Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Organocatalytic Asymmetric Synthesis of both *cis*- and *trans*-Configured Pyrano[2,3-*b*]chromenes via Different Dehydration Pathway

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Supporting Information

Contents

A. General information

The ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz for ^{1}H and at 125 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). 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: $CHCl_3$).

Note: NMR signals containing common solvent contaminants were list. H_2O in $CDCl_3$ at 1.56 ppm ^{1}H NMR, Ethyl acetate in $CDCl_3$ at 2.05 (s), 4.12 (q), 1.26 (t) ppm ^{1}H NMR; Dichloromethane in $CDCl_3$ at 5.30 (s) ppm ^{1}H NMR; Acetone in $CDCl_3$ at 2.17 (s) ppm ^{1}H NMR.

All the reactions were set up under air and using freshly distilled 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 an 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.

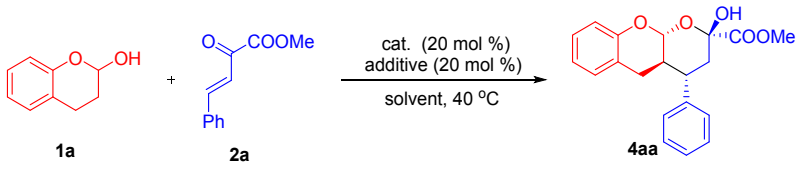
HPLC analyses on chiral stationary phase were performed on a Hitachi Chromaste. Daicel Chiralpak IA, IC or IB columns with *n*-hexane/*i*-PrOH as the eluent were used. HPLC traces were compared to racemic samples which prepared by mixture of two enantiomeric final products obtained using (*S*) and (*R*)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

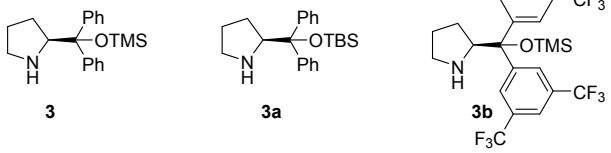
Commercial reagents and solvents were purchased from Sigma Aldrich, Fluka, and Alfa Aesar used as received, without further purification. All the lactols[1], β,γ-unsaturated α-ketoesters[2] were synthesized according to literature procedures.

[1] R. Miyaji, K. Asano, S. Matsubara, *Org. Biomol. Chem.* **2014**, 12, 119-122.

[2] Y.-Z. Hua, M.-M. Liu, P.-J. Huang, X.-X. Song, M.-C. Wang, J.-B. Chang. *Chem. Eur. J.* **2015**, 21, 11994.

B. Optimization of the [3+3] reaction pathway

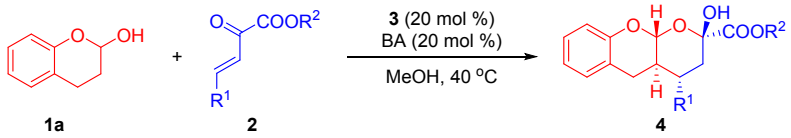




Entry[a]	cat.	solvent	additive	time (h)	yield (%)[b]	*ee* (%)[c]	dr[d]
1	**3**	MeOH	PhCOOH	6	77/67[e]	>99	>20:1
2	**3a**	MeOH	PhCOOH	7	79	>99	>20:1
3	**3b**	MeOH	PhCOOH	10	76	>99	>20:1
4	**3**	CH_2Cl_2	PhCOOH	29	62	>99	>20:1
5	**3**	$CHCl_3$	PhCOOH	36	60	>99	>20:1
6	**3**	DMF	PhCOOH	24	60	>99	>20:1
7	**3**	THF	PhCOOH	20	62	>99	>20:1
8	**3**	CH_3CN	PhCOOH	12	76	>99	>20:1
9	**3**	toluene	PhCOOH	36	81	>99	>20:1
10	**3**	MeOH	2-FPhCOOH	10	60	>99	>20:1
11	**3**	MeOH	4-NO_2PhCOOH	10	59	>99	>20:1
12	**3**	MeOH	$(CH_3)_3CCOOH$	14	53	>99	>20:1

[*a*] Unless otherwise specified, all reactions were carried out using **1a** (0.1 mmol, 1.0 equiv) and unsaturated ketoester **2a** (0.12 mmol, 1.2 equiv) in solvent (0.2 mL) with cat. **3** (20 mol %) and additive (20 mol %) at 40 °C. After workup, the mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 12:1) to get product **4aa**. [*b*] Isolated yield of **4aa** for one step. [*c*] Determined by HPLC analyses of isolated compound **4aa** on chiral stationary phases. [*d*] Determined by ^{1}H NMR. [*e*] Isolated yield of **4aa** was given based on filtration. DMF = *N*,*N*-dimethylformamide; THF = tetrahydrofuran.

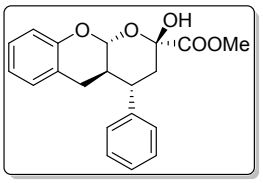
C. Procedures for [3+3] reaction and characterization of products



1a 2 4

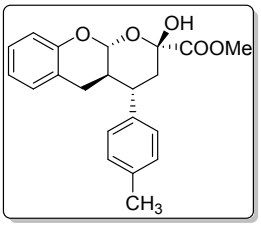
General procedure: A glass vial equipped with a magnetic stirring bar was charged with lactol **1a** (0.10 mmol, 1.0 equiv), and unsaturated ketoester **2** (0.12 mmol, 1.2 equiv) in MeOH (0.2 mL) with **3** (20 mol %) and BA (PhCOOH) (20 mol %) at 40 °C until the material **1a** disappeared. After completion of the reaction, the reaction mixture was purified by filtration to afford **4** for NMR and HPLC analysis after washed twice with methanol.

Methyl(2*S*,4*S*,4a*R*,10a*R*)-2-hydroxy-4-phenyl-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4aa)



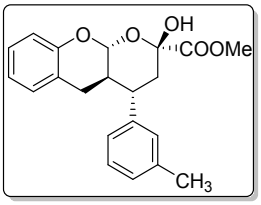
White solid, **67%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) 7.37 (t, *J* = 7.4 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.84 (dd, *J* = 10.7, 4.1 Hz, 1H), 5.52 (d, *J* = 8.9 Hz, 1H), 4.27 (d, *J* = 1.9 Hz, 1H), 3.89 (s, 3H), 3.09 (td, *J* = 12.7, 3.7 Hz, 1H), 2.59 – 2.44 (m, 3H), 2.18 (tdd, *J* = 11.5, 8.9, 5.7 Hz, 1H), 2.02 (dd, *J* = 13.4, 3.8 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) 170.0, 152.9, 141.0, 129.3, 129.1, 127.8, 127.8, 127.5, 121.5, 121.4, 117.1, 98.2, 96.1, 53.9, 41.5, 40.7, 38.7, 28.6 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{20}NaO_5^+$ m/z: 363.1203; found: 363.1200. **$[\alpha]_D^{20}$** +39.8 (*c* = 2.68 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 210 nm, t_{major} = 14.67 min, t_{minor} = 8.49 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(2*S*,4*S*,4a*R*,10a*R*)-2-hydroxy-4-(*p*-tolyl)-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4ab)



White solid, **72%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (s, 4H), 7.10 (t, J = 7.5 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.84 (t, J = 7.3 Hz, 1H), 5.51 (d, J = 8.9 Hz, 1H), 4.25 (d, J = 1.7 Hz, 1H), 3.88 (s, 3H), 3.05 (td, J = 12.7, 3.7 Hz, 1H), 2.54 – 2.41 (m, 3H), 2.36 (s, 3H), 2.21 – 2.11 (m, 1H), 1.99 (dd, J = 13.4, 3.7 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.8, 152.7, 137.7, 136.9, 129.5, 129.1, 127.6, 127.4, 121.3, 121.2, 116.9, 98.1, 95.9, 53.6, 40.8, 40.6, 38.6, 28.4, 21.1 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{21}H_{22}NaO_5^+$ m/z: 377.1359; found: 377.1352. **$[\alpha]_D^{20}$** +45.0 (c = 1.34 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 210 nm, t_{major} = 14.52 min, t_{minor} = 8.06 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

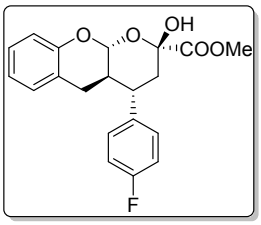
Methyl(2*S*,4*S*,4a*R*,10a*R*)-2-hydroxy-4-(*m*-tolyl)-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4ac)



White solid, **59%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (dd, J = 9.1, 5.6 Hz, 1H), 7.09 (dd, J = 13.1, 8.3 Hz, 4H), 6.95 – 6.89 (m, 2H), 6.84 (t, J = 7.4 Hz, 1H), 5.51 (d, J = 8.9 Hz, 1H), 4.27 (d, J = 1.8 Hz, 1H), 3.89 (s, 3H), 3.05 (td, J = 12.5, 3.6 Hz, 1H), 2.55 – 2.43 (m, 3H), 2.37 (s, 3H), 2.23 – 2.13 (m, 1H), 2.00 (dd, J = 13.4, 3.7 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.8, 152.8, 140.7, 138.5, 129.1, 128.74, 128.2, 128.0, 127.6, 124.6, 121.3, 121.2, 116.9, 98.1, 95.9, 53.6, 41.2, 40.5, 38.6, 28.4, 21.5 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{21}H_{22}NaO_5^+$ m/z: 377.1359; found: 377.1355. **$[\alpha]_D^{20}$** +44.9 (c = 1.79 in $CHCl_3$). The

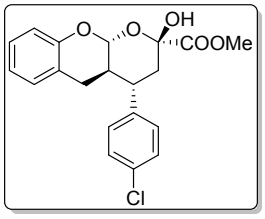
enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 210 nm, t_{major} = 9.85 min, t_{minor} = 6.99 min, ***ee* > 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(2*S*,4*S*,4a*R*,10a*R*)-4-(4-fluorophenyl)-2-hydroxy-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4ad)



White solid, **68%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.08 (dt, *J* = 17.2, 8.1 Hz, 3H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 5.50 (d, *J* = 8.8 Hz, 1H), 4.25 (d, *J* = 1.8 Hz, 1H), 3.89 (s, 3H), 3.08 (td, *J* = 12.7, 3.7 Hz, 1H), 2.57 – 2.40 (m, 3H), 2.13 (tdd, *J* = 11.6, 8.9, 5.5 Hz, 1H), 1.99 (dd, *J* = 13.4, 3.7 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.7, 162.9, 160.9, 152.7, 136.5, 129.1, 129.0, 128.9, 127.7, 121.3, 121.0, 116.9, 115.8, 115.7, 97.9, 95.8, 53.7, 40.8, 40.6, 38.6, 28.3 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{19}FNaO_5^+$ m/z: 381.1109; found: 381.1110. **$[\alpha]_D^{20}$** +41.3 (*c* = 2.00 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 210 nm, t_{major} = 16.67 min, t_{minor} = 8.61 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

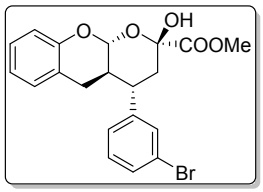
Methyl(2*S*,4*S*,4a*R*,10a*R*)-4-(4-chlorophenyl)-2-hydroxy-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4ae)



White solid, **73%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.91 (d, *J* = 9.1 Hz, 2H), 6.85 (t, *J* = 7.4 Hz, 1H), 5.50 (d, *J* = 8.8 Hz, 1H), 4.29 (d, *J* = 1.3 Hz, 1H), 3.89 (s, 3H), 3.08 (td, *J* = 12.5, 3.6 Hz, 1H), 2.56

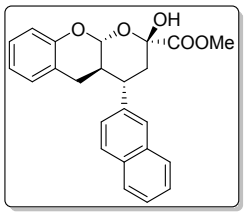
– 2.39 (m, 3H), 2.13 (dtd, *J* = 11.6, 9.1, 5.6 Hz, 1H), 1.99 (dd, *J* = 13.4, 3.6 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.6, 152.7, 139.2, 133.0, 129.1, 129.0, 128.9, 127.7, 121.3, 121.0, 116.9, 97.9, 95.8, 53.7, 40.8, 40.6, 38.4, 28.3 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{19}ClNaO_5^+$ m/z: 397.0813; found: 397.0815. **$[\alpha]_D^{20}$** +38.9 (*c* = 0.91 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 210 nm, t_{major} = 17.41 min, t_{minor} = 9.03 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(2*S*,4*S*,4a*R*,10a*R*)-4-(3-bromophenyl)-2-hydroxy-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4af)



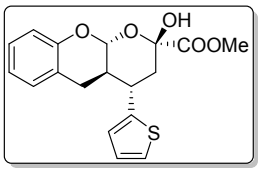
White solid, **57%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.25 – 7.19 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.92 (dd, *J* = 6.9, 4.9 Hz, 2H), 6.85 (t, *J* = 7.3 Hz, 1H), 5.50 (d, *J* = 8.8 Hz, 1H), 4.25 (d, *J* = 1.8 Hz, 1H), 3.89 (s, 3H), 3.07 (td, *J* = 12.7, 3.7 Hz, 1H), 2.56 – 2.39 (m, 3H), 2.14 (m, 1H), 2.00 (dd, *J* = 13.4, 3.7 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.6, 152.7, 143.2, 130.6, 130.5, 130.5, 129.1, 127.7, 126.3, 123.0, 121.4, 120.9, 116.9, 97.8, 95.7, 53.7, 41.1, 40.5, 38.4, 28.3 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{19}{}^{79}BrNaO_5^+$ m/z: 441.0308; found: 441.0313; For $C_{20}H_{19}{}^{81}BrNaO_5^+$ m/z: 443.0288; found: 443.0298. **$[\alpha]_D^{20}$** +26.6 (*c* = 2.11 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 230 nm, t_{major} = 11.01 min, t_{minor} = 8.08 min, ***ee* = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(2*S*,4*S*,4a*R*,10a*R*)-2-hydroxy-4-(naphthalen-2-yl)-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4ag)



White solid, **63%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (ddd, J = 11.4, 8.6, 6.3 Hz, 3H), 7.74 (s, 1H), 7.54 – 7.45 (m, 2H), 7.42 (dd, J = 8.5, 1.4 Hz, 1H), 7.10 (t, J = 6.9 Hz, 1H), 6.93 (d, J = 8.2 Hz, 1H), 6.88 – 6.79 (m, 2H), 5.57 (d, J = 8.8 Hz, 1H), 4.28 (d, J = 1.9 Hz, 1H), 3.90 (s, 3H), 3.27 (td, J = 12.6, 3.7 Hz, 1H), 2.64 – 2.54 (m, 2H), 2.49 (dd, J = 16.6, 5.2 Hz, 1H), 2.38 – 2.24 (m, 1H), 2.08 (dd, J = 13.4, 3.7 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.8, 152.7, 138.1, 133.5, 132.7, 129.1, 128.7, 127.7, 127.6, 126.5, 126.4, 125.9, 125.3, 121.3, 121.2, 116.9, 98.1, 95.9, 53.7, 41.5, 40.5, 38.5, 28.4 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{24}H_{22}NaO_5^+$ m/z: 413.1359; found: 413.1363. **$[\alpha]_D^{20}$** +24.0 (c = 0.79 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (n-hexane/i-PrOH = 85/15, 1 mL/min), λ = 230 nm, t_{major} = 15.06 min, t_{minor} = 9.23 min, ***ee* = 96%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

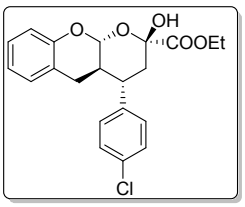
Methyl(2*S*,4*S*,4a*R*,10a*R*)-2-hydroxy-4-(thiophen-2-yl)-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4ah)



White solid, **69%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, J = 6.0 Hz, 2H), 7.22 (t, J = 8.6 Hz, 2H), 7.11 (t, J = 7.6 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.86 (q, J = 7.7 Hz, 1H), 5.50 (d, J = 8.8 Hz, 1H), 4.31 (s, 1H), 3.89 (s, 3H), 3.12 – 3.01 (m, 1H), 2.48 (dt, J = 26.3, 12.6 Hz, 3H), 2.22 – 2.08 (m, 1H), 2.00 (dd, J = 13.3, 3.3 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.6, 152.6, 144.5, 129.2, 127.7, 126.9, 124.6, 123.9, 121.3, 121.1, 116.8, 97.8, 95.6, 53.7, 42.2, 39.7, 36.8, 28.5 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{18}H_{18}NaO_5S^+$ m/z: 369.0767;

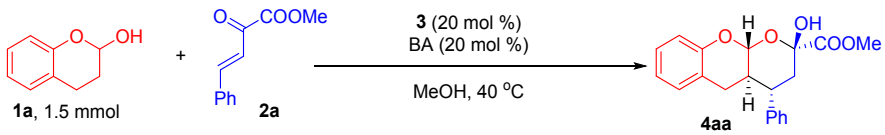
found: 369.0765. **$[\alpha]_D^{20}$** +24.5 (c = 0.2 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 210 nm, t_{major} = 13.20 min, t_{minor} = 9.17 min, ***ee* = 94%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Ethyl(2*S*,4*S*,4a*R*,10a*R*)-4-(4-chlorophenyl)-2-hydroxy-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (4ai)



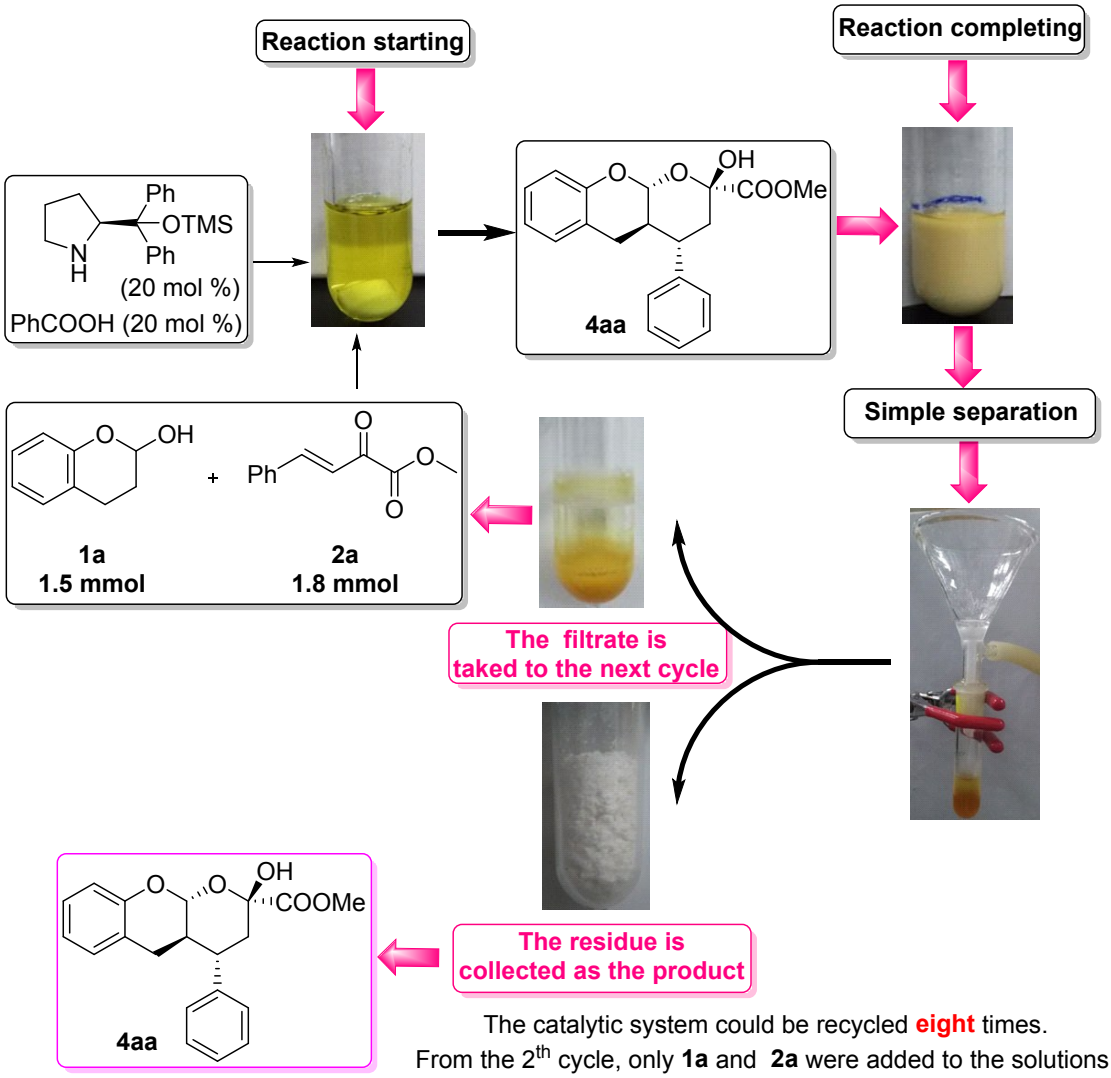
White solid, **72%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.2 Hz, 2H), 7.10 (t, J = 7.6 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.85 (t, J = 7.4 Hz, 1H), 5.50 (d, J = 8.8 Hz, 1H), 4.43 – 4.21 (m, 3H), 3.11 – 3.04 (m, 1H), 2.56 – 2.39 (m, 3H), 2.19 – 2.09 (m, 1H), 1.98 (dd, J = 13.3, 3.4 Hz, 1H), 1.37 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 169.1, 152.7, 139.4, 135.1, 133.0, 129.1, 128.9, 127.7, 121.3, 121.0, 116.9, 97.9, 95.7, 63.2, 40.8, 40.5, 38.4, 28.3, 14.0 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{21}H_{21}ClNaO_5^+$ m/z: 411.0970; found: 411.0973. **$[\alpha]_D^{20}$** +50.2 (c = 1.30 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 210 nm, t_{major} = 19.71 min, t_{minor} = 9.65 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

D. Catalyst recycling studies



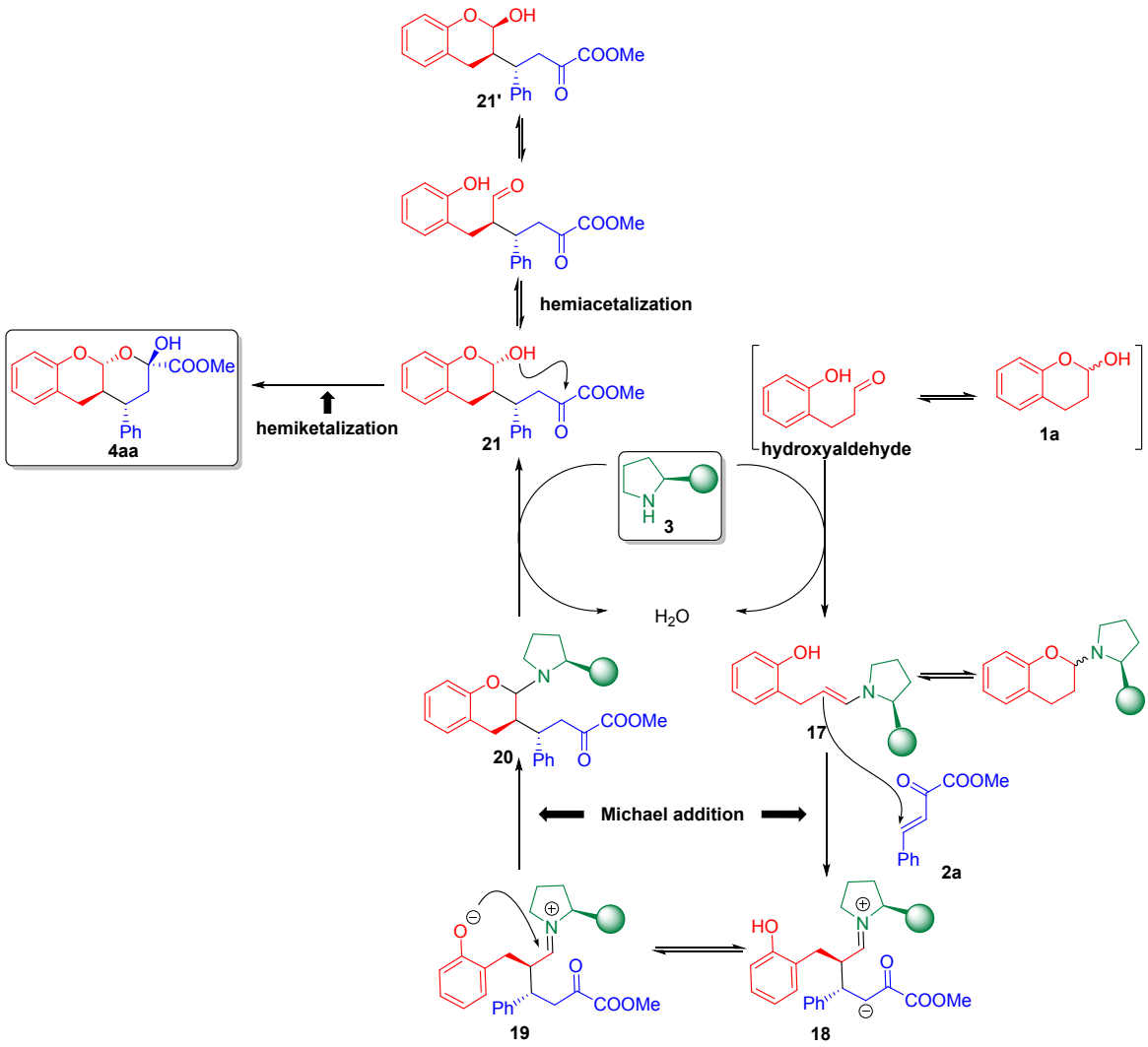
recycle	*t*[h]	yield (%)	*ee* (%)	recycle	*t*[h]	yield (%)	*ee* (%)
1	6	61	>99	5	66	71	>99
2	16	59	>99	6	120	57	96
3	22	87	>99	7	163	84	96
4	54	77	>99	8	200	66	93

A glass vial equipped with a magnetic stirring bar was charged with lactol **1a** (1.5 mmol, 1.0 equiv), and unsaturated ketoester **2a** (1.8 mmol, 1.2 equiv) in MeOH (1.5 mL) with **3** (20 mol %) and BA (PhCOOH) (20 mol %) at 40 °C until the material **1a** disappeared. After completion of the reaction, the reaction mixture was purified by filtration to afford **4aa** for NMR and HPLC analysis after washed twice with methanol. The filtrate was evaporated under vacuum and the remaining catalyst **3** and BA was used in the next run. In the seventh running, only lactol **1a** (1.5 mmol, 1.0 equiv) was added in the solution of filtrate.



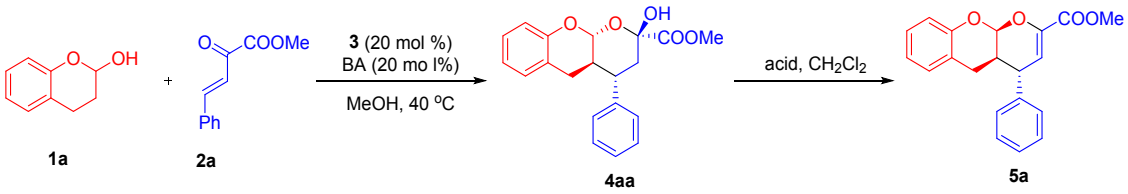
The catalytic system could be recycled **eight** times.
From the 2th cycle, only **1a** and **2a** were added to the solutions.

E. Mechanism of [3+3] reaction pathway



The reaction could start with the addition of **3** to the hydroxyaldehyde, which is from the equilibrium of lactol **1a**, providing the intermediate enamine **17**, and then the enamine **17** would react with the *β,γ*-unsaturated α-ketoester **2a** in a Michael reaction to generate **18**. Zwitterion **18** would undergo proton transfer delivering **19**, which could provide aminoacetal **20** after an intramolecular aminoacetalization. Hydrolysis of aminoacetal **20** releasing catalyst was followed by spontaneous intramolecular hemiacetalization to afford substituted hemiacetal **21** and **21'**. Because of the steric hindrance of substituted hemiacetal, the hydroxyl group of the hemiacetal attacked the keto of product **21** from its *Re*-face to get the product **4aa**. While the product **21'**, which is the equilibrium of **21** , cannot complete the attack, that can effectively convert to the substituted hemiacetal **21** to finish the hemiketalization.

F. Optimization of the dehydration reaction

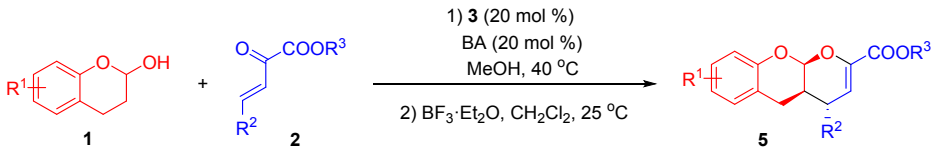


1a 2a 4aa 5a

Entry[a]	acid	acid loading	time (h)	yield (%)[b]	*ee* (%)[c]	dr[d]
1[e]	*p*-TsOH	1.0	>24	63	>99	>20:1
2	$BF_3{\cdot}OEt_2$	1.0	>24	70	>99	>20:1
3	$BF_3{\cdot}OEt_2$	5.0	7	77	>99	>20:1
4	$BF_3{\cdot}OEt_2$	10.0	7	78	>99	>20:1
5	$BF_3{\cdot}OEt_2$	15.0	6	77	>99	>20:1

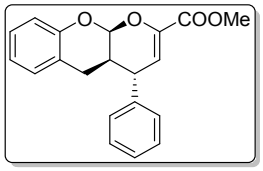
[*a*] Unless otherwise specified, all reactions were carried out using **1a** (0.1 mmol, 1.0 equiv) and unsaturated ketoester **2a** (0.12 mmol, 1.2 equiv) in MeOH (0.2 mL) with **3** (20 mol %) and BA (PhCOOH) (20 mol %) at 40 °C. After workup, the mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 12:1) to get product **4aa**. The acid was added to the solution of compound **4aa** dissolved in redistilled CH_2Cl_2 (0.2 mmol in 1 mL) at 25 °C. After full conversion of the second step, the reaction mixture was purified by flash chromatography on gel (petroleum ether/ethyl acetate = 25/1) to give product **5a**. [*b*] Isolated yield of **5a** for two steps. [*c*] Determined by HPLC analyses of isolated compound **5a** on chiral stationary phases. [*d*] Determined by ^{1}H NMR. [*e*] The acid was added to the solution of compound **4aa** dissolved in redistilled CH_2Cl_2 at 40 °C. *p*-TsOH = *p*-Toluenesulfonic acid.

G. Procedures for *cis*-5 and characterization of products



General procedure: A glass vial equipped with a magnetic stirring bar was charged with lactol **1** (0.10 mmol, 1.0 equiv), and unsaturated ketoester **2** (0.12 mmol, 1.2 equiv) in MeOH (0.2 mL) with **3** (20 mol %) and BA (PhCOOH) (20 mol %) at 40 °C until the material **1** disappeared. After completion of the reaction, the mixture was purified by flash chromatography on silica gel to afford the hemiketal intermediate **4**. The $BF_3{\cdot}OEt_2$ (5.0 equiv) was added to the solution of compound **4** (1.0 equiv) dissolved in redistilled CH_2Cl_2 (0.2 mmol in 1 mL) at 25 °C. After full conversion of the second step, the reaction mixture was purified by flash chromatography on gel to give product **5** for NMR and HPLC analysis.

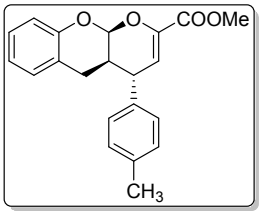
Methyl(4*S*,4a*R*,10a*S*)-4-phenyl-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5a)



White solid, **77%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, J = 7.4 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 7.16 (t, J = 6.6 Hz, 3H), 7.05 (d, J = 7.4 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.25 (d, J = 3.4 Hz, 1H), 5.75 (d, J = 1.8 Hz, 1H), 3.85 (s, 3H), 3.45 (dd, J = 7.5, 3.3 Hz, 1H), 2.91 (dd, J = 16.7, 5.7 Hz, 1H), 2.71 (dd, J = 16.7, 6.1 Hz, 1H), 2.38 (dt, J = 7.7, 3.9 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.6, 151.3, 141.7, 140.8, 129.3, 128.9, 128.3, 128.0, 127.3, 121.7, 119.4, 117.1, 113.7, 94.6, 52.4, 39.6, 36.0, 26.7 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{18}NaO_4^+$ m/z: 345.1097; found: 345.1099. **$[\alpha]_D^{20}$** +80.4 (c = 1.67 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IB column

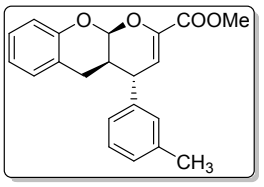
(*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 230 nm, t_{major} = 8.30 min, t_{minor} = 6.76 min, ***ee*** **>99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr*** **>20:1**.

Methyl(4*S*,4a*R*,10a*S*)-4-(p-tolyl)-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5b)



White solid, **71%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 – 7.12 (m, 3H), 7.08 – 7.01 (m, 3H), 6.94 – 6.83 (m, 2H), 6.24 (d, *J* = 3.4 Hz, 1H), 5.74 (d, *J* = 1.9 Hz, 1H), 3.84 (s, 3H), 3.42 (dd, *J* = 7.4, 3.4 Hz, 1H), 2.90 (dd, *J* = 16.7, 5.7 Hz, 1H), 2.71 (dd, *J* = 16.7, 6.1 Hz, 1H), 2.39 – 2.35 (m, 1H), 2.35 (s, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.6, 151.3, 140.7, 138.7, 137.0, 129.5, 129.3, 128.1, 128.0, 121.7, 119.5, 117.1, 114.0, 94.6, 52.4, 39.2, 36.0, 26.7, 21.0 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{21}H_{20}NaO_4^+$ m/z: 359.1254; found: 359.1260. **$[\alpha]_D^{20}$** +84.4 (*c* = 1.78 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 13.09 min, t_{minor} = 8.75 min, ***ee*** **= 94%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr*** **>20:1**.

