Supporting Information

Bismuth(III) Triflate-catalysed Tandem Cyclisations Towards Complex Polycyclic Ethers

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1 General Experimental

All reactions with air or moisture sensitive reagents were conducted in dried glassware under an atmosphere of nitrogen using anhydrous solvents. Unless otherwise stated, all reagents and catalysts were purchased with the classification *reagent-grade* and used as received from their suppliers without further purification. Solvents for flash and thin layer chromatography [petroleum ether (PE), ethyl acetate (EtOAc), diethyl ether (Et_2O), pentane (P)] were used as received without further purification. All solvents for the use in reactions were freshly distilled. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium/benzophenone ketyl, dichloromethane (CH_2Cl_2) and dimethyl-sulfoxide (DMSO) were dried by distillation over CaH_2. Methyllithium and *tert*-butyllithium were purchased as a 1.6 M solution in diethyl ether and a 1.9 M solution in pentane respectively and titrate before use. [1]

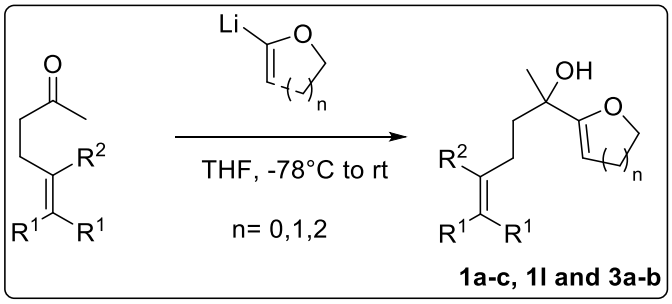
Reactions were monitored by analytical Thin Layer Chromatography (TLC), which was performed on 0.20 mm precoated silica plates (Silica gel 60, F_{254}, *Macherey-Nagel*). UV-active substances were detected by fluorescence detection with UV-light at wavelengths of 254 nm and 366 nm respectively. Detection of non UV-active substances was carried out by staining with *p*-anisaldehyde (0.7 mL *p*-anisaldehyde, 1.7 mL acetic acid and 9.5 mL conc. sulfuric acid in 250 mL ethanol), and subsequent heating. Separations via column chromatography were carried out on a Combi*Flash*®*Rf*+ (Teledyne Isco, USA), using CHROMABOND® Flash columns (Macherey-Nagel GmbH & Co. KG, Germany).
NMR spectra (^{1}H, ^{13}C, COSY, DEPT135, HSQC, HMBC, NOESY) were recorded on a *Bruker* AV-200 or AV-500 spectrometer at a temperature of 300 K. Chemical shifts (δ) are given in parts per million (ppm) and refer to the residual proton signal of the used solvent. In ^{1}H-spectra the $CDCl_3$ residual peak was applied as an internal standard with a chemical shift of 7.26 ppm. ^{13}C-spectra were calibrated according to the deuterium-coupled signals of the used solvent ($CDCl_3$ = 77.16 ppm).[1] Coupling constants ^{3}J are given in Hertz (Hz) and result from averaging of the experimentally found values. Spectral splitting patterns are designated as: s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintet), sept. (septet), m (multiplet), m_c (*centered* multiplet), br (broad), *virt.* (virtual). COSY, HSQC, HMBC, and NOESY correlations were established to identify the structures of some cyclic molecules. Infrared spectra were recorded on a Jasco FT/IR-4600 spectrometer. Samples were analyzed directly in substance with the attenuated total reflexion method (ATR). Absorption maxima are reported in wavenumbers (cm^{-1}) and characterised with the following symbols, according to their form and intensity: s (strong), m (medium), w (weak), b (broad). Analytical GC analyses were performed on a Shimadzu GC-2025 capillary gas chromatograph. Analytical GC/MS analyses were performed on a *Shimadzu* QP2010S-MS chromatograph (EI, 70 eV) equipped with a SLB-5ms capillary column (thickness: 0.25 mm, length: 30 m, inside diameter: 0.25 mm). High resolution mass spectrometry (HRMS) was performed on a mass spectrometer LTQ-Orbitrap hybrid.

2 Experimental Procedures

2.1 Synthesis of the starting materials

2.1.1 Synthesis of dihydropyranyl and dihydrofuranyl derivatives 1a, 1b, 1c, 1l, 3a and 3b.

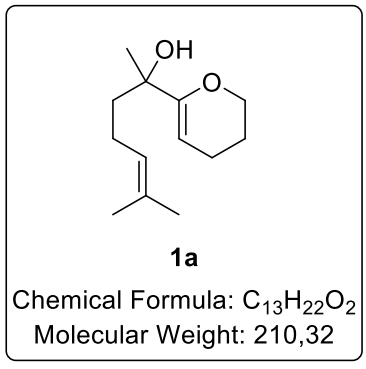
The starting dienols were generally synthesised in one step from the corresponding ketones, 2,3-dihydrofuran or 3,4-dihydro-1*H*-pyran using *tert*-butyllithium in THF at -78 °C. In the cases where the ketone was not directly available, different procedures were necessary.



General procedure 1: *tert*-BuLi mediated addition of enol ethers to aldehydes and ketones

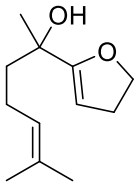
To a 2 M solution of the enol ether (1.2-1.3 eq.) in anhydrous THF, *tert*-BuLi (1.9 M in pentane, 1.0 – 1.2 eq.) was added dropwise at –78 °C. The mixture was allowed to warm to -5 °C and stirred at this temperature for 3 hours, before being recooled to –78 °C, followed by addition of the adequate ketone or aldehyde (1.0 eq.). The solution was slowly warmed to room temperature and stirred for an additional 2 – 3 hours. Then 5 mL of a saturated aqueous NH_4Cl solution were added, the forming precipitate was dissolved in water and the aqueous phase was extracted with ether (3 × 50 mL). The organic extracts were washed with brine, dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was purified via flash column chromatography on NEt_3 basified silica gel to afford the alcohols in good yields.

2-(3,4-dihydro-2H-pyran-6-yl)-6-methylhept-5-en-2-ol (1a)



Compound **1a** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (2.52 g, 30.0 mmol, 2.71 mL) and 6-methylhept-5-en-2-one (3.16 g,25.0 mmol, 3.69 mL). The crude product was purified by flash chromatography (PE + 3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (3.53 g, 16.8 mmol, 67%). **TLC**: R_f = 0.32 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 1.28 (s, 3H), 1.55 (bs, 3H), 1.68 (bs, 3H), 1.55-2.09 (m, 8H), 2.13 (bs, 1H, OH), 4.00 (t, ^3J = 5.1 Hz, 2H), 4.79 (t, ^3J = 3.8 Hz, 1H), 5.09-5.16 (m_c, 1H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 17.6, 20.0, 22.4, 23.1, 25.7, 25.8, 40.2, 66.3, 73.6, 94.1, 124.5, 131.7, 157.2. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3464 (b, OH), 2967 (m), 2927 (m), 2850 (m), 1670 (m), 1985 (s), 918 (s). **ESI-HRMS**: *m/z* calcd. for $C_{13}H_{23}O_2$ $[MH]^+$: 211.1693, found: 211.1693.

2-(4,5-dihydrofuran-2-yl)-6-methylhept-5-en-2-ol (1b)

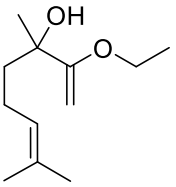


1b

Chemical Formula: $C_{12}H_{20}O_2$
Molecular Weight: 196,29

Compound **1b** was synthesised according to **general procedure 1** starting from 2,3-dihydrofuran (3.33 g, 47.5 mmol, 3.60 mL) and 6-methylhept-5-en-2-one (5.00 g, 39.6 mmol). Purification by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) afforded the title compound **1b** as a yellow oil (5.24 g, 26.7 mmol, 67%). **TLC**: R_f = 0.30 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 1.31 (s, 3H), 1.56 (s, 3H), 1.63 (s, 3H), 1.50-1.72 (m, 2H), 1.90-2.04 (m, 2H), 2.25 (s, 1H, OH), 2.60 (td, ^3J = 9.3 Hz, 2.4 Hz, 2H), 4.31 (t, ^3J = 9.3 Hz, 2H), 4.76 (t, ^3J = 2.4 Hz, 1H), 5.05-5.12 (m_c, 1H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 17.6, 22.9, 25.6, 25.9, 30.0, 40.2, 70.3, 71.4, 93.7, 124.2, 131.7, 162.3. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3402 (b, OH), 2967 (s), 2924 (s), 2857 (s), 1644 (w), 1447 (m), 1376 (m), 1175 (m). **APGC-HRMS**: *m/z* calcd. for $C_{12}H_{19}O_2$ $[M-H]^+$: 195.1385, found: 195.1378.

2-ethoxy-3,7-dimethylocta-1,6-dien-3-ol (1c)

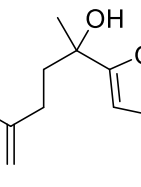


1c

Chemical Formula: $C_{12}H_{22}O_2$
Molecular Weight: 198,31

Compound **1c** was synthesised according to **general procedure 1** starting from ethyl vinyl ether (3.23 g, 44.4 mmol, 4.30 mL) and 6-methylhept-5-en-2-one (2.36 g, 18.5 mmol). Purification by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) afforded the title compound **1c** as a yellow oil (2.17 g, 10.93 mmol, 59%). **TLC**: R_f = 0.34 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 1.24-1.39 (m, 6H), 1.49-1.78 (m, 8H), 1.85-2.08 (m, 2H), 2.21 (s, 1H, OH), 3.74 (q, ^3J = 7.0 Hz, 2H), 3.95 (d, ^3J = 2.5 Hz, 1H), 4.19 (d, ^3J = 2.5 Hz, 1H), 5.01-5.22 (m_c, 1H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 14.42, 17.58, 22.89, 25.67, 26.54, 40.49, 62.99, 74.15, 79.37, 124.42, 131.69, 166.27. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3472 (b, OH), 2977 (m), 2914 (m), 1656 (w), 1615 (m), 1445 (m), 1186 (s), 1120 (s), 1060 (s), 809 (s). **ESI-HRMS**: *m/z* calcd. for $C_{12}H_{23}O_2$ $[MH]^+$: 199.1694, found: 199.1693.

2-(4,5-dihydrofuran-2-yl)-5-methylhex-5-en-2-ol (3a)

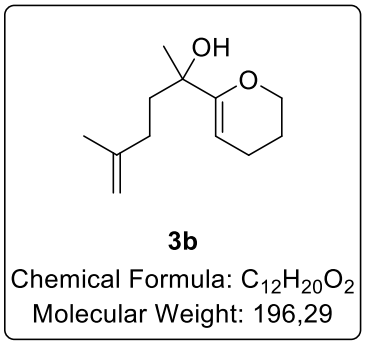


3a

Chemical Formula: $C_{11}H_{18}O_2$
Molecular Weight: 182,26

Compound **3a** was synthesised according to **general procedure 1** starting from 2,3-dihydrofuran (2.01 g, 28.7 mmol, 2.17 mL) and 5-methylhex-5-en-2-one (2.50 g, 22.1 mmol, 2.89 mL). Purification by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) afforded the title compound **3a** as a yellow oil (3.96 g, 21.7 mmol, 98%). **TLC**: R_f = 0.47 (PE/EtOAc = 9:1), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 4.78 (t, ^3J = 2.4 Hz, 1H), 4.67 (m_c, 2H), 4.33 (t, ^3J = 9.3 Hz, 2H), 2.62 (td, ^3J = 9.3, 2.5 Hz, 2H), 2.22 (s, 1H, OH), 2.07 – 1.94 (m, 2H), 1.80 – 1.66 (m, 5H), 1.34 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 162.16, 146.01, 109.70, 93.79, 71.30, 70.35, 38.25, 32.29, 29.98, 25.90, 22.59. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3452 (b, OH), 2933 (m), 2860 (m), 1650 (m), 1449 (m), 1366 (m), 1175 (m), 1082 (s), 934 (s), 883 (s). **ESI-HRMS**: *m/z* calcd. for $C_{11}H_{19}O_2$ $[MH]^+$: 183.1380, found: 183.1380.

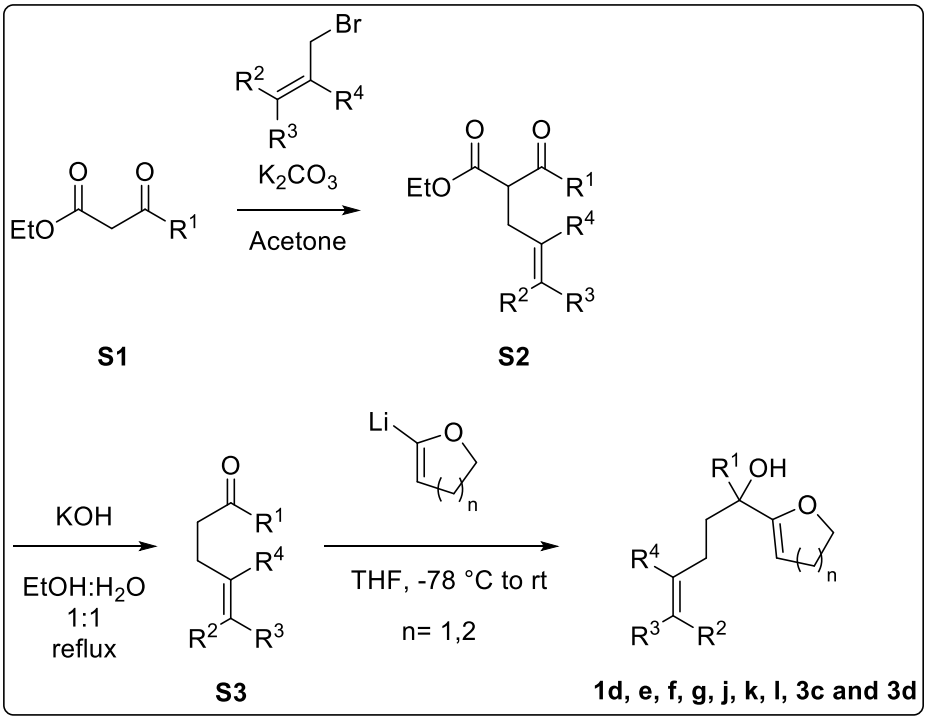
2-(3,4-dihydro-2H-pyran-6-yl)-5-methylhex-5-en-2-ol (3b)



Compound **3b** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (2.49 g, 28.7 mmol, 2.70 mL) and 5-methylhex-5-en-2-one (2.50 g, 22.1 mmol, 2.89 mL). Purification by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) afforded the title compound **3b** as a yellow oil (4.04 g, 20.6 mmol, 93%). **TLC**: R_f = 0.27 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 4.79 (t, ^3J = 3.8 Hz, 1H), 4.72 – 4.66 (m_c, 2H), 3.98 (t, ^3J = 5.0 Hz, 2H), 2.17 (s, 1H, OH), 2.12 – 1.88 (m, 4H), 1.86 – 1.63 (m, 7H), 1.29 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 157.05, 146.35, 109.57, 94.18, 73.45, 66.27, 38.27, 32.50, 25.77, 22.62, 22.34, 19.94. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3446 (b, OH), 2930 (m), 2849 (m), 1670 (m), 1447 (m), 1372 (w), 1285 (w), 1095 (s), 1067 (m), 917 (s), 883 (s). **ESI-HRMS**: *m/z* calcd. for $C_{12}H_{21}O_2$ $[MH]^+$: 197.1536, found: 197.1536.

2.1.2 Synthesis of dienols 1d, 1e, 1f, 1g, 1j, 1k, 1l, 3c and 3d

Alcohols **1d, 1e, 1f, 1g, 1j, 1k,** *(E)*-**1l,** *(Z)*-**1l, 3c** and **3**d were synthesised in three steps starting from the corresponding *β*-keto ester **S1**. Deprotonation of **S1** and subsequent alkylation afforded **S2**. Decarboxylation in the presence of potassium hydroxide afforded the ketones **S3**, which were then subjected to the conditions described in **general procedure 1**.

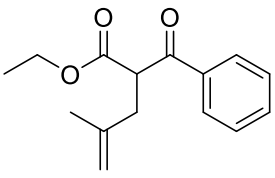


General procedure 2: Synthesis of S2 from the corresponding *β*-keto esters

To a 0.5 M solution of *β*-keto ester **S1** and potassium carbonate in acetone was added the halide derivative. The mixture was stirred at room temperature for 20 h. After completion (monitored by TLC or GC-MS) the solution was quenched with a hydrochloric acid solution 1 N. The organic layer

was extracted with diethyl ether. The organic extracts were washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure to give the desired product as a yellow oil. The residue was purified via flash column chromatography on silica gel to afford the corresponding *β*-keto esters **S2**.

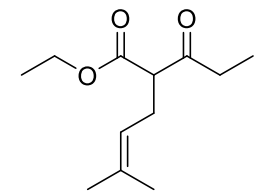
Ethyl 2-benzoyl-4-methylpent-4-enoate (S2c'-d')



S2c'-d'
Chemical Formula: $C_{15}H_{18}O_3$
Molecular Weight: 246,31

Compound **S2c'-d'** was synthesised according to **general procedure 2** starting from ethyl benzoylacetate (1.35g, 70.0 mmol, 12.22 mL) and methallyl chloride (7.24 g, 80.0 mmol, 7.89 mL). Crude product was used in the next step without further purification. The title compound was obtain as a yellow oil (6.87 g, 27.9 mmol, 40%). **TLC**: R_f = 0.76 (PE/EtOAc = 98:2), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 8.06 – 7.96 (m, 2H), 7.60 – 7.42 (m, 3H), 4.83 – 4.69 (m, 2H), 4.55 (dd, ^3J = 7.8, 6.8 Hz, 1H), 4.14 (q, ^3J = 7.1 Hz, 2H), 2.73 (m, 2H), 1.77 (s, 3H), 1.17 (t, ^3J = 7.2 Hz, 3H). **CAS number:** 118067-01-9**.** The experimental data are in accordance with those reported in the literature.[1]

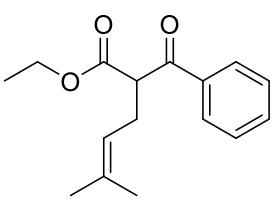
Ethyl 5-methyl-2-propionylhex-4-enoate (S2d-e)



S2d-e
Chemical Formula: $C_{12}H_{20}O_3$
Molecular Weight: 212,29

Compound **S2d-e** was synthesised according to **general procedure 2** starting from ethyl 3-oxopentanoate (7.00 g, 47.1 mmol, 6.92 mL) and prenyl bromide (7.16 g, 47.1 mmol, 5.55 mL). Crude product was used in the next step without further purification. The title compound was obtain as a yellow oil (10.0 g, 47.1 mmol, 90%). **TLC**: R_f = 0.61 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.00 (m_c, 1H), 4.16 (q, ^3J = 7.1 Hz, 2H), 3.50 – 3.37 (m_c, 1H), 2.62 – 2.41 (m, 4H), 1.69 – 1.58 (m, 6H), 1.24 (t, ^3J = 7.1 Hz, 2H), 1.04 (t, ^3J = 7.2 Hz, 2H).**^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 205.79, 169.68, 134.60, 119.89, 61.18 , 58.77, 35.42, 27.03, 25.69, 17.70, 14.06, 7.57. **CAS number**: 105519-89-9. The experimental data are in accordance with those reported in the literature.[1]

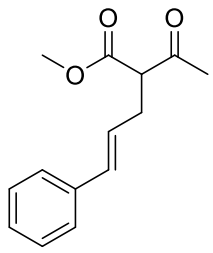
Ethyl 2-benzoyl-5-methylhex-4-enoate (S2f-g)



S2f-g
Chemical Formula: $C_{16}H_{20}O_3$
Molecular Weight: 260,33

Compound **S2f-g** was synthesised according to **general procedure 2** starting from ethyl benzoylacetate (12.50 g, 58.5 mmol, 11.26 mL) and prenyl bromide (9.69 g, 58.5 mmol, 7.51 mL). Crude product was used in the next step without further purification. The title compound was obtain as a yellow oil (10.0 g, 47.1 mmol, 90%). **TLC**: R_f = 0.53 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.98 (m, 2H), 7.50 (m, 3H), 5.15-5.06 (m, 1H), 4.29 (t, ^3J = 7.3 Hz, 1H), 4.13 (q, ^3J = 7.1 Hz, 2H), 2.64-2.73 (m, 2H), 1.64 (s, 3H), 1.62 (s, 3H), 1.16 (t, ^3J = 7.1 Hz, 3H). **CAS number**: 4535-59-5. The experimental data are in accordance with those reported in the literature.[1]

Methyl (*E*)-2-acetyl-5-phenylpent-4-enoate (S2j-k)

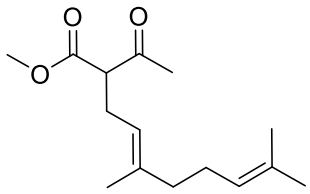


S2j-k

Chemical Formula: $C_{14}H_{16}O_3$
Molecular Weight: 232,28

Compound **S2j-k** was synthesised according to slightly modified **general procedure 2**. Methyl acetoacetate (2.32 g, 20.0 mmol, 2.15 mL) was added dropwise to a 0 °C suspension of NaH (0.96 g, 24.0 mmol, 1.2 eq.) in 35 mL THF. After 15 minutes a solution of cinnamyl bromide (3.94 g, 20.0 mmol, 2.96 mL, 1.0 eq.) in 35 mL THF was added carefully at 0 °C. The ice bath was removed and the mixture was stirred overnight (17 h) at room temperature until TLC showed full conversion of the starting material. The reaction was quenched with H_2O, and the aqueous phase was extracted with EtOAc (3 × 40°mL).The organic extracts were washed with water and brine, dried over $MgSO_4$ and the solvent was evaporated under reduced pressure to afford the crude product as a 2:1 mixture of the title compound **S2j-k** and the double alkylated product. Purification by flash chromatography afforded the mono alkylated compound (1.89 g, 8.12 mmol, 41%).**TLC**: R_f = 0.45 (PE/EtOAc = 9:1), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 2.26 (s,3H), 2.76 (ddd, ^3J = 7.3 Hz, 1.2 Hz, 2H), 3.61 (t, ^3J = 7.4 Hz, 1H), 3.75 (s, 3H), 6.11 (dt, ^3J = 15.8 Hz, 7.1 Hz, 1H), 6.46 (br d, ^3J = 15.8 Hz, 1H), 7.19-7.36 (m, 5H).**CAS number**: 85217-77-2. The experimental data are in accordance with those reported in the literature.[1]

Methyl (E)-2-acetyl-5,9-dimethyldeca-4,8-dienoate (*(E)*-S2l)

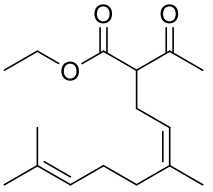


***(E)*-S2l**

Chemical Formula: $C_{15}H_{24}O_3$
Molecular Weight: 252,35

Compound *(E)*-**S2l** was synthesised according to **general procedure 2** starting from methyl acetoacetate (1.0 g, 3.97 mmol, 0.98 mL) and geranyl bromide (862 mg, 3.97 mmol, 0.78 mL).). Purification by flash chromatography afforded the title compound as a yellow oil (652 g, 2.58 mmol, 65%). **TLC**: R_f = 0.62 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.09 – 4.95 (m, 2H), 3.72 (s, 3H), 3.46 (t, ^3J = 7.5 Hz, 1H), 2.55 (t, ^3J = 7.6 Hz, 2H), 2.22 (s, 3H), 2.11 – 1.86 (m, 4H), 1.70 – 1.55 (m, 9H). **CAS number**: 51933-45-0. The experimental data are in accordance with those reported in the literature.[1]

Ethyl (Z)-2-acetyl-5,9-dimethyldeca-4,8-dienoate (*(Z)*-S2l)



(Z)-**S2l**

Chemical Formula: $C_{16}H_{26}O_3$
Molecular Weight: 266,38

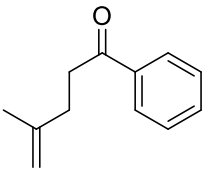
Compound *(Z)*-**S2l** was synthesised according to **general procedure 2** starting from ethyl acetoacetate (900 mg, 6.8 mmol, 0.88 mL) and freshly prepared neryl bromide (1.21 g, 5.5 mmol, 0.94 mL) from nerol (To a solution of nerol in THF was added PBr_3 at 0 °C. The solution was stirred at 0 °C for 15 min, and was then diluted with ether/water and washed with saturated $NaHCO_3$, water and brine and dried over Na_2SO_4. The solvent was removed *in vacuo* and neryl bromide was obtined as a brown oil which was used in the next step without further purification). Purification by flash chromatography afforded the title compound as a yellow oil (691 mg, 2.59 mmol, 47%). **TLC**: R_f = 0.62 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **CAS**

number: 72444-96-3.

General procedure 3: Synthesis of ketones S3 from decarboxylation of S2

To a solution of potassium hydroxide in Ethanol:Water (1:1) stirred at room temperature was added **S2**. The mixture was stirred at reflux (100°C) for 3h. After completion (monitored by TLC) the mixture was cooled to room temperature and extracted with diethyl ether. The organic extracts were washed with water and brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified via flash column chromatography on silica gel to afford the corresponding ketones **S3**.

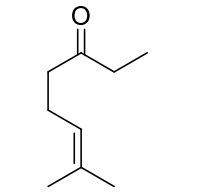
4-methyl-1-phenylpent-4-en-1-one (S3c'-d')



S3c'-d'
Chemical Formula: $C_{12}H_{14}O$
Molecular Weight: 174,24

Compound **S3c'-d'** was synthesised according to **general procedure 3** starting from **S2c'-d'** (6.0 g, 24.4 mmol) and KOH (1.7 g, 30.4 mmol). The crude product was engaged in the next step without further purification. The title compound was obtain as a yellow oil (3.8 g, 21.9 mmol, 90%). **TLC**: R_f = 0.79 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 8.02 – 7.90 (m, 2H), 7.63 – 7.40 (m, 3H), 4.80 – 4.67 (m, 2H), 3.18 – 3.05 (m, 2H), 2.51 – 2.39 (m, 2H), 1.79 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 199.86, 144.83, 133.13, 128.73, 128.44, 128.17, 110.33, 36.98, 32.03, 22.91. **CAS number**: 1078-36-0. The experimental data are in accordance with those reported in the literature.[1]

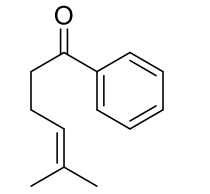
7-methyloct-6-en-3-one (S3d-e)



S3d-e
Chemical Formula: $C_9H_{16}O$
Molecular Weight: 140,23

Compound **S3d-e** was synthesised according to **general procedure 3** starting from **S2d-e** (10.0 g, 47.1 mmol) and KOH (3.3 g, 58.9 mmol). The crude product was engaged in the next step without further purification. The title compound was obtain as a yellow oil (6.1 g, 43.4 mmol, 92%). **TLC**: R_f = 0.78 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.11 – 4.96 (m, 1H), 2.47 – 2.33 (m, 4H), 2.25 (t, ^3J = 7.4 Hz, 2H), 1.65 (s, 3H), 1.60 (s, 3H), 1.03 (t, ^3J = 7.3 Hz, 3H). **CAS number**: 762-47-0. The experimental data are in accordance with those reported in the literature.[1]

5-methyl-1-phenylhex-4-en-1-one (S3f-g)

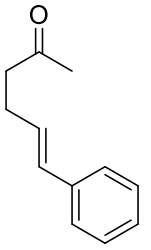


S3f-g
Chemical Formula: $C_{13}H_{16}O$
Molecular Weight: 188,27

Compound **S3f-g** was synthesised according to **general procedure 3** starting from **S2f-g** (15.0 g, 57.6 mmol) and KOH (4.0 g, 72.0 mmol). The crude product was engaged in the next step without further purification. The title compound was obtain as a yellow oil (10.0 g, 53.3 mmol, 93%). **TLC**: R_f = 0.76 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.99 – 7.94 (m, 2H), 7.56 – 7.41 (m, 3H), 5.21 – 5.13 (m, 1H), 3.00 (dd, ^3J = 8.0, 6.8 Hz, 2H), 2.42 (q, ^3J = 7.4 Hz, 2H), 1.74 – 1.51 (m, 6H). **^{13}C-NMR**

(50 MHz, $CDCl_3$): δ [ppm] = 200.20, 137.17, 133.03, 128.68, 128.44, 128.18, 123.07, 38.90, 25.84, 23.07, 17.83. **CAS number**: 4535-64-2. The experimental data are in accordance with those reported in the literature.[1]

(*E*)-6-phenylhex-5-en-2-one (S3j-k)

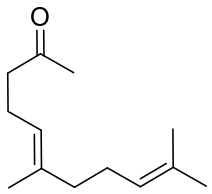


S3j-k

Chemical Formula: $C_{12}H_{14}O$
Molecular Weight: 174,24

Compound **S3j-k** was synthesised according to **general procedure 3** starting from **S2j-k** (1.87 g, 8.06 mmol) and KOH (0.57 g, 10.1 mmol). The residue was purified by flash chromatography on silica (PE/EtOAc = 95/5) to give compound **S3j-k** as a pale yellow oil (1.28 g, 7.36 mmol, 91%). **TLC**: R_f = 0.40 (PE/EtOAc = 9:1), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] =2.06 (s, 3H), 2.32-2.43 (m, 2H), 2.47-2.55 (m, 2H), 6.10 (dt, ^3J = 15.8 Hz, 6.4 Hz, 1H), 6.31 (d, ^3J = 15.8 Hz, 1H), 7.06-7.27 (m, 5H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 27.14, 30.1, 43.2, 126.1, 127.1, 128.6, 128.9, 130.8, 137.4, 208.03. **CAS number**: 33599-88-1. The experimental data are in accordance with those reported in the literature.[1]

(E)-6,10-dimethylundeca-5,9-dien-2-one (*(E)*-S3l)

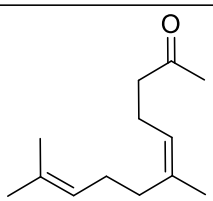


(E)-**S3l**

Chemical Formula: $C_{13}H_{22}O$
Molecular Weight: 194,32

Compound *(E)*-**S3l** was synthesised according to **general procedure 3** starting from *(E)*-**S2l** (1.00 g, 3.96 mmol) and KOH (278 mg, 4.95 mmol). The residue was purified by flash chromatography on silica (PE/EtOAc = 95/5) to give compound *(E)*-**S3l** as a pale yellow oil (703 mg, 3.61 mmol, 91%). **TLC**: R_f = 0.76 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.10 – 5.04 (m, 2H), 2.45 (t, ^3J = 7.4 Hz, 2H), 2.30 – 2.22 (m, 2H), 2.13 (s, 3H), 2.09 – 2.02 (m, 2H), 1.99 – 1.93 (m, 2H), 1.68 – 1.66 (m, 3H), 1.61 – 1.60 (m, 3H), 1.60 – 1.59 (m, 3H). **^{13}C-NMR** 125 MHz, $CDCl_3$): δ [ppm] = 209.02 , 136.52 , 131.55 , 124.32 , 122.66 , 43.91 , 39.78 , 30.09 , 26.76 , 25.83 , 22.62 , 17.82 , 16.12 . **CAS number**: 3796-70-1. The experimental data are in accordance with those reported in the literature.[1]

(Z)-6,10-dimethylundeca-5,9-dien-2-one (*(Z)*-S3l)

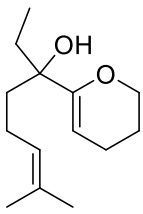


(Z)-**S3l**

Chemical Formula: $C_{13}H_{22}O$
Molecular Weight: 194,32

Compound *(Z)*-**S3l** was synthesised according to **general procedure 3** starting from *(Z)*-**S2l** (690 mg, 2.59 mmol) and KOH (182 mg, 3.24 mmol). The residue was purified by flash chromatography on silica (PE/EtOAc = 95/5) to give compound *(Z)*-**S3l** as a pale yellow oil (467 mg, 2.40 mmol, 93%). **TLC**: R_f = 0.79 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.16 – 4.98 (m, 2H), 2.51 – 2.38 (m, 2H), 2.32 – 2.17 (m, 2H), 2.13 (s, 3H), 2.07 – 1.91 (m, 4H), 1.71 – 1.65 (m, 6H), 1.60 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 208.95, 136.63, 131.82, 124.29, 123.45, 44.15, 32.01, 30.07, 26.64, 25.86, 23.50, 22.41, 17.79. **CAS number**: 3879-26-3. The experimental data are in accordance with those reported in the literature.[1]

3-(3,4-dihydro-2H-pyran-6-yl)-7-methyloct-6-en-3-ol (1d)

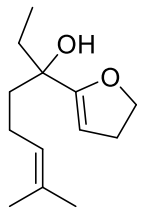


1d

Chemical Formula: $C_{14}H_{24}O_2$
Molecular Weight: 224,34

Compound **1d** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (2.29 g, 26.4 mmol, 2.49 mL) and **S3d-e** (3.00 g, 20.3 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (2.42 g, 10.8 mmol, 53%). **TLC**: R_f = 0.72 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.24 – 5.06 (m, 1H), 4.79 (t, ^3J = 3.7 Hz, 1H), 4.02 – 3.88 (m, 2H), 2.13 – 1.93 (m, 4H), 1.85 – 1.38 (m, 12H), 0.82 (t, ^3J = 7.4 Hz, 2H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 155.58, 131.68, 124.74, 95.25, 76.22, 66.14, 38.46, 31.69, 25.71, 22.58, 22.47, 20.07, 17.63, 7.74. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3417 (b, OH), 2966 (m), 2929 (m), 2882 (w), 1715 (m), 1667 (w), 1450 (m), 1376 (m), 1059 (s). **ESI-HRMS**: *m/z* calcd. for $C_{14}H_{25}O_2$ $[MH]^+$: 225.1848, found: 225.1849.

3-(4,5-dihydrofuran-2-yl)-7-methyloct-6-en-3-ol (1e)

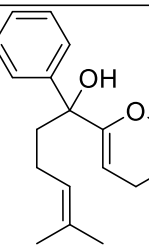


1e

Chemical Formula: $C_{13}H_{22}O_2$
Molecular Weight: 210,32

Compound **1e** was synthesised according to **general procedure 1** starting from 2,3-dihydrofuran (1.85 g, 26.4 mmol, 2.00 mL) and **S3d-e** (3.00 g, 20.3 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (3.22 g, 15.3 mmol, 75%). **TLC**: R_f = 0.64 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.20 – 5.09 (m, 1H), 4.81 (t, ^3J = 2.4 Hz, 1H), 4.34 (t, ^3J = 9.3 Hz, 2H), 2.64 (td, ^3J = 9.3, 2.4 Hz, 2H), 2.12 – 1.90 (m, 3H), 1.77 – 1.47 (m, 10H), 0.86 (t, ^3J = 7.4 Hz, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 161.21, 132.07, 124.60, 95.18, 74.79, 70.53, 38.49, 31.82, 30.17, 25.88, 22.70, 17.82, 7.95. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3487 (b, OH), 2966 (m), 2924 (m), 2858 (m), 2355 (w), 1659 (m), 1453 (m), 1375 (m), 1160 (m), 1094 (m), 1001 (m), 936 (s). **ESI-HRMS**: *m/z* calcd. for $C_{13}H_{23}O_2$ $[MH]^+$: 211.1693, found: 211.1693.

1-(3,4-dihydro-2H-pyran-6-yl)-5-methyl-1-phenylhex-4-en-1-ol (1f)

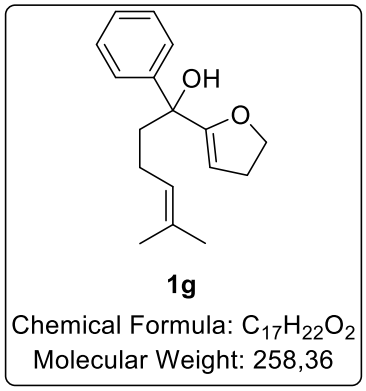


1f

Chemical Formula: $C_{18}H_{24}O_2$
Molecular Weight: 272,39

Compound **1f** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (2.03 g, 23.4 mmol, 2.20 mL) and **S3f-g** (3.50 g, 18.0 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (2.60 g, 9.54 mmol, 53%). **TLC**: R_f = 0.56 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.55 – 7.46 (m, 2H), 7.38 – 7.21 (m, 3H), 5.16 – 5.05 (m_c, 1H), 4.95 (t, ^3J = 3.8 Hz, 1H), 3.96 (t, ^3J = 5.1 Hz, 2H), 2.74 (s, 1H, OH), 2.19 – 1.72 (m, 8H), 1.65 (s, 3H), 1.53 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 156.31, 145.06, 131.83, 127.83, 126.75, 125.55, 124.39, 96.33, 77.37, 66.45, 39.24, 25.68, 22.43, 22.22, 20.06, 17.58. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3568 (b, OH), 2967 (m), 2926 (m), 2850 (m), 1668 (m), 1446 (m), 1062 (s), 916 (s), 764 (m), 700 (s). **ESI-HRMS**: *m/z* calcd. for $C_{18}H_{25}O_2$ $[MH]^+$: 273.1848, found: 273.1849.

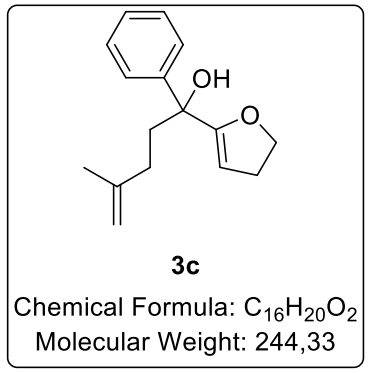
1-(4,5-dihydrofuran-2-yl)-5-methyl-1-phenylhex-4-en-1-ol (1g)



1g
Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

Compound **1g** was synthesised according to **general procedure 1** starting from 2,3-dihydrofuran (2.03 g, 23.4 mmol, 2.20 mL) and **S3f-g** (3.50 g, 18.0 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (2.60 g, 9.54 mmol, 53%). **TLC**: R_f = 0.56 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.65 – 7.41 (m, 2H), 7.42 – 7.08 (m, 3H), 5.19 – 5.07 (m, 1H), 4.93 (t, ^3J = 2.5 Hz, 1H), 4.34 (t, ^3J = 9.3 Hz, 2H), 2.67 (td, ^3J = 9.5, 2.7 Hz, 2H), 2.59 (s, 1H), 2.19 – 1.81 (m, 4H), 1.65 (s, 3H), 1.53 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 161.39, 144.19, 132.25, 128.13, 127.21, 125.51, 124.26, 95.72, 75.41, 70.58, 40.20, 30.19, 25.83, 22.51, 17.76. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3481 (b, OH), 2965 (m), 2921 (m), 2858 (m), 1655 (w), 1446 (m), 1067 (m), 1005 (m), 935 (s), 760 (m), 701 (s). **ESI-HRMS**: *m/z* calcd. for $C_{17}H_{23}O_2$ $[MH]^+$: 259.1693, found: 259.1693.

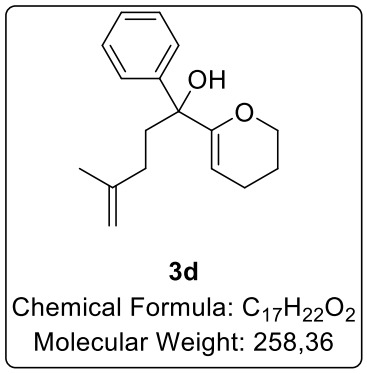
1-(4,5-dihydrofuran-2-yl)-4-methyl-1-phenylpent-4-en-1-ol (3c)



3c
Chemical Formula: $C_{16}H_{20}O_2$
Molecular Weight: 244,33

Compound **3c** was synthesised according to **general procedure 1** starting from 2,3-dihydrofuran (1.05 g, 14.9 mmol, 1.13 mL) and **S3c'-d'** (2.00 g, 11.5 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (1.93 g, 7.9 mmol, 69%). **TLC**: R_f = 0.44 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.56 – 7.46 (m, 2H), 7.41 – 7.25 (m, 3H), 4.94 (t, ^3J = 2.5 Hz, 1H), 4.71 – 4.63 (m, 2H), 4.44 – 4.28 (m, 2H), 2.69 (td, ^3J = 9.4, 2.5 Hz, 2H), 2.59 (s, 1H), 2.27 – 2.01 (m, 3H), 1.99 – 1.79 (m, 1H), 1.70 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 161.20, 146.22, 144.09, 128.19, 127.28, 125.49, 109.76, 95.83, 75.22, 70.58, 38.35, 31.74, 30.20, 22.87. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3484 (b, OH), 2961 (m), 2631 (m), 2360 (m), 1649 (m), 1446 (m), 1006 (m), 935 (s), 884 (m), 700 (s). **ESI-HRMS**: *m/z* calcd. for $C_{16}H_{21}O_2$ $[MH]^+$: 245.1536, found: 245.1536.

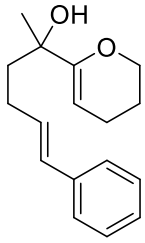
1-(3,4-dihydro-2H-pyran-6-yl)-4-methyl-1-phenylpent-4-en-1-ol (3d)



3d
Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

Compound **3d** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (1.25 g, 14.5 mmol, 1.36 mL) and **S3c'-d'** (1.80 g, 10.3 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (1.86 g, 7.2 mmol, 70%). **TLC**: R_f = 0.47 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.56 – 7.47 (m, 2H), 7.40 – 7.23 (m, 3H), 4.95 (t, ^3J = 3.8 Hz, 1H), 4.72 – 4.61 (m, 2H), 4.05 – 3.89 (m_c, 2H), 2.78 (s, 1H), 2.23 – 1.75 (m, 8H), 1.70 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 156.30, 146.50, 145.14, 128.04, 126.98, 125.71, 109.56, 96.63, 77.38, 66.64, 37.56, 31.84, 22.91, 22.35, 20.19. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3564 (b, OH), 2931 (m), 2848 (w), 2358 (w), 1668 (m), 1446 (m), 1286 (m), 1233 (m), 1063 (s), 916 (m), 883 (m), 765 (m), 700 (s). **ESI-HRMS**: *m/z* calcd. for $C_{17}H_{23}O_2$ $[MH]^+$: 259.1693, found: 259.1693.

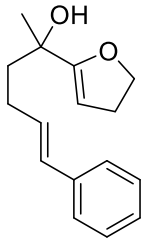
(*E*)-2-(3,4-dihydro-2*H*-pyran-6-yl)-6-phenylhex-5-en-2-ol (1j)



1j
Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

Compound **1j** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (348 mg, 4.13 mmol, 0.37 mL, 1.2 eq.) and ketone **S3j-k** (600 mg, 3.44 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (783 mg, 3.03 mmol, 73%). TLC: R_f = 0.27 (PE/EtOAc = 9/1), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 1.26 (s, 3H), 1.64-1.81 (m, 4H), 1.98 (s, 1H), 1.95-2.20 (m, 4H), 3.94 (t, ^3J = 4.4 Hz, 2H), 4.75 (t, ^3J = 3.8 Hz, 1H), 6.16 (dt, ^3J = 15.8 Hz, 6.4 Hz, 1H), 6.33 (d, ^3J = 15.8 Hz, 1H), 7.07-7.29 (m, 5H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 20.1, 22.5, 26.0, 28.2, 40.0, 66.5, 73.5, 94.4, 126.0, 126.9, 128.6, 129.8, 131.1, 138.0, 157.2. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3443 (b, OH), 2928 (m), 2847 (m), 1670 (m), 1446 (m), 1285 (m), 1085 (s), 1067 (s), 962 (s), 917 (s), 741 (s), 691 (s). **ESI-HRMS**: *m/z* calcd. for $C_{17}H_{23}O_2$ $[MH]^+$: 259.1693, found: 259.1693.

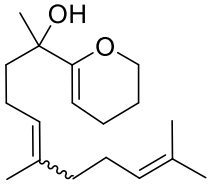
(*E*)-2-(4,5-dihydrofuran-2-yl)-6-phenylhex-5-en-2-ol (1k)



1k
Chemical Formula: $C_{16}H_{20}O_2$
Molecular Weight: 244,33

Compound **1k** was synthesized according to **general procedure 1** starting from 2,3-dihydrofuran (290 mg, 4.13 mmol, 0.31 mL, 1.2 eq.) and ketone **S3j-k** (600 mg, 3.44 mmol). Purification by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) afforded the title compound **1k** as a yellow oil (742 mg, 3.04 mmol, 74%). **TLC**: R_f = 0.26 (PE/EtOAc = 9/1), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 1.32 (s, 3H), 1.69-1.78 (m, 2H), 1.97 (s, 1H), 2.12-2.24 (m, 2H), 2.58 (td, ^3J = 9.4 Hz, 2.5 Hz, 2H), 4.30 (t, ^3J = 9.3 Hz, 2H), 4.76 (t, ^3J = 2.4 Hz, 1H), 6.16 (dt, ^3J = 15.8 Hz, 6.4 Hz, 1H), 6.34 (d, ^3J = 15.8 Hz, 1H), 7.07-7.29 (m, 5H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 26.2, 28.0, 30.2, 40.0, 70.6, 71.4, 94.1, 126.0, 127.0, 128.6, 130.0, 130.8, 137.9, 162.2. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3453 (b, OH), 2926 (m), 2858 (w), 1659 (w), 1447 (w), 1364 (w), 1175 (w), 1072 (m), 961 (s), 934 (s), 739 (s), 691 (s). **ESI-HRMS**: *m/z* calcd. for $C_{16}H_{21}O_2$ $[MH]^+$: 245.1536, found: 245.1536.

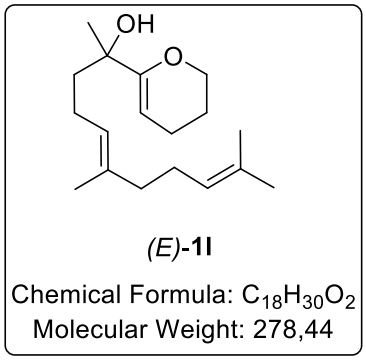
2-(3,4-dihydro-2H-pyran-6-yl)-6,10-dimethylundeca-5,9-dien-2-ol (1l)



1l
Chemical Formula: $C_{18}H_{30}O_2$
Molecular Weight: 278,44

Compound **1l** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (2.01 g, 23.2 mmol, 2.18 mL) and geranyl acetone (3.5 g, 17.8 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (3.35 g, 12.0 mmol, 68%). **TLC**: R_f = 0.30 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.21 – 5.00 (m, 2H), 4.79 (td, ^3J = 3.8, 1.2 Hz, 1H), 4.06 – 3.89 (m, 2H), 2.21 – 1.88 (m, 9H), 1.86 – 1.53 (m, 13H), 1.28 (s, 3H).

