Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Hydrogenative Cyclopropanation and Hydrogenative Metathesis

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SUPPORTING INFORMATION

Contents

GENERAL

Unless stated otherwise, all reactions were carried out under argon atmosphere in flame dried Schlenk glassware. The solvents were purified by distillation over the indicated drying agents under argon: THF, Et_2O (Mg/anthacene), hexanes (Na/K), EtOH, MeOH (Mg), 1,2-dichloroethane, CD_2Cl_2, EtOAc, THP (CaH_2), 2-butanone (B_2O_3). DMF, MeCN and Et_3N were dried by an absorption solvent purification system based on molecular sieves. 1,2-Dichloroethane, CD_2Cl_2, THP and 2-butanone were degassed via freeze-pump-thaw procedure (3 x) and stored over molecular sieves (except 2-butanone). Flash chromatography: Merck Geduran silica gel 60 (40 – 63 µm). TLCs were stained with $KMnO_4$, anisaldehyde or PMA.

NMR spectra were recorded on Bruker DPX 300, AMX 300, AV 400 or AV III 600 spectrometers in the solvents indicated; chemical shifts are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 54.00 ppm; residual $CHDCl_2$: δ_H = 5.32 ppm; C_6D_6: δ_C = 128.06 ppm; residual C_6HD_5 : δ_H = 7.16 ppm). Proton and carbon assignments were established using HSQC, HMBC and NOESY experiments.

IR: Alpha Platinum ATR (Bruker), wavenumbers ($\tilde{\nu}$) in cm^{-1}.

MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker) or Thermo Scientific LTQ-FT or Thermo Scientific Exactive. HRMS: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan) or Thermo Scientific LTQ-FT or Thermo Scientific Exactive. GC-MS was measured on a Shimadzu GCMS-QP2010 Ultra instrument.

Headspace GC-FID samples were measured on an Agilent Technology 6890 or 7890 with a 30 m HP-plot Al_2O_3 column (0.25 mm Ø, 5 µm film) using H_2 as the carrier gas. Headspace GC/MS samples were measured on an Agilent Technology 7890A instrument with AT 5975C MSD detection.

Unless stated otherwise, all commercially available compounds (abcr, Acros, TCI, Aldrich, Alfa Aesar) were used as received. The ruthenium complexes $[Cp^*RuCl]_4$,[1] $[Cp^*Ru(cod)Cl]$,[1] and $[Cp^*Ru(NCMe)_3][PF_6]$[2] were prepared according to literature procedures.

SUPPORTING CRYSTALLOGRAPHIC INFORMATION

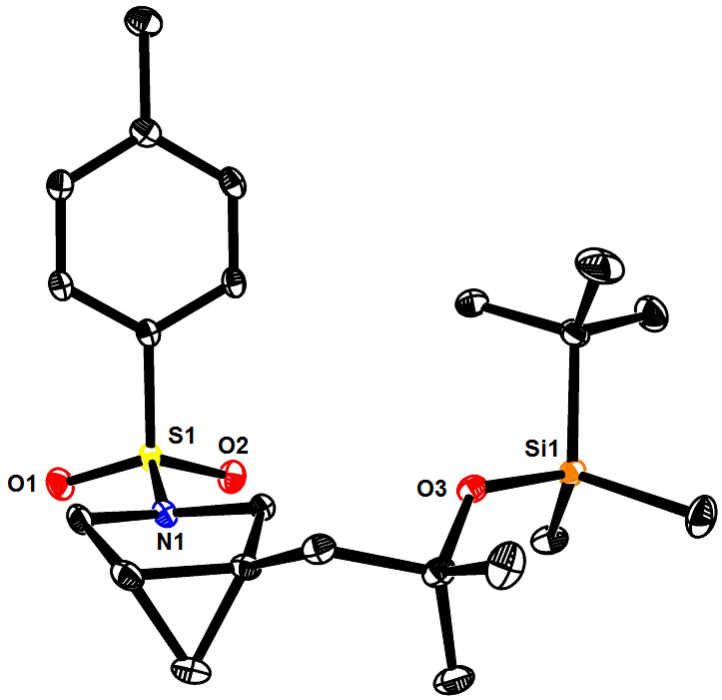


Figure S1. The structure of cyclopropane **4e** in the solid state; only one of the two independent molecules in the unit cell is shown, H-atoms are omitted for clarity

X-ray Crystal Structure Analysis of Compound 4e: $C_{22}H_{37}NO_3SSi$, *Mr* = 423.67 g · mol^{-1}, colorless plate, crystal size 0.131 x 0.052 x 0.042 mm^3, monoclinic, space group $P2_1$, *a* = 6.835(2) Å, *b* = 17.816(5) Å, *c* = 19.511(6) Å, β = 93.141(6)°, *V* = 2372.2(12) Å^3, *T* = 150(2) K, *Z* = 4, D_{calc} = 1.186 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 0.208 mm^{-1}, Gaussian absorption correction (T_{min} = 0.98, T_{max} = 0.99), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 2.985 < Θ < 35.156°, 79614 measured reflections, 20656 independent reflections, 15380 reflections with $I > 2\sigma(I)$, R_{int} = 0.066.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.045 [$I > 2\sigma(I)$], wR_2 = 0.100, 521 parameters. The H atoms were refined using a riding model, *S* = 1.070, absolute structure parameter = 0.03(2), residual electron density 0.3 (0.73 Å from O2)/ -0.3 (0.55 Å from S1) e · Å^{-3}. **CCDC-1905682**.

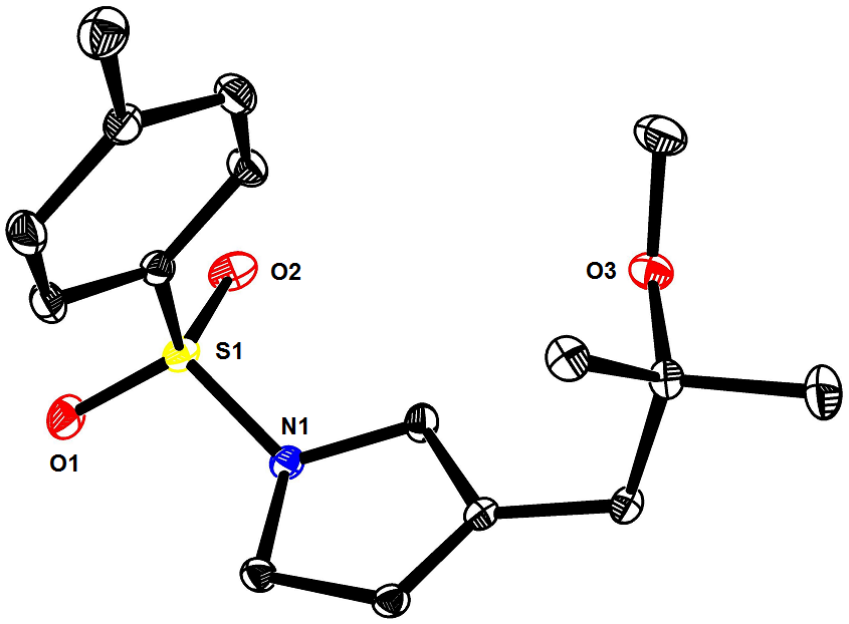


Figure S2. The structure of cycloalkene **12b** in the solid state; H-atoms are omitted for clarity.

X-ray Crystal Structure Analysis of Compound 12b: $C_{16}H_{23}NO_3S$, *Mr* = 309.41 g · mol^{-1}, colorless plate, crystal size 0.177 x 0.087 x 0.048 mm^3, triclinic, space group *P*$\bar{1}$, *a* = 7.9011(18) Å, *b* = 8.0298(19) Å, *c* = 14.549(3) Å, α = 91.943(4)°, β = 98.836(4)°, γ = 118.012(4)°, *V* = 799.2(3) Å^3, *T* = 160(2) K, *Z* = 2, D_{calc} = 1.286 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 0.212 mm^{-1}, Gaussian absorption correction (T_{min} = 0.98, T_{max} = 0.99), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 2.976 < Θ < 36.474°, 37819 measured reflections, 7683 independent reflections, 5904 reflections with $I > 2\sigma(I)$, R_{int} = 0.035.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.042 [$I > 2\sigma(I)$], wR_2 = 0.120, 194 parameters. The H atoms were refined using a riding model, *S* = 1.031, residual electron density 0.5 (0.64 Å from C3)/ -0.5 (0.62 Å from S1) e · Å^{-3}. **CCDC-1905683**.

HEADSPACE GC ANALYSES

The reactions were setup as described in the Experimental Section (see below). After completion of the reaction, the mixture was allowed to cool to room temperature and a needle connected to a gas tight analysis bag was pierced through the septum used to seal the Schlenk tube. The headspace gases were transferred by purging the Schlenk tube into the gas bag by a stream of argon (approx. 50 mL). An aliquot of the gas mixture was immediately analyzed by GC-FID and GC-MS. Retention times and fragmentation patterns of the analytes were compared with reference samples ("Phillips 40"), which unambiguously confirmed the formation of propane/propene from enyne **1f** and of isobutane/isobutene from enyne **1e** as the starting material.

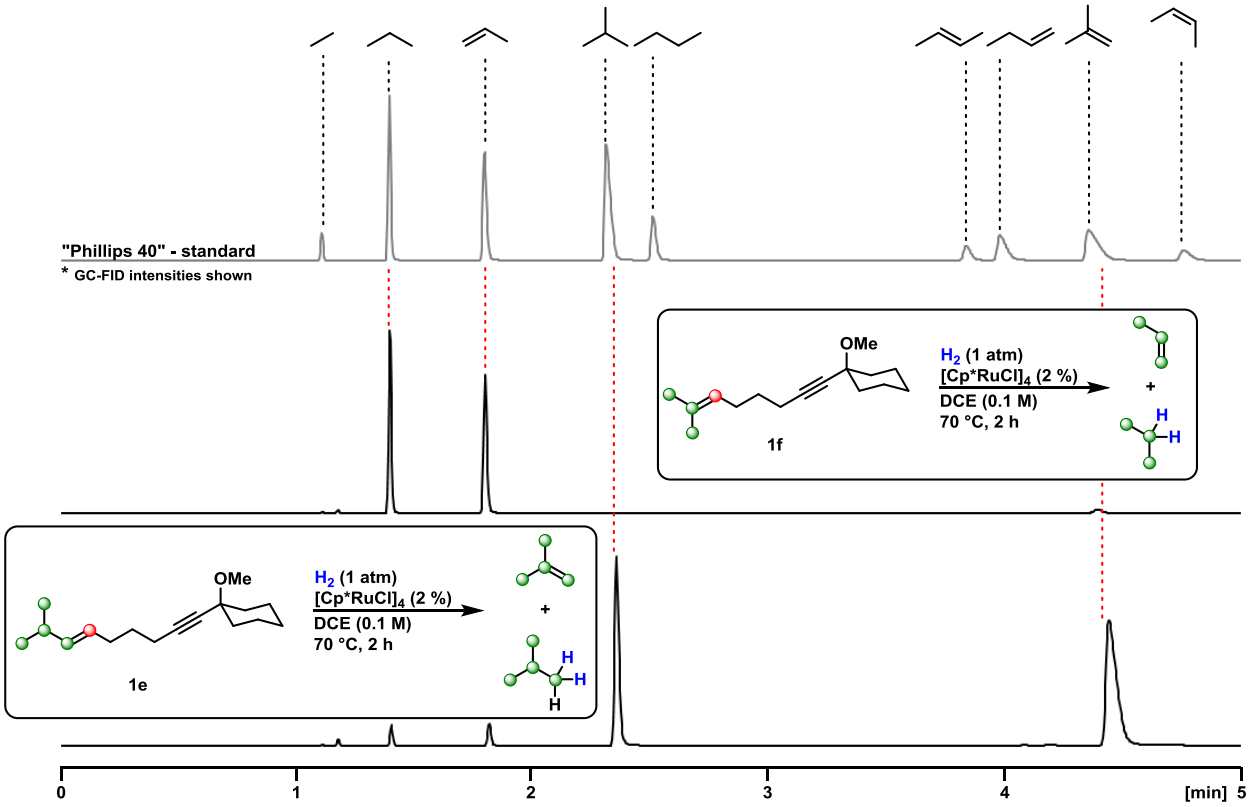
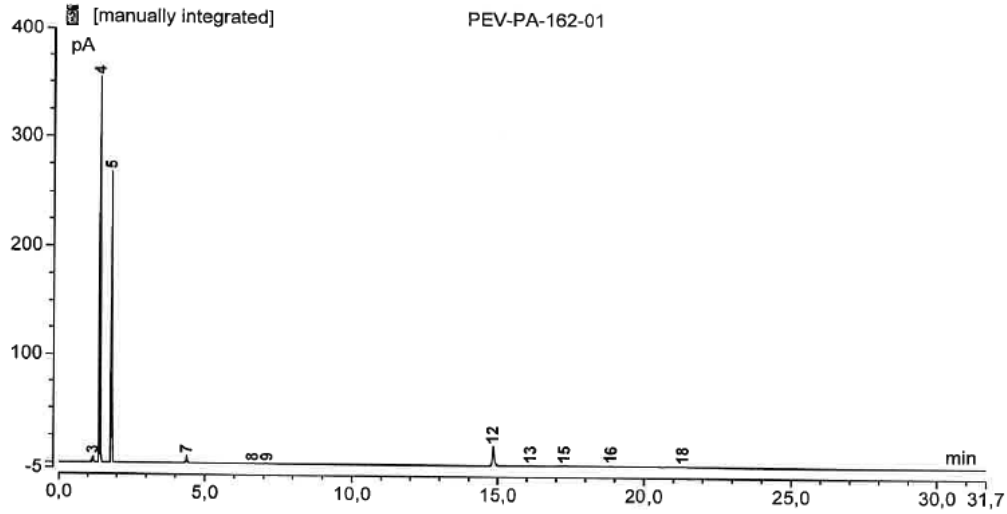


Figure S3: Excerpt of GC-FID traces of the headspace analytes formed in the shown reactions.



Sample:	**PEV-PA-162-01**	Instrument:	**GC_123**
Sequenz:	**5030 PEV-PA VD**	Measured:	**23.07.18 10:53**
Sequenz date:	**23.07.18**	Processing M.:	**Übersicht PEV-PA**
		Report-File:	**Übersicht 162-01**

Zuordnung mit Vergleichssubstanzen (Gasmischung Phillips 40)

No.	Ret.Time min	area-% %	Peak Name
1	1,04	0,06	
2	1,12	0,19	
3	1,19	0,61	
4	1,40	42,65	Propan
5	1,81	40,35	Propen
6	3,99	0,07	
7	4,38	2,39	
8	6,62	0,19	
9	7,11	0,36	
10	8,14	0,02	
11	10,07	0,02	
12	14,83	12,11	
13	16,12	0,22	
14	17,03	0,01	
15	17,28	0,25	
16	18,89	0,15	
17	19,81	0,03	
18	21,32	0,21	
19	21,82	0,02	
20	26,43	0,06	

Instrument parameters:

Column:	30,0 m	HP-Plot/Al203 0,25/5,0df G/425
Temperature:	220/ 80, 10 min iso 6/min 180, 5 min iso/ 350	
Gas:	0,80 bar	H2
Sample size:	250,0 µL	

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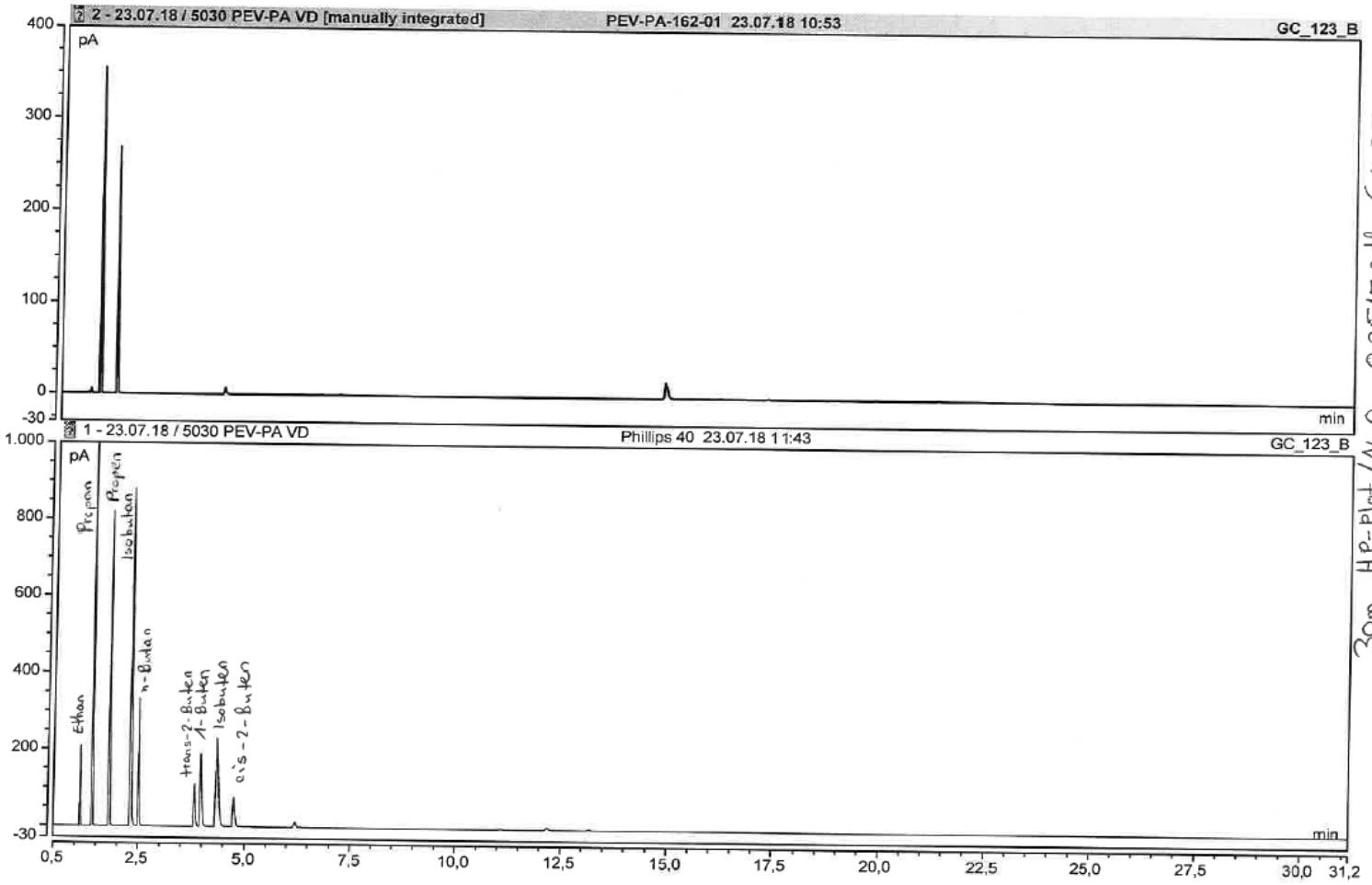
Sequence: 5030 PEV-PA VD
Injection #2: PEV-PA-162-01

Chromatogram



30m HP-Plot/Al_2O_3 0,25/15,0µl 6/425
220/80,10min iso 6/min 180,5 min iso/350
0,8bar H_2

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Version 7.2.5.9717, Thermo Fisher Scientific

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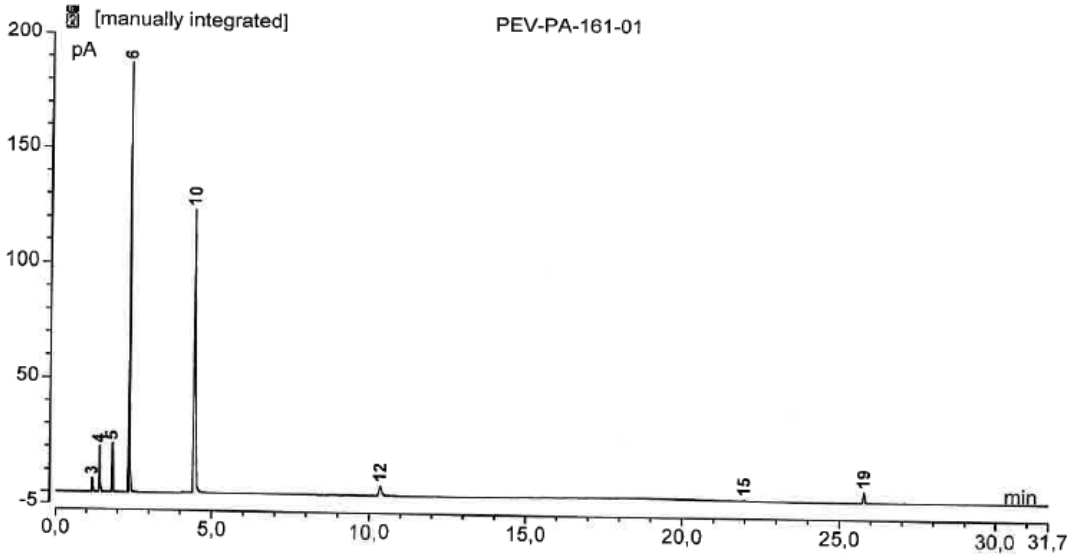


Sample: **PEV-PA-161-01**
Sequenz: **5031 PEV-PA VD**
Sequenz date: **23.07.18**

Instrument: **GC_123**
Measured: **23.07.18 13:55**
Processing M.: **Übersicht PEV-PA**
Report-File: **Übersicht 161-01**

Zuordnung mit Vergleichssubstanzen (Gasmischung Phillips 40)

No.	Ret.Time min	area-% %	Peak Name
1	1,04	0,07	
2	1,12	0,06	
3	1,19	0,63	
4	1,41	2,19	Propan
5	1,82	2,93	Propen
6	2,36	33,46	Isobutan
7	2,55	0,01	
8	4,07	0,17	
9	4,18	0,59	
10	4,43	53,96	Isobuten
11	7,30	0,03	
12	10,35	3,25	
13	15,14	0,06	
14	17,55	0,05	
15	21,97	0,23	
16	22,09	0,04	
17	22,37	0,02	
18	23,30	0,04	
19	25,77	2,18	
20	27,08	0,04	

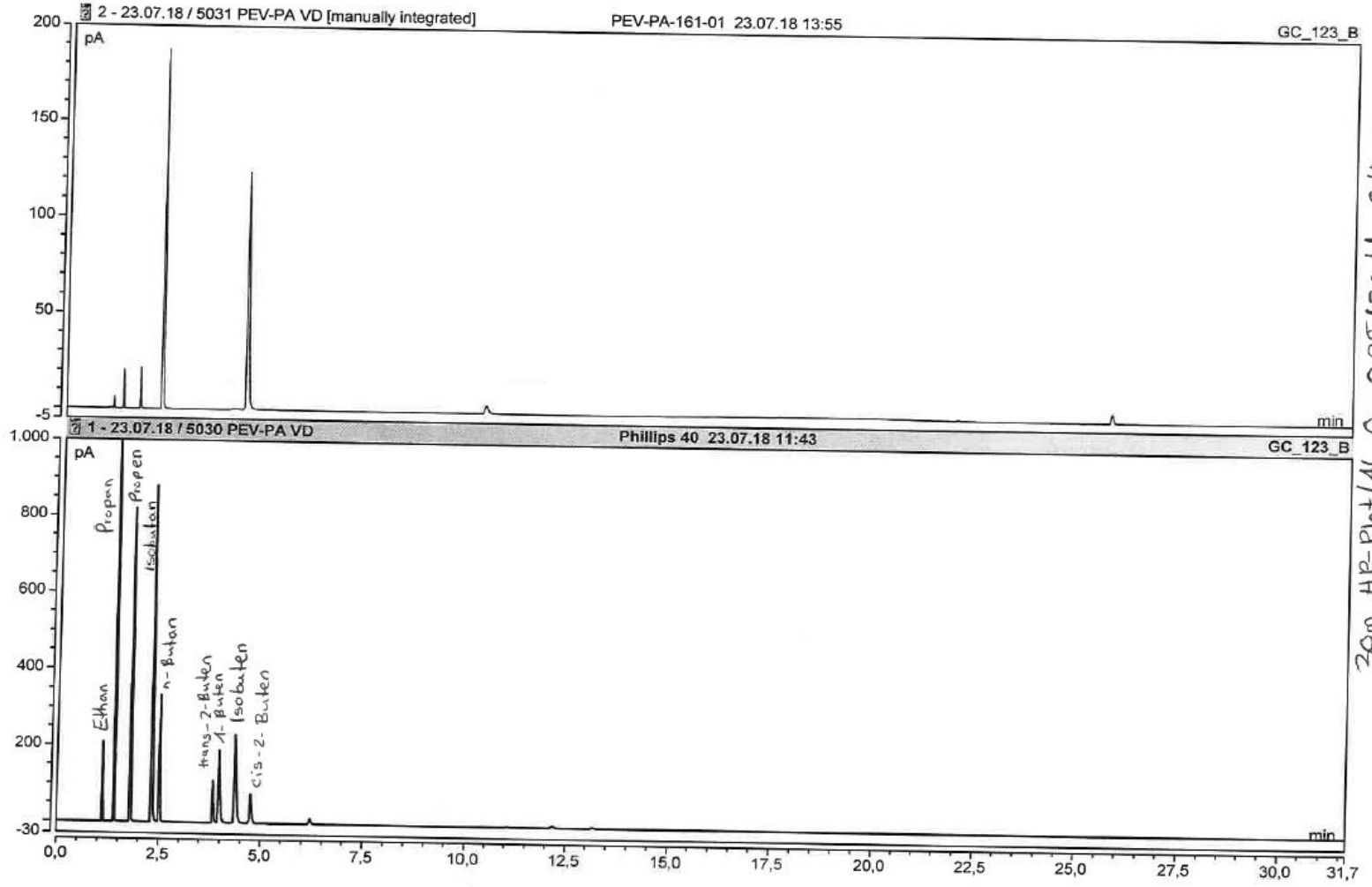
Instrument parameters:

Column:	30,0 m	HP-Plot/Al203 0,25/5,0df G/425
Temperature:	220/ 80, 10 min iso 6/min 180, 5 min iso/ 350	
Gas:	0,80 bar	H2
Sample size:	250,0 µL	

V. Diehl

Sequence: 5030 PEV-PA VD
Injection #3: Phillips 40

Chromatogram



30m HP-Plot/Al2O3 0,25 15,0d4 G/425
220/80, 10min iso 6/min 180, 5min iso 1350
0,8 bar H2

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Version 7.2.5.9717, Thermo Fisher Scientific

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THE BRIDGED CARBENOID 16

A. Variable-temperature NMR Control of the Stoichiometric Reaction of Enyne 1f with $[Cp^*RuCl]_4$ under H_2. $[Cp^*RuCl]_4$ (16.1 mg, 0.015 mmol) was added to a stirred solution of enyne **1f** (13.9 mg, 0.059 mmol) in CD_2Cl_2 (0.7 mL) under argon in a flame-dried Schlenk tube. The mixture was transferred into a flame-dried J-Young-NMR tube under argon before it was cooled to −78 °C (dry ice/acetone bath). The atmosphere was exchanged for H_2 by purging the system with a H_2 for 2 min and the NMR tube was quickly sealed in a H_2 current. The NMR tube was shaken before being introduced into the NMR spectrometer, the internal temperature of which had been set to −50°C. ^{1}H NMR spectra were recorded at temperatures from −50 °C to room temperature using 10 °C intervals (series of ^{1}H excerpts see **Fig. S4**).

Figures S4 and S5*: The formation of the metathesis product **11a** starts at −30 °C (signals **C** + **D**) with steady increase of conversion upon raising the temperature in increments of 10°C. An additional signal (**E**) appears in parallel which was attributed to the bridged carbenoid **16**. Conversion was incomplete even at room temperature, likely because of insufficient H_2 in solution and slow transfer from the gas phase.*

B. Room Temperature NMR Spectra of a Stoichiometric Reaction of Enyne 1f with $[Cp^*RuCl]_4$ under H_2. $[Cp^*RuCl]_4$ (15.3 mg, 0.014 mmol) was added to a stirred solution of enyne **1f** (14.5 mg, 0.062 mmol) in CD_2Cl_2 (0.7 mL) under argon in a flame dried Schlenk tube at room temperature. H_2 was bubbled gently through the mixture for 2 min and stirring was continued for 30 min under a H_2 atmosphere. The mixture was transferred into a flame dried J-Young-NMR tube under argon, sealed and immediately analyzed.

Figures S7-S10: *The spectra show complete conversion of enyne* **1f** *(signals **A** + **B** missing) to product **11a** (signals **C** + **D**). Significant quantities of bridged carbenoid **16** are detected (approx. 15% by comparison of signals **D** and **E**). ^{13}C NMR, HSQC and HMBC spectra were recorded to characterize the carbenoid species; the data are summarized in* **Figure S5**.

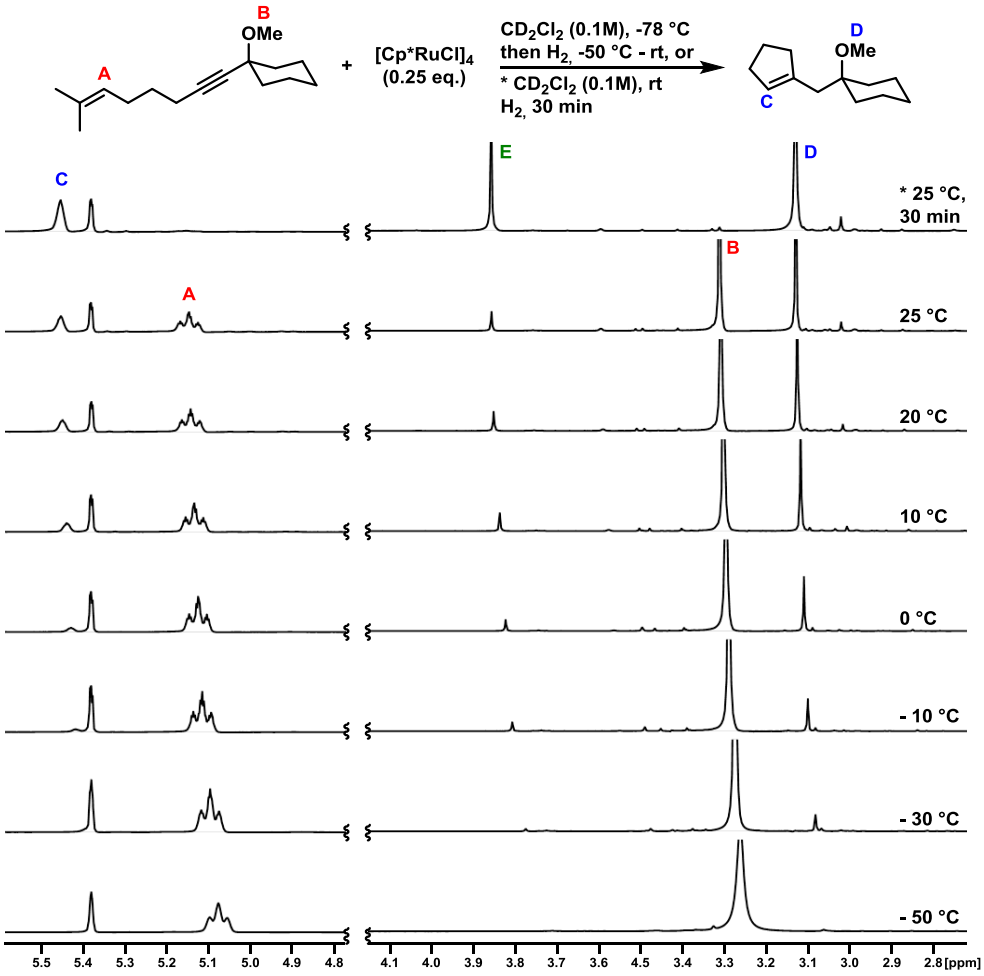


Figure S4: Low and room temperature stoichiometric NMR experiments. Shown is the relevant region in the ^{1}H spectra recorded at the specified temperatures (complete spectra see below). Excerpt 1 (top) refers to experiment **B**, excerpts 2 – 8 refer to experiment **A**.

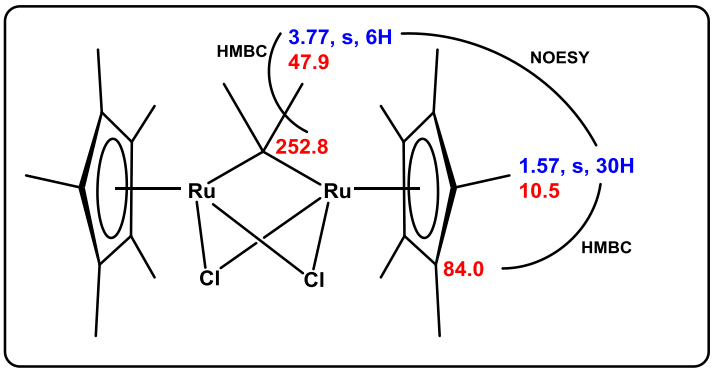


Figure S5: NMR assignments of carbenoid **16** based on the spectra shown in Fig. S7 – S14.

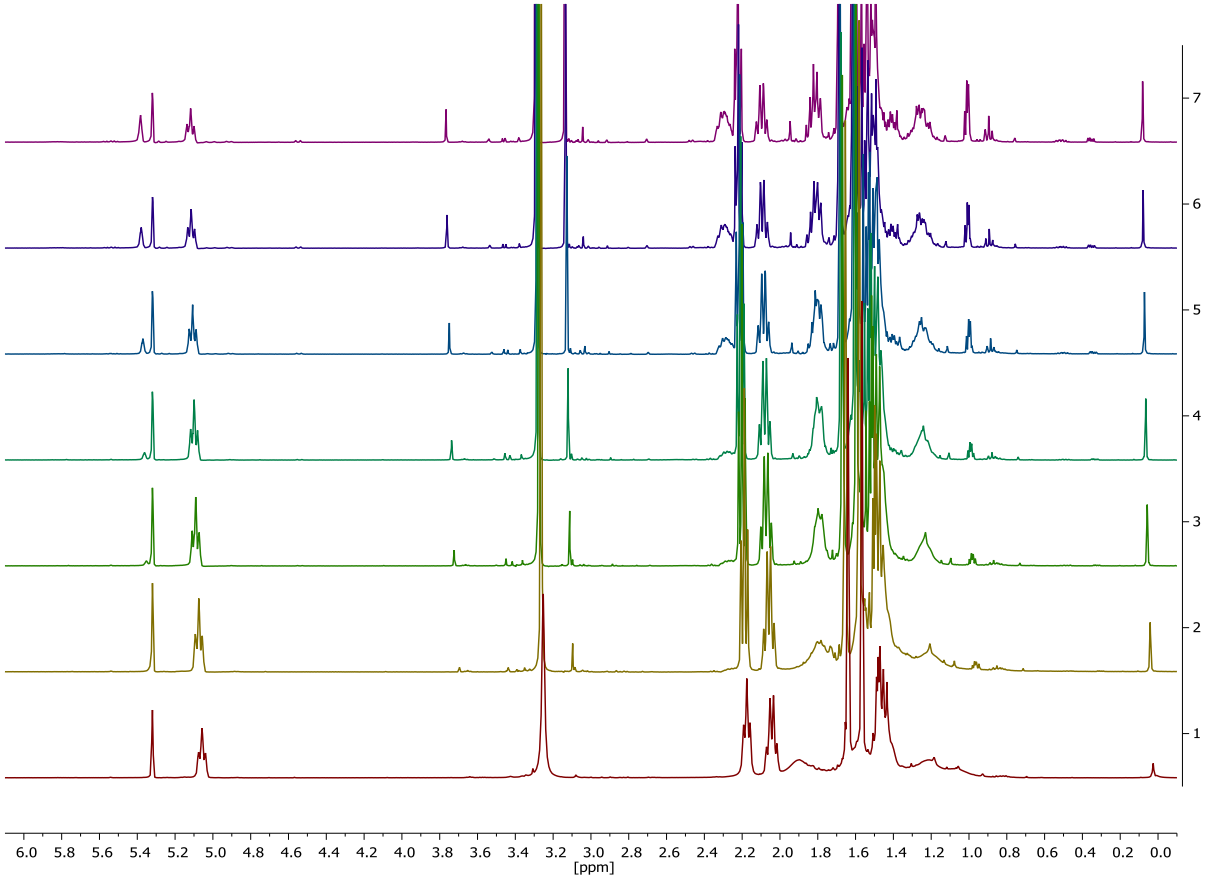


Figure S6. ^{1}H NMR spectra of low temperature stoichiometric NMR experiment **A**. Spectra are stacked according to Fig. S4 (1 @ −50 °C to 7 @ 25 °C)

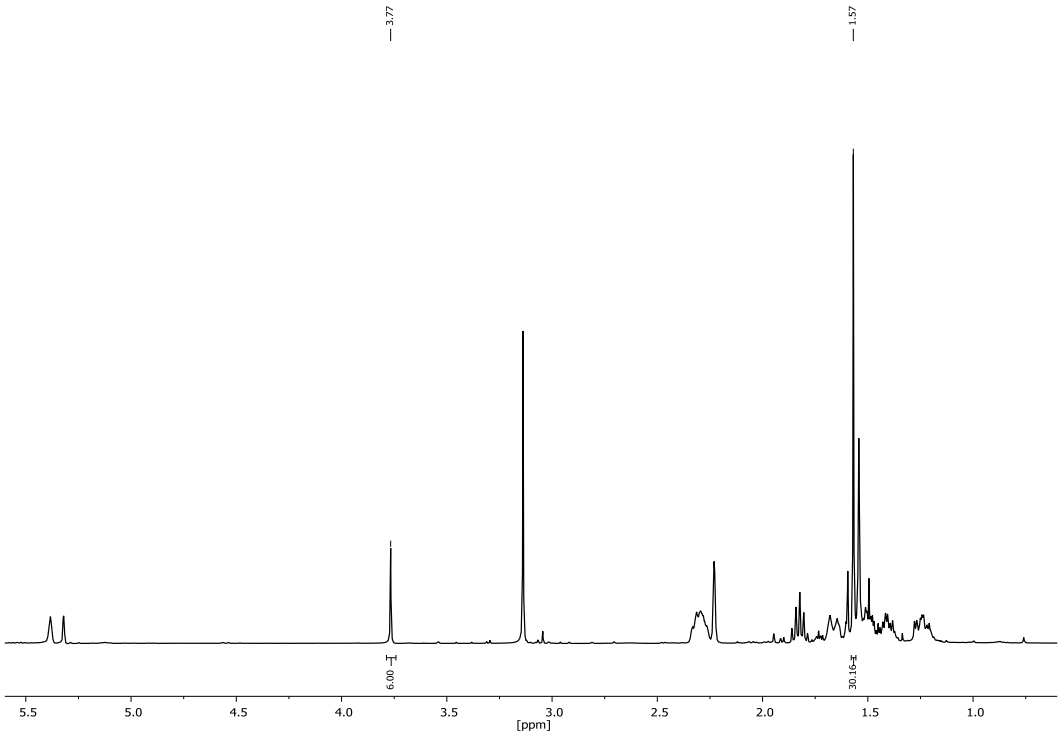


Figure S7. ^{1}H NMR spectrum of room temperature stoichiometric NMR experiment **B**; peak-picking and integrals shown for signals attributed to carbenoid **16**.

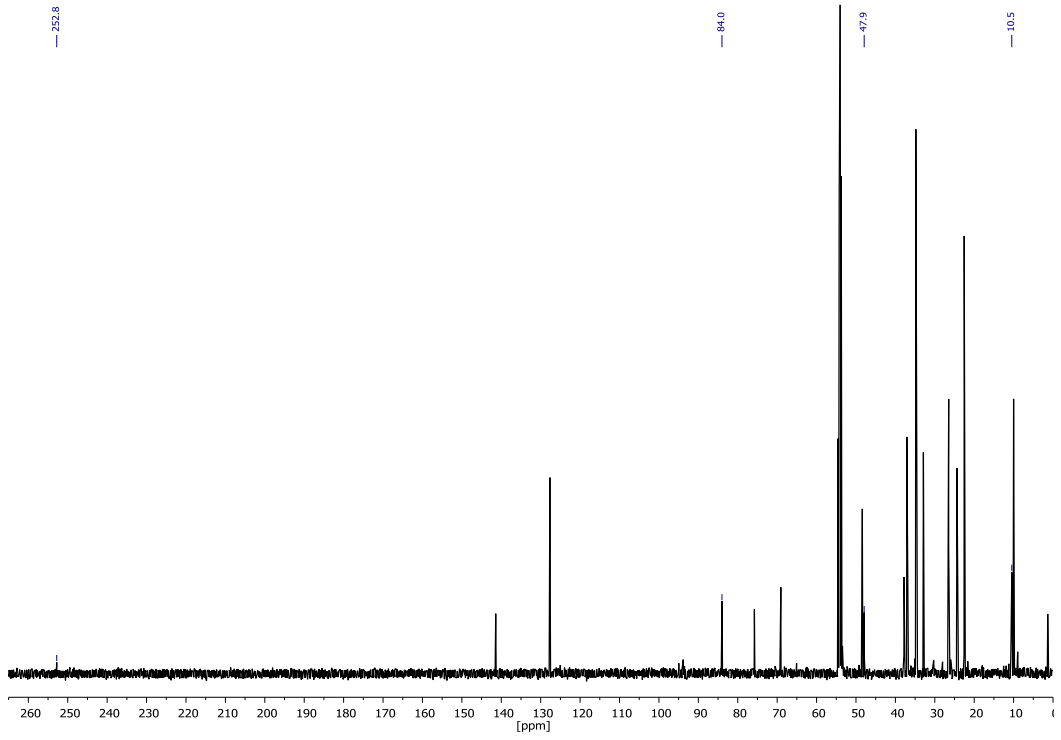


Figure S8: ^{13}C NMR spectrum of the room temperature stoichiometric NMR experiment **B**; peak-picking shown for signals attributed to carbenoid **16**.

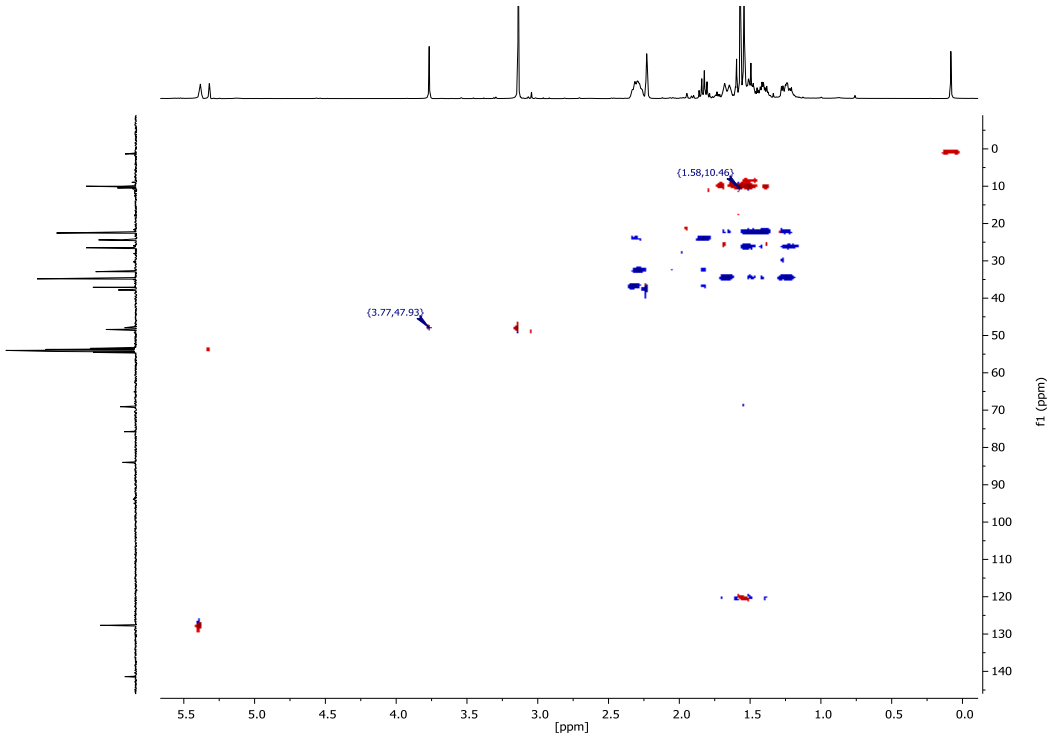


Figure S9: HSQC of experiment **B**, cross-peaks for carbenoid **16** are indicated

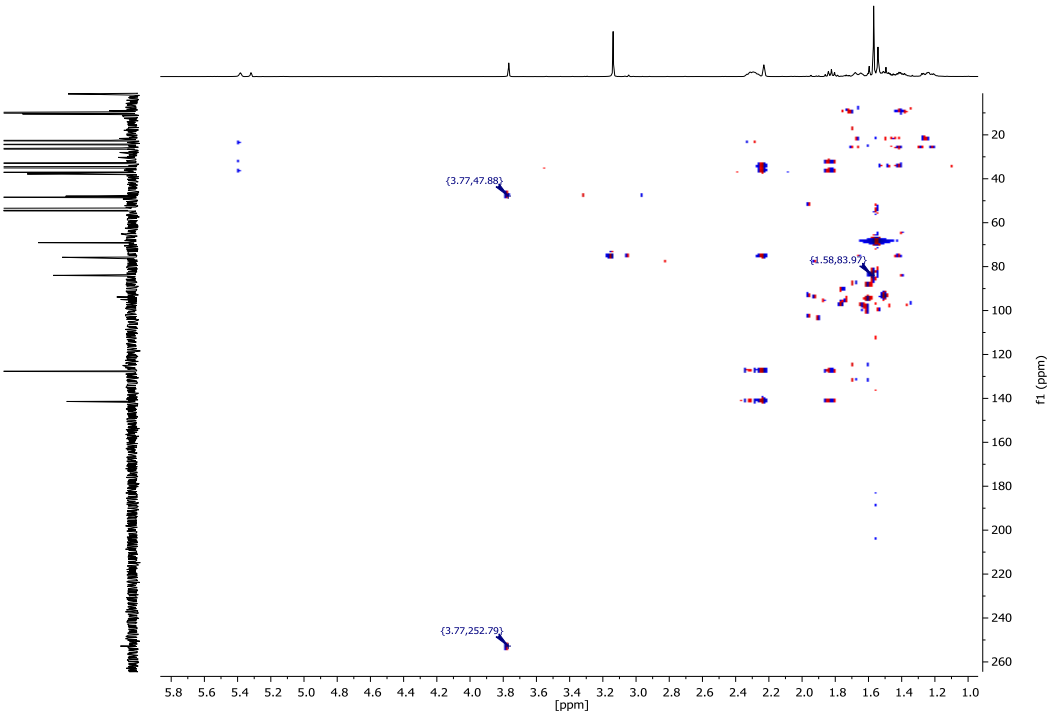


Figure S10: HMBC of experiment **B**, cross-peaks for carbenoid **16** are indicated

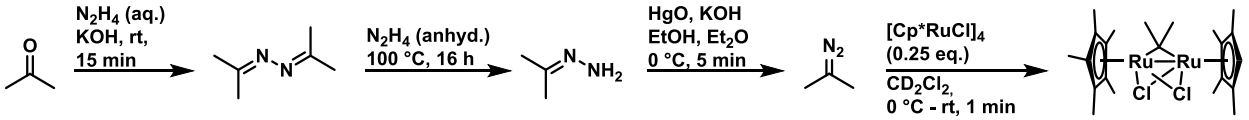


Figure S11: Synthesis of bridged carbenoid **16** from 2-diazopropane.

Independent Synthesis. 2-Diazopropane (0.2 M in Et_2O, 92 µL, 0.02 mmol)[3][4] was added dropwise to a stirred solution of $[Cp^*RuCl]_4$ (10 mg, 0.01 mmol) in CH_2Cl_2 (0.4 mL) at 0 °C in a flame-dried Schlenk tube under argon. The mixture was stirred for 1 min before it was allowed to warm to room temperature. The solvent was removed by purging with argon and subsequent evacuation of the tube, and the green residue was dissolved in CD_2Cl_2 and immediately analyzed.

Figures S12-S14*: Identical sets of ^1H and ^{13}C resonances (**Figs. S12 – S13**) were found as for the in-situ generated carbenoid* **16** *from NMR experiment* **B** *by metathesis, thus strongly supporting the structural assignment. nOe data confirm the shown 3D structure, which is also consistent with a previously reported dimeric carbenoid.*[5]

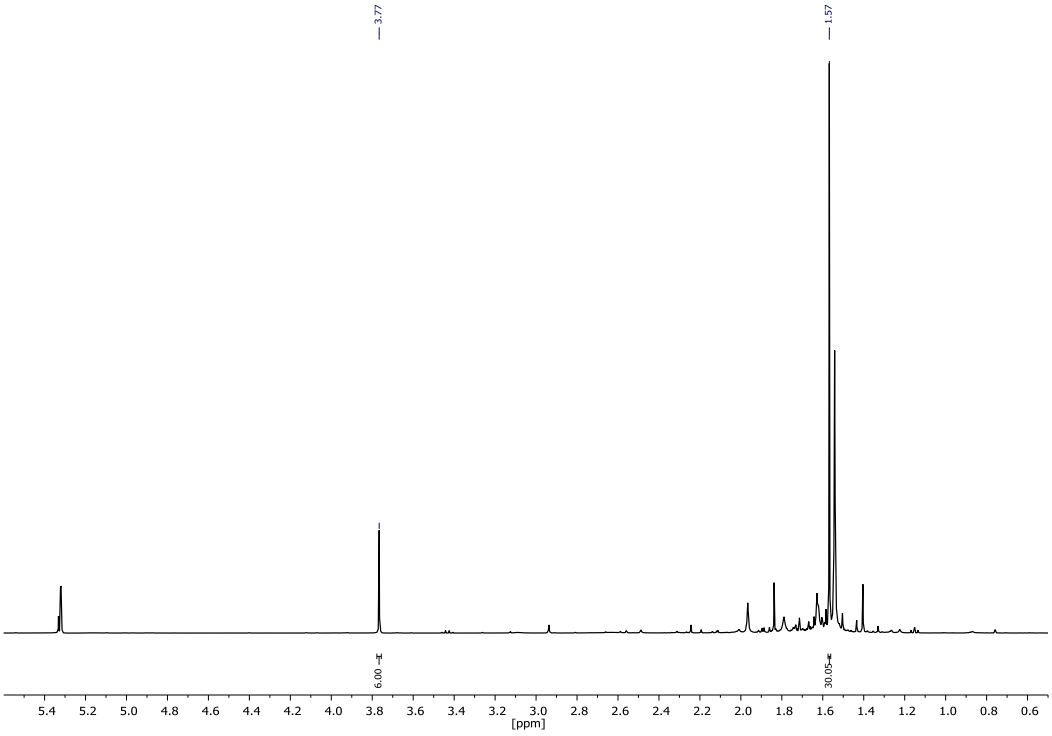


Figure S12: ^1H NMR spectrum of the crude reaction mixture comprising carbenoid **16** prepared by decomposition of 2-diazopropane

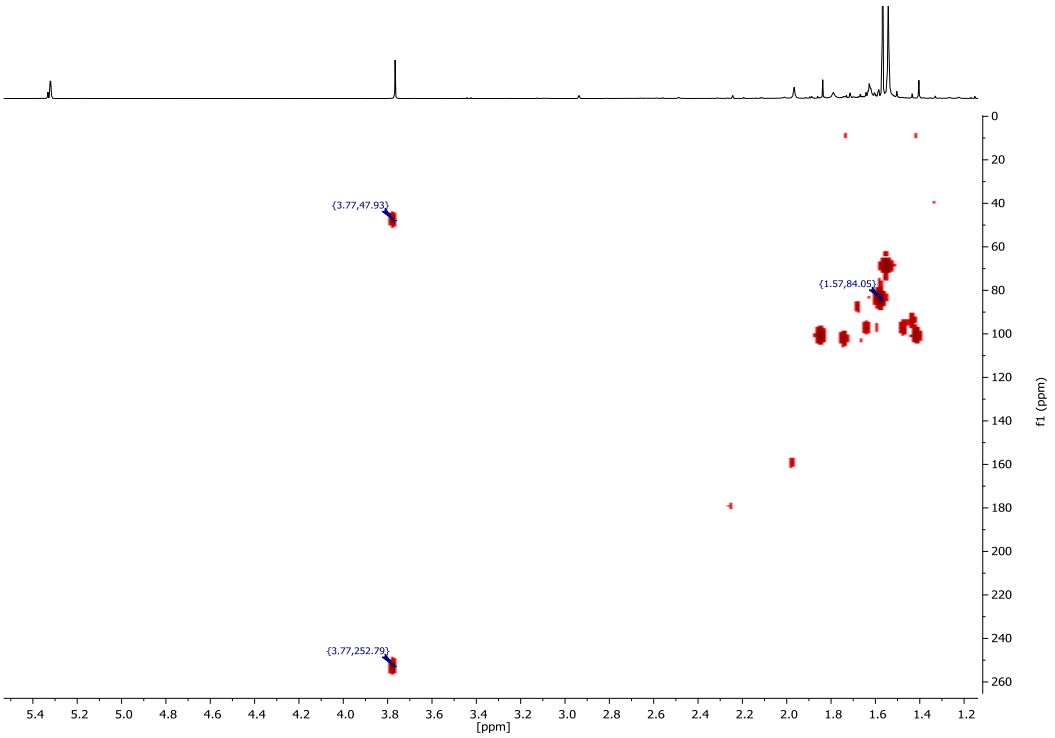


Figure S13: HMBC of carbenoid **16** generated from diazopropane

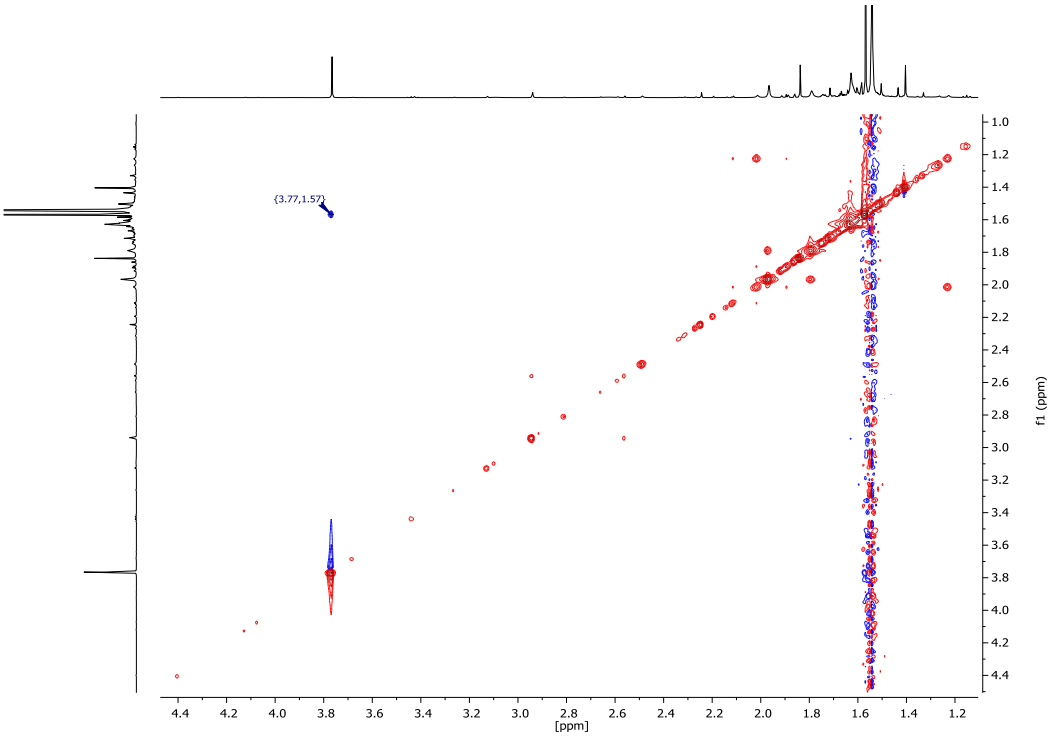
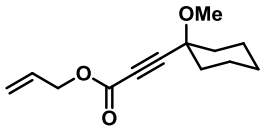
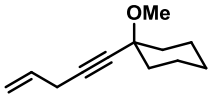
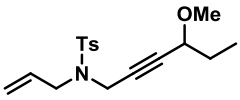
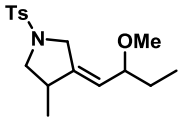
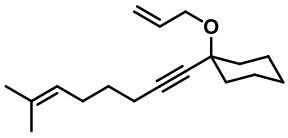
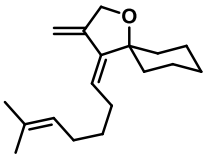
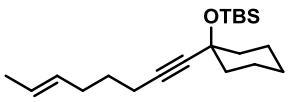
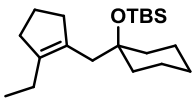
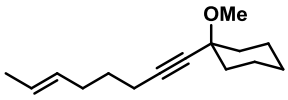
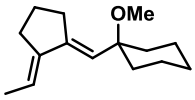
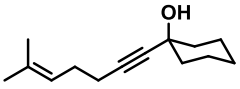
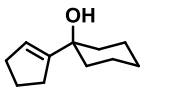
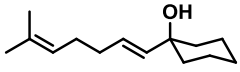
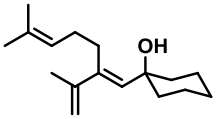


Figure S14: NOESY of of carbenoid **16** generated from diazopropane

SIDE REACTIONS

A compilation of side products identified in the reactions of the shown substrates is presented in Table S1. As can be seen from entry 1 and 2 the scope of hydrogenative cyclopropanation is limited by the higher propensity of such substrates to get activated either by allylic substitution (entry 1) or oxidative cyclization (entry 2) of the terminal alkene compared to the internal alkenes used for hydrogenative metathesis. Oxidative enyne cyclization can also be observed by the "competition"-substrate (entry 3) where the non-hydrogenative cyclization outcompetes carbene formation by *gem*-hydrogenation. Products of oxidative cyclization were also observed with 1,2-disubstituted enynes (entries 4 and 5). Finally, a propargylic alcohol (entry 6) yielded a mixture of products formed by hydrogenative metathesis, *trans*-hydrogenation and enyne addition/isomerization.

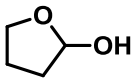
Table S1: Identified side products formed upon treatment of the shown substrates under standard conditions ((Cp*RuCl)$_4$ cat., H_2, 1,2-DCE, 70 °C, 3 h).

entry	substrate	identified side products	comment
1			allylic substitution/ decarboxylation
2			oxidative cyclization/ hydrogenation
3			oxidative cyclization
4			oxidative cyclization/ hydrogenation
5			oxidative cyclization
6			hydrogenative metathesis
			*trans*-hydrogenation
			enyne addition/ isomerization

SUBSTRATES

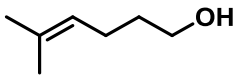
Building Blocks

Tetrahydrofuran-2-ol (S1). DIBAL-H (1 M in CH_2Cl_2, 34.8 mL, 34.8 mmol) was slowly added to a solution of



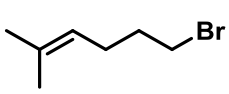
γ-butyrolactone (2.5 g, 29.0 mmol) in CH_2Cl_2 (12 mL) at −78 °C and stirring was continued for 1.5 h at that temperature. MeOH (3 mL) and sat. Rochelle salt solution (3 mL) were introduced, the mixture was warmed to room temperature and vigorously stirred for 2 h until clean separation of the layers was reached. The aqueous phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was used without further purification (colorless oil, 1.06 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dd, *J* = 4.4, 1.6 Hz, 1H), 4.04 (td, *J* = 7.7, 7.2, 4.9 Hz, 1H), 3.89 – 3.80 (m, 1H), 2.12 – 1.99 (m, 1H), 1.99 – 1.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 98.5, 67.5, 33.3, 23.6. The spectral data is consistent with previously reported values.[6]

5-Methylhex-4-en-1-ol (S2). KO^{t}Bu (1.16 g, 10.4 mmol dissolved in 7.7 mL THF) was added to a



suspension of isopropyltriphenylphosphonium iodide (4.1 g, 9.5 mmol) in THF (10.0 mL) at −78 °C. The mixture was warmed to 0 °C and stirred for 30 min at that temperature before a solution of lactol **S1** (0.76 g, 8.63 mmol) in THF (4.2 mL) was introduced. The mixture was stirred at room temperature for 18 h before water (10 mL) and Et_2O (50 mL) were added and the layers were separated. The aqueous phase was extracted with Et_2O (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, pentane/Et_2O 7:3) to furnish the product as a colorless liquid (444 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.11 – 2.02 (m, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.65 – 1.57 (m, 5H), 1.40 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 124.0, 62.9, 32.9, 25.9, 24.5, 17.8. The spectral data is consistent with previously reported values.[7]

6-Bromo-2-methylhex-2-ene (S3). Br_2 (0.38 mL, 7.2 mmol) was added dropwise to a solution of PPh_3



(2.0 g, 7.7 mmol) and imidazole (870 mg, 12.7 mmol) in CH_2Cl_2 (13.6 mL) at 0 °C. The mixture was stirred for 15 min before alcohol **S2** (440 mg, 3.9 mmol) was added at 0 °C. Stirring was continued for 45 min at 0 °C and for another 1 h at room temperature. The suspension was successively washed with H_2O_2 solution (3 % H_2O_2 in water, 2 x 3 mL) and aq. $Na_2S_2O_3$ solution (1 M, 2 x 10 mL). The combined thiosulfate layers were extracted with CH_2Cl_2 (2 x 40 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure. The solid residue was suspended in hexanes (20 mL) by means of short ultrasonication and the resulting suspension filtered through a short plug of silica, thoroughly rinsing with hexanes (200 mL). The combined filtrates were concentrated under reduced pressure to give the product as a colorless liquid (622 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (tdq, *J* = 7.3, 2.9, 1.3 Hz, 1H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.13 (q, *J* = 7.1 Hz, 2H), 1.89 (p, *J* = 6.9 Hz, 2H), 1.70 (q, *J* = 1.3 Hz, 3H), 1.63 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.3, 122.6, 33.8, 33.0, 26.6, 25.9, 17.9. The spectral data is consistent with previously reported values.[8]

4-Methylpent-4-en-1-ol (S4). $LiAlH_4$ (570 mg, 15 mmol) was added in portions to a solution of ethyl 4-methylpent-4-enoate (1.1 g, 7.5 mmol) in Et_2O (8 mL) at 0 °C. The mixture was stirred room temperature for 4 h before water (0.52 mL) and NaOH (0.52 mL, 15% in water) was carefully added. The mixture was stirred for 15 min at room temperature before more water (0.85 mL) was added. Stirring was continued for 15 min, the suspension was filtrated through a glas frit, the residue was washed with Et_2O (20 mL) and the combined filtrates were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, pentane/Et_2O 2:1) to give the title compound as a colorless liquid (502 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.72 (s, 1H), 4.71 (s, 1H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.10 (t, *J* = 7.6 Hz, 2H), 1.76 – 1.67 (m, 5H), 1.53 – 1.44 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.7, 110.3, 62.9, 34.2, 30.7, 22.5. The spectral data is consistent with previously reported values.[9]

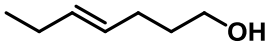
5-Bromo-2-methylpent-1-ene (S5). Br_2 (0.49 mL, 9.5 mmol) was added dropwise to a solution of PPh_3 (2.6 g, 10.0 mmol) and imidazole (1.13 g, 16.5 mmol) in CH_2Cl_2 (17.7 mL) at 0 °C. The mixture was stirred for 15 min before alcohol **S4** (502 mg, 5.0 mmol) was added at 0 °C. Stirring was continued for 45 min at 0 °C and for 1 h at reach room temperature. The suspension was washed H_2O_2 solution (3 % H_2O_2 in water, 2 x 4 mL) and $Na_2S_2O_3$ solution (1 M, 2 x 15 mL). The combined thiosulfate layers were extracted with CH_2Cl_2 (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure. The solid white residue was suspended in hexanes (20 mL) by means of short ultrasonication and insoluble material filtered off through a short plug of silica. The filter cake and silica were thoroughly rinsed with hexanes (200 mL) and the combined filtrates were concentrated under reduced pressure to give the product as a colorless liquid (427 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.80 – 4.73 (m, 1H), 4.75 – 4.69 (m, 1H), 3.41 (t, *J* = 6.7 Hz, 2H), 2.20 – 2.12 (m, 2H), 2.04 – 1.94 (m, 2H), 1.75 – 1.69 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.1, 111.2, 36.2, 33.5, 30.7, 22.5. The spectral data is consistent with previously reported values.[10]

Pent-1-en-3-ol (S6). Freshly distilled propionaldehyd (2.42 g, 41.7 mmol) in Et_2O (42 mL) was added over 30 min to a stirred solution of vinylmagnesium bromide (1 M in THF, 50 mL, 50 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C before it was allowed to reach room temperature. The mixture was acidified with aqueous HCl (1 M, 55 mL) and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the crude product as a pale yellow liquid, which was used without further purification (3.28 g, 91%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 16.9, 10.4, 6.2 Hz, 1H), 5.22 (dt, *J* = 17.2, 1.4 Hz, 1H), 5.16 – 5.07 (m, 1H), 4.08 – 3.98 (m, 1H), 1.63 – 1.50 (m, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 114.9, 74.7, 30.0, 9.7. The spectral data is consistent with previously reported values.[11]

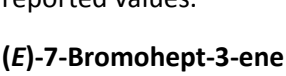
Methyl (*E*)-hept-4-enoate (S7). Alcohol **S6** (3.28 g, 38.0 mmol) was added to trimethylorthoacetate (14.5 mL, 114 mmol) and propionic acid (140 mg, 1.9 mmol) in a thick-walled pressure Schlenk flask. The flask was sealed and immersed into a pre-heated oil bath at 120 °C and the mixture stirred at this temperature for 14 h. The mixture was cooled to room temperature before being reheated to 120 °C in air. After reaching room

temperature, the solution was diluted with CH_2Cl_2 (50 mL) and aqueous HCl (1 M, 10 mL) and the mixture was stirred for 1 h before the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 100 mL), the combined organic layers were washed with sat. $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude product used without further purification (colorless oil, 4.77 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (dtt, *J* = 14.9, 6.0, 1.1 Hz, 1H), 5.38 (dtt, *J* = 15.2, 6.2, 1.4 Hz, 1H), 3.67 (s, 3H), 2.42 – 2.33 (m, 2H), 2.34 – 2.26 (m, 2H), 2.05 – 1.93 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 133.5, 127.0, 51.6, 34.3, 28.0, 25.7, 13.9. The spectral data is consistent with previously reported values.[12]

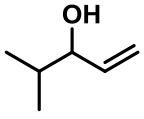
(*E*)-Hept-4-en-1-ol (S8). $LiAlH_4$ (1.87 g, 49 mmol) was added in portions to a solution of ester **S7** (2.0 g, 14.1 mmol) in Et_2O (44 mL) at 0 °C. The mixture was stirred at room temperature for 4 h before water (2 mL) and NaOH (2 mL, 15% in water) were carefully added. The mixture was stirred for 15 min before more water (6 mL) was added. Stirring was continued for another 15 min, the suspension was filtrated through a glas frit, the residue was washed with Et_2O (20 mL) and the combined filtrates were dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude product used without further purification (colorless liquid, 1.49 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 – 5.46 (m, 1H), 5.47 – 5.34 (m, 1H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.11 – 2.03 (m, 2H), 2.03 – 1.95 (m, 2H), 1.68 – 1.59 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9, 128.6, 62.8, 32.6, 29.0, 25.7, 14.1. The spectral data is consistent with previously reported values.[13]



(*E*)-7-Bromohept-3-ene (S9). Br_2 (0.72 mL, 14.0 mmol) was added dropwise to a solution of PPh_3 (3.86 g, 14.7 mmol) and imidazole (1.65 g, 24.3 mmol) in CH_2Cl_2 (26 mL) at 0 °C. The mixture was stirred for 15 min before alcohol **S8** (840 mg, 7.4 mmol) was added at 0 °C. Stirring was continued for 45 min at 0 °C and at room temperature for 1 h. The suspension was washed H_2O_2 solution (3 % H_2O_2 in water, 2 x 6 mL) and $Na_2S_2O_3$ solution (1 M, 2 x 20 mL). The combined thiosulfate layers were extracted with CH_2Cl_2 (2 x 80 mL) and the combined organic layers dried over $MgSO_4$. The solvent was removed under reduced pressure. The white residue was suspended in hexanes (30 mL) by means of short ultrasonication and insoluble materials were filtered off through a plug of silica. The filter cake and silica were thoroughly rinsed with hexanes (300 mL) and the combined filtrate were concentrated under reduced pressure to give the title compound as a colorless liquid (1.06 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (dtt, *J* = 15.3, 6.2, 1.3 Hz, 1H), 5.34 (dtt, *J* = 15.1, 6.7, 1.5 Hz, 1H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.14 (dddd, *J* = 8.6, 7.5, 6.1, 1.3 Hz, 2H), 2.00 (qdq, *J* = 7.5, 6.4, 1.2 Hz, 2H), 1.91 (p, *J* = 7.0 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.9, 127.0, 33.5, 32.6, 31.0, 25.7, 14.0. The spectral data is consistent with previously reported values.[13]

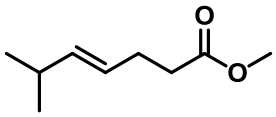


4-Methylpent-1-en-3-ol (S10). Freshly distilled isobutyraldehyd (3.02 g, 41.7 mmol) in Et_2O (44 mL) was added over 30 min to a stirred solution of vinylmagnesium bromide (1 M in THF, 50 mL, 50 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C before being allowed to reach room temperature. The mixture was acidified with aqueous HCl (1 M, 55 mL) and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced



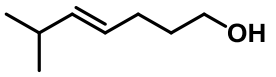
pressure and the resulting crude product used without further purification (light yellow liquid, 3.75 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 17.1, 10.4, 6.4 Hz, 1H), 5.22 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.15 (ddd, *J* = 10.4, 1.7, 1.1 Hz, 1H), 3.88 – 3.83 (m, 1H), 1.80 – 1.67 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 115.7, 78.4, 33.7, 18.3, 17.9. The spectral data is consistent with previously reported values.[14]

Methyl (*E*)-6-methylhept-4-enoate (S11). Alcohol **S10** (3.75 g, 37.4 mmol) was added to



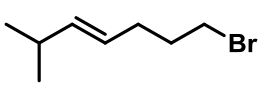
trimethylorthoacetate (14.3 mL, 112 mmol) and propionic acid (138 mg, 1.9 mmol) in a thick-walled pressure Schlenk flask. The sealed flask was immersed in a heating bath at 120 °C and the mixture stirred for 14 h. The mixture was allowed to cool to room temperature and then stirred again at 120 °C open to air. After reaching ambient temperature, the solution was diluted with CH_2Cl_2 (50 mL) and aqueous HCl (1 M, 10 mL). The mixture was stirred for 1 h at room temperature before the layers were separated and the aqueous phase extracted with CH_2Cl_2 (2 x 100 mL). The combined organic layers were washed with sat. $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude product was used without further purification in the next step (colorless oil, 5.45 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (ddt, *J* = 15.4, 6.2, 1.0 Hz, 1H), 5.34 (dtd, *J* = 15.3, 6.0, 1.0 Hz, 1H), 3.66 (s, 3H), 2.40 – 2.33 (m, 2H), 2.33 – 2.26 (m, 2H), 2.26 – 2.17 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 139.1, 125.0, 51.6, 34.4, 31.1, 28.0, 22.7.