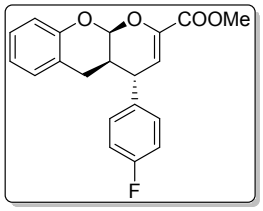
Methyl(4*S*,4a*R*,10a*S*)-4-(m-tolyl)-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5c)



White solid, **74%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 6.9 Hz, 1H), 7.01 – 6.86 (m, 4H), 6.25 (d, *J* = 3.4 Hz, 1H), 5.74 (d, *J* = 1.9 Hz, 1H), 3.85 (s, 3H), 3.42 (dd, *J* = 7.3, 3.4 Hz, 1H), 2.90 (dd,

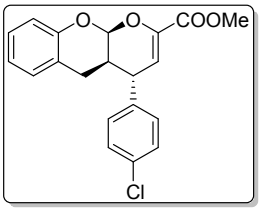
J = 16.7, 5.7 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.43 – 2.36 (m, 1H), 2.35 (s, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.6, 151.3, 141.7, 140.7, 138.6, 129.3, 128.9, 128.7, 128.1, 128.0, 125.4, 121.7, 119.5, 117.1, 113.8, 94.6, 52.4, 39.6, 35.9, 26.7, 21.4 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{21}H_{20}NaO_4^+$ m/z: 359.1254; found: 359.1254. **$[\alpha]_D^{20}$** +88.6 (*c* = 1.77 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 12.95 min, t_{minor} = 8.06 min, ***ee* = 97%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(4*S*,4a*R*,10a*S*)-4-(4-fluorophenyl)-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5d)



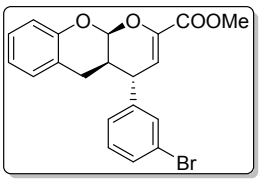
White solid, **85%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 – 7.08 (m, 3H), 7.03 (t, *J* = 8.6 Hz, 3H), 6.92 (dd, *J* = 13.0, 7.7 Hz, 2H), 6.21 (d, *J* = 3.3 Hz, 1H), 5.73 (d, *J* = 1.7 Hz, 1H), 3.85 (s, 3H), 3.44 (dd, *J* = 7.6, 3.3 Hz, 1H), 2.92 (dd, *J* = 16.7, 5.6 Hz, 1H), 2.68 (dd, *J* = 16.8, 5.9 Hz, 1H), 2.34 (td, *J* = 7.6, 1.9 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.0, 162.58, 151.2, 140.9, 137.4, 129.8, 129.7, 129.30, 128.1, 121.8, 119.2, 117.1, 115.8, 115.6, 113.4, 94.6, 52.5, 38.7, 36.1, 26.6 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{17}FNaO_4^+$ m/z: 363.1003; found: 363.1002. **$[\alpha]_D^{20}$** +14.0 (*c* = 7.48 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 13.38 min, t_{minor} = 8.97 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(4*S*,4a*R*,10a*S*)-4-(4-chlorophenyl)-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5e)



White solid, **61%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.2 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 8.3 Hz, 2H), 7.04 (d, J = 7.4 Hz, 1H), 6.92 (dd, J = 14.2, 7.7 Hz, 2H), 6.20 (d, J = 3.2 Hz, 1H), 5.73 (d, J = 1.5 Hz, 1H), 3.85 (s, 3H), 3.43 (dd, J = 7.7, 3.2 Hz, 1H), 2.92 (dd, J = 16.8, 5.6 Hz, 1H), 2.67 (dd, J = 16.8, 5.8 Hz, 1H), 2.39 – 2.10 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4, 151.2, 141.0, 140.2, 133.2, 129.6, 129.3, 129.0, 128.1, 121.8, 119.1, 117.1, 113.0, 94.5, 52.5, 38.8, 36.0, 26.6 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{17}ClNaO_4^+$ m/z: 379.0708; found: 379.0703. **$[\alpha]_D^{20}$** +100.0 (c = 5.10 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 13.23 min, t_{minor} = 9.25 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

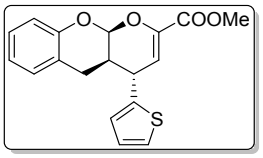
Methyl(4*S*,4a*R*,10a*S*)-4-(3-bromophenyl)-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5f)



White solid, **83%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.9 Hz, 1H), 7.32 (s, 1H), 7.22 (t, J = 7.8 Hz, 1H), 7.16 (dd, J = 11.2, 4.2 Hz, 1H), 7.07 (dd, J = 19.3, 7.5 Hz, 2H), 6.93 (dd, J = 15.5, 7.8 Hz, 2H), 6.19 (d, J = 3.4 Hz, 1H), 5.73 (d, J = 1.9 Hz, 1H), 3.85 (s, 3H), 3.42 (dd, J = 7.6, 3.3 Hz, 1H), 2.93 (dd, J = 16.8, 5.7 Hz, 1H), 2.69 (dd, J = 16.8, 6.0 Hz, 1H), 2.37 (qd, J = 5.9, 2.0 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4, 151.2, 144.0, 141.1, 131.2, 130.6, 130.4, 129.3, 128.1, 127.0, 123.0, 121.9, 119.1, 117.1, 112.7, 94.5, 52.5, 39.2, 35.9, 26.6 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{17}{}^{79}BrNaO_4^+$ m/z: 423.0202; found: 423.0205. For $C_{20}H_{17}{}^{81}BrNaO_4^+$ m/z: 425.0182; found: 425.0192. **$[\alpha]_D^{20}$** +82.8 (c = 2.05 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel

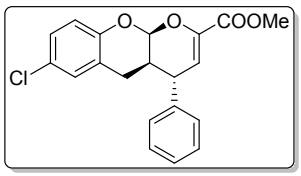
Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 13.75 min, t_{minor} = 8.37 min, ***ee* = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(4*S*,4a*R*,10a*S*)-4-(thiophen-2-yl)-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5g)



White solid, **57%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.18 – 7.13 (m, 1H), 7.05 (d, *J* = 7.9 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.93 (dd, *J* = 11.6, 4.3 Hz, 2H), 6.86 (d, *J* = 3.3 Hz, 1H), 6.29 (d, *J* = 3.8 Hz, 1H), 5.75 (d, *J* = 1.9 Hz, 1H), 3.84 (s, 3H), 3.76 (dd, *J* = 6.0, 3.9 Hz, 1H), 2.92 (dd, *J* = 16.6, 5.8 Hz, 1H), 2.78 (dd, *J* = 16.6, 7.6 Hz, 1H), 2.48 (qd, *J* = 6.0, 1.9 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4, 151.1, 145.0, 140.4, 129.4, 128.0, 127.0, 125.5, 124.7, 121.8, 119.5, 117.1, 112.5, 94.3, 52.5, 36.5, 35.8, 26.3 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{18}H_{16}NaO_4S^+$ m/z: 351.0662; found: 351.0669. **$[\alpha]_D^{20}$** +67.8 (*c* = 1.29 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 13.43 min, t_{minor} = 18.85 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

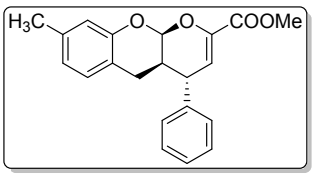
Methyl(4*S*,4a*R*,10a*S*)-7-chloro-4-phenyl-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5h)



White solid, **62%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.16 (d, *J* = 7.1 Hz, 2H), 7.11 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.03 (d, *J* = 2.1 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.25 (d, *J* = 3.4 Hz, 1H), 5.72 (d, *J* = 1.8 Hz, 1H), 3.84 (s, 3H), 3.42

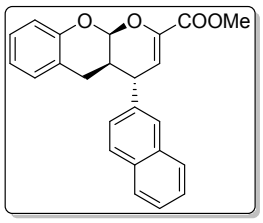
(dd, *J* = 7.3, 3.4 Hz, 1H), 2.88 (dd, *J* = 16.9, 5.6 Hz, 1H), 2.68 (dd, *J* = 16.9, 6.3 Hz, 1H), 2.42 – 2.31 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4, 149.9 141.4, 140.8 128.9, 128.9 128.2, 128.1 127.5 126.5 121.1, 118.5 113.5 94.5, 52.5 39.6, 35.7 26.5 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{17}ClNaO_4^+$ m/z: 379.0708; found: 379.0700. **$[\alpha]_D^{20}$** +82.3 (*c* = 0.96 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 14.78 min, t_{minor} = 7.64 min, ***ee* = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(4*S*,4a*R*,10a*S*)-8-methyl-4-phenyl-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5i)



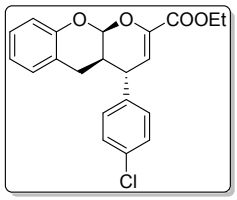
White solid, **53%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.87 – 6.78 (m, 2H), 6.25 (d, *J* = 3.3 Hz, 1H), 5.72 (d, *J* = 1.5 Hz, 1H), 3.84 (s, 3H), 3.45 (dd, *J* = 7.5, 3.3 Hz, 1H), 2.87 (dd, *J* = 16.7, 5.6 Hz, 1H), 2.67 (dd, *J* = 16.7, 5.9 Hz, 1H), 2.37 (q, *J* = 5.7 Hz, 1H), 2.27 (s, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.6, 149.0, 141.8 140.8, 131.0, 129.6, 128.8, 128.6, 128.3 127.3 119.0, 116.8, 113.7, 94.7, 52.4, 39.5, 36.1 26.7, 20.5 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{21}H_{20}NaO_4^+$ m/z: 359.1254; found: 359.1260. **$[\alpha]_D^{20}$** +63.9 (*c* = 1.04 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 15.52 min, t_{minor} = 9.05 min, ***ee* = 93%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(4*S*,4a*R*,10a*S*)-4-(naphthalen-2-yl)-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5j)



White solid, **67%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.5 Hz, 2H), 7.81 – 7.77 (m, 1H), 7.59 (s, 1H), 7.53 – 7.47 (m, 2H), 7.31 (dd, J = 8.5, 1.6 Hz, 1H), 7.18 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.34 (d, J = 3.4 Hz, 1H), 5.79 (d, J = 1.9 Hz, 1H), 3.87 (s, 3H), 3.63 (dd, J = 7.4, 3.4 Hz, 1H), 2.93 (dd, J = 16.7, 5.7 Hz, 1H), 2.76 (dd, J = 16.8, 6.1 Hz, 1H), 2.50 (td, J = 7.7, 1.9 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.6, 151.3, 141.0, 139.0, 133.3, 132.6, 129.4, 128.8, 128.0, 127.7, 127.7, 127.2, 126.5, 126.1, 126.1, 121.8, 119.5, 117.2, 113.5, 94.6, 52.5, 39.7, 35.8, 26.7 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{24}H_{20}NaO_4^+$ m/z: 395.1254; found: 395.1255. **$[\alpha]_D^{20}$** +128.1 (c = 1.88 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (n-hexane/i-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 15.32 min, t_{minor} 9.94 min, ***ee* = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

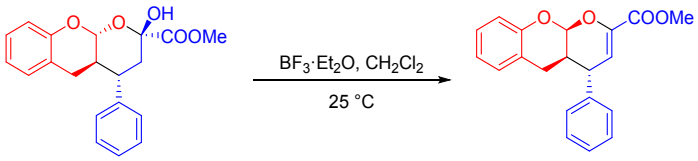
Ethyl(4*S*,4a*R*,10a*S*)-4-(4-chlorophenyl)-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (5k)



White solid, **70%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.4 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 7.3 Hz, 1H), 6.96 – 6.88 (m, 2H), 6.18 (d, J = 3.2 Hz, 1H), 5.74 (d, J = 1.9 Hz, 1H), 4.41 – 4.22 (m, 2H), 3.42 (dd, J = 8.0, 3.2 Hz, 1H), 2.92 (dd, J = 16.8, 5.6 Hz, 1H), 2.67 (dd, J = 16.8, 5.5 Hz, 1H), 2.37 – 2.28 (m, 1H), 1.34 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.0, 151.3, 141.2, 140.2, 133.2, 129.6, 129.3, 129.0, 128.1, 121.8, 119.1, 117.2, 112.8, 94.6, 61.6, 38.7, 35.9, 26.7, 14.2 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{21}H_{19}ClNaO_4^+$ m/z: 393.0864; found: 393.0861. **$[\alpha]_D^{20}$** +38.3 (c = 3.42 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel

Chiralpak IC column (*n*-hexane/*i*-PrOH = 75/25, 1 mL/min), λ = 230 nm, t_{major} = 14.15 min, t_{minor} = 9.23 min, ***ee* >99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

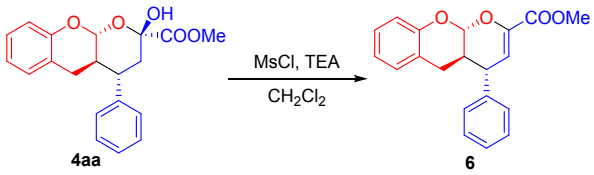
H. The larger scale transformation of 5a



4aa **5a**

A glass vial equipped with a magnetic stirring bar was charged with **4aa** (1.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) at 0 °C. To the reaction mixture was added $BF_3{\cdot}OEt_2$ (617μL, 5.0 equiv) at 0 °C. Then return the reaction mixture to 25 °C until **4aa** consumed for about 10 h. After completion of the reaction, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 25/1) to give product **5a** (95%, >99% *ee*).

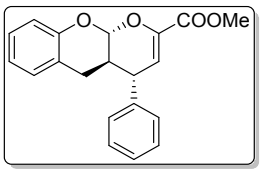
I. Procedure for *trans*-6 and characterization of product



4aa **6**

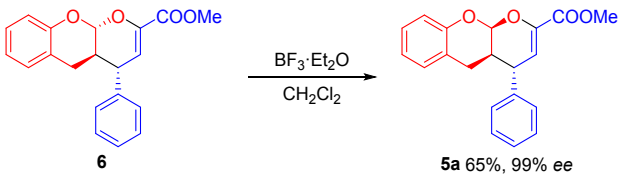
A glass vial equipped with a magnetic stirring bar was charged with **4aa** (1.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) at 0 °C. To the reaction mixture was added TEA (834 μL, 6.0 mmol, 6.0 equiv) and MsCl (232 μL, 3.0 mmol, 3.0 equiv) at 0 °C. Then return the reaction mixture to 25 °C for 15 h. After completion of the reaction, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **6** for NMR and HPLC analysis.

Methyl(4*S*,4a*R*,10a*R*)-4-phenyl-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (6)



White solid, **66%** yield, **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (t, J = 7.3 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.23 (d, J = 7.2 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 6.94 (d, J = 7.4 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.17 (d, J = 1.9 Hz, 1H), 5.56 (d, J = 9.2 Hz, 1H), 3.86 (s, 3H), 3.42 (dd, J = 10.4, 1.7 Hz, 1H), 2.76 (dd, J = 16.4, 5.3 Hz, 1H), 2.64 (dd, J = 16.2, 12.3 Hz, 1H), 2.23 – 2.17 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.4, 152.4, 142.1, 140.1, 129.0, 128.8, 127.9, 127.9, 127.6, 121.4, 120.5, 116.8, 115.0, 110.0, 99.5, 52.5, 44.9, 39.0, 28.8 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{18}NaO_4^+$ m/z: 345.1097; found: 345.1099. **$[\alpha]_D^{20}$** +102.2 (c = 1.06 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 = 230 nm, t_{major} = 8.51 min, t_{minor} = 6.97 min, ***ee* = 99%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

J. Transformation between 6 and 5a

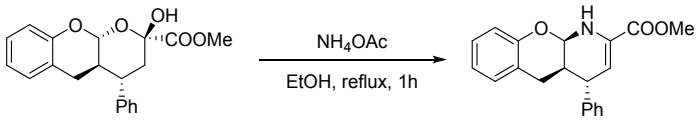


6 **5a** 65%, 99% *ee*

A glass vial equipped with a magnetic stirring bar was charged with **6** (0.1 mmol, 1.0 equiv) in CH_2Cl_2 (0.5 mL) at 0 °C. To the reaction mixture was added $BF_3{\cdot}OEt_2$ (62 μL, 5.0 equiv) at 0 °C. Then return the reaction mixture to 25 °C until **6** consumed. After completion of the reaction, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 25/1) to give product **5a** (65%, 99% *ee*).

K. Synthetic transformation

Methyl(4*S*,4a*R*,10a*R*)-4-phenyl-1,4a,5,10a-tetrahydro-4*H*-chromeno[2,3-*b*]pyridine-2-carboxylate (7)

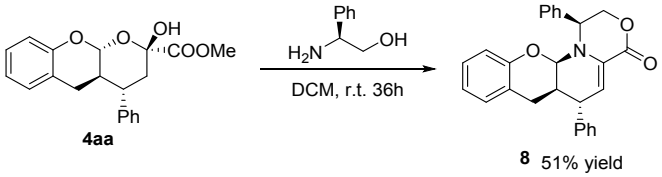


4a **7**

98% yield

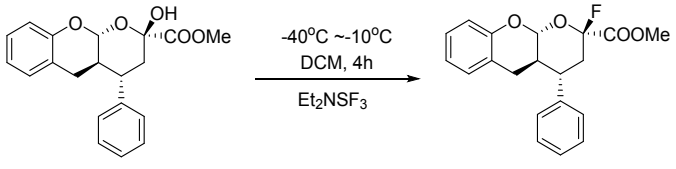
To the solution of **4a** (68 mg, 0.2 mmol) in the EtOH (1 mL) was added NH_4OAc (31 mg, 0.4 mmol) at room temperature. Then return the reaction to the 80 °C and reflux for 1 h. After completion of the reaction, the solvent was removed under vacuum. The product was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate = 25/1) to afford the desired product **7** as a colorless oil (63 mg, 98%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.27 (dd, *J* = 9.7, 4.7 Hz, 1H), 7.16 (dd, *J* = 8.8, 7.7 Hz, 3H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.89 (t, *J* = 7.3 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 5.81 (d, *J* = 1.7 Hz, 1H), 5.30 – 5.25 (m, 2H), 3.81 (s, 3H), 3.44 (dd, *J* = 11.6, 2.5 Hz, 1H), 2.94 (dd, *J* = 17.0, 6.0 Hz, 1H), 2.57 (d, *J* = 16.9 Hz, 1H), 2.38 (dd, *J* = 11.6, 6.0 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.4, 152.0, 143.1, 129.8, 129.5, 128.6, 128.6, 128.1, 127.9, 126.9, 120.9, 119.2, 117.1, 111.9, 80.4, 52.2, 39.4, 36.1, 28.0 ppm. **HRMS:** $[M+H]^+$ *calcd*. For $C_{20}H_{20}NO_3^+$ m/z: 322.1438; found: 322.1437. **$[\alpha]_D^{20}$** -67.5 (*c* = 2.77 in $CHCl_3$). The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

(1*S*,6*S*,6a*R*,12a*R*)-1,6-diphenyl-1,2,6a,12a-tetrahydro-7*H*-chromeno[3',2':5,6]pyrido[2,1-*c*][1,4]oxazin-4(6*H*)-one (8)



To the solution of **4aa** (68 mg, 0.2 mmol) in the CH_2Cl_2 (1 mL) was added *D*-2-Phenylglycinol (55 mg, 0.4 mmol) at room temperature. After stirring at room temprerature for 36 h, remove the soluvent under vacuum and the mixture was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate = 20/1) to afford the desired product **8** as a white solid (42 mg, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 5H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.16 (dd, *J* = 13.1, 6.1 Hz, 3H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.37 (d, *J* = 2.9 Hz, 1H), 4.86 (dd, *J* = 9.4, 3.3 Hz, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 4.56 (dd, *J* = 11.3, 9.5 Hz, 1H), 4.45 (dd, *J* = 11.4, 3.3 Hz, 1H), 3.46 (dd, *J* = 11.6, 2.8 Hz, 1H), 2.78 (dd, *J* = 17.0, 5.8 Hz, 1H), 2.53 (d, *J* = 16.7 Hz, 1H), 2.46 – 2.38 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.4, 151.9, 142.0, 135.0, 129.9, 129.7, 129.2, 129.1, 128.7, 128.6, 128.2, 127.9, 127.1, 121.1, 119.3, 119.0, 117.0, 82.3, 71.4, 56.8, 40.3, 36.3, 28.1 ppm. **HRMS:** $[M+H]^+$ *calcd*. For $C_{27}H_{24}NO_3^+$ m/z: 410.1751; found: 410.1751. **$[\alpha]_D^{20}$** -80.2 (*c* = 2.06 in $CHCl_3$). The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(2*R*,4*S*,4a*R*,10a*R*)-2-fluoro-4-phenyl-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (9)

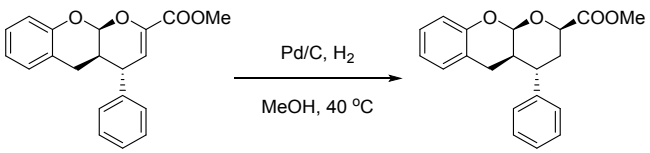


4aa **9**

47% yield

To the solution of **4aa** (68 mg, 0.2 mmol) in the CH_2Cl_2 (1 mL) was added drop wise DAST (Et_2NSF_3, 0.22 mmol) at -40 °C under N_2 atmosphere. Then return the reaction to -10 °C gradually and stir at the temperature for 4 h until the material **4aa** consumed. The product was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate = 25/1) to afford the desired product **9** as a colorless oil (32 mg, 47%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.87 (t, *J* = 7.3 Hz, 1H), 5.50 (d, *J* = 9.0 Hz, 1H), 3.90 (s, 3H), 3.05 (td, *J* = 11.5, 5.3 Hz, 1H), 2.53 (d, *J* = 8.5 Hz, 2H), 2.44 – 2.32 (m, 2H), 2.31 – 2.17 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 165.7, 165.4, 152.4, 139.6, 129.1, 127.8, 127.6, 127.5, 121.6, 120.8, 117.0, 109.3, 107.5, 98.9, 53.4, 40.6, 39.7, 37.9, 28.2 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{19}FNaO_4^+$ m/z: 365.1160; found: 365.1154. **$[\alpha]_D^{20}$** +42.9 (*c* = 1.26 in $CHCl_3$). The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

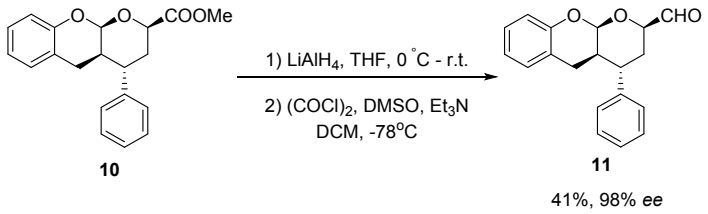
Methyl(2*R*,4*S*,4a*R*,10a*R*)-4-phenyl-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (10)



5a **10**
90%, 97% *ee*

Hydrogenate a solution of **5a** (32 mg, 0.1 mmol) in MeOH (1 mL) at atmospheric pressure using 10% Pd/C (3 mg) as the catalyst. And the reaction mixture was stirred at 40 °C for 48 h. After completion of the reaction, filter the catalyst and the solvent was removed under vacuum. The product was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate = 25/1) to afford the desired product **10** as a white solid (29 mg, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, J = 7.3 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.10 (dd, J = 11.7, 4.3 Hz, 3H), 6.83 (q, J = 7.6 Hz, 2H), 6.72 (d, J = 8.2 Hz, 1H), 5.62 (s, 1H), 4.52 (d, J = 4.9 Hz, 1H), 3.87 (s, 3H), 3.04 (td, J = 11.9, 3.5 Hz, 1H), 2.78 (dd, J = 16.7, 5.3 Hz, 1H), 2.37 (t, J = 16.2 Hz, 3H), 2.15 – 2.05 (m, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.9, 152.8, 142.5, 129.4, 128.9, 127.8, 127.8, 127.1, 121.4, 119.1, 116.5, 97.2, 70.3, 52.2, 37.3, 34.7, 32.0, 27.5 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{20}NaO_4^+$ m/z: 347.1254; found: 347.1255; **$[\alpha]_D^{20}$** -3.74 (c = 2.81 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IA column (*n*-hexane/*i*-PrOH = 85/15, 1 mL/min), λ = 210 nm, t_{major} = 9.13 min, t_{minor} = 10.21 min, ***ee* = 97%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

(2*R*,4*S*,4a*R*,10a*R*)-4-phenyl-3,4,4a,10a-tetrahydro-2*H*,5*H*-pyrano[2,3-*b*]chromene-2-carbaldehyde (11)



10 **11**

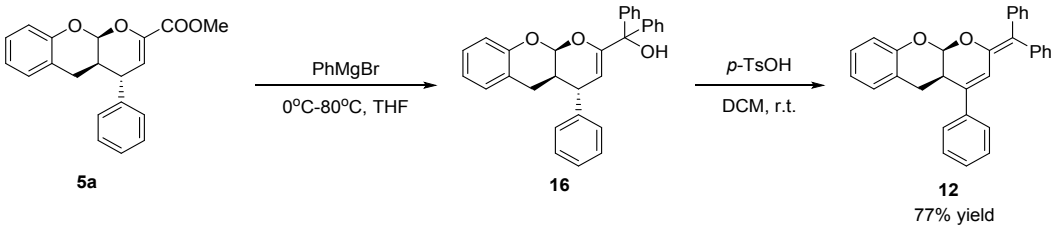
41%, 98% *ee*

To a magnetically stirred suspension of $LiAlH_4$ (29 mg, 0.75 mmol) in 1 mL of anhydrous tetrahydrofuran (THF), cooled to 0 °C, was added drop wise a solution of **10** (80 mg, 0.25 mmol) in anhydrous tetrahydrofuran (1 mL) under N_2 atmosphere. After stirring at this temperature for about 1 h (TLC monitoring) the mixture was diluted with a small amount of 15% KOH solution. The white suspension was filtered, the filtrate was evaporated and obtained crude was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate = 8/1) to get reduction product as a white solid (68 mg, 93 %).

To the solution of reduction product in the CH_2Cl_2 (3 mL) was added drop wise $(CO)_2Cl_2$ (63 µL, 0.75 mmol) and DMSO (159 µL, 2.25 mmol) in CH_2Cl_2 (2.5 mL) at –78 °C. After stirring at this temperature for 30 min, TEA (521 µL, 3.75 mmol) was added. When the reaction finished, the mixture was diluted with NH_4Cl (aq.) and extracted with ethyl acetate (3 x 5mL) and H_2O (3 x 5mL) until no product was visible in TLC. The organic layer was dried with Na_2SO_4, filtered and the filtrate was evaporated and obtained crude was purified by column chromatography on a silica gel (petroleum ether/ethyl acetate = 8/1) to get product **11** as colorless oil (30 mg, 41%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.16 (dd, *J* = 11.4, 4.9 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 2H), 6.90 (dd, *J* = 10.7, 7.9 Hz, 3H), 5.75 (d, *J* = 2.6 Hz, 1H), 4.70 (dd, *J* = 12.3, 2.6 Hz, 1H), 2.92 – 2.81 (m, 2H), 2.44 – 2.38 (m, 1H), 2.38 – 2.33 (m, 1H), 2.15 – 2.08 (m, 1H), 1.81 (dd, *J* = 25.6, 12.6 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.2, 153.1, 141.8, 129.3, 128.8, 127.7, 127.4, 127.2, 121.3, 118.7, 116.3, 96.7, 75.0, 38.3, 37.4, 32.7, 27.1 ppm. **HRMS:** $[M+H]^+$ *calcd*. For $C_{19}H_{19}O_3^+$ m/z: 295.1329; found: 295.1328; **$[\alpha]_D^{20}$** –17.9 (*c* = 0.68 in $CHCl_3$). The enantiomeric excess was determined by HPLC analysis on Daicel Chiralpak IC column (*n*-hexane/*i*-PrOH = 80/20, 1 mL/min), λ = 210 nm, t_{major} = 8.75 min,

t_{minor} = 9.34 min, ***ee* = 98%**. The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

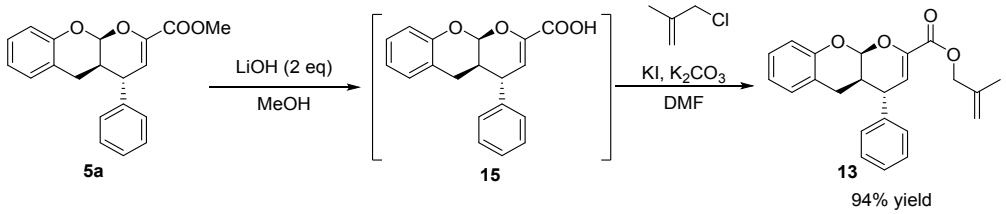
(4a*R*,10a*R*)-2-(diphenylmethylene)-4-phenyl-4a,10a-dihydro-2*H*,5*H*-pyrano[2,3-*b*]chromene (12)



5a **16** **12**
77% yield

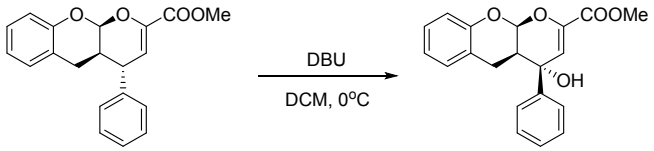
To a solution of **5a** (32 mg, 0.1 mmol) in 2 mL of anhydrous tetrahydrofuran (THF) was added drop wise PhMgBr (0.4 mmol in Et_2O, 4.0 eq.) at 0 °C. Then return the reaction to 80 °C for 12 h until the material is consumed. When the reaction finished, the mixture was diluted with NH_4Cl (aq.) and extracted with ethyl acetate (3 x 5mL) and H_2O (3 x 5mL) until no product was visible in TLC. The organic layer was dried with Na_2SO_4, filtered and the filtrate was evaporated and obtained crude was purified by column chromatography on a silica gel to get product **16** as white solid. To the solution of **16** in CH_2Cl_2 (400 µL) was added *p*-TsOH (20 mol %) and stirred at room temperature for 2 h until the compound **16** was consumed. The mixture was purified by column chromatography on a silica gel to get product **12** as white solid (33 mg, 77%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.42 – 7.32 (m, 8H), 7.31 – 7.26 (m, 5H), 7.21 – 7.14 (m, 2H), 7.03 (dd, *J* = 16.1, 7.6 Hz, 2H), 6.96 – 6.91 (m, 1H), 6.69 (s, 1H), 5.87 (d, *J* = 2.2 Hz, 1H), 3.26 (ddd, *J* = 9.8, 7.7, 2.2 Hz, 1H), 2.99 (d, *J* = 8.1 Hz, 2H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.3, 145.9, 140.5, 139.3, 138.3, 137.3, 131.7, 130.5, 128.9, 128.8, 128.2, 128.2, 127.9, 127.6, 127.1, 126.5, 125.1, 124.0, 121.4, 120.7, 118.4, 116.8, 95.6, 33.4, 26.9 ppm. **HRMS:** $[M+H]^+$ *calcd*. For $C_{31}H_{25}O_2^+$ m/z: 429.1849; found: 429.1848. **$[\alpha]_D^{20}$** +195.6 (*c* = 1.27 in $CHCl_3$). The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

2-methylallyl(4*S*,4a*R*,10a*S*)-4-phenyl-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (13)



To a solvent of **5a** (32mg, 0.1 mmol) in MeOH (400 µL) was added LiOH (0.2 mmol, 2.0 eq.). The reaction mixture was stirred at room temperature for 12 h. After the reaction completed (detected by TLC), the reaction mixture was acidified to pH=1 with 1 N HCl. The mixture was then extracted with ethyl acetate (3 x 10mL) until no product was visible in TLC, the organic layer was dried with Na_2SO_4, filtered and the solvent was removed under vacuum to get crude product **15** as a white solid. To a solvent of **15** in dry DMF (200 µL) was added KI (33 mg, 2.0 eq.), K_2CO_3 (28 mg, 2.0 eq.) and 3-chloro-2-methylprop-1-ene (20 µL, 2.0 eq.) The solution was stirred at room temperature for 12 h. After completion of the reaction, the reaction mixture was purified by flash chromatography to get **13** as a light yellow oil (34 mg, 94%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 10.0, 4.6 Hz, 2H), 7.29 (dd, *J* = 8.4, 6.2 Hz, 1H), 7.17 (dd, *J* = 9.9, 3.0 Hz, 3H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.96 – 6.89 (m, 2H), 6.26 (d, *J* = 3.3 Hz, 1H), 5.76 (d, *J* = 2.0 Hz, 1H), 5.03 (s, 1H), 4.96 (s, 1H), 4.67 (dd, *J* = 32.1, 13.1 Hz, 2H), 3.45 (dd, *J* = 7.9, 3.3 Hz, 1H), 2.92 (dd, *J* = 16.8, 5.7 Hz, 1H), 2.71 (dd, *J* = 16.8, 5.6 Hz, 1H), 2.39 (dtd, *J* = 7.8, 5.7, 2.0 Hz, 1H), 1.79 (s, 3H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 161.7, 151.3, 141.7, 140.8, 139.4, 129.3, 128.9, 128.3, 128.0, 127.3, 121.7, 119.3, 117.1, 113.8, 113.5, 94.7, 68.5, 39.3, 36.0, 26.7, 19.6 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{23}H_{22}NaO_4^+$ m/z: 385.1410; found: 385.1414. **$[\alpha]_D^{20}$** +32.2 (*c* = 1.74 in $CHCl_3$). The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

Methyl(4*S*,4a*R*,10a*S*)-4-hydroxy-4-phenyl-4a,10a-dihydro-4*H*,5*H*-pyrano[2,3-*b*]chromene-2-carboxylate (14)

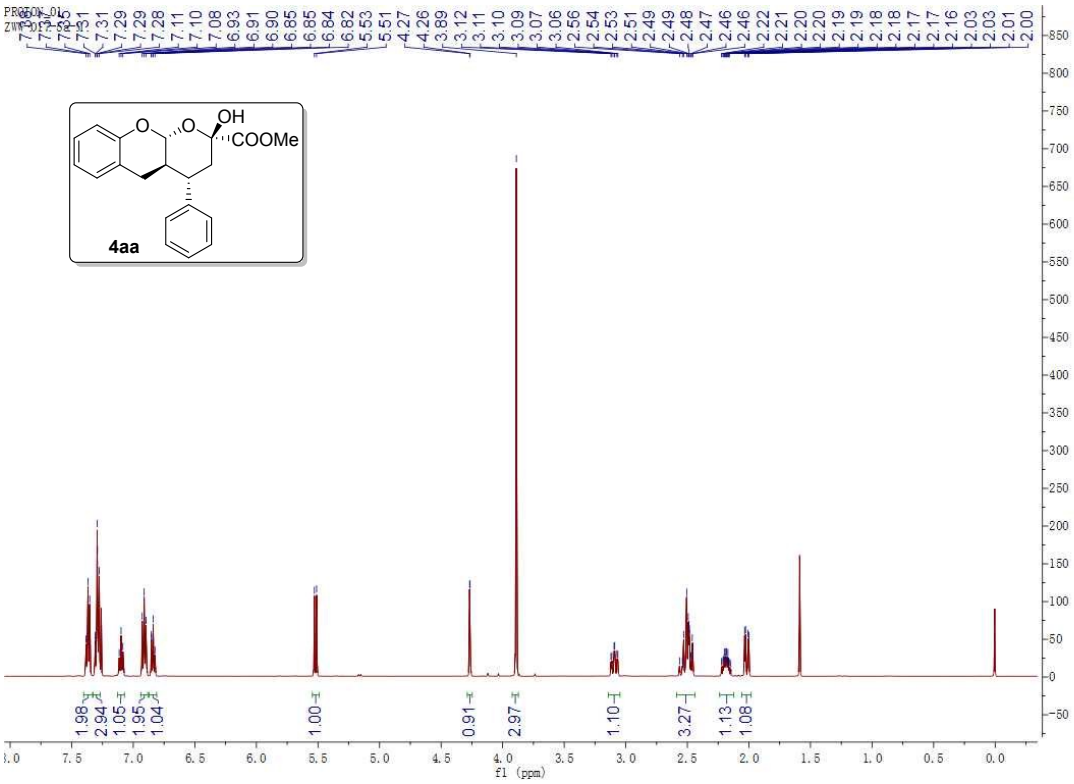


5a **14**
45% yield

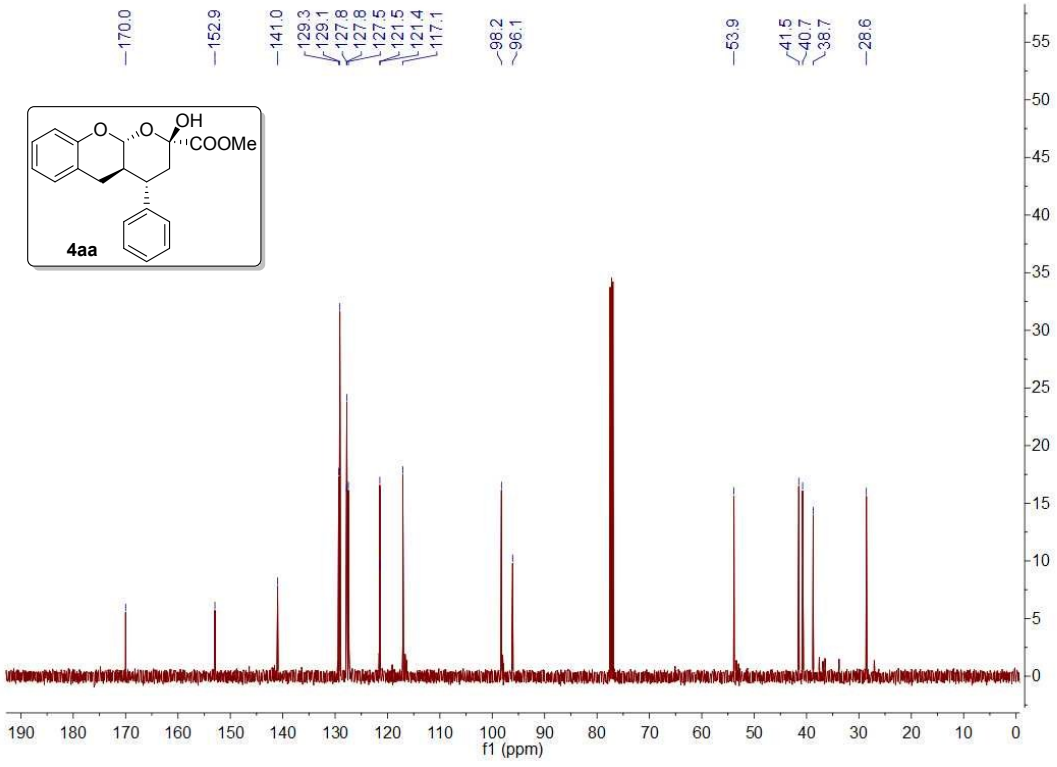
To a solvent of **5a** (32 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) with a magnetic rotor was added DBU (15 mg, 1.0 eq., 0.1 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. After the reaction completed (detected by TLC), reaction mixture was purified by column chromatograph on a silica gel (petroleum ether/ethyl acetate = 10/1) to get product **14** as a white solid (15 mg, 45%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, J = 7.3 Hz, 2H), 7.41 (dt, J = 20.9, 7.0 Hz, 3H), 7.11 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 8.1 Hz, 1H), 6.86 – 6.77 (m, 2H), 6.42 (d, J = 1.2 Hz, 1H), 6.13 (s, 1H), 3.84 (s, 3H), 2.53 – 2.44 (m, 2H), 2.35 – 2.25 (m, 1H), 1.69 (dd, J = 16.1, 5.6 Hz, 1H) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$) δ 162.7, 150.9, 143.8, 142.6, 129.6, 128.8, 128.6, 127.9, 126.1, 121.9, 120.9, 117.2, 112.4, 95.8, 73.1, 52.9, 40.3, 22.8 ppm. **HRMS:** $[M+Na]^+$ *calcd*. For $C_{20}H_{18}NaO_4^+$ m/z: 361.0837; found: 361.0842. **$[\alpha]_D^{20}$** +174.9 (c = 0.51 in $CHCl_3$). The diastereomeric ratio was determined by ^{1}H NMR, ***dr* >20:1**.

