# Supporting Information

# Stereoselective Construction of Cyclic Quaternary Stereocenters by Prins Cyclization with Ketones

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## 1. GENERAL PROCEDURES

Unless otherwise noted, experiments were carried out with dry solvents under nitrogen atmosphere. Dichloromethane was dried with preactivated molecular sieves. Flash column chromatography was performed using Silica Gel 60 (230-400 mesh ASTM). Thin layer chromatography (TLC) was performed using aluminium backed plate, pre-coated with silica gel (0.20 mm, silica gel 60) with a fluorescent indicator (254 nm) from Macherey. NMR spectra were recorded at nuclear magnetic resonance service of the Laboratory of Instrumental Techniques (L.T.I., www.laboratoriotecnicasinstrumentales.es) University of Valladolid at Varian 400 MHz ($^{1}$H, 399.85 MHz; $^{13}$C, 100.6 MHz), Varian 500 MHz ($^{1}$H, 500.12 MHz; $^{13}$C, 126 MHz), Bruker 500 MHz ($^{1}$H, 500.12 MHz; $^{13}$C, 126 MHz) spectrometers at room temperature (25 °C). Chemical shifts (δ) were reported in parts per million (ppm) relative to the residual solvent peaks recorded, rounded to the nearest 0.01 for $^{1}$H-NMR and 0.1 for $^{13}$C-NMR (reference: $CDCl_3$ [$^{1}$H: 7.26, $^{13}$C: 77.2]). Spin-spin coupling constants (*J*) in $^{1}$H-NMR were given in Hz to the nearest 0.1 Hz, and peak multiplicity was indicated as follows s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). $^{13}$C NMR were recorded with complete proton decoupling. Carbon types, structure assignments and attribution of peaks were determined from two-dimensional correlation experiments (HSQC, COSY and HMBC). The relative stereochemistry of tetrahydropyrans was assigned based on the 2D-NOE experiments, considering the signals corresponding to the interactions highlighted in the Figure S1-A, and the coupling constants (*J*) of the corresponding protons highlighted in the Figure S1-B. High-resolution mass spectra (HRMS) were measured at mass spectrometry service of the University of Burgos, on a 6545 Q-TOF Agilent LC-MS mass spectrometer (positive electrospray ionization mode, ESI (+)) and at mass spectrometry service of the Laboratory of Instrumental Techniques of the University of Valladolid, using a quadrupole spectrometer equipped with a TOF analyzer, on a UPLC-MS system (UPLC: Waters ACQUITY H-class UPLC; MS: Bruker Maxis Impact) by positive electrospray ionization (ESI(+)). X-ray diffraction studies were performed at University of Burgos on a Bruker D8 VENTURE diffractometer.

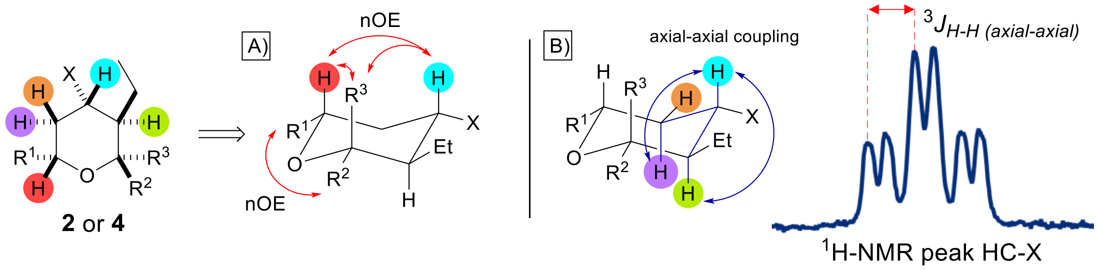
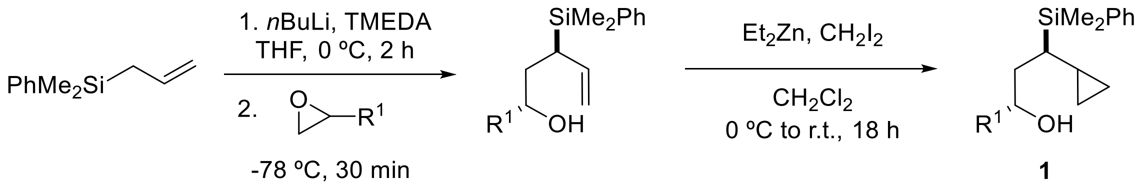


***Figure S1.*** *Assignment of the relative stereochemistry based on (**A**) 2D-NOE experiments and (**B**) the coupling constants (J) of the corresponding protons.*

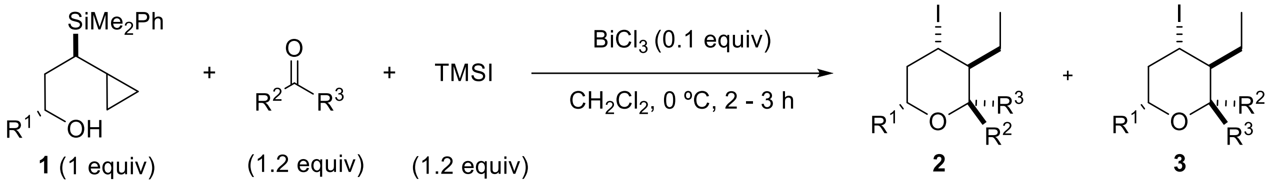
## 2. EXPERIMENTAL SECTION

### 2.1 Synthesis of cyclopropylsilyl alcohols **1**



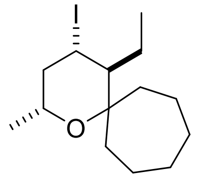
The synthesis of starting materials **1** was carried out following previously reported methodology.[1]

### 2.2. TMSI/BiCl$_3$-promoted cyclization of cyclopropylsilyl alcohols **1** with ketones

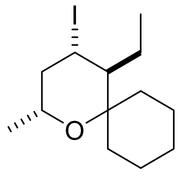


**1a**, R$^1$ = Me
**1b**, R$^1$ = (CH$_2$)$_7$CH$_3$
**1c**, R$^1$ = $^t$Bu

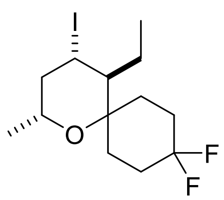
A solution of BiCl$_3$ (0.1 equiv) and the corresponding ketone (1.2 equiv) in 5 mL of dry dichloromethane (0.05 M) was cooled to 0 °C under nitrogen. Alcohol **1** (80 mg, 1.0 equiv) was then dissolved in 1 mL of dry dichloromethane and added to the reaction mixture. Finally, the Lewis acid, TMSI (1.2 equiv), was added dropwise. The mixture was stirred at 0 ˚C for 2-3 hours while monitored by TLC. Upon complete consumption of the starting materials, the reaction was quenched with 5 mL of Na$_2$S$_2$O$_3$ (sat.). Phases were separated and the aqueous phase was extracted three times with dichloromethane (3 x 10 mL). The combined organic layers were washed with NaCl sat. (20 mL) and dried over anhydrous Na$_2$SO$_4$. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography in silica gel, using mixtures of hexane-ethyl acetate, to afford tetrahydropyrans **2** and **3**.



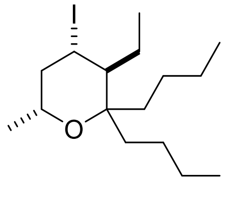
(2*R**,4*S**,5*S**)-5-ethyl-4-iodo-2-methyl-1-oxaspiro[5.6]dodecane (**2a**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (500.0 mg, 2.0 mmol), cycloheptanone (0.28 mL, 2.4 mmol) and TMSI (0.29 mL, 2.4 mmol). Purification by column chromatography (hexane/EtOAc: 100:1) afforded a yellow oil (371.7 mg, 55%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.39 (td, *J* = 12.1, 4.5 Hz, 1H, *H*C-I), 3.56 – 3.45 (m, 1H, *H*C-O), 2.43 (ddd, *J* = 12.6, 4.5, 2.2 Hz, 1H, C*H*H), 2.10 (td, *J* = 12.6, 12.1, Hz, 1H, CH*H*), 1.91 – 1.84 (m, 1H, Cy), 1.80 – 1.69 (m, 2H), 1.69 – 1.59 (m, 3H), 1.59 – 1.49 (m, 5H), 1.49 – 1.40 (m, 3H, Cy), 1.40 – 1.32 (m, 1H, Cy), 1.10 (d, *J* = 6.2 Hz, 3H, CH$_3$), 1.04 (t, *J* = 7.5 Hz, 3H, CH$_2$-*CH$_3$*). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 81.4 (O-C), 66.9 (HC-O), 57.0 (CH), 49.6 (CH$_2$), 43.1 (CH$_2$), 36.6 (HC-I), 28.7 (CH$_2$), 28.3 (2*CH$_2$), 25.9 (CH$_2$), 22.7 (CH$_2$), 21.6 (CH$_3$), 21.2 (CH$_2$), 14.7 (CH$_3$). **HRMS (ESI+)** m/z calc. for C$_{14}$H$_{26}$IO ([M+H]$^+$): 337.1023, found 337.1020.



(2*R**,*4S**,5*S**)-5-ethyl-4-iodo-2-methyl-1-oxaspiro[5.5]undecane (**2b**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), cyclohexanone (39 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 100:1) afforded a white solid (72.2 mg, 70%). **$^{1}$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.42 (td, *J* = 12.1, 4.5 Hz, 1H, *H*C-I), 3.62 – 3.55 (m, 1H, *H*C-O), 2.47 (ddd, *J* = 12.9, 4.5, 2.3 Hz, 1H, C*H*H), 2.17 – 2.08 (m, 1H, C*H*H), 1.99 – 1.93 (m, 1H, Cy), 1.74 (qt, *J* = 12.5, 3.8 Hz, 1H, Cy), 1.68 – 1.59 (m, 2H), 1.57 – 1.49 (m, 2H), 1.47 – 1.30 (m, 5H), 1.24 (td, *J* = 13.4, 3.9 Hz, 1H, Cy), 1.16 – 1.09 (m, 1H, Cy), 1.13 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.02 (t, *J* = 7.4 Hz, 3H, $CH_2$-$\mathit{CH_3}$). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 78.4 (C-O), 66.3 (HC-O), 56.3 (CH), 49.9 ($CH_2$), 37.6 ($CH_2$), 36.4 (HC-I), 26.3 ($CH_2$), 26.2 ($CH_2$), 25.1 ($CH_2$), 21.6 ($CH_2$), 21.6 ($CH_3$), 20.5 ($CH_2$), 14.8 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{13}H_{24}IO$ ($[M+H]^+$): 323.0866, found 323.0871. **Melting point** = 41.1 – 42.8 ˚C.

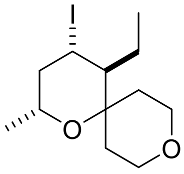


(2*R**,*4S**,5*S**)-5-ethyl-9,9-difluoro-4-iodo-2-methyl-1-oxaspiro[5.5]undecane (**2c**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 4,4-difluorocyclohexanone (50.9 mg, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 50:1) afforded a white solid (80.2 mg, 72%). **$^{1}$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.33 (td, *J* = 12.3, 4.4 Hz, 1H, *H*C-I), 3.58 – 3.50 (m, 1H, *H*C-O), 2.49 (ddd, *J* = 13.0, 4.4, 2.2 Hz, 1H, C*H*H), 2.27 – 2.13 (m, 2H), 2.05 – 1.99 (m, 1H, Cy), 1.98 – 1.91 (m, 1H, Cy), 1.91 – 1.71 (m, 3H), 1.67 – 1.59 (m, 2H), 1.58 – 1.37 (m, 3H, Cy), 1.13 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.03 (t, *J* = 7.6 Hz, 3H, $CH_2$-$\mathit{CH_3}$).**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 123.6 (dd, $^{1}J$ = 242.9, 238.4 Hz, C-$F_2$), 76.6 (d, $^{4}J_{C\text{-}F}$ = 1.8 Hz, C-O), 67.1 (HC-O), 54.8 (d, $^{5}J_{C\text{-}F}$ = 2.1 Hz, C-O), 49.4 ($CH_2$), 34.1 (HC-I), 34.0 ($CH_2$), 29.5 (dd, $^{2}J$ = 24.9, 23.6 Hz, $CH_2$), 28.7 (dd, $^{2}J$ = 25.6, 23.8 Hz, $CH_2$), 25.9 ($CH_2$), 21.5 ($CH_3$), 21.3 (d, $^{3}J$ = 10.0 Hz, $CH_2$), 14.7 ($CH_3$). **$^{19}$F NMR (470 MHz, $CDCl_3$)** δ (ppm) -91.1 (d, $^{1}J_{F\text{-}F}$ = 234.7 Hz), -103.4 (dddt, $^{1}J_{F\text{-}F}$ = 234.7 Hz, $^{3}J_{F\text{-}H}$ = 36.5, 34.0, 11.6 Hz). **HRMS (ESI+)** m/z calc. for $C_{13}H_{22}F_2IO$ ($[M+H]^+$): 359.0678, found 359.0681. **Melting point** = 65.1 – 66.7 ˚C.

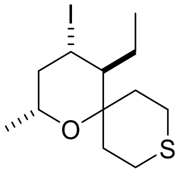


(3*S**,4*S**,6*R**)-2,2-dibutyl-3-ethyl-4-iodo-6-methyltetrahydro-2*H* pyran (**2d**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 5-nonanona (66 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 80:1) afforded a yellow oil (77.4 mg, 66%). **$^{1}$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.49 (td, *J* = 12.2, 4.4 Hz, 1H, *H*C-I), 3.53 – 3.45 (m, 1H, *H*C-O), 2.44 (ddd, *J* = 12.9, 4.4, 2.1 Hz, 1H, C*H*H), 2.09 (td, *J* = 12.9, 12.2, Hz, 1H, CH*H*), 1.94 (ddd, *J* = 12.2, 4.8, 3.6, 1H, CH), 1.81 – 1.73 (m, 1H), 1.65 – 1.58 (m, 1H), 1.56 – 1.46 (m, 2H), 1.45 – 1.36 (m, 2H), 1.36 – 1.22 (m, 7H, chain), 1.22 – 1.4 (m, 1H, chain), 1.09 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.04 (t, *J* = 7.6 Hz, 3H, $CH_2$-$\mathit{CH_3}$), 0.93 (t, *J* = 7.1 Hz, 3H, $CH_3$), 0.92 (t, *J* = 7.1 Hz, 3H, $CH_3$). **$^{13}$C NMR (101 MHz,**

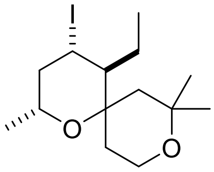
**$CDCl_3$)** δ (ppm) 80.6 (O-C), 67.4 (HC-O), 50.5 (CH), 49.7 ($CH_2$), 37.6 ($CH_2$), 36.9 (HC-I), 30.5 ($CH_2$), 25.8 ($CH_2$), 25.2 ($CH_2$), 24.1 ($CH_2$), 23.6 ($CH_2$), 23.4 ($CH_2$), 21.5 ($CH_3$), 14.4 ($CH_3$), 14.4 ($CH_3$), 13.7 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{32}IO$ ($[M+H]^+$): 367.1492, found 367.1485.



(2*R**,*4S**,5*S**)-5-ethyl-4-iodo-2-methyl-1,9-dioxaspiro[5.5]undecane (**2e**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), tetrahydro-4*H*-pyran-4-one (35 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 5:1) afforded a white solid (98.6 mg, 95%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.42 (td, *J* = 12.3, 4.3 Hz, 1H, *H*C-I), 3.85 (ddd, *J* = 13.3, 11.1, 2.3 Hz, 1H, C*H*H-O), 3.75 – 3.52 (m, 4H), 2.49 (ddd, *J* = 12.9, 4.3, 2.3 Hz, 1H, C*H*H), 2.18 – 2.10 (m, 1H, CH*H*), 2.04 (td, *J* = 12.9, 5.3, 1H, Cy), 1.88 – 1.80 (m, 1H, Cy), 1.70 (ddd, *J* = 13.4, 12.9, 4.8 Hz, 1H, Cy), 1.62 – 1.52 (m, 2H), 1.47 – 1.36 (m, 1H), 1.34 – 1.27 (m, 1H, Cy), 1.15 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.05 (t, *J* = 7.4 Hz, 3H, $CH_2$-*$CH_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 75.9 (C-O), 66.8 (HC-O), 63.6 (O-$CH_2$), 62.7 (O-$CH_2$), 55.7 (CH), 49.7 ($CH_2$), 37.5 ($CH_2$), 34.2 (HC-I), 26.0 ($CH_2$), 25.7 ($CH_2$), 21.5 ($CH_3$), 14.8 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{12}H_{22}IO_2$ ($[M+H]^+$): 325.0659, found 325.0655. **Melting point** = 49.3 – 50.3 ˚C.

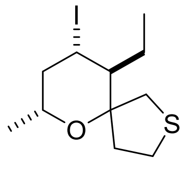


(2*R**,*4S**,5*S**)-5-ethyl-4-iodo-2-methyl-1-oxa-9-thiaspiro[5.5]undecane (**2f**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), tetrahydrothiopyran-4-one (44.1 mg, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 30:1) afforded a white solid (101.3 mg, 93%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.38 (td, *J* = 12.5, 4.9 Hz, 1H, *H*C-I), 3.63 – 3.52 (m, 1H, *H*C-O), 3.24 (td, *J* = 12.9, 2.9 Hz, 1H, C*H*H-S), 2.81 (br t, *J* = 12.5 Hz, 1H, C*H*H-S), 2.47 (ddd, *J* = 12.9, 4.4, 2.2 Hz, 1H, C*H*H), 2.33 – 2.19 (m, 3H, Cy), 2.16 – 2.00 (m, 2H), 1.79 – 1.66 (m, 2H, Cy), 1.65 – 1.6 (m, 3H), 1.14 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.03 (t, *J* = 7.5 Hz, 3H, $CH_2$-*$CH_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 76.6 (C-O), 66.4 (HC-O), 56.6 (CH), 49.5 ($CH_2$), 39.1 ($CH_2$), 34.1 (HC-I), 27.2 ($CH_2$), 25.8 ($CH_2$), 23.8 (S-$CH_2$), 22.8 (S-$CH_2$), 21.5 ($CH_3$), 14.6 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{12}H_{22}IOS$ ($[M+H]^+$): 341.0431, found 341.0325. **Melting point** = 82.6 – 84.3 ˚C.



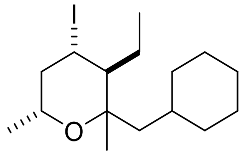
(2*R**,*4S**,5*S**)-5-ethyl-4-iodo-2,8,8-trimethyl-1,9-dioxaspiro[5.5]undecanes (**2g** and **3g**) were obtained as a mixture of separable epimers (C-6) following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 2,2-dimethyldihydro-2*H*-pyran-4(3*H*)-one (51 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 9:1) afforded two yellow oils (85.7 mg, 76%). Compound **2g (6*S**)**: **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.34 (td, *J* = 12.3, 4.4 Hz, 1H, *H*C-I), 3.77 (ddd, *J* = 13.6, 11.5, 1.9 Hz, 1H, C*H*H-O), 3.64 – 3.55 (m, 2H), 2.47 (ddd, *J* = 12.9, 4.4, 2.3 Hz, 1H, C*H*H), 2.13 (dd, *J* = 12.9, 12.3 Hz, 1H, CH*H*), 1.83 (ddd, *J* = 14.2, 4.1, 1.9 Hz, 1H, Cy), 1.71 (d, *J* = 13.8 Hz, 1H, Cy), 1.62 – 1.50 (m, 3H), 1.41 – 1.37 (m, 2H), 1.36 (s, 3H, CH$_3$), 1.17 (s, 3H, CH$_3$), 1.14 (d, *J* = 6.1 Hz, 3H, CH$_3$), 1.04 (t, *J* = 7.4 Hz, 3H, CH$_2$-*CH$_3$*). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 77.9 (C), 71.9 (C-O), 66.9 (HC-O), 57.0 (O-CH$_2$), 55.7 (CH), 49.6 (CH$_2$), 45.8 (CH$_2$), 34.6 (HC-I), 33.2 (CH$_3$), 26.6 (CH$_2$), 24.7 (CH$_2$), 24.4 (CH$_3$), 21.6 (CH$_3$), 15.1 (CH$_3$). **HRMS (ESI+)** m/z calc. for C$_{14}$H$_{26}$IO$_2$ ([M+H]$^+$): 353.0972, found 353.0975.

Compound **3g (6*R**)**: **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.35 (td, *J* = 12.2, 4.4 Hz, 1H, *H*C-I), 4.01 (td, *J* = 12.3, 2.2 Hz, 1H, C*H*H-O), 3.70 – 3.62 (m, 1H, *H*C-O), 3.54 (ddd, *J* = 12.2, 5.3, 1.5 Hz, 1H, CH*H*-O), 2.47 (ddd, *J* = 12.9, 4.4, 2.4 Hz, 1H, C*H*H), 2.15 (td, *J* = 12.9, 12.2 Hz, 1H, CH*H*), 1.96 (td, *J* = 13.0, 5.4 Hz, 1H, Cy), 1.88 (dd, *J* = 14.6, 2.5 Hz, 1H, Cy), 1.59 – 1.48 (m, 2H), 1.40 – 1.34 (m, 2H, Cy), 1.31 (s, 3H, CH$_3$), 1.32 – 1.28 (m, 1H, Cy), 1.19 (s, 3H, CH$_3$), 1.13 (d, *J* = 6.1 Hz, 3H, CH$_3$), 1.05 (t, *J* = 7.4 Hz, 3H, CH$_2$-*CH$_3$*).**$^{13}$C NMR (101 MHz, CDCl$_3$)** δ (ppm) 77.2 (C), 71.0 (C-O), 67.3 (HC-O), 57.8 (O-CH$_2$), 56.7 (CH), 49.8 (CH$_2$), 36.7 (CH$_2$), 34.56 (HC-I), 33.3 (CH$_3$), 33.0 (CH$_2$), 26.9 (CH$_2$), 22.9 (CH$_3$), 21.2 (CH$_3$), 15.3 (CH$_3$). **HRMS (ESI+)** m/z calc. for C$_{14}$H$_{25}$INaO$_2$ ([M+Na]$^+$): 375.0791, found 375.0800.



(7*R**,9*S**,10*S**)-10-ethyl-9-iodo-7-methyl-6-oxa-2-thiaspiro[4.5]decanes (**2h** and **3h**) were obtained as a mixture of separable epimers (C-5) following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), dihydrothiophen-3(2*H*)-one (33 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 20:1) afforded two white solids (67.9 mg, 65%). Compound **2h (5*R**): $^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.22 (td, *J* = 12.2, 4.3 Hz, 1H, *H*C-I), 3.62 – 3.55 (m, 1H, *H*C-O), 3.08 (d, *J* = 11.4 Hz, 1H, C*H*H-S), 2.87 (ddd, *J* = 12.0, 10.1, 5.1 Hz, 1H, C*H*H-S), 2.80 (dd, *J* = 10.1, 6.9 Hz, 1H, CH*H*-S), 2.76 (d, *J* = 11.4 Hz, 1H, CH*H*-S), 2.49 – 2.39 (m, 2H), 2.19 – 2.11 (m, 1H, CH*H*), 1.95 (dt, *J* = 12.2, 3.9 Hz, 1H, CH), 1.72 – 1.61 (m, 1H, Cy), 1.53 – 1.39 (m, 2H, CH$_2$), 1.13 (d, *J* = 6.1 Hz, 3H, CH$_3$), 1.08 (t, *J* = 7.6 Hz, 3H, CH$_2$-*CH$_3$*). **$^{13}$C NMR isomer 2h (126 MHz, CDCl$_3$)** δ (ppm) 89.3 (C-O), 68.0 (HC-O), 51.5 (CH), 49.3 (CH$_2$), 42.0 (CH$_2$), 34.0 (HC-I), 30.6 (CH$_2$), 29.3 (CH$_2$), 26.2 (CH$_2$), 21.6 (CH$_3$), 14.9 (CH$_3$). **HRMS (ESI+)** m/z calc. for C$_{11}$H$_{20}$IOS ([M+H]$^+$): 327.0274, found 327.0271. **Melting point** = 50.8 – 54.0 ˚C.

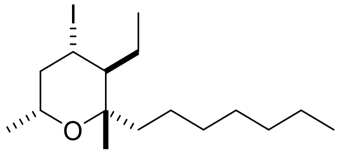
Compound **3h (5*S**): $^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.17 (td, *J* = 12.3, 4.2 Hz, 1H, *H*C-I), 3.70 – 3.62 (m, 1H, *H*C-O), 3.05 (d, *J* = 12.1 Hz, 1H, C*H*H-S), 3.06 – 2.97 (m, 1H, C*H*H-S), 2.74 – 2.67 (m, 1H, CH*H*-S), 2.69 (d, *J* = 12.1 Hz, 1H, CH*H*-S), 2.47 (ddd, *J* = 13.1, 4.2, 2.3 Hz, 1H, C*H*H), 2.17 – 2.01 (m, 3H), 1.92 (dt, *J* = 12.3, 3.7 Hz, 1H, CH), 1.49 – 1.36 (m, 2H, CH$_2$), 1.13 (d, *J* = 6.9 Hz, 3H, CH$_3$), 1.08 (t, *J* = 7.5 Hz, 3H, CH$_2$-*CH$_3$*). **$^{13}$C NMR (101 MHz, CDCl$_3$)** δ (ppm) 89.7 (C-O), 68.0 (HC-O), 52.8 (CH), 49.5 (CH$_2$), 43.4 (CH$_2$), 34.8 (HC-I), 30.6 (CH$_2$), 28.8 (CH$_2$), 26.8 (CH$_2$), 21.4 (CH$_3$), 15.7 (CH$_3$). **Melting point** = 63.6 – 65.1 ˚C. **HRMS (ESI+)** m/z calc. for C$_{11}$H$_{20}$IOS ([M+H]$^+$): 327.0274, found 327.0277.



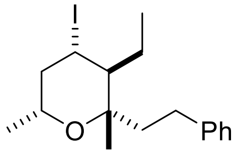
(3*S**,4*S**,6*R**)-2-(cyclohexylmethyl)-3-ethyl-4-iodo-2,6-dimethyltetrahydro-2*H*-pyrans (**2i and 3i**) were obtained as a mixture of separable epimers (C-2) following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 1-cyclohexylpropan-2-one (59 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 100:1) afforded a white solid (**2j**) and a yellow oil (**3j**) (69.9 mg, 60%). Compound **2i**

**(2*S**)**: **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.41 (td, *J* = 12.2, 4.4 Hz, 1H, *H*C-I), 3.65 – 3.57 (m, 1H, *H*C-O), 2.43 (ddd, *J* = 12.8, 4.4, 2.2 Hz, 1H, C*H*H), 2.09 (dd, *J* = 12.8, 12.2 Hz, 1H, CH*H*), 1.87 – 1.75 (m, 2H, Cy), 1.71 (dt, *J* = 12.2, 3.9 Hz, 1H, CH), 1.68 – 1.57 (m, 3H), 1.49 – 1.32 (m, 5H), 1.31 – 1.17 (m, 3H), 1.12 (s, 3H, $CH_3$), 1.06 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.02 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*$H_3$*), 1.01 – 0.86 (m, 2H). **$^{13}$C NMR of isomer 2i (101 MHz, $CDCl_3$)** δ (ppm) 79.9 (O-C), 67.3 (HC-O), 53.7 (CH), 49.8 ($CH_2$), 49.5 ($CH_2$), 36.6 (HC-I), 35.5 ($CH_2$), 35.3 ($CH_2$), 33.3 (CH), 26.8 ($CH_2$), 26.7 ($CH_2$), 26.6 ($CH_2$), 26.56 ($CH_2$), 21.7 ($CH_3$), 18.4 ($CH_3$), 14.1 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{30}IO$ ([M+H]$^+$): 365.1336, found 365.1331. **Melting point** = 38.6 – 41.3 ˚C.

Compound **3i (2*R**)**: **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.42 (td, *J* = 12.2, 4.4 Hz, 1H, *H*C-I), 3.67 – 3.59 (m, 1H, *H*C-O), 2.44 (ddd, *J* = 12.8, 4.4, 2.3 Hz, 1H, C*H*H), 2.12 (td, *J* = 12.8, 12.2 Hz, 1H, CH*H*), 1.87 – 1.80 (m, 1H, Cy), 1.75 – 1.58 (m, 6H), 1.53 – 1.44 (m, 2H), 1.43 – 1.33 (m, 1H), 1.28 – 1.21 (m, 1H), 1.26 (s, 3H, $CH_3$), 1.19 – 1.11 (m, 3H), 1.09 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.04 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*$H_3$*), 1.00 – 0.88 (m, 2H). **$^{1\,3}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 80.3 (O-C), 67.5 (HC-O), 57.8 (CH), 49.9 ($CH_2$), 36.2 ($CH_2$), 35.9 (HC-I), 35.8 ($CH_2$), 34.6 ($CH_2$), 32.7 (CH), 27.7 ($CH_3$), 26.8 (2x$CH_2$), 26.7 ($CH_2$), 26.5 ($CH_2$), 21.4 ($CH_3$), 14.9 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{30}IO$ ([M+H]$^+$): 365.1336, found 365.1330.



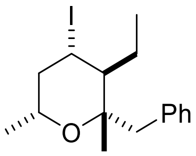
(2*S**,3*S**,4*S**,6*R**)-3-ethyl-2-heptyl-4-iodo-2,6-dimethyltetrahydro-2*H*-pyran (**2j**) was obtained as the major isomer (C-2) of a partially separable mixture of epimers, following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 2-nonanona (66 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 90:1) afforded a yellow oil (84.4 mg, 72%), from which compound **2j** could be isolated. **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.41 (td, *J* = 12.3, 4.4 Hz, 1H, *H*C-I), 3.67 – 3.58 (m, 1H, *H*C-O), 2.43 (ddd, *J* = 12.9, 4.4, 2.2 Hz, 1H, C*H*H), 2.13 – 2.03 (m, 1H, CH*H*), 1.75 – 1.67 (m, 1H, CH), 1.53 – 1.46 (m, 2H, $CH_2$), 1.46 – 1.35 (m, 4H, chain), 1.34 – 1.20 (m, 8H, chain), 1.11 (s, 3H, $CH_3$), 1.08 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.02 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*$H_3$*), 0.88 (t, *J* = 7.0 Hz, 3H, $CH_3$).**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 78.9 (O-C), 67.5 (HC-O), 53.2 (CH), 49.8 ($CH_2$), 42.5 ($CH_2$), 36.7 (HC-I), 32.1 ($CH_2$), 30.3 ($CH_2$), 29.6 ($CH_2$), 26.6 ($CH_2$), 22.8 ($CH_2$), 22.7 ($CH_2$), 21.7 ($CH_3$), 18.5 ($CH_3$), 14.3 ($CH_3$), 14.1 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{32}IO$ ([M+H]$^+$): 367.1492, found 367.1496.



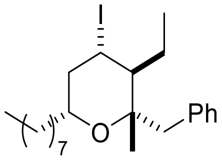
(2*S**,3*S**,4*S**,6*R**)-3-ethyl-4-iodo-2,6-dimethyl-2-phenethyltetrahydro-2*H*-pyran (**2k**) was obtained as the major isomer (C-2) of an inseparable mixture of epimers, following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 4-phenylbutan-2-one (57 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 40:1) afforded a yellow oil (89.3 mg, 75%), from which compound **2k** could be isolated. **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 7.30 – 7.26 (m, 2H, Ar-*H*), 7.23 – 7.15 (m, 3H, Ar-*H*), 4.44 (td, *J* = 12.3, 4.4 Hz, 1H, *H*C-I), 3.71 – 3.64 (m, 1H, *H*C-O), 2.76 – 2.71 (m, 2H, C*$H_2$*-Ph), 2.50 – 2.44 (m, 1H, C*H*H), 2.16 – 2.08 (m, 1H, CH*H*), 1.86 – 1.72 (m, 3H), 1.52 – 1.40 (m, 2H, C*$H_2$*-$CH_3$), 1.19 (s, 3H, $CH_3$), 1.12 (d, *J* = 6.0 Hz, 3H, $CH_3$), 1.05 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*$H_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 143.1 (C), 128.6 (2xCH), 128.5 (2xCH), 125.7 (CH), 78.5 (O-

C), 67.6 (HC-O), 53.3 (CH), 49.8 ($CH_2$), 44.4 ($CH_2$), 36.1 (HC-I), 29.2 ($CH_2$), 26.6 ($CH_2$), 21.7 ($CH_3$), 18.4 ($CH_3$), 14.3 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{17}H_{26}IO$ ($[M+H]^+$): 373.1023, found 373.1023.

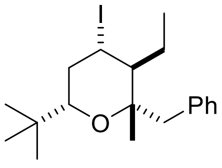
Distinctive signals of minor isomer **3k**: **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.41 (td, *J* = 12.2, 4.4 Hz, 1H, *H*C-I), 3.65 – 3.59 (m, 1H, *H*C-O), 1.33 (s, 3H, $CH_3$), 1.17 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.04 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*H*$_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 79.0 (O-C), 67.6 (HC-O), 56.7 (CH), 49.5 ($CH_2$), 34.9 (HC-I), 32.1 ($CH_2$), 28.7 ($CH_2$), 27.0 ($CH_3$), 26.3 ($CH_2$), 21.6 ($CH_3$), 14.6 ($CH_3$).



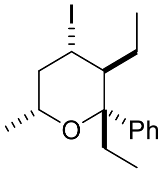
(2*S**,3*S**,4*S**,6*R**)-2-benzyl-3-ethyl-4-iodo-2,6-dimethyltetrahydro-2*H*-pyran (**2l**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), benzyl methyl ketone (57 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 30:1) afforded a white solid (80.3 mg, 70%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 7.33 – 7.19 (m, 5H, Ar-*H*), 4.41 (td, *J* = 12.2, 4.4 Hz, 1H, *H*C-I), 3.62 – 3.55 (m, 1H, *H*C-O), 2.85 (d, *J* = 14.0 Hz, 1H, C*H*H-Ph), 2.82 (d, *J* = 14.0 Hz, 1H, CH*H*-Ph), 2.43 (ddd, *J* = 12.7, 4.4, 2.2 Hz, 1H, C*H*H), 2.07 (td, *J* = 12.7, 12.2, Hz, 1H, CH*H*), 1.69 (dt, *J* = 12.2, 3.9, 1H, CH), 1.65 – 1.56 (m, 1H, C*H*H-$CH_3$), 1.53 – 1.44 (m, 1H, CH*H*-$CH_3$), 1.11 (d, *J* = 6.0 Hz, 3H, $CH_3$), 1.09 (t, *J* = 7.6 Hz, 3H, $CH_2$-*CH*$_3$), 1.05 (s, 3H, $CH_3$). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ (ppm) 137.6 (C), 131.3 (2xCH), 127.7 (2xCH), 126.2 (CH), 79.4 (O-C), 67.5 (HC-O), 53.2 (CH), 49.6 ($CH_2$), 48.0 ($CH_2$), 35.3 (HC-I), 26.4 ($CH_2$), 21.6 ($CH_3$), 17.6 ($CH_3$), 13.9 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{24}IO$ ($[M+H]^+$): 359.0866, found 359.0868. **Melting point** = 79.9 – 81.0 ˚C.



(2*S**,3*S**,4*S**,6*S**)-2-benzyl-3-ethyl-4-iodo-2-methyl-6-octyltetrahydro-2*H*-pyran (**2m**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1c** (80.0 mg, 0.23 mmol), benzyl methyl ketone ne (37 µL, 0.28 mmol) and TMSI (40 µL, 0.28 mmol). Purification by column chromatography (hexane/EtOAc: 90:1) afforded a white solid (78.7 mg, 75%), from which compound **2m** could be isolated. **$^1$H NMR (400 MHz, $CDCl_3$)** δ (ppm) 7.29 – 7.18 (m, 5H, Ar-*H*), 4.40 (td, *J* = 12.2, 4.4 Hz, 1H, *H*C-I), 3.40 – 3.31 (m, 1H, *H*C-O), 2.82 (s, 2H, C*H*$_2$-Ph), 2.41 (ddd, *J* = 12.8, 4.4, 2.2 Hz, 1H, C*H*H), 2.12 – 2.01 (m, 1H, CH*H*), 1.70 (dt, *J* = 12.2, 3.8, 1H, CH), 1.64 – 1.55 (m, 1H), 1.52 – 1.38 (m, 2H), 1.36 – 1.17 (m, 13H, chain), 1.09 (t, *J* = 7.5 Hz, 3H, $CH_2$-*CH*$_3$), 1.00 (s, 3H, $CH_3$), 0.88 (t, *J* = 6.9 Hz, 3H, $CH_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 137.5 (C), 131.3 (2xCH), 127.6 (2xCH), 126.2 (CH), 79.2 (O-C), 71.2 (HC-O), 54.0 (CH), 48.1 ($CH_2$), 48.1 ($CH_2$), 36.0 ($CH_2$), 35.9 (HC-I), 32.1 ($CH_2$), 29.7 ($CH_2$), 29.6 ($CH_2$), 29.4 ($CH_2$), 26.5 ($CH_2$), 25.5 ($CH_2$), 22.8 ($CH_2$), 17.4 ($CH_3$), 14.3 ($CH_3$), 14.0 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{23}H_{38}IO$ ($[M+H]^+$): 457.1962, found 457.1965. **Melting point** = 35.6 – 37.7 ˚C.

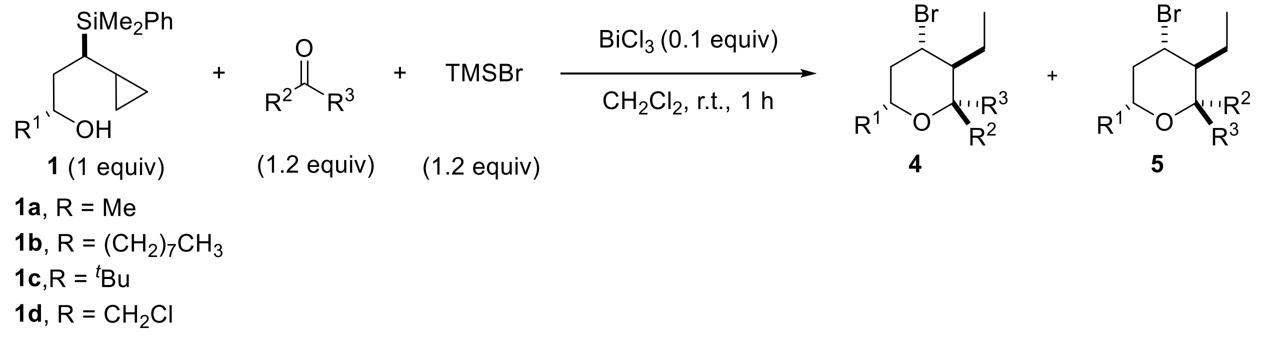


(2*S**,3*S**,4*S**,6*S**)-2-benzyl-6-(*tert*-butyl)-3-ethyl-4-iodo-2-methyltetrahydro-2*H*-pyran (**2n**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1c** (80.0 mg, 0.28 mmol), benzyl methyl ketone (45 µL, 0.34 mmol) and TMSI (48 µL, 0.34 mmol). Purification by column chromatography (hexane/EtOAc: 90:1) afforded a yellow oil (42.6 mg, 38%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 7.29 – 7.17 (m, 5H, Ar-*H*), 4.40 (td, *J* = 12.1, 4.4 Hz, 1H, *H*C-I), 2.99 (dd, *J* = 11.6, 1.9 Hz, 1H, *H*C-O), 2.84 (s, 2H, C*H$_2$*-Ph), 2.39 (ddd, *J* = 12.5, 4.4, 1.9Hz, 1H, C*H*H), 2.12 – 2.02 (m, 1H, CH*H*), 1.70 (dt, *J* = 12.1, 3.9, 1H, CH), 1.67 – 1.56 (m, 1H, C*H*H), 1.53 – 1.46 (m, 1H, CH*H*), 1.10 (t, *J* = 7.6 Hz, 3H, CH$_2$-*CH$_3$*), 1.01 (s, 3H, CH$_3$), 0.83 (s, 9H, CH$_3$). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 137.4 (C), 131.5 (CH), 127.5 (2xCH), 126.2 (2xCH), 79.0 (O-C), 78.8 (HC-O), 53.9 (CH), 48.3 (CH$_2$), 42.6 (CH$_2$), 37.2 (HC-I), 34.1 (C), 26.4 (CH$_2$), 26.1 (3xCH$_3$), 17.7 (CH$_3$), 13.8 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{19}H_{30}IO$ ([M+H]$^+$): 401.1336, found 401.1332.

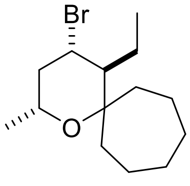


(2*R**,3*S**,4*S**,6*R**)-2,3-diethyl-4-iodo-6-methyl-2-phenyltetrahydro-2*H*-pyran (**2o**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), ethyl phenyl ketone (50 µL, 0.38 mmol) and TMSI (55 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 30:1) afforded a yellow oil (44.7 mg, 39%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 7.54 – 7.50 (m, 2H, Ar-*H*), 7.38 – 7.32 (m, 2H, Ar-*H*), 7.29 – 7.23 (m, 1H, Ar-*H*), 4.57 (td, *J* = 12.2, 4.4 Hz, 1H, *H*C-I), 3.81 – 3.72 (m, 1H, *H*C-O), 2.62 (ddd, *J* = 13.0, 4.4, 2.2 Hz, 1H, C*H*H), 2.39 – 2.30 (m, 1H, CH*H*), 2.18 (dq, *J* = 15.1, 7.4 Hz, 1H, C*H*H-CH$_3$), 2.10 (dq, *J* = 15.1, 7.4 Hz, 1H, CH*H*-CH$_3$), 1.88 (ddd, *J* = 12.2, 5.2, 3.9, 1H, CH), 1.53 – 1.43 (m, 1H, C*H*H-CH$_3$), 1.36 – 1.27 (m, 1H, CH*H*-CH$_3$), 1.24 (d, *J* = 6.1 Hz, 3H, CH$_3$), 0.81 (t, *J* = 7.2 Hz, 3H, CH$_2$-*CH$_3$*), 0.49 (t, *J* = 7.4 Hz, 3H, CH$_3$). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 143.7 (C), 128.2 (CH), 127.1 (CH), 126.7 (CH), 83.0 (O-C), 67.2 (HC-O), 57.6 (CH), 49.7 (CH$_2$), 35.1 (HC-I), 25.0 (CH$_2$), 21.7 (CH$_3$), 18.8 (CH$_2$), 13.2 (CH$_3$), 6.9 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{24}IO$ ([M+H]$^+$): 359.0866, found 359.0870.

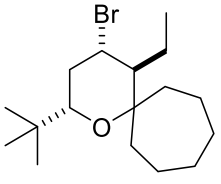
## 2.3 TMSBr/BiCl$_3$-promoted cyclization of cyclopropylsilyl alcohols **1** with ketones



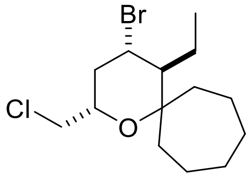
A solution of BiCl$_3$ (0.1 equiv) and the corresponding ketone (1.2 equiv) in 5 mL of dry dichloromethane (0.05 M) was prepared under nitrogen. Alcohol **1** (80 mg, 1.0 equiv) was then dissolved in 1 mL of dry dichloromethane and added to the reaction mixture. Finally, the Lewis acid, TMSBr (1.2 equiv), was added dropwise. The mixture was stirred at room temperature for 1 hour while monitored by TLC. Upon complete consumption of the starting materials, the reaction was quenched with 5 mL of $NaHCO_3$ (sat.). Phases were separated and the aqueous phase was extracted three times with dichloromethane (3 x 10 mL). The combined organic layers were washed with NaCl sat. (20 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the crude mixture was purified by column chromatography in silica gel, using mixtures of hexane-ethyl acetate, to afford tetrahydropyrans **4** and **5**.



(2*R**,4*S**,5*S**)-4-bromo-5-ethyl-2-methyl-1-oxaspiro[5.6]dodecane (**4a**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), cycloheptanone (34 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 100:1) afforded a yellow oil (52.8 mg, 57%). **$^{1}$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.22 (ddd, *J* = 12.2, 11.1, 4.6 Hz, 1H, *H*C-Br), 3.56 – 3.49 (m, 1H, *H*C-O), 2.26 (ddd, *J* = 12.7, 4.6, 2.1 Hz, 1H, C*H*H), 1.88 – 1.73 (m, 4H), 1.73 – 1.69 (m, 1H, Cy), 1.69 – 1.59 (m, 3H, Cy), 1.58 – 1.40 (m, 8H), 1.14 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.06 (t, *J* = 7.4 Hz, 3H, $CH_2$-C*$H_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 81.6 (O-C), 65.7 (HC-O), 56.7 (CH), 56.4 (HC-Br), 46.9 ($CH_2$), 42.9 ($CH_2$), 28.7 ($CH_2$), 28.5 ($CH_2$), 28.3 ($CH_2$), 23.7 ($CH_2$), 22.8 ($CH_2$), 21.9 ($CH_3$), 21.2 ($CH_2$), 15.3 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{14}H_{26}BrO$ ([M+H]$^+$): 289.1162, found 289.1159.

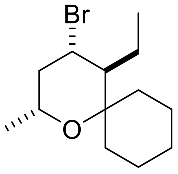


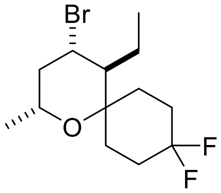
(2*S**,4*S**,5*S**)-4-bromo-2-(*tert*-butyl)-5-ethyl-1-oxaspiro[5.6]dodecane (**4b**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1c** (80.0 mg, 0.28 mmol), cycloheptanone (30 µL, 0.34 mmol) and and TMSBr (44 µL, 0.34 mmol). Purification by column chromatography (hexane) afforded a white solid (23.2 mg, 25%). **$^{1}$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.26 (td, *J* = 11.5, 4.5 Hz, 1H, *H*C-Br), 3.06 (dd, *J* = 11.8, 2.0 Hz, 1H, *H*C-O), 2.25 (ddd, *J* = 12.4, 4.5, 2.0 Hz, 1H, C*H*H), 1.90 – 1.73 (m, 4H), 1.69 – 1.37 (m, 12H, Cy), 1.06 (t, *J* = 7.4 Hz, 3H, $CH_2$-C*$H_3$*), 0.91 (s, 9H, $CH_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 81.1 (O-C), 76.5 (HC-O), 58.3 (HC-Br), 57.3 (CH), 42.7 ($CH_2$), 40.0 ($CH_2$), 34.6 ($CH_2$), 29.0 ($CH_2$), 28.8 ($CH_2$), 28.3 ($CH_2$), 26.12 (3x$CH_3$), 23.9 ($CH_2$), 22.6 ($CH_2$), 21.6 ($CH_2$), 15.4 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{17}H_{32}BrO$ ([M+H]$^+$): 331.1631, found 331.1627. **Melting point** = 32.7 – 34.4 ˚C.

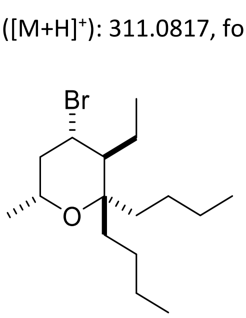


(2*S**,4*S**,5*S**)-4-bromo-2-(chloromethyl)-5-ethyl-1-oxaspiro[5.6]dodecane (**4c**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1d** (80.0 mg, 0.28 mmol) cycloheptanone (30 µL, 0.34 mmol) and and TMSBr (44 µL, 0.34 mmol). Purification by column chromatography (hexane/EtOAc: 100:1) afforded a white solid (32.6 mg, 36%). **$^{1}$H NMR (400 MHz, $CDCl_3$)** δ (ppm) 4.20 (td, *J* = 11.7, 4.6 Hz, 1H, *H*C-Br), 3.66 – 3.57 (m, 1H, *H*C-O), 3.48 (dd, *J* = 11.1, 6.4 Hz, 1H, C*H*H-Cl), 3.40 (dd, *J* = 11.1, 5.2 Hz, 1H, CH*H*-Cl), 2.42 (ddd, *J* = 12.5, 4.6, 2.1 Hz, 1H, C*H*H), 1.93 – 1.71 (m, 4H), 1.70 – 1.58 (m, 5H, Cy), 1.57 – 1.40 (m, 7H), 1.07 (t, *J* = 7.4 Hz, 3H, $CH_2$-C*$H_3$*). **$^{13}$C NMR (101**

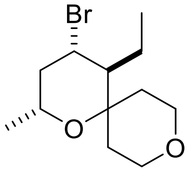
**MHz, $CDCl_3$)** δ (ppm) 82.2 (O-C), 69.9 (HC-O), 56.7 (CH), 54.7 (HC-Br), 47.1 ($CH_2$-Cl), 42.6 ($CH_2$), 42.5 ($CH_2$), 28.6 ($CH_2$), 28.6 ($CH_2$), 28.1 ($CH_2$), 23.6 ($CH_2$), 22.7 ($CH_2$), 21.1 ($CH_2$), 15.2 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{14}H_{25}BrClO$ ($[M+H]^+$): 323.0772, found 323.0775. **Melting point** = 24.0 – 26.1 ˚C.


(2*R**,*4S**,5*S**)-4-bromo-5-ethyl-2-methyl-1-oxaspiro[5.5]undecane (**4d**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), cyclohexanone (39 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol. Purification by column chromatography (hexane/EtOAc: 100:1) afforded a yellow oil (72.2 mg, 82%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.22 (td, *J* = 11.8, 4.6 Hz, 1H, *H*C-Br), 3.63 – 3.53 (m, 1H, *H*C-O), 2.28 (ddd, *J* = 12.7, 4.6, 2.2 Hz, 1H, C*H*H), 1.91 – 1.78 (m, 2H), 1.72 (qt, *J* = 12.7, 3.8 Hz, 1H, Cy), 1.66 – 1.57 (m, 2H), 1.51 – 1.48 (m, 6H), 1.34 (qt, *J* = 12.7, 3.4 Hz, 1H, Cy), 1.27 – 1.20 (m, 1H, Cy), 1.20 – 1.08 (m, 1H, Cy), 1.14 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.03 (t, *J* = 7.4 Hz, 3H, $CH_2$-*$CH_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 78.6 (C), 65.1 (HC-O), 56.1 (HC-Br), 55.9 (CH), 47.2 ($CH_2$), 37.3 ($CH_2$), 26.3 ($CH_2$), 25.3 ($CH_2$), 23.8 ($CH_2$), 21.9 ($CH_3$), 21.6 ($CH_2$), 20.5 ($CH_2$), 15.4 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{13}H_{24}BrO$ ($[M+H]^+$): 275.1005, found 275.1007.

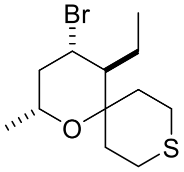

(2*R**,*4S**,5*S**)-4-bromo-5-ethyl-9,9-difluoro-2-methyl-1-oxaspiro[5.5]undecane (**4e**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80 mg, 0.32 mmol), 4,4-difluorocyclohexanone (50.9 mg, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 50:1) afforded a white solid (54.8 mg, 55%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.16 (td, *J* = 11.9, 4.6 Hz, 1H, *H*C-Br), 3.59 – 3.52 (m, 1H, *H*C-O), 2.32 (ddd, *J* = 12.9, 4.6, 2.2 Hz, 1H, C*H*H), 2.26 – 2.11 (m, 1H, Cy), 1.99 – 1.91 (m, 2H), 1.92 – 1.70 (m, 4H), 1.61 (ddd, *J* = 14.0, 4.2, 1.7 Hz, 1H, Cy), 1.58 – 1.50 (m, 2H), 1.49 – 1.39 (m, 2H), 1.16 (d, *J* = 6.0 Hz, 3H, $CH_3$), 1.05 (t, *J* = 7.5 Hz, 3H, $CH_2$-*$CH_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 123.6 (dd, $^1J$ = 239.1, 230.3 Hz C-$F_2$), 76.8 (C-O), 65.9 (HC-O), 54.5 (HC-Br), 54.4 (d, $^5J_{C-F}$ = 2.1 Hz, CH-O), 46.7 ($CH_2$), 33.9 (d, $^3J$ = 9.9 Hz, $CH_2$), 29.5 (dd, $^2J$ = 24.7, 23.7 Hz, $CH_2$), 28.7 (dd, $^2J$ = 25.5, 23.8 Hz, $CH_2$), 23.6 ($CH_2$), 21.8 ($CH_3$), 21.5 (d, $^3J$ = 9.9 Hz, $CH_2$), 15.2 ($CH_3$). **$^{19}$F NMR (470 MHz, $CDCl_3$)** δ (ppm) -91.0 (d, $^1J_{F-F}$ = 235.4 Hz), -103.4 (dddt, $^1J_{F-F}$ = 235.4 Hz, $^3J_{F-H}$ = 36.4, 35.0, 11.5 Hz). **HRMS (ESI+)** m/z calc. for $C_{13}H_{22}BrF_2O$ ($[M+H]^+$): 311.0817, found 311.0818. **Melting point** = 35.8 – 37.1 ˚C.


