same level to verify that optimized structures are local minimums and to evaluate zero-point vibrational energies (ZPVE) and thermal corrections at 298 K. Then the energies of the optimized structures in toluene were computed at the more accurate M062X/6-311+G(d,p) level with the SMD model.

Reference

[1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision D.01; Gaussian Inc.: Wallingford, CT, **2013**.

[2] Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215-241.

H2. Computational results

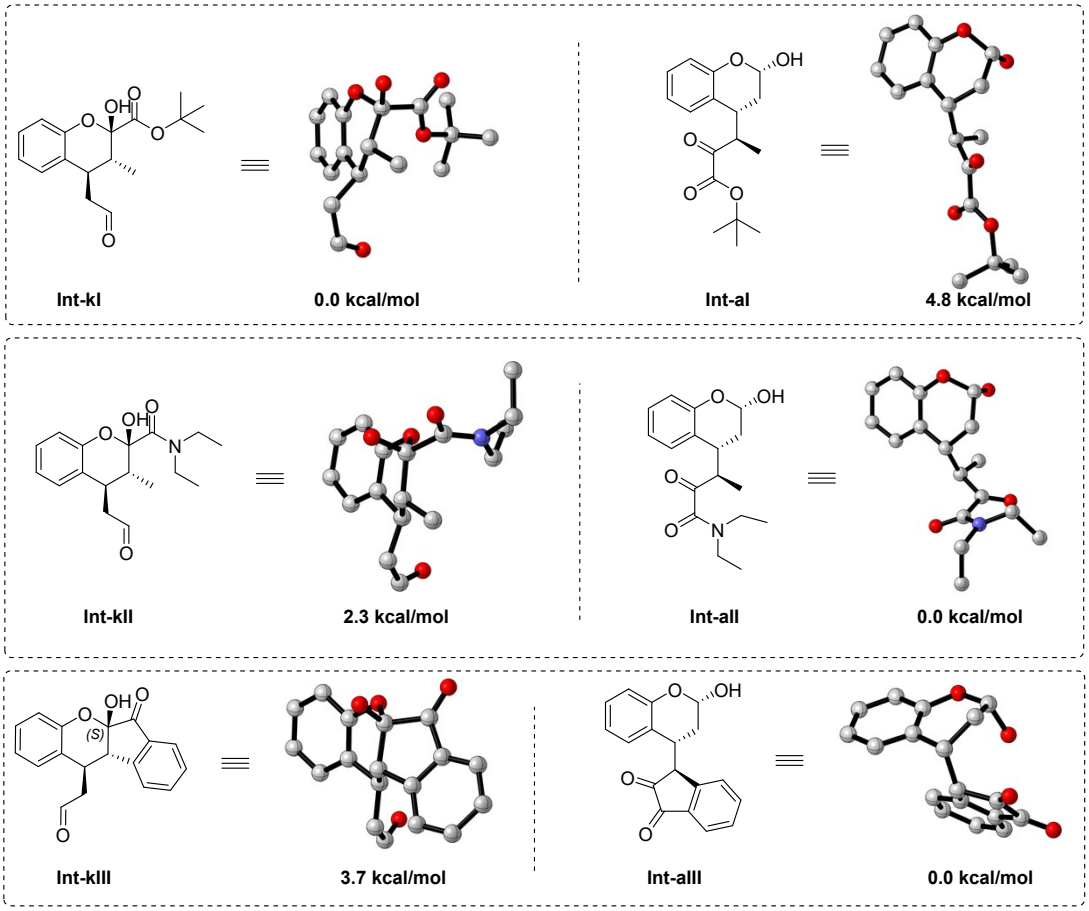


Figure. DFT calculation of ΔG_{sol} (in kcal mol^{-1}) at the SMD (toluene)-M06-2X/6–311+G(d,p)//M06-2X/6–31G(d) level of theory and the computed transition-state.

There were two competitive reaction pathways for the formation of 1) desired hemiketal intermediates via the attack of the phenolic hydroxyl group onto the 2-oxo group and 2) undesired hemiacetal intermediates via the attack of the phenolic hydroxyl group onto the aldehyde carbonyl group. During the reaction of 2-hydroxycinnamaldehyde **1a** and 2-oxocarboxylic ester, the desired hemiketal intermediate (**Int-kI**) is more favorable than the hemiacetal intermediate (**Int-aI**); while in the reaction of 2-hydroxycinnamaldehyde **1a** with 2-oxocarboxylic amide **7** and indan-1,2-dione **11**, respectively, both of the undesired hemiacetal intermediates **Int-aII** and **Int-aIII** are more preferred than the corresponding hemiketal intermediates **Int-kII** and **Int-kIII**.

H3. Coordinates and energies of stationary points

Int-kI

C	2.285375	2.750485	-0.317452
C	2.231724	1.444003	0.155429
C	1.393244	0.487124	-0.424620
C	0.584384	0.894731	-1.489021
C	0.630317	2.201001	-1.976853
C	1.485347	3.126507	-1.395235
H	2.946227	3.470745	0.153807
H	2.837248	1.158625	1.010761
H	-0.014460	2.460642	2.810014
H	1.520563	4.141778	-1.778016
O	-0.284523	0.049280	-2.126363
C	1.335238	-0.935058	0.096787
H	0.906304	-0.896100	1.105459
C	0.442083	-1.845373	-0.769516
H	1.029411	-2.197060	-1.629563
C	-0.727692	-1.114040	-1.423651
O	-1.308422	-1.953269	-2.344480
H	-2.232537	-1.660006	-2.443508
C	2.737292	-1.553690	0.225917
H	2.710300	-2.640413	0.056546
C	3.385089	-1.366706	1.576148
O	2.882896	-0.787010	2.507874
H	3.421807	-1.160037	-0.537992
H	4.390580	-1.825287	1.680647
C	-0.069524	-3.047618	0.021748
H	0.757987	-3.615874	0.457328
H	-0.707761	-2.713025	0.848404
H	-0.647441	-3.715576	-0.619754
C	-1.833681	-0.602031	-0.472861
O	-1.324196	-0.050023	0.614301
O	-3.001339	-0.655653	-0.786276
C	-2.120424	0.784105	1.517127
C	-3.177195	-0.072405	2.203280
H	-3.698400	0.529241	2.954461
H	-3.906111	-0.448133	1.483249
H	-2.703905	-0.918657	2.711281
C	-1.074955	1.285078	2.505148
H	-0.601849	0.445792	3.024047
H	-0.297485	1.846933	1.977838
H	-1.544831	1.936830	3.247552

C	-2.720951	1.941696	0.727732
H	-3.476320	1.593117	0.021486
H	-3.188269	2.645744	1.423068
H	-1.930422	2.467280	0.181830

Int-aI

C	-3.821314	2.621163	-0.098135
C	-2.646125	1.920388	-0.334628
C	-2.619100	0.522071	-0.401064
C	-3.832975	-0.155124	-0.222595
C	-5.020521	0.538055	0.016848
C	-5.016374	1.923235	0.073785
H	-3.806709	3.705259	-0.055850
H	-1.725654	2.475878	-0.494872
H	-5.928246	-0.039981	0.154378
H	-5.942902	2.458003	0.257946
O	-3.925086	-1.519172	-0.287068
C	-1.345079	-0.234613	-0.754243
H	-1.117729	0.007842	-1.799522
C	-1.559013	-1.767674	-0.699308
H	-1.729125	-2.137629	-1.714261
H	-0.669809	-2.281171	-0.325127
C	-2.754511	-2.199648	0.140464
H	-2.971203	-3.256579	-0.020390
O	-2.568546	-2.060474	1.518035
H	-2.448368	-1.118399	1.714869
C	-0.124991	0.255045	0.050783
H	-0.047318	1.346473	-0.034658
C	1.158524	-0.263198	-0.568229
C	2.456878	0.386053	-0.023574
O	1.221955	-1.064920	-1.465919
O	2.434532	1.443803	0.562419
O	3.516632	-0.344937	-0.317339
C	4.861857	0.109620	0.040860
C	-0.170657	-0.057807	1.553282
H	-0.247392	-1.131908	1.744017
H	0.717241	0.331421	2.056013
H	-1.037326	0.444344	1.998521
C	5.746566	-1.019301	-0.471055
H	5.611262	-1.150608	-1.548011
H	6.796648	-0.787119	-0.272075
H	5.493429	-1.958561	0.028442
C	5.169774	1.414999	-0.685555
H	5.020993	1.289345	-1.762340

H	4.536545	2.227876	-0.326851
H	6.216704	1.682373	-0.512503
C	4.979821	0.246419	1.555912
H	4.377030	1.074543	1.930972
H	4.662268	-0.681076	2.042509
H	6.027201	0.427179	1.816478

Int-kII

C	3.763714	2.014621	0.226621
C	3.351010	0.698544	0.025101
C	1.997657	0.374638	-0.033684
C	1.074136	1.413359	0.101555
C	1.463136	2.729843	0.297245
C	2.820783	3.028032	0.368611
H	4.823188	2.244021	0.276319
H	4.103898	-0.078111	-0.072479
H	0.699056	3.494369	0.387519
H	3.140412	4.053443	0.525821
O	-0.266903	1.108227	0.076349
C	1.418375	-1.013508	-0.225061
H	1.037294	-1.351550	0.748536
C	0.254995	-0.946380	-1.242092
H	0.709961	-0.766646	-2.222235
C	-0.655064	0.311851	-1.046155
O	-0.566585	1.047968	-2.213219
H	-1.480751	1.304698	-2.444229
C	2.470416	-2.033527	-0.654744
H	2.000633	-2.948872	-1.040417
C	3.369146	-2.487149	0.472176
O	3.170641	-2.248212	1.636867
H	3.089061	-1.652515	-1.478396
H	4.242294	-3.100251	0.164463
C	-0.560938	-2.239397	-1.336900
H	0.036358	-3.056846	-1.748640
H	-0.941695	-2.558633	-0.360991
H	-1.415046	-2.098320	-2.007187
C	-2.175547	0.043824	-0.800166
O	-2.942551	0.351466	-1.711522
C	-4.081051	-0.595651	0.496794
H	-4.262570	-1.265684	1.343080
H	-4.458723	-1.079556	-0.408208
C	-1.814440	-0.821315	1.522771
H	-2.112169	-1.830155	1.836331
H	-0.773030	-0.868596	1.220054

C	-1.960917	0.163564	2.676568
H	-2.987869	0.189880	3.053613
H	-1.306438	-0.130016	3.502284
H	-1.677625	1.164576	2.341482
C	-4.789953	0.740511	0.699715
H	-4.616206	1.385848	-0.163308
H	-5.867409	0.580196	0.801913
H	-4.429547	1.247955	1.598452
N	-2.626093	-0.463715	0.364043

Int-aII

C	-3.800643	2.356699	0.443117
C	-2.518772	1.825759	0.491326
C	-2.207063	0.603332	-0.114276
C	-3.235975	-0.074532	-0.779609
C	-4.528496	0.448855	-0.833587
C	-4.808932	1.664162	-0.228022
H	-4.010596	3.309104	0.918576
H	-1.730255	2.383418	0.990184
H	-5.288660	-0.121025	-1.357257
H	-5.814594	2.070106	-0.275333
O	-3.027878	-1.266135	-1.423411
C	-0.780275	0.078059	-0.140397
H	-0.216072	0.783202	-0.763274
C	-0.692517	-1.310110	-0.819625
H	-0.379799	-1.183477	-1.861059
H	0.051412	-1.948430	-0.328512
C	-2.015104	-2.071984	-0.843166
H	-1.943172	-2.943531	-1.494988
O	-2.409689	-2.562989	0.400718
H	-2.544253	-1.810900	0.998594
C	-0.092379	0.125417	1.252972
H	-0.082621	1.175976	1.564992
C	1.365765	-0.242021	1.068926
C	2.167107	0.731225	0.179617
O	1.901953	-1.173334	1.625874
O	1.884691	1.922627	0.258736
C	3.972637	1.247853	-1.302038
H	4.513116	0.722139	-2.094653
H	3.292724	1.966913	-1.768696
C	-0.735125	-0.736678	2.328275
H	-0.690454	-1.798853	2.071258
H	-0.213707	-0.611254	3.280183

H	-1.778893	-0.436635	2.476821
C	3.475160	-1.163943	-0.797337
H	2.606280	-1.763060	-0.526993
H	3.644906	-1.306781	-1.870767
C	4.690712	-1.615626	0.002360
H	4.884151	-2.678017	-0.172167
H	5.585481	-1.056886	-0.289044
H	4.504560	-1.463097	1.067857
C	4.938735	1.981317	-0.376836
H	5.516243	2.716537	-0.944951
H	4.380427	2.507554	0.400166
H	5.636335	1.286038	0.098140
N	3.159403	0.250414	-0.600658

Int-kIII

C	-4.302782	0.227926	-0.511770
C	-3.103216	0.930463	-0.406573
C	-1.926997	0.274009	-0.057737
C	-1.983552	-1.104071	0.162156
C	-3.165134	-1.821662	0.064787
C	-4.333795	-1.142465	-0.270373
H	-5.213527	0.755740	-0.774988
H	-3.099562	2.002241	-0.583746
H	-3.148528	-2.889877	0.250668
H	-5.268718	-1.688312	-0.348893
O	-0.831284	-1.751039	0.550697
C	-0.552322	0.891083	0.083983
H	-0.258232	0.821344	1.141797
C	0.406050	-0.011217	-0.730325
H	0.097927	0.023129	-1.782838
C	0.300922	-1.471960	-0.206946
O	0.330564	-2.407277	-1.258924
H	1.079512	-2.197843	-1.837992
C	-0.484043	2.355617	-0.321012
H	0.560135	2.696635	-0.355433
C	-1.181850	3.277173	0.654270
O	-1.601056	2.929748	1.728340
H	-0.891518	2.522134	-1.328069
H	-1.267484	4.335042	0.327744
C	1.552585	-1.661088	0.696360
O	1.713950	-2.540399	1.501550
C	2.506024	-0.594560	0.305455
C	1.879090	0.307137	-0.556983

C	3.848321	-0.479252	0.654313
C	2.626882	1.335545	-1.127234
C	4.581350	0.565205	0.104535
H	4.293233	-1.203052	1.330752
C	3.973378	1.456650	-0.786836
H	2.178822	2.026634	-1.836407
H	5.631425	0.685818	0.350737
H	4.563657	2.254899	-1.227040

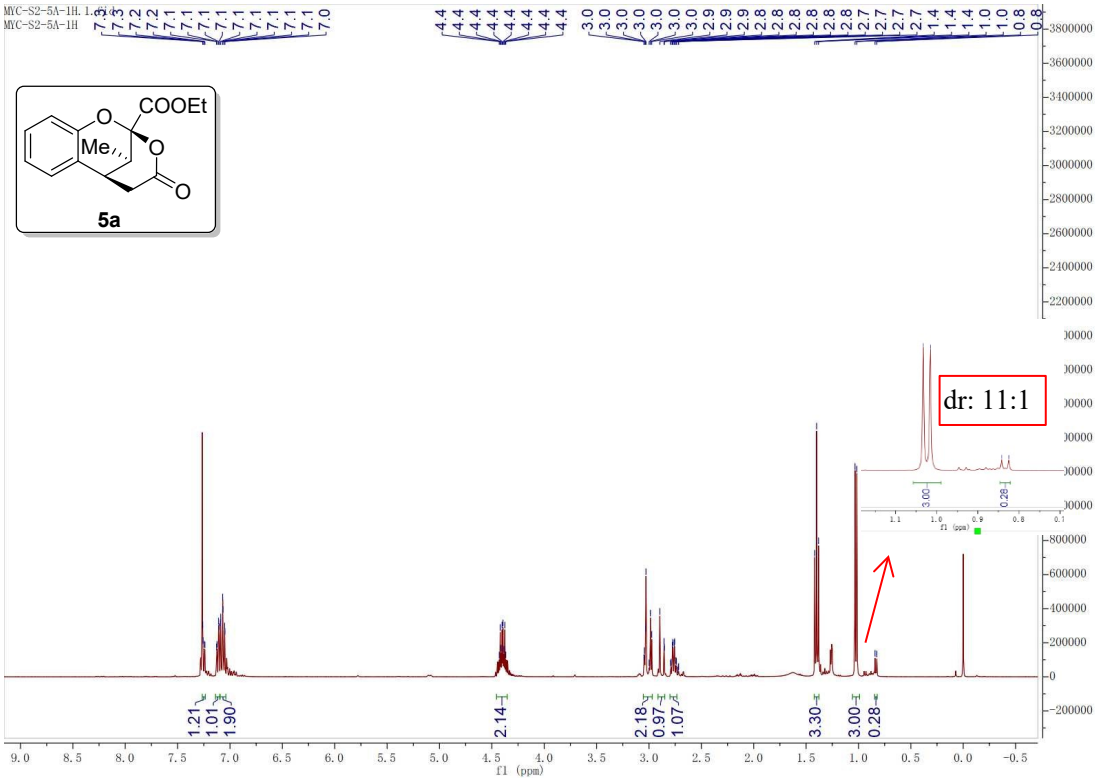
Int-aIII

C	-3.676176	0.581354	-1.411702
C	-2.583519	-0.253389	-1.610087
C	-1.806185	-0.702313	-0.540938
C	-2.169952	-0.322005	0.754248
C	-3.265877	0.515622	0.966783
C	-4.008132	0.972208	-0.113307
H	-4.265565	0.921508	-2.256687
H	-2.306008	-0.559811	-2.616814
H	-3.513524	0.791725	1.986425
H	-4.856933	1.626556	0.059842
O	-1.517012	-0.746337	1.880239
C	-0.559506	-1.521346	-0.745790
H	-0.715895	-2.203612	-1.587932
C	-0.366127	-2.401059	0.496554
H	-1.199703	-3.110161	0.538843
H	0.561581	-2.975045	0.453328
C	-0.373375	-1.577722	1.764254
H	-0.414284	-2.206806	2.660730
O	0.795832	-0.810742	1.750703
H	0.741446	-0.145190	2.453485
C	0.837769	0.786267	-0.597661
C	2.146724	0.980866	-0.134724
C	-0.052434	1.857443	-0.552311
C	2.583056	2.191466	0.392690
C	0.379949	3.073949	-0.021626
H	-1.067515	1.767043	-0.924050
C	1.682568	3.247567	0.453660
H	3.607710	2.285459	0.740788
H	-0.315802	3.907118	0.016382
H	1.988393	4.207705	0.857132
C	1.988673	-1.282613	-0.933786
C	2.940535	-0.252055	-0.277120
C	0.639704	-0.610188	-1.182174

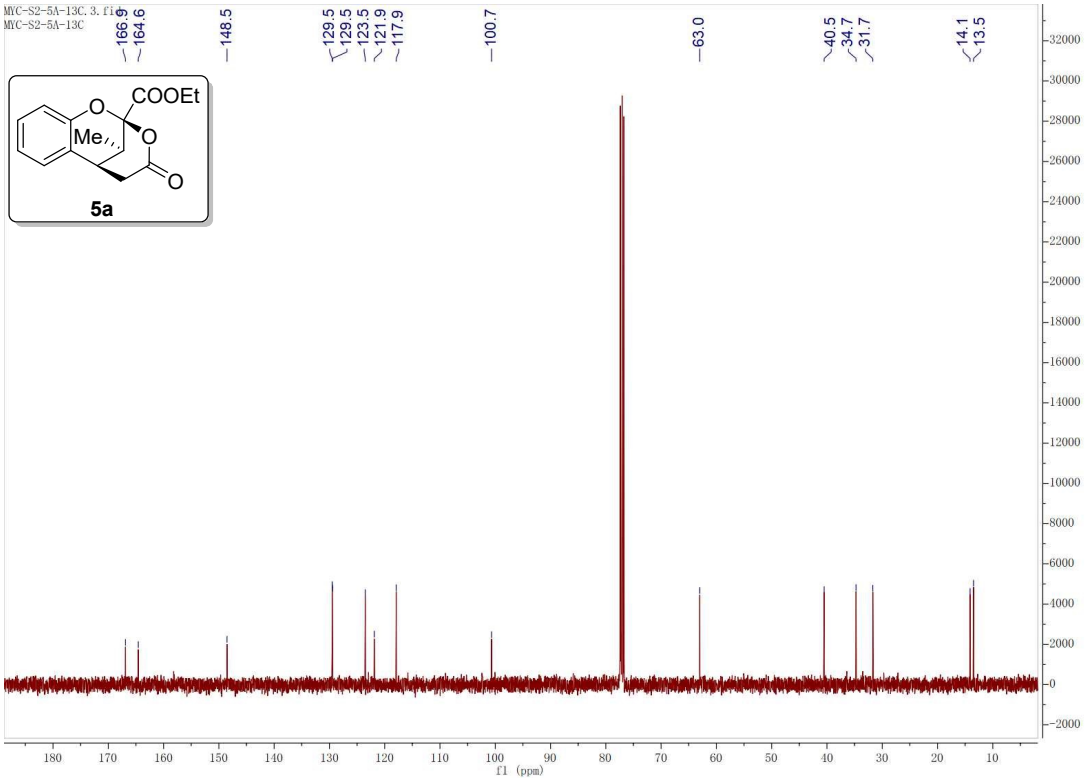
H	0.535742	-0.497275	-2.270935
O	2.279751	-2.420589	-1.192024
O	4.090702	-0.461522	0.017041

I. NMR spectra and HPLC traces

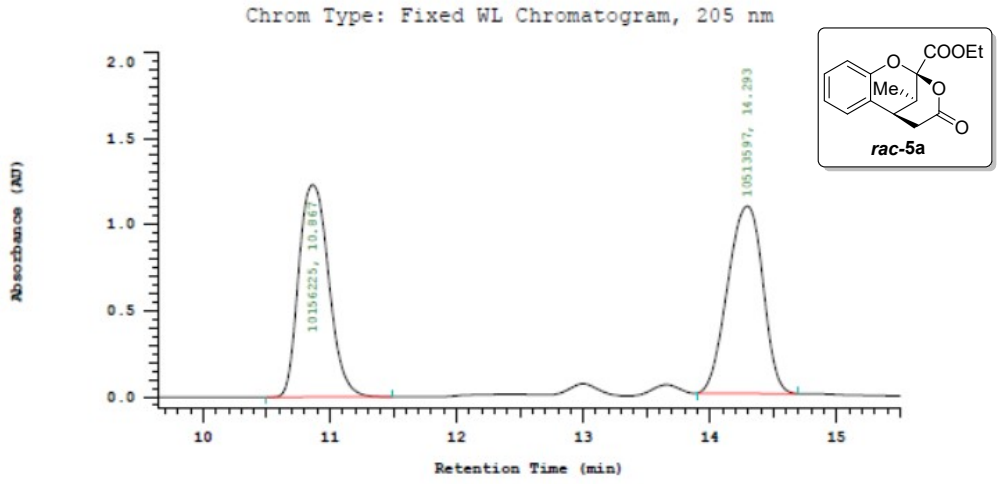
The ^{1}H NMR spectrum of 5a (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5a (100 MHz, $CDCl_3$)



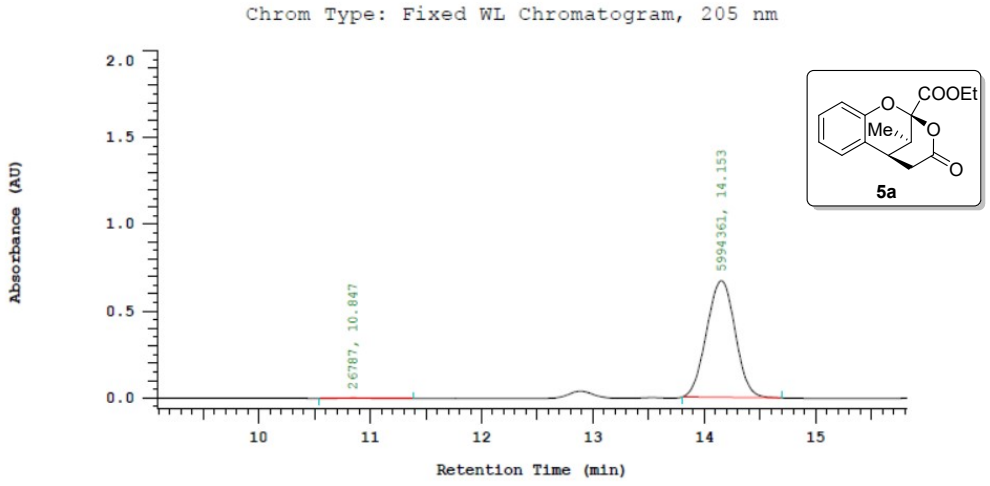
The HPLC of racemic 5a



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.867	10156225	49.136	BB
2	14.293	10513597	50.864	BB
		20669822	100.000	

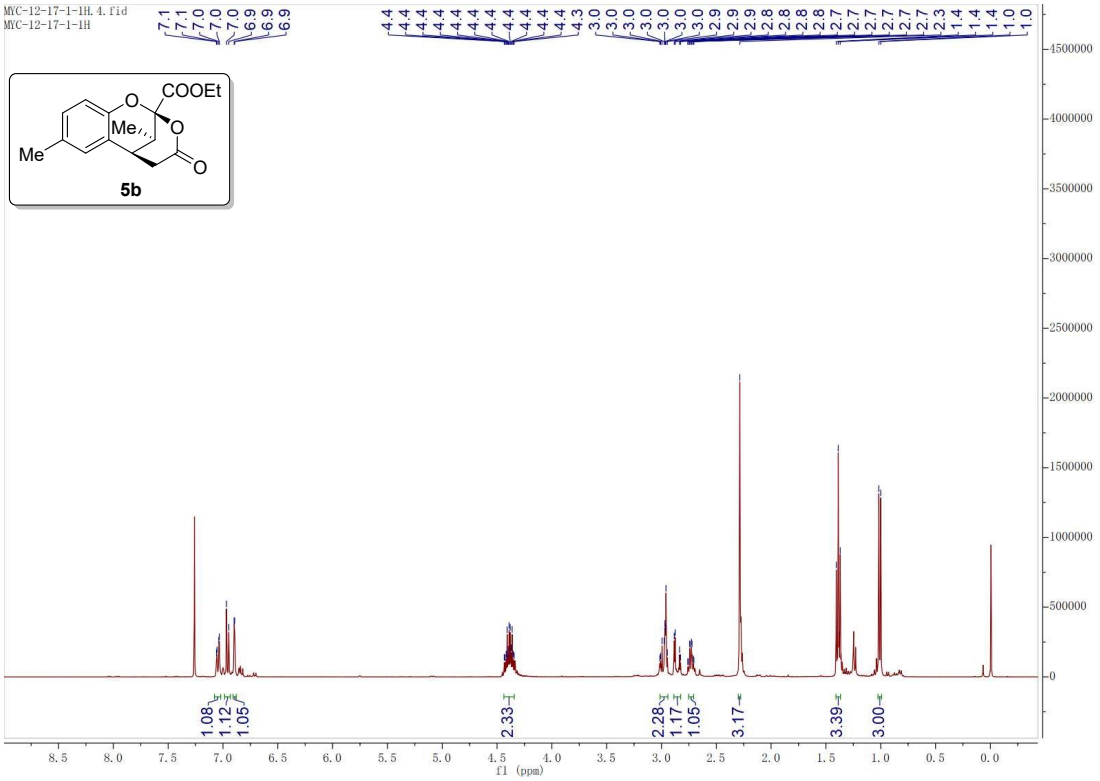
The HPLC of chiral 5a



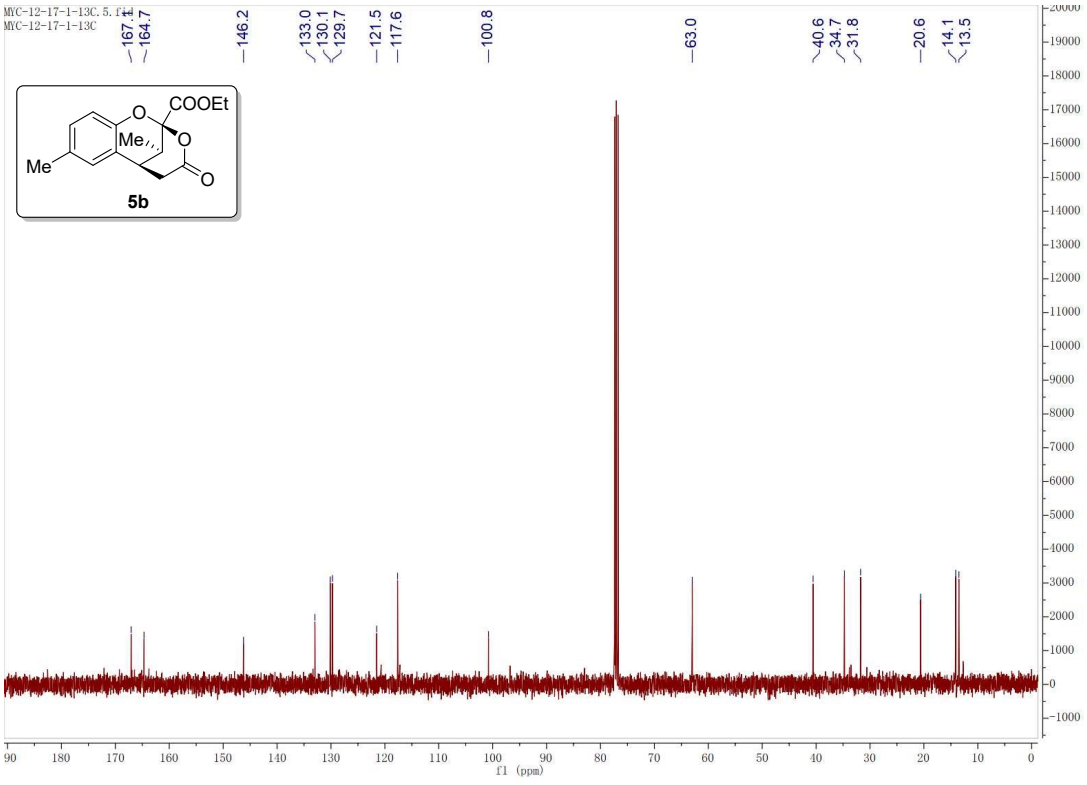
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.847	26787	0.445	BB
2	14.153	5994361	99.555	BB
		6021148	100.000	

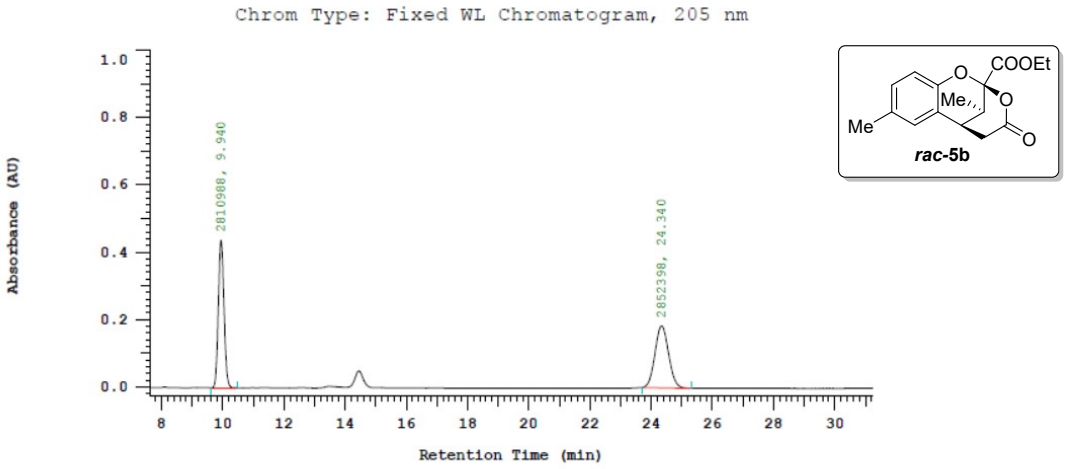
The ^{1}H NMR spectrum of 5b (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5b (100 MHz, $CDCl_3$)



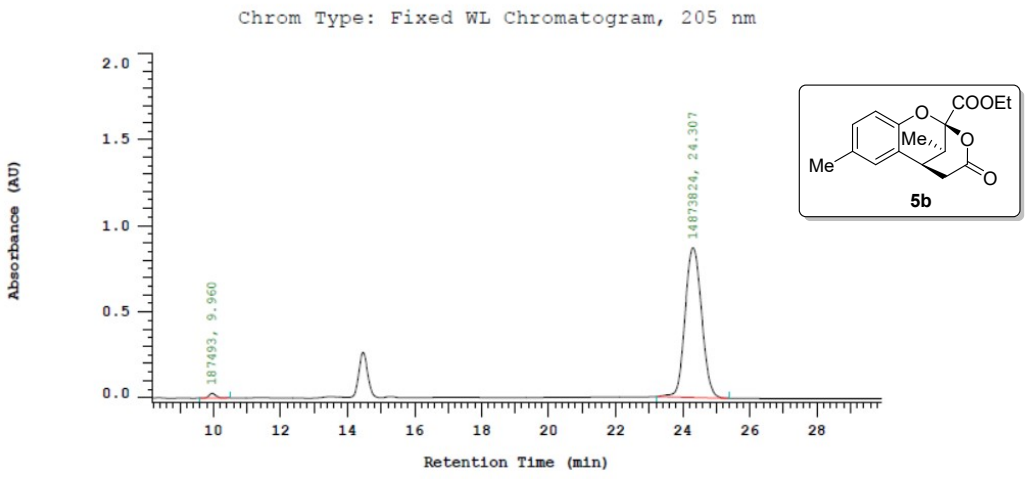
The HPLC of racemic 5b



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.940	2810988	49.634	BB
2	24.340	2852398	50.366	BB
		5663386	100.000	

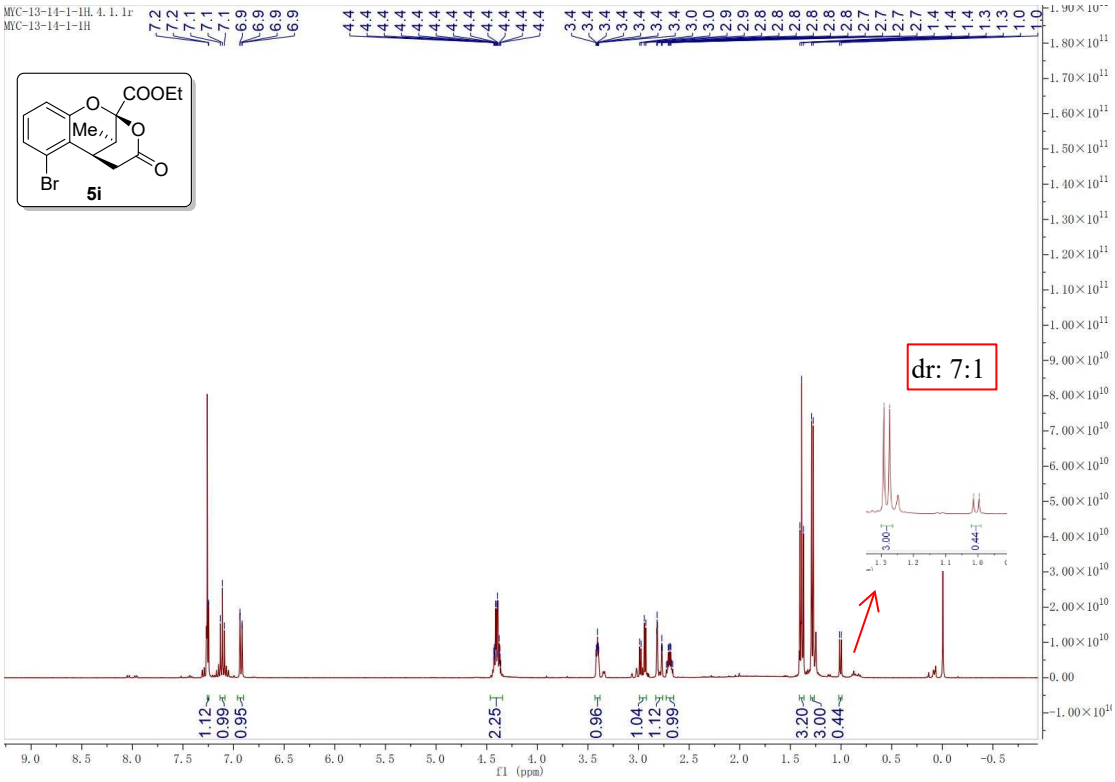
The HPLC of chiral 5b



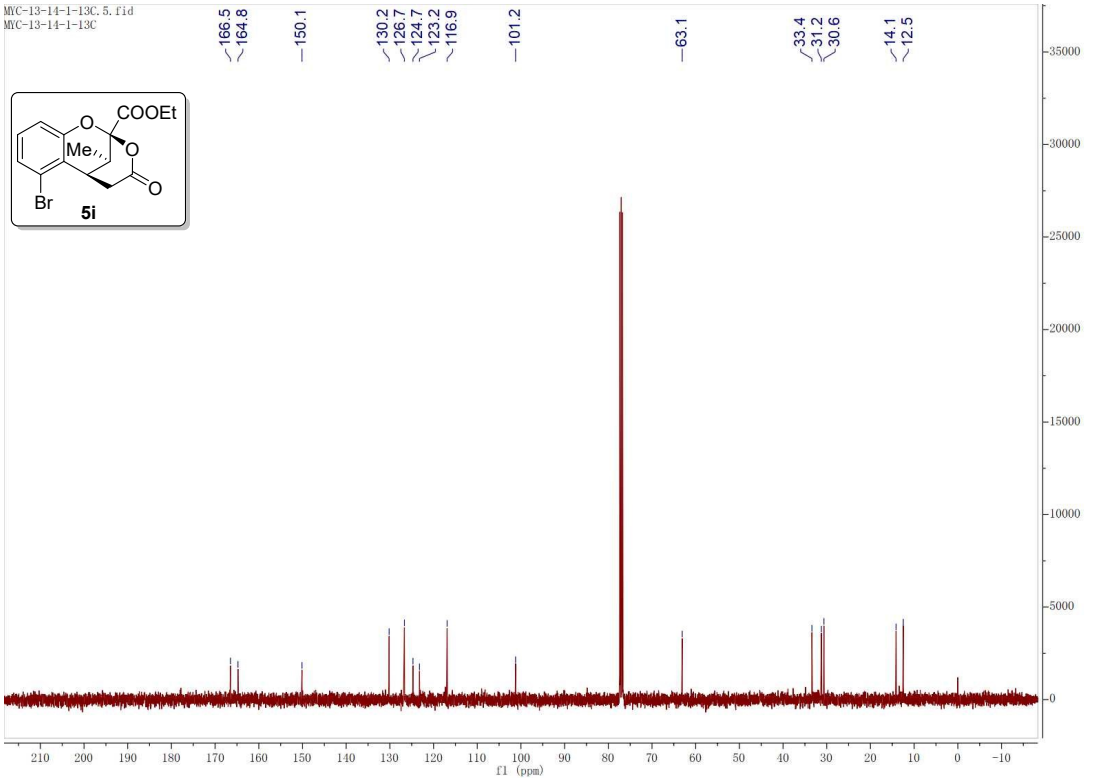
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.960	187493	1.245	BB
2	24.307	14873824	98.755	BB
		15061317	100.000	

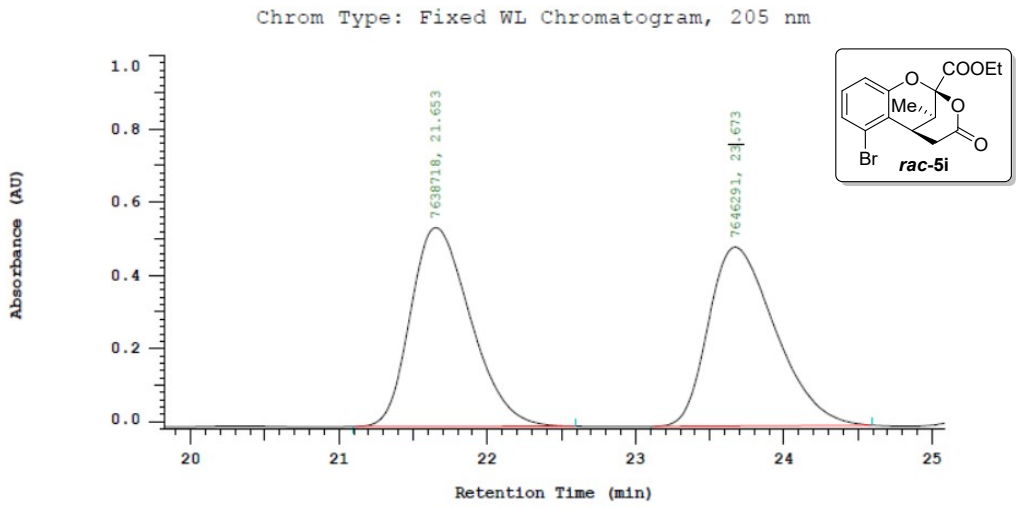
The ^{1}H NMR spectrum of 5i (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5i (100 MHz, $CDCl_3$)



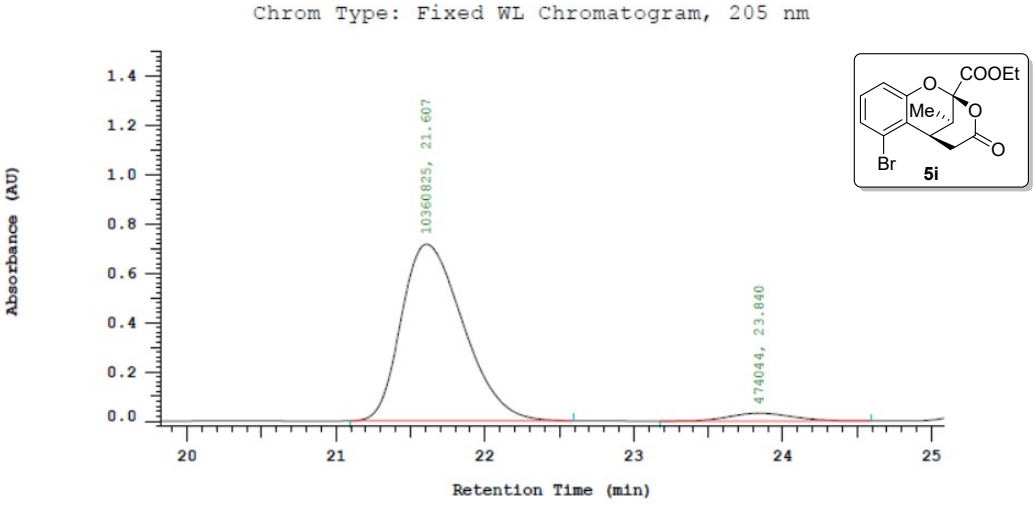
The HPLC of racemic 5i



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	21.653	7638718	49.975	BB
2	23.673	7646291	50.025	BB
		15285009	100.000	

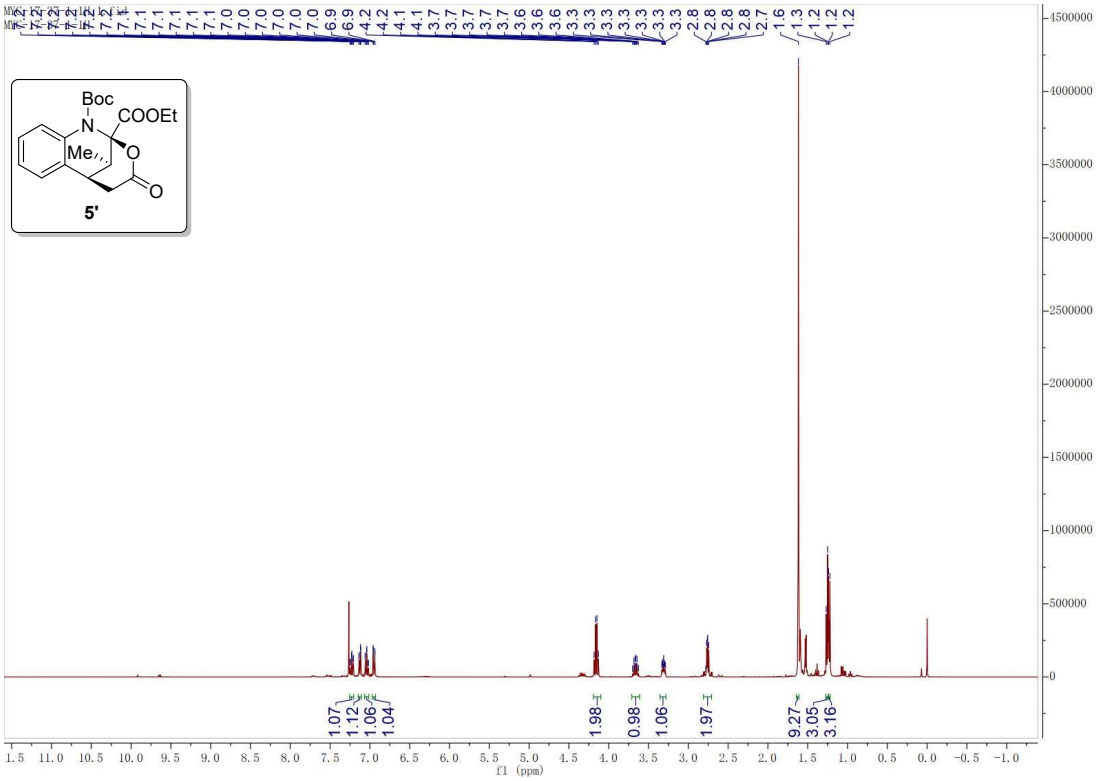
The HPLC of chiral 5i



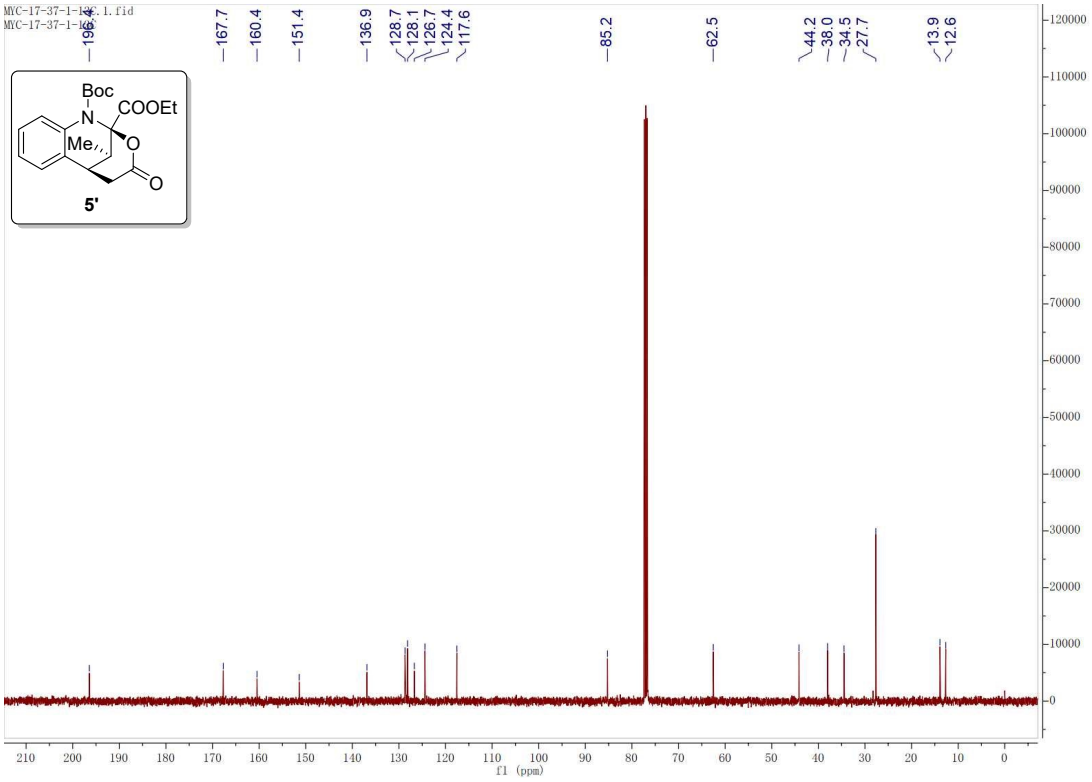
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	21.607	10360825	95.625	BB
2	23.840	474044	4.375	BB
		10834869	100.000	

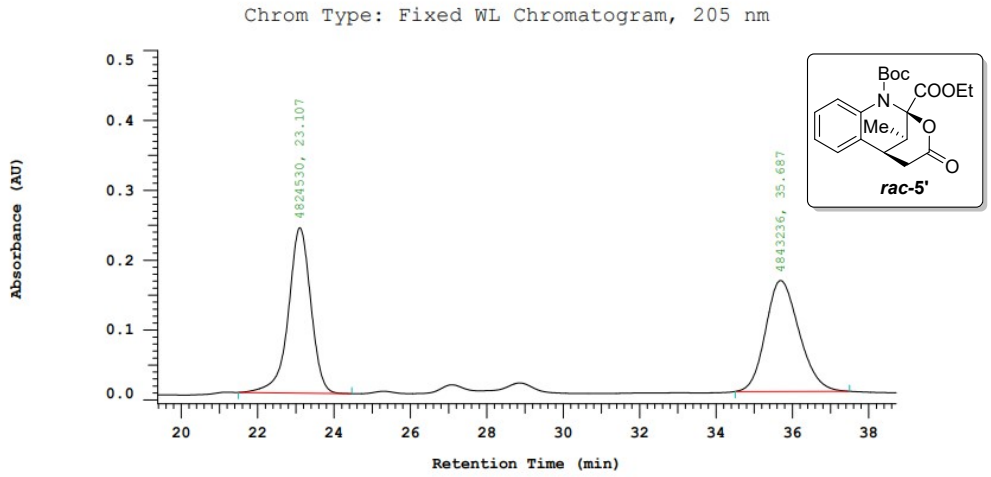
The ^{1}H NMR spectrum of 5' (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5' (100 MHz, $CDCl_3$)