L. NMR spectra and HPLC traces

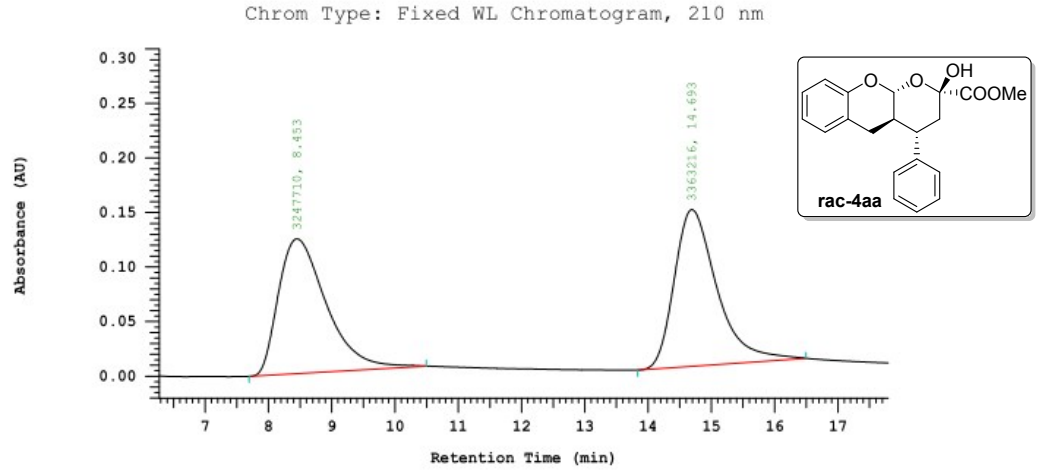
The ^{1}H NMR spectrum of 4aa (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4aa (125 MHz, $CDCl_3$)



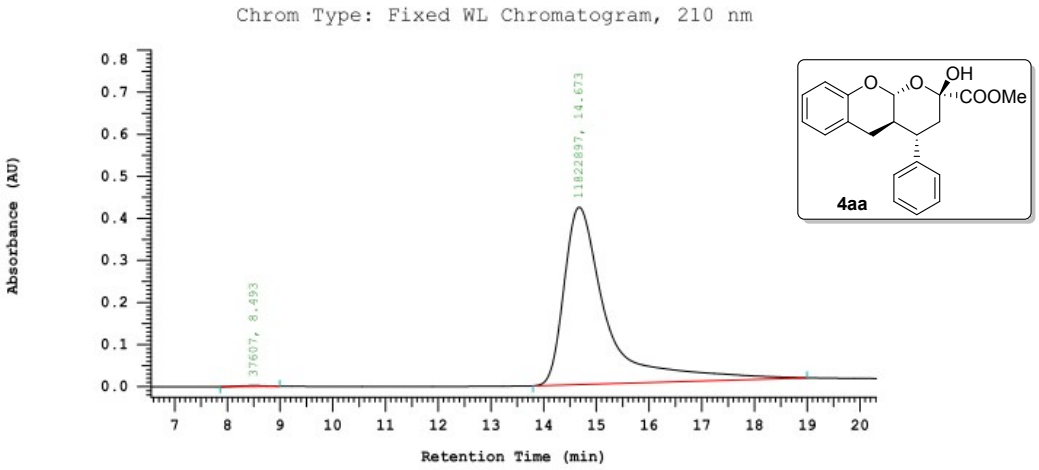
The HPLC of racemic 4aa



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.453	3247710	49.126	BB
2	14.693	3363216	50.874	BB
		6610926	100.000	

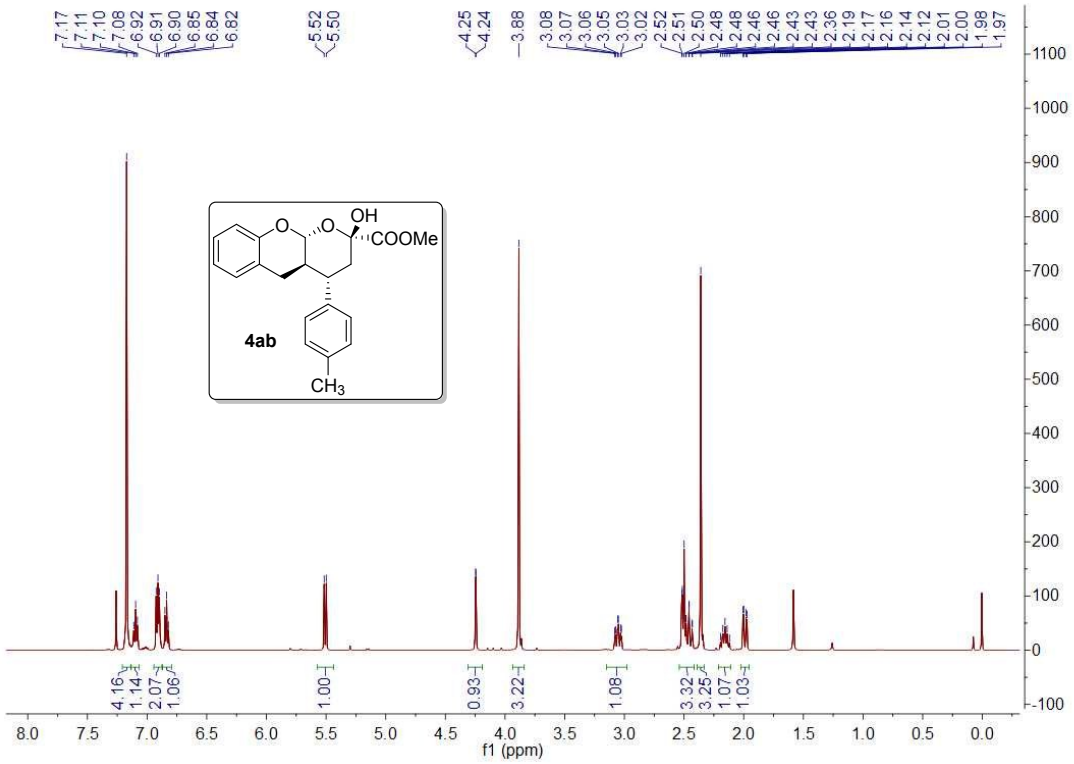
The HPLC of chiral 4aa



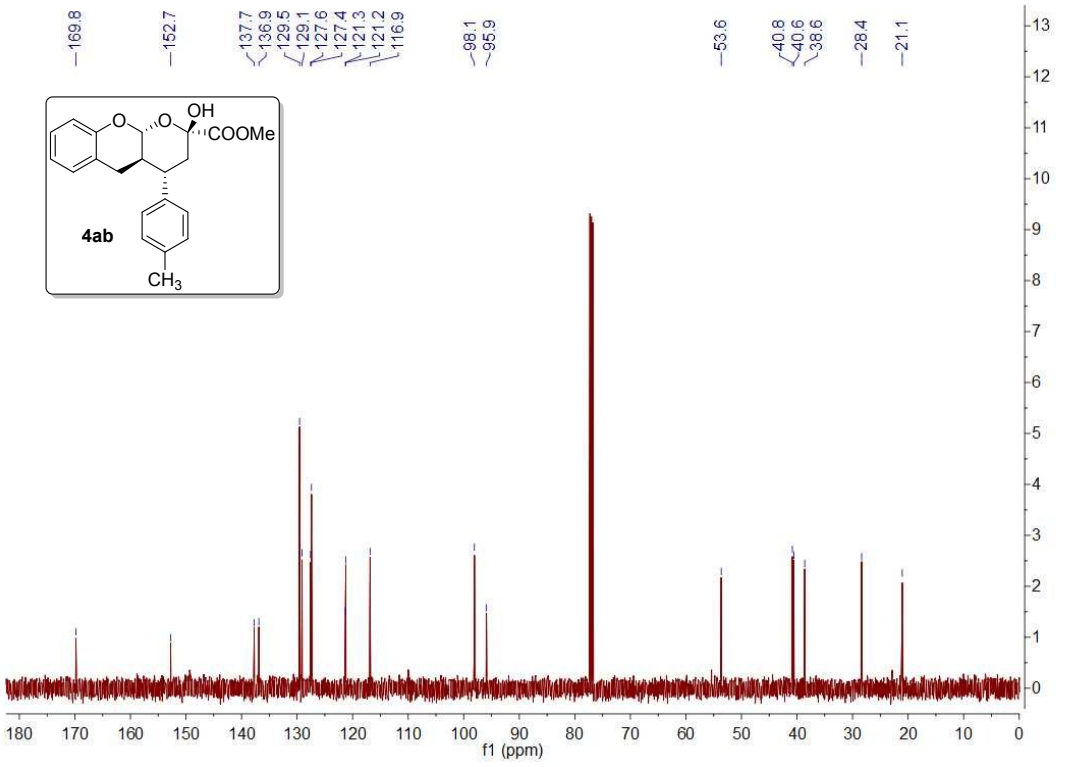
Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.493	37607	0.317	BB
2	14.673	11822897	99.683	BB
		11860504	100.000	

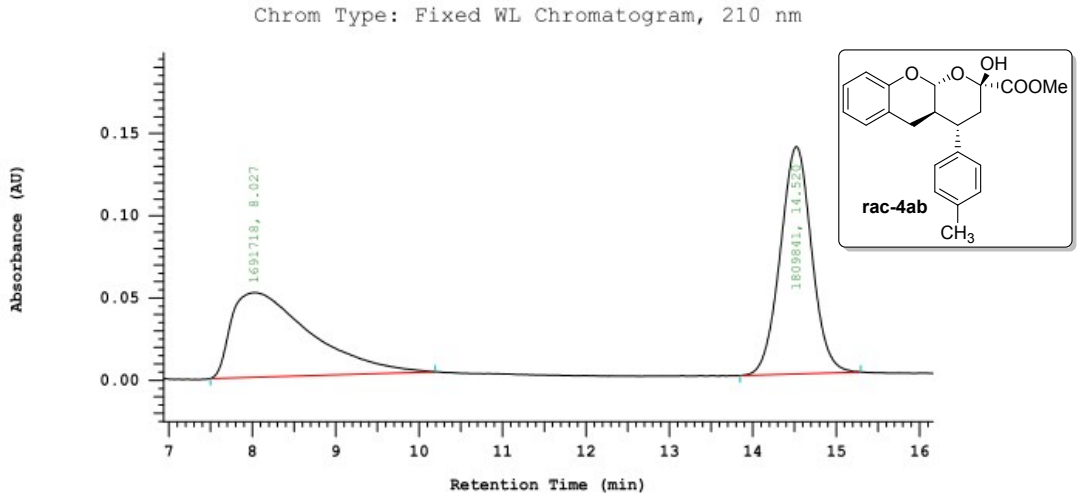
The ^{1}H NMR spectrum of 4ab (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4ab (125 MHz, $CDCl_3$)



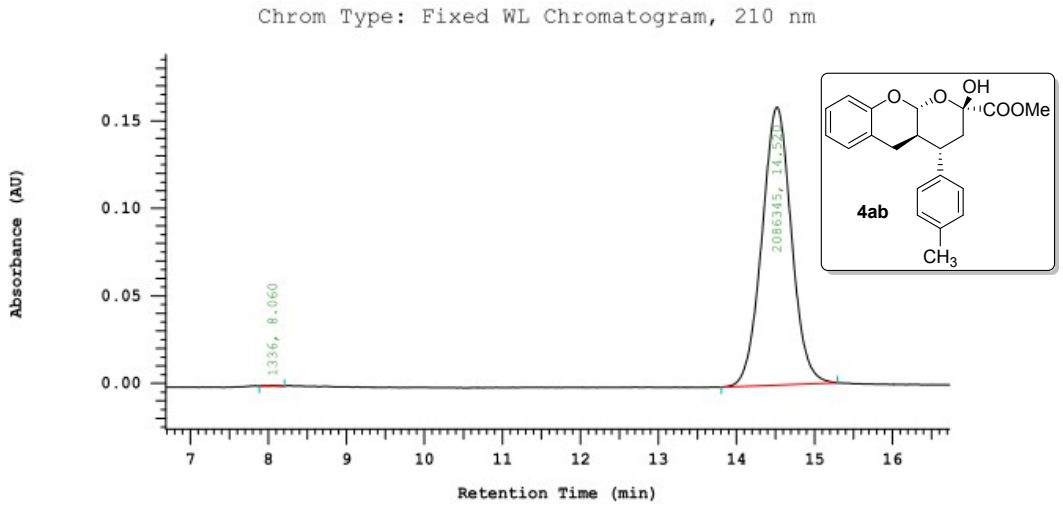
The HPLC of racemic 4ab



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.027	1691718	48.313	BB
2	14.520	1809841	51.687	BB
		3501559	100.000	

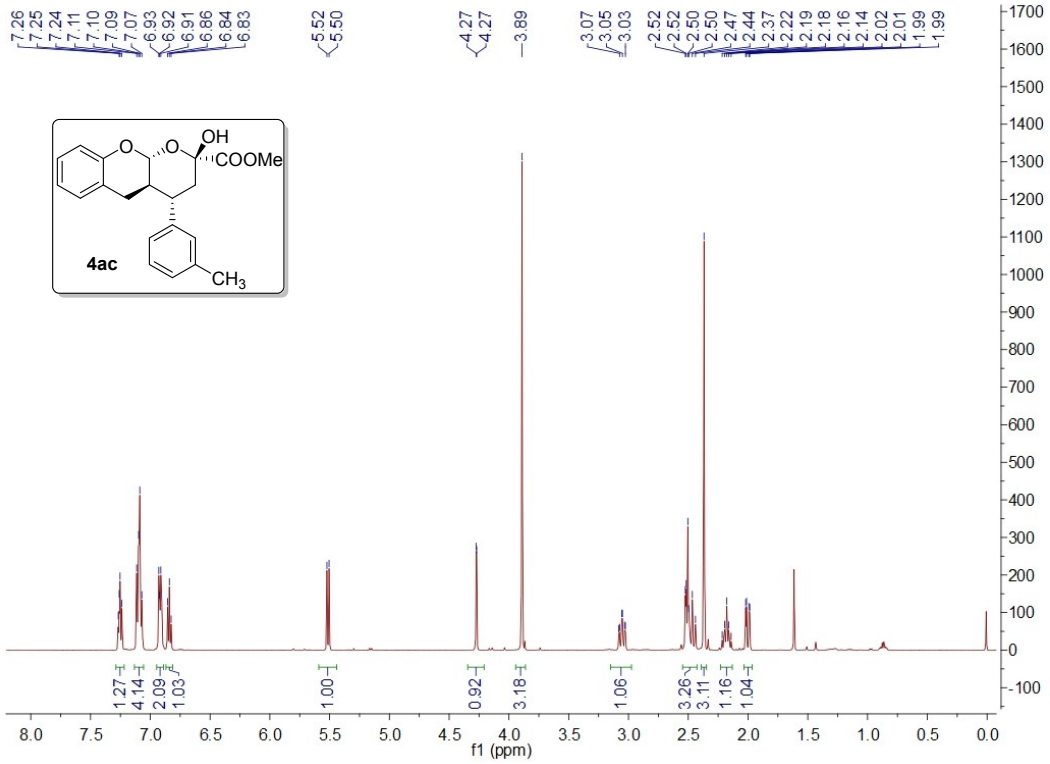
The HPLC of chiral 4ab



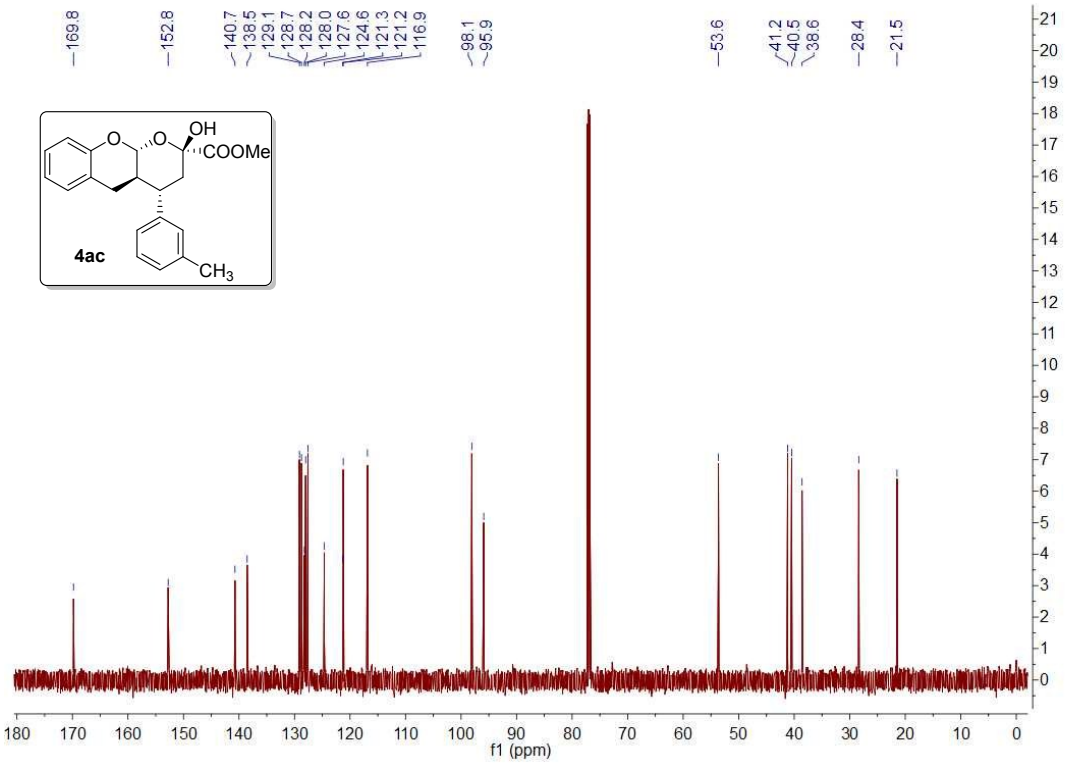
Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.060	1336	0.064	BB
2	14.520	2086345	99.936	BB
		2087681	100.000	

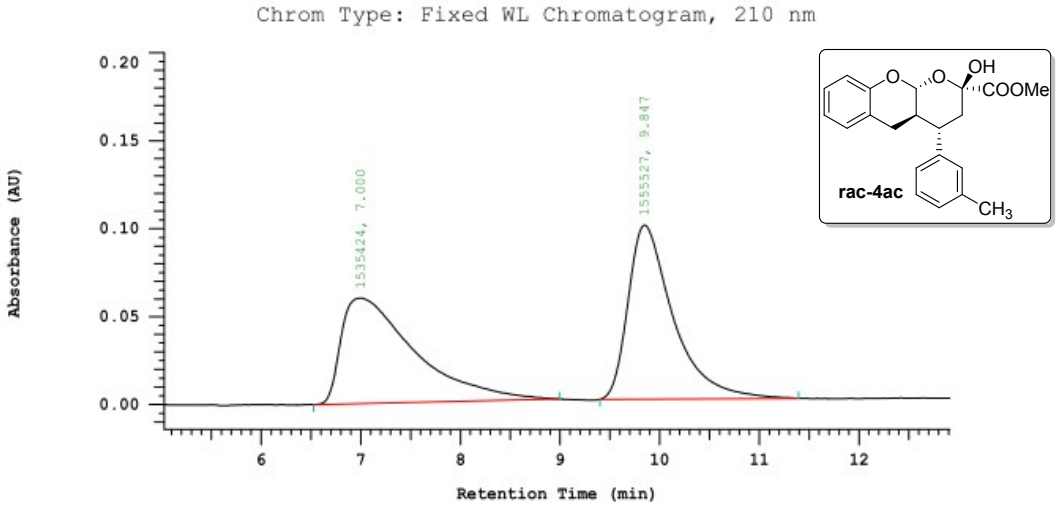
The ^{1}H NMR spectrum of 4ac (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4ac (125 MHz, $CDCl_3$)



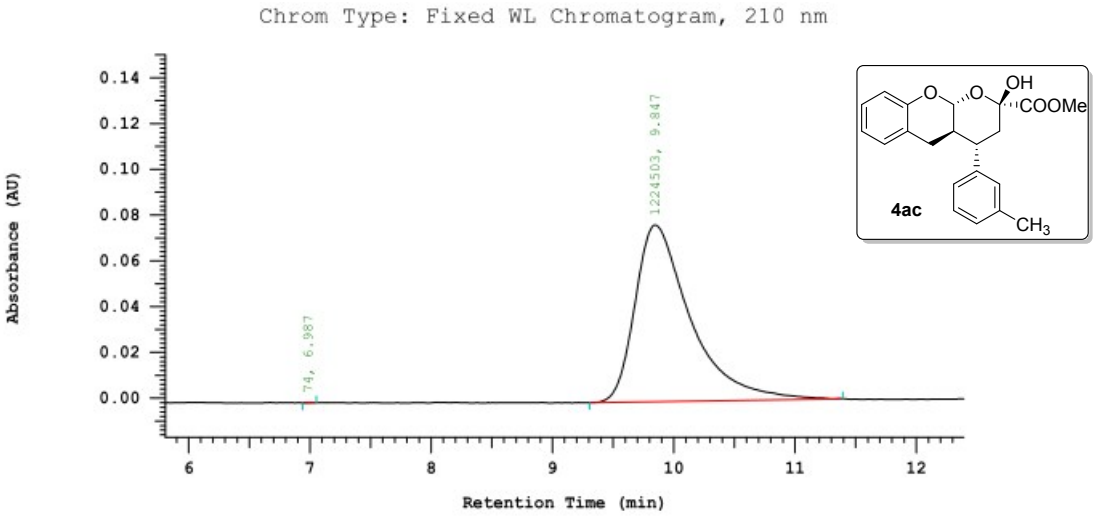
The HPLC of racemic 4ac



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.000	1535424	49.675	BB
2	9.847	1555527	50.325	BB
		3090951	100.000	

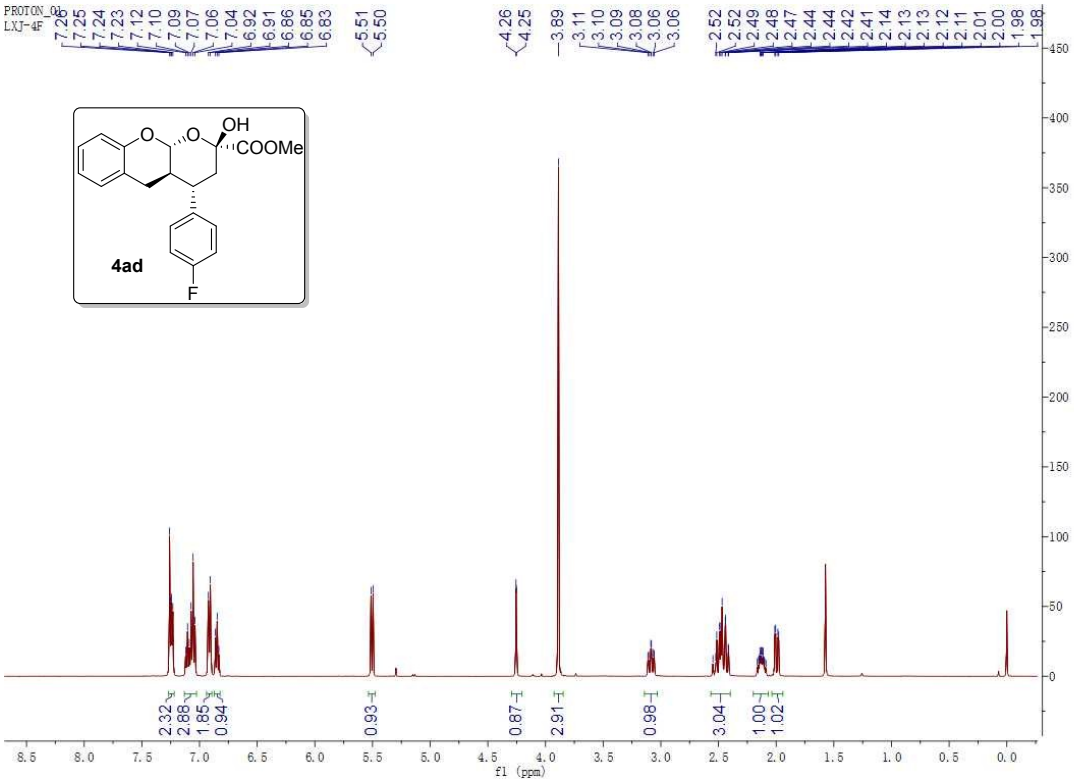
The HPLC of chiral 4ac



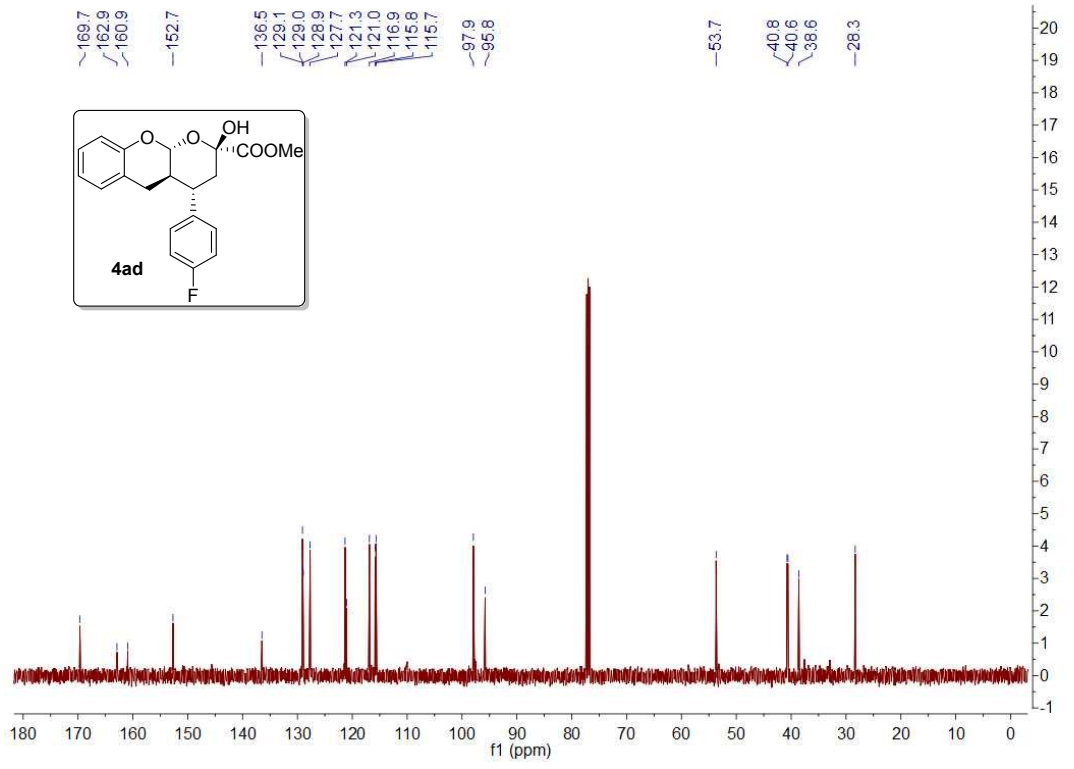
Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.987	74	0.006	BB
2	9.847	1224503	99.994	BB
		1224577	100.000	

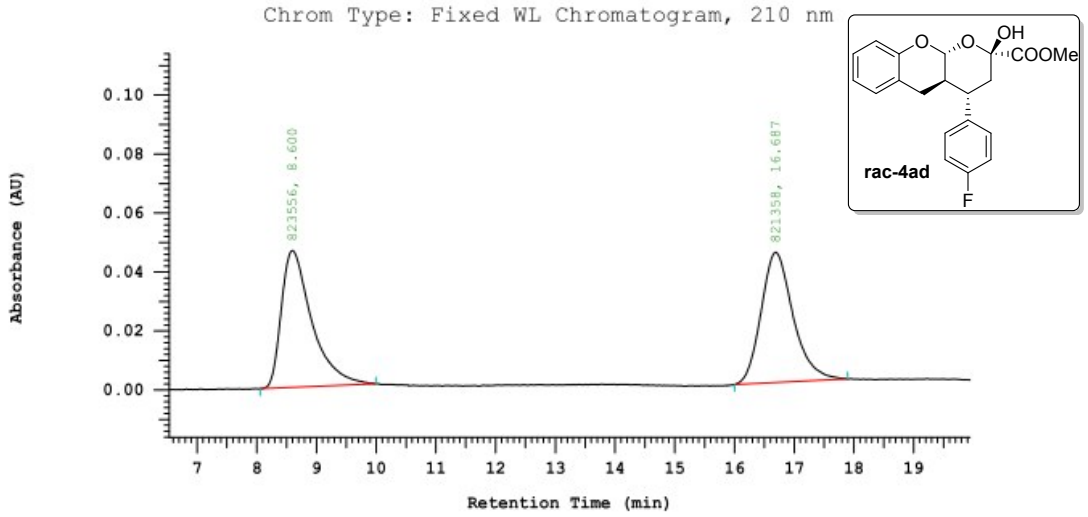
The ^{1}H NMR spectrum of 4ad (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4ad (125 MHz, $CDCl_3$)



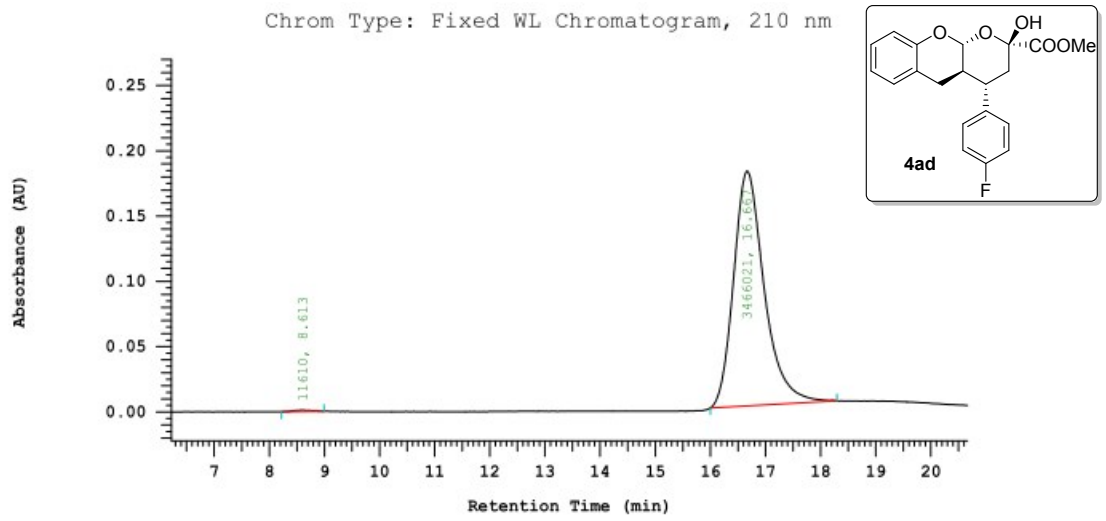
The HPLC of racemic 4ad



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.600	823556	50.067	BB
2	16.687	821358	49.933	BB
		1644914	100.000	

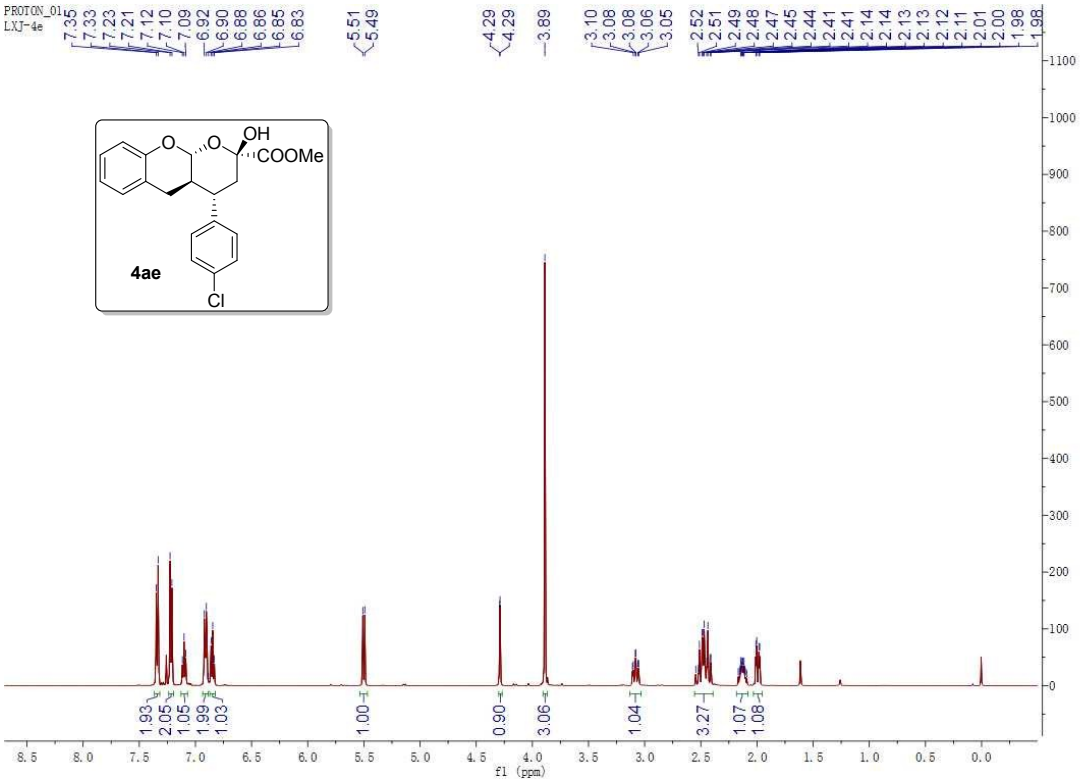
The HPLC of chiral 4ad



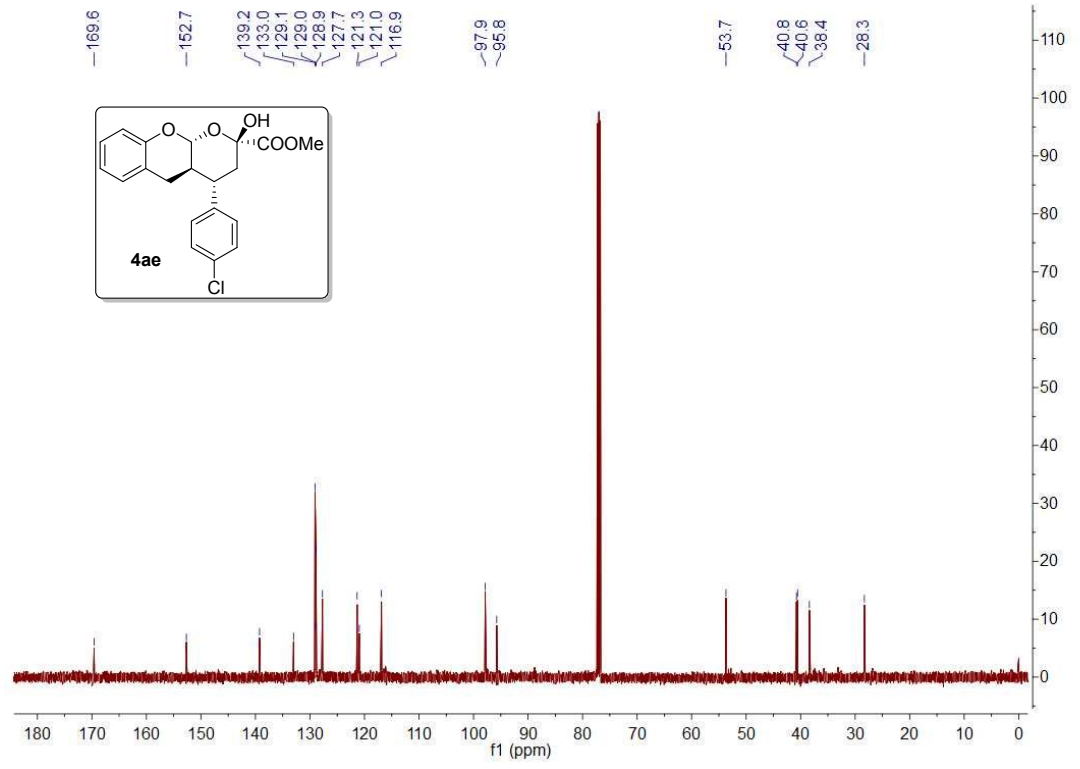
Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.613	11610	0.334	BB
2	16.667	3466021	99.666	BB
		3477631	100.000	

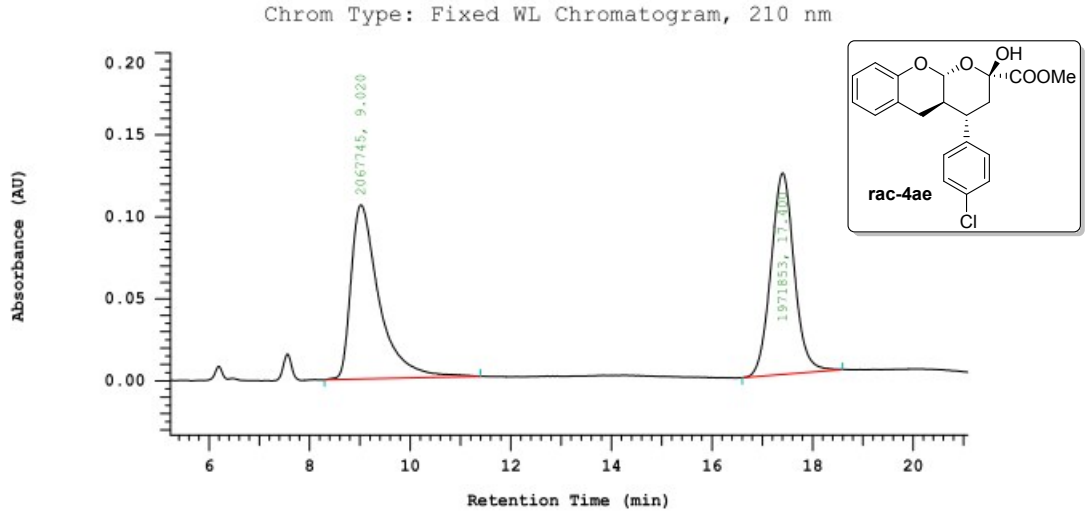
The ^{1}H NMR spectrum of 4ae (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4ae (125 MHz, $CDCl_3$)



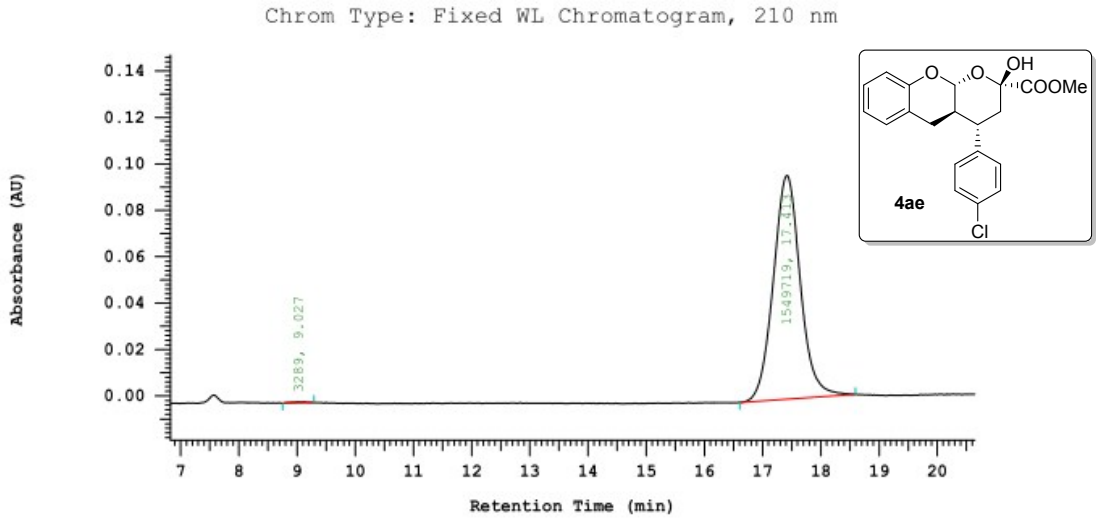
The HPLC of racemic 4ae



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.020	2067745	51.187	BB
2	17.400	1971853	48.813	BB
		4039598	100.000	

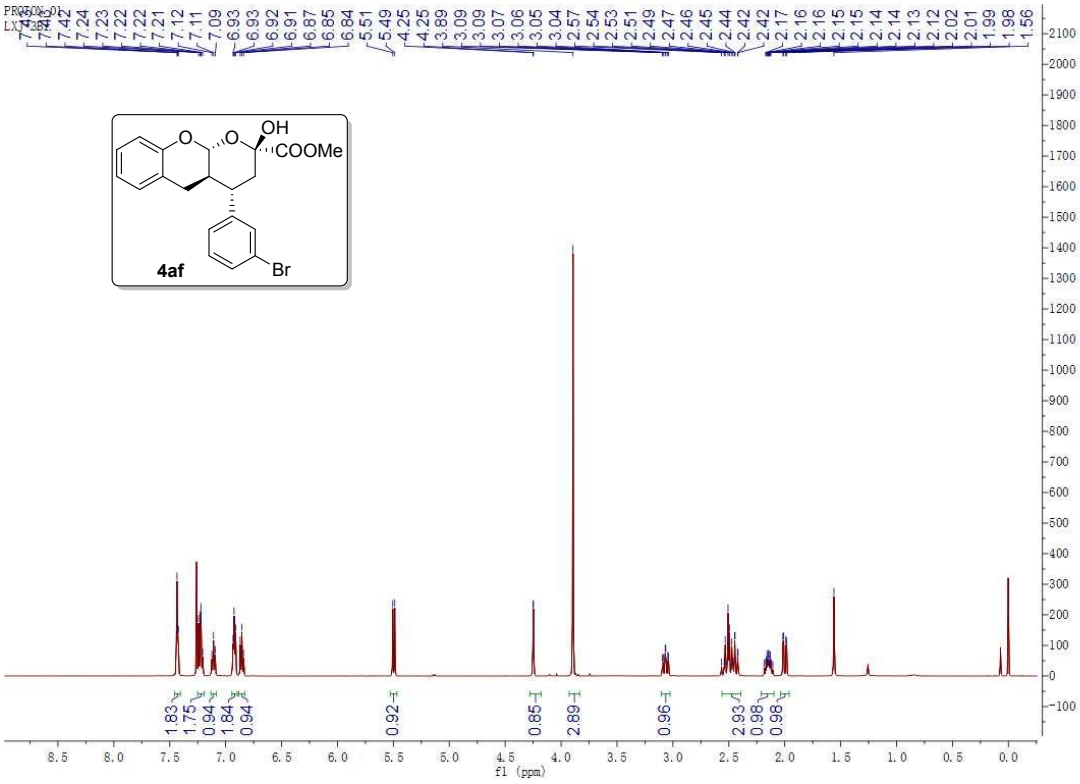
The HPLC of chiral 4ae



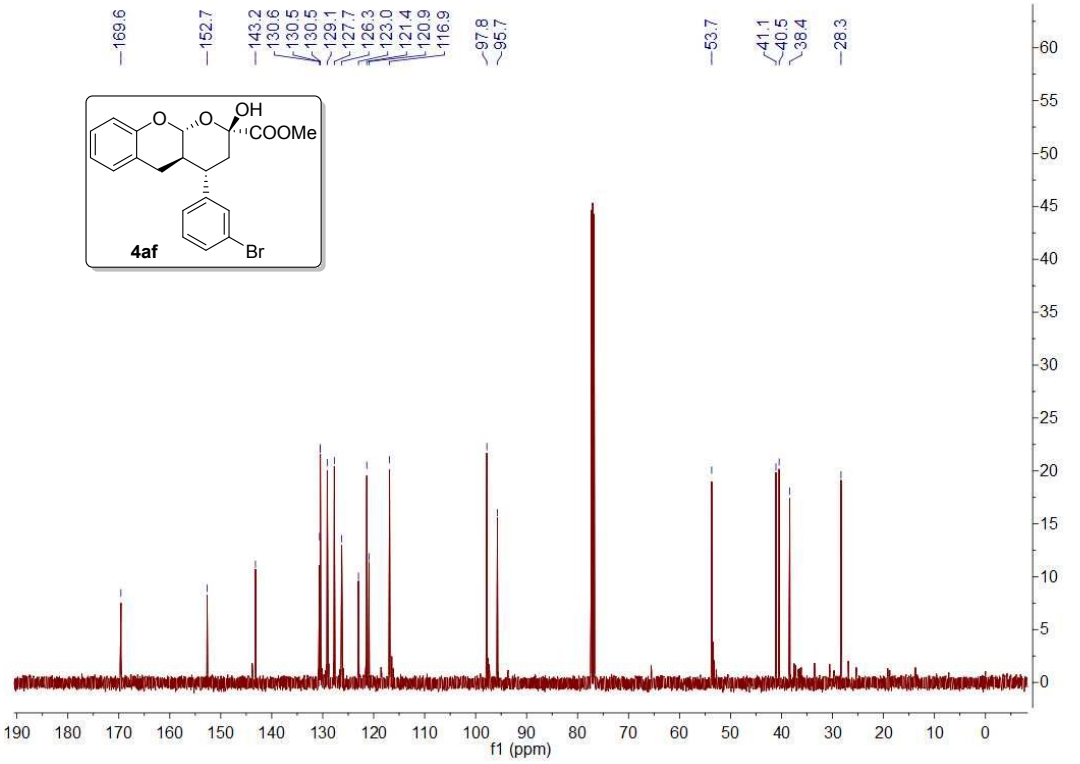
Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.027	3289	0.212	BB
2	17.413	1549719	99.788	BB
		1553008	100.000	

