Supporting Information

Ir/Brønsted acid dual-catalyzed asymmetric synthesis of bisbenzannulated spiroketals and spiroaminals from isochroman ketals

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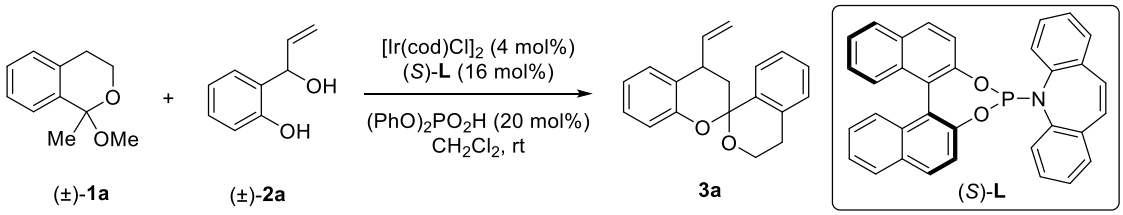
1. General information

^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The spectra are interpreted as: s, singlet; d, doublet; t, triplet; m, multiplet; dd, double doublet; ddd, double double doublet; ddq, double double quartet; coupling constant(s) *J* are reported in Hz and relative integrations are reported. ^{13}C NMR (100 MHz) spectrum were recorded on a Bruker DPX 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.16 ppm as a standard; ^{19}F NMR (376 or 565 MHz) spectra were recorded on a Bruker DPX 400 or 600 MHz spectrometer in $CDCl_3$ and referenced relative to $CFCl_3$. Optical rotations were measured on an AUTOPOL V. Enantiomeric excesses were determined by analysis of HPLC traces, obtained by using Chiralpak AD-H, IA, IB, IC, IF, IG and Chiralcel OD-H, OJ-H, columns with *n*-hexane and ethanol or isopropanol as solvents. (Chiralpak AD-H, IA, IB, IC, IF, IG and Chiralcel OD-H, OJ-H columns were purchased from Daicel Chiral Technologies (China) Co., LTD.) Melting points were obtained in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected. High-resolution mass spectra (HRMS) were recorded on a Waters GCT Premier mass spectrometer using EI-TOF (electron ionization-time of flight). Commercially available materials purchased from Adamas-beta and Bidepharm, which were used as received. Solvent was purified according to the procedure from *Purification of Laboratory Chemicals*. $[Ir(cod)Cl]_2$ purchased from laajoo and Bidepharm. Carreira's ligand (*S*)-**L**,[1] substrates isochroman ketals (±)-**1**,[2] 2-(1-hydroxyallyl)phenols (±)-**2**,[3] and *N*-protected-2-(1-hydroxyallyl)anilines (±)-**4**[4-6] were prepared according to the literature procedures.

2. Optimization study

1) The optimization studies for synthesis of bisbenzannulated spiroketal 3a

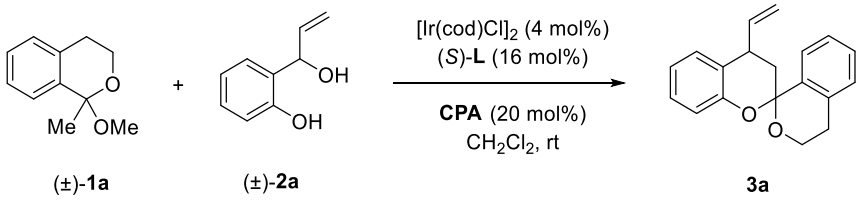
Table S1: The dr value of product **3a** along with the course of the reaction.



entry[a]	time	ee (%)[b]	dr[c]
1	5 min	98	3:1
2	10 min	98	5:1
3	30 min	98	11:1
4	1 h	98	11:1
5	2 h	98	12:1
6	6 h	98	12:1
7	12 h	98	12:1
8	24 h	98	12:1
9	48 h	98	12:1

[a] The reaction was carried out with (±)-**1a** (0.20 mmol), (±)-**2a** (0.40 mmol), $[Ir(cod)Cl]_2$ (4 mol%), (*S*)-**L** (16 mol%), $(PhO)_2PO_2H$ (20 mol%) in dry CH_2Cl_2 (2.0 mL) at room temperature. [b] Determined by HPLC analysis on a chiral stationary phase. [c] Determined by ^1H NMR analysis and HPLC analysis.

Table S2: The dr value of product **3a** along with the course of the reaction by using **CPA**.



entry[a]	**CPA**	time	ee (%)[b]	dr[c]
1	(*R*)-**A**	5 min	96	1:2
2	(*R*)-**A**	10 min	96	1:1.7
3	(*R*)-**A**	30 min	96	1:1.5
4	(*R*)-**A**	1 h	96	1:1.2
5	(*R*)-**A**	2 h	96	1:1.1
6	(*R*)-**A**	12 h	96	6:1
7	(*R*)-**A**	24 h	96	12:1
8	(*R*)-**A**	48 h	96	12:1
9	(*S*)-**A**	5 min	96	1:1.2
10	(*S*)-**A**	10 min	96	1:1.1
11	(*S*)-**A**	30 min	96	1:1
12	(*S*)-**A**	1 h	96	1.1:1

13	(*S*)-**A**	2 h	96	1.6:1
14	(*S*)-**A**	12 h	96	7:1
15	(*S*)-**A**	24 h	96	12:1
16	(*S*)-**A**	48 h	96	12:1

[a] The reaction was carried out with (±)-**1a** (0.20 mmol), (±)-**2a** (0.40 mmol), $[Ir(cod)Cl]_2$ (4 mol%), (*S*)-**L** (16 mol%), **CPA** (0.2 equiv) in dry CH_2Cl_2 (2.0 mL) at room temperature. [b] Determined by HPLC analysis on a chiral stationary phase. [c] Determined by ^1H NMR analysis and HPLC analysis.

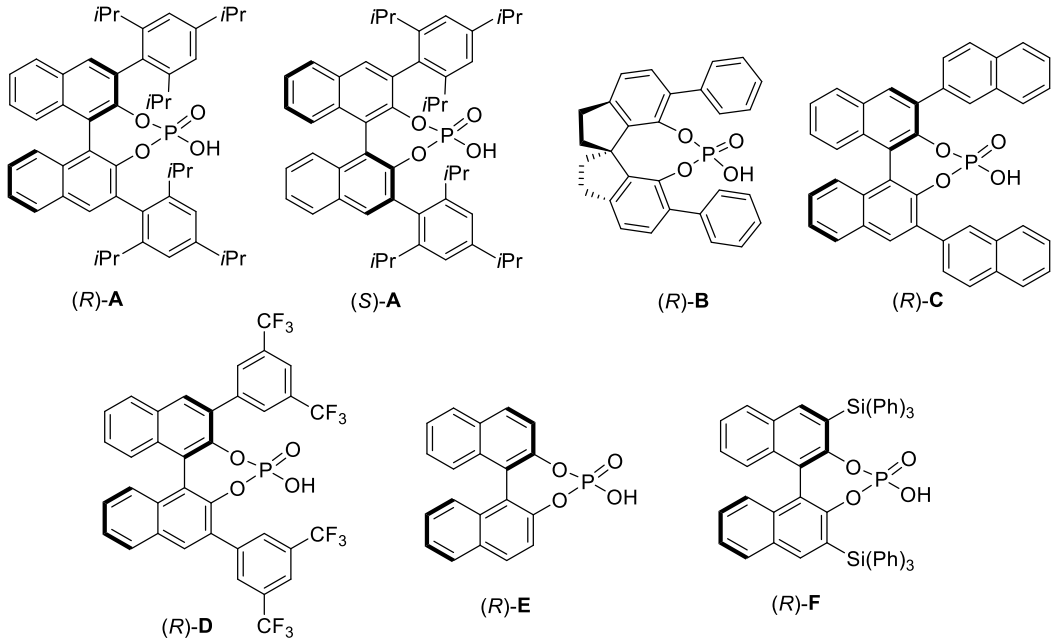
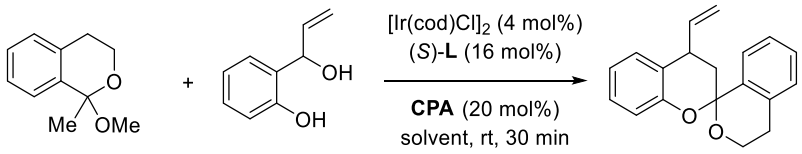


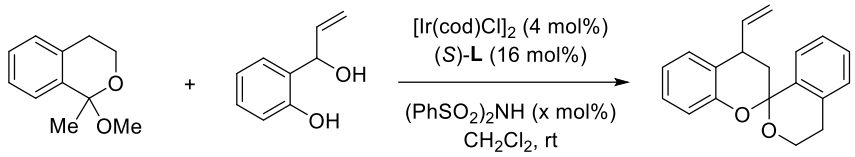
Table S3: The screening of various **CPA**.



entry[a]	**CPA**	solvent	yield (%)[b]	ee (%)[c]	dr[d]
1	(*R*)-**A**	CH_2Cl_2	76	96	1:1.5
2	(*S*)-**A**	CH_2Cl_2	86	96	1.6:1
3	(*R*)-**B**	CH_2Cl_2	68	98	1:1.2
4	(*R*)-**C**	CH_2Cl_2	88	98	10:1
5	(*R*)-**D**	CH_2Cl_2	92	97	12:1
6	(*R*)-**E**	CH_2Cl_2	97	98	12:1
7	(*R*)-**F**	CH_2Cl_2	73	95	1:1.1
8	(*R*)-**A**	toluene	32	95	1:1.2
9	(*R*)-**A**	THF	9	99	1:1.2

[a] The reaction was carried out with (±)-**1a** (0.20 mmol), (±)-**2a** (0.40 mmol), $[Ir(cod)Cl]_2$ (4 mol%), (*S*)-**L** (16 mol%), **CPA** (20 mol%) in dry solvent (2.0 mL) at room temperature. [b] Yield of the diastereomeric mixtures. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Determined by ^1H NMR analysis and HPLC analysis.

Table S4: The screening of the amount of $(PhSO_2)_2NH$ and additives.



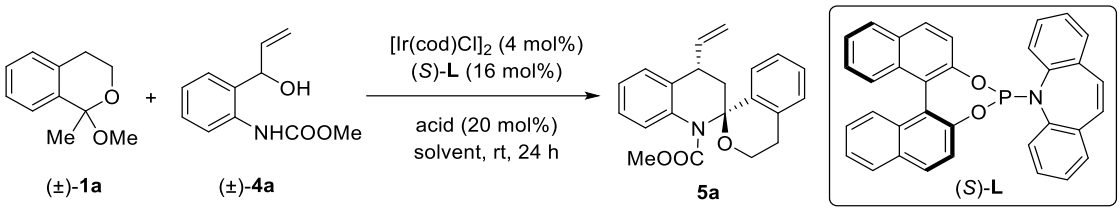
(±)-**1a** (±)-**2a** **3a**

entry[a]	$(PhSO_2)_2NH$	additive	t (h)	yield (%)[b]	ee (%)[c]	dr[d]
1	20 mol%	-	2	99	99	12:1
2	10 mol%	-	4	99	99	6:1
3	10 mol%	-	24	99	99	7:1
4	20 mol%	3Å MS	12	99	99	6:1
5	20 mol%	4Å MS	12	99	99	3:1
6	20 mol%	5Å MS	12	99	99	11:1

[a] The reaction was carried out with (±)-**1a** (0.20 mmol), (±)-**2a** (0.40 mmol), $[Ir(cod)Cl]_2$ (4 mol%), (*S*)-**L** (16 mol%), $(PhSO_2)_2NH$ (x mol%), and additive (50.0 mg) in dry CH_2Cl_2 (2.0 mL) at room temperature. [b] Yield of the diastereomeric mixtures. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Determined by ^1H NMR analysis and HPLC analysis.

2) The optimization studies for synthesis of bisbenzannulated spiroaminal 5a

Table S5: The optimization studies for synthesis of bisbenzannulated spiroaminal **5a**.

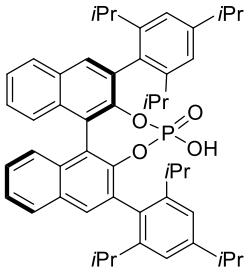


(±)-**1a** (±)-**4a** **5a**

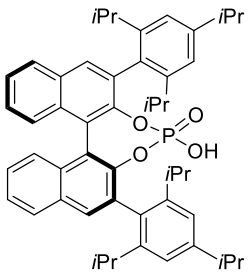
entry[a]	acid	solvent	yield (%)[b]	ee (%)[c]	dr[d]
1	CF_3CO_2H	CH_2Cl_2	78	99	5:1
2	$(PhSO_2)_2NH$	CH_2Cl_2	77	98	5:1
3	$Zn(OTf)_2$	CH_2Cl_2	71	99	5:1
4	$Sc(OTf)_3$	CH_2Cl_2	75	98	5:1
5	$Fe(OTf)_2$	CH_2Cl_2	76	98	5:1
6	(*R*)-**A**	CH_2Cl_2	16	99	5:1
7	(*S*)-**A**	CH_2Cl_2	31	99	4:1
8	(*R*)-**D**	CH_2Cl_2	79	97	6:1
9	(*S*)-**D**	CH_2Cl_2	80	97	6:1
10	(*R*)-**E**	CH_2Cl_2	74	99	6:1
11	(*S*)-**E**	CH_2Cl_2	78	99	6:1
12	(*R*)-**F**	CH_2Cl_2	0	-	-
13	(*S*)-**F**	CH_2Cl_2	0	-	-
14	CF_3CO_2H	toluene	72	99	6:1
15	CF_3CO_2H	THF	55	99	5:1
16	CF_3CO_2H	CH_3CN	56	91	6:1
17	CF_3CO_2H	1,4-dioxane	76	99	5:1

18	CF_3CO_2H	DCE	78	99	5:1
19	CF_3CO_2H	$PhCF_3$	78	99	5:1
20[e]	CF_3CO_2H	CH_2Cl_2	76	99	6:1
21[f]	CF_3CO_2H	CH_2Cl_2	60	99	6:1

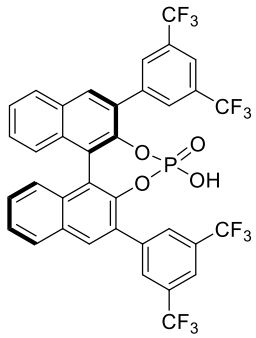
[a] The reaction was carried out with (±)-**1a** (0.10 mmol), (±)-**4a** (0.20 mmol), $[Ir(cod)Cl]_2$ (4 mol%), (*S*)-**L** (16 mol%), acid (20 mol%) in dry solvent (1.0 mL) at room temperature. [b] Yield of the diastereomeric mixtures. [c] Determined by HPLC analysis on a chiral stationary phase. [d] Determined by ^1H NMR analysis and HPLC analysis. [e] $[Ir(cod)Cl]_2$ (2 mol%) and (*S*)-**L** (8 mol%) were used. [f] $[Ir(cod)Cl]_2$ (1 mol%) and (*S*)-**L** (4 mol%) were used.



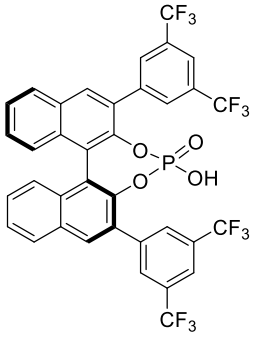
(*R*)-**A**



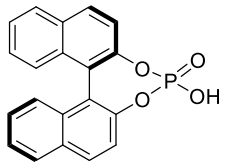
(*S*)-**A**



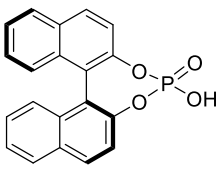
(*R*)-**D**



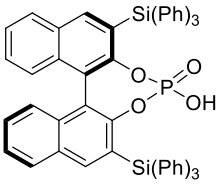
(*S*)-**D**



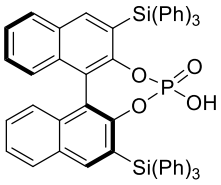
(*R*)-**E**



(*S*)-**E**

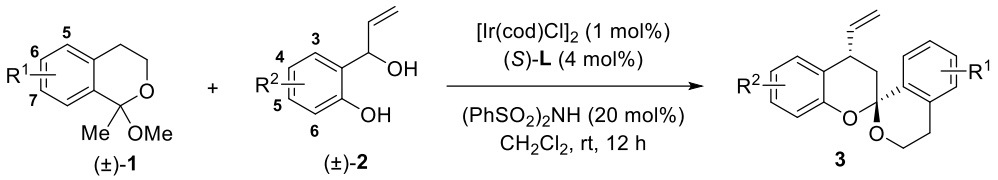


(*R*)-**F**



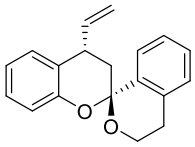
(*S*)-**F**

3. General procedure and characterization data for bisbenzannulated spiroketals 3



General procedure A: Under a nitrogen atmosphere, a flame dried 10 mL Schlenk tube was charged with $[Ir(cod)Cl]_2$ (2.0 mg, 0.003 mmol, 1 mol%), Carreira's ligand (*S*)-**L** (6.1 mg, 0.012 mmol, 4 mol%). After the tube was evacuated and backfilled with nitrogen, freshly distilled CH_2Cl_2 (3.0 mL) was added, then stirred at room temperature for 15 minutes while the solution turned dark red. Then, 2-(1-hydroxyallyl)phenols (±)-**2** (0.6 mmol, 2.0 equiv) were added and the reaction mixture immediately turned light yellow. Isochroman ketals (±)-**1** (0.3 mmol, 1.0 equiv) and $(PhSO_2)_2NH$ (18.0 mg, 0.06 mmol, 0.2 equiv) were added sequentially. The reaction mixture was stirred at room temperature for 12 h, which was directly purified by silica gel flash column chromatography (petroleum ether/EtOAc = 10/1) to afford bisbenzannulated spiroketals **3**.

Corresponding racemic products rac-**3** were prepared according to the general procedure **A** using racemic ligand which had the same skeleton with (*S*)-**L**.



(2*R*,4*S*)-4-Vinylspiro[chromane-2,1'-isochromane] (3a): Following the general procedure **A**, compound **3a** was obtained as a white solid in 99% yield of the diastereomeric mixtures (82.6 mg), 12:1 dr and 99% ee; R_f = 0.8 (petroleum ether/EtOAc = 10/1), m.p: 84 – 86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 1H), 7.29 – 7.22 (m, 3H), 7.20 – 7.12 (m, 2H), 7.01 – 6.90 (m, 1H), 6.86 (dd, *J* = 8.2, 1.2 Hz, 1H), 5.89 (ddd, *J* = 17.0, 9.5, 8.4 Hz, 1H), 5.33 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.25 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.21 – 4.11 (m, 1H), 3.95 – 3.87 (m, 2H), 3.15 – 3.06 (m, 1H), 2.70 – 2.63 (m, 1H), 2.31 (dd, *J* = 13.3, 12.9 Hz, 1H), 2.10 (dd, *J* = 13.3, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 140.1, 136.5, 134.6, 128.8, 128.7, 128.4, 127.9, 126.9, 126.6, 124.4, 121.0, 117.5(4), 117.4(5), 96.8, 59.5, 39.2, 37.5, 28.9; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{18}O_2$: 278.1301, found: 278.1302; $[\alpha]_D^{25}$ = +35.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R =

7.286 min (*trans*-minor), 9.282 min (*cis*-major), 10.938 min (*cis*-minor), 11.996 min (*trans*-major).

The preparation and X-ray analysis of the single crystal: Compound **3a** (10.0 mg) was dissolved in 1.0 mL dichloromethane in a screw-top vial and drops of *n*-hexane were added. The lid was then loosely screwed on the vial, and a single crystal was obtained by natural volatilization at room temperature. The data set was collected by a Bruker APEX-II CCD at 293(2) K equipped with Cu radiation source (Kα = 1.54178 Å). Applied with multi-scan absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package. CCDC 2342942 contains the supplementary crystallographic data, and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

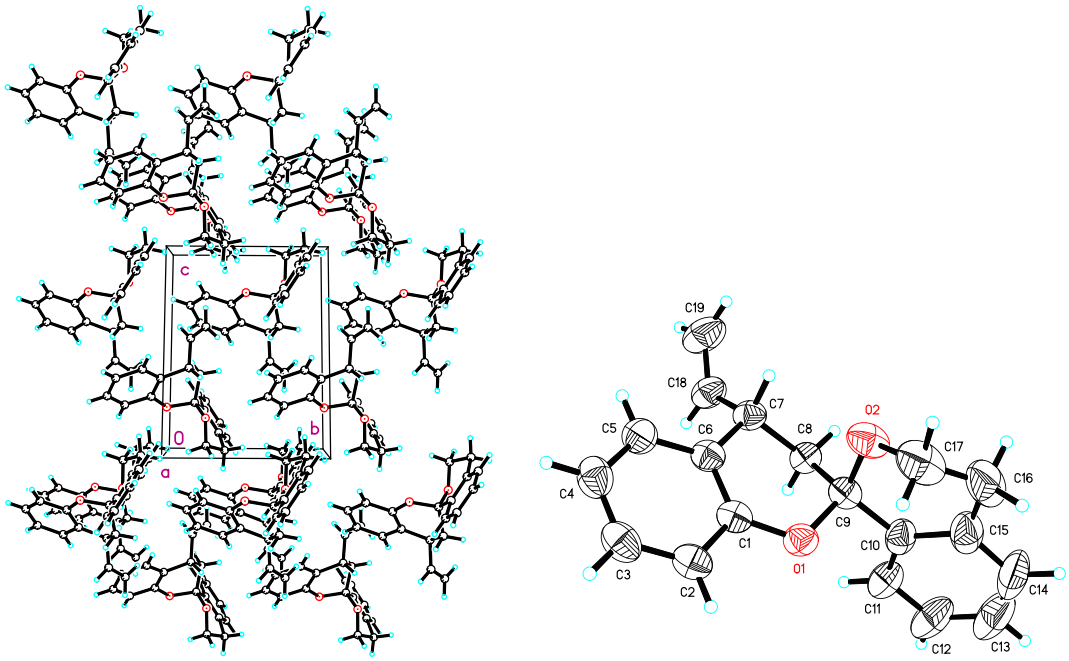
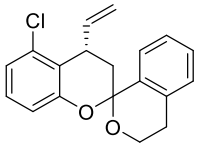


Fig S1. The thermal ellipsoid plot for X-ray structure of (2*R*,4*S*)-**3a** with the ellipsoid contour at 30% probability levels

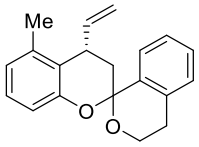
Crystal data and structure refinement for (2*R*,4*S*)-3a

Identification code	cu_dd22077_0m	
Empirical formula	C19 H18 O2	
Formula weight	278.33	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 9.2482(5) Å	= 90 °.
	b = 8.0146(4) Å	= 111.655(2) °.
	c = 11.0460(6) Å	= 90 °.

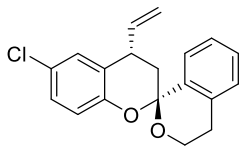
Volume	760.95(7) $Å^3$
Z	2
Density (calculated)	1.215 Mg/m^3
Absorption coefficient	0.612 mm^{-1}
F (000)	296
Crystal size	0.180 x 0.120 x 0.050 mm^3
Theta range for data collection	4.306 to 67.488 °.
Index ranges	-11<=h<=11, -9<=k<=9, -12<=l<=13
Reflections collected	15380
Independent reflections	2676 [R(int) = 0.0637]
Completeness to theta = 67.679 °	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.5406
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2676 / 1 / 191
Goodness-of-fit on F^2	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.1177
R indices (all data)	R1 = 0.0498, wR2 = 0.1251
Absolute structure parameter	-0.07(16)
Extinction coefficient	0.14(2)
Largest diff. peak and hole	0.106 and -0.114 $e.Å^{-3}$



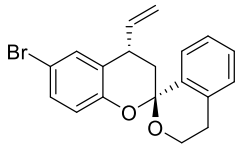
(2*R*,4*S*)-5-Chloro-4-vinylspiro[chromane-2,1'-isochromane] (3b): Following the general procedure **A**, compound **3b** was obtained as a colorless oil in 99% yield of the diastereomeric mixtures (92.7 mg), 2:1 dr and 98% / 93% ee [*The product **3b** was treated with CF_3CO_2H (20 mol%) in CH_2Cl_2 for 12 h, the dr value had not been changed*], R_f = 0.8 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 3H), 7.20 – 7.13 (m, 1H), 7.13 – 7.04 (m, 1H), 7.04 – 6.96 (m, 1H), 6.86 – 6.75 (m, 1H), 6.21 (ddd, *J* = 17.7, 10.1, 8.1 Hz, 1H), 5.23 – 4.99 (m, 2H), 4.18 – 4.08 (m, 1H), 3.96 – 3.89 (m, 1H), 3.88 – 3.81 (m, 1H), 3.09 (ddd, *J* = 17.3, 12.2, 5.8 Hz, 1H), 2.72 – 2.58 (m, 2H), 2.32 – 2.18 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 141.2, 136.4, 135.4, 134.8, 128.9, 128.5, 128.3, 126.8, 126.7, 123.4, 122.4, 116.4, 114.9, 97.3, 59.4, 38.9, 37.5, 28.7; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}{}^{35}ClO_2$: 312.0912, found: 312.0916; $C_{19}H_{17}{}^{37}ClO_2$: 314.0883, found: 314.0893; $[\alpha]_D^{25}$ = +56.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 6.923 min (*cis*-minor), 10.875 min (*trans*-major), 11.529 min (*trans*-minor), 12.263 min (*cis*-major).



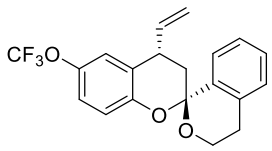
(2*R*,4*S*)-5-Methyl-4-vinylspiro[chromane-2,1'-isochromane] (3c): Following the general procedure **A**, compound **3c** was obtained as a white solid in 99% yield of the diastereomeric mixtures (86.7 mg), 1.6:1 dr and 99% / 99% ee [*The product **3c** was treated with CF_3CO_2H (20 mol%) in CH_2Cl_2 for 12 h, the dr value had not been changed*], R_f = 0.8 (petroleum ether/EtOAc = 10/1), m.p: 95 – 97 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 3H), 7.18 – 7.12 (m, 1H), 7.10 – 7.00 (m, 1H), 6.82 – 6.68 (m, 2H), 6.24 (ddd, *J* = 17.7, 9.4, 8.1 Hz, 1H), 5.18 – 4.99 (m, 2H), 4.19 – 4.09 (m, 1H), 3.94 – 3.83 (m, 1H), 3.66 – 3.58 (m, 1H), 3.09 (ddd, *J* = 17.6, 12.2, 6.1 Hz, 1H), 2.77 – 2.55 (m, 2H), 2.29 (s, 3H), 2.24 – 2.12 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 142.8, 138.7, 137.0, 134.8, 128.8, 128.3, 127.5, 126.9, 126.8, 124.1, 123.2, 115.6, 114.1, 96.7, 59.2, 39.5, 37.5, 28.8, 19.6; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{20}O_2$: 292.1458, found: 292.1466; $[\alpha]_D^{25}$ = +68.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 6.458 min (*cis*-minor), 8.310 min (*trans*-major), 10.336 min (*cis*-major), 13.882 min (*trans*-minor).



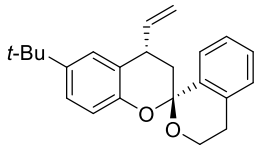
(2*R*,4*S*)-6-Chloro-4-vinylspiro[chromane-2,1'-isochromane] (3d): Following the general procedure **A**, compound **3d** was obtained as a white solid in 99% yield of the diastereomeric mixtures (92.9 mg), 14:1 dr and 99% ee; R_f = 0.8 (petroleum ether/EtOAc = 10/1), m.p: 99 – 101 °C; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 1H), 7.24 – 7.15 (m, 2H), 7.14 – 7.05 (m, 2H), 7.03 – 6.97 (m, 1H), 6.70 (dd, *J* = 8.7, 2.0 Hz, 1H), 5.69 (ddd, *J* = 16.8, 9.5, 8.4 Hz, 1H), 5.25 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.19 (dd, *J* = 9.5, 1.8 Hz, 1H), 4.13 – 3.99 (m, 1H), 3.88 – 3.73 (m, 2H), 3.07 – 2.96 (m, 1H), 2.62 – 2.52 (m, 1H), 2.19 (dd, *J* = 13.0, 12.6 Hz, 1H), 2.01 (dd, *J* = 13.4, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 139.2, 136.0, 134.6, 128.9, 128.6, 128.4, 127.8, 126.9, 126.6, 126.2, 125.9, 118.8, 118.3, 96.9, 59.6, 38.8, 37.6, 28.8; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}{}^{35}ClO_2$: 312.0912, found: 312.0918; $C_{19}H_{17}{}^{37}ClO_2$: 314.0883, found: 314.0892; $[\alpha]_D^{25}$ = +57.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OD-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 3.854 min (minor), 4.070 min (major).



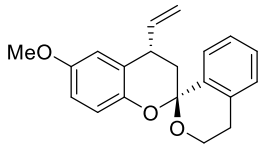
(2*R*,4*S*)-6-Bromo-4-vinylspiro[chromane-2,1'-isochromane] (3e): Following the general procedure **A**, compound **3e** was obtained as a colorless oil in 99% yield of the diastereomeric mixtures (106.0 mg), 14:1 dr and 99% ee; R_f = 0.8 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.22 – 7.16 (m, 2H), 7.14 – 7.07 (m, 2H), 6.64 (d, *J* = 8.6 Hz, 1H), 5.68 (ddd, *J* = 17.2, 9.5, 8.4 Hz, 1H), 5.24 (dd, *J* = 16.8, 1.8 Hz, 1H), 5.18 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.14 – 3.98 (m, 1H), 3.87 – 3.72 (m, 2H), 3.06 – 2.94 (m, 1H), 2.59 – 2.50 (m, 1H), 2.18 (dd, *J* = 13.0, 12.6 Hz, 1H), 2.00 (dd, *J* = 13.5, 5.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.9, 139.2, 136.0, 134.6, 131.4, 130.7, 128.9, 128.6, 126.9, 126.8, 126.5, 119.3, 118.3, 113.3, 96.9, 59.6, 38.8, 37.5, 28.7; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}{}^{79}BrO_2$: 356.0406, found: 356.0415; $C_{19}H_{17}{}^{81}BrO_2$: 358.0386, found: 358.0395; $[\alpha]_D^{25}$ = +47.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralpak IB, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 4.013 min (minor), 4.341 min (major).



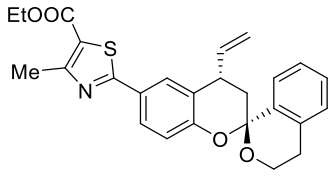
(2*R*,4*S*)-6-(Trifluoromethoxy)-4-vinylspiro[chromane-2,1'-isochromane] (3f): Following the general procedure **A**, compound **3f** was obtained as a colorless oil in 88% yield of the diastereomeric mixtures (95.6 mg), 14:1 dr and 97% ee; R_f = 0.8 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.19 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.78 (ddd, *J* = 17.0, 9.5, 8.4 Hz, 1H), 5.35 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.29 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.15 (ddd, *J* = 12.6, 11.2, 2.9 Hz, 1H), 4.01 – 3.82 (m, 2H), 3.20 – 3.04 (m, 1H), 2.72 – 2.60 (m, 1H), 2.28 (dd, *J* = 13.2, 13.0 Hz, 1H), 2.11 (dd, *J* = 13.4, 5.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.3, 143.0, 139.1, 136.0, 134.7, 128.9, 128.6, 127.0, 126.6, 125.8, 121.6, 120.9, 120.8 (q, C-F, $^1J_{C\text{-}F}$ = 329.0 Hz), 118.4, 118.3, 97.0, 59.7, 38.8, 37.6, 28.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.19 (s); **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{17}F_3O_3$: 362.1124, found: 362.1133; $[\alpha]_D^{25}$ = +35.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 4.927 min (*trans*-minor), 5.821 min (*cis*-major), 7.204 min (*cis*-minor), 7.892 min (*trans*-major).



(2*R*,4*S*)-6-(*tert*-Butyl)-4-vinylspiro[chromane-2,1'-isochromane] (3g): Following the general procedure **A**, compound **3g** was obtained as a white solid in 80% yield of the diastereomeric mixtures (80.2 mg), 13:1 dr and 96% ee [*The product **3g** was treated with CF_3CO_2H (20 mol%) in CH_2Cl_2 for 12 h, the dr value changed from 2:1 to 13:*1], R_f = 0.8 (petroleum ether/EtOAc = 10/1), m.p: 127 – 129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 1H), 7.28 – 7.21 (m, 3H), 7.19 – 7.11 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 5.82 (ddd, *J* = 17.2, 9.5, 8.4 Hz, 1H), 5.32 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.24 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.22 – 4.11 (m, 1H), 3.96 – 3.83 (m, 2H), 3.14 – 3.02 (m, 1H), 2.67 – 2.58 (m, 1H), 2.29 (dd, *J* = 12.9, 12.8 Hz, 1H), 2.08 (dd, *J* = 13.4, 5.7 Hz, 1H), 1.29 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.4, 143.6, 140.2, 136.6, 134.6, 128.8, 128.4, 126.9, 126.6, 125.3, 124.9, 123.4, 117.5, 116.8, 96.7, 59.5, 39.4, 37.6, 34.3, 31.7 (3C), 28.9; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{23}H_{26}O_2$: 334.1927, found: 334.1936; $[\alpha]_D^{25}$ = +34.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 5.315 min (*trans*-minor), 7.257 min (*cis*-major), 7.863 min (*cis*-minor), 11.389 min (*trans*-major).

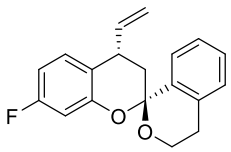


(2*R*,4*S*)-6-Methoxy-4-vinylspiro[chromane-2,1'-isochromane] (3h): Following the general procedure **A**, compound **3h** was obtained as a colorless oil in 98% yield of the diastereomeric mixtures (90.6 mg), 14:1 dr and 98% ee [*The product **3h** was treated with CF_3CO_2H (20 mol%) in CH_2Cl_2 for 12 h, the dr value changed from 8:1 to 14:1*], R_f = 0.8 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 6.4, 2.6 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.17 (dd, *J* = 6.4, 2.5 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.75 – 6.67 (m, 1H), 5.81 (ddd, *J* = 17.1, 9.5, 8.4 Hz, 1H), 5.32 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.24 (dd, *J* = 9.9, 1.7 Hz, 1H), 4.16 (ddd, *J* = 12.7, 11.2, 2.9 Hz, 1H), 3.96 – 3.81 (m, 2H), 3.75 (s, 3H), 3.09 (ddd, *J* = 17.6, 12.5, 6.0 Hz, 1H), 2.68 – 2.59 (m, 1H), 2.29 (dd, *J* = 13.0, 12.9 Hz, 1H), 2.08 (dd, *J* = 13.3, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.9, 146.7, 140.0, 136.5, 134.6, 128.8, 128.4, 126.9, 126.6, 125.0, 118.0, 117.6, 113.7, 113.6, 96.6, 59.4, 55.8, 39.1, 37.8, 28.8; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{20}O_3$: 308.1407, found: 308.1416; $[\alpha]_D^{25}$ = +53.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 14.027 min (*trans*-minor), 17.086 min (*cis*-major), 24.586 min (*cis*-minor), 26.904 min (*trans*-major).

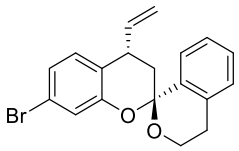


Ethyl 4-methyl-2-((2*R*,4*S*)-4-vinylspiro[chromane-2,1'-isochroman]-6-yl) thiazole-5-carboxylate (3i): Following the general procedure **A**, compound **3i** was obtained as a white solid in 99% yield of the diastereomeric mixtures (132.8 mg), 14:1 dr and 93% ee; R_f = 0.4 (petroleum ether/EtOAc = 10/1), m.p: 75 – 77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.33 – 7.23 (m, 2H), 7.19 (d, *J* = 7.0 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 5.85 (ddd, *J* = 17.0, 9.7, 8.4 Hz, 1H), 5.41 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.33 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.21 – 4.10 (m, 1H), 4.02 – 3.87 (m, 2H), 3.11 (ddd, *J* = 17.6, 12.5, 5.8 Hz, 1H), 2.76 (s, 3H), 2.70 – 2.61 (m, 1H), 2.32 (dd, *J* = 13.2, 13.0 Hz, 1H), 2.14 (dd, *J* = 13.8, 5.7 Hz, 1H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 162.6, 161.2, 155.5, 139.2, 135.8, 134.6, 128.9, 128.6, 127.6, 127.0, 126.8, 126.6, 126.3, 125.3, 120.9, 118.5, 118.2, 97.3, 61.2, 59.7, 39.1, 37.4, 28.7, 17.7, 14.5; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{26}H_{25}NO_4S$: 447.1499, found: 447.1508; $[\alpha]_D^{25}$ = +53.0 (*c* 0.20,

CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 9.729 min (minor), 10.635 min (major).

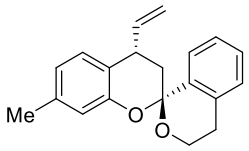


(2*R*,4*S*)-7-Fluoro-4-vinylspiro[chromane-2,1'-isochromane] (3j): Following the general procedure **A**, compound **3j** was obtained as a colorless oil in 96% yield of the diastereomeric mixtures (85.2 mg), 12:1 dr and 99% ee; R_f = 0.8 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 1H), 7.40 – 7.34 (m, 2H), 7.31 – 7.20 (m, 2H), 6.78 – 6.69 (m, 1H), 6.67 (dd, *J* = 10.1, 2.5 Hz, 1H), 5.85 (ddd, *J* = 16.9, 10.0, 8.4 Hz, 1H), 5.40 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.33 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.33 – 4.20 (m, 1H), 4.06– 3.98 (m, 1H), 3.96– 3.86 (m, 1H), 3.25 – 3.12 (m, 1H), 2.78 – 2.69 (m, 1H), 2.36 (dd, *J* = 13.7, 13.0 Hz, 1H), 2.18 (dd, *J* = 13.7, 5.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4 (d, C-F, $^1J_{C\text{-}F}$ = 243.9 Hz), 153.7 (d, C-F, $^3J_{C\text{-}F}$ = 11.8 Hz), 139.9, 136.0, 134.6, 129.7 (d, C-F, $^3J_{C\text{-}F}$ = 9.5 Hz), 128.9, 128.6, 126.9, 126.6, 120.2 (d, C-F, $^4J_{C\text{-}F}$ = 3.2 Hz), 117.7, 108.0 (d, C-F, $^2J_{C\text{-}F}$ = 21.3 Hz), 104.5 (d, C-F, $^2J_{C\text{-}F}$ = 24.4 Hz), 97.1, 59.6, 39.1, 37.1, 28.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.59 – -114.97 (m); **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}FO_2$: 296.1207, found: 296.1210; $[\alpha]_D^{25}$ = +24.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 3.546 min (minor), 3.807 min (major).

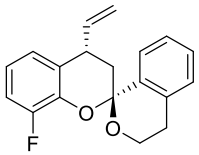


(2*R*,4*S*)-7-Bromo-4-vinylspiro[chromane-2,1'-isochromane] (3k): Following the general procedure **A**, compound **3k** was obtained as a white solid in 99% yield of the diastereomeric mixtures (106.0 mg), 14:1 dr and 99% ee [*The product **3k** was treated with CF_3CO_2H (20 mol%) in CH_2Cl_2 for 12 h, the dr value changed from 12:1 to 14:1*], R_f = 0.8 (petroleum ether/EtOAc = 10/1), m.p: 114 – 116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.31 – 7.25 (m, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.21 – 7.09 (m, 3H), 5.86 (ddd, *J* = 16.9, 10.7, 8.4 Hz, 1H), 5.42 (dd, *J* = 16.9, 1.8 Hz, 1H), 5.35 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.31 – 4.17 (m, 1H), 4.07 – 3.99 (m, 1H), 3.93 (ddd, *J* = 12.8, 7.6, 6.0 Hz, 1H), 3.26 – 3.12 (m, 1H), 2.80 – 2.69 (m, 1H), 2.37 (dd, *J* = 13.4, 12.4 Hz, 1H), 2.20 (dd, *J* = 13.4, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 139.4, 135.9, 134.6, 130.1, 128.9, 128.6, 126.9, 126.6, 124.0, 123.6, 120.7, 120.5, 118.0, 97.1, 59.7, 39.0, 37.2, 28.7; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}{}^{79}BrO_2$:

356.0406, found: 356.0414; $C_{19}H_{17}{}^{81}BrO_2$: 358.0386, found: 358.0397; $[\alpha]_D^{25}$ = +47.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralpak IG, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 3.759 min (minor), 4.006 min (major).

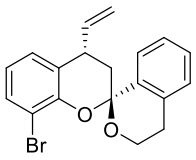


(2*R*,4*S*)-7-Methyl-4-vinylspiro[chromane-2,1'-isochromane] (3l): Following the general procedure **A**, compound **3l** was obtained as a white solid in 61% yield of the diastereomeric mixtures (53.4 mg), 14:1 dr and 99% ee; R_f = 0.8 (petroleum ether/EtOAc = 10/1), m.p: 84 – 86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.0, 2.7 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.17 (d, *J* = 6.3 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.69 (s, 1H), 5.79 (ddd, *J* = 17.0, 9.2, 8.4 Hz, 1H), 5.31 (dd, *J* = 16.8, 1.8 Hz, 1H), 5.23 (dd, *J* = 9.6, 1.8 Hz, 1H), 4.28 – 4.13 (m, 1H), 3.97 – 3.79 (m, 2H), 3.17 – 3.03 (m, 1H), 2.69 – 2.59 (m, 1H), 2.32 – 2.21 (m, 4H), 2.06 (dd, *J* = 13.2, 5.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.5, 140.2, 137.9, 136.5, 134.6, 128.8, 128.5, 128.3, 126.9, 126.6, 121.9, 121.4, 117.8, 117.3, 96.7, 59.5, 39.3, 37.2, 28.8, 21.1; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{20}O_2$: 292.1458, found: 292.1466; $[\alpha]_D^{25}$ = +38.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 6.684 min (*trans*-minor), 7.347 min (*cis*-major), 11.129 min (*cis*-minor), 12.234 min (*trans*-major).

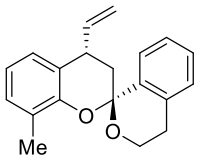


(2*R*,4*S*)-8-Fluoro-4-vinylspiro[chromane-2,1'-isochromane] (3m): Following the general procedure **A**, compound **3m** was obtained as a colorless oil in 99% yield of the diastereomeric mixtures (87.9 mg), 11:1 dr and 98% ee; R_f = 0.8 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 1H), 7.31 – 7.23 (m, 2H), 7.19 – 7.13 (m, 1H), 7.01 – 6.96 (m, 1H), 6.96 – 6.90 (m, 1H), 6.88 – 6.79 (m, 1H), 5.79 (ddd, *J* = 17.3, 9.6, 8.4 Hz, 1H), 5.32 (dd, *J* = 17.2, 1.9 Hz, 1H), 5.25 (dd, *J* = 9.9, 1.9 Hz, 1H), 4.24 – 4.14 (m, 1H), 3.9 – 3.84 (m, 2H), 3.10 (ddd, *J* = 17.5, 12.5, 5.8 Hz, 1H), 2.70 – 2.60 (m, 1H), 2.32 (dd, *J* = 13.5, 12.9 Hz, 1H), 2.11 (dd, *J* = 13.5, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1 (d, C-F, $^1J_{C\text{-}F}$ = 245.0 Hz), 141.2 (d, C-F, $^2J_{C\text{-}F}$ = 10.9 Hz), 139.6, 135.8, 134.7, 128.8, 128.6, 127.1, 126.9, 126.8, 123.6 (d, $^3J_{C\text{-}F}$ = 3.3 Hz), 120.1 (d, C-F, $^3J_{C\text{-}F}$ = 7.4 Hz), 117.8, 114.4 (d, C-F, $^2J_{C\text{-}F}$ = 18.4 Hz), 97.0, 59.8, 39.2, 37.5 (d, C-F, $^4J_{C\text{-}F}$ = 2.6 Hz), 28.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -

136.19 – -136.32 (m); **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}FO_2$: 296.1207, found: 296.1216; $[\alpha]_D^{25}$ = +36.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 8.603 min (minor), 10.228 min (major).

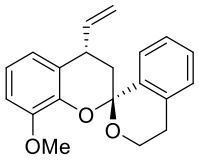


(2*R*,4*S*)-8-Bromo-4-vinylspiro[chromane-2,1'-isochromane] (3n): Following the general procedure **A**, compound **3n** was obtained as a colorless oil in 91% yield of the diastereomeric mixtures (97.5 mg), 14:1 dr, and 98% ee [*The product **3n** was treated with CF_3CO_2H (20 mol%) in CH_2Cl_2 for 12 h, the dr changed from 7:1 to 14:1*]; R_f = 0.8 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.13 (m, 2H), 6.86 – 6.75 (m, 1H), 5.78 (ddd, *J* = 18.0, 9.6, 8.4 Hz, 1H), 5.32 (dd, *J* = 17.8, 1.9 Hz, 1H), 5.25 (dd, *J* = 9.9, 1.9 Hz, 1H), 4.28 – 4.11 (m, 1H), 3.98 – 3.82 (m, 2H), 3.11 (ddd, *J* = 17.7, 12.5, 5.8 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.32 (dd, *J* = 13.2, 13.0 Hz, 1H), 2.10 (dd, *J* = 13.5, 6.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6, 139.6, 135.9, 134.6, 131.6, 128.8, 128.5, 127.9, 126.8(3), 126.8(0), 126.3, 121.6, 117.9, 111.8, 97.5, 59.8, 39.1, 37.9, 28.8; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}{}^{79}BrO_2$: 356.0406, found: 356.0414; $C_{19}H_{17}{}^{81}BrO_2$: 358.0386, found: 358.0394; $[\alpha]_D^{25}$ = +54.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralpak IG, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 4.031 min (major), 4.873 min (minor).

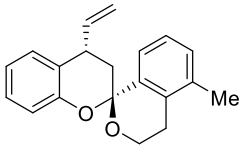


(2*R*,4*S*)-8-Methyl-4-vinylspiro[chromane-2,1'-isochromane] (3o): Following the general procedure **A**, compound **3o** was obtained as a white solid in 99% yield of the diastereomeric mixtures (86.7 mg), 12:1 dr and 99% ee [*The product **3o** was treated with CF_3CO_2H (20 mol%) in CH_2Cl_2 for 12 h, the dr value changed from 3:1 to 12:1*]; R_f = 0.8 (petroleum ether/EtOAc = 10/1), m.p: 65 – 67 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.88 – 6.78 (m, 1H), 5.80 (ddd, *J* = 17.2, 9.5, 8.4 Hz, 1H), 5.29 (dd, *J* = 17.0, 1.9 Hz, 1H), 5.21 (dd, *J* = 10.0, 1.9 Hz, 1H), 4.20 – 4.04 (m, 1H), 3.96 – 3.82 (m, 2H), 3.09 (ddd, *J* = 17.9, 12.8, 5.9 Hz, 1H), 2.69 – 2.55 (m, 1H), 2.28 (dd, *J* = 13.2, 13.0 Hz, 1H), 2.21 – 1.98 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.8, 140.4, 136.9, 134.7, 129.1, 128.7, 128.2, 126.9, 126.7, 126.4, 126.2, 123.8, 120.3, 117.2, 96.6, 59.5, 39.3, 37.6, 29.0, 16.4; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for

$C_{20}H_{20}O_2$: 292.1458, found: 292.1465; $[\alpha]_D^{25}$ = +34.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralpak AD-H, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 3.363 min (minor), 3.596 min (major).

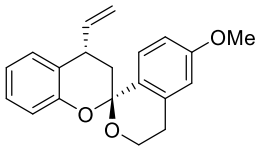


(2*R*,4*S*)-8-Methoxy-4-vinylspiro[chromane-2,1'-isochromane] (3p): Following the general procedure **A**, compound **3p** was obtained as a colorless oil in 98% yield of the diastereomeric mixtures (90.6 mg), 11:1 dr and >99% ee; R_f = 0.8 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 6.7, 2.5 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.19 – 7.12 (m, 1H), 6.87 (d, *J* = 7.3 Hz, 2H), 6.78 (dd, *J* = 7.0, 2.5 Hz, 1H), 5.81 (ddd, *J* = 16.8, 9.5, 8.4 Hz, 1H), 5.30 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.21 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.25 – 4.13 (m, 1H), 3.97 – 3.83 (m, 2H), 3.77 (s, 3H), 3.10 (ddd, *J* = 17.8, 12.5, 5.9 Hz, 1H), 2.70 – 2.61 (m, 1H), 2.31 (dd, *J* = 13.4, 12.9 Hz, 1H), 2.08 (dd, *J* = 13.4, 5.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 142.5, 140.3, 136.5, 134.7, 128.7, 128.3, 127.0, 126.9, 125.4, 120.6, 120.3, 117.2, 110.6, 96.7, 59.6, 56.3, 39.4, 37.7, 28.9; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{20}O_3$: 308.1407, found: 308.1415; $[\alpha]_D^{25}$ = +41.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 9.795 min (*cis*-major), 10.604 min (*trans*-minor), 25.423 min (*cis*-minor), 29.495 min (*trans*-major).

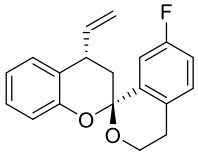


(2*R*,4*S*)-5'-Methyl-4-vinylspiro[chromane-2,1'-isochromane] (3q): Following the general procedure **A**, CF_3CO_2H (4.6 μL/6.8 mg, 18 mg, 0.06 mmol, 0.2 equiv) was used instead of $(PhSO_2)_2NH$, compound **3q** was obtained as a white solid in 52% yield of the diastereomeric mixtures (45.6 mg), 17:1 dr and 91% ee; R_f = 0.6 (petroleum ether/EtOAc = 10/1), m.p: 100 – 102 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2H), 7.28 – 7.18 (m, 3H), 7.07 – 6.99 (m, 1H), 6.95 (dd, *J* = 8.0, 1.3 Hz, 1H), 5.89 (ddd, *J* = 16.9, 9.5, 8.5 Hz, 1H), 5.40 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.32 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.31 – 4.23 (m, 1H), 4.09 – 4.03 (m, 1H), 3.97 (ddd, *J* = 12.7, 9.0, 5.9 Hz, 1H), 2.95 (ddd, *J* = 18.0, 12.4, 6.1 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.44 – 2.34 (m, 4H), 2.15 (dd, *J* = 13.3, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 140.1, 136.3, 136.2, 133.2, 129.7, 128.7, 127.9, 126.4, 124.5, 124.2, 121.0, 117.5(2), 117.4(6), 96.9, 59.1, 39.2, 37.6, 26.3, 19.3; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{20}O_2$: 292.1458, found:

292.1465; $[\alpha]_D^{25}$ = +18.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 7.817 min (*trans*-minor), 10.175 min (*cis*-major), 13.777 min (*cis*-minor), 16.227 min (*trans*-major).

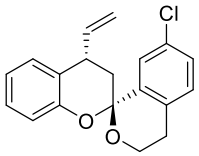


(2*R*,4*S*)-6'-Methoxy-4-vinylspiro[chromane-2,1'-isochromane] (3r): Following the general procedure **A**, CF_3CO_2H (4.6 μL/6.8 mg, 18 mg, 0.06 mmol, 0.2 equiv) was used instead of $(PhSO_2)_2NH$, compound **3r** was obtained as a white solid in 63% yield of the diastereomeric mixtures (58.2 mg), 15:1 dr and 93% ee; R_f = 0.6 (petroleum ether/EtOAc = 10/1), m.p: 106 – 108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.17 – 7.10 (m, 1H), 6.97 – 6.90 (m, 1H), 6.88 – 6.79 (m, 2H), 6.70 (d, *J* = 2.6 Hz, 1H), 5.81 (ddd, *J* = 16.9, 9.5, 8.4 Hz, 1H), 5.32 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.24 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.25 – 4.12 (m, 1H), 3.95 – 3.84 (m, 2H), 3.80 (s, 3H), 3.09 (ddd, *J* = 17.8, 12.6, 5.9 Hz, 1H), 2.67 – 2.56 (m, 1H), 2.29 (dd, *J* = 13.2, 12.9 Hz, 1H), 2.09 (dd, *J* = 13.4, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 152.8, 140.1, 136.2, 129.0, 128.7, 127.9(0), 127.8(7), 124.4, 121.0, 117.5(0), 117.4(5), 113.2(2), 113.1(9), 96.7, 59.4, 55.4, 39.2, 37.6, 29.2; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{20}O_3$: 308.1407, found: 308.1414; $[\alpha]_D^{25}$ = +14.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 11.511 min (*trans*-minor), 13.177 min (*cis*-major), 24.047 min (*trans*-major), 29.947 min (*cis*-minor).

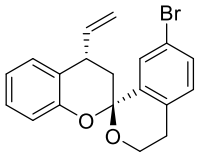


(2*R*,4*S*)-7-Fluoro-4-vinylspiro[chromane-2,1'-isochromane] (3s): Following the general procedure **A**, CF_3CO_2H (4.6 μL/6.8 mg, 18 mg, 0.06 mmol, 0.2 equiv) was used instead of $(PhSO_2)_2NH$, compound **3s** was obtained as a white solid in 85% yield of the diastereomeric mixtures (75.5 mg), 13:1 dr and >99% ee; R_f = 0.6 (petroleum ether/EtOAc = 10/1), m.p: 108 – 110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.09 (m, 4H), 6.98 (m, 2H), 7.05 – 6.91 (d, *J* = 8.1 Hz, 1H), 5.81 (ddd, *J* = 17.2, 9.5, 8.4 Hz, 1H), 5.33 (dd, *J* = 17.2, 1.9 Hz, 1H), 5.26 (dd, *J* = 10.0, 1.9 Hz, 1H), 4.22 – 4.07 (m, 1H), 4.02 – 3.79 (m, 2H), 3.04 – 2.96 (ddd, *J* = 17.8, 12.5, 5.6 Hz, 1H), 2.64 (m, 1H), 2.24 (dd, *J* = 12.9, 12.8 Hz, 1H), 2.11 (dd, *J* = 13.3, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6 (d, C-F, $^1J_{C\text{-}F}$ = 244.7 Hz), 152.4, 139.8, 138.1 (d, C-F, $^3J_{C\text{-}F}$ = 6.7 Hz), 130.4, 130.3, 128.7, 128.0, 124.3, 121.2, 117.8, 117.4, 115.8 (d, C-F, $^2J_{C\text{-}}$

$_F$ = 21.6 Hz), 113.4 (d, C-F, $^2J_{C\text{-}F}$ = 22.3 Hz), 96.4, 59.6, 39.1, 37.4, 28.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.09 – -115.25 (m). **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}FO_2$: 296.1207, found: 296.1216; $[\alpha]_D^{25}$ = +46.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 5.844 min (minor), 7.238 min (major).