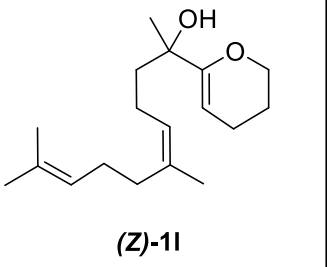
(E)-2-(3,4-dihydro-2H-pyran-6-yl)-6,10-dimethylundeca-5,9-dien-2-ol (*(E)*-1l)



(E)-**1l**
Chemical Formula: $C_{18}H_{30}O_2$
Molecular Weight: 278,44

Compound *(E)*-**1l** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (402 mg, 4.64 mmol, 0.44 mL) and *(E)*-**S3l** (700 mg, 3.57 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (804 mg, 2.89 mmol, 81%). **TLC**: R_f = 0.31 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.21 – 5.01 (m, 2H), 4.79 (t, ^3J = 3.8 Hz, 1H), 3.99 (dd, ^3J = 5.7, 4.5 Hz, 2H), 2.15 (s, 1H), 2.10 – 1.91 (m, 8H), 1.86 – 1.74 (m, 2H), 1.72 – 1.54 (m, 11H), 1.28 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 157.40, 135.46, 131.54, 124.55, 124.43, 94.27, 73.80, 66.42, 40.36, 39.87, 26.82, 25.95, 25.85, 23.22, 22.55, 20.16, 17.83, 16.10. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3456 (b, OH), 2968 (m), 2927 (m), 2851 (m), 1670 (m), 1447 (m), 1375 (m), 1285 (m) 1086 (s), 1066 (s), 919 (s).

***(Z)*-2-(3,4-dihydro-2H-pyran-6-yl)-6,10-dimethylundeca-5,9-dien-2-ol (*(Z)*-1l)**

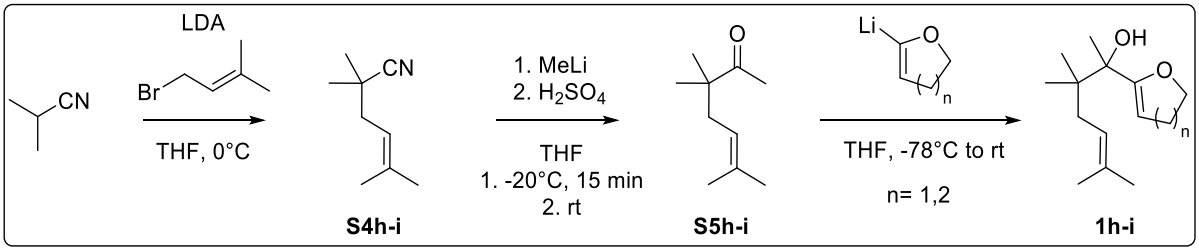


***(Z)*-1l**
Chemical Formula: $C_{18}H_{30}O_2$
Molecular Weight: 278,44

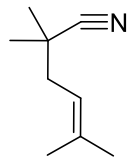
Compound *(Z)*-**1l** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (268 mg, 3.09 mmol, 0.29 mL) and *(Z)*-**S3l** (467 mg, 2.38 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (623 mg, 2.24 mmol, 94%). **TLC**: R_f = 0.31 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.22 – 5.06 (m, 2H), 4.79 (t, ^3J = 3.8 Hz, 1H), 3.99 (dd, ^3J = 5.6, 4.6 Hz, 2H), 2.16 – 1.89 (m, 9H), 1.86 – 1.75 (m, 2H), 1.73 – 1.56 (m, 11H), 1.28 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 157.34, 135.54, 131.65, 125.33, 124.51, 94.29, 73.71, 66.42, 40.73, 32.07, 26.76, 25.87, 23.57, 23.06, 22.53, 20.15, 17.79. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3439 (b, OH), 2929 (m), 2854 (m), 2360 (m), 1670 (m), 1448 (m), 1286 (m), 1086 (s), 1067 (s), 918 (s).

2.1.3 Synthesis of dienols 1h and 1i

Alcohols **1h** and **1i** were synthesised in three steps from iso-butyronitrile and prenyl bromide. Nitriles **S4h-i** were reduced using MeLi and subsequent acid hydrolysis afforded the corresponding ketone **S5h-i**. Introduction of the enol ether moiety following the conditions described in **general procedure 1** afforded the tertiary alcohol.



2,2,5-trimethylhex-4-enenitrile (S4h-i)[1]

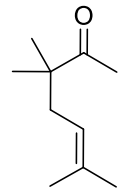


S4h-i

Chemical Formula: $C_9H_{15}N$
Molecular Weight: 137,23

A solution of *n*-butyllithium (2.5 M in cyclohexane, 1 eq.) was added dropwise to an ice cold solution of diisopropylamine (1 eq.) in dry THF. After stirring for 10 minutes at this temperature, isobutyronitrile (5 eq., 11.2 g, 160 mmol, 14.7 mL) was added to the mixture. Prenyl bromide (1 eq., 5.30 g, 32.0 mmol, 4.11 mL) was added after another mixing of 10 minutes at 0° C. Reaction conversion was followed by GC-MS and seen as complete after 15 minutes stirring at 0° C. The reaction was quenched by addition of saturated NH_4Cl aqueous solution and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified using a quick filtration over silica by elution with a PE-Et_2O mixture (9-1). Concentration of the eluent under reduced pressure resulted in the compound **S4h-i** as a pale yellow oil (4.20 g, 30.6 mmol, 96%). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.29 – 5.19 (m_c, 1H), 2.22 (d, ^3J = 7.6 Hz, 2H), 1.78 – 1.74 (m, 3H), 1.64 (s, 3H), 1.31 (s, 6H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 136.41, 125.22, 118.14, 39.13, 32.81, 26.21, 25.92, 18.05. **CAS number:** 13899-89-3**.**

3,3,6-trimethylhept-5-en-2-one (S5h-i)[1]

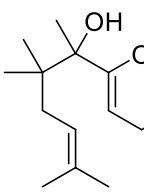


S5h-i

Chemical Formula: $C_{10}H_{18}O$
Molecular Weight: 154,25

A methyllithium solution (1.2 eq., 1.6M in pentane, 21.9 mmol, 13.7 mL) was added dropwise to a solution of the nitrile **S4h-i** (1 eq., 2.50 g, 18.2 mmol) in dry THF (0.5M) at -20° C. After stirring for 15 minutes at -10/-20° C., full conversion was observed by GC-MS. The reaction was quenched with a H_2SO_4 solution (2 eq., 2 M, 36.4 mmol, 18.2 mL) and stirred at ambient temperature till full hydrolysis of the *in situ* formed imine was observed. The mixture was then extracted with Et_2O and washed with a saturated $NaHCO_3$ aqueous solution. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting oil was purified with column chromatography by eluting with a PE-Et_2O mixture (95-5). Concentration of the desired fractions under reduced pressure resulted in the compound **S5h-i** as a colorless oil. (2.20 g, 14.3 mmol, 78%). **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 4.99 (m, 1H), 2.20 (d, ^3J = 7.3 Hz, 2H), 2.11 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.10 (s, 6H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 214.01, 134.20, 119.58, 48.25, 37.98, 25.91, 25.23, 24.04, 17.88. **CAS number:** 2550-19-8.

2-(3,4-dihydro-2H-pyran-6-yl)-3,3,6-trimethylhept-5-en-2-ol (1h)



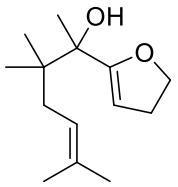
1h

Chemical Formula: $C_{15}H_{26}O_2$
Molecular Weight: 238,37

Compound **1h** was synthesised according to **general procedure 1** starting from 3,4-dihydropyran (0.95 g, 11.0 mmol, 1.03 mL) and ketone **S5h-i** (1.30 g, 8.43 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (1.40 g, 5.86 mmol, 69%). **TLC**: R_f = 0.61 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.29 – 5.16 (m_c, 1H), 4.74 (t, ^3J = 3.8 Hz, 1H), 4.06 – 3.89 (m, 2H), 2.52 (s, 1H), 2.17 – 1.96 (m, 4H), 1.87 – 1.67 (m, 5H), 1.60 (bs, 3H), 1.28 (s, 3H), 0.87 (m, 6H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] =

156.76, 132.78, 121.89, 96.68, 78.12, 65.82, 41.61, 35.31, 26.12, 22.39, 22.26, 22.23, 22.06, 20.13, 17.87. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3511 (OH, b), 2966 (m), 2927 (m), 2875 (m), 2359 (w), 2342 (w), 1662 (m), 1449 (m), 1375 (m), 1329 (m), 1266 (m), 1074 (s), 920 (s). **ESI-HRMS**: *m/z* calcd. for $C_{15}H_{27}O_2$ $[MH]^+$: 239.2005, found: 239.2006.

2-(4,5-dihydrofuran-2-yl)-3,3,6-trimethylhept-5-en-2-ol (1i)



1i
Chemical Formula: $C_{14}H_{24}O_2$
Molecular Weight: 224,34

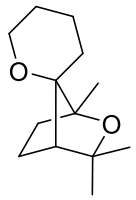
Compound **1i** was synthesised according to **general procedure 1** starting from 2,3-dihydrofuran (1.13 g, 16.0 mmol, 1.22 mL) and ketone **S5h-i** (1.90 g, 12.3 mmol). The crude product was purified by flash chromatography (PE+3% NEt_3/EtOAc = 95/5) and isolated as a yellow oil (1.74 g, 7.77 mmol, 63%). **TLC**: R_f = 0.57 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 5.29 – 5.15 (m, 1H), 4.76 (t, ^3J = 2.5 Hz, 1H), 4.32 (t, ^3J = 9.3 Hz, 2H), 2.63 (td, ^3J = 9.3, 2.5 Hz, 2H), 2.26 (s, 1H), 2.01 – 2.10 (m, 2H), 1.71 (s, 3H), 1.60 (s, 3H), 1.32 (s, 3H), 0.90 (d, ^3J = 2.1 Hz, 6H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 162.23, 133.08, 121.57, 95.46, 76.78, 70.00, 41.20, 35.29, 30.04, 26.11, 22.41, 22.30, 21.88, 17.89. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3498 (b, OH), 2966 (m), 2920 (m), 1650 (m), 1452 (m), 1365 (m), 1083 (m), 1060 (s), 936 (s). **ESI-HRMS**: *m/z* calcd. for $C_{14}H_{25}O_2$ $[MH]^+$: 225.1849, found: 225.1849.

2.2 Cyclisation products 2a-l, 4a-d, 7a-c

General procedure 4: Bi(OTf)$_3$ catalysed cyclisation reactions

$Bi(OTf)_3$ was added to a 0.1 M solution of the cyclisation precursor in the corresponding solvent (CH_2Cl_2 or CH_3NO_2) at room temperature and the reaction was followed by TLC and/or GC. Upon completion, the reaction was quenched by addition of a saturated aqueous $NaHCO_3$ solution. The aqueous phase was extracted with CH_2Cl_2 and the combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography afforded the corresponding cyclisation products.

Polycyclic ether (2a)

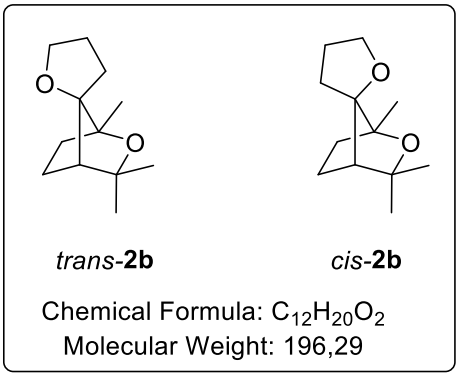


trans-**2a**
Chemical Formula: $C_{13}H_{22}O_2$
Molecular Weight: 210,32

Compound **2a** was synthesised according to **general procedure 4** starting from dienol **1a** (1.50 g, 7.13 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 47 mg, 0.07 mmol) were added and the mixture was stirred for 1.5 h. Purification by flash chromatography (P/Et_2O = 95/5) afforded **2a** (936 mg, 4.45 mmol, 62%) as a pale yellow oil. **TLC**: R_f = 0.34 (P/Et_2O = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.03 (s, 3H), 1.20 (s, 3H), 1.21 (s, 3H), 1.46-1.49 (m, 1H), 1.51-1.64 (m, 6H), 1.69- 1.74 (m, 1H), 1.78-1.81 (m, 1H), 2.09-2.11 (m, 1H), 2.33 (bs, 1H), 3.38-3.43 (m_c, 1H), 3.74-3.77 (m, 1H). **^{13}C-NMR** (125 MHz,

$CDCl_3$): δ [ppm] = 15.2, 21.0, 21.3, 26.5, 27.2, 29.2, 29.2, 33.9, 47.0, 64.8, 77.4, 85.3, 86.9. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2695 (m), 2932 (m), 2857 (w), 1442 (w), 1376 (m), 1200 (m), 1178 (m), 1100 (s), 1074 (s), 989 (s), 909 (s). **APGC-HRMS**: *m/z* calcd. for $C_{13}H_{22}O_2$ $[M]^{\bullet+}$: 210.1624, found: 210.1624.

Polycyclic ethers (*trans*-2b) and (*cis*-2b)

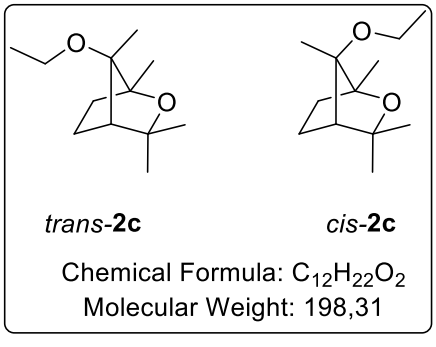


Compounds **2b** were synthesised according to **general procedure 4** starting from dienol **1b** (1.00 g, 6.0 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 33 mg, 0.05 mmol) was added and the mixture was stirred for 30 minutes. Purification by flash chromatography (P/Et_2O = 95/5) afforded *trans*-**2b** (275 mg, 1.40 mmol, 28%) as a pale yellow oil and *cis*-**2b** (580 mg, 3.00 mmol, 58%) as a pale yellow oil. The overall yield of cycloisomerisation products was 86%.

trans-**2b**: **TLC**: R_f = 0.50 (PE/EtOAc = 9:1), [*p*-anisaldehyde]. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.07 (s, 3H), 1.22 (s, 3H), 1.25 (s, 3H), 1.48-1.55 (m, 1H), 1.69-1.78 (m, 3H), 1.84-2.05 (m, 4H), 2.22-2.26 (m, 1H), 3.65-3.70 (m, 1H), 3.88-3.91 (m, 1H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 15.8 , 23.1, 27.1, 28.2, 28.4, 29.6, 34.0, 52.6, 67.1, 77.7, 84.8, 94.2. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2965 (m), 2932 (w), 2871 (w), 1460 (w), 1377 (m), 1175 (m), 1080 (s), 917 (m). **APGC-HRMS**: *m/z* calcd. for $C_{12}H_{21}O_2$ $[MH]^+$: 197.1542, found: 197.1532.

cis-**2b**: **TLC**: R_f = 0.23 (PE/EtOAc = 9:1), [*p*-anisaldehyde]. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.12 (s, 3H), 1.25 (s, 3H), 1.43 (s, 3H), 1.45-1.50 (m, 1H), 1.52- 1.58 (m, 2H), 1.71-1.78 (m, 3H), 1.80-1.92 (m, 2H), 1.95-2.01 (dt, ^3J = 12.4 Hz, 8.1 Hz, 1H), 3.78-3.82 (dt, ^3J = 6.6 Hz, 8.1 Hz, 1H), 3.95-3.99 (m, 1H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 15.3, 21.4, 25.9, 28.1, 28.5, 29.6, 33.1, 51.0, 68.2, 79.3, 85.0, 94.8. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2965 (m), 2929 (m), 2860 (w), 1457 (w), 1375 (m), 1240 (w), 1121 (w), 1090 (s), 1059 (s), 914 (s). **APGC-HRMS**: *m/z* calcd. for $C_{12}H_{19}O_2$ $[M-H]^+$: 195. 1385, found: 195.1398.

Polycyclic ethers (*trans*-2c) and (*cis*-2c)



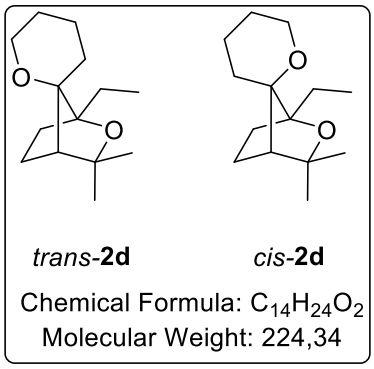
Compounds **2c** were synthesised according to **general procedure 4** starting from dienol **1c** (100 mg, 0.5 mmol) in CH_3NO_2 and 4Å molecular sieves at room temperature, $Bi(OTf)_3$ (1 mol%, 3.3 mg, 0.005 mmol) was added and the mixture was stirred for 5 minutes. Purification by flash chromatography (P/Et_2O = 95/5) afforded *trans*-**2c** (53 mg, 0.267 mmol, 53%) as a pale yellow oil and *cis*-**2c** (29 mg, 0.146 mmol, 29%) as a pale yellow oil. The overall isolated yield of cycloisomerisation products was 82%.

trans-**2c**: **TLC**: R_f = 0.79 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.54 (dq, ^3J = 8.9, 7.0 Hz, 1H), 3.25 (dq, ^3J = 8.9, 7.0 Hz, 1H), 2.02 (bs, 1H), 1.91 – 1.77 (m, 1H), 1.70 – 1.59 (m, 2H), 1.59 – 1.46 (m, 1H), 1.44 (s, 3H), 1.23 (s, 6H), 1.14 (t, ^3J = 7.0 Hz, 3H), 1.06 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 86.24, 86.01, 77.70, 59.23, 51.01, 34.17, 29.06, 28.80, 22.16, 17.85, 16.20, 14.85. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2970 (m), 2934 (w), 1444 (w), 1377 (m), 1181 (m),

1155 (s), 1113 (s), 1100 (s), 1062 (m). **ESI-HRMS**: *m/z* calcd. for $C_{12}H_{23}O_2$ $[MH]^+$: 199.1693, found: 199.1694.

cis-**2c**: **TLC**: R_f = 0. $[MH]^+$54 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.71 – 3.52 (m, 1H), 3.45 – 3.23 (m, 1H), 2.00 (d, ^3J = 3.3 Hz, 2H), 1.87 – 1.70 (m, 1H), 1.68 – 1.54 (m, 3H), 1.37 (s, 4H), 1.29 – 1.19 (m, 8H), 1.16 (d, ^3J = 4.2 Hz, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 86.84, 86.64, 78.72, 58.95, 48.91, 33.80, 29.01, 28.45, 21.53, 17.17, 15.72, 14.94. **ESI-HRMS**: *m/z* calcd. for $C_{12}H_{23}O_2$ $[MH]^+$: 199.1693, found: 199.1693.

Polycyclic ethers (*trans*-2d) and (*cis*-2d)

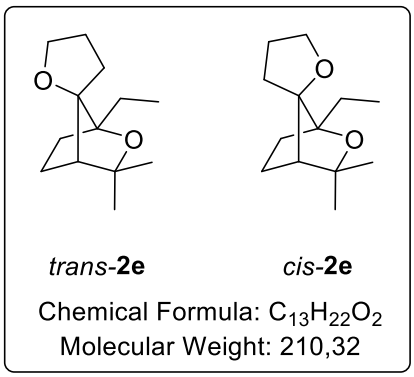


Compounds **2d** were synthesised according to **general procedure 4** starting from dienol **1d** (100 mg, 0.45 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (0.1 mol%, 0.3 mg, 0.0004 mmol) was added and the mixture was stirred for 1.5 h. Purification by flash chromatography (P/Et_2O = 95/5) afforded *trans*-**2d** (69 mg, 0.308 mmol, 69%) as a pale yellow oil and *cis*-**2d** (12 mg, 0.053 mmol, 12%) as white cristals. The overall isolated yield of cycloisomerisation products was 81%.

trans-**2d**: **TLC**: R_f = 0.78 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.96 – 3.81 (m, 1H), 3.63 – 3.43 (m, 1H), 2.48 (s, 1H), 2.31 – 2.15 (m, 1H), 1.99 – 1.49 (m, 11H), 1.35 (s, 3H), 1.33 (s, 3H), 1.01 (t, ^3J = 7.5 Hz, 3H. **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 88.1, 87.43, 77.36, 64.75, 47.19, 30.59, 29.29, 29.26, 27.35, 26.62, 23.02, 21.14, 21.09, 8.69. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2962 (m), 2934 (m), 2361 (w), 1456 (m), 1377 (m), 1273 (m), 1195 (m), 1175 (m), 1100 (s), 1076 (s), 1042 (s), 973 (s), 910 (s), 884 (s), 856 (s).

cis-**2d**: **TLC**: R_f = 0.44 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.92 – 3.76 (m, 1H), 3.53 (td, ^3J = 11.4, 3.4 Hz, 1H), 2.32 (d, ^3J = 3.0 Hz, 1H), 1.90 – 1.34 (m, 12H), 1.38 (s, 3H), 1.26 (s, 3H), 0.93 (t, ^3J = 7.5 Hz, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 88.91, 88.04, 78.75, 64.91, 44.94, 29.95, 28.79, 27.99, 26.50, 22.50, 21.72, 20.95, 8.84. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2955 (s), 2929 (s), 2849 (m), 2362 (m), 1438 (w), 1354 (w), 1239 (m), 1104 (s), 1078 (s), 1051 (s), 972 (s), 917 (s). **APGC-HRMS**: *m/z* calcd. for $C_{14}H_{24}O_2$ $[M]^{\bullet+}$: 224.1776, found: 224.1779.

Polycyclic ethers (*trans*-2e) and (*cis*-2e)



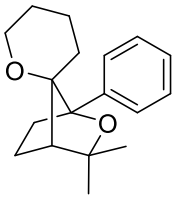
Compounds **2e** were synthesised according to **general procedure 4** starting from dienol **1e** (100 mg, 0.475 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (0.1 mol%, 0.3 mg, 0.0005 mmol) was added and the mixture was stirred for 5 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded *trans*-**2e** (22 mg, 0.105 mmol, 22%) as a pale yellow oil and *cis*-**2e** (61 mg, 0.290 mmol, 61%) as a pale yellow oil. The overall isolated yield of cycloisomerisation products was 83%.

trans-**2e**: **TLC**: R_f = 0.59 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.97 – 3.81 (m, 1H), 3.72 – 3.56 (m, 1H), 2.30 – 2.17 (m, 1H), 2.11 – 1.81 (m, 4H), 1.80 – 1.35 (m, 6H), 1.24 (s, 3H), 1.20

(s, 3H), 0.91 (t, ^{3}J = 7.5 Hz, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 94.57, 87.67, 77.50, 67.13, 52.73, 30.60, 29.72, 28.47, 28.20, 27.22, 23.22, 22.69, 9.07. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2965 (m), 2934 (m), 1460 (m), 1377 (m), 1363 (m), 1174 (m), 1103 (m), 1000 (s), 966 (s), 911 (w), 855 (w).

cis-**2e**: **TLC**: R_f = 0.41 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 4.10 – 3.97 (m, 1H), 3.90 – 3.76 (m, 1H), 2.11 – 1.63 (m, 8H), 1.61 – 1.33 (m, 5H), 1.31 (s, 3H), 1.01 (t, ^{3}J = 7.5 Hz, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 95.01, 87.65, 78.94, 67.98, 51.20, 30.15, 29.58, 28.59, 28.03, 25.92, 22.98, 21.08, 8.90. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2964 (m), 2935 (m), 1464 (m), 1375 (m), 1359 (m), 1194 (m), 1118 (m), 1096 (s), 1069 (s), 966 (s), 908 (m), 856 (m). **APGC-HRMS**: *m/z* calcd. for $C_{13}H_{21}O_2$ $[M-H]^+$: 209.1543, found: 209.1543.

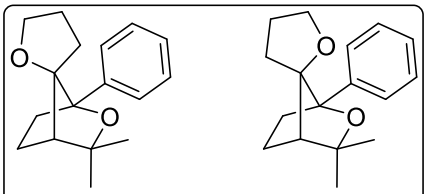
Polycyclic ether (2f)



trans-**2f**
Chemical Formula: $C_{18}H_{24}O_2$
Molecular Weight: 272,39

Compound **2f** was synthesised according to **general procedure 4** starting from dienol **1f** (100 mg, 0.37 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 2.4 mg, 0.004 mmol) was added and the mixture was stirred for 6 h. Purification by flash chromatography (P/Et_2O = 95/5) afforded *trans*-**2f** (67 mg, 0.246 mmol, 67%) as a white solid. **TLC**: R_f = 0.65 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.55 – 7.37 (m, 2H), 7.34 – 7.09 (m, 3H), 3.85 – 3.70 (m, 1H), 3.55 – 3.31 (m, 1H), 2.55 – 2.49 (m, 1H), 2.40 – 2.19 (m, 1H), 2.10 – 1.66 (m, 4H), 1.66 – 1.36 (m, 4H), 1.30 (s, 6H), 1.13 – 0.92 (m, 1H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 139.34, 127.68, 126.76, 126.27, 88.77, 88.53, 77.67, 64.73, 48.43, 35.49, 29.70, 29.51, 27.80, 26.35, 22.12, 21.00. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) =2965 (w), 2938 (m), 2859 (w), 1444 (w), 1276 (w), 1092 (m), 1075 (m), 1034 (s), 759 (s), 699 (s). **ESI-HRMS**: *m/z* calcd. for $C_{18}H_{25}O_2$ $[MH]^+$: 273.1855, found: 273.1841.

Polycyclic ethers (*trans*-2g) and (*cis*-2g)



trans-**2g** *cis*-**2g**
Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

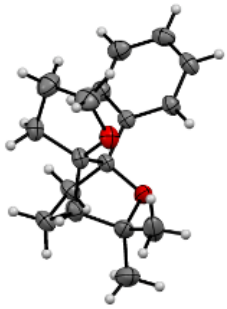
Compounds **2g** were synthesised according to **general procedure 4** starting from dienol **1g** (100 mg, 0.387 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (0.1 mol%, 0.3 mg, 0.0004 mmol) was added and the mixture was stirred for 10 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded *trans*-**2g** (22 mg, 0.085 mmol, 22%) as a pale yellow oil and *cis*-**2g** (75 mg, 0.290 mmol, 75%) as white cristals. The overall isolated yield of cycloisomerisation products was 99%.

trans-**2g**: **TLC**: R_f = 0.59 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.57 – 7.48 (m, 2H), 7.36 – 7.23 (m, 3H), 3.84 – 3.73 (m, 1H), 3.66 – 3.48 (m, 1H), 2.56 – 2.39 (m, 1H), 2.28 – 1.71 (m, 6H), 1.65 – 1.45 (m, 1H), 1.38 (s, 3H), 1.35 (s, 3H), 0.82 – 0.50 (m, 1H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 139.15, 127.72, 126.89, 125.72, 96.58, 87.50, 77.94, 67.58, 54.31, 34.71, 30.07, 28.49, 28.41, 26.24, 23.67. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2968 (m), 2941 (m), 1446 (w), 1271 (w), 1079 (s), 1032 (m), 984 (m), 849 (m), 758 (s), 699 (s).

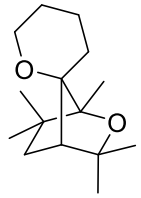
cis-**2g**: **TLC**: R_f = 0.47 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.62 – 7.52 (m, 2H), 7.36 – 7.20 (m, 3H), 3.67 (dt, ^{3}J = 8.1, 7.1 Hz, 1H), 3.42 – 3.29 (m, 1H), 2.44 – 2.28 (m, 1H), 2.07 – 1.52 (m, 10H), 1.38 – 1.33 (m, 3H), 1.26 – 1.10 (m, 1H). **^{13}C-NMR** (50 MHz,

$CDCl_3$): δ [ppm] = 138.19, 127.81, 127.33, 126.99, 96.59, 87.70, 80.04, 68.19, 52.96, 30.98, 29.85, 28.50, 28.25, 25.01, 21.43. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2969 (m), 2925 (w), 2862 (w), 1446 (m), 1377 (m), 1084 (m), 1037 (m), 981 (m), 967 (s), 757 (s), 698 (s). **APGC-HRMS**: *m/z* calcd. for $C_{17}H_{22}O_2$ $[M]^{\bullet+}$: 258.1624, found: 258.1623.

X-ray crystal structure of *cis*-2g (CCDC number 1452479)



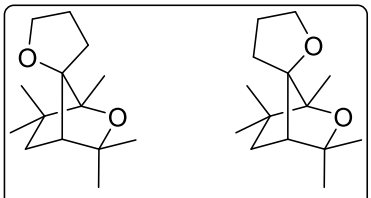
Polycyclic ether (*trans*-2h)



trans-**2h**
Chemical Formula: $C_{15}H_{26}O_2$
Molecular Weight: 238,37

Compound **2h** was synthesised according to **general procedure 4** starting from dienol **1h** (100 mg, 0.42 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 2.8 mg, 0.004 mmol) was added and the mixture was stirred for 7 h. Purification by flash chromatography (P/Et_2O = 95/5) afforded *trans*-**2h** (50 mg, 0.210 mmol, 50%) as a pale yellow oil. **TLC**: R_f = 0.78 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.89 – 3.72 (m, 1H), 3.57 – 3.37 (m, 1H), 2.43 (t, ^3J = 2.3 Hz, 1H), 2.27 – 2.15 (m, 1H), 1.86 – 1.51 (m, 7H), 1.32 (s, 3H), 1.31 (s, 3H), 1.12 (s, 3H), 1.10 (s, 3H), 0.97 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 89.52, 88.77, 77.54, 64.25, 47.60, 40.99, 36.57, 30.13, 29.60, 29.12, 27.85, 26.56, 24.33, 21.08, 11.39. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2934 (m), 2860 (w), 1447 (w), 1375 (m), ,1042 (m), 1092 (s), 1082 (s), 1071 (s), 987 (s). **APGC-HRMS**: *m/z* calcd. for $C_{15}H_{27}O_2$ $[MH]^+$: 239.2006, found: 239.2006.

Polycyclic ethers (*trans*-2i) and (*cis*-2i)



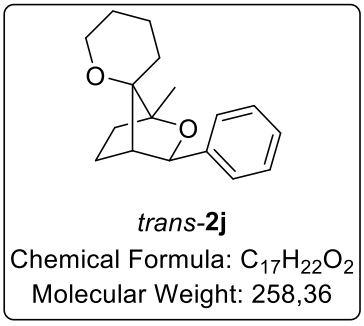
trans-**2i** *cis*-**2i**
Chemical Formula: $C_{14}H_{24}O_2$
Molecular Weight: 224,34

Compounds **2i** were synthesised according to **general procedure 4** starting from dienol **1i** (100 mg, 0.45 mmol) in CH_3NO_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 2.95 mg, 0.002 mmol) was added and the mixture was stirred for 10 minutes. Purification by flash chromatography (P/Et_2O = 95/5) afforded *trans*-**2i** (21 mg, 0.094 mmol, 21%) as a pale yellow oil and *cis*-**2i** (61 mg, 0.272 mmol, 61%) as a pale yellow oil. The overall yield of cycloisomerisation products was 82%.

trans-**2i**: **TLC**: R_f = 0.71 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.97 – 3.78 (m, 1H), 3.78 – 3.62 (m, 1H), 2.43 – 2.23 (m, 1H), 2.14 – 1.62 (m, 6H), 1.30 (s, 6H), 1.12 (s, 3H), 1.10 (s, 3H), 0.97 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 96.29, 87.81, 77.62, 65.84, 52.92, 41.02, 38.24, 31.80, 29.36, 28.69, 26.75, 26.30, 24.12, 11.77. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2964 (m), 2865 (w), 1451 (w), 1379 (m), 1159 (w), 1077 (s), 978 (w), 926 (m), 896 (m).

cis-**2i**: **TLC**: R_f = 0.46 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.87 – 3.67 (m, 2H), 2.10 – 1.86 (m, 3H), 1.85 – 1.66 (m, 3H), 1.46 (s, 3H), 1.42 – 1.32 (m, 1H), 1.31 (s, 3H), 1.12 (s, 3H), 1.01 (s, 3H), 0.94 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 95.30, 89.21, 79.24, 65.17, 49.73, 38.88, 37.31, 31.06, 29.35, 28.25, 26.82, 26.07, 24.38, 10.35. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2955 (m), 2858 (w), 1467 (w), 1374 (m), 1080 (s), 1054 (m), 885 (m). **APGC-HRMS**: *m/z* calcd. for $C_{14}H_{25}O_2$ $[MH]^+$: 225.1855, found: 225.1855.

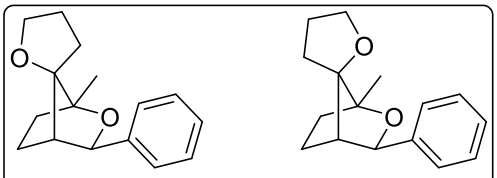
Polycyclic ether (2j)



trans-**2j**
Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

Compound **2j** was synthesised according to **general procedure 4** starting from dienol **1j** (100 mg, 0.39 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 2.54 mg, 0.003 mmol) were added and the mixture was stirred for 15 min. Purification by flash chromatography (P/Et_2O = 98:2) afforded *trans*-**2j** (58 mg, 0.23 mmol, 58%) as a pale yellow oil. **TLC**: R_f = 0.76 (P/Et_2O = 98:2), [*p*-anisaldehyde]. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.07 – 1.21 (m, 1H), 1.26 – 1.36 (m, 4H), 1.37 – 1.49 (m, 3H), 1.50 – 1.66 (m, 2H), 1.80-1.85 (m, 1H), 1.94 – 2.10 (m, 2H), 2.98 (d, ^3J = 3.3 Hz, 1H), 3.47 (m_c, 1H), 3.85 (m_c, 1H), 4.83 (s, 1H), 7.22 (m_c, 1H), 7.32-7.38 (m, 4H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 14.6, 20.7, 24.9, 26.0, 27.2, 35.4, 43.7, 65.1, 82.1, 84.5, 85.2, 124.5, 126.3, 128.1, 143.3.

Polycyclic ethers (*trans*-2k) and (*cis*-2k)



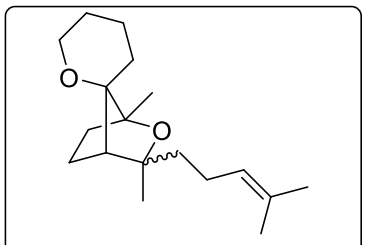
trans-**2k** *cis*-**2k**
Chemical Formula: $C_{16}H_{20}O_2$
Molecular Weight: 244,33

Compounds **2k** were synthesised according to **general procedure 4** starting from dienol **1k** (100 mg, 0.41 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 2.69 mg, 0.004 mmol) were added and the mixture was stirred for 10 min. Purification by flash chromatography (P/Et_2O = 98:2) afforded *trans*-**2k** (65 mg, 0.27 mmol, 65%) as a pale yellow oil and *cis*-**2k** (23 mg, 0.09 mmol, 23%) as a pale yellow oil. The overall yield of cycloisomerisation products was 88%.

trans-**2k**: **TLC**: R_f = 0.76 (P/Et_2O = 98:2), [*p*-anisaldehyde]. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.14-1.20 (m, 1H), 1.27 (s, 3H), 1.67-1.79 (m, 4H), 1.83-1.89 (m, 1H), 2.02 (td, ^3J = 12.1 Hz, 3.5 Hz, 1H), 2.14-2.20 (m, 1H), 2.36 (d, ^3J = 3.8 Hz, 1H), 3.61-3.65 (m, 1H), 3.80-3.84 (m, 1H), 4.80 (s, 1H), 7.22-7.25 (m, 1H), 7.32-7.37 (m, 4H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 14.8, 26.7, 27.3, 28.3, 35.4, 50.6, 67.5, 82.2, 83.9, 91.7, 124.9, 126.3, 128.0, 143.1.

cis-**2k**: **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 1.29 (s, 3H), 1.66 – 1.75 (m, 3H), 1.76 – 1.90 (m, 4H), 1.91 – 1.97 (m, 1H), 2.36 (d, ^3J = 3.5 Hz, 1H), 3.45 – 3.52 (m, 1H), 3.68 – 3.76 (m, 1H), 4.81 (s, 1H), 7.16 – 7.21 (m, 1H), 7.28 – 7.33 (m, 2H), 7.40 – 7.42 (m, 2H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 14.33, 25.87, 26.92, 28.40, 34.08, 49.09, 67.74, 83.97, 84.84, 92.18, 125.72, 125.94, 127.57, 143.84.

Polycyclic ether (2l)

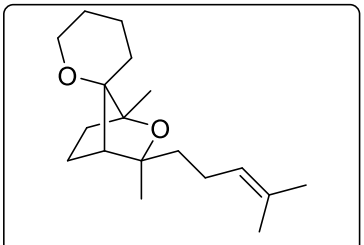


2l

Chemical Formula: $C_{18}H_{30}O_2$
Molecular Weight: 278,44

Compound **2l** was synthesised according to **general procedure 4** starting from dienol **1l** (100 mg, 0.36 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 2.4 mg, 0.004 mmol) were added and the mixture was stirred for 5 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded a mixture of *endo* and *exo* compounds **2l** which were not separated (50 mg, 0.18 mmol, 50%) as a pale yellow oil. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.11 (ddt, ^3J = 7.1, 5.6, 1.4 Hz, 1H), 5.07 (ddt, ^3J = 7.1, 5.7, 1.4 Hz, 1H), 3.83 – 3.80 (m, 1H), 3.80 – 3.78 (m, 1H), 3.45 (tdd, ^3J = 12.0, 6.4, 2.6 Hz, 2H), 2.42 (d, ^3J = 3.3 Hz, 1H), 2.39 (d, ^3J = 1.8 Hz, 1H), 2.19 – 1.89 (m, 5H), 1.86 – 1.47 (m, 34H), 1.37 (ddd, ^3J = 13.6, 12.2, 4.9 Hz, 1H), 1.27 (s, 3H), 1.24 (s, 3H), 1.08 (s, 6H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 131.65, 131.54, 124.62, 124.55, 87.02, 86.94, 85.16, 84.92, 79.67, 79.29, 64.93, 64.86, 46.73, 46.02, 41.82, 40.84, 34.32, 34.26, 27.53, 27.23, 26.61, 26.59, 26.19, 26.12, 25.86, 25.83, 24.21, 22.44, 21.31, 21.21, 21.16, 17.87, 17.73, 15.31, 15.24.

Polycyclic ether (*exo*-2l)

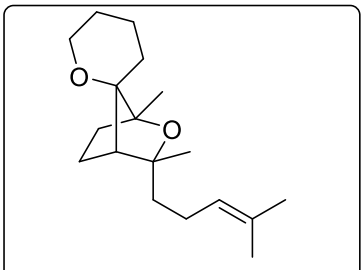


exo-**2l**

Chemical Formula: $C_{18}H_{30}O_2$
Molecular Weight: 278,44

Compound *exo*-**2l** was synthesised according to **general procedure 4** starting from dienol *(E)*-**1l** (100 mg, 0.36 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 2.4 mg, 0.004 mmol) were added and the mixture was stirred for 5 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded *exo*-**2l** (51 mg, 0.18 mmol, 51%) as a pale yellow oil. **TLC**: R_f = 0.76 (P/Et_2O = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.07 (ddt, ^3J = 8.6, 5.7, 1.4 Hz, 1H), 3.83 – 3.78 (m, 1H), 3.45 (td, ^3J = 11.9, 2.6 Hz, 1H), 2.40 – 2.37 (m, 1H), 2.15 – 2.06 (m, 1H), 2.05 – 1.93 (m, 3H), 1.88 – 1.80 (m, 1H), 1.80 – 1.74 (m, 1H), 1.72 – 1.63 (m, 6H), 1.63 – 1.51 (m, 7H), 1.37 (ddd, ^3J = 13.6, 12.2, 5.2 Hz, 1H), 1.24 (s, 3H), 1.08 (s, 3H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 131.65, 124.62, 87.02, 85.16, 79.29, 64.93, 46.73, 40.84, 34.27, 27.24, 26.61, 26.12, 25.85, 22.44, 21.31, 21.16, 17.73, 15.24. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2966 (m), 2931 (m), 2854 (w), 2358 (s), 2341 (s), 1442 (w), 1373 (w), 1185 (m), 1075 (m), 989 (m), 910 (m).

Polycyclic ether (*endo*-2l)



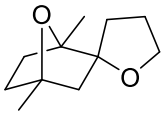
endo-**2l**

Chemical Formula: $C_{18}H_{30}O_2$
Molecular Weight: 278,44

Compound *endo*-**2l** was synthesised according to **general procedure 4** starting from dienol *(Z)*-**1l** (100 mg, 0.36 mmol) in CH_2Cl_2 at room temperature, $Bi(OTf)_3$ (1 mol%, 2.4 mg, 0.004 mmol) were added and the mixture was stirred for 5 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded *endo*-**2l** (53 mg, 0.19 mmol, 53%) as a pale yellow oil. **TLC**: R_f = 0.74 (P/Et_2O = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (500 MHz, $CDCl_3$): δ [ppm] = 5.11 (ddt, ^3J

= 7.0, 5.6, 1.4 Hz, 1H), 3.84 – 3.77 (m, 1H), 3.46 (td, ^3J = 11.8, 2.7 Hz, 1H), 2.42 (d, ^3J = 3.5 Hz, 1H), 2.19 – 2.12 (m, 1H), 2.05 – 1.96 (m, 1H), 1.97 – 1.86 (m, 1H), 1.86 – 1.81 (m, 1H), 1.78 – 1.48 (m, 16H), 1.27 (s, 3H), 1.07 (s, 3H). **^{13}C-NMR** (125 MHz, $CDCl_3$): δ [ppm] = 131.53, 124.55, 86.94, 84.92, 79.66, 64.86, 46.02, 41.82, 34.32, 27.53, 26.58, 26.19, 25.83, 24.21, 21.21, 21.16, 17.86, 15.31. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2965 (m), 2933 (s), 2858 (m), 1444 (m), 1374 (m), 1204 (m), 1095 (s), 1073 (s), 1043 (s), 990 (m), 910 (s).

Polycyclic ether (4a)

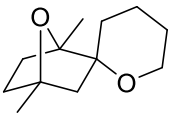


4a

Chemical Formula: $C_{11}H_{18}O_2$
Molecular Weight: 182,26

Compound **4a** was synthesised according to **general procedure 4** starting from dienol **3a** (100 mg, 0.55 mmol) and $Bi(OTf)_3$ (1 mol%, 3.6 mg, 0.005 mmol) in CH_3NO_2 stirred at room temperature for 5 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded **4a** as a pale yellow oil (79 mg, 0.43 mmol, 79%). **TLC**: R_f = 0.48 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.88 – 3.67 (m, 2H), 2.38 (ddd, ^3J = 11.5, 8.9, 4.5 Hz, 1H), 2.16 (ddd, ^3J = 12.1, 7.7, 5.5 Hz, 1H), 1.98 – 1.77 (m, 3H), 1.74 – 1.41 (m, 5H), 1.37 (s, 3H), 1.31 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 90.90, 86.11, 83.63, 67.79, 52.90, 37.74, 36.07, 32.84, 25.81, 21.98, 17.21. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2966 (m), 2932 (m), 2868 (w), 1445 (w), 1375 (m), 1232 (m), 1126 (m), 1071 (m), 1047 (s), 905 (m), 856 (s). **ESI-HRMS**: *m/z* calcd. for $C_{11}H_{19}O_2$ $[MH]^+$: 183.1385, found: 183.1382.

Polycyclic ether (4b)

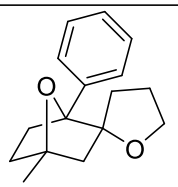


4b

Chemical Formula: $C_{12}H_{20}O_2$
Molecular Weight: 196,29

Compound **4b** was synthesised according to **general procedure 4** starting from dienol **3b** (100 mg, 0.51 mmol) and $Bi(OTf)_3$ (1 mol%, 3.3 mg, 0.005 mmol) in CH_3NO_2 stirred at room temperature for 5 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded **4b** as a pale yellow oil (78 mg, 0.40 mmol, 78%). **TLC**: R_f = 0.57 (PE/EtOAc = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 3.83 (dd, ^3J = 11.1, 2.4 Hz, 1H), 3.55 – 3.31 (m, 1H), 2.50 – 2.26 (m, 1H), 1.75 – 1.40 (m, 11H), 1.38 (s, 3H), 1.31 (s, 3H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 87.26, 83.53, 83.22, 65.76, 46.03, 38.12, 32.48, 31.95, 26.25, 22.24, 19.14, 17.20. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2935 (m), 2860 (w), 1443 (w), 1375 (m), 1233 (m), 1207 (m), 1132 (m), 1083 (s), 1067 (s), 1036 (m), 998 (m), 902 (m), 861 (s). **ESI-HRMS**: *m/z* calcd. for $C_{12}H_{21}O_2$ $[MH]^+$: 197.1537, found: 197.1536.

Polycyclic ether (4c)



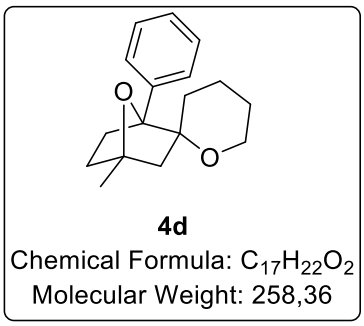
4c

Chemical Formula: $C_{16}H_{20}O_2$
Molecular Weight: 244,33

Compound **4c** was synthesised according to **general procedure 4** starting from dienol **3c** (100 mg, 0.41 mmol) and $Bi(OTf)_3$ (1 mol%, 2.7 mg, 0.004 mmol) in CH_3NO_2 stirred at room temperature for 15 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded **4c** as a pale yellow oil (95 mg, 0.39 mmol, 79%). **TLC**: R_f = 0.8 (PE/Et_2O = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 7.53 – 7.17 (m, 5H), 3.85 – 3.56 (m, 2H), 3.04 – 2.83 (m, 1H), 2.02 – 1.37 (m, 8H), 1.49 (s, 3H), 1.18 – 0.96 (m, 1H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 140.90, 127.77, 126.84, 125.79, 92.33, 90.10, 83.64, 68.59, 53.59, 37.58, 37.46, 32.61, 25.56, 22.11. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2965 (m),

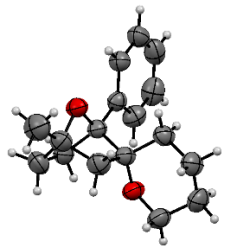
2866 (w), 1446 (m), 1112 (m), 1036 (s), 851 (m), 759 (s), 700 (s). **APGC-HRMS**: *m/z* calcd. for $C_{16}H_{21}O_2$ $[MH]^+$: 245.1542, found: 245,1550.