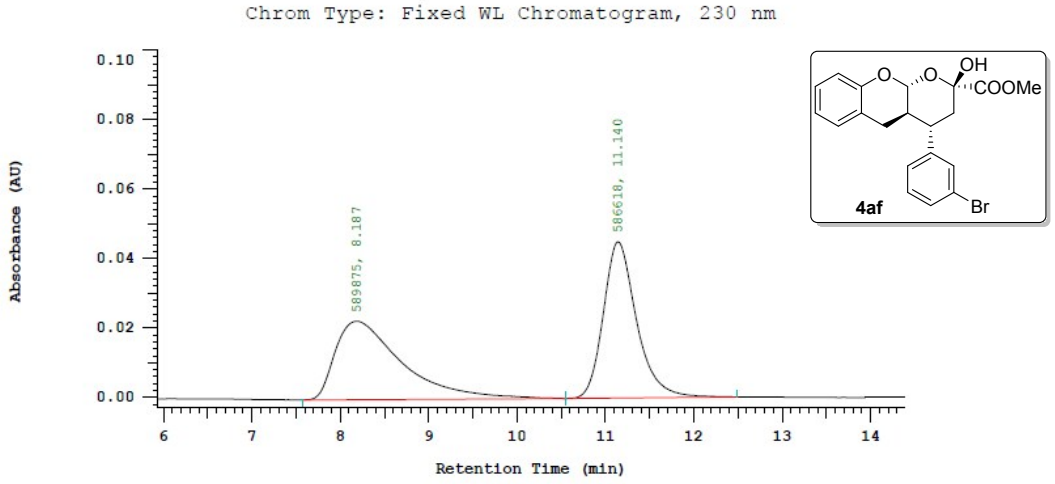
The ^{1}H NMR spectrum of 4af (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4af (125 MHz, $CDCl_3$)



The HPLC of racemic 4af



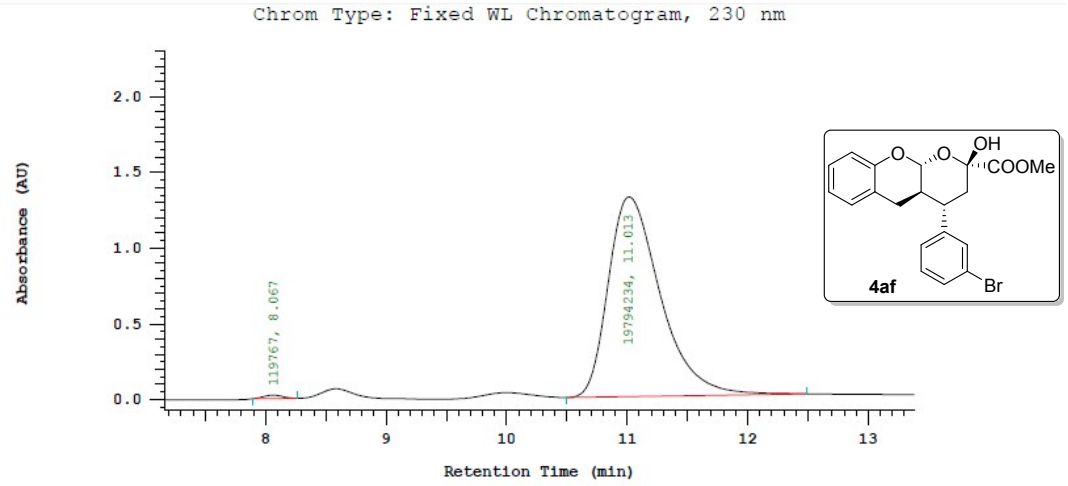
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.187	589875	50.138	BB
2	11.140	586618	49.862	BB
		1176493	100.000	

The HPLC of chiral 4af



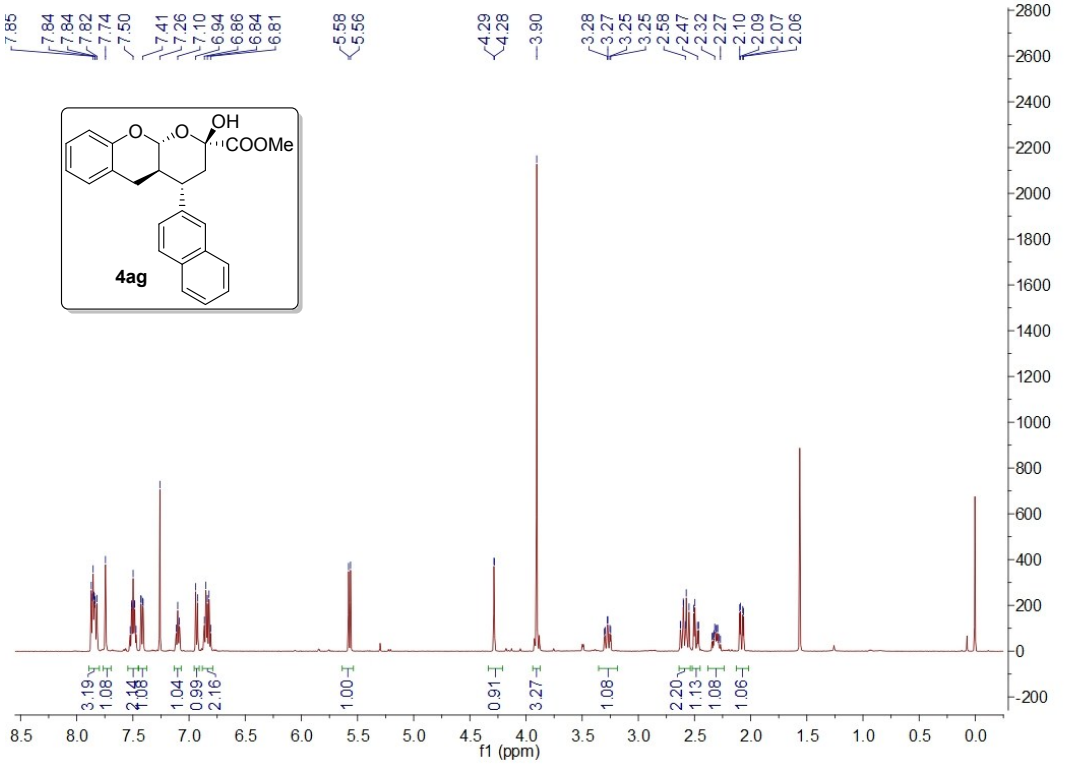
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

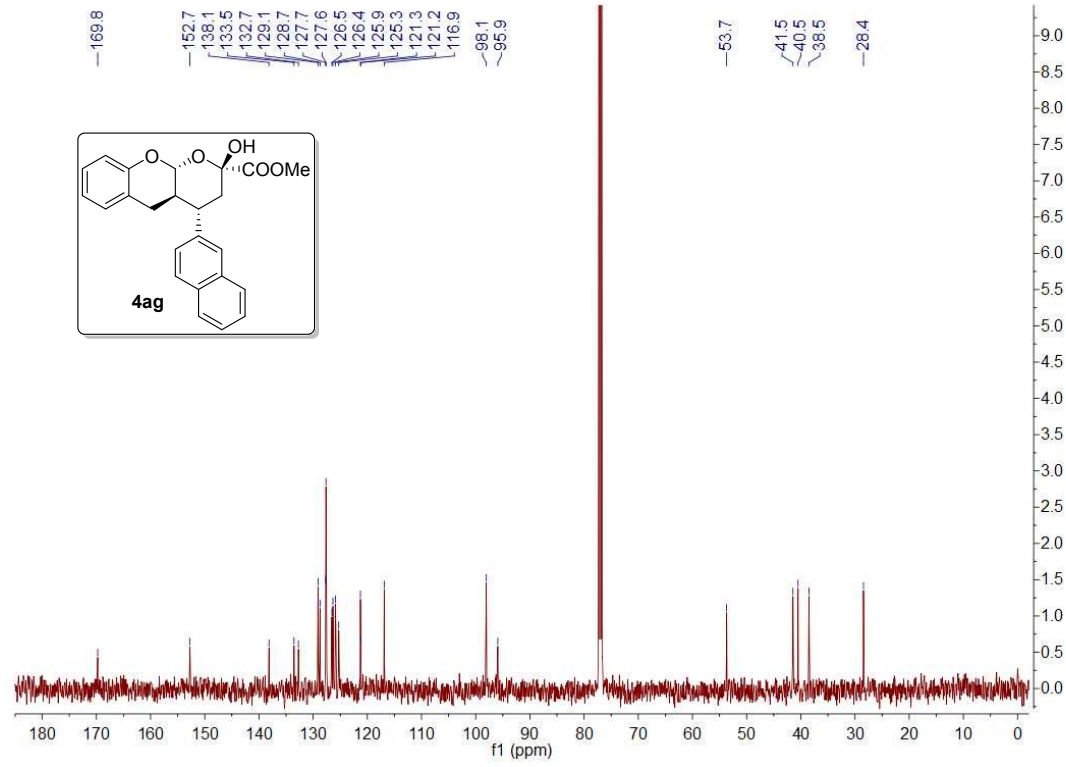
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.067	119767	0.601	BB
2	11.013	19794234	99.399	BB
		19914001	100.000	

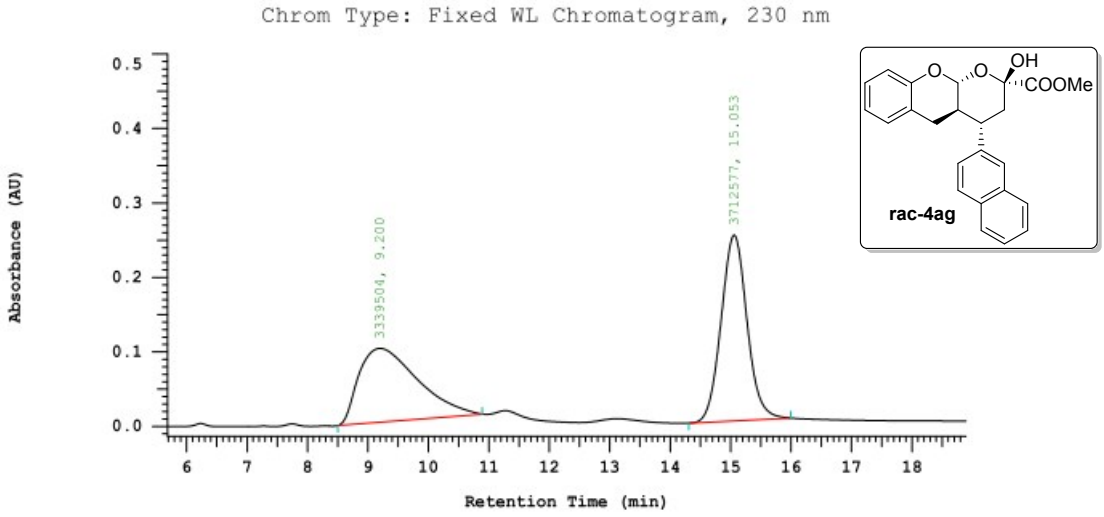
The ^{1}H NMR spectrum of 4ag (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4ag (125 MHz, $CDCl_3$)



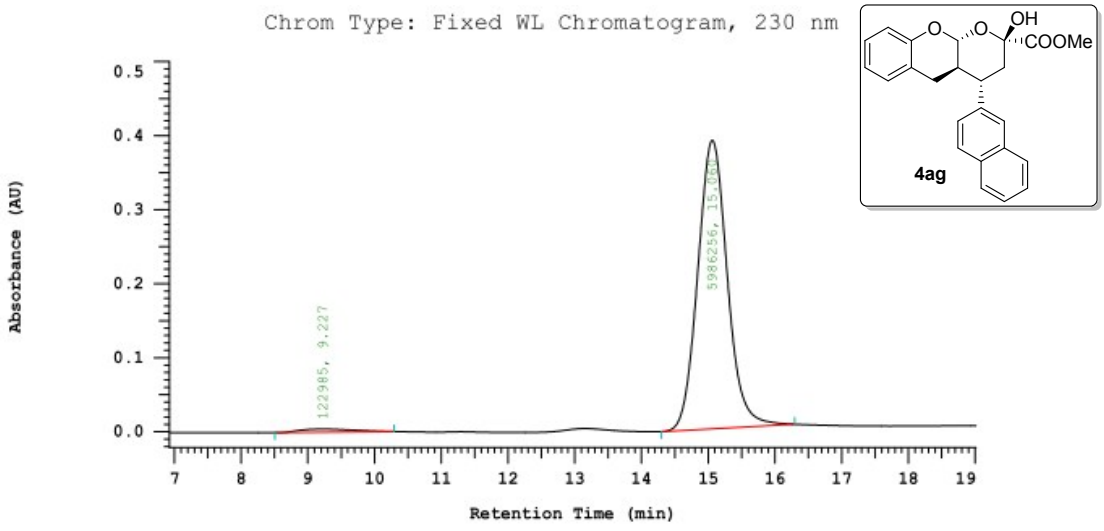
The HPLC of racemic 4ag



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.200	3339504	47.355	BB
2	15.053	3712577	52.645	BB
		7052081	100.000	

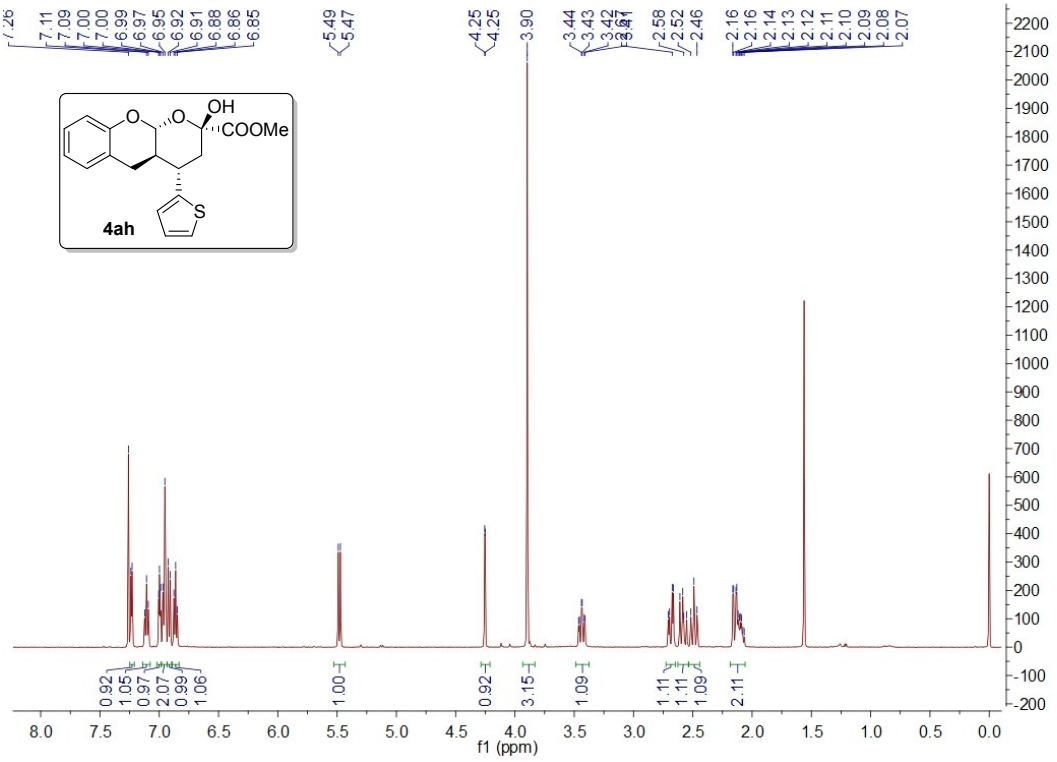
The HPLC of chiral 4g



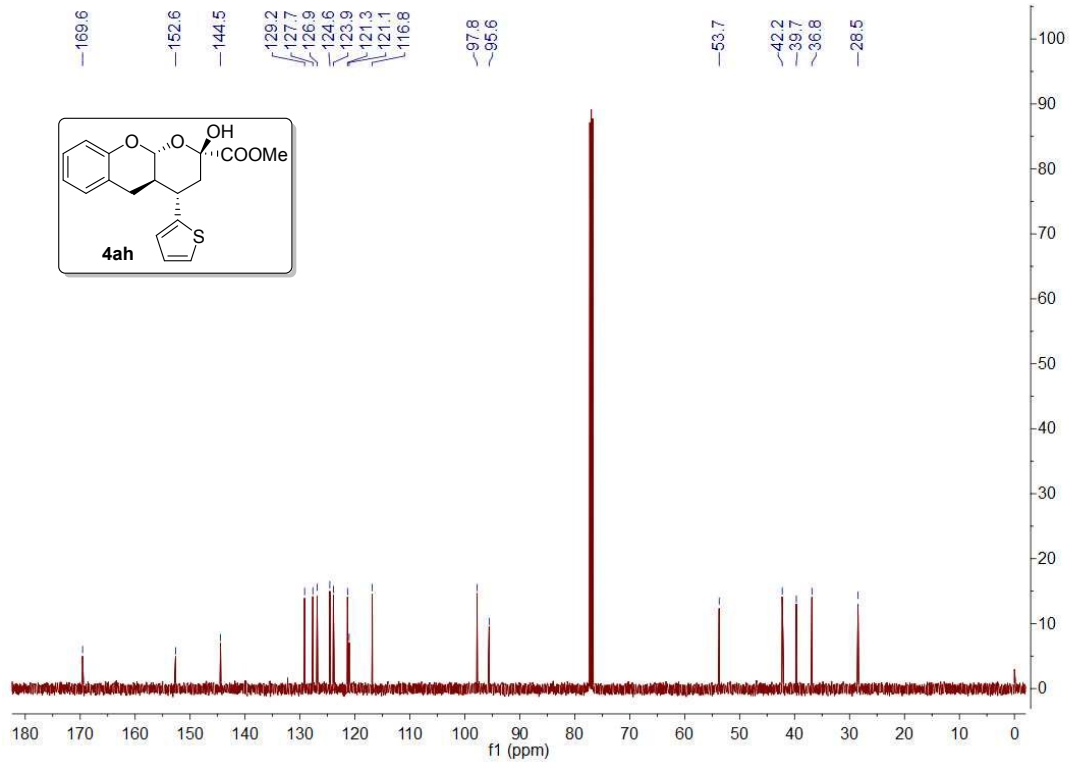
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.227	122985	2.013	BB
2	15.060	5986256	97.987	BB
		6109241	100.000	

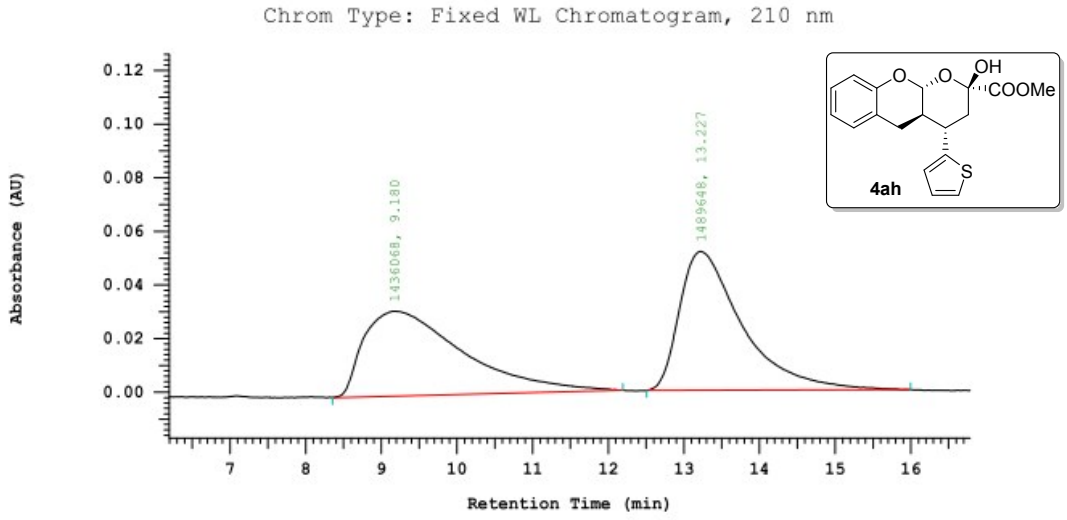
The ^{1}H NMR spectrum of 4ah (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4ah (125 MHz, $CDCl_3$)



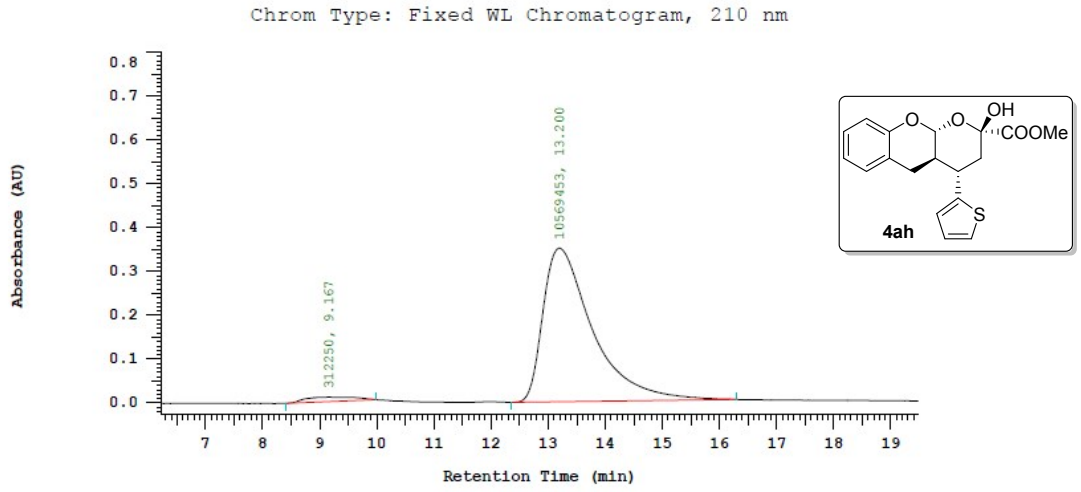
The HPLC of racemic 4ah



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.180	1436068	49.084	BB
2	13.227	1489648	50.916	BB
		2925716	100.000	

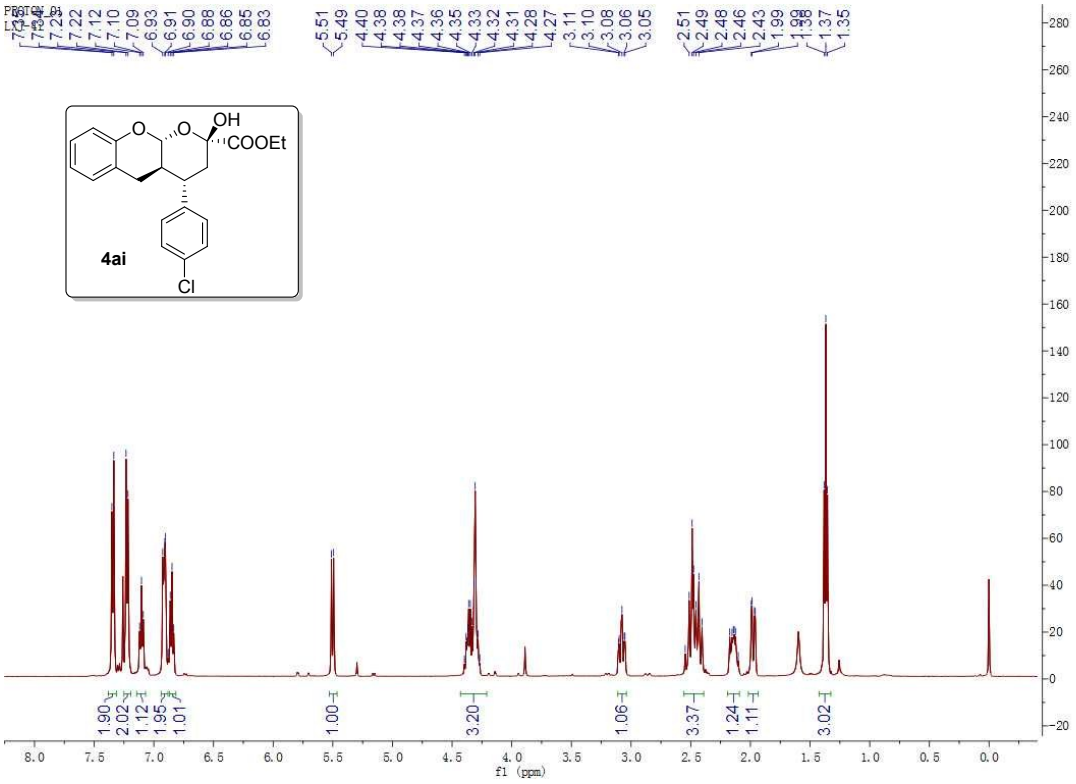
The HPLC of chiral 4ah



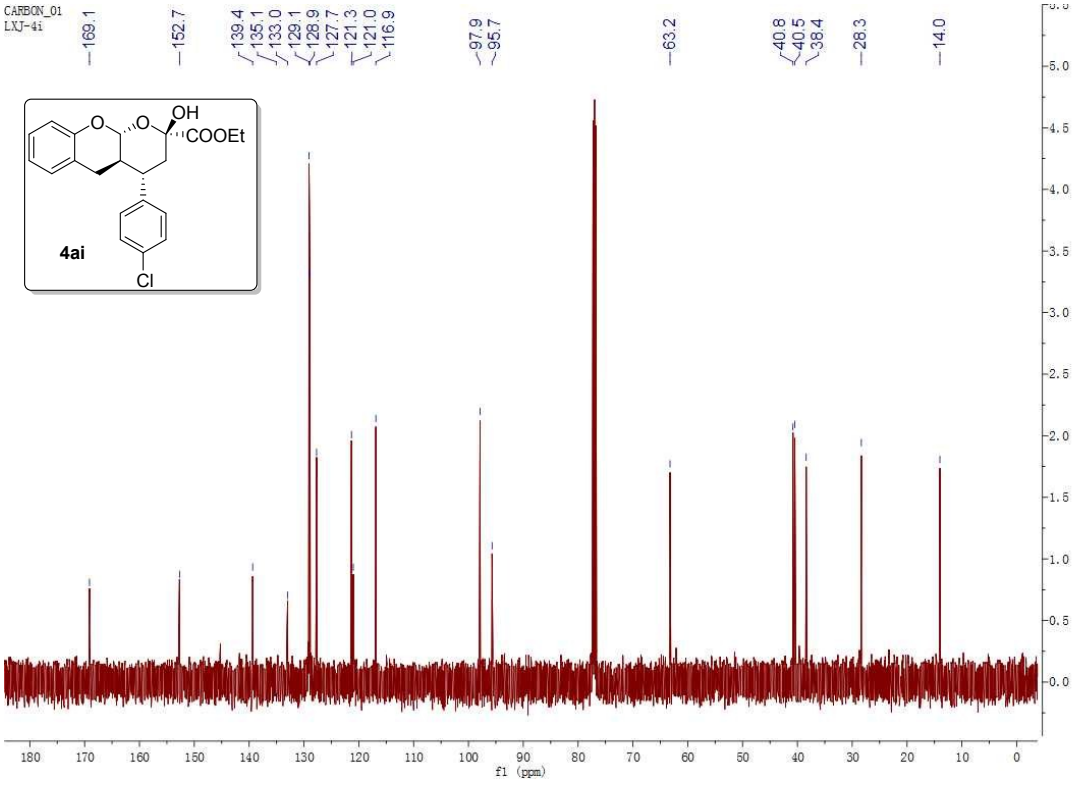
Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.167	312250	2.870	BB
2	13.200	10569453	97.130	BB
		10881703	100.000	

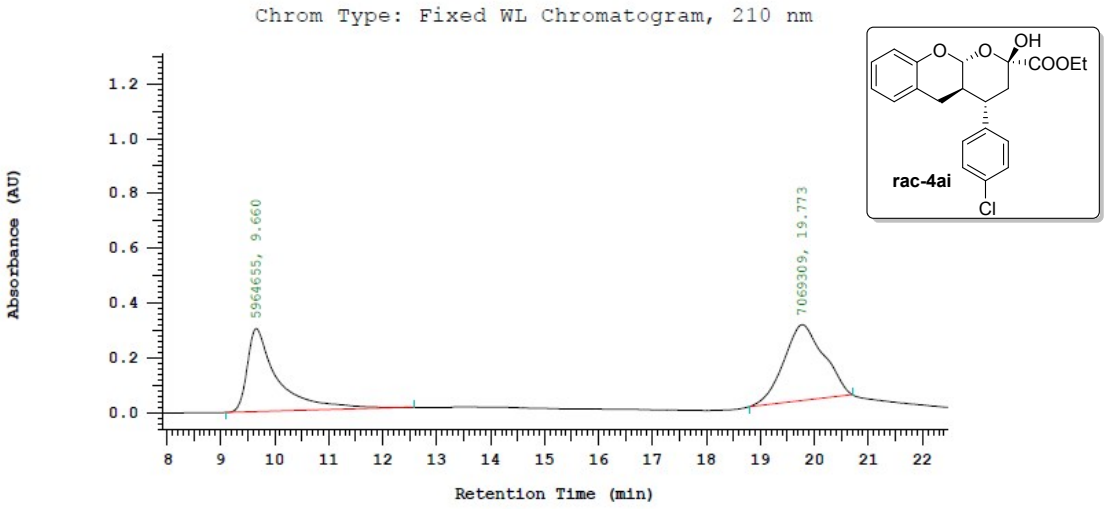
The ^{1}H NMR spectrum of 4ai (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 4ai (125 MHz, $CDCl_3$)



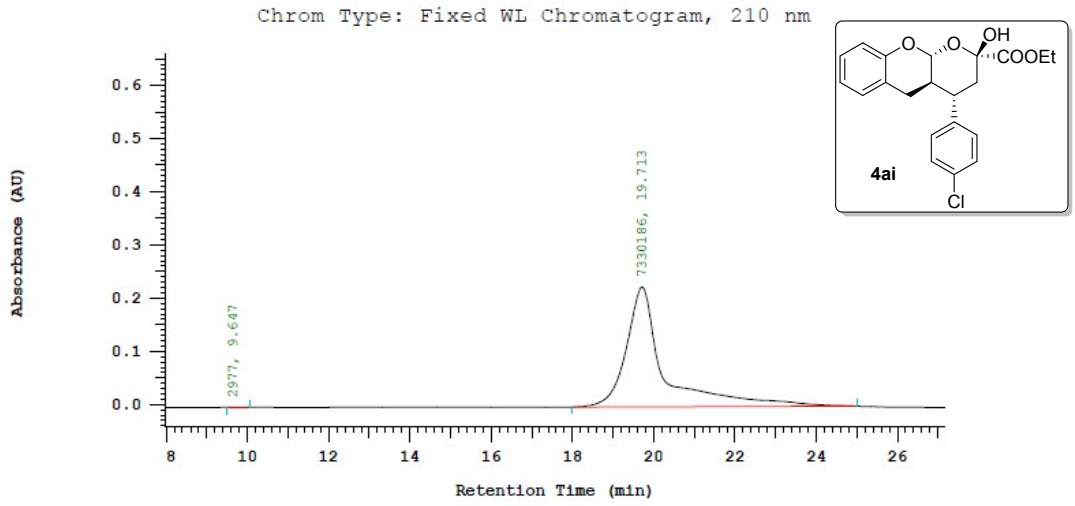
The HPLC of racemic 4ai



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.660	5964655	45.762	BB
2	19.773	7069309	54.238	BB
		13033964	100.000	

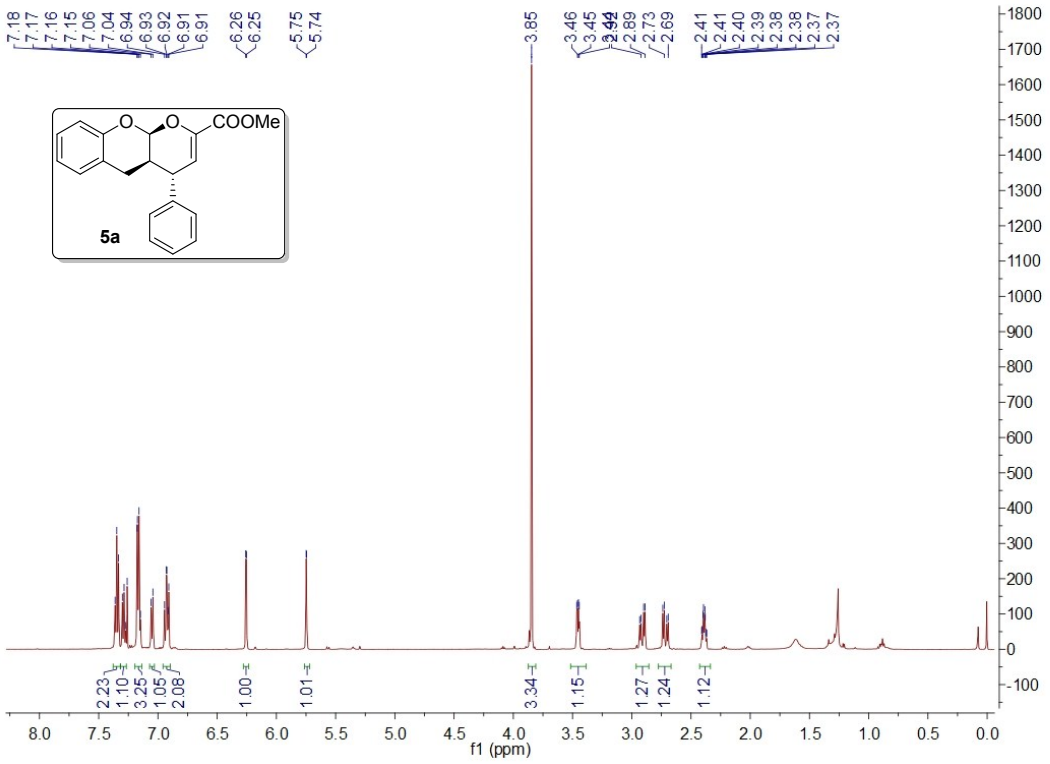
The HPLC of chiral 4ai



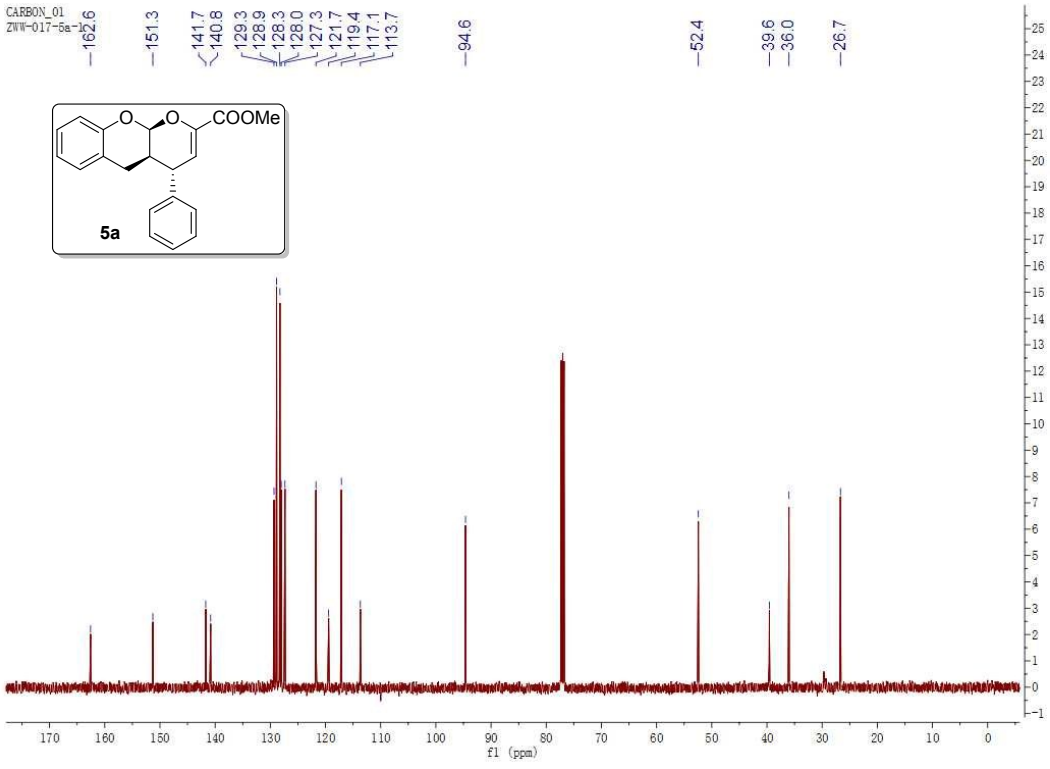
Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.647	2977	0.041	BB
2	19.713	7330186	99.959	BB
		7333163	100.000	

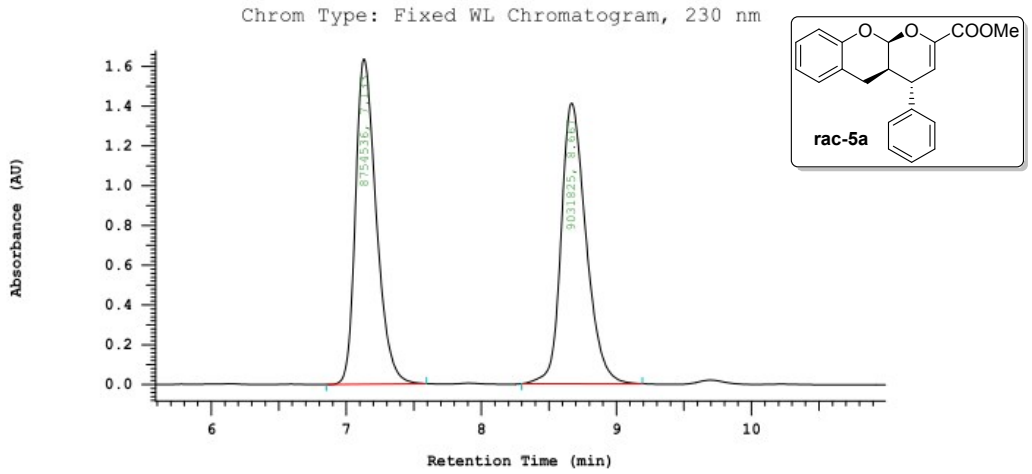
The ^{1}H NMR spectrum of 5a (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5a (125 MHz, $CDCl_3$)



The HPLC of racemic 5a



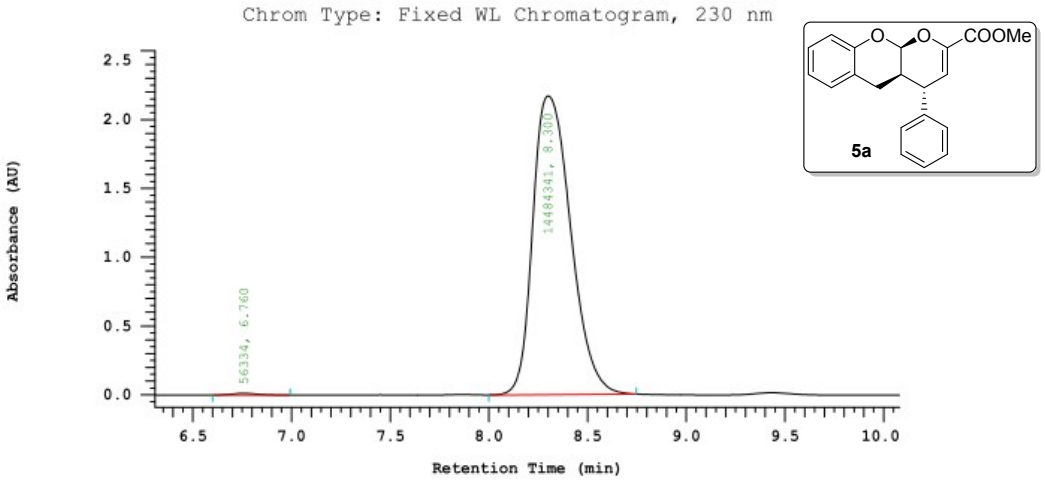
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.133	8754536	49.221	BB
2	8.667	9031825	50.779	BB
		17786361	100.000	