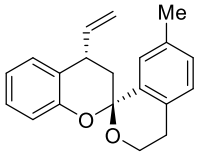


(2*R*,4*S*)-7'-Chloro-4-vinylspiro[chromane-2,1'-isochromane] (3t): Following the general procedure **A**, CF_3CO_2H (4.6 μL/6.8 mg, 18 mg, 0.06 mmol, 0.2 equiv) was used instead of $(PhSO_2)_2NH$, compound **3t** was obtained as a white solid in 80% yield of the diastereomeric mixtures (74.5 mg), 12:1 dr and >99% ee; R_f = 0.6 (petroleum ether/EtOAc = 10/1), m.p: 137 – 139 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.28 – 7.21 (m, 2H), 7.18 – 7.09 (m, 2H), 6.99 – 6.92 (m, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 5.81 (ddd, *J* = 17.2, 9.5, 8.4 Hz, 1H), 5.33 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.26 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.18 – 4.08 (m, 1H), 3.99 – 3.82 (m, 2H), 3.05 (ddd, *J* = 17.7, 12.4, 5.9 Hz, 1H), 2.73 – 2.57 (m, 1H), 2.26 (dd, *J* = 12.9, 12.8 Hz, 1H), 2.10 (dd, *J* = 13.3, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 139.8, 138.1, 133.1, 132.5, 130.2, 128.7(1), 128.6(7), 128.0, 126.9, 124.3, 121.3, 117.8, 117.4, 96.3, 59.4, 39.1, 37.4, 28.3. **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}{}^{35}ClO_2$: 312.0912, found: 312.0919; $C_{19}H_{17}{}^{37}ClO_2$: 314.0883, found: 314.0887; $[\alpha]_D^{25}$ = +25.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 5.741 min (minor), 7.162 min (major).

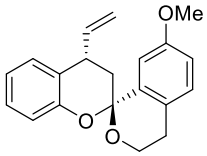


(2*R*,4*S*)-7'-Bromo-4-vinylspiro[chromane-2,1'-isochromane] (3u): Following the general procedure **A**, CF_3CO_2H (4.6 μL/6.8 mg, 18 mg, 0.06 mmol, 0.2 equiv) was used instead of $(PhSO_2)_2NH$, compound **3u** was obtained as a white solid in 79% yield of the diastereomeric mixtures (83.4 mg), 12:1 dr and 94% ee; R_f = 0.6 (petroleum ether/EtOAc = 10/1), m.p: 190 – 192 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.0 Hz, 1H), 7.42 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.24 (d, *J* = 9.9 Hz, 1H), 7.19 – 7.12 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.00 – 6.92 (m, 1H), 6.86 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.81 (ddd, *J* = 17.0, 9.6, 8.4 Hz, 1H), 5.33 (dd, *J* = 17.0, 1.8 Hz, 1H), 5.26 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.14 (ddd, *J* = 12.4, 11.3, 2.9 Hz, 1H), 3.98 – 3.83 (m, 2H), 3.03 (ddd, *J* = 17.3, 12.3, 5.9 Hz, 1H), 2.69 – 2.59 (m, 1H), 2.25 (dd, *J* =13.3, 12.9 Hz, 1H),

2.10 (dd, *J* = 13.3, 5.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4, 139.8, 138.5, 133.6, 131.6, 130.5, 129.8, 128.7, 128.0, 124.3, 121.3, 120.4, 117.8, 117.4, 96.2, 59.3, 39.1, 37.4, 28.4; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{17}{}^{79}BrO_2$: 356.0406, found: 356.0411; $C_{19}H_{17}{}^{81}BrO_2$: 358.0386, found: 358.0396; $[\alpha]_D^{25}$ = +16.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 6.113 min (minor), 7.722 min (major).



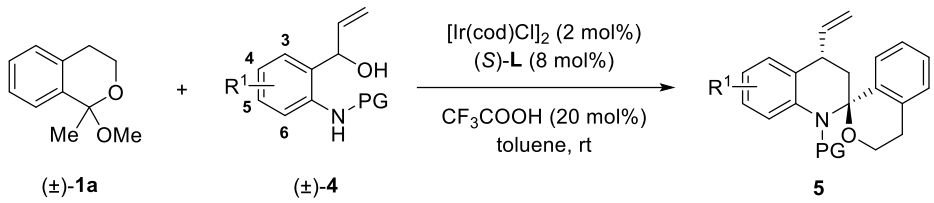
(2*R*,4*S*)-7'-Methyl-4-vinylspiro[chromane-2,1'-isochromane] (3v): Following the general procedure **A**, CF_3CO_2H (4.6 μL/6.8 mg, 18 mg, 0.06 mmol, 0.2 equiv) was used instead of $(PhSO_2)_2NH$, compound **3v** was obtained as a white solid in 85% yield of the diastereomeric mixtures (78.8 mg), 16:1 dr and >99% ee; R_f = 0.6 (petroleum ether/EtOAc = 10/1), m.p: 140 – 142 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19 – 7.10 (m, 2H), 7.03 – 6.97 (m, 3H), 6.89 – 6.82 (m, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 5.74 (ddd, *J* = 17.2, 9.6, 8.4 Hz, 1H), 5.24 (dd, *J* = 17.0, 1.9 Hz, 1H), 5.16 (dd, *J* = 9.9, 1.9 Hz, 1H), 4.13 – 4.02 (m, 1H), 3.89 – 3.75 (m, 2H), 2.97 (ddd, *J* = 17.8, 12.6, 6.0 Hz, 1H), 2.57 – 2.47 (m, 1H), 2.33 – 2.16 (m, 4H), 2.02 (dd, *J* = 13.2, 5.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 140.1, 136.5, 136.2, 131.6, 129.4, 128.7(3), 128.6(8), 127.9, 127.0, 124.5, 121.0, 117.5, 117.4, 96.8, 59.7, 39.2, 37.5, 28.5, 21.4; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{20}O_2$: 292.1458, found: 292.1467; $[\alpha]_D^{25}$ = +26.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 4.938 min (minor), 7.344 min (major).



(2*R*,4*S*)-7'-Methoxy-4-vinylspiro[chromane-2,1'-isochromane] (3w): Following the general procedure **A**, CF_3CO_2H (4.6 μL/6.8 mg, 18 mg, 0.06 mmol, 0.2 equiv) was used instead of $(PhSO_2)_2NH$, compound **3w** was obtained as a white solid in 87% yield of the diastereomeric mixtures (80.4 mg), 16:1 dr and 96% ee; R_f = 0.6 (petroleum ether/EtOAc = 10/1), m.p: 98 – 100 ℃; **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 7.18 – 7.06 (m, 2H), 6.99 – 6.92 (m, 1H), 6.91 – 6.85 (m, 3H), 5.82 (ddd, *J* = 16.7, 9.6, 8.5 Hz, 1H), 5.33 (dd, *J* = 17.0, 2.0 Hz, 1H), 5.25 (dd, *J* = 9.9, 1.9 Hz, 1H), 4.13 (ddd, *J* = 13.7, 8.4, 2.8 Hz, 1H), 3.90 (ddd, *J* = 13.9, 9.7, 5.4 Hz, 2H), 3.77 (s, 3H), 3.02 (ddd, *J* = 15.2, 12.6, 5.8 Hz, 1H), 2.63 – 2.55 (m, 1H), 2.29

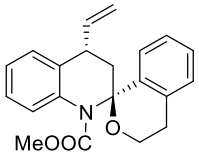
(dd, *J* = 13.2, 12.5 Hz, 1H), 2.11 (dd, *J* = 12.7, 5.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 152.7, 140.0, 137.2, 129.8, 128.7, 127.9, 126.7, 124.4, 121.1, 117.6, 117.5, 115.2, 111.1, 96.8, 59.8, 55.5, 39.3, 37.5, 28.0; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{20}H_{20}O_3$:308.1412, found: 308.1414; $[\alpha]_D^{25}$ = +36.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 7.519 min (*trans*-minor), 8.690 min (*cis*-major), 10.342 min (*trans*-major), 18.356 min (*cis*-minor).

4. General procedure and characterization data for bisbenzannulated spiroaminals 5



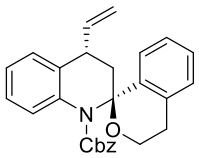
General procedure B: Under a nitrogen atmosphere, a flame dried 10 mL Schlenk tube was charged with $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), Carreira's ligand (*S*)-**L** (8.1 mg, 0.016 mmol, 8 mol%). After the tube was evacuated and backfilled with nitrogen, freshly distilled toluene (2.0 mL) was added, then stirred at room temperature for 15 minutes while the solution turned dark red. Then, 2-(1-hydroxyallyl)anilines (±)-**4** (0.4 mmol, 2.0 equiv) were added and the reaction mixture immediately turned light yellow. Isochroman ketals (±)-**1a** (35.6 mg, 0.2 mmol, 1.0 equiv) and CF_3CO_2H (4.6 mg, 0.04 mmol, 0.2 equiv) were added sequentially. The reaction mixture was stirred at room temperature for 24 h, which was directly purified by silica gel flash column chromatography (petroleum ether/EtOAc = 10/1) to afford bisbenzannulated spiroaminals **5**.

Corresponding racemic products rac-**5** were prepared according to the general procedure **B** using racemic ligand which had the same skeleton with (*S*)-**L**.

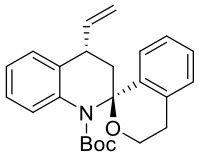


Methyl (1*S*,4'*S*)-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5a): Following the general procedure **B**, compound **5a** was obtained as a colorless oil in 76% yield of the diastereomeric mixtures (51.0 mg), 6:1 dr and 99% ee; R_f = 0.4 (petroleum ether/EtOAc = 10/1); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.16 – 7.12 (m, 2H), 7.11 – 7.04 (m, 1H), 7.05 – 7.03 (m, 1H), 5.88 (ddd, *J* = 16.9, 10.5, 8.9 Hz, 1H), 5.34 – 5.28 (m, 2H), 4.25 – 4.11 (m, 2H), 3.78 (ddd, *J* = 12.1, 8.9, 2.7 Hz, 1H), 3.60 (s, 3H), 3.13 (ddd, *J* = 14.7, 9.0, 4.9 Hz, 1H), 2.73 (dt, *J* = 15.8, 4.2 Hz, 1H), 2.45 (dd, *J* = 13.6, 2.9 Hz, 1H), 1.73 (dd, *J* = 13.6, 12.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 140.3, 138.3, 137.8, 134.7(2), 134.7(0), 127.9, 127.0, 126.6, 126.5, 125.3, 124.5, 123.7, 123.4, 117.8, 87.9, 62.5, 52.7, 46.3, 37.7, 28.6; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{21}H_{21}NO_3$: 335.1516, found: 335.1519; $[\alpha]_D^{25}$ = +29.3 (*c* 0.80, CH_2Cl_2); **HPLC** (Chiralpak IB, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 8.224 min (*cis*-major),

8.704 min (*trans*-major), 9.729 min (*cis*-minor), 10.795 min (*trans*-minor).

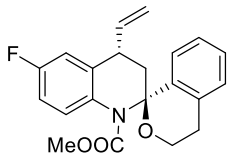


Benzyl (1*S*,4'*S*)-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5b): Following the general procedure **B**, compound **5b** was obtained as a colorless oil in 60% yield of the diastereomeric mixtures (49.4 mg), 6:1 dr and 99% ee; R_f = 0.4 (petroleum ether/EtOAc = 10/1); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.21 – 7.12 (m, 3H), 7.11 – 7.03 (m, 2H), 7.02 – 6.96 (m, 1H), 6.97 – 6.91 (m, 2H), 5.86 (ddd, *J* = 17.0, 10.4, 8.8 Hz, 1H), 5.34 – 5.26 (m, 2H), 5.10 – 4.98 (m, 2H), 4.08 (dd, *J* = 7.1, 4.2 Hz, 2H), 3.78 (ddd, *J* = 12.1, 8.8, 2.7 Hz, 1H), 2.83 – 2.66 (m, 1H), 2.56 (dt, *J* = 15.8, 4.2 Hz, 1H), 2.44 (dd, *J* = 13.7, 2.8 Hz, 1H), 1.72 (dd, *J* = 13.7, 12.3 Hz, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 155.0, 140.5, 138.3, 137.8, 135.8, 134.8, 134.5, 128.4 (2C), 128.2, 128.0(1) (2C), 128.0(0), 126.9, 126.6, 126.4, 125.2, 124.5, 123.9, 123.3, 117.7, 87.9, 67.6, 62.2, 46.3, 37.6, 28.3; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{27}H_{25}NO_3$: 411.1829, found: 411.1833; $[\alpha]_D^{25}$ = +48.8 (*c* 0.40, CH_2Cl_2); **HPLC** (Chiralpak IB, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 9.578 min (*cis*-major), 10.403 min (*trans*-major), 11.905 min (*cis*-minor), 13.504 min (*trans*-minor).

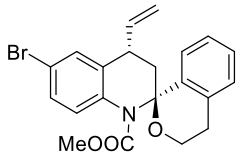


***tert*-Butyl (1*S*,4'*S*)-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5c):** Following the general procedure **B**, compound **5c** was obtained as a colorless oil in 63% yield of the diastereomeric mixtures (47.6 mg), 4:1 dr and 99% ee; R_f = 0.6 (petroleum ether/EtOAc = 15/1); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.20 – 7.12 (m, 4H), 7.15 -7.08 (m, 2H), 7.03 – 6.98 (m, 1H), 5.83 (ddd, *J* = 17.0, 10.1, 8.9 Hz, 1H), 5.34 – 5.23 (m, 2H), 4.28 – 4.18 (m, 1H), 4.19 – 4.13 (m, 1H), 3.78 (ddd, *J* = 12.4, 8.8, 3.1 Hz, 1H), 3.05 (ddd, *J* = 16.0, 7.9, 5.1 Hz, 1H), 2.79 (dt, *J* = 15.9, 5.1 Hz, 1H), 2.39 (dd, *J* = 13.6, 3.3 Hz, 1H), 1.74 (dd, *J* = 13.7, 12.5 Hz, 1H), 1.24 (s, 9H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 154.3, 141.1, 139.0, 138.3, 133.7, 133.1, 128.2, 126.8, 126.6, 126.3, 125.8, 124.6, 123.3, 122.5, 117.5, 87.1, 81.3, 61.7, 46.0, 37.7, 28.6, 28.0 (3C); **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{24}H_{27}NO_3$: 377.1986, found: 377.1988; $[\alpha]_D^{25}$ = +59.2 (*c* 0.40, CH_2Cl_2); **HPLC** (Chiralpak IF, *n*-hexane/isopropanol = 99.5/0.5, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 4.471 min (*trans*-

major), 4.846 min (*trans*-minor), 5.169 min (*cis*-major), 5.552 min (*cis*-minor).

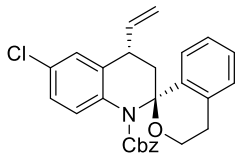


Methyl (1*S*,4'*S*)-6'-fluoro-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5d): Following the general procedure **B**, compound **5d** was obtained as a colorless oil in 54% yield of the diastereomeric mixtures (38.2 mg), 7:1 dr and 99% ee; R_f = 0.4 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.38 (m, 1H), 7.18 (d, *J* = 1.6 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.04 – 6.98 (m, 1H), 6.93 – 6.88 (m, 2H), 5.89 – 5.76 (m, 1H), 5.37 – 5.28 (m, 2H), 4.24 – 4.11 (m, 2H), 3.80 – 3.72 (m, 1H), 3.59 (s, 3H), 3.18 – 3.07 (m, 1H), 2.72 (dt, *J* = 15.8, 4.2 Hz, 1H), 2.45 (dd, *J* = 13.7, 2.8 Hz, 1H), 1.71 (dd, *J* = 13.7, 12.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.9 (d, $^1J_{C\text{-}F}$ = 243.1 Hz), 155.1, 140.0, 137.5, 137.0 (d, $^3J_{C\text{-}F}$ = 7.0 Hz), 134.6, 133.7 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 128.0, 127.1, 126.7, 125.1 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 124.4, 118.5, 113.1 (d, $^2J_{C\text{-}F}$ = 22.6 Hz), 112.0 (d, $^2J_{C\text{-}F}$ = 23.6 Hz), 87.8, 62.5, 52.7, 46.1, 37.7, 28.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.51 – -119.61 (m); **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{21}H_{20}FNO_3$: 353.1422, found: 353.1430; $[\alpha]_D^{25}$ = +15.8 (*c* 0.40, CH_2Cl_2); **HPLC** (Chiralpak IG, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 7.411 min (*trans*-major), 8.765 min (*trans*-minor), 9.178 min (*cis*-minor), 14.895 min (*cis*-major).



Methyl (1*S*,4'*S*)-6'-bromo-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5e): Following the general procedure **B**, compound **5e** was obtained as a colorless oil in 42% yield of the diastereomeric mixtures (34.8 mg), 4:1 dr and 98% ee; R_f = 0.4 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.30 (d, *J* = 1.9 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.13 – 7.10 (m, 1H), 7.03 – 6.96 (m, 1H), 5.82 (ddd, *J* = 16.5, 10.6, 8.8 Hz, 1H), 5.37 – 5.28 (m, 2H), 4.25 – 4.02 (m, 2H), 3.82 – 3.70 (m, 1H), 3.58 (s, 3H), 3.11 (ddd, *J* = 14.6, 9.0, 4.9 Hz, 1H), 2.72 (dt, *J* = 15.8, 4.2 Hz, 1H), 2.43 (dd, *J* = 13.7, 2.9 Hz, 1H), 1.72 (dd, *J* = 13.7, 12.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 139.8, 137.4, 136.9, 136.8, 134.6, 129.5, 128.3, 128.0, 127.1, 126.7, 125.3, 124.3, 118.6, 116.5, 87.8, 62.5, 52.8, 46.0, 37.6, 28.5; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{21}H_{20}{}^{79}BrNO_3$: 413.0622, found: 413.0624; $C_{21}H_{20}{}^{81}BrNO_3$: 415.0601, found: 415.0608; $[\alpha]_D^{25}$ = +13.8 (*c* 0.40, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 95/5, flow rate = 1.0 mL/min, λ = 220 nm) t_R =

7.342 min (*trans*-minor), 7.728 min (*trans*-major), 8.654 min (*cis*-minor), 10.667 min (*cis*-major).



Benzyl (1*S*,4'*S*)-6'-chloro-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5f): Following the general procedure **B**, compound **5f** was obtained as a white solid in 54% yield of the diastereomeric mixtures (48.2 mg), 5:1 dr and 99% ee; R_f = 0.5 (petroleum ether/EtOAc = 10/1); m.p: 109 – 111 ℃; ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 1H), 7.25 – 7.22 (m, 3H), 7.18 – 7.14 (m, 4H), 7.04 – 6.96 (m, 2H), 6.95 – 6.91 (m, 2H), 5.81 (ddd, *J* = 16.6, 10.7, 8.7 Hz, 1H), 5.36 – 5.27 (m, 2H), 5.06 – 4.98 (m, 2H), 4.06 (dd, *J* = 7.1, 4.2 Hz, 2H), 3.75 (ddd, *J* = 12.0, 8.7, 2.7 Hz, 1H), 2.80 – 2.65 (m, 1H), 2.55 (dt, *J* = 15.9, 4.2 Hz, 1H), 2.43 (dd, *J* = 13.8, 2.9 Hz, 1H), 1.70 (dd, *J* = 13.7, 12.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 140.1, 137.5, 136.5, 136.4, 135.6, 134.4, 128.7, 128.4 (2C), 128.3, 128.1(8), 128.1(5) (2C), 127.0, 126.7, 126.4, 125.3, 125.1, 124.3, 118.6, 87.8, 67.8, 62.2, 46.0, 37.5, 28.2; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{27}H_{24}{}^{35}ClNO_3$: 445.1440, found: 445.1443; $C_{27}H_{24}{}^{37}ClNO_3$: 447.1410, found: 447.1412; $[\alpha]_D^{25}$ = +47.5 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralpak IG, *n*-hexane/isopropanol = 95/5, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 9.902 min (minor), 11.020 min (major).

The preparation and X-ray analysis of the single crystal: Compound **5f** (10.0 mg) was dissolved in 5.0 mL ethanol in a round-bottom flask. A single crystal was obtained after placing at -20 ℃ for 12 hours. The data set was collected by a Bruker APEX-II CCD at 293(2) K equipped with Mo radiation source (Kα = 0.71073 Å). Applied with multi-scan absorption correction, the structure solution was solved and refinement was processed by SHELXTL program package. CCDC 2342944 contains the supplementary crystallographic data, and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

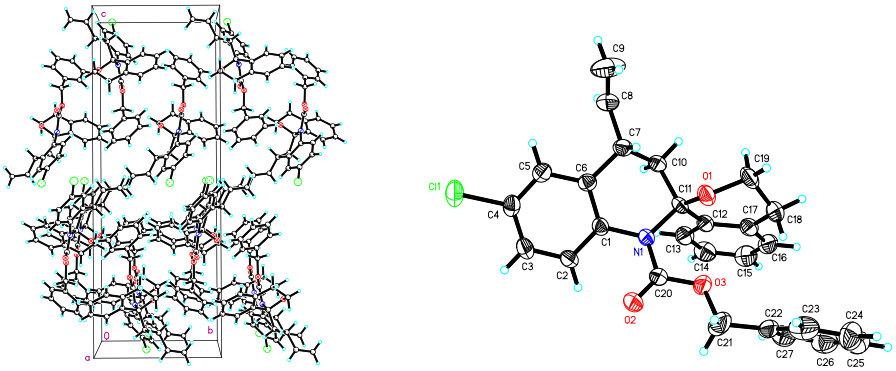
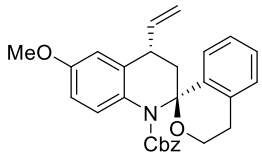


Fig S2. The thermal ellipsoid plot for X-ray structure of (1*S*,4′*S*)-**5f** with the ellipsoid contour at 30% probability levels

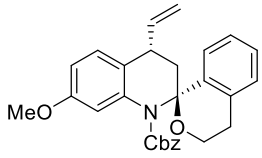
Crystal data and structure refinement for (1*S*,4′*S*)-5f

Identification code	mo_d8v23612_0m	
Empirical formula	C27 H24 Cl N O3	
Formula weight	445.92	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.740(2) Å	α= 90°.
	b = 9.775(3) Å	β= 90 °.
	c = 26.948(6) Å	γ= 90°.
Volume	2302.5(10) Å^3	
Z	4	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.195 mm^{-1}	
F (000)	936	
Crystal size	0.150 x 0.100 x 0.060 mm^3	
Theta range for data collection	2.574 to 26.499 °.	
Index ranges	-10<=h<=10, -12<=k<=10, -33<=l<=32	
Reflections collected	19725	
Independent reflections	4756 [R(int) = 0.0788]	
Completeness to theta = 25.242 °	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6685	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4756 / 0 / 290	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0618, wR2 = 0.1205	
R indices (all data)	R1 = 0.1249, wR2 = 0.1488	
Absolute structure parameter	0.12(5)	

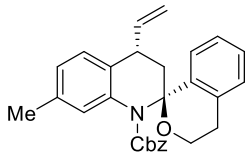
Extinction coefficient	0.0058(18)
Largest diff. peak and hole	0.343 and -0.182 e.Å^{-3}



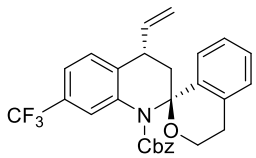
Benzyl (1*S*,4'*S*)-6'-methoxy-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5g): Following the general procedure **B**, compound **5g** was obtained as a colorless oil in 89% yield of the diastereomeric mixtures (78.6 mg), 5:1 dr and 99% ee; R_f = 0.4 (petroleum ether/EtOAc = 5/1); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.8 Hz, 1H), 7.24 – 7.21 (m, 3H), 7.18 – 7.13 (m, 2H), 7.10 – 7.03 (m, 1H), 7.00 – 6.97 (m, 1H), 6.96 – 6.93 (m, 2H), 6.78 – 6.72 (m, 2H), 5.91 – 5.78 (m, 1H), 5.33 – 5.27 (m, 2H), 5.08 – 5.00 (m, 2H), 4.07 (dd, *J* = 7.1, 4.1 Hz, 2H), 3.80 (s, 3H), 3.81 – 3.71 (m, 1H), 2.81 – 2.71 (m, 1H), 2.55 (dt, *J* = 15.9, 4.2 Hz, 1H), 2.43 (dd, *J* = 13.7, 2.7 Hz, 1H), 1.70 (dd, *J* = 13.6, 12.3 Hz, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 155.6, 154.9, 140.6, 138.1, 136.5, 136.0, 134.5, 131.0, 128.4 (2C), 128.1, 127.9(7) (2C), 127.9(1), 126.9, 126.6, 125.0, 124.5, 118.0, 111.5, 110.8, 87.9, 67.5, 62.3, 55.6, 46.4, 37.7, 28.3; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{28}H_{27}NO_4$: 441.1935, found: 441.1938; $[\alpha]_D^{25}$ = +38.4 (*c* 0.80, CH_2Cl_2); **HPLC** (Chiralpak IA, *n*-hexane/isopropanol = 97/3, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 16.775 min (minor), 19.329 min (major).



Benzyl (1*S*,4'*S*)-7'-methoxy-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5h): Following the general procedure **B**, compound **5h** was obtained as a colorless oil in 63% yield of the diastereomeric mixtures (55.6 mg), 10:1 dr and 99% ee; R_f = 0.3 (petroleum ether/EtOAc = 10/1); ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 3H), 7.18 – 7.14 (m, 3H), 7.10 – 7.05 (m, 2H), 7.01 – 6.97 (m, 3H) , 6.62 (dd, *J* = 8.5, 2.6 Hz, 1H), 5.82 (ddd, *J* = 17.1, 10.1, 8.9 Hz, 1H), 5.32 – 5.22 (m, 2H), 5.12 – 4.95 (m, 2H), 4.10 – 4.05 (m, 2H), 3.74 – 3.69 (m, 1H), 3.69 (s, 3H), 2.82 – 2.72 (m, 1H), 2.57 (dt, *J* = 15.8, 4.3 Hz, 1H), 2.41 (dd, *J* = 13.7, 2.9 Hz, 1H), 1.70 (dd, *J* = 13.6, 12.3 Hz, 1H); ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 158.2, 154.8, 140.6, 138.7, 138.5, 135.7, 134.4, 128.4 (2C), 128.2(1), 128.2(0) (2C), 128.0, 126.9(7), 126.9(5), 126.6, 125.9, 124.4, 117.5, 109.5, 109.5, 88.0, 67.7, 62.2, 55.5, 46.3, 37.0, 28.2; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{28}H_{27}NO_4$: 441.1935, found: 441.1942; $[\alpha]_D^{25}$ = +33.8 (*c* 0.40, CH_2Cl_2); **HPLC** (Chiralcel OD-H, *n*-hexane/isopropanol = 97/3, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 11.286 min (*cis*-major), 12.543 min (*trans*-major), 17.334 min (*trans*-minor), 20.954 min (*cis*-minor).



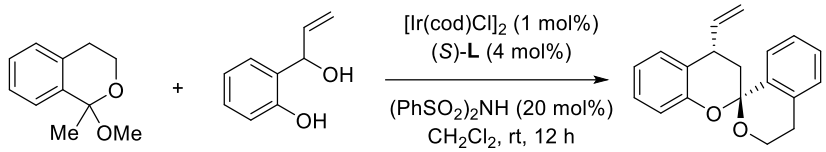
Benzyl (1*S*,4'*S*)-7'-methyl-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5i): Following the general procedure **B**, compound **5i** was obtained as a colorless oil in 69% yield of the diastereomeric mixtures (58.7 mg), 5:1 dr and 99% ee; R_f = 0.5 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.25 – 7.23 (m, 3H), 7.18 – 7.13 (m, 2H), 7.09 – 7.04 (m, 2H), 7.01 – 6.97 (m, 3H), 6.88 – 6.85 (m, 1H), 5.84 (ddd, *J* = 17.0, 10.2, 8.8 Hz, 1H), 5.33 – 5.23 (m, 2H), 5.14 – 4.95 (m, 2H), 4.08 (dd, *J* = 7.0, 4.2 Hz, 2H), 3.79 – 3.68 (m, 1H), 2.84 – 2.74 (m, 1H), 2.57 (dt, *J* = 15.9, 4.2 Hz, 1H), 2.42 (dd, *J* = 13.7, 2.8 Hz, 1H), 2.30 (s, 3H), 1.70 (dd, *J* = 13.6, 12.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 140.6, 138.6, 137.5, 136.0, 135.9, 134.5, 131.8, 128.4 (2C), 128.2, 128.1 (2C), 128.0, 126.9, 126.6, 125.1, 124.5(3), 124.5(0), 124.2, 117.5, 87.9, 67.6, 62.2, 46.4, 37.3, 28.3, 21.4; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{28}H_{27}NO_3$: 425.1986, found: 425.1993; $[\alpha]_D^{25}$ = +43.5 (*c* 0.40, CH_2Cl_2); **HPLC** (Chiralpak IC, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 8.310 min (*cis*-major), 10.121 min (*cis*-minor), 10.879 min (*trans*-major), 13.481 min (*trans*-minor).



Benzyl (1*S*,4'*S*)-7'-(trifluoromethyl)-4'-vinyl-3',4'-dihydro-1'*H*-spiro[isochromane-1,2'-quinoline]-1'-carboxylate (5j): Following the general procedure **B**, compound **5j** was obtained as a colorless oil in 40% yield of the diastereomeric mixtures (38.4 mg), 6:1 dr and 99% ee; R_f = 0.5 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.30 – 7.28 (m, 2H), 7.27 – 7.24 (m, 3H), 7.20 – 7.16 (m, 2H), 7.06 – 7.01 (m, 2H), 7.01 – 6.98 (m, 2H), 5.90 – 5.77 (m, 1H), 5.38 – 5.29 (m, 2H), 5.13 – 4.97 (m, 2H), 4.11 – 4.06 (m, 2H), 3.81 (t, *J* = 10.8 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.58 (dt, *J* = 15.8, 4.3 Hz, 1H), 2.45 (dd, *J* = 13.8, 2.9 Hz, 1H), 1.78 – 1.67 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 139.8, 138.2(9), 138.2(5), 137.5, 135.3, 134.5, 128.6 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 128.5 (2C), 128.3, 128.2(4) (2C), 128.2(2), 127.1, 126.8, 125.9, 125.5 (q, $^1J_{C\text{-}F}$ = 239.0 Hz), 124.3, 120.9 (q, $^3J_{C\text{-}F}$ = 4.1 Hz), 119.9 (q, $^3J_{C\text{-}F}$ = 3.9 Hz), 118.6, 87.8, 68.1, 62.4, 45.9, 37.6, 28.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.21 (s); **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{28}H_{24}F_3NO_3$: 479.1703, found: 479.1705; $[\alpha]_D^{25}$ = +34.0 (*c* 0.40, CH_2Cl_2); **HPLC** (Chiralpak IB, *n*-hexane/isopropanol = 99/1, flow rate = 1.0 mL/min,

λ = 220 nm) t_R = 6.547 min (*cis*-major), 6.943 min (*trans*-major), 7.835 min (*trans*-minor), 10.471 min (*cis*-minor).

5. Gram-scale preparation of bisbenzannulated spiroketal 3a



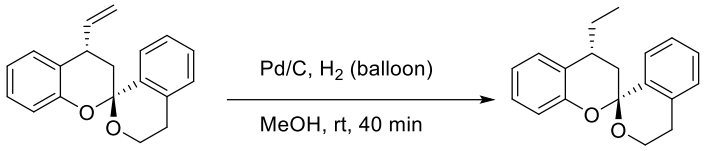
(±)-**1a**
5.0 mmol
891 mg

(±)-**2a**
10.0 mmol
1.50 g

3a
1.28 g, 92% yield
12:1 dr, 99% ee

Under a nitrogen atmosphere, a flame dried 100 mL Schlenk tube was charged with $[Ir(cod)Cl]_2$ (34 mg, 0.05 mmol, 1 mol%), Carreira's ligand (*S*)-**L** (102 mg, 0.2 mmol, 4 mol%). After the tube was evacuated and backfilled with nitrogen, freshly distilled CH_2Cl_2 (50 mL) was added, then stirred at room temperature for 15 minutes while the solution turned dark red. Then, 2-(1-hydroxyallyl)phenol (±)-**2a** (1.50 g, 10.0 mmol, 2.0 equiv) were added and the reaction mixture immediately turned light yellow. Isochroman ketal **1a** (891 mg, 5.0 mmol, 1.0 equiv) and $(PhSO_2)_2NH$ (300 mg, 1.0 mmol, 0.2 equiv) were added sequentially. The reaction mixture was stirred at room temperature until **1a** were consumed (monitored by TLC), which was directly purified by flash column chromatography silica gel (petroleum ether/EtOAc = 10/1) to afford spiroketal **3a** in 92% yield (1.28 g) with 12:1 dr and 99% ee.

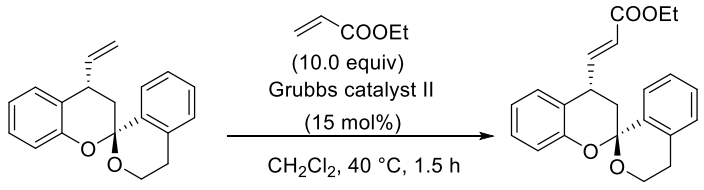
6. Synthetic transformations of bisbenzannulated spiroketal 3a



3a
99% ee

6
95% yield
95% ee

A stirred suspension of compound **3a** (83.4 mg, 0.3 mmol, 1.0 equiv) in MeOH (3.0 mL) and palladium on activated carbon (63.9 mg, 10 mol%) was added. The reaction mixture was stirred under H_2 atmosphere (H_2 ballon) at room temperature for 40 min. The mixture was filtered over SiO_2 and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 15:1) to afford the title product **6** (79.8 mg, 95% yield, 95% ee) as a white solid. R_f = 0.8 (petroleum ether/EtOAc = 10/1), m.p: 76 – 78 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 1H), 7.33 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.31 – 7.24 (m, 2H), 7.21 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H), 6.98 – 6.92 (m, 1H), 6.86 (dd, *J* = 8.1, 1.5 Hz, 1H), 4.22 – 4.10 (m, 1H), 3.96 – 3.86 (m, 1H), 3.25 – 3.16 (m, 1H), 3.10 (ddd, *J* = 17.5, 12.4, 5.8 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.22 – 2.05 (m, 3H), 1.64 (ddq, *J* = 14.1, 9.2, 7.1 Hz, 1H), 0.98 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 136.9, 134.6, 128.8, 128.3, 127.2, 126.9, 126.8, 126.7, 126.4, 121.1, 117.6, 97.0, 59.4, 37.7, 31.6, 28.9, 26.2, 10.7; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{19}H_{20}O_2$: 280.1458, found: 280.1460; $[\alpha]_D^{25}$ = –30.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OJ-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 6.779 min (minor), 9.355 min (major).

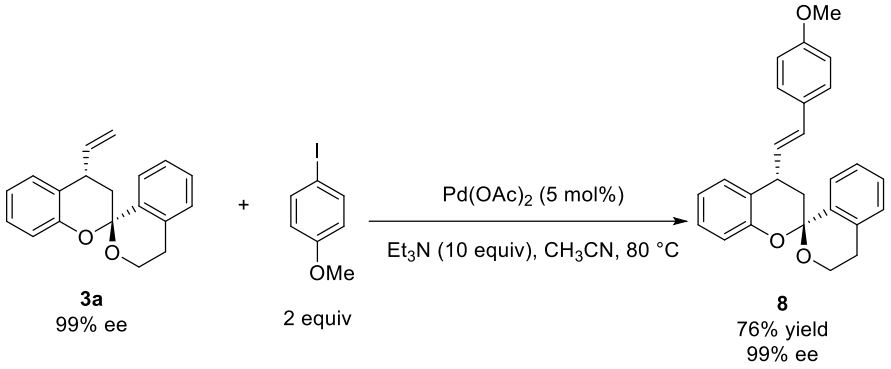


3a
99% ee

7
70% yield
98% ee

Compound **3a** (83.4 mg, 0.3 mmol, 1.0 equiv), ethyl acrylate (0.3 mL, 3.0 mmol, 10.0 equiv) and Grubbs catalyst II (39.0 mg, 0.045 mmol, 15 mol%) were dissolved in CH_2Cl_2 (3.0 mL). After stirring at 40 °C for 1.5 h, the reaction mixture was directly purified by silica gel flash column chromatography (petroleum ether/EtOAc = 10:1) to afford the title product **7** as a white solid (73.5 mg, 70% yield, 98% ee). R_f = 0.3 (petroleum ether/EtOAc = 10/1), m.p: 94 – 96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.1 Hz, 1H), 7.29 (d, *J* = 6.0 Hz, 2H), 7.22 – 7.14 (m, 2H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.03 – 6.91 (m, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.11 (d, *J* = 15.6 Hz, 1H), 4.27 – 4.03 (m, 4H), 3.98 – 3.90 (m, 1H), 3.11 (ddd, *J* = 17.8, 12.6, 5.9 Hz, 1H),

2.72 – 2.62 (m, 1H), 2.37 (dd, *J* = 12.9, 12.8 Hz, 1H), 2.11 (dd, *J* = 13.3, 6.0 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 152.6, 149.4, 136.0, 134.6, 128.9, 128.8, 128.6, 128.4, 127.0, 126.6, 123.9, 122.6, 121.3, 117.8, 96.4, 60.6, 59.6, 38.3, 35.9, 28.8, 14.4. **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{22}H_{22}O_4$: 350.1513, found: 350.1516; $[\alpha]_D^{25}$ = +69.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OD-H, *n*-hexane/ethanol = 90/10, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 4.930 min (minor), 6.570 min (major).



Under nitrogen atmosphere, to a stirring solution of **3a** (83.4 mg, 0.3 mmol, 1.0 equiv) in anhydrous CH_3CN (3.0 mL) were added $Pd(OAc)_2$ (2.5 mg, 0.015 mmol, 5 mol%), Et_3N (0.42 mL, 3 mmol, 10 equiv), and 4-iodophenyl methyl ether (140.4 mg, 0.6 mmol, 2 equiv). The mixture was then stirred for 24 hours at 80 °C (oil bath temperature), which was cooled down to room temperature, diluted with water, and extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 15:1) to give **8** (87.5 mg, 76% yield, 99% ee) as colorless oil. R_f = 0.4 (petroleum ether/EtOAc = 10/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.22 – 7.12 (m, 2H), 6.96 – 6.91 (m, 1H), 6.90 – 6.83 (m, 3H), 6.63 (d, *J* = 15.7 Hz, 1H), 6.06 (dd, *J* = 15.7, 9.3 Hz, 1H), 4.21 (ddd, *J* = 12.3, 11.9, 2.9 Hz, 1H), 4.04 (ddd, *J* = 14.1, 9.0, 6.0 Hz, 1H), 3.99– 3.92 (dd, *J* = 11.3, 5.8 Hz, 1H), 3.81 (s, 3H), 3.13 (ddd, *J* = 17.6, 12.4, 5.8 Hz, 1H), 2.72 – 2.64 (dd, *J* = 16.5, 2.7 Hz, 1H), 2.39 (dd, *J* = 13.0, 12.8 Hz, 1H), 2.16 (dd, *J* = 13.3, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 152.8, 136.4, 134.6, 132.1, 130.1, 129.5, 129.0, 128.9, 128.5, 128.0, 127.5 (2C), 126.9, 126.6, 125.0, 121.1, 117.5, 114.2 (2C), 96.8, 59.6, 55.5, 39.5, 36.7, 28.9; **HRMS** (EI-TOF) m/z: $[M]^+$ calcd for $C_{26}H_{24}O_3$: 384.1720, found: 384.1723; $[\alpha]_D^{25}$ = +50.0 (*c* 0.20, CH_2Cl_2); **HPLC** (Chiralcel OD-H, *n*-hexane/ethanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 11.990 min (minor), 37.067 min (major).

7. *In-vitro* antifungal activity against four species of pathogenic fungi

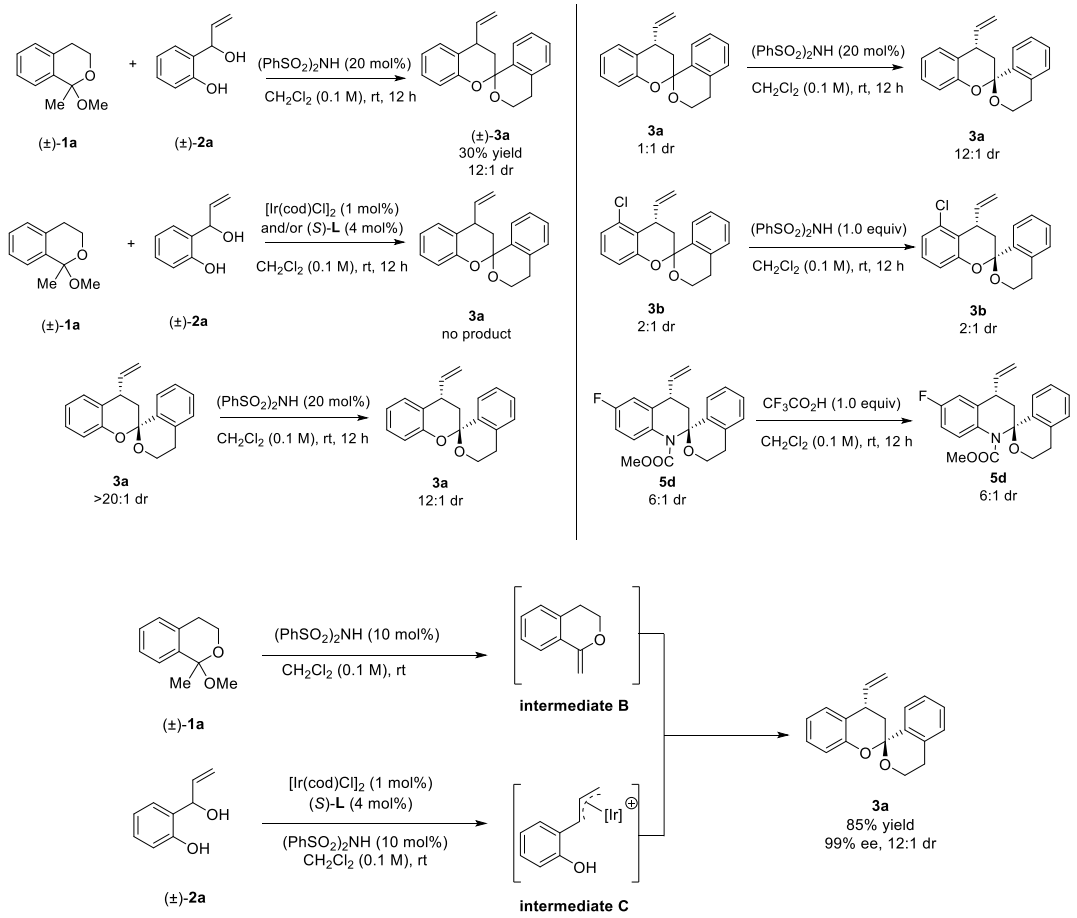
In-vitro antifungal activities of target compounds against *Rhizoctonia solani* (*R. s.*), *Botrytis cinerea* (*B. c.*), *Sclerotinia sclerotiorum* (*S. s.*), and *Fusarium graminearum* (*F. g.*) which were provided by GreenTech Laboratory, were tested using the mycelium growth rate method. All compounds were tested at 100 mg/L as well as the positive control reagent Spiroxamine. Each compound was dissolved with dimethyl sulfoxide (DMSO) for preparing 1000 mg/L stock solution and diluted with the melted potato dextrose agar (PDA) media to prepared the target concentrations of compounds. A blank control was established by incorporating 0.5% DMSO (v/v) into PDA media. The mycelial disks, with a diameter of 5 mm, from phytopathogenic fungi were placed onto PDA plates and then were incubated at 25 °C under 80% moisturizing conditions in the dark. Diameters (mm) of the colony were measured by the cross-bracketing method. The growth inhibition rates were calculated according to the following formula percentage inhibition (%) = [(C − T)/(C – 5 mm)] × 100, where C and T represent diameters of the colony cultured on blank control and dosed PDA, respectively. Each experiment was conducted three times.

Table S6: *In-vitro* antifungal activity against four species of pathogenic fungi.

compounds	Inhibition Rates (%)/100 mg/L			
	R. s.	*B. c.*	*S. s.*	*F. g.*
3a	**60.5**	21.0	34.0	49.3
3b	48.8	11.3	23.0	39.5
3c	53.9	10.9	24.8	42.0
3d	47.6	16.5	1.4	48.1
3e	44.8	17.4	-8.3	46.7
3f	**61.5**	21.0	-38.2	23.8
3g	36.9	6.4	-36.7	22.0
3h	50.3	24.4	18.0	46.7
3i	37.4	6.4	-10.6	25.9
3j	**61.4**	8.5	26.2	42.3
3k	44.0	-2.4	35.3	11.3
3l	45.7	9.6	15.7	11.3
3m	**61.1**	12.0	27.7	50.2
3n	53.1	14.9	0.5	**61.4**
3o	**60.7**	24.1	30.9	51.2
3p	58.2	33.9	36.8	55.4

3q	52.6	14.7	30.9	19.1
3r	49.2	16.7	37.0	15.7
3s	30.0	-15.2	20.1	0.6
3t	23.2	-15.4	24.8	13.2
3u	33.1	-16.5	16.3	3.4
3v	49.2	-8.5	29.7	16.0
3w	45.7	9.2	13.4	30.1
5a	56.4	44.1	56.1	36.7
5b	0.7	17.1	7.0	19.0
5c	28.6	31.4	21.0	21.4
5d	27.5	19.3	54.1	49.0
5e	48.0	24.0	29.5	25.4
5f	25.7	0.7	5.6	1.5
5g	30.2	24.0	14.2	9.1
5h	11.2	14.8	-5.8	14.2
5i	12.6	13.6	7.4	10.9
5j	3.0	6.8	5.3	10.3
6	58.4	21.5	30.9	41.7
7	44.4	17.1	29.7	24.5
8	36.2	-0.7	11.1	11.3
Spiroxamine	91.3	92.6	94.9	67.1

8. Control experiments for mechanism study



According to our experiment, the intermediate **B** is unstable, and the attempt to separate it was failed. In addition, the intermediate **B** was prepared in advance and used directly in our reaction, affording product **3a** in 85% yield with 99%ee and 12:1 dr. This result revealed that intermediate **B** is indeed generated in this reaction.

9. DFT calculations

Computational details: All density functional theory (DFT) calculations were performed using Gaussian 16.[7] The geometry optimizations and frequencies were calculated using the B3LYP-D3(BJ) hybrid density functional theory[8] with 6-31G(d,p) basis set for all elements. Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). To obtain more accurate electronic energies, single-point energy calculations were performed at the M06-2X/def2TZVP level of theory[9-10] with the optimized structures. Grimme's quasi-RRHO correction[11] for the frequencies that are below 100 cm^{-1} and concentration correction for all species (from 1 atm to 1 mol/L) are implemented by the GoodVibes program.[12]

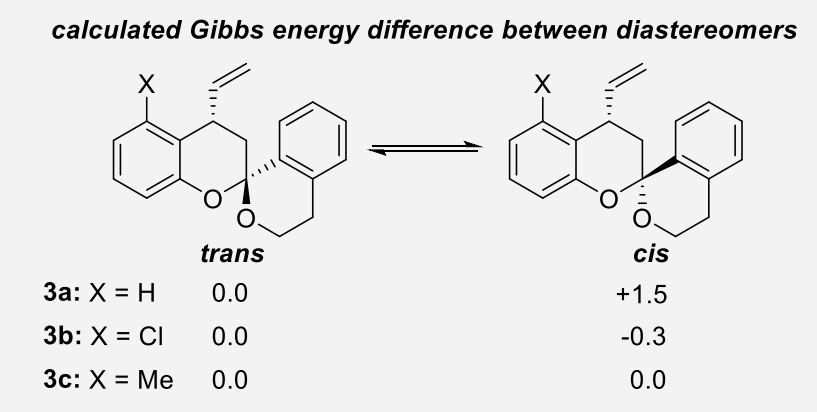


Fig S4. Calculated Gibbs free energy of diastereomers.