(*E*)-6-Methylhept-4-en-1-ol (S12). $LiAlH_4$ (1.7 g, 45 mmol) was added in portions to a solution of ester



S11 (2.0 g, 12.8 mmol) in Et_2O (40 mL) at 0 °C. The mixture was warmed to room temperature and stirring was continued for 4 h before water (2 mL) and NaOH (2 mL, 15% in water) were carefully added. The mixture was stirred for 15 min at room temperature before more water (6 mL) was added. After stirring for additional 15 min, the suspension was filtrated through a glass frit, the residue was washed with Et_2O (20 mL) and the combined filtrates were dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude material used in the next step without further purification (colorless liquid, 1.65 g, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 – 5.32 (m, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.30 – 2.17 (m, 1H), 2.11 – 2.03 (m, 2H), 1.69 – 1.57 (m, 2H), 0.96 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 126.5, 62.8, 32.6, 31.1, 29.0, 22.8. The spectral data is consistent with previously reported values.[15]

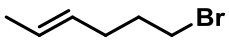
(*E*)-7-Bromo-2-methylhept-3-ene (S13). Br_2 (0.67 mL, 13.0 mmol) was added dropwise to a solution of



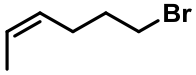
PPh_3 (3.60 g, 13.7 mmol) and imidazole (1.54 g, 22.6 mmol) in CH_2Cl_2 (24 mL) at 0 °C. The mixture was stirred for 15 min before alcohol **S12** (880 mg, 6.9 mmol) was added at 0 °C. Stirring was continued for 30 min at 0 °C and for 1 h at ambient temperature. The suspension was washed with H_2O_2 solution (3 % H_2O_2 in water, 2 x 6 mL) and $Na_2S_2O_3$ solution (1 M, 2 x 20 mL). The combined thiosulfate layers were extracted with CH_2Cl_2 (2 x 80 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure. The solid white residue was suspended in hexanes (30 mL) by means of short ultrasonication and the suspension filtered through a plug of silica. The filter cake and silica were thoroughly rinsed with hexanes (300 mL) and the combined filtrates were evaporated to give the product as a colorless liquid

(1.08 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (ddt, *J* = 15.3, 6.5, 1.3 Hz, 1H), 5.30 (dtd, *J* = 15.3, 6.7, 1.2 Hz, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.31 – 2.17 (m, 1H), 2.18 – 2.07 (m, 2H), 1.91 (p, *J* = 7.0 Hz, 2H), 0.96 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 124.9, 33.5, 32.7, 31.2, 31.0, 22.7.

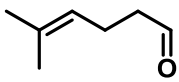
(*E*)-6-Bromohex-2-ene (S14). Br_2 (1.86 mL, 36.3 mmol) was added dropwise to a solution of PPh_3 (10.1 g, 38.5 mmol) and imidazole (4.4 g, 64.1 mmol) in CH_2Cl_2 (75 mL) at 0 °C. The mixture was stirred for 15 min before *trans*-4-hexen-1-ol (2.14 g, 21.4 mmol) was added at 0 °C. Stirring was continued for 45 min at 0 °C and at room temperature for another 30 min. The suspension was washed with H_2O_2 solution (3 % H_2O_2 in water, 2 x 15 mL) and $Na_2S_2O_3$ solution (1 M, 2 x 30 mL). The combined thiosulfate layers were extracted with CH_2Cl_2 (2 x 80 mL) and the combined extracts were dried over $MgSO_4$. The solvent was evaporated, the solid residue was suspended in hexanes (30 mL) by means of short ultrasonication and the suspension filtered through a plug of silica. The filter cake and silica were thoroughly rinsed with hexanes (300 mL), the combined filtrates were evaporated to give the title compound as a colorless liquid (1.56 g, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.50 (dqt, *J* = 14.8, 6.1, 1.2 Hz, 1H), 5.37 (dtq, *J* = 15.1, 6.9, 1.5 Hz, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.13 (m, 2H), 1.90 (p, *J* = 6.7 Hz, 2H), 1.65 (dq, *J* = 6.3, 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.3, 126.6, 33.5, 32.6, 31.0, 18.1. The spectral data is consistent with previously reported values.[16]



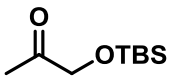
(*Z*)-6-Bromohex-2-ene (S15). Prepared analogously from *cis*-4-hexen-1-ol (1.0 g, 10.0 mmol) as a colorless liquid (1.10 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (dddd, *J* = 10.7, 8.3, 6.8, 5.2 Hz, 1H), 5.38 – 5.29 (m, 1H), 3.41 (t, *J* = 6.7 Hz, 2H), 2.26 – 2.17 (m, 2H), 1.92 (dq, *J* = 8.1, 6.7 Hz, 2H), 1.64 (ddt, *J* = 6.8, 1.8, 0.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.5, 125.7, 33.6, 32.6, 25.4, 13.0. The spectral data is consistent with previously reported values.[17]



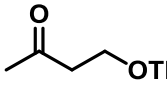
5-Methylhex-4-enal (S16). 2-Methyl-3-buten-2-ol (8.0 g, 93 mmol), ethyl vinyl ether (17.8 mL, 186 mmol) and H_3PO_4 (85%, 0.1 mL, 1.4 mmol) were stirred in a sealed thick-walled pressure Schlenk flask for 2.5 h at 150 °C. The mixture was cooled to room temperature before Et_3N (0.6 mL, 4.2 mmol) was added. The crude product was purified by distillation under reduced pressure (60 mbar, 120 °C bath temperature). The product was obtained as a colorless oil by collecting the fraction boiling at ≈72 °C (2.38 g, 23%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.8 Hz, 1H), 5.09 (tdq, *J* = 7.1, 2.9, 1.5 Hz, 1H), 2.48 – 2.43 (m, 2H), 2.37 – 2.26 (m, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.63 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 133.4, 122.3, 44.1, 25.8, 21.1, 17.9. The spectral data is consistent with previously reported values.[18]



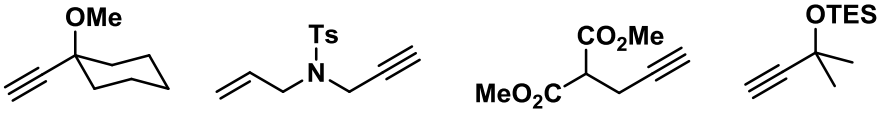
1-((*tert*-Butyldimethylsilyl)oxy)propan-2-one (S17). Imidazole (1.0 g, 14.8 mmol) was added in portions to a stirred solution of hydroxyacetone (90%, 555 mg, 6.7 mmol) and TBSCl (1.53 g, 10.1 mmol) in CH_2Cl_2 (26 mL) at 0 °C. The mixture was stirred at room temperature for 1 h before brine (10 mL) was added. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated and the crude product purified by flash chromatography (silica, pentane/Et_2O 20:1 – 10:1) to give the title compound as a colorless oil (1.1 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (s, 2H), 2.17 (s, 3H), 0.92 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 69.7, 26.1, 25.9, 18.4, -5.4. The spectral data is consistent with previously reported values.[19]



4-((*tert*-Butyldimethylsilyl)oxy)butan-2-one (S18). Imidazole (3.2 g, 47.1 mmol) was added in portions to a stirred solution of 4-hydroxy-2-butanone (90%, 2.1 g, 21.5 mmol) and TBSCl (4.85 g, 32.2 mmol) in CH_2Cl_2 (83 mL) at 0 °C. The mixture was stirred at room temperature for 1 h before brine (20 mL) was added and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 100 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, pentane/Et_2O 20:1 – 10:1) to give the title compound as a colorless oil (4.05 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (t, *J* = 6.3 Hz, 1H), 2.61 (t, *J* = 6.3 Hz, 1H), 2.18 (s, 1H), 0.87 (s, 4H), 0.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 59.0, 46.7, 31.0, 26.0, 18.4, -5.3. The spectral data is consistent with previously reported values.[20]



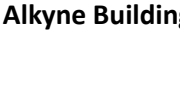
Alkyne Building Blocks



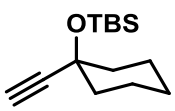
S19 **S20** **S21** **S22**

The alkynes **S19,**[21] **S20,**[22] **S21**,[23] **and S22**[24] were prepared according to literature procedures

1-Ethynyl-1-(methoxymethoxy)cyclohexane (S23). A solution of 1-ethynyl-1-cyclohexanol (4.0 g, 32.2 mmol) in THF (15 mL) was added to a stirred suspension of NaH (1.55 g, 64.4 mmol) in THF (65 mL) at 0 °C. The mixture was stirred for 30 min at room temperature before MOMCl (0.61 mL, 8.1 mmol) was added at 0 °C. Stirring was continued for 2 h at room temperature before aq. sat. NH_4Cl (6 mL), water (4 mL) and *tert*-butyl methyl ether (80 mL) were added. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaported and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to give the title compound as colorless oil (5.06 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (s, 2H), 3.40 (s, 3H), 2.52 (s, 1H), 2.01 – 1.91 (m, 2H), 1.73 – 1.48 (m, 7H), 1.33 – 1.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 92.9, 84.9, 74.8, 74.7, 56.0, 38.6, 25.4, 23.0. IR (film) $\tilde{\nu}$ 3305, 3264, 2934, 1149, 1023 cm^{-1}. HRMS (ESI$^+$) for $C_{10}H_{16}O_2$ $[M+Na]^+$: calcd: 191.1042, found: 191.1042.



***tert*-Butyl((1-ethynylcyclohexyl)oxy)dimethylsilane (S24)**. TBSOTf (0.83 mL, 3.6 mmol) was added to a solution of 1-ethynyl-1-cyclohexanol (500 mg, 4.0 mmol) and 2,6-lutidine (0.94 mL, 8.1 mmol) in CH_2Cl_2 (10.8 mL) at 0 °C. The mixture was stirred for 2 h before water (2 mL) was added. After reaching room temperature, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes) to yield the title compound as a colorless oil (610 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 1H), 1.84 – 1.74 (m, 2H), 1.71 – 1.57 (m, 4H), 1.57 – 1.47 (m, 2H), 1.47 – 1.38 (m, 1H), 1.37 – 1.25 (m, 1H), 0.88 (s, 9H), 0.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$)



δ 88.7, 72.8, 69.2, 41.2, 26.0, 25.4, 22.8, 18.3, -2.7. IR (film) $\tilde{\nu}$ 3310, 2932, 2856, 1252, 1101, 835, 774 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{26}OSi$ $[M+H]^+$: calcd: 239.1826, found: 239.1825.

N-(4-(1-Methoxycyclohexyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S25). *n*-BuLi (1.6 M in hexanes, 2.0 mL, 3.2 mmol) was slowly added to a solution of alkyne **S19** (400 mg, 2.9 mmol) in THF (5.0 mL) at 0 °C. A solution of *N*-tosylaziridine (428 mg, 2.2 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was slowly added and the mixture was stirred at room temperature for 3 h. sat. NH_4Cl solution (2 mL), water (2 mL) and EtOAc (20 mL) were introduced before the layers were separated and the aqueous phase extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 5:1 – 4:1 – 3:1) to give the title compound as a colorless oil (405 mg, 56%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.34 – 7.29 (m, 2H), 4.71 (t, *J* = 6.3 Hz, 1H), 3.28 (s, 3H), 3.10 (q, *J* = 6.5 Hz, 2H), 2.45 – 2.39 (m, 5H), 1.84 – 1.74 (m, 2H), 1.68 – 1.57 (m, 2H), 1.57 – 1.36 (m, 5H), 1.34 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 137.1, 129.9, 127.2, 84.0, 81.9, 74.0, 50.7, 42.2, 36.9, 25.5, 22.9, 21.7, 20.1. IR (film) $\tilde{\nu}$ 3283 (br), 2933, 2857, 1446, 1090 cm^{-1}. HRMS (ESI^+) for $C_{18}H_{25}NO_3S$ $[M+Na]^+$: calcd: 358.1447, found: 358.1444.

4-Methyl-N-(3-methylbut-2-en-1-yl)-N-(prop-2-yn-1-yl)benzenesulfonamide (S26). 1-Bromo-3-methyl-2-butene (0.66 mL, 5.7 mmol) was added to a solution of N-tosylpropargylamine (1.00 g, 4.8 mmol)[25] and K_2CO_3 (1.32 g, 9.6 mmol) in MeCN (8 mL). The mixture was stirred at 60 °C for 6 h before it was cooled to room temperature and diluted with MeCN (10 mL). The suspension was filtered through a pad of Celite and the filter cake was washed with EtOAc (40 mL). The combined filtrates were evaporated and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 4:1) to give the title compound as a colorless oil (923 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.31 – 7.27 (m, 2H), 5.10 (tdq, *J* = 7.2, 2.8, 1.4 Hz, 1H), 4.07 (d, *J* = 2.5 Hz, 2H), 3.81 (d, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 1.98 (t, *J* = 2.5 Hz, 1H), 1.72 (q, *J* = 1.1 Hz, 3H), 1.67 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.2, 136.3, 129.5, 128.0, 118.1, 77.2, 73.5, 44.1, 35.5, 26.0, 21.7, 18.0. The spectral data is consistent with previously reported values.[26]

Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(prop-2-yn-1-yl)malonate (S27). Cs_2CO_3 (1.45 g, 4.5 mmol) and 1-bromo-3-methyl-2-butene (0.67 mL, 5.8 mmol) were added to a solution of malonate **S21** (330 mg, 1.9 mmol) in acetone (12.8 mL). The mixture was stirred at reflux temperature for 18 h before it was allowed to cool to room temperature and diluted with *tert*-butyl methyl ether (40 mL). The mixture was filtered through a pad of Celite and the filter cake was washed with *tert*-butyl methyl ether (100 mL). The combined filtrates were evaporated and the crude product was purified by flash chromatography (silica, hexanes/*tert*-butyl methyl ether 1:0 – 20:1 – 10:1 – 6:1) to give the title compound as a colorless oil (412 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.89 (tdq, *J* = 7.3, 2.9, 1.4 Hz, 1H), 3.73 (s, 6H), 2.80 – 2.76 (m, 4H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.70 (q, *J* = 1.2 Hz, 3H), 1.66 – 1.64 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 137.1, 117.1, 79.4, 71.3, 57.3, 52.9, 30.9, 26.2, 22.7, 18.1. The spectral data is consistent with previously reported values.[27]

3-Methylbut-2-en-1-yl propiolate (S28). Propiolic acid (500 mg, 7.1 mmol) and 1-bromo-3-methyl-2-butene (1.65 mL, 14.3 mmol) were added to a stirred suspension of $NaHCO_3$ (1.2 g, 14.3 mmol) in DMF (8.8 mL) at room temperature. The mixture was stirred for 18 h before it was diluted with water (60 mL) and Et_2O (30 mL). The aqueous phase was extracted with Et_2O (2 x 30 mL) and the combined organic layers were washed with water (60 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, pentane/Et_2O 10:1) to give the title compound as a colorless oil (993 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (tdq, *J* = 7.2, 2.9, 1.5 Hz, 1H), 4.69 (dt, *J* = 7.4, 0.8 Hz, 2H), 2.85 (s, 1H), 1.80 – 1.74 (m, 3H), 1.75 – 1.70 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.91, 140.95, 117.46, 74.90, 74.57, 63.22, 25.93, 18.21. IR (film) ν 3271, 2975, 2937, 2119, 1707 cm^{-1}. HRMS (ESI$^+$) for $C_8H_{10}O_2$ $[M+H]^+$: calcd: 139.0734, found: 139.0754.

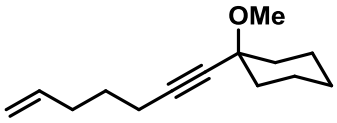
Preparation of the Substrates for Hydrogenative Cyclopropanation or Metathesis

1-(6-Methylhept-5-en-1-yn-1-yl)cyclohexan-1-ol (S29). *n*-BuLi (1.6 M in hexanes, 3.2 mL, 5.1 mmol) was added to a solution of 1-ethynyl-1-cyclohexanol (315 mg, 2.5 mmol) in THF (6.9 mL) and DMPU (2.6 mL) at 0 °C in a thick-walled pressure Schlenk flask. The mixture was stirred for 1 h at 0 °C before 5-bromo-2-methyl-2-pentene (0.28 mL, 2.1 mmol) in THF (1.7 mL) was added. The flask was sealed and the mixture stirred at 65 °C for 16 h. Water (2 mL) and *tert*-butyl methyl ether (5 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 7:1 – 5:1) to give the title compound as a colorless oil (50 mg, 11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 – 5.11 (m, 1H), 2.26 – 2.15 (m, 4H), 1.90 – 1.80 (m, 2H), 1.77 – 1.61 (m, 2H), 1.70 (d, *J* = 1.3 Hz, 3H), 1.63 (d, *J* = 1.3 Hz, 3H), 1.60 – 1.46 (m, 6H), 1.29 – 1.14 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0, 123.1, 84.8, 84.0, 69.0, 40.4, 27.8, 25.9, 25.4, 23.6, 19.3, 18.0. IR (film) $\tilde{\nu}$ 3357 (br), 2930, 2856, 1446, 1057, 962 cm^{-1}. HRMS (ESI$^+$) for $C_{14}H_{22}O$ $[M+Na]^+$: calcd: 229.1563, found: 229.1564.

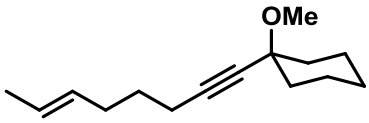
1-Methoxy-1-(6-methylhept-6-en-1-yn-1-yl)cyclohexane (S30). *n*-BuLi (1.6 M in hexanes, 1.08 mL, 1.74 mmol) was slowly added to a solution of alkyne **S19** (200 mg, 1.45 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S5** (283 mg, 1.74 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was added. The mixture was warmed to room temperature and stirring was continued stirring for 18 h. sat. NH_4Cl solution (2 mL), *tert*-butyl methyl ether (10 mL) and water (2 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to give the title compound as a colorless oil (203 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 (m, 1H), 4.70 (m, 1H), 3.35 (s, 3H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.13 (t, *J* = 7.6 Hz, 2H), 1.91 – 1.81 (m, 2H), 1.72 (dd, *J* = 1.4, 0.8 Hz, 3H), 1.71 – 1.59 (m, 4H), 1.59 –

1.46 (m, 5H), 1.34 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 110.6, 86.3, 81.5, 74.2, 50.6, 37.2, 37.00, 27.1, 25.7, 23.1, 22.5, 18.4. IR (film) $\tilde{\nu}$ 3074, 2933, 2857, 1650, 1447, 1093 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O$ [M+Na]$^+$: calcd: 243.1719, found: 243.1720.

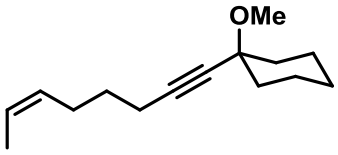
1-(Hept-6-en-1-yn-1-yl)-1-methoxycyclohexane (1a). A detailed procedure as well as analytical and spectroscopic data of this compound and copies of the spectra are contained in the Supporting Information of our previous publication.[28]



(*E*)-1-Methoxy-1-(oct-6-en-1-yn-1-yl)cyclohexane (1b). *n*-BuLi (1.6 M in hexanes, 1.08 mL, 1.74 mmol) was slowly added to a solution of alkyne **S19** (200 mg, 1.45 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S14** (283 mg, 1.74 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was added. The mixture was then stirred at room temperature for 18 h. sat. NH_4Cl solution (2 mL), *tert*-butyl methyl ether (10 mL) and water (2 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to give the title compound as a colorless oil (204 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 – 5.35 (m, 2H), 3.35 (s, 3H), 2.23 (t, *J* = 7.1 Hz, 2H), 2.14 – 2.05 (m, 2H), 1.85 (t, *J* = 8.3 Hz, 2H), 1.69 – 1.45 (m, 12H), 1.26 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 130.5, 125.8, 86.4, 81.3, 74.2, 50.6, 37.2, 31.8, 28.9, 25.7, 23.1, 18.2, 18.1. IR (film) $\tilde{\nu}$ 2932, 2856, 1447, 1092 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O$ [M+Na]$^+$: calcd: 243.1719, found: 243.1721.



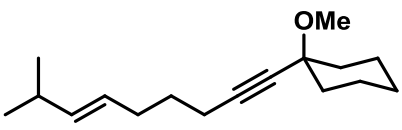
(*Z*)-1-Methoxy-1-(oct-6-en-1-yn-1-yl)cyclohexane (1c). Prepared analogously as a colorless oil (184 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.54 – 5.44 (m, 1H), 5.43 – 5.31 (m, 1H), 3.35 (s, 3H), 2.25 (t, *J* = 7.0 Hz, 2H), 2.22 – 2.11 (m, 2H), 1.91 – 1.82 (m, 2H), 1.69 – 1.46 (m, 12H), 1.33 – 1.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.7, 124.9, 86.4, 81.3, 74.2, 50.6, 37.2, 28.9, 26.1, 25.7, 23.1, 18.3, 12.9. IR (film) $\tilde{\nu}$ 3013, 2933, 2857, 1446, 1092 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O$ [M+Na]$^+$: calcd: 243.1719, found: 243.1720.



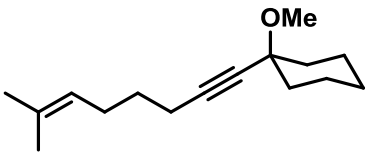
(*E*)-1-Methoxy-1-(non-6-en-1-yn-1-yl)cyclohexane (1d). *n*-BuLi (1.6 M in hexanes, 1.08 mL, 1.74 mmol) was added slowly to a solution of alkyne **S19** (200 mg, 1.45 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S9** (308 mg, 1.74 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was added. The mixture was stirred at ambient temperature for 18 h. sat. NH_4Cl solution (2 mL), *tert*-butyl methyl ether (10 mL) and water (2 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to furnish the product as a colorless oil (193 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 – 5.44 (m, 1H), 5.43 – 5.31 (m, 1H), 3.35 (s, 3H), 2.23 (t, *J* = 7.1 Hz, 2H), 2.15 –

2.04 (m, 2H), 2.06 – 1.94 (m, 2H), 1.90 – 1.82 (m, 2H), 1.70 – 1.46 (m, 9H), 1.33 – 1.24 (m, 1H), 0.97 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.1, 128.2, 86.4, 81.3, 74.2, 50.6, 37.2, 31.8, 29.0, 25.8, 25.7, 23.1, 18.2, 14.1. IR (film) $\tilde{\nu}$ 2932, 2856, 2822, 1447, 1092 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{26}O$ [M+Na]$^+$: calcd: 257.1876, found: 257.1876.

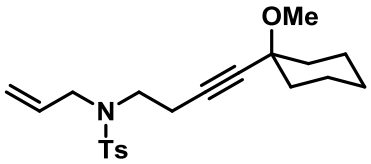
(*E*)-1-Methoxy-1-(8-methylnon-6-en-1-yn-1-yl)cyclohexane (1e). *n*-BuLi (1.6 M in hexanes, 1.08 mL, 1.74 mmol) was added slowly to a solution of alkyne **S19** (200 mg, 1.45 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S13** (332 mg, 1.74 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was introduced. The mixture was stirred at room temperature for 18 h. sat. NH_4Cl solution (2 mL), *tert*-butyl methyl ether (10 mL) and water (2 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to give the product as a colorless oil (216 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (ddt, *J* = 15.3, 6.1, 1.0 Hz, 1H), 5.32 (dtd, *J* = 15.3, 6.4, 0.9 Hz, 1H), 3.35 (s, 3H), 2.23 (t, *J* = 7.1 Hz, 2H), 2.24 (m, 1H), 2.09 (m, 2H), 1.90 – 1.82 (m, 2H), 1.70 – 1.46 (m, 9H), 1.28 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 126.1, 86.4, 81.3, 74.2, 50.6, 37.2, 31.8, 31.2, 29.0, 25.7, 23.1, 22.8, 18.2. IR (film) $\tilde{\nu}$ 2932, 2858, 2822, 1448, 1093 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{28}O$ [M+Na]$^+$: calcd: 271.2032, found: 271.2032.



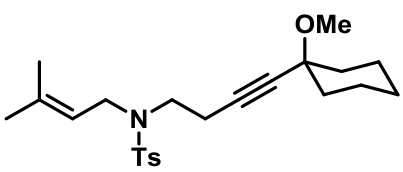
1-Methoxy-1-(7-methyloct-6-en-1-yn-1-yl)cyclohexane (1f). *n*-BuLi (1.6 M in hexanes, 1.08 mL, 1.74 mmol) was slowly added to a solution of alkyne **S19** (200 mg, 1.45 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S3** (307 mg, 1.74 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was added. The mixture was warmed to room temperature and stirring was continued for 18 h. Sat. NH_4Cl solution (2 mL), *tert*-butyl methyl ether (10 mL) and water (2 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to give the product as a colorless oil (183 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (tdq, *J* = 7.2, 2.9, 1.5 Hz, 1H), 3.35 (s, 3H), 2.24 (d, *J* = 7.0 Hz, 2H), 2.09 (q, *J* = 7.3 Hz, 2H), 1.90 – 1.81 (m, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.65 – 1.60 (m, 2H), 1.62 (s, 3H), 1.59 – 1.47 (m, 7H), 1.26 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 123.8, 86.6, 81.2, 74.2, 50.6, 37.2, 29.3, 27.3, 25.9, 25.7, 23.1, 18.4, 17.8. IR (film) $\tilde{\nu}$ 2932, 2857, 1446, 1092 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{26}O$ [M+Na]$^+$: calcd: 257.1876, found: 257.1877.



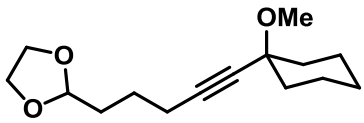
N-Allyl-N-(4-(1-methoxycyclohexyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S31). Allyl bromide (0.08 mL, 0.95 mmol) was added to a stirred suspension of K_2CO_3 (131 mg, 0.95 mmol) and sulfonamide **S25** (160 mg, 0.48 mmol) in MeCN (0.8 mL) at room temperature. After stirring for 18 h at 60 °C the mixture was allowed to cool to ambient temperature and diluted with MeCN (10 mL). The suspension was filtered through a plug of cotton wool and the filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 6:1) to yield the title compound as a colorless oil (105 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 5.66 (ddt, *J* = 17.1, 10.1, 6.3 Hz, 1H), 5.23 – 5.14 (m, 2H), 3.85 (dt, *J* = 6.3, 1.4 Hz, 2H), 3.32 – 3.26 (m, 5H), 2.55 – 2.48 (m, 2H), 2.43 (s, 3H), 1.86 – 1.76 (m, 2H), 1.67 – 1.42 (m, 7H), 1.35 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.2, 133.2, 129.9, 127.3, 119.2, 83.1, 82.6, 74.0, 51.4, 50.7, 46.5, 36.9, 25.6, 22.9, 21.7, 19.7. IR (film) $\tilde{\nu}$ 2935, 2857, 1449, 1345, 1158, 1092 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{29}NO_3S$ [M+Na]$^+$: calcd: 398.1760, found: 398.1762.



N-(4-(1-Methoxycyclohexyl)but-3-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S32). 1-Bromo-3-methyl-2-butene (0.28 mL, 2.4 mmol) was added to a stirred suspension of K_2CO_3 (494 mg, 3.6 mmol) and sulfonamide **S25** (400 mg, 1.2 mmol) in MeCN (3.8 mL). The mixture was stirred at 60 °C for 2 h before additional K_2CO_3 (494 mg, 3.6 mmol) and 1-bromo-3-methyl-2-butene (0.28 mL, 2.4 mmol) were added. After stirring for another 18 h at 60 °C, the mixture was cooled to room temperature and diluted with MeCN (10 mL). The suspension was filtered through a plug of cotton wool and the filtrate was evaporated. The residue was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 6:1) to yield the title compound as pale yellow oil (306 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.32 – 7.27 (m, 2H), 5.01 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 3.82 (d, *J* = 7.1 Hz, 2H), 3.31 (s, 3H), 3.28 – 3.22 (m, 2H), 2.53 – 2.47 (m, 2H), 2.42 (s, 3H), 1.85 – 1.77 (m, 2H), 1.66 (q, *J* = 1.2 Hz, 3H), 1.65 – 1.57 (m, 5H), 1.57 – 1.41 (m, 5H), 1.32 – 1.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.4, 137.3, 129.7, 127.3, 119.1, 83.0, 82.8, 74.0, 50.6, 46.5, 46.2, 36.9, 25.9, 25.6, 22.9, 21.6, 19.8, 17.9. IR (film) $\tilde{\nu}$ 2933, 2857, 1448, 1341, 1157 cm^{-1}. HRMS (ESI$^+$) for $C_{23}H_{33}NO_3S$ [M+Na]$^+$: calcd: 426.1073, found: 426.2072.

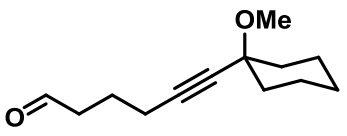


2-(5-(1-Methoxycyclohexyl)pent-4-yn-1-yl)-1,3-dioxolane (S33). *n*-BuLi (1.6 M in hexanes, 1.63 mL, 2.60 mmol) was added slowly to a solution of alkyne **S19** (300 mg, 2.17 mmol) in THF (7.6 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of 2-(3-bromopropyl)-1,3-dioxolane (508 mg, 2.60 mmol) in THF (4.9 mL) and DMPU (1.3 mL) was added. The mixture was stirred at room temperature for 18 h. sat. NH_4Cl solution (3 mL), *tert*-butyl methyl ether (20 mL) and water (3 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 40 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to give the product as a colorless oil (301 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 (t, *J* = 4.7 Hz, 1H), 4.01 – 3.92 (m, 2H), 3.90 – 3.81 (m, 2H), 3.34 (s,

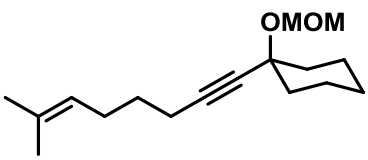


3H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.82 – 1.74 (m, 2H), 1.65 (m, 5H), 1.57 – 1.45 (m, 4H), 1.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.36, 85.93, 81.62, 74.16, 65.03, 50.63, 37.16, 33.15, 25.70, 23.61, 23.06, 18.82. IR (film) $\tilde{\nu}$ 2935, 2859, 1449, 1142, 1091 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O_3$ [M+Na]$^+$: calcd: 275.1618, found: 275.1618.

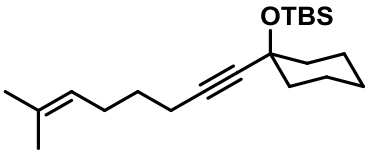
6-(1-Methoxycyclohexyl)hex-5-ynal (S34). A solution of dioxolane **S33** (150 mg, 0.59 mmol) in acetone (2.7 mL) was added to a solution of *p*-TsOH·H_2O (6 mg, 0.03 mmol) in water (2.7 mL). The mixture was stirred at 70 °C for 3 h before sat. $NaHCO_3$ solution (2 mL) was added. The mixture was diluted with *tert*-butyl methyl ether (10 mL) and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to give the title compound as a colorless oil (110 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (t, *J* = 1.4 Hz, 1H), 3.33 (s, 3H), 2.59 (td, *J* = 7.2, 1.4 Hz, 2H), 2.33 (t, *J* = 6.9 Hz, 2H), 1.90 – 1.80 (m, 4H), 1.69 – 1.59 (m, 2H), 1.59 – 1.44 (m, 5H), 1.33 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 84.9, 82.5, 74.1, 50.6, 43.0, 37.1, 25.6, 23.0, 21.5, 18.3. IR (film) $\tilde{\nu}$ 2935, 2857, 1725, 1448, 1091 cm^{-1}. HRMS (ESI$^+$) for $C_{13}H_{20}O_2$ [M+Na]$^+$: calcd: 231.1355, found: 231.1357.



1-(Methoxymethoxy)-1-(7-methyloct-6-en-1-yn-1-yl)cyclohexane (S35). *n*-BuLi (1.6 M in hexanes, 12.2 mL, 19.5 mmol) was slowly added to a solution of alkyne **S23** (2.73 g, 16.2 mmol) in THF (57 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S3** (3.73 g, 21.1 mmol) in THF (37 mL) and DMPU (9.8 mL) was added. The resulting mixture was stirred at room temperature for 18 h. sat. NH_4Cl solution (10 mL), *tert*-butyl methyl ether (50 mL) and water (10 mL) were added, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a colorless oil (4.12 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.94 (s, 2H), 3.39 (s, 3H), 2.23 (t, *J* = 7.1 Hz, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.68 – 1.62 (m, 3H), 1.61 (s, 3H), 1.59 – 1.48 (m, 6H), 1.30 – 1.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 123.8, 92.9, 87.5, 80.9, 75.5, 55.8, 39.1, 29.2, 27.3, 25.9, 25.6, 23.4, 18.4, 17.8. IR (film) $\tilde{\nu}$ 2931, 2857, 1447, 1149, 1026 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{28}O_2$ [M+Na]$^+$: calcd: 287.1981, found: 287.1980.

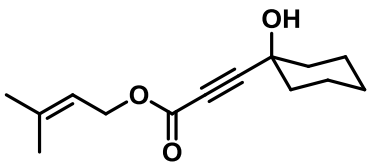


***tert*-Butyldimethyl((1-(7-methyloct-6-en-1-yn-1-yl)cyclohexyl)oxy)silane (S36)**. *n*-BuLi (1.6 M in hexanes, 1.3 mL, 2.1 mmol) was slowly added to a solution of alkyne **S24** (412 mg, 1.7 mmol) in THF (6.0 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S3** (398 mg, 2.2 mmol) in THF (3.9 mL) and DMPU (1.0 mL) was added. The mixture was stirred at room temperature for 18 h. sat. NH_4Cl solution (3 mL), *tert*-butyl methyl ether (20 mL) and water (2 mL) were added, the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and

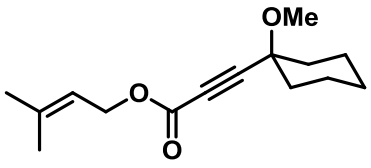


the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes) to give the title compound as a colorless oil (523 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (m, 1H), 2.20 (t, *J* = 7.1 Hz, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.70 (q, *J* = 1.3 Hz, 3H), 1.67 – 1.59 (m, 2H), 1.62 (s, 3H), 1.59 – 1.45 (m, 6H), 1.46 – 1.34 (m, 1H), 1.35 – 1.24 (m, 1H), 0.88 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 123.9, 85.0, 84.9, 69.4, 41.6, 29.1, 27.4, 26.1, 25.9, 25.6, 23.0, 18.5, 18.3, 17.9, -2.7. IR (film) $\tilde{\nu}$ 2930, 2855, 1446, 1250, 1095, 1052 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{38}OSi$ [M+Na]$^+$: calcd: 357.2584, found: 257.2585.

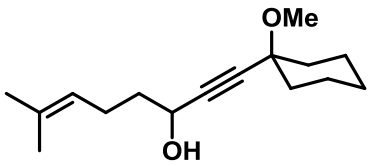
3-Methylbut-2-en-1-yl 3-(1-hydroxycyclohexyl)propiolate (S37). LiHMDS (1 M in THF, 1.7 mL, 1.7 mmol) was slowly added to a solution of alkyne **S28** (200 mg, 1.45 mmol) in THF (14.1 mL) at −78 °C and the resulting mixture was stirred for 30 min at that temperature. Cyclohexanone (0.23 mL, 2.17 mmol) was slowly added at −78 °C to the mixture allowed to reach room temperature. After 5 min sat., NH_4Cl solution (1 mL) and EtOAc (20 mL) were introduced, the layers were separated, the aqueous phase was extracted with EtOAc (3 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 7:1 – 5:1) to give the title compound as a colorless oil (312 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.60 (d, *J* = 7.4 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.70 (d, *J* = 1.3 Hz, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.65 – 1.41 (m, 7H), 1.28 – 1.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 140.4, 117.6, 90.3, 76.0, 68.5, 62.9, 39.1, 25.8, 24.9, 22.8, 18.1. IR (film) $\tilde{\nu}$ 3401 (br), 2935, 2860, 2227, 1709, 1228 cm^{-1}. HRMS (ESI$^+$) for $C_{14}H_{20}O_3$ [M+Na]$^+$: calcd: 259.1346, found: 259.1304.



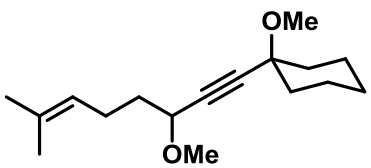
3-Methylbut-2-en-1-yl 3-(1-methoxycyclohexyl)propiolate (S38). A solution of alcohol **S37** (300 mg, 1.27 mmol) in THF (1 mL) was slowly added to a suspension of NaH (152 mg, 6.3 mmol) in THF (5.5 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.80 mL, 12.7 mmol) was carefully added at 0 °C. Stirring was continued for 1 h at room temperature before water (2 mL) and *tert*-butyl methyl ether (30 mL) were introduced. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless oil (129 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (ddp, *J* = 8.8, 5.7, 1.4 Hz, 1H), 4.67 (dt, *J* = 7.3, 0.9 Hz, 2H), 3.37 (s, 3H), 1.98 – 1.85 (m, 2H), 1.77 (d, *J* = 1.2 Hz, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.73 – 1.58 (m, 4H), 1.59 – 1.44 (m, 4H), 1.38 – 1.25 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 140.4, 117.8, 88.5, 77.9, 73.9, 63.0, 51.4, 36.1, 26.0, 25.3, 22.5, 18.2. IR (film) $\tilde{\nu}$ 2937, 2860, 2238, 1711, 1230 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{23}O_3$ [M+Na]$^+$: calcd: 273.1461, found: 273.1459.



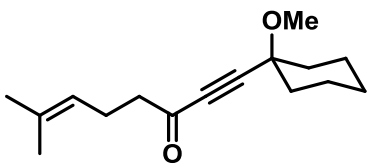
1-(1-Methoxycyclohexyl)-7-methyloct-6-en-1-yn-3-ol (S39). *n*-BuLi (1.6 M in hexanes, 3.6 mL, 5.8 mmol) was slowly added to a solution of alkyne **S19** (800 mg, 5.8 mmol) in THF (47 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of the freshly distilled aldehyde **S16** (500 mg, 4.5 mmol) in THF (3 mL) was introduced. After warming to room temperature the mixture was stirred for 10 min before water (5 mL) and EtOAc (50 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 7:1 - 5:1) to yield the title compound as a colorless oil (647 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.44 (t, *J* = 6.5 Hz, 1H), 3.35 (s, 3H), 2.27 – 2.08 (m, 2H), 1.93 – 1.83 (m, 2H), 1.81 – 1.67 (m, 2H), 1.70 (q, *J* = 4.0 Hz, 3H), 1.70 – 1.62 (m, 2H), 1.63 (s, 3H), 1.61 – 1.46 (m, 5H), 1.35 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.8, 123.4, 87.2, 86.1, 74.0, 62.4, 50.8, 38.2, 36.9, 36.8, 25.9, 25.6, 24.0, 23.0, 17.8. IR (film) $\tilde{\nu}$ 3416 (br), 2933, 2857, 1446, 1079 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{26}O_2$ $[M+Na]^+$: calcd: 273.1825, found: 273.1823.



1-Methoxy-1-(3-methoxy-7-methyloct-6-en-1-yn-1-yl)cyclohexane (S40). A solution of alcohol **S39** (200 mg, 0.8 mmol) in THF (1 mL) was added to a stirred suspension of NaH (96 mg, 4.0 mmol) in THF (3.2 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.50 mL, 8.0 mmol) was introduced. After stirring for 1 h at room temperature, sat. NH_4Cl solution (2 mL), water (4 mL) and *tert*-butyl methyl ether (30 mL) were added and the layers separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a colorless oil (184 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.11 (tdq, *J* = 7.3, 2.9, 1.4 Hz, 1H), 4.00 (t, *J* = 6.6 Hz, 1H), 3.40 (s, 3H), 3.37 (s, 3H), 2.19 – 2.10 (m, 2H), 1.95 – 1.86 (m, 2H), 1.82 – 1.71 (m, 2H), 1.69 (d, *J* = 1.0 Hz, 3H), 1.70 – 1.60 (m, 2H), 1.62 (s, 3H), 1.60 – 1.47 (m, 5H), 1.35 – 1.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 123.5, 87.0, 85.1, 74.2, 70.9, 56.5, 50.8, 37.0, 36.0, 25.9, 25.6, 24.1, 23.1, 17.8. IR (film) $\tilde{\nu}$ 2934, 2857, 1447, 1290, 1094 cm^{-1}. HRMS (EI) for $C_{17}H_{28}O_2$ $[M]^+$: calcd: 264.1084, found: 264.2085.

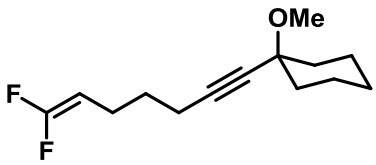


1-(1-Methoxycyclohexyl)-7-methyloct-6-en-1-yn-3-one (S41). $NaHCO_3$ (336 mg, 4.0 mmol) and Dess-Martin periodinane (508 mg, 1.2 mmol) were added to a solution of alcohol **S39** (200 mg, 0.8 mmol) in wet CH_2Cl_2 (7.4 mL) at 0 °C. The mixture was stirred at room temperature for 30 min before aq. sat. $Na_2S_2O_3$ (3 mL) and water (3 mL) were added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 30:1 – 20:1) to give the product as a colorless oil (193 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (tdq, *J* = 7.2, 2.9, 1.5 Hz, 1H), 3.38 (s, 3H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.36 (q, *J* = 7.5 Hz, 2H), 1.99 – 1.88 (m, 2H), 1.70 –

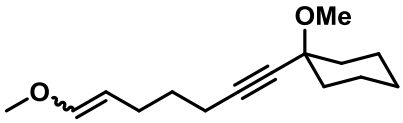


1.61 (m, 3H), 1.68 (q, *J* = 1.4 Hz, 3H), 1.62 (s, 3H), 1.59 – 1.45 (m, 4H), 1.38 – 1.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 133.5, 122.1, 93.2, 85.1, 74.0, 51.4, 46.0, 36.2, 25.8, 25.4, 23.0, 22.6, 17.8. IR (film) $\tilde{\nu}$ 2934, 2859, 2204, 1676, 1120 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{24}O_2$ [M+Na]$^+$: calcd: 271.1668, found: 271.1668.

1-(7,7-Difluorohept-6-en-1-yn-1-yl)-1-methoxycyclohexane (22). A solution of aldehyde **S34** (110 mg, 0.53 mmol) in DMF (2.3 mL) was added to solid PPh_3 (277 mg, 1.06 mmol) and sodium chlorodifluoroacetate (161 mg, 1.06 mmol). The mixture was stirred at 100 °C for 10 min before it was allowed to reach room temperature. Water (3 mL) and *tert*-butyl methyl ether (10 mL) were added and the layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 10 mL) and the combined organic layers were washed with brine (2 mL), H_2O_2 solution (6% in water, 4 mL) and again brine. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 50:1) to give the title compound as a colorless oil (62 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (dtd, *J* = 25.3, 7.9, 2.5 Hz, 1H), 3.34 (s, 3H), 2.27 (t, *J* = 7.0 Hz, 2H), 2.11 (qt, *J* = 7.6, 1.8 Hz, 2H), 1.89 – 1.78 (m, 2H), 1.71 – 1.43 (m, 9H), 1.34 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (dd, *J* = 287.5, 285.1 Hz), 85.3, 81.7, 77.3 (d, *J* = 21.6 Hz), 74.0, 50.4, 37.0, 28.6 (t, *J* = 2.5 Hz), 25.5, 22.9, 21.3 (d, *J* = 4.5 Hz), 19.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -88.8 (d, *J* = 47.3 Hz), -91.3 (d, *J* = 47.4 Hz). IR (film) $\tilde{\nu}$ 2935, 2859, 1746, 1448, 1229, 1092 cm^{-1}. HRMS (EI) for $C_{14}H_{20}F_2O$ [M-H]$^+$: calcd: 241.1398, found: 241.1398.



1-Methoxy-1-(7-methoxyhept-6-en-1-yn-1-yl)cyclohexane (23). PhLi (1.8 M in *n*-Bu_2O, 0.41 mL, 0.73 mmol) was slowly added to a solution of (methoxymethyl)triphenylphosphonium chloride (263 mg, 0.77 mmol) in Et_2O (3.2 mL) at 0 °C. The mixture was stirred for 10 min at 0 °C before a solution of aldehyde **S34** (80 mg, 0.38 mmol) in Et_2O (1 mL) was introduced. The mixture was stirred at room temperature for 10 min sat. NH_4Cl solution (1 mL) and *tert*-butyl methyl ether (5 mL) were added, the layers were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a pale yellow oil (44 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (mixture of *E*/*Z* isomers: 54/46) 6.30 (dt, *J* = 12.7, 1.2 Hz, 0.54H), 5.90 (dt, *J* = 6.2, 1.4 Hz, 0.46H), 4.70 (dt, *J* = 12.6, 7.4 Hz, 0.54H), 4.33 (td, *J* = 7.4, 6.2 Hz, 0.46H), 3.57 (s, 1.08H), 3.51 (s, 1.62H), 3.35 (s, s, 3H), 2.24 (t, *J* = 7.1 Hz, 2H), 2.17 (qd, *J* = 7.4, 1.5 Hz, 0.92H), 2.05 (qd, *J* = 7.4, 1.2 Hz, 1.08H), 1.90 – 1.80 (m, 2H), 1.68 – 1.45 (m, 9H), 1.33 – 1.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.8, 105.9, 102.0, 86.6, 86.2, 81.4, 81.2, 74.2, 74.2, 59.6, 56.1, 50.6, 37.2, 37.2, 30.0, 29.3, 26.9, 25.8, 25.7, 23.3, 23.1, 18.4, 18.0. IR (film) $\tilde{\nu}$ 2932, 2856, 1656, 1448, 1210, 1110, 1090 cm^{-1}. HRMS (EI) for $C_{15}H_{24}O_2$ [M]$^+$: calcd: 236.1771, found: 236.1773.



N-Allyl-N-(4-hydroxy-4-methylpent-2-yn-1-yl)-4-methylbenzenesulfonamide (S42). *n*-BuLi (1.6 M in hexanes, 0.59 mL, 0.94 mmol) was added slowly to a solution of alkyne **S20** (181 mg, 0.73 mmol) in THF (7.6 mL) at 0 °C. The solution was stirred for 30 min at 0 °C before acetone (0.75 mL, 10.1 mmol) was introduced. The mixture was warmed to room temperature and stirring continued for 30 min. sat. NH_4Cl solution (3 mL) and EtOAc (30 mL) were added, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 2:1 – 1:1) to yield the title compound as a pale yellow amorphous solid (72 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.75 (ddt, *J* = 17.1, 10.0, 6.5 Hz, 1H), 5.32 – 5.22 (m, 2H), 4.10 (s, 2H), 3.82 (dt, *J* = 6.4, 1.2 Hz, 2H), 2.43 (s, 3H), 1.45 (br, 1H), 1.27 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 136.4, 132.1, 129.7, 128.1, 120.0, 90.6, 74.8, 64.9, 49.2, 36.1, 31.2, 21.6. IR (neat) $\tilde{\nu}$ 3510, 2981, 2929, 1598, 1160 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{22}NO_3S$ [M+Na]$^+$: calcd: 308.1315, found: 308.1316.

N-Allyl-N-(4-((*tert*-butyldimethylsilyl)oxy)-4-methylpent-2-yn-1-yl)-4-methylbenzenesulfonamide (S43). TBSOTf (54 µL, 0.23 mmol) was added to a solution of alcohol **S42** (60 mg, 0.20 mmol) and 2,6-lutidine (46 µL, 0.39 mmol) in CH_2Cl_2 (0.6 mL) at −15 °C (ice/acetone bath). The mixture was stirred for 2 h before water (0.5 mL) was added. After reaching room temperature the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless amorphous solid (67 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.0, 6.4 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.23 (dq, *J* = 10.1, 1.2 Hz, 1H), 4.12 (s, 2H), 3.83 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 1.21 (s, 6H), 0.82 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.6, 132.2, 129.7, 127.8, 119.9, 91.1, 75.1, 66.2, 49.1, 36.1, 32.8, 25.8, 21.6, 18.0, -2.8. IR (film) $\tilde{\nu}$ 2929, 2856, 1352, 1162, 1042 cm^{-1}. HRMS (ESI$^+$) for $C_{22}H_{35}NO_3SSi$ [M+Na]$^+$: calcd: 444.1999, found: 444.2001.

N-allyl-N-(4-methoxy-4-methylpent-2-yn-1-yl)-4-methylbenzenesulfonamide (9a). NaH (62 mg, 2.60 mmol) was added to a solution of alcohol **S42** (320 mg, 1.04 mmol) in THF (4.5 mL) at room temperature. The suspension was stirred for 10 min before MeI (0.33 mL, 5.20 mmol) was slowly added. Stirring was continued for 1 h before water (2 mL) and *tert*-butyl methyl ether (20 mL) were added. The aqueous phase was etracted with *tert*-butyl methyl ether (2 x 20 mL) and the combined organic phases were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (269 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.33 – 7.27 (m, 2H), 5.75 (ddt, *J* = 17.2, 10.0, 6.5 Hz, 1H), 5.32 – 5.22 (m, 2H), 4.15 (s, 2H), 3.83 (dt, *J* = 6.5, 1.3 Hz, 2H), 3.12 (s, 3H), 2.42 (s, 3H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 136.4, 132.2, 129.7,

127.8, 120.0, 87.7, 76.8, 70.3, 51.6, 49.2, 36.1, 28.2, 21.6. IR (film) $\tilde{\nu}$ 2984, 2934, 1350, 1163, 1075 cm^{-1}. HRMS (ESI^+) for $C_{17}H_{23}NO_3S$ $[M+Na]^+$: calcd 344.1291, found 344.1293.

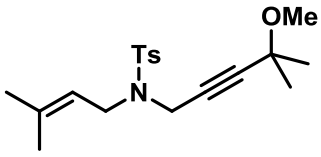
N-Allyl-N-(4-hydroxybut-2-yn-1-yl)-4-methylbenzenesulfonamide (S44). *n*-BuLi (1.6 M in hexanes, 1.68 mL, 2.69 mmol) was added slowly to a solution of alkyne **S20** (515 mg, 2.07 mmol) in THF (21 mL) at 0 °C. The solution was stirred for 30 min before powdered paraformaldehyde (93 mg, 3.10 mmol) was introduced. After stirring for another 2 h at room temperature, the reaction was quenched with NH_4Cl solution (5 mL) and EtOAc (30 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 2:1 – 3:2) to yield the title compound as a light yellow oil (310 mg, 54%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.34 – 7.29 (m, 2H), 5.73 (ddt, *J* = 17.1, 10.0, 6.4 Hz, 1H), 5.32 – 5.21 (m, 2H), 4.10 (t, *J* = 2.0 Hz, 2H), 3.98 (t, *J* = 2.0 Hz, 2H), 3.82 (dt, *J* = 6.4, 1.3 Hz, 2H), 2.43 (s, 3H), 1.23 (s (br), 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 136.3, 132.1, 129.5, 128.1, 120.1, 83.9, 78.7, 50.9, 49.4, 36.2, 21.7. IR (film) $\tilde{\nu}$ 3510 (br), 2924, 2867, 1432, 1345, 1160 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{17}NO_3S$ $[M+Na]^+$: calcd 302.0821, found 302.0824.

N-allyl-N-(4-methoxybut-2-yn-1-yl)-4-methylbenzenesulfonamide (9b). NaH (68 mg, 2.77 mmol) was added to a solution of alcohol **S44** (310 mg, 1.11 mmol) in THF (4.8 mL) and the resulting suspension stirred for 10 min before MeI (0.35 mL, 5.55 mmol) was slowly added. Stirring was continued for 1 h before water (2 mL) and *tert*-butyl methyl ether (20 mL) were introduced. The layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 5:1) to yield the title compound as a colorless oil (270 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.32 – 7.27 (m, 2H), 5.74 (ddt, *J* = 17.1, 10.1, 6.4 Hz, 1H), 5.31 – 5.21 (m, 2H), 4.13 (t, *J* = 1.9 Hz, 2H), 3.83 (t, *J* = 1.9 Hz, 3H), 3.81 (t, *J* = 1.3 Hz, 1H), 3.19 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 136.2, 132.1, 129.6, 127.9, 120.0, 81.5, 79.3, 59.7, 57.53, 49.3, 36.2, 21.7. IR (film) $\tilde{\nu}$ 2984, 2929, 1598, 1447, 1348, 1162, 1093 cm^{-1}. HRMS (ESI^+) for $C_{15}H_{19}NO_3S$ $[M+Na]^+$: calcd 316.0978, found 316.0977.

N-(4-Hydroxy-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S45). *n*-BuLi (1.6 M in hexanes, 1.35 mL, 2.16 mmol) was slowly added to a solution of alkyne **S26** (460 mg, 1.66 mmol) in THF (17.5 mL) at 0 °C. The solution was stirred for 30 min at 0 °C before acetone (1.22 mL, 16.6 mmol) was introduced. After stirring at room temperature for 30 min, sat. NH_4Cl solution (3 mL) and EtOAc (30 mL) were added, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 4:1 – 2:1) to yield the title compound as a light yellow amorphous solid (297 mg, 53%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.34 – 7.29 (m, 2H),

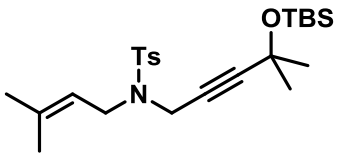
5.11 (ddq, *J* = 8.8, 5.8, 1.4 Hz, 1H), 4.07 (s, 2H), 3.81 (d, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 1.73 (s, 3H), 1.68 (s, 3H), 1.47 (br, 1H), 1.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.1, 136.6, 129.6, 128.1, 118.1, 90.1, 75.3, 64.9, 44.1, 35.7, 31.1, 26.0, 21.6, 18.0. IR (film) $\tilde{\nu}$ 3522, 2979, 2921, 1596, 1327, 1152 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{25}O_3S$ [M+Na]$^+$: calcd: 358.1447, found: 358.1444.

N-(4-Methoxy-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S46).

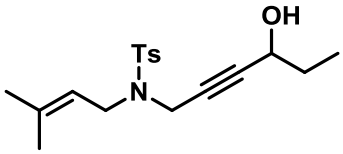


NaH (38 mg, 1.58 mmol) was added to a solution of alcohol **S45** (106 mg, 0.32 mmol) in THF (1.4 mL) at room temperature. The suspension was stirred for 10 min before MeI (0.2 mL, 3.16 mmol) was slowly added. After stirring for another 1 h at room temperature, water (1 mL) and *tert*-butyl methyl ether (5 mL) were introduced, the layers were separated, the aqueous phase was etracted with *tert*-butyl methyl ether (2 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (106 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.32 – 7.27 (m, 2H), 5.13 (tdq, *J* = 7.3, 2.9, 1.3 Hz, 1H), 4.12 (s, 2H), 3.82 (d, *J* = 7.3 Hz, 2H), 3.11 (s, 3H), 2.41 (s, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.8, 136.5, 129.5, 127.7, 118.1, 87.0, 77.2, 70.2, 51.5, 43.9, 35.6, 28.0, 25.9, 21.5, 17.9. IR (film) $\tilde{\nu}$ 2982, 2932, 1738, 1346, 1159 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{27}NO_3S$ [M+Na]$^+$: calcd: 372.1604, found: 372.1603.

N-(4-((*tert*-butyldimethylsilyl)oxy)-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)-benzenesulfonamide (S47). TBSOTf (82 µL, 0.36 mmol) was added to a solution of alcohol **S45** (100 mg, 0.30 mmol) and 2,6-lutidine (69 µL, 0.60 mmol) in CH_2Cl_2 (0.8 mL) at −15 °C (ice/acetone bath). Stirring was continued for 2 h before water (0.5 mL) was added. After reaching room temperature, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless amorphous solid (126 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.30 – 7.27 (m, 2H), 5.12 (dddd, *J* = 8.6, 5.7, 2.8, 1.4 Hz, 1H), 4.09 (s, 2H), 3.81 (d, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.72 (s, 3H), 1.67 (s, 3H), 1.21 (s, 6H), 0.82 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 138.6, 136.6, 130.0, 127.7, 118.2, 90.5, 75.4, 66.1, 44.0, 35.7, 32.6, 25.8, 25.6, 21.5, 17.9, 17.9, -3.0. IR (film) $\tilde{\nu}$ 2929, 2855, 1451, 1343, 1160 cm^{-1}. HRMS (ESI$^+$) for $C_{24}H_{39}NO_3SSi$ [M+Na]$^+$: calcd: 472.2312, found: 472.2313.



N-(4-Hydroxyhex-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S48). *n*-BuLi (1.6 M in hexanes, 1.35 mL, 2.16 mmol) was added slowly to a solution of alkyne **S26** (460 mg, 1.66 mmol) in THF (17.5 mL) at 0 °C. The solution was stirred for 30 min at 0 °C before freshly distilled propionaldehyde (1.20 mL, 16.6 mmol) was introduced. Stirring was continued at room temperature for 30 min before sat. NH_4Cl solution (3 mL) and EtOAc (30 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic



layers were washed with brine and dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 8:1 – 4:1 – 3:1) to yield the title compound as a light yellow oil which was directly used in the subsequent step.

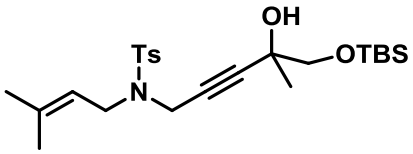
N-(4-Methoxyhex-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S49). A solution of alcohol **S48** in THF (3 mL) was slowly added to a suspension of NaH (214 mg, 8.9 mmol) in THF (7.7 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (1.12 mL, 17.9 mmol) was carefully added at 0 °C. After stirring for another 1 h at room temperature, water (1 mL) and *tert*-butyl methyl ether (10 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL), the combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (235 mg, 40% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.30 – 7.26 (m, 2H), 5.12 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.14 (d, *J* = 1.8 Hz, 2H), 3.81 (d, *J* = 7.3 Hz, 2H), 3.61 (tt, *J* = 6.3, 1.8 Hz, 1H), 3.18 (s, 2H), 2.41 (s, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.57 – 1.36 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 139.0, 136.5, 129.6, 127.9, 118.2, 84.1, 79.1, 72.4, 56.4, 44.1, 35.8, 28.6, 26.0, 21.6, 18.0, 9.7. IR (film) $\tilde{\nu}$ 2971, 2932, 1449, 1343, 1159 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{27}NO_3S$ [M+Na]$^+$: calcd: 372.1604, found: 372.1604.

N-(4-Hydroxybut-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S50). *n*-BuLi (1.6 M in hexanes, 0.59 mL, 0.94 mmol) was slowly added to a solution of alkyne **S26** (200 mg, 0.72 mmol) in THF (7.6 mL) at −78 °C. The solution was stirred for 3 h at −78 °C before powdered paraformaldehyde (28 mg, 0.94 mmol) was introduced. After stirring at room temperature for 1 h, sat. NH_4Cl solution (3 mL) and EtOAc (30 mL) were added, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1 – 2:1) to yield the title compound as a light yellow oil (159 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.34 – 7.28 (m, 2H), 5.10 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.07 (t, *J* = 2.0 Hz, 2H), 3.97 (dt, *J* = 6.1, 2.0 Hz, 2H), 3.80 (d, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.67 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 139.2, 136.4, 129.4, 128.1, 118.0, 83.5, 79.2, 50.9, 44.2, 35.8, 26.0, 21.7, 18.0. The spectral data is consistent with previously reported values.[29]

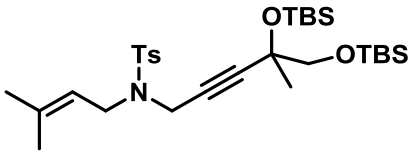
N-(4-Methoxybut-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S51). A solution of alcohol **S50** (150 mg, 0.49 mmol) in THF (2 mL) was slowly added to a suspension of NaH (59 mg, 2.4 mmol) in THF (2.1 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.31 mL, 4.9 mmol) was carefully added at 0 °C. Stirring was continued for 1 h at room temperature before water (0.5 mL) and *tert*-butyl methyl ether (10 mL) were introduced and the

layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (126 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.32 – 7.27 (m, 2H), 5.11 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.10 (t, *J* = 1.9 Hz, 2H), 3.82 (t, *J* = 1.9 Hz, 2H), 3.80 (d, *J* = 7.3 Hz, 3H), 3.18 (s, 3H), 2.42 (s, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.66 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 139.1, 136.3, 129.5, 128.0, 118.1, 81.2, 79.8, 59.7, 57.5, 44.2, 35.9, 26.0, 21.7, 18.0. IR (film) $\tilde{\nu}$ 2975, 2926, 1598, 1343, 1090 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{23}NO_3S$ [M+Na]$^+$: calcd: 344.1291, found: 344.1294.

N-(5-((*tert*-Butyldimethylsilyl)oxy)-4-hydroxy-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S52). *n*-BuLi (1.6 M in hexanes, 1.46 mL, 2.34 mmol) was slowly added to a solution of alkyne **S26** (500 mg, 1.80 mmol) in THF (19.0 mL) at 0 °C. The solution was stirred for 20 min at 0 °C before ketone **S17** (509 mg, 2.7 mmol) was introduced. The mixture was warmed to room temperature and stirred for 5 min before sat. NH_4Cl solution (10 mL) and EtOAc (50 mL) were added. The aqueous phase was extracted with EtOAc (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 4:1) to yield the title compound as a colorless oil (503 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.32 – 7.27 (m, 2H), 5.11 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.09 (s, 2H), 3.81 (d, *J* = 7.3 Hz, 2H), 3.40 (d, *J* = 9.5 Hz, 1H), 3.29 (d, *J* = 9.4 Hz, 1H), 2.51 (br, 1H), 2.42 (s, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.15 (s, 3H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 139.0, 136.6, 129.6, 128.0, 118.2, 87.7, 76.5, 70.8, 67.8, 44.0, 35.8, 26.0, 26.0, 25.2, 21.7, 18.5, 18.1, -5.2, -5.3. IR (film) $\tilde{\nu}$ 3513 (br), 2929, 2858, 1347, 1160, 1093 cm^{-1}. HRMS (ESI$^+$) for $C_{24}H_{39}NO_4SSi$ [M+Na]$^+$: calcd: 488.2261, found: 488.2264.



N-(4,5-bis((*tert*-Butyldimethylsilyl)oxy)-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S53). TBSOTf (0.15 mL, 0.64 mmol) was added to a solution of alcohol **S52** (250 mg, 0.0.54 mmol) and 2,6-lutidine (0.13 mL, 1.07 mmol) in CH_2Cl_2 (2.1 mL) at −78 °C. The mixture was allowed to reach room temperature and was stirred for 2 h before sat. NH_4Cl solution (0.5 mL) was added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to yield the title compound as a light yellow oil (281 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.30 – 7.26 (m, 2H), 5.12 (tdq, *J* = 7.2, 2.9, 1.3 Hz, 1H), 4.10 (s, 2H), 3.82 (d, *J* = 7.2 Hz, 2H), 3.29 (s, 2H), 2.41 (s, 3H), 1.71 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.18 (s, 3H), 0.87 (s, 9H), 0.82 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.7, 136.9, 129.6, 127.8, 118.3, 88.5, 77.4, 71.6, 70.0, 44.0, 35.9, 27.2, 26.0, 26.0, 25.8, 21.7, 18.5, 18.1, -2.7, -2.9, -5.2. IR (film) $\tilde{\nu}$ 2929, 2857, 1351, 1162, 1112 cm^{-1}. HRMS (ESI$^+$) for $C_{30}H_{53}NO_4SSi_2$ [M+Na]$^+$: calcd: 602.3126, found: 602.3128.



