Supporting Information

Brønsted Acid Catalyzed [4 + 2] Cycloaddition for the Synthesis of Bisbenzannulated Spiroketals with Antifungal Activities

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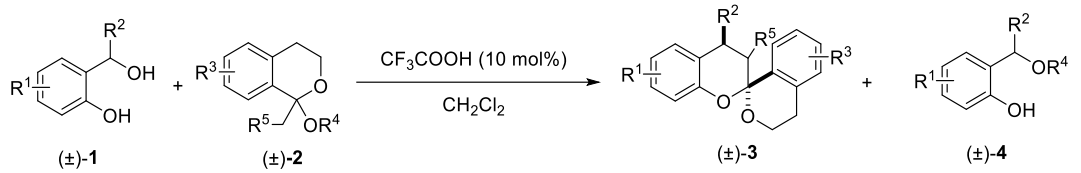
1. General information

^{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; q, quartet; m, multiplet; dd, double doublet; dt, double triplet; ddd, double double doublet; td, triple doublet; 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 (565 MHz) spectra were recorded on a Bruker DPX 600 MHz spectrometer in $CDCl_3$ and referenced relative to $CFCl_3$. Enantiomeric excesses were determined by analysis of HPLC traces, obtained by using Chiralcel OD-H, columns with *n*-hexane and *i*-propanol as solvents (Chiralcel OD-H columns were purchased from Daicel Chiral Technologies (China) Co., Ldq.). Melting points were obtained in open capillary tubes using SGW X-4 micro melting point apparatus which were uncorrected or Optimelt MPA 100 automatic melting point apparatus. 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. Solvents were purified according to the procedure from *Purification of Laboratory Chemicals*. Feng's chiral *N,N*' -dioxide ligands **8** were prepared according to the literature procedure.[1] Substrates *o*-hydroxyl benzyl alcohols **(±)-1**[2] and isochroman ketals **(±)-2**[3] were prepared according to the literature procedures.

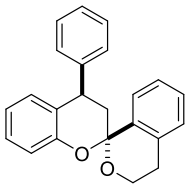
2. Synthesis and characterization data of bisbenzannulated spiroketals 3 and product 4



General procedure A: *o*-Hydroxy benzyl alcohols **(±)-1** (0.6 mmol, 2.0 equiv), CF_3COOH (0.03 mmol, 0.1 equiv) and freshly distilled CH_2Cl_2 (3.0 mL) were added sequentially to a flame dried 10 mL Schlenk tube. Then, isochroman ketals **(±)-2** (0.3 mmol, 1.0 equiv) were added. The reaction mixture was stirred at room temperature until **(±)-2** were consumed (monitored by TLC), which was directly purified by flash column chromatography silica gel (petroleum ether/EtOAc = 20/1) to afford bisbenzannulated spiroketals **(±)-3** and ether products **(±)-4**.

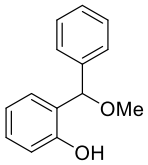
General procedure B: *o*-Hydroxy benzyl alcohols **(±)-1** (0.6 mmol, 2.0 equiv), CF_3COOH (0.03 mmol, 0.1 equiv) and freshly distilled CH_2Cl_2 (3.0 mL) were added sequentially to a flame dried 10 mL Schlenk tube. Then, isochroman ketals **(±)-2** (0.3 mmol, 1.0 equiv) were added. The reaction mixture was stirred at 40 °C until **(±)-2** were consumed (monitored by TLC), which was directly purified by flash column chromatography silica gel (petroleum ether/EtOAc = 20/1) to afford bisbenzannulated spiroketals **(±)-3** and ether products **(±)-4**.

General procedure C: *o*-Hydroxy benzyl alcohols **(±)-1** (0.6 mmol, 2.0 equiv), CF_3COOH (0.15 mmol, 0.5 equiv) and freshly distilled CH_2Cl_2 (3.0 mL) were added sequentially to a flame dried 10 mL Schlenk tube. Then, isochroman ketals **(±)-2** (0.3 mmol, 1.0 equiv) were added. The reaction mixture was stirred at room temperature until **(±)-2** were consumed (monitored by TLC), which was directly purified by flash column chromatography silica gel (petroleum ether/EtOAc = 20/1) to afford bisbenzannulated spiroketals **(±)-3** and ether products **(±)-4**.

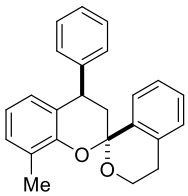


4-Phenylspiro[chromane-2,1'-isochromane] ((±)-3a): Following the general procedure A, compound **(±)-3a** was obtained as a white solid in 97% yield (95.4 mg);

R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 99-103 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 6.9, 2.2 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.22 – 7.10 (m, 4H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.86 – 6.79 (m, 1H), 4.51 (dd, *J* = 12.8, 5.8 Hz, 1H), 4.29 – 4.18 (m, 1H), 4.04 – 3.93 (m, 1H), 3.13 (ddd, *J* = 17.5, 12.7, 5.9 Hz, 1H), 2.72 – 2.63 (m, 1H), 2.59 (dd, *J* = 13.4, 12.8 Hz, 1H), 2.26 (dd, *J* = 13.4, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 144.5, 136.3, 134.6, 129.6, 129.1(2C), 128.9, 128.8(2C), 128.5, 127.7, 126.8(8), 126.8(6), 126.6, 126.2, 121.1, 117.4, 97.0, 59.5, 42.0, 39.3, 28.8; **HRMS** (EI, m/z): calcd for $C_{23}H_{20}O_2$ $[M]^+$: 328.1458, found: 328.1466.

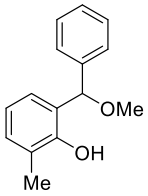


2-(Methoxy(phenyl)methyl)phenol((±)-4a)[4]: Following the general procedure A, compound **(±)-4a** was obtained as a colorless oily liquid in 60% yield (42.3 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.36 – 7.30 (m, 5H), 7.22 – 7.16 (m, 1H), 6.92 – 6.86 (m, 2H), 6.84 – 6.78 (m, 1H), 5.44 (s, 1H), 3.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.7, 139.9, 129.5, 129.0, 128.7(2C), 128.3, 127.4(2C), 124.9, 119.9, 117.3, 86.8, 57.4.

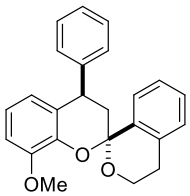


8-Methyl-4-phenylspiro[chromane-2,1'-isochromane](±)-3b): Following the general procedure A, compound **(±)-3b** was obtained as a white solid in 45% yield (35.9 mg); R_f = 0.85 (petroleum ether/EtOAc = 4/1); mp = 112-115 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.1, 4.0 Hz, 1H), 7.36 – 7.30 (m, 5H), 7.26 – 7.17 (m, 5H), 7.01 (t, *J* = 5.6 Hz, 1H), 6.76 – 6.70 (m, 1H), 6.67 – 6.60 (m, 1H), 4.50 (dd, *J* = 11.9, 5.0 Hz, 1H), 4.25 – 4.12 (m, 1H), 4.01 – 3.93 (m, 1H), 3.14 (ddd, *J* = 17.1, 11.1, 4.9 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.58 (dd, *J* = 13.2, 11.9 Hz, 1H), 2.25 (dd, *J* = 13.2, 5.0 Hz, 1H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 144.8, 136.8, 134.7,

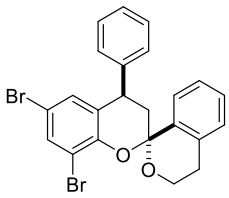
129.1(2C), 128.9(0), 128.8(9), 128.7(2C), 128.2, 127.2, 126.9, 126.8, 126.7, 126.4, 125.6, 120.3, 96.9, 59.6, 42.1, 39.40, 29.0, 16.5; **HRMS** (EI, m/z): calcd for $C_{23}H_{19}FO_2$ $[M]^+$: 342.1614, found: 342.1622.



2-(Methoxy(phenyl)methyl)-6-methylphenol((±)-4b): Following the general procedure A, compound **(±)-4b** was obtained as a colorless oily liquid in 38% yield (28.7 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.38 – 7.25 (m, 5H), 6.73 (d, *J* = 6.1 Hz, 2H), 5.42 (s, 1H), 3.47 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.8, 140.0, 130.7, 128.7(2C), 128.2, 127.3(2C), 126.7, 126.2, 124.1, 119.4, 86.9, 57.4, 16.0;**HRMS** (EI, m/z): calcd for $C_{14}H_{13}FO_2$ $[M]^+$: 228.1150, found: 228.1152.



8-Methoxy-4-phenylspiro[chromane-2,1'-isochromane](±)-3c): Following the general procedure B, compound **(±)-3c** was obtained as a white solid in 80% yield (85.9 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 98-101 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 5.7, 3.6 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.30 – 7.23 (m, 5H), 7.16 (d, *J* = 7.1 Hz, 1H), 6.82 – 6.70 (m, 2H), 6.42 (dd, *J* = 5.7, 2.6 Hz, 1H), 4.50 (dd, *J* = 12.5, 5.5 Hz, 1H), 4.31 – 4.20 (m, 1H), 4.01 – 3.92 (m, 1H), 3.81 (s, 3H), 3.13 (ddd, *J* = 17.8, 12.6, 5.9 Hz, 1H), 2.73 – 2.66 (m, 1H), 2.59 (dd, *J* = 13.3, 12.5 Hz, 1H), 2.25 (dd, *J* = 13.3, 5.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 144.8, 143.1, 136.3, 134.7, 129.1(2C), 128.7(5), 128.7(3)(2C), 128.3, 127.1, 126.9(4), 126.8(6), 126.8, 121.5, 120.3, 110.1, 97.0, 59.7, 56.2, 42.2, 39.5, 28.9; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_3$ $[M]^+$: 358.1563, found: 358.1566.



6,8-Dibromo-4-phenylspiro[chromane-2,1'-isochromane]((±)-3d): Following the general procedure B, compound **(±)-3d** was obtained as a white solid in 62% yield (90.3 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 121-123 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.51 (m, 1H), 7.43 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.31 – 7.24 (m, 5H), 7.22 – 7.17 (m, 1H), 6.88 (dd, *J* = 2.4, 1.2 Hz, 1H), 4.48 (dd, *J* = 12.8, 6.0 Hz, 1H), 4.19 (ddd, *J* = 12.6, 11.1, 2.9 Hz, 1H), 4.01 – 3.93 (m, 1H), 3.13 (ddd, *J* = 17.8, 12.6, 5.9 Hz, 1H), 2.74 – 2.67 (m, 1H), 2.57 (dd, *J* = 13.6, 12.8 Hz, 1H), 2.25 (dd, *J* = 13.6, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.6, 143.2, 135.3, 134.6, 133.6, 131.4, 129.9, 129.1(2C), 129.0(2C), 128.8, 128.7, 127.4, 126.9, 126.7, 113.1, 112.8, 98.1, 60.0, 41.8, 39.8, 28.7; **HRMS** (EI, m/z): calcd for $C_{23}H_{18}{}^{79}Br_2O_2$ $[M]^+$: 483.9668, found: 483.9673, calcd for $C_{23}H_{18}{}^{79}Br^{81}BrO_2$ $[M]^+$: 485.9648, found: 485.9659, calcd for $C_{23}H_{18}{}^{81}Br_2O_2$ $[M]^+$: 489.9628, found: 489.9637.

The preparation and X-ray analysis of the single crystal: Compound **(±)-3d** (10.0 mg) was dissolved in 1.0 mL of $CHCl_3$ in a screw-top vial and drops of 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 213(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 2340632 contains the supplementary crystallographic data, and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

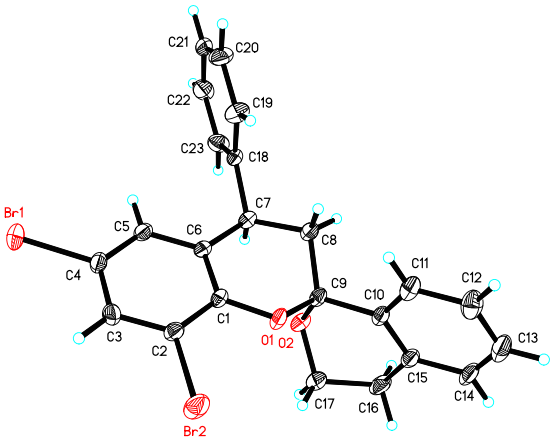


Figure S1. The thermal ellipsoid plot for X-ray structure of compound **(±)-3d** with the ellipsoid contour

The crystallographic data of compound (±)-3d

Identification code mo_dd23006_0m

Empirical formula C23 H18 Br2 O2

Formula weight 486.19

Temperature 213(2) K

Wavelength 0.71073 Å

Crystal system Monoclinic

Space group P 21/c

Unit cell dimensions a = 10.2643(5) Å a= 90Å

b = 9.0256(5) Å b= 94.116(2)Å

c = 21.2231(13) Å g = 90Å

Volume 1961.07(19) $Å^3$

Z 4

Density (calculated) 1.647 Mg/m^3

Absorption coefficient 4.149 mm^{-1}

F(000) 968

Crystal size 0.160 x 0.140 x 0.100 mm^3

Theta range for data collection 2.667 to 25.999°

Index ranges -12<=h<=12, -11<=k<=11, -26<=l<=26

Reflections collected 18359

Independent reflections 3855 [R(int) = 0.0533]

Completeness to theta = 25.242° 99.9 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7456 and 0.5165

Refinement method Full-matrix least-squares on F2

Data / restraints / parameters 3855 / 0 / 244

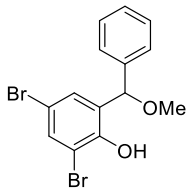
Goodness-of-fit on F2 1.021

Final R indices [I>2sigma(I)] R1 = 0.0345, wR2 = 0.0681

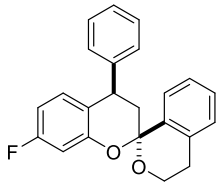
R indices (all data) R1 = 0.0587, wR2 = 0.0772

Extinction coefficient n/a

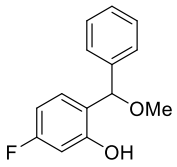
Largest diff. peak and hole 0.514 and -0.465 $e.Å^{-3}$



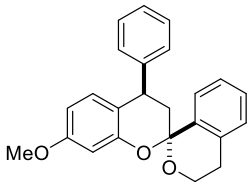
2,4-Dibromo-6-(methoxy(phenyl)methyl)phenol((±)-4d): Following the general procedure B, compound **(±)-4d** was obtained as a colorless oily liquid in 45% yield (54.4 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.36 – 7.31 (m, 4H), 7.25 (s, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 5.44 (s, 1H), 3.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 139.2, 134.2, 130.3, 129.1, 128.9(2C), 128.7, 127.3(2C), 112.2, 111.9, 84.0, 57.5; **HRMS** (EI, m/z): calcd for $C_{14}H_{12}{}^{79}Br_2O_2$ $[M]^+$: 369.9199, found: 369.9207. $C_{14}H_{12}{}^{79}Br^{81}BrO_2$ $[M]^+$: 371.9179, found: 371.9203, $C_{14}H_{12}{}^{81}Br_2O_2$ $[M]^+$: 373.9159, found: 373.9163.



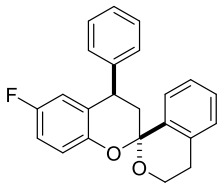
7-Fluoro-4-phenylspiro[chromane-2,1'-isochromane](±)-3e): Following the general procedure A, compound **(±)-3e** was obtained as a white solid in 98% yield (101.7 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 115-118 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.27 – 7.23 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 6.78 – 6.71 (m, 1H), 6.62 (dd, *J* = 10.1, 2.6 Hz, 1H), 6.58 – 6.50 (m, 1H), 4.44 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.27 – 4.13 (m, 1H), 4.06 – 3.95 (m, 1H), 3.13 (ddd, *J* = 17.7, 12.5, 5.9 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.55 (dd, *J* = 13.5, 12.9 Hz, 1H), 2.25 (dd, *J* = 13.5, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2 (d, C-F, $^1J_{C\text{-}F}$ = 244.0 Hz), 154.2 (d, C-F, $^3J_{C\text{-}F}$ = 11.9 Hz), 144.2, 135.9, 134.6, 130.6 (d, C-F, $^3J_{C\text{-}F}$ = 9.5 Hz), 129.0 (2C), 128.9(1), 128.8(7) (2C), 128.6, 127.0, 126.9, 126.6, 122.0 (d, C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 108.2 (d, C-F, $^2J_{C\text{-}F}$ = 21.3 Hz), 104.5 (d, C-F, $^2J_{C\text{-}F}$ = 24.2 Hz), 97.4, 59.7, 41.9, 38.8, 28.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -112.63 – -117.49 (m); **HRMS** (EI, m/z): calcd for $C_{23}H_{19}FO_2$ $[M]^+$: 346.1364, found: 346.1371.



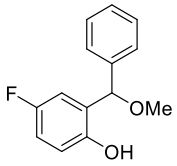
5-Fluoro-2-(methoxy(phenyl)methyl)phenol((±)-4e): Following the general procedure A, compound **(±)-4e** was obtained as a colorless oily liquid in 45% yield (41.7 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.39 – 7.29 (m, 5H), 6.78 (dd, *J* = 8.5, 6.5 Hz, 1H), 6.64 – 6.59 (m, 1H), 6.54 – 6.47 (m, 1H), 5.41 (s, 1H), 3.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.5 (d, C-F, $^1J_{C\text{-}F}$ = 245.3 Hz), 157.2 (d, C-F, $^3J_{C\text{-}F}$ = 12.2 Hz), 139.6, 129.9 (d, C-F, $^3J_{C\text{-}F}$ = 10.2 Hz), 128.8 (2C), 128.5, 127.4 (2C), 120.9 (d, C-F, $^4J_{C\text{-}F}$ = 3.1 Hz), 106.8 (d, C-F, $^2J_{C\text{-}F}$ = 21.7 Hz), 104.7 (d, C-F, $^2J_{C\text{-}F}$ = 24.4 Hz), 86.3, 57.3;**^{19}F NMR** (565 MHz, $CDCl_3$) δ -110.11 – -115.06 (m); **HRMS** (EI, m/z): calcd for $C_{14}H_{13}FO_2$ $[M]^+$: 232.0900, found: 232.0898.



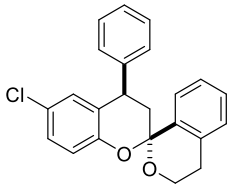
7-Methoxy-4-phenylspiro[chromane-2,1'-isochromane](±)-3f): Following the general procedure A, compound **(±)-3f** was obtained as a white solid in 65% yield (69.8 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 95-97 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 1H), 7.35 – 7.31 (m, 2H), 7.31 – 7.24 (m, 5H), 7.19 (dd, *J* = 6.6, 2.2 Hz, 1H), 6.70 (dd, *J* = 8.5, 1.1 Hz, 1H), 6.49 (d, *J* = 2.6 Hz, 1H), 6.43 (dd, *J* = 8.6, 2.6 Hz, 1H), 4.43 (dd, *J* = 12.8, 5.7 Hz, 1H), 4.24 (ddd, *J* = 12.5, 11.3, 3.0 Hz, 1H), 4.00 (ddd, *J* = 11.2, 5.9, 1.2 Hz, 1H), 3.19 – 3.08 (m, 1H), 2.78 – 2.65 (m, 1H), 2.55 (dd, *J* = 13.4, 12.8 Hz, 1H), 2.25 (dd, *J* = 13.4, 5.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 154.0, 144.7, 136.2, 134.6, 130.2, 129.0(2C), 128.9, 128.8(2C), 128.5, 126.9, 126.8, 126.6, 118.4, 108.0, 102.1, 97.3, 59.6, 55.4, 42.2, 38.7, 28.8; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_3$[M]$^+$: 358.1563, found: 358.1572.



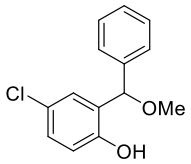
6-Fluoro-4-phenylspiro[chromane-2,1'-isochromane]((±)-3g): Following the general procedure , compound **(±)-3g** was obtained as a white solid in 85% yield (95.8 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 113-117 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 5H), 7.22 – 7.17 (m, 1H), 6.83 (d, *J* = 5.9 Hz, 2H), 6.52 (d, *J* = 9.5 Hz, 1H), 4.47 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.26 – 4.14 (m, 1H), 4.04 – 3.94 (m, 1H), 3.13 (ddd, *J* = 17.8, 12.6, 5.9 Hz, 1H), 2.75 – 2.65 (m, 1H), 2.56 (dd, *J* = 13.5, 12.9 Hz, 1H), 2.26 (dd, *J* = 13.5, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.3 (d, C-F, $^1J_{C-F}$ = 238.4 Hz), 149.3 (d, C-F, $^4J_{C-F}$ = 2.3 Hz), 143.7, 136.1, 134.6, 129.0(2C), 128.9(2C), 128.9, 128.6, 127.5 (d, C-F, $^3J_{C-F}$ = 7.0 Hz), 127.1, 126.9, 126.5, 118.3 (d, C-F, $^3J_{C-F}$ = 7.9 Hz), 115.6 (d, C-F, $^2J_{C-F}$ = 23.5 Hz), 114.5 (d, C-F, $^2J_{C-F}$ = 23.2 Hz), 97.1, 59.5, 41.6, 39.5, 28.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -122.82 – -122.97 (m); **HRMS** (EI, m/z): calcd for $C_{23}H_{19}FO_2$ $[M]^+$: 346.1364, found: 346.1366.



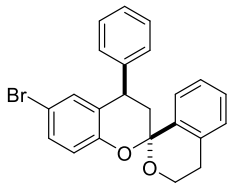
4-Fluoro-2-(methoxy(phenyl)methyl)phenol((±)-4g): Following the general procedure A, compound **(±)-4g** was obtained as a colorless oily liquid in 41% yield (28.5 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.39 – 7.26 (m, 5H), 6.92 – 6.70 (m, 2H), 6.65 – 6.49 (m, 1H), 5.38 (s, 1H), 3.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4 (d, C-F, $^1J_{C-F}$ = 237.5 Hz), 151.4 (d, *J* = 2.2 Hz), 139.3, 128.8(2C), 128.5, 127.4(2C), 126.17 (d, C-F, $^3J_{C-F}$ = 6.5 Hz), 118.0 (d, C-F, $^3J_{C-F}$ = 7.8 Hz), 115.7 (d, C-F, $^2J_{C-F}$ = 22.9 Hz), 115.0 (d, C-F, $^2J_{C-F}$ = 23.9 Hz), 85.8 , 57.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -124.40 – -125.08 (m); **HRMS** (EI, m/z): calcd for $C_{14}H_{13}FO_2$ $[M]^+$: 232.0900, found: 232.0903.



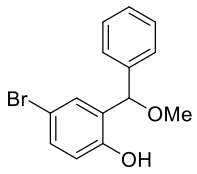
6-Chloro-4-phenylspiro[chromane-2,1'-isochromane]((±)-3h): Following the general procedure A, compound **(±)-3h** was obtained as a white solid in 91% yield (99.9 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 110-112 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.31 – 7.26 (m, 4H), 7.24 (s, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.08 (dd, *J* = 8.7, 2.6 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 1H), 6.80 – 6.78 (m, 1H), 4.46 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.24 – 4.14 (m, 1H), 4.02 – 3.95 (m, 1H), 3.13 (ddd, *J* = 17.8, 12.7, 5.9 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.56 (dd, *J* = 13.5, 12.9 Hz, 1H), 2.25 (dd, *J* = 13.5, 5.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 143.6, 135.9, 134.6, 129.2, 129.0(4)(2C), 129.0(1)(2C), 128.9, 128.6, 127.9, 127.8, 127.2, 126.9, 126.5, 125.9, 118.9, 97.2, 59.6, 41.7, 39.3, 28.8; **HRMS** (EI, m/z): calcd for $C_{23}H_{19}{}^{35}ClO_2$ $[M]^+$: 362.1068, found: 362.1070, calcd for $C_{23}H_{19}{}^{37}ClO_2$ $[M]^+$: 364.1039, found: 364.1050.



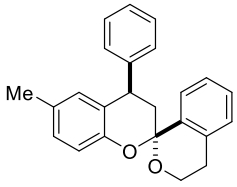
4-Chloro-2-(methoxy(phenyl)methyl)phenol((±)-4h): Following the general procedure A, compound **(±)-4h** was obtained as a colorless oily liquid in 40% yield (29.7 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.39 – 7.30 (m, 5H), 7.16 – 7.08 (m, 1H), 6.88 – 6.77 (m, 2H), 5.37 (s, 1H), 3.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.0, 143.6, 135.9, 134.6, 129.2, 129.0(4)(2C), 129.0(1)(2C), 128.9, 128.6, 127.9, 127.8, 127.2, 126.9, 126.5, 125.9, 118.9, 97.2, 59.6, 41.7, 39.3, 28.8; **HRMS** (EI, m/z): calcd for $C_{14}H_{13}{}^{35}ClO_2$ $[M]^+$: 248.0599, found: 248.0607, calcd for $C_{14}H_{13}{}^{37}ClO_2$ $[M]^+$: 250.0570, found: 250.0578.



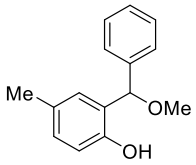
6-Bromo-4-phenylspiro[chromane-2,1'-isochromane]((±)-3i): Following the general procedure A, compound **(±)-3i** was obtained as a white solid in 93% yield (113.2 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 95-98 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.37 – 7.28 (m, 5H), 7.25 – 7.18 (m, 4H), 6.93 (dd, *J* = 2.5, 1.2 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 4.47 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.19 (ddd, *J* = 12.5, 11.2, 3.0 Hz, 1H), 3.98 (ddd, *J* = 11.2, 6.0, 1.2 Hz, 1H), 3.13 (ddd, *J* = 17.6, 12.5, 5.9 Hz, 1H), 2.74 – 2.63 (m, 1H), 2.55 (dd, *J* = 13.5,12.9 Hz, 1H), 2.25 (dd, *J* = 13.5, 5.8Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.5, 143.6, 135.8, 134.6, 132.1, 130.7, 129.0(1)(2C), 129.0(0)(2C), 128.9, 128.6, 128.5, 127.2, 126.9, 126.5, 119.4, 113.4, 97.2, 59.6, 41.7, 39.3, 28.8; **HRMS** (EI, m/z): calcd for $C_{23}H_{19}{}^{79}BrO_2$ $[M]^+$: 406.0563, found: 406.0565, calcd for $C_{23}H_{19}{}^{81}BrO_2$ $[M]^+$: 408.0543, found: 408.0552.



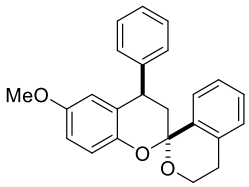
4-Bromo-2-(methoxy(phenyl)methyl)phenol((±)-4i): Following the general procedure A, compound **(±)-4i** was obtained as a colorless oily liquid in 50% yield (43.8 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1);**^{1}H NMR** (400 MHz, CDCl3) δ 8.11 (s, 1H), 7.38 – 7.31 (m, 5H), 7.29 – 7.25 (m, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 5.37 (s, 1H), 3.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.7, 139.2, 132.2, 131.4, 128.9(2C), 128.7, 127.4(2C), 127.0, 119.2, 111.8, 86.2, 57.4; **HRMS** (EI, m/z): calcd for $C_{14}H_{13}{}^{79}BrO_2$ $[M]^+$: 292.0094, found: 292.0098, calcd for $C_{14}H_{13}{}^{81}BrO_2$ $[M]^+$: 294.0073, found: 294.0081.



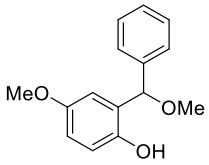
6-Methyl-4-phenylspiro[chromane-2,1'-isochromane]((±)-3j): Following the general procedure A, compound **(±)-3j** was obtained as a white solid in 98% yield (100.5 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 100-102 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 1H), 7.37 – 7.32 (m, 2H), 7.32 – 7.26 (m, 5H), 7.21 – 7.16 (m, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.62 (s, 1H), 4.47 (dd, *J* = 13.0, 5.7 Hz, 1H), 4.28 – 4.16 (m, 1H), 4.03 – 3.92 (m, 1H), 3.13 (ddd, *J* = 17.6, 12.6, 5.8 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.57 (dd, *J* = 13.5, 13.0 Hz, 1H), 2.24 (dd, *J* = 13.5, 5.7 Hz, 1H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 144.7, 136.4, 134.6, 130.3, 129.8, 129.1(2C), 128.9, 128.8(2C), 128.4(3), 128.4(2), 126.9, 126.8, 126.6, 125.7, 117.3, 96.9, 59.5, 42.2, 39.3, 28.9, 20.8; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_2$ $[M]^+$: 342.1614, found: 342.1623.



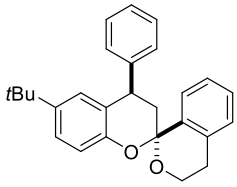
4-(Methoxy(phenyl)methyl)-4-methylphenol((±)-4j): Following the general procedure A, compound **(±)-4j** was obtained as a colorless oily liquid in 60% yield (41.0 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.43 – 7.21 (m, 5H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.71 (s, 1H), 5.38 (s, 1H), 3.46 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 140.1, 130.0, 129.4, 129.0, 128.7(2C), 128.3, 127.4(2C), 124.4, 117.1, 86.9, 57.4, 20.6; **HRMS** (EI, m/z): calcd for $C_{15}H_{16}O_2$ $[M]^+$: 228.1150, found: 228.1152.



6-Methoxy-4-phenylspiro[chromane-2,1'-isochromane]((±)-3k): Following the general procedure A, compound **(±)-3k** was obtained as a white solid in 80% yield (85.9 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 98-100 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.30 – 7.24 (m, 5H), 7.18 (d, *J* = 6.9 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 6.36 (s, 1H), 4.48 (dd, *J* = 12.9, 6.0 Hz, 1H), 4.28 – 4.15 (m, 1H), 4.02 – 3.93 (m, 1H), 3.61 (s, 3H), 3.13 (ddd, *J* = 18.3, 12.5, 6.1 Hz, 1H), 2.73 – 2.63 (m, 1H), 2.57 (dd, *J* = 13.8, 12.9 Hz, 1H), 2.25 (dd, *J* = 13.8, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.8, 147.4, 144.3, 136.4, 134.6, 129.1(2C), 128.9, 128.8(2C), 128.4, 126.9(0), 126.8(8), 126.8, 126.6, 118.0, 114.6, 113.6, 96.9, 59.5, 55.8, 42.0, 39.6, 28.9; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_3$ $[M]^+$: 358.1569, found: 358.1567.

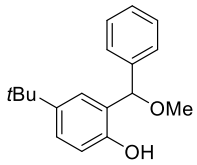


4-Methoxy-2-(methoxy(phenyl)methyl)phenol((±)-4k): Following the general procedure A, compound **(±)-4k** was obtained as a colorless oily liquid in 53% yield (36.7 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.37 – 7.32 (m, 4H), 7.29 – 7.23 (m, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.75 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.48 (d, *J* = 3.0 Hz, 1H), 5.38 (s, 1H), 3.69 (s, 3H), 3.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 149.4, 139.8, 128.7(2C), 127.4(2C), 125.6, 117.8, 114.6, 114.3, 86.5, 57.4, 55.8; **HRMS** (EI, m/z): calcd for $C_{15}H_{16}O_3$ $[M]^+$: 244.1099, found: 244.1096.

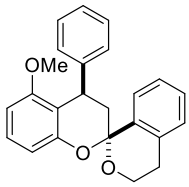


6-(*tert*-Butyl)-4-phenylspiro[chromane-2,1'-isochromane]((±)-3l): Following the general procedure A, compound **(±)-3l** was obtained as a white solid in 98% yield (111.7 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 120-122 ℃; **^{1}H NMR** (400

MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.0 Hz, 1H), 7.35 – 7.30 (m, 4H), 7.29 – 7.25 (m, 3H), 7.21 – 7.13 (m, 2H), 6.86 (s, 1H), 6.85 – 6.80 (m, 1H), 4.50 (dd, *J* = 12.9, 5.7 Hz, 1H), 4.29 – 4.18 (m, 1H), 4.04 – 3.94 (m, 1H), 3.13 (ddd, *J* = 17.9, 12.5, 5.9 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.55 (dd, *J* = 13.4, 12.9 Hz, 1H), 2.25 (dd, *J* = 13.4, 5.7 Hz, 1H), 1.16 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.1, 144.6, 143.6, 136.5, 134.6, 129.1(2C), 128.9, 128.7(2C), 128.4, 126.9, 126.8, 126.6(2), 126.5(5), 125.0, 124.6, 116.7, 96.9, 59.5, 42.4, 39.4, 34.2, 31.6(3C), 28.9; **HRMS** (EI, m/z): calcd for $C_{27}H_{28}O_2$ $[M]^+$: 384.2084, found: 384.2091.

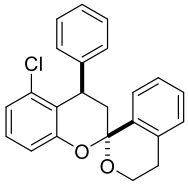


4-(*tert*-Butyl)-2-(methoxy(phenyl)methyl)phenol((±)-4l): Following the general procedure A, compound **(±)-4l** was obtained as a colorless oily liquid in 34% yield (28.34 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.36 – 7.32 (m, 4H), 7.26 – 7.19 (m, 2H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 5.42 (s, 1H), 3.48 (s, 3H), 1.23 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.1, 142.6, 140.2, 128.7(2C), 128.2, 127.4(2C), 126.3, 125.7, 123.9, 116.7, 87.2, 57.4, 34.1, 31.6; **HRMS** (EI, m/z): calcd for $C_{18}H_{22}O_2$ $[M]^+$: 270.1620, found: 270.1623.

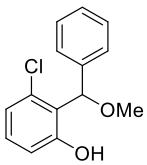


5-Methoxy-4-phenylspiro[chromane-2,1'-isochromane](±)-3m): Following the general procedure B, compound **(±)-3m** was obtained as a white solid in 83% yield (89.3 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 81-85 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.22 (m, 4H), 7.20 – 7.11 (m, 5H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.45 (d, *J* = 8.1 Hz, 1H), 4.38 (dd, *J* = 11.8, 7.5 Hz, 1H), 4.18 – 4.04 (m, 1H), 3.94 – 3.86 (m, 1H), 3.35 (s, 3H), 3.12 (ddd, *J* = 17.7, 12.6, 6.0 Hz, 1H), 2.70 – 2.61 (m, 1H), 2.47 (dd, *J* = 13.8, 11.8 Hz, 1H), 2.36 (dd, *J* = 13.8, 7.5 Hz, 1H);

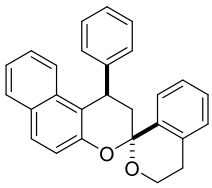
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 154.5, 147.5, 136.1, 134.6, 128.8, 128.4, 128.2(2C), 127.9, 127.0(2C), 126.9, 126.7, 125.6, 115.1, 110.7, 104.8, 97.0, 59.5, 55.4, 43.9, 36.9, 28.8; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_3$ $[M]^+$: 358.1563, found: 358.1567.



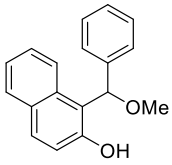
5-Chloro-4-phenylspiro[chromane-2,1'-isochromane]((±)-3n): Following the general procedure B, compound **(±)-3n** was obtained as a white solid in 60% yield (65.1 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); mp = 120-121 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.32 – 7.24 (m, 4H), 7.21 – 7.08 (m, 5H), 6.96 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.50 (dd, *J* = 11.3, 7.9 Hz, 1H), 4.06 (ddd, *J* = 12.5, 11.2, 3.0 Hz, 1H), 3.94 – 3.87 (m, 1H), 3.13 (ddd, *J* = 17.8, 12.6, 6.0 Hz, 1H), 2.70 – 2.63 (m, 1H), 2.53 (dd, *J* = 14.0, 11.3 Hz, 1H), 2.45 (dd, *J* = 14.0, 7.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 146.0, 135.5, 135.1, 134.6, 128.9, 128.8(2C), 128.7, 128.3, 127.6(2C), 126.9, 126.7, 126.1, 124.6, 123.5, 116.8, 97.2, 59.6, 44.8, 39.5, 28.7; **HRMS** (EI, m/z): calcd for $C_{23}H_{19}{}^{35}ClO_2$ $[M]^+$: 362.1068, found: 362.1071, calcd for $C_{23}H_{19}{}^{37}ClO_2$ $[M]^+$: 364.1039, found: 364.1047.



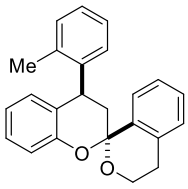
3-Chloro-2-(methoxy(phenyl)methyl)phenol((±)-4n): Following the general procedure B, compound **(±)-4n** was obtained as a colorless oily liquid in 40% yield (29.6 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.42 – 7.37 (m, 2H), 7.36 – 7.29 (m, 3H), 7.16 – 7.11 (m, 1H), 6.91 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.84 (dd, *J* = 8.3, 1.2 Hz, 1H), 5.94 (s, 1H), 3.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 138.6, 133.4, 129.9, 128.7(2C), 128.6, 127.4(2C), 122.5, 121.3, 116.4, 84.0, 57.8; **HRMS** (EI, m/z): calcd for $C_{14}H_{13}{}^{35}ClO_2$ $[M]^+$: 248.0604, found: 248.0607, calcd for $C_{14}H_{13}{}^{37}ClO_2$ $[M]^+$: 250.0570, found: 250.0577.



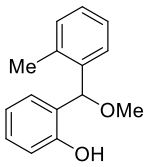
1-Phenyl-1,2-dihydrospiro[benzo[*f*]chromene-3,1'-isochromane]((±)-3o):
Following the general procedure A, compound **(±)-3o** was obtained as a white solid in 92% yield (104.3 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 115-117 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 11.6, 8.5 Hz, 2H), 7.42 (dd, *J* = 17.5, 8.0 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.25 – 7.21 (m, 4H), 7.21 – 7.18 (m, 2H), 7.17 – 7.12 (m, 4H), 4.84 (dd, *J* = 10.9, 8.2 Hz, 1H), 4.18 – 4.06 (m, 1H), 3.94 – 3.82 (m, 1H), 3.15 (ddd, *J* = 17.9, 12.7, 5.9 Hz, 1H), 2.71 – 2.64 (m, 1H), 2.61 – 2.58 (m, 1H), 2.57 – 2.52 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 147.2, 135.9, 134.7, 132.5, 130.3, 129.0(2C), 128.8(8), 128.8(7), 128.6, 128.4(2C), 127.7, 126.9, 126.8, 126.2, 125.6, 125.5(6), 123.2, 119.8, 117.2, 96.7, 59.6, 45.3, 38.4, 28.8; **HRMS** (EI, m/z): calcd for $C_{27}H_{22}O_2$ $[M]^+$: 378.1614, found: 378.1623.



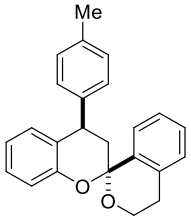
1-(Methoxy(phenyl)methyl)naphthalen-2-ol((±)-4o): Following the general procedure A, compound **(±)-4o** was obtained as a colorless oily liquid in 53% yield (41.9 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.83 – 7.65 (m, 3H), 7.45 – 7.35 (m, 3H), 7.35 – 7.24 (m, 5H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.21 (s, 1H), 3.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.3, 139.4, 132.4, 130.4, 129.0, 128.9, 128.8(2C), 128.5, 127.8(2C), 126.9, 123.1, 121.4, 119.8, 114.3, 83.7, 58.0; **HRMS** (EI, m/z): calcd for $C_{18}H_{16}O_2$ $[M]^+$: 264.1150, found: 264.1147.



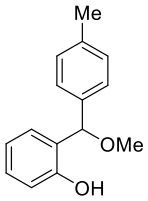
4-(*o*-Tolyl)spiro[chromane-2,1'-isochromane]((±)-3p): Following the general procedure A, compound **(±)-3p** was obtained as a white solid in 90% yield (94.3 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 111-113 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 1H), 7.29 – 7.24 (m, 2H), δ 7.20 – 7.17 (m, 2H), 7.17 – 7.09 (m, 4H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.78 (d, *J* = 7.7 Hz, 1H), 4.84 (dd, *J* = 12.7, 5.7 Hz, 1H), 4.27 – 4.18 (m, 1H), 4.01 – 3.94 (m, 1H), 3.14 (ddd, *J* = 17.7, 12.5, 5.9 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.53 (dd, *J* = 13.4, 12.7 Hz, 1H), 2.48 (s, 3H), 2.23 (dd, *J* = 13.4, 5.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 142.9, 136.9, 136.4, 134.7, 130.3, 129.5, 128.9, 128.5, 128.2, 127.5, 1269, 126.7, 126.6, 126.5, 126.4, 121.1, 117.5, 97.1, 59.5, 40.8, 34.1, 28.8, 19.8; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_2$ $[M]^+$: 342.1614, found: 342.1619.



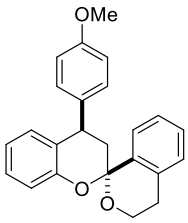
2-(Methoxy(*o*-tolyl)methyl)phenol((±)-4p): Following the general procedure A, compound **(±)-4p** was obtained as a colorless oily liquid in 36% yield (24.6 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.27 – 7.20 (m, 3H), 7.19 – 7.15 (m, 2H), 6.94 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.80 – 6.74 (m, 1H), 6.69 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.68 (s, 1H), 3.44 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 137.4, 137.0, 131.0, 129.5, 128.7, 128.6, 128.4, 126.4, 123.9, 120.0, 117.1, 84.2, 57.1, 19.5; **HRMS** (EI, m/z): calcd for $C_{15}H_{16}O_2$ $[M]^+$: 228.1150, found: 228.1151.



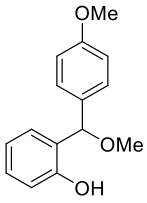
4-(*p*-Tolyl)spiro[chromane-2,1'-isochromane]((±)-3q): Following the general procedure A, compound **(±)-3q** was obtained as a white solid in 97% yield (100.5 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 100-103 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.1 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.21 – 7.17 (m, 3H), 7.17 – 7.11 (m, 3H), 6.90 (d, J = 8.1 Hz, 1H), 6.85 – 6.80 (m, 2H), 4.47 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.30 – 4.16 (m, 1H), 4.03 – 3.93 (m, 1H), 3.13 (ddd, *J* = 17.7, 12.6, 5.9 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.58 (dd, *J* = 13.4, 12.9 Hz, 1H), 2.35 (s, 3H), 2.24 (dd, *J* = 13.4, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 141.4, 136.4, 136.4, 134.6, 129.6, 129.5(2C), 129.0(2C), 128.9, 128.5, 127.6, 126.9, 126.6, 126.4, 121.0, 117.4, 97.0, 59.5, 42.0, 38.8, 28.8, 21.2; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_2$ $[M]^+$: 342.1614, found: 342.1622.



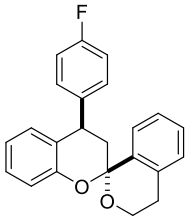
2-(Methoxy(*p*-tolyl)methyl)phenol((±)-4q): Following the general procedure A, compound **(±)-4q** was obtained as a colorless oily liquid in 56% yield (38.2 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.25 – 7.13 (m, 5H), 6.92 – 6.84 (m, 2H), 6.82 – 6.76 (m, 1H), 5.41 (s, 1H), 3.45 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.6, 138.1, 136.9, 129.4(2C), 129.3, 128.9, 127.4(2C), 125.0, 119.9, 117.3, 86.7, 57.2, 21.3; **HRMS** (EI, m/z): calcd for $C_{15}H_{16}O_2$ $[M]^+$: 228.1150, found: 228.1151.



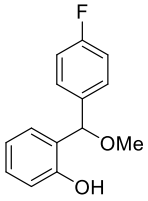
4-(4-Methoxyphenyl)spiro[chromane-2,1'-isochromane]((±)-3r): Following the general procedure A, compound **(±)-3r** was obtained as a white solid in 96% yield (99.7 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 80-85 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 1H), 7.30 – 7.24 (m, 2H), 7.23 – 7.18 (m, 3H), 7.14 – 7.09 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 1.9 Hz, 1H), 6.84 – 6.80 (m, 2H), 4.46 (dd, *J* = 12.9, 5.7 Hz, 1H), 4.23 (ddd, *J* = 12.5, 11.2, 3.0 Hz, 1H), 3.97 (ddd, *J* = 11.3, 6.0, 1.1 Hz, 1H), 3.79 (s, 3H), 3.20 – 3.04 (m, 1H), 2.72 – 2.62 (m, 1H), 2.56 (dd, *J* = 13.4, 12.8 Hz, 1H), 2.24 (dd, *J* = 13.4, 5.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 153.3, 136.4, 136.3(5), 134.6, 130.0(2C), 129.5, 128.9, 128.4, 127.6, 126.9, 126.6, 126.5, 121.0, 117.4, 114.2(2C), 97.1, 59.5, 55.4, 42.0, 38.4, 28.8; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_3$ $[M]^+$: 358.1563, found: 358.1571.



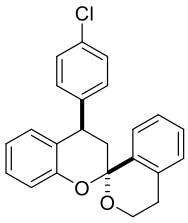
2-(Methoxy(4-methoxyphenyl)methyl)phenol((±)-4r): Following the general procedure A, compound **(±)-4r** was obtained as a colorless oily liquid in 30% yield (22.0 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.25 – 7.17 (m, 3H), 6.91 – 6.79 (m, 5H), 5.40 (s, 1H), 3.79 (s, 3H), 3.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 155.7, 132.0, 129.4, 129.0, 128.9(2C), 125.0, 119.9, 117.3, 114.1(2C), 86.5, 57.1, 55.4; **HRMS** (EI, m/z): calcd for $C_{15}H_{16}O_3$ $[M]^+$: 244.1099, found: 244.1097.



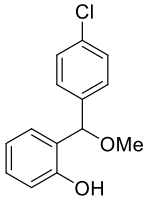
4-(4-Fluorophenyl)spiro[chromane-2,1'-isochromane]((±)-3s): Following the general procedure A, compound **(±)-3s** was obtained as a white solid in 86% yield (89.2 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 110-113 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 6.8, 2.2 Hz, 1H), 7.29 – 7.22 (m, 4H), 7.21 – 7.17 (m, 1H), 7.15 – 7.10 (m, 1H), 7.04 – 6.97 (m, 2H), 6.90 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.79 – 6.75 (m, 1H), 4.50 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.22 (ddd, *J* = 12.6, 11.2, 2.9 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.12 (ddd, *J* = 16.4, 12.4, 6 Hz, 1H), 2.70 – 2.63 (m, 1H), 2.54 (dd, *J* = 13.4, 12.9 Hz, 1H), 2.24 (dd, *J* = 13.4, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8 (d, C-F, $^1J_{C\text{-}F}$ = 244.8 Hz), 153.3, 140.1 (d, C-F, $^4J_{C\text{-}F}$ = 3.2 Hz), 136.2, 134.6, 130.5(2C) (d, C-F, $^3J_{C\text{-}F}$ = 7.9 Hz), 129.4, 128.9, 128.5, 127.8, 126.9, 126.6, 126.0, 121.1, 117.5, 115.6(2C) (d, C-F, $^2J_{C\text{-}F}$ = 21.2 Hz), 97.0, 59.5, 42.1, 38.6, 28.8; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -112.02 – -120.09 (m). **HRMS** (EI, m/z): calcd for $C_{23}H_{19}FO_2$ $[M]^+$: 346.1364, found: 346.1366.