The calculated Cartesian coordinates of optimized structures

trans-**3a**

C	-3.39365	-2.58487	-0.40294
C	-2.01331	-2.41422	-0.41013
C	-1.46687	-1.14097	-0.23088
C	-2.29077	-0.02108	-0.04598
C	-3.67573	-0.22054	-0.03636
C	-4.2326	-1.48496	-0.21077
H	-3.81261	-3.57656	-0.54407
H	-1.33624	-3.24958	-0.55315
C	-1.68365	1.35849	0.1532
H	-4.31824	0.64339	0.10464
H	-5.31046	-1.61105	-0.20052
C	-0.23554	1.35612	-0.36376
O	-0.0932	-1.07069	-0.27602
H	-1.65121	1.57003	1.22856
H	-0.22765	1.31257	-1.45685
H	0.28289	2.26798	-0.06028
C	3.53901	0.0299	-2.14515
C	2.2301	0.07184	-1.67583
C	1.96258	0.06565	-0.30279
C	3.02156	-0.02716	0.6116
C	4.33458	-0.06934	0.12924
C	4.59776	-0.03201	-1.23665
H	3.73321	0.03924	-3.21305
H	1.4052	0.09672	-2.37999
C	2.72895	-0.1214	2.09122
H	5.15449	-0.14544	0.83867
H	5.62266	-0.0672	-1.59325
C	1.30622	-0.61945	2.29549
H	3.44773	-0.79022	2.57789
H	2.83159	0.86373	2.56468
H	1.1937	-1.65136	1.9404
H	0.99778	-0.5718	3.3419
C	0.52202	0.14536	0.1814
O	0.41577	0.24059	1.5831

C	-2.48227	2.43866	-0.52522
H	-2.60637	2.32484	-1.60251
C	-3.01791	3.48863	0.09514
H	-3.5731	4.2501	-0.44382
H	-2.91685	3.62343	1.16917

M06-2X/def2TZVP-SMD(CH_2Cl_2): E = -885.281768 hartree

Corrected Gibbs Free Energy = -884.998858 hartree

cis-**3a**

C	3.46592	-2.46978	0.58604
C	2.08236	-2.33497	0.55756
C	1.50631	-1.16338	0.05828
C	2.30275	-0.11764	-0.42324
C	3.69264	-0.2703	-0.36869
C	4.27988	-1.4309	0.12573
H	3.90868	-3.38225	0.97361
H	1.42527	-3.11994	0.91644
C	1.68612	1.15158	-0.98895
H	4.31363	0.54867	-0.72156
H	5.36055	-1.5263	0.15348
C	0.1692	0.96001	-1.20149
O	0.13005	-1.12769	0.04666
H	2.12795	1.32648	-1.9781
H	-0.33438	1.92472	-1.2937
H	0.00601	0.40837	-2.13052
C	-3.6963	-1.01603	-1.75045
C	-2.35248	-0.76842	-1.48904
C	-1.9599	-0.11975	-0.31335
C	-2.92715	0.2441	0.63471
C	-4.27617	-0.00922	0.36222
C	-4.66466	-0.62494	-0.82361
H	-3.98704	-1.51666	-2.66862
H	-1.59765	-1.09398	-2.19687
C	-2.49846	0.85795	1.94743
H	-5.02405	0.27022	1.09973
H	-5.71581	-0.81512	-1.01776
C	-1.04727	0.49648	2.22306
H	-2.59041	1.95113	1.90787
H	-3.14662	0.50786	2.75865
H	-0.64527	1.02685	3.0887
H	-0.93095	-0.58243	2.38364
C	-0.48427	0.16683	-0.06878
O	-0.25846	0.91076	1.10639
C	2.03003	2.34836	-0.13341
H	1.68677	2.30303	0.89545
C	2.71662	3.40045	-0.57692
H	2.95382	4.24109	0.068
H	3.06587	3.46121	-1.60541

M06-2X/def2TZVP-SMD(CH_2Cl_2): E = -885.279528 hartree

Corrected Gibbs Free Energy = -884.99648 hartree

trans-**3b**

C	2.73778	2.74875	-0.94329
C	1.38374	2.44509	-0.99175
C	0.94126	1.18109	-0.5968
C	1.83191	0.17601	-0.17367
C	3.18085	0.5529	-0.08246
C	3.64793	1.80716	-0.46744
H	3.08656	3.72914	-1.25133
H	0.6451	3.16804	-1.31881
C	1.32286	-1.21297	0.18128
H	4.70309	2.03573	-0.38173
C	-0.16998	-1.35276	-0.18681
O	-0.41773	0.99575	-0.65307
H	1.42606	-1.35142	1.26324
H	-0.26899	-1.54933	-1.25765
H	-0.60158	-2.20293	0.34445
C	-4.1365	-0.59939	-1.88819
C	-2.79456	-0.4982	-1.53531
C	-2.42308	-0.15946	-0.22993
C	-3.41152	0.12241	0.7242
C	-4.75813	0.01754	0.35887
C	-5.12364	-0.3488	-0.93295
H	-4.41177	-0.86694	-2.90344
H	-2.02672	-0.67145	-2.28171
C	-3.01036	0.57043	2.11069
H	-5.52357	0.23957	1.09781
H	-6.17347	-0.42373	-1.19934
C	-1.59997	1.13831	2.07215
H	-3.71839	1.31698	2.48752
H	-3.0327	-0.27745	2.80758
H	-1.56088	2.06045	1.47896
H	-1.20907	1.34505	3.07035

C	-0.94963	-0.08687	0.13849
O	-0.72931	0.15711	1.50491
C	2.05552	-2.32979	-0.52941
H	2.28228	-2.14688	-1.57927
C	2.3391	-3.50885	0.01777
H	2.80515	-4.3051	-0.55351
H	2.13004	-3.71345	1.06486
Cl	4.36728	-0.56381	0.5897

M06-2X/def2TZVP-SMD(CH_2Cl_2): E = -1344.882219 hartree

Corrected Gibbs Free Energy = -1344.611155 hartree

cis-**3b**

C	-2.81893	2.70705	0.95089
C	-1.45561	2.44647	0.91225
C	-0.99159	1.25259	0.35373
C	-1.87268	0.29039	-0.16971
C	-3.23885	0.60479	-0.12145
C	-3.7266	1.78645	0.42839
H	-3.18127	3.63358	1.38448
H	-0.72726	3.14926	1.30051
C	-1.34666	-1.00845	-0.7522
H	-4.79273	1.97657	0.43873
C	0.15018	-0.85176	-1.08986
O	0.3739	1.12522	0.3131
H	-1.87106	-1.19608	-1.69555
H	0.59975	-1.82679	-1.28741
H	0.24961	-0.2453	-1.99366
C	3.97192	1.11324	-1.90032
C	2.66029	0.86729	-1.50772
C	2.38605	0.11768	-0.35862
C	3.44412	-0.35216	0.43256
C	4.76004	-0.0995	0.02894
C	5.02806	0.61798	-1.13267
H	4.17031	1.69286	-2.79629
H	1.83943	1.27242	-2.08998
C	3.14884	-1.07644	1.72514
H	5.57874	-0.46113	0.64549
H	6.05517	0.80588	-1.43005
C	1.7549	-0.70151	2.20236
H	3.19204	-2.16306	1.57596
H	3.89966	-0.82293	2.4818
H	1.43661	-1.29606	3.06102
H	1.69907	0.36158	2.46752
C	0.93934	-0.16698	0.02558
O	0.82475	-0.99416	1.1576
C	-1.62614	-2.18564	0.15942
H	-1.27998	-2.08113	1.18197
C	-2.23593	-3.29891	-0.24064
H	-2.40583	-4.12948	0.43751
H	-2.59715	-3.41766	-1.25916
Cl	-4.41404	-0.51039	-0.81558

M06-2X/def2TZVP-SMD(CH_2Cl_2): E = -1344.88325 hartree

Corrected Gibbs Free Energy = -1344.611577 hartree

trans-**3c**

C	-3.03421	-2.6277	-0.90508
C	-1.67532	-2.35607	-0.97739
C	-1.2025	-1.10872	-0.56541
C	-2.06717	-0.10217	-0.10633
C	-3.43893	-0.41521	0.01994
C	-3.90443	-1.66856	-0.38933
H	-3.41237	-3.59443	-1.22335
H	-0.95824	-3.08802	-1.33248
C	-1.51174	1.26455	0.27491
H	-4.96219	-1.89421	-0.29145
C	-0.025	1.38795	-0.12128
O	0.16488	-0.95343	-0.64289
H	-1.58331	1.38093	1.36336
H	0.05528	1.60696	-1.18959
H	0.43798	2.21538	0.42007
C	3.88621	0.59702	-1.92847
C	2.5506	0.51429	-1.54764
C	2.20052	0.1504	-0.24313
C	3.20397	-0.17713	0.68028
C	4.54416	-0.09092	0.28711
C	4.8889	0.30144	-1.00277
H	4.1444	0.88459	-2.94281
H	1.76993	0.72126	-2.27181
C	2.82512	-0.65413	2.06351
H	5.32086	-0.34856	1.00246
H	5.93397	0.36132	-1.29099
C	1.39978	-1.1854	2.0446
H	3.52341	-1.42795	2.40182
H	2.88593	0.17318	2.78261

H	1.323	-2.09003	1.42859
H	1.02878	-1.40997	3.04676
C	0.733	0.09688	0.15509
O	0.54248	-0.16817	1.52512
C	-2.23448	2.41508	-0.38648
H	-2.40667	2.29949	-1.45683
C	-2.58664	3.54518	0.22312
H	-3.04938	4.36583	-0.31594
H	-2.42921	3.68652	1.28974
C	-4.42379	0.5602	0.62064
H	-4.03798	1.00768	1.5419
H	-4.65047	1.39055	-0.05376
H	-5.36085	0.05038	0.85857

M06-2X/def2TZVP-SMD(CH_2Cl_2): E = -924.589307 hartree

Corrected Gibbs Free Energy = -924.280306 hartree

cis-**3c**

C	3.13455	-2.59183	0.85553
C	1.7642	-2.37345	0.84271
C	1.26063	-1.19932	0.27707
C	2.10827	-0.22912	-0.27653
C	3.49992	-0.46805	-0.26537
C	3.99601	-1.6445	0.30197
H	3.53318	-3.50204	1.29315
H	1.06265	-3.08974	1.25595
C	1.52694	1.04308	-0.87154
H	5.0678	-1.81887	0.30452
C	0.02339	0.85191	-1.16
O	-0.11395	-1.10776	0.27035
H	2.00922	1.22741	-1.83956
H	-0.45562	1.81262	-1.35997
H	-0.08983	0.227	-2.04951
C	-3.79581	-1.17885	-1.80259
C	-2.47402	-0.9074	-1.46441
C	-2.16675	-0.14429	-0.33274
C	-3.20061	0.31249	0.49726
C	-4.52706	0.03396	0.14863
C	-4.829	-0.6964	-0.99653
H	-4.01967	-1.76878	-2.68582
H	-1.66978	-1.3032	-2.07553
C	-2.8675	1.051	1.77268
H	-5.32661	0.38548	0.79553
H	-5.86379	-0.9044	-1.25098
C	-1.44635	0.71058	2.19308
H	-2.94149	2.13547	1.61945
H	-3.58057	0.78571	2.56129
H	-1.10648	1.31853	3.03414
H	-1.3557	-0.34889	2.46303
C	-0.71001	0.16555	-0.00839
O	-0.56904	1.01497	1.10797
C	1.80359	2.25106	-0.00061
H	1.51844	2.15194	1.04137
C	2.34115	3.38421	-0.45043
H	2.50861	4.2353	0.20256
H	2.63159	3.50399	-1.49198
C	4.46034	0.52118	-0.87822
H	4.23241	0.70089	-1.93577
H	4.4124	1.49325	-0.37948
H	5.48604	0.14987	-0.81837

M06-2X/def2TZVP-SMD(CH_2Cl_2): E = --924.589572 hartree

Corrected Gibbs Free Energy = -924.280303 hartree

10. References

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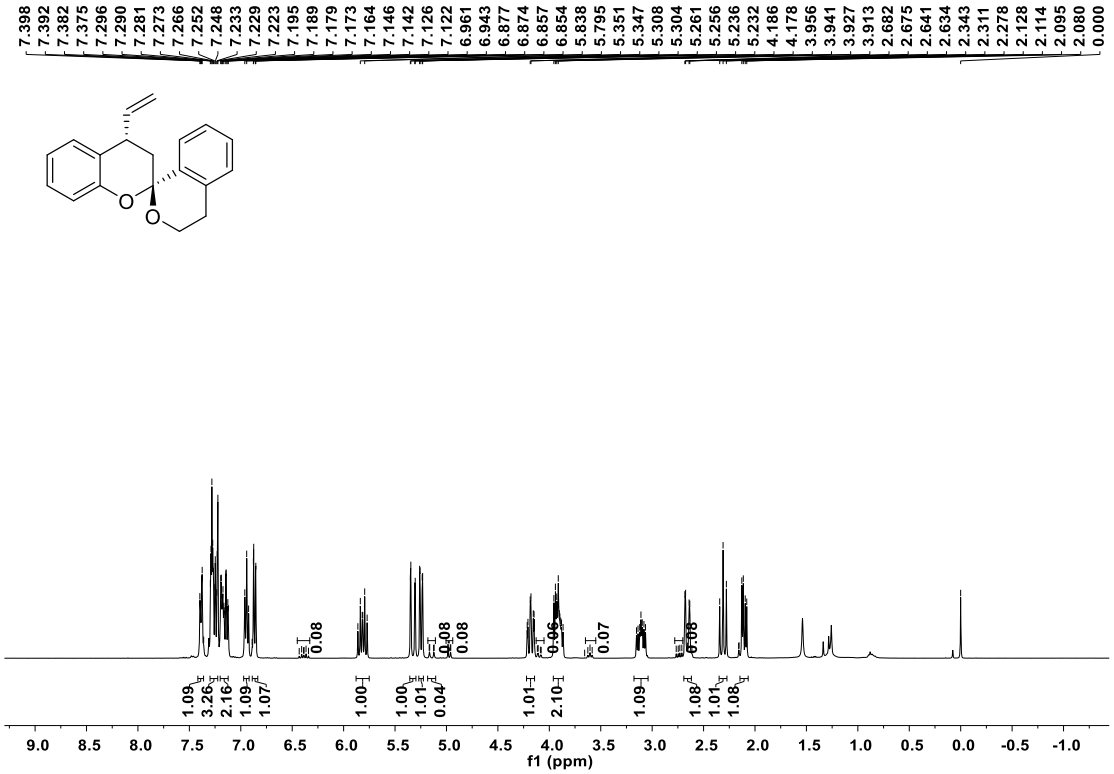
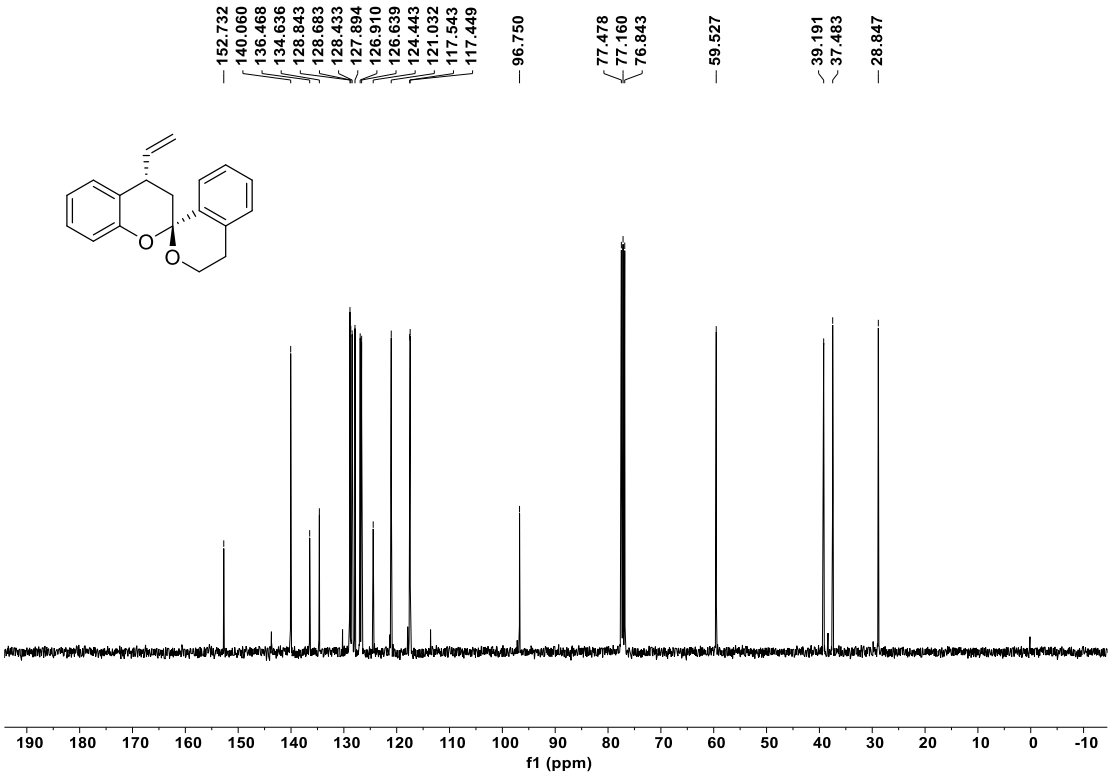
11. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

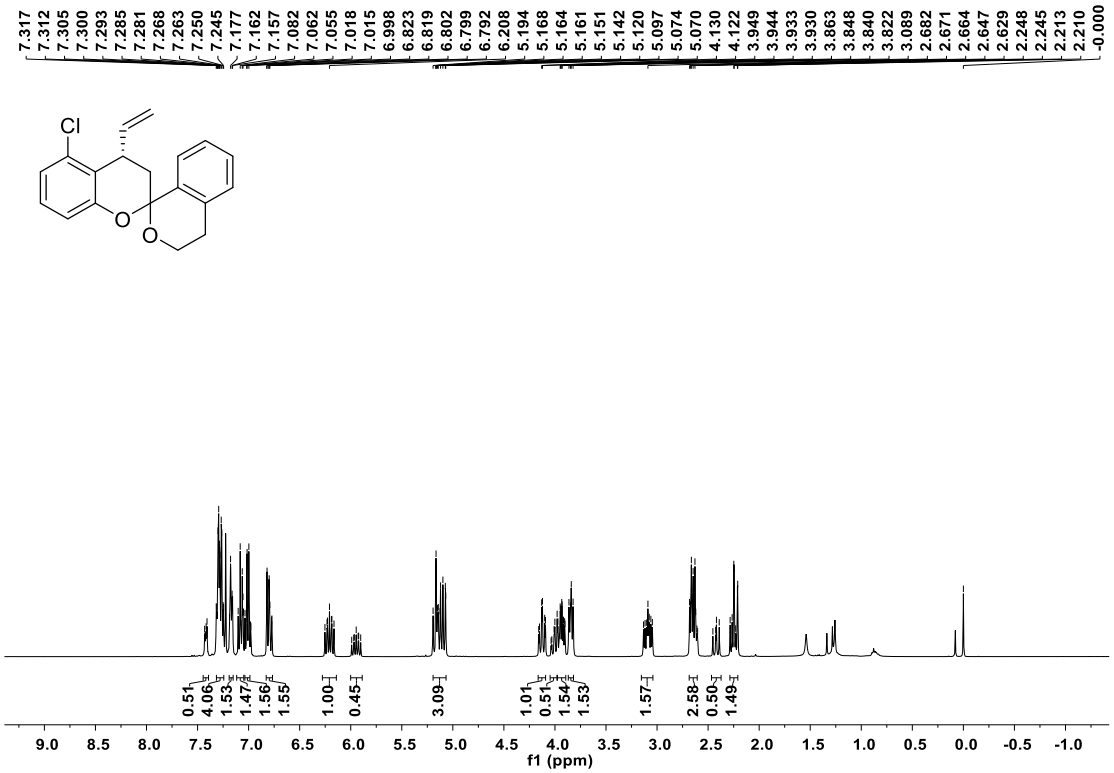
^{1}H NMR spectrum of product **3a** (400 MHz, $CDCl_3$, 12:1 dr)



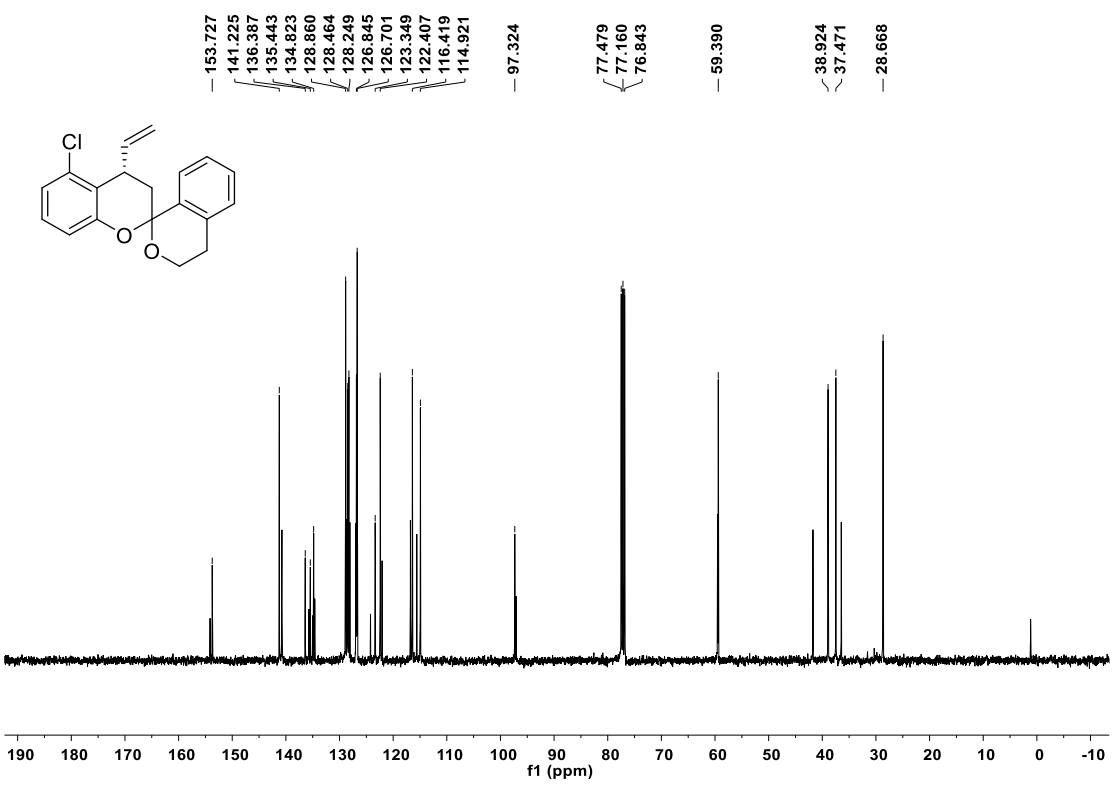
^{13}C NMR spectrum of product **3a** (100 MHz, $CDCl_3$, 12:1 dr)



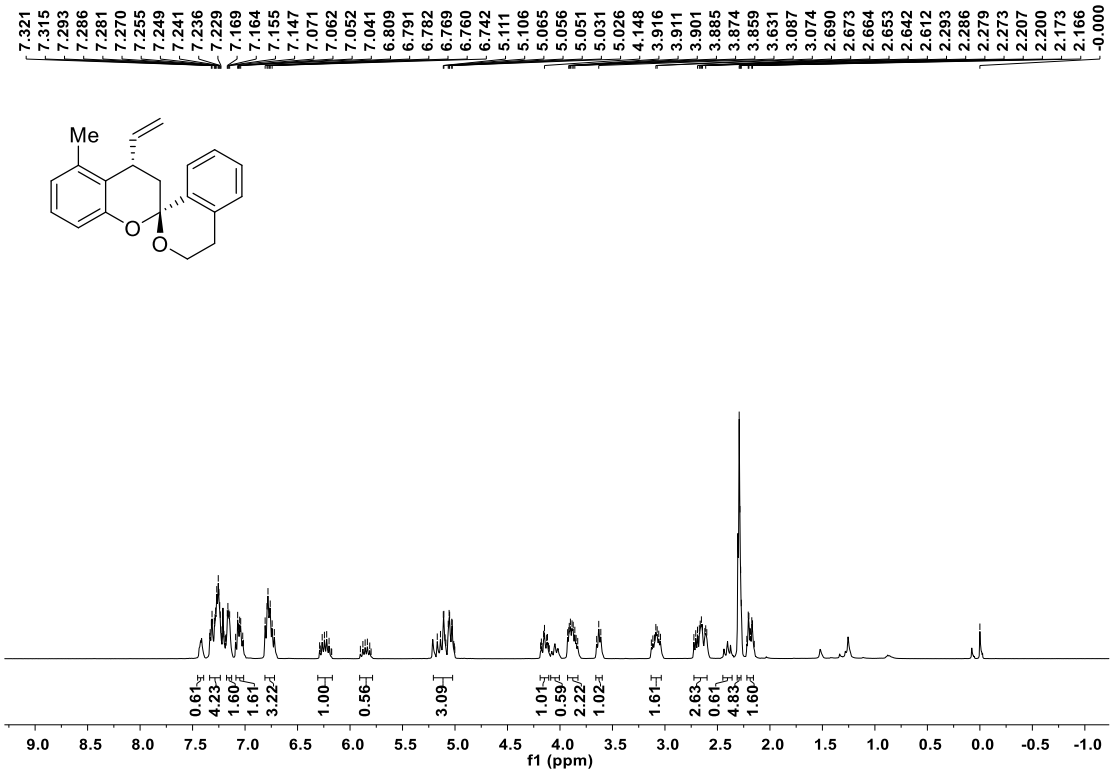
^{1}H NMR spectrum of product **3b** (400 MHz, $CDCl_3$, 2:1 dr)



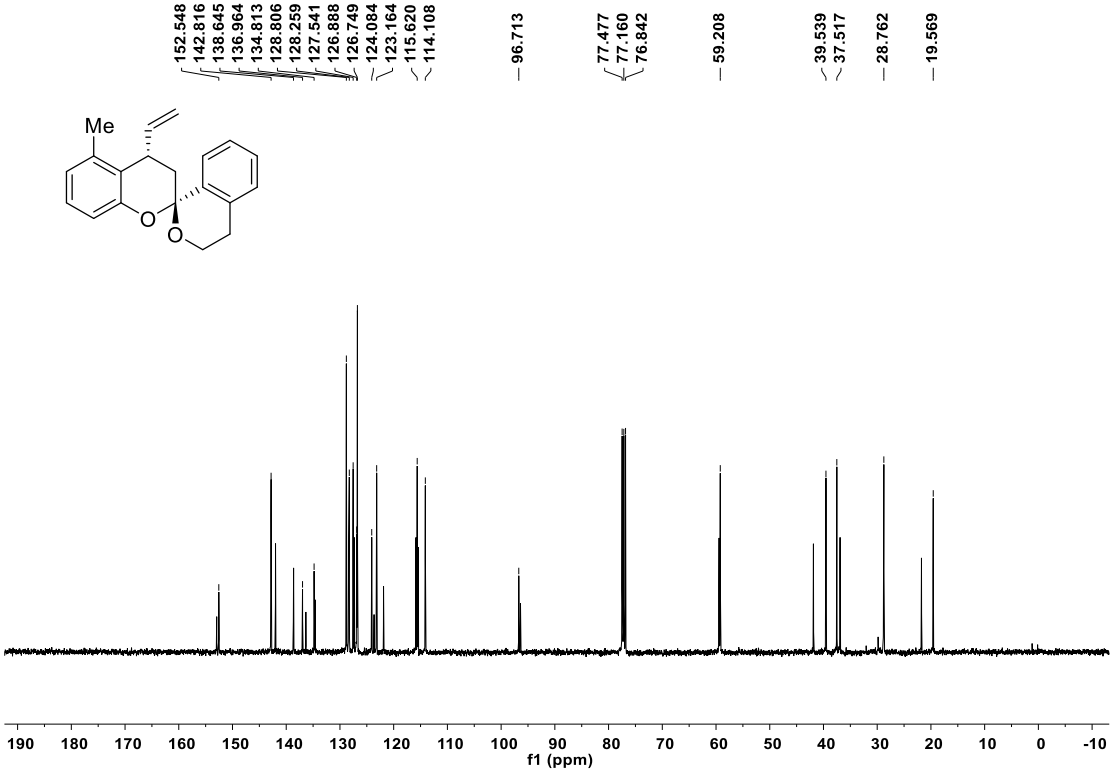
^{13}C NMR spectrum of product **3b** (100 MHz, $CDCl_3$, 2:1 dr)



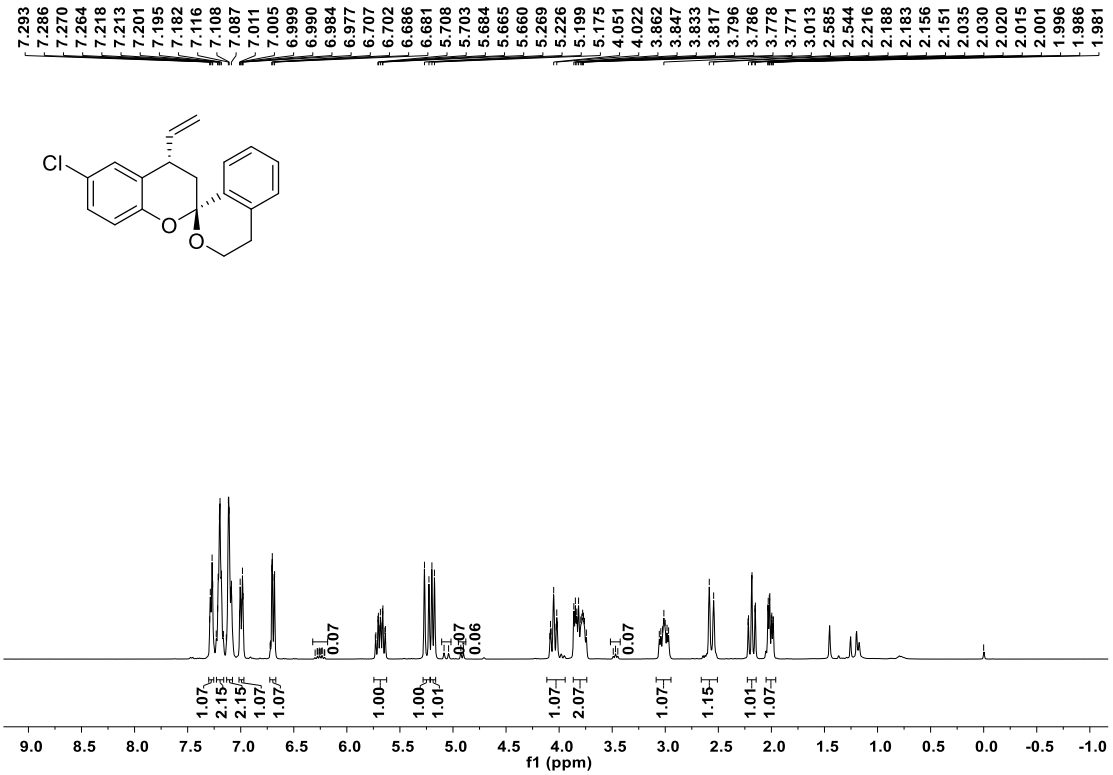
^{1}H NMR spectrum of product **3c** (400 MHz, $CDCl_3$, 1.6:1 dr)



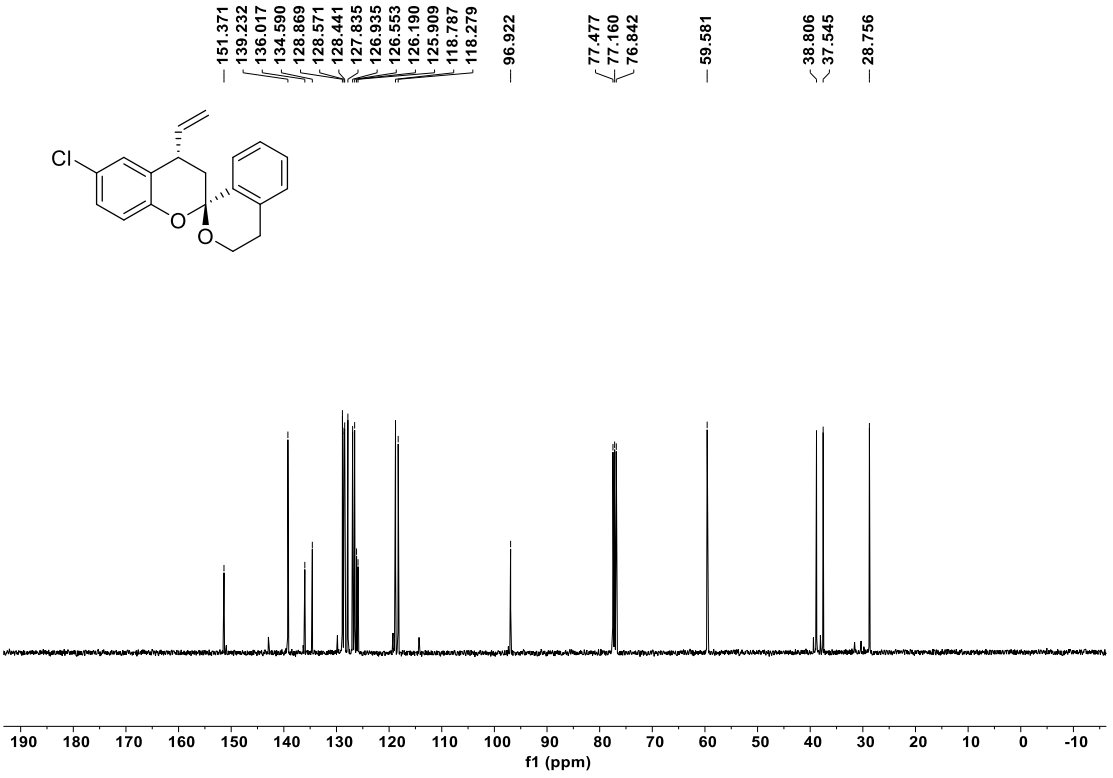
^{13}C NMR spectrum of product **3c** (100 MHz, $CDCl_3$, 1.6:1 dr)



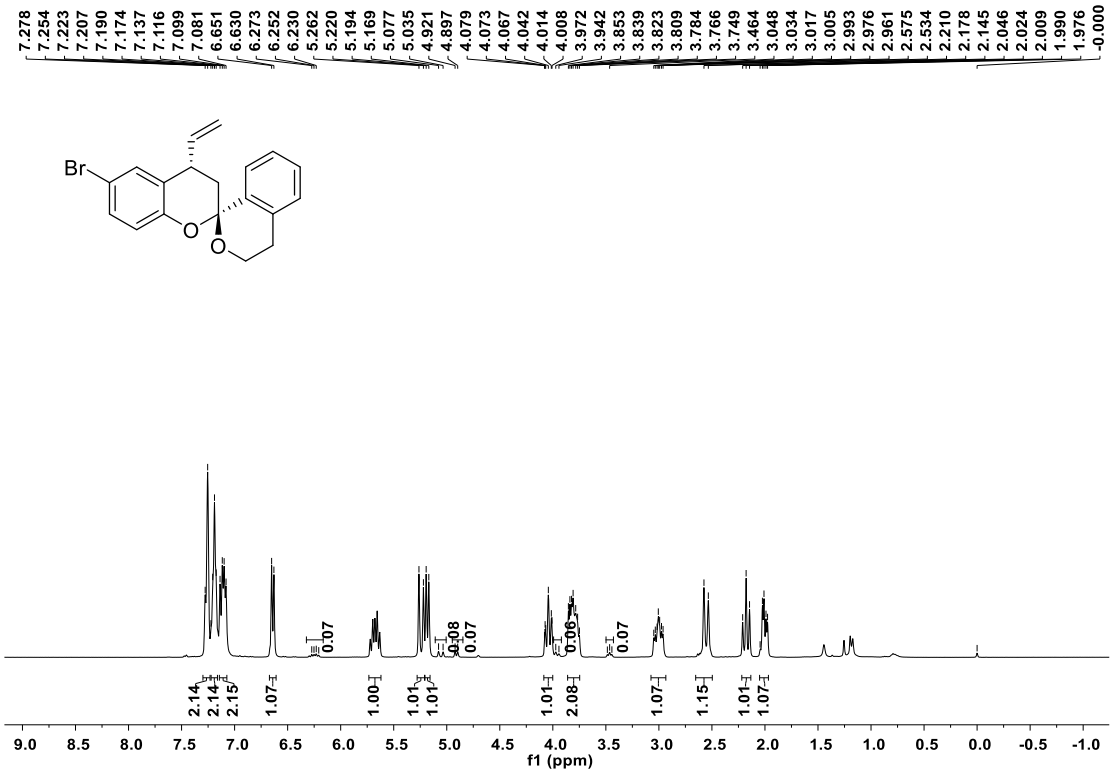
^{1}H NMR spectrum of product **3d** (400 MHz, $CDCl_3$, 14:1 dr)



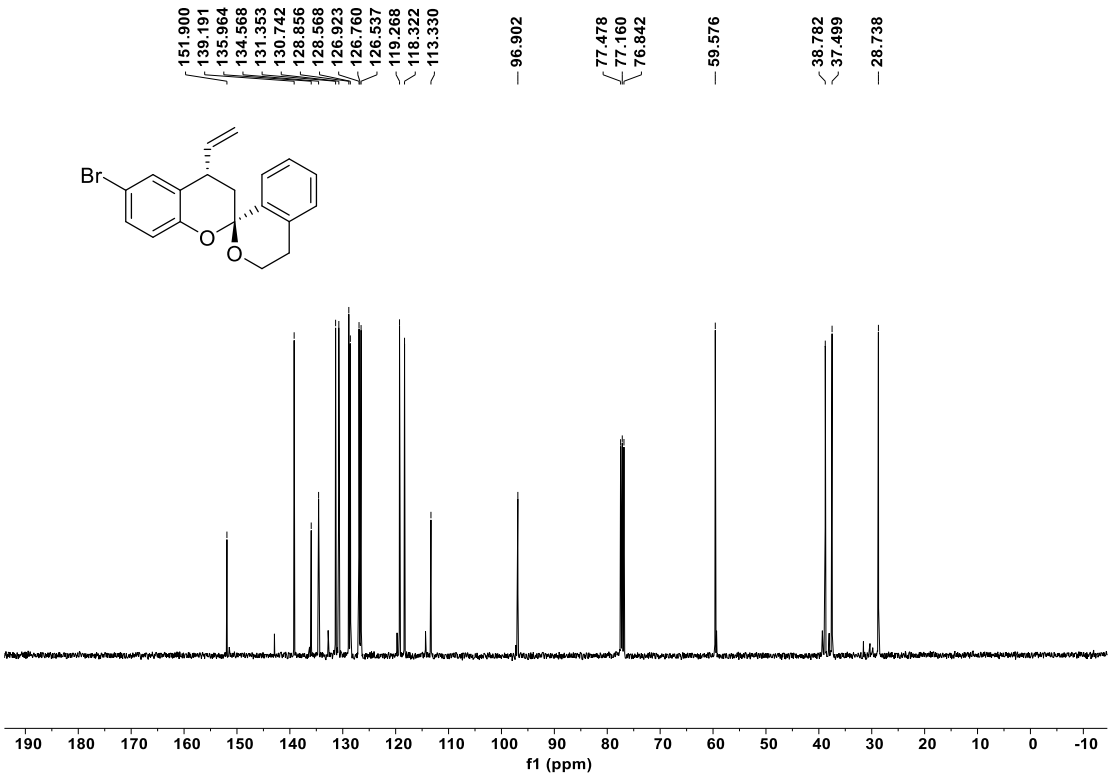
^{13}C NMR spectrum of product **3d** (100 MHz, $CDCl_3$, 14:1 dr)



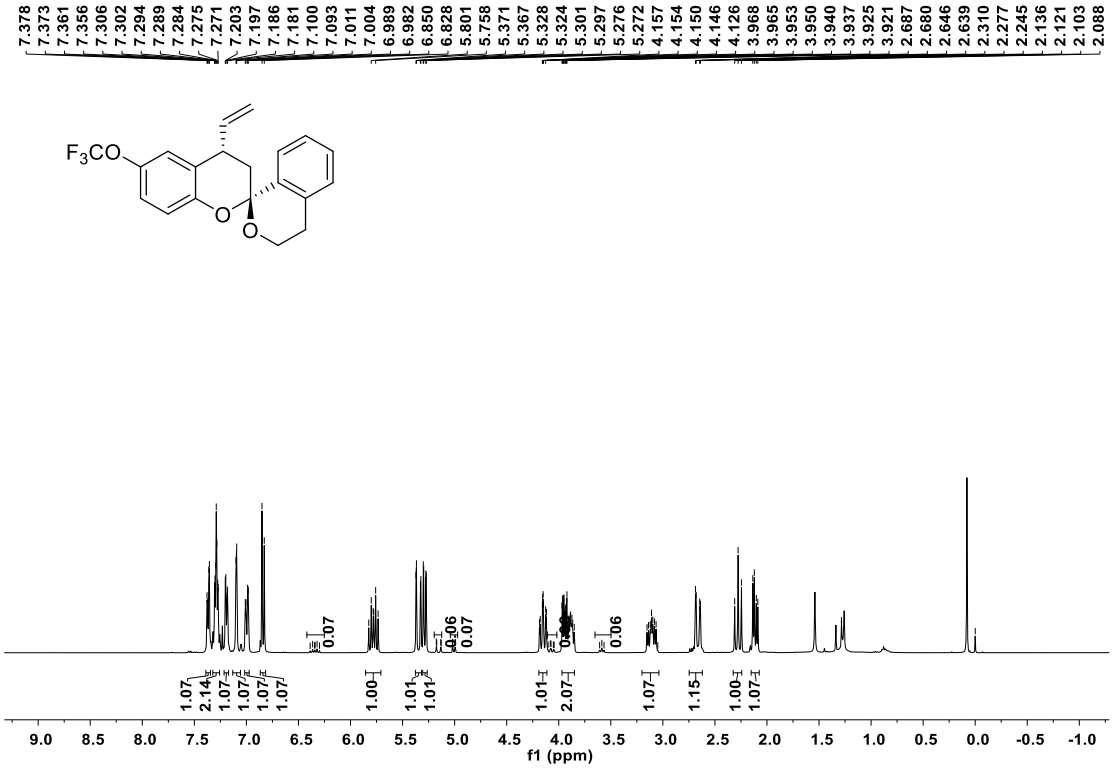
^{1}H NMR spectrum of product **3e** (400 MHz, $CDCl_3$, 14:1 dr)



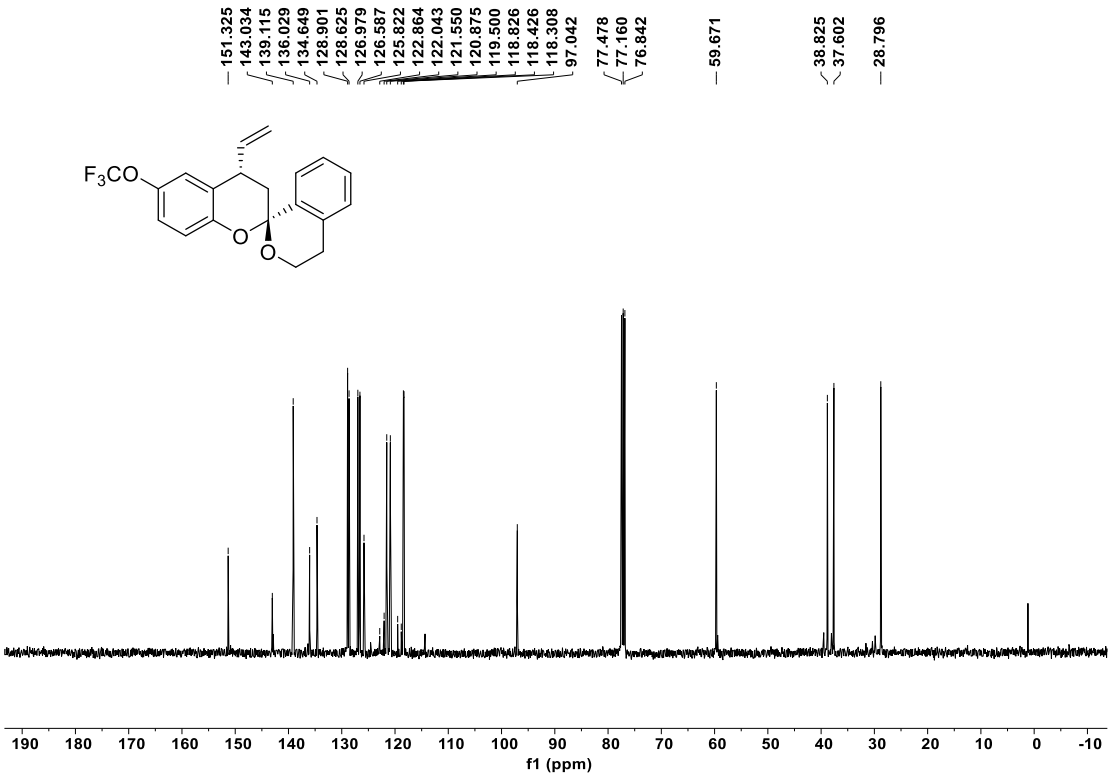
^{13}C NMR spectrum of product **3e** (100 MHz, $CDCl_3$, 14:1 dr)



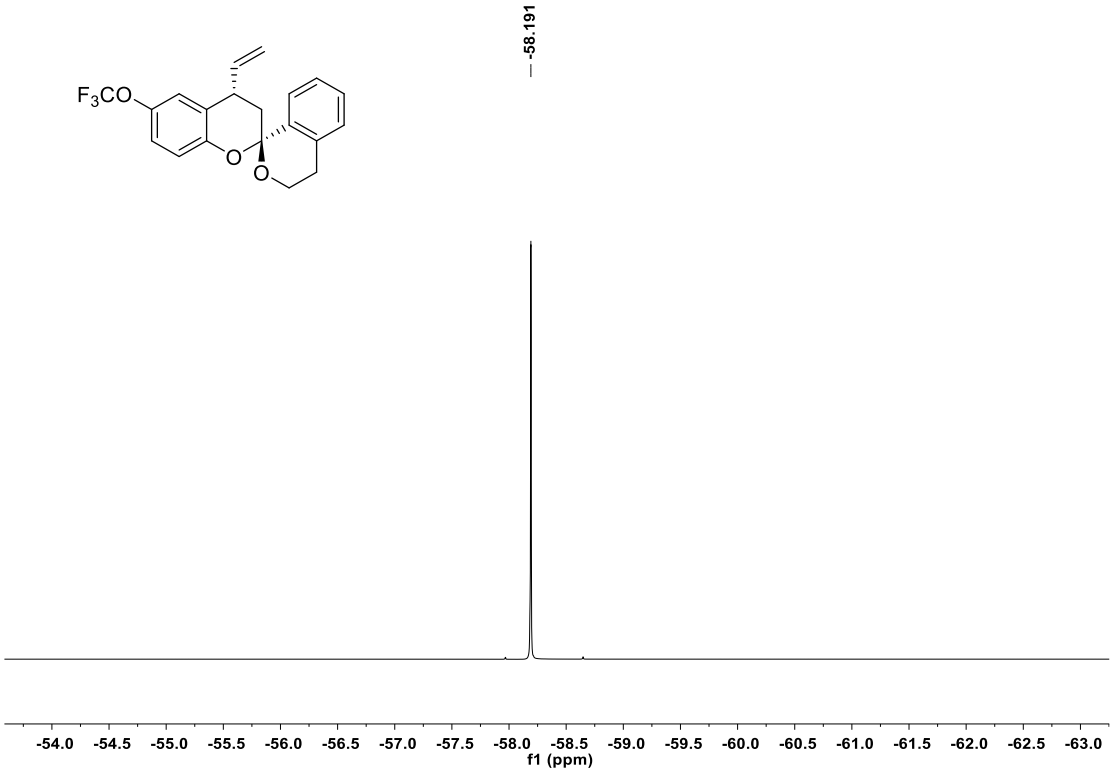
^{1}H NMR spectrum of product **3f** (400 MHz, $CDCl_3$, 14:1 dr)



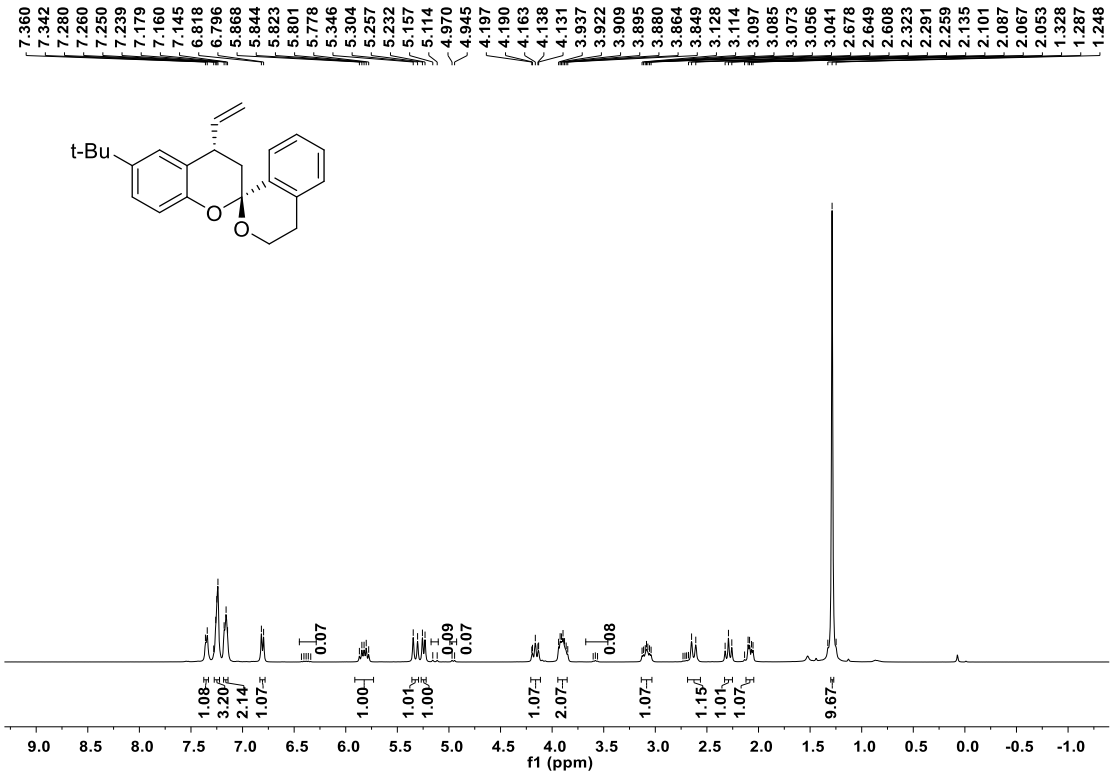
^{13}C NMR spectrum of product **3f** (100 MHz, $CDCl_3$, 14:1 dr)



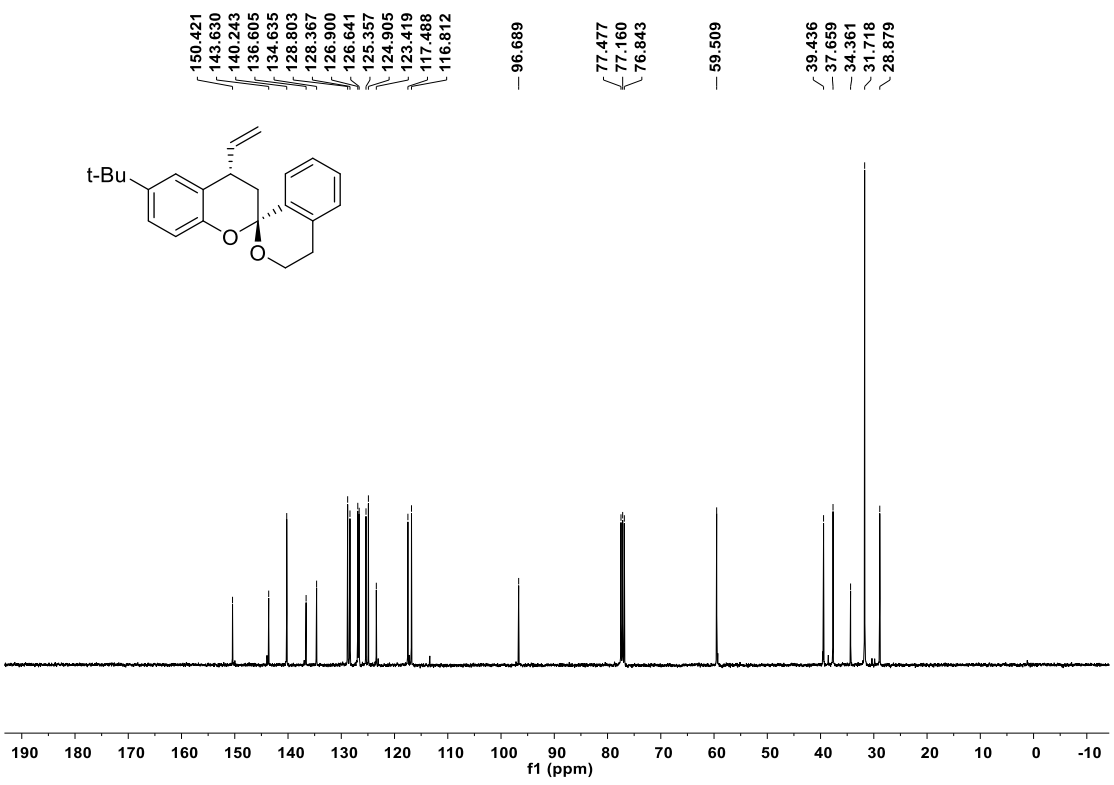
^{19}F NMR spectrum of product **3f** (376 MHz, $CDCl_3$, 14:1 dr)



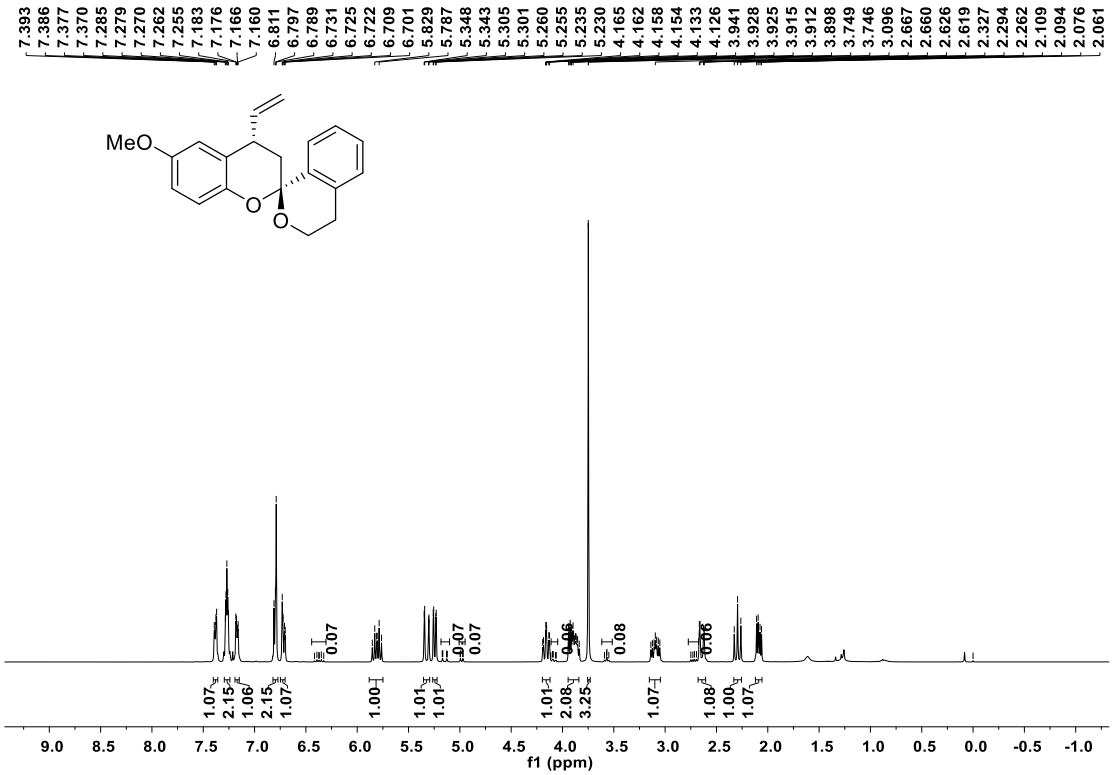
^{1}H NMR spectrum of product **3g** (400 MHz, $CDCl_3$, 13:1 dr)



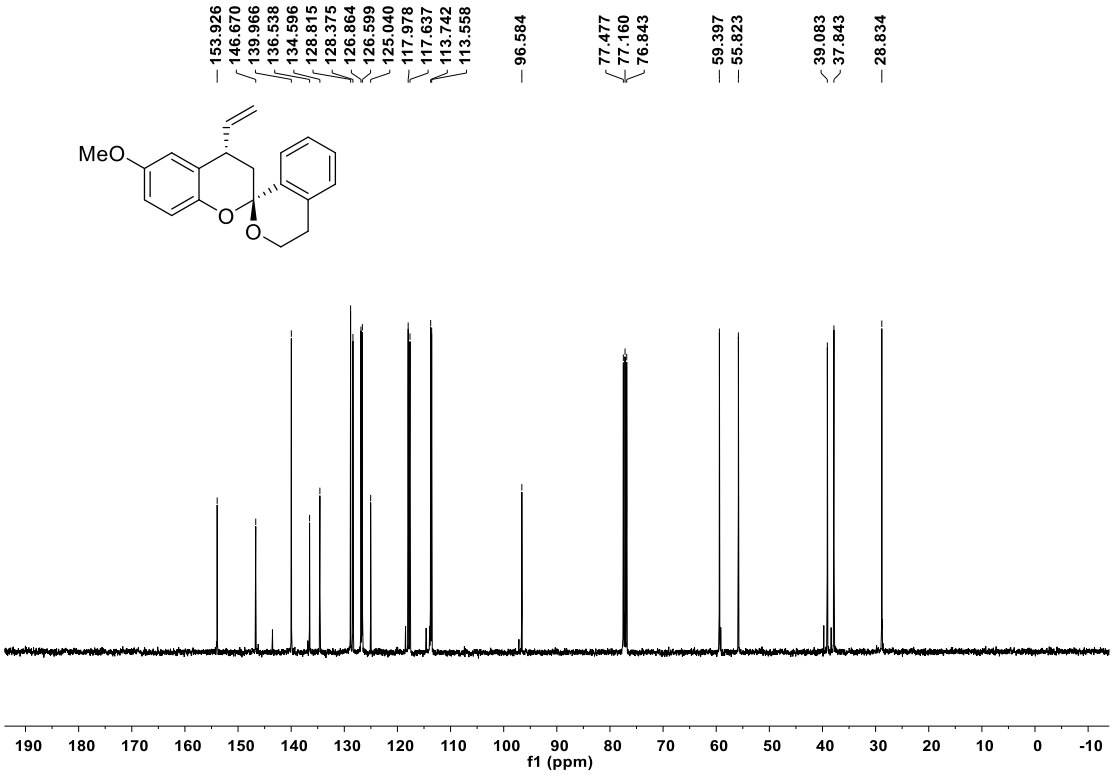
^{13}C NMR spectrum of product **3g** (100 MHz, $CDCl_3$, 13:1 dr)



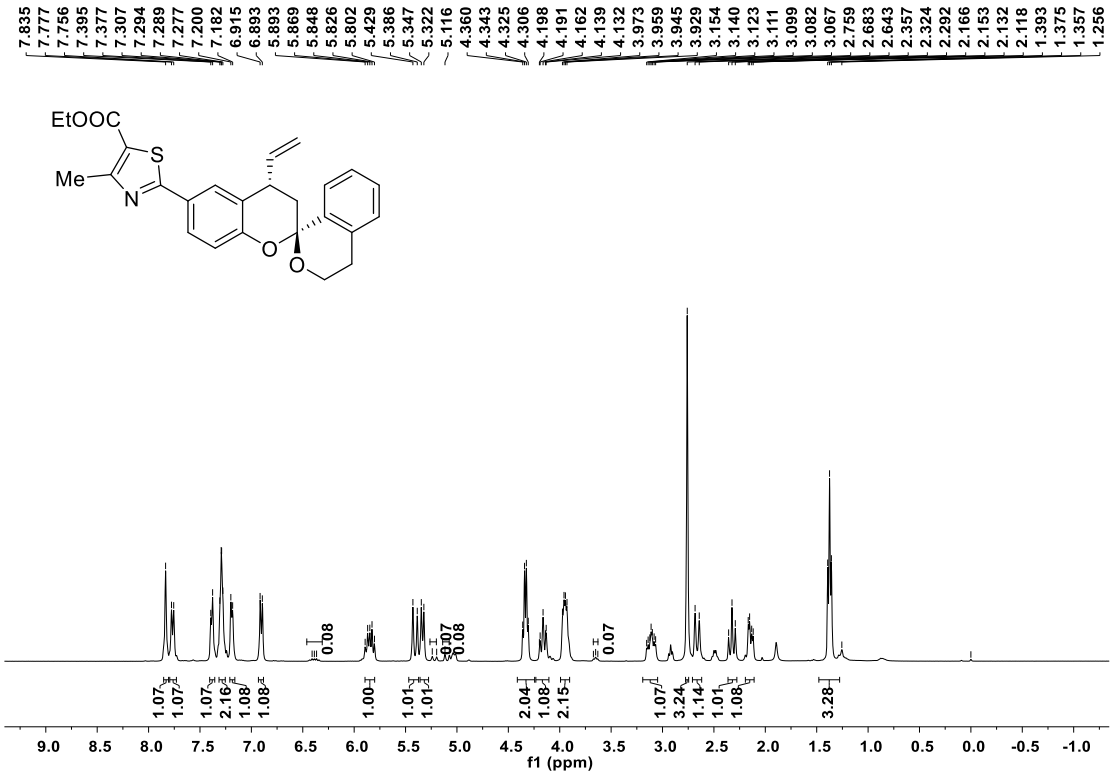
^{1}H NMR spectrum of product **3h** (400 MHz, $CDCl_3$, 14:1 dr)



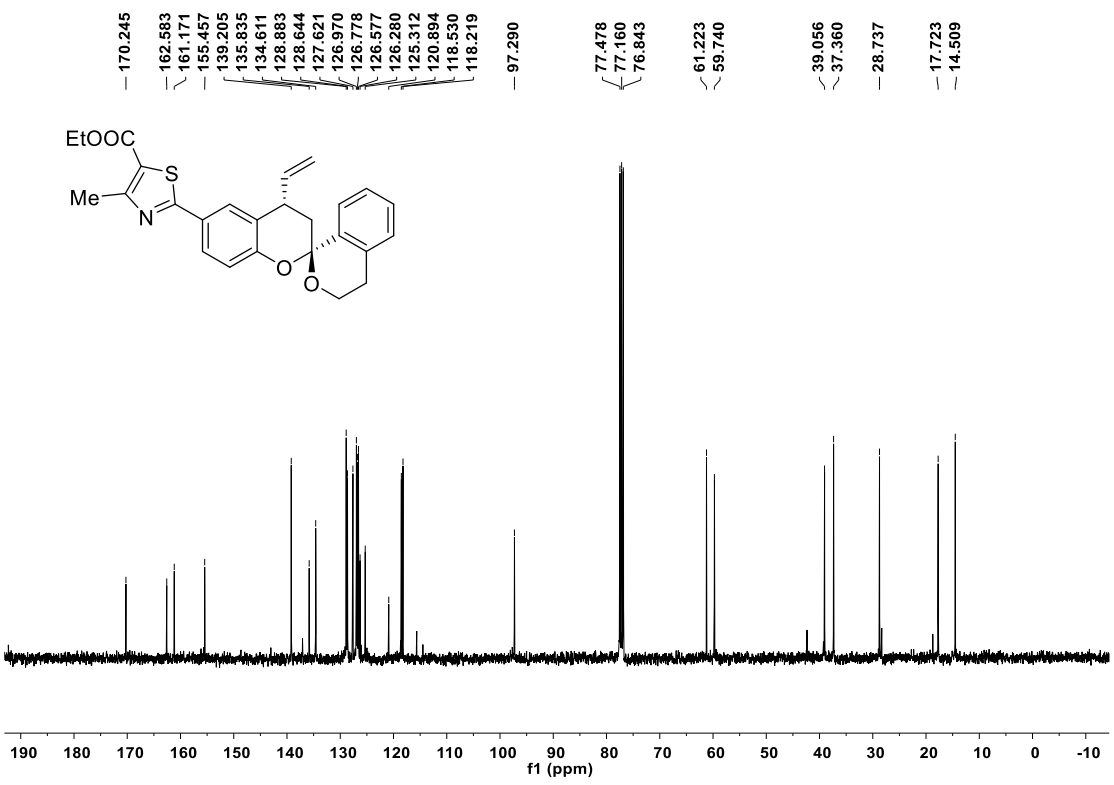
^{13}C NMR spectrum of product **3h** (100 MHz, $CDCl_3$, 14:1 dr)