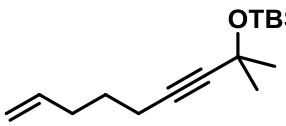
4-Methyl-N-(3-methylbut-2-en-1-yl)-N-(4-oxopent-2-yn-1-yl)benzenesulfonamide (S54). *n*-BuLi (1.6 M in hexanes, 1.46 mL, 2.34 mmol) was slowly added to a solution of alkyne **S26** (500 mg, 1.80 mmol) in THF (19.0 mL) at 0 °C. The solution was stirred for 20 min at 0 °C before *N*-methoxy-*N*-methylacetamide (0.29 mL, 2.7 mmol) was introduced. After reaching room temperature, the mixture was stirred for 5 min before sat. NH_4Cl solution (10 mL) and EtOAc (50 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 4:1) to yield the title compound as a yellow oil (248 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.36 – 7.29 (m, 2H), 5.10 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.21 (s, 2H), 3.82 (d, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 2.08 (s, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.66 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3, 144.0, 139.9, 135.8, 129.8, 127.9, 117.6, 84.9, 84.6, 44.6, 35.7, 32.4, 26.0, 21.7, 18.0. IR (film) $\tilde{\nu}$ 2974, 2921, 2209, 1679, 1348, 1162 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{21}NO_3S$ [M+Na]$^+$: calcd: 342.1134, found: 342.1135.

4-Methyl-N-(3-(2-methyl-1,3-dioxolan-2-yl)prop-2-yn-1-yl)-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S55). *p*-TsOH · H_2O (7.4 mg, 0.04 mmol) was added to a vigorously stirred suspension of ynone **S54** (125 mg, 0.39 mmol) and triethylorthoformate (70 mg, 0.47 mmol) in ethylene glycol (1.9 mL). The mixture was stirred at room temperature for 24 h before solid $NaHCO_3$ (30 mg) and sat. $NaHCO_3$ solution (1 mL) were added. The mixture was diluted with EtOAc (20 mL) and water (5 mL), the layers were separated, the aqueous phase was extracted with EtOAc (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 4:1) to give the title compound as a colorless amorphous solid (116 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.34 – 7.29 (m, 2H), 5.10 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.11 (s, 2H), 3.91 – 3.83 (m, 2H), 3.82 – 3.77 (m, 4H), 2.42 (s, 3H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.1, 136.3, 129.7, 127.8, 118.1, 100.5, 83.9, 76.3, 64.6, 44.2, 35.6, 26.2, 26.0, 21.7, 18.0. IR (film) $\tilde{\nu}$ 2973, 2895, 1347, 1185, 1161 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{25}NO_4S$ [M+Na]$^+$: calcd: 386.1397, found: 386.1399.

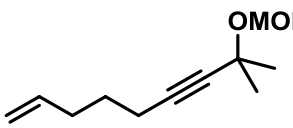
2-Methylnon-8-en-3-yn-2-ol (S56). *n*-BuLi (1.6 M in hexanes, 19.3 mL, 30.1 mmol) was added at 0 °C to a solution of 2-methyl-3-butin-2-ol (1.50 mL, 15.5 mmol) in THF (45 mL) and HMPA (18 mL). After 1 h at 0 °C, the reaction mixture was cooled to −78 °C and 5-bromo-1-pentene (1.53 mL, 12.9 mmol) was slowly introduced. The mixture was warmed to room temperature during 1 h and then stirred at 70 °C for another 18 h. The mixture was cooled to room temperature and the reaction quenched with sat. NH_4Cl solution (50 mL). The aqueous phase was extracted with Et_2O (3 x 40 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 5:1) to give the title compound as a colorless oil (1.54 g, 78%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.08 – 4.95 (m, 2H), 2.19 (t, *J* = 7.1 Hz, 2H), 2.17 – 2.10 (m, 2H), 1.86 (s, 1H), 1.63 – 1.55 (m, 1H), 1.50

(s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 115.1, 85.4, 82.2, 65.3, 32.8, 31.7, 27.8, 18.0. IR (film) $\tilde{\nu}$ 3331, 2980, 2933, 1641, 1439, 1364, 1240, 1163, 1133, 1083, 950, 912, 838 cm^{-1}. HRMS (ESI$^+$) for $C_{10}H_{16}O$ [M+Na]$^+$: calcd: 175.1093, found: 175.1094.

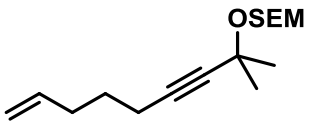
***tert*-Butyldimethyl((2-methylnon-8-en-3-yn-2-yl)oxy)silane (S57)**. 2,6-Lutidine (0.4 mL, 3.4 mmol) and TBSOTf (0.47 mL, 2.0 mmol) were added at −15 °C to a solution of alcohol **S56** (260 mg, 1.7 mmol) in CH_2Cl_2 (8 mL).The mixture was warmed to ambient temperature over the course of 2 h and stirring was continued for 14 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 100:1) to give the title compound as a colorless oil (349 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 4.88 (ddd, *J* = 17.1, 1.7, 1.7 Hz, 1H), 4.85 – 4.80 (m, 1H), 2.08 – 1.93 (m, 5H), 1.50 – 1.37 (m, 2H), 1.27 (s, 6H), 0.71 (s, 9H), 0.00 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$): δ 138.1, 115.2, 86.1, 82.5, 66.5, 33.4, 33.0, 28.0, 25.9, 25.9, 18.2, 18.1, -2.8. IR (film) $\tilde{\nu}$ 2930, 1247, 1159, 1035, 834, 774 cm^{-1}. HRMS (CI) for $C_{16}H_{30}OSi$ [M+H]$^+$: calcd: 267.2137, found: 267.2139.



8-(Methoxymethoxy)-8-methylnon-1-en-6-yne (S58). Hünig's base (1.17 mL, 6.7 mmol) and MOMCl (0.26 mL, 3.37 mmol) were added at 0 °C to a solution of alcohol **S56** (171 mg, 1.12 mmol) in CH_2Cl_2 (5 mL). The mixture was warmed to ambient temperature over 2 h and stirring was continued for another 14 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 97:3) to give the title compound as a colorless oil (156 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.89 (s, 2H), 3.37 (s, 3H), 2.21 (t, *J* = 7.1 Hz, 2H), 2.18 – 2.11 (m, 2H), 1.64 – 1.56 (m, 2H), 1.48 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 115.3, 93.2, 85.1, 82.3, 71.4, 55.5, 32.9, 30.7, 28.0, 18.1. IR (film) $\tilde{\nu}$ 2934, 1256, 1144, 1031, 1001, 917, 810 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{20}O_2$ [M+Na]$^+$: calcd: 219.1356, found: 219.1356.

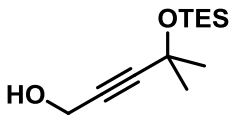


Trimethyl(2-(((2-methylnon-8-en-3-yn-2-yl)oxy)methoxy)ethyl)silane (S59). Hünig's base (1.21 mL, 6.9 mmol) and SEMCl (0.62 mL, 3.48 mmol) were added at 0 °C to a solution of alcohol **S56** (176.9 mg, 1.16 mmol) in CH_2Cl_2(5 mL). The mixture was warmed to ambient temperature over 2 h and stirring was continued for another 14 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 100:1) to give the title compound as a colorless oil (311 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.94 (s, 2H), 3.71 – 3.59 (m, 2H), 2.21 (t, *J* = 7.1 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.67 – 1.55 (m, 2H), 1.48 (s, 6H), 0.99 – 0.89 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 116.6, 92.7, 86.2, 83.7, 72.5, 66.6,

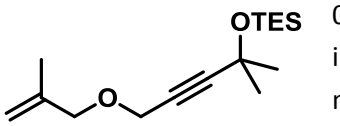


34.2, 31.9, 29.3, 19.6, 19.4, 0.0. IR (film) $\tilde{\nu}$ 2953, 1248, 1095, 1027, 919, 857, 834 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{30}O_2Si$ $[M+Na]^+$: calcd: 305.1907, found: 305.1908.

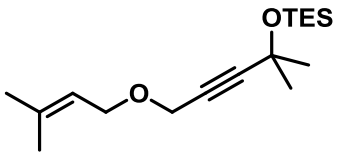
4-Methyl-4-((triethylsilyl)oxy)pent-2-yn-1-ol (S60). *n*-BuLi (1.6 M in hexanes, 1.57 mL, 2.5 mmol) was added at 0 °C to a solution of alkyne **S22** (500 mg, 2.5mmol) in THF (10 mL). The mixture was stirred for 1 h at this temperature before powdered paraformaldehyde (90 mg, 3.0 mmol) was slowly introduced and stirring was continued overnight at ambient temperature. The reaction was quenched with sat. NH_4Cl solution (10 mL). The aqueous phase was extracted with Et_2O (3 x 40 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 9:1) to give the title compound as a colorless oil (529 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.28 (d, *J* = 6.2 Hz, 2H), 1.42 (t, *J* = 6.2 Hz, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.74 – 0.62 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 91.4, 80.4, 66.3, 51.4, 33.1, 7.1, 6.2. IR (film) $\tilde{\nu}$ 3340, 2955, 2876, 1377, 1239, 1160, 1035, 1002, 724 cm^{-1}. HRMS (ESI^+) for $C_{12}H_{24}O_2Si$ $[M+Na]^+$: calcd: 251.1438, found: 251.1436.



Triethyl((2-methyl-5-((2-methylallyl)oxy)pent-3-yn-2-yl)oxy)silane (S61). Alcohol **S60** (150 mg, 0.66 mmol) was added at 0 °C to a suspension of NaH (15.7 mg, 0.66 mmol) in THF (5 mL). The mixture was stirred for 1 h at 0 °C before 3-bromo-2-methylpropene (0.13 mL, 1.3 mmol) was slowly introduced. The mixture was allowed to reach ambient temperature overnight. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 3 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 98:2) to give the title compound as a colorless oil (145.8 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.99 (s, 1H), 4.92 (s, 1H), 4.16 – 4.10 (m, 2H), 3.96 (s, 2H), 1.80 – 1.70 (m, 3H), 1.49 (d, *J* = 1.0 Hz, 6H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 113.0, 91.7, 78.5, 73.6, 66.3, 57.5, 33.2, 19.7, 7.1, 6.2. IR (film) $\tilde{\nu}$ 2954, 2876, 1458, 1359, 1239, 1161, 1035, 1004, 725 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{30}O_2Si$ $[M+Na]^+$: calcd: 305.1907, found: 305.1903.

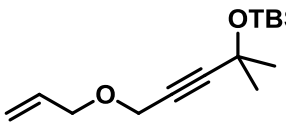


Triethyl((2-methyl-5-((3-methylbut-2-en-1-yl)oxy)pent-3-yn-2-yl)oxy)silane (S62). Alcohol **S60** (150 mg, 0.66 mmol) was added at 0 °C to a suspension of NaH (15.7 mg, 0.66 mmol) in THF (5 mL). The mixture was stirred for 1 h at 0 °C before 1-bromo-3-methyl-2-butene (0.15 mL, 1.3 mmol) was slowly introduced. The mixture was allowed to reach ambient temperature overnight. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 3 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 50:1) to give the title compound as a colorless oil (126 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.26 (m, 1H), 4.14 (s, 2H), 4.03 (d, *J* = 6.7 Hz, 2H), 1.81 – 1.67 (m, 6H), 1.48 (s, 6H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 120.6, 91.6, 78.7, 66.3, 66.0,



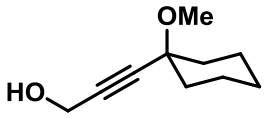
57.4, 33.2, 26.0, 18.1, 7.1, 6.2. IR (film) $\tilde{\nu}$ 2956, 1716, 1362, 1237, 1163, 1037, 1004, 726 cm^{-1}. HRMS (ESI^+) for $C_{17}H_{32}O_2Si$ $[M+Na]^+$: calcd: 319.2064, found: 319.2063.

((5-(Allyloxy)-2-methylpent-3-yn-2-yl)oxy)(*tert*-butyl)dimethylsilane (S63). To a solution of allyl propargyl ether (150 mg, 1.5 mmol)[30] in THF (6 mL) was added *n*-BuLi (1.6 M in hexanes, 0.97 mL, 1.56 mmol) at −78 °C. The mixture was stirred for 1 h at this temperature before acetone (0.17 mL, 2.3 mmol) was slowly introduced. The mixture was allowed to reach ambient temperature overnight. The reaction was quenched with sat. NH_4Cl solution (10 mL). The aqueous phase was extracted with Et_2O (3 x 10 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was used directly for the next step.

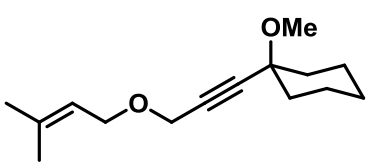


2,6-Lutidine (0.2 mL, 1.74 mmol) and TBSOTf (0.24 mL, 1 mmol) were added at −15 °C to a solution of the crude alcohol (134 mg, 0.89 mmol) in CH_2Cl_2 (2.5 mL). The mixture was warmed to ambient temperature over 2 h and stirring was continued for another 14 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 3 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 99:1) to give the title compound as a colorless oil (220 mg, 94%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.31 (ddd, *J* = 17.2, 1.6, 1.6 Hz, 1H), 5.22 (ddd, *J* = 10.4, 1.4, 1.3 Hz, 1H), 4.17 (s, 2H), 4.05 (dt, *J* = 5.8, 1.4 Hz, 2H), 1.46 (s, 6H), 0.86 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 117.9, 91.9, 78.4, 70.6, 66.4, 57.6, 33.0, 25.8, 18.1, -2.8. IR (film) $\tilde{\nu}$ 2930, 1721, 1360, 1248, 1162, 1035, 828, 775, 678 cm^{-1}. HRMS (ESI^+) for $C_{15}H_{28}O_2Si$ $[M+H]^+$: calcd: 269.1931, found: 269.1933.

3-(1-Methoxycyclohexyl)prop-2-yn-1-ol (S64). *n*-BuLi (1.6 M in hexanes, 2.94 mL, 4.7 mmol) was slowly added to a solution of alkyne **S19** (500 mg, 3.6 mmol) in THF (38 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before powdered paraformaldehyde (141 mg, 4.7 mmol) was introduced. After stirring at room temperature for 18 h the reaction was quenched with water (10 mL) and EtOAc (50 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1) to yield the title compound as a colorless oil (371 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.33 (s, 2H), 3.35 (s, 3H), 1.92 – 1.83 (m, 2H), 1.70 – 1.44 (m, 8H), 1.37 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.0, 84.1, 73.9, 51.3, 50.8, 36.7, 25.5, 22.8. IR (film) $\tilde{\nu}$ 3423 (br), 2935, 2858, 1448, 1077 cm^{-1}. HRMS (ESI^+) for $C_{10}H_{16}O_2$ $[M+Na]^+$: calcd: 191.1042, found: 191.1042.

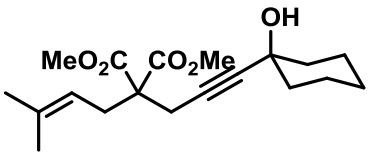


1-Methoxy-1-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-yn-1-yl)cyclohexane (S65). A solution of alcohol **S64** (360 mg, 2.1 mmol) in THF (1 mL) was added to a stirred suspension of NaH (87 mg, 3.6 mmol) in THF (13.9 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before 1-bromo-3-methyl-2-butene (0.30 mL, 2.6 mmol) was added. After stirring for 1 h at room temperature, the reaction was quenched with sat. NH_4Cl solution (2 mL), water (4 mL) and *tert*-

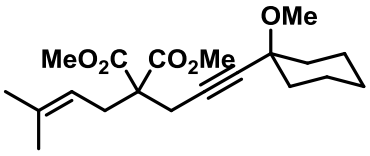


butyl methyl ether (30 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 40:1 – 20:1) to give the title compound as a colorless oil (266 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.20 (s, 2H), 4.06 (d, *J* = 7.1 Hz, 2H), 3.36 (s, 3H), 1.94 – 1.82 (m, 2H), 1.76 (s, 3H), 1.70 (s, 3H), 1.69 – 1.45 (m, 7H), 1.37 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 120.5, 87.3, 82.2, 74.1, 65.9, 57.28, 50.9, 36.8, 26.0, 25.6, 22.9, 18.2. IR (film) $\tilde{\nu}$ 2933, 2856, 1674, 1446, 1073 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O_2$ [M+Na]$^+$: calcd: 259.1668, found: 259.1669.

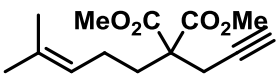
Dimethyl 2-(3-(1-hydroxycyclohexyl)prop-2-yn-1-yl)-2-(3-methylbut-2-en-1-yl)malonate (S66). LiHMDS (1 M in THF, 1.0 mL, 1.0 mmol) was slowly added to a solution of alkyne **S27** (200 mg, 0.84 mmol) in THF (8.2 mL) at −78 °C and the resulting mixture was stirred for 30 min at that temperature. Cyclohexanone (0.13 mL, 1.26 mmol) was slowly added at −78 °C and the resulting mixture warmed to room temperature. After 5 min, sat. NH_4Cl solution (1 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to give the title compound as a colorless oil (189 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (tp, *J* = 7.7, 1.5 Hz, 1H), 3.72 (s, 6H), 2.79 (s, 2H), 2.76 (d, *J* = 7.7 Hz, 2H), 1.87 – 1.72 (m, 5H), 1.70 (d, *J* = 1.4 Hz, 3H), 1.65 (d, *J* = 1.4 Hz, 3H), 1.58 – 1.44 (m, 5H), 1.23 – 1.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.9, 117.2, 87.1, 79.6, 68.9, 57.6, 52.8, 40.2, 31.0, 26.2, 25.3, 23.5, 22.9, 18.1. IR (film) $\tilde{\nu}$ 3468 (br), 2933, 2858, 1732, 1437 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{28}O_5$ [M+Na]$^+$: calcd: 359.1829, found: 359.1829.



Dimethyl 2-(3-(1-methoxycyclohexyl)prop-2-yn-1-yl)-2-(3-methylbut-2-en-1-yl)malonate (S67). A solution of alcohol **S66** (180 mg, 0.54 mmol) in THF (1 mL) was slowly added to a suspension of NaH (64 mg, 2.7 mmol) in THF (2.2 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.34 mL, 5.4 mmol) was carefully added at 0 °C. After stirring for 1 h at room temperature, water (0.5 mL) and *tert*-butyl methyl ether (10 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 40:1 – 20:1 – 15:1) to yield the title compound as a colorless oil (84 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (dddd, *J* = 9.2, 5.9, 2.9, 1.5 Hz, 1H), 3.72 (s, 6H), 3.31 (s, 3H), 2.83 (s, 2H), 2.77 (d, *J* = 7.8 Hz, 2H), 1.88 – 1.77 (m, 2H), 1.70 (d, *J* = 1.3 Hz, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.64 – 1.41 (m, 8H), 1.31 – 1.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.9, 117.3, 84.2, 81.2, 74.1, 57.6, 52.8, 50.7, 37.0, 31.0, 26.2, 25.6, 23.0, 22.9, 18.1. IR (film) $\tilde{\nu}$ 2935, 2857, 1738, 1437, 1224 cm^{-1}. HRMS (ESI$^+$) for $C_{20}H_{30}O_5$ [M+Na]$^+$: calcd: 373.1985, found: 373.1983.

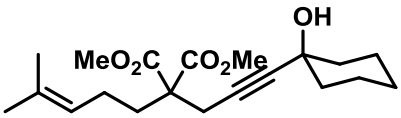


Dimethyl 2-(4-methylpent-3-en-1-yl)-2-(prop-2-yn-1-yl)malonate (S68). Cs_2CO_3 (3.4 g, 10.5 mmol) and 5-bromo-2-methyl-2-pentene (1.40 mL, 10.5 mmol) were added to a solution of malonate **S21** (594 mg, 3.5 mmol) in acetone (23.1 mL). The mixture was

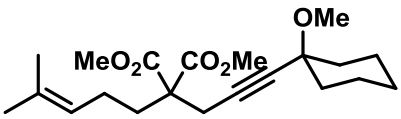


stirred at reflux temperature for 18 h before it was cooled to room temperature and diluted with *tert*-butyl methyl ether (40 mL). The mixture was filtered through a pad of Celite and the filter cake was washed with *tert*-butyl methyl ether (100 mL). The combined filtrates were evaporated and the residue was purified by flash chromatography (silica, hexanes/*tert*-butyl methyl ether 40:1 – 20:1 – 15:1 – 10:1) to give the title compound as a colorless oil (740 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (tdq, *J* = 6.9, 2.6, 1.3 Hz, 1H), 3.73 (s, 6H), 2.85 (d, *J* = 2.7 Hz, 2H), 2.12 – 2.06 (m, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.93 – 1.85 (m, 2H), 1.67 (q, *J* = 1.3 Hz, 3H), 1.58 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 133.0, 122.9, 79.0, 71.4, 56.8, 52.9, 32.2, 25.8, 23.0, 22.9, 17.7. The spectral data is consistent with previously reported values.[31]

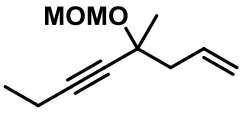
Dimethyl 2-(3-(1-hydroxycyclohexyl)prop-2-yn-1-yl)-2-(4-methylpent-3-en-1-yl)malonate (S69). LiHMDS (1 M in THF, 1.9 mL, 1.9 mmol) was slowly added to a solution of alkyne **S68** (400 mg, 1.59 mmol) in THF (15.4 mL) at −78 °C and the resulting mixture was stirred for 30 min at this temperature. Cyclohexanone (0.25 mL, 2.38 mmol) was slowly added at −78 °C and the resulting mixture was warmed to room temperature. After 5 min, sat. NH_4Cl solution (1 mL) and EtOAc (20 mL) were introduced and the layers were separated, the aqueous phase was extracted with EtOAc (3 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1). The product was obtained as a colorless oil (351 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 3.72 (s, 6H), 2.87 (s, 2H), 2.11 – 2.03 (m, 2H), 1.93 – 1.77 (m, 5H), 1.70 – 1.63 (m, 5H), 1.58 (d, *J* = 1.4 Hz, 3H), 1.50 (qd, *J* = 10.6, 9.6, 3.2 Hz, 5H), 1.25 – 1.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 132.9, 123.0, 87.1, 79.2, 68.9, 57.2, 52.8, 40.3, 32.3, 25.8, 25.3, 23.5, 23.2, 22.9, 17.7. IR (film) $\tilde{\nu}$ 3498 (br), 2933, 2857, 1733, 1438, 1171 cm^{-1}. HRMS (ESI$^+$) for $C_{20}H_{30}O_5$ [M+Na]$^+$: calcd: 373.1985, found: 373.1983.



Dimethyl 2-(3-(1-methoxycyclohexyl)prop-2-yn-1-yl)-2-(4-methylpent-3-en-1-yl)malonate (17). A solution of alcohol **S69** (340 mg, 0.97 mmol) in THF (1 mL) was slowly added to a suspension of NaH (70 mg, 2.9 mmol) in THF (3.9 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.31 mL, 4.9 mmol) was carefully added at 0 °C. Stirring was continued for 1 h at room temperature before water (1 mL) and *tert*-butyl methyl ether (20 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (263 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 3.72 (s, 6H), 3.31 (s, 3H), 2.90 (s, 2H), 2.12 – 2.00 (m, 2H), 1.93 – 1.78 (m, 4H), 1.70 – 1.56 (m, 3H), 1.67 (q, *J* = 1.9 Hz, 3H), 1.58 (s, 3H), 1.55 – 1.40 (m, 6H), 1.30 – 1.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 132.8, 123.0, 84.3, 80.9, 74.2, 57.2, 52.8, 50.7, 37.0, 32.3, 25.8, 25.6, 23.2, 23.0, 22.9, 17.7. IR (film) $\tilde{\nu}$ 2934, 2857, 1735, 1436, 1167 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{32}O_5$ [M+Na]$^+$: calcd: 387.2142, found: 387.2142.

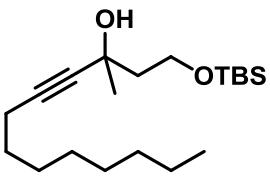


4-(Methoxymethoxy)-4-methyloct-1-en-5-yne (S70). Allylmagnesium chloride (2 M in THF, 0.59 mL, 1.19 mmol) was added to a stirred solution of 3-hexyn-2-one (57.0 mg, 0.59 mmol) in THF (2 mL) at 0 °C. The mixture was warmed to room temperature and stirring was continued for 18 h before sat. NH_4Cl solution (3 mL) and Et_2O (5 mL) were introduced. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was directly used in the next step without further purification.

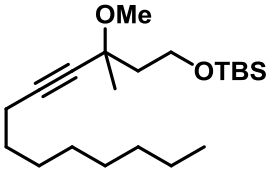


Hünig's base (0.54 mL, 3.1 mmol) and MOMCl (0.12 mL, 1.6 mmol) were added at 0 °C to a solution of the crude alcohol (82 mg, 0.59 mmol) in CH_2Cl_2 (2.1 mL). The mixture was warmed to ambient temperature over 2 h and stirring was continued for another 14 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 98:2) to give the title compound as a colorless oil (67 mg, 62% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ6.01 – 5.81 (m, 1H), 5.14 – 5.07 (m, 2H), 4.98 (d, *J* = 7.0 Hz, 1H), 4.85 (d, *J* = 7.0 Hz, 1H), 3.38 (s, 3H), 2.56 – 2.48 (m, 1H), 2.45 – 2.37 (m, 1H), 2.23 (q, *J* = 7.5 Hz, 2H), 1.43 (s, 3H), 1.14 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 117.9, 93.2, 88.6, 74.0, 55.7, 47.6, 28.1, 14.1, 12.5, 1.2. IR (film) $\tilde{\nu}$ 2979, 1320, 1143, 1092, 1024, 917 cm^{-1}. HRMS (ESI$^+$) for $C_{11}H_{18}O_2$ $[M+Na]^+$: calcd: 205.1199, found: 205.1201.

1-((*tert*-Butyldimethylsilyl)oxy)-3-methyltridec-4-yn-3-ol (S71). *n*-BuLi (1.6 M in hexanes, 7.04 mL, 11.3 mmol) was slowly added to a solution of 1-decyne (2.03 mL, 11.3 mmol) in THF (100 mL) at 0 °C. The solution was stirred for 20 min at 0 °C before ketone **S18** (1.9 g, 9.4 mmol) was introduced. After stirring at room temperature for 20 min, aq. sat. NH_4Cl (10 mL) and *tert*-butyl methyl ether (100 mL) were added. The layers were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 100 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to yield the title compound as a colorless oil (2.65 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (br, 1H), 4.23 (ddd, *J* = 10.8, 10.0, 3.1 Hz, 1H), 3.87 (ddd, *J* = 10.1, 4.5, 3.4 Hz, 1H), 2.20 (t, *J* = 7.1 Hz, 2H), 1.95 (ddd, *J* = 14.1, 10.8, 4.5 Hz, 1H), 1.69 (dt, *J* = 14.1, 3.2 Hz, 1H), 1.56 – 1.45 (m, 2H), 1.46 (s, 3H), 1.42 – 1.33 (m, 2H), 1.33 – 1.22 (m, 8H), 0.91 (s, 9H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.11 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.1, 83.5, 68.8, 62.1, 43.6, 32.0, 30.9, 29.4, 29.3, 29.1, 29.0, 26.0, 22.8, 18.9, 18.3, 14.3, -5.4, -5.5. IR (film) $\tilde{\nu}$ 3503 (br), 2954, 2928, 2856, 1255, 1093 cm^{-1}. HRMS (ESI$^+$) for $C_{20}H_{40}O_2Si$ $[M+Na]^+$: calcd: 363.2690, found: 363.2691.

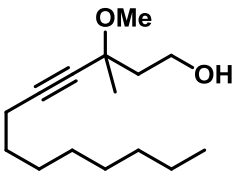


***tert*-Butyl((3-methoxy-3-methyltridec-4-yn-1-yl)oxy)dimethylsilane (S72)**. A solution of alcohol **S71** (1.8 g, 5.3 mmol) in THF (5 mL) was added to a stirred suspension of NaH (317 mg, 13.2 mmol) in THF (23 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (1.66 mL, 26.4 mmol) was added. After stirring for 1 h at room temperature sat. NH_4Cl solution (10 mL), water (10 mL) and *tert*-butyl methyl ether (60 mL) were added to the mixture and the layers were



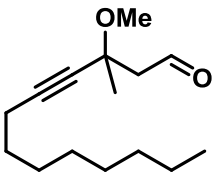
separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a colorless oil (1.77 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (ddd, *J* = 7.9, 6.6, 1.1 Hz, 2H), 3.31 (s, 3H), 2.20 (t, *J* = 7.0 Hz, 2H), 1.99 – 1.84 (m, 2H), 1.54 – 1.46 (m, 2H), 1.42 – 1.34 (m, 2H), 1.39 (s, 3H), 1.34 – 1.21 (m, 8H), 0.89 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.2, 80.8, 72.5, 60.0, 51.2, 44.2, 32.0, 29.4, 29.2, 29.0, 28.9, 26.6, 26.1, 22.8, 18.8, 18.5, 14.3, -5.1, -5.1. IR (film) $\tilde{\nu}$ 2955, 2928, 2856, 1463, 1254, 1079 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{42}O_2Si$ [M+Na]$^+$: calcd: 377.2846, found: 377.2846.

3-Methoxy-3-methyltridec-4-yn-1-ol (S73). TBAF (1 M in THF) was added to a solution of silyl ether **S72**



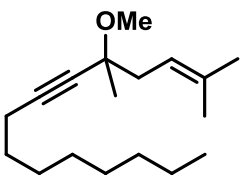
(1.77 g, 4.98 mmol) in THF (32 mL) at room temperature. The mixture was stirred for 1 h before sat. NH_4Cl solution (5 mL), water (5 mL) and EtOAc (30 mL) were added. The aqueous phase was extracted with EtOAc (2 x 80 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1) to give the title compound as a colorless oil (1.03 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (ddd, *J* = 11.6, 8.3, 3.5 Hz, 1H), 3.76 (ddd, *J* = 11.3, 6.0, 3.8 Hz, 1H), 3.34 (s, 3H), 2.74 (br, 1H), 2.21 (t, *J* = 7.1 Hz, 2H), 1.97 (ddd, *J* = 14.4, 8.3, 3.9 Hz, 1H), 1.86 (ddd, *J* = 14.4, 6.0, 3.5 Hz, 1H), 1.56 – 1.46 (m, 2H), 1.42 (s, 3H), 1.38 (m, 2H), 1.33 – 1.22 (m, 8H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.3, 80.2, 75.0, 60.4, 51.3, 44.1, 32.0, 29.3, 29.2, 29.0, 28.9, 26.1, 22.8, 18.7, 14.3. IR (film) $\tilde{\nu}$ 3424 (br), 2927, 2856, 1464, 1078 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{28}O_2$ [M+Na]$^+$: calcd: 263.1981, found: 263.1981.

3-Methoxy-3-methyltridec-4-ynal (S74). $NaHCO_3$ (874 mg, 10.4 mmol) and Dess-Martin periodinane



(1.06 g, 2.5 mmol) were added to a solution of alcohol **S73** (500 mg, 2.08 mmol) in wet CH_2Cl_2 (19 mL) at 0 °C. The mixture was stirred at room temperature for 30 min before sat. $Na_2S_2O_3$ solution (7 mL) and water (4 mL) were introduced. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 60 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1). The product was obtained as a colorless oil (421 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (t, *J* = 2.9 Hz, 1H), 3.37 (s, 3H), 2.64 (dd, *J* = 15.3, 3.0 Hz, 1H), 2.58 (dd, *J* = 15.3, 2.8 Hz, 1H), 2.22 (t, *J* = 7.1 Hz, 2H), 1.51 (m, 2H), 1.47 (s, 3H), 1.42 – 1.33 (m, 2H), 1.27 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.9, 88.4, 79.5, 70.9, 54.5, 51.6, 32.0, 29.3, 29.2, 29.0, 28.7, 26.5, 22.8, 18.7, 14.3. IR (film) $\tilde{\nu}$ 2928, 2856, 1726, 1463, 1075 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{26}O_2$ [M+Na]$^+$: calcd: 261.1825, found: 261.1827.

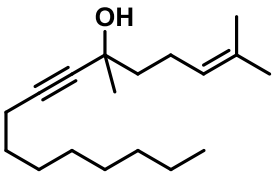
5-Methoxy-2,5-dimethylpentadec-2-en-6-yne (S75). *n*-BuLi (1.6 M in hexanes, 0.60 mL, 0.96 mmol) was



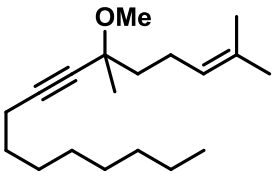
slowly added to a stirred suspension of isopropyltriphenylphosphonium iodide (492 mg, 1.14 mmol) in THF (5.7 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of aldehyde **S74** (208 mg, 0.88 mmol) in THF (1.4 mL) was added. After stirring at 0 °C for 1 h, sat. NH_4Cl solution (2 mL) and *tert*-butyl

methyl ether (10 mL) were introduced and the layers separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 75:1 – 50:1) to yield the title compound as a colorless oil (55 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 3.35 (s, 3H), 2.43 – 2.30 (m, 2H), 2.21 (t, *J* = 7.0 Hz, 2H), 1.74 (q, *J* = 1.3 Hz, 3H), 1.63 (s, 3H), 1.55 – 1.46 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 (s, 3H), 1.32 – 1.23 (m, 8H), 0.91 – 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 119.5, 85.9, 81.4, 74.0, 51.4, 39.8, 32.0, 29.4, 29.2, 29.0, 26.2, 25.9, 22.8, 18.8, 18.3, 14.3. IR (film) $\tilde{\nu}$ 2928, 2857, 1458, 1367, 1089 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{32}O$ [M+H]$^+$: calcd: 265.2526, found: 265.2526.

2,6-Dimethylhexadec-2-en-7-yn-6-ol (S76). *n*-BuLi (1.6 M in hexanes, 1.78 mL, 2.85 mmol) was added slowly to a solution of 1-decyne (0.51 mL, 2.85 mmol) in THF (25 mL) at 0 °C. The solution was stirred for 20 min at 0 °C before 6-methyl-5-hepten-2-one (300 mg, 2.38 mmol) was introduced. After stirring at room temperature for 20 min, sat. NH_4Cl solution (2 mL) and *tert*-butyl methyl ether (25 mL) were added, the layers were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 25 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless oil (546 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 – 5.14 (m, 1H), 2.32 – 2.22 (m, 1H), 2.19 (t, *J* = 7.1 Hz, 2H), 1.85 (br, 1H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.68 – 1.66 (m, 2H), 1.65 (d, *J* = 1.2 Hz, 3H), 1.54 – 1.46 (m, 2H), 1.45 (s, 3H), 1.42 – 1.33 (m, 2H), 1.32 – 1.22 (m, 9H), 0.91 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 124.2, 84.2, 84.0, 68.7, 43.8, 32.0, 30.4, 29.3, 29.2, 29.0, 28.9, 25.9, 24.0, 22.8, 18.8, 17.8, 14.3. IR (film) $\tilde{\nu}$ 3384 (br), 2925, 2856, 1455, 1375 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{32}O$ [M+Na]$^+$: calcd: 287.2345, found: 287.2345.



6-Methoxy-2,6-dimethylhexadec-2-en-7-yne (S77). A solution of alcohol **S76** (300 mg, 1.13 mmol) in THF (1 mL) was added to a stirred suspension of NaH (68 mg, 2.84 mmol) in THF (4.9 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.36 mL, 5.67 mmol) was added and stirring continued for 1 h at room temperature. sat. NH_4Cl solution (2 mL), water (2 mL) and *tert*-butyl methyl ether (20 mL) were introduced and the layers separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the product as a colorless oil (284 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 3.33 (s, 3H), 2.21 (t, *J* = 7.0 Hz, 2H), 2.17 – 2.06 (m, 3H), 1.68 (q, *J* = 1.2 Hz, 3H), 1.67 – 1.58 (m, 2H), 1.62 (d, *J* = 1.2 Hz, 3H), 1.54 – 1.46 (m, 2H), 1.42 – 1.35 (m, 2H), 1.37 (s, 3H), 1.33 – 1.23 (m, 8H), 0.91 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 124.3, 86.0, 81.2, 73.7, 51.3, 41.6, 32.0, 29.4, 29.2, 29.0, 29.0, 26.1, 25.9, 23.4, 22.8, 18.8, 17.8, 14.3. IR (film) $\tilde{\nu}$ 2926, 2856, 1459, 1173, 1088, 1073 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{34}O$ [M+H]$^+$: calcd: 279.2682, found: 279.2680.



HYDROGENATIVE CYCLOPROPANATION AND METATHESIS REACTIONS

Representative Procedure A. Preparation of cycloalkene 11a. $[Cp^*RuCl]_4$ (2.3 mg, 2 mol%) was added to a stirred solution of enyne **1f** (24.8 mg, 0.11 mmol) in 1,2-dichloroethane (1 mL, 0.1 M) in a flame dried Schlenk tube under argon. H_2 was bubbled through the mixture for 2 min before After stirring for 3 h at 70 °C, the mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, pentane/Et_2O 100:1) to yield the title product as colorless oil (20.4 mg, 93%).

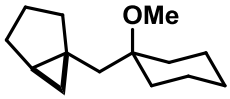
Representative Procedure B. Preparation of cycloalkene 18. TBACl (0.021 M in 1,2-dichloroethane, 0.42 mL, 11 mol%) was added to solid $[Cp(Me_2CO_2Et)Ru(NCMe)_3][PF_6]$ **21** (4.3 mg, 10 mol%) in a flame dried Schlenk tube under argon. The mixture was stirred for 5 min at room temperature before enyne **17** (29.3 mg, 0.08 mmol) in 1,2-dichloroethane (0.5 mL, 0.1 M) was added. H_2 was bubbled through the mixture for 2 min before the flask was immersed into a pre-heated oil bath at 70 °C keeping a static H_2 atmosphere (ambient pressure, H_2 filled balloon). After stirring for 3 h at 70 °C, the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 40:1 – 20:1 – 10:1) to yield the title product as light grey oil (16.9 mg, 65%).

Representative Procedure C. Preparation of cyclopropane 4a. $[Cp^*RuCl]_4$ (2.6 mg, 2 mol%) was added to a stirred solution of enyne **S57** (31.6 mg, 0.12 mmol) in CH_2Cl_2 (1.2 mL, 0.1 M) in a flame dried Schlenk tube under argon. H_2 was bubbled through the mixture for 2 min and stirring was continued for 18h under H_2 atmosphere (ambient pressure, H_2 filled balloon). The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 100:1) to yield the title product as colorless oil (29.1 mg, 91%).

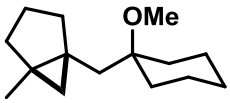
Representative Procedure D. Preparation of cyclopropane 3b. $[Cp^*RuCl]_4$ (3.5 mg, 2 mol%) was added to a stirred solution of enyne **S30** (35.0 mg, 0.16 mmol) in 1,2-dichloroethane (1.6 mL, 0.1 M) in a flame dried Schlenk tube under argon. H_2 was bubbled through the mixture for 2 min before before the flask was immersed into a pre-heated oil bath at 70 °C keeping a static H_2 atmosphere (ambient pressure, H_2 filled balloon). After stirring was continued for 18 h at 70 °C, the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 50:1) to yield the title product as colorless oil (32.2 mg, 91%).

Representative Procedure E. Preparation of cyclopropane 4e. $[Cp^*RuCl]_4$ (1.0 mg, 2 mol%) was added to a stirred solution of enyne **S43** (20.0 mg, 0.05 mmol) in 1,2-dichloroethane (1 mL, 0.5 M) in a flame dried thick-walled Schlenk tube under argon. H_2 was bubbled through the mixture for 2 min before the tube was sealed and immersed into a pre-heated oil bath at 90 °C keeping a static H_2 atmosphere. The mixture was stirred for 18 h at 90 °C before it was cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 97:3) to yield the title product as colorless solid (15.6 mg, 78%).

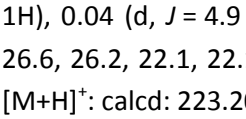
(1S*,5R*)-1-((1-methoxycyclohexyl)methyl)bicyclo[3.1.0]hexane (3a). A detailed procedure for the preparation of this compound, a compilation of analytical and spectroscopic data as well as copies of the spectra are contained in the Supporting Information of our previous publication.[28]



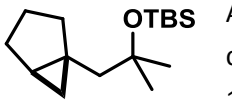
(1S*,5R*)-1-((1-methoxycyclohexyl)methyl)-5-methylbicyclo[3.1.0]hexane [3.1.0]hexane (3b). According to the Representative Procedure A from enyne **S30** (35.0 mg, 0.16 mmol); colorless oil (32.2 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.15 (s, 3H), 1.97 (dd, *J* = 12.4, 7.8 Hz, 1H), 1.87 – 1.70 (m, 3H), 1.71 – 1.62 (m, 1H), 1.62 – 1.51 (m, 4H), 1.53 – 1.38 (m, 5H), 1.40 – 1.22 (m, 3H), 1.13 (d, *J* = 14.9 Hz, 1H), 1.08 (s, 3H), 0.53 (d, *J* = 4.8 Hz, 1H), 0.04 (d, *J* = 4.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 76.7, 48.2, 38.8, 35.1, 34.5, 34.5, 34.2, 27.8, 26.6, 26.2, 22.1, 22.1, 20.8, 19.2, 18.6. IR (film) $\tilde{\nu}$ 2928, 2851, 1445, 1081 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{26}O$ $[M+H]^+$: calcd: 223.2056, found: 223.2055.



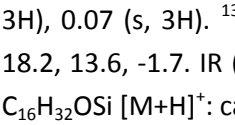
((1-((1S*,5R*)-bicyclo[3.1.0]hexan-1-yl)-2-methylpropan-2-yl)oxy)(tert-butyl)dimethylsilane (4a). According to the Representative Procedure C from enyne **S57** (31.6 mg, 0.12 mmol); colorless oil (29.1 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (dd, *J* = 14.1, 1.4 Hz, 1H), 1.81 (dd, *J* = 12.0, 7.8 Hz, 1H), 1.74 – 1.51 (m, 4H), 1.29 (d, *J* = 14.4 Hz, 1H), 1.27 (s, 3H), 1.24 (s, 3H), 1.18 (d, *J* = 8.3 Hz, 1H), 0.87 – 0.86 (m, 1H), 0.86 (s, 9H), 0.44 – 0.31 (m, 2H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.6, 52.2, 33.1, 30.9, 30.3, 27.0, 26.1, 26.0, 24.0, 22.3, 18.2, 13.6, -1.7. IR (film) $\tilde{\nu}$ 2954, 2929, 2857, 1462, 1251, 1144, 1031, 832, 769, 689 cm^{-1}. HRMS (CI) for $C_{16}H_{32}OSi$ $[M+H]^+$: calcd: 269.2295, found: 269.2295.



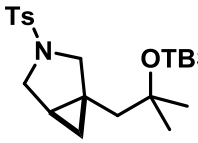
(2-(((1-((1S*,5R*)-bicyclo[3.1.0]hexan-1-yl)-2-methylpropan-2-yl)oxy)methoxy)ethyl)trimethylsilane (4b). According to the Representative Procedure C from enyne **S59** (27.6 mg, 0.10 mmol); colorless oil (28.0 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 – 4.71 (m, 2H), 3.67 – 3.55 (m, 2H), 1.97 (d, *J* = 14.4 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.70 – 1.48 (m, 4H), 1.34 (d, *J* = 14.5 Hz, 1H), 1.28 (s, 3H), 1.24 (s, 3H), 1.18 – 1.07 (m, 1H), 0.97 – 0.82 (m, 3H), 0.43 – 0.38 (m, 1H), 0.34 (dd, *J* = 7.9, 4.8 Hz, 1H), -0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 89.3, 77.9, 64.9, 48.6, 33.0, 27.3, 27.0, 25.7, 24.1, 22.3, 18.4, 13.6, -1.2. IR (film) $\tilde{\nu}$ 2955, 1259, 1091, 1023, 858, 833, 797, 692 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{32}O_2Si$ $[M+Na]^+$: calcd: 307.2064, found: 307.2066.



(1S*,5R*)-1-(2-(methoxymethoxy)-2-methylpropyl)bicyclo[3.1.0]hexane (4c). According to the Representative Procedure C from enyne **S58** (34.3 mg, 0.17 mmol); colorless oil (27.4 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (q, *J* = 7.2 Hz, 2H), 3.36 (s, 3H), 2.00 (dd, *J* = 14.4, 1.5 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.73 – 1.48 (m, 5H), 1.35 (d, *J* = 14.4 Hz, 1H), 1.29 (s, 3H), 1.26 (s, 3H), 1.22 – 1.08 (m, 1H), 0.87 (dt, *J* = 8.2, 4.1 Hz, 1H), 0.45 – 0.40 (m, 1H), 0.39 – 0.32 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 91.1, 78.1, 55.2, 48.6, 33.0, 27.3, 27.0, 26.9, 25.6, 24.1, 22.3, 13.6. IR (film) $\tilde{\nu}$ 2928, 1715, 1449, 1259, 1087, 1030, 919, 806 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{22}O_2$ $[M+Na]^+$: calcd: 221.1511, found: 221.1514.

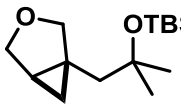


(1R*,5R*)-1-(2-((tert-butyldimethylsilyl)oxy)-2-methylpropyl)-3-tosyl-3-azabicyclo[3.1.0]hexane (4e).



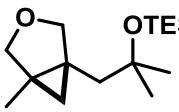
According to the Representative Procedure E from enyne **S43** (20.0 mg, 0.05 mmol); colorless solid (15.6 mg, 78%). Single crystals suitable for X-ray analysis were grown by slowly cooling a saturated solution of product in Et_2O to −20 °C. m.p.: 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 2H), 3.64 (d, *J* = 9.6 Hz, 1H), 3.47 (d, *J* = 9.0 Hz, 1H), 2.98 (dd, *J* = 9.0, 3.9 Hz, 1H), 2.91 (d, *J* = 9.9 Hz, 1H), 2.43 (s, 3H), 1.96 (d, *J* = 14.2 Hz, 1H), 1.26 (s, 3H), 1.18 (s, 3H), 1.09 – 0.97 (m, 2H), 0.89 (s, 9H), 0.74 (t, *J* = 4.9 Hz, 1H), 0.59 (dd, *J* = 7.9, 5.1 Hz, 1H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 133.6, 129.6, 127.8, 74.9, 54.3, 49.6, 49.2, 31.4, 28.8, 26.2, 25.0, 21.7, 21.2, 18.2, 15.2, -1.7, -1.7. IR (film) $\tilde{\nu}$ 2928, 2855, 1462, 1347, 1163, 1132, 1027, 832, 771, 664, 567, 548 cm^{-1}. HRMS (ESI$^+$) for $C_{22}H_{37}NO_3SSi$ [M+Na]$^+$: calcd: 446.2156, found: 446.2155.

((1-((1R*,5R*)-3-oxabicyclo[3.1.0]hexan-1-yl)-2-methylpropan-2-yl)oxy)(tert-butyl)dimethylsilane (4f).



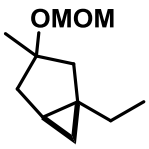
According to the Representative Procedure E from enyne **S63** (22.3 mg, 0.08 mmol), flash chromatography (silica, hexanes/EtOAc 97:3), colorless oil (12.7 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (d, *J* = 8.5 Hz, 1H), 3.76 – 3.64 (m, 2H), 3.62 (d, *J* = 8.5 Hz, 1H), 2.13 (d, *J* = 14.2 Hz, 1H), 1.32 (d, *J* = 14.3 Hz, 1H), 1.28 (s, 3H), 1.24 (s, 3H), 1.20 (d, *J* = 12.1 Hz, 1H), 1.13 (td, *J* = 6.0, 2.8 Hz, 1H), 0.86 (s, 9H), 0.63 (d, *J* = 6.4 Hz, 2H), 0.10 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.0, 74.1, 69.0, 48.8, 31.2, 29.2, 26.1, 25.9, 22.9, 18.2, 14.7, -1.7. IR (film) $\tilde{\nu}$ 2956, 2856, 1780, 1364, 1252, 1131, 1024, 830, 770, 690 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{30}O_2Si$ [M+H]$^+$: calcd: 271.2088, found: 271.2087.

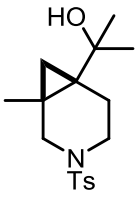
triethyl((2-methyl-1-((1R*,5R*)-5-methyl-3-oxabicyclo[3.1.0]hexan-1-yl)propan-2-yl)oxy)silane (4g).



According to the Representative Procedure E from enyne **S61** (21.0 mg, 0.07 mmol); colorless oil (18.8 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 (d, *J* = 8.7 Hz, 1H), 3.73 (d, *J* = 7.9 Hz, 1H), 3.58 (d, *J* = 8.8 Hz, 1H), 3.42 (d, *J* = 8.0 Hz, 1H), 1.91 (d, *J* = 13.9 Hz, 1H), 1.26 (s, 6H), 1.16 (d, *J* = 14.1 Hz, 1H), 1.09 (s, 3H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.70 (d, *J* = 4.4 Hz, 1H), 0.58 (q, *J* = 7.8 Hz, 6H), 0.33 (d, *J* = 4.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.1, 74.6, 74.1, 45.2, 31.5, 29.3, 28.4, 25.8, 19.7, 13.6, 7.3, 6.9. IR (film) $\tilde{\nu}$ 2956, 2876, 1458, 1225, 1173, 1097, 1035, 925, 719 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{32}O_2Si$ [M+Na]$^+$: calcd: 307.2064, found: 307.2064.

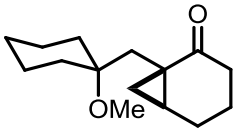
(1R*,5S*)-1-ethyl-3-(methoxymethoxy)-3-methylbicyclo[3.1.0]hexane (5). According to the Representative Procedure D (using additional $[Cp^*RuCl]_4$ (2 mol%) added after 12 h and stirring was continued for another 12 h) from enyne **S70** (24.0 mg, 0.14 mmol); colorless oil (19.5 mg, 80%, mixture of diastereomers 1.3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 – 4.63 (m, 1H), 4.64 (s, 1H), 3.37 (s, 1.35H), 3.34 (s, 1.65H), 2.32 (dd, *J* = 13.9, 6.2 Hz, 0.55H), 2.12 – 1.82 (m, 2H), 1.71 – 1.48 (m, 2.75H), 1.31 (s, 1.65H), 1.29 – 1.24 (m, 0.7H), 1.22 (s, 1.35H), 1.17 – 1.09 (m, 0.45H); 1.04 – 0.94 (m, 55H), 0.94 – 0.85 (m, 3H), 0.84 – 0.78 (m, 0.55H), 0.59 – 0.52 (m, 0.45H), 0.41 – 0.34 (m, 0.55H), 0.23 – 0.16 (m, 0.45H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 92.0, 91.7, 89.4, 86.5, 55.5, 55.3, 46.9, 45.3, 43.6, 42.0, 31.5, 30.2, 29.8, 29.4, 27.6, 27.0, 23.8, 22.9, 22.0, 17.5, 12.0, 11.9. IR (film) $\tilde{\nu}$ 2959, 2626, 2727, 1461, 1259, 1074, 1019, 796 cm^{-1}. HRMS (ESI$^+$) for $C_{11}H_{20}O_2$ [M+Na]$^+$: calcd: 207.1356, found: 207.1357.





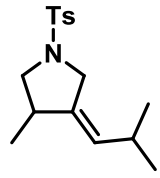
2-((1S*,6R*)-1-Methyl-3-tosyl-3-azabicyclo[4.1.0]heptan-6-yl)propan-2-ol (6). A detailed procedure for the preparation of this compound, a compilation of analytical and spectroscopic data as well as copies of the spectra are contained in the Supporting Information of our previous publication.[28]

(1R*,6R*)-6-((1-methoxycyclohexyl)methyl)-3-tosyl-3-azabicyclo[4.1.0]heptane (7). According to the Representative Procedure A from enyne **S31** (35.0 mg, 0.09 mmol); colorless oil (27.2 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.31 – 7.28 (m, 2H), 3.31 (dt, *J* = 11.4, 1.4 Hz, 1H), 3.22 (dd, *J* = 11.6, 5.4 Hz, 1H), 3.08 (s, 3H), 2.91 – 2.84 (m, 1H), 2.71 (ddd, *J* = 12.0, 8.2, 5.3 Hz, 1H), 2.42 (s, 3H), 2.12 (dt, *J* = 13.7, 5.8 Hz, 1H), 1.92 (ddd, *J* = 13.8, 8.2, 5.3 Hz, 1H), 1.81 – 1.67 (m, 2H), 1.60 – 1.33 (m, 6H), 1.28 – 1.08 (m, 4H), 0.82 (dtd, *J* = 8.8, 5.4, 1.9 Hz, 1H), 0.51 (dd, *J* = 8.7, 4.9 Hz, 1H), 0.42 (t, *J* = 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 133.9, 129.7, 127.7, 76.7, 47.9, 45.0, 44.9, 42.9, 35.1, 34.9, 28.0, 26.0, 21.9, 21.8, 21.7, 17.8, 17.2, 15.1. IR (film) $\tilde{\nu}$ 2929, 2854, 1455, 1339, 1160, 1075 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{31}NO_3S$ [M+Na]$^+$: calcd: 400.1917, found: 400.1917.

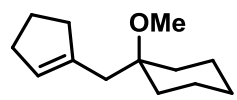


(1S*,6S*)-1-((1-Methoxycyclohexyl)methyl)bicyclo[4.1.0]heptan-2-one (8). A detailed procedure for the preparation of this compound, a compilation of analytical and spectroscopic data as well as copies of the spectra are contained in the Supporting Information of our previous publication.[28]

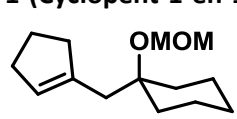
(*Z*)-3-Methyl-4-(2-methylpropylidene)-1-tosylpyrrolidine (10a). According to the Representative Procedure A from enyne **9a** (28.9 mg, 0.09 mmol); colorless solid (20.2 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.35 – 7.30 (m, 2H), 4.98 (dq, *J* = 9.5, 2.4 Hz, 1H), 3.88 (ddd, *J* = 13.9, 2.6, 1.0 Hz, 1H), 3.73 (ddd, *J* = 14.0, 2.5, 1.8 Hz, 1H), 3.55 – 3.47 (m, 1H), 2.66 – 2.61 (m, 1H), 2.60 (q, *J* = 2.4, 1.6 Hz, 1H), 2.43 (s, 3H), 2.24 – 2.13 (m, 1H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 137.4, 133.1, 129.8, 129.3, 127.9, 55.0, 49.5, 37.2, 29.1, 22.8, 22.8, 21.7, 16.8. IR (film) $\tilde{\nu}$ 2958, 2928, 2868, 1462, 1344, 1160 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{23}NO_2S$ [M+Na]$^+$: calcd 294.1522, found 294.1521.



1-(Cyclopent-1-en-1-ylmethyl)-1-methoxycyclohexane (11a). According to the Representative Procedure A from enyne **1f** (24.8 mg, 0.11 mmol), colorless oil (20.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.36 (m, 1H), 3.18 (s, 3H), 2.36 – 2.26 (m, 4H), 2.27 – 2.21 (m, 2H), 1.90 – 1.77 (m, 2H), 1.73 – 1.64 (m, 2H), 1.59 – 1.37 (m, 5H), 1.32 – 1.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 127.6, 75.6, 48.3, 37. 5, 36.9, 34.5, 32.6, 26.0, 23.9, 22.1. IR (film) $\tilde{\nu}$ 3038, 2929, 2848, 1455, 1444, 1081 cm^{-1}. HRMS (ESI$^+$) for $C_{13}H_{22}O$ [M+H]$^+$: calcd: 195.1734, found: 195.1741.

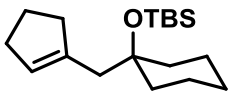


1-(Cyclopent-1-en-1-ylmethyl)-1-(methoxymethoxy)cyclohexane (11b). According to the Representative Procedure A from enyne **S35** (26.6 mg, 0.10 mmol), flash chromatography (silica, hexanes/EtOAc 1:0 – 40:1 – 30:1), colorless oil (18.0 mg, 80%). ^{1}H NMR (400 MHz,



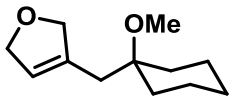
$CDCl_3$) δ 5.43 – 5.38 (m, 1H), 4.73 (s, 2H), 3.41 (s, 3H), 2.34 – 2.26 (m, 6H), 1.83 (m, 2H), 1.76 – 1.20 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 128.1, 90.8, 77.8, 55.9, 39.5, 37.1, 35.5, 32.6, 25.9, 24.0, 22.5. IR (film) $\tilde{\nu}$ 2927, 2849, 1448, 1140, 1028 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{24}O_2$ $[M+Na]^+$: calcd: 247.1668, found: 247.1671.

***tert*-Butyl((1-(cyclopent-1-en-1-ylmethyl)cyclohexyl)oxy)dimethylsilane (11c)**. According to the



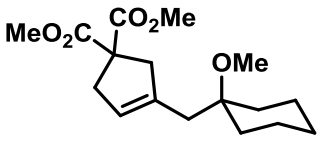
Representative Procedure A from enyne **S36** (31.4 mg, 0.09 mmol), colorless oil (19.0 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.40 (m, 1H), 2.34 – 2.25 (m, 6H), 1.83 (m, 2H), 1.70 – 1.57 (m, 2H), 1.53 – 1.24 (m, 8H), 0.88 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 127.9, 75.9, 43.8, 38.2, 37.4, 32.6, 26.3, 25.9, 24.2, 23.0, 18.6, -1.4. IR (film) $\tilde{\nu}$ 2927, 2853, 1471, 1251, 1056, 769 cm^{-1}. HRMS (ESI^+) for C18H34OSi $[M+Na]^+$: calcd: 317.2271, found: 317.2271.

3-((1-Methoxycyclohexyl)methyl)-2,5-dihydrofuran (11e). According to the Representative Procedure A



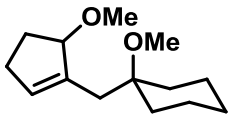
from enyne **S65** (25.9 mg, 0.11 mmol); light yellow oil (16.9 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.60 – 5.52 (m, 1H), 4.67 – 4.61 (m, 2H), 4.61 – 4.55 (m, 2H), 3.16 (s, 3H), 2.31 – 2.28 (m, 2H), 1.76 – 1.65 (m, 2H), 1.65 – 1.48 (m, 3H), 1.48 – 1.37 (m, 2H), 1.34 – 1.21 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 122.6, 77.9, 75.7, 75.2, 48.3, 34.3, 34.1, 25.9, 22.1. IR (film) $\tilde{\nu}$ 2932, 2855, 1750, 1145, 1073 cm^{-1}. HRMS (ESI^+) for $C_{12}H_{20}O_2$ $[M+Na]^+$: calcd: 219.1357, found: 219.1355.

Dimethyl 3-((1-methoxycyclohexyl)methyl)cyclopent-3-ene-1,1-dicarboxylate (11f). According to the



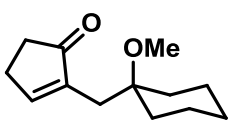
Representative Procedure A from enyne **S67** (24.6 mg, 0.07 mmol); colorless oil (16.8 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.27 (m, 1H), 3.72 (s, 6H), 3.17 (s, 3H), 3.03 – 2.96 (m, 4H), 2.22 (q, *J* = 1.2 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.57 – 1.45 (m, 3H), 1.46 – 1.35 (m, 2H), 1.31 – 1.17 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 138.1, 124.2, 75.5, 59.6, 52.9, 48.3, 44.4, 40.6, 36.9, 3.3, 25.9, 22.1. IR (film) $\tilde{\nu}$ 2931, 2855, 1734, 1434, 1250 cm^{-1}. HRMS (ESI^+) for $C_{17}H_{26}O_5$ $[M+Na]^+$: calcd: 333.1672, found: 333.1673.

1-Methoxy-1-((5-methoxycyclopent-1-en-1-yl)methyl)cyclohexane (11g). According to the



Representative Procedure A from enyne **S40** (30.5 mg, 0.12 mmol); colorless oil (13.7 mg, 53%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.67 (m, 1H), 4.42 – 4.36 (m, 1H), 3.28 (s, 3H), 3.21 (s, 3H), 2.45 – 2.35 (m, 2H), 2.29 – 2.18 (m, 1H), 2.17 – 2.04 (m, 2H), 1.82 – 1.70 (m, 2H), 1.69 – 1.60 (m, 2H), 1.59 – 1.37 (m, 3H), 1.34 – 1.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 132.0, 87.9, 75.7, 55.6, 48.3, 35.0, 34.2, 33.5, 30.3, 28.9, 26.1, 22.1, 22.0. IR (film) $\tilde{\nu}$ 2931, 2853, 1456, 1260, 1083 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{24}O_2$ $[M+Na]^+$: calcd: 247.1668, found: 247.1668.

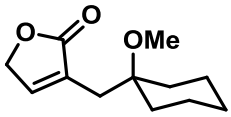
2-((1-Methoxycyclohexyl)methyl)cyclopent-2-en-1-one (11h). According to the Representative



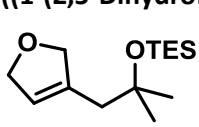
Procedure A from enyne **S41** (25.4 mg, 0.10 mmol); yellow oil (14.5 mg, 68%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 1H), 3.22 (s, 3H), 2.64 – 2.55 (m, 2H), 2.40 – 2.36 (m, 2H), 2.34 (q, *J* = 1.3 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.58 – 1.49 (m, 1H), 1.49 – 1.41 (m, 4H), 1.32 – 1.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 160.8,

141.9, 75.4, 48.5, 34.2, 34.0, 30.1, 26.9, 25.9, 21.9. IR (film) $\tilde{\nu}$ 2931, 2856, 1700, 1444, 1074 cm^{-1}. HRMS (ESI^+) for $C_{13}H_{20}O_2$ $[M+Na]^+$: calcd: 231.1355, found: 231.1357.

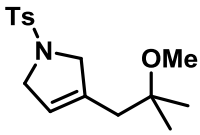
3-((1-Methoxycyclohexyl)methyl)furan-2(5*H*)-one (11i). According to the Representative Procedure A from enyne **S38** (27.1 mg, 0.11 mmol); light yellow oil (11.9 mg, 52%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (p, *J* = 1.6 Hz, 1H), 4.80 (q, *J* = 1.7 Hz, 2H), 3.22 (s, 3H), 2.46 (q, *J* = 1.6 Hz, 2H), 1.75 – 1.67 (m, 2H), 1.59 – 1.42 (m, 5H), 1.36 – 1.20 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 147.4, 129.6, 75.3, 70.5, 48.6, 34.1, 30.8, 25.8, 21.8. IR (film) $\tilde{\nu}$ 2931, 2856, 1730, 1455, 1346, 1071 cm^{-1}. HRMS (ESI^+) for $C_{12}H_{18}O_3$ $[M+H]^+$: calcd: 211.1329, found: 211.1329.



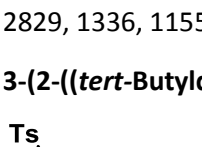
((1-(2,5-Dihydrofuran-3-yl)-2-methylpropan-2-yl)oxy)triethylsilane (12a). According to the Representative Procedure A from enyne **S62** (27.0 mg, 0.09 mmol), colorless oil (22.2 mg, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.54 – 5.50 (m, 1H), 4.67 – 4.57 (m, 4H), 2.29 (s, 2H), 1.23 (s, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.63 – 0.54 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.0, 122.6, 78.1, 75.5, 73.3, 43.7, 30.1, 7.2, 6.9. IR (film) $\tilde{\nu}$ 3412, 2973, 1735, 1370, 1234, 1072, 1010, 901, 736 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{28}O_2Si$ $[M+Na]^+$: calcd: 279.1751; found: 279.1753.



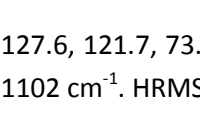
3-(2-Methoxy-2-methylpropyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (12b). According to the Representative Procedure A from enyne **S46** (34.8 mg, 0.1 mmol), colorless solid (24.0 mg, 78%). Single crystals suitable for X-ray analysis were grown by vapor diffusion of pentane into a saturated solution of product in CH_2Cl_2 at room temperature. mp.: 76-77 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 5.33 – 5.29 (m, 1H), 4.14 – 4.05 (m, 4H), 3.14 (s, 3H), 2.42 (s, 3H), 2.17 (s, 2H), 1.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 136.7, 134.5, 129.8, 127.6, 121.7, 74.5, 57.6, 54.9, 49.4, 40.2, 24.8, 21.7. IR (film) $\tilde{\nu}$ 2962, 2860, 2829, 1336, 1155, 1055 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{23}NO_3S$ $[M+Na]^+$: calcd: 332.1291, found: 332.1288.



3-(2-((*tert*-Butyldimethylsilyl)oxy)-2-methylpropyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (12c). According to the Representative Procedure A from enyne **S47** (44.8 mg, 0.10 mmol); colorless solid (31.0 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 5.34 – 5.27 (m, 1H), 4.14 – 4.03 (m, 4H), 2.42 (s, 3H), 2.15 (s, 2H), 1.13 (s, 6H), 0.83 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 137.1, 134.6, 129.8, 127.6, 121.7, 73.5, 57.7, 54.8, 45.0, 30.0, 26.0, 21.7, 18.1, -1.9. IR (film) $\tilde{\nu}$ 3039, 2928, 2856, 1337, 1161, 1102 cm^{-1}. HRMS (ESI^+) for $C_{21}H_{35}NO_3SSi$ $[M+Na]^+$: calcd: 432.1999, found: 432.2000.



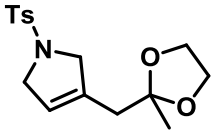
3-(2-Methoxybutyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (12d). According to the Representative Procedure A from enyne **S49** (41.8 mg, 0.12 mmol), light brown oil (13.3 mg, 36%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.32 (s, 1H), 4.13 – 3.99 (m, 4H), 3.25 (s, 3H), 3.16 – 3.09 (m, 1H), 2.42 (s, 3H), 2.17 (d, *J* = 5.9 Hz, 2H), 1.48 – 1.31 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.0, 134.4, 129.8, 127.6, 120.3, 80.5, 57.1, 56.6, 55.1, 32.8, 25.8, 21.7, 9.3. IR (film) $\tilde{\nu}$ 2967, 2930, 1598, 1341, 1160 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{23}NO_3S$ $[M+Na]^+$: calcd: 332.1291, found: 332.1291.



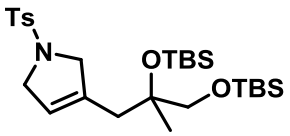
3-(2-Methoxyethyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (12e). According to the Representative Procedure A from enyne **S51** (34.8 mg, 0.11 mmol), colorless oil (3.5 mg, 11%). ^1H NMR (400 MHz,

$CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.34 – 7.29 (m, 2H), 5.34 (hept, *J* = 1.6 Hz, 1H), 4.13 – 4.05 (m, 2H), 4.06 – 4.01 (m, 2H), 3.42 (t, *J* = 6.3 Hz, 2H), 3.30 (s, 3H), 2.43 (s, 3H), 2.31 – 2.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.0, 134.5, 129.9, 127.6, 119.6, 70.5, 58.8, 56.8, 55.1, 29.3, 21.7. IR (film) $\tilde{\nu}$ 2921, 2863, 1341, 1160, 1100 cm^{-1}. HRMS (ESI$^+$) for $C_{14}H_{19}NO_3S$ [M+H]$^+$: calcd: 282.1158, found: 282.1158.

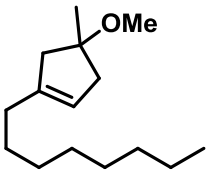
3-((2-methyl-1,3-dioxolan-2-yl)methyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (13). According to the Representative Procedure A from enyne **S55** (36.0 mg, 0.10 mmol), colorless oil (17.3 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.34 – 7.28 (m, 2H), 5.39 (m, 1H), 4.09 (s, 4H), 3.91 – 3.84 (m, 2H), 3.84 – 3.77 (m, 2H), 2.41 (s, 3H), 2.35 (s, 2H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 135.2, 134.4, 129.8, 127.6, 122.4, 109.0, 64.8, 57.3, 55.1, 38.9, 23.9, 21.6. IR (film) $\tilde{\nu}$ 2983, 2875, 1341, 1161, 1046 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{21}NO_4S$ [M+Na]$^+$: calcd: 346.1084, found: 346.1083.