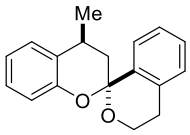
2-((4-Fluorophenyl)(methoxy)methyl)phenol((±)-4s): Following the general procedure A, compound **(±)-4s** was obtained as a colorless oily liquid in 54% yield (37.6 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.34 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 7.05 – 6.98 (m, 2H), 6.92 – 6.88 (m, 2H), 6.85 – 6.79 (m, 1H), 5.42 (s, 1H), 3.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.6 (d, C-F, $^1J_{C\text{-}F}$ = 246.7 Hz), 155.5, 135.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 129.5, 129.1(2C) (d, $^3J_{C\text{-}F}$ = 8.2 Hz), 128.8, 124.6, 120.0, 117.3, 115.5(2C) (d, *J* = 21.5 Hz), 85.8, 57.3; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -111.84 – -115.06 (m). **HRMS** (EI, m/z): calcd for $C_{14}H_{13}FO_2[M]^+$: 232.0900, found: 232.0903.



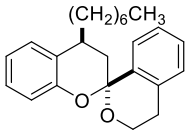
4-(4-Chlorophenyl)spiro[chromane-2,1'-isochromane]((±)-3t): Following the general procedure A, compound **(±)-3t** was obtained as a white solid in 95% yield (105.3 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 110-113 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 1H), δ 7.33 – 7.25 (m, 5H), 7.24 – 7.18 (m, 2H), 7.18 – 7.12 (m, 1H), 6.91 (dd, *J* = 8.3, 3.7 Hz, 1H), 6.85 (dd, *J* = 7.4, 2.4 Hz, 1H), 6.80 – 6.75 (m, 1H), 4.50 (dd, *J* = 13.0, 4.7 Hz, 1H), 4.28 – 4.18 (m, 1H), 3.98 (ddd, *J* = 11.4, 6.0, 2.2 Hz, 1H), 3.21 – 3.05 (m, 1H), 2.76 – 2.64 (m, 1H), 2.53 (dd, *J* = 13.5, 13.1 Hz, 1H), 2.24 (dd, *J* = 13.5, 4.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 143.0, 136.1, 134.6, 132.6, 130.5(2C), 129.4, 129.0(2C), 128.9, 128.6, 127.9, 126.9, 126.6, 125.6, 121.2, 117.6, 96.9, 59.6, 42.0, 38.8, 28.8; **HRMS** (EI, m/z): calcd for $C_{23}H_{19}{}^{35}ClO_2$ $[M]^+$: 362.1068, found: 362.1070, calcd for $C_{23}H_{19}{}^{37}ClO_2$ $[M]^+$: 364.1039, found: 364.1052.



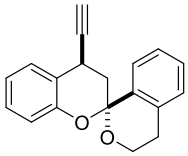
2-((4-Chlorophenyl)(methoxy)methyl)phenol((±)-4t): Following the general procedure A, compound **(±)-4t** was obtained as a colorless oily liquid in 45% yield (33.5 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.33 – 7.25 (m, 4H), 7.22 – 7.17 (m, 1H), 6.92 – 6.87 (m, 2H), 6.83 (dd, *J* = 7.4, 1.2 Hz, 1H), 5.40 (s, 1H), 3.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 138.6, 134.1, 129.7, 128.8(9)(2C), 128.8(7)(2C), 128.7, 124.4, 120.1, 117.4, 85.8, 57.4; **HRMS** (EI, m/z): calcd for $C_{14}H_{13}{}^{35}ClO_2$ $[M]^+$: 248.0599, found: 248.0603, calcd for $C_{14}H_{13}{}^{37}ClO_2$ $[M]^+$: 250.0570, found: 250.0581.



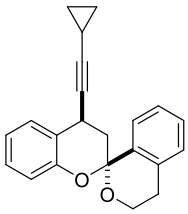
4-Methylspiro[chromane-2,1'-isochromane]((±)-3u): Following the general procedure C, compound **(±)-3u** was obtained as a yellow solid in 50% yield (40.0 mg); R_f = 0.85 (petroleum ether/EtOAc = 4/1); mp = 80-83 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 6.8, 2.4 Hz, 1H), 7.33 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.20 – 7.17 (m, 1H), 7.16 – 7.10 (m, 1H), 7.00 – 6.94 (m, 1H), 6.86 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.24 – 4.13 (m, 1H), 3.92 (ddd, *J* = 11.3, 5.8, 1.3 Hz, 1H), 3.40 – 3.28 (m, 1H), 3.10 (ddd, *J* = 17.6, 12.4, 5.9 Hz, 1H), 2.71 – 2.61 (m, 1H), 2.13 (dd, *J* = 13.4, 11.4 Hz, 1H), 2.09 (dd, *J* = 13.4, 6.3 Hz, 1H), 1.40 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.7, 136.7, 134.6, 128.8, 128.4, 127.6, 127.4, 126.9, 126.9, 126.7, 121.1, 117.4, 96.9, 59.5, 41.4, 28.9, 25.7, 19.4; **HRMS** (EI, m/z): calcd for $C_{18}H_{18}O_2$ $[M]^+$: 266.1301, found: 266.1304.



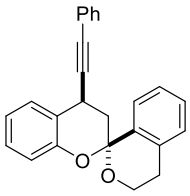
4-Heptylspiro[chromane-2,1'-isochromane]((±)-3v): Following the general procedure C, compound **(±)-3v** was obtained as a white solid in 97% yield (101.8 mg);12:1 dr; R_f = 0.8 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.28 (dd, *J* = 5.9, 2.9 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.13 – 7.08 (m, 1H), 6.98 – 6.93 (m, 1H), 6.85 (dd, *J* = 8.3, 1.3 Hz, 1H), 4.15 (td, *J* = 11.9, 2.9 Hz, 1H), 3.92 – 3.86 (m, 1H), 3.30 – 3.19 (m, 1H), 3.09 (ddd, *J* = 17.8, 12.5, 5.9 Hz, 1H), 2.67 – 2.59 (m, 1H), 2.20 – 2.14 (m, 1H), 2.10 – 2.06 (m, 1H), 1.40 – 1.22 (m, 12H), 0.88 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 137.0, 134.6, 129.3, 128.8, 128.3, 127.2, 126.9, 126.8, 126.7, 121.1, 117.6, 97.0, 59.4, 38.3, 33.8, 32.0, 30.4, 30.1, 29.4, 28.9, 26.5, 22.8, 14.2; **HRMS** (EI, m/z): calcd for $C_{24}H_{30}O_2$ $[M]^+$: 350.2240, found: 350.2245.



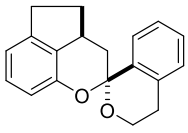
4-Ethynylspiro[chromane-2,1'-isochromane]((±)-3w): Following the general procedure A, compound **(±)-3w** was obtained as a yellow solid in 75% yield (62.1 mg); R_f = 0.85 (petroleum ether/EtOAc = 4/1); mp = 85-88 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 1H), 7.40 – 7.34 (m, 1H), 7.32 – 7.25 (m, 2H), 7.22 – 7.14 (m, 2H), 7.05 – 6.95 (m, 1H), 6.85 (dd, *J* = 8.2, 3.3 Hz, 1H), 4.33 (dd, *J* = 12.9, 5.4 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.95 – 3.84 (m, 1H), 3.08 (ddd, *J* = 16.5, 10.8, 5.0 Hz, 1H), 2.70 – 2.61 (m, 1H), 2.54 (dd, *J* = 13.3, 12.9 Hz, 1H), 2.36 (dd, *J* = 13.3, 5.4 Hz, 1H), 2.22 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.2, 135.8, 134.6, 128.9, 128.6, 128.6, 128.4, 127.0, 126.6, 121.5, 121.3, 117.4, 96.3, 85.1, 70.2, 59.5, 38.7, 28.7, 25.2; **HRMS** (EI, m/z): calcd for $C_{19}H_{16}O_2$ $[M]^+$: 276.1145, found: 276.1147.



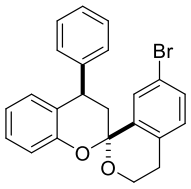
4-(Cyclopropylethynyl)spiro[chromane-2,1'-isochromane]((±)-3x): Following the general procedure A, compound **(±)-3x** was obtained as a yellow solid in 78% yield (73.1 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 80-83 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 1H), 7.36 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.19 – 7.12 (m, 2H), 7.02 – 6.96 (m, 1H), 6.84 – 6.80 (m, 1H), 4.24 (dd, *J* = 12.8, 5.5 Hz, 1H), 4.14 (ddd, *J* = 12.5, 11.2, 2.9 Hz, 1H), 3.90 (ddd, *J* = 11.2, 5.9, 1.2 Hz, 1H), 3.14 – 2.99 (m, 1H), 2.70 – 2.59 (m, 1H), 2.46 (dd, *J* = 13.3, 12.8 Hz, 1H), 2.28 (dd, *J* = 13.3, 5.5 Hz, 1H), 1.27 (dddd, *J* = 13.1, 8.2, 5.0, 1.9 Hz, 1H), 0.77 – 0.72 (m, 2H), 0.69 – 0.62 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.2, 136.0, 134.6, 128.8, 128.7, 128.5, 128.1, 126.9, 126.6, 122.8, 121.2, 117.3, 96.5, 85.3, 76.0, 59.5, 39.2, 28.7, 25.2, 8.4, 8.3, -0.3; **HRMS** (EI, m/z): calcd for $C_{22}H_{20}O_2$ $[M]^+$: 316.1458, found: 316.1461.



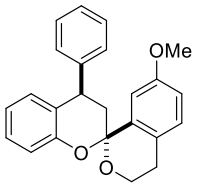
4-(Phenylethynyl)spiro[chromane-2,1'-isochromane]((±)-3y): Following the general procedure A, compound **(±)-3y** was obtained as a yellow solid in 79% yield (83.2 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 99-102 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.31 – 7.26 (m, 5H), 7.22 – 7.17 (m, 2H), 7.05 – 6.98 (m, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 4.54 (dd, *J* = 12.7, 5.5 Hz, 1H), 4.22 – 4.12 (m, 1H), 3.98 – 3.90 (m, 1H), 3.16 – 3.01 (m, 1H), 2.70 – 2.63 (m, 1H), 2.60 (dd, *J* = 13.2, 12.7 Hz, 1H), 2.43 (dd, *J* = 13.2, 5.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3, 135.9, 134.6, 131.8, 128.9, 128.8, 128.6, 128.3(8)(2C), 128.3(7)(2C), 128.1, 127.0, 126.6, 123.6, 122.2, 121.3, 117.5, 96.5, 90.5, 82.3, 59.5, 38.8, 28.8, 25.9; **HRMS** (EI, m/z): calcd for $C_{25}H_{20}O_2$ $[M]^+$: 352.1458, found: 352.1462.



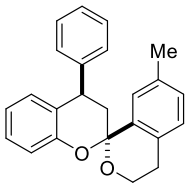
3,3a,4,5-Tetrahydrospiro[cyclopenta[*de*]chromene-2,1'-isochromane]((±)-3z):
Following the general procedure A, compound **(±)-3z** was obtained as a white solid in 63% yield (52.5 mg); R_f = 0.85 (petroleum ether/EtOAc = 4/1); mp = 105-107 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.17 (m, 4H), 7.11 – 7.05 (m, 1H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 4.28 (ddd, *J* = 12.6, 11.2, 2.9 Hz, 1H), 3.98 (ddd, *J* = 11.2, 5.9, 1.2 Hz, 1H), 3.54 – 3.40 (m, 1H), 3.12 (ddd, *J* = 16.5, 12.5, 5.9 Hz, 1H), 3.07 – 2.97 (m, 1H), 2.83 (dd, *J* = 15.3, 7.9 Hz, 1H), 2.68 (dd, *J* = 16.3, 2.8 Hz, 1H), 1.99 – 1.90 (m, 1H), 1.77 – 1.62 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 144.9, 136.7, 134.6, 129.9, 128.8, 128.3, 128.2, 126.9, 126.6, 116.7, 112.5, 99.1, 59.6, 39.4, 35.5, 34.1, 32.9, 28.8; **HRMS** (EI, m/z): calcd for $C_{19}H_{18}O_2$ $[M]^+$: 278.1305, found: 278.1310.



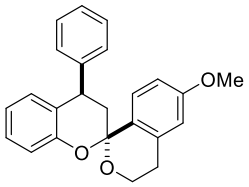
7'-Bromo-4-phenylspiro[chromane-2,1'-isochromane](±)-3aa): Following the general procedure A, compound **(±)-3aa** was obtained as a white solid in 92% yield (112.1 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 97-99 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 2.1 Hz, 1H), 7.45 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.42 – 7.32 (m, 5H), 7.22 – 7.16 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 1H), 6.95 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.92 – 6.85 (m, 2H), 4.54 (dd, *J* = 12.8, 5.8 Hz, 1H), 4.23 (ddd, *J* = 12.5, 11.3, 3.0 Hz, 1H), 4.03 (ddd, *J* = 11.3, 6.0, 1.2 Hz, 1H), 3.16 – 3.04 (m, 1H), 2.74 – 2.65 (m, 1H), 2.57 (dd, *J* = 13.4, 12.8 Hz, 1H), 2.31 (dd, *J* = 13.4, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.0, 144.2, 138.3, 133.6, 131.6, 130.6, 129.7, 129.6, 129.1(2C), 128.8(2C), 127.8, 127.0, 126.0, 121.3, 120.4, 117.4, 96.5, 59.3, 42.0, 39.2, 28.4; **HRMS** (EI, m/z): calcd for $C_{23}H_{19}BrO_2$ $[M]^+$: 406.0563, found: 406.0565.



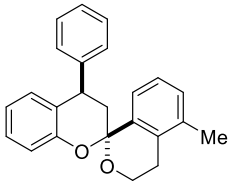
7'-Methoxy-4-phenylspiro[chromane-2,1'-isochromane](±)-3ab): Following the general procedure A, compound **(±)-3ab** was obtained as a white solid in 87% yield (93.4 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 112-115 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 7.16 – 7.09 (m, 2H), 6.96 – 6.90 (m, 2H), 6.87 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.85 – 6.79 (m, 2H), 4.51 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.24 – 4.15 (m, 1H), 4.01 – 3.95 (m, 1H), 3.79 (s, 3H), 3.05 (ddd, *J* = 17.6, 12.4, 5.8 Hz, 1H), 2.66 – 2.60 (m, 1H), 2.55 (dd, *J* = 13.4, 12.9 Hz, 1H), 2.27 (dd, *J* = 13.4, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 153.3, 144.4, 137.1, 129.9, 129.6, 129.1(2C), 128.8(2C), 127.7, 126.9, 126.7, 126.2, 121.1, 117.5, 115.2, 111.3, 97.1, 59.8, 55.6, 42.1, 39.3, 28.1; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_3$ $[M]^+$: 358.1563, found: 358.1572.



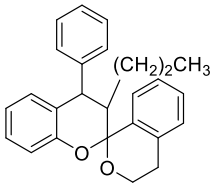
7'-Methyl-4-phenylspiro[chromane-2,1'-isochromane]((±)-3ac): Following the general procedure A, compound **(±)-3ac** was obtained as a white solid in 96% yield (99.6 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 108-110 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 7.13 (dd, J = 7.7, 5.2 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.85 – 6.80 (m, 2H), 4.51 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.21 (ddd, *J* = 12.7, 11.1, 2.9 Hz, 1H), 4.00 – 3.93 (m, 1H), 3.08 (ddd, *J* = 17.8, 12.5, 5.9 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.57 (dd, *J* = 13.4, 12.9 Hz, 1H), 2.32 (s, 3H), 2.26 (dd, *J* = 13.4, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 144.6, 136.5, 136.0, 131.5, 129.6, 129.4, 129.1, 128.7(8)(2C), 128.7(7)(2C), 127.7, 127.0, 126.8, 126.2, 121.1, 117.5, 97.1, 59.7, 42.1, 39.3, 28.5, 21.4; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_2$ $[M]^+$: 342.1614, found: 342.1617.



6'-Methoxy-4-phenylspiro[chromane-2,1'-isochromane]((±)-3ad): Following the general procedure A, compound **(±)-3ad** was obtained as a white solid in 67% yield (72.0 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 115-118 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.29 – 7.21 (m, 2H) 6.90 (d, *J* = 8.1 Hz, 1H), 6.82 (s, 1H), 6.81 – 6.77 (m, 3H), 6.69 (d, *J* = 2.7 Hz, 1H), 4.50 (dd, *J* = 12.9, 5.8 Hz, 1H), 4.27 – 4.17 (m, 1H), 3.98 – 3.92 (m, 1H), 3.79 (s, 3H), 3.11 (ddd, *J* = 17.7, 12.6, 5.9 Hz, 1H), 2.68 – 2.61 (m, 1H), 2.55 (dd, *J* = 13.4, 12.9 Hz, 1H), 2.25 (dd, *J* = 13.4, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 153.4, 144.5, 136.2, 129.6, 129.1(2C), 128.8(2C), 128.8, 127.9, 127.7, 126.8, 126.1, 121.0, 117.4, 113.2, 97.0, 59.4, 55.4, 42.0, 39.3, 29.2; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_3$ $[M]^+$: 358.1563, found: 358.1567.

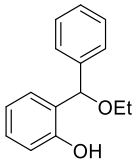


5'-Methyl-4-phenylspiro[chromane-2,1'-isochromane]((±)-3ae): Following the general procedure A, compound **(±)-3ae** was obtained as a white solid in 63% yield (64.6 mg); R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 104-107 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 4H), 7.30 – 7.23 (m, 2H), 7.19 – 7.10 (m, 3H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.85 – 6.78 (m, 2H), 4.50 (dd, *J* = 12.8, 5.8 Hz, 1H), 4.33 – 4.17 (m, 1H), 4.09 – 3.96 (m, 1H), 2.90 (ddd, *J* = 18.1, 12.2, 6.0 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.58 (dd, *J* = 13.5, 12.8 Hz, 1H), 2.28 (s, 3H), 2.24 (dd, *J* = 13.5, 5.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.3, 144.6, 136.2, 136.1, 133.2, 129.8, 129.6, 129.1(2C), 128.8(2C), 127.7, 126.8, 126.4, 126.2, 124.2, 121.0, 117.5, 97.2, 59.1, 42.1, 39.4, 26.3, 19.3; **HRMS** (EI, m/z): calcd for $C_{24}H_{22}O_2$ $[M]^+$: 342.1614, found: 342.1622.



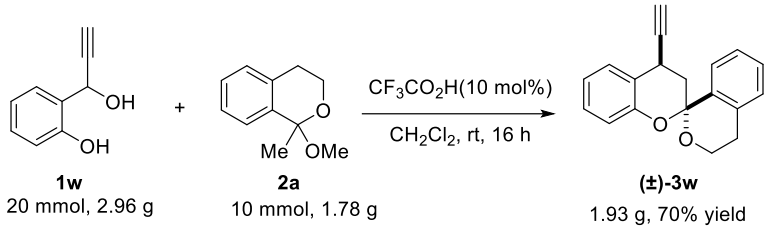
4-Phenyl-3-propylspiro[chromane-2,1'-isochromane]((±)-3af): Following the general procedure A, compound **(±)-3af** was obtained as a white solid in 80% yield (88.8 mg);1:1 dr; R_f = 0.8 (petroleum ether/EtOAc = 4/1); mp = 98-102 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) 1H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.44 (m, 1H), 7.41 – 7.36 (m, 1H), 7.35 – 7.29, 7.29 – 7.26 (m, 5H), 7.25 – 7.21 (m, 3H), 7.21 – 7.16 (m, 3H), 7.15 – 7.13 (m, 2H), 7.11 – 7.04 (m, 2H), 6.93 – 6.88, 6.86 – 6.81 (m, 2H), 6.80 – 6.75 (m, 1H), 6.70 – 6.65 (m, 1H), 4.37 (d, J = 7.7 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.15 – 4.13 (m, 1H), 4.12 – 4.06 (m, 1H), 3.95 (dd, *J* = 11.2, 5.7 Hz, 1H), 3.82 (dd, *J* = 11.0, 5.7 Hz, 1H), 3.10 (ddd, *J* = 17.8, 12.8, 5.7 Hz, 1H), 2.91 (ddd, *J* = 17.8, 12.7, 5.8 Hz, 1H), 2.83 – 2.76 (m, 1H), 2.64 (dd, *J* = 16.3, 2.5 Hz, 1H), 2.57 – 2.54 (m, 1H), 2.53 – 2.49 (m, 1H), 1.20 – 1.13 (m, 2H), 1.13 – 1.06 (m, 2H), 0.90 – 0.79 (m, 2H), 0.67 (t, *J* = 6.9 Hz, 3H), 0.61 – 0.37 (m, 2H), 0.33 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.5(7), 152.5(6), 144.2, 143.0, 136.7, 135.8, 135.7, 135.5, 131.9(2C), 131.3, 130.0(1), 130.0(0), 129.9(5), 128.6(7), 128.6(4), 128.6(2C), 128.26, 128.1, 127.8, 127.5,

127.4, 127.3(2C), 127.0(2C), 126.8(4), 126.8(0), 126.7, 126.4, 126.1, 121.1, 120.9, 117.6, 117.1, 100.5, 100.4, 59.6, 58.8, 46.9, 46.2, 44.8, 43.5, 32.5, 29.5, 28.9, 28.7, 21.1(0), 21.1(5), 14.4, 13.9.; **HRMS** (EI, m/z): calcd for $C_{26}H_{26}O_2$ $[M]^+$: 370.1928, found: 370.1935.



2-(Ethoxy(phenyl)methyl)phenol((±)-4aa)[4]**:** Following the general procedure A , compound **(±)-4aa** was obtained as a colorless oily liquid in 50% yield (34.3 mg); R_f = 0.7 (petroleum ether/EtOAc = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.38 – 7.27 (m, 4H), 7.22 – 7.15 (m, 1H), 6.92 – 6.86 (m, 2H), 6.83 – 6.77 (m, 1H), 5.55 (s, 1H), 3.73-3.55 (m, 2H), 1.31 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.8, 140.3, 129.4, 128.9, 128.7(2C), 128.2, 127.4(2C), 125.2, 119.8, 117.3, 85.0, 65.4, 15.3; **HRMS** (EI, m/z): calcd for $C_{15}H_{16}O_2$ $[M]^+$: 228.1150, found: 228.1152.

3. Gram-scale preparation of bisbenzannulated spiroketal 3w



1w
20 mmol, 2.96 g

2a
10 mmol, 1.78 g

(±)-3w
1.93 g, 70% yield

o-Hydroxy benzyl alcohols **(±)-1w** (20 mmol, 2.0 equiv), CF_3COOH (1 mmol, 0.1 equiv) and freshly distilled CH_2Cl_2 (30.0 mL) were added sequentially to a flame dried 100 mL Schlenk tube. Then, isochroman ketals **(±)-2a** (10 mmol, 1.0 equiv) were added. The reaction mixture was stirred at room temperature until **(±)-2a** were consumed (monitored by TLC), which was directly purified by flash column chromatography silica gel (petroleum ether/EtOAc = 20/1) to afford bisbenzannulated spiroketals (±)-**3w** (1.93 g, 70% yield, >20:1 dr).

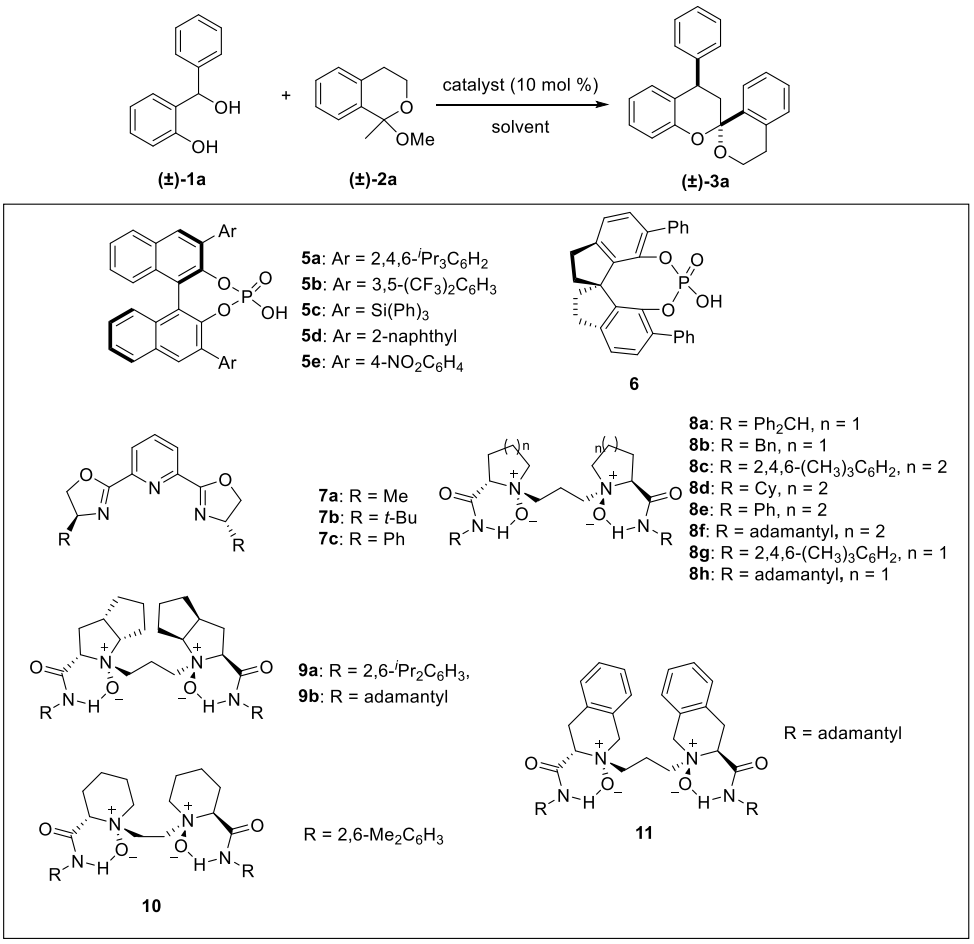
4. Synthetic transformations of product 3w

3w **5**
88% yield

A scintillation vial was charged with copper(I) thiophene-2-carboxylate (CuTC, 0.012 g, 0.06 mmol, 0.1 equiv in regards to alkyne), toluene (3 mL), and the **3w** (0.6 mmol, 1.0 equiv). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (0.6 mmol, 1 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture allowed to warm to room temperature and stir until judged complete by TLC. The reaction was diluted with saturated aq NH4Cl (5 mL) and extracted into EtOAc (2 × 5 mL). The combined organics were dried (Na_2SO_4) and filtered through celite. The eluent was concentrated in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc = 15:1) to afford the product **5** (249 mg, 88% yield) as white solid. R_f = 0.3 (petroleum ether/EtOAc = 4/1); mp = 80-84ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 3.4 Hz, 2H), 7.99 (s, 1H), 7.44 – 7.36 (m, 3H), 7.31 – 7.24 (m, 2H), 7.21 – 7.11 (m, 2H), 6.92 – 6.82 (m, 3H), 4.83 (dd, *J* = 12.9, 5.6 Hz, 1H), 4.22 – 4.14 (m, 1H), 3.95 (dd, *J* = 11.3, 5.7 Hz, 1H), 3.09 (ddd, *J* = 17.6, 12.4, 5.9 Hz, 1H), 2.73 – 2.68 (m, 1H), 2.67 – 2.61 (m, 1H), 2.45 (s, 3H), 2.29 (dd, *J* = 13.2, 5.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.9, 150.0, 147.4, 135.8, 134.7, 133.2, 130.6(2C), 128.9, 128.8(2C), 128.6, 128.4, 128.3, 127.0, 126.6, 123.0, 121.4, 121.3, 117.9, 96.6, 59.6, 39.5, 30.3, 28.8, 22.0; **HRMS** (EI, m/z): calcd for $C_{26}H_{23}N_3O_4S$ $[M]^+$: 473.1404, found: 473.1406.

5. Optimization studies for the asymmetric synthesis

Table S1 Optimization of asymmetric reaction conditions.



entry[a]	catalyst (10 mol%)	temp. (°C)	solvent	yield (%)[b]	ee %[c]	dr[d]
1	**5a**	25	CH_2Cl_2	59	<10	>20:1
2	**5b**	25	CH_2Cl_2	85	<10	>20:1
3	**5c**	25	CH_2Cl_2	31	<10	>20:1
4	**5d**	25	CH_2Cl_2	72	<10	>20:1
5	**5e**	25	CH_2Cl_2	90	<10	>20:1
6	**6**	25	CH_2Cl_2	37	<10	>20:1
7	**7a**/$Sc(OTf)_3$	25	CH_2Cl_2	14	<10	>20:1
8	**7b**/$Sc(OTf)_3$	25	CH_2Cl_2	32	<10	>20:1
9	**7c**/$Sc(OTf)_3$	25	CH_2Cl_2	18	11	>20:1
10	**8a**/$Sc(OTf)_3$	25	CH_2Cl_2	88	45	>20:1
11	**8b**/$Sc(OTf)_3$	25	CH_2Cl_2	45	50	4:1
12	**8c**/$Sc(OTf)_3$	25	CH_2Cl_2	56	20	>20:1

13	**8d**/$Sc(OTf)_3$	25	CH_2Cl_2	96	50	>20:1
14	**9a**/$Sc(OTf)_3$	25	CH_2Cl_2	93	30	>20:1
15	**9b**/$Sc(OTf)_3$	25	CH_2Cl_2	90	53	>20:1
16	**10**/$Sc(OTf)_3$	25	CH_2Cl_2	80	39	>20:1
17	**11**/$Sc(OTf)_3$	25	CH_2Cl_2	75	52	>20:1
18	**8e**/$Sc(OTf)_3$	25	CH_2Cl_2	95	56	>20:1
19	**8f**/$Sc(OTf)_3$	25	CH_2Cl_2	90	61	>20:1
20	**8f**/$Sc(OTf)_3$	25	THF	-	-	-
21	**8f**/$Sc(OTf)_3$	25	$C_6H_5CF_3$	60	59	15:1
22	**8f**/$Sc(OTf)_3$	25	EtOAc	56	60	12:1
23	**8f**/$Sc(OTf)_3$	25	CH_3CN	40	42	>20:1
24	**8f**/$Sc(OTf)_3$	25	C_6H_6	45	53	>20:1
25	**8f**/$Sc(OTf)_3$	25	$CHCl_3$	60	59	>20:1
26	**8f**/$Sc(OTf)_3$	25	DCE	65	60	>20:1
27	**8f**/$Sc(OTf)_3$	25	1,4-dioxane	75	<10	>20:1
28	**8g**/$Sc(OTf)_3$	25	CH_2Cl_2	85	40	>20:1
29	**8h**/$Sc(OTf)_3$	25	CH_2Cl_2	76	60	>20:1
30	**8f**/$Sc(OTf)_3$	0	CH_2Cl_2	75	60	>20:1
31	**8h**/$Sc(OTf)_3$	0	CH_2Cl_2	50	61	>20:1
32	**8f**/$Sc(OTf)_3$	-20	CH_2Cl_2	53	47	>20:1
33	**8f**/$Sc(OTf)_3$	40	CH_2Cl_2	75	54	9:1

[a] Unless others stated, the reactions were performed with **1a** (0.20 mmol), **2a** (0.10 mmol), catalyst (10 mol%) in dry solvent (1.5 mL) at the indicated temperature for 16 h. [b] Yield of isolated product **3a**. [c] The ee value was determined by chiral HPLC analysis. [d] The dr was determined by ^1H NMR.

6. Preliminary *in vitro* antifungal activities of bisbenzannulated spiroketal products 3

The *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 S2 Preliminary *in vitro* antifungal activities of bisbenzannulated spiroketal products **3**

compounds	Inhibition Rate (%)/100 mg/L			
	B. c.	S. s.	R. s.	F. g.
3a	31.2	25.6	44.2	46.2
3b	15.5	23.6	35.2	39.8
3c	22.8	27.5	24.2	29.5
3d	23.7	33.4	34.5	24.6
3e	15.8	20.6	17.5	23.8
3f	12.5	34.7	26.4	29.5
3g	36.5	26.1	17.5	16.2
3h	6.64	20.6	10.2	12.3
3i	34.5	35.2	36.2	40.5
3j	15.6	26.5	30.2	18.2
3k	42.1	42.3	39.5	20.4
3l	25.8	33.5	28.3	41.0

3m	42.2	34.3	23.7	46.2
3n	37.2	42.5	29.3	44.3
3o	19.2	28.5	36.2	42.3
3p	19.5	42.3	18.2	15.3
3q	17.5	27.2	16.0	13.2
3r	12.3	14.6	19.3	20.4
3s	49.2	56.1	48.5	45.9
3t	52.2	59.3	61.4	57.2
3u	37.5	30.2	26.3	30.2
3v	18.2	42.0	20.3	37.3
3w	17.8	43.3	37.6	26.5
3w	43.1	50.3	55.2	23.5
3x	45.2	67.3	61.2	42.5
3y	47.2	60.2	62.5	53.2
3z	16.4	19.3	6.5	12.3
3aa	20.1	30.6	38.2	18.8
3ab	26.4	29.2	13.2	19.4
3ac	18.6	22.5	35.2	30.0
3ad	20.4	26.5	17.2	20.1
3ae	10.2	16.8	26.4	32.5
Spiroxamine	92.6	94.9	91.3	67.1

7. References

1. Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. Feng, *Synlett* 2005, 2445-2448.

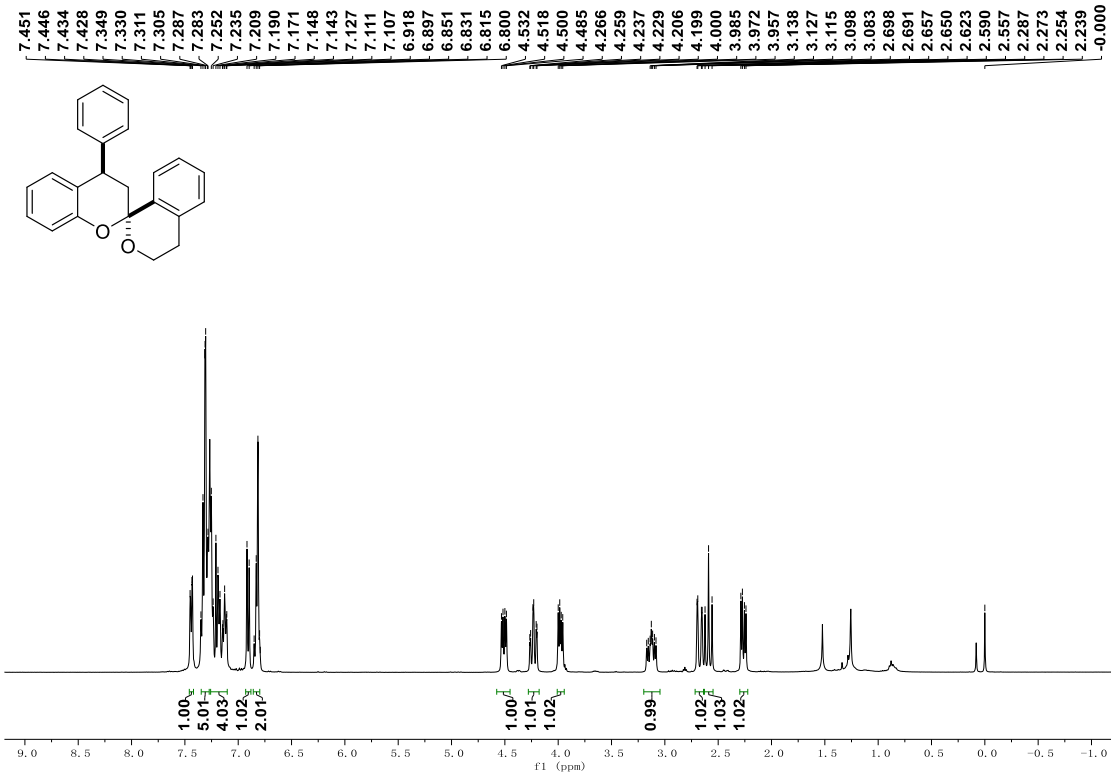
2. a) J. Fan, Z. Wang, *Chem. Commun.* 2008, 5381-5383. b) B. Wu, X. Gao,M.-W. Chen, Y.-G. Zhou, *Chin. J. Org. Chem*, 2014. **32**, 981-984;

3. T. Yang, Y. Sun, H. Wang, Z. Lin, J. Wen, X. Zhang, *Angew. Chem., Int. Ed*, 2020, **59**, 6108-6114.

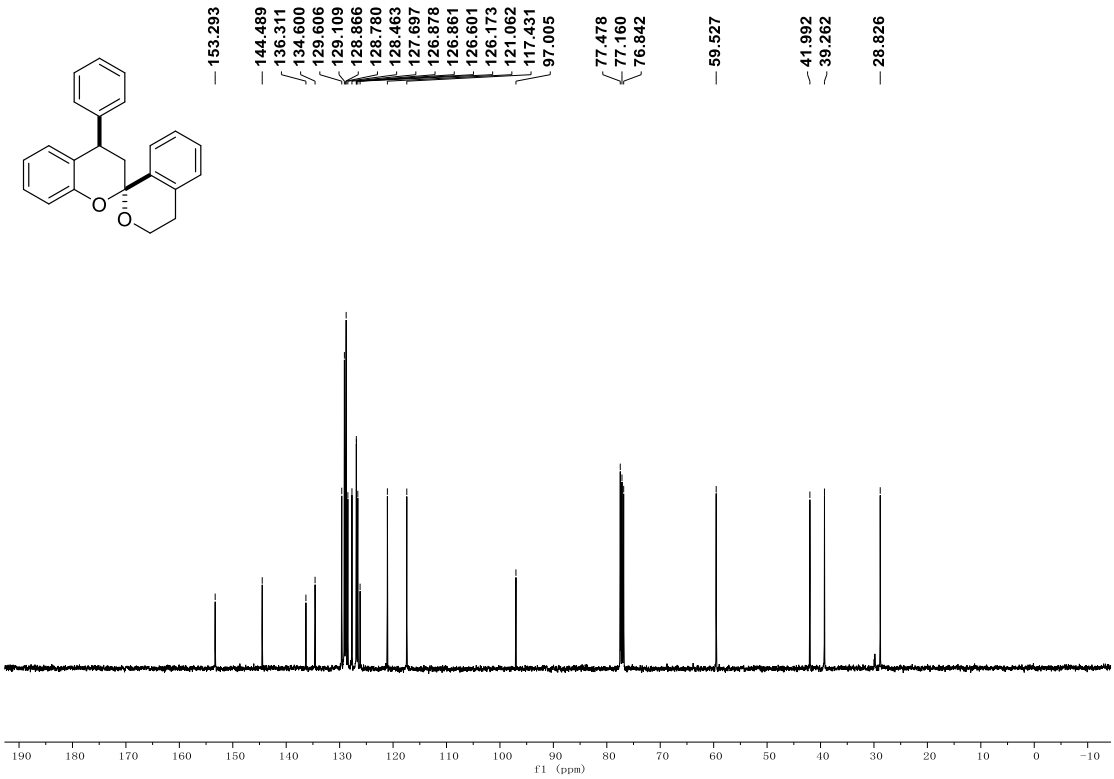
4. Z. Lai, Z. Wang, J. Sun, *Org. Lett*. 2015, **17**, 6058-6061.

8. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

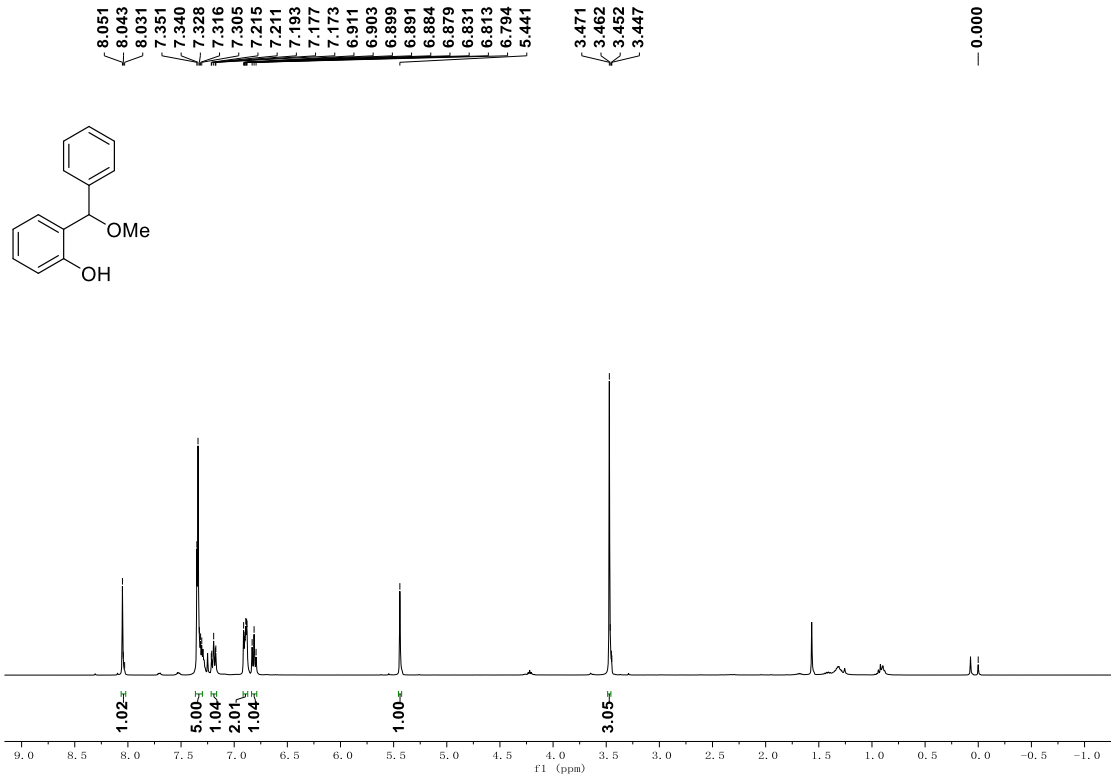
^{1}H NMR (400 MHz) of **(±)-3a** in $CDCl_3$



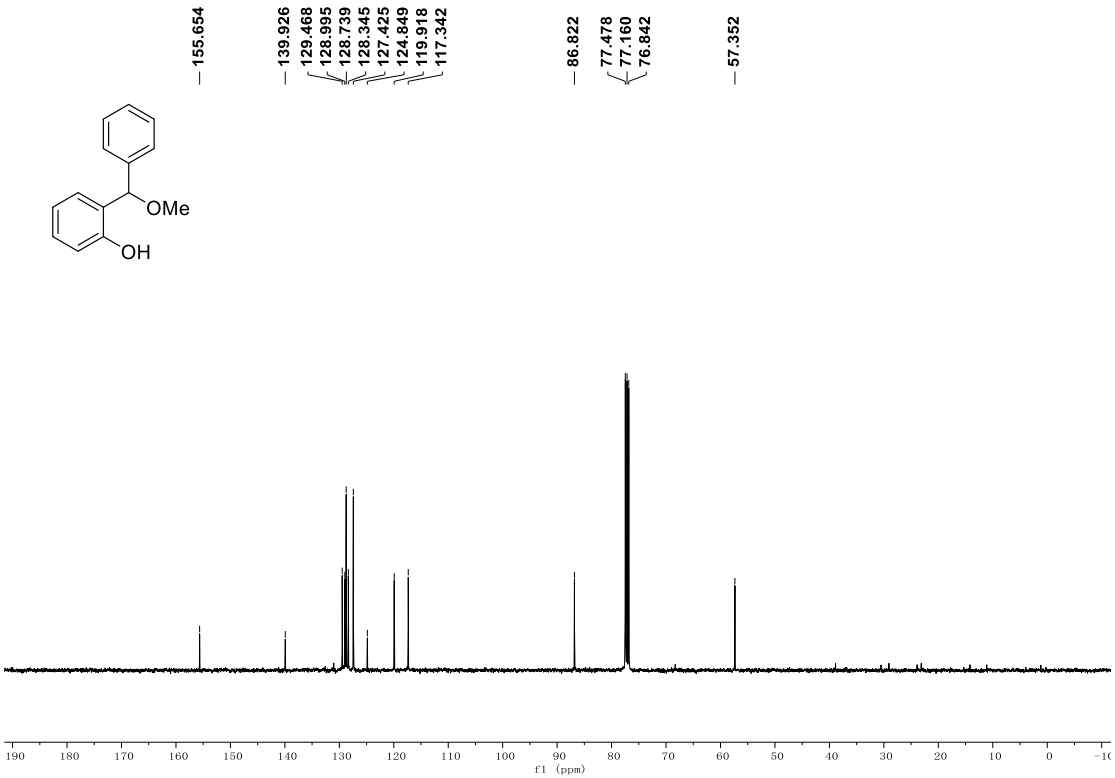
^{13}C NMR (100 MHz) of **(±)-3a** in $CDCl_3$



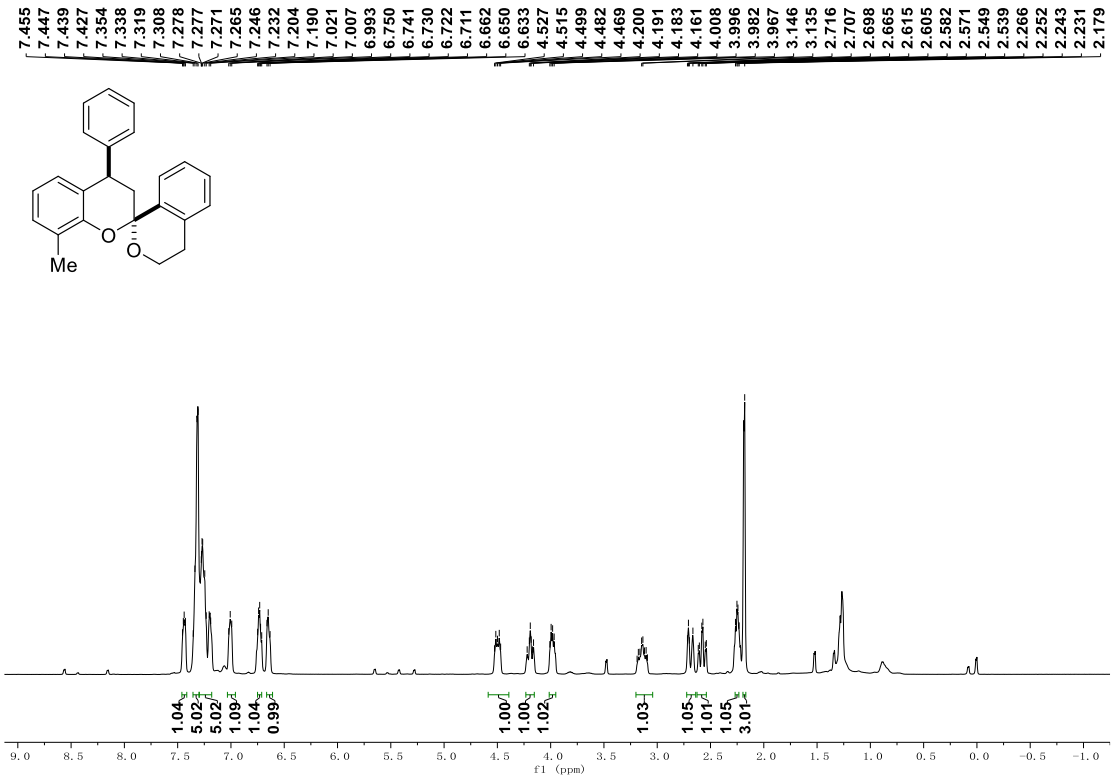
^{1}H NMR (400 MHz) of **(±)-4a** in $CDCl_3$



