Supporting Information

Diastereoselective Synthesis of Spiro[2,n]alkanes via Intramolecular Carbolithiation

Contents

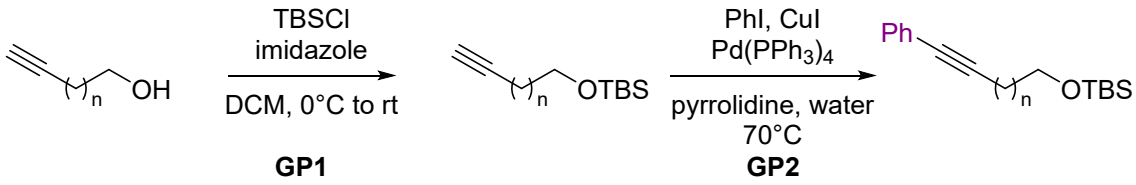
Experimental Procedures

General Information

Unless stated otherwise, reactions were conducted in flame-dried glassware under a positive pressure of argon. Ether and THF were dried from Pure-Solv® Purification System (Innovative Technology©). Allyl bromide, acetyl chloride and benzaldehyde were distilled before use and stored under argon. TMSCl was distilled over calcium hydride and stored under argon. All other commercially obtained reagents were used as received. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 pre-coated plates (0.25 mm), and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, cerium ammonium molybdate or potassium permanganate solutions. Column chromatography was performed using Fluka silica gel 60 Å (40-63mm, 230-400 mesh) or an ISCO flash system using pre-packed columns. NMR spectra were recorded on Bruker spectrometers (AVHD300, AVIII400, AVHD400, AVHD500) and are reported relative to deuterated solvent signals. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal $CDCl_3$ (^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.16). Peak multiplicities are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were obtained by the mass spectrometry facility at the Technion or recorded on a DFS-EI-Mass Spectrometer or an ESI-Exactive Plus Orbitrap Mass Spectrometer (both Thermo Fisher Scientific). The X-ray intensity data were collected at 100 K on a Bruker D8 VENTURE three-angle diffractometer.

Note: All cyclopropenes were stored under argon at -20°C to prevent dimerization.

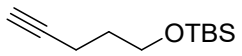
Synthesis of Starting Materials



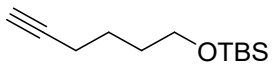
GP1 **GP2**

GP1: TBS protection.[1]

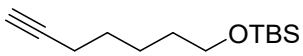
Imidazole (1.16 eq.) and TBS chloride (1.15 eq.) were added sequentially to a solution of alkynol (1.0 eq.) in dry DCM (0.5 M) at 0°C under argon. The reaction mixture was allowed to warm to room temperature and stirred until complete conversion (monitored by TLC). The reaction was quenched with sat. aq. NH_4Cl and extracted with DCM (3x). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The protected alkynols were purified by column chromatography (SiO_2, PE).



tert-butyldimethyl(pent-4-yn-1-yloxy)silane, data in agreement with the literature.[2]



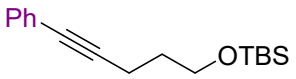
tert-butyl(hex-5-yn-1-yloxy)dimethylsilane, data in agreement with the literature.[3]



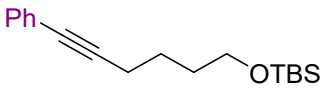
tert-butyl(hept-6-yn-1-yloxy)dimethylsilane, data in agreement with the literature.[4]

GP2: Sonogashira coupling.[5]

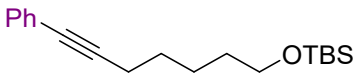
A round bottom flask fitted with a reflux condenser was charged with phenyl iodide (2 equiv.), terminal alkyne (1 equiv.), pyrrolidine (3 equiv.), $Pd(PPh_3)_4$ (0.5 mol %), CuI (1 mol %), and water (0.5 M) and heated to 70°C. After vigorous stirring for 30 min, the intensely colored reaction mixture was cooled to room temperature and extracted with ether. The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The internal alkynes were purified by column chromatography (SiO_2, PE to 2% Et_2O in PE).



tert-butyldimethyl((5-phenylpent-4-yn-1-yl)oxy)silane, data agreement with the literature.[6]

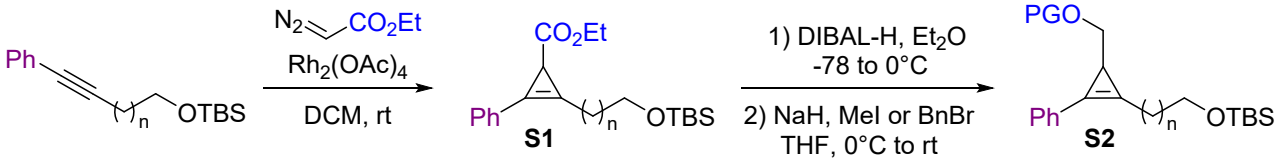


tert-butyldimethyl((6-phenylhex-5-yn-1-yl)oxy)silane, data agreement with the literature.[7]



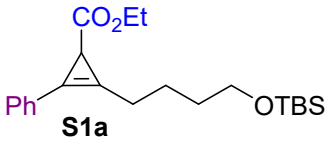
tert-butyldimethyl((7-phenylhept-6-yn-1-yl)oxy)silane, data agreement with the literature.[8]

GP3: Cyclopropenation.[5]



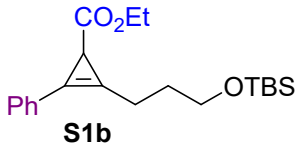
An oven-dried round bottom flask was charged with alkyne (1.0 eq.), Rh_2OAc_4 (0.25 mol%) and dry DCM under an argon atmosphere. A solution of ethyl diazoacetate in DCM (1.5 eq.) was added over a period of 10-15 h via a syringe pump at room temperature. After completion of the addition, the solvent was removed under reduced pressure and the corresponding cyclopropene **S1** was purified by column chromatography (SiO_2, PE to 2% EtOAc in PE).

Ethyl 2-(4-((*tert*-butyldimethylsilyl)oxy)butyl)-3-phenylcycloprop-2-ene-1-carboxylate (S1a)



186 mmol scale, colorless liquid, 26.57 g, 70.9 mmol, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.29 (m, 1H), 4.18 – 4.10 (m, 2H), 3.67 (t, *J* = 6.2 Hz, 2H), 2.70 (td, *J* = 7.3, 1.4 Hz, 2H), 2.44 (s, 1H), 1.90 – 1.75 (m, 2H), 1.65 (dq, *J* = 9.7, 6.3 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.9, 129.5, 128.8, 128.7, 127.2, 110.4, 105.0, 62.9, 60.2, 32.6, 26.1, 25.5, 24.1, 22.4, 18.5, 14.5, -5.2 ppm. **HR-ESI-MS**: m/z calcd. for $C_{22}H_{35}O_3Si^+$ 375.2355; found 375.2346.

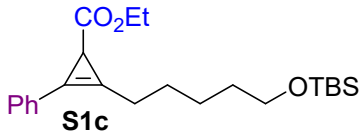
Ethyl 2-(3-((*tert*-butyldimethylsilyl)oxy)propyl)-3-phenylcycloprop-2-ene-1-carboxylate (S1b)



S1b

92 mmol scale, colorless liquid, 5.25 g, 14.6 mmol, 24% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.39 (dd, *J* = 8.3, 6.7 Hz, 2H), 7.35 – 7.29 (m, 1H), 4.20 – 4.05 (m, 2H), 3.71 (td, *J* = 6.2, 2.9 Hz, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.44 (s, 1H), 1.94 (ddd, *J* = 13.5, 7.3, 6.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.05 (d, *J* = 0.7 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.0, 129.5, 128.8, 128.7, 127.2, 110.2, 105.2, 62.3, 60.3, 30.7, 26.1, 22.4, 22.1, 18.5, 14.6, -5.2 ppm. **HR-ESI-MS**: m/z calcd. for $C_{21}H_{32}O_3SiNa^+$ 383.2018; found 383.2017.

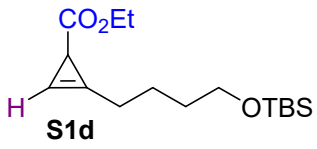
Ethyl 2-(3-((*tert*-butyldimethylsilyl)oxy)pentyl)-3-phenylcycloprop-2-ene-1-carboxylate (S1c)



S1c

57.2 mmol scale, pale yellow liquid, 4.58 g, 11.8 mmol, 31% yield, contains trace amounts of the corresponding dimer. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.42 – 7.35 (m, 2H), 7.35 – 7.28 (m, 1H), 4.21 – 4.09 (m, 2H), 3.62 (t, *J* = 6.5 Hz, 2H), 2.68 (td, *J* = 7.3, 1.6 Hz, 2H), 2.43 (s, 1H),1.76 (p, *J* = 7.4 Hz, 2H), 1.63 – 1.52 (m, 2H), 1.52 – 1.42 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.0, 129.4, 128.8, 128.7, 127.3, 110.5, 104.9, 63.2, 60.2, 32.7, 27.4, 26.1, 25.8, 25.6, 22.3, 18.5, 14.6, -5.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{23}H_{37}O_3Si^+$ 389.2512; found 389.2532.

Ethyl 2-(4-((*tert*-butyldimethylsilyl)oxy)butyl)cycloprop-2-ene-1-carboxylate (S1d)



S1d

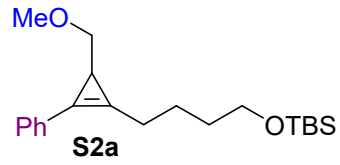
50 mmol scale, pale yellow liquid, 7.015 g, 23.5 mmol, 47% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.33 (q, *J* = 1.5 Hz, 1H), 4.12 (qt, *J* = 7.4, 4.1 Hz, 2H), 3.62 (t, *J* = 6.1 Hz, 2H), 2.52 (td, *J* = 7.1, 1.4 Hz, 2H), 2.12 (d, *J* = 1.6 Hz, 1H), 1.72 – 1.43 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.04 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.7, 115.6, 94.3, 62.8, 60.3, 32.3, 26.1, 24.9, 23.3, 19.8, 18.5, 14.5, -5.2 ppm. **HR-ESI-MS**: m/z calcd. for $[3M+Na]^+$ $C_{48}H_{90}O_9Si_3Na^+$ 917.5785; found 917.5794.

GP4: Synthesis of methyl cyclopropenylcarbinols.[9]

A flame-dried round bottom flask was charged with cyclopropene ester (1.0 eq.) and dry Et_2O (0.2 M) and cooled to -78°C. A solution of DIBAL-H (1.0 M in hexanes or 1.1 M in toluene, 2.2 eq.) was added dropwise and the reaction mixture was allowed to gradually warm to 0°C. Upon completion of the reduction, the reaction mixture was diluted with Et_2O and quenched by careful addition of water (0.04 mL per mmol DIBAL-H), 15% aq. NaOH (0.04 mL per mmol DIBAL-H) and again water (0.1 mL per mmol DIBAL-H). The mixture was stirred at room temperature for 15 min before $MgSO_4$ and celite were added, and stirring was continued for another 15 min. The resulting slurry was filtered and washed with copious amounts of DCM. The filtrate was concentrated under reduced pressure and the crude alcohols were protected without purification.

The crude alcohol was suspended in dry THF (0.15 M) under an atmosphere of argon and cooled to 0°C. NaH (60wt% in mineral oil, 2.0 eq.) and iodomethane (2.5 eq.) [or benzyl bromide (2.5 eq.)] were added sequentially and the mixture was allowed to warm gradually to room temperature overnight. A saturated solution of $NaHCO_3$ was added carefully and the aqueous layer was extracted with Et_2O (3x). The combined

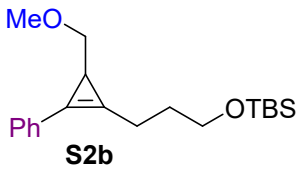
organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. Cyclopropylcarbinol ethers **S2** were purified by column chromatography (SiO_2, PE to 2.5% EtOAc in PE).



S2a

***tert*-Butyl(4-(3-(methoxymethyl)-2-phenylcycloprop-1-en-1-yl)butoxy)dimethylsilane (S2a)**

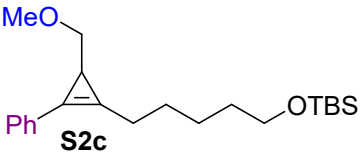
Synthesized according to **GP4**. 12.8 mmol scale, colorless liquid, 4.005 g, 11.56 mmol, 90% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.41 – 7.35 (m, 2H), 7.29 – 7.23 (m, 1H), 3.67 (t, *J* = 6.3 Hz, 2H), 3.47 (dd, *J* = 9.8, 5.2 Hz, 1H), 3.37 (d, *J* = 8.6 Hz, 1H), 3.37 (s, 3H), 2.69 (t, *J* = 7.3 Hz, 2H), 1.97 (t, *J* = 5.2 Hz, 1H), 1.85 – 1.73 (m, 2H), 1.69 – 1.57 (m, 2H), 0.90 (s, 9H), 0.06 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.8, 129.2, 128.6, 127.8, 119.3, 113.3, 79.9, 63.0, 58.6, 32.7, 26.7, 26.1, 24.6, 20.2, -5.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{21}H_{35}O_2Si^+$ 347.2406; found 347.2422.



S2b

***tert*-Butyl(3-(3-(methoxymethyl)-2-phenylcycloprop-1-en-1-yl)propoxy)dimethylsilane (S2b)**

Synthesized according to **GP4**. 7.47 mmol scale, colorless liquid, 2.10 g, 6.31 mmol, 85% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.41 – 7.35 (m, 2H), 7.31 – 7.25 (m, 1H), 3.71 (t, *J* = 6.3 Hz, 2H), 3.48 (dd, *J* = 9.8, 5.2 Hz, 1H), 3.37 (s, 3H), 3.39 – 3.34 (m, 1H), 2.75 (t, *J* = 7.3 Hz, 2H), 1.98 (t, *J* = 5.3 Hz, 1H), 1.95 (q, *J* = 7.4, 6.9 Hz, 1H), 1.93 (q, *J* = 7.1, 6.7 Hz, 1H), 0.91 (s, 9H), 0.05 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.8, 129.2, 128.6, 127.9, 119.0, 113.5, 79.8, 62.6, 58.6, 31.2, 26.1, 23.2, 20.3, 18.5, -5.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{20}H_{32}O_2SiNa^+$ 355.2069; found 355.2056.

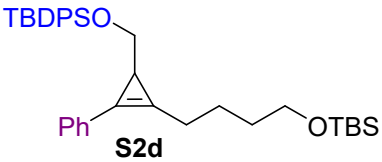


S2c

***tert*-Butyl((5-(3-(methoxymethyl)-2-phenylcycloprop-1-en-1-yl)pentyl)oxy)dimethylsilane (S2c)**

Synthesized according to **GP4**. 14.45 mmol scale, colorless liquid, 4.850 g, 13.45 mmol, 93% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 2H), 7.41 – 7.34 (m, 2H), 7.27 (tt, *J* = 6.2, 1.4 Hz, 1H), 3.62 (t, *J* = 6.5 Hz, 2H), 3.47 (dd, *J* = 9.7, 5.2 Hz, 1H), 3.37 (s, 3H), 3.38 – 3.33 (m, 1H), 2.68 (t, *J* = 7.3 Hz, 2H), 1.97 (t, *J* = 5.3 Hz, 1H), 1.74 (p, *J* = 7.4 Hz, 2H), 1.59 (dq, *J* = 8.8, 6.4 Hz, 2H), 1.50 – 1.38 (m, 2H), 0.88 (s, 9H), 0.04 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.9, 129.2, 128.7, 127.8, 119.4, 113.3, 79.9, 63.3, 58.6, 32.8, 27.9, 26.8, 26.1, 26.0, 20.3, 18.5, -5.1 pppm. **HR-ESI-MS**: m/z calcd. for $[M-H]^+$ $C_{22}H_{35}O_2Si^+$ 359.2401; found 359.2407.

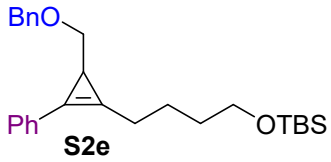
***tert*-Butyl((2-(4-((*tert*-butyldimethylsilyl)oxy)butyl)-3-phenylcycloprop-2-en-1-yl)methoxy)diphenylsilane (S2d)**



S2d

The reduction of **S1d** was performed according to **GP4** and the protection of the cyclopropylcarbinol was performed according to **GP1** with TBDPSCl. 1.51 mmol scale, 667.7 mg, 1.334 mmol, 89% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 4H), 7.59 – 7.57 (m, 2H), 7.44 – 7.32 (m, 8H), 7.30 – 7.26 (m, 1H), 3.79 (dd, *J* = 10.3, 4.5 Hz, 1H), 3.69 – 3.66 (m, 2H), 3.66 – 3.63 (m, 1H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.04 (t, *J* = 4.9 Hz, 1H), 1.78 (p, *J* = 7.4 Hz, 2H), 1.64 (dt, *J* = 9.8, 6.5 Hz, 2H), 1.07 (s, 9H), 0.91 (s, 9H), 0.06 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.8, 135.8, 134.4, 134.4, 130.1, 129.5, 129.5, 129.4, 128.5, 127.8, 127.7, 127.7, 127.7, 119.3, 113.8, 70.4, 63.1, 32.8, 27.0, 27.0, 26.7, 26.1, 24.6, 22.6, 19.3, 18.5, -5.1 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{36}H_{51}O_2Si_2^+$ 571.3428; found 571.3425.

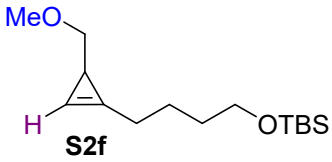
(4-(3-((Benzyloxy)methyl)-2-phenylcycloprop-1-en-1-yl)butoxy)(*tert*-butyl)dimethylsilane (S2e)



S2e

Synthesized according to **GP4**. 2.50 mmol scale, colorless liquid, 544 2mg, 1.287 mmol, 52% yield over two steps, containing trace amounts of the dimer. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.44 – 7.27 (m, 8H), 4.56 (s, 2H), 3.68 (t, *J* = 6.3 Hz, 2H), 3.61 – 3.46 (m, 2H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.06 (t, *J* = 5.3 Hz, 1H), 1.81 (dtd, *J* = 8.8, 7.7, 7.0, 5.9 Hz, 2H), 1.76 – 1.49 (m, 2H), 0.93 (s, 9H), 0.08 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.2, 129.8, 129.3, 128.6, 128.5, 128.4, 127.7, 127.4, 119.2, 113.4, 72.8, 72.2, 63.0, 32.8, 26.7, 26.1, 24.6, 20.3, 18.5, -5.1 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{27}H_{38}O_2SiNa^+$ 445.2533; found 445.2546.

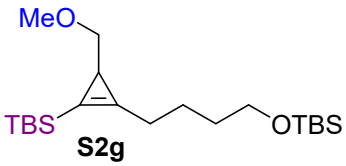
***tert*-Butyl(4-(3-(methoxymethyl)cycloprop-1-en-1-yl)butoxy)dimethylsilane (S2f)**



S2f

Synthesized according to **GP4**. 5.07 mmol scale, colorless liquid, 712 mg, 2.63 mmol, 52% yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.63 (q, *J* = 1.4 Hz, 1H), 3.71 – 3.54 (m, 2H), 3.32 (s, 3H), 3.29 (dd, *J* = 9.3, 4.6 Hz, 1H), 3.22 (ddd, *J* = 9.8, 5.3, 0.6 Hz, 1H), 2.49 (td, *J* = 6.9, 1.3 Hz, 2H), 1.65 (dd, *J* = 5.1, 1.5 Hz, 1H), 1.64 – 1.53 (m, 4H), 0.88 (s, 9H), 0.04 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 125.4, 102.7, 80.5, 63.0, 58.4, 32.5, 26.2, 26.1, 23.7, 18.5, 17.8, -5.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{15}H_{31}O_2Si^+$ 271.2088; found 271.2099.

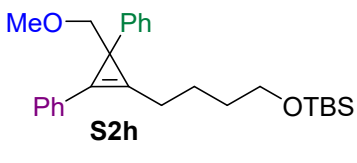
***tert*-Butyl(4-(2-(*tert*-butyldimethylsilyl)-3-(methoxymethyl)cycloprop-1-en-1-yl)butoxy)dimethylsilane (S2g)**



S2g

Cyclopropene **S1d** (1.0 eq.) was dissolved in anhydrous THF and cooled to -78°C. TBSCl (1.1 eq.) was added, followed by dropwise addition of freshly prepared LiHMDS (1 M in THF, 1.2 eq.). The reaction mixture was allowed to warm to 0°C and quenched with sat. aqueous NH_4Cl. The aqueous layer was extracted with Et_2O (3x) and the combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude silylated cyclopropane ester was transformed into the corresponding methyl ether according to **GP4**. 2.81 mmol scale, colorless liquid, contains TBSOTBS as an inseparable impurity, 1.1122 g, 76wt-% purity, 2.197 mmol, 78% corrected yield over three steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.62 (t, J = 6.1 Hz, 2H), 3.42 (dd, J = 9.8, 4.6 Hz, 1H), 3.30 (s, 3H), 3.01 – 2.84 (m, 1H), 2.58 (t, J = 7.2 Hz, 2H), 1.71 – 1.53 (m, 4H), 1.50 (dd, J = 6.0, 4.6 Hz, 1H), 0.91 (s, 8H), 0.89 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H), 0.04 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.8, 109.3, 81.6, 63.0, 58.2, 32.7, 28.1, 26.6, 26.1, 23.9, 19.3, 18.5, 17.0, -5.16, -5.19, -5.21 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{21}H_{44}O_2Si_2Na^+$ 407.2778; found 407.2768.

***tert*-Butyl(4-(3-(methoxymethyl)-2,3-diphenylcycloprop-1-en-1-yl)butoxy)dimethylsilane (S2h)**

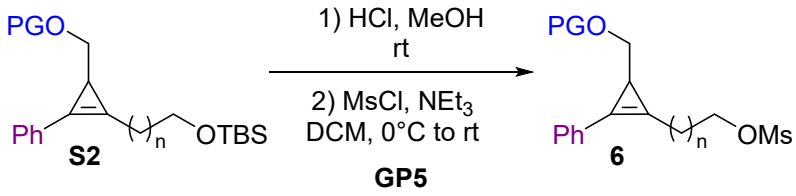


S2h

Methyl phenyldiazoacetate (7.53 mmol, 1.0 eq.) in DCM (10 mL) was added in the dark via a syringe pump over 10 h to a solution of alkyne (8.28 mmol, 1.1 eq.) and AgOTf (0.753 mmol, 0.10 eq) in DCM (27 mL) under argon atmosphere.[10] Upon complete addition, the black mixture was concentrated under reduced pressure and filtered over silica gel (eluting with 2% Et_2O in PE). The product-containing fraction was concentrated and the crude product was subjected to reduction and methylation according to according to **GP4**. 7.53 mmol scale, colorless liquid, 611.0 mg,

1.446 mmol, 19.3% yield over three steps. **^{1}H NMR** (300 MHz, $CDCl_3$*d*) δ 7.62 – 7.54 (m, 2H), 7.45 – 7.25 (m, 8H), 7.17 (ddt, *J* = 8.4, 6.5, 1.5 Hz, 1H), 4.04 (s, 1H), 3.71 (t, *J* = 6.2 Hz, 2H), 3.46 (s, 2H), 2.77 (td, *J* = 7.3, 3.3 Hz, 2H), 1.88 (p, *J* = 7.3 Hz, 2H), 1.78 – 1.66 (m, 2H), 0.98 (s, 9H), 0.12 (s, 6H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.6, 129.5, 128.7, 128.3, 128.1, 126.3, 125.0, 119.7, 113.0, 80.2, 62.9, 58.8, 32.7, 31.8, 26.1, 25.2, 24.8, 18.5, -5.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{27}H_{28}O_2SiNa^+$ 445.2533; found 445.2529.

GP5: TBS deprotection and mesylation

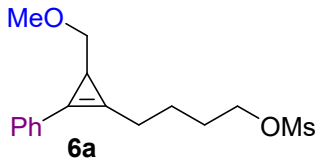


A solution of 1wt% HCl in MeOH (1.7 eq., 1.6 M) was added to a solution of the TBS ether (1.0 eq.) in DCM (0.2 M) and stirred for 15 min at room temperature. The reaction mixture was neutralized with $NaHCO_3$ (solid), diluted with DCM and filtered over $Na_2SO_4$to remove salts. The filtrate was concentrated under reduced pressure and the crude alcohol was used in the next step without further purification.

Note: The TBS deprotection works similarly well with TBAF in THF for compounds not containing another silyl moiety.

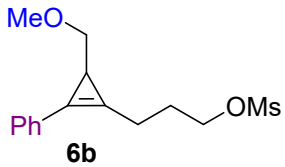
The crude alcohol (1.0 eq.) was dissolved in DCM (0.2 M) and cooled to 0°C. Methanesulfonyl chloride (1.5 eq.) and triethylamine (1.5 eq.) were added dropwise and the reaction mixture was allowed to stir at room temperature for 1 h. Upon completion, water was added and the mixture was stirred for an additional 20 min. The layers were separated and the aqueous layer was extracted with DCM (3x). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The methyl ethers were purified by column chromatography (SiO_2, PE/EtOAc 9/1 to 3/1).

4-(3-(Methoxymethyl)-2-phenylcycloprop-1-en-1-yl)butyl methanesulfonate (6a)



Synthesized according to **GP5**. 11.9 mmol scale, colorless liquid, 3.420 g (contains 2.7wt% EtOAc), 10.73 mmol, 91% corrected yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 1H), 4.28 (t, *J* = 5.3 Hz, 2H), 3.52 (dd, *J* = 9.8, 5.0 Hz, 1H), 3.36 (s, 3H), 3.32 (dd, *J* = 9.9, 5.6 Hz, 1H), 3.00 (s, 3H), 2.74 (t, *J* = 6.4 Hz, 3H), 1.99 (t, *J* = 5.3 Hz, 1H), 1.92 – 1.80 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.5, 129.2, 128.7, 128.1, 118.2, 113.9, 79.6, 69.7, 58.7, 37.5, 29.0, 26.0, 24.0, 20.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{16}H_{22}O_4SNa^+$ 333.1136; found 333.1141.

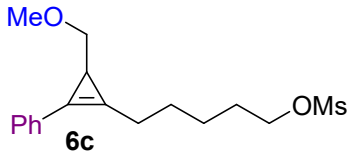
3-(3-(Methoxymethyl)-2-phenylcycloprop-1-en-1-yl)propyl methanesulfonate (6b)



Synthesized according to **GP5**. 1.688 mmol scale, colorless liquid, 553.3 mg (contains 2.5wt% EtOAc), 1.551 mmol, 92% corrected yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.45 – 7.36 (m, 2H), 7.35 – 7.28 (m, 1H), 4.54 (td, *J* = 6.6, 1.2 Hz, 2H), 3.55 (dd, *J* = 9.7, 4.8 Hz, 1H), 3.35 (s, 3H), 3.30 (dd, *J* = 9.7, 5.6 Hz, 1H), 3.21 – 3.11 (m, 2H), 3.01 (d, *J* = 0.9 Hz, 3H), 2.08 – 2.01 (m,

1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.4, 128.9, 128.8, 128.6, 116.2, 113.3, 79.1, 67.4, 58.7, 37.7, 31.7, 27.1, 20.1 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{15}H_{20}O_4SNa^+$ 319.0980; found 319.0956.

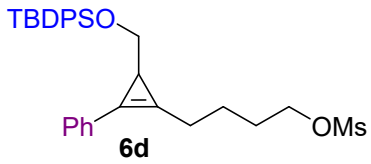
5-(3-(Methoxymethyl)-2-phenylcycloprop-1-en-1-yl)pentyl methanesulfonate (6c)



6c

Synthesized according to **GP5**. 5.128 mmol scale, colorless liquid, 1.256 g, 3.871 mmol, 75% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.32 – 7.25 (m, 1H), 4.24 (t, *J* = 6.5 Hz, 2H), 3.50 (dd, *J* = 9.7, 5.0 Hz, 1H), 3.36 (s, 3H), 3.33 (dd, *J* = 9.8, 5.5 Hz, 1H), 2.97 (s, 3H), 2.70 (t, *J* = 7.3 Hz, 2H), 1.97 (t, *J* = 5.2 Hz, 1H), 1.79 (dq, *J* = 20.0, 7.5 Hz, 4H), 1.52 (tt, *J* = 9.6, 6.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.7, 129.2, 128.7, 128.0, 118.8, 113.5, 79.7, 70.0, 58.6, 37.5, 29.1, 27.4, 26.5, 25.4, 20.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{17}H_{25}O_4S^+$ 325.1468; found 325.1460.

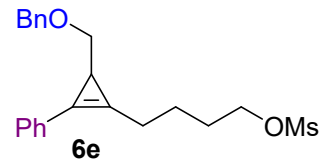
4-(3-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-2-phenylcycloprop-1-en-1-yl)butyl methanesulfonate (6d)



6d

Synthesized according to **GP5**. 1.186 mmol scale, colorless liquid, contains 8 wt-% EtOAc, 318.1 mg, 0.547 mmol, 46% corrected yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (tt, J = 6.9, 1.5 Hz, 4H), 7.56 – 7.51 (m, 2H), 7.44 – 7.24 (m, 9H), 4.26 – 4.21 (m, 2H), 3.75 (dd, J = 10.3, 4.6 Hz, 1H), 3.69 (dd, J = 10.3, 5.1 Hz, 1H), 2.95 (s, 3H), 2.73 – 2.65 (m, 2H), 1.88 – 1.78 (m, 4H), 1.06 (s, 9H); **^{13}C NMR** (101 MHz, CDCl3) δ 135.8, 135.7, 134.3, 134.2, 129.7, 129.6, 129.6, 129.4, 128.6, 128.0, 127.7, 127.7, 118.2, 114.3, 70.2, 69.7, 37.5, 29.0, 27.0, 26.1, 24.0, 22.5, 19.3 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{31}H_{39}O_4SSi^+$ 535.2333; not found.

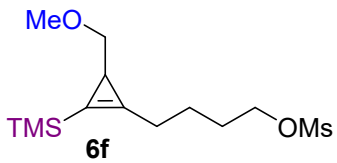
4-(3-((Benzyloxy)methyl)-2-phenylcycloprop-1-en-1-yl)butyl methanesulfonate (6e)



6e

Synthesized according to **GP5**. 1.207 mmol scale, colorless liquid, 291.1 mg, 0.753 mmol, 62% yield over two steps, containing traces (<2wt-%) of the dimer. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.40 – 7.21 (m, 8H), 4.51 (s, 2H), 4.27 – 4.19 (m, 2H), 3.58 (dd, *J* = 9.6, 5.0 Hz, 1H), 3.42 (dd, *J* = 9.6, 5.4 Hz, 1H), 2.94 (s, 3H), 2.77 – 2.66 (m, 2H), 2.03 (t, *J* = 5.2 Hz, 1H), 1.89 – 1.77 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.0, 129.5, 129.2, 128.7, 128.6, 128.5, 128.4, 128.1, 127.7, 127.5, 118.2, 114.0, 77.2, 72.9, 69.7, 37.4, 29.0, 26.0, 24.0, 20.3 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{22}H_{26}O_4SNa^+$ 409.1444; found 409.1447.

4-(3-(Methoxymethyl)-2-(trimethylsilyl)cycloprop-1-en-1-yl)butyl methanesulfonate (6f)

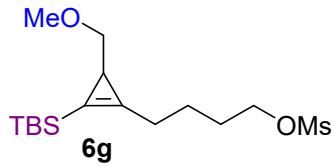


6f

In a flame-dried Schlenk flask, **S2f** was dissolved in dry THF (0.25 M) and cooled to -78°C. *n*BuLi (2.0 eq.) was added dropwise, followed by addition of TMSCl (2.3 eq.). The reaction mixture was allowed to gradually warm to rt, diluted with brine and extracted with Et_2O (3x). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude TBSether was subjected to deprotection according to **GP5**. 2.00 mmol scale, colorless liquid, 500 mg (contains DCM and MsCl, 37wt% purity), 0.604 mmol, 30% corrected yield over three

steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.24 (t, *J* = 6.3 Hz, 2H), 3.36 (dd, *J* = 9.8, 4.8 Hz, 1H), 3.30 (s, 3H), 3.05 – 3.01 (m, 1H), 3.00 (s, 3H), 2.59 (t, *J* = 7.1 Hz, 2H), 1.86 – 1.74 (m, 2H), 1.74 – 1.64 (m, 2H), 1.53 (dd, *J* = 5.8, 4.8 Hz, 1H), 0.15 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.5, 111.8, 81.2, 69.8, 58.2, 37.5, 31.7, 27.5, 23.5, 19.2, -1.0 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{13}H_{26}O_4SSi^+$ 306.1321; found 306.1320.

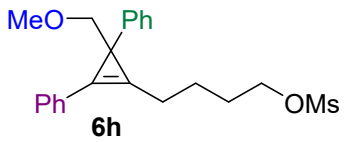
4-(2-(*tert*-Butyldimethylsilyl)-3-(methoxymethyl)cycloprop-1-en-1-yl)butyl methanesulfonate (6g)



6g

Synthesized according to **GP5**. 0.936 mmol scale, colorless liquid, 264.8 mg, 0.760 mmol, 81% yield over two steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 4.24 (t, *J* = 6.4 Hz, 2H), 3.45 (dd, *J* = 9.7, 4.2 Hz, 1H), 3.29 (d, *J* = 1.9 Hz, 5H), 3.00 (s, 3H), 2.95 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.61 (t, *J* = 7.1 Hz, 2H), 1.84 – 1.76 (m, 2H), 1.75 – 1.66 (m, 2H), 1.54 – 1.49 (m, 1H), 0.90 (s, 9H), 0.09 (s, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.9, 110.2, 81.4, 69.8, 58.3, 37.5, 28.9, 27.5, 26.5, 23.4, 19.3, 17.0, -5.3 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{16}H_{32}O_4SSiNa^+$ 371.1688; found 371.1686.

4-(3-(methoxymethyl)-2,3-diphenylcycloprop-1-en-1-yl)butyl methanesulfonate (6h)

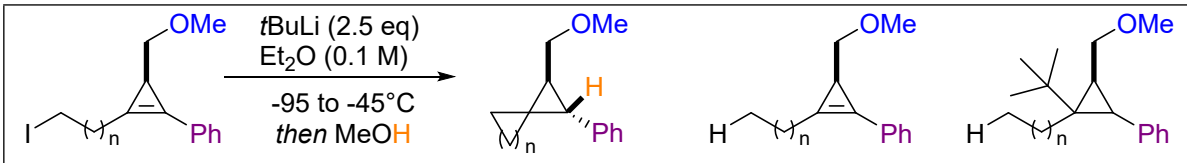


6h

Synthesized according to **GP5**. 1.453 mmol scale, colorless liquid, 551.5 mg, 1.427 mmol, 98% yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.32 – 7.19 (m, 5H), 7.11 (tt, *J* = 6.8, 1.9 Hz, 1H), 4.27 – 4.15 (m, 2H), 4.03 (d, *J* = 9.9 Hz, 1H), 3.92 (dt, *J* = 9.8, 1.1 Hz, 1H), 3.40 (s, 3H), 2.93 (s, 3H), 2.83 – 2.68 (m, 2H), 1.83 (p, *J* = 3.4, 2.9 Hz, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 145.4, 129.4, 128.8, 128.3, 128.1, 128.0, 126.2, 125.1, 118.8, 113.4, 79.8, 69.7, 58.8, 37.2, 31.8, 28.8, 24.6, 24.0 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{22}H_{26}O_4SNa^+$ 409.1444; found 409.1438.

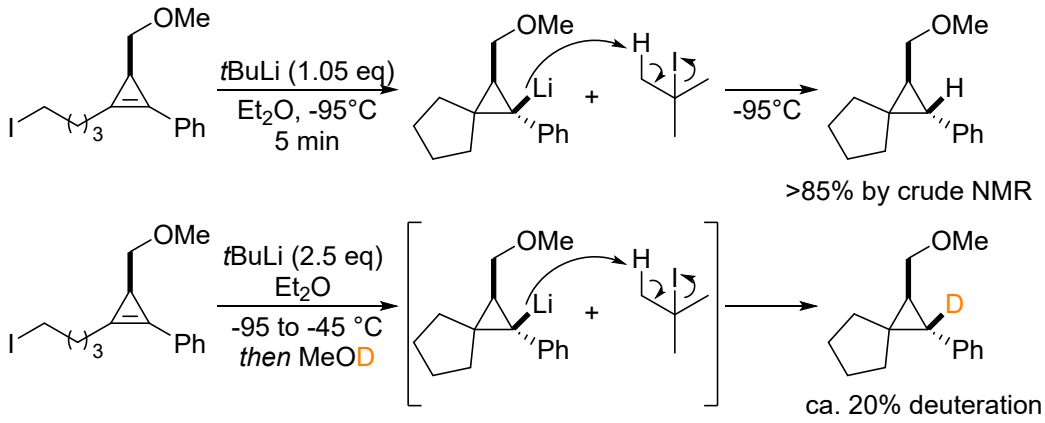
Optimization of the Intramolecular Carbolithiation

Table S1: Optimization of intramolecular Carbolithiation.



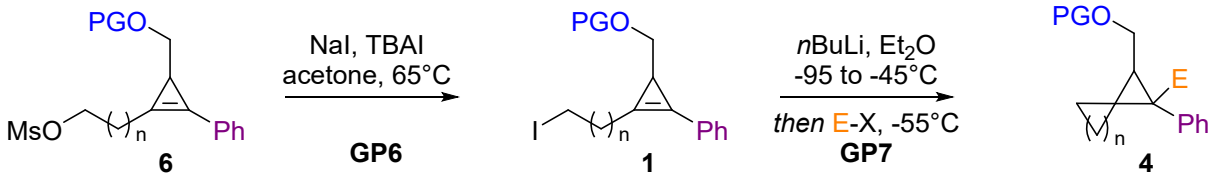
entry	Deviation from above	observation
1	none	≥85% **4a** by crude ^{1}H NMR
2	-95 to -70°C	≥85% **4a** by crude ^{1}H NMR
3	-95 to -20°C	≥85% **4a** by crude ^{1}H NMR
4	-95 to 0°C	Complex mixture, **4a** major
5	THF instead of Et_2O	ratio **4a:5a** ca. 2.4:1
6	*n*hexane instead of Et_2O	**5a** only
7	3.0 eq. *t*BuLi	≥85% **4a** by crude ^{1}H NMR, 80% isolated
8	1.1 eq. *t*BuLi	≥85% **4a** by crude ^{1}H NMR
9	1.1 eq. *t*BuLi, -95°C	≥85% **4a** by crude ^{1}H NMR
10	1.1 eq, *t*BuLi, internal quench with MeOH-d_4	≥85% **4a** by crude ^{1}H NMR, less then 40%D
11	Quench with MeOH-d_4	≥85% **4a** by crude ^{1}H NMR, ca. 20% D
12	1.1 eq. *n*BuLi	≥85% **4a** by crude ^{1}H NMR, 85% isolated
13	1.1 eq. *n*BuLi, quench with MeOH-d_4	≥85% **4a** by crude ^{1}H NMR, 69% isolated, 83%D
14	**1c** (n=4) instead of **1a**	**7c** only
15	**1c** (n=4) instead of **1a**, 1.1 eq. *t*BuLi	**1c**:**5c**:**4c** 1:1:2.8, 40% **5c** isolated
16	**1c** (n=4) instead of **1a,** 1.1 eq. *n*BuLi	≥85% **4c** by crude ^{1}H NMR, 72% isolated
17	**1b** (n=2) instead of **1a**	Complex mixture
18	**1b** (n=2) instead of **1a**, *n*BuLi (1.1 eq.)	Complex mixture containing **4b** and **5b** as major species
19	**1b** (n=2) instead of **1a,** *n*BuLi (1.1 eq.), 30 min at -45°C	75% **4b** by crude ^{1}H NMR, 66% isolated
Standard conditions: Substrate **1a** (1 eq.) in Et_2O (0.08M), *t*BuLi added dropwise at -95°C, allowed to warm gradually to -45°C, then excess MeOH (0.1 mL) was added in one portion.		

Upon dropwise addition of *t*BuLi to the iodide at -95°C, the reaction mixture was allowed to warm gradually to the specified temperature to enable the carbometallation. For substrate **1a**, the cyclisation took place already at -95°C (entry 9) and reaction temperatures up to -20°C were tolerated. Warming the mixture to 0°C before methanol addition led to a less clean reaction profile. Using THF instead of diethyl ether led to full I-Li exchange but incomplete carbometallation, with the reduced product **5** being the major side product. In hexane, no carbometallation was observed. Larger excess of *t*BuLi was well-tolerated, and surprisingly, even 1.1 eq. of *t*BuLi were sufficient for this reaction. Low degrees of deuteration were observed when MeOH-d_4 was used as an electrophile. This observation, together with the efficiency of the reaction with only 1.1 eq. of *t*BuLi, suggest that the tertiary cyclopropyllithium species formed in the carbolithiation is more reactive than *t*BuLi under the reaction conditions (T<-80°C). Consequently, the tertiary cyclopropyllithium reacts with the *tert*-butyl iodide formed in situ, yielding the protonated spirocycle **4a**.



As this side reaction cannot be suppressed, *n*BuLi was tested for the I-Li exchange, even though an equilibrium between linear iodide **1a** and the corresponding linear alkyllithium would be expected for the I-Li exchange with *n*BuLi. Gratifyingly, the intramolecular carbolithiation provides a sufficient driving force for the reaction to proceed, giving similar results as with *t*BuLi. Importantly, a significantly higher degree of deuteration (83%, entry 13) was observed when MeOH-d_4 was used as electrophile. The advantage of *n*BuLi over *t*BuLi was further corroborated by the finding that iodide **1c**, containing one more carbon in the alkyl chain, reacted with excess *t*BuLi in an intermolecular carbolithiation. As expected, the I-Li exchange is faster than the carbolithiation between *t*BuLi and cyclopropene **1c**, but incomplete conversion was observed with 1.1 eq. *t*BuLi. 1.1 eq. *n*BuLi, on the contrary, led to a smooth spirocyclisation, enabling the isolation of spiro[2.5]octane **4c** in 72% yield. The formation of spiro[2.3]hexane **4b** was also efficient with *n*BuLi, although the carbolithiation seemed to require higher temperatures than for spiro[2.4]heptane **4a**. The reaction was allowed to warm to -45°C and stirred additional 30 min at this temperature to achieve full conversion.

General Procedure for the Intramolecular Carbolithiation



GP6: Finkelstein

An oven-dried round bottom flask was charged with the mesylate **6** (1.0 eq.), NaI (4 eq.), TBAI (0.4 eq.) and anhydrous acetone (0.2 M). The reaction mixture was heated to 65°C for 45 min, allowed to cool to room temperature and treated with sat. aq. $Na_2S_2O_3$. The acetone was removed under reduced pressure, and the residue was extracted with DCM (3x). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was filtered over a plug of silica gel (5% to 10% Et_2O in PE) to remove polar side products. The crude iodides 1 were used directly in the subsequent spirocyclization. Spectral data are not reported, as significant decomposition was observed even after few hours in deacidified $CDCl_3$.

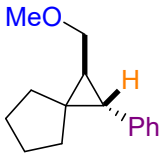
As the iodides decomposed upon column chromatography, the iodides (purity typically 80-95%) were used without further purification. The iodides can be stored overnight under argon in the dark at -20°C, but decompose upon prolonged storage (both neat and in Et_2O solution; solutions were stable at -78°C for at least several days).

GP7: Intramolecular carbolithiation

A flame-dried Schlenk tube was charged with a solution of the crude alkyl iodide **1a-h** (1.0 eq.) in dry Et_2O (0.08 M) under argon and cooled to -95°C (EtOH/liquid nitrogen bath). *n*BuLi (1.1 eq.) was added dropwise and the reaction mixture was allowed to gradually warm to -45°C (typically within 1-1.5 h). The mixture was kept at that temperature (-50 to -40°C) for 30 minutes before the electrophile was added at -55°C. The reaction mixture was stirred for another 10 minutes at -55°C before the cooling bath was removed and Et_2O (10 mL) and brine (5 mL) were added. The aqueous layer was extracted with Et_2O (3x), and the combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The products were purified by column chromatography.

Characterization of Spiro[2.n]alkanes

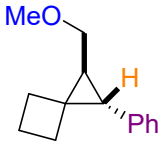
(1*S,2*S**)-1-(Methoxymethyl)-2-phenylspiro[2.4]heptane (4a)**



4a

4a was synthesized from **1a** according to **GP6** and **GP7** by trapping with MeOH. 0.185 mmol scale, colorless liquid, *dr* > 95:5, 29.6 mg, 0.137 mmol, 74% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.11 (m, 1H), 7.11 – 7.07 (m, 2H), 3.63 (dd, *J* = 10.3, 6.1 Hz, 1H), 3.45 – 3.38 (m, 1H), 3.38 (s, 3H), 1.87 (dt, *J* = 11.9, 7.4 Hz, 1H), 1.80 (d, *J* = 5.7 Hz, 1H), 1.77 – 1.67 (m, 1H), 1.69 – 1.47 (m, 5H), 1.41 (ddd, *J* = 13.3, 7.7, 5.7 Hz, 1H), 1.25 (dt, *J* = 14.1, 7.2 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.9, 128.2, 128.1, 125.6, 74.1, 58.5, 35.4, 32.5, 31.1, 28.0, 26.5, 26.1 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{15}H_{21}O^+$ 217.1587; found 217.1568.

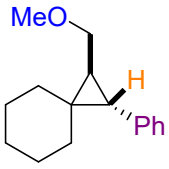
(1*S,2*S**)-1-(Methoxymethyl)-2-phenylspiro[2.3]hexane (4b)**



4b

4b was synthesized from **6b** according to **GP6** and **GP7** by trapping with MeOH. 0.254 mmol scale, colorless liquid, *dr* > 95:5, 27.4 mg, 0.135 mmol, 53% yield over two steps**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.17 – 7.11 (m, 1H), 6.99 – 6.93 (m, 2H), 3.52 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.38 (s, 3H), 3.30 (dd, *J* = 10.2, 8.0 Hz, 1H), 2.31 (ddd, *J* = 9.1, 7.4, 4.5 Hz, 1H), 2.18 – 2.05 (m, 3H), 1.99 – 1.92 (m, 2H), 1.65 (d, *J* = 5.3 Hz, 1H), 1.40 (dt, *J* = 8.0, 5.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.3, 128.2, 127.0, 125.3, 73.7, 58.5, 33.2, 32.7, 29.6, 27.3, 26.6, 17.0 ppm. **HR-ESI-MS**: m/z calcd. for $[M-OMe]^+$ $C_{13}H_{15}^+$ 171.1168; found 171.1159.

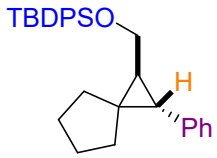
(1*S,2*S**)-1-(Methoxymethyl)-2-phenylspiro[2.5]octane (4c)**



4c

4c was synthesized from **6c** according to **GP6** and **GP7** by trapping with MeOH. 0.293 mmol scale, colorless liquid, *dr* > 95:5, 41.3 mg, 0.179 mmol, 61% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 4H), 7.19 – 7.13 (m, 1H), 3.65 – 3.48 (m, 2H), 3.39 (s, 3H), 1.79 (d, *J* = 5.8 Hz, 1H), 1.72 – 1.50 (m, 4H), 1.48 – 1.40 (m, 2H), 1.35 – 1.14 (m, 4H), 1.12 – 1.05 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.1, 128.9, 127.9, 125.7, 72.4, 58.4, 34.4, 32.6, 32.1, 30.9, 27.9, 26.5, 26.0, 25.0 ppm. **HR-ESI-MS**: m/z calcd. for $[M-OMe]^+$ $C_{15}H_{19}^+$ 199.1481; found 199.1478.

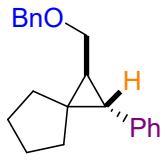
***tert*-Butyldiphenyl(((1*S**,2*S**)-2-phenylspiro[2.4]heptan-1-yl)methoxy)silane (4d)**



4d

4d was synthesized from **6d** according to **GP6** and **GP7** by trapping with MeOH. 0.229 mmol scale, colorless liquid, *dr* 5:1, 80.5 mg, 0.183 mmol, 74% yield over two steps. Resonances of major diastereomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 4H), 7.48 – 7.35 (m, 7H), 7.29 – 7.23 (m, 2H), 7.20 – 7.13 (m, 1H), 7.09 – 7.02 (m, 2H), 3.95 (dd, *J* = 11.0, 5.9 Hz, 1H), 3.69 (dd, *J* = 11.0, 8.1 Hz, 1H), 1.89 (dt, *J* = 12.3, 7.3 Hz, 1H), 1.78 – 1.69 (m, 2H), 1.68 – 1.48 (m, 4H), 1.39 (ddd, *J* = 12.8, 7.5, 5.5 Hz, 1H), 1.31 – 1.23 (m, 2H), 1.08 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.3, 135.8, 135.8, 134.3, 134.2, 129.7, 128.3, 128.3, 128.0, 127.8, 127.7, 127.7, 125.5, 65.5, 35.4, 34.8, 32.2, 31.5, 31.2, 27.0, 26.5, 26.1, 19.4 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{30}H_{27}OSi^+$ 441.2614; found 441.2609.

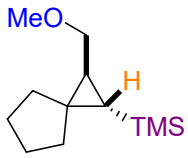
(1*S,2*S**)-1-((Benzyloxy)methyl)-2-phenylspiro[2.4]heptane (4e)**



4e

4e was synthesized from **6e** according to **GP6** and **GP7** by trapping with MeOH. 0.287 mmol scale, colorless liquid, *dr* > 95:5, 62.8 mg, 0.215 mmol, 75% yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 7H), 7.20 – 7.12 (m, 1H), 7.11 – 7.05 (m, 2H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 3.74 (dd, *J* = 10.3, 5.9 Hz, 1H), 3.47 (dd, *J* = 10.3, 8.2 Hz, 1H), 1.93 – 1.81 (m, 1H), 1.79 (d, *J* = 5.6 Hz, 1H), 1.76 – 1.67 (m, 1H), 1.68 – 1.33 (m, 6H), 1.26 (dt, *J* = 13.1, 6.8 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.9, 138.8, 128.7, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 125.6, 72.7, 71.7, 35.5, 35.2, 32.5, 31.1, 28.3, 26.5, 26.0 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{21}H_{25}O^+$ 293.1900; found 293.1898.

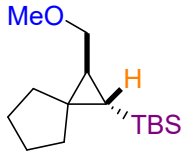
((1*S,2*S**)-2-(Methoxymethyl)spiro[2.4]heptan-1-yl)trimethylsilane (4f)**



4f

4f was synthesized from **6f** according to **GP6** and **GP7** by trapping with MeOH. 0.234 mmol scale, colorless liquid, *dr* > 95:5, contains traces (<1 wt-%) of silicon grease, 47.6 mg, 0.187 mmol, 80% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.49 (dd, *J* = 10.4, 5.5 Hz, 1H), 3.33 (d, *J* = 1.0 Hz, 3H), 3.22 – 3.16 (m, 1H), 1.76 – 1.55 (m, 5H), 1.50 – 1.38 (m, 2H), 1.00 (td, *J* = 7.8, 5.7 Hz, 1H), 0.94 – 0.82 (m, 1H), 0.00 (s, 9H), -0.54 (d, *J* = 7.1 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 75.5, 58.3, 34.4, 32.5, 32.3, 27.4, 26.4, 25.9, 17.2, -0.5 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{12}H_{25}OSi^+$ 213.1675; found 213.1665.