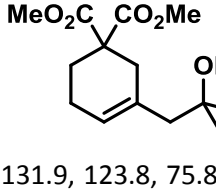
3-(2,3-bis((*tert*-Butyldimethylsilyl)oxy)-2-methylpropyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (14). According to the Representative Procedure A from enyne **S53** (55.0 mg, 0.09 mmol), colorless oil (34.2 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 5.32 (m, 1H), 4.11 – 4.01 (m, 4H), 3.26 – 3.20 (m, 2H), 2.42 (s, 3H), 2.27 – 2.21 (m, 1H), 2.20 – 2.11 (m, 1H), 1.10 (s, 3H), 0.86 (s, 9H), 0.83 (s, 9H), 0.03 (s, 3H), 0.03 (s, 3H), 0.00 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 136.6, 134.5, 129.8, 127.7, 121.8, 76.2, 69.8, 57.9, 54.8, 39.6, 26.1, 26.0, 25.4, 21.7, 18.4, 18.3, -1.7, -1.8, -5.4, −5.4. IR (film) $\tilde{\nu}$ 2954, 2929, 2856, 1163, 1096 cm^{-1}. HRMS (ESI$^+$) for $C_{27}H_{49}NO_4SSi_2$ [M+Na]$^+$: calcd: 562.2813, found: 562.2814.



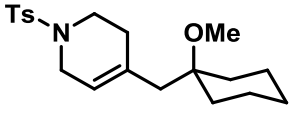
4-Methoxy-4-methyl-1-octylcyclopent-1-ene (15). According to the Representative Procedure A from enyne **S75** (30.3 mg, 0.11 mmol), colorless oil (25.2 mg, 98%). An aliquot was further purified by HPLC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (hept, *J* = 2.2 Hz, 1H), 3.20 (s, 3H), 2.58 – 2.45 (m, 2H), 2.28 – 2.12 (m, 2H), 2.05 – 1.97 (m, 2H), 1.46 – 1.35 (m, 2H), 1.33 (s, 3H), 1.30 – 1.23 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 121.0, 83.9, 50.7, 47.0, 44.5, 32.0, 31.5, 29.6, 29.6, 29.4, 27.7, 25.6, 22.8, 14.3. IR (film) $\tilde{\nu}$ 2959, 2924, 2854, 1461, 1077 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{28}O$ [M+Na]+: calcd: 247.2032, found: 247.2032.



Dimethyl 3-((1-methoxycyclohexyl)methyl)cyclohex-3-ene-1,1-dicarboxylate (18). According to the Representative Procedure B from enyne **17** (29.3 mg, 0.08 mmol), colorless oil (16.9 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (m, 1H), 3.71 (s, 6H), 3.18 (s, 3H), 2.58 (s, 2H), 2.13 (s, 2H), 2.09 (s, 4H), 1.68 (dt, *J* = 13.4, 4.0 Hz, 2H), 1.60 – 1.36 (m, 5H), 1.29 – 1.14 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 131.9, 123.8, 75.8, 53.9, 52.7, 48.3, 44.0, 35.4, 34.3, 27.3, 26.0, 22.8, 22.1. IR (film) $\tilde{\nu}$ 2931, 2852, 1733, 1435, 1253 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{28}O_5$ [M+Na]$^+$: calcd: 347.1829, found: 347.1830.

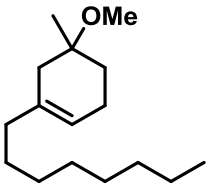


4-((1-Methoxycyclohexyl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (19). According to the Representative Procedure B from enyne **S32** (33.7 mg, 0.08 mmol), colorless oil (17.9 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.33 – 7.28

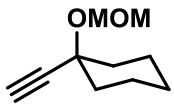


(m, 2H), 5.36 – 5.28 (m, 1H), 3.60 – 3.52 (m, 2H), 3.14 (t, *J* = 5.7 Hz, 2H), 3.13 (s, 3H), 2.42 (s, 3H), 2.28 – 2.22 (m, 2H), 2.07 (s, 2H), 1.68 – 1.31 (m, 6H), 1.31 – 1.11 (m, 3H), 0.96 – 0.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.6, 133.5, 129.7, 127.9, 120.0, 75.7, 48.2, 45.0, 43.2, 42.7, 34.4, 29.9, 25.9, 22.0, 21.7. IR (film) $\tilde{\nu}$ 2929, 2854, 1458, 1341, 1161 cm^{-1}. HRMS (ESI$^+$) for $C_{20}H_{29}NO_3S$ [M+Na]$^+$: calcd: 386.1760, found: 386.1758.

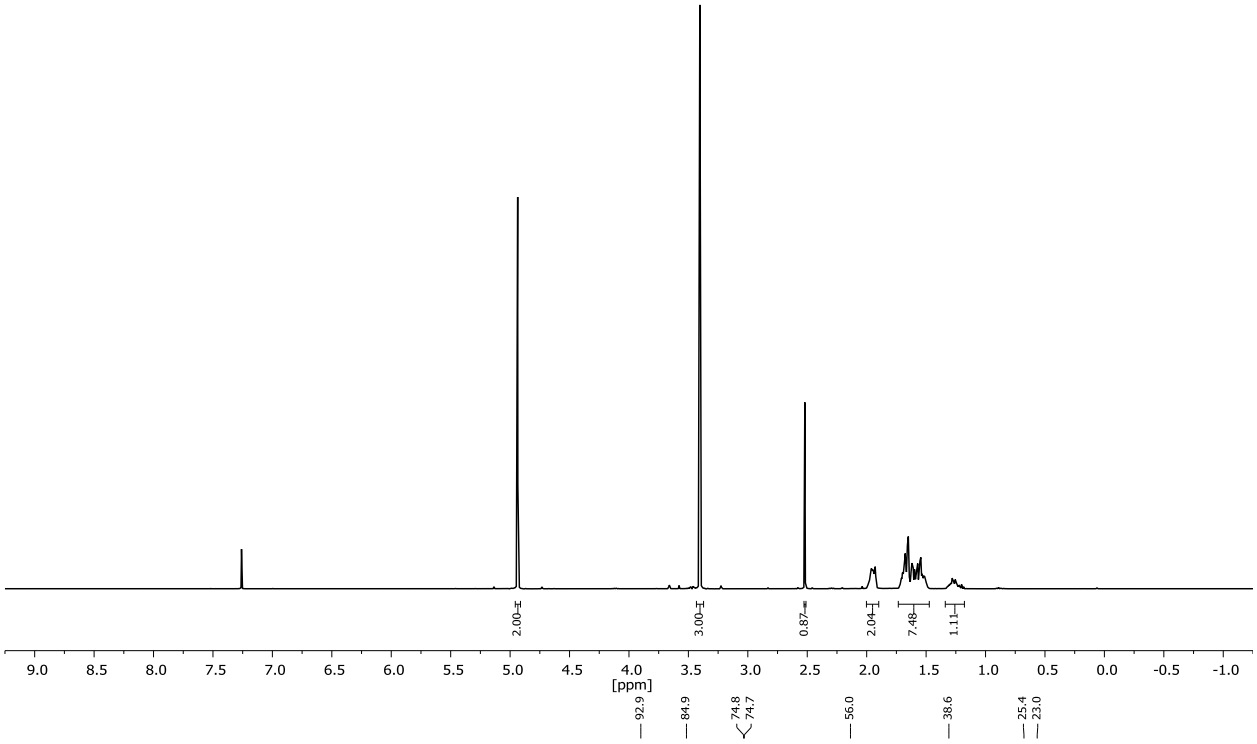
5-Methoxy-5-methyl-1-octylcyclohex-1-ene (20). According to the Representative Procedure B from

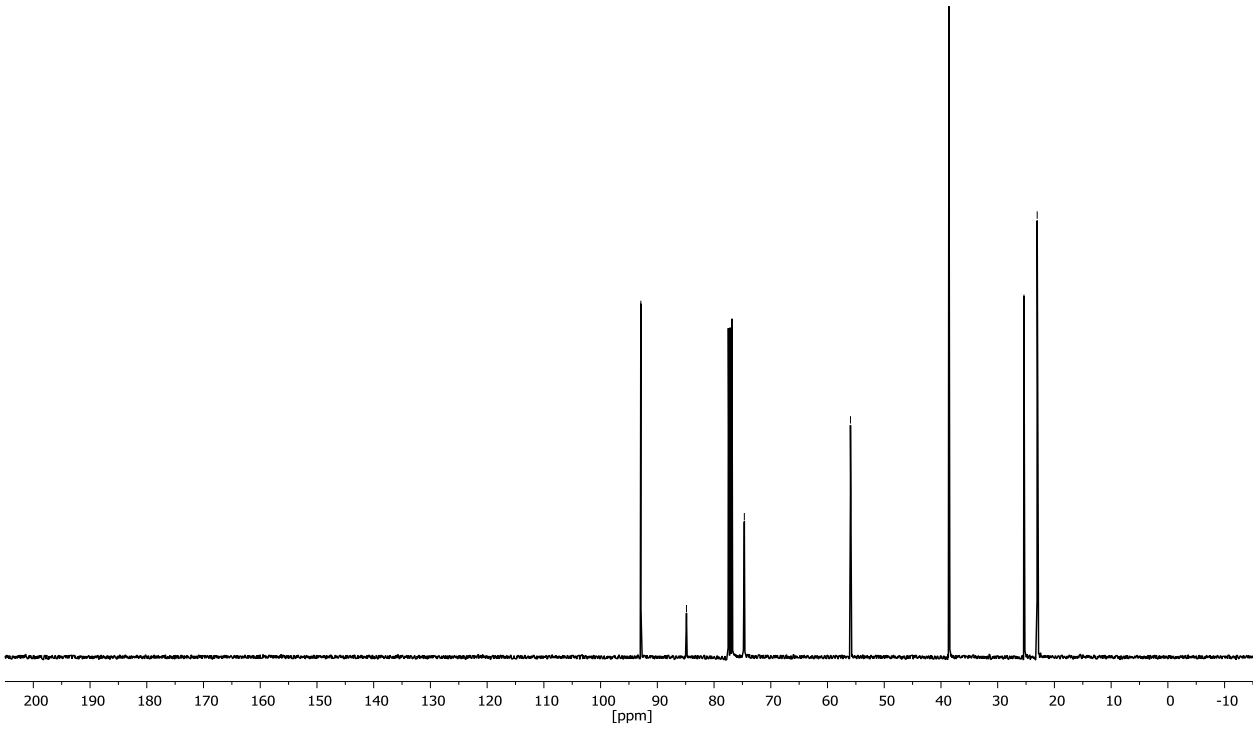


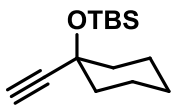
enyne **S77** (31.0 mg, 0.11 mmol), colorless oil (22.7 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.32 (m, 1H), 3.24 (s, 3H), 2.20 – 2.05 (m, 2H), 2.04 – 1.88 (m, 4H), 1.73 – 1.65 (m, 1H), 1.57 – 1.48 (m, 1H), 1.38 (m, 2H), 1.26 (m, 10H), 1.16 (s, 3H), 0.91 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 119.4, 73.5, 49.0, 39.9, 37.9, 32.1, 31.9, 29.7, 29.5, 29.5, 27.8, 23.5, 22.8, 22.7, 14.3. IR (film) $\tilde{\nu}$ 2923, 2853, 1462, 1369, 1095 cm^{-1}. HRMS (CI) for $C_{16}H_{30}O$ [M+NH_4]$^+$: calcd: 256.2635, found: 256.2632.


OMOM

S23

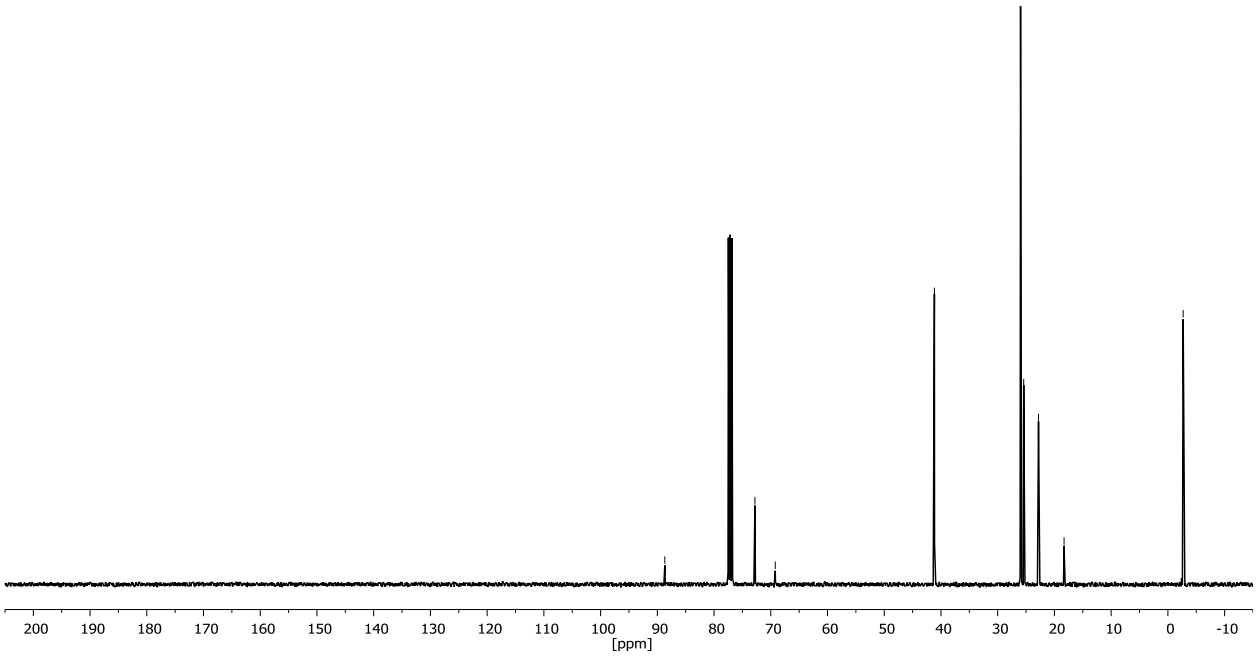

2.00
3.00
0.87
2.04
7.48
1.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
92.9
84.9
74.8
74.7
56.0
38.6
25.4
23.0

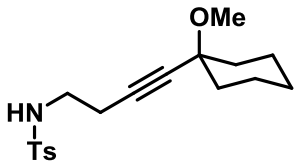

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTBS

S24

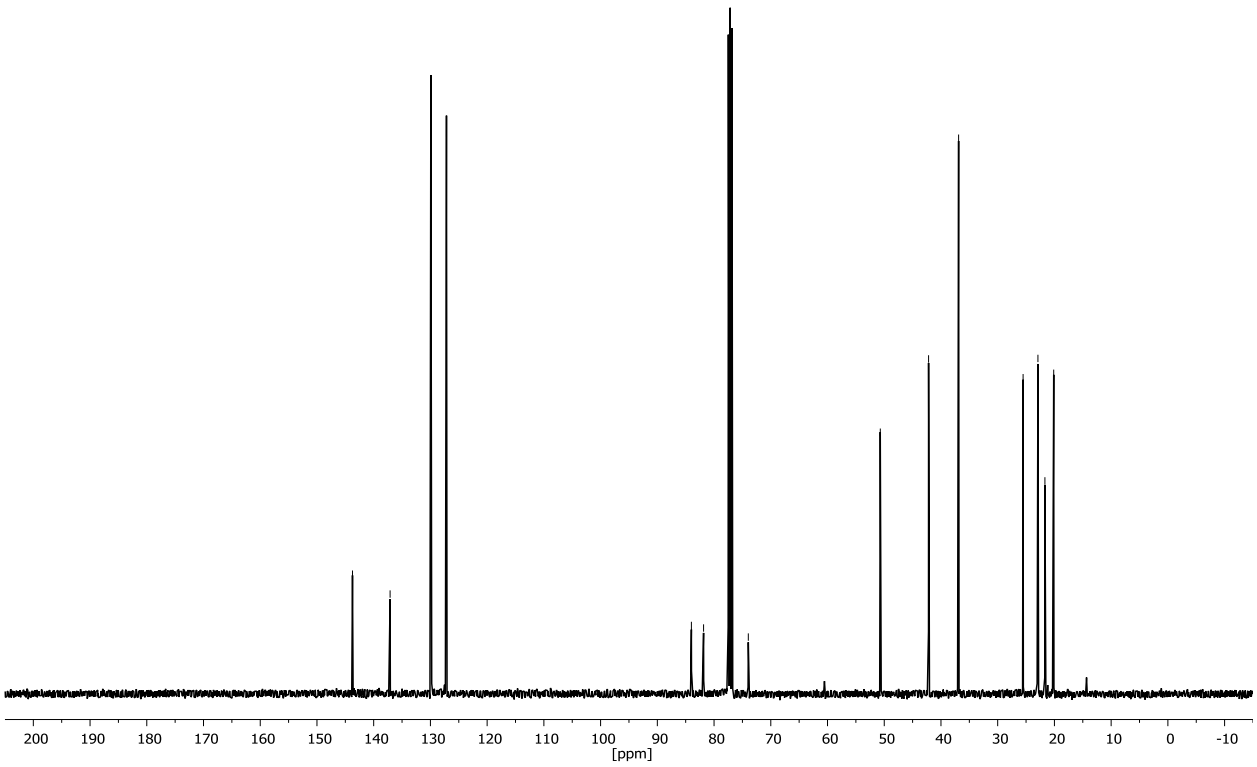
1.00
2.31
4.64
2.65
1.23
1.15
10.37
6.56
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
88.7
72.8
69.2
41.2
26.0
25.4
22.8
18.3
-2.7

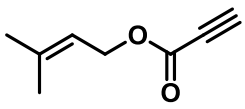

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
HN
Ts

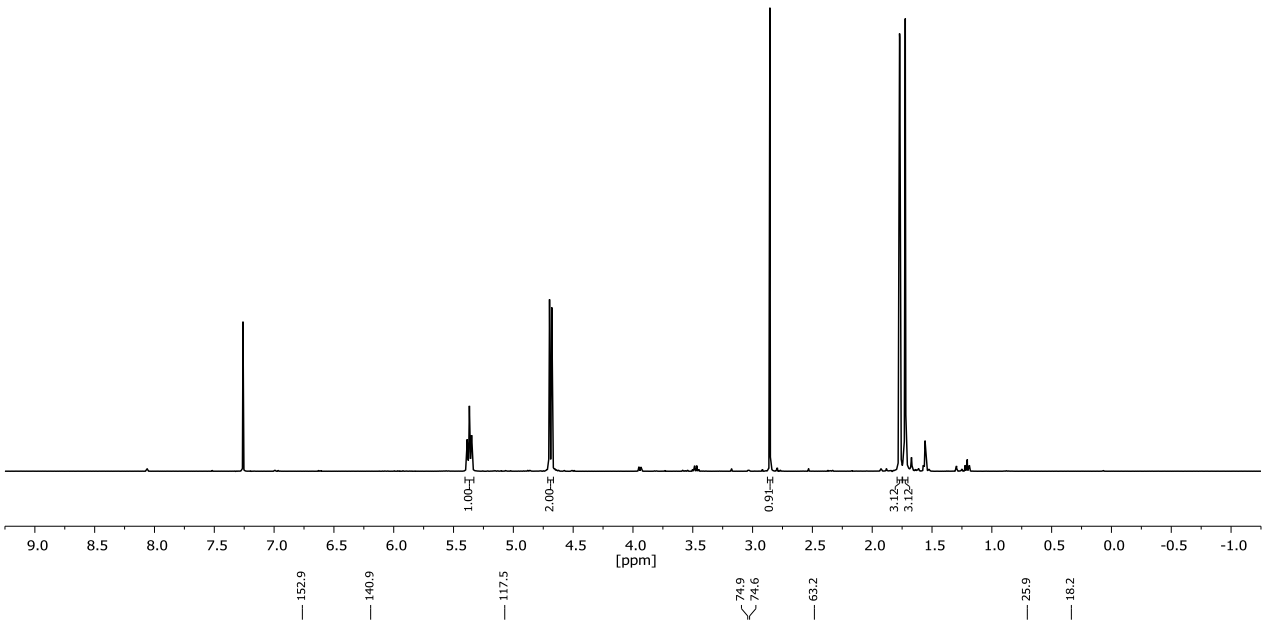
S25

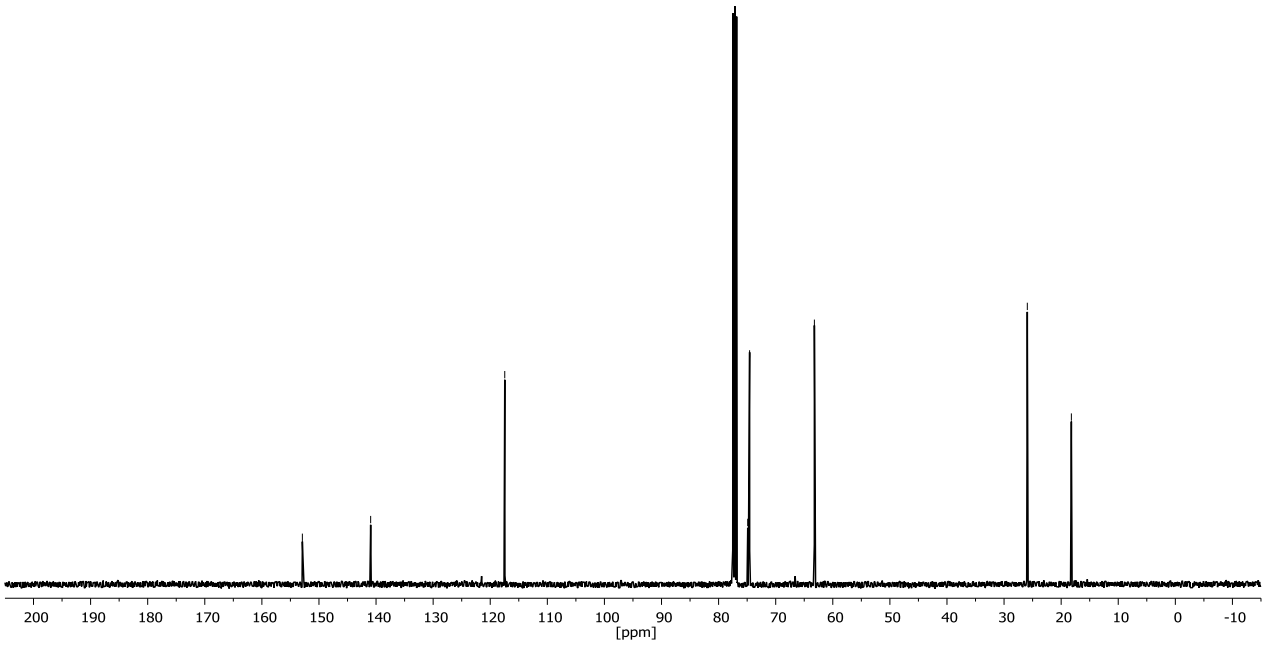
2.00
2.03
0.93
3.06
2.10
5.19
2.07
2.63
5.52
1.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.7
137.1
129.9
127.2
84.0
81.8
74.0
50.7
42.2
36.9
25.5
22.9
21.7
20.1

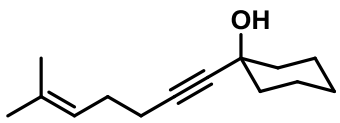

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]



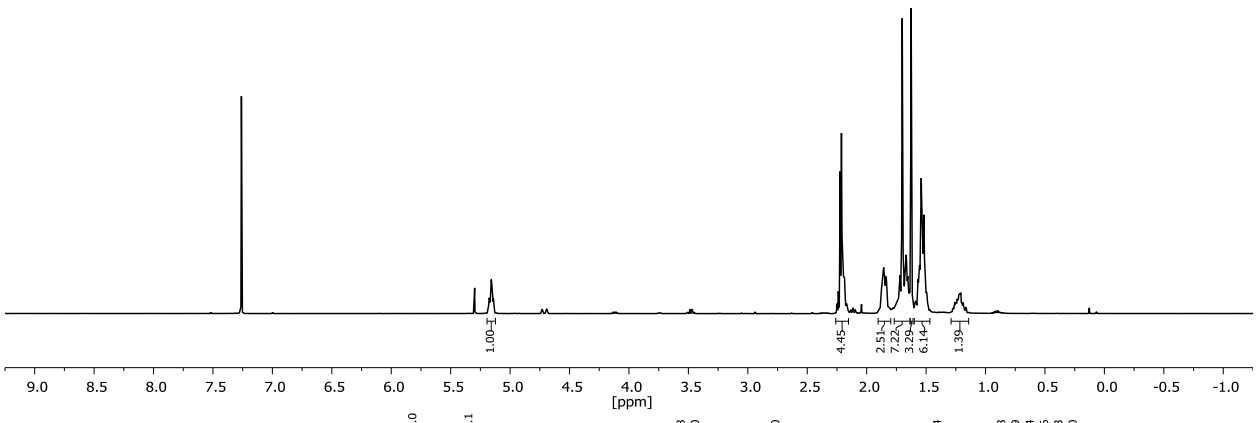
S28

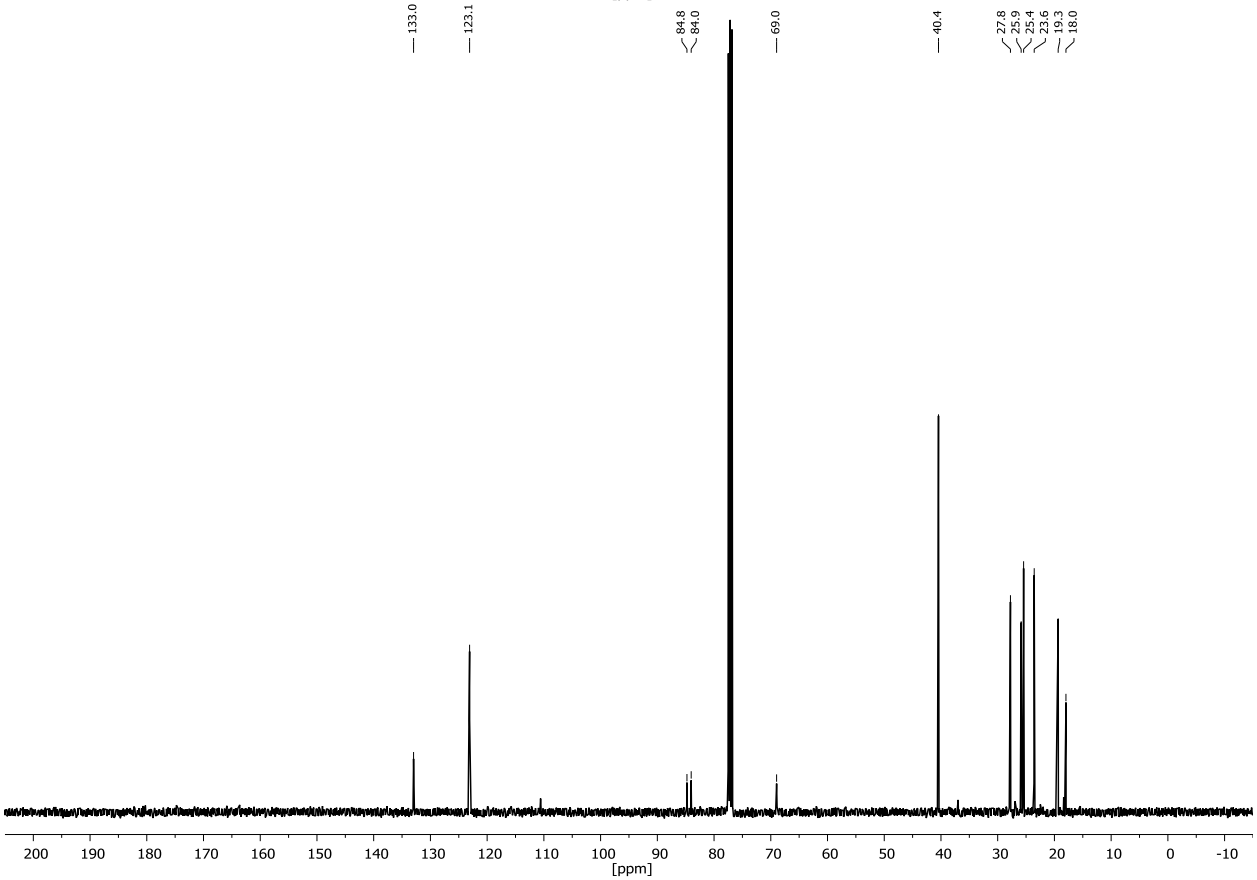

1.00
2.00
0.91
3.12
3.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
152.9
140.9
117.5
74.9
74.6
63.2
25.9
18.2

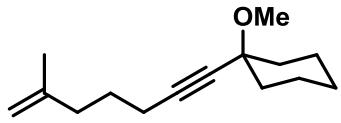

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OH

S29

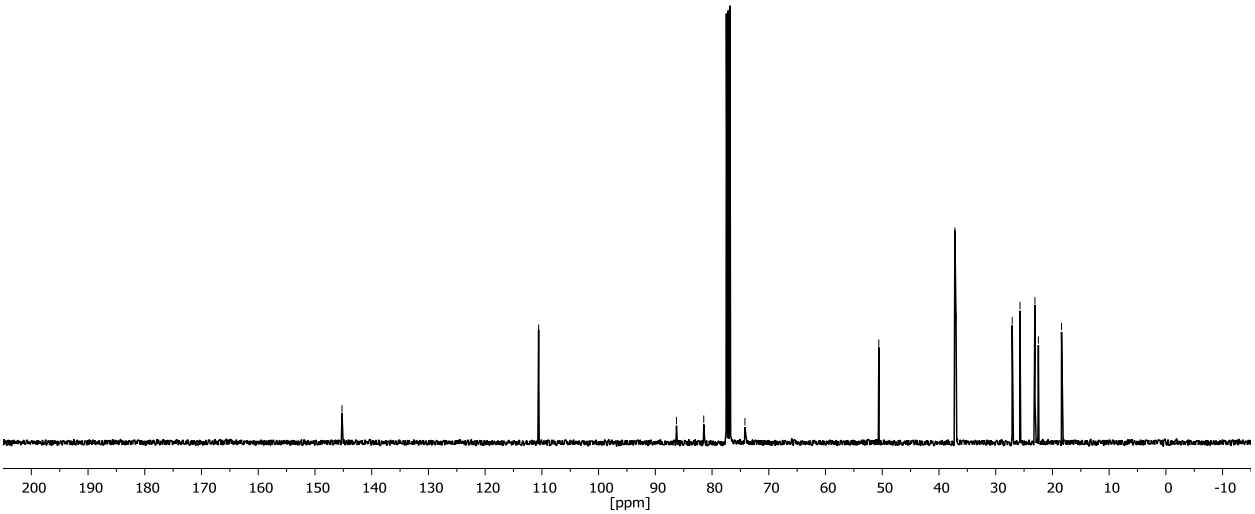

1.00
4.45
2.51
7.22
3.29
6.14
1.39
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

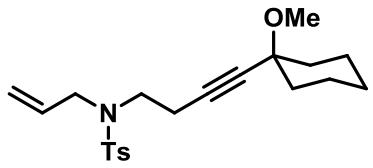

133.0
123.1
84.8
84.0
69.0
40.4
27.8
25.9
25.4
23.6
19.3
18.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

S30

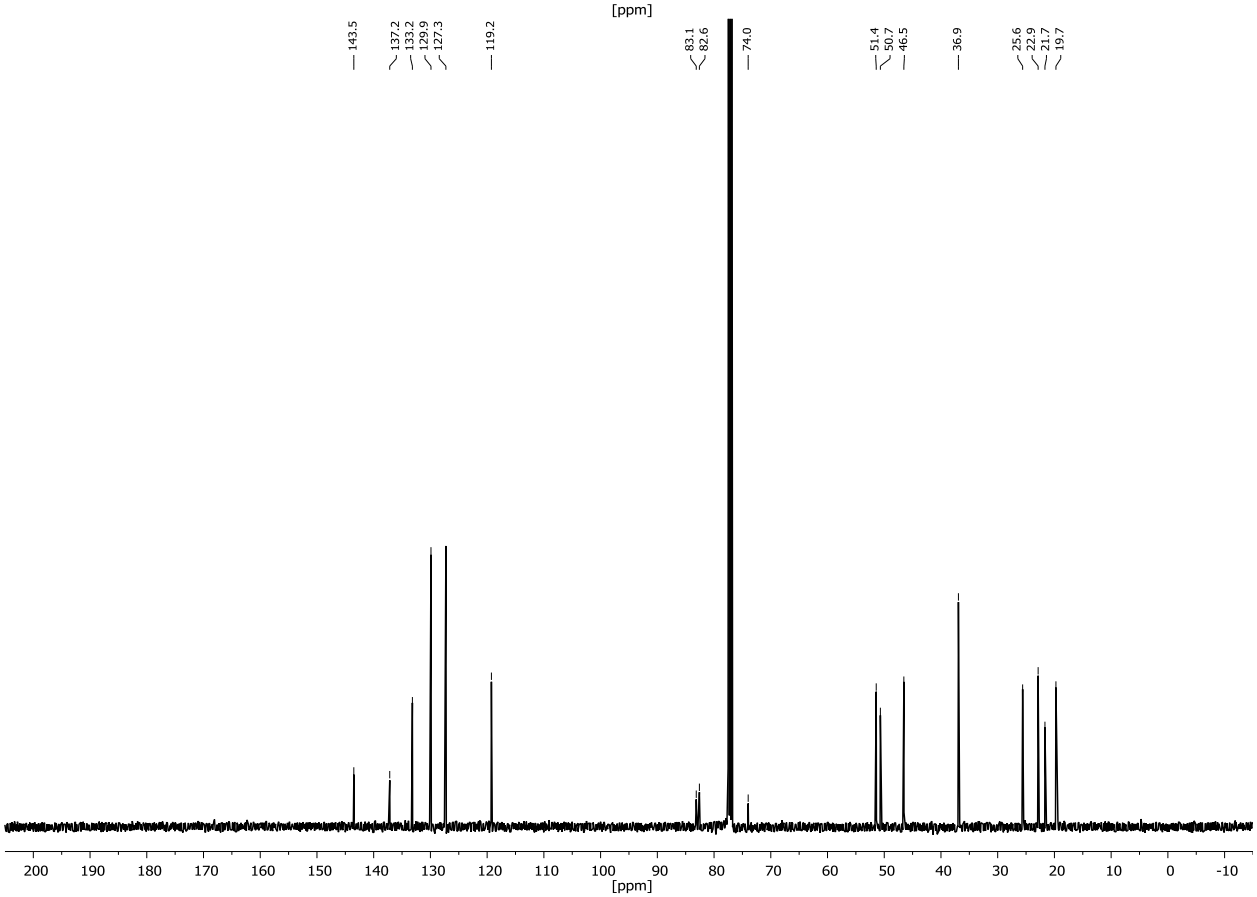
1.00
1.12
3.29
2.09
2.13
2.18
3.09
4.68
6.89
1.31
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
145.2
110.6
86.3
81.5
74.2
50.6
37.2
37.0
27.1
25.7
23.1
22.5
18.4

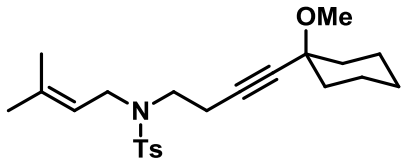

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
N
Ts

S31

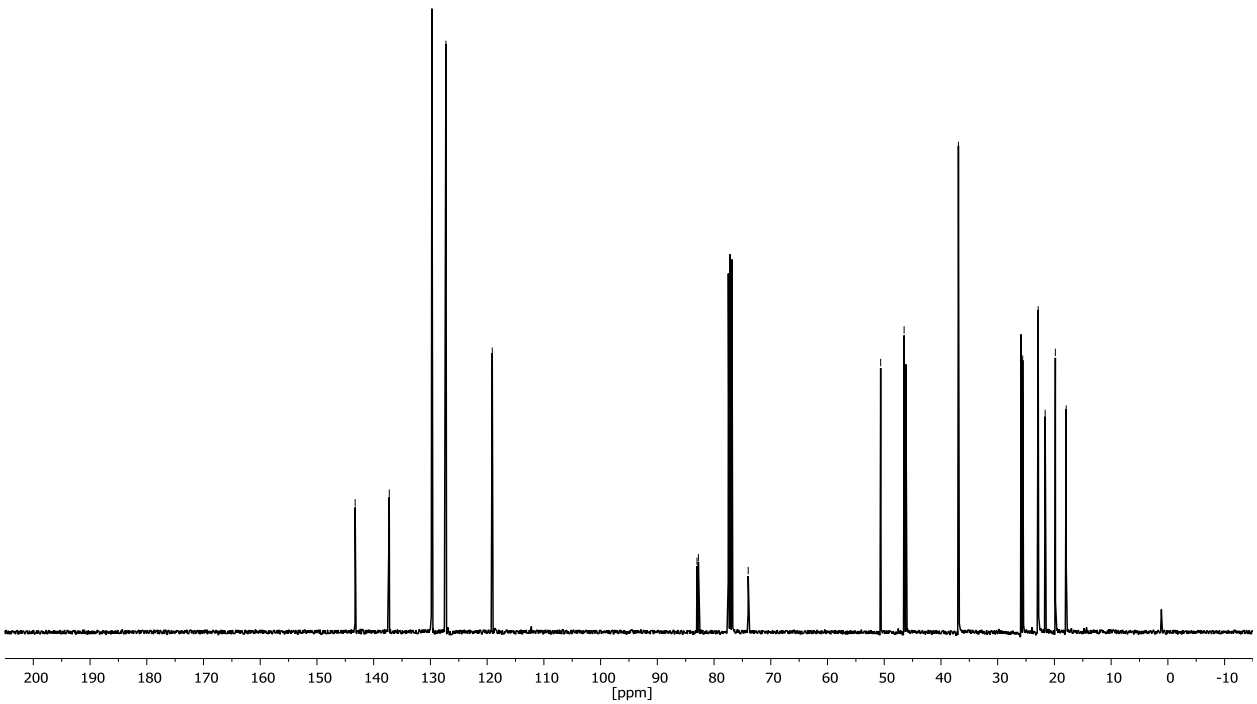
2.00
2.02
1.00
2.08
2.09
5.19
2.13
3.09
2.12
8.61
1.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

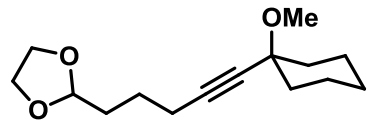

143.5
137.2
133.2
129.9
127.3
119.2
83.1
82.6
74.0
51.4
50.7
46.5
36.9
25.6
22.9
21.7
19.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
N
Ts

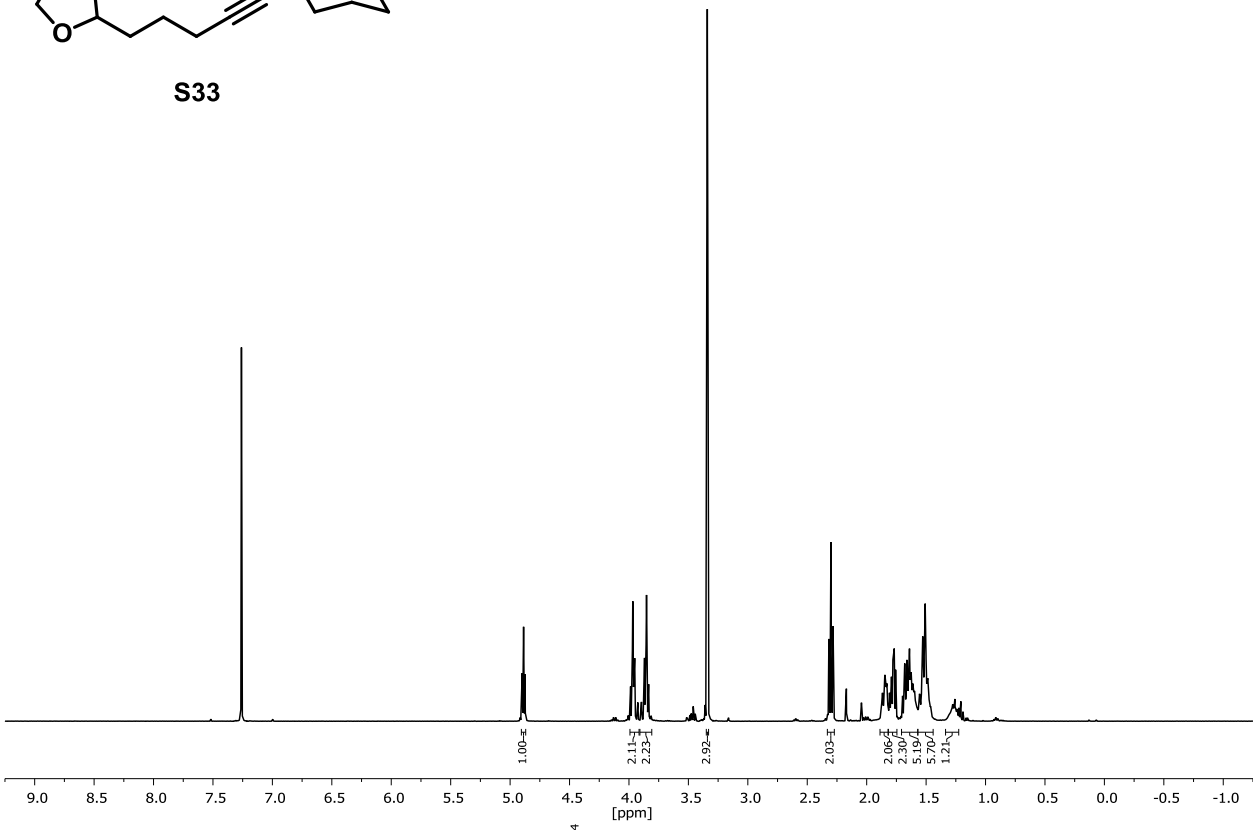
S32

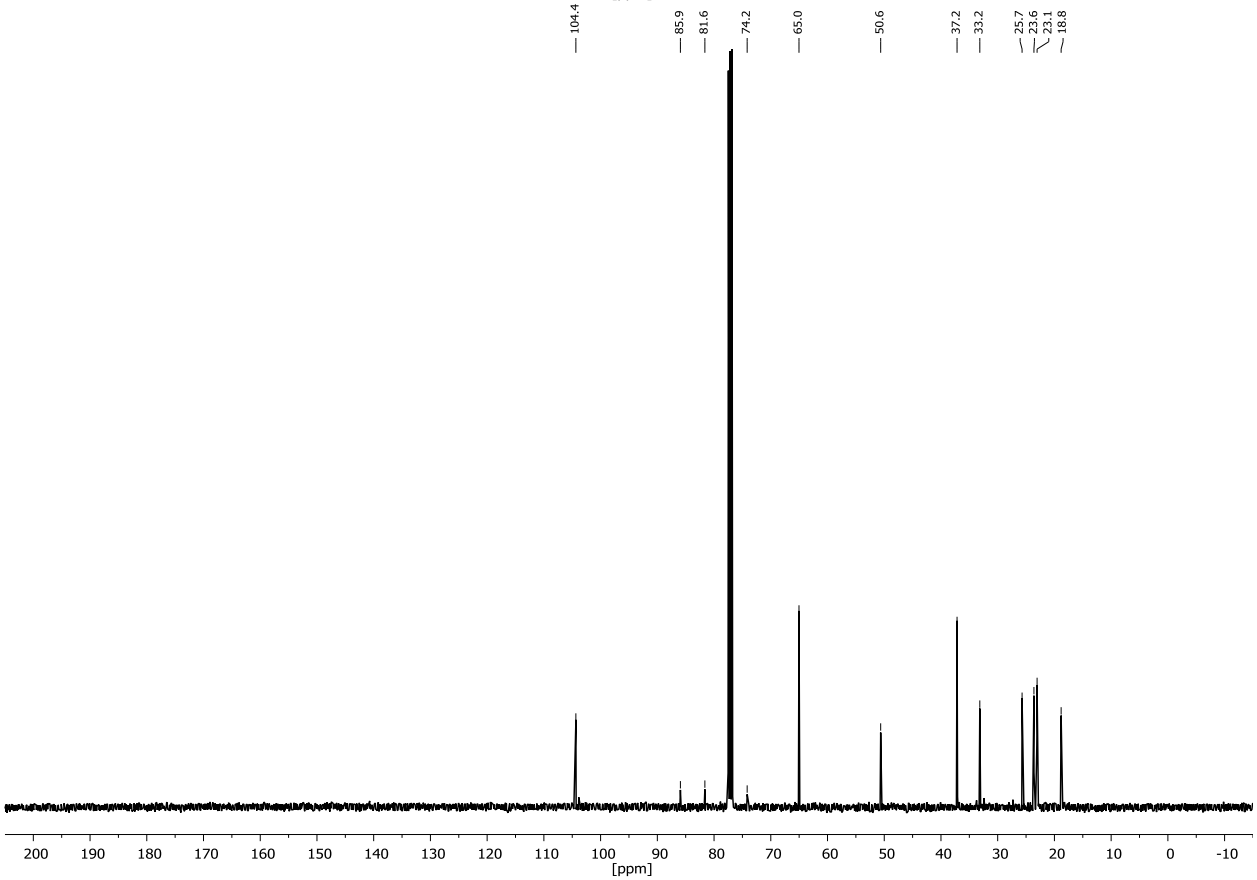
2.06
2.05
1.00
2.01
3.09
2.09
2.03
3.09
2.03
3.09
5.51
5.61
1.30
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.3
137.4
137.3
129.7
127.3
119.1
83.0
82.8
74.0
50.6
46.5
46.2
36.9
25.9
25.6
22.9
21.6
19.8
17.9

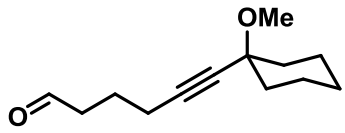

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
O
O

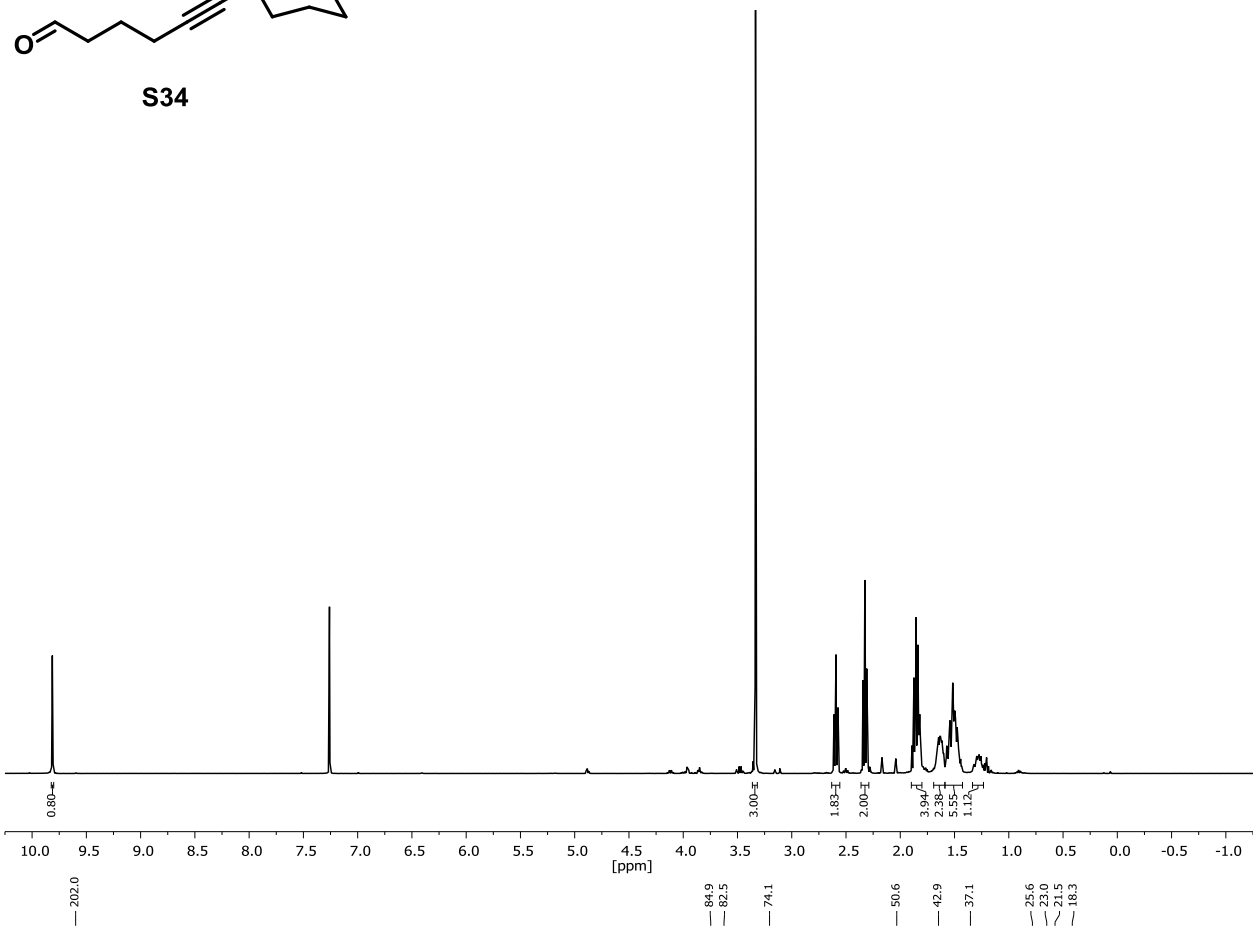
S33

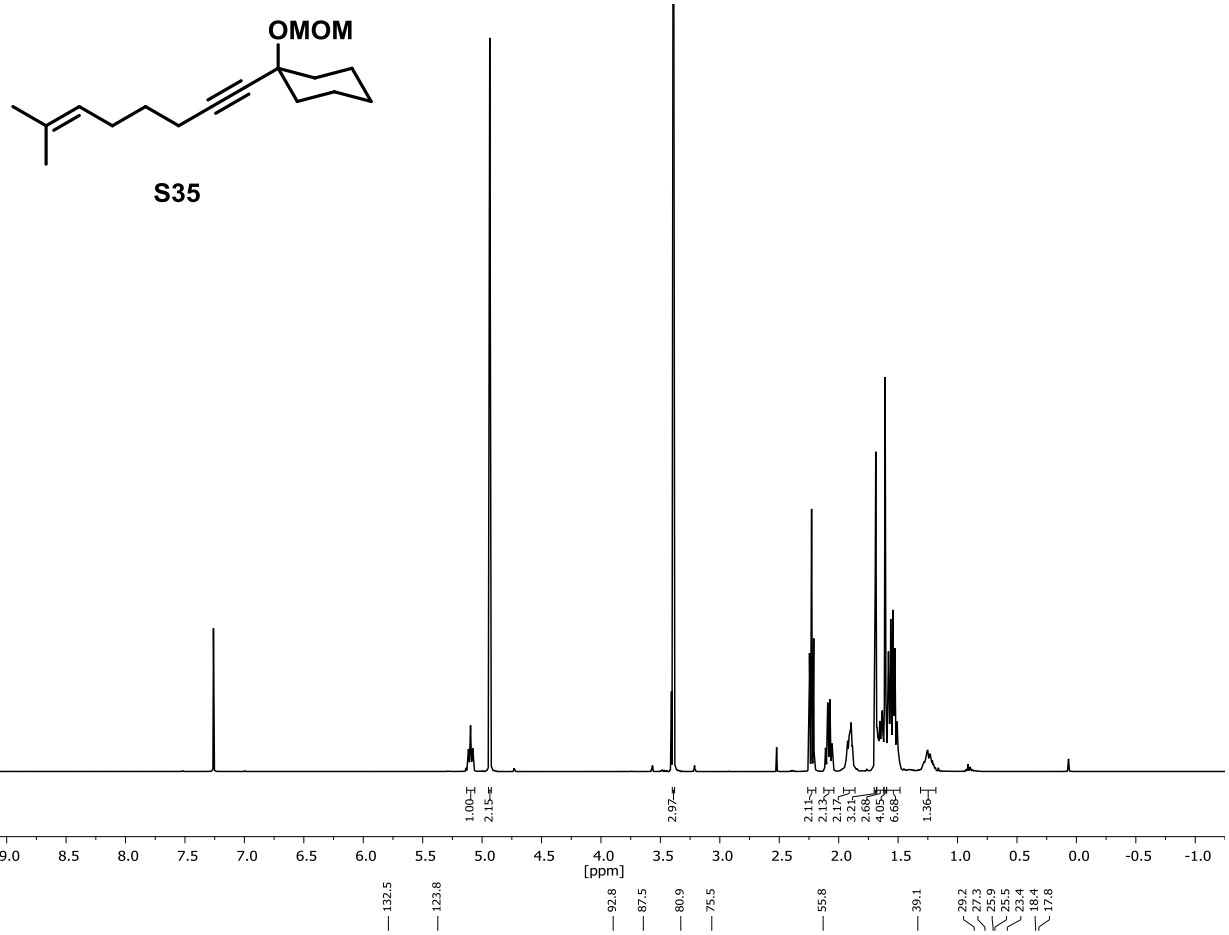

1.00
2.11
2.23
2.92
2.03
2.06
2.30
5.19
5.70
1.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

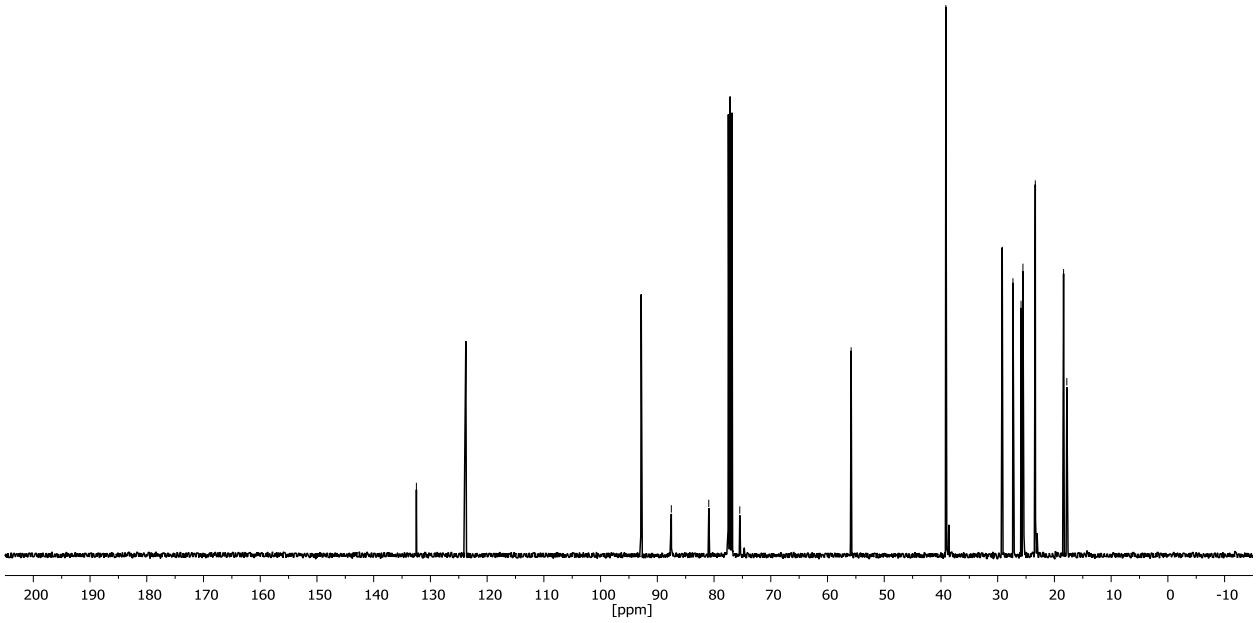

104.4
85.9
81.6
74.2
65.0
50.6
37.2
33.2
25.7
23.6
23.1
18.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

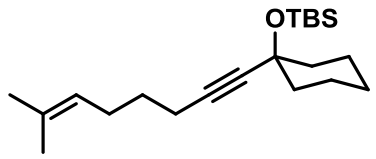

OMe
O

S34


0.80
3.00
1.83
2.00
3.94
2.38
5.55
1.12
10.0 9.5 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 -0.5 -1.0
[ppm]
202.0
84.9
82.5
74.1
50.6
42.9
37.1
25.6
23.0
21.5
18.3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

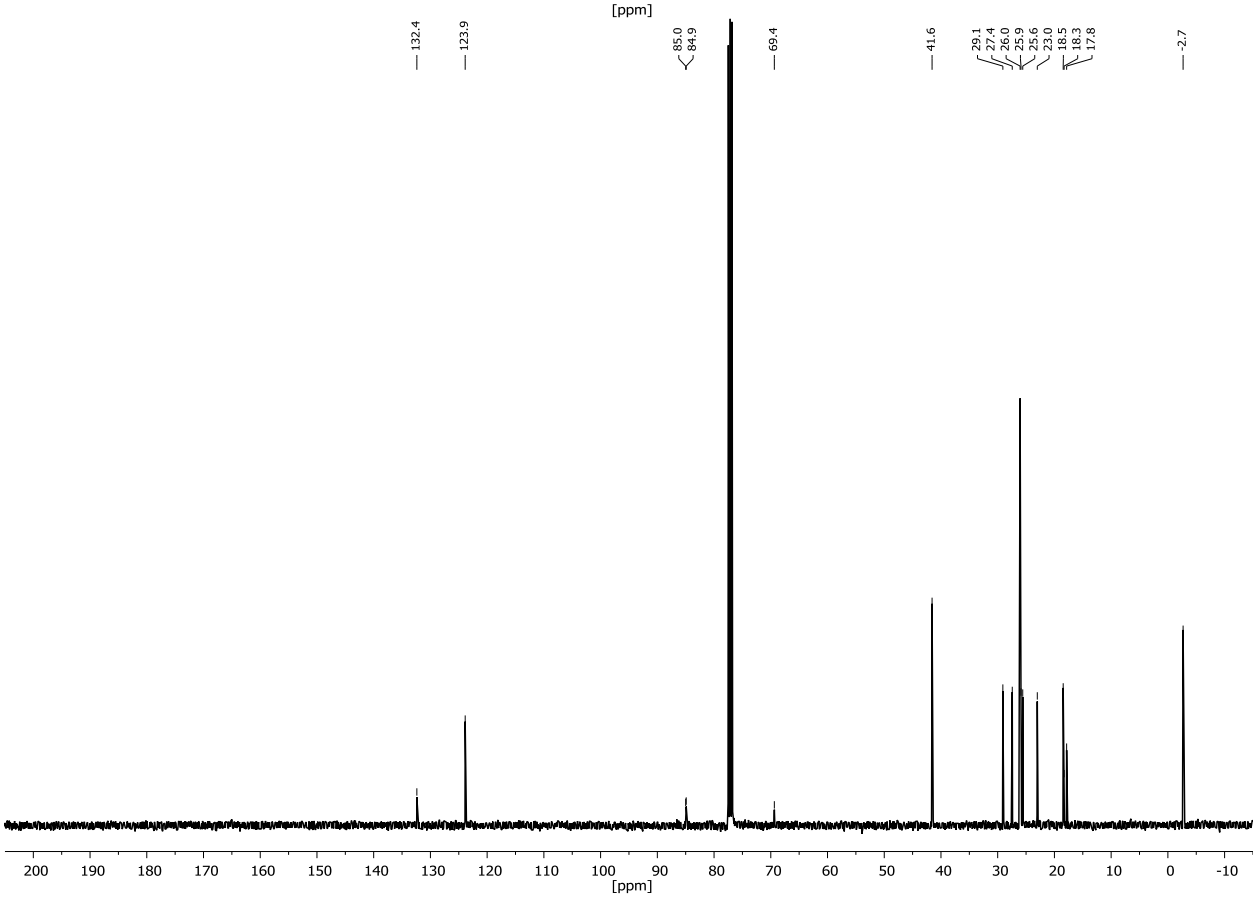

OMOM
S35
1.00
2.15
2.97
2.11
2.13
2.17
2.21
2.68
4.05
6.68
1.36
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
132.5
123.8
92.8
87.5
80.9
75.5
55.8
39.1
29.2
27.3
25.9
25.5
23.4
18.4
17.8

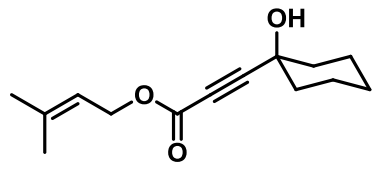

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTBS

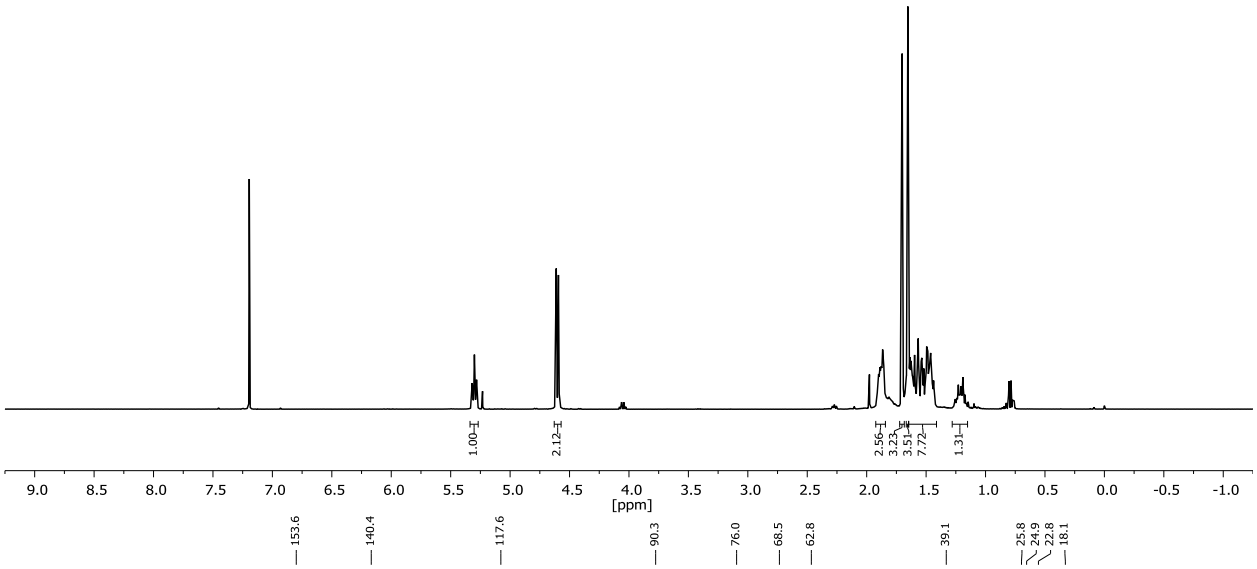
S36

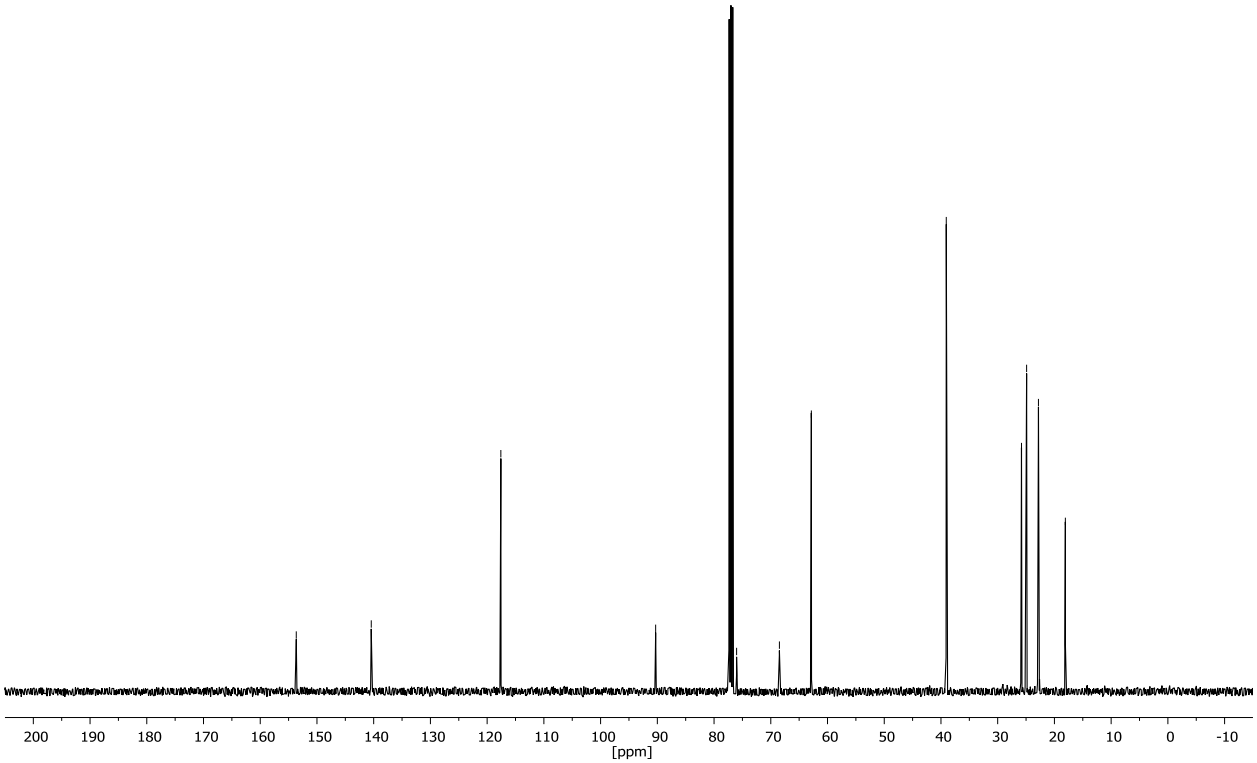
1.00
2.07
2.08
1.55
3.66
13.13
9.78
6.41
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

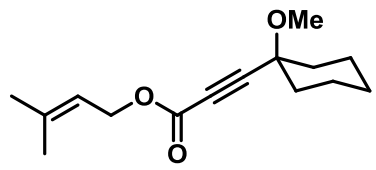

132.4
123.9
85.0
84.9
69.4
41.6
29.1
27.4
26.0
25.9
25.6
23.0
18.5
18.3
17.8
-2.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OH
O
O