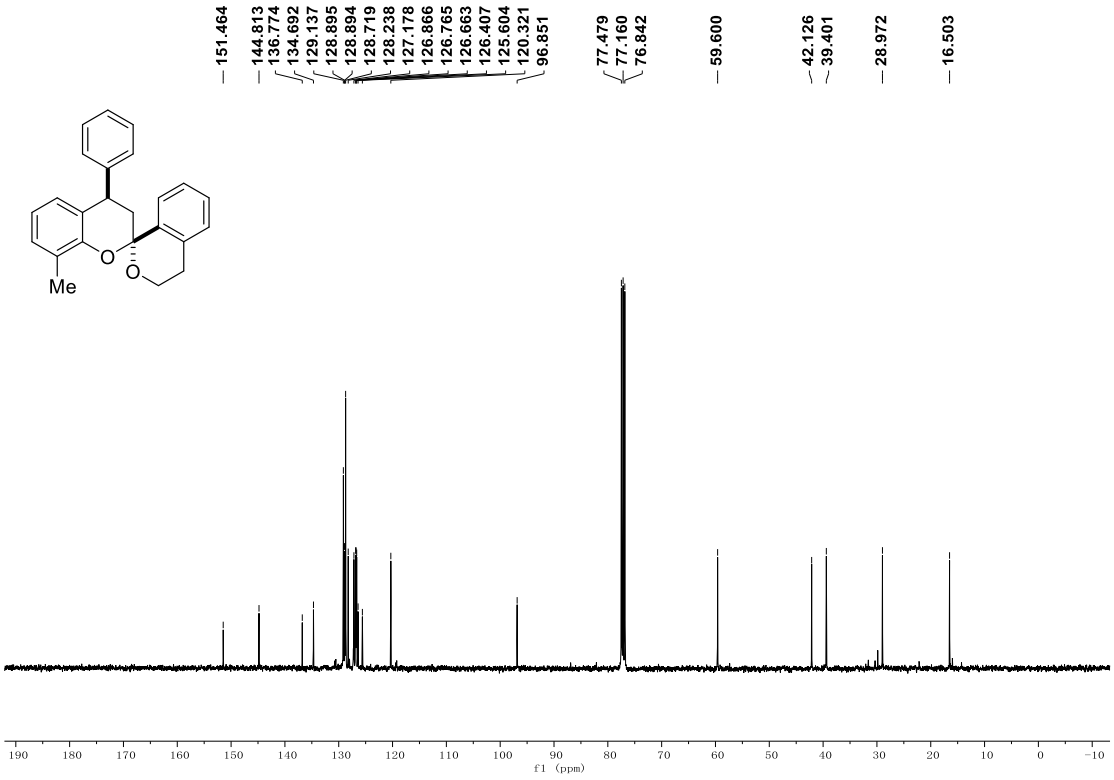
^{13}C NMR (100 MHz) of **(±)-4a** in $CDCl_3$



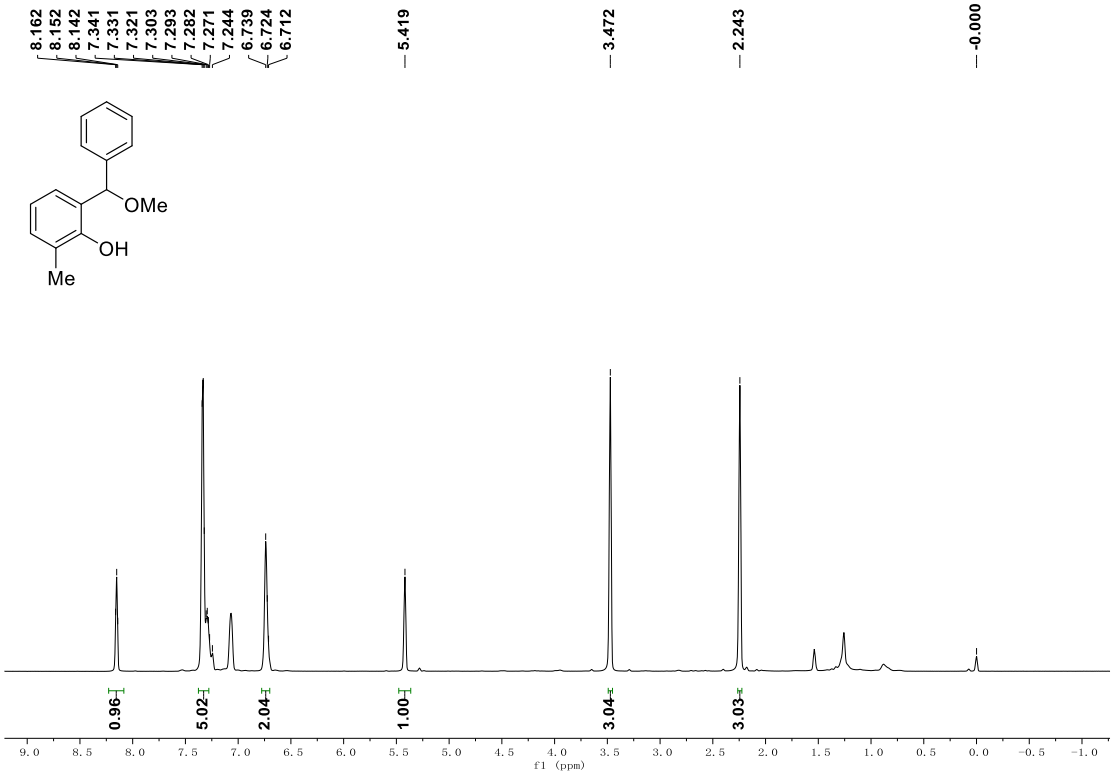
^{1}H NMR (400 MHz) of **(±)-3b** in $CDCl_3$



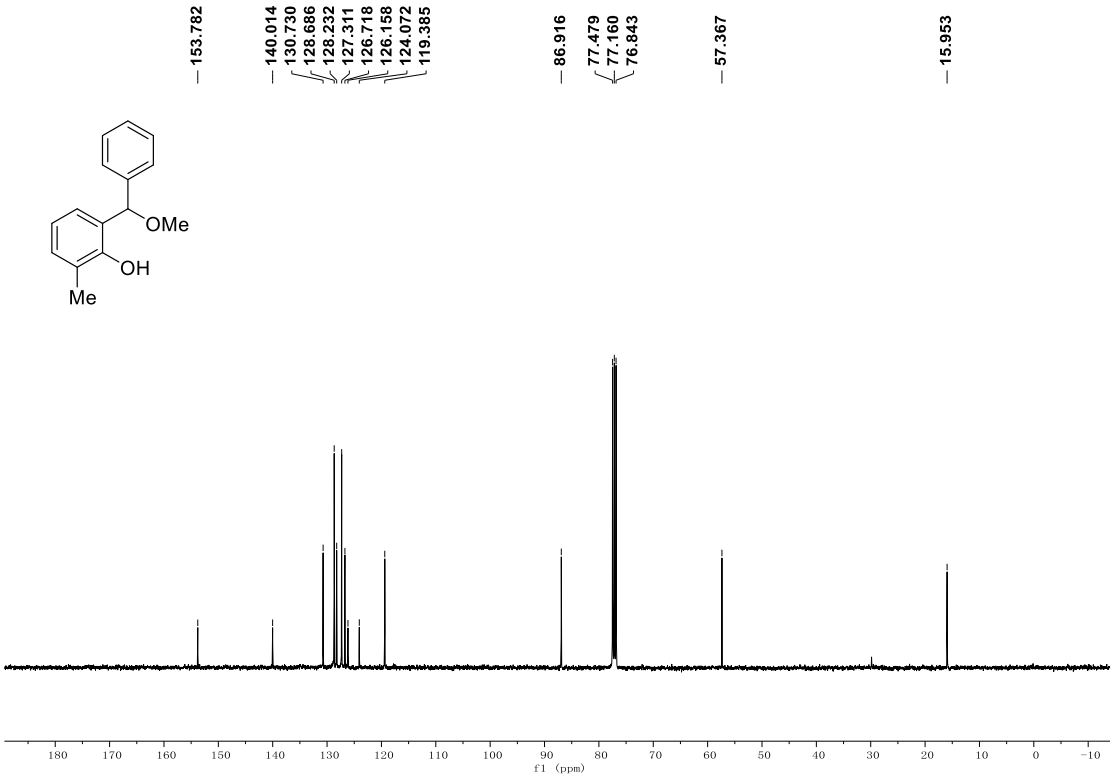
^{13}C NMR (100 MHz) of **(±)-3b** in $CDCl_3$



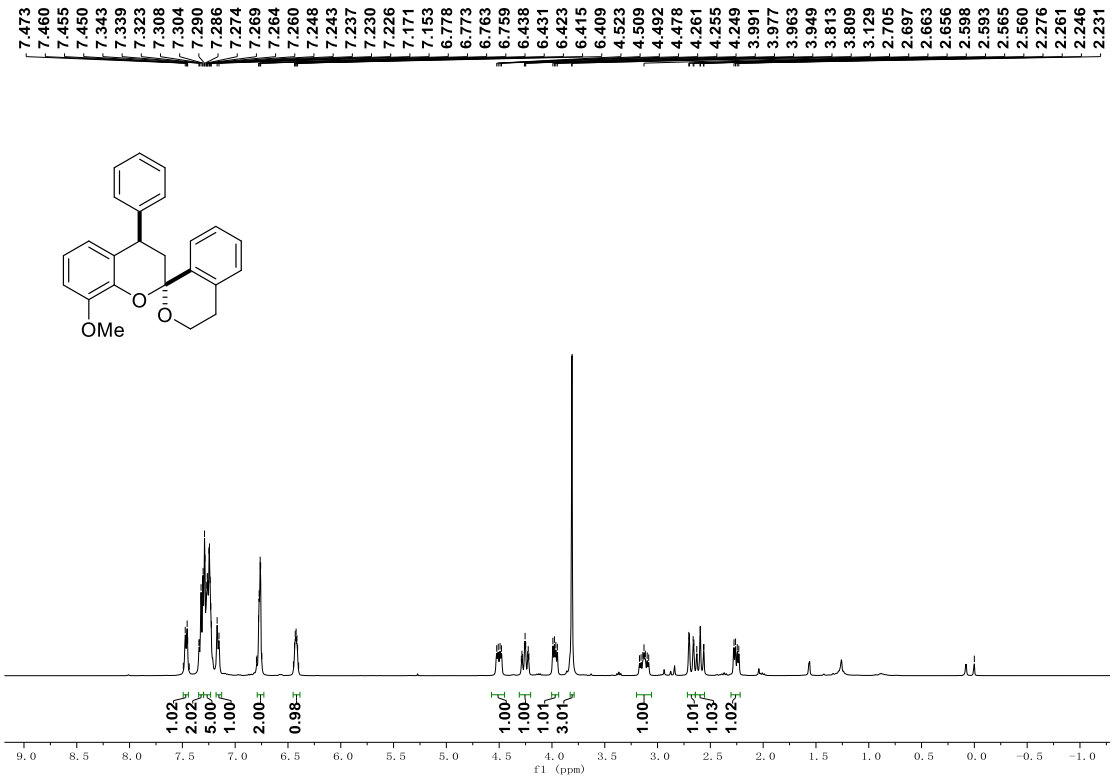
^{1}H NMR (400 MHz) of **(±)-4b** in $CDCl_3$



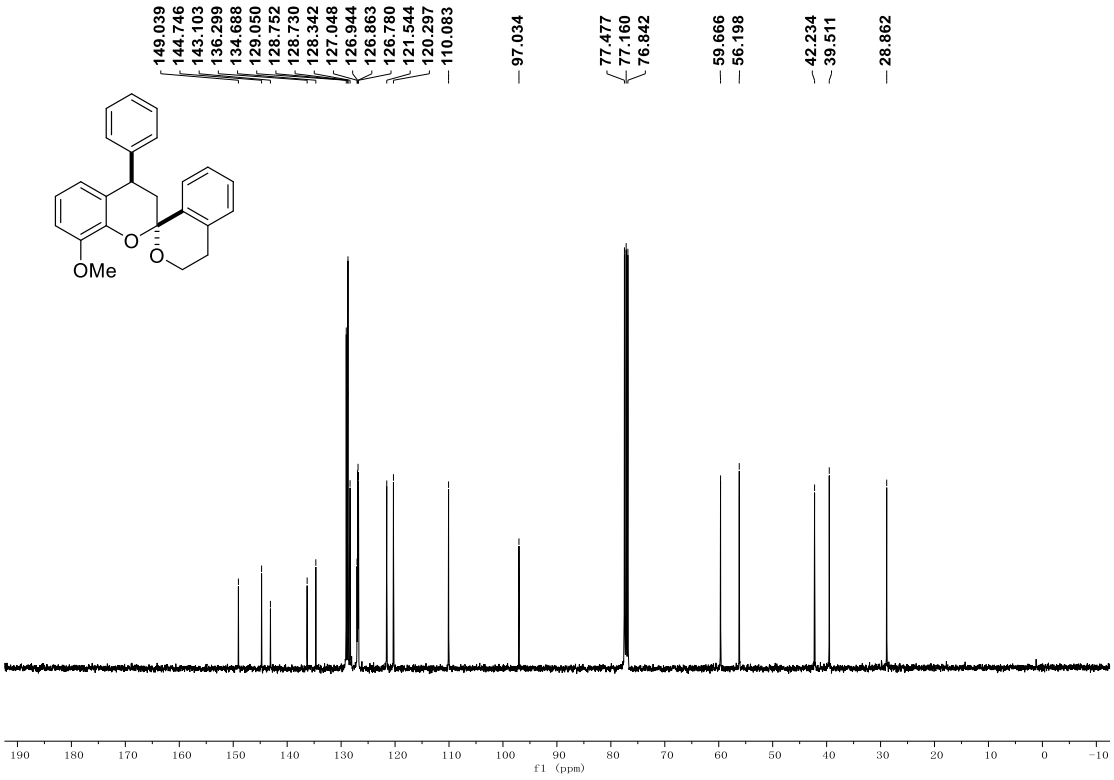
^{13}C NMR (100 MHz) of **(±)-4b** in $CDCl_3$



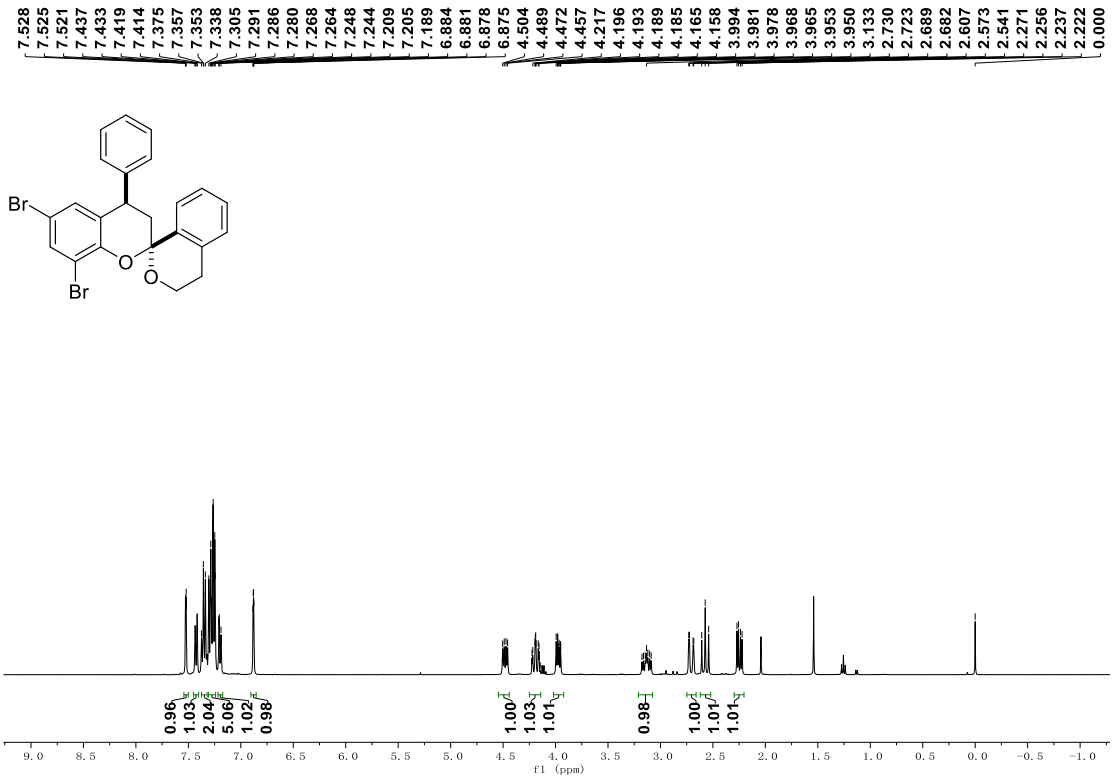
^{1}H NMR (400 MHz) of **(±)-3c** in $CDCl_3$



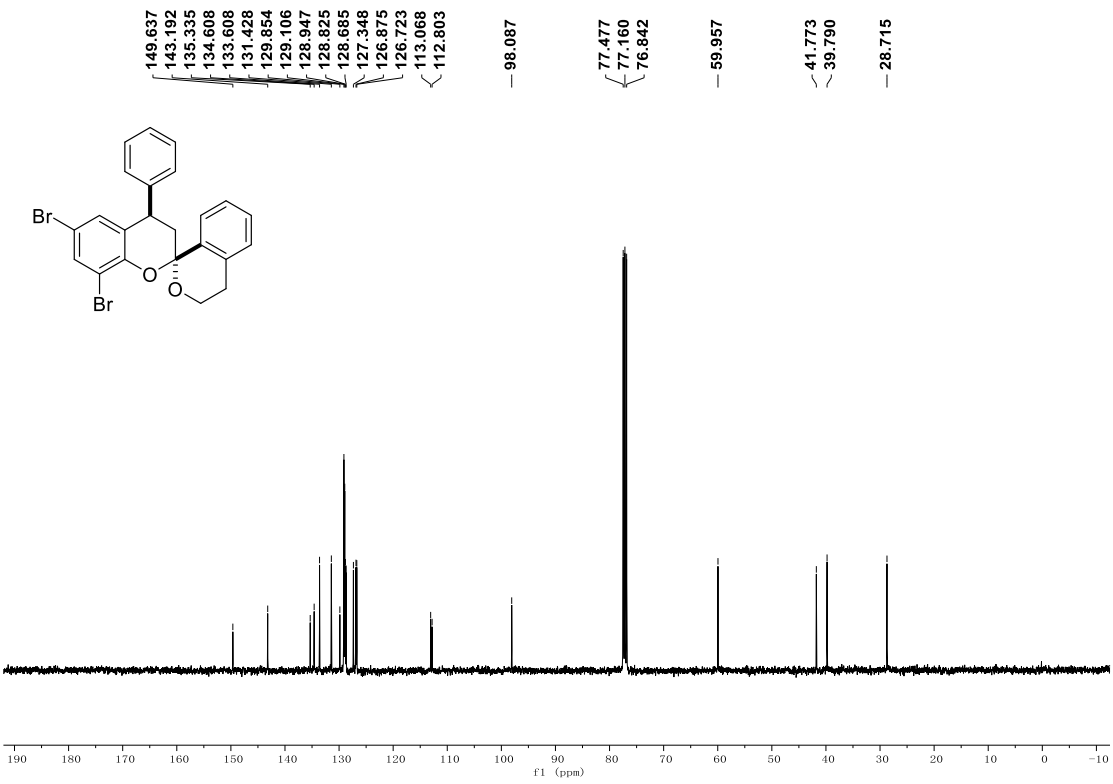
^{13}C NMR (100 MHz) of **(±)-3c** in $CDCl_3$



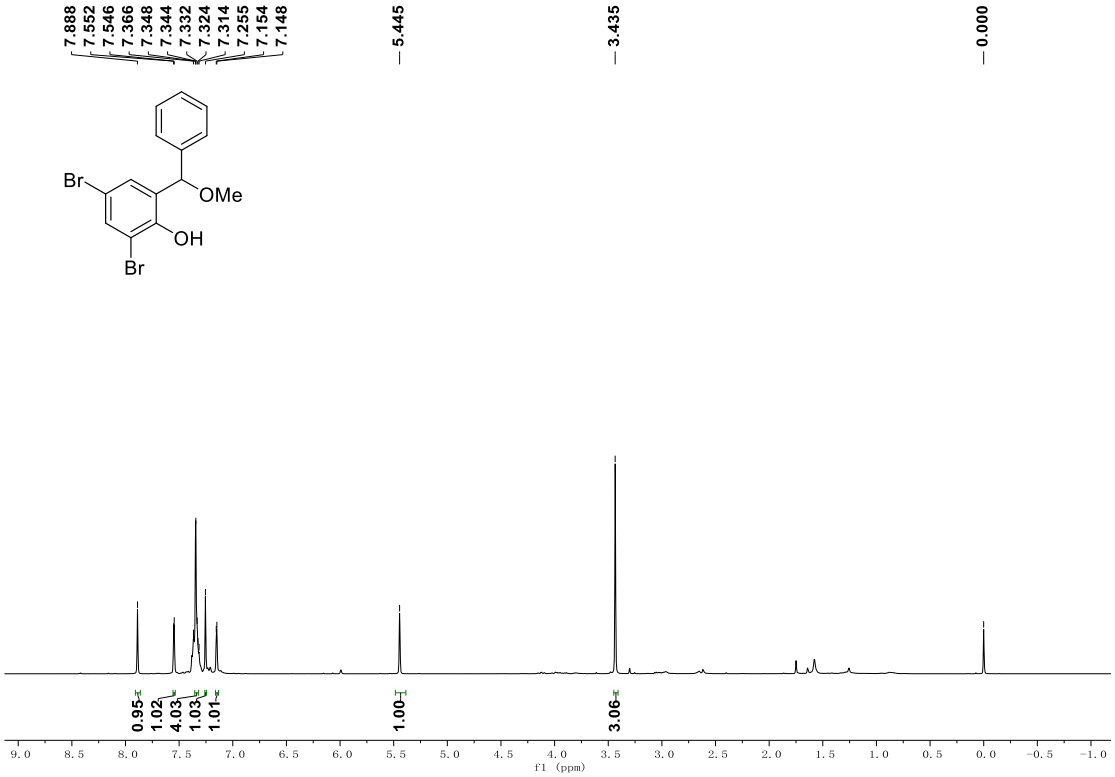
^{1}H NMR (400 MHz) of **(±)-3d** in $CDCl_3$



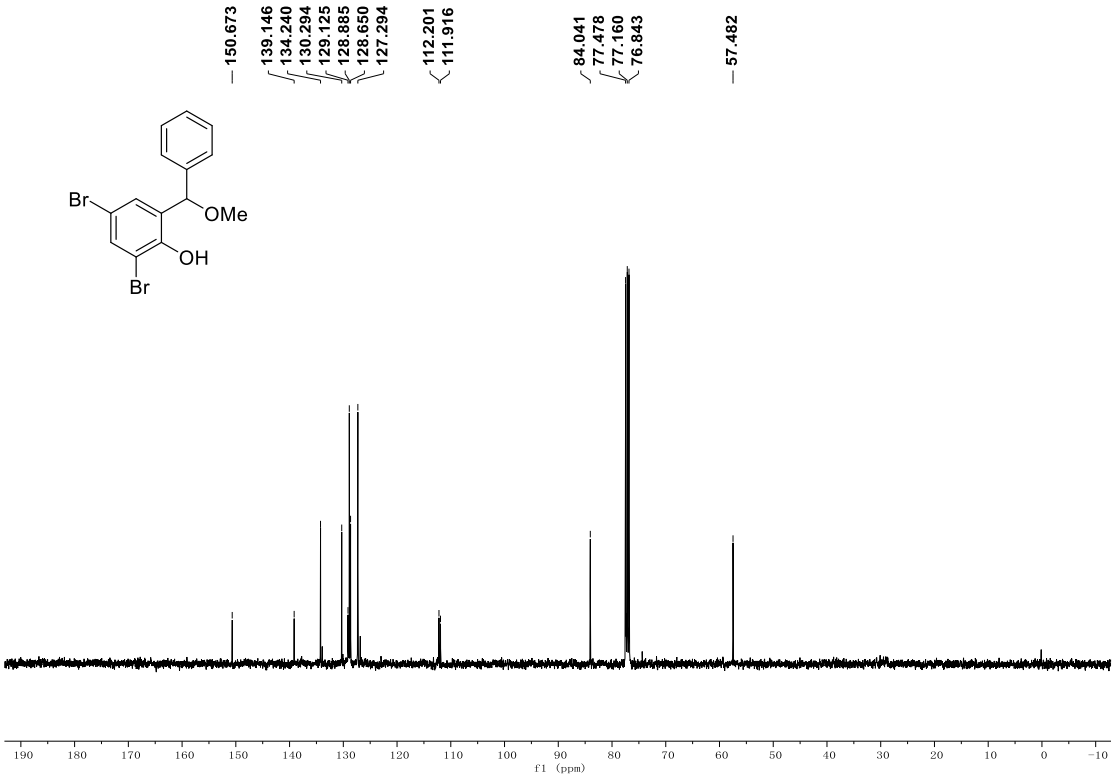
^{13}C NMR (100 MHz) of **(±)-3d** in $CDCl_3$



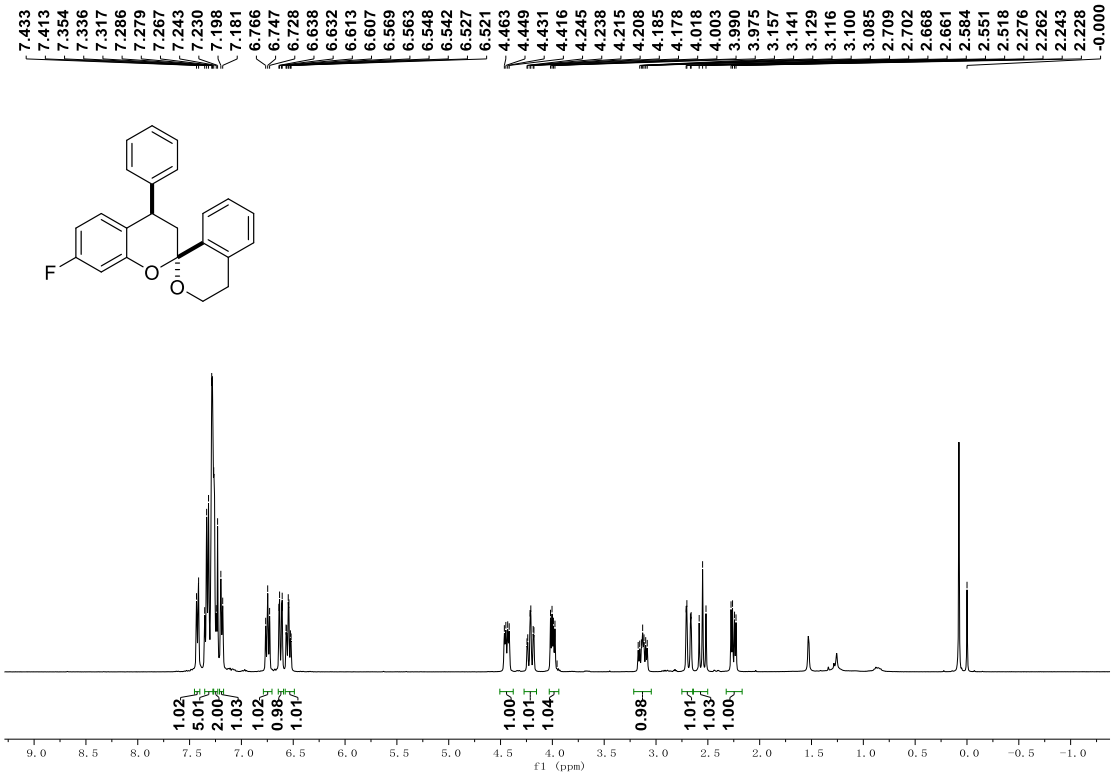
^{1}H NMR (400 MHz) of **(±)-4d** in $CDCl_3$



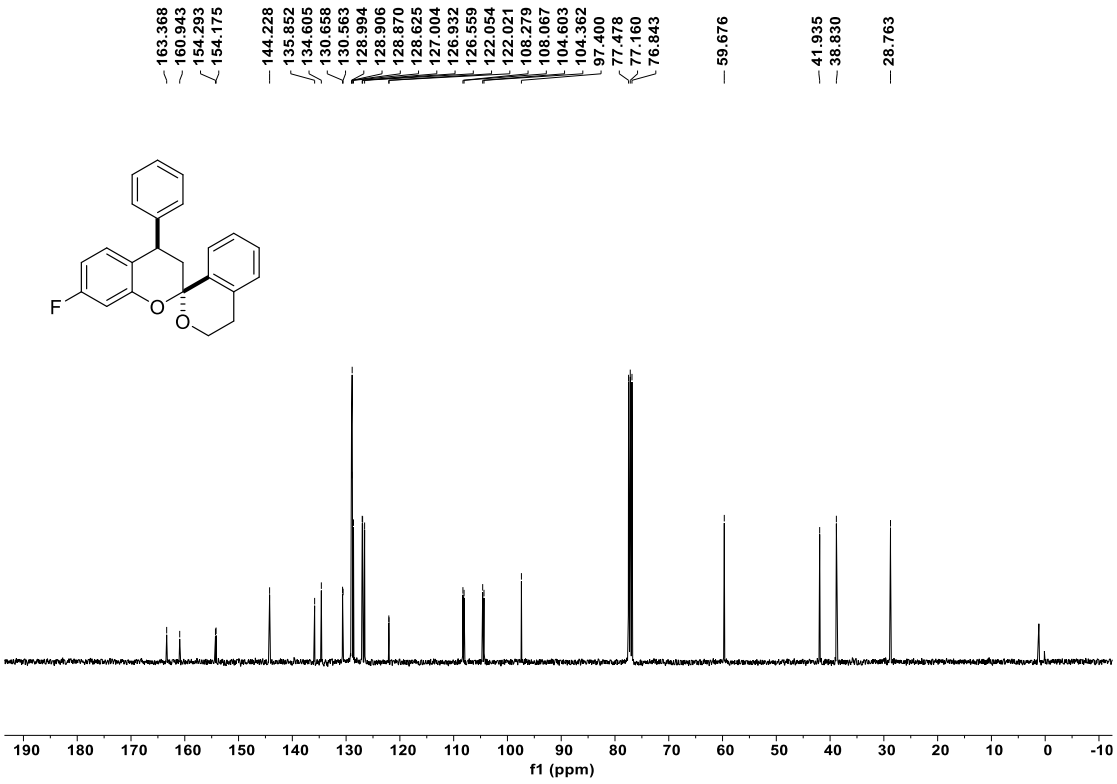
^{13}C NMR (100 MHz) of **(±)-4d** in $CDCl_3$



^{1}H NMR (400 MHz) of **(±)-3e** in $CDCl_3$

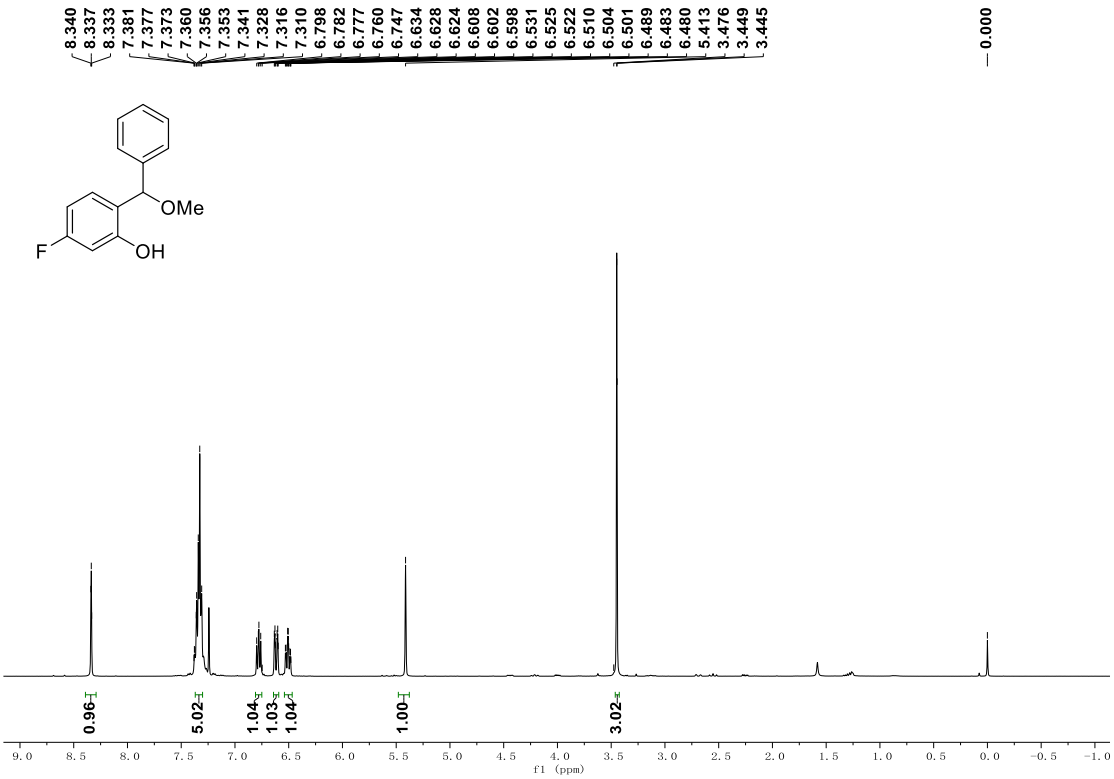


^{13}C NMR (100 MHz) of **(±)-3e** in $CDCl_3$

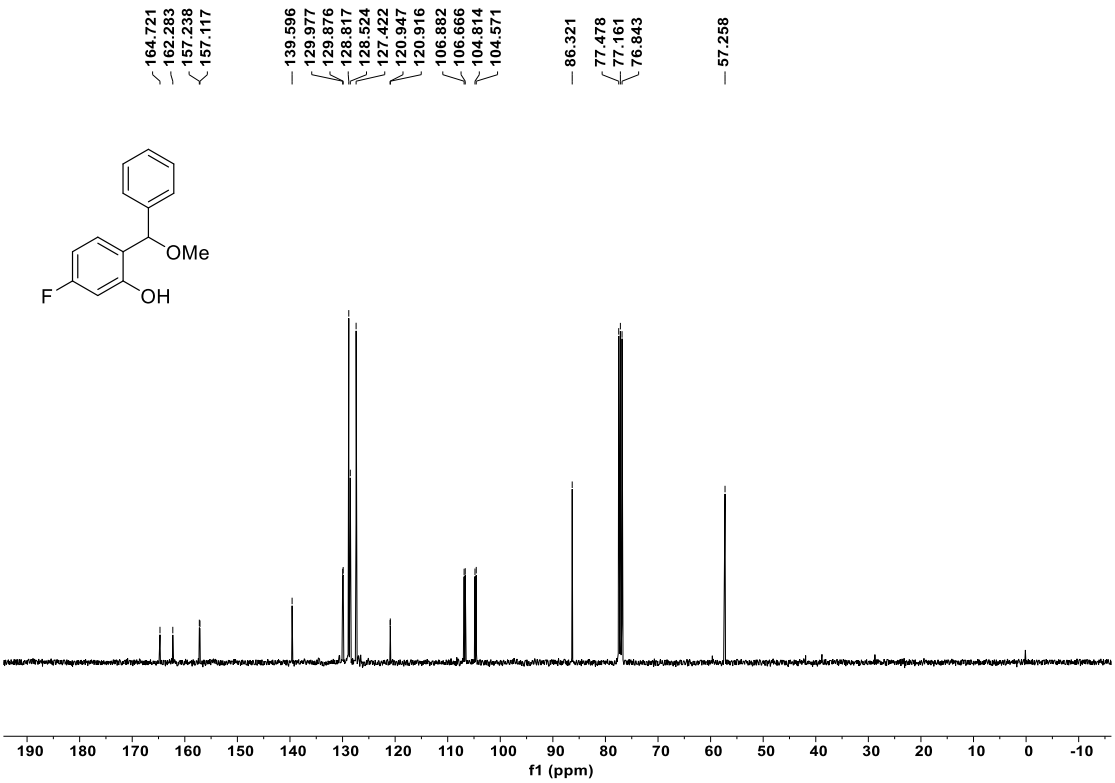


^{19}F NMR (565 MHz) of **(±)-3e** in $CDCl_3$

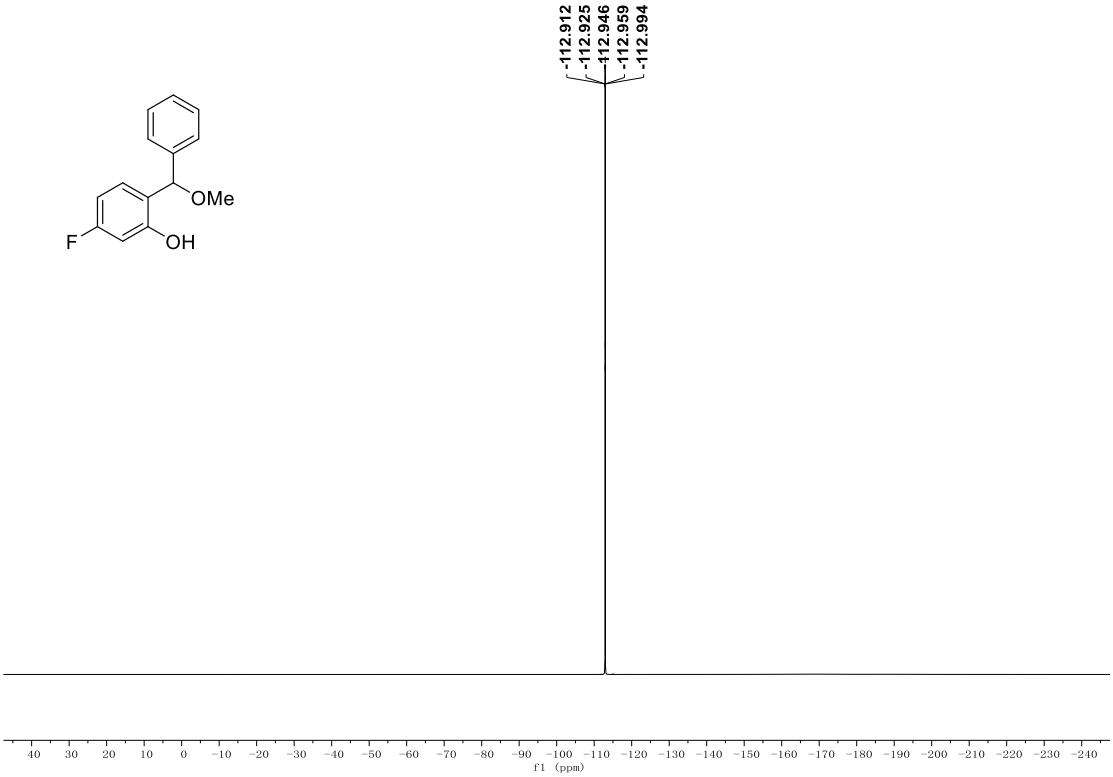
^{1}H NMR (400 MHz) of **(±)-4e** in $CDCl_3$



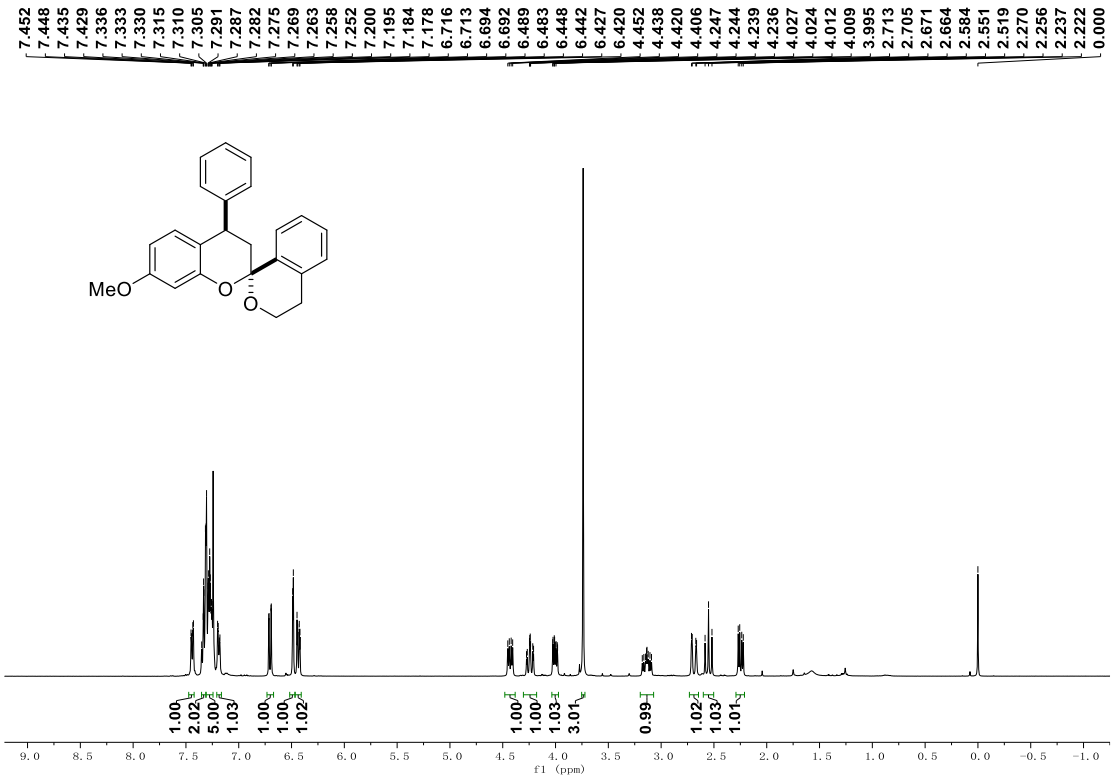
^{13}C NMR (100 MHz) of **(±)-4e** in $CDCl_3$



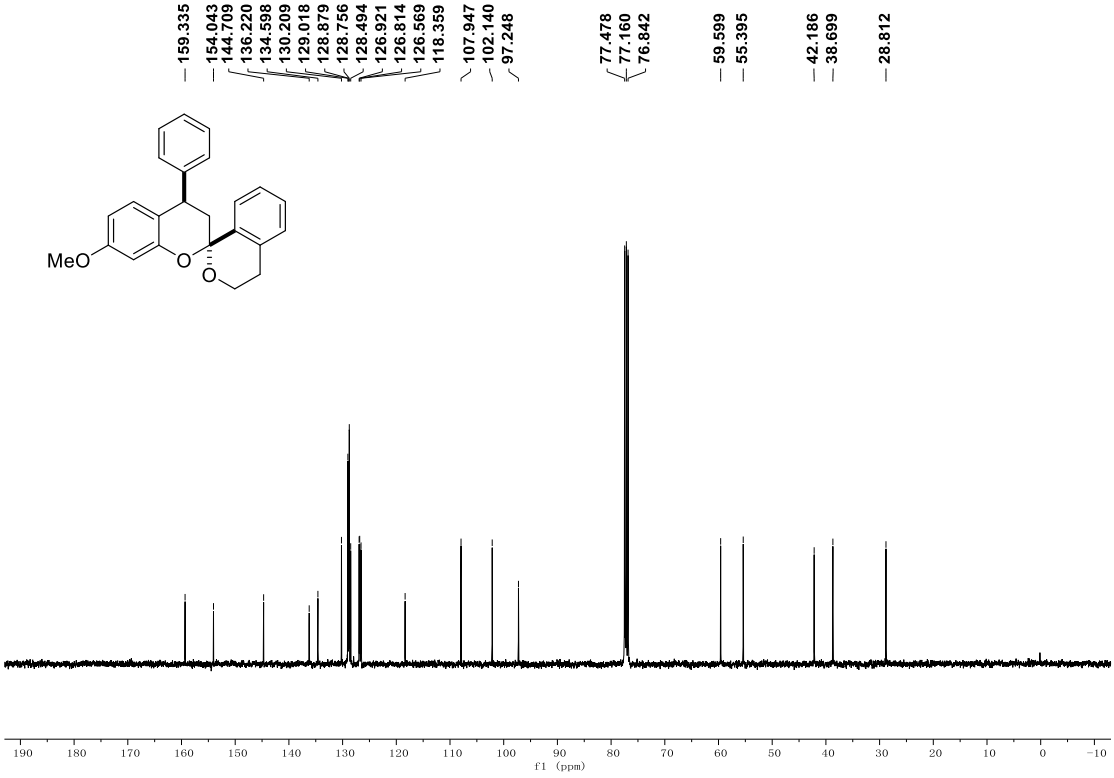
^{19}F NMR (565 MHz) of **(±)-4e** in $CDCl_3$



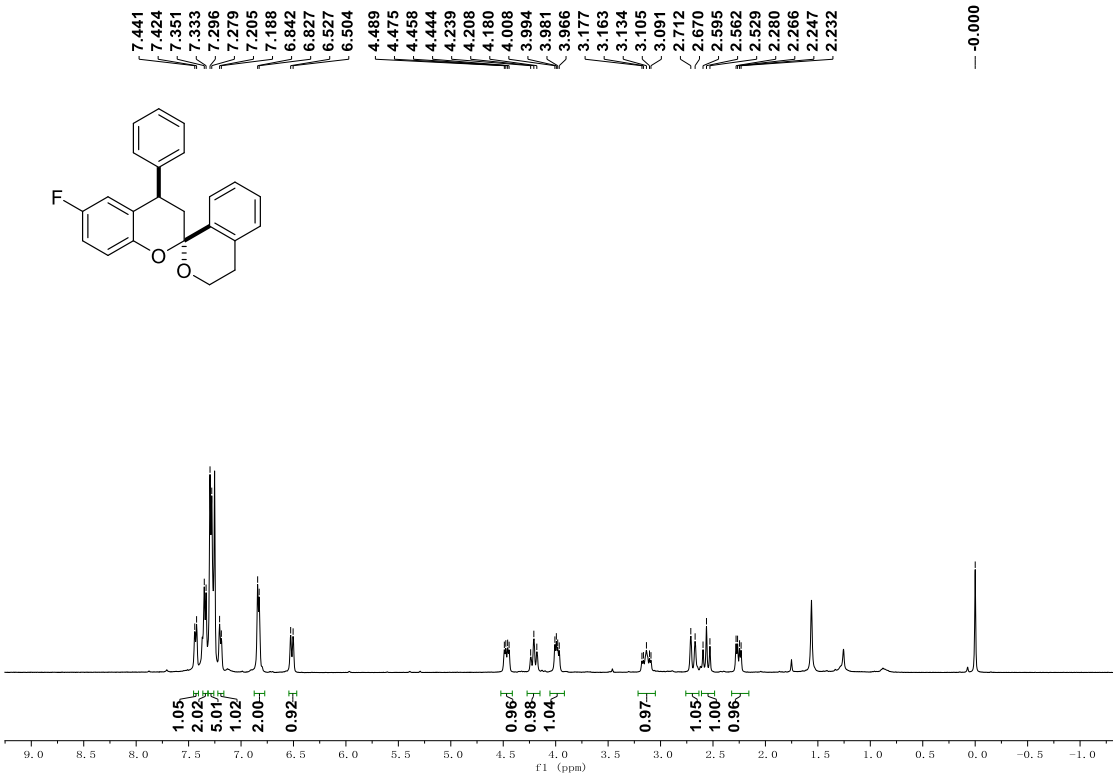
^{1}H NMR (400 MHz) of **(±)-3f** in $CDCl_3$