Polycyclic ether (4d)

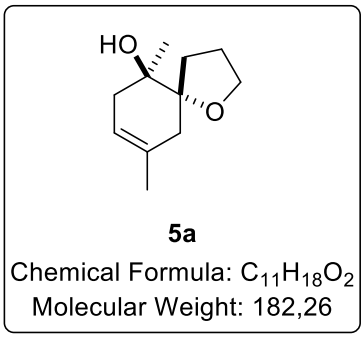


Compound **4d** was synthesised according to **general procedure 4** starting from dienol **3d** (100 mg, 0.39 mmol) and $Bi(OTf)_3$ (1 mol%, 2.5 mg, 0.004 mmol) in CH_3NO_2 stirred at room temperature for 15 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded **4d** as a white powder (83 mg, 0.32 mmol, 83%). **TLC**: R_f = 0.78 (PE/Et_2O = 95/5), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] =7.73 – 7.21 (m, 5H), 4.07 – 3.85 (m, 1H), 3.53 (ddd, ^3J = 11.4, 9.0, 4.9 Hz, 1H), 3.18 – 2.85 (m, 1H), 1.97 – 1.32 (m, 10H), 1.60 (s, 3H), 1.04 – 0.76 (m, 1H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 141.26, 127.75, 126.60, 125.78, 91.27, 84.29, 83.67, 65.83, 46.21, 38.00, 33.58, 31.94, 26.05, 22.43, 19.01. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 2941 (m), 2858 (w), 1449 (m), 1121 (m), 1071 (s), 1044 (s), 1021 (s), 988 (m), 761 (s), 701 (s). **ESI-HRMS**: *m/z* calcd. for $C_{17}H_{23}O_2$ $[MH]^+$: 259.1693, found: 259.1693.

X-ray crystal structure of 4d (CCDC number 1452480)



Polycyclic ether (5a)



Compound **5a** was synthesised according to **general procedure 4** starting from dienol **3a** (100 mg, 0.55 mmol) and $Bi(OTf)_3$ (1 mol%, 3.6 mg, 0.005 mmol) in CH_2Cl_2 stirred at room temperature for 5 min. Purification by flash chromatography (P/Et_2O = 95/5) afforded 4**a** (23 mg, 0.13 mmol, 23%) as a pale yellow oil and **5a** (50 mg, 0.27 mmol, 53%). **5a: TLC**: R_f = 0.27 (PE/EtOAc = 9/1), [*p*-anisaldehyde]. **^{1}H-NMR** (200 MHz, $CDCl_3$): δ [ppm] = 1.23 (s, 3H), 1.37-1.58 (m, 1H), 1.59-1.72 (m, 3H), 1.82-2.30 (m, 7H), 3.85 (m, 2H), 5.27 (m, 1H). **^{13}C-NMR** (50 MHz, $CDCl_3$): δ [ppm] = 23.20, 23.25, 26.27, 30.77, 38.41, 41.88, 68.59, 72.09, 86.02, 119.57, 132.59. **IR** (neat): $\tilde{\nu}$ (cm^{-1}) = 3465 (b, OH), 2967 (m), 2901 (m), 1441 (m), 1366 (m), 1128 (m), 1108 (m), 1065 (s).

3 References

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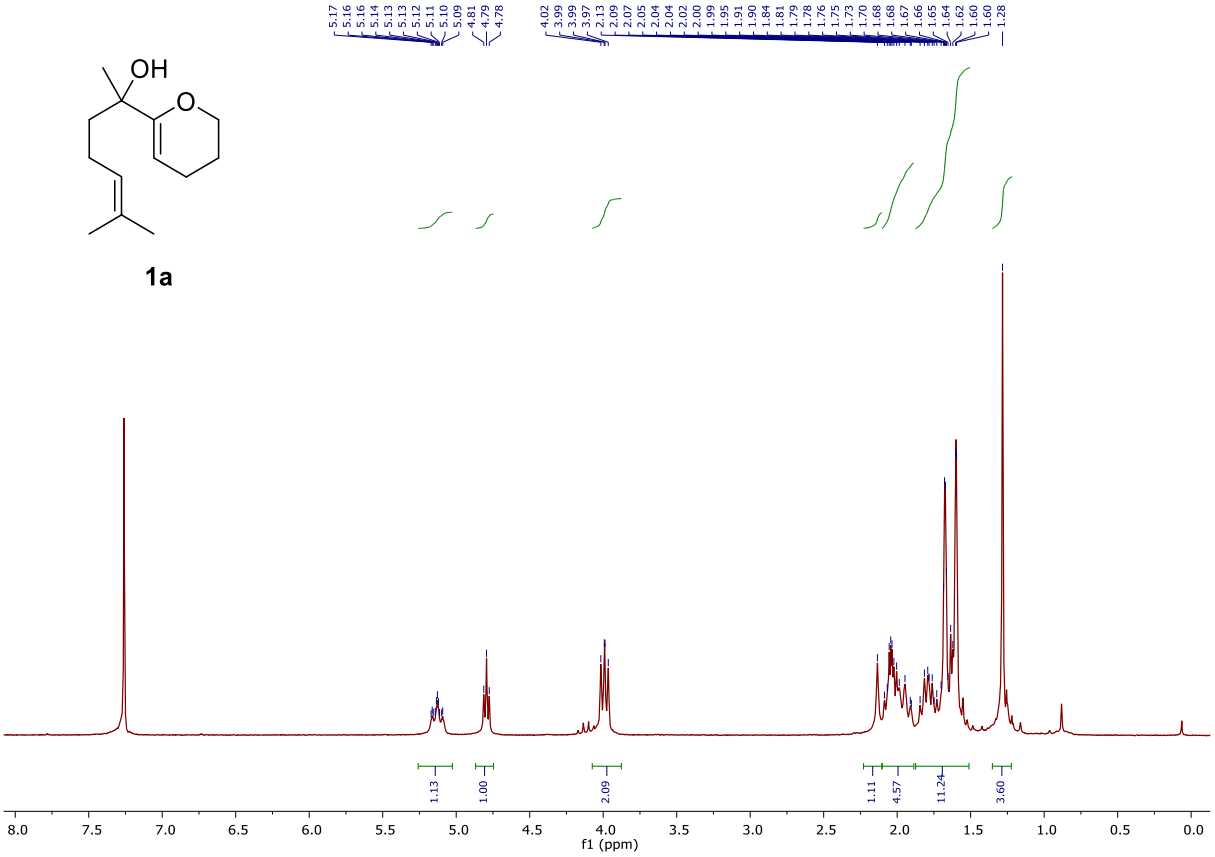
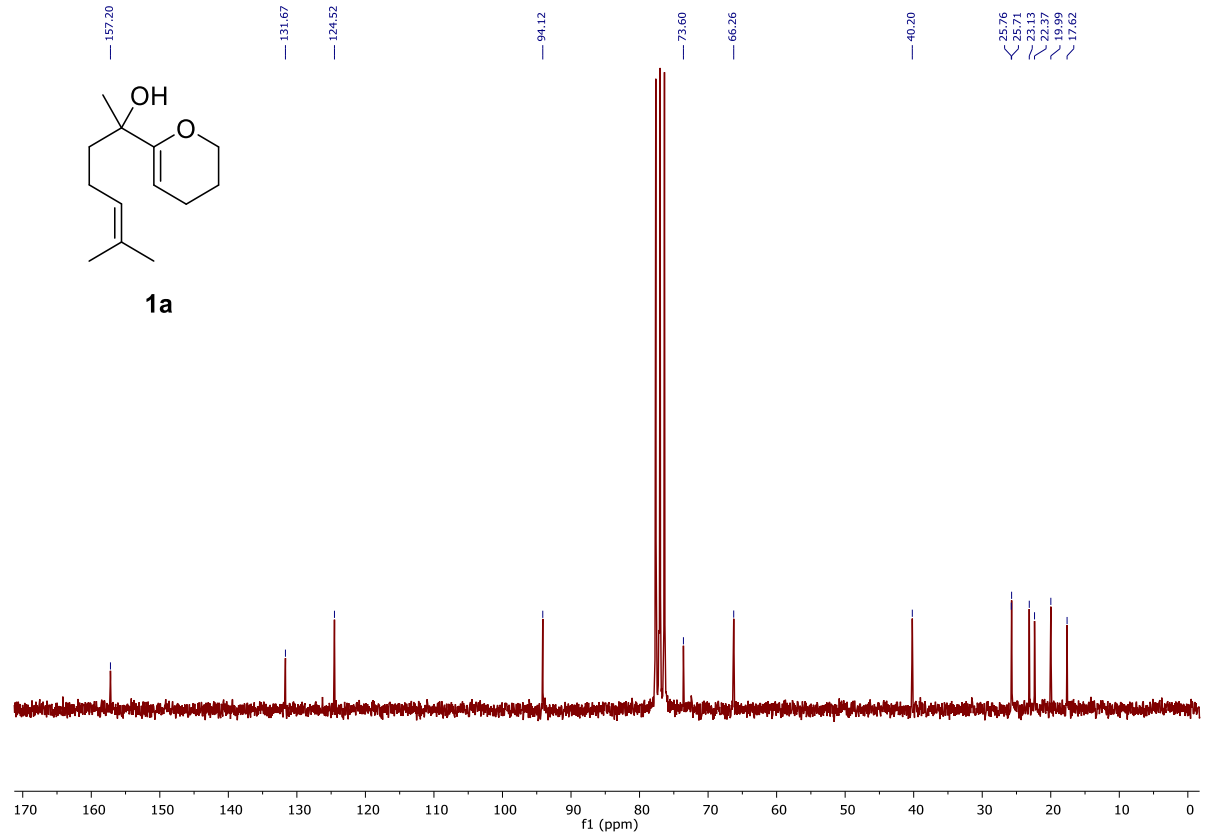
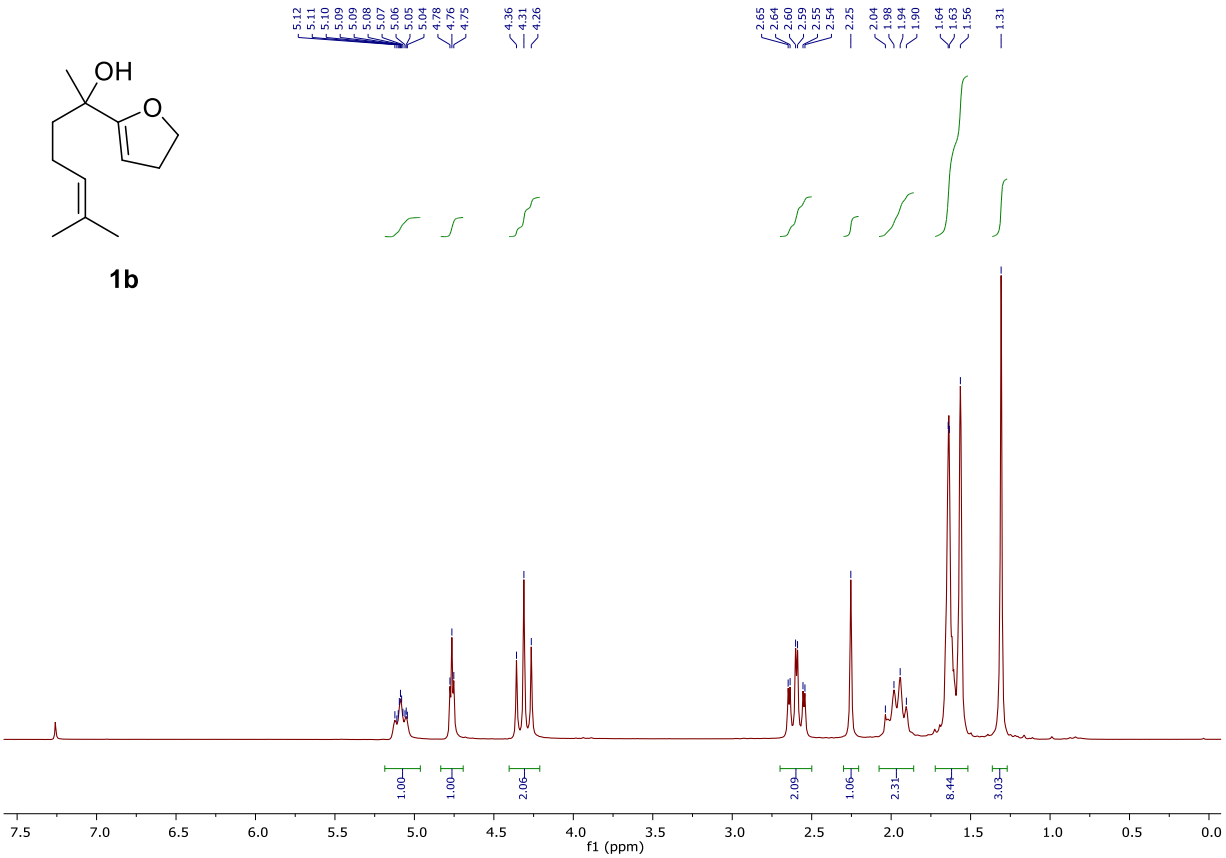
4 NMR spectra



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5.05
5.04
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6.5
6.0
5.5
5.0
4.5
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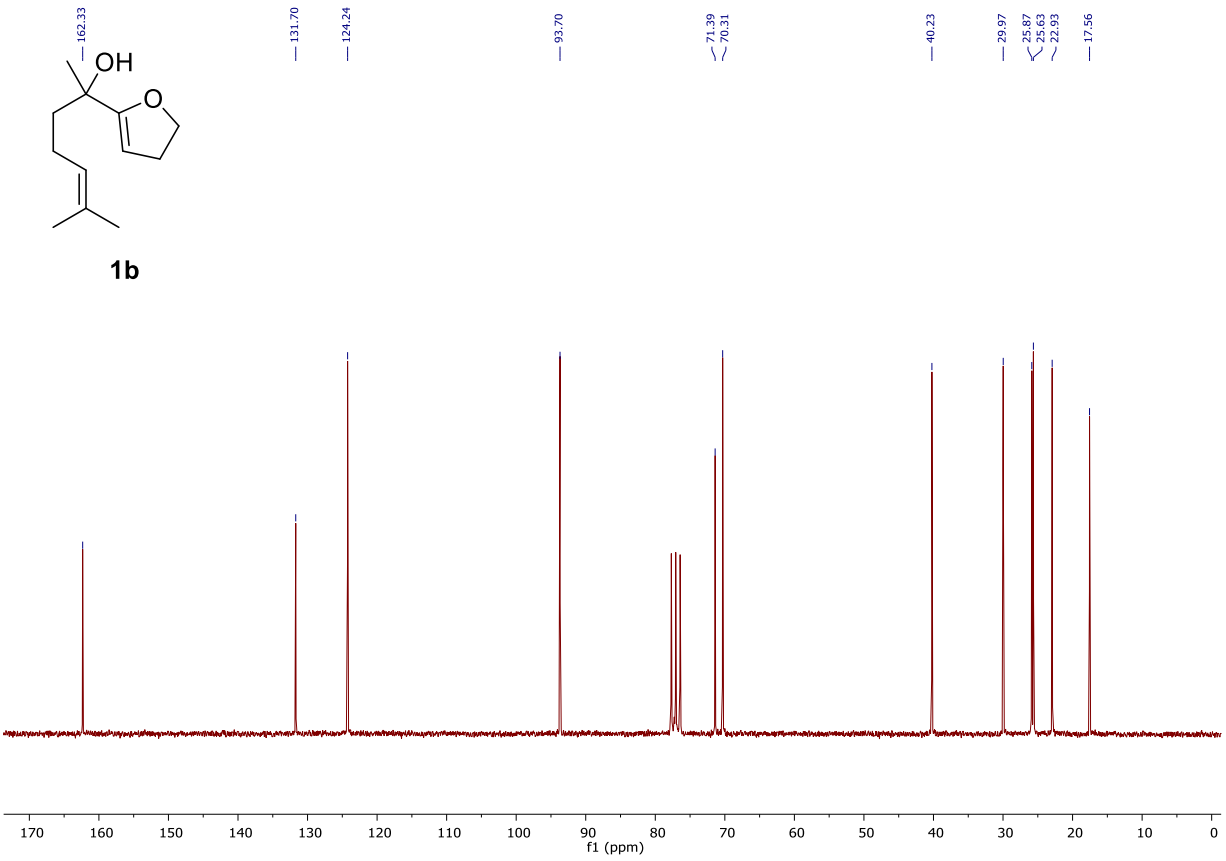
f1 (ppm)

1b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17.56
170
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100
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40
30
20
10
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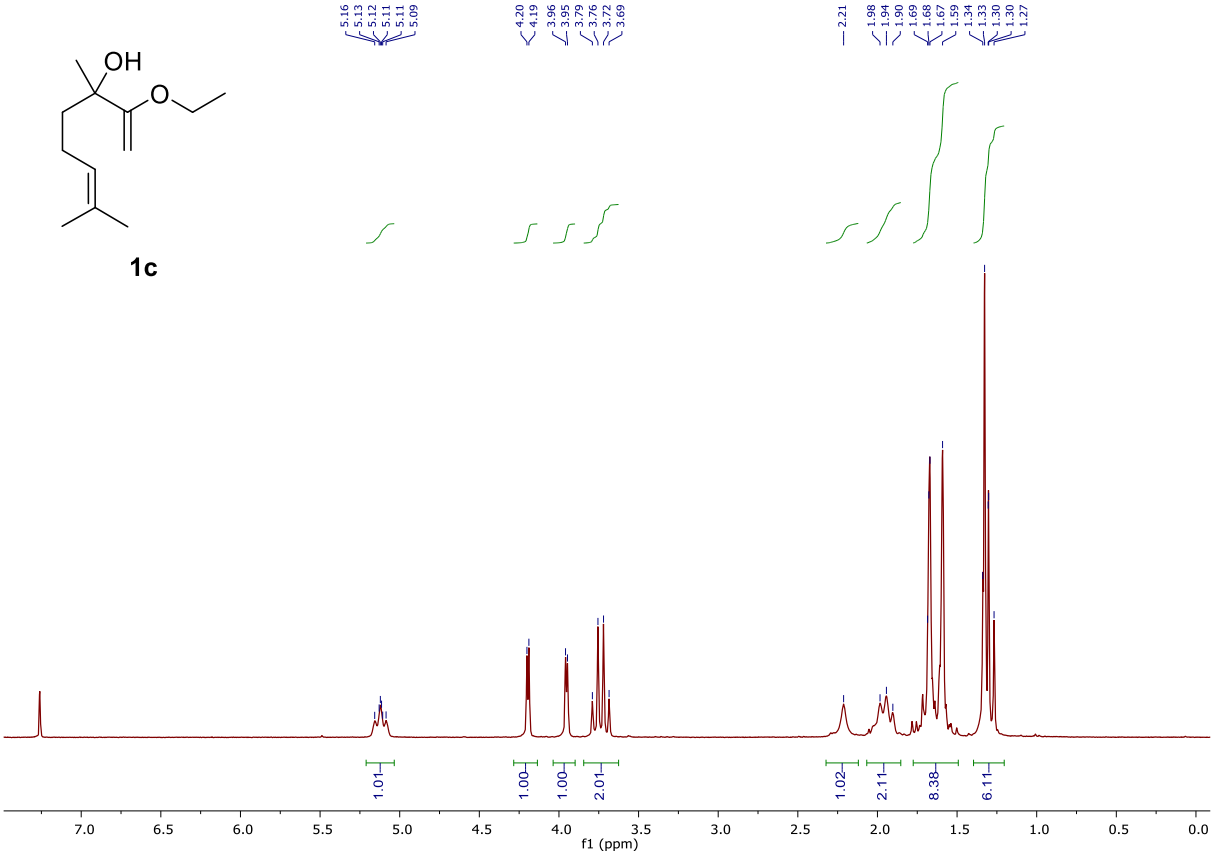
f1 (ppm)

1b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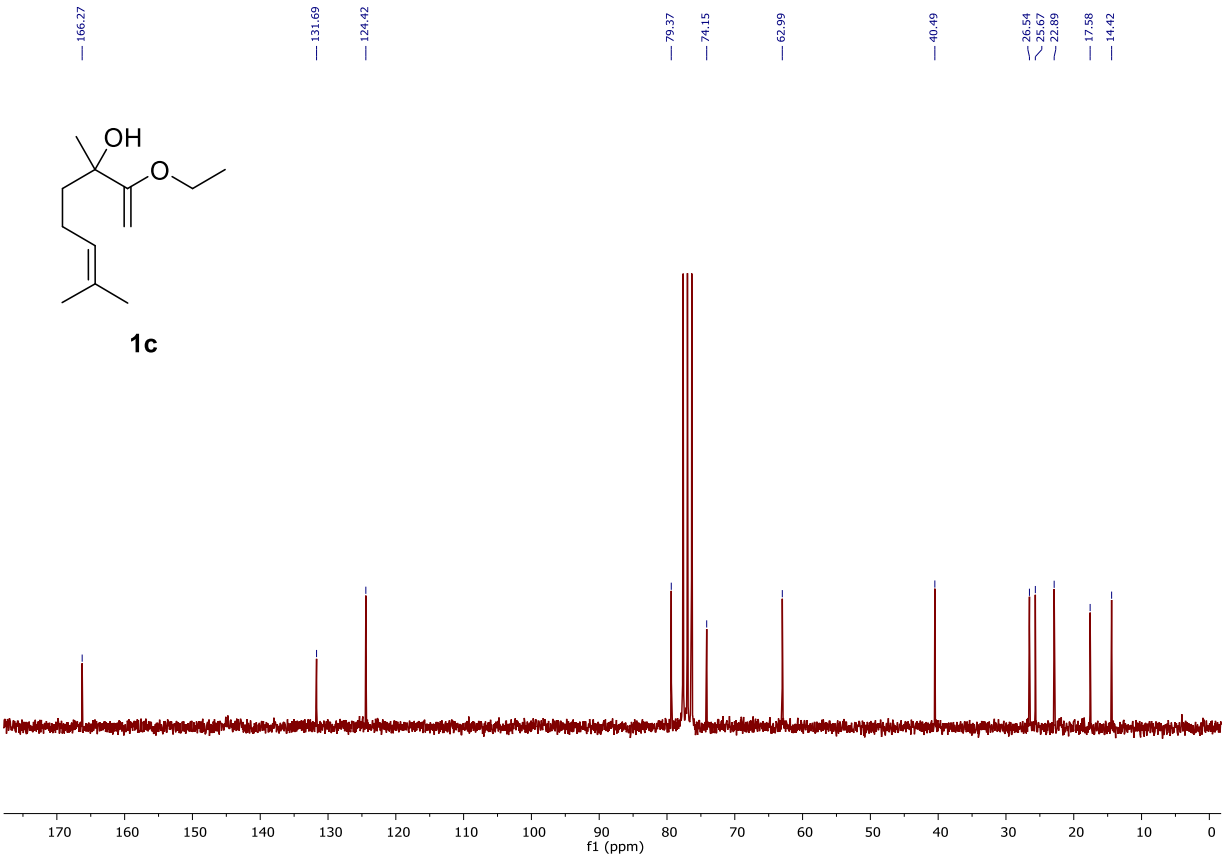
f1 (ppm)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50
40
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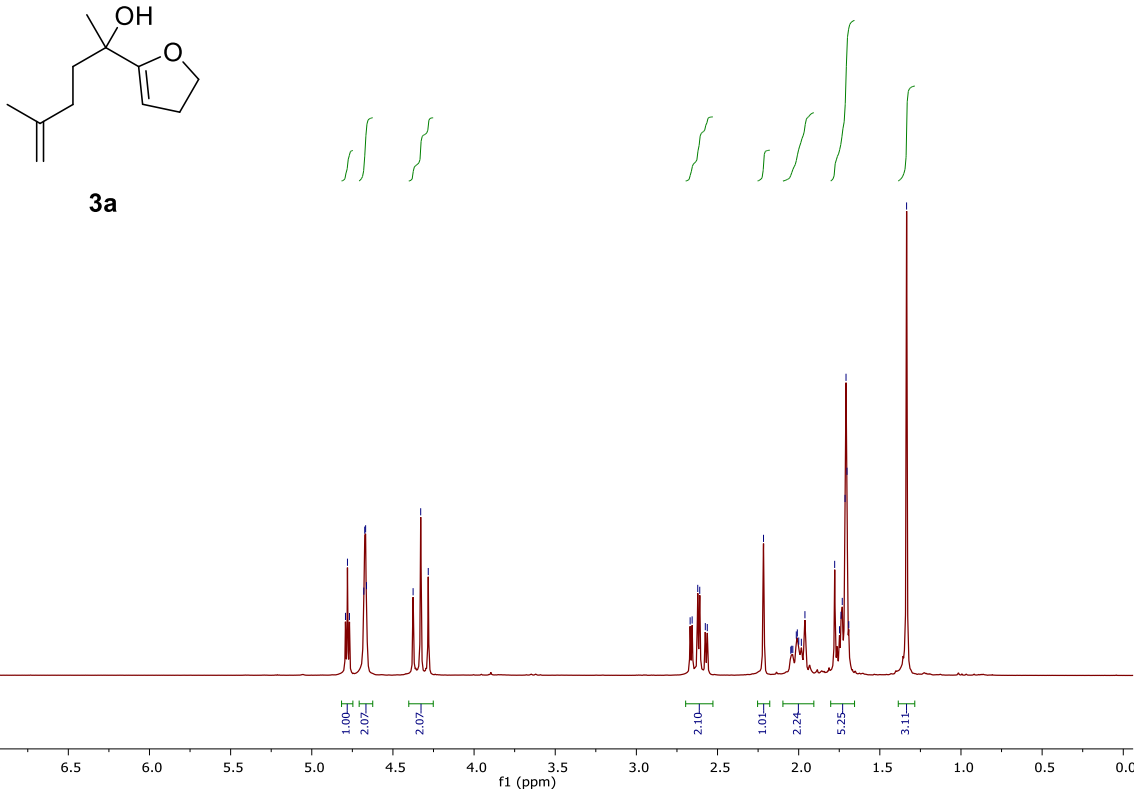
0
f1 (ppm)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6.5
6.0
5.5
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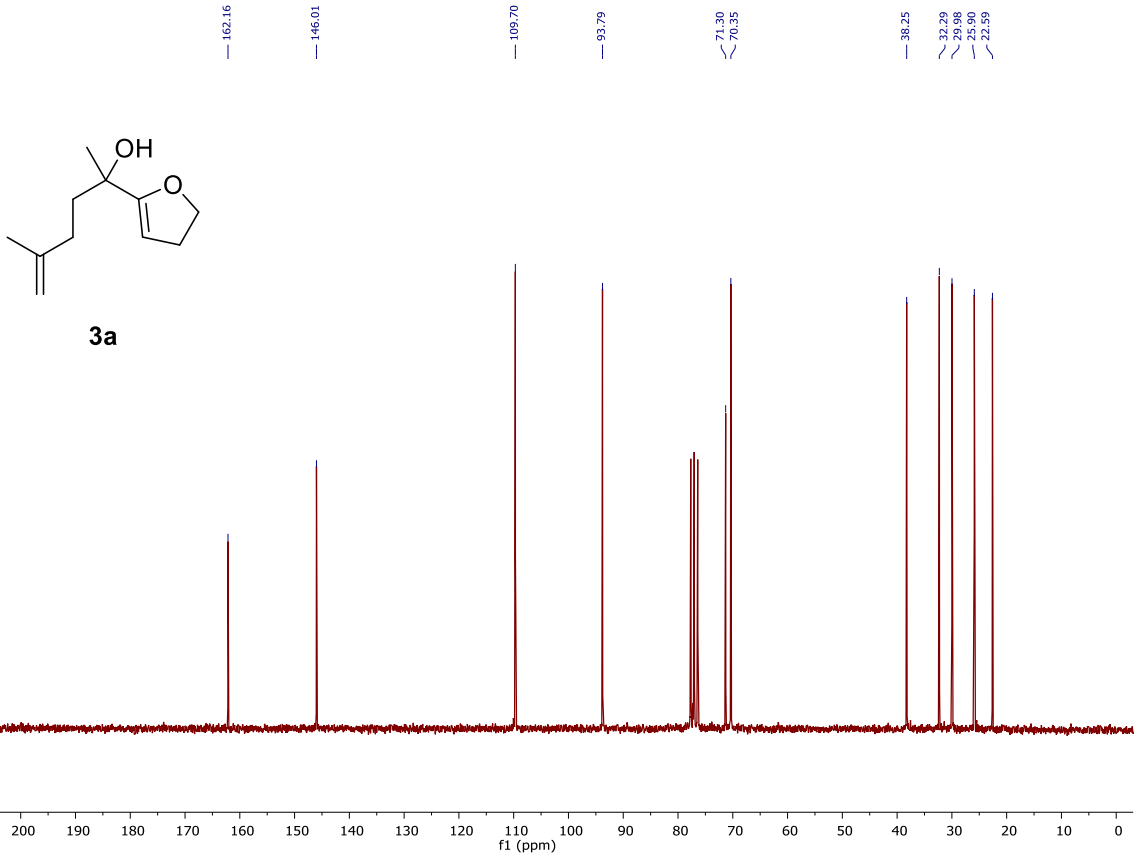
f1 (ppm)

3a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170
160
150
140
130
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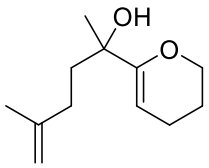
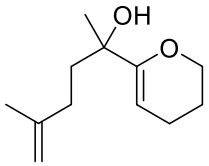
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3a


OH
O

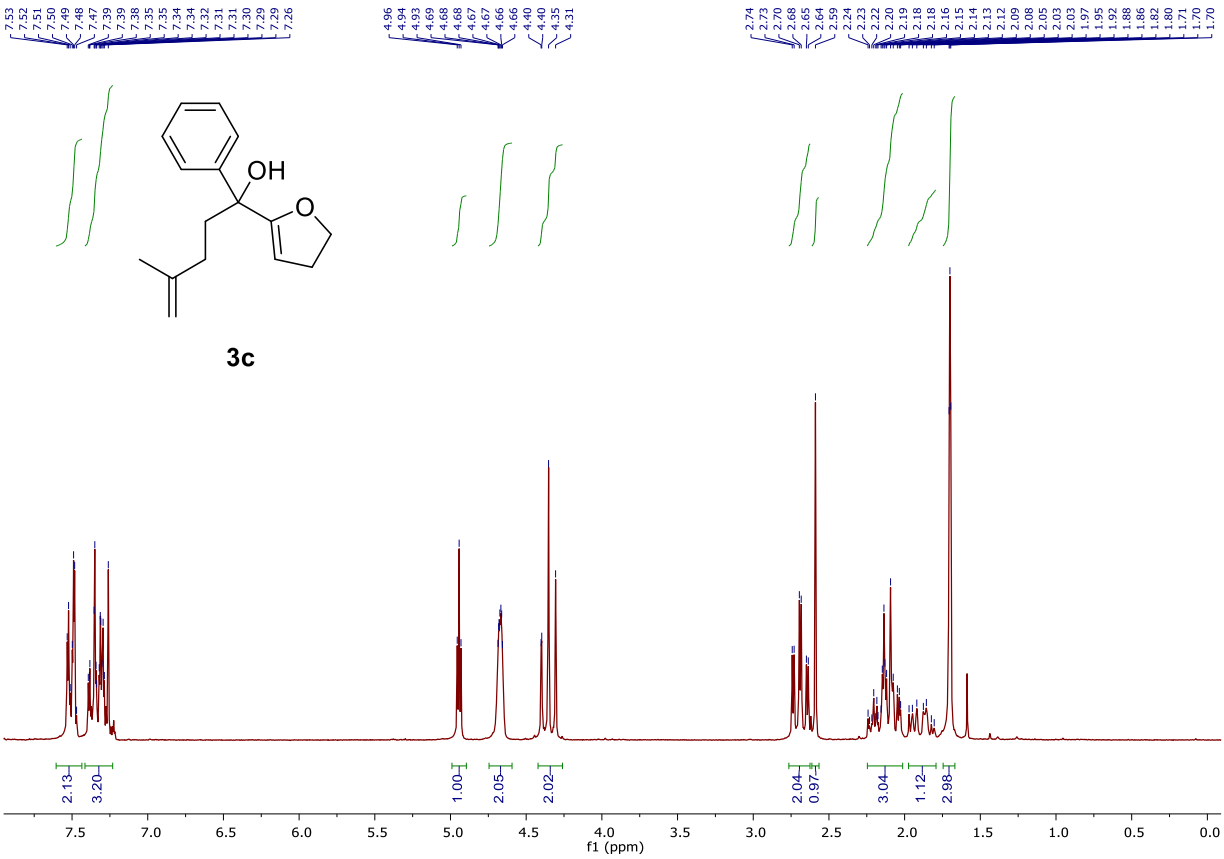
3b

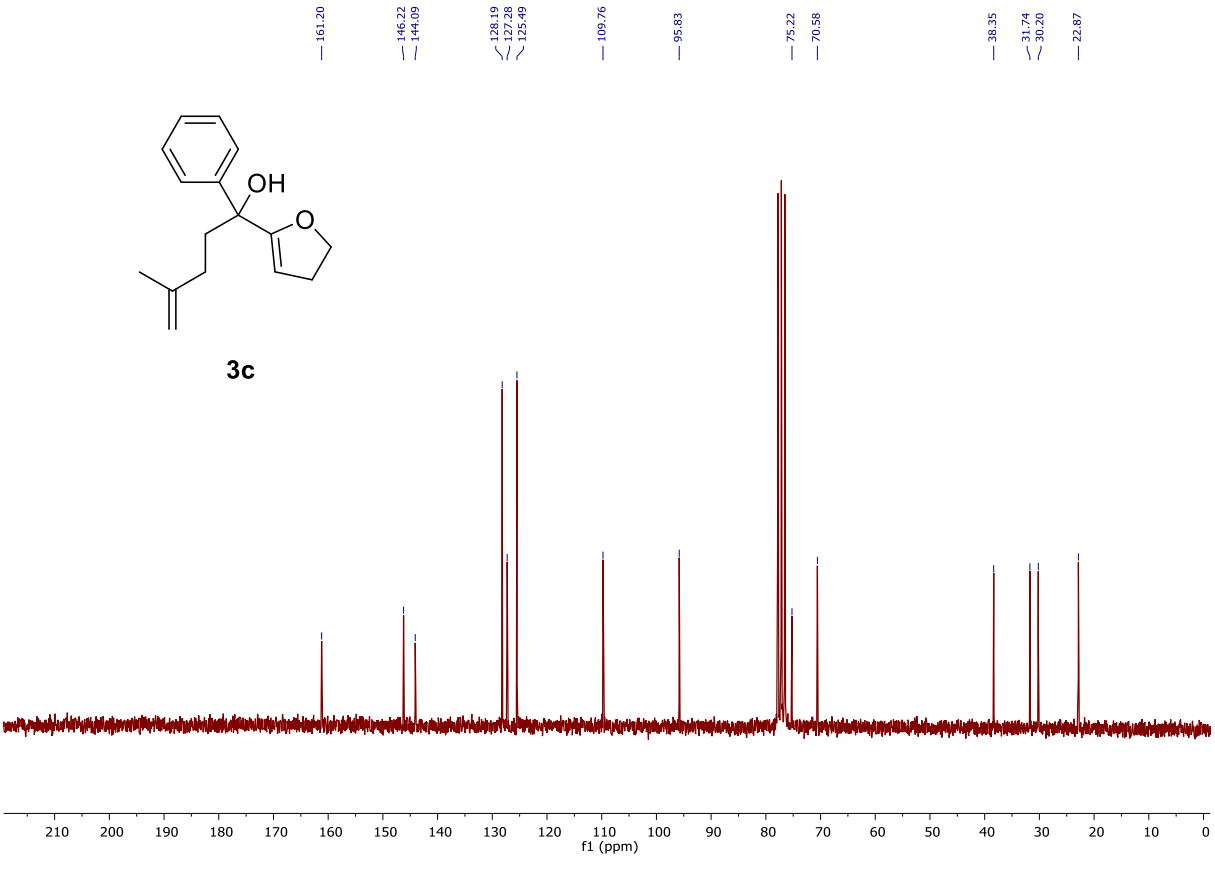
4.81
4.79
4.77
4.68
4.68
4.01
3.98
3.96
2.17
2.08
2.05
2.03
2.02
2.00
1.99
1.95
1.84
1.81
1.78
1.76
1.75
1.72
1.70
1.69
1.68
1.66
1.29
1.00
2.35
2.03
1.11
4.21
8.01
3.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

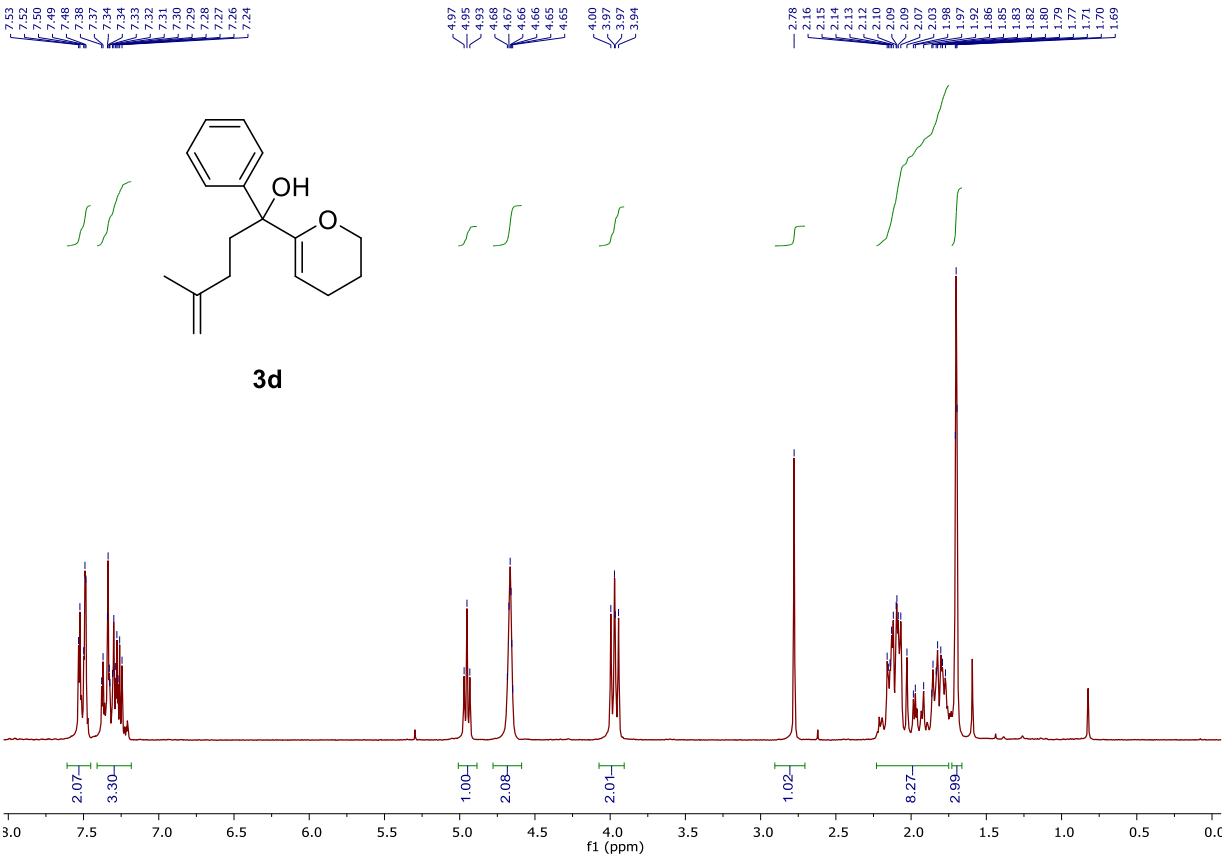

OH
O

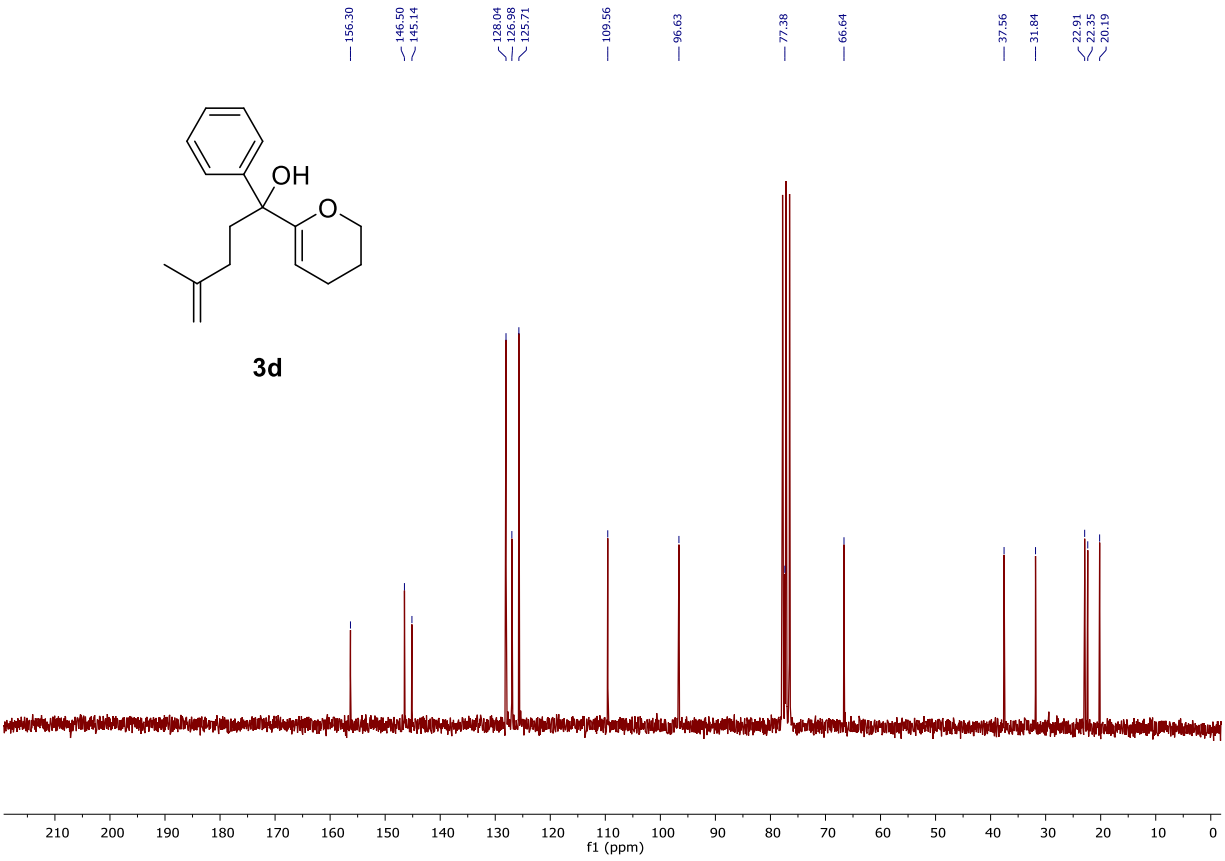
3b

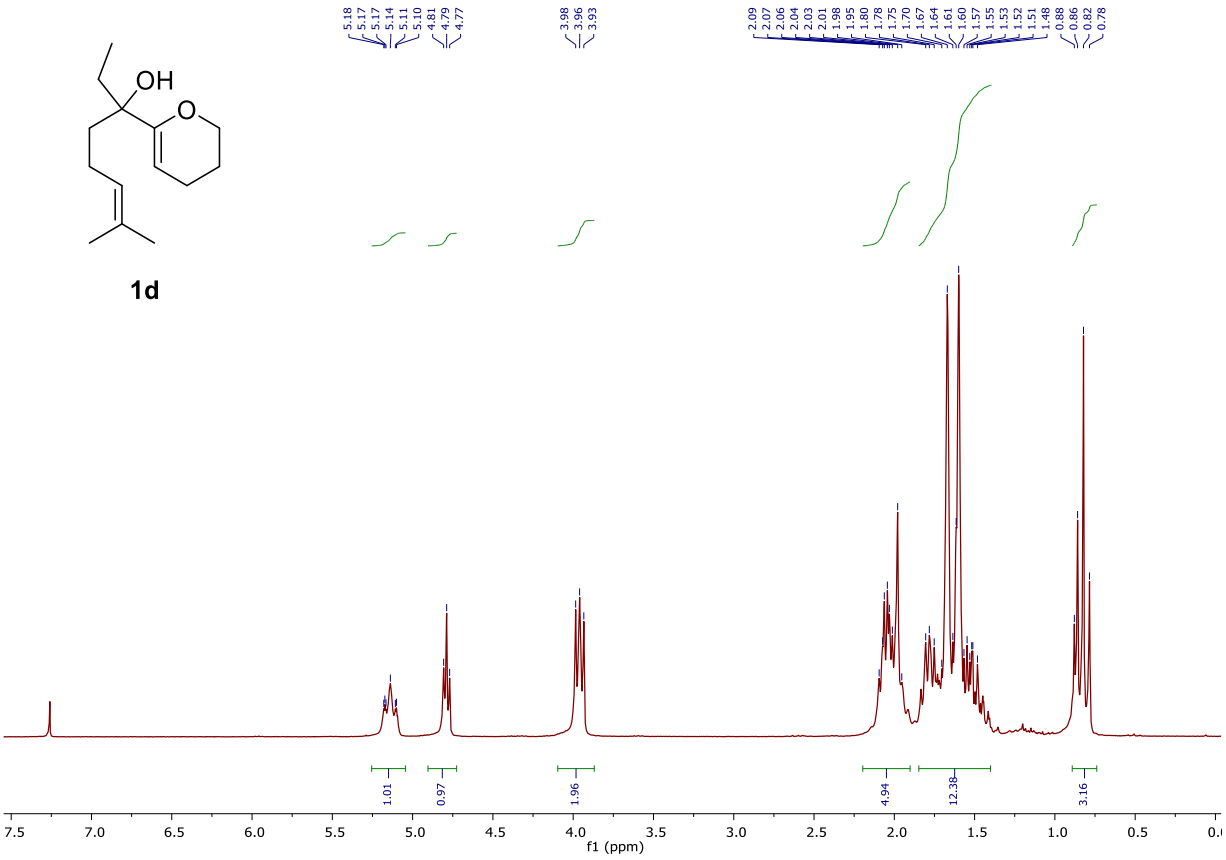
157.05
146.35
109.57
94.18
73.45
66.27
38.27
32.50
25.77
22.62
22.34
19.94
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