S37

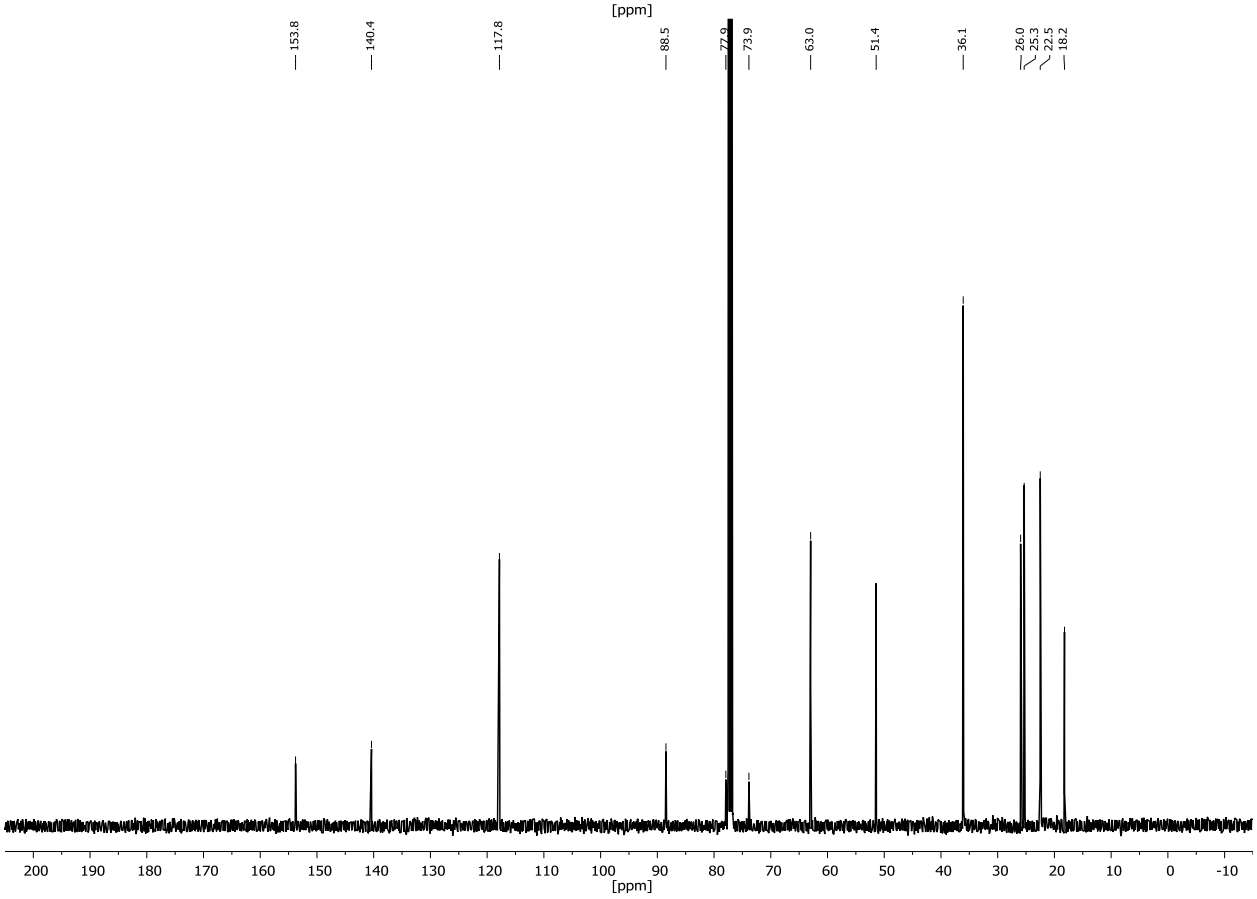

1.00
2.12
2.56
3.23
3.51
7.72
1.31
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
153.6
140.4
117.6
90.3
76.0
68.5
62.8
39.1
25.8
24.9
22.8
18.1

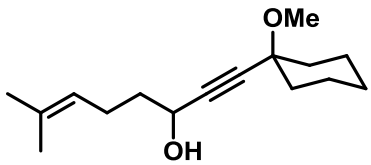

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
O
O

S38

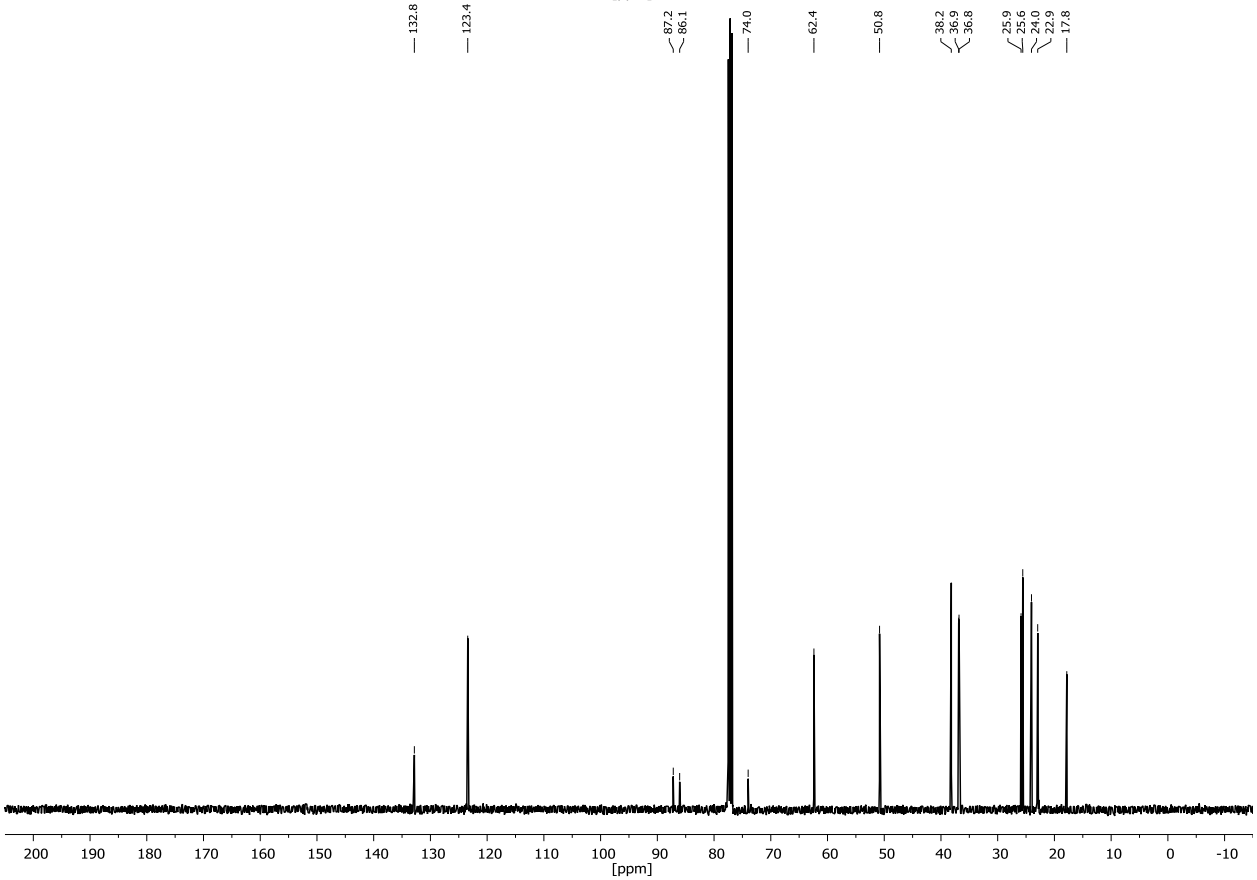
1.00
2.07
3.22
2.06
3.05
3.09
4.66
4.46
1.45
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

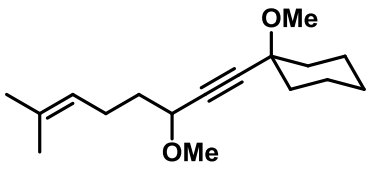

153.8
140.4
117.8
88.5
77.9
73.9
63.0
51.4
36.1
26.0
25.3
22.5
18.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
OH

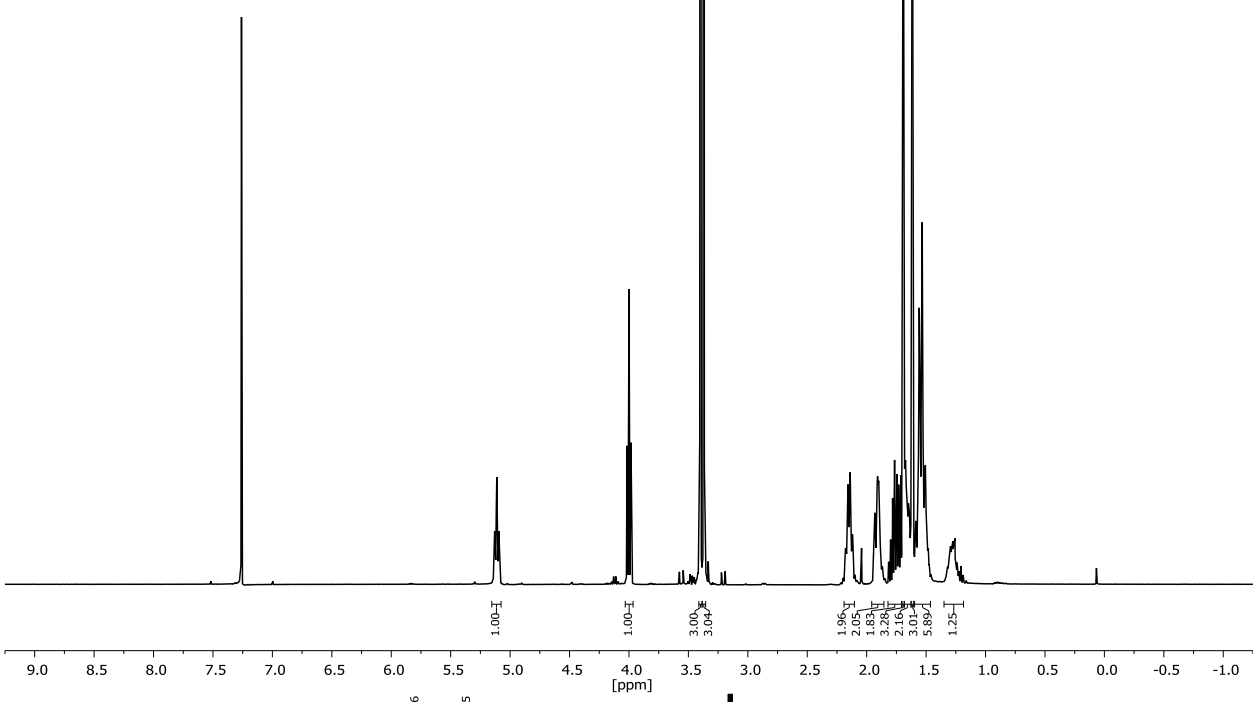
S39

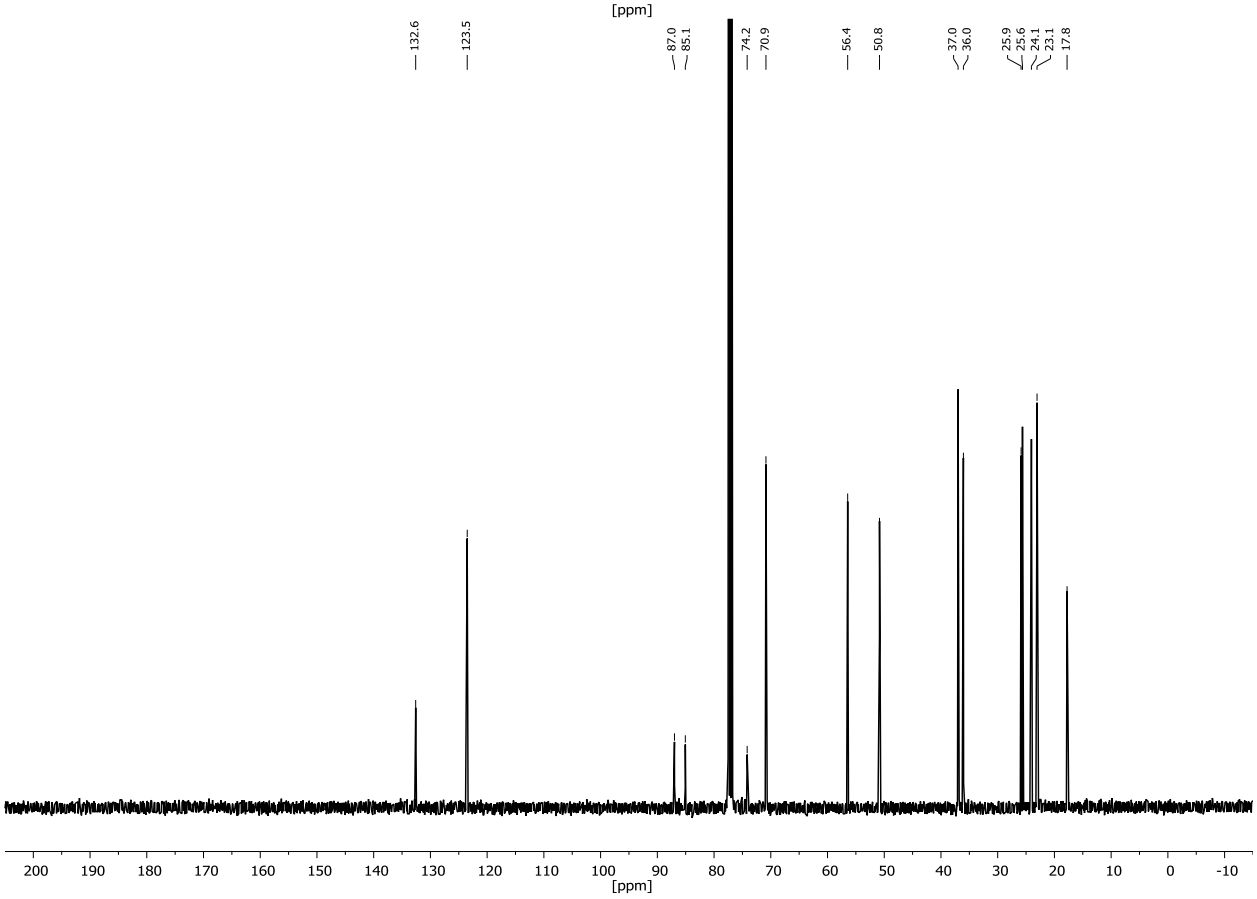
1.00
0.98
2.98
2.17
2.30
2.72
3.63
1.53
3.75
5.79
1.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

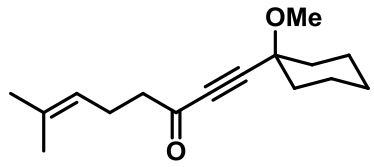

132.8
123.4
87.2
86.1
74.0
62.4
50.8
38.2
36.9
36.8
25.9
25.6
24.0
22.9
17.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
OMe

S40

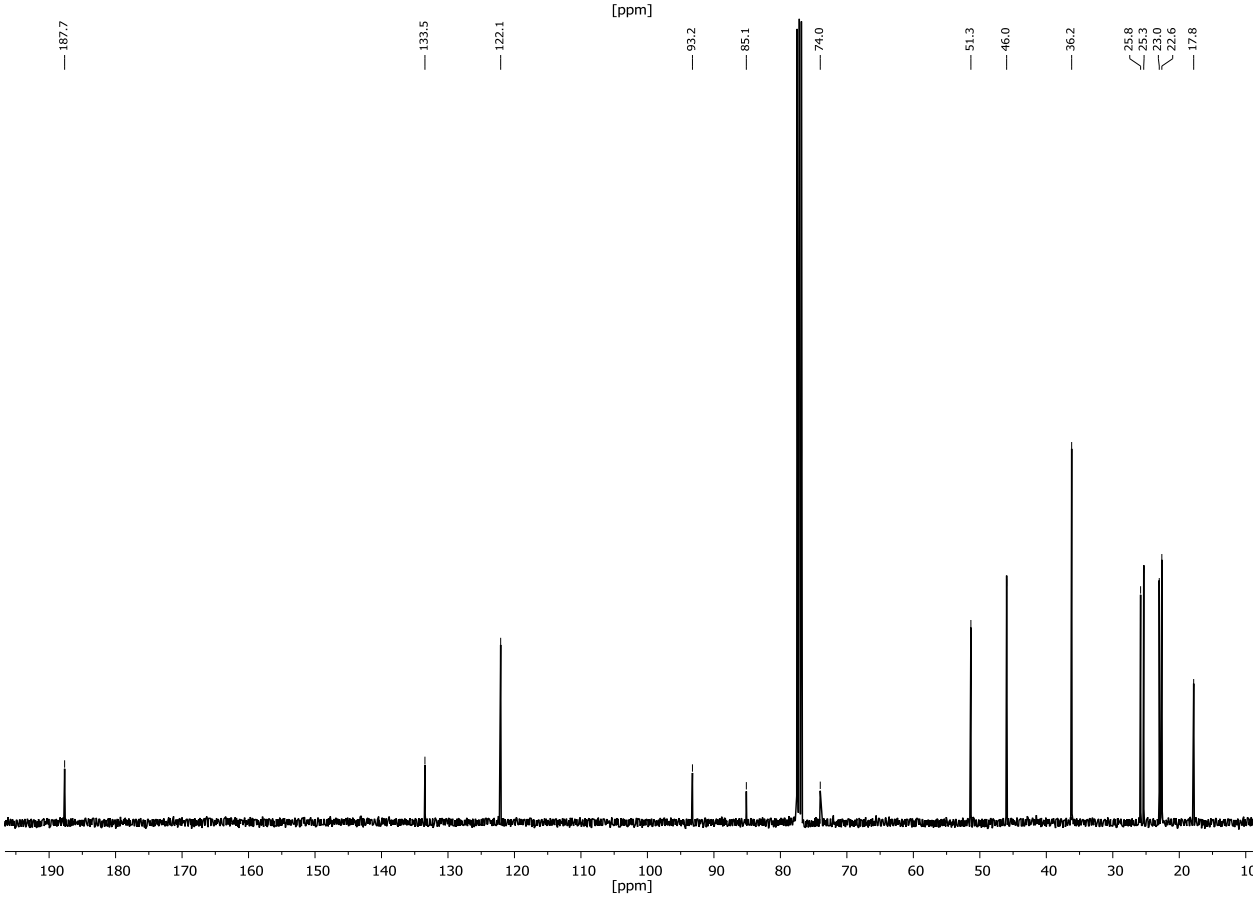

1.00
1.00
3.00
3.04
1.96
2.05
1.83
3.28
2.16
3.01
5.89
1.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

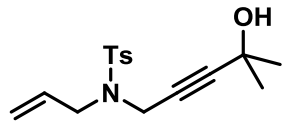

132.6
123.5
87.0
85.1
74.2
70.9
56.4
50.8
37.0
36.0
25.9
25.6
24.1
23.1
17.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
O

S41

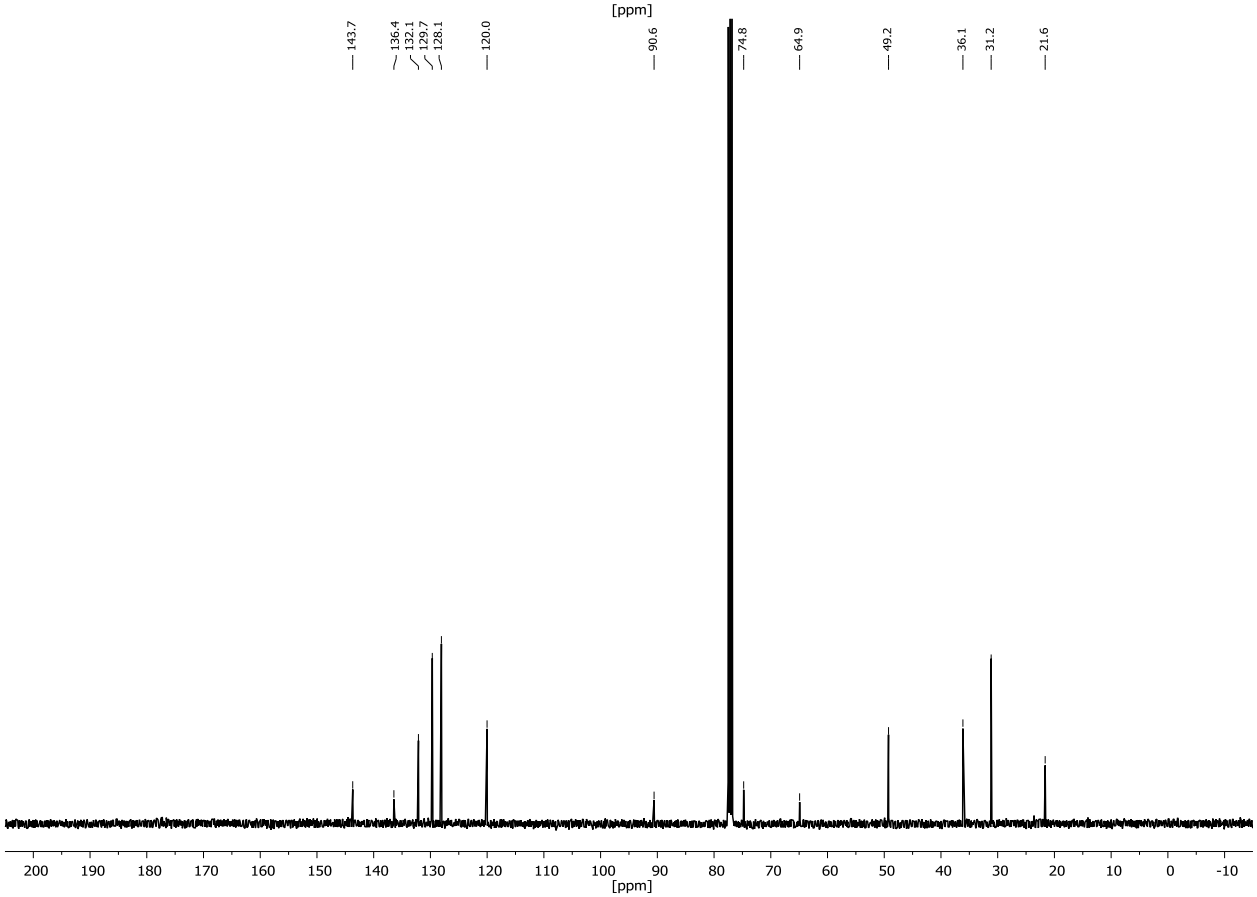
1.00
3.12
2.10
2.11
2.14
3.54
3.17
4.38
1.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

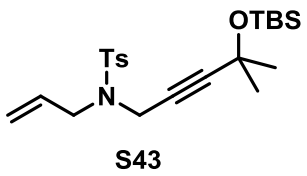

187.7
133.5
122.1
93.2
85.1
74.0
51.3
46.0
36.2
25.8
25.3
23.0
22.6
17.8
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
[ppm]


OH
Ts
N

S42

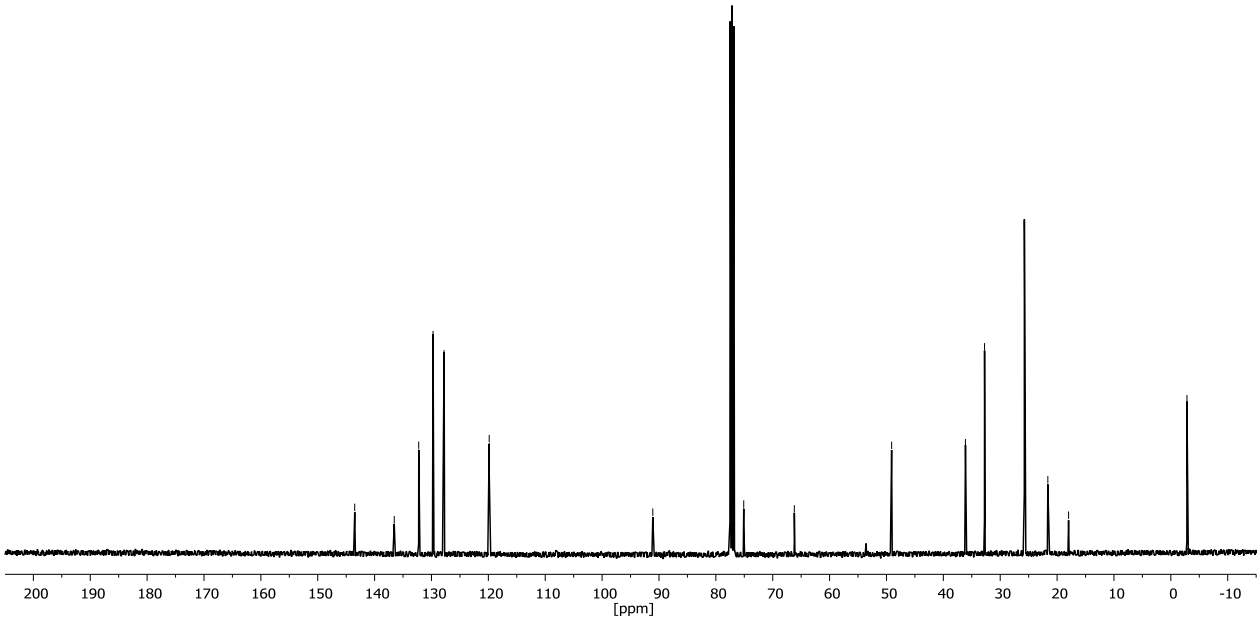
2.04
2.09
1.00
2.09
2.12
2.11
3.21
0.83
6.69
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

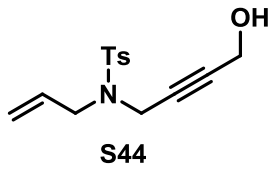

143.7
136.4
132.1
129.7
128.1
120.0
90.6
74.8
64.9
49.2
36.1
31.2
21.6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTBS
Ts
N

S43

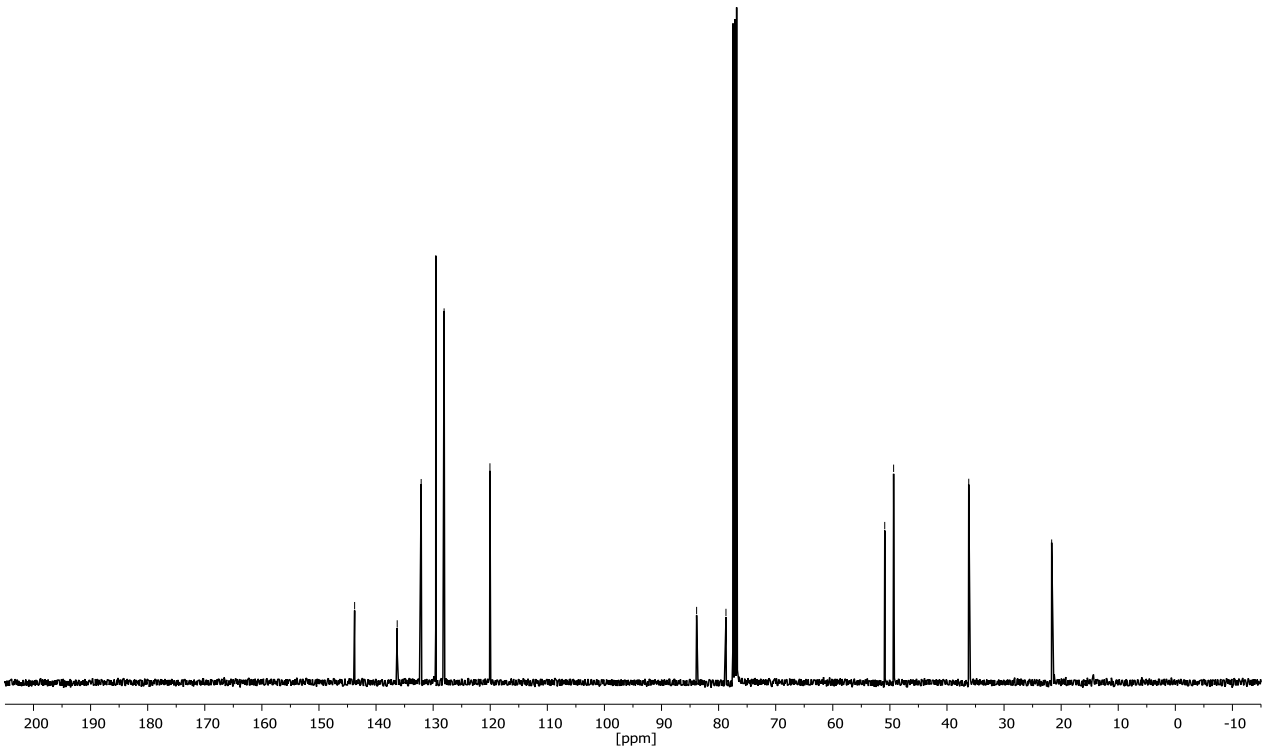
2.01
2.05
1.00
2.30
2.13
2.10
3.05
6.20
9.38
6.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.5
136.5
132.2
129.7
127.8
119.9
91.1
75.1
66.2
49.1
36.1
32.8
25.8
21.6
18.0
-2.8

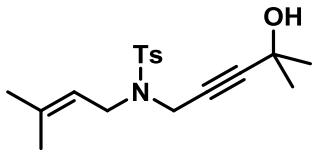

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OH
Ts
N

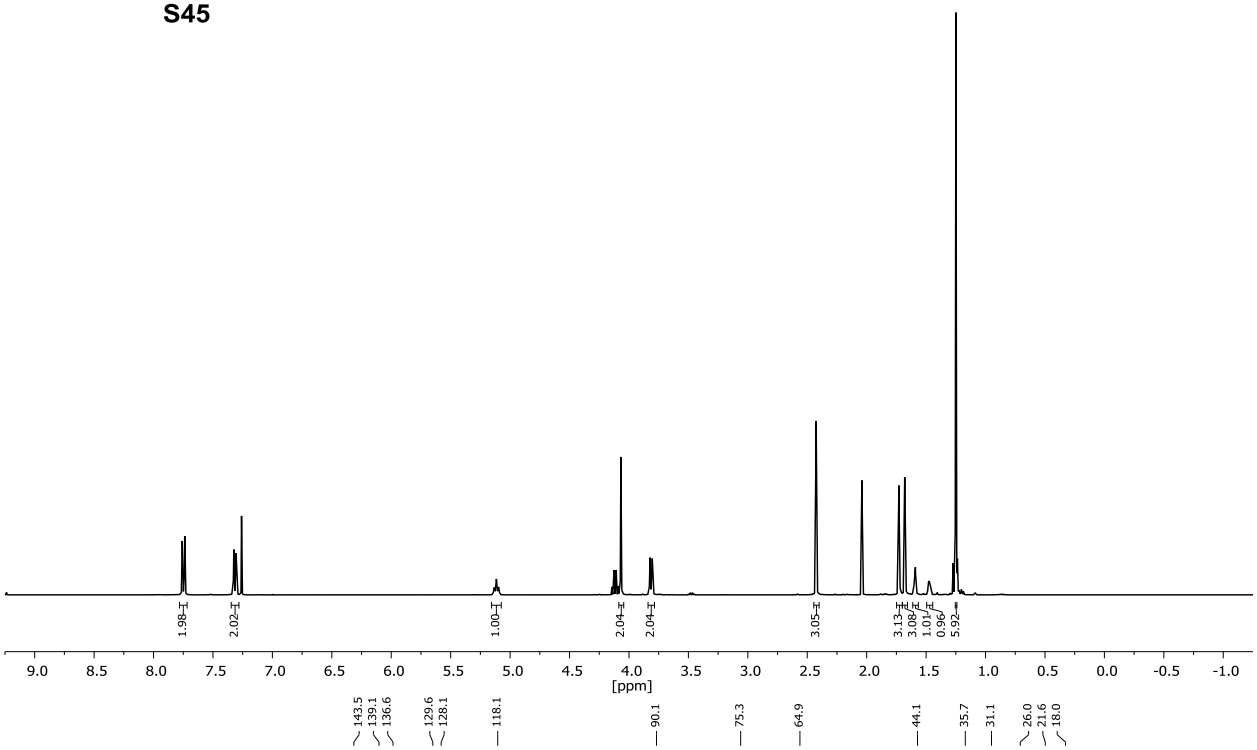
S44

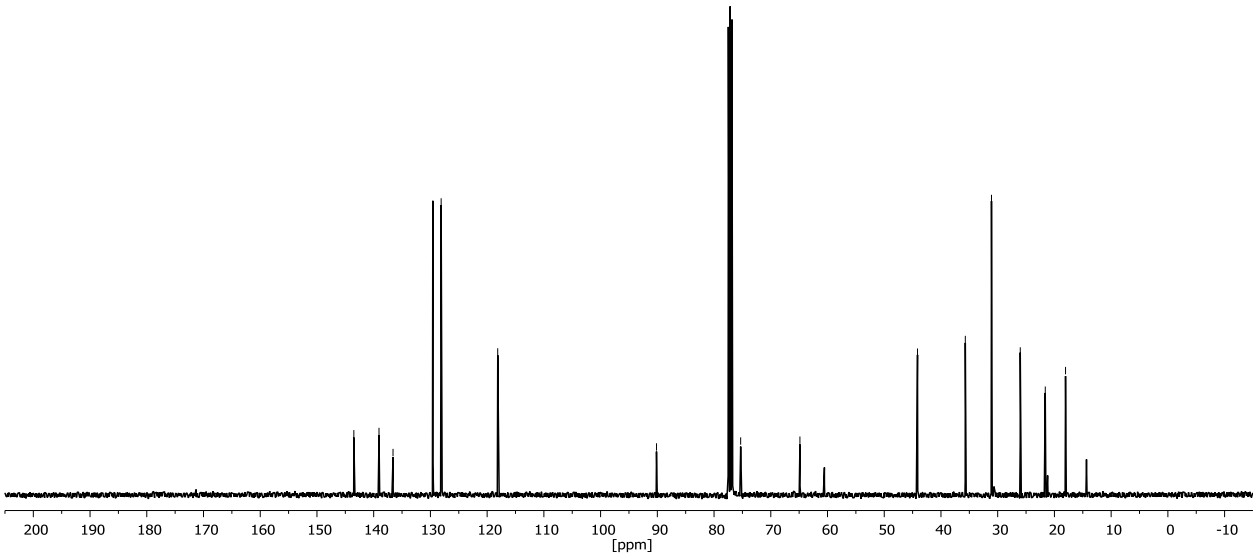
1.98
2.03
1.00
2.07
2.16
2.03
2.12
3.14
0.94
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.8
136.3
132.1
129.5
128.1
120.1
83.9
78.7
50.9
49.3
36.2
21.7

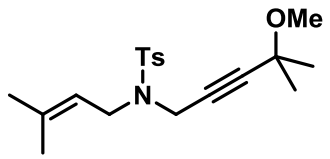

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OH
Ts
N

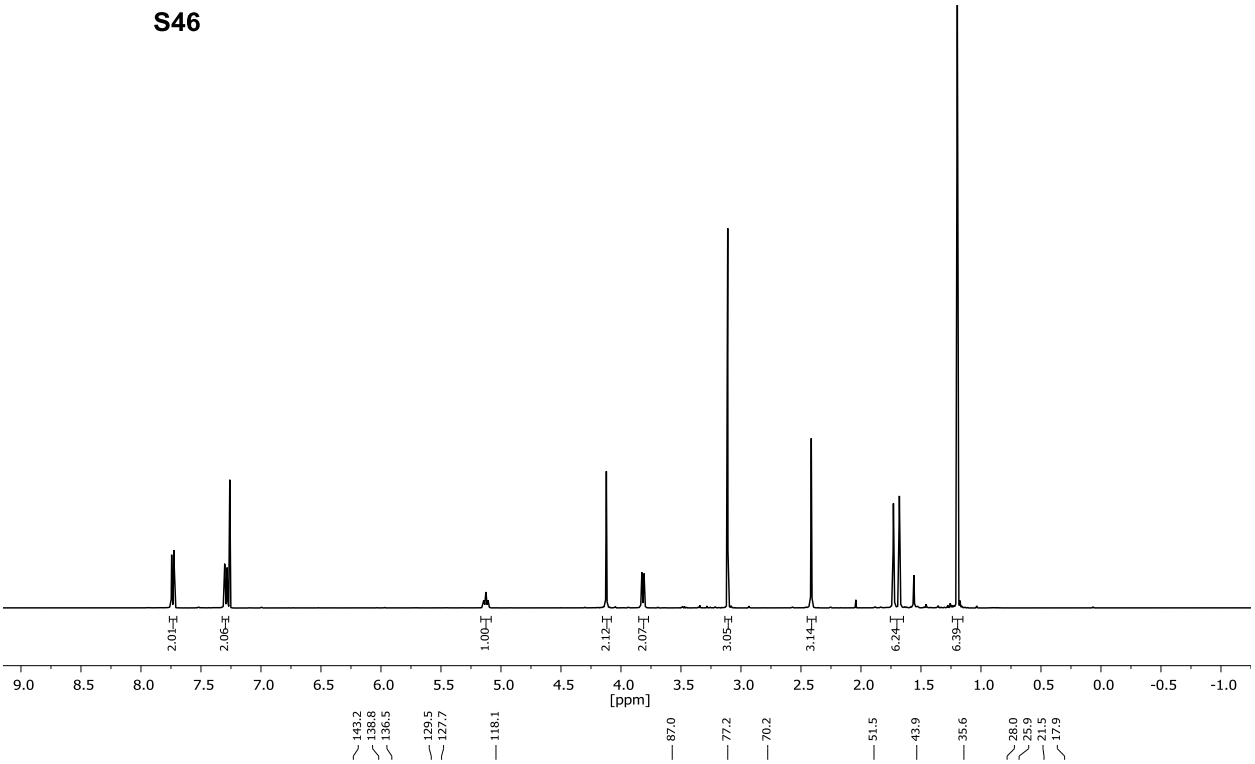
S45

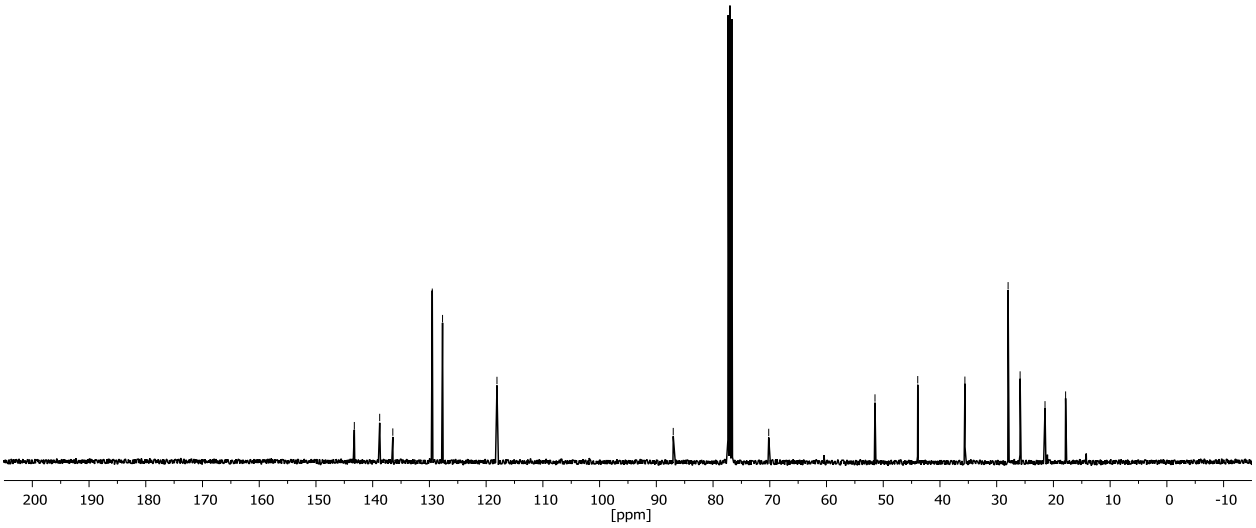

1.98
2.02
1.00
2.04
2.04
3.05
3.13
3.08
1.01
0.96
5.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.5
139.1
136.6
129.6
128.1
118.1
90.1
75.3
64.9
44.1
35.7
31.1
26.0
21.6
18.0

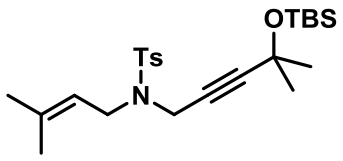

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
Ts
N

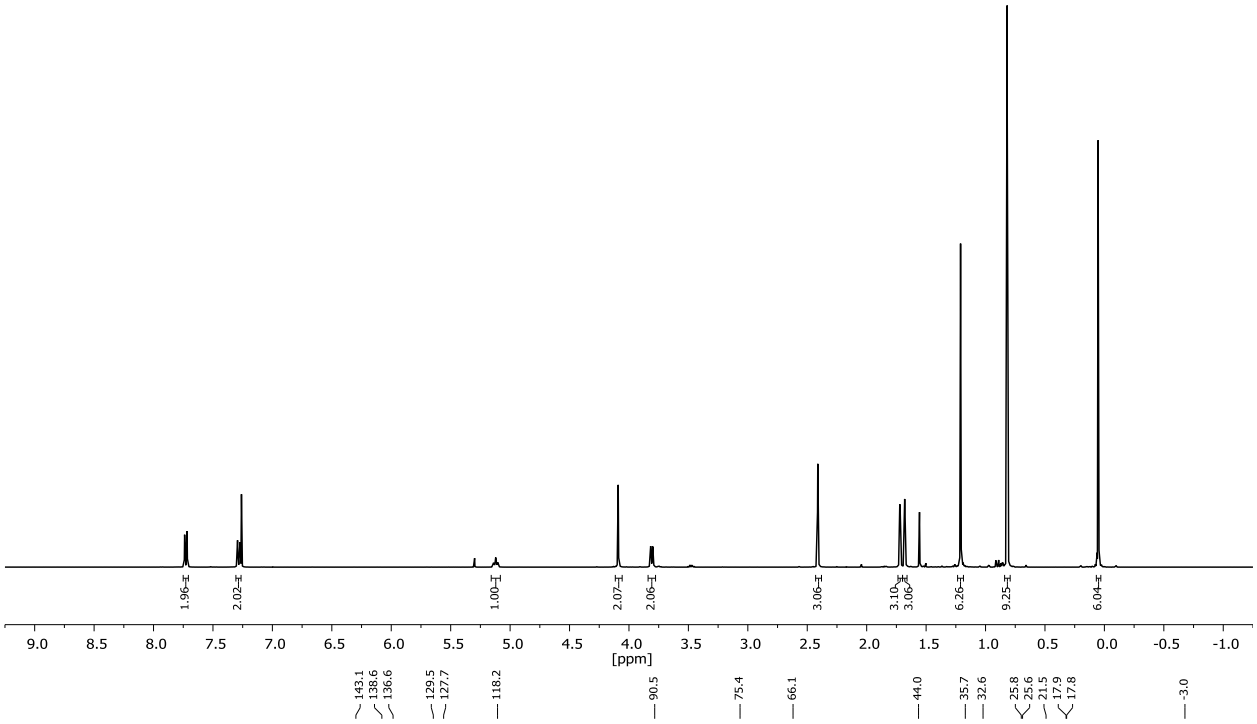
S46

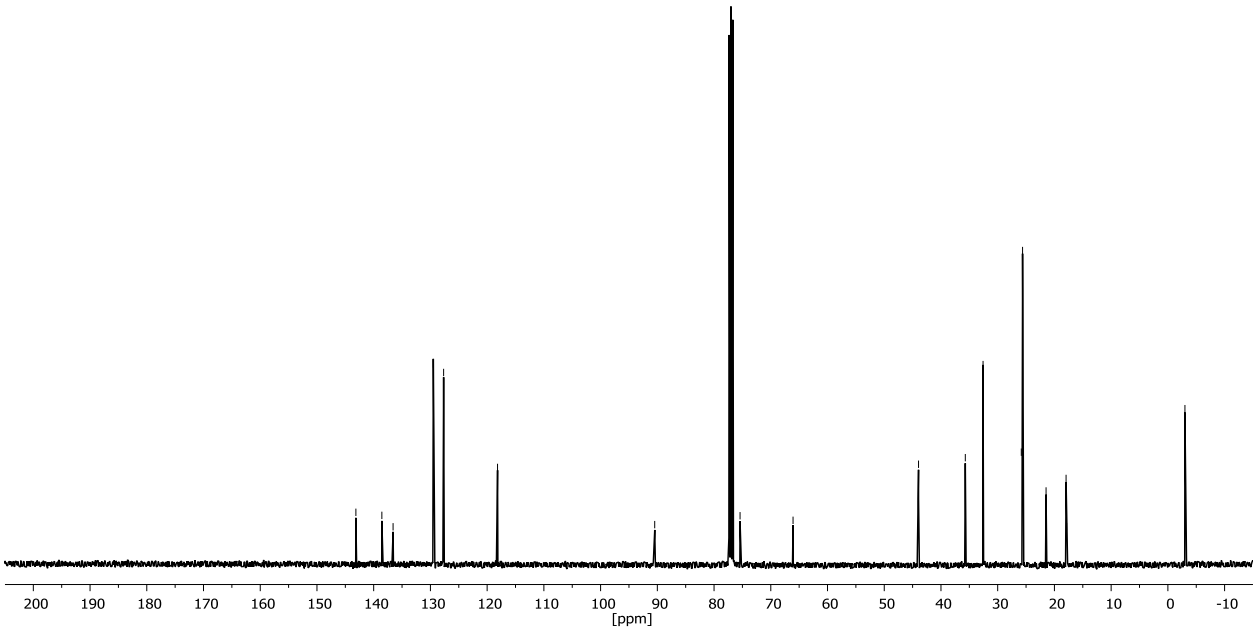

2.01
2.06
1.00
2.12
2.07
3.05
3.14
6.24
6.39
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.2
138.8
136.5
129.5
127.7
118.1
87.0
77.2
70.2
51.5
43.9
35.6
28.0
25.9
21.5
17.9

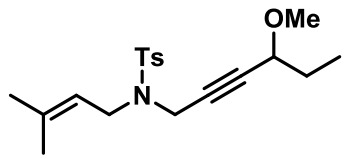

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTBS
Ts
N

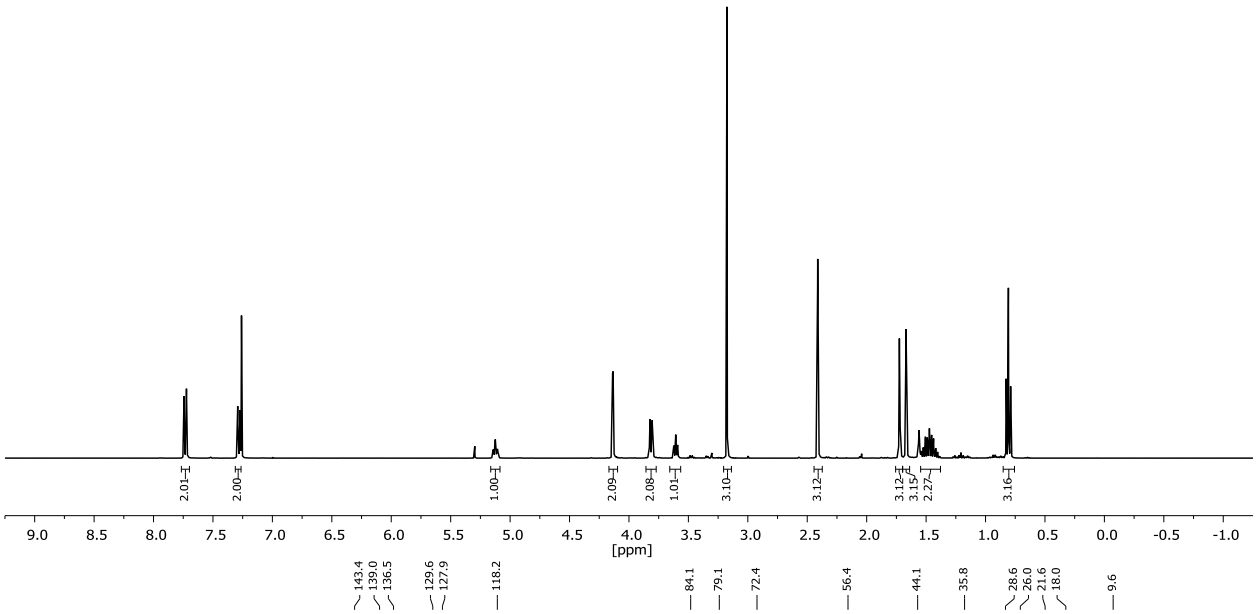
S47

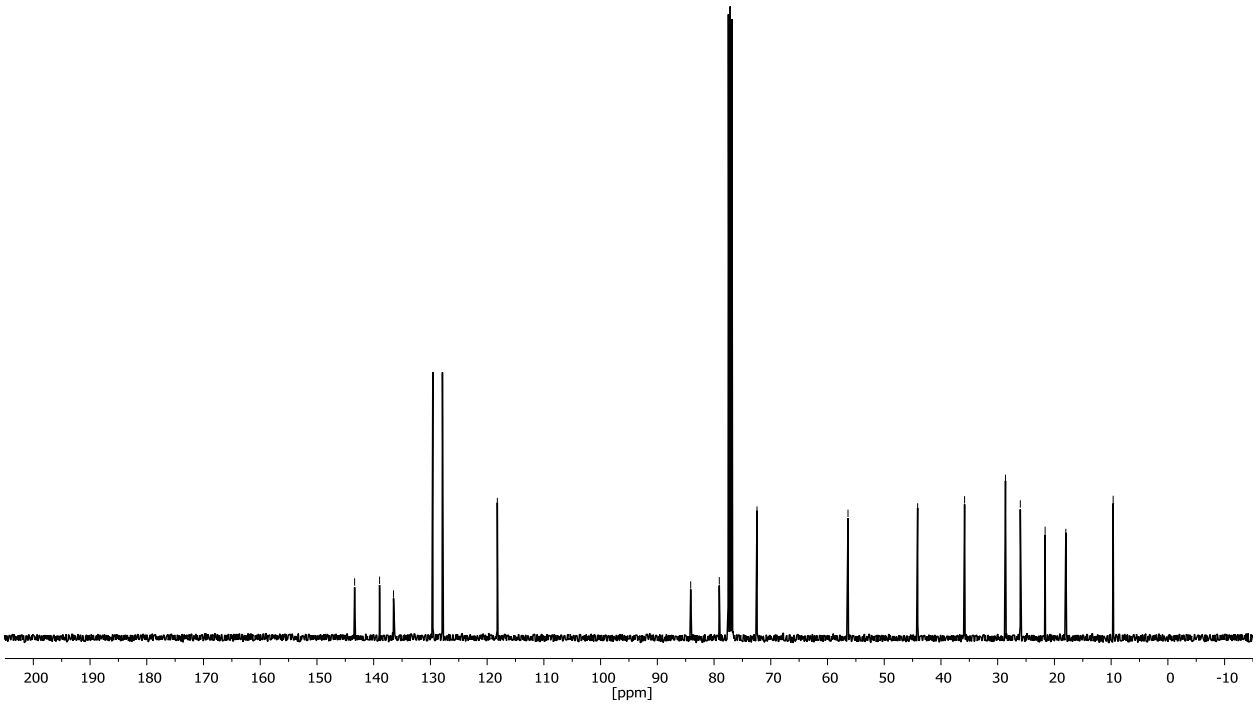

1.96
2.02
1.00
2.07
2.06
3.06
3.10
3.06
6.26
9.25
6.04
[ppm]
143.1
138.6
136.6
129.5
127.7
118.2
90.5
75.4
66.1
44.0
35.7
32.6
25.8
25.6
21.5
17.9
17.8
-3.0

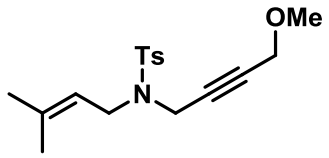

[ppm]


OMe
Ts
N

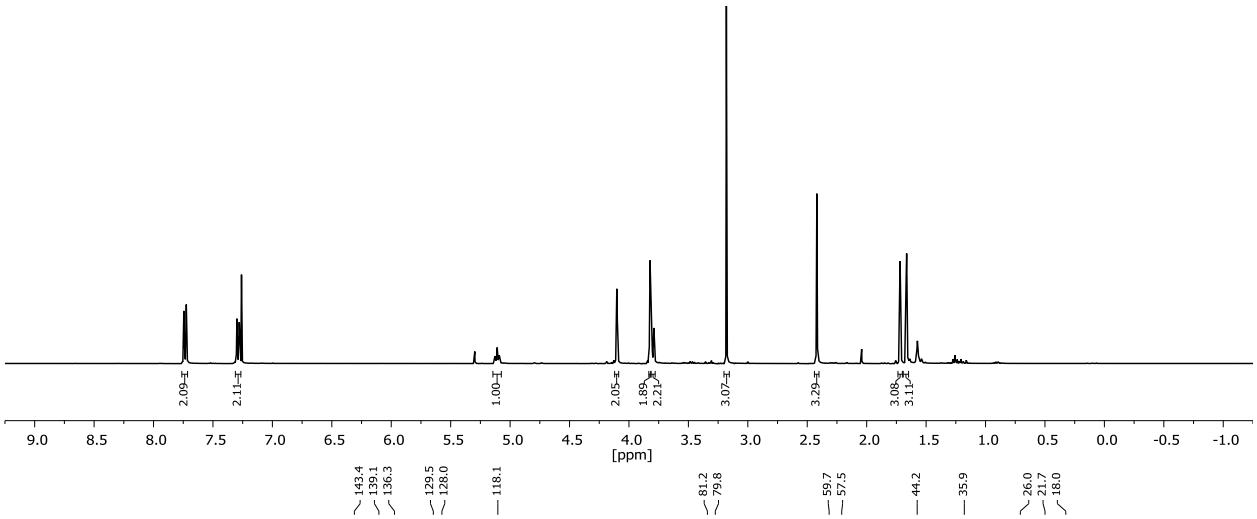
S49

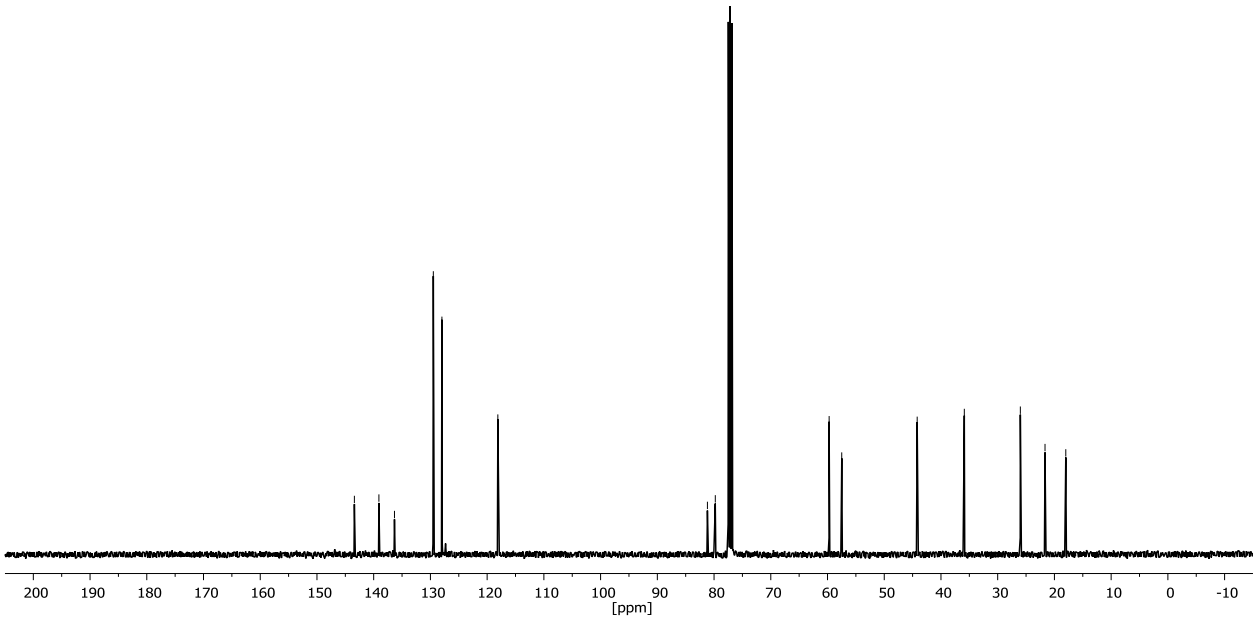

2.01
2.00
1.00
2.09
2.08
1.01
3.10
3.12
3.12
3.15
2.27
3.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.4
139.0
136.5
129.6
127.9
118.2
84.1
79.1
72.4
56.4
44.1
35.8
28.6
26.0
21.6
18.0
9.6

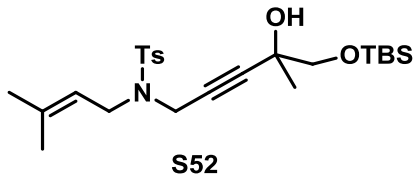

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
Ts
N

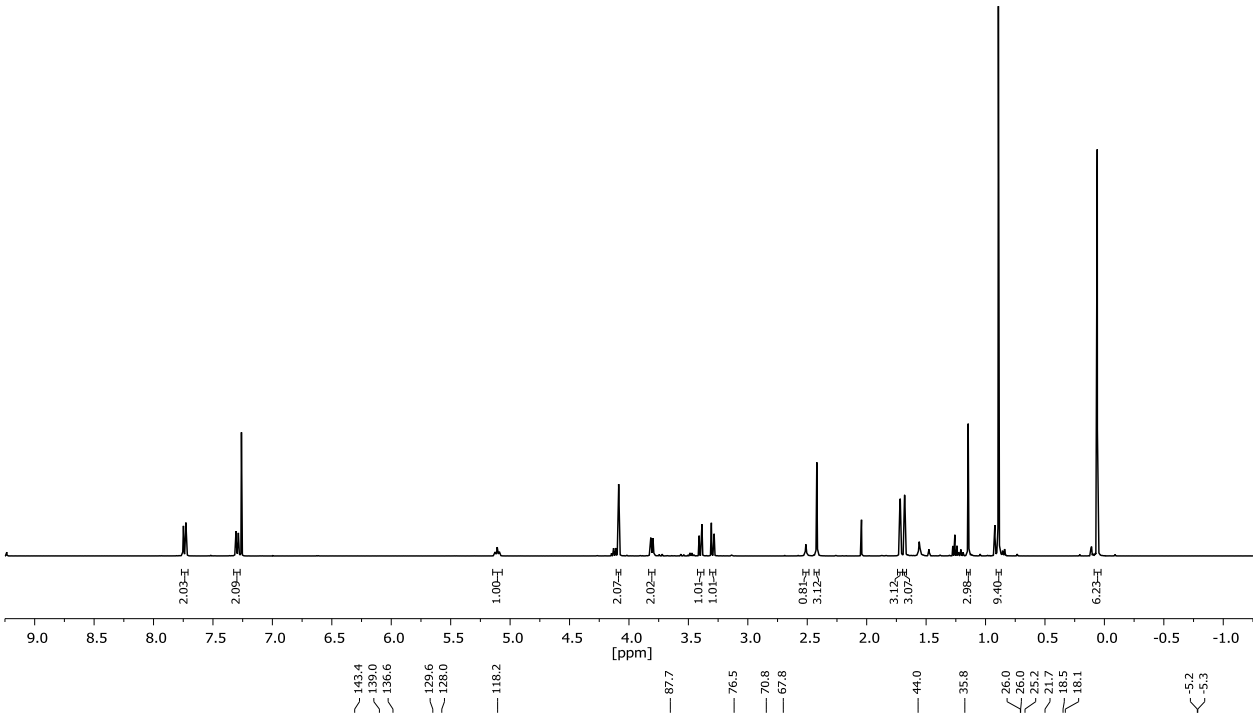
S51

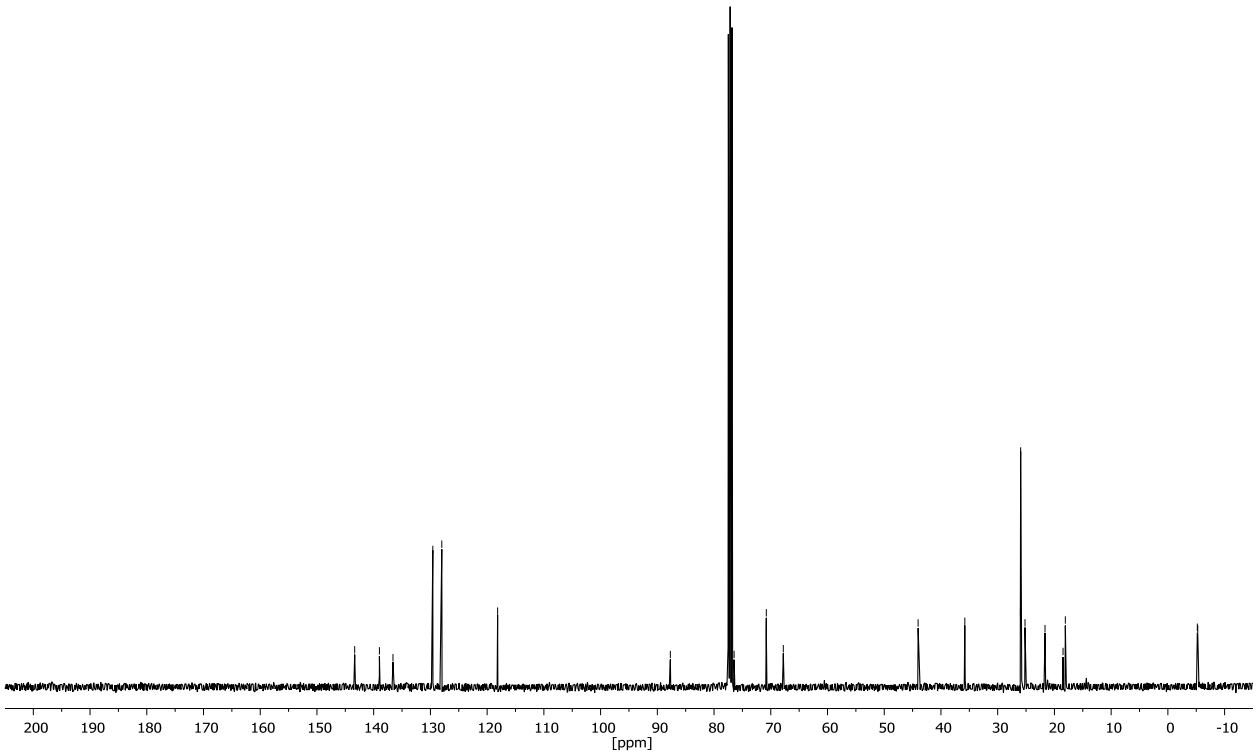

2.09
2.11
1.00
2.05
1.89
2.21
3.07
3.29
3.08
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.4
139.1
136.3
129.5
128.0
118.1
81.2
79.8
59.7
57.5
44.2
35.9
26.0
21.7
18.0

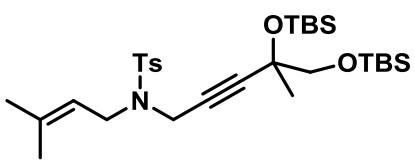

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OH
Ts
N
OTBS

S52

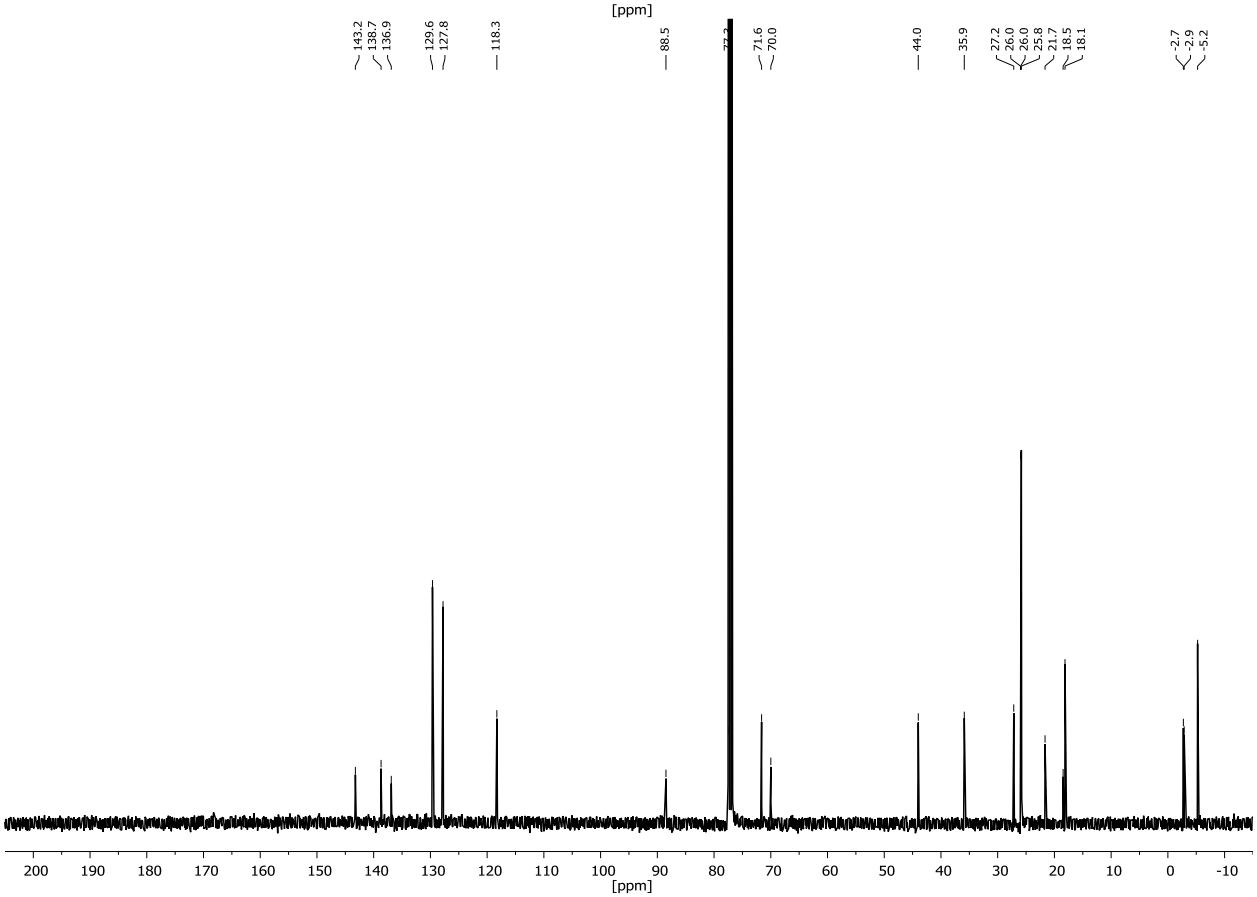

2.03
2.09
1.00
2.07
2.02
1.01
1.01
0.81
3.12
3.12
3.07
2.98
9.40
6.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.4
139.0
136.6
129.6
128.0
118.2
87.7
76.5
70.8
67.8
44.0
35.8
26.0
26.0
25.2
21.7
18.5
18.1
-5.2
-5.3

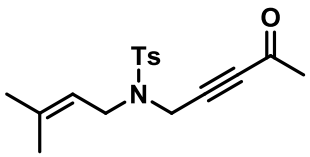

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTBS
Ts
N
OTBS

S53

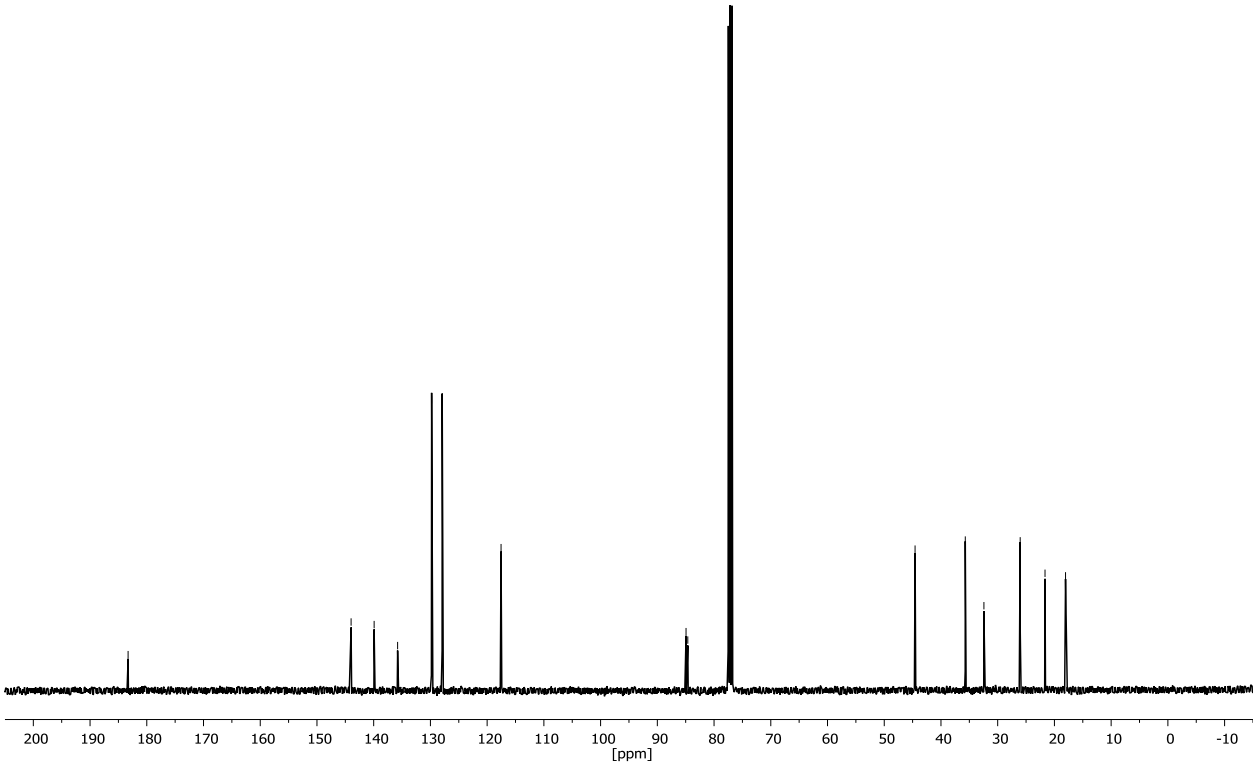
2.05
4.06
1.00
2.03
2.02
2.01
3.16
3.12
3.10
3.11
10.12
9.58
3.15
3.12
6.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