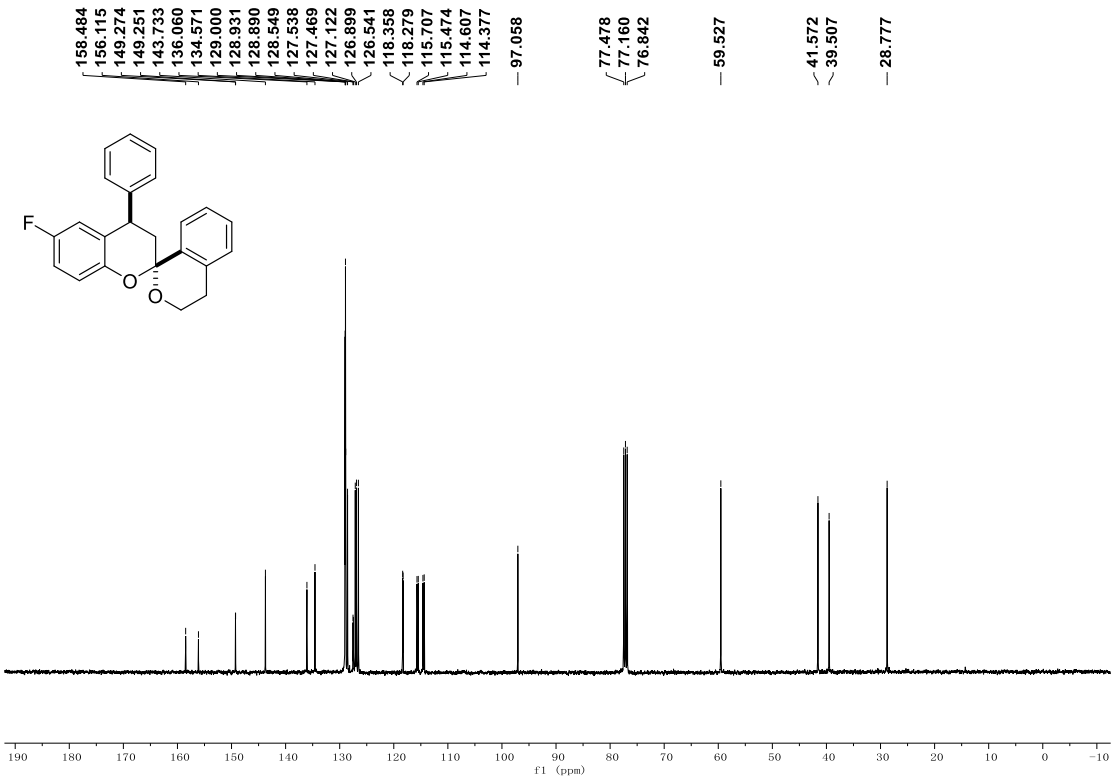
^{13}C NMR (100 MHz) of **(±)-3f** in $CDCl_3$



^{1}H NMR (400 MHz) of **(±)-3g** in $CDCl_3$

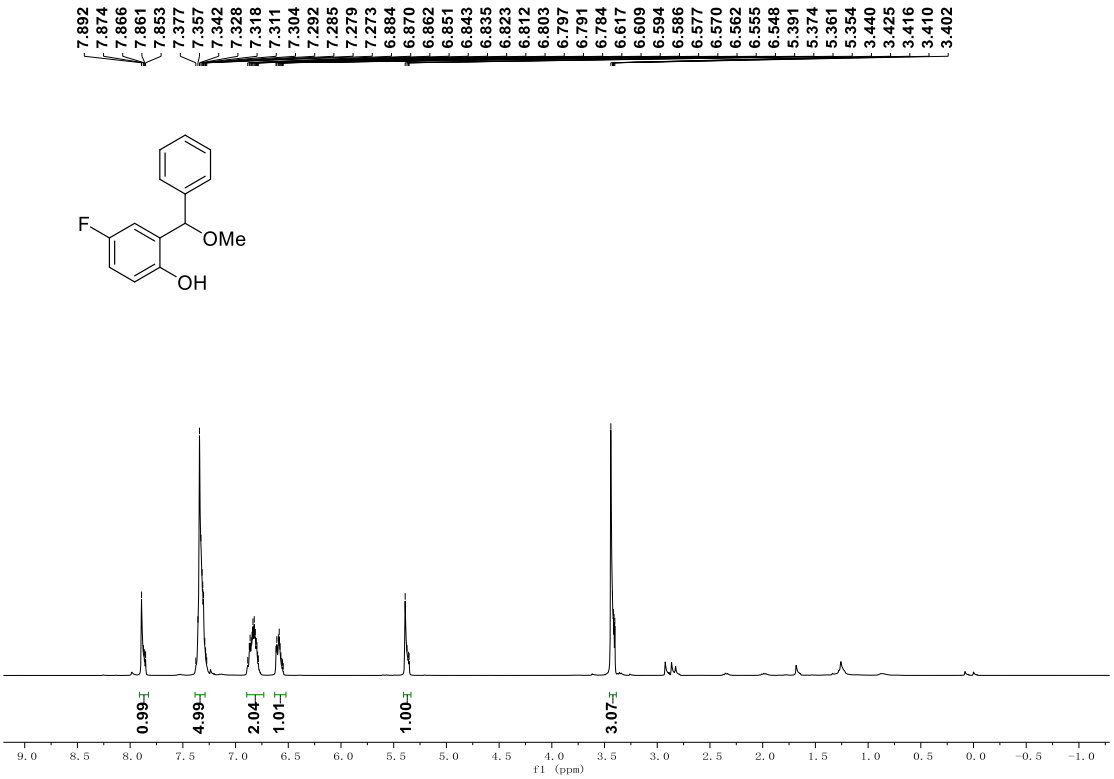


^{13}C NMR (100 MHz) of **(±)-3g** in $CDCl_3$

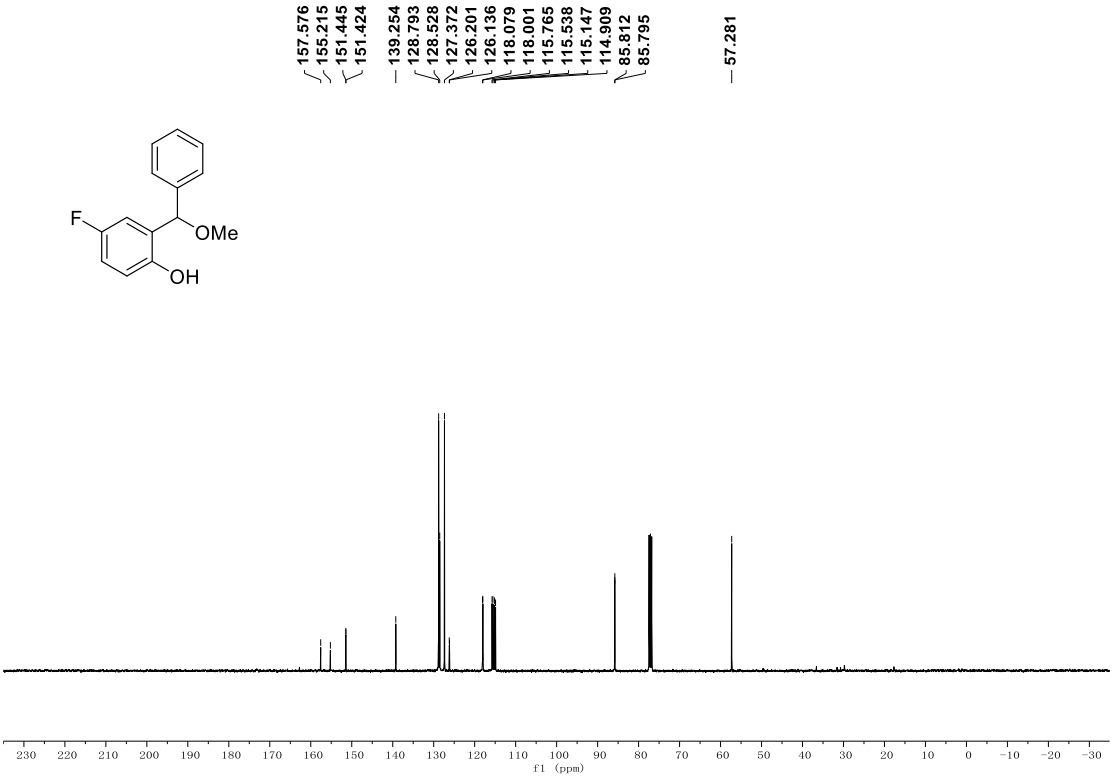


^{19}F NMR (565 MHz) of **(±)-3g** in $CDCl_3$

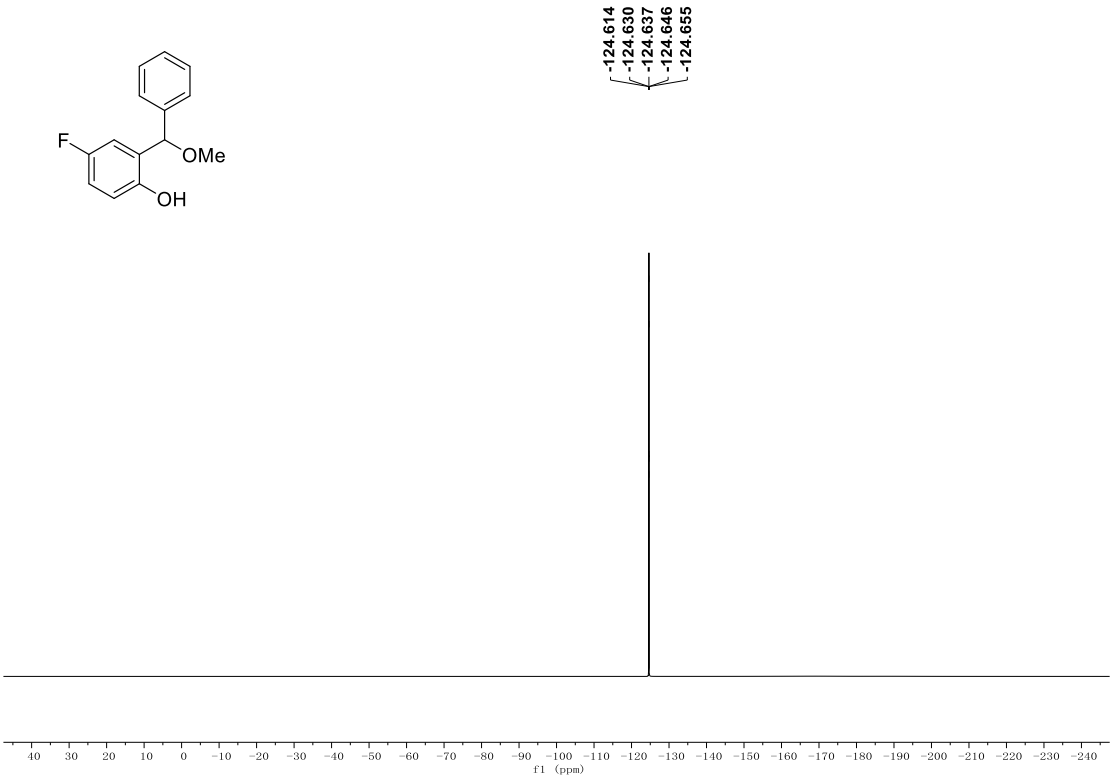
^{1}H NMR (400 MHz) of **(±)-4g** in $CDCl_3$



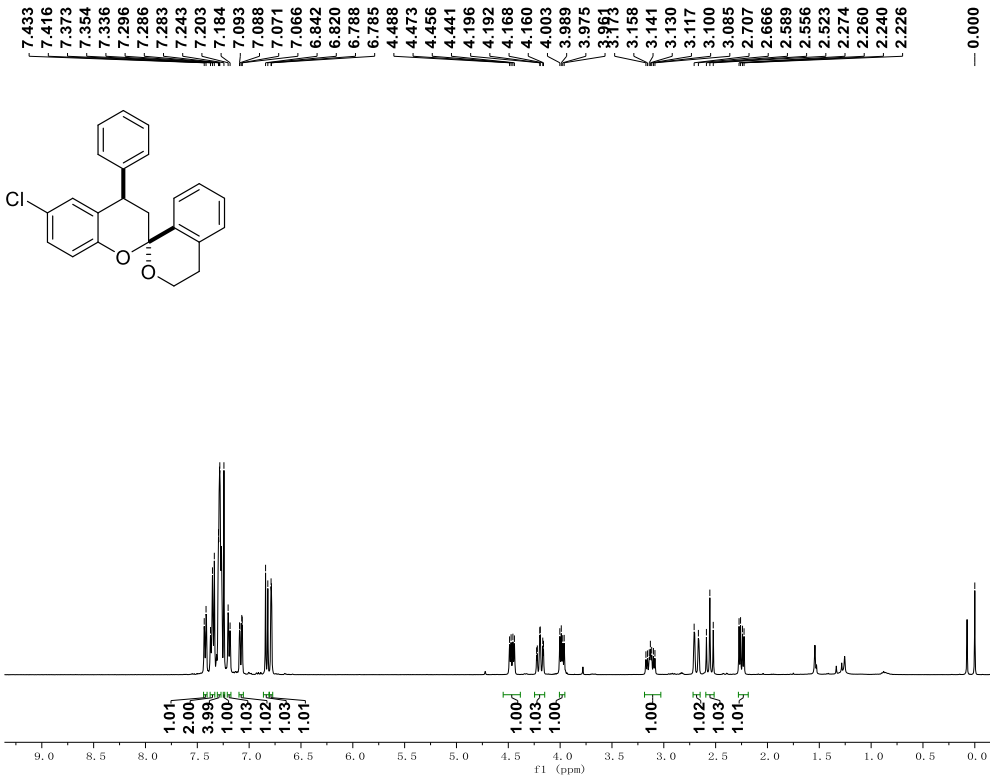
^{13}C NMR (100 MHz) of **(±)-4g** in $CDCl_3$



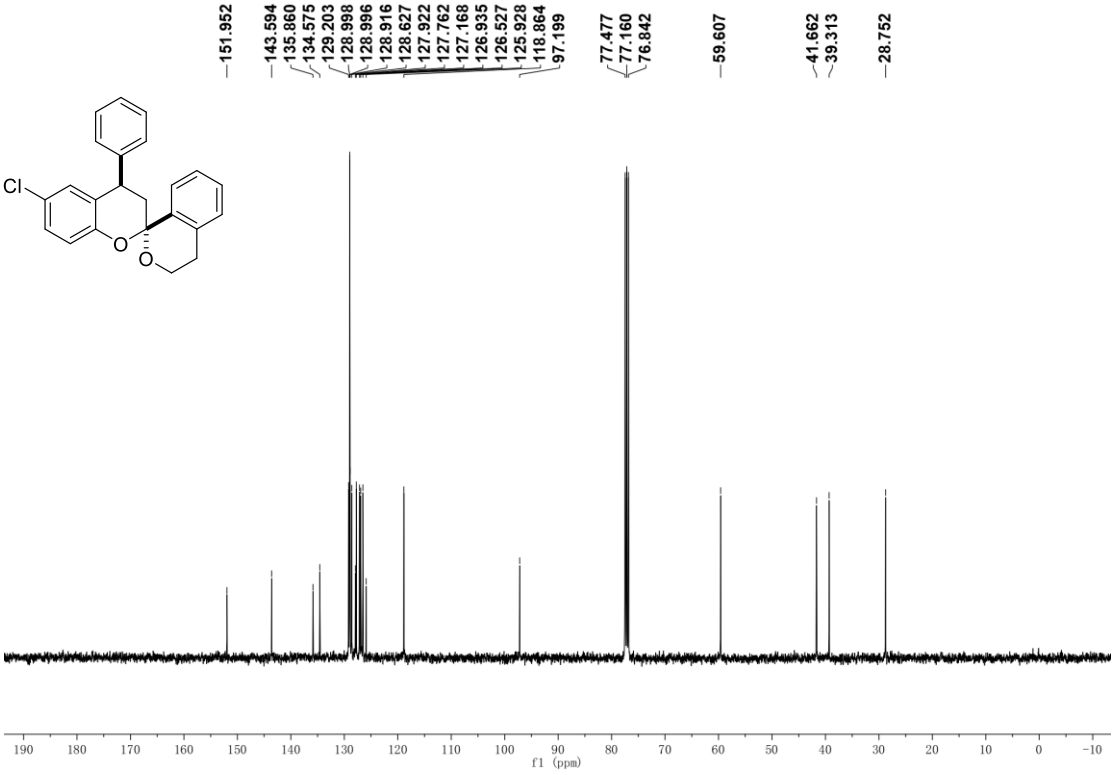
^{19}F NMR (565 MHz) of **(±)-4g** in $CDCl_3$



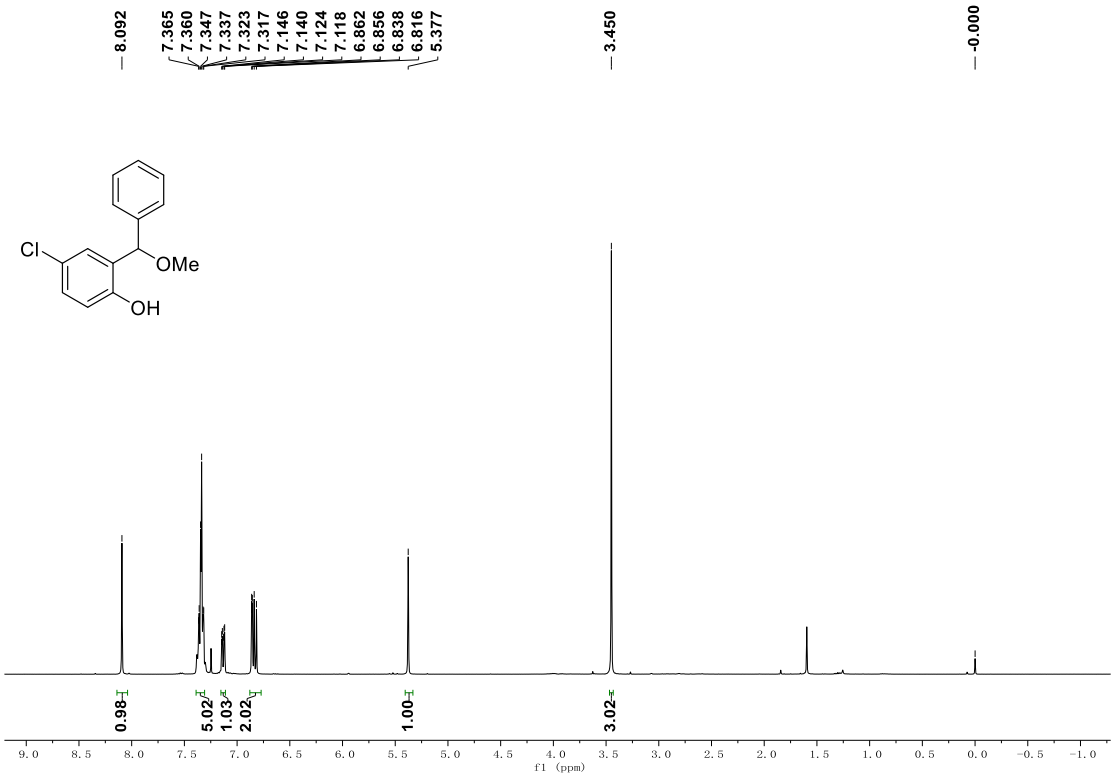
^{1}H NMR (400 MHz) of **(±)-3h** in $CDCl_3$



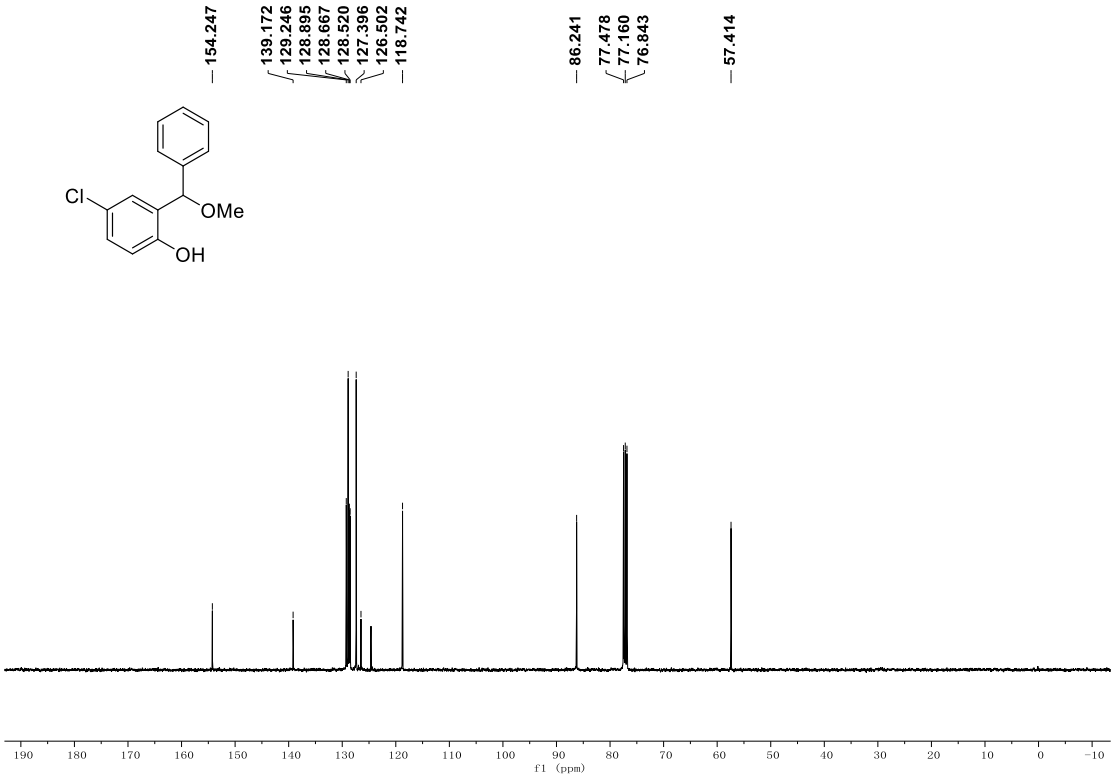
^{13}C NMR (100 MHz) of **(±)-3h** in $CDCl_3$



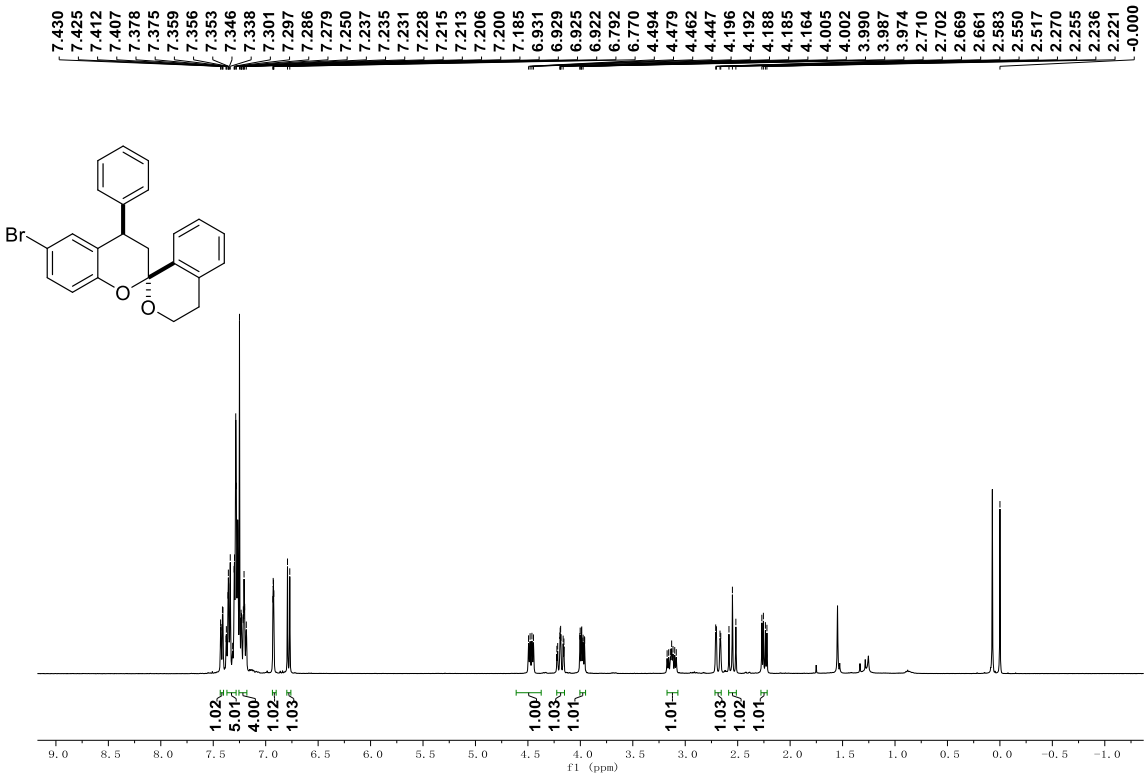
^{1}H NMR (400 MHz) of **(±)-4h** in $CDCl_3$



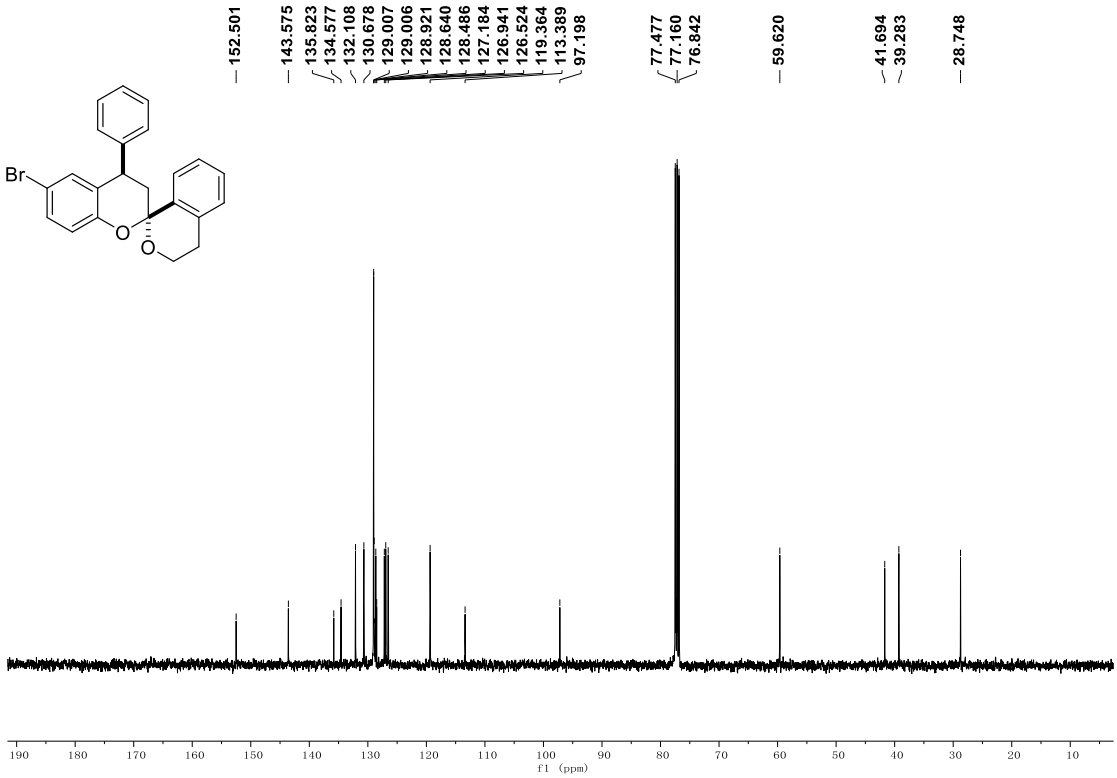
^{13}C NMR (100 MHz) of **(±)-4h** in $CDCl_3$



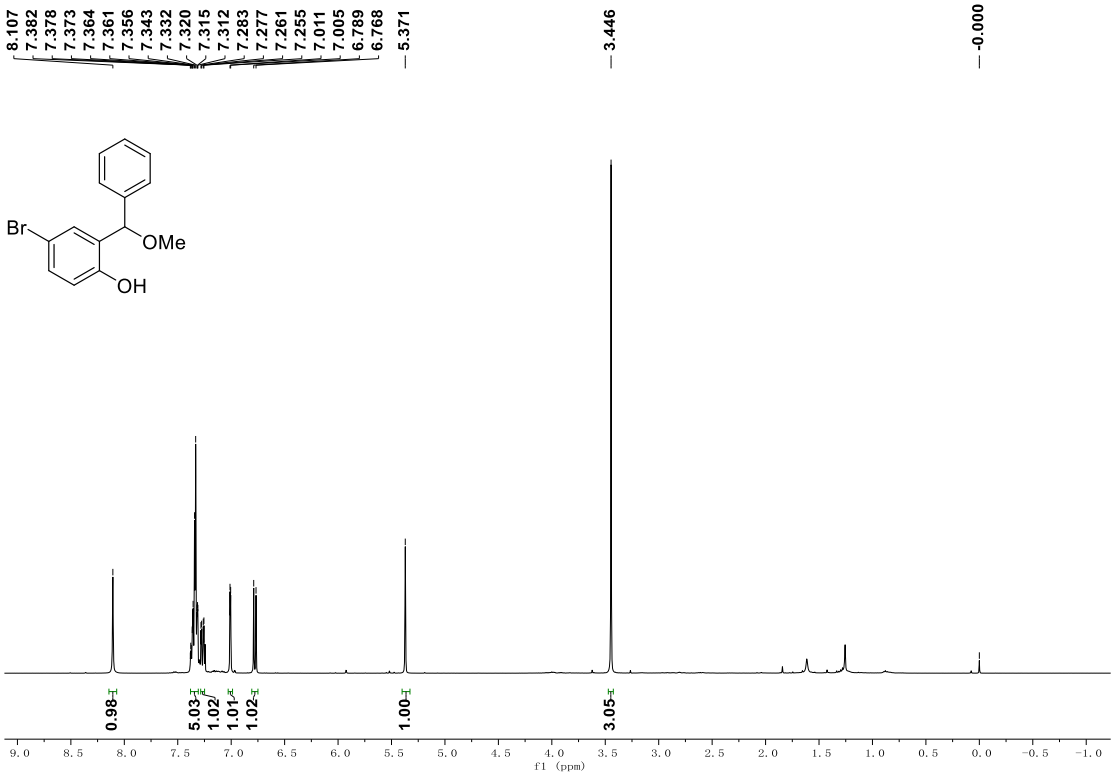
^{1}H NMR (400 MHz) of **(±)-3i** in $CDCl_3$



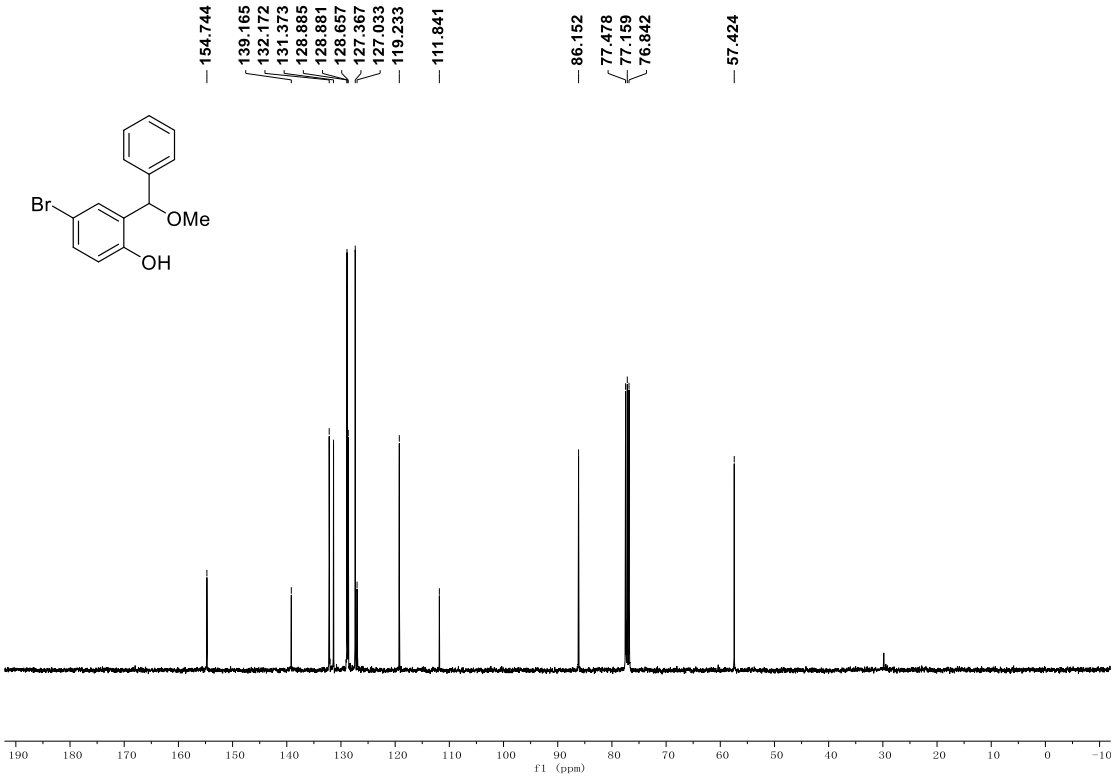
^{13}C NMR (100 MHz) of **(±)-3i** in $CDCl_3$



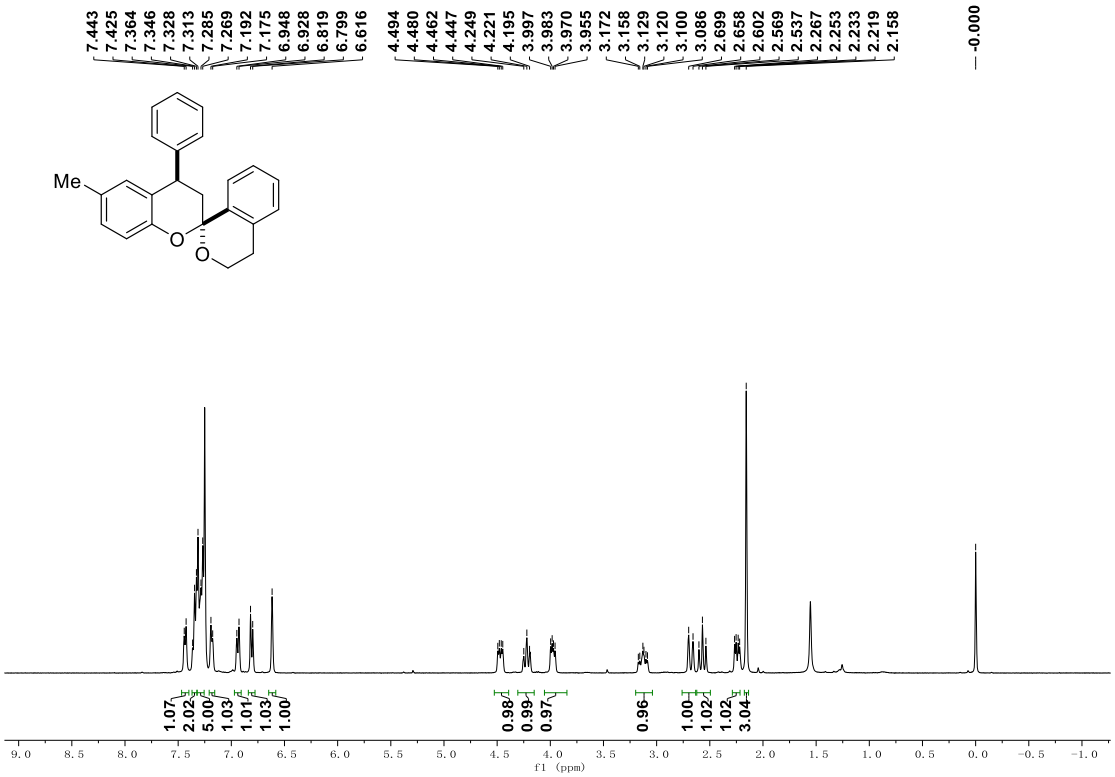
^{1}H NMR (400 MHz) of **(±)-4i** in $CDCl_3$



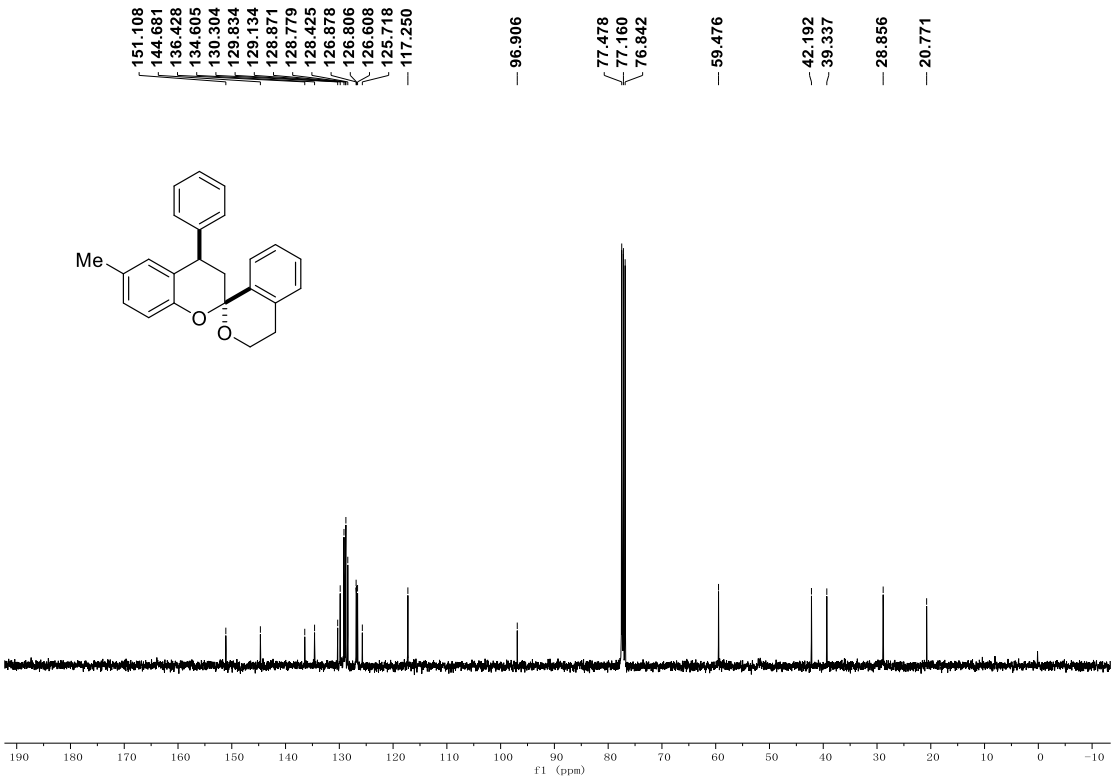
^{13}C NMR (100 MHz) of **(±)-4i** in $CDCl_3$



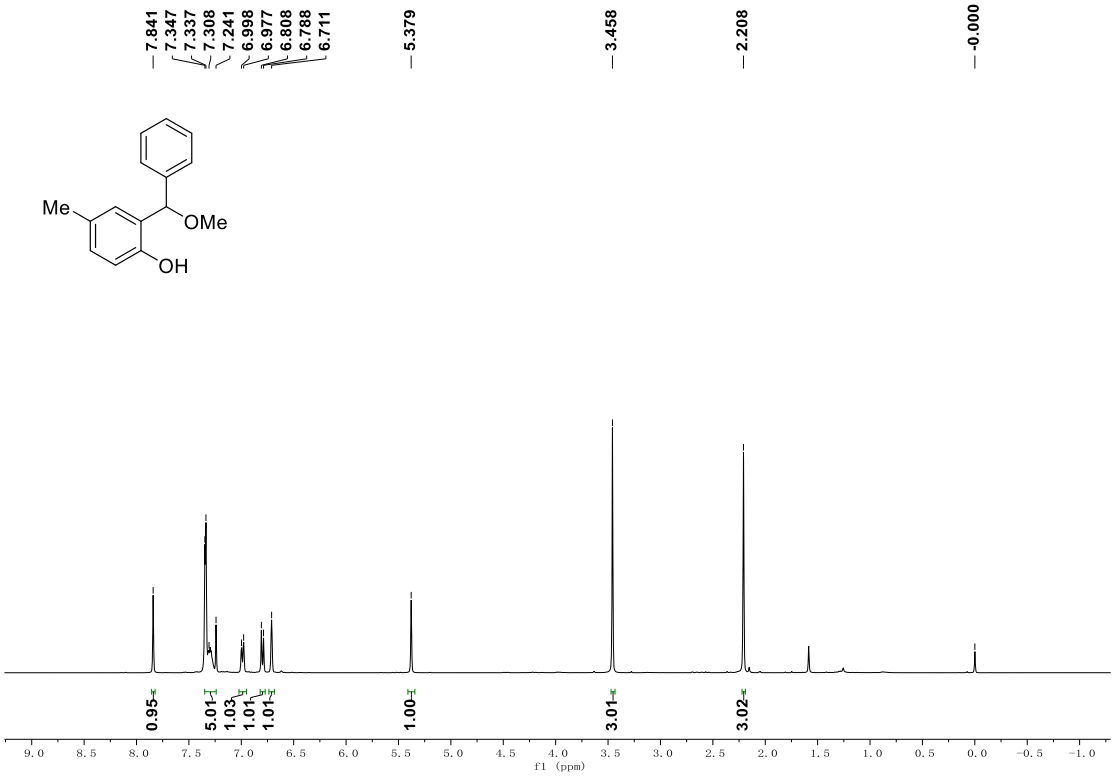
^{1}H NMR (400 MHz) of **(±)-3j** in $CDCl_3$



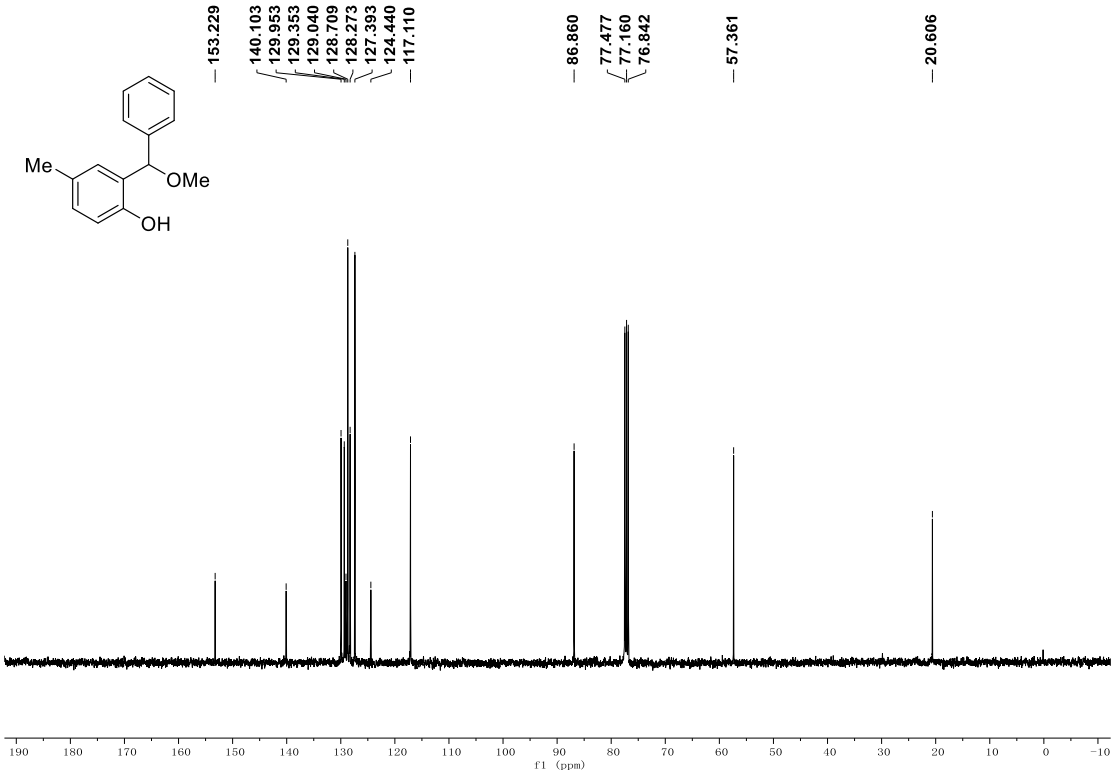
^{13}C NMR (100 MHz) of **(±)-3j** in $CDCl_3$



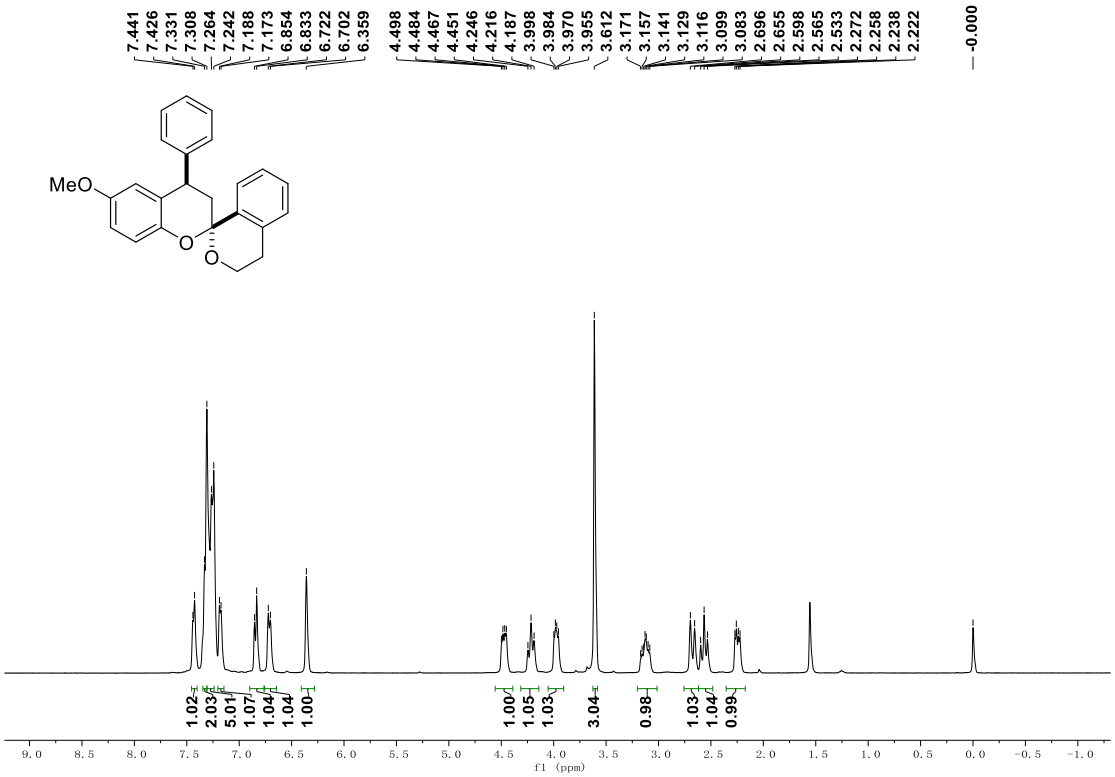
^{1}H NMR (400 MHz) of **(±)-4j** in $CDCl_3$