The HPLC of chiral 5a



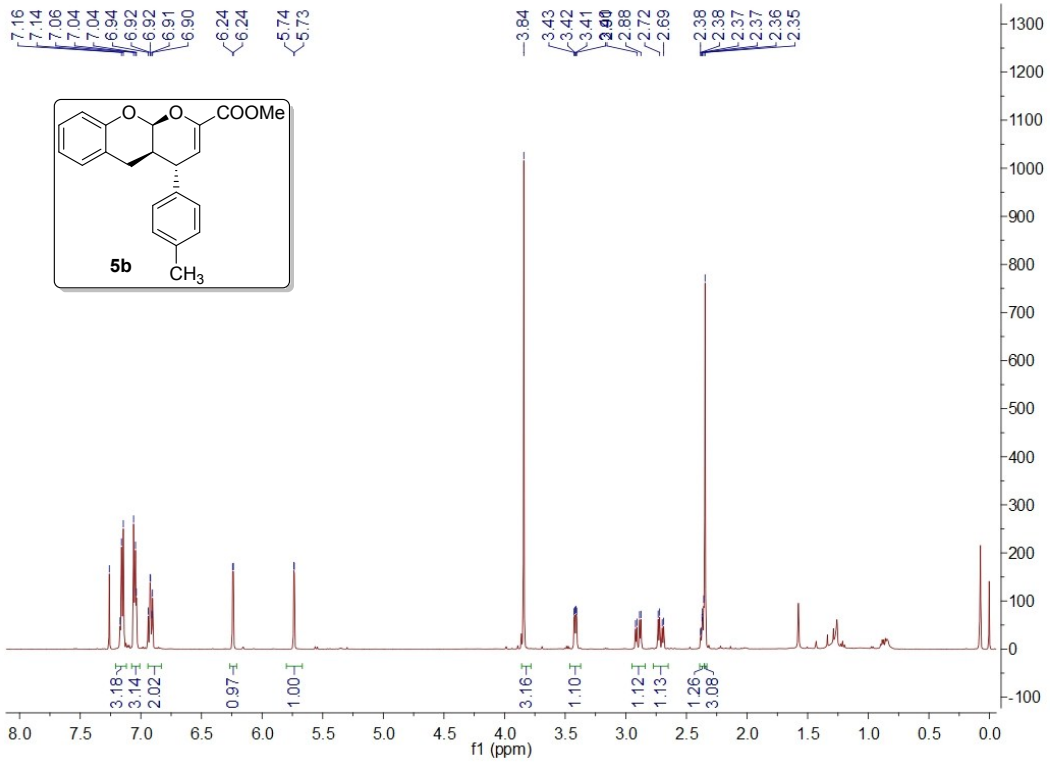
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

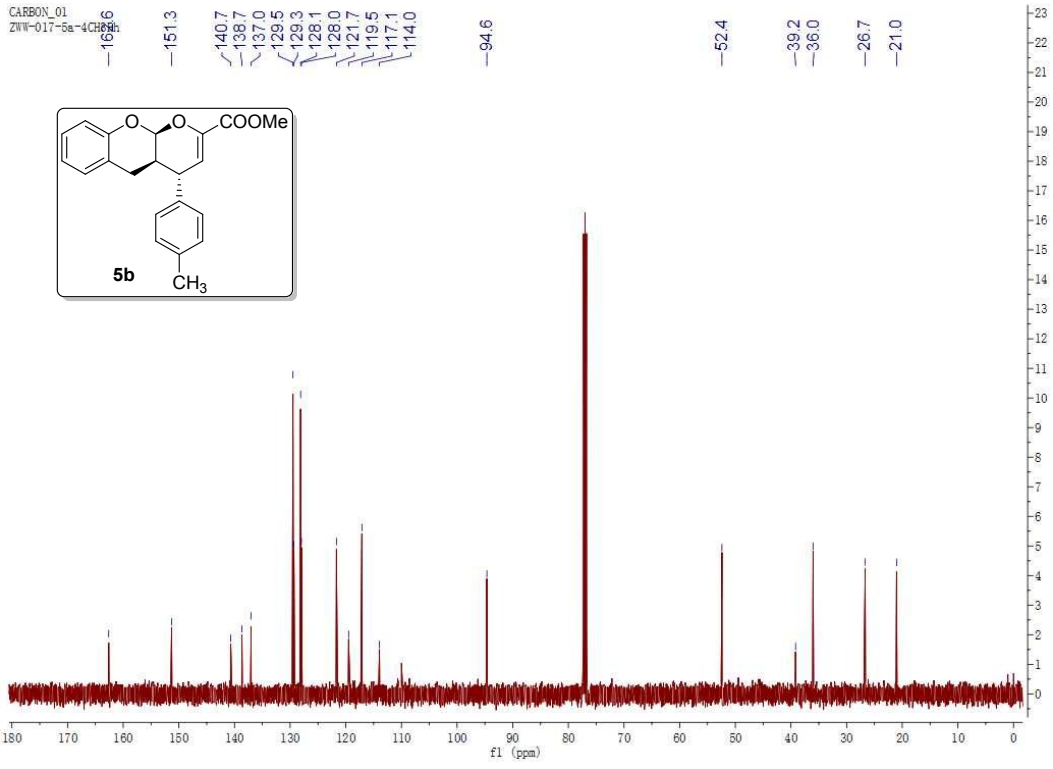
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.760	56334	0.387	BB
2	8.300	14484341	99.613	BB
		14540675	100.000	

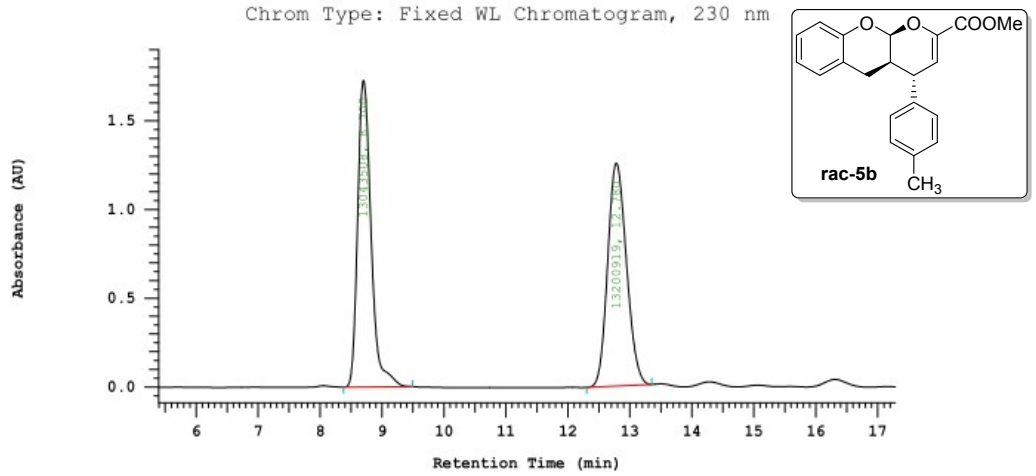
The ^{1}H NMR spectrum of 5b (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5b (125 MHz, $CDCl_3$)



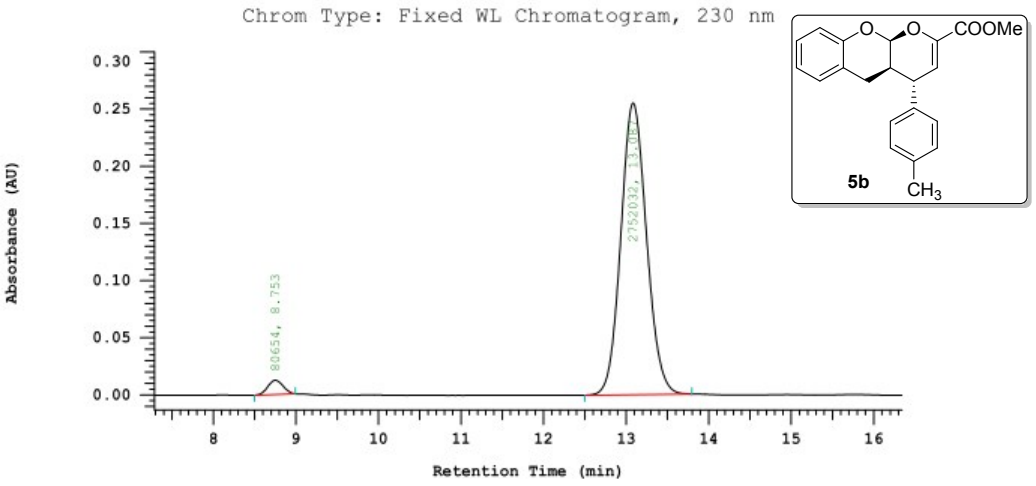
The HPLC of racemic 5b



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.700	13043508	49.700	BB
2	12.780	13200919	50.300	BB
		26244427	100.000	

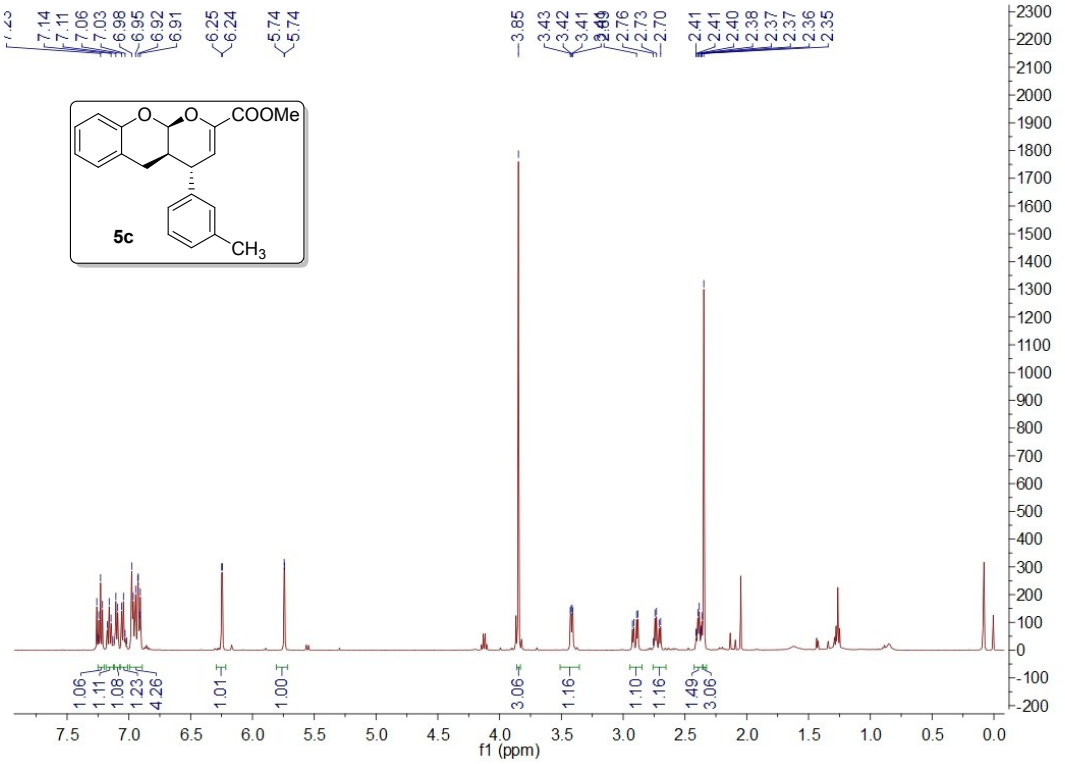
The HPLC of chiral 5b



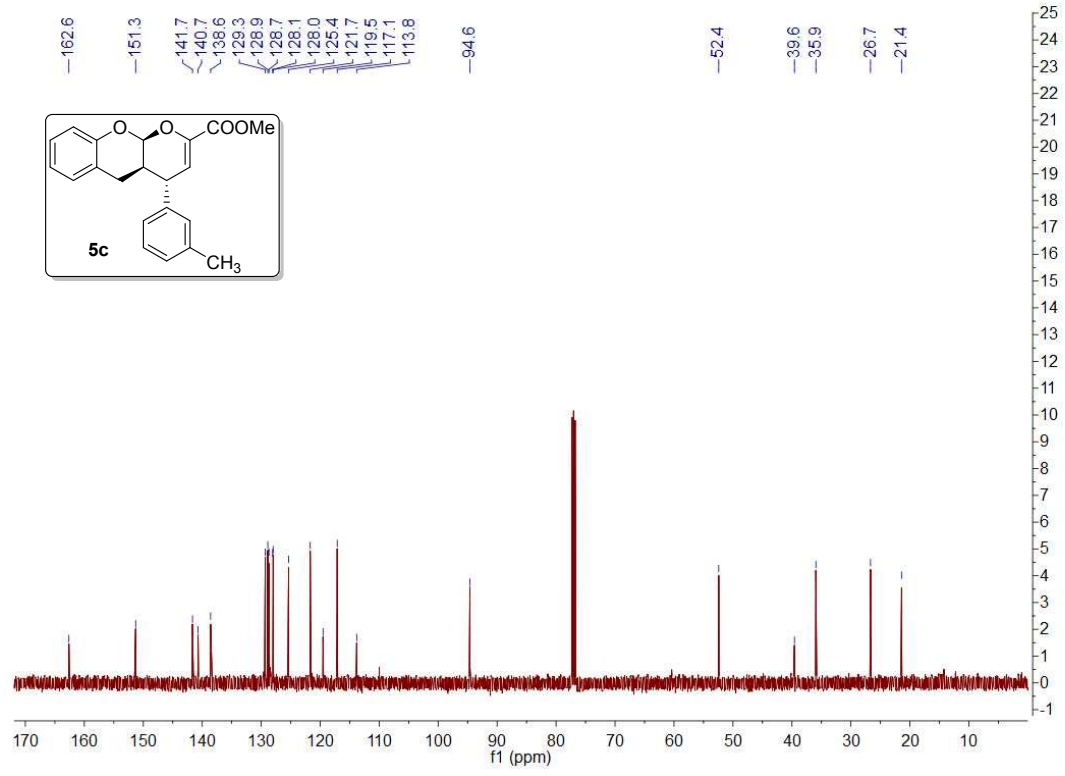
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.753	80654	2.847	BB
2	13.087	2752032	97.153	BB
		2832686	100.000	

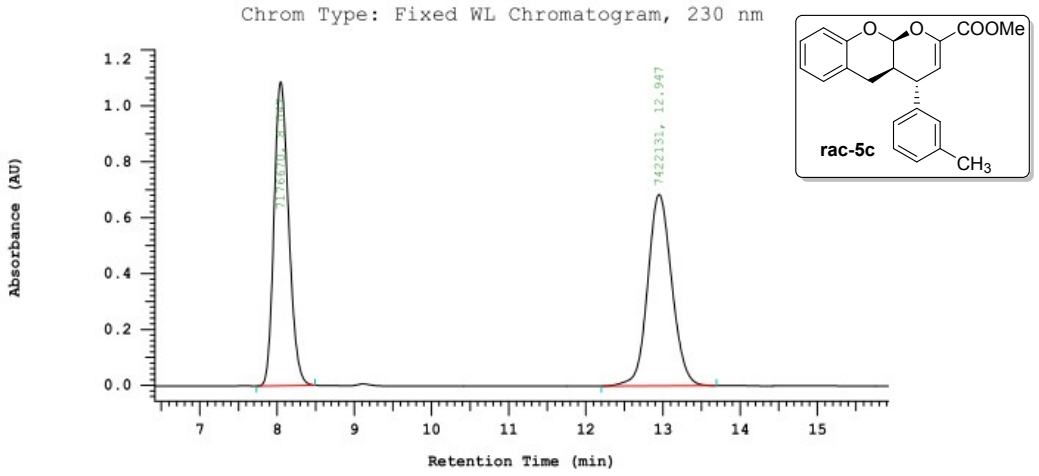
The ^{1}H NMR spectrum of 5c (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5c (125 MHz, $CDCl_3$)



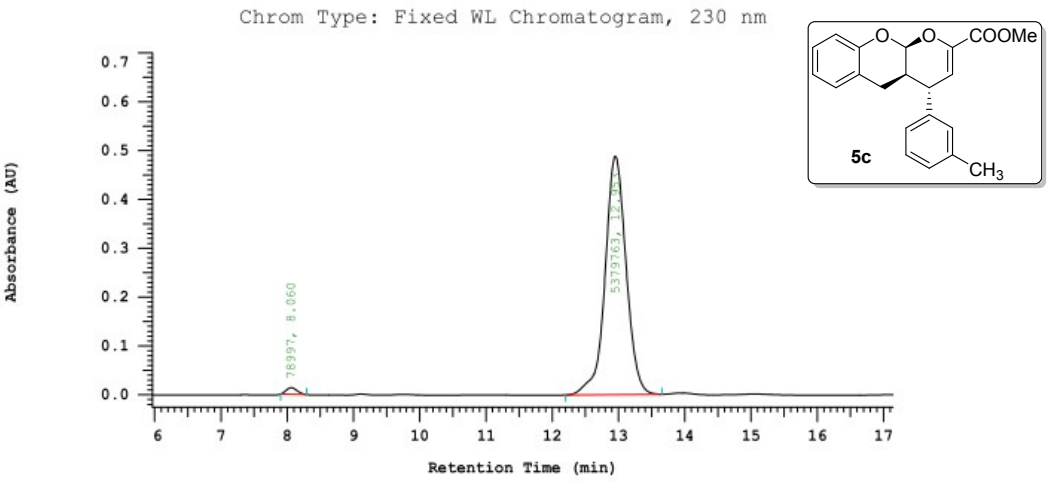
The HPLC of racemic 5c



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.047	7176670	49.159	BB
2	12.947	7422131	50.841	BB
		14598801	100.000	

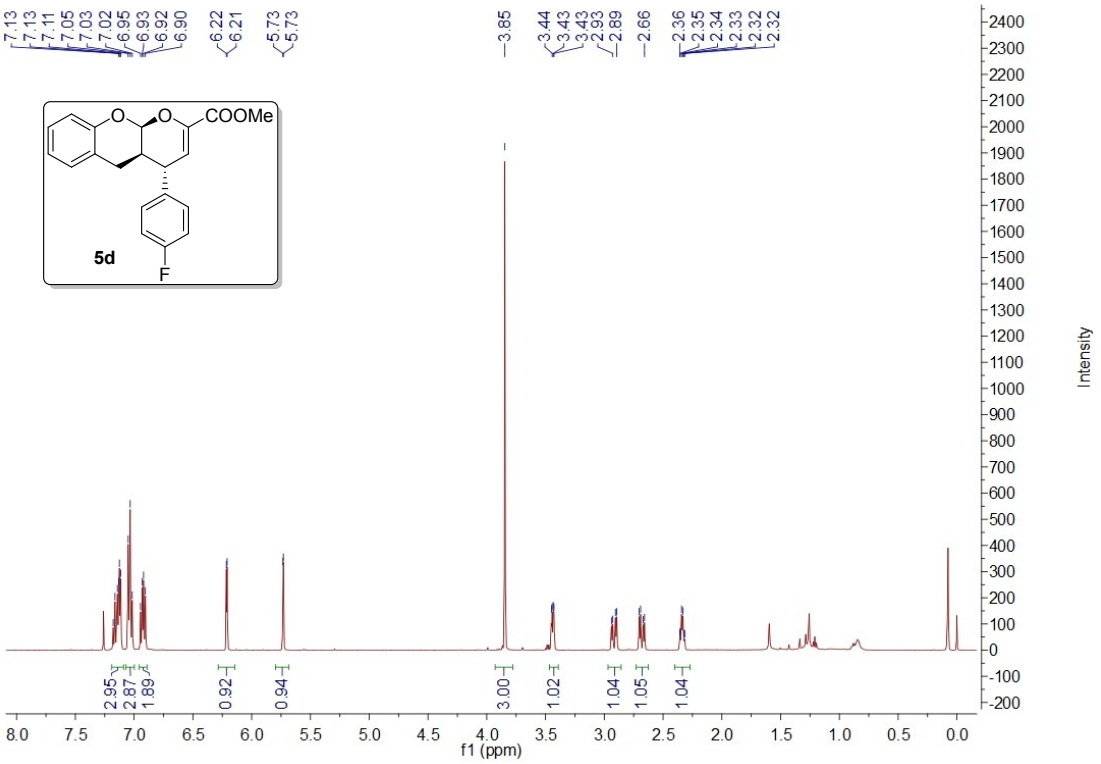
The HPLC of chiral 5c



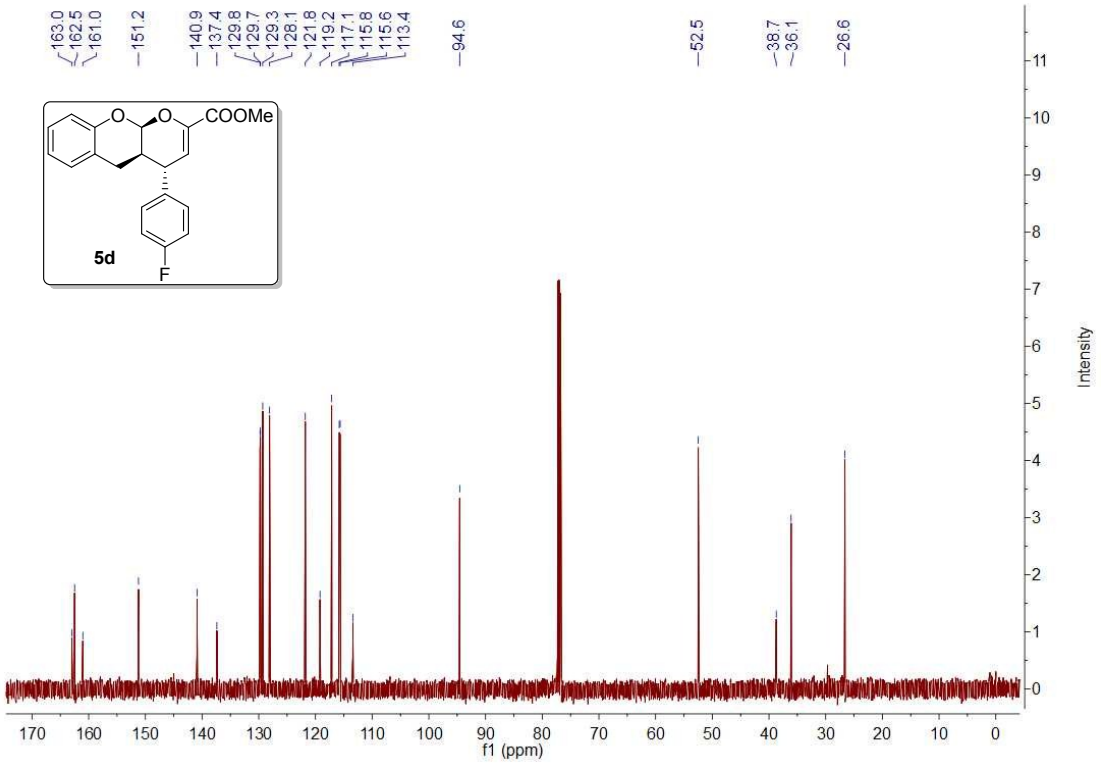
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.060	78997	1.447	BB
2	12.953	5379763	98.553	BB
		5458760	100.000	

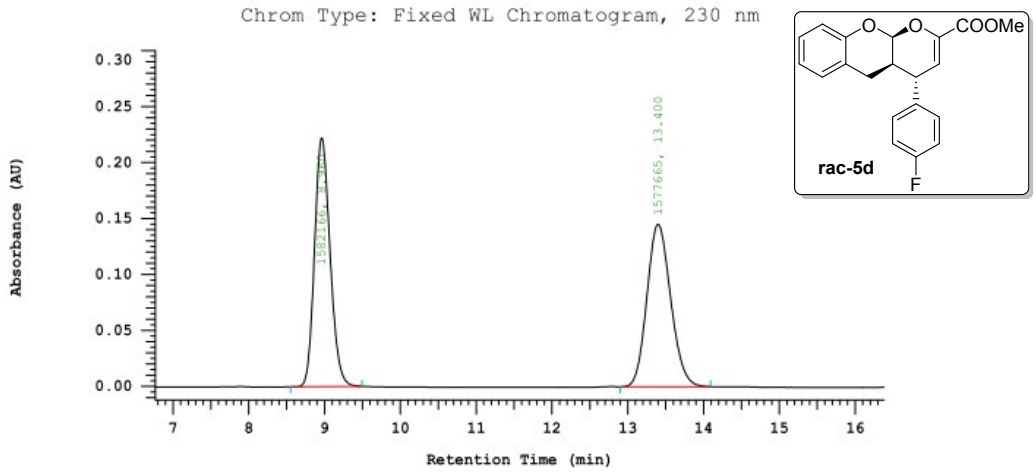
The ^{1}H NMR spectrum of 5d (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5d (125 MHz, $CDCl_3$)



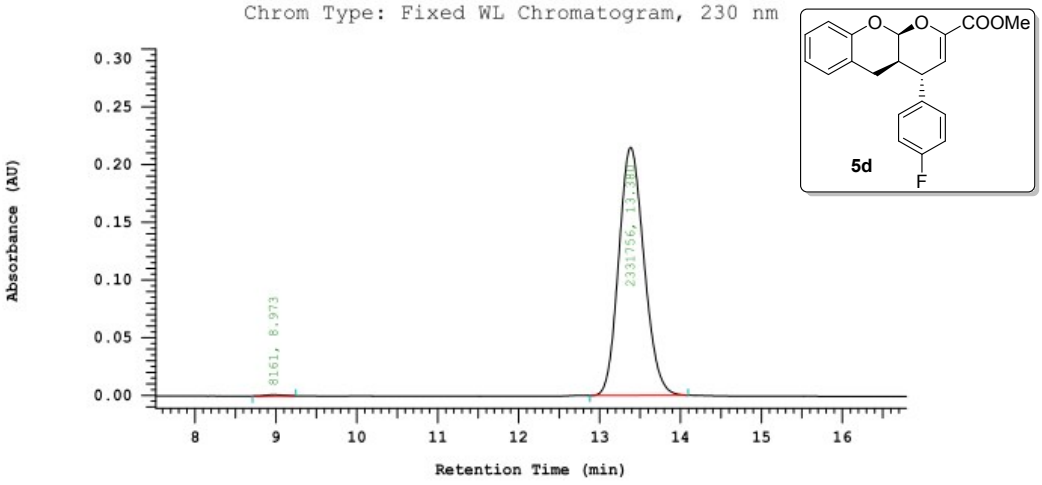
The HPLC of racemic 5d



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.960	1582166	50.071	BB
2	13.400	1577665	49.929	BB
		3159831	100.000	

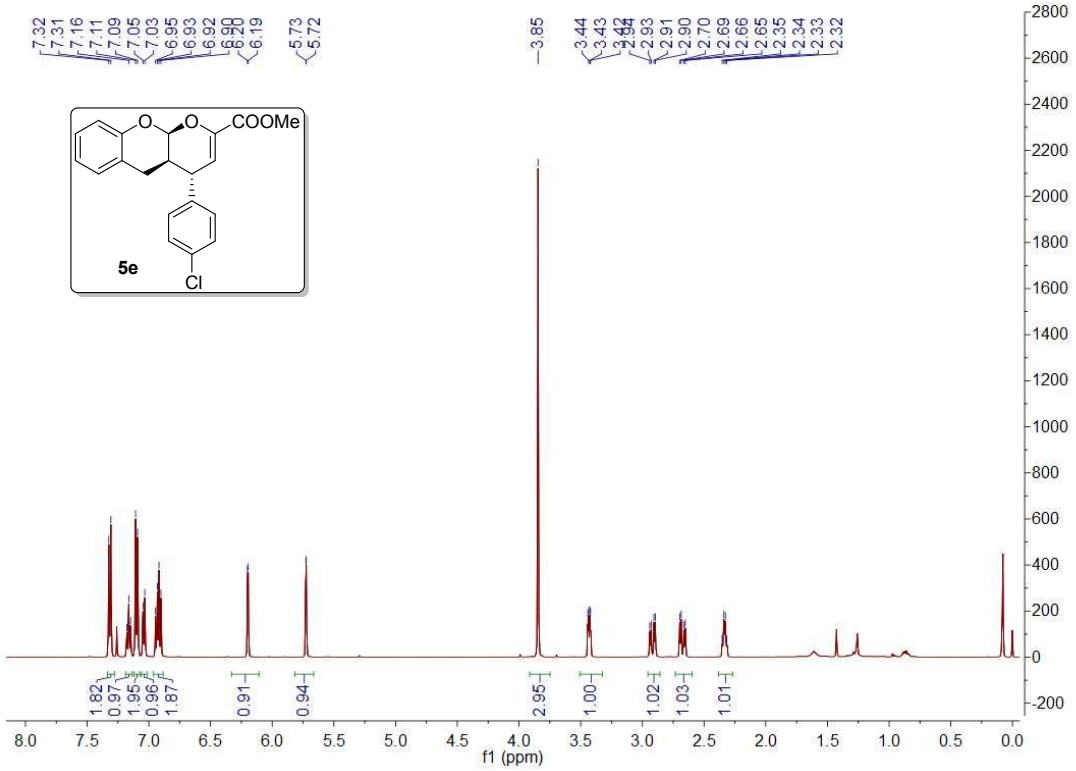
The HPLC of chiral 5d



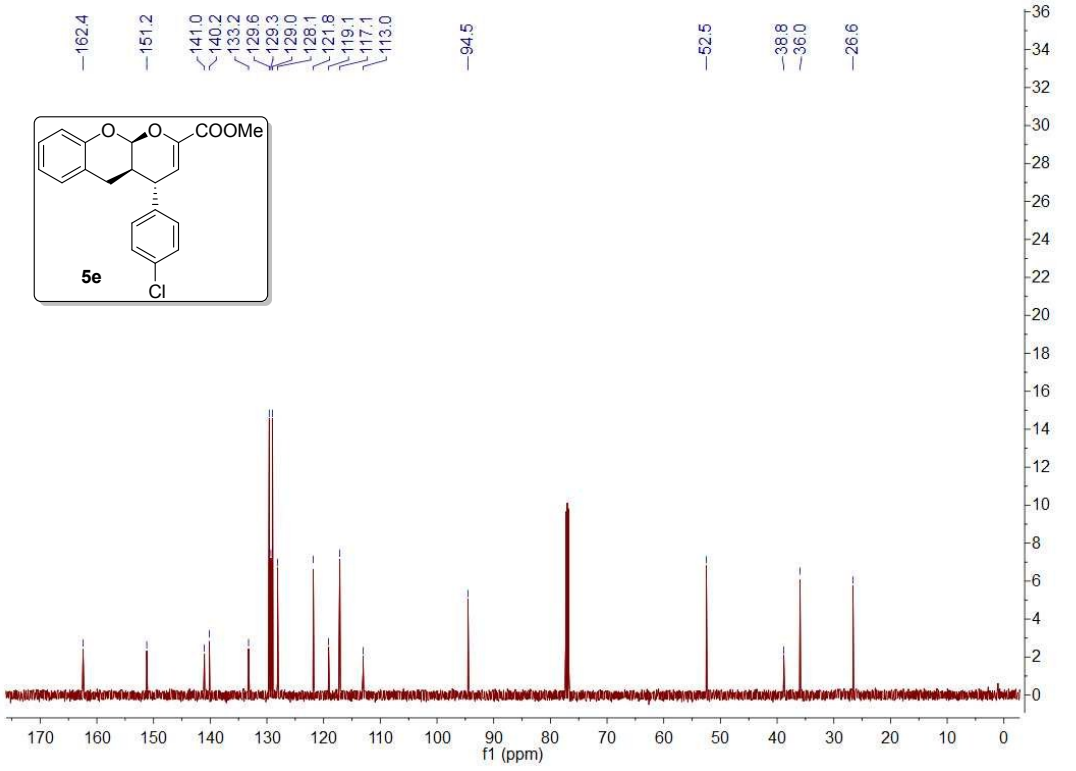
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.973	8161	0.349	BB
2	13.380	2331756	99.651	BB
		2339917	100.000	

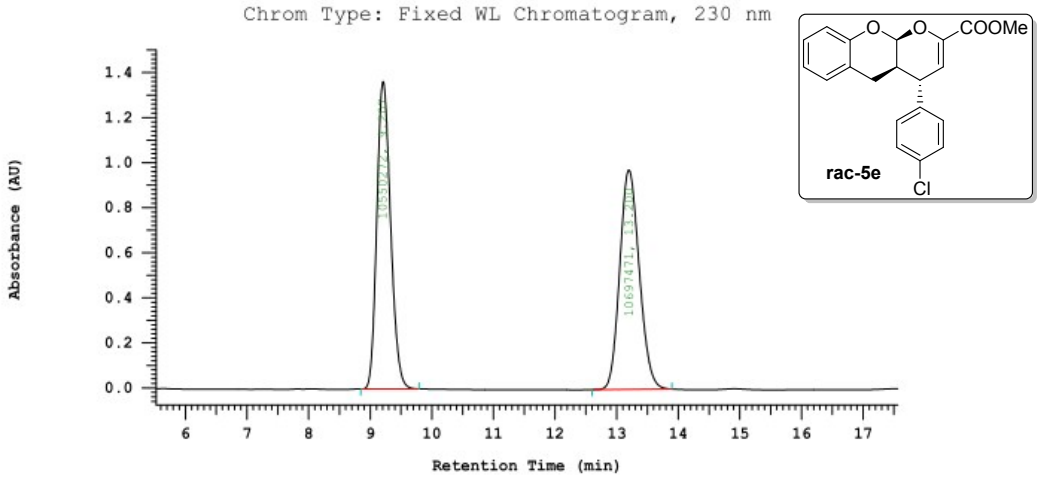
The ^{1}H NMR spectrum of 5e (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5e (125 MHz, $CDCl_3$)



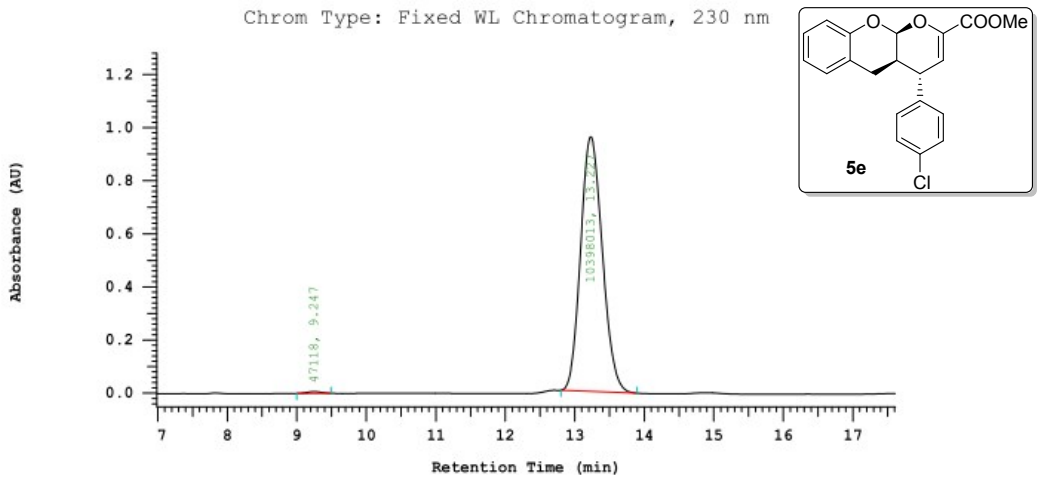
The HPLC of racemic 5e



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.207	10550272	49.654	BB
2	13.200	10697471	50.346	BB
		21247743	100.000	

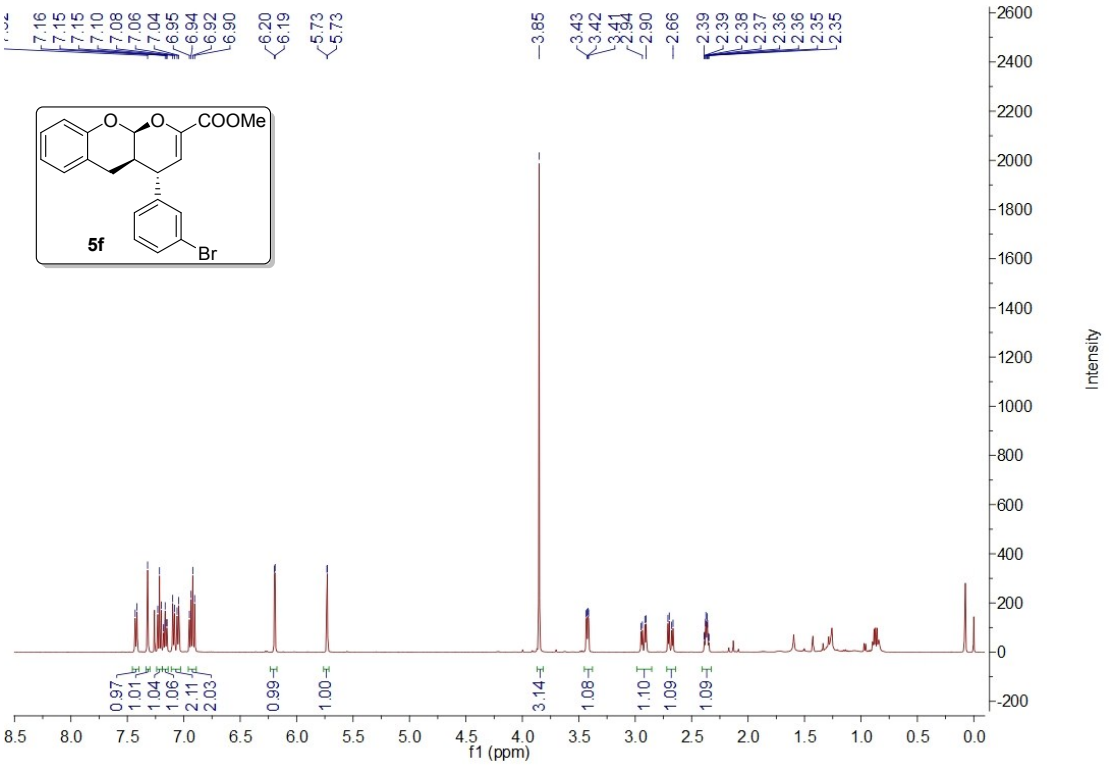
The HPLC of chiral 5e



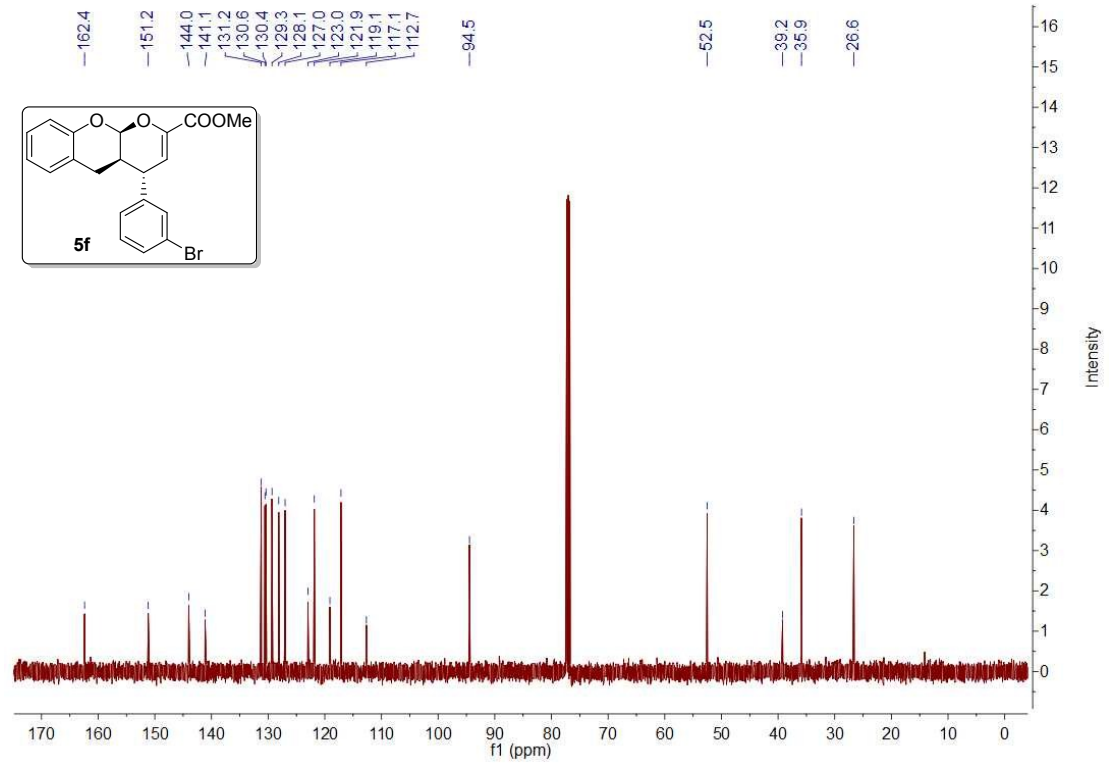
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.247	47118	0.451	BB
2	13.227	10398013	99.549	BB
		10445131	100.000	