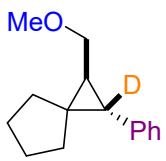
***tert*-Butyl((1*S**,2*S**)-2-(methoxymethyl)spiro[2.4]heptan-1-yl)dimethylsilane (4g)**



4g

4g was synthesized from **6g** according to **GP6** and **GP7** by trapping with MeOH. 0.234 mmol scale, colorless liquid, *dr* > 95:5, 47.6 mg, 0.187 mmol, 80% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.58 (dd, *J* = 10.2, 4.9 Hz, 1H), 3.33 (s, 3H), 3.09 (dd, *J* = 10.2, 9.0 Hz, 1H), 1.78 – 1.57 (m, 6H), 1.47 – 1.39 (m, 2H), 0.97 (ddd, *J* = 9.2, 7.0, 5.0 Hz, 1H), 0.89 (s, 9H), -0.06 (s, 3H), -0.11 (s, 3H), -0.52 (d, *J* = 7.4 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 75.5, 58.4, 34.6, 32.6, 32.1, 27.8, 26.8, 26.4, 25.9, 17.1, 13.3, -5.4, -5.4 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{15}H_{31}OSi^+$ 255.2140; found 255.2139.

(1*S,2*S**)-1-(Methoxymethyl)-2-phenylspiro[2.4]heptane-2-*d* ($4a_D$)**

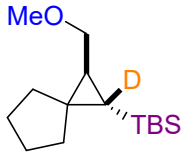


$4a_D$

$4a_D$ was synthesized from **6a** according to **GP6** and **GP7** by trapping with MeOH-d_4. 0.369 mmol scale, colorless liquid, *dr* > 95:5, 83% deuteration, 55.0 mg, 0.254 mmol, 69%

yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.19 – 7.14 (m, 1H), 7.13 – 7.09 (m, 2H), 3.64 (dd, *J* = 10.3, 6.1 Hz, 1H), 3.43 (dd, *J* = 10.3, 8.1 Hz, 1H), 3.40 (s, 3H), 1.89 (dt, *J* = 11.9, 7.4 Hz, 1H), 1.79 – 1.49 (m, 6H), 1.44 (ddd, *J* = 13.4, 7.7, 5.7 Hz, 1H), 1.32 – 1.21 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.8, 128.2, 128.1, 125.6, 74.1, 58.5, 35.4, 35.0 (t, *J* = 23.8 Hz), 32.4, 31.1, 28.0, 26.5, 26.1 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{15}H_{20}OD^+$ 218.1655; found 218.1658.

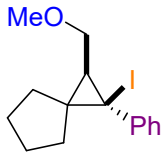
tert-Butyl((1S*,2S*)-2-(methoxymethyl)spiro[2.4]heptan-1-yl-1-d)dimethylsilane ($4g_D$)



$4g_D$

$4g_D$ was synthesized from **6g** according to **GP6** and **GP7** by trapping with MeOH-d_4. 0.234 mmol scale, colorless liquid, *dr* > 95:5, ≥95% deuteration, 45.3 mg, 0.178 mmol, 76% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.57 (dd, *J* = 10.3, 4.9 Hz, 1H), 3.33 (s, 3H), 3.09 (dd, *J* = 10.2, 9.0 Hz, 1H), 1.77 – 1.59 (m, 6H), 1.45 (ddd, *J* = 10.9, 7.3, 3.2 Hz, 2H), 1.00 – 0.92 (m, 1H), 0.89 (s, 9H), -0.06 (s, 3H), -0.12 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 75.4, 58.4, 34.6, 32.5, 32.0, 27.7, 26.8, 26.4, 25.9, 17.1, 12.83 (t, *J* = 20.7 Hz), -5.4, -5.5 ppm. **HR-EI-MS**: m/z calcd. for $[M]^+$ $C_{15}H_{29}DOSi^+$ 255.2123; found 255.2118.

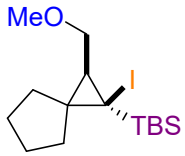
(1R*,2S*)-1-Iodo-2-(methoxymethyl)-1-phenylspiro[2.4]heptane (4h)



4h

4h was synthesized from **6a** according to **GP6** and **GP7** by trapping with a solution of iodine (2.0 eq.) in dry THF (0.5 mL). 0.269 mmol scale, colorless liquid, *dr* > 95:5, contains 14 wt-% H-quenched product (**4a**), 47.2 mg, 0.110 mmol, 44% corrected yield over two steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 2H), 7.20 – 7.16 (m, 1H), 3.59 (dd, *J* = 6.7, 2.7 Hz, 2H), 3.47 (s, 3H), 1.92 – 1.86 (m, 1H), 1.85 – 1.62 (m, 6H), 1.51 (ddd, *J* = 13.4, 7.4, 6.1 Hz, 1H), 1.18 (dd, *J* = 7.3, 5.7 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.9, 129.3, 128.5, 127.4, 77.1, 76.9, 59.0, 37.1, 35.8, 34.3, 31.5, 31.3, 26.50, 26.46 ppm. . **HR-EI-MS**: m/z calcd. for $[M]^+$ $C_{15}H_{19}OI^+$ 342.0475; found 342.0489.

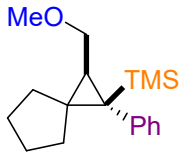
***tert*-Butyl((1R*,2S*)-1-iodo-2-(methoxymethyl)spiro[2.4]heptan-1-yl)dimethylsilane (4i)**



4i

4i was synthesized from **6g** according to **GP6** and **GP7** by trapping with iodine (2.5 eq.) in dry THF (1 mL). 0.234 mmol scale, colorless liquid, *dr* > 95:5, 64.8 mg, 90 wt-% purity (contains 10 wt-% H-quenched product **4g**), 0.153 mmol, 66% corrected yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.50 (dd, *J* = 10.3, 5.8 Hz, 1H), 3.43 (dd, *J* = 10.3, 7.0 Hz, 1H), 3.37 (s, 3H), 1.97 – 1.84 (m, 1H), 1.81 – 1.56 (m, 6H), 1.55 – 1.45 (m, 1H), 1.05 (s, 9H), 0.76 (dd, *J* = 7.0, 5.9 Hz, 1H), 0.21 (s, 3H), 0.02 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 77.2, 58.8, 38.0, 35.8, 35.4, 30.3, 29.0, 27.4, 25.9, 22.3, 18.5, -1.2, -3.6 ppm. **HR-EI-MS**: m/z calcd. for $[M-C_4H_9]^+$ $C_{11}H_{20}OSiI^+$ 323.0323; found 323.0317 and for $[M-MeOH-I]^+$ $C_{14}H_{15}OSi^+$ 221.1720; found 221.1720.

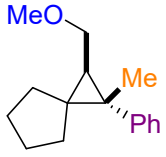
((1R*,2S*)-2-(Methoxymethyl)-1-phenylspiro[2.4]heptan-1-yl)trimethylsilane (4j)



4j

4j was synthesized from **6a** according to **GP6** and **GP7** by trapping with TMSCl (2.0 eq.). 0.234 mmol scale, colorless liquid, *dr* > 95:5, ≥83 wt-% purity, 27.6 mg, 0.079 mmol, 30% corrected yield over two steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 – 7.13 (m, 4H), 7.12 – 7.07 (m, 1H), 3.65 – 3.60 (m, 2H), 3.42 (s, 3H), 1.86 – 1.50 (m, 8H), 1.47 – 1.40 (m, 1H), -0.02 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.5, 131.1, 127.9, 124.9, 71.5, 58.4, 37.7, 37.3, 36.0, 30.2, 28.9, 26.3, 24.9, 1.0 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{18}H_{28}OSiNa^+$ 311.1807; found 311.1814.

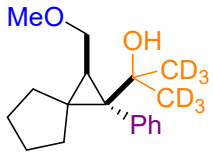
(1S*,2R*)-2-(Methoxymethyl)-1-methyl-1-phenylspiro[2.4]heptane (4k)



4k

4k was synthesized from **6a** according to **GP6** and **GP7** by trapping with MeI (3.0 eq.). 0.302 mmol scale, colorless liquid, *dr* > 95:5, 40.1 mg, 0.174 mmol, 57% yield over two steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.25 – 7.22 (m, 2H), 7.19 – 7.14 (m, 1H), 3.56 (dd, *J* = 7.2, 1.5 Hz, 2H), 3.42 (s, 3H), 1.77 – 1.66 (m, 3H), 1.60 – 1.48 (m, 3H), 1.40 (t, *J* = 7.2 Hz, 1H), 1.33 – 1.26 (m, 1H), 1.28 (s, 3H), 1.10 – 1.02 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.8, 128.9, 128.3, 125.8, 70.7, 58.6, 35.1, 32.1, 30.3, 29.8, 26.7, 26.3, 26.1, 19.2 ppm. **HR-EI-MS**: m/z calcd. for $[M]^+$ $C_{16}H_{22}O^+$ 230.1665; found 230.1664.

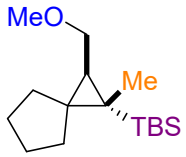
2-((1R*,2R*)-2-(Methoxymethyl)-1-phenylspiro[2.4]heptan-1-yl)propan-1,1,1,3,3,3-d6-2-ol (4l)



4l

4l was synthesized from **6a** according to **GP6** and **GP7** by trapping with acetone-d_6. 0.350 mmol scale, colorless liquid, *dr* > 95:5, 37.6 mg, 0.134 mmol, 38% yield over two steps (major side product: H/D trapping, 33% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 1H), 7.30 – 7.13 (m, 4H), 3.91 (dd, *J* = 10.6, 8.1 Hz, 1H), 3.82 (dd, *J* = 10.5, 8.1 Hz, 1H), 3.45 (s, 3H), 2.63 (br s, 1H, OH), 2.10 (ddd, *J* = 13.5, 8.8, 7.3 Hz, 1H), 2.00 – 1.87 (m, 1H), 1.82 – 1.55 (m, 5H), 1.52 – 1.39 (m, 1H), 1.33 (t, *J* = 8.1 Hz, 1H), 0.70 (ddd, *J* = 11.6, 7.3, 3.8 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.0, 132.0, 131.4, 127.9, 126.7, 126.0, 73.0, 70.7, 58.3, 46.1, 38.7, 36.3, 34.9, 26.6, 25.9, 24.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{18}H_{20}O_2D_6Na^+$ 303.2202; found 303.2203.

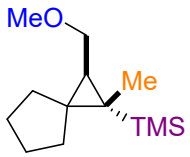
***tert*-Butyl((1S*,2S*)-2-(methoxymethyl)-1-methylspiro[2.4]heptan-1-yl)dimethylsilane (4m)**



4m

4m was synthesized from **6g** according to **GP6** and **GP7** by trapping with MeI (3.0 eq.). 0.250 mmol scale, colorless liquid, *dr* > 95:5, 42.5 mg, 87 wt-% purity (contains 13 wt-% H-quenched product **4g**), 0.138 mmol, 55% corrected yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.52 – 3.42 (m, 1H), 3.41 – 3.34 (m, 1H), 3.33 (s, 3H), 1.80 – 1.38 (m, 8H), 0.97 (s, 3H), 0.95 (s, 9H), 0.95 – 0.84 (m, 1H), 0.01 (s, 3H), -0.09 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 70.0, 58.5, 36.6, 34.5, 30.0, 28.4, 27.3, 26.8, 26.5, 25.8, 18.2, 14.1, -4.5, -4.7 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{16}H_{32}OSiNa^+$ 291.2120; found 291.2127.

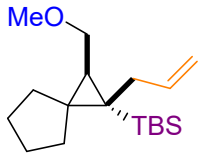
((1S*,2S*)-2-(Methoxymethyl)-1-methylspiro[2.4]heptan-1-yl)trimethylsilane (4n)



4n

4n was synthesized from **6f** according to **GP6** and **GP7** by trapping with MeI (3.0 eq.). 0.295 mmol scale, colorless liquid, *dr* > 95:5, 47.1 mg, 81 wt-% purity (contains 19 wt-% H-quenched product **4f**), 0.167 mmol, 56% corrected yield over two steps**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.39 (dd, *J* = 6.9, 4.6 Hz, 2H), 3.32 (s, 3H), 1.72 – 1.55 (m, 5H), 1.54 – 1.38 (m, 3H), 0.91 (s, 3H), 0.89 (td, *J* = 6.9, 0.0 Hz, 1H), 0.00 (d, *J* = 2.5 Hz, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 70.2, 58.4, 35.8, 29.4, 26.9, 26.5, 25.9, 13.7, 12.5, -1.4 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{13}H_{27}OSi^+$ 227.1831; found 227.1821.

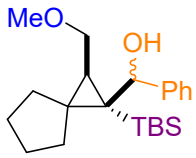
((1S*,2S*)-1-Allyl-2-(methoxymethyl)spiro[2.4]heptan-1-yl)(tert-butyl)dimethylsilane (4o)



4o

4o was synthesized from **6g** according to **GP6** and **GP7** by trapping with allyl bromide (3.0 eq.). 0.250 mmol scale, colorless liquid, *dr* 7:3, 45.1 mg, 0.153 mmol, 61% yield over two steps. Resonances of the major diastereomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.85 – 5.68 (m, 1H), 4.97 – 4.90 (m, 1H), 4.88 (dq, *J* = 17.2, 1.7 Hz, 1H), 3.49 (dd, *J* = 10.2, 6.1 Hz, 1H), 3.43 – 3.36 (m, 1H), 3.33 (s, 3H), 2.53 (ddt, *J* = 15.9, 6.0, 1.7 Hz, 1H), 2.15 – 2.00 (m, 1H), 1.85 (dt, *J* = 12.4, 8.1 Hz, 1H), 1.68 – 1.47 (m, 7H), 1.47 – 1.35 (m, 1H), 0.96 (s, 9H), 0.93 (d, *J* = 8.5 Hz, 1H), 0.07 (s, 3H), 0.02 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 139.6, 115.0, 71.4, 58.4, 38.9, 36.2, 34.4, 30.1, 28.9, 28.3, 26.8, 25.0, 19.0, 18.5, -0.3, -1.1 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{19}H_{34}OSi^+$ 295.2452; found 295.2451.

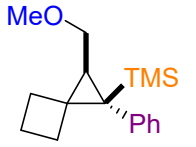
((1S*,2S*)-1-*(tert*-Butyldimethylsilyl)-2-(methoxymethyl)spiro[2.4]heptan-1-yl)(phenyl)methanol (4p)



4p

4p was synthesized from **6g** according to **GP6** and **GP7** by trapping with benzaldehyde (2.0 eq.). To facilitate the purification, excess benzaldehyde was reduced with $NaBH_4$ (2.0 eq.) prior to the aqueous workup. 0.250 mmol scale, colorless liquid, *dr* 3.5:1, 57.2 mg, 0.159 mmol, 64% yield over two steps. Major diastereomer isolated for spectroscopic analysis. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (dt, *J* = 8.2, 1.2 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.25 – 7.18 (m, 1H), 4.87 (d, *J* = 3.0 Hz, 1H), 3.65 (dd, *J* = 10.0, 6.9 Hz, 1H), 3.51 (dd, *J* = 10.0, 7.4 Hz, 1H), 3.36 (s, 3H), 2.11 (d, *J* = 3.8 Hz, 1H), 2.06 – 1.96 (m, 1H), 1.73 – 1.61 (m, 5H), 1.61 – 1.57 (m, 1H), 1.53 (t, *J* = 7.1 Hz, 1H), 0.97 (s, 9H), -0.23 (s, 3H), -0.29 (s, 3H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.9, 127.8, 126.6, 126.6, 74.7, 71.4, 58.8, 37.0, 35.4, 32.9, 28.8, 28.1, 26.9, 25.9, 25.7, 19.0, -0.7, -1.5 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{22}H_{36}O_2SiNa^+$ 383.2377; found 383.2372.

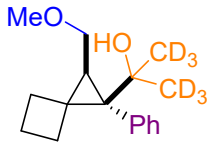
((1R*,2S*)-2-(Methoxymethyl)-1-phenylspiro[2.3]hexan-1-yl)trimethylsilane (4q)



4q

4q was synthesized from **6b** according to **GP6** and **GP7** by trapping with TMSCl (3.0 eq.). 0.190 mmol scale, colorless liquid, *dr* >95:5, 26.4 mg, 83.6 wt-% purity (contains 6.4 wt-% TMSOMe and 10 wt-% TMS_2O), 0.081 mmol, 42% corrected yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.26 – 7.05 (m, 5H), 3.61 (dd, *J* = 7.5, 2.8 Hz, 2H), 3.45 (s, 3H), 2.48 – 2.34 (m, 2H), 2.16 – 2.03 (m, 2H), 2.06 – 1.94 (m, 1H), 1.62 – 1.49 (m, 1H), 1.42 (t, *J* = 7.6 Hz, 1H), -0.03 (s, 9H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 144.4, 131.1, 127.6, 125.0, 71.4, 58.4, 36.5, 34.7, 30.8, 29.6, 27.3, 17.9, 0.3 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{17}H_{26}OSiNa^+$ 297.1645; found 297.1581.

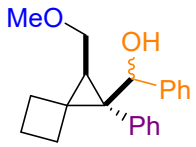
2-((1R*,2R*)-2-(Methoxymethyl)-1-phenylspiro[2.3]hexan-1-yl)propan-1,1,1,3,3,3-d6-2-ol (4r)



4r

4r was synthesized from **6b** according to **GP6** and **GP7** by trapping with acetone-d_6. 0.289 mmol scale, colorless liquid, *dr* > 95:5, 29.1 mg, 0.109 mmol, 41% yield over two steps. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.28 – 7.21 (m, 2H), 7.20 – 7.14 (m, 1H), 3.98 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.89 (dd, *J* = 10.5, 7.1 Hz, 1H), 3.47 (s, 3H), 2.69 – 2.58 (m, 1H), 2.37 (dt, *J* = 11.6, 8.8 Hz, 1H), 2.19 (ddd, *J* = 11.7, 8.0, 3.8 Hz, 1H), 2.09 (br s, 1H, OH), 2.07 – 2.00 (m, 1H), 1.94 (dddd, *J* = 17.1, 10.8, 8.8, 4.2 Hz, 1H), 1.45 – 1.35 (m, 1H), 1.33 (t, *J* = 7.6 Hz, 1H); ^{2}H NMR (77 MHz, $CDCl_3$) δ 1.02 (s, 3D), 0.80 (s, 3D); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 132.2, 127.5, 126.2, 73.2, 70.3, 58.3, 44.5, 34.1, 33.5, 32.1, 26.2, 18.0 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{17}H_{17}D_6O^+$ 249.2126; found 249.2128.

((1R*,2R)*-2-(Methoxymethyl)-1-phenylspiro[2.3]hexan-1-yl)(phenyl)methanol (4s)

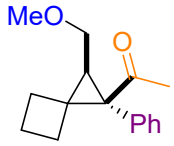


4s

4s was synthesized from **6b** according to **GP6** and **GP7** by trapping with benzaldehyde (3.0 eq.). 0.190 mmol scale, colorless liquid, *dr* 1:1:0:0, 33.2 mg, 0.108 mmol, 57% yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.23 – 7.06 (m, 13H), 7.04 – 6.98 (m, 2H), 6.85 – 6.80 (m, 4H), 4.75 (s, 1H), 4.56 (br s, 2H, OH), 4.38 (s, 1H), 4.09 (dd, *J* = 10.5, 5.6 Hz, 1H), 3.83 (dd, *J* = 10.0, 5.7 Hz, 1H), 3.64 (dd, *J* = 8.9, 7.6 Hz, 1H), 3.61 – 3.55 (m, 1H), 3.54 (s, 3H), 3.46 (s, 3H), 2.77 – 2.50 (m, 2H), 2.39 – 2.26 (m, 2H), 2.26 – 1.97 (m, 6H), 1.81 – 1.71 (m, 1H), 1.70 – 1.59 (m, 1H), 1.53 (dd, *J* = 11.4, 5.5 Hz, 1H), 1.38 (dd, *J* = 8.7, 5.7 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 142.7, 141.6, 138.6, 138.5, 132.6, 132.3, 127.7, 127.6, 127.3, 127.0, 126.9, 126.8, 126.7, 126.6,

126.3, 74.7, 73.8, 71.2, 70.4, 58.9, 58.7, 44.2, 41.6, 34.6, 33.3, 33.2, 32.9, 30.1, 29.3, 25.9, 24.3, 18.2, 17.3 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{21}H_{24}O_2Na^+$ 331.1669; found 331.1683.

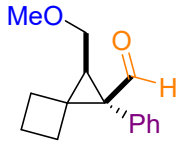
1-((1R*,2R*)-2-(Methoxymethyl)-1-phenylspiro[2.3]hexan-1-yl)ethan-1-one (4t)



4t

4t was synthesized from **6b** according to **GP6** and **GP7** by trapping with AcCl (5.0 eq.). 0.185 mmol scale, colorless liquid, *dr* > 95:5, 20.1 mg, 0.082 mmol, 44% yield over two steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.30 – 7.27 (m, 1H), 3.74 (dd, *J* = 10.4, 5.9 Hz, 1H), 3.49 (dd, *J* = 10.4, 8.4 Hz, 1H), 3.35 (s, 3H), 2.64 – 2.54 (m, 1H)p, 2.28 – 2.20 (m, 1H), 2.15 – 2.07 (m, 1H), 2.03 – 1.93 (m, 2H), 1.91 (s, 3H), 1.49 (tdd, *J* = 9.1, 4.7, 2.8 Hz, 1H), 0.95 – 0.86 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 206.9, 139.7, 130.9, 128.8, 127.3, 67.5, 58.8, 46.7, 39.7, 39.3, 31.9, 30.0, 25.8, 17.0 ppm. **HR-ESI-MS**: m/z calcd. for $[M+K]^+$ $C_{16}H_{20}O_2K^+$ 283.1100; found 283.1098.

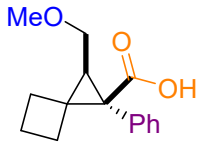
(1R*,2R*)-2-(Methoxymethyl)-1-phenylspiro[2.3]hexane-1-carbaldehyde (4u)



4u

4u was synthesized from **6b** according to **GP6** and **GP7** by trapping with DMF (6.0 eq.). 0.190 mmol scale, colorless liquid, *dr* > 95:5, 27.0 mg, 0.117 mmol, 62% yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.42 – 7.34 (m, 2H), 7.34 – 7.26 (m, 3H), 3.88 (dd, *J* = 10.5, 6.9 Hz, 1H), 3.70 (dd, *J* = 10.5, 7.6 Hz, 1H), 3.39 (s, 3H), 2.51 – 2.32 (m, 2H), 2.22 (t, *J* = 7.3 Hz, 1H), 2.12 – 1.91 (m, 3H), 1.75 – 1.67 (m, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 200.7, 136.8, 130.5, 128.8, 127.6, 66.9, 58.8, 47.7, 42.5, 39.0, 29.2, 25.0, 17.2 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{15}H_{18}O_2Na^+$ 253.1199; found 253.1202.

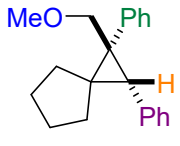
(1R*,2R*)-2-(Methoxymethyl)-1-phenylspiro[2.3]hexane-1-carboxylic acid (4v)



4v

4v was synthesized from **6b** according to **GP6** and **GP7** by trapping with CO_2. 0.190 mmol scale, colorless crystals, *dr* > 95:5, 19.8 mg, 0.080 mmol, 42% yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 – 7.19 (m, 5H), 3.78 (dd, *J* = 10.5, 6.9 Hz, 1H), 3.72 (dd, *J* = 10.5, 7.1 Hz, 1H), 3.40 (s, 3H), 2.55 – 2.41 (m, 1H), 2.31 – 2.10 (m, 2H), 2.06 – 1.88 (m, 3H), 1.57 (dtd, *J* = 10.8, 7.8, 7.3, 3.5 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.9, 137.6, 130.8, 128.4, 127.4, 68.1, 58.8, 39.3, 39.2, 37.0, 29.2, 25.6, 16.4 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{15}H_{18}O_3Na^+$ 269.1148; found 269.1155.

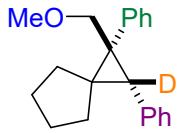
(1S*,2R*)-1-(Methoxymethyl)-1,2-diphenylspiro[2.4]heptane (4w)



4w

4w was synthesized from **6h** according to **GP6** and **GP7** by trapping with MeOH. 0.232 mmol scale, colorless liquid, *dr* > 95:5, 51.5 mg, 0.176 mmol, 76% yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 3H), 7.10 (qd, *J* = 2.6, 1.3 Hz, 3H), 7.06 – 7.00 (m, 2H), 6.65 – 6.60 (m, 2H), 3.70 (d, *J* = 9.8 Hz, 1H), 3.52 (d, *J* = 9.8 Hz, 1H), 3.21 (s, 3H), 2.31 – 2.17 (m, 1H), 2.23 (s, 1H), 1.94 – 1.57 (m, 6H), 1.36 (ddd, *J* = 12.6, 9.0, 7.4 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.8, 137.7, 132.5, 130.0, 127.7, 127.2, 126.5, 125.0, 81.9, 59.1, 40.6, 40.1, 38.9, 34.7, 29.2, 27.1, 26.7 ppm. **HR-ESI-MS**: m/z calcd. for $[M+H]^+$ $C_{21}H_{25}O^+$ 293.1900; found 293.1895.

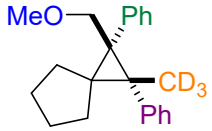
(1S*,2R*)-1-(Methoxymethyl)-1,2-diphenylspiro[2.4]heptane-2-*d* ($4w_D$)



$4w_D$

$4w_D$ was synthesized from **6h** according to **GP6** and **GP7** by trapping with MeOH-d_4. 0.232 mmol scale, colorless liquid, *dr* > 95:5, >95% deuteration, 54.7 mg, 0.186 mmol, 80% yield over two steps. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.16 (m, 3H), 7.17 – 6.96 (m, 5H), 6.69 – 6.55 (m, 2H), 3.69 (d, *J* = 9.8 Hz, 1H), 3.51 (d, *J* = 9.8 Hz, 1H), 3.21 (s, 3H), 2.33 – 2.16 (m, 1H), 1.93 – 1.53 (m, 5H), 1.35 (ddd, *J* = 12.5, 8.9, 7.2 Hz, 1H); **^{13}C NMR** (75 MHz, $CDCl_3$) δ 138.7, 137.7, 132.5, 129.9, 127.7, 127.2, 126.5, 125.0, 81.8, 59.1, 40.0, 38.8, 34.6, 29.2, 27.1, 26.7 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{21}H_{23}DONa^+$ 316.1788; found 316.1785.

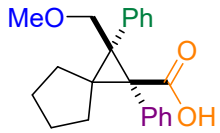
(1R*,2R*)-1-(Methoxymethyl)-2-(methyl-*d*3)-1,2-diphenylspiro[2.4]heptane (4x)



4x

4x was synthesized from **6h** according to **GP6** and **GP7** by trapping with CD_3I. 0.232 mmol scale, colorless liquid, *dr* > 95:5, 40.2 mg, 96 wt-% purity (contains 4 wt-% pentane), 0.130 mmol, 54% corrected yield over two steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 8H), 7.27 – 7.22 (m, 2H), 3.32 (d, *J* = 9.6 Hz, 1H), 3.12 (d, *J* = 9.5 Hz, 1H), 3.03 (s, 3H), 1.92 – 1.84 (m, 1H), 1.84 – 1.77 (m, 1H), 1.78 – 1.62 (m, 5H), 1.61 – 1.49 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.2, 140.4, 132.1, 130.2, 128.6, 127.9, 126.1, 126.0, 79.1, 59.0, 39.3, 38.5, 36.9, 30.2, 29.3, 26.9 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{22}H_{23}D_3ONa^+$ 332.2070; found 332.2195.

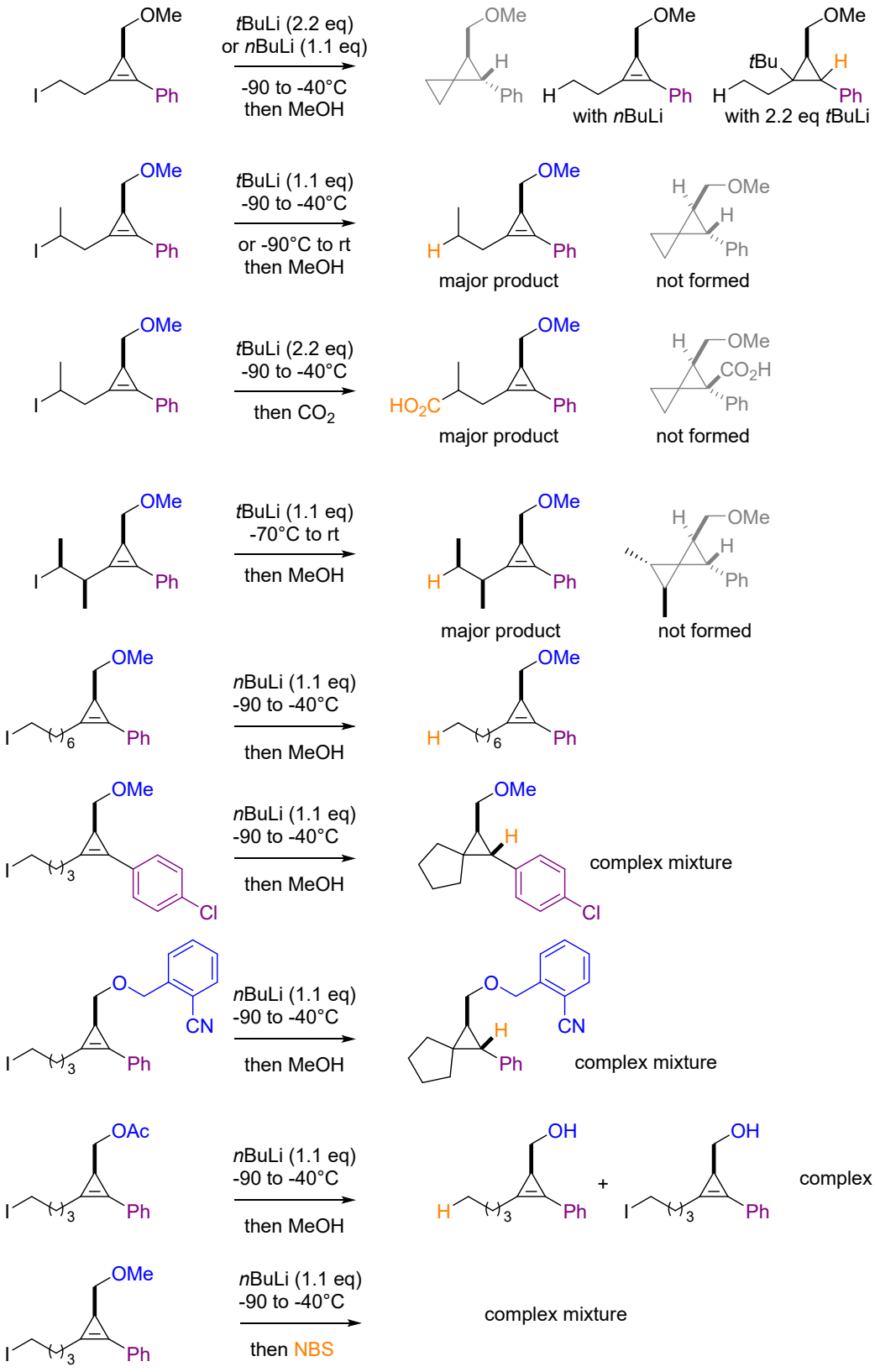
(1S*,2R*)-2-(Methoxymethyl)-1,2-diphenylspiro[2.4]heptane-1-carboxylic acid (4y)



4y

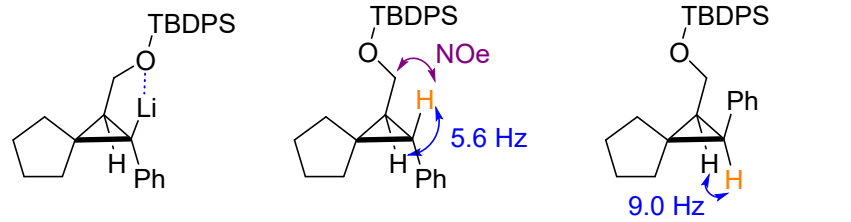
4y was synthesized from **6h** according to **GP6** and **GP7** by trapping with CO_2. 0.232 mmol scale, colorless liquid, *dr* > 95:5, 61.3 mg, 96 wt-% purity (contains 4 wt-% pentanoic acid), 0.174 mmol, 75% corrected yield over two steps. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 5H), 7.15 (s, 5H), 3.92 (d, *J* = 10.2 Hz, 1H), 3.70 (d, *J* = 10.2 Hz, 1H), 3.25 (s, 3H), 2.29 (dt, *J* = 12.8, 6.2 Hz, 1H), 2.01 (dt, *J* = 13.0, 7.7 Hz, 1H), 1.96 – 1.73 (m, 5H), 1.67 – 1.54 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.8, 137.9, 135.6, 131.5, 130.9, 127.9, 127.6, 127.0, 126.6, 78.9, 59.3, 47.4, 42.8, 40.8, 31.0, 30.9, 25.8, 25.7 ppm. **HR-ESI-MS**: m/z calcd. for $[M+Na]^+$ $C_{22}H_{24}O_3Na^+$ 359.1618; found 359.1606.

Unsuccessful Substrates



Stereochemical Assignment of Compounds 4d and 4l

For compound **4d**, both diastereomers were formed in the spirocyclisation. NMR analysis of the coupling constants revealed the expected *syn*-diastereomer (formed by directing effect of the silyl ether) to be the major diastereomer. The coupling constants of all other proton-quenched spirocycles in this study agree with being the *syn*-diastereomer and the stereochemistry was thus assigned by analogy.



syn-intermediate

4d major diastereomer via *syn*-carbolithiation

4d' minor diastereomer via *anti*-carbolithiation

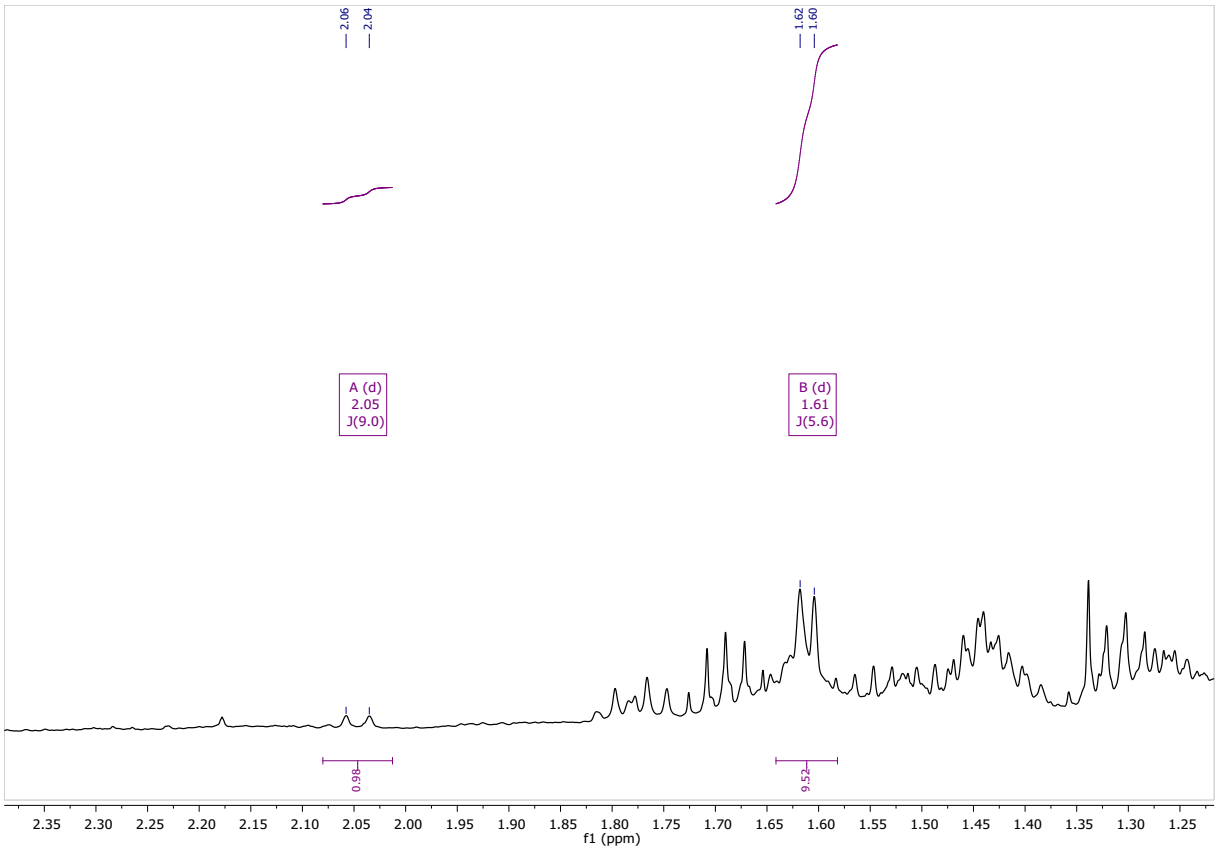
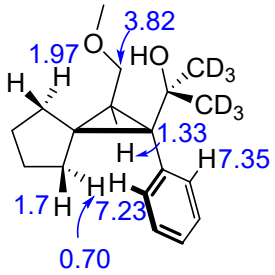
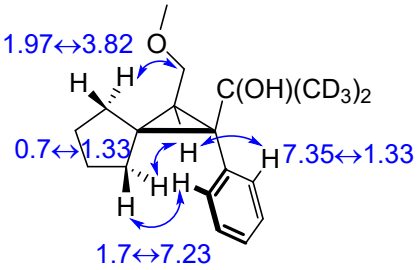


*Figure S1. Excerpt from the crude ^{1}H-NMR spectrum of compound **4d** containing both diastereomers.*

For compound **4l**, the *syn*-carbolithiation with respect to the carbinol was confirmed by Noe analysis.

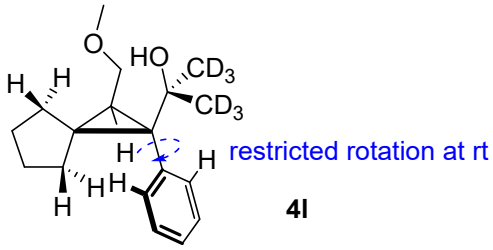


assignment of relevant resonances in ppm



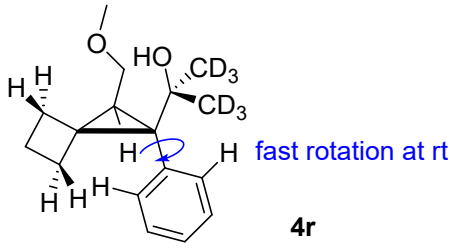
observed NOes confirming *syn*-diastereomer

Comparing compounds **4l** and **4r** it is striking that the rotation around the C(cyclopropane)-C(Ph) bond is restricted at ambient temperature in $CDCl_3$ for **4l** but not for **4r**. The reason is likely the angle compression of the cyclobutene fragment reducing steric congestion around the highly substituted cyclopropane unit.



4l

^{13}C resonances of Ph:
145.0, 132.0, 131.4, 127.9, 126.7, 126.0 ppm



4r

^{13}C resonances of Ph:
143.4, 132.2, 127.5, 126.2 ppm

SC-XRD Structure Report for Compound 4v

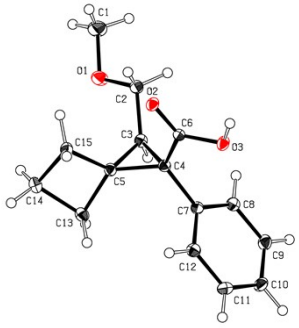


*Figure S2. ORTEP representation of the solid-state structure of compound **4v** (C = black, O = red) shown with 50 % probability displacement ellipsoids.*

A colourless, block-shaped crystal of $C_{15}H_{18}O_3$ coated with perfluorinated ether and fixed on top of a Kapton micro sampler was used for X-ray crystallographic analysis. The X-ray intensity data were collected at 100(2) K on a Bruker D8 VENTURE three-angle diffractometer with a TXS rotating anode with MoK_α radiation (λ=0.71073 Å) using APEX4.[11] The diffractometer was equipped with a Helios optic monochromator, a Bruker PHOTON III detector, and an Oxford Cryostreamlow temperature device.

A matrix scan was used to determine the initial lattice parameters. All data were integrated with the Bruker SAINT V8.40B software package using a narrow-frame algorithm and the reflections were corrected for Lorentz and polarisation effects, scan speed, and background.[12] The integration of the data using a monoclinic unit cell yielded a total of 69964 reflections within a 2θ range [°] of 4.96 to 53.01 (0.80 Å), of which 2726 were independent. Data were corrected for absorption effects including odd and even ordered spherical harmonics by the multi-scan method (SADABS 2016/2).[13] Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure.

The structure was solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ using SHELXL in conjunction with SHELXLE.[14-16] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and a C–H distance of 0.98 Å. Non-methyl hydrogen atoms were refined using a riding model with methylene, aromatic, and other C–H distances of 0.99 Å, 0.95 Å, and 1.00 Å, respectively, and U_{iso} values constrained to 1.2 times the U_{eq} of their pivot atoms.

Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.[17] Supplementary crystallographic data reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2476391) and can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[18]

Table S2. Crystal data and structure refinement for compound 4v.

CCDC number	2476391
Empirical formula	$C_{15}H_{18}O_3$
Formula weight	246.29
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	10.7981(8)
b [Å]	7.4662(5)
c [Å]	16.4344(12)
α [°]	90
β [°]	93.101(3)
γ [°]	90
Volume [Å^3]	1323.01(16)
Z	4
ρ_{calc} [gcm^{-3}]	1.237
μ [mm^{-1}]	0.085
F(000)	528
Crystal size [mm^3]	0.040×0.089×0.098
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.96 to 53.01 (0.80 Å)
Index ranges	−13 ≤ h ≤ 13 −9 ≤ k ≤ 9 −20 ≤ l ≤ 20
Reflections collected	69964
Independent reflections	2726 R_{int} = 0.0755 R_{sigma} = 0.0213
Completeness to θ = 25.242°	99.9
Data / Restraints / Parameters	2726 / 0 / 166
Goodness-of-fit on F^2	1.065
Final *R* indexes [*I*≥2σ(*I*)]	R_1 = 0.0351 wR_2 = 0.0905
Final *R* indexes [all data]	R_1 = 0.0448 wR_2 = 0.0971
Largest peak/hole [eÅ^{-3}]	0.28/−0.19

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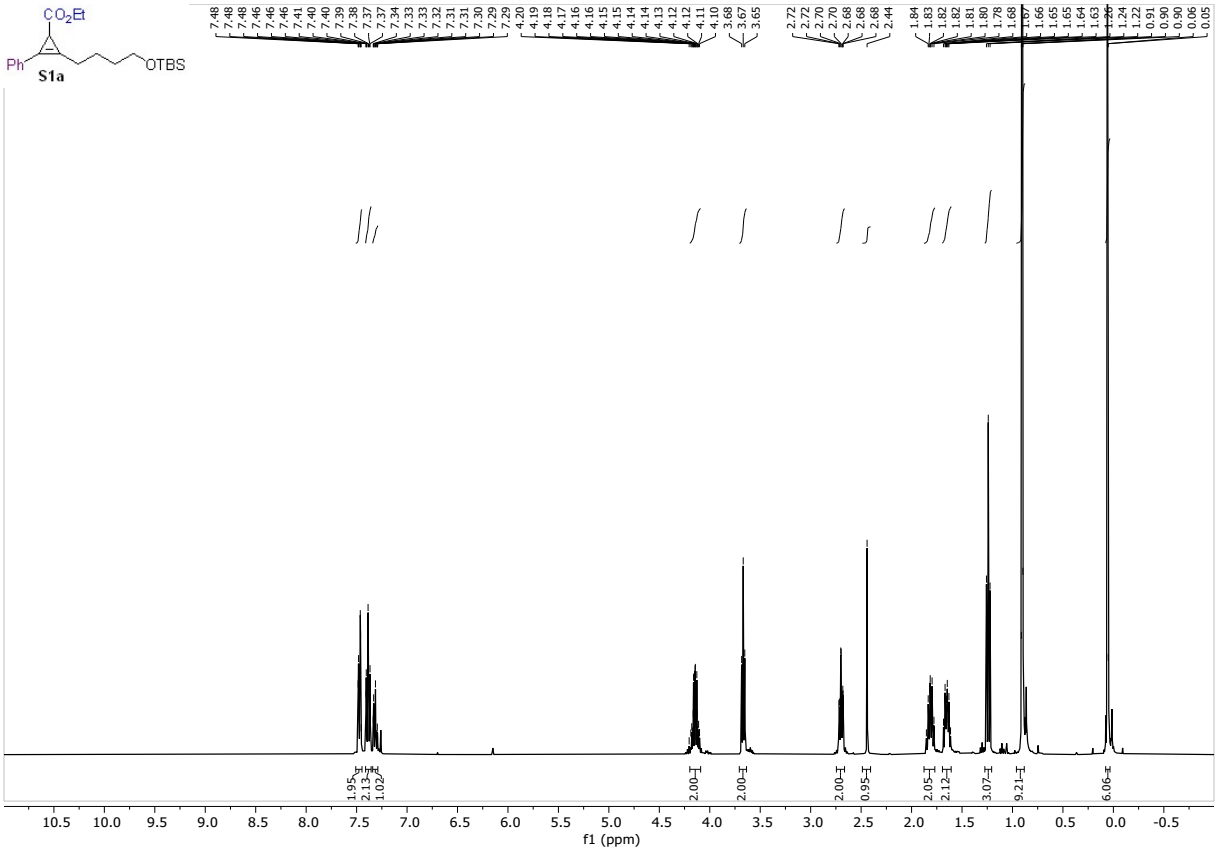
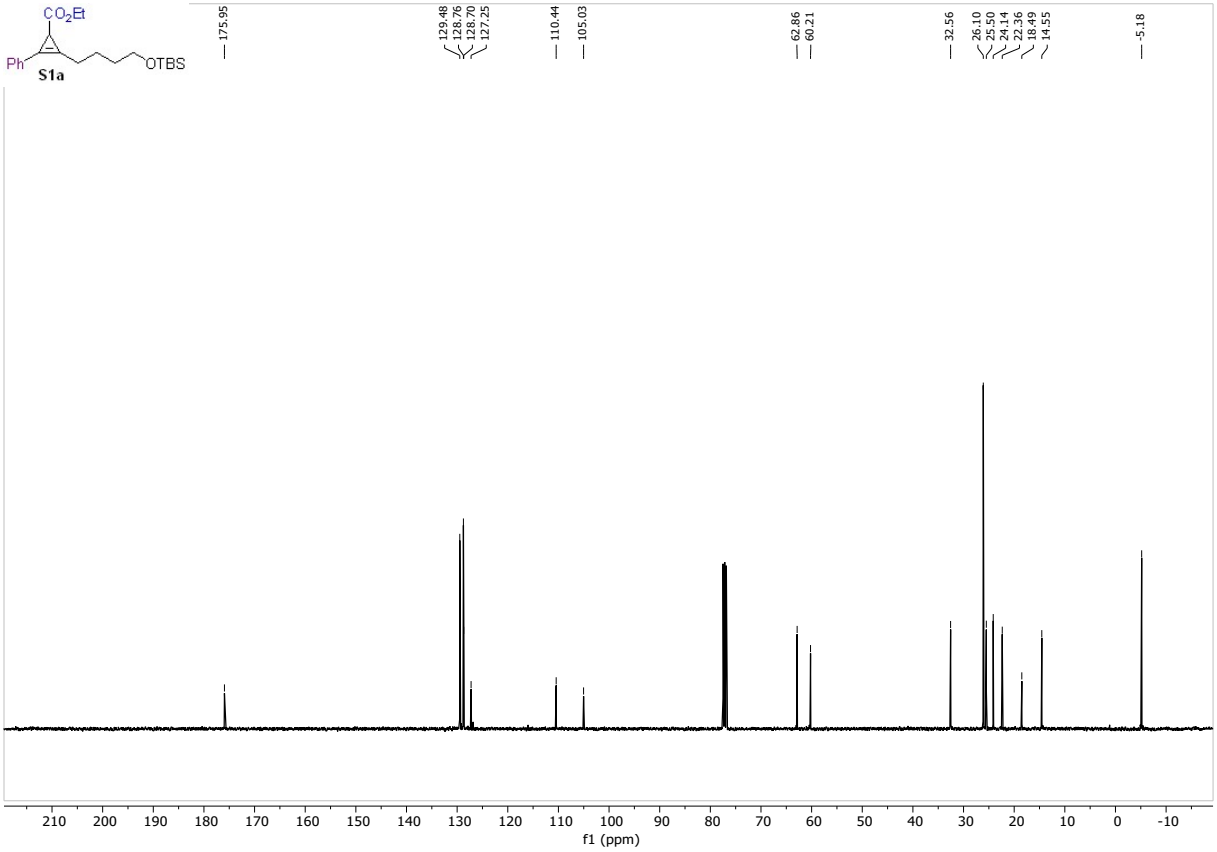
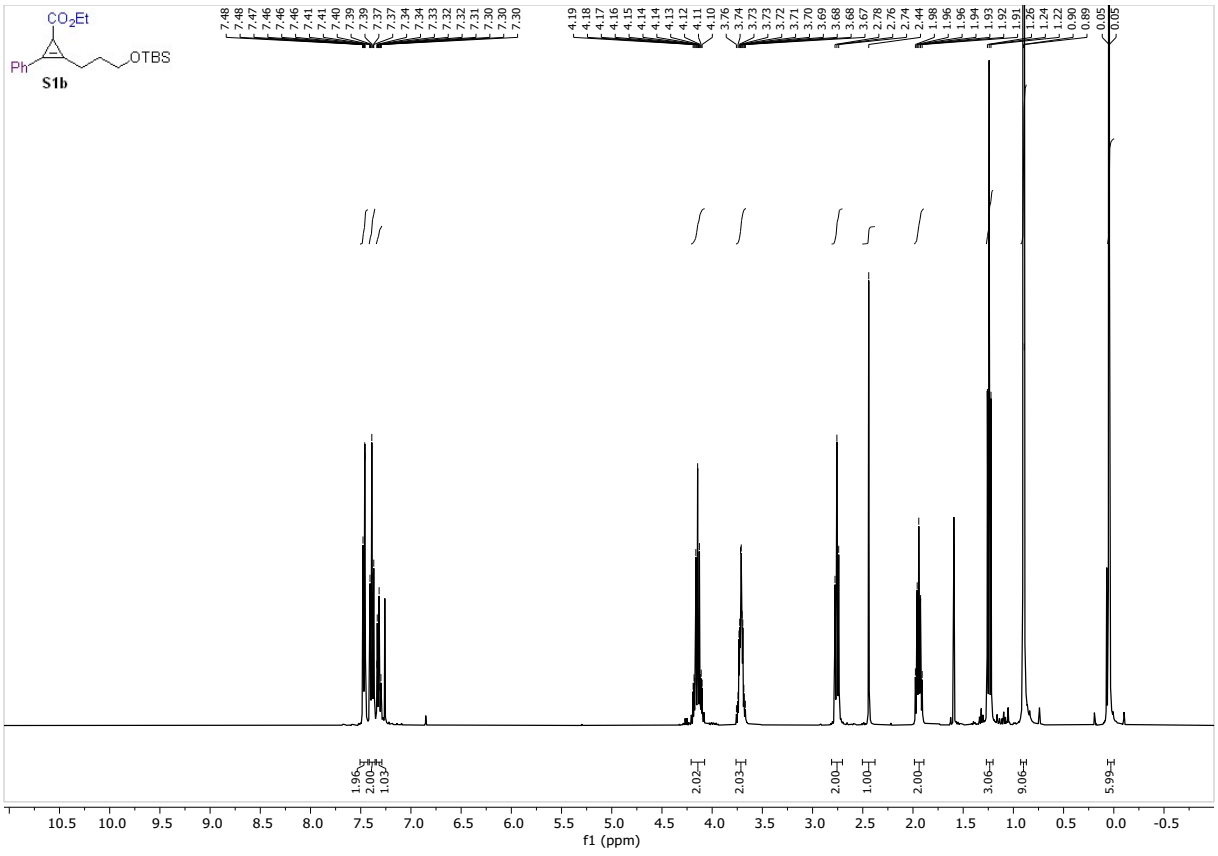
NMR Spectra of New Compounds



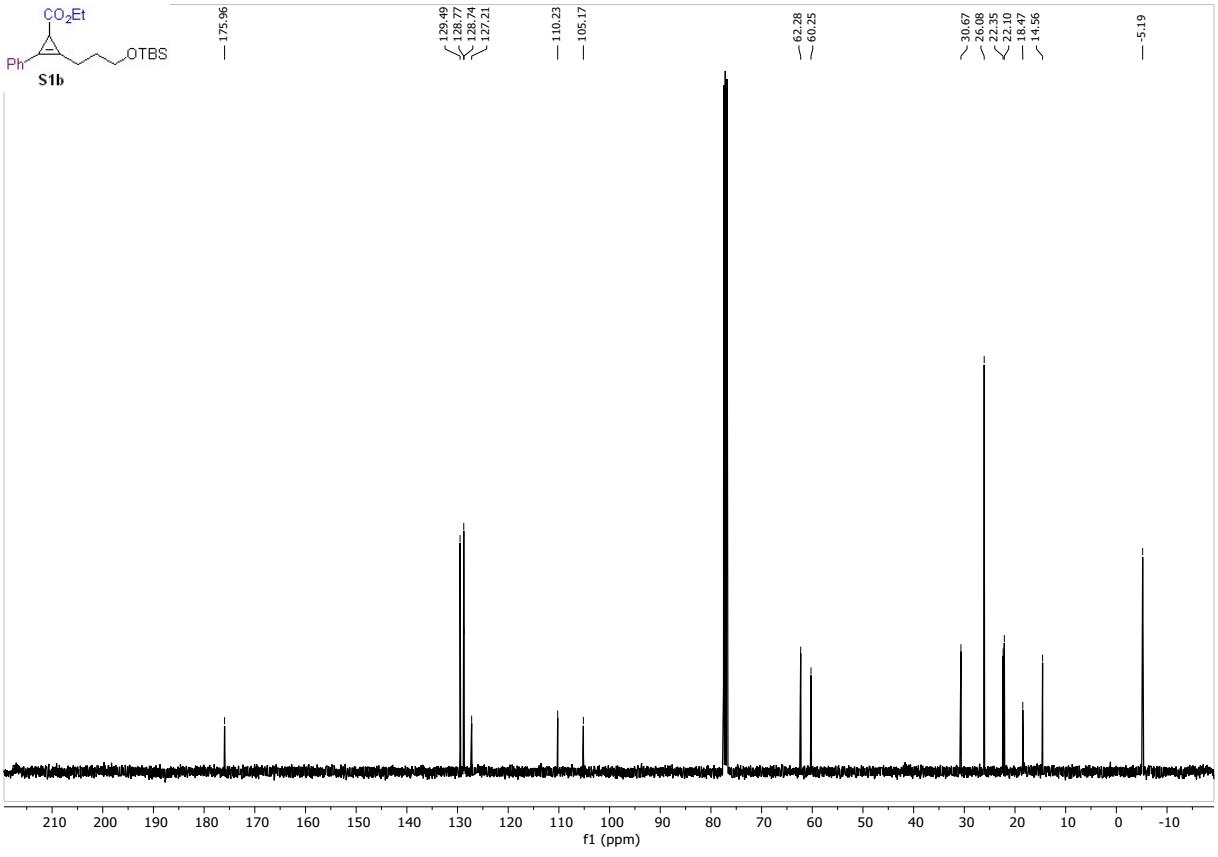
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S1a**.