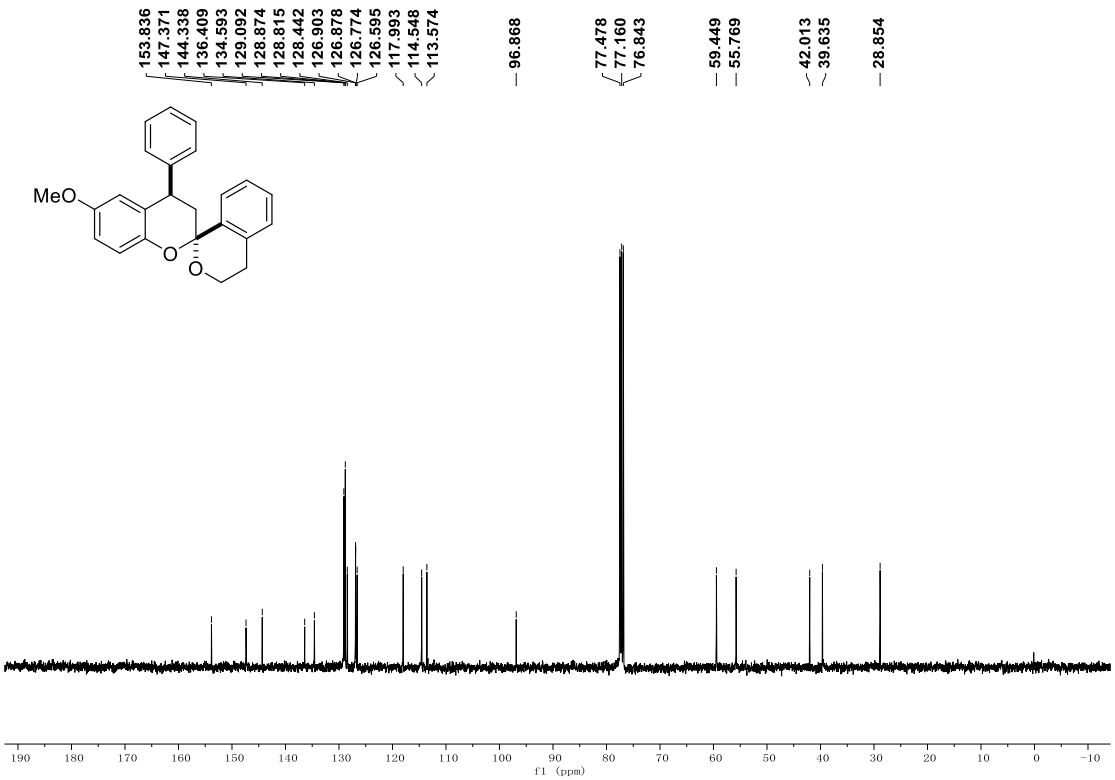
^{13}C NMR (100 MHz) of **(±)-4j** in $CDCl_3$



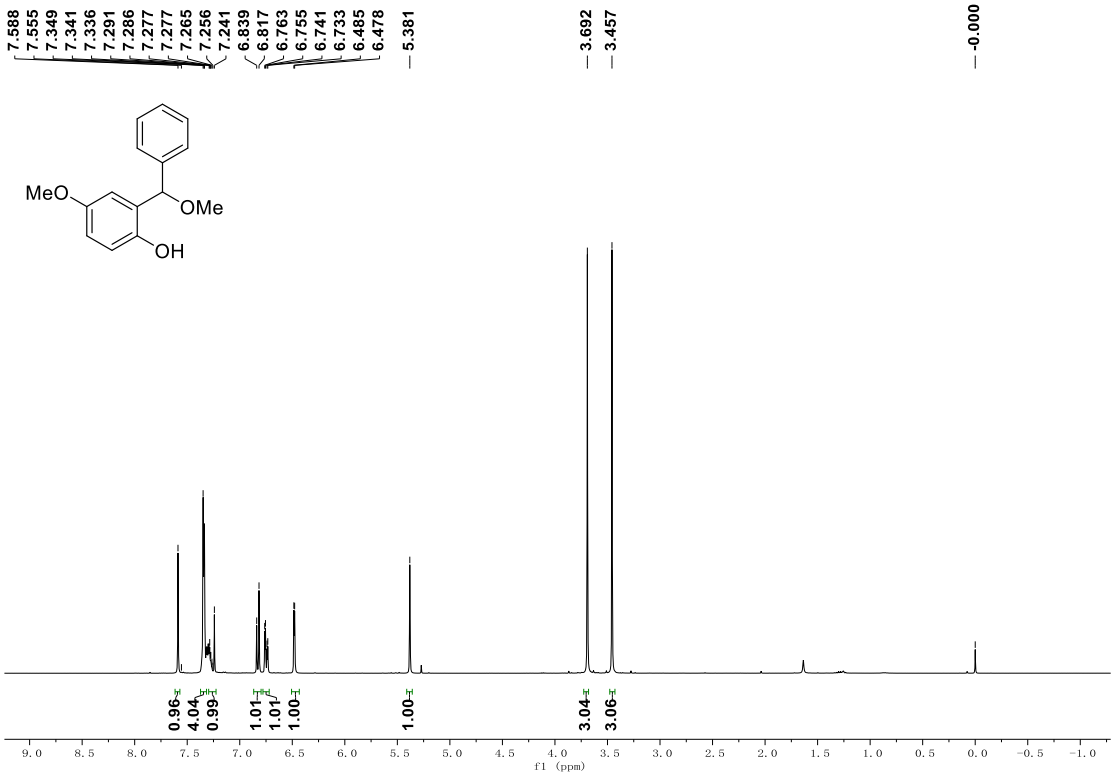
^{1}H NMR (400 MHz) of **(±)-3k** in $CDCl_3$



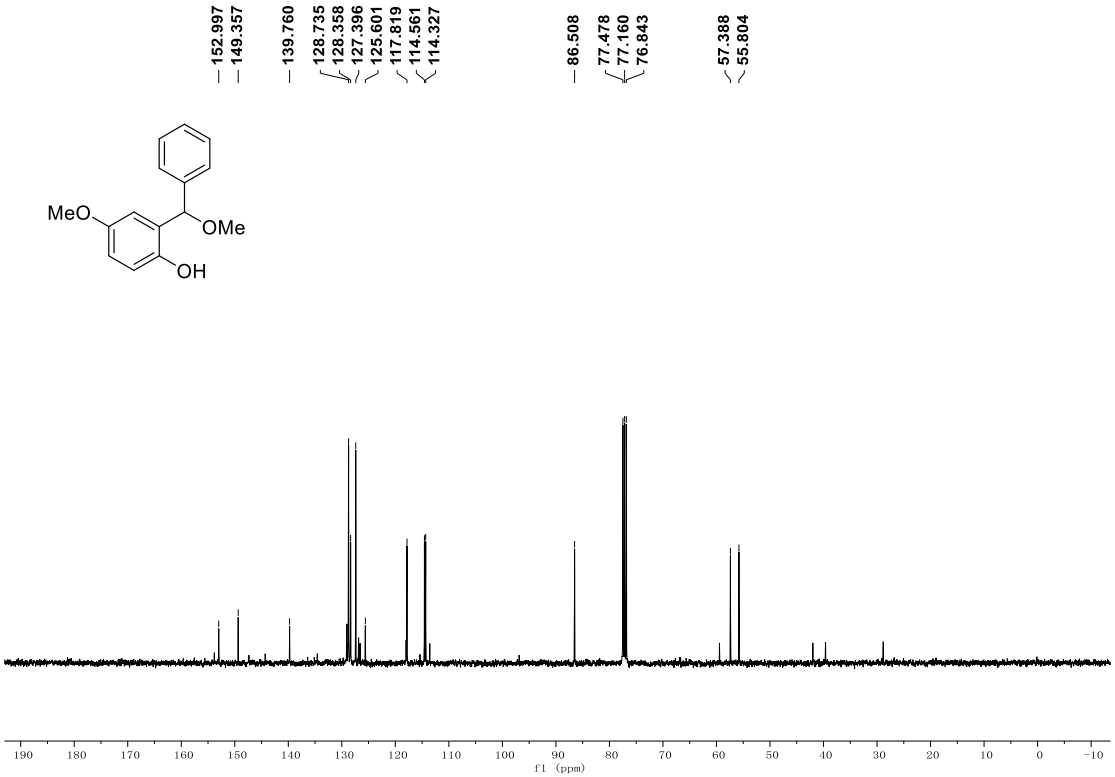
^{13}C NMR (100 MHz) of **(±)-3k** in $CDCl_3$



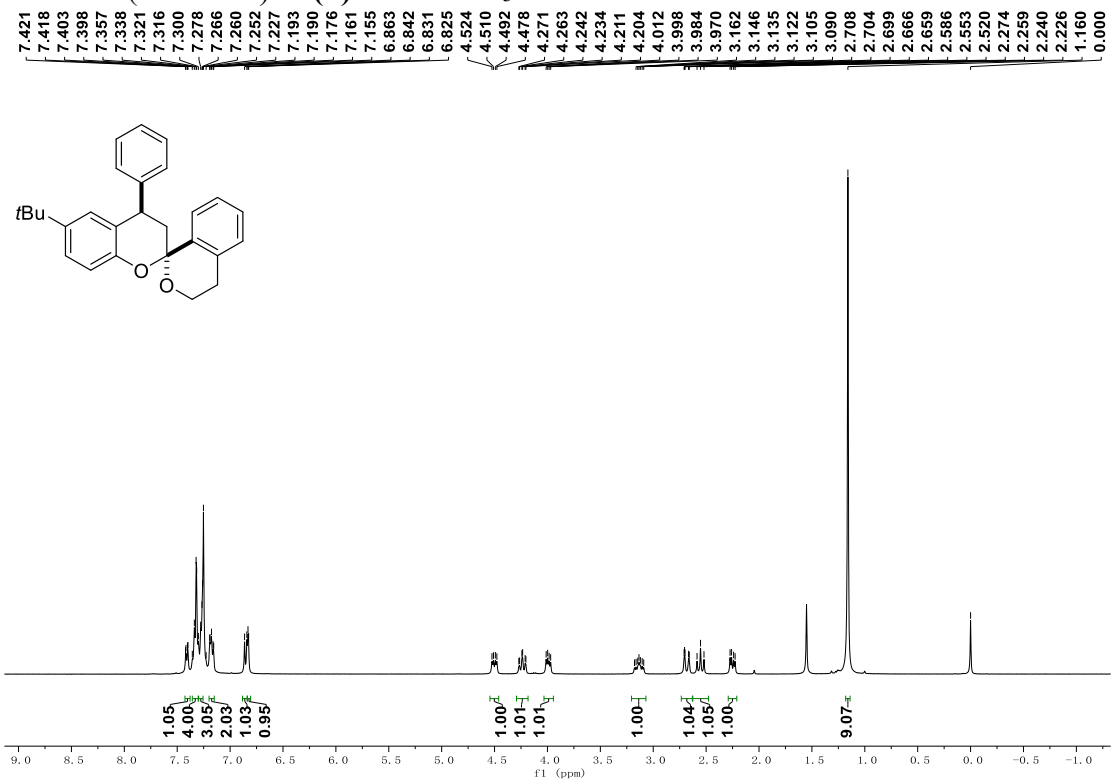
^{1}H NMR (400 MHz) of **(±)-4k** in $CDCl_3$



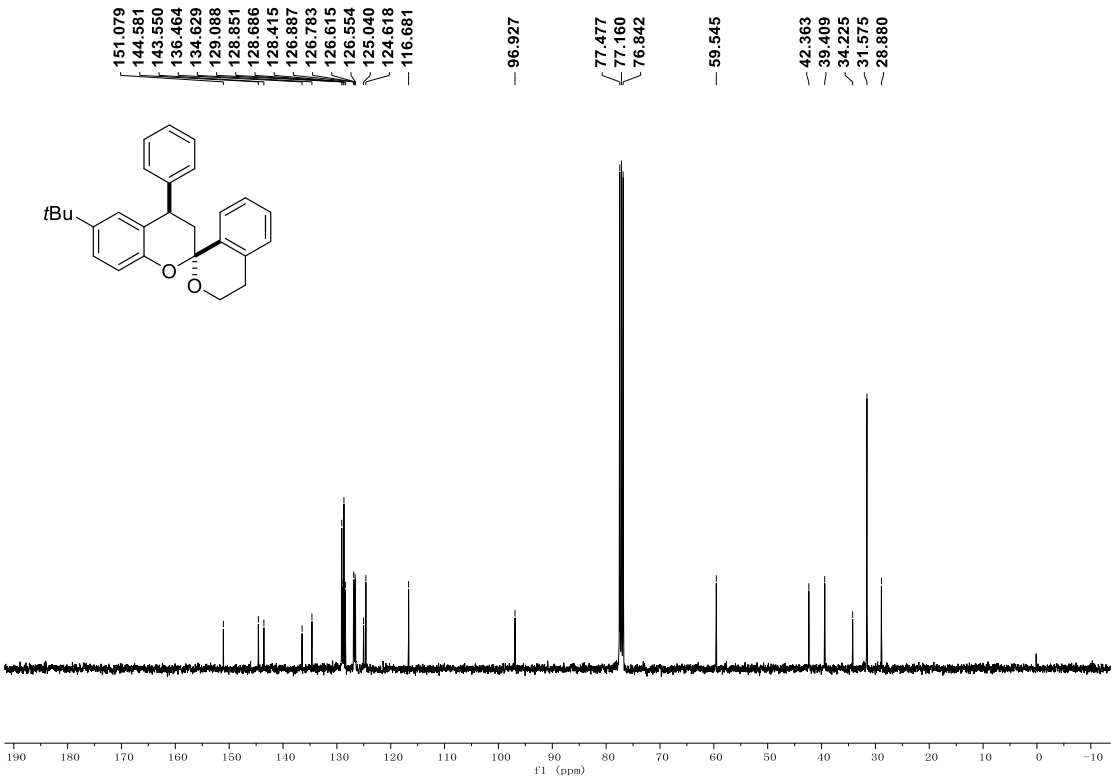
^{13}C NMR (100 MHz) of **(±)-4k** in $CDCl_3$



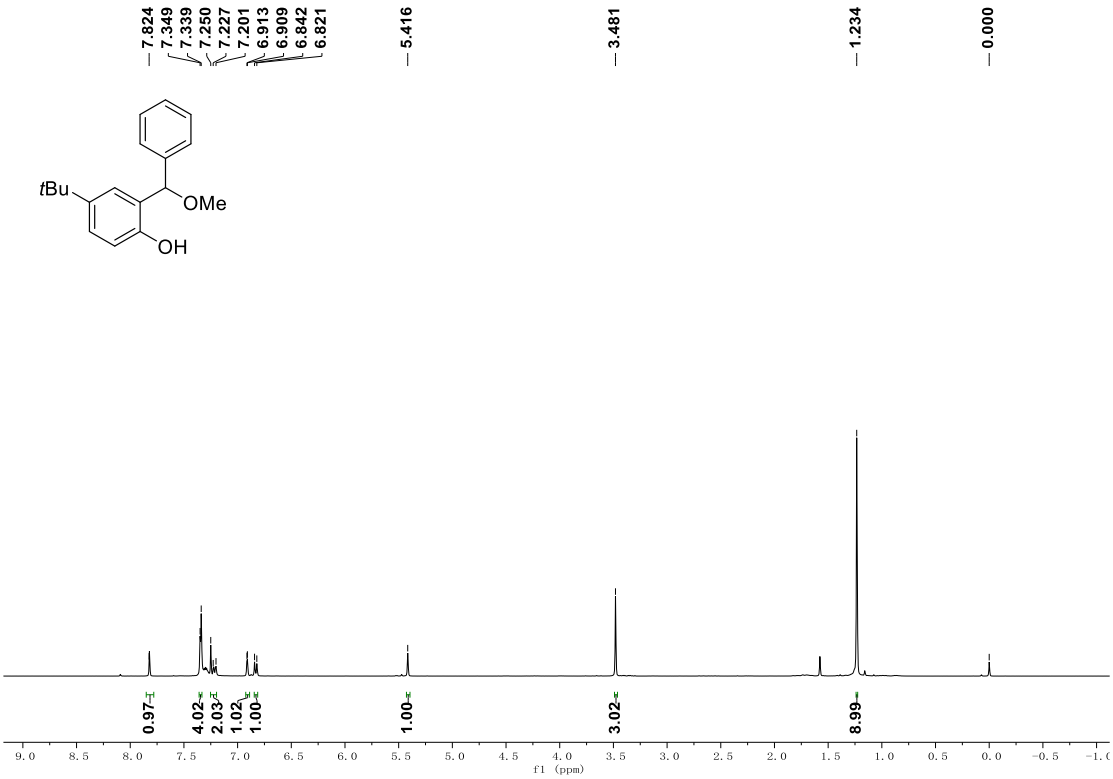
^{1}H NMR (400 MHz) of **(±)-3l** in $CDCl_3$



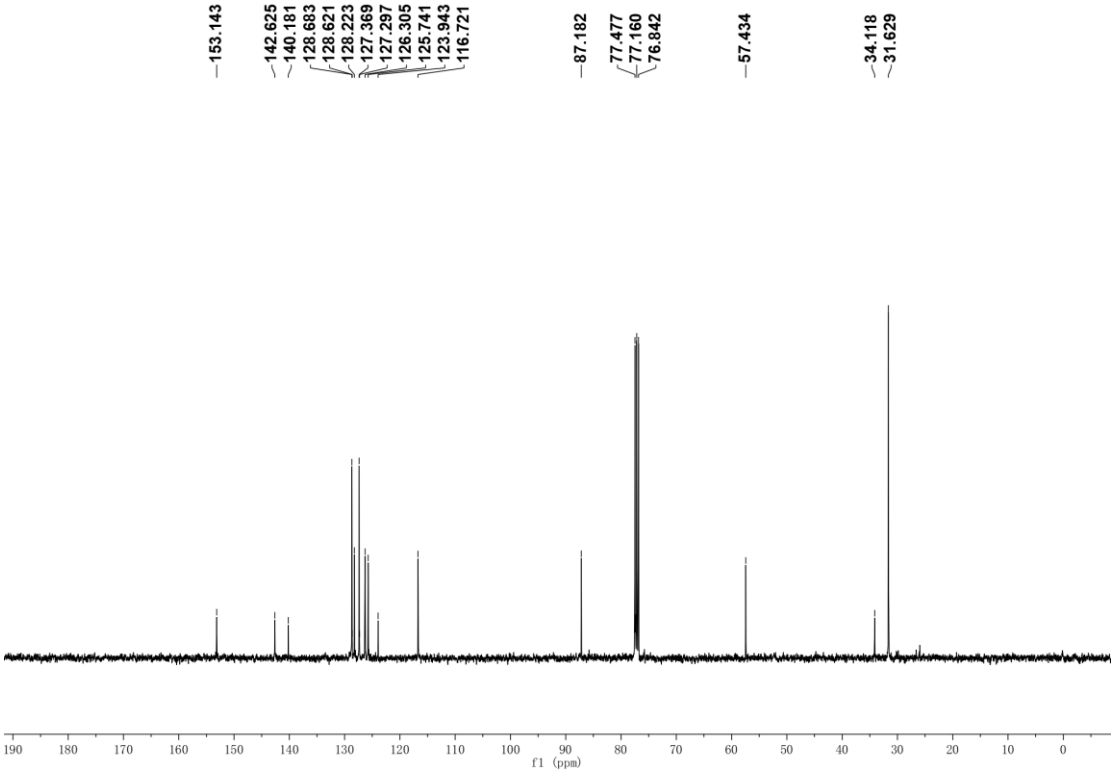
^{13}C NMR (100 MHz) of **(±)-3l** in $CDCl_3$



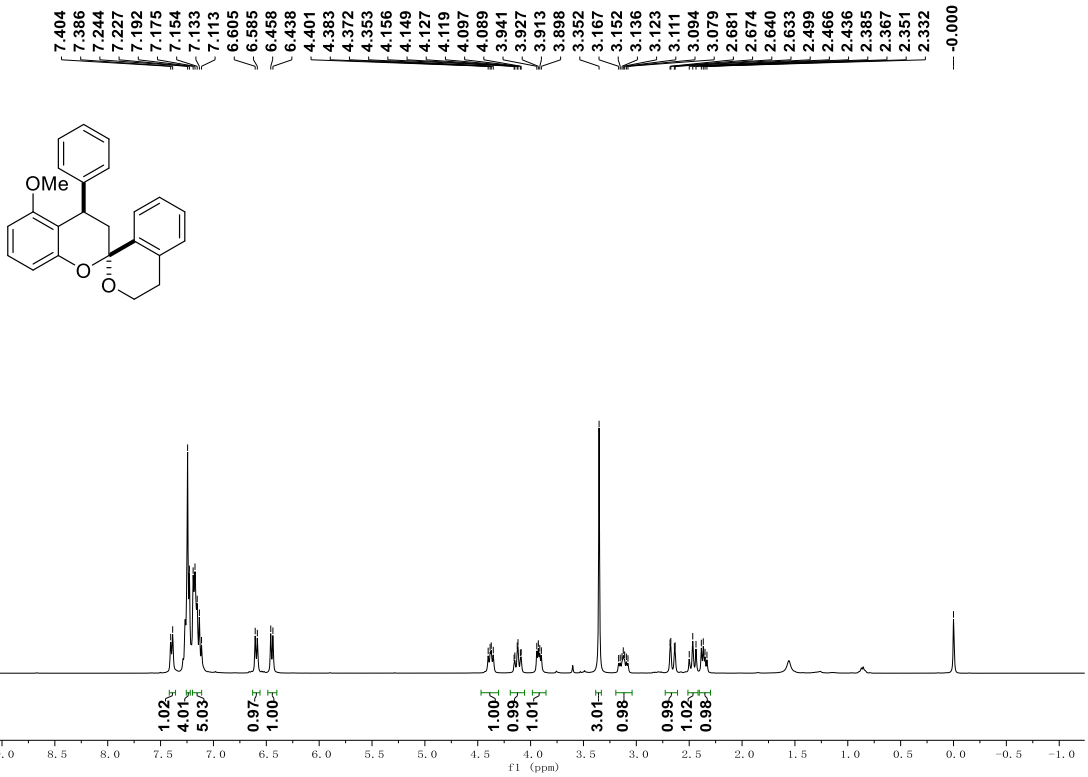
^{1}H NMR (400 MHz) of **(±)-4l** in $CDCl_3$



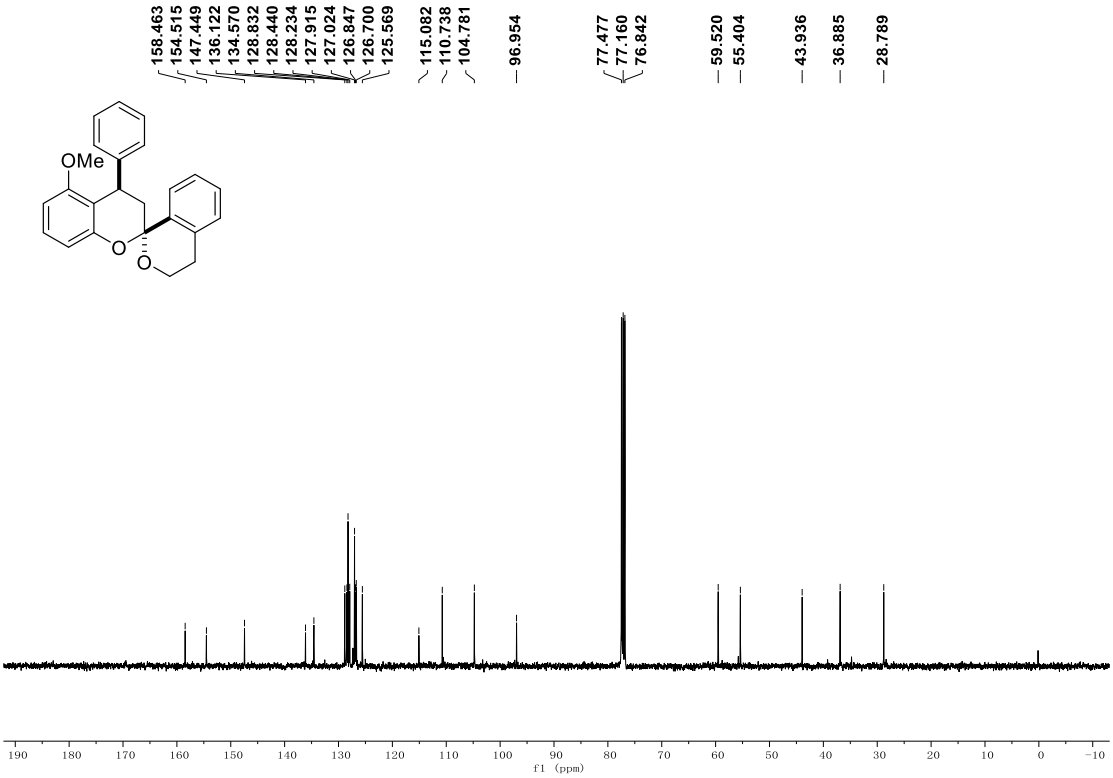
^{13}C NMR (100 MHz) of **(±)-4l** in $CDCl_3$



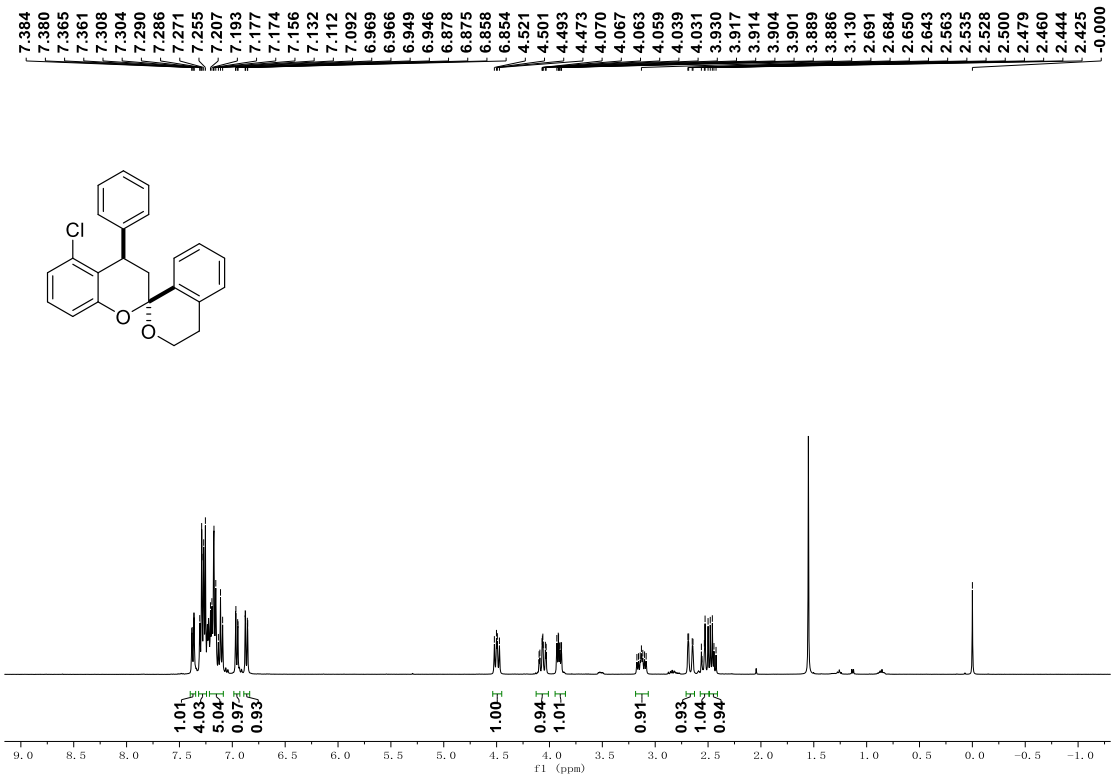
^{1}H NMR (400 MHz) of **(±)-3m** in $CDCl_3$



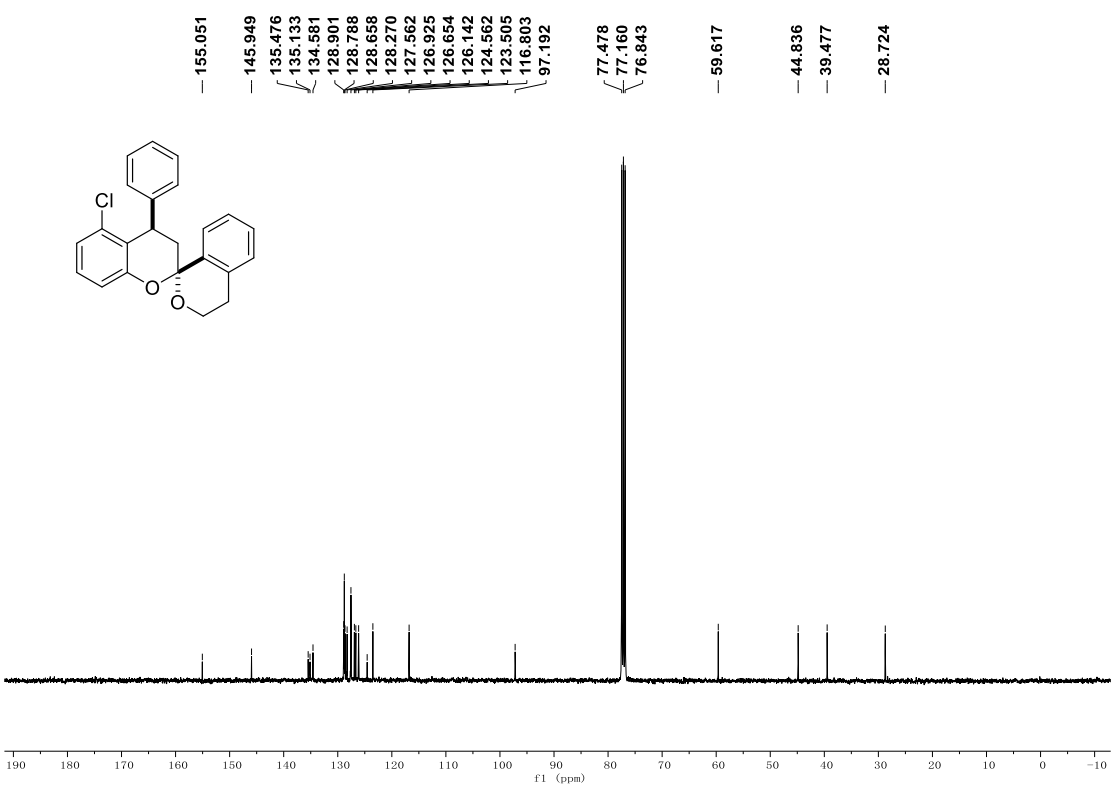
^{13}C NMR (100 MHz) of **(±)-3m** in $CDCl_3$



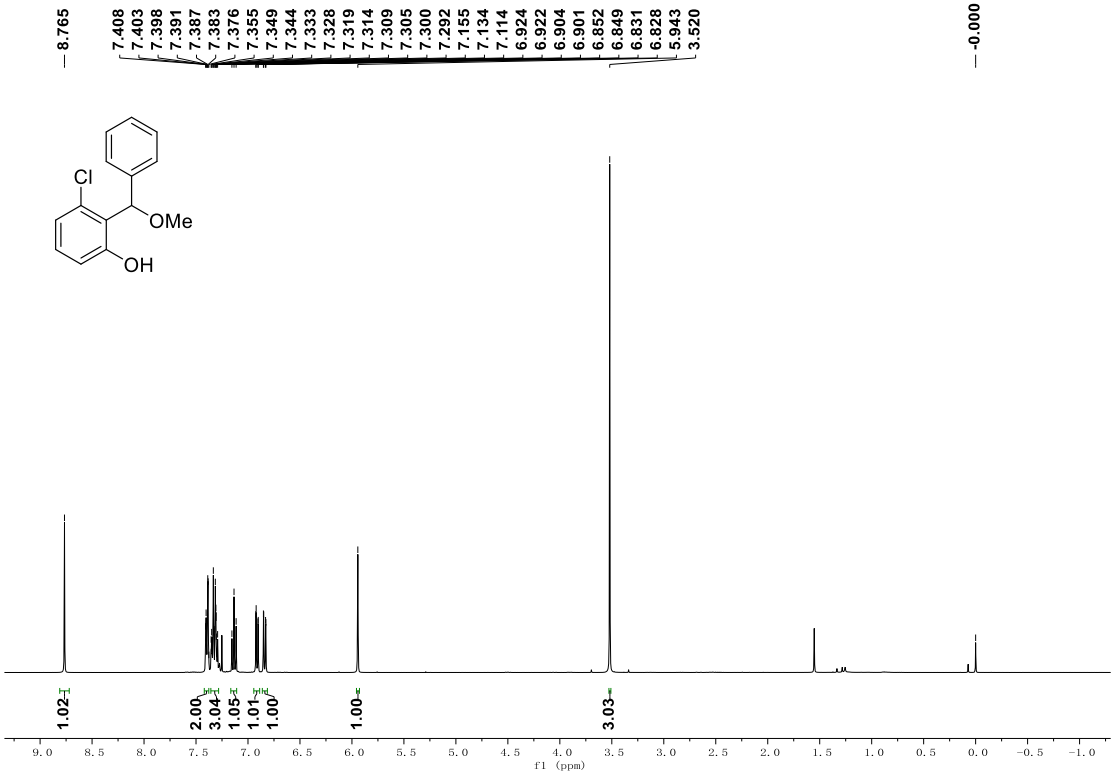
^{1}H NMR (400 MHz) of **(±)-3n** in $CDCl_3$



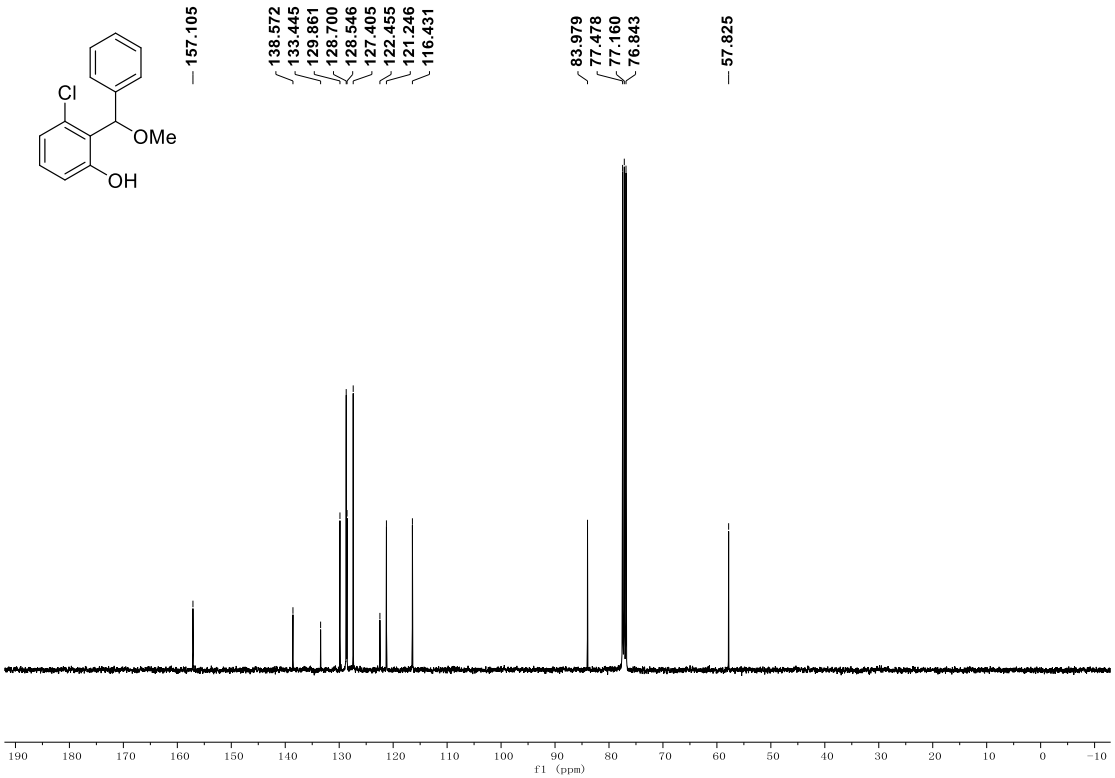
^{13}C NMR (100 MHz) of **(±)-3n** in $CDCl_3$



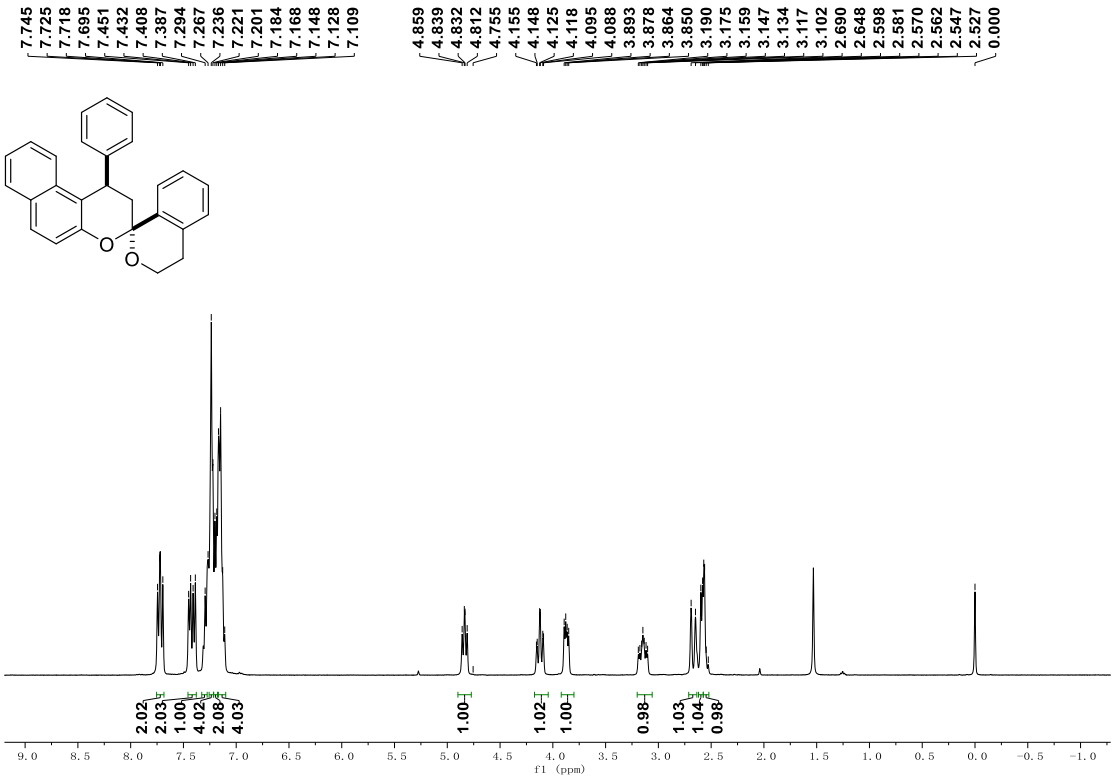
^{1}H NMR (400 MHz) of **(±)-4n** in $CDCl_3$



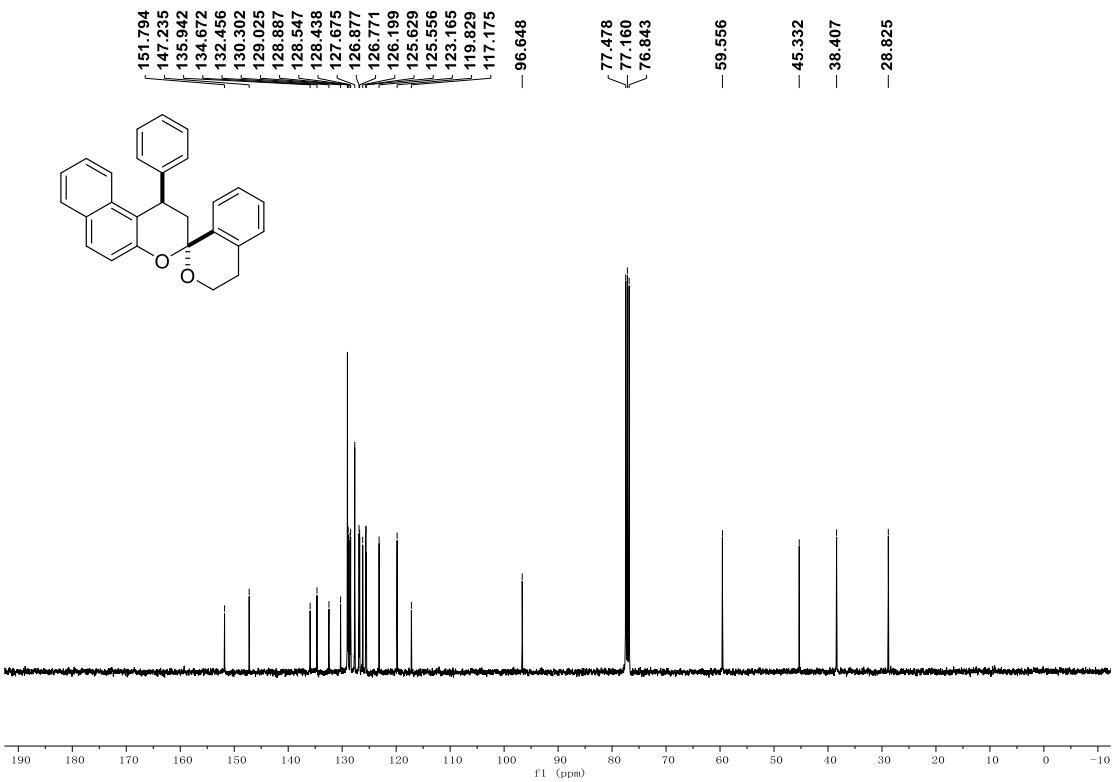
^{13}C NMR (100 MHz) of **(±)-4n** in $CDCl_3$



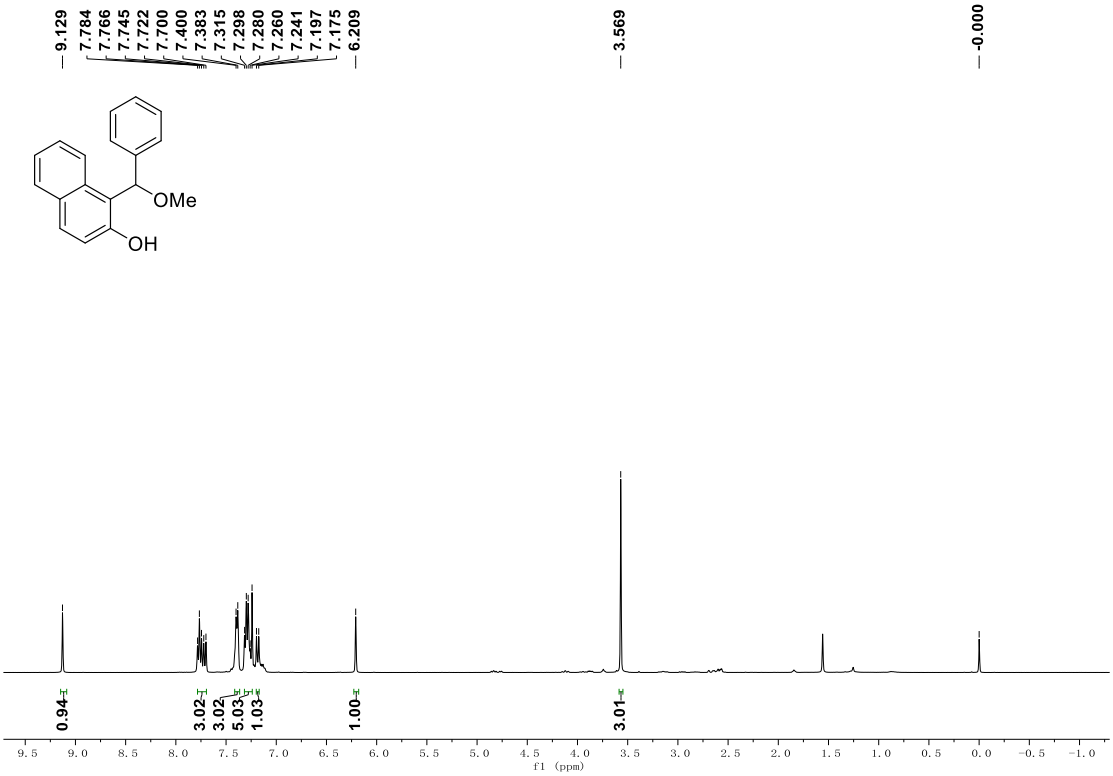
^{1}H NMR (400 MHz) of **(±)-3o** in $CDCl_3$



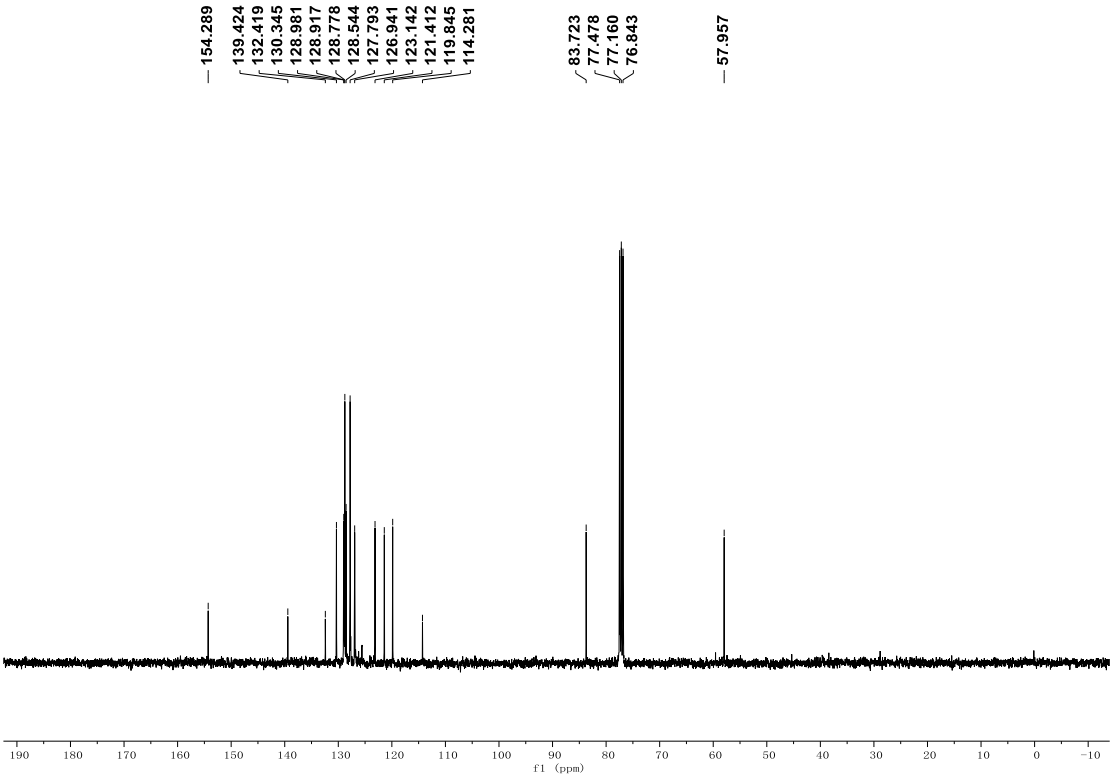
^{13}C NMR (100 MHz) of **(±)-3o** in $CDCl_3$