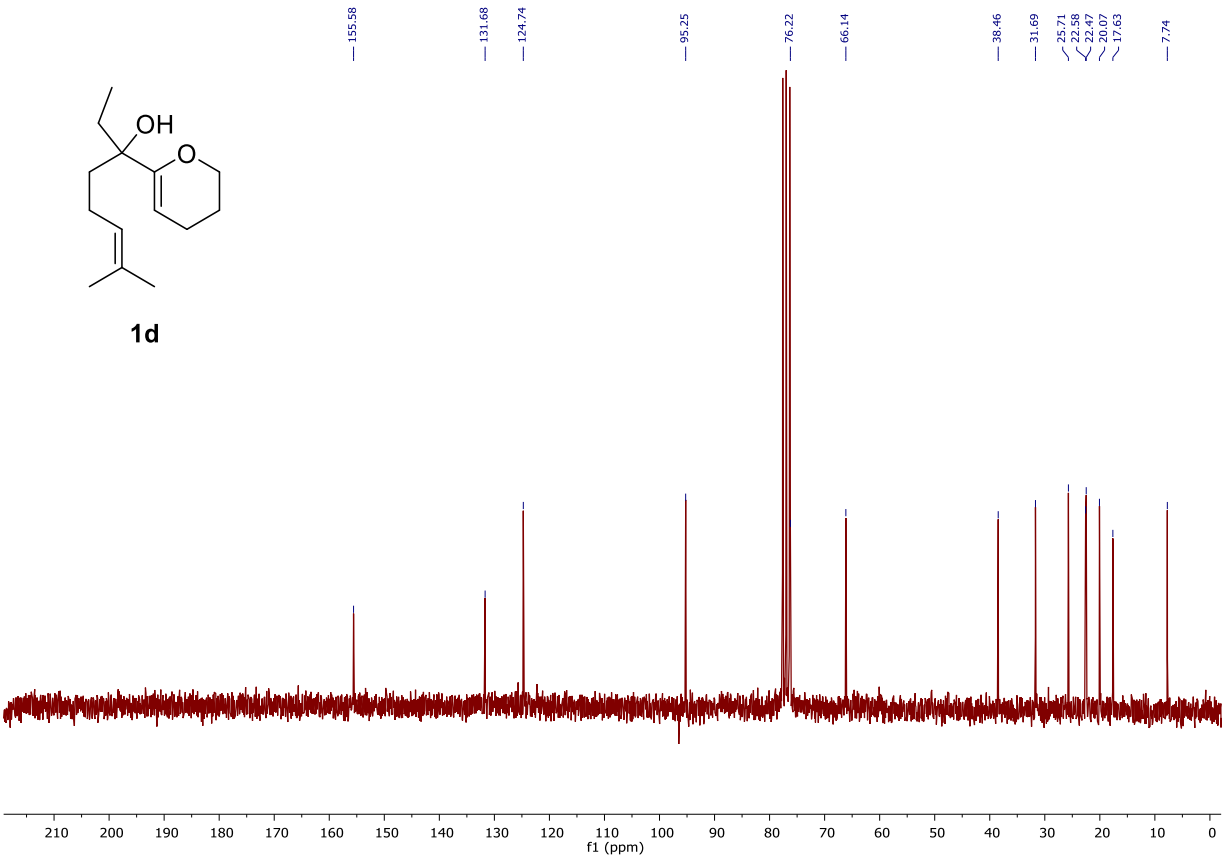

7.53 7.52 7.51 7.50 7.49 7.48 7.47 7.39 7.39 7.38 7.35 7.35 7.35 7.34 7.34 7.32 7.31 7.31 7.30 7.29 7.29 7.26
4.96 4.94 4.93 4.69 4.68 4.68 4.67 4.67 4.66 4.66 4.40 4.40 4.35 4.31
2.74 2.73 2.70 2.68 2.65 2.64 2.59 2.24 2.23 2.22 2.20 2.19 2.18 2.18 2.16 2.15 2.14 2.13 2.12 2.09 2.08 2.05 2.03 2.03 1.97 1.95 1.92 1.88 1.86 1.82 1.80 1.71 1.70 1.70
OH
O
3c
2.13
3.20
1.00
2.05
2.02
2.04
0.97
3.04
1.12
2.98
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

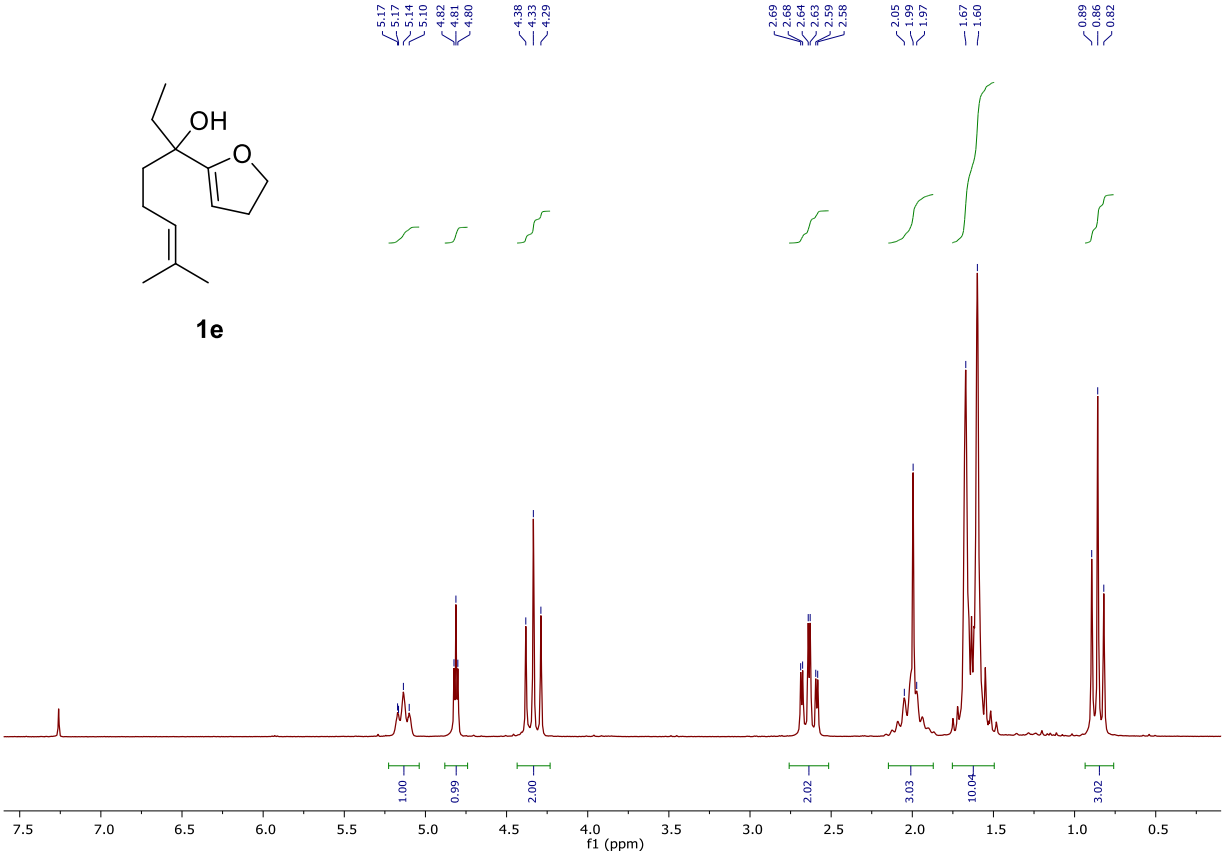

161.20
146.22
144.09
128.19
127.28
125.49
109.76
95.83
75.22
70.58
38.35
31.74
30.20
22.87
OH
O
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

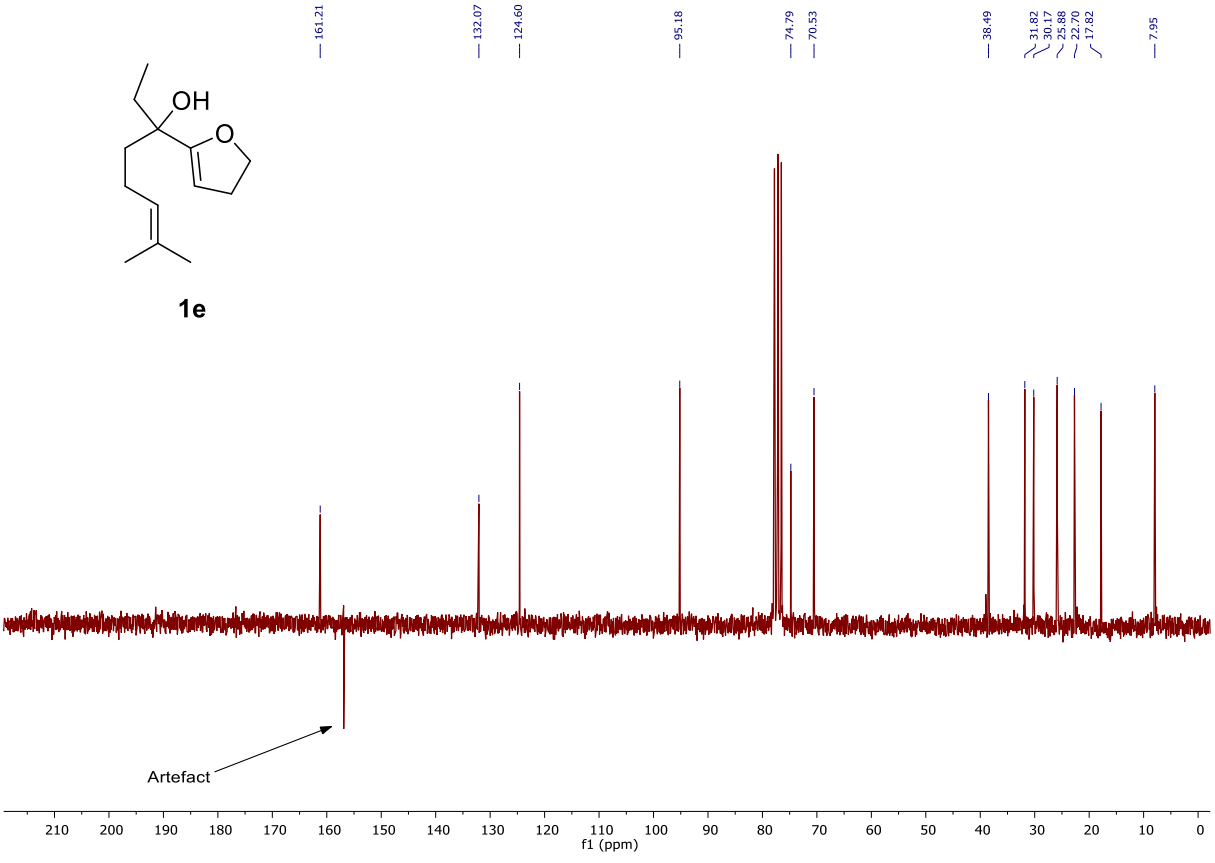

OH
O
3d
f1 (ppm)

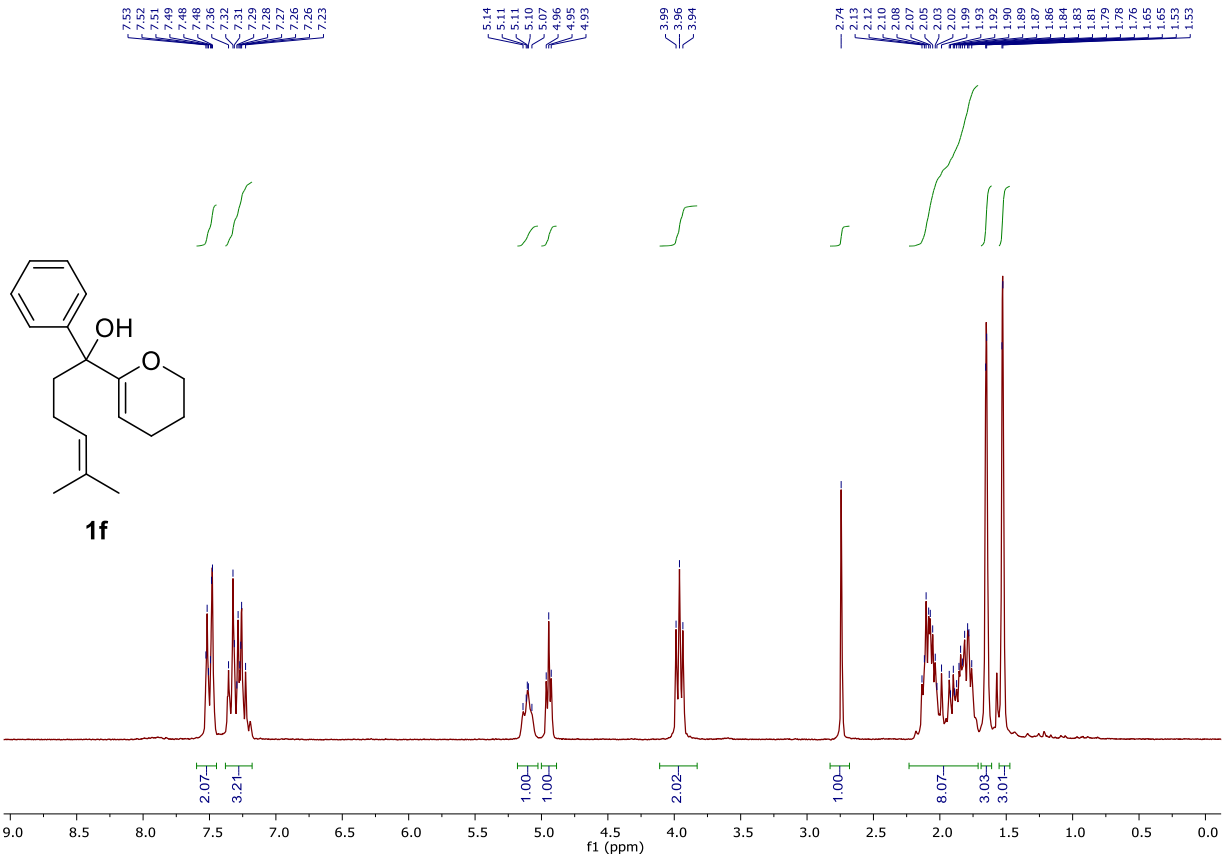

OH
O
3d
f1 (ppm)

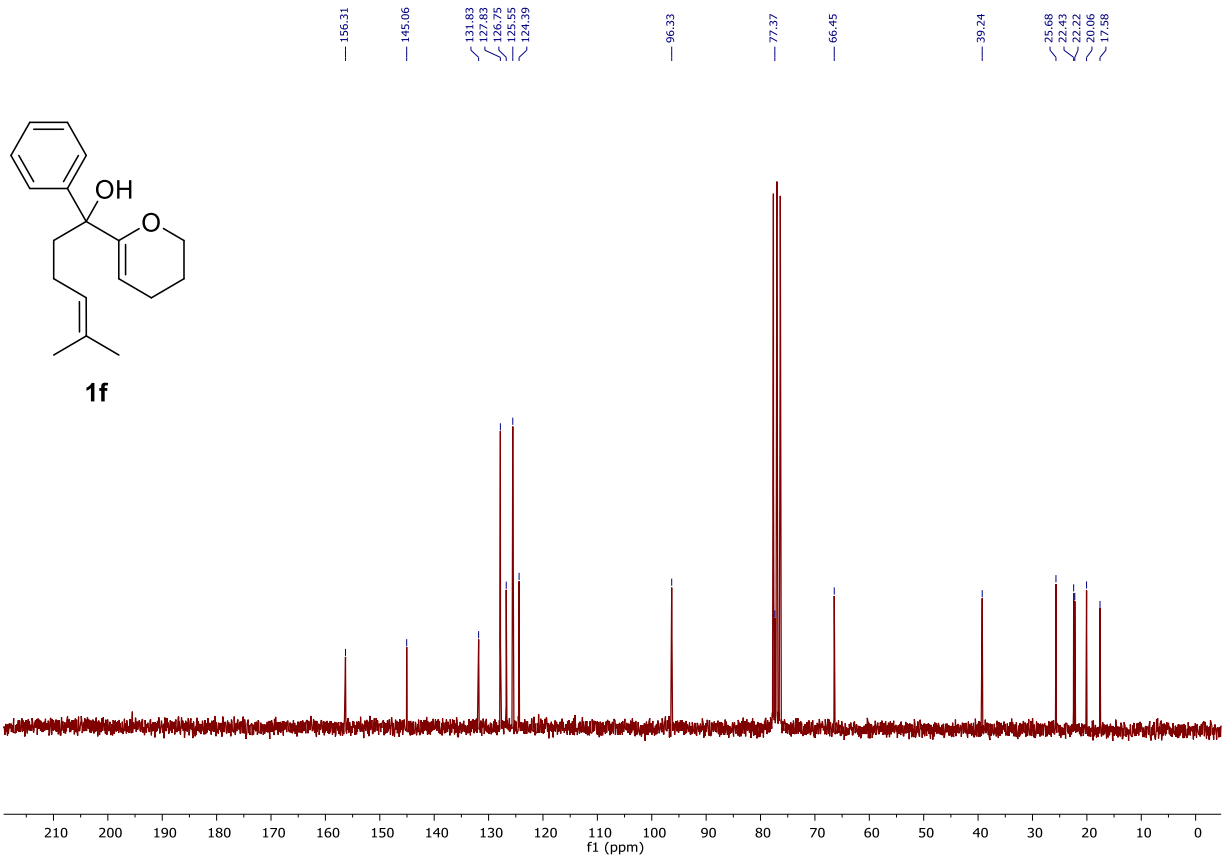

OH
O
1d
5.18
5.17
5.17
5.14
5.11
5.10
4.81
4.79
4.77
3.98
3.96
3.93
2.09
2.07
2.06
2.04
2.03
2.01
1.98
1.95
1.80
1.78
1.75
1.70
1.67
1.64
1.61
1.60
1.57
1.55
1.53
1.52
1.51
1.48
0.88
0.86
0.82
0.78
1.01
0.97
1.96
4.94
12.38
3.16
f1 (ppm)

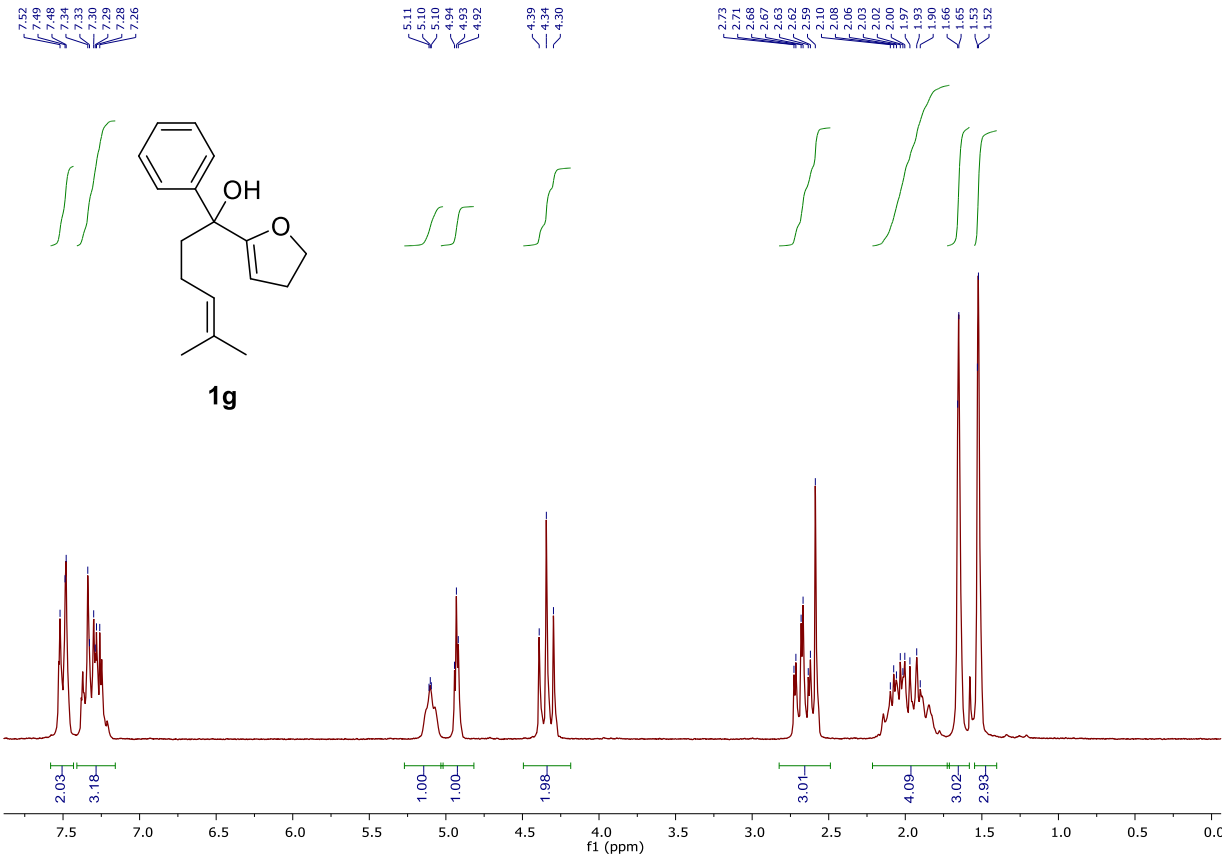

OH
O
1d
155.58
131.68
124.74
95.25
76.22
66.14
38.46
31.69
25.71
22.58
22.47
20.07
17.63
7.74
f1 (ppm)


OH
O
1e
5.17
5.17
5.14
5.10
4.82
4.81
4.80
4.38
4.33
4.29
2.69
2.68
2.64
2.63
2.59
2.58
2.05
1.99
1.97
1.67
1.60
0.89
0.86
0.82
1.00
0.99
2.00
2.02
3.03
10.04
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

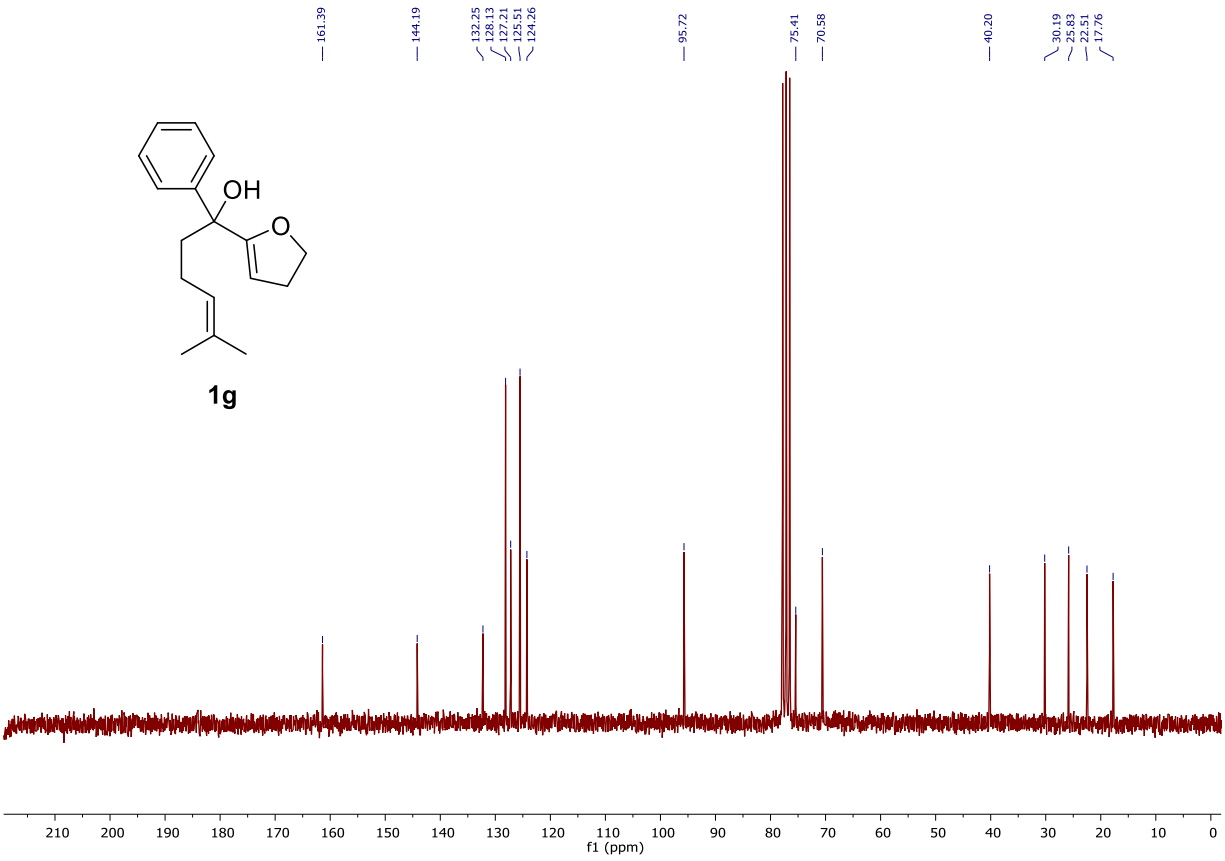

OH
O
1e
161.21
132.07
124.60
95.18
74.79
70.53
38.49
31.82
30.17
25.88
22.70
17.82
7.95
Artefact
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.53
7.52
7.51
7.49
7.48
7.48
7.36
7.32
7.31
7.29
7.28
7.27
7.26
7.26
7.23
5.14
5.11
5.11
5.11
5.10
5.07
4.96
4.95
4.93
3.99
3.96
3.94
2.74
2.13
2.12
2.10
2.08
2.07
2.05
2.03
2.02
1.99
1.93
1.92
1.90
1.89
1.87
1.86
1.84
1.83
1.81
1.79
1.78
1.76
1.65
1.65
1.53
1.53
OH
O
1f
2.07
3.21
1.00
1.00
2.02
1.00
8.07
3.03
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

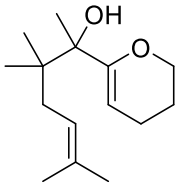

156.31
145.06
131.83
127.83
126.75
125.55
124.39
96.33
77.37
66.45
39.24
25.68
22.43
22.22
20.06
17.58
OH
O
1f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.52
7.49
7.48
7.34
7.33
7.30
7.29
7.28
7.26
5.11
5.10
5.10
4.94
4.93
4.92
4.39
4.34
4.30
2.73
2.71
2.68
2.67
2.63
2.62
2.59
2.10
2.08
2.06
2.03
2.02
2.00
1.97
1.93
1.90
1.66
1.65
1.53
1.52
OH
O
2.03
3.18
1.00
1.00
1.98
3.01
4.09
3.02
2.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

1g

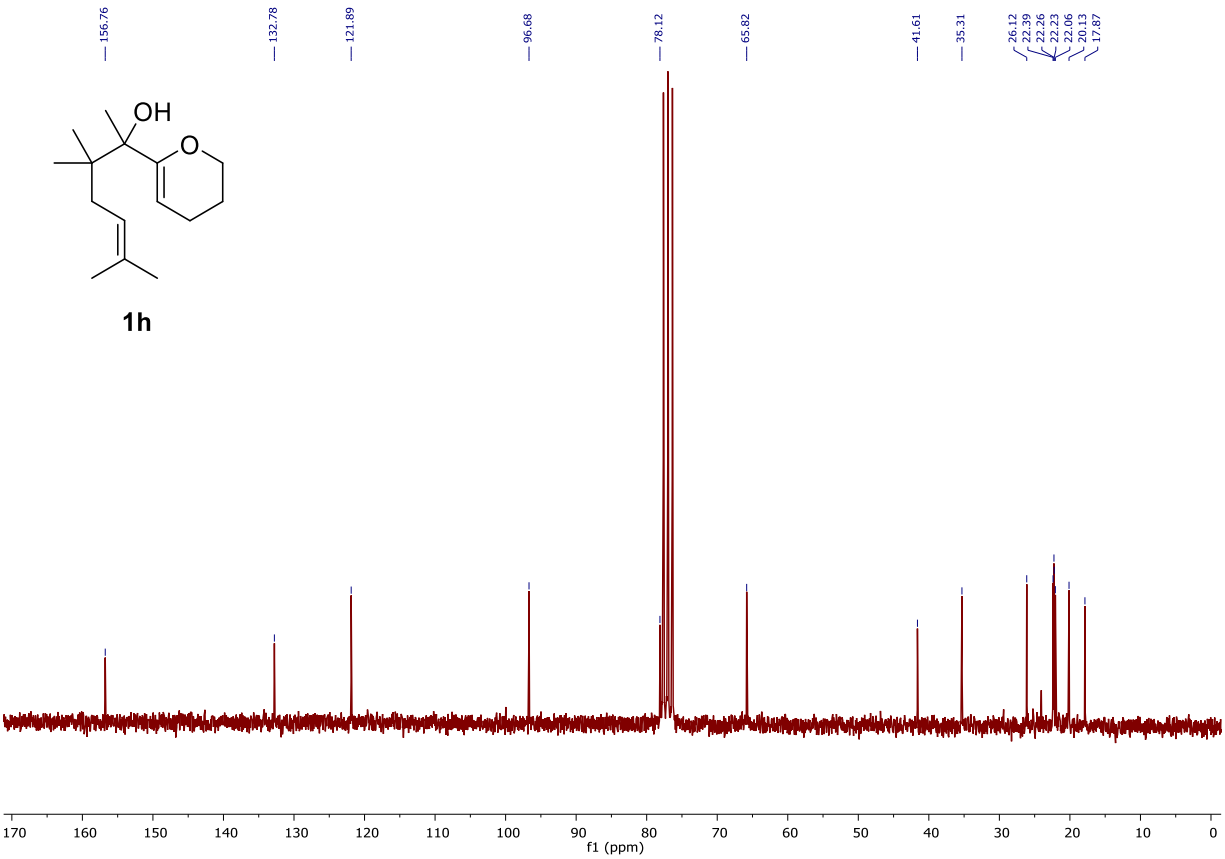

161.39
144.19
132.25
128.13
127.21
125.51
124.26
95.72
75.41
70.58
40.20
30.19
25.83
22.51
17.76
OH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

1g


OH
O

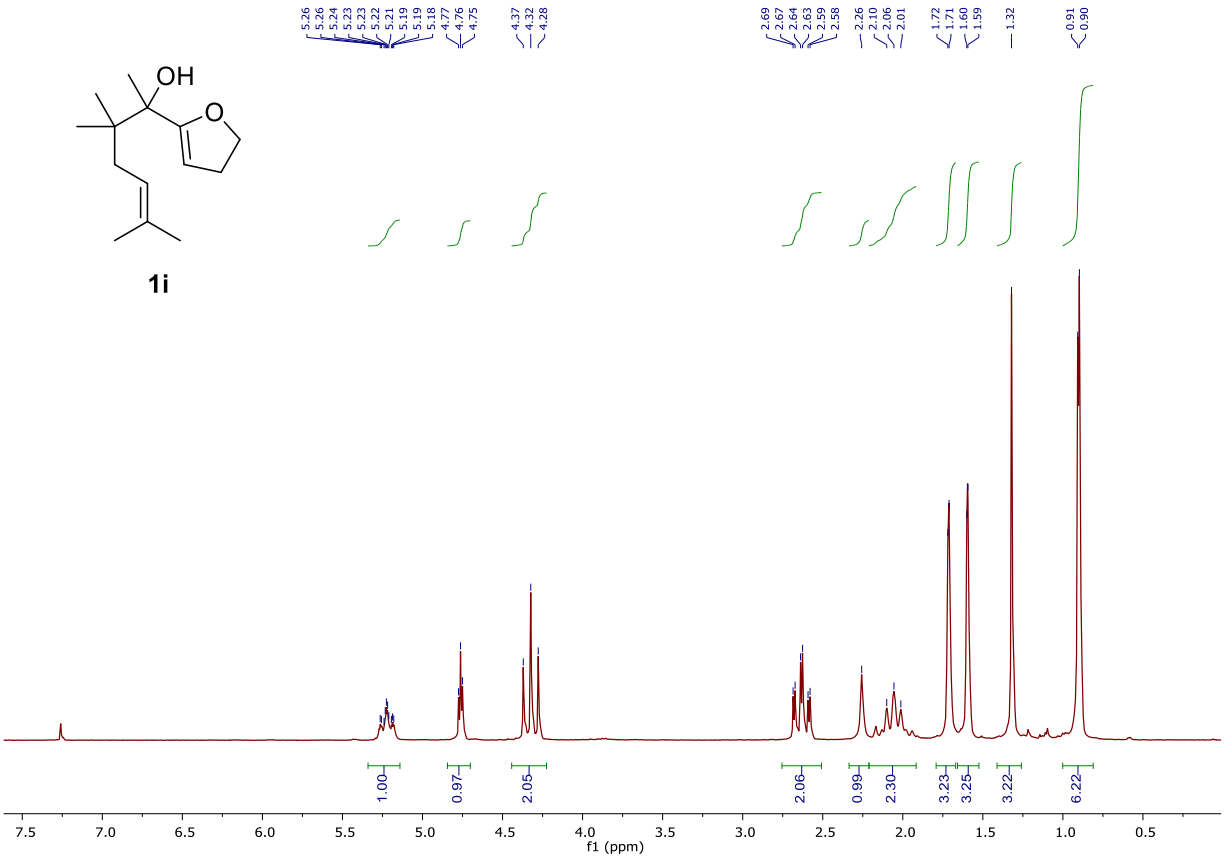
1h

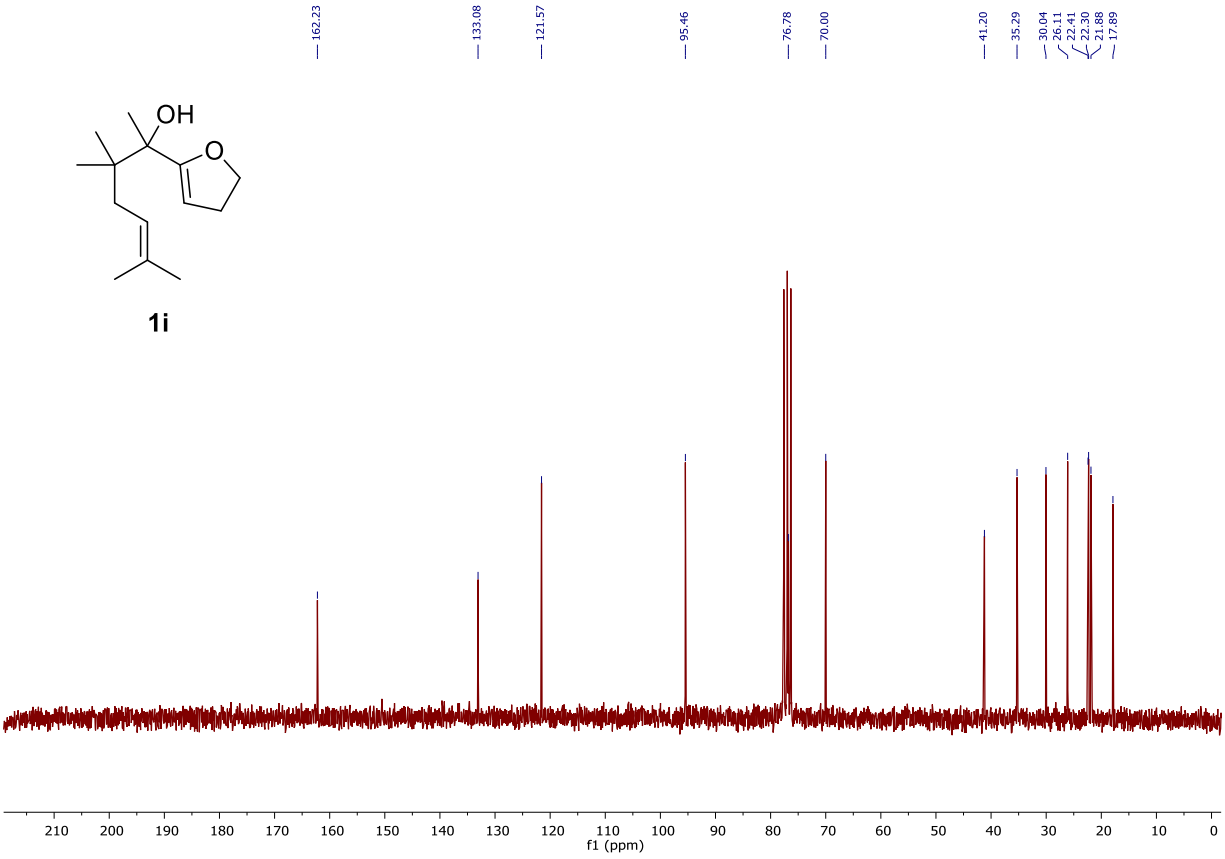
5.27 5.26 5.25 5.23 5.22 5.21 5.19 5.18 5.17 4.76 4.74 4.73
4.00 3.99 3.98 3.97 3.96 3.94 3.93
2.52 2.11 2.09 2.09 2.08 2.06 2.05 2.04 2.03 2.00 1.82 1.81 1.79 1.77 1.77 1.76 1.75 1.74 1.72 1.72 1.71 1.71 1.69 1.68 1.61 1.60 1.59 1.28 1.10 0.88 0.87
1.02 1.00 2.05 1.00 4.53 5.42 3.75 3.00 6.24
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

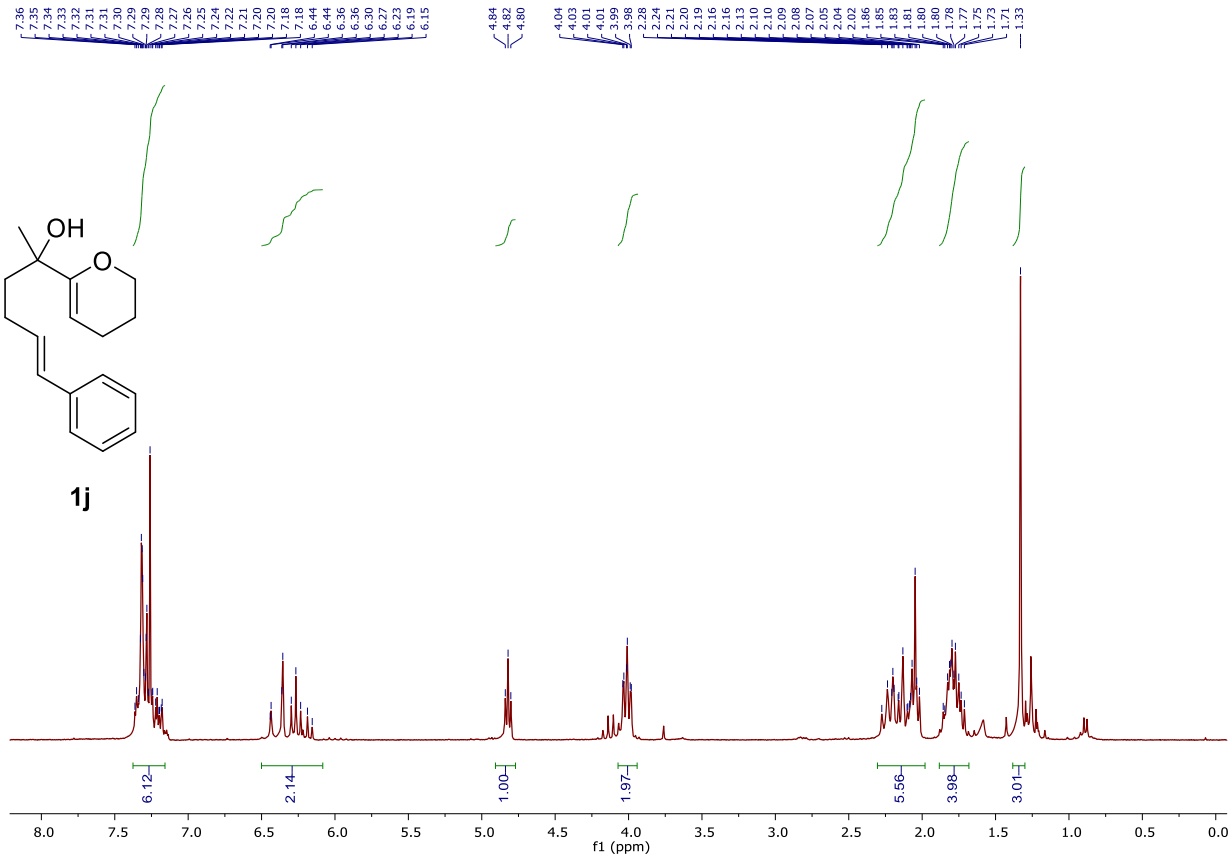

156.76
132.78
121.89
96.68
78.12
65.82
41.61
35.31
26.12 22.39 22.26 22.23 22.06 20.13 17.87
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

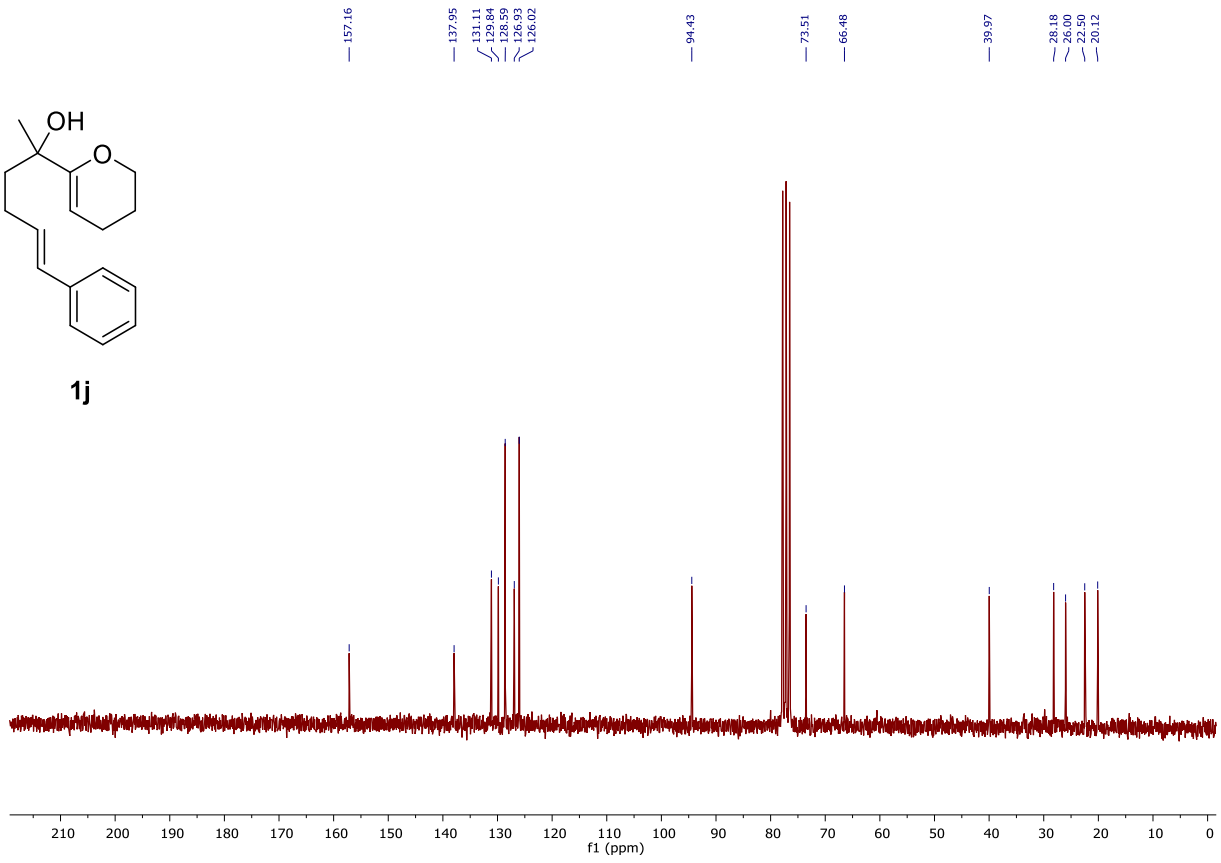
OH
O

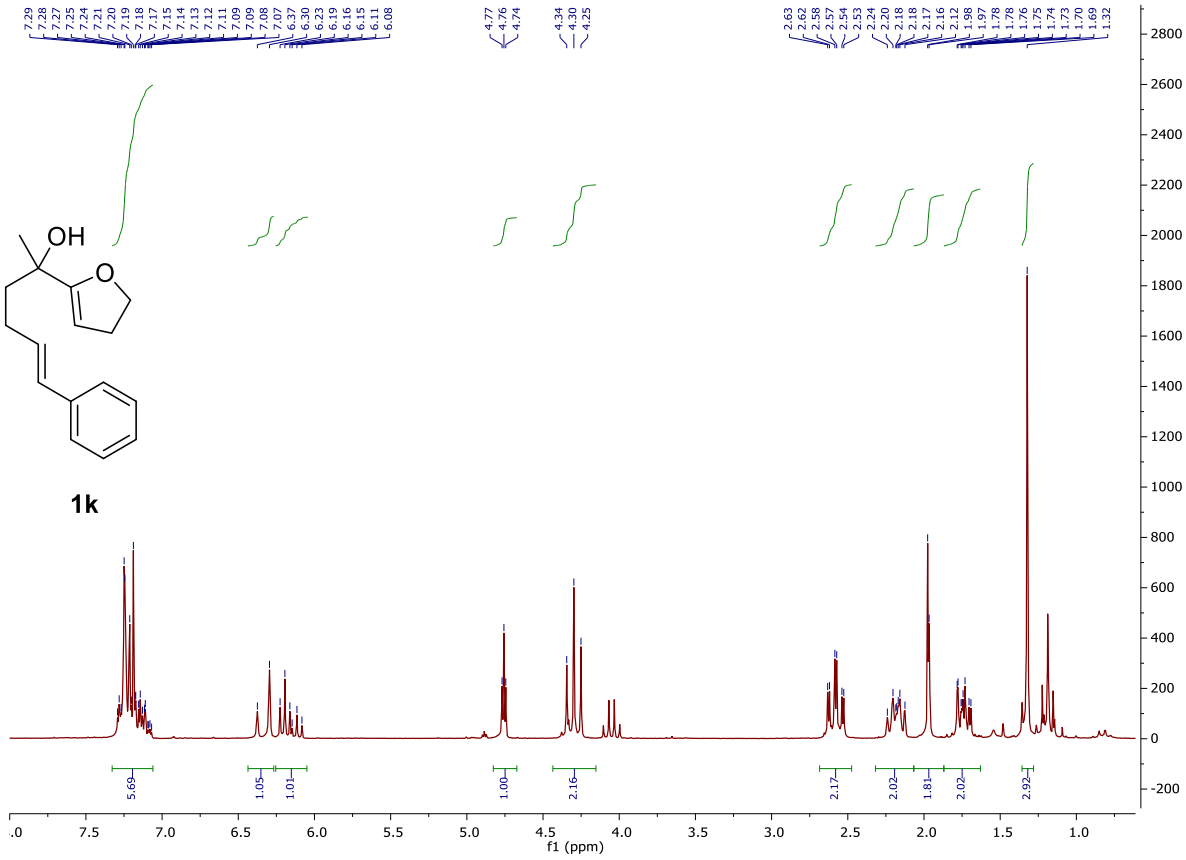
1h

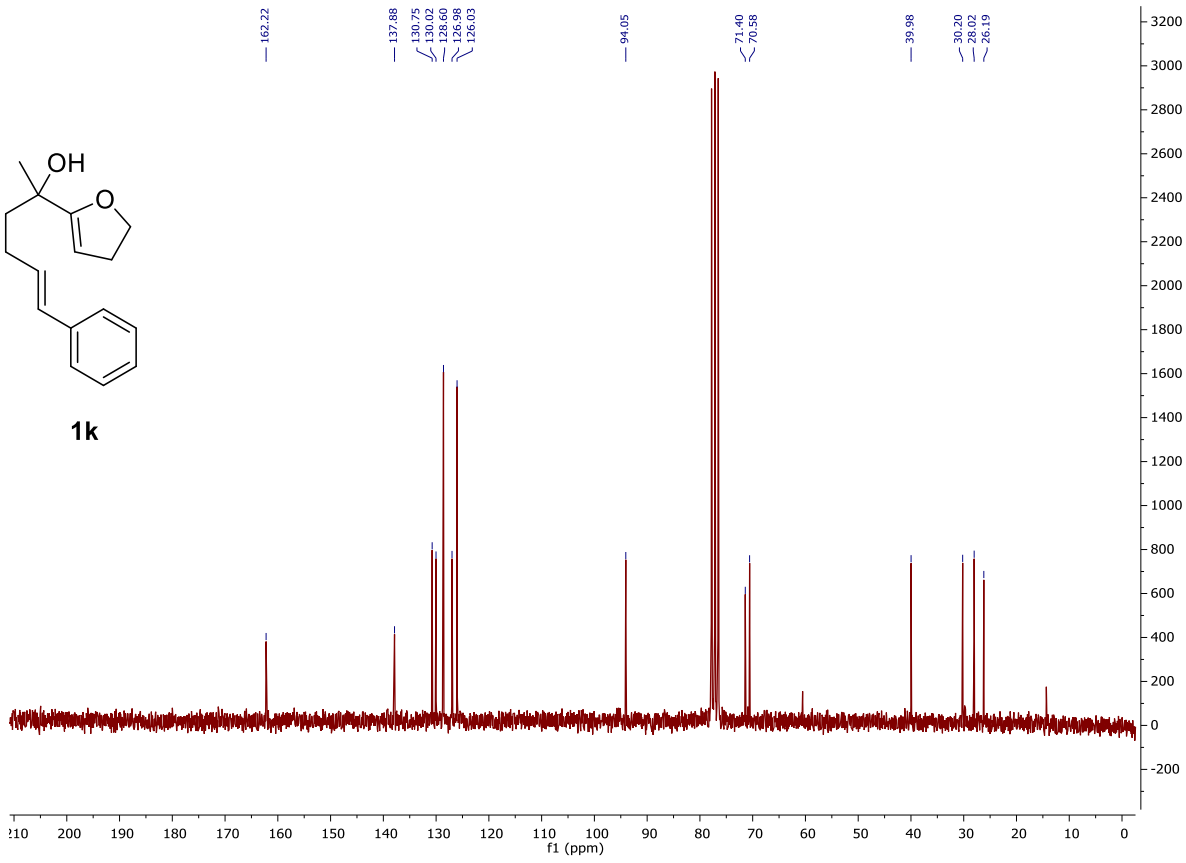

OH
O
1i
5.26
5.26
5.24
5.23
5.23
5.22
5.21
5.19
5.19
5.18
4.77
4.76
4.75
4.37
4.32
4.28
2.69
2.67
2.64
2.63
2.59
2.58
2.26
2.10
2.06
2.01
1.72
1.71
1.60
1.59
1.32
0.91
0.90
1.00
0.97
2.05
2.06
0.99
2.30
3.23
3.25
3.22
6.22
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