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S1a**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S1b**.



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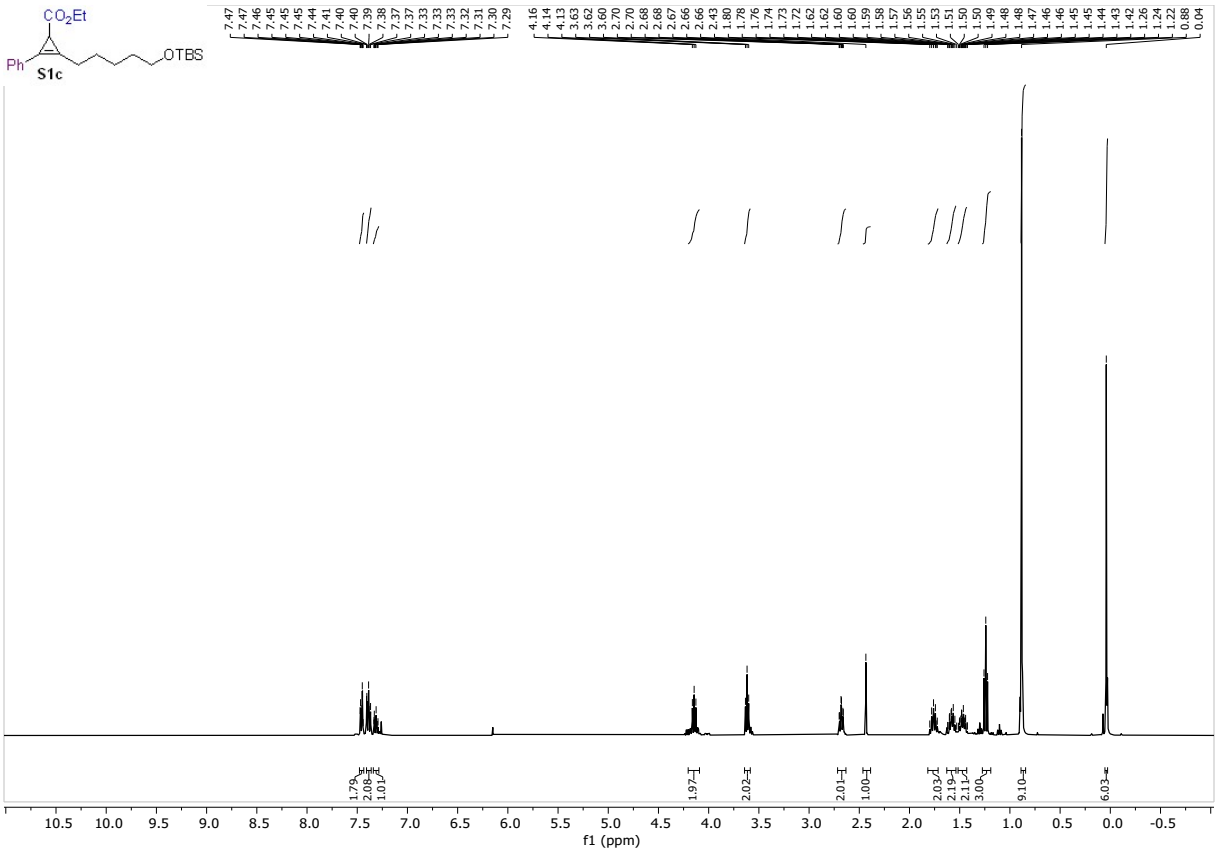
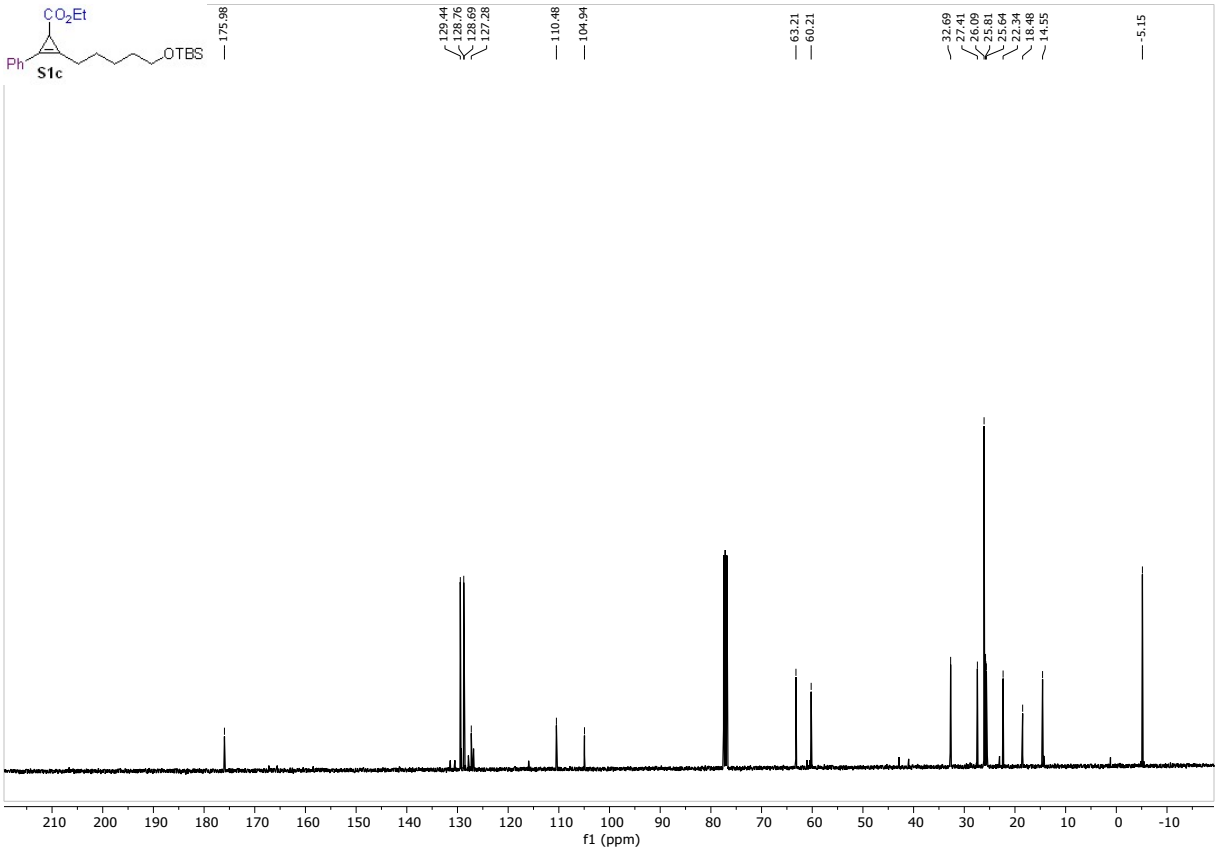
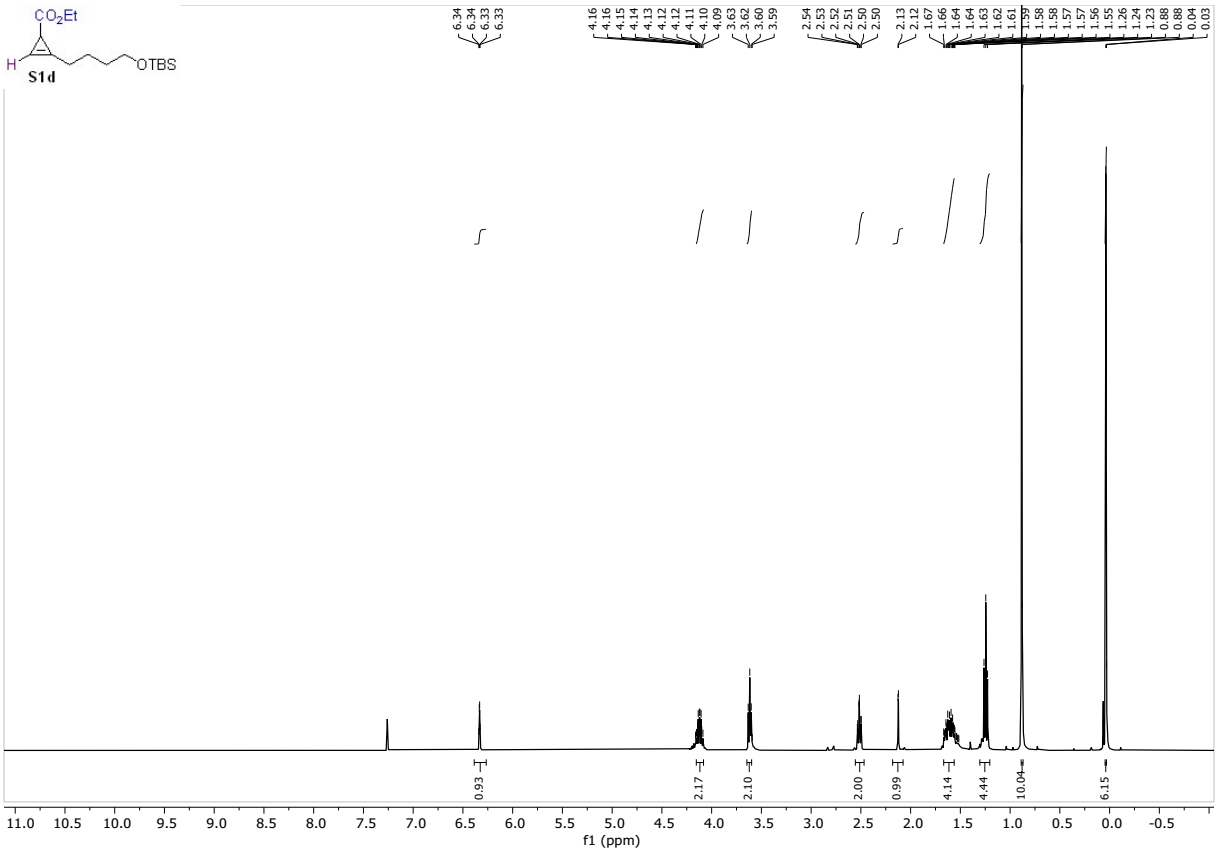


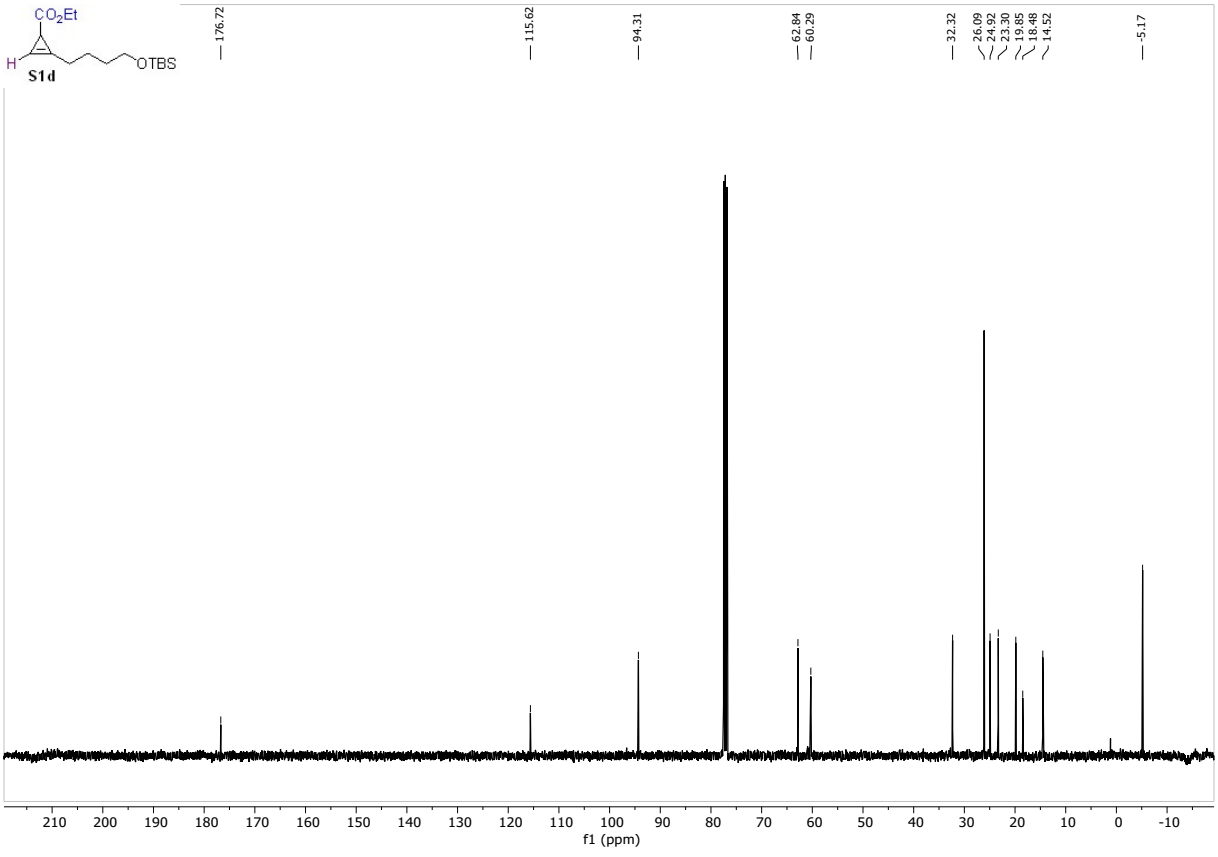
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S1c**.



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S1c**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S1d**.



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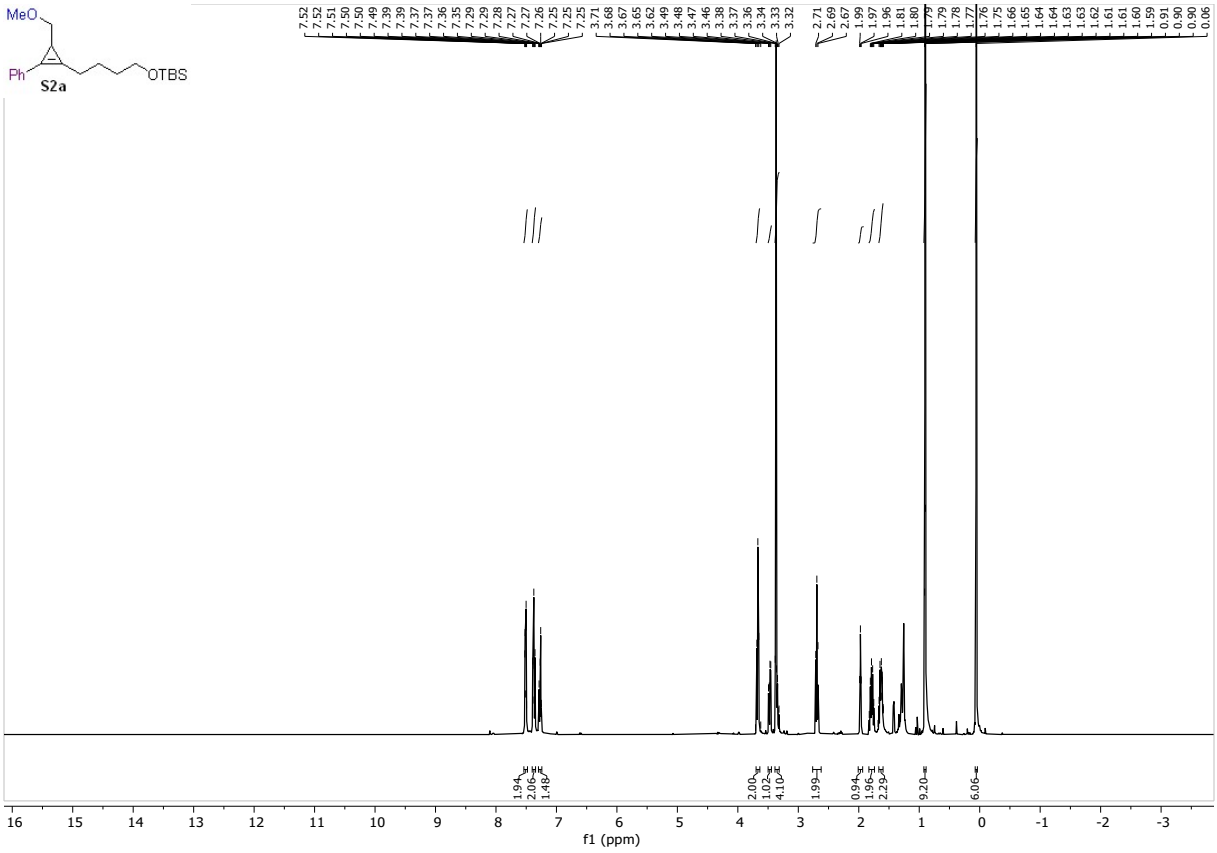
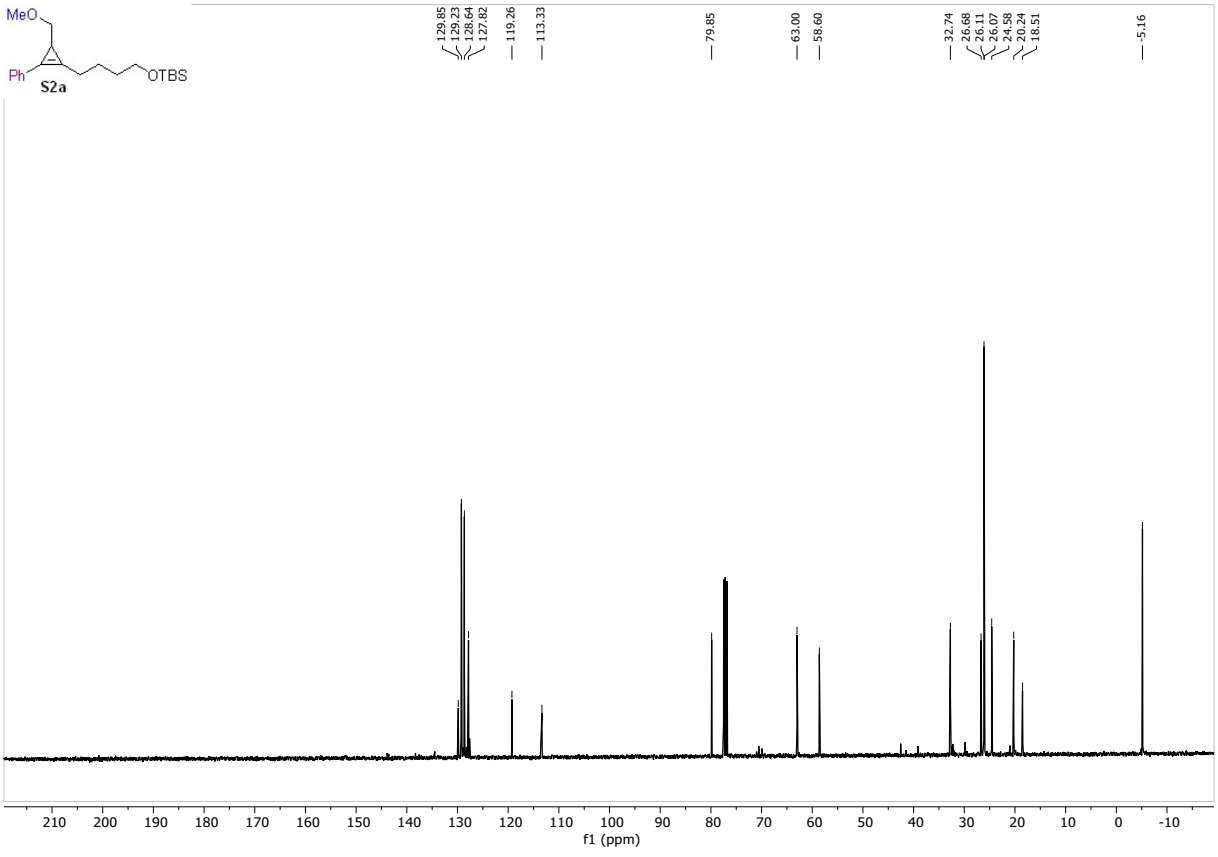
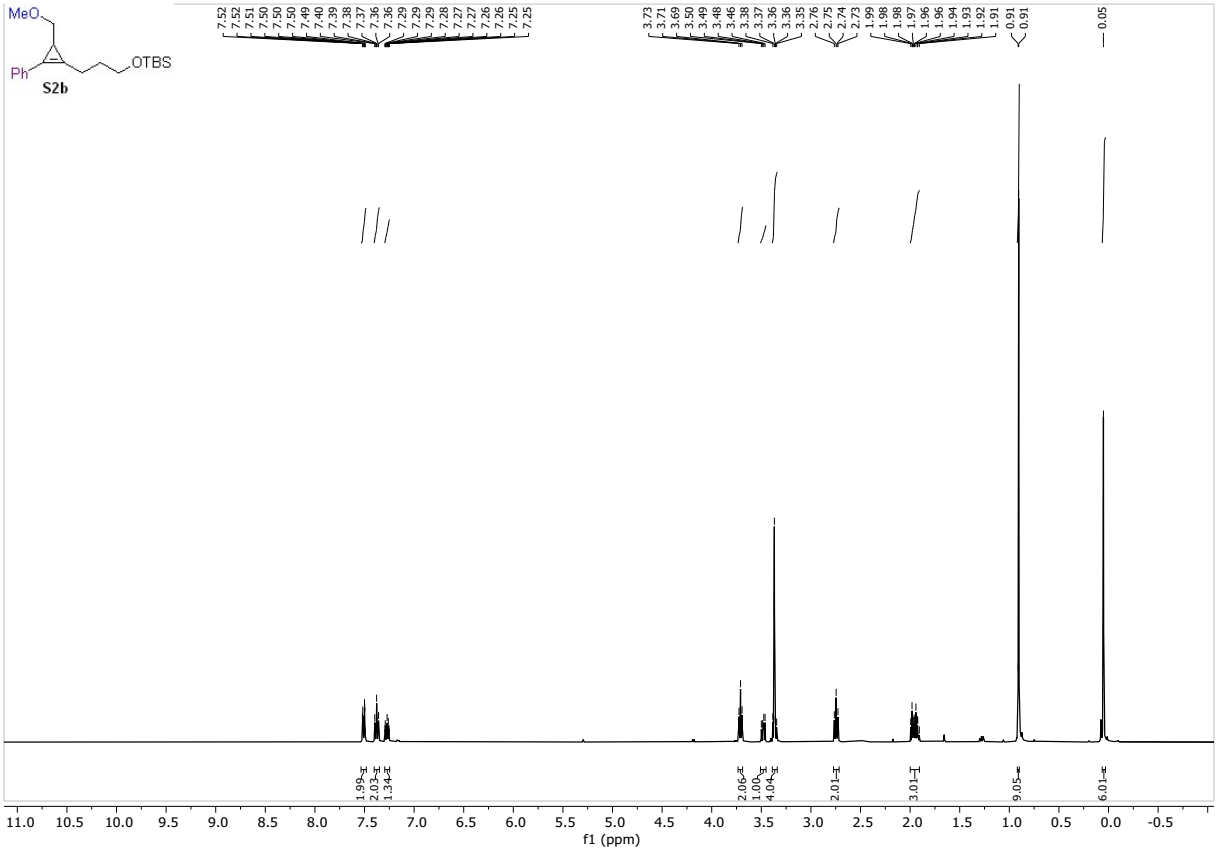


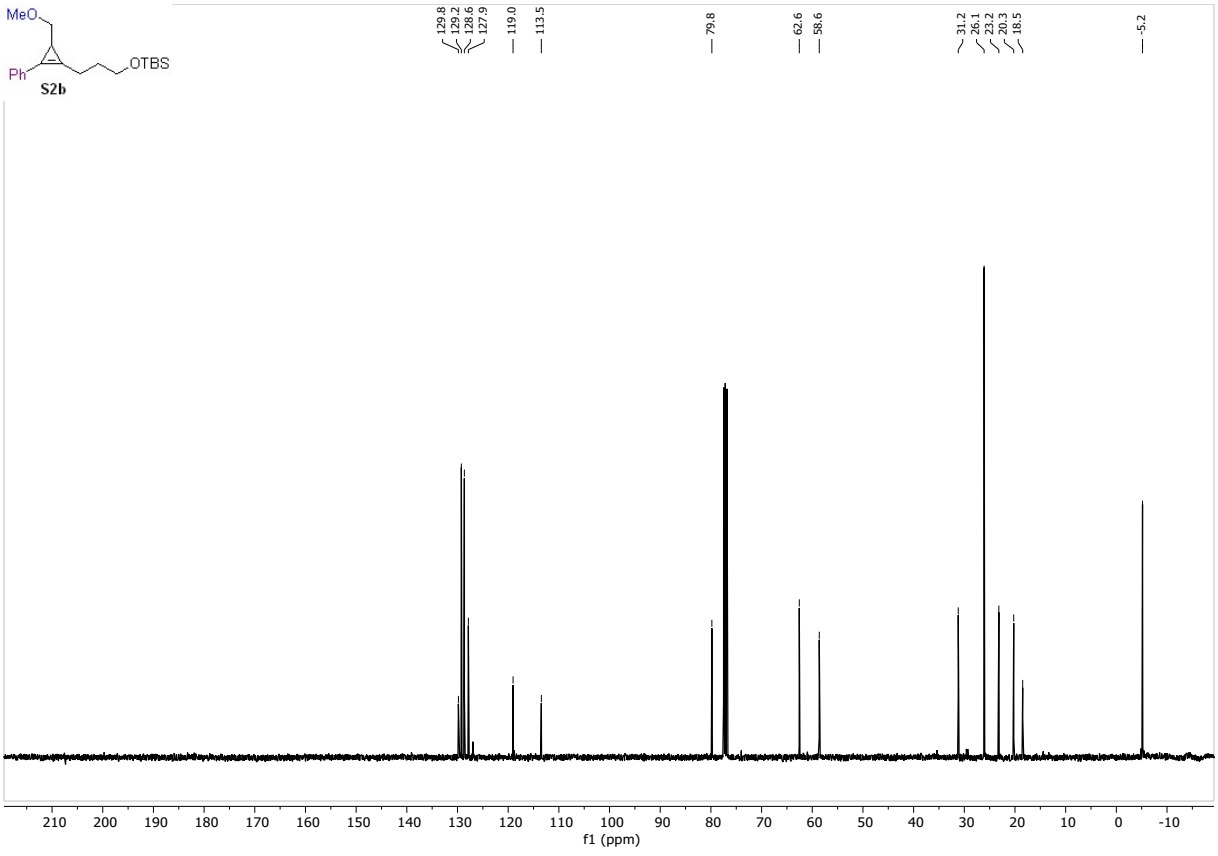
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S2a**.



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S2a**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S2b**.



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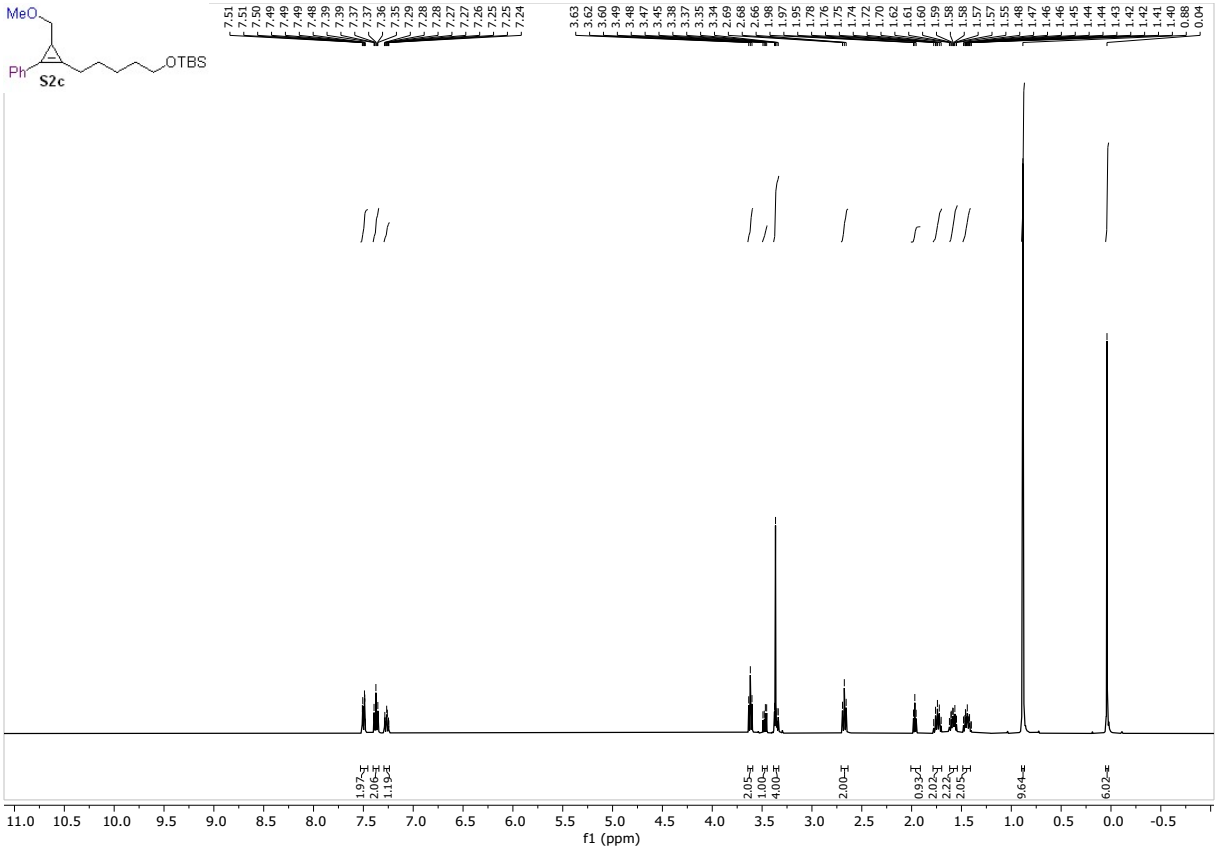
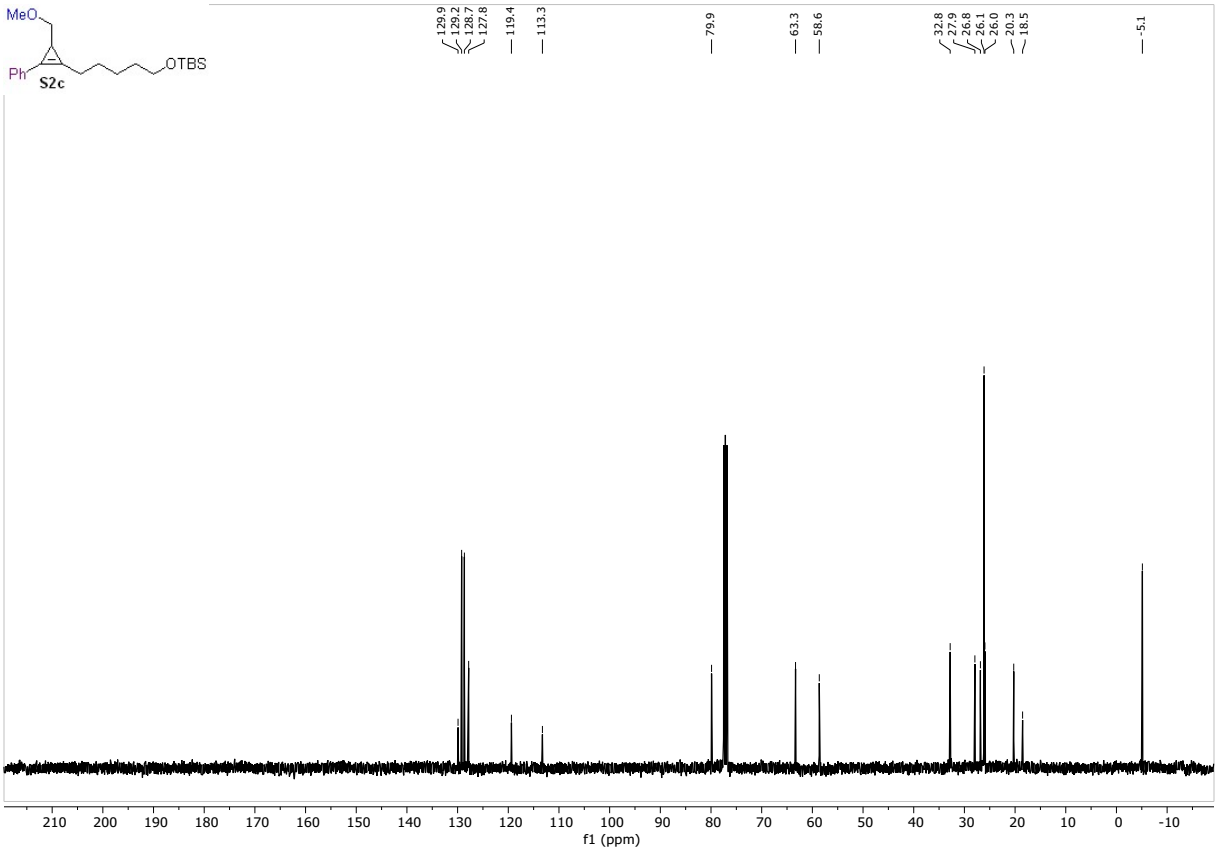
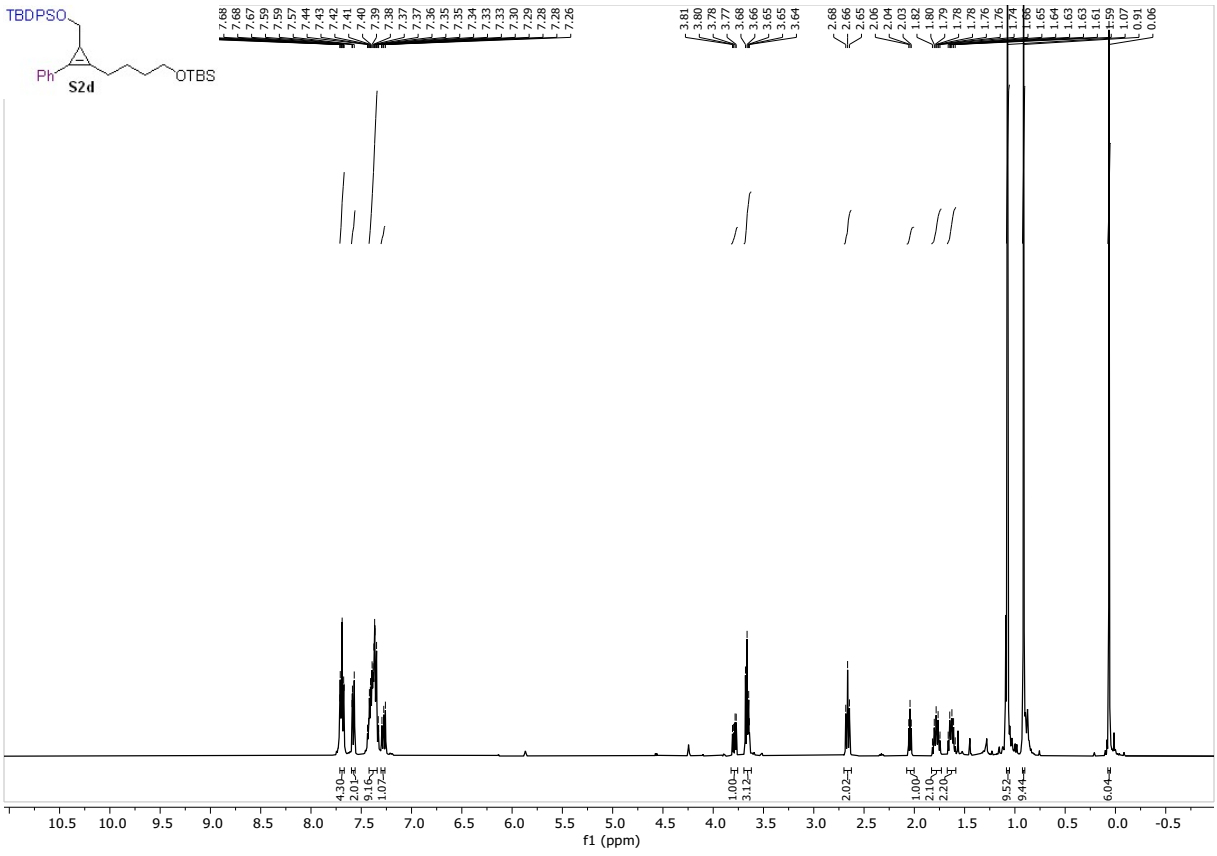


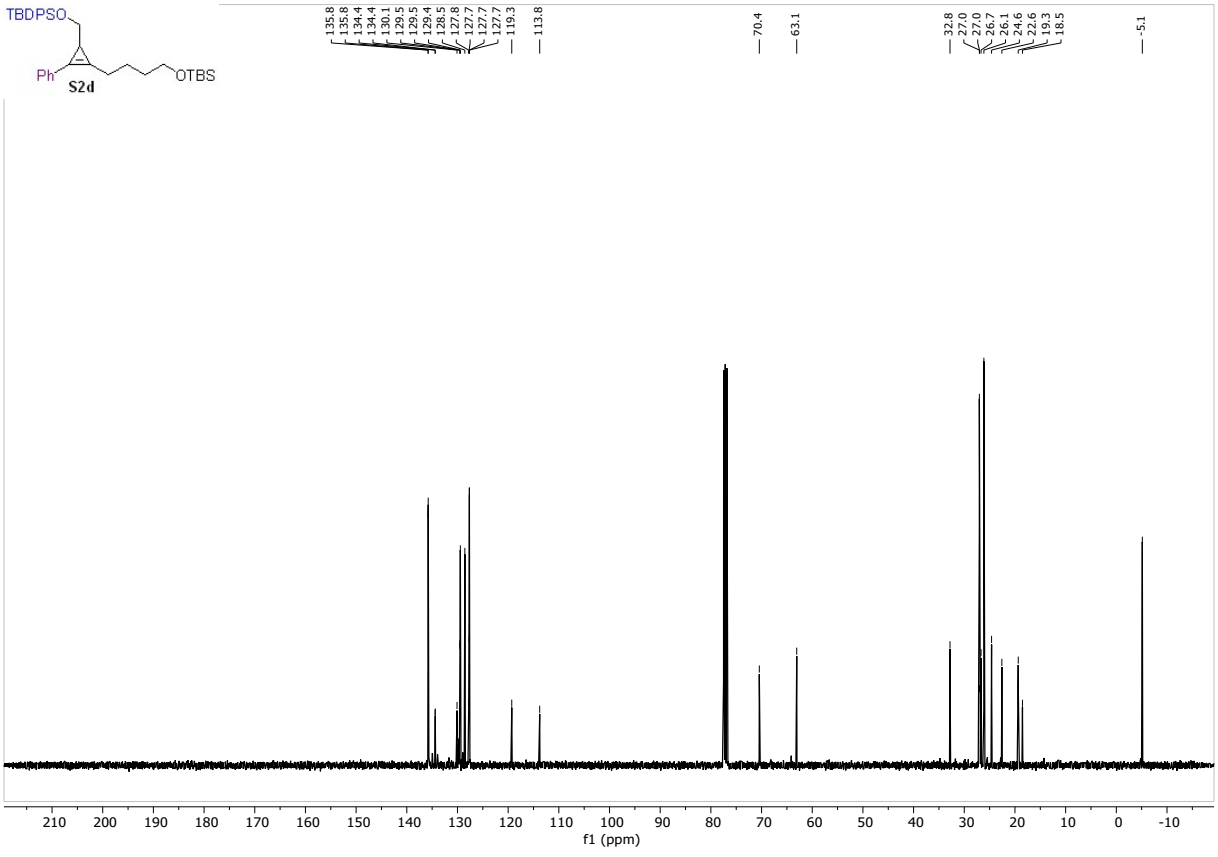
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S2c**.



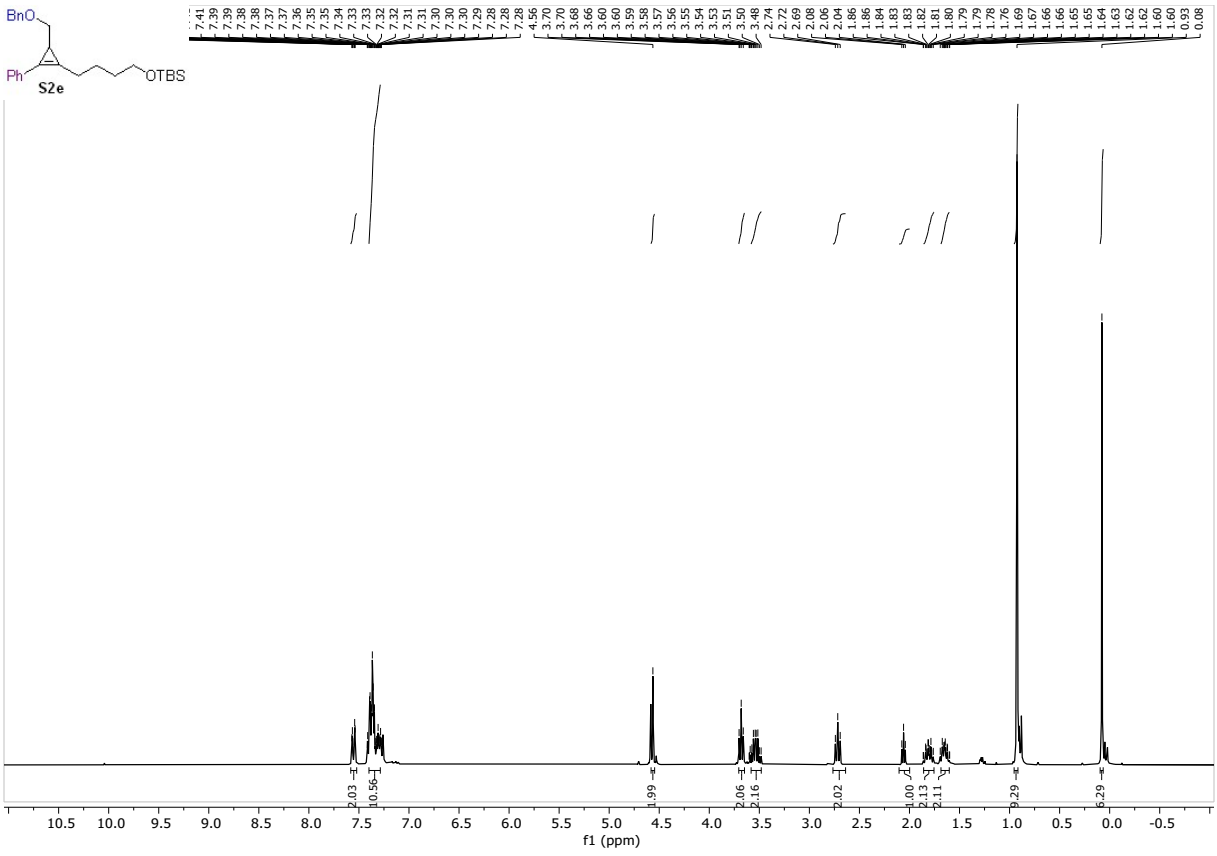
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S2c**.



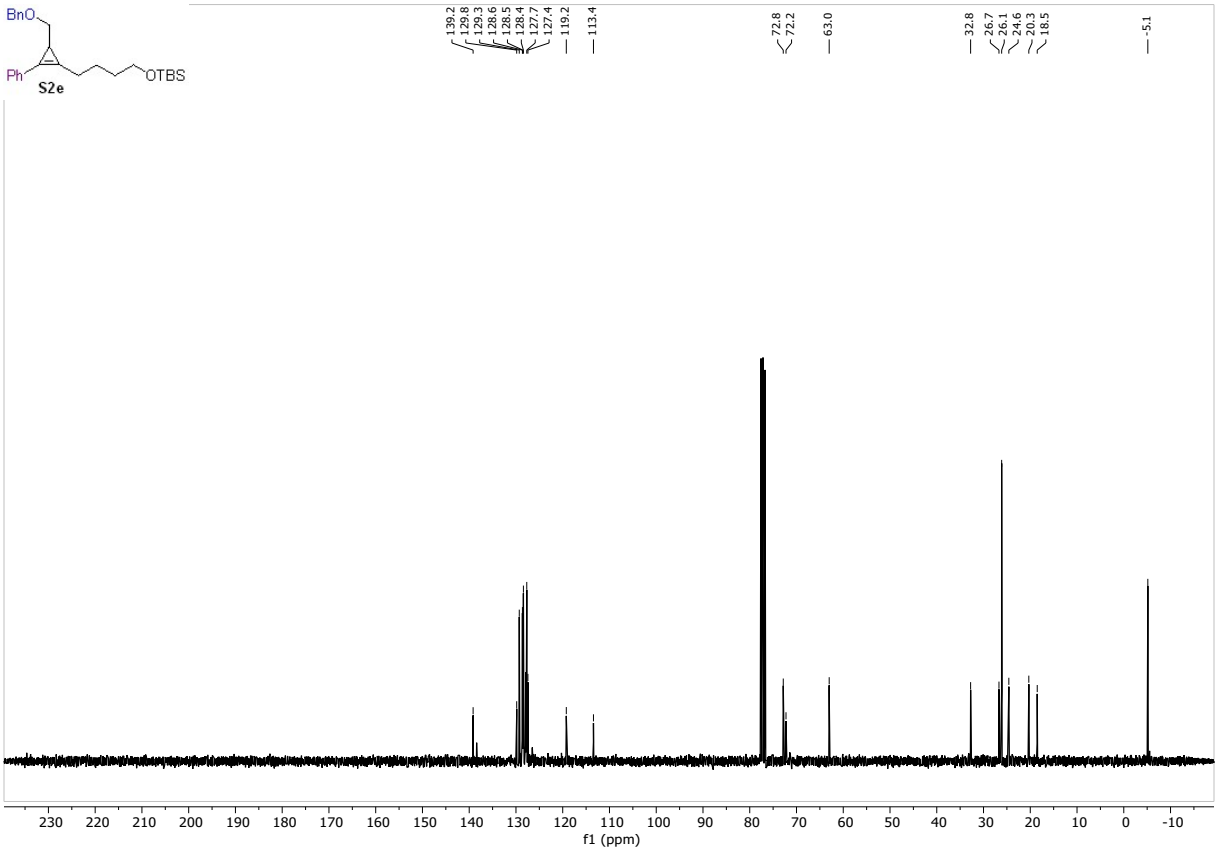
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S2d**.



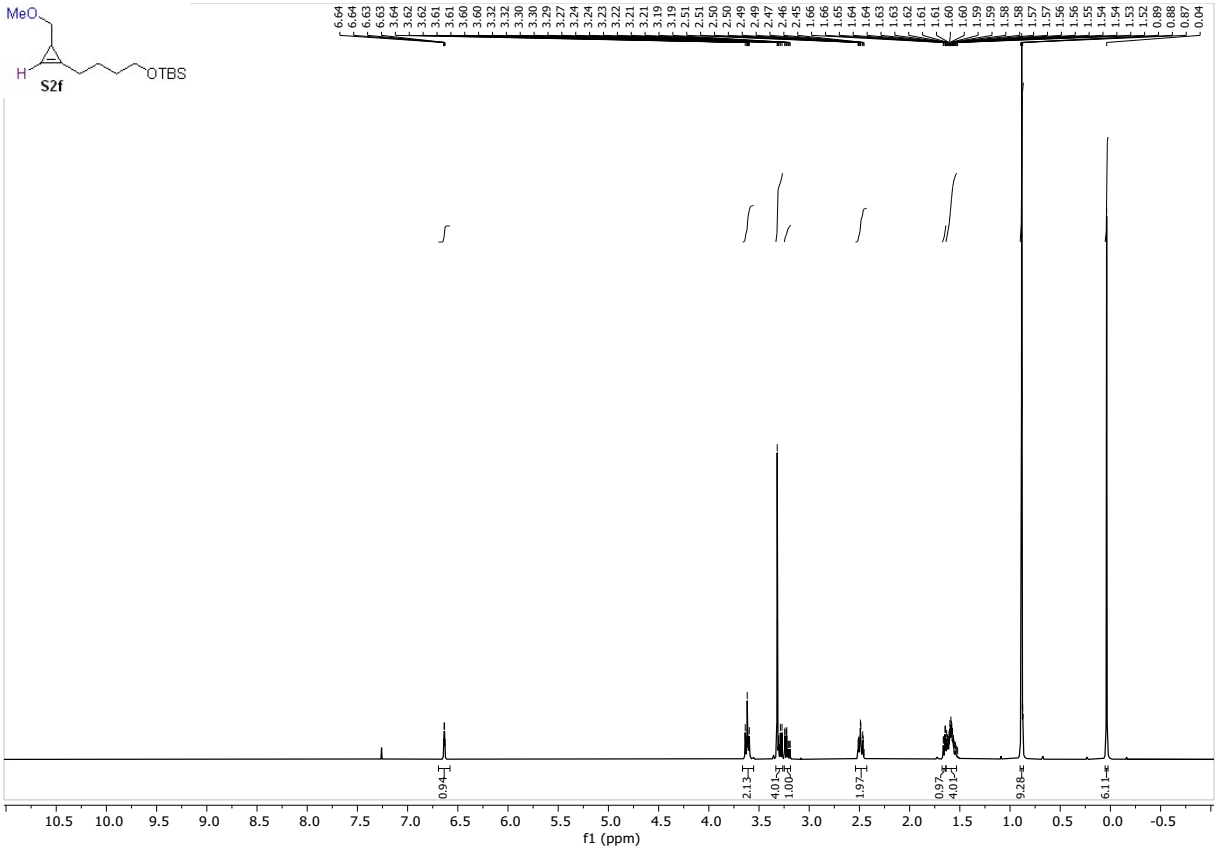
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S2d**.