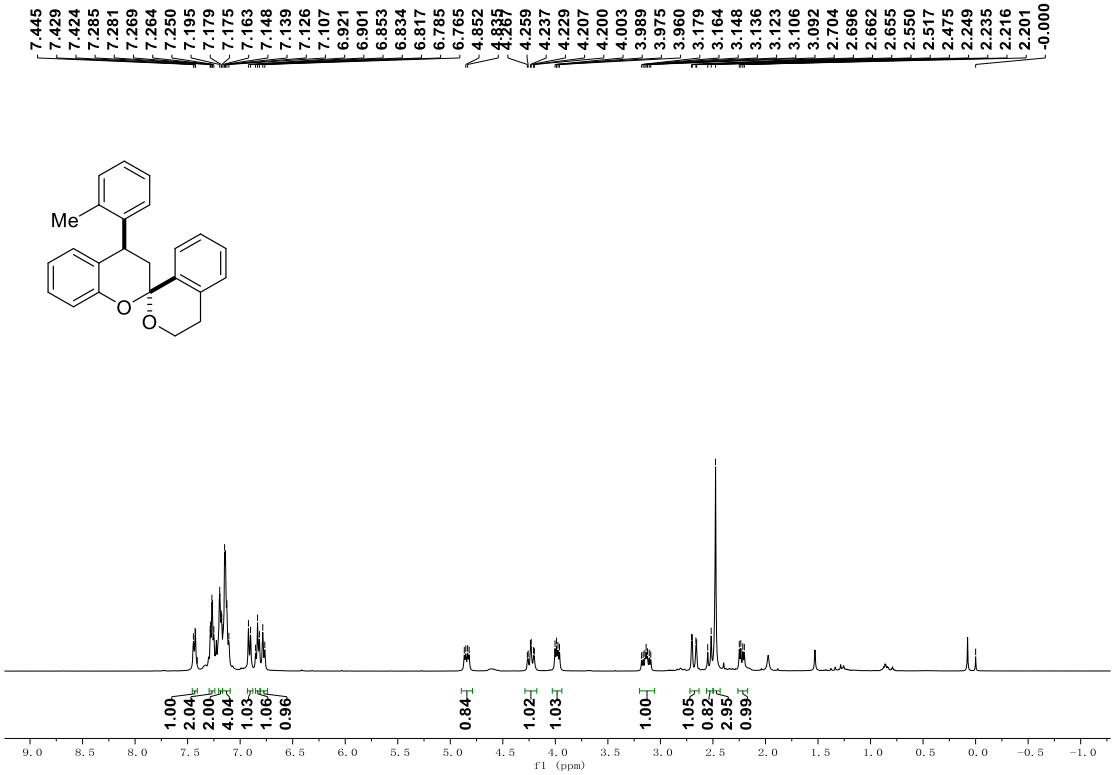
^{1}H NMR (400 MHz) of **(±)-4o** in $CDCl_3$



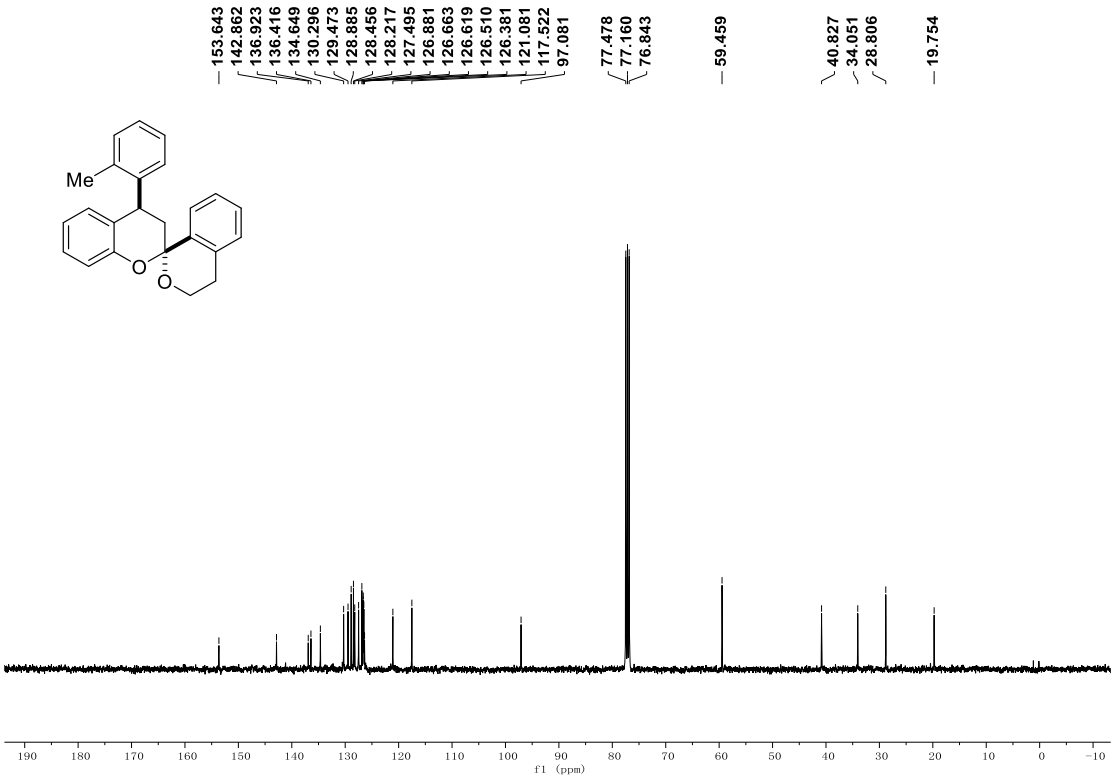
^{13}C NMR (100 MHz) of **(±)-4o** in $CDCl_3$



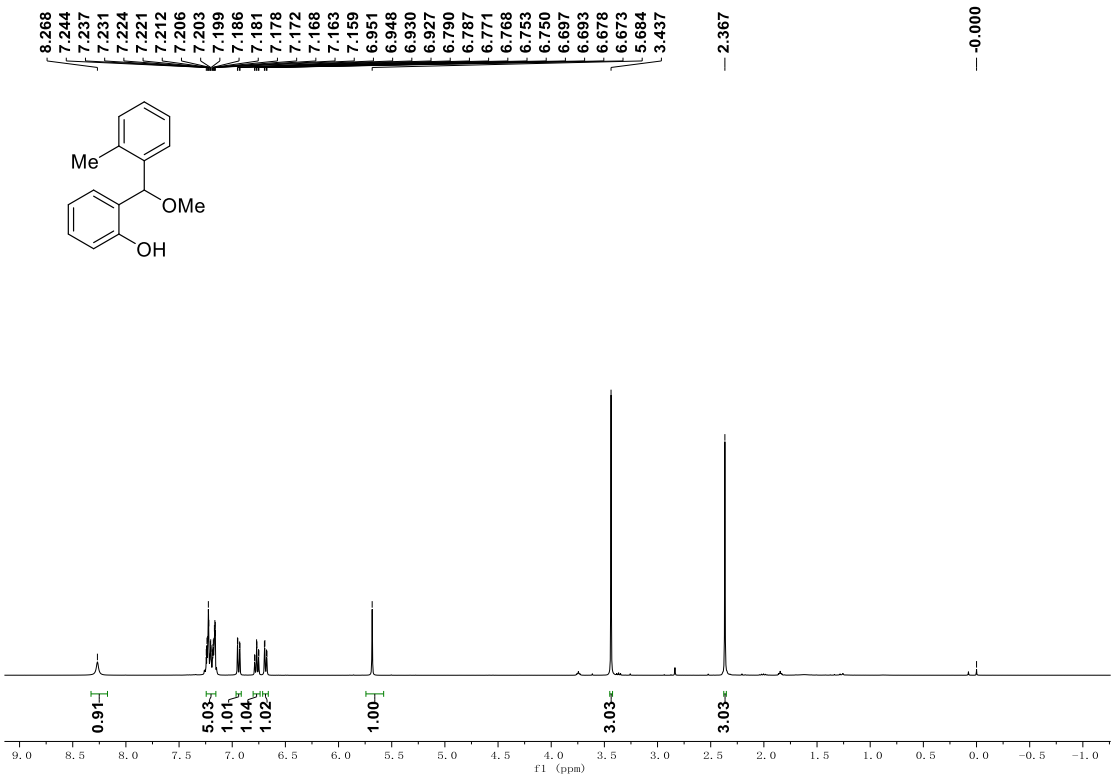
^{1}H NMR (400 MHz) of **(±)-3p** in $CDCl_3$



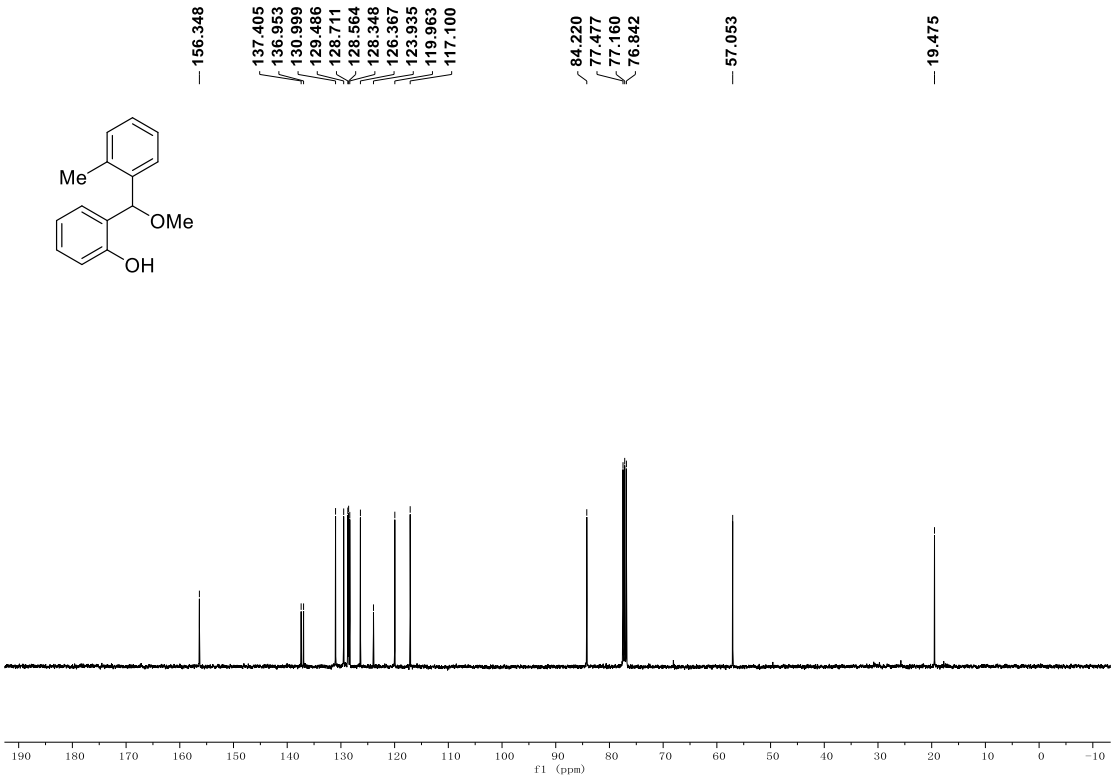
^{13}C NMR (100 MHz) of **(±)-3p** in $CDCl_3$



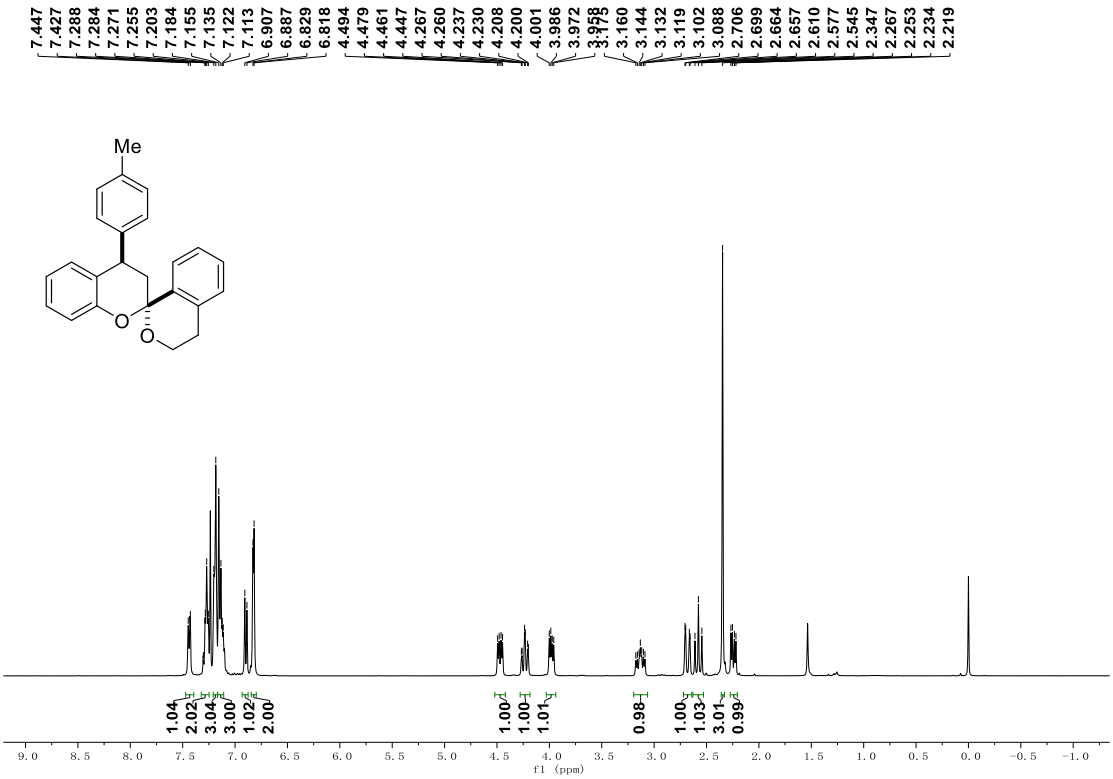
^{1}H NMR (400 MHz) of **(±)-4p** in $CDCl_3$



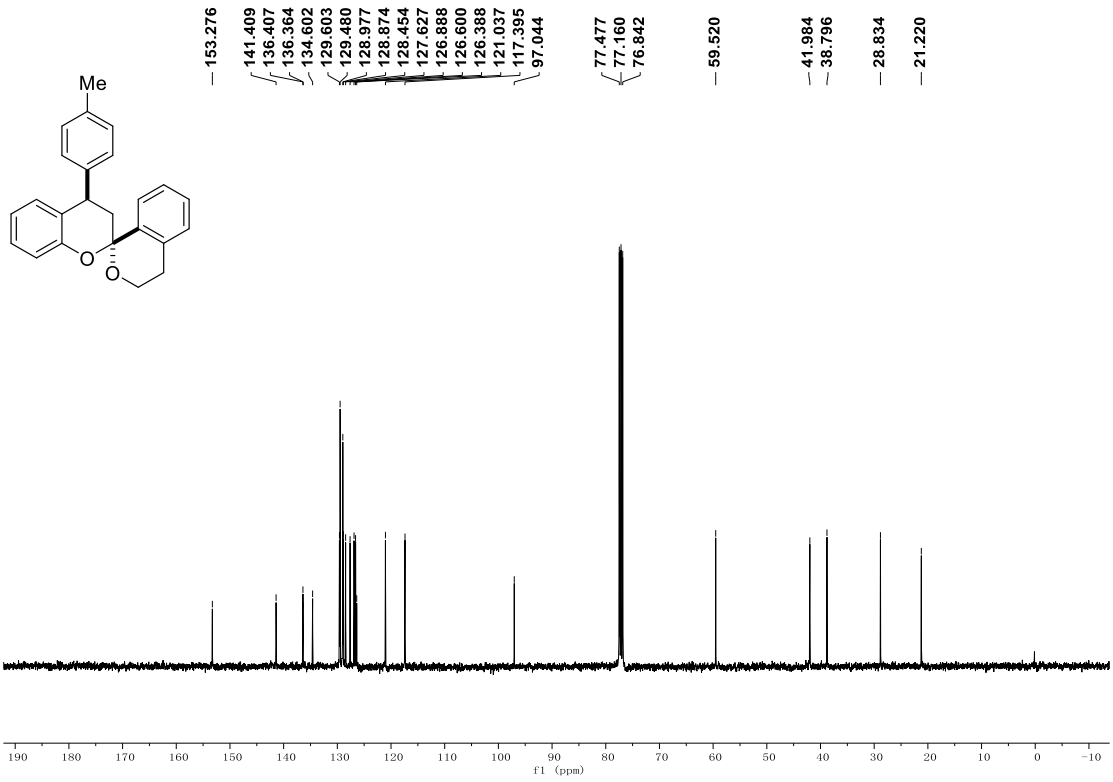
^{13}C NMR (100 MHz) of **(±)-4p** in $CDCl_3$



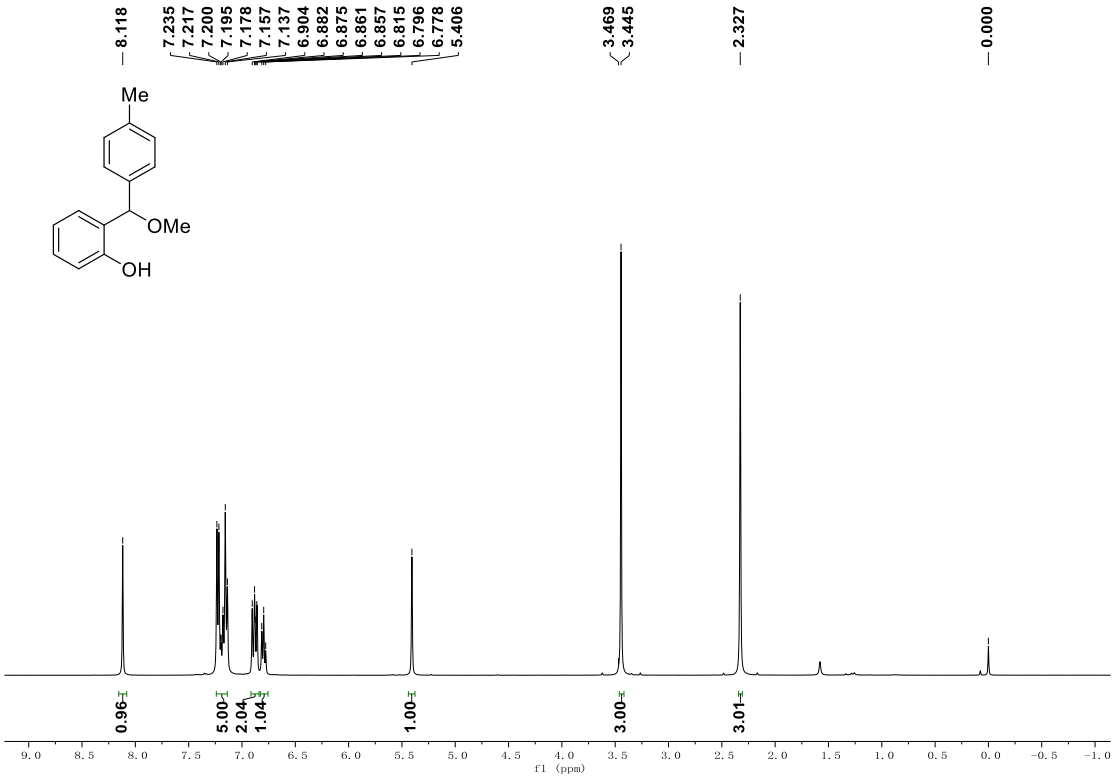
^{1}H NMR (400 MHz) of **(±)-3q** in $CDCl_3$



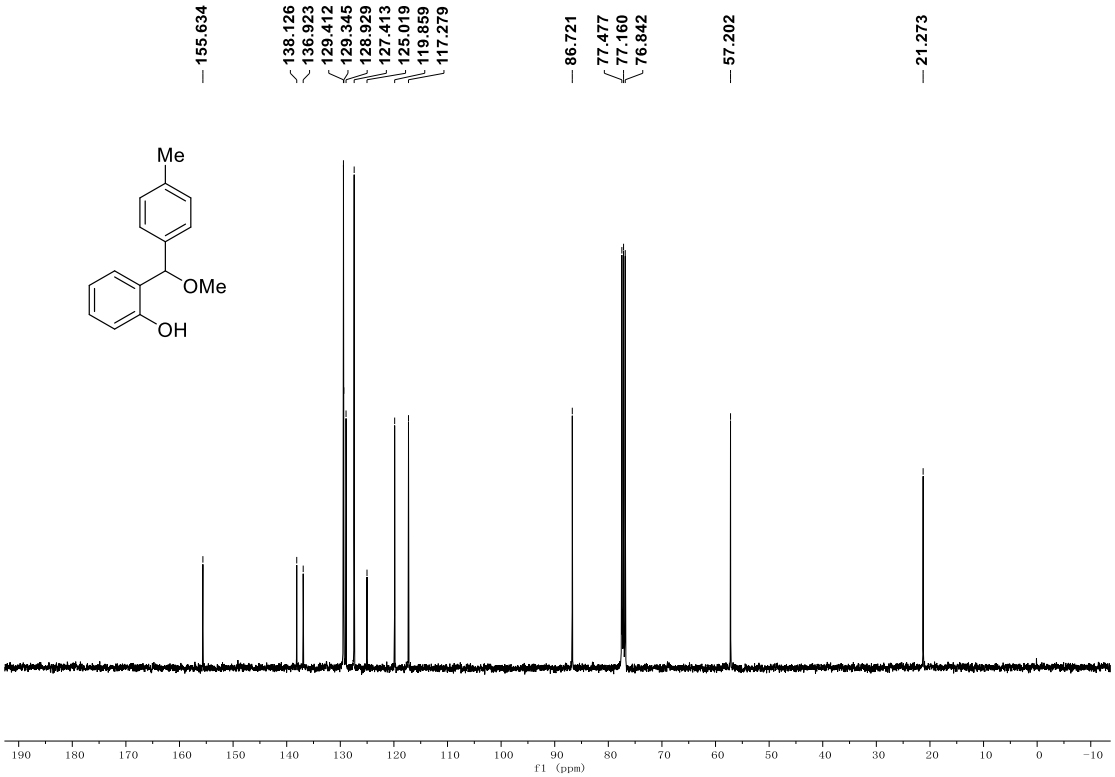
^{13}C NMR (100 MHz) of **(±)-3q** in $CDCl_3$



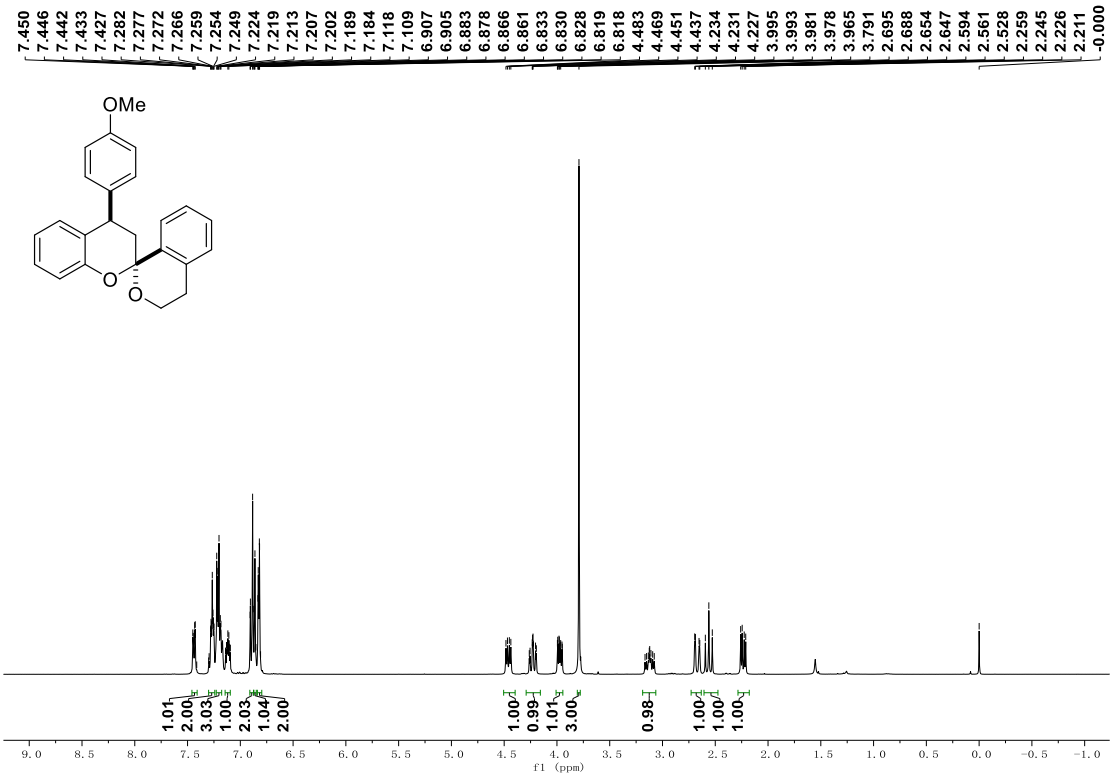
^{1}H NMR (400 MHz) of **(±)-4q** in $CDCl_3$



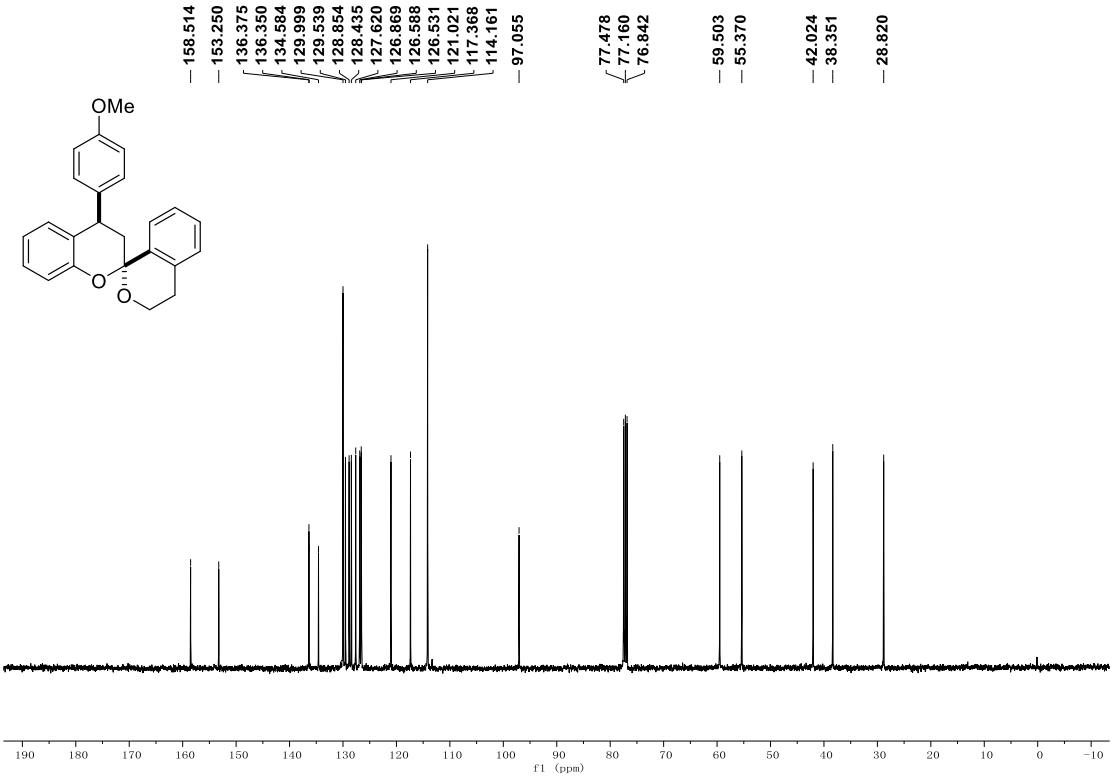
^{13}C NMR (100 MHz) of **(±)-4q** in $CDCl_3$



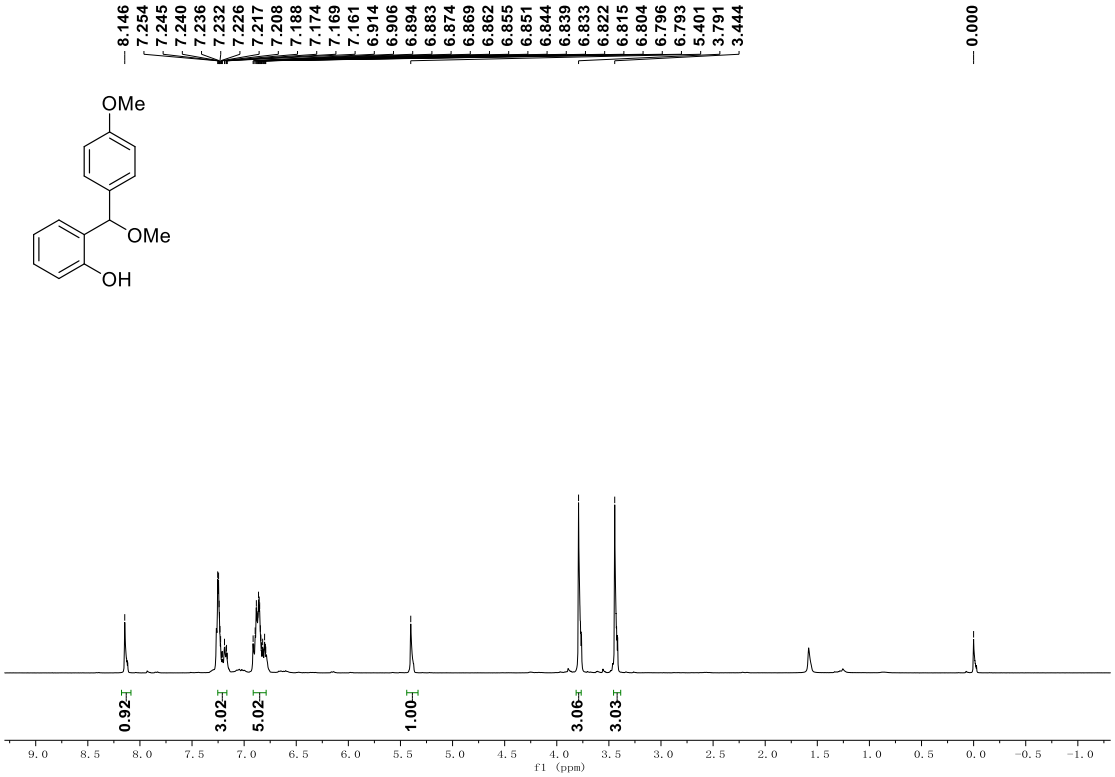
^{1}H NMR (400 MHz) of **(±)-3r** in $CDCl_3$



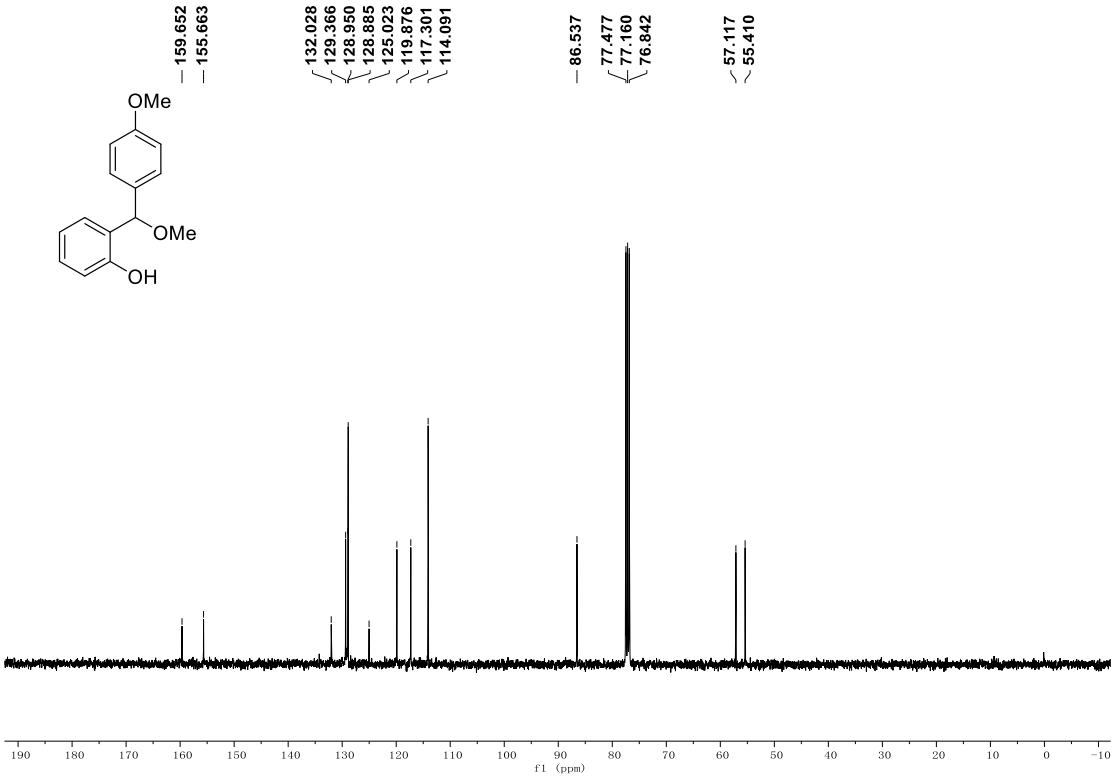
^{13}C NMR (100 MHz) of **(±)-3r** in $CDCl_3$



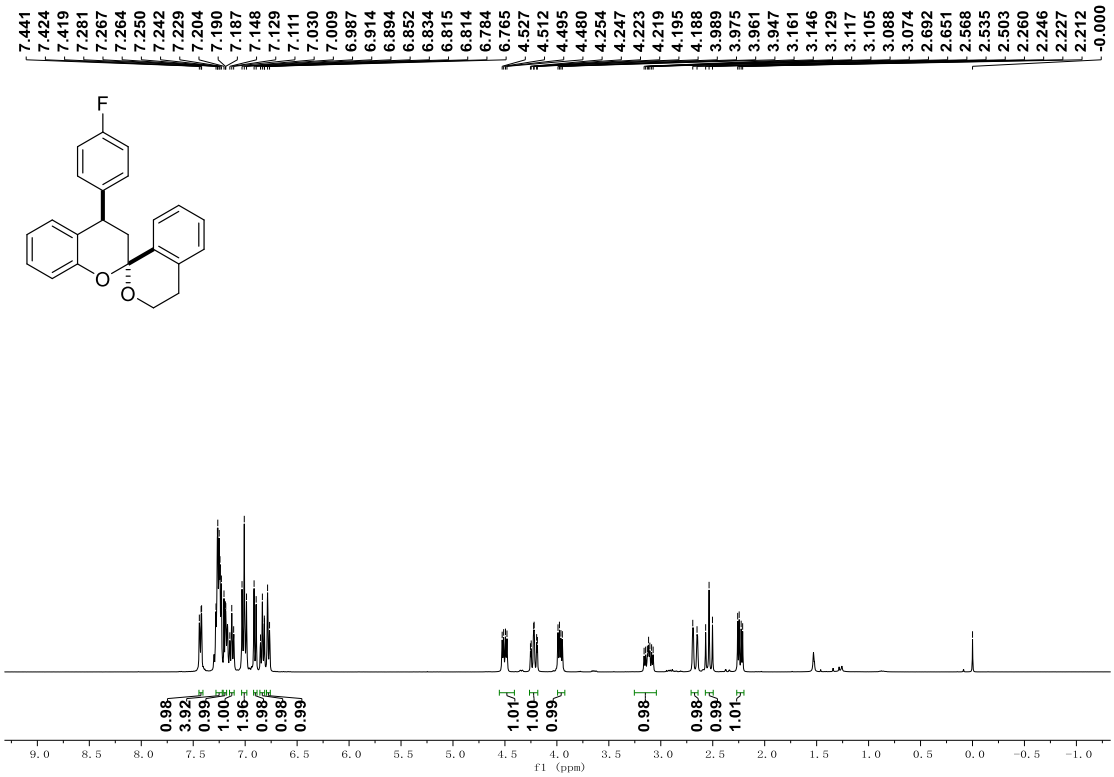
^{1}H NMR (400 MHz) of **(±)-4r** in $CDCl_3$



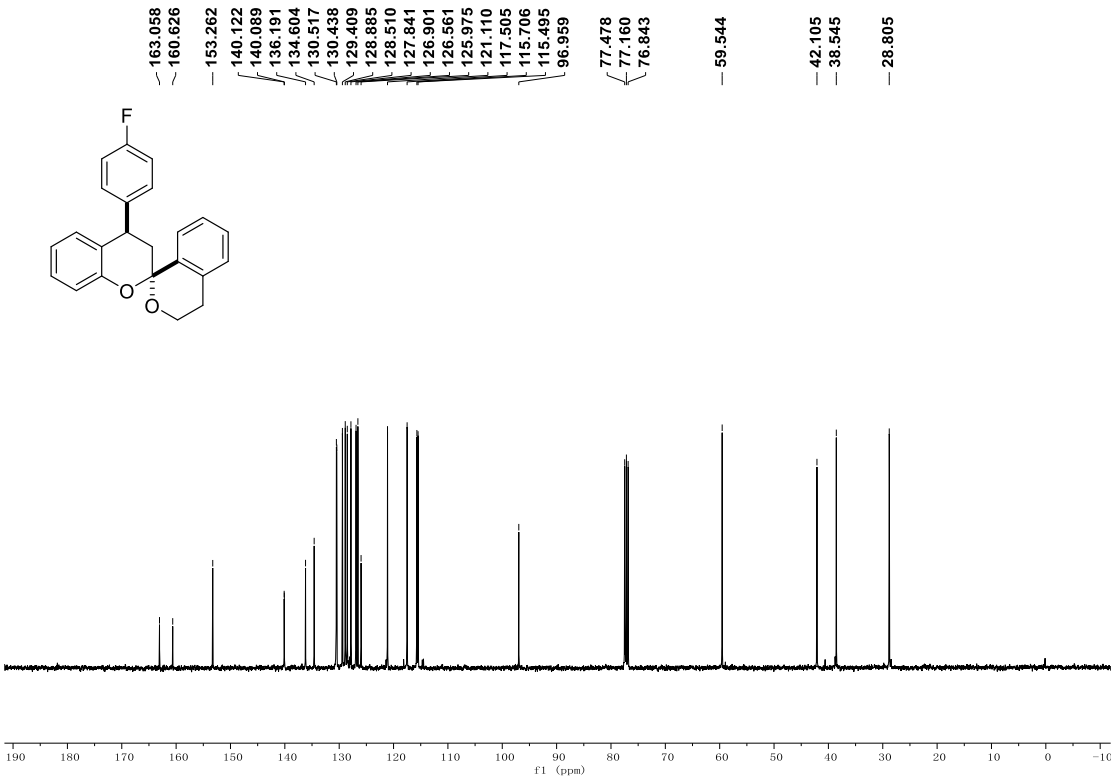
^{13}C NMR (100 MHz) of **(±)-4r** in $CDCl_3$



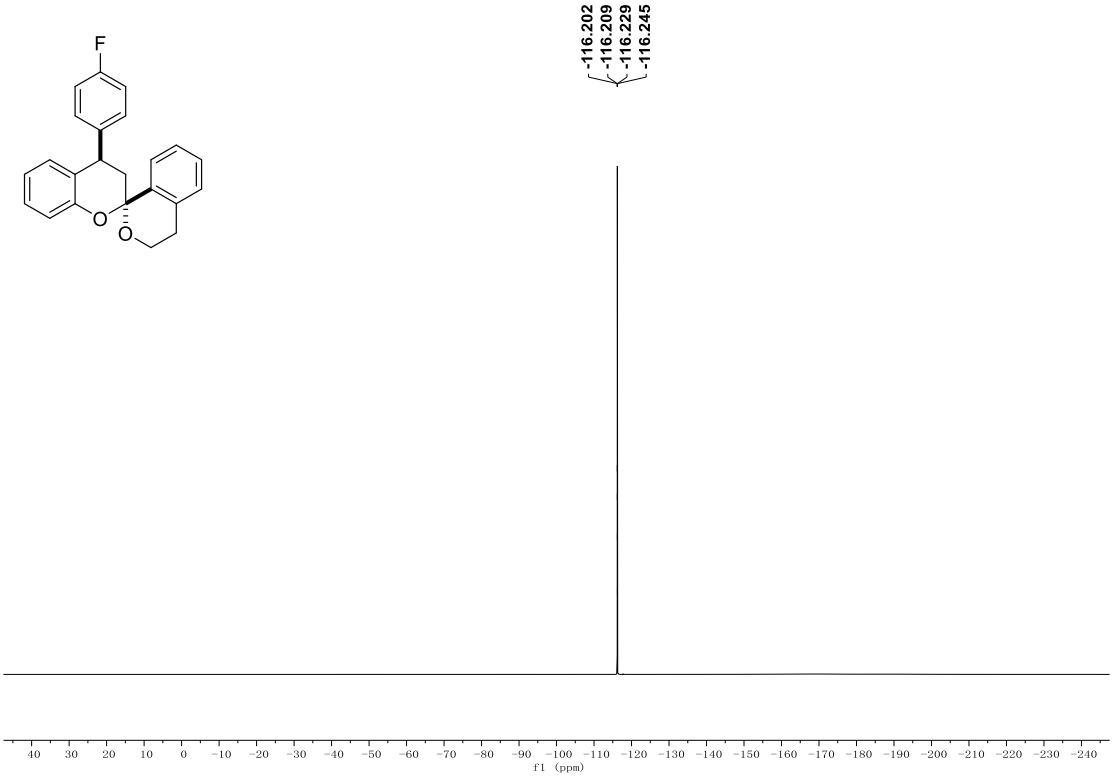
^{1}H NMR (400 MHz) of **(±)-3s** in $CDCl_3$



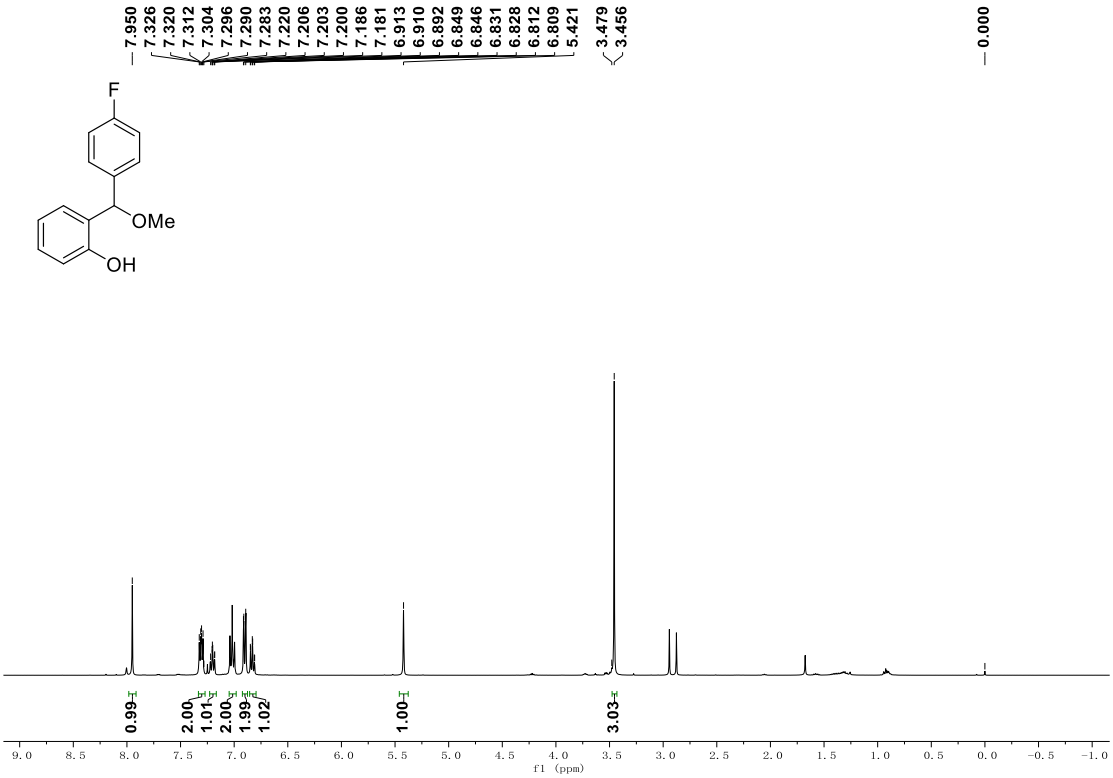
^{13}C NMR (100 MHz) of **(±)-3s** in $CDCl_3$



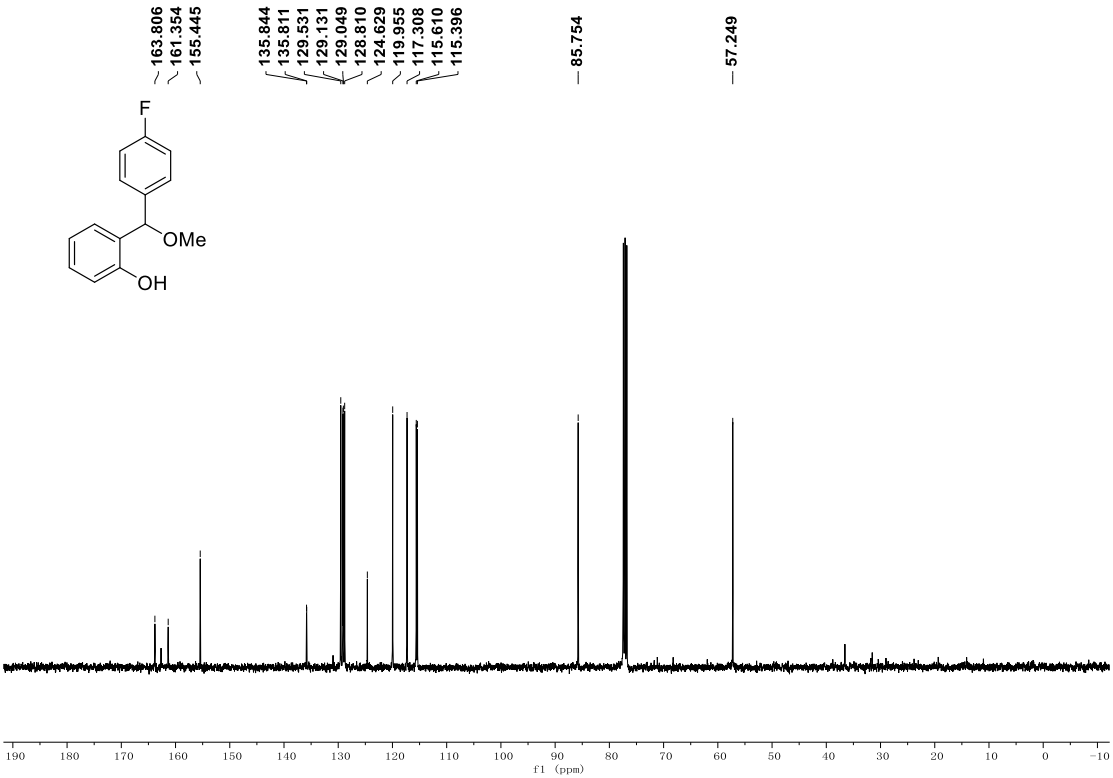
^{19}F NMR (565 MHz) of **(±)-3s** in $CDCl_3$