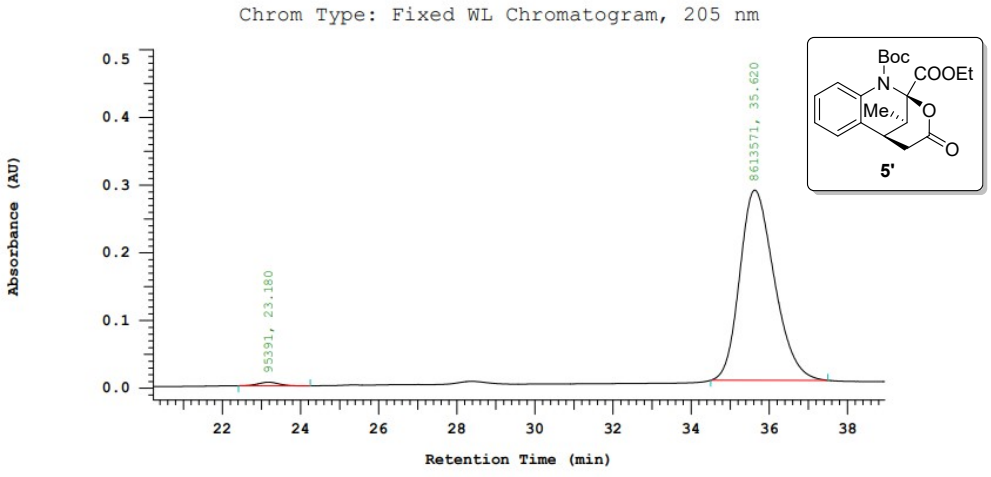
The HPLC of racemic 5’



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	23.107	4824530	49.903	BB
2	35.687	4843236	50.097	BB
		9667766	100.000	

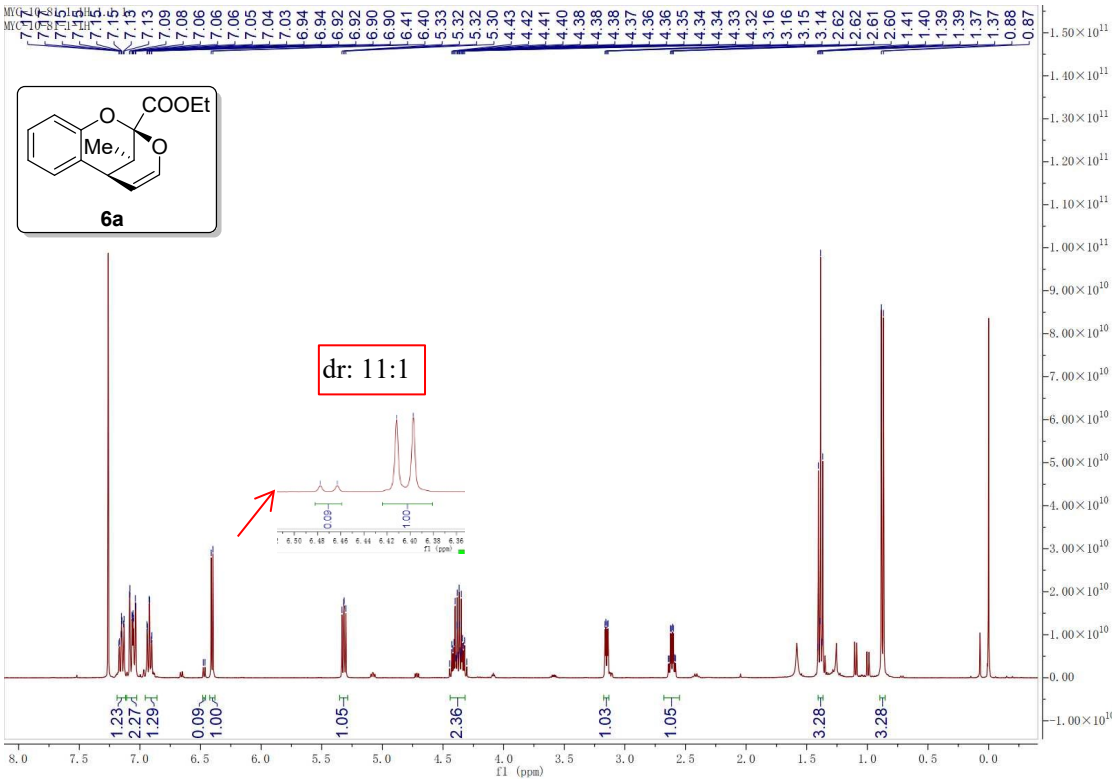
The HPLC of chiral 5’



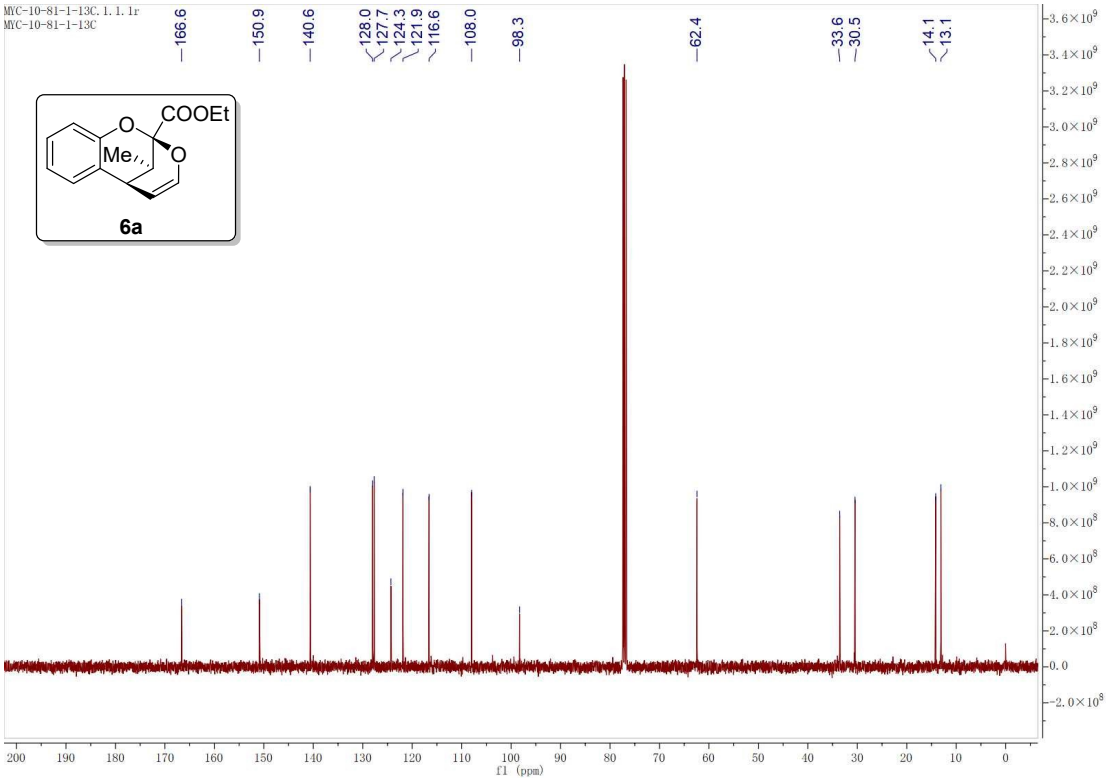
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	23.180	95391	1.095	BB
2	35.620	8613571	98.905	BB
		8708962	100.000	

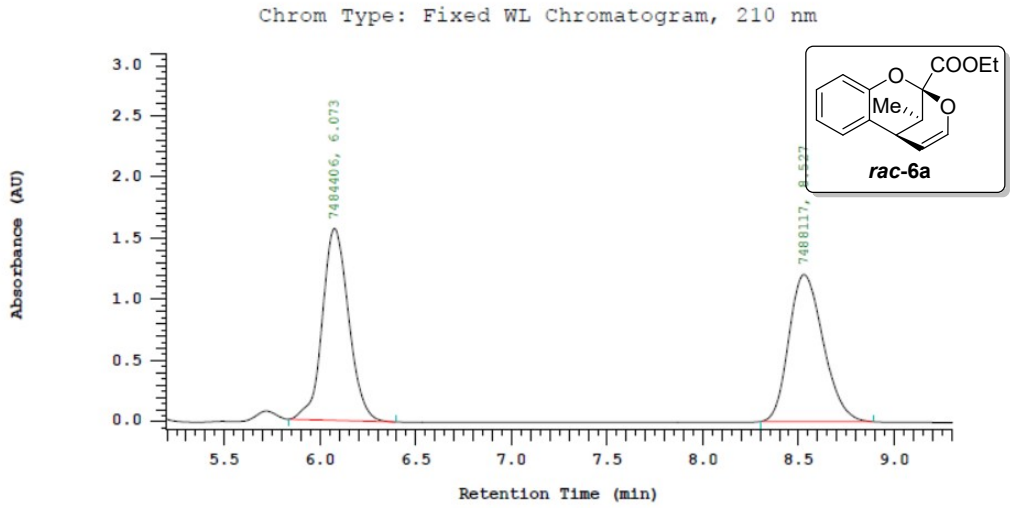
The ^{1}H NMR spectrum of 6a (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6a (100 MHz, $CDCl_3$)



The HPLC of racemic 6a



Chrom Type: Fixed WL Chromatogram, 210 nm

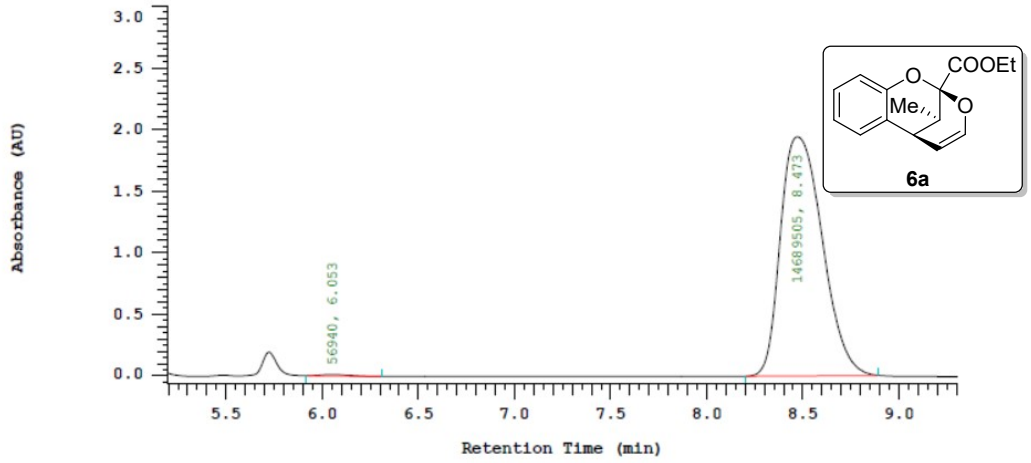
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.073	7484406	49.988	BB
2	8.527	7488117	50.012	BB
		14972523	100.000	

The HPLC of chiral 6a

Chrom Type: Fixed WL Chromatogram, 210 nm



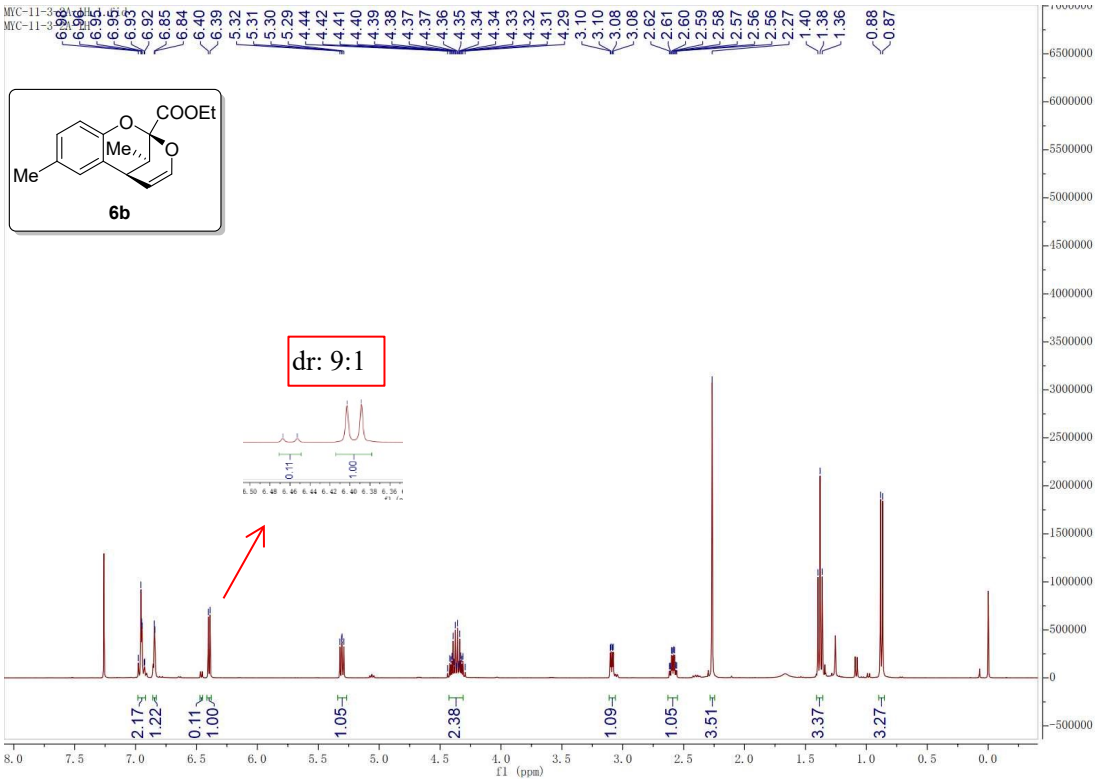
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

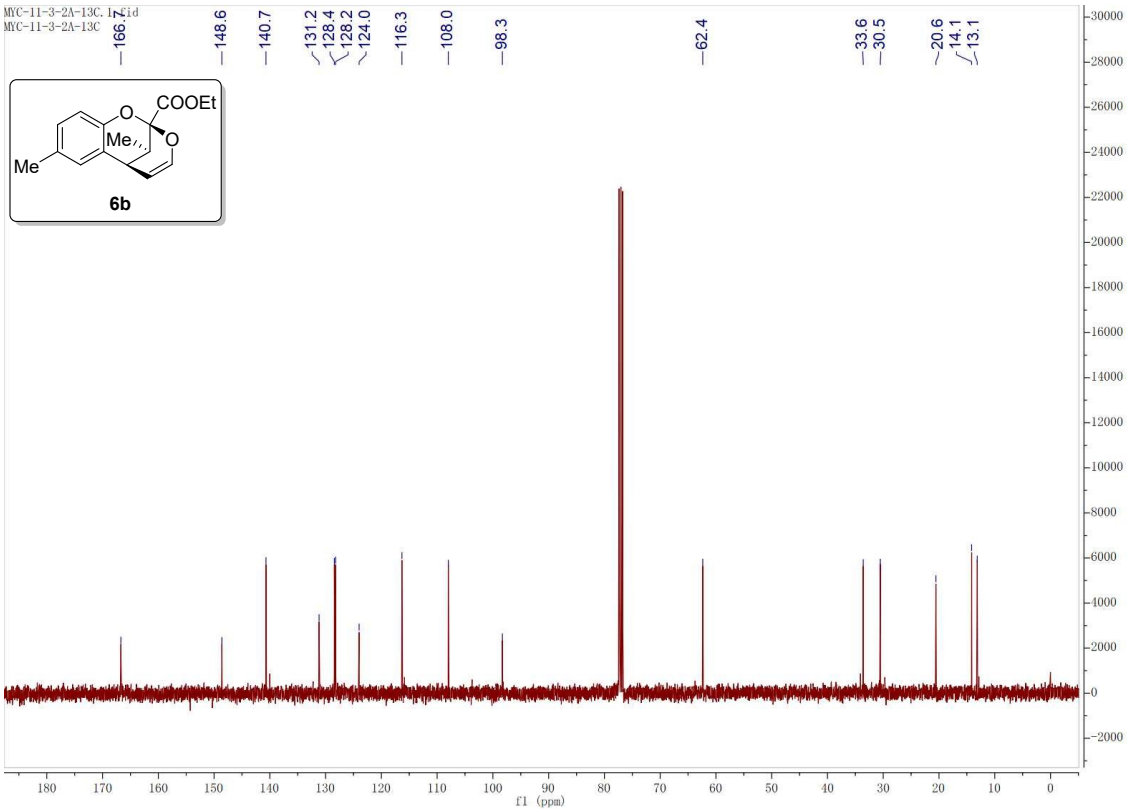
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.053	56940	0.386	BB
2	8.473	14689505	99.614	BB
		14746445	100.000	

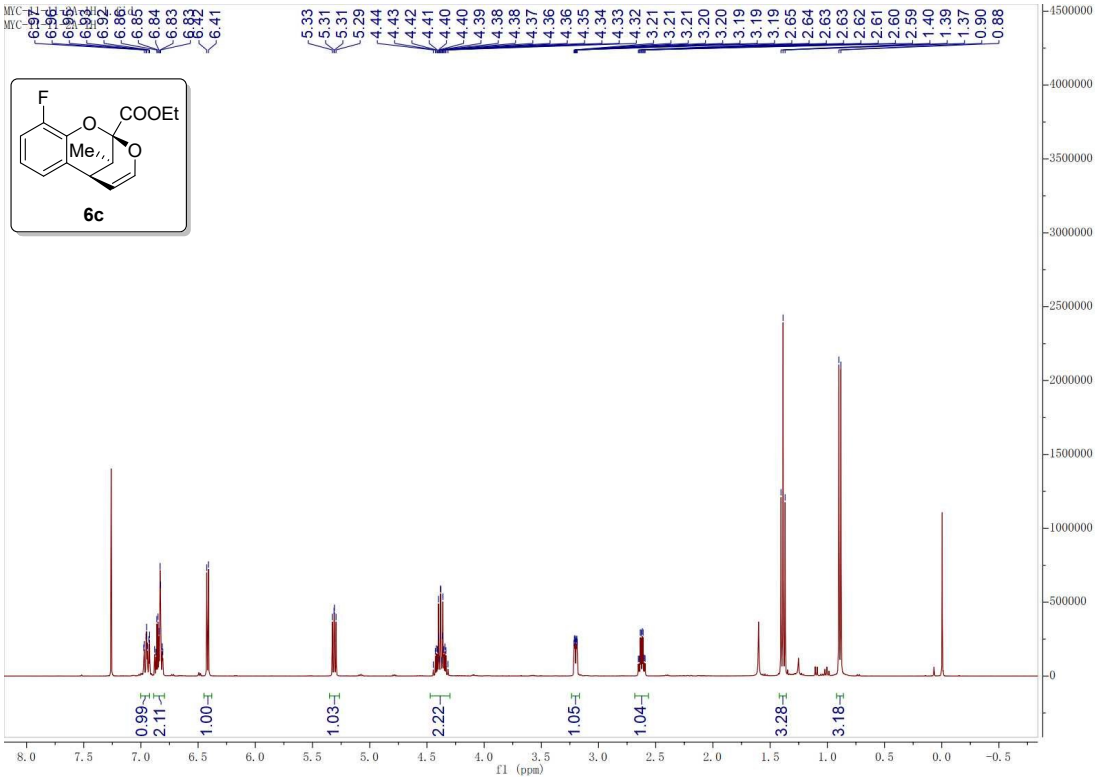
The ^{1}H NMR spectrum of 6b (400 MHz, $CDCl_3$)



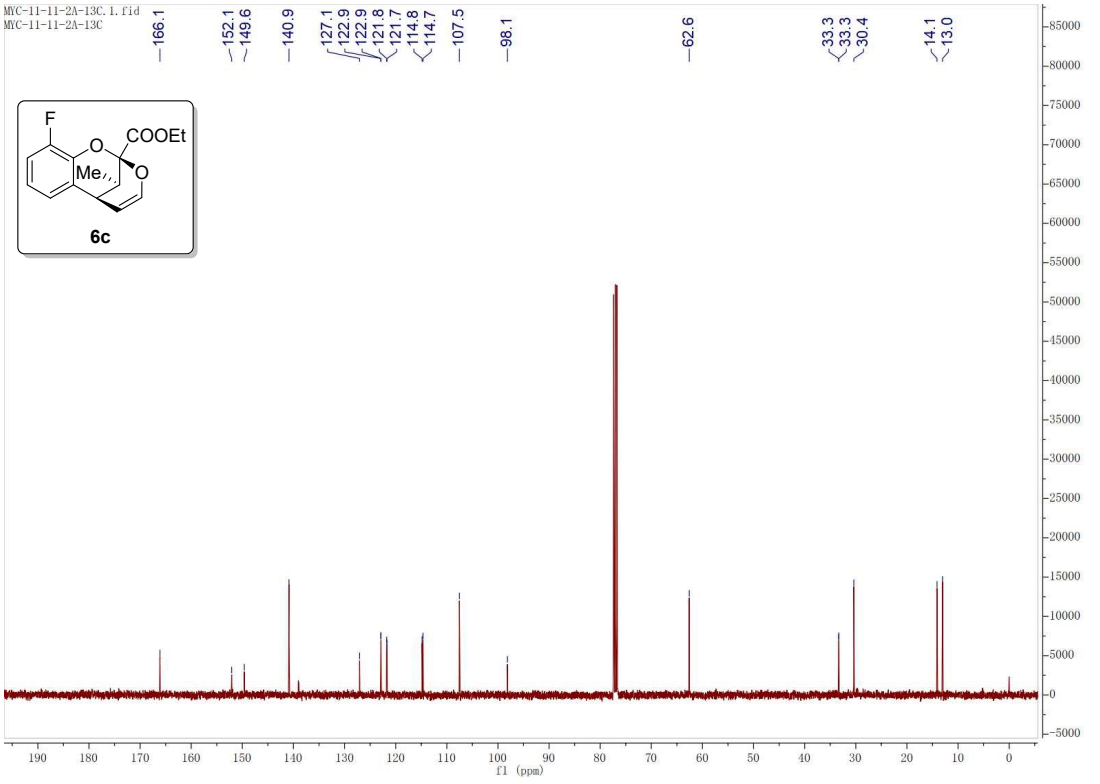
The ^{13}C NMR spectrum of 6b (100 MHz, $CDCl_3$)



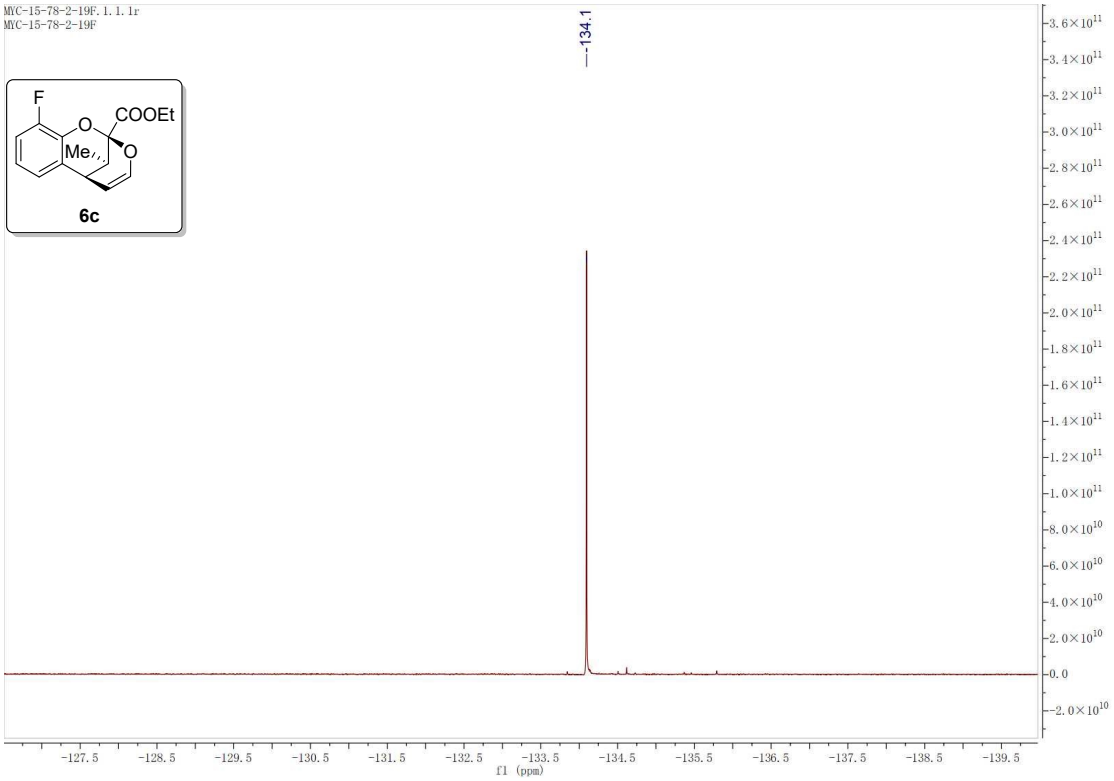
The ^{1}H NMR spectrum of 6c (400 MHz, $CDCl_3$)



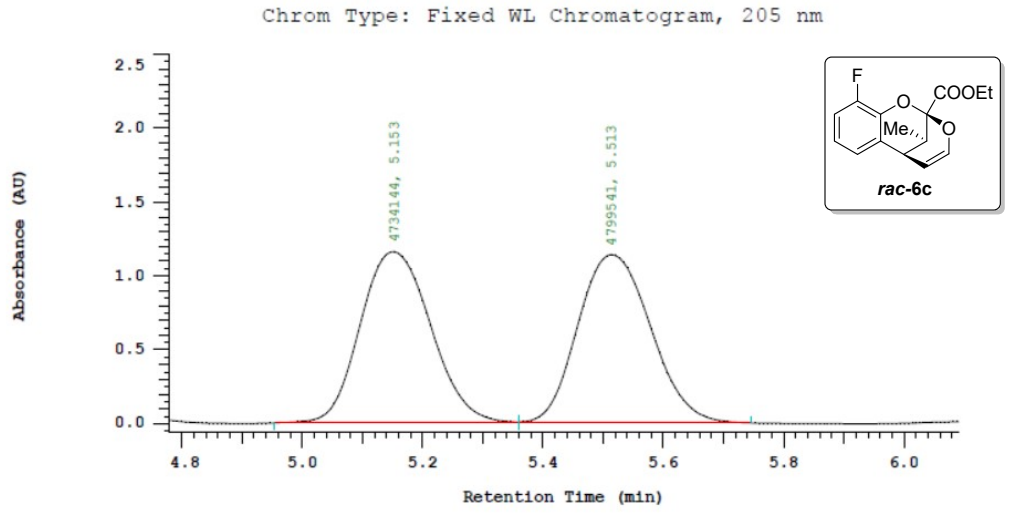
The ^{13}C NMR spectrum of 6c (100 MHz, $CDCl_3$)



The ^{19}F NMR spectrum of 6c (376 MHz, $CDCl_3$)



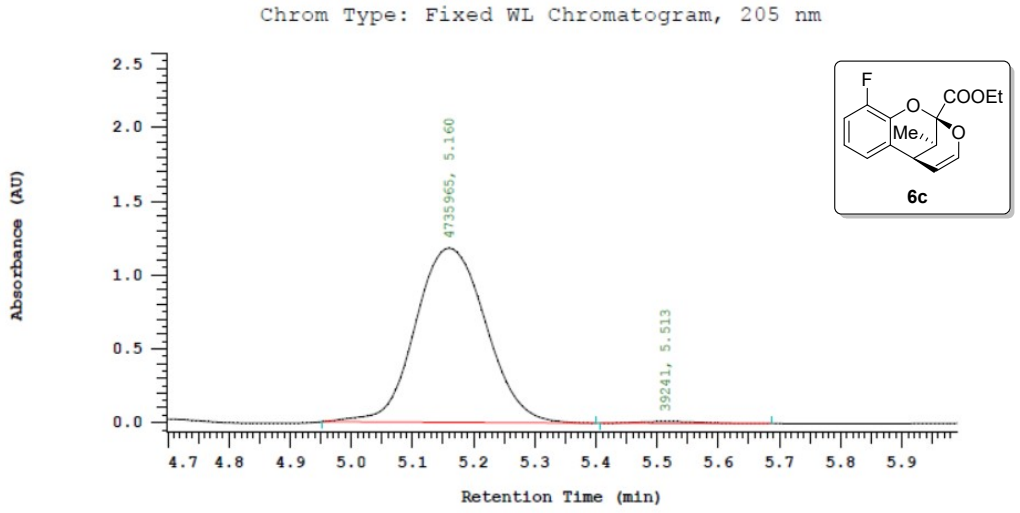
The HPLC of racemic 6c



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	5.153	4734144	49.657	BV
2	5.513	4799541	50.343	VB
		9533685	100.000	

The HPLC of chiral 6c



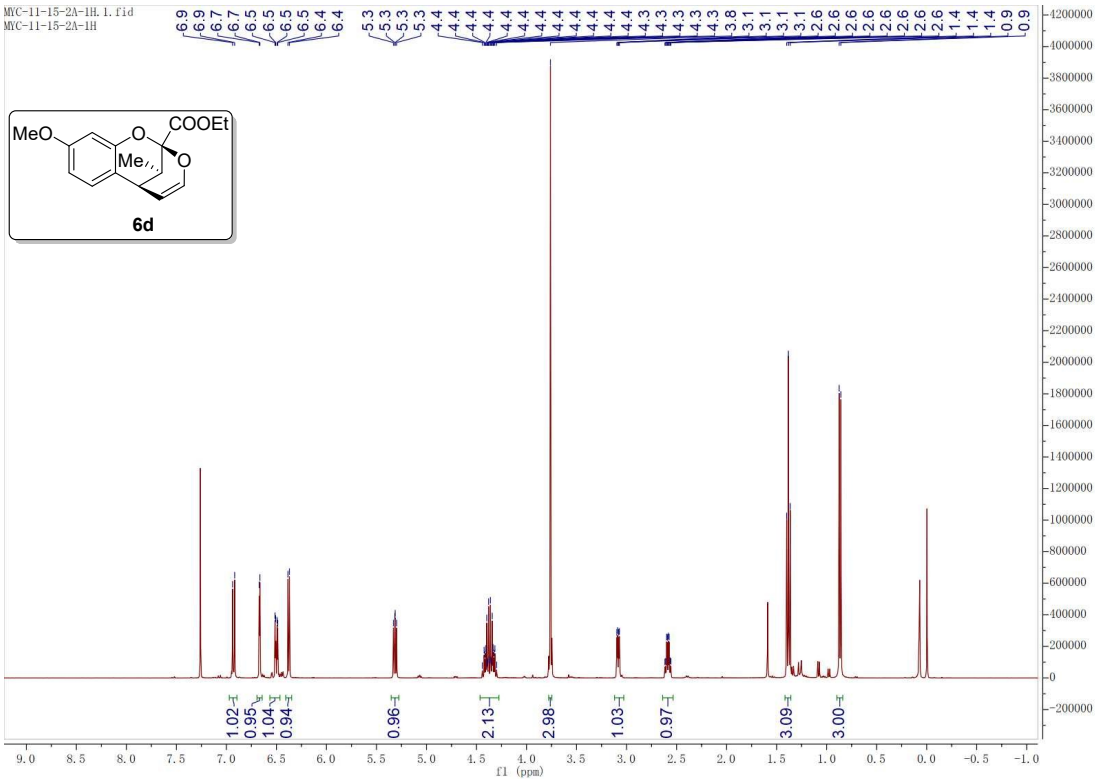
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

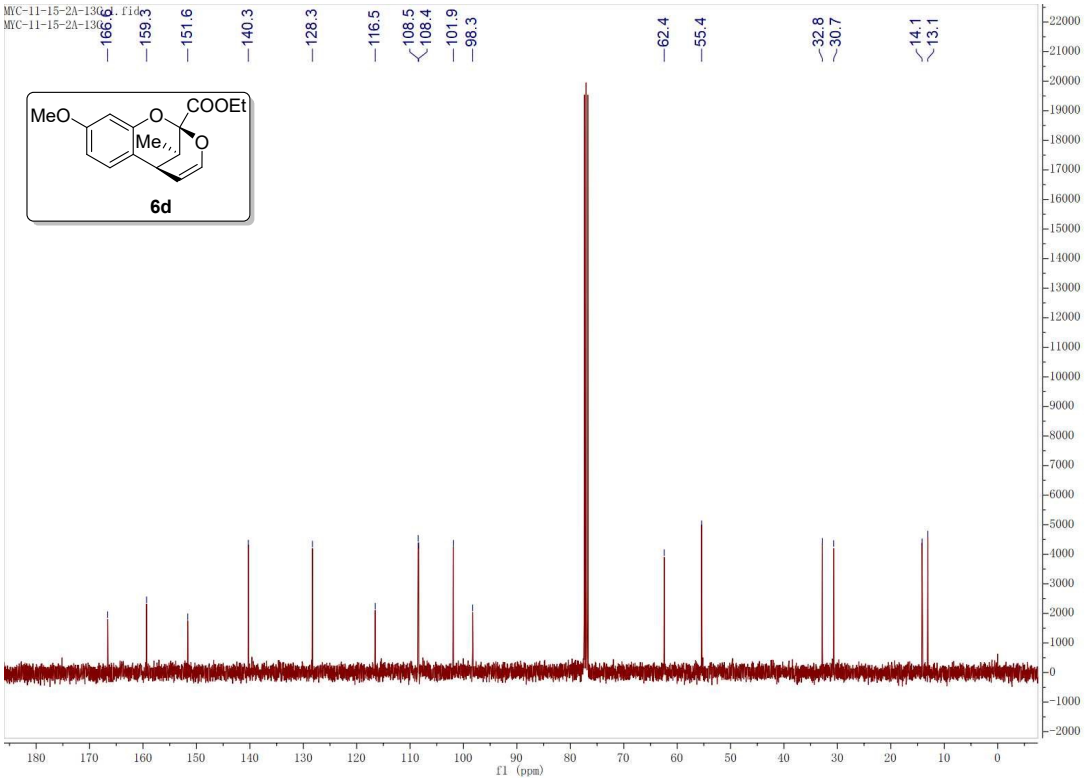
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	5.160	4735965	99.178	BB
2	5.513	39241	0.822	BB
		4775206	100.000	

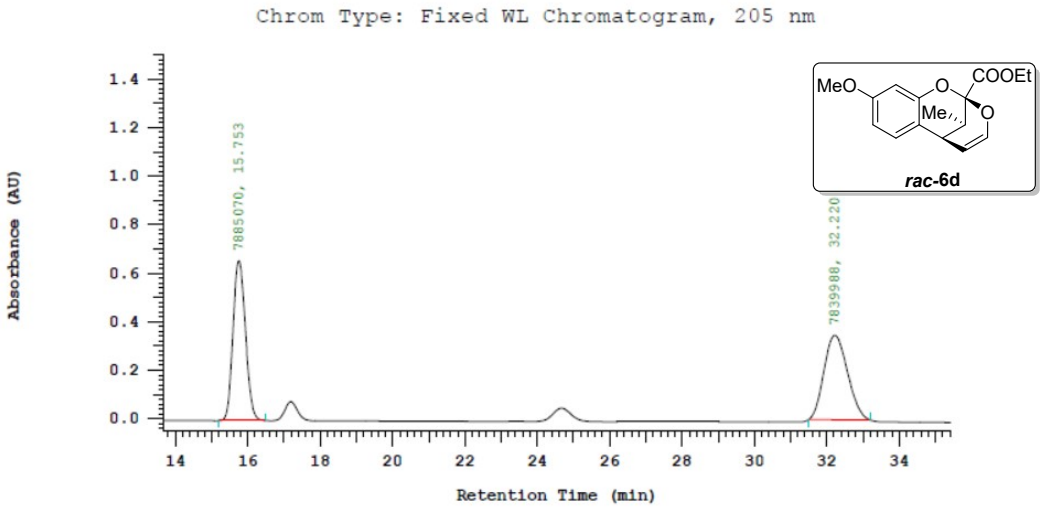
The ^{1}H NMR spectrum of 6d (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6d (100 MHz, $CDCl_3$)



The HPLC of racemic 6d



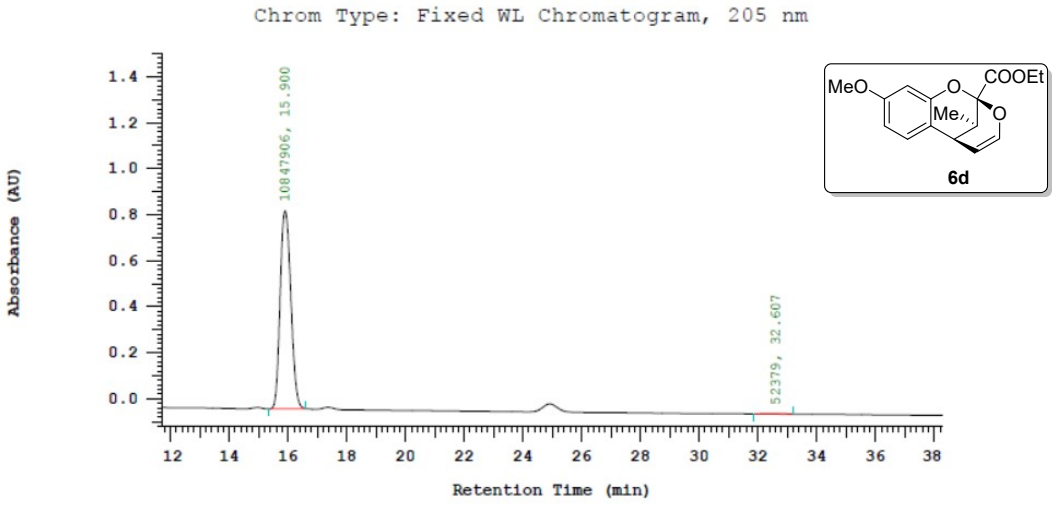
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.753	7885070	50.143	BB
2	32.220	7839988	49.857	BB
		15725058	100.000	

The HPLC of chiral 6d



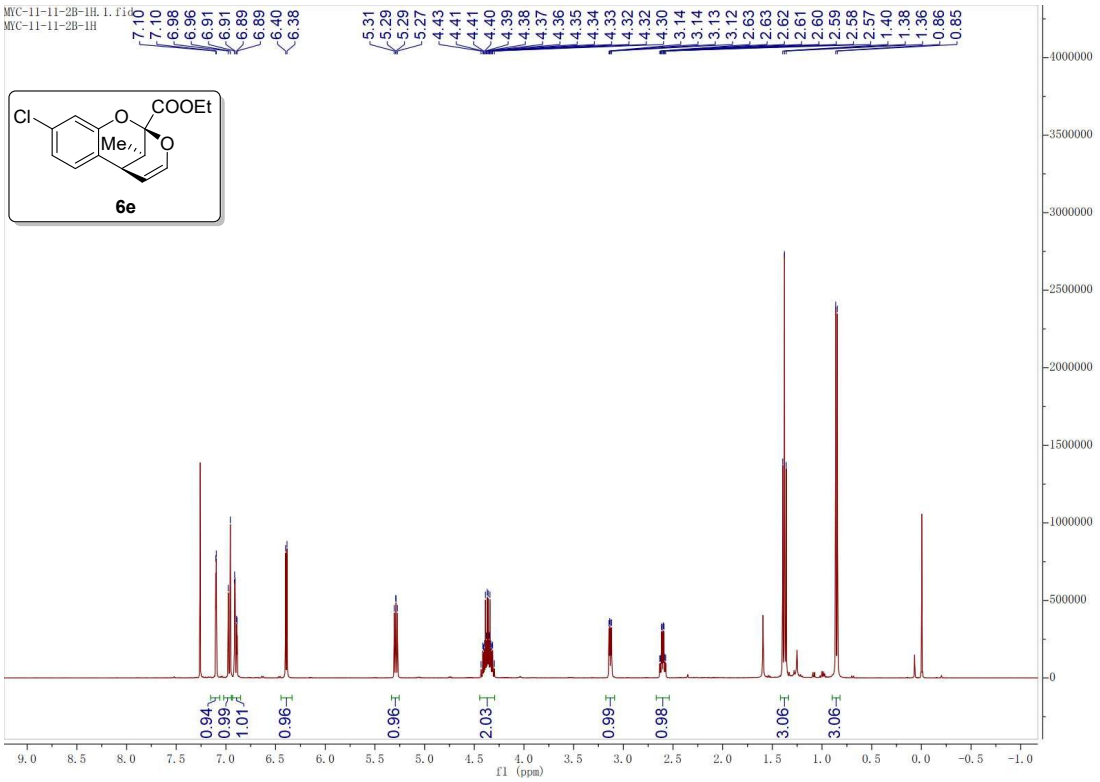
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

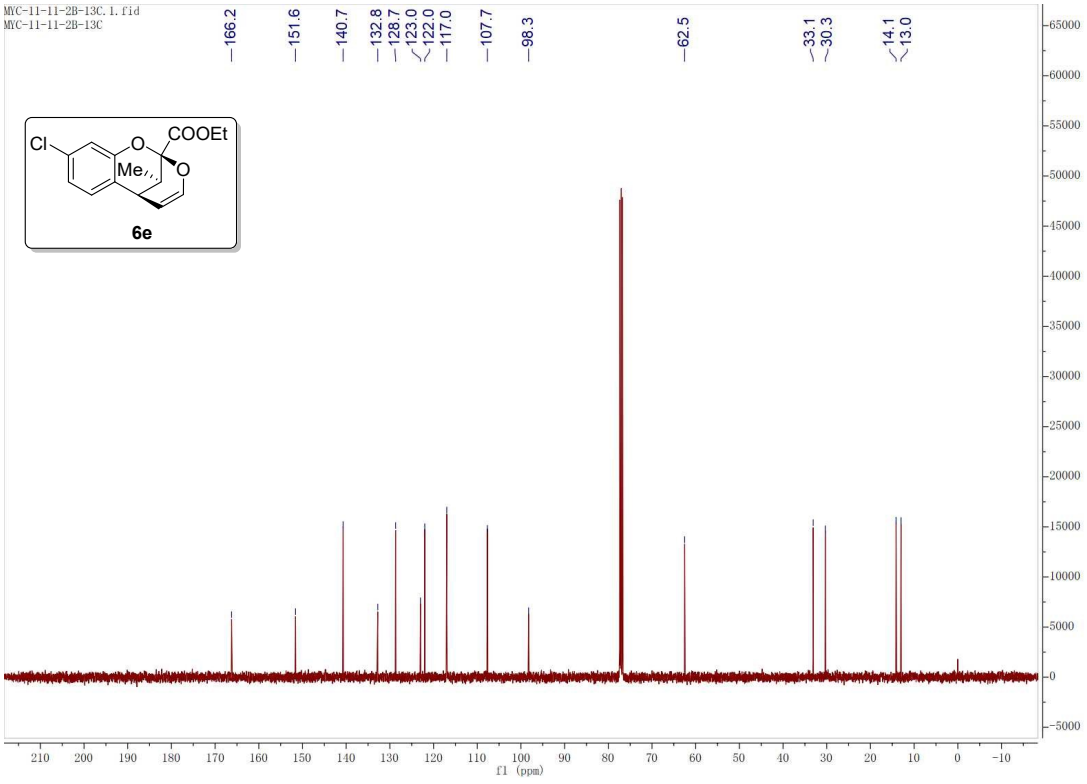
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.900	10847906	99.519	BB
2	32.607	52379	0.481	BB
		10900285	100.000	

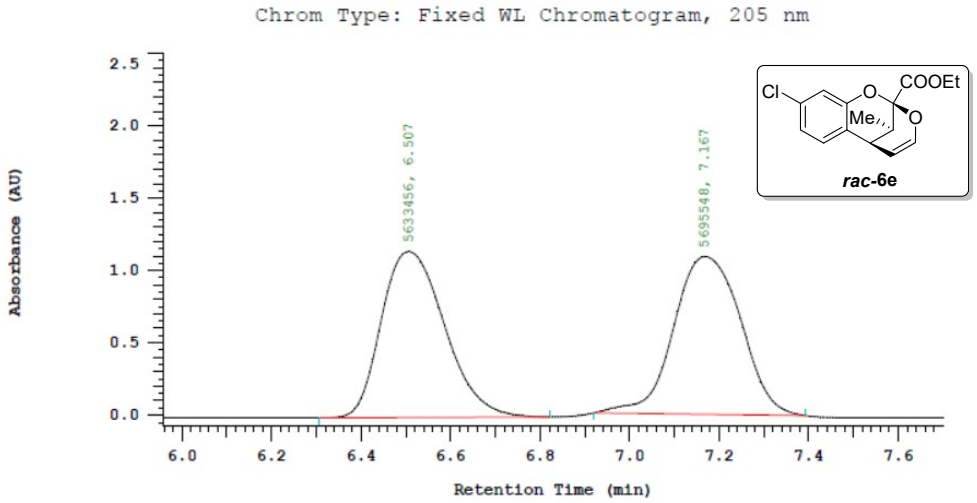
The ^{1}H NMR spectrum of 6e (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6e (100 MHz, $CDCl_3$)



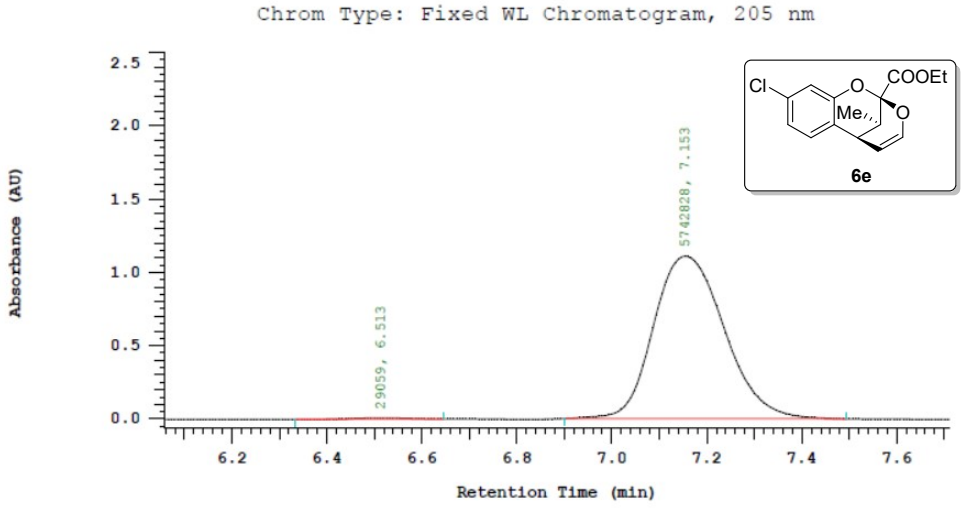
The HPLC of racemic 6e



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.507	5633456	49.726	BB
2	7.167	5695548	50.274	BB
		11329004	100.000	

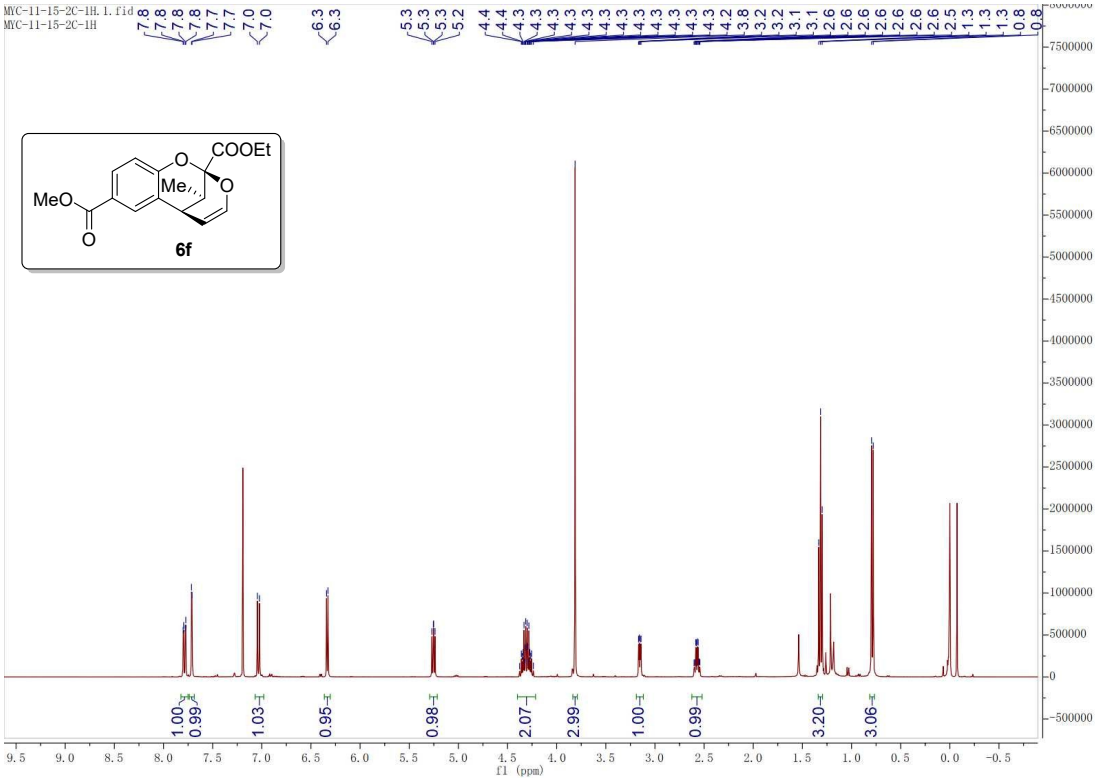
The HPLC of chiral 6e



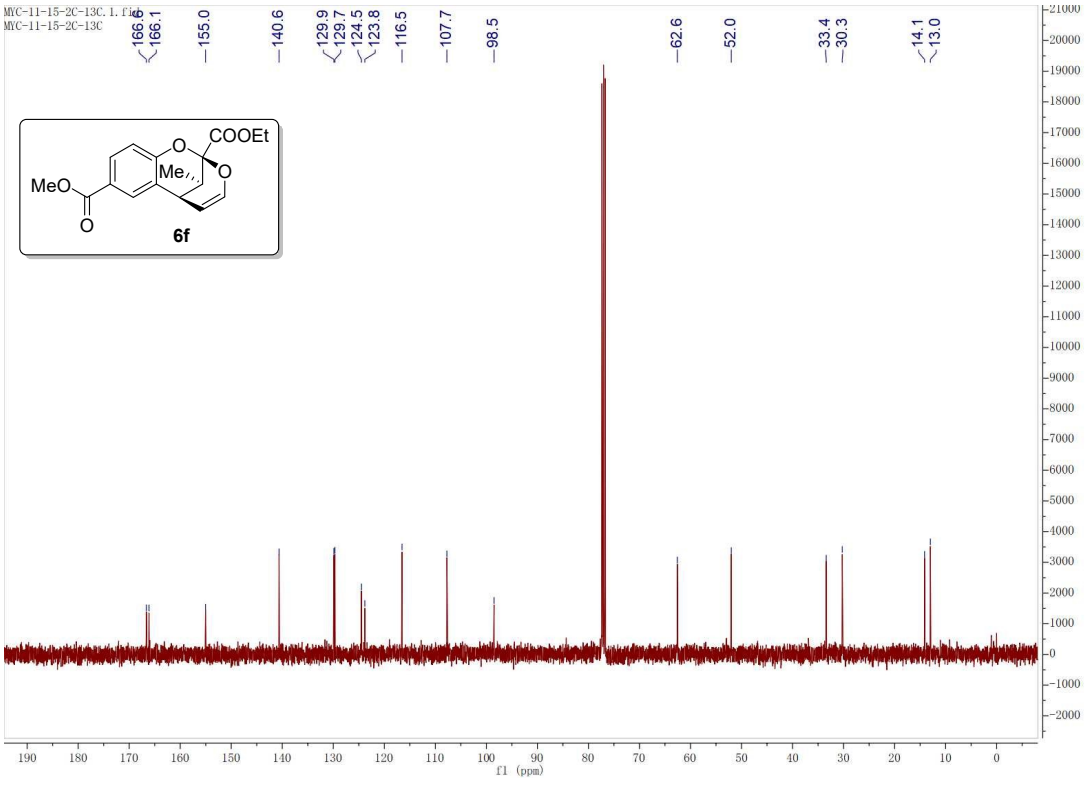
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.513	29059	0.503	BB
2	7.153	5742828	99.497	BB
		5771887	100.000	