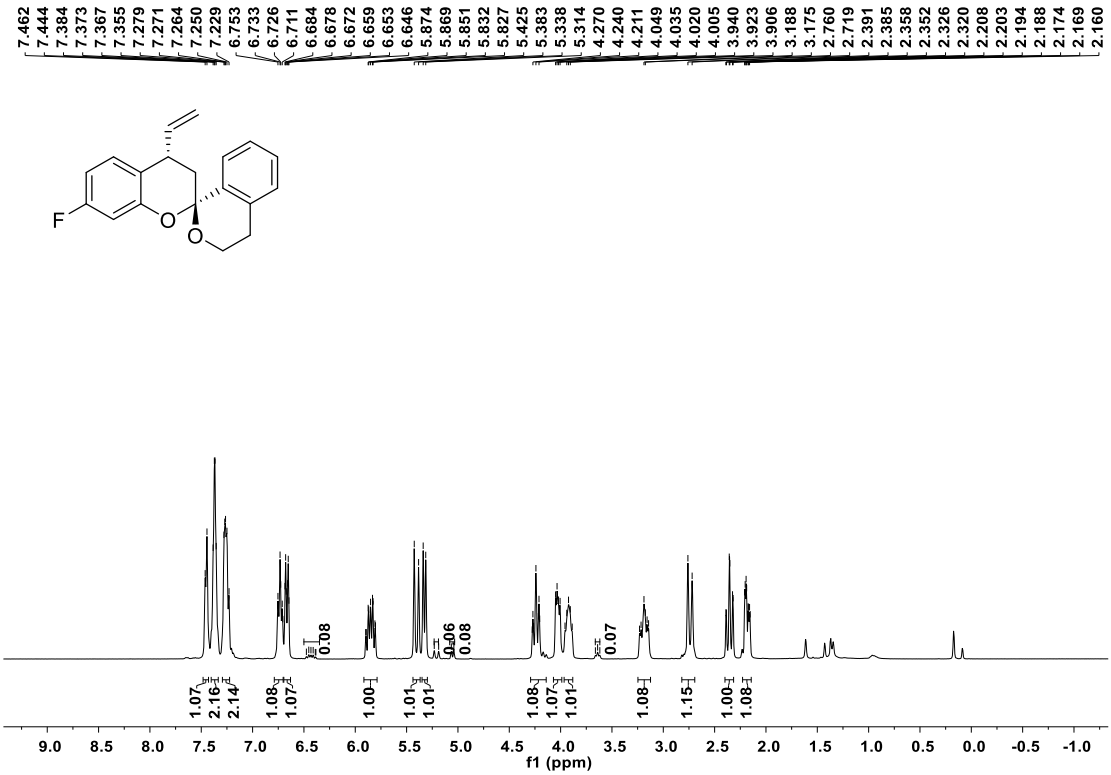
^{1}H NMR spectrum of product **3i** (400 MHz, $CDCl_3$, 14:1 dr)



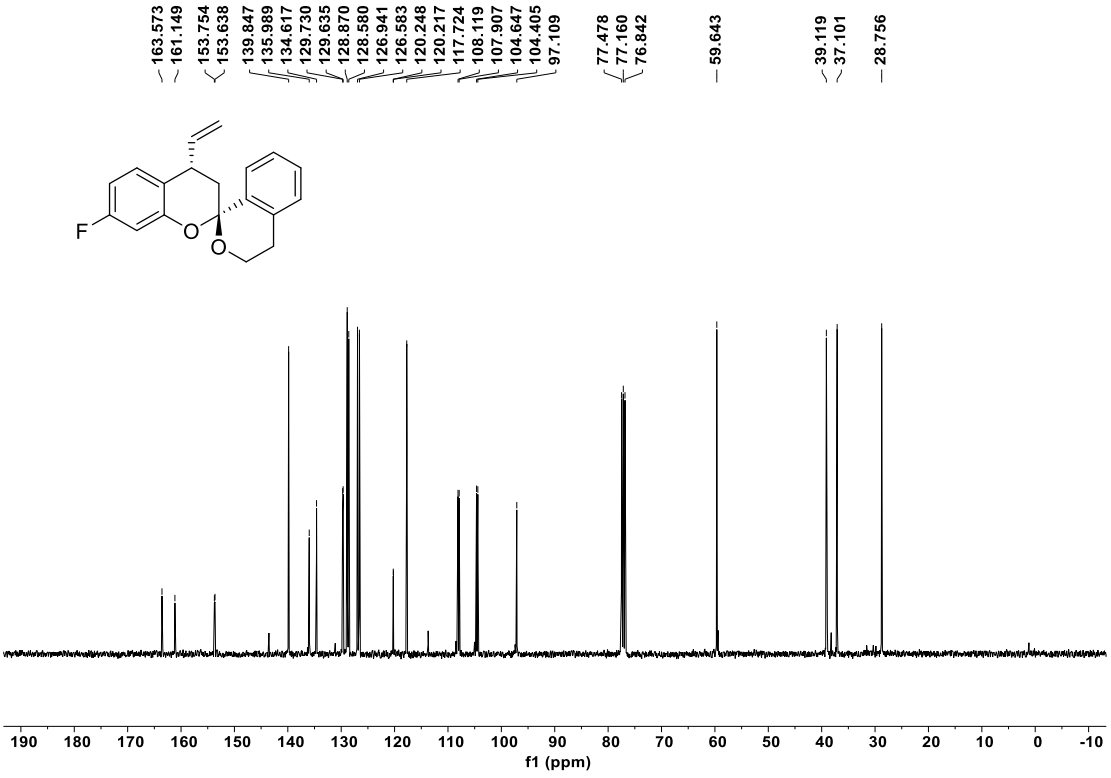
^{13}C NMR spectrum of product **3i** (100 MHz, $CDCl_3$, 14:1 dr)



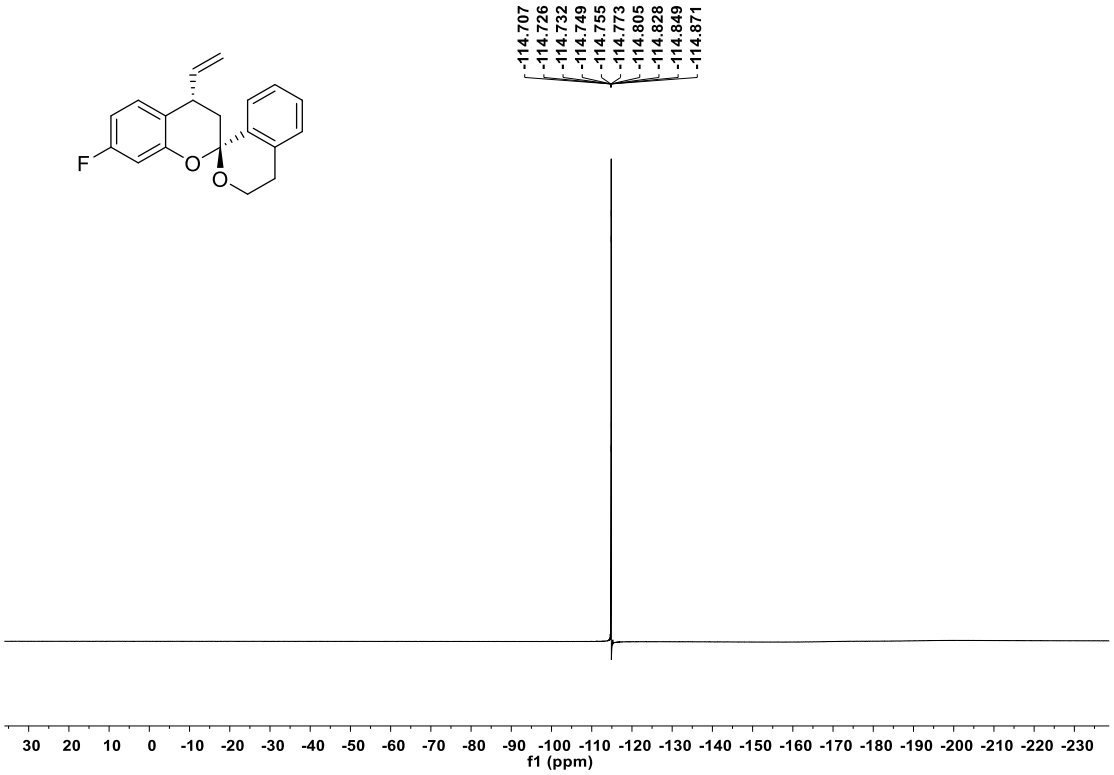
^{1}H NMR spectrum of product **3j** (400 MHz, $CDCl_3$, 12:1 dr)



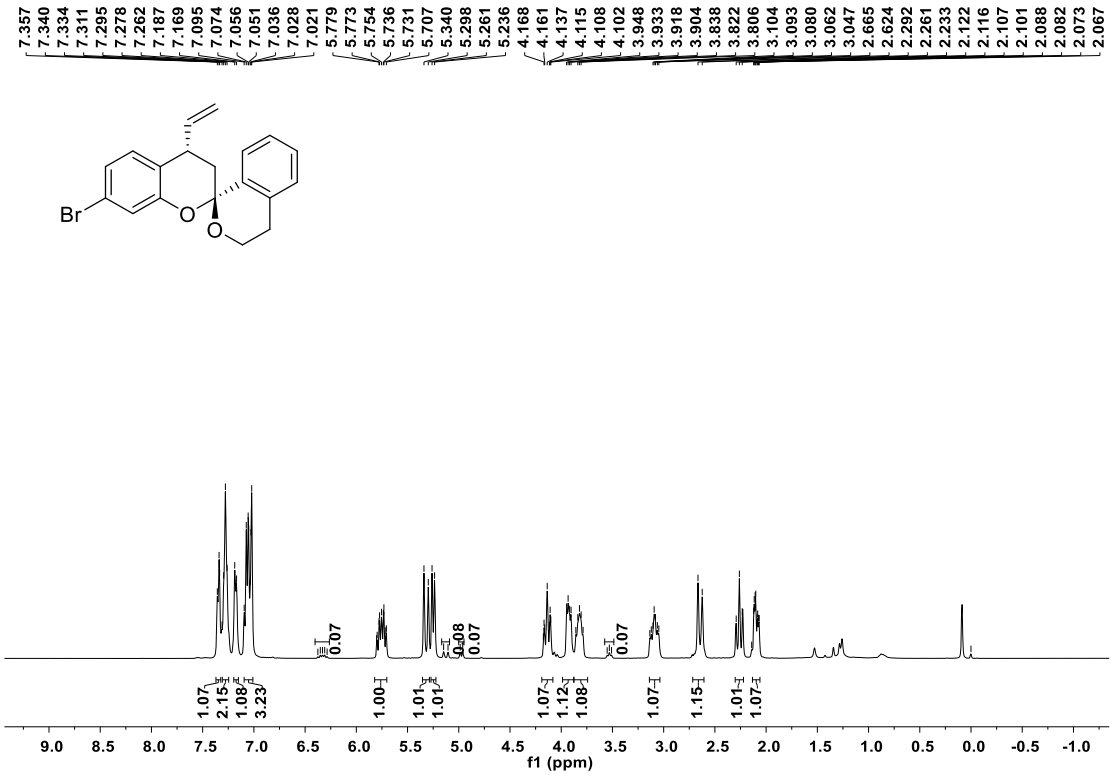
^{13}C NMR spectrum of product **3j** (100 MHz, $CDCl_3$, 12:1 dr)



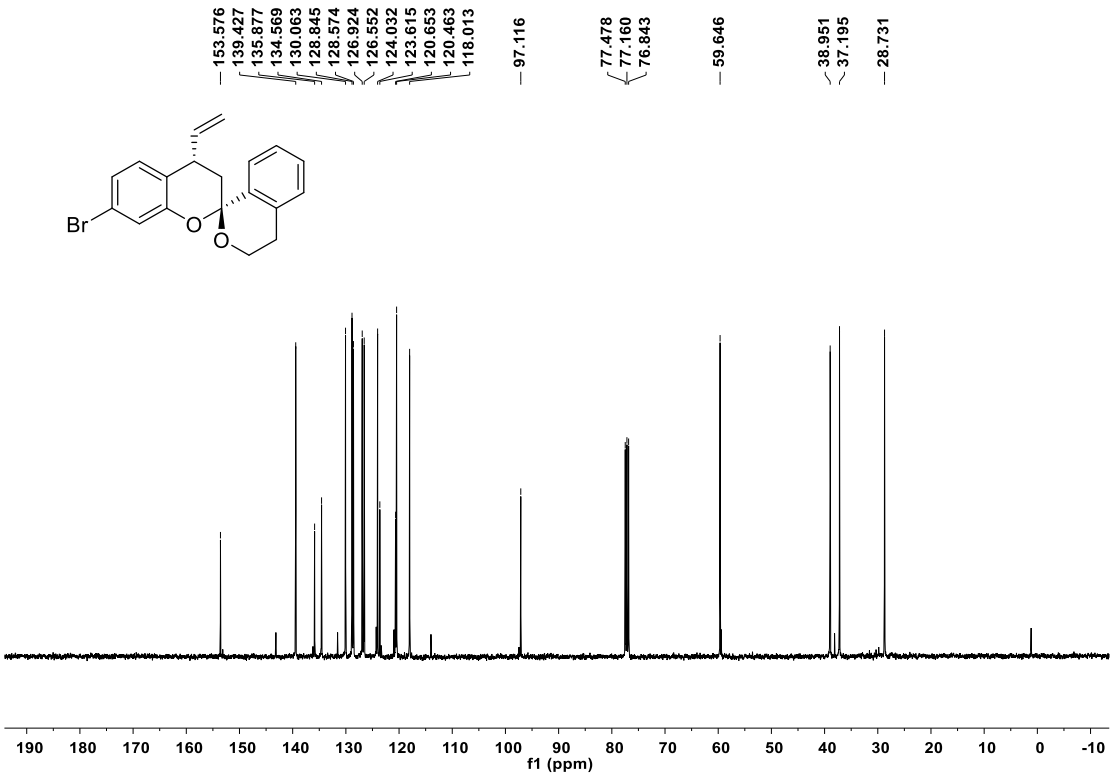
^{19}F NMR spectrum of product **3j** (376 MHz, $CDCl_3$, 12:1 dr)



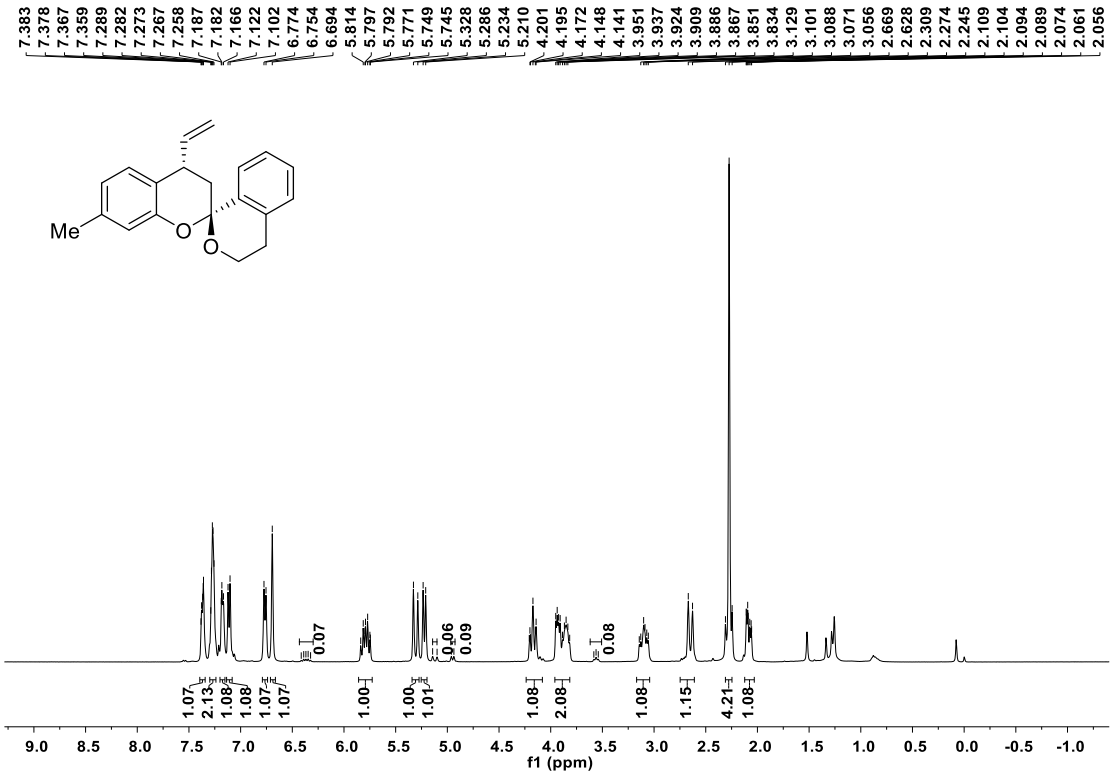
^{1}H NMR spectrum of product **3k** (400 MHz, $CDCl_3$, 14:1 dr)



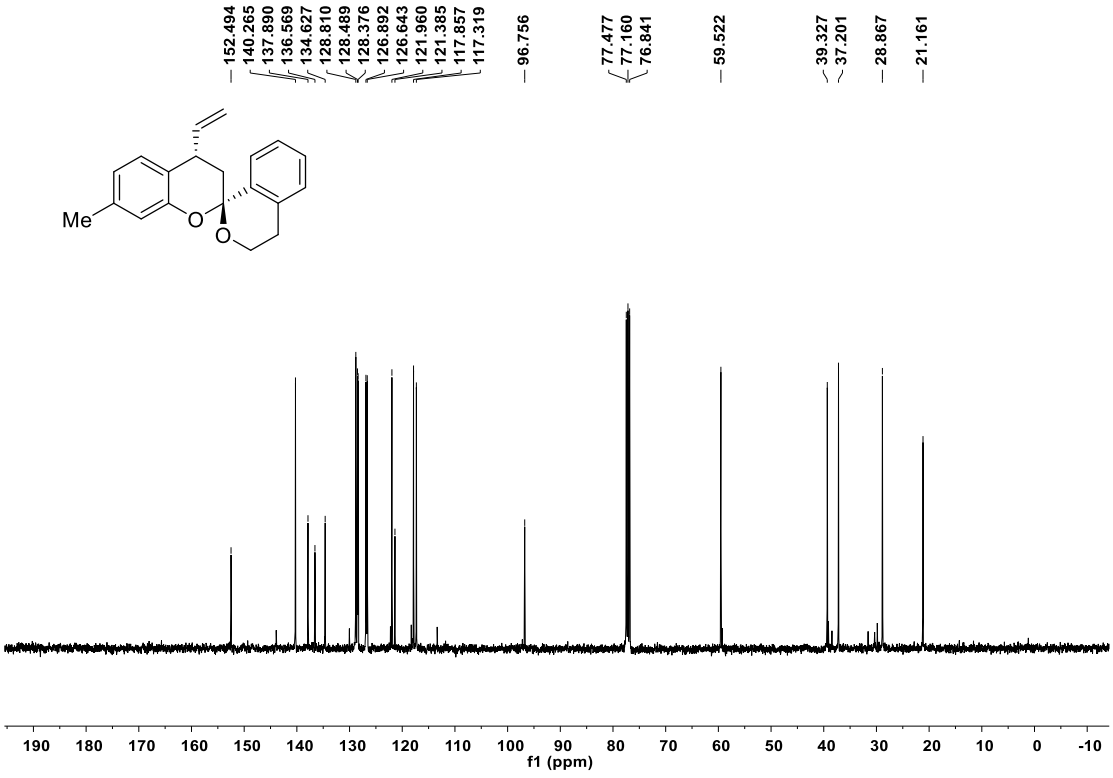
^{13}C NMR spectrum of product **3k** (100 MHz, $CDCl_3$, 14:1 dr)



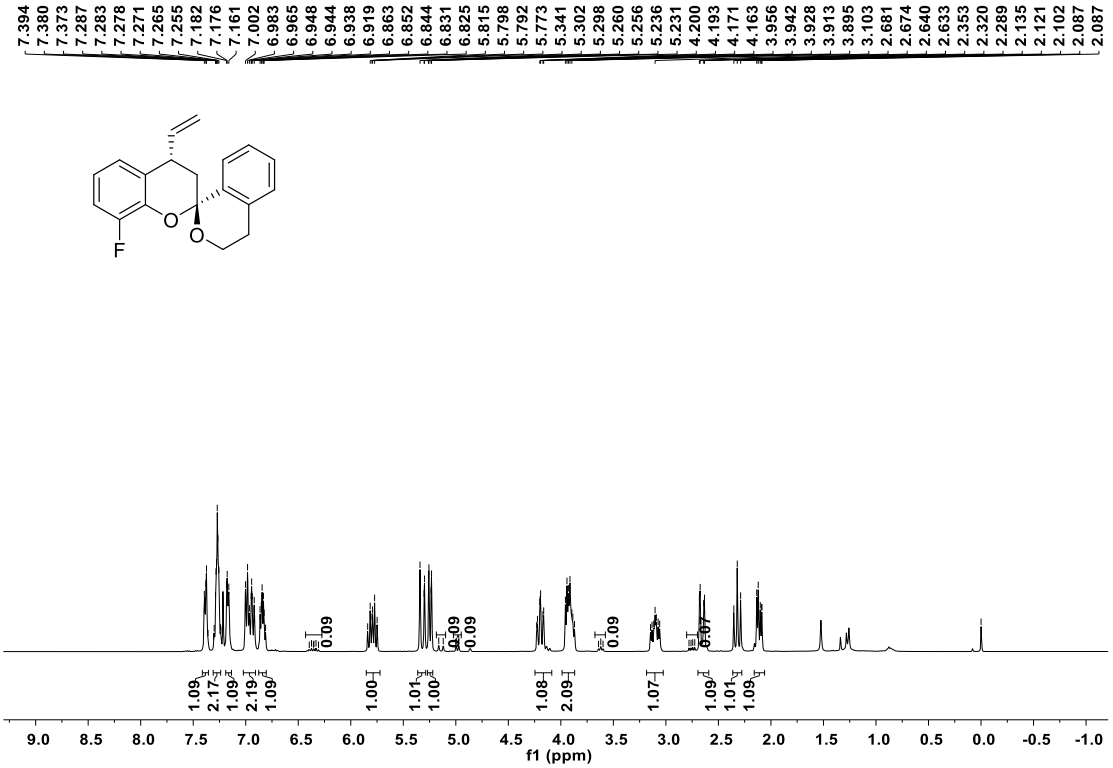
^{1}H NMR spectrum of product **3l** (400 MHz, $CDCl_3$, 14:1 dr)



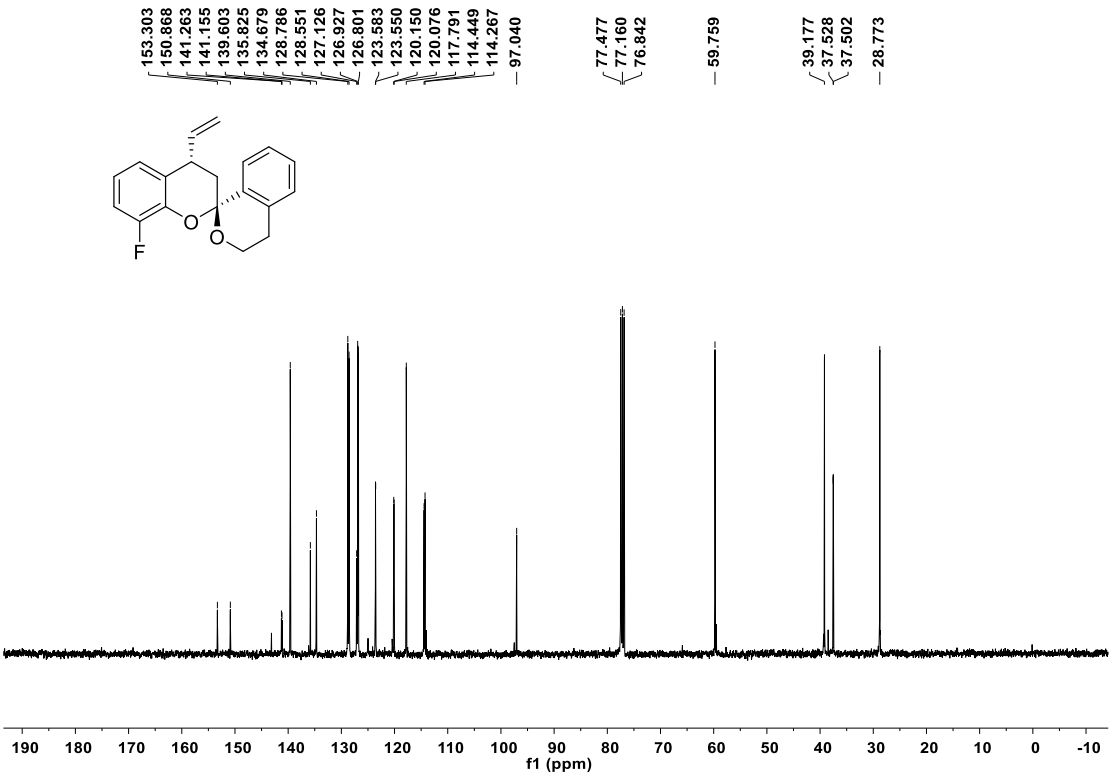
^{13}C NMR spectrum of product **3l** (100 MHz, $CDCl_3$, 14:1 dr)



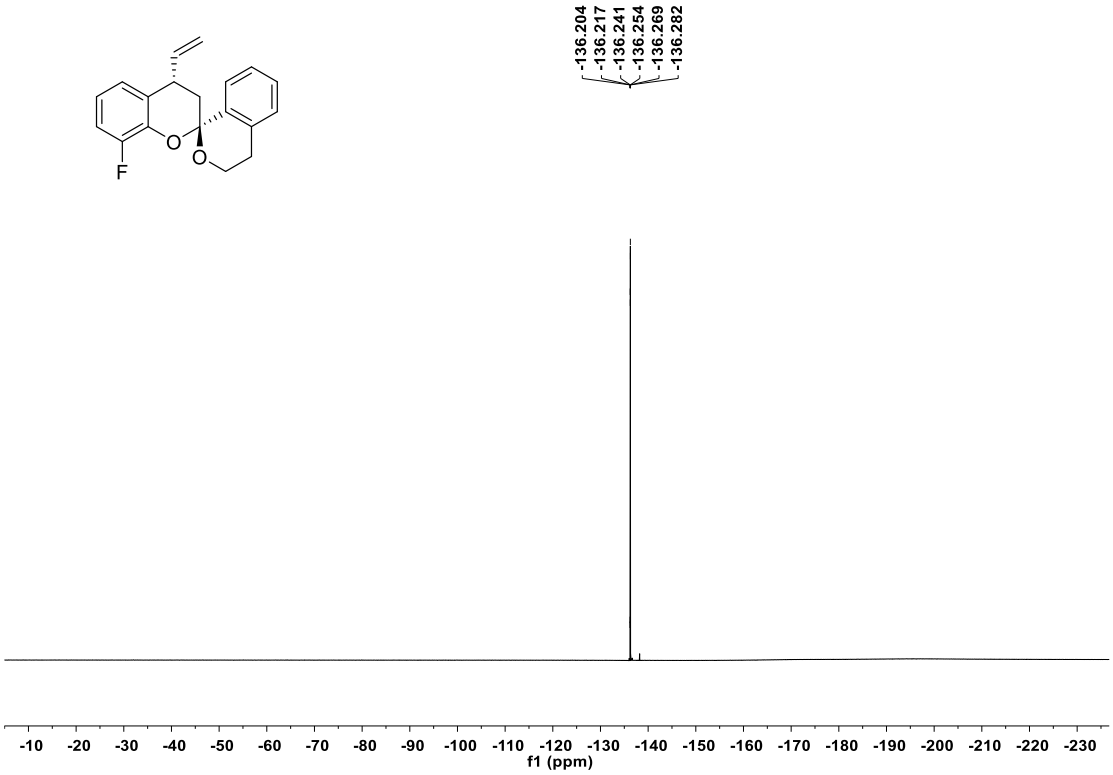
^{1}H NMR spectrum of product **3m** (400 MHz, $CDCl_3$, 11:1 dr)



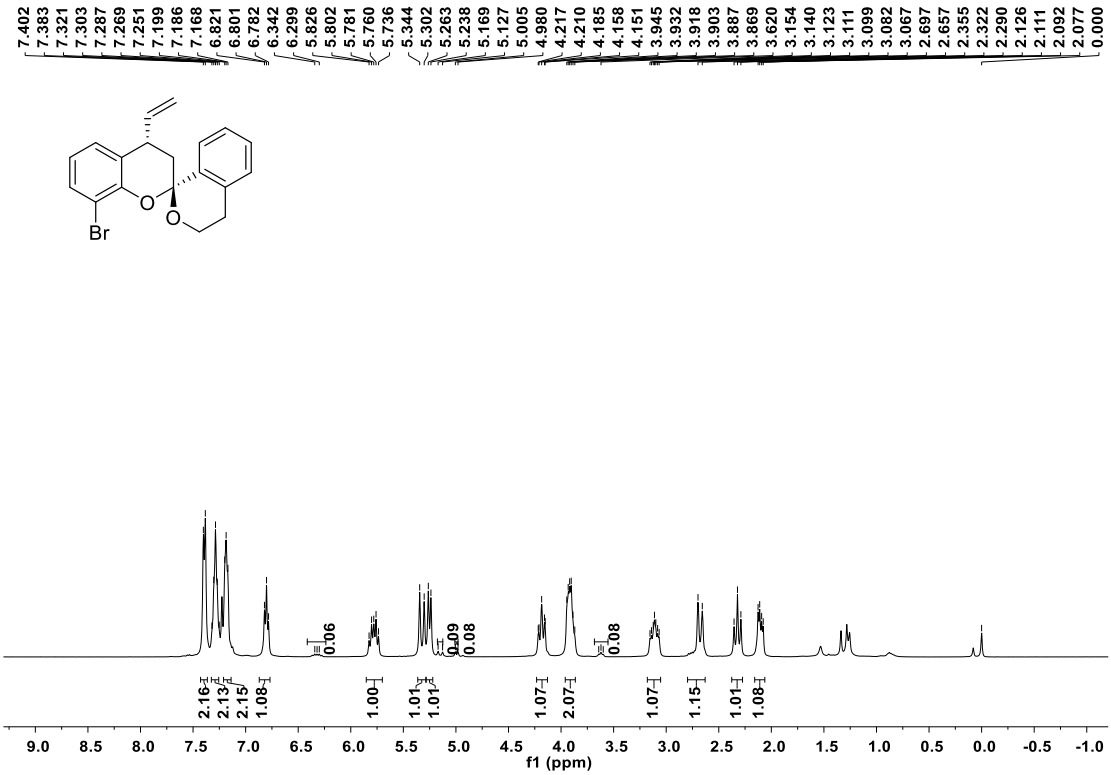
^{13}C NMR spectrum of product **3m** (100 MHz, $CDCl_3$, 11:1 dr)



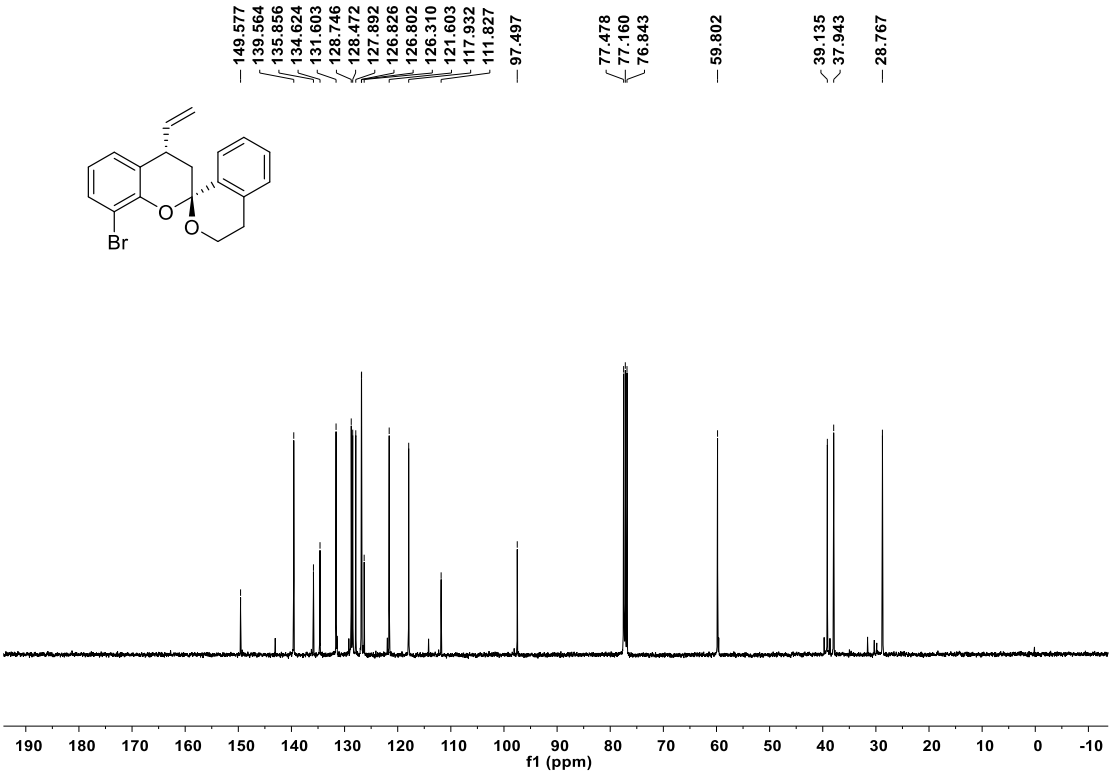
^{19}F NMR spectrum of product **3m** (376 MHz, $CDCl_3$, 11:1 dr)



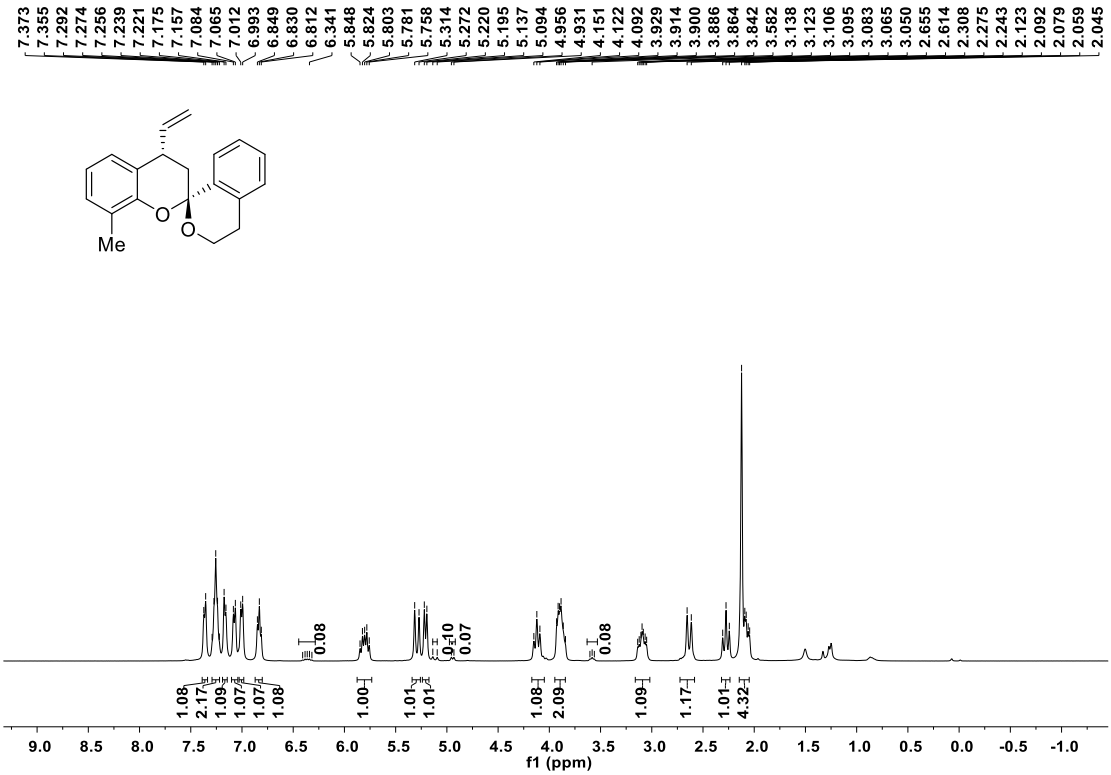
^{1}H NMR spectrum of product **3n** (400 MHz, $CDCl_3$, 14:1 dr)



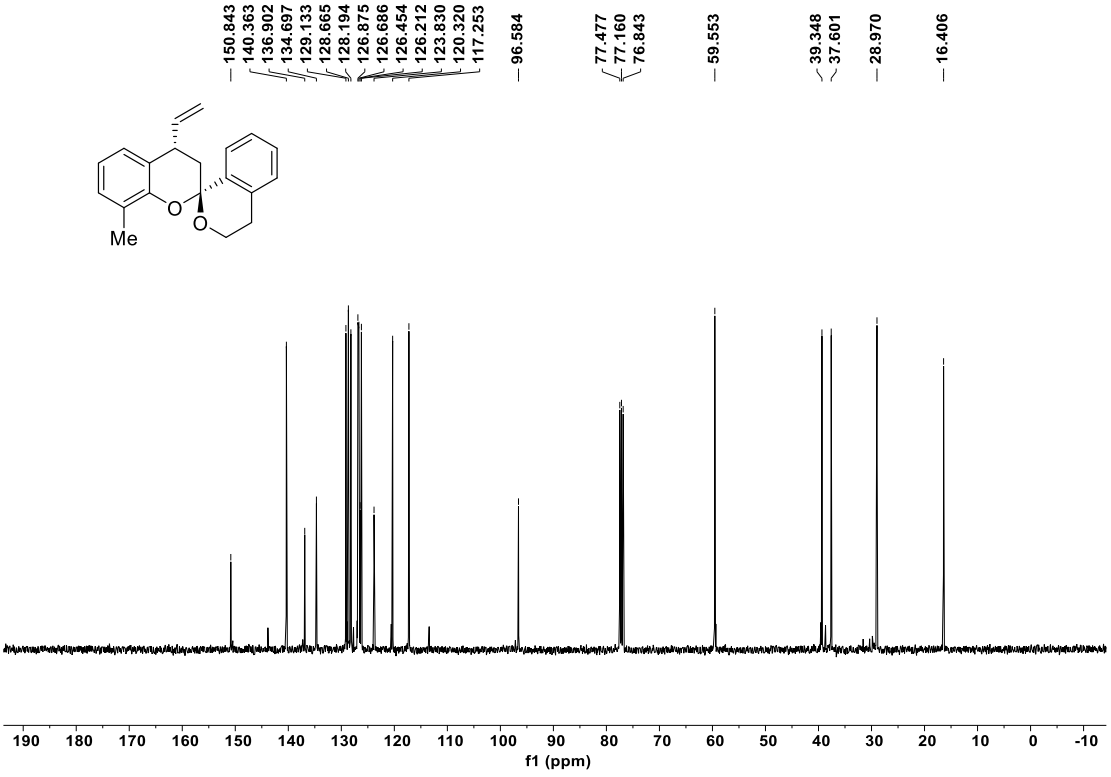
^{13}C NMR spectrum of product **3n** (100 MHz, $CDCl_3$, 14:1 dr)



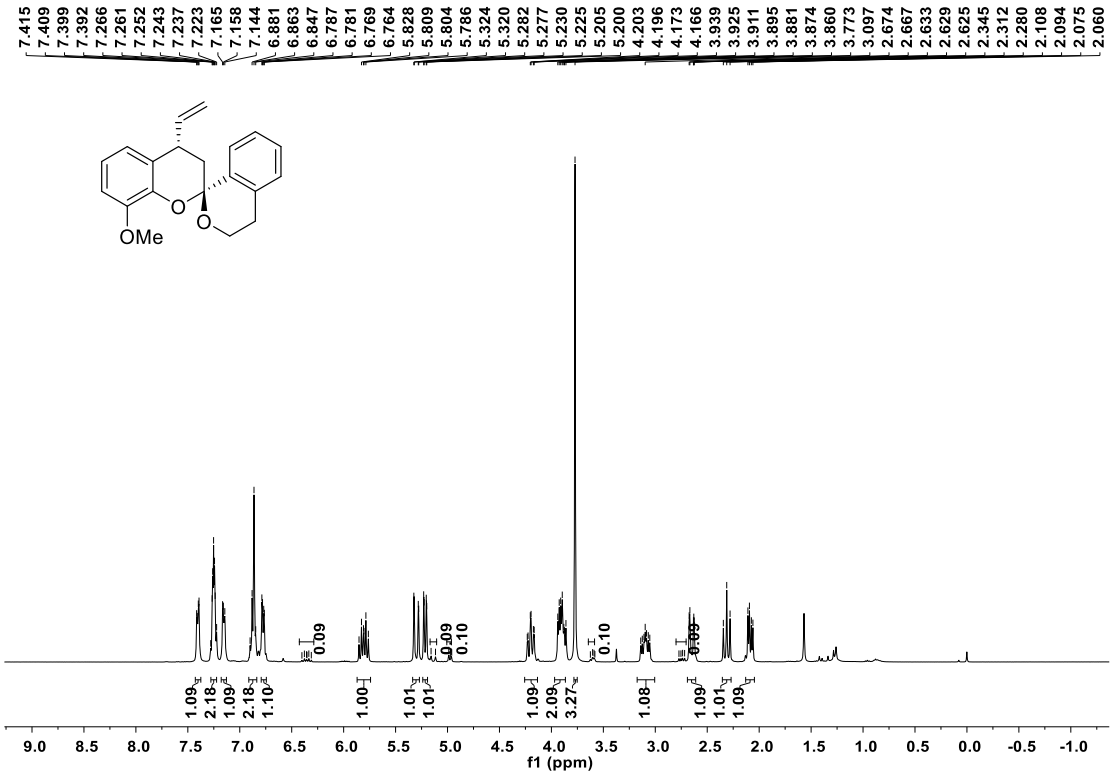
^{1}H NMR spectrum of product **3o** (400 MHz, $CDCl_3$, 12:1 dr)



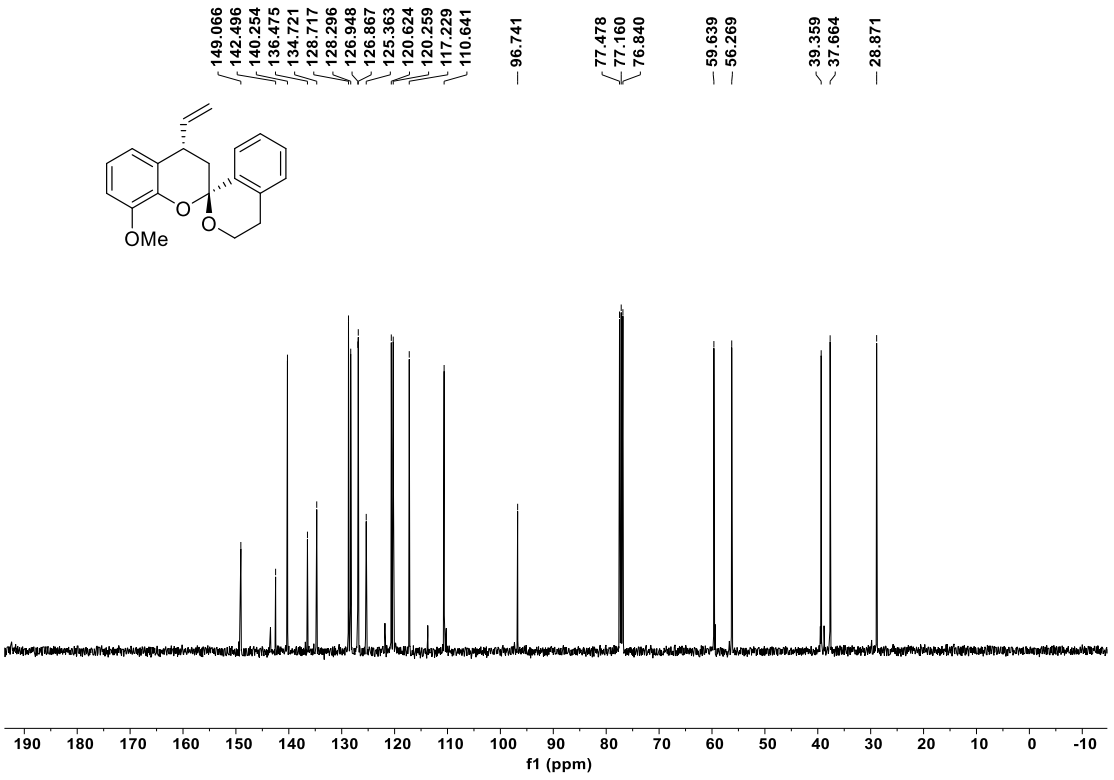
^{13}C NMR spectrum of product **3o** (100 MHz, $CDCl_3$, 12:1 dr)



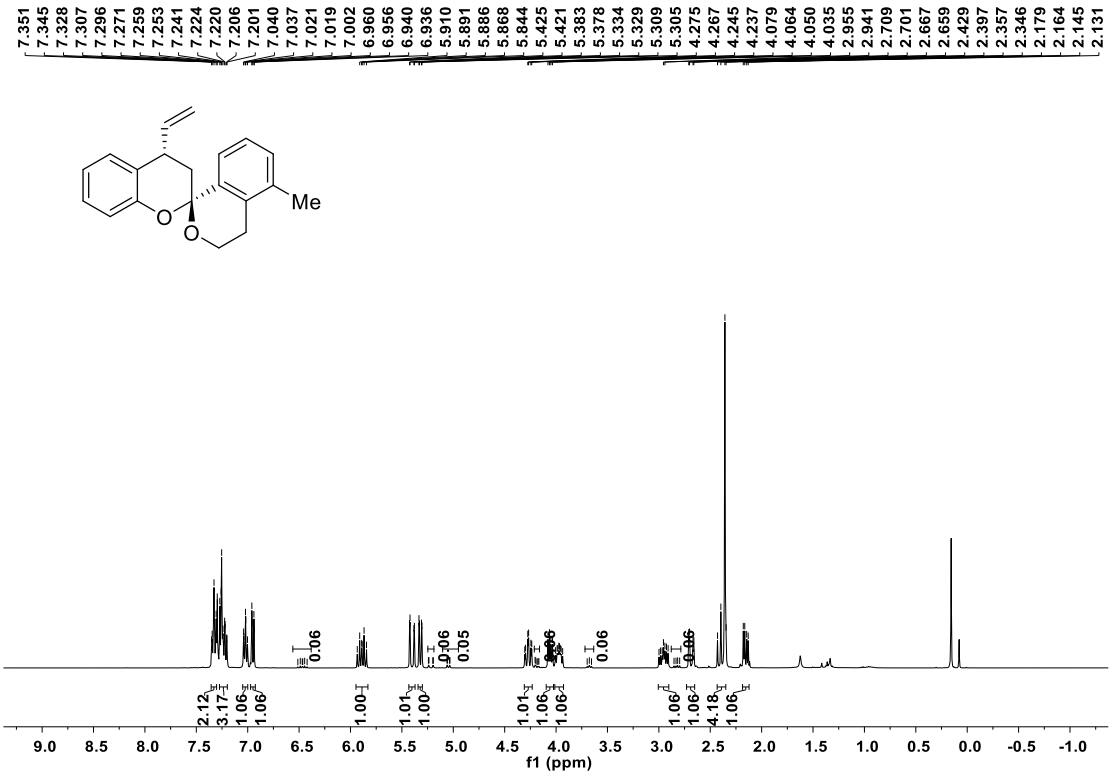
^{1}H NMR spectrum of product **3p** (400 MHz, $CDCl_3$, 11:1 dr)



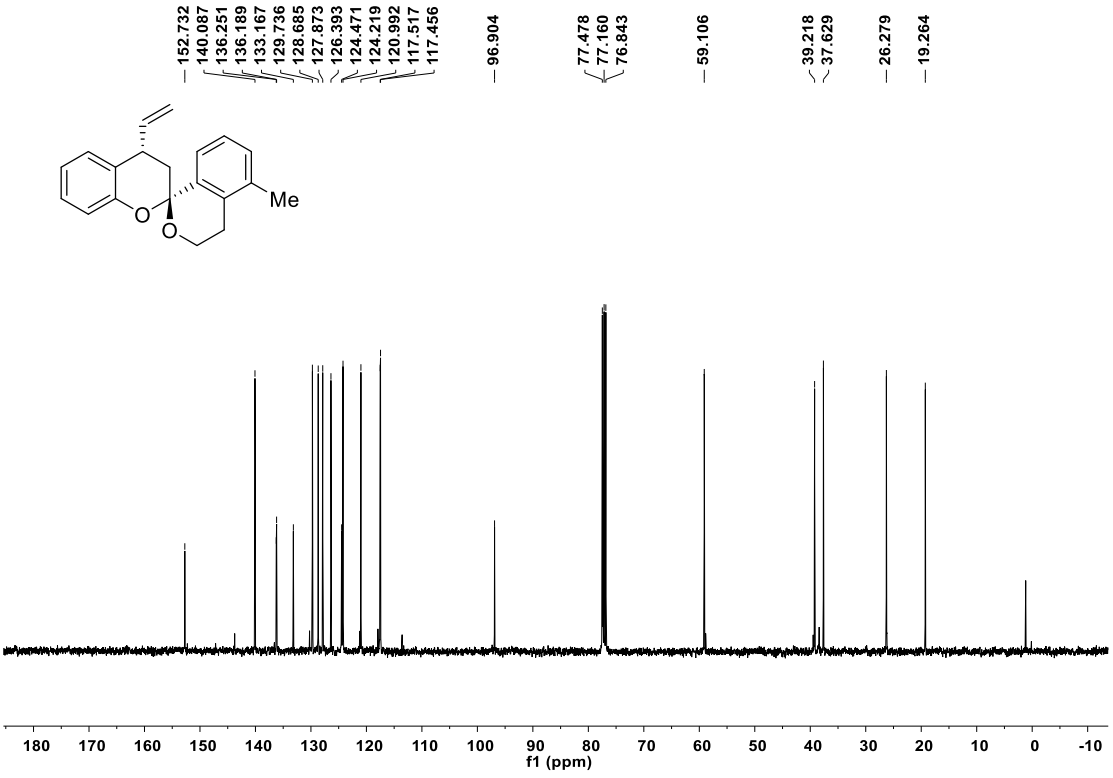
^{13}C NMR spectrum of product **3p** (100 MHz, $CDCl_3$, 11:1 dr)



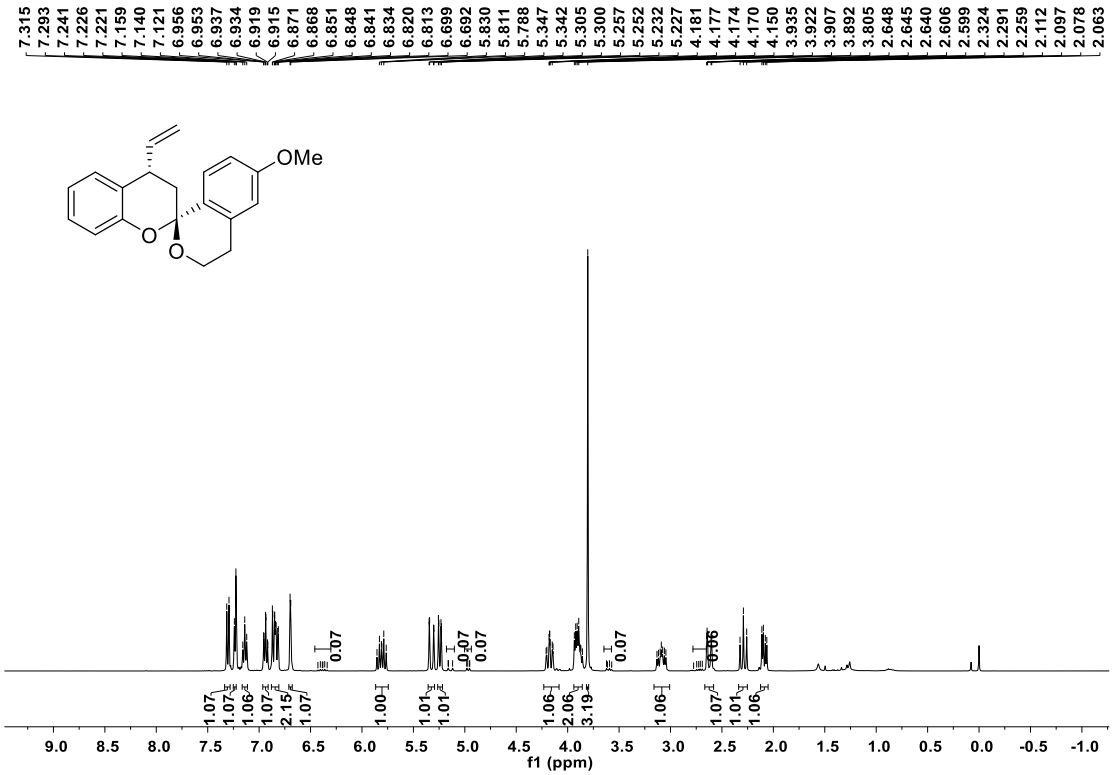
^{1}H NMR spectrum of product **3q** (400 MHz, $CDCl_3$, 17:1 dr)