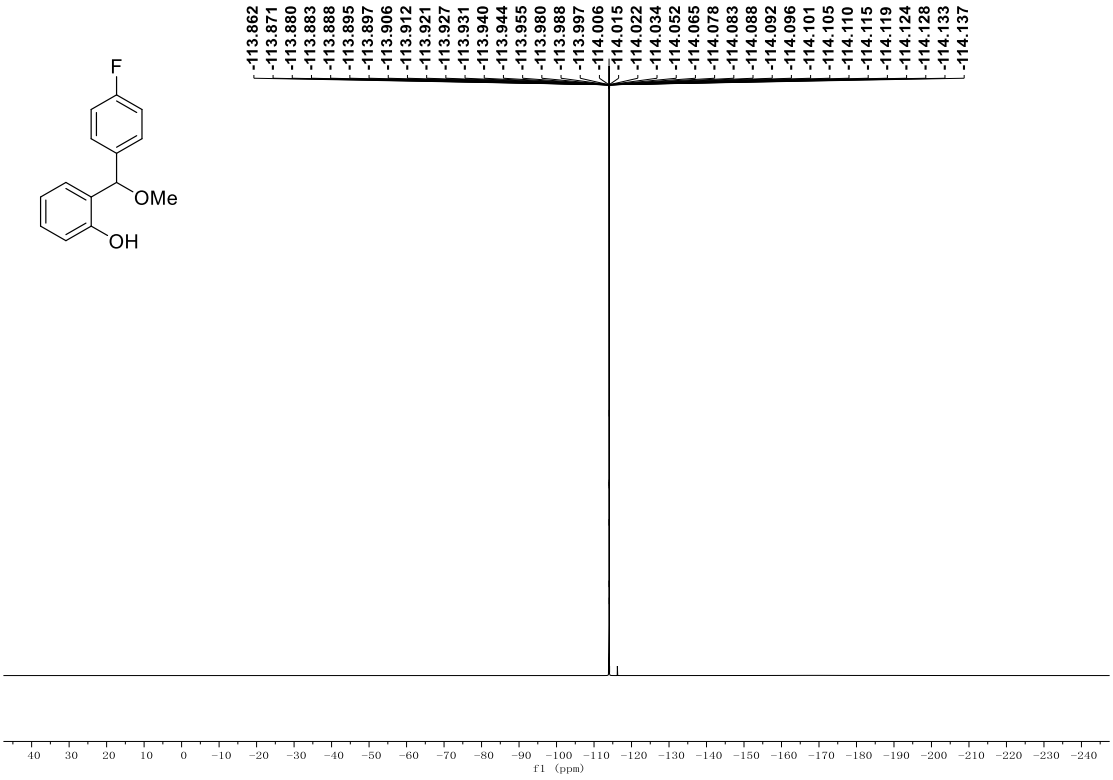
^{1}H NMR (400 MHz) of **(±)-4s** in $CDCl_3$



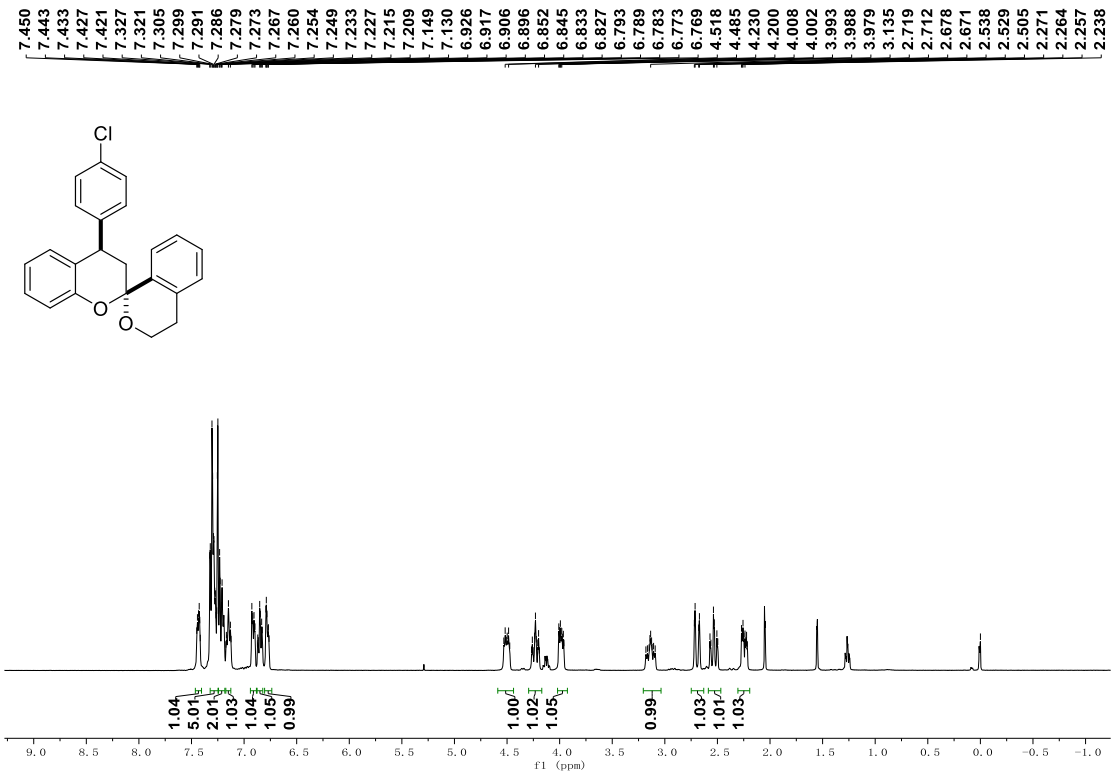
^{13}C NMR (100 MHz) of **(±)-4s** in $CDCl_3$



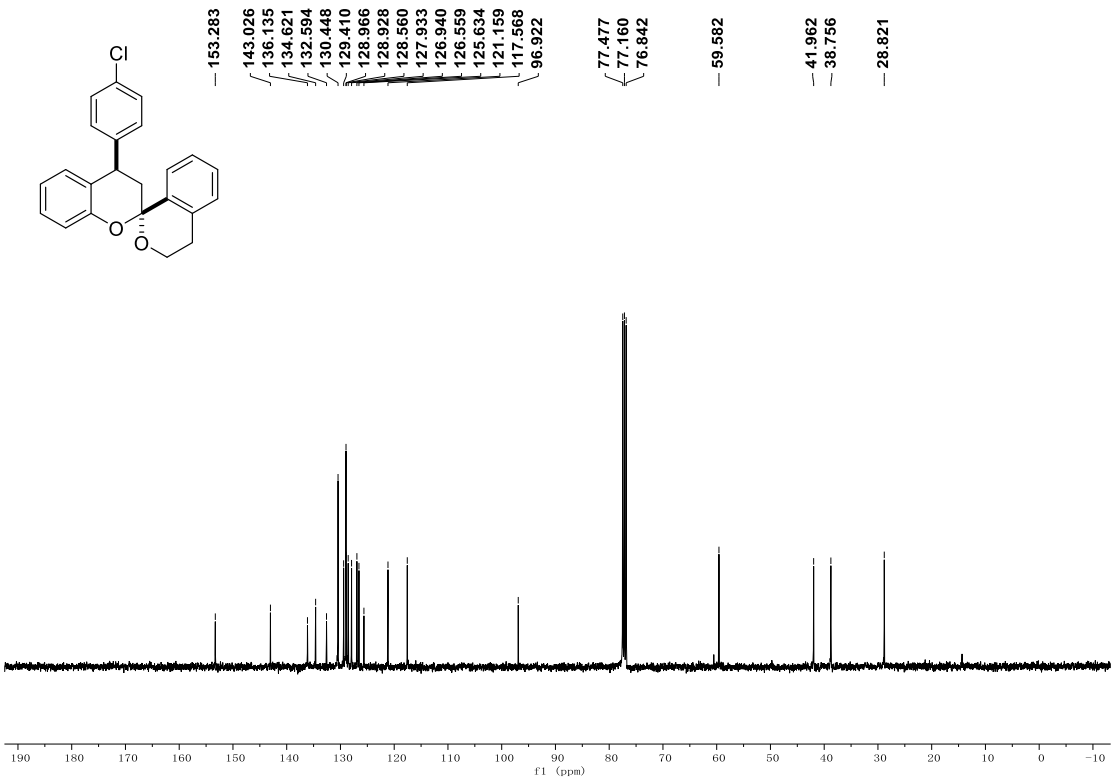
^{19}F NMR (565 MHz) of **(±)-4s** in $CDCl_3$



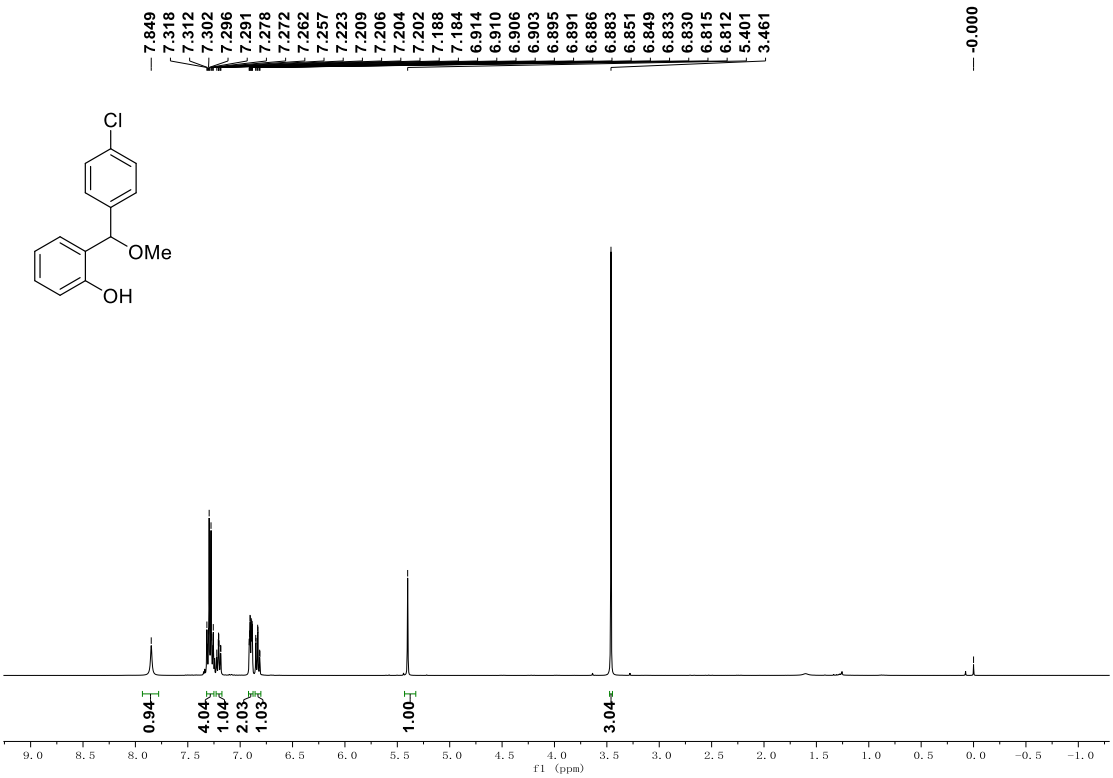
^{1}H NMR (400 MHz) of **(±)-3t** in $CDCl_3$



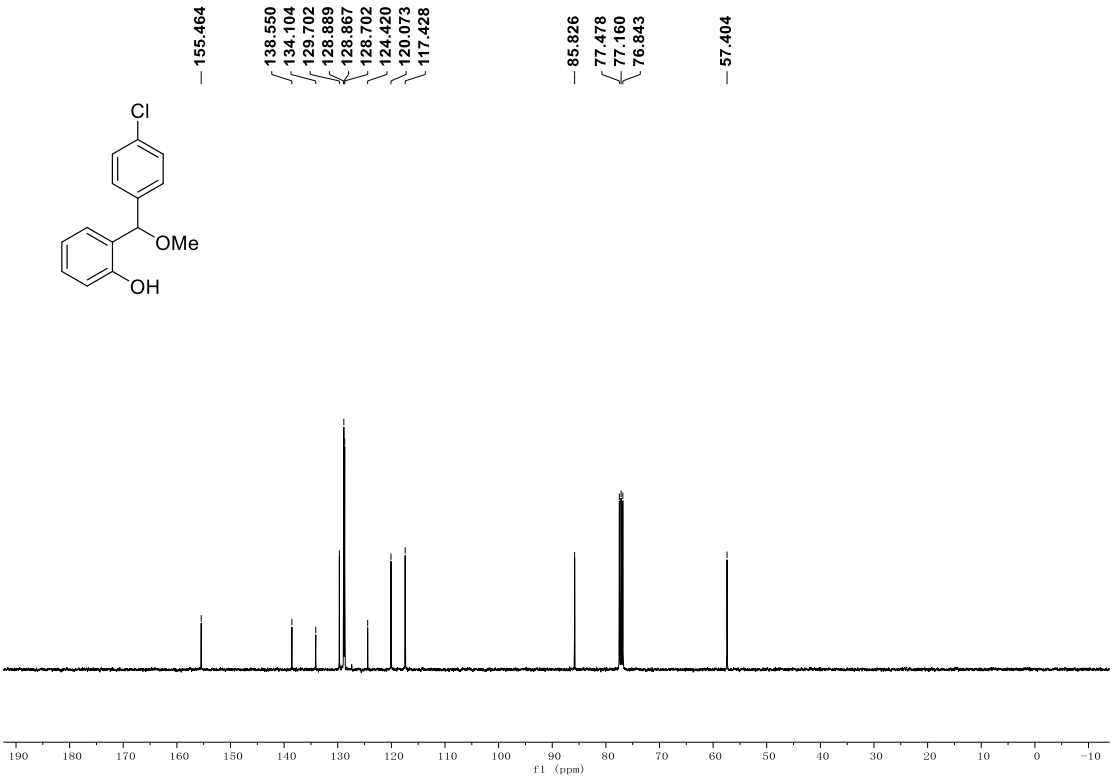
^{13}C NMR (100 MHz) of **(±)-3t** in $CDCl_3$



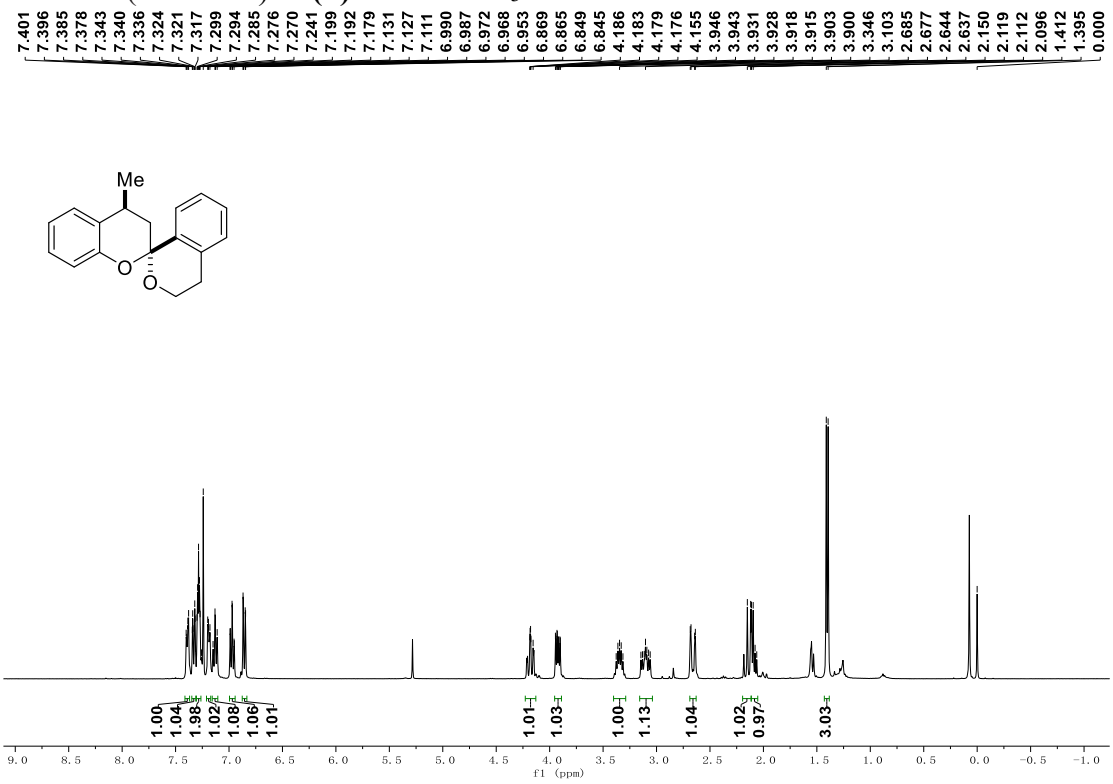
^{1}H NMR (400 MHz) of **(±)-4t** in $CDCl_3$



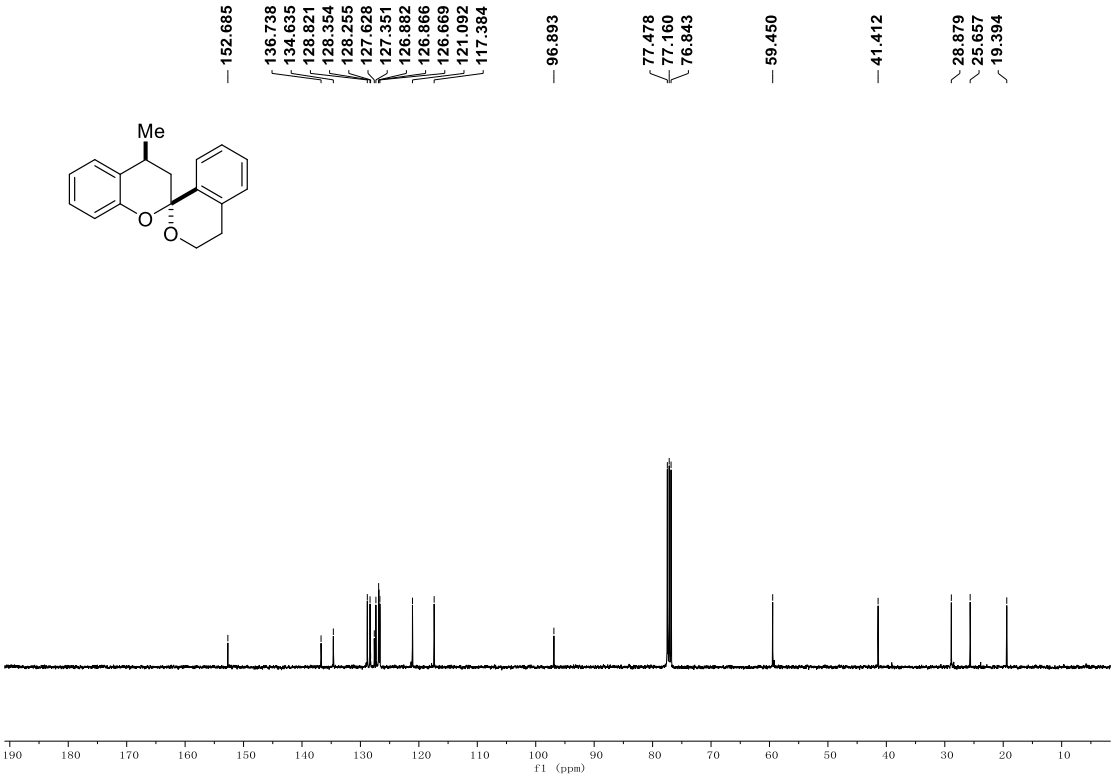
^{13}C NMR (100 MHz) of **(±)-4t** in $CDCl_3$



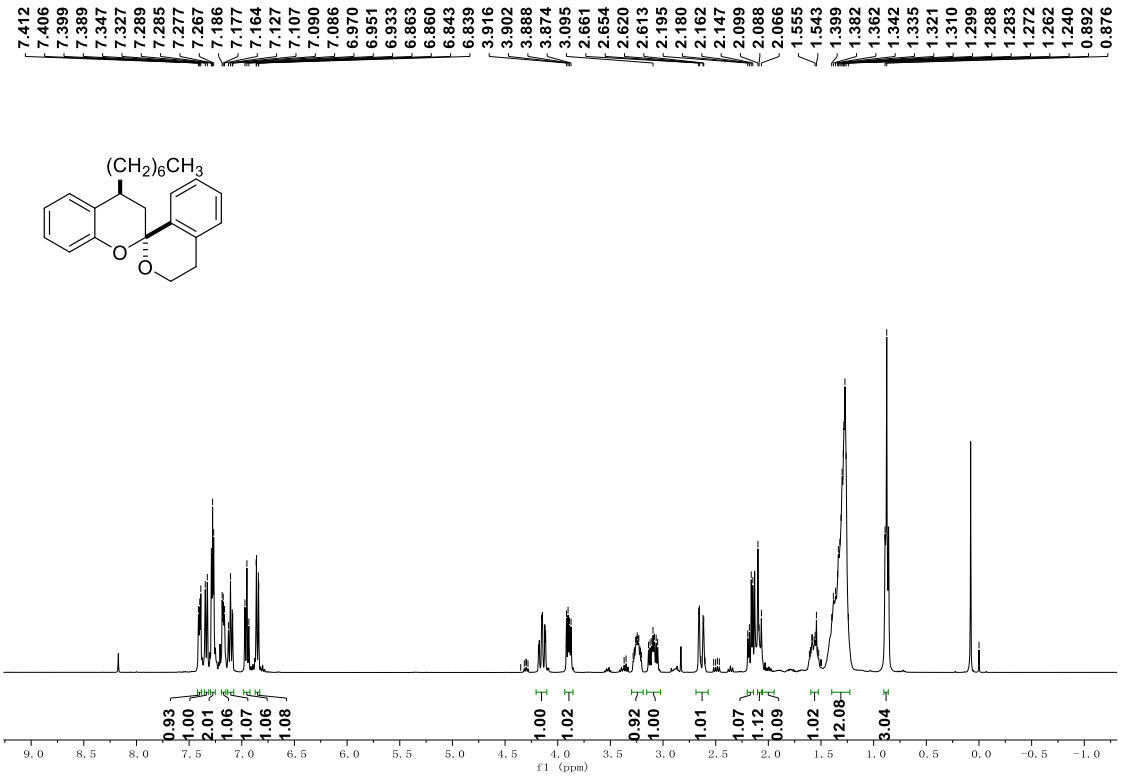
^{1}H NMR (400 MHz) of **(±)-3u** in $CDCl_3$



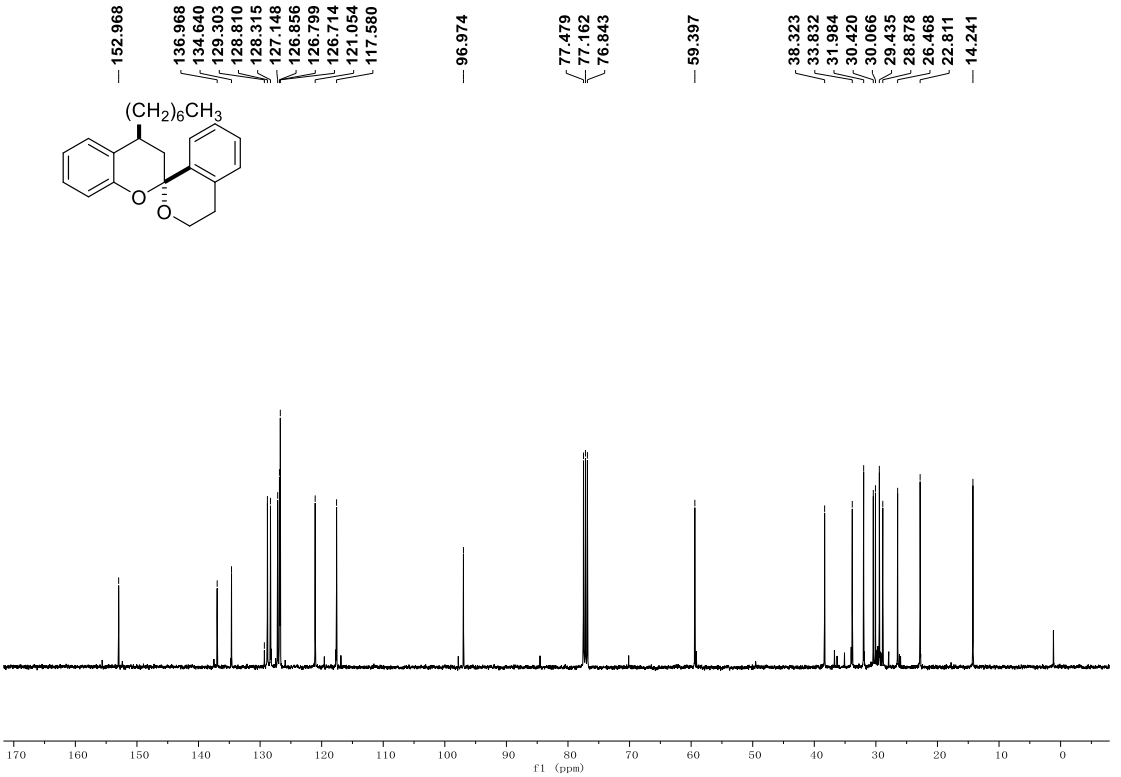
^{13}C NMR (100 MHz) of **(±)-3u** in $CDCl_3$



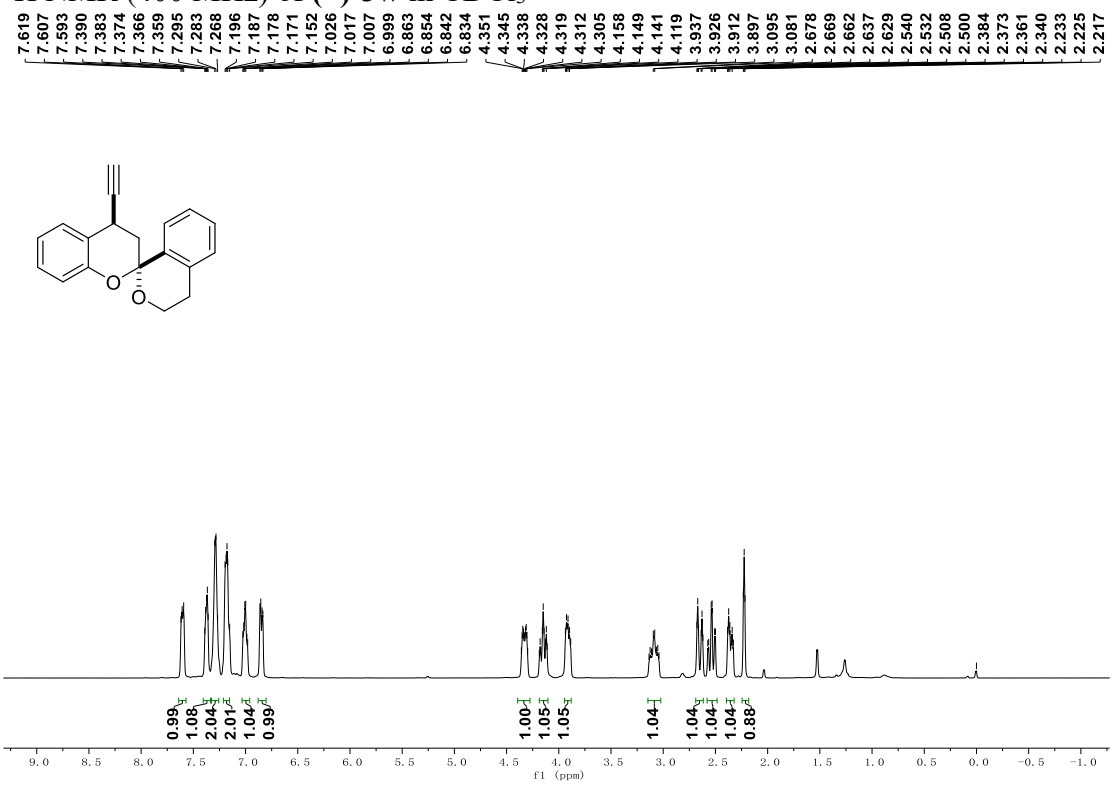
^{1}H NMR (400 MHz) of **(±)-3v** in $CDCl_3$ (12:1 dr)



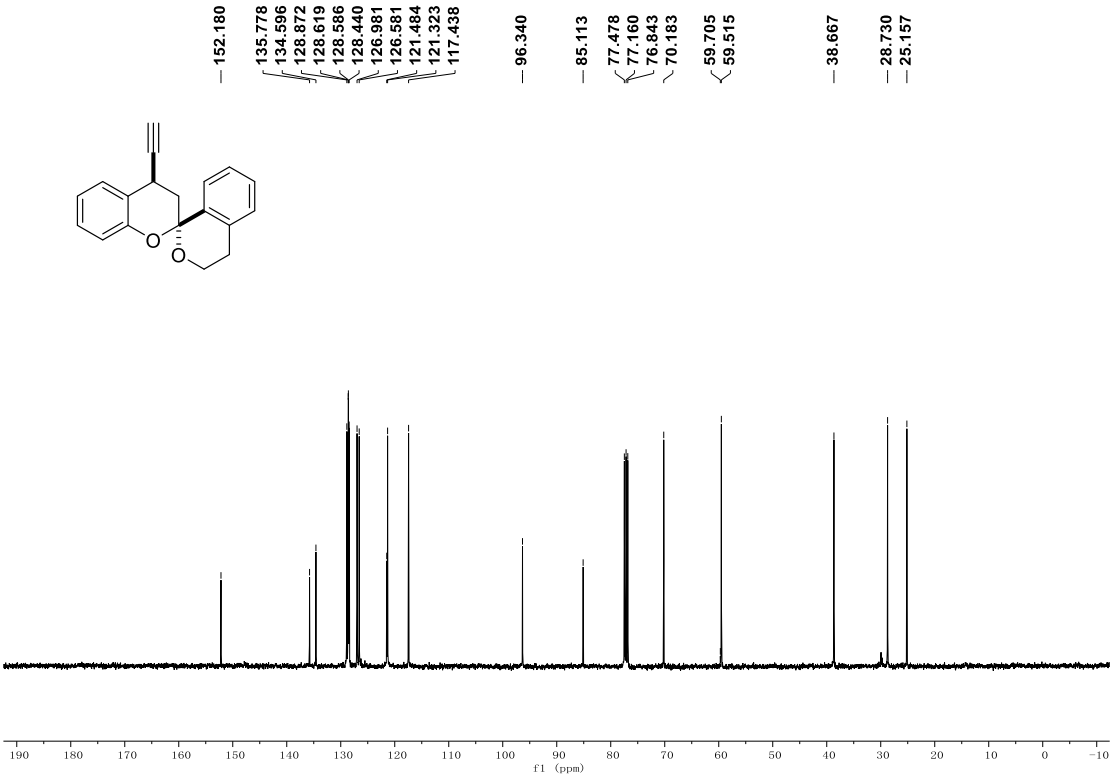
^{13}C NMR (100 MHz) of **(±)-3v** in $CDCl_3$ (12:1 dr)



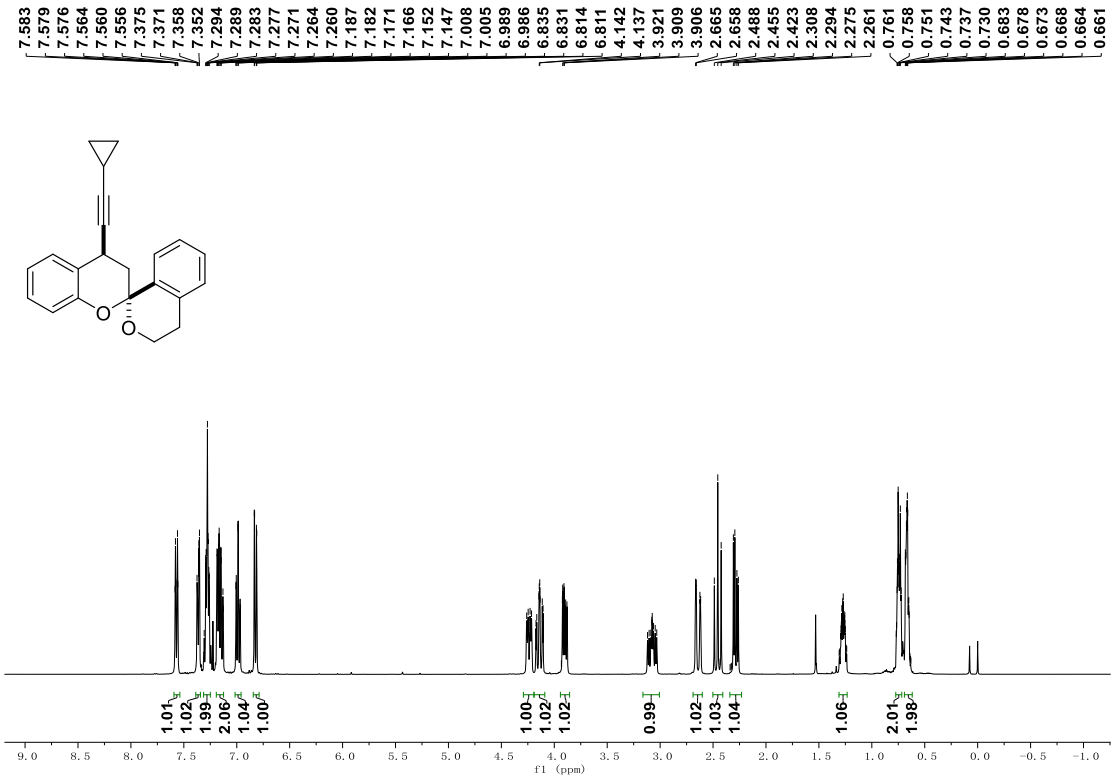
^{1}H NMR (400 MHz) of **(±)-3w** in $CDCl_3$



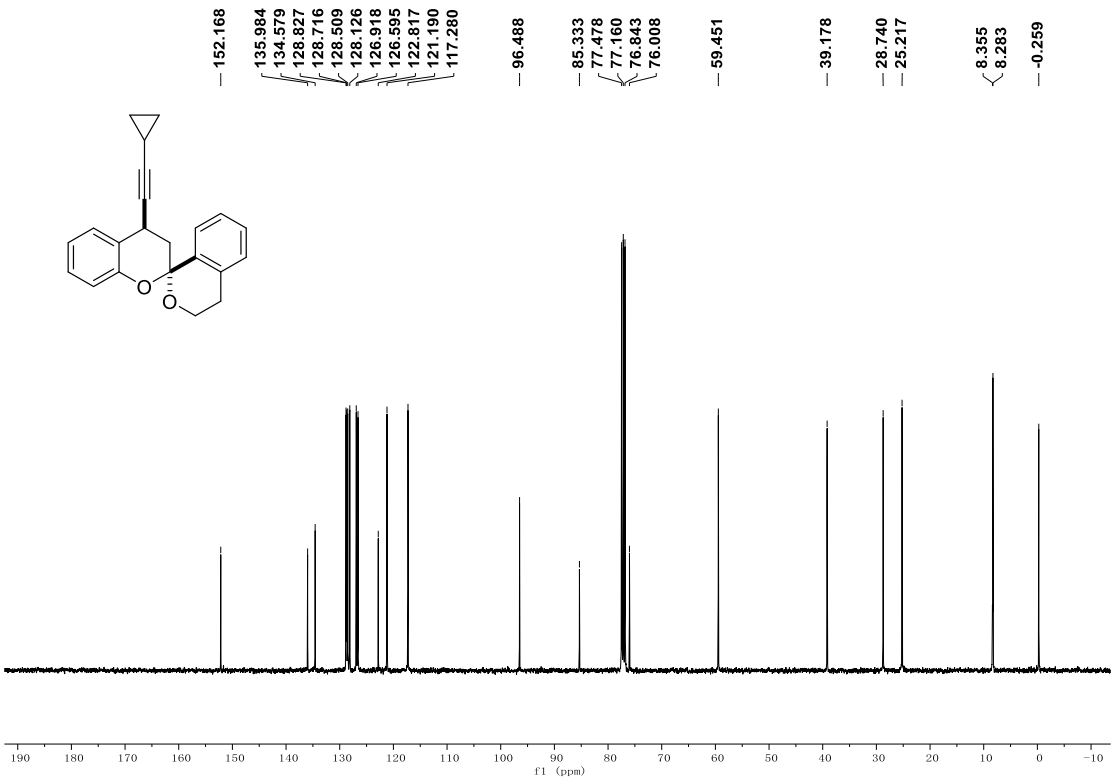
^{13}C NMR (100 MHz) of **(±)-3w** in $CDCl_3$



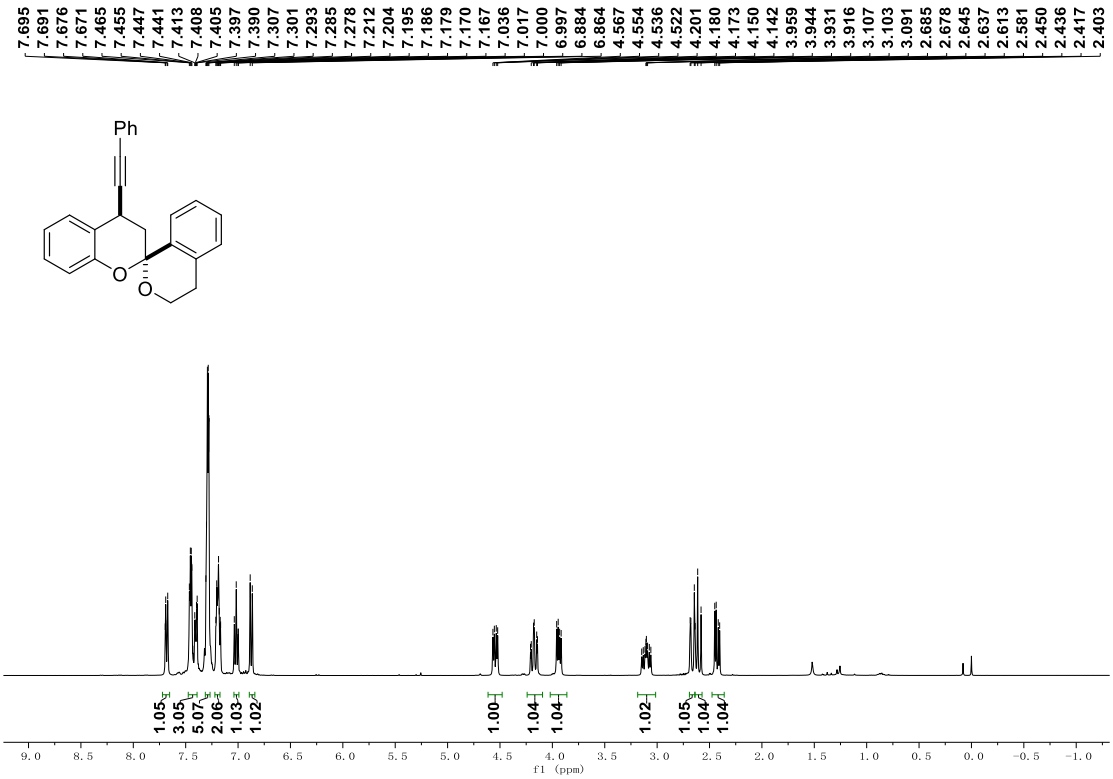
^{1}H NMR (400 MHz) of **(±)-3x** in $CDCl_3$



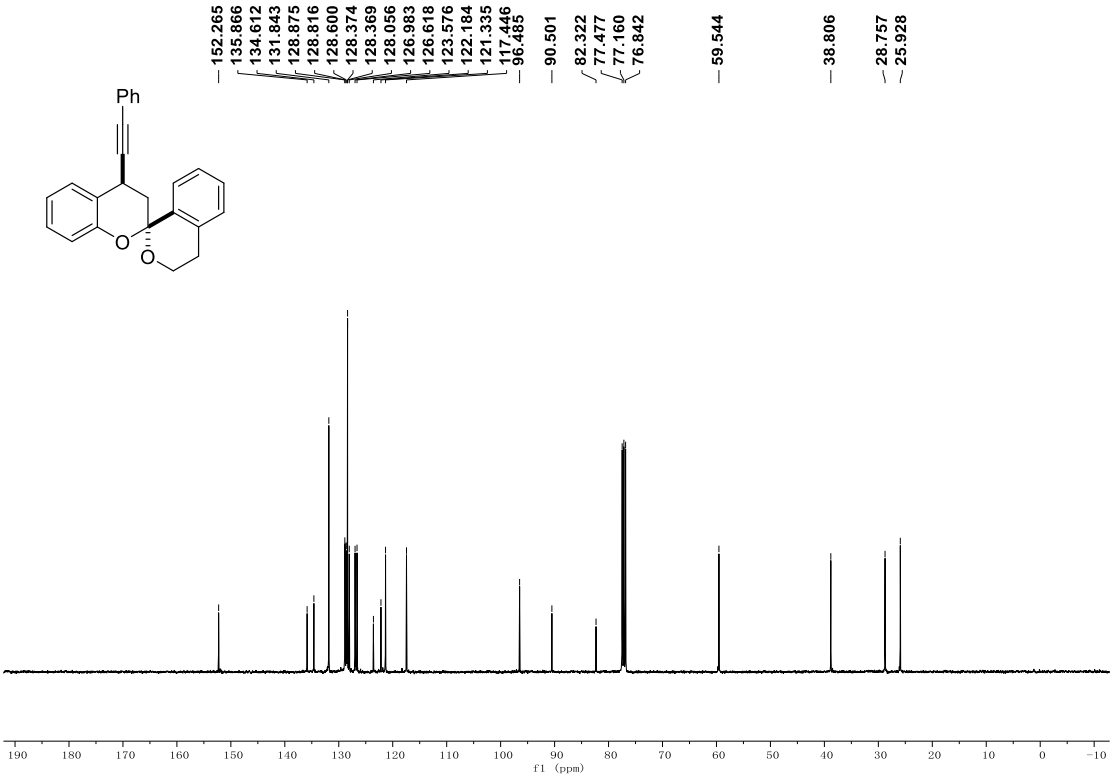
^{13}C NMR (100 MHz) of **(±)-3x** in $CDCl_3$



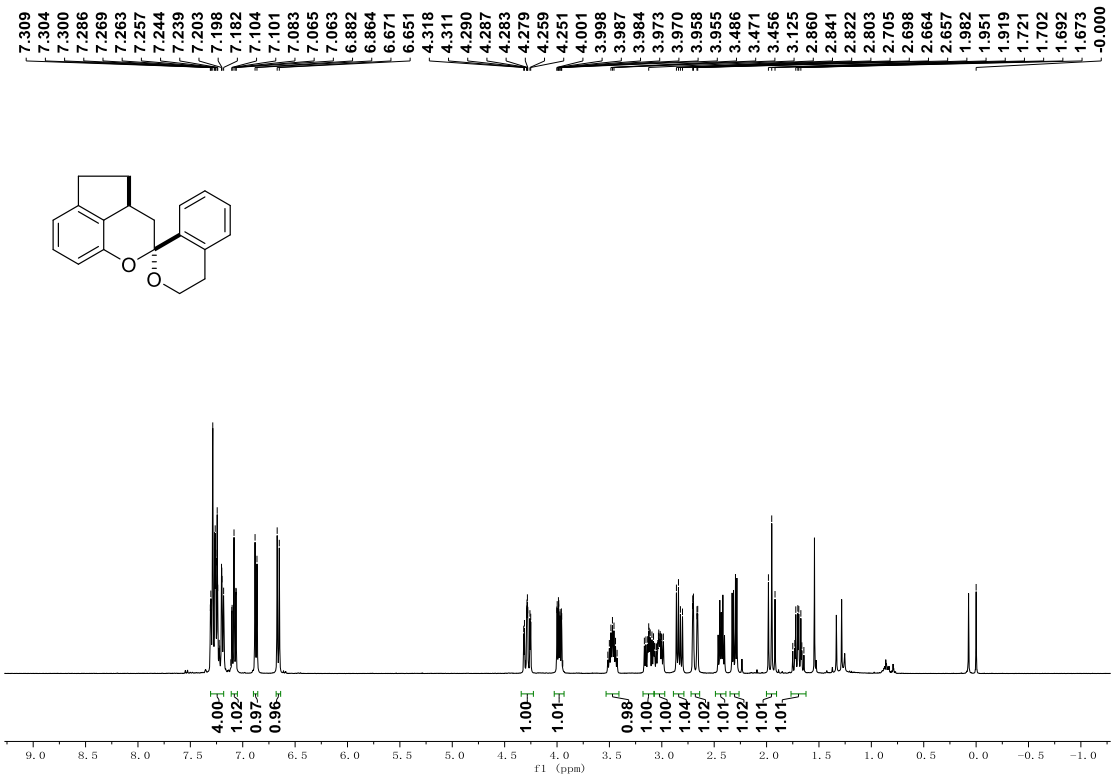
^{1}H NMR (400 MHz) of **(±)-3y** in $CDCl_3$



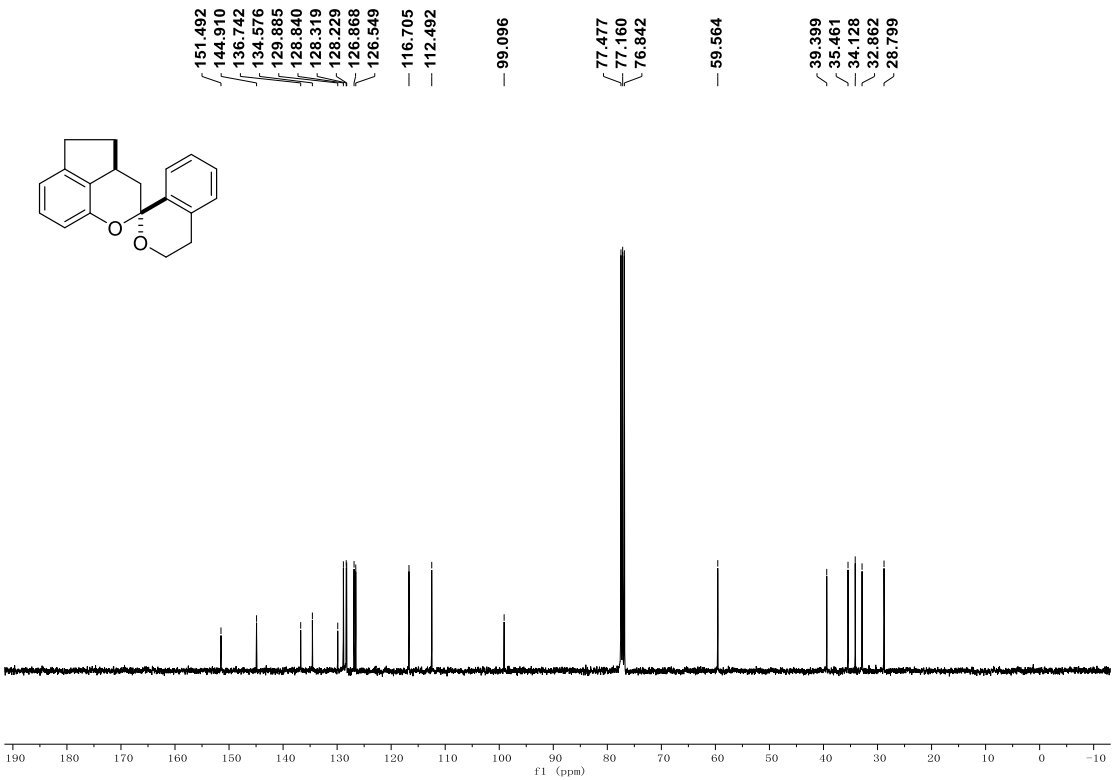
^{13}C NMR (100 MHz) of **(±)-3y** in $CDCl_3$