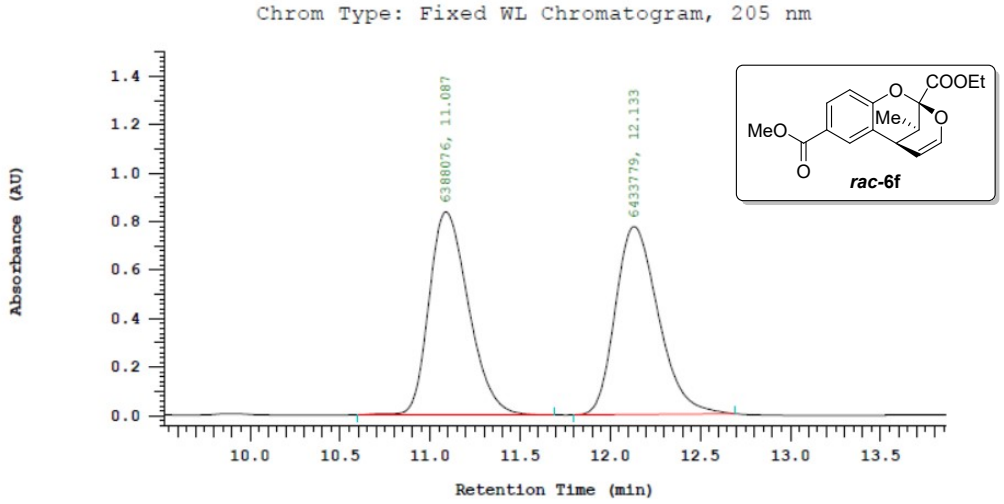
The ^{1}H NMR spectrum of 6f (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6f (100 MHz, $CDCl_3$)



The HPLC of racemic 6f



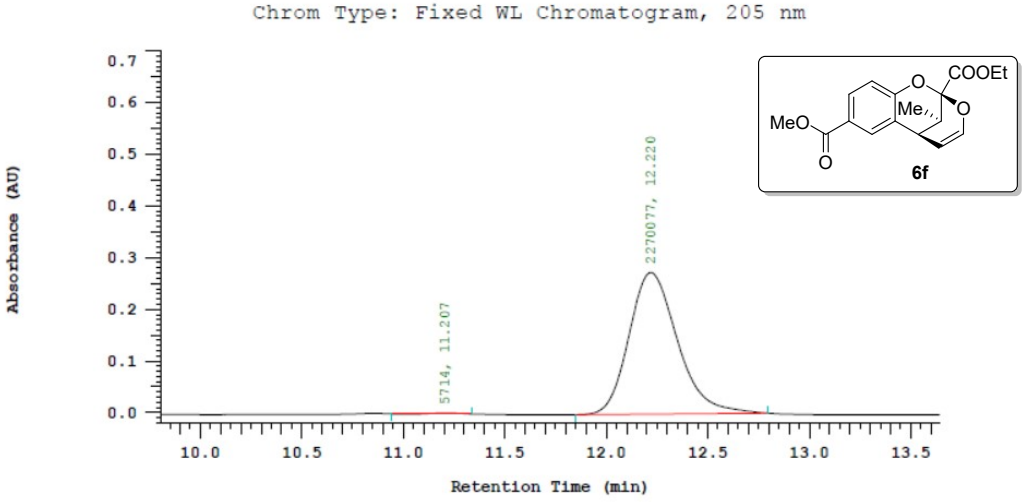
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.087	6388076	49.822	BB
2	12.133	6433779	50.178	BB
		12821855	100.000	

The HPLC of chiral 6f



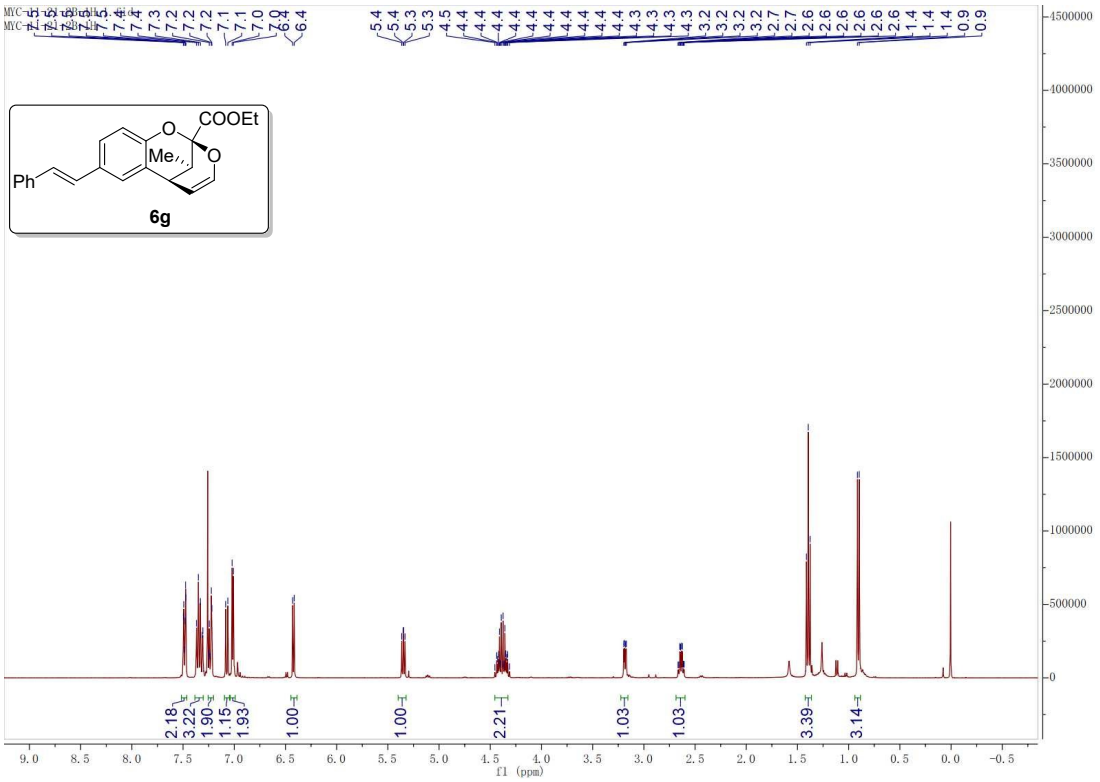
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

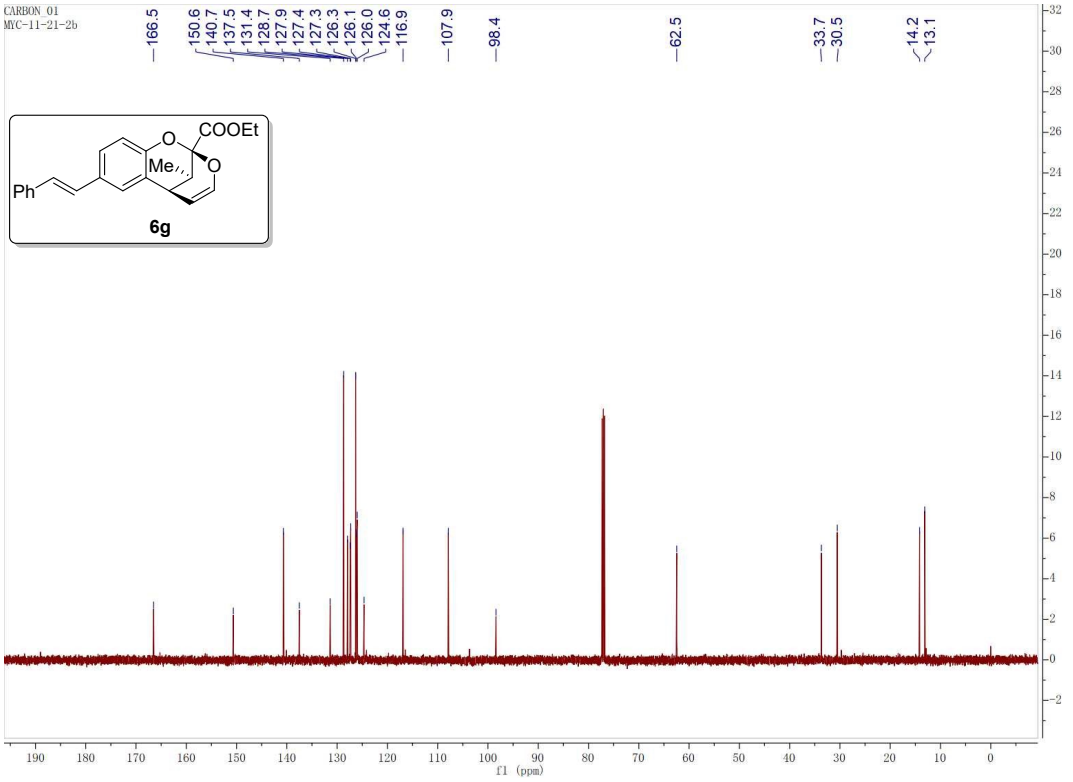
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.207	5714	0.251	BB
2	12.220	2270077	99.749	BB
		2275791	100.000	

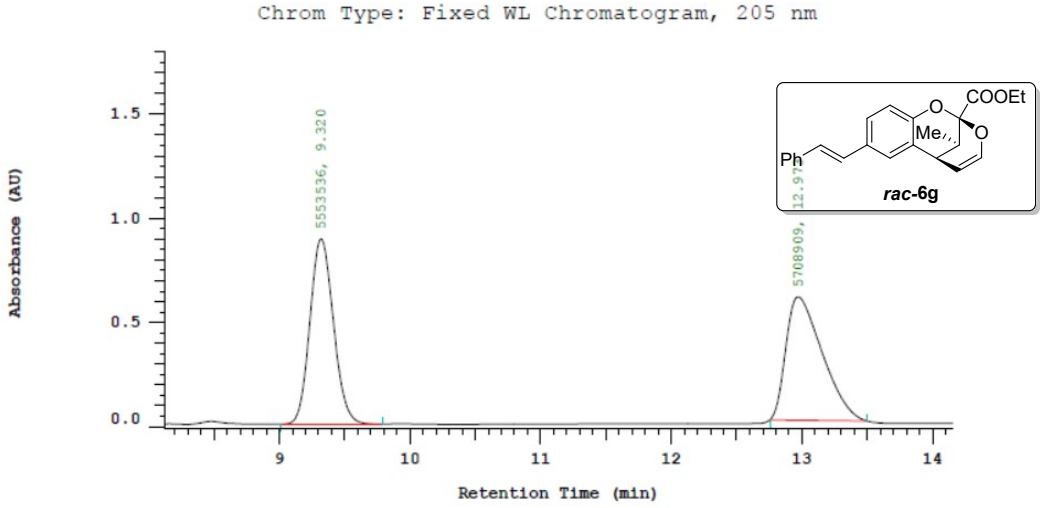
The ^{1}H NMR spectrum of 6g (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6g (100 MHz, $CDCl_3$)



The HPLC of racemic 6g

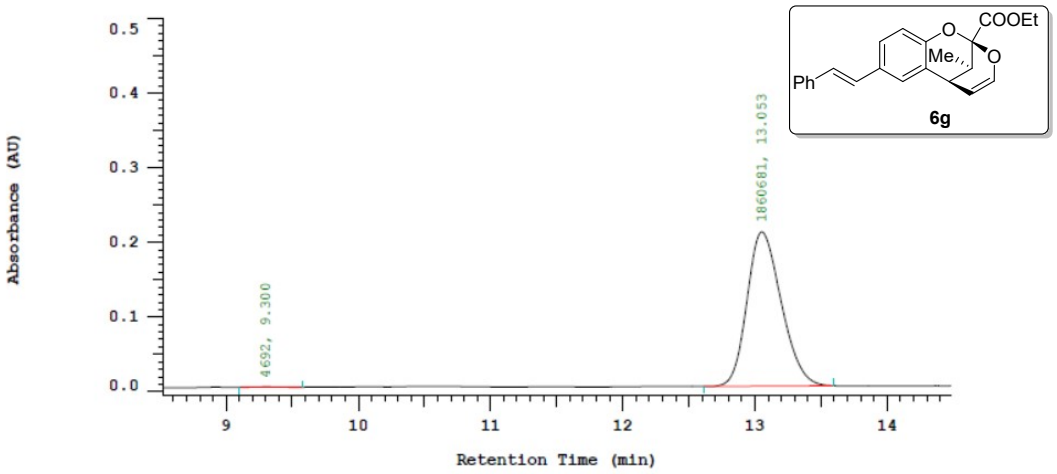


Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.320	5553536	49.310	BB
2	12.973	5708909	50.690	BB
		11262445	100.000	

The HPLC of chiral 6g

Chrom Type: Fixed WL Chromatogram, 205 nm



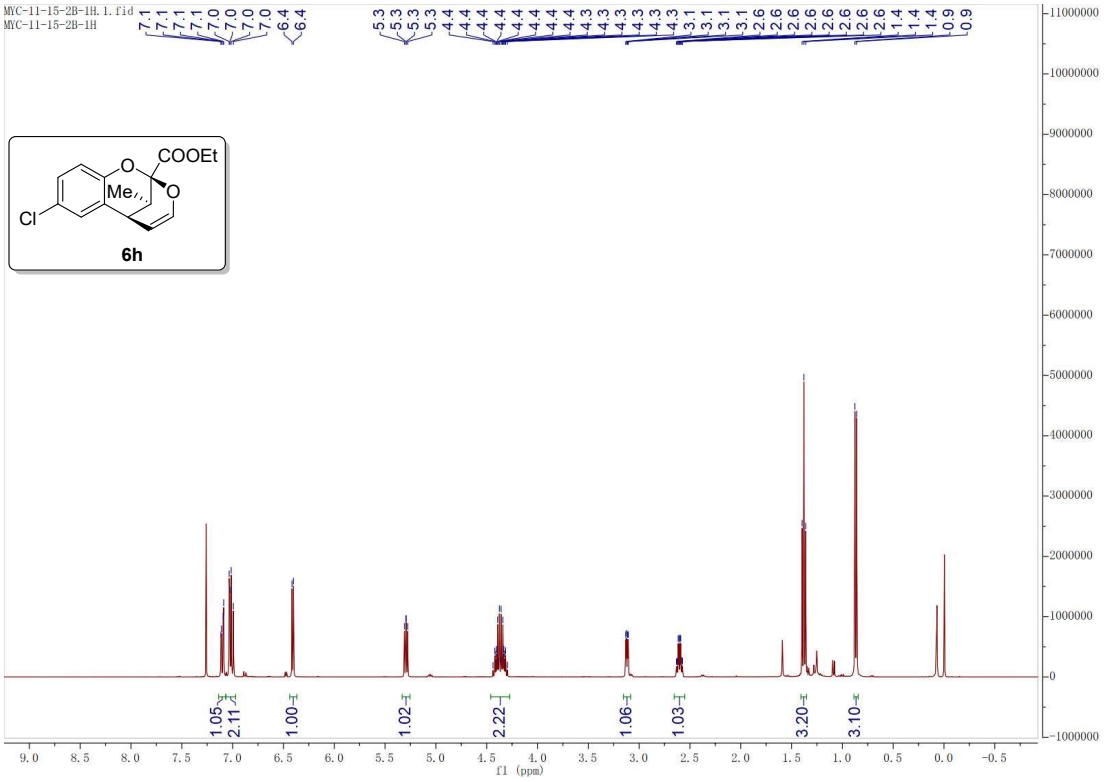
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

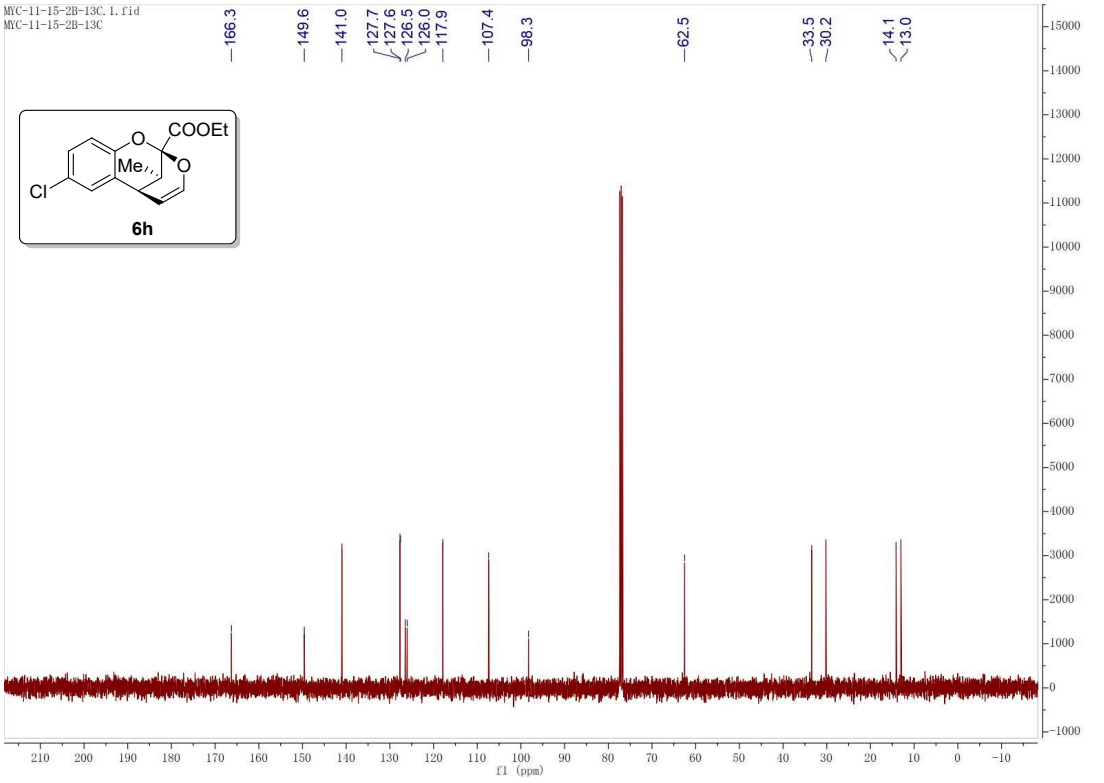
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.300	4692	0.252	BB
2	13.053	1860681	99.748	BB
		1865373	100.000	

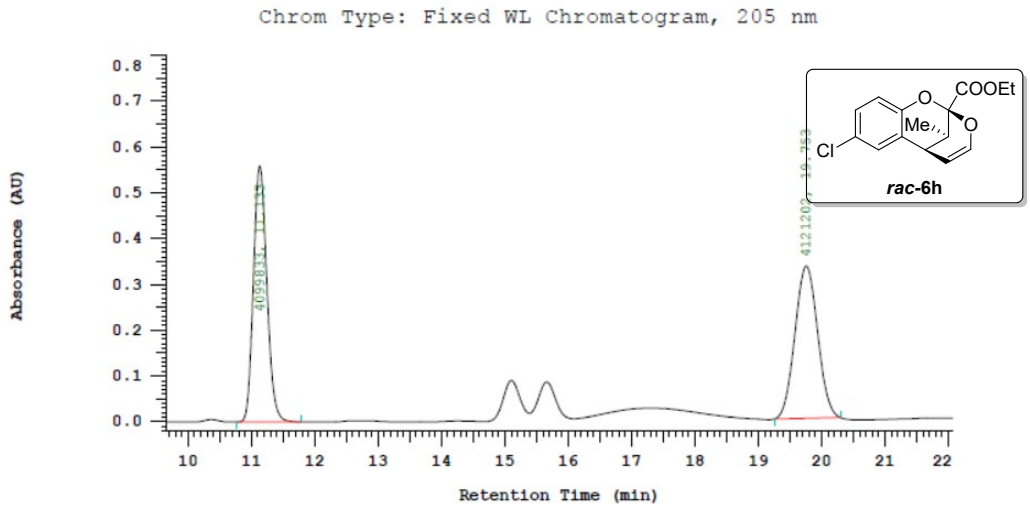
The ^{1}H NMR spectrum of 6h (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6h (100 MHz, $CDCl_3$)



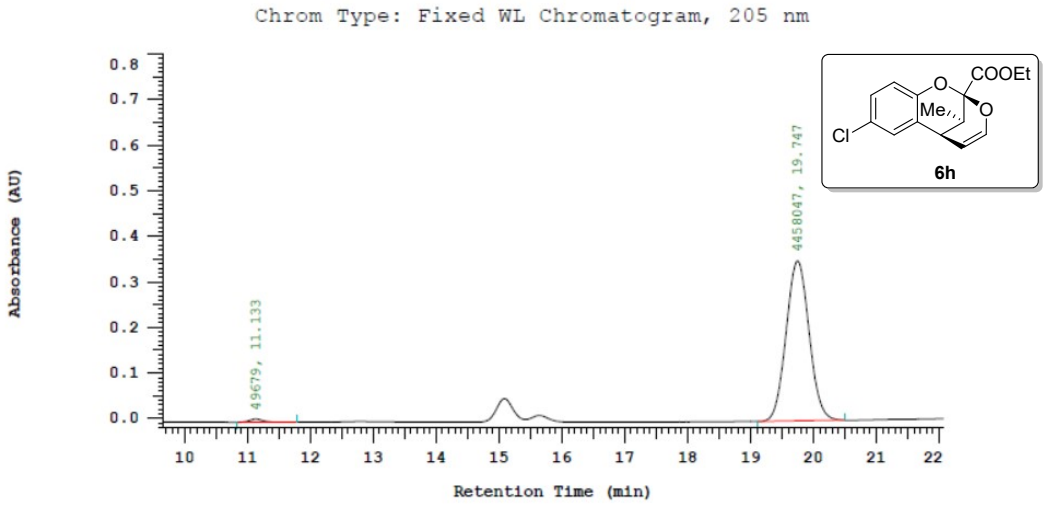
The HPLC of racemic 6h



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.133	4099833	49.870	BB
2	19.753	4121202	50.130	BB
		8221035	100.000	

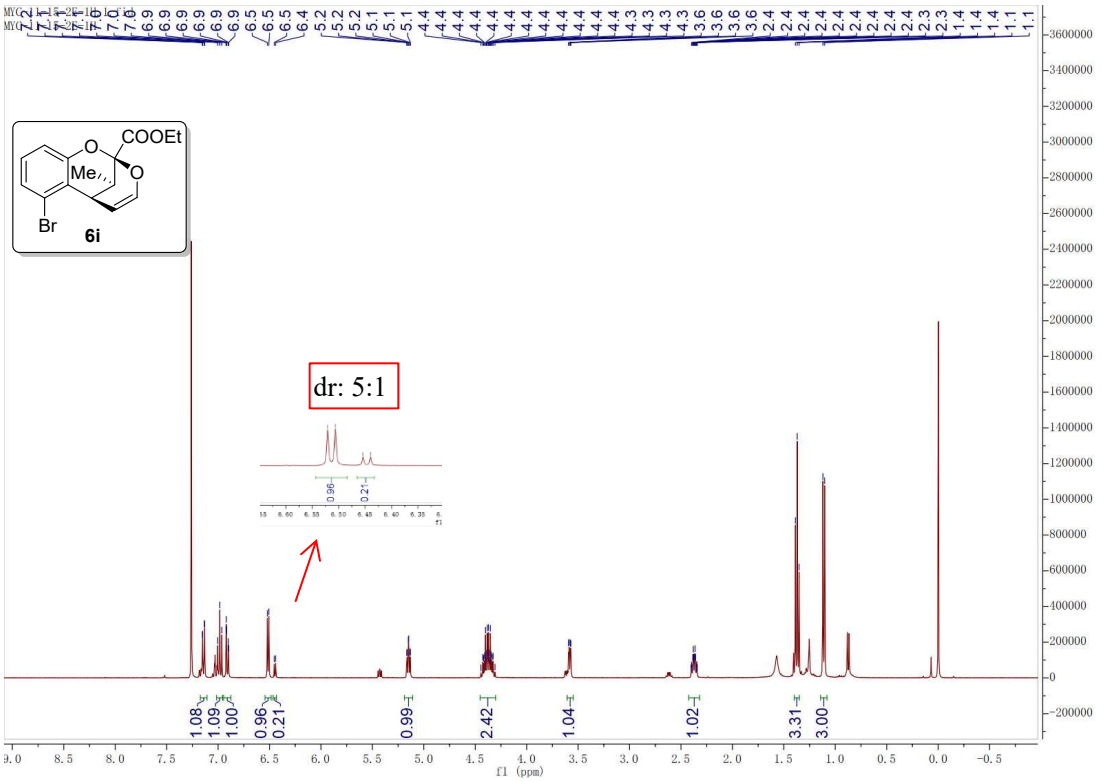
The HPLC of chiral 6h



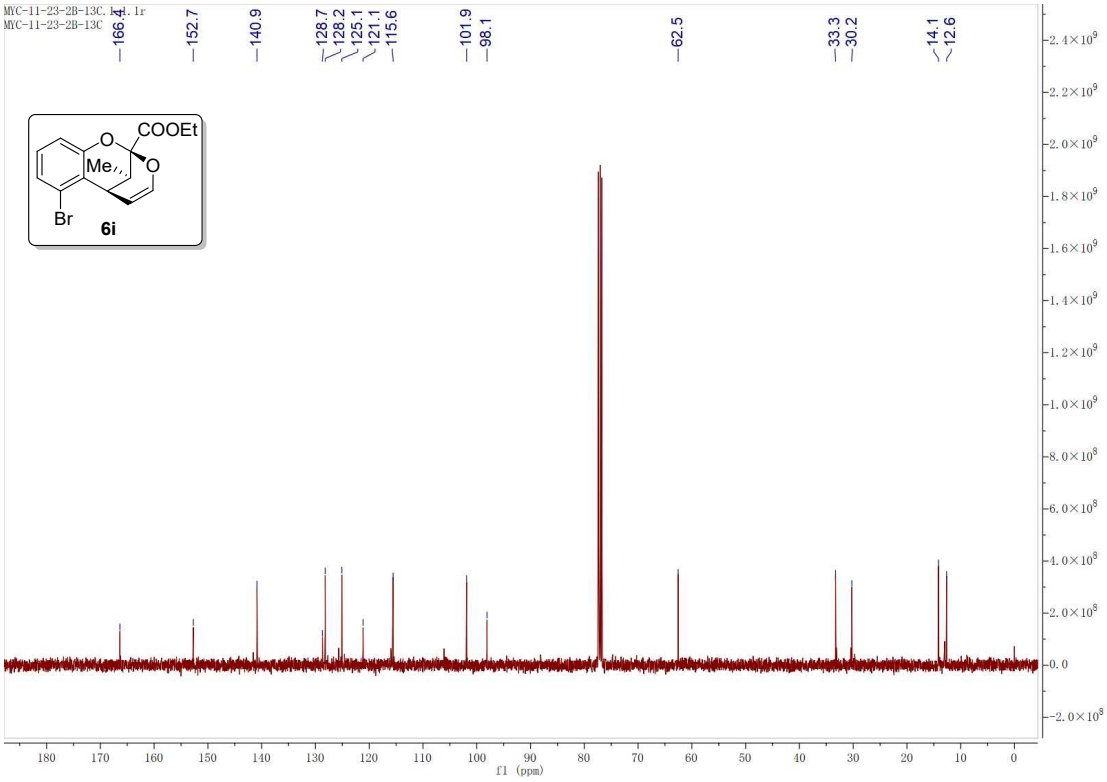
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.133	49679	1.102	BB
2	19.747	4458047	98.898	BB
		4507726	100.000	

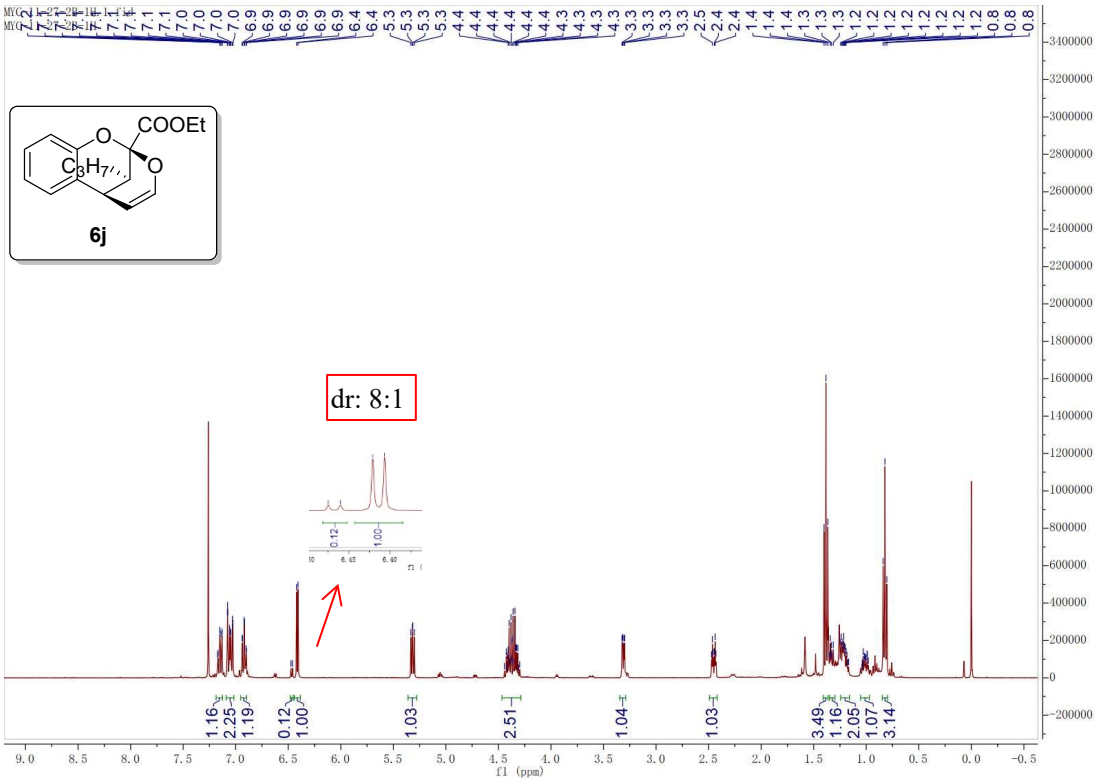
The ^{1}H NMR spectrum of 6i (400 MHz, $CDCl_3$)



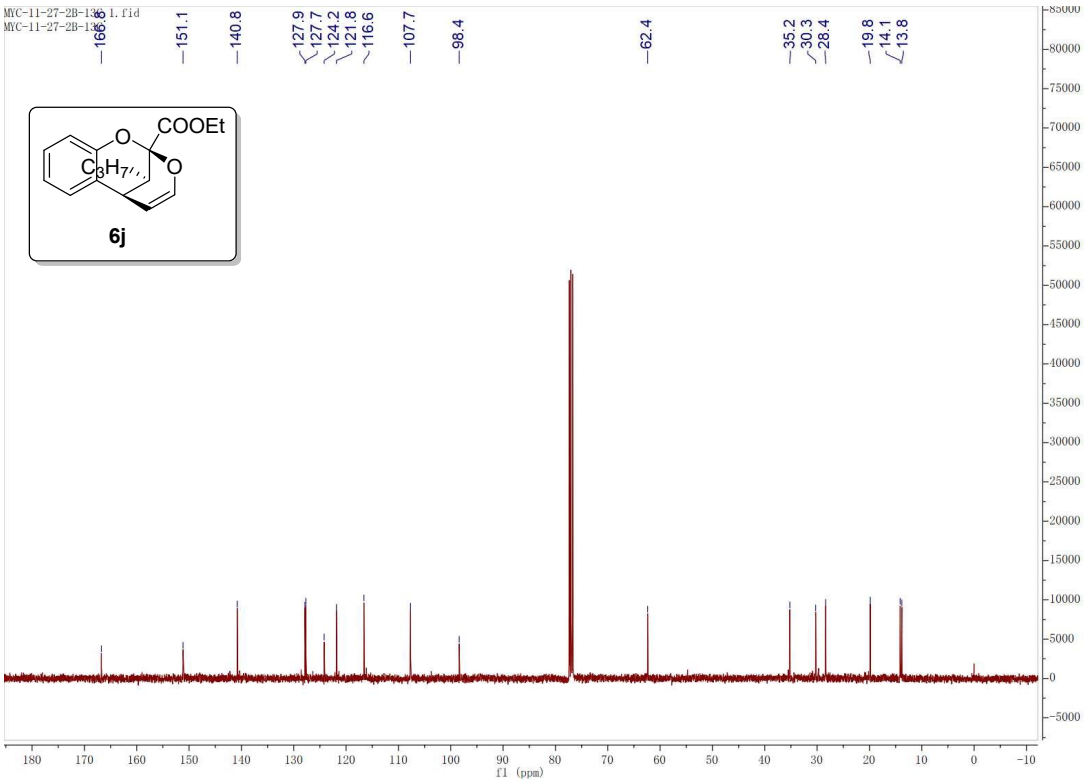
The ^{13}C NMR spectrum of 6i (100 MHz, $CDCl_3$)



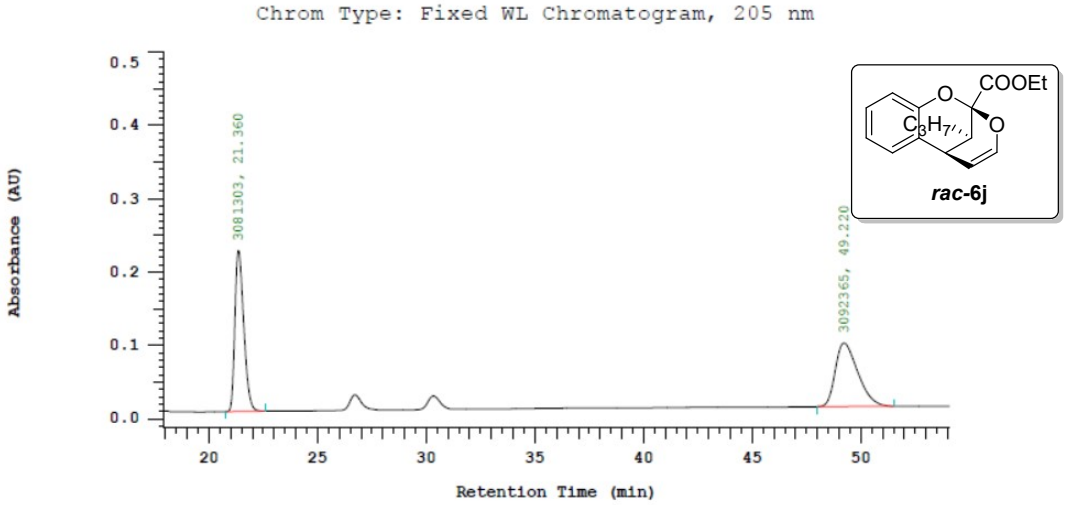
The ^{1}H NMR spectrum of 6j (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6j (100 MHz, $CDCl_3$)



The HPLC of racemic 6j

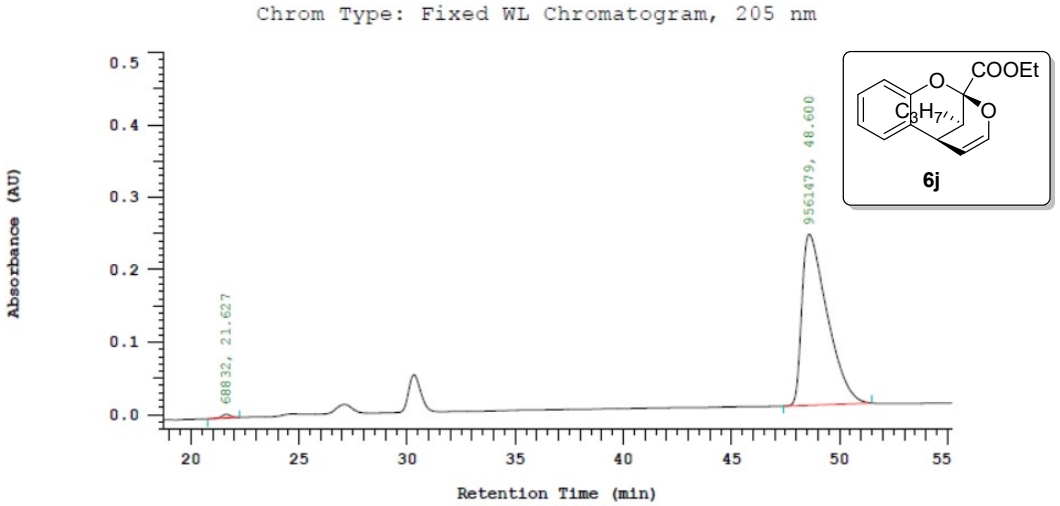


Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	21.360	3081303	49.910	BB
2	49.220	3092365	50.090	BB
		6173668	100.000	

The HPLC of chiral 6j

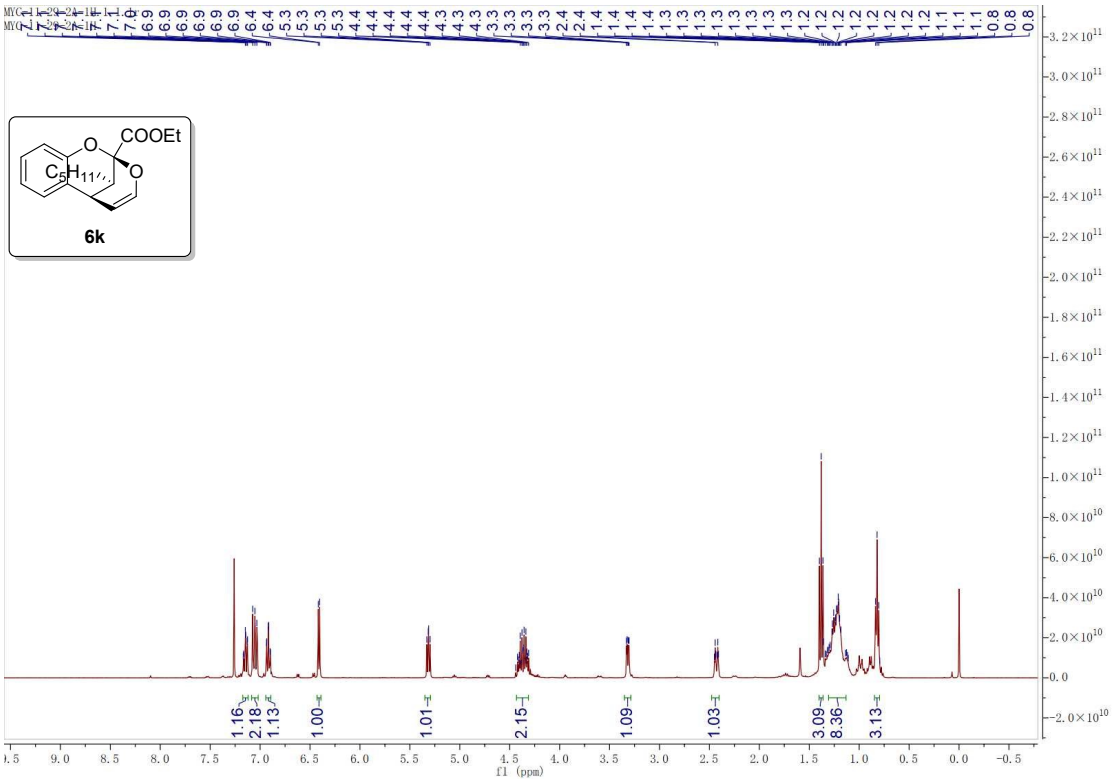


Chrom Type: Fixed WL Chromatogram, 205 nm

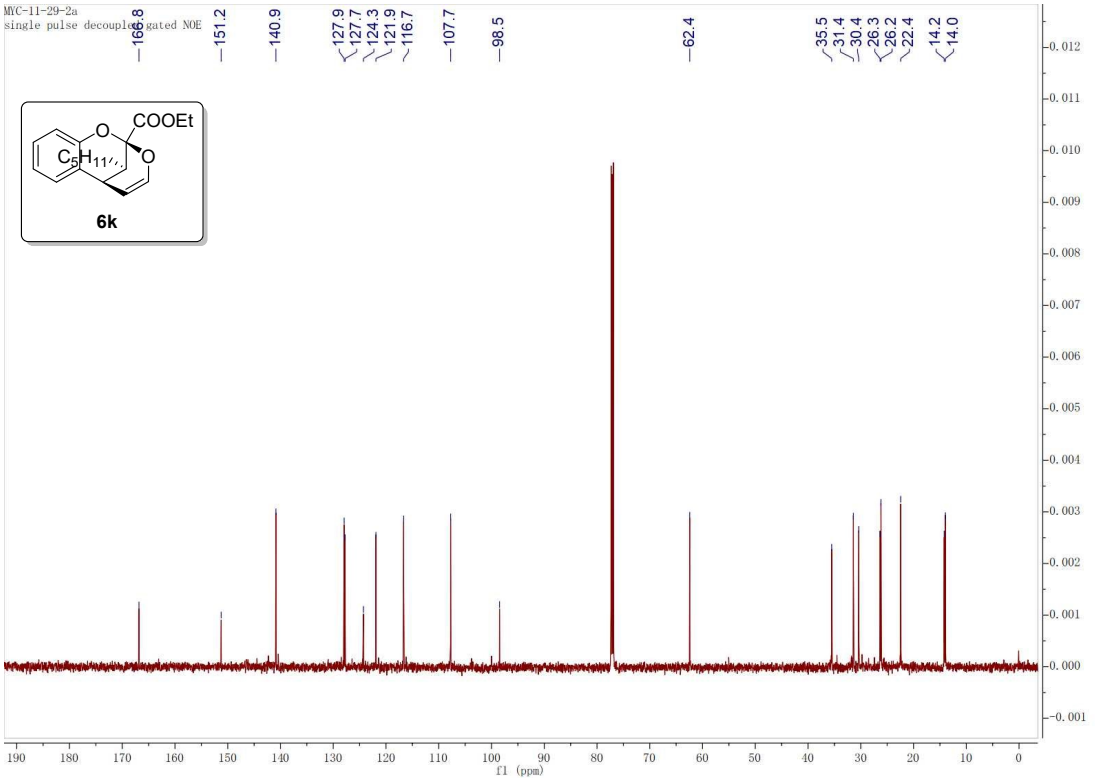
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	21.627	68832	0.715	BB
2	48.600	9561479	99.285	BB
		9630311	100.000	

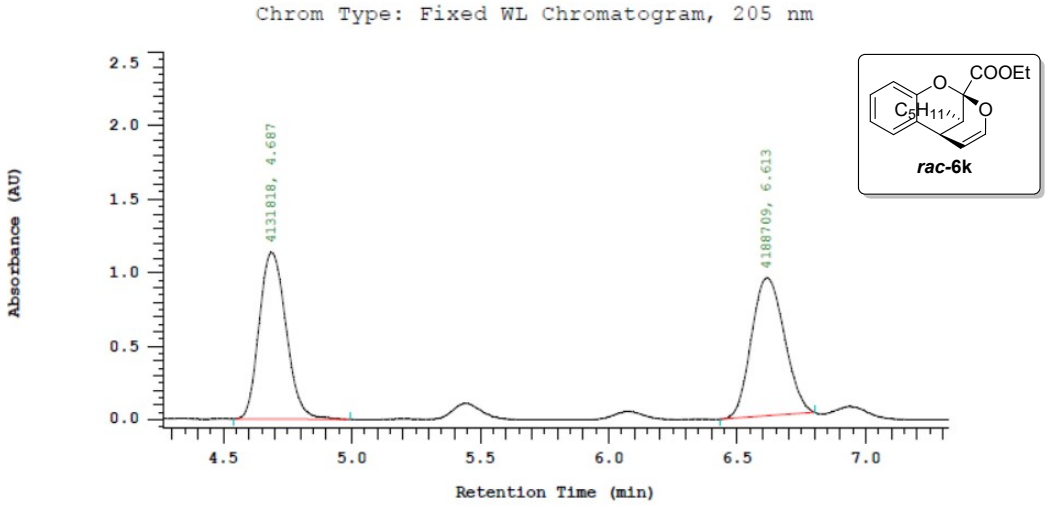
The ^{1}H NMR spectrum of 6k (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6k (150 MHz, $CDCl_3$)



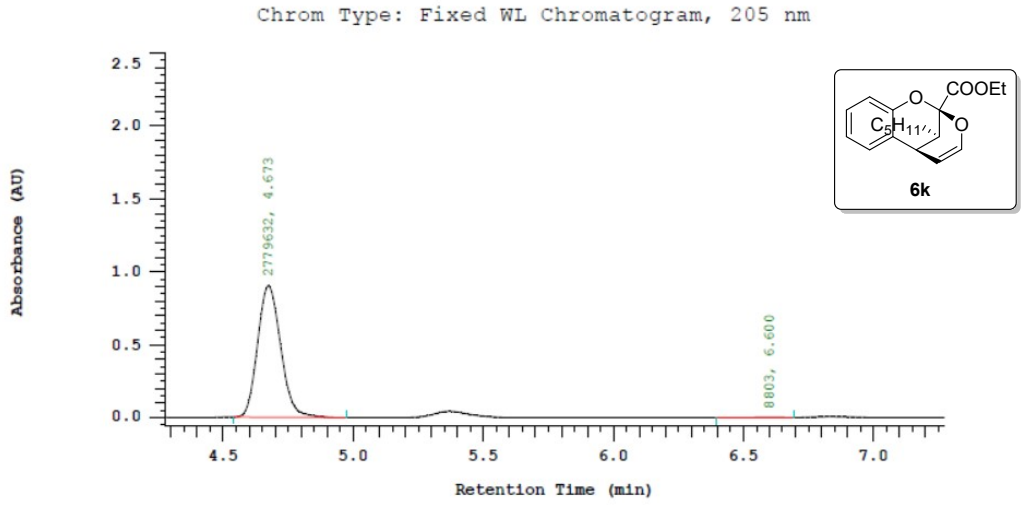
The HPLC of racemic 6k



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	4.687	4131818	49.658	BB
2	6.613	4188709	50.342	BB
		8320527	100.000	