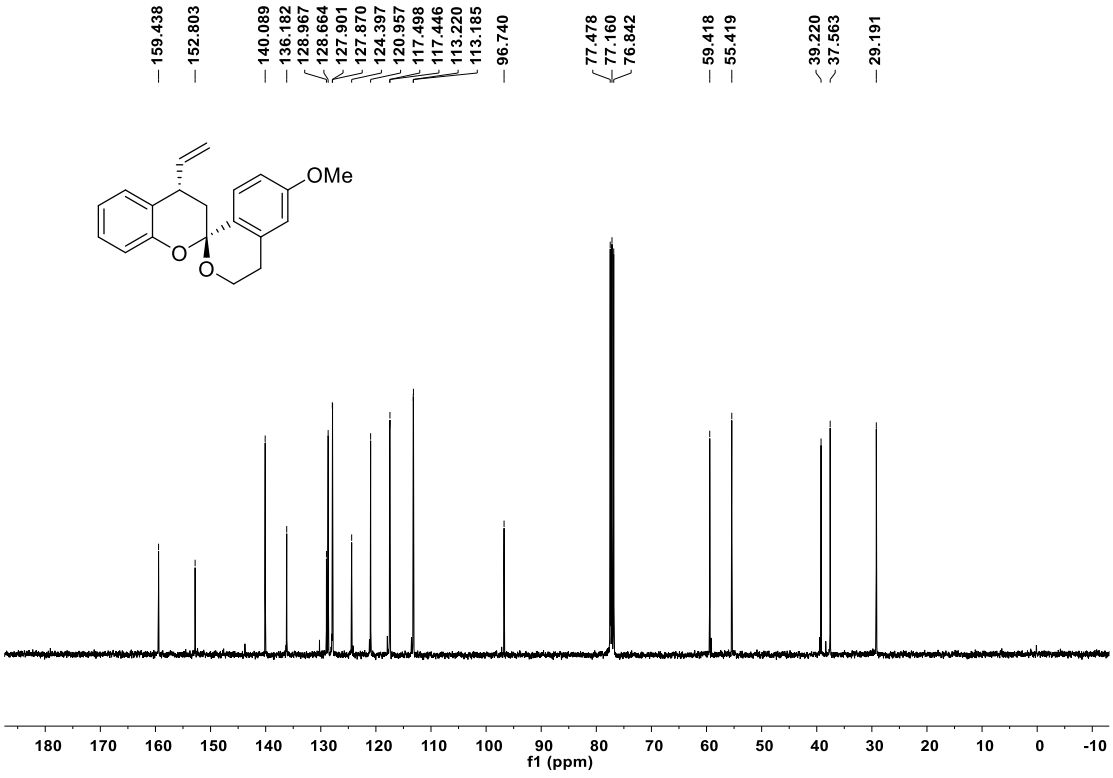
^{13}C NMR spectrum of product **3q** (100 MHz, $CDCl_3$, 17:1 dr)



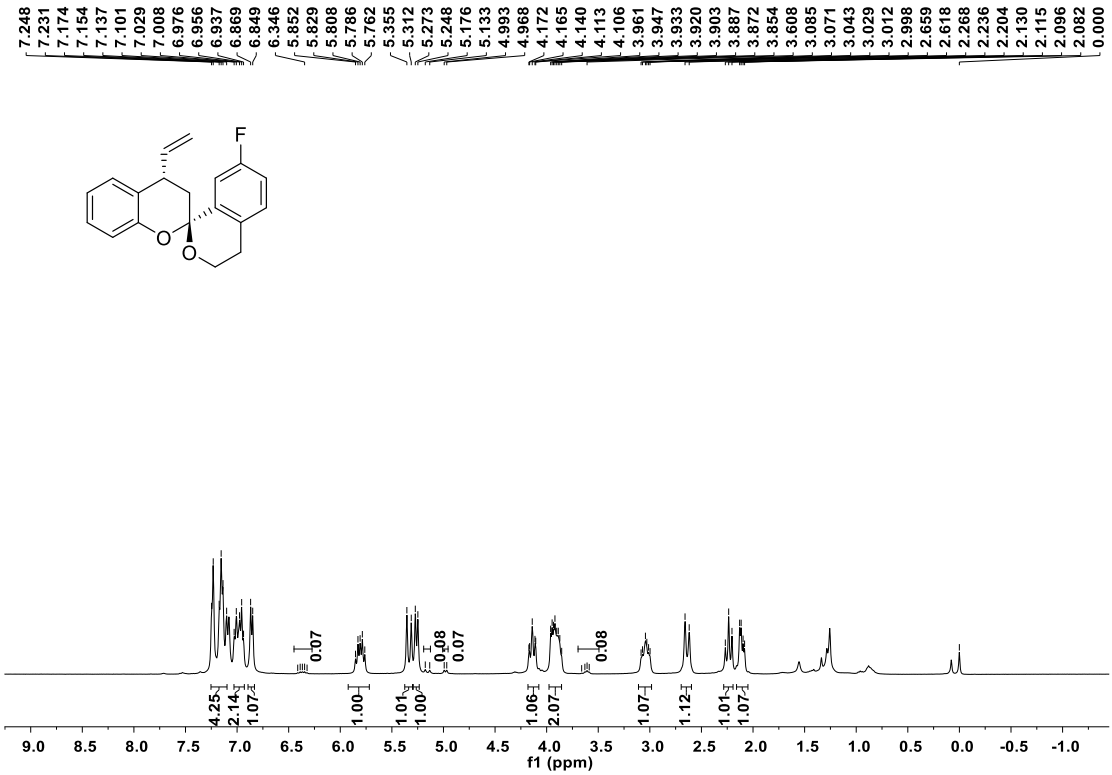
^{1}H NMR spectrum of product **3r** (400 MHz, $CDCl_3$, 15:1 dr)



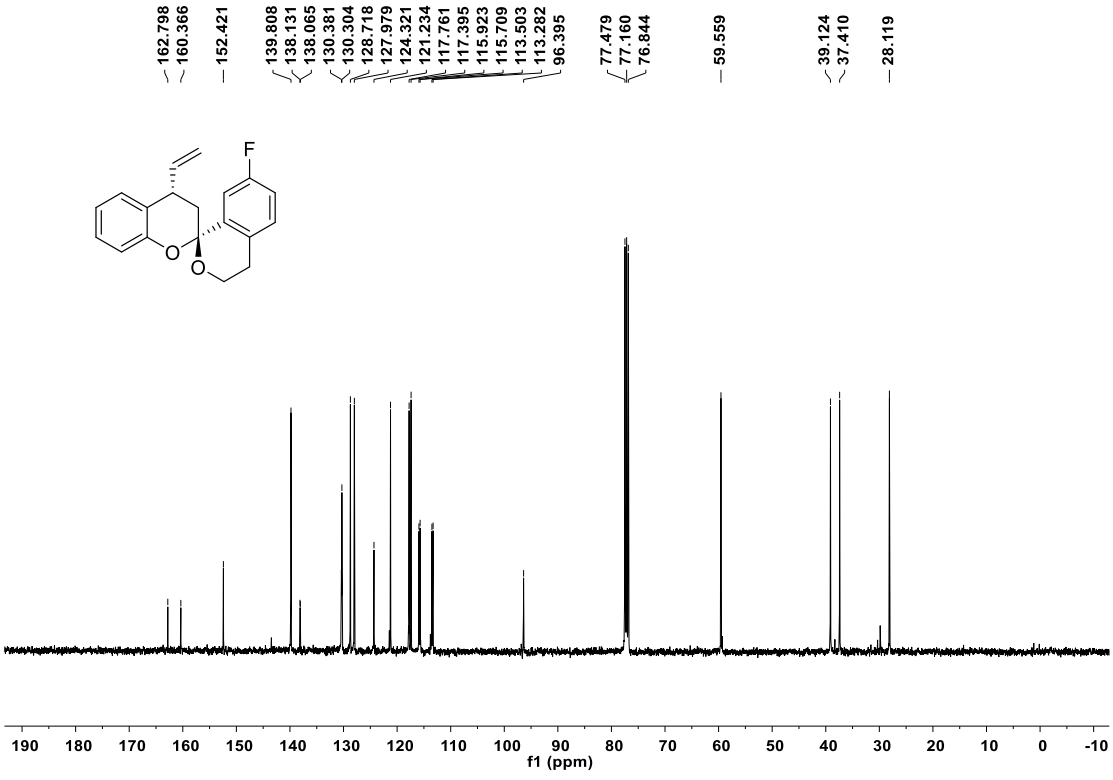
^{13}C NMR spectrum of product **3r** (100 MHz, $CDCl_3$, 15:1 dr)



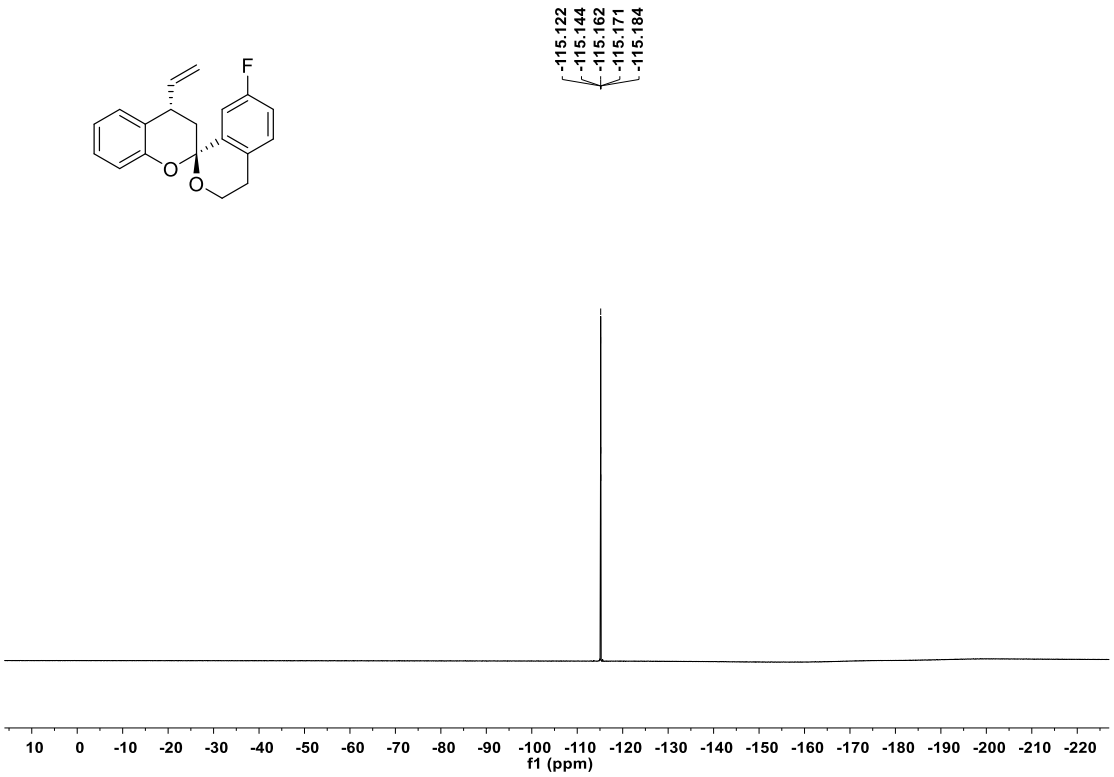
^{1}H NMR spectrum of product **3s** (400 MHz, $CDCl_3$, 13:1 dr)



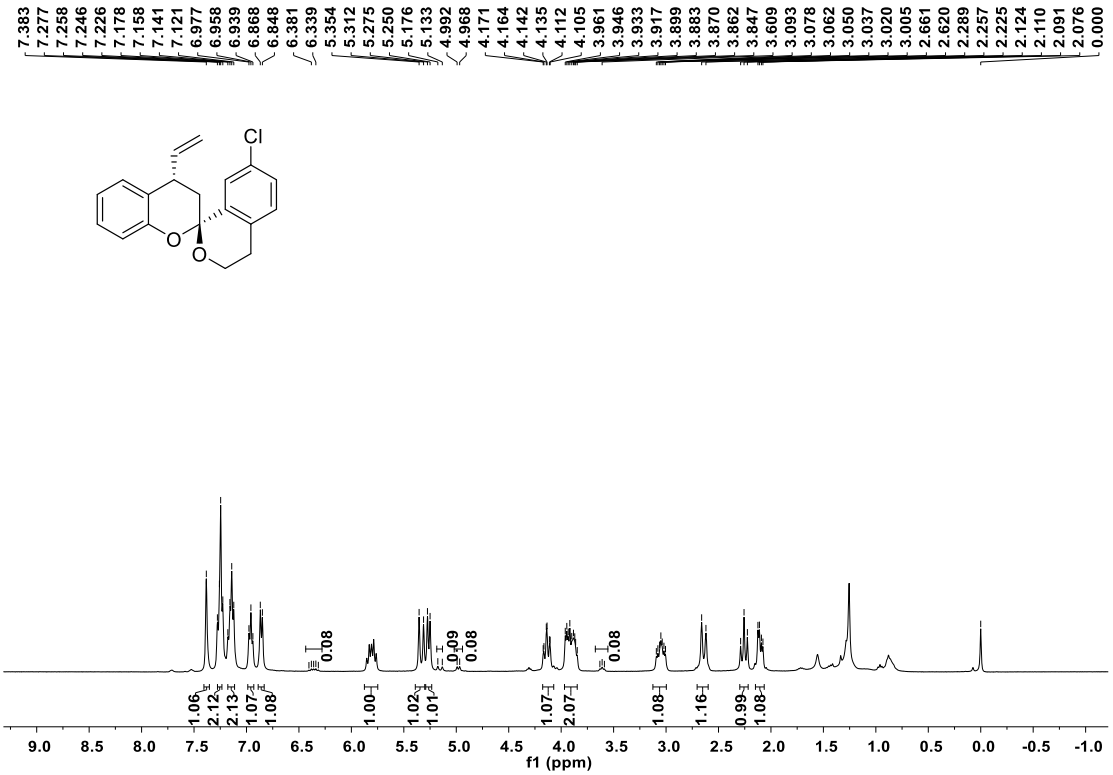
^{13}C NMR spectrum of product **3s** (100 MHz, $CDCl_3$, 13:1 dr)



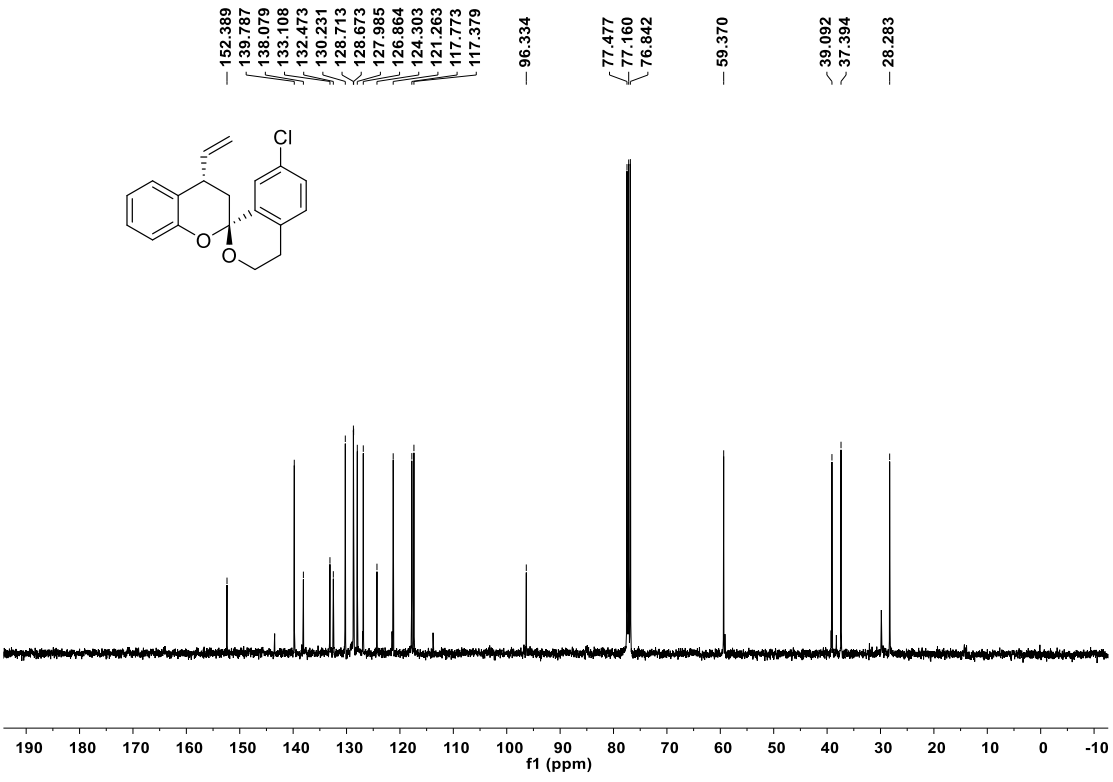
^{19}F NMR spectrum of product **3s** (376 MHz, $CDCl_3$, 13:1 dr)



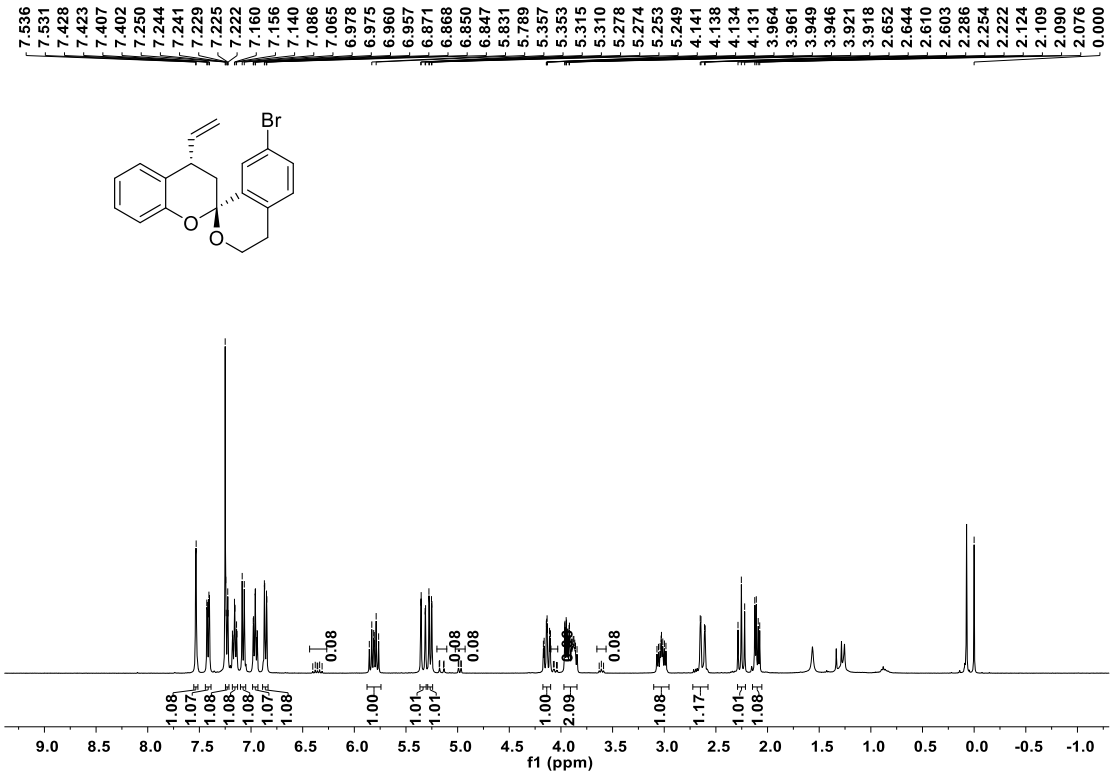
^{1}H NMR spectrum of product **3t** (400 MHz, $CDCl_3$, 12:1 dr)



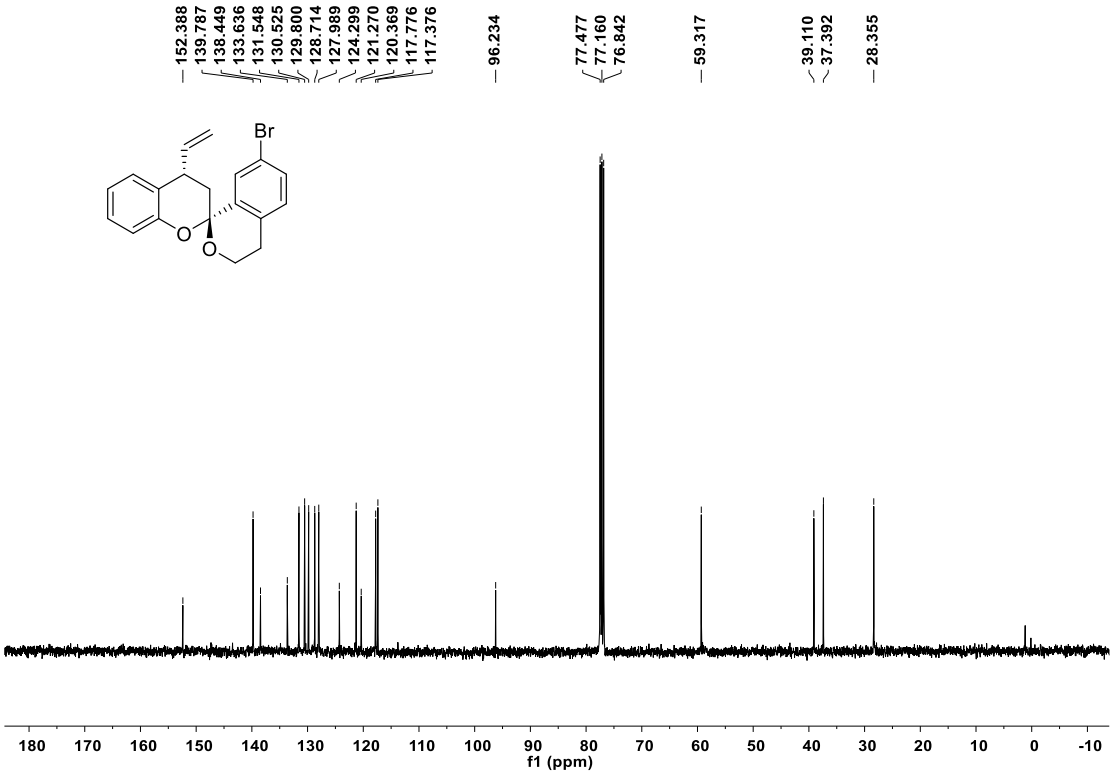
^{13}C NMR spectrum of product **3t** (100 MHz, $CDCl_3$, 12:1 dr)



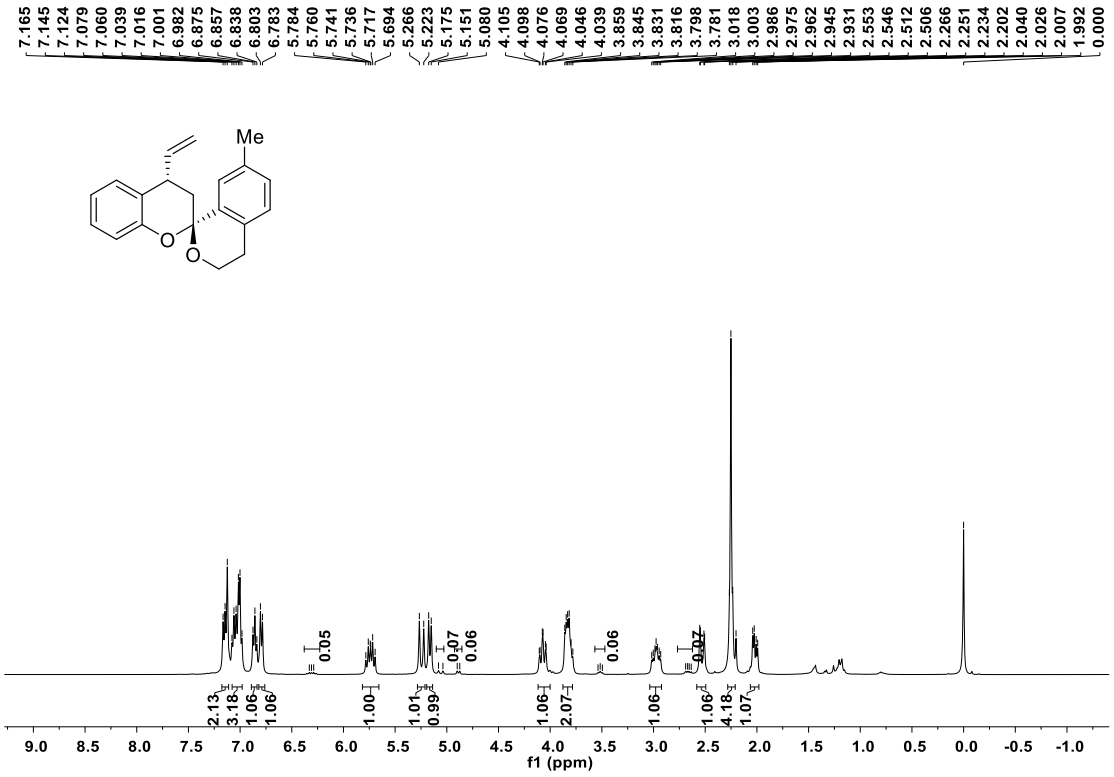
^{1}H NMR spectrum of product **3u** (400 MHz, $CDCl_3$, 12:1 dr)



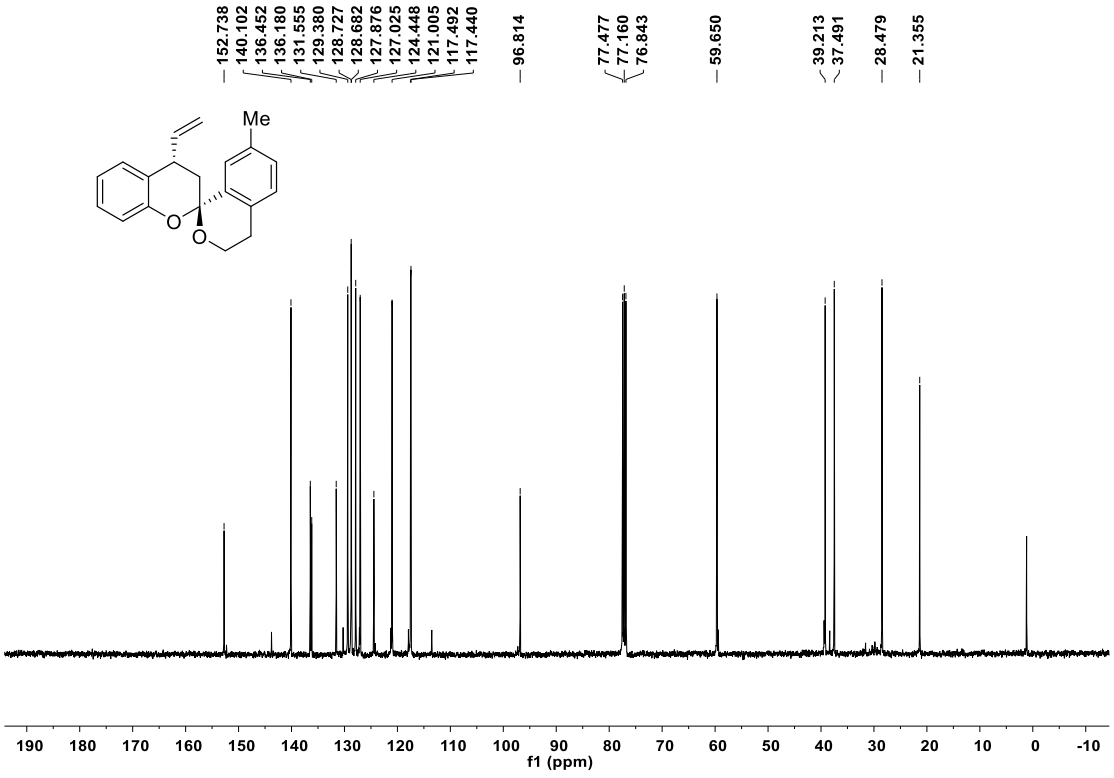
^{13}C NMR spectrum of product **3u** (100 MHz, $CDCl_3$, 12:1 dr)



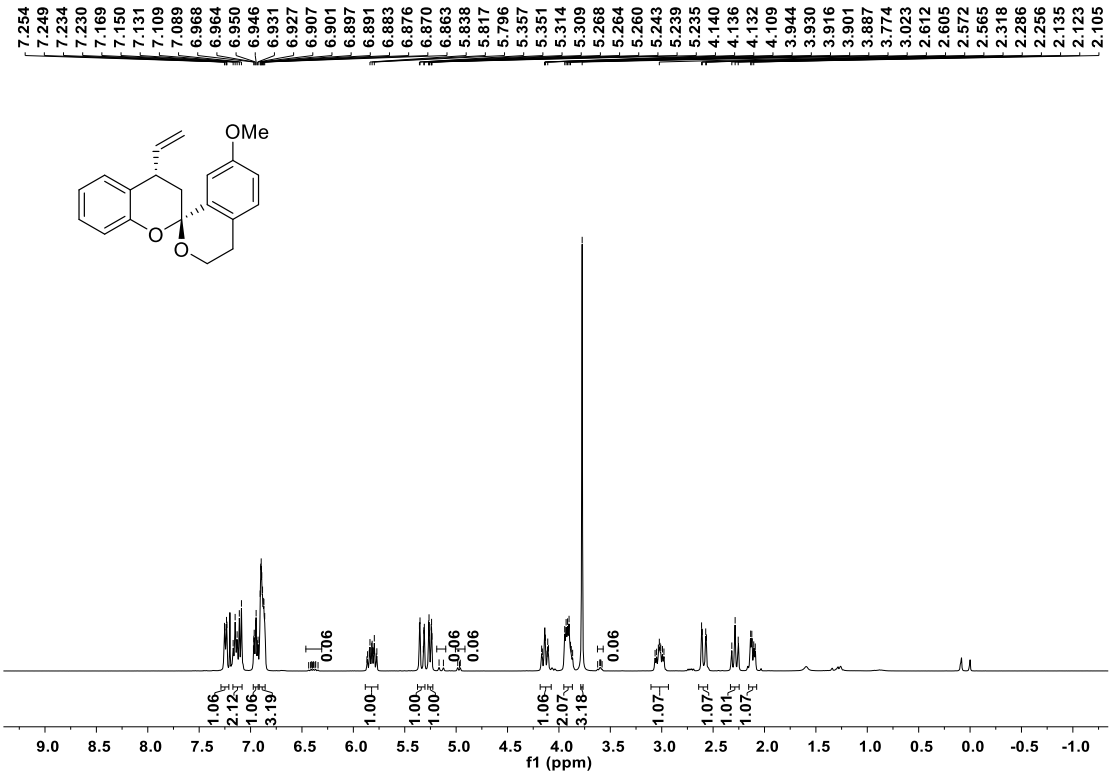
^{1}H NMR spectrum of product **3v** (400 MHz, $CDCl_3$, 16:1 dr)



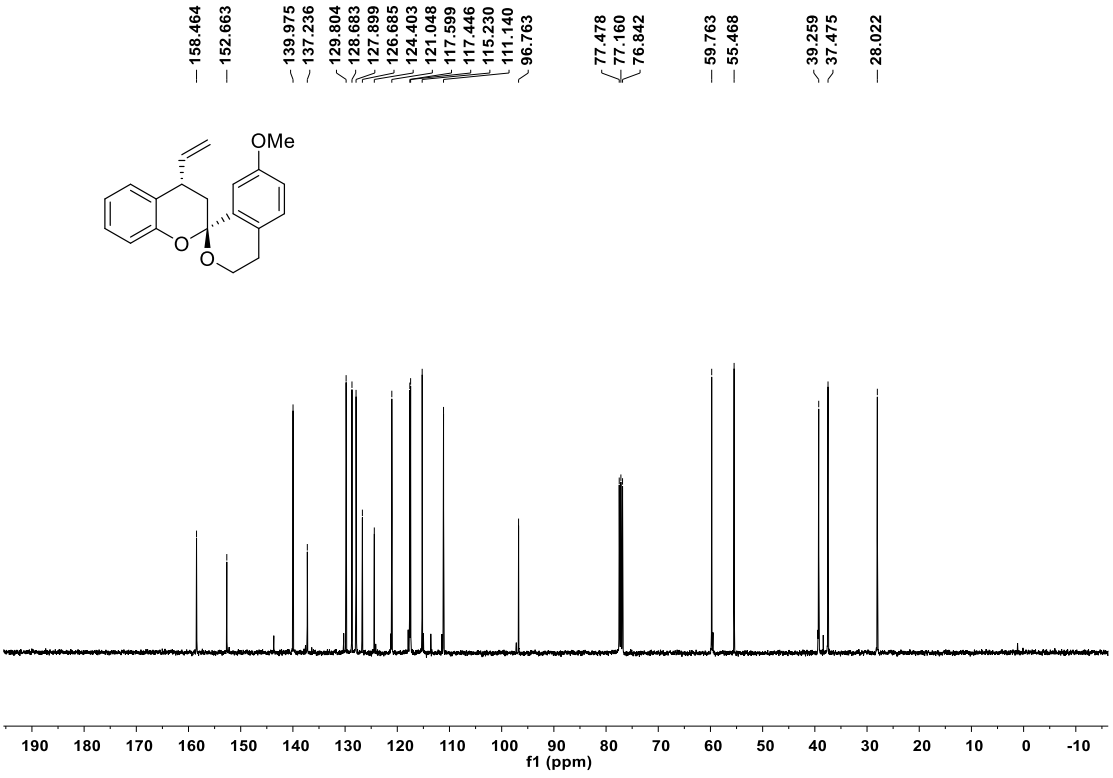
^{13}C NMR spectrum of product **3v** (100 MHz, $CDCl_3$, 16:1 dr)



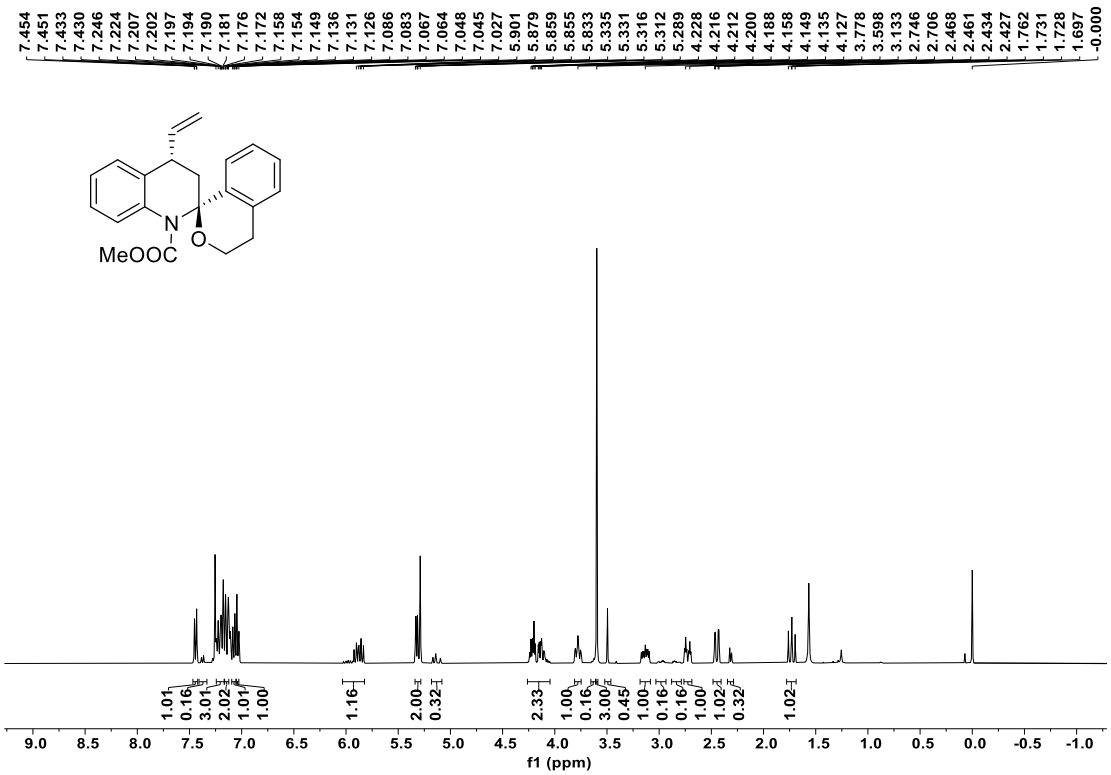
^{1}H NMR spectrum of product **3w** (400 MHz, $CDCl_3$, 16:1 dr)



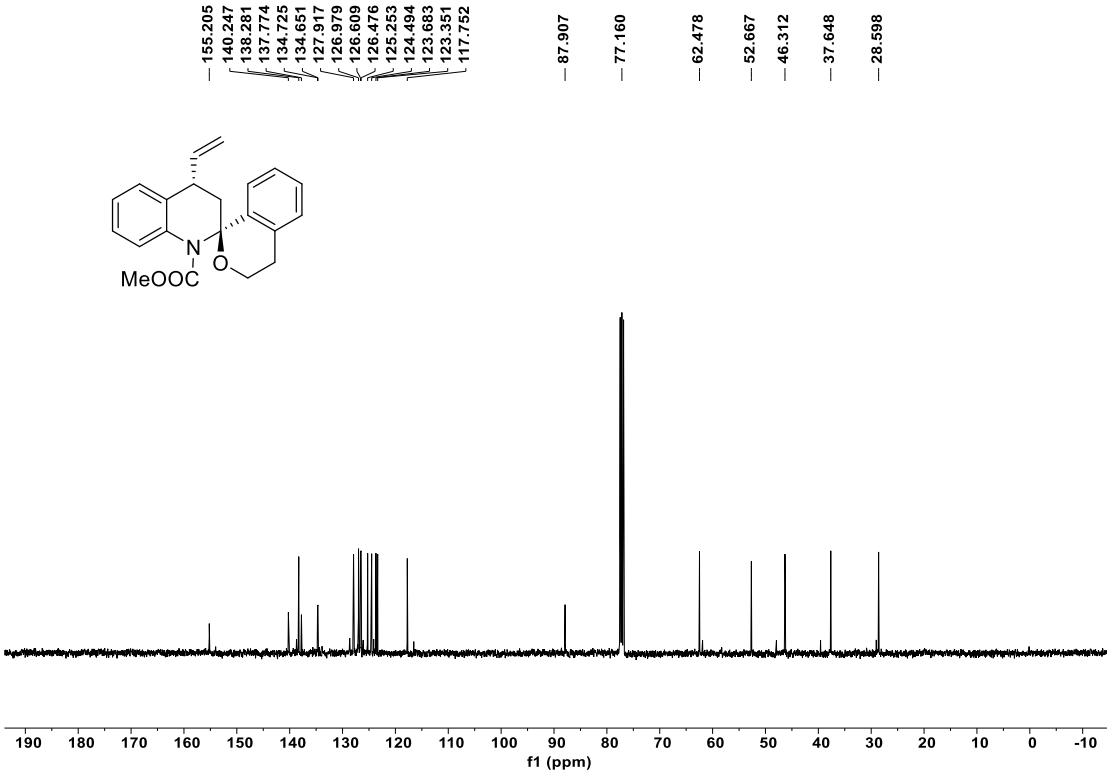
^{13}C NMR spectrum of product **3w** (100 MHz, $CDCl_3$, 16:1 dr)



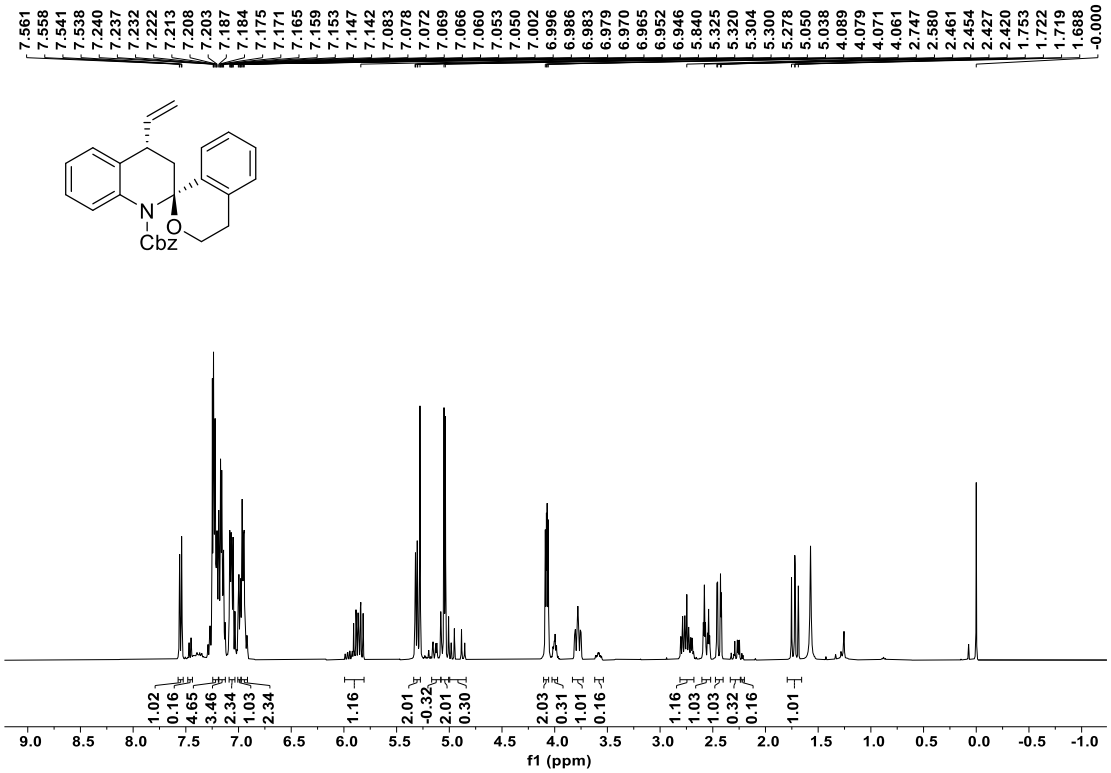
^{1}H NMR spectrum of product **5a** (400 MHz, $CDCl_3$, 6:1 dr)



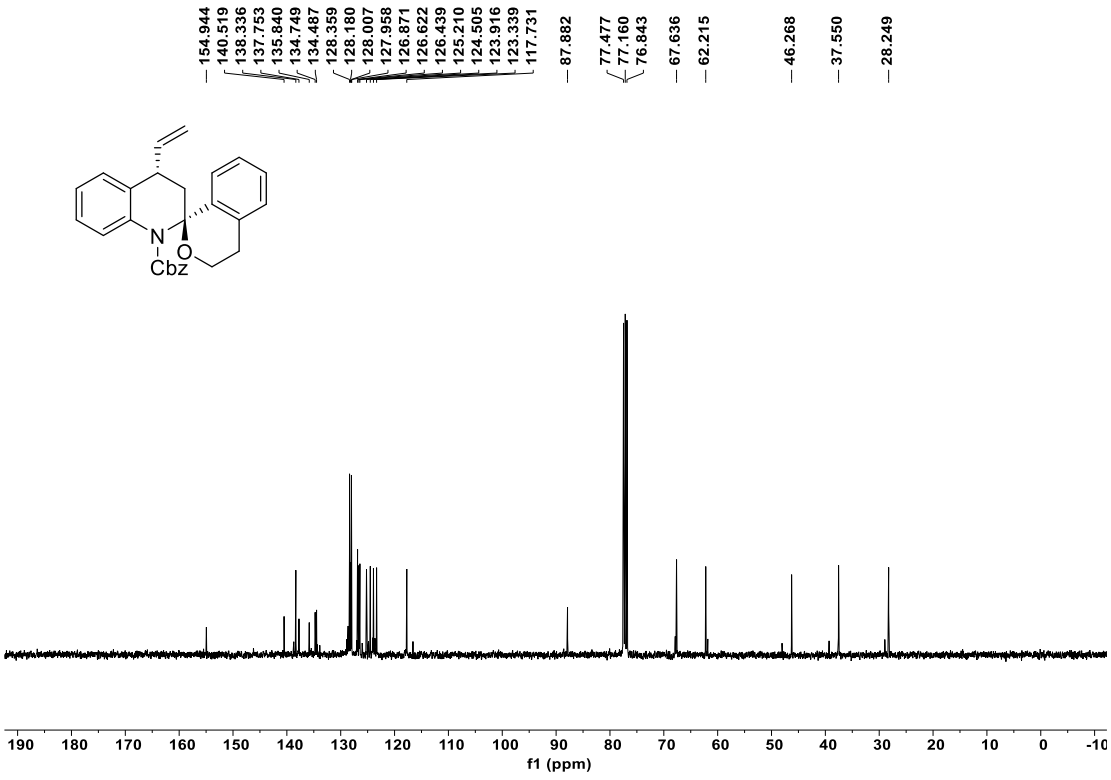
^{13}C NMR spectrum of product **5a** (100 MHz, $CDCl_3$, 6:1 dr)



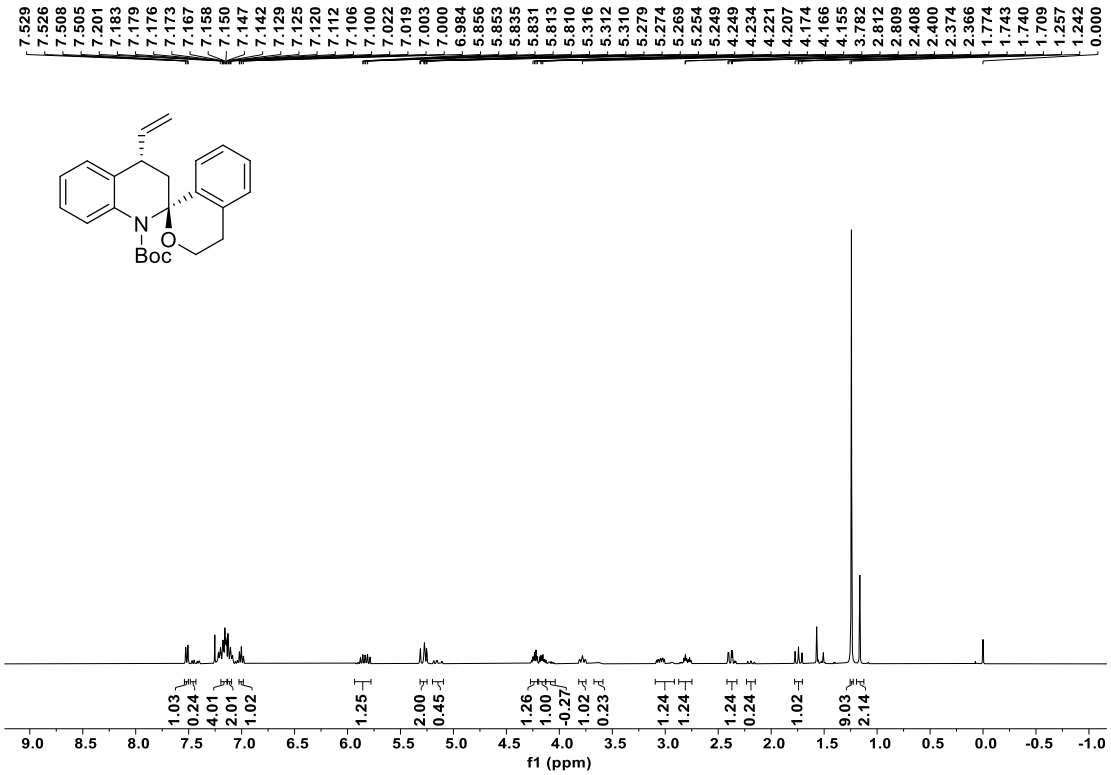
^{1}H NMR spectrum of product **5b** (400 MHz, $CDCl_3$, 6:1 dr)



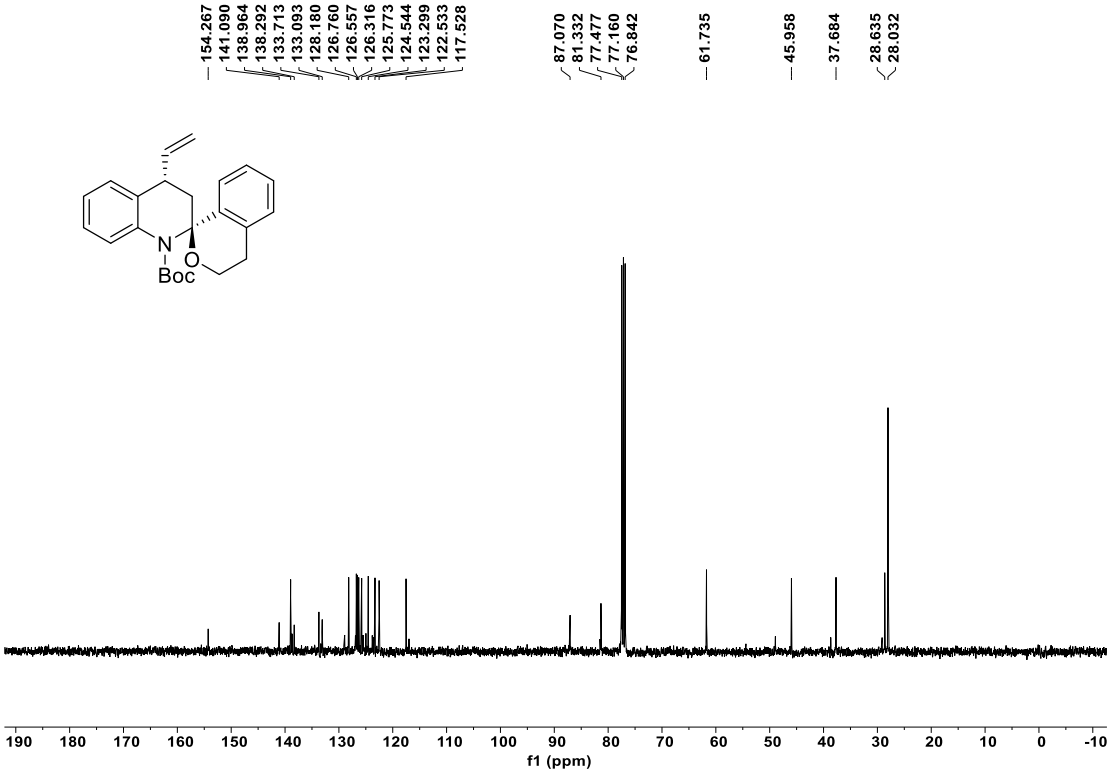
^{13}C NMR spectrum of product **5b** (100 MHz, $CDCl_3$, 6:1 dr)



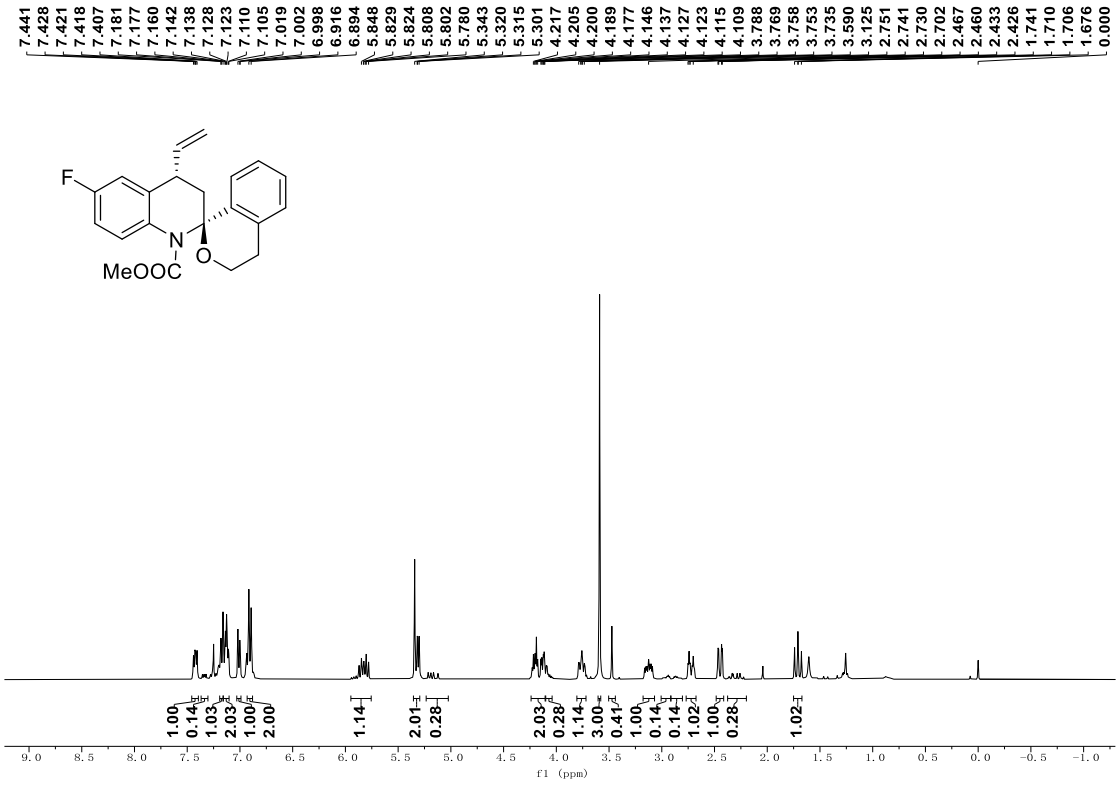
^{1}H NMR spectrum of product **5c** (400 MHz, $CDCl_3$, 4:1 dr)



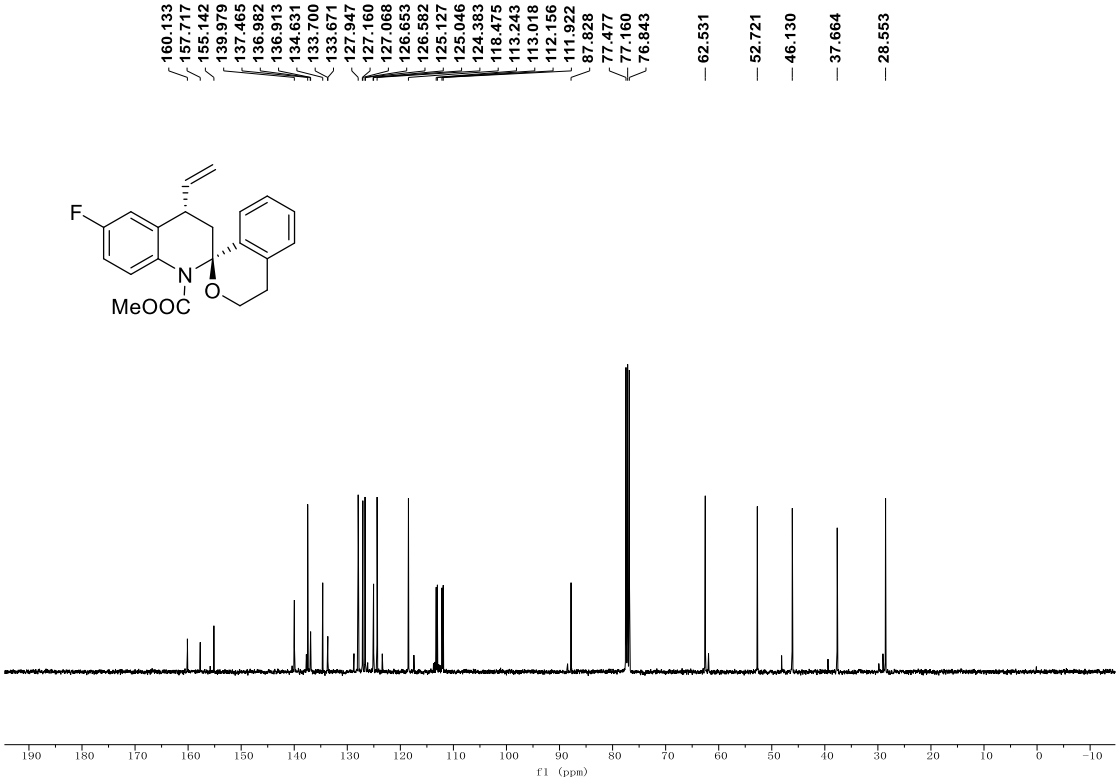
^{13}C NMR spectrum of product **5c** (100 MHz, $CDCl_3$, 4:1 dr)