(3*S**,4*S**,6*R**)-4-bromo-2,2-dibutyl-3-ethyl-6-methyltetrahydro-2*H*-pyran (**4f**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 5-nonanona (66 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 80:1) afforded a yellow oil

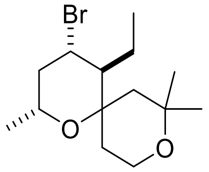
(49.0 mg, 48%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.49 (td, *J* = 11.8, 4.5 Hz, 1H, *H*C-Br), 3.53 – 3.45 (m, 1H, *H*C-O), 2.25 (ddd, *J* = 12.7, 4.5, 2.2 Hz, 1H, C*H*H), 1.87 – 1.76 (m, 2H), 1.73 – 1.58 (m, 2H, chain), 1.53 – 1.37 (m, 4H), 1.36 – 1.14 (m, 8H), 1.11 (d, *J* = 6.0 Hz, 3H, CH$_3$), 1.05 (t, *J* = 7.6 Hz, 3H, CH$_2$-C*H$_3$*), 0.91 (t, *J* = 7.1 Hz, 3H, CH$_3$), 0.91 (t, *J* = 7.1 Hz, 3H, CH$_3$). **$^{13}$C NMR (101 MHz, CDCl$_3$)** δ (ppm) 80.8 (O-C), 66.1 (HC-O), 56.7 (HC-Br), 50.1 (CH), 47.0 (CH$_2$), 37.3 (CH$_2$), 30.7 (CH$_2$), 25.2 (CH$_2$), 24.1 (CH$_2$), 23.6 (2xCH$_2$), 23.4 (CH$_2$), 21.8 (CH$_3$), 14.4 (CH$_3$), 14.4 (CH$_3$), 14.3 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{32}BrO$ ([M+H]$^+$): 319.1631, found 319.1630.



(2*R**,4*S**,5*S**)-4-bromo-5-ethyl-2-methyl-1,9-dioxaspiro[5.5]undecane (**4g**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), tetrahydro-4*H*-pyran-4-one (35 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol).. Purification by column chromatography (hexane/EtOAc: 5:1) afforded a white solid (67.4 mg, 76%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.17 (ddd, *J* = 12.2, 11.4, 4.5 Hz, 1H, *H*C-Br), 3.85 (ddd, *J* = 12.4, 11.1, 2.3 Hz, 1H, *H*HC-O), 3.73 – 3.67 (m, 2H, Cy), 3.66 – 3.59 (m, 1H, *H*C-O), 3.56 (ddd, *J* = 12.1, 11.1, 2.3 Hz, 1H, O-C*H*H), 2.32 (ddd, *J* = 12.7, 4.5, 2.3 Hz, 1H, C*H*H), 2.04 (ddd, *J* = 13.5, 12.4, 5.3 Hz, 1H, Cy), 1.88 (td, *J* = 12.7, 11.4 Hz, 1H, CH*H*), 1.78 (dq, *J* = 14.5, 2.3 Hz, 1H, Cy), 1.70 (ddd, *J* = 14.5, 12.1, 4.9 Hz, 1H, Cy), 1.56 – 1.43 (m, 3H), 1.29 (dq, *J* = 13.5, 2.3 Hz, 1H, Cy), 1.19 (d, *J* = 6.1 Hz, 3H, CH$_3$), 1.07 (t, *J* = 7.4 Hz, 3H, CH$_2$-*CH$_3$*). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 76.2 (C), 65.6 (HC-O), 63.6 (O-CH$_2$), 62.6 (H$_2$C-O), 55.3 (HC-Br), 54.6 (CH), 46.9 (CH$_2$), 37.2 (CH$_2$), 25.8 (CH$_2$), 23.6 (CH$_2$), 21.8 (CH$_3$), 15.3 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{12}H_{22}BrO_2$ ([M+H]$^+$): 277.0798, found 277.0797. **Melting point** = 35.4 – 37.9 ˚C.

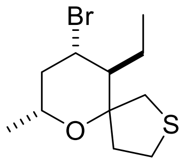


(2*R**,4*S**,5*S**)-4-bromo-5-ethyl-2-methyl-1-oxa-9-thiaspiro[5.5]undecane (**4h**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80 mg, 0.32 mmol), tetrahydrothiopyran-4-one (44.1 mg, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 30:1) afforded a white solid (56 mg, 60%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.21 (td, *J* = 11.9, 4.6 Hz, 1H, *H*C-Br), 3.63 – 3.54 (m, 1H, *H*C-O), 3.25 (td, *J* = 13.1, 2.7 Hz, 1H, *H*HC-S), 2.82 (td, *J* = 13.0, 2.2 Hz, 1H, S-C*H*H), 2.30 (ddd, *J* = 12.9, 4.6, 2.2 Hz, 1H, C*H*H), 2.28 – 2.16 (m, 4H, Cy), 2.06 (td, *J* = 13.1, 3.9 Hz, 1H, Cy), 1.89 – 1.81 (m, 1H, CH*H*), 1.78 – 1.68 (m, 1H, Cy), 1.61 – 1.47 (m, 2H, CH$_2$), 1.41 (dt, *J* = 11.9, 4.0 Hz, 1H, C*H*), 1.18 (d, *J* = 6.1 Hz, 3H, CH$_3$), 1.06 (t, *J* = 7.4 Hz, 3H, CH$_2$-*CH$_3$*). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 76.8 (C), 65.2 (HC-O), 56.2 (HC-Br), 54.5 (CH), 46.7 (CH$_2$), 38.8 (CH$_2$), 27.4 (CH$_2$), 23.7 (S-CH$_2$), 23.4 (CH$_2$), 22.7 (H$_2$C-S), 21.8 (CH$_3$), 15.1 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{12}H_{22}BrOS$ ([M+H]$^+$): 293.0569, found 293.0567. **Melting point** = 68.7 – 71.1 ˚C.



(2R*,4*S**,5*S**)-4-bromo-5-ethyl-2,8,8-trimethyl-1,9-dioxaspiro[5.5]undecane (**4i** and **5i**) were obtained as a mixture of separable epimers (C-6) following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 2,2-dimethyldihydro-2*H*-pyran-4(3*H*)-one (51 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 9:1) afforded two yellow oils (80.1 mg, 82%). Compound **4i (6*S**)**: **$^{1}$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.18 (td, *J* = 11.9, 4.5 Hz, 1H, *H*C-Br), 4.01 (ddd, *J* = 12.5, 11.7, 2.2 Hz, 1H, O-C*H*H), 3.72 – 3.63 (m, 1H, *H*C-O), 3.57 (ddd, *J* = 12.5, 5.4, 1.5 Hz, 1H, O-CH*H*), 2.32 (ddd, *J* = 12.8, 4.5, 2.3 Hz, 1H, C*H*H), 1.99 – 1.90 (m, 1H, Cy), 1.92 – 1.84 (m, 1H, CH*H*), 1.81 (dd, *J* = 14.6, 2.5 Hz, 1H, Cy), 1.51 – 1.34 (m, 5H), 1.32 (s, 3H, $CH_3$), 1.18 (s, 3H, $CH_3$), 1.16 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.07 (t, *J* = 7.4 Hz, 3H, $CH_2$-*$CH_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 77.7 (C), 71.0 (C), 66.1 (HC-O), 57.8 ($H_2C$-O), 56.3 (CH), 54.9 (HC-Br), 47.1 ($CH_2$), 36.3 ($CH_2$), 33.6 ($CH_2$), 33.0 ($CH_3$), 24.5 ($CH_2$), 22.9 ($CH_3$), 21.5 ($CH_3$), 15.8 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{14}H_{26}BrO_2$ ($[M+H]^+$): 305.1111, found 305.1113.

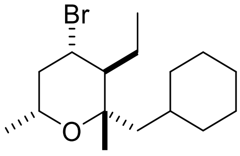
Compound **5i (6*R**)**: **$^{1}$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.17 (td, *J* = 11.7, 4.5 Hz, 1H, *H*C-Br), 3.77 (ddd, *J* = 12.5, 11.5, 2.0 Hz, 1H, O-C*H*H), 3.64 – 3.53 (m, 2H), 2.29 (ddd, *J* = 12.8, 4.6, 2.3 Hz, 1H, C*H*H), 1.6 (td, *J* = 12.8, 11.7 Hz, 1H, CH*H*), 1.78 – 1.73 (m, 1H, Cy), 1.70 (d, *J* = 13.8 Hz, 1H, Cy), 1.58 (ddd, *J* = 14.3, 11.7, 4.8 Hz, 1H, Cy), 1.53 – 1.38 (m, 4H), 1.37 (s, 3H, $CH_3$), 1.17 (s, 3H, $CH_3$), 1.17 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.05 (t, *J* = 7.4 Hz, 3H, $CH_2$-*$CH_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 78.1 (C), 71.8 (C), 65.7 (HC-O), 56.9 ($H_2C$-O), 55.4 (CH), 54.9 (HC-Br), 46.9 ($CH_2$), 45.5 ($CH_2$), 33.2 ($CH_3$), 24.9 ($CH_2$), 24.3 ($CH_2$), 24.3 ($CH_3$), 21.8 ($CH_3$), 15.6 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{14}H_{25}BrNaO_2$ ($[M+Na]^+$): 327.0930 found 327.0933.



(7*R**,9*S**,10*S**)-9-bromo-10-ethyl-7-methyl-6-oxa-2-thiaspiro[4.5]decane (**4j** and **5j**) were obtained as a mixture of separable epimers (C-5) following the general procedure, from cyclopropylsilyl alcohol **1a** (80 mg, 0.32 mmol), dihydrothiophen-3(2*H*)-one (33 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 20:1) afforded two white solids (59.0 mg, 66%). Compound **4j (5*R**)**: **$^{1}$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.07 (td, *J* = 11.9, 4.4 Hz, 1H, *H*C-Br), 3.64 – 3.55 (m, 1H, *H*C-O), 3.07 (d, *J* = 11.4 Hz, 1H, C*H*H-S), 2.87 (ddd, *J* = 12.0, 10.1, 5.1 Hz, 1H, S-C*H*H), 2.82 – 2.77 (m, 1H, S-CH*H*), 2.76 (dd, *J* = 11.4, 1.4 Hz, 1H, CH*H*-S), 2.36 (dd, *J* = 13.4, 5.1 Hz, 1H, Cy), 2.29 (ddd, *J* = 12.9, 4.4, 2.2 Hz, 1H, C*H*H), 1.94 – 1.82 (m, 2H), 1.66 (ddd, *J* = 13.4, 12.0, 7.1 Hz, 1H, Cy), 1.55 – 1.40 (m, 2H, $CH_2$), 1.16 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.09 (t, *J* = 7.5 Hz, 3H, $CH_2$-*$CH_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 89.6 (C), 66.7 (HC-O), 55.0 (HC-Br), 51.3 (CH), 46.6 ($CH_2$), 42.0 ($CH_2$), 30.7 ($CH_2$), 29.4 ($CH_2$), 24.1 ($CH_2$), 21.9 ($CH_3$), 15.4 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{11}H_{20}BrOS$ ($[M+H]^+$): 279.0413, found 279.0410. **Melting point** = 55.1 – 56.3 ˚C.

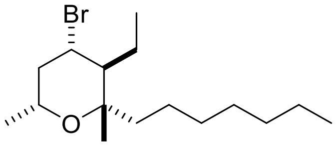
Compound **5j (5*S**)**: **$^{1}$H NMR (400 MHz, $CDCl_3$)** δ (ppm) 4.01 (td, *J* = 12.0, 4.3 Hz, 1H, *H*C-Br), 3.72 – 3.62 (m, 1H, *H*C-O), 3.07 – 2.98 (m, 2H), 2.74 (dd, *J* = 10.0, 6.6, 2.0 Hz, 1H, S-C*H*H), 2.70 (d, *J* = 12.0 Hz, 1H, C*H*H-S), 2.31 (ddd, *J* = 13.0, 4.3, 2.3 Hz, 1H, C*H*H), 2.14 – 2.03 (m, 2H, Cy), 1.92 – 1.80 (m, 2H), 1.58 – 1.47 (m, 1H, C*H*H), 1.45 – 1.35 (m, 1H, CH*H*), 1.17 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.10 (t, *J* = 7.5 Hz, 3H, $CH_2$-*$CH_3$*). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 90.0 (C), 66.9 (HC-O), 55.5 (HC-

Br), 52.5 (CH), 46.8 ($CH_2$), 43.2 ($CH_2$), 30.8 ($CH_2$), 28.8 ($CH_2$), 24.4 ($CH_2$), 21.7 ($CH_3$), 16.1 ($CH_3$). **Melting point** = 33.9 – 36.0 ˚C. **HRMS (ESI+)** m/z calc. for $C_{11}H_{20}BrOS$ ($[M+H]^+$): 301.0232, found 301.0240.



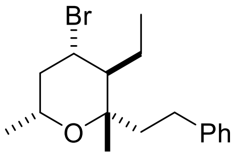
(2*S**,3*S**,4*S**,6*R**)-4-bromo-2-(cyclohexylmethyl)-3-ethyl-2,6-dimethyltetrahydro-2*H*-pyran (**4k**) was obtained as the major isomer (C-2) of a partially separable mixture of epimers, following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 1-cyclohexylpropan-2-one (59 µL, 0.38 mmol) and TMSBr (550 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 100:1), afforded a yellow oil (41 mg, 40%), from which compound **4k** could be isolated. **$^1$H NMR (400 MHz, $CDCl_3$) δ (ppm)** 4.24 (td, *J* = 11.9, 4.5 Hz, 1H, *H*C-Br), 3.66 – 3.57 (m, 1H, *H*C-O), 2.26 (ddd, *J* = 12.7, 4.5, 2.2 Hz, 1H, C*H*H), 1.89 – 1.73 (m, 3H), 1.70 – 1.58 (m, 4H), 1.57 – 1.48 (m, 1H, Cy), 1.47 – 1.37 (m, 4H, Cy), 1.33 – 1.11 (m, 3H, Cy), 1.10 (s, 3H, $CH_3$), 1.09 (d, *J* = 6.3 Hz, 3H, $CH_3$), 1.04 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*$H_3$*), 1.00 – 0.87 (m, 2H). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 80.1 (O-C), 66.2 (HC-O), 56.5 (HC-Br), 53.2 (CH), 49.2 ($CH_2$), 47.1 ($CH_2$), 35.5 ($CH_2$), 35.3 ($CH_2$), 33.3 ($CH_2$), 26.8 ($CH_2$), 26.7 ($CH_2$), 26.6 ($CH_2$), 24.4 ($CH_2$), 22.0 ($CH_3$), 18.6 ($CH_3$), 14.7 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{30}BrO$ ($[M+H]^+$): 317.1475, found 317.1477.

Distinctive signals of minor isomer **5k**: **$^1$H NMR (500 MHz, $CDCl_3$) δ (ppm)** 4.24 (td, *J* = 11.9, 4.5 Hz, 1H, *H*C-I), 3.69 – 3.56 (m, 1H, *H*C-O), 1.26 (s, 3H, $CH_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm) 80.6 (O-C), 66.3 (HC-O), 57.4 (HC-Br), 55.7 (CH), 47.1 ($CH_2$), 36.2 ($CH_2$), 36.1 ($CH_2$), 34.5 ($CH_2$), 32.7 ($CH_2$), 27.3 ($CH_2$), 26.7 ($CH_2$), 26.5 ($CH_2$), 24.5 ($CH_2$), 21.7 ($CH_3$), 18.6 ($CH_3$), 15.4 ($CH_3$).

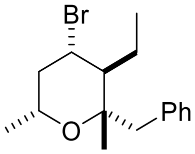


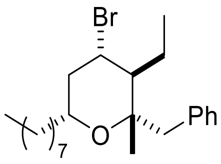
(2*S**,3*S**,4*S**,6*R**)-4-bromo-3-ethyl-2-heptyl-2,6-dimethyltetrahydro-2*H*-pyran (**4l**) was obtained as the major isomer (C-2) of a partially separable mixture of epimers, following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 2-nonanona (66 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 80:1) afforded a yellow oil (51.1 mg, 50%), from which compound **4l** could be isolated. **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.24 (td, *J* = 11.6, 4.5 Hz, 1H, *H*C-Br), 3.67 – 3.60 (m, 1H, *H*C-O), 2.26 (ddd, *J* = 12.7, 4.5, 2.1 Hz, 1H, C*H*H), 1.84 – 1.76 (m, 1H, CH*H*), 1.62 (dt, *J* = 11.6, 4.1 Hz, 1H, CH), 1.53 – 1.46 (m, 3H), 1.45 – 1.36 (m, 4H, chain), 1.33 – 1.23 (m, 7H, chain), 1.11 (d, *J* = 6.0 Hz, 3H, $CH_3$), 1.10 (s, 3H, $CH_3$), 1.04 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*$H_3$*), 0.88 (t, *J* = 6.8 Hz, 3H, $CH_3$). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ (ppm) 79.1 (O-C), 66.3 (HC-O), 56.5 (HC-Br), 52.7 (CH), 47.1 ($CH_2$), 42.2 ($CH_2$), 32.1 ($CH_2$), 30.3 ($CH_2$), 29.6 ($CH_2$), 24.2 ($CH_2$), 22.8 ($CH_2$), 22.7 ($CH_2$), 22.0 ($CH_3$), 18.6 ($CH_3$), 14.7 ($CH_3$), 14.3 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{32}BrO$ ($[M+H]^+$): 319.1631, found 319.1639.

Distinctive signals of minor isomer **5l**: **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 4.26 (td, *J* = 11.6, 4.5 Hz, 1H, *H*C-Br), 3.53 – 3.46 (m, 1H, *H*C-O), 1.22 (s, 3H, $CH_3$), 1.13 (d, *J* = 6.1 Hz, 3H, $CH_3$), 1.06 (t, *J* = 7.4 Hz, 3H, $CH_2$-C*$H_3$*), 0.89 (t, *J* = 6.9 Hz, 3H, $CH_3$). **$^{13}$C NMR (101 MHz, $CDCl_3$)** δ (ppm), 66.3 (HC-O), 56.5 (HC-Br), 55.6 (CH), 46.9 ($CH_2$), 32.0 ($CH_2$), 30.4 ($CH_2$), 29.9 ($CH_2$), 29.5 ($CH_2$), 26.7 ($CH_3$), 24.0 ($CH_2$), 22.8 ($CH_2$), 21.9 ($CH_3$), 15.1 ($CH_3$).

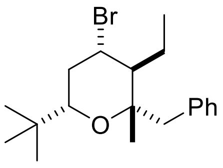

(2*S**,3*S**,4*S**,6*R**)-4-bromo-3-ethyl-2,6-dimethyl-2-phenethyltetrahydro-2*H*-pyran (**4m**) was obtained as the major isomer (C-2) of an inseparable mixture of epimers, following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol, 4-phenylbutan-2-one (57 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 40:1) afforded a yellow oil (62.5 mg, 60%). Compound **4m**: **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 7.30 – 7.26 (m, 2H, Ar-*H*), 7.23 – 7.15 (m, 3H, Ar-*H*), 4.27 (td, *J* = 11.9, 4.6 Hz, 1H, *H*C-Br), 3.73 – 3.66 (m, 1H, *H*C-O), 2.77 – 2.71 (m, 2H, C*H*$_2$-Ph), 2.30 (ddd, *J* = 12.8, 4.4, 2.2 Hz, 1H, C*H*H), 1.94 – 1.78 (m, 3H), 1.69 (dt, *J* = 11.9, 4.0 Hz, 1H, CH), 1.53 – 1.41 (m, 2H, C*H*$_2$-CH$_3$), 1.17 (s, 3H, CH$_3$), 1.16 (d, *J* = 6.1 Hz, 3H, CH$_3$), 1.07 (t, *J* = 7.6 Hz, 3H, CH$_2$-C*H*$_3$). **$^{13}$C NMR (101 MHz, CDCl$_3$)** δ (ppm) 143.1 (C), 128.6 (2xCH), 128.5 (2xCH), 125.8 (CH), 78.8 (O-C), 66.4 (HC-O), 56.1 (HC-Br), 52.8 (CH), 47.1 (CH$_2$), 44.1 (CH$_2$), 29.2 (CH$_2$), 24.2 (CH$_2$), 22.0 (CH$_3$), 18.6 (CH$_3$), 14.8 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{17}H_{26}BrO$ ([M+H]$^+$): 325.1162, found 325.1163.

Distinctive signals of minor isomer **5m**: **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.24 (td, *J* = 11.8, 4.5 Hz, 1H, *H*C-Br), 3.68 – 3.60 (m, 1H, *H*C-O), 2.67 – 2.59 (m, 1H, C*H*H-Ph), 2.58 – 2.50 (m, 1H, CH*H*-Ph), 1.33 (s, 3H, CH$_3$), 1.20 (d, *J* = 6.1 Hz, 3H, CH$_3$), 1.06 (t, *J* = 7.5 Hz, 3H, CH$_2$-C*H*$_3$). **$^{13}$C NMR (101 MHz, CDCl$_3$)** δ (ppm) 79.3 (O-C), 56.3 (CH), 55.1 (HC-Br), 46.8 (CH$_2$), 32.4 (CH$_2$), 28.7 (CH$_2$), 24.0 (CH$_2$), 21.9 (CH$_3$), 15.1 (CH$_3$).

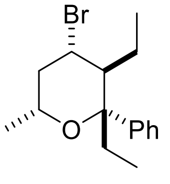

(2*S**,3*S**,4*S**,6*R**)-2-benzyl-4-bromo-3-ethyl-2,6-dimethyltetrahydro-2*H*-pyran (**4n**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), benzyl methyl ketone (57 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 30:1) afforded a colourless oil (59.8 mg, 60%). **$^1$H NMR (400 MHz, CDCl$_3$)** δ (ppm) 7.32 – 7.19 (m, 5H, Ar-*H*), 4.24 (td, *J* = 11.6, 4.5 Hz, 1H, *H*C-Br), 3.65 – 3.55 (m, 1H, *H*C-O), 2.86 (d, *J* = 13.9 Hz, 1H, C*H*H-Ph), 2.81 (d, *J* = 13.9 Hz, 1H, CH*H*-Ph), 2.25 (ddd, *J* = 12.7, 4.5, 2.2 Hz, 1H, C*H*H), 1.84 – 1.73 (m, 1H, CH*H*), 1.64 – 1.48 (m, 3H), 1.14 (d, *J* = 6.0 Hz, 3H, CH$_3$), 1.10 (t, *J* = 7.4 Hz, 3H, CH$_2$-C*H*$_3$), 1.04 (s, 3H, CH$_3$). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 137.5 (C), 131.3 (2xCH), 127.7 (2xCH), 126.3 (CH), 79.8 (O-C), 66.3 (HC-O), 55.7 (HC-Br), 52.6 (CH), 47.7 (CH$_2$), 46.9 (CH$_2$), 24.4 (CH$_2$), 21.9 (CH$_3$), 17.9 (CH$_3$), 14.4 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{24}BrO$ ([M+H]$^+$): 311.1005, found 311.1012.


(2*S**,3*S**,4*S**,6*S**)-2-benzyl-4-bromo-3-ethyl-2-methyl-6-octyltetrahydro-2*H*-pyran (**4o**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1c** (80.0 mg, 0.23 mmol), benzyl methyl ketone ne (37 µL, 0.28 mmol) and TMSBr (37 µL, 0.28 mmol). Purification by column chromatography (hexane/EtOAc: 90:1) afforded a yellow oil (59.3 mg, 63%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 7.31– 7.20 (m, 5H, Ar-*H*), 4.25 (td, *J* = 11.7, 4.5 Hz, 1H, *H*C-Br), 3.44 – 3.37 (m, 1H, *H*C-O), 2.86 (d, *J* = 13.9 Hz, 1H C*H*H-Ph), 2.82 (d, *J* = 13.9 Hz, 1H, C*H*H-Ph), 2.25 (ddd, *J* =

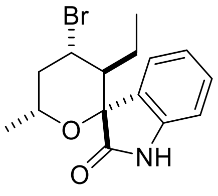
12.6, 4.3, 1.8 Hz, 1H, C*H*H), 1.85 – 1.76 (m, 1H, CH*H*), 1.64 – 1.55 (m, 4H), 1.41 – 1.22 (m, 13H, chain), 1.12 (t, *J* = 7.4 Hz, 3H, $CH_2$-$\mathit{CH_3}$), 1.01 (s, 3H, $CH_3$), 0.90 (t, *J* = 6.7 Hz, 3H, $CH_3$). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ (ppm) 137.5 (C), 131.4 (2xCH), 127.6 (2xCH), 126.2 (CH), 79.5 (O-C), 69.9 (HC-O), 56.1 (HC-Br), 53.4 (CH), 47.8 ($CH_2$), 45.4 ($CH_2$), 36.2 ($CH_2$), 32.1 (CH), 29.7 ($CH_2$), 29.6 ($CH_2$), 29.4 ($CH_2$), 25.5 ($CH_2$), 24.4 ($CH_2$), 22.8 ($CH_2$), 17.7 ($CH_3$), 14.5 ($CH_3$), 14.3 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{23}H_{38}BrO$ ($[M+H]^+$): 409.2101, found 409.2105.



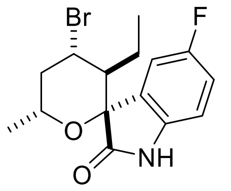
(2*S**,3*S**,4*S**,6*S**)-2-benzyl-4-bromo-6-(*tert*-butyl)-3-ethyl-2-methyltetrahydro-2*H*-pyran (**4p**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1c** (80.0 mg, 0.28 mmol), benzyl methyl ketone (45 µL, 0.34 mmol) and TMSBr (45 µL, 0.34 mmol). Purification by column chromatography (hexane/EtOAc: 100:1) afforded a yellow oil (29.7 mg, 30%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 7.28 – 7.18 (m, 5H, Ar-*H*), 4.25 (td, *J* = 11.6, 4.5 Hz, 1H, *H*C-Br), 3.02 (dd, *J* = 11.7, 2.0 Hz, 1H, *H*C-O), 2.86 (d, *J* = 13.5 Hz, 1H, C*H*H-Ph), 2.82 (d, *J* = 13.5 Hz, 1H, CH*H*-Ph), 2.22 (ddd, *J* = 12.3, 4.5, 1.9Hz, 1H, C*H*H), 1.84 – 1.74 (m, 1H, CH*H*), 1.63 – 1.53 (m, 1H, CH), 1.67 – 1.56 (m, 3H), 1.12 (t, *J* = 7.4 Hz, 3H, $CH_2$-$\mathit{CH_3}$), 1.01 (s, 3H, $CH_3$), 0.84 (s, 9H, $CH_3$). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ (ppm) 137.4 (C), 131.5 (CH), 127.6 (2xCH), 126.2 (2xCH), 79.3 (O-C), 77.6 (HC-O), 57.4 (HC-Br), 53.2 (CH), 48.0 ($CH_2$), 39.8 ($CH_2$), 34.3 (C), 26.1 ($CH_2$), 24.3 (3x$CH_3$), 17.9 ($CH_3$), 14.4 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{19}H_{30}BrO$ ($[M+H]^+$): 353.1475, found 353.1471.



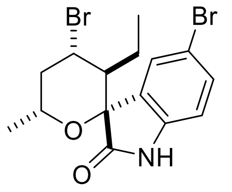
(2*R**,3*S**,4*S**,6*R**)-4-bromo-2,3-diethyl-6-methyl-2-phenyltetrahydro-2*H*-pyran (**4q**) was obtained as following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), ethyl phenyl ketone (50 µL, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 30:1) afforded a yellow oil (29.9 mg, 30%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 7.56 – 7.47 (m, 2H, Ar-*H*), 7.38 – 7.32 (m, 2H, Ar-*H*), 7.29 – 7.22 (m, 1H, Ar-*H*), 4.40 (td, *J* = 12.0, 4.6 Hz, 1H, *H*C-Br), 3.81 – 3.73 (m, 1H, *H*C-O), 2.45 (ddd, *J* = 12.9, 4.6, 2.2 Hz, 1H, C*H*H), 2.23 – 2.14 (m, 1H, C*H*H), 2.11 – 1.99 (m, 2H), 1.78 (ddd, *J* = 12.0, 4.8, 3.4, 1H, CH), 1.49 – 1.35 (m, 2H, $C\mathit{H_2}$-$CH_3$), 1.27 (d, *J* = 6.1 Hz, 3H, $CH_3$), 0.81 (t, *J* = 7.2 Hz, 3H, $CH_2$-$\mathit{CH_3}$), 0.53 (t, *J* = 7.5 Hz, 3H, $CH_3$). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ (ppm) 143.6 (C), 128.2 (2xCH), 127.2 (CH), 126.8 (2xCH), 83.4 (O-C), 66.1 (HC-O), 57.2 (CH), 55.2 (HC-Br), 47.0 ($CH_2$), 22.5 ($CH_2$), 22.0 ($CH_3$), 19.1 ($CH_2$), 13.8 ($CH_3$), 6.9 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{24}BrO$ ($[M+H]^+$): 311.1005, found 311.1019.



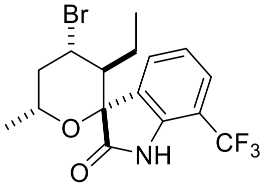
(3*R**,3'*S**,4'*S**,6'*R**)-4'-bromo-3'-ethyl-6'-methyl-3',4',5',6'-tetrahydrospiro[indoline-3,2'-pyran]-2-one (**4r**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), isatine (55.9 mg, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 10:1) afforded a white solid (67.4 mg, 65%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 7.44 (s, 1H, NH), 7.31 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.28 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.10 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 6.82 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 4.95 (td, *J* = 11.8, 4.4 Hz, 1H, *H*C-Br), 4.76 – 4.68 (m, 1H, *H*C-O), 2.50 (ddd, *J* = 13.0, 4.4, 2.2 Hz, 1H, C*H*H), 2.18 (ddd, *J* = 11.8, 5.9, 3.1 Hz, 1H, CH), 2.13 – 2.03 (m, 1H, CH*H*), 1.60 – 1.50 (m, 1H, C*H*H-CH$_3$), 1.29 – 1.19 (m, 1H, CH*H*-CH$_3$), 1.17 (d, *J* = 6.2 Hz, 3H, CH$_3$), 0.67 (t, *J* = 7.6 Hz, 3H, CH$_2$-C*H*$_3$). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 176.5 (C), 140.7 (C), 130.2 (CH), 130.1 (C), 124.5 (CH), 123.4 (CH), 109.9 (CH), 81.2 (O-C), 67.9 (HC-O), 52.2 (HC-Br), 50.8 (CH), 46.1 (CH$_2$), 22.8 (CH$_2$), 21.56 (CH$_3$), 13.2 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{15}H_{19}BrNO_2$ ([M+H]$^+$): 324.0594, found 324.0597. **Melting point** = 138.5 – 140.0 ˚C.



(3*R**,3'*S**,4'*S**,6'*R**)-4'-bromo-3'-ethyl-5-fluoro-6'-methyl-3',4',5',6'-tetrahydrospiro[indoline-3,2'-pyran]-2-one (**4s**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 5-fluoroisatin (62.7 mg, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 5:1) afforded a white solid (38.3 mg, 35%). **$^{1}$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 8.06 (s, 1H, NH), 7.05 (dd, *J* = 8.5, 4.1 Hz, 1H, Ar-*H*), 6.98 (ddd, *J* = 9.0, 8.5, 2.6 Hz, 1H, Ar-*H*), 6.78 (dd, *J* = 8.5, 4.1 Hz, 1H, Ar-*H*), 4.91 (td, *J* = 11.8, 4.4 Hz, 1H, *H*C-Br), 4.74 – 4.66 (m, 1H, *H*C-O), 2.49 (ddd, *J* = 13.1, 4.4, 2.2 Hz, 1H, C*H*H), 2.11 (ddd, *J* = 11.8, 5.7, 3.2 Hz, 1H, CH), 2.10 – 2.02 (m, 1H, CH*H*), 1.61 – 1.52 (m, 1H, C*H*H-CH$_3$), 1.26 – 1.18 (m, 1H, CH*H*-CH$_3$), 1.17 (d, *J* = 6.2 Hz, 3H, CH$_3$), 0.69 (t, *J* = 7.6 Hz, 3H, CH$_2$-C*H*$_3$). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 177.0 (C), 159.6 (d, $^{1}J_{\text{C-F}}$ = 242.5 Hz, C), 136.7 (C), 131.7 (C), 116.6 (d, $^{2}J_{\text{C-F}}$ = 23.7 Hz, CH), 112.5 (d, $^{2}J_{\text{C-F}}$ = 24.8 Hz, CH), 110.8 (d, $^{3}J_{\text{C-F}}$ = 7.9 Hz, CH), 81.5 (O-C), 68.1 (HC-O), 51.6 (HC-Br), 50.8 (CH), 46.0 (CH$_2$), 22.7 (CH$_2$), 21.5 (CH$_3$), 13.2 (CH$_3$). **$^{19}$F NMR (470 MHz, CDCl$_3$)** δ (ppm) -119.1 (ddd, $^{3}J_{\text{F-H}}$ = 9.1, 7.5 Hz, $^{4}J_{\text{F-H}}$ = 4.2 Hz). **HRMS (ESI+)** m/z calc. for $C_{15}H_{17}BrFNNaO_2$ ([M+Na]$^+$): 364.0319, found 364.0316. **Melting point** = 142.1 – 144.5 ˚C.

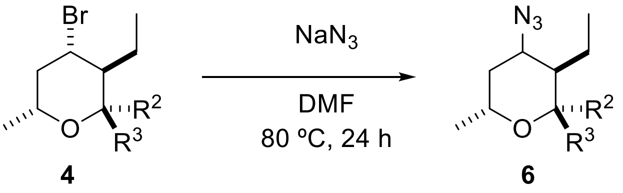


(3*R**,3'*S**,4'*S**,6'*R**)-4’,5-dibromo-3'-ethyl-6'-methyl-3',4',5',6'-tetrahydrospiro[indoline-3,2'-pyran]-2-one (**4t**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol) and 5-bromoisatin (85.9 mg, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 5:1) afforded a white solid (38.7 mg, 30%). **$^{1}$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 8.36 (s, 1H, NH), 7.43 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 7.40 (dd, *J* = 8.3, 2.0 Hz, 1H, Ar-*H*), 6.74 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 4.88 (td, *J* = 11.8, 4.4 Hz, 1H, *H*C-Br), 4.73 – 4.64 (m, 1H, *H*C-O), 2.49 (ddd, *J* = 13.0, 4.4, 2.2 Hz, 1H, C*H*H), 2.13 (ddd, *J* = 11.8, 5.9, 3.2 Hz, 1H, CH), 2.10 – 2.00 (m, 1H, CH*H*), 1.61 – 1.49 (m, 1H, C*H*H-CH$_3$), 1.28 – 1.17 (m, 1H, CH*H*-CH$_3$), 1.17 (d, *J* = 6.2 Hz, 3H, CH$_3$), 0.69 (t, *J* = 7.6 Hz, 3H, CH$_2$-C*H*$_3$). **$^{13}$C NMR (101 MHz, CDCl$_3$)** δ (ppm) 176.9 (C), 139.9 (C), 133.0 (CH), 132.1 (C), 127.7 (CH), 116.1 (C), 111.6 (CH), 81.3 (O-C), 68.2 (HC-O), 51.4 (HC-Br), 50.6 (CH), 45.9 (CH$_2$), 22.7 (CH$_2$), 21.5 (CH$_3$), 13.2 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{15}H_{17}Br_2NNaO_2$ ([M+Na]$^+$): 423.9518, found 423.9517. **Melting point** = 164.9 – 166.1 ˚C.

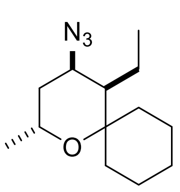


(3*R**,3'*S**,4'*S**,6'*R**)-4'-bromo-3'-ethyl-6'-methyl-7-(trifluoromethyl)-3',4',5',6'-tetrahydrospiro[indoline-3,2'-pyran]-2-one (**4u**) was obtained following the general procedure, from cyclopropylsilyl alcohol **1a** (80.0 mg, 0.32 mmol), 7-trifluoromethylisatin (81.7 mg, 0.38 mmol) and TMSBr (50 µL, 0.38 mmol). Purification by column chromatography (hexane/EtOAc: 5:1) afforded a white solid (37.7 mg, 30%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 8.10 (s, 1H, NH), 7.51 – 7.46 (m, 2H, Ar-*H*), 7.19 (t, *J* = 7.7 Hz, 1H, Ar-*H*), 4.91 (td, *J* = 11.8, 4.4 Hz, 1H, *H*C-Br), 4.76 – 4.63 (m, 1H, *H*C-O), 2.51 (ddd, *J* = 13.0, 4.4, 2.2 Hz, 1H, C*H*H), 2.20 – 2.13 (m, 1H, CH), 2.12 – 2.02 (m, 1H, CH*H*), 1.63 – 1.51 (m, 1H, C*H*H-CH$_3$), 1.29 – 1.18 (m, 1H, CH*H*-CH$_3$), 1.17 (d, *J* = 6.2 Hz, 3H, CH$_3$), 0.66 (t, *J* = 7.6 Hz, 3H, CH$_2$-C*H*$_3$). **$^{13}$C NMR (101 MHz, CDCl$_3$)** δ (ppm) 176.2 (C), 138.5 (q, $^4J_{C\text{-}F}$ = 2.0 Hz, CH), 131.7 (C), 127.8 (CH), 126.9 (q, $^3J_{C\text{-}F}$ = 4.1 Hz, CH), 123.7 (q, $^1J_{C\text{-}F}$ = 271.7 Hz, C-F$_3$), 123.2 (CH), 112.5 (q, $^2J_{C\text{-}F}$ = 33.4 Hz, C), 80.1 (O-C), 68.2 (HC-O), 51.4 (HC-Br), 50.6 (CH), 45.9 (CH$_2$), 22.7 (CH$_2$), 21.4 (CH$_3$), 13.3 (CH$_3$). **$^{19}$F NMR (470 MHz, CDCl$_3$)** δ (ppm) -60.6 (s, CF$_3$). **HRMS (ESI+)** m/z calc. for $C_{16}H_{17}BrF_3NNaO_2$ ([M+Na]$^+$): 414.0287, found 414.0289. **Melting point** = 155.5 – 158.6 ˚C.

## 2.4. Synthesis of azide derivatives 6

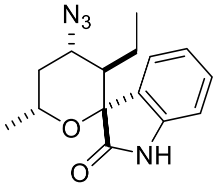


A solution of the corresponding bromo derivative **4** (80 mg, 1 equiv) and NaN$_3$ (2 or 3 equiv) in DMF (0.2 M) was heated at 80 ˚C. The reaction mixture was stirred for 24 hours while monitored by TLC. Upon complete consumption of the starting material, ethyl acetate was added., and the resulting mixture was washed with water (3x10 mL) and NaCl sat. (20 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using mixtures of hexane-ethyl acetate as eluents to afford tetrahydropyrans **6**.



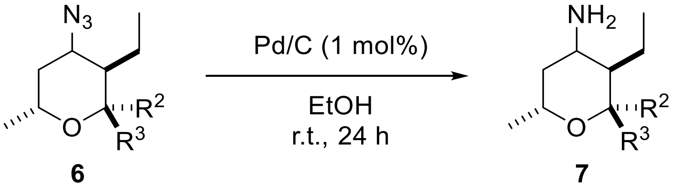
(2*R**,4*R**,5*R**)-4-azido-5-ethyl-2-methyl-1-oxaspiro[5.5]undecane (**6d**) was obtained following the general procedure from bromo derivative **4d** (80.0 mg, 0.29 mmol) and sodium azide (56.6 mg, 0.87 mmol, 3 equiv). Purification by column chromatography (hexane/EtOAc: 50:1) afforded a yellow oil (35.1 mg, 51%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 4.00 (q, *J* = 3.4 Hz, 1H, *H*C-N$_3$), 3.80 – 3.73 (m, 1H, *H*C-O), 2.33 – 2.26 (m, 1H, Cy), 1.91 (dt, *J* = 13.9, 2.4 Hz, 1H, C*H*H), 1.75 (qt, *J* = 13.0, 3.7 Hz, 1H, Cy), 1.66 – 1.57 (m, 2H), 1.53 – 1.34 (m, 5H), 1.30 – 1.21 (m, 1H, Cy), 1.27 – 1.20 (m, 1H, Cy), 1.20 – 1.16 (m, 2H, CH), 1.18 (d, *J* = 6.2 Hz, 3H, CH$_3$), 1.14 – 0.98 (m, 1H, Cy), 0.93 (t, *J* = 7.4 Hz, 3H, CH$_2$-*CH*$_3$). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 75.6 (C), 59.7 (HC-O), 57.6 (HC-N$_3$), 49.6 (CH), 37.8 (CH$_2$), 37.5 (CH$_2$), 27.2 (CH$_2$), 26.2

($CH_2$), 22.0 ($CH_3$), 21.5 ($CH_2$), 20.9 ($CH_2$), 19.8 ($CH_2$), 12.0 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{13}H_{24}N_3O$ ($[M+H]^+$): 238.1914, found 238.1916

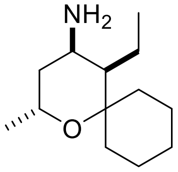


(3*R**,3'*R**,4'*S**,6'*R**)-4'-azido-3'-ethyl-6'-methyl-3',4',5',6'-tetrahydrospiro[indoline-3,2'-pyran]-2-one (**6q**) was obtained following the general procedure, from bromo derivative **4q** (80.0 mg, 0.25 mmol) and sodium azide (32.5 mg, 0.5 mmol, 2 equiv). Purification by column chromatography (hexane/EtOAc: 5:1) afforded a yellowish solid (68.0 mg, 95%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 7.30 – 7.24 (m, 2H Ar-*H*), 7.21 (s, 1H, NH), 7.08 (t, *J* = 7.6 Hz, 1H, Ar-*H*), 6.80 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 4.76 – 4.69 (m, 1H, *H*C-O), 4.20 (td, *J* = 11.4, 4.4 Hz, 1H, *H*C-$N_3$), 2.19 (ddd, *J* = 12.7, 4.6, 2.3 Hz, 1H, C*H*H), 1.75 (dt, *J* = 10.6, 4.4 Hz, 1H, CH), 1.60 -1.52 (m, 1H, CH*H*), 1.51 – 1.41 (m, 1H, C*H*H-$CH_3$), 1.20 (d, *J* = 6.2 Hz, 3H, $CH_3$), 1.13 – 1.03 (m, 1H, CH*H*-$CH_3$), 0.70 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*H₃*). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ (ppm) 176.5 (C), 140.8 (C), 130.2 (CH), 130.1 (C), 124.4 (CH), 123.5 (CH), 109.8 (CH), 79.8 (O-C), 66.5 (HC-O), 59.0 (HC-$N_3$), 47.1 (CH), 39.1 ($CH_2$), 21.8 ($CH_3$), 21.4 ($CH_2$), 13.5 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{15}H_{18}N_4NaO_2$ ($[M+Na]^+$): 309.1322, found 309.1328. **Melting point** = 140.7 – 142.9 ˚C.

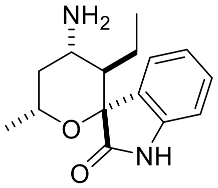
## 2.5. Synthesis of amine derivatives **7**



A solution of azide derivative **6** (1 equiv) in EtOH (0.1 M) at room temperature was added Pd/C (10 wt.%, 0.01 equiv). The mixture was stirred under a hydrogen atmosphere for 24 hours. The catalyst was then removed by filtration through celite and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using mixtures of dicloromethane-methanol as eluents to afford the desired products **7**.

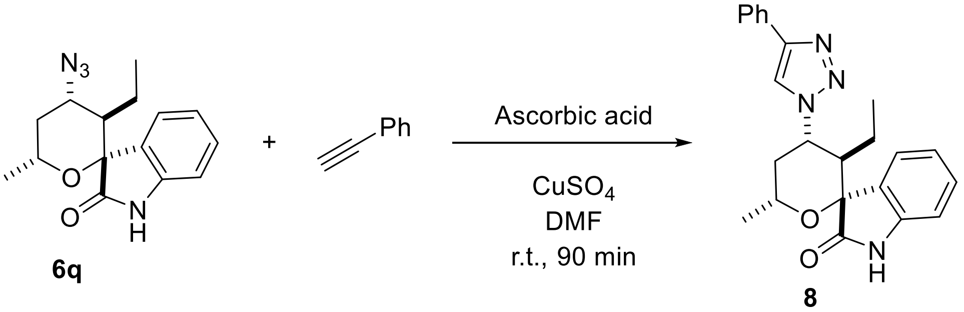


(2*R**,*4R**,5*R**)-5-ethyl-2-methyl-1-oxaspiro[5.5]undecan-4-amine (**7d**) was obtained following the general procedure from azide derivative **6d** (47.0 mg, 0.2 mmol). Purification by column chromatography ($CH_2Cl_2$/$CH_3OH$: 15:1) afforded a yellow oil (22.8 mg, 54%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 3.93 – 3.83 (m, 1H, *H*C-O), 3.35 (br s, 1H, *H*C-$NH_2$), 2.41 (d, *J* = 14.0 Hz, 1H, C*H*H), 1.77 (qt, *J* = 13.0, 3.8 Hz, 1H, Cy), 1.68– 1.55 (m, 3H), 1.54 – 1.35 (m, 5H), 1.34 – 1.23 (m, 2H), 1.18 – 1.01 (m, 5H), 1.17 (d, *J* = 6.2 Hz, 3H, $CH_3$), 0.92 (t, *J* = 7.4 Hz, 3H, $CH_2$-C*H₃*). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ (ppm) 75.7 (C), 59.2 (HC-O), 50.0 (CH), 44.9 (HC-$NH_2$), 42.1 ($CH_2$), 37.8 ($CH_2$), 28.7 ($CH_2$), 26.3 ($CH_2$), 22.3 ($CH_3$), 21.6 ($CH_2$), 21.2 ($CH_2$), 19.5 ($CH_2$), 12.0 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{13}H_{26}NO$ ($[M+H]^+$): 212.2009, found 212.2003.

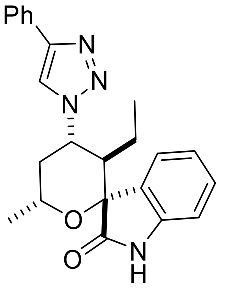


(3*R**,3'*R**,4'*S**,6'*R**)-4'-amino-3'-ethyl-6'-methyl-3',4',5',6'-tetrahydrospiro[indoline-3,2'-pyran]-2-one (**7q**) was obtained following the general procedure, from bromo derivative **6q** (80.0 mg, 0.28 mmol). Purification by column chromatography ($CH_2Cl_2$/$CH_3OH$: 10:1) afforded a white solid (53.9 mg, 74%). **$^1$H NMR (500 MHz, $CDCl_3$)** δ (ppm) 7.69 (s, 1H, NH), 7.26 (dd, *J* = 7.6, 0.9 Hz, 1H, Ar-*H*), 7.21 (td, *J* = 7.6, 0.9 Hz, 1H, Ar-*H*), 7.03 (td, *J* = 7.6 Hz, 0.9 Hz, 1H, Ar-*H*), 6.80 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 4.77 – 4.69 (m, 1H, *H*C-O), 3.61 (td, *J* = 11.2, 3.8 Hz, 1H, *H*C-$NH_2$), 1.97 (ddd, *J* = 12.8, 4.2, 2.2 Hz, 1H, C*H*H), 1.55 (ddd, *J* = 10.5, 5.2, 4.2 Hz, 1H, CH), 1.48 -1.34 (m, 2H), 1.29 (dt, *J* = 12.8, 11.2 Hz, 1H, CH*H*), 1.51 – 1.41 (m, 1H, C*H*H-$CH_3$), 1.15 (d, *J* = 6.2 Hz, 3H, $CH_3$), 1.13 – 1.03 (m, 1H, CH*H*-$CH_3$), 0.67 (t, *J* = 7.6 Hz, 3H, $CH_2$-C*$H_3$*). **$^{13}$C NMR (126 MHz, $CDCl_3$)** δ (ppm) 178.1 (C), 141.2 (C), 131.0 (CH), 129.7 (C), 124.1 (CH), 123.1 (CH), 109.8 (CH), 80.7 (O-C), 67.0 (HC-O), 50.7 (CH), 47.9 (HC-$NH_2$), 43.9 ($CH_2$), 22.0 ($CH_3$), 20.7 ($CH_2$), 14.2 ($CH_3$). **HRMS (ESI+)** m/z calc. for $C_{15}H_{21}N_2O_2$ ($[M+H]^+$): 261.1598, found 261.1604. **Melting point** = 175.6 – 178.2 ˚C.

### 2.6. Click reaction: Synthesis of triazole derivative **8**



A solution of azide derivative **6q** (60.0 mg, 0.21 mmol, 1.0 equiv), ascorbic acid (40.5 mg, 0.23 mmol, 1.1 equiv) and copper sulphate (20.4 mg, 0.13 mmol, 0.6 equiv) in DMF (2.1 mL, 0.1 M) at room temperature was treated with ethenylbenzene (20 µL, 0.21 mmol, 1.0 equiv). The reaction mixture was stirred a room temperature. Upon complete consumption of the starting materials after 90 min (as monitored by TLC), 5 mL of water were added. The aqueous phase was extracted with dichloromethane (3*10 mL). The combined organic fractions were washed with water (3*15 mL) and NaCl sat. (15 mL). The organic layer was dried over anhydrous $Na_2SO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of hexane-ethyl acetate (2:1) as eluent to afford triazole derivative **8**.



(3*R**,3'*R**,4'*S**,6'*R**)-3'-ethyl-6'-methyl-4'-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-3',4',5',6'-tetrahydrospiro[indoline-3,2'-pyran]-2-one (**8**) was obtained as a white solid (75.9 mg, 93%). **$^1$H NMR (500 MHz, CDCl$_3$)** δ (ppm) 8.63 (s, 1H, NH), 7.89 (s, 1H, =C*H*), 7.86 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.46 – 7.38 (m, 3H, Ar-*H*), 7.33 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.28 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 7.10 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 6.90 (d, *J* = 7.4 Hz, 1H, Ar-*H*), 5.50 (td, *J* = 11.2, 5.2 Hz, 1H, *H*C-triaz.), 4.96 – 4.87 (m, 1H, *H*C-O), 2.58 (dt, *J* = 11.0, 5.2 Hz, 1H, CH), 2.33 – 2.22 (m, 2H, CH$_2$), 1.25 (d, *J* = 6.2 Hz, 3H, CH$_3$), 1.24 – 1.16 (m, 1H, C*H*H-CH$_3$), 1.07 – 0.96 (m, 1H, CH*H*-CH$_3$), 0.19 (t, *J* = 7.6 Hz, 3H, CH$_2$-C*H$_3$*). **$^{13}$C NMR (126 MHz, CDCl$_3$)** δ (ppm) 177.1 (C), 147.5 (C), 141.1 (C),130.6 (C), 130.2 (CH), 129.8 (C), 129.0 (2xCH), 128.3 (CH), 125.8 (2xCH), 124.3 (CH), 123.5 (CH), 119.4 (CH), 110.2 (CH), 80.5 (O-C), 66.9 (HC-O), 58.9 (HC-triaz.), 47.4 (CH), 40.9 (CH$_2$), 21.8 (CH$_3$), 21.0 (CH$_2$), 12.9 (CH$_3$). **HRMS (ESI+)** m/z calc. for $C_{23}H_{24}N_4NaO_2$ ([M+Na]$^+$): 411.1791, found 411.1789. **Melting point** = 134.8 – 137.0 ˚C.