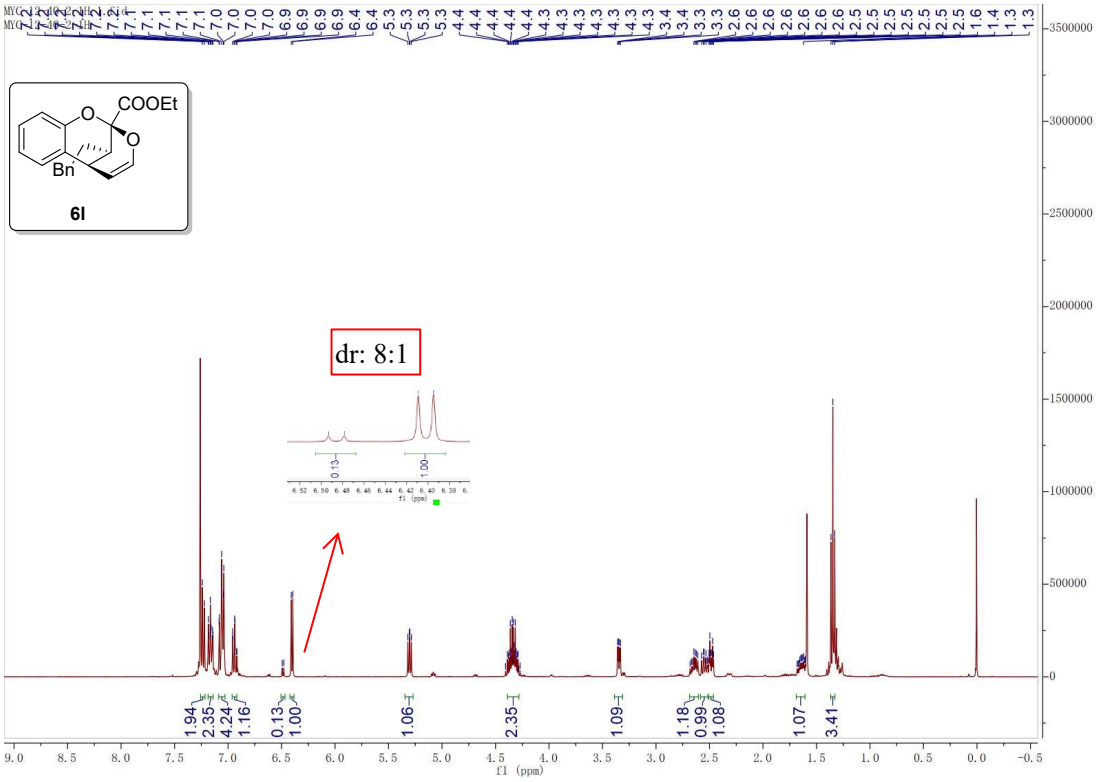
The HPLC of chiral 6k



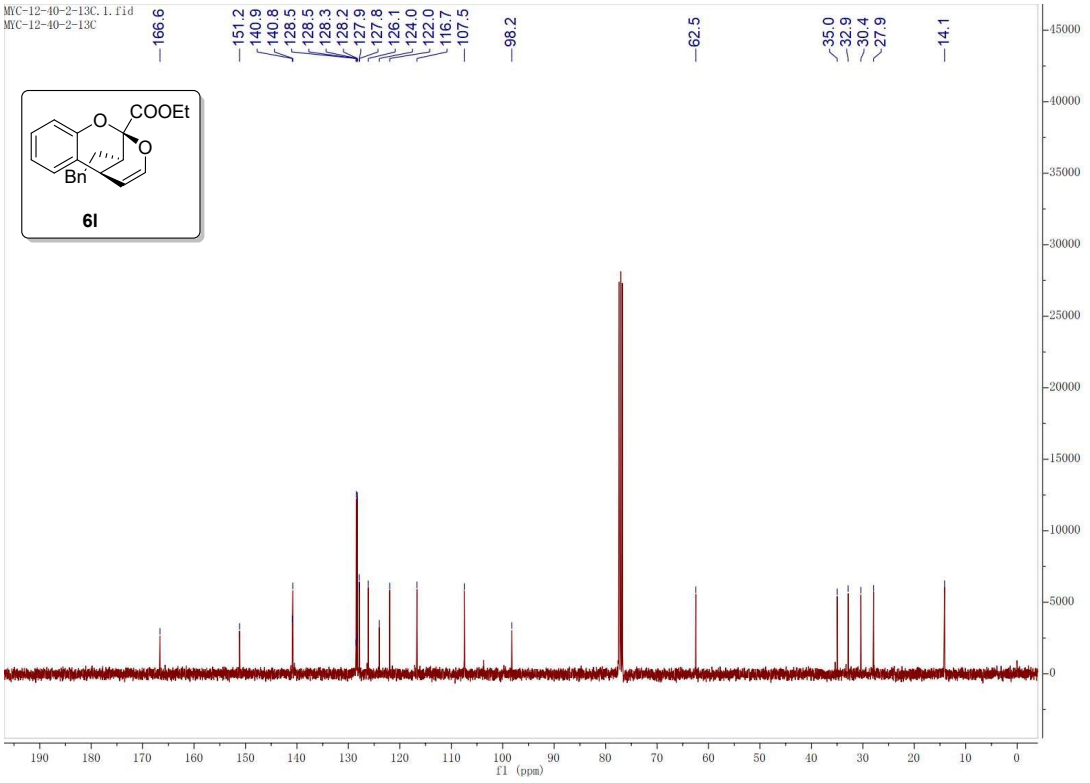
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	4.673	2779632	99.684	BB
2	6.600	8803	0.316	BB
		2788435	100.000	

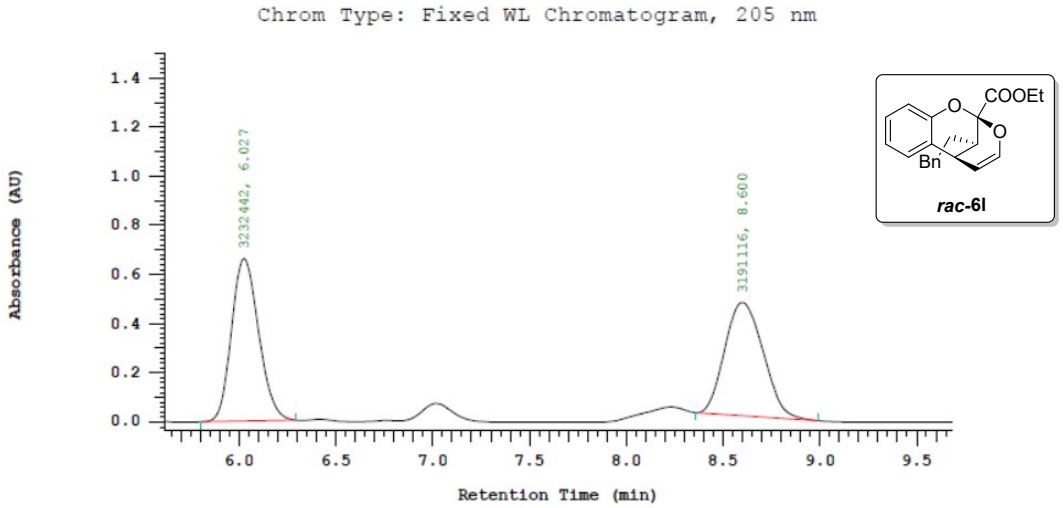
The ^{1}H NMR spectrum of 6l (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6l (100 MHz, $CDCl_3$)



The HPLC of racemic 6l



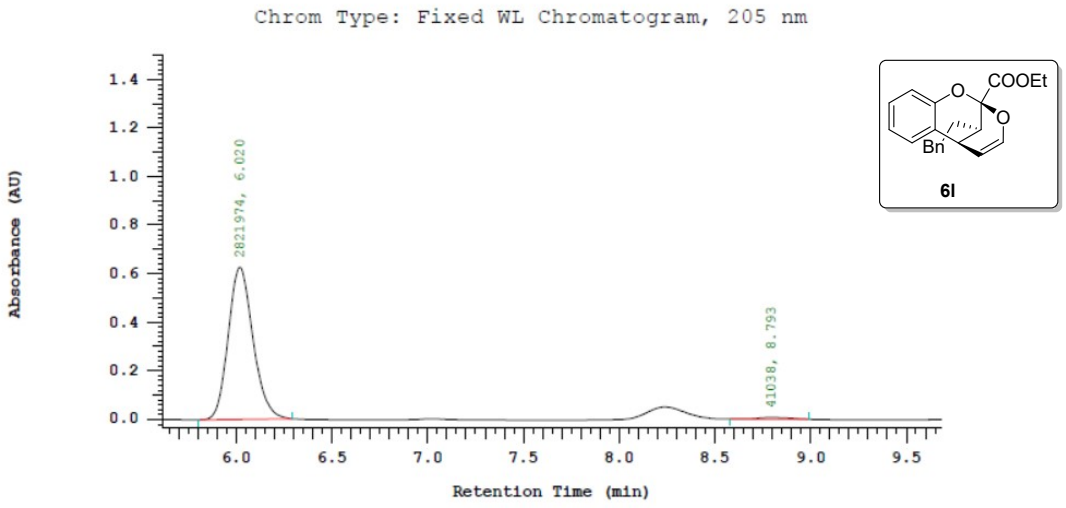
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.027	3232442	50.322	BB
2	8.600	3191116	49.678	BB
		6423558	100.000	

The HPLC of chiral 6l



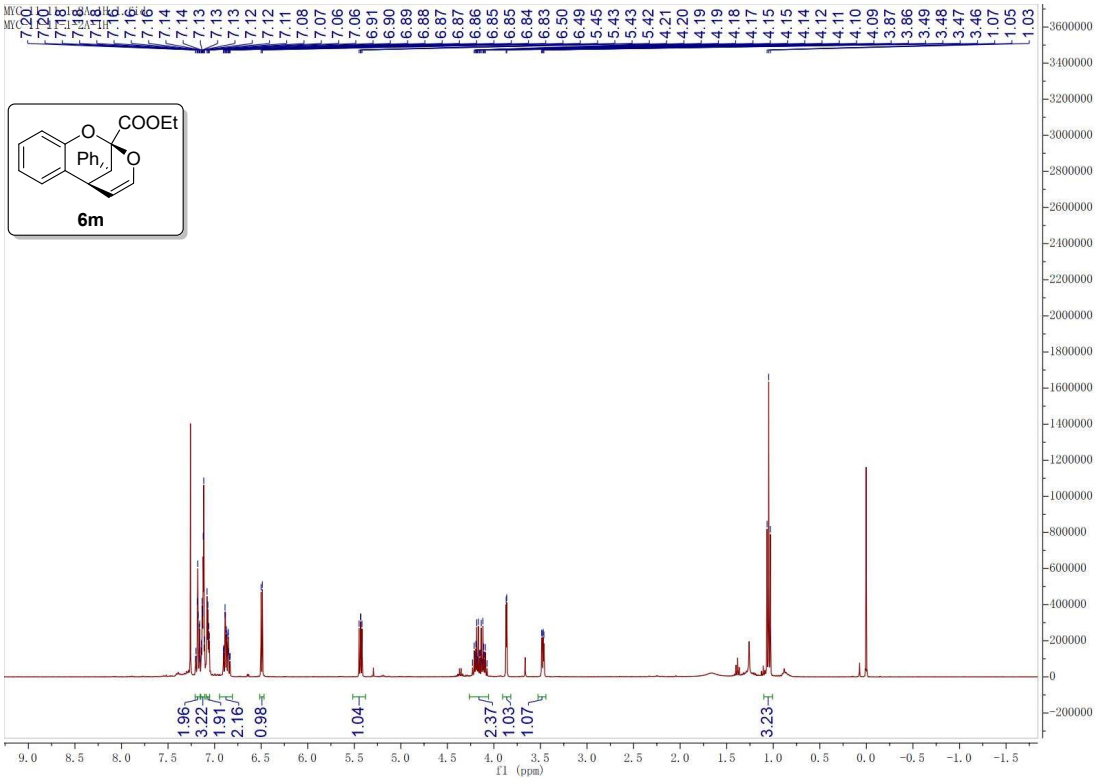
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

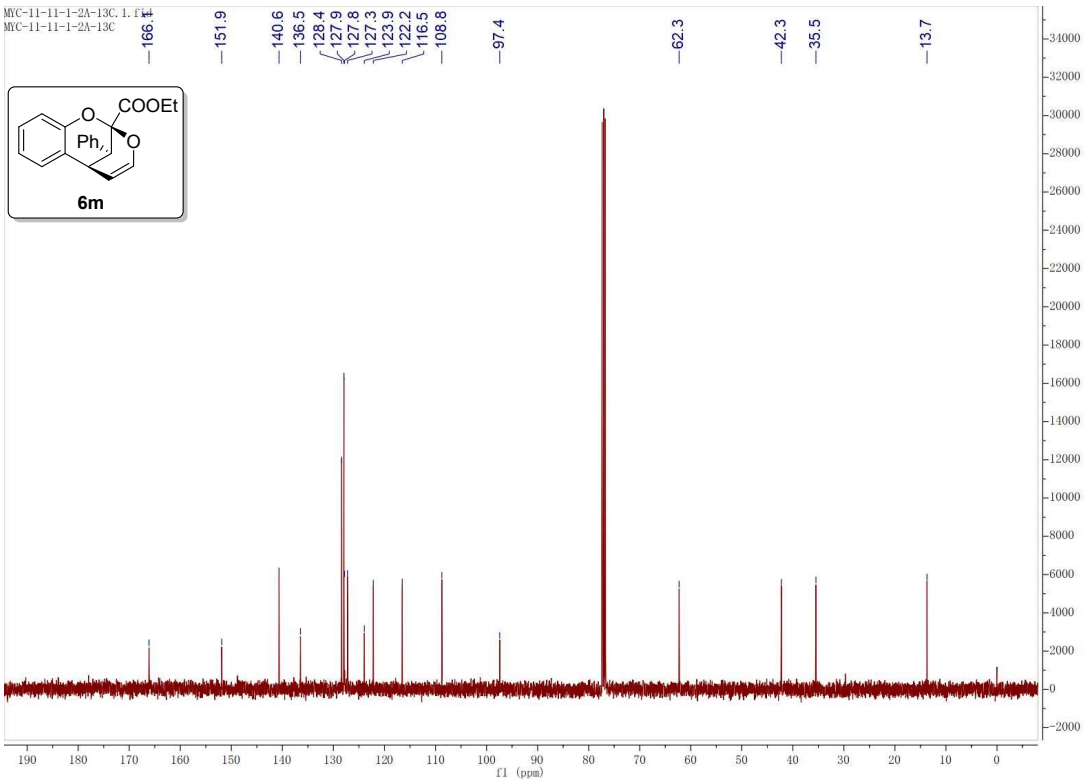
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.020	2821974	98.567	BB
2	8.793	41038	1.433	BB
		2863012	100.000	

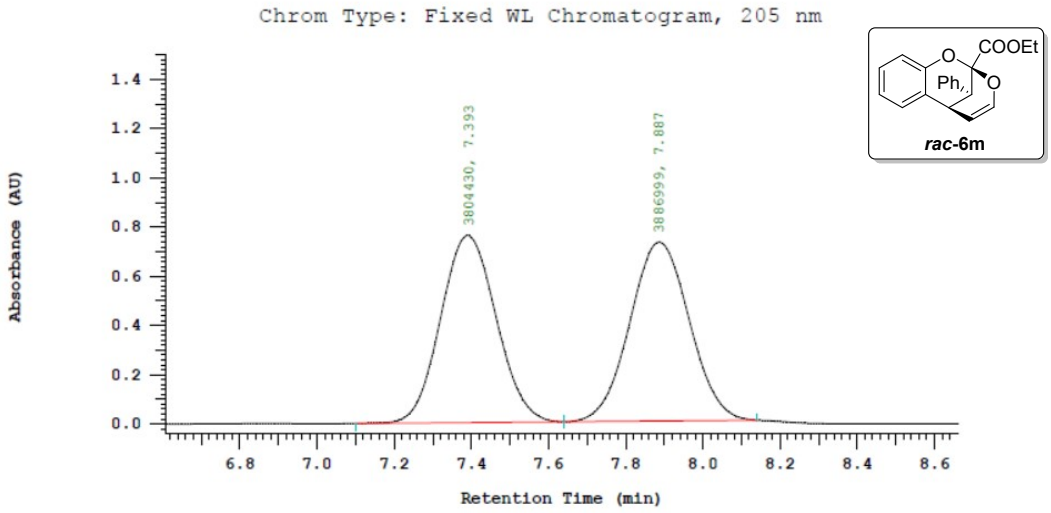
The ^{1}H NMR spectrum of 6m (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6m (100 MHz, $CDCl_3$)



The HPLC of racemic 6m



Chrom Type: Fixed WL Chromatogram, 205 nm

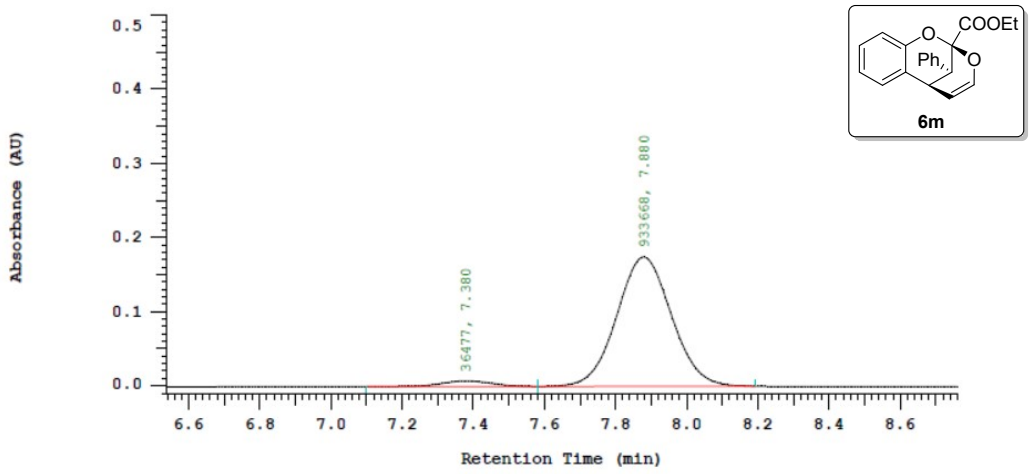
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.393	3804430	49.463	BB
2	7.887	3886999	50.537	BB
		7691429	100.000	

The HPLC of chiral 6m

Chrom Type: Fixed WL Chromatogram, 205 nm



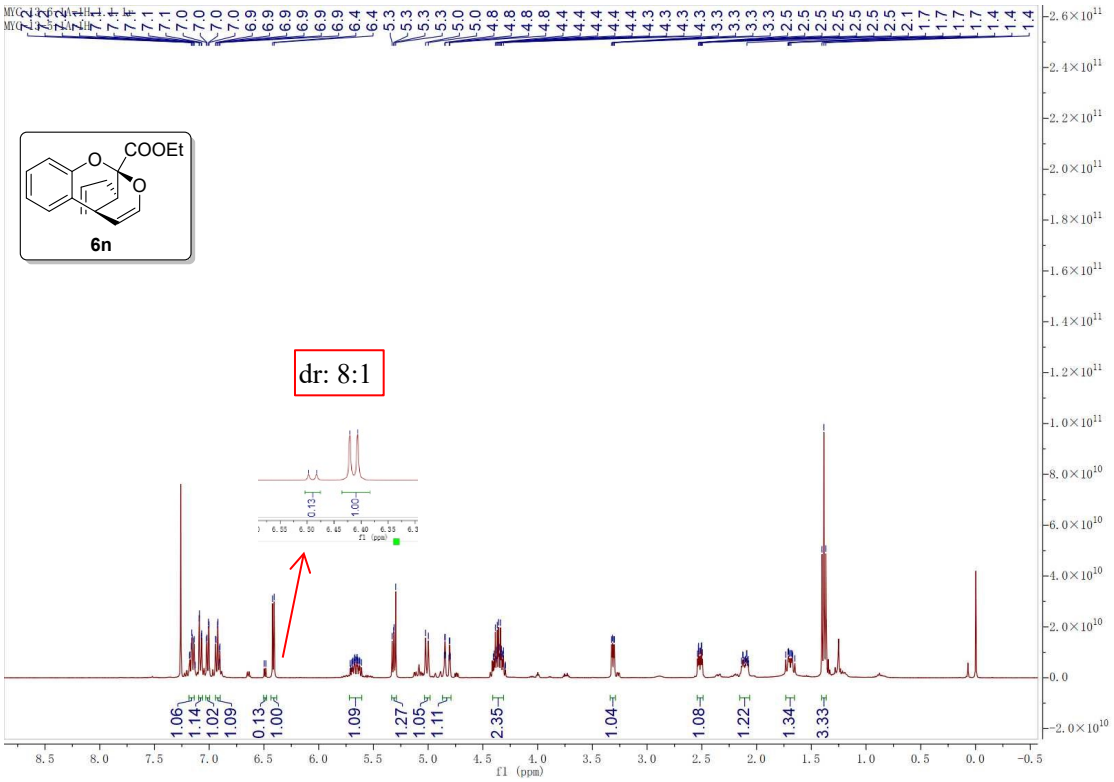
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

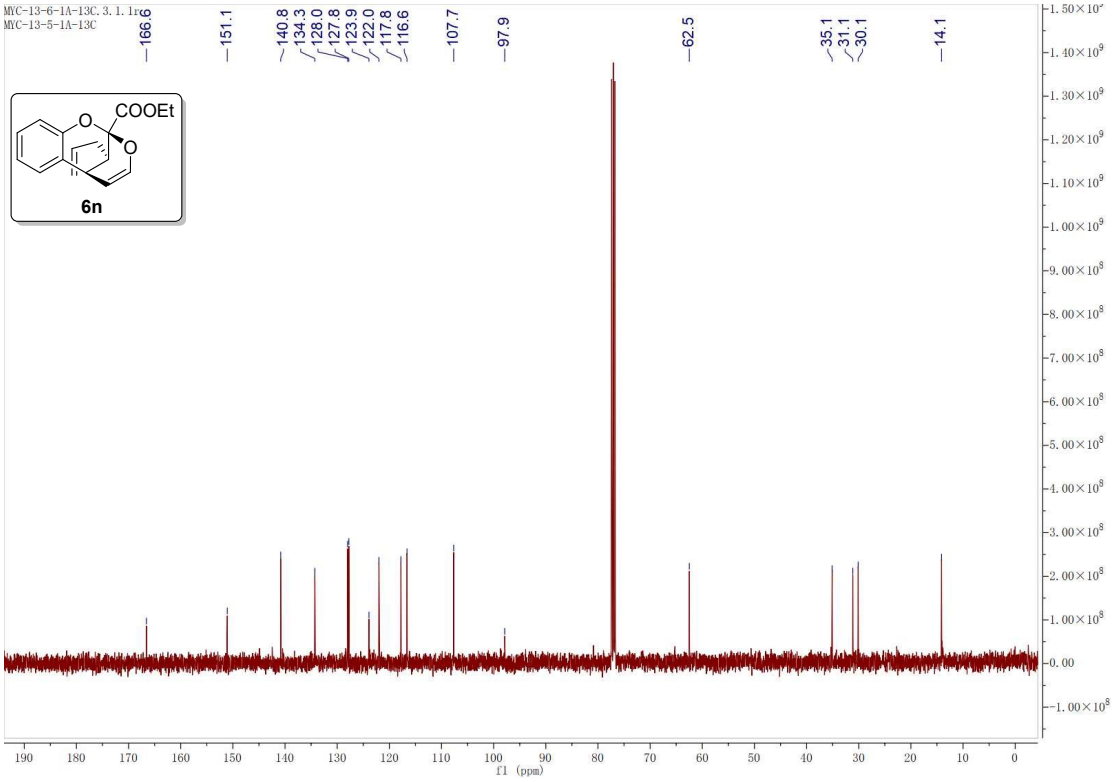
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.380	36477	3.760	BB
2	7.880	933668	96.240	BB
		970145	100.000	

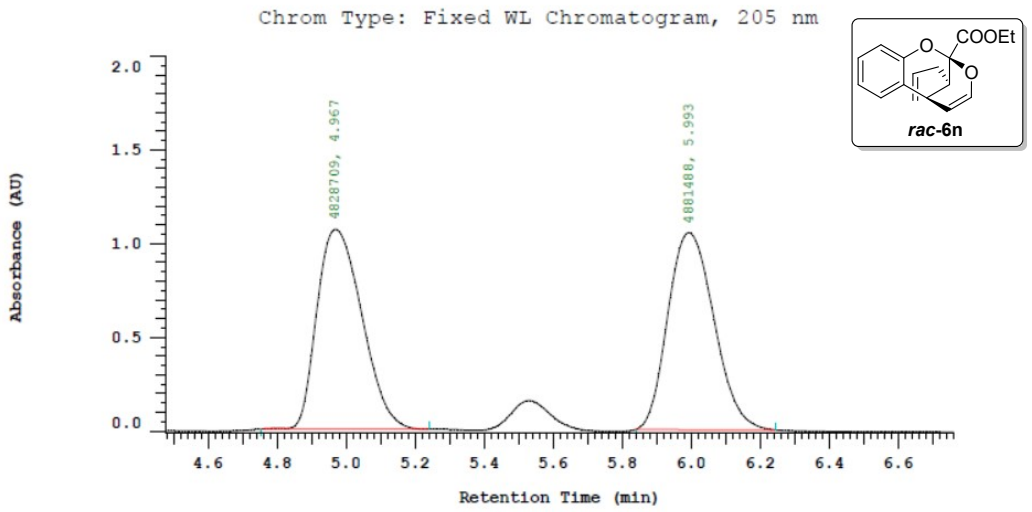
The ^{1}H NMR spectrum of 6n (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6n (100 MHz, $CDCl_3$)



The HPLC of racemic 6n



Chrom Type: Fixed WL Chromatogram, 205 nm

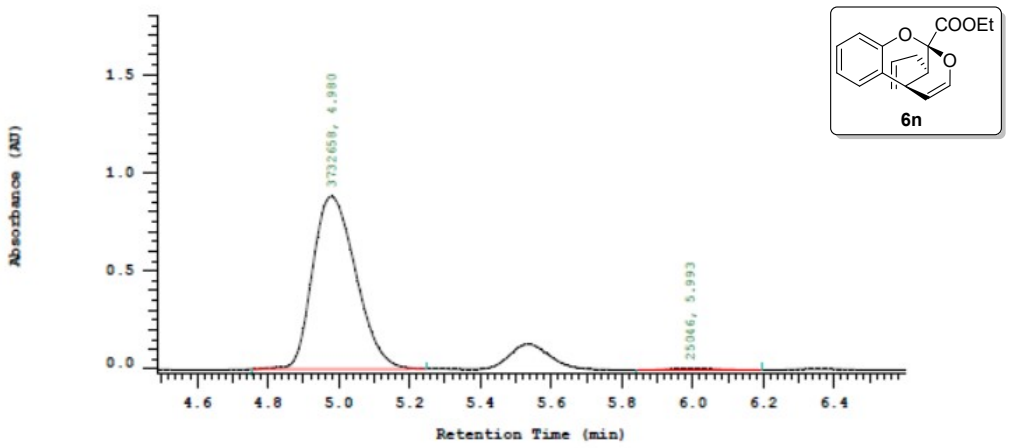
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	4.967	4828709	49.728	BB
2	5.993	4881488	50.272	BB
		9710197	100.000	

The HPLC of chiral 6n

Chrom Type: Fixed WL Chromatogram, 205 nm

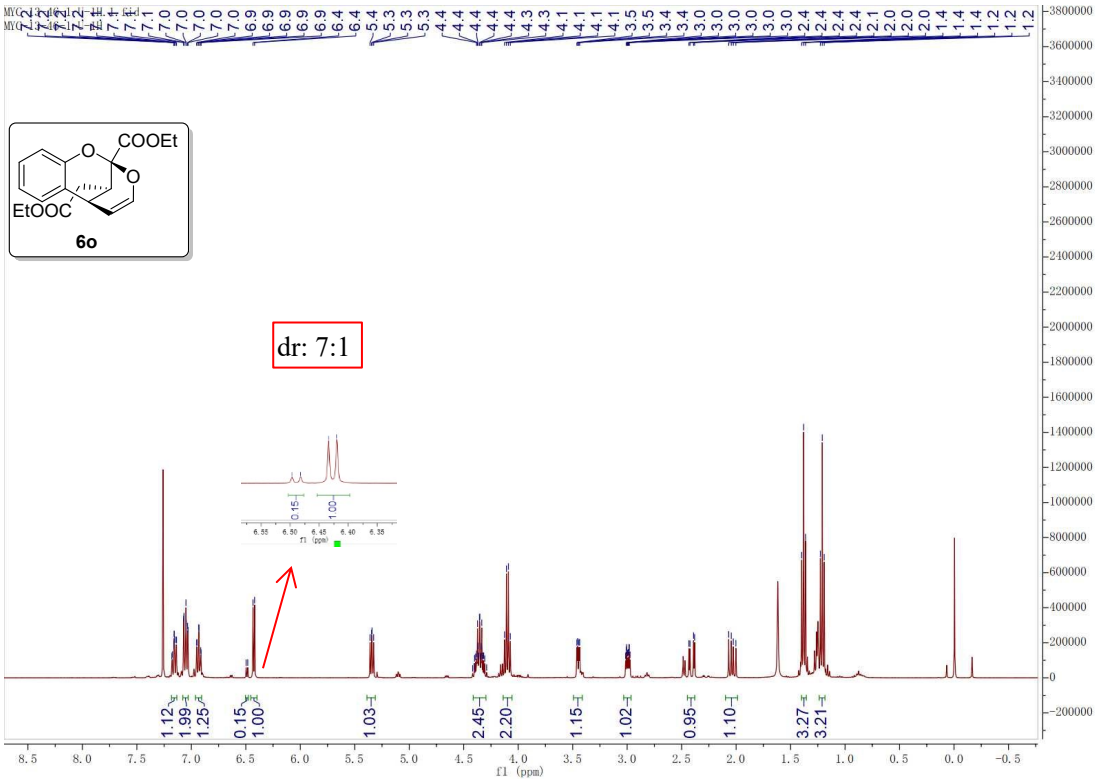


Chrom Type: Fixed WL Chromatogram, 205 nm

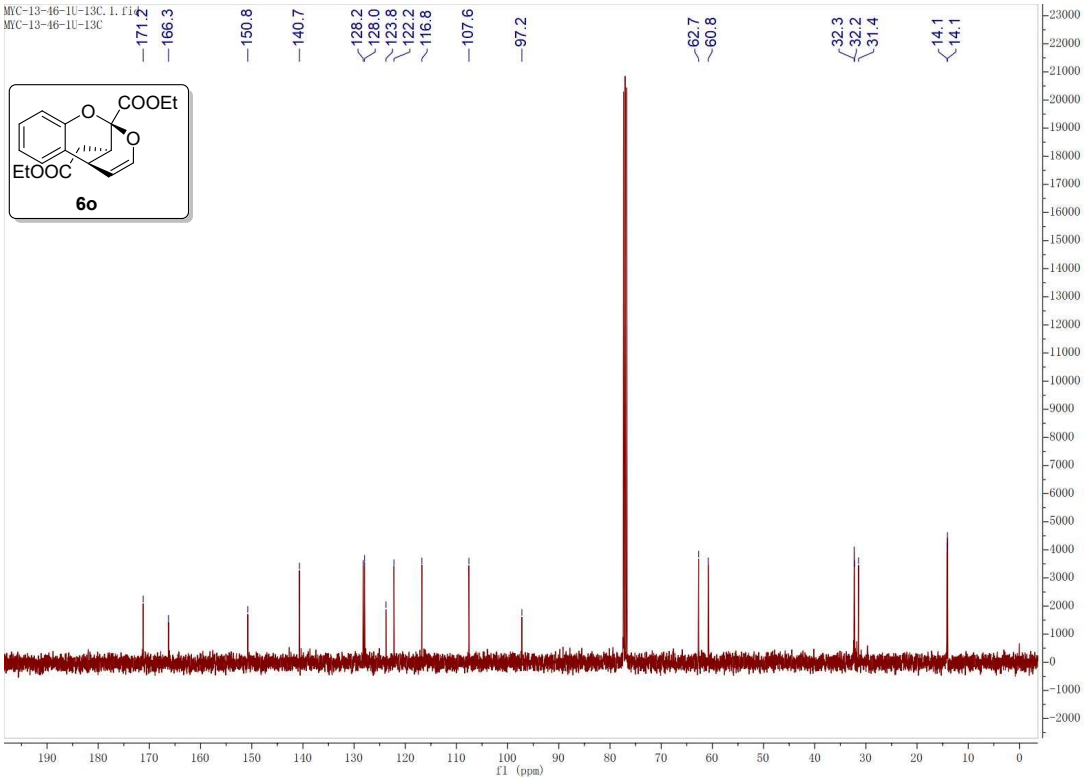
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	4.980	3732658	99.333	BB
2	5.993	25046	0.667	BB
		3757704	100.000	

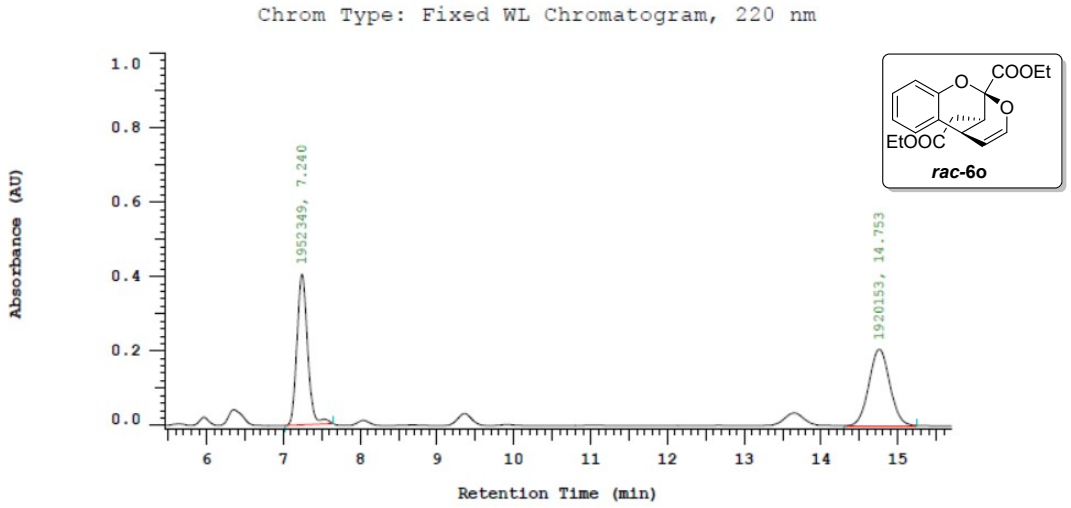
The ^{1}H NMR spectrum of 6o (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6o (100 MHz, $CDCl_3$)



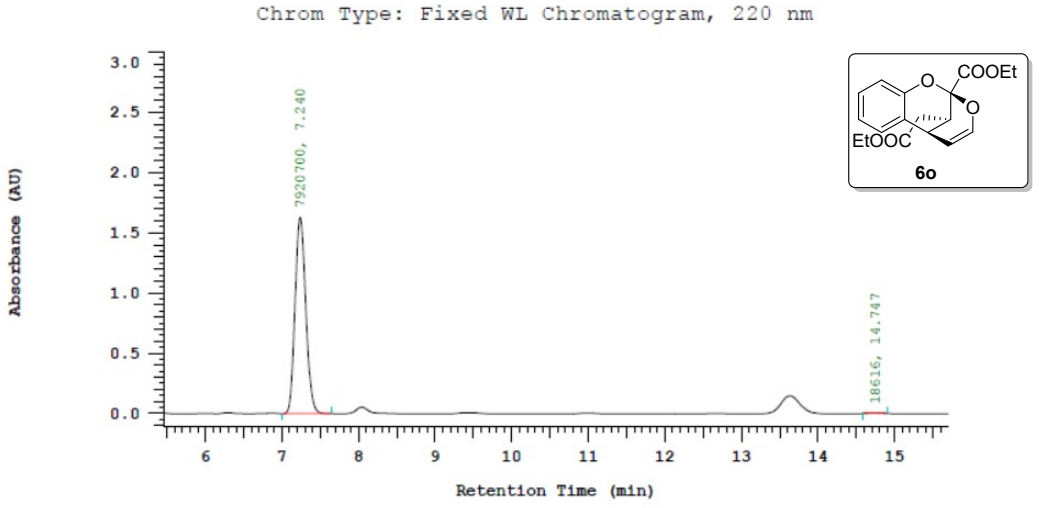
The HPLC of racemic 6o



Chrom Type: Fixed WL Chromatogram, 220 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.240	1952349	50.416	BB
2	14.753	1920153	49.584	BB
		3872502	100.000	

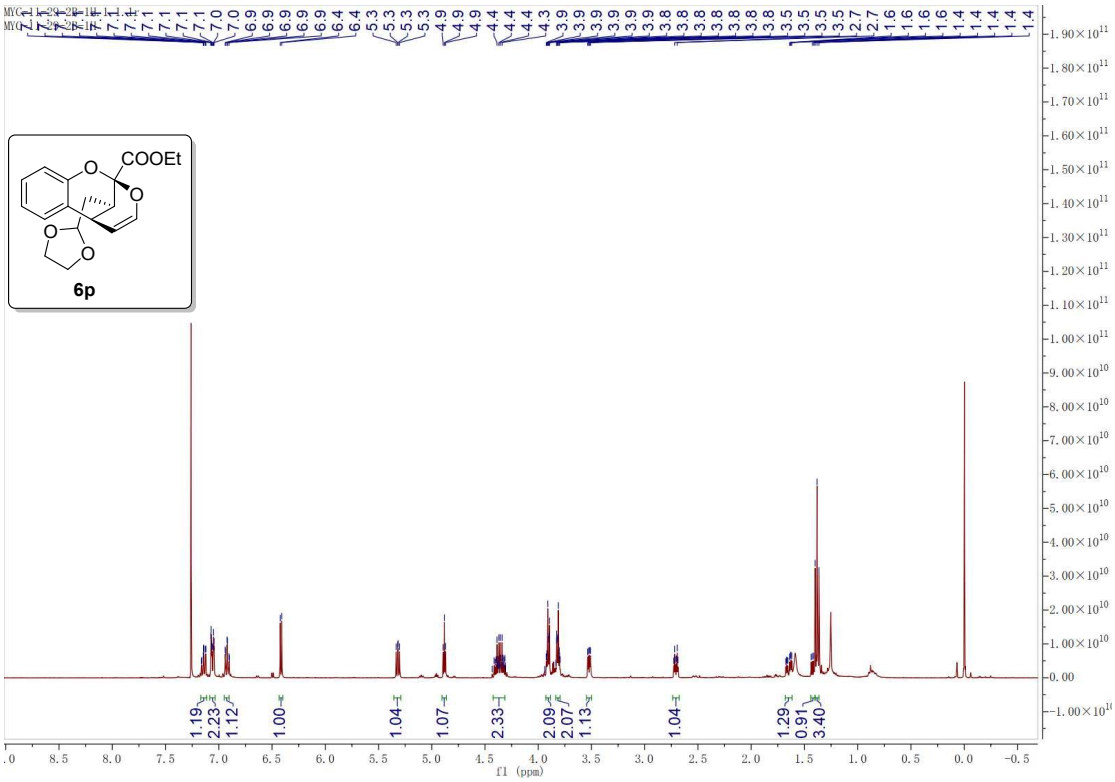
The HPLC of chiral 6o



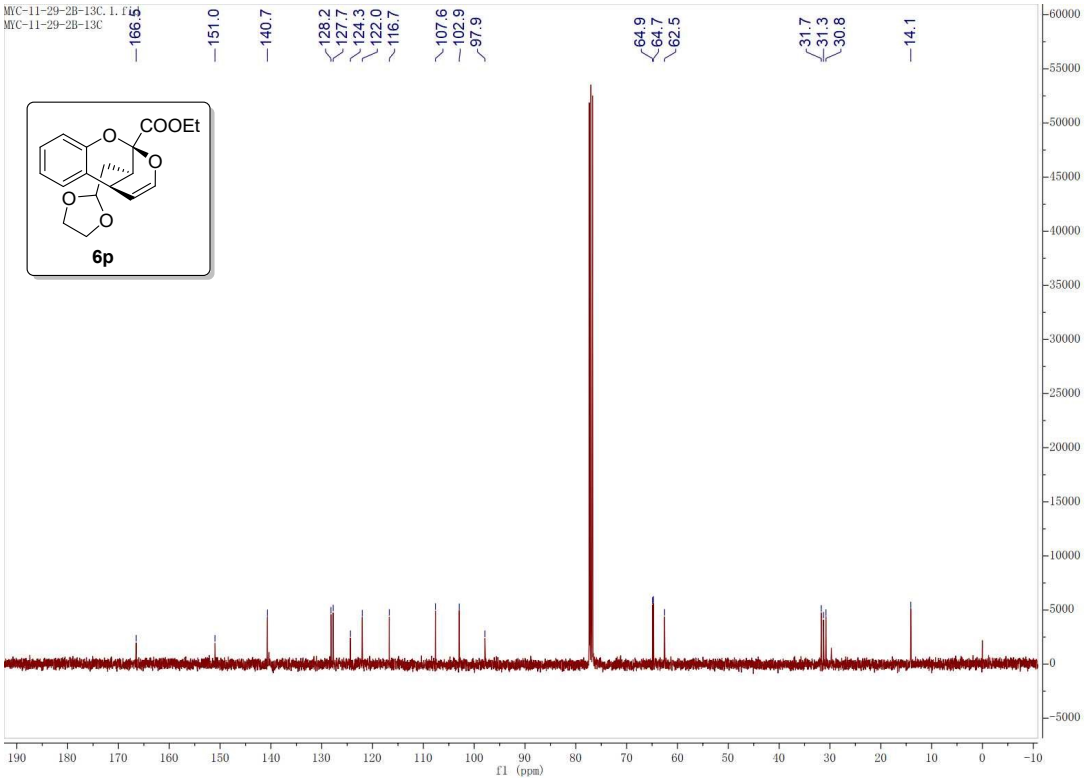
Chrom Type: Fixed WL Chromatogram, 220 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.240	7920700	99.766	BB
2	14.747	18616	0.234	BB
		7939316	100.000	

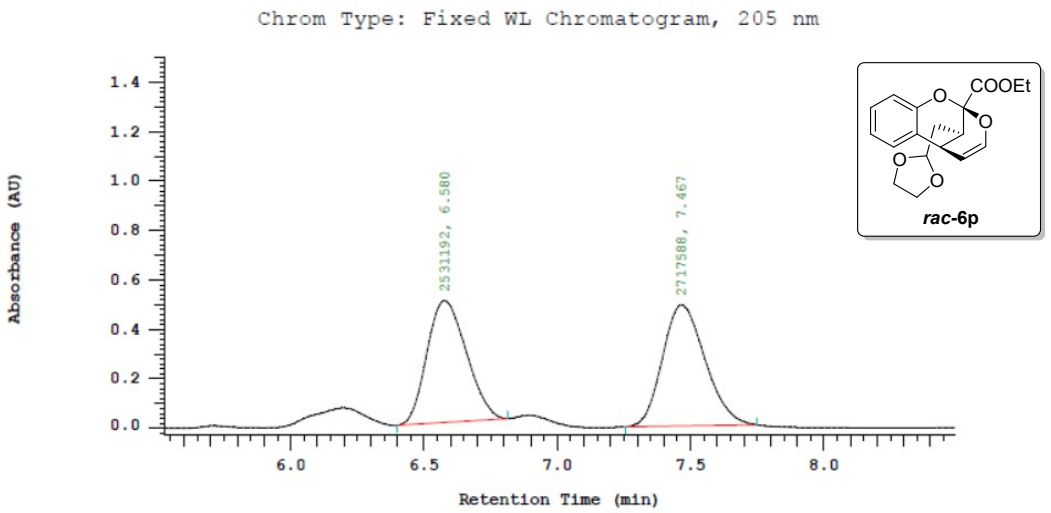
The ^{1}H NMR spectrum of 6p (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6p (100 MHz, $CDCl_3$)



The HPLC of racemic 6p



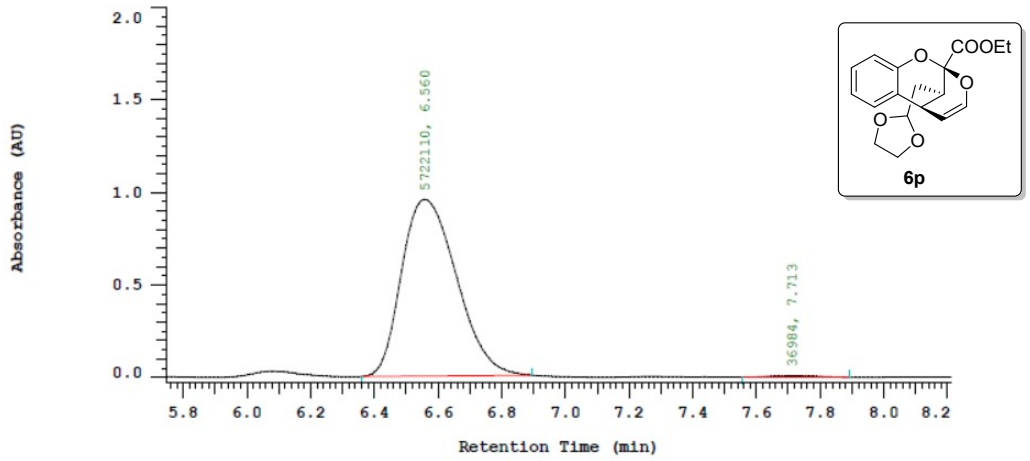
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.580	2531192	48.224	BB
2	7.467	2717588	51.776	BB
		5248780	100.000	

The HPLC of chiral 6p

Chrom Type: Fixed WL Chromatogram, 205 nm



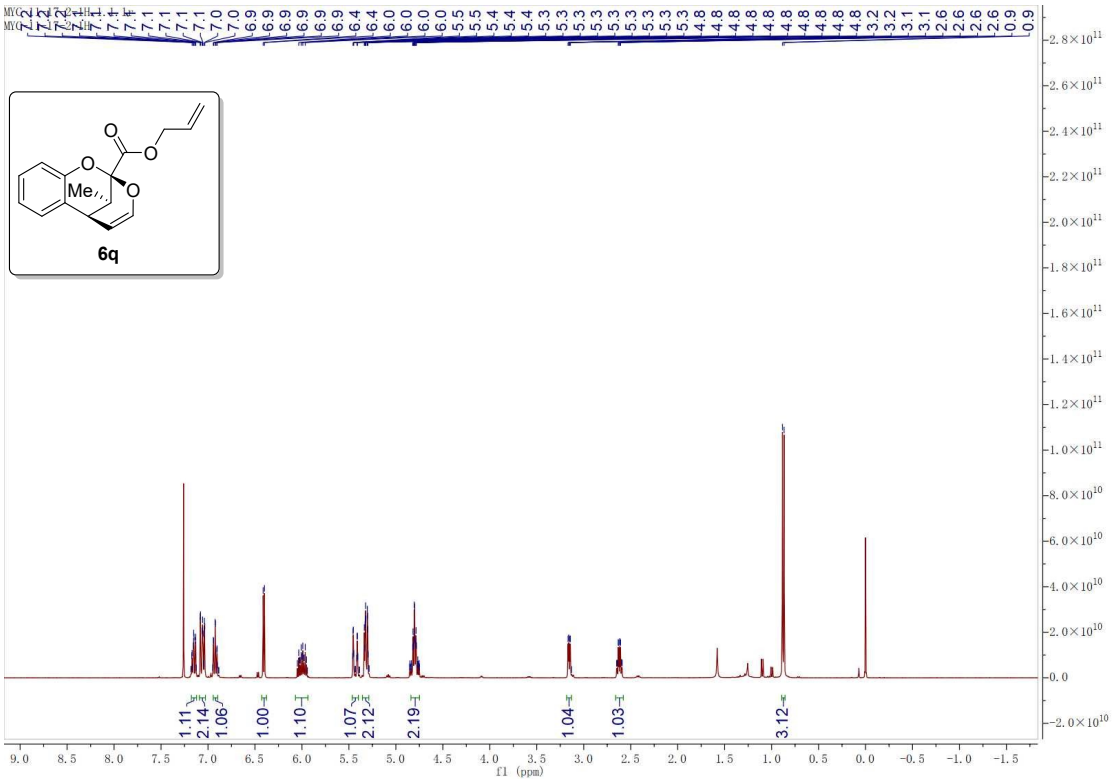
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

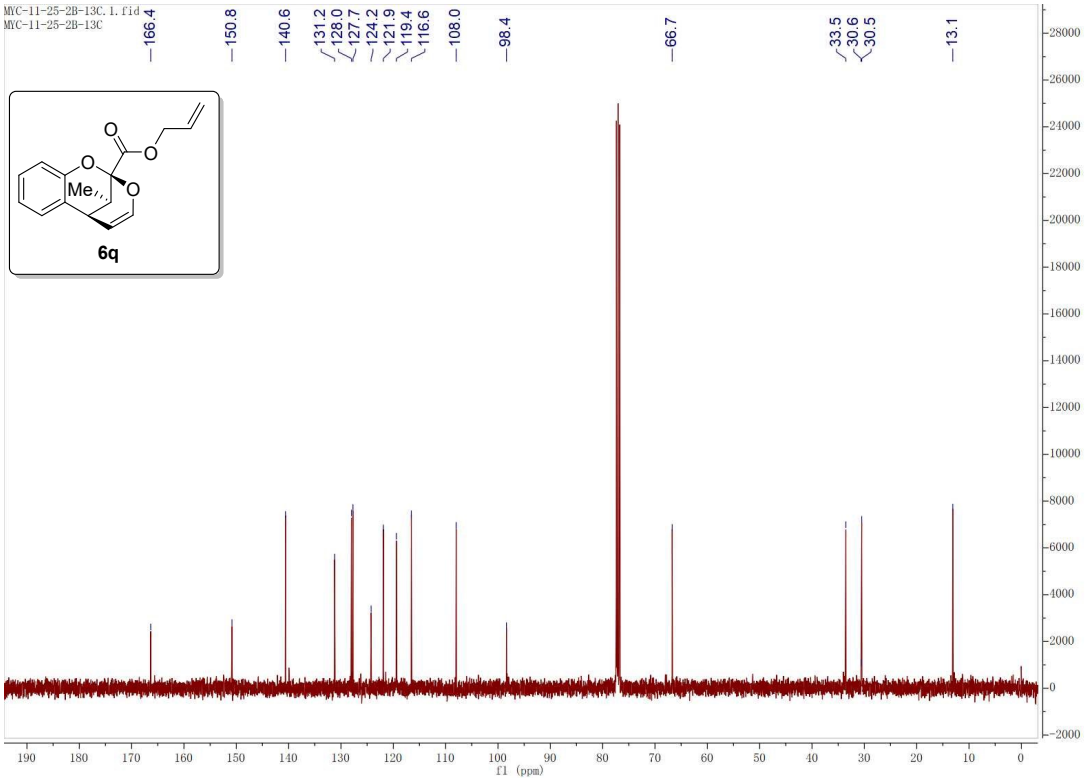
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.560	5722110	99.358	BB
2	7.713	36984	0.642	BB
		5759094	100.000	

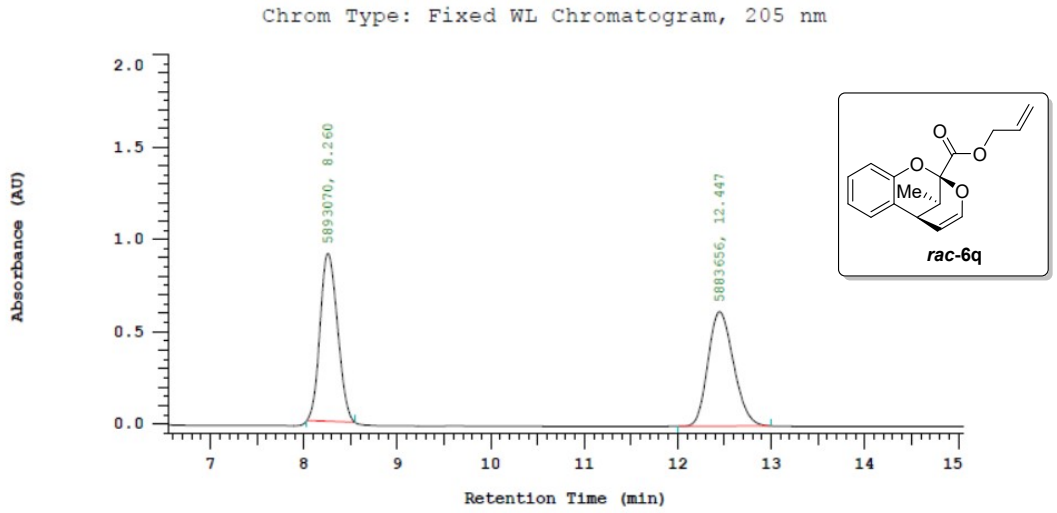
The ^{1}H NMR spectrum of 6q (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6q (100 MHz, $CDCl_3$)