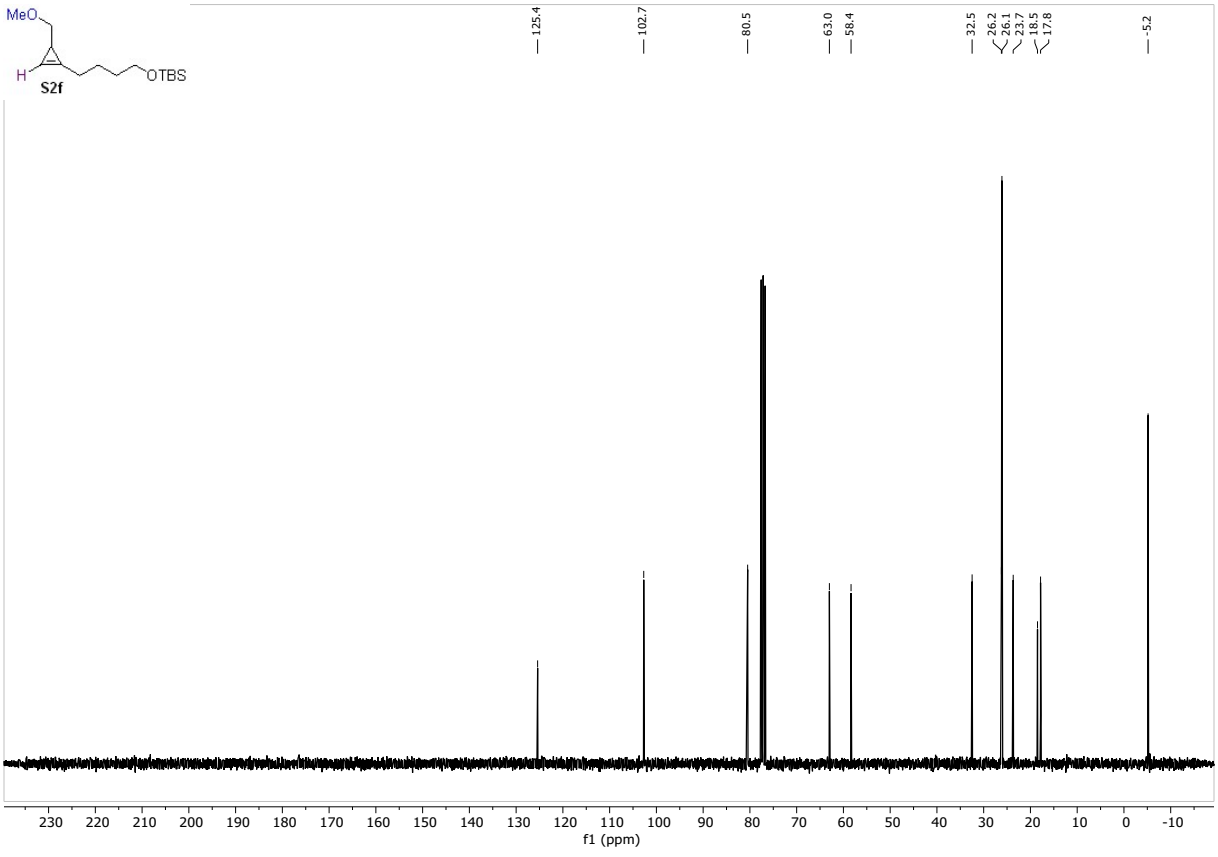
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **S2e**.



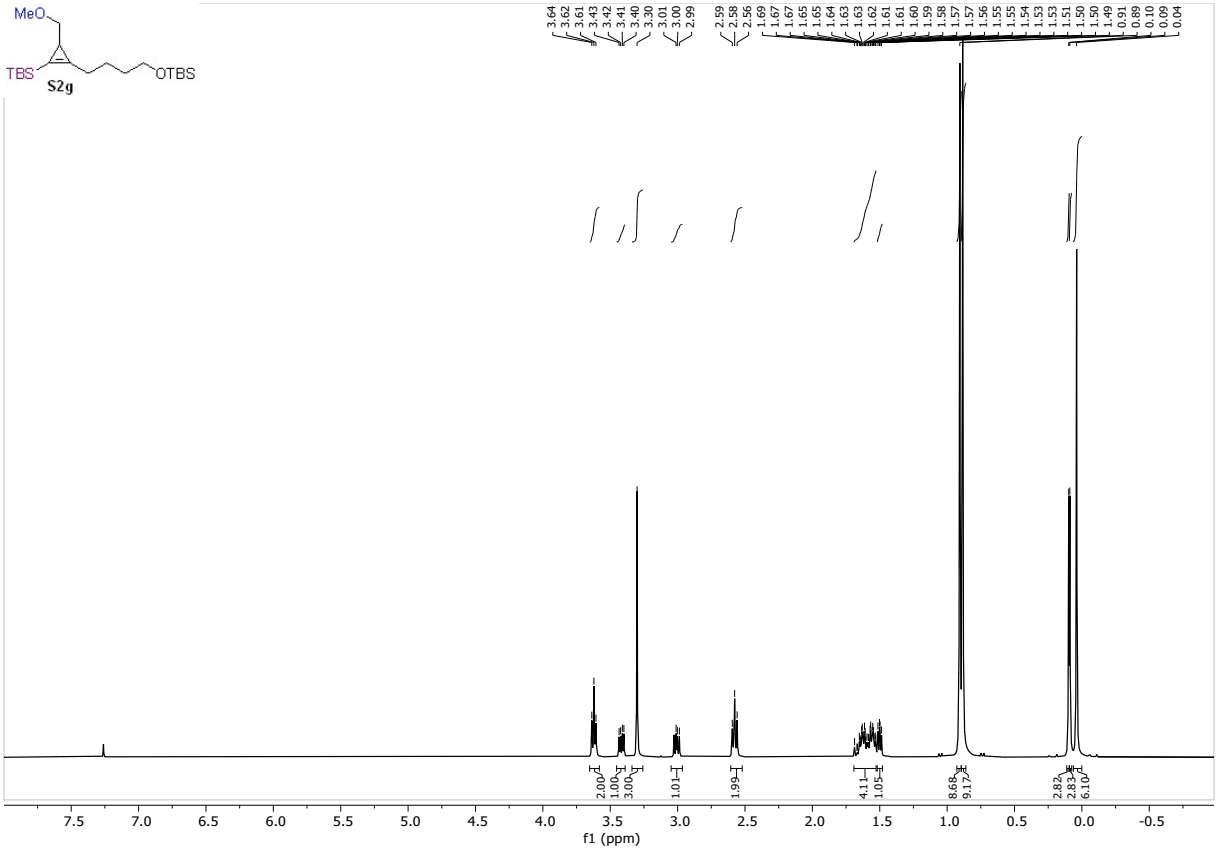
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **S2e**.



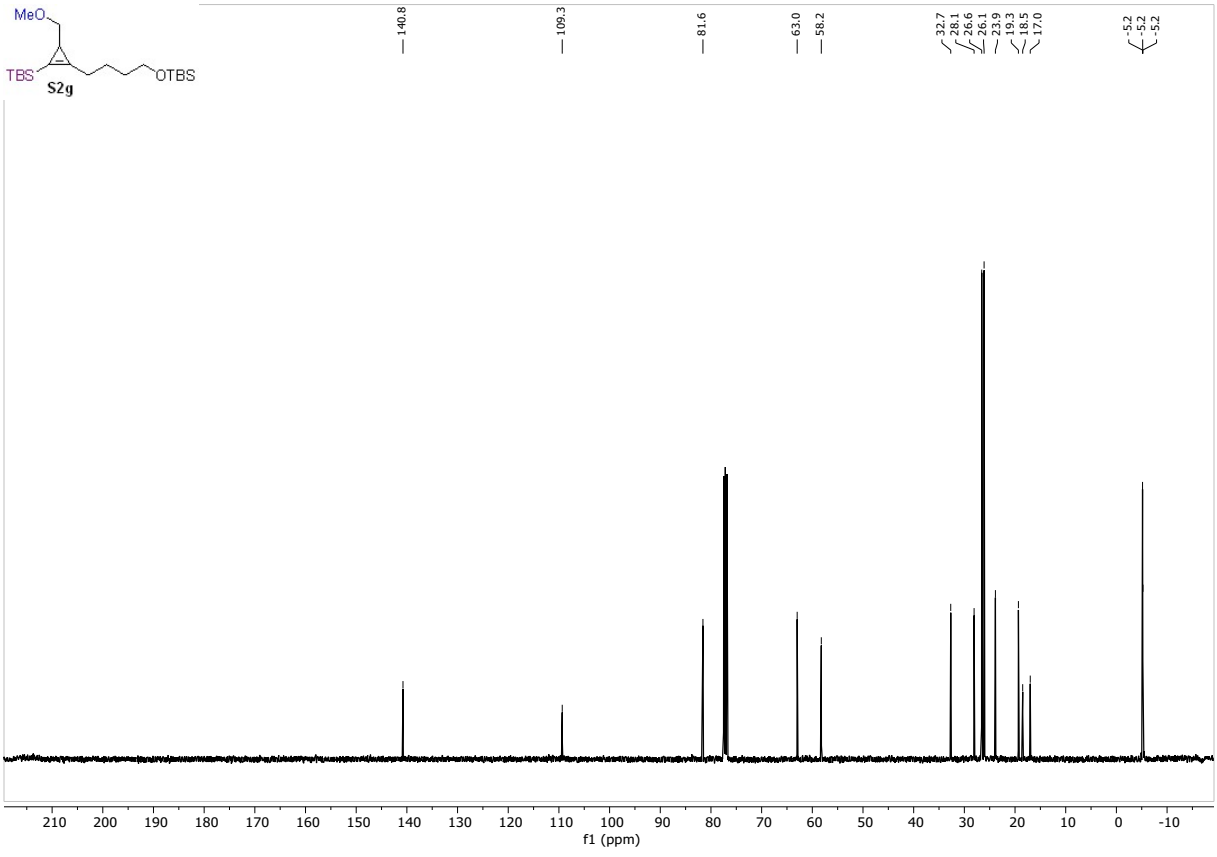
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **S2f**.



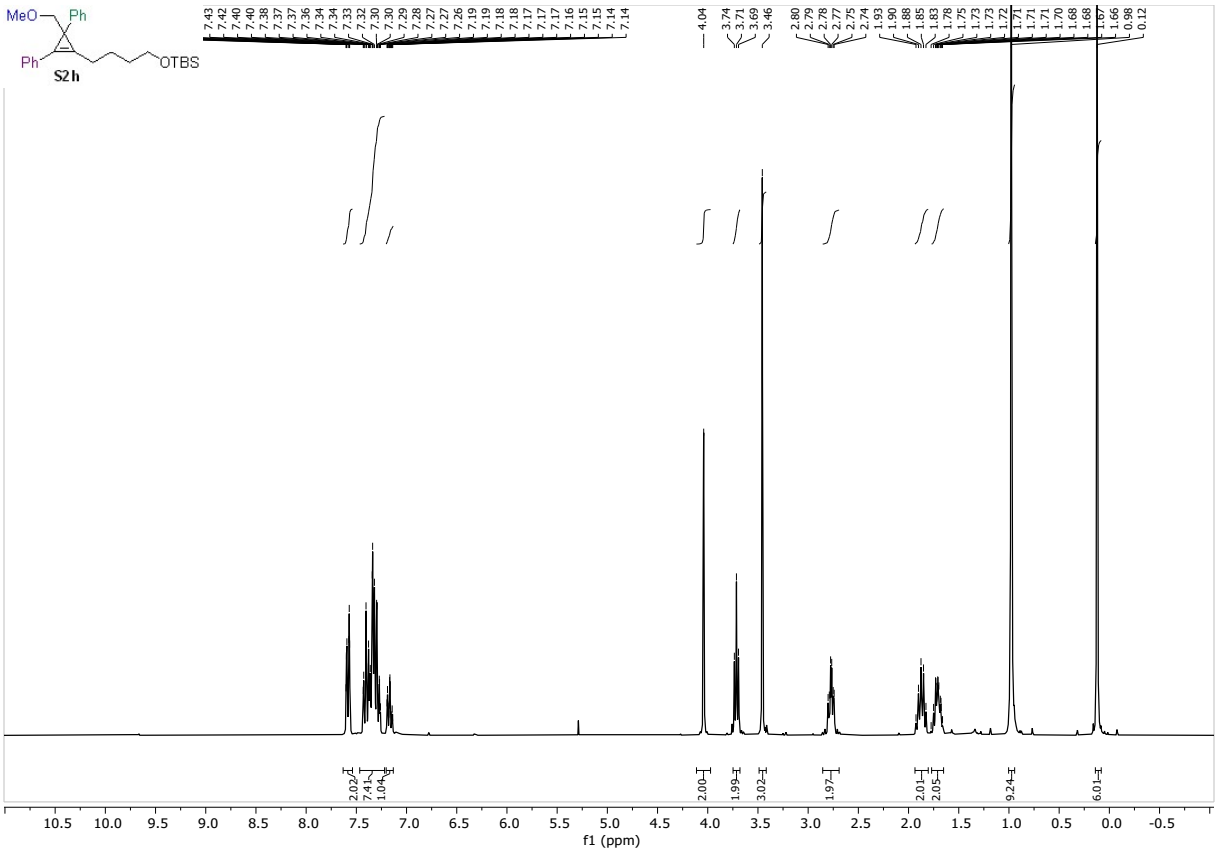
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **S2f**.



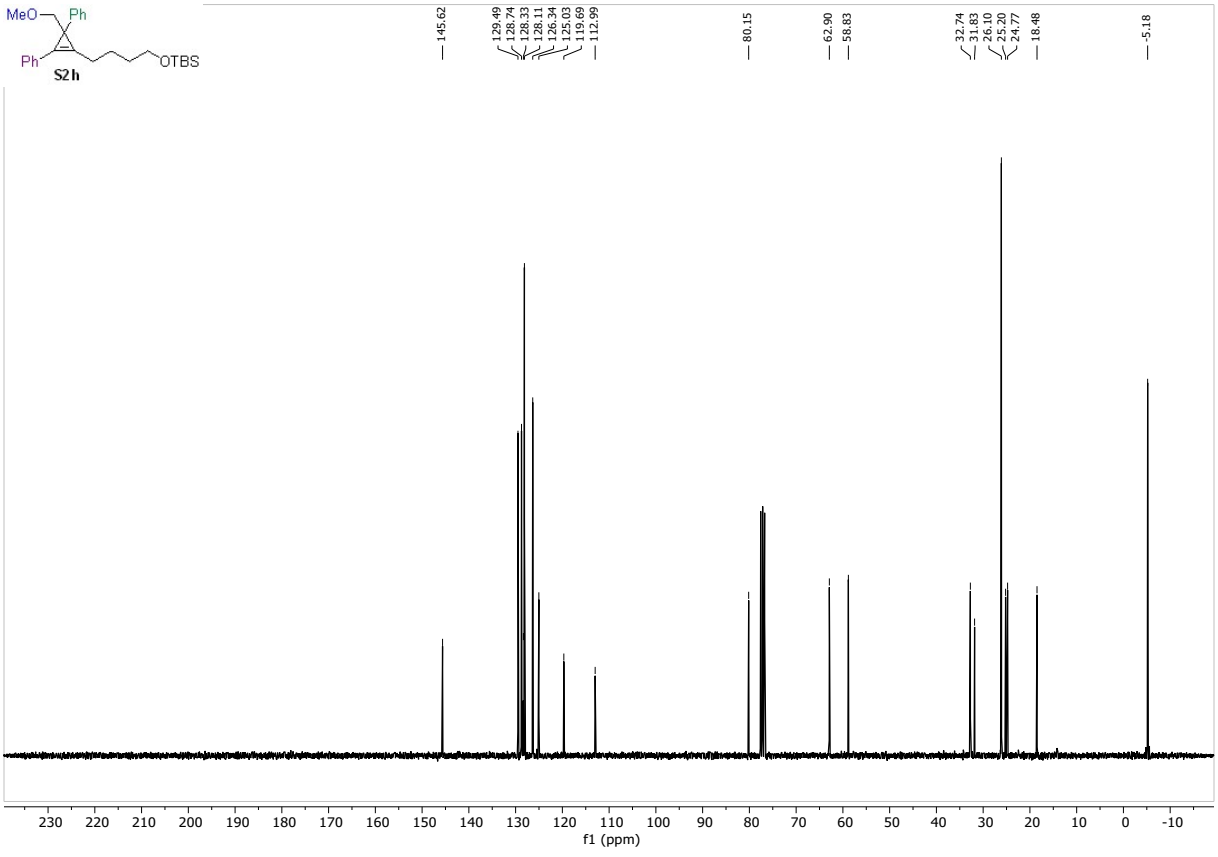
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **S2g**.



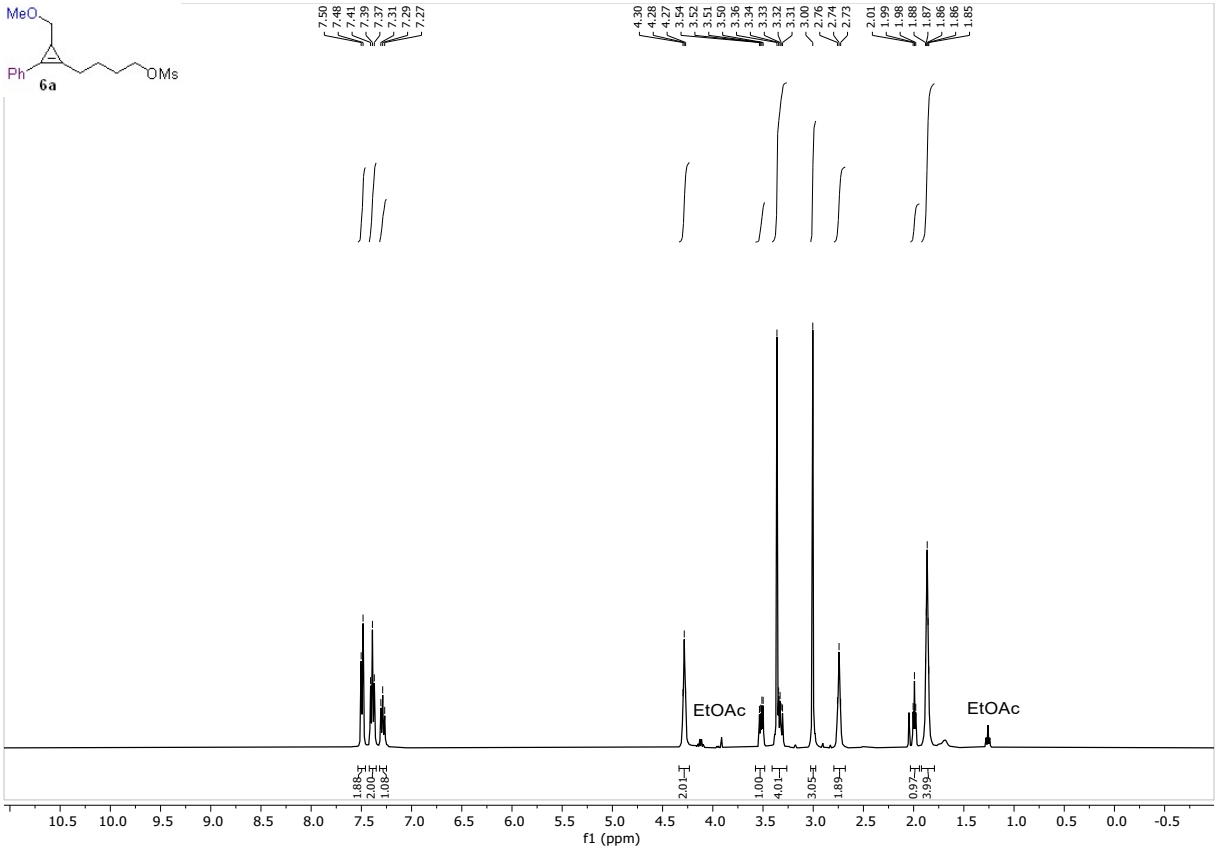
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **S2g**.



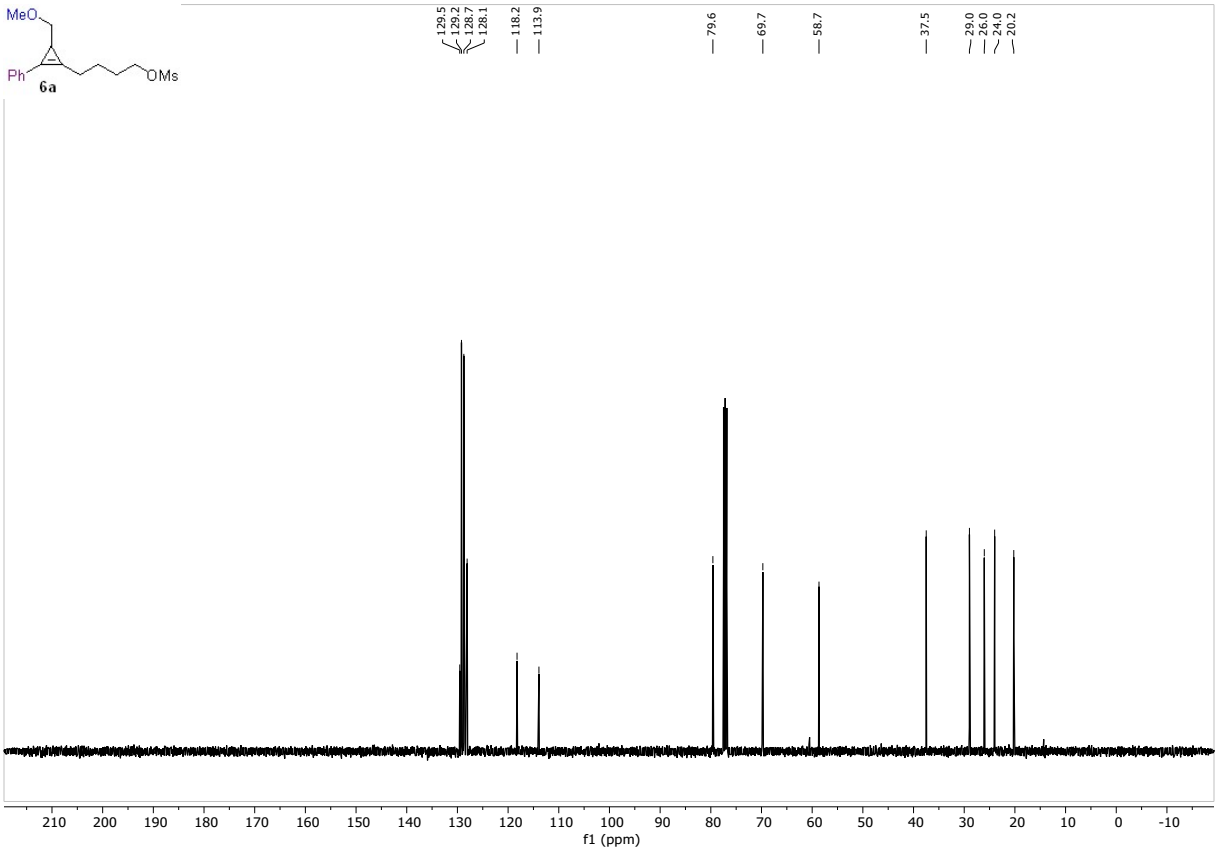
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **S2h**.



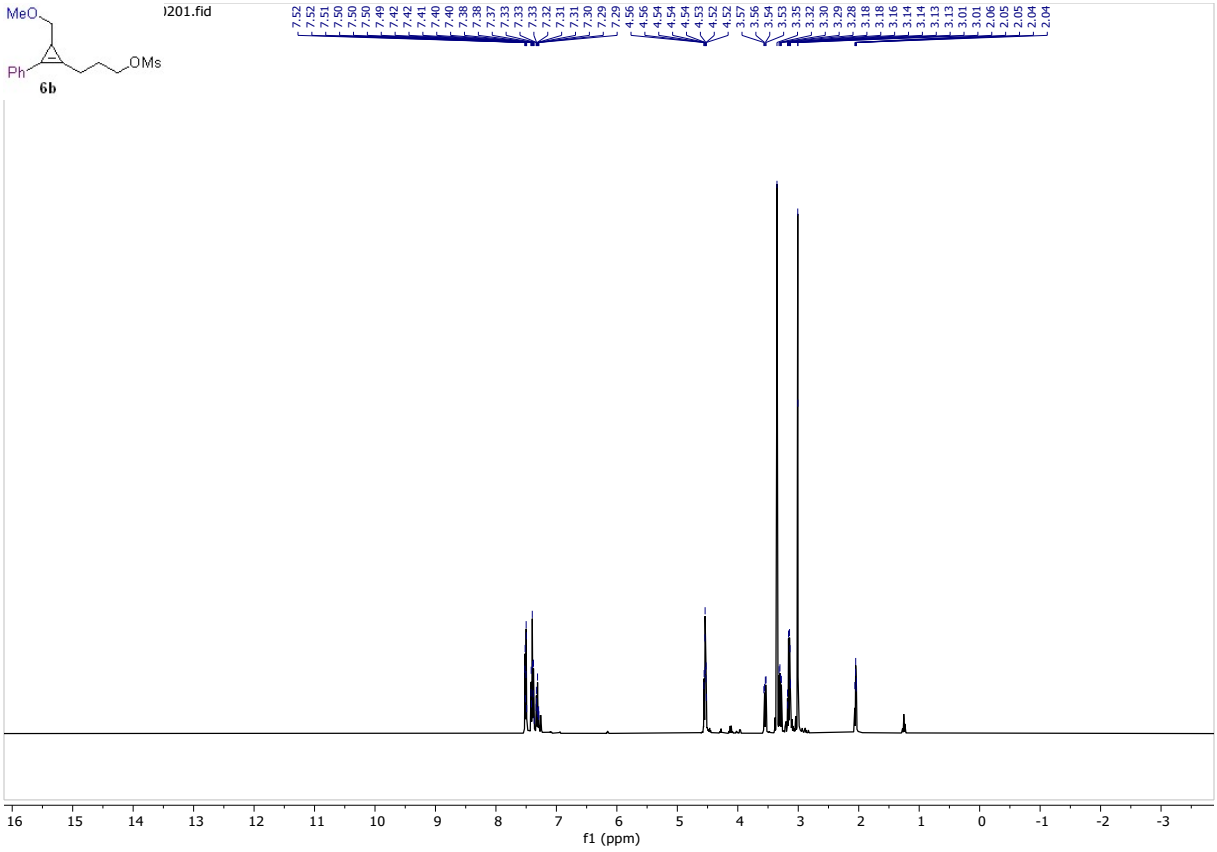
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **S2h**.



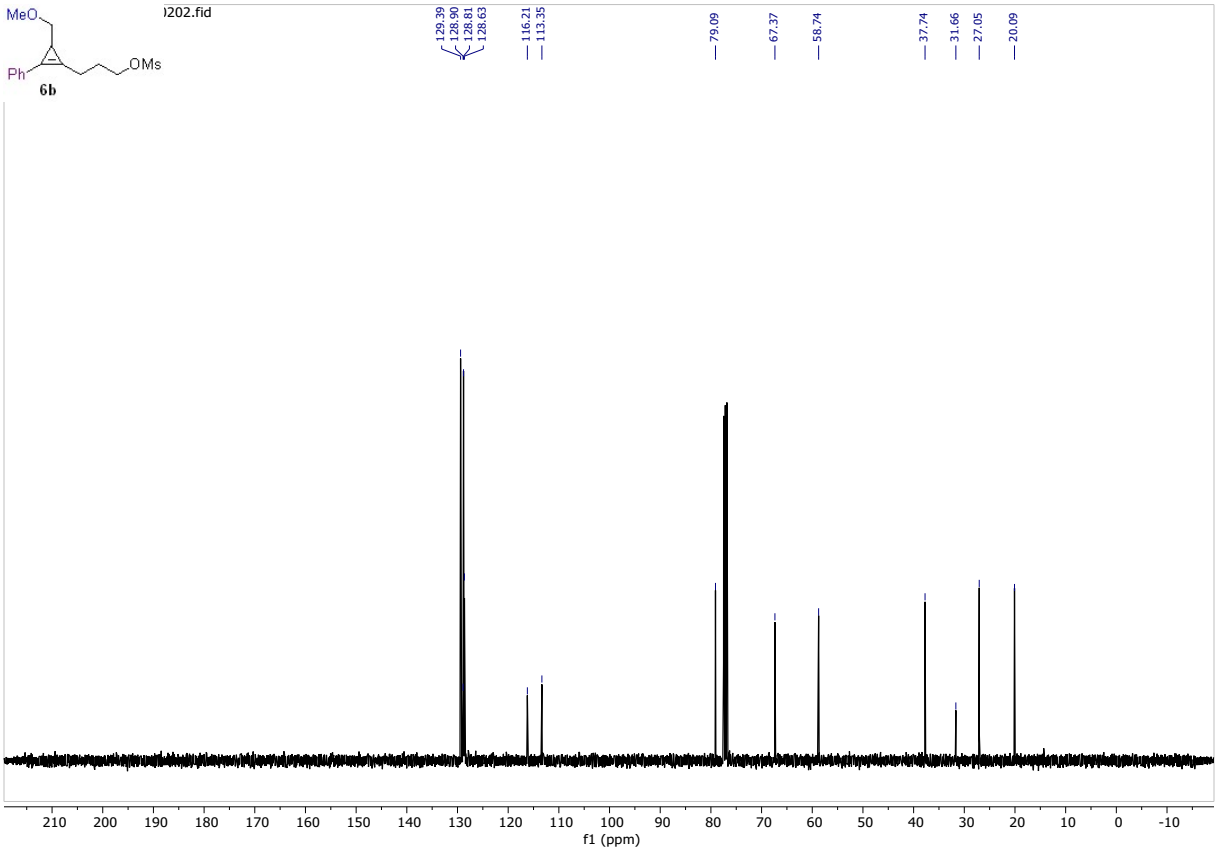
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6a**.



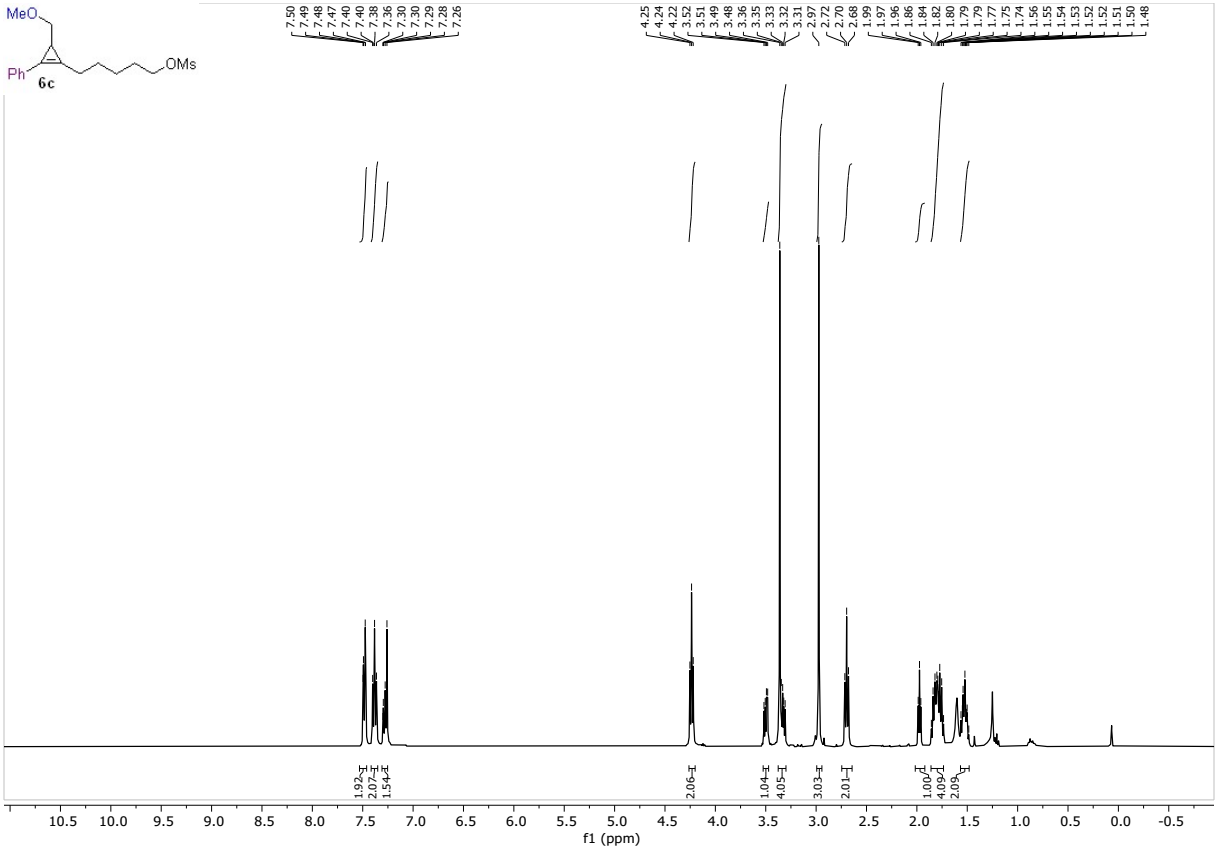
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **6a**.



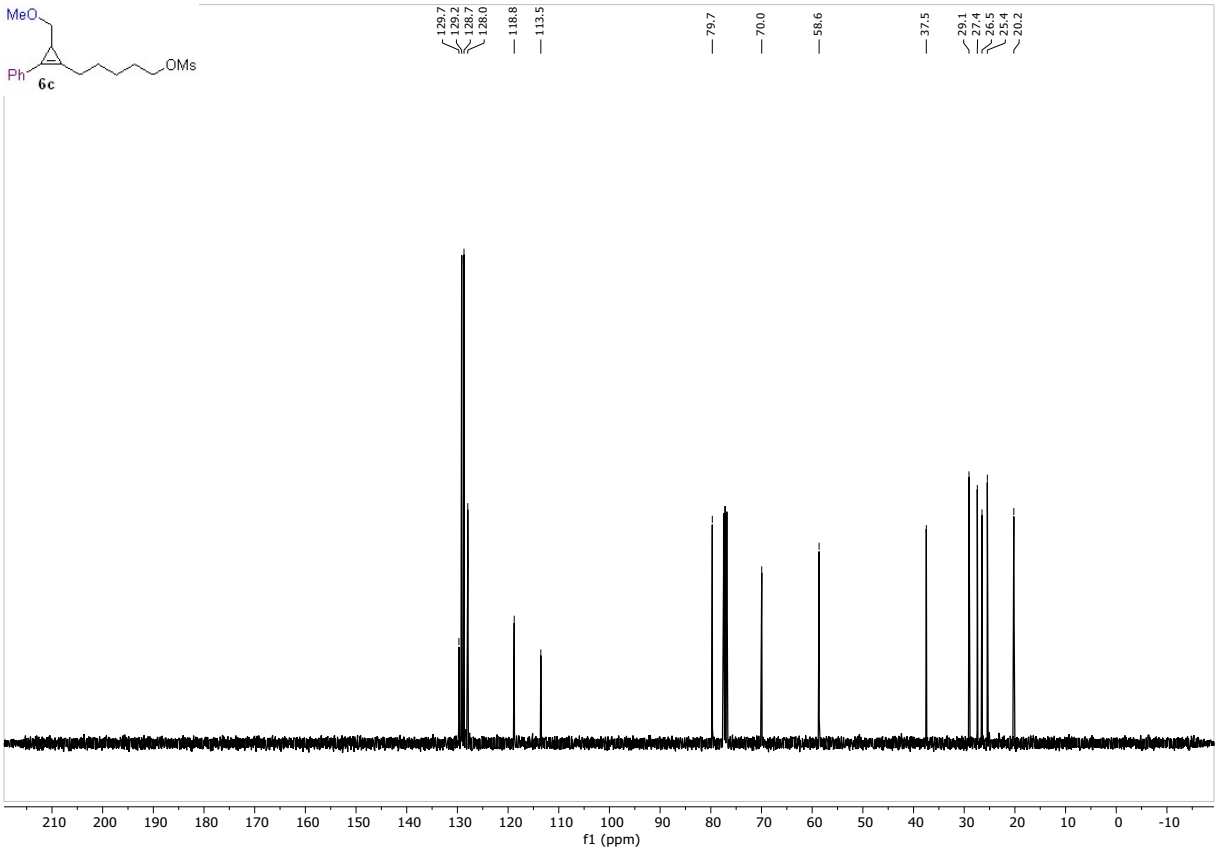
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6b**.



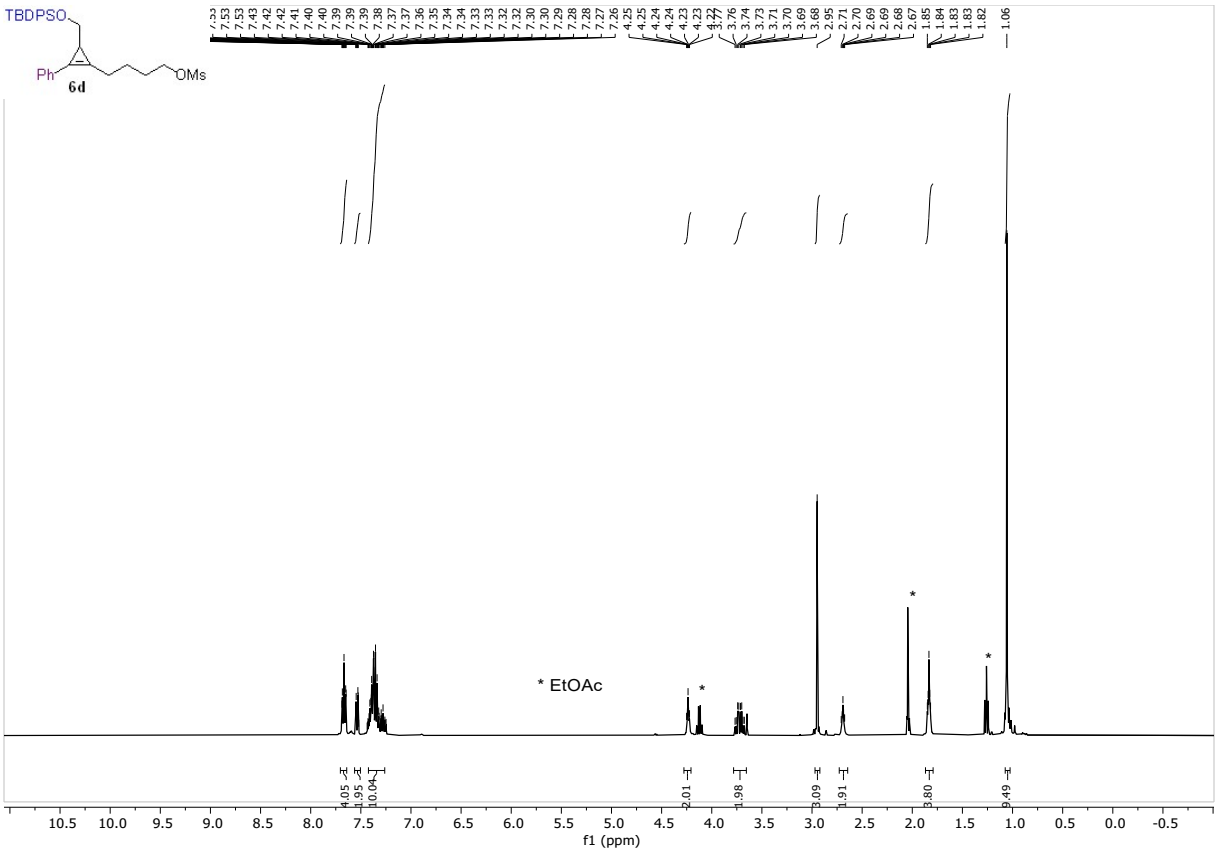
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **6b**.



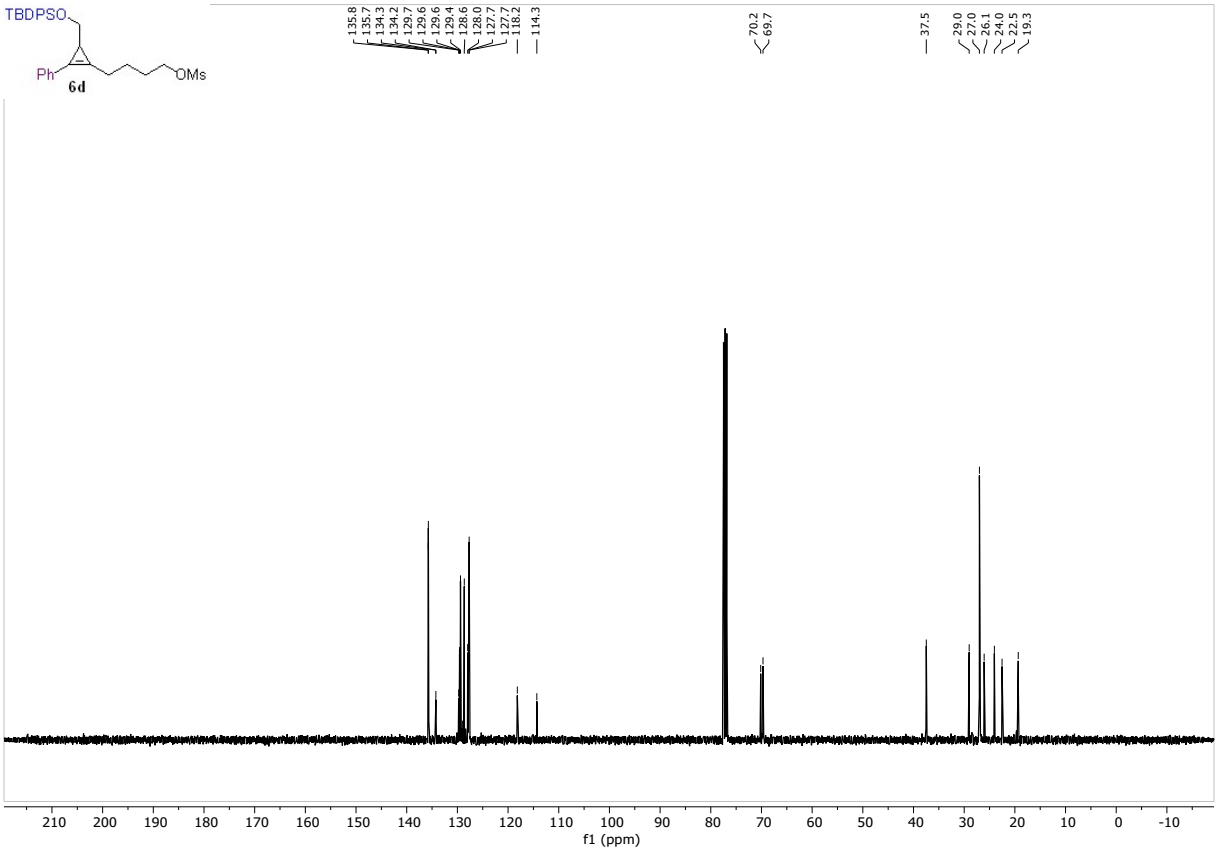
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6c**.



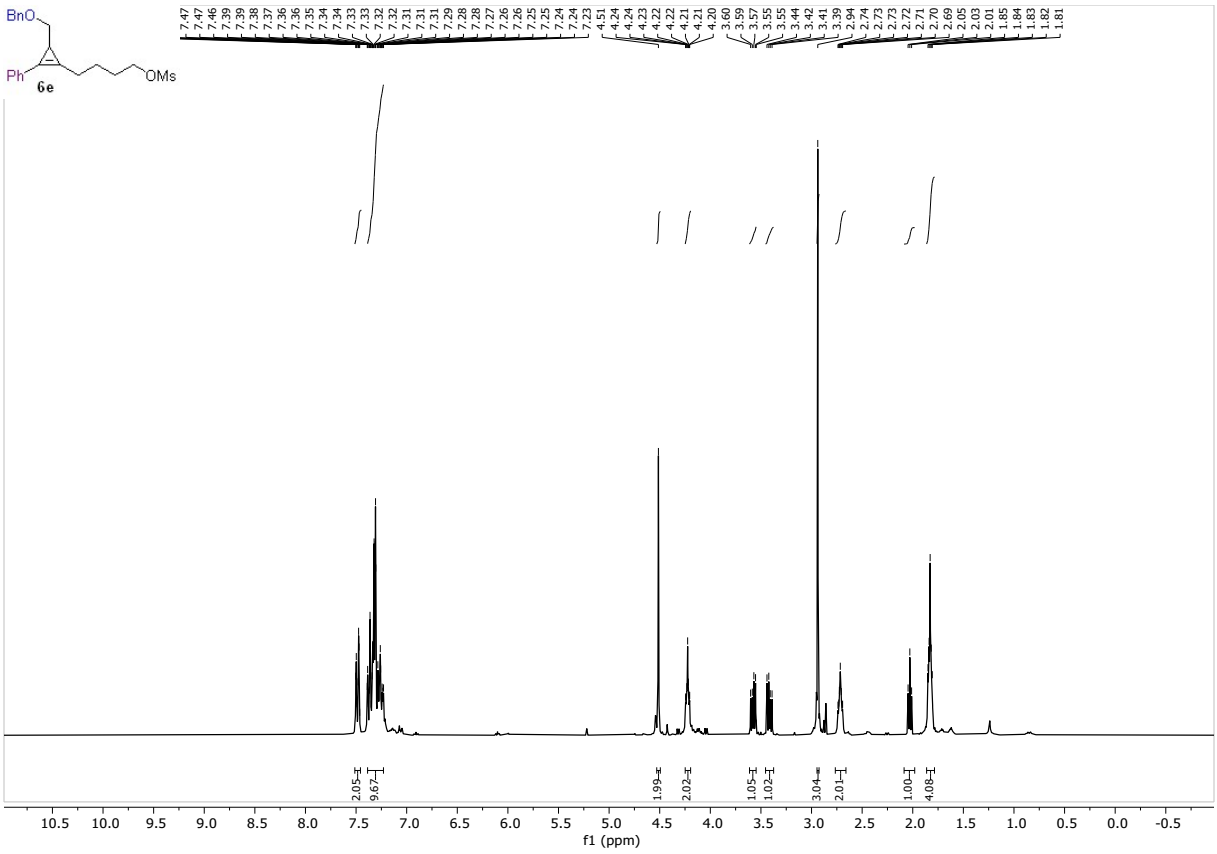
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **6c**.



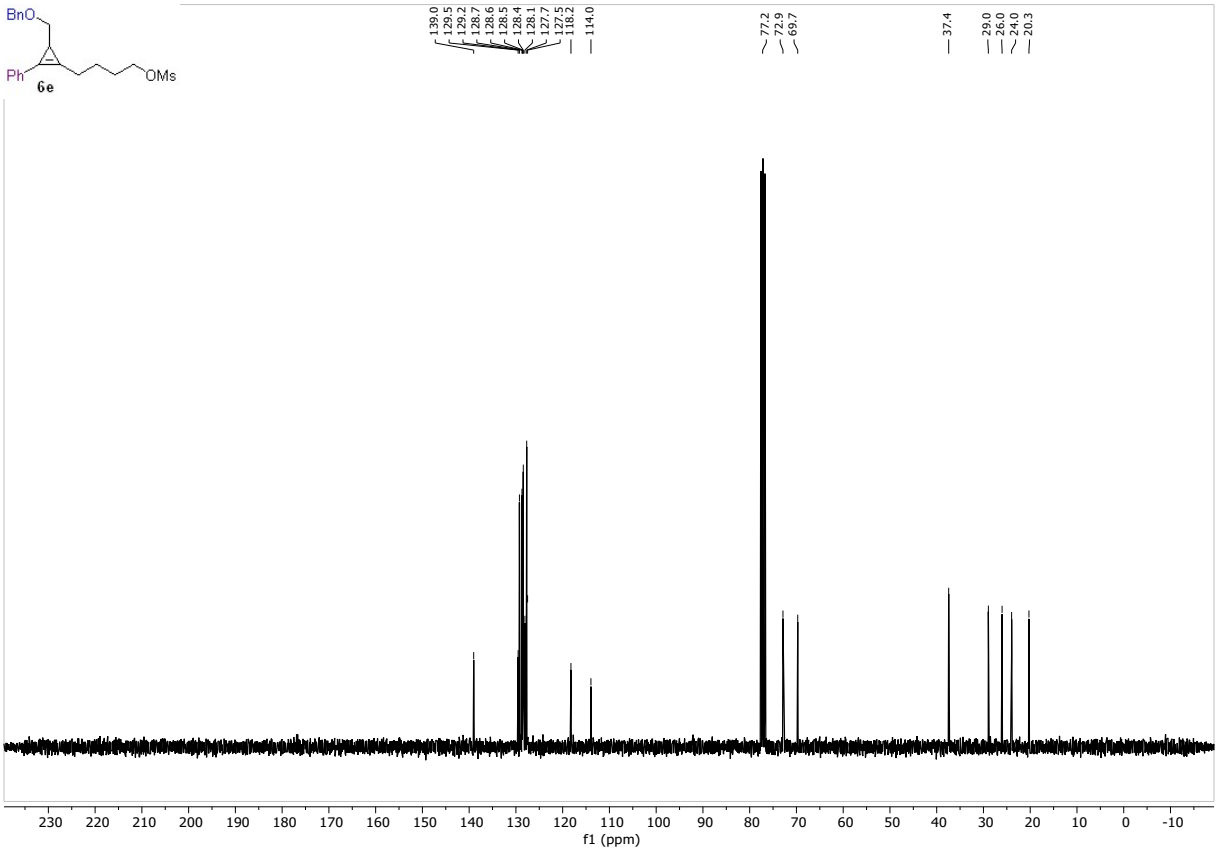
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6d**.