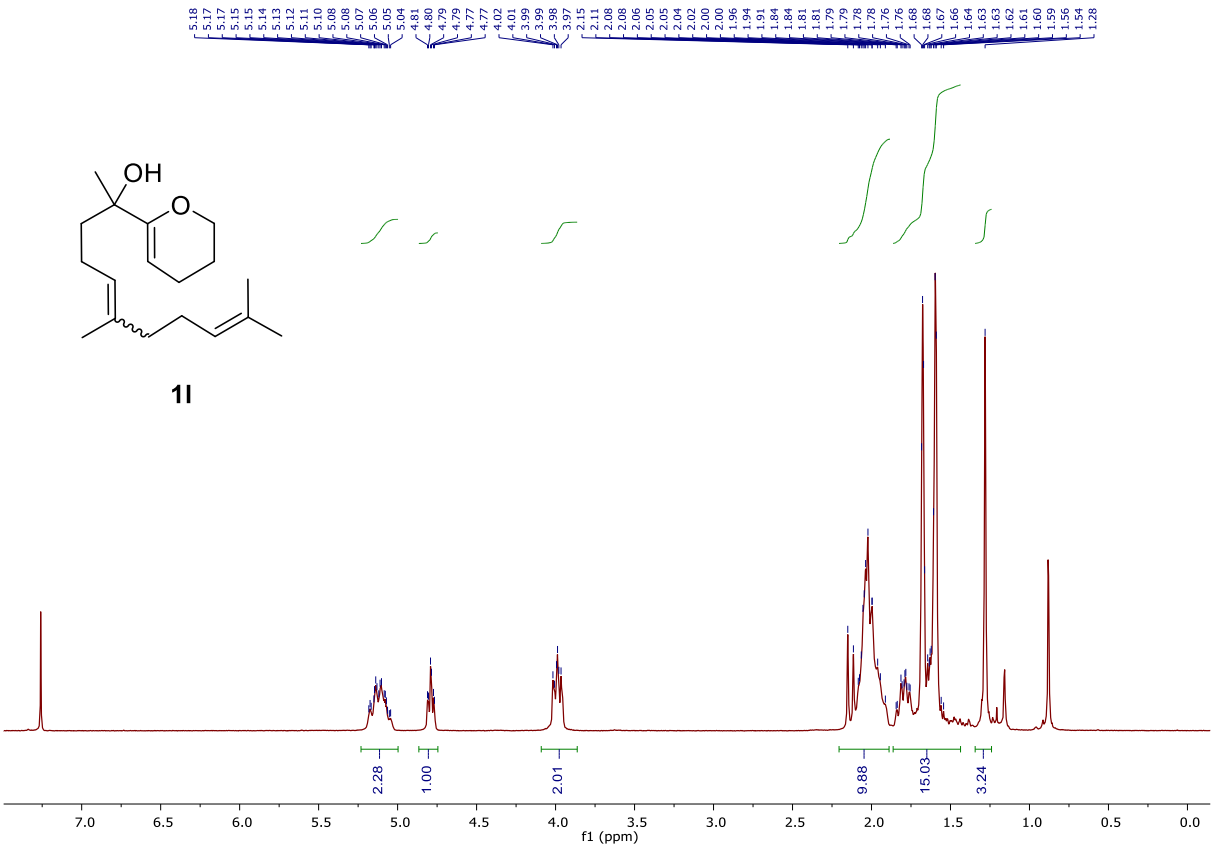

OH
O
1i
162.23
133.08
121.57
95.46
76.78
70.00
41.20
35.29
30.04
26.11
22.41
22.30
21.88
17.89
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

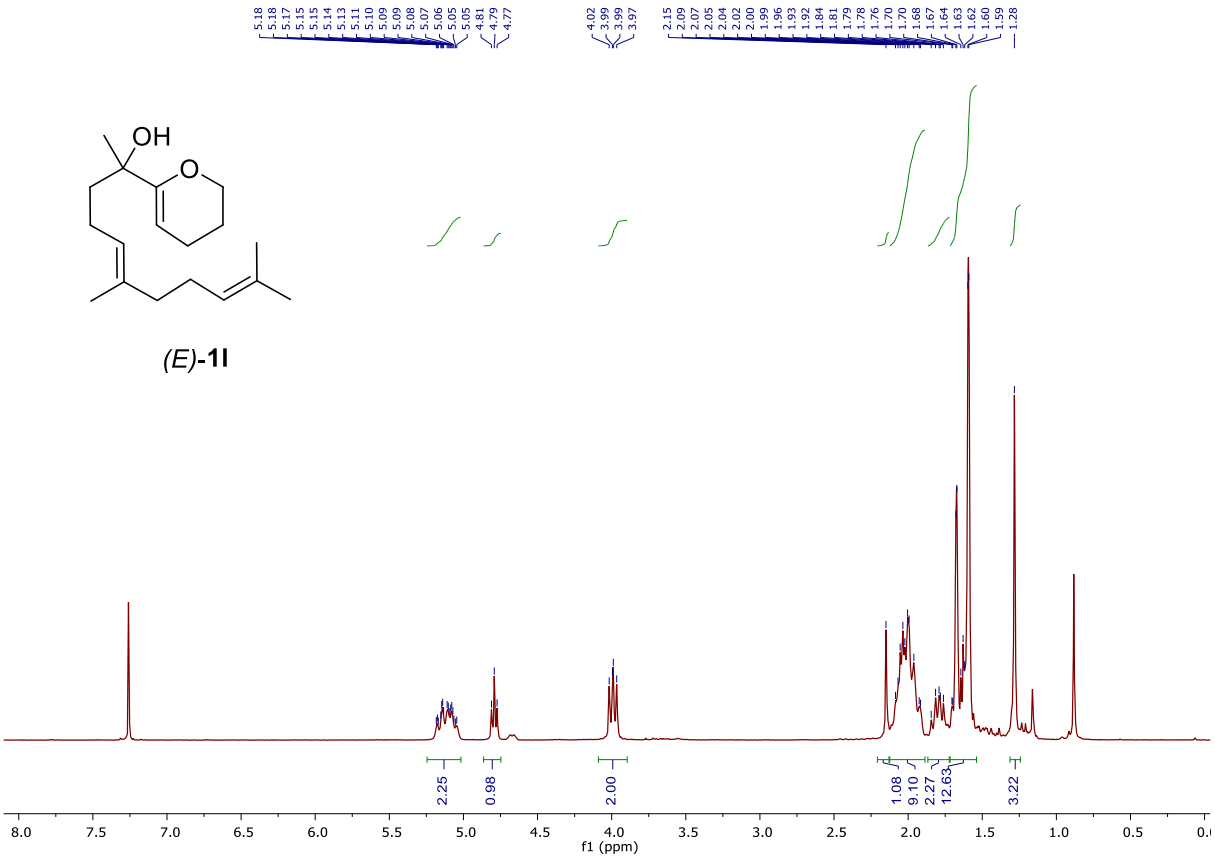

OH
O
1j
f1 (ppm)


OH
O
1j
f1 (ppm)

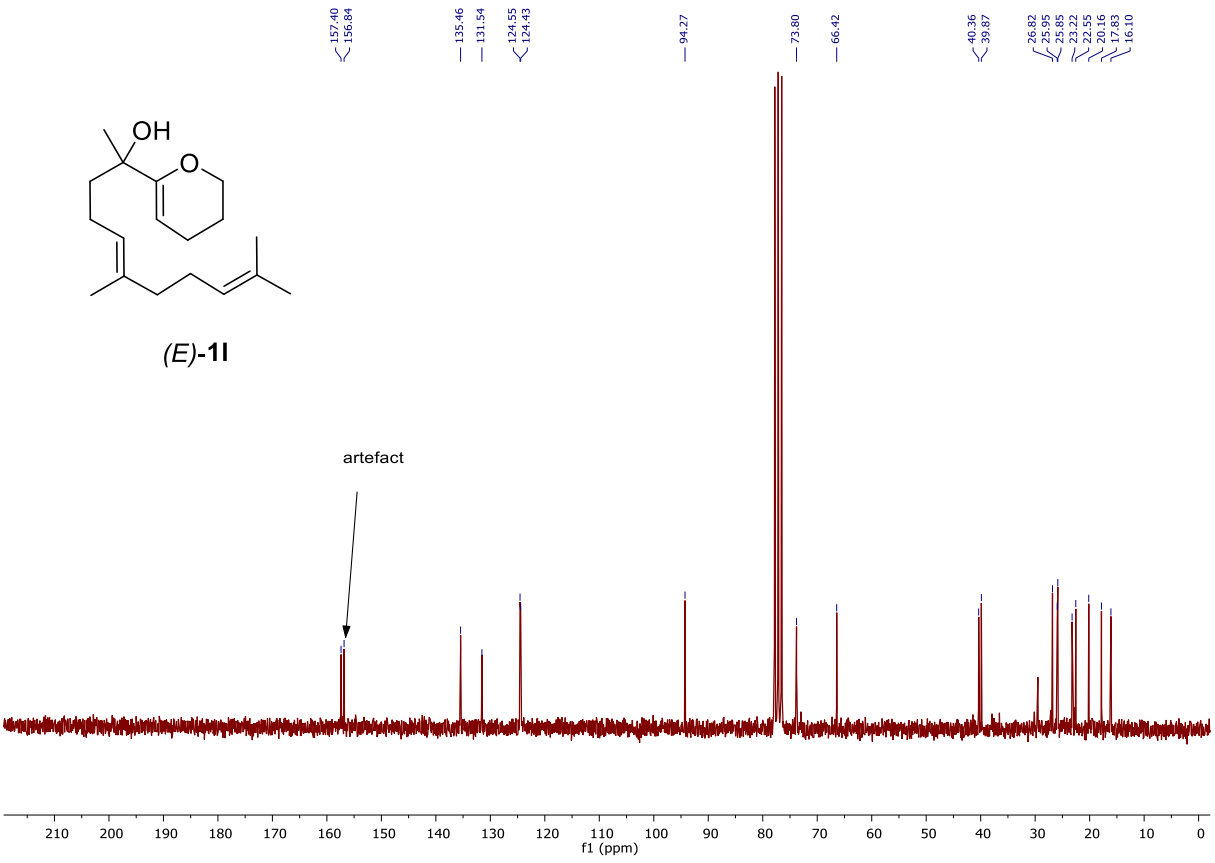

OH
O
1k
f1 (ppm)


OH
O
1k
f1 (ppm)

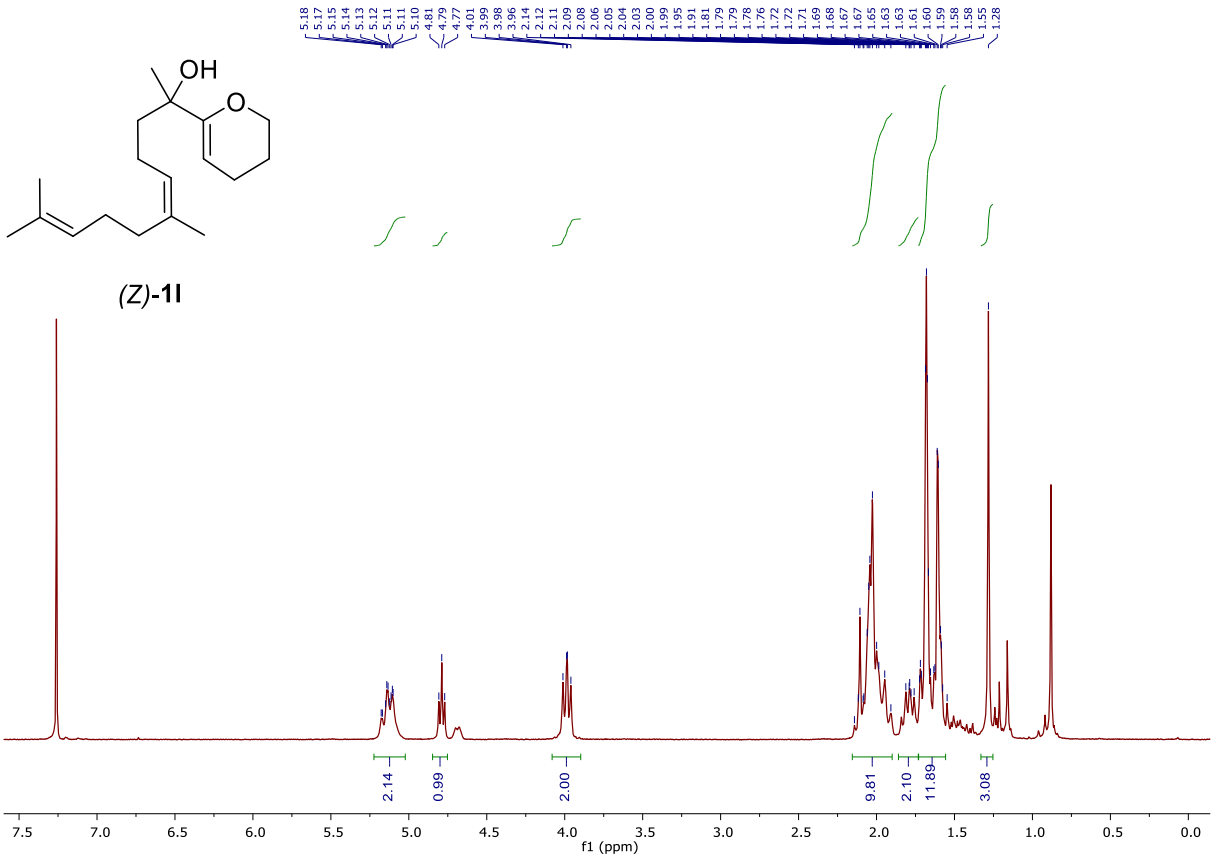

OH
O
1l
5.18 5.17 5.17 5.17 5.15 5.15 5.14 5.13 5.12 5.11 5.10 5.08 5.08 5.07 5.06 5.05 5.04 4.81 4.80 4.79 4.79 4.77 4.77 4.02 4.01 3.99 3.99 3.98 3.97 2.15 2.11 2.08 2.08 2.06 2.05 2.05 2.04 2.02 2.00 2.00 1.96 1.94 1.91 1.84 1.84 1.81 1.81 1.79 1.79 1.78 1.78 1.76 1.76 1.68 1.68 1.67 1.66 1.64 1.63 1.62 1.61 1.60 1.59 1.56 1.54 1.28
2.28
1.00
2.01
9.88
15.03
3.24
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

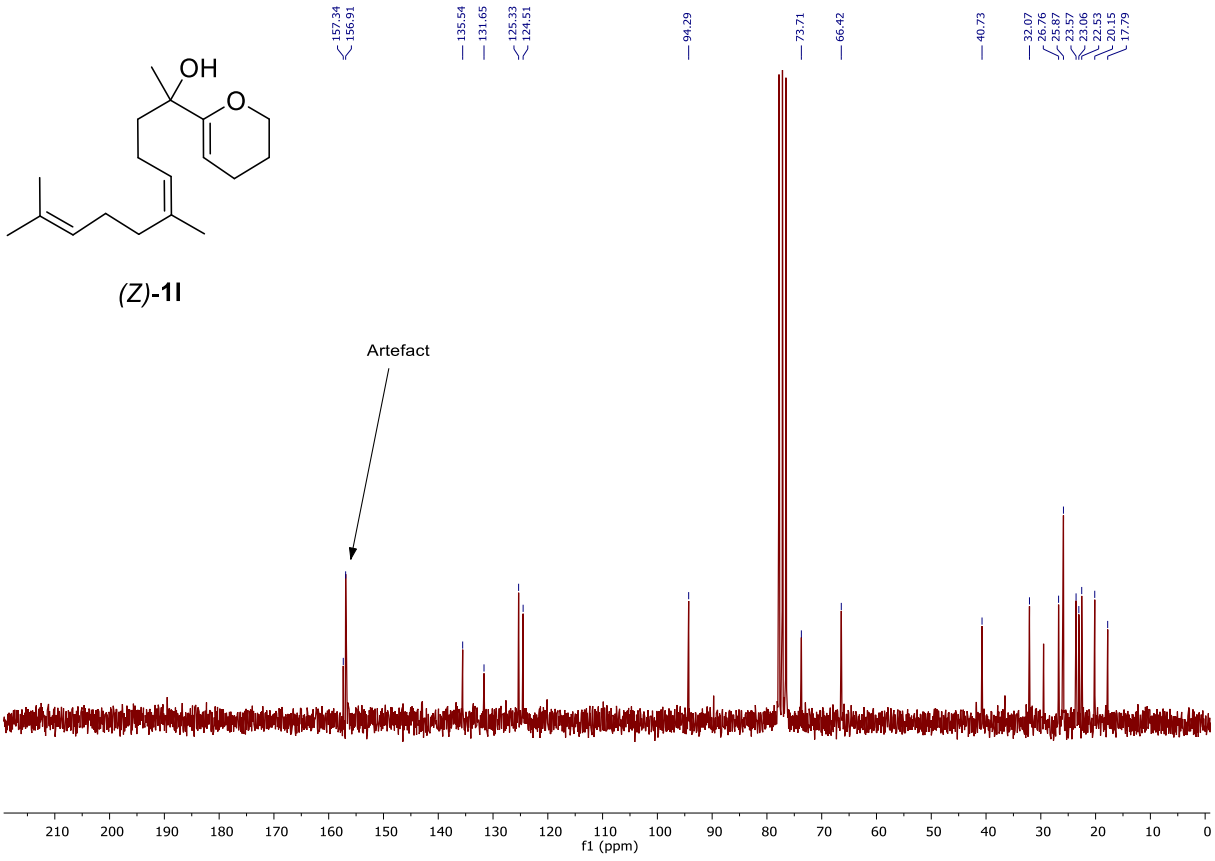

OH
O
5.18 5.18 5.17 5.15 5.15 5.14 5.13 5.11 5.10 5.09 5.09 5.08 5.07 5.06 5.05 5.05 4.81 4.79 4.77
4.02 3.99 3.99 3.97
2.15 2.09 2.07 2.05 2.04 2.02 2.00 1.99 1.96 1.93 1.92 1.84 1.81 1.79 1.78 1.76 1.70 1.70 1.68 1.67 1.64 1.63 1.62 1.60 1.59 1.28
2.25
0.98
2.00
1.08
9.10
2.27
12.63
3.22
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

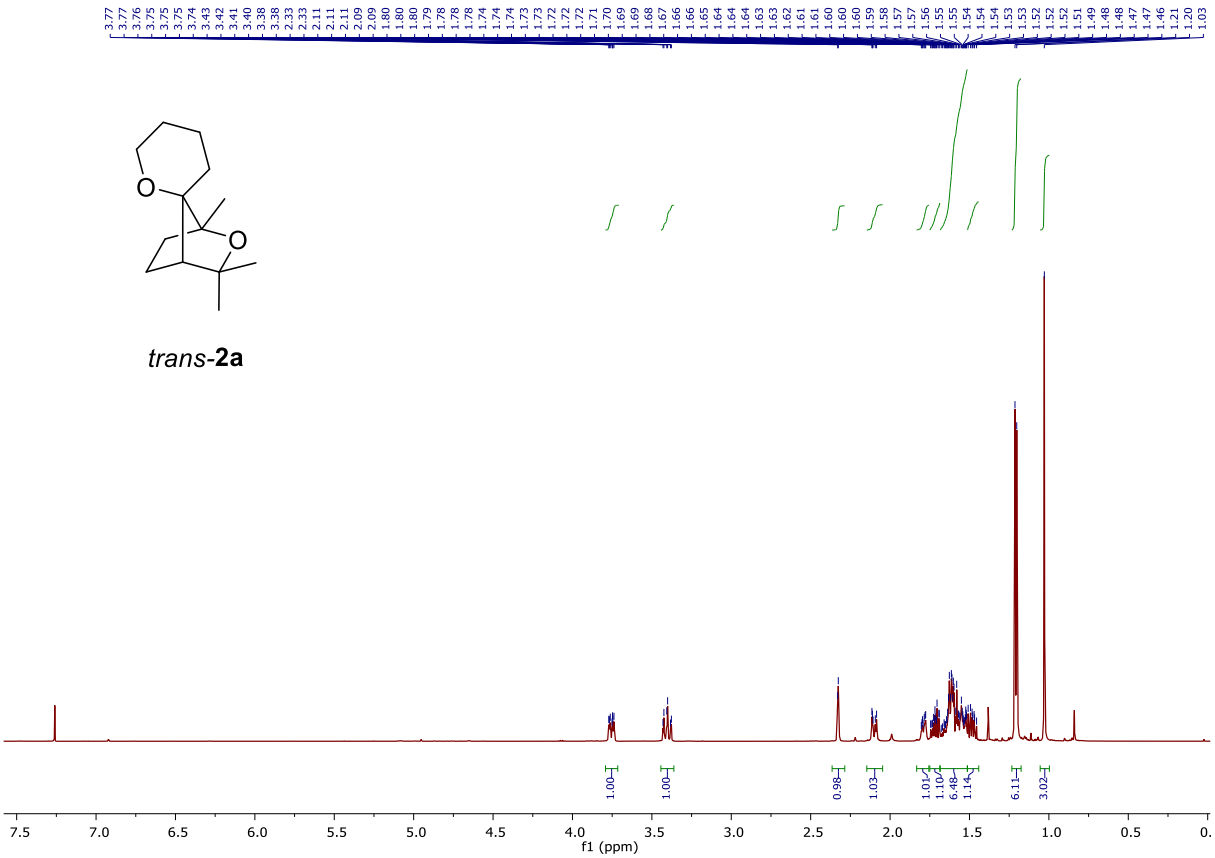
(E)-**1l**


OH
O
157.40
156.84
135.46
131.54
124.55
124.43
94.27
73.80
66.42
40.36
39.87
26.82
25.95
25.85
23.22
22.55
20.16
17.83
16.10
artefact
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

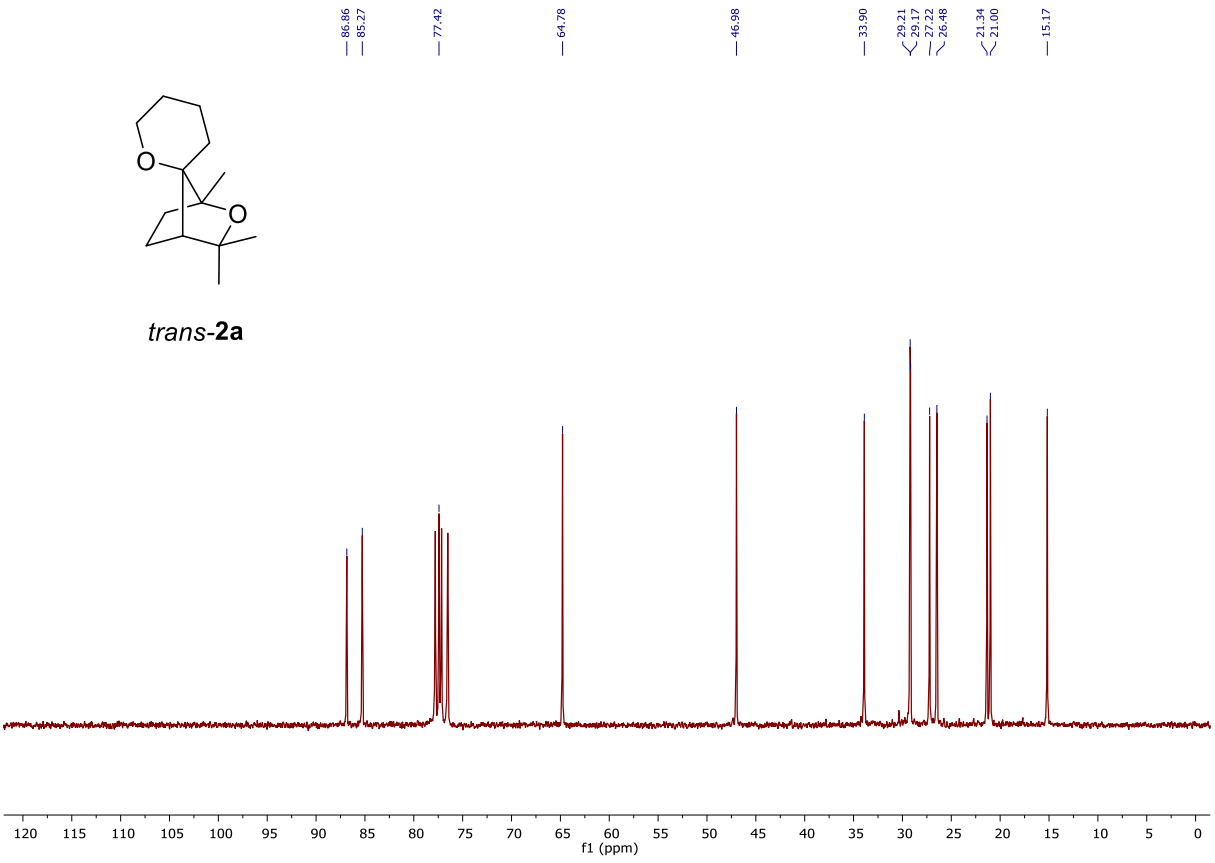
(E)-**1l**


OH
O
(Z)-1l
5.18 5.17 5.15 5.14 5.13 5.12 5.11 5.11 5.10 4.81 4.79 4.77 4.01 3.99 3.98 3.96 2.14 2.12 2.11 2.09 2.08 2.06 2.05 2.04 2.03 2.00 1.99 1.95 1.91 1.81 1.79 1.79 1.78 1.76 1.72 1.72 1.71 1.69 1.68 1.67 1.67 1.65 1.63 1.63 1.61 1.60 1.59 1.58 1.58 1.55 1.28
2.14
0.99
2.00
9.81
2.10
11.89
3.08
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

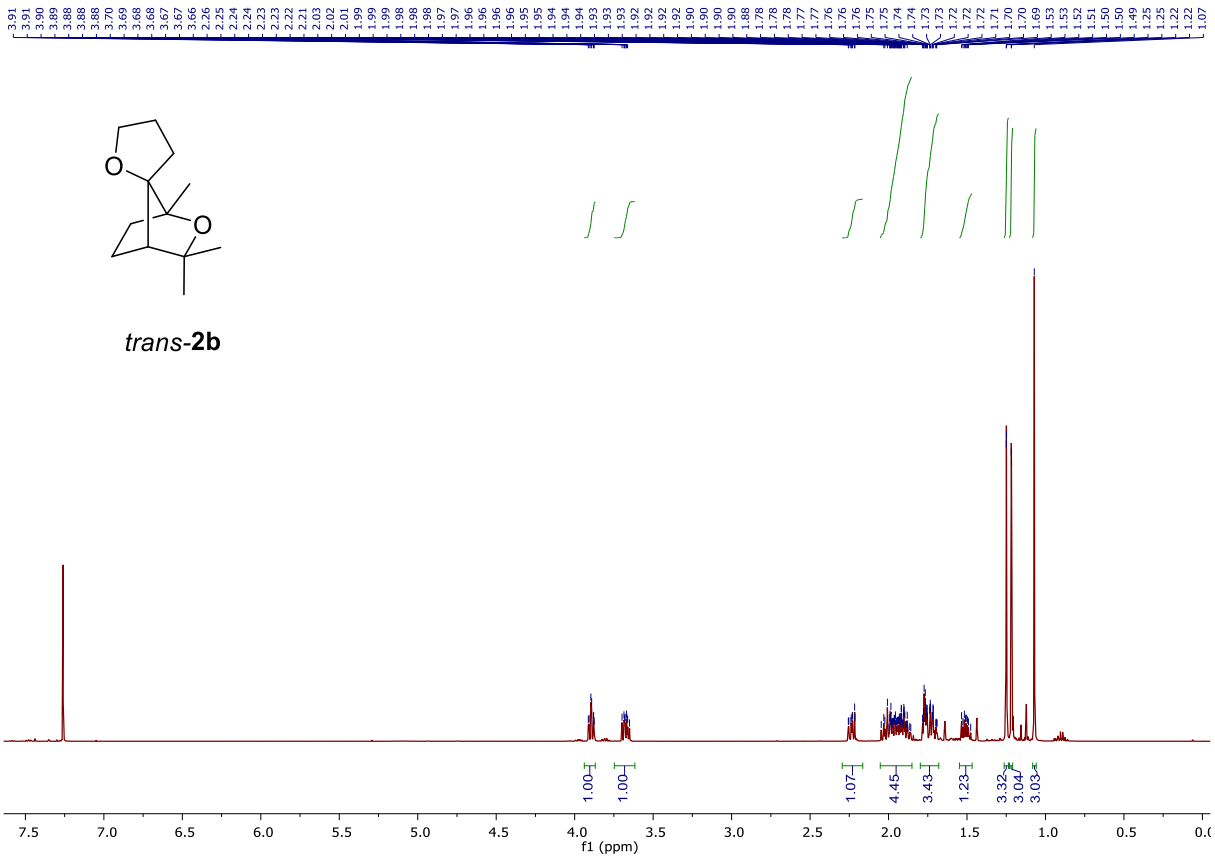

OH
O
(Z)-1l
157.34 156.91 135.54 131.65 125.33 124.51 94.29 73.71 66.42 40.73 32.07 26.76 25.87 23.57 23.06 22.53 20.15 17.79
Artefact
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

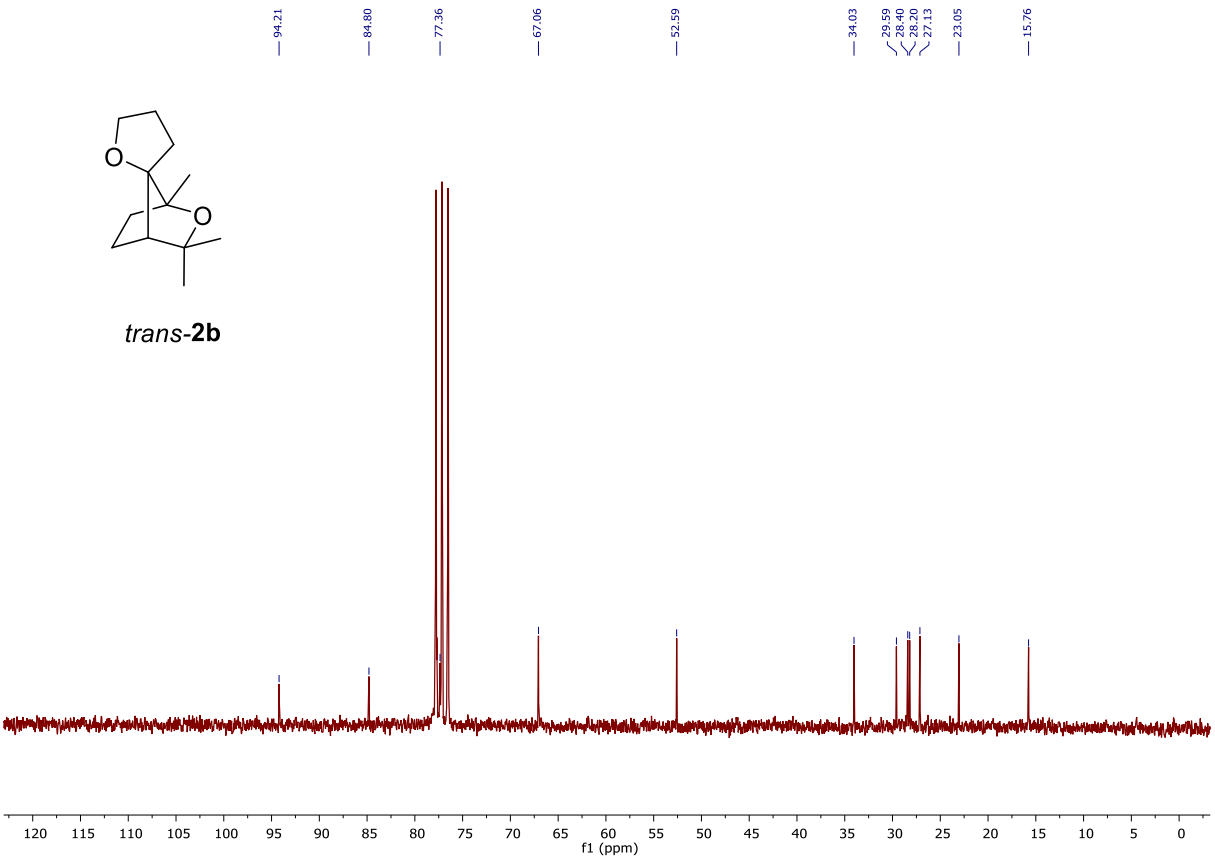


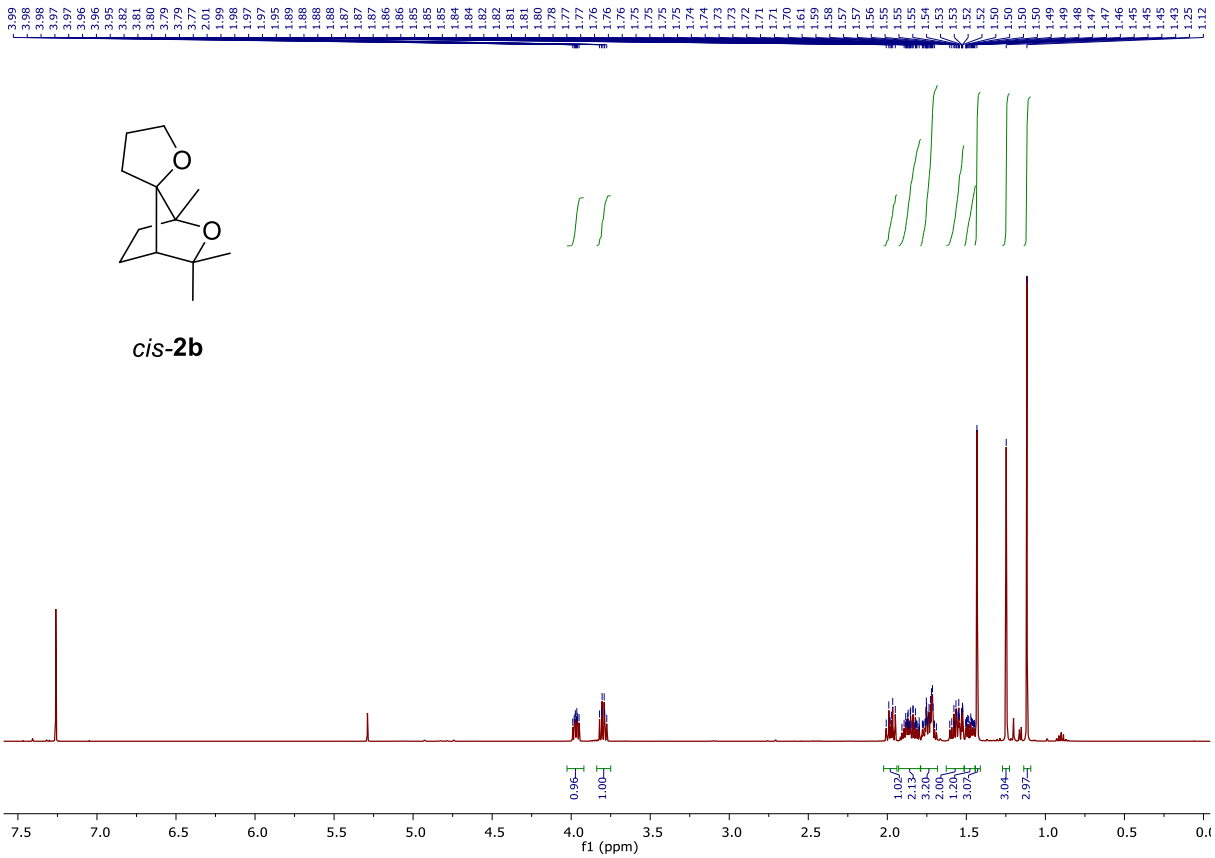
trans-**2a**

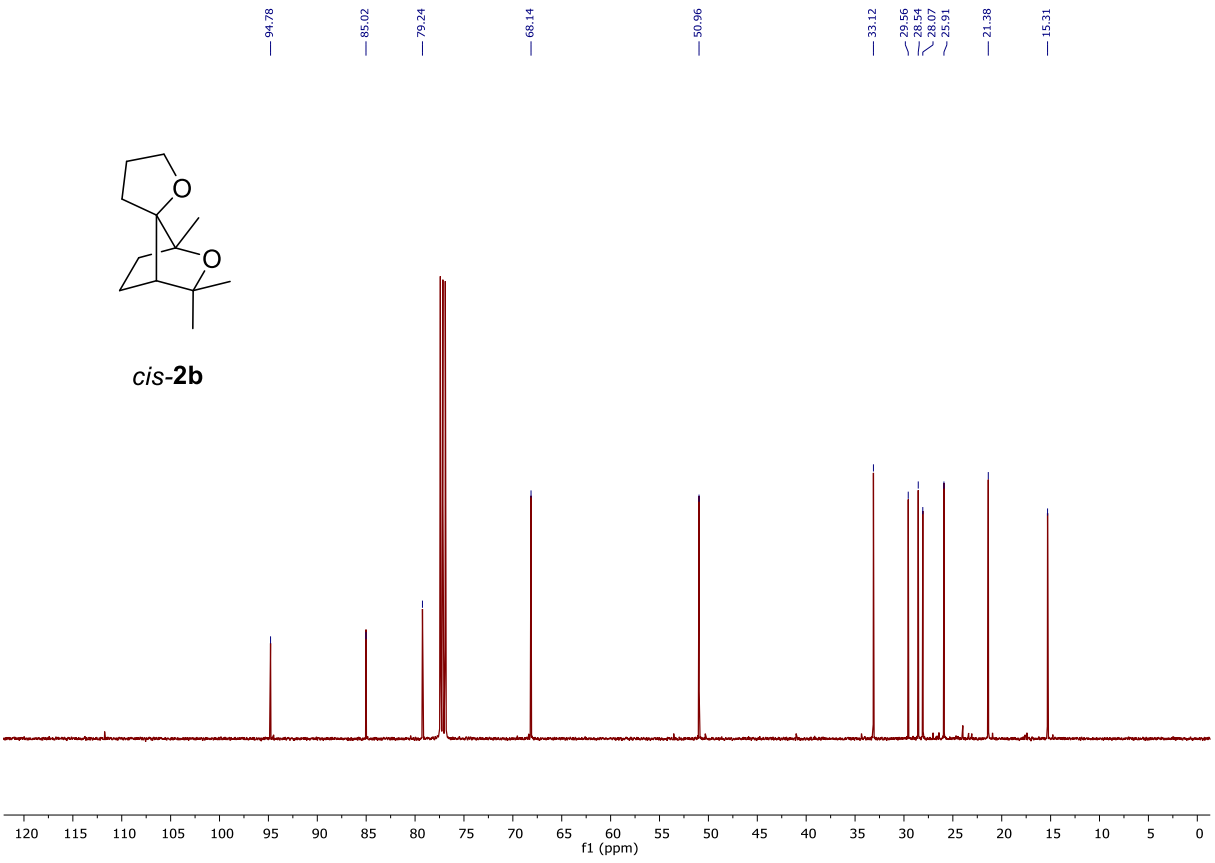


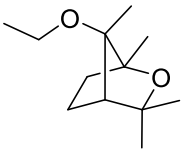
trans-**2a**


3.91 3.91 3.90 3.89 3.88 3.88 3.88 3.70 3.69 3.68 3.68 3.67 3.67 3.66 2.26 2.25 2.24 2.24 2.23 2.22 2.21 2.03 2.02 2.01 1.99 1.99 1.98 1.98 1.97 1.97 1.96 1.96 1.96 1.95 1.95 1.94 1.94 1.93 1.93 1.92 1.92 1.92 1.90 1.90 1.90 1.90 1.88 1.78 1.78 1.77 1.77 1.76 1.76 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.72 1.72 1.72 1.71 1.70 1.70 1.69 1.53 1.53 1.52 1.51 1.50 1.50 1.49 1.25 1.22 1.22 1.07
O
O
trans-2b
1.00 1.00 1.07 4.45 3.43 1.23 3.32 3.04 3.03
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

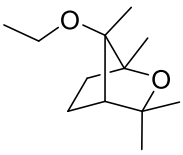

94.21 84.80 77.36 67.06 52.59 34.03 29.59 28.40 28.20 27.13 23.05 15.76
O
O
trans-2b
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


O
O
cis-2b
0.96
1.00
1.02
2.13
3.20
2.00
1.20
3.07
3.04
2.97
f1 (ppm)

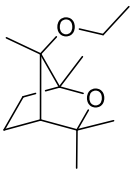

94.78
85.02
79.24
68.14
50.96
33.12
29.56
28.54
28.07
25.91
21.38
15.31
O
O
cis-2b
f1 (ppm)



trans-**2c**

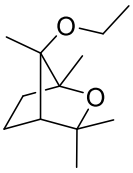


trans-**2c**



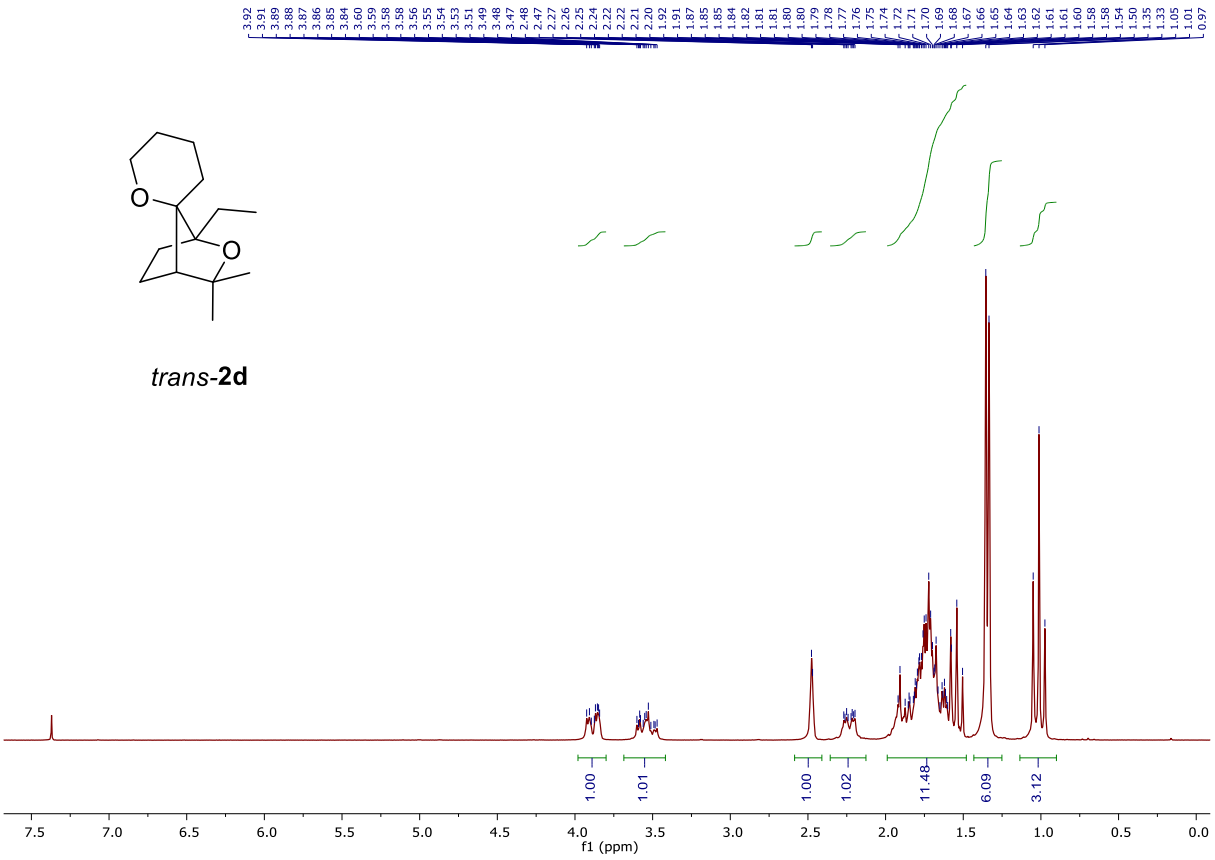
cis-**2c**

3.68
3.65
3.61
3.60
3.57
3.53
3.41
3.38
3.34
3.33
3.31
3.30
3.27
2.01
1.99
1.83
1.81
1.78
1.76
1.73
1.71
1.63
1.59
1.56
1.49
1.44
1.43
1.37
1.33
1.27
1.26
1.24
1.21
1.20
1.17
1.16
1.15
1.00
0.95
0.99
1.13
2.70
4.48
8.81
3.63
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