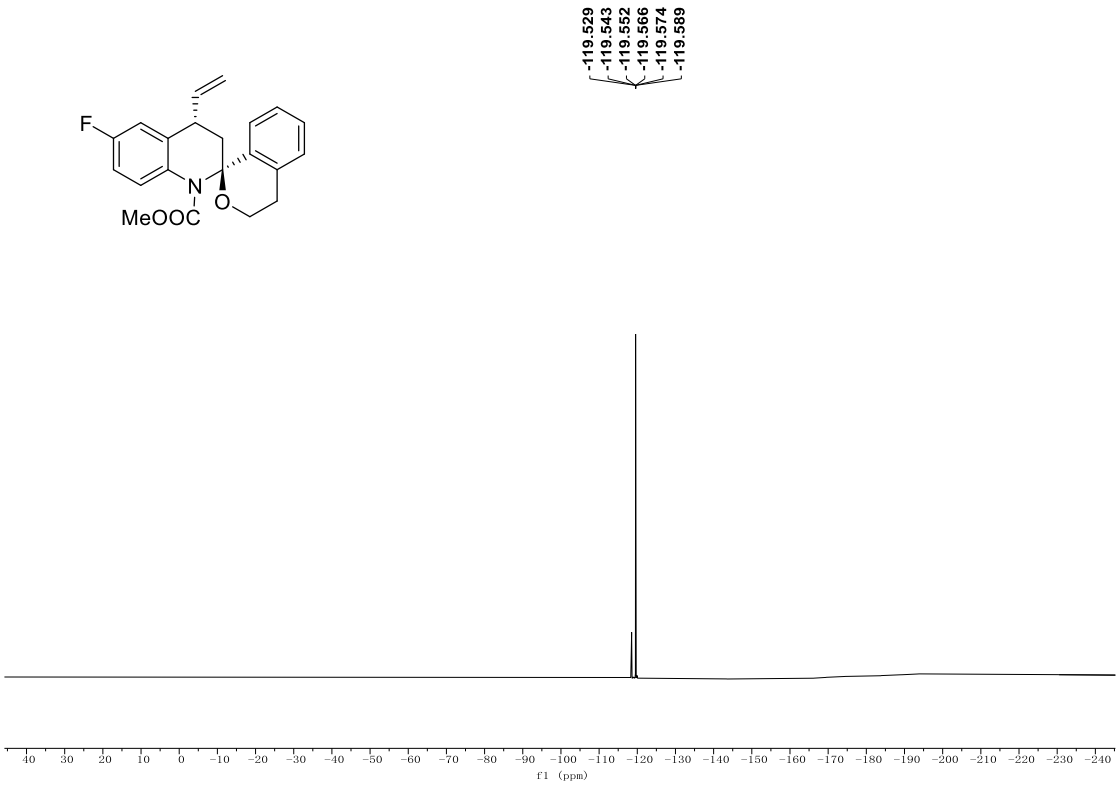
^{1}H NMR spectrum of product **5d** (400 MHz, $CDCl_3$, 7:1 dr)



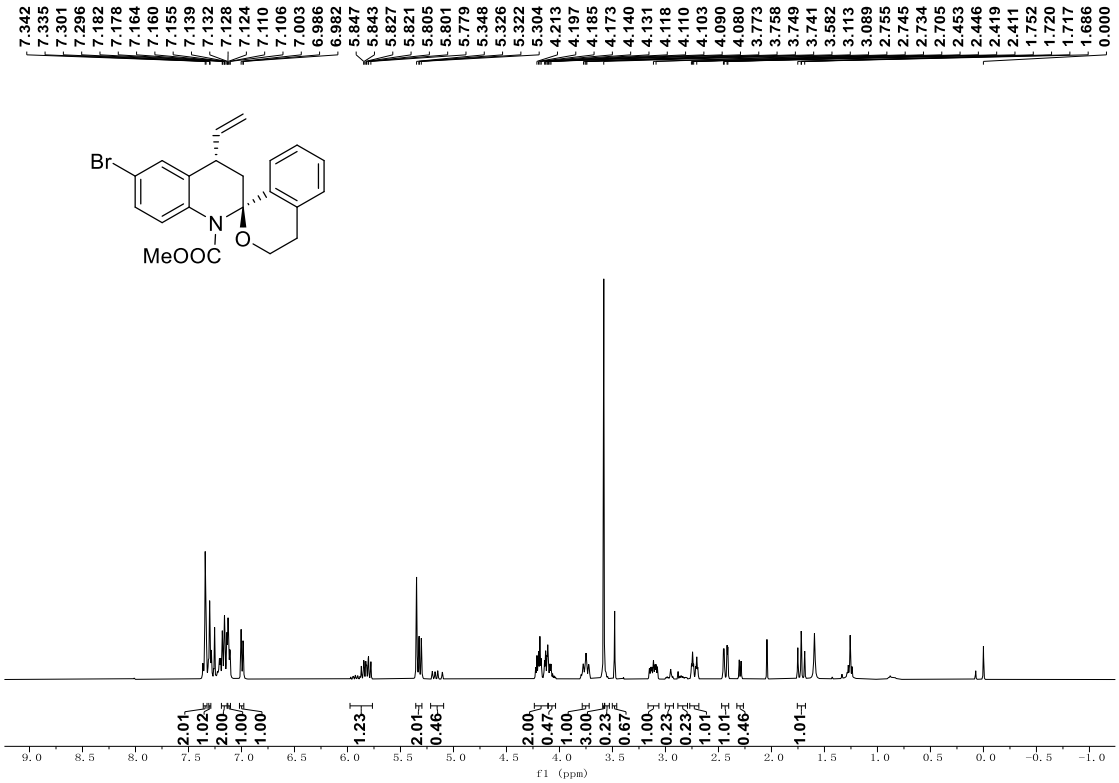
^{13}C NMR spectrum of product **5d** (100 MHz, $CDCl_3$, 7:1 dr)



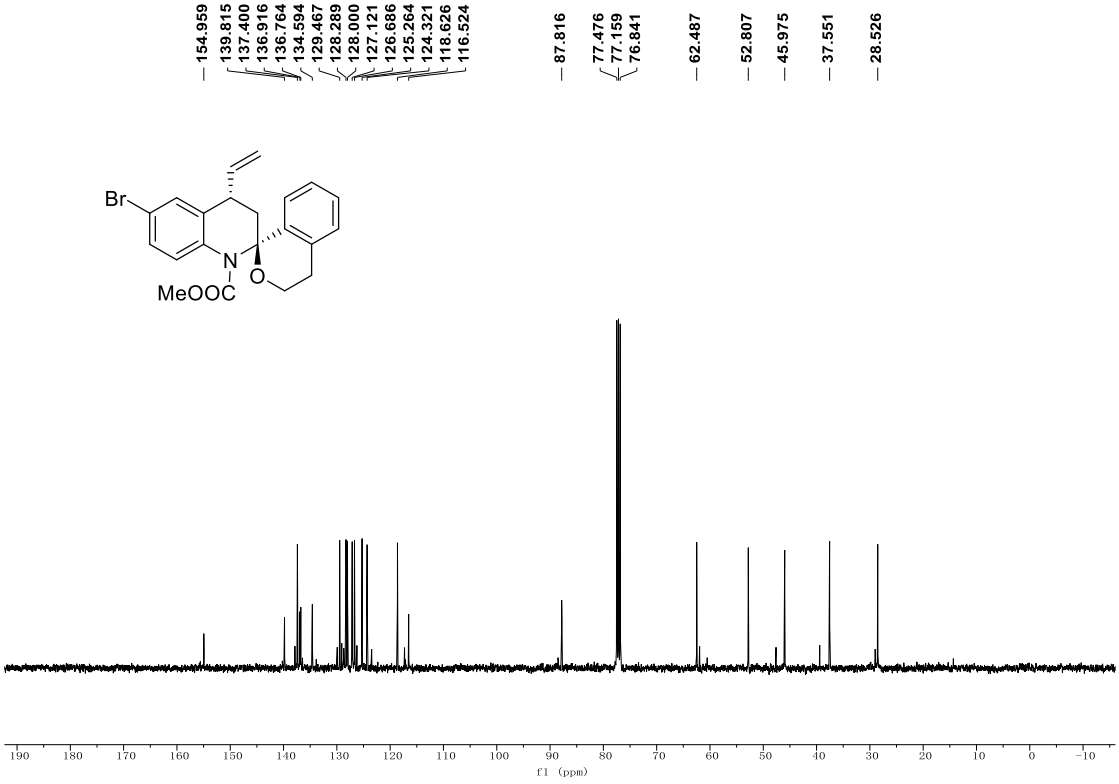
^{19}F NMR spectrum of product **5d** (376 MHz, $CDCl_3$, 7:1 dr)



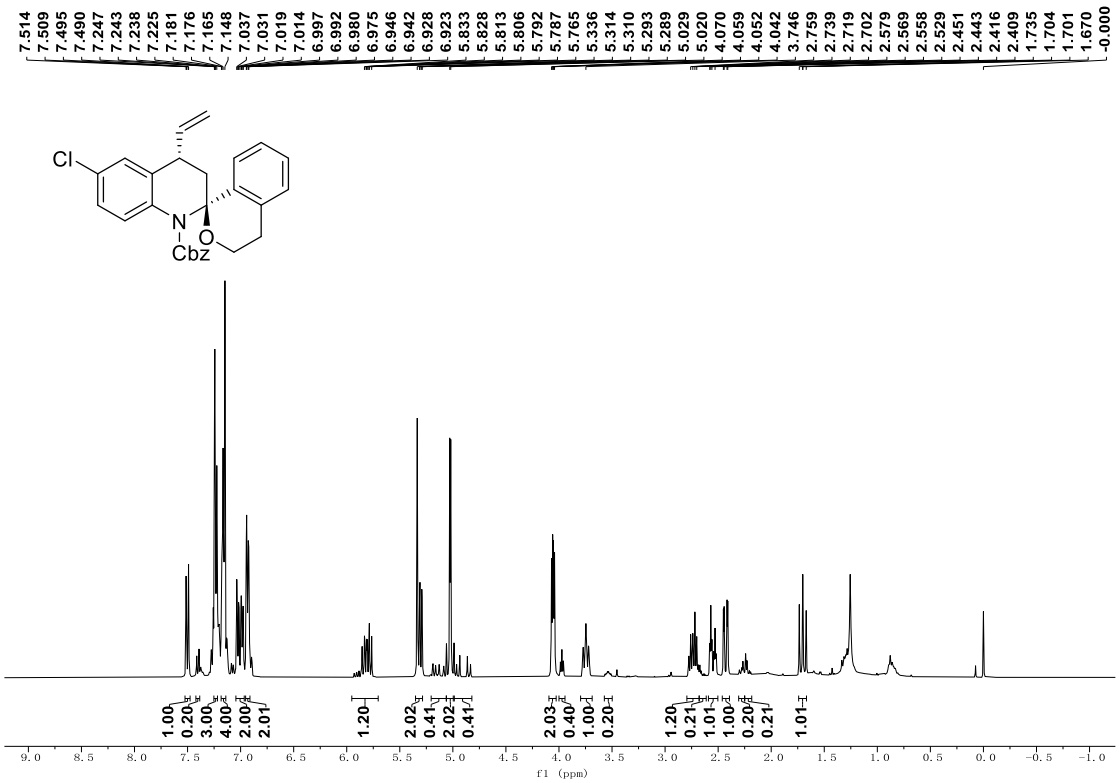
^{1}H NMR spectrum of product **5e** (400 MHz, $CDCl_3$, 4:1 dr)



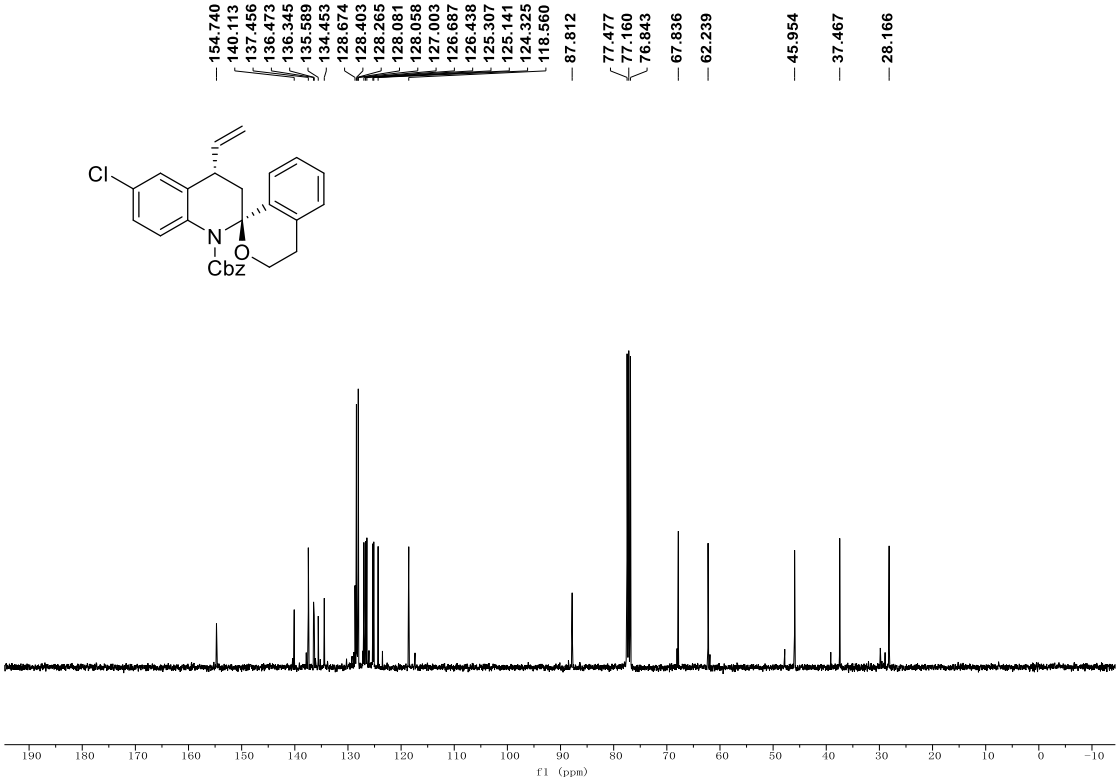
^{13}C NMR spectrum of product **5e** (100 MHz, $CDCl_3$, 5:1 dr)



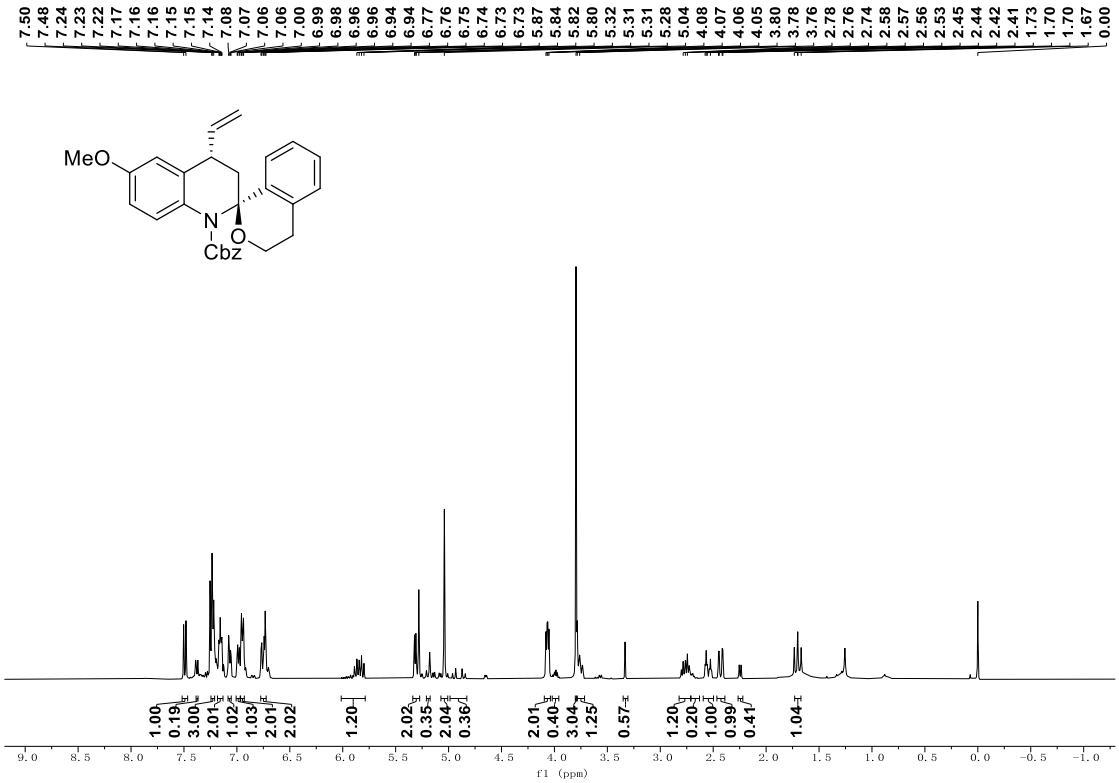
^{1}H NMR spectrum of product **5f** (400 MHz, $CDCl_3$, 5:1 dr)



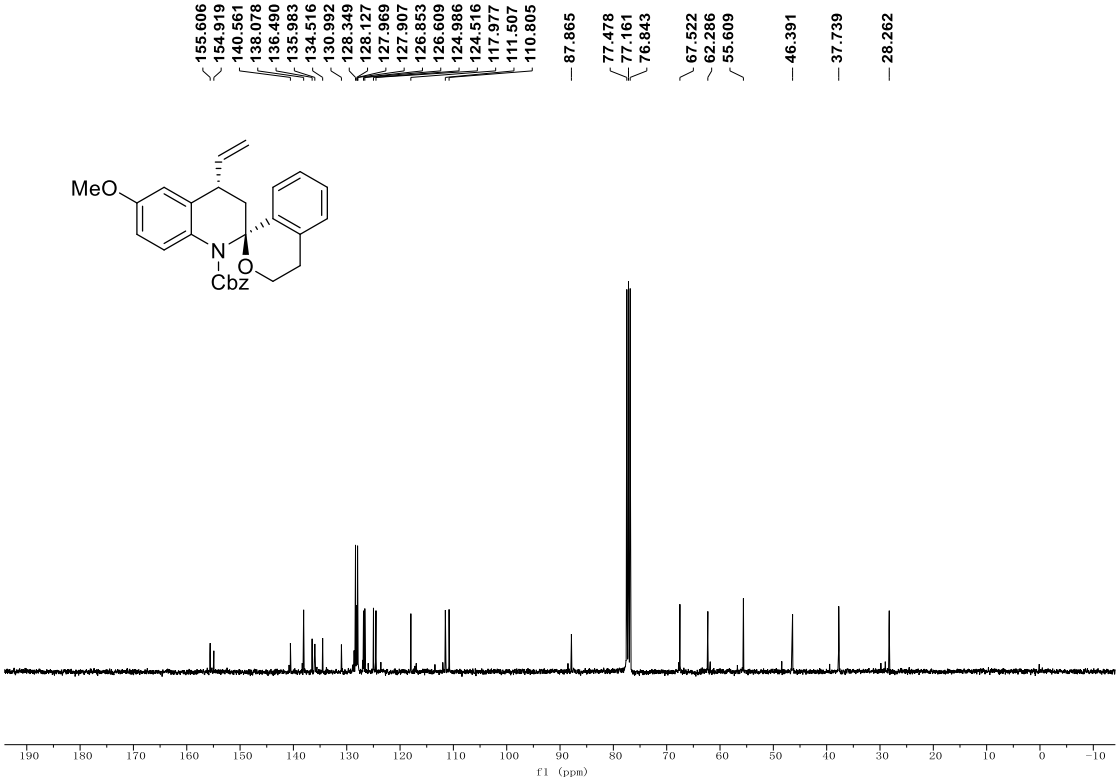
^{13}C NMR spectrum of product **5f** (100 MHz, $CDCl_3$, 5:1 dr)



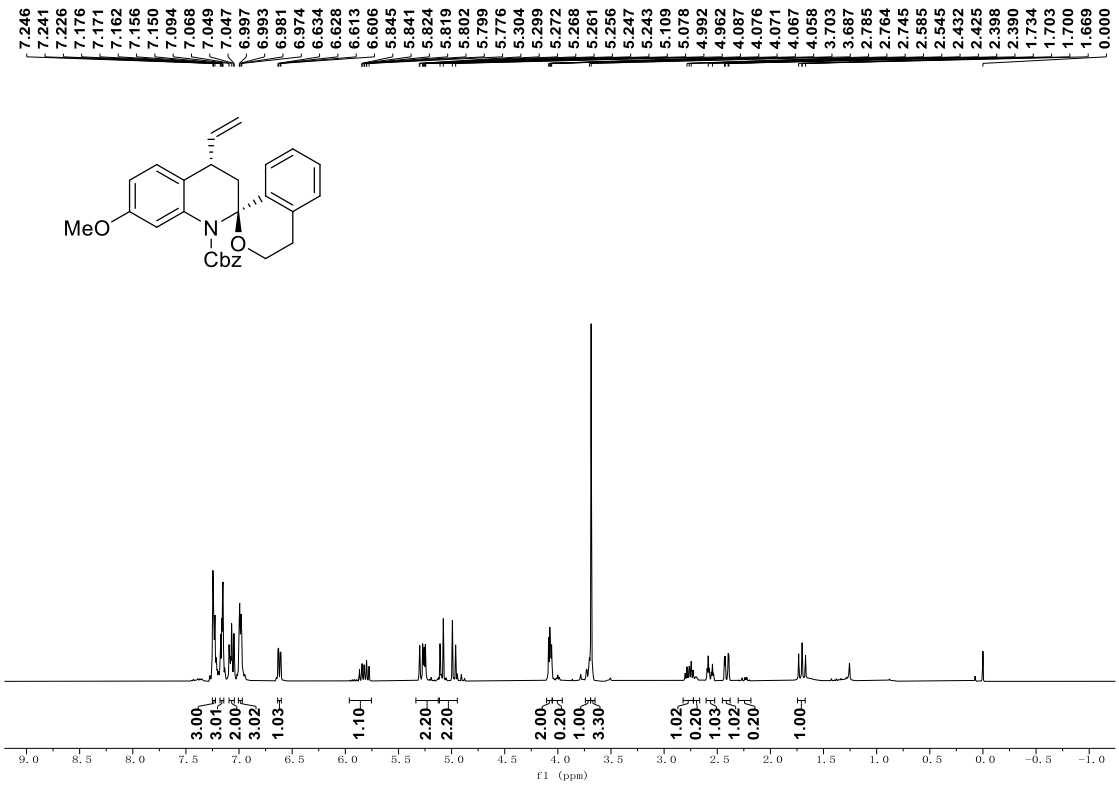
^{1}H NMR spectrum of product **5g** (400 MHz, $CDCl_3$, 5:1 dr)



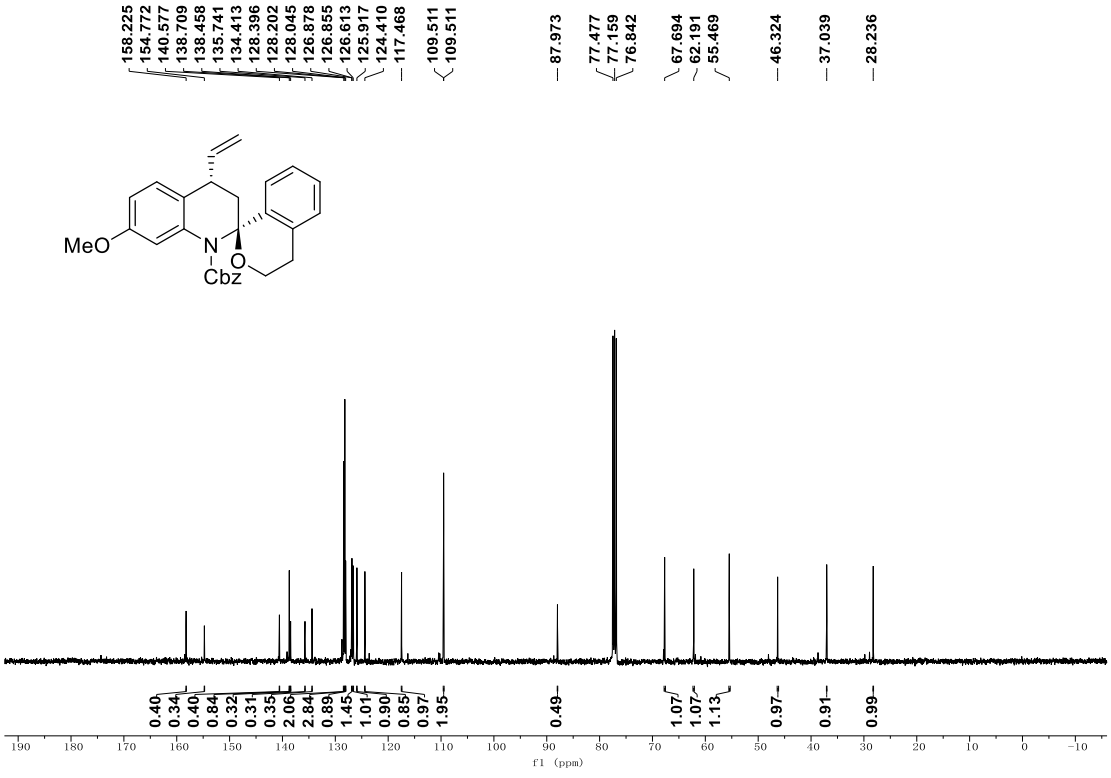
^{13}C NMR spectrum of product **5g** (100 MHz, $CDCl_3$, 5:1 dr)



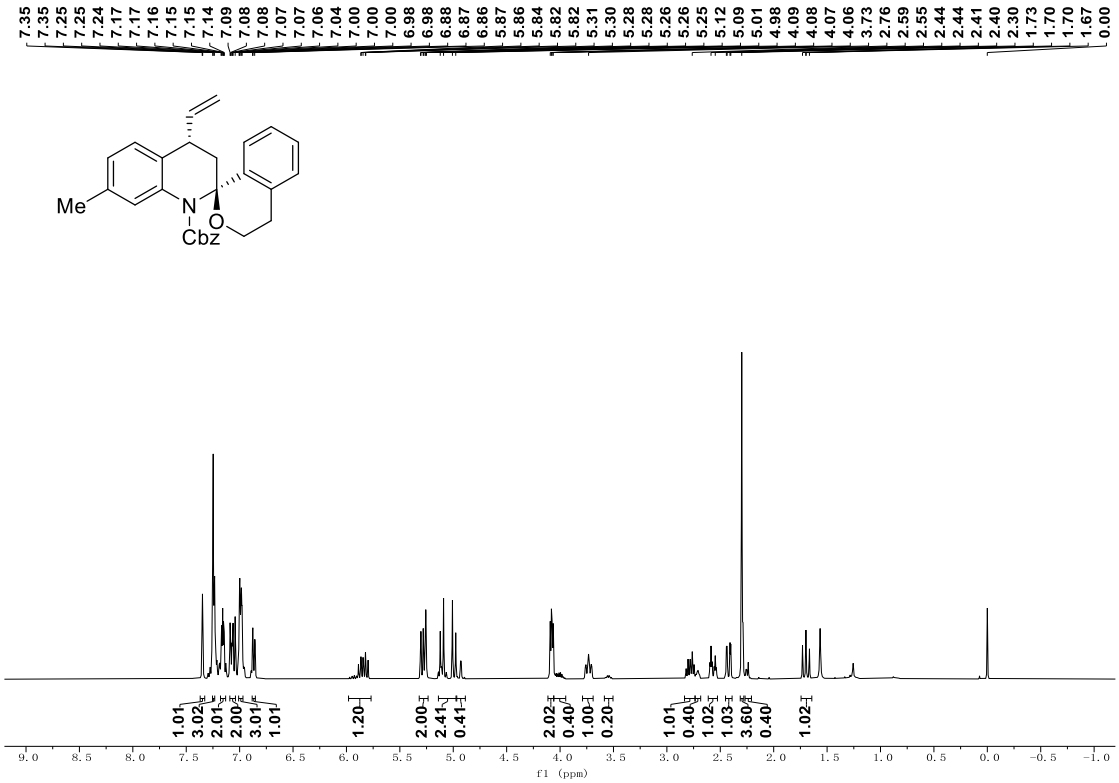
^{1}H NMR spectrum of product **5h** (400 MHz, $CDCl_3$, 10:1 dr)



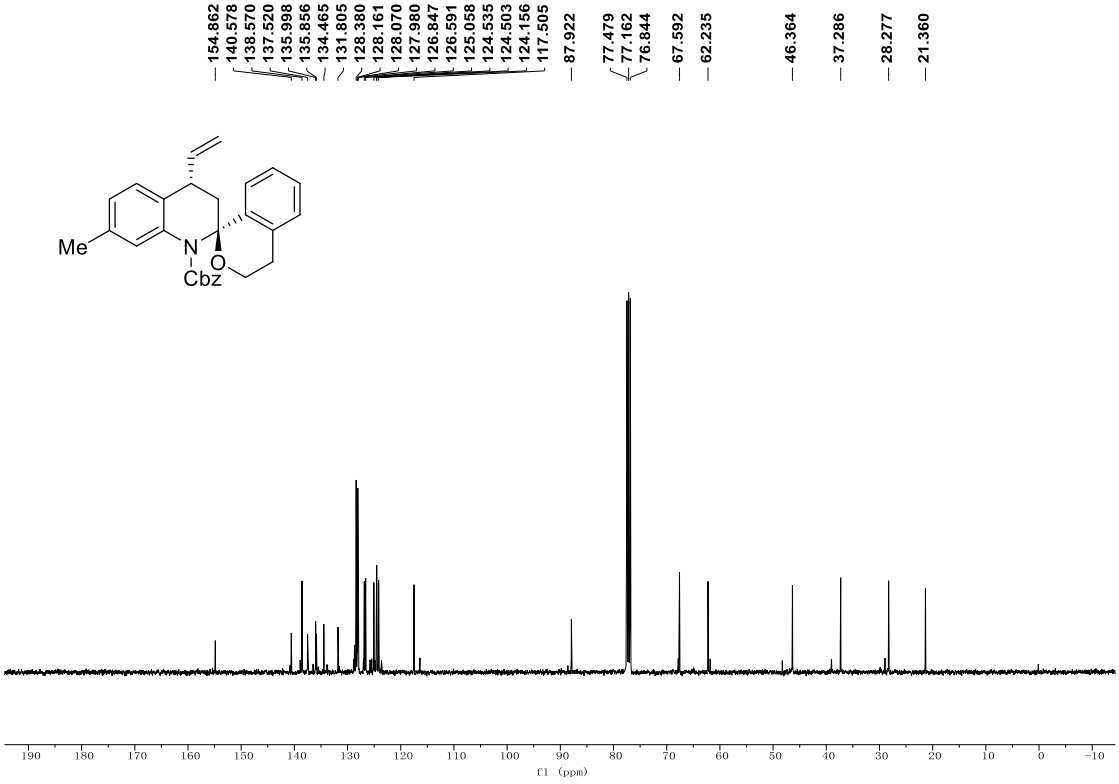
^{13}C NMR spectrum of product **5h** (100 MHz, $CDCl_3$, 10:1 dr)



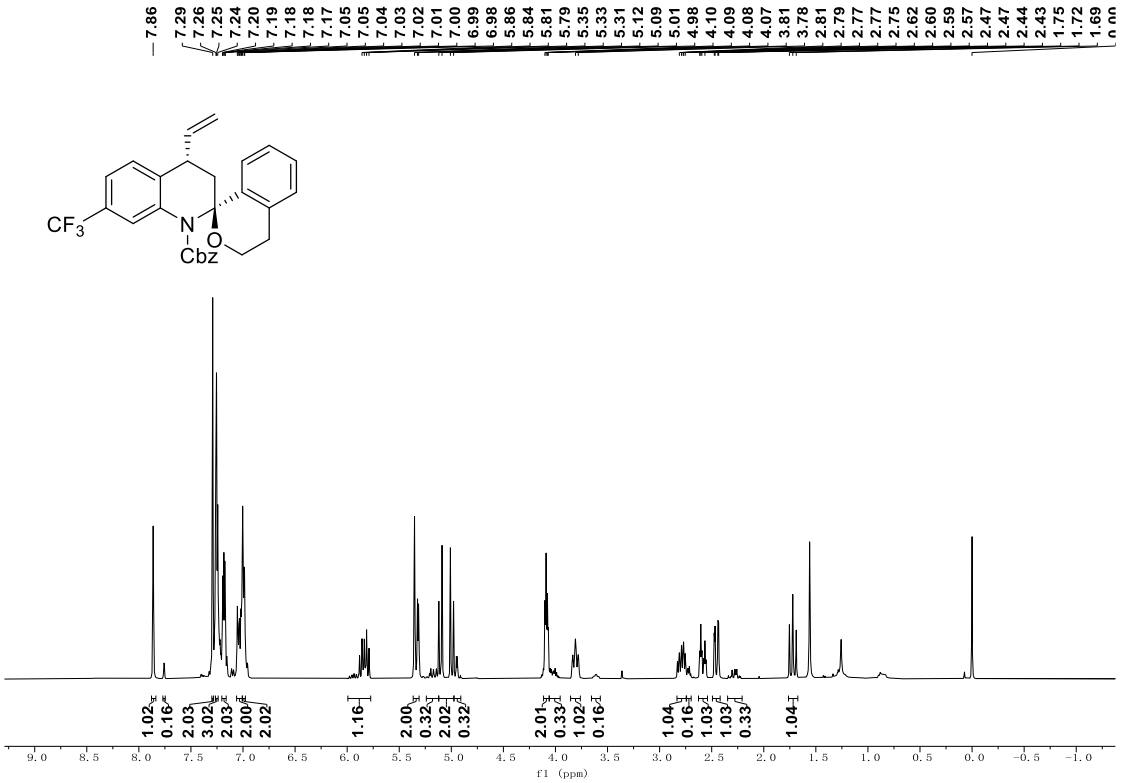
^{1}H NMR spectrum of product **5i** (400 MHz, $CDCl_3$, 5:1 dr)



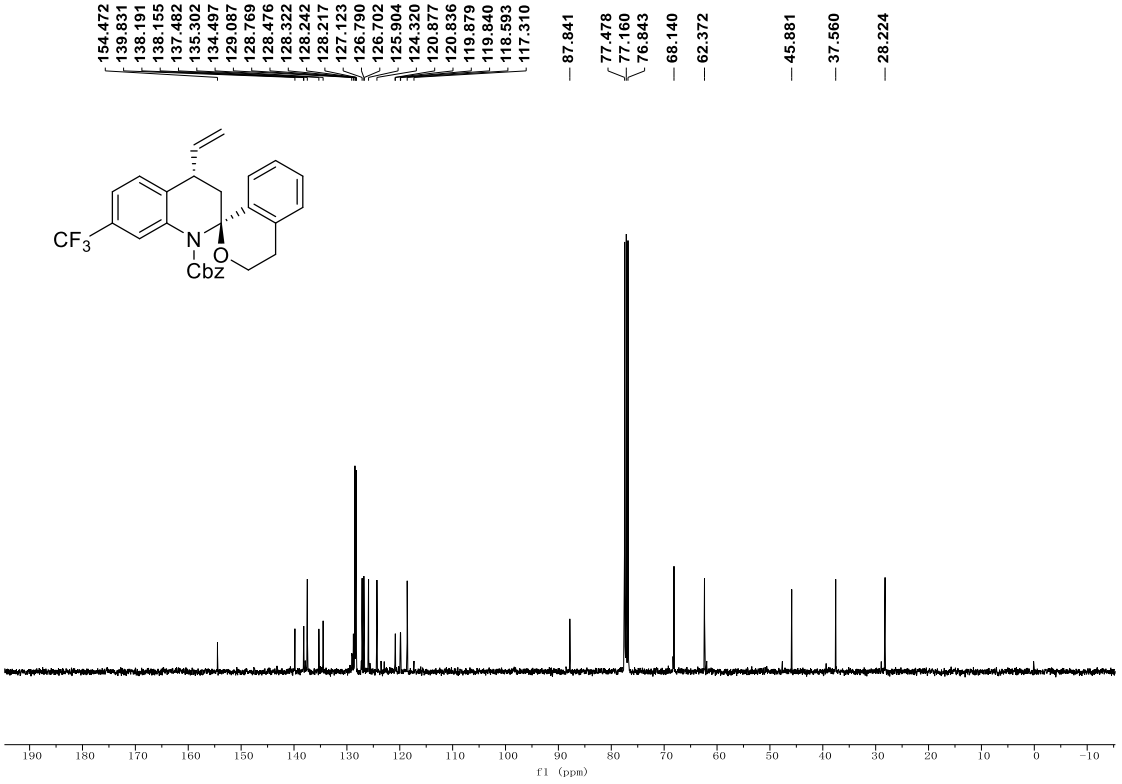
^{13}C NMR spectrum of product **5i** (100 MHz, $CDCl_3$, 5:1 dr)



^{1}H NMR spectrum of product **5j** (400 MHz, $CDCl_3$, 6:1 dr)

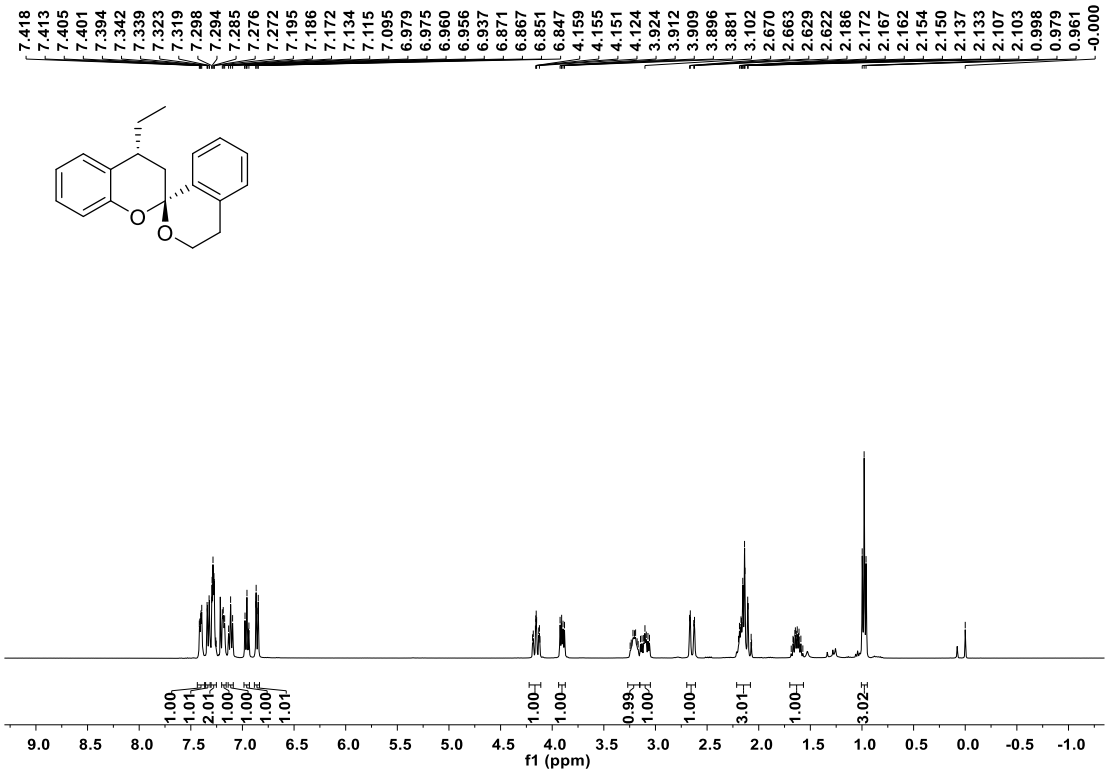


^{13}C NMR spectrum of product **5j** (100 MHz, $CDCl_3$, 6:1 dr)

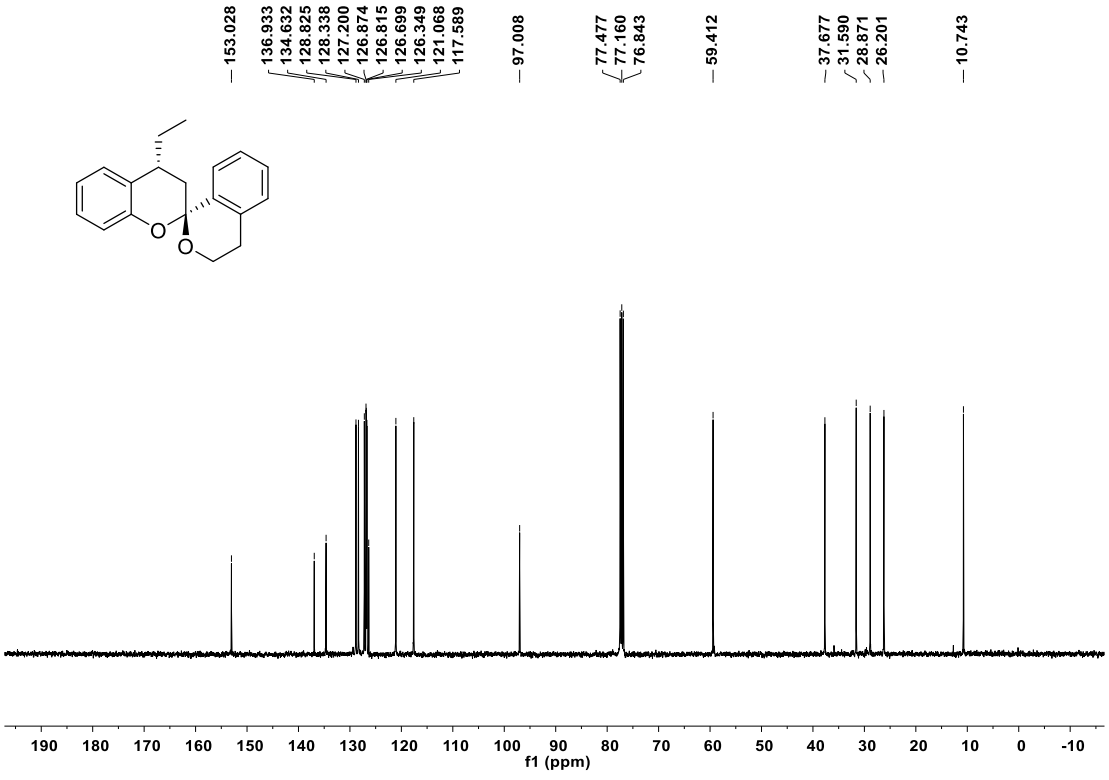


^{19}F NMR spectrum of product **5j** (376 MHz, $CDCl_3$, 6:1 dr)

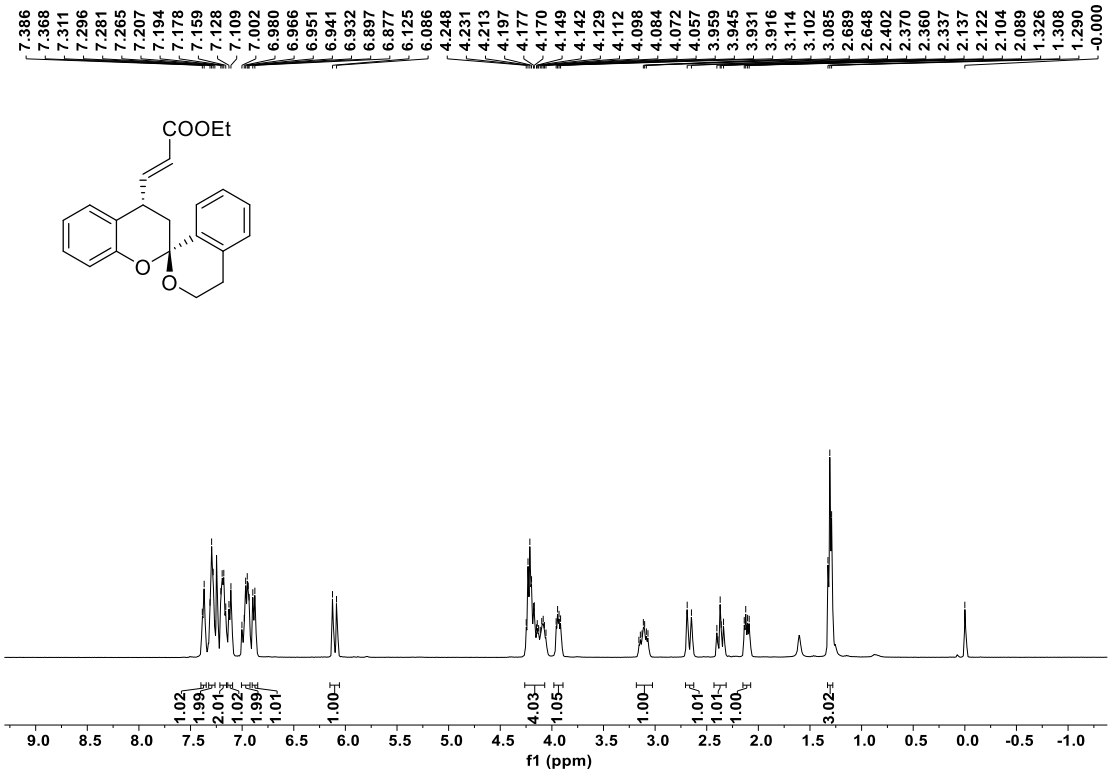
^{1}H NMR spectrum of product **6** (400 MHz, $CDCl_3$)



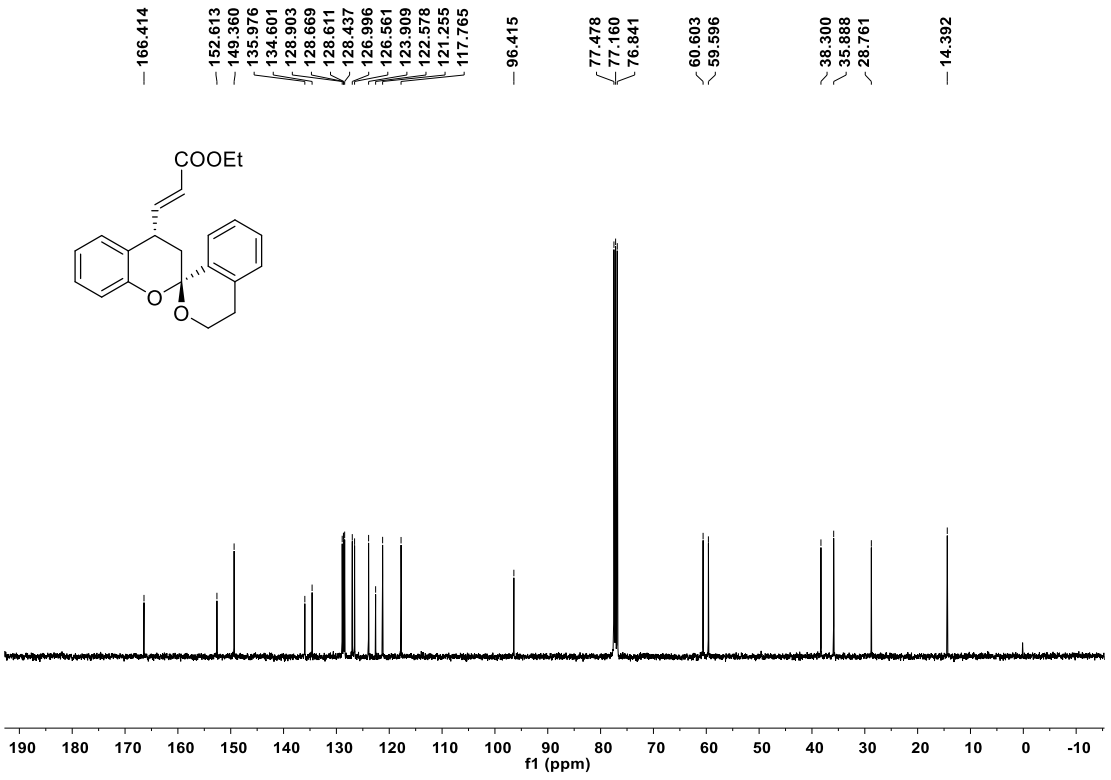
^{13}C NMR spectrum of product **6** (100 MHz, $CDCl_3$)



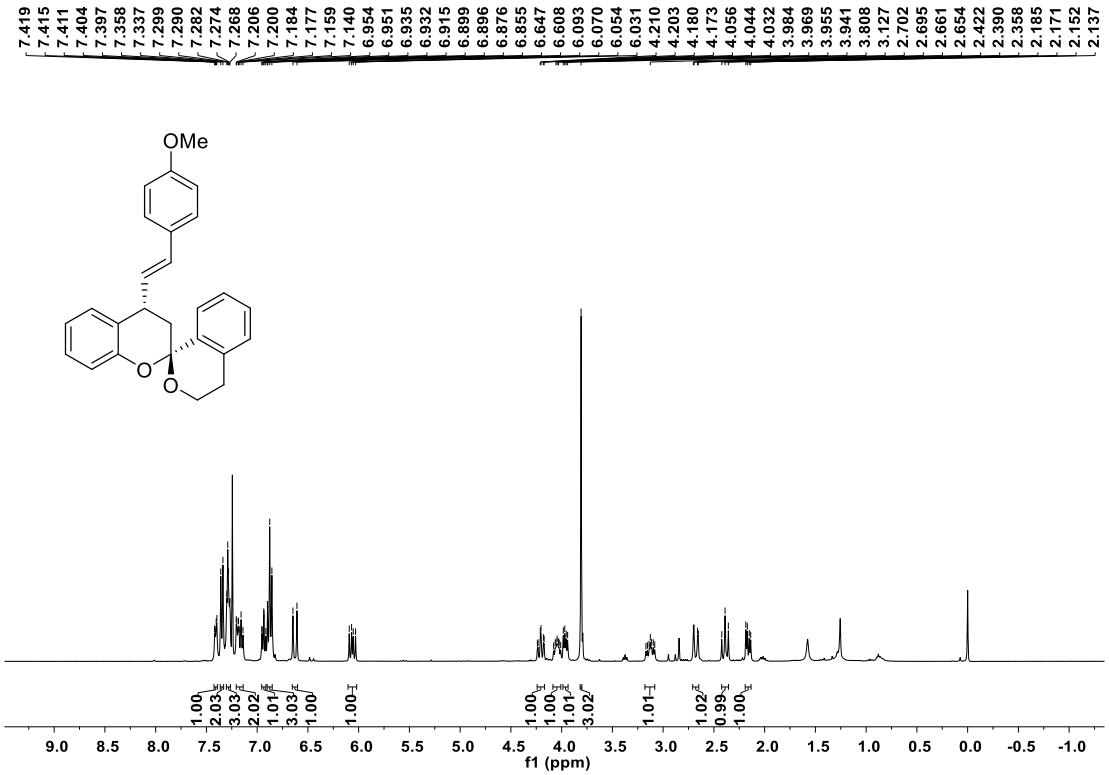
^{1}H NMR spectrum of product **7** (400 MHz, $CDCl_3$)



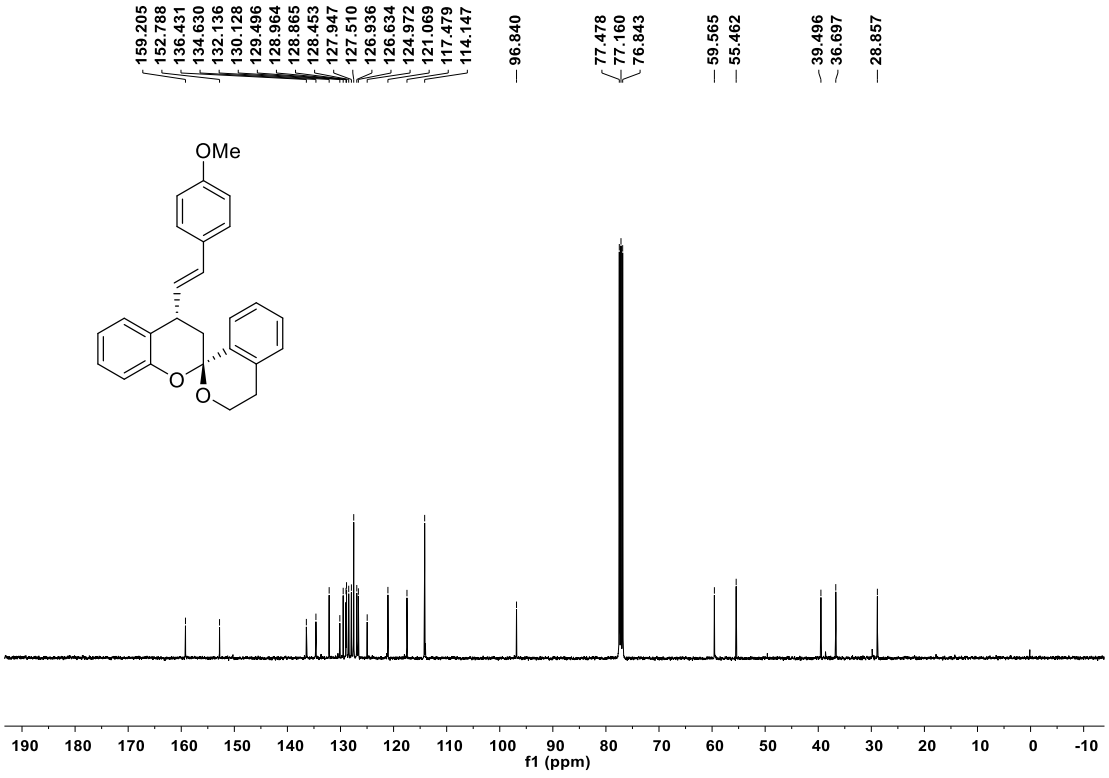
^{13}C NMR spectrum of product **7** (100 MHz, $CDCl_3$)



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

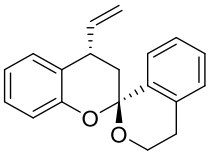


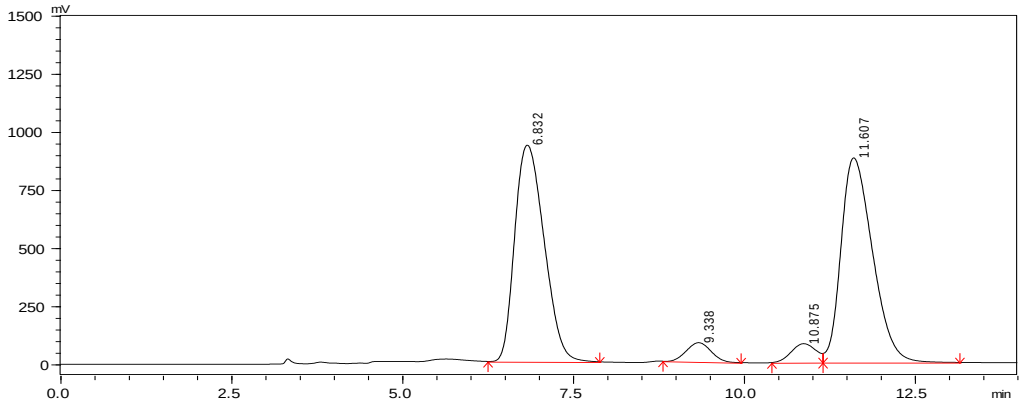
^{13}C NMR spectrum of product **8** (100 MHz, $CDCl_3$)



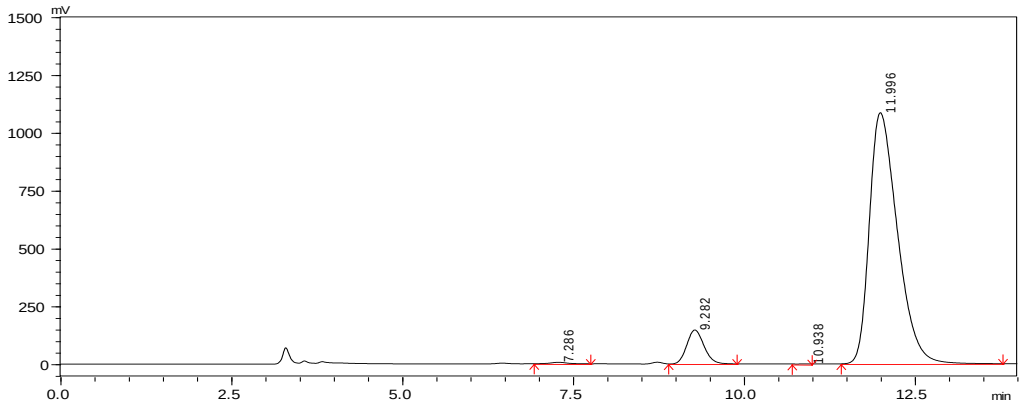
12. HPLC chromatograms

HPLC chromatogram of compound **3a** (99% ee, 12:1 dr)