## 3. X-RAY CRYSTALLOGRAPHIC DATA FOR COMPOUND 2f

The crystal structure has been deposited at the Cambridge Crystallographic Date Center and allocated the deposition number CCDC: 2524379. This data can be obtained free of charge from the Cambridge Crystallographic Date Center via www.ccdc.cam.ac.uk/data_request/ci

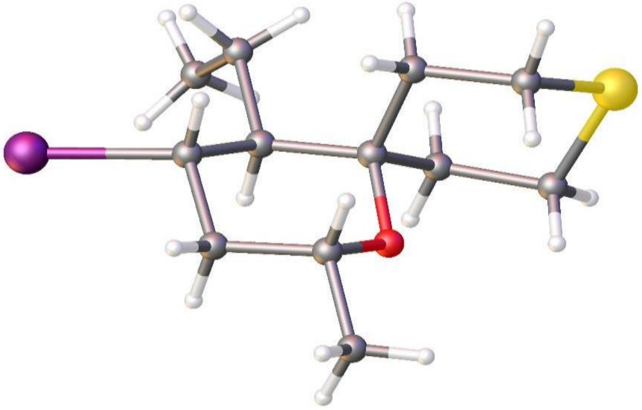


**Figure S2**. X-Ray crystal structure of (2R*,4S*,5S*)-5-ethyl-4-iodo-2-methyl-1-oxa-9-thiaspiro[5.5]undecane (**2f**).

**Experimental.** Single crystals of $C_{12}H_{21}IOS$ (**2f**) were grown from a dichloromethane saturated solution, by slow evaporation. A colourless specimen of $C_{12}H_{21}IOS$, approximate dimensions 0.200 mm x 0.200 mm x 0.300 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 1.54184 Å). A total of 1999 frames were collected. The total exposure time was 5.55 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.[2] The integration of the data using a monoclinic unit cell yielded a total of 41276 reflections to a maximum θ angle of 72.36° (0.81 Å resolution). The final cell constants of a = 9.0806(9) Å, b = 10.7383(11) Å, c = 14.1798(15) Å, β = 99.703(3)°, volume = 1362.9(3) Å$^3$, are based upon the refinement of the XYZ-centroids of 9790 reflections above 20 σ(I) with 6.323° < 2θ < 144.5°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.363. The structure was solved by direct methods and refined with XT, VERSION 2014/5.[3,4] Graphic was made using MERCURY.[5]

**Table S1.** Crystal data and structure refinement for **2f.**

| | |
|---|---|
| Empirical formula | $C_{12}H_{21}IOS$ |
| Formula weight | 340.25 |
| Temperature/K | 300.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 9.0806(9) |
| b/Å | 10.7383(11) |

| | |
|---|---|
| c/Å | 14.1798(15) |
| α/° | 90 |
| β/° | 99.703(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 1362.9(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.658 |
| μ/mm$^{-1}$ | 19.684 |
| F(000) | 680.0 |
| Crystal size/mm$^3$ | 0.3 × 0.2 × 0.2 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 10.388 to 145.208 |
| Index ranges | -11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17 |
| Reflections collected | 33602 |
| Independent reflections | 2703 [$R_{int}$ = 0.1255, $R_{sigma}$ = 0.0483] |
| Data/restraints/parameters | 2703/0/84 |
| Goodness-of-fit on F$^2$ | 1.299 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1026, $wR_2$ = 0.2610 |
| Final R indexes [all data] | $R_1$ = 0.1045, $wR_2$ = 0.2721 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.90/-4.97 |

**Table 2.** Sample and crystal data for **2f.**

| | | |
|---|---|---|
| **Chemical formula** | $C_{12}H_{21}IOS$ | |
| **Formula weight** | 340.26 g/mol | |
| **Wavelength** | 1.54184 Å | |
| **Crystal size** | 0.200 x 0.200 x 0.300 mm | |
| **Crystal habit** | colorless prism | |
| **Crystal system** | monoclinic | |
| **Unit cell dimensions** | a = 9.0806(9) Å | α = 90° |

| | | |
|---|---|---|
| | b = 10.7383(11) Å | β = 99.703(3)° |
| | c = 14.1798(15) Å | γ = 90° |
| **Volume** | 1362.9(3) Å$^3$ | |
| **Z** | 2 | |

**Table 3.** Data collection and structure refinement for **2f.**

| | |
|---|---|
| **Reflections collected** | 41276 |
| **Absorption correction** | Multi-Scan |
| **Structure solution technique** | direct methods |
| **Structure solution program** | XT, VERSION 2014/5 |

## 4. REFERENCES

[1] L. F. Peña, A. Barbero, Terminal cyclopropylsilyl alcohols as useful key units to access 2,3,4,6-tetrasubstituted tetrahydropyran scaffolds by stereocontrolled Prins cyclization, *Org. Lett.,* 2024, **26**, 5202−5207.

[2] CrysAlisPro-Data Collection and Integration Software, Agilent Technologies UK Ltd, Oxford, UK, 2011.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.,* 2009, **42**, 339–341.

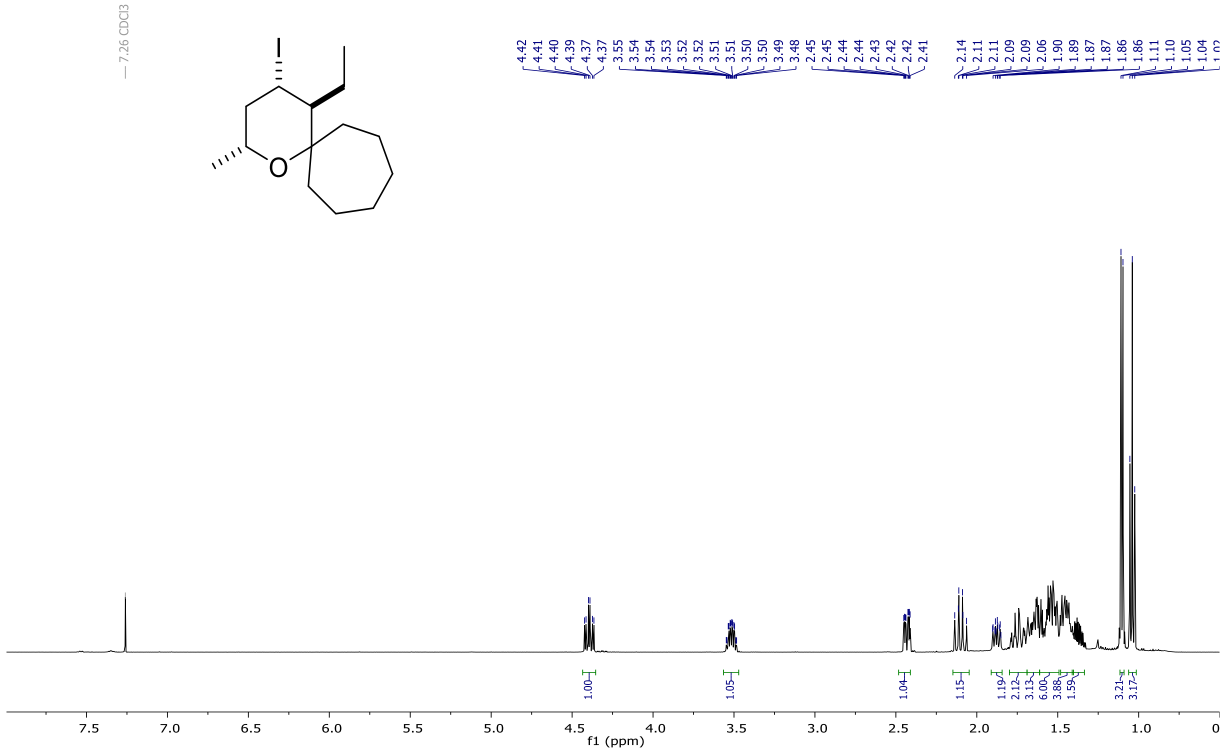
[4] G. M. Sheldrick, Crystal Structure Refinement with SHELXL. *Acta Crystallogr., Sect. C.,* 2015, **71**, 3–8.

[5] C. F. Macrae, I. Sovago, S. J. Cottrell, P. T. A. Galek, P. McCabe, E. Pidcock, M. Platings, G. P. Shields, J. S. Stevens, M. Towler, P. A. Wood, Mercury 4.0: from visualization to analysis, design and prediction. *J. Appl. Crystallogr.,* 2020, **53**, 226-235.

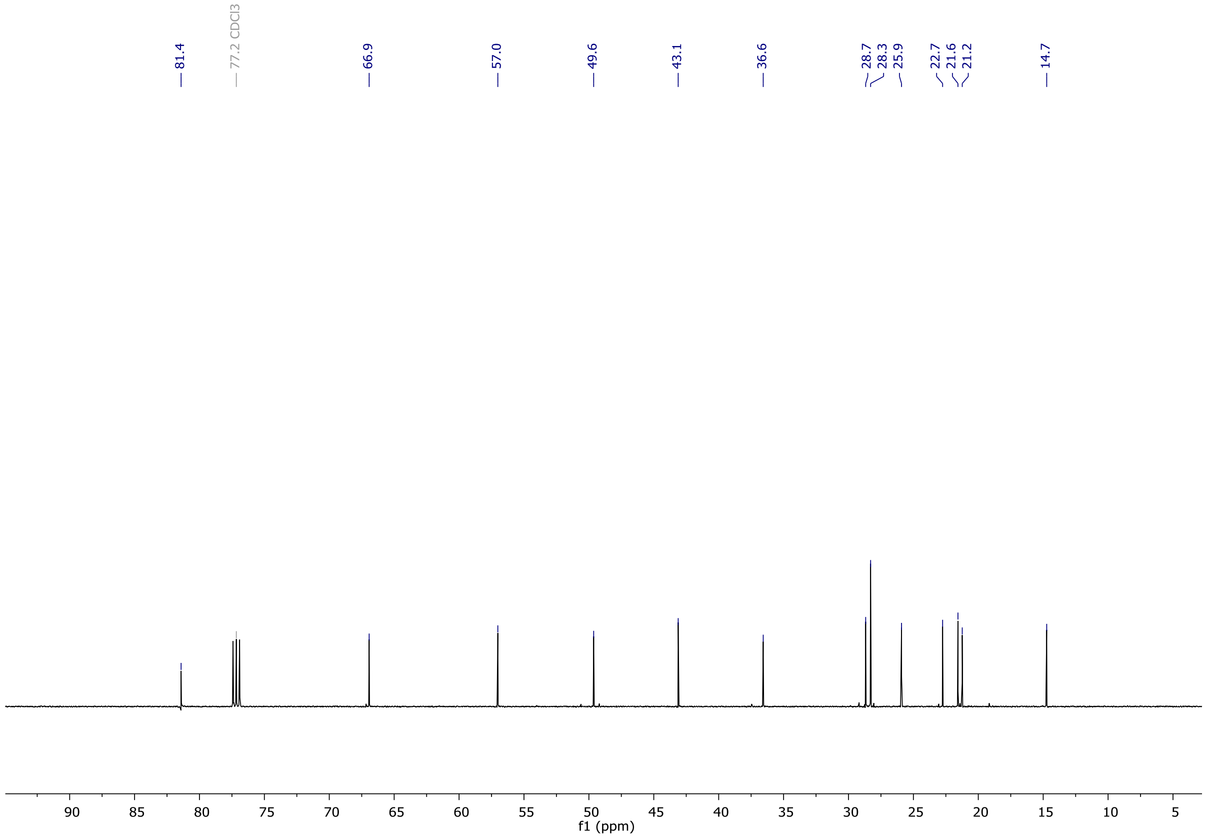
## 5. SPECTROSCOPY CHARACTERIZATION

### Compound 2a

**$^1$H NMR** (500 MHz, CDCl$_3$)

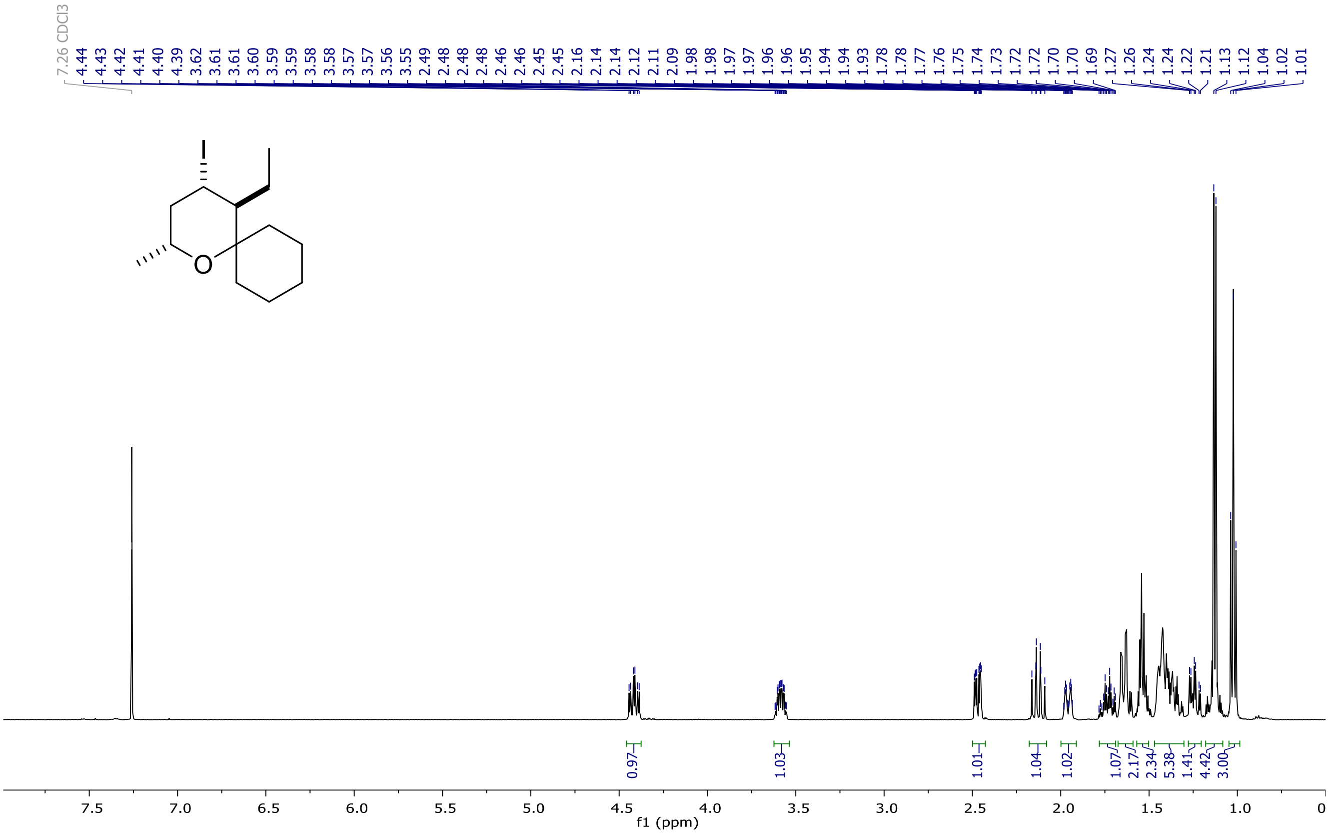


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

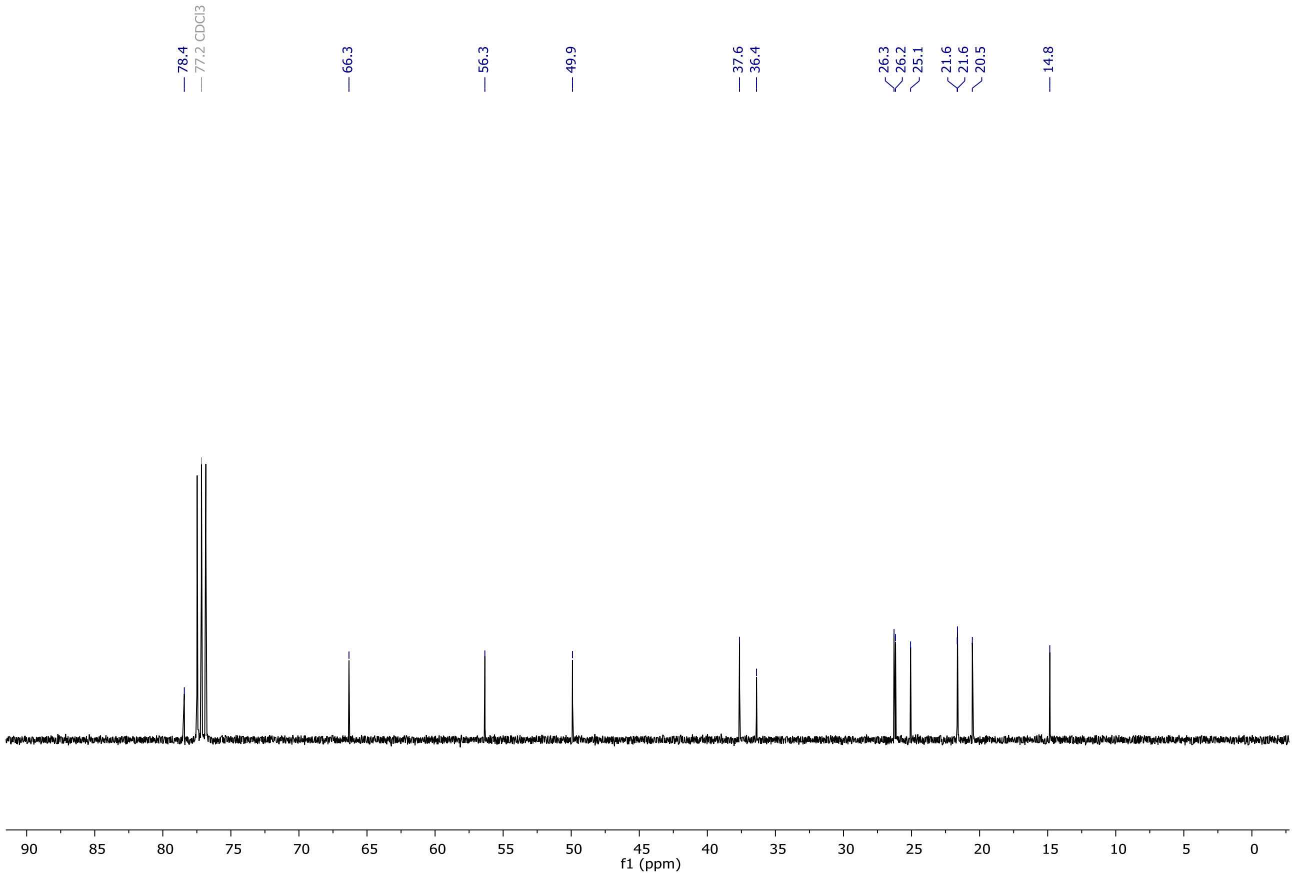


**Compound 2b**

**$^{1}$H NMR** (500 MHz, CDCl$_3$)

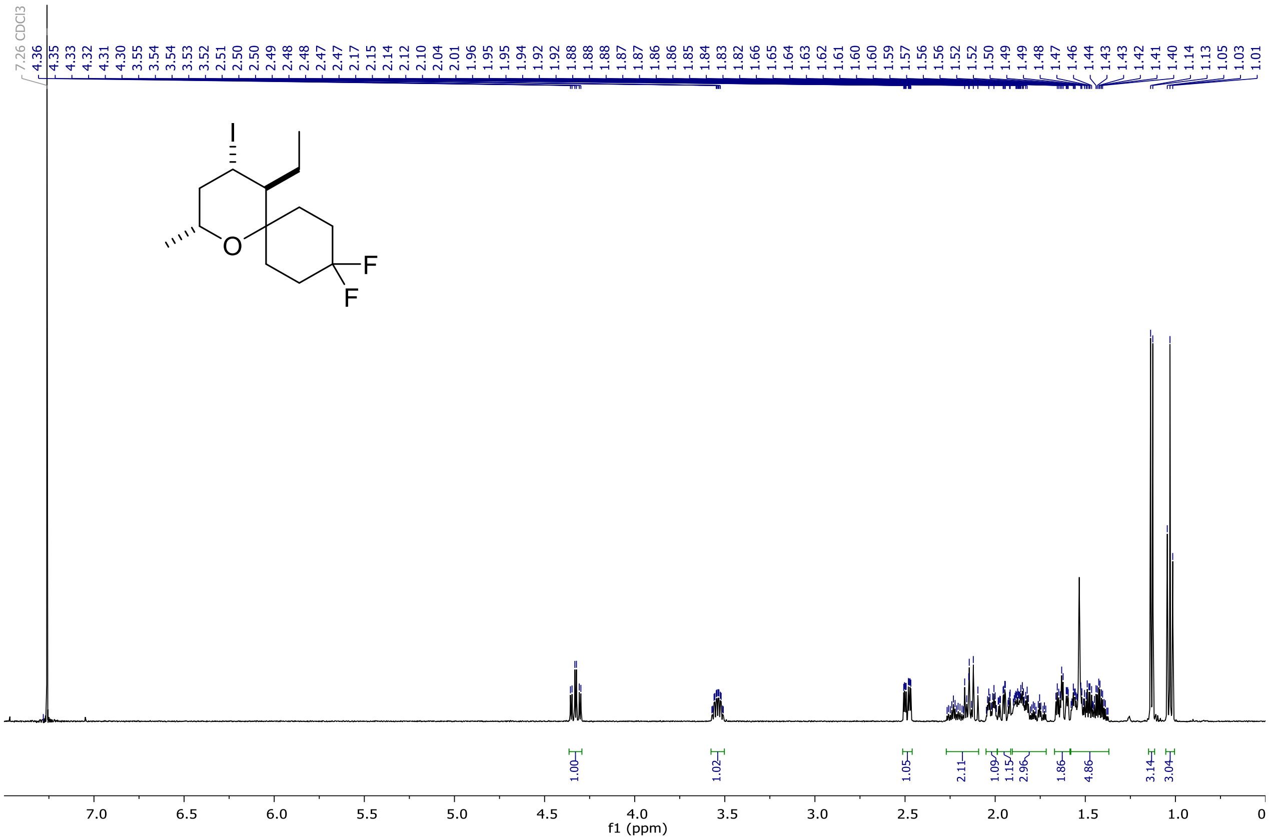


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

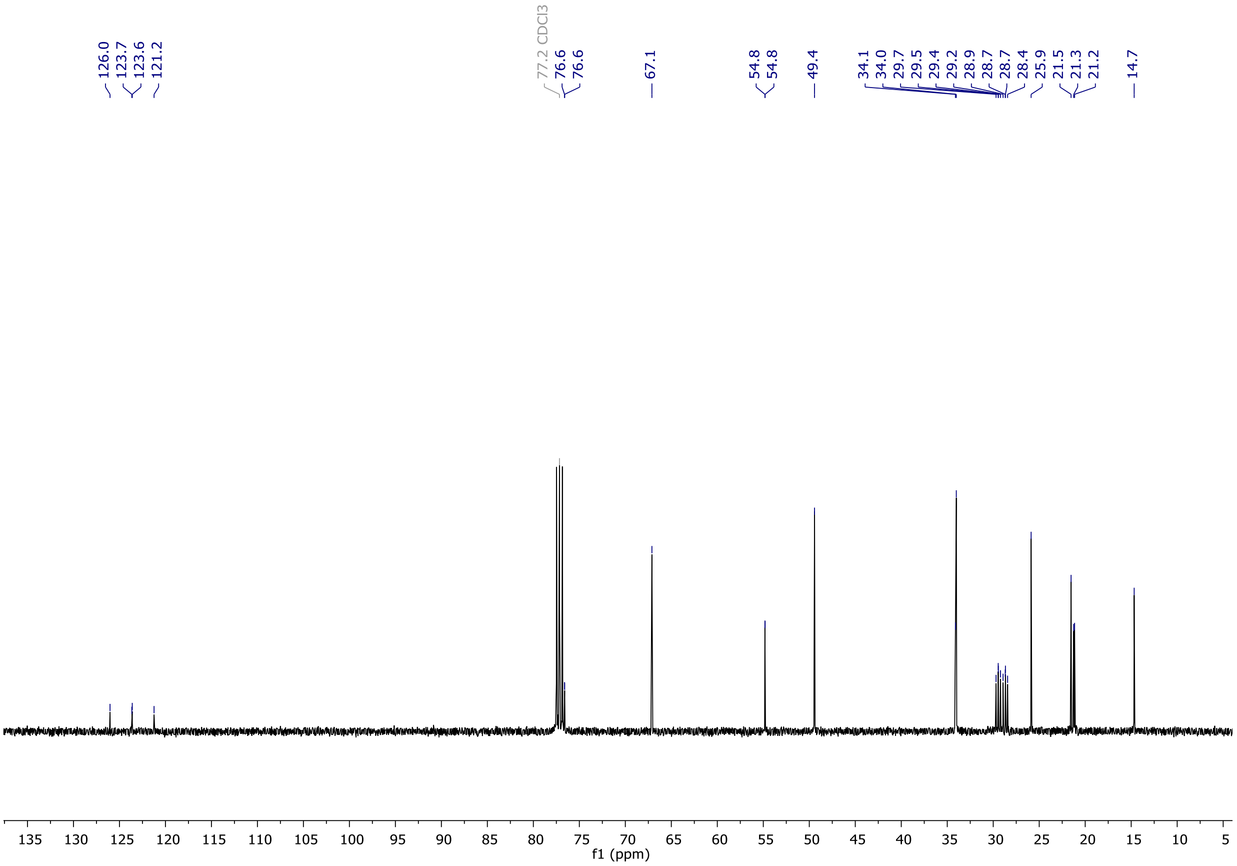


## Compound 2c

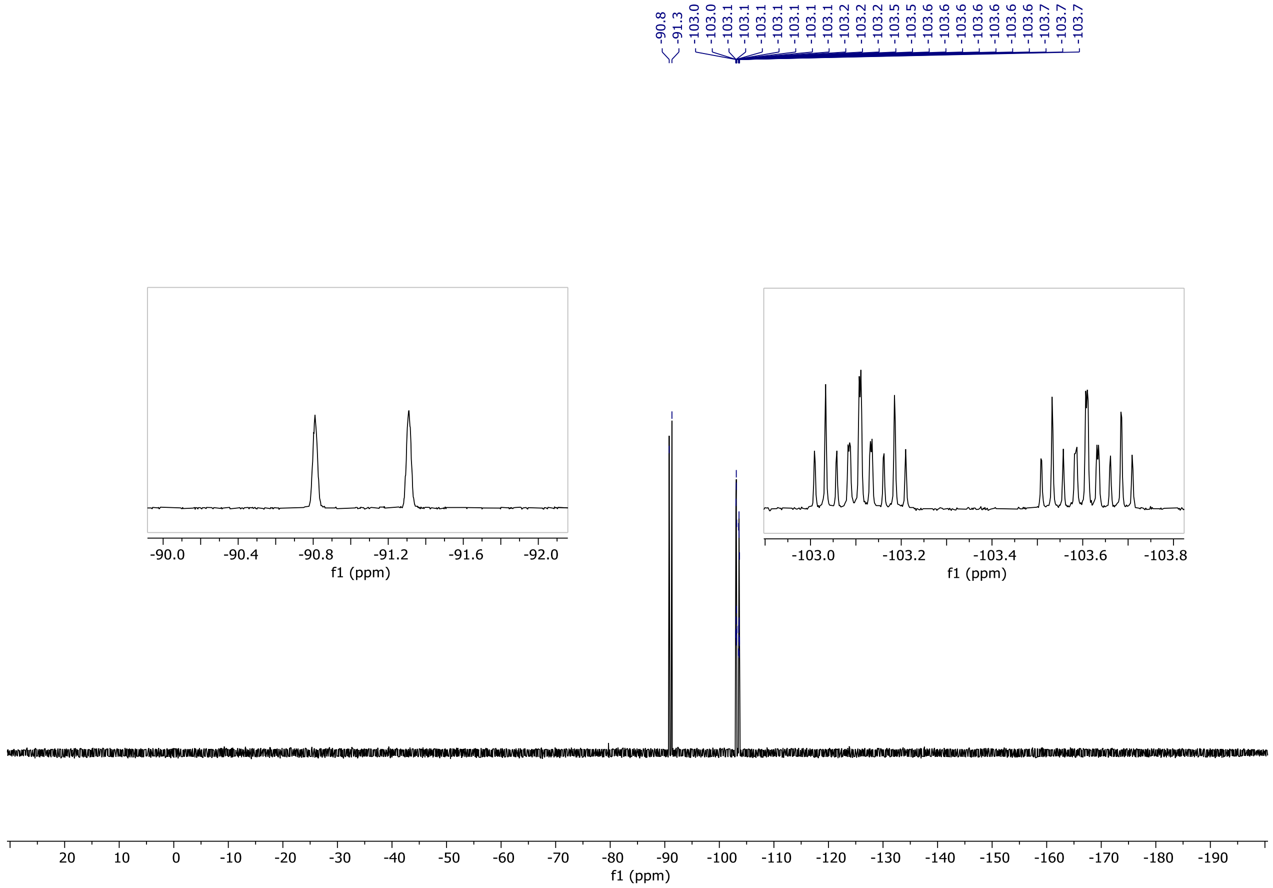
**$^{1}$H NMR** (500 MHz, CDCl$_3$)



**$^{13}$C NMR** (101 MHz, CDCl$_3$)

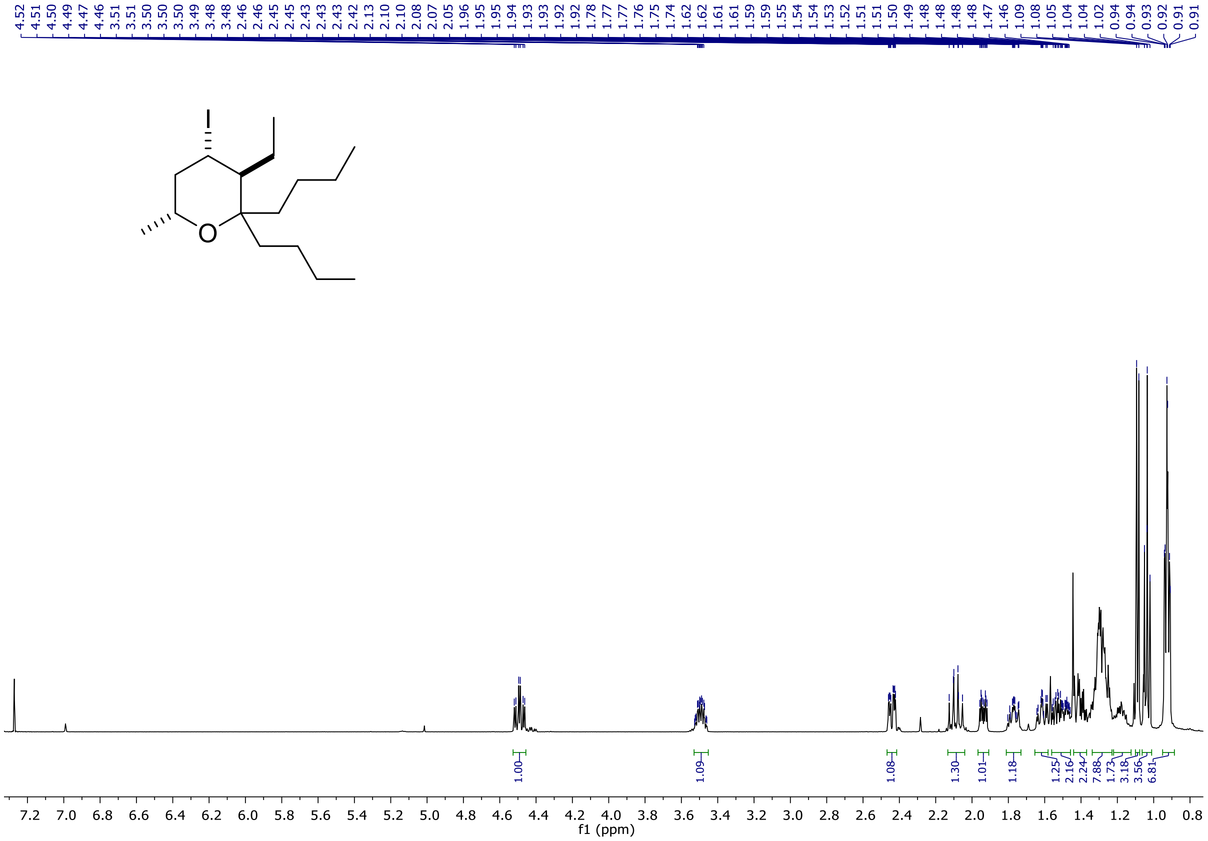


$^{19}$**F NMR** (470 MHz, $CDCl_3$)