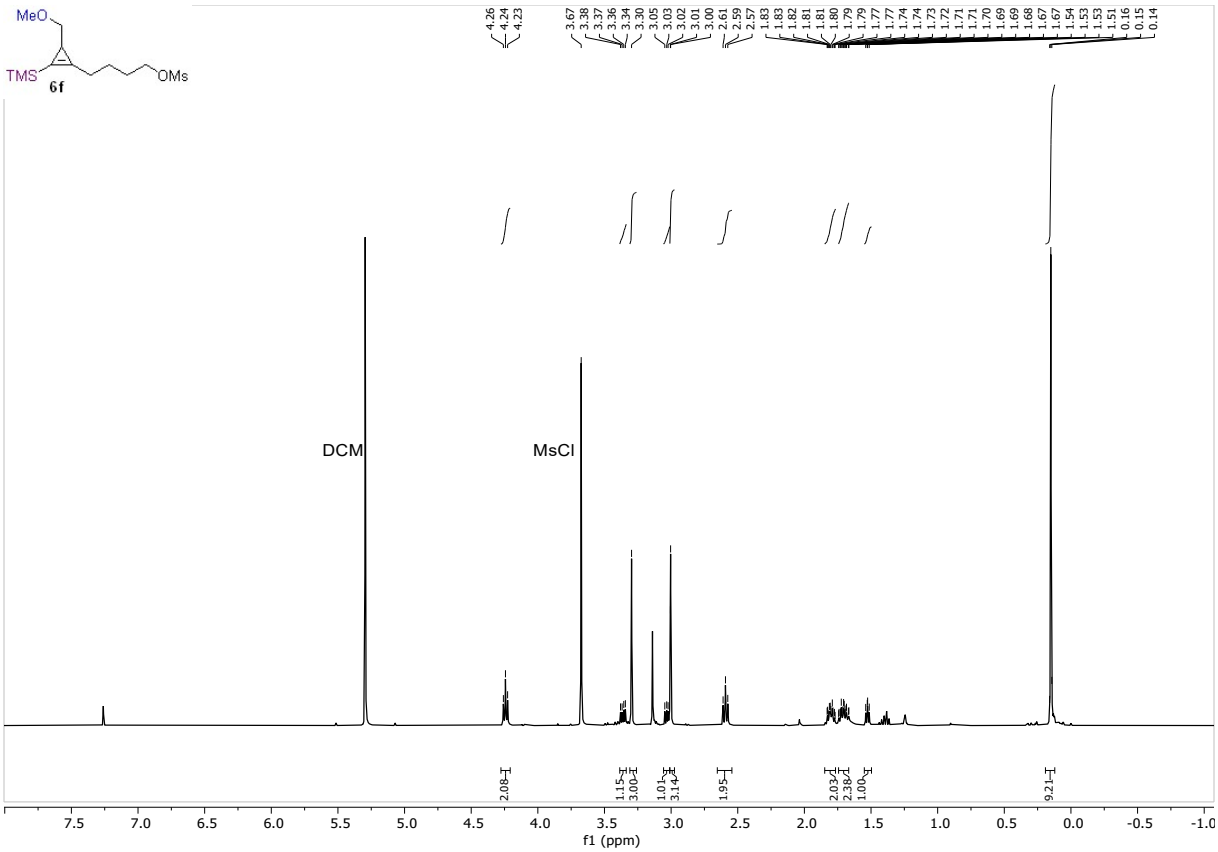
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **6d**.



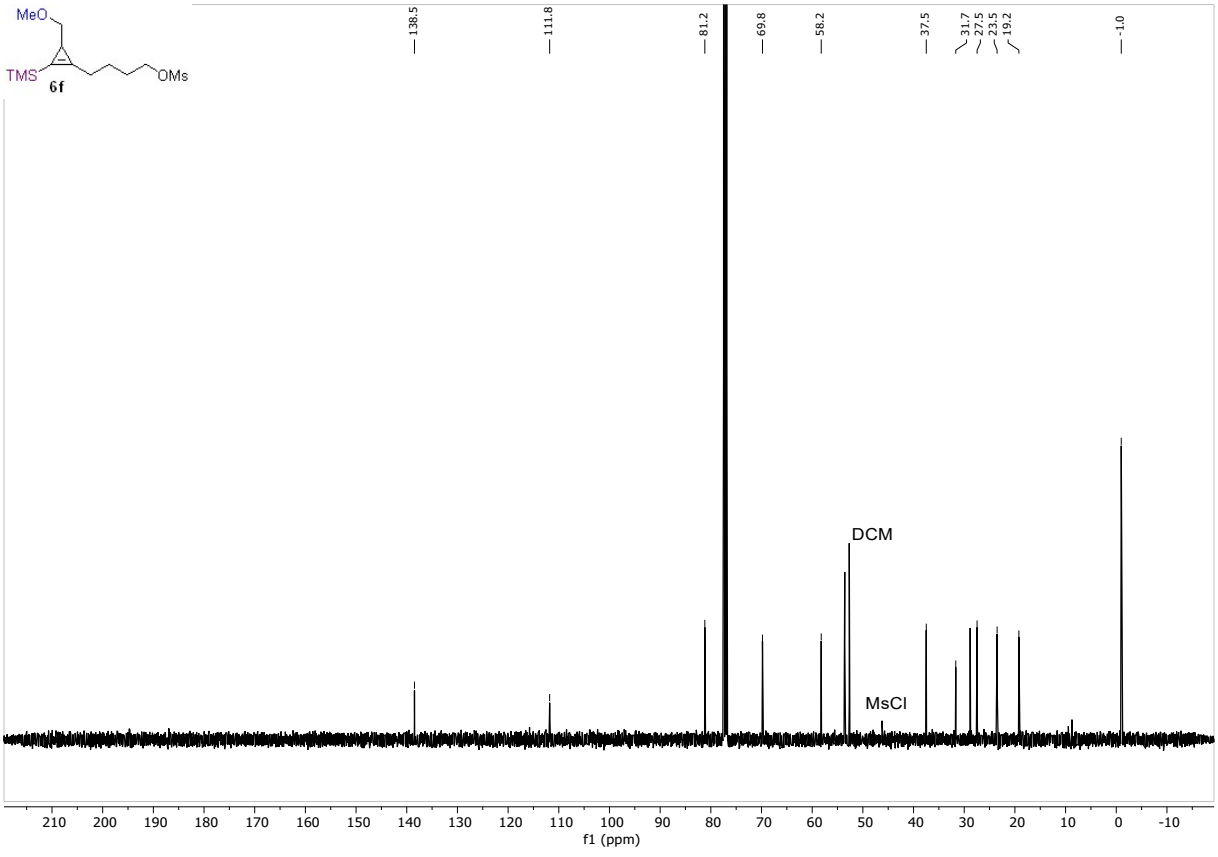
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **6e**.



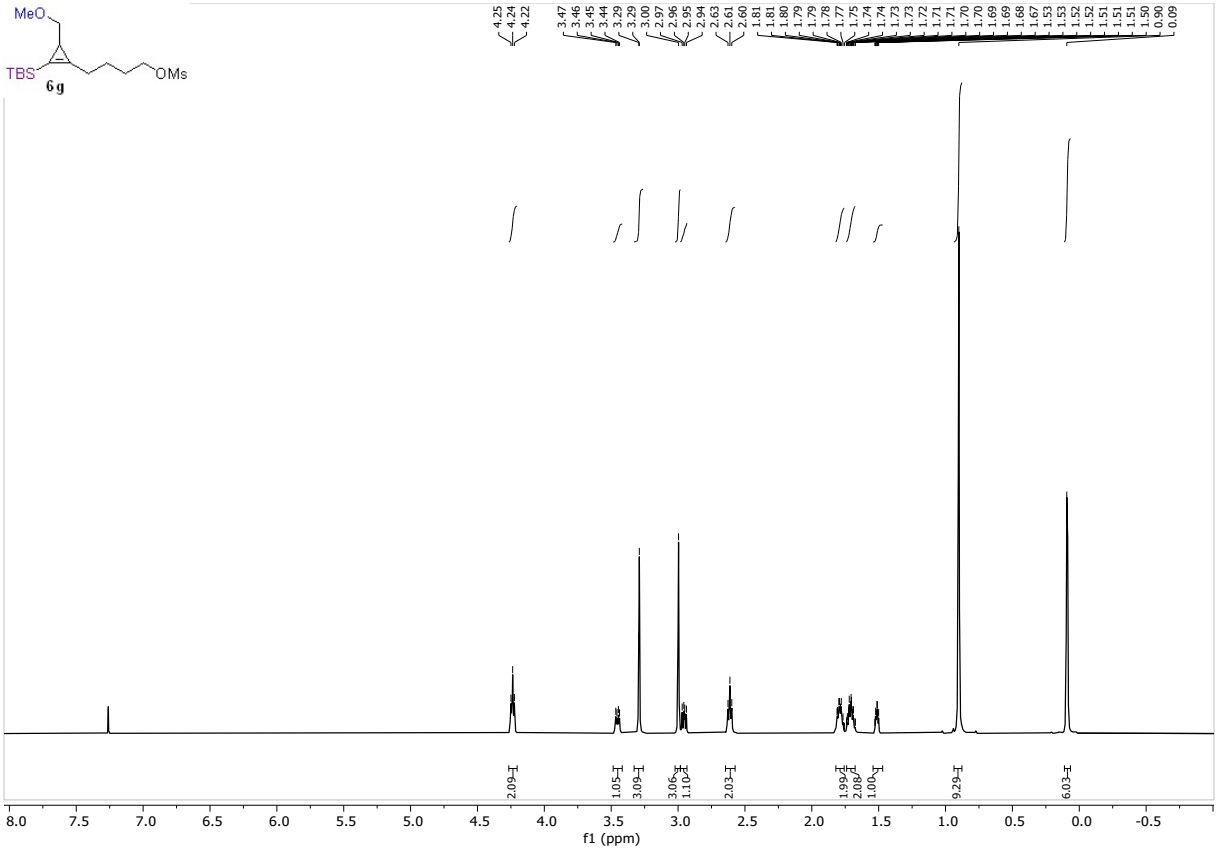
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **6e**.



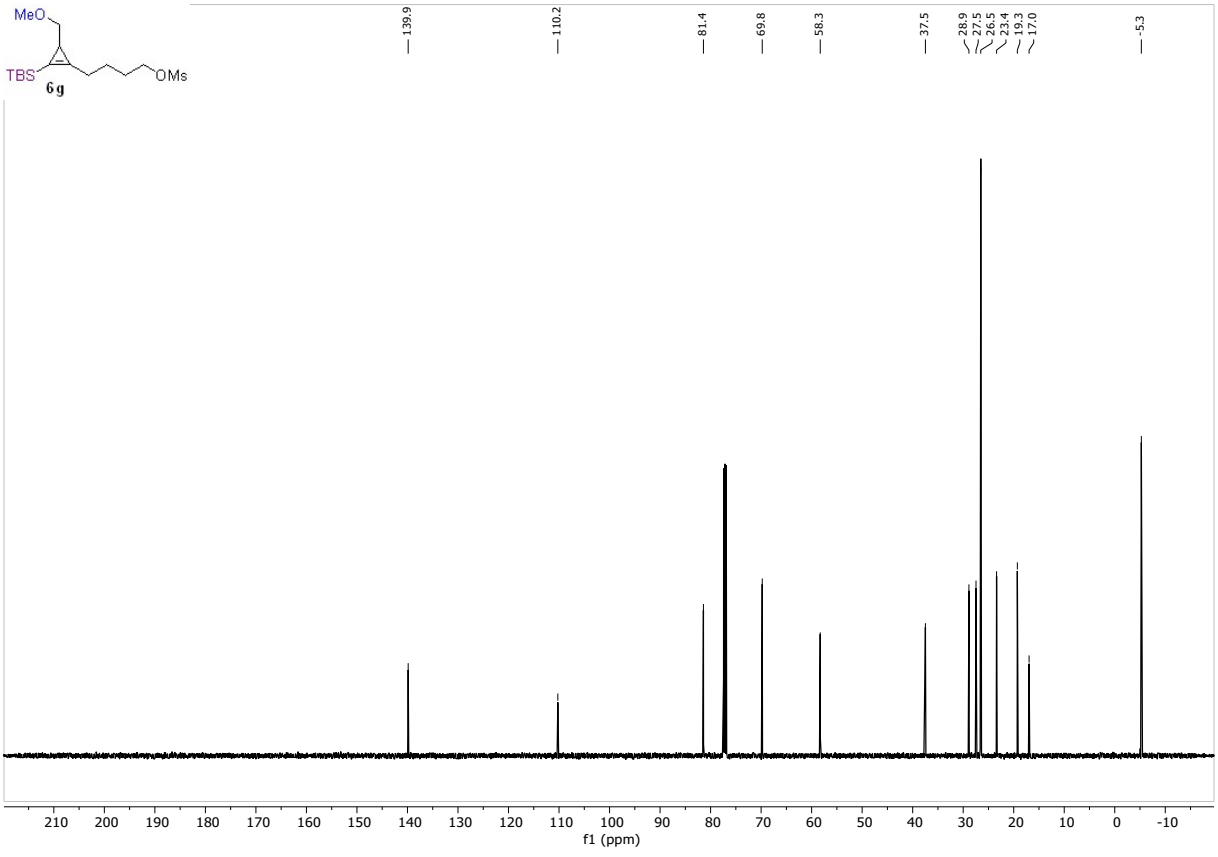
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6f**.



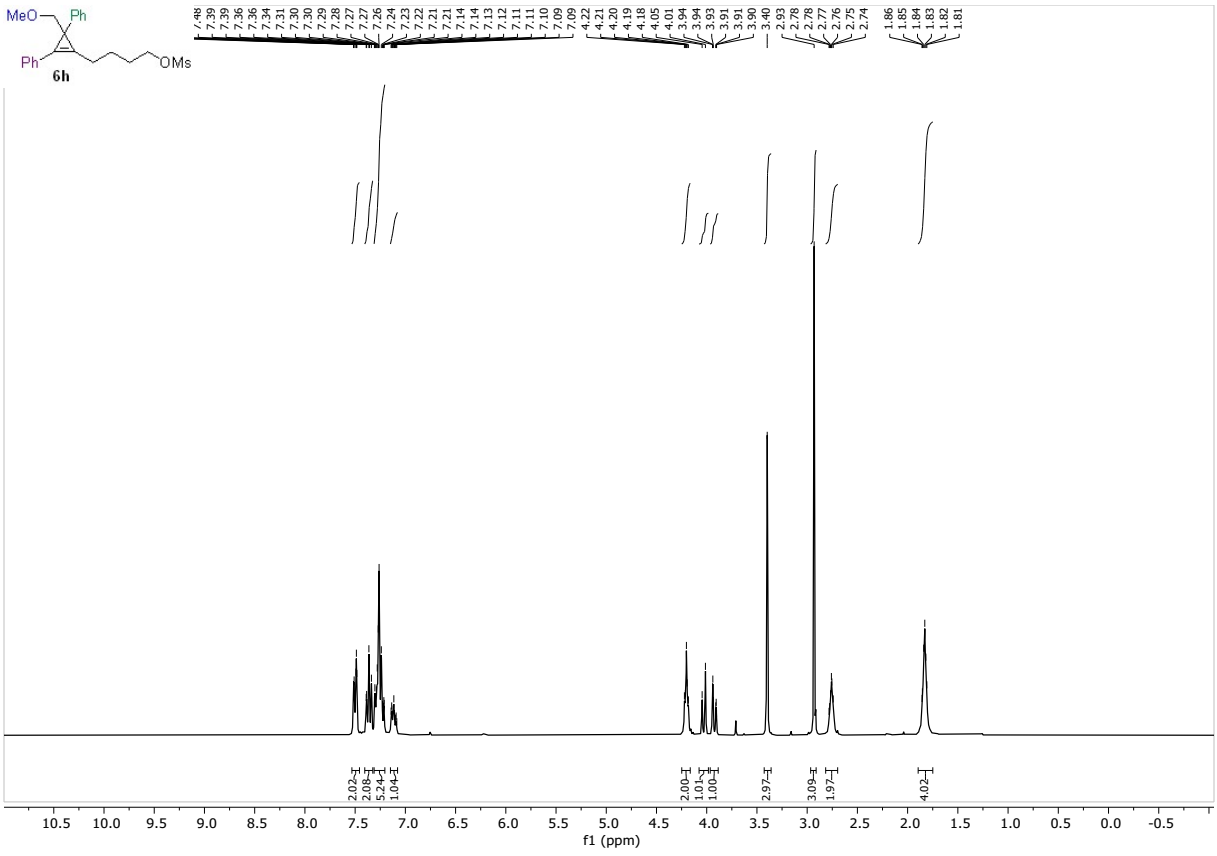
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **6f**.



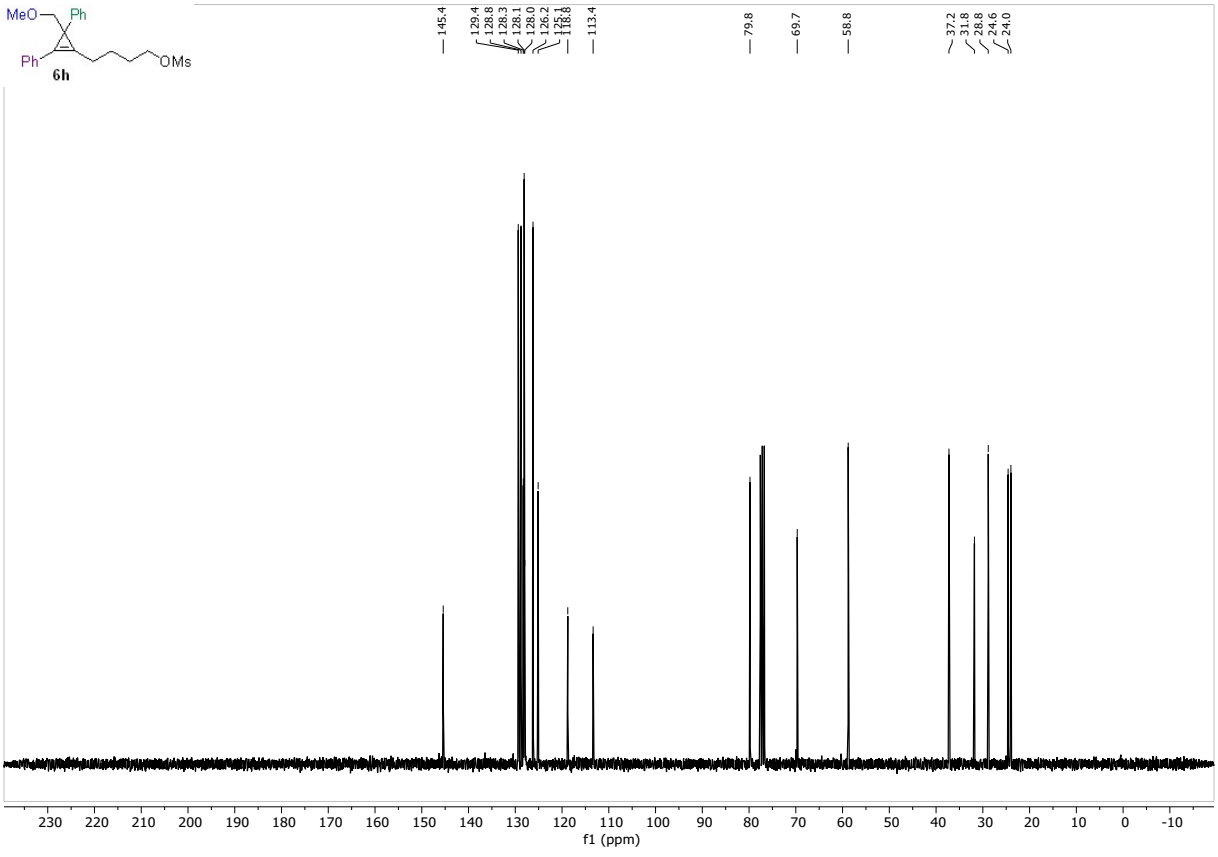
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **6g**.



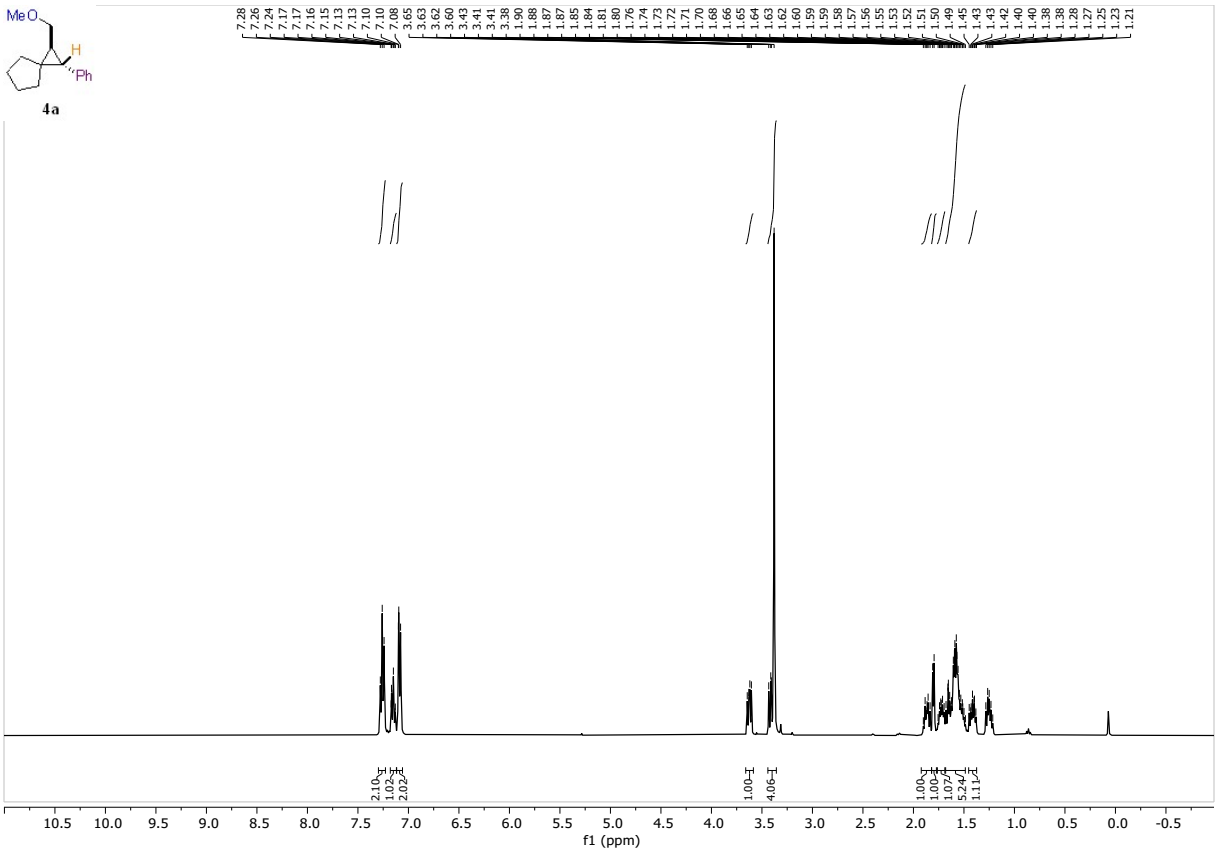
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **6g**.



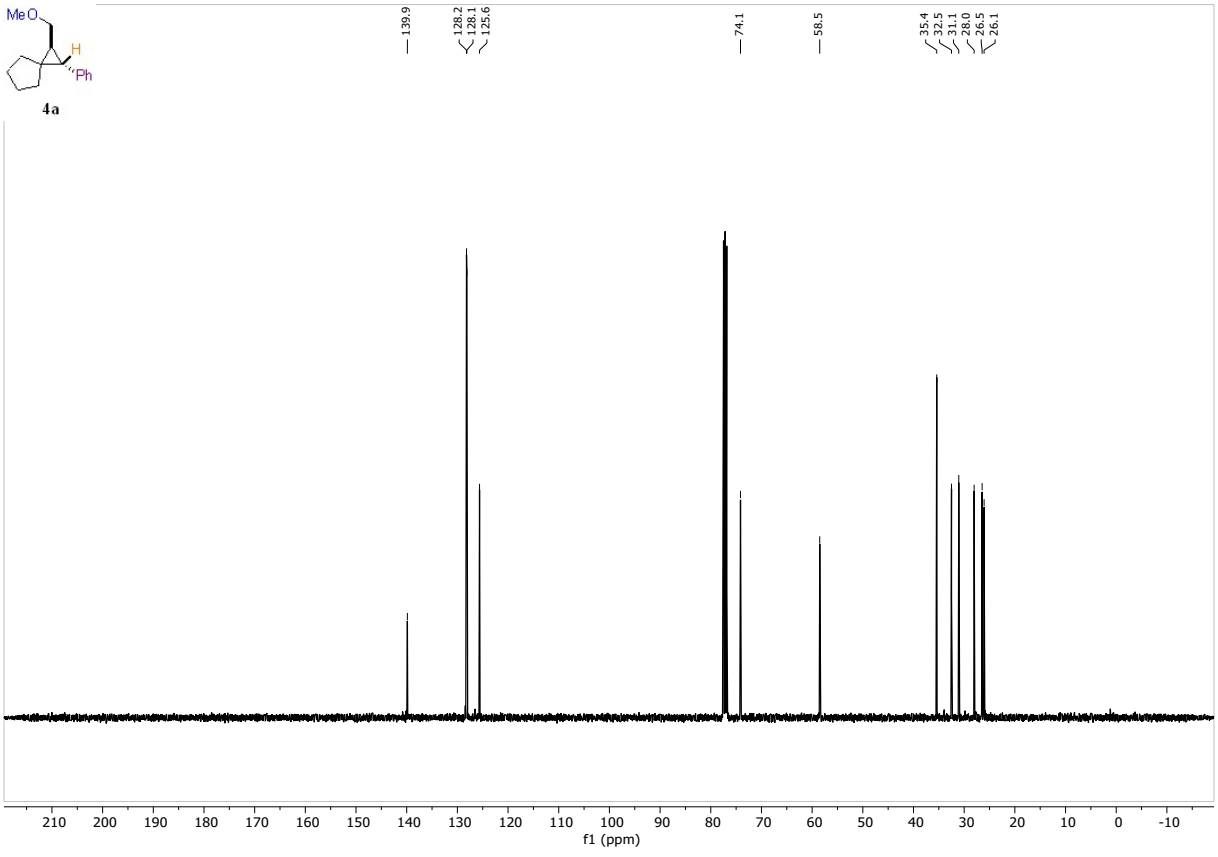
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **6h**.



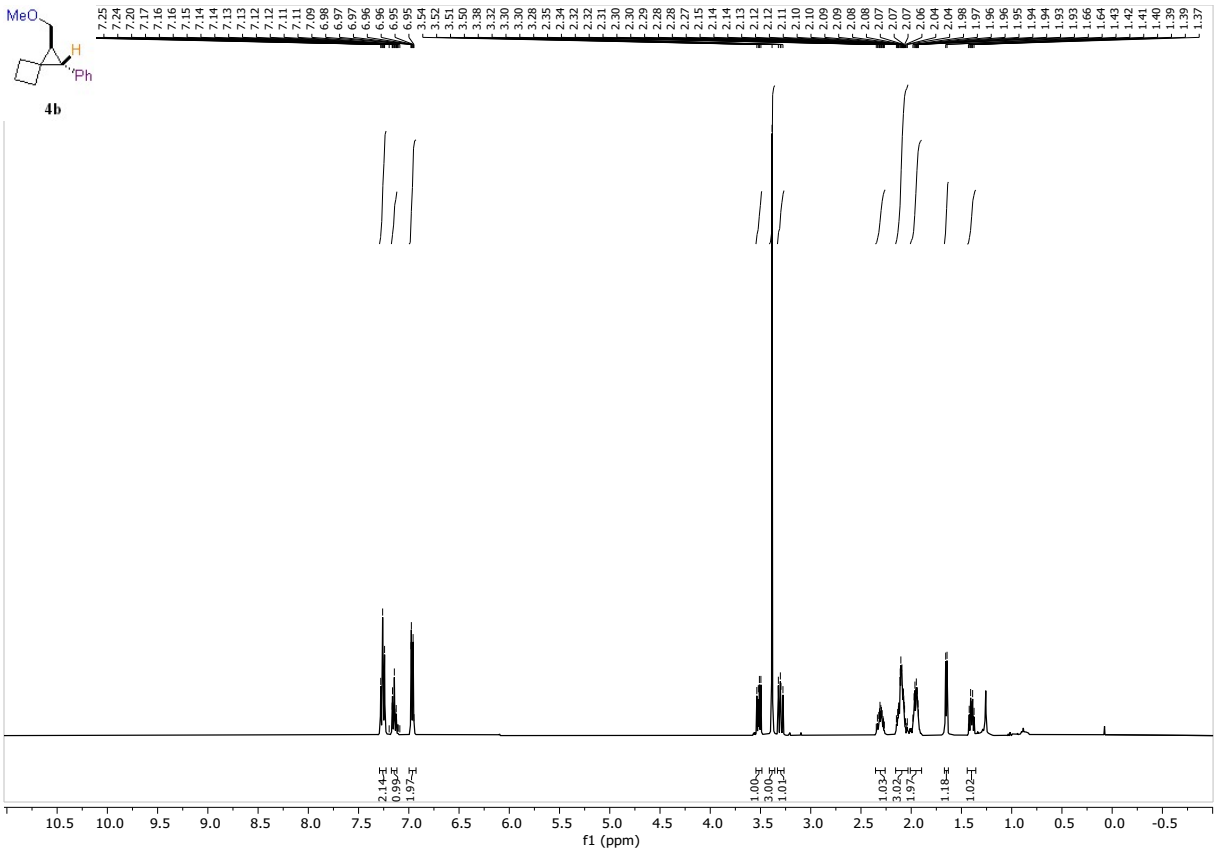
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **6h**.



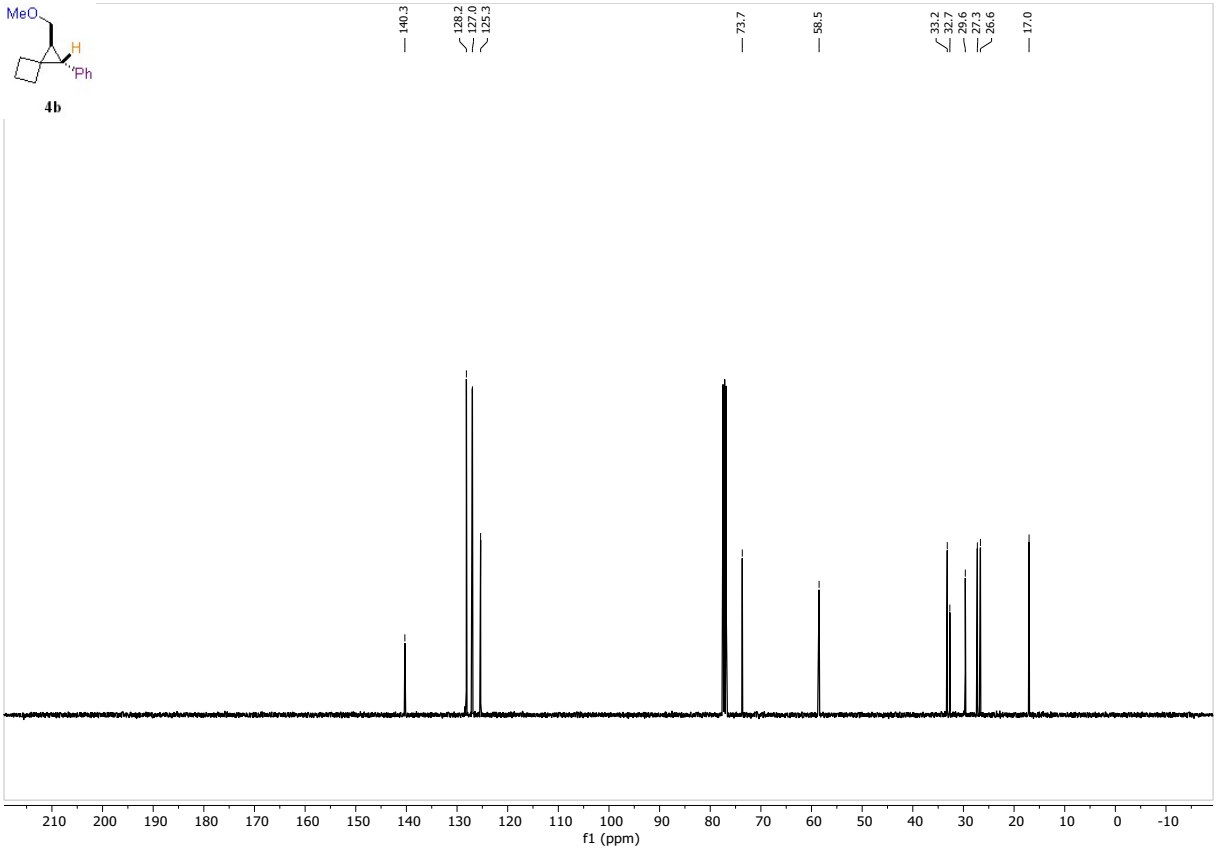
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4a**.



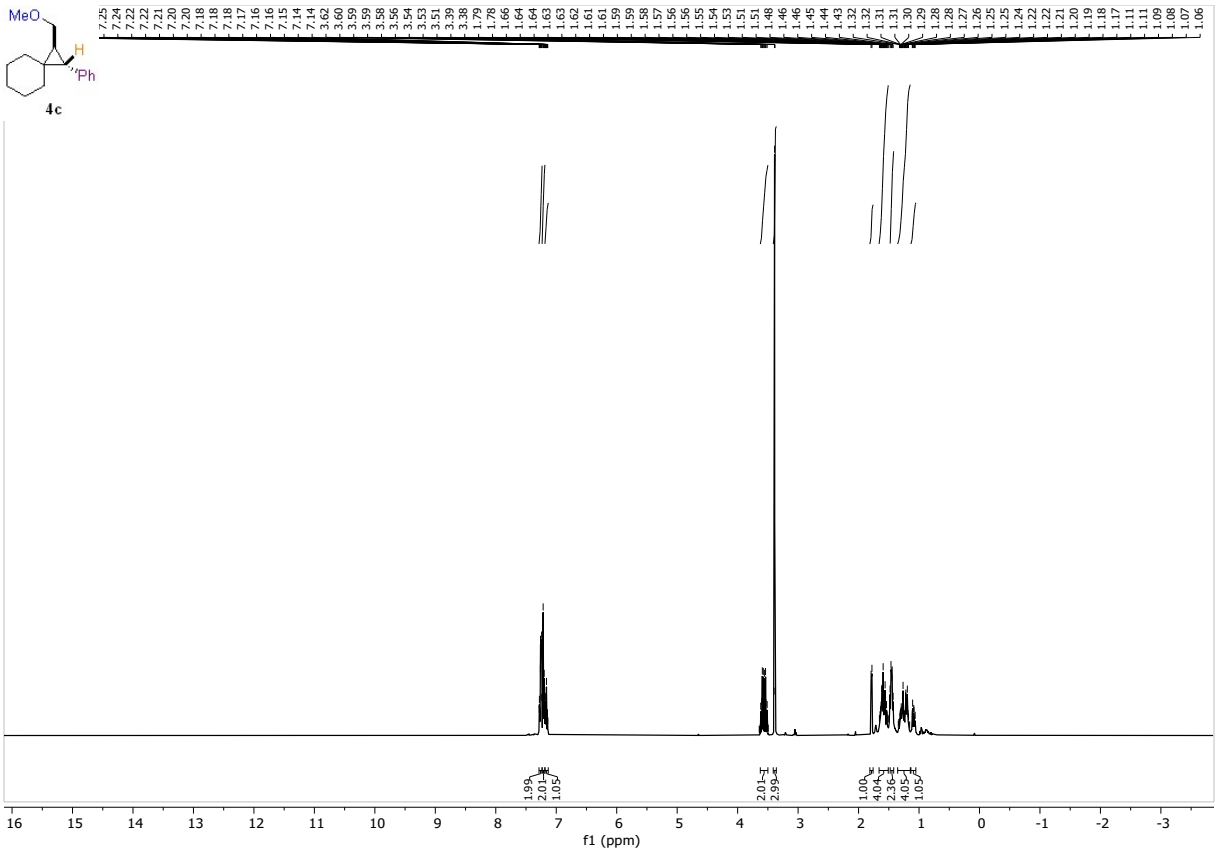
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4a**.



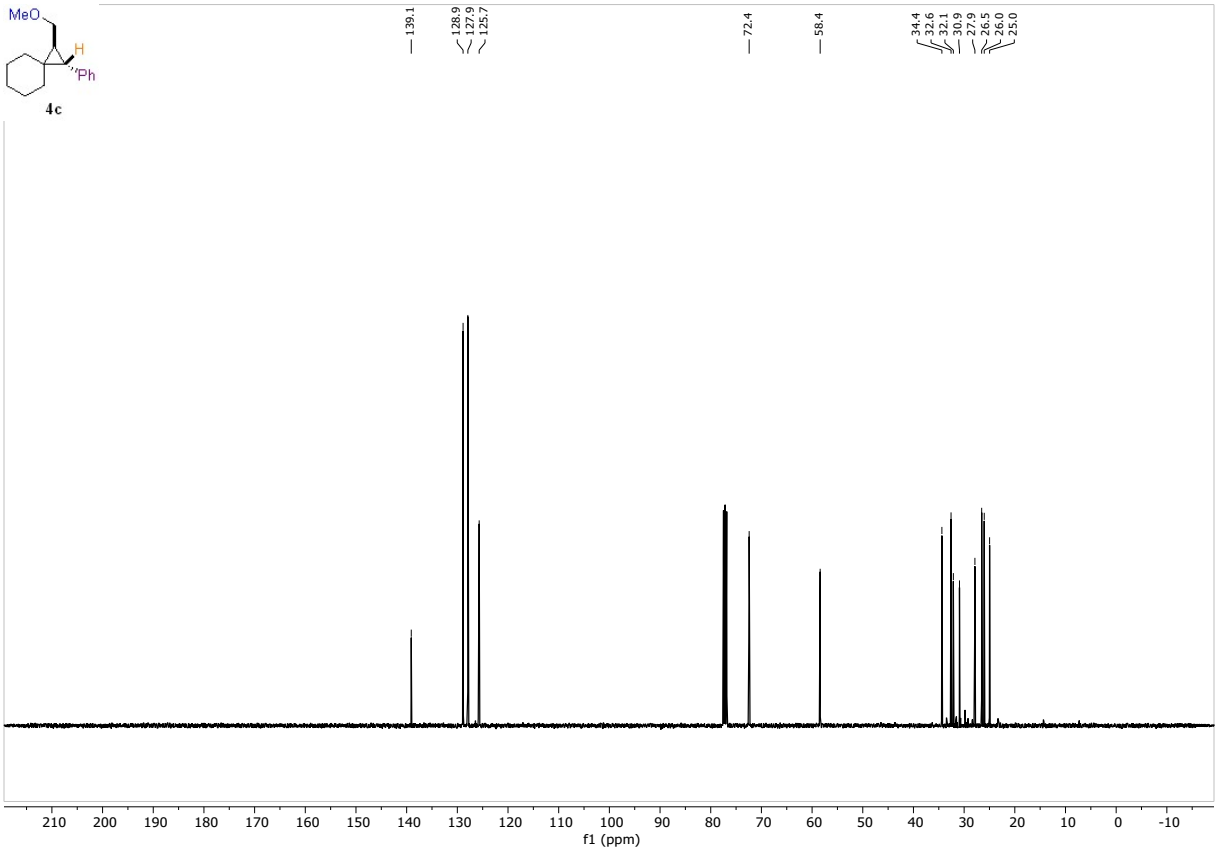
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4b**.



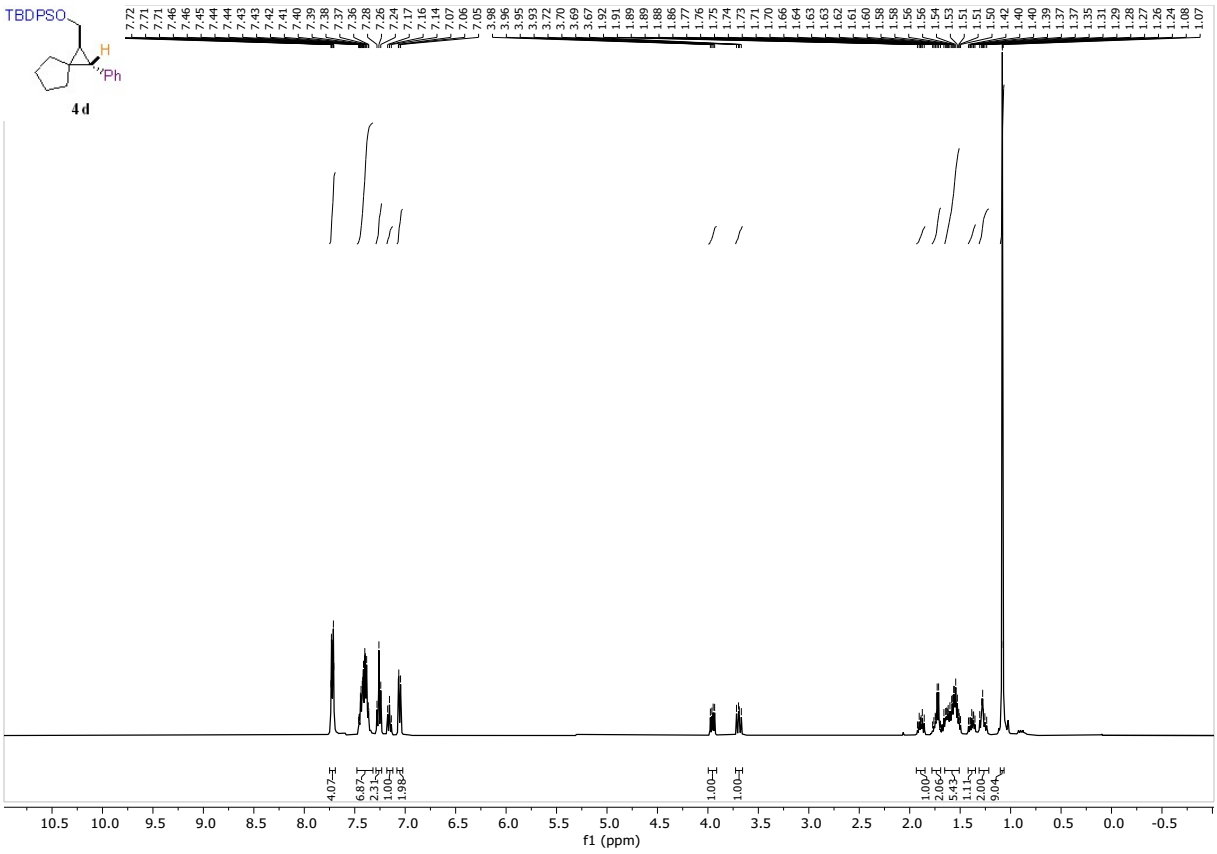
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4b**.



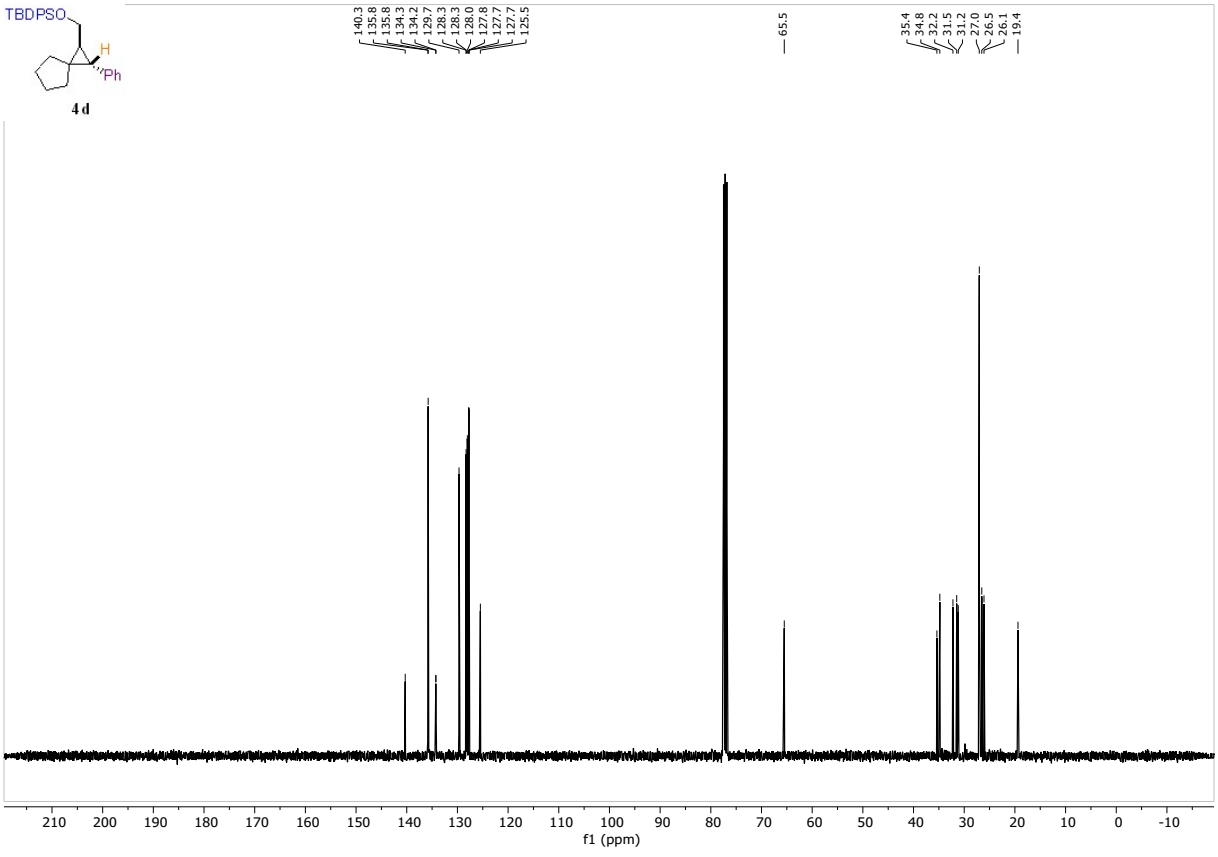
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4c**.



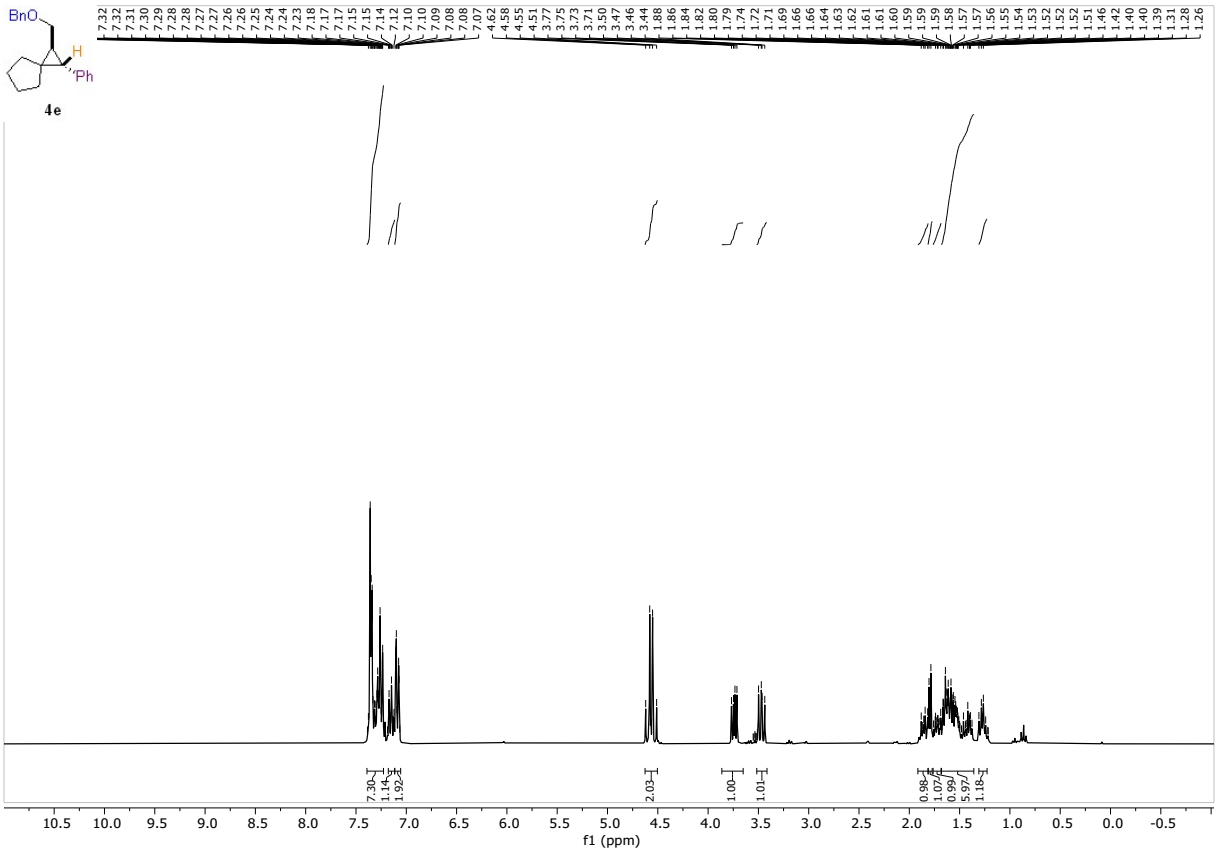
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4c**.



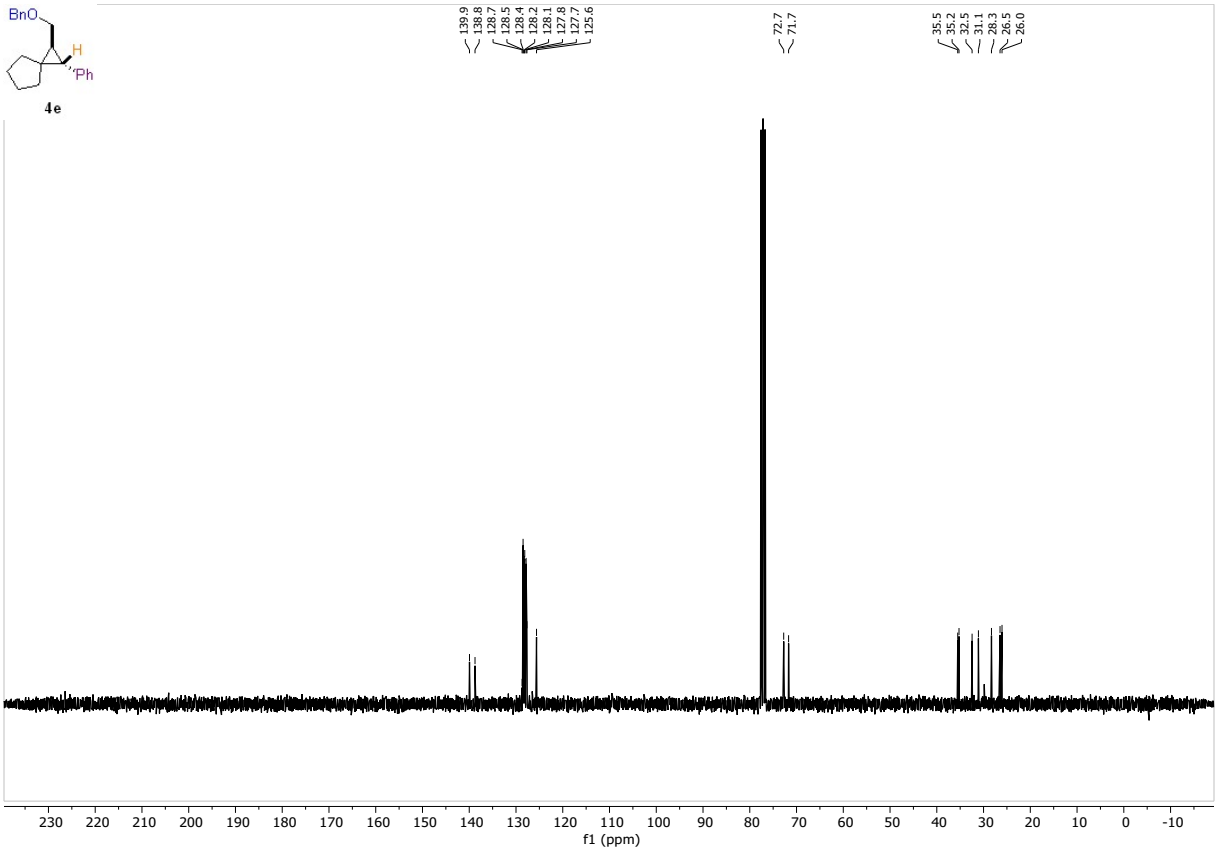
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4d**.