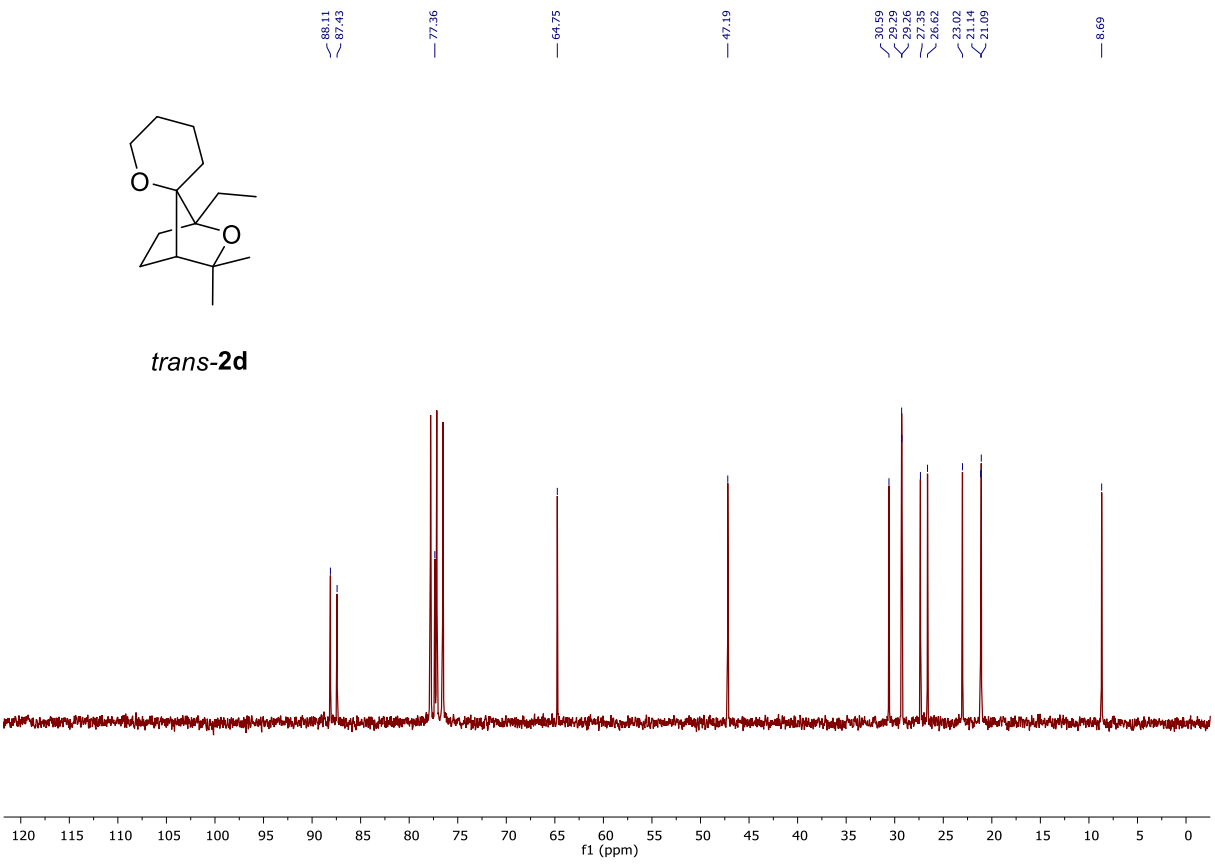


cis-**2c**

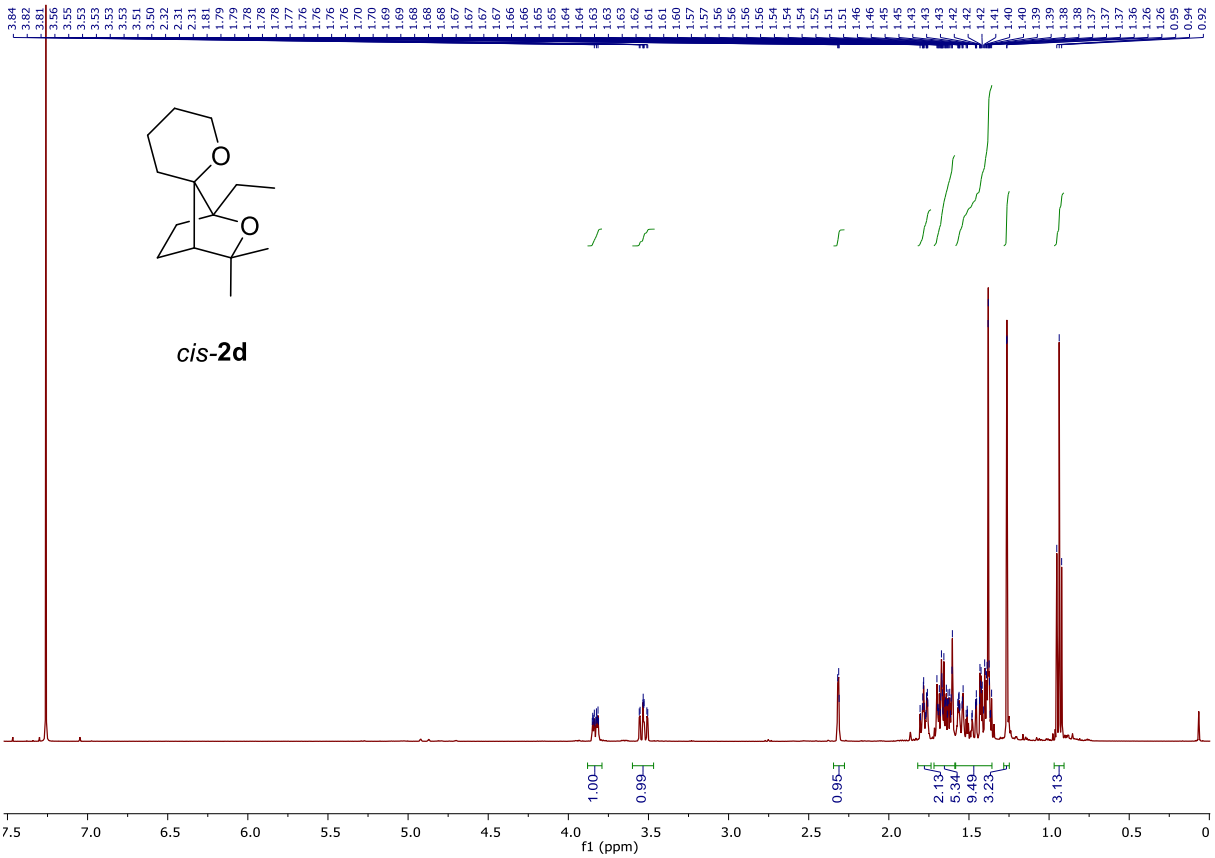
86.85
86.65
78.72
58.95
48.97
33.83
29.04
28.45
21.54
17.16
15.72
14.95
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

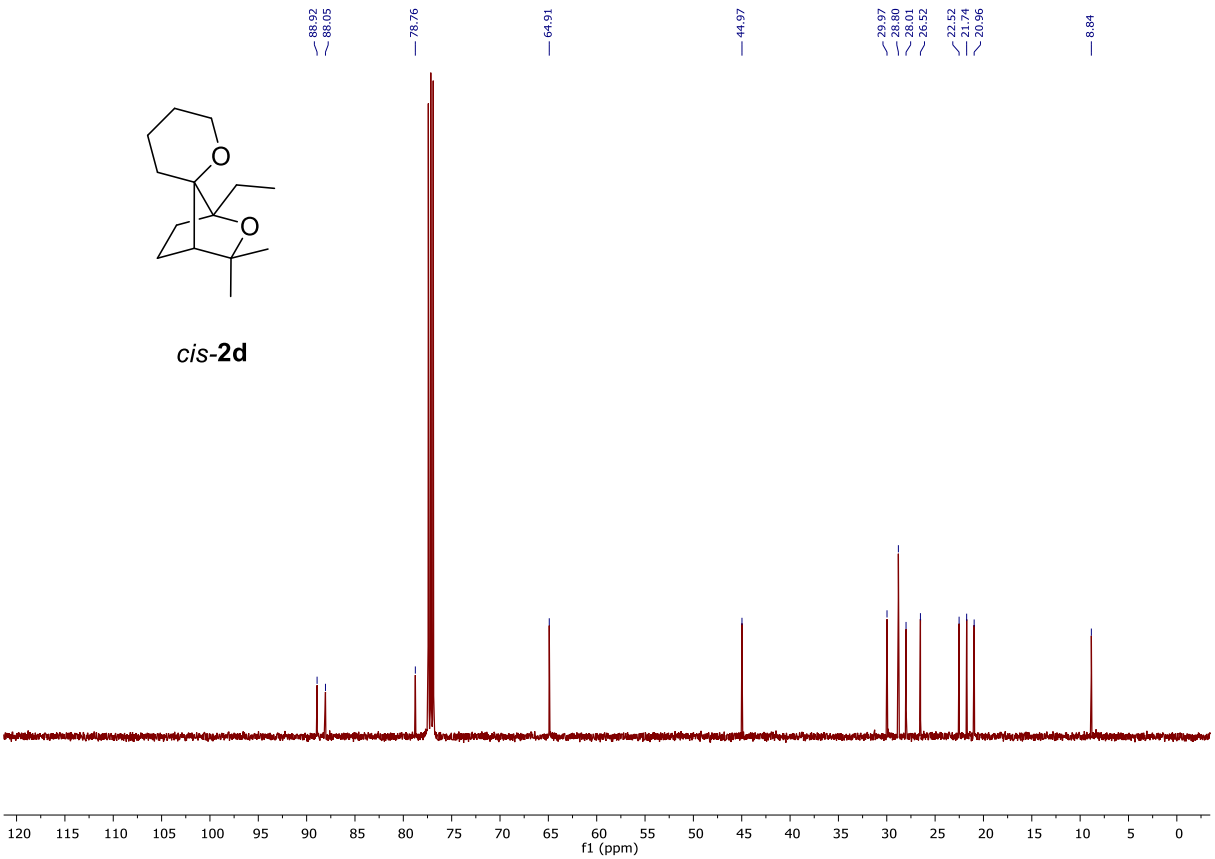


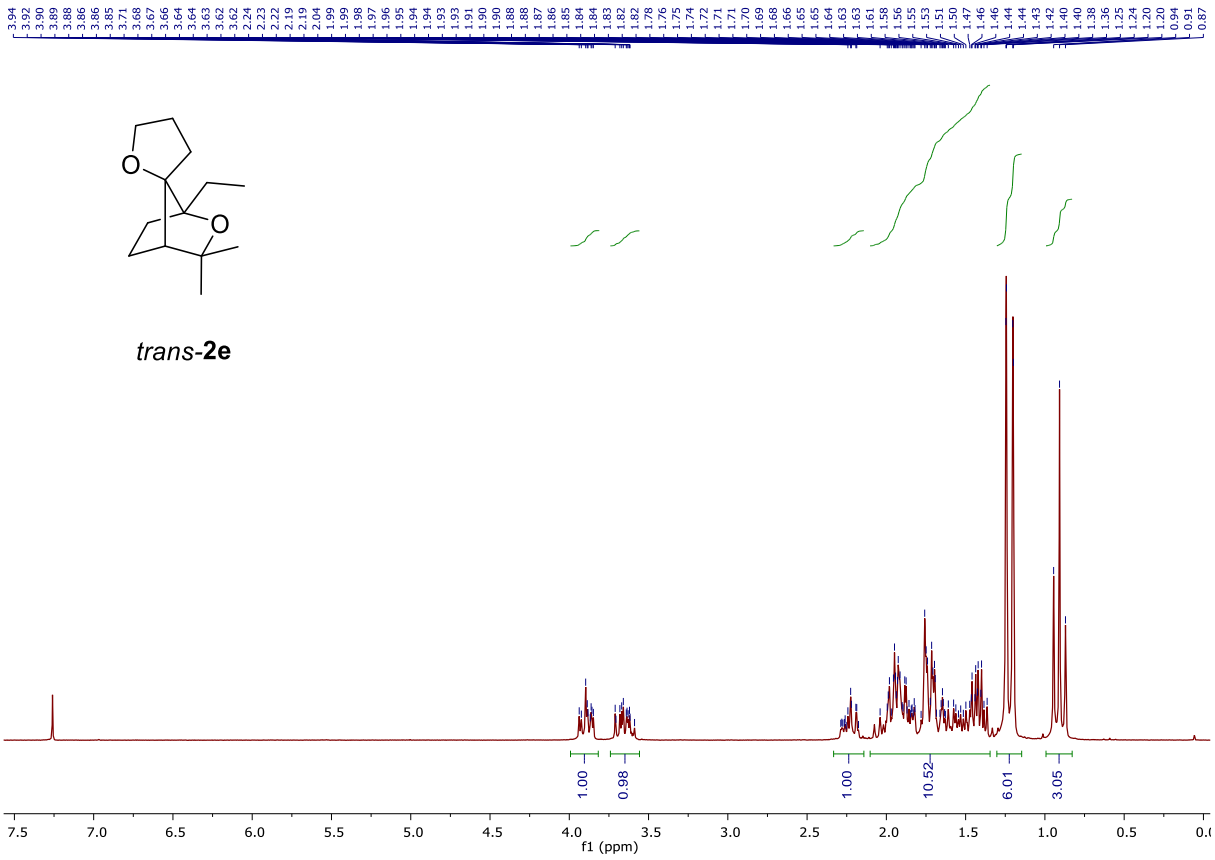
trans-**2d**



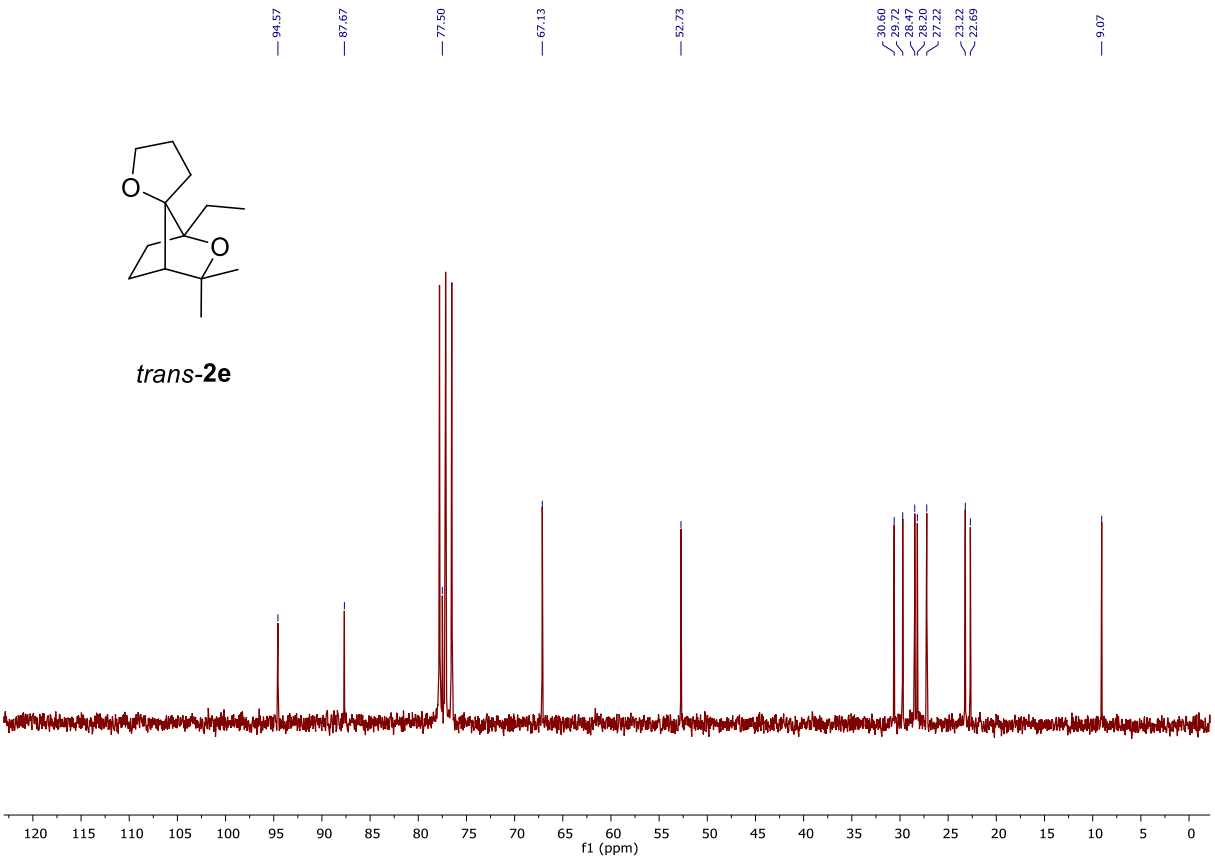
trans-**2d**


O
O
cis-2d
1.00
0.99
0.95
2.13
5.34
9.49
3.23
3.13
f1 (ppm)

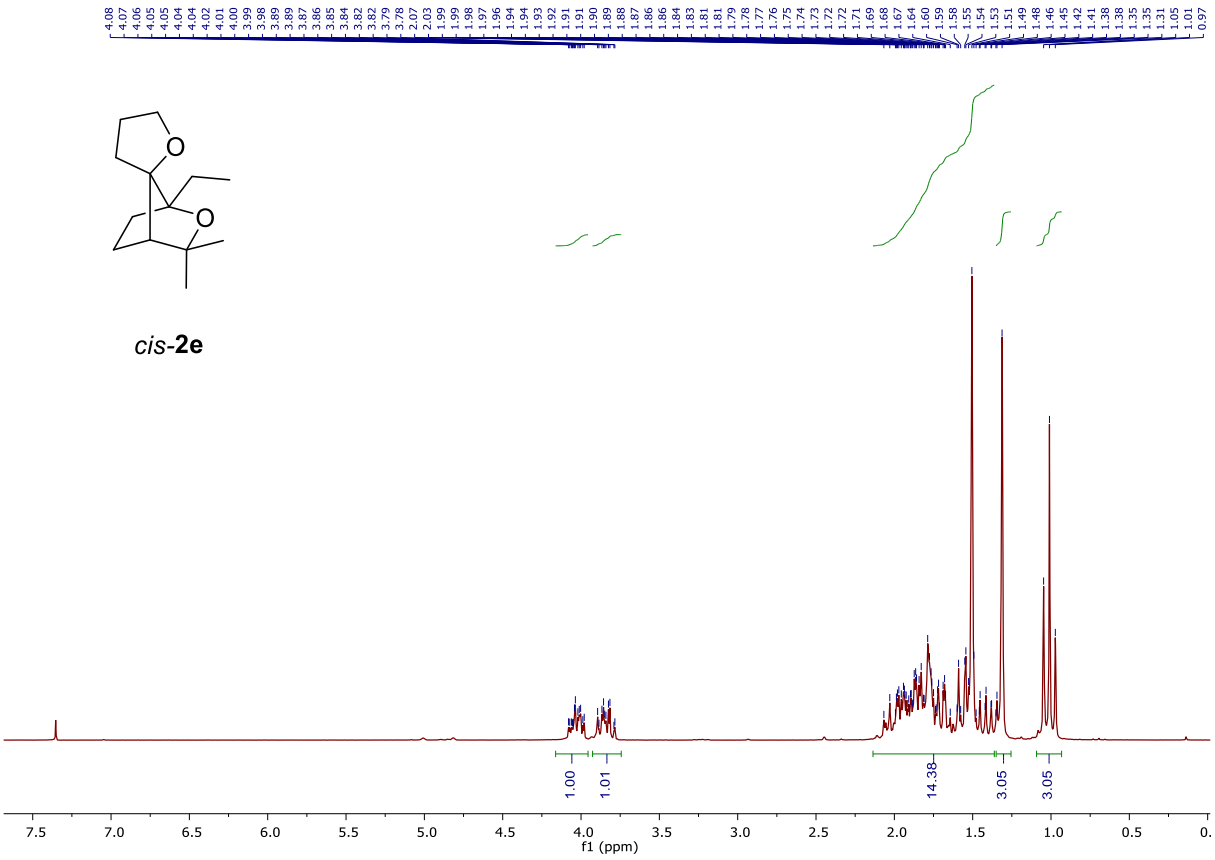

88.92
88.05
78.76
64.91
44.97
29.97
28.80
28.01
26.52
22.52
21.74
20.96
8.84
O
O
cis-2d
f1 (ppm)

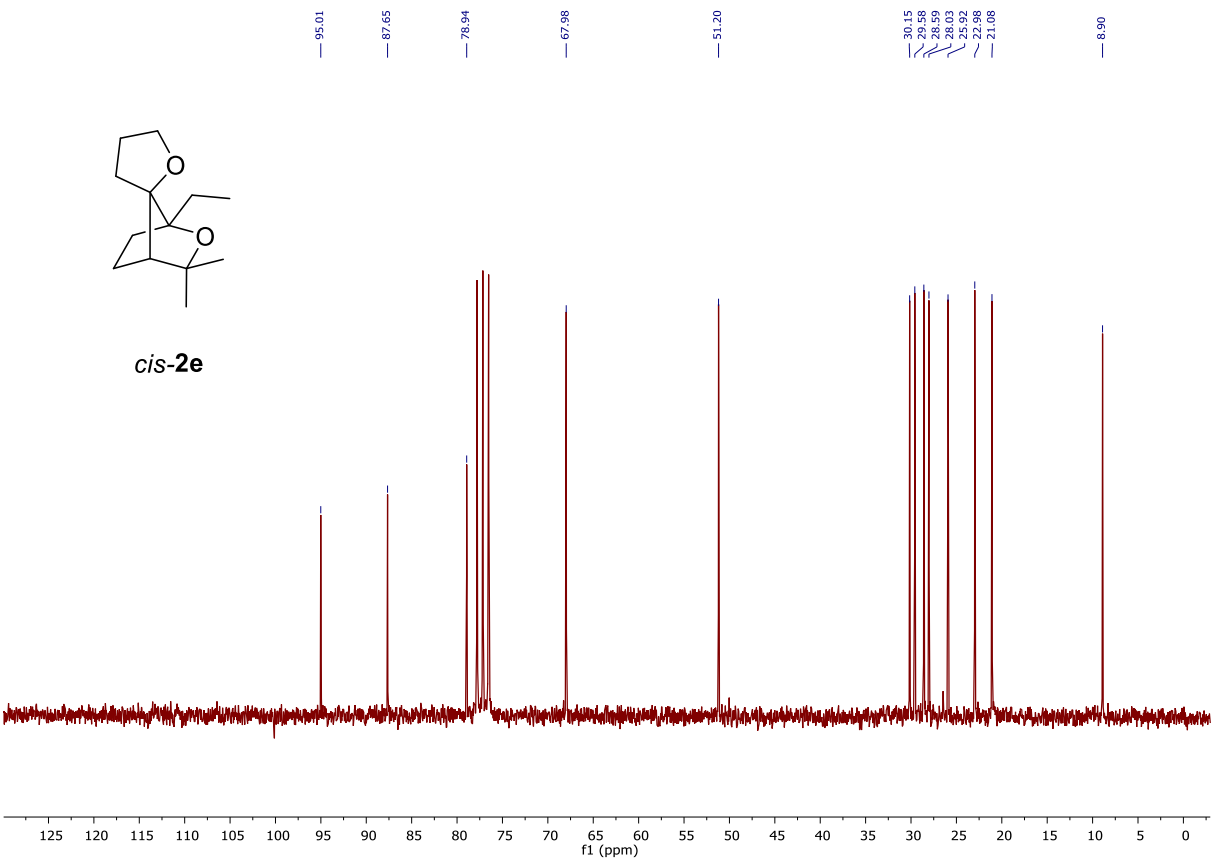


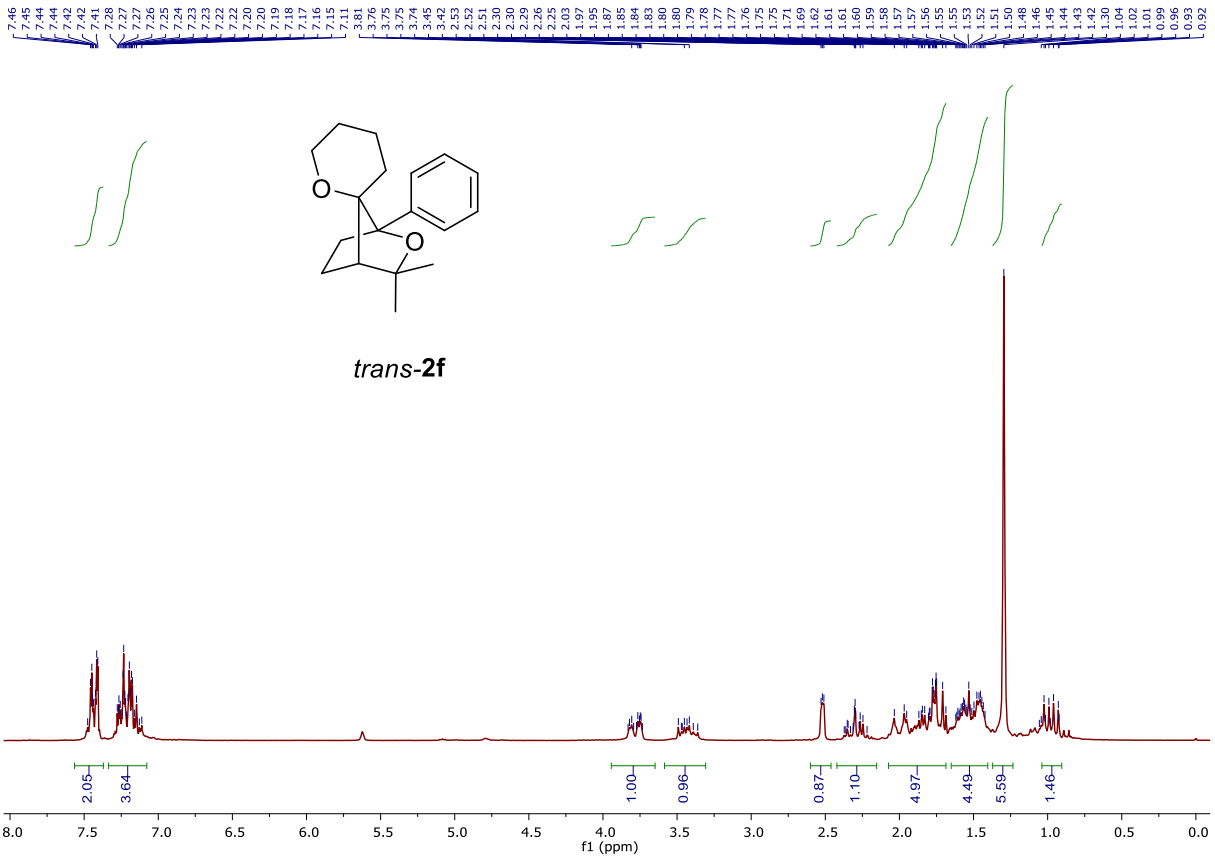
trans-**2e**



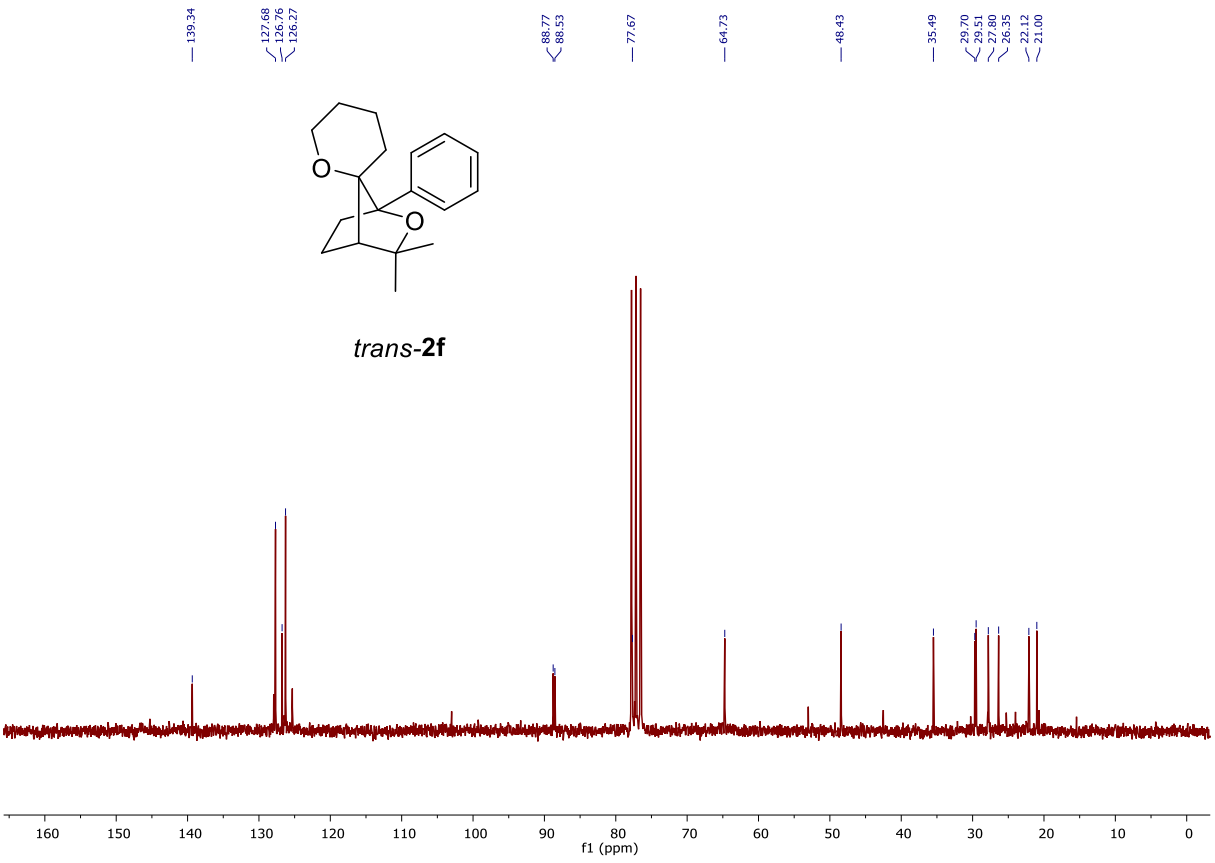
trans-**2e**


O
O
cis-2e
1.00
1.01
14.38
3.05
3.05
f1 (ppm)

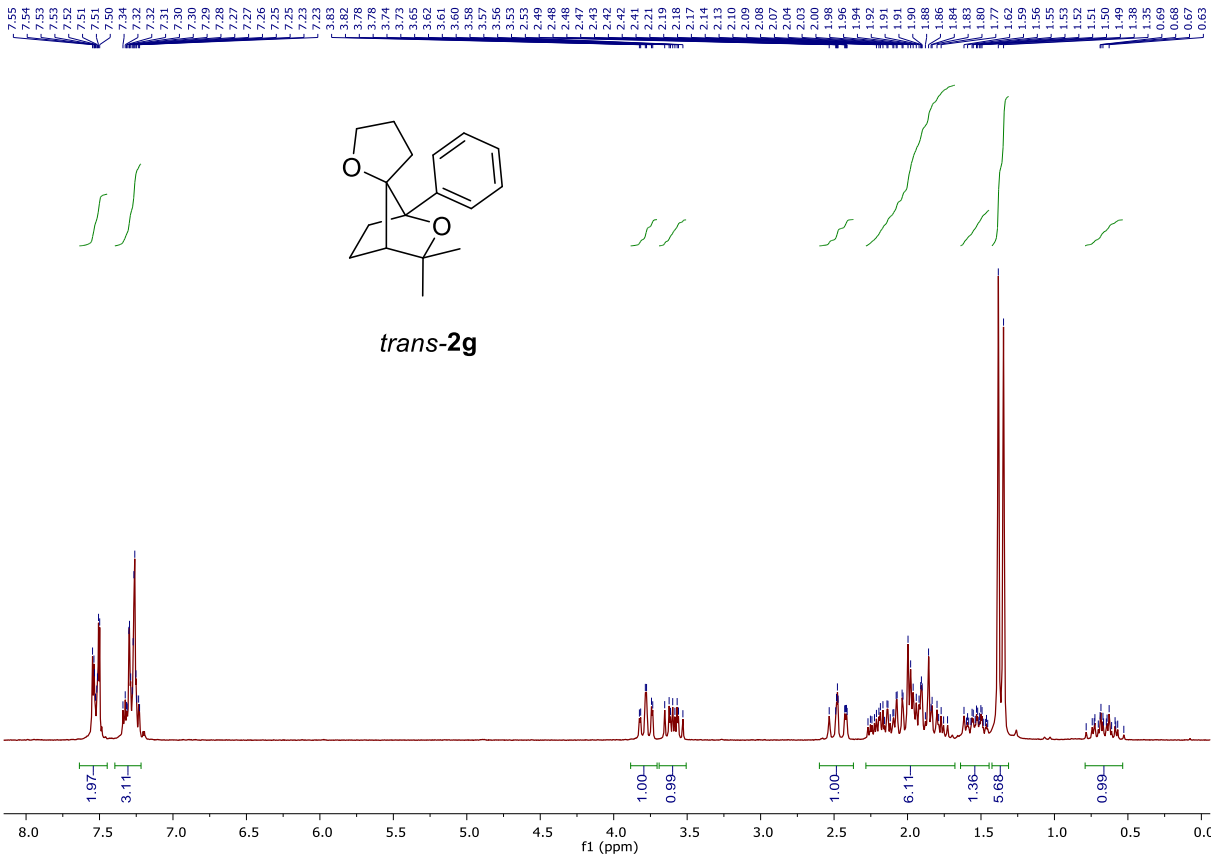

95.01
87.65
78.94
67.98
51.20
30.15
29.58
28.59
28.03
25.92
22.98
21.08
8.90
O
O
cis-2e
f1 (ppm)



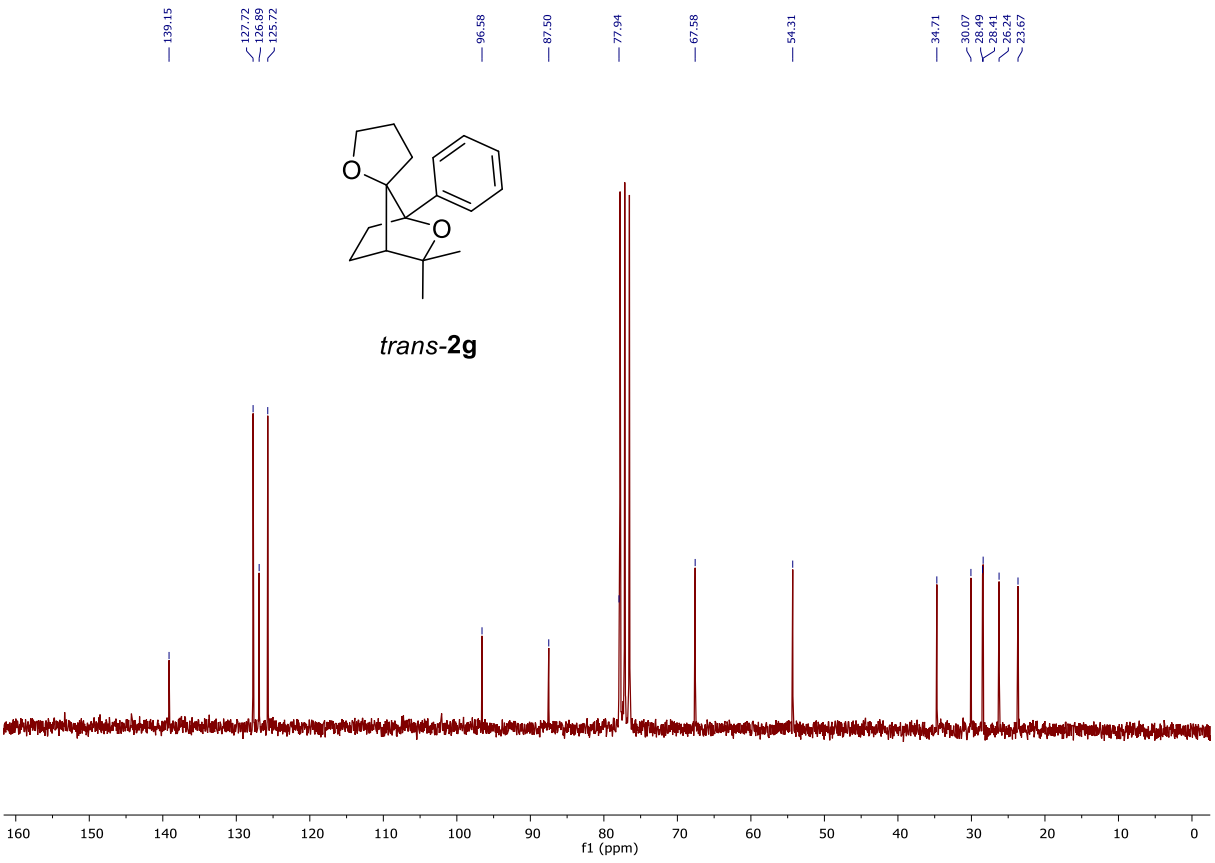
trans-**2f**



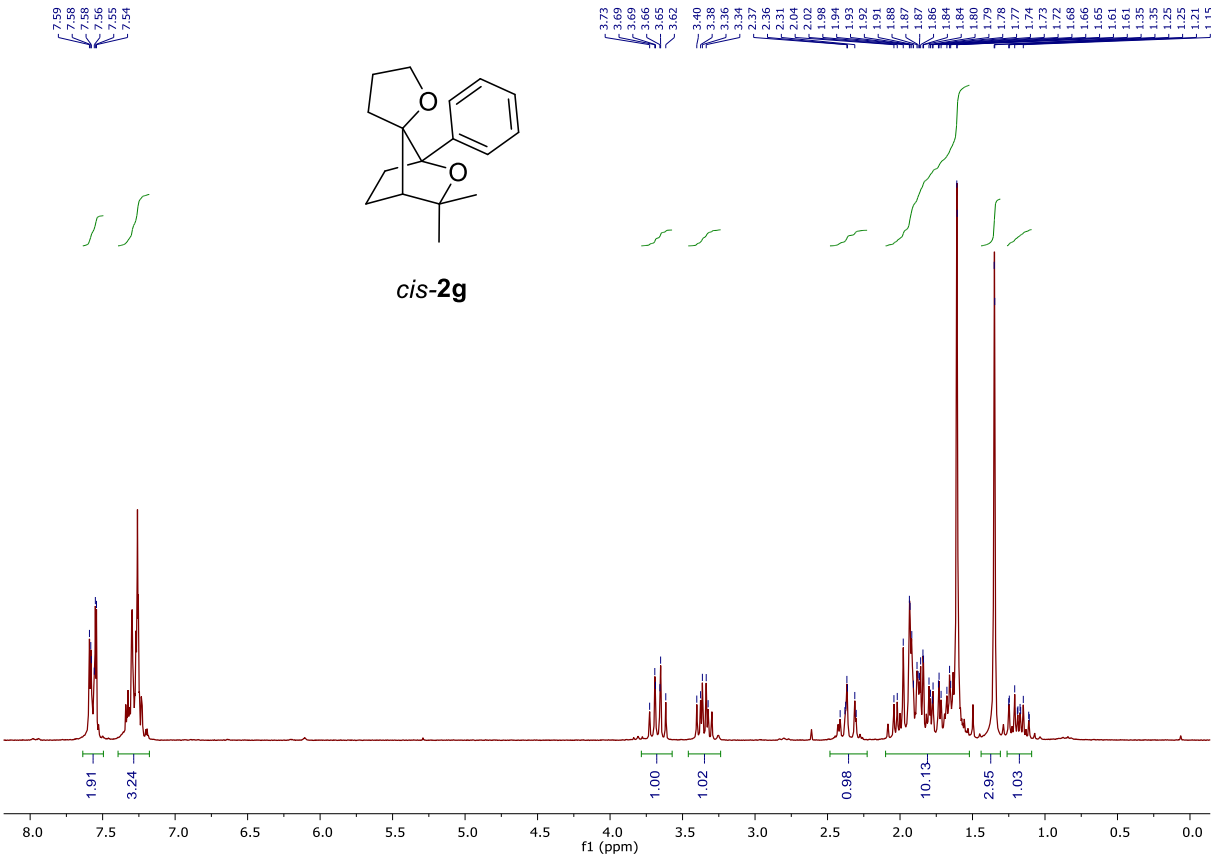
trans-**2f**



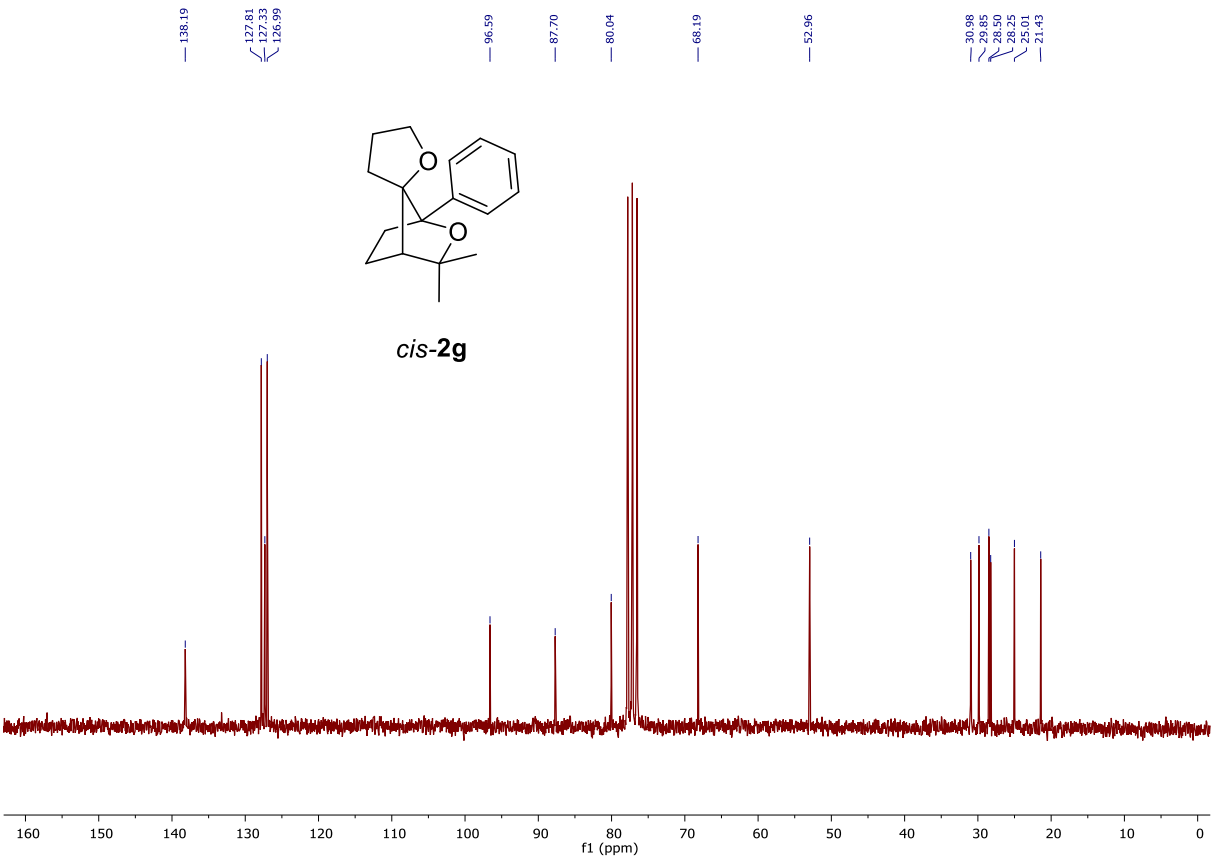
trans-**2g**



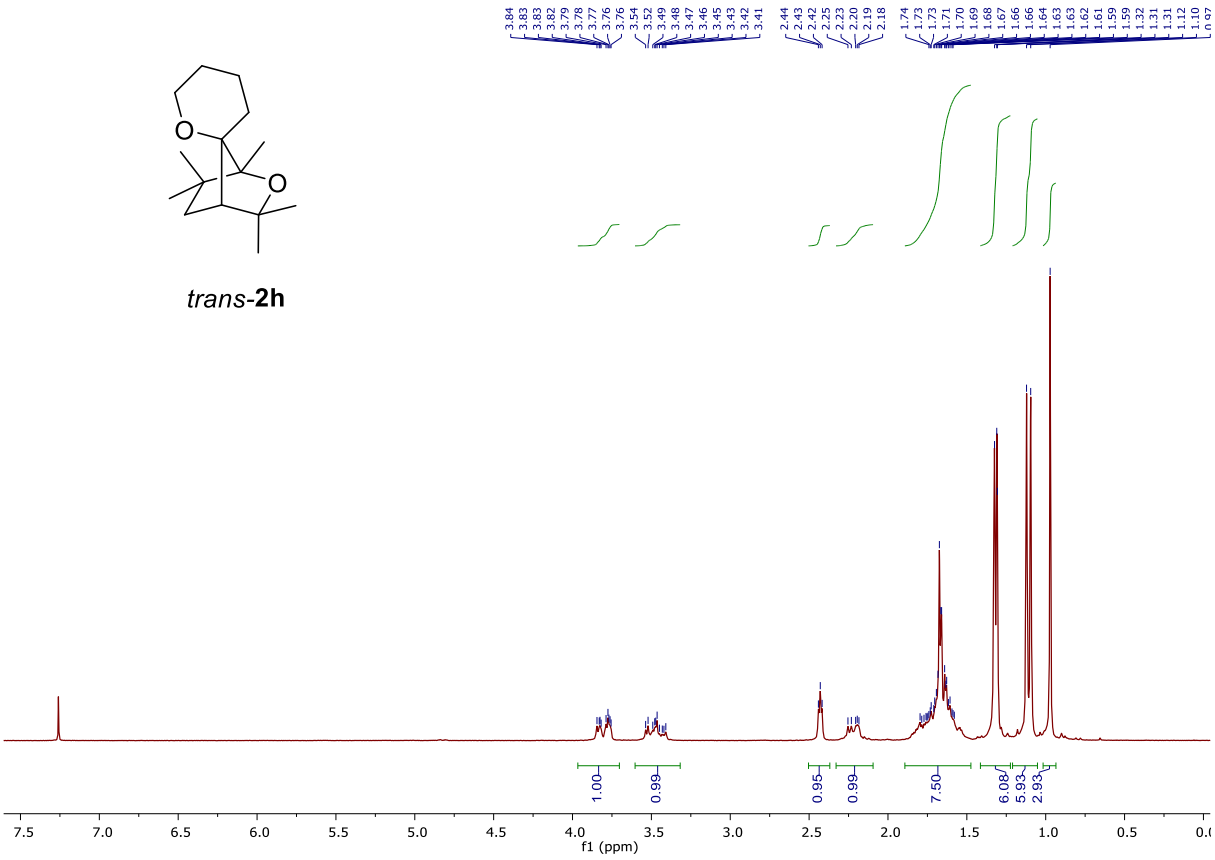
trans-**2g**


7.59
7.58
7.58
7.56
7.55
7.54
3.73
3.69
3.69
3.66
3.65
3.62
3.40
3.38
3.36
3.34
2.37
2.36
2.31
2.04
2.02
1.98
1.94
1.93
1.92
1.91
1.88
1.87
1.87
1.86
1.84
1.84
1.80
1.79
1.78
1.77
1.74
1.73
1.72
1.68
1.66
1.65
1.61
1.61
1.35
1.25
1.25
1.21
O
O
1.91
3.24
1.00
1.02
0.98
10.13
2.95
1.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