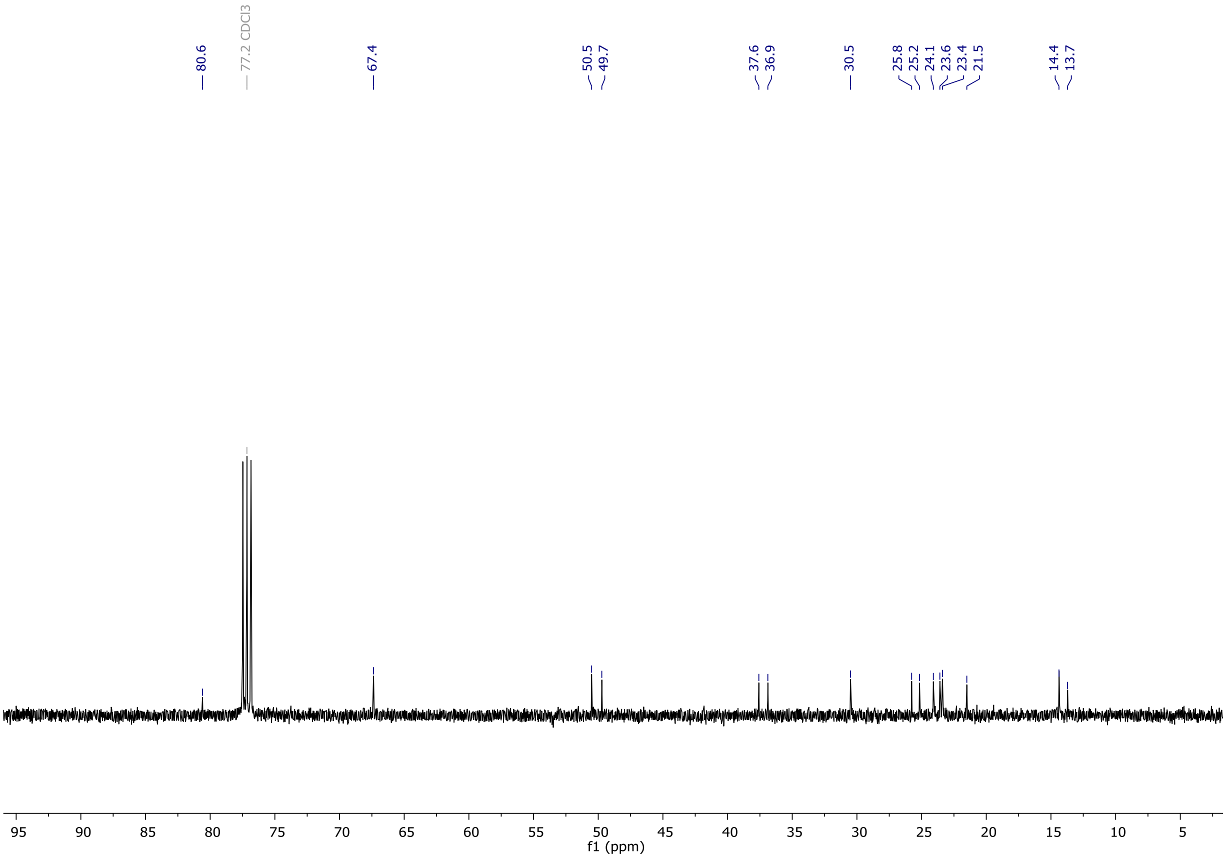


**Compound 2d**

**$^1$H NMR** (500 MHz, CDCl$_3$)

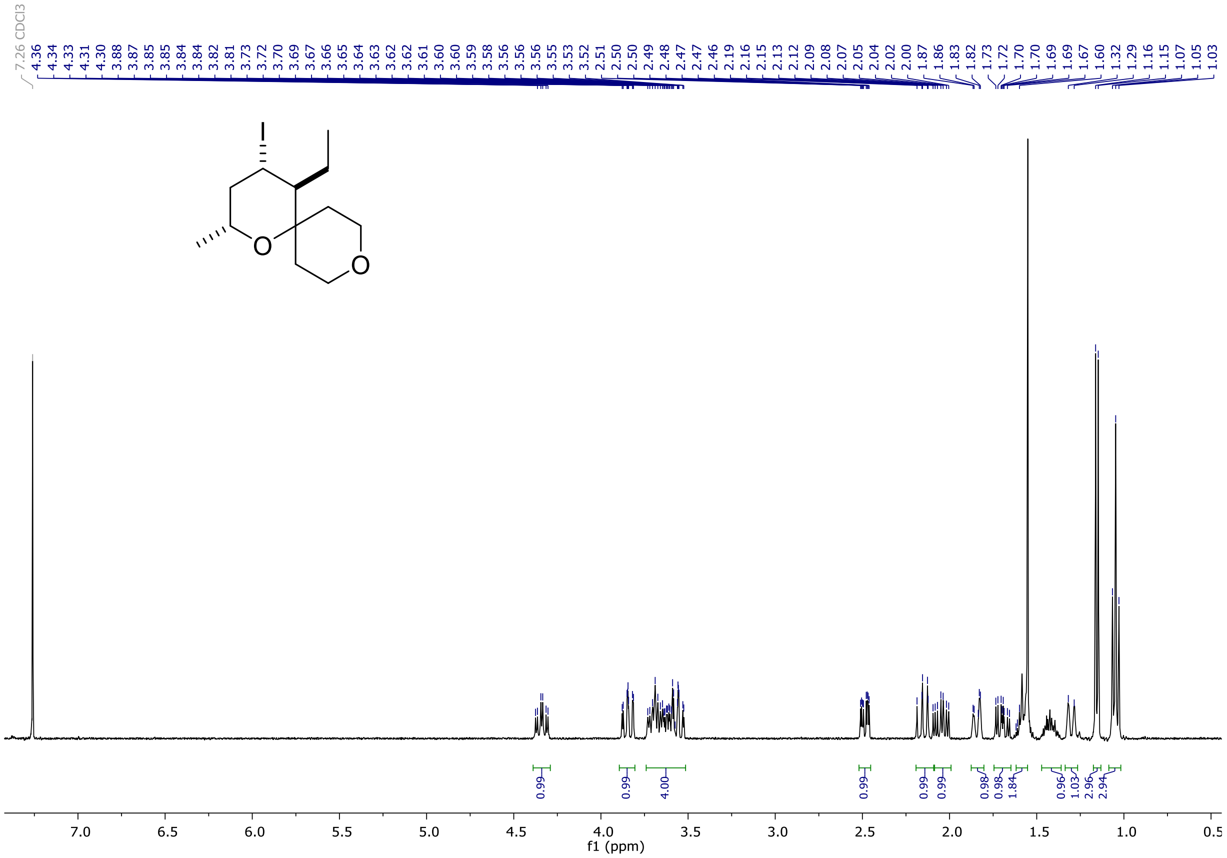


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

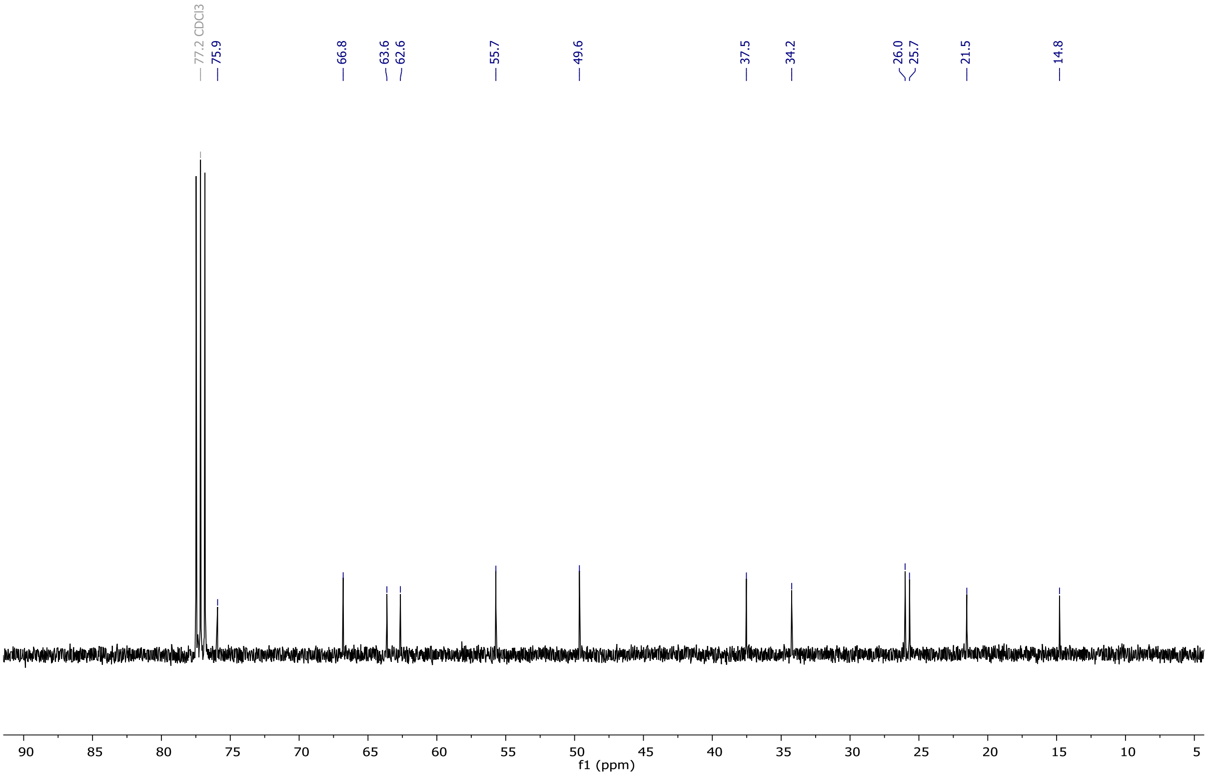


**Compound 2e**

**$^{1}$H NMR** (500 MHz, CDCl$_3$)

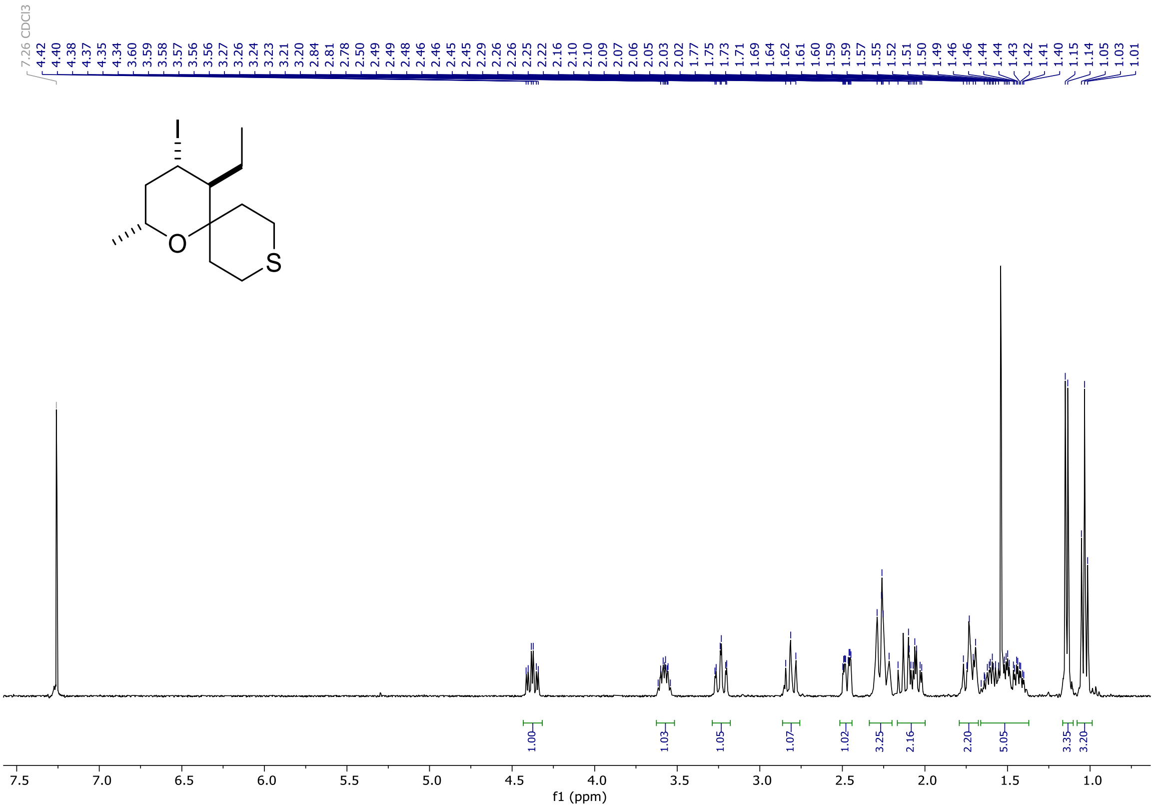


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

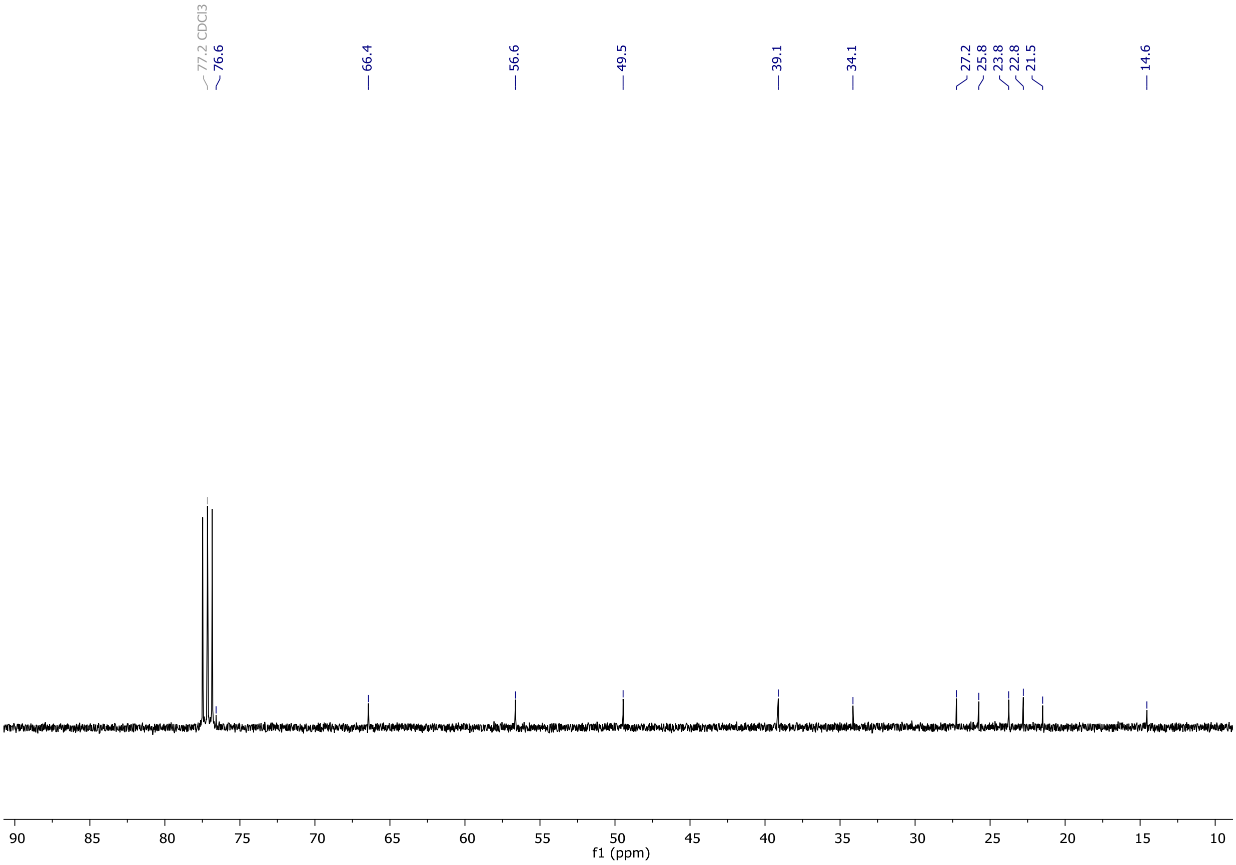


**Compound 2f**

**$^1$H NMR** (500 MHz, CDCl$_3$)

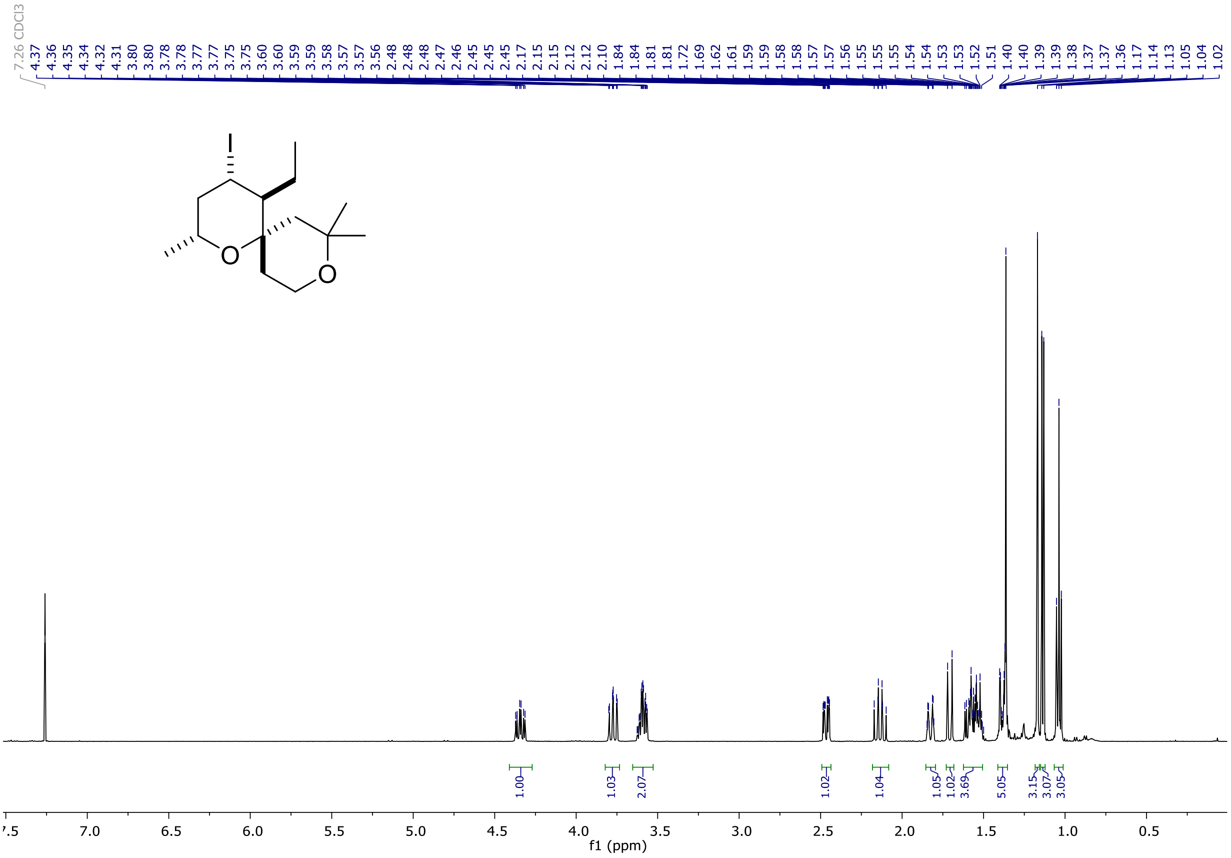


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

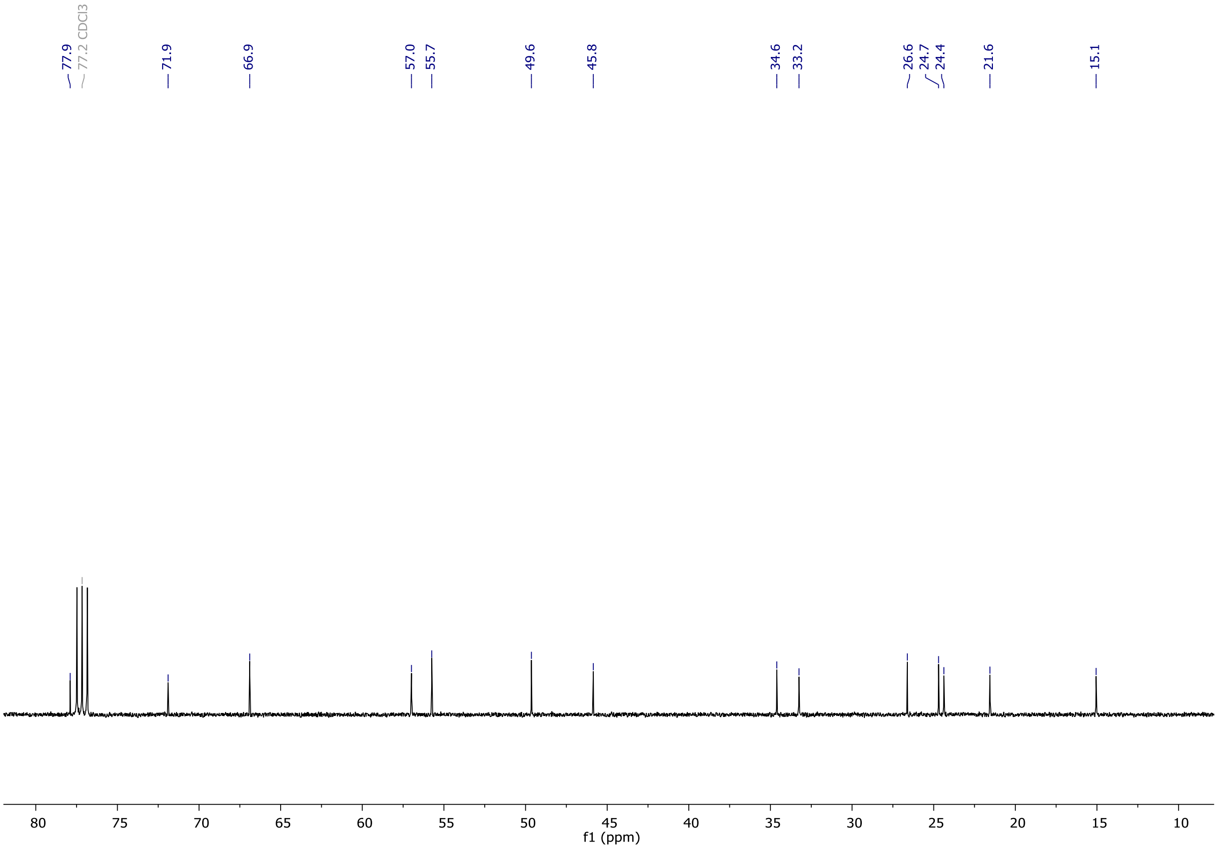


**Compound 2g**

**$^1$H NMR** (500 MHz, CDCl$_3$)

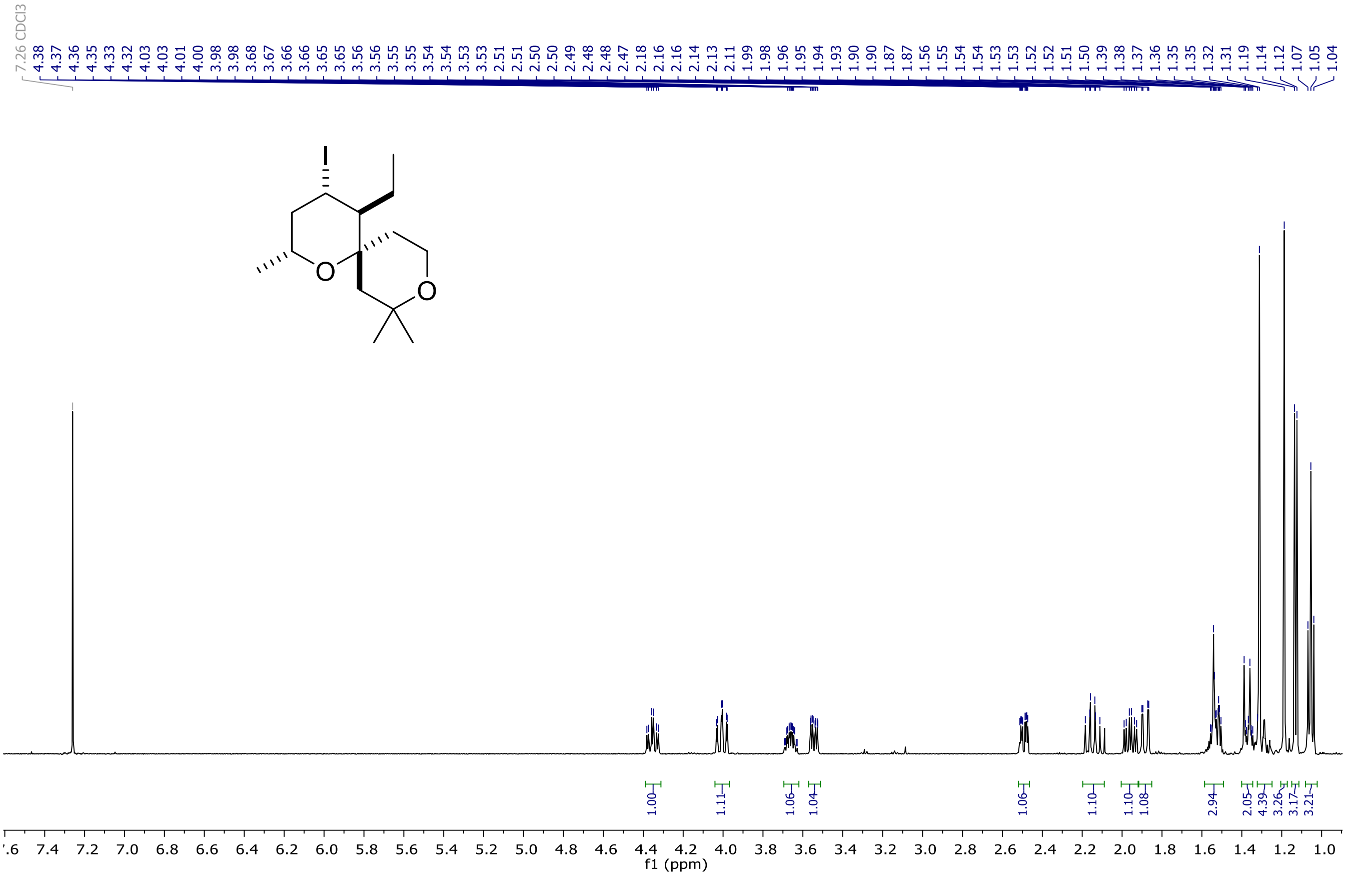


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

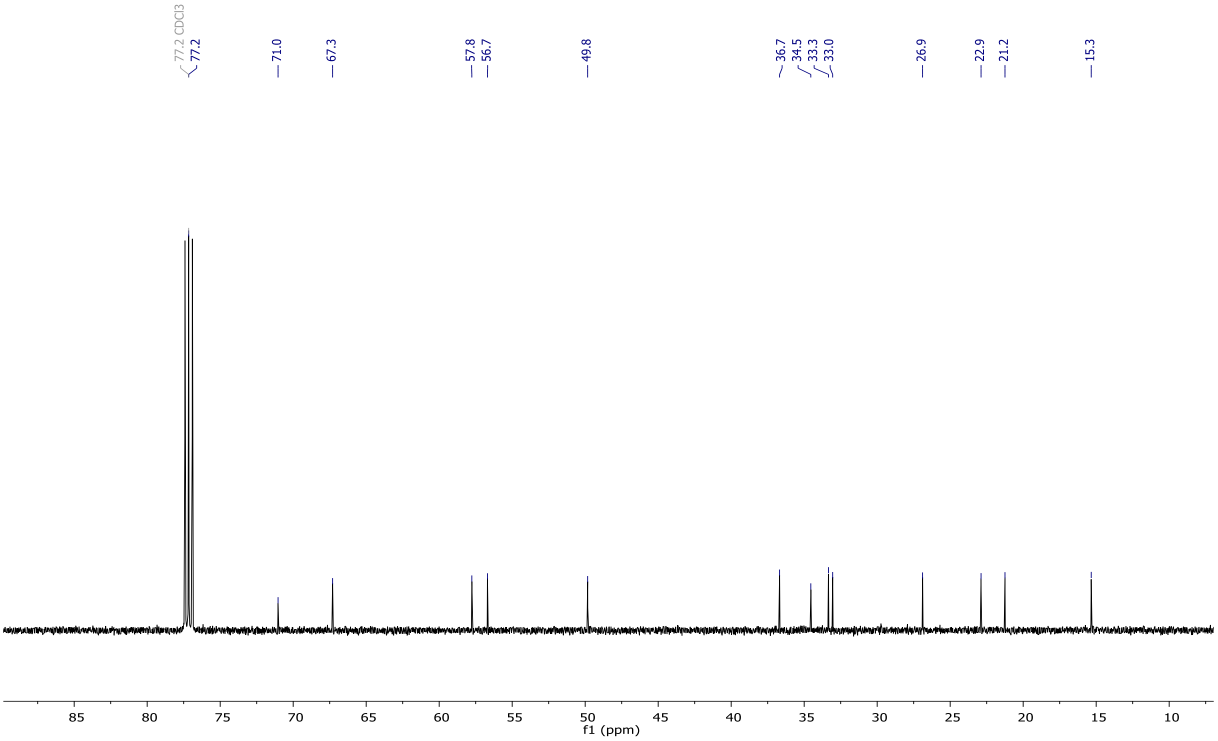


**Compound 3g**

**$^1$H NMR** (500 MHz, CDCl$_3$)

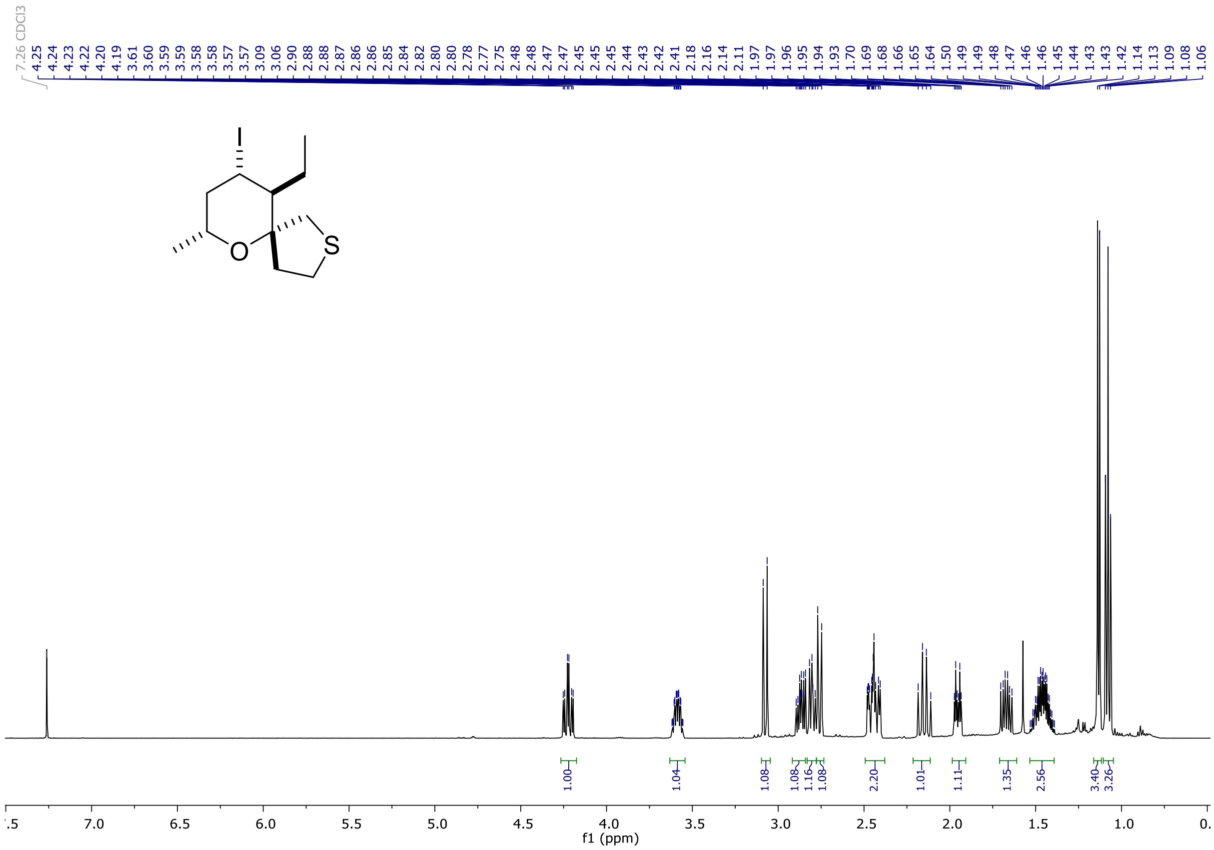


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

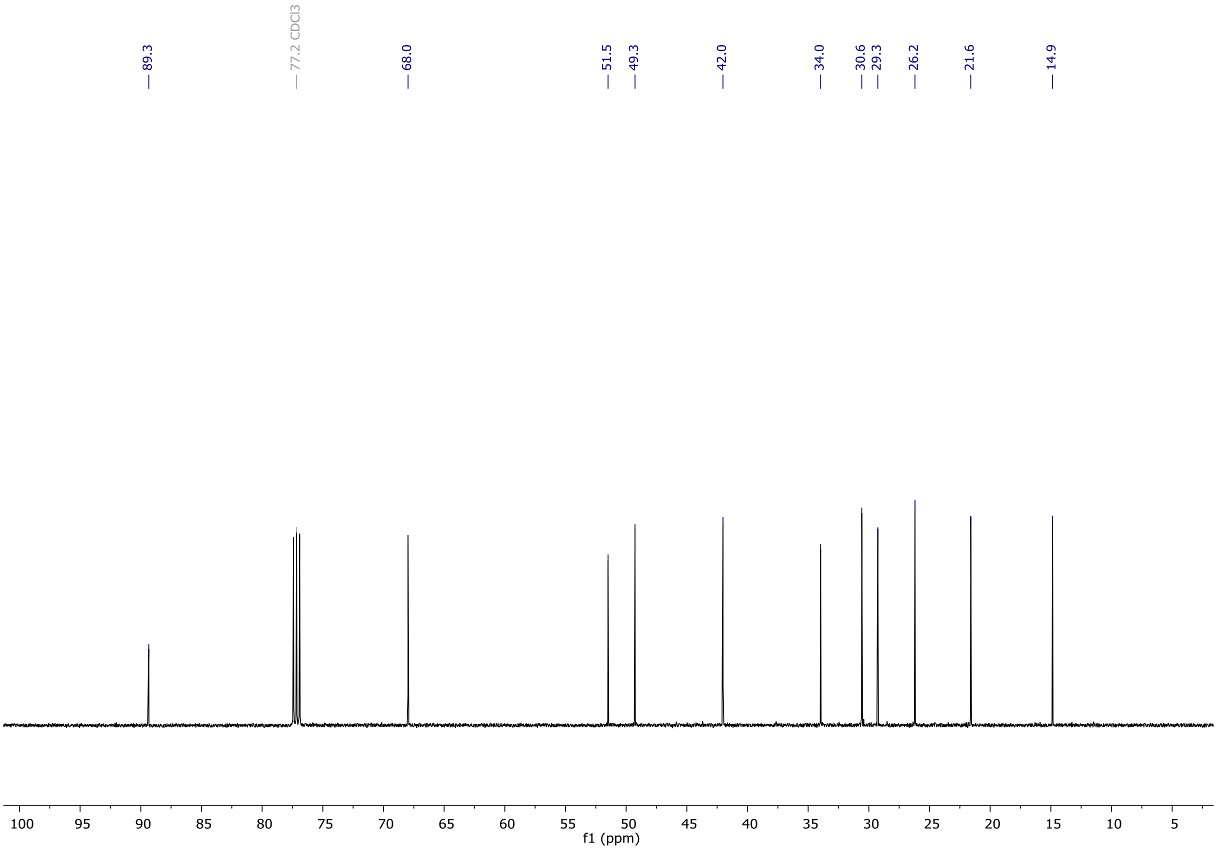


**Compound 2h**

**$^1$H NMR** (500 MHz, CDCl$_3$)

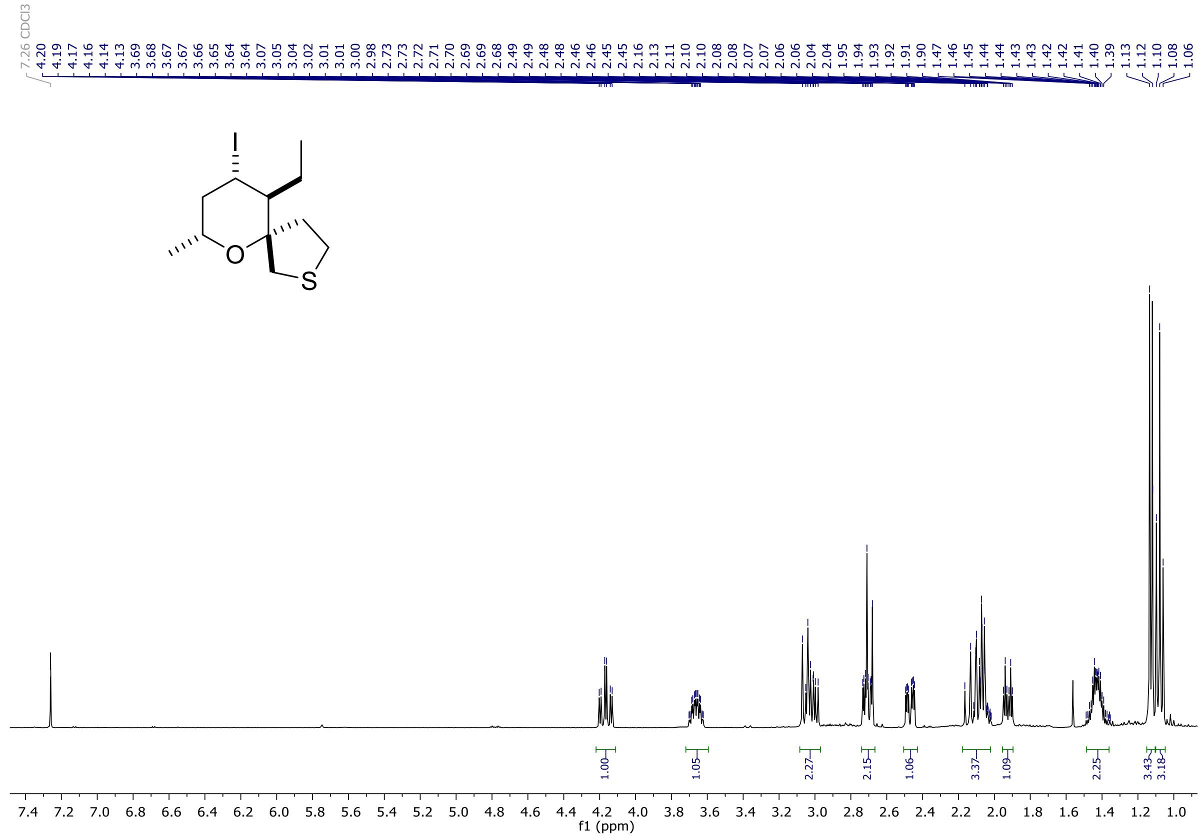


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

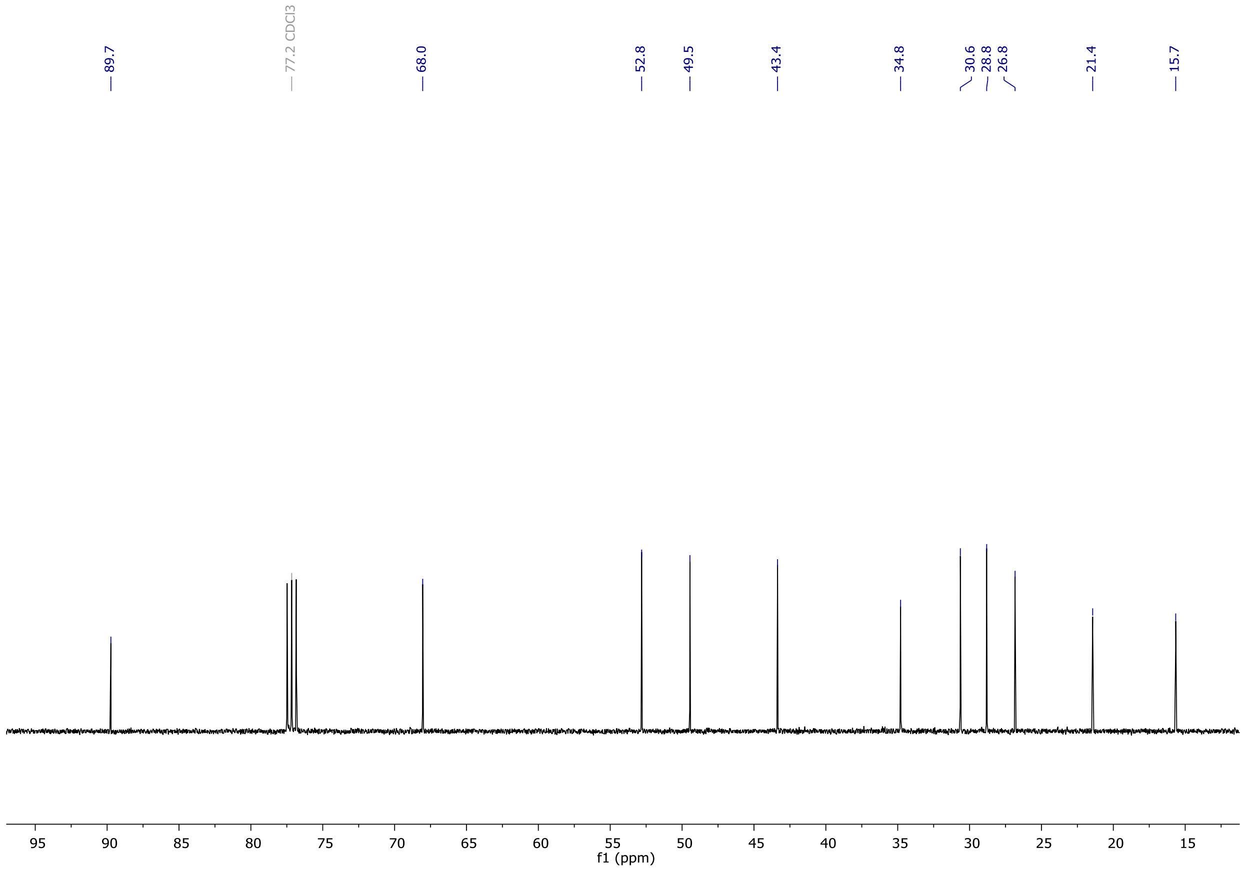


## Compound 3h

### $^1$H NMR (500 MHz, CDCl$_3$)

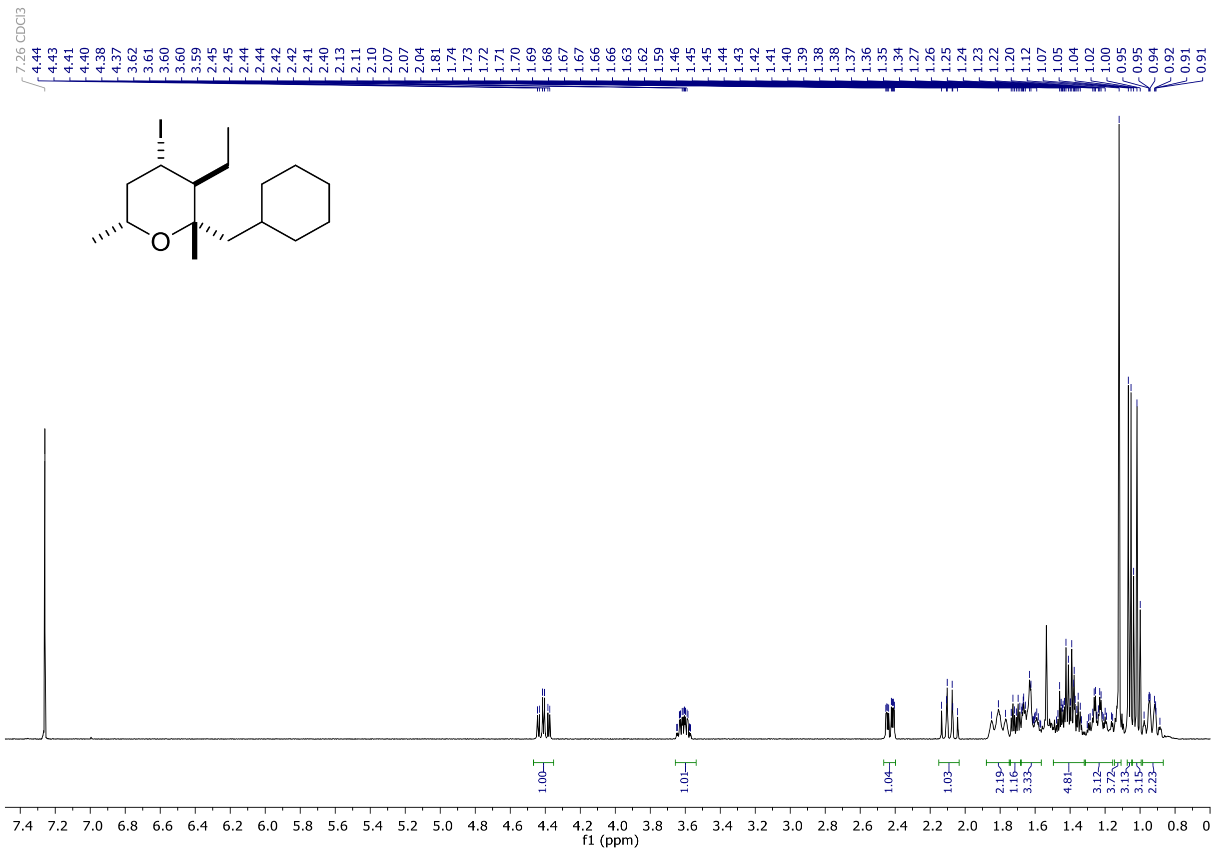


### $^{13}$C NMR (101 MHz, CDCl$_3$)

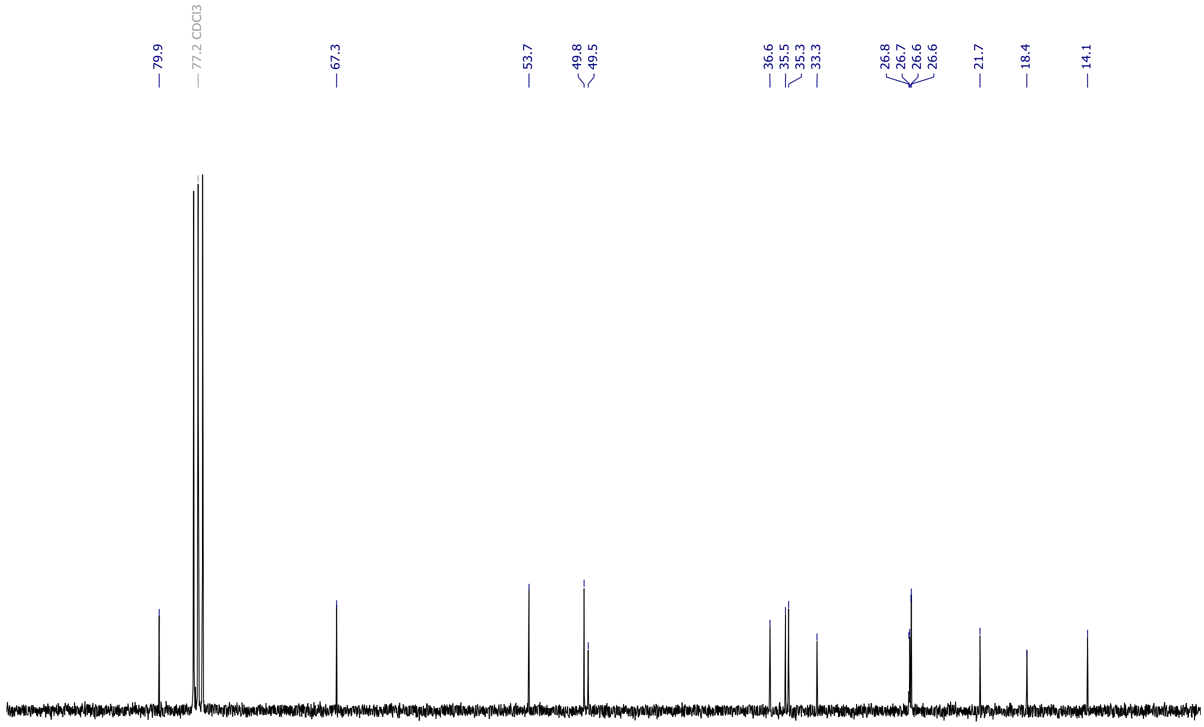


**Compound 2i**

$^{1}$**H NMR** (500 MHz, CDCl$_3$)

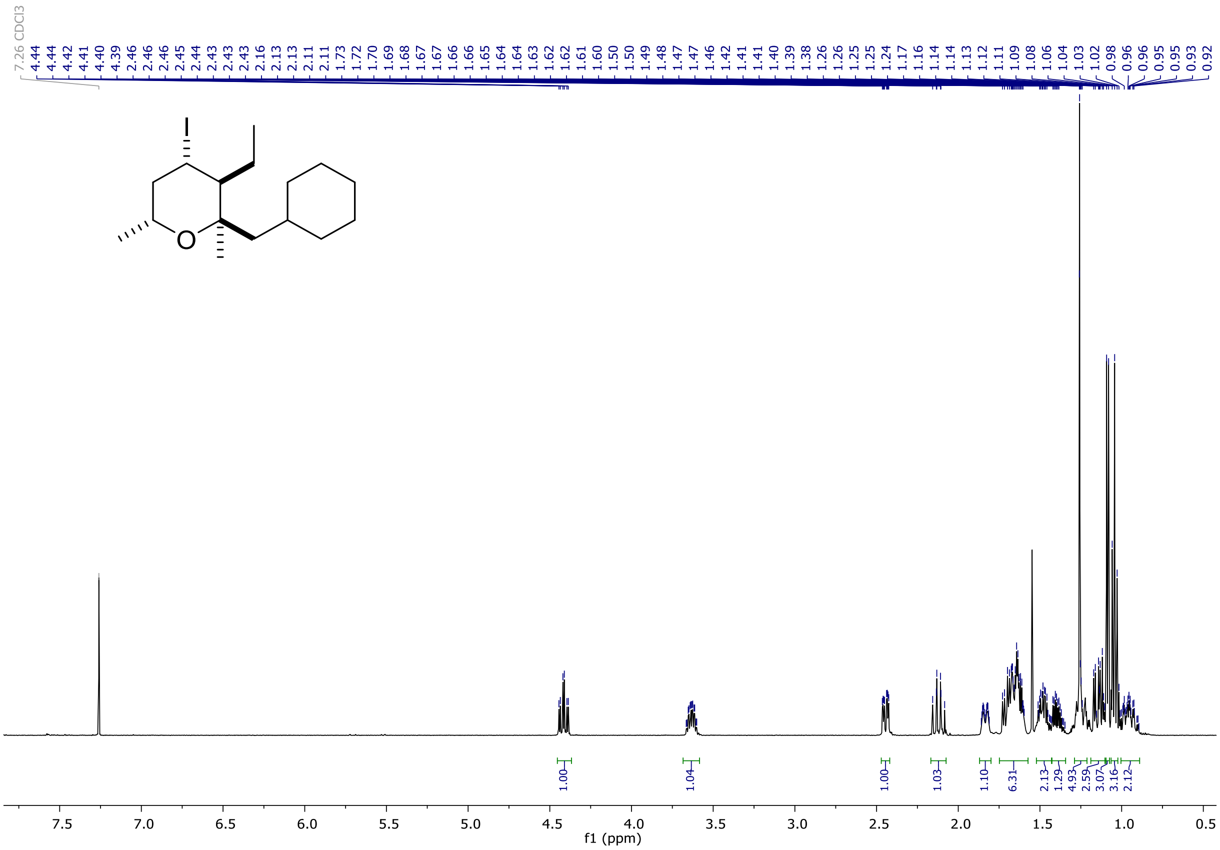


$^{13}$**C NMR** (101MHz, CDCl$_3$)