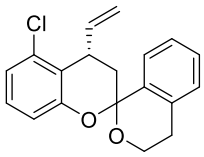


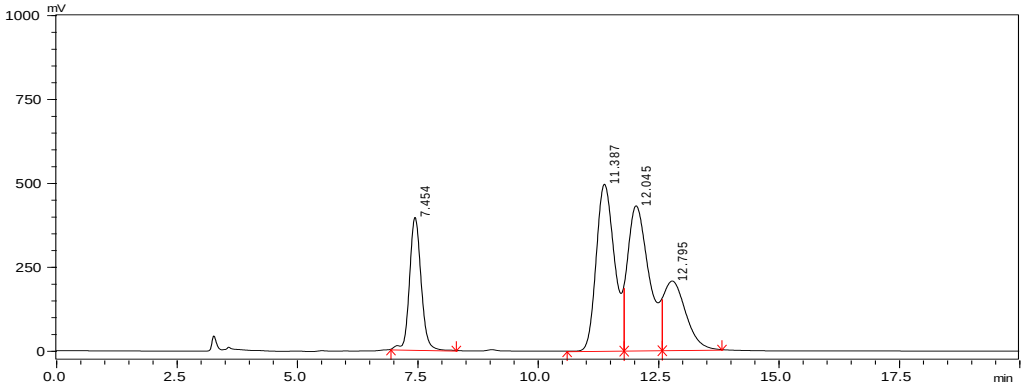
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.832	931366	27819100	46.220
2	9.338	82543	2061916	3.426
3	10.875	81411	2041438	3.392
4	11.607	880597	28266633	6.963
total		1975918	60189088	100.000



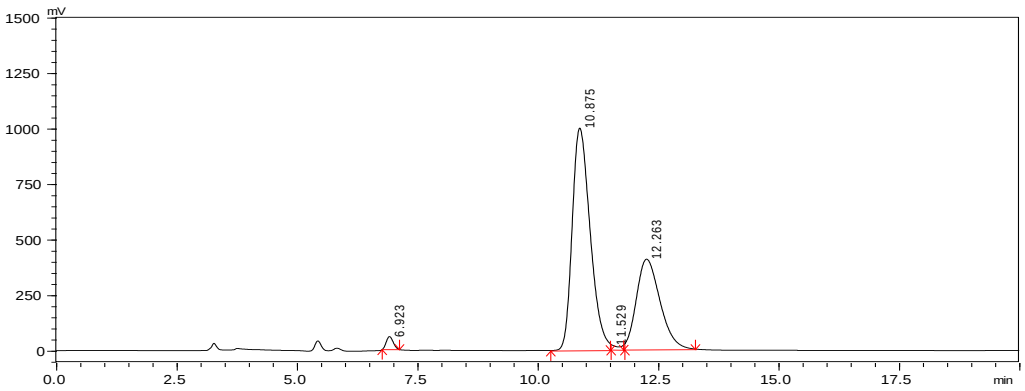
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.286	6280	107382	0.319
2	9.282	146644	2563647	7.614
3	10.938	2252	29962	0.089
4	11.996	1085357	30970419	91.978
total		1240533	33671409	100.000

HPLC chromatogram of compound **3b** (98% / 93% ee, 2:1 dr)



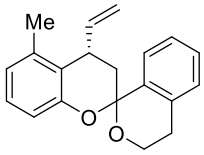


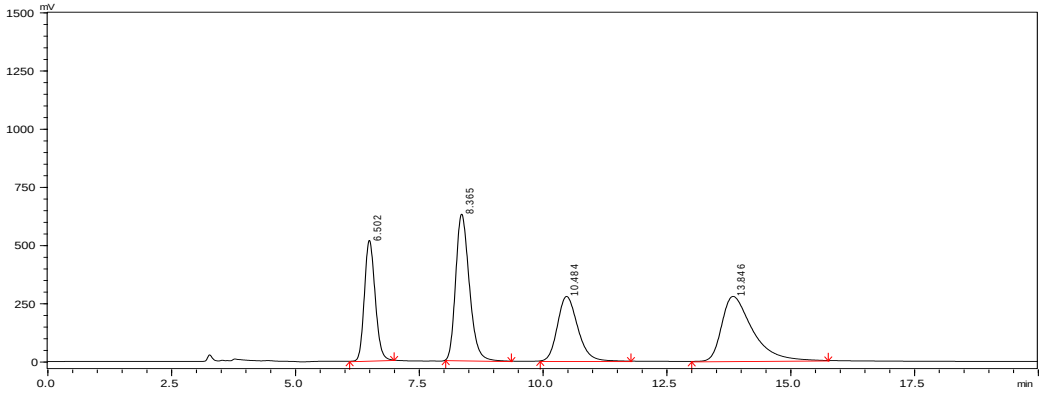
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.454	394191	6553538	16.610
2	11.387	496288	13189999	33.430
3	12.045	431019	13236572	33.548
4	12.795	205863	6475698	16.413
total		1527360	39455807	100.000



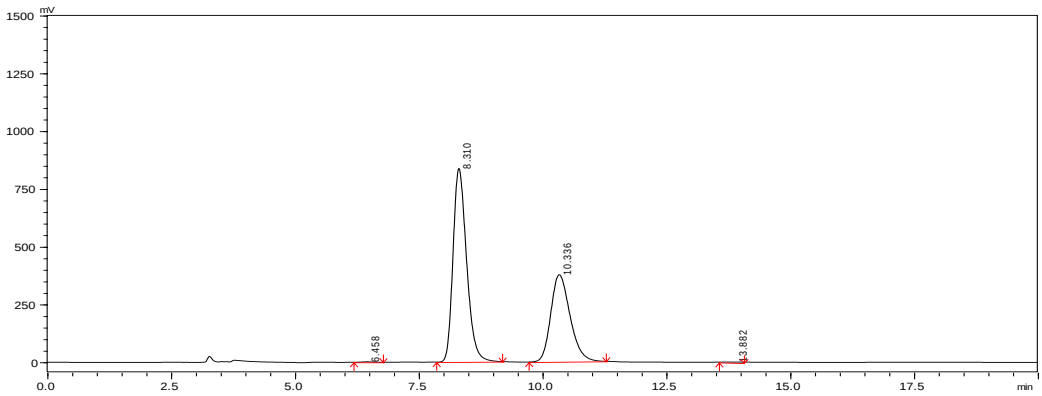
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.923	56019	538325	1.329
2	10.875	1000829	25901553	63.956
3	11.529	22966	235116	0.581
4	12.263	405963	13823816	34.134
total		1485777	40498810	100.000

HPLC chromatogram of compound **3c** (99% / 99% ee, 1.6:1 dr)



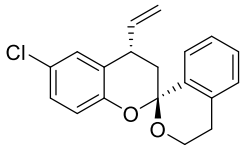


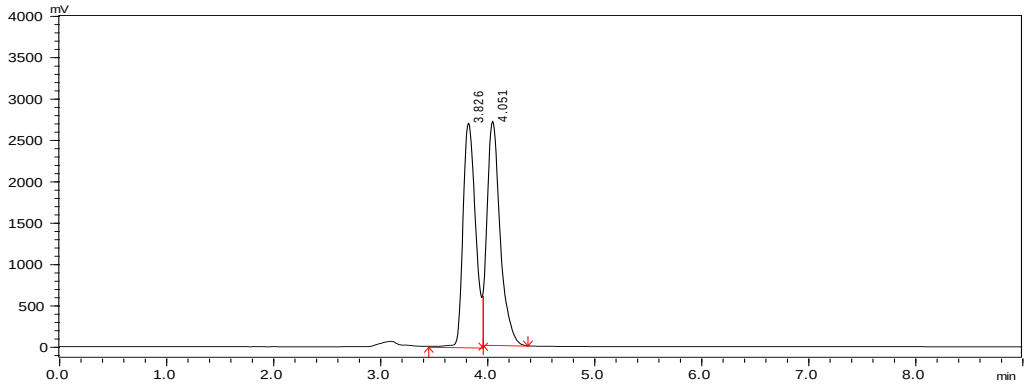
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.502	516743	7767034	19.665
2	8.365	628308	11989617	30.356
3	10.484	277365	7849132	19.873
4	13.846	277948	11891452	30.107
total		1700363	39497235	100.000



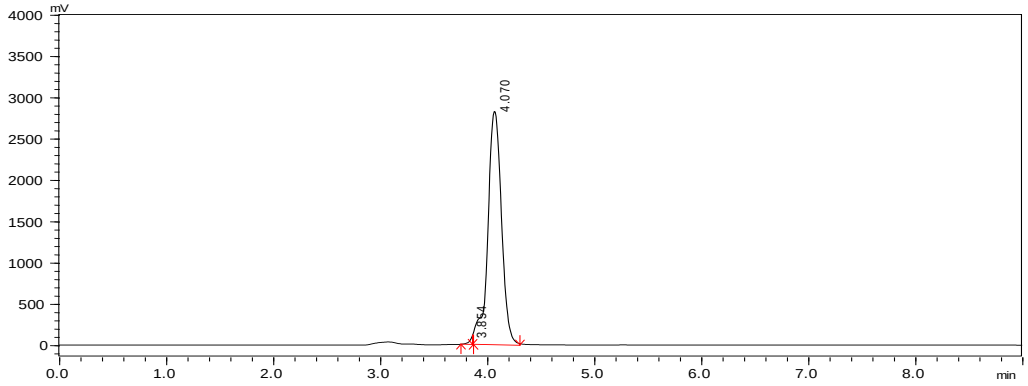
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.458	1797	28257	0.108
2	8.310	836452	15941307	60.822
3	10.336	376303	10163075	38.776
4	13.882	2991	77052	0.294
total		1217544	26209690	100.000

HPLC chromatogram of compound **3d** (99% ee)



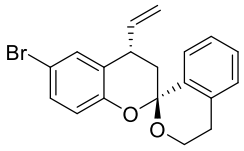


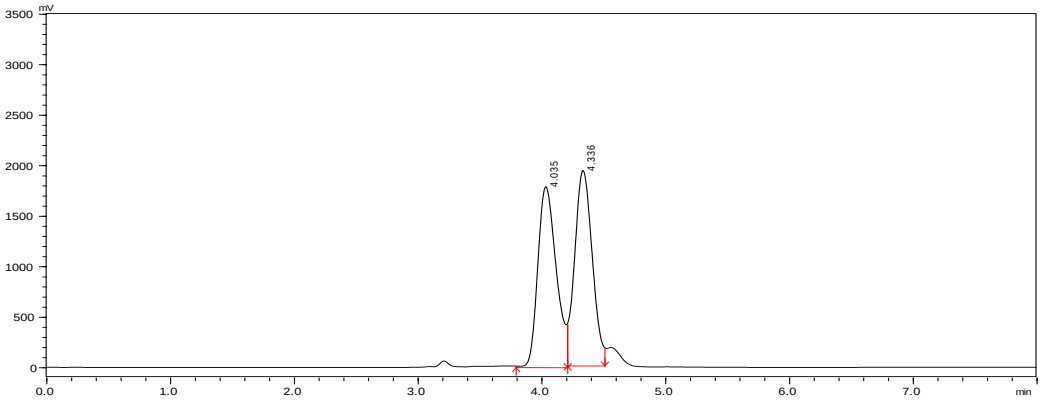
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	3.826	2709788	22083925	49.060
2	4.051	2702999	22930054	50.940
total		5412786	45013978	100.000



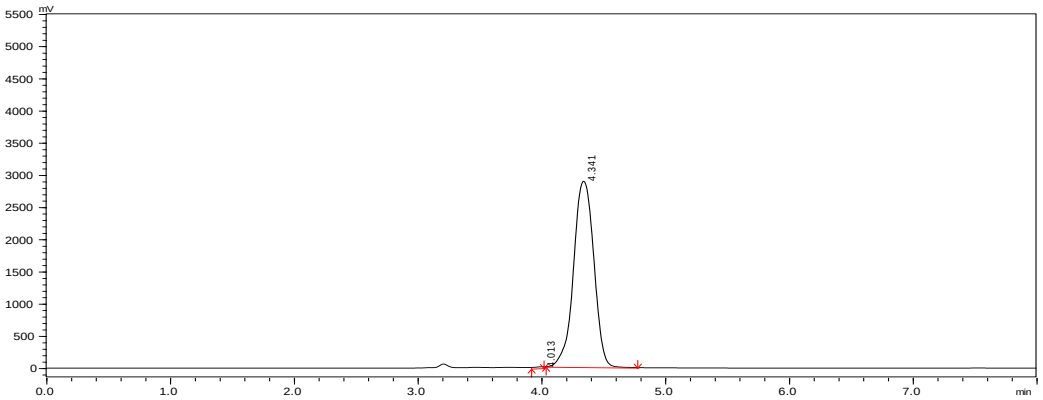
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	3.854	58843	103610	0.414
2	4.070	2815653	24908707	99.586
total		2874496	25012317	100.000

HPLC chromatogram of compound **3e** (99% ee)



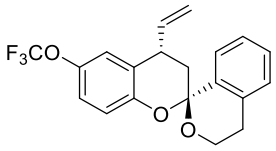


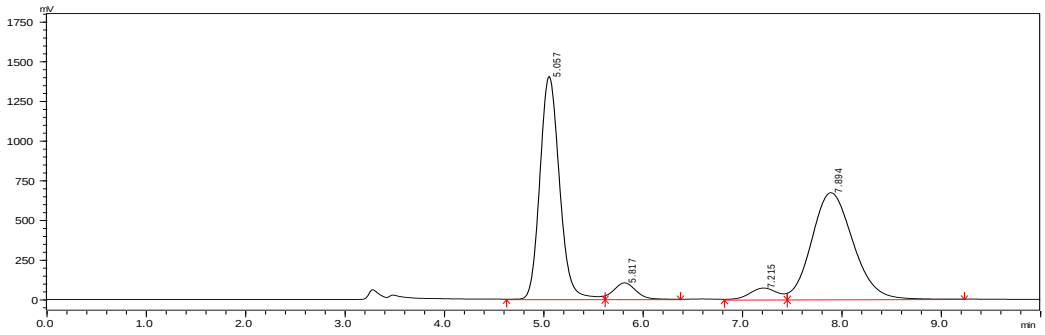
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.035	1786723	18581296	49.479
2	4.336	1930701	18972907	50.521
total		3717424	37554203	100.000



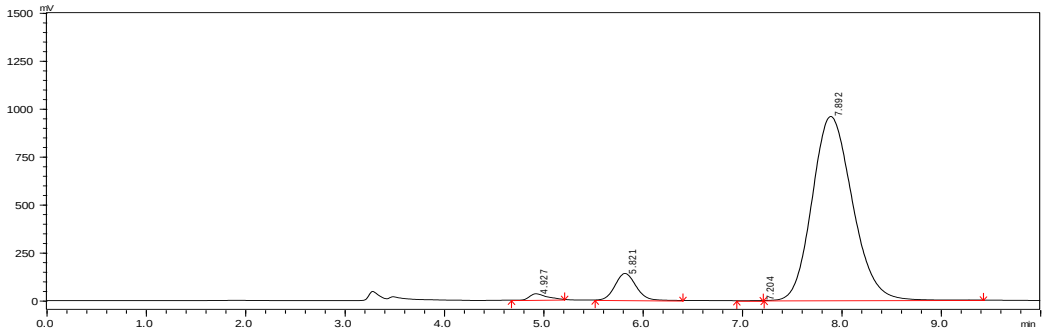
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.013	22062	125224	0.379
2	4.341	2887124	32897250	99.621
total		2909186	33022474	100.000

HPLC chromatogram of compound **3f** (97% ee, 14:1 dr)



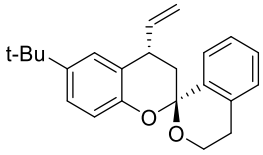


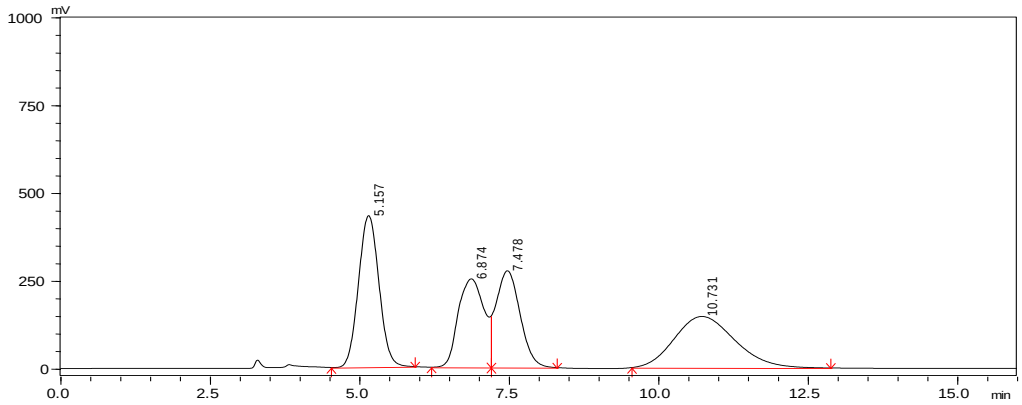
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.057	1402619	19173991	46.040
2	5.817	102926	1562585	3.752
3	7.215	72524	1429127	3.432
4	7.894	672596	19480480	46.776
total		2250665	41646183	100.000



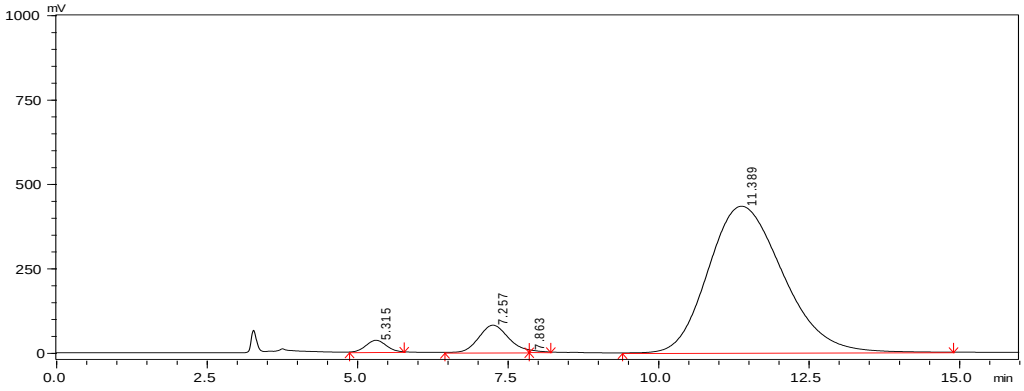
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.927	31191	357202	1.220
2	5.821	138893	2007193	6.857
3	7.204	1619	9283	0.032
4	7.892	958649	26900132	91.891
total		1130352	29273810	100.000

HPLC chromatogram of compound **3g** (96% ee, 13:1 dr)





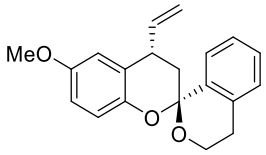
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.157	431295	10271925	28.710
2	6.874	251832	7596124	21.231
3	7.478	275139	7668268	21.433
4	10.731	145953	10242314	28.627
total		1104218	35778630	100.000

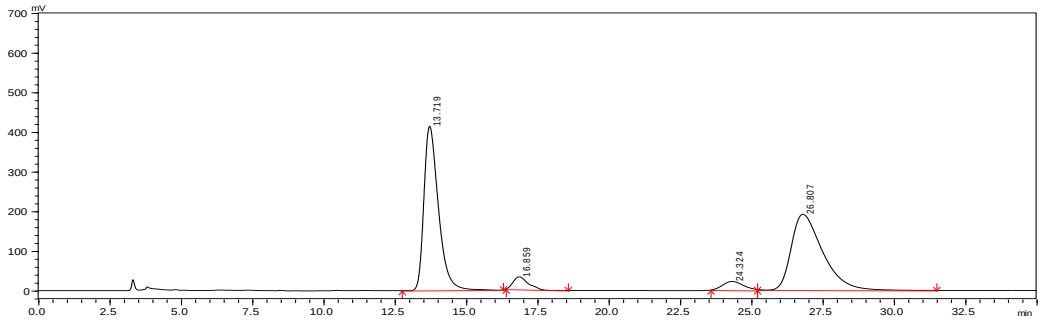


#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.315	34500	789840	1.928
2	7.257	80939	2757384	6.731
3	7.863	6505	58255	0.142
4	11.389	433617	37359071	91.199
total		555560	40964550	100.000

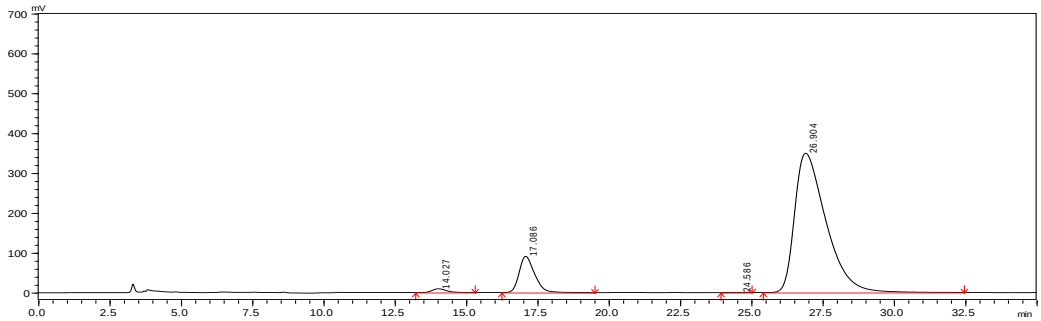
HPLC chromatogram of compound **3h** (98% ee, 14:1 dr)

[*the dr values from HPLC analysis and NMR analysis were inconsistent, so, we determined the dr value by NMR analysis*]



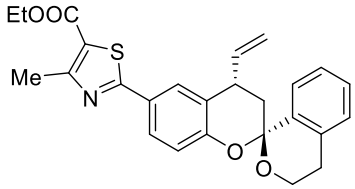


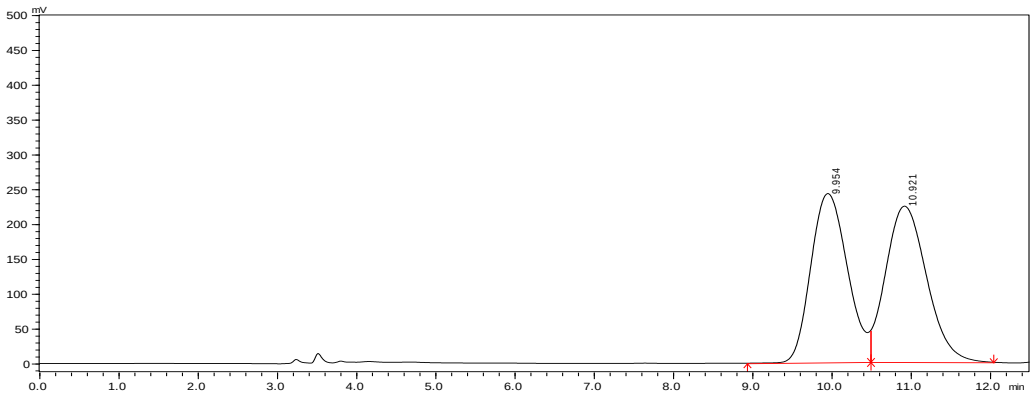
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	13.719	414329	14641984	46.437
2	16.859	31887	1139320	3.613
3	24.324	21979	1104083	3.502
4	26.807	191387	14645257	46.448
total		659582	31530645	100.000



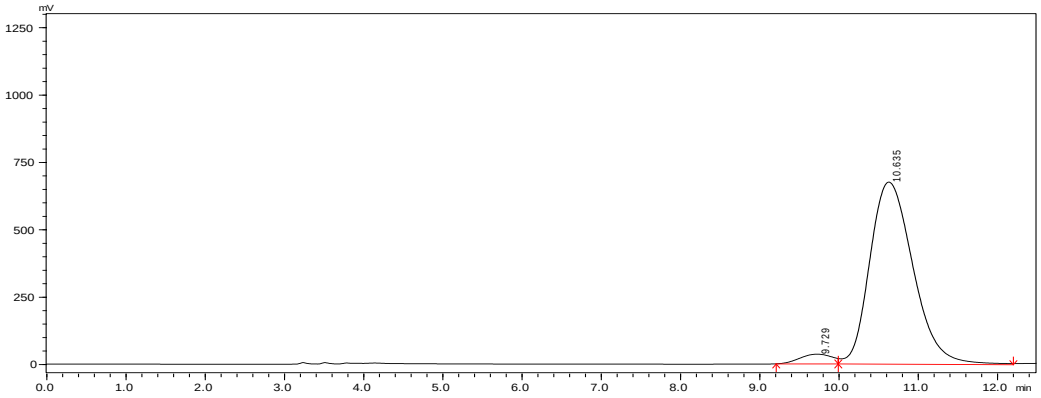
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	14.027	9521	332788	1.092
2	17.086	90992	3419846	11.219
3	24.586	522	19897	0.065
4	26.904	349377	26709673	87.624
total		450412	30482203	100.000

HPLC chromatogram of compound **3i** (93% ee)



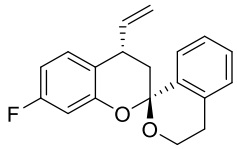


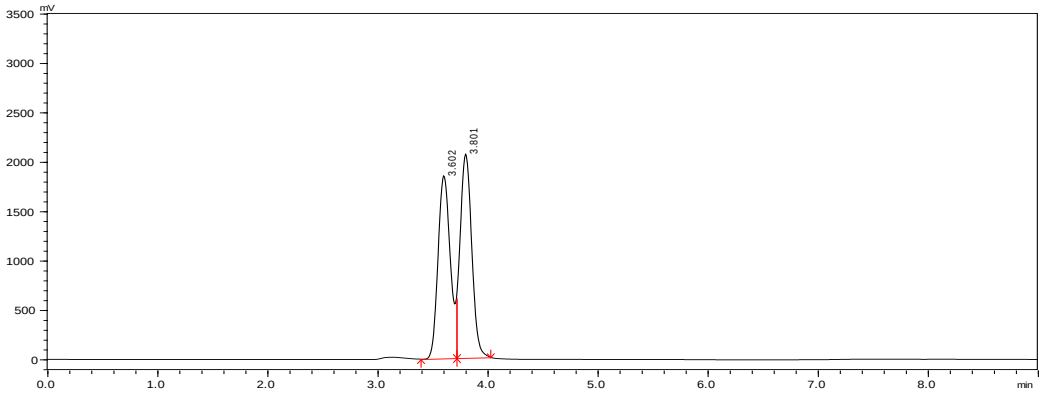
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.729	34281	926466	3.508
2	10.635	673831	25485145	96.492
total		708112	26411611	100.000



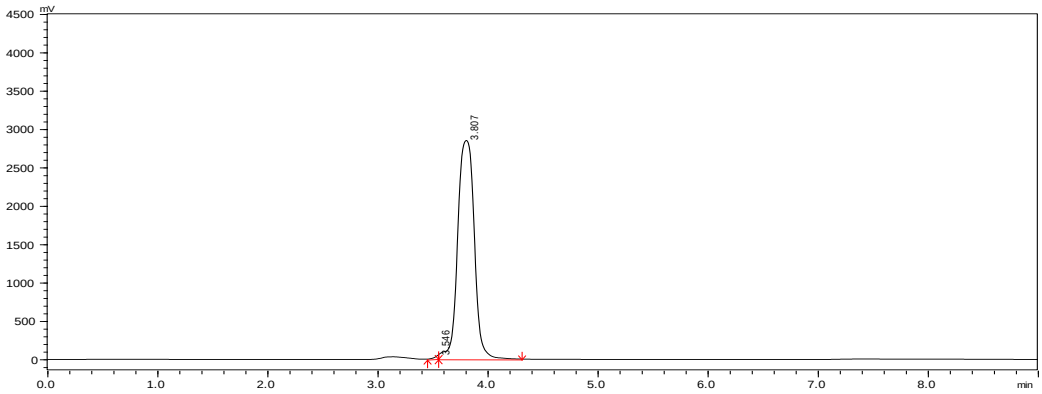
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.729	34281	926466	3.508
2	10.635	673831	25485145	96.492
total		708112	26411611	100.000

HPLC chromatogram of compound **3j** (99% ee)



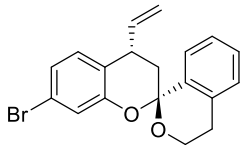


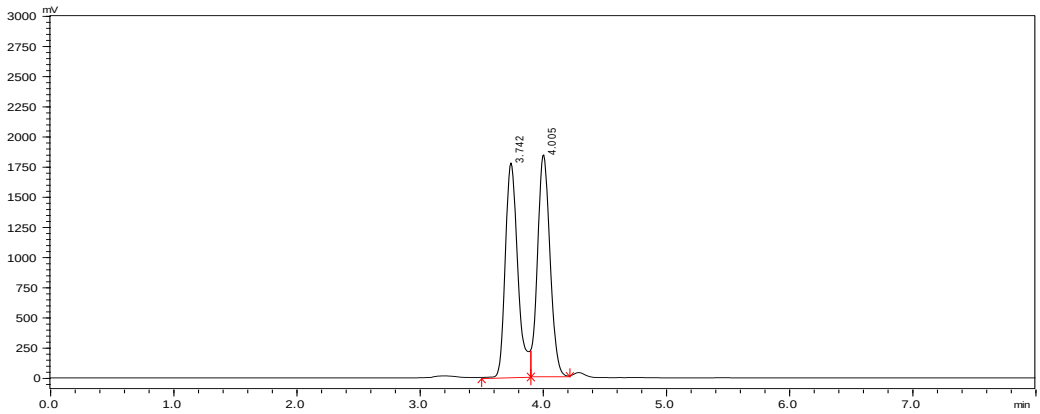
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	3.602	1849602	14456177	49.081
2	3.801	2064089	14997823	50.919
total		3913691	29454000	100.000



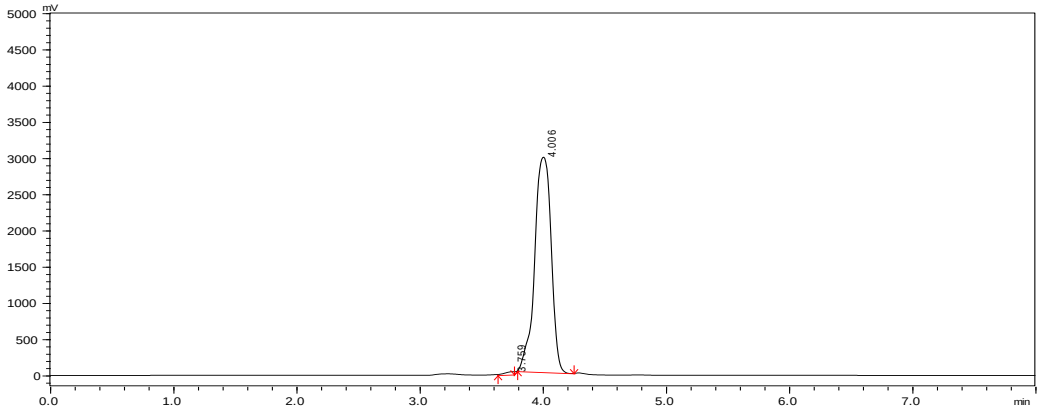
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	3.546	42613	127266	0.423
2	3.807	2851304	29989093	99.577
total		2893917	30116360	100.000

HPLC chromatogram of compound **3k** (99% ee)



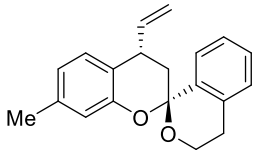


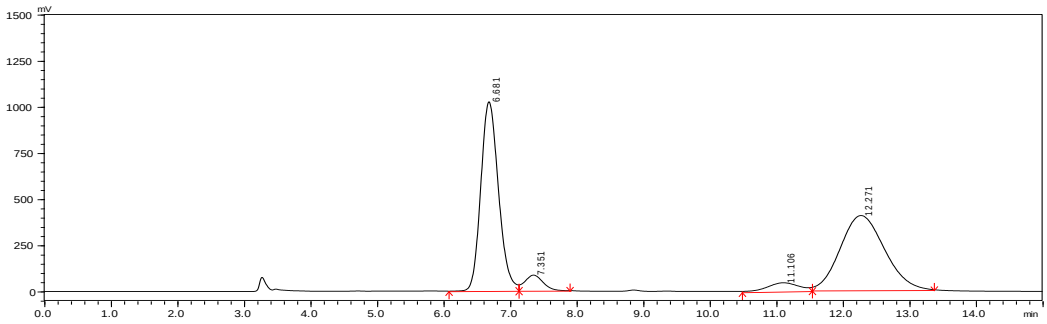
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	3.742	1777039	12620764	49.493
2	4.005	1835084	12879314	50.507
total		3612124	25500079	100.000



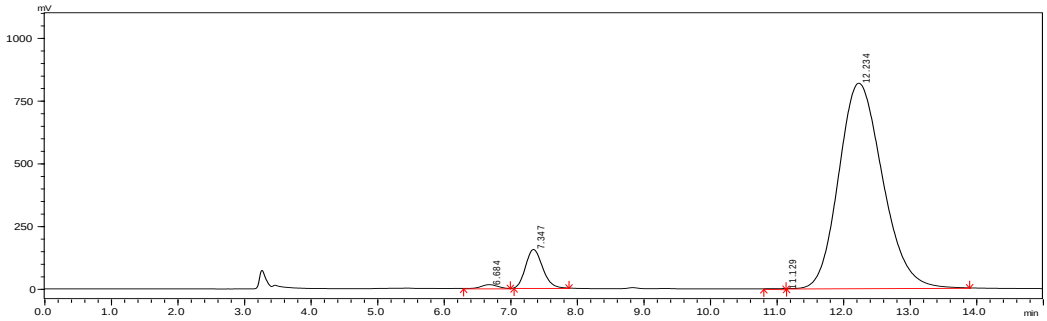
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	3.759	36641	203995	0.731
2	4.006	2968195	27699897	99.269
total		3004836	27903892	100.000

HPLC chromatogram of compound **3l** (99% ee, 14:1 dr)



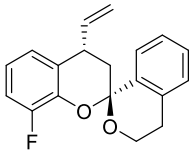


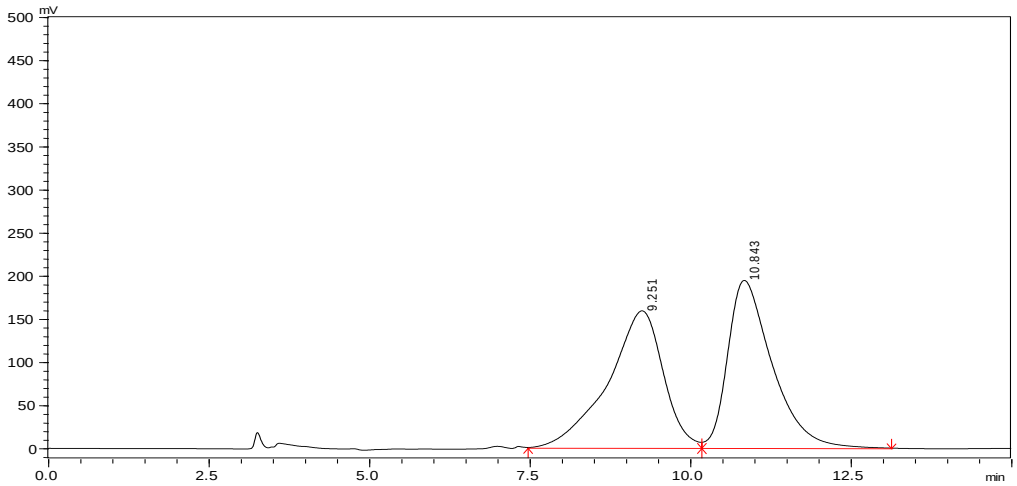
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.681	1025229	18941758	46.183
2	7.351	84926	1625694	3.964
3	11.106	47668	1631201	3.977
4	12.271	405656	18815848	45.876
total		1563479	41014501	100.000



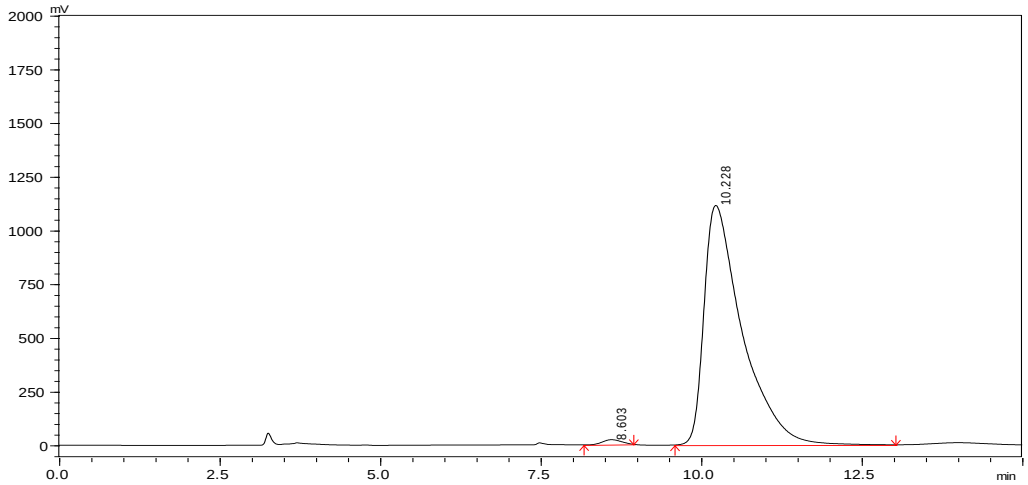
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.684	15123	247421	0.614
2	7.347	153327	2699127	6.700
3	11.129	2676	27401	0.068
4	12.234	817447	37310067	92.618
total		988574	40284015	100.000

HPLC chromatogram of compound **3m** (98% ee)



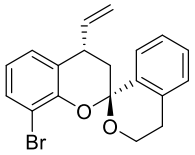


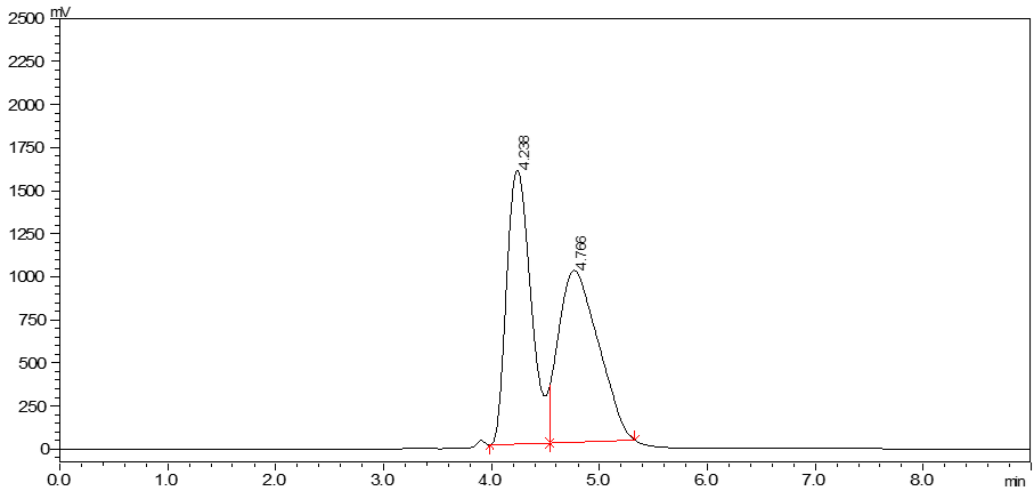
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.251	158650	9459319	50.314
2	10.843	194062	9341224	49.686
total		352712	18800543	100.000



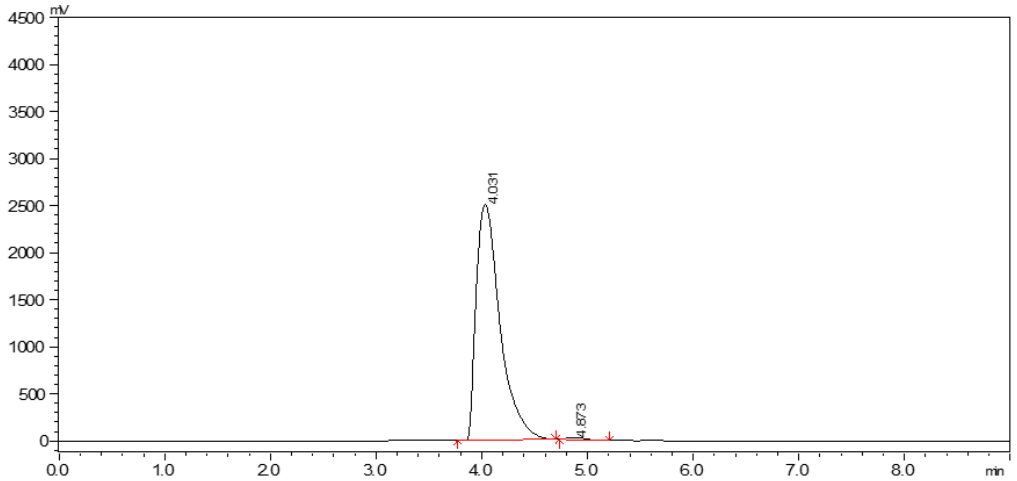
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.603	22470	454995	0.979
2	10.228	1114651	46032714	99.021
total		1137121	46487709	100.000

HPLC chromatogram of compound **3n** (98% ee)



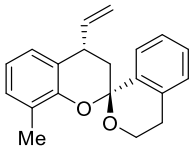


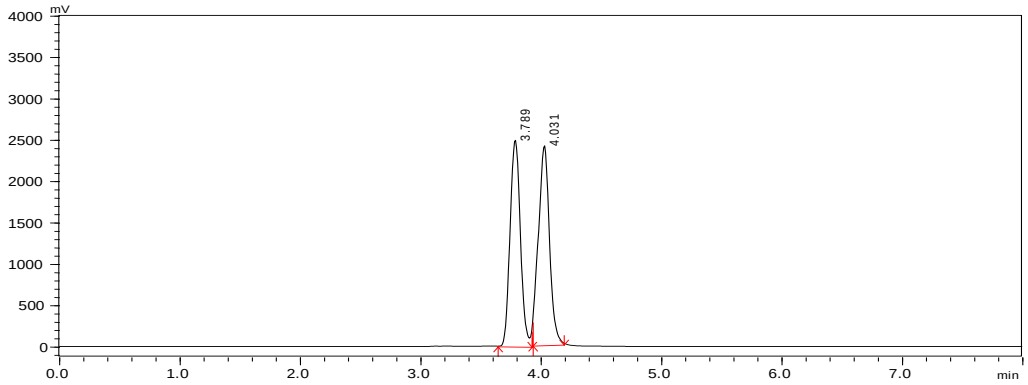
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.238	1590301	25186460	49.260
2	4.766	996794	25942710	50.740
total		2587095	51129169	100.000



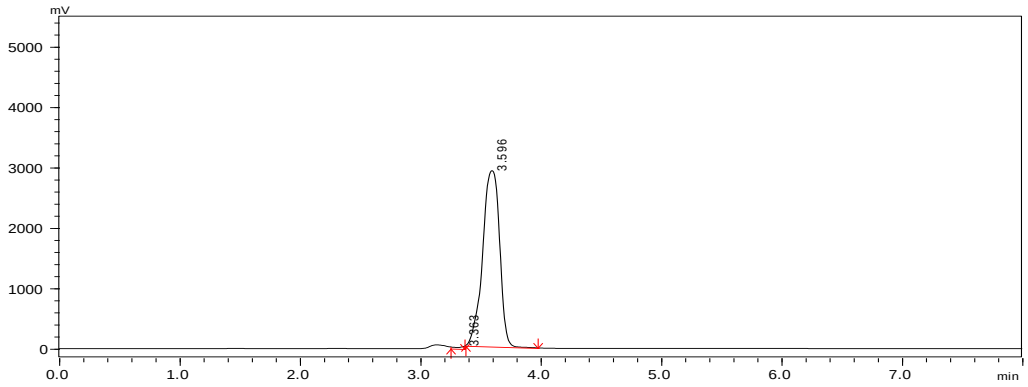
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.031	2498044	39130218	99.241
2	4.873	27145	299444	0.759
total		2525188	39429662	100.000

HPLC chromatogram of compound **3o** (99% ee)



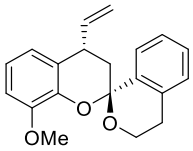


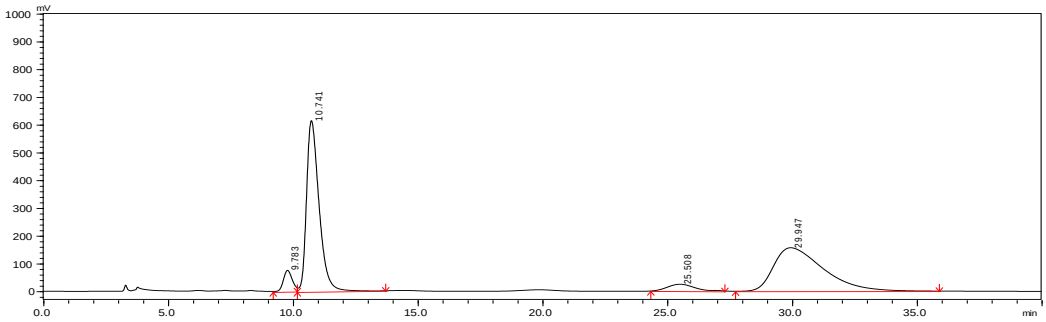
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	3.789	2490962	15006166	49.371
2	4.031	2407221	15388414	50.629
total		4898183	30394580	100.000



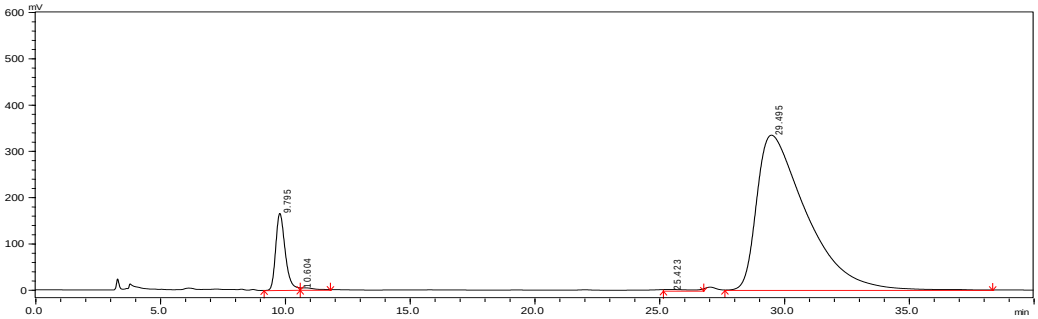
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	3.363	36259	173693	0.605
2	3.596	2909865	28558912	99.395
total		2946123	28732605	100.000

HPLC chromatogram of compound **3p** (99% ee, 11:1 dr)



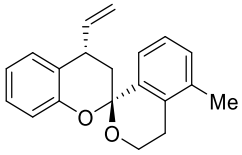


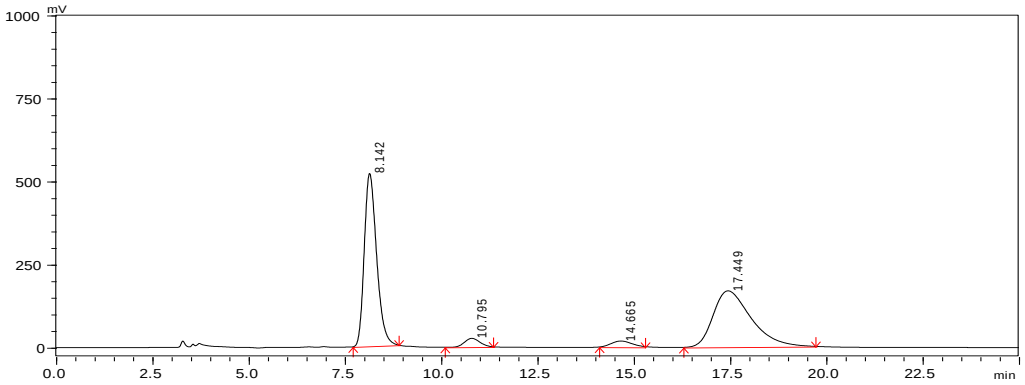
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.783	77207	1925764	4.088
2	10.741	616554	21608259	45.865
3	25.508	24968	1925674	4.087
4	29.947	156608	21652605	45.960
total		875337	47112303	100.000



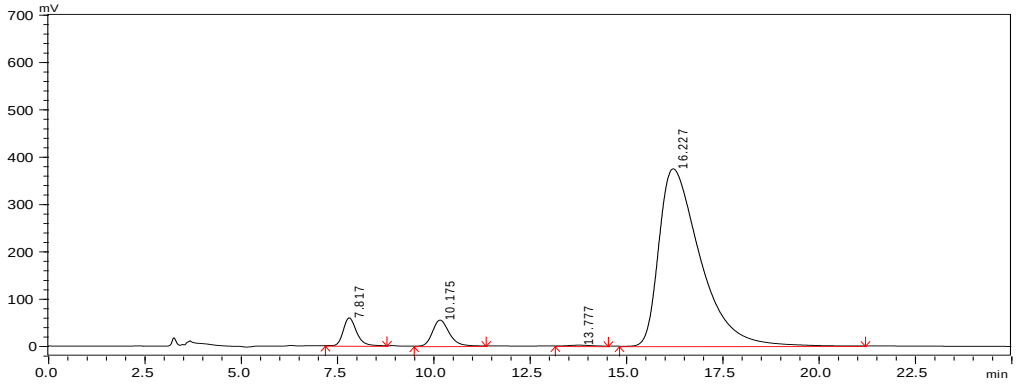
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.795	165565	4355814	8.595
2	10.604	4128	153478	0.303
3	25.423	2474	198174	0.391
4	29.495	334498	45968192	90.711
total		506665	50675657	100.000

HPLC chromatogram of compound **3q** (91% ee, 17:1 dr)



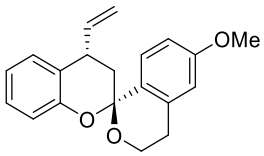


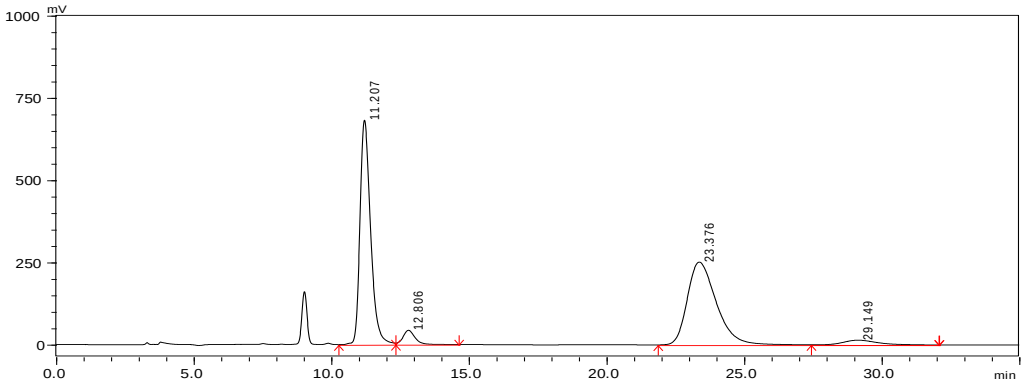
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.142	520123	11604958	47.236
2	10.795	25814	703221	2.862
3	14.665	18278	681493	2.774
4	17.449	169182	11578410	47.128
total		733396	24568083	100.000



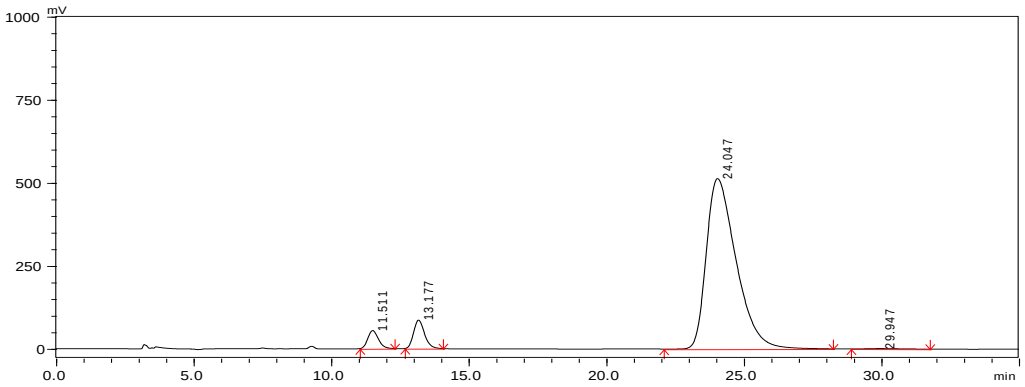
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.817	58734	1388465	4.481
2	10.175	54852	1635813	5.279
3	13.777	1776	65877	0.213
4	16.227	374528	27895863	90.027
total		489890	30986018	100.000

HPLC chromatogram of compound **3r** (93% ee, 15:1 dr)



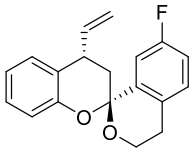


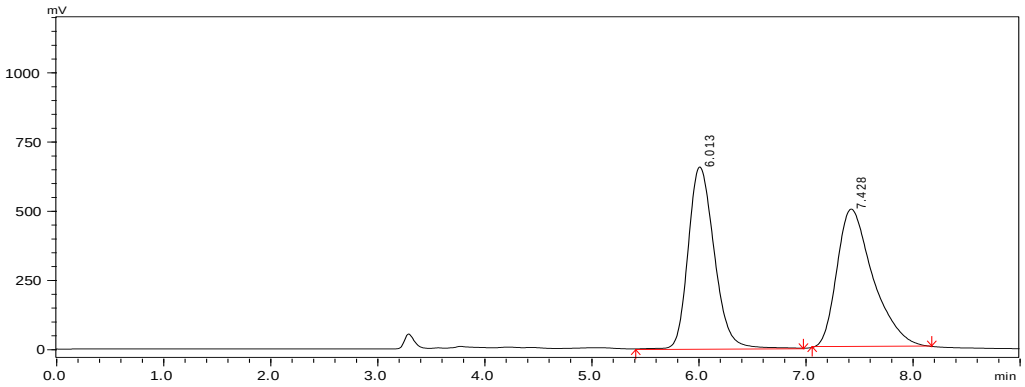
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.207	682303	18295322	46.565
2	12.806	43600	1332342	3.391
3	23.376	251550	18434520	46.919
4	29.149	14369	1228064	3.126
total		991821	39290247	100.000