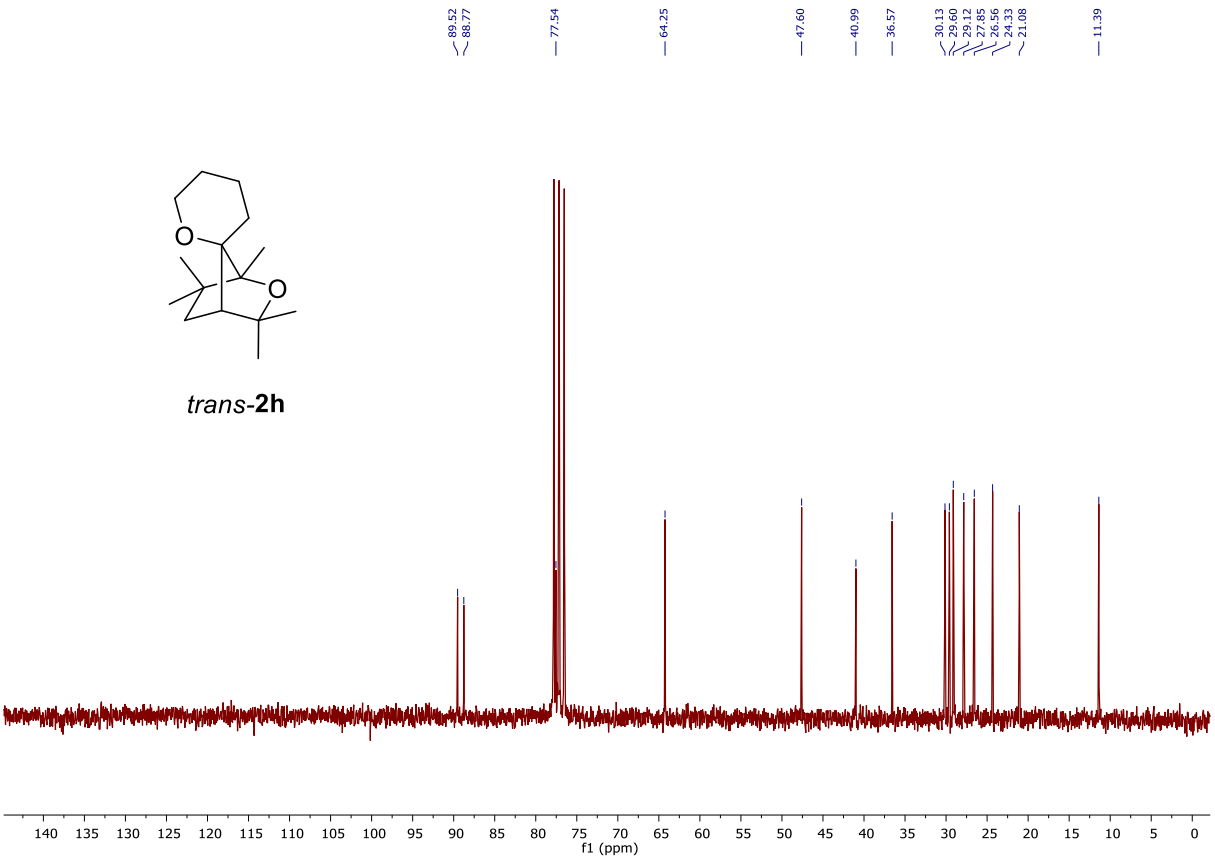
cis-**2g**


138.19
127.81
127.33
126.99
96.59
87.70
80.04
68.19
52.96
30.98
29.85
28.50
28.25
25.01
21.43
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

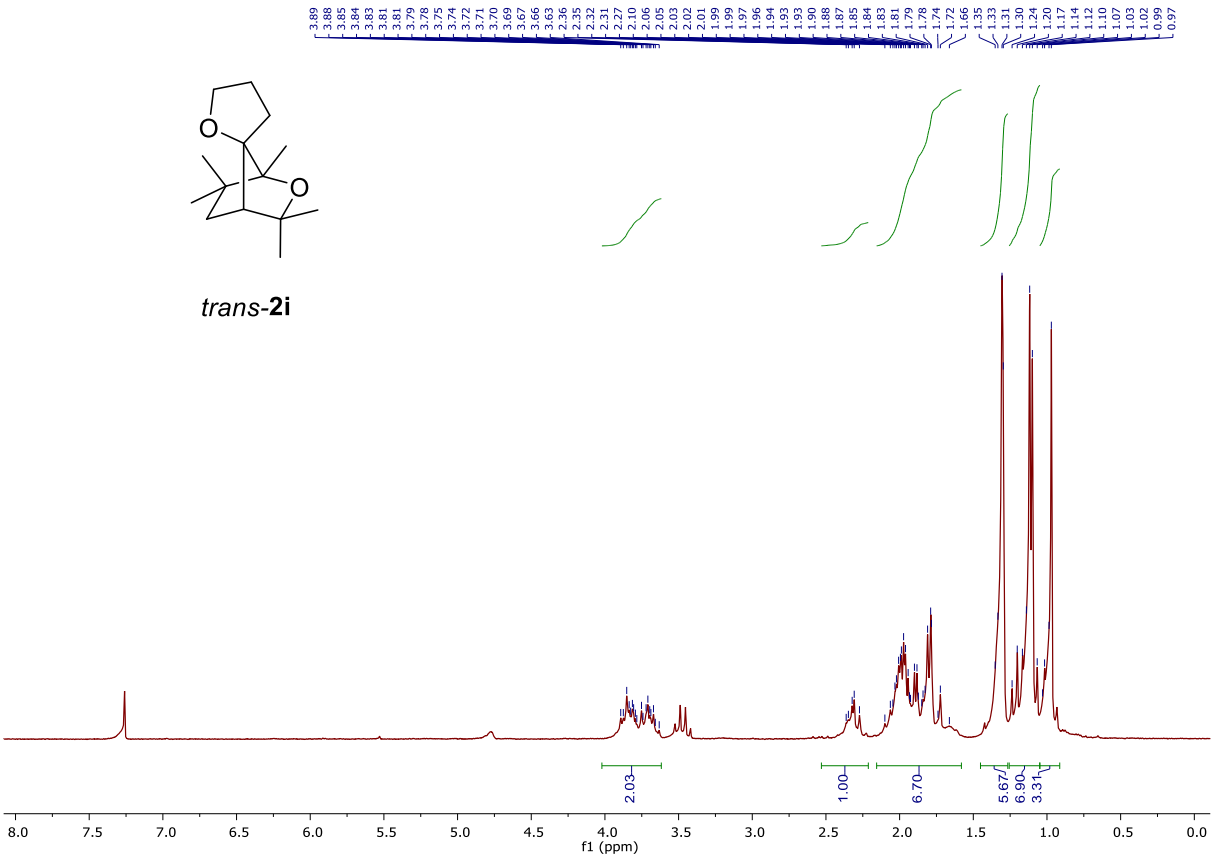
cis-**2g**

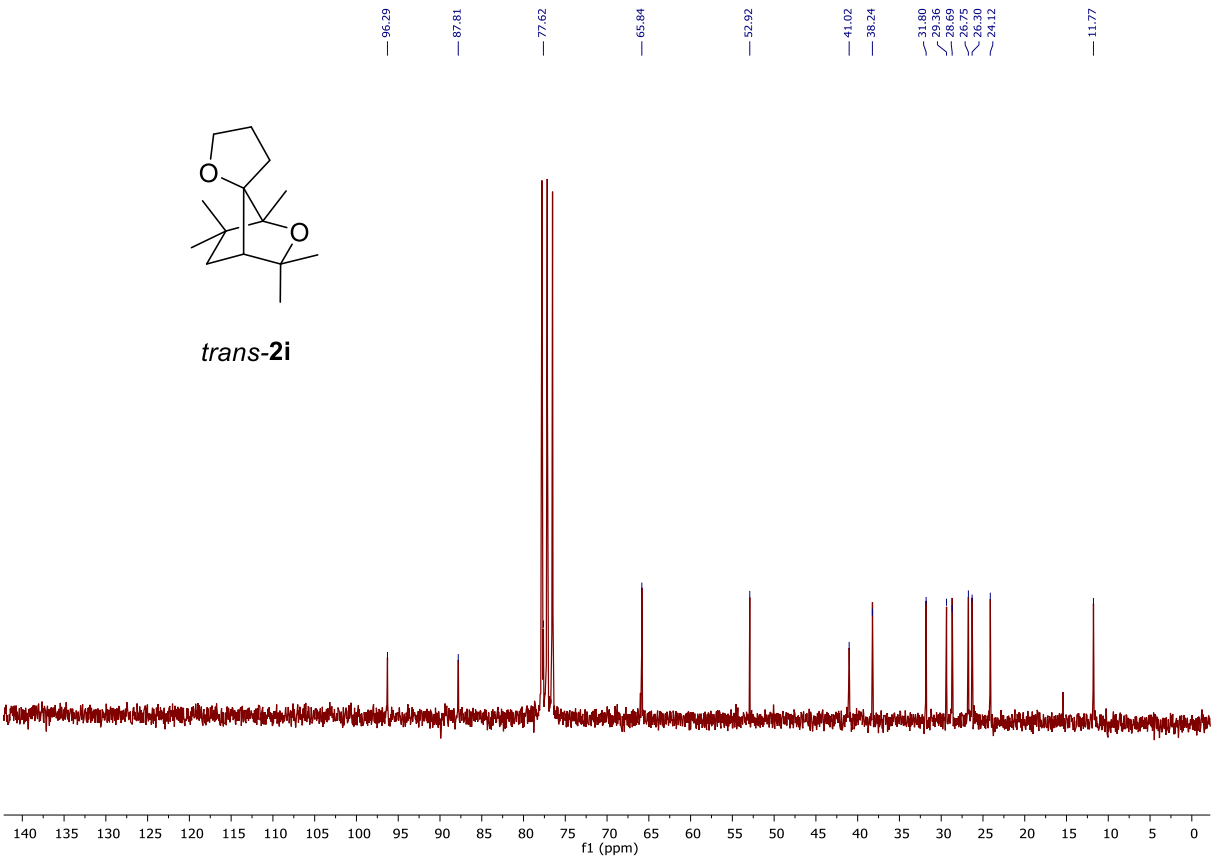


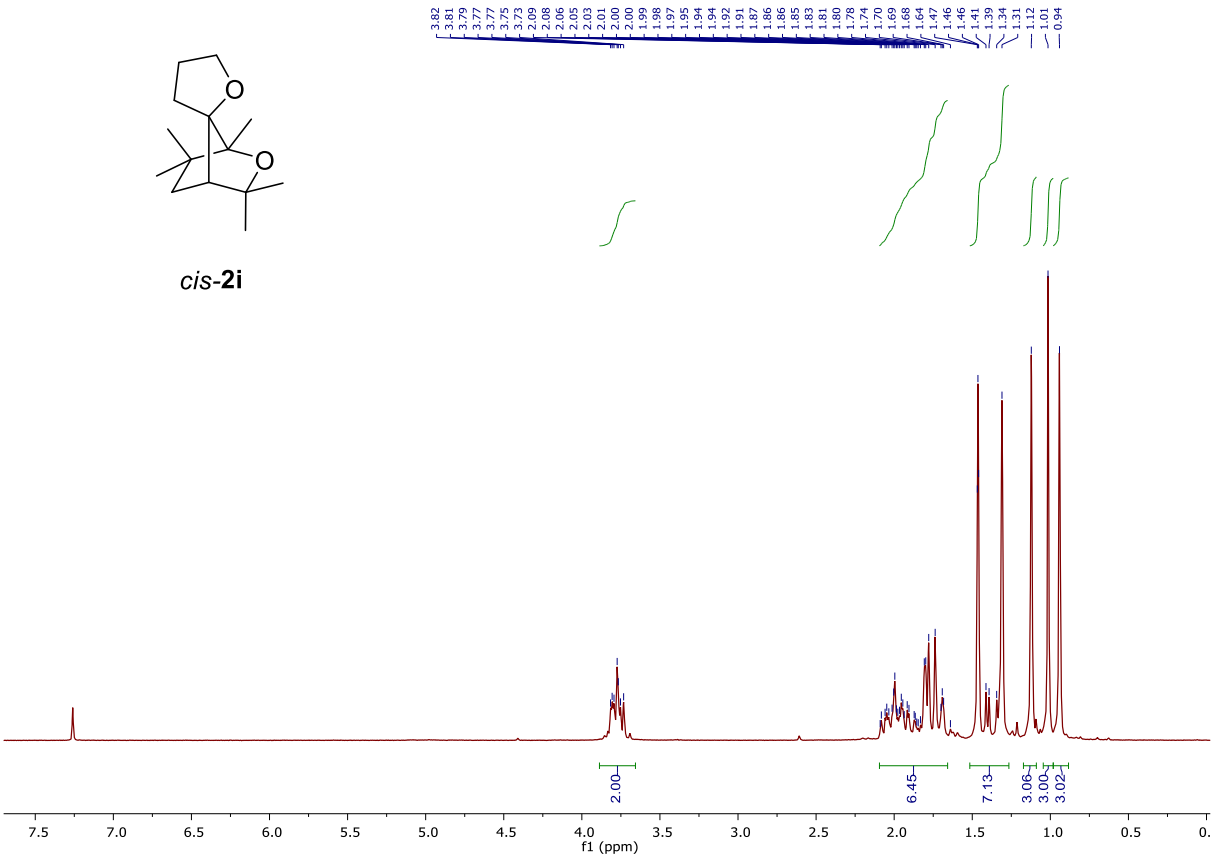
trans-**2h**



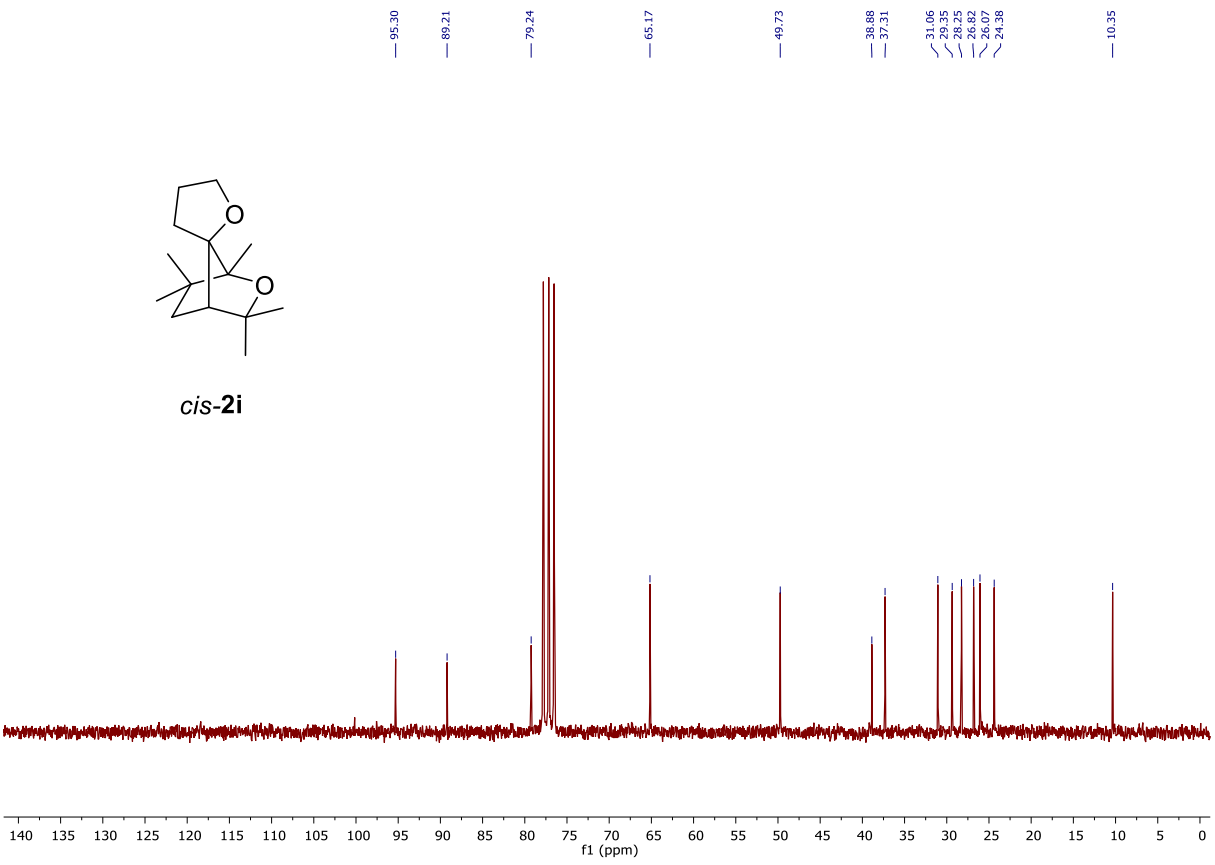
trans-**2h**


3.89 3.88 3.85 3.84 3.83 3.81 3.81 3.79 3.78 3.75 3.74 3.72 3.71 3.70 3.69 3.67 3.66 3.63 2.36 2.35 2.32 2.31 2.27 2.10 2.06 2.05 2.03 2.02 2.01 1.99 1.99 1.97 1.96 1.94 1.93 1.93 1.90 1.88 1.87 1.85 1.84 1.83 1.81 1.79 1.78 1.74 1.72 1.66 1.35 1.33 1.31 1.30 1.24 1.20 1.17 1.14 1.12 1.10 1.07 1.03 1.02 0.99 0.97
O
O
trans-2i
2.03
1.00
6.70
5.67
6.90
3.31
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

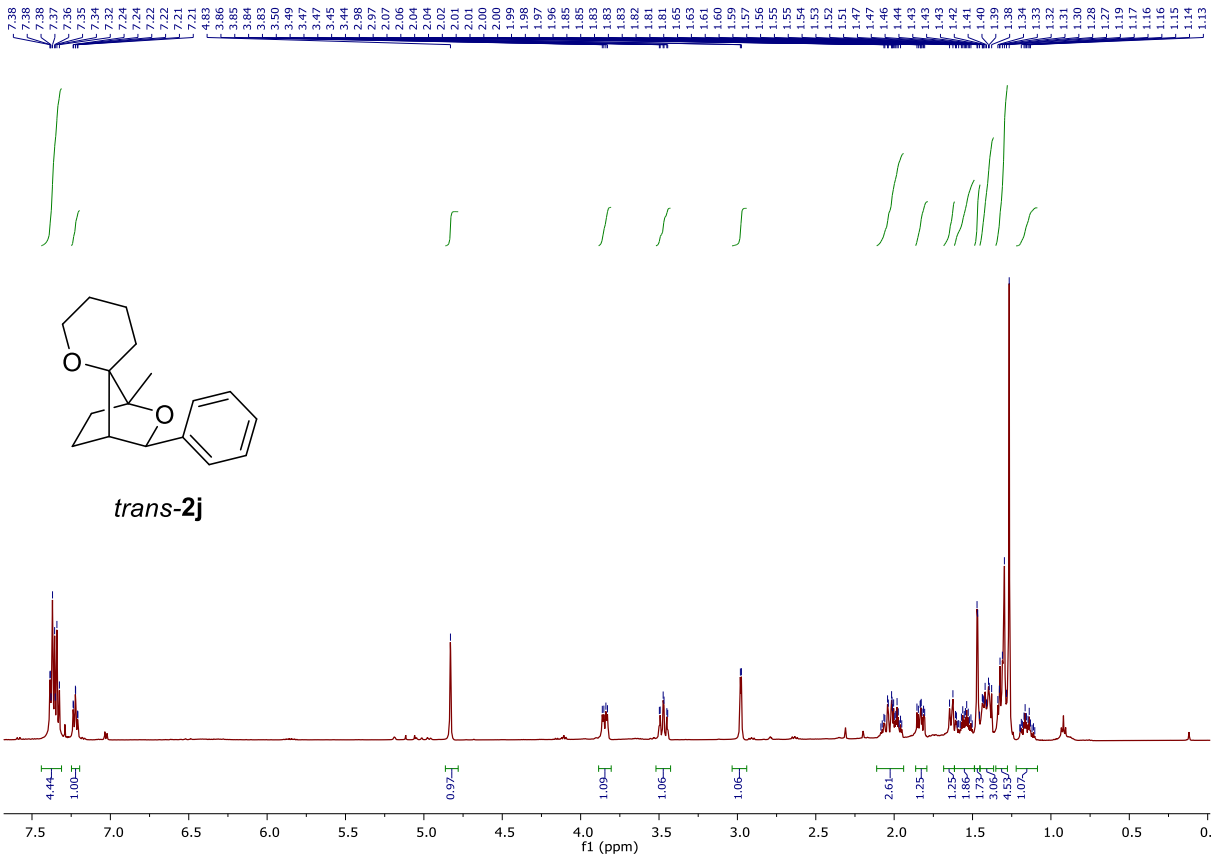

96.29
87.81
77.62
65.84
52.92
41.02
38.24
31.80
29.36
28.69
26.75
26.30
24.12
11.77
O
O
trans-2i
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

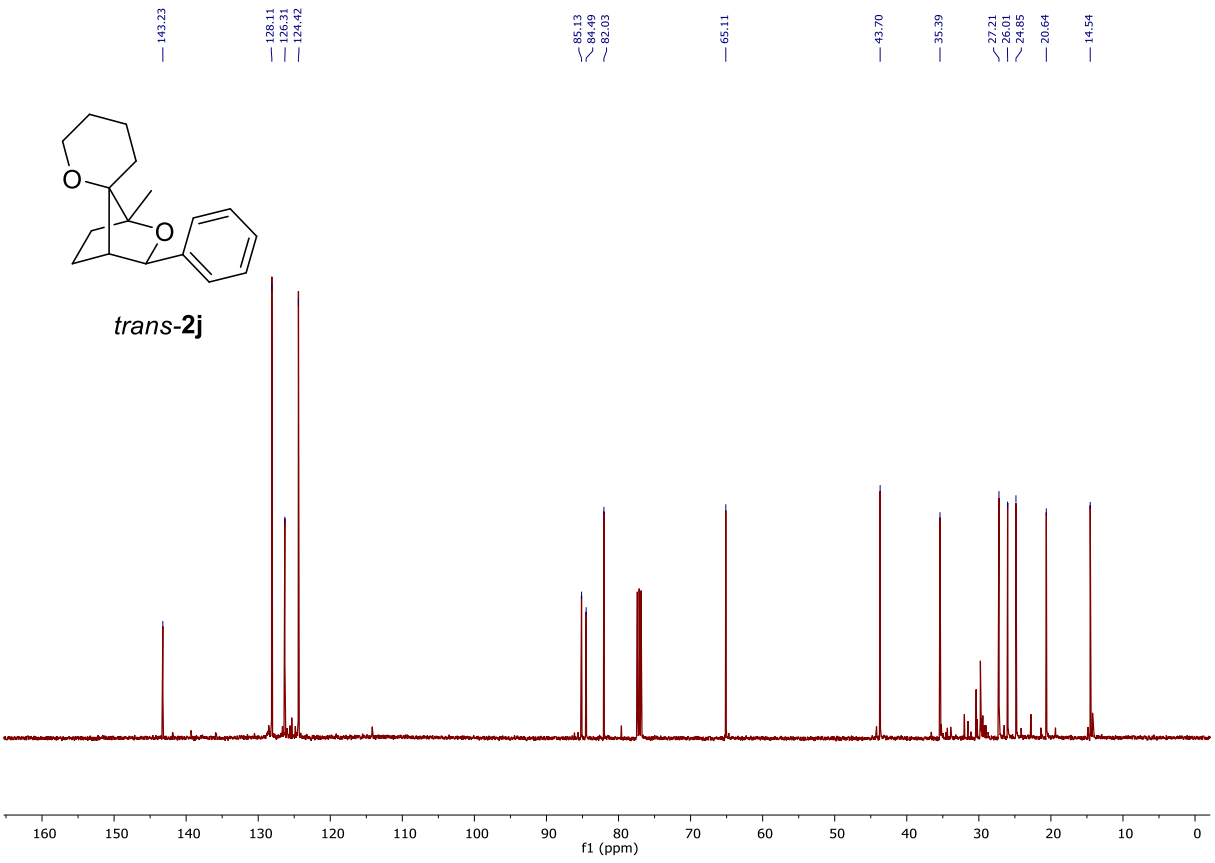

3.82
3.81
3.79
3.77
3.77
3.75
3.73
2.09
2.08
2.06
2.05
2.03
2.01
2.00
2.00
1.99
1.98
1.97
1.95
1.94
1.94
1.92
1.91
1.87
1.86
1.86
1.85
1.83
1.81
1.80
1.78
1.74
1.70
1.69
1.68
1.64
1.47
1.46
1.46
1.41
1.39
1.34
1.31
1.12
1.01
0.94
O
O
2.00
6.45
7.13
3.06
3.00
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

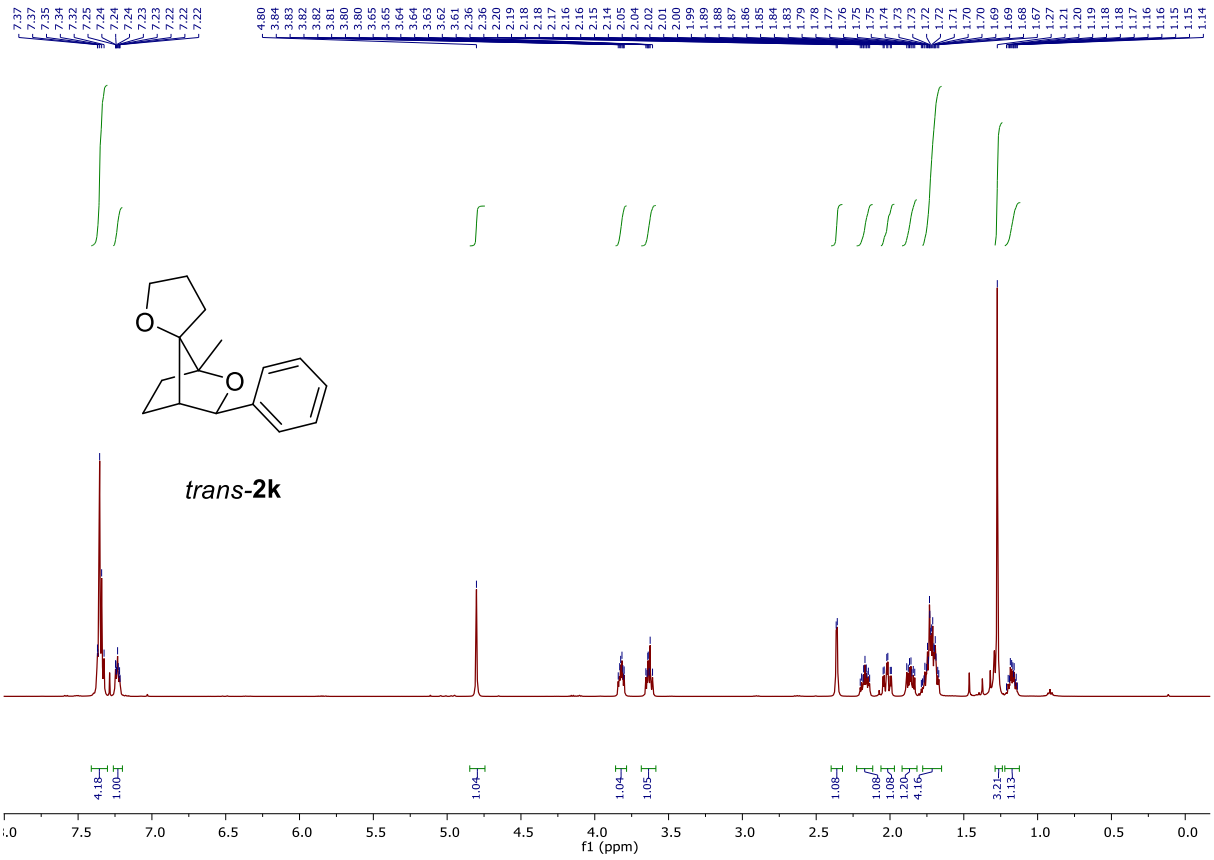
cis-**2i**

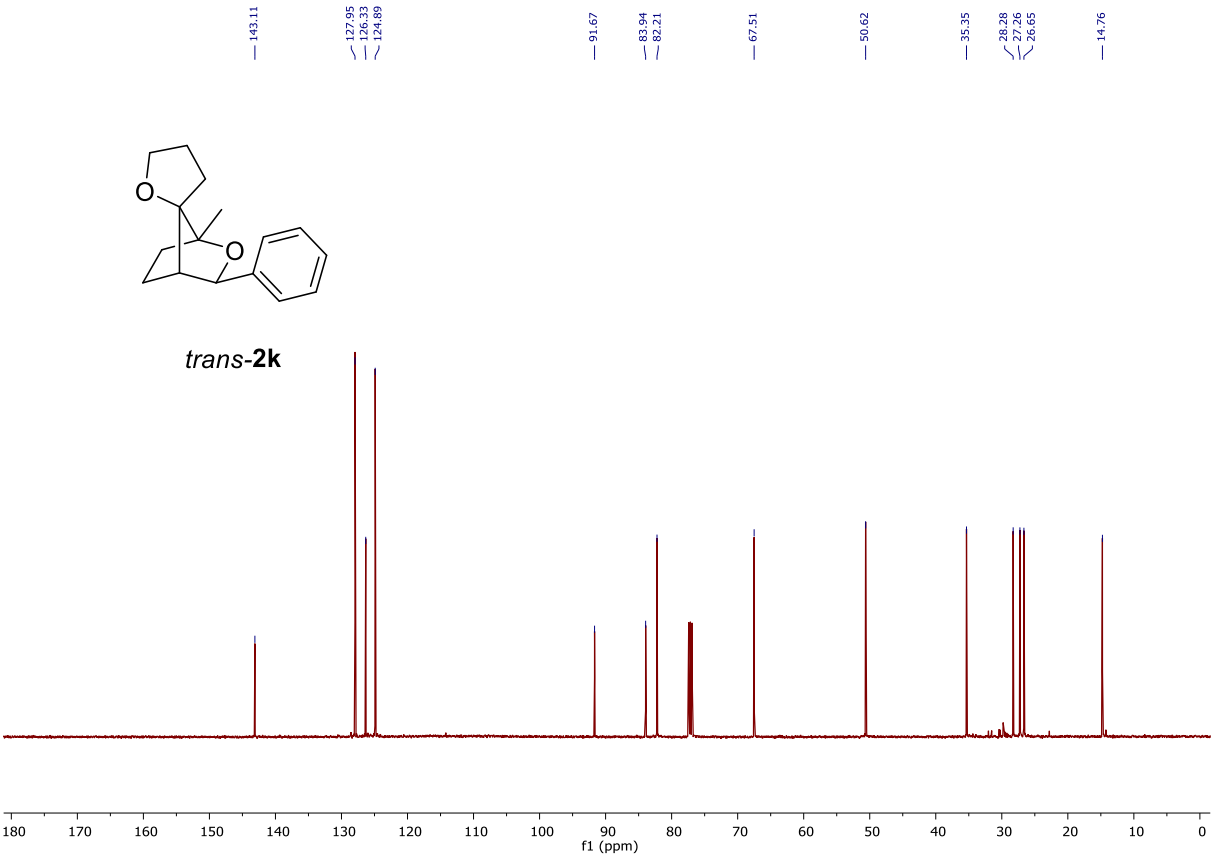

95.30
89.21
79.24
65.17
49.73
38.88
37.31
31.06
29.35
28.25
26.82
26.07
24.38
10.35
O
O
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

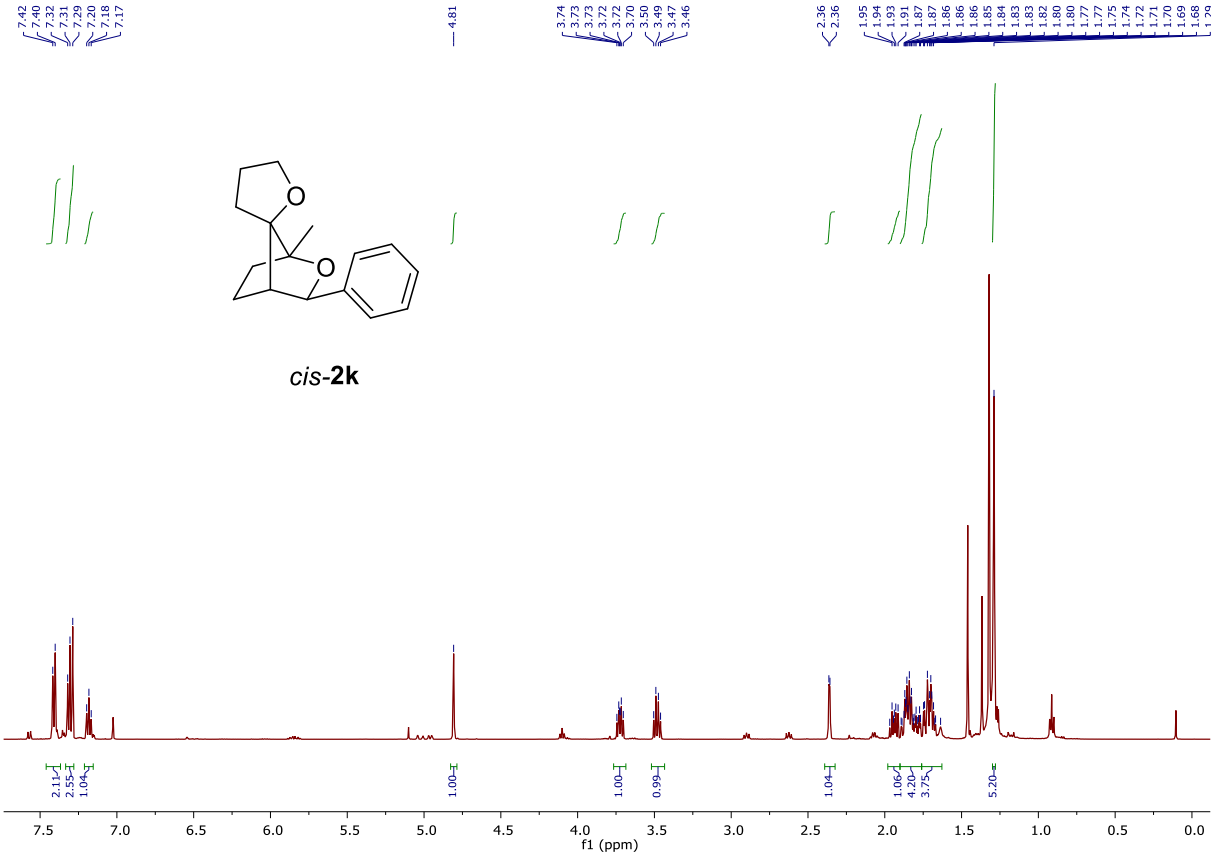
cis-**2i**


trans-2j
f1 (ppm)

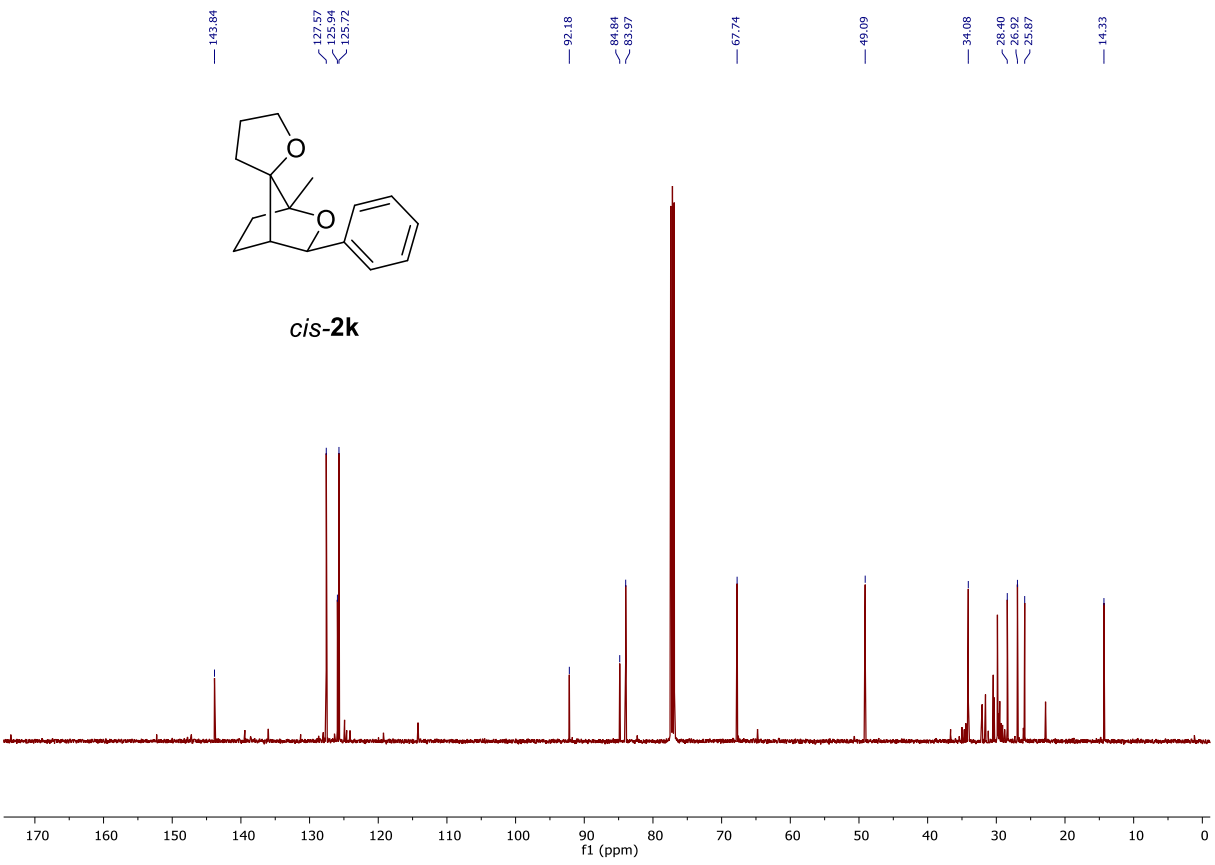

trans-2j
f1 (ppm)


O
O
trans-2k
4.18
1.00
1.04
1.04
1.05
1.08
1.09
1.08
1.20
4.16
3.21
1.13
f1 (ppm)

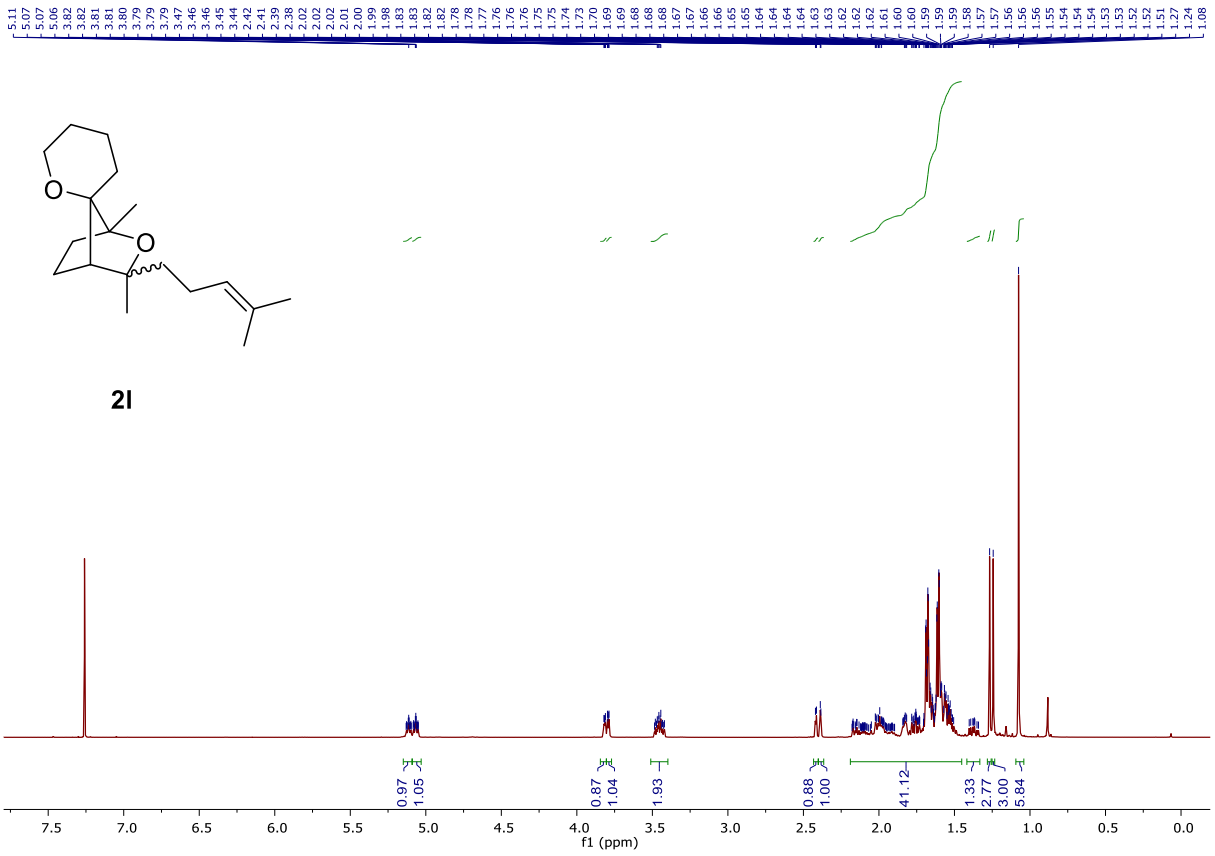

143.11
127.95
126.33
124.89
91.67
83.94
82.21
67.51
50.62
35.35
28.28
27.26
26.65
14.76
O
O
trans-2k
f1 (ppm)

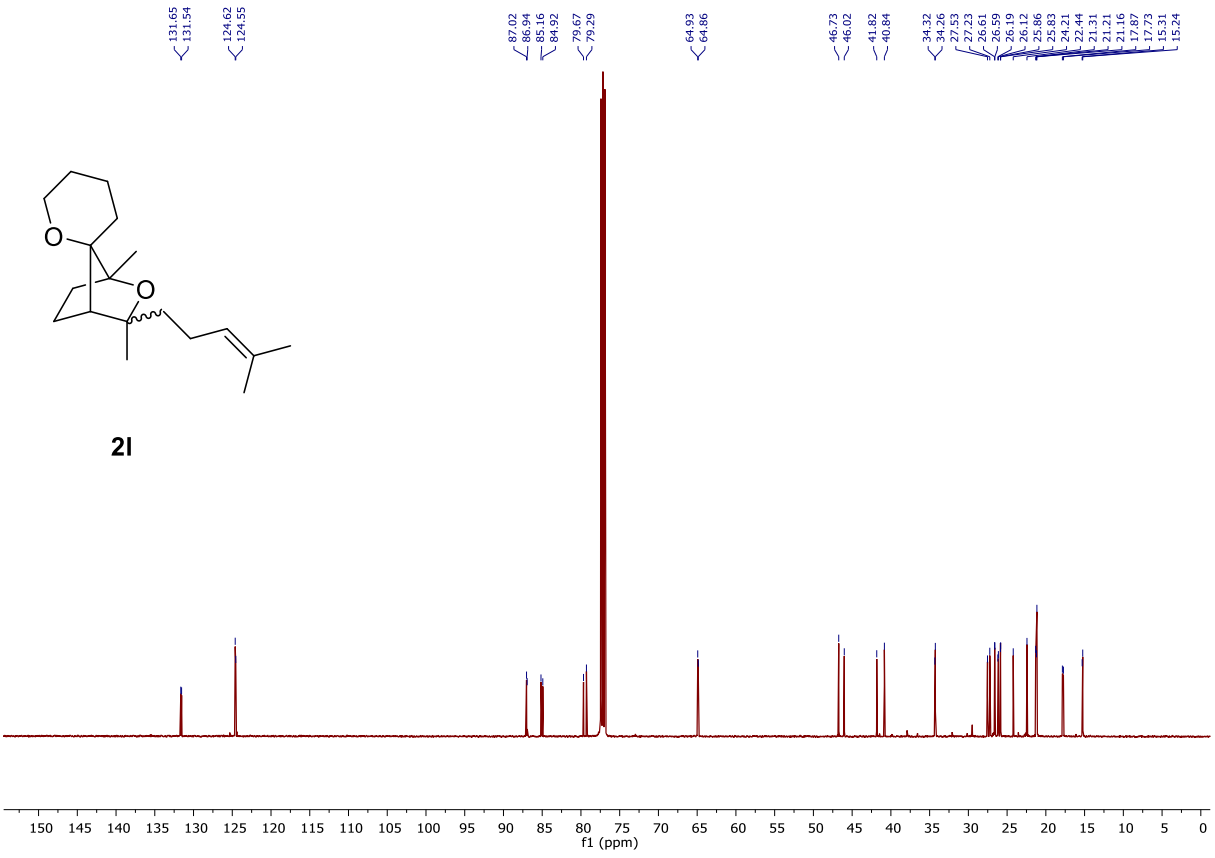

7.42
7.40
7.32
7.31
7.29
7.20
7.18
7.17
4.81
3.74
3.73
3.73
3.72
3.72
3.70
3.50
3.49
3.47
3.46
2.36
2.36
1.95
1.94
1.93
1.91
1.87
1.87
1.86
1.86
1.86
1.85
1.84
1.83
1.83
1.82
1.80
1.80
1.77
1.77
1.75
1.74
1.72
1.71
1.70
1.69
1.68
2.11
2.55
1.04
1.00
1.00
0.99
1.04
1.06
4.20
3.75
5.20
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