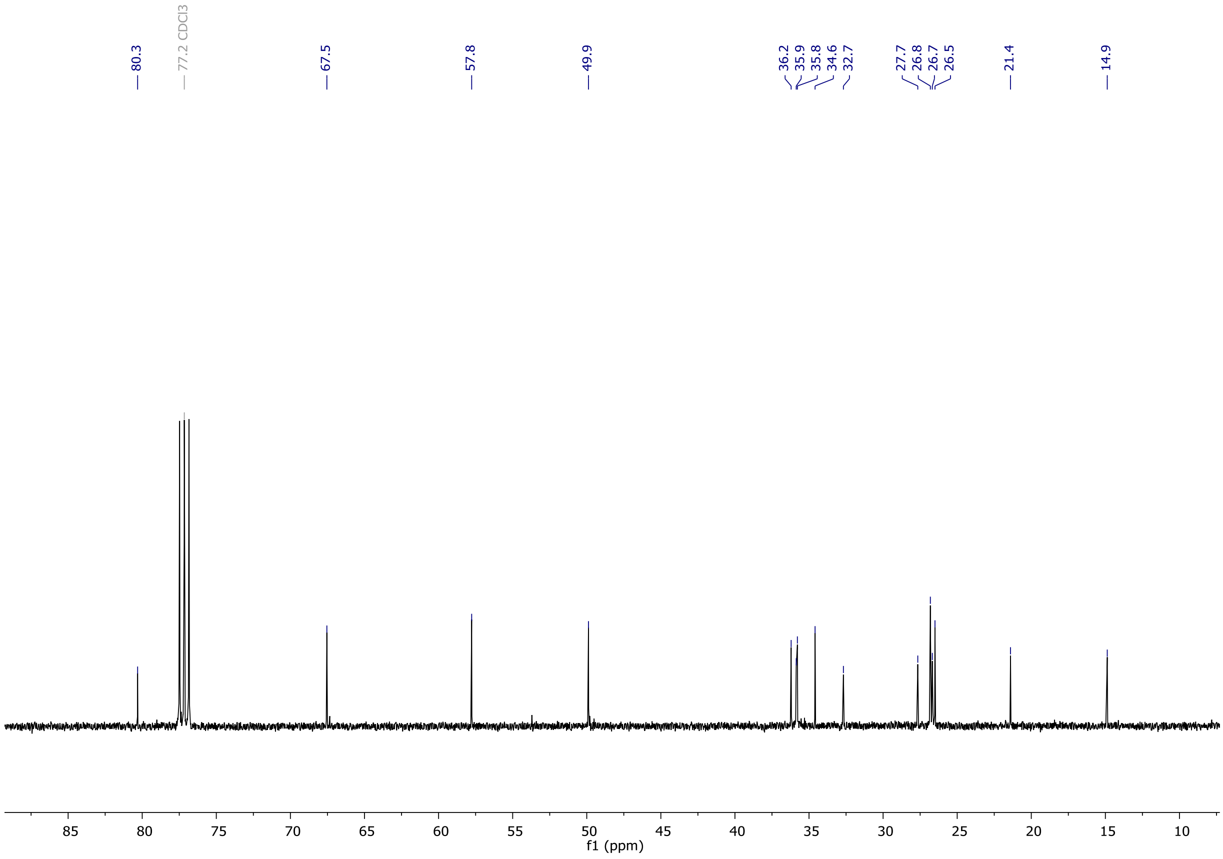


**Compound 3i**

**$^{1}$H NMR** (500 MHz, CDCl$_3$)

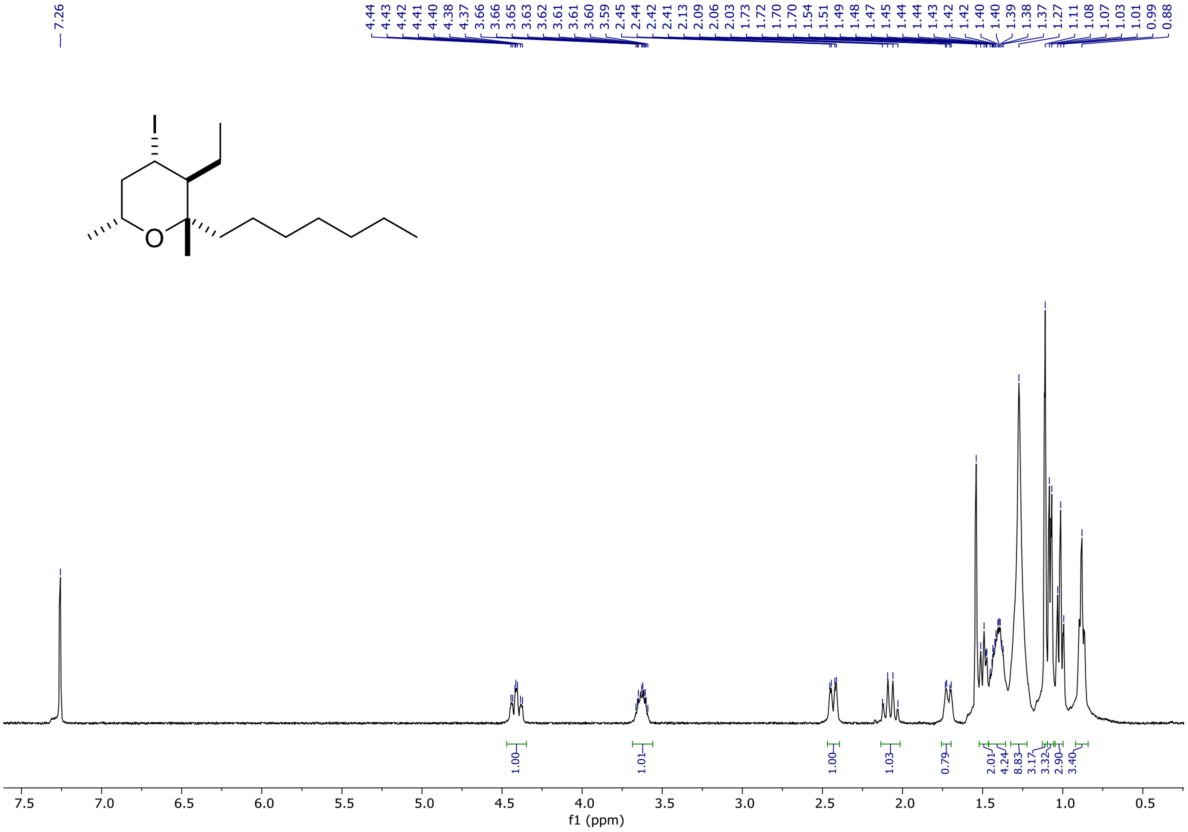


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

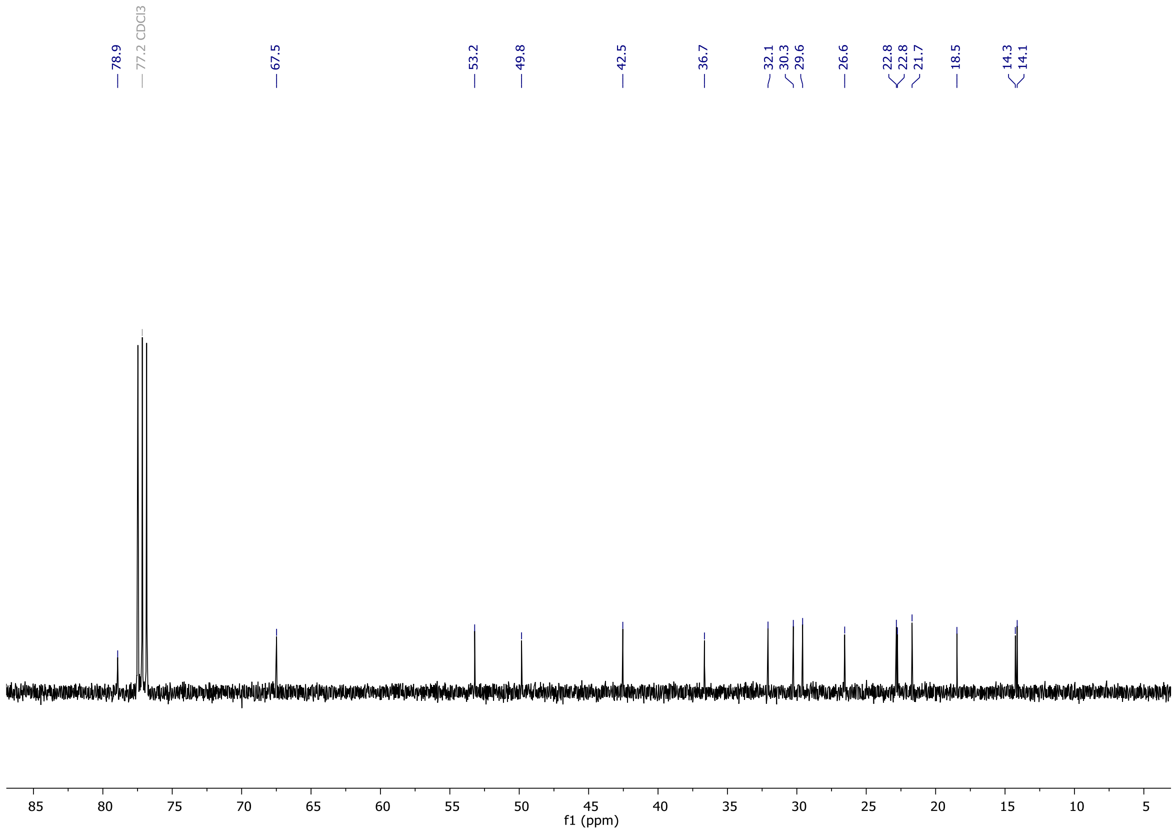


**Compound 2j**

**$^1$H NMR** (500 MHz, CDCl$_3$)

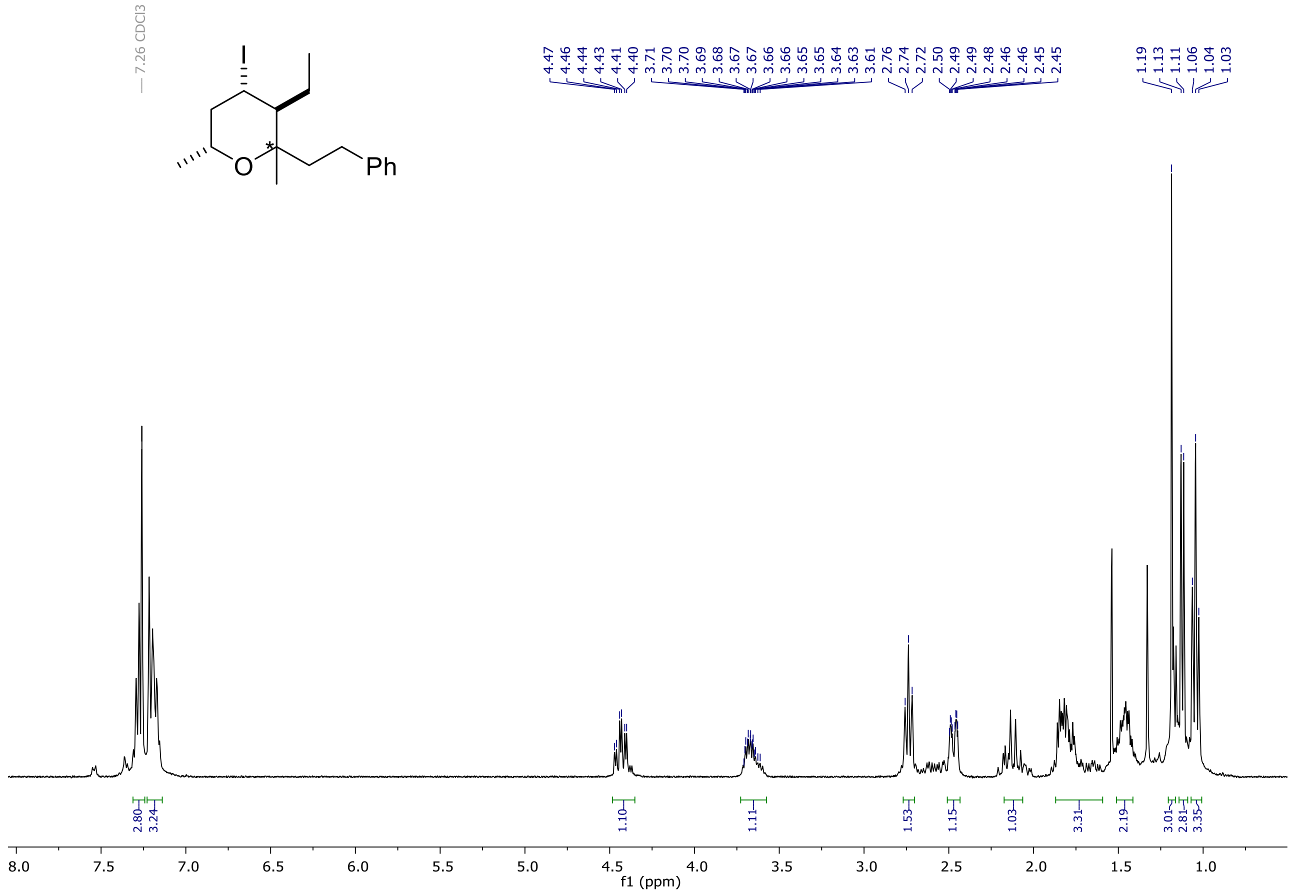


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

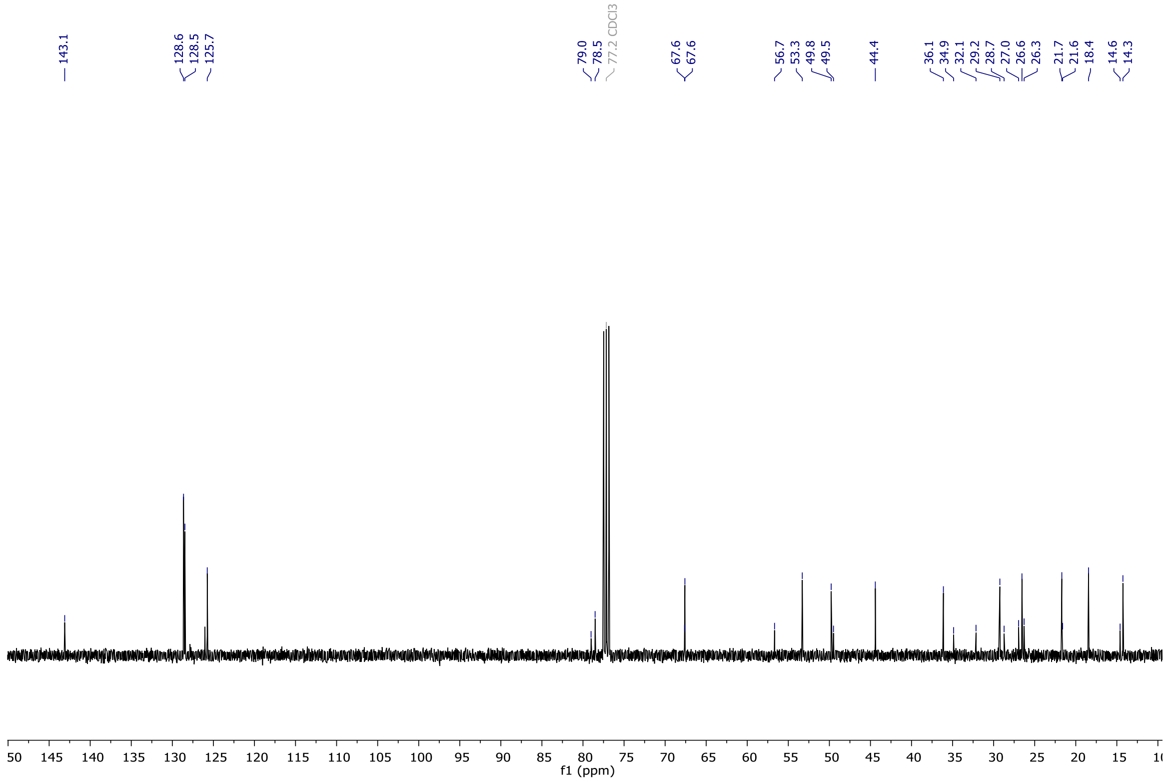


## Compound 2k and 3k

**$^{1}$H NMR** (500 MHz, $CDCl_3$)

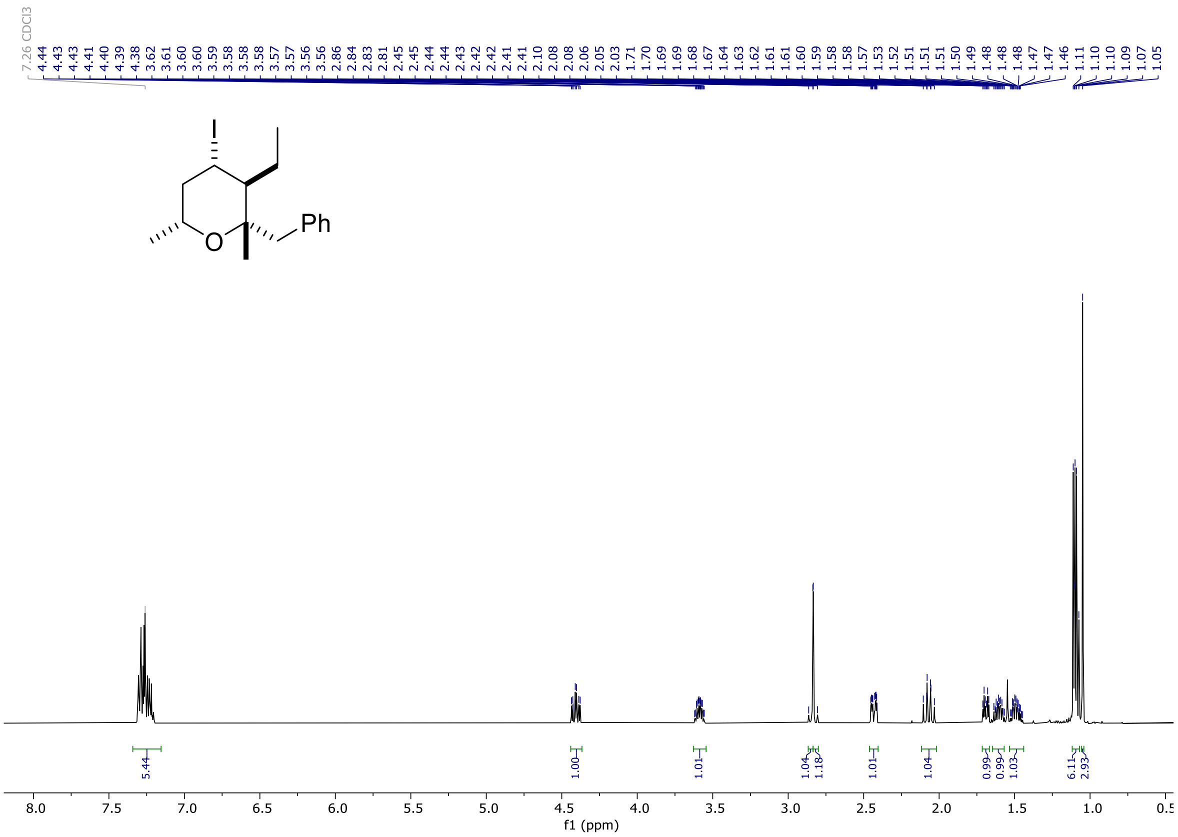


**$^{13}$C NMR** (101 MHz, $CDCl_3$)

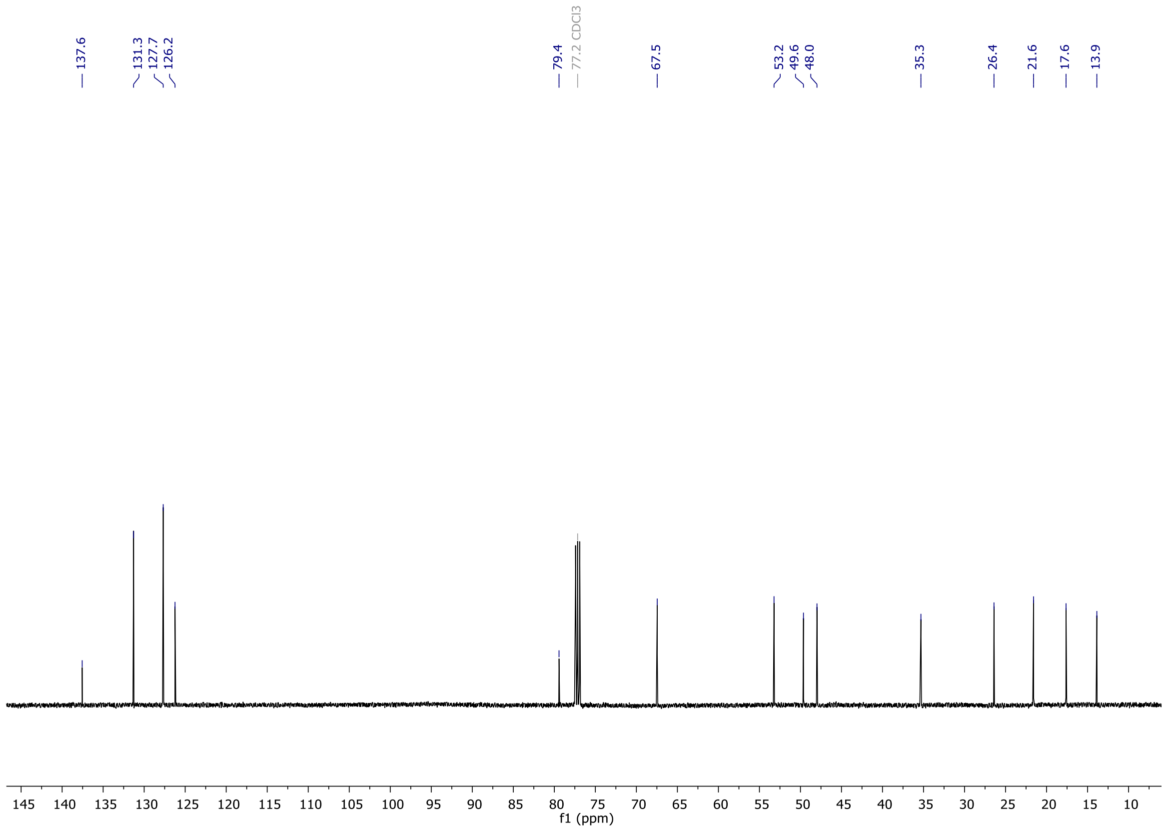


## Compound 2l

**$^{1}$H NMR** (500 MHz, CDCl$_3$)

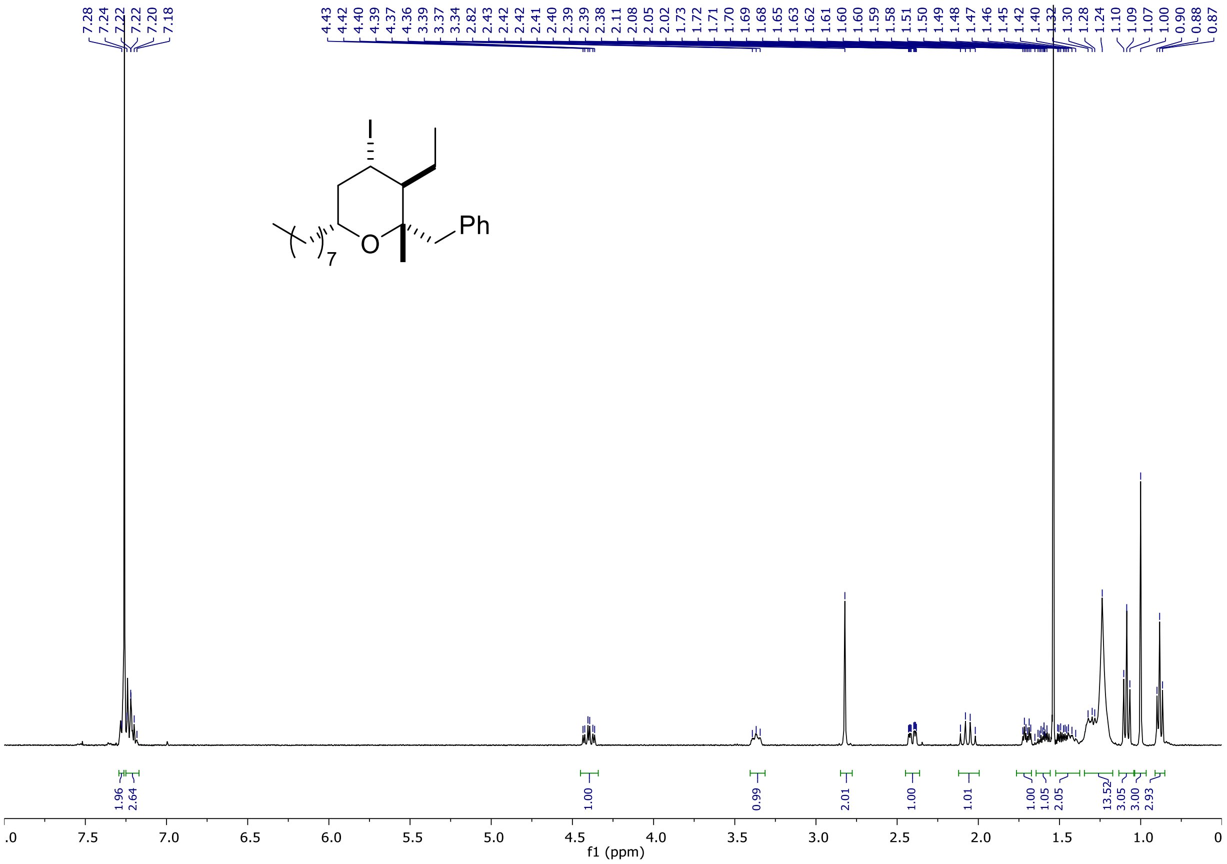


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

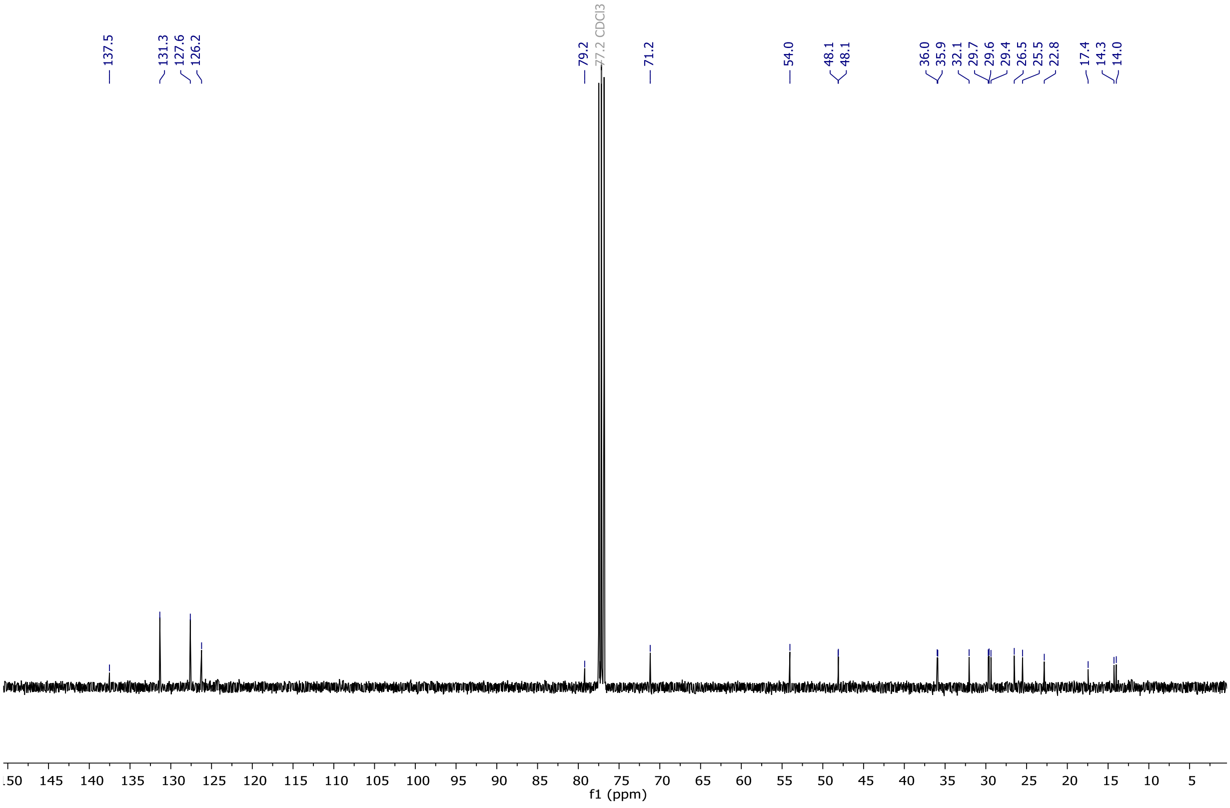


**Compound 2m**

**$^{1}$H NMR** (400 MHz, CDCl$_3$)

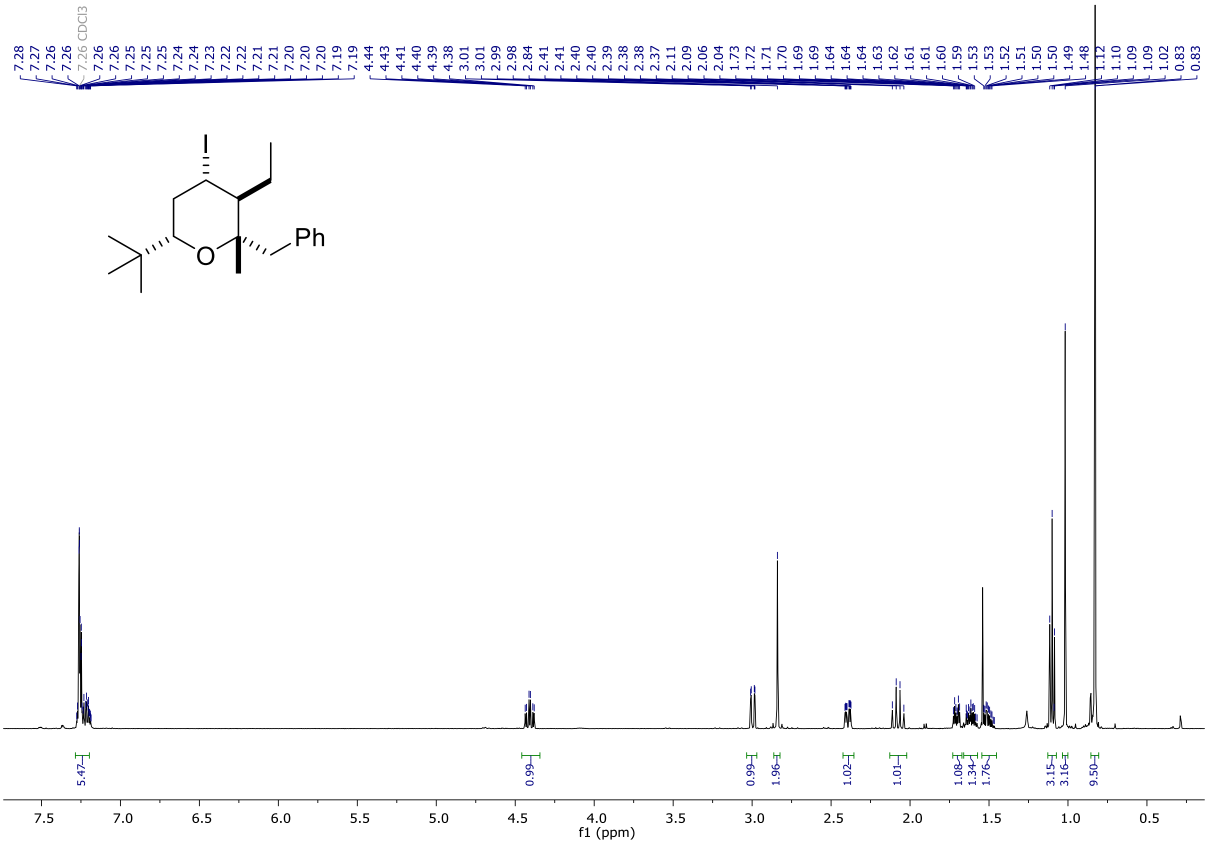


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

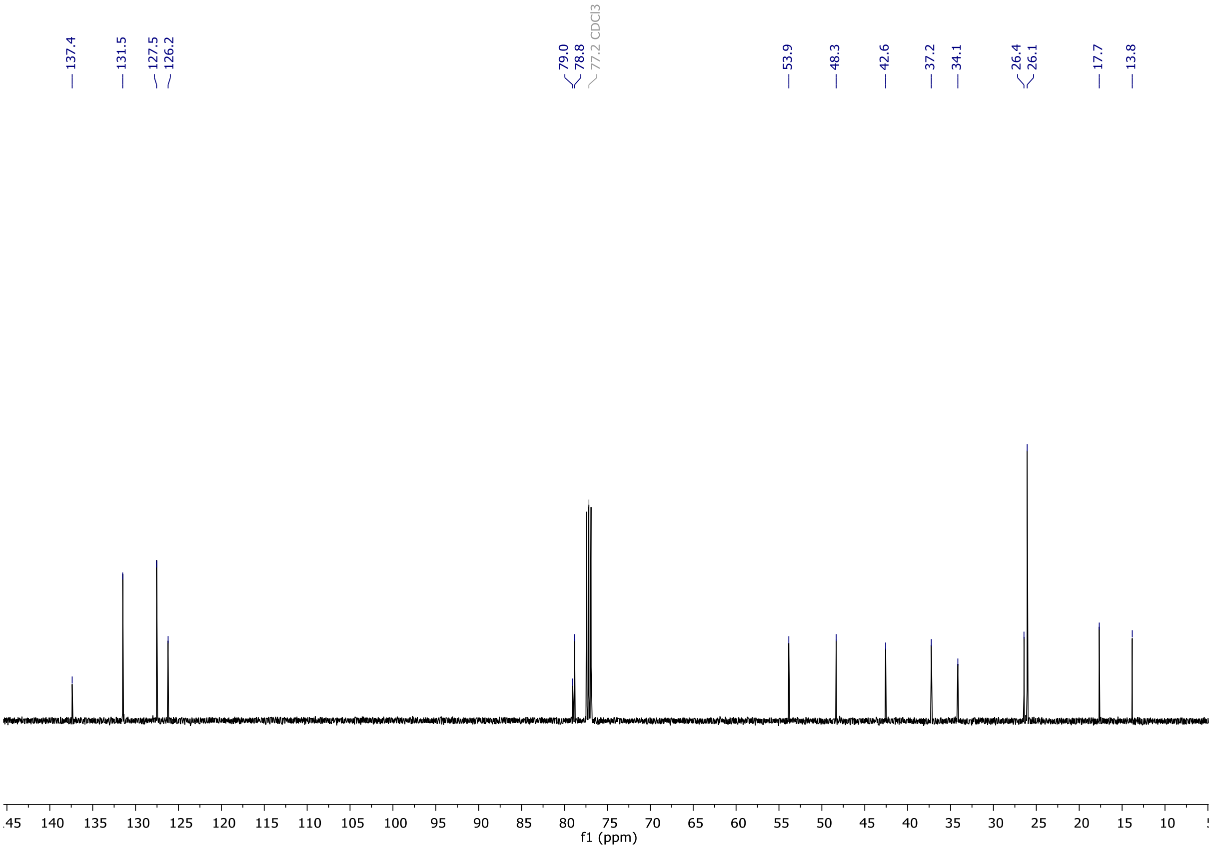


**Compound 2n**

**$^1$H NMR** (500 MHz, CDCl$_3$)

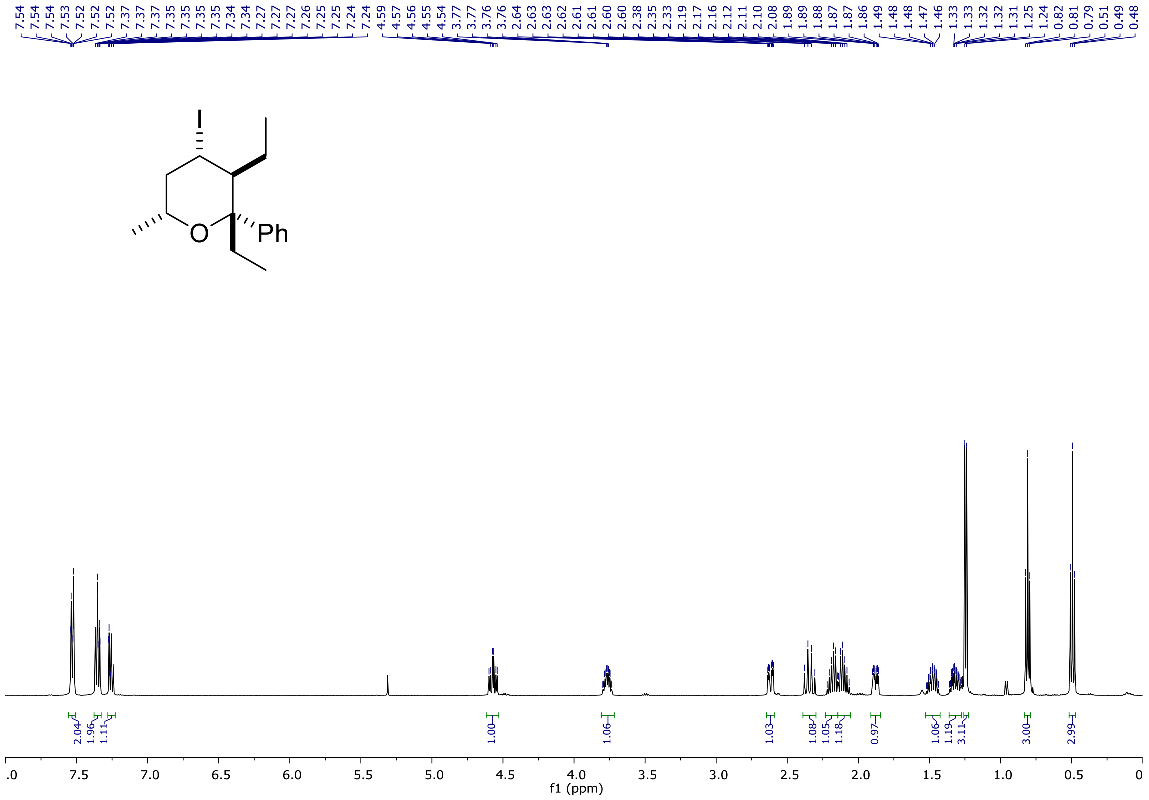


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

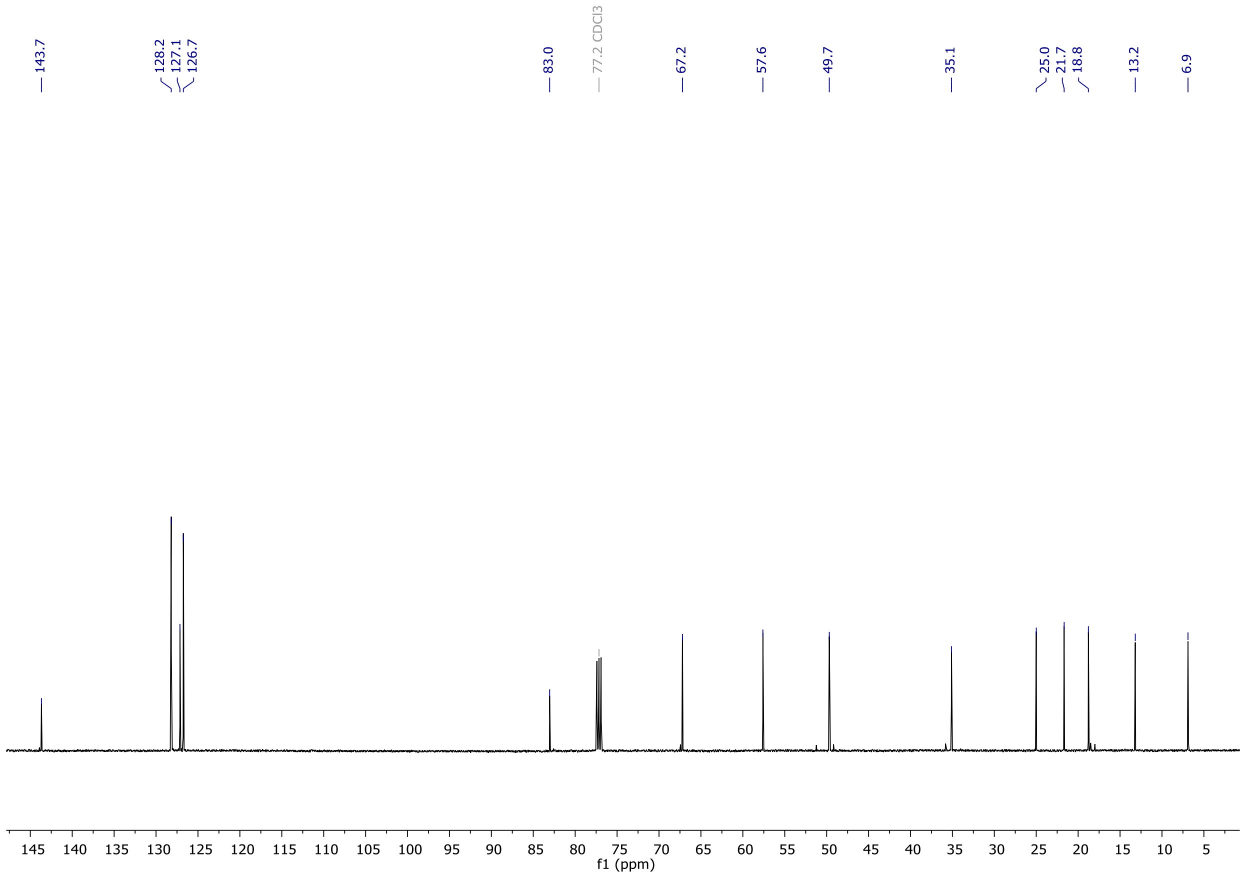


**Compound 2o**

**$^1$H NMR** (500 MHz, CDCl$_3$)

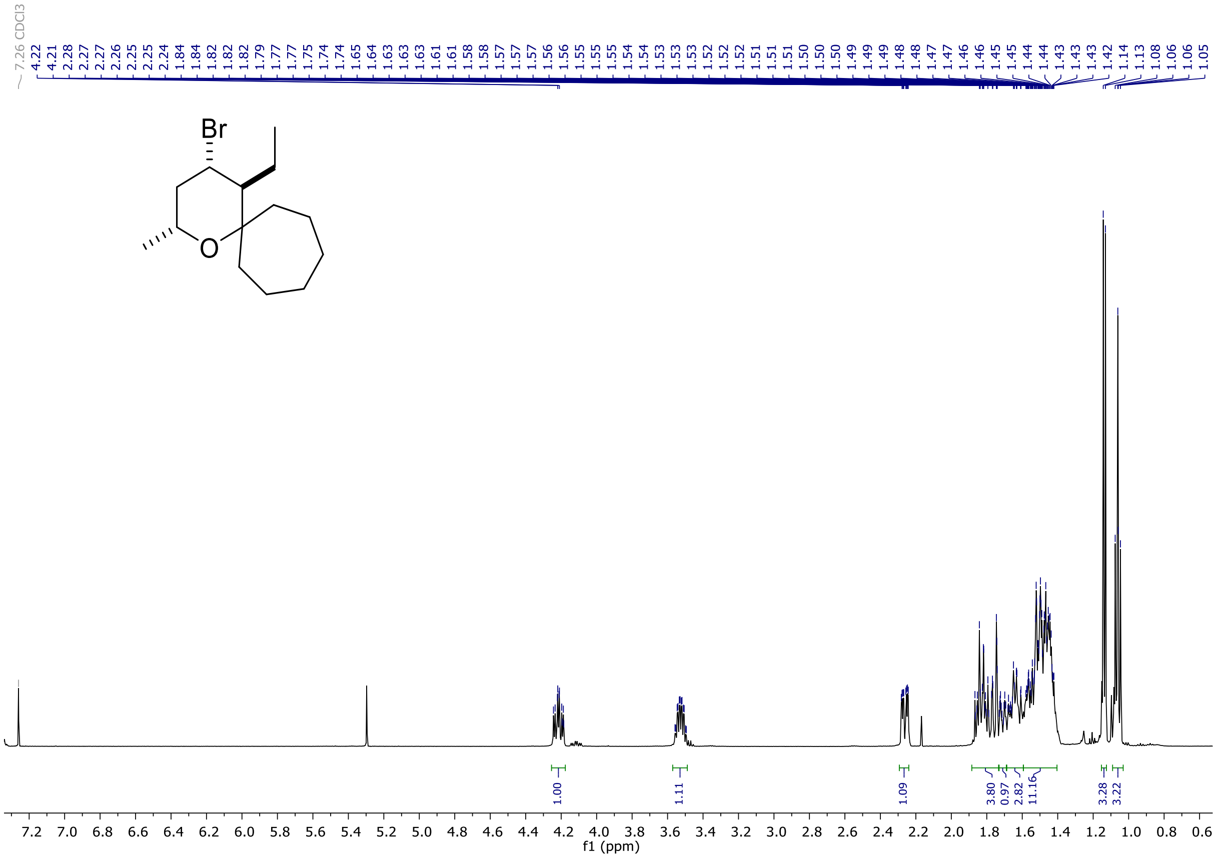


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

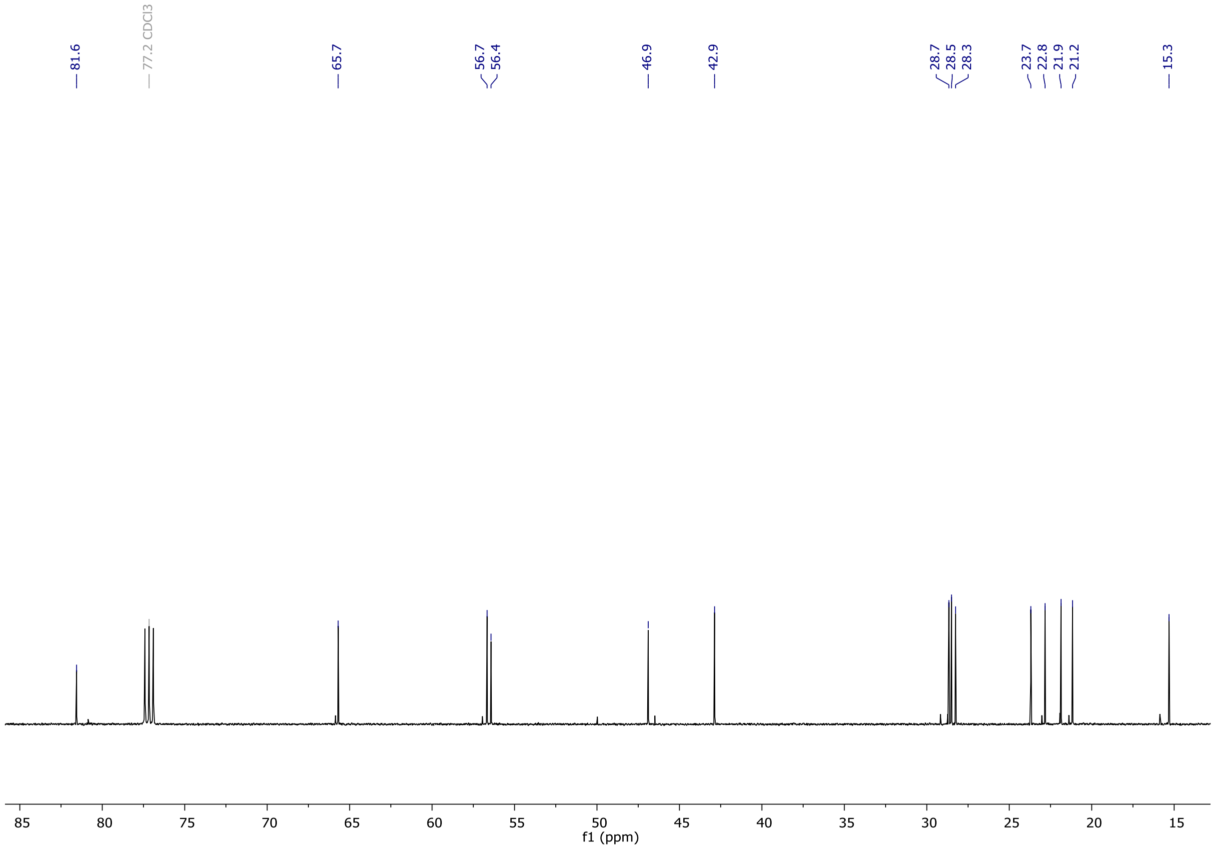


## Compound 4a

**$^{1}$H NMR** (500 MHz, CDCl$_3$)

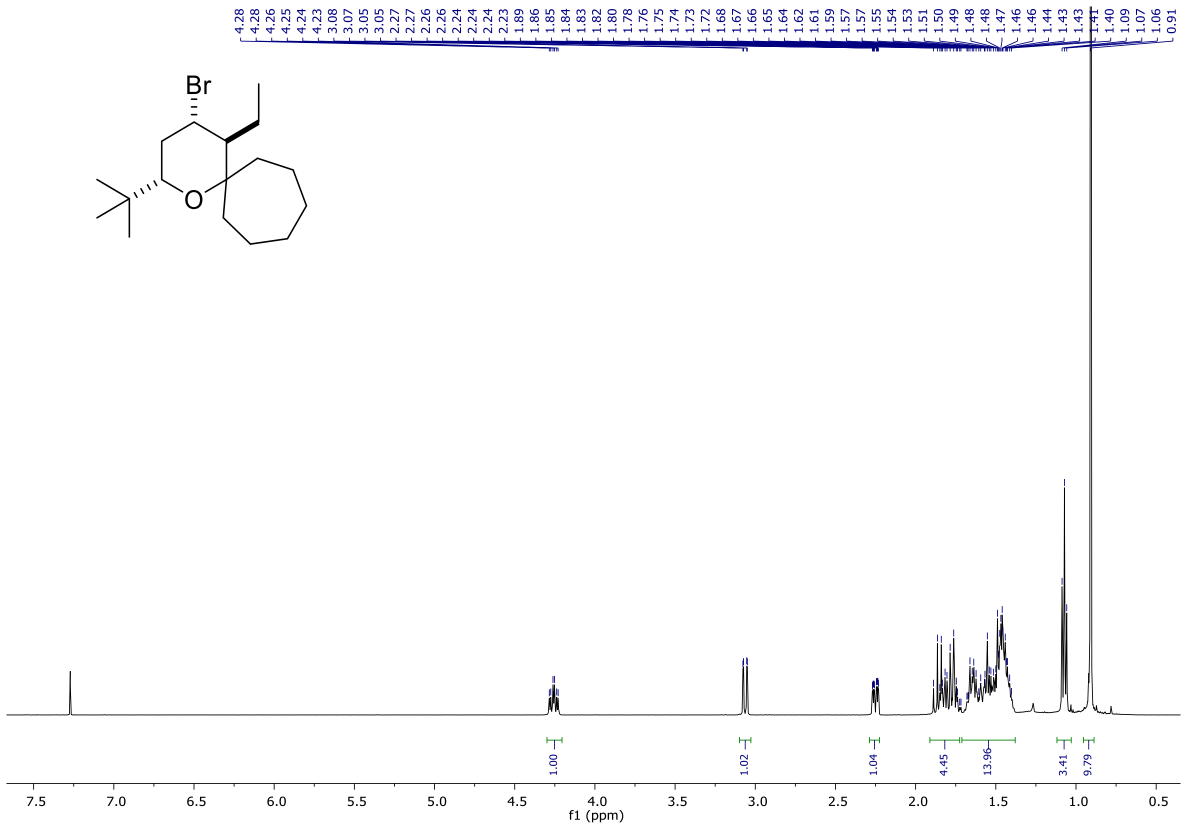


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

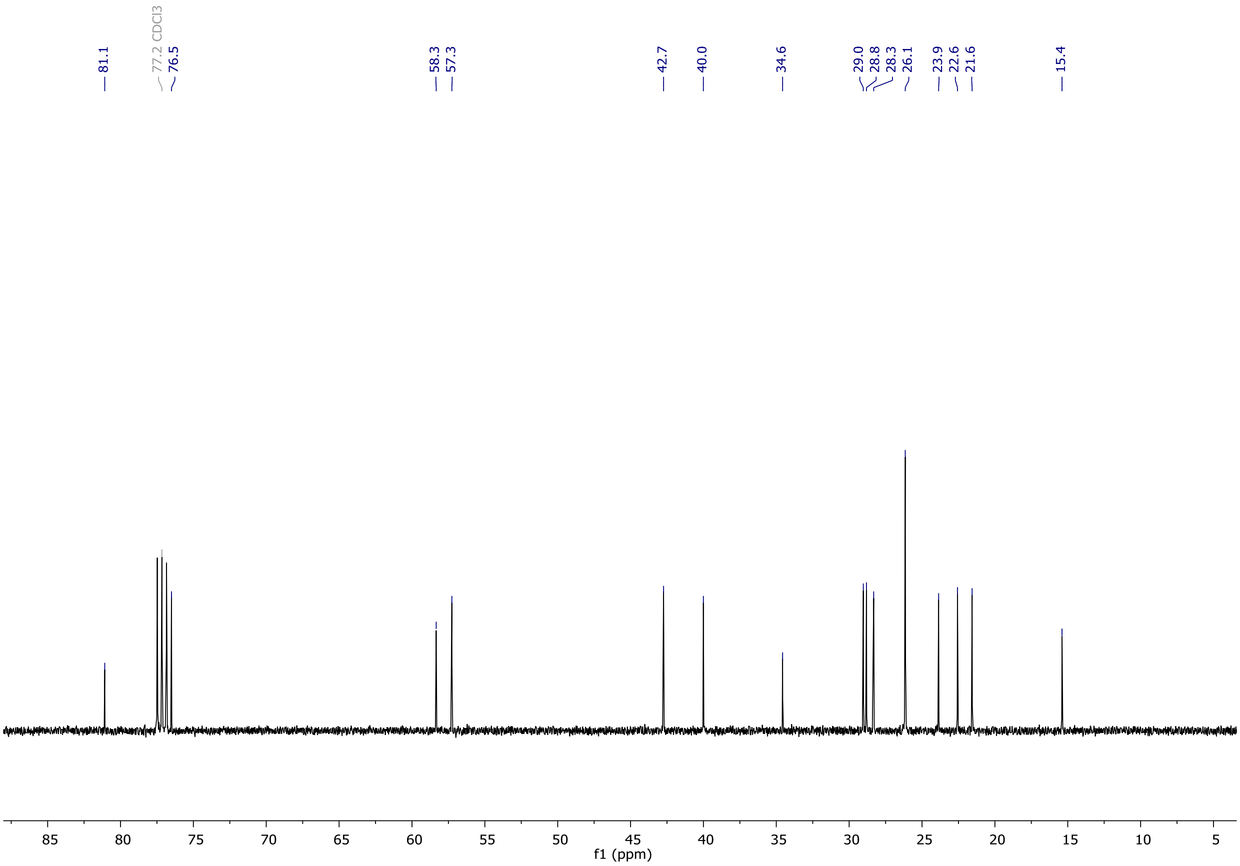


**Compound 4b**

**$^1$H NMR** (500 MHz, $CDCl_3$)



**$^{13}$C NMR** (101 MHz, $CDCl_3$)



**Compound 4c**

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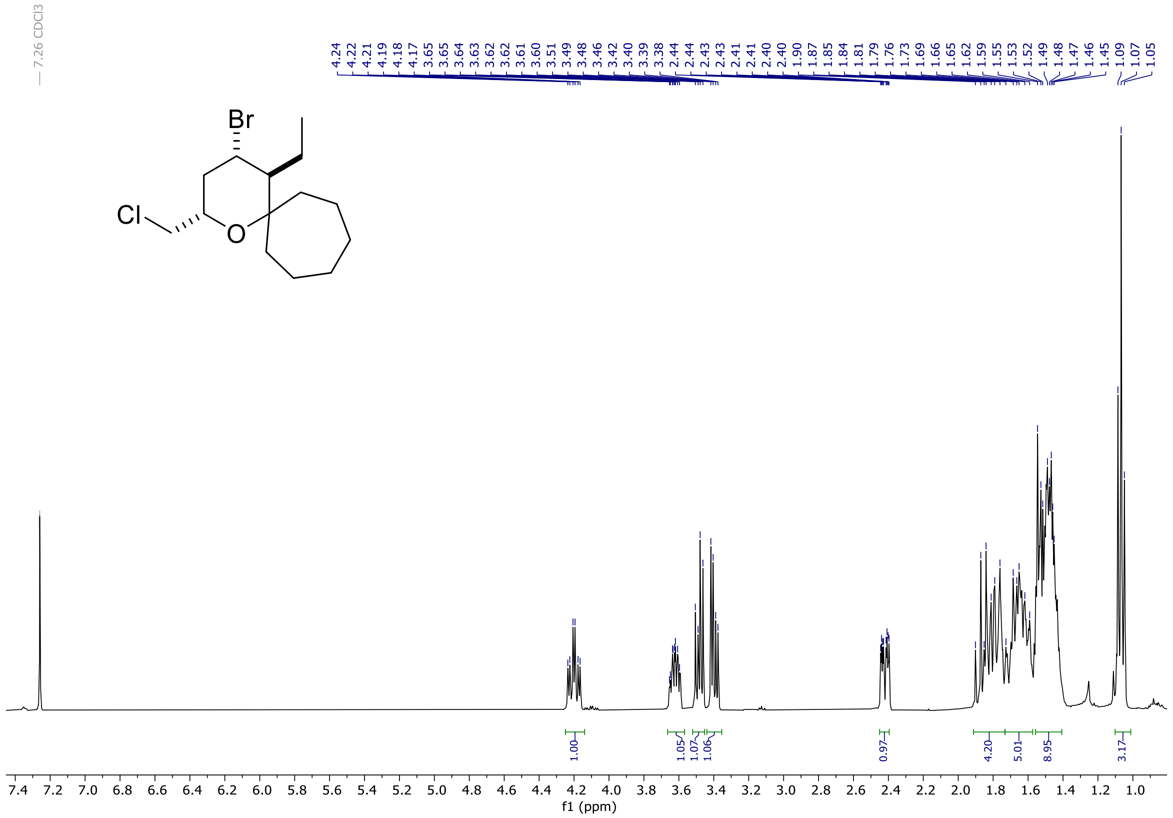
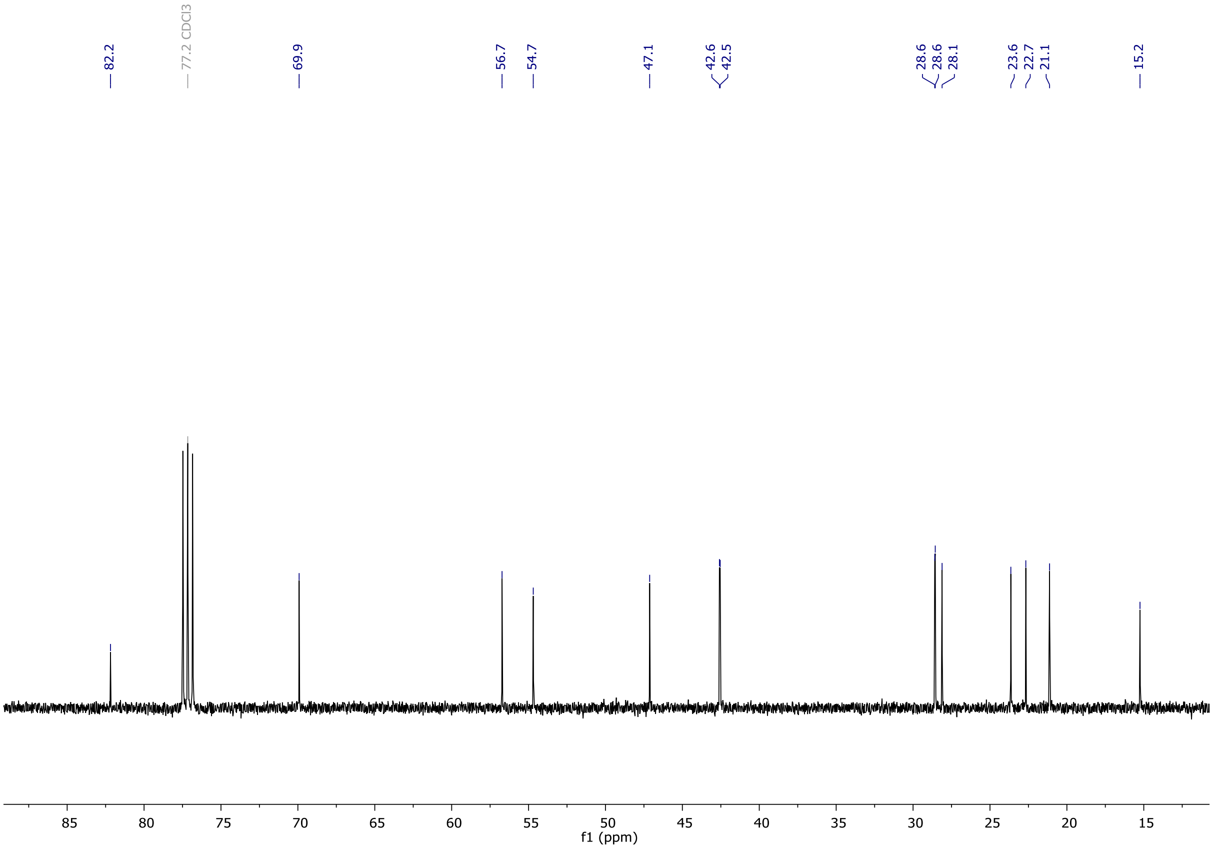


**$^{13}$C NMR** (101 MHz, CDCl$_3$)



## Compound 4d

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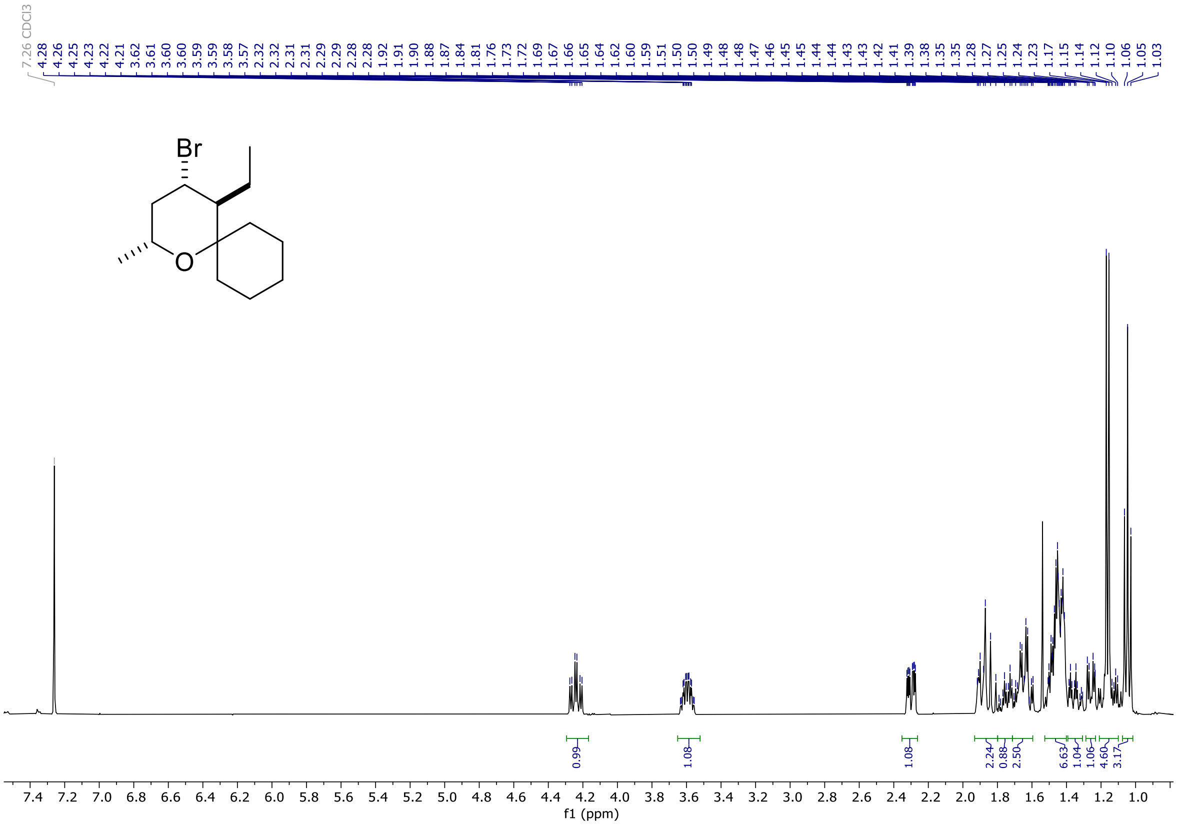
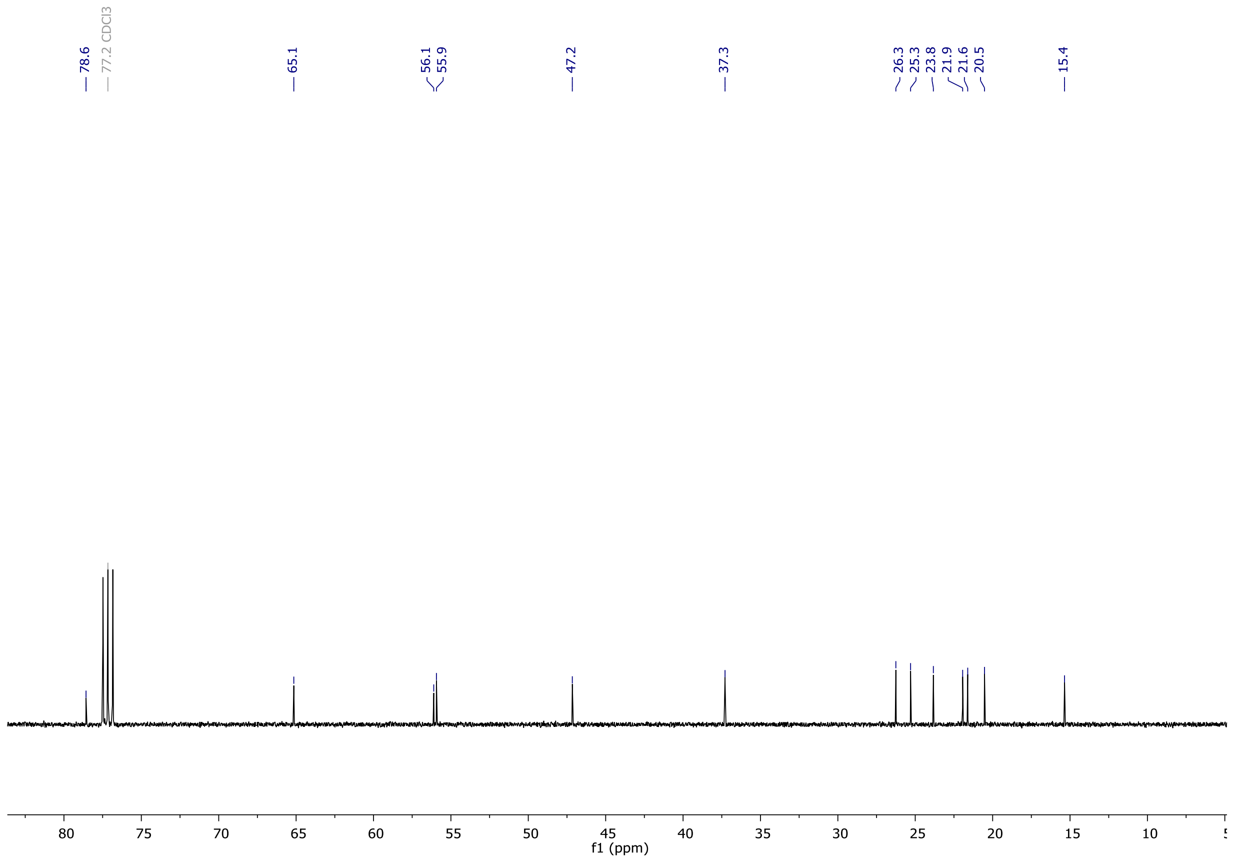
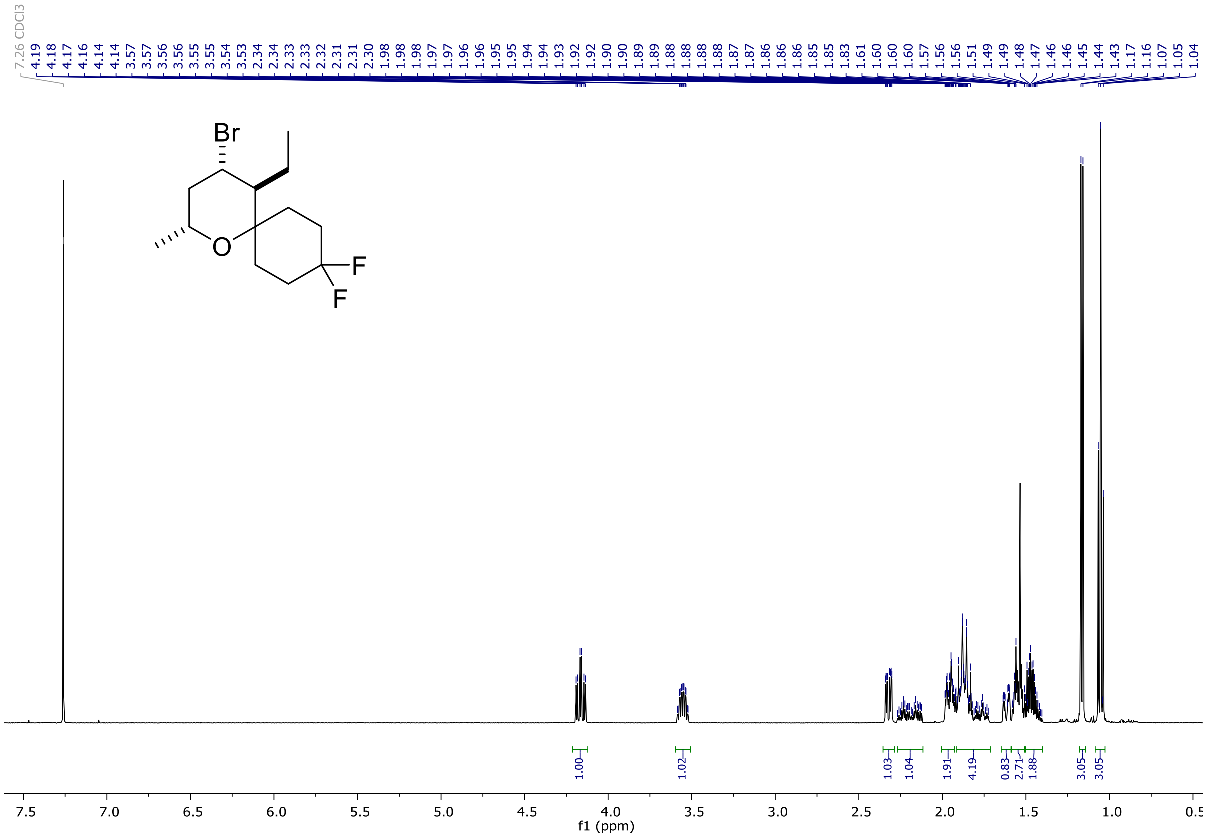


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

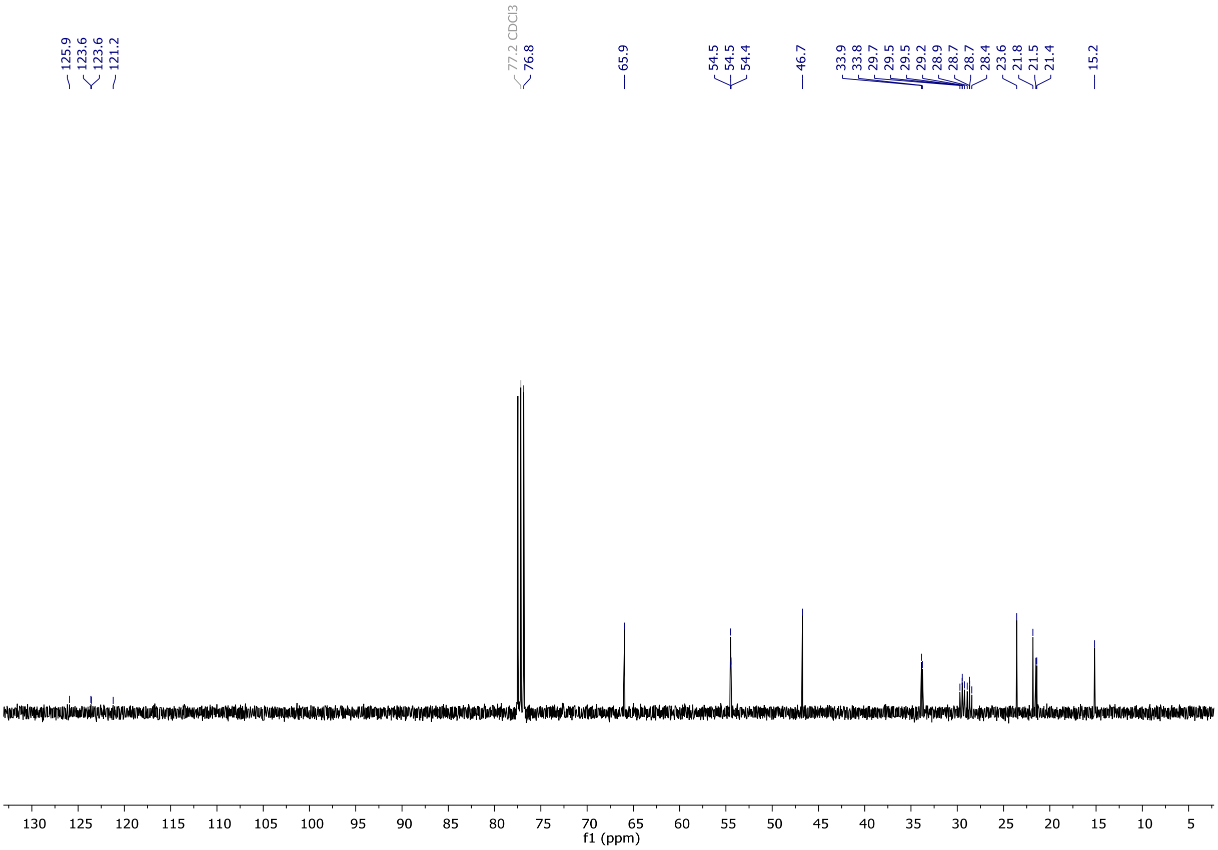


## Compound 4e

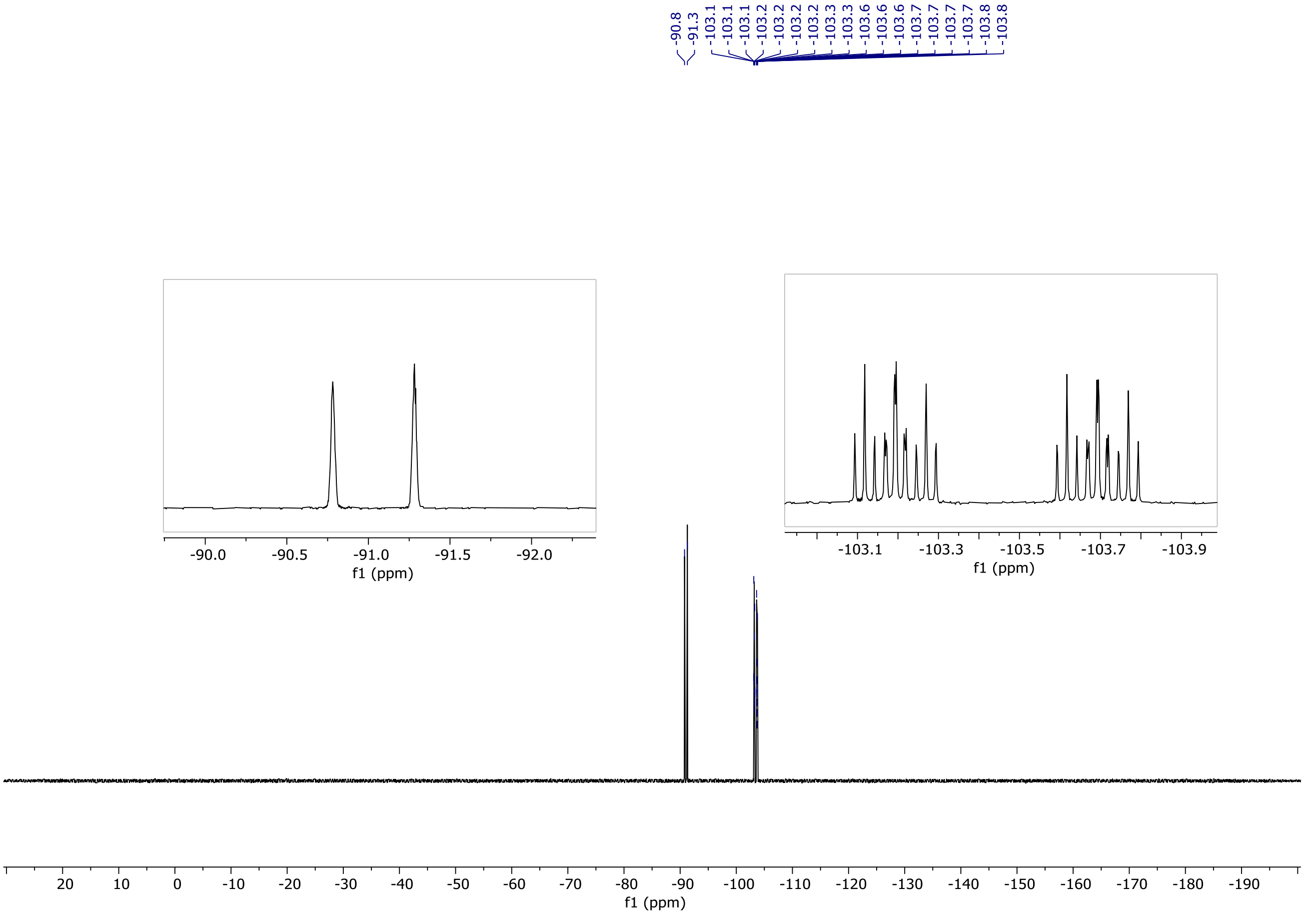
**$^{1}$H NMR** (500 MHz, $CDCl_3$)