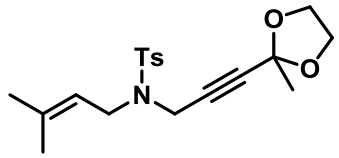

143.2
138.7
136.9
129.6
127.8
118.3
88.5
77.2
71.6
70.0
44.0
35.9
27.2
26.0
26.0
25.8
21.7
18.5
18.1
-2.7
-2.9
-5.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


O
Ts
N

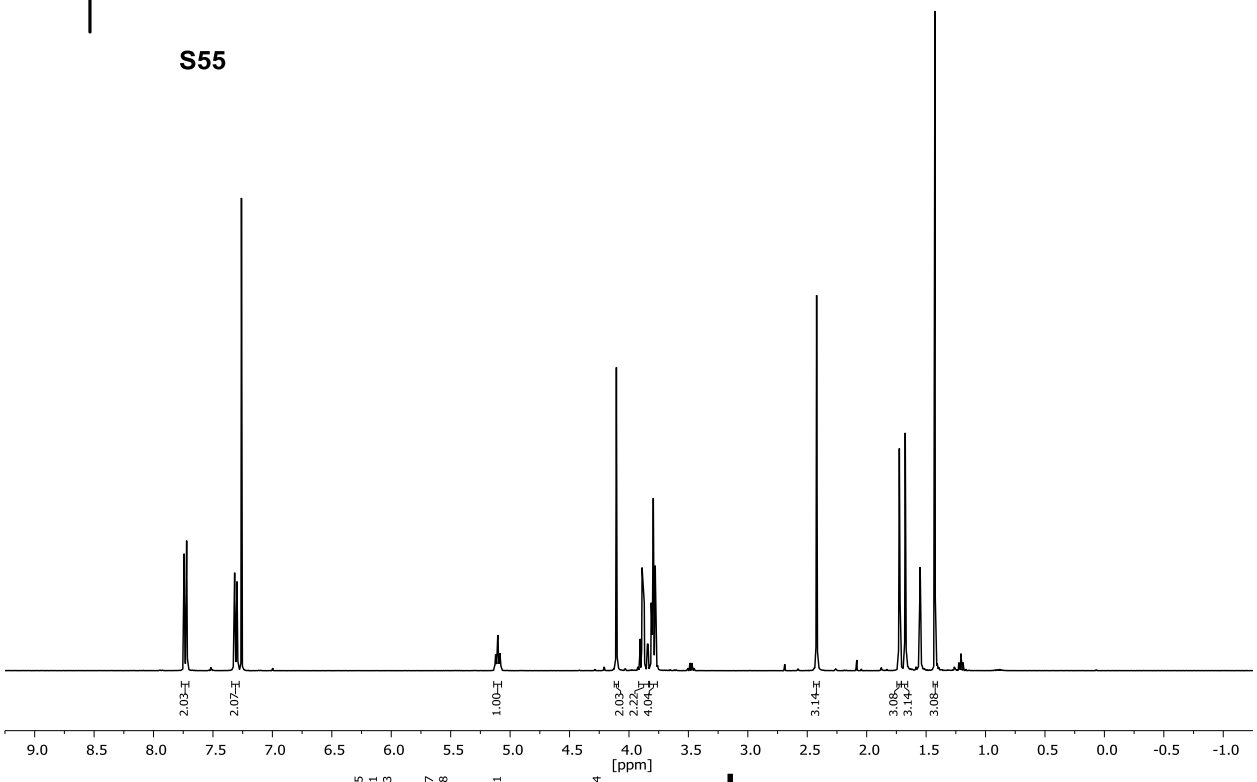
S54

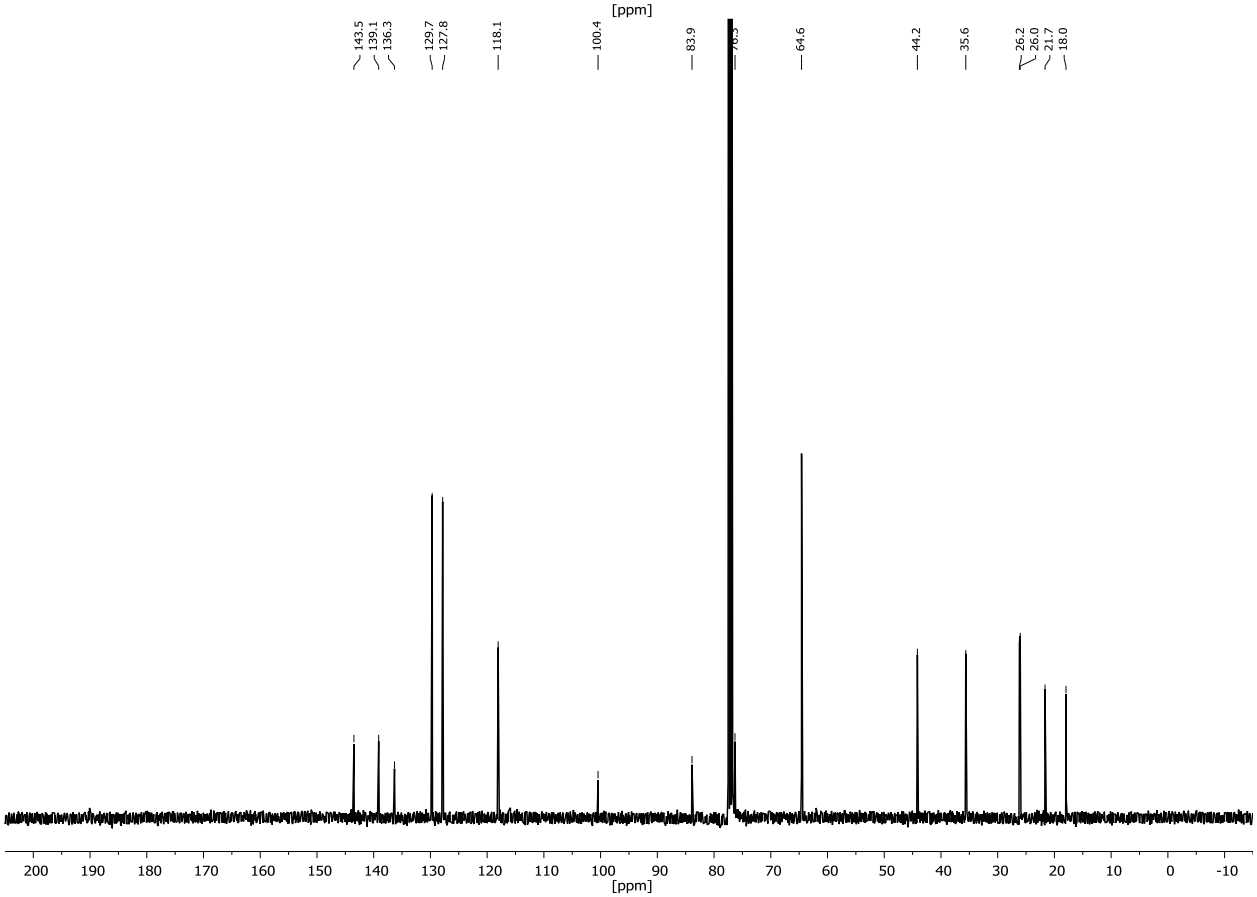
1.98
2.05
1.00
2.06
2.08
3.15
3.00
3.15
3.13
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
183.3
144.0
139.9
135.8
129.8
127.9
117.5
84.9
84.6
44.6
35.7
32.4
26.0
21.7
18.0

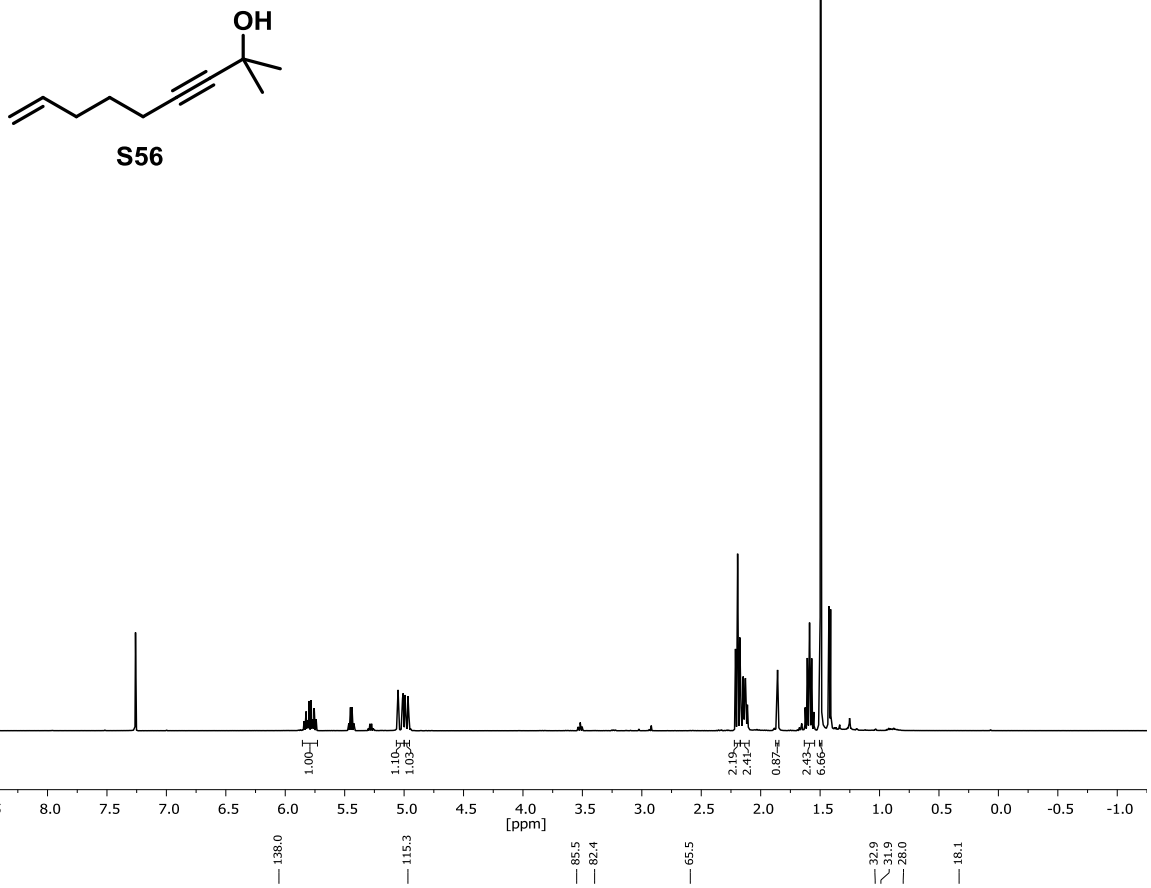

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

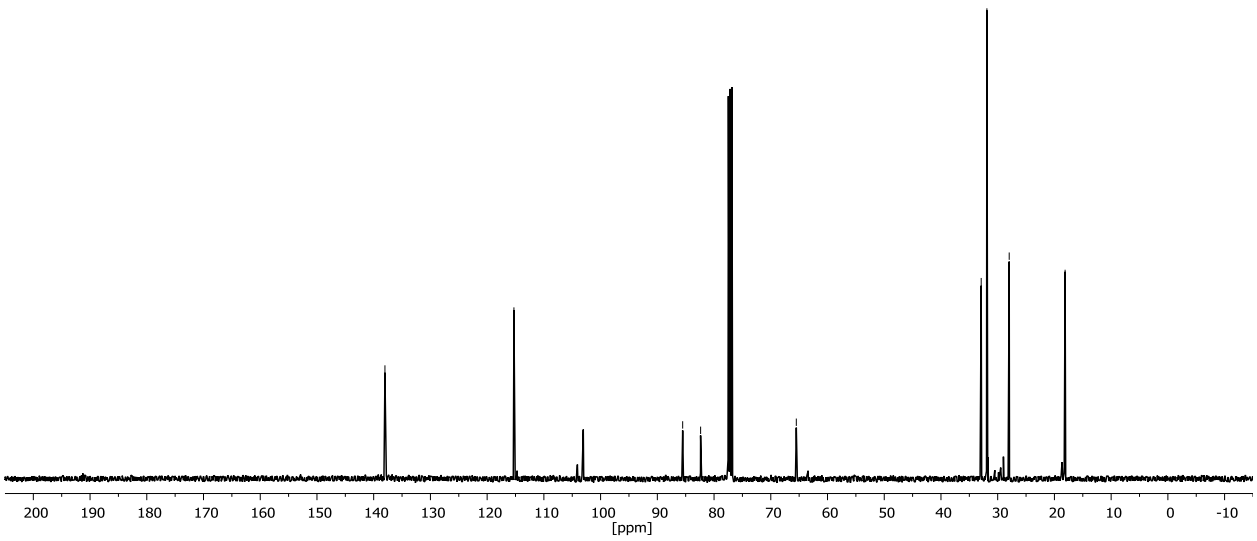

Ts
N
O
O

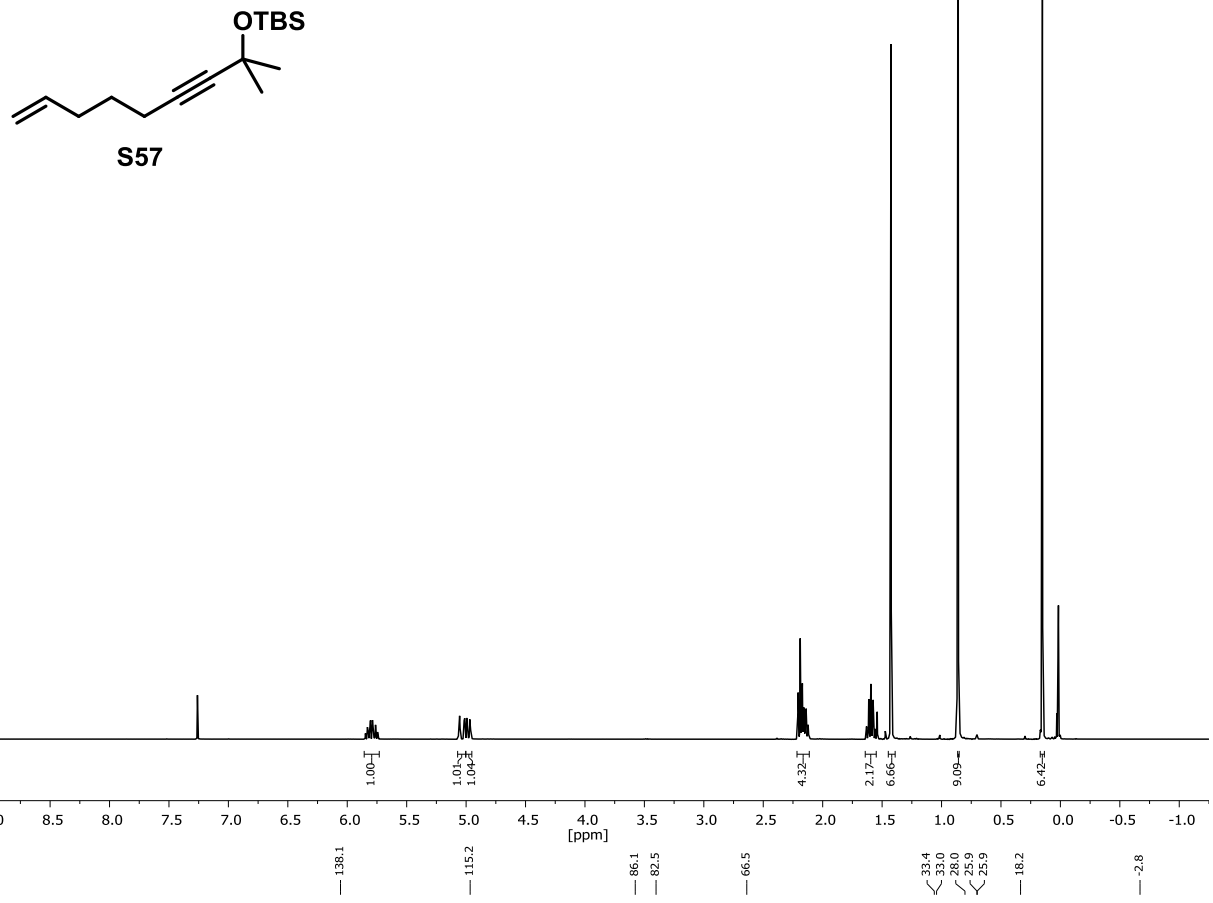
S55

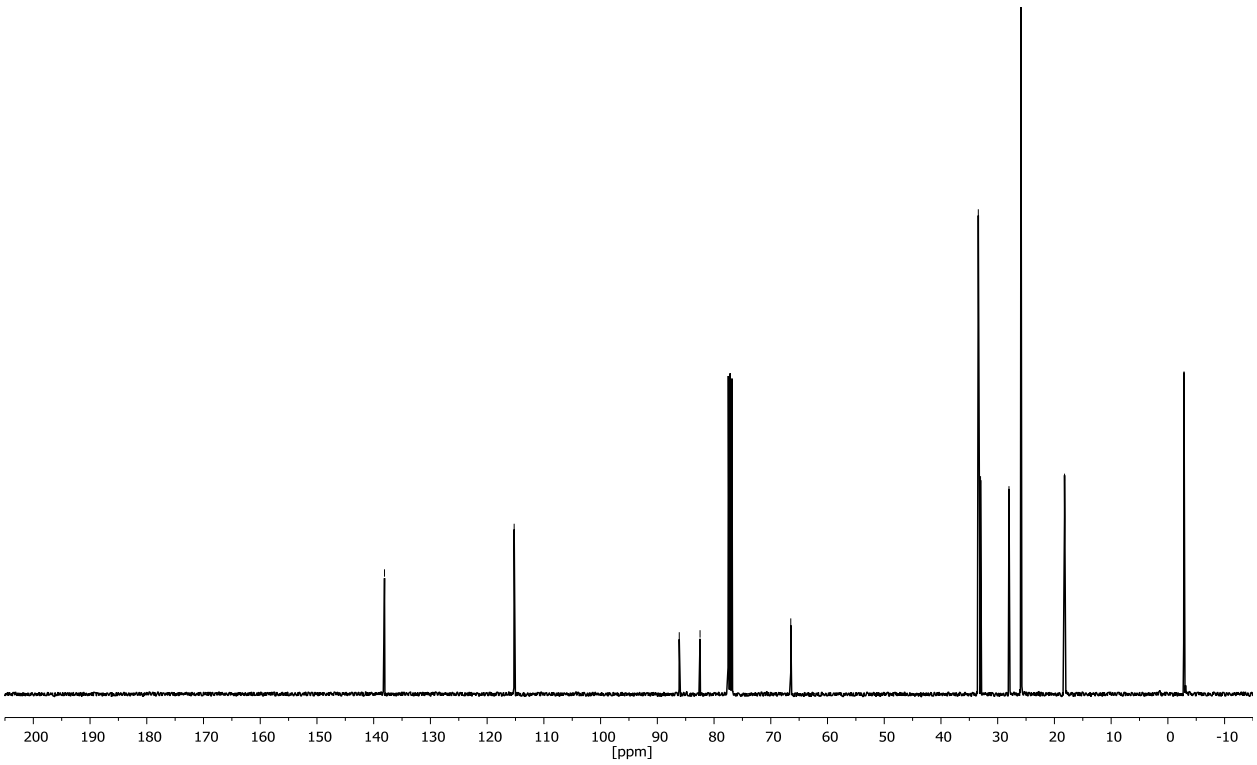

2.03
2.07
1.00
2.03
2.22
4.04
3.14
3.08
3.14
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

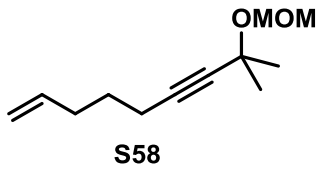

143.5
139.1
136.3
129.7
127.8
118.1
100.4
83.9
78.3
64.6
44.2
35.6
26.2
26.0
21.7
18.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OH
S56
1.00
1.10
1.03
2.19
2.41
0.87
2.43
6.66
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 -0.5 -1.0
[ppm]
138.0
115.3
85.5
82.4
65.5
32.9
31.9
28.0
18.1

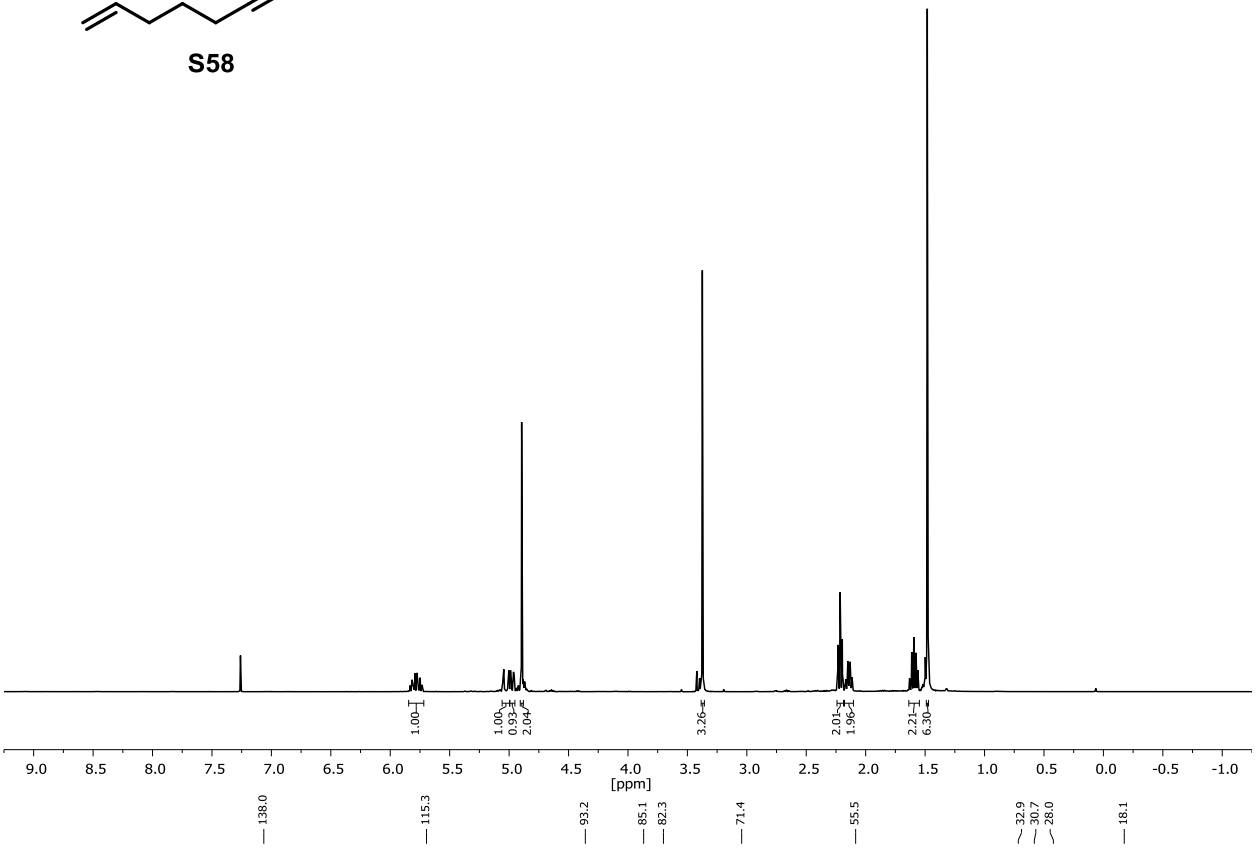

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

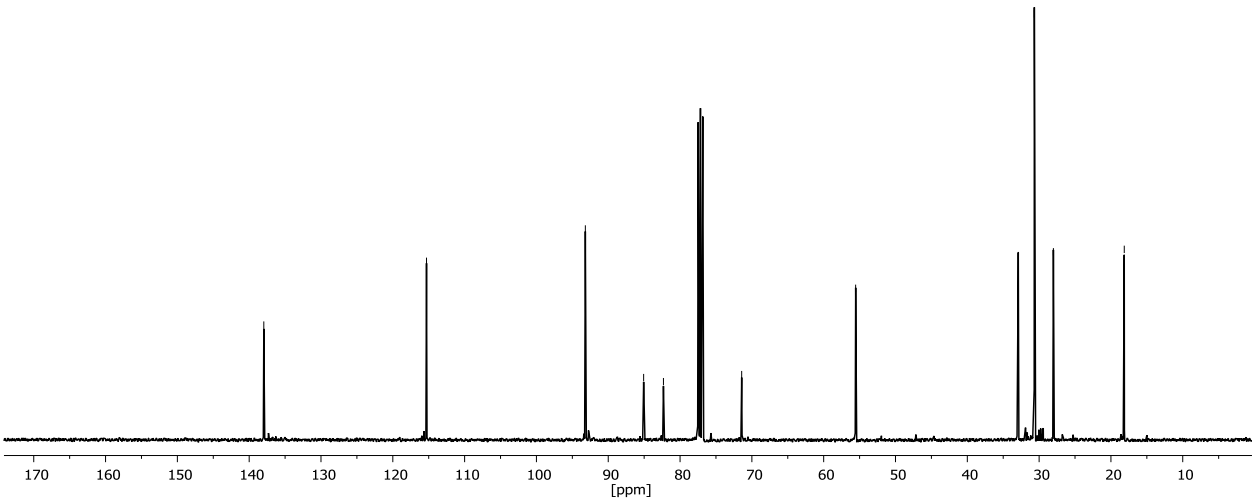

OTBS
S57
1.00
1.01
1.04
4.32
2.17
6.66
9.09
6.42
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
138.1
115.2
86.1
82.5
66.5
33.4
33.0
28.0
25.9
25.9
18.2
-2.8

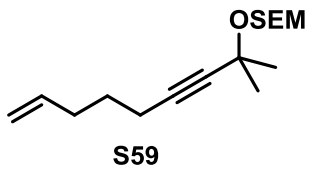

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMOM

S58

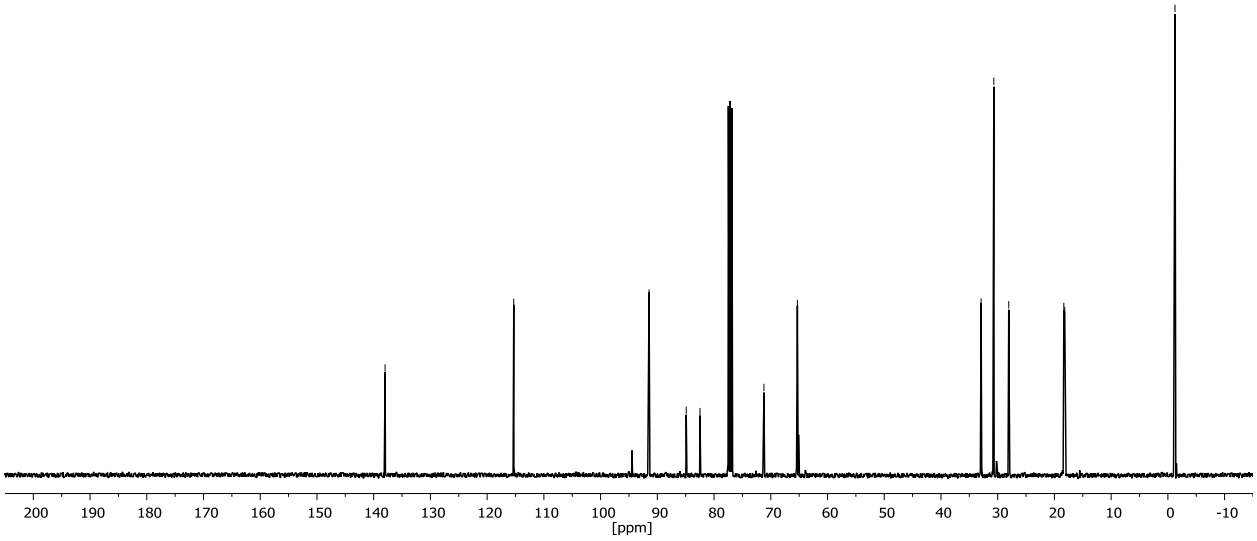

1.00
0.93
2.04
3.26
2.01
1.96
2.21
6.30
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
138.0
115.3
93.2
85.1
82.3
71.4
55.5
32.9
30.7
28.0
18.1

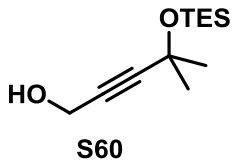

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
[ppm]


OSEM

S59

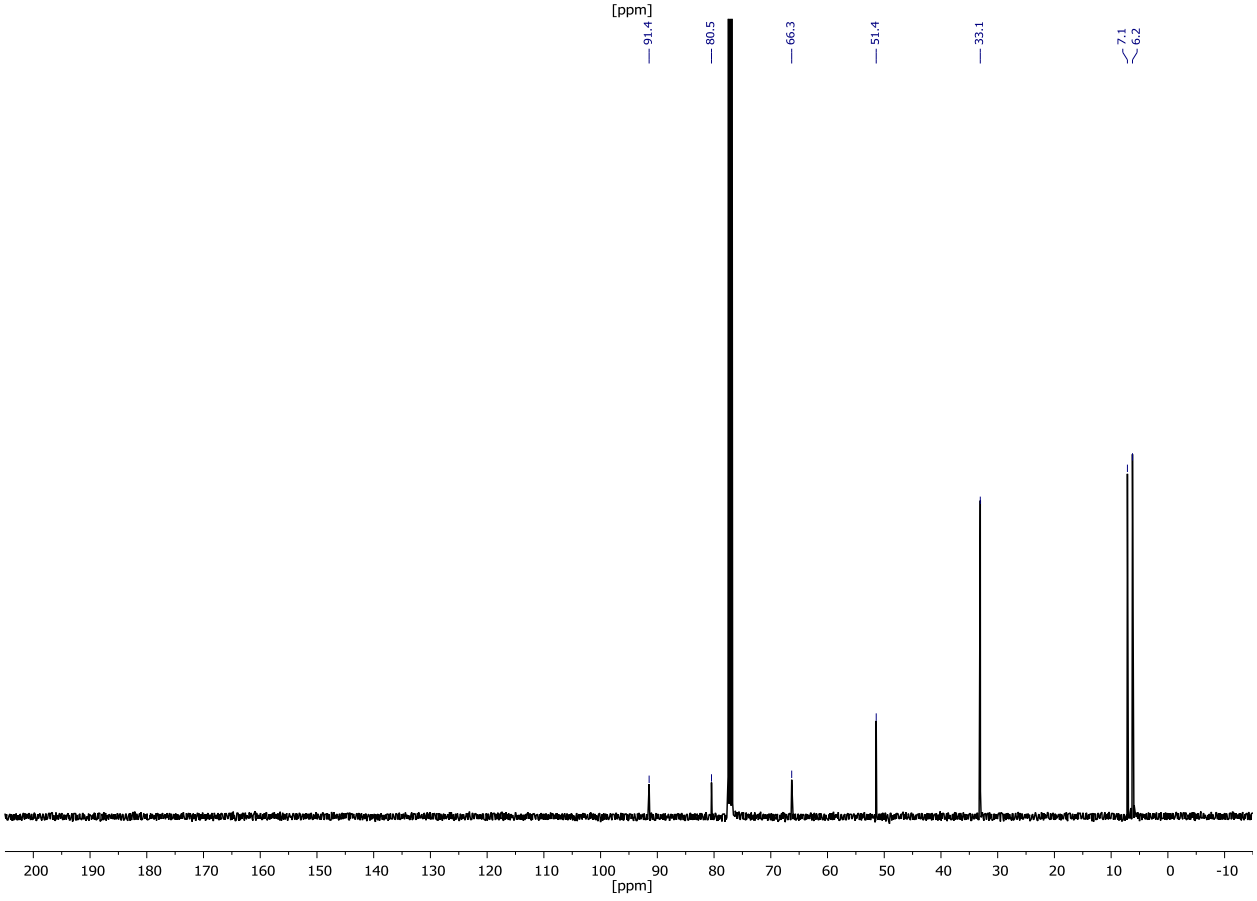
1.00
1.07
1.07
2.13
2.64
2.26
2.33
2.45
6.44
2.82
9.73
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
138.0
115.3
91.5
84.9
82.5
71.2
65.3
32.9
30.7
28.1
18.3
18.2
-1.3

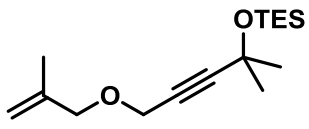

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTES
HO

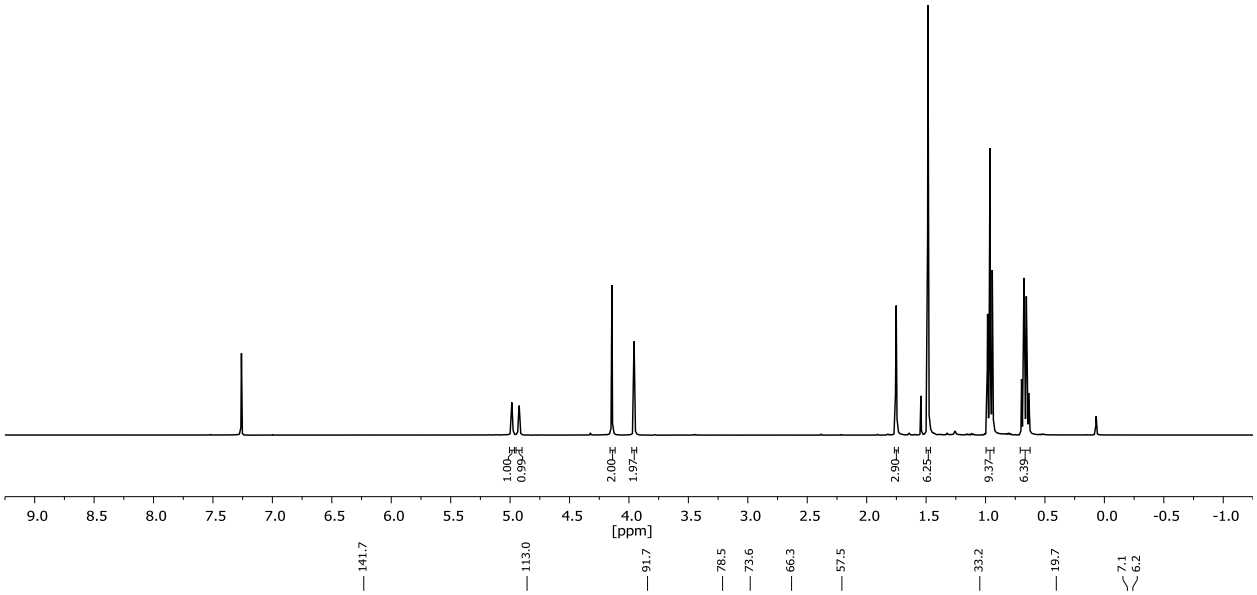
S60

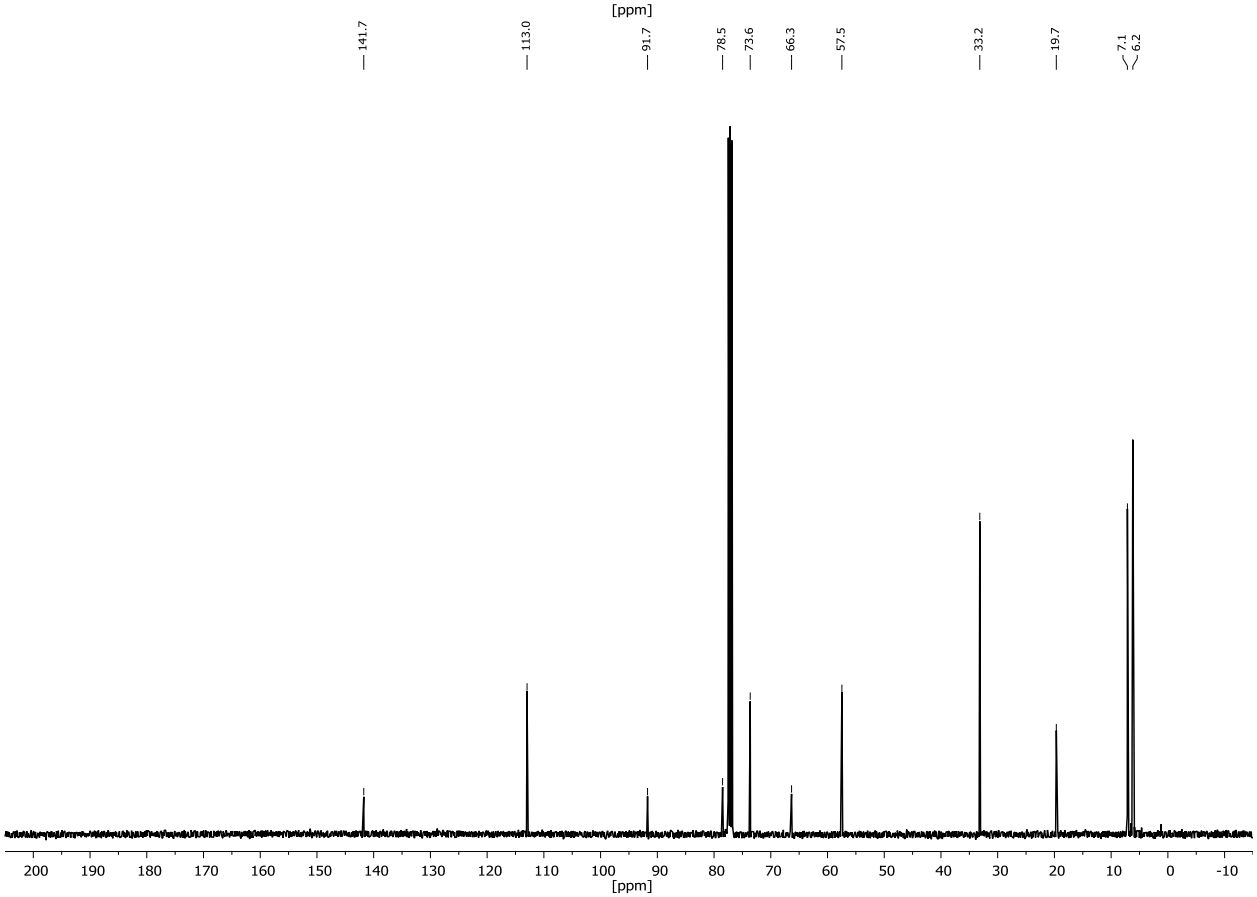
1.90
6.00
0.93
8.79
5.90
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

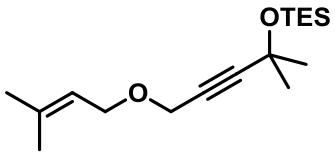

91.4
80.5
66.3
51.4
33.1
7.1
6.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTES
O

S61

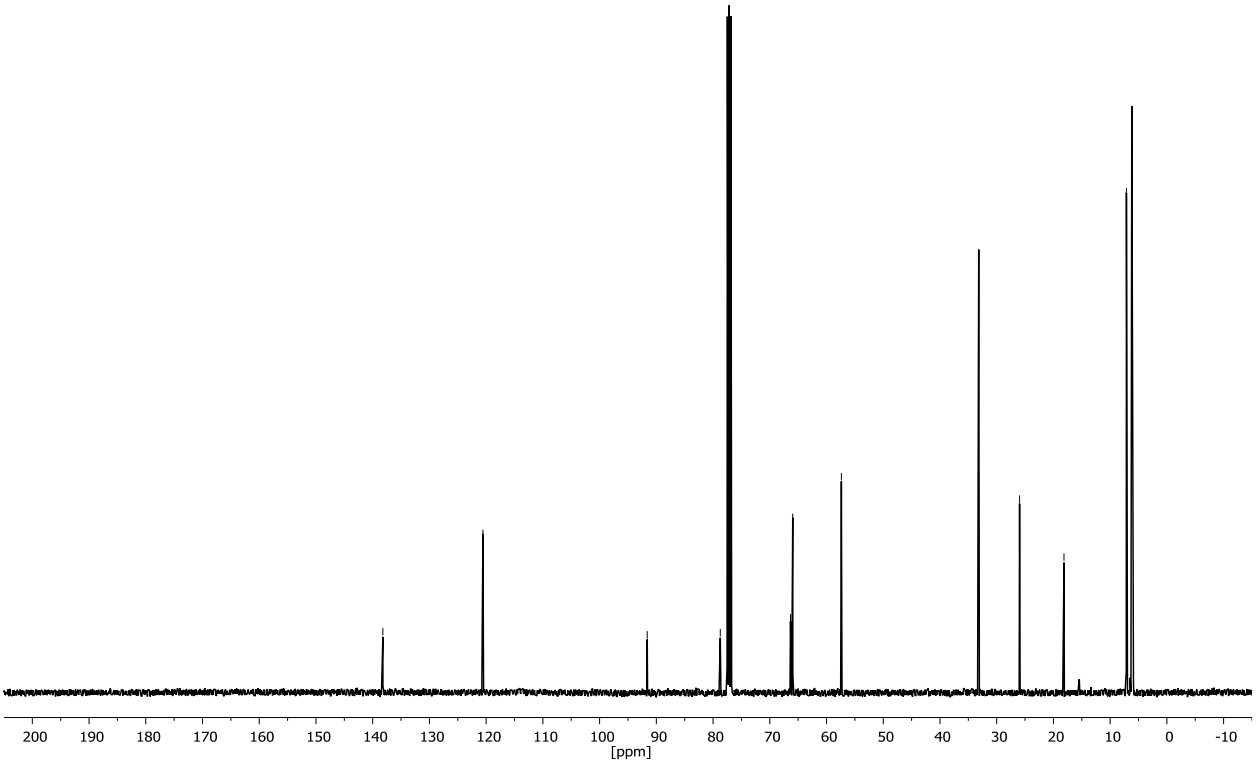

1.00
0.99
2.00
1.97
2.90
6.25
9.37
6.39
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

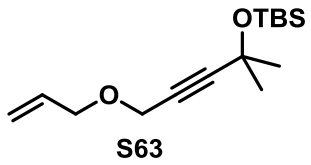

141.7
113.0
91.7
78.5
73.6
66.3
57.5
33.2
19.7
7.1
6.2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTES
O

S62

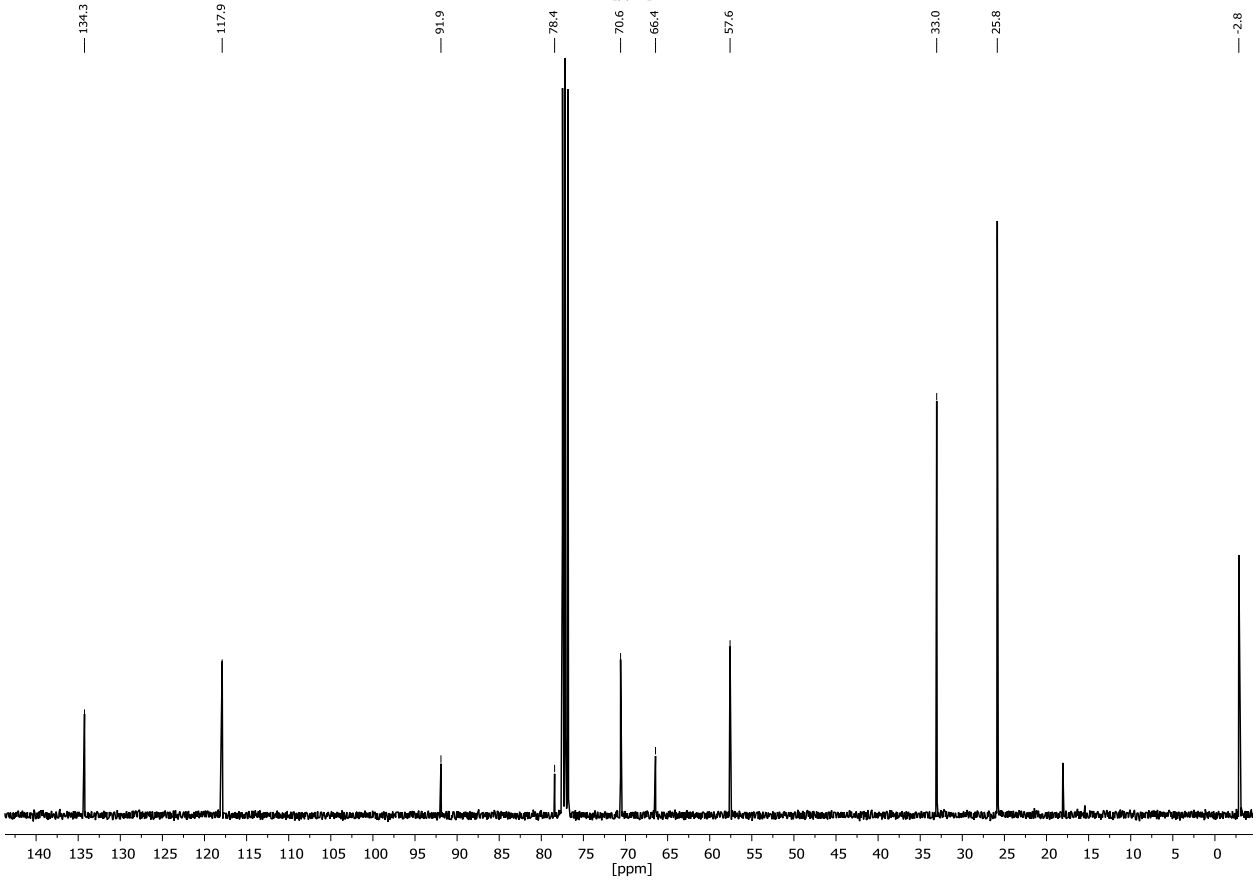
1.00
2.12
2.11
3.16
3.13
6.45
9.44
6.42
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
138.2
120.6
91.6
78.7
66.3
66.0
57.4
33.2
26.0
18.1
7.1
6.2

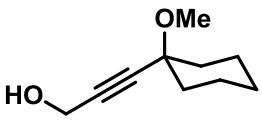

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTBS
O

S63

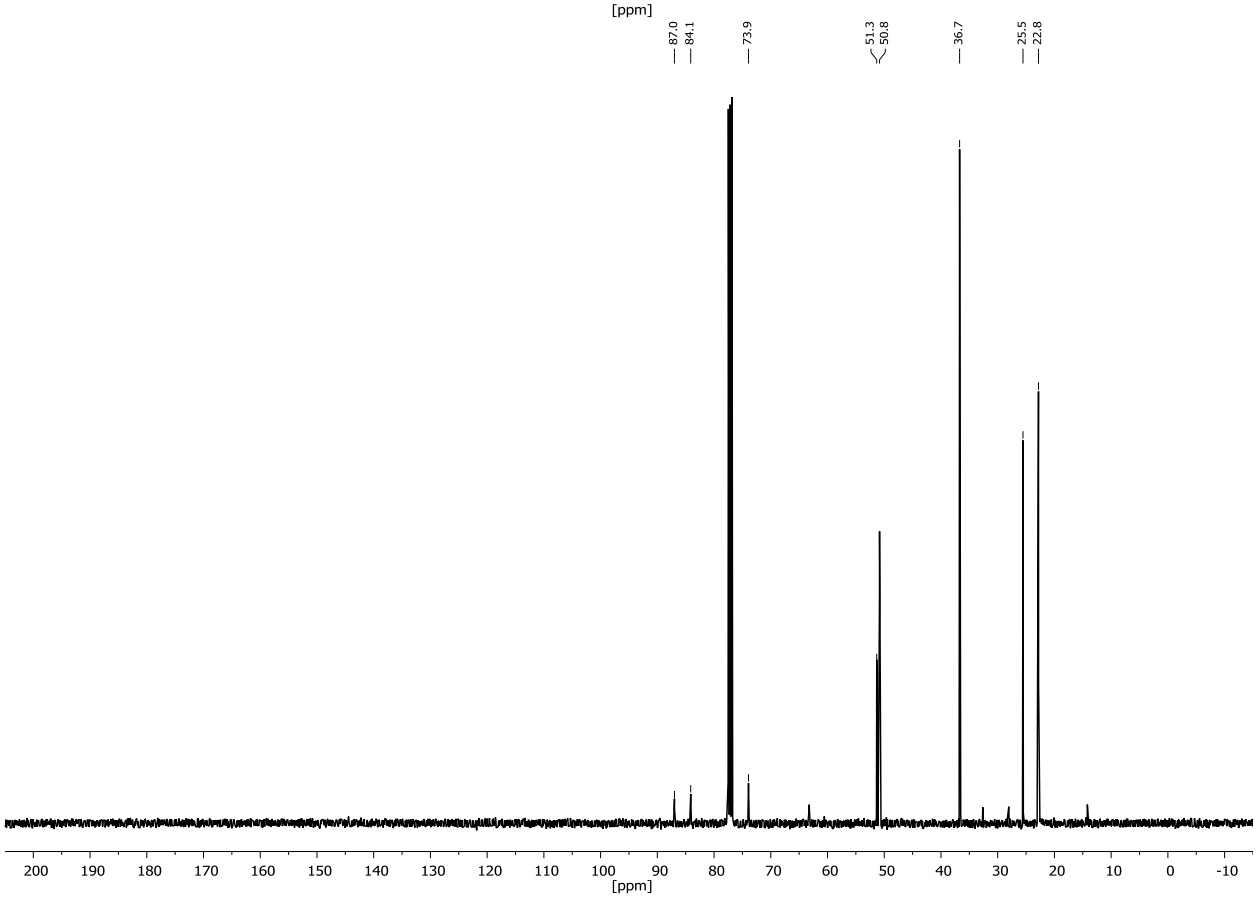
1.00
1.03
1.03
2.12
2.12
6.79
10.18
6.59
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

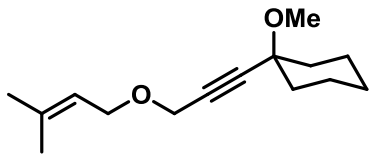

134.3
117.9
91.9
78.4
70.6
66.4
57.6
33.0
25.8
-2.8
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
[ppm]


OMe
HO

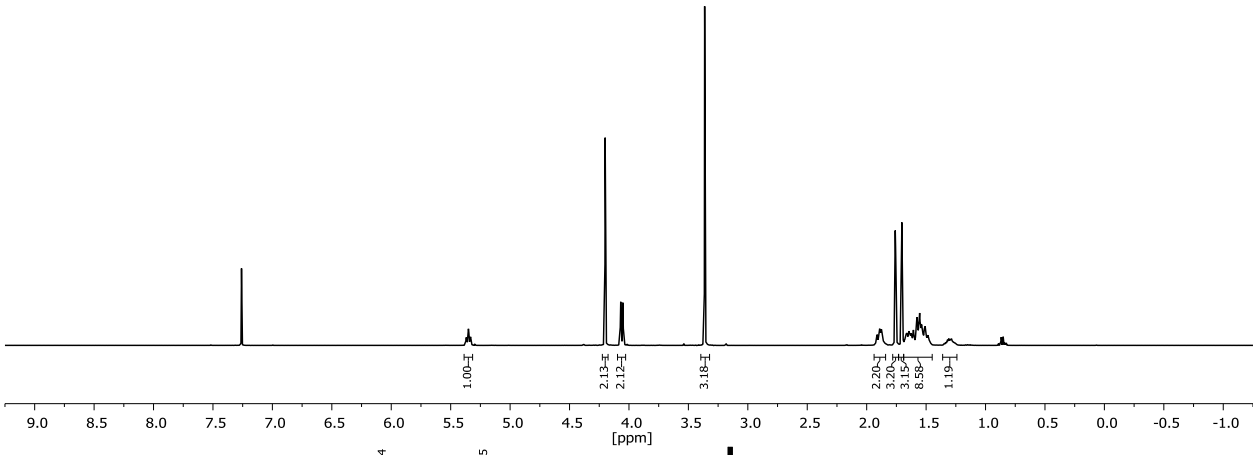
S64

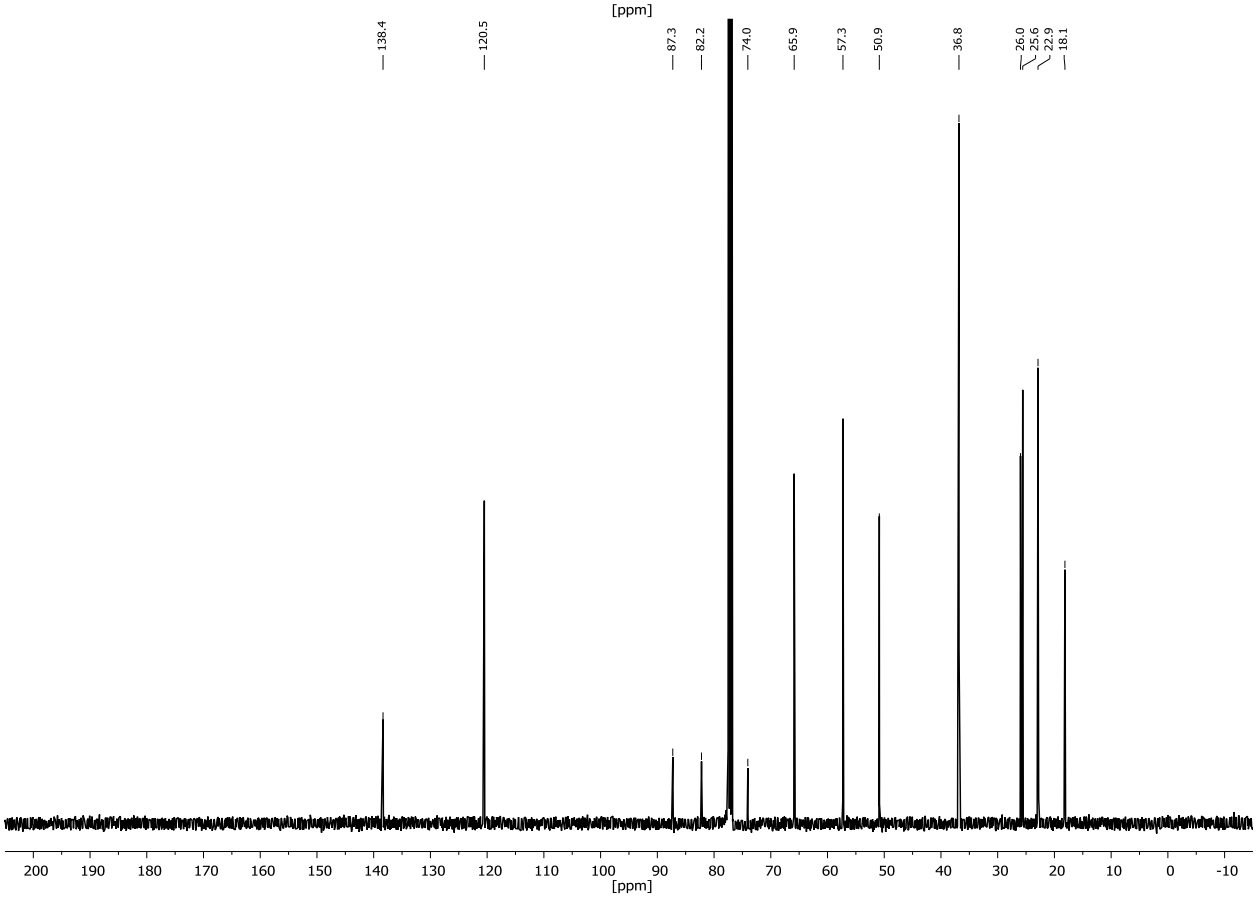
2.00
3.06
2.18
9.20
1.43
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

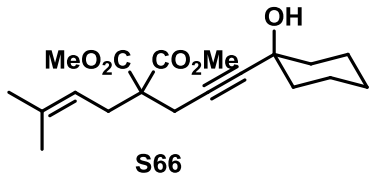

87.0
84.1
73.9
51.3
50.8
36.7
25.5
22.8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
O

S65

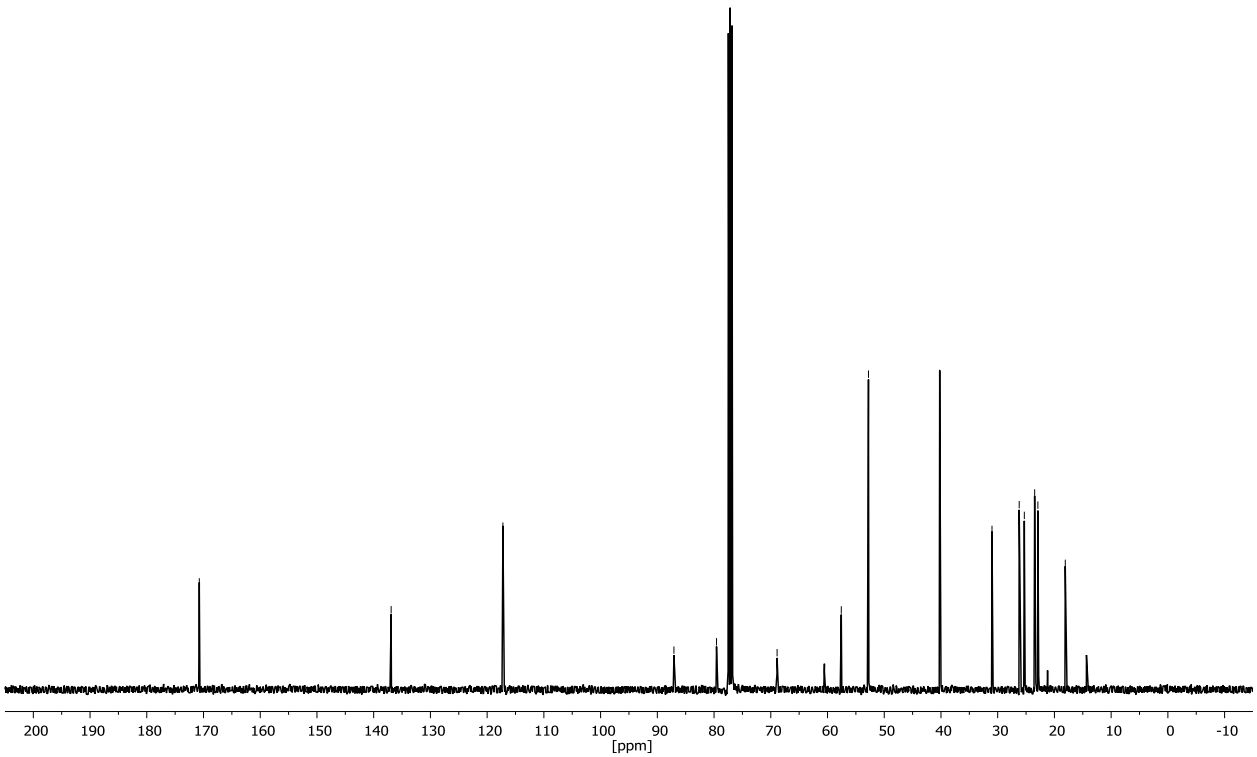

1.00
2.13
2.12
3.18
2.20
3.20
3.15
8.58
1.19
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

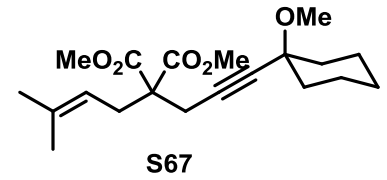

138.4
120.5
87.3
82.2
74.0
65.9
57.3
50.9
36.8
26.0
25.6
22.9
18.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OH
MeO2C
CO2Me

S66

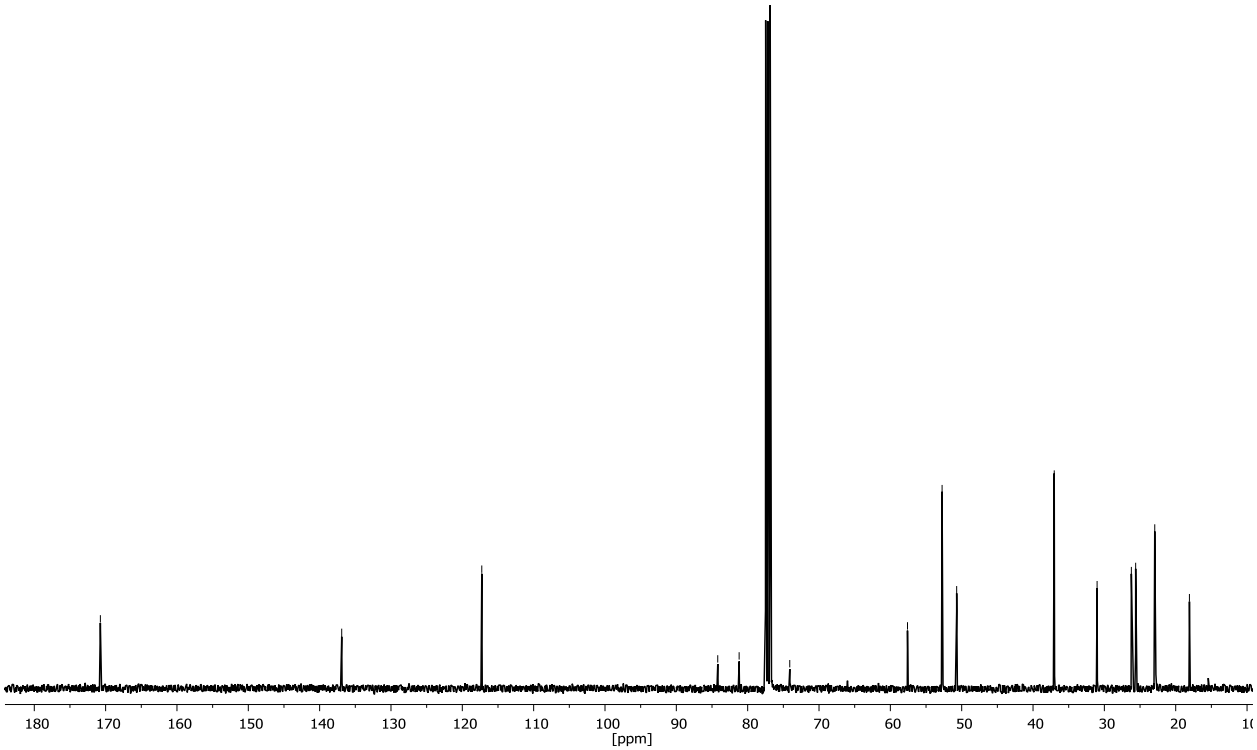
1.00
6.15
1.94
2.13
3.97
3.38
3.54
5.46
1.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
170.7
136.9
117.2
87.1
79.6
68.9
57.6
52.8
40.2
31.0
26.2
25.3
23.5
22.9
18.1

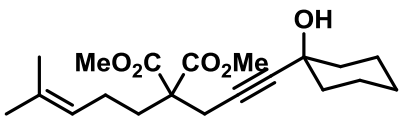

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
MeO2C
CO2Me

S67

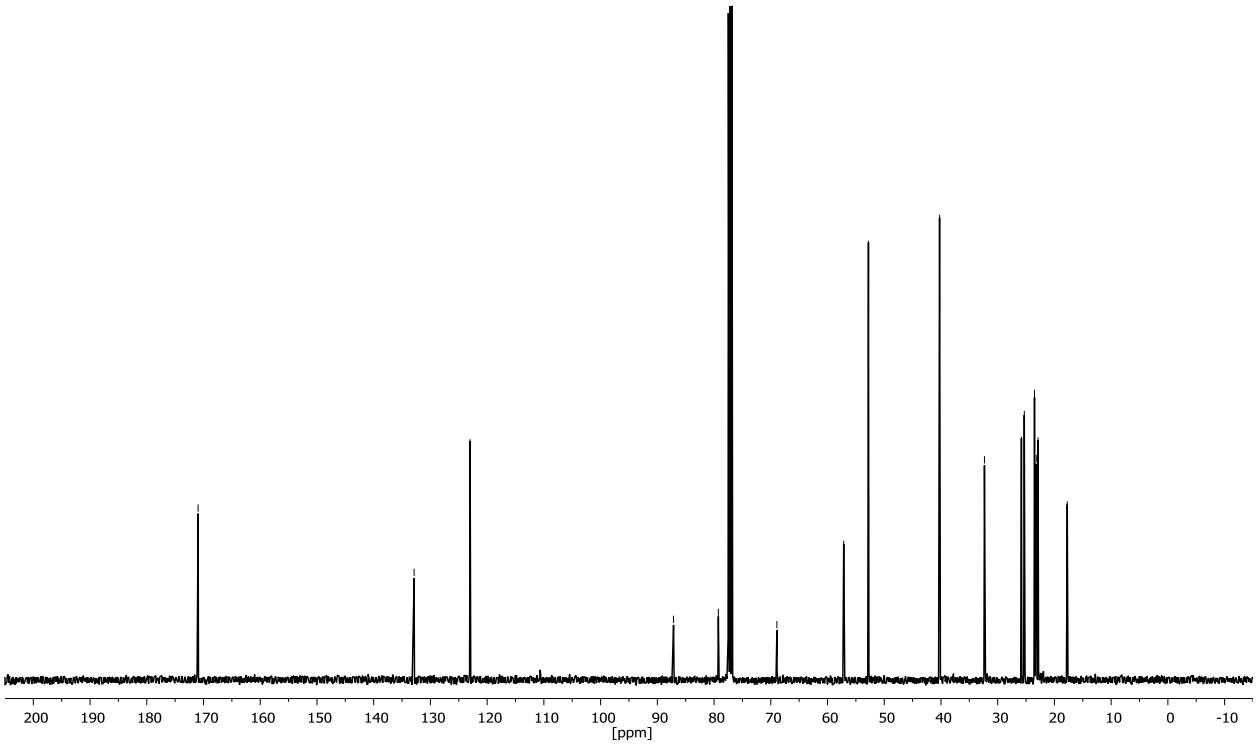
1.00
5.91
3.01
2.02
2.10
2.09
3.11
3.55
8.55
1.32
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
170.7
136.9
117.3
84.2
81.2
74.1
57.6
52.7
50.7
37.0
31.0
26.2
25.6
23.0
22.9
18.1

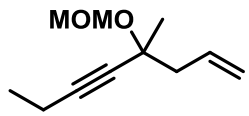

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
[ppm]