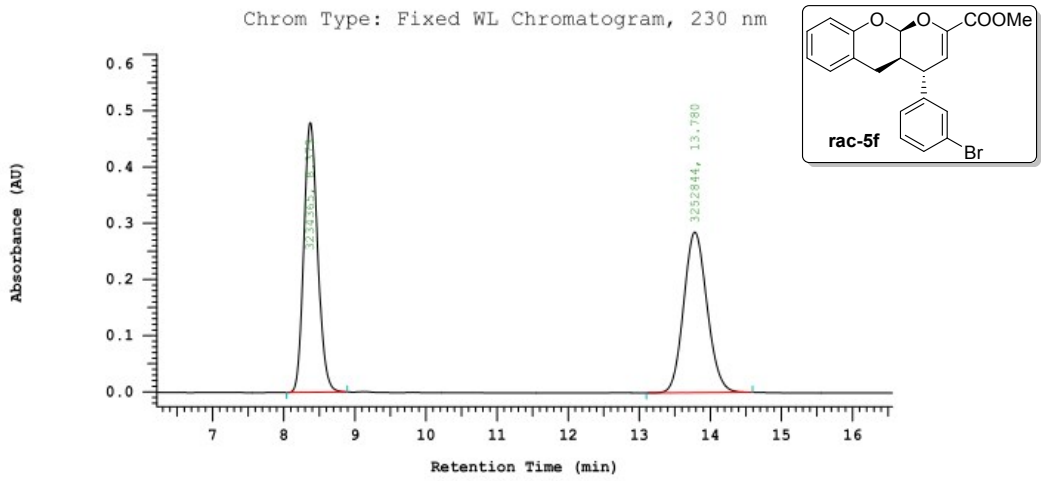
The ^{1}H NMR spectrum of 5f (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5f (125 MHz, $CDCl_3$)



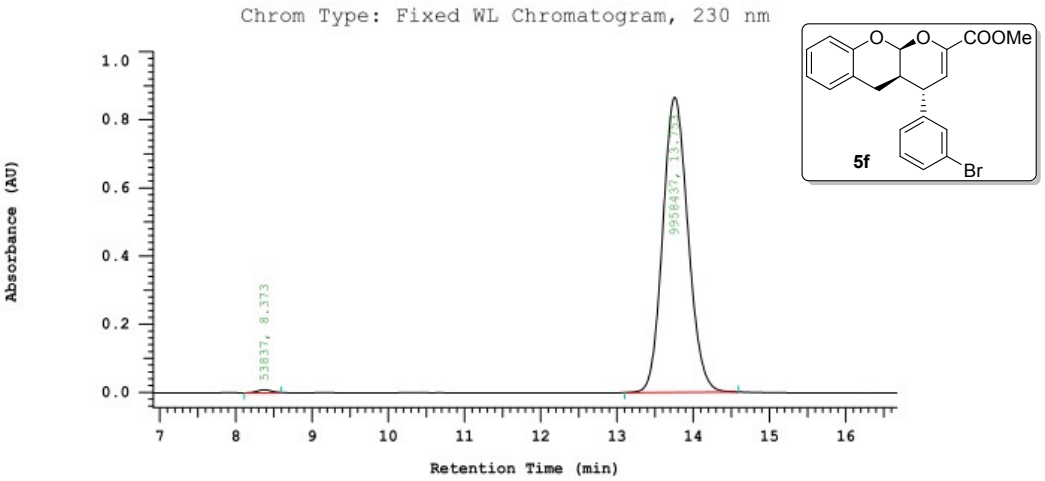
The HPLC of racemic 5f



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.373	3234365	49.858	BB
2	13.780	3252844	50.142	BB
		6487209	100.000	

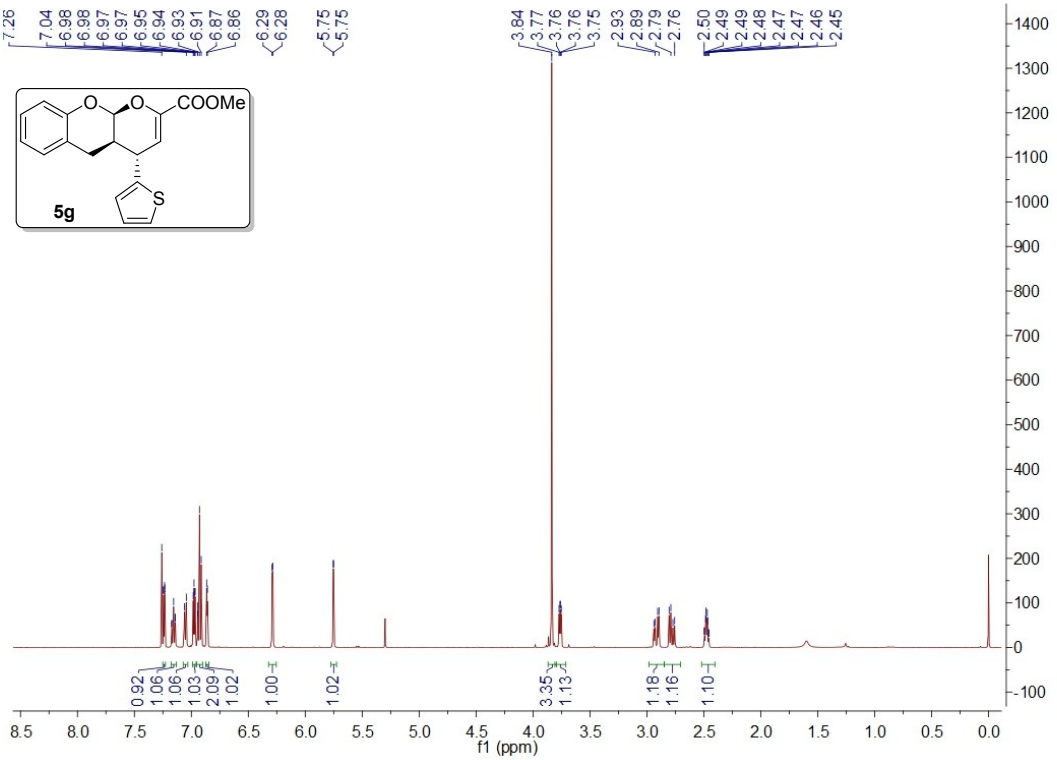
The HPLC of chiral 5f



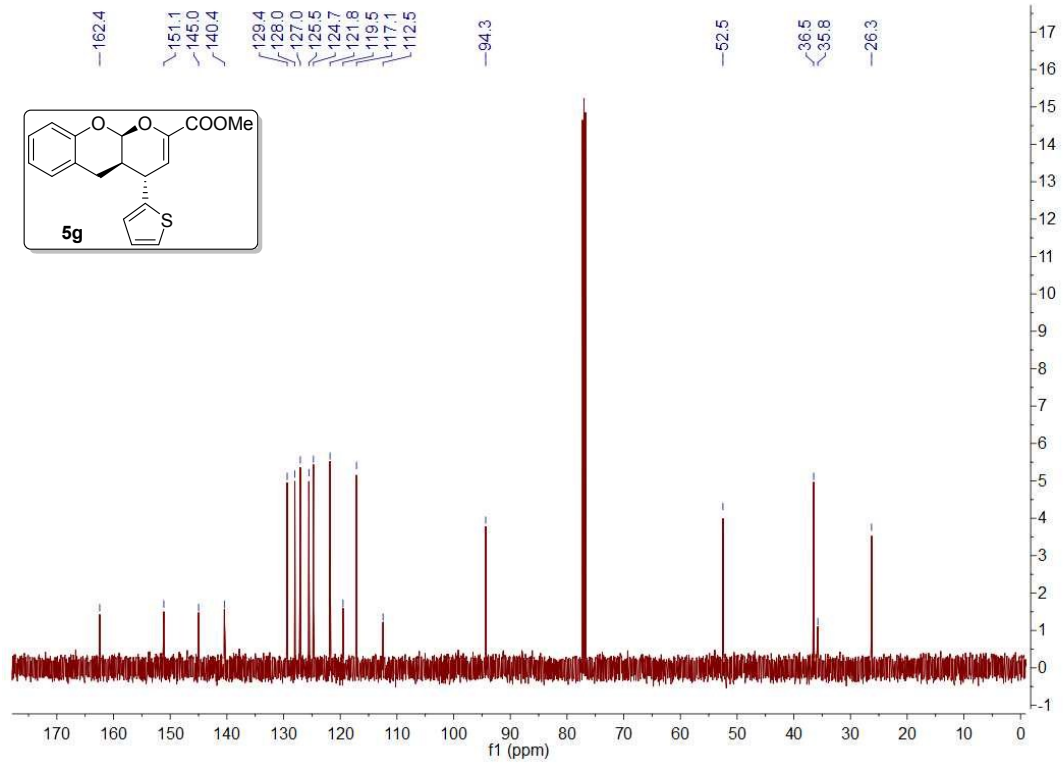
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.373	53837	0.538	BB
2	13.753	9958437	99.462	BB
		10012274	100.000	

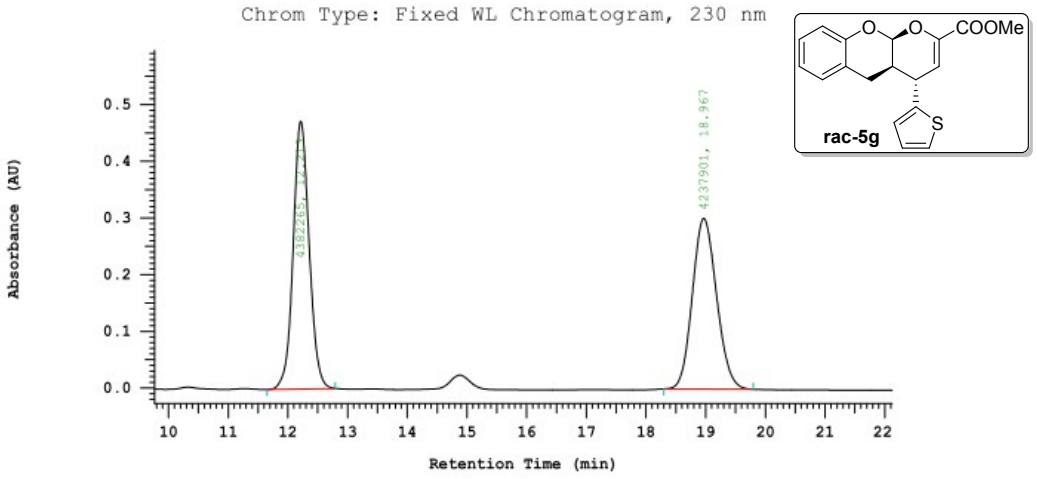
The ^{1}H NMR spectrum of 5g (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5g (125 MHz, $CDCl_3$)



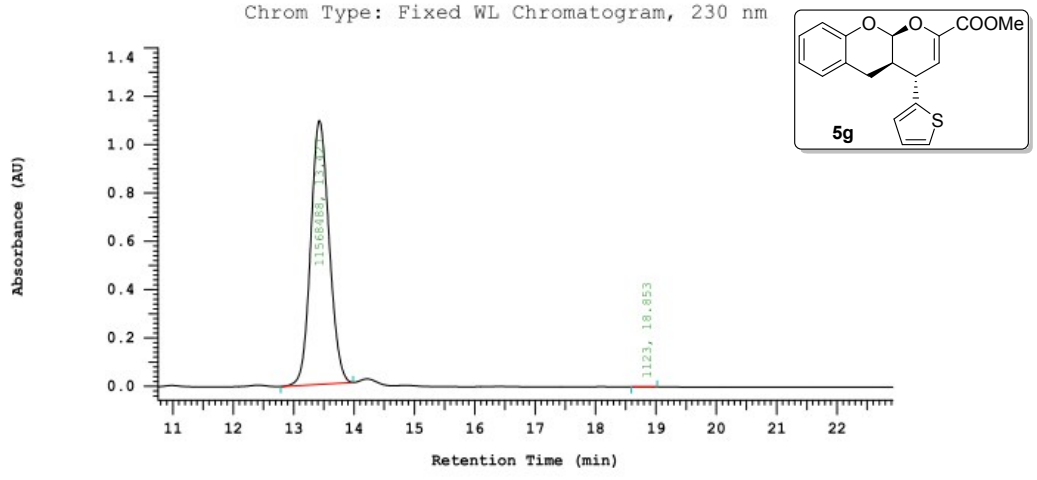
The HPLC of racemic 5g



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.213	4382265	50.837	BB
2	18.967	4237901	49.163	BB
		8620166	100.000	

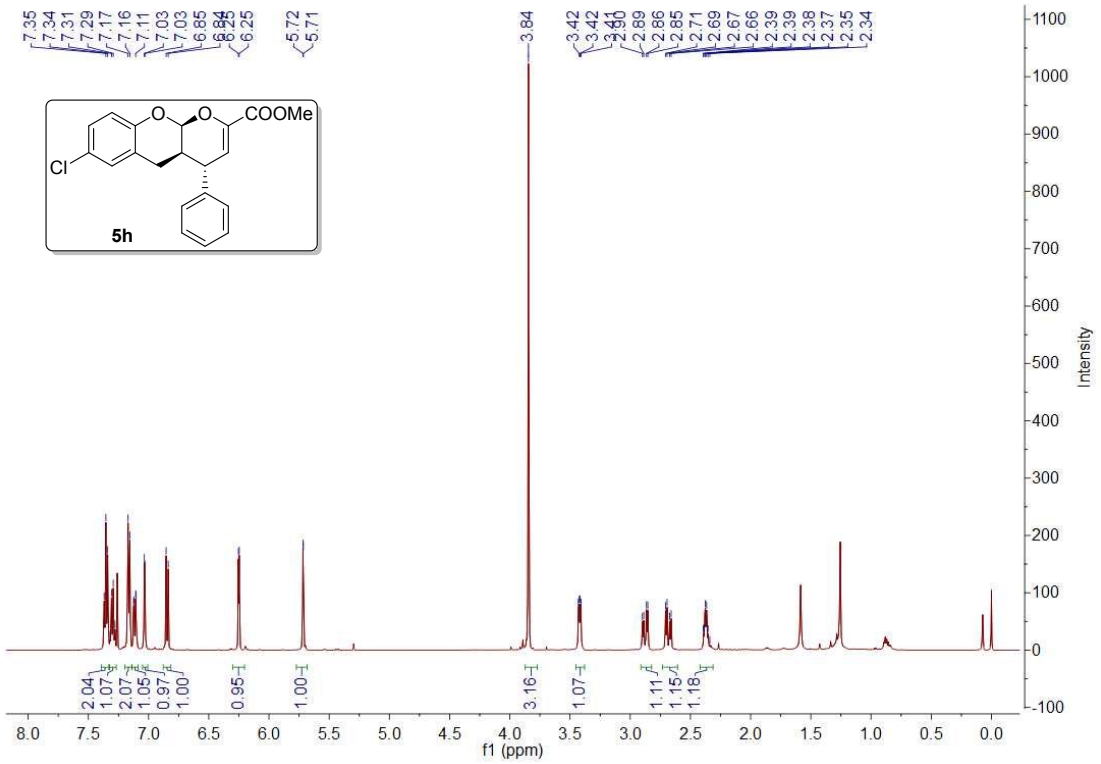
The HPLC of chiral 5g



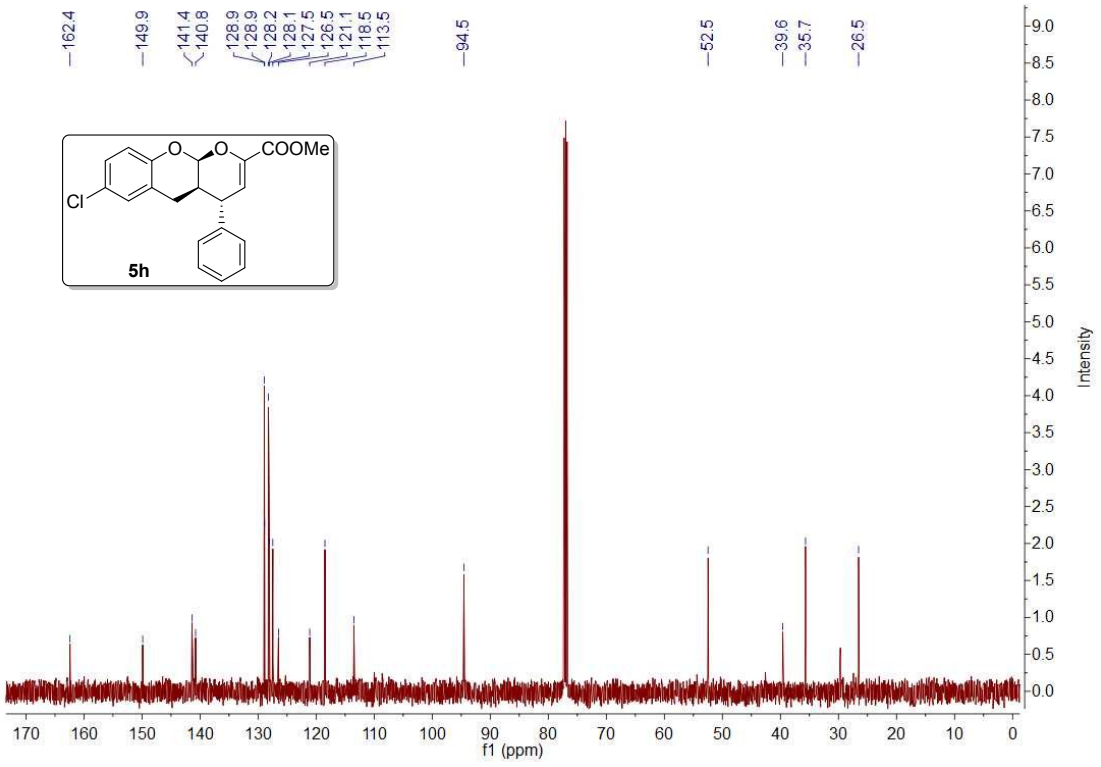
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.427	11568488	99.990	BB
2	18.853	1123	0.010	BB
		11569611	100.000	

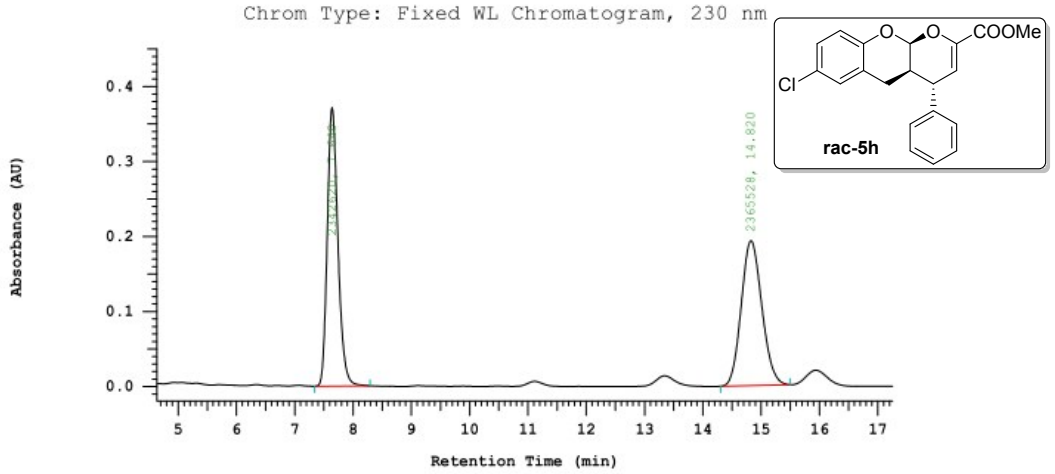
The ^{1}H NMR spectrum of 5h (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5h (125 MHz, $CDCl_3$)



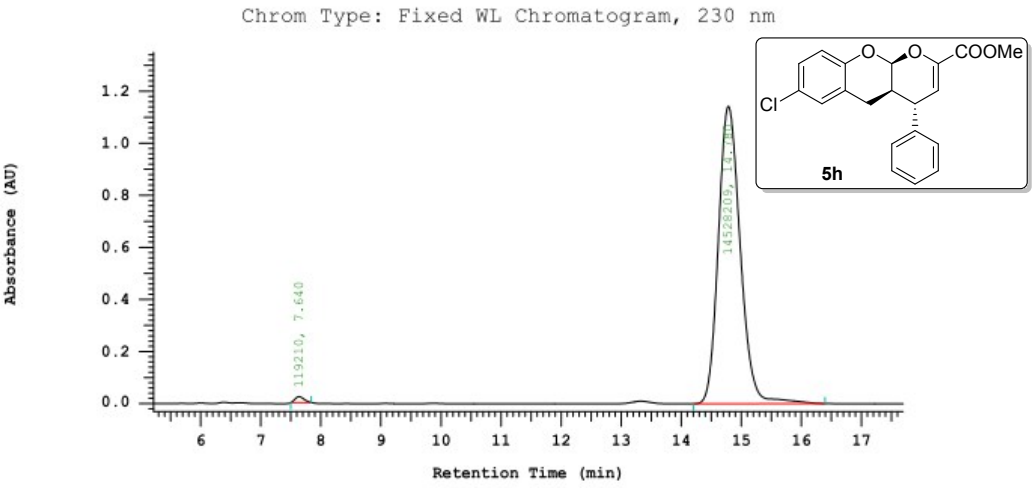
The HPLC of racemic 5h



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.640	2342620	49.757	BB
2	14.820	2365528	50.243	BB
		4708148	100.000	

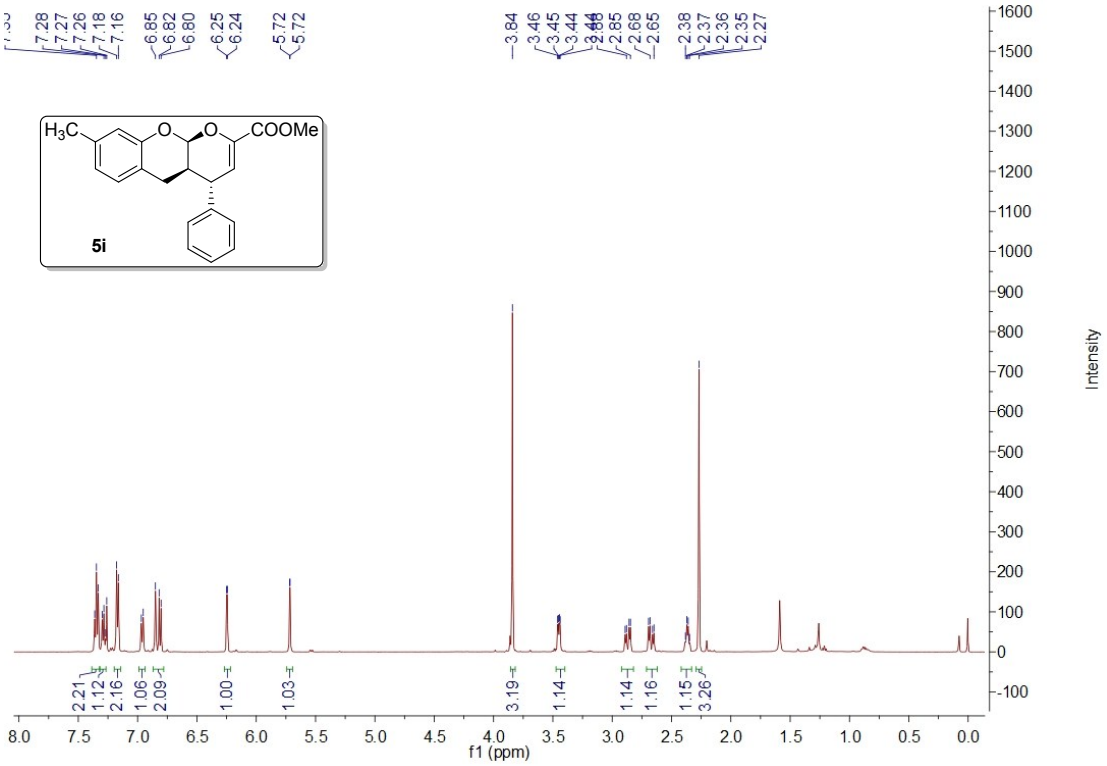
The HPLC of chiral 5h



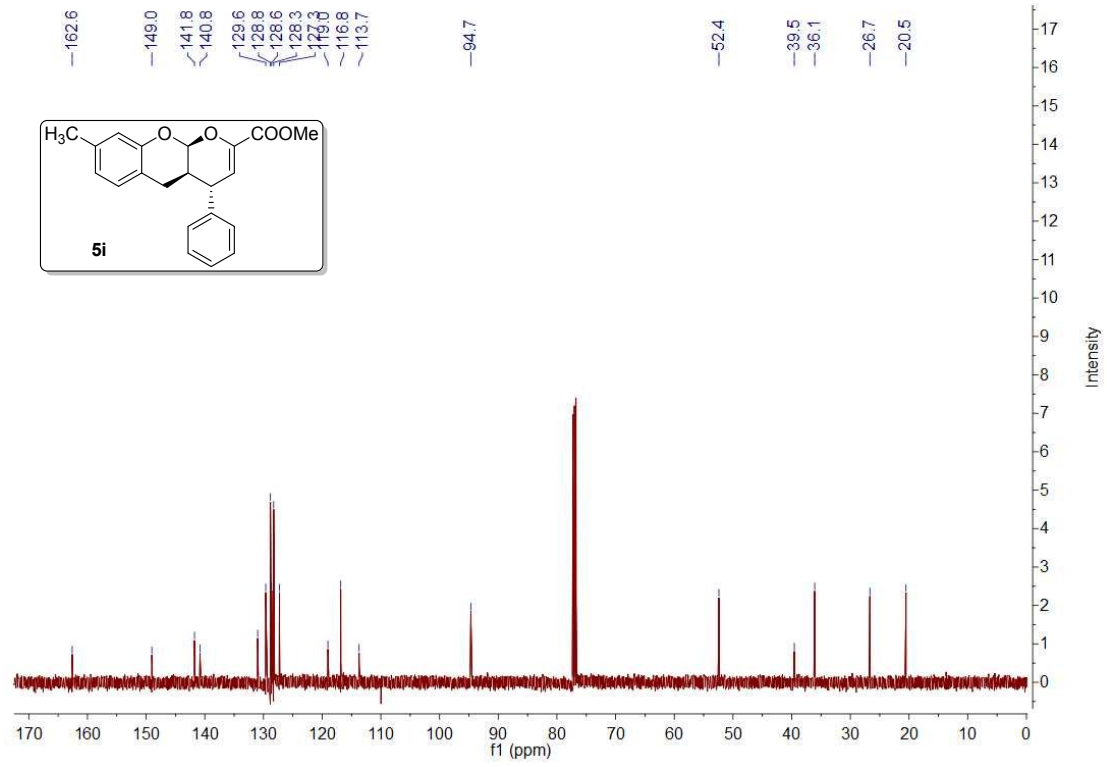
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.640	119210	0.814	BB
2	14.780	14528209	99.186	BB
		14647419	100.000	

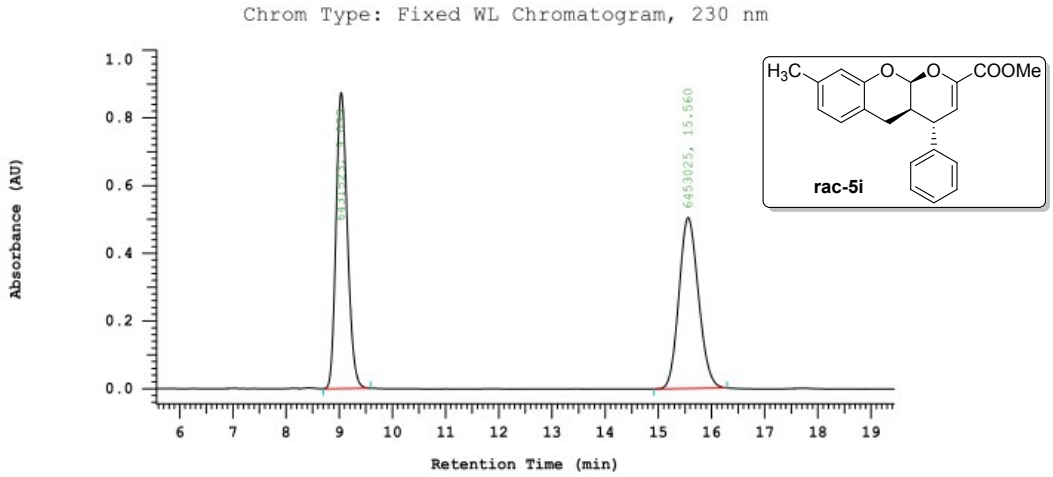
The ^{1}H NMR spectrum of 5i (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5i (125 MHz, $CDCl_3$)



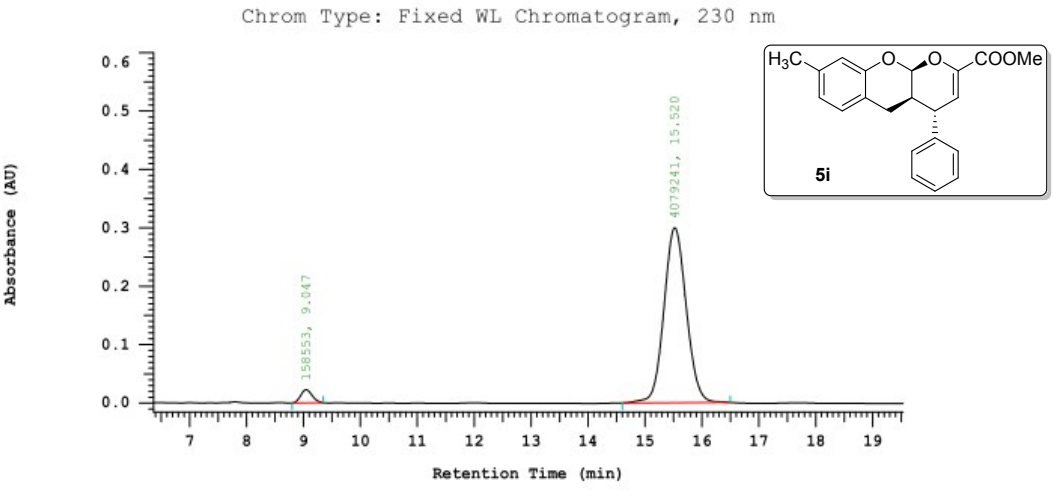
The HPLC of racemic 5i



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.033	6431523	49.917	BB
2	15.560	6453025	50.083	BB
		12884548	100.000	

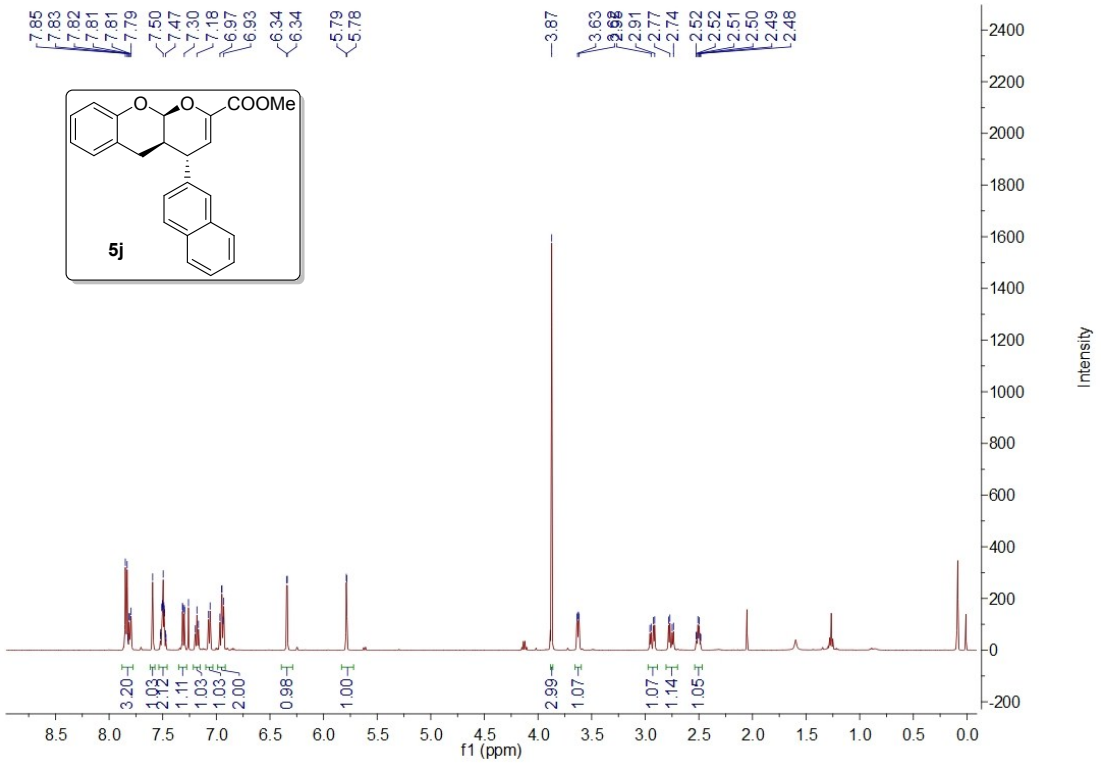
The HPLC of chiral 5i



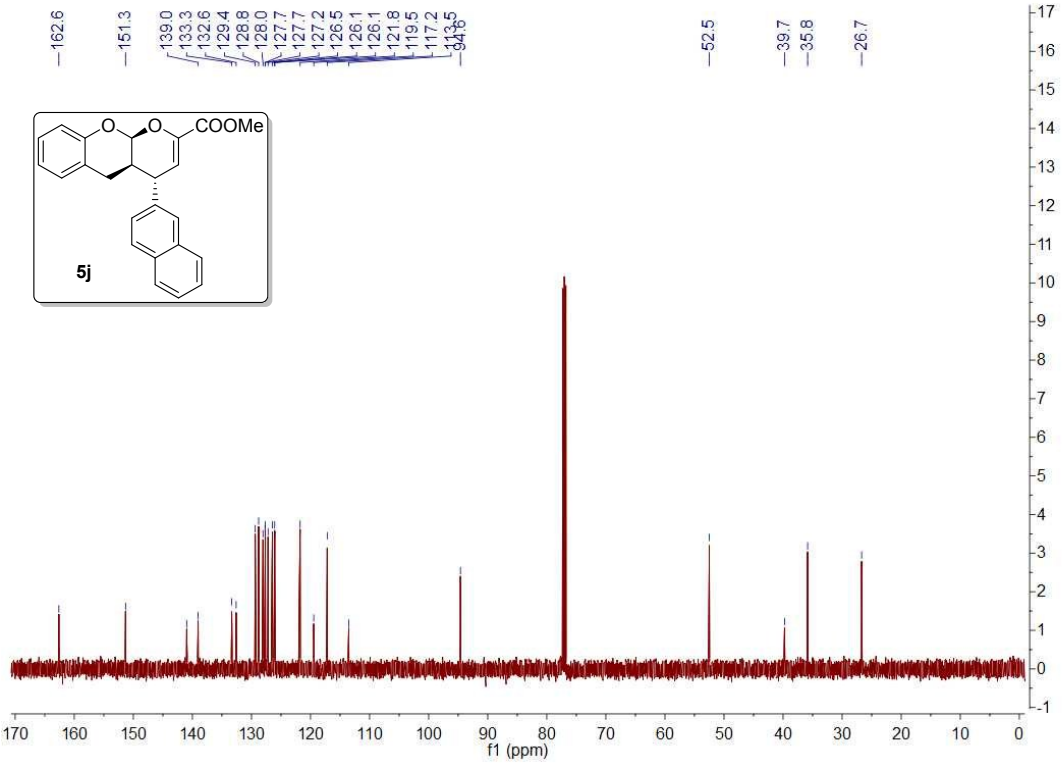
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.047	158553	3.741	BB
2	15.520	4079241	96.259	BB
		4237794	100.000	

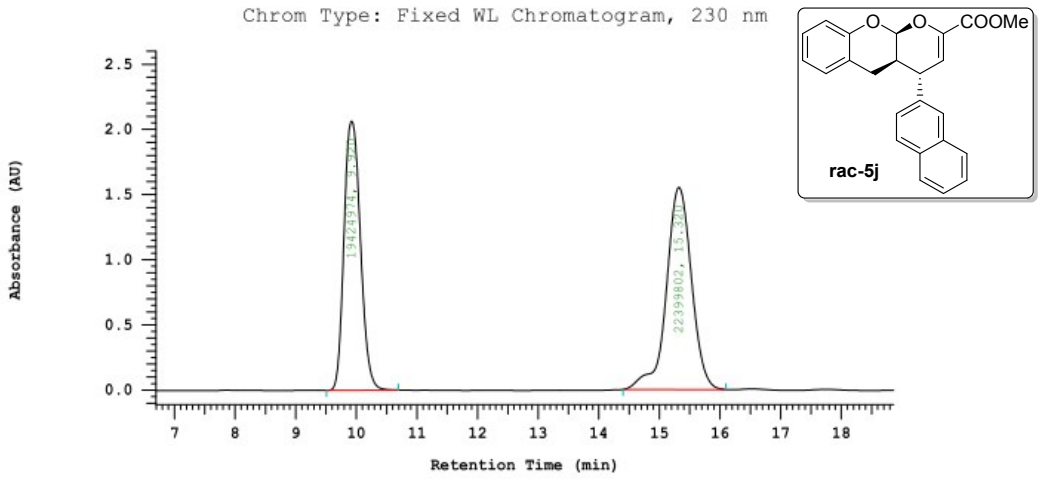
The ^{1}H NMR spectrum of 5j (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5j (125 MHz, $CDCl_3$)



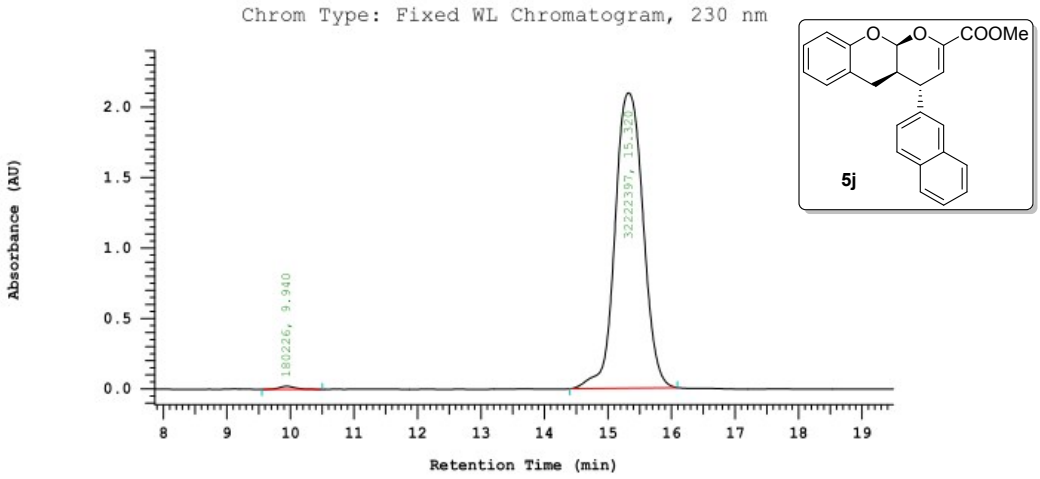
The HPLC of racemic 5j



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.920	19424974	46.444	BB
2	15.320	22399802	53.556	BB
		41824776	100.000	