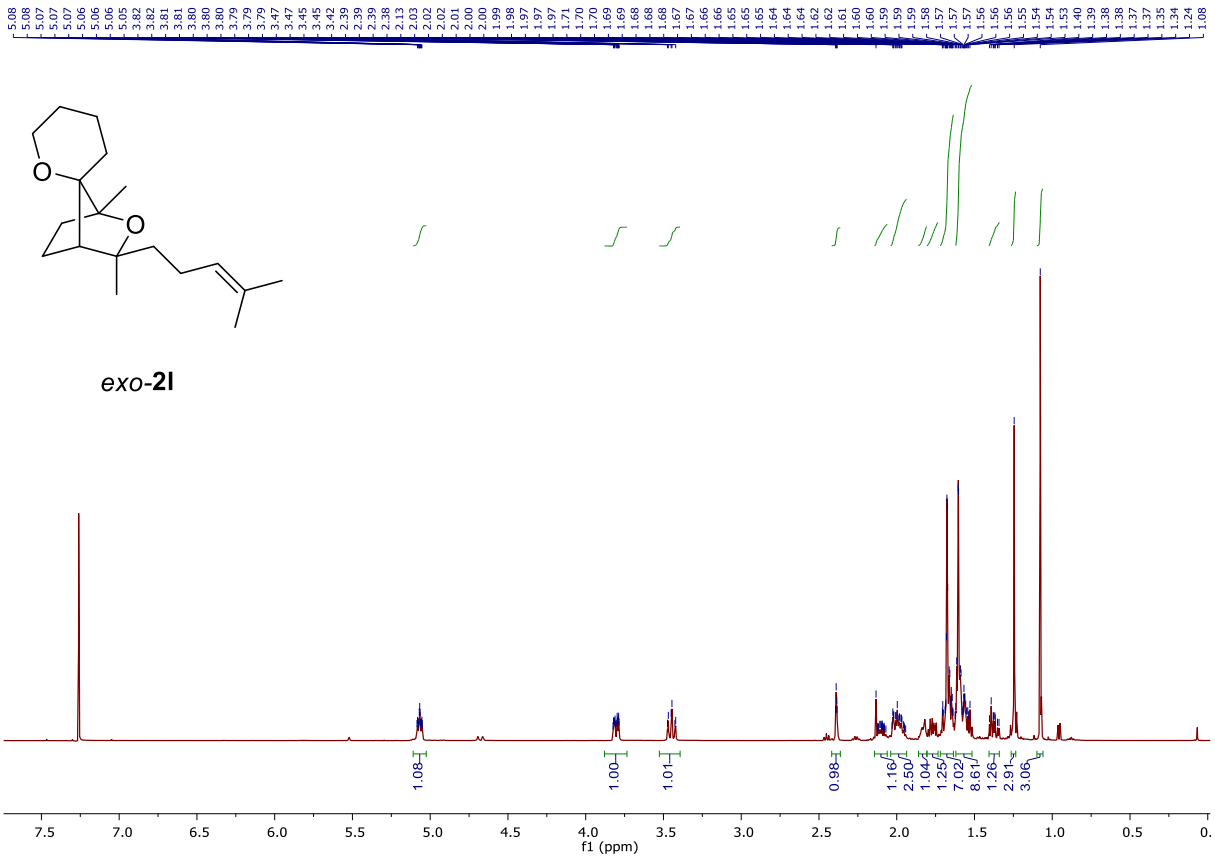
cis-**2k**

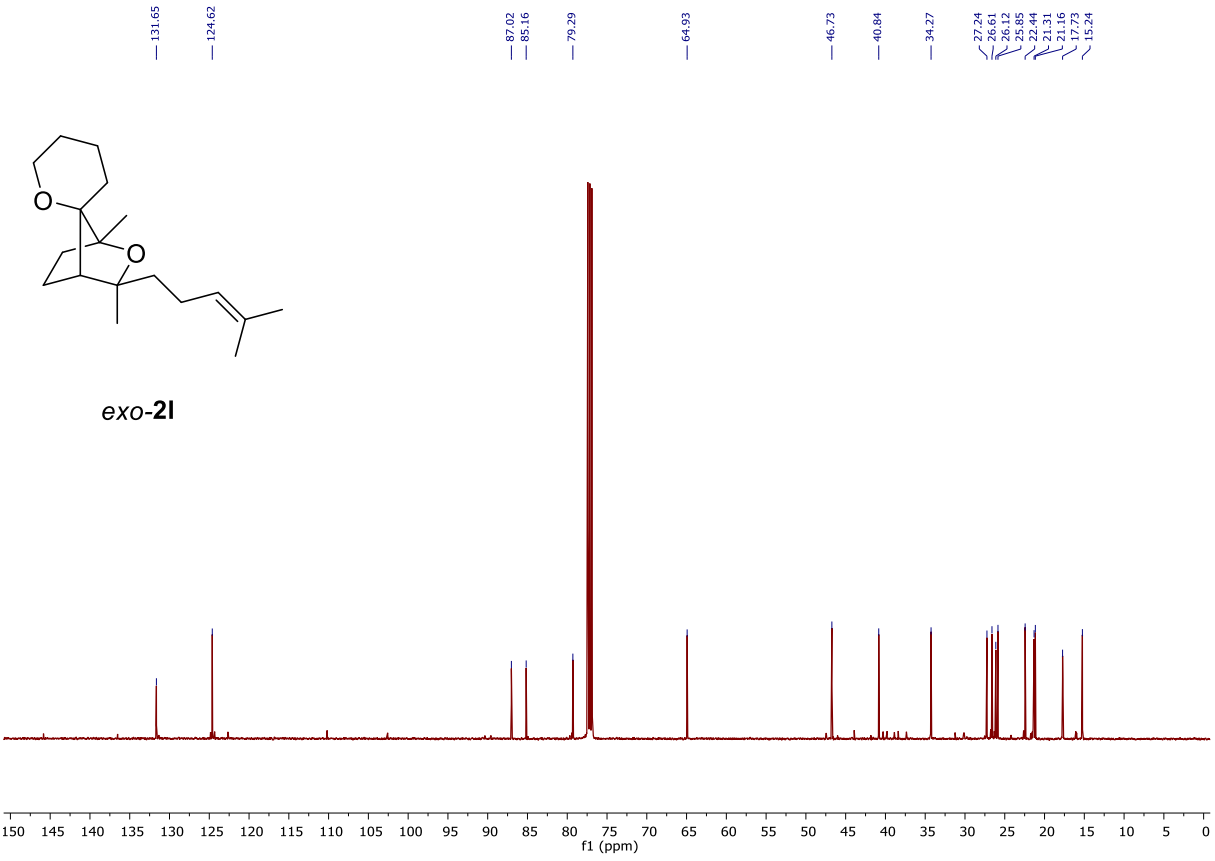

143.84
127.57
125.94
125.72
92.18
84.84
83.97
67.74
49.09
34.08
28.40
26.92
25.87
14.33
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

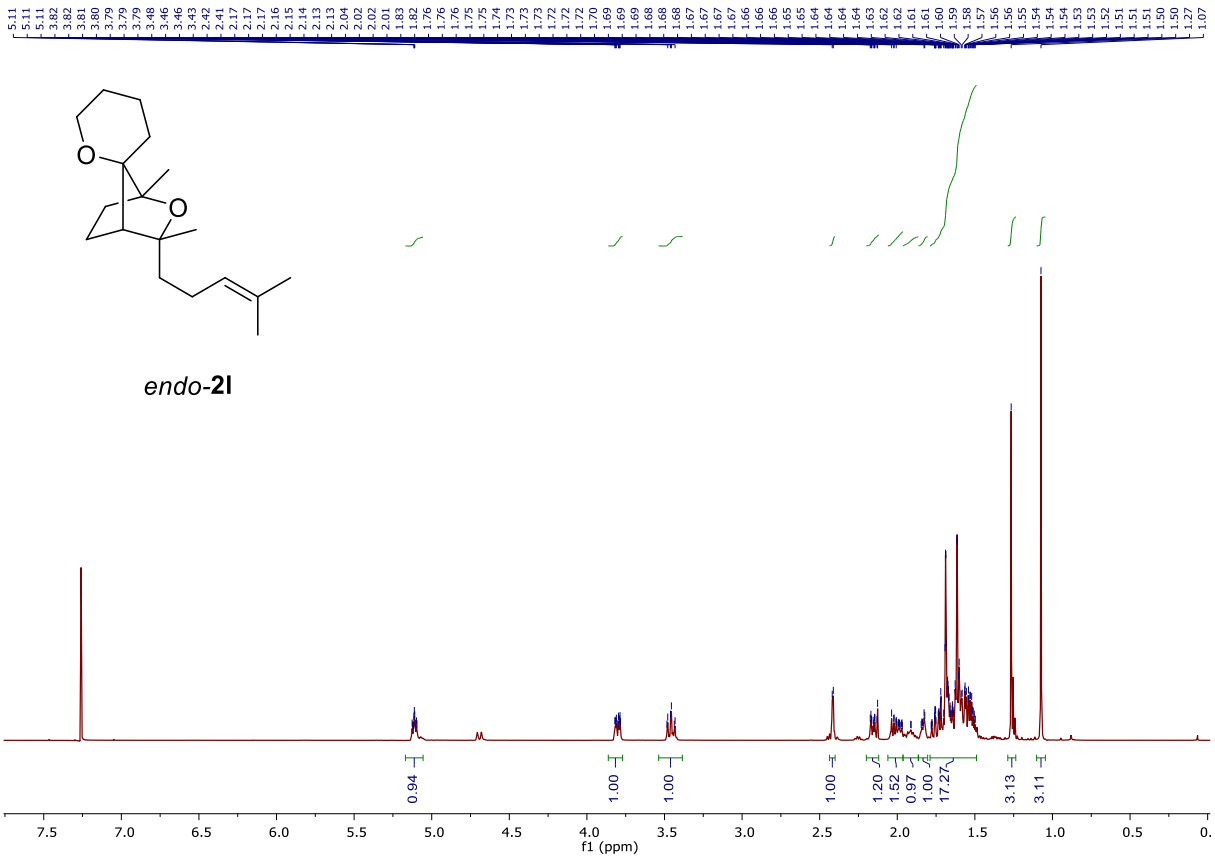
cis-**2k**

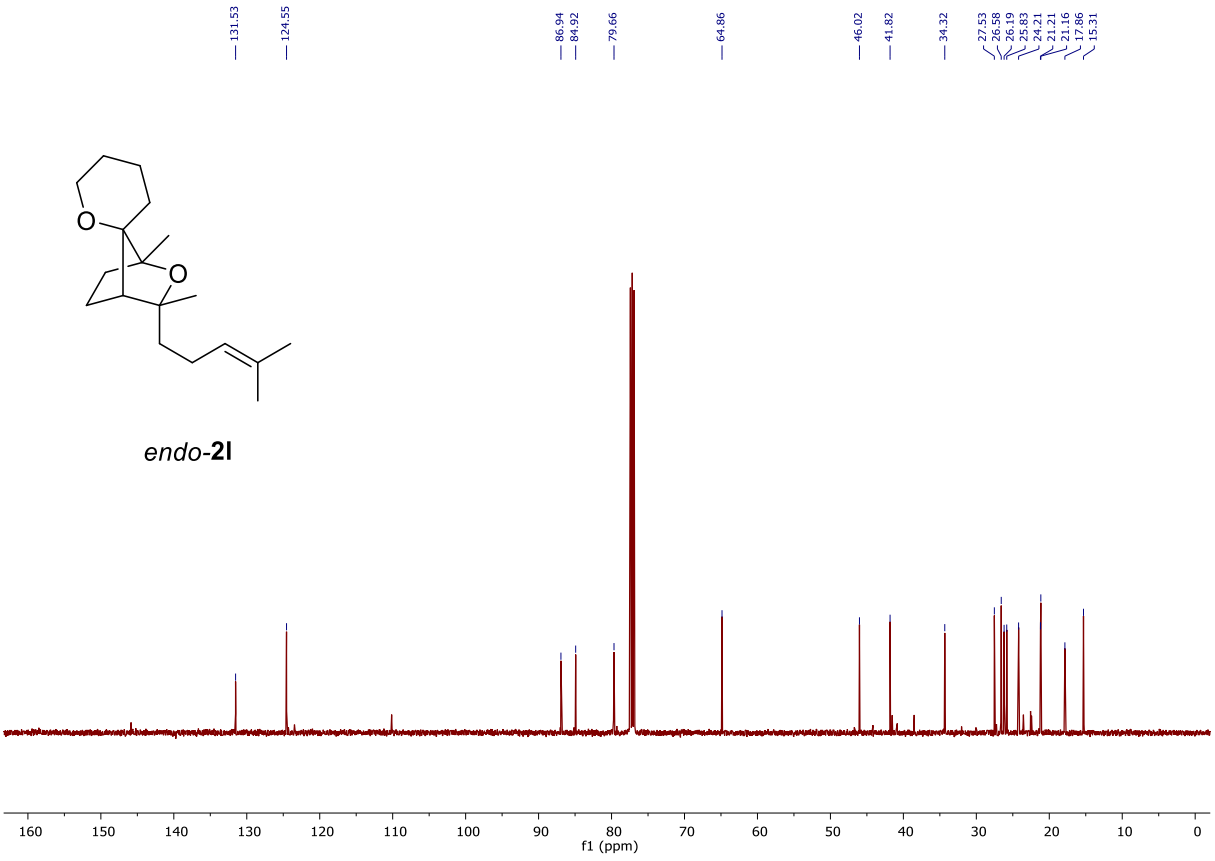

5.11 5.07 5.07 5.06 3.82 3.82 3.81 3.81 3.80 3.79 3.79 3.47 3.46 3.46 3.45 3.44 2.42 2.41 2.39 2.38 2.02 2.02 2.02 2.01 2.00 1.99 1.98 1.83 1.83 1.82 1.82 1.78 1.78 1.77 1.76 1.76 1.76 1.75 1.75 1.74 1.73 1.70 1.69 1.69 1.68 1.68 1.68 1.67 1.67 1.66 1.66 1.65 1.65 1.64 1.64 1.64 1.64 1.63 1.63 1.62 1.62 1.62 1.61 1.61 1.60 1.60 1.59 1.59 1.59 1.58 1.57 1.57 1.56 1.56 1.56 1.55 1.54 1.54 1.54 1.53 1.53 1.52 1.52 1.51 1.27 1.24 1.08
O
O
2l
0.97
1.05
0.87
1.04
1.93
0.88
1.00
41.12
1.33
2.77
3.00
5.84
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

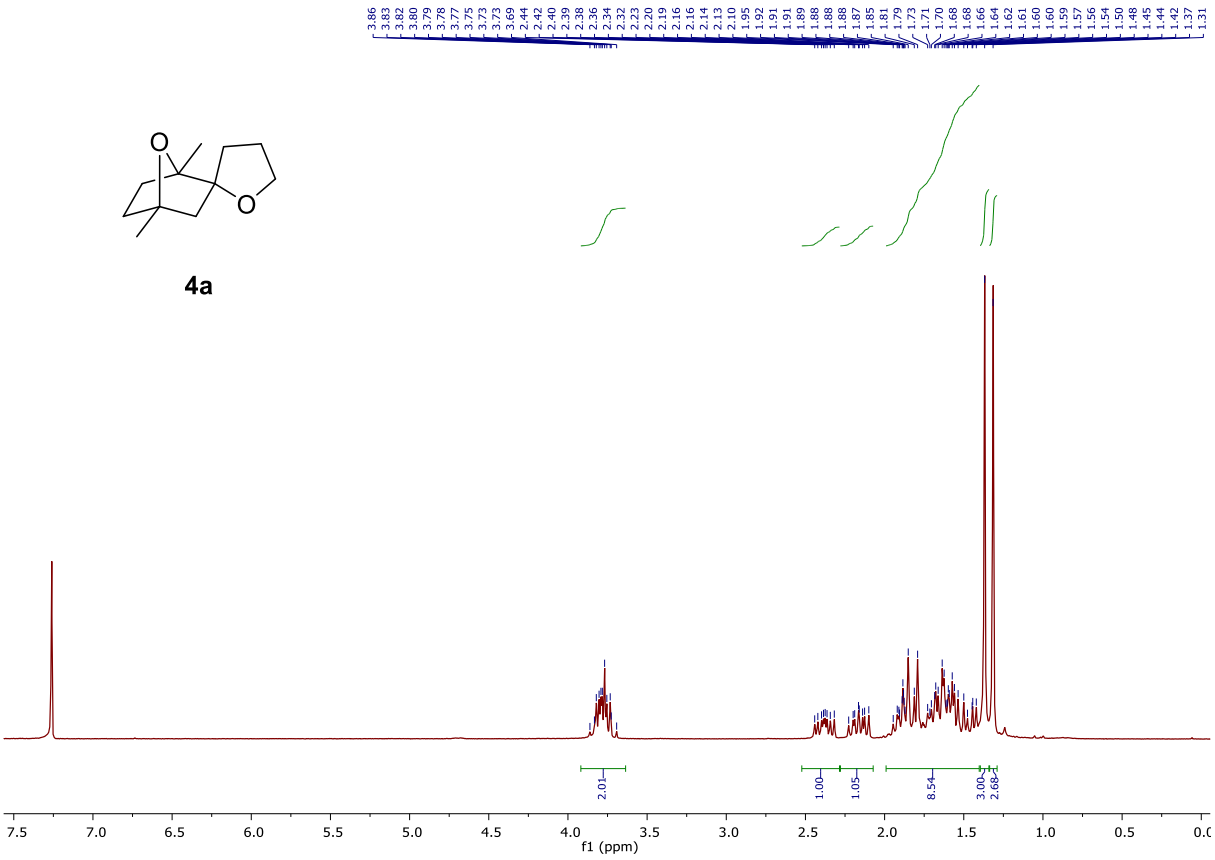

131.65
131.54
124.62
124.55
87.02
86.94
85.16
84.92
79.67
79.29
64.93
64.86
46.73
46.02
41.82
40.84
34.32
34.26
27.53
27.23
26.61
26.59
26.19
26.12
25.86
25.83
24.21
22.44
21.31
21.21
21.16
17.87
17.73
15.31
15.24
O
O
2l
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

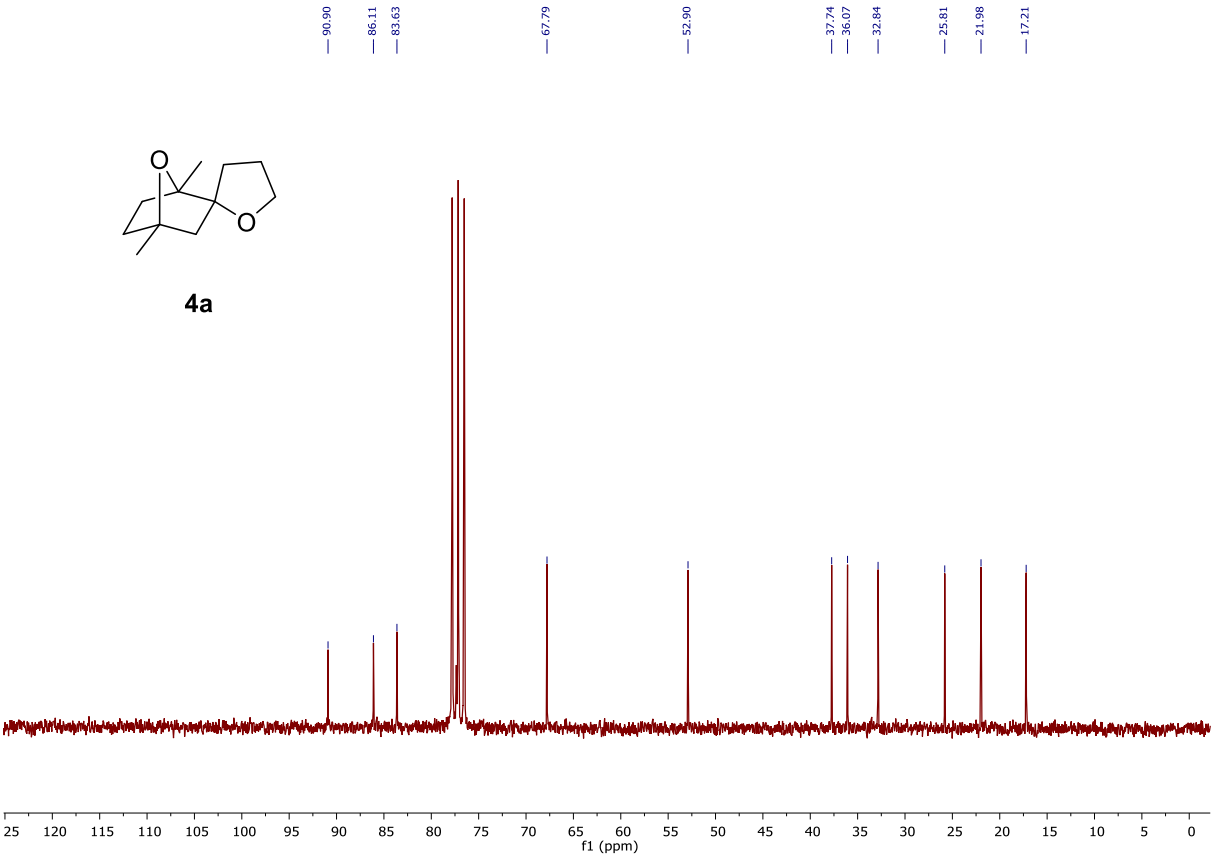

exo-2l
f1 (ppm)

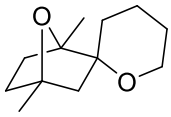

exo-2l
f1 (ppm)


O
O
endo-2l
0.94
1.00
1.00
1.00
1.20
1.52
0.97
1.00
17.27
3.13
3.11
f1 (ppm)


131.53
124.55
86.94
84.92
79.66
64.86
46.02
41.82
34.32
27.53
26.58
26.19
25.83
24.21
21.21
21.16
17.86
15.31
O
O
endo-2l
f1 (ppm)

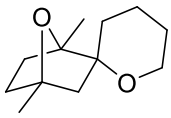

4a
f1 (ppm)


4a
f1 (ppm)



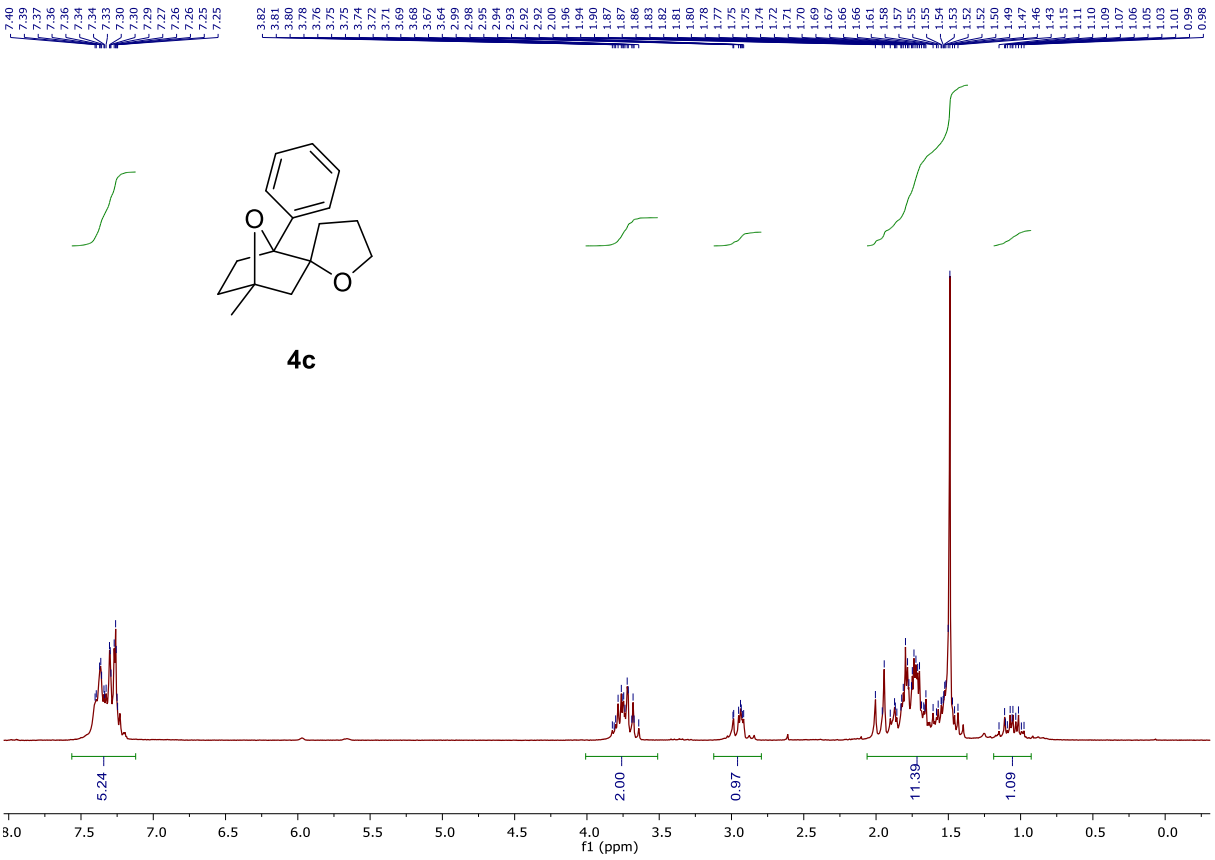
4b

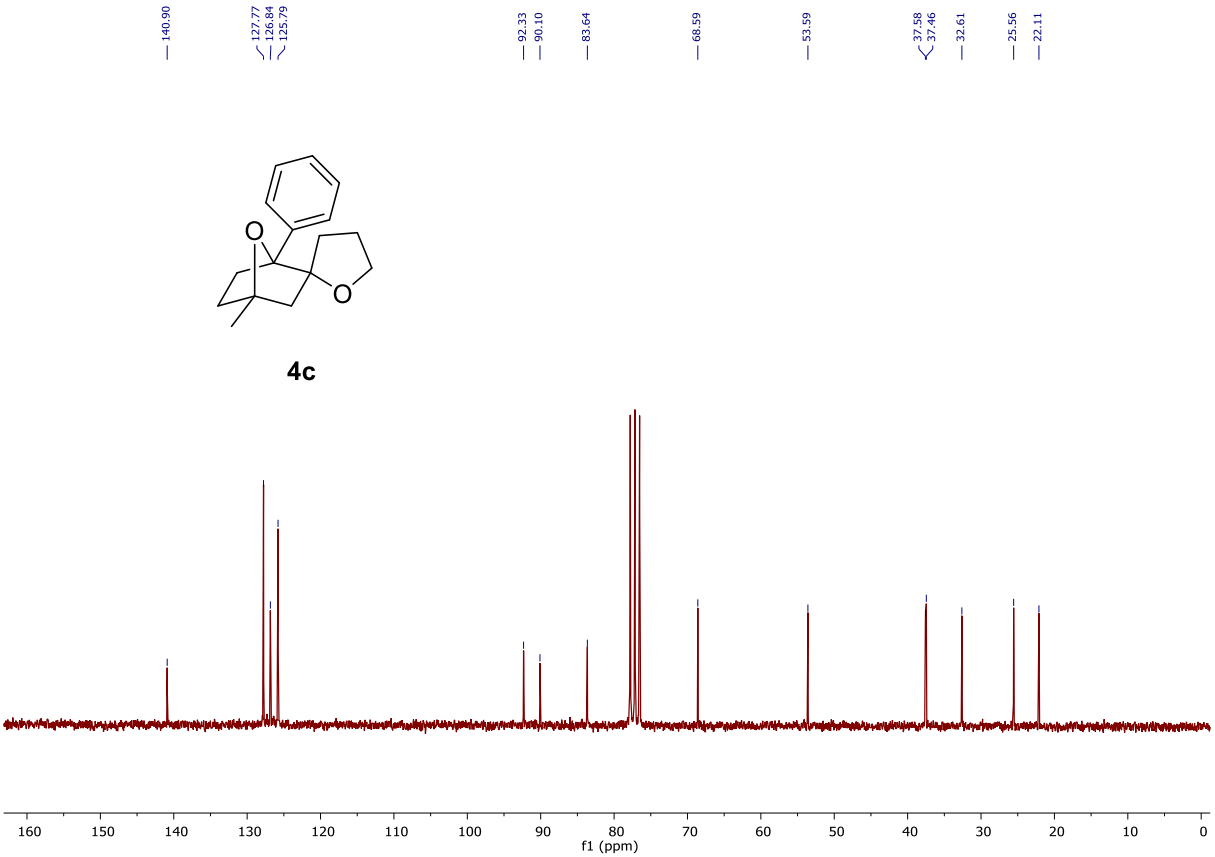
3.86
3.85
3.81
3.79
3.49
3.47
3.45
3.44
3.42
3.38
3.36
2.46
2.44
2.42
2.41
2.39
2.37
2.34
1.73
1.71
1.70
1.67
1.65
1.65
1.64
1.62
1.61
1.60
1.59
1.58
1.57
1.55
1.52
1.48
1.44
1.43
1.42
1.41
1.38
1.31
1.00
0.98
1.00
10.26
3.09
2.80
f1 (ppm)

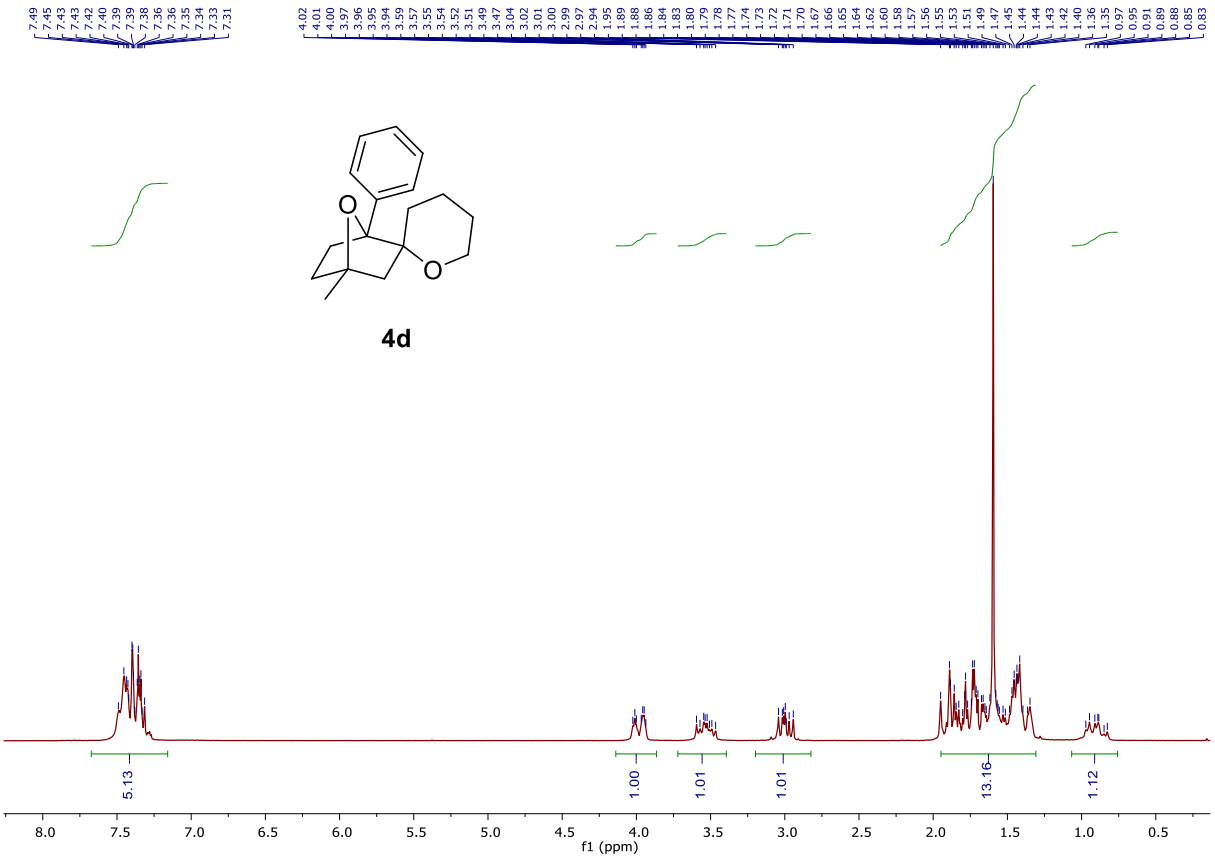


4b

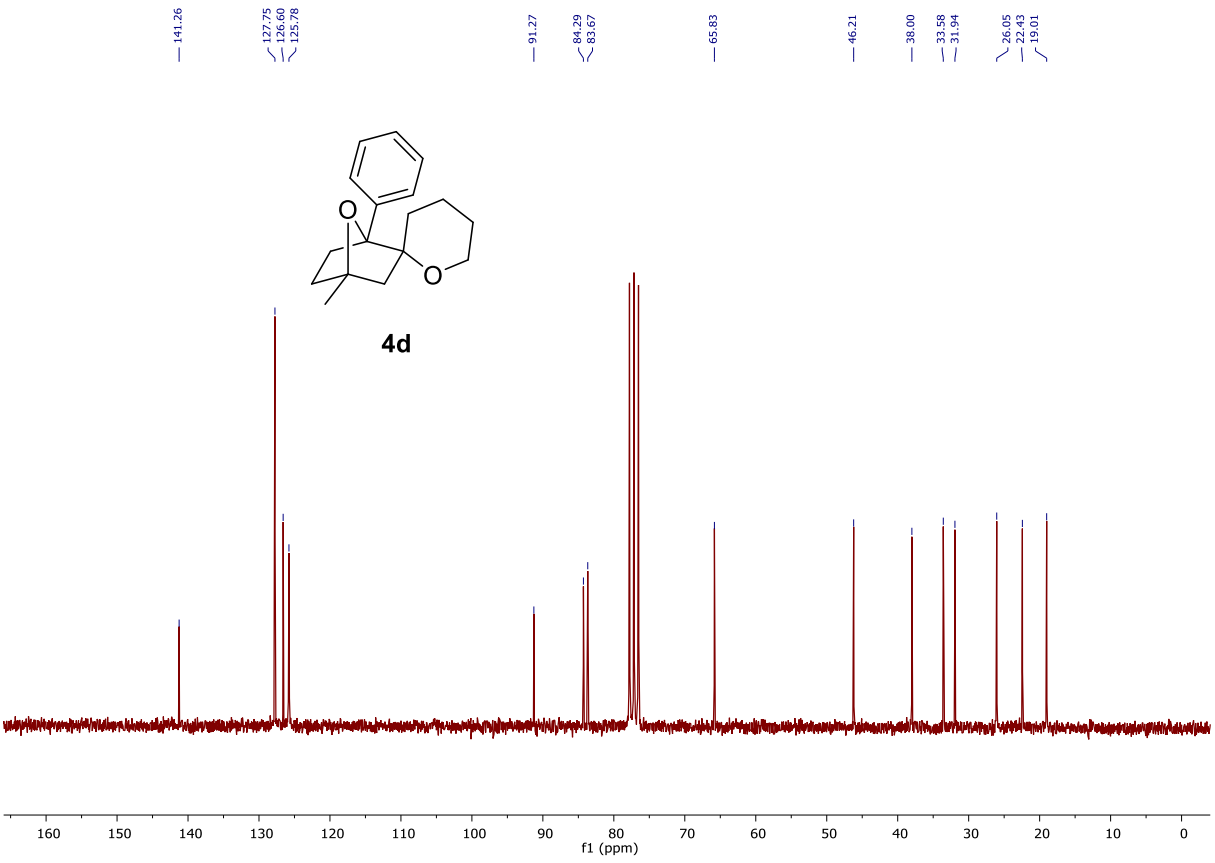
87.26
83.53
83.22
65.76
46.03
38.12
32.48
31.95
26.25
22.24
19.14
17.20
f1 (ppm)


7.40 7.39 7.37 7.36 7.36 7.34 7.34 7.33 7.30 7.30 7.29 7.27 7.26 7.27 7.26 7.25 7.25
3.82 3.81 3.80 3.78 3.76 3.75 3.75 3.74 3.72 3.71 3.69 3.68 3.67 3.64 2.99 2.98 2.95 2.94 2.93 2.92 2.92 2.00 1.96 1.94 1.90 1.87 1.87 1.86 1.83 1.82 1.81 1.80 1.78 1.77 1.75 1.75 1.74 1.72 1.71 1.70 1.69 1.67 1.66 1.66 1.61 1.58 1.57 1.55 1.55 1.54 1.53 1.52 1.52 1.50 1.49 1.47 1.46 1.43 1.15 1.11 1.10 1.09 1.09 1.07 1.06 1.05 1.03 1.01 0.99 0.98
O
O
4c
5.24
2.00
0.97
11.39
1.09
f1 (ppm)

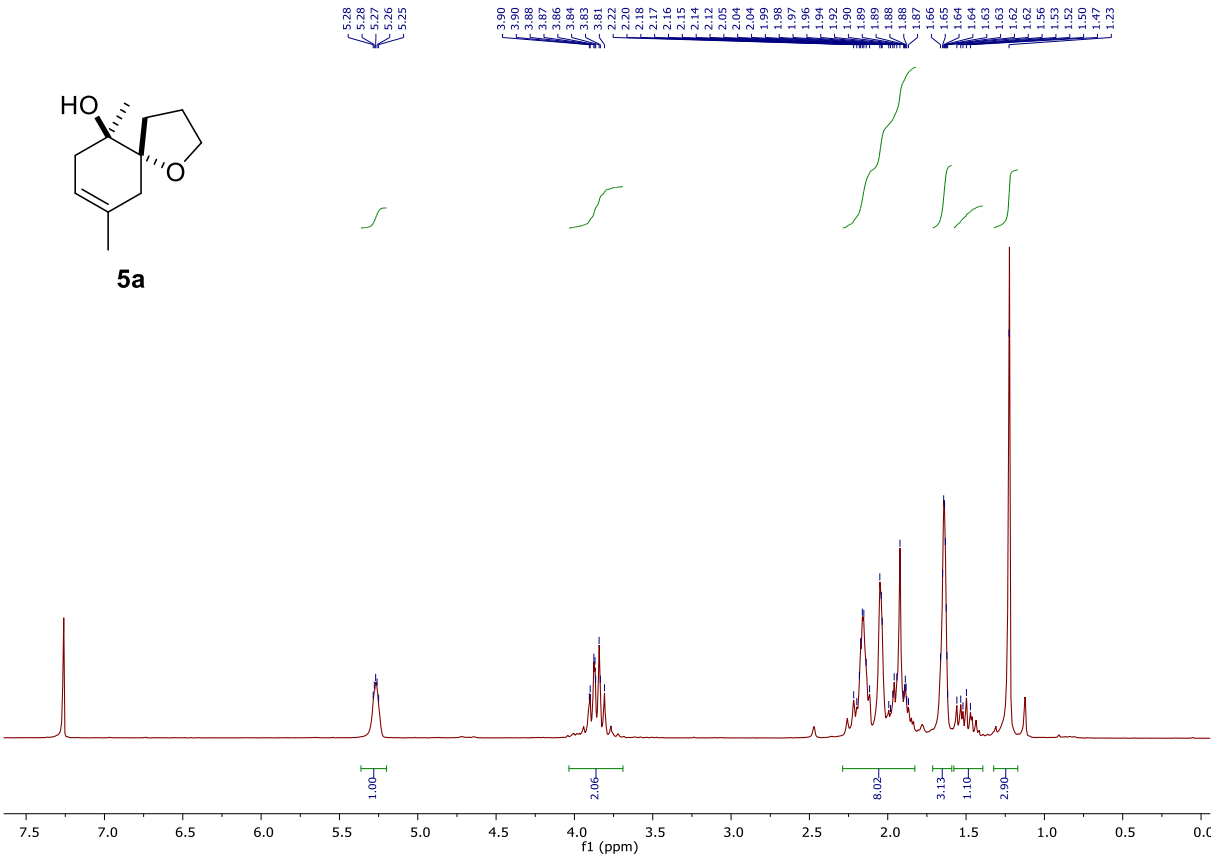

140.90
127.77
126.84
125.79
92.33
90.10
83.64
68.59
53.59
37.58
37.46
32.61
25.56
22.11
O
O
4c
f1 (ppm)

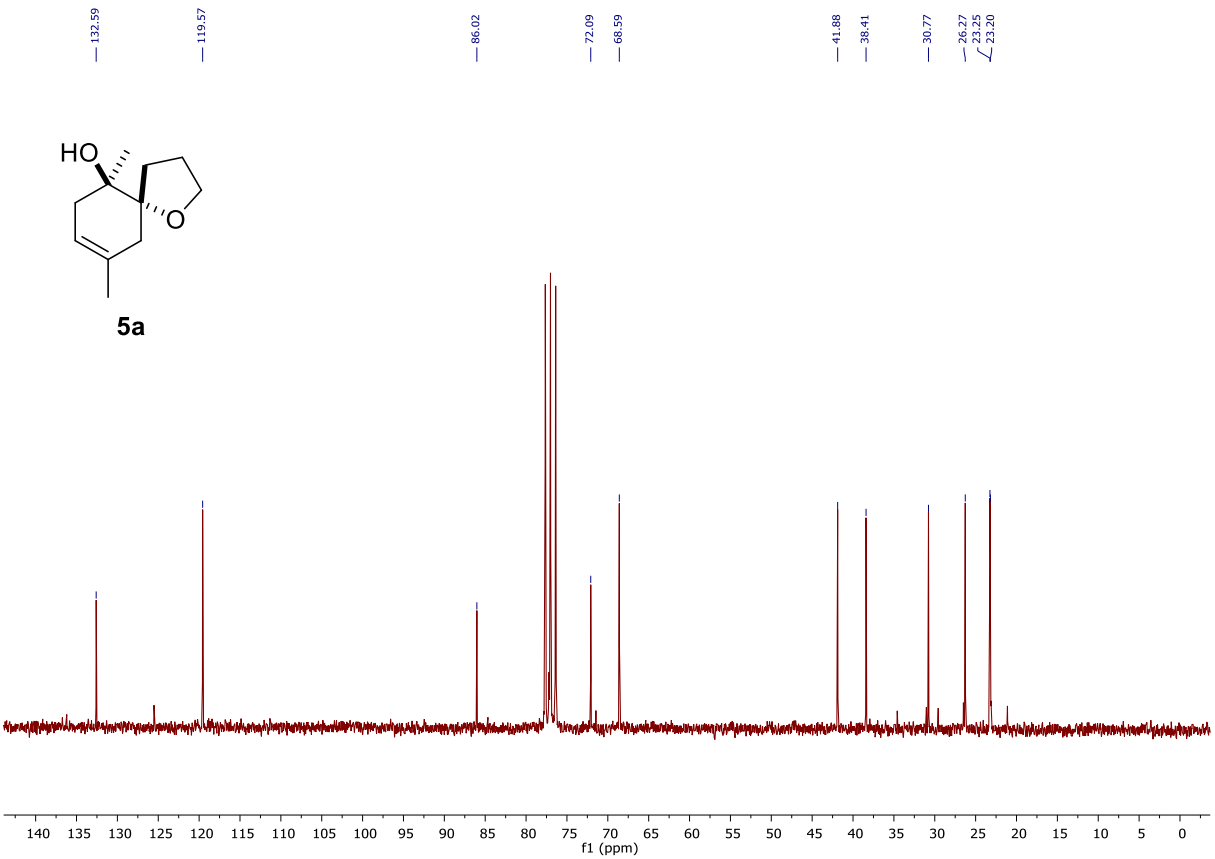

7.49 7.45 7.43 7.43 7.42 7.40 7.39 7.39 7.38 7.36 7.36 7.35 7.34 7.33 7.31
4.02 4.01 4.00 3.97 3.96 3.95 3.94 3.59 3.57 3.55 3.54 3.52 3.51 3.49 3.47 3.04 3.02 3.01 3.00 2.99 2.97 2.94 1.95 1.89 1.88 1.86 1.84 1.83 1.80 1.79 1.78 1.77 1.74 1.73 1.72 1.71 1.70 1.67 1.66 1.65 1.64 1.62 1.60 1.58 1.57 1.56 1.55 1.53 1.51 1.49 1.47 1.45 1.44 1.44 1.43 1.42 1.40 1.36 1.35 0.97 0.95 0.91 0.89 0.88 0.85 0.83
O
O
5.13
1.00
1.01
1.01
13.16
1.12
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

4d


141.26
127.75
126.60
125.78
91.27
84.29
83.67
65.83
46.21
38.00
33.58
31.94
26.05
22.43
19.01
O
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4d


HO
O
5a
5.28
5.28
5.27
5.26
5.25
3.90
3.90
3.88
3.87
3.86
3.84
3.83
3.81
2.22
2.20
2.18
2.17
2.16
2.15
2.14
2.12
2.05
2.04
2.04
1.99
1.98
1.97
1.96
1.94
1.92
1.90
1.89
1.89
1.88
1.88
1.87
1.66
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.56
1.53
1.52
1.50
1.47
1.23
1.00
2.06
8.02
3.13
1.10
2.90
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


132.59
119.57
86.02
72.09
68.59
41.88
38.41
30.77
26.27
23.25
23.20
HO
O
5a
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)