The HPLC of racemic 6q



Chrom Type: Fixed WL Chromatogram, 205 nm

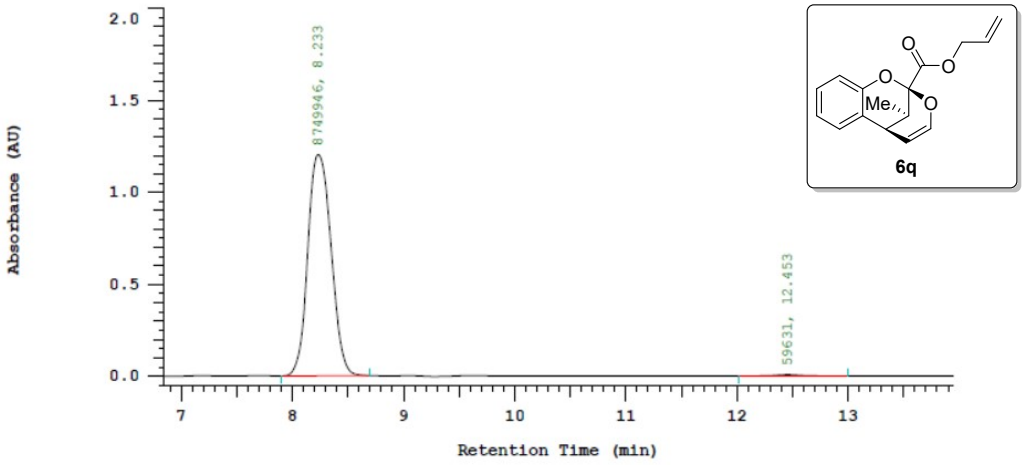
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.260	5893070	50.040	BB
2	12.447	5883656	49.960	BB
		11776726	100.000	

The HPLC of chiral 6q

Chrom Type: Fixed WL Chromatogram, 205 nm



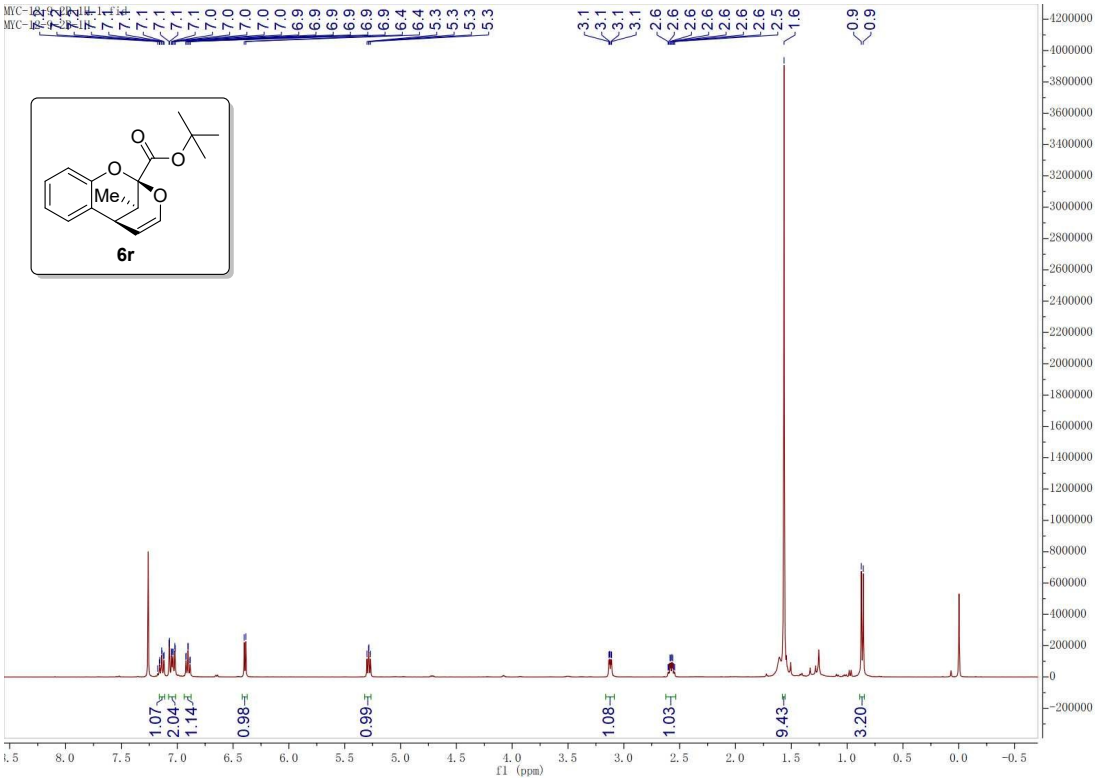
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

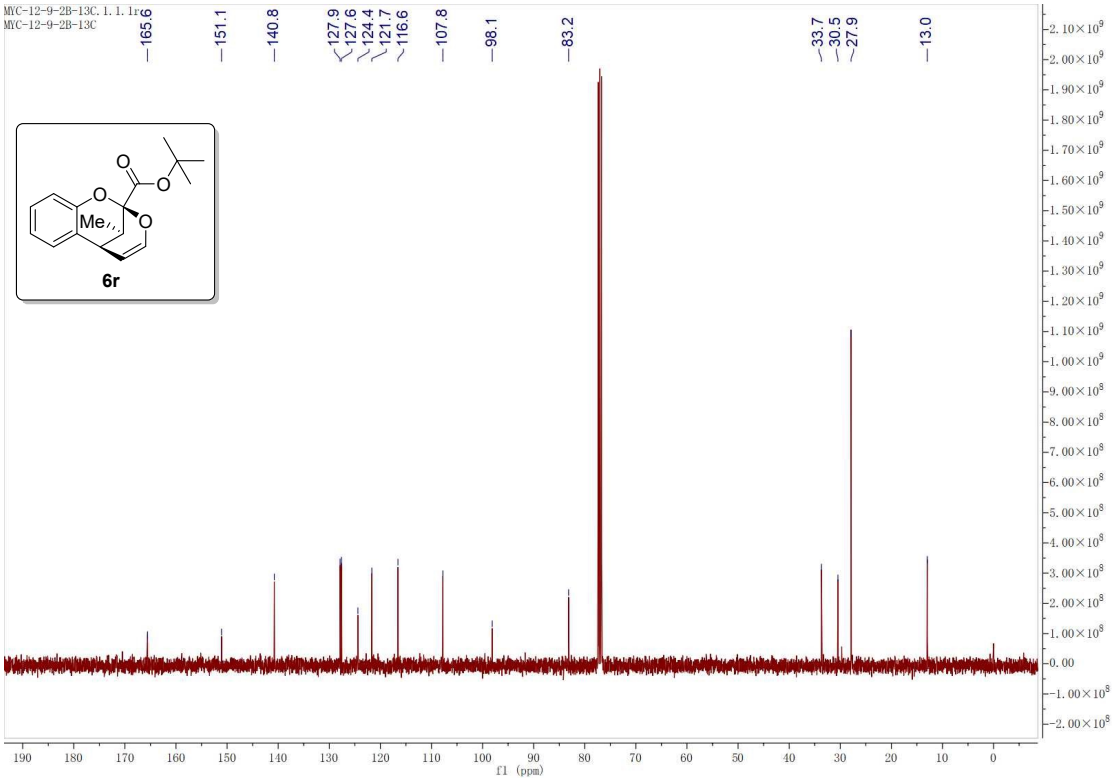
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.233	8749946	99.323	BB
2	12.453	59631	0.677	BB
		8809577	100.000	

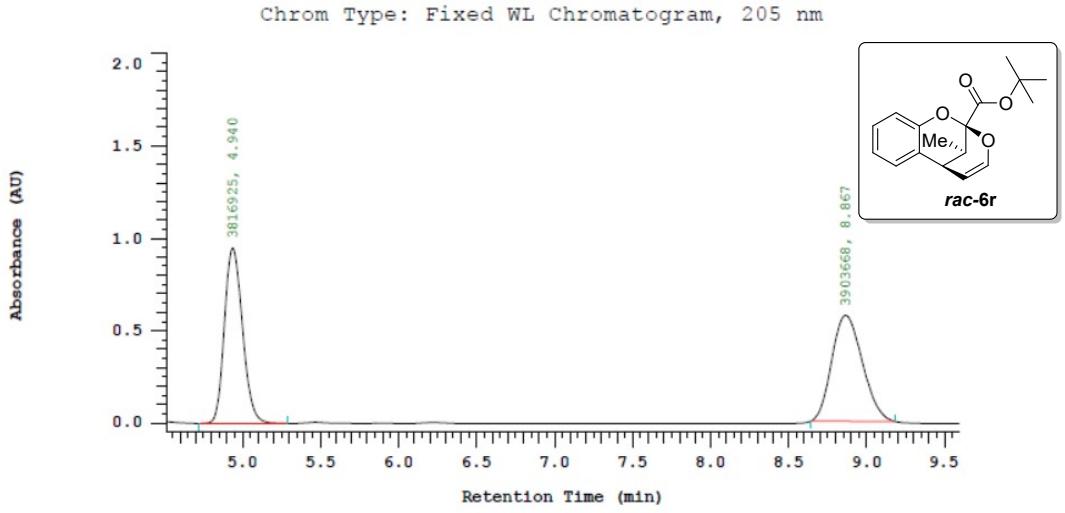
The ^{1}H NMR spectrum of 6r (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6r (100 MHz, $CDCl_3$)



The HPLC of racemic 6r



Chrom Type: Fixed WL Chromatogram, 205 nm

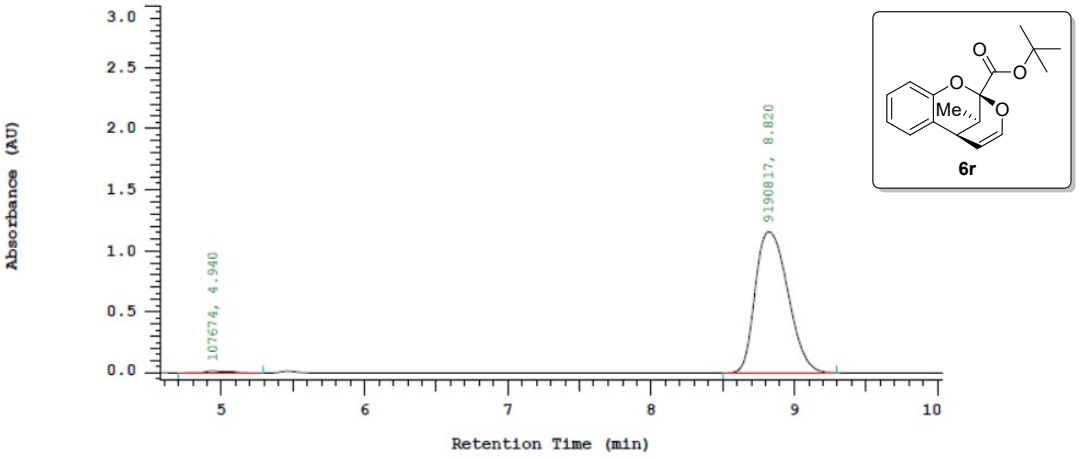
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	4.940	3816925	49.438	BB
2	8.867	3903668	50.562	BB
		7720593	100.000	

The HPLC of chiral 6r

Chrom Type: Fixed WL Chromatogram, 205 nm

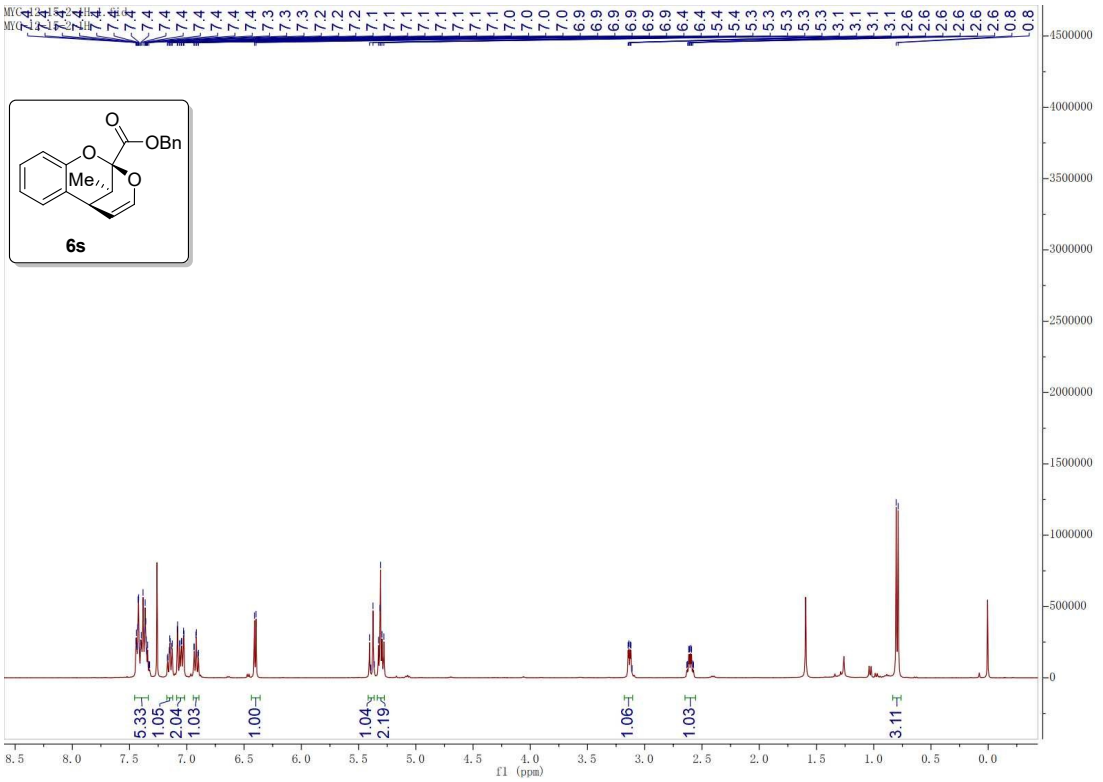


Chrom Type: Fixed WL Chromatogram, 205 nm

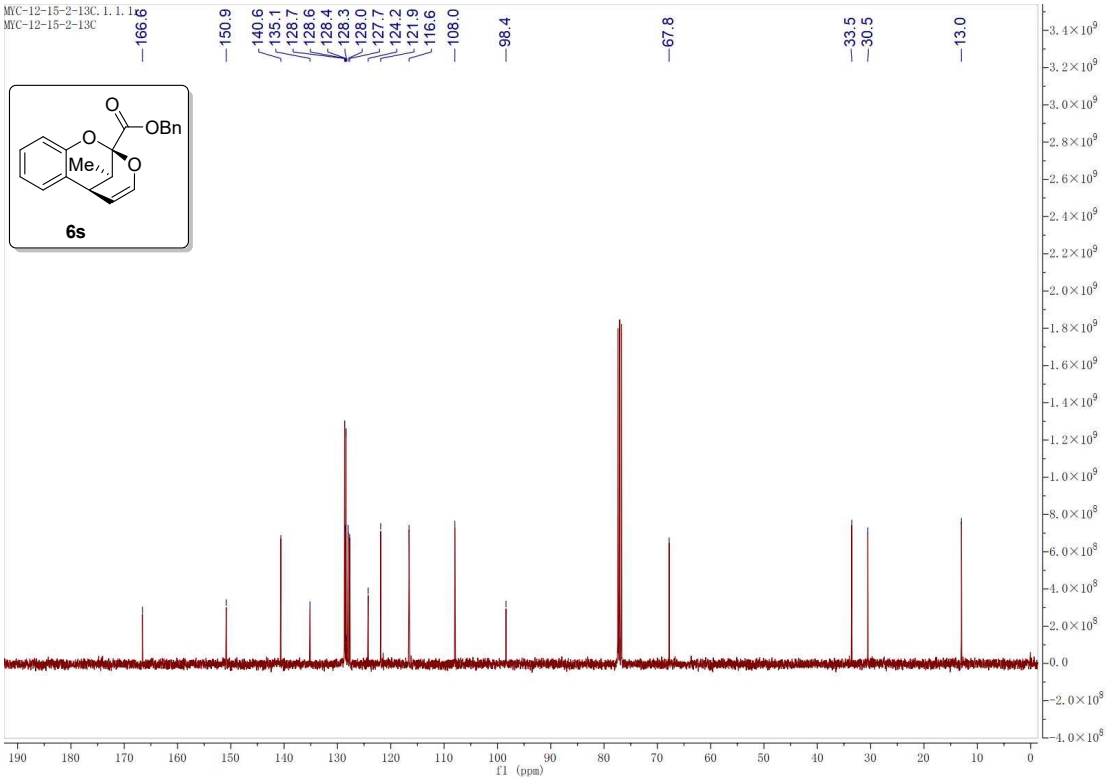
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	4.940	107674	1.158	BB
2	8.820	9190817	98.842	BB
		9298491	100.000	

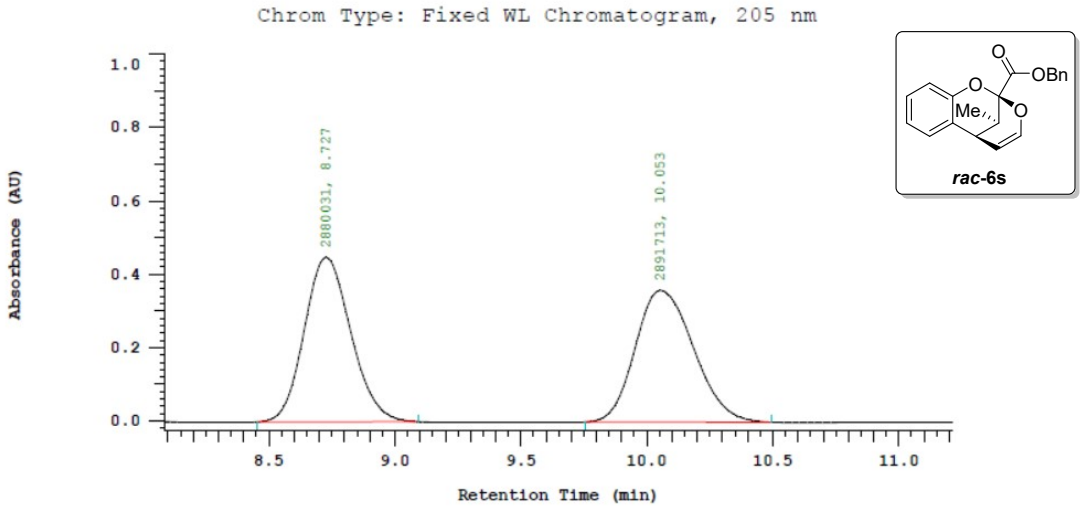
The ^{1}H NMR spectrum of 6s (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6s (100 MHz, $CDCl_3$)



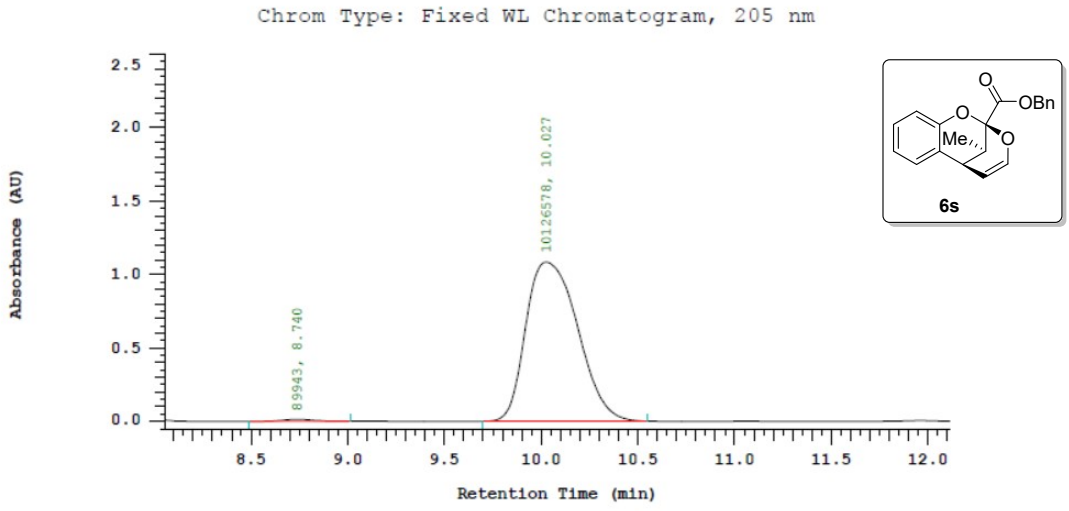
The HPLC of racemic 6s



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.727	2880031	49.899	BB
2	10.053	2891713	50.101	BB
		5771744	100.000	

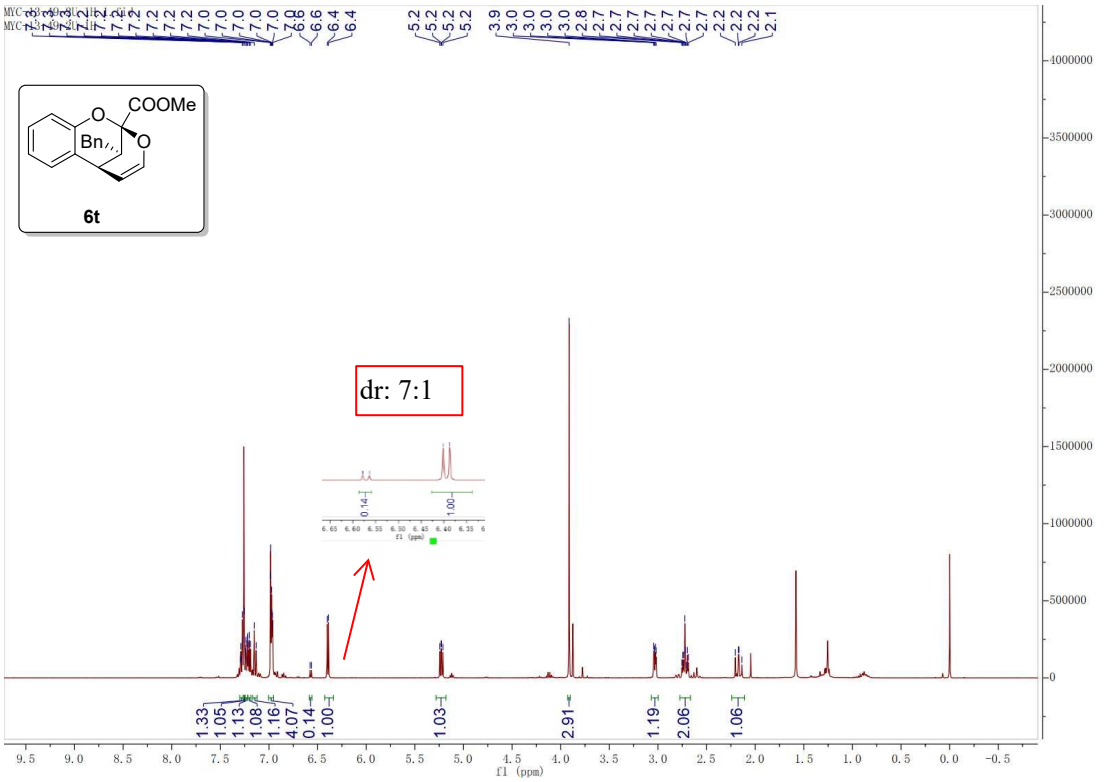
The HPLC of chiral 6s



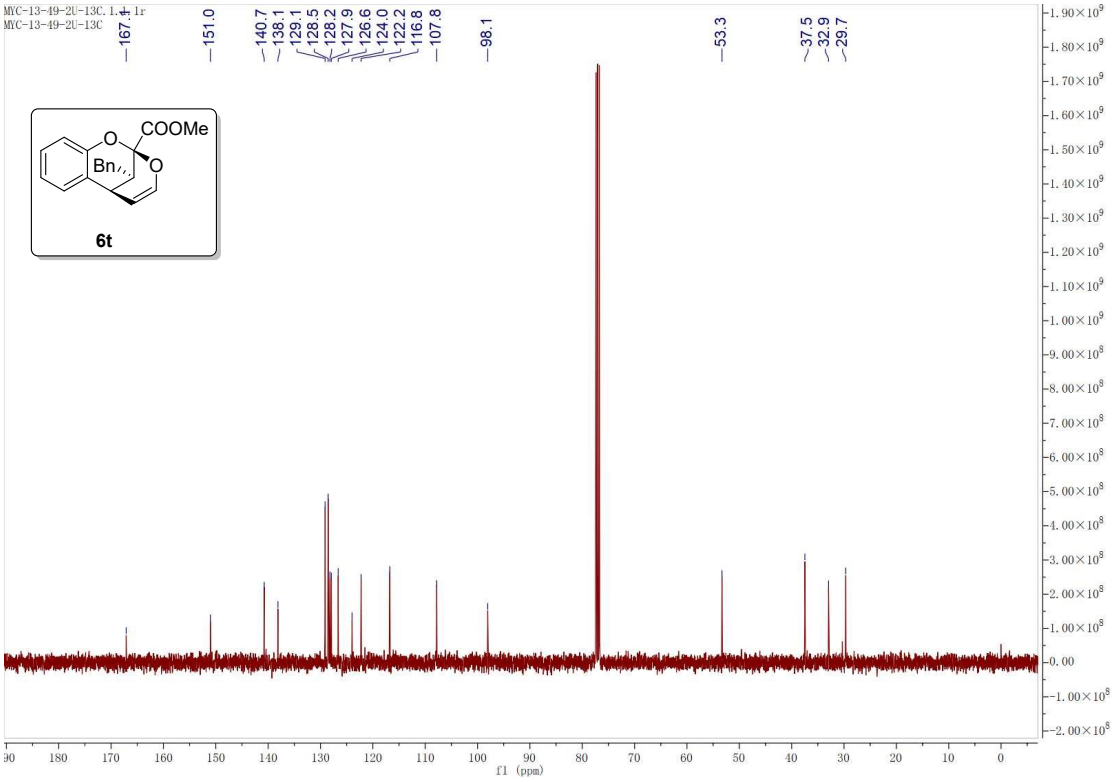
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.740	89943	0.880	BB
2	10.027	10126578	99.120	BB
		10216521	100.000	

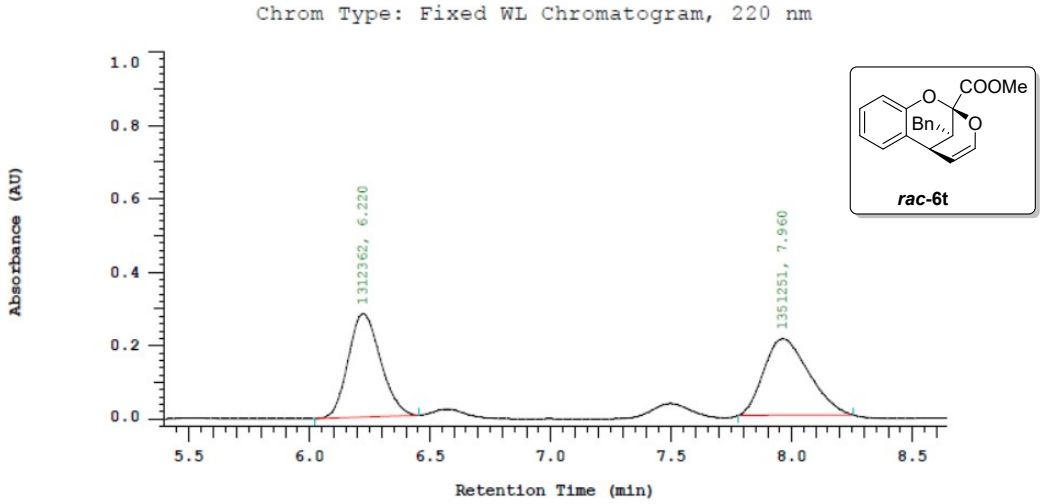
The ^{1}H NMR spectrum of 6t (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6t (100 MHz, $CDCl_3$)



The HPLC of racemic 6t



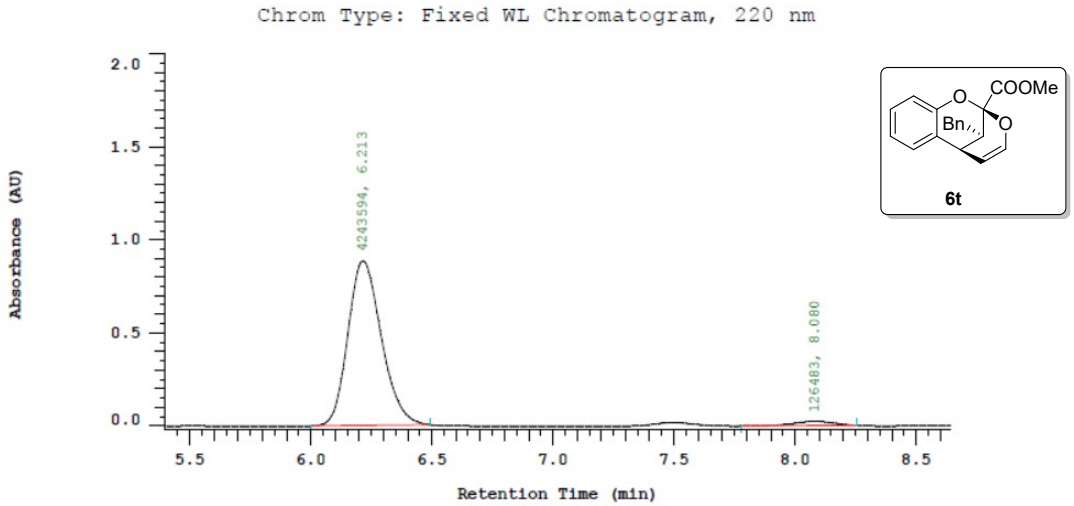
Chrom Type: Fixed WL Chromatogram, 220 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.220	1312362	49.270	BB
2	7.960	1351251	50.730	BB
		2663613	100.000	

The HPLC of chiral 6t



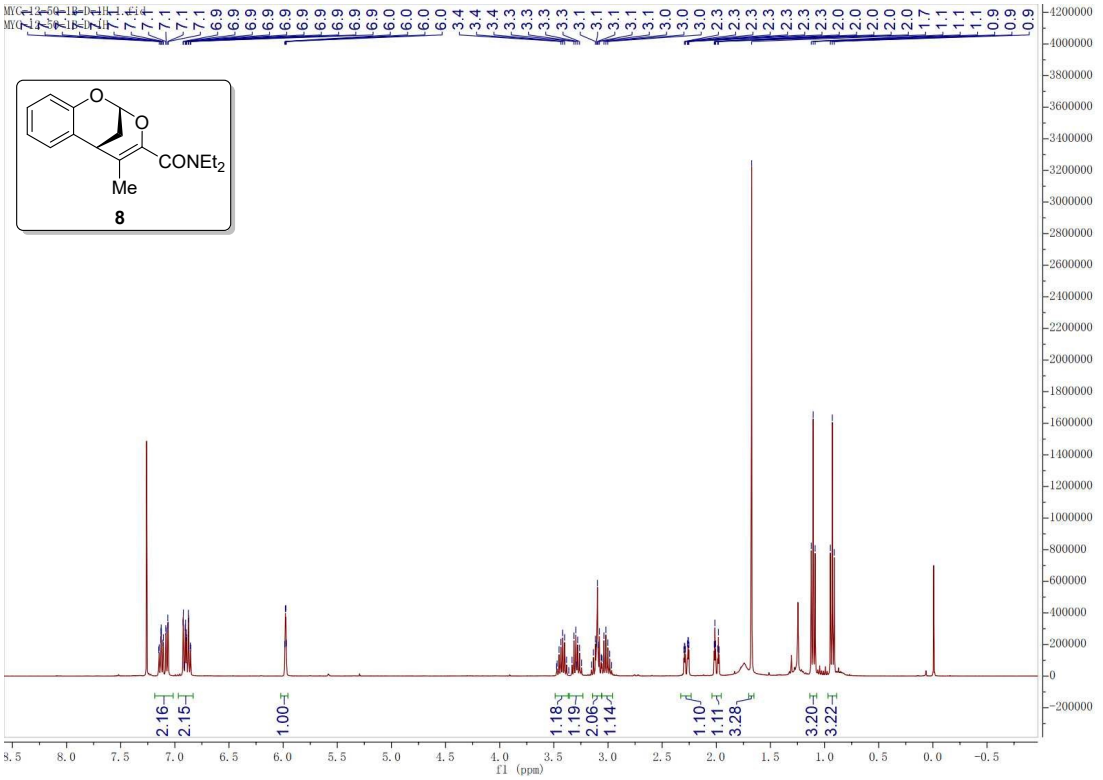
Chrom Type: Fixed WL Chromatogram, 220 nm

Peak Quantitation: AREA

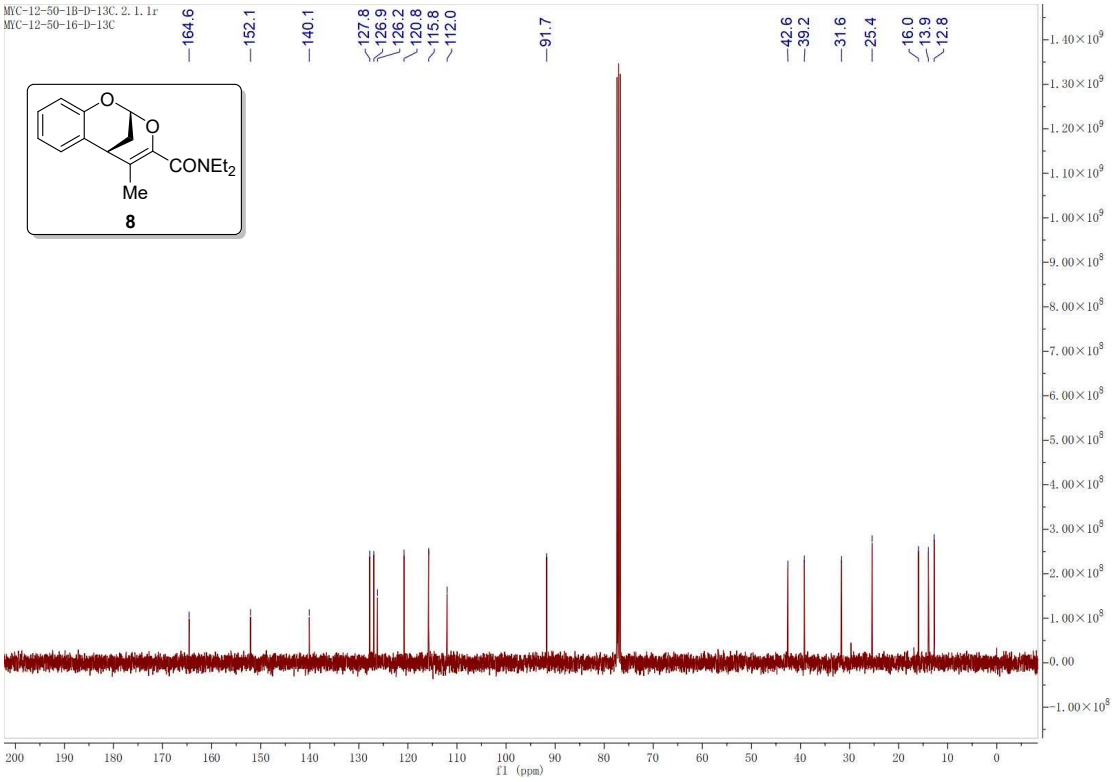
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.213	4243594	97.106	BB
2	8.080	126483	2.894	BB
		4370077	100.000	

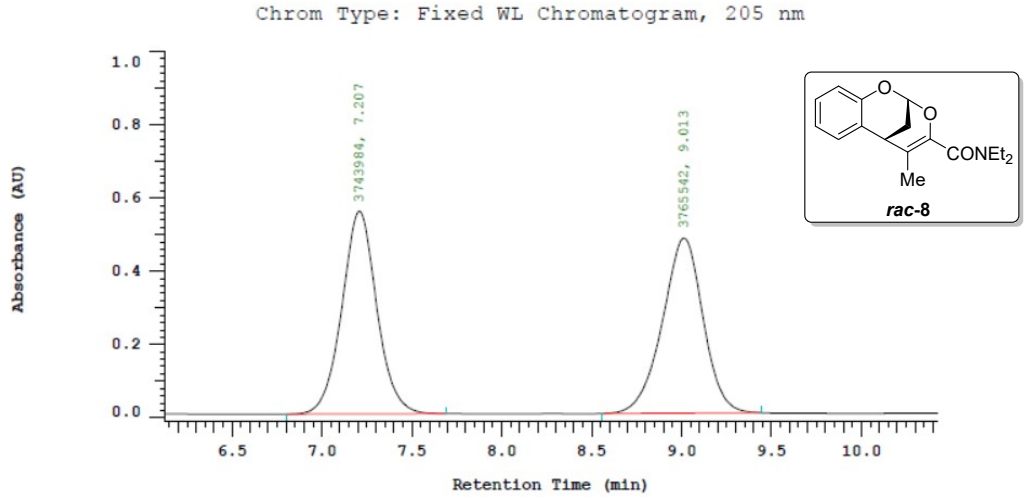
The ^{1}H NMR spectrum of 8 (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 8 (100 MHz, $CDCl_3$)



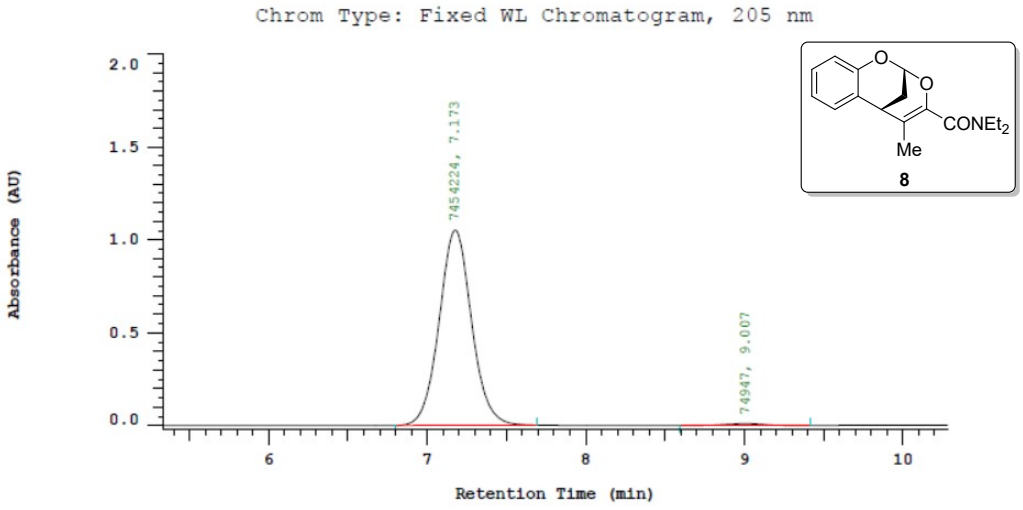
The HPLC of racemic 8



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.207	3743984	49.856	BB
2	9.013	3765542	50.144	BB
		7509526	100.000	

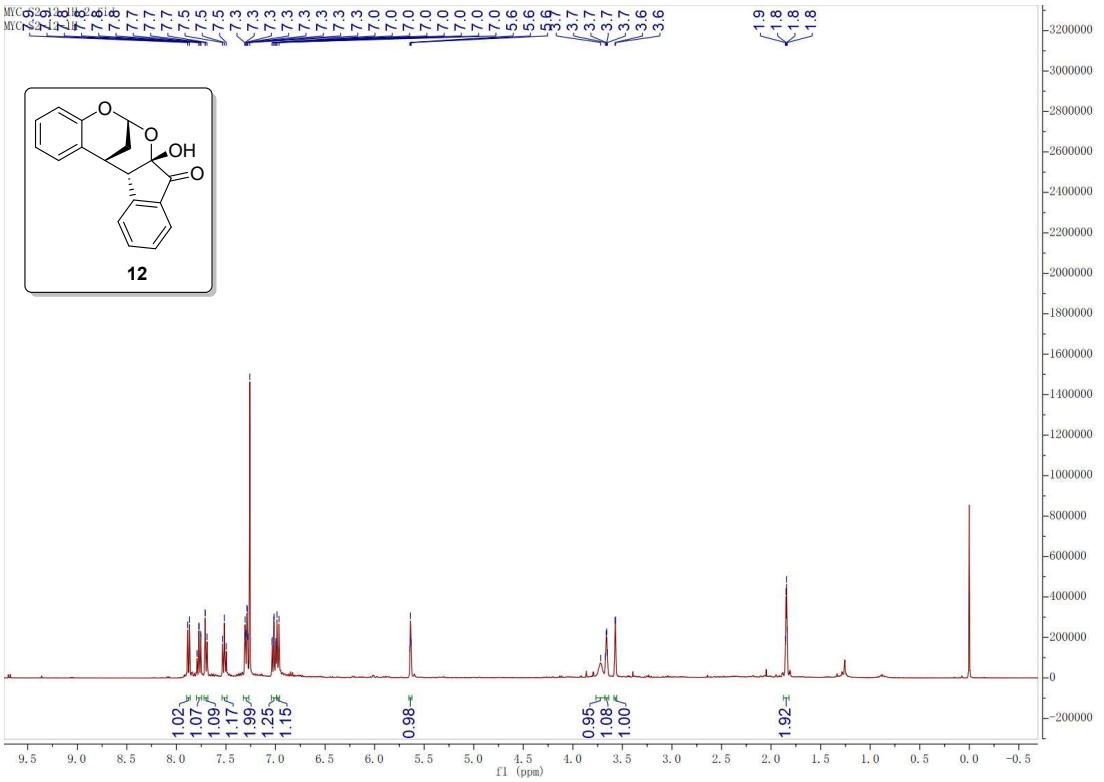
The HPLC of chiral 8



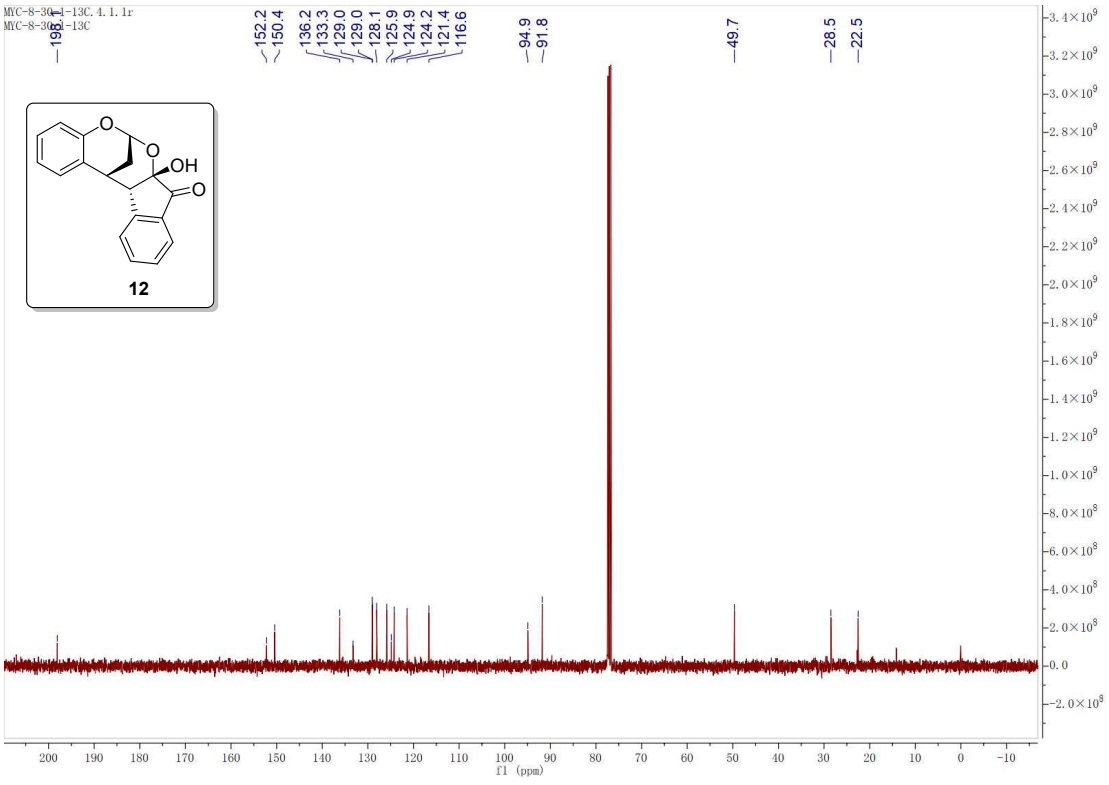
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.173	7454224	99.005	BB
2	9.007	74947	0.995	BB
		7529171	100.000	

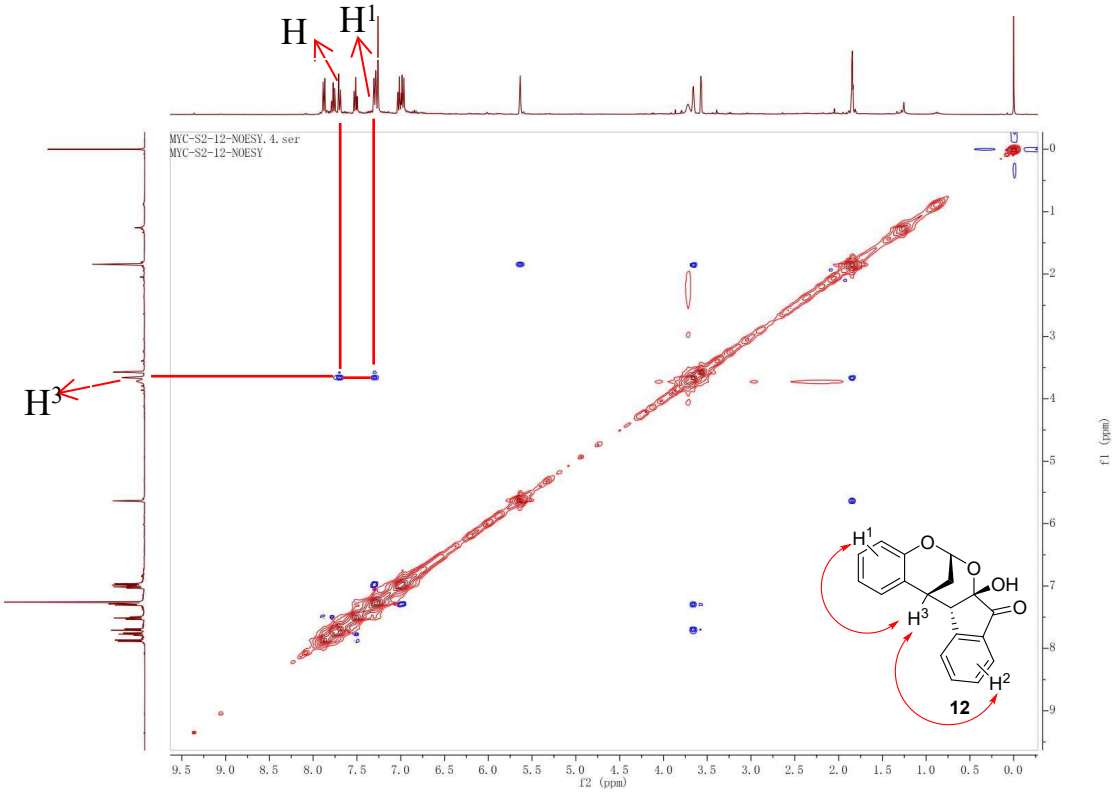
The ^{1}H NMR spectrum of 12 (400 MHz, $CDCl_3$)



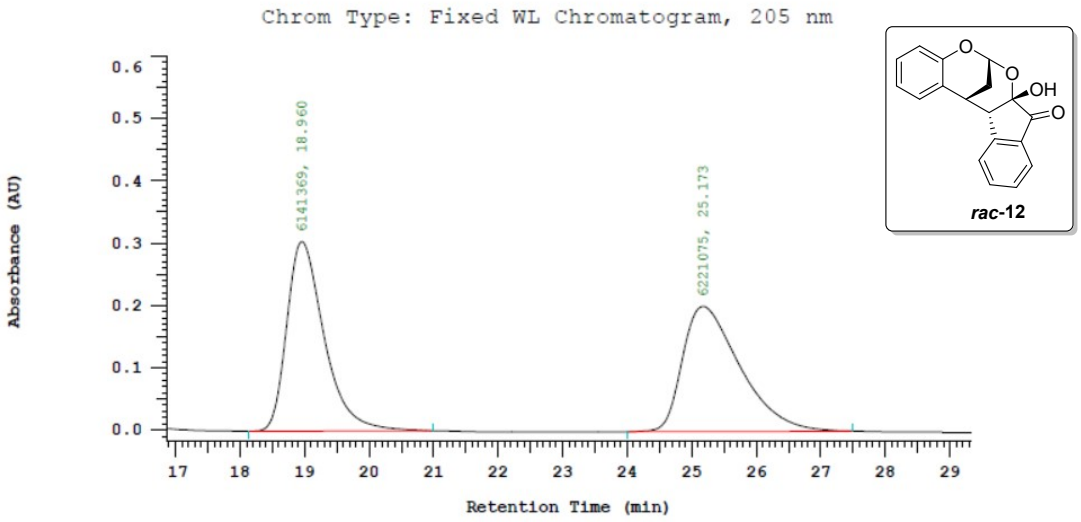
The ^{13}C NMR spectrum of 12 (100 MHz, $CDCl_3$)



The NOSEY spectrum of 12 (400 MHz, $CDCl_3$)