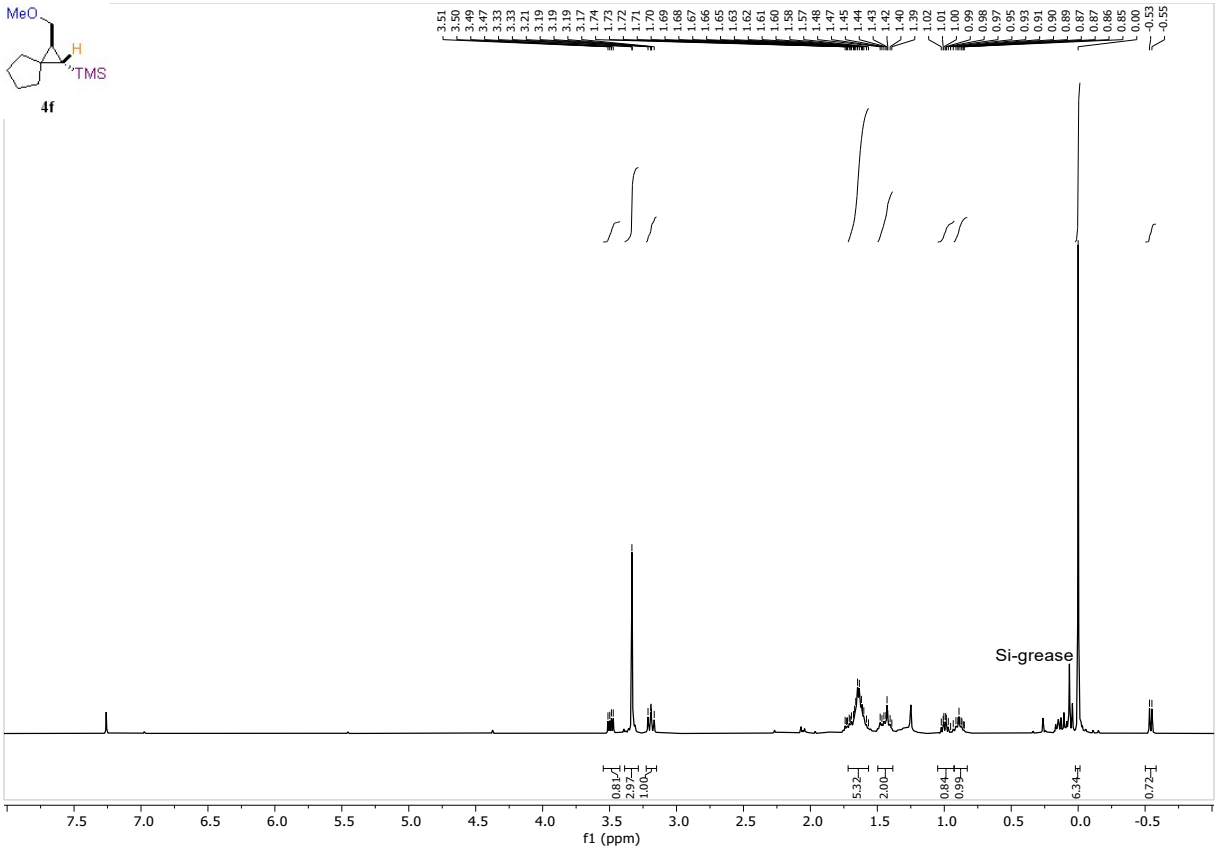
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4d**.



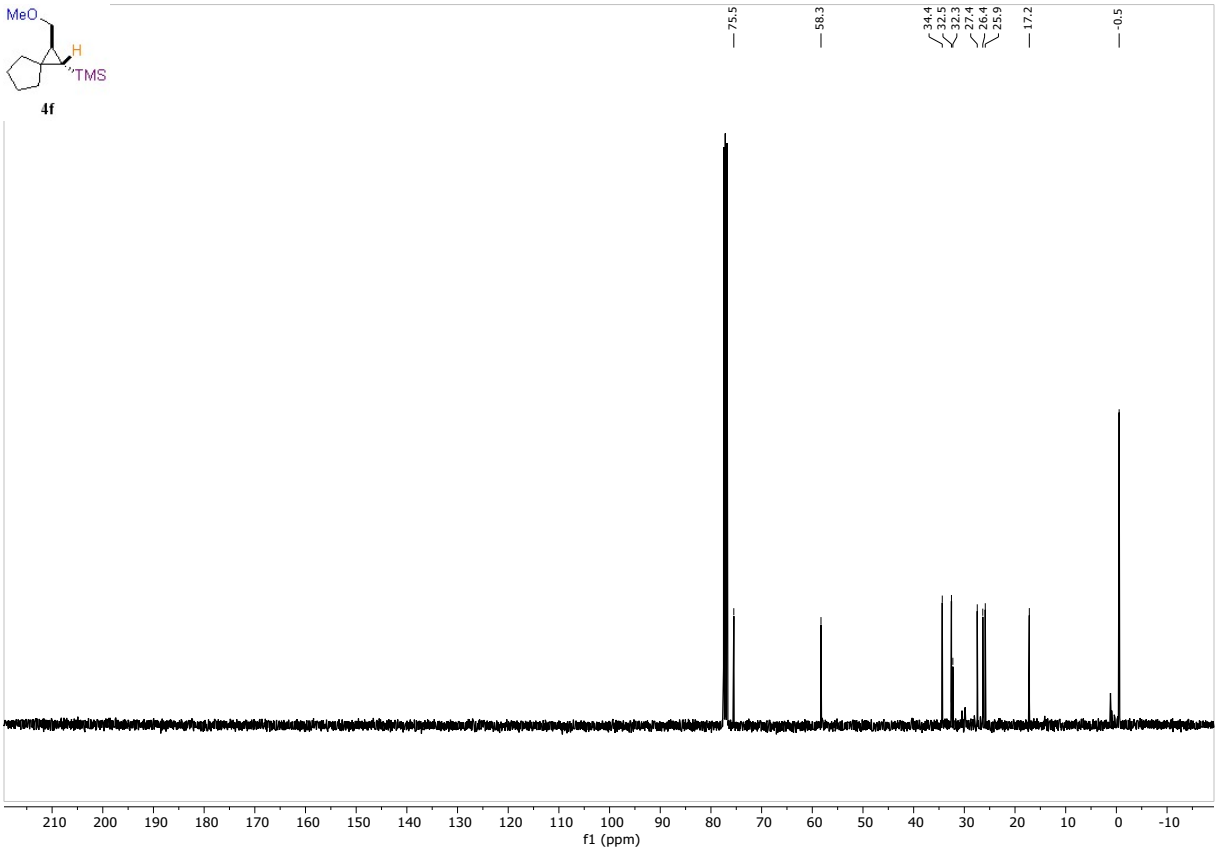
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4e**.



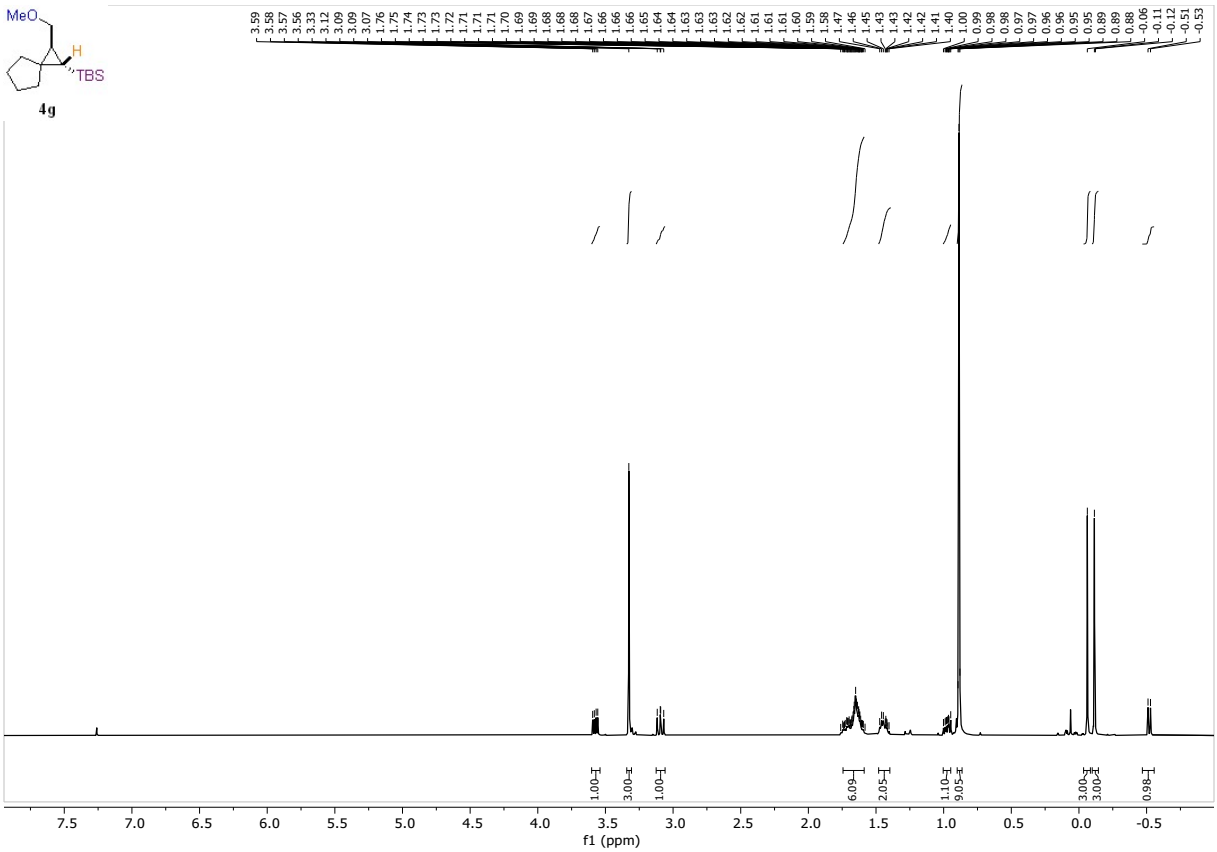
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4e**.



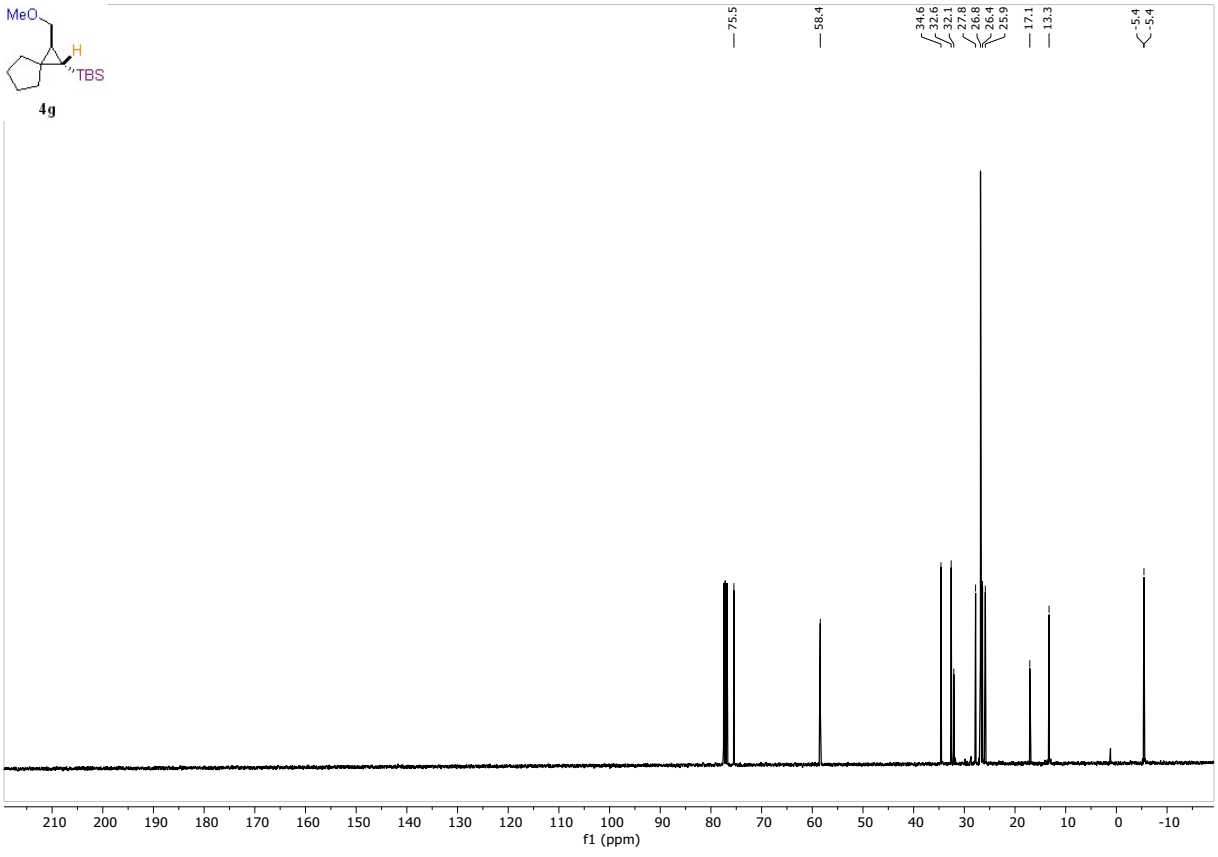
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4f**.



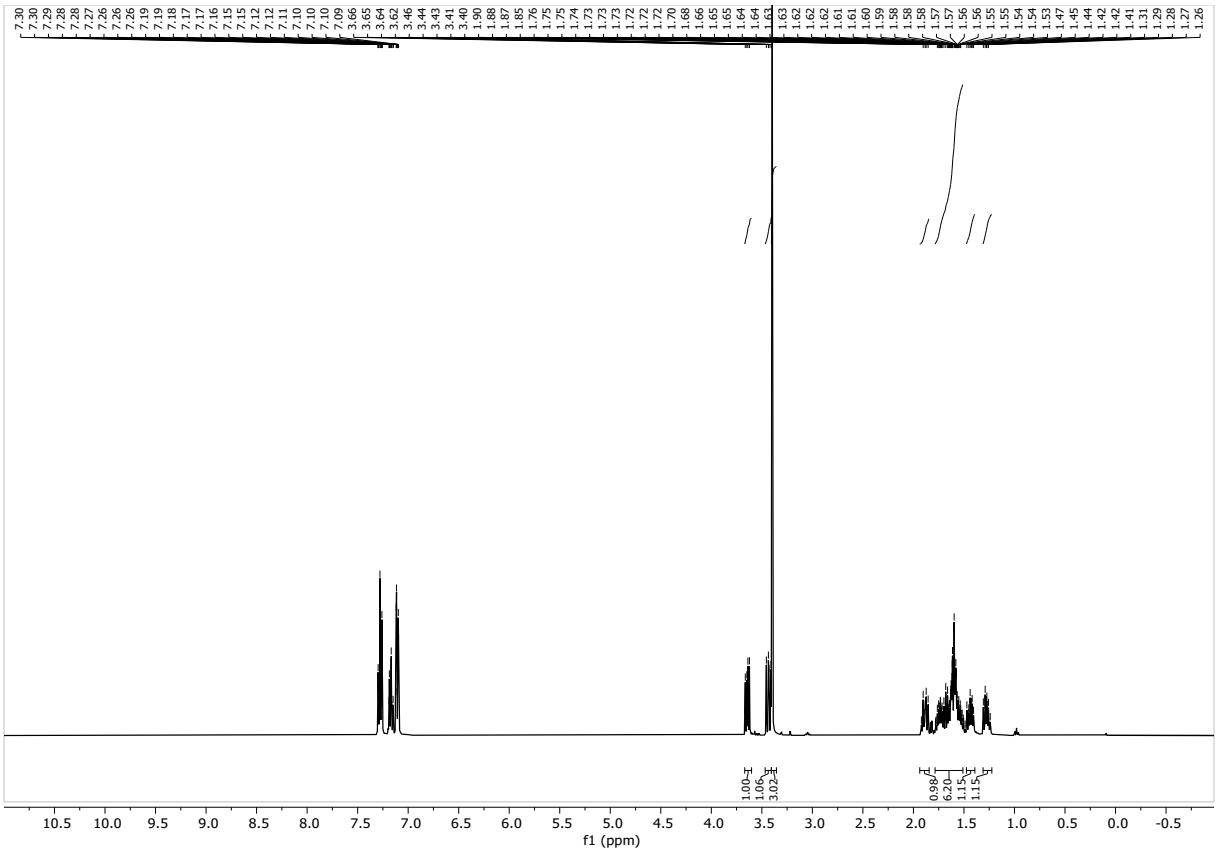
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4f**.



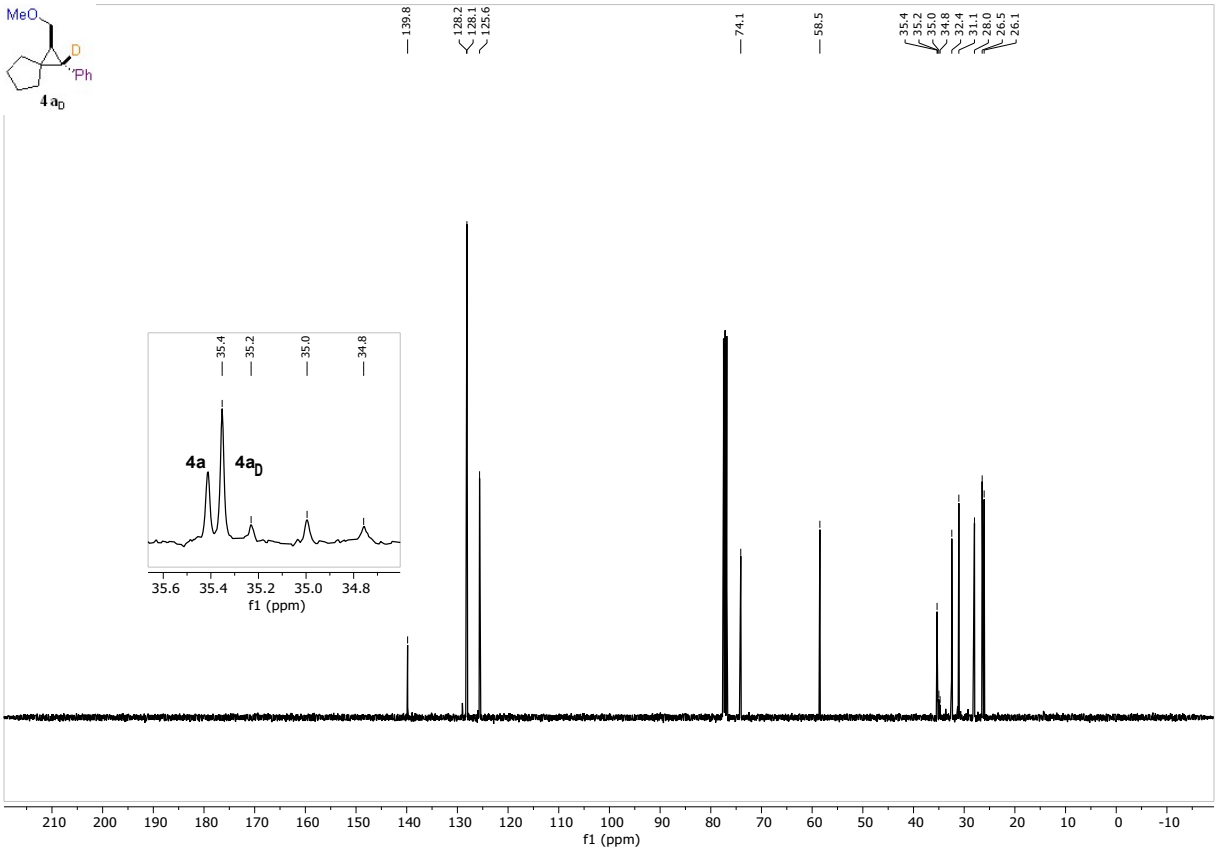
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4g**.



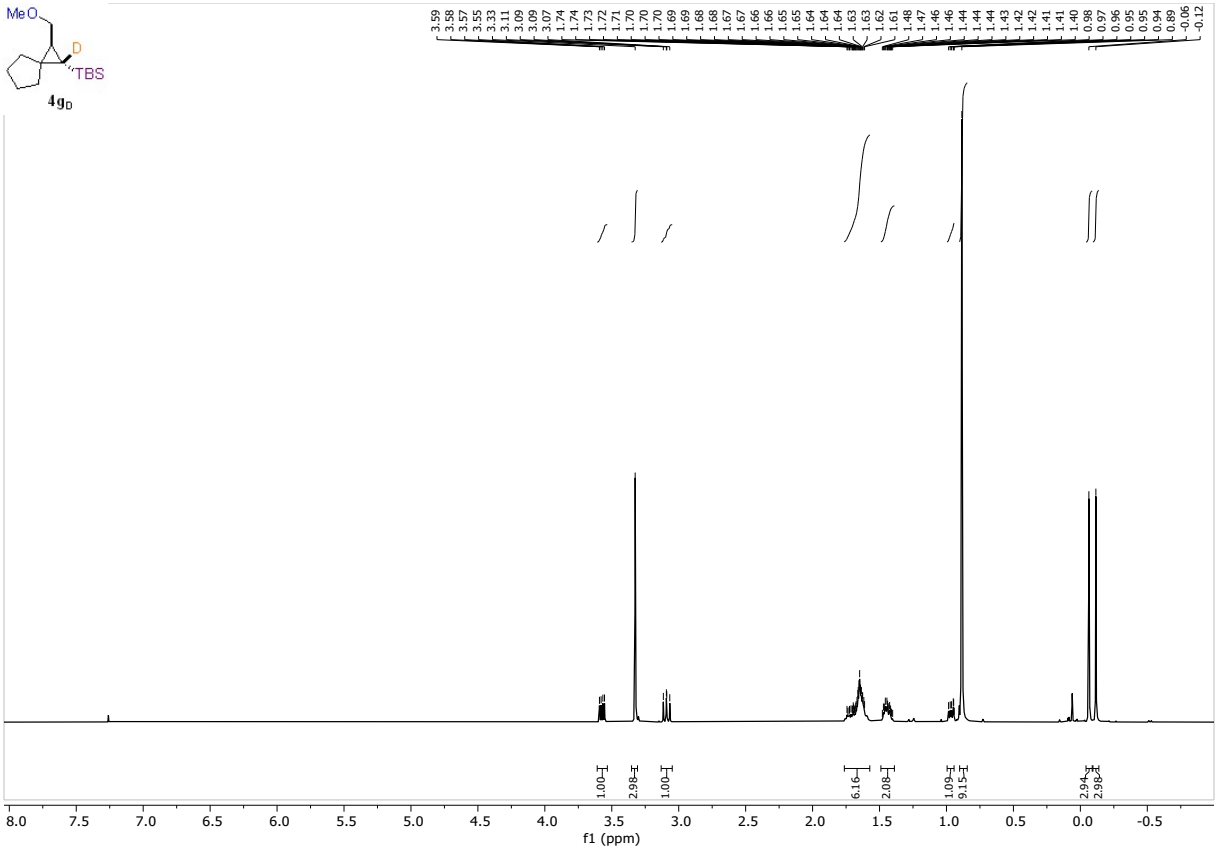
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4g**.



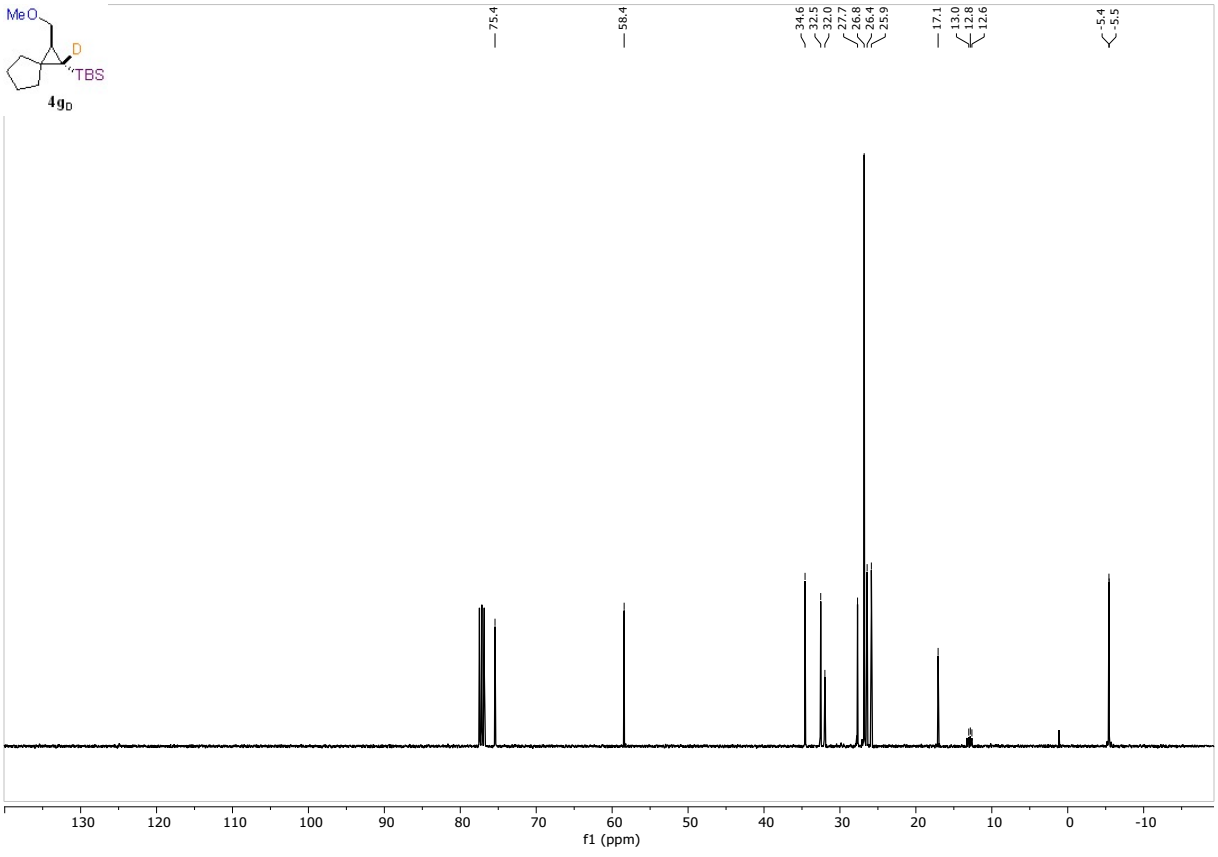
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4a$_D$**.



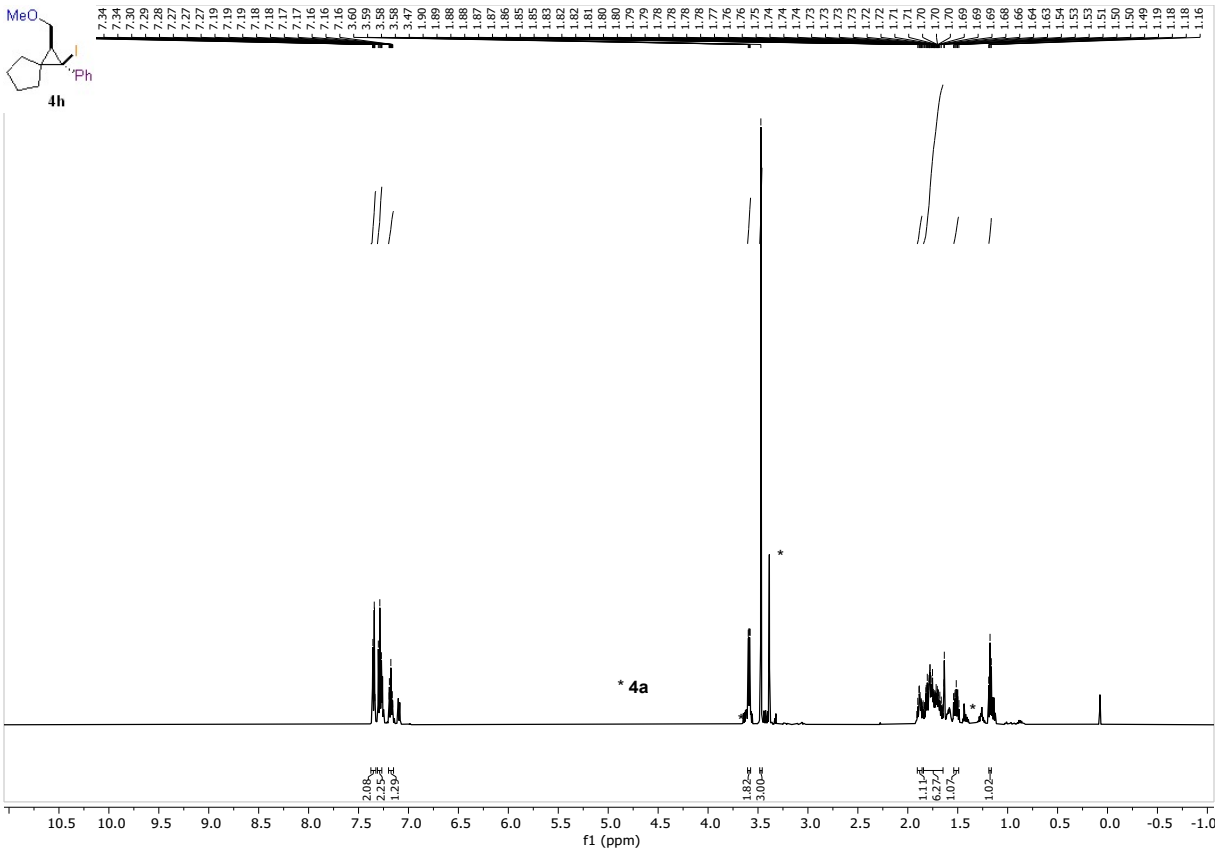
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4a$_D$**.



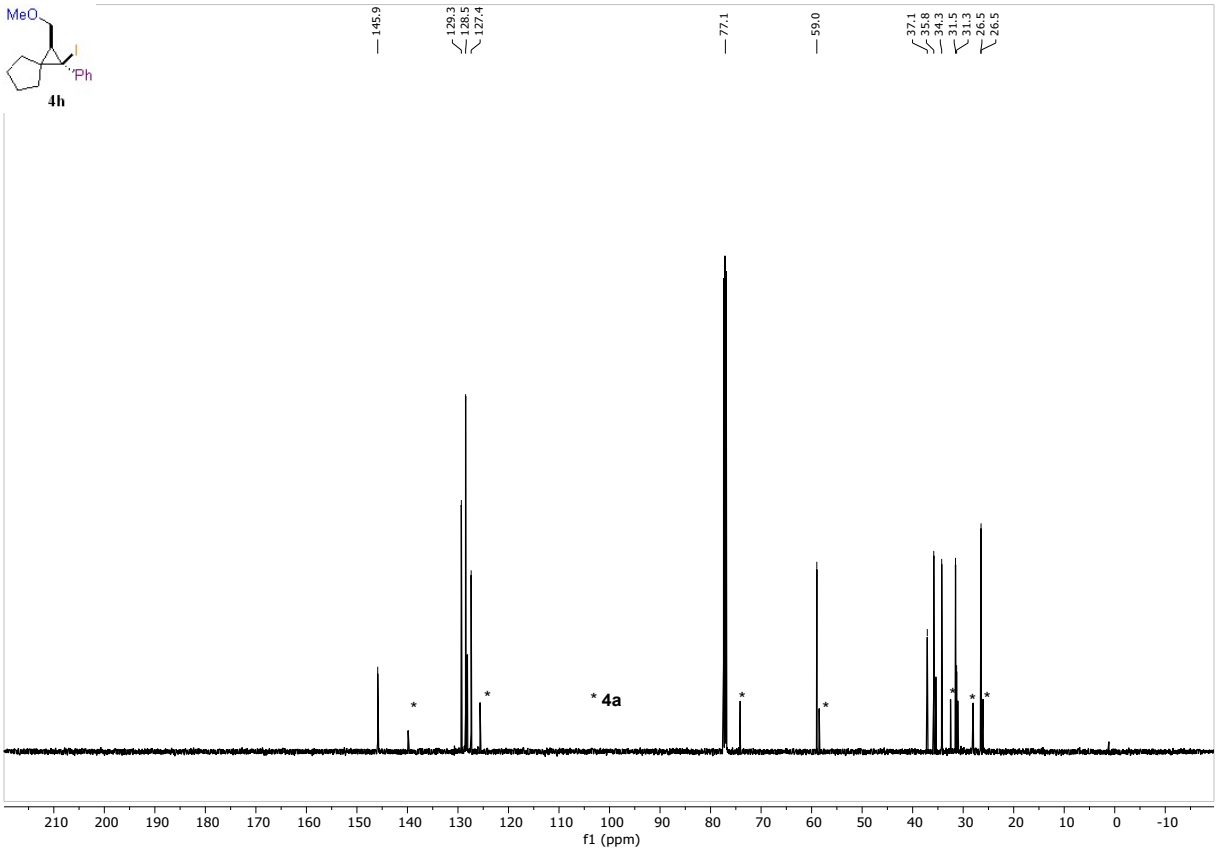
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **$4g_D$**.



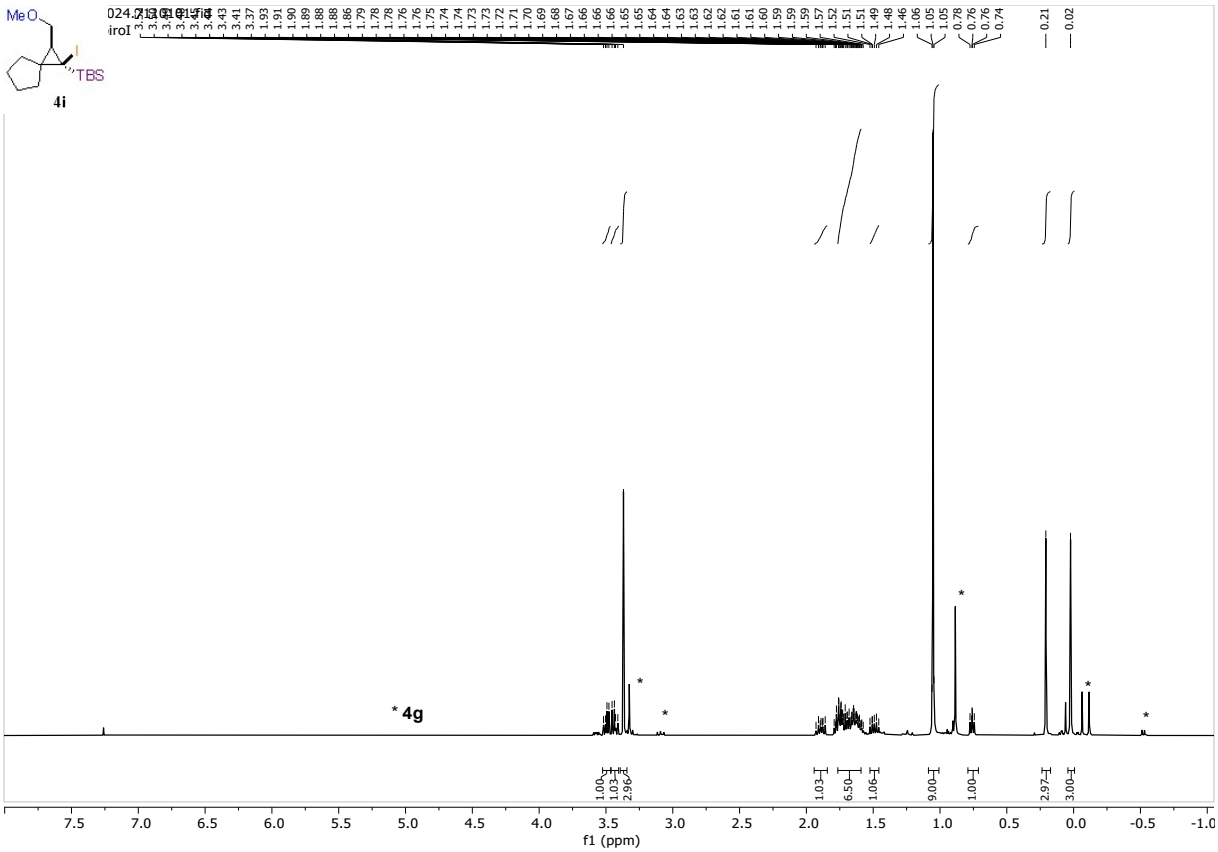
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **$4g_D$**.



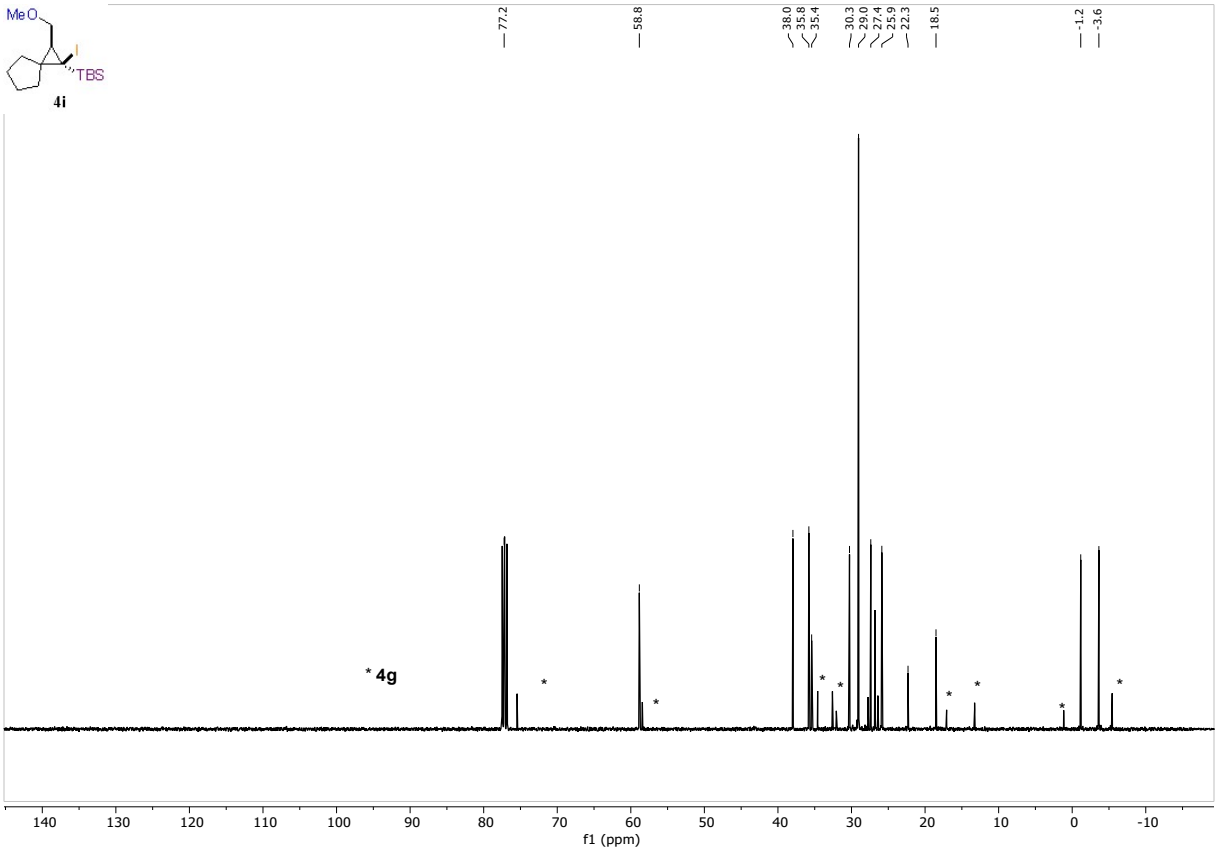
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4h**.



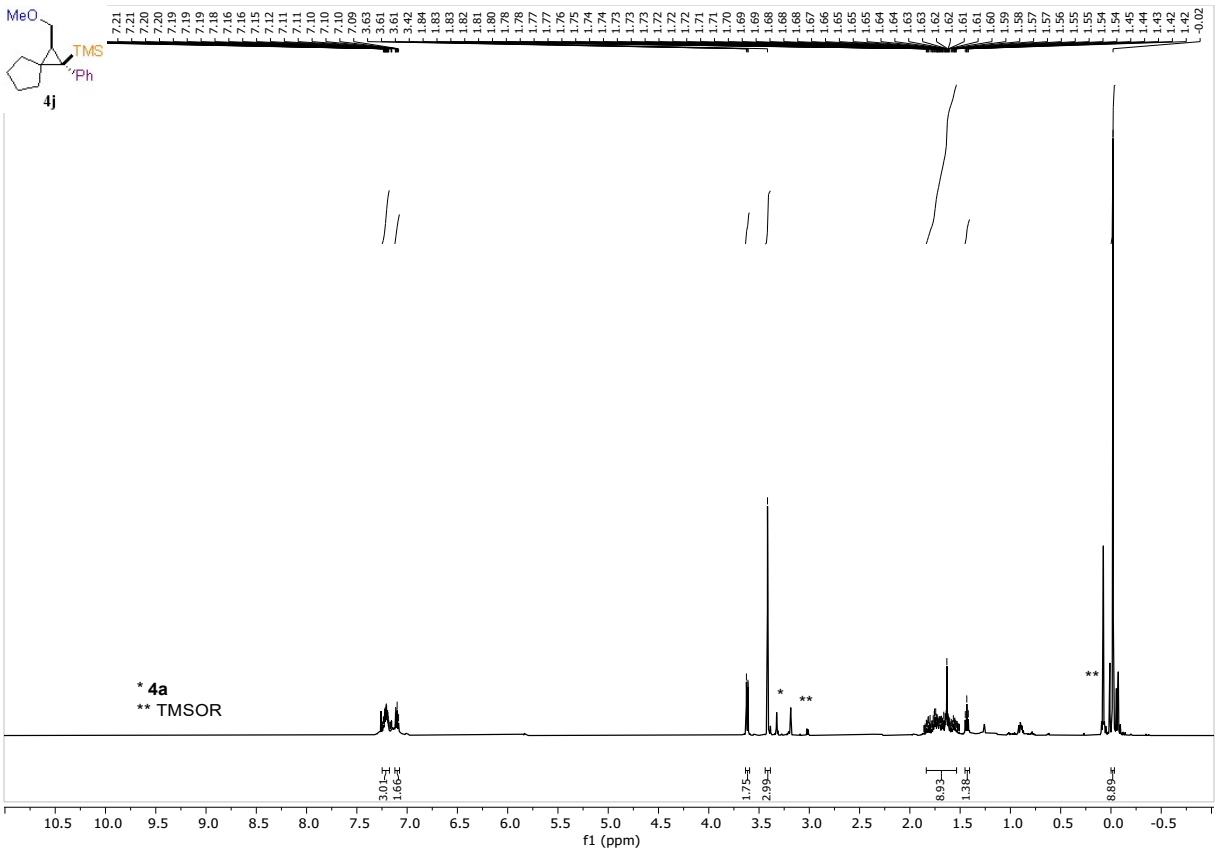
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4h**.



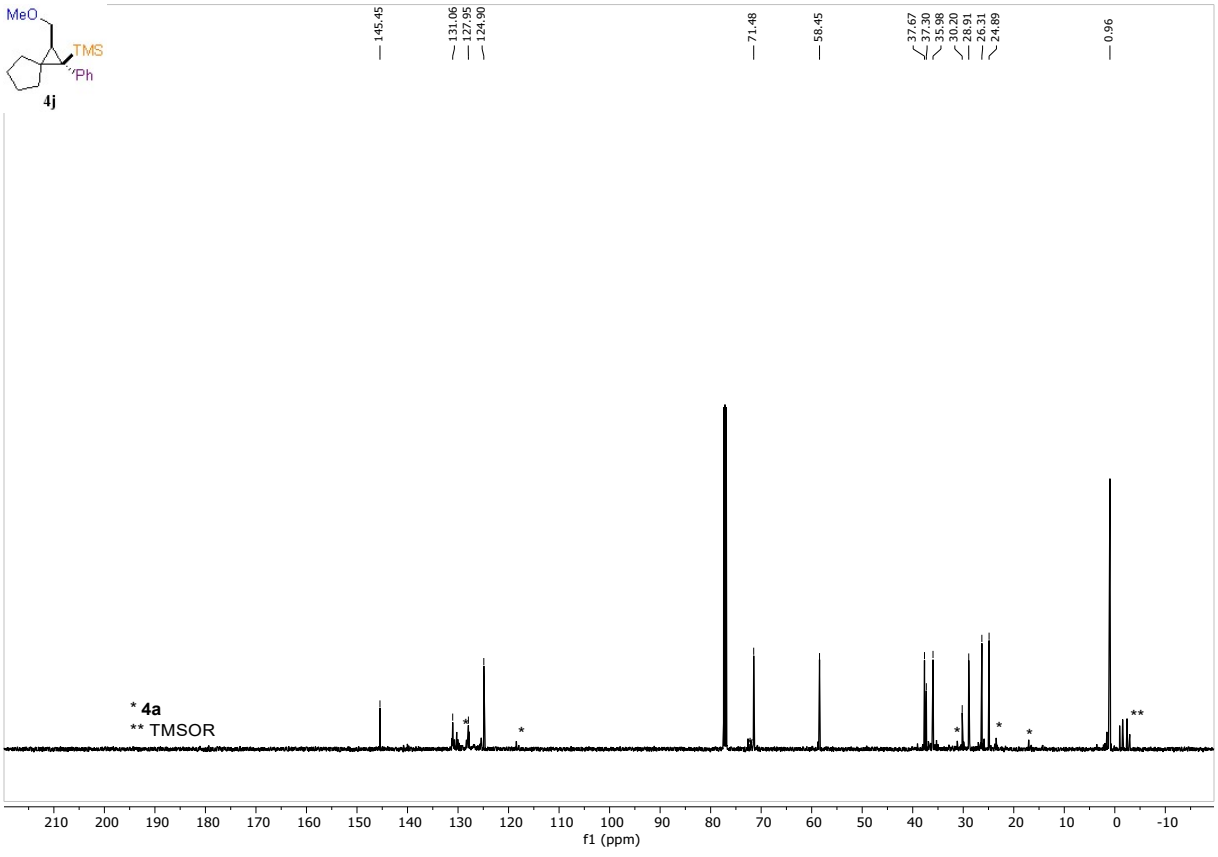
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4i**.



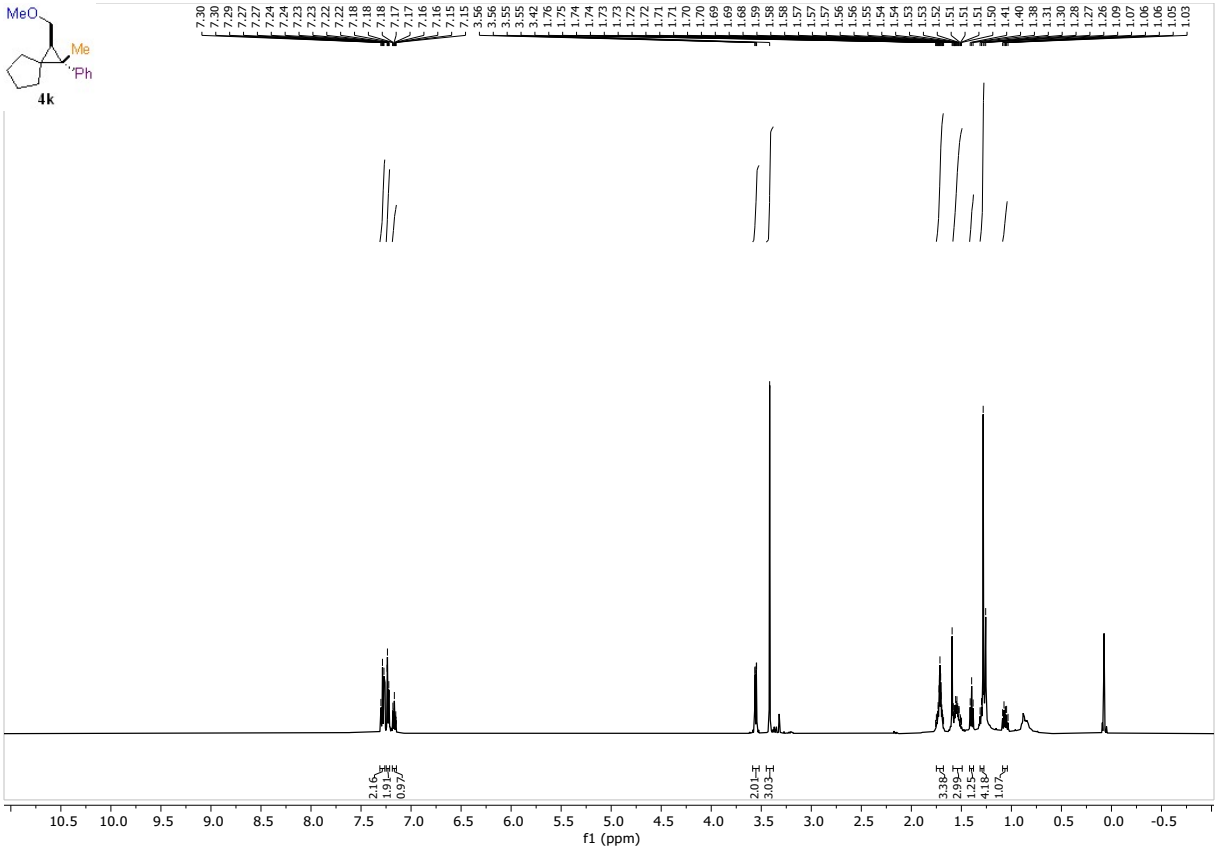
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4i**.



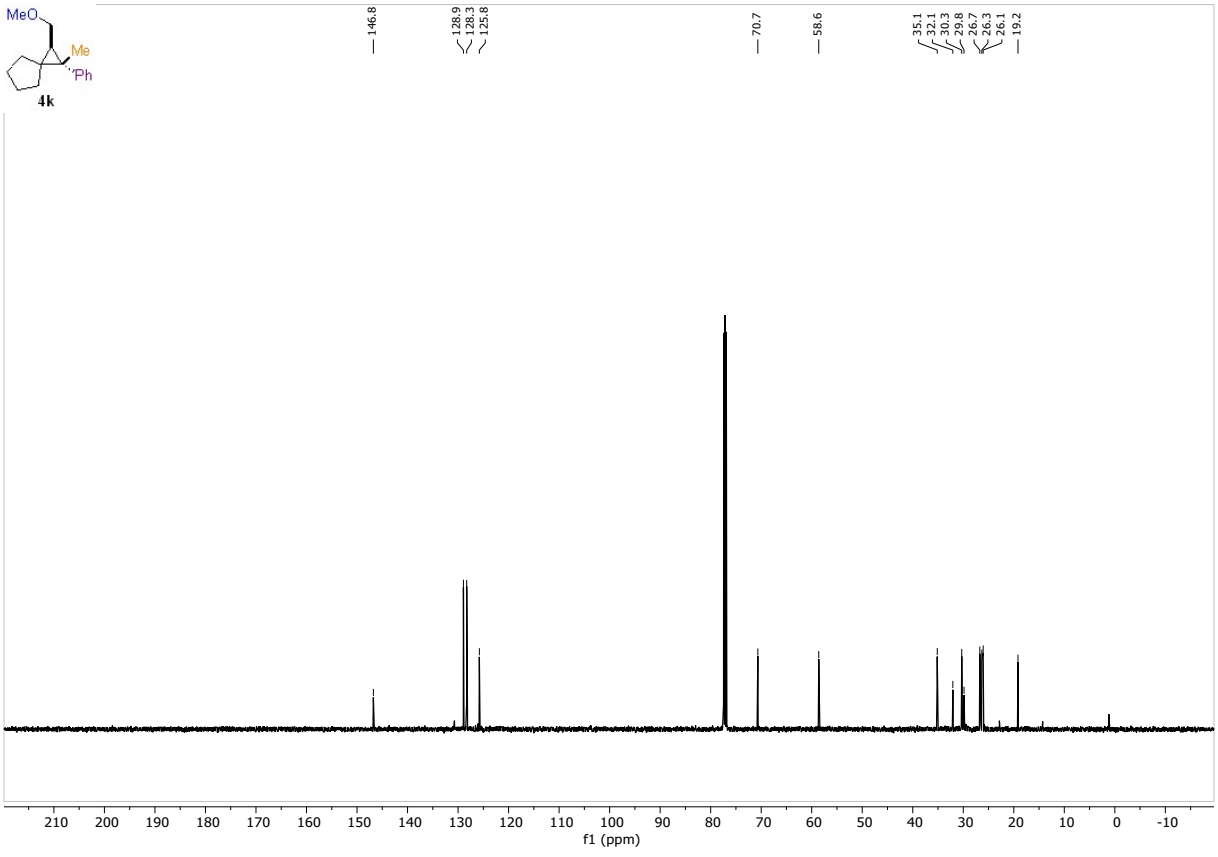
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4j**.