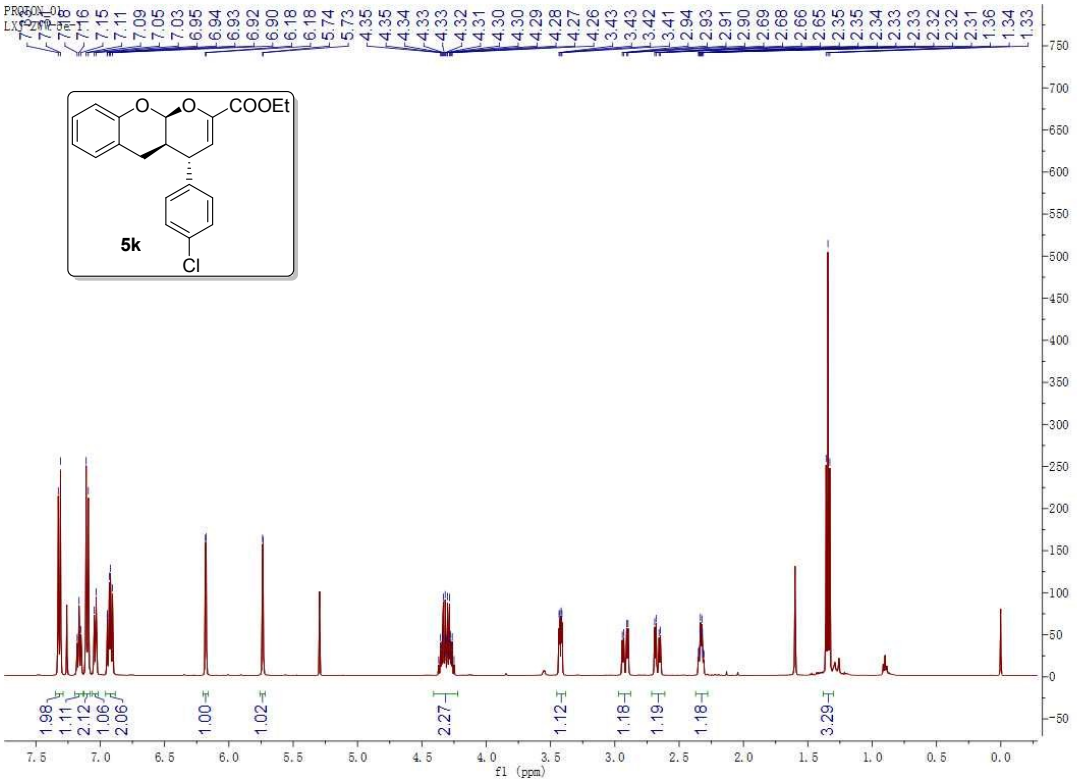
The HPLC of chiral 5j



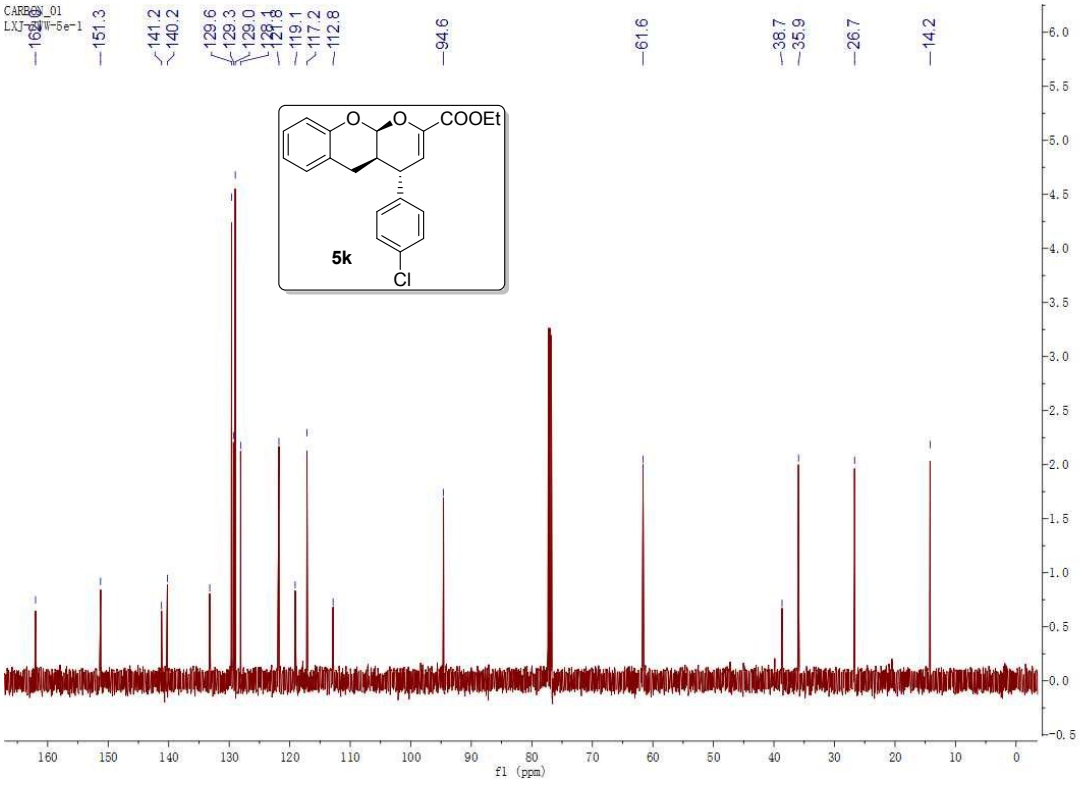
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.940	180226	0.556	BB
2	15.320	32222397	99.444	BB
		32402623	100.000	

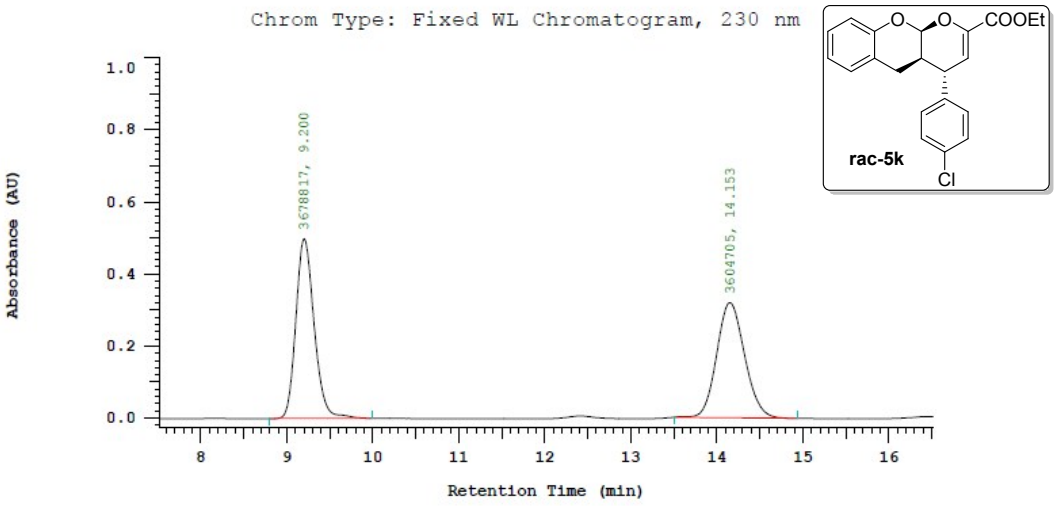
The ^{1}H NMR spectrum of 5k (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 5k (125 MHz, $CDCl_3$)



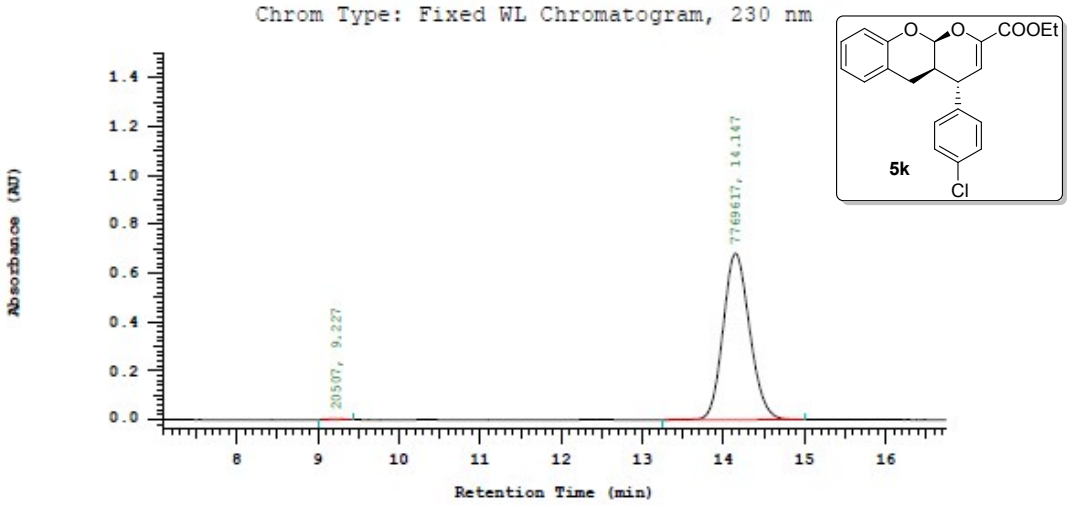
The HPLC of racemic 5k



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.200	3678817	50.509	BB
2	14.153	3604705	49.491	BB
		7283522	100.000	

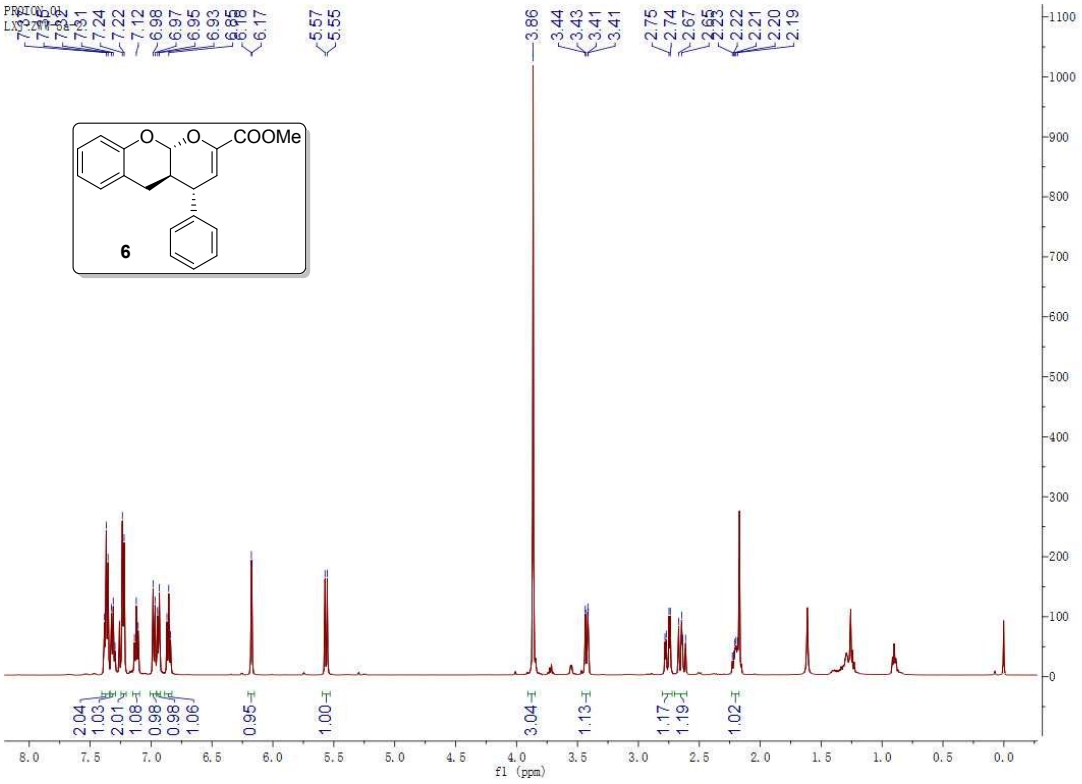
The HPLC of chiral 5k



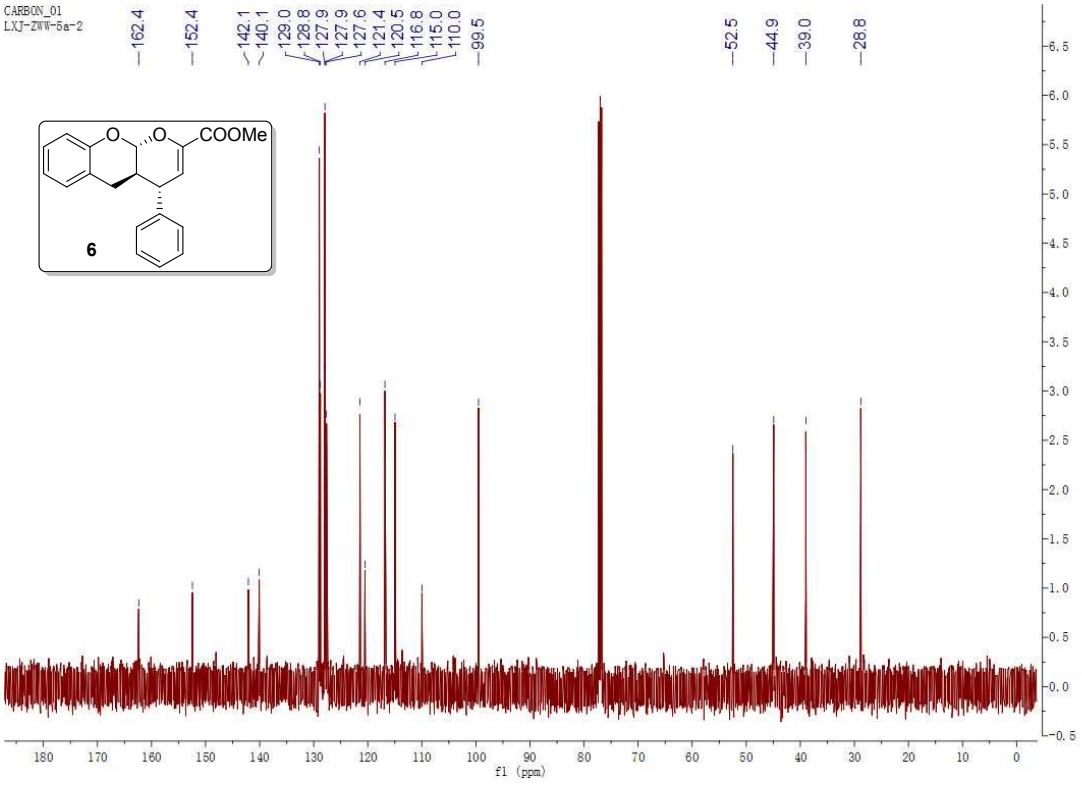
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.227	20507	0.263	BB
2	14.147	7769617	99.737	BB
		7790124	100.000	

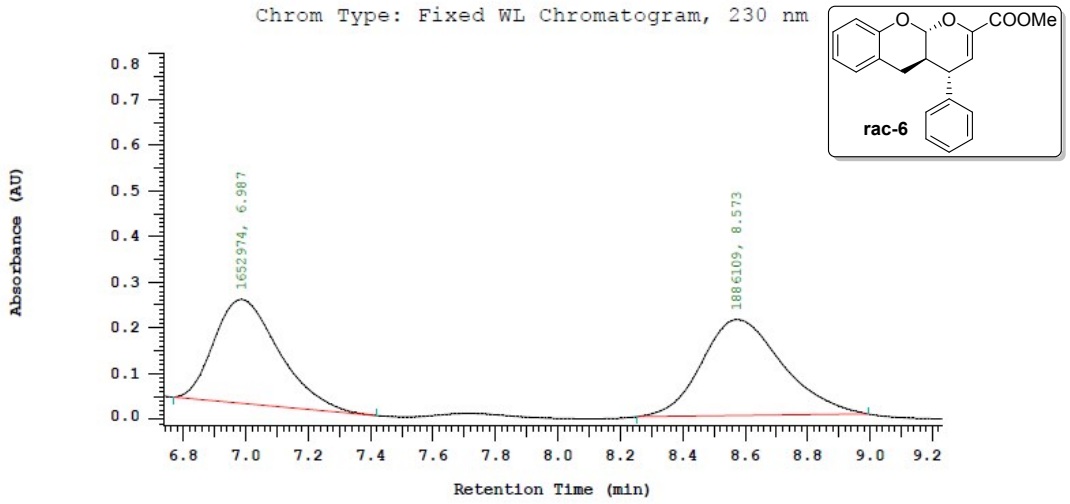
The ^{1}H NMR spectrum of 6 (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 6 (125 MHz, $CDCl_3$)



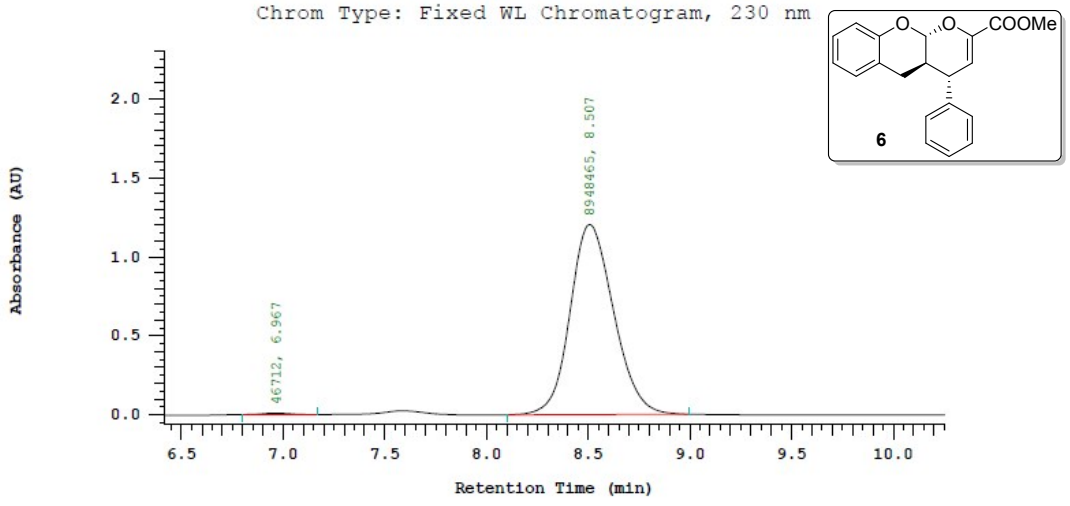
The HPLC of racemic 6



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.987	1652974	46.706	BB
2	8.573	1886109	53.294	BB
		3539083	100.000	

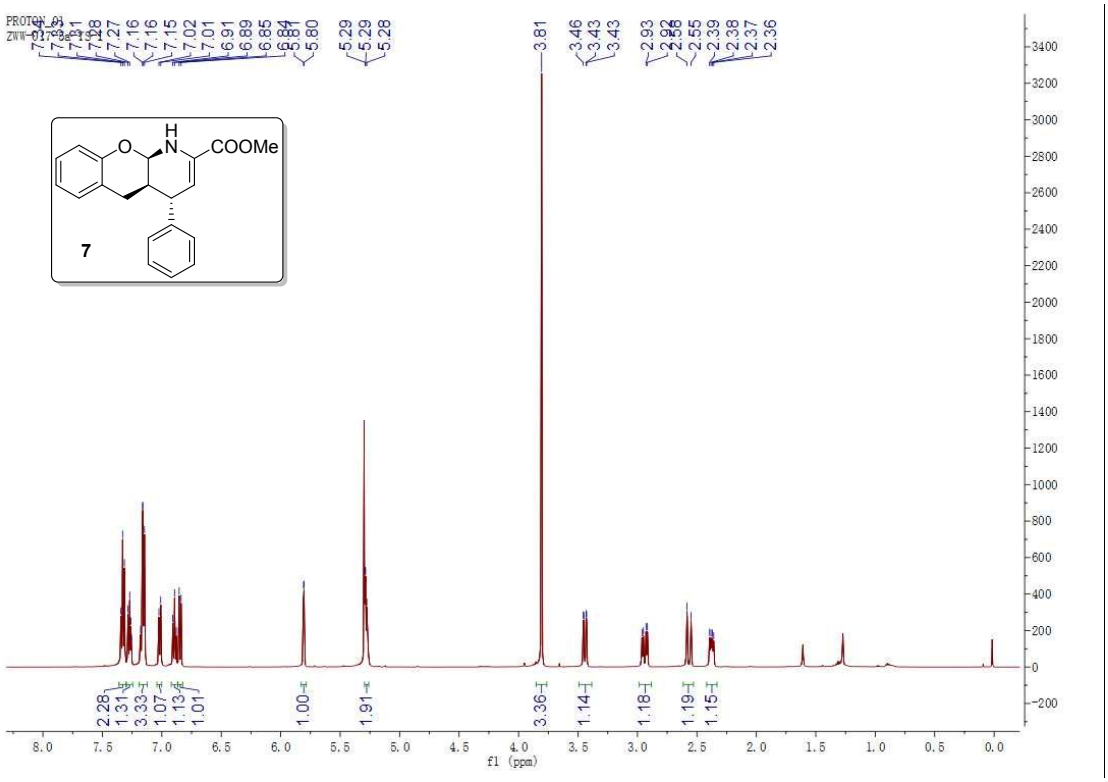
The HPLC of chiral 6



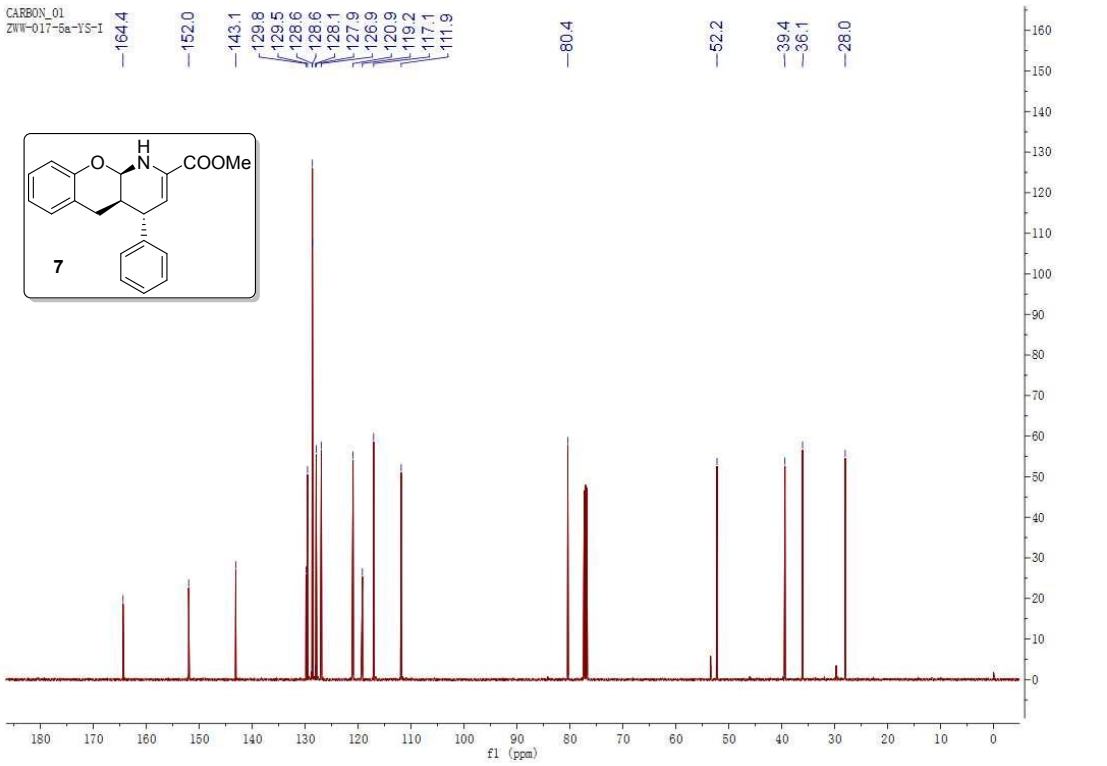
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.967	46712	0.519	BB
2	8.507	8948465	99.481	BB
		8995177	100.000	

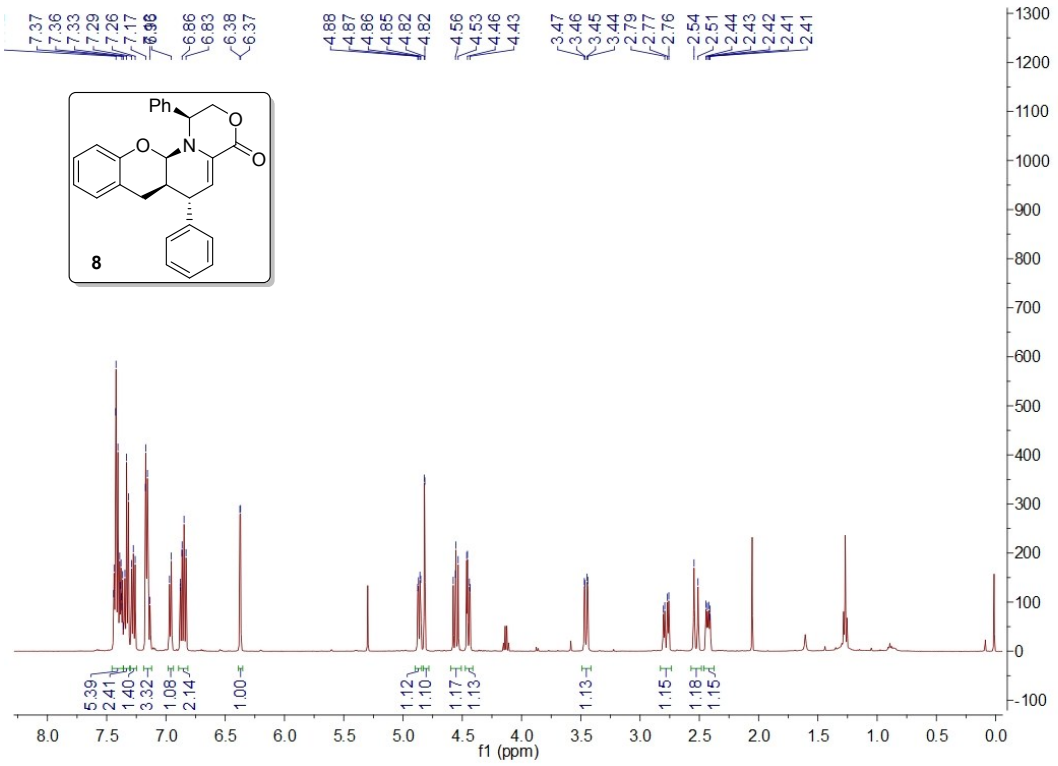
The ^{1}H NMR spectrum of 7 (500 MHz, $CDCl_3$)



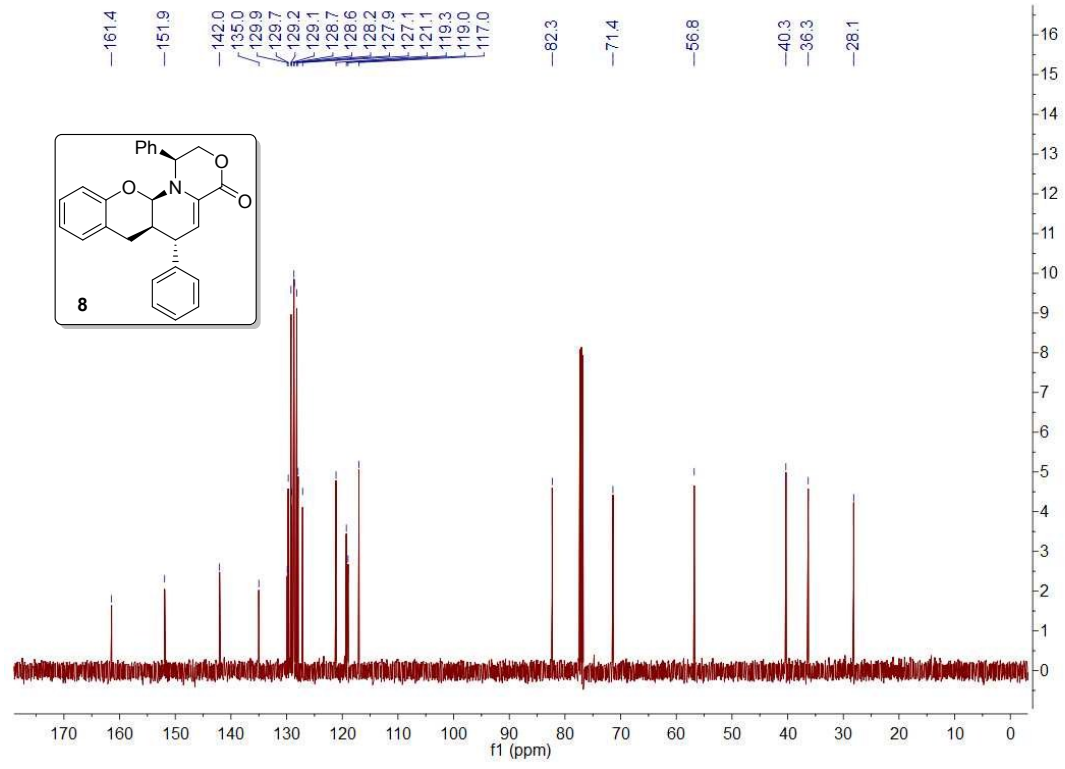
The ^{13}C NMR spectrum of 7 (125 MHz, $CDCl_3$)



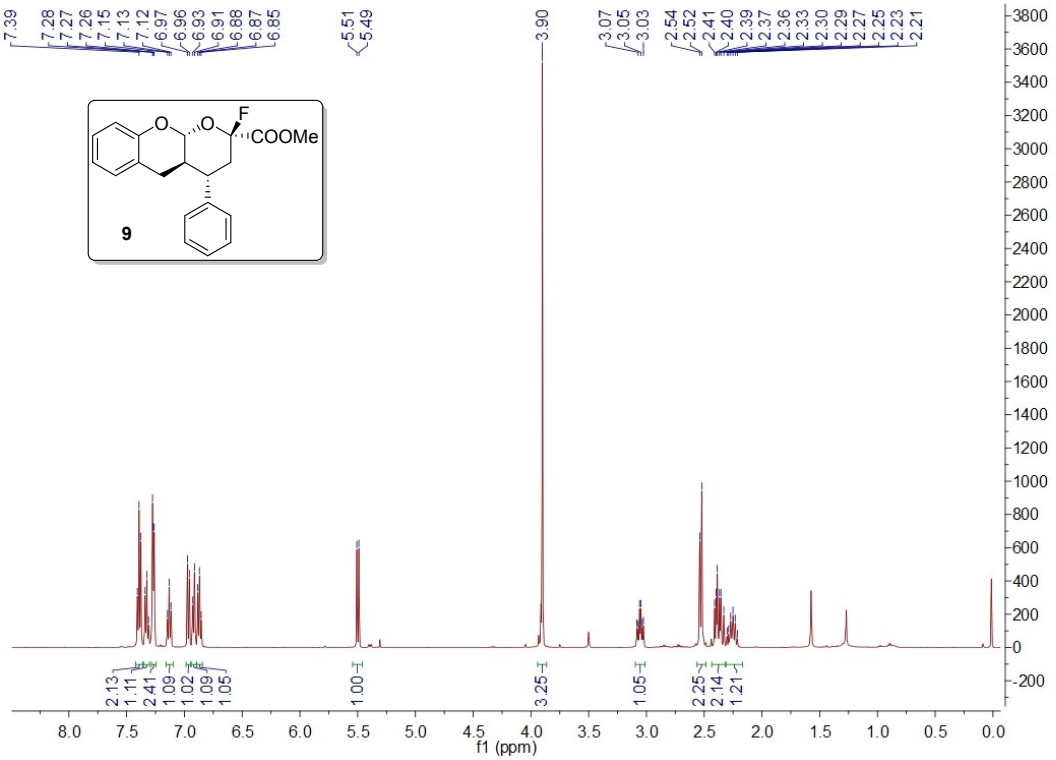
The ^{1}H NMR spectrum of 8 (500 MHz, $CDCl_3$)



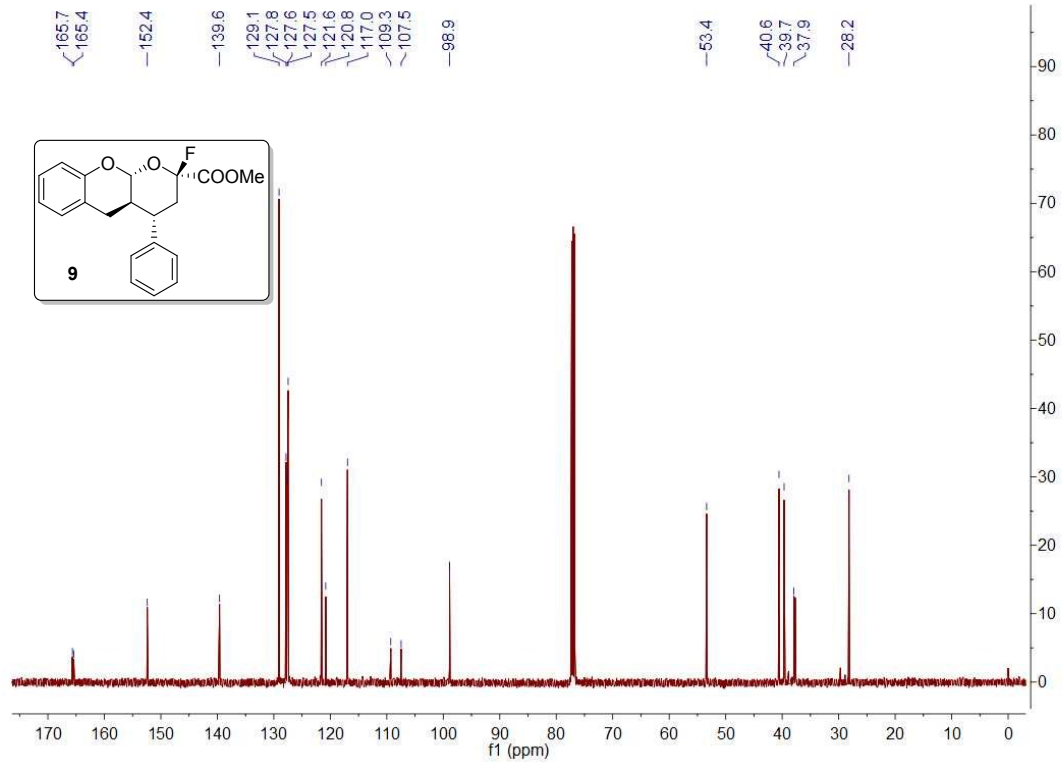
The ^{13}C NMR spectrum of 8 (125 MHz, $CDCl_3$)



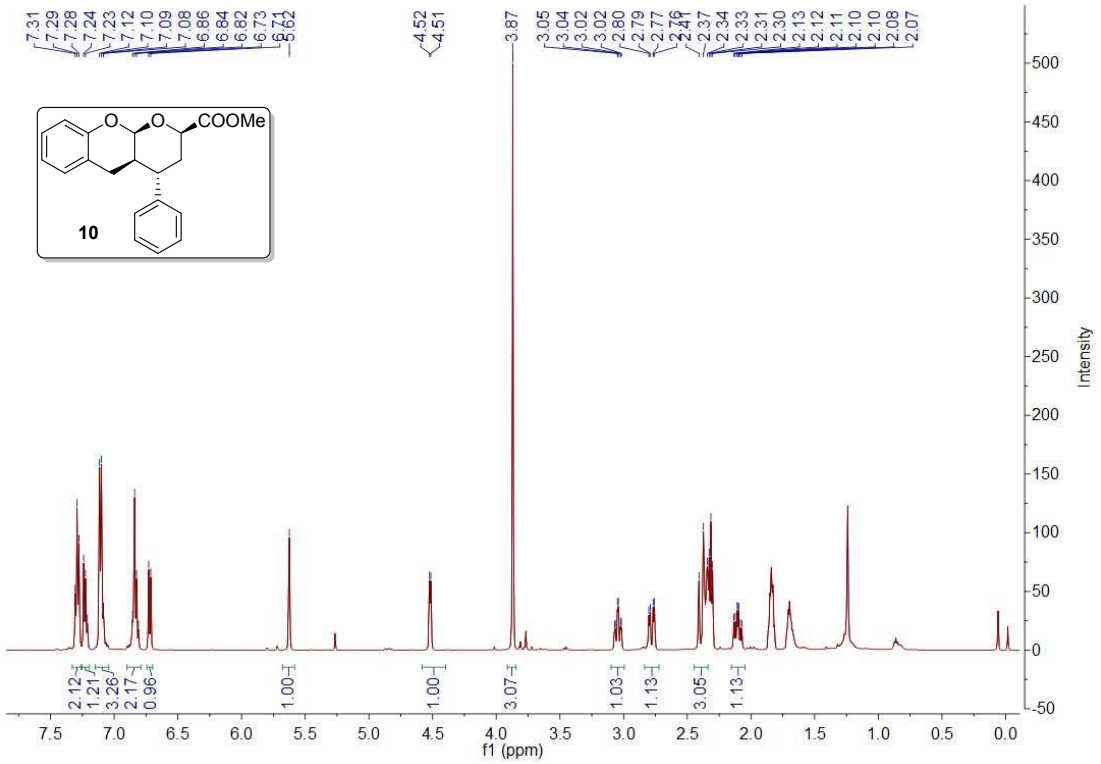
The ^{1}H NMR spectrum of 9 (500 MHz, $CDCl_3$)



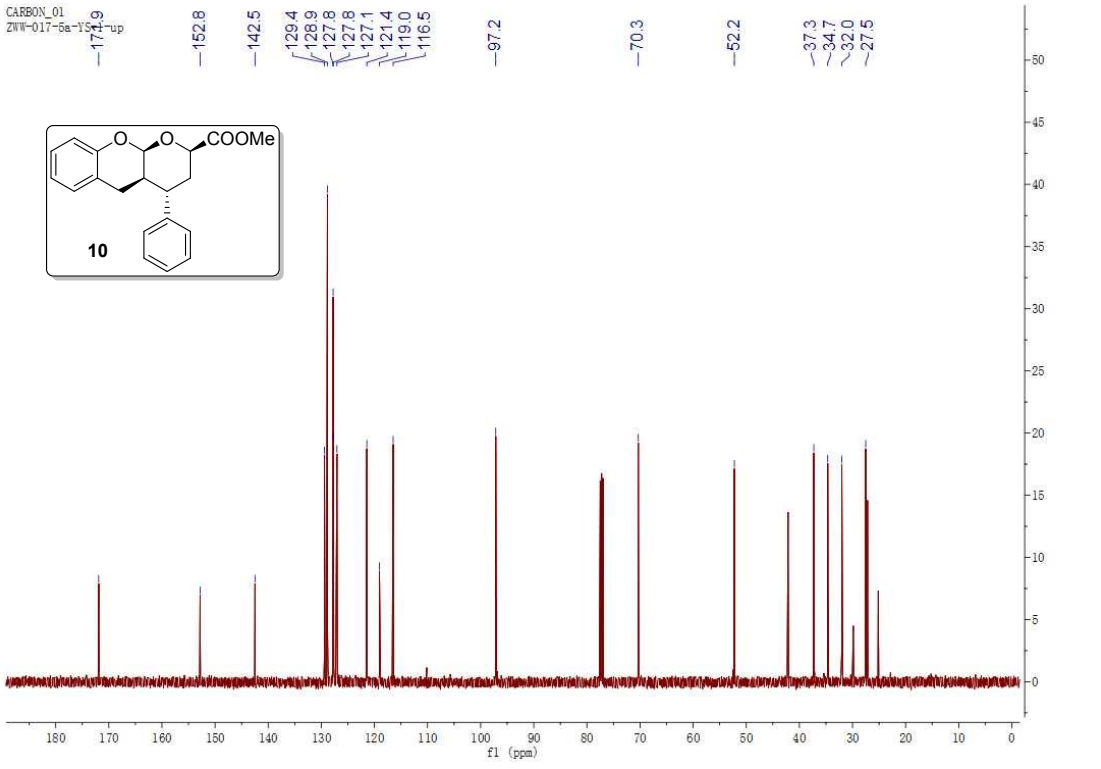
The ^{13}C NMR spectrum of 9 (125 MHz, $CDCl_3$)