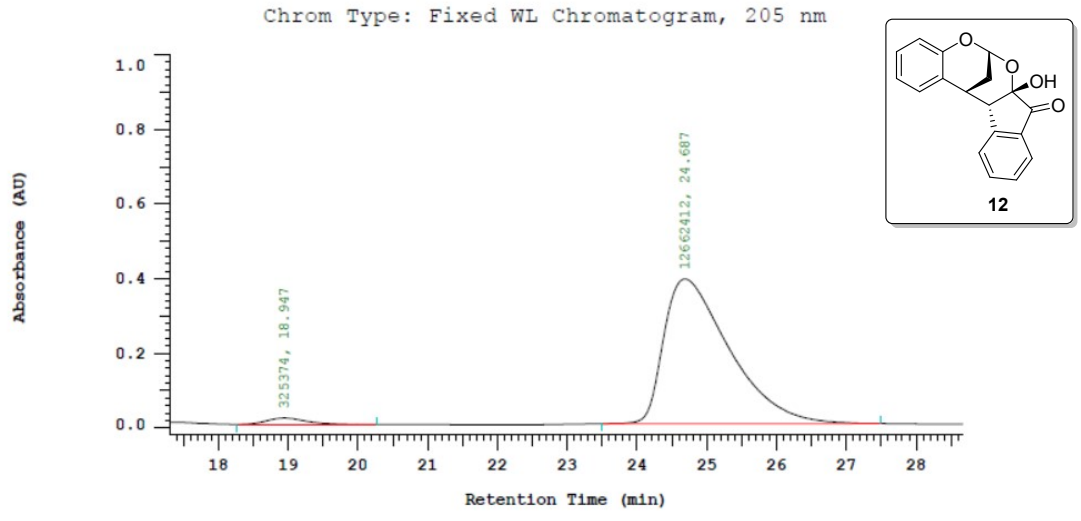
The HPLC of racemic 12



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.960	6141369	49.678	BB
2	25.173	6221075	50.322	BB
		12362444	100.000	

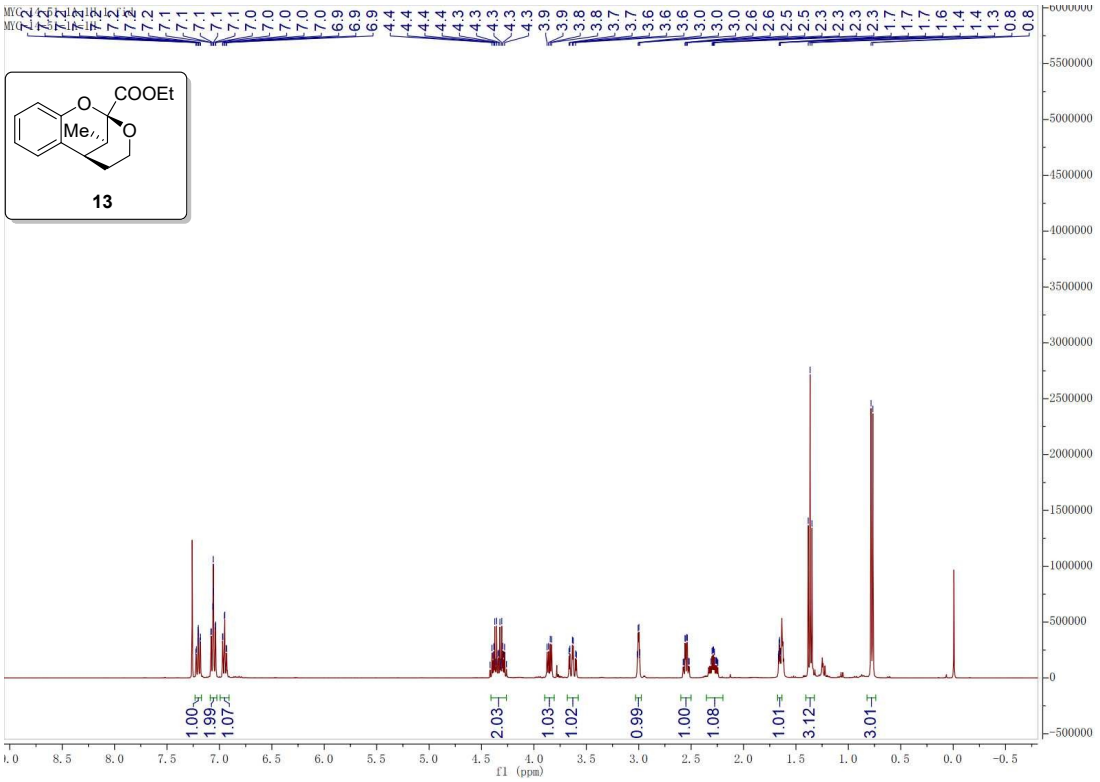
The HPLC of chiral 12



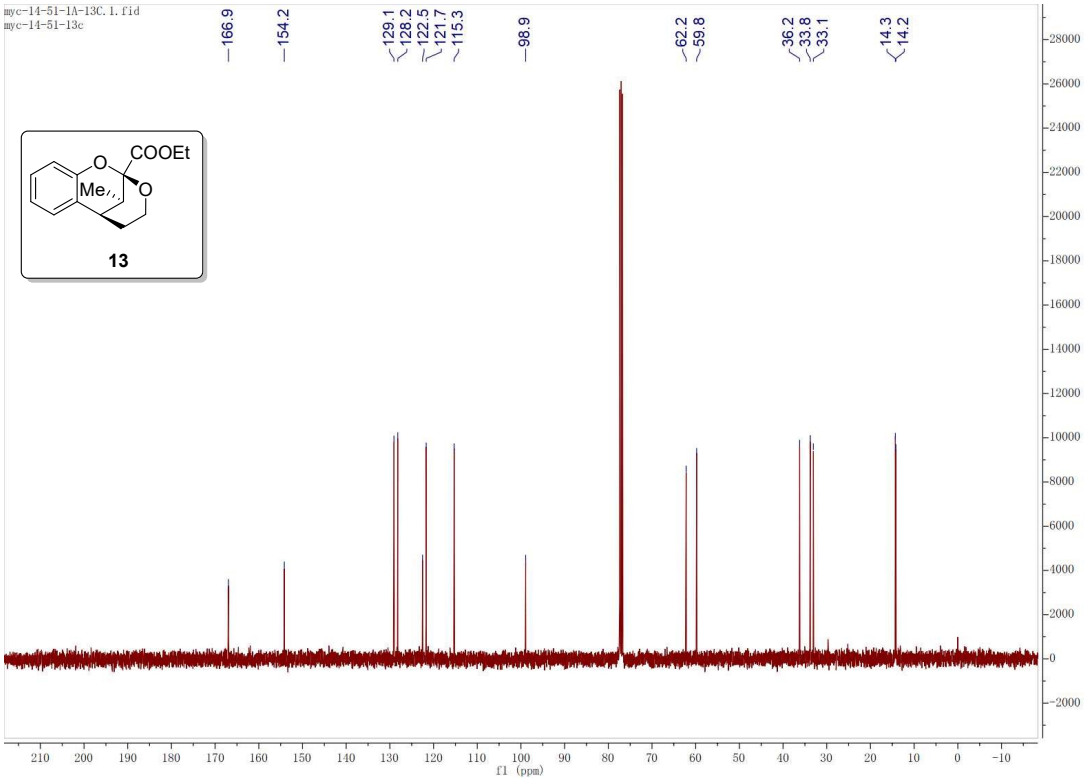
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.947	325374	2.505	BB
2	24.687	12662412	97.495	BB
		12987786	100.000	

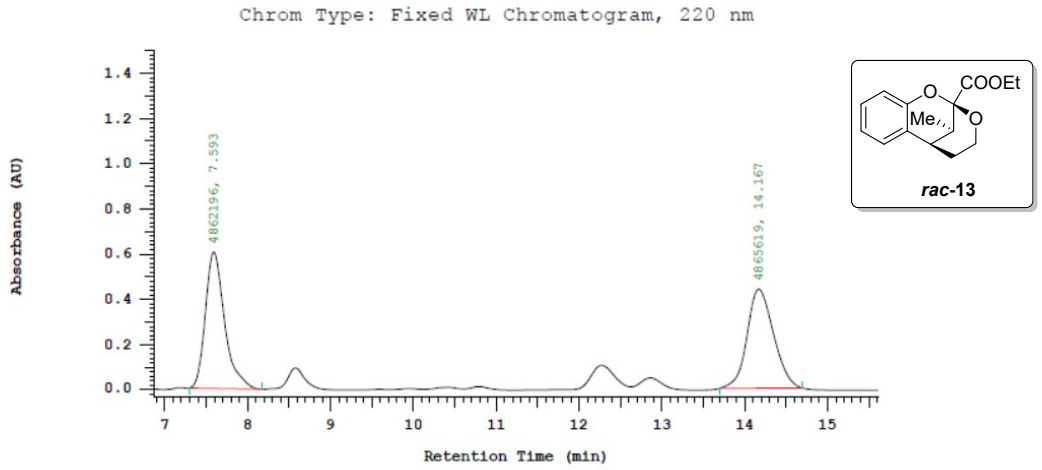
The ^{1}H NMR spectrum of 13 (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 13 (100 MHz, $CDCl_3$)



The HPLC of racemic 13



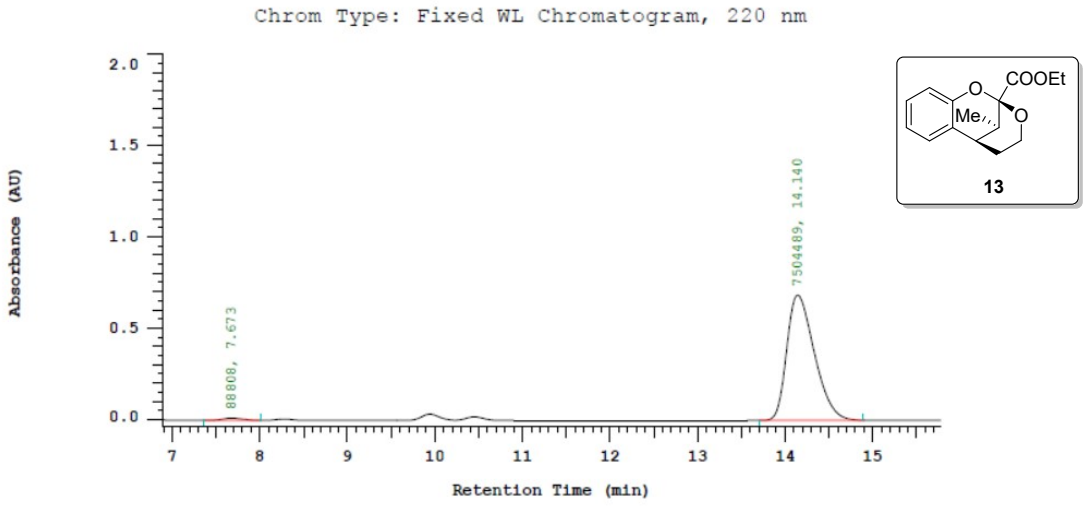
Chrom Type: Fixed WL Chromatogram, 220 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.593	4862196	49.982	BB
2	14.167	4865619	50.018	BB
		9727815	100.000	

The HPLC of chiral 13



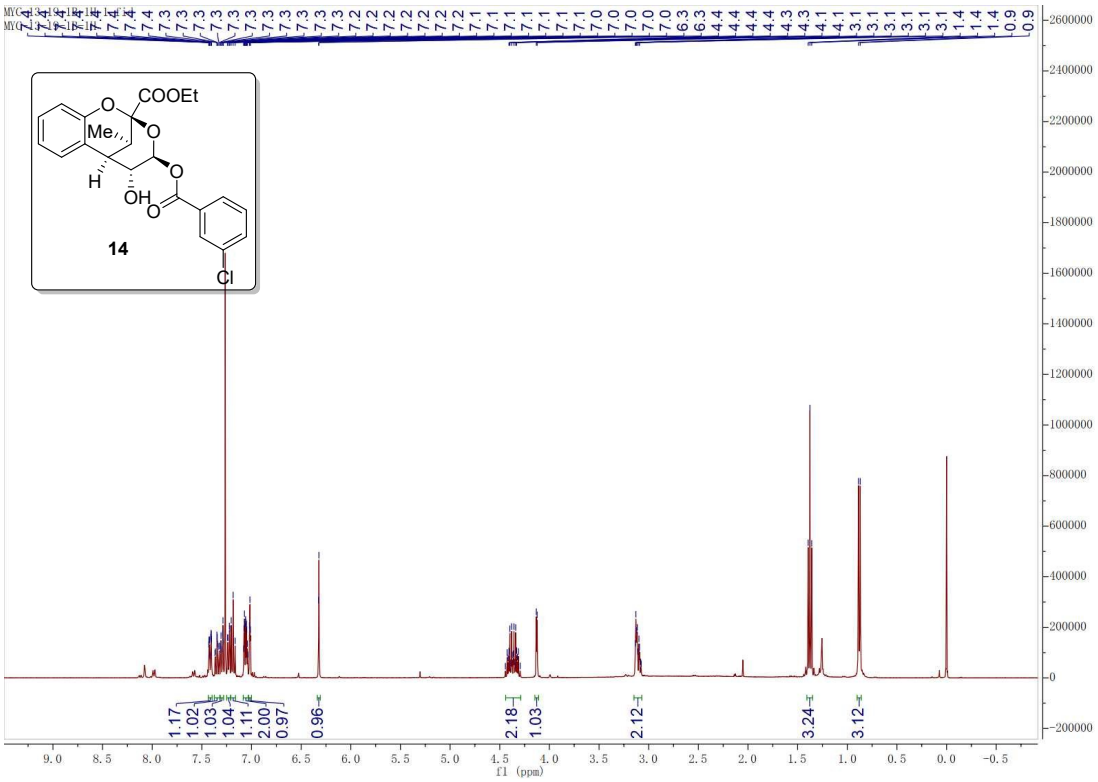
Chrom Type: Fixed WL Chromatogram, 220 nm

Peak Quantitation: AREA

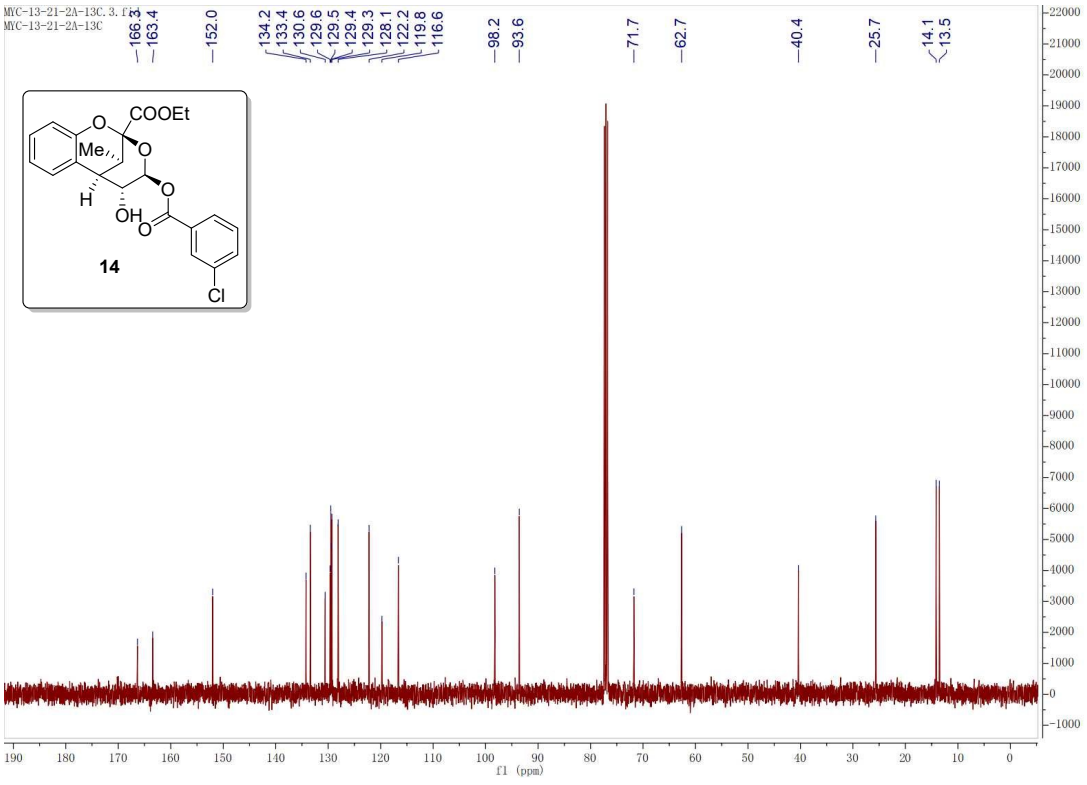
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.673	88808	1.170	BB
2	14.140	7504489	98.830	BB
		7593297	100.000	

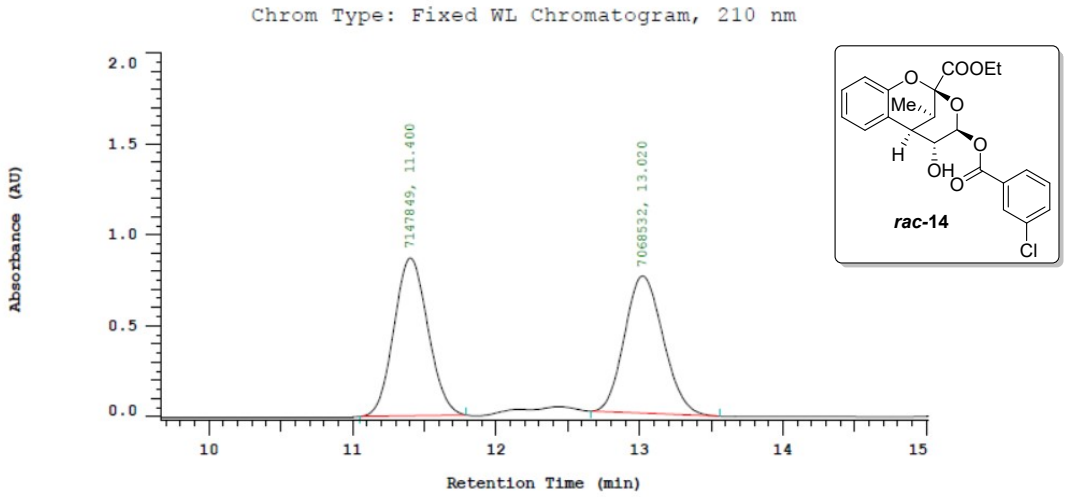
The ^{1}H NMR spectrum of 14 (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 14 (100 MHz, $CDCl_3$)



The HPLC of racemic 14



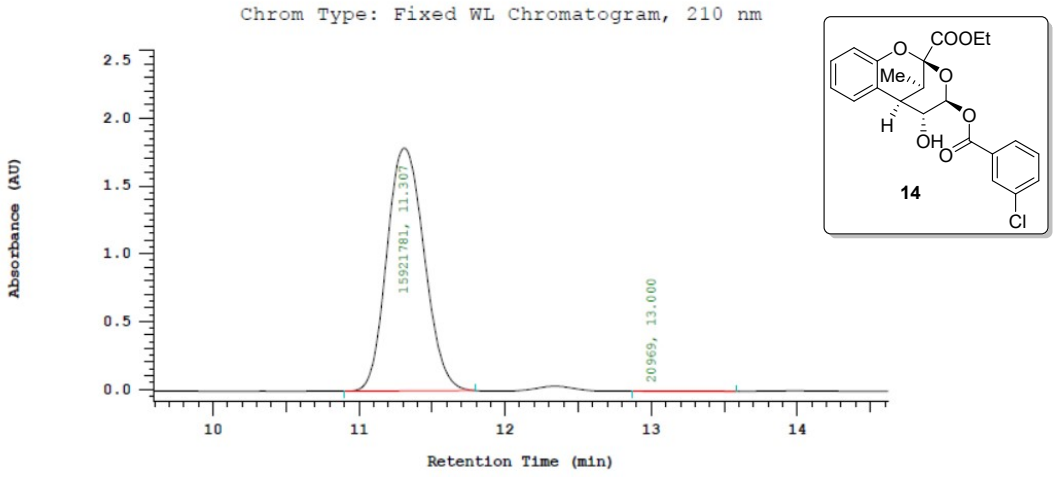
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.400	7147849	50.279	BB
2	13.020	7068532	49.721	BB
		14216381	100.000	

The HPLC of chiral 14



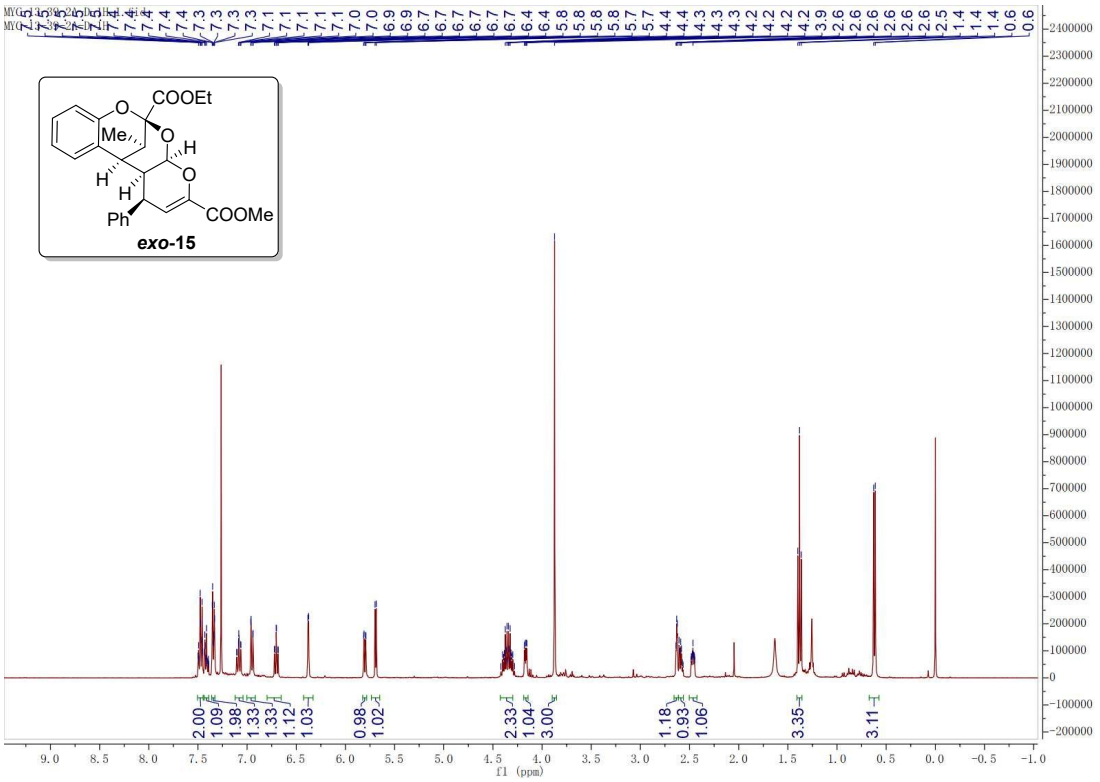
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

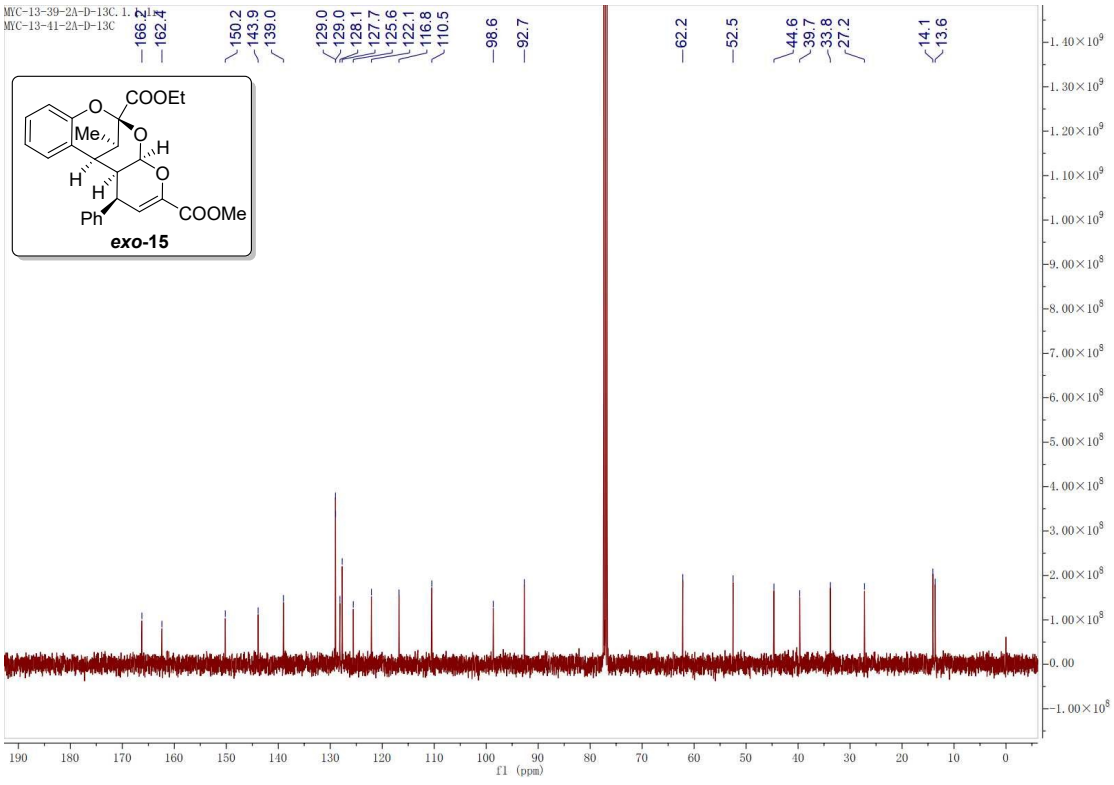
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.307	15921781	99.868	BB
2	13.000	20969	0.132	BB
		15942750	100.000	

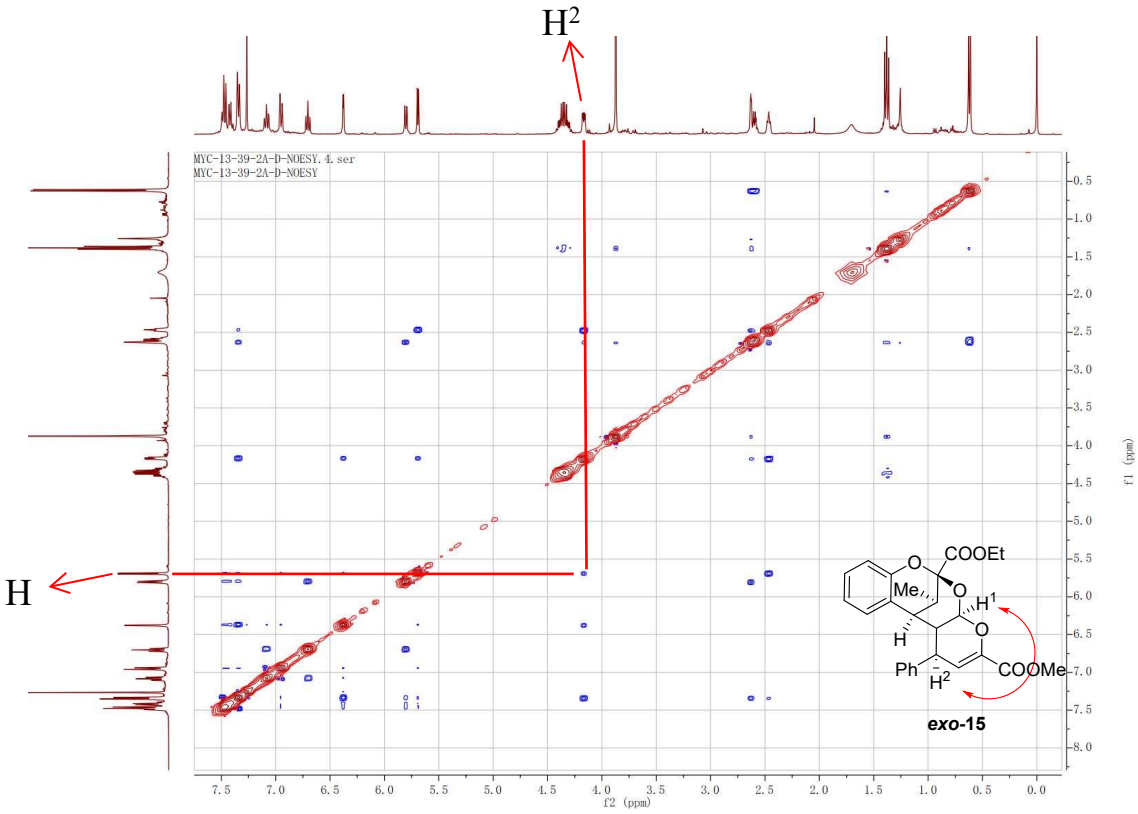
The ^{1}H NMR spectrum of *exo*-15 (400 MHz, $CDCl_3$)



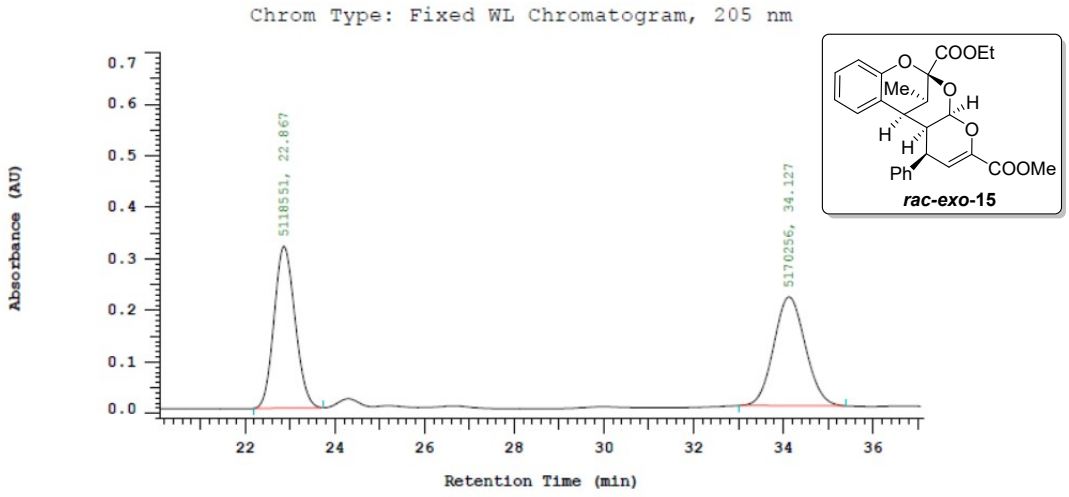
The ^{13}C NMR spectrum of *exo*-15 (100 MHz, $CDCl_3$)



The NOSEY spectrum of *exo*-15 (400 MHz, $CDCl_3$)



The HPLC of racemic *exo*-15



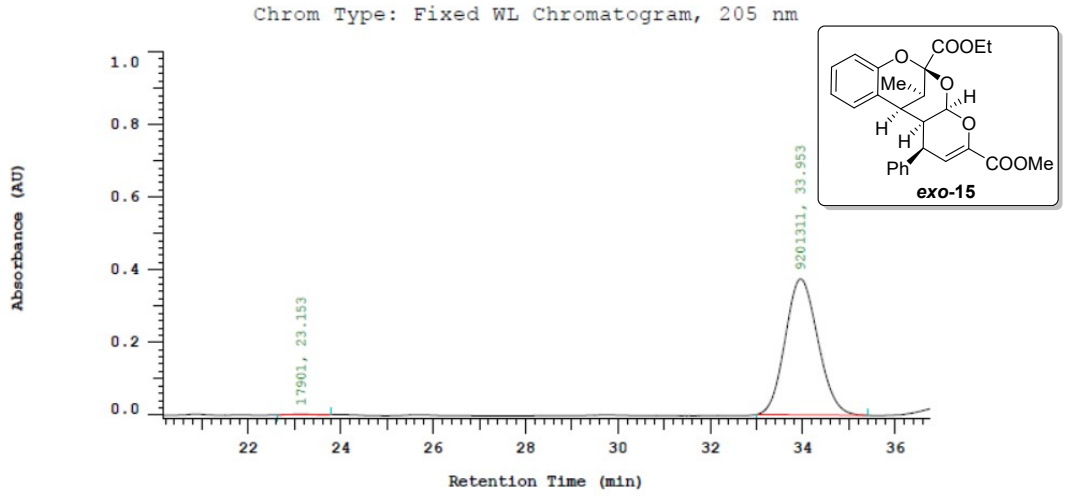
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	22.867	5118551	49.749	BB
2	34.127	5170256	50.251	BB
		10288807	100.000	

The HPLC of chiral *exo*-15



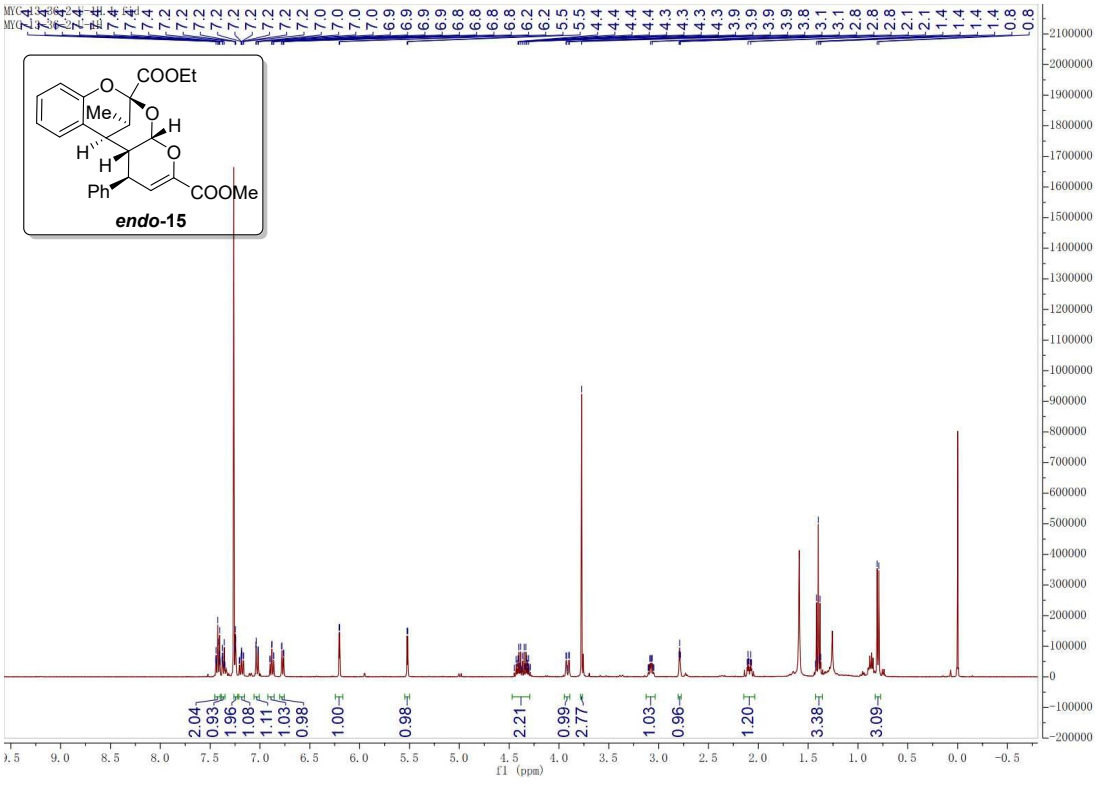
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

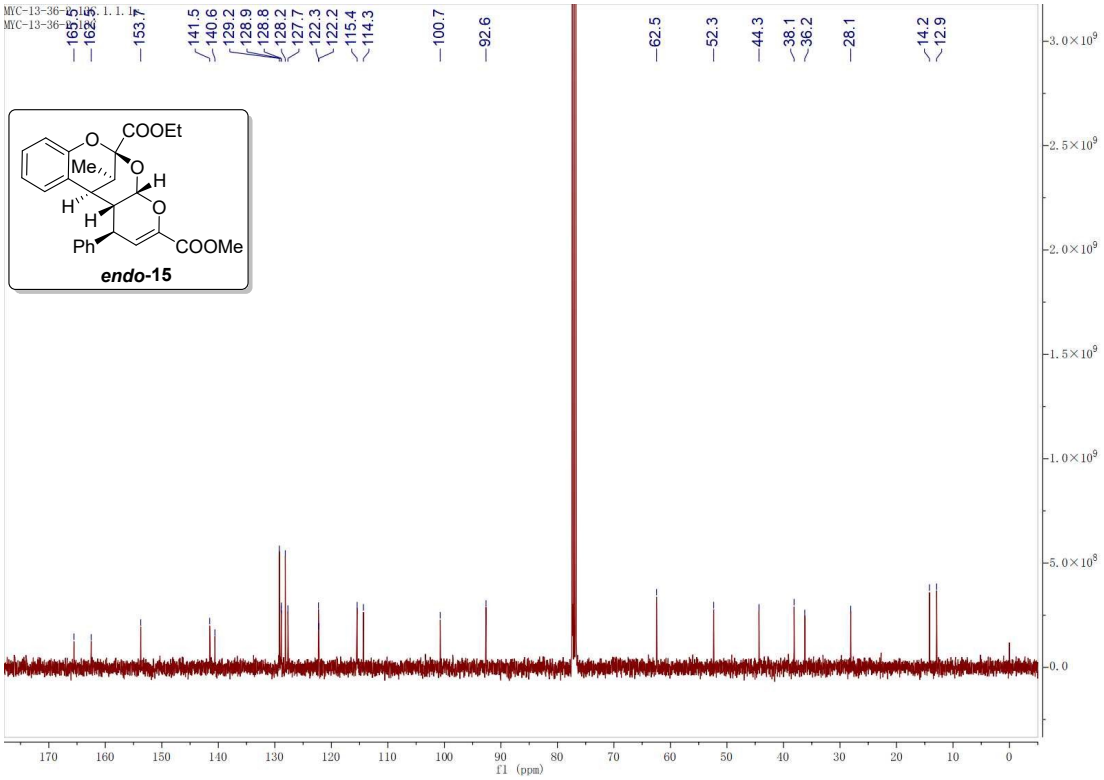
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	23.153	17901	0.194	BB
2	33.953	9201311	99.806	BB
		9219212	100.000	

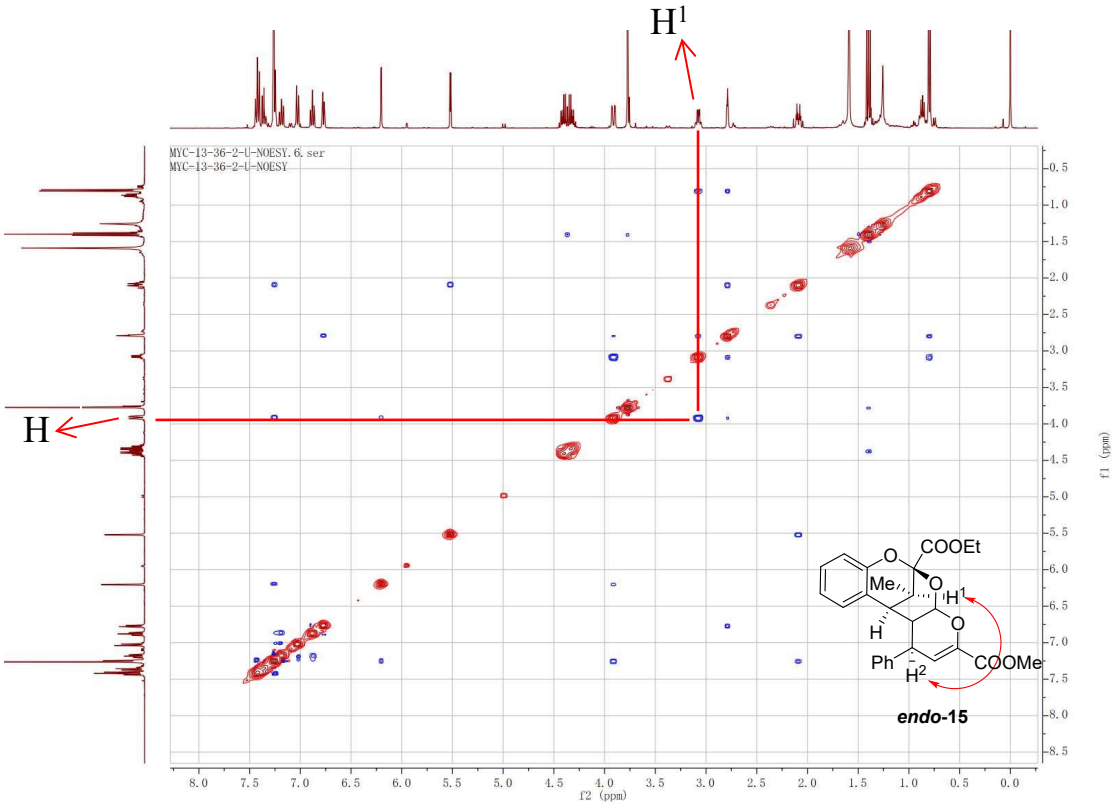
The ^{1}H NMR spectrum of *endo*-15 (400 MHz, $CDCl_3$)



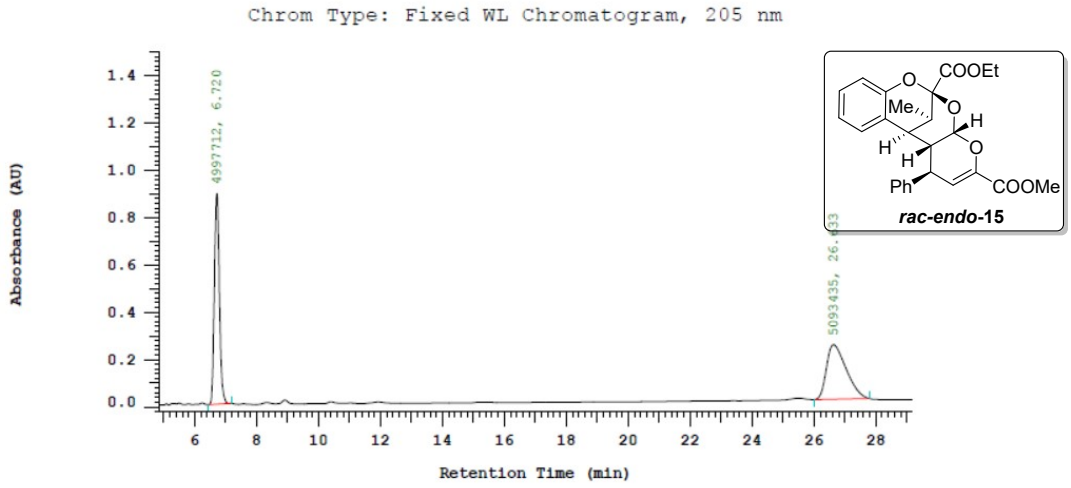
The ^{13}C NMR spectrum of *endo*-15 (100 MHz, $CDCl_3$)



The NOSEY spectrum of *endo*-15 (400 MHz, $CDCl_3$)



The HPLC of racemic *endo*-15



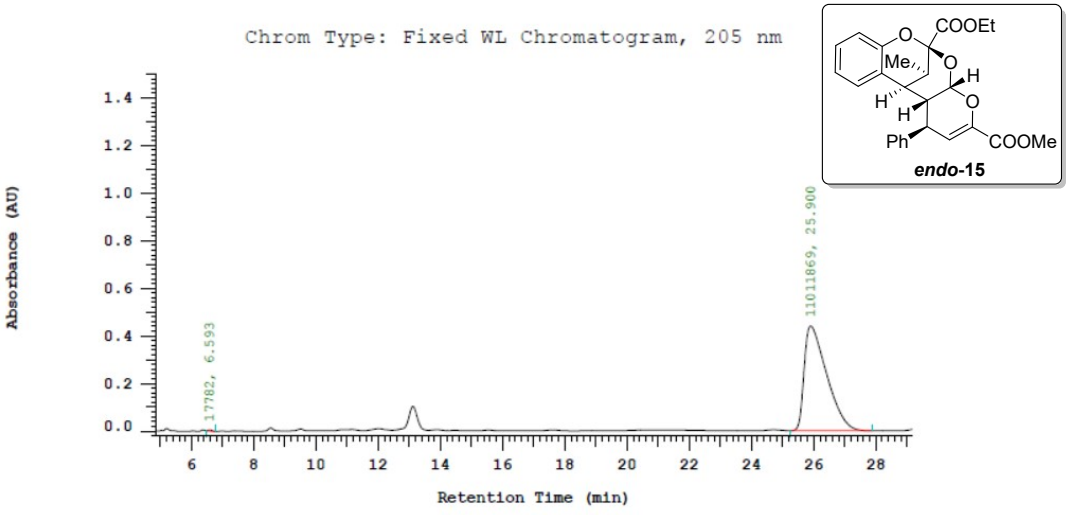
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.720	4997712	49.526	BB
2	26.633	5093435	50.474	BB
		10091147	100.000	

The HPLC of chiral *endo*-15



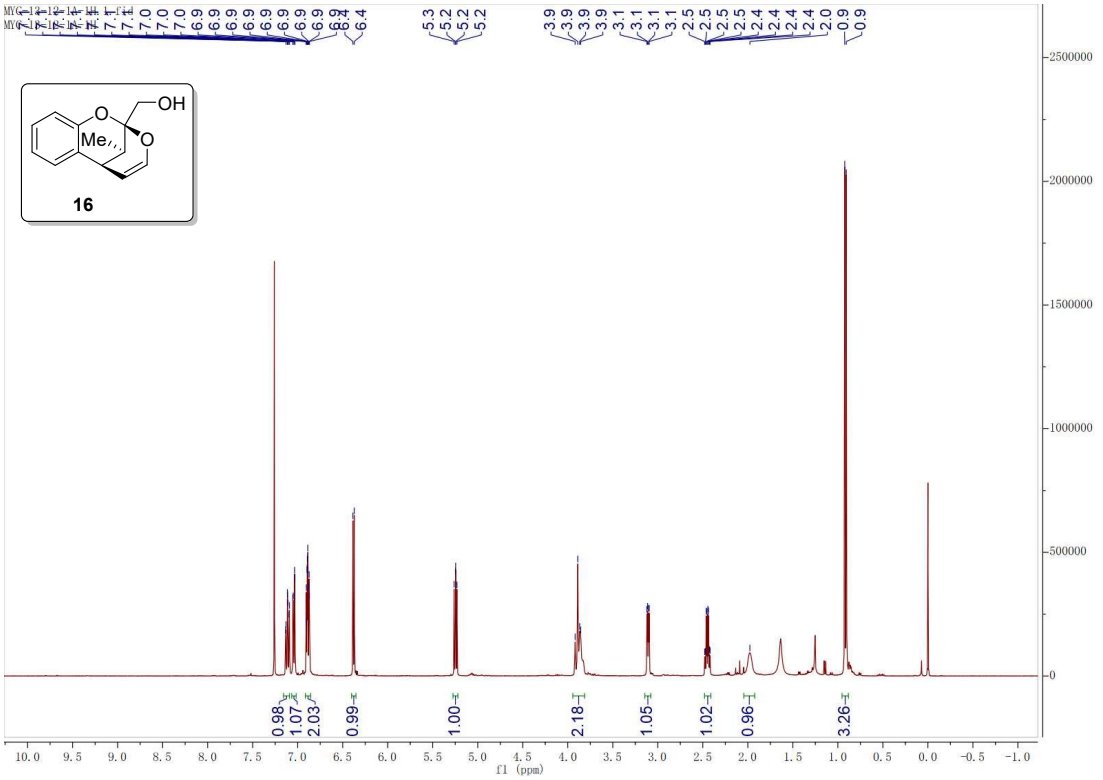
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

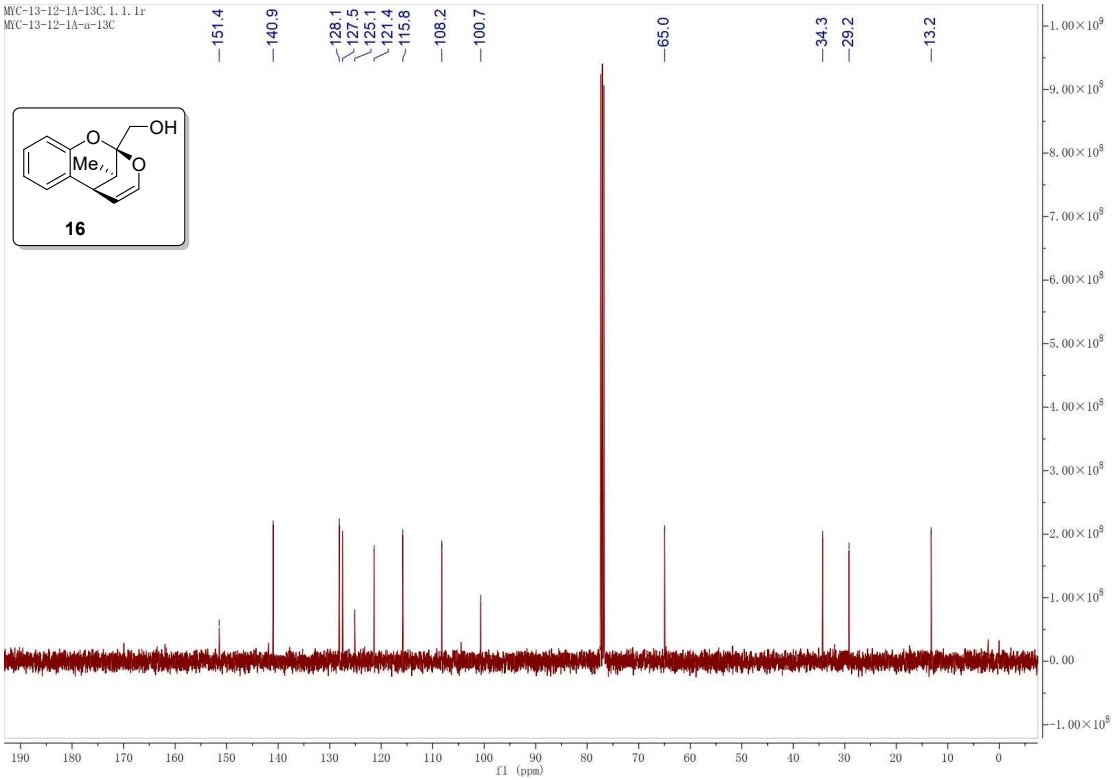
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.593	17782	0.161	BB
2	25.900	11011869	99.839	BB
		11029651	100.000	