OH
MeO2C
CO2Me

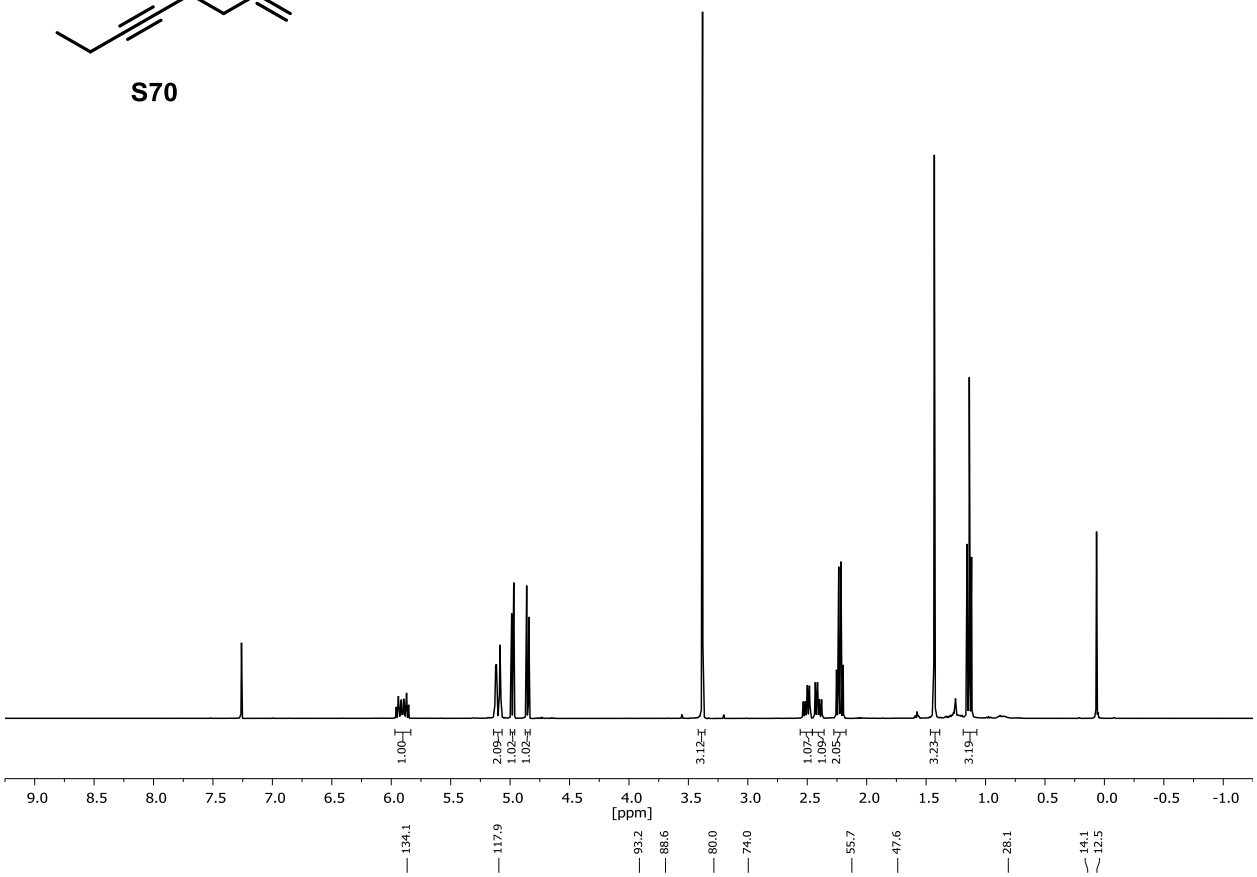
S69

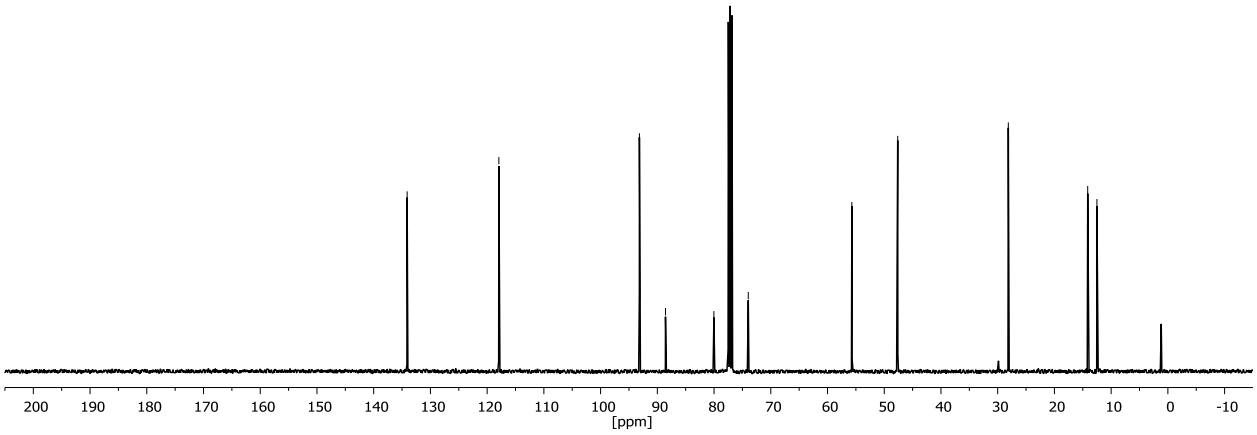
1.00
6.34
2.09
2.24
5.73
5.46
2.92
5.42
1.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
170.9
132.9
123.0
87.1
79.2
68.9
57.1
52.8
40.2
32.3
25.8
25.3
23.5
23.2
22.9
17.7

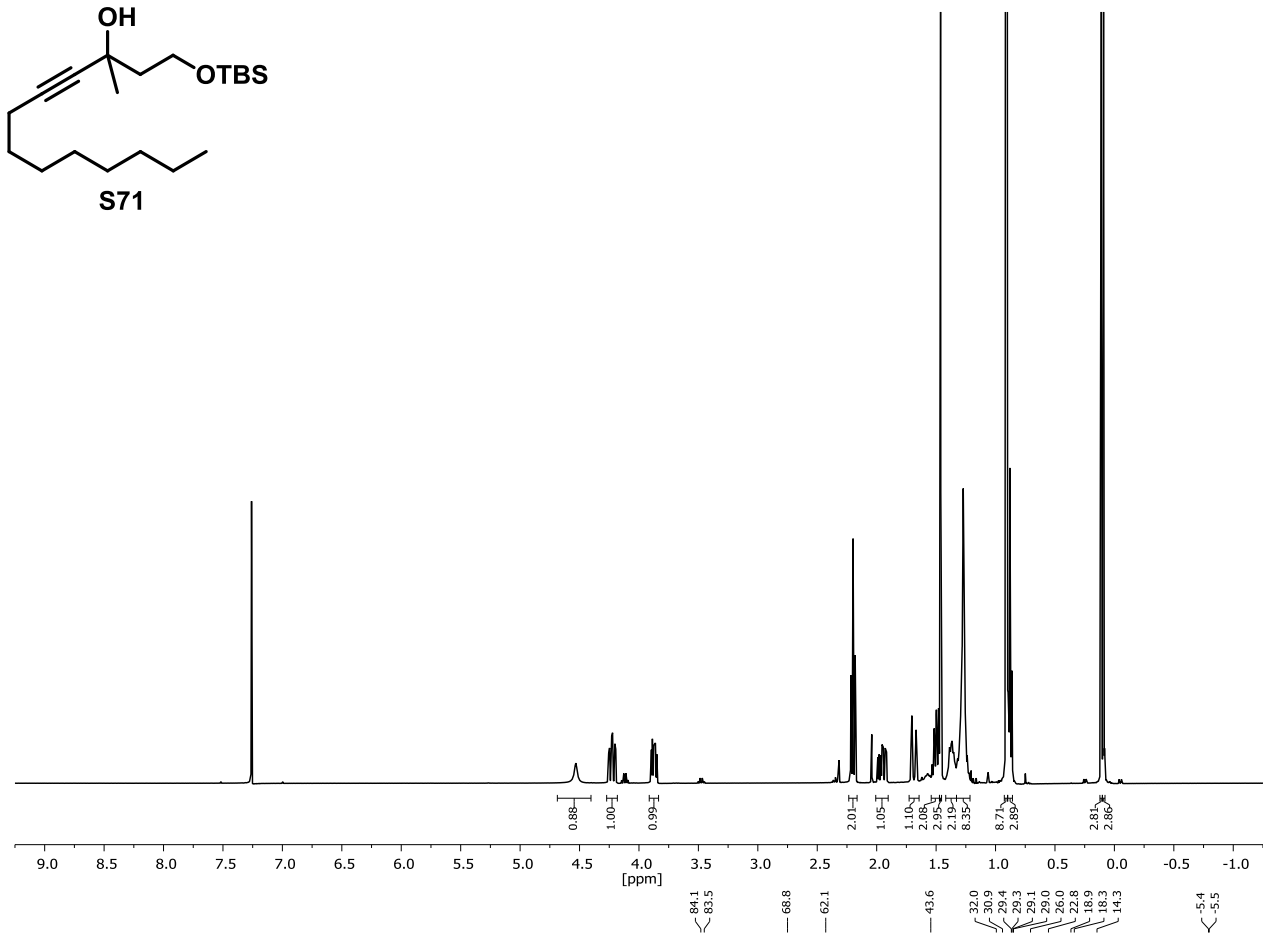

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

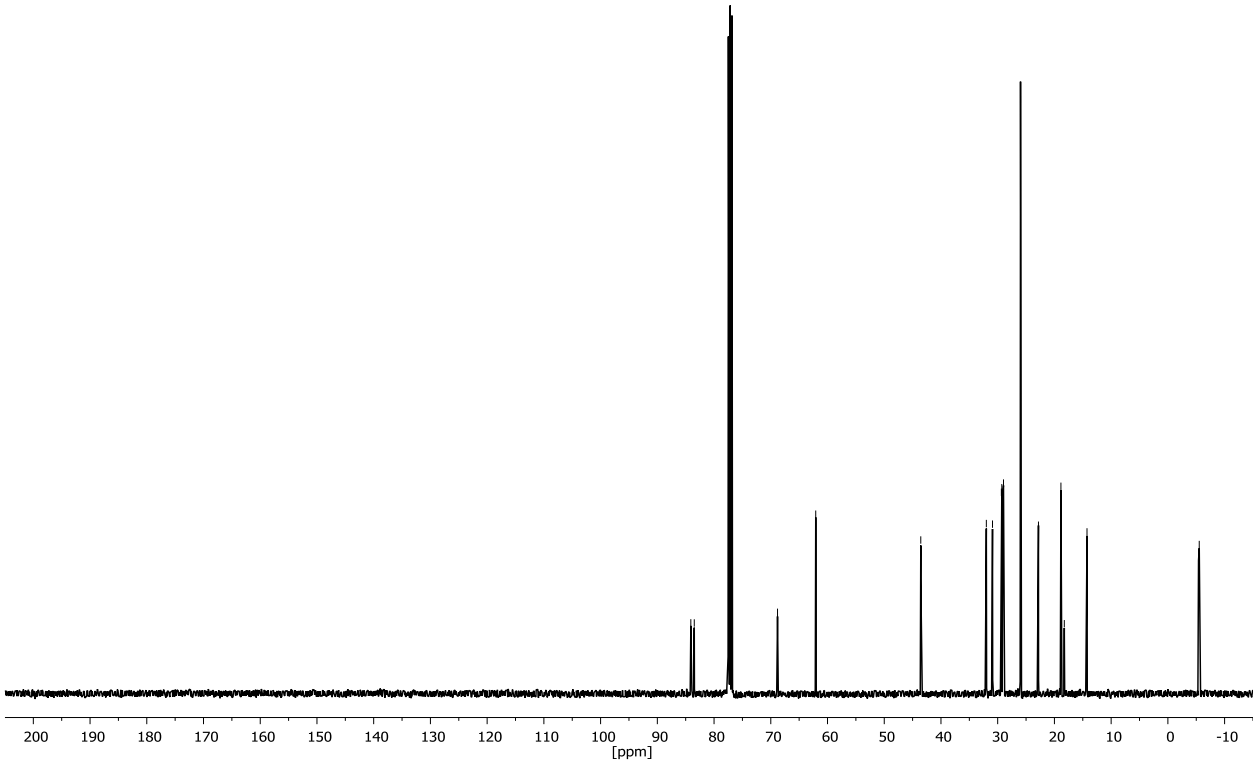

MOMO

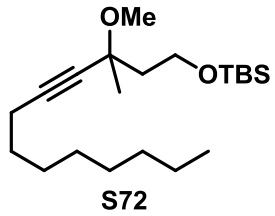
S70


1.00
2.09
1.02
1.02
3.12
1.07
1.09
2.05
3.23
3.19
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 -0.5 -1.0
[ppm]
134.1
117.9
93.2
88.6
80.0
74.0
55.7
47.6
28.1
14.1
12.5


200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

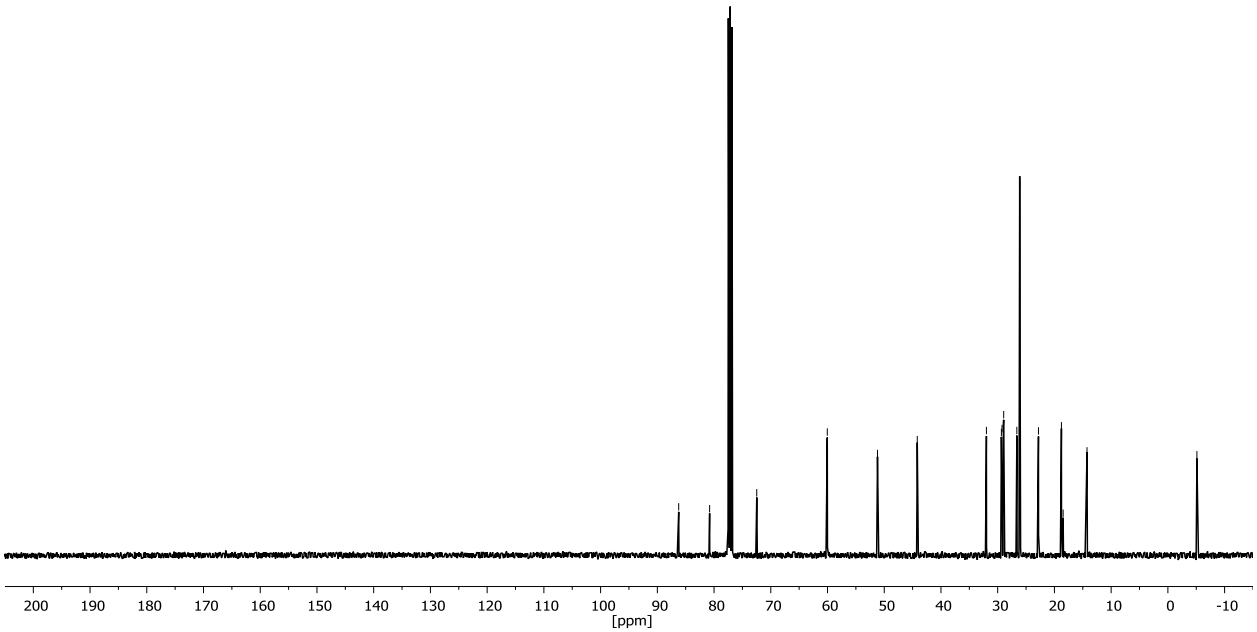

OH
OTBS
S71
0.88
1.00
0.99
2.01
1.05
1.10
2.08
2.95
2.19
8.35
8.71
2.89
2.81
2.86
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
84.1
83.5
68.8
62.1
43.6
32.0
30.9
29.4
29.3
29.1
29.0
26.0
22.8
18.9
18.3
14.3
-5.4
-5.5

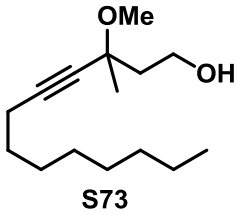

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
OTBS

S72

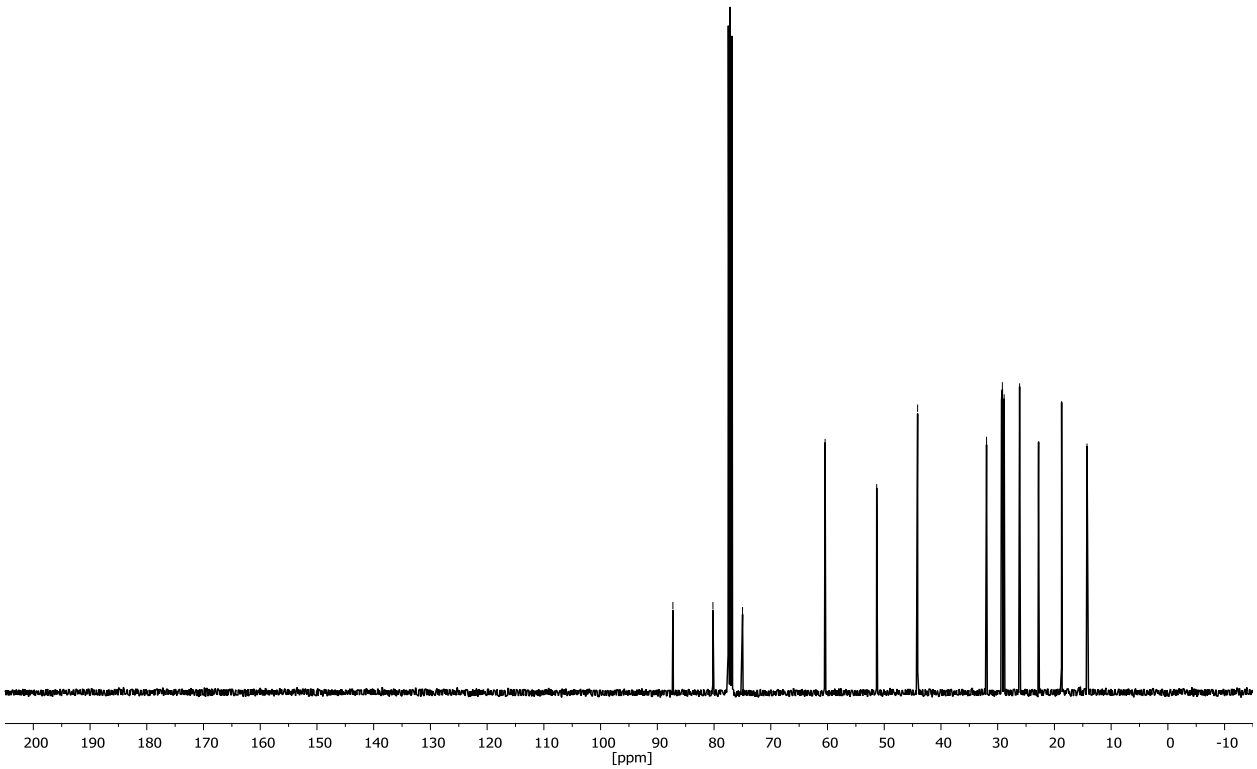
2.00
2.99
2.05
2.07
2.20
5.30
8.38
12.05
5.87
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
86.2
80.8
72.5
60.0
51.2
44.2
32.0
29.4
29.2
29.0
28.9
26.6
26.1
22.8
18.8
18.5
14.3
-5.1
-5.1

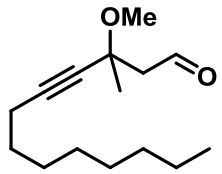

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
OH

S73

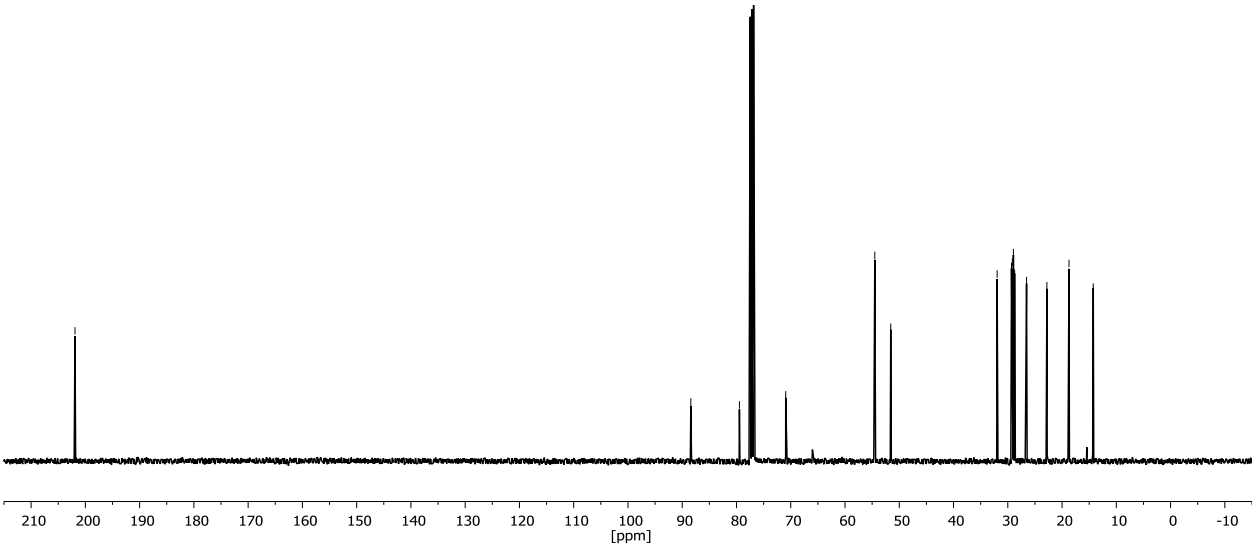
1.00
0.99
3.00
2.04
1.01
1.03
1.97
3.06
2.06
8.22
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
87.3
80.2
75.0
60.4
51.3
44.1
32.0
29.3
29.2
29.0
28.9
26.1
22.8
18.7
14.3

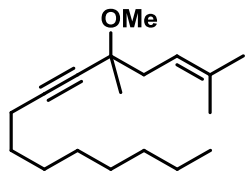

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
O

S74

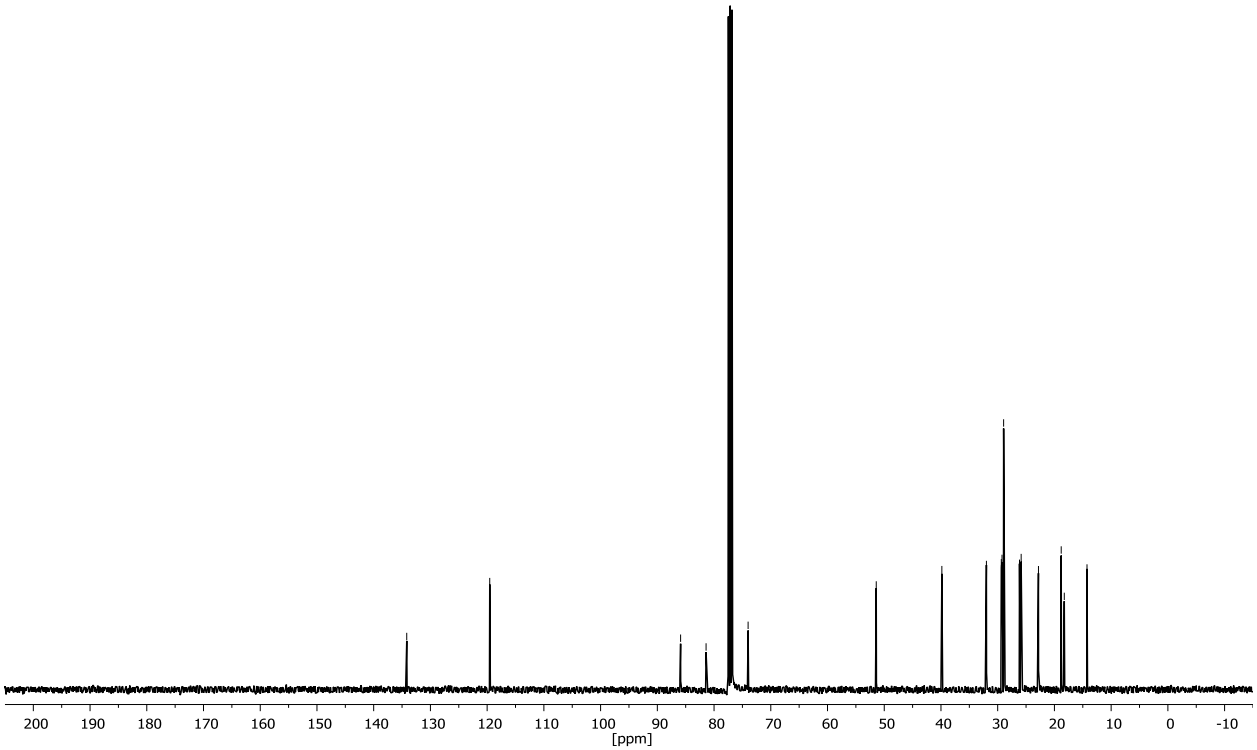
0.85
2.91
2.00
2.02
2.03
3.13
2.06
8.26
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
201.9
88.4
79.5
70.9
54.5
51.6
32.0
29.3
29.2
29.0
28.7
26.5
22.8
18.7
14.3

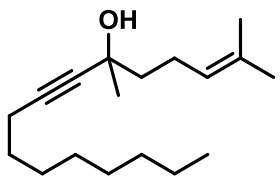

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

S75

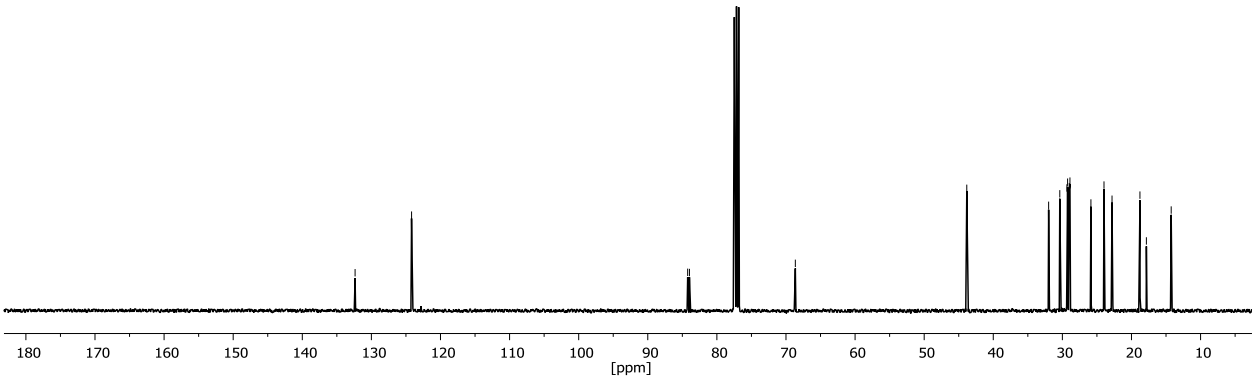
1.00
3.07
2.14
2.07
3.07
2.99
2.27
2.13
3.19
8.49
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
134.2
119.5
85.9
81.4
74.0
51.4
39.8
32.0
29.4
29.2
29.0
26.2
25.9
22.8
18.8
18.3
14.3

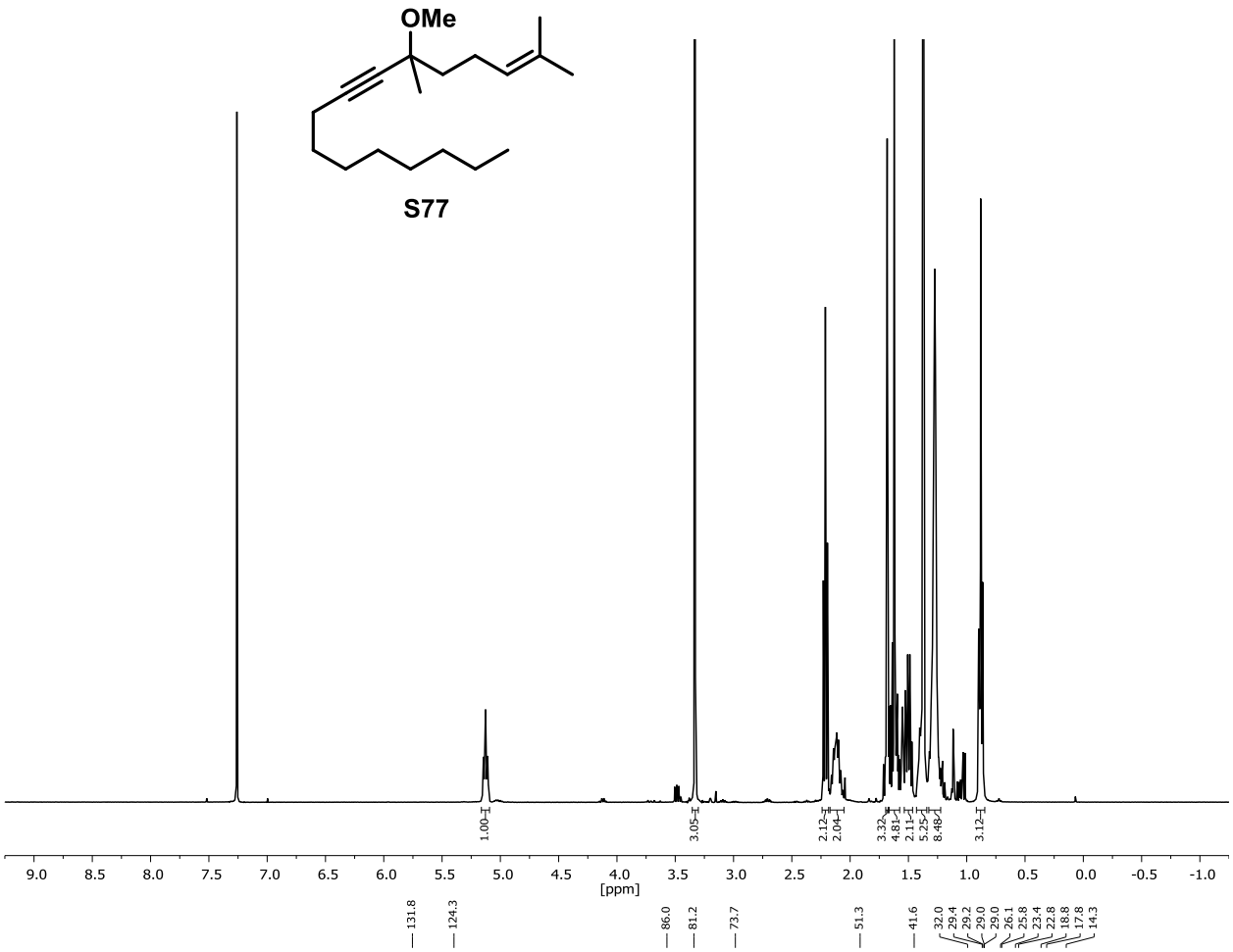

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

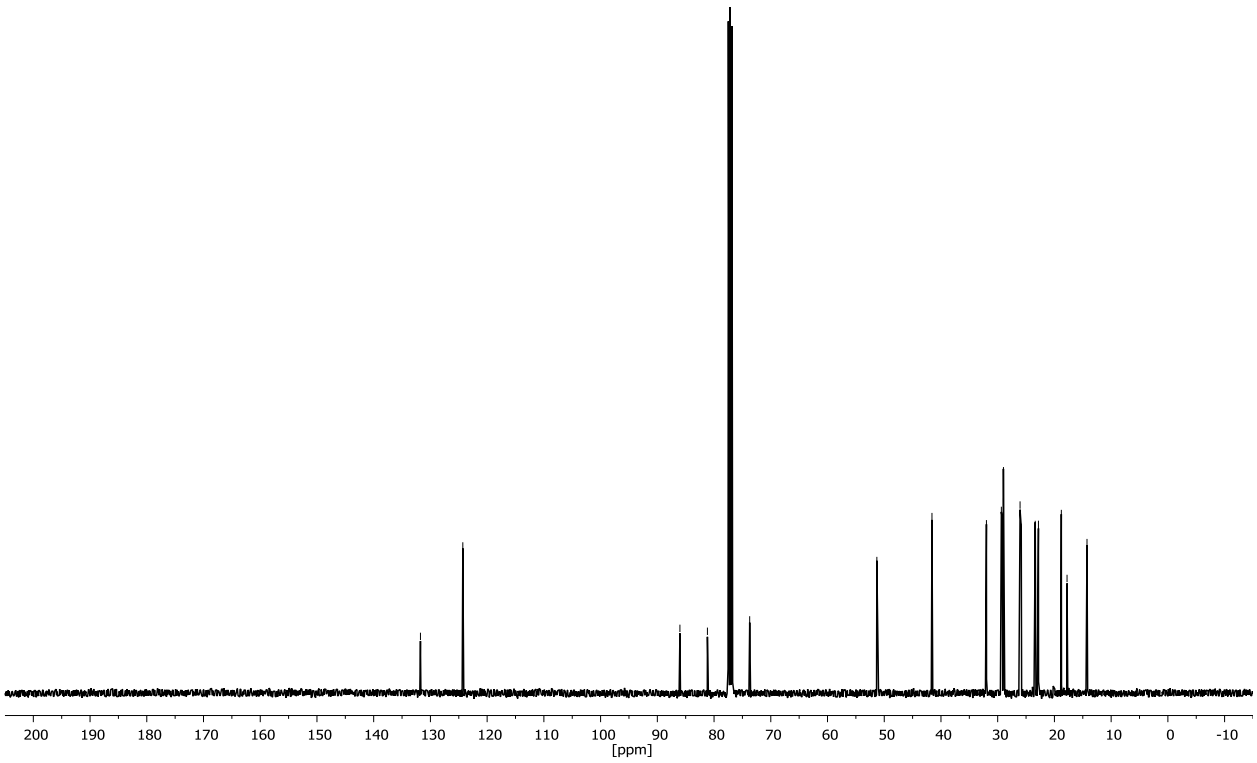

OH

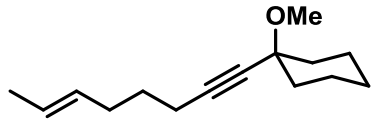
S76

1.00
1.09
2.71
0.95
3.01
1.11
3.90
2.00
3.31
2.18
8.80
3.10
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 -0.5 -1.0
[ppm]
132.4
124.2
84.2
84.0
68.6
43.8
32.0
30.4
29.3
29.2
29.0
28.9
25.9
24.0
22.8
18.8
17.8
14.3

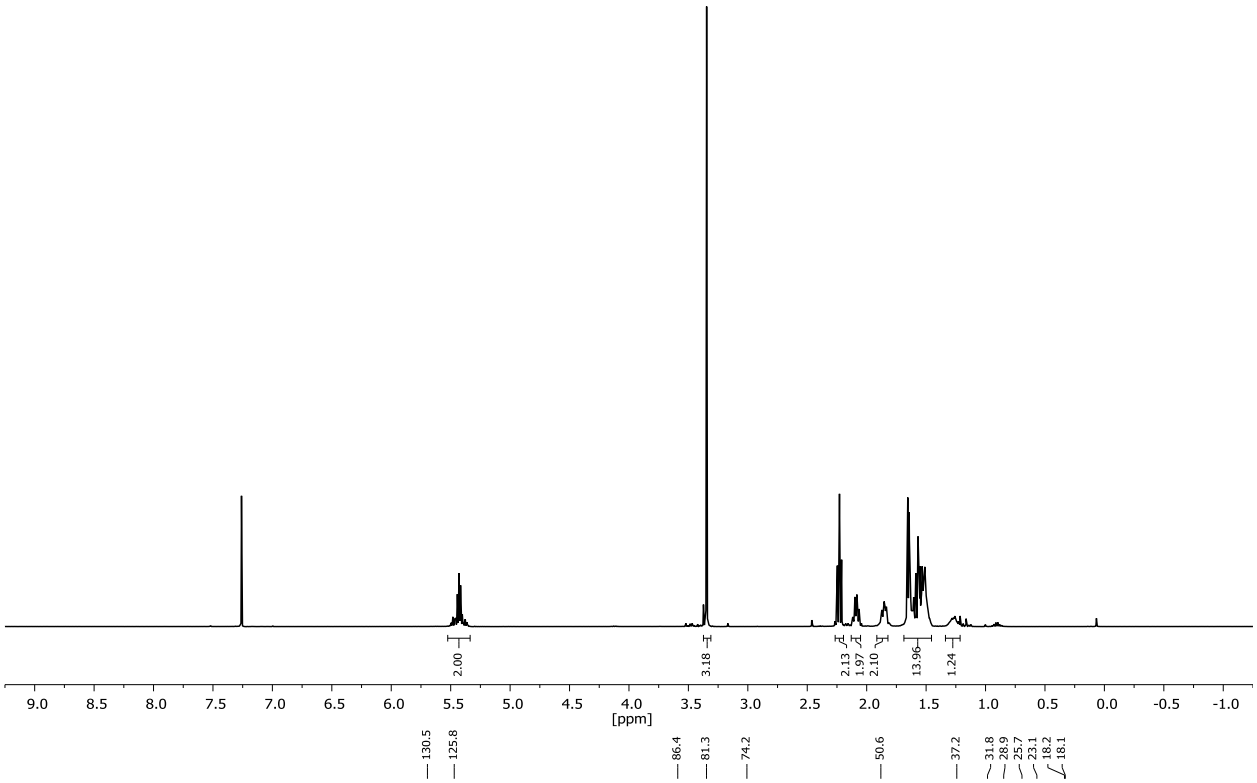

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
[ppm]

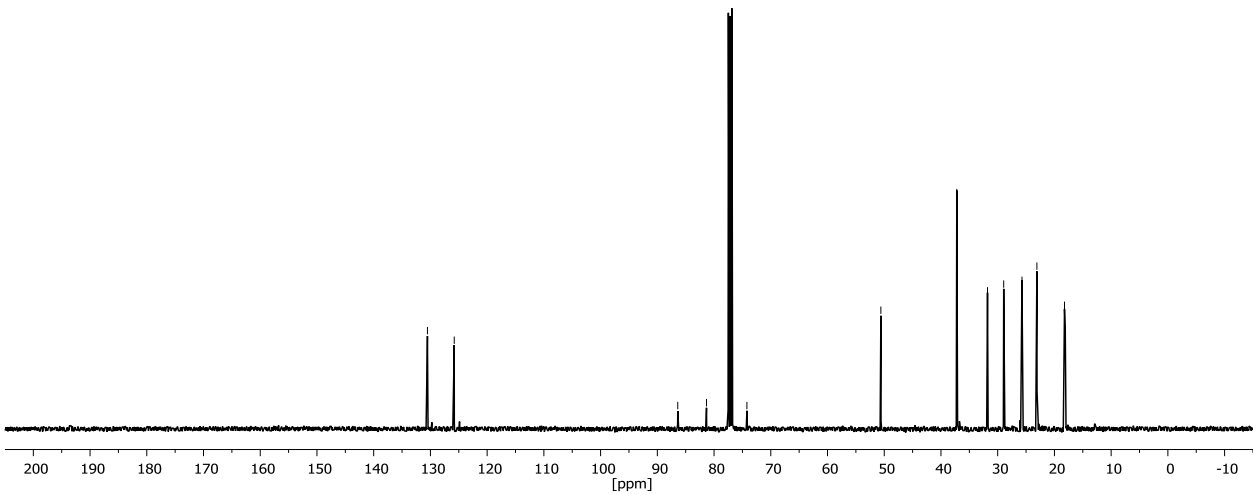

OMe
S77
1.00
3.05
2.12
2.04
3.32
4.81
2.11
5.25
8.48
3.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
131.8
124.3
86.0
81.2
73.7
51.3
41.6
32.0
29.4
29.2
29.0
29.0
26.1
25.8
23.4
22.8
18.8
17.8
14.3

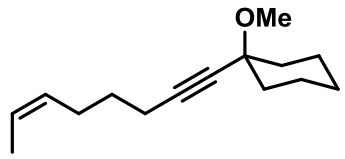

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

1b

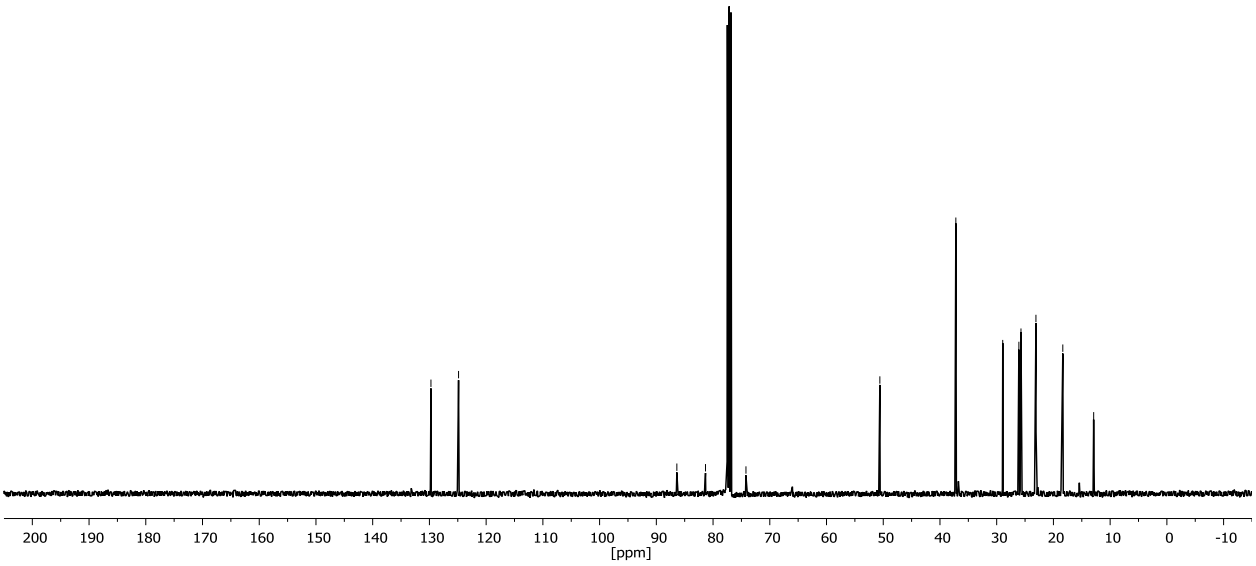

2.00
3.18
2.13
1.97
2.10
13.96
1.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
[ppm]
130.5
125.8
86.4
81.3
74.2
50.6
37.2
31.8
28.9
25.7
23.1
18.2
18.1

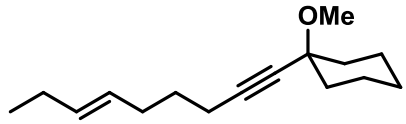

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
[ppm]


OMe

1c

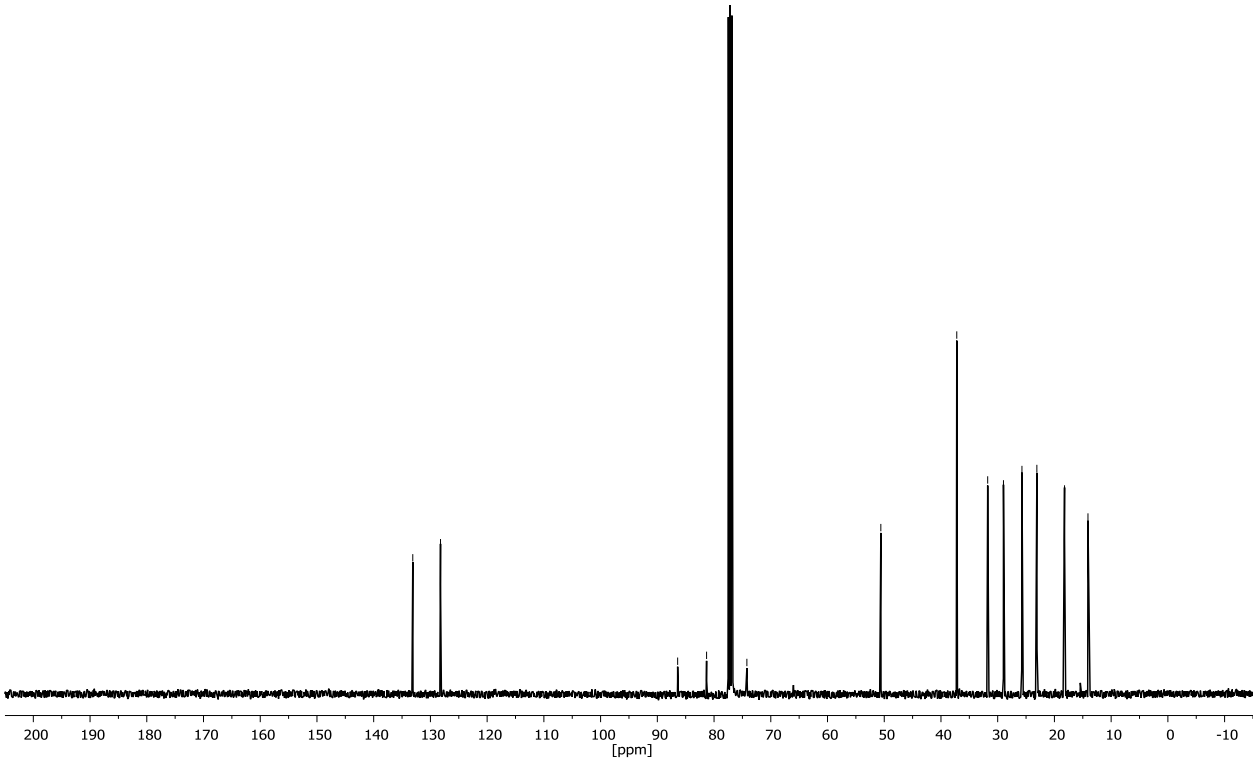
1.00
1.01
3.19
2.15
2.15
2.17
14.47
1.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
[ppm]
129.7
124.9
86.4
81.3
74.2
50.6
37.2
28.9
26.1
25.7
23.1
18.3
12.9

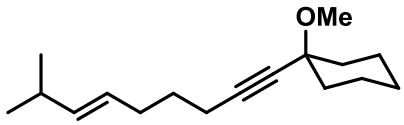

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
[ppm]


OMe

1d

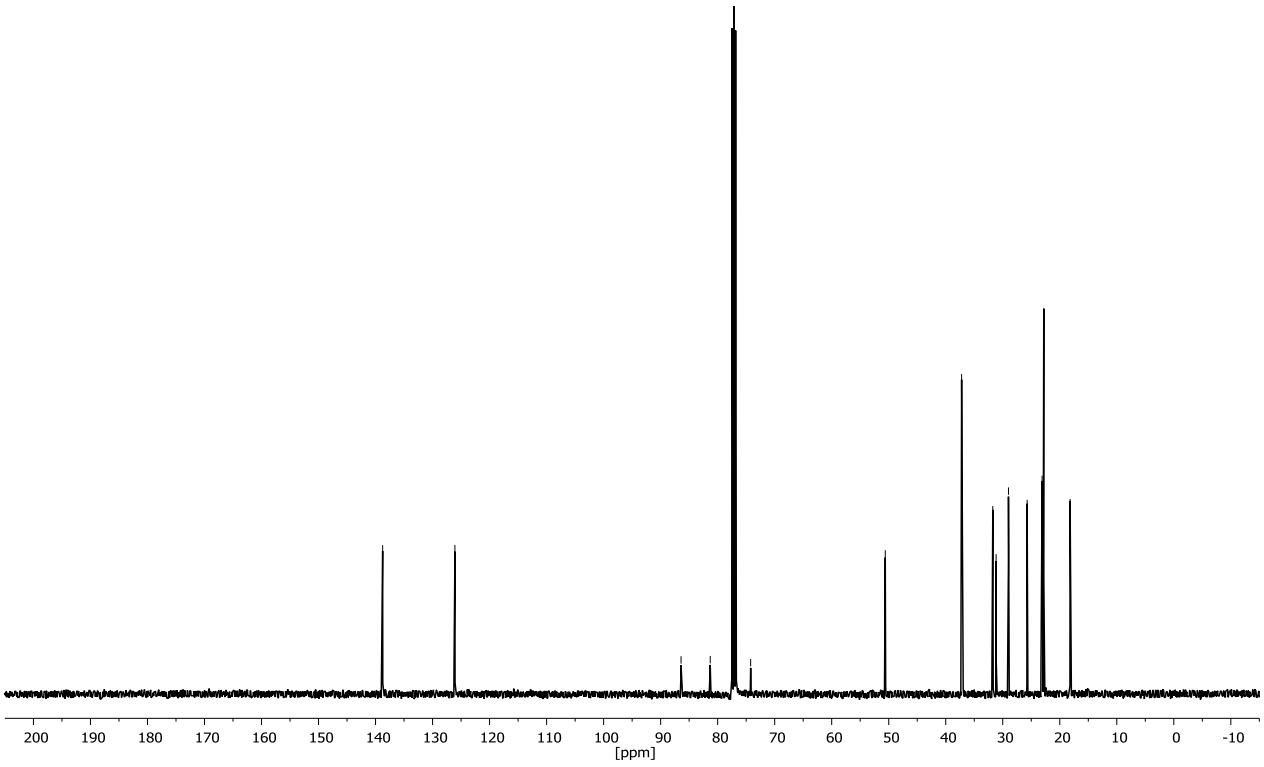
1.00
1.01
3.09
2.14
2.13
2.13
2.06
10.84
1.07
3.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
133.1
128.2
86.4
81.3
74.2
50.6
37.2
31.8
29.0
25.8
25.7
23.1
18.2
14.1

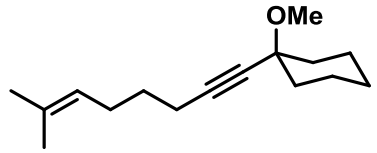

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

1e

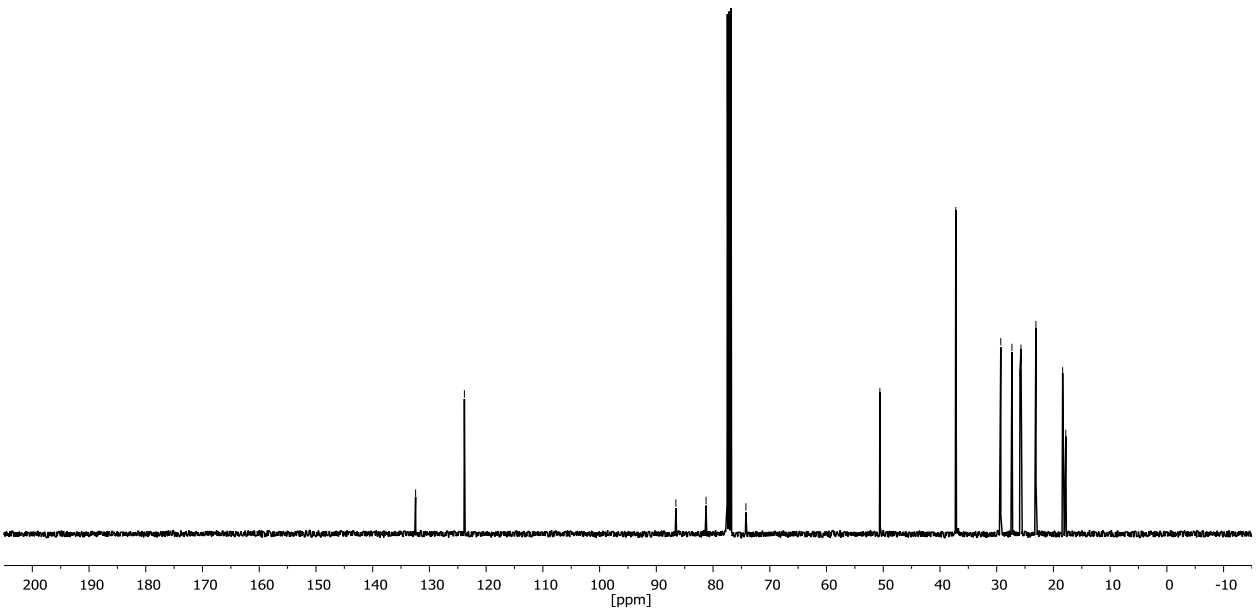
1.00
1.06
3.13
3.21
2.16
2.13
11.12
1.16
6.38
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
138.8
126.1
86.4
81.3
74.2
50.6
37.2
31.7
31.2
29.0
25.7
23.1
22.8
18.2

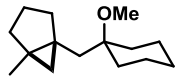

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

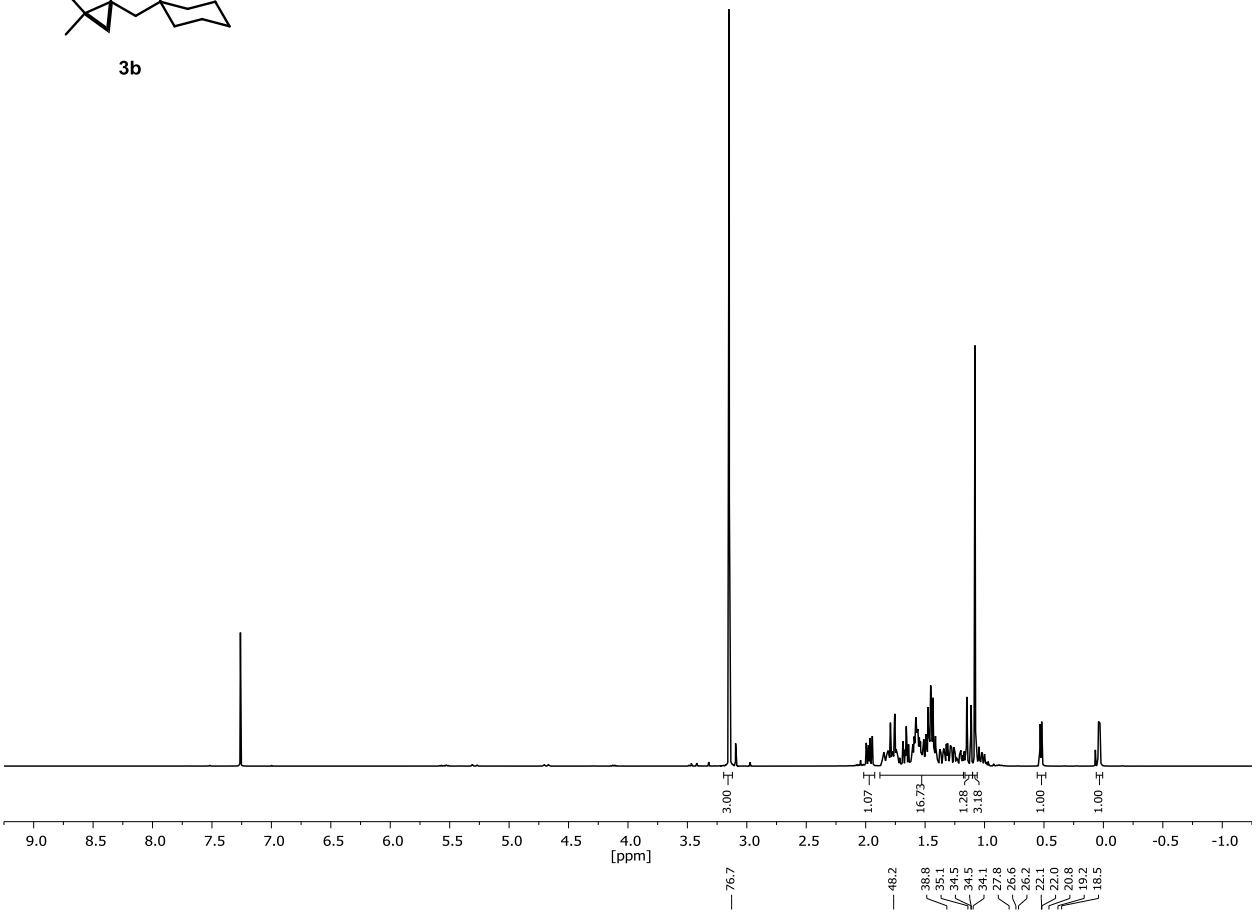
1f

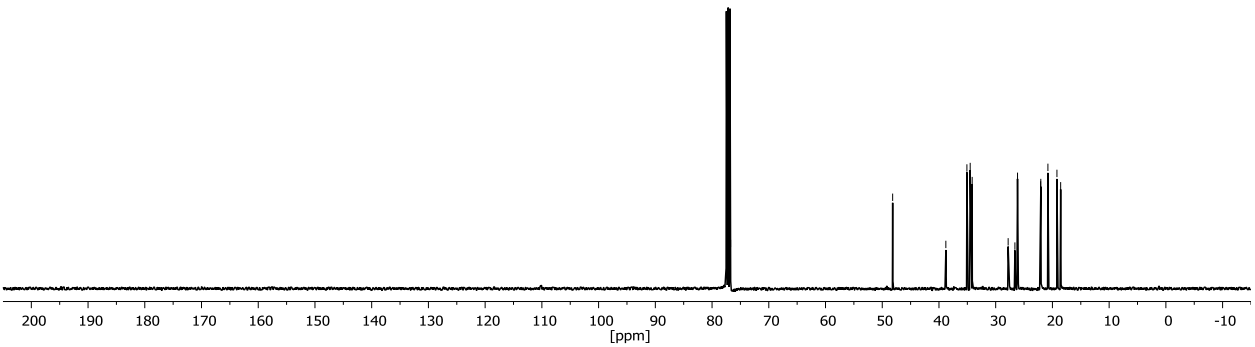
1.00
3.08
2.11
2.14
2.09
3.14
3.39
8.46
1.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
132.4
123.8
86.6
81.2
74.2
50.6
37.2
29.3
27.3
25.9
25.7
23.1
18.4
17.8

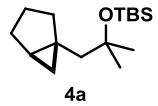

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

3b

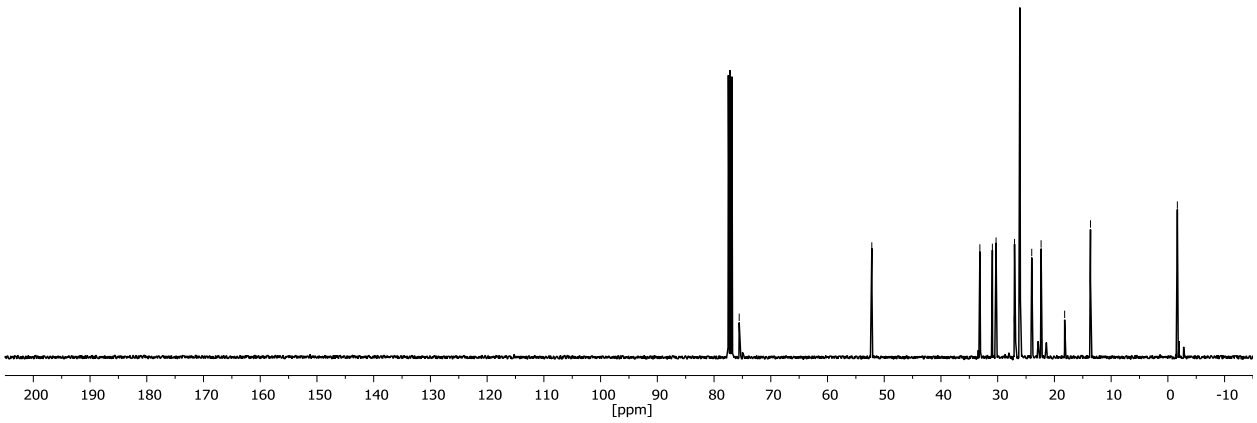

3.00
1.07
16.73
1.28
3.18
1.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
76.7
48.2
38.8
35.1
34.5
34.5
34.1
27.8
26.6
26.2
22.1
22.0
20.8
19.2
18.5

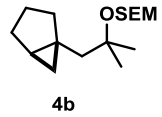

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTBS

4a

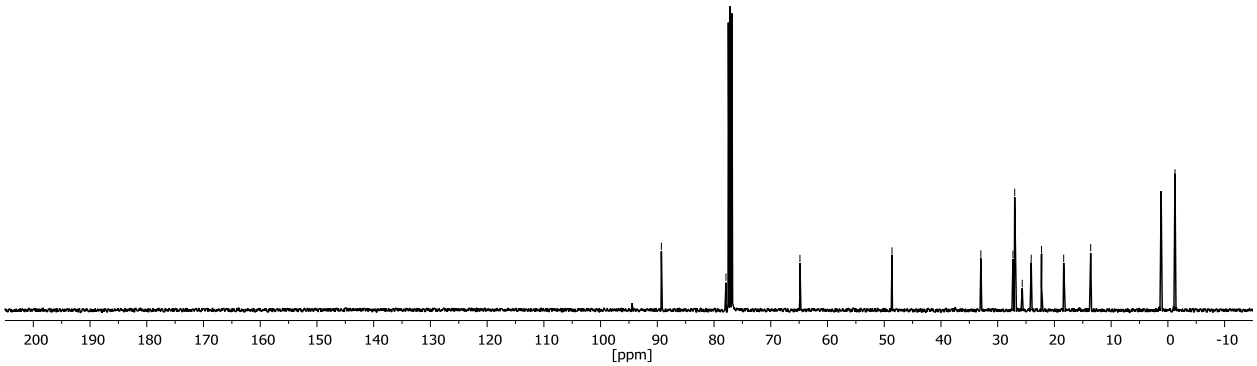
1.00
1.02
4.44
1.18
2.97
3.12
1.27
10.61
0.99
1.01
2.88
2.81
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
[ppm]
75.6
52.2
33.1
30.9
30.3
27.1
27.0
26.1
26.0
24.0
22.3
18.2
13.6
-1.7

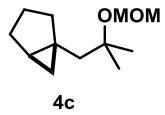

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
[ppm]


OSEM

4b

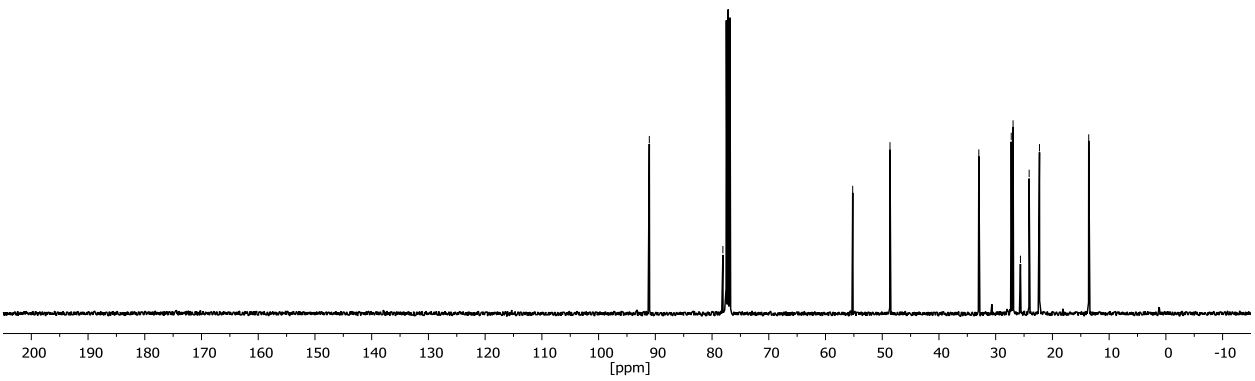
2.05
2.62
1.00
1.04
4.72
1.41
2.93
3.37
1.50
2.65
1.09
0.99
0.99
8.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
89.3
77.9
64.9
48.6
33.0
27.3
27.0
25.7
24.1
22.3
18.4
13.6
-1.3

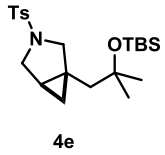

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMOM

4c

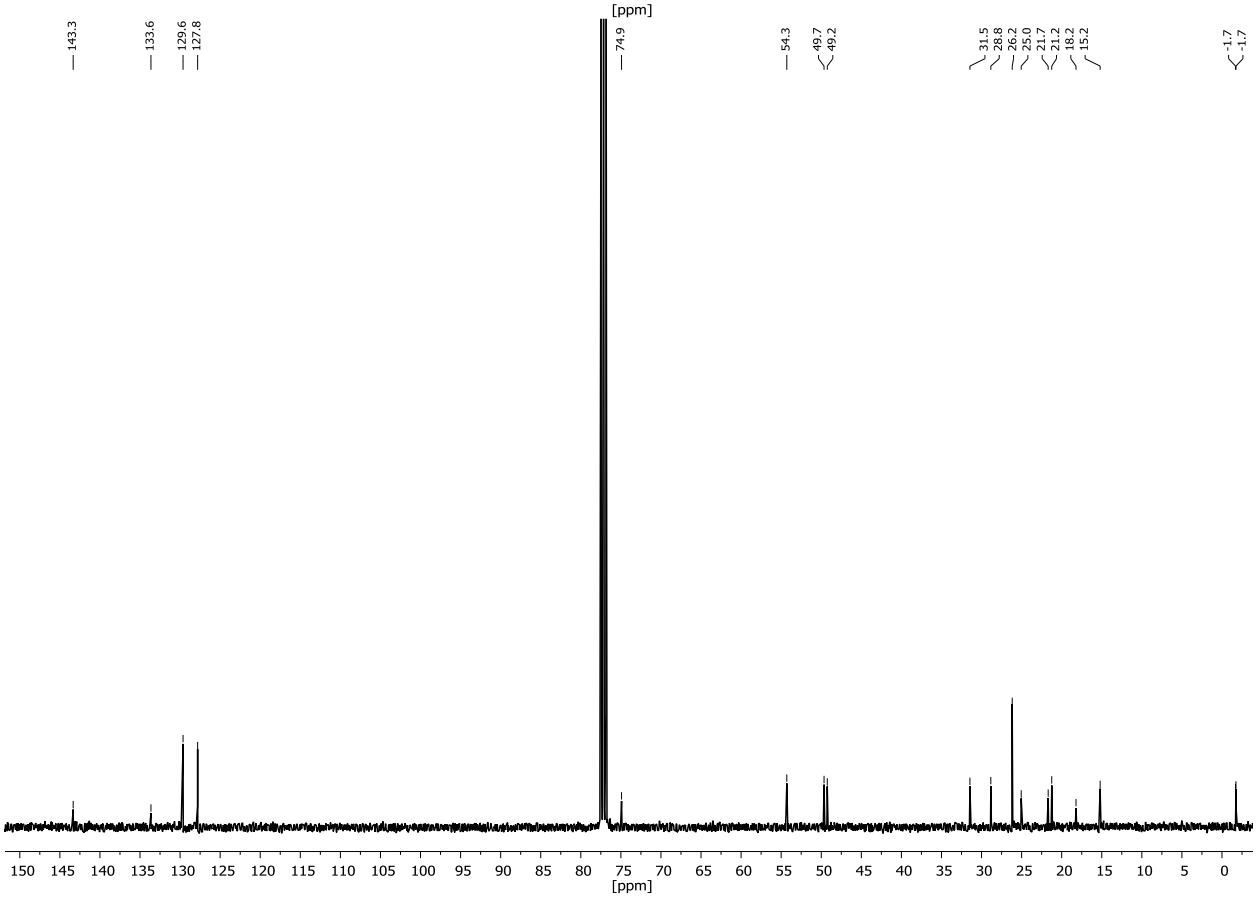
2.00
3.01
1.03
1.09
4.87
1.29
3.10
2.97
1.15
0.98
1.03
0.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
91.1
78.1
55.2
48.6
33.0
27.3
27.0
26.9
25.6
24.1
22.3
13.6