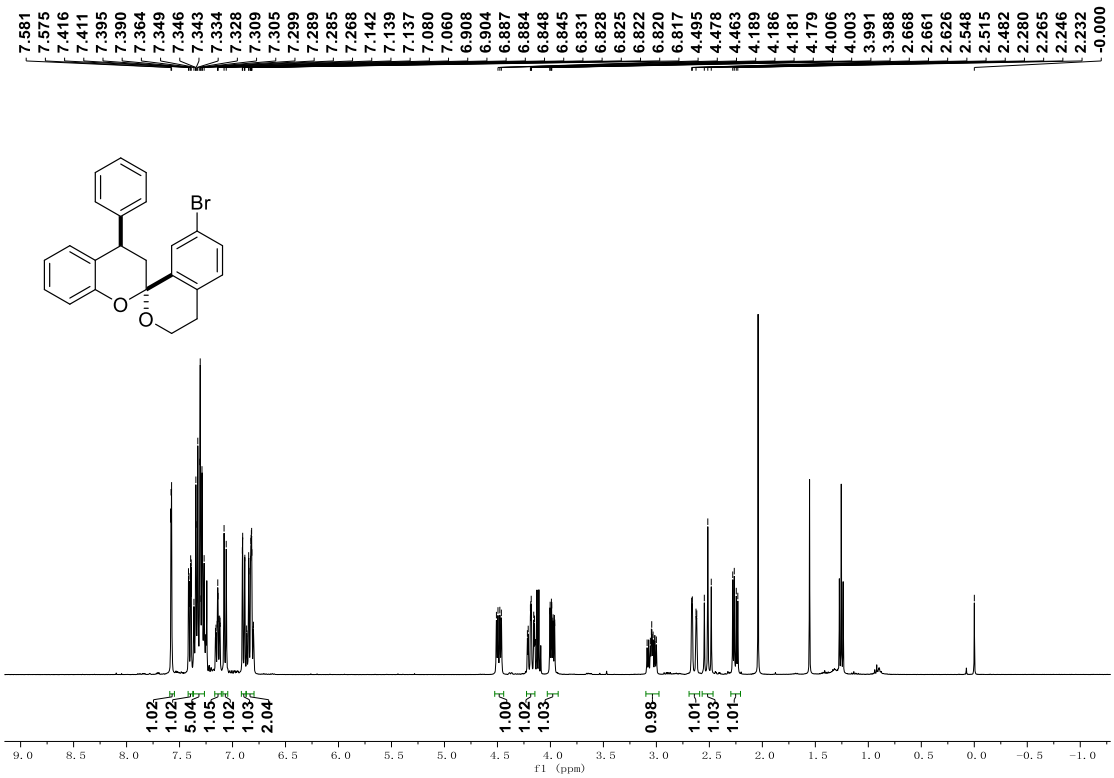
^{1}H NMR (400 MHz) of **(±)-3z** in $CDCl_3$



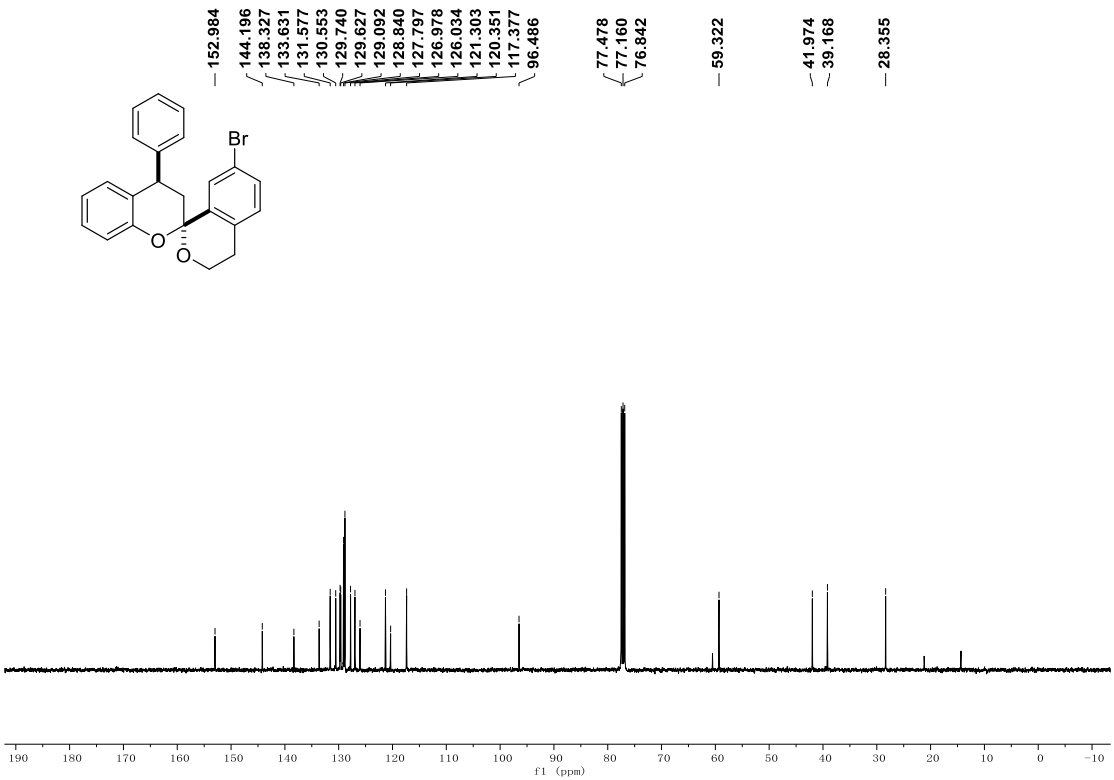
^{13}C NMR (100 MHz) of **(±)-3z** in $CDCl_3$



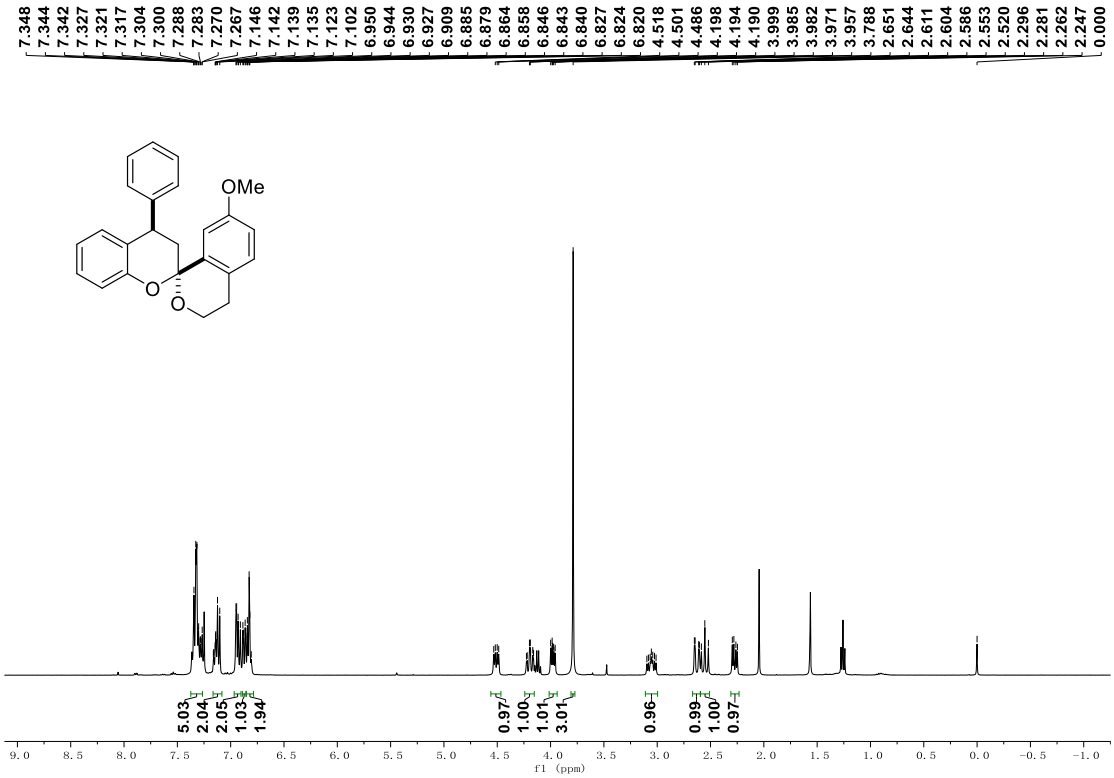
^{1}H NMR (400 MHz) of **(±)-3aa** in $CDCl_3$



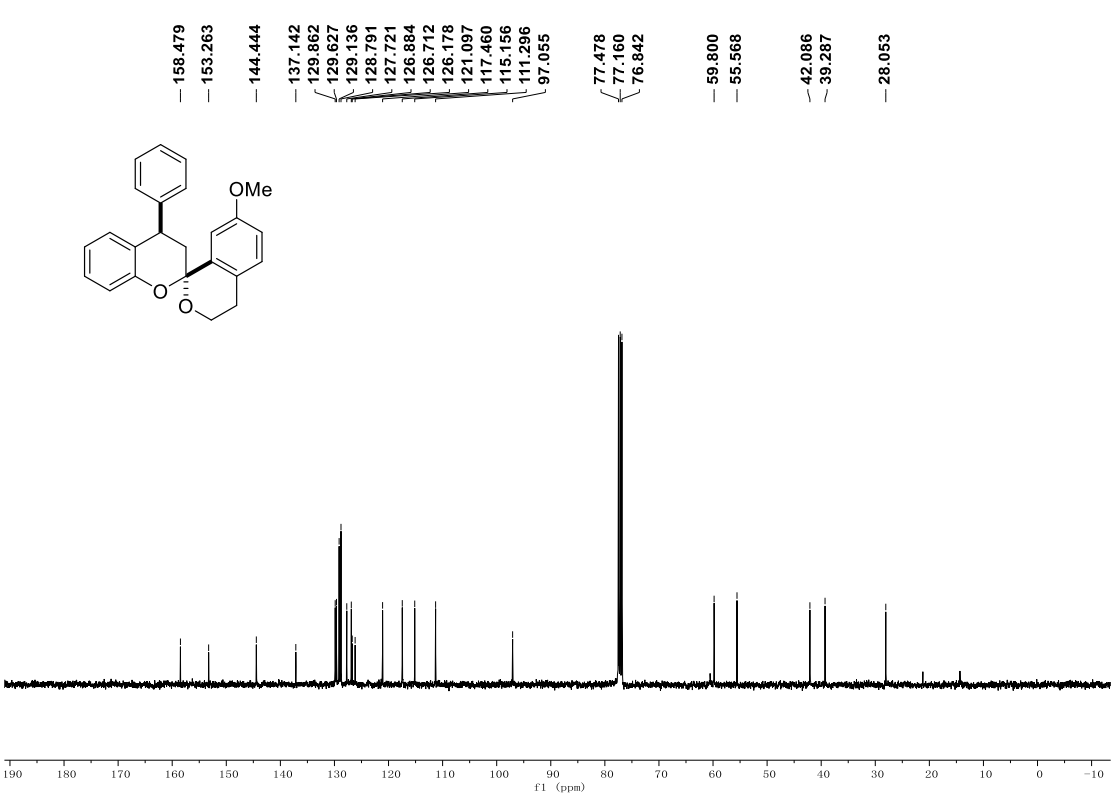
^{13}C NMR (100 MHz) of **(±)-3aa** in $CDCl_3$



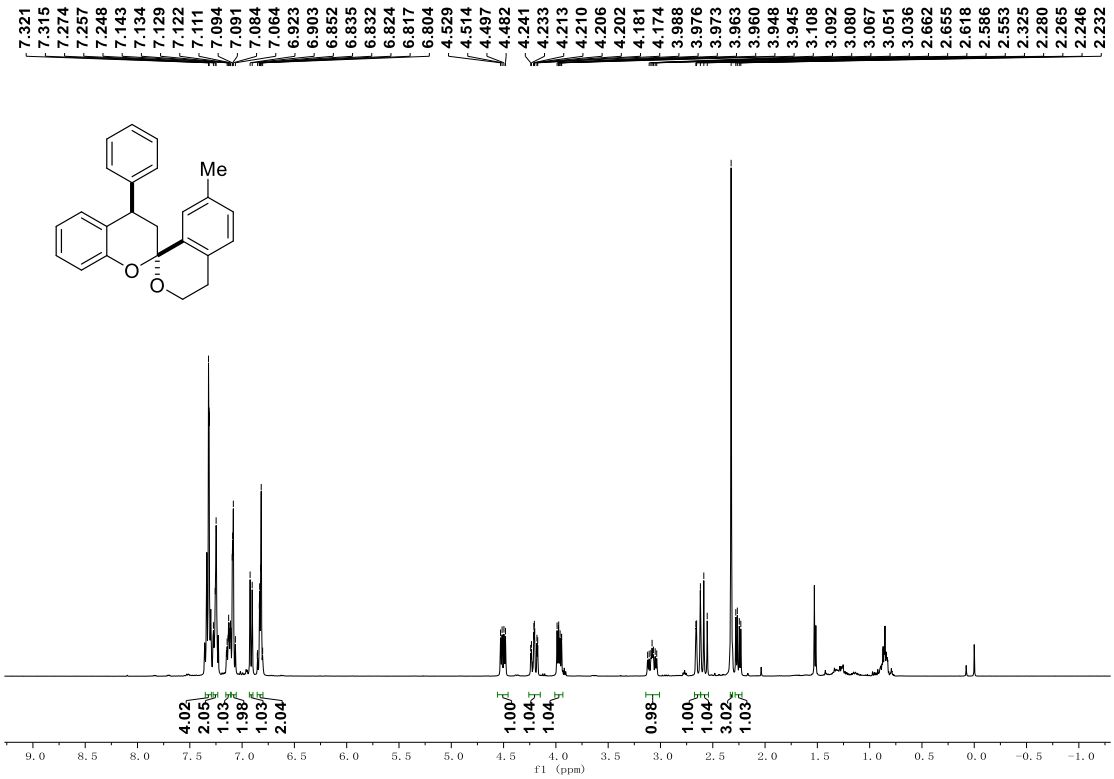
^{1}H NMR (400 MHz) of **(±)-3ab** in $CDCl_3$



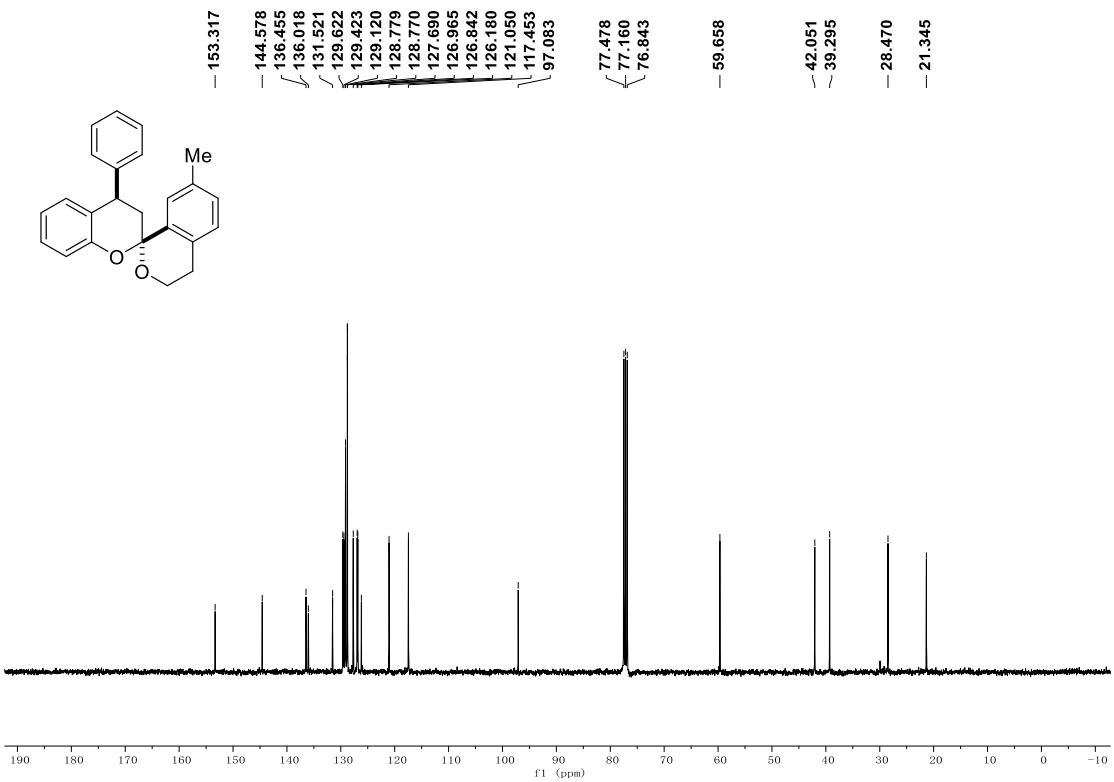
^{13}C NMR (100 MHz) of **(±)-3ab** in $CDCl_3$



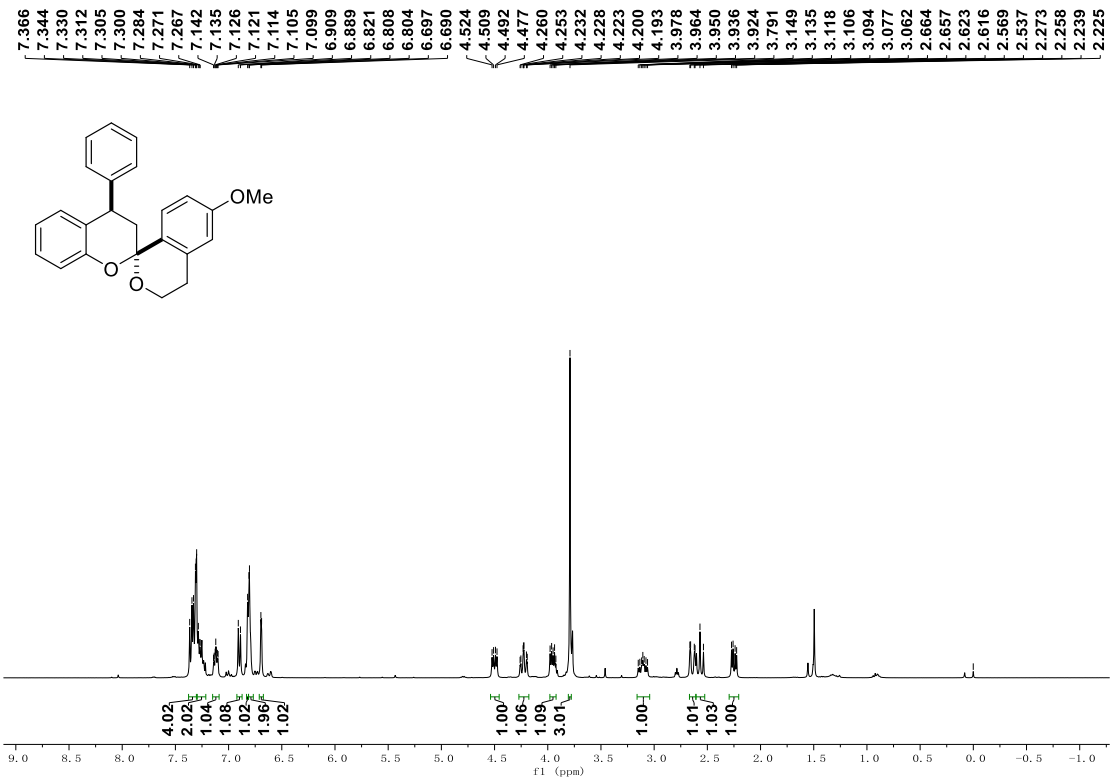
^{1}H NMR (400 MHz) of **(±)-3ac** in $CDCl_3$



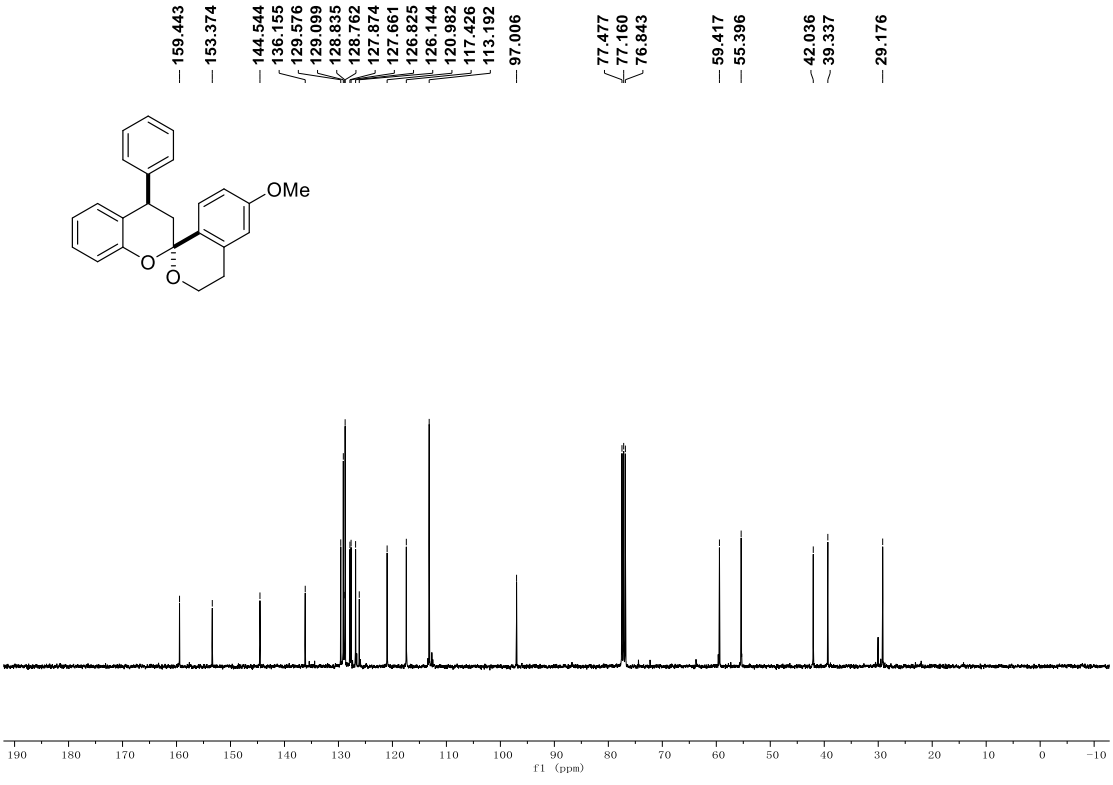
^{13}C NMR (100 MHz) of **(±)-3ac** in $CDCl_3$



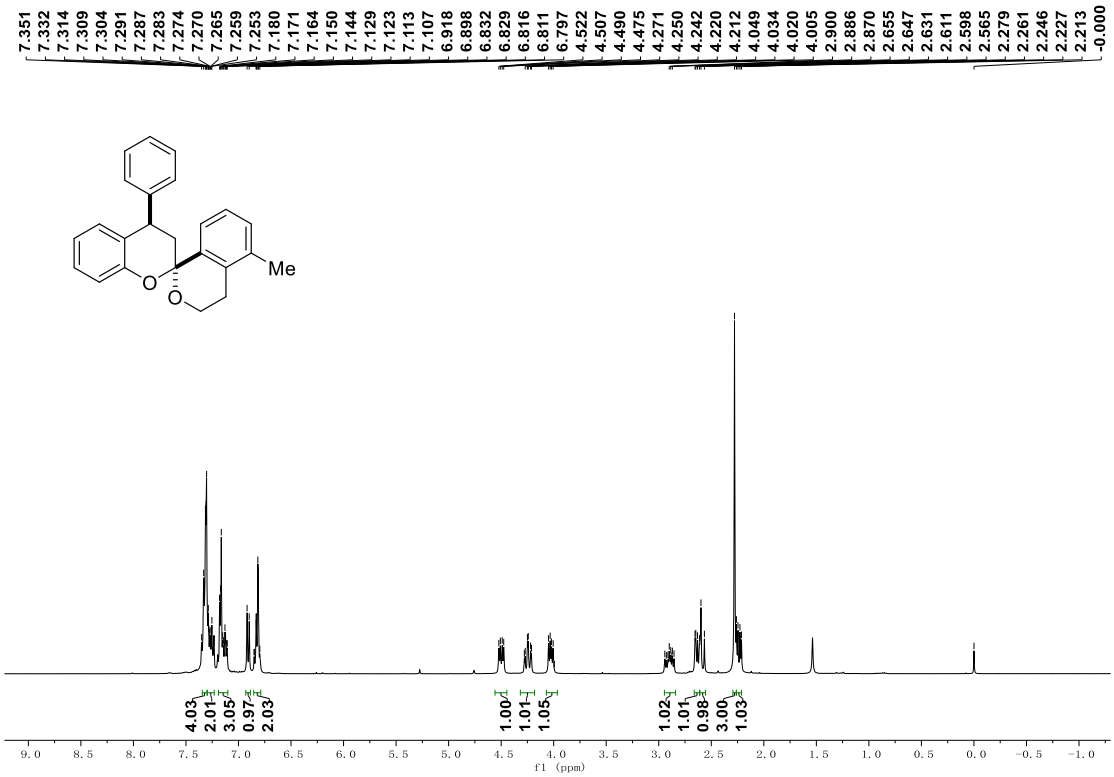
^{1}H NMR (400 MHz) of **(±)-3ad** in $CDCl_3$



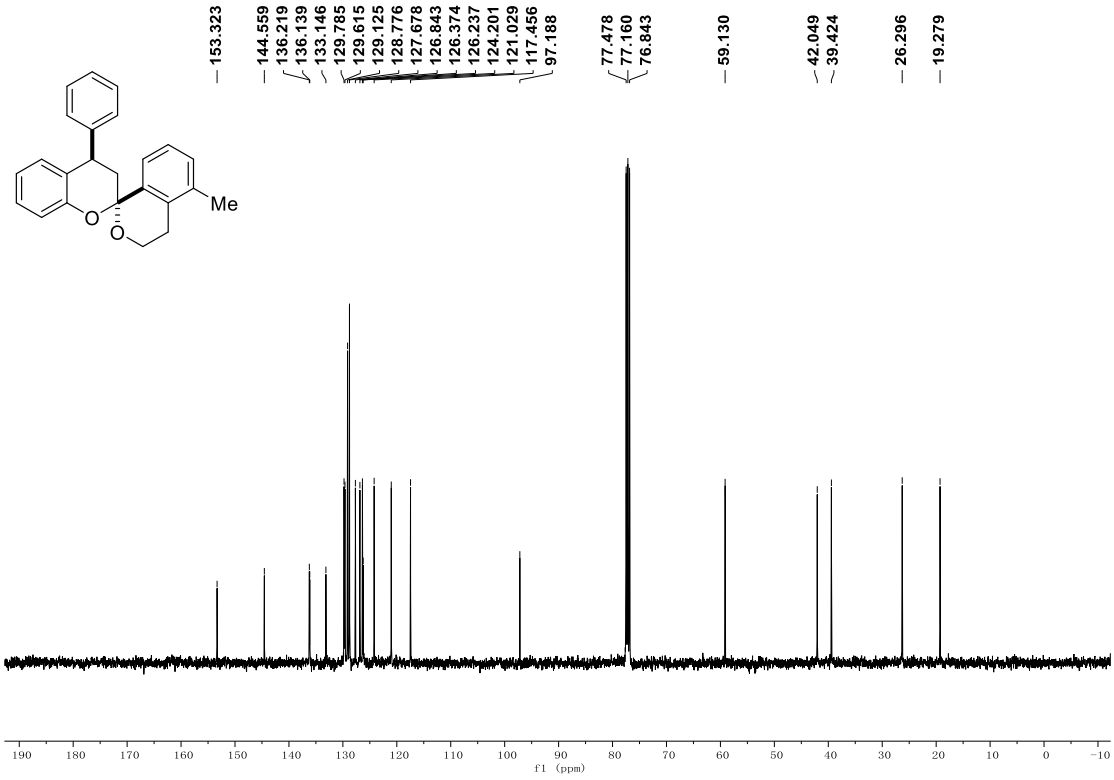
^{13}C NMR (100 MHz) of **(±)-3ad** in $CDCl_3$



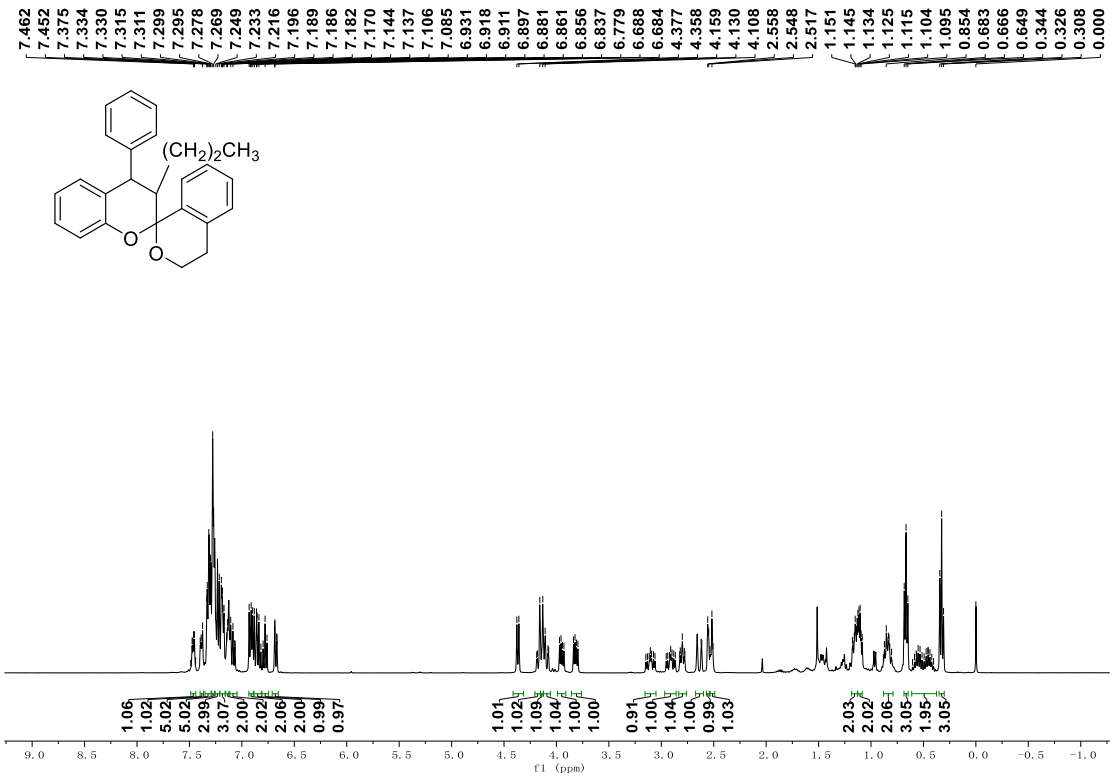
^{1}H NMR (400 MHz) of **(±)-3ae** in $CDCl_3$



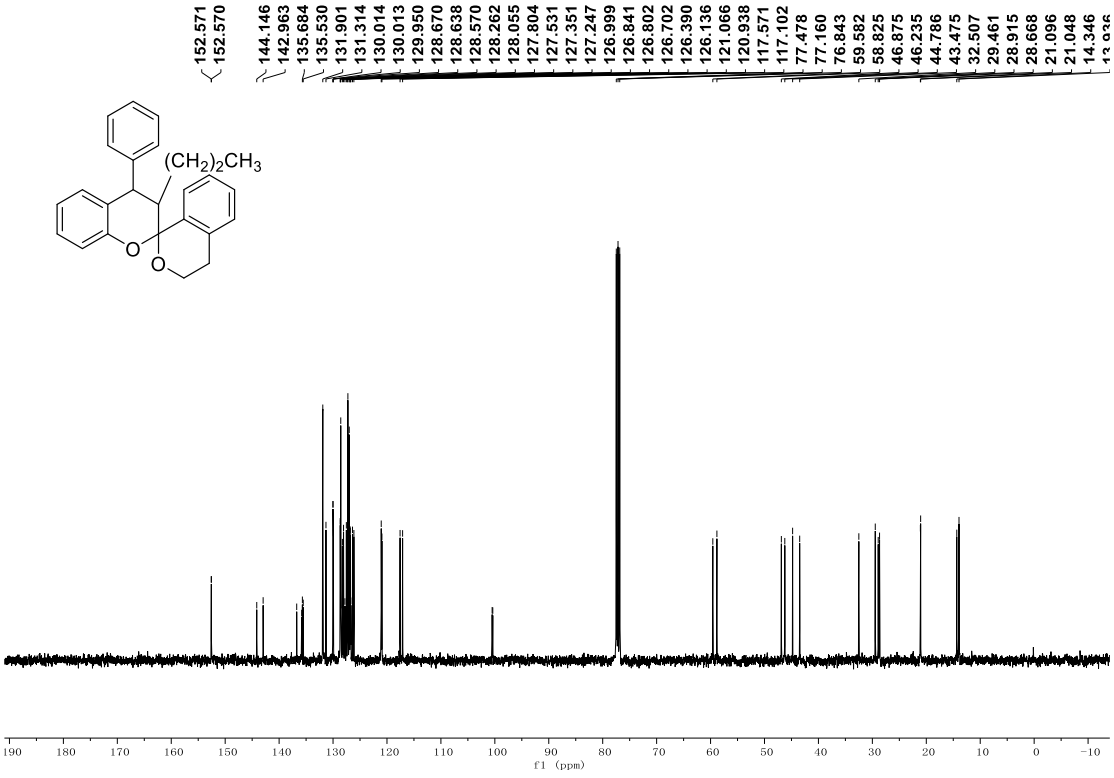
^{13}C NMR (100 MHz) of **(±)-3ae** in $CDCl_3$



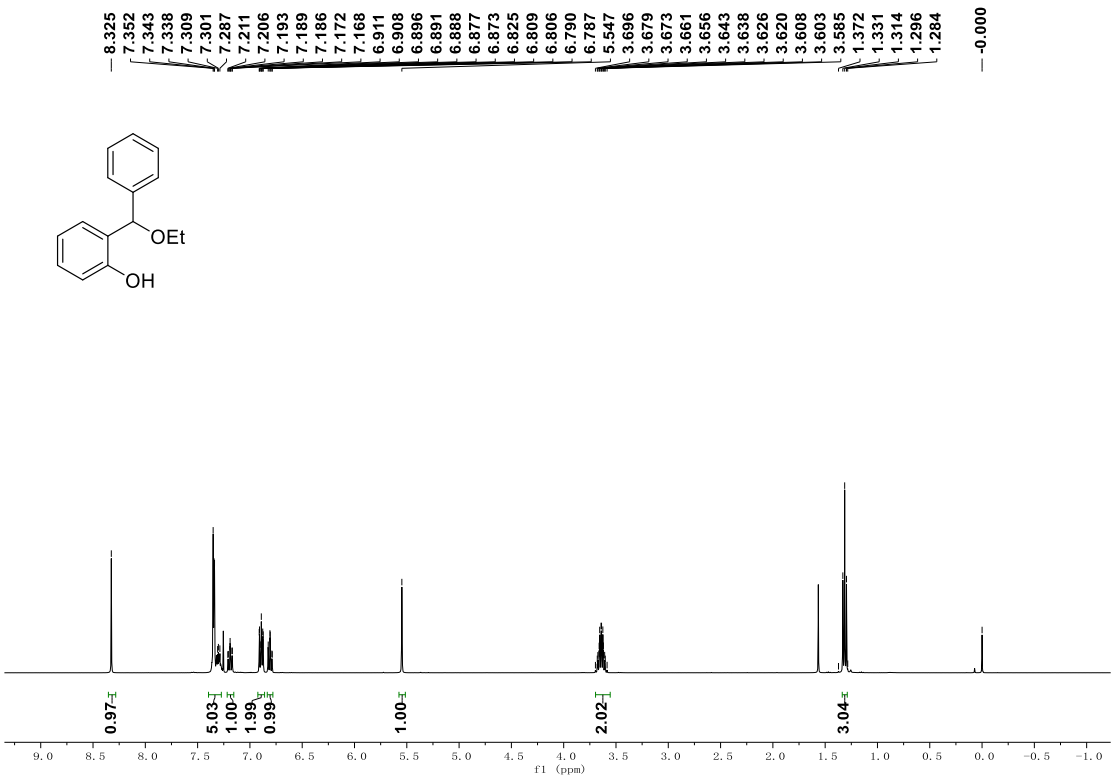
^{1}H NMR (400 MHz) of **(±)-3af** in $CDCl_3$ (1:1 dr)



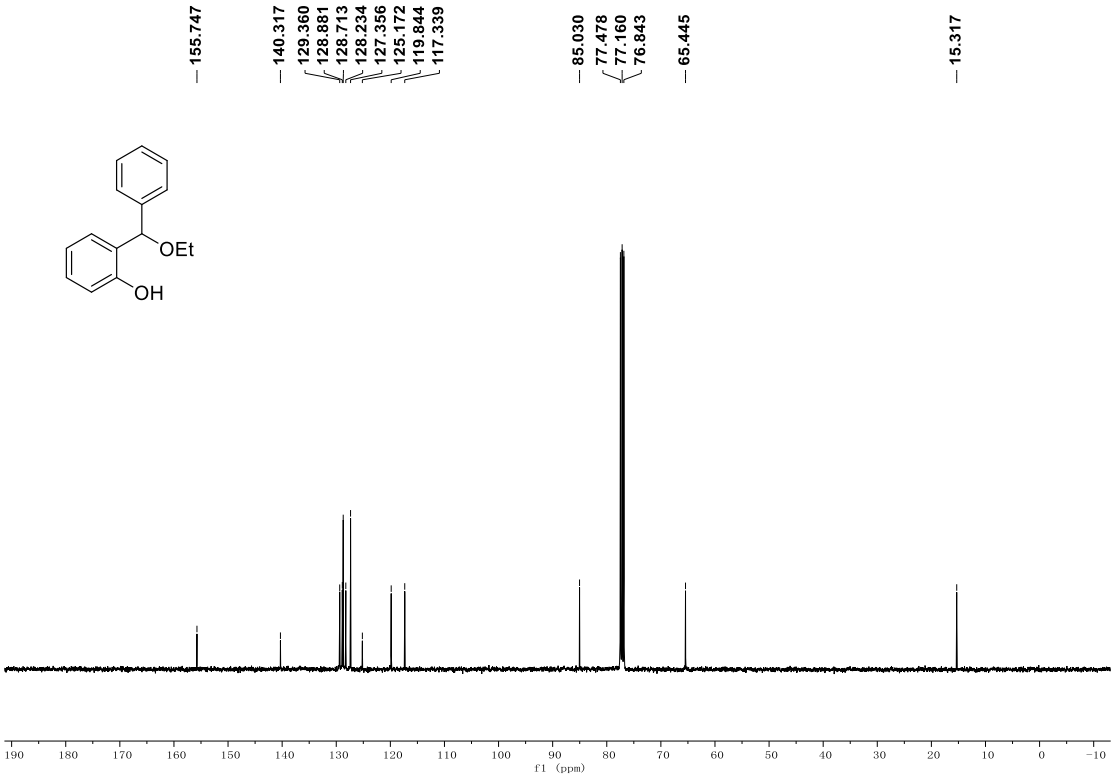
^{13}C NMR (100 MHz) of **(±)-3ae** in $CDCl_3$ (1:1 dr)



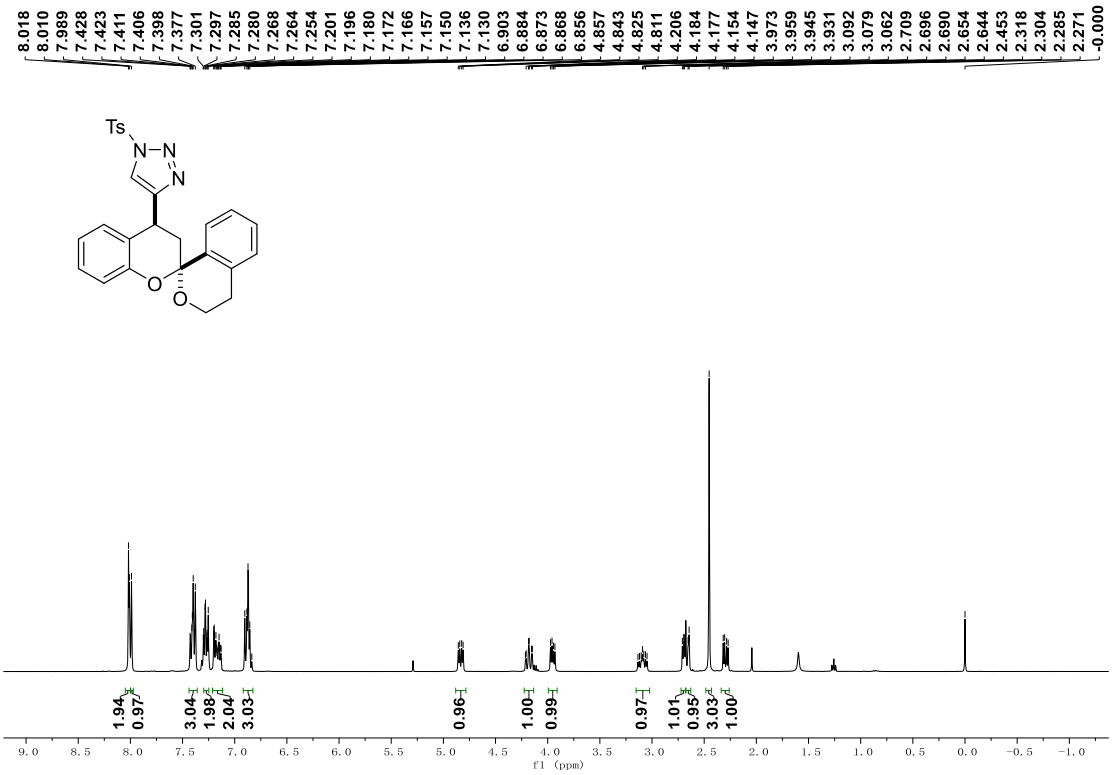
^{1}H NMR (400 MHz) of **(±)-4aa** in $CDCl_3$



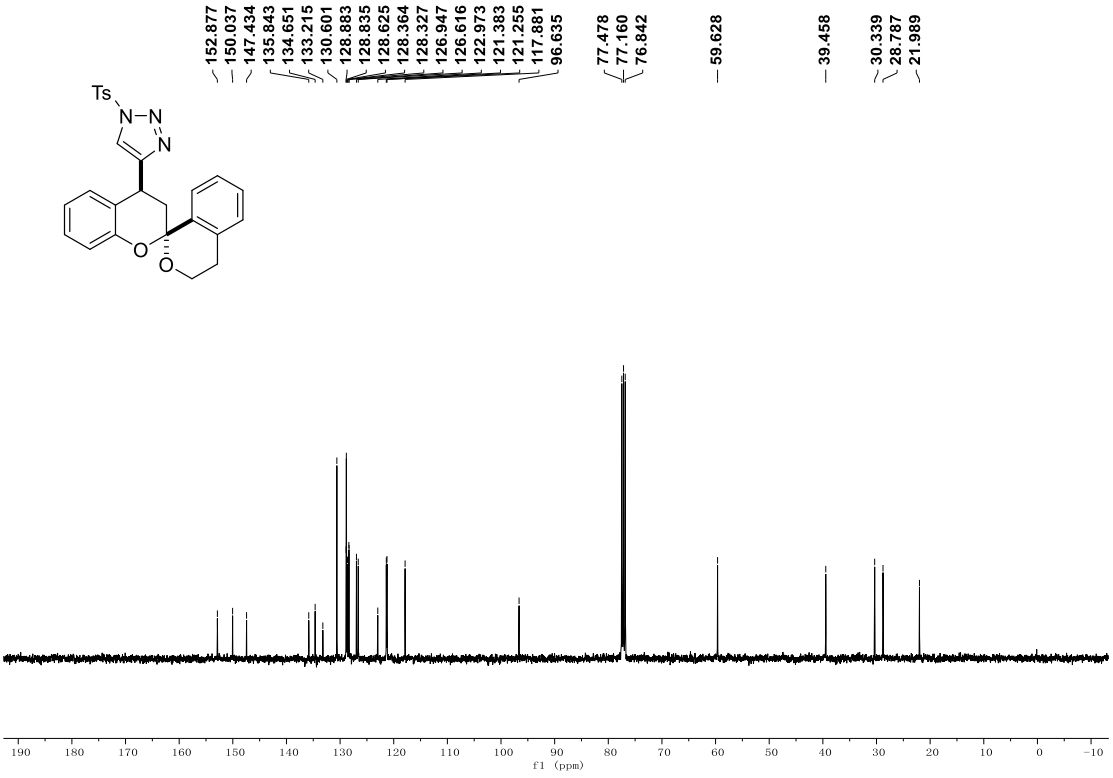
^{13}C NMR (100 MHz) of **(±)-4aa** in $CDCl_3$



^{1}H NMR (400 MHz) of **(±)-5** in $CDCl_3$

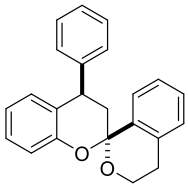


^{13}C NMR (100 MHz) of **(±)-5** in $CDCl_3$

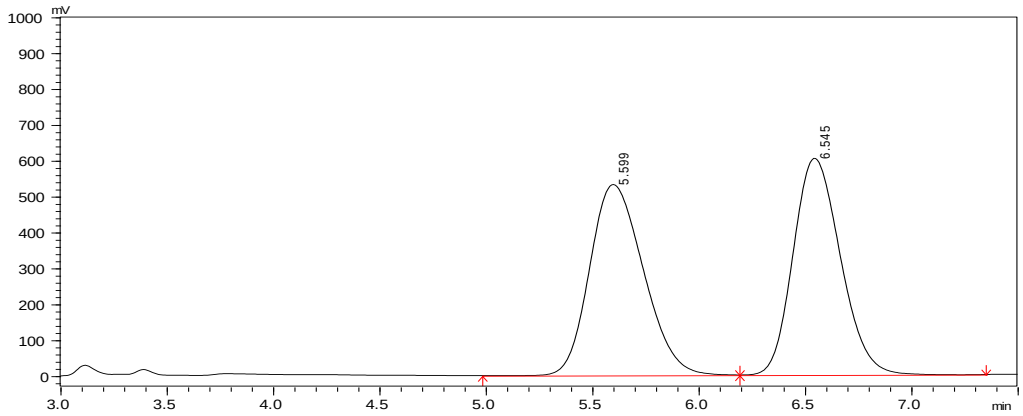


9. HPLC chromatograms

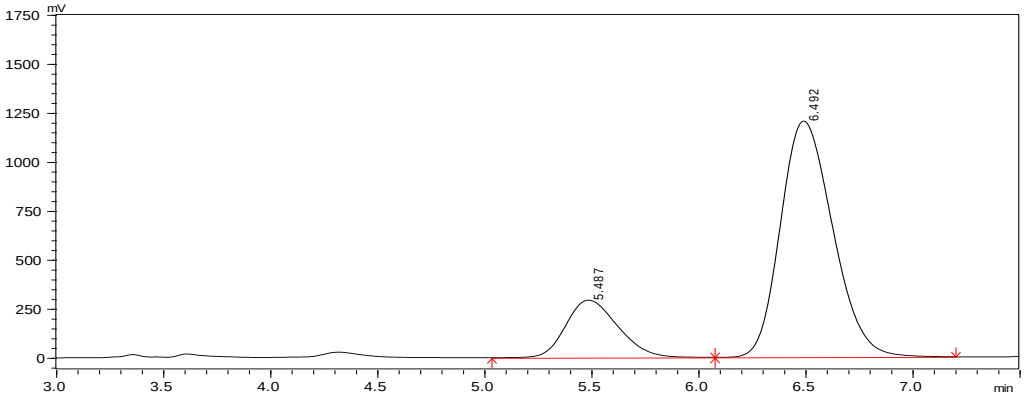
HPLC chromatogram of compound **3a** (61% ee)



HPLC (Chiralcel OD-H, *n*-hexane/*i*-propanol = 99/1, flow rate = 1.0 mL/min, λ = 220 nm) t_R = 5.599 min (minor), 6.545 min (major).



#	Ret Time (min)	Height (μV)	Area (μV.sec)	Area (%)
1	5.599	531967	9343997	50.088
2	6.545	603495	9319585	49.912
total		1161571	1905733	100.000



#	Ret Time (min)	Height (μV)	Area (μV)	Area (%)
1	5.487	292787	4934573	19.429
2	6.492	1204794	20463269	80.571

total	1588601	26843200	100.000