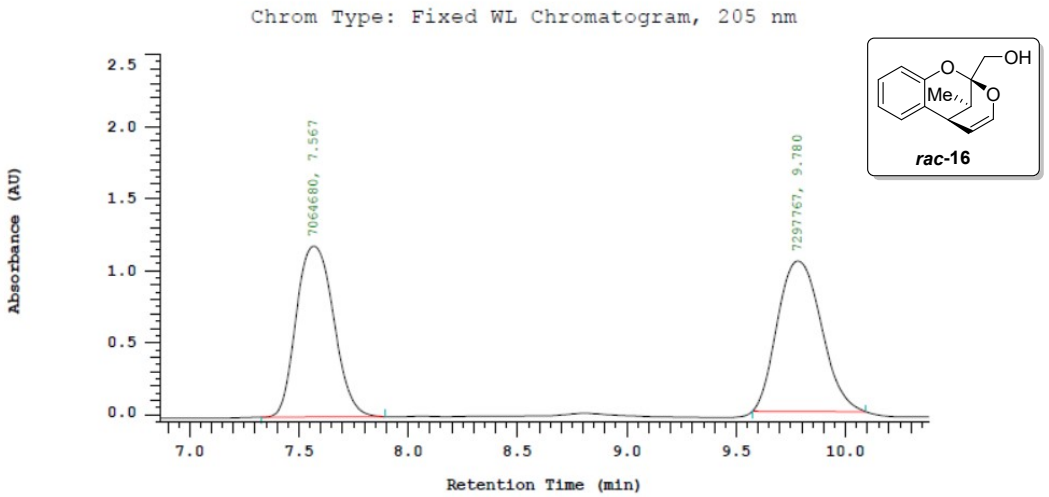
The ^{1}H NMR spectrum of 16 (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 16 (100 MHz, $CDCl_3$)



The HPLC of racemic 16

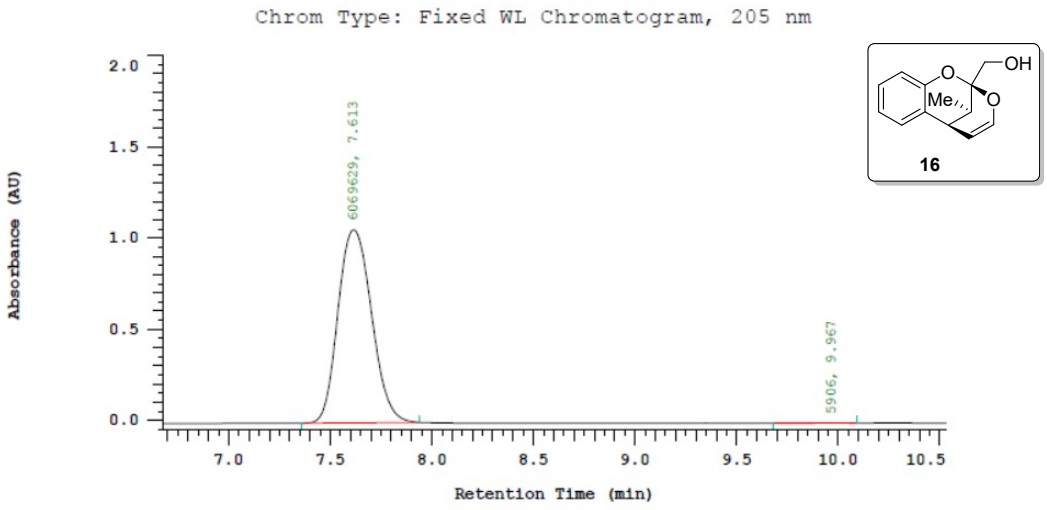


Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.567	7064680	49.189	BB
2	9.780	7297767	50.811	BB
		14362447	100.000	

The HPLC of chiral 16

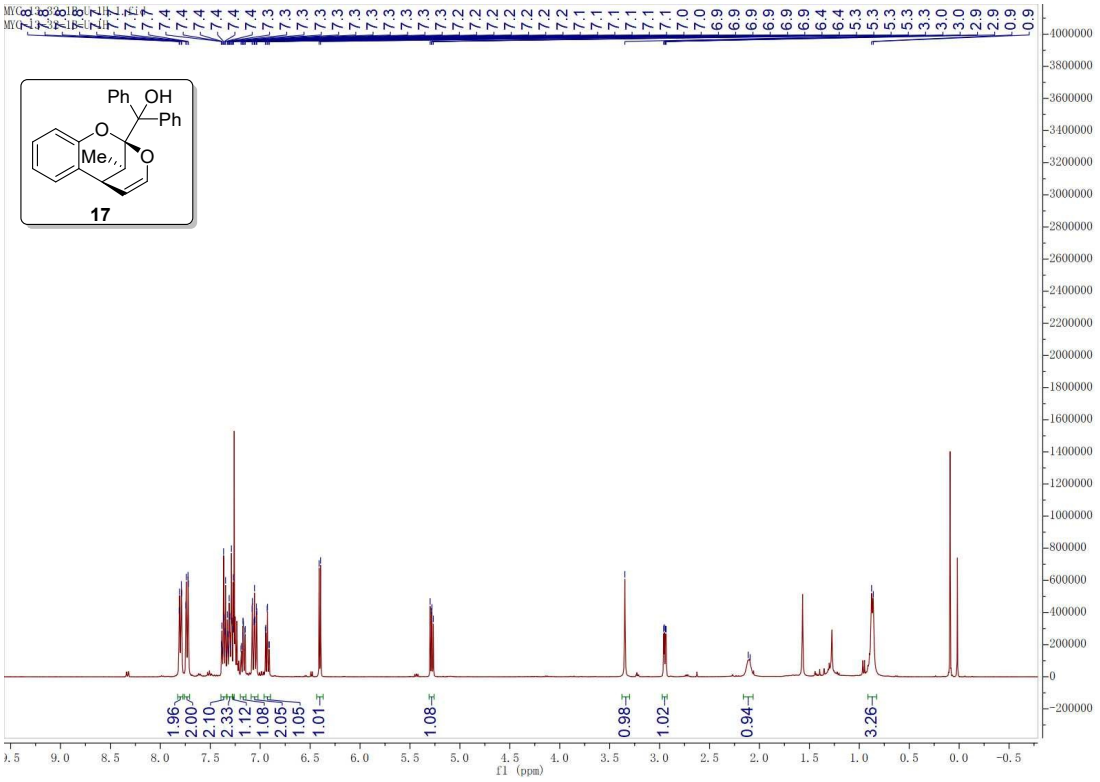


Chrom Type: Fixed WL Chromatogram, 205 nm

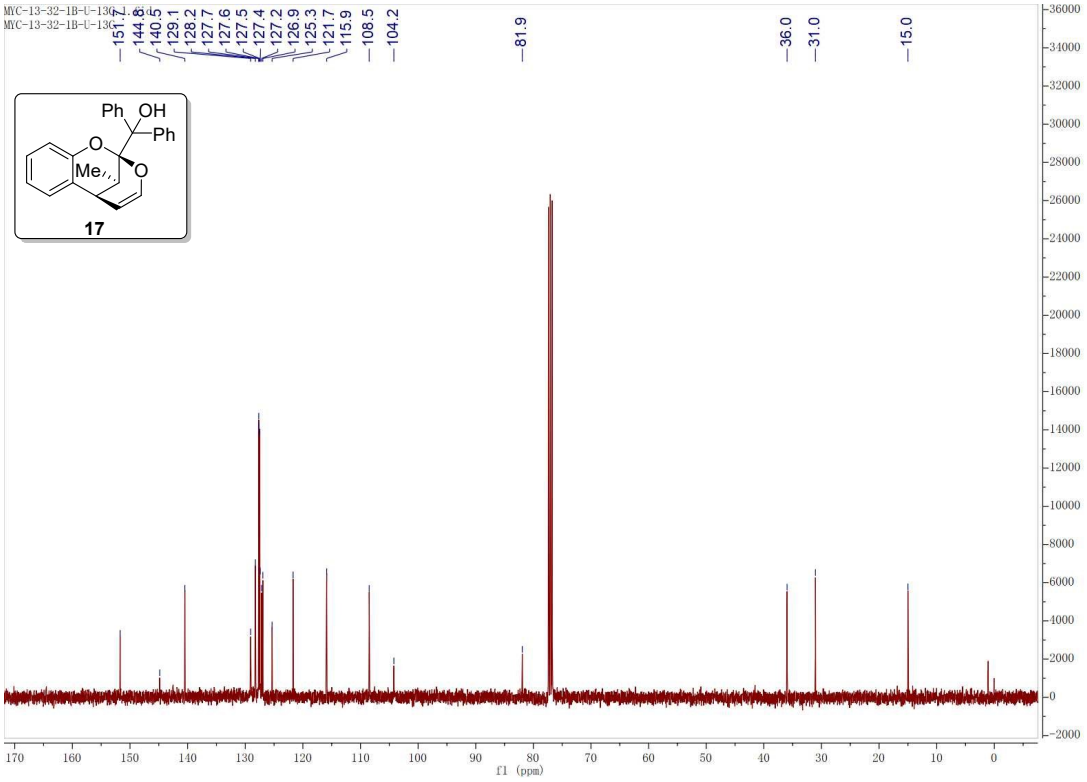
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.613	6069629	99.903	BB
2	9.967	5906	0.097	BB
		6075535	100.000	

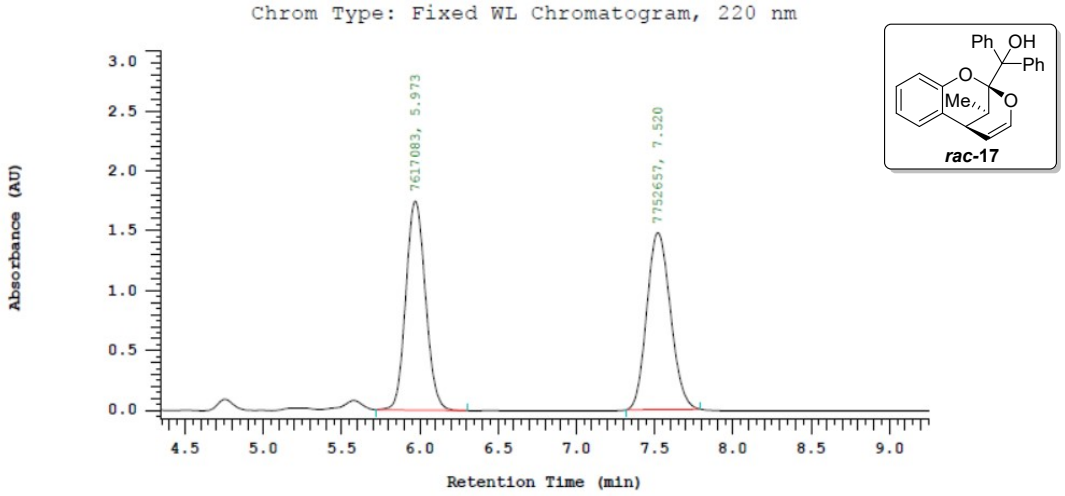
The ^{1}H NMR spectrum of 17 (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 17 (100 MHz, $CDCl_3$)



The HPLC of racemic 17



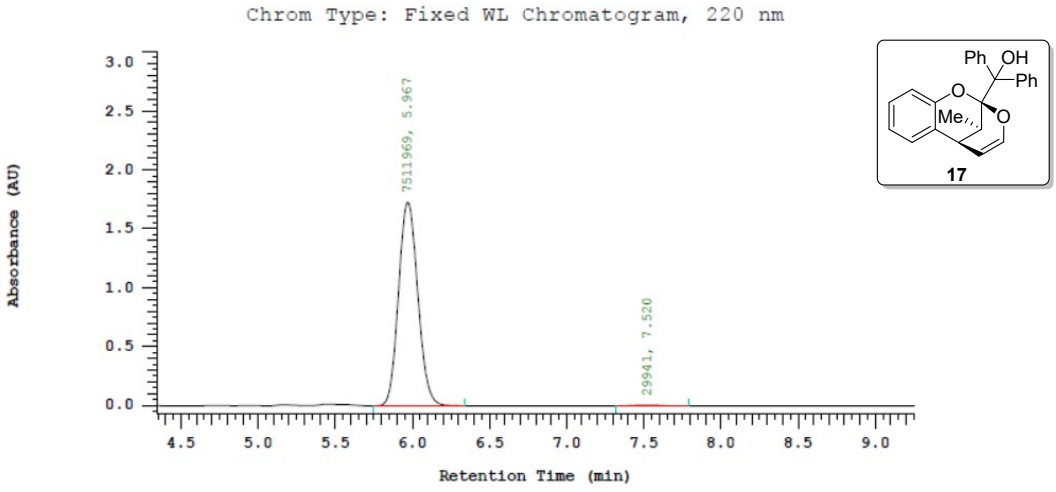
Chrom Type: Fixed WL Chromatogram, 220 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	5.973	7617083	49.559	BB
2	7.520	7752657	50.441	BB
		15369740	100.000	

The HPLC of chiral 17



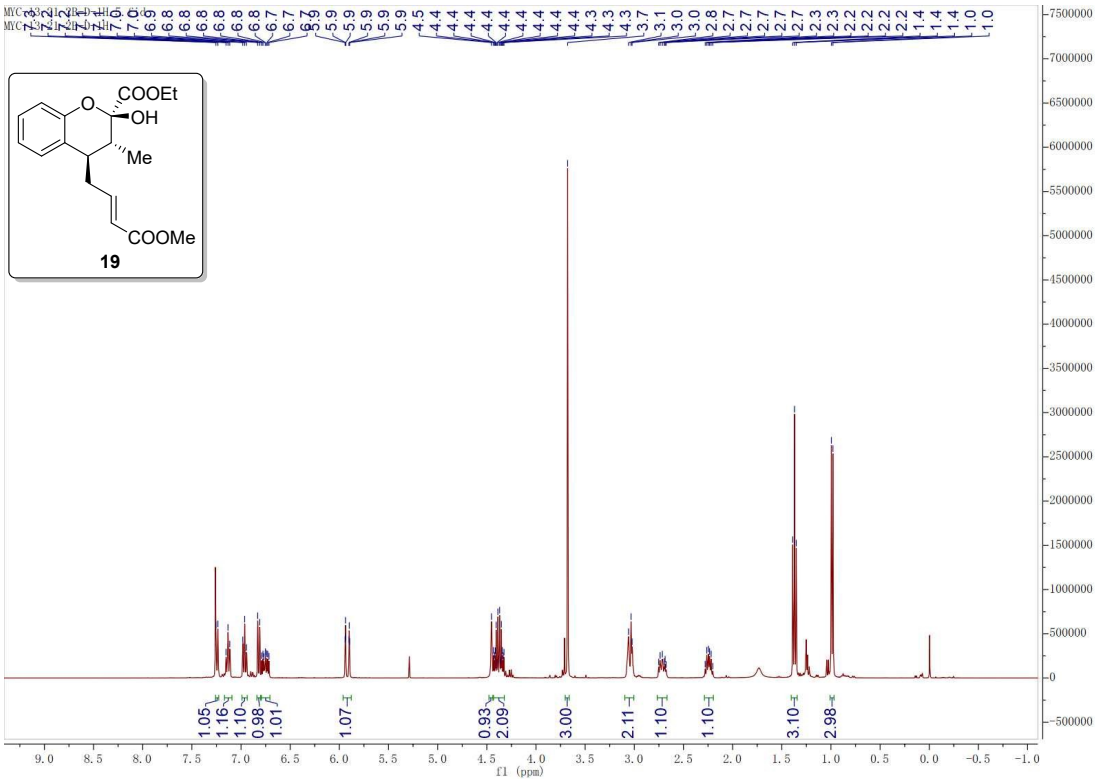
Chrom Type: Fixed WL Chromatogram, 220 nm

Peak Quantitation: AREA

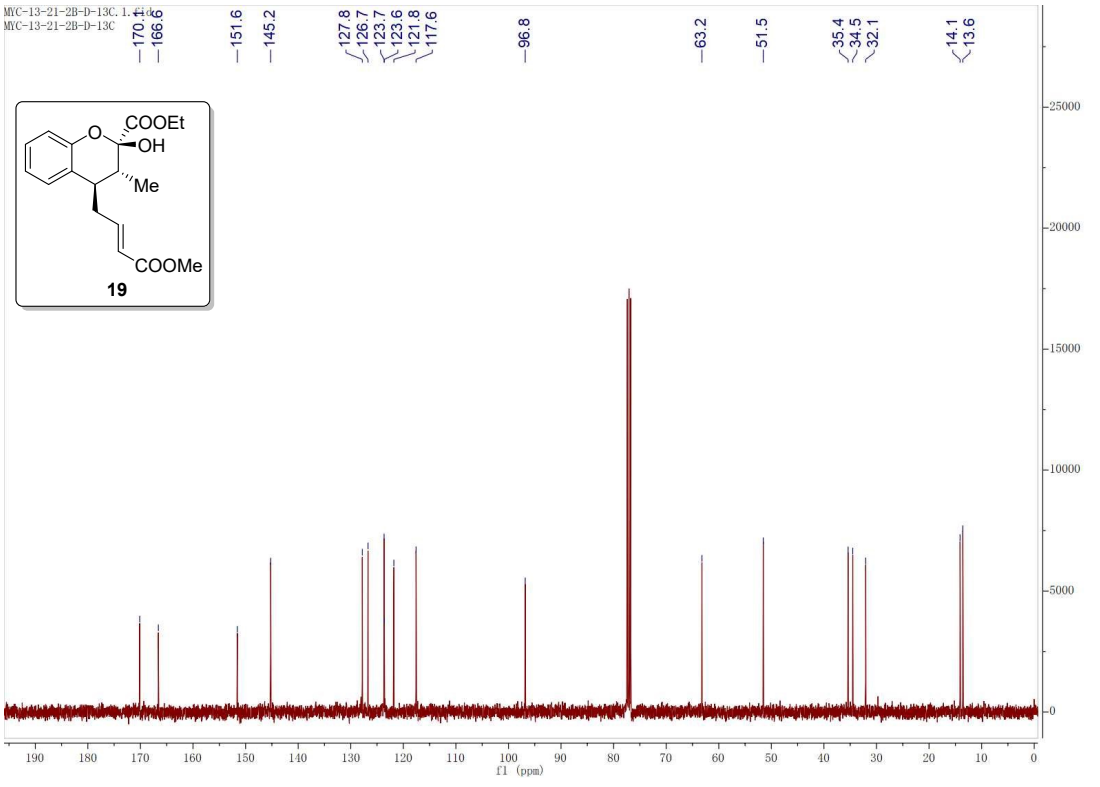
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	5.967	7511969	99.603	BB
2	7.520	29941	0.397	BB
		7541910	100.000	

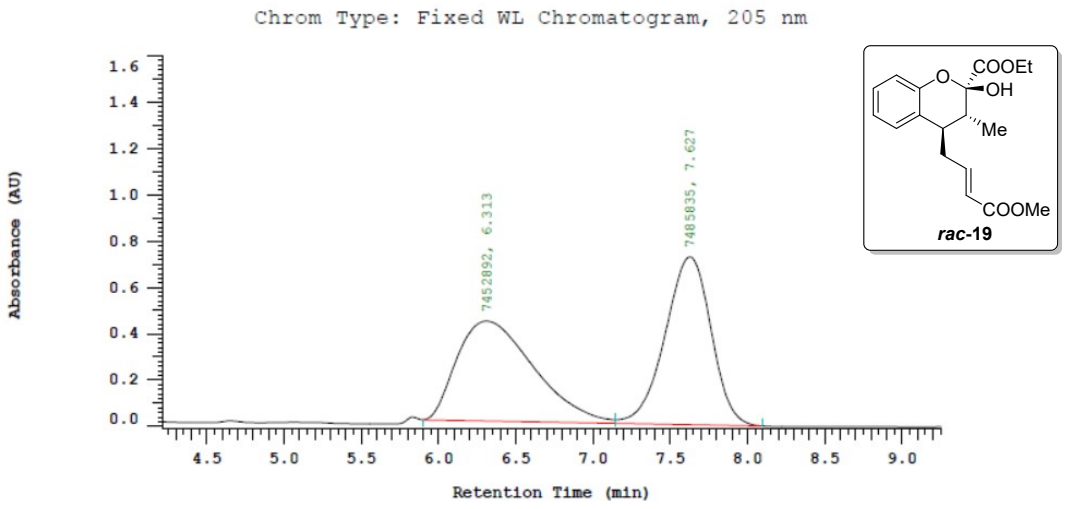
The ^{1}H NMR spectrum of 19 (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 19(100 MHz, $CDCl_3$)



The HPLC of racemic 19



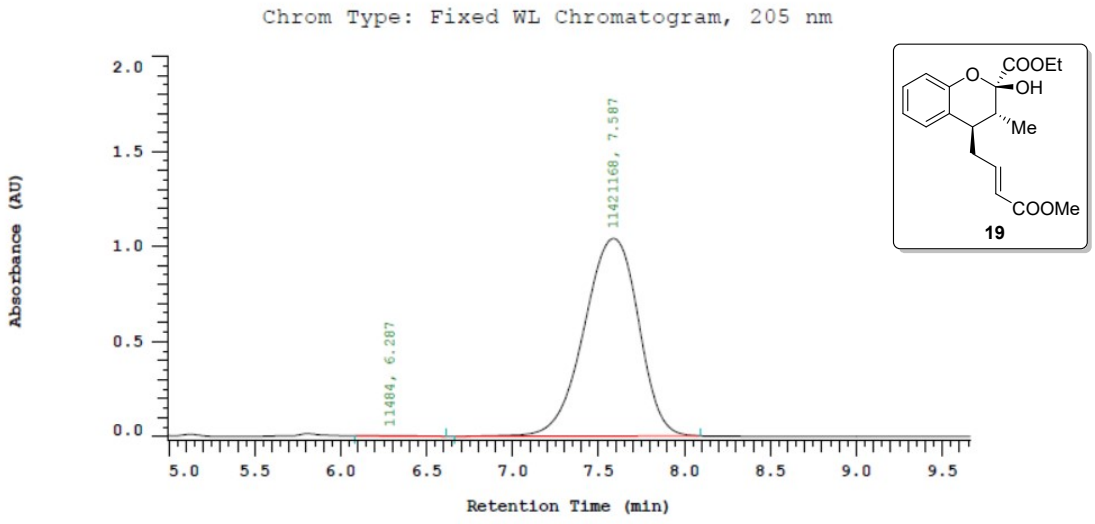
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.313	7452892	49.890	BV
2	7.627	7485835	50.110	VB
		14938727	100.000	

The HPLC of chiral 19



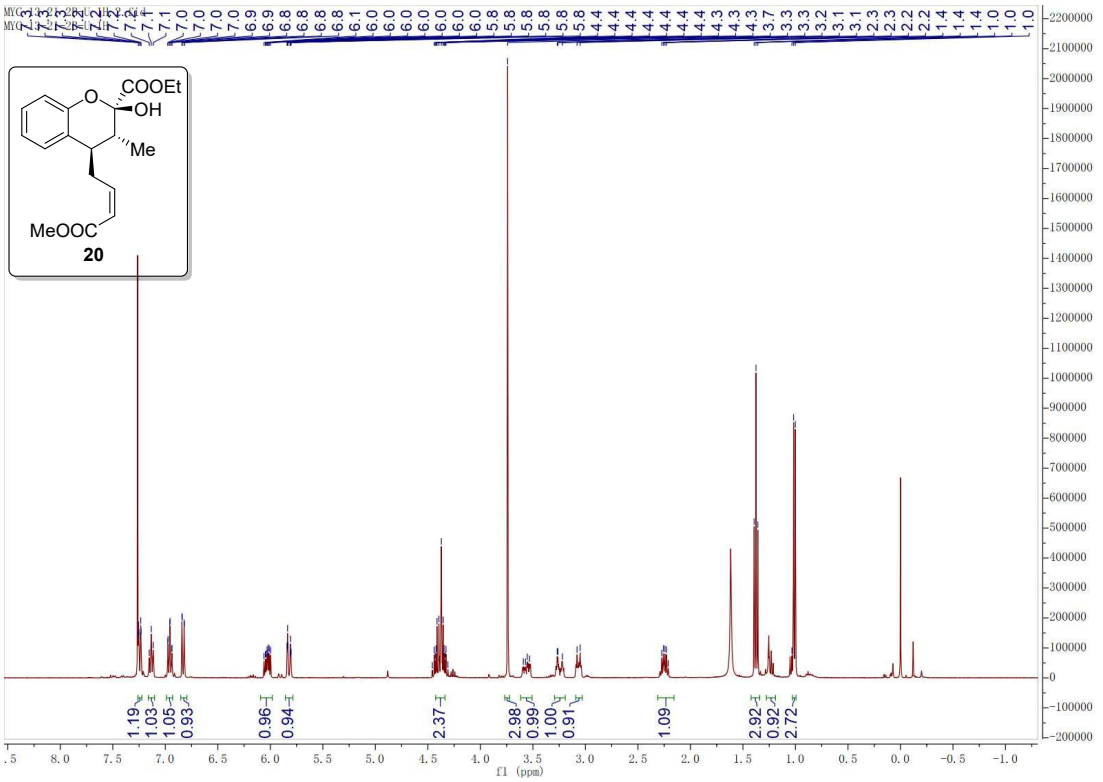
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

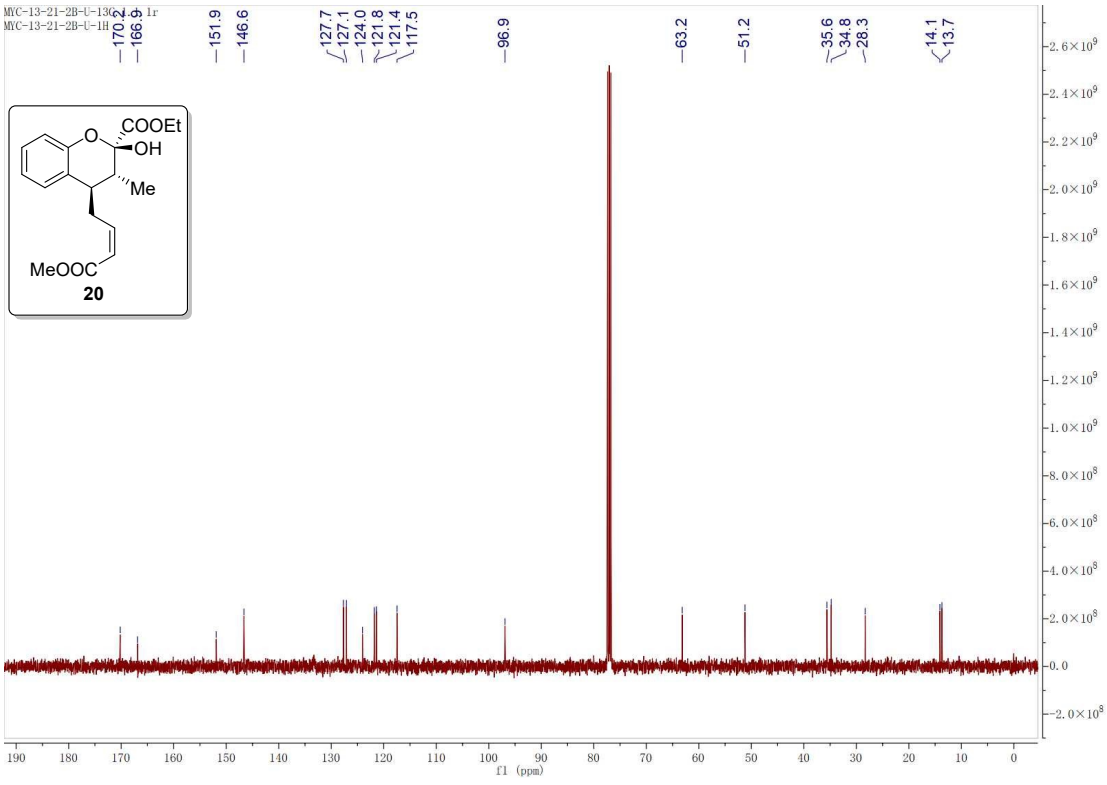
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.287	11484	0.100	BB
2	7.587	11421168	99.900	BB
		11432652	100.000	

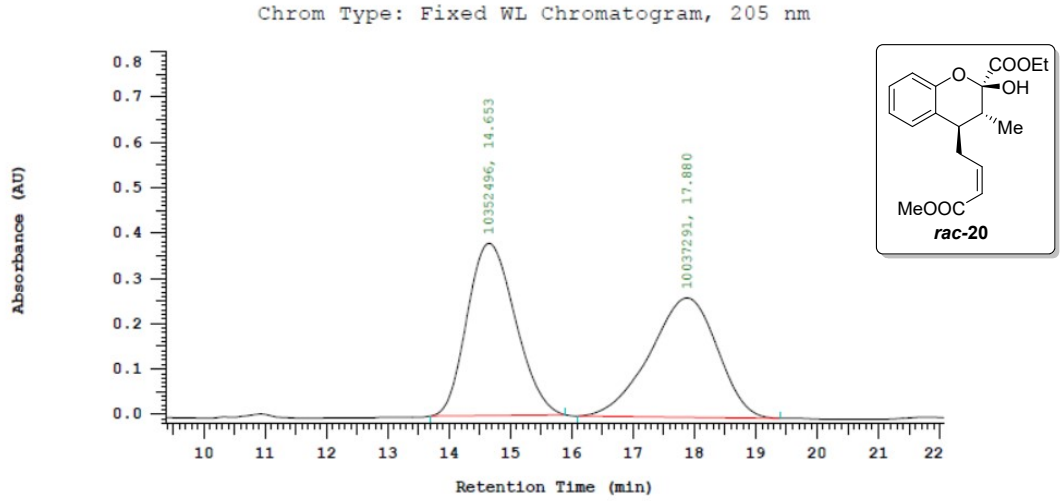
The ^{1}H NMR spectrum of 20 (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 20(100 MHz, $CDCl_3$)



The HPLC of racemic 20



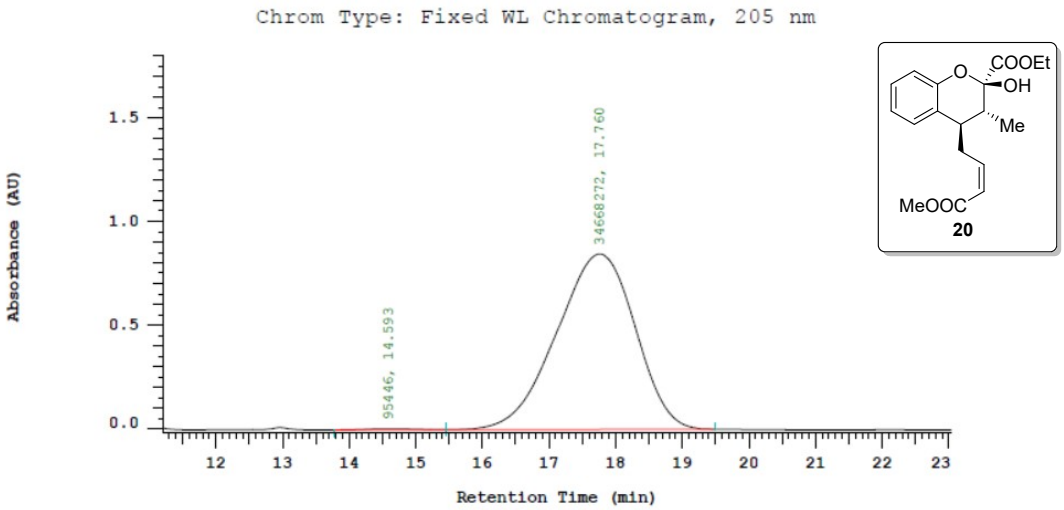
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	14.653	10352496	50.773	BB
2	17.880	10037291	49.227	BB
		20389787	100.000	

The HPLC of chiral 20



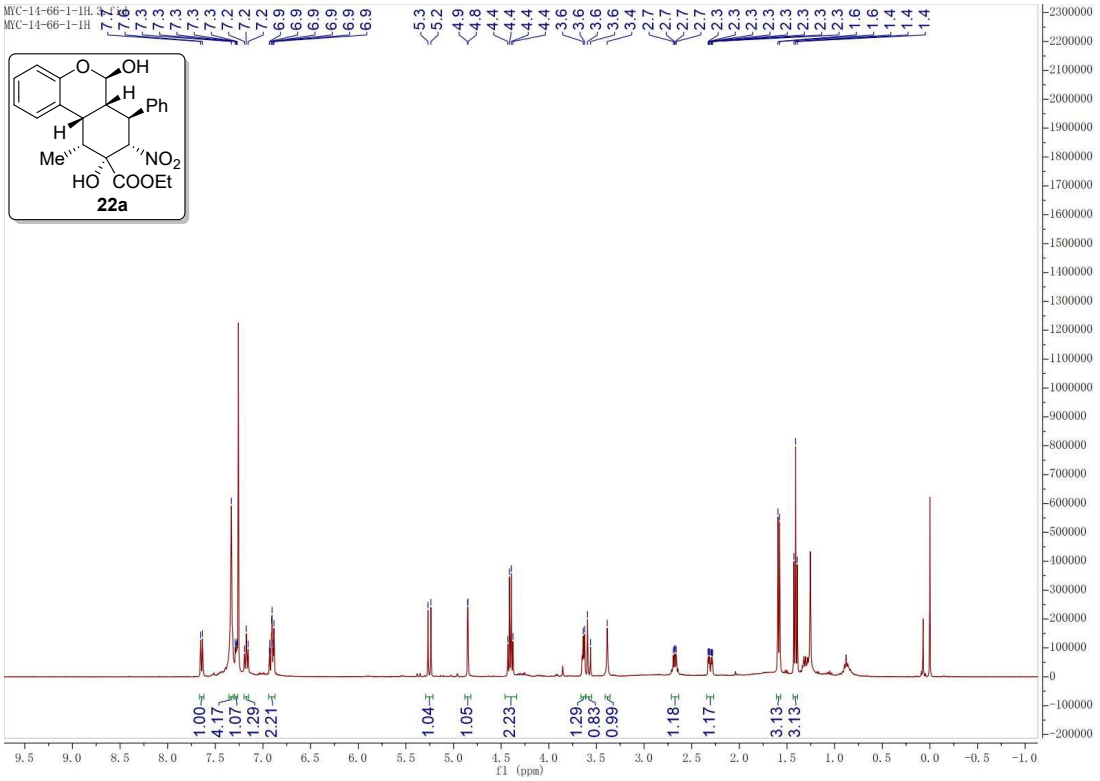
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

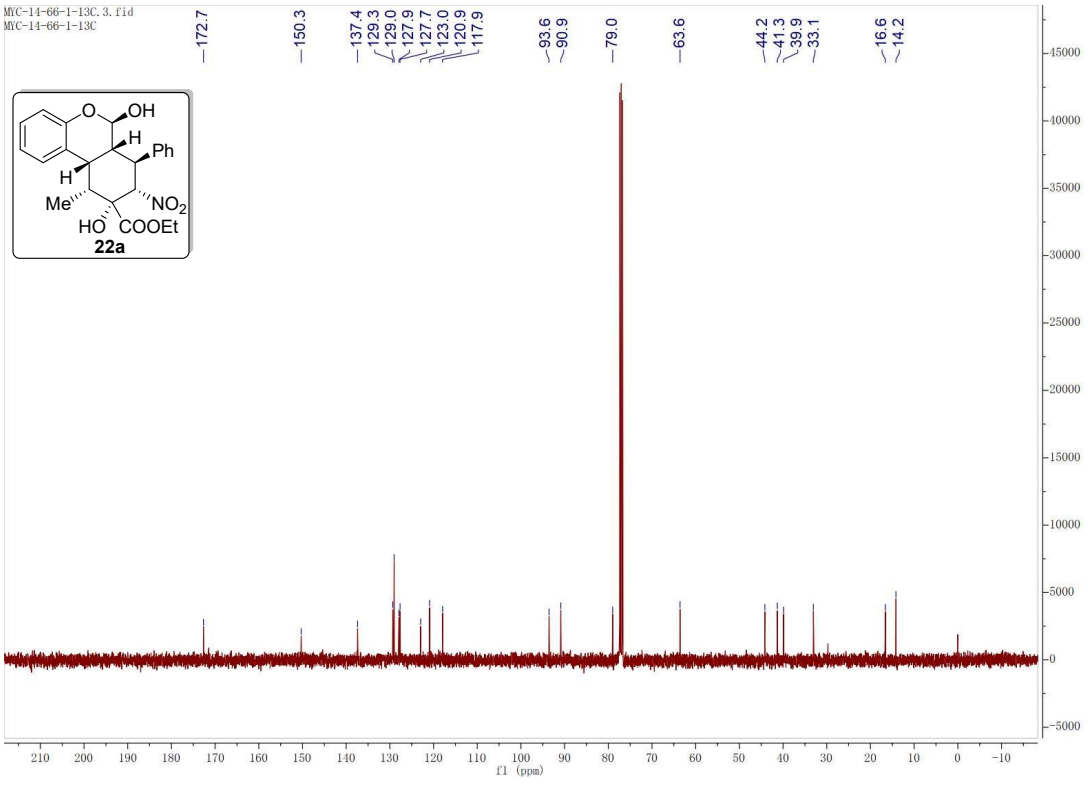
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	14.593	95446	0.275	BV
2	17.760	34668272	99.725	VB
		34763718	100.000	

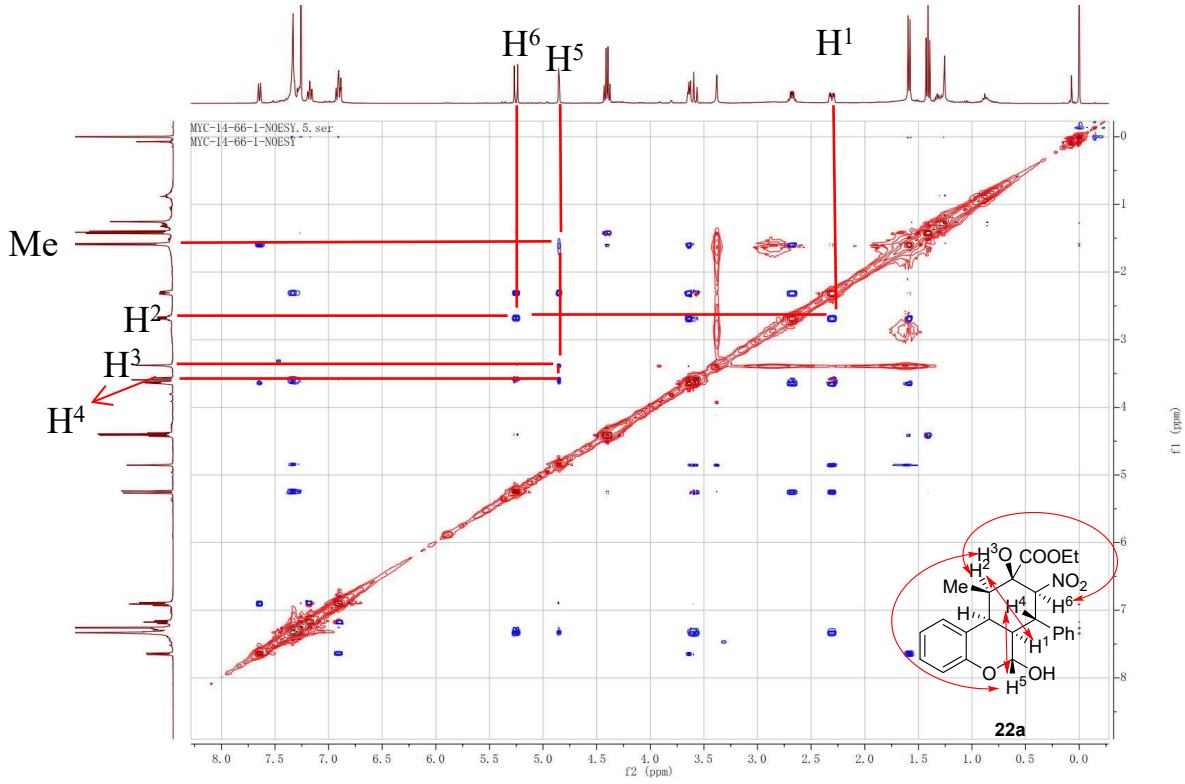
The ^{1}H NMR spectrum of 22a (400 MHz, $CDCl_3$)



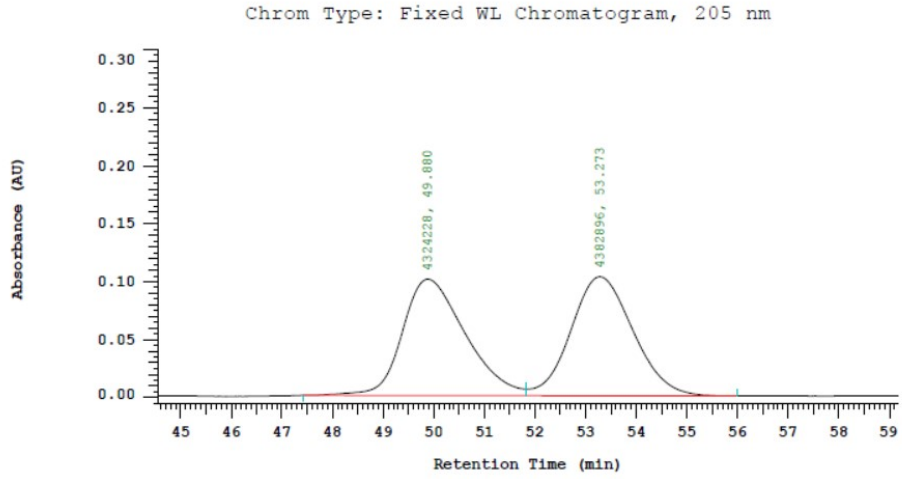
The ^{13}C NMR spectrum of 22a(100 MHz, $CDCl_3$)



The NOSEY spectrum of 22a (400 MHz, $CDCl_3$)



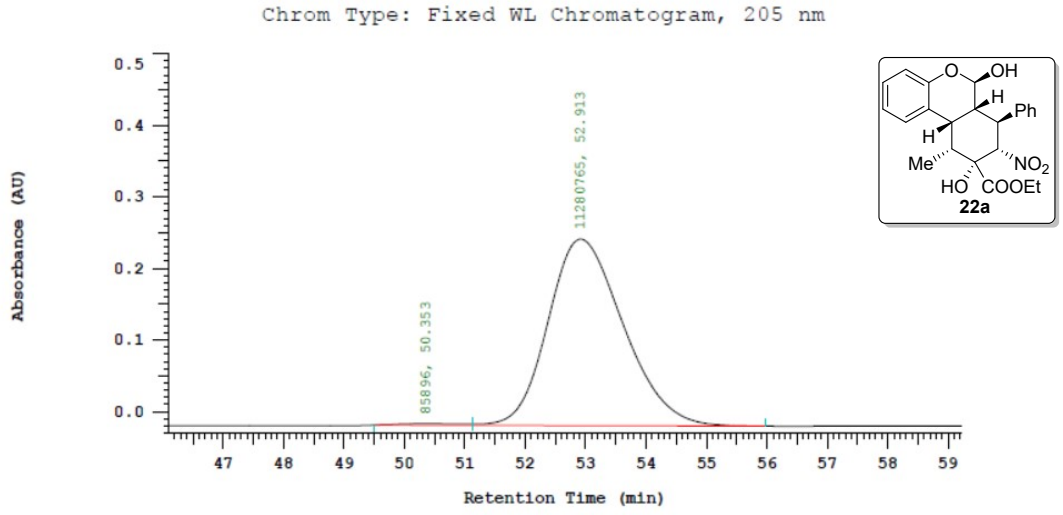
The HPLC of racemic 22a



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	49.880	4324228	49.663	BV
2	53.273	4382896	50.337	VB
		8707124	100.000	

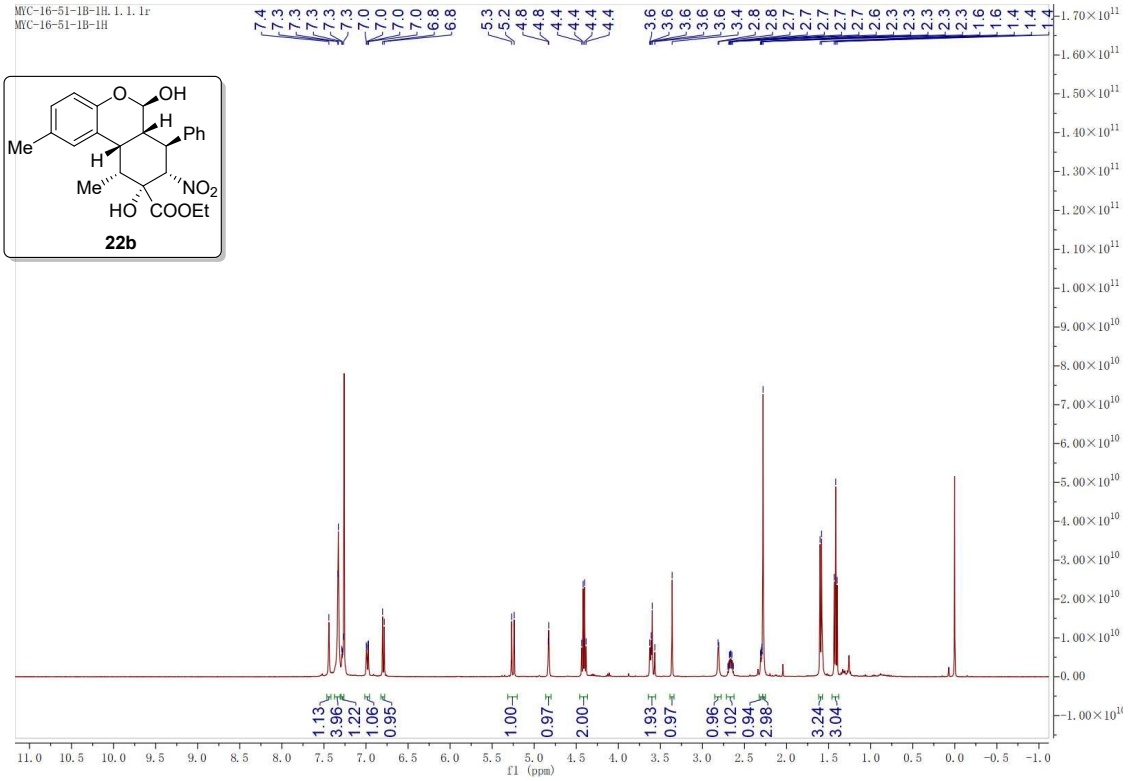
The HPLC of chiral 22a



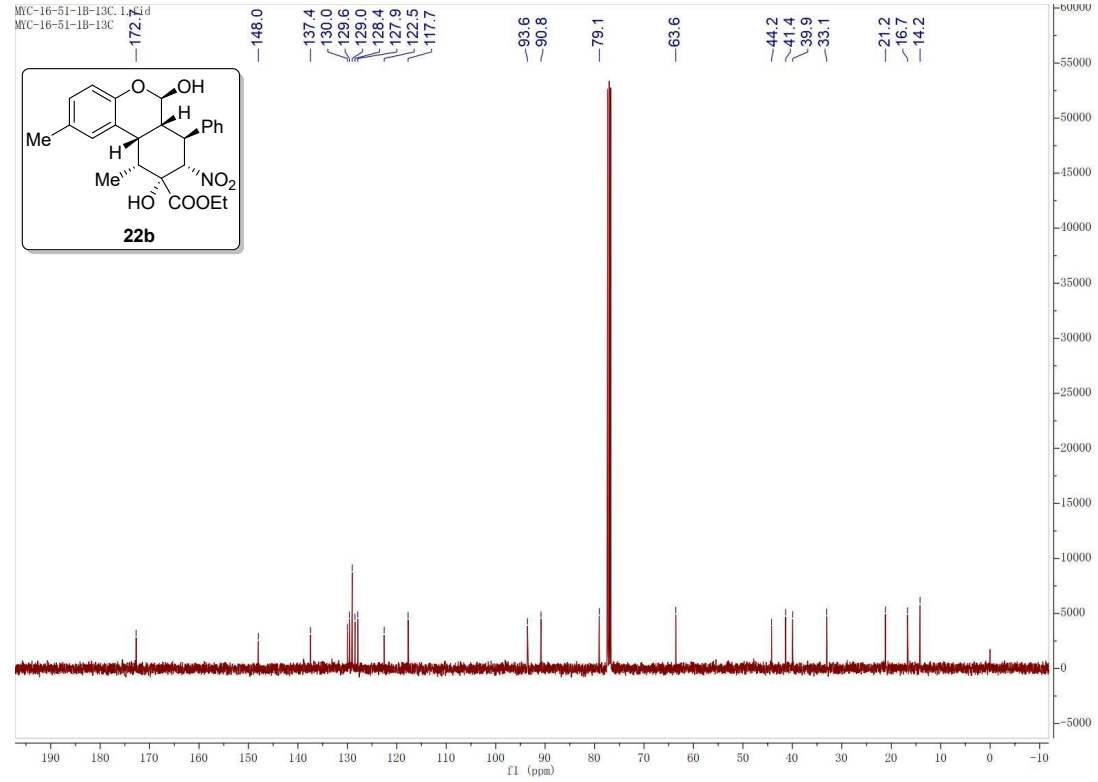
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	50.353	85896	0.756	BV
2	52.913	11280765	99.244	VB
		11366661	100.000	