**$^{13}$C NMR** (101MHz, $CDCl_3$)

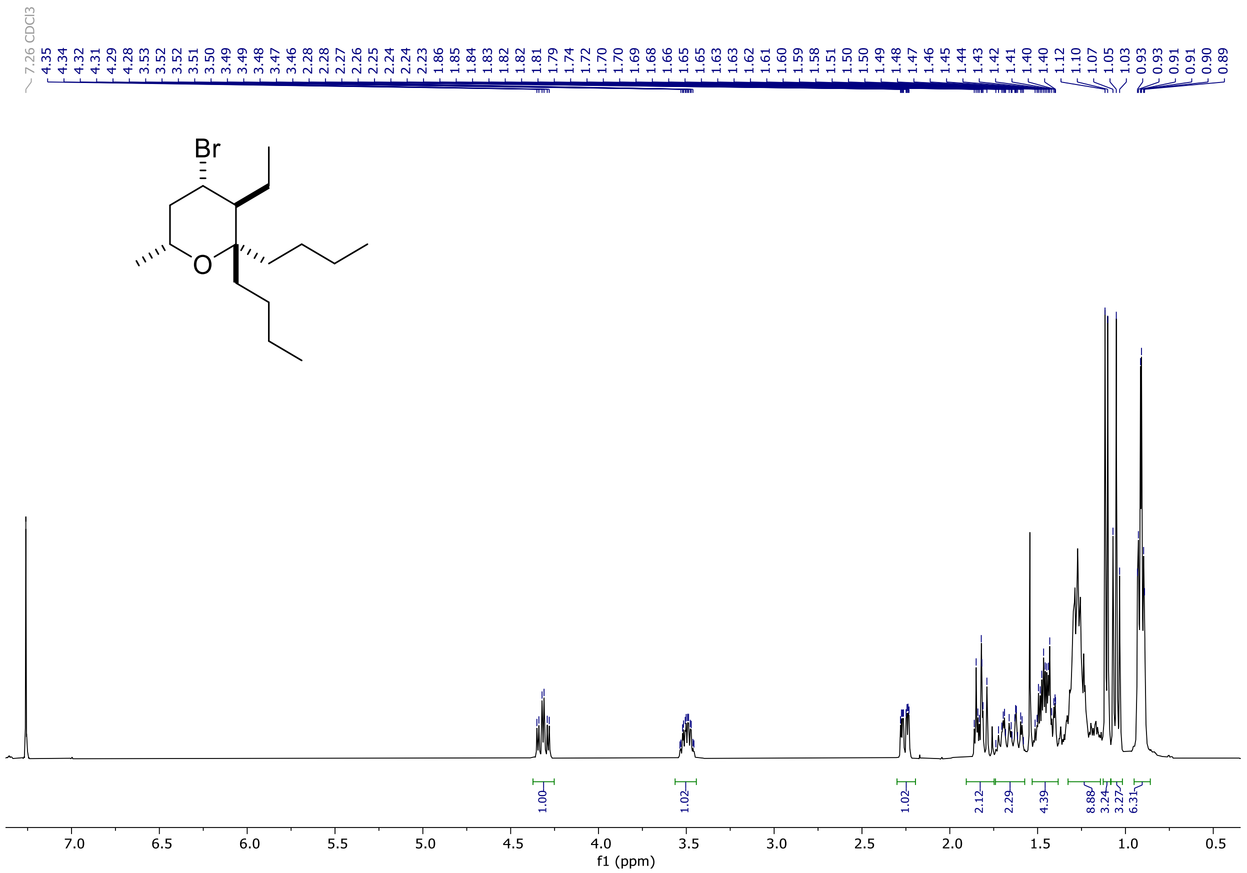


**$^{19}$F NMR** (470 MHz, $CDCl_3$)

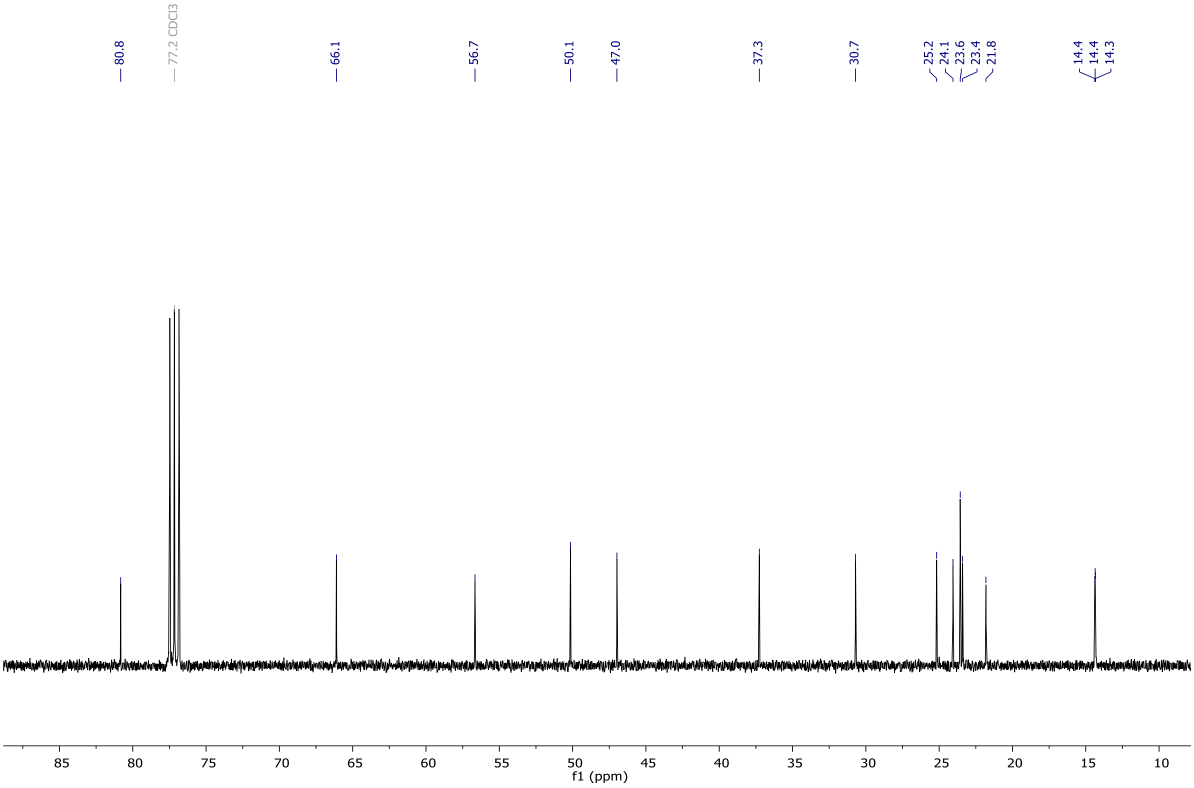


**Compound 4f**

**$^1$H NMR** (500 MHz, CDCl$_3$)

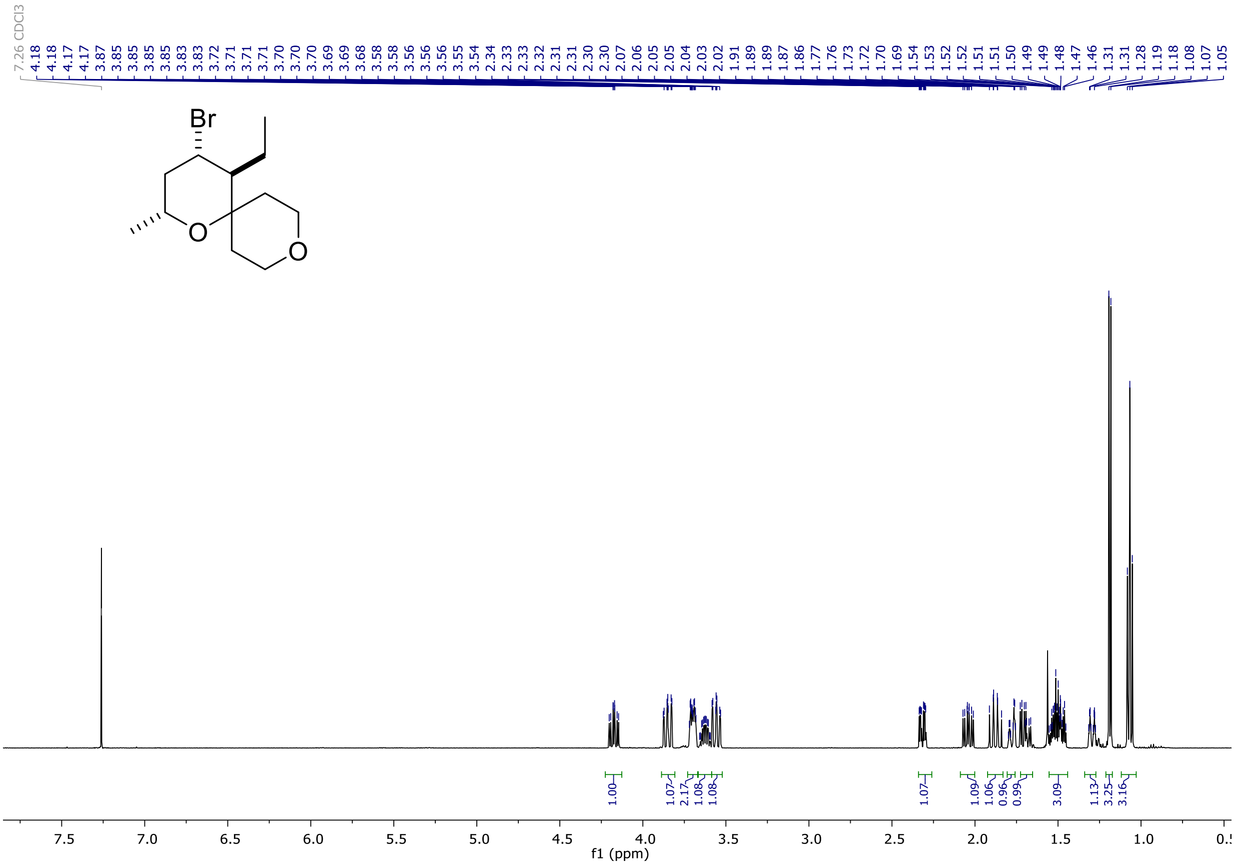


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

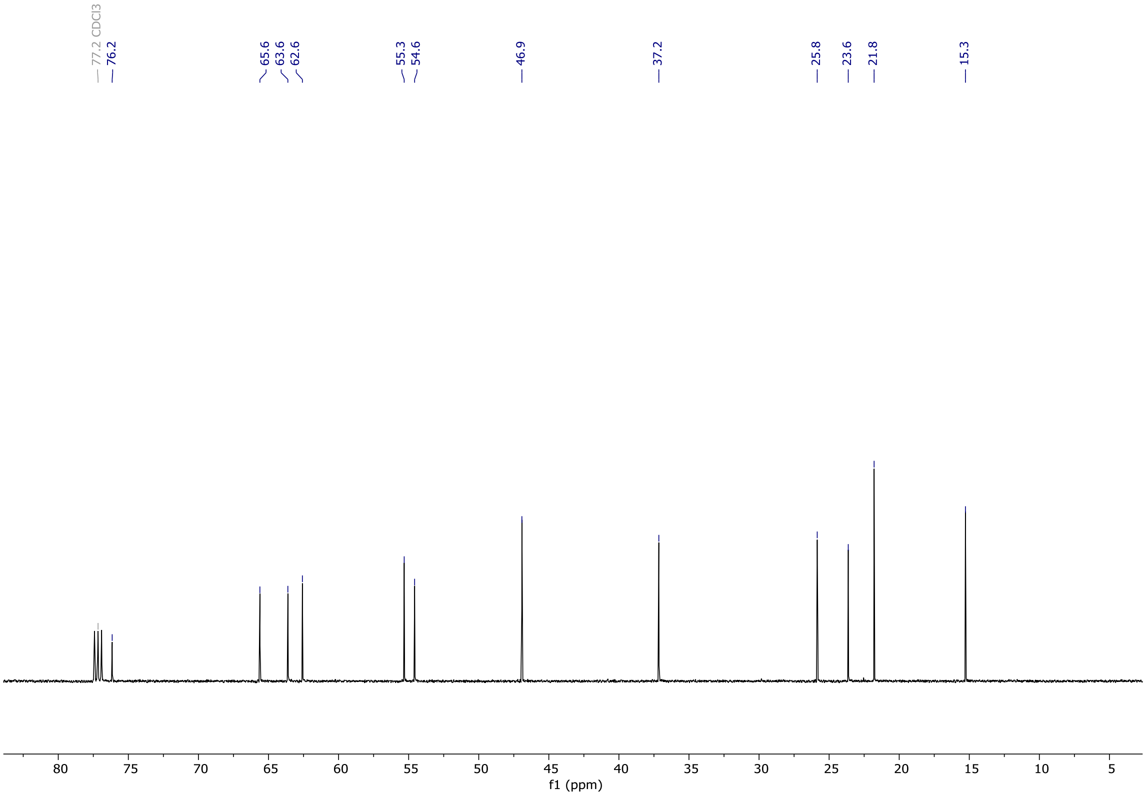


**Compound 4g**

**$^1$H NMR** (500 MHz, $CDCl_3$)

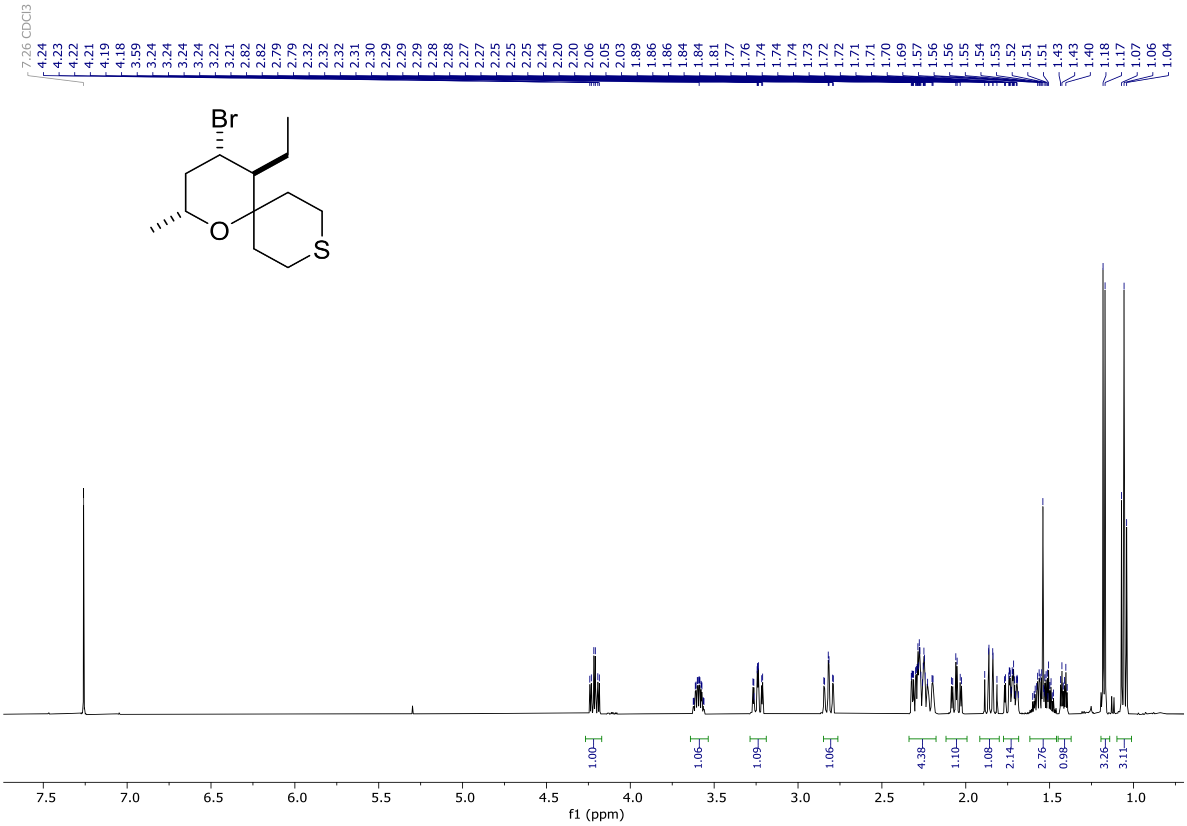


**$^{13}$C NMR** (126 MHz, $CDCl_3$)

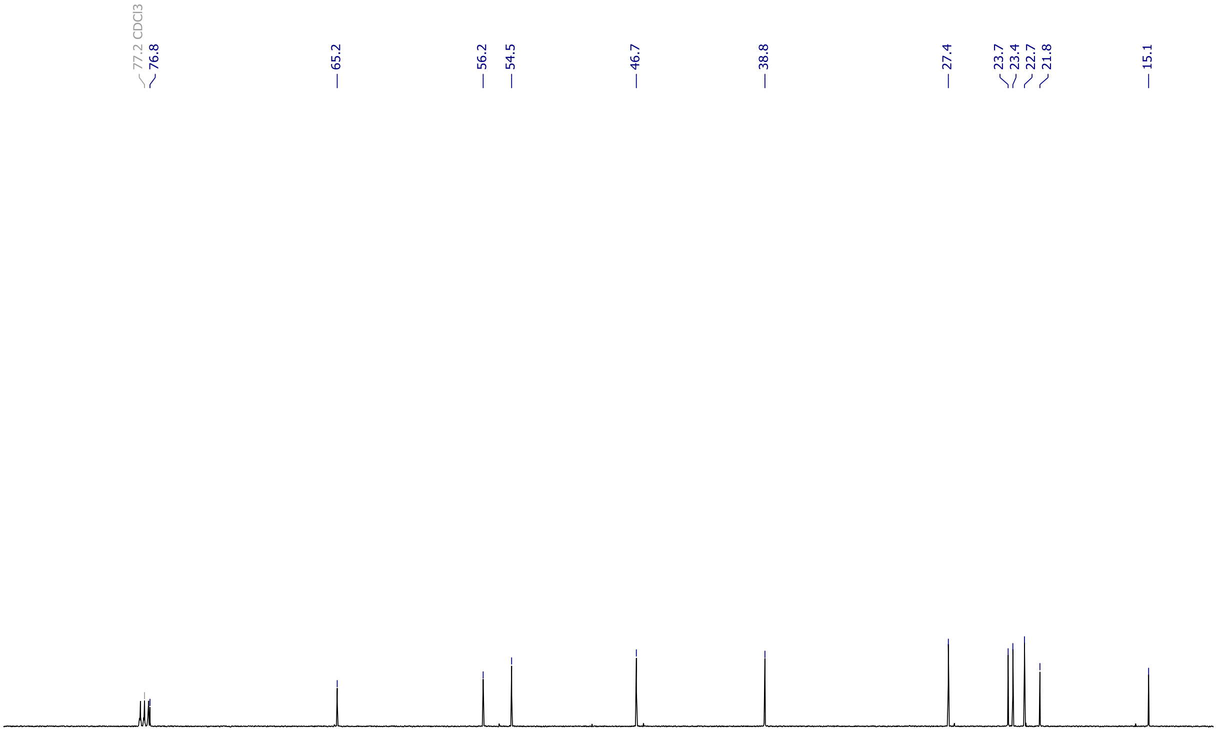


**Compound 4h**

**$^1$H NMR** (500 MHz, $CDCl_3$)

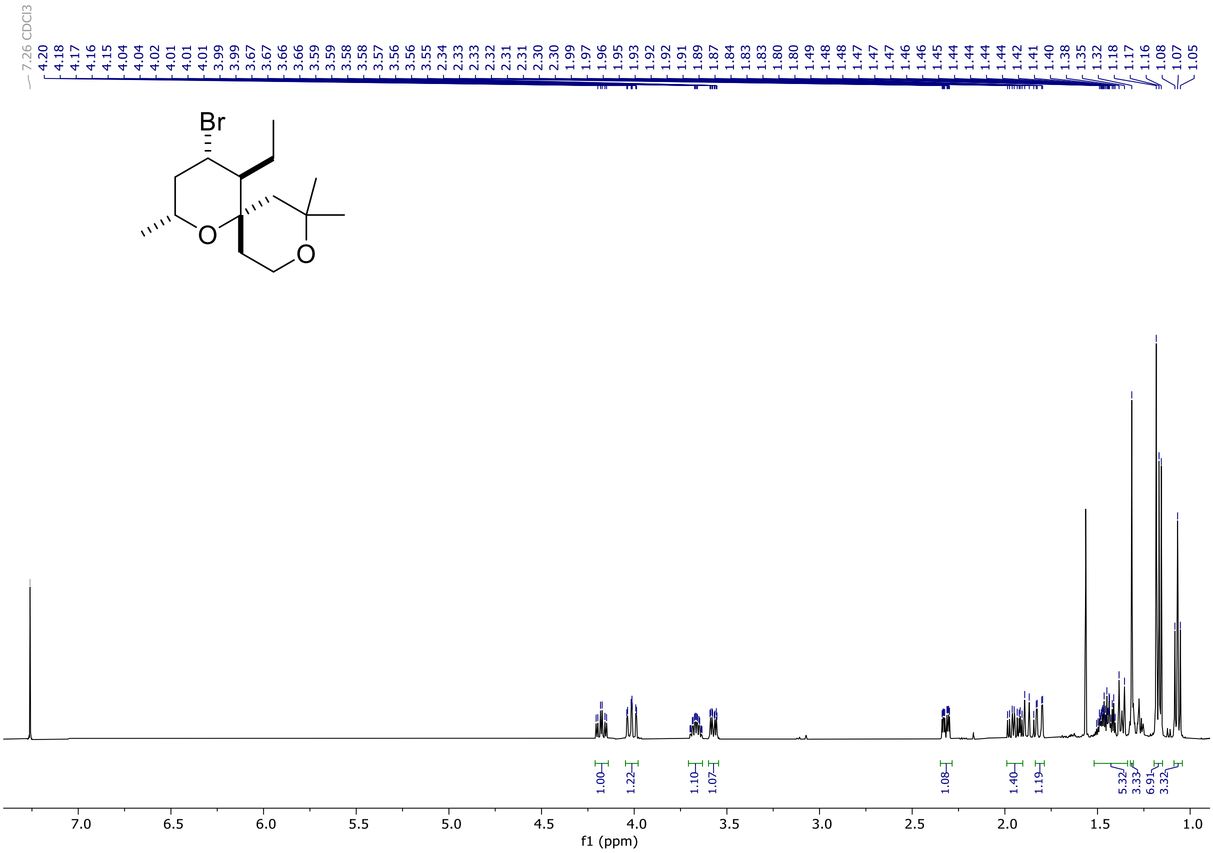


**$^{13}$C NMR** (126 MHz, $CDCl_3$)

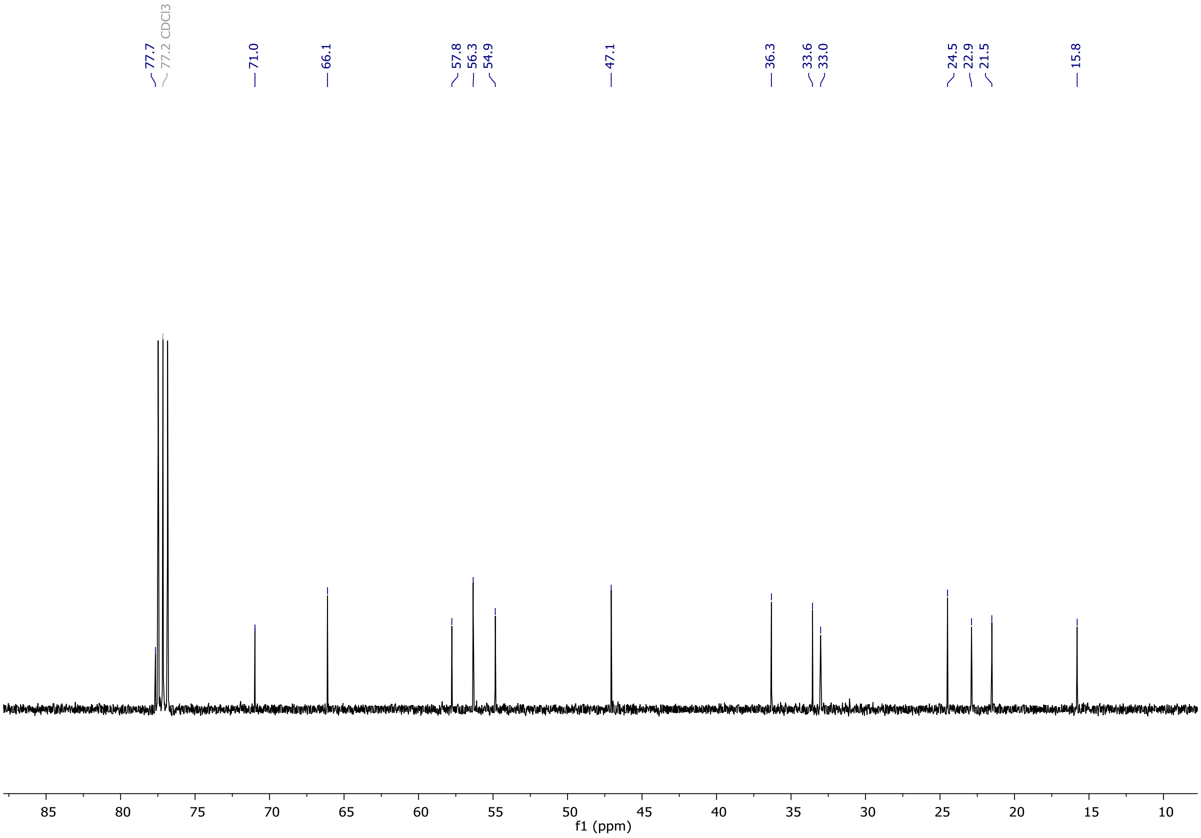


**Compound 4i**

**$^{1}$H NMR** (500 MHz, CDCl$_3$)

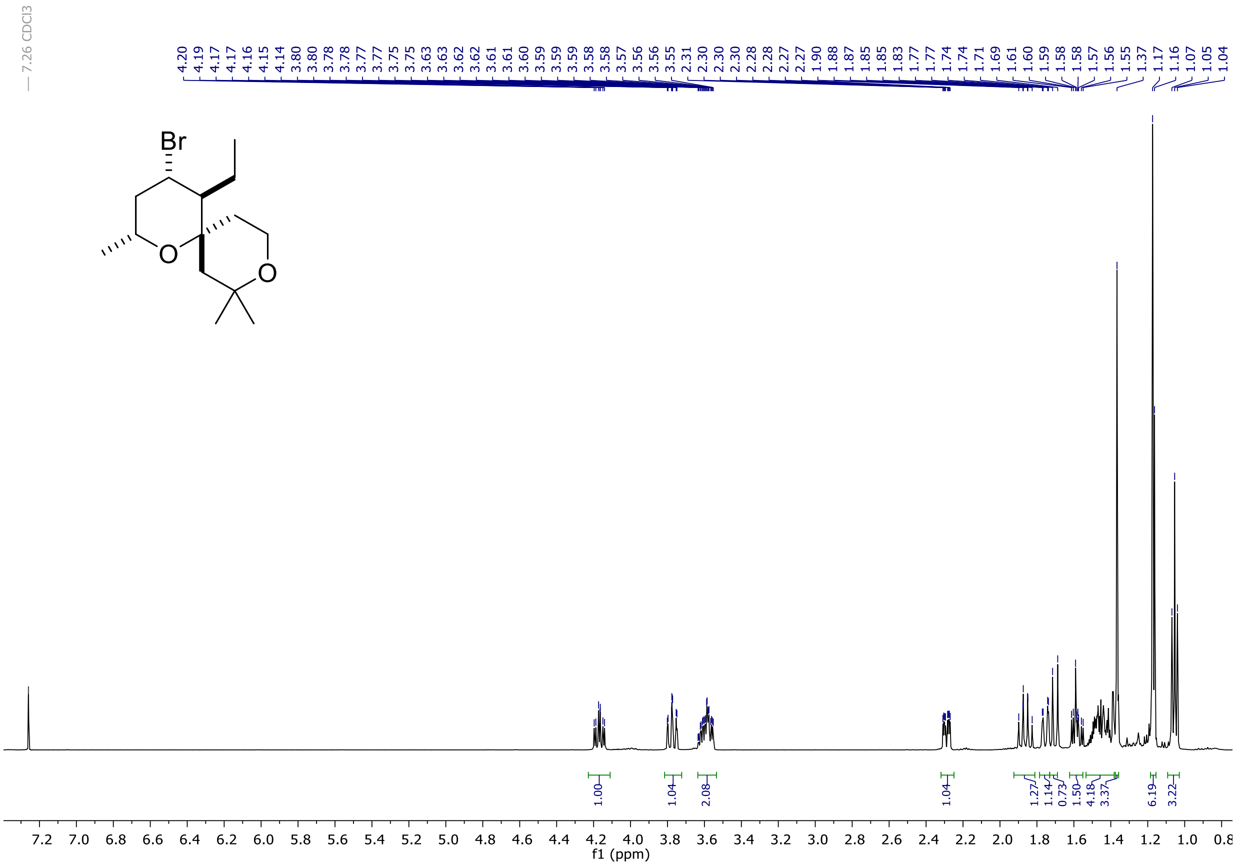


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

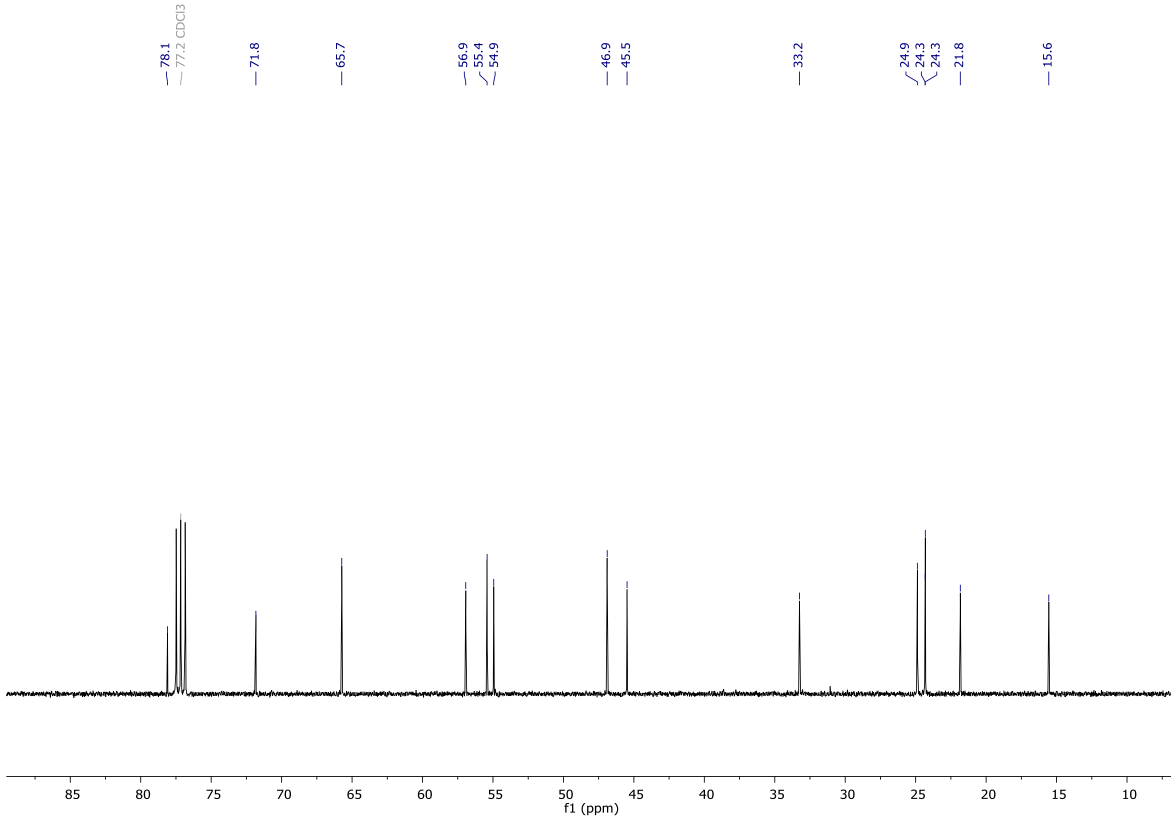


**Compound 5i**

**$^1$H NMR** (500 MHz, CDCl$_3$)

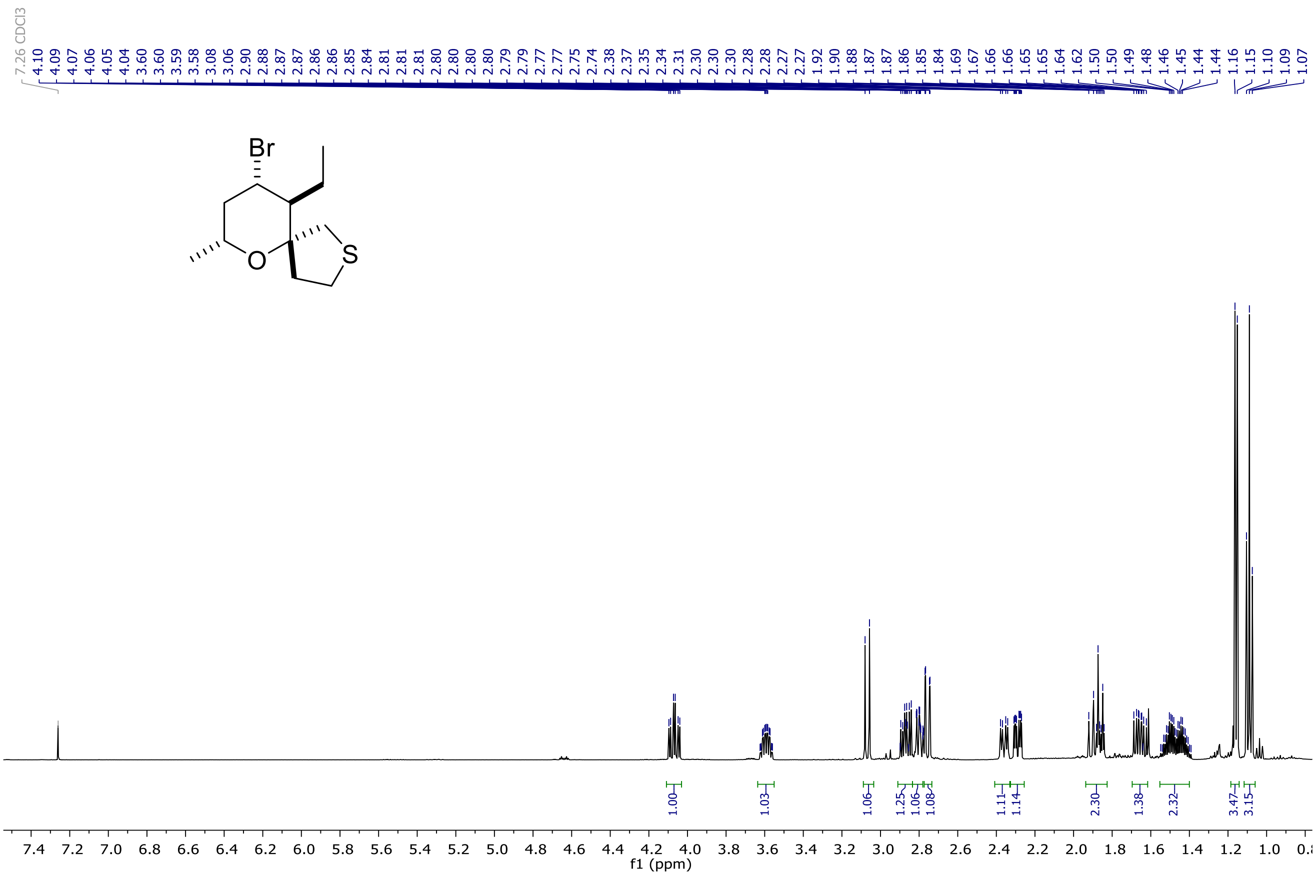


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

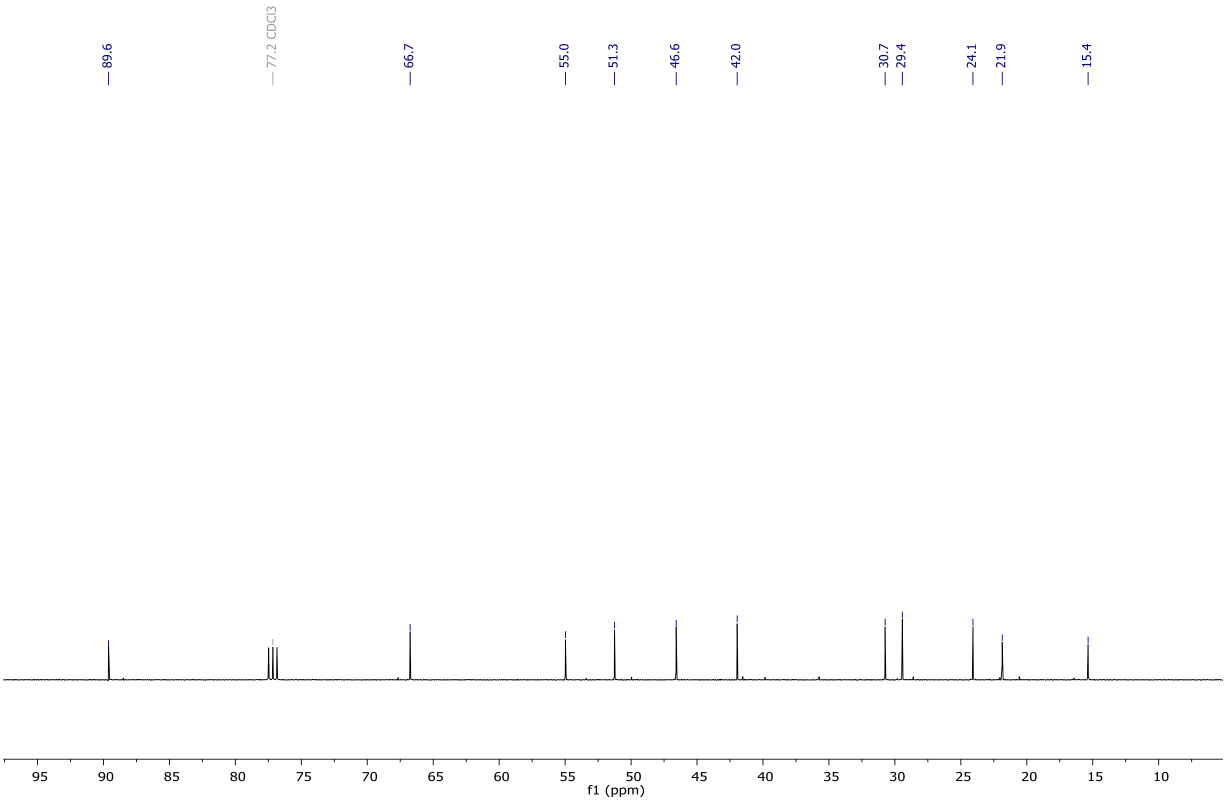


## Compound 4j

**¹H NMR** (500 MHz, CDCl₃)

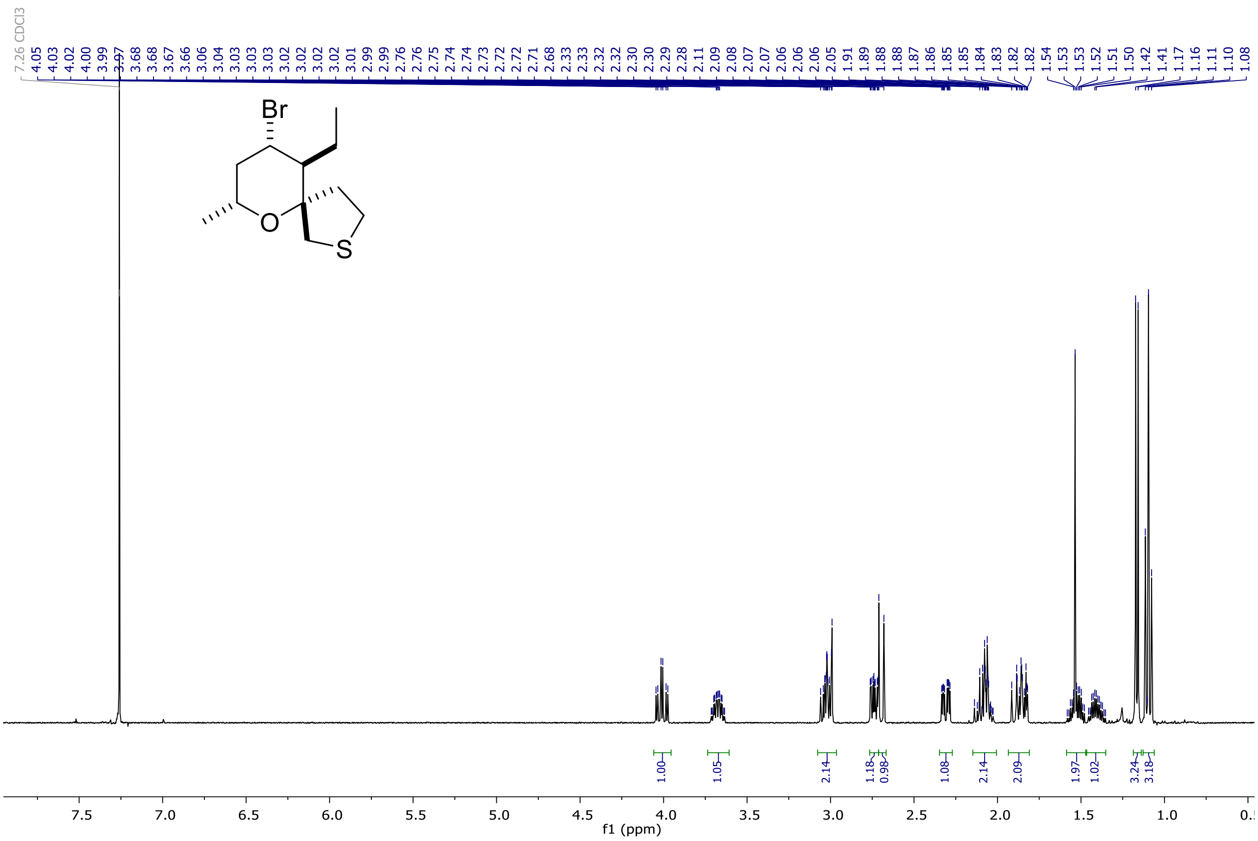


**¹³C NMR** (101 MHz, CDCl₃)

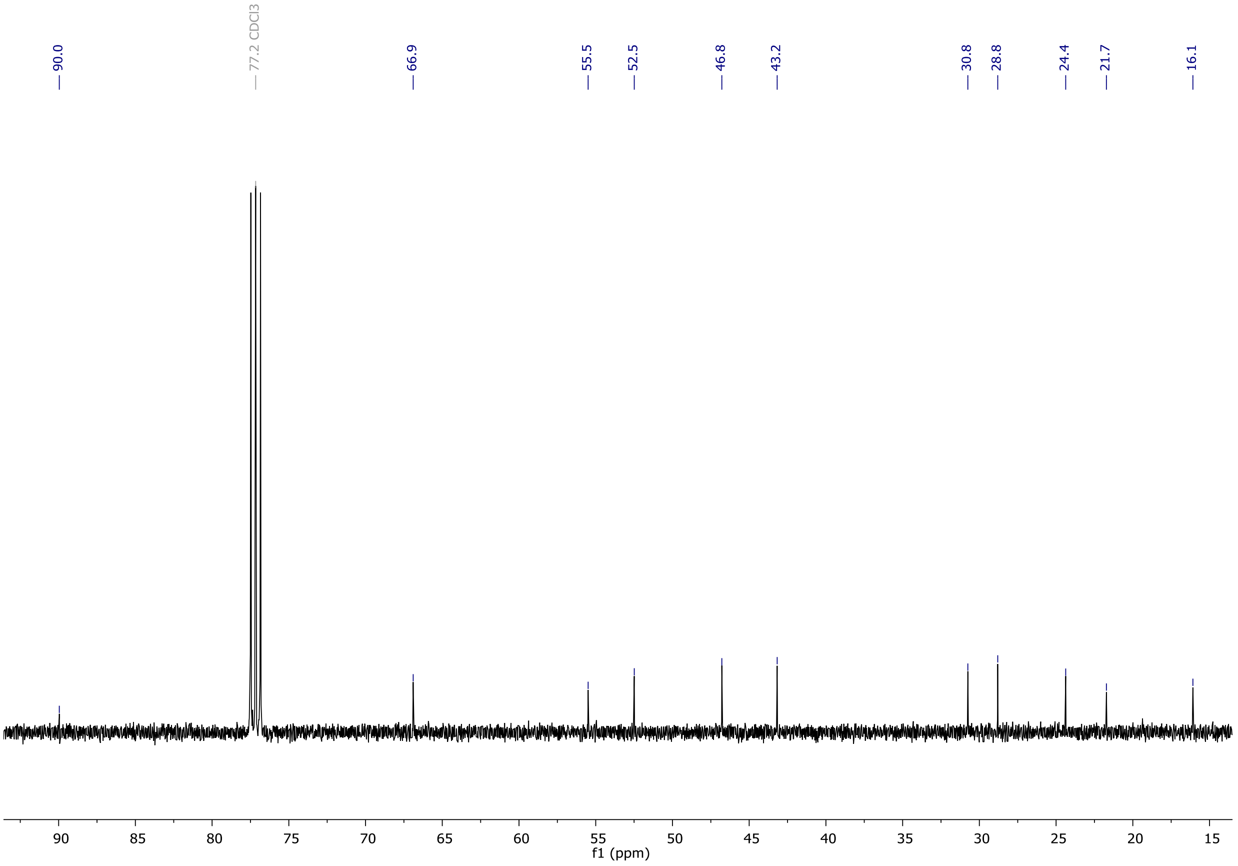


## Compound 5j

**$^{1}$H NMR** (400 MHz, CDCl$_3$)

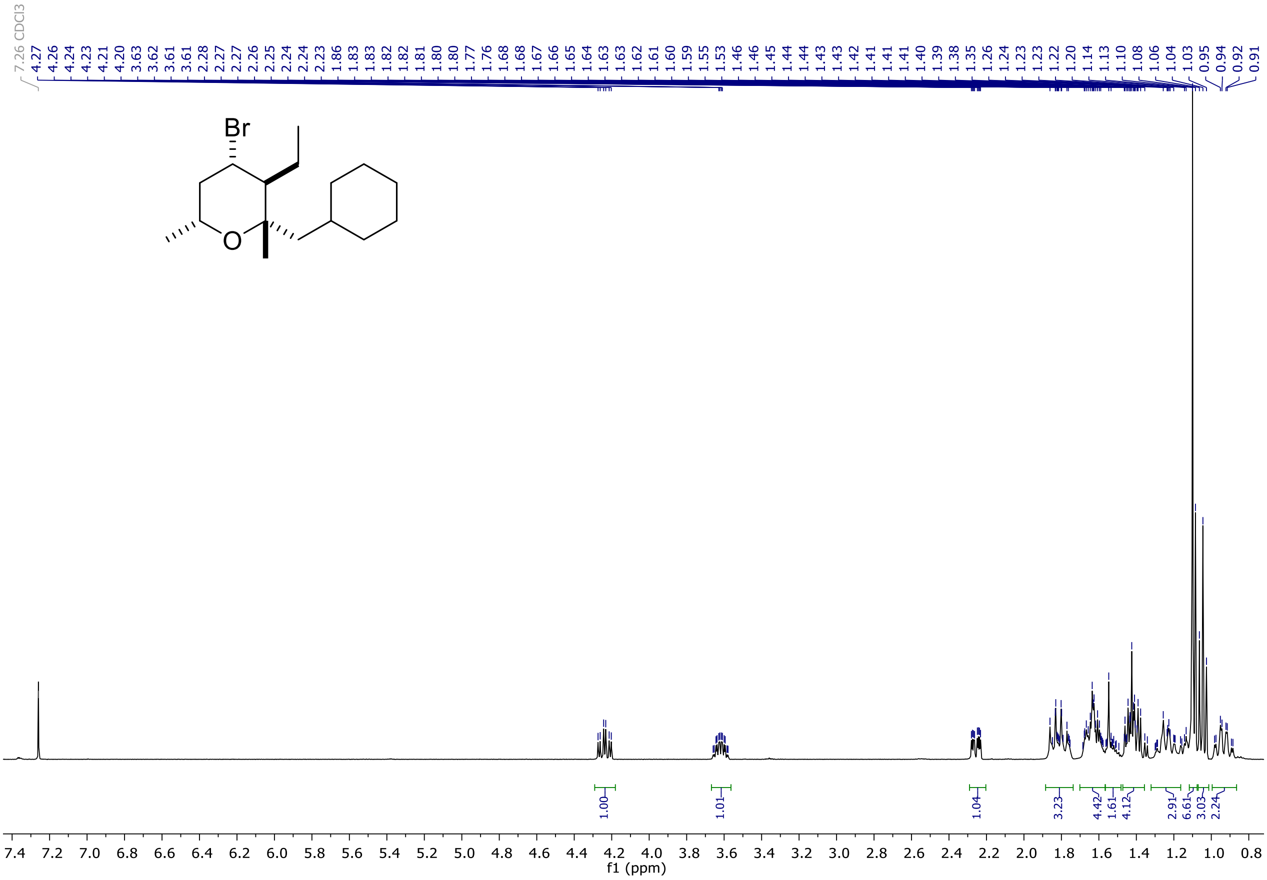


**$^{13}$C NMR** (101 MHz, CDCl$_3$)

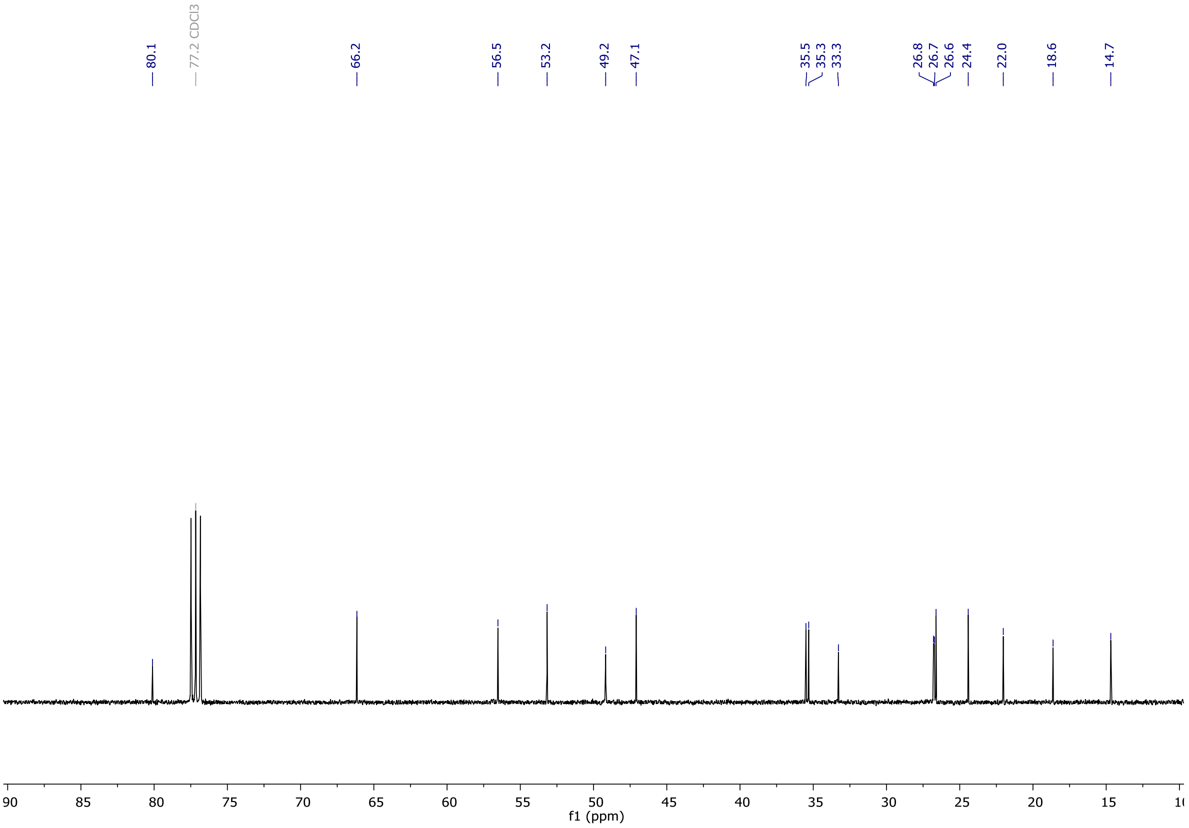


## Compound 4k

**$^{1}$H NMR** (400 MHz, CDCl$_3$)

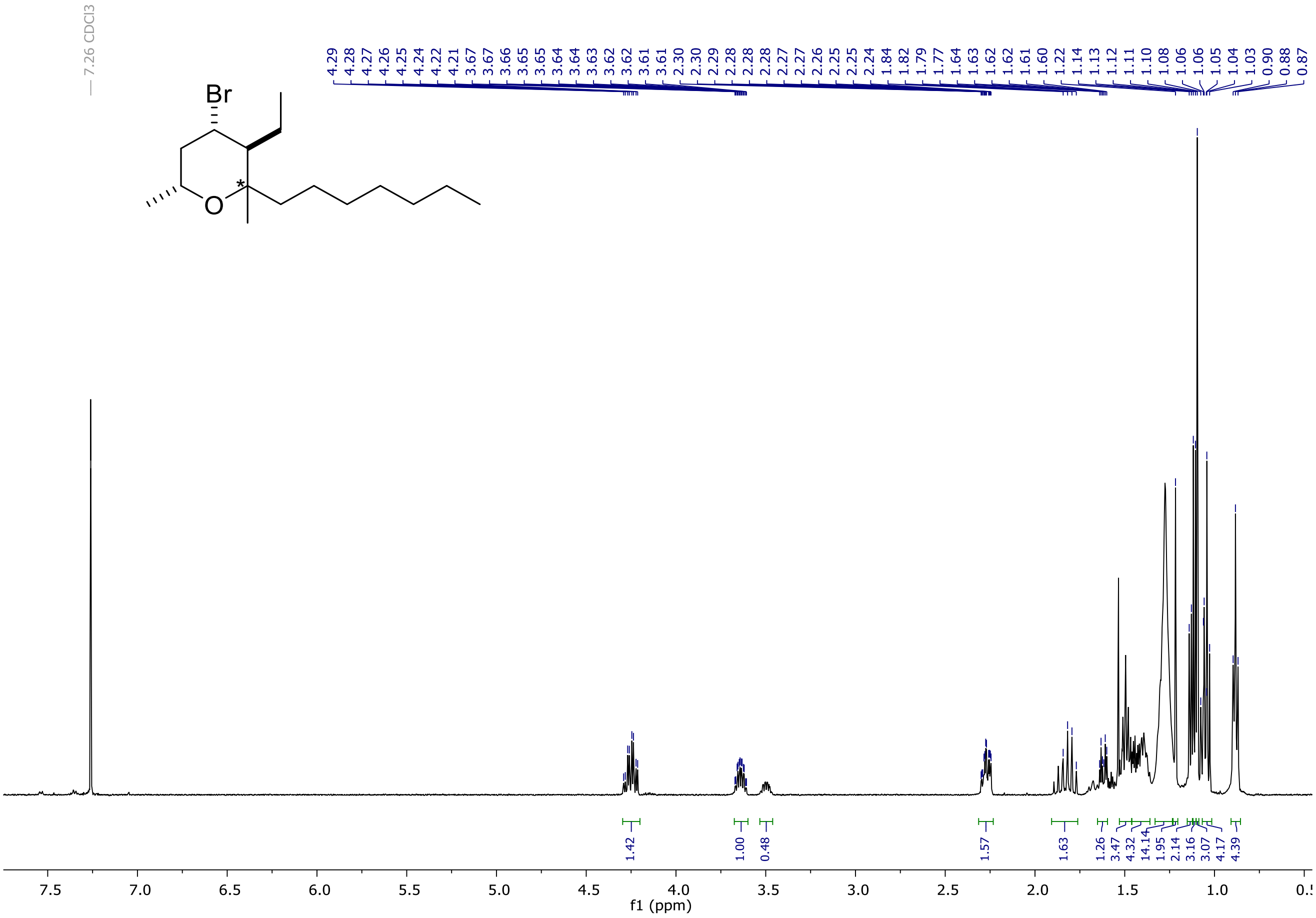