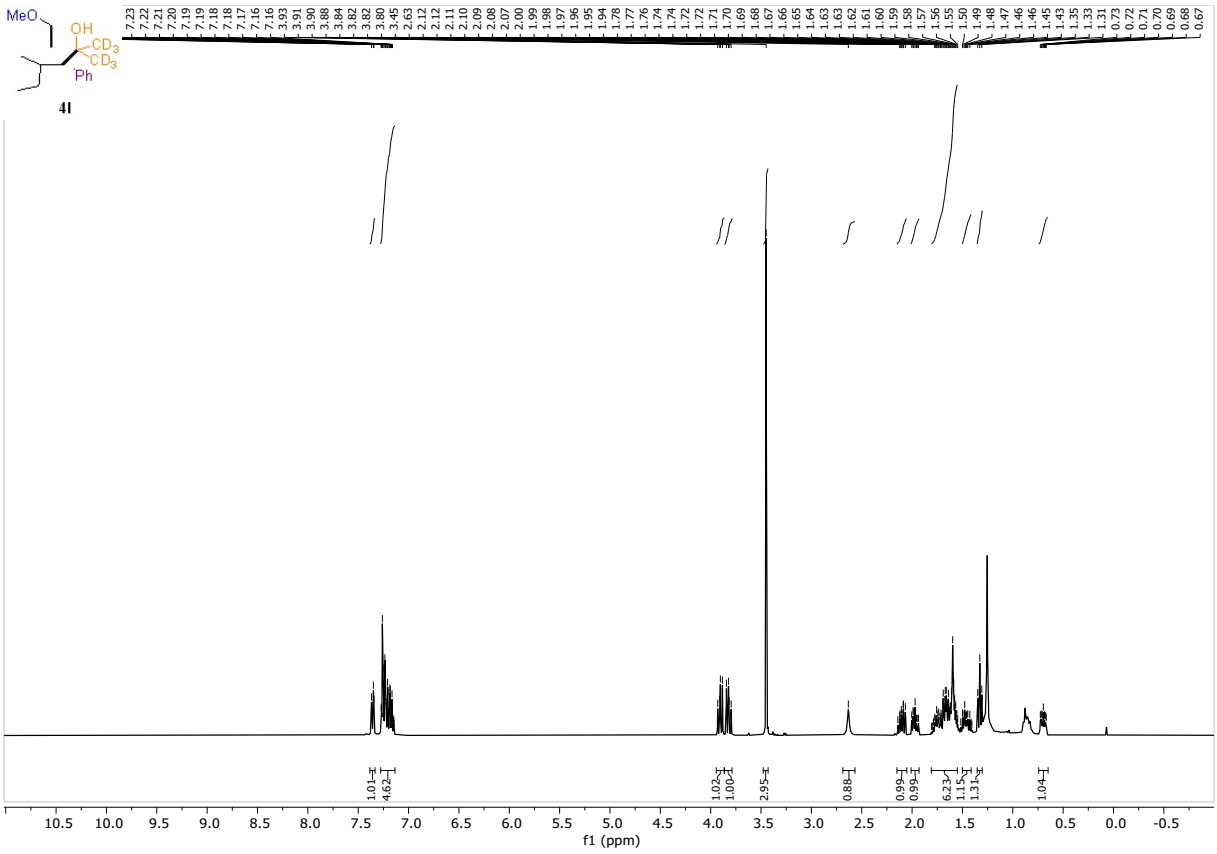
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4j**.



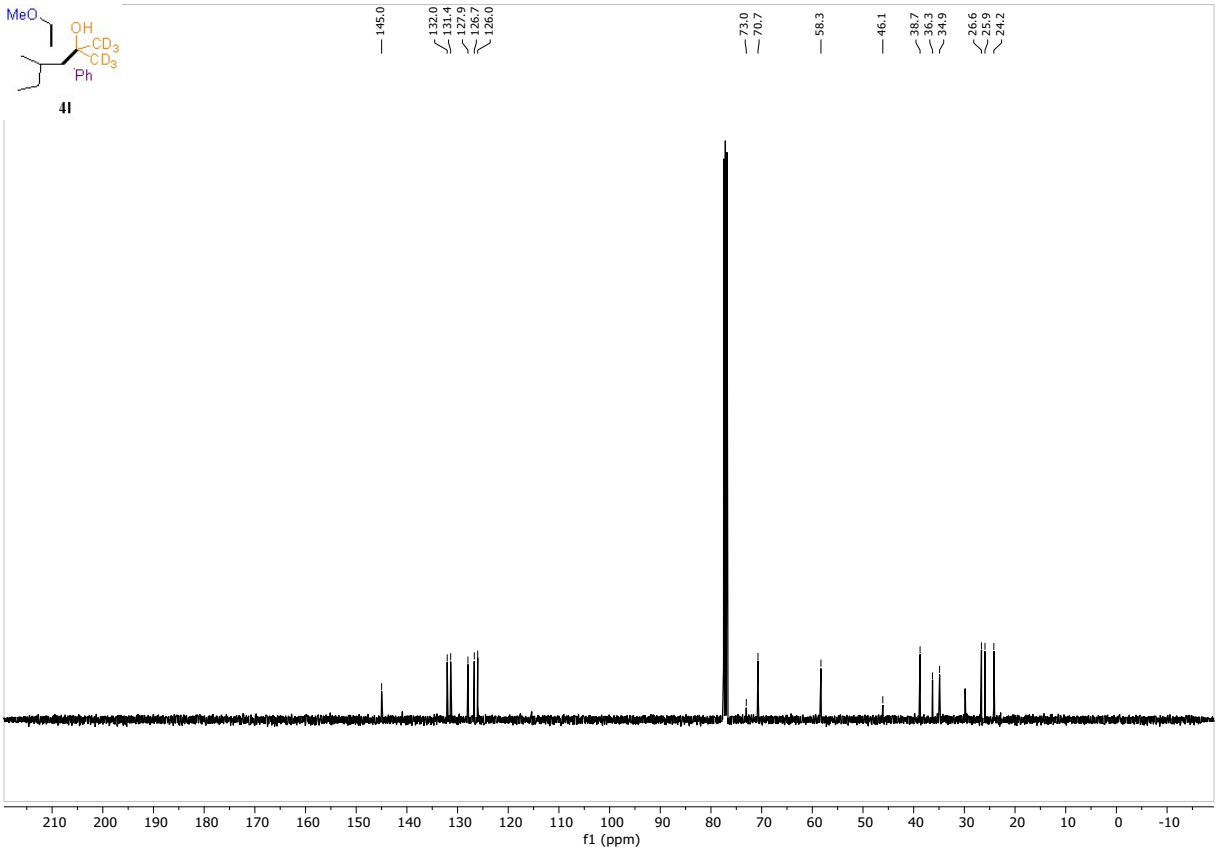
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4k**.



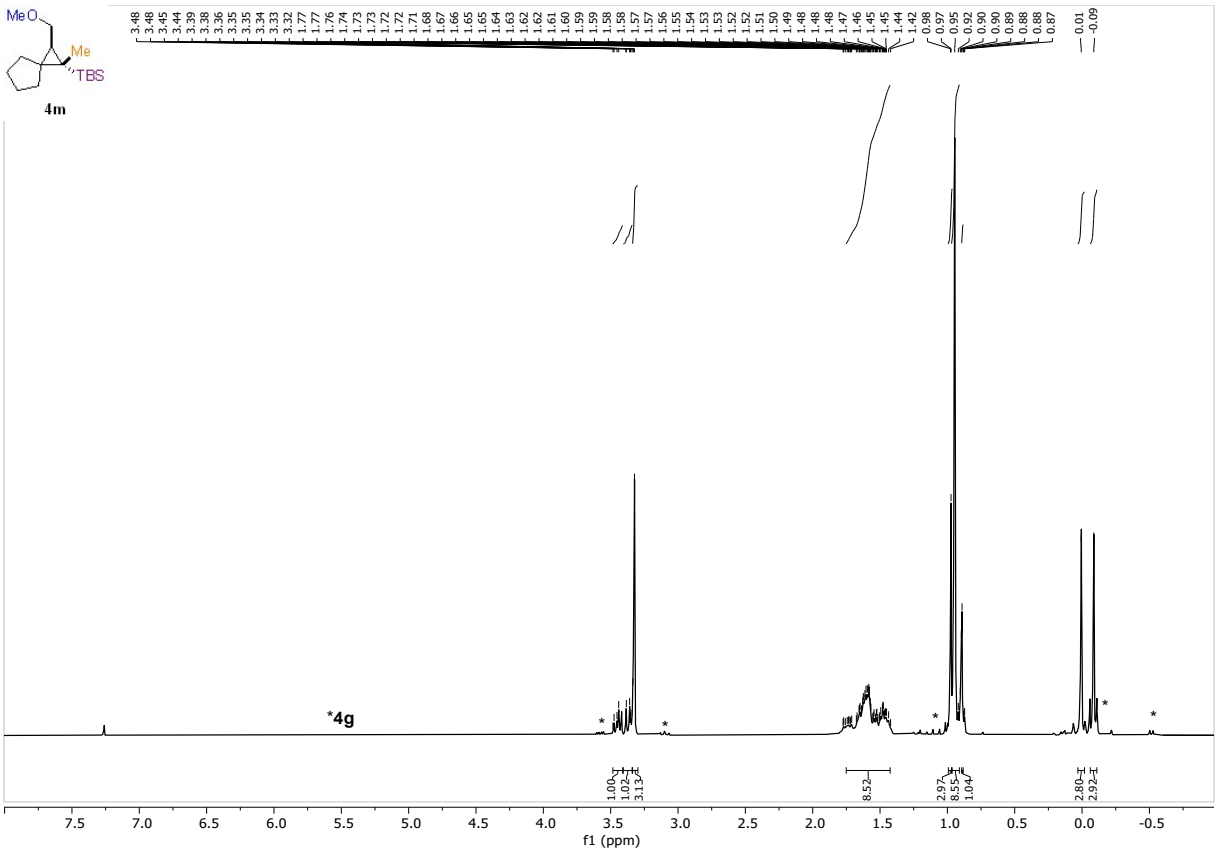
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4k**.



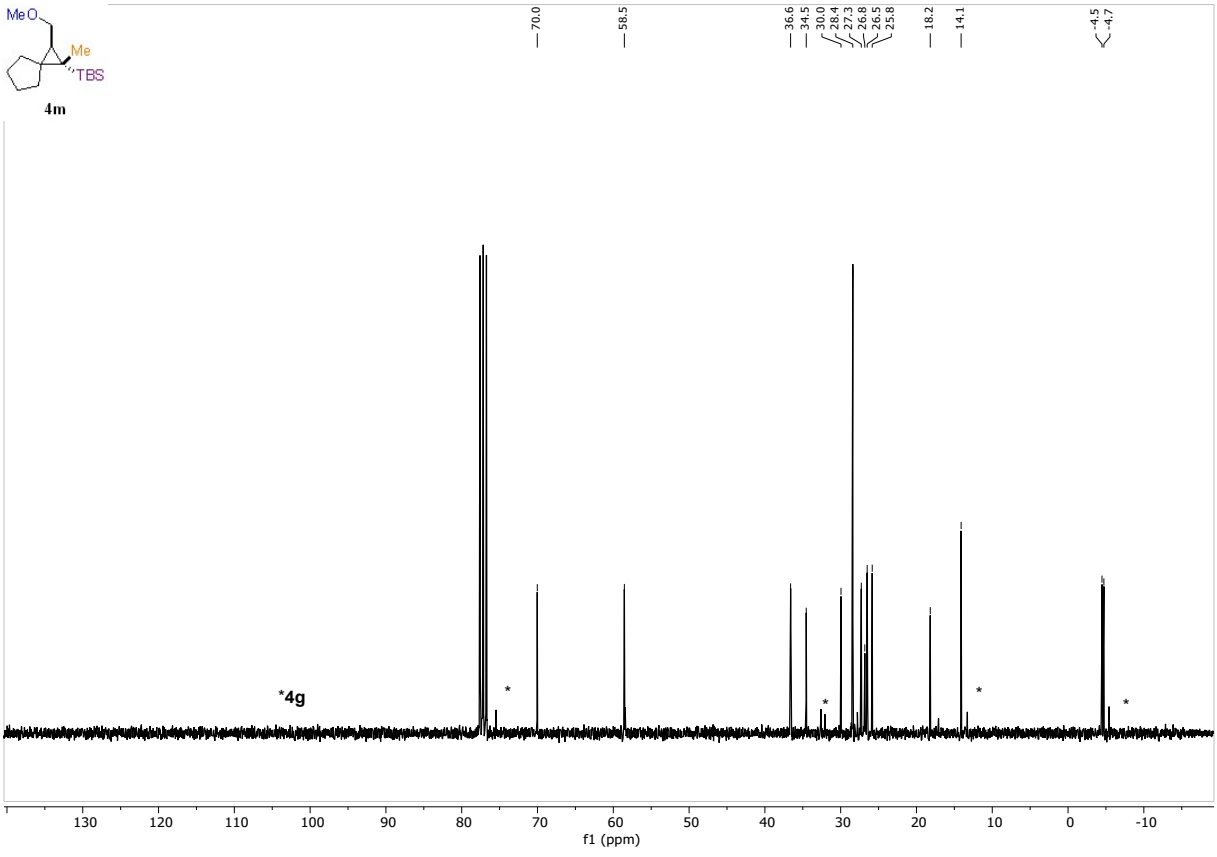
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4l**.



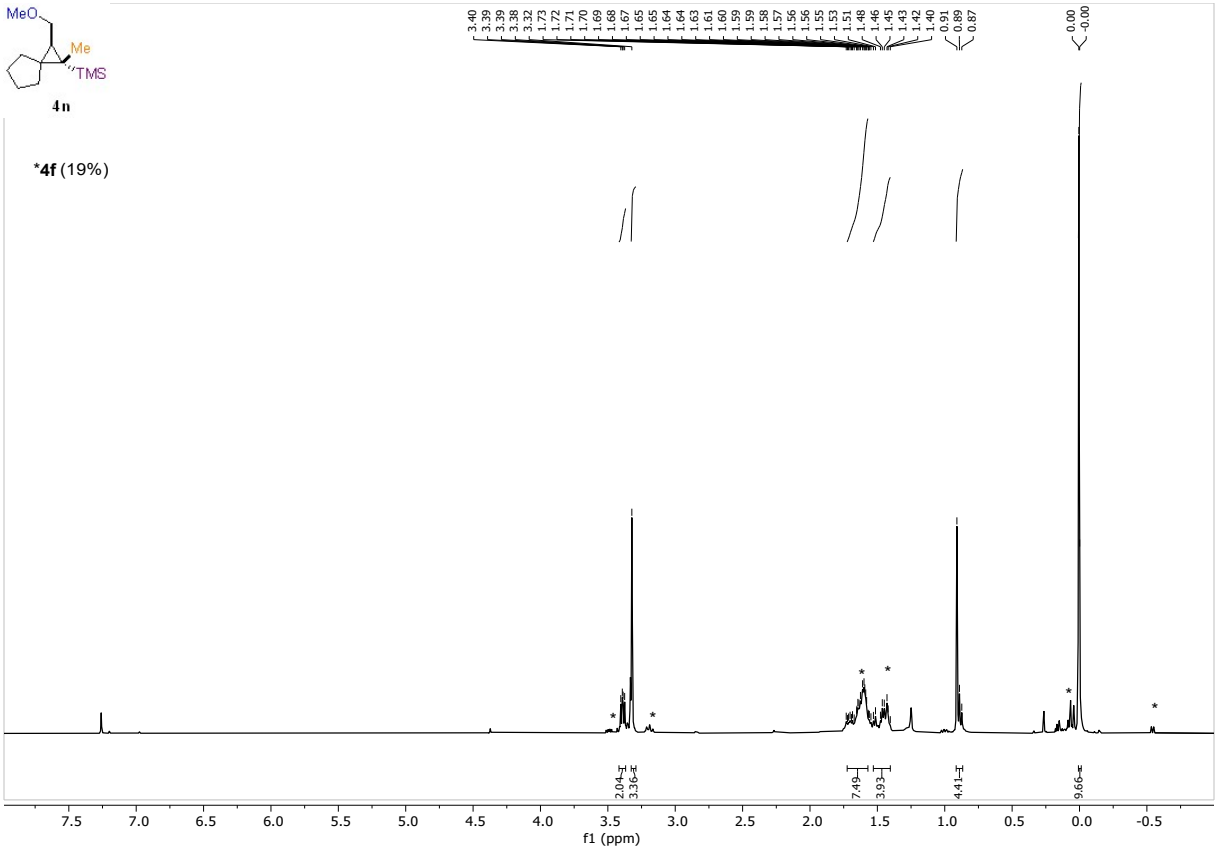
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4l**.



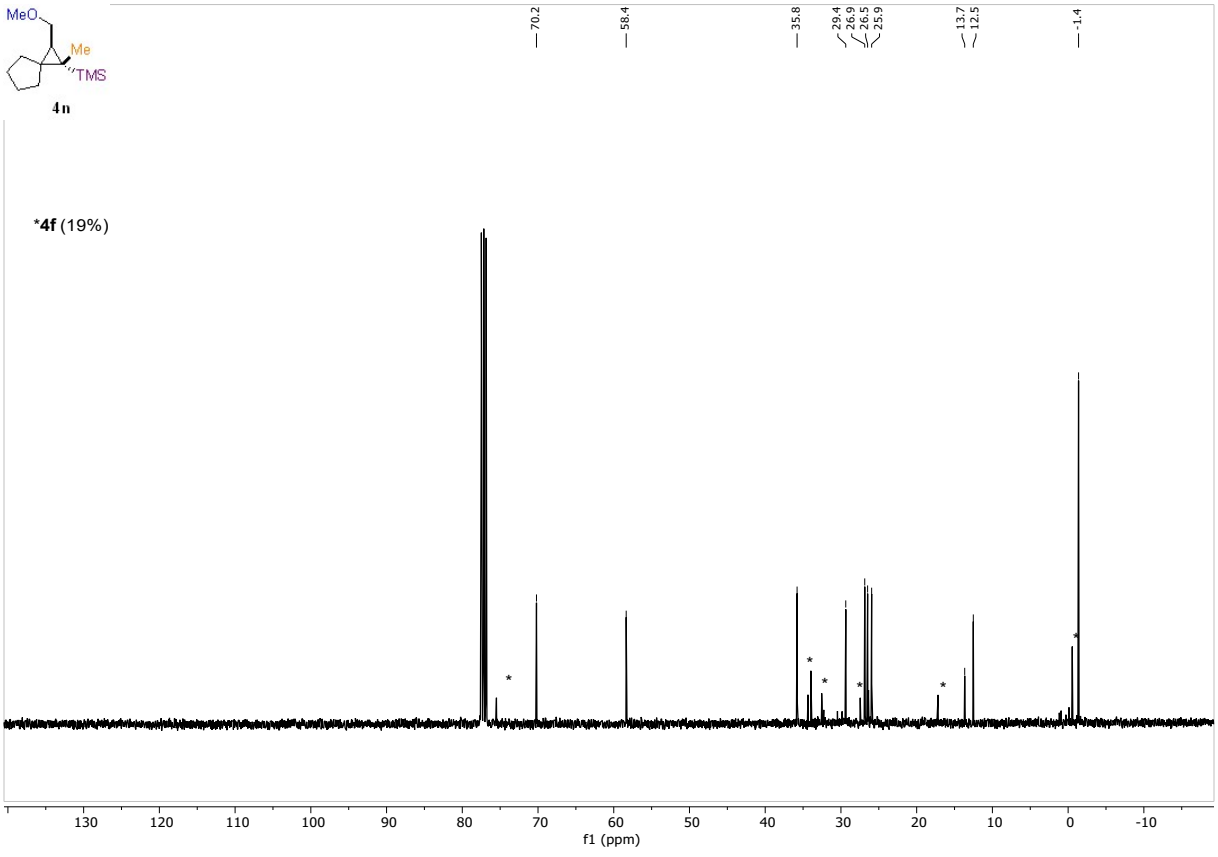
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4m**.



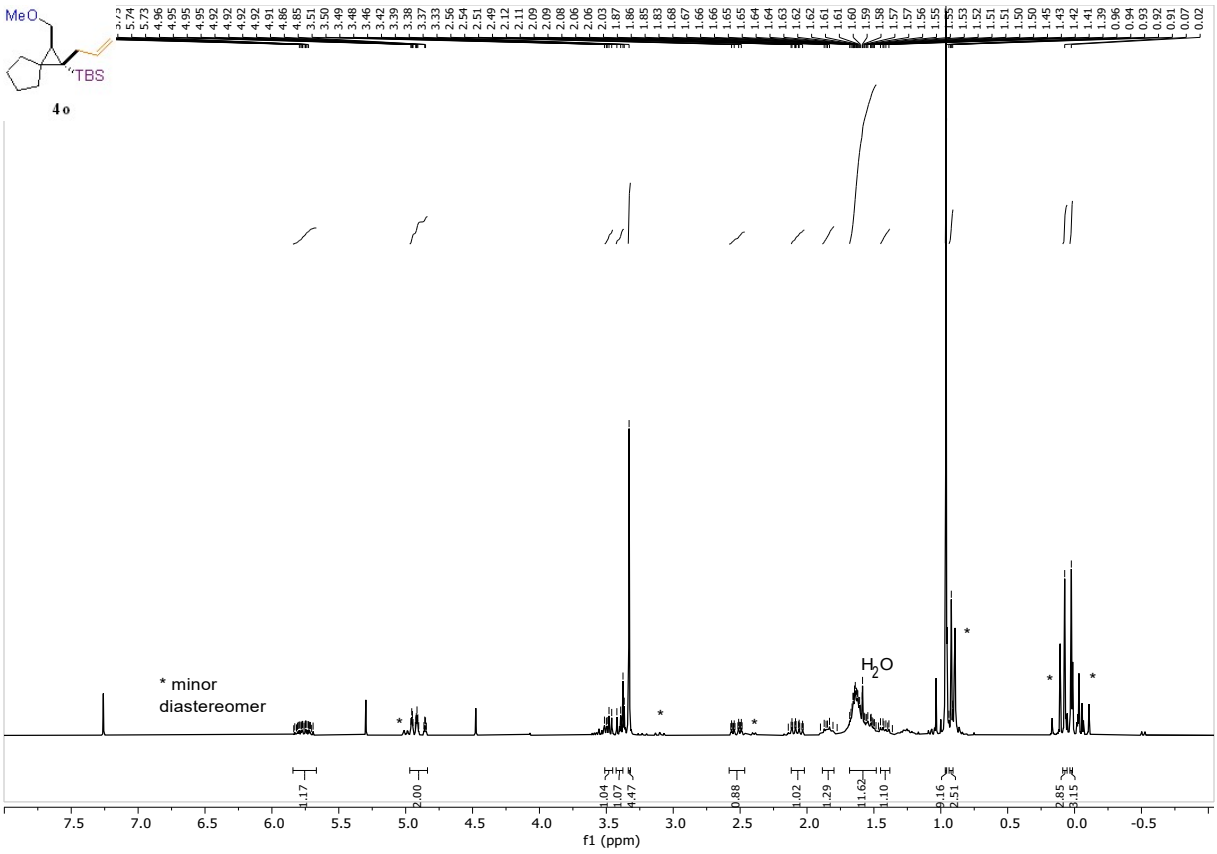
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4m**.



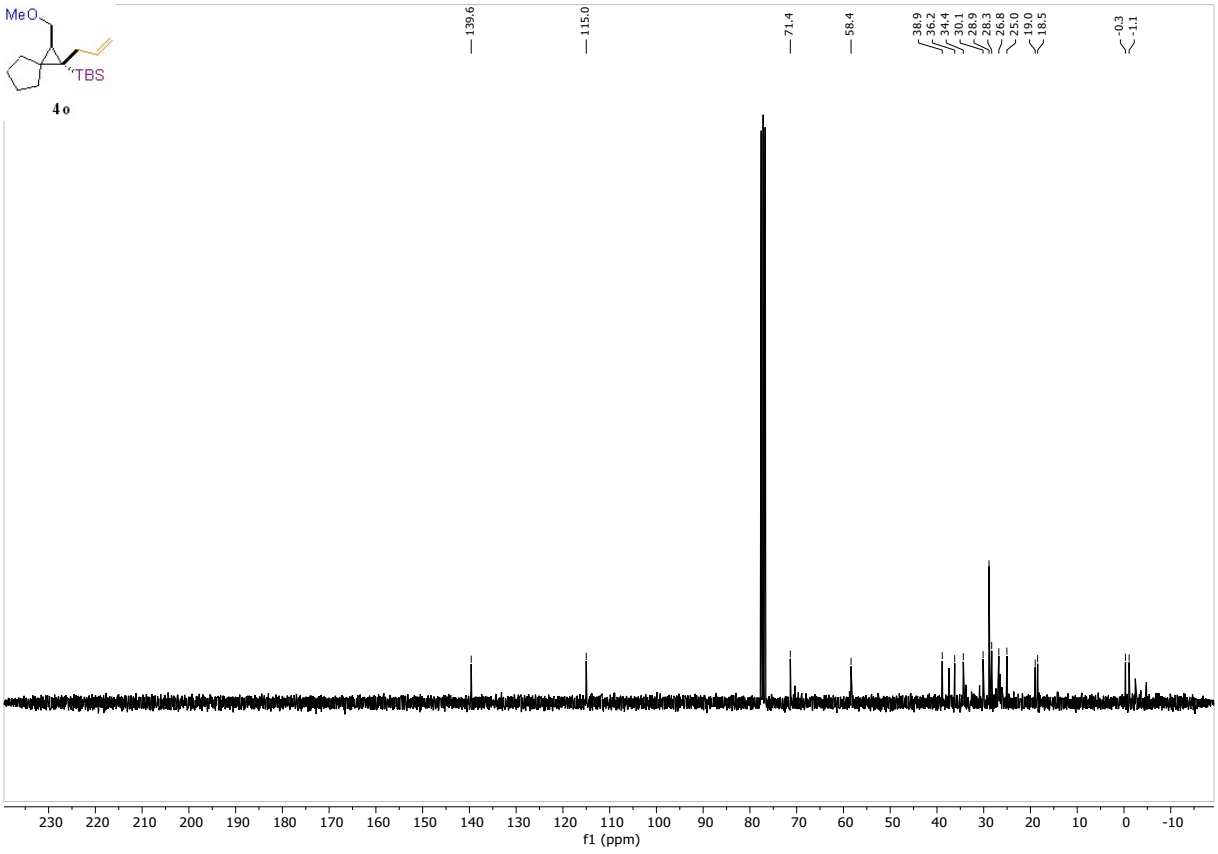
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4n**.



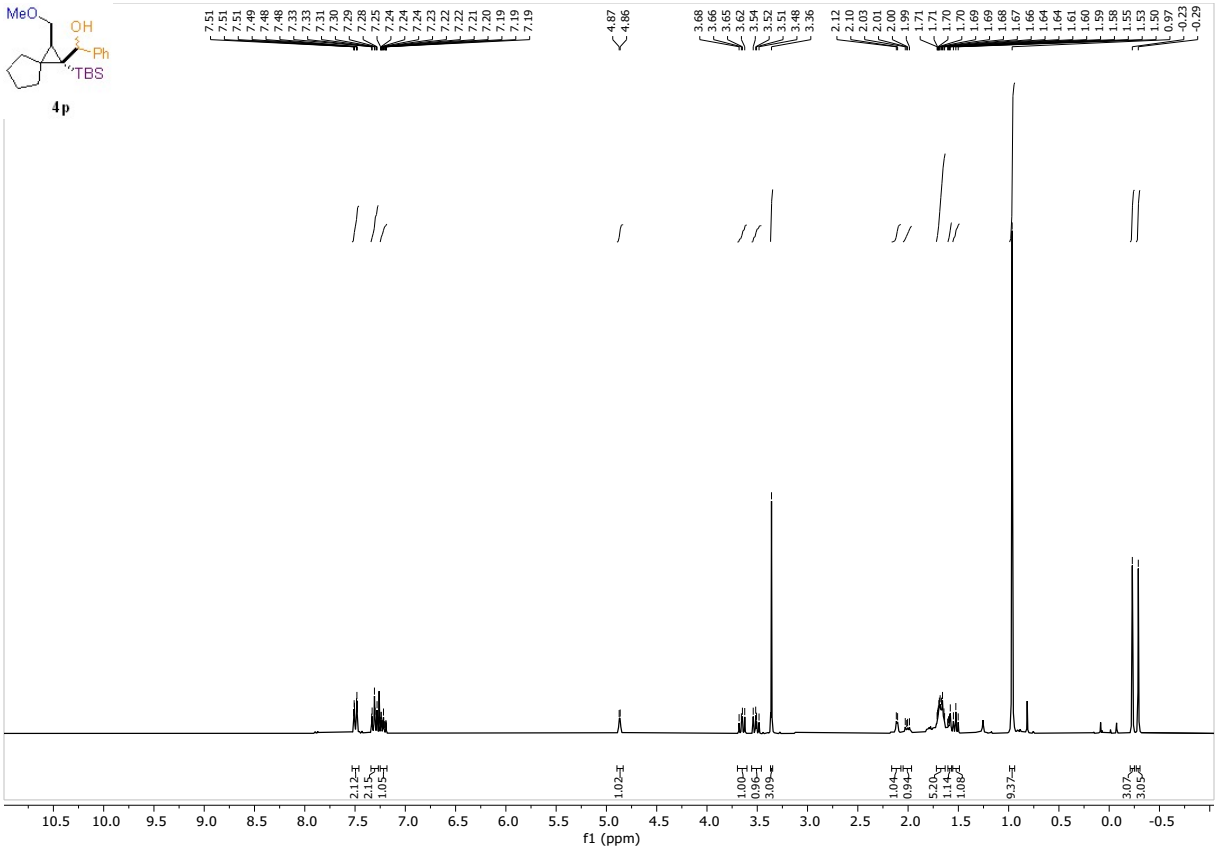
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4n** containing 19wt-% of compound **4f**.



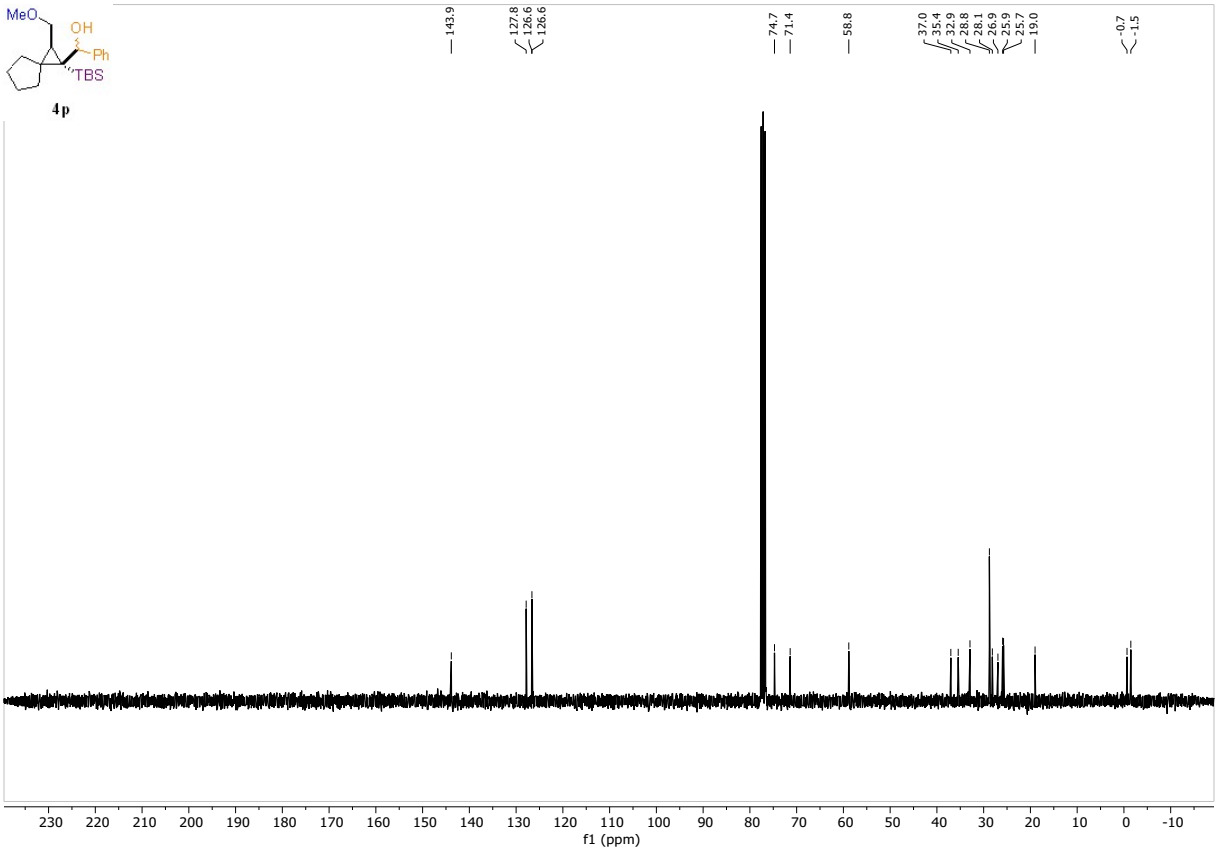
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4o**.



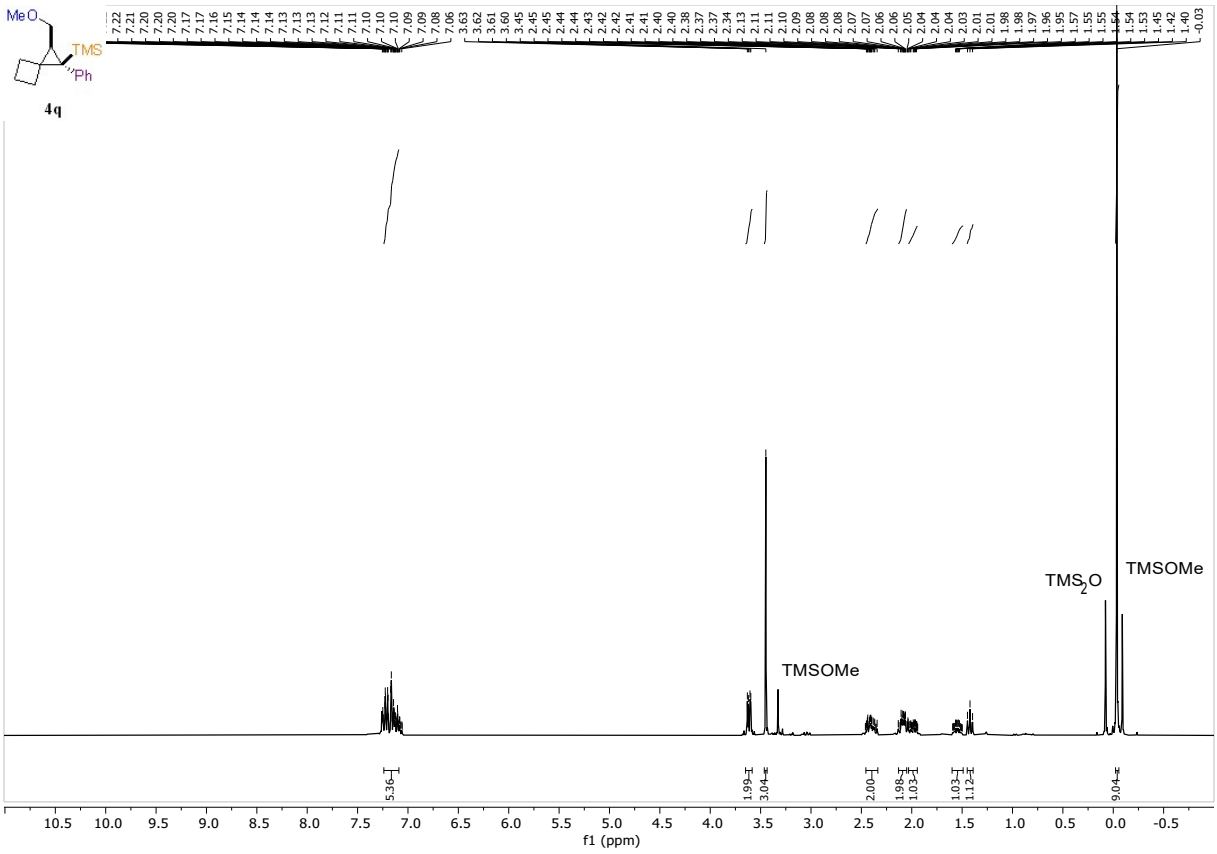
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4o**.



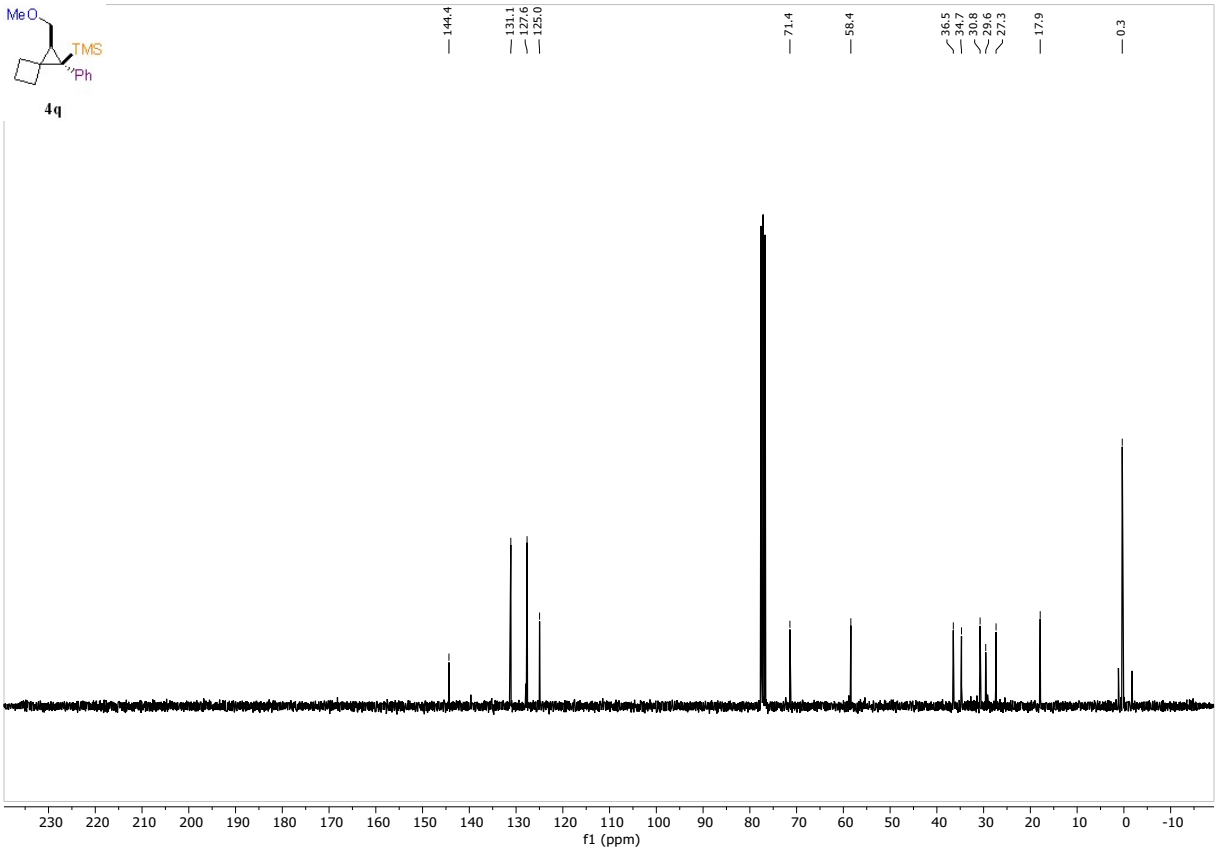
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4p**.



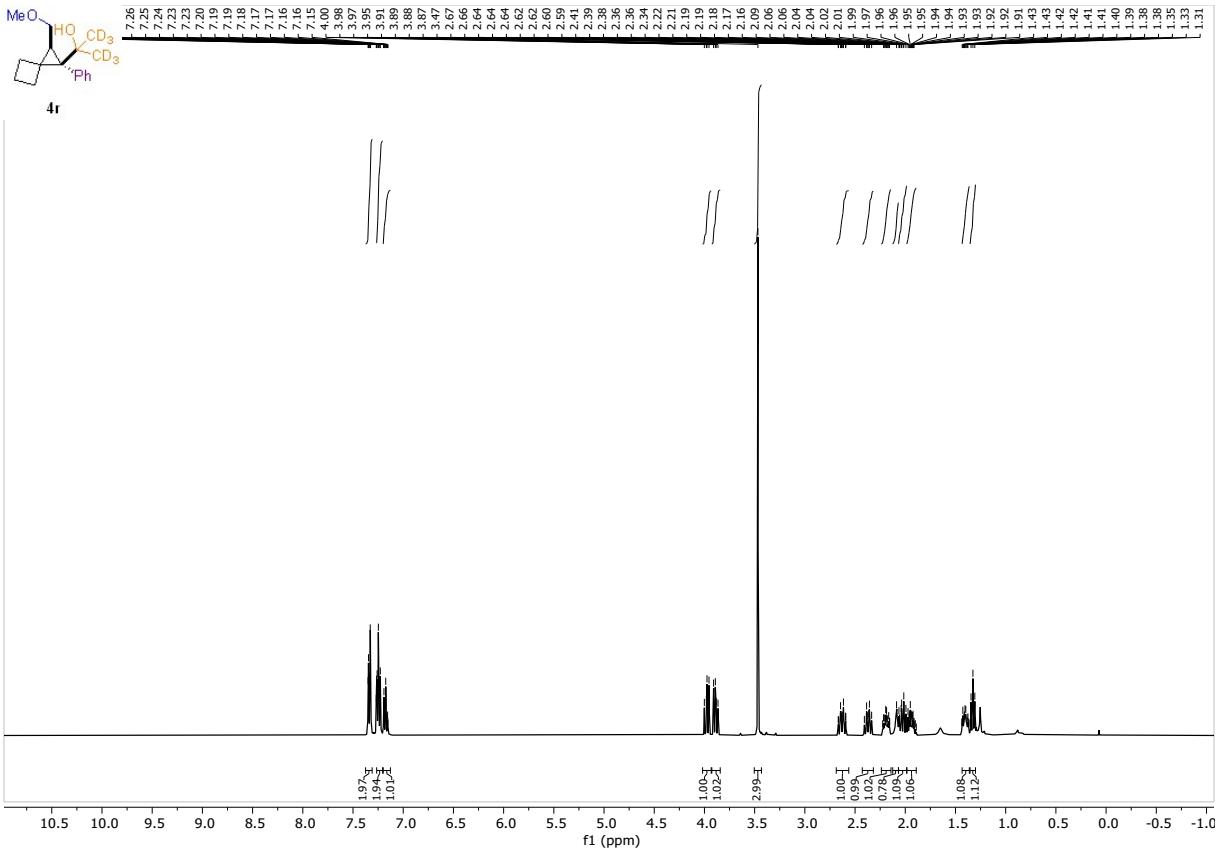
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4p**.



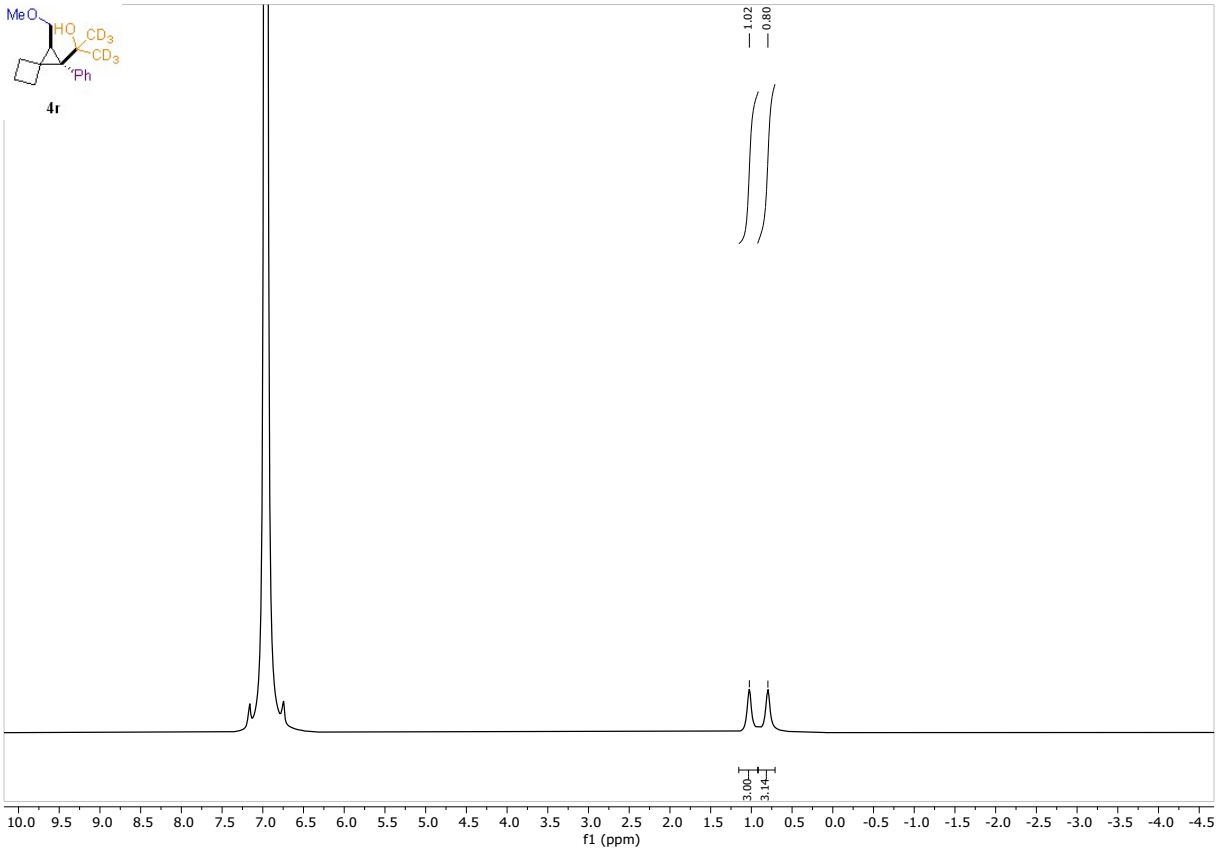
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4q**.



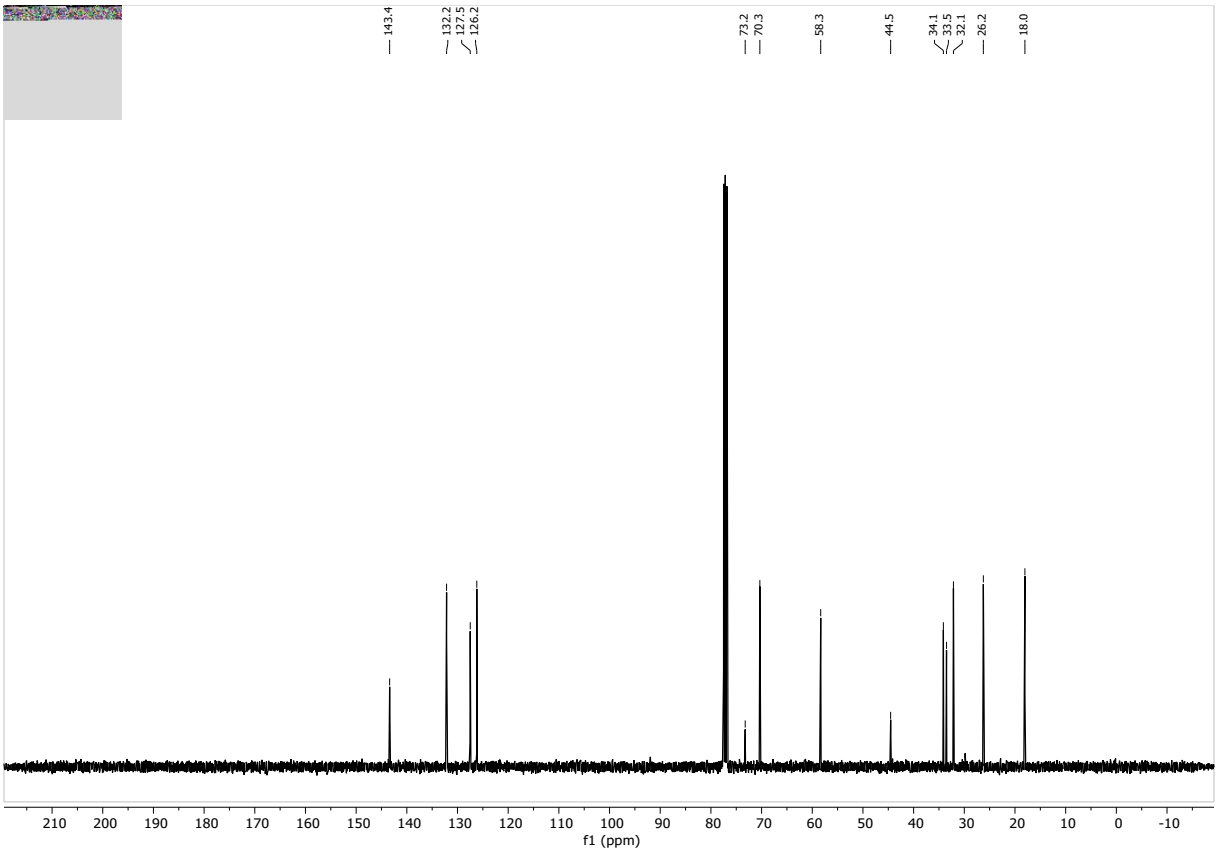
#^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4q**.