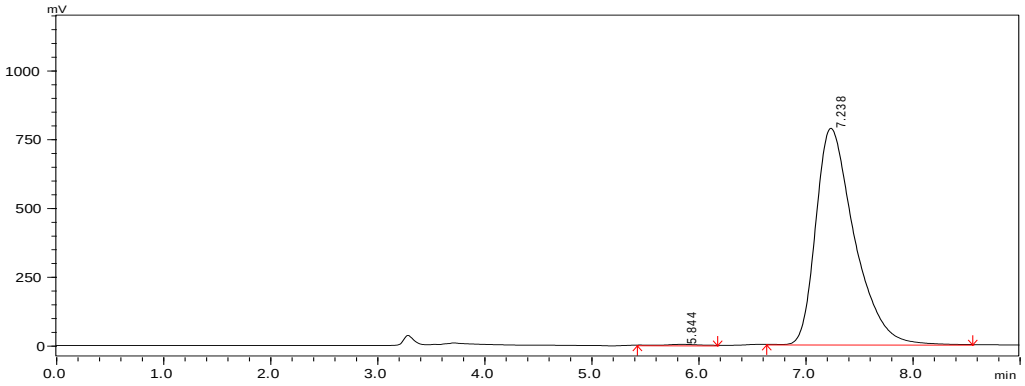
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.511	54376	1453687	3.417
2	13.177	85774	2376027	5.585
3	24.047	512820	38625020	90.784
4	29.947	1203	91119	0.214
total		654173	42545852	100.000

HPLC chromatogram of compound **3s** (>99% ee)



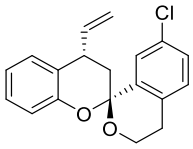


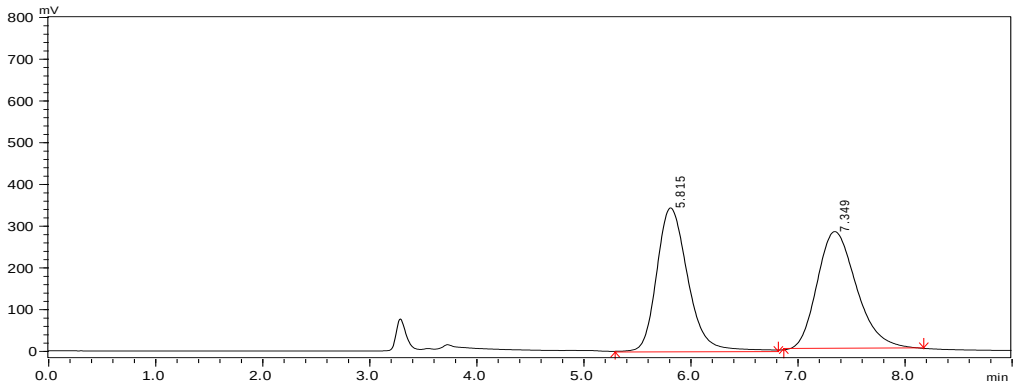
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.013	656353	11056555	49.178
2	7.428	493887	11426329	50.822
total		1150240	22482885	100.000



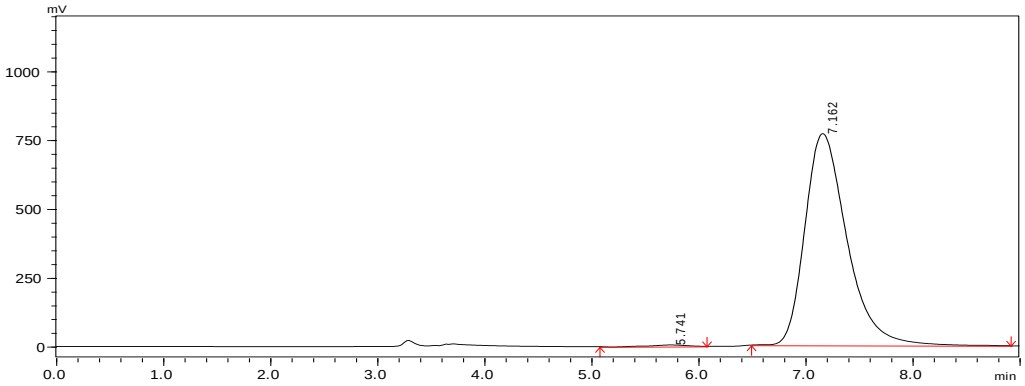
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.844	2818	38860	0.198
2	7.238	785232	19560072	99.802
total		788050	19598932	100.000

HPLC chromatogram of compound **3t** (>99% ee)



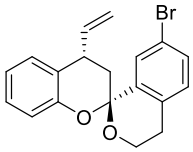


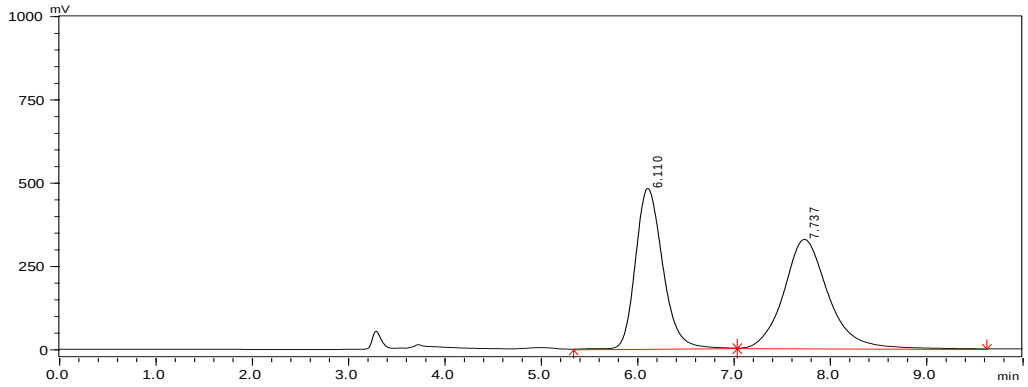
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.815	343188	6904674	49.738
2	7.349	278027	6977353	50.262
total		621215	13882027	100.000



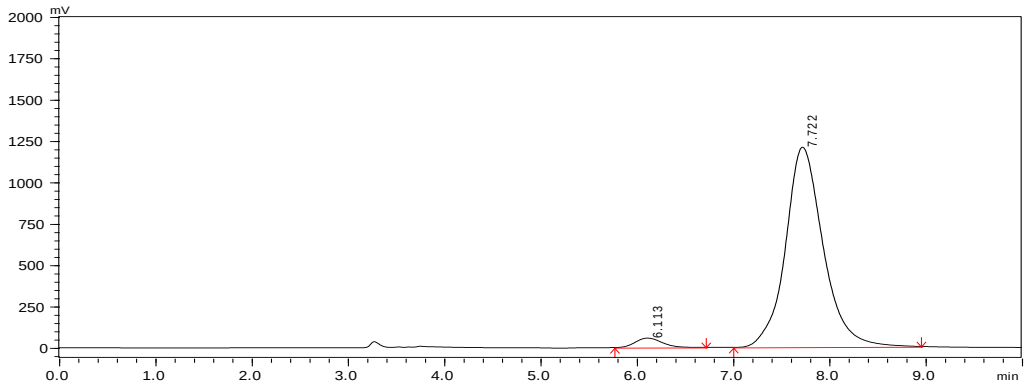
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.741	5375	101772	0.483
2	7.162	768580	20972506	99.517
total		773955	21074278	100.000

HPLC chromatogram of compound **3u** (94% ee)



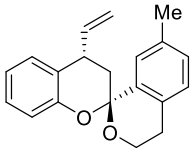


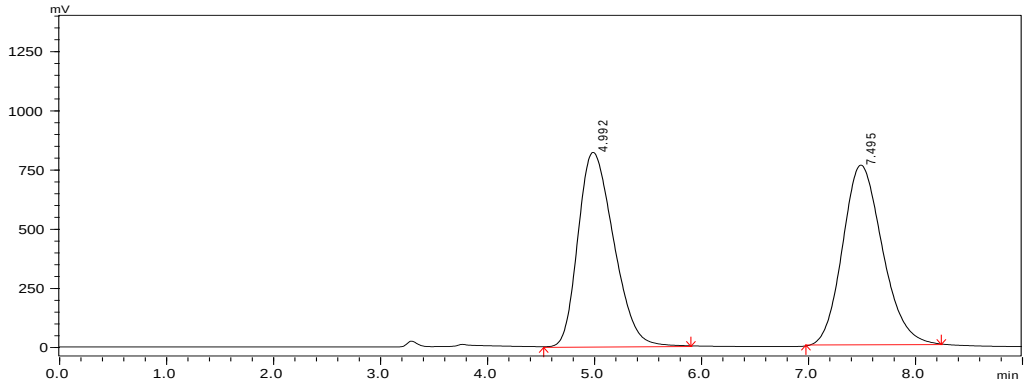
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.110	480991	9432222	49.870
2	7.737	317383	9481363	50.130
total		798374	18913585	100.000



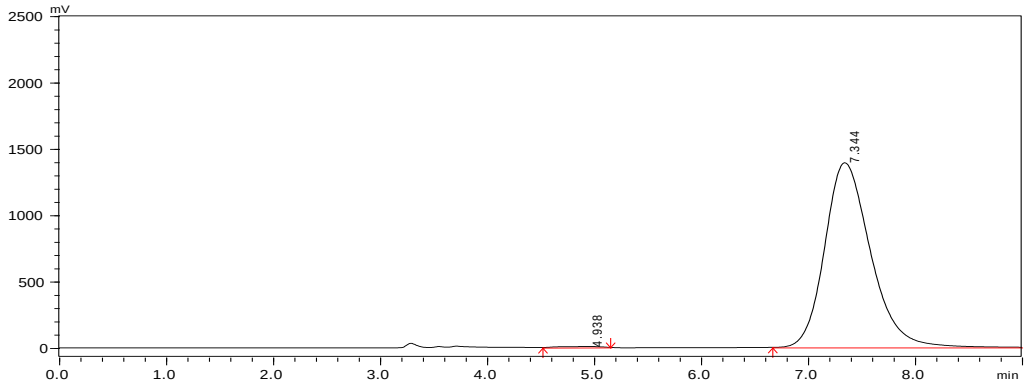
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.113	57054	1092248	3.217
2	7.722	1207597	32860276	96.783
total		1264651	33952524	100.000

HPLC chromatogram of compound **3v** (>99% ee)



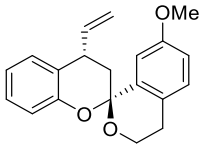


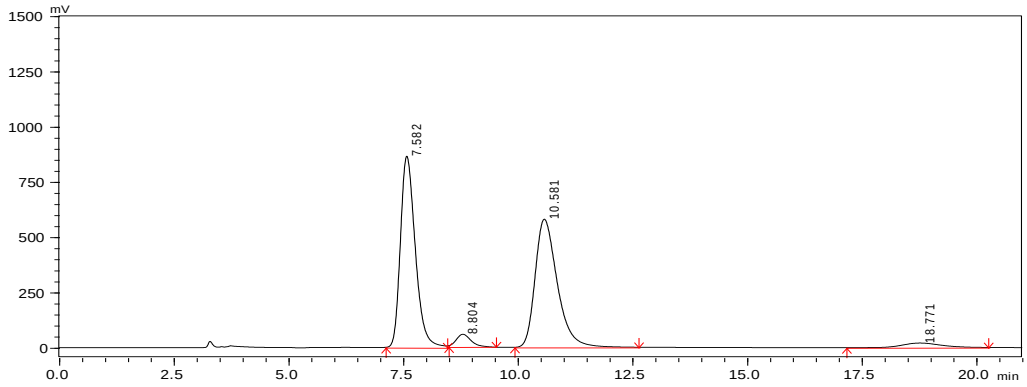
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.992	819698	18939852	49.325
2	7.495	756125	19457968	50.675
total		1575823	38397821	100.000



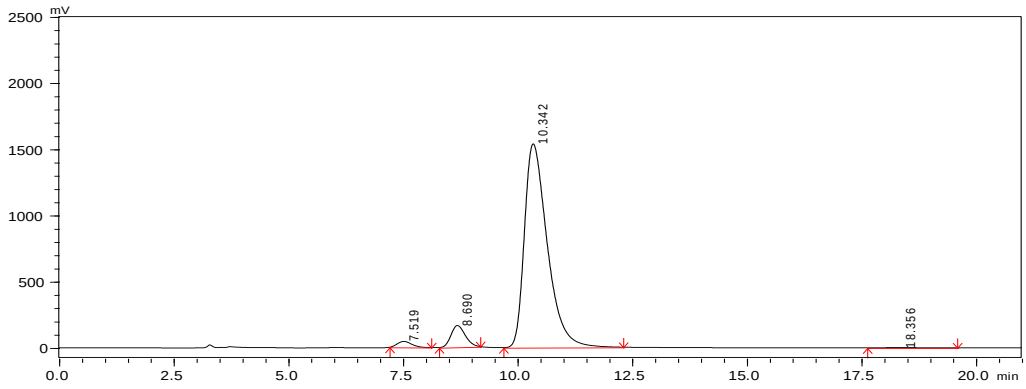
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.938	7186	178229	0.429
2	7.344	1390785	41378581	99.571
total		1397972	41556810	100.000

HPLC chromatogram of compound **3w** (96% ee, 16:1 dr)



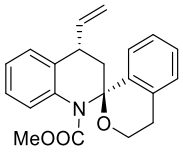


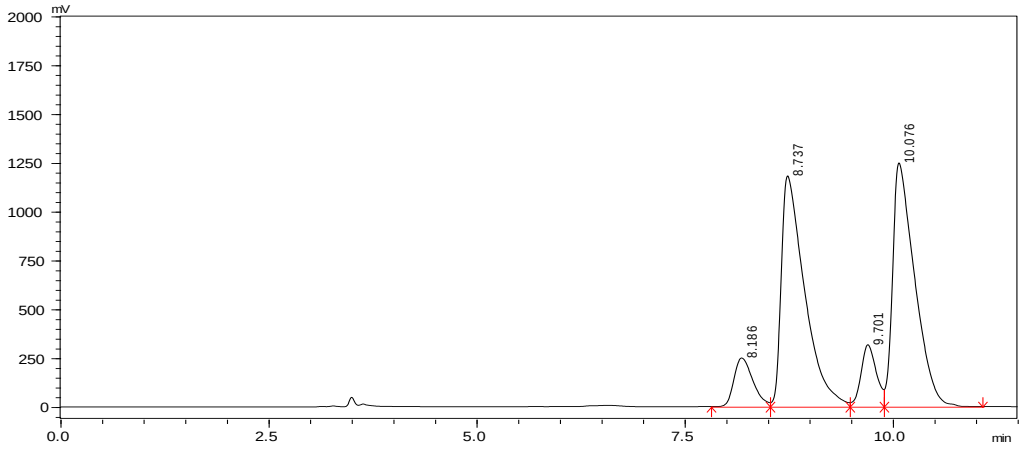
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.582	865745	19533598	47.244
2	8.804	56353	1220830	2.953
3	10.581	579637	19405896	46.935
4	18.771	20393	1185830	2.868
total		1522127	41346154	100.000



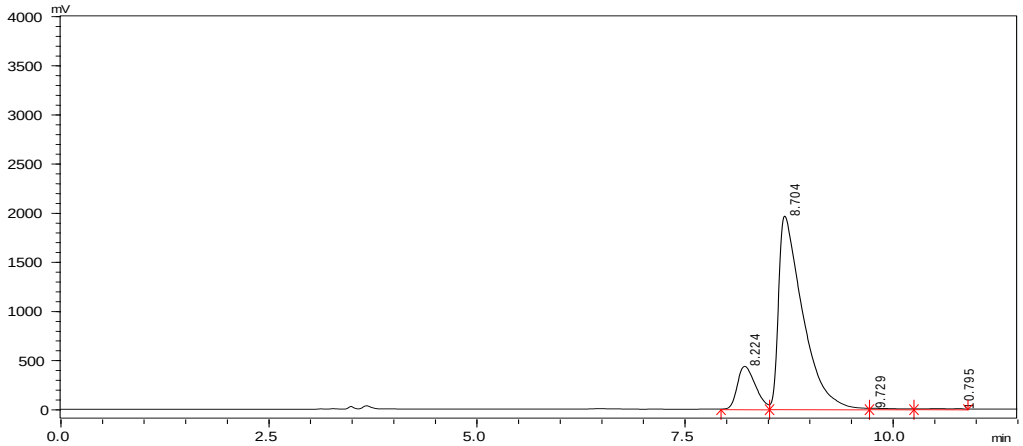
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.519	44982	988333	1.706
2	8.690	163427	3508163	6.054
3	10.342	1538174	53374821	92.115
4	18.356	1257	72220	0.125
total		1747839	57943537	100.000

HPLC chromatogram of compound **5a** (99% ee, 6:1 dr)



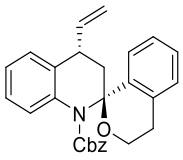


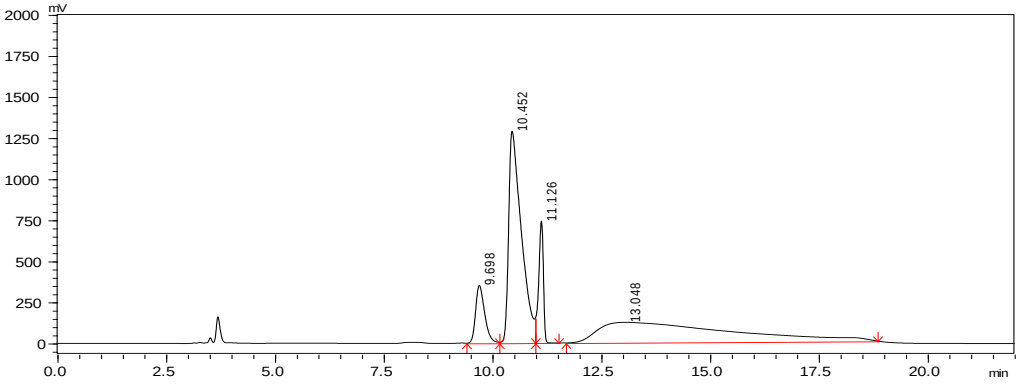
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.186	248992	3939288	7.298
2	8.737	1181213	23060016	42.719
3	9.701	316601	4044467	7.492
4	10.076	1247555	22937505	42.492
total		2994361	53981276	100.000



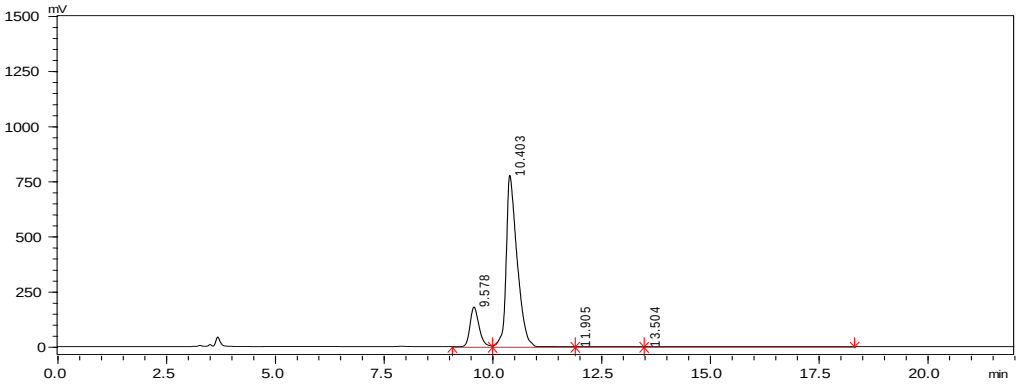
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.224	434394	6526848	14.104
2	8.704	1962490	39514320	85.385
3	9.729	7422	134712	0.291
4	10.795	4850	101972	0.220
total		2409155	46277851	100.000

HPLC chromatogram of compound **5b** (99% ee, 6:1 dr)



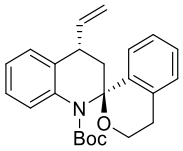


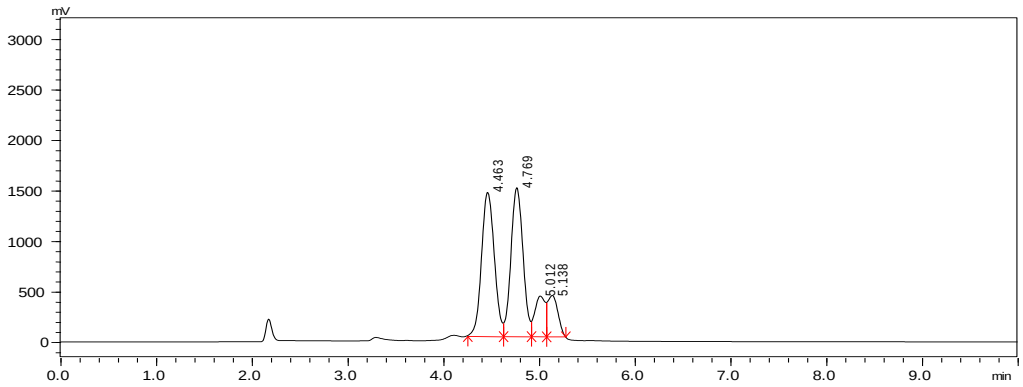
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.698	351144	5085532	8.073
2	10.452	1289744	26244983	41.663
3	11.126	741930	5617986	8.918
4	13.048	123303	26044939	41.345
total		2506121	62993440	100.000



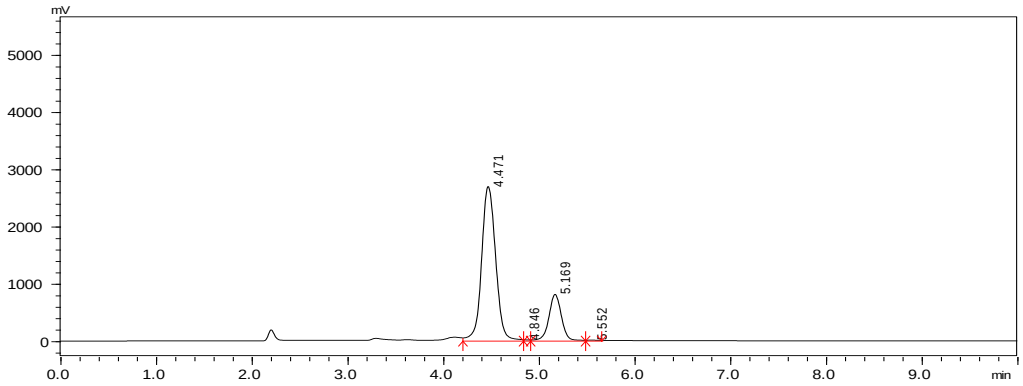
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.578	180009	2598851	16.010
2	10.403	776960	13534900	83.379
3	11.905	458	36404	0.224
4	13.504	349	62893	0.387
total		957776	16233048	100.000

HPLC chromatogram of compound **5c** (99% ee, 4:1 dr)



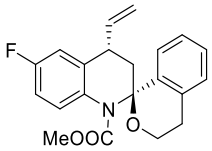


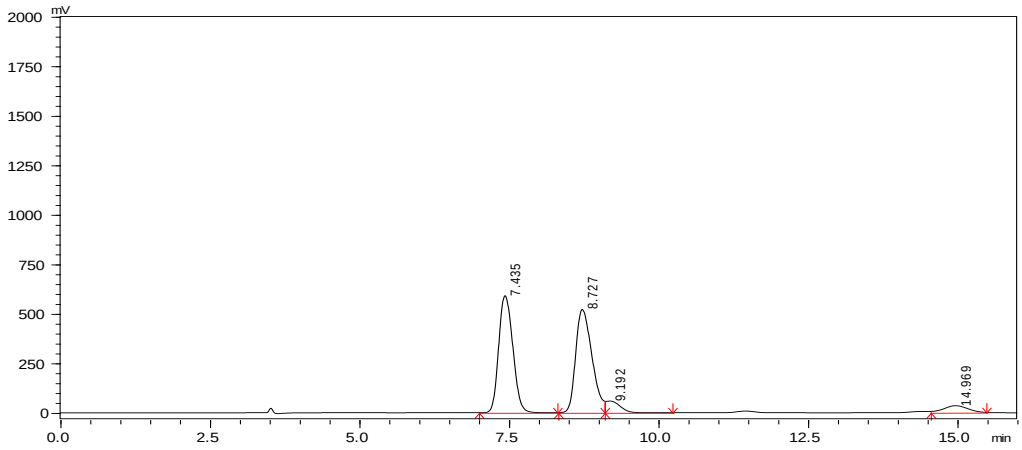
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.463	1420420	13155510	41.162
2	4.769	1468286	12822704	40.120
3	5.012	396610	2996626	9.376
4	5.138	403684	2985784	9.342
total		3689000	31960625	100.000



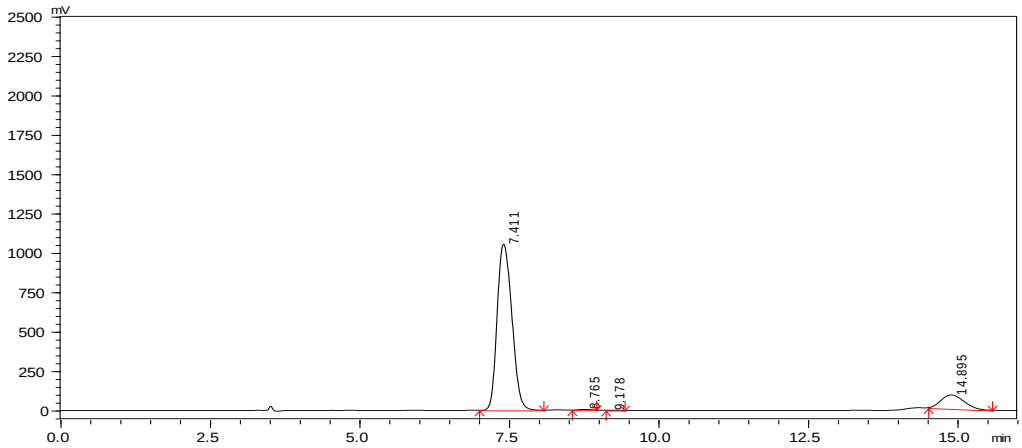
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.471	2688064	27356214	78.762
2	4.846	15225	56231	0.162
3	5.169	806563	7259850	20.902
4	5.552	8303	60341	0.174
total		3518155	34732637	100.000

HPLC chromatogram of compound **5d** (99% ee, 7:1 dr)



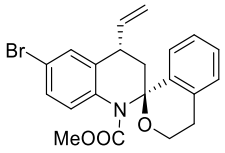


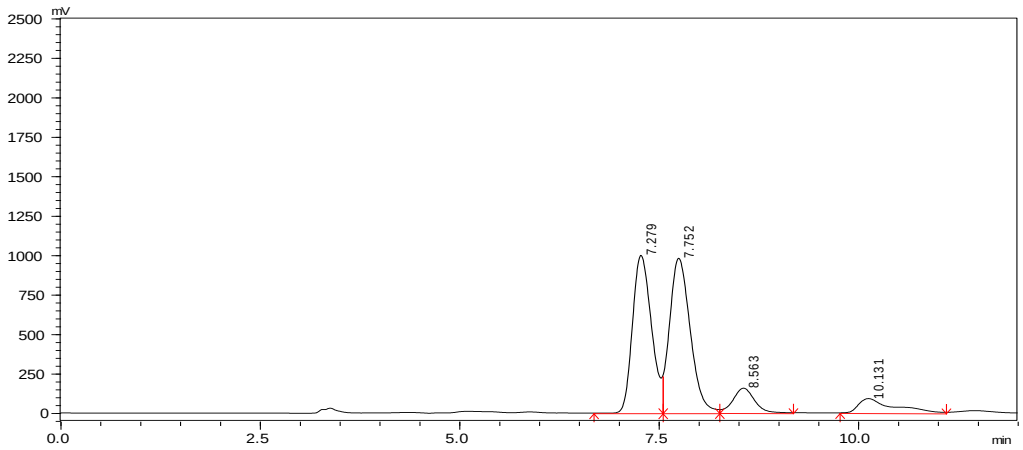
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.435	591020	9721267	45.132
2	8.727	521327	9860443	45.778
3	9.192	59013	994963	4.619
4	14.969	34399	963051	4.471
total		1205758	21539724	100.000



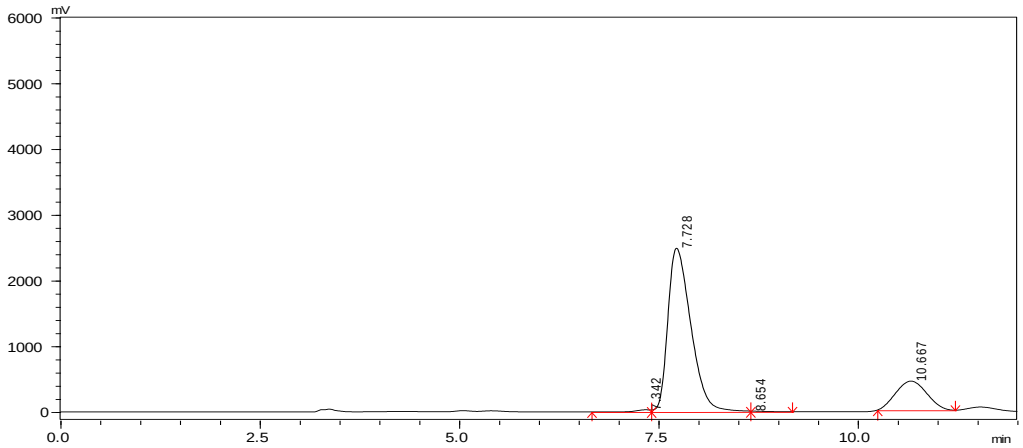
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.411	1054371	18092488	88.301
2	8.765	4159	57321	0.280
3	9.178	506	5995	0.029
4	14.895	87659	2333644	11.389
total		1146694	20489449	100.000

HPLC chromatogram of compound **5e** (98% ee, 4:1 dr)



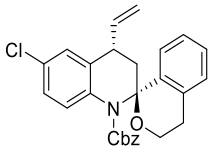


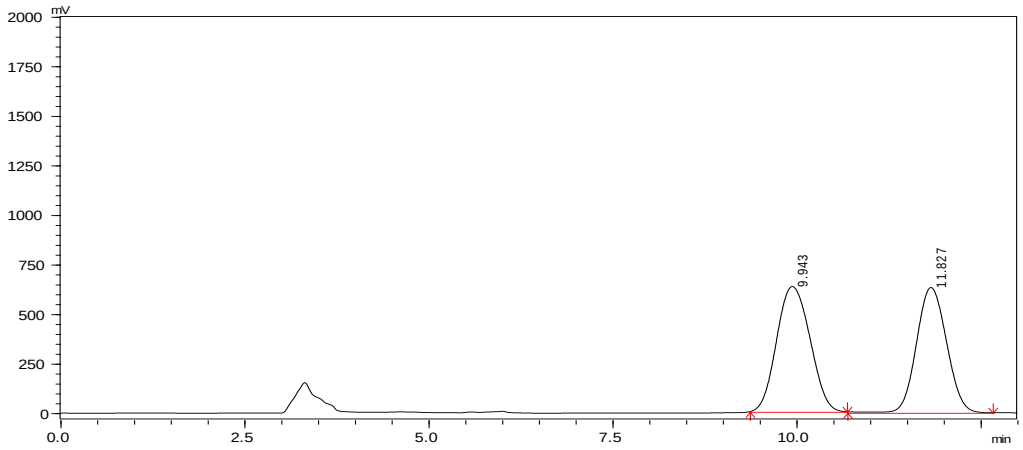
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.279	999182	16611332	41.512
2	7.752	981248	17621811	44.037
3	8.563	156744	2933340	7.330
4	10.131	91103	2849456	7.121
total		2228277	40015939	100.000



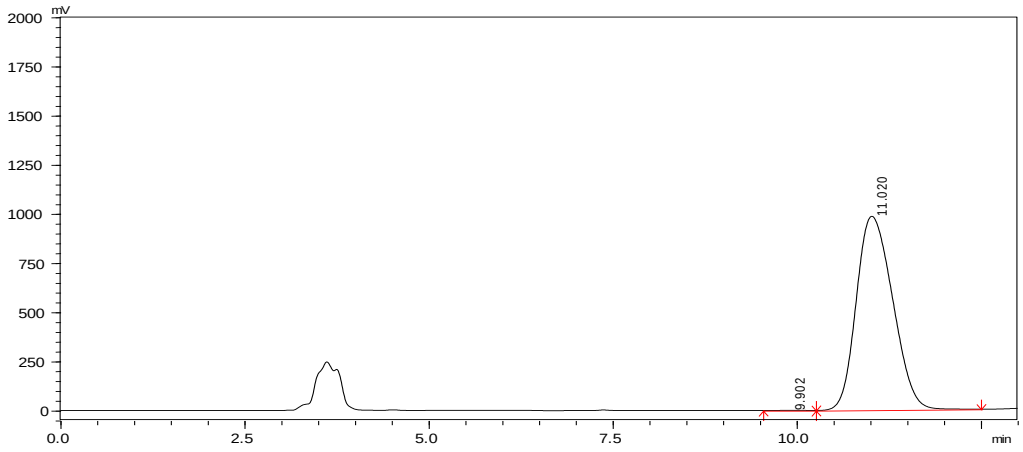
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	7.342	31483	379313	0.608
2	7.728	2487139	49967390	80.078
3	8.654	10859	114205	0.183
4	10.667	440975	11937104	19.131
total		2970455	62398012	100.000

HPLC chromatogram of compound **5f** (99% ee)



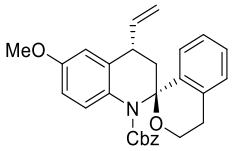


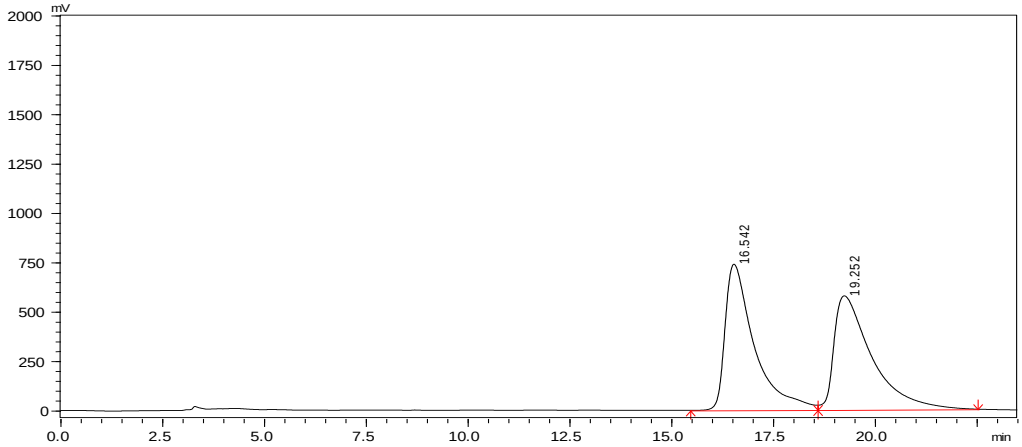
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.943	631295	19886569	52.565
2	11.827	631609	17945995	47.435
total		1262904	37832563	100.000



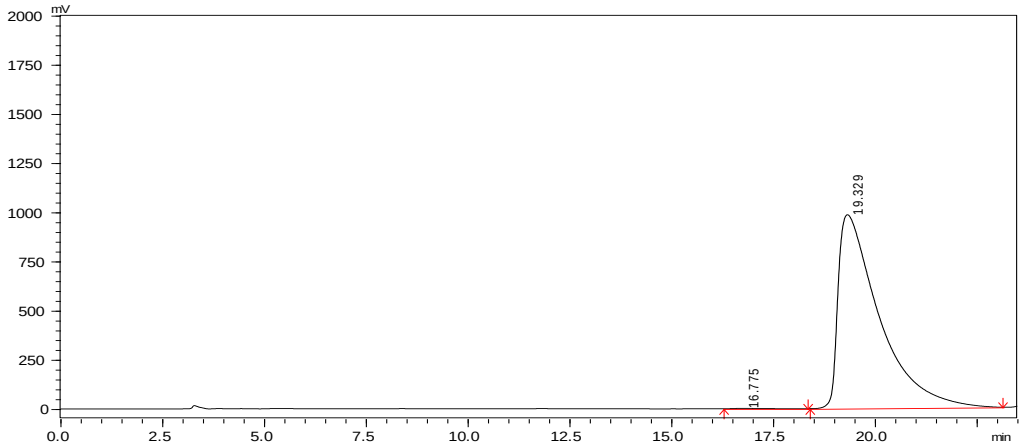
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	9.902	518	8396	0.025
2	11.020	985111	33880161	99.975
total		985629	33888557	100.000

HPLC chromatogram of compound **5g** (99% ee)



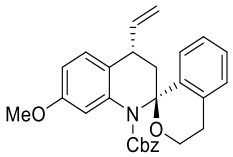


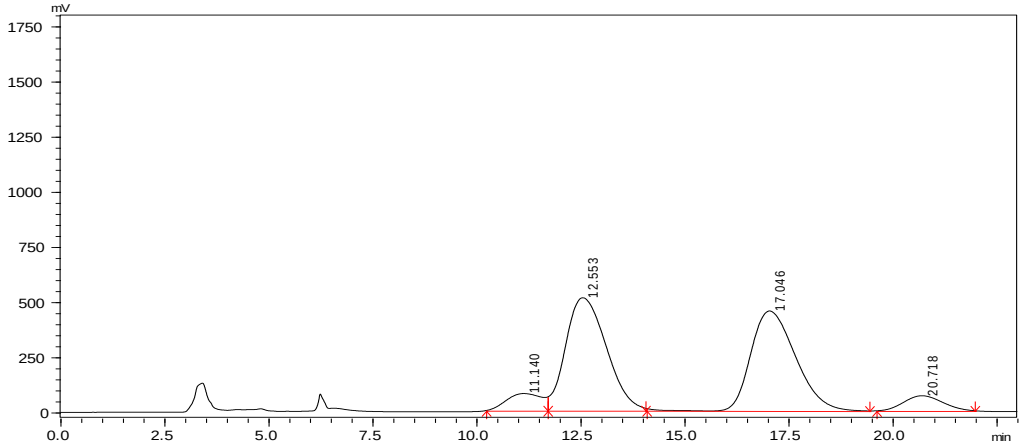
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	16.542	739165	36821868	49.781
2	19.252	576552	37146218	50.219
total		1315717	73968086	100.000



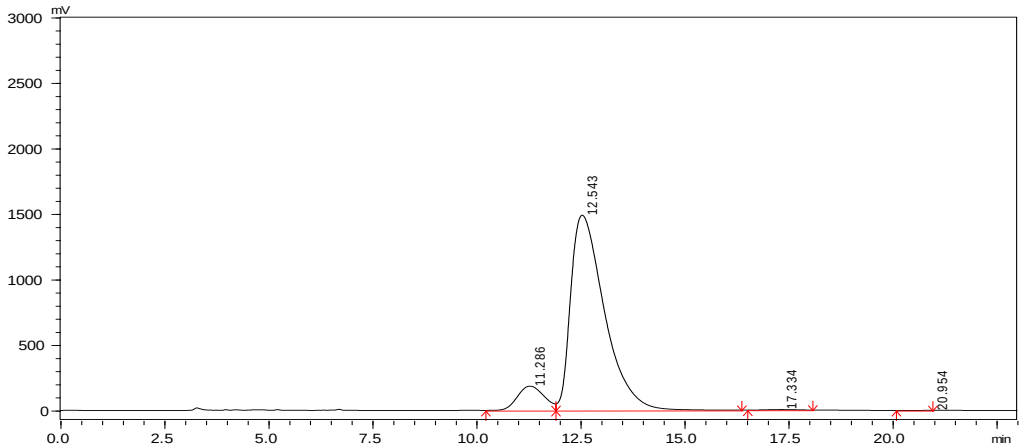
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	16.775	2105	74744	0.108
2	19.329	984560	69088860	99.892
total		986665	69163603	100.000

HPLC chromatogram of compound **5h** (99% ee, 10:1 dr)



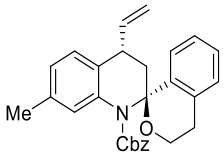


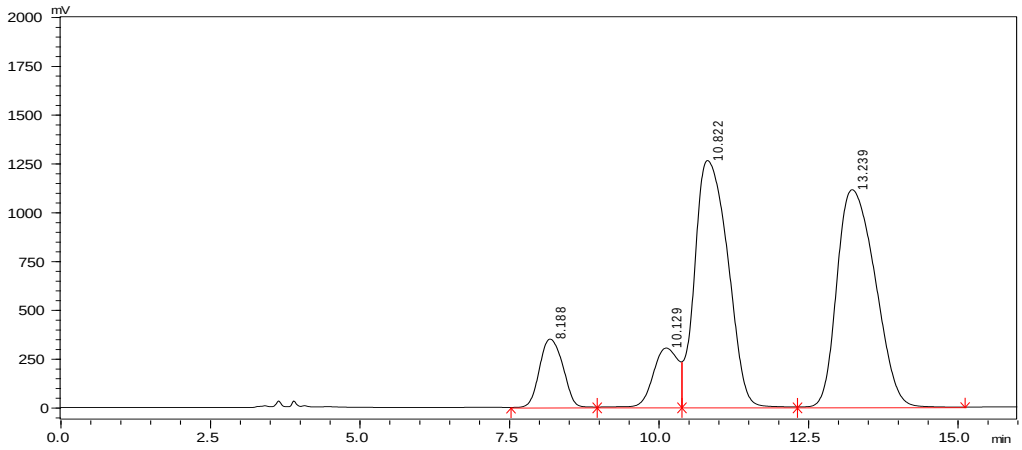
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.140	77472	4574173	5.911
2	12.553	511332	34804350	44.978
3	17.046	452354	33617848	43.445
4	20.718	68144	4384648	5.666
total		1109302	77381020	100.000



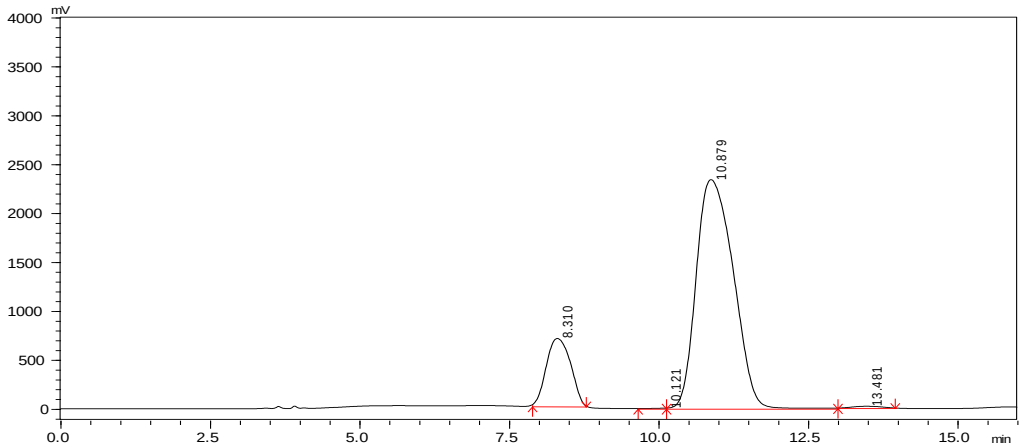
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.286	184970	8173087	8.834
2	12.543	1489941	84164459	90.968
3	17.334	3777	177230	0.192
4	20.954	275	5991	0.006
total		1678963	92520767	100.000

HPLC chromatogram of compound **5i** (99% ee, 5:1 dr)



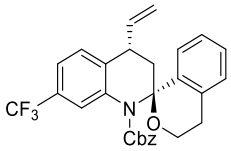


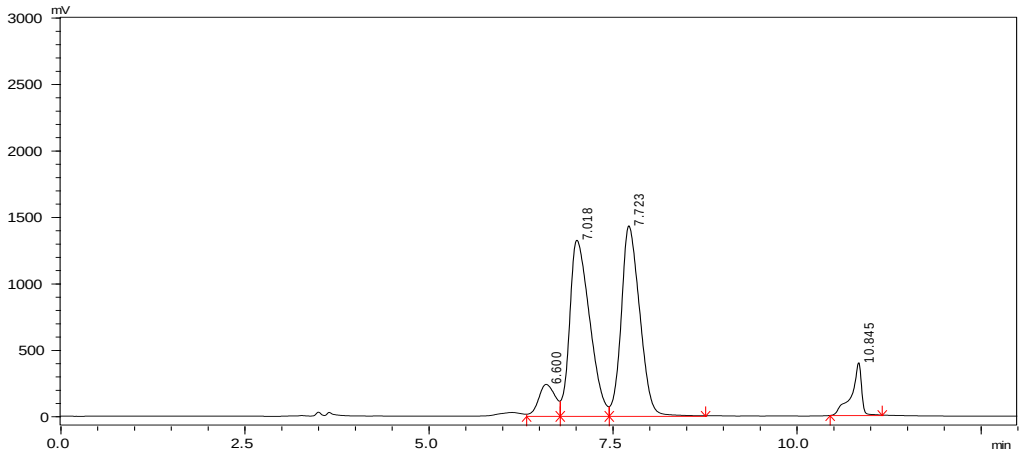
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.188	349513	9490404	8.149
2	10.129	303325	8747137	7.510
3	10.822	1263120	48732265	41.842
4	13.239	1114022	49497452	42.499
total		3029980	116467258	100.000



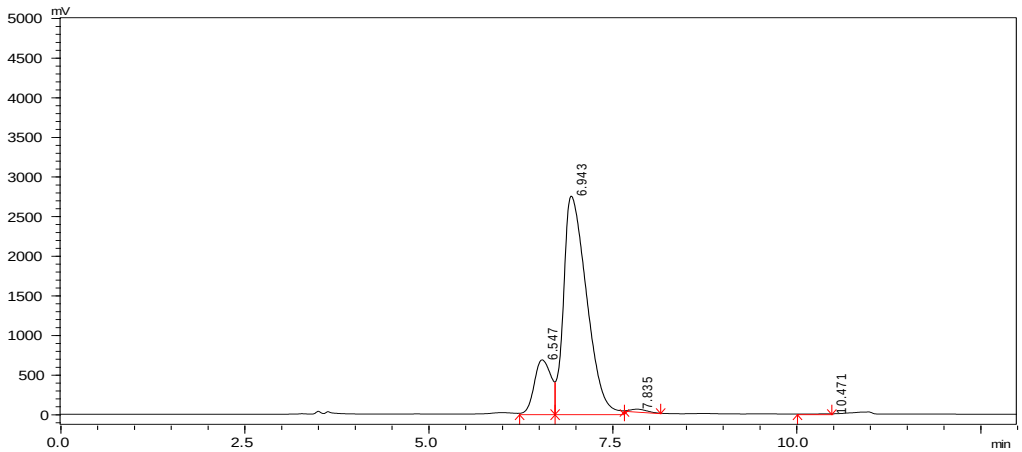
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	8.310	693176	19603383	16.198
2	10.121	4885	52985	0.044
3	10.879	2339986	100791125	83.280
4	13.481	17992	578849	0.478
total		3056038	121026342	100.000

HPLC chromatogram of compound **5j** (99% ee, 6:1 dr)



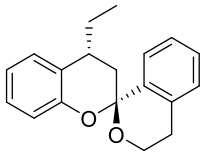


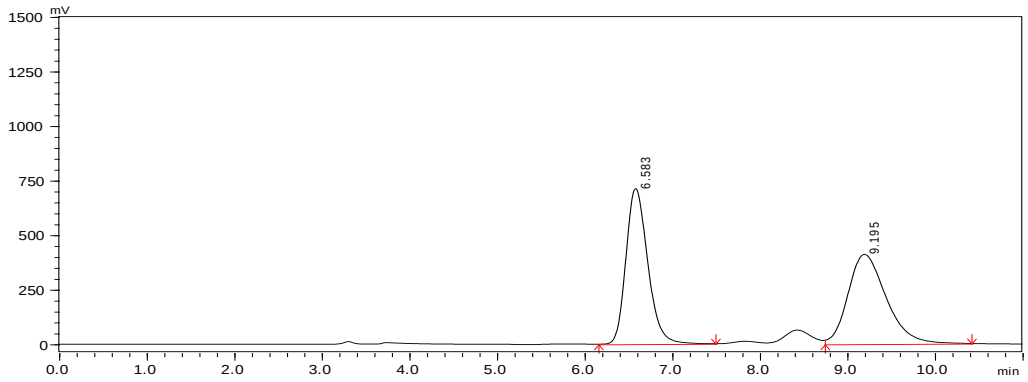
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.600	236714	3647812	6.403
2	7.018	1321175	24862405	43.639
3	7.723	1429196	24780938	43.496
4	10.845	392670	3681720	6.462
total		3379754	56972875	100.000



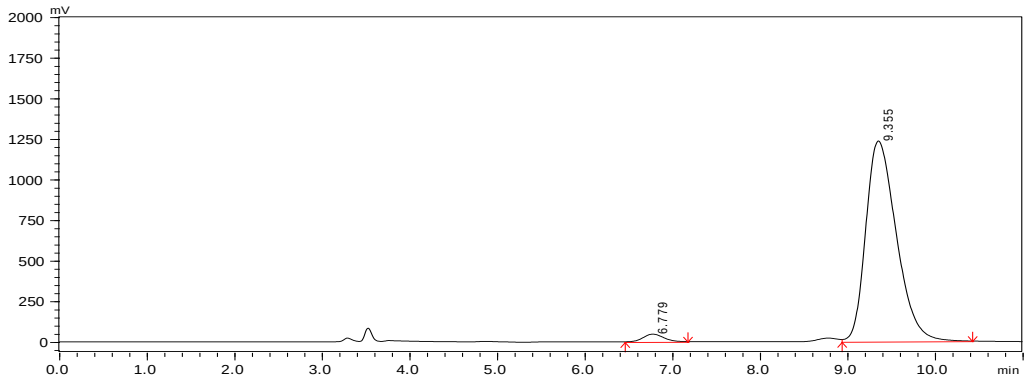
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.547	682477	10769672	15.156
2	6.943	2748653	59851600	84.230
3	7.835	30942	413076	0.581
4	10.471	2346	23064	0.032
total		3464417	71057412	100.000

HPLC chromatogram of compound **6** (95% ee)



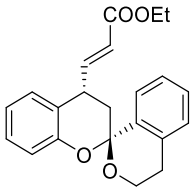


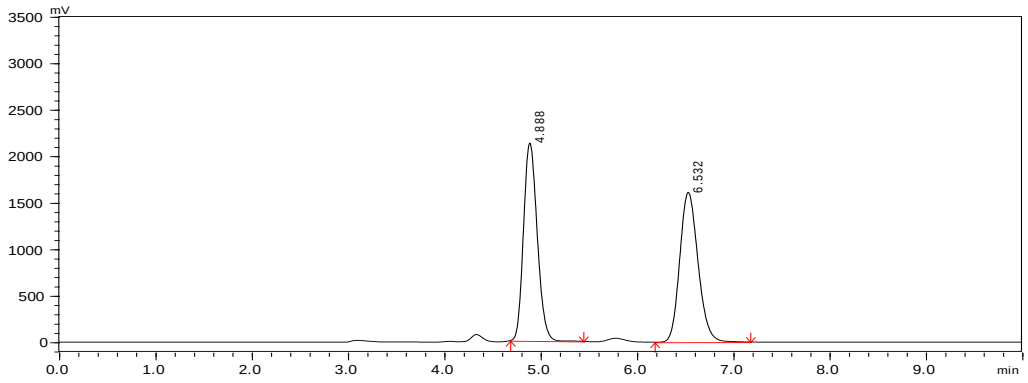
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.583	712398	12321774	49.727
2	9.195	410815	12457021	50.273
total		1123213	24778794	100.000



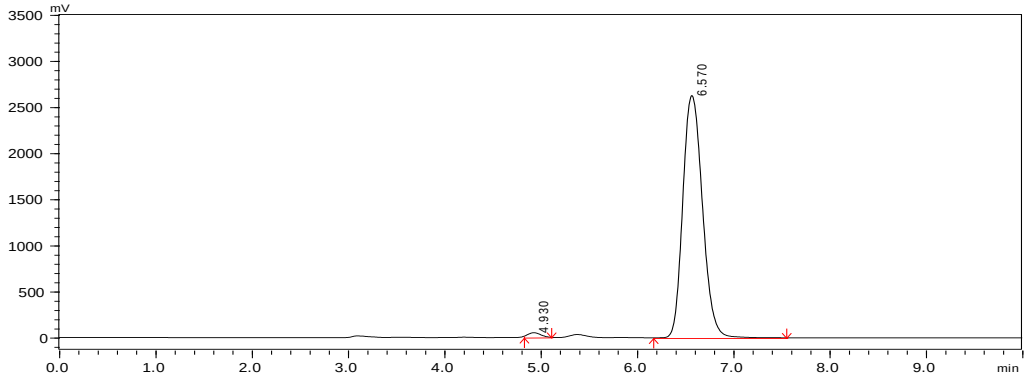
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	6.779	46475	736244	2.393
2	9.355	1234772	30031829	97.607
total		1281247	30768073	100.000

HPLC chromatogram of compound **7** (98% ee)



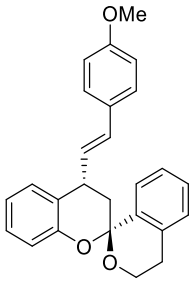


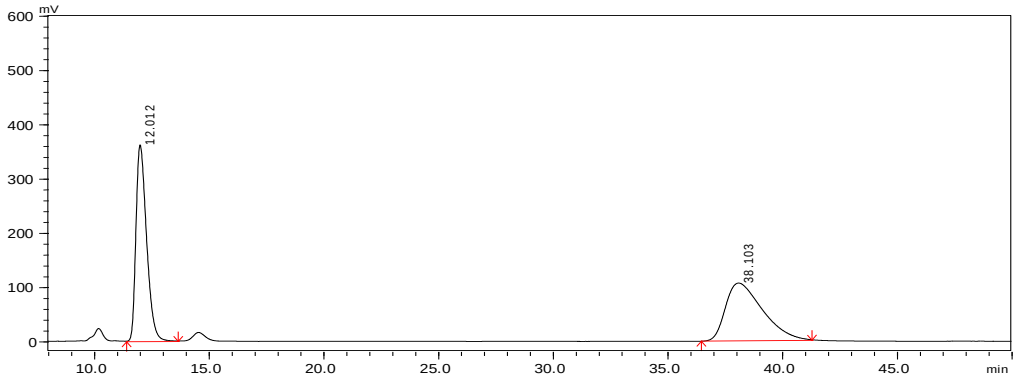
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.888	2126824	21043754	49.796
2	6.532	1610059	21216299	50.204
total		3736883	42260053	100.000



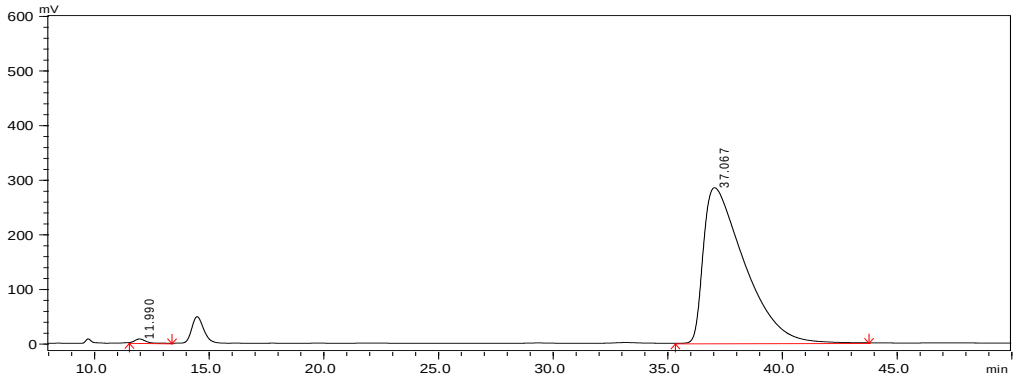
#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	4.930	50237	462967	1.227
2	6.570	2624985	37256381	98.773
total		2675222	37719347	100.000

HPLC chromatogram of compound **8** (99% ee)





#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	12.012	361467	11604708	50.015
2	38.103	105248	11597734	49.985
total		466715	23202443	100.000



#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	11.990	7010	192279	0.540
2	37.067	284679	35419503	99.460
total		291689	35611782	100.000