**$^{13}$C NMR** (101MHz, CDCl$_3$)

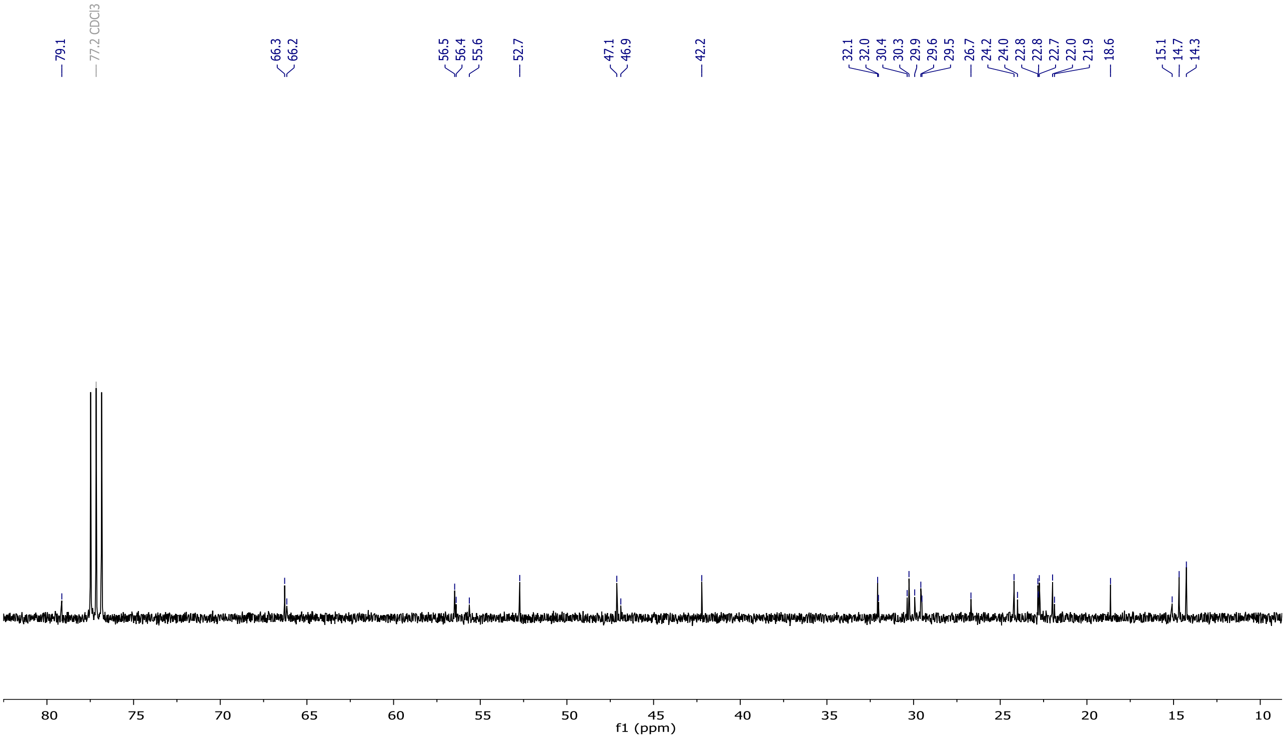


## Compound 4l and 5l

**$^1$H NMR** (500 MHz, CDCl$_3$)

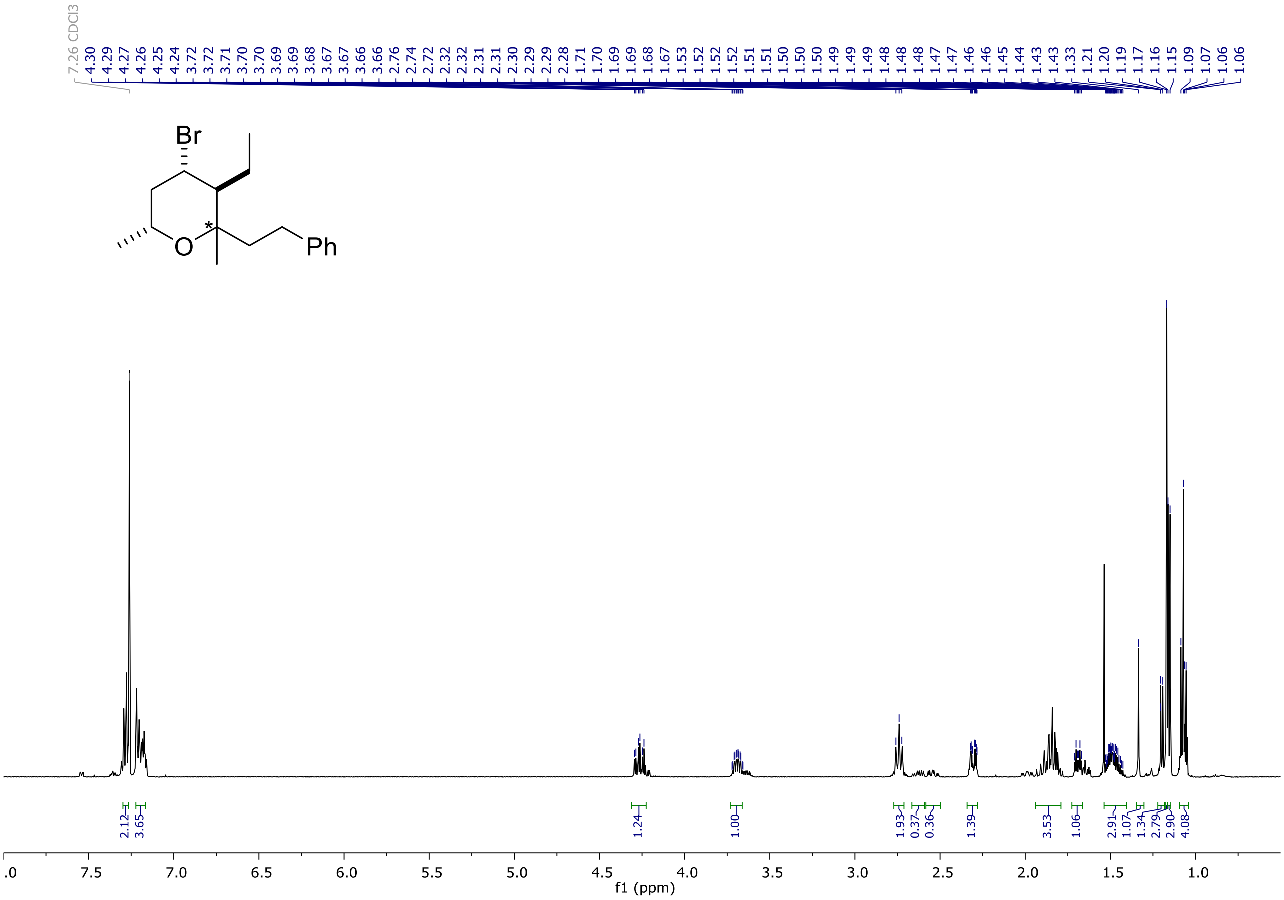


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

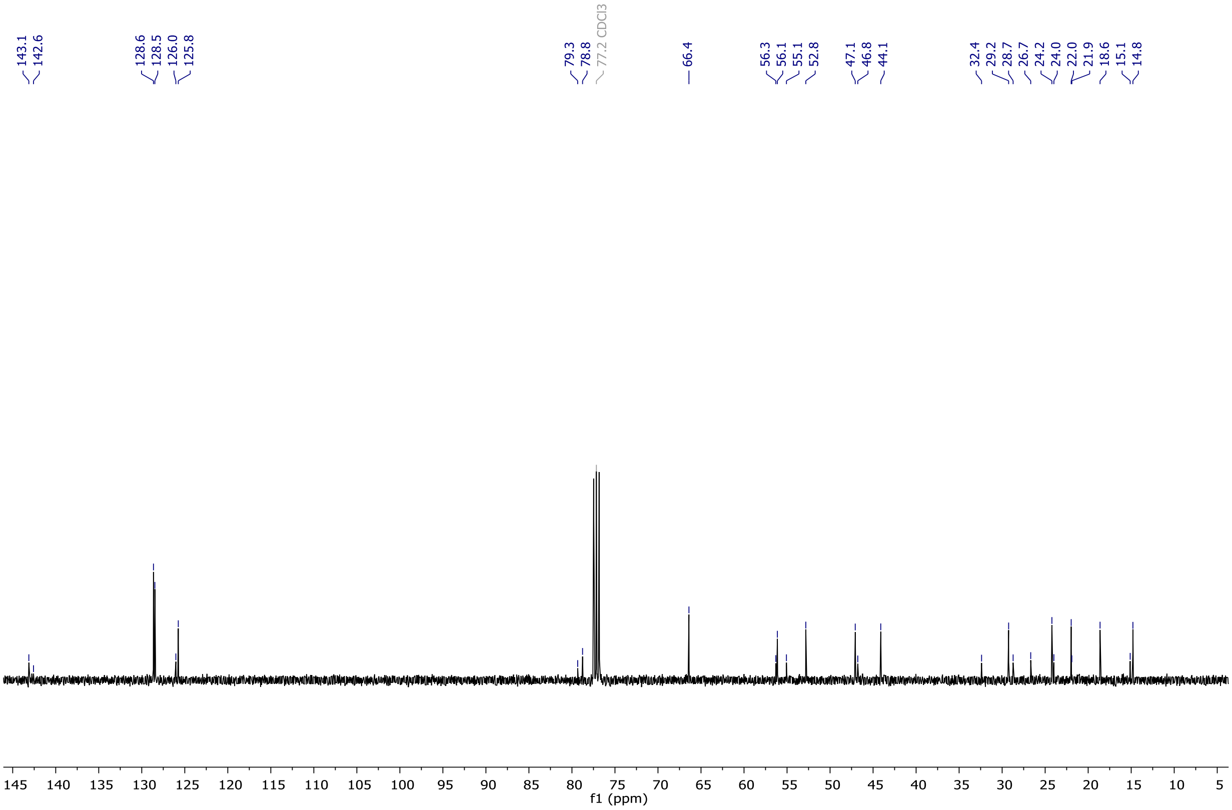


## Compound 4m and 5m

**$^1$H NMR** (500 MHz, $CDCl_3$)

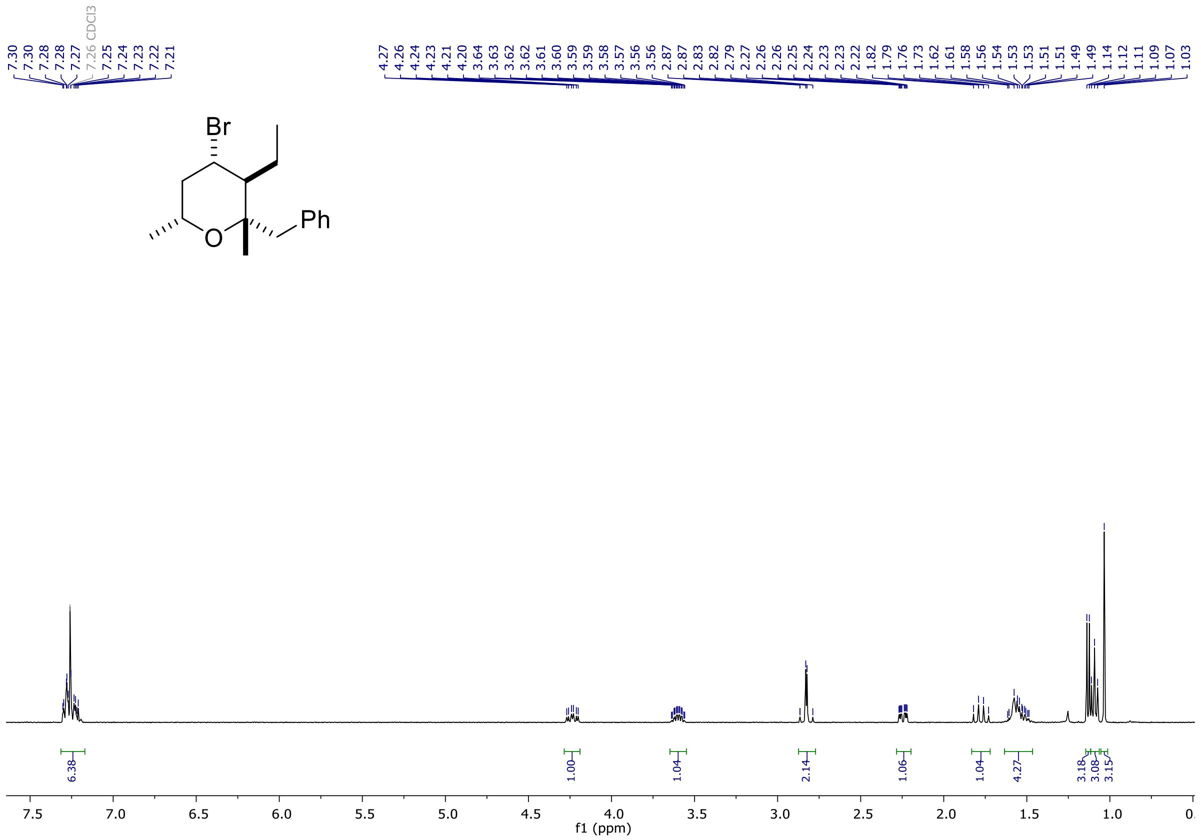


**$^{13}$C NMR** (101 MHz, $CDCl_3$)

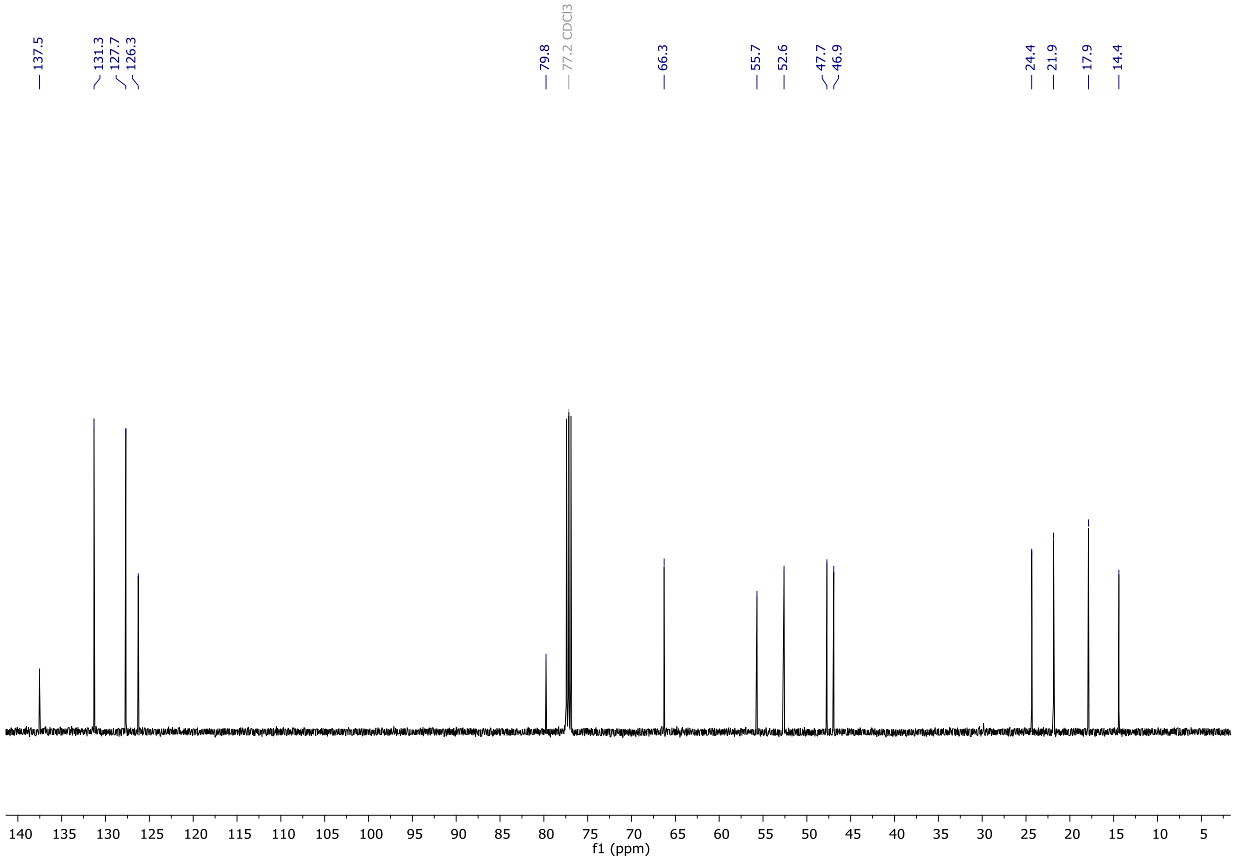


## Compound 4n

### **$^{1}$H NMR** (500 MHz, CDCl$_3$)

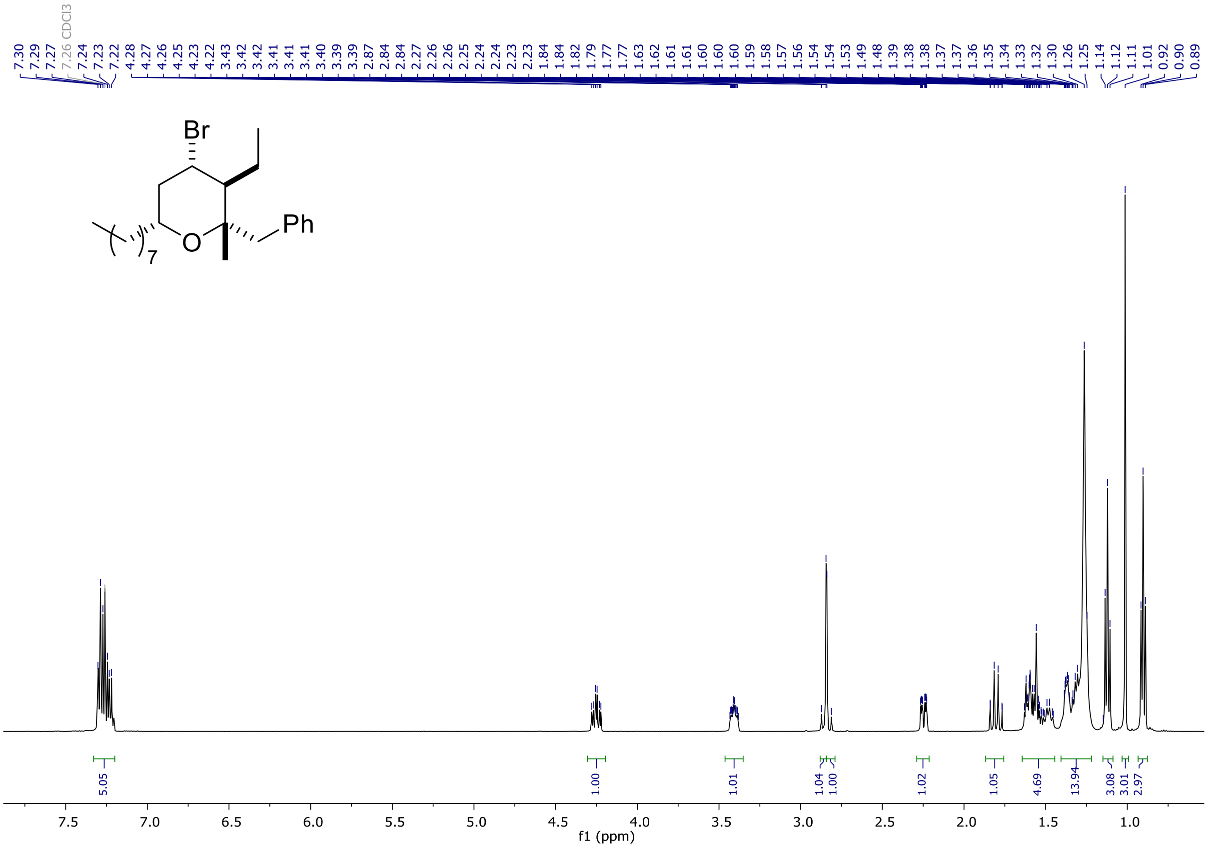


### **$^{13}$C NMR** (126 MHz, CDCl$_3$)

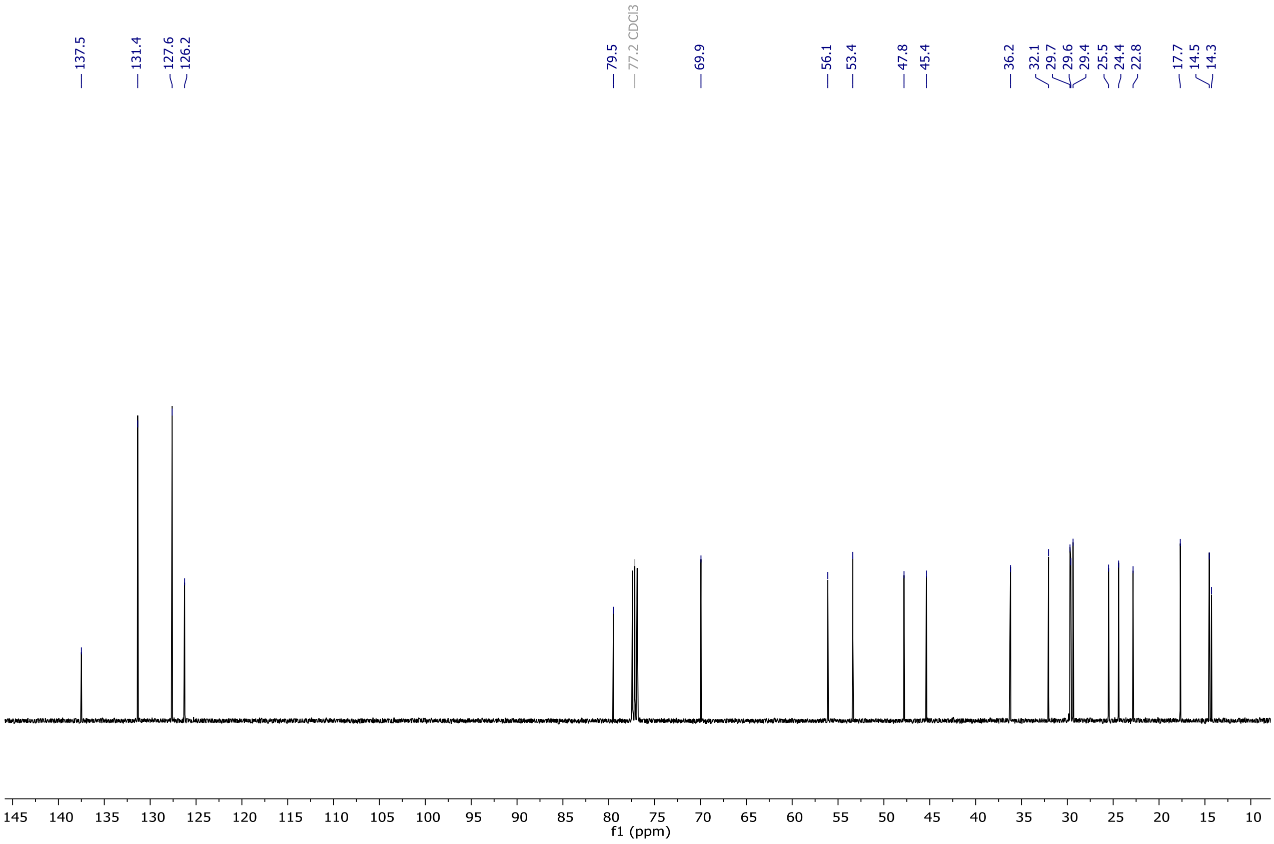


## Compound 4o

**$^1$H NMR** (500 MHz, CDCl$_3$)

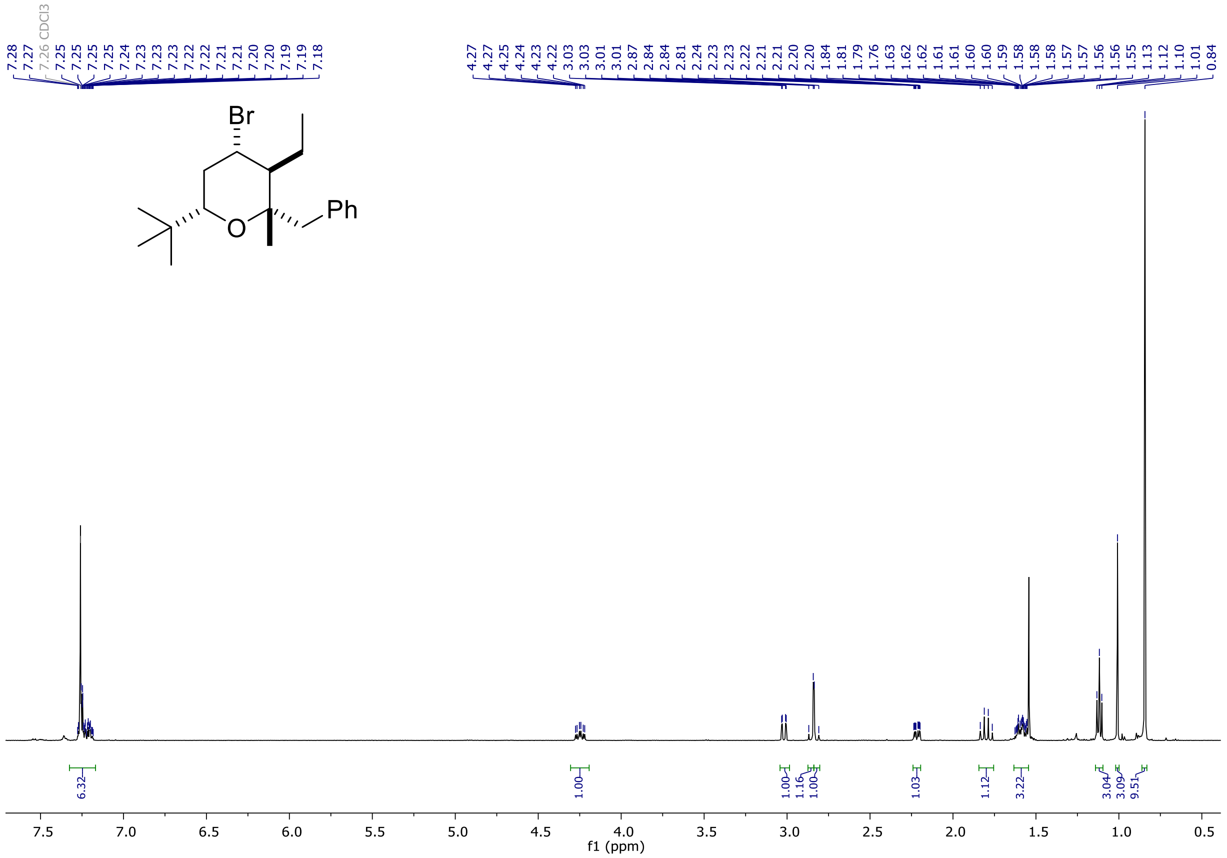


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

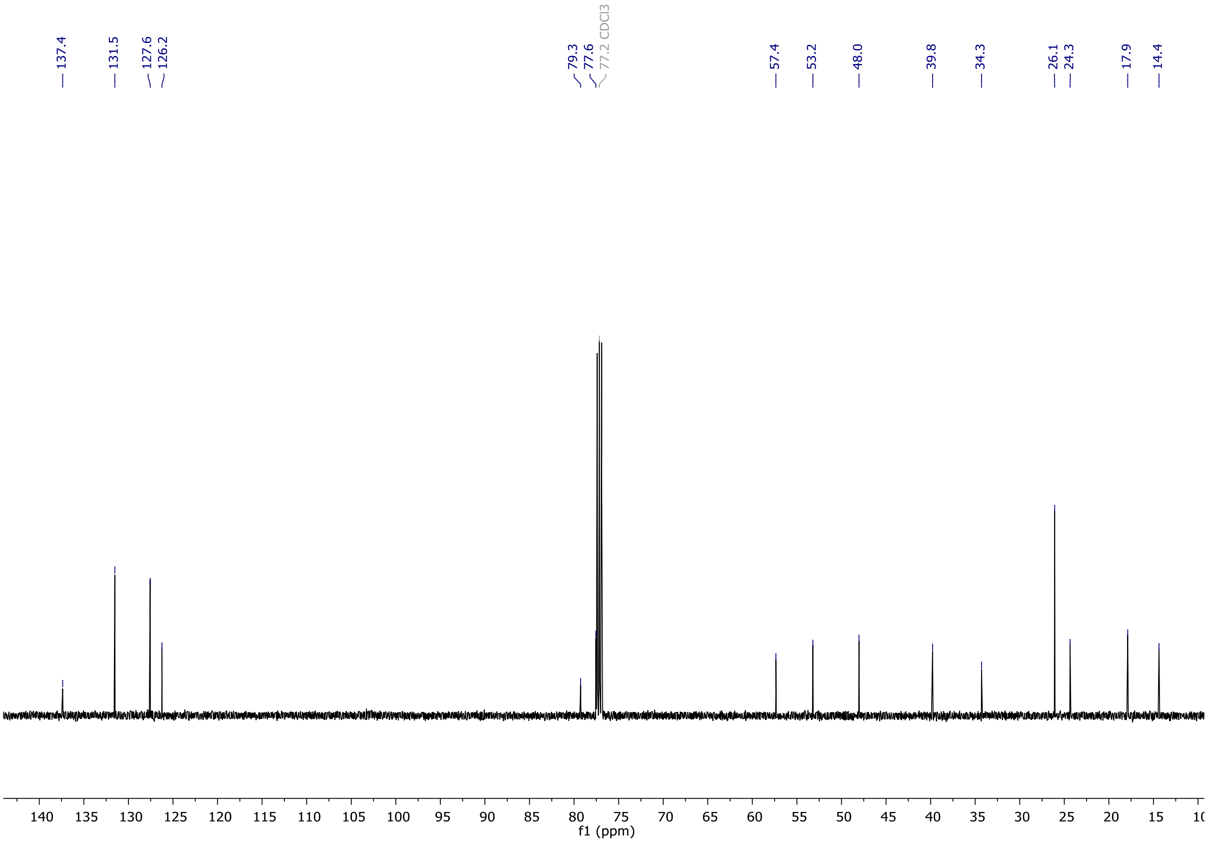


### Compound 4p

**$^1$H NMR** (500 MHz, CDCl$_3$)

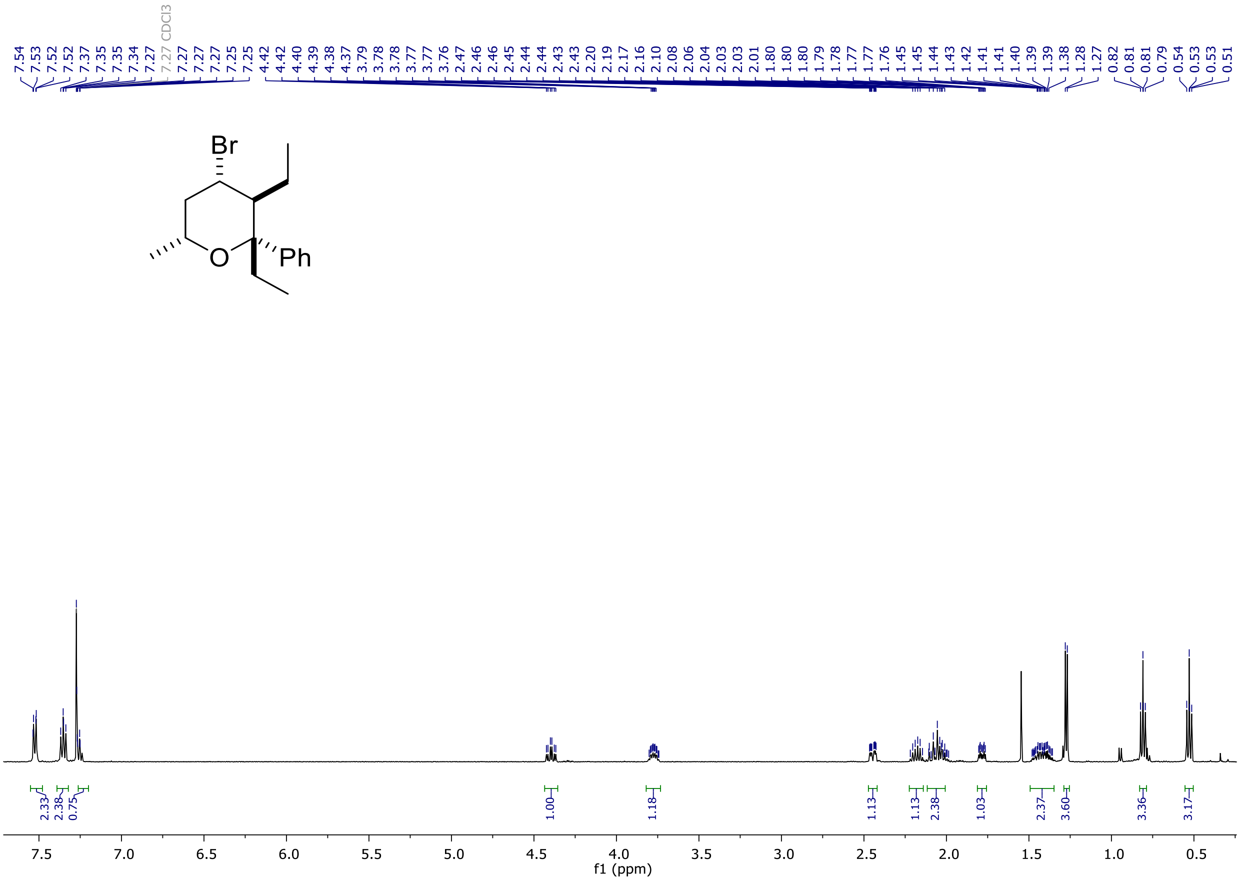


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

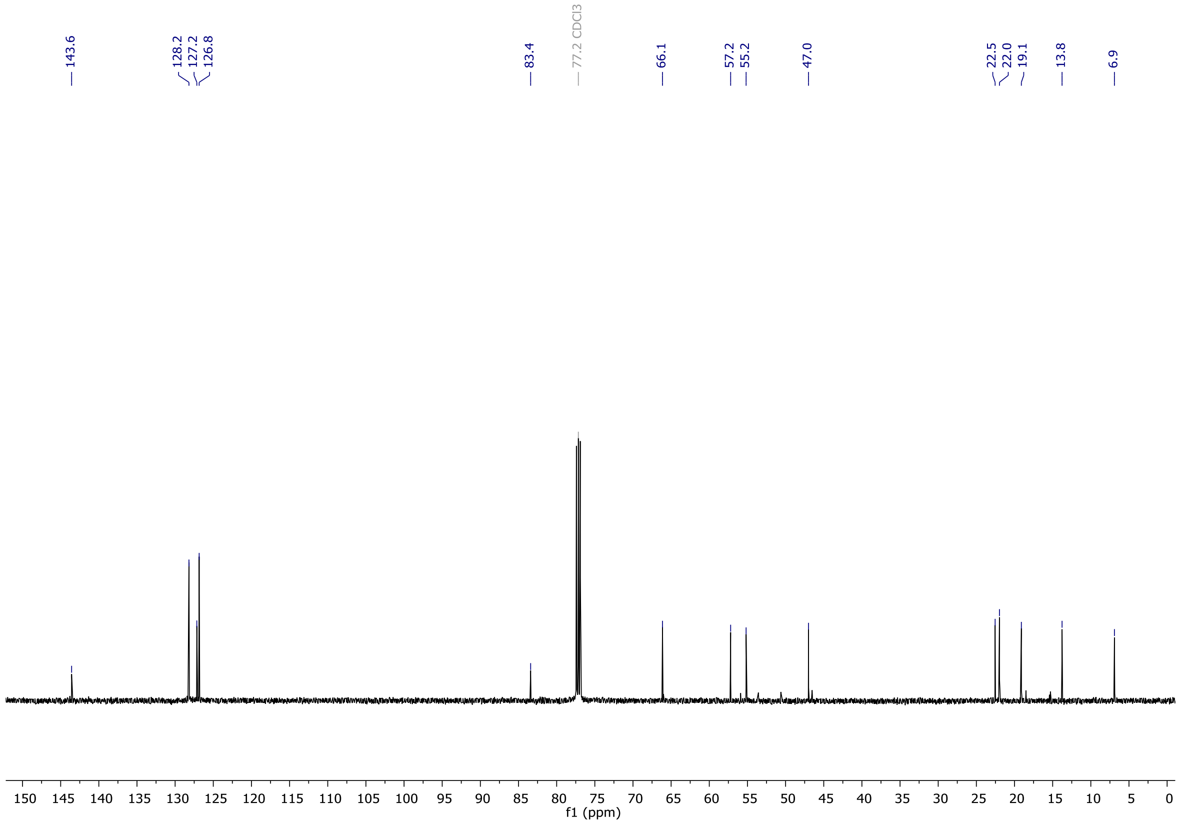


**Compound 4q**

**$^{1}$H NMR** (500 MHz, $CDCl_3$)

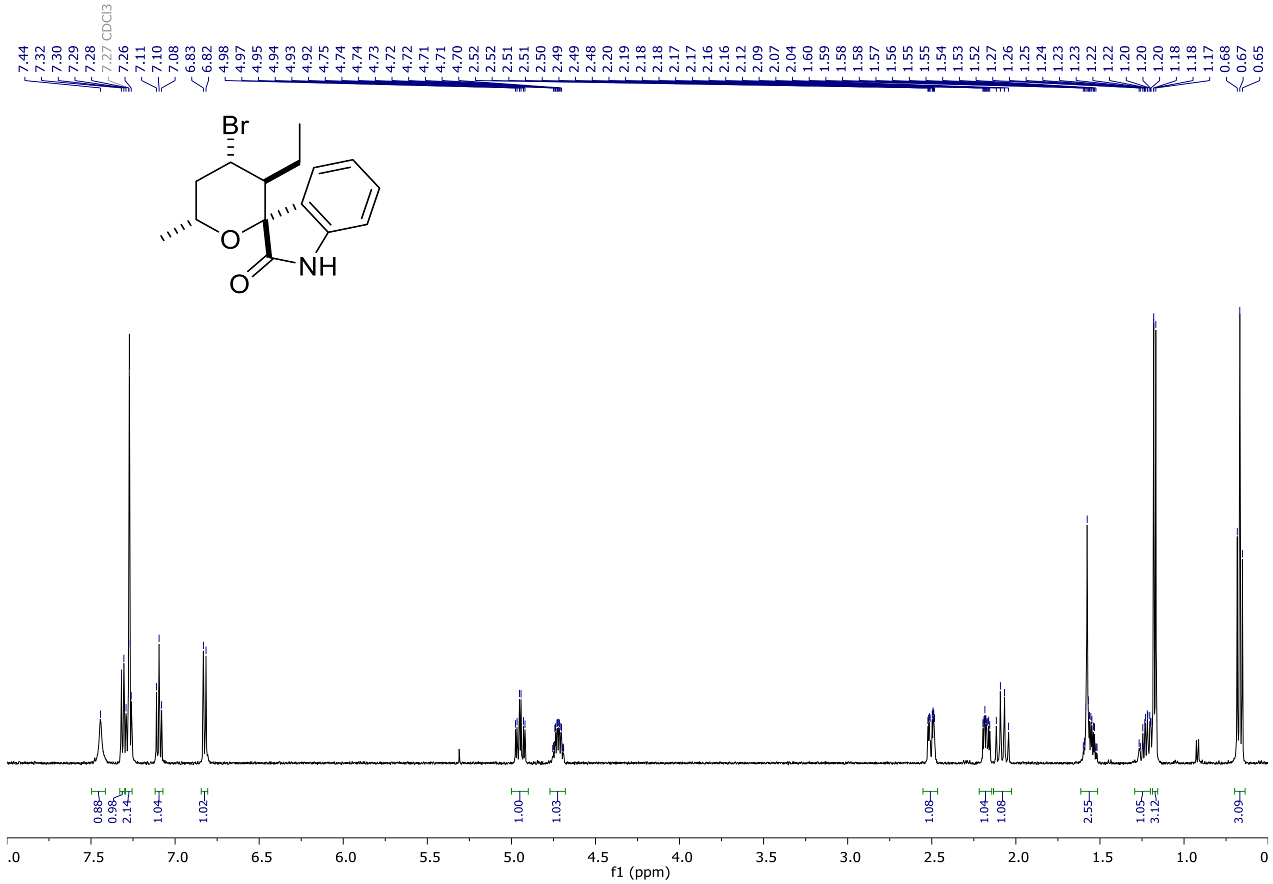


**$^{13}$C NMR** (126 MHz, $CDCl_3$)

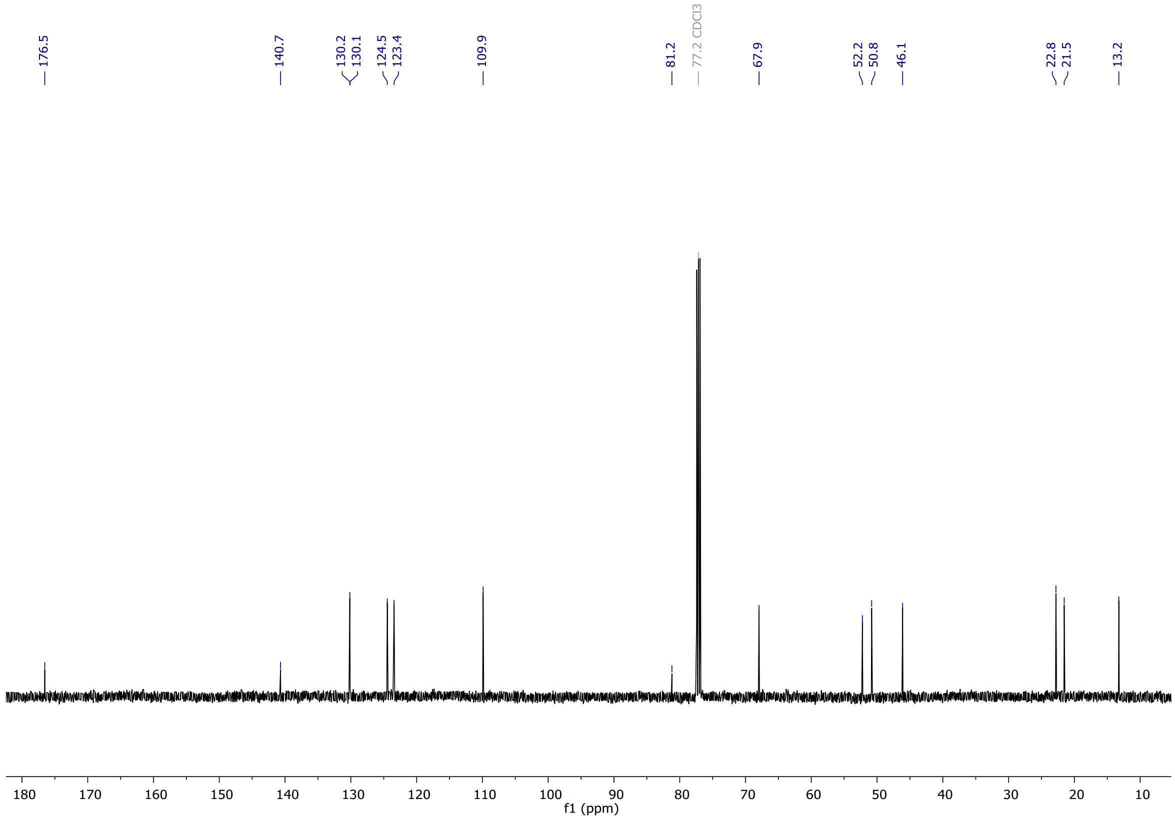


## Compound 4r

**$^1$H NMR** (500 MHz, $CDCl_3$)

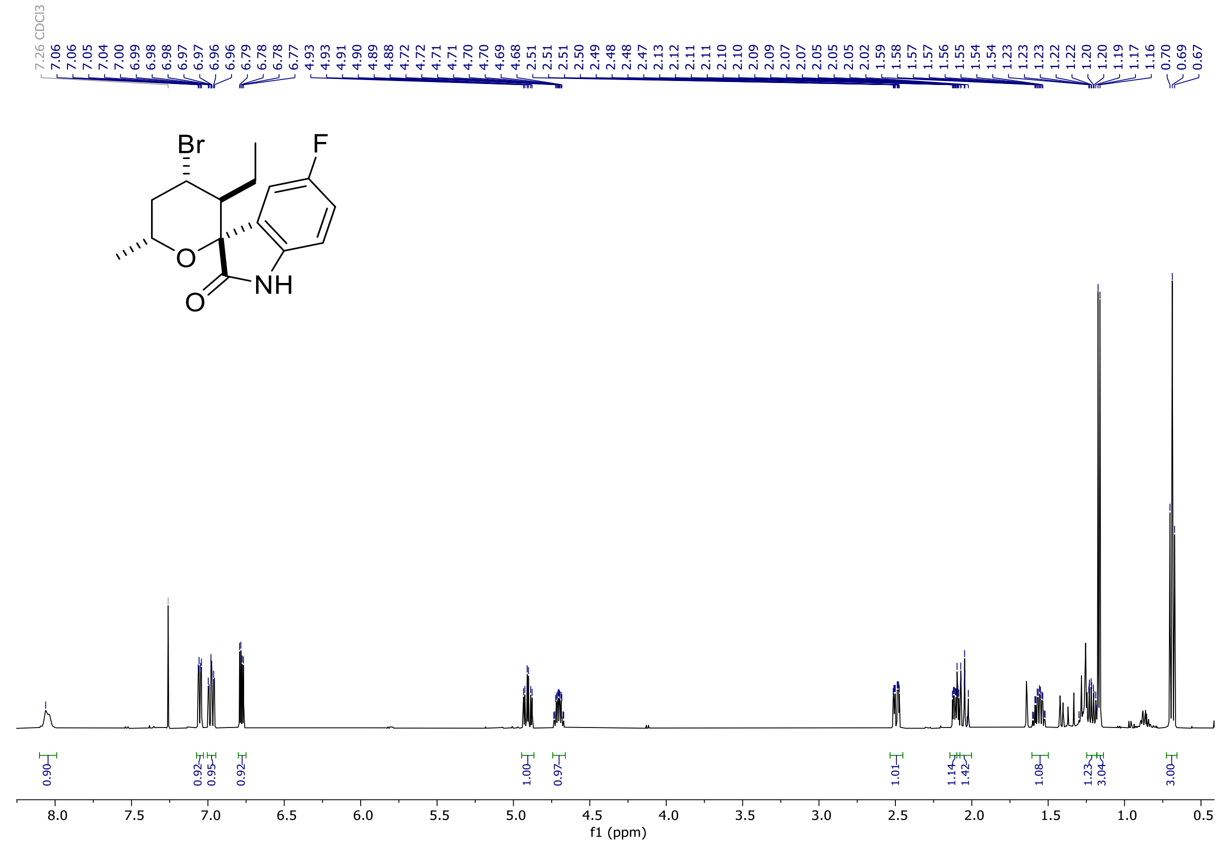


**$^{13}$C NMR** (126 MHz, $CDCl_3$)

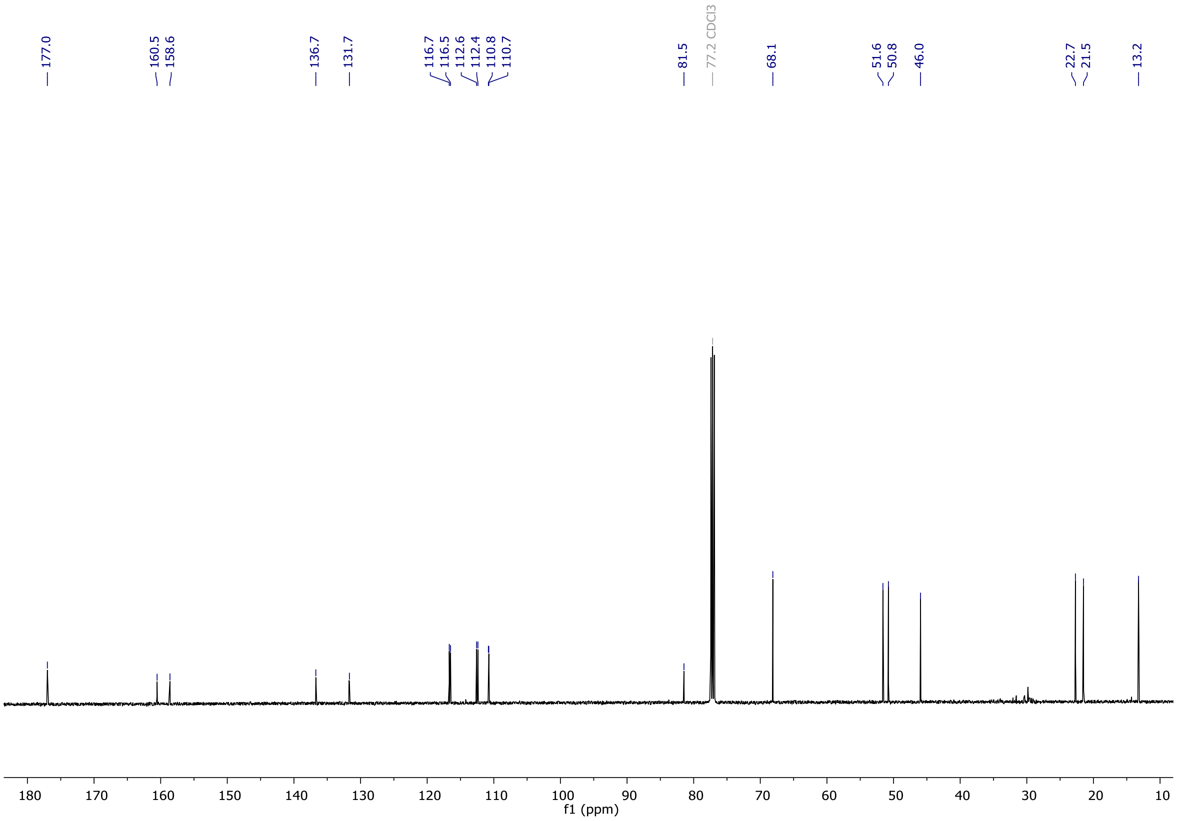


## Compound 4s

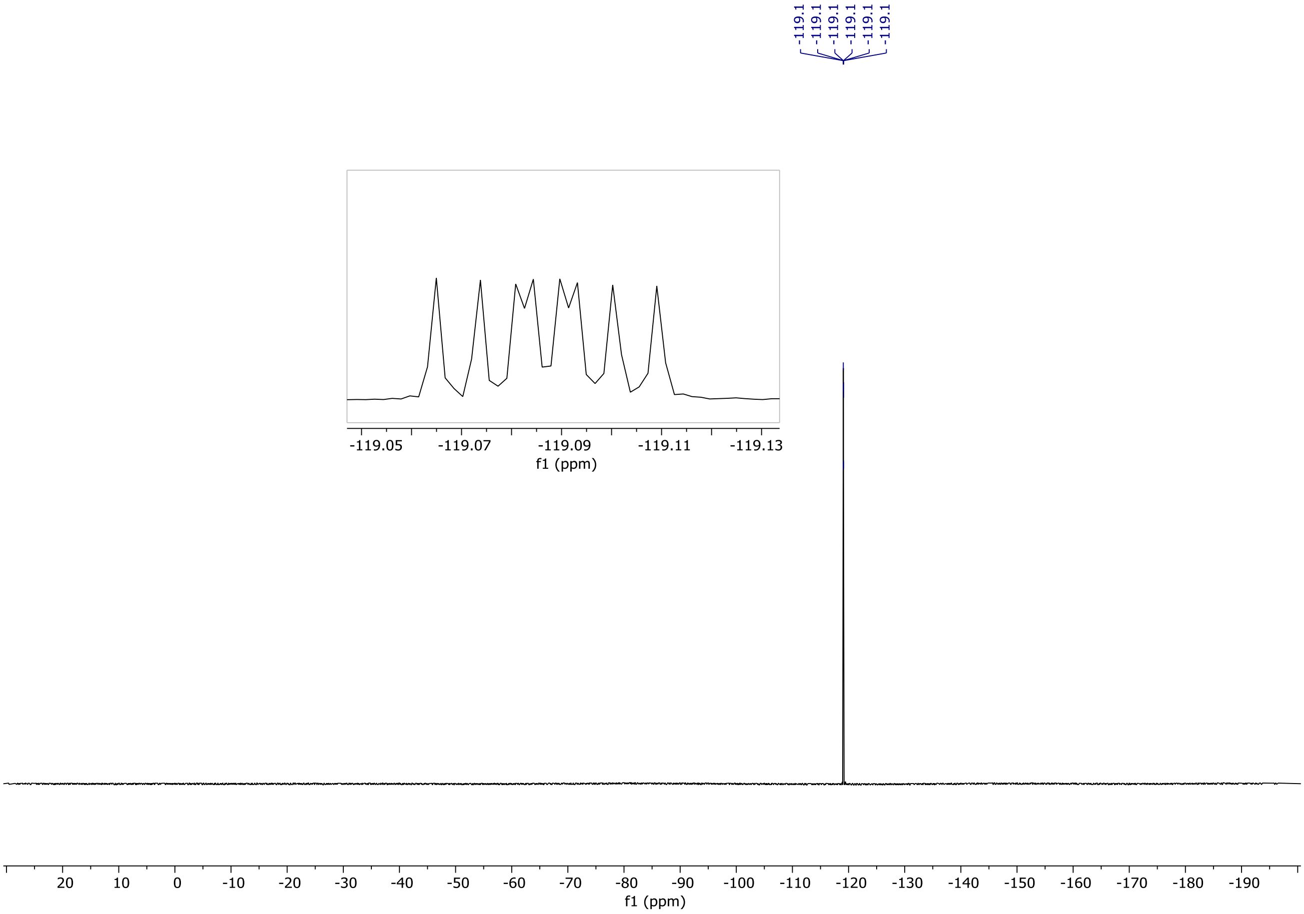
**$^{1}$H NMR** (500 MHz, CDCl$_3$)