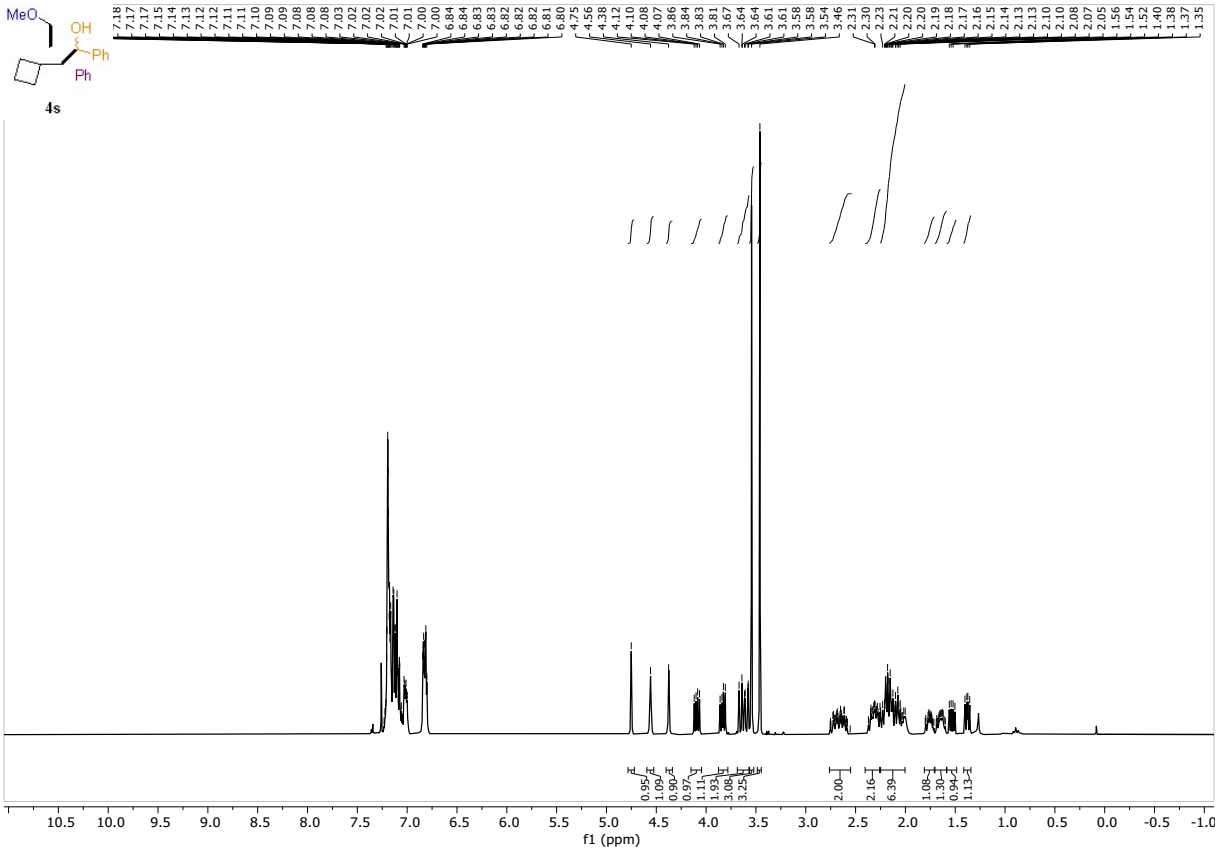
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4r**.



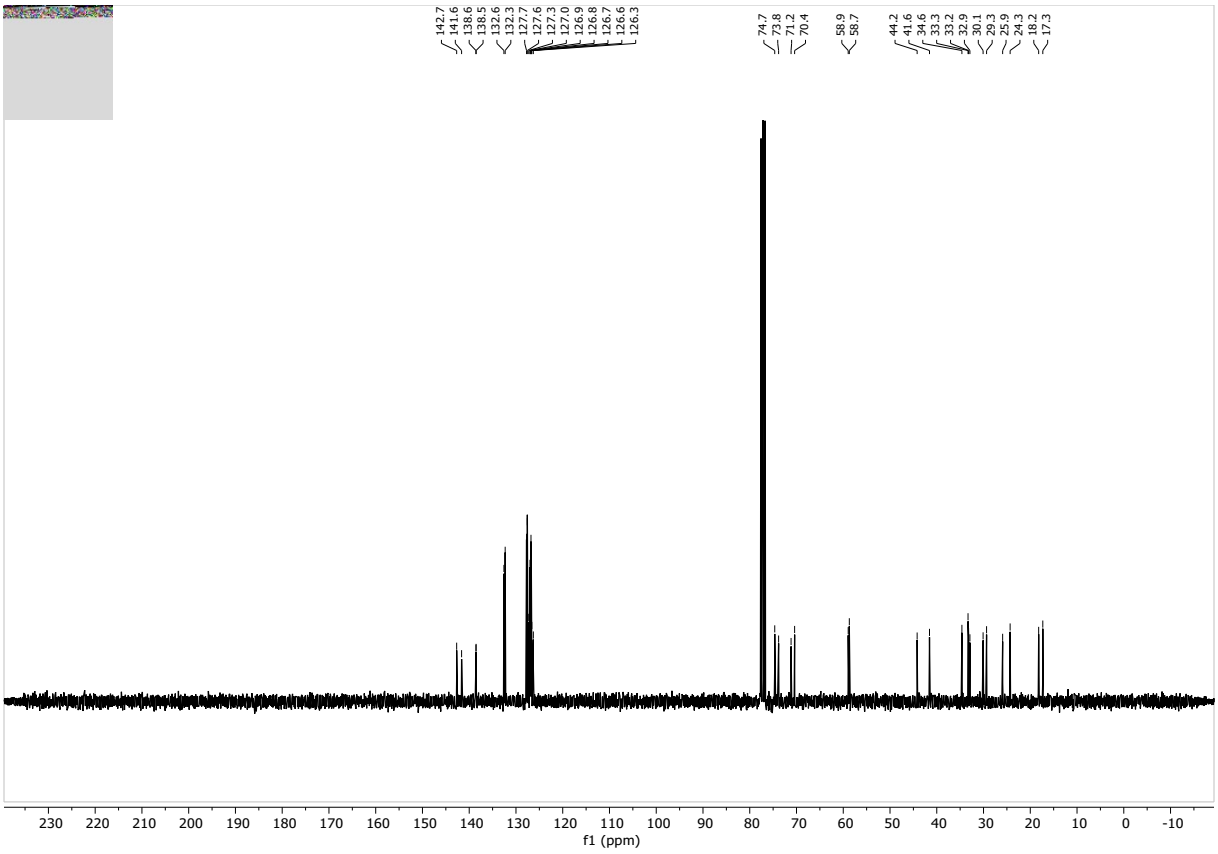
^{2}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4r**.



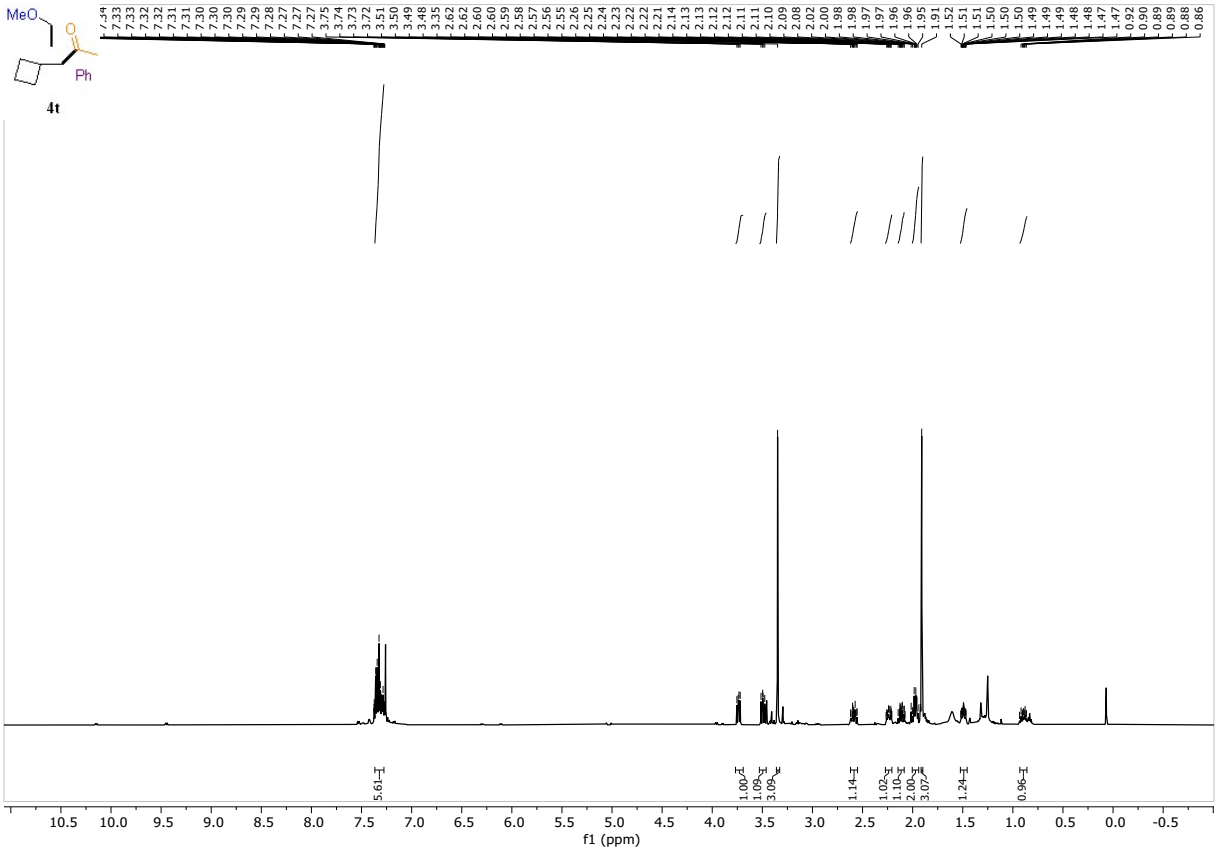
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of compound **4r**.



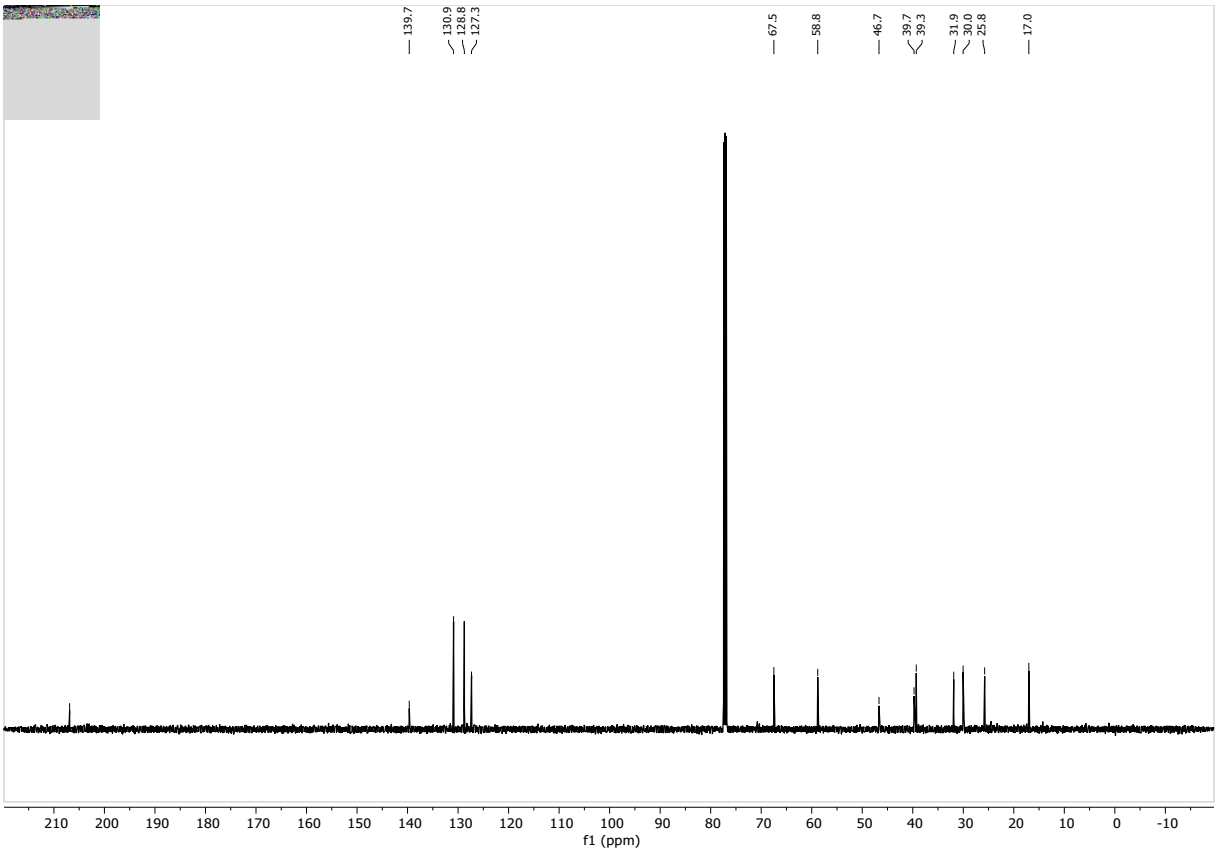
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4s**.



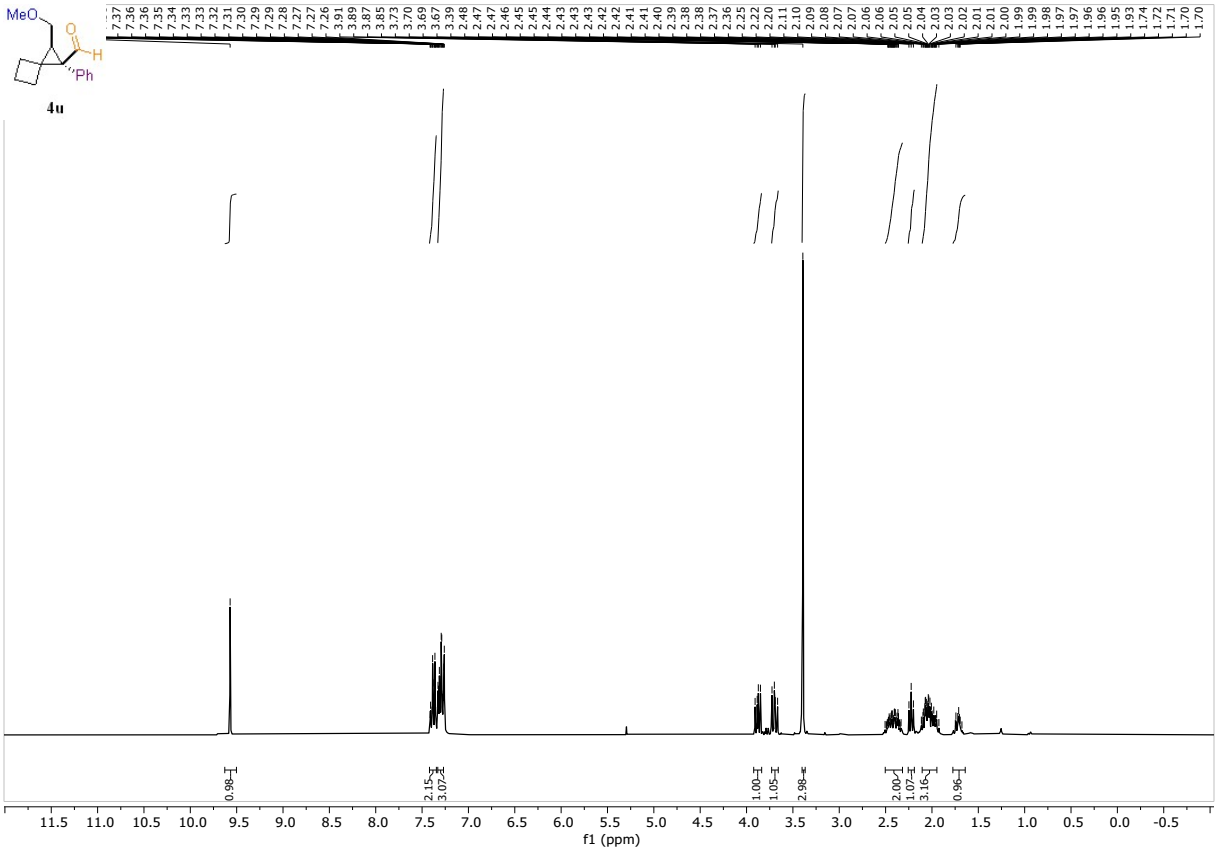
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4s**.



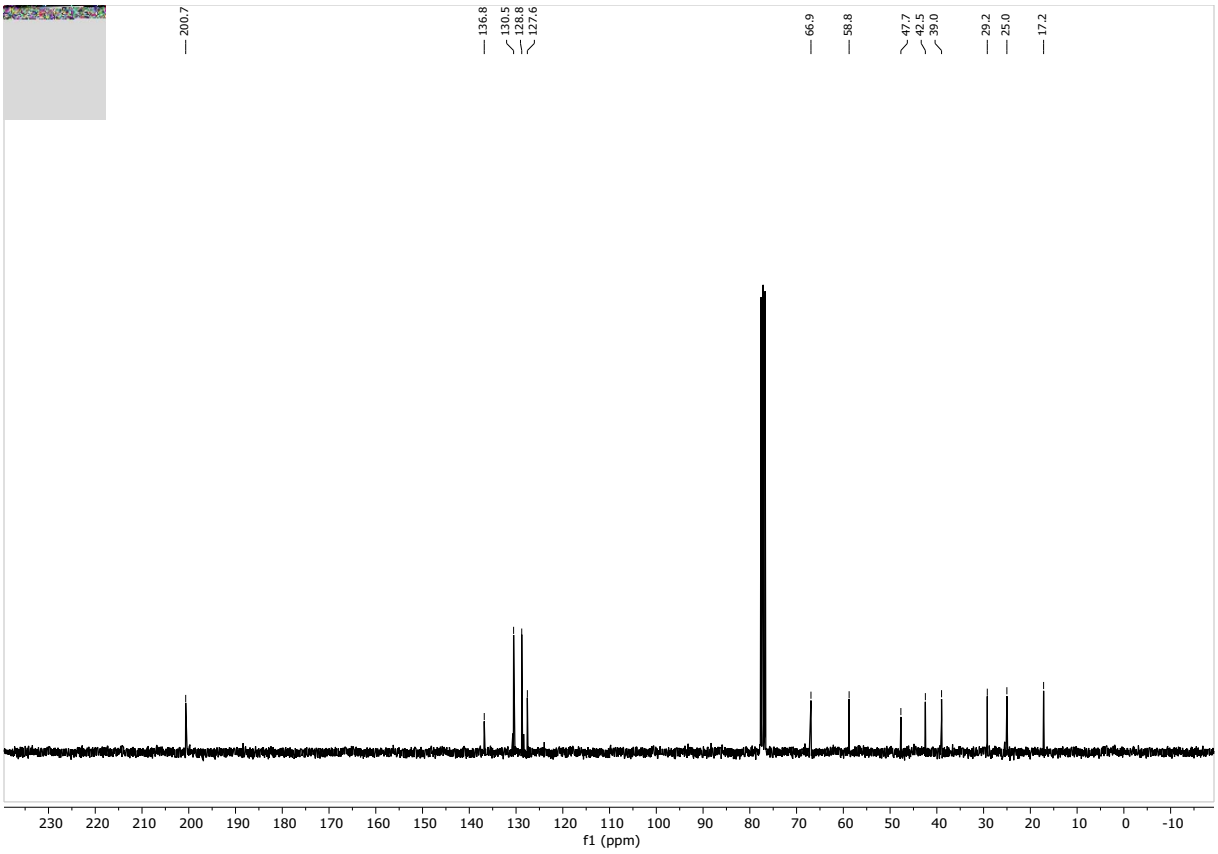
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4t**.



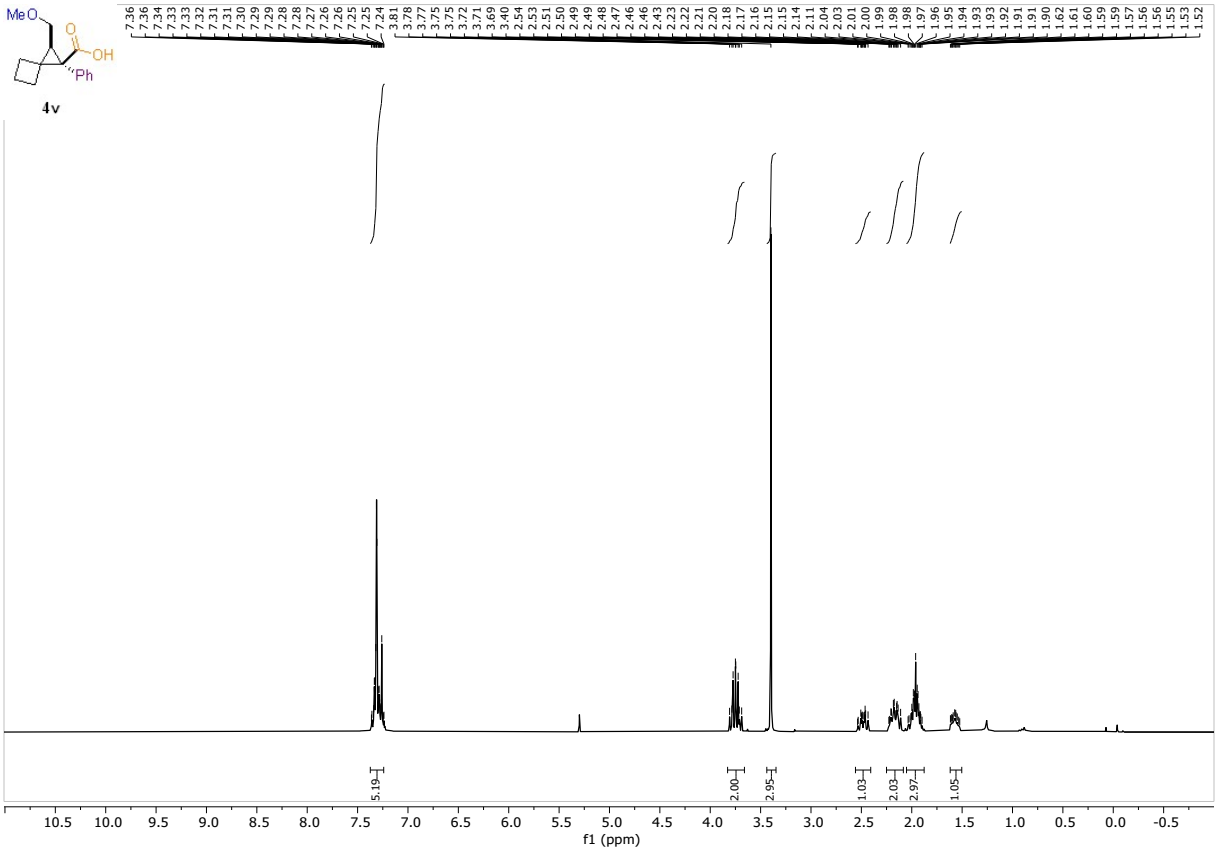
^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4t**.



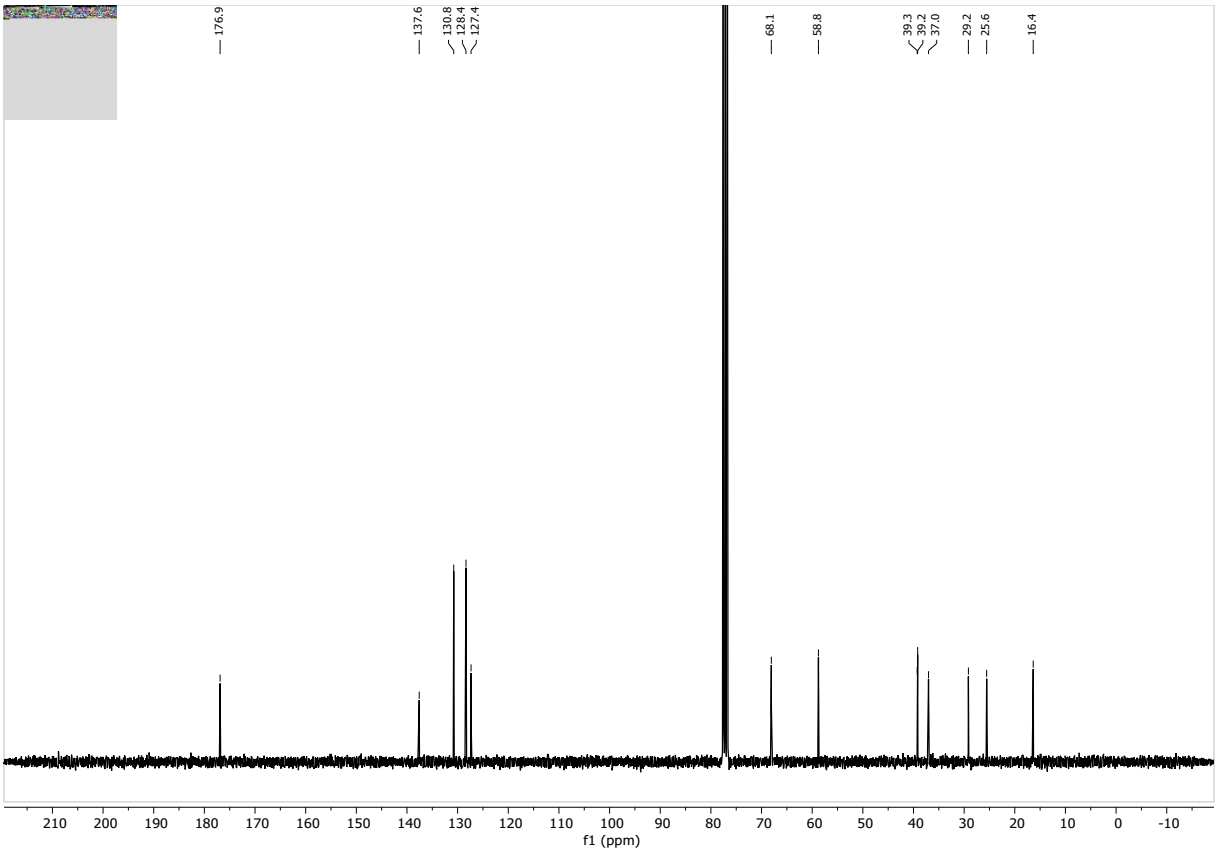
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4u**.



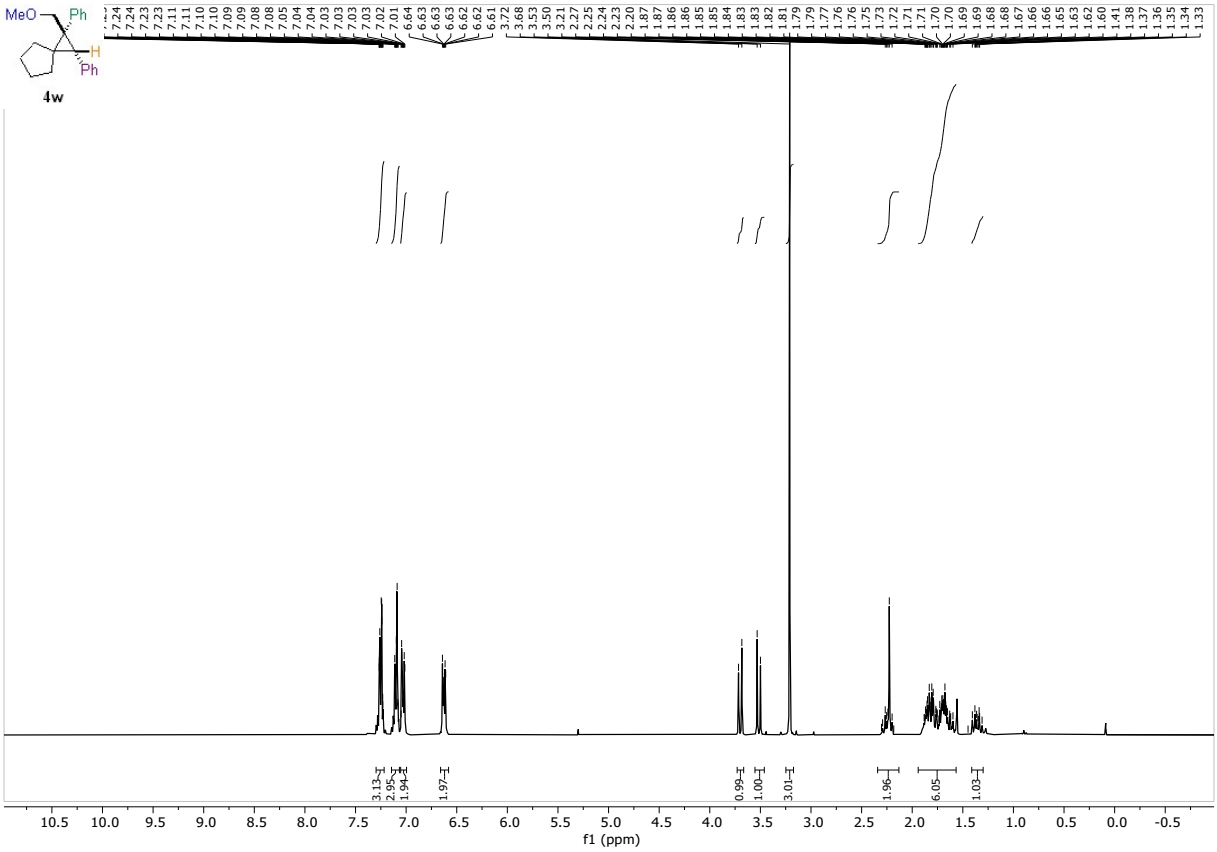
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4u**.



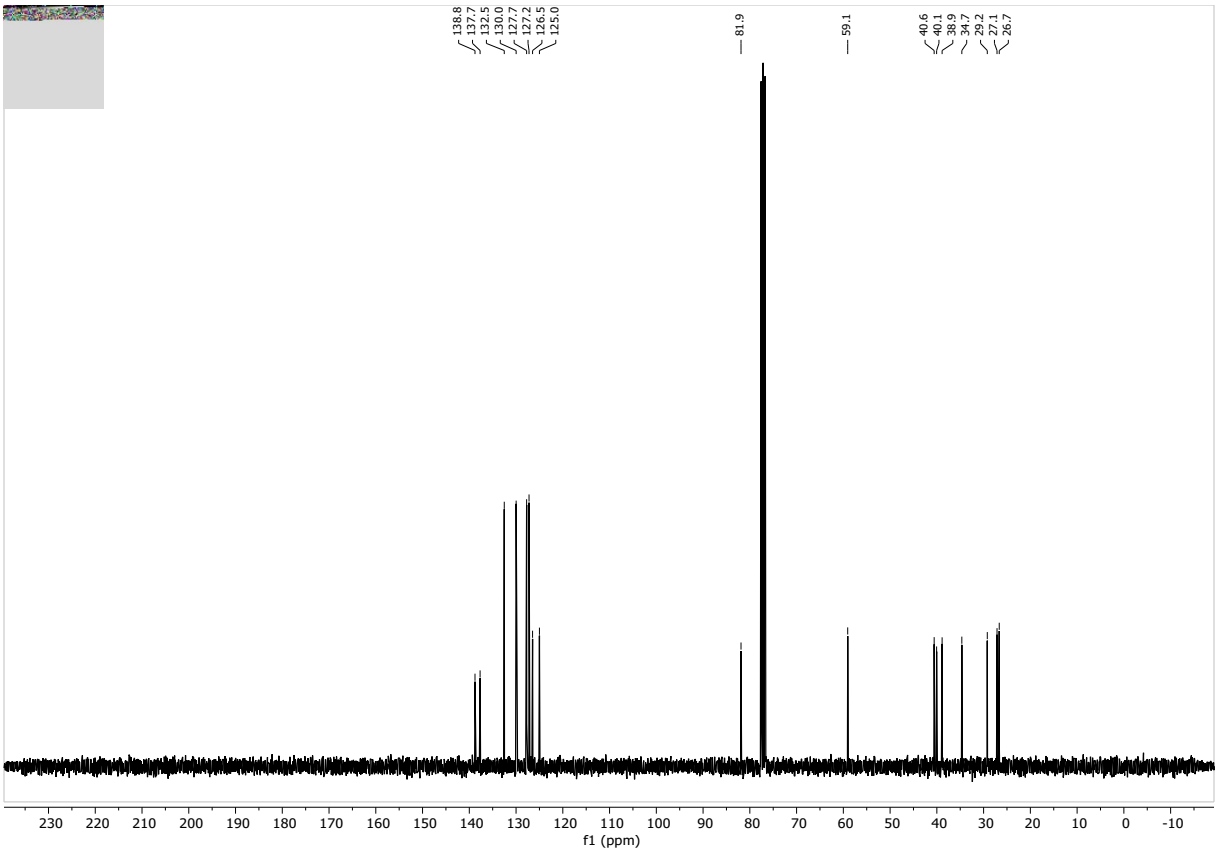
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4v**.



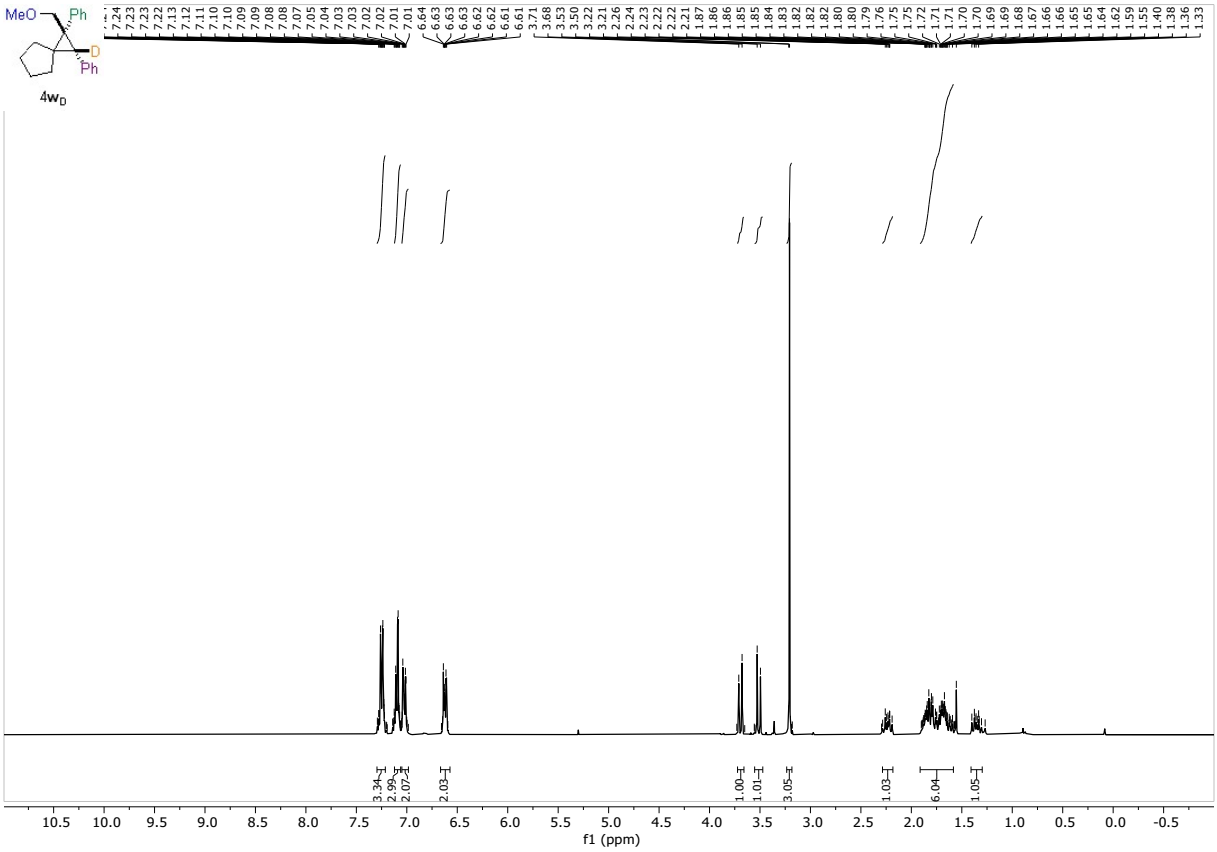
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4v**.



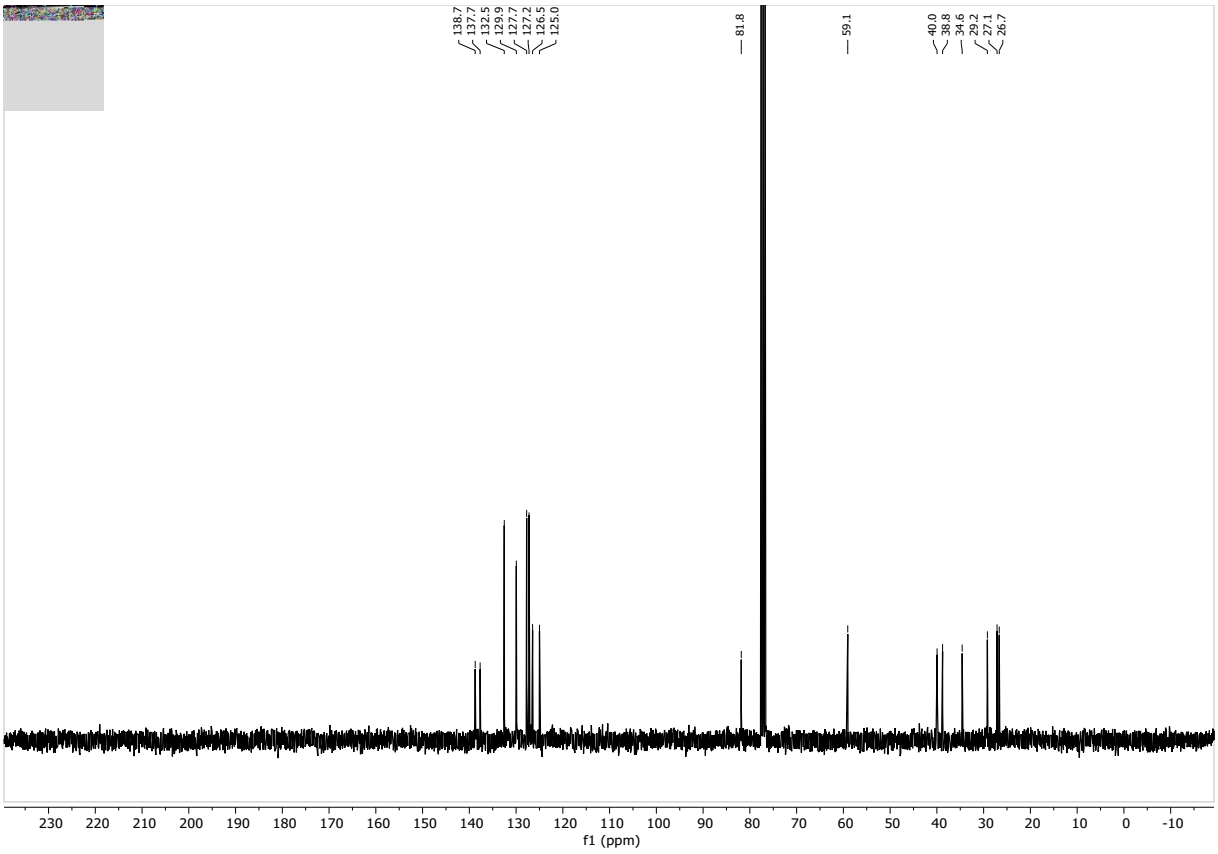
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4w**.



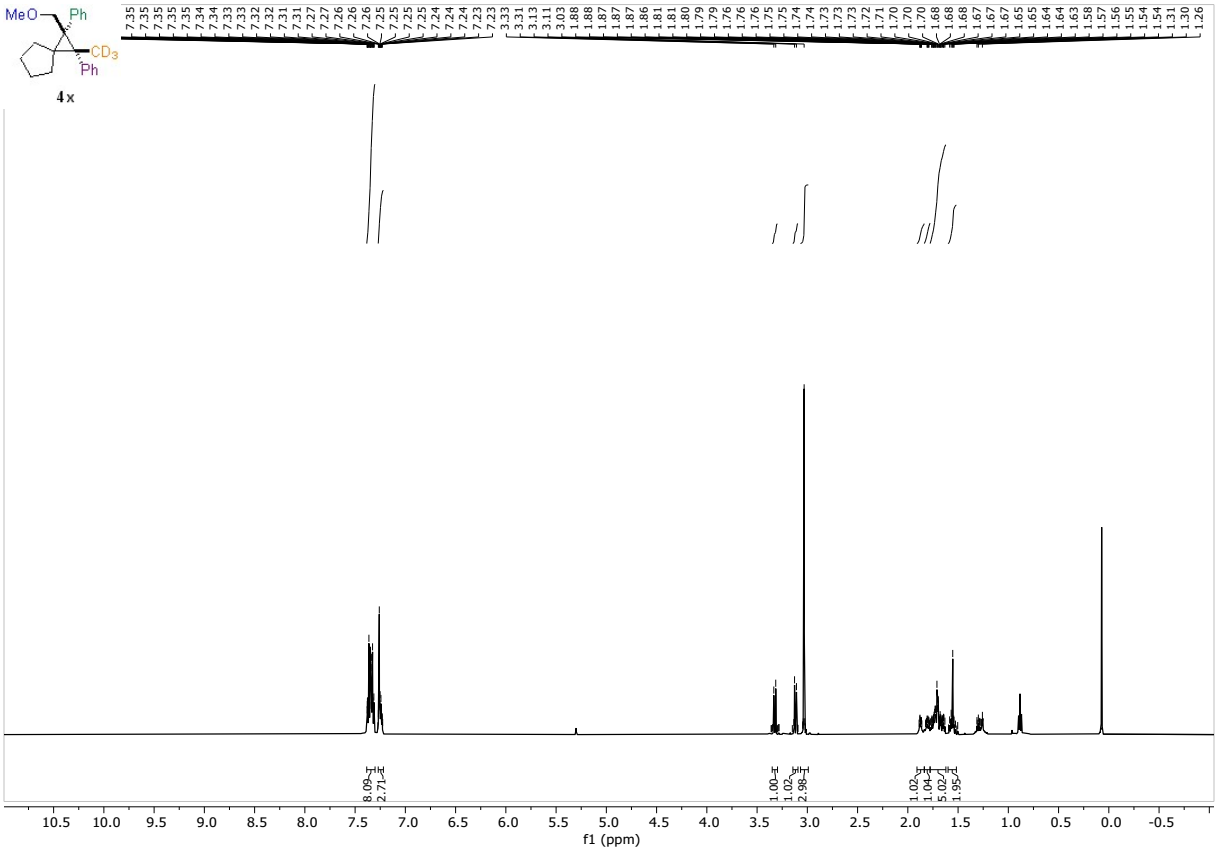
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4w**.



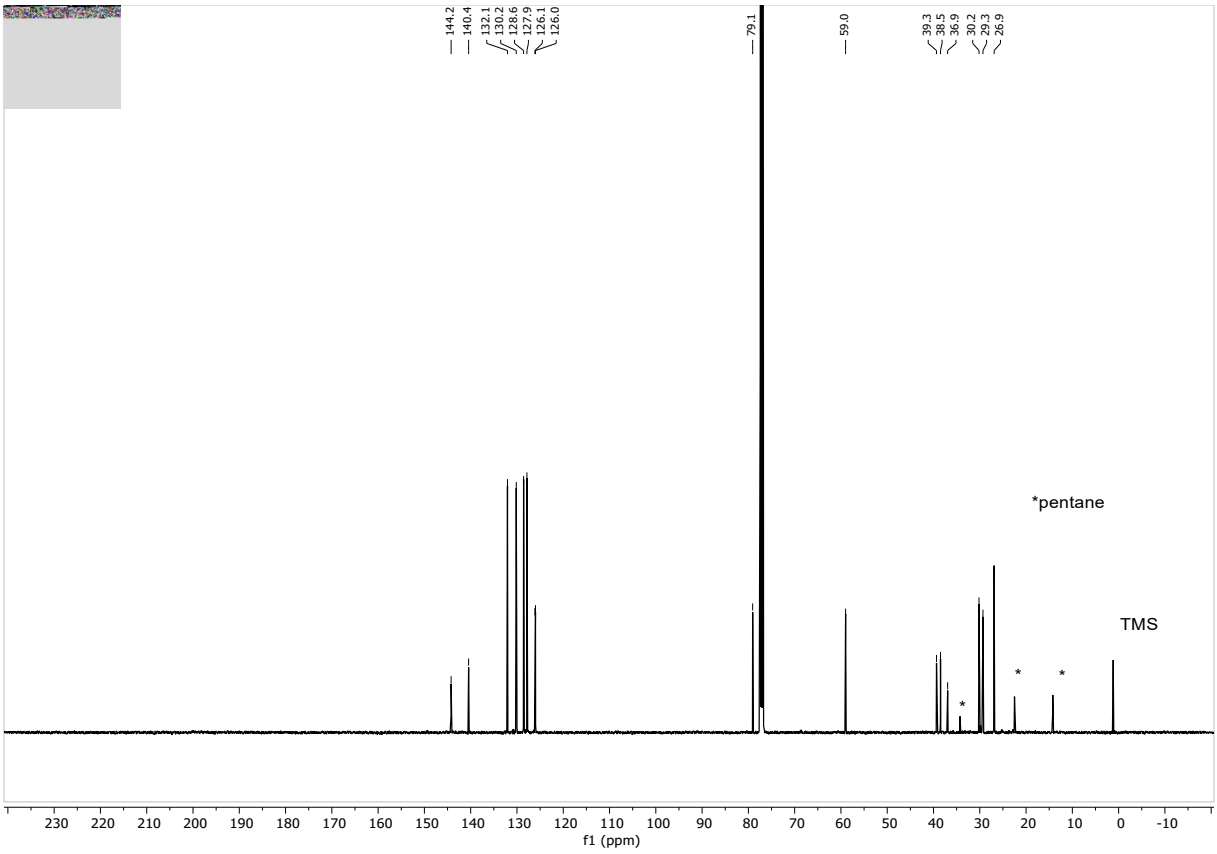
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4w$_D$**.



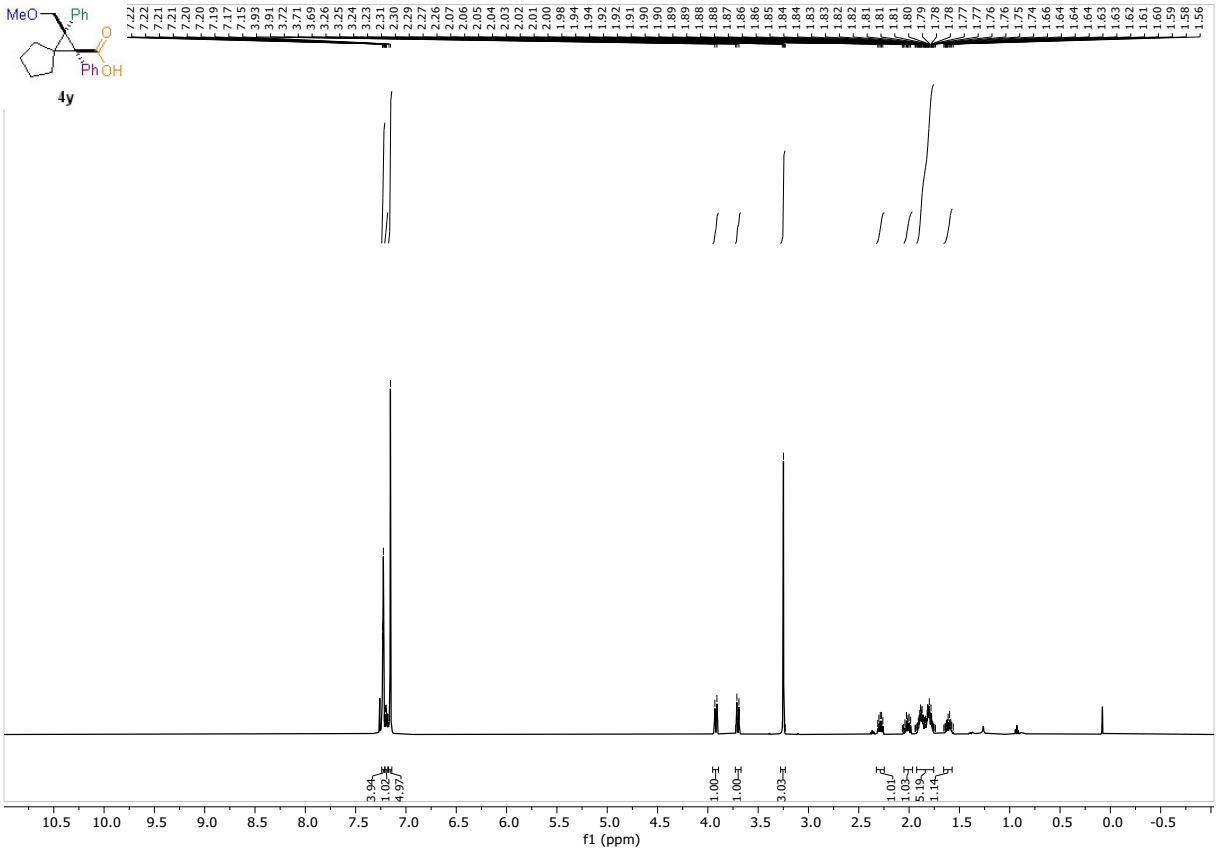
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4w$_D$**.



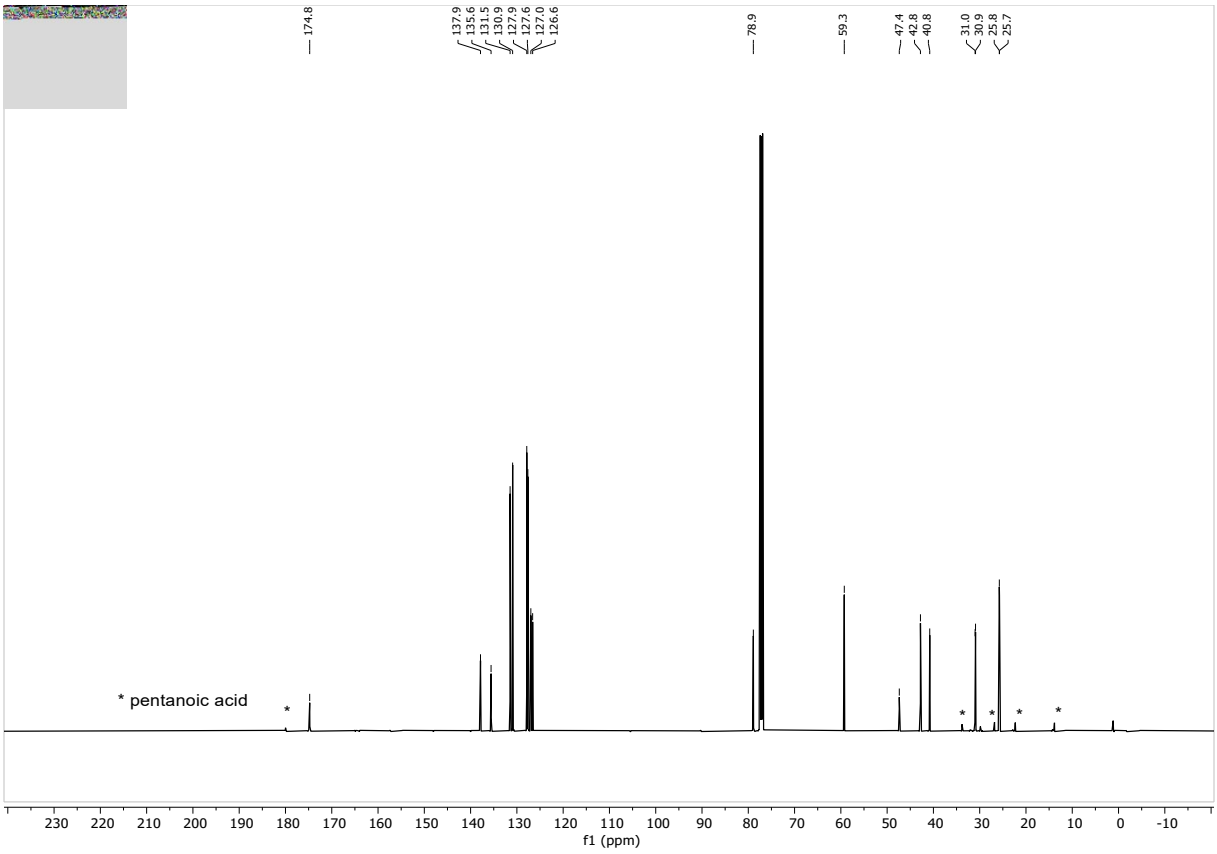
^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4x**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4x**.



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4y**.



^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4y**.