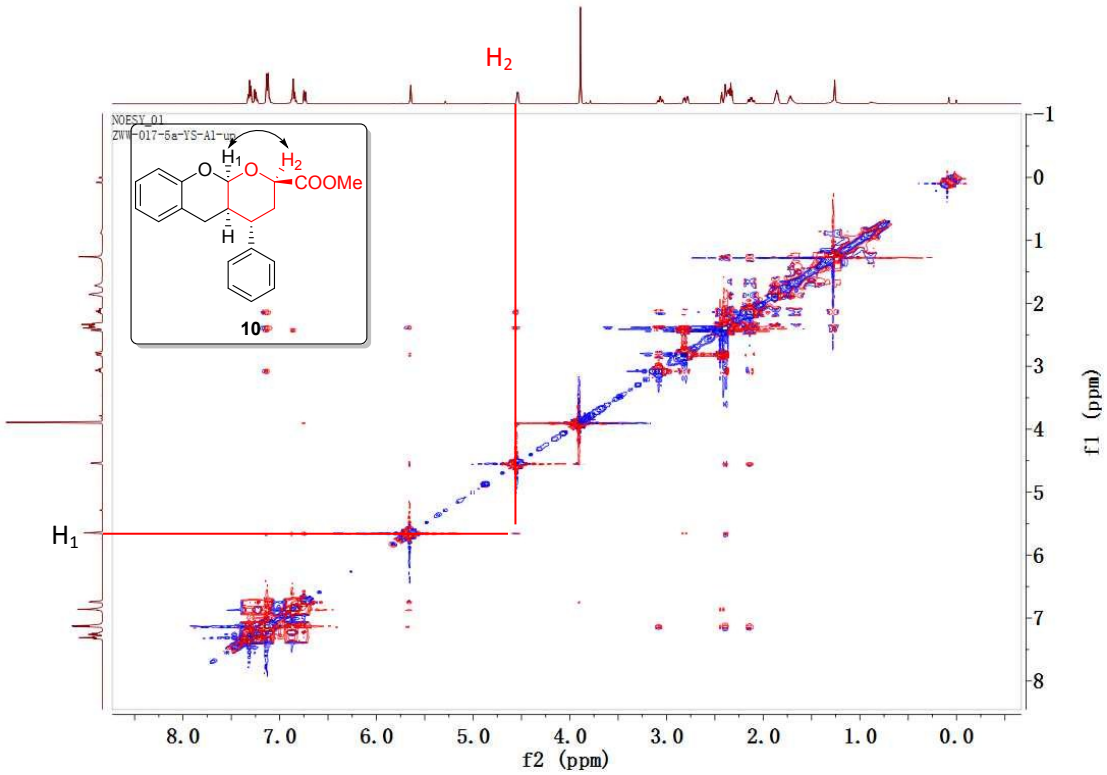
The ^{1}H NMR spectrum of 10 (500 MHz, $CDCl_3$)



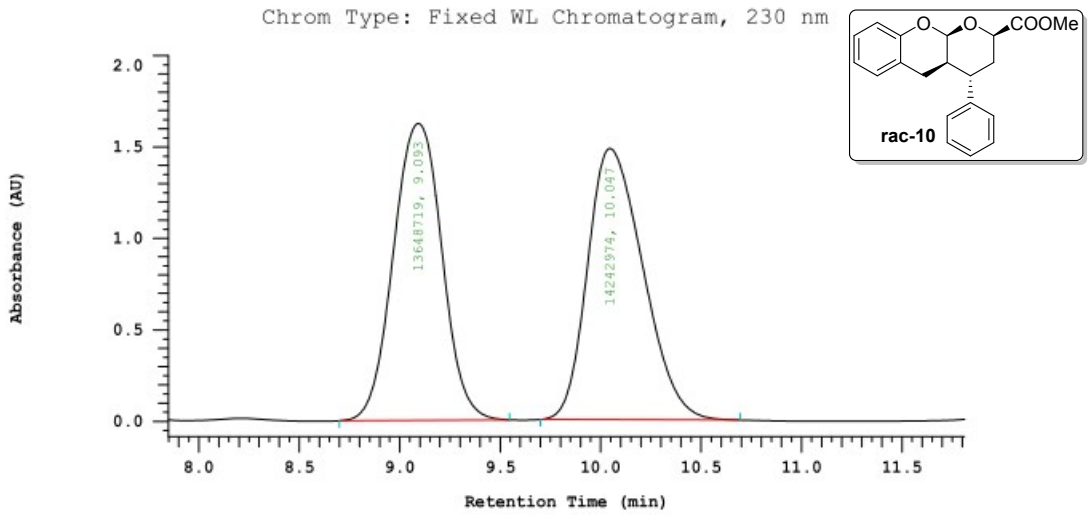
The ^{13}C NMR spectrum of 10 (125 MHz, $CDCl_3$)



The NOSEY spectrum of 10 (500 MHz, $CDCl_3$)



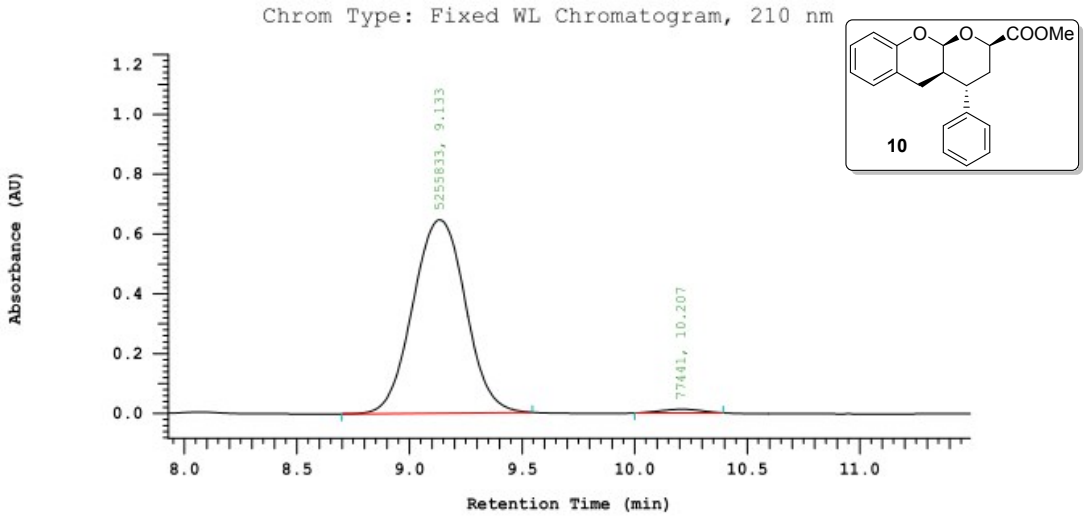
The HPLC of racemic 10



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.093	13648719	48.935	BB
2	10.047	14242974	51.065	BB
		27891693	100.000	

The HPLC of chiral 10



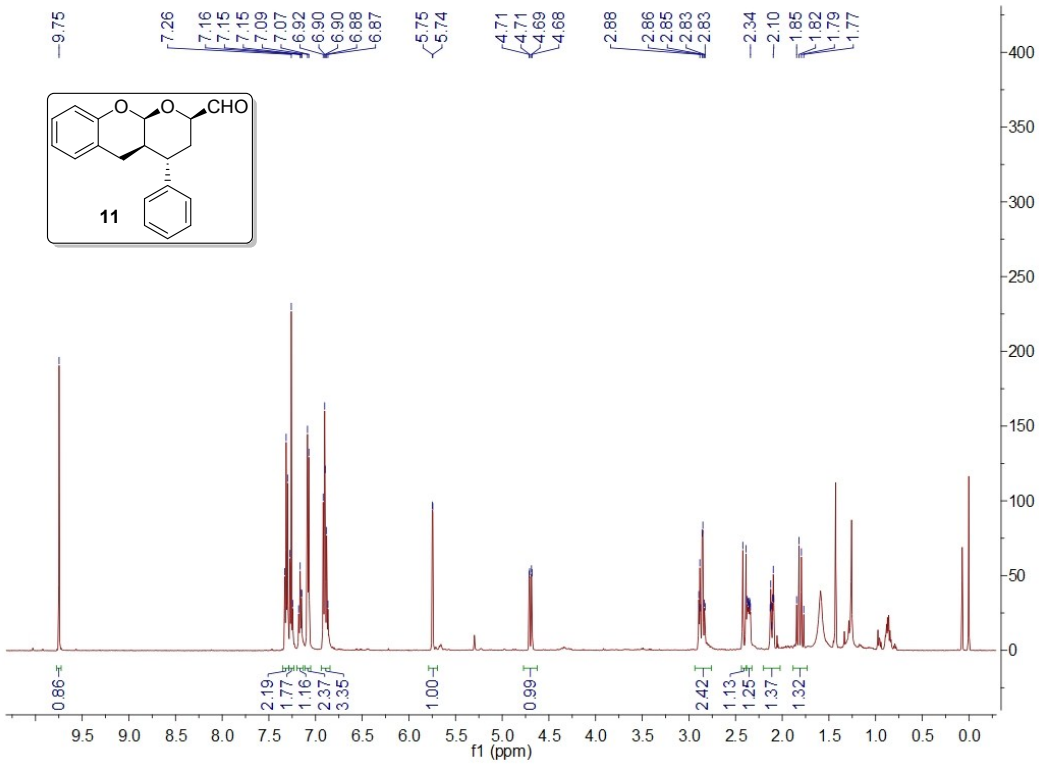
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

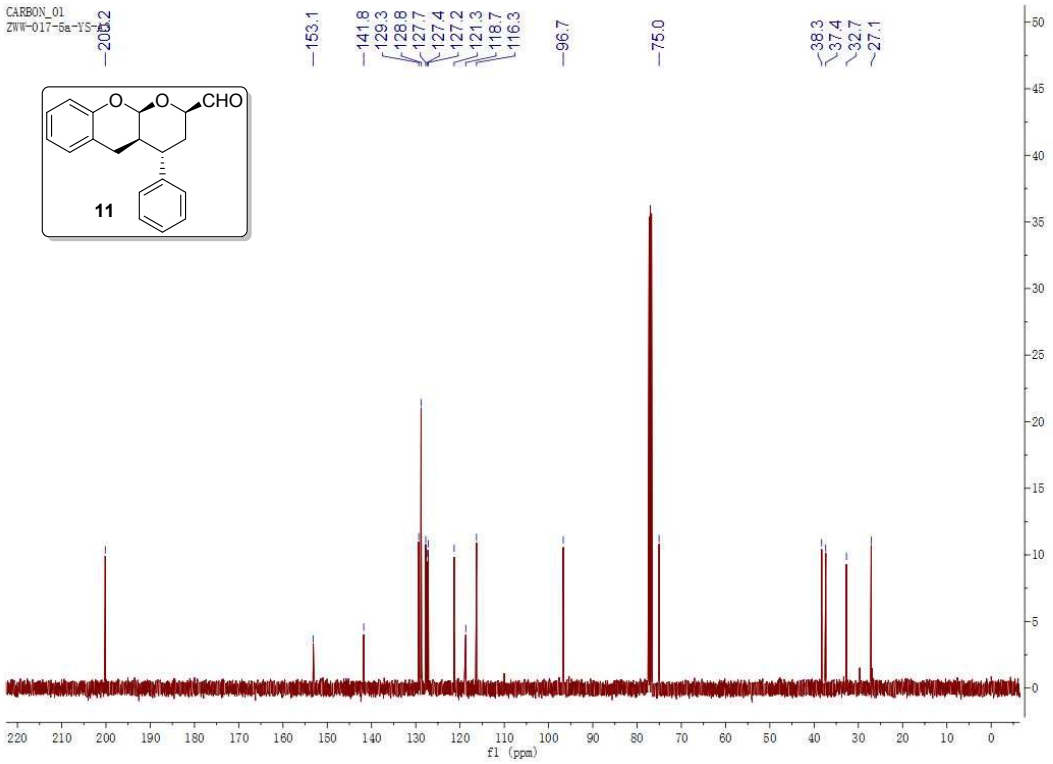
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.133	5255833	98.548	BB
2	10.207	77441	1.452	BB
		5333274	100.000	

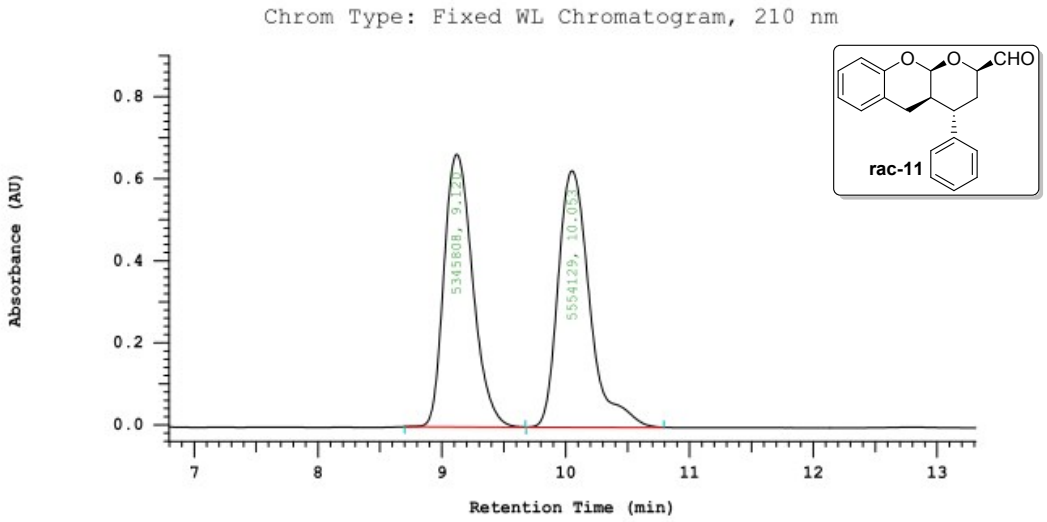
The ^{1}H NMR spectrum of 11 (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 11 (125 MHz, $CDCl_3$)



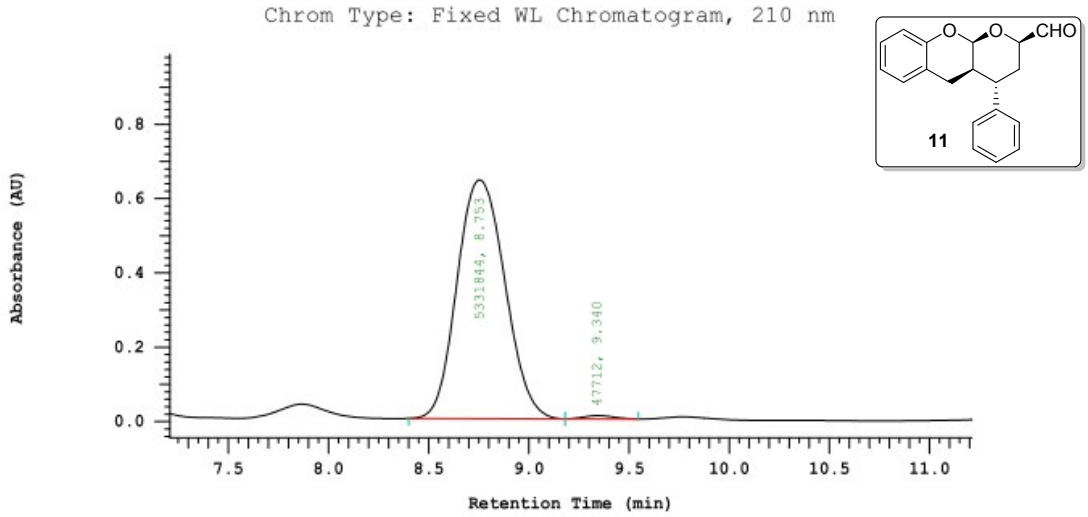
The HPLC of racemic 11



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.120	5345808	49.044	BB
2	10.053	5554129	50.956	BB
		10899937	100.000	

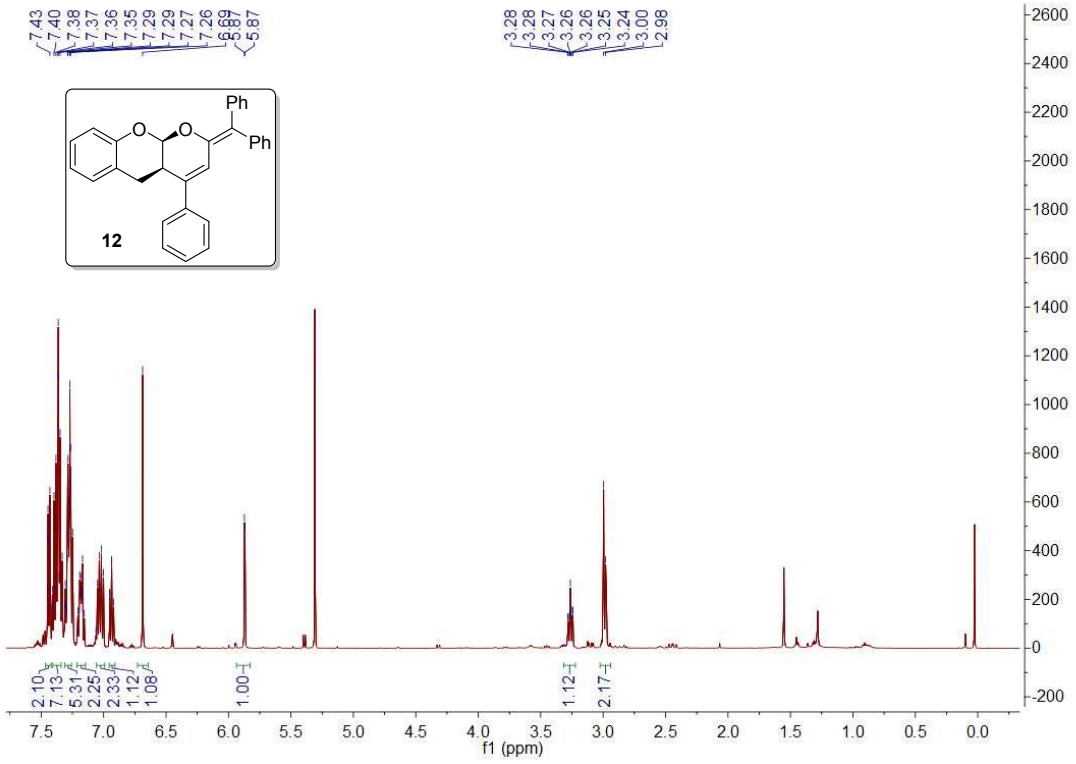
The HPLC of chiral 11



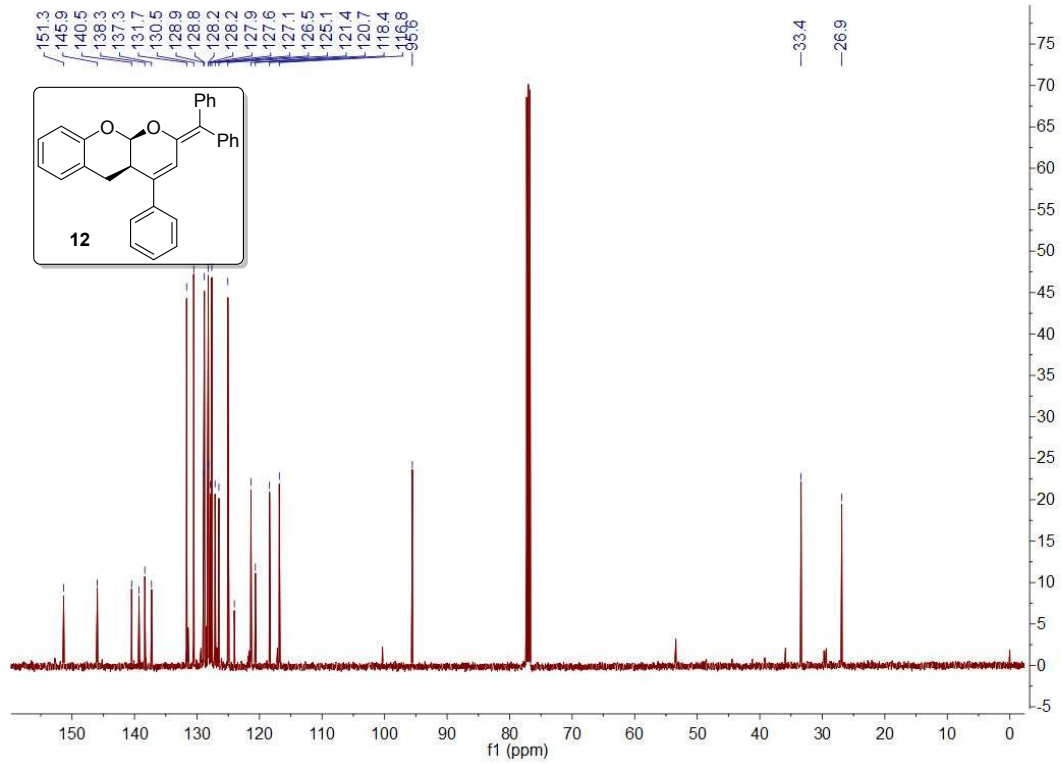
Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.753	5331844	99.113	BB
2	9.340	47712	0.887	BB
		5379556	100.000	

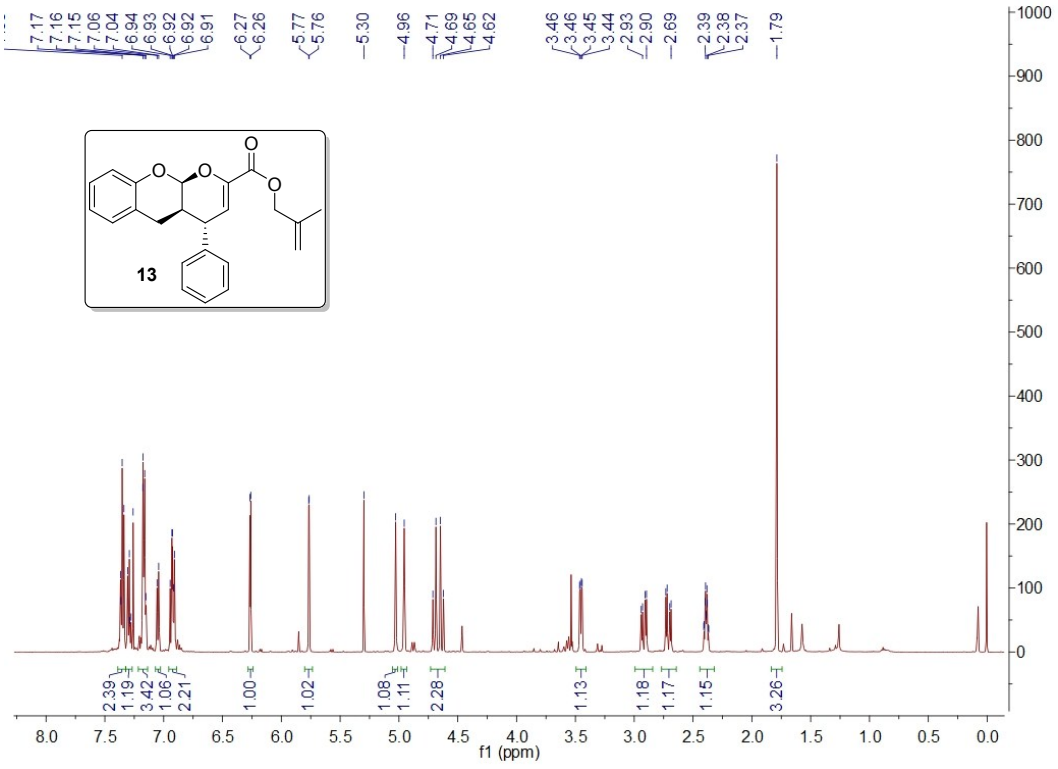
The ^{1}H NMR spectrum of 12 (500 MHz, $CDCl_3$)



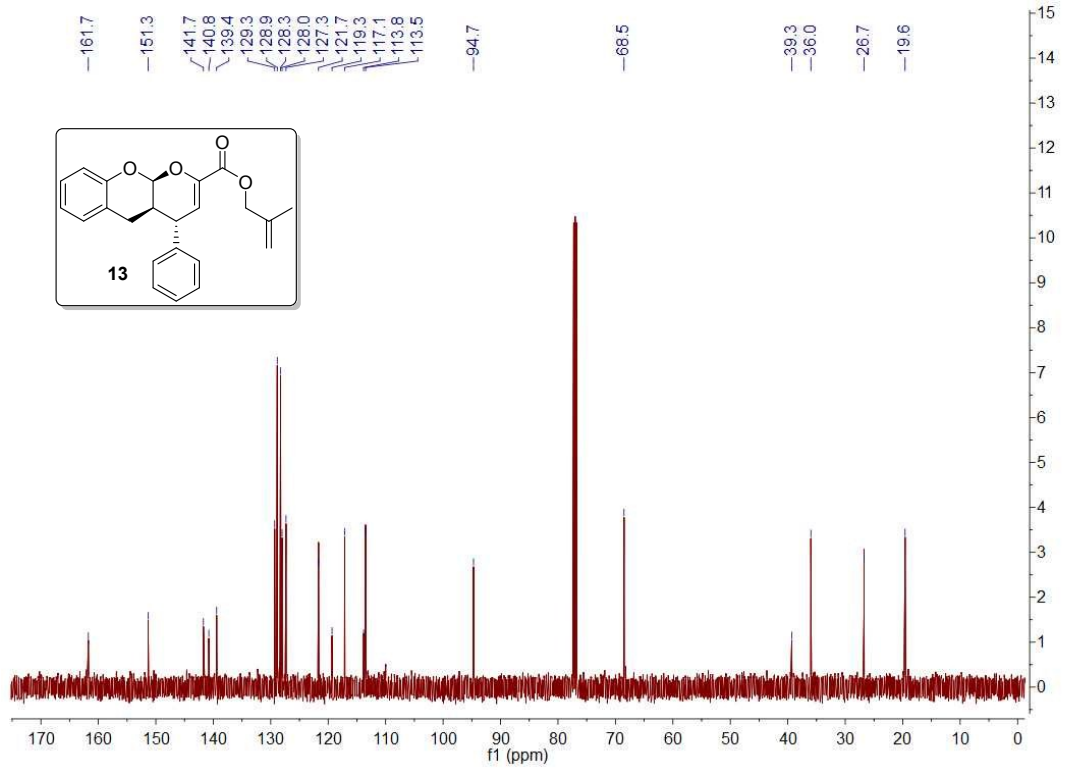
The ^{13}C NMR spectrum of 12 (125 MHz, $CDCl_3$)



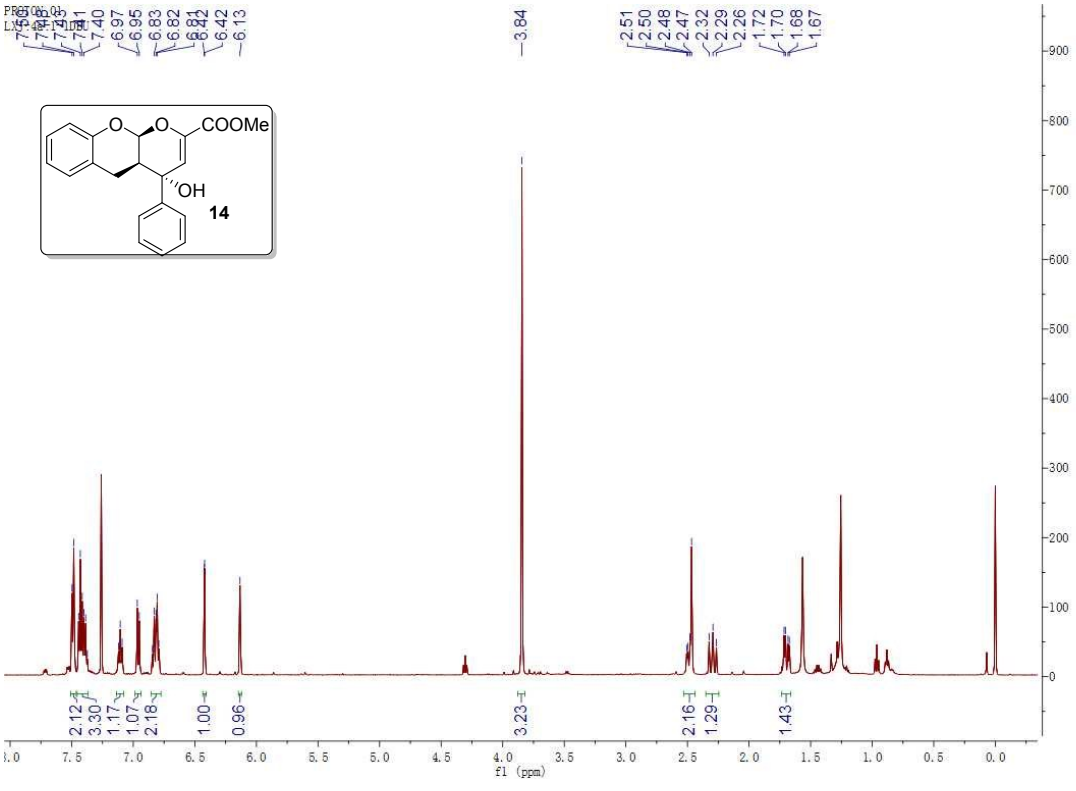
The ^{1}H NMR spectrum of 13 (500 MHz, $CDCl_3$)



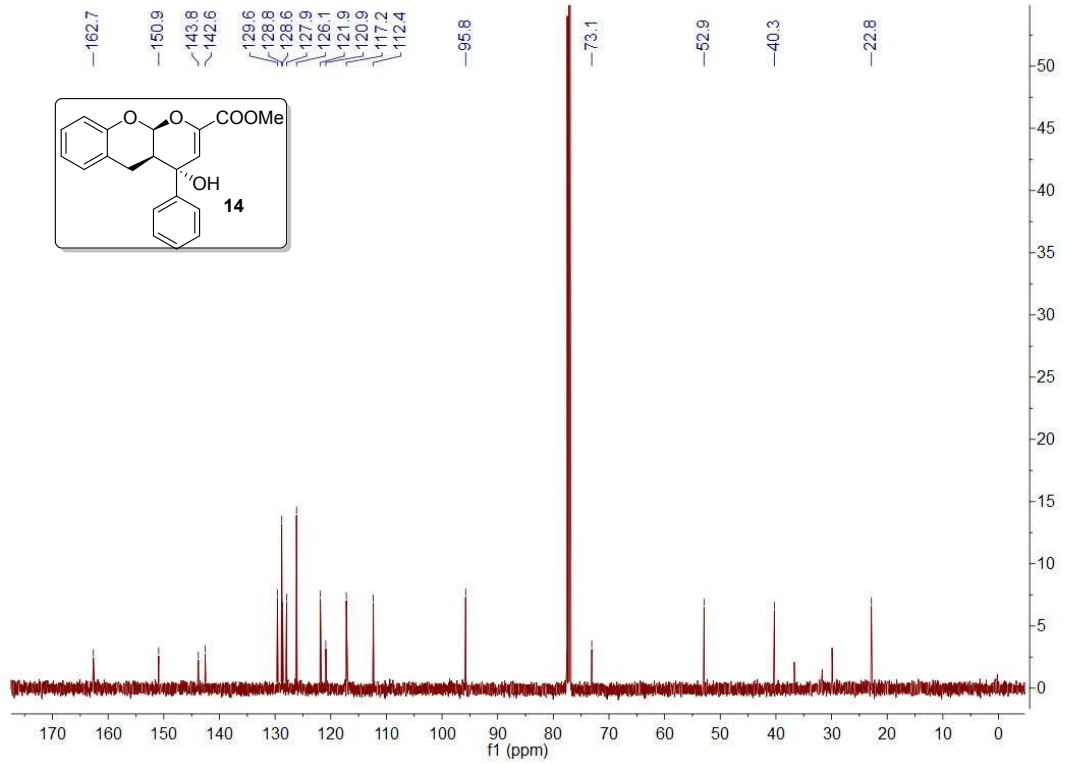
The ^{13}C NMR spectrum of 13 (125 MHz, $CDCl_3$)



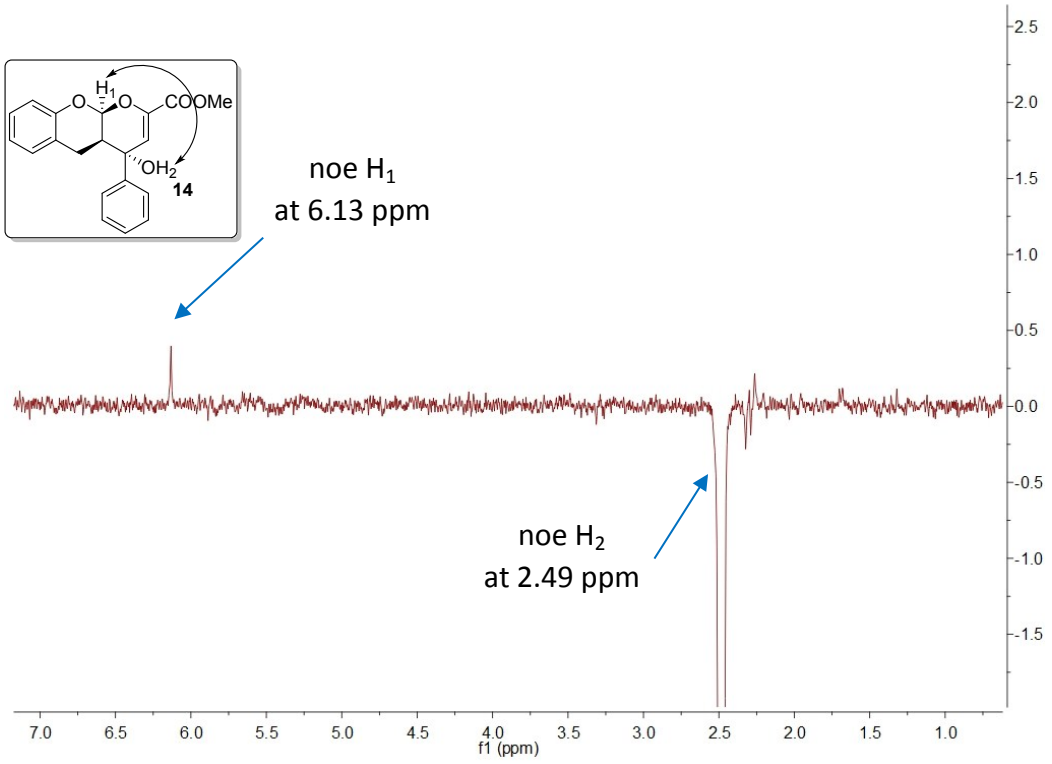
The ^{1}H NMR spectrum of 14 (500 MHz, $CDCl_3$)



The ^{13}C NMR spectrum of 14 (125 MHz, $CDCl_3$)



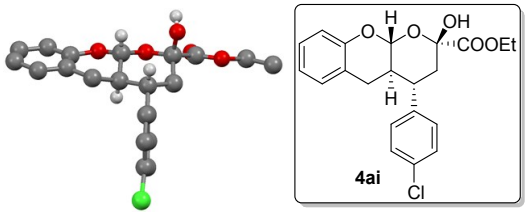
The NOE pectrum of 14 (500 MHz, $CDCl_3$)



M. Single crystal X-Ray diffraction data

[CCDC 1895258-1895260 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 **4ai** - CCDC 1895258



Bond precision: C-C = 0.0095 A Wavelength=0.71073

Cell: a=7.229(4) b=11.212(6) c=22.921(12)
alpha=90 beta=90 gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1857.8(17)	1857.8(17)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C21 H21 Cl O5	C21 H21 Cl O5
Sum formula	C21 H21 Cl O5	C21 H21 Cl O5
Mr	388.83	388.83
Dx,g cm-3	1.390	1.390
Z	4	4
Mu (mm-1)	0.236	0.236
F000	816.0	816.0
F000'	817.00	
h,k,lmax	8,13,27	8,13,27
Nref	3279[1908]	3263
Tmin,Tmax		0.500,0.746
Tmin'		

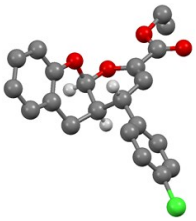
Correction method= # Reported T Limits: Tmin=0.500 Tmax=0.746
AbsCorr = MULTI-SCAN

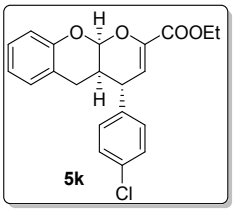
Data completeness= 1.71/1.00 Theta(max)= 25.014

R(reflections)= 0.0738(2359) wR2(reflections)= 0.2015(3263)

S = 1.002 Npar= 245

Absolute configuration of **5k** - CCDC 1895259





Bond precision: C-C = 0.0046 A Wavelength=0.71073

Cell: a=10.5134(13) b=7.5193(9) c=22.921(3)
alpha=90 beta=90 gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1812.0(4)	1812.0(4)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C21 H19 Cl O4	C21 H19 Cl O4
Sum formula	C21 H19 Cl O4	C21 H19 Cl O4
Mr	370.81	370.81
Dx,g cm-3	1.359	1.359
Z	4	4
Mu (mm-1)	0.234	0.234
F000	776.0	776.0
F000'	776.96	
h,k,lmax	13,9,29	13,9,29
Nref	4195[2410]	4139
Tmin,Tmax		0.694,0.746
Tmin'		

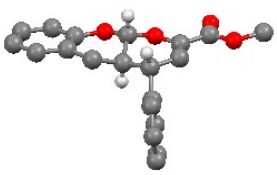
Correction method= # Reported T Limits: Tmin=0.694 Tmax=0.746
AbsCorr = MULTI-SCAN

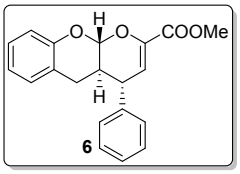
Data completeness= 1.72/0.99 Theta(max)= 27.593

R(reflections)= 0.0472(3342) wR2(reflections)= 0.1190(4139)

S = 1.036 Npar= 236

Relative configuration of **6** - CCDC 1895260





Bond precision: C-C = 0.0037 A Wavelength=0.71073

Cell: a=10.3231(13) b=8.3376(10) c=10.6510(13)
alpha=90 beta=116.926(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	817.35(17)	817.35(17)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C20 H18 O4	C20 H18 O4
Sum formula	C20 H18 O4	C20 H18 O4
Mr	322.34	322.34
Dx,g cm-3	1.310	1.310
Z	2	2
Mu (mm-1)	0.091	0.091
F000	340.0	340.0
F000'	340.18	
h,k,lmax	13,10,13	13,10,13
Nref	3766[2013]	3389
Tmin,Tmax		0.688,0.746
Tmin'		

Correction method= # Reported T Limits: Tmin=0.688 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.68/0.90 Theta(max)= 27.530

R(reflections)= 0.0357(3014) wR2(reflections)= 0.0905(3389)

S = 1.048 Npar= 218