**$^{13}$C NMR** (126 MHz, CDCl$_3$)

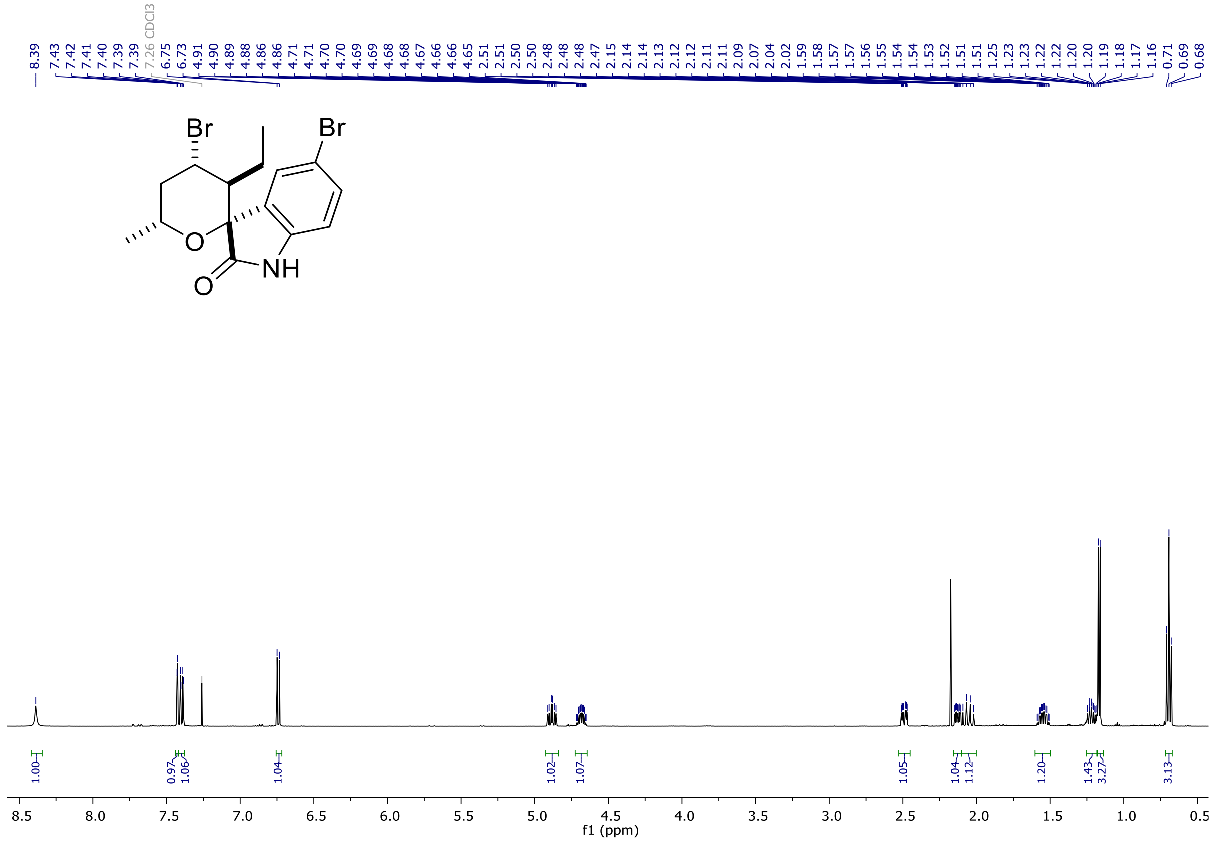


**$^{19}$F NMR** (470 MHz, $CDCl_3$)

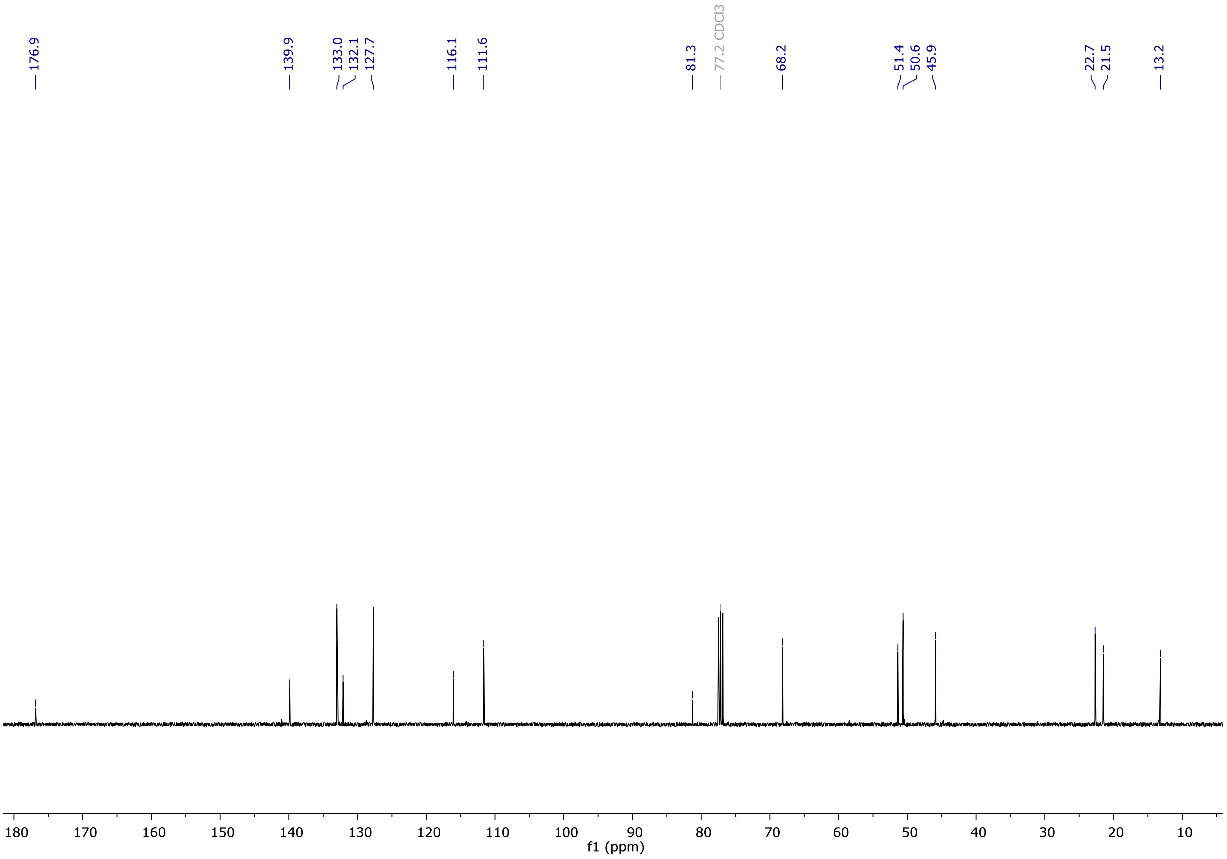


**Compound 4t**

**$^1$H NMR** (500 MHz, CDCl$_3$)

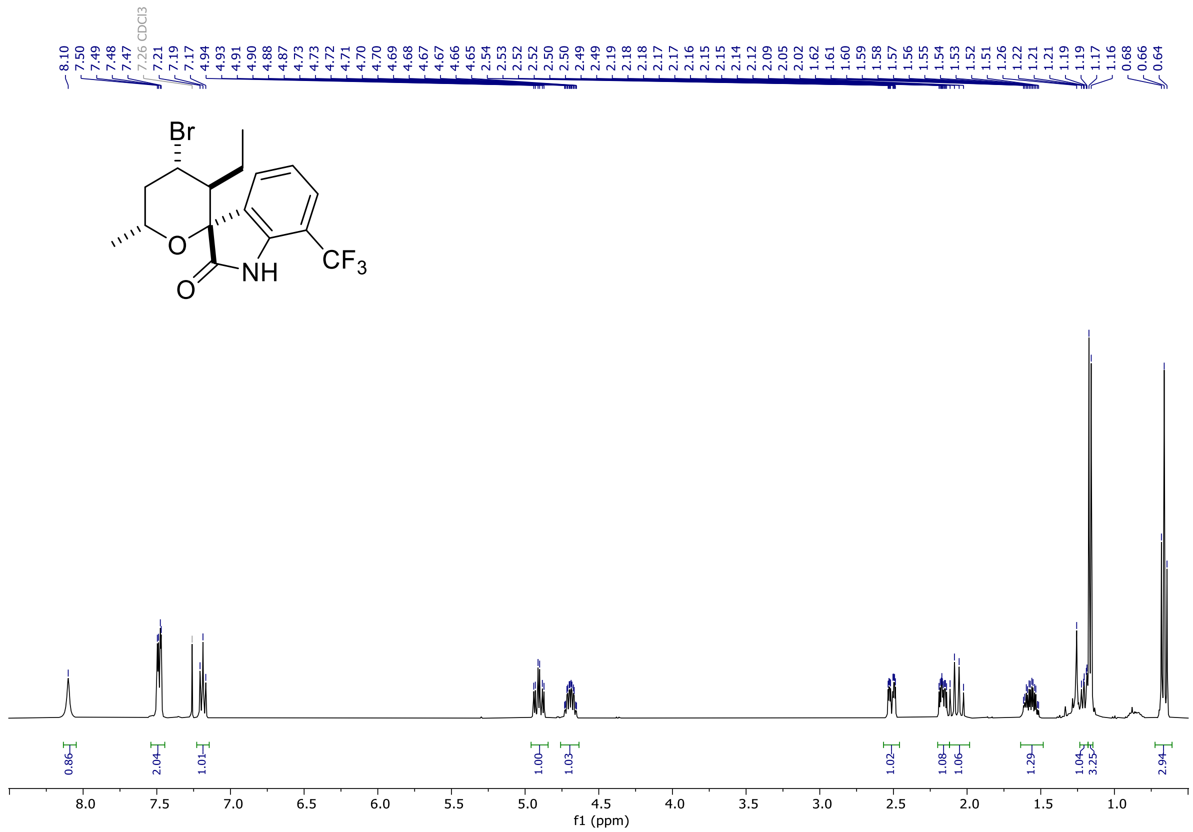


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

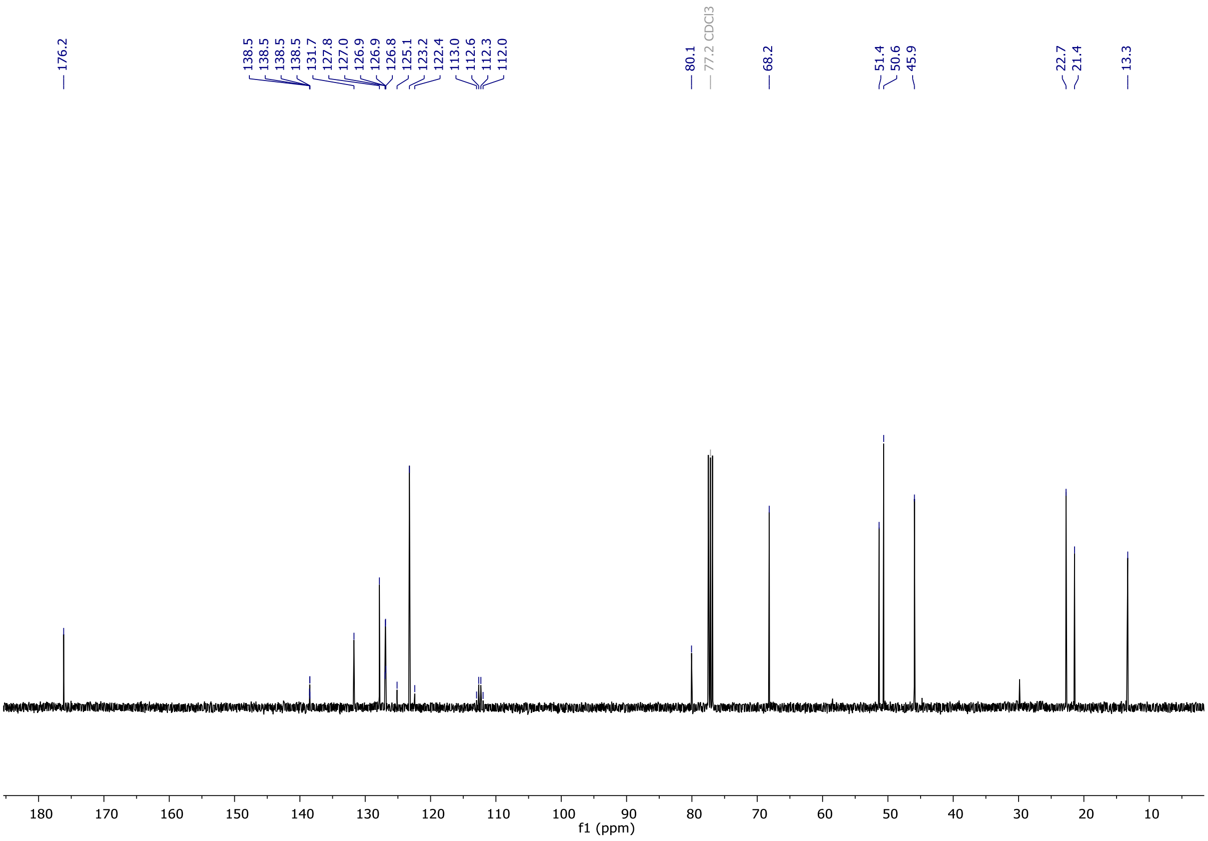


## Compound 4u

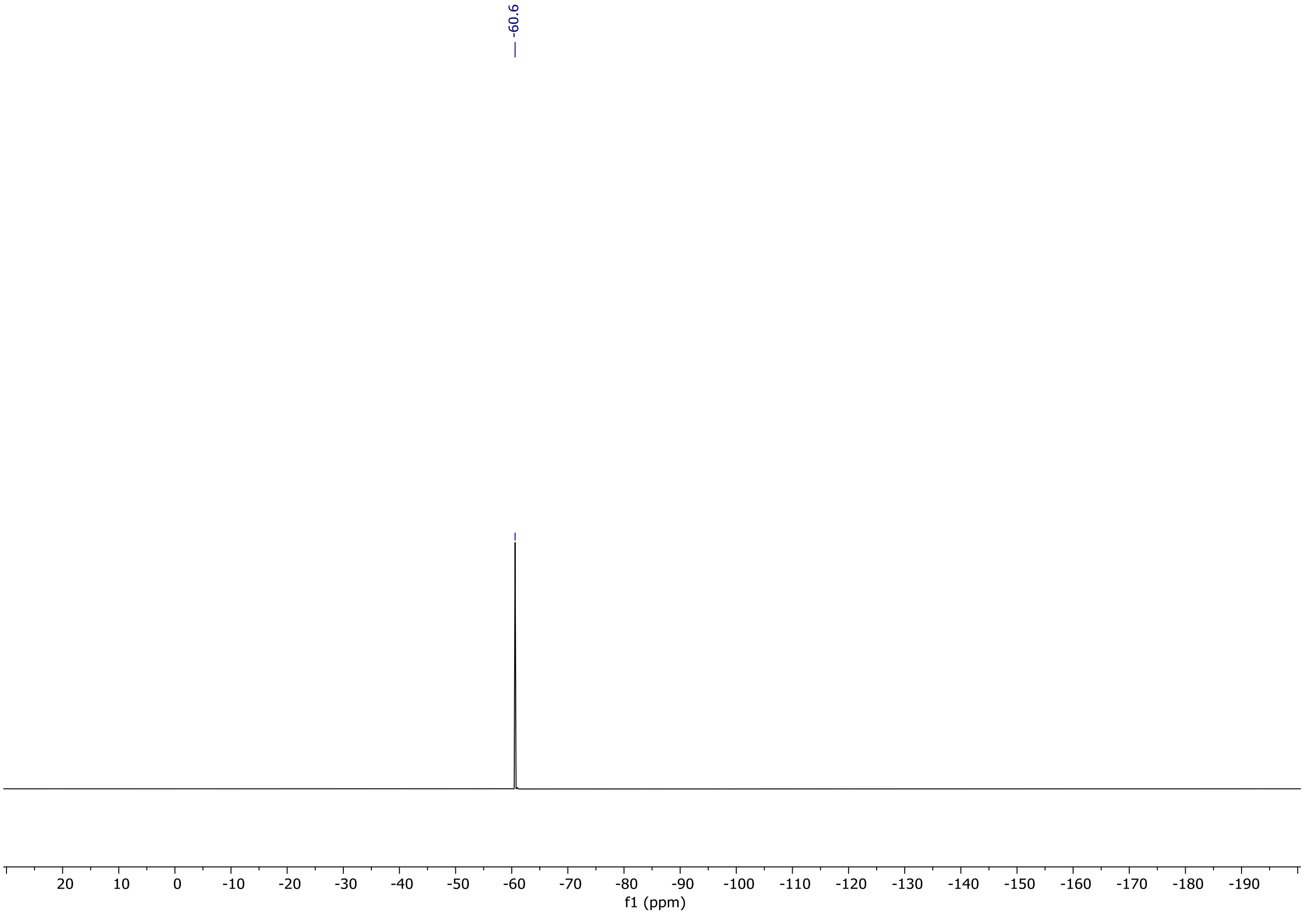
**$^1$H NMR** (500 MHz, CDCl$_3$)



**$^{13}$C NMR** (126 MHz, CDCl$_3$)

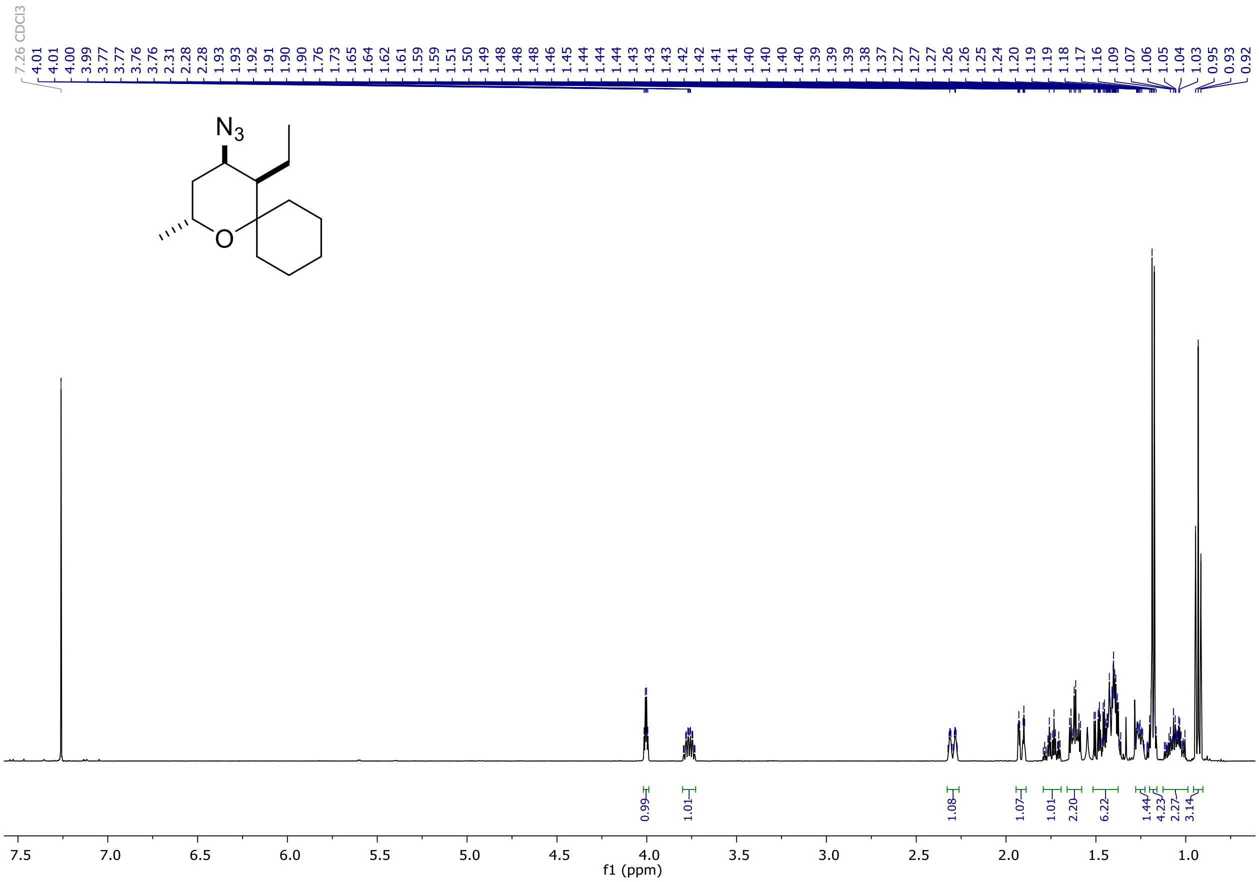


**$^{19}$F NMR** (470 MHz, CDCl$_3$)

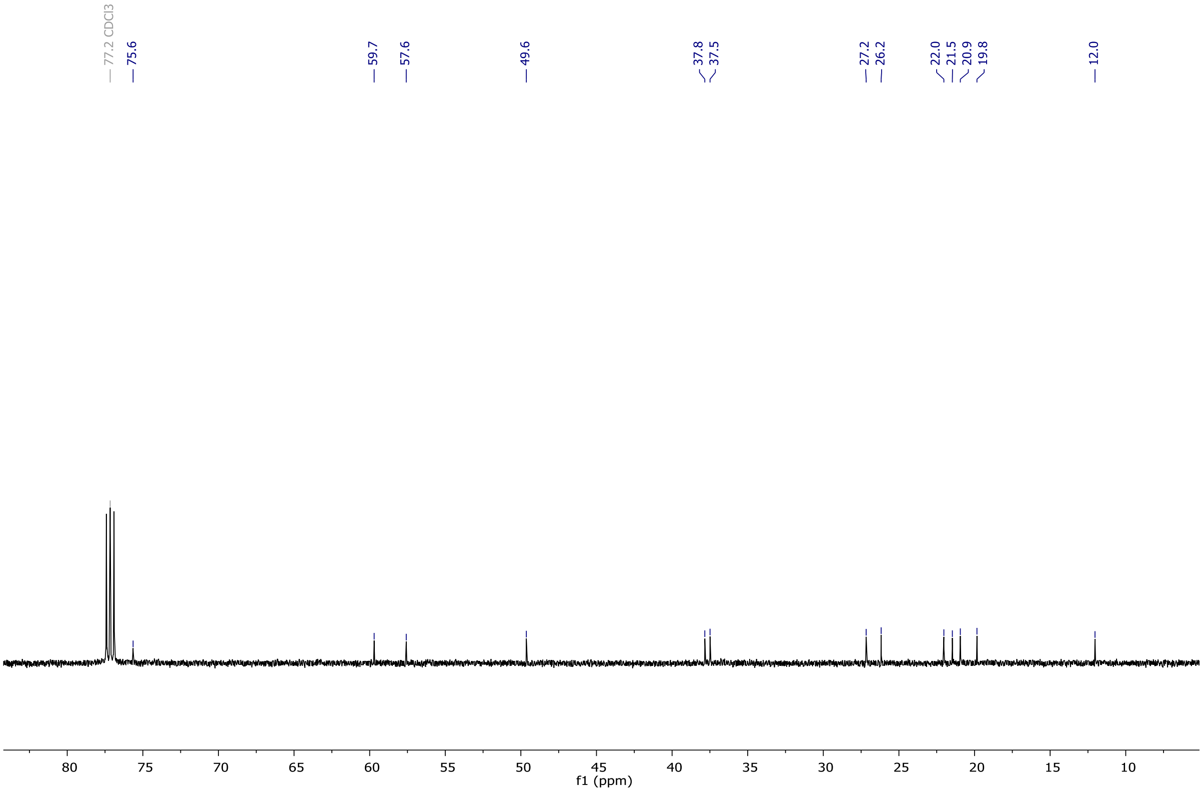


## Compound 6d

**$^1$H NMR** (500 MHz, $CDCl_3$)

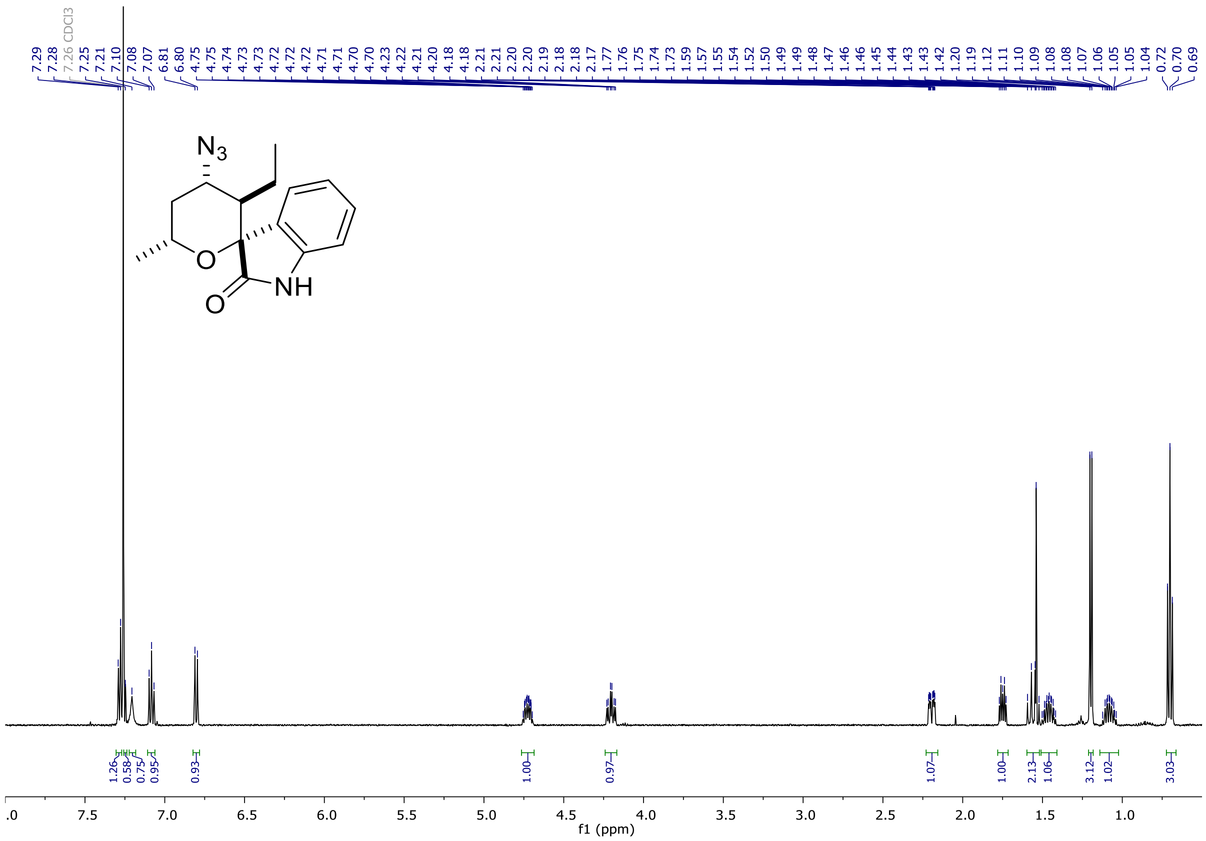


**$^{13}$C NMR** (126 MHz, $CDCl_3$)

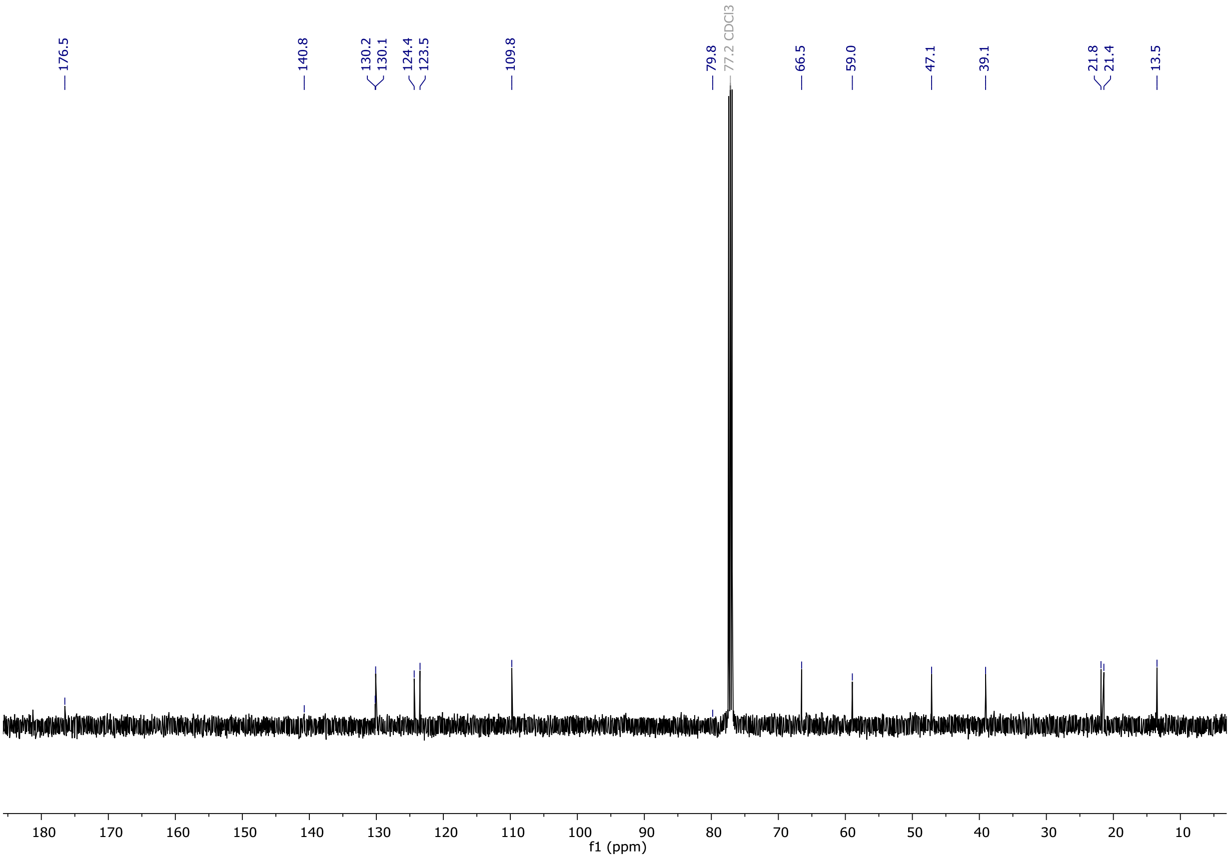


**Compound 6q**

**$^{1}$H NMR** (500 MHz, CDCl$_3$)

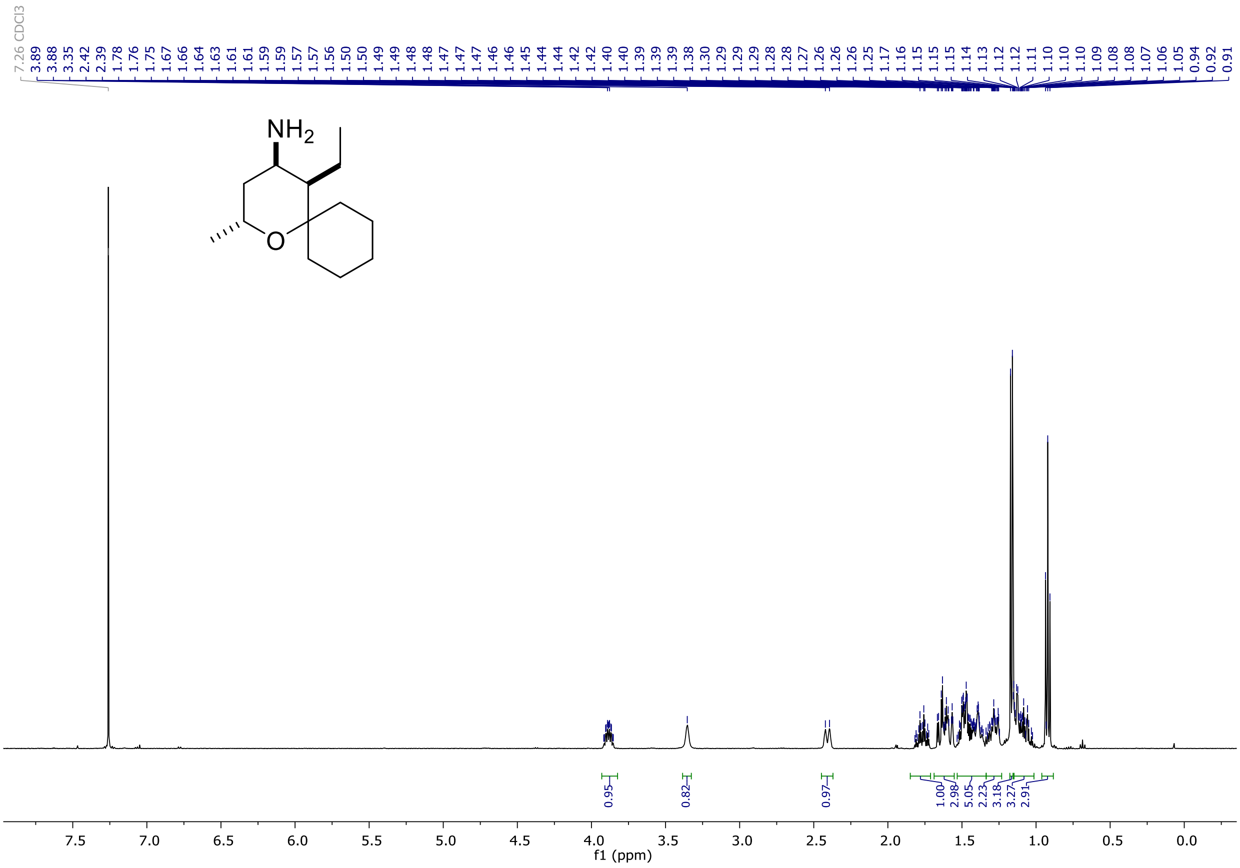


**$^{13}$C NMR** (126 MHz, CDCl$_3$)

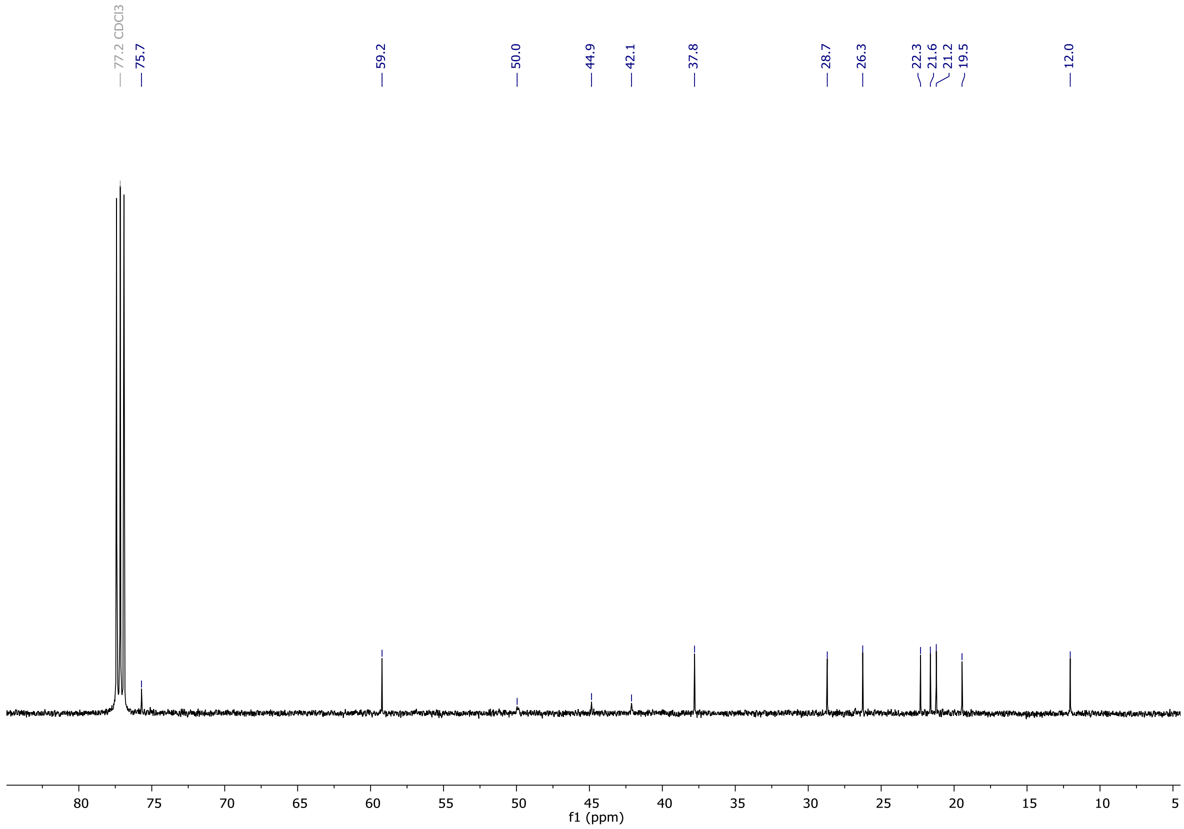


**Compound 7d**

$^1$**H NMR** (500 MHz, CDCl$_3$)

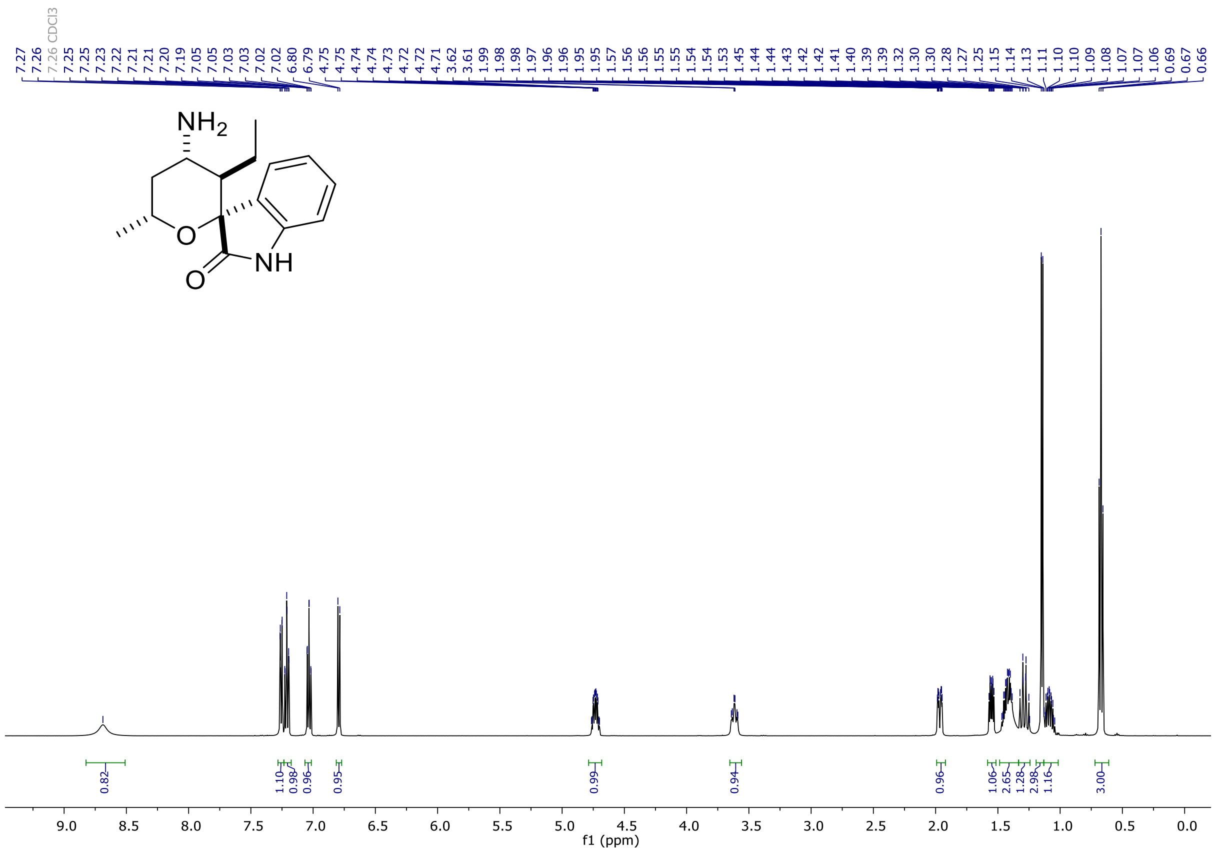


$^{13}$**C NMR** (126 MHz, CDCl$_3$)

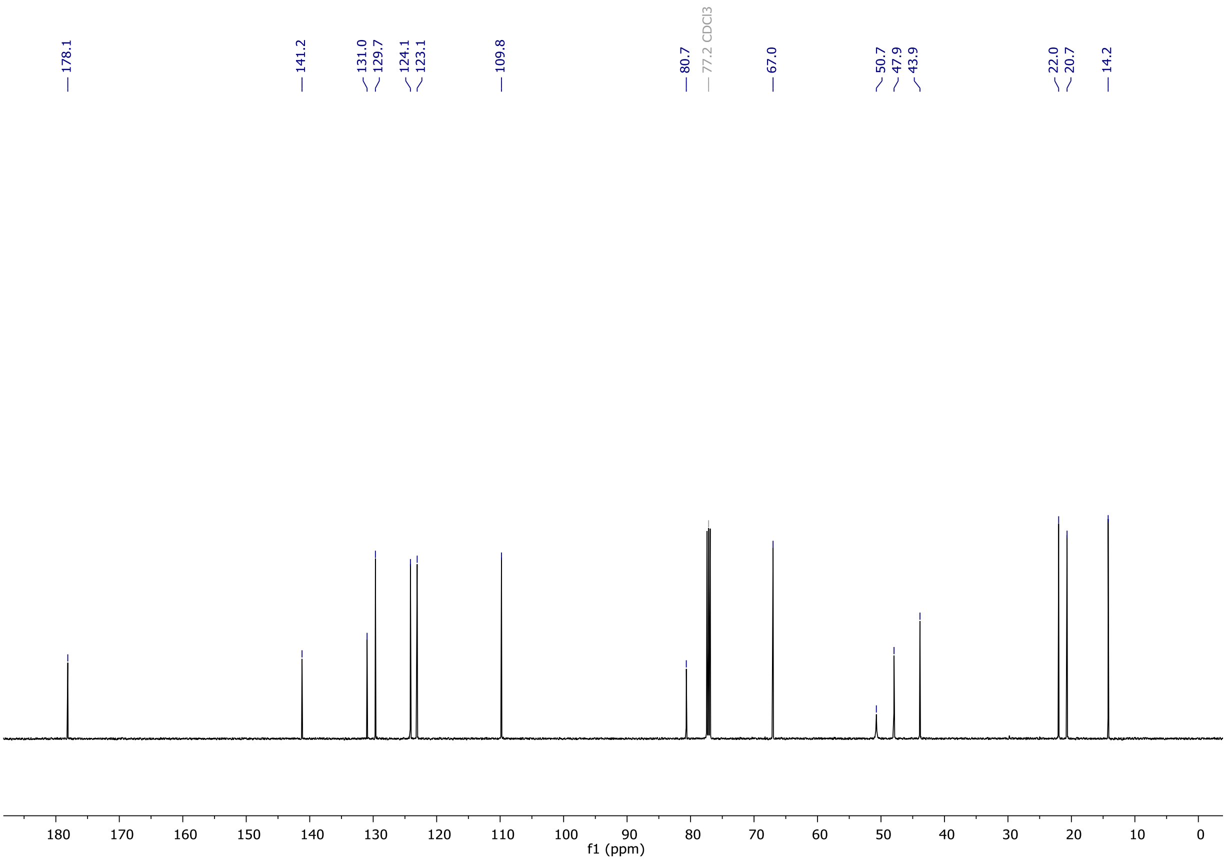


**Compound 7q**

**$^1$H NMR** (500 MHz, CDCl$_3$)

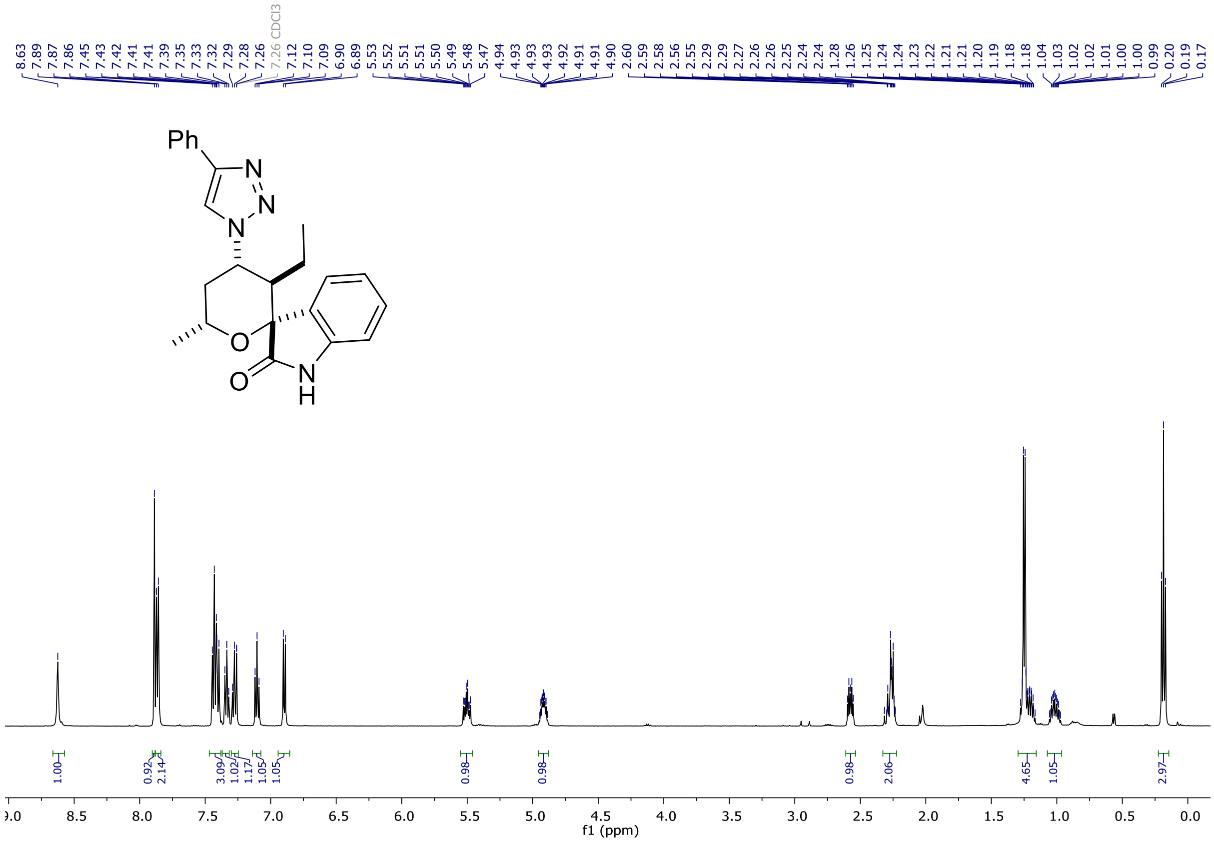


**$^{13}$C NMR** (126 MHz, CDCl$_3$)



## Compound 8

### $^1$H NMR (500 MHz, CDCl$_3$)



### $^{13}$C NMR (126 MHz, CDCl$_3$)