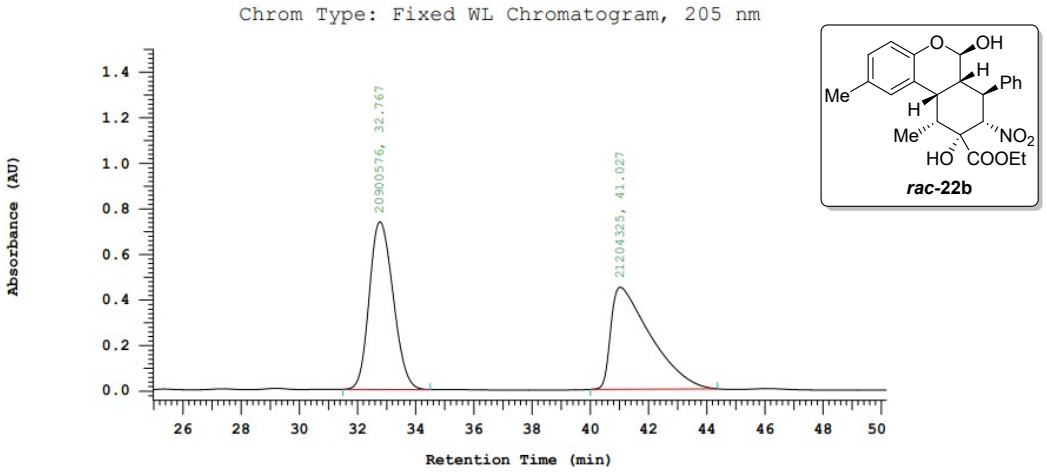
The ^{1}H NMR spectrum of 22b (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 22b (100 MHz, $CDCl_3$)



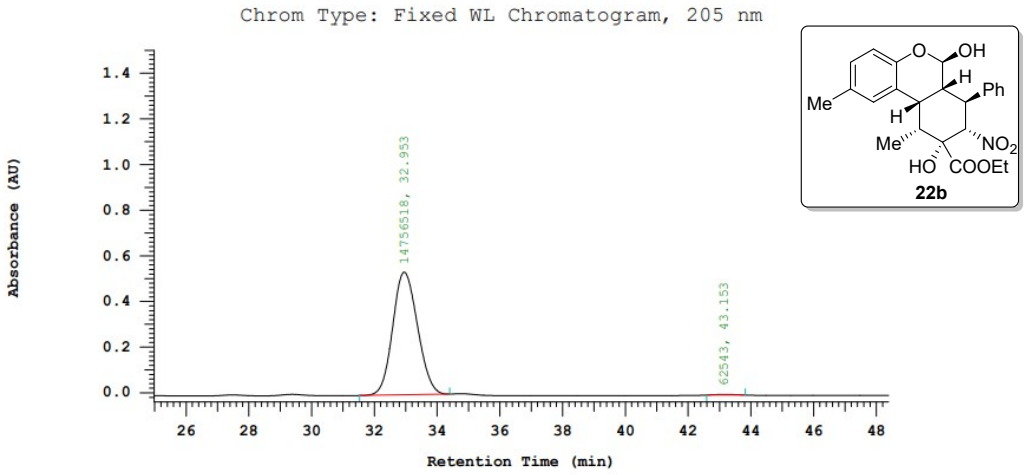
The HPLC of racemic 22b



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	32.767	20900576	49.639	BB
2	41.027	21204325	50.361	BB
		42104901	100.000	

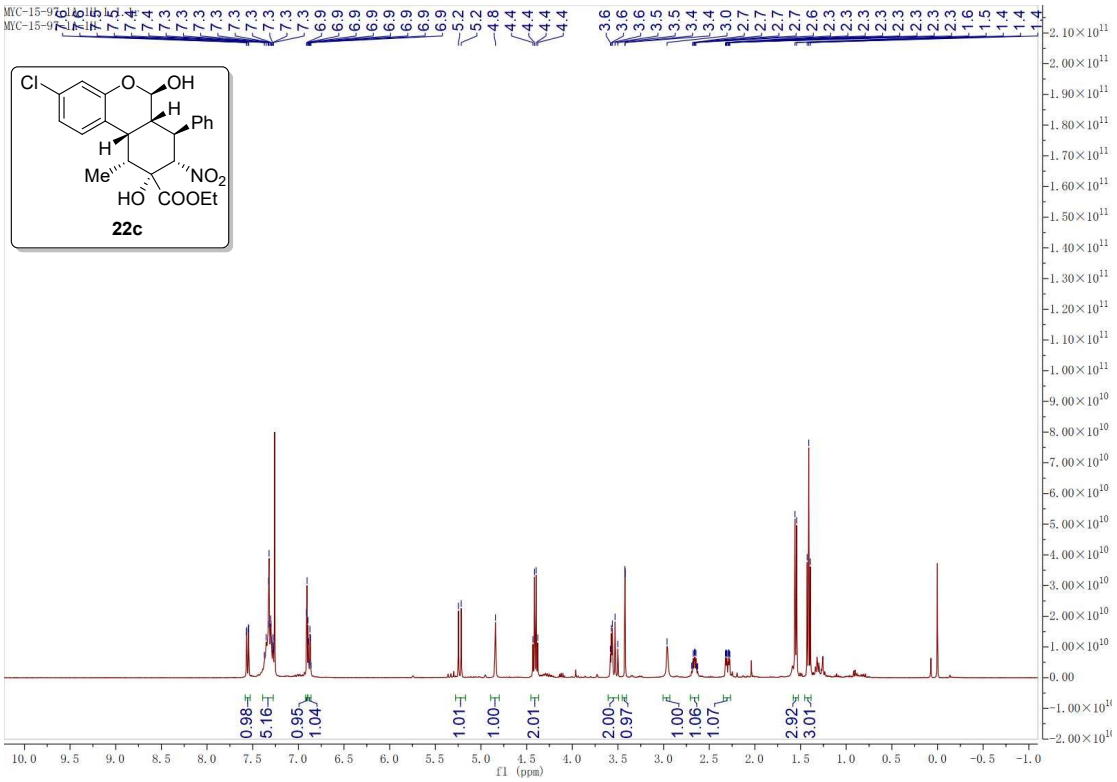
The HPLC of chiral 22b



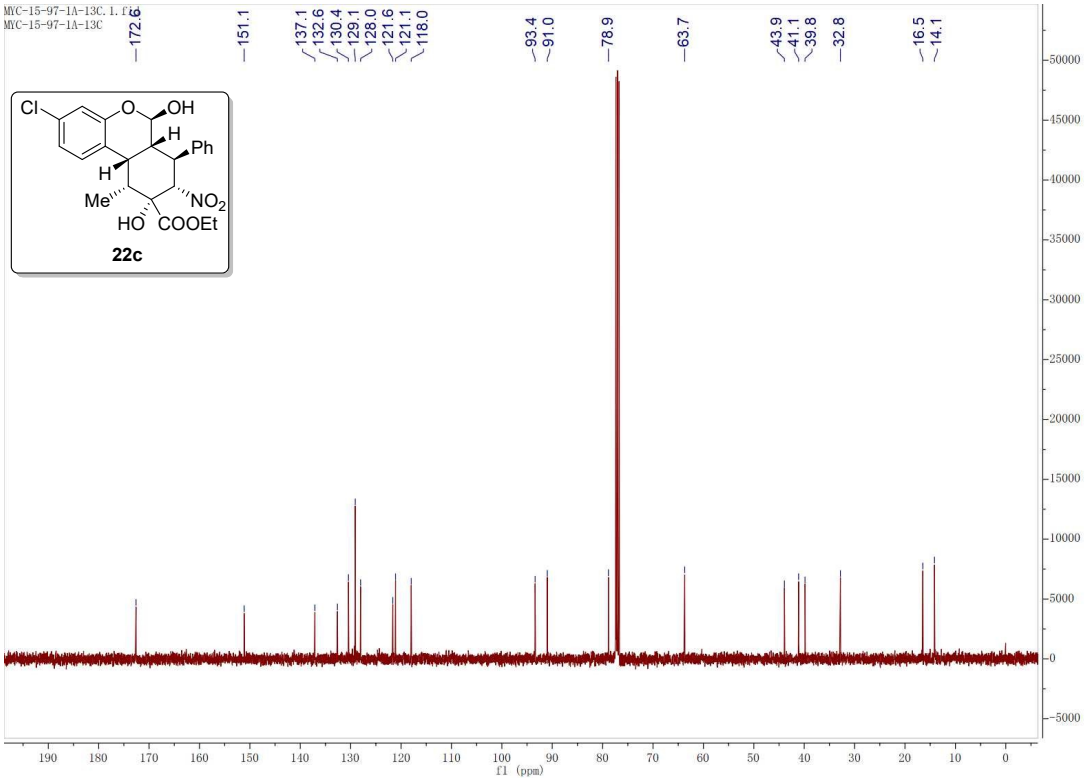
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	32.953	14756518	99.578	BB
2	43.153	62543	0.422	BB
		14819061	100.000	

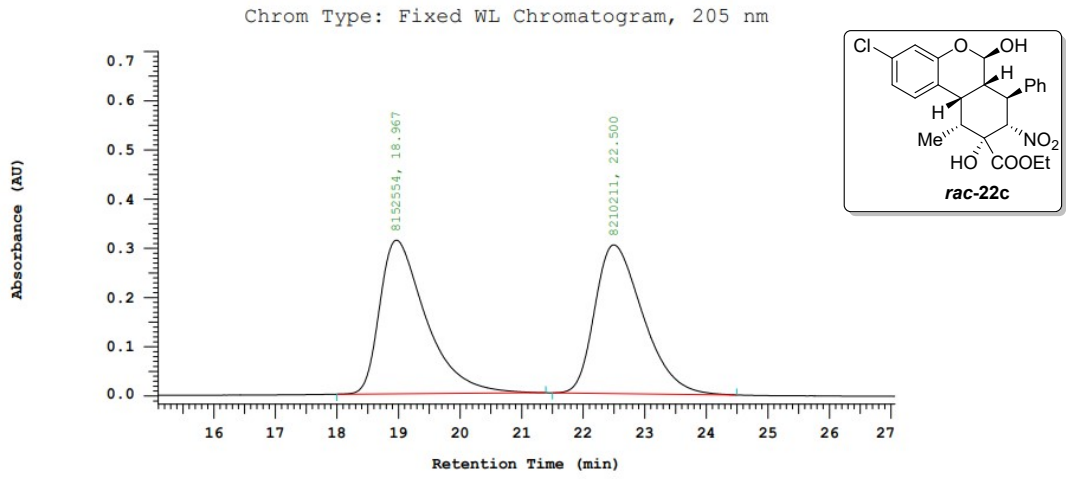
The ^{1}H NMR spectrum of 22c (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 22c (100 MHz, $CDCl_3$)



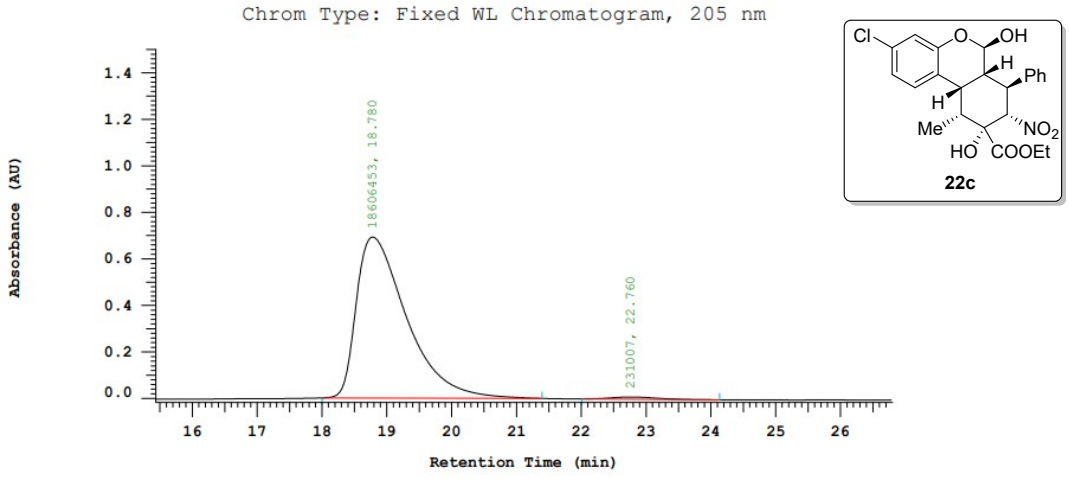
The HPLC of racemic 22c



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.967	8152554	49.824	BB
2	22.500	8210211	50.176	BB
		16362765	100.000	

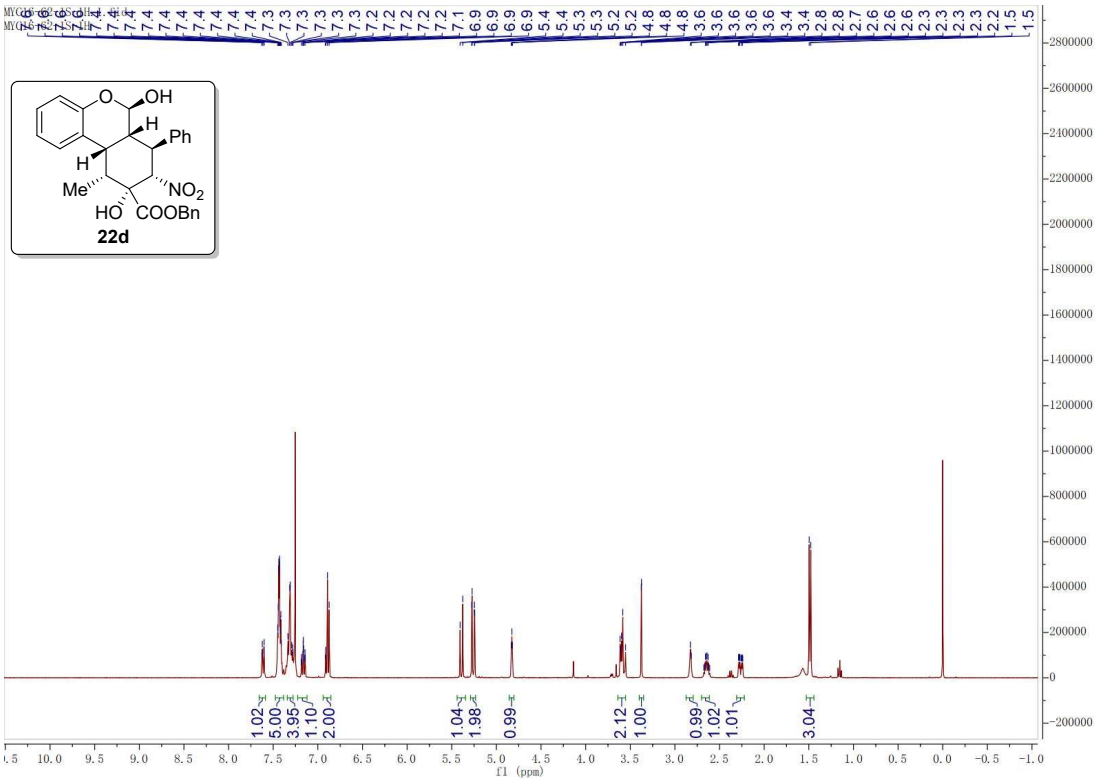
The HPLC of chiral 22c



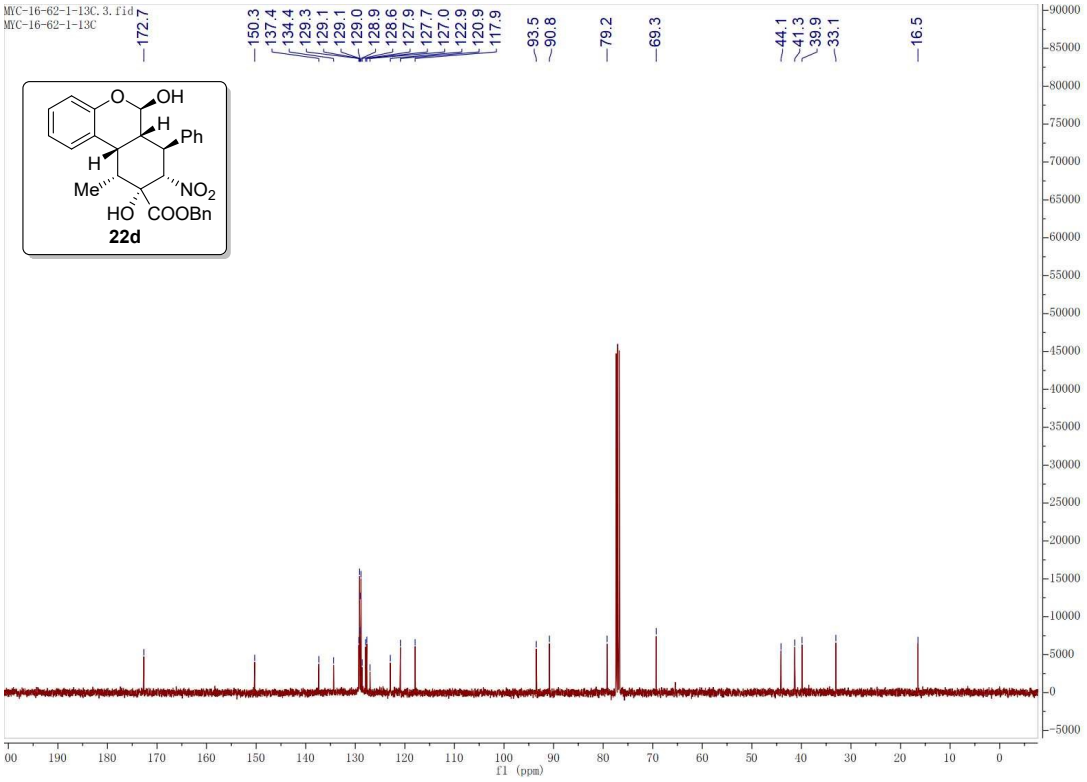
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.780	18606453	98.774	BB
2	22.760	231007	1.226	BB
		18837460	100.000	

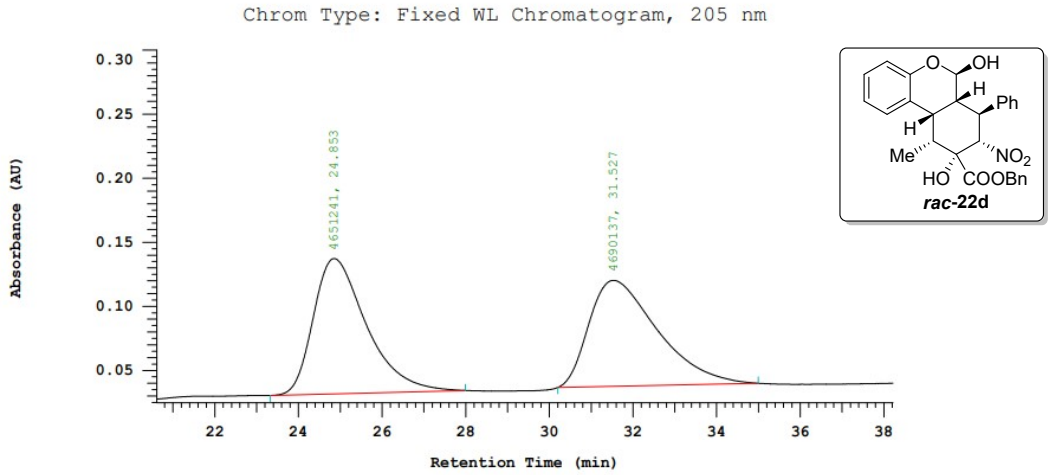
The ^{1}H NMR spectrum of 22d (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 22d (100 MHz, $CDCl_3$)



The HPLC of racemic 22d



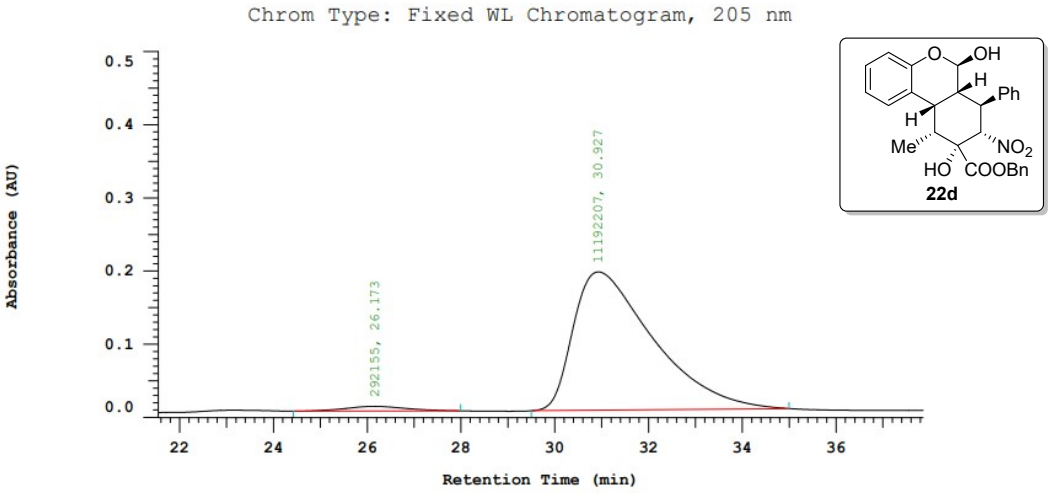
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	24.853	4651241	49.792	BB
2	31.527	4690137	50.208	BB
		9341378	100.000	

The HPLC of chiral 22d



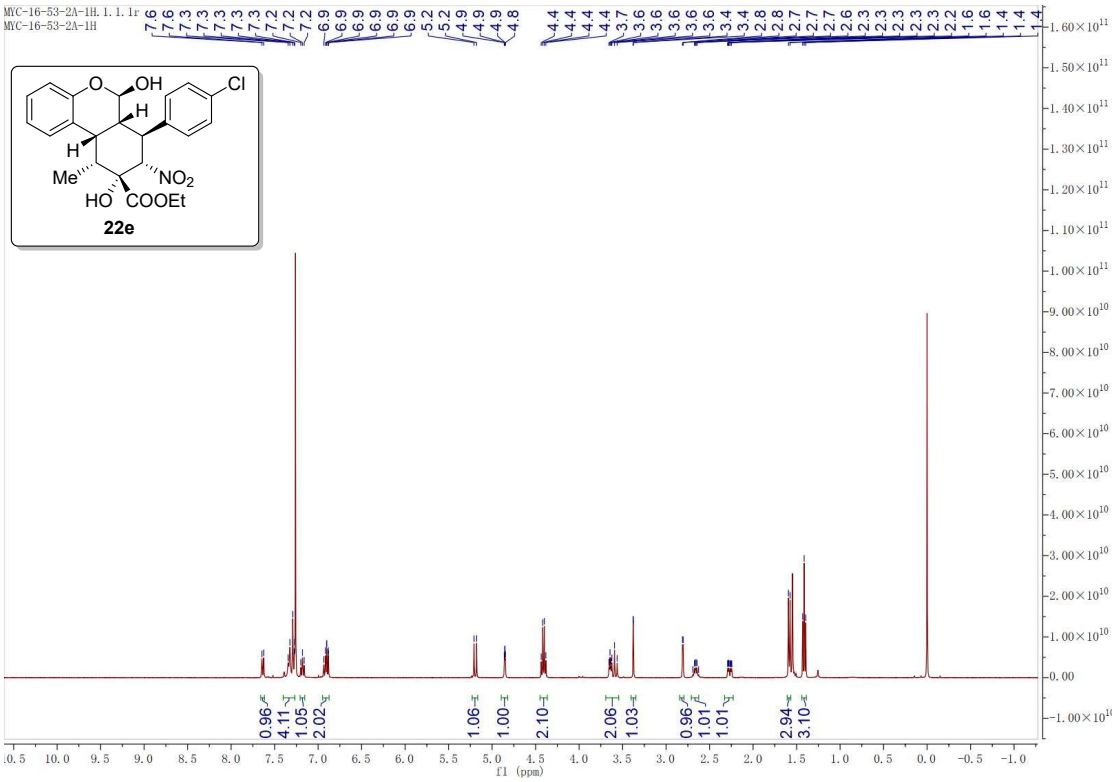
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

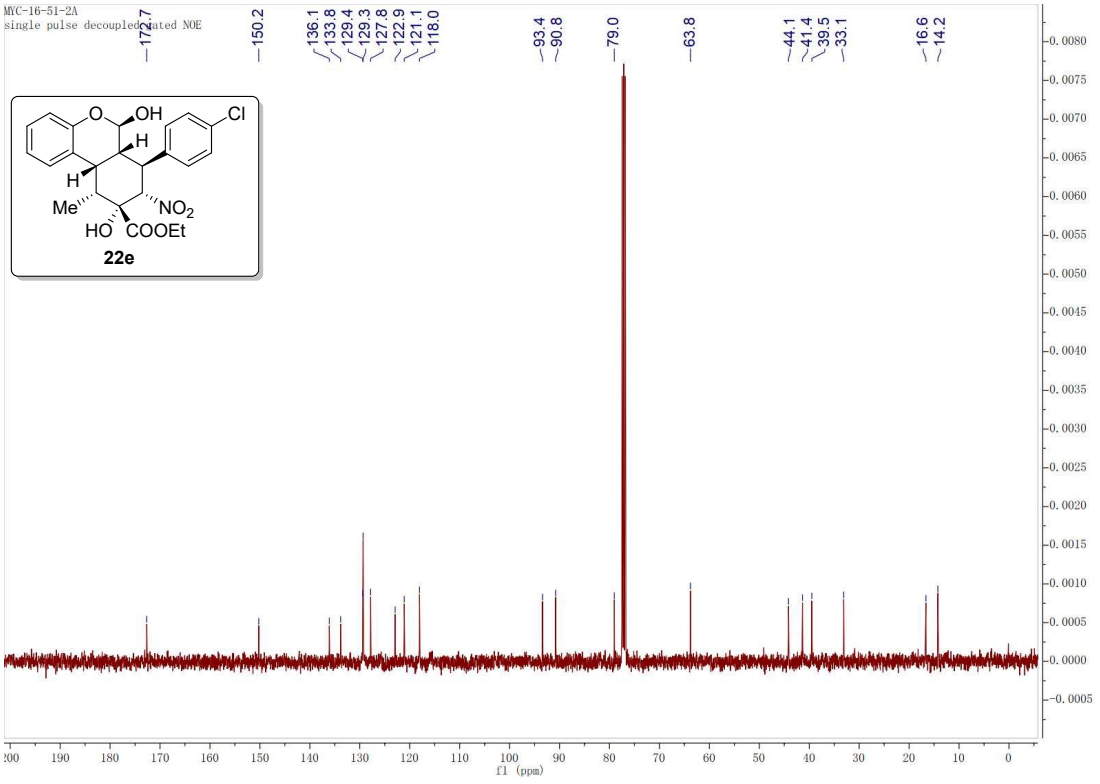
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	26.173	292155	2.544	BB
2	30.927	11192207	97.456	BB
		11484362	100.000	

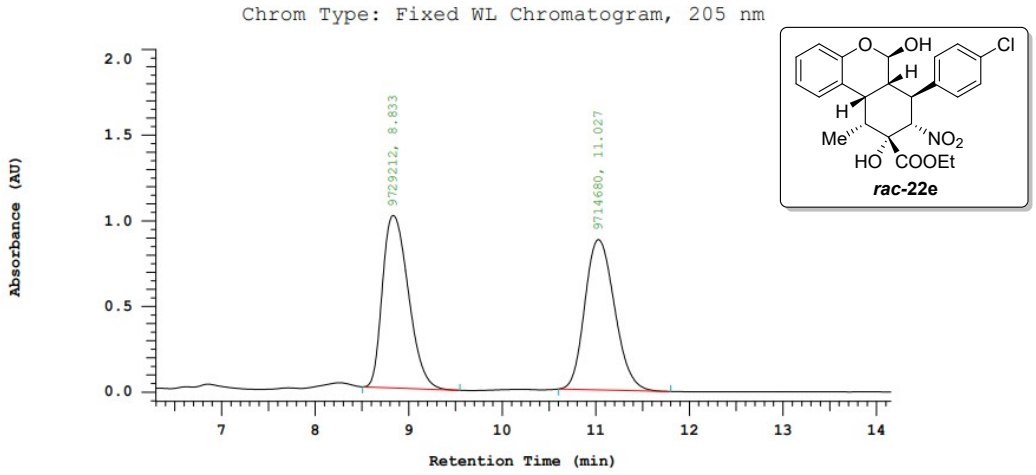
The ^{1}H NMR spectrum of 22e (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 22e (100 MHz, $CDCl_3$)



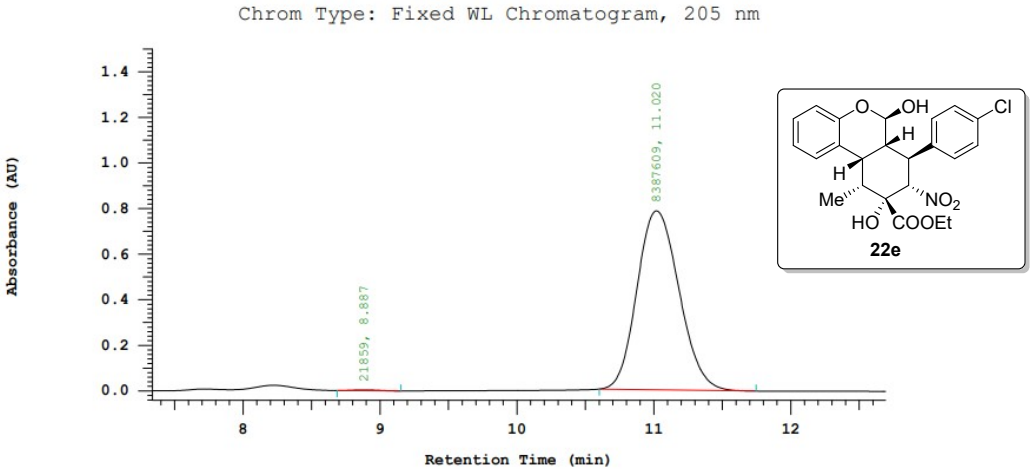
The HPLC of racemic 22e



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.833	9729212	50.037	BB
2	11.027	9714680	49.963	BB
		19443892	100.000	

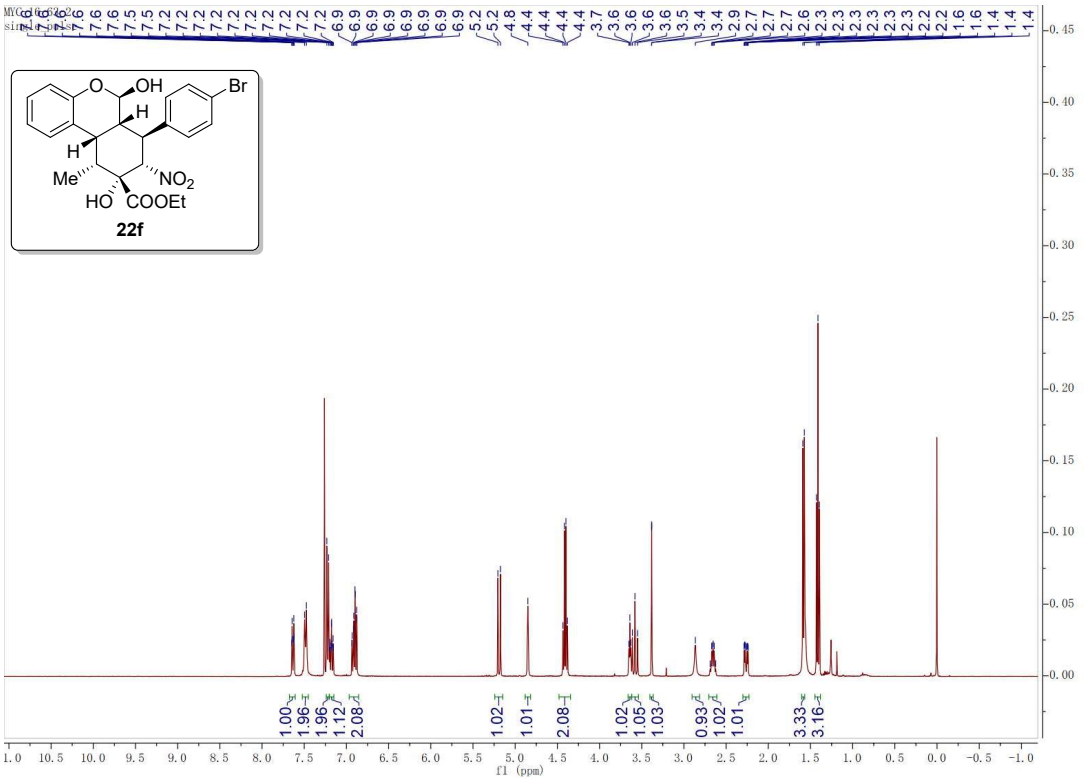
The HPLC of chiral 22e



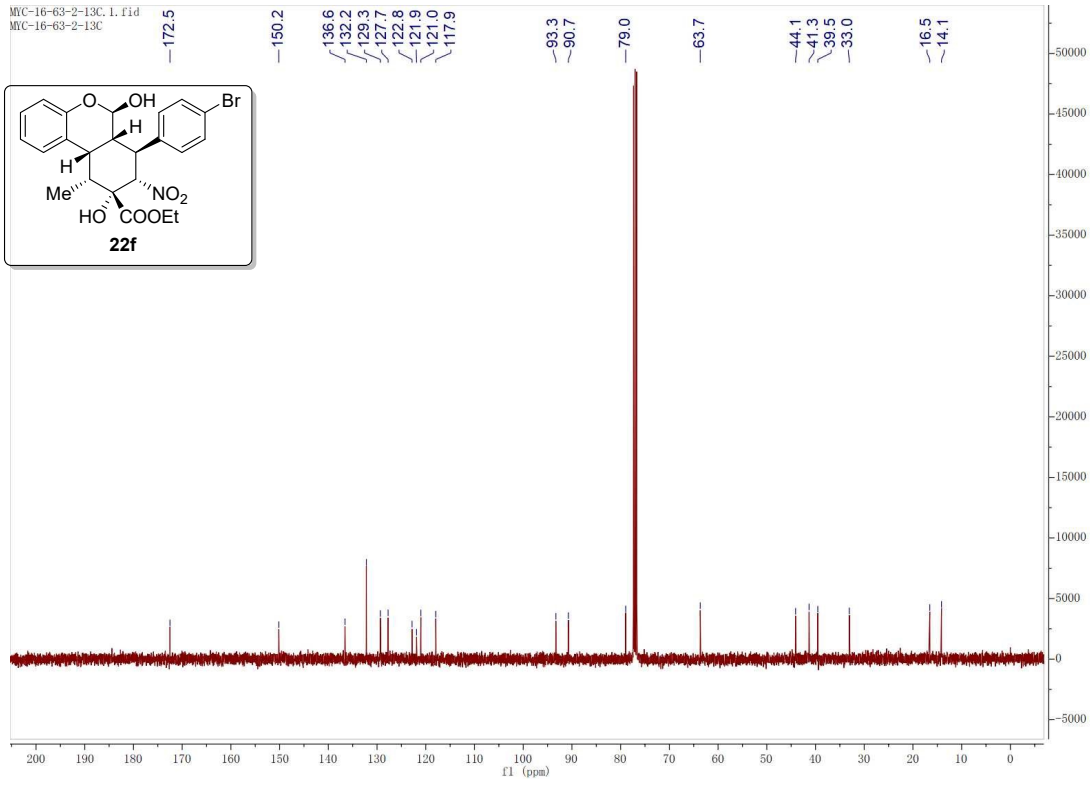
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.887	21859	0.260	BB
2	11.020	8387609	99.740	BB
		8409468	100.000	

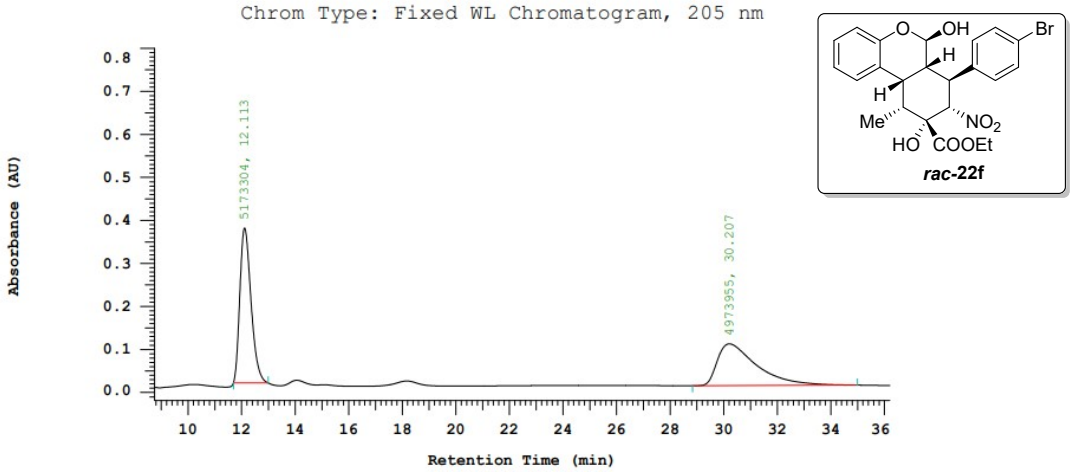
The ^{1}H NMR spectrum of 22f (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 22f (100 MHz, $CDCl_3$)



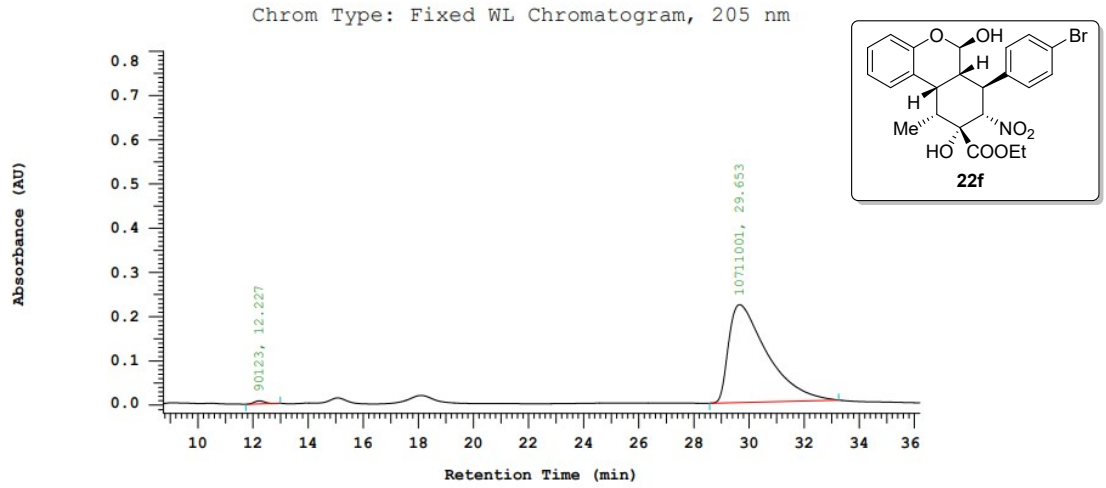
The HPLC of racemic 22f



Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.113	5173304	50.982	BB
2	30.207	4973955	49.018	BB
		10147259	100.000	

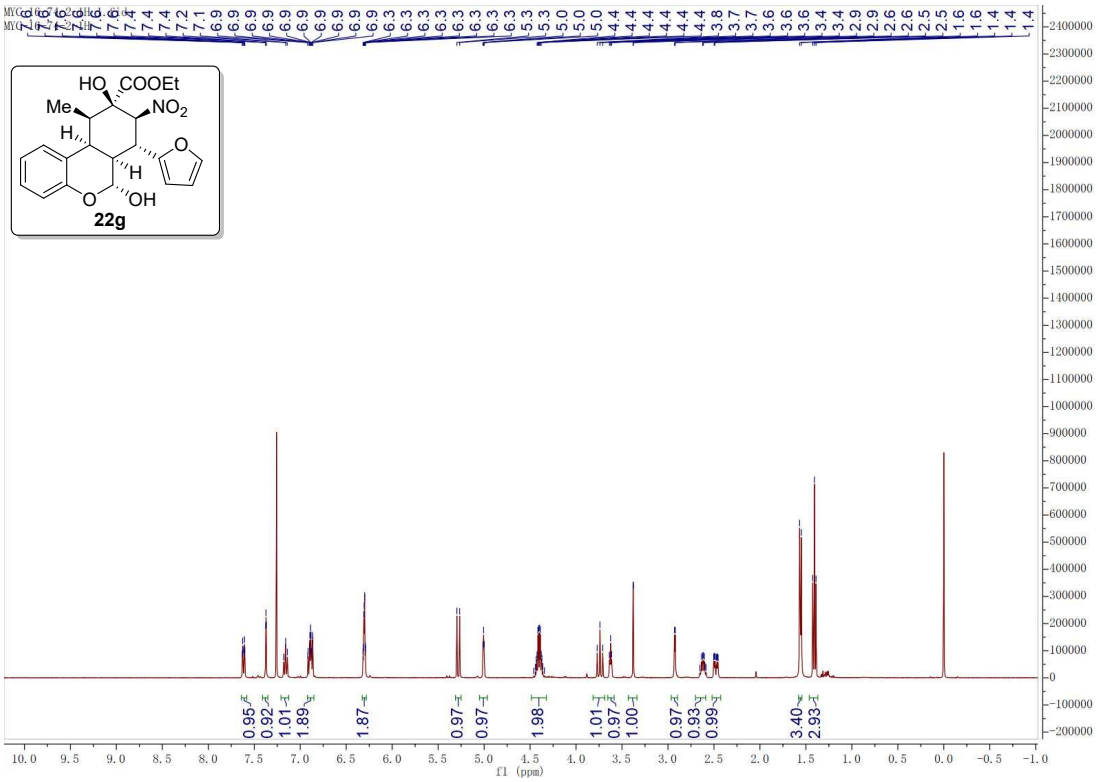
The HPLC of chiral 22f



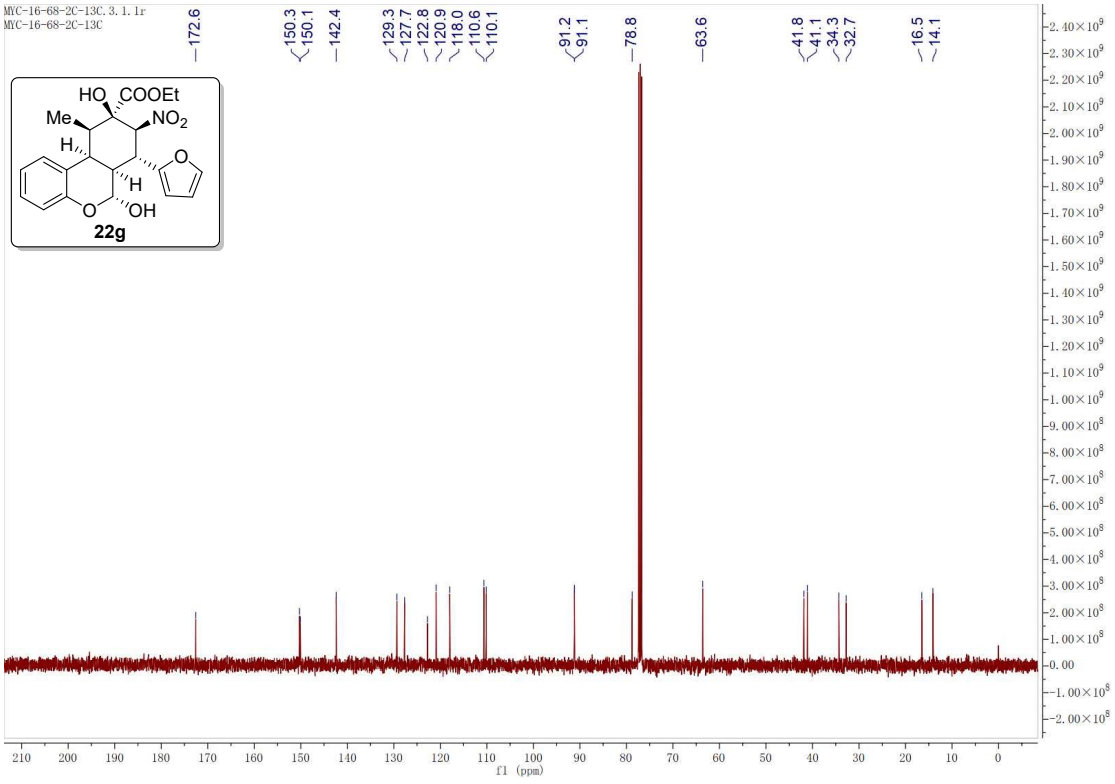
Chrom Type: Fixed WL Chromatogram, 205 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.227	90123	0.834	BB
2	29.653	10711001	99.166	BB
		10801124	100.000	

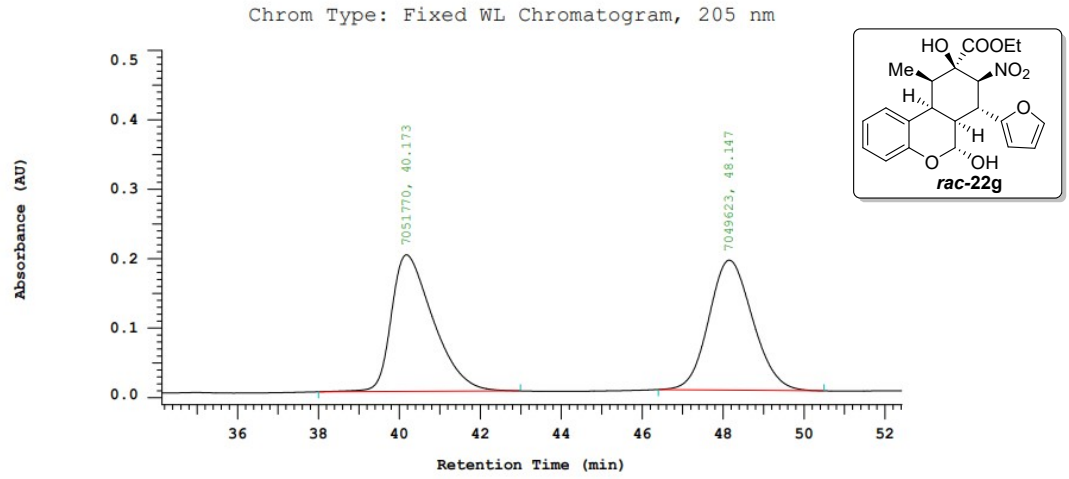
The ^{1}H NMR spectrum of 22g (400 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 22g (100 MHz, $CDCl_3$)



The HPLC of racemic 22g



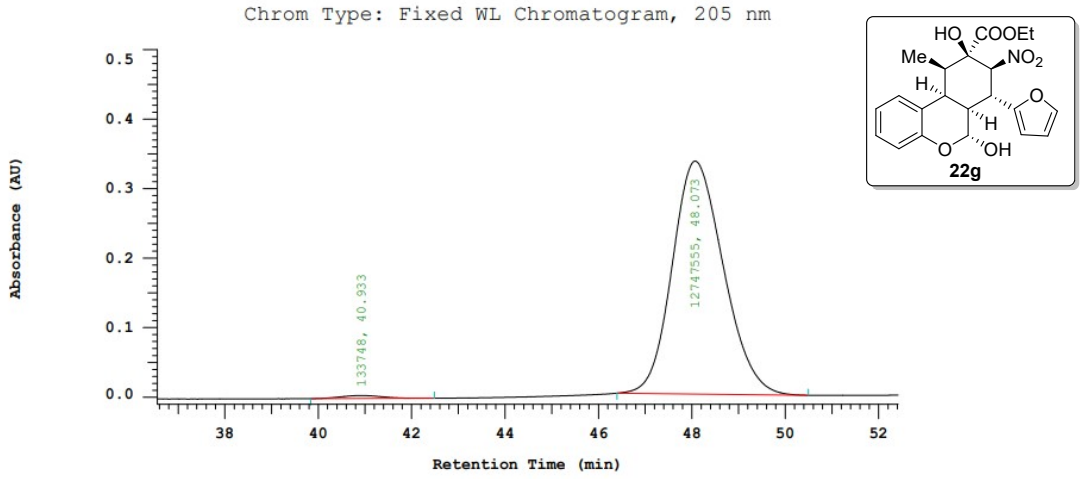
Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	40.173	7051770	50.008	BB
2	48.147	7049623	49.992	BB
		14101393	100.000	

The HPLC of chiral 22g



Chrom Type: Fixed WL Chromatogram, 205 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	40.933	133748	1.038	BB
2	48.073	12747555	98.962	BB
		12881303	100.000	

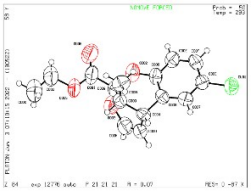
J. Single crystal X-Ray diffraction data

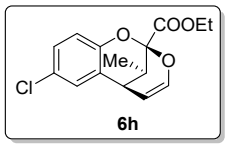
Single crystal preparation: 6h was dissolved in CH_2Cl_2 (0.1 mL), diluted with MeOH (1 mL), sealed, cultured in standing, and the solvent was volatilized at room temperature. After a week, single crystals were formed.

The instrumentation used: Gemini E/Eos of Rigaku.

[CCDC 2210634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.].

Absolute configuration of **6h** - CCDC 2210634





```
Bond precision:   C-C = 0.0138 A          Wavelength=1.54184

Cell:              a=6.0599(8)      b=13.909(2)      c=17.1498(18)
                   alpha=90         beta=90          gamma=90
Temperature:       293 K

                  Calculated                Reported
Volume            1445.5(3)                 1445.5(3)
Space group       P 21 21 21                P 21 21 21
Hall group        P 2ac 2ab                 P 2ac 2ab
Moiety formula    C15 H15 Cl O4             C15 H15 Cl O4
Sum formula       C15 H15 Cl O4             C15 H15 Cl O4
Mr                294.72                    294.72
Dx,g cm-3         1.354                     1.354
Z                 4                         4
Mu (mm-1)         2.439                     2.439
F000              616.0                     616.0
F000'             619.28
h,k,lmax          7,17,21                   7,16,20
Nref              2788[ 1635]               2226
Tmin,Tmax         0.677,0.784               0.680,1.000
Tmin'             0.585

Correction method= # Reported T Limits: Tmin=0.680 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.36/0.80        Theta(max)= 70.940

R(reflections)= 0.0656( 1138)                wR2(reflections)=
                                             0.2282( 2226)
S = 1.137                  Npar= 184
```

K. Proposed reaction mechanism