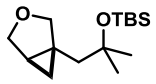

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


Ts
N
OTBS

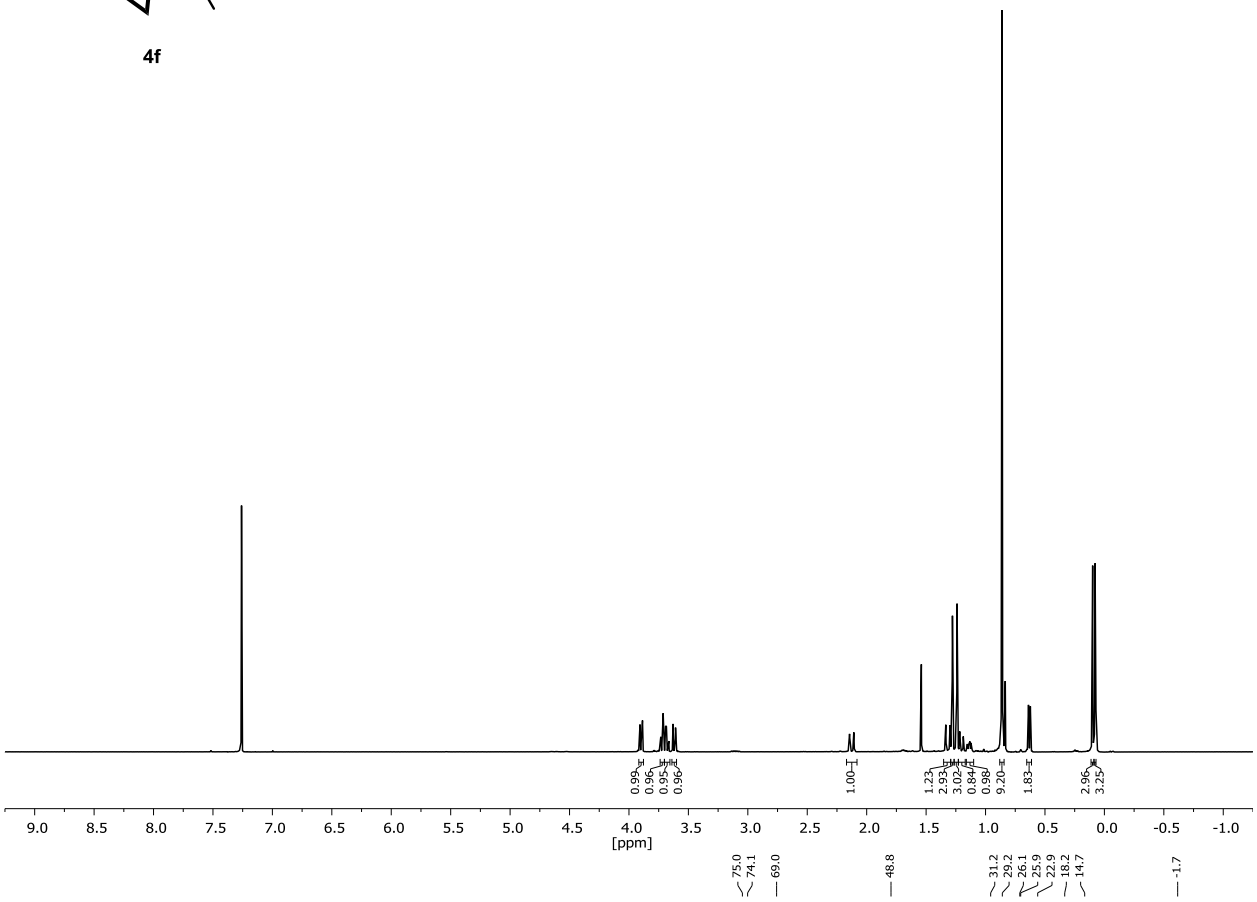
4e

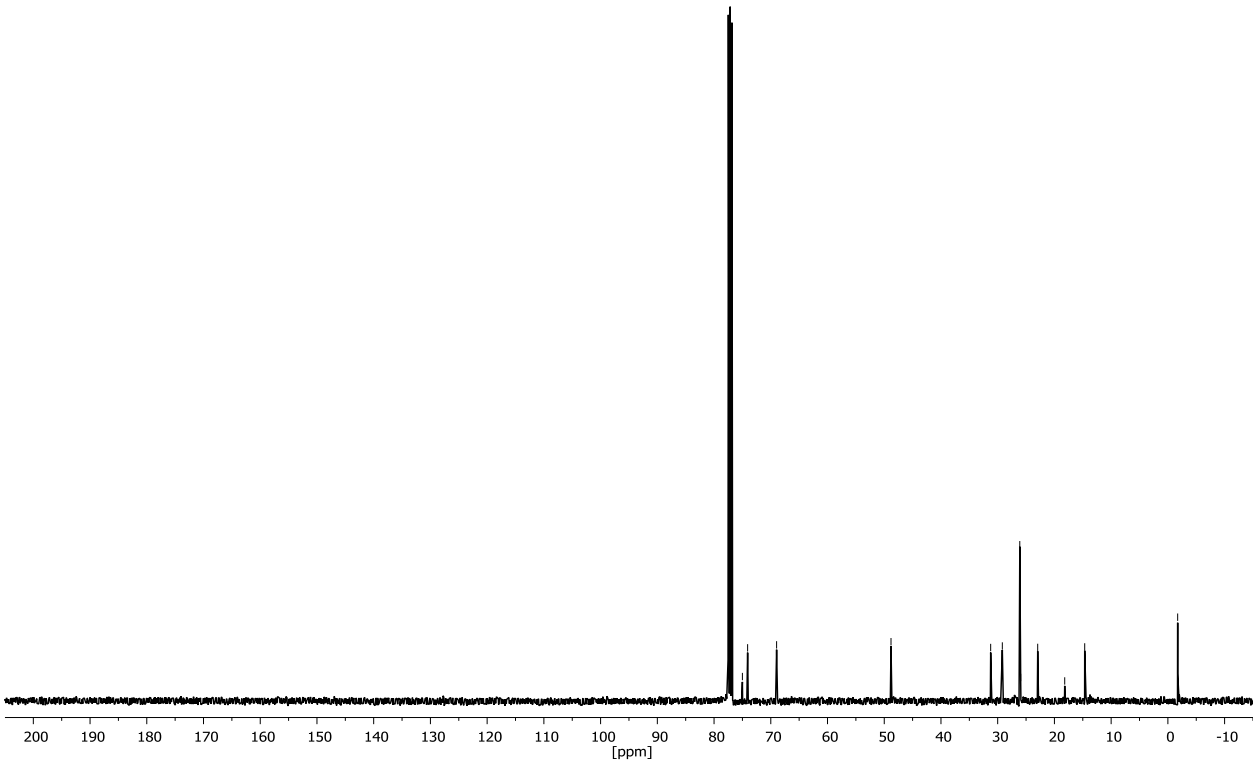
1.95
2.09
1.00
1.00
1.00
1.00
3.08
1.02
3.76
3.19
2.23
9.64
1.11
1.01
2.78
2.89
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

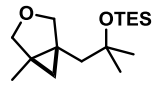

143.3
133.6
129.6
127.8
74.9
54.3
49.7
49.2
31.5
28.8
26.2
25.0
21.7
21.2
18.2
15.2
-1.7
-1.7
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
[ppm]


O
OTBS

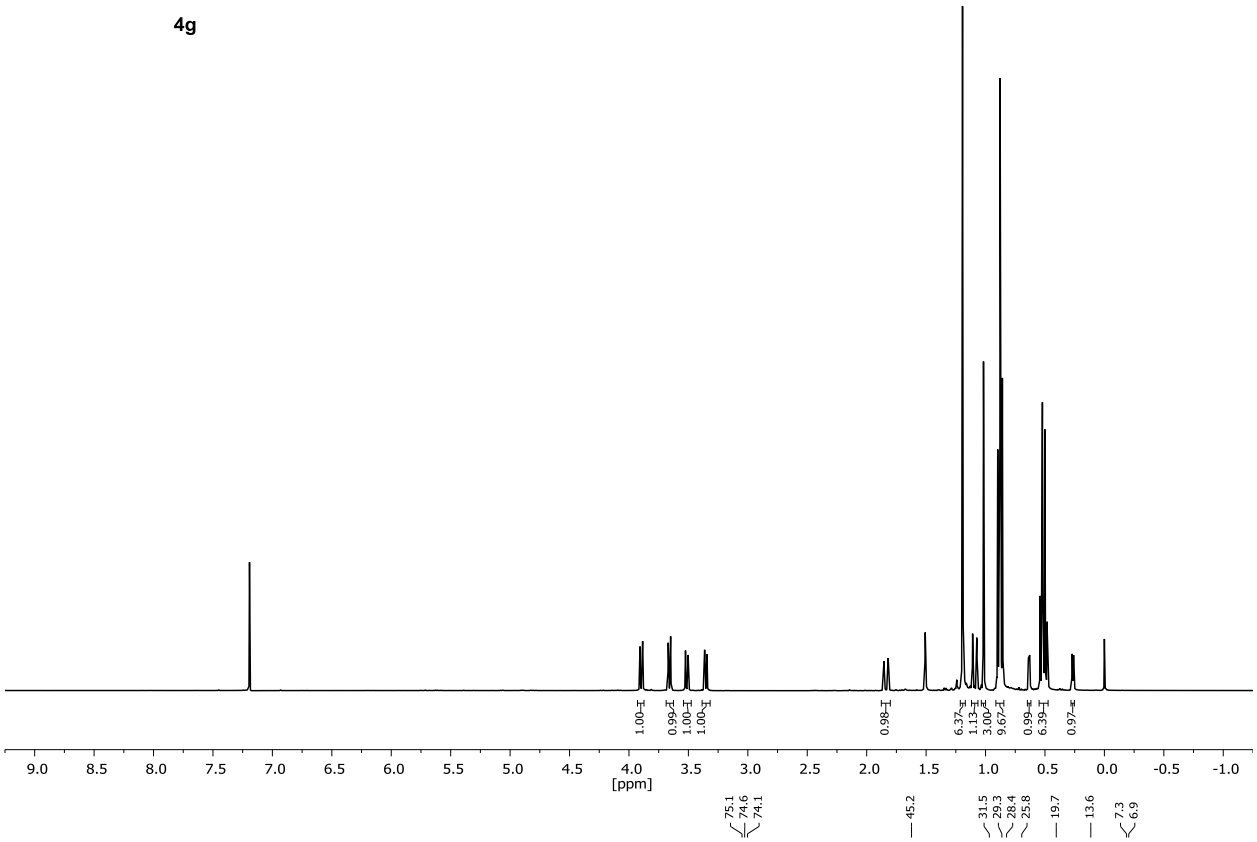
4f

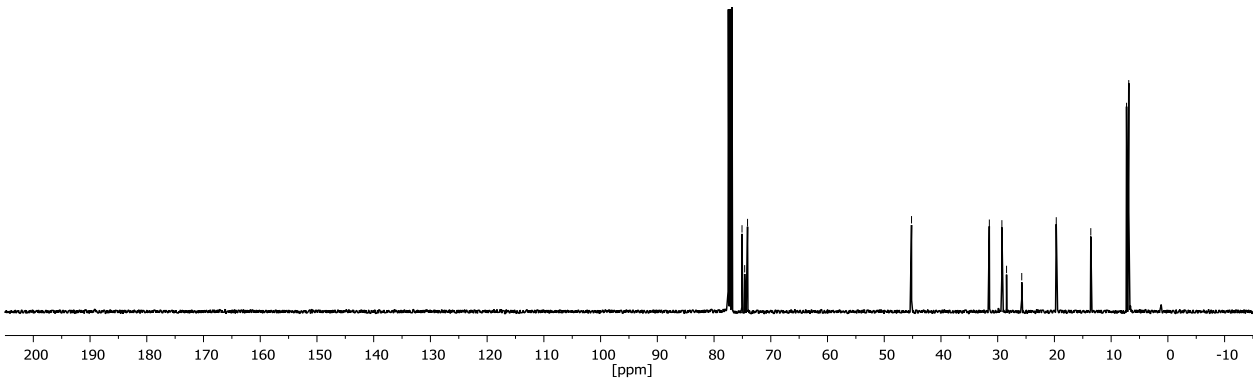

0.99
0.96
0.95
0.96
1.00
1.23
2.93
3.02
0.84
0.98
9.20
1.83
2.96
3.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

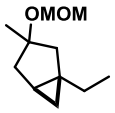

75.0
74.1
69.0
48.8
31.2
29.2
26.1
25.9
22.9
18.2
14.7
-1.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


O
OTES

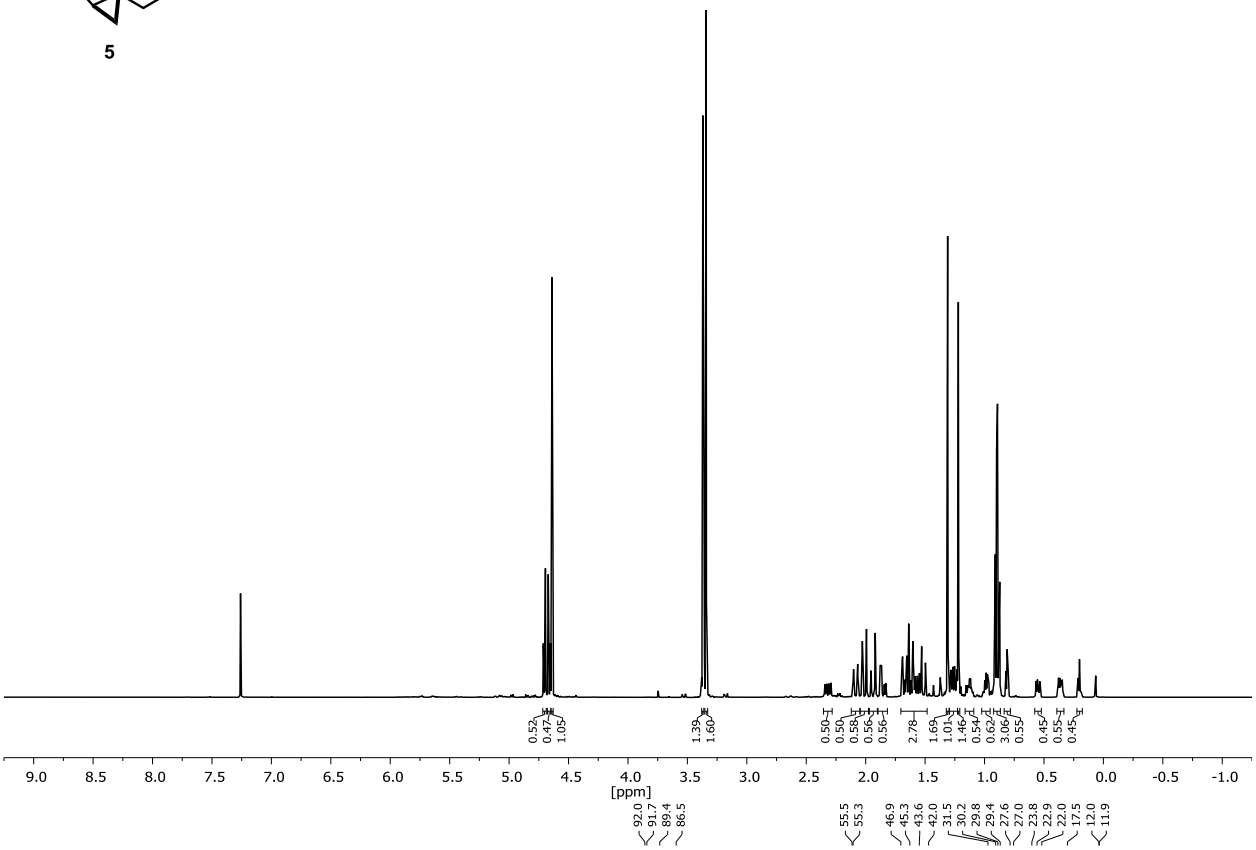
4g

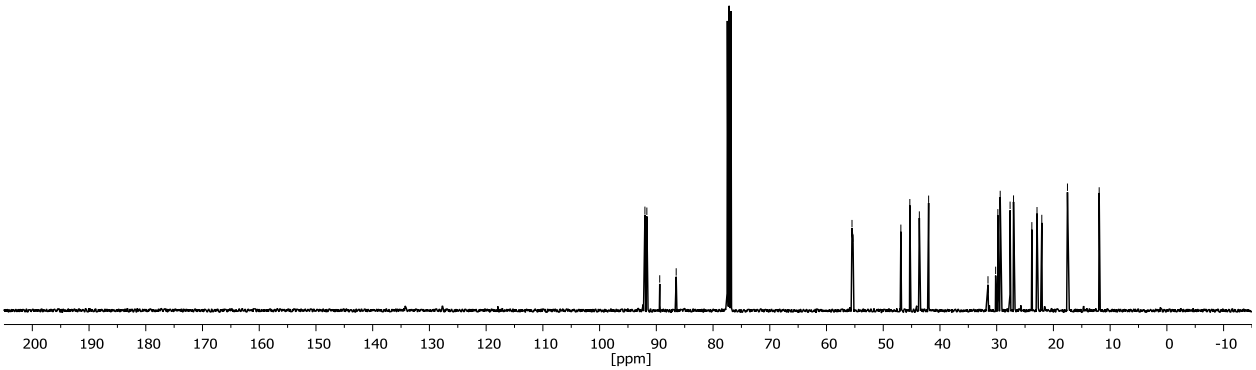

1.00
0.99
1.00
1.00
0.98
6.37
1.13
3.00
9.67
0.99
6.39
0.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
75.1
74.6
74.1
45.2
31.5
29.3
28.4
25.8
19.7
13.6
7.3
6.9

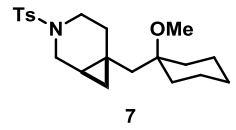

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMOM

5

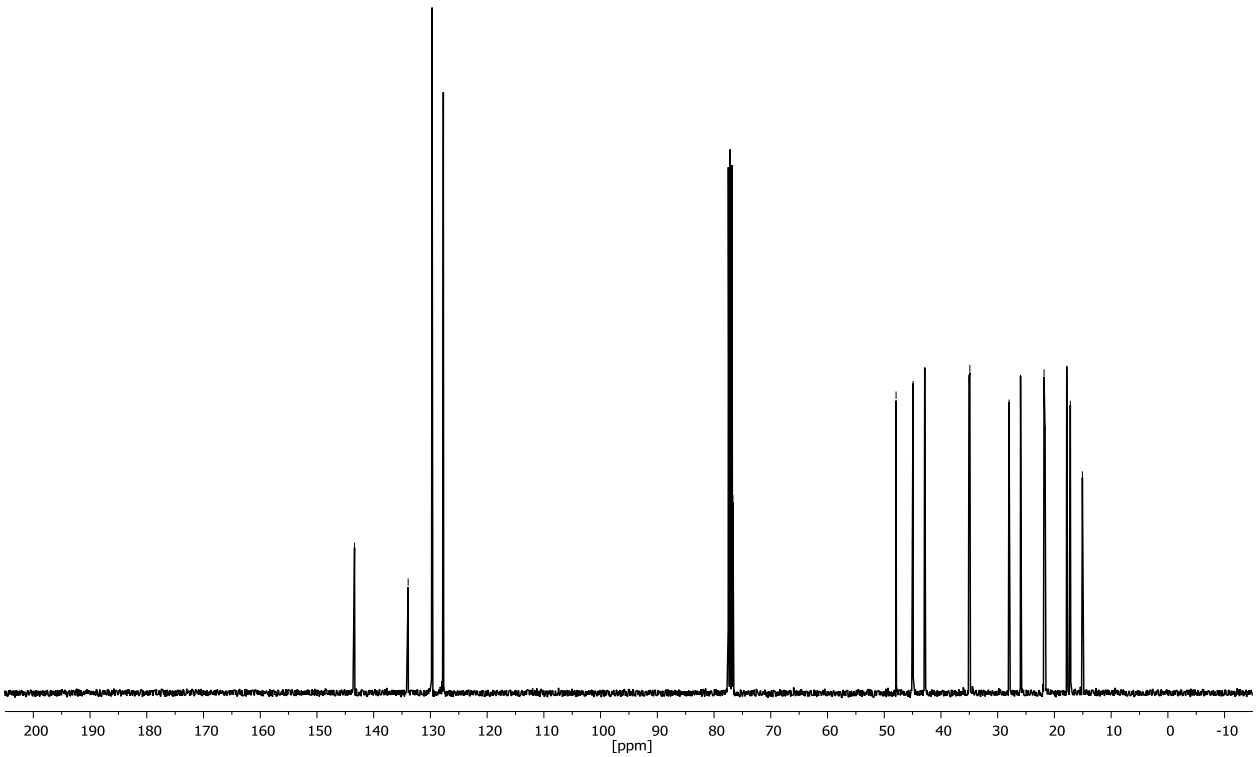

0.52
0.47
1.05
1.39
1.60
0.50
0.50
0.58
0.56
0.56
2.78
1.69
1.01
1.46
0.54
0.67
3.06
0.55
0.45
0.55
0.45
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
92.0
91.7
89.4
86.5
55.5
55.3
46.9
45.3
43.6
42.0
31.5
30.2
29.8
29.4
27.6
27.0
23.8
22.9
22.0
17.5
12.0
11.9

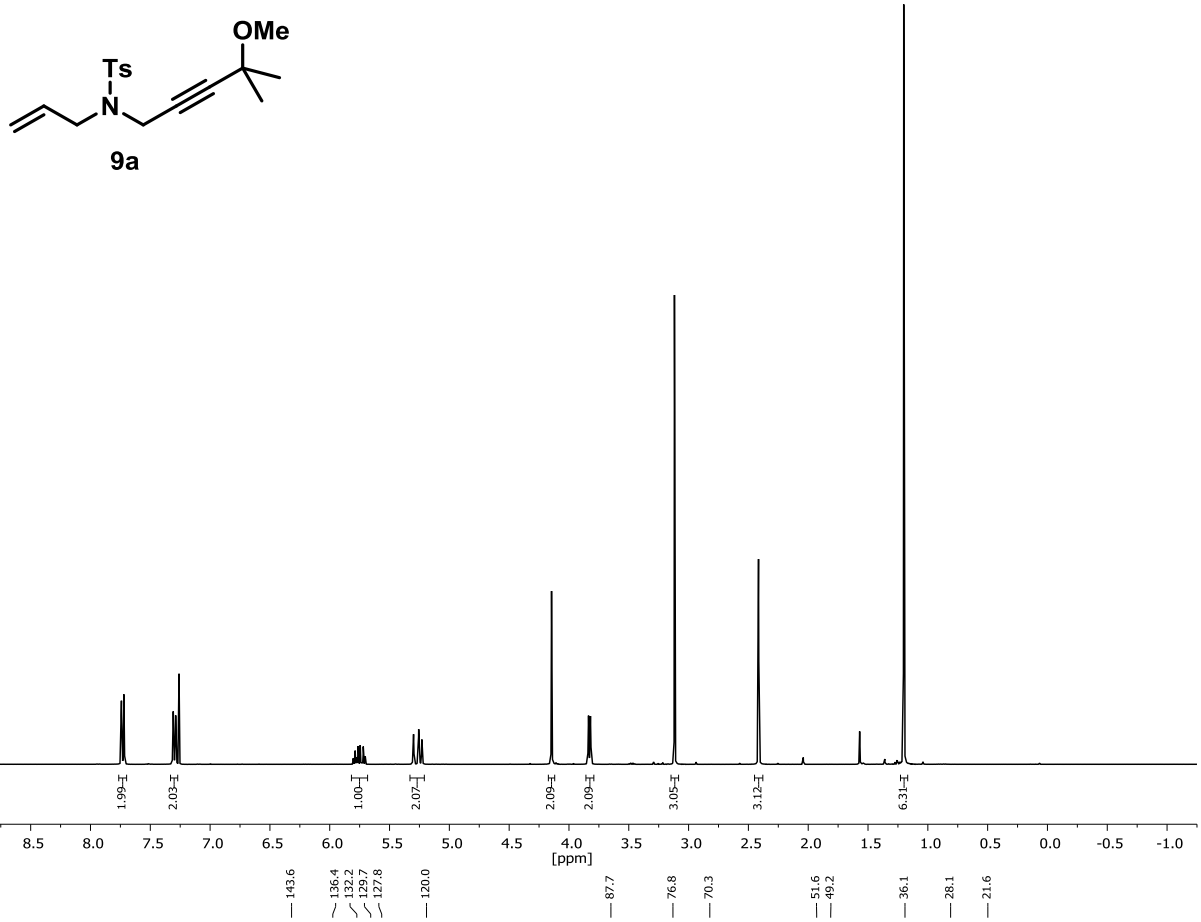

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

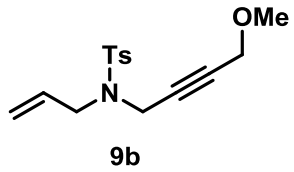

Ts
N
OMe

7

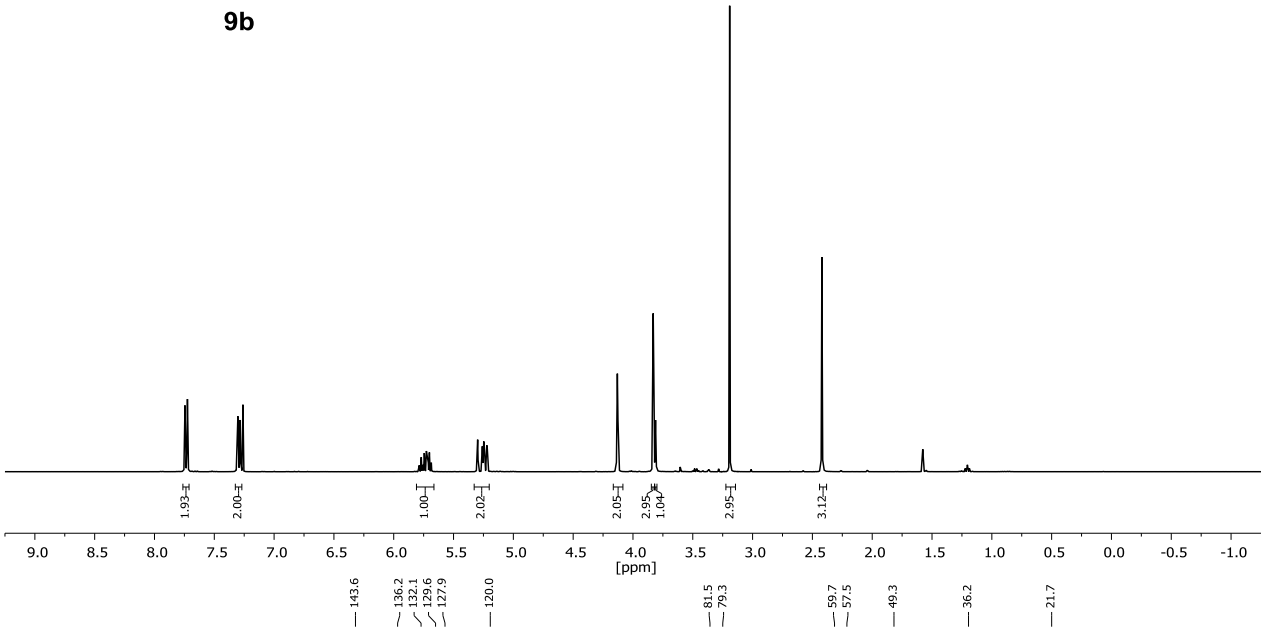
1.95
2.05
1.00
1.01
3.00
1.01
1.03
3.15
1.03
1.01
2.13
6.68
4.51
1.03
0.99
0.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.4
133.9
129.7
127.7
76.7
47.9
45.0
44.9
42.9
35.1
34.9
28.0
26.0
21.9
21.8
21.6
17.8
17.2
15.1

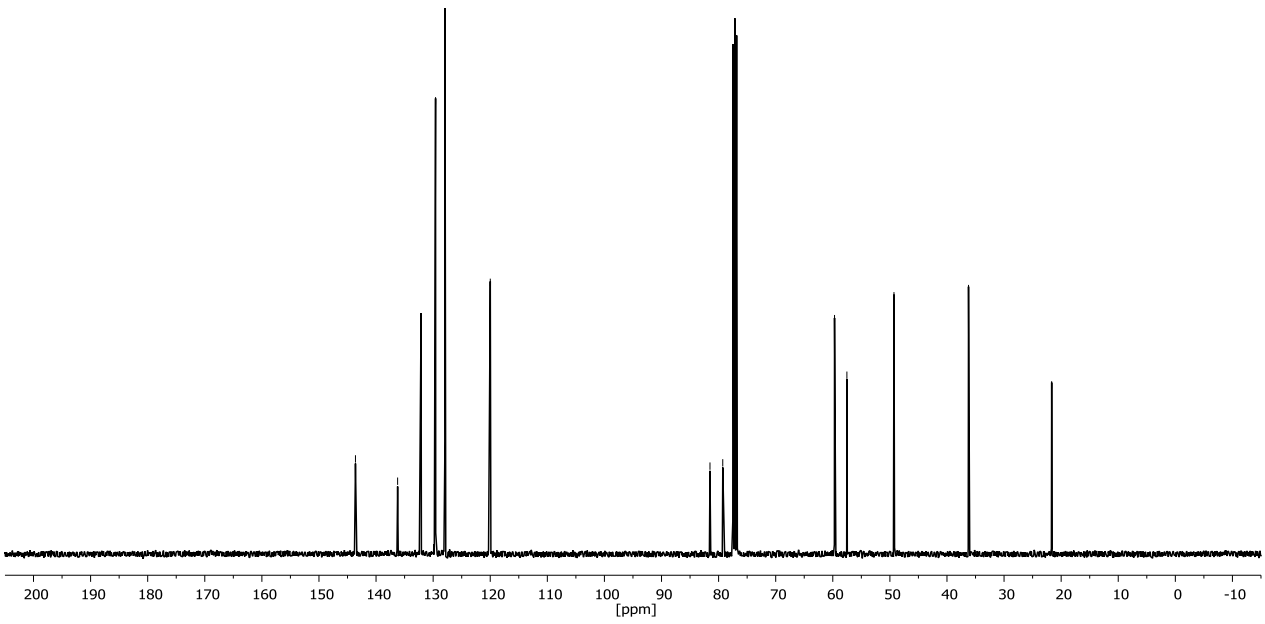

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

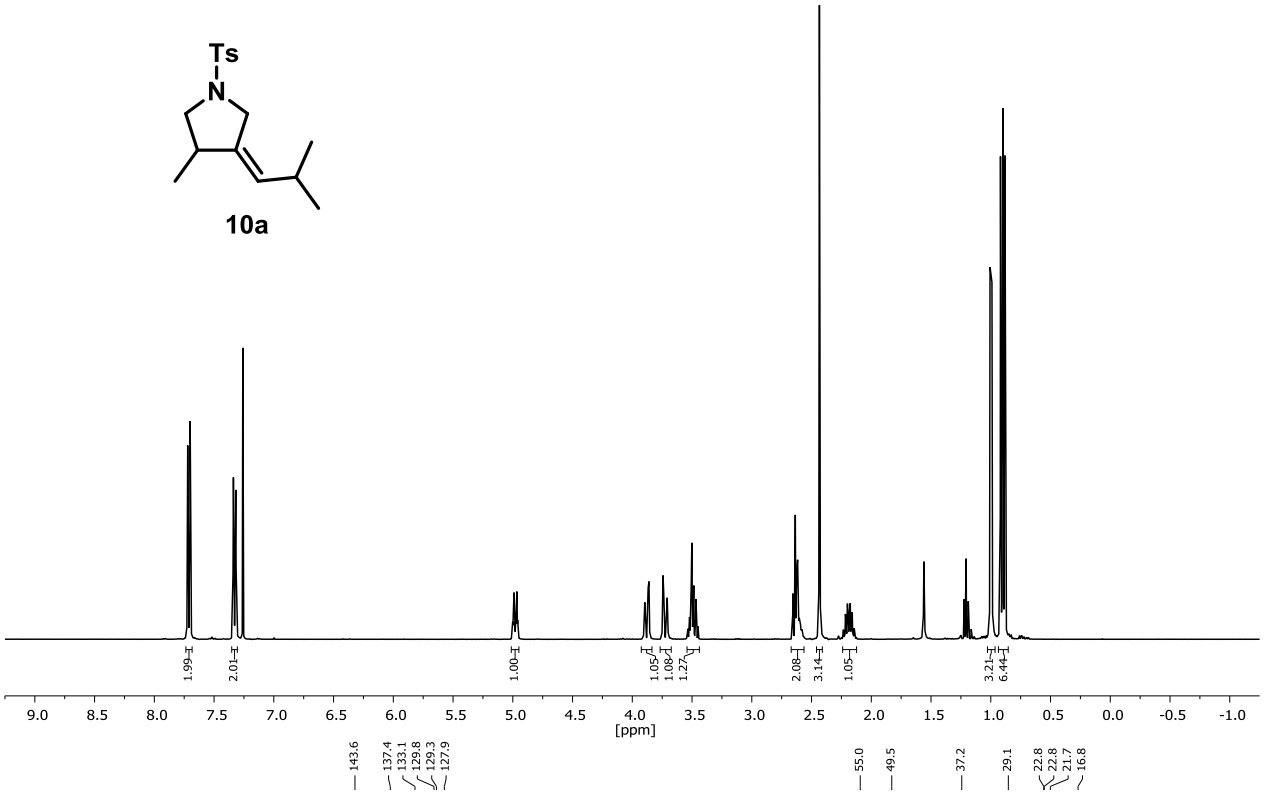

OMe
Ts
N
9a
1.99
2.03
1.00
2.07
2.09
2.09
3.05
3.12
6.31
[ppm]
143.6
136.4
132.2
129.7
127.8
120.0
87.7
76.8
70.3
51.6
49.2
36.1
28.1
21.6
[ppm]

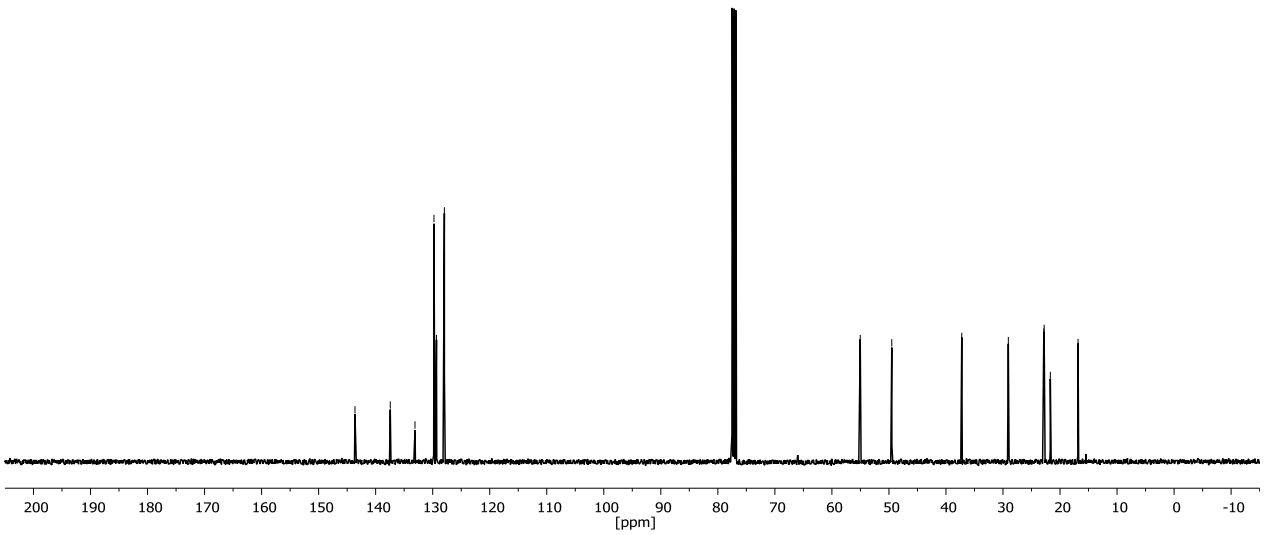

OMe
Ts
N

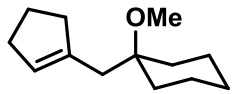
9b


1.93
2.00
1.00
2.02
2.05
2.95
1.04
2.95
3.12
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 -0.5 -1.0
[ppm]
143.6
136.2
132.1
129.6
127.9
120.0
81.5
79.3
59.7
57.5
49.3
36.2
21.7

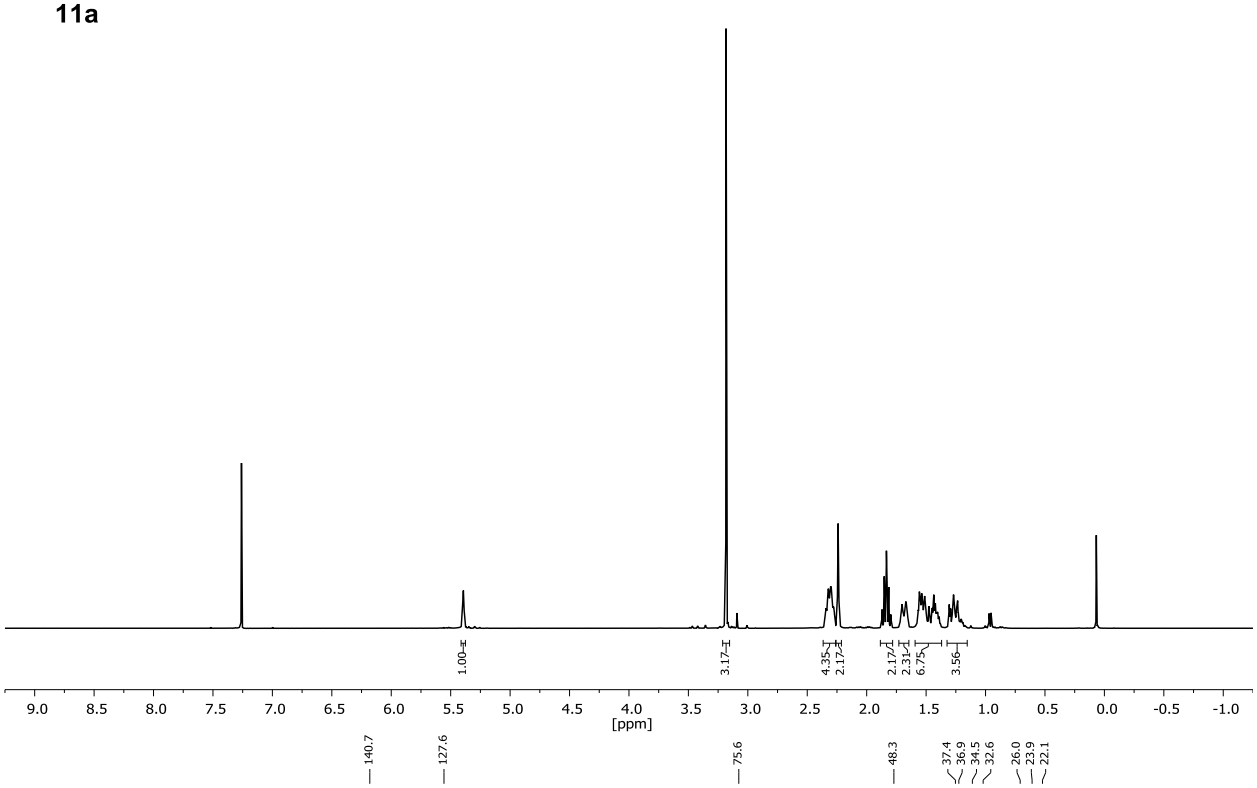

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

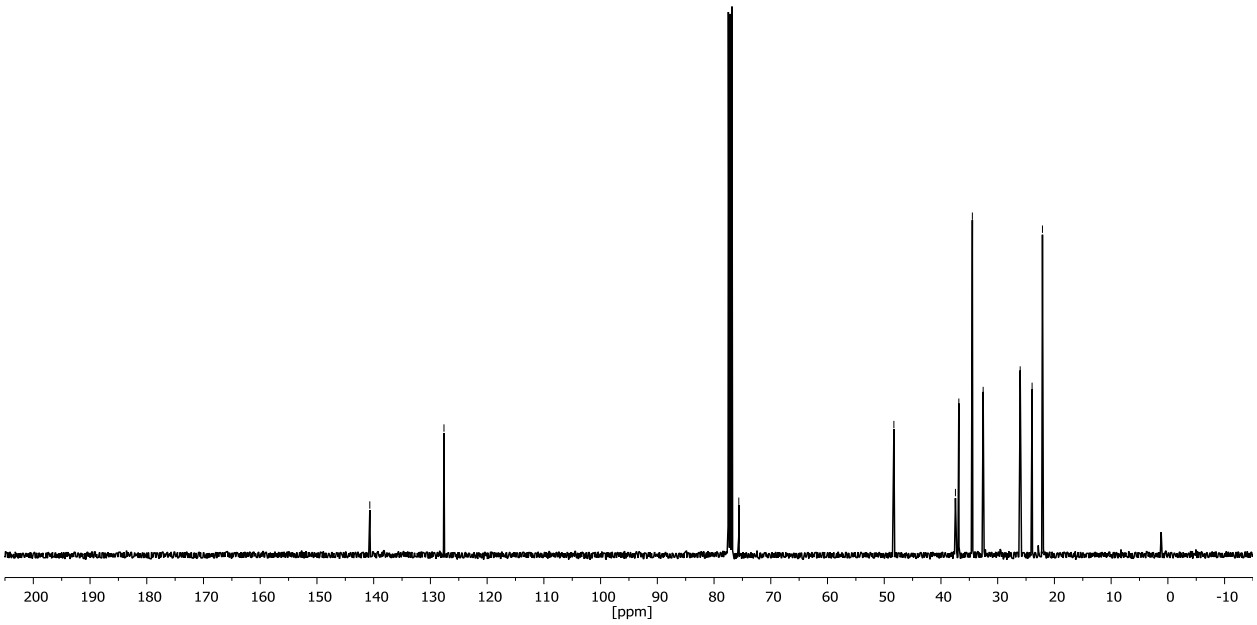

Ts
N
10a
1.99
2.01
1.00
1.05
1.08
1.27
2.08
3.14
1.05
3.21
6.44
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.6
137.4
133.1
129.8
129.3
127.9
55.0
49.5
37.2
29.1
22.8
22.8
21.7
16.8

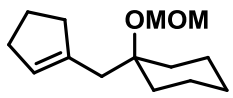

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

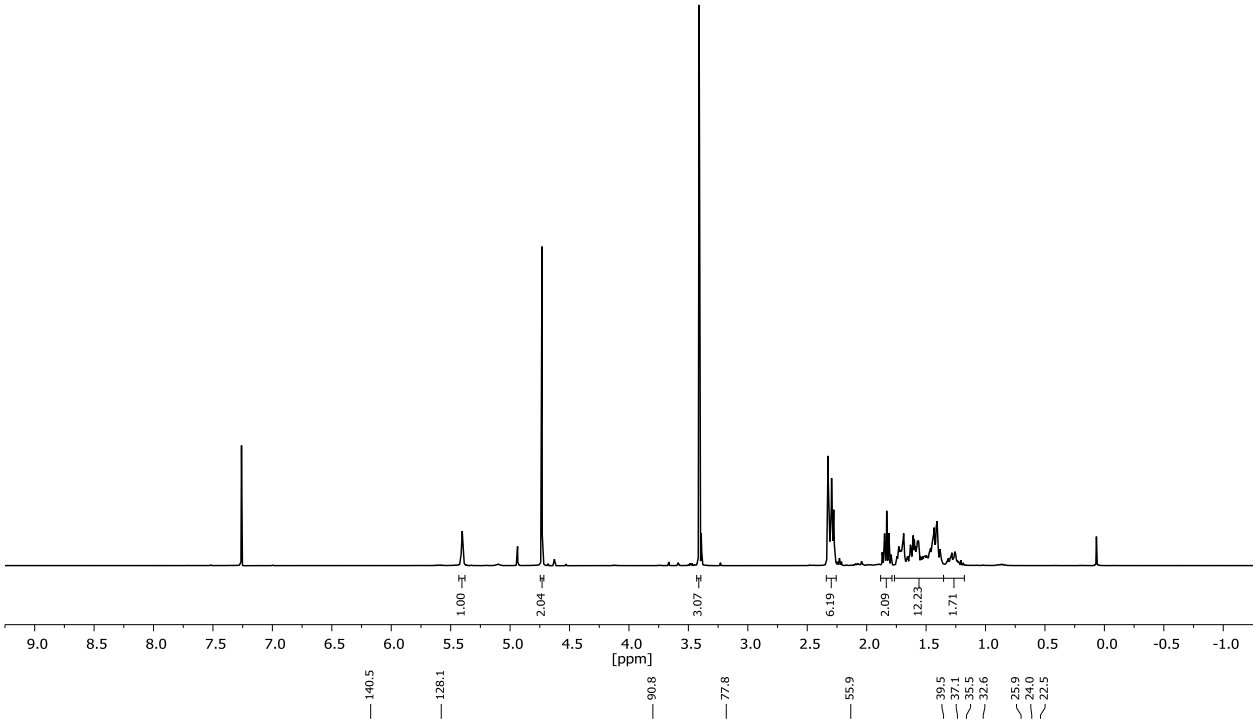
11a

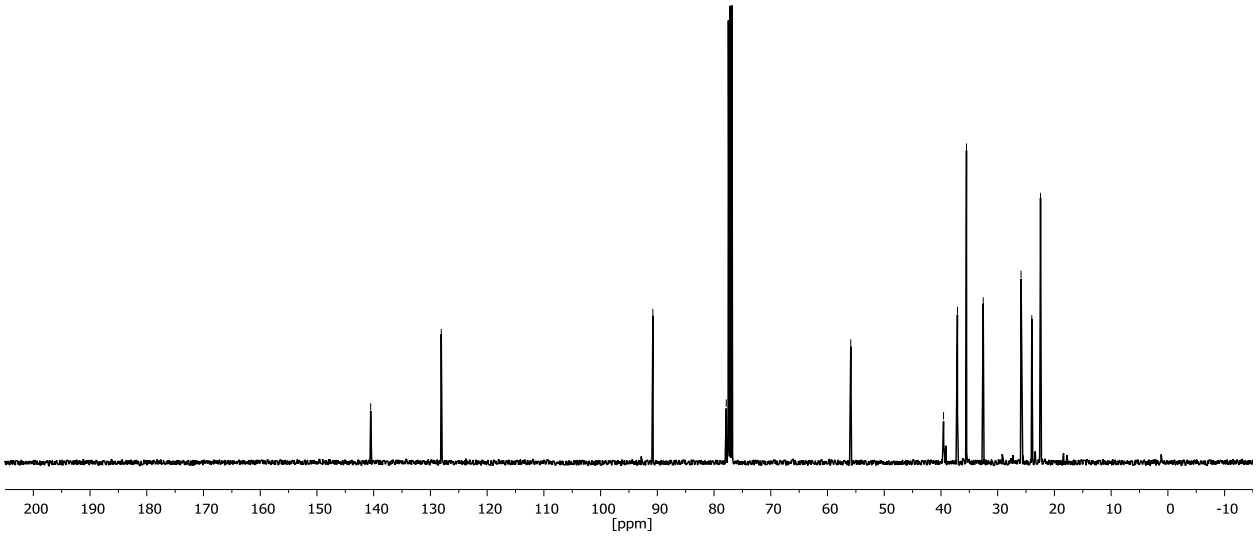

1.00
3.17
4.35
2.17
2.17
2.31
6.75
3.56
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
140.7
127.6
75.6
48.3
37.4
36.9
34.5
32.6
26.0
23.9
22.1

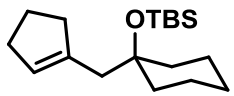

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMOM

11b

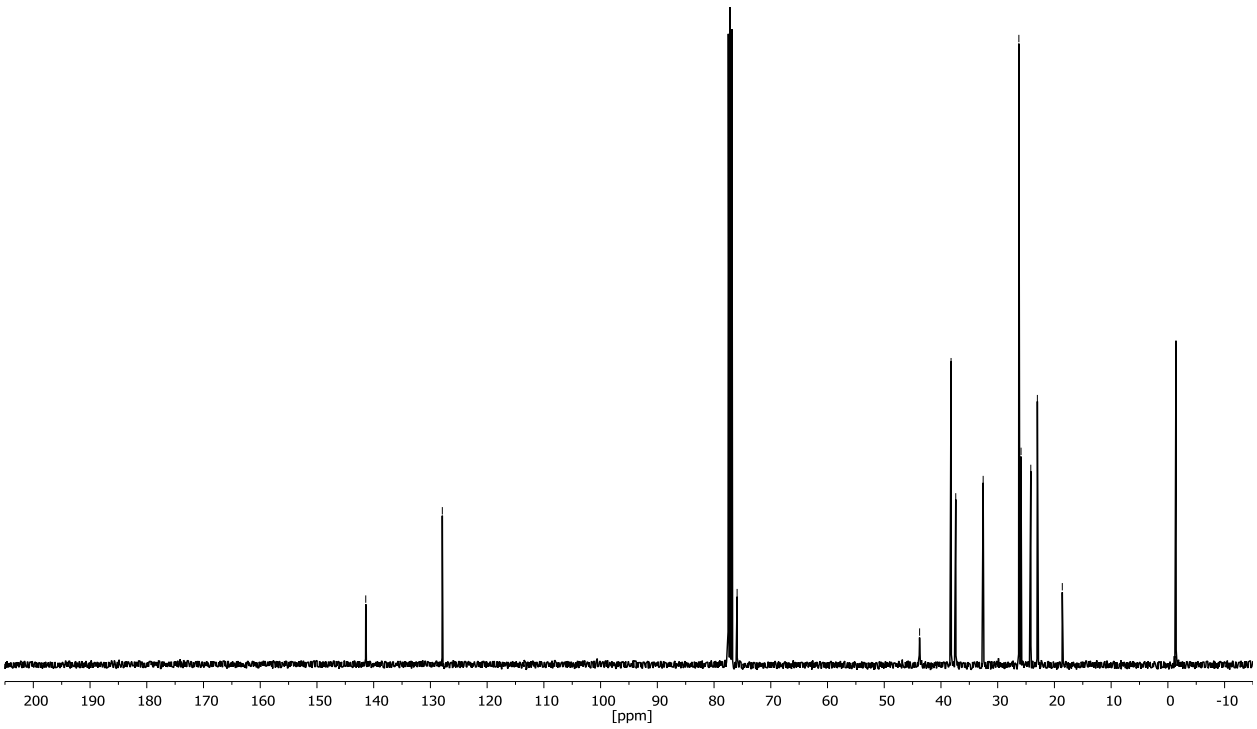

1.00
2.04
3.07
6.19
2.09
12.23
1.71
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
140.5
128.1
90.8
77.8
55.9
39.5
37.1
35.5
32.6
25.9
24.0
22.5

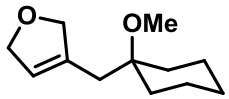

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OTBS

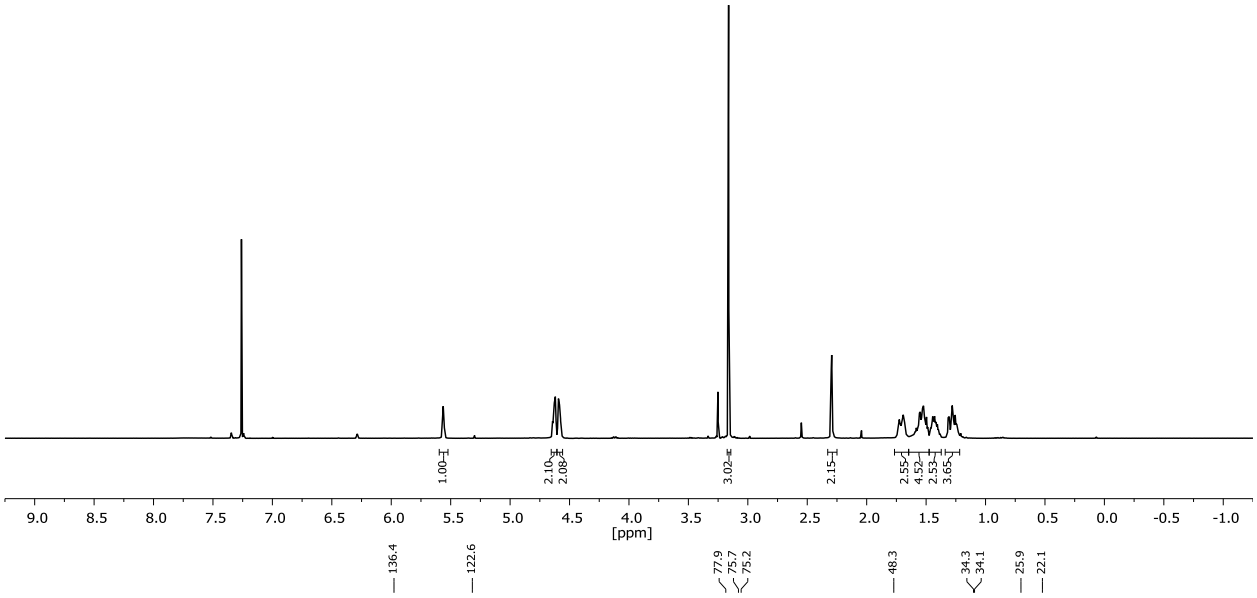
11c

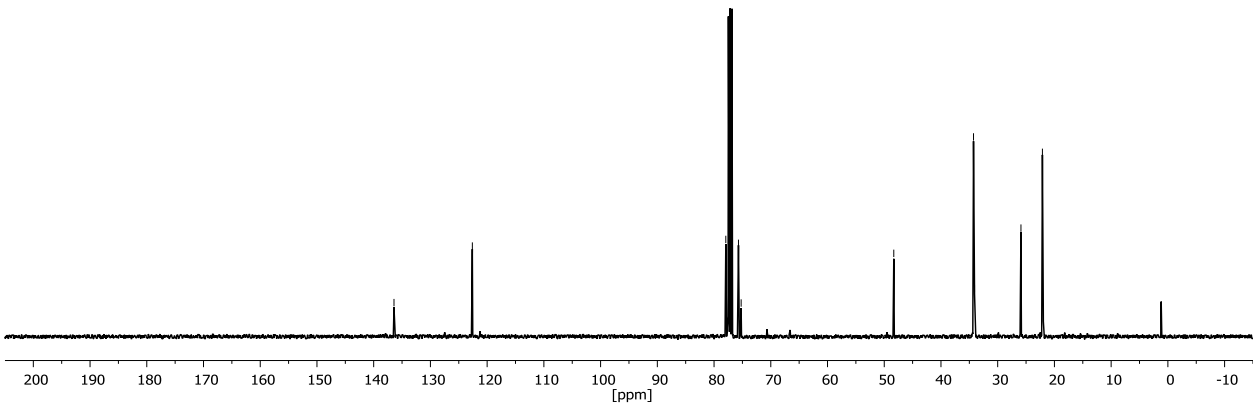
1.00
6.45
2.18
2.43
8.92
9.97
6.42
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
141.4
127.9
75.9
43.8
38.2
37.4
32.6
26.3
25.9
24.2
23.0
18.6
-1.4

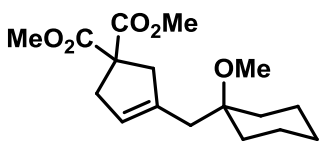

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


O
OMe

11e

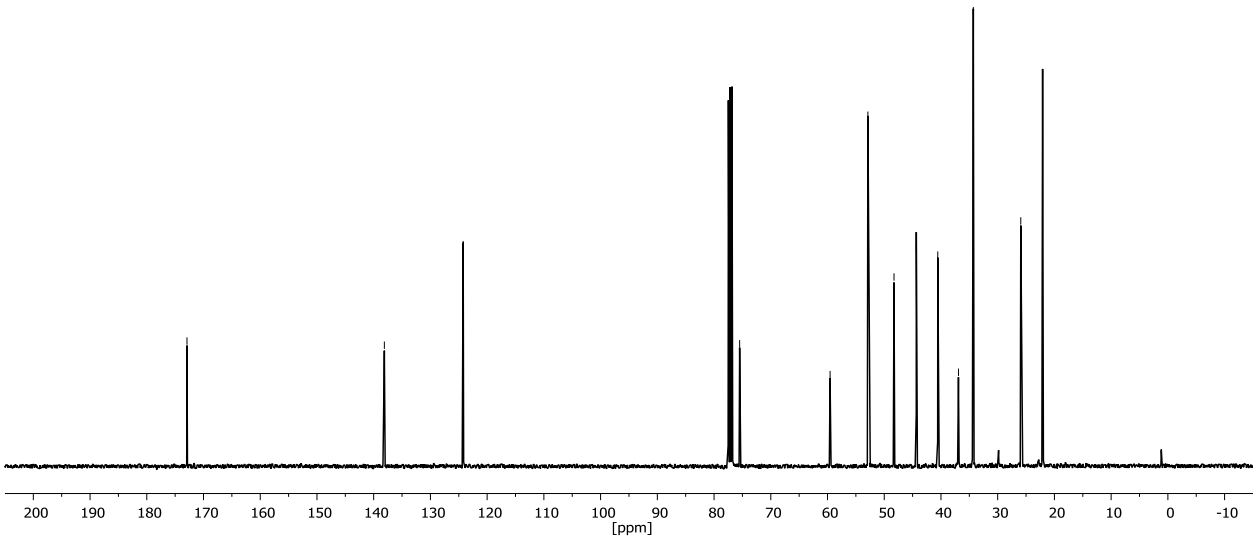

1.00
2.10
2.08
3.02
2.15
2.55
4.52
2.53
3.65
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
136.4
122.6
77.9
75.7
75.2
48.3
34.3
34.1
25.9
22.1

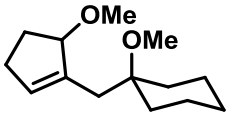

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


MeO2C
CO2Me
OMe

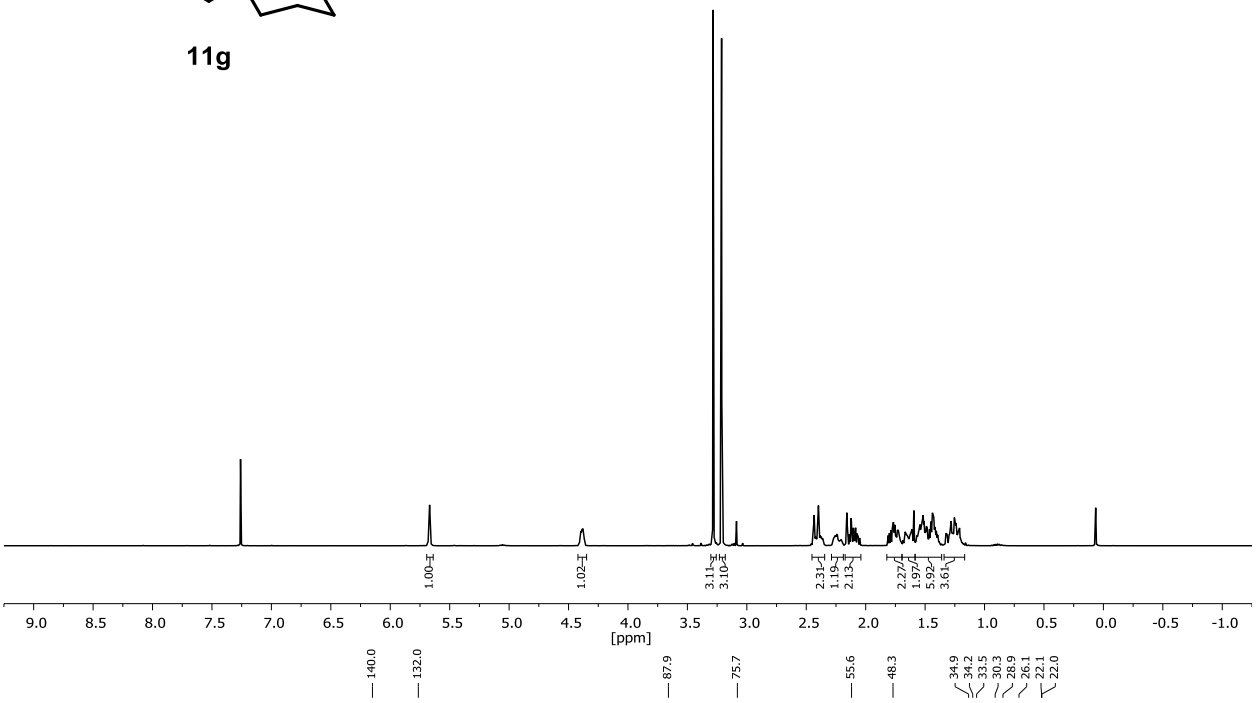
11f

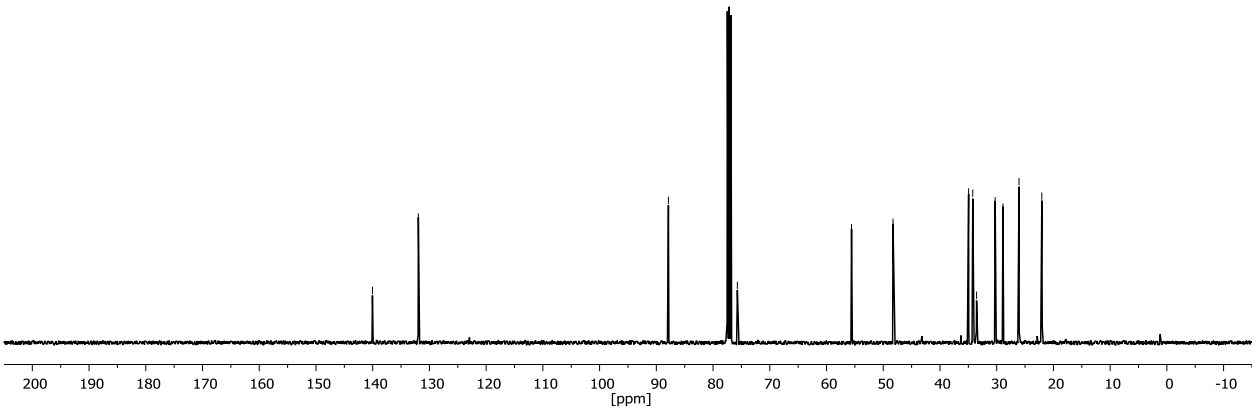
1.00
6.16
3.08
4.16
2.06
2.70
3.43
2.32
3.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
172.9
138.1
124.2
75.5
59.5
52.9
48.3
44.3
40.6
36.9
34.3
25.9
22.1

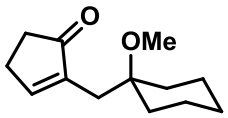

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
OMe

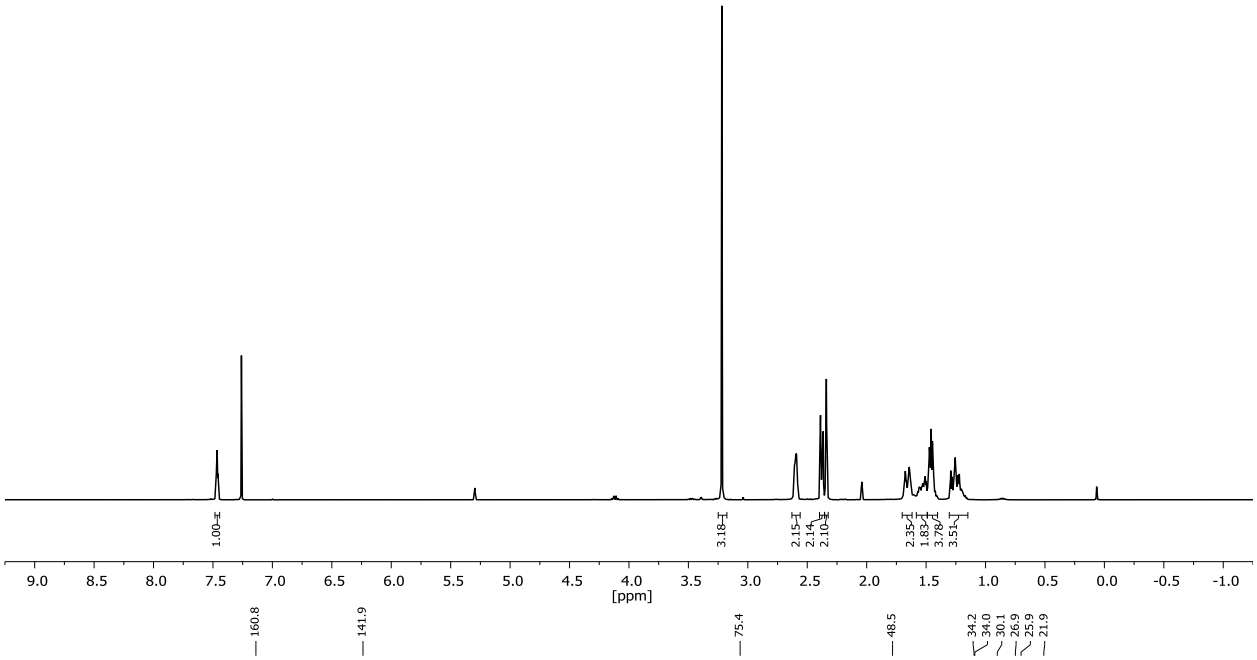
11g

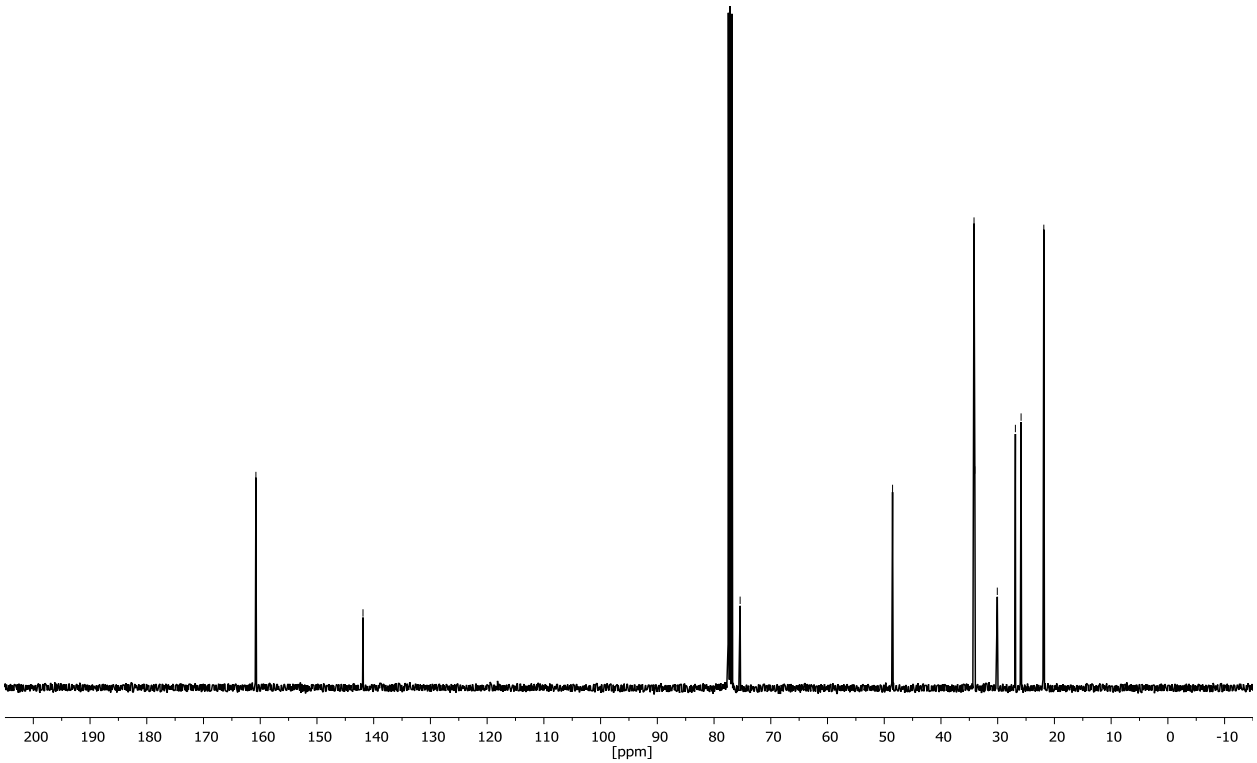

1.00
1.02
3.11
3.10
2.31
1.19
2.13
2.27
1.97
5.92
3.61
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
140.0
132.0
87.9
75.7
55.6
48.3
34.9
34.2
33.5
30.3
28.9
26.1
22.1
22.0

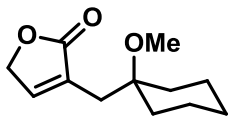

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


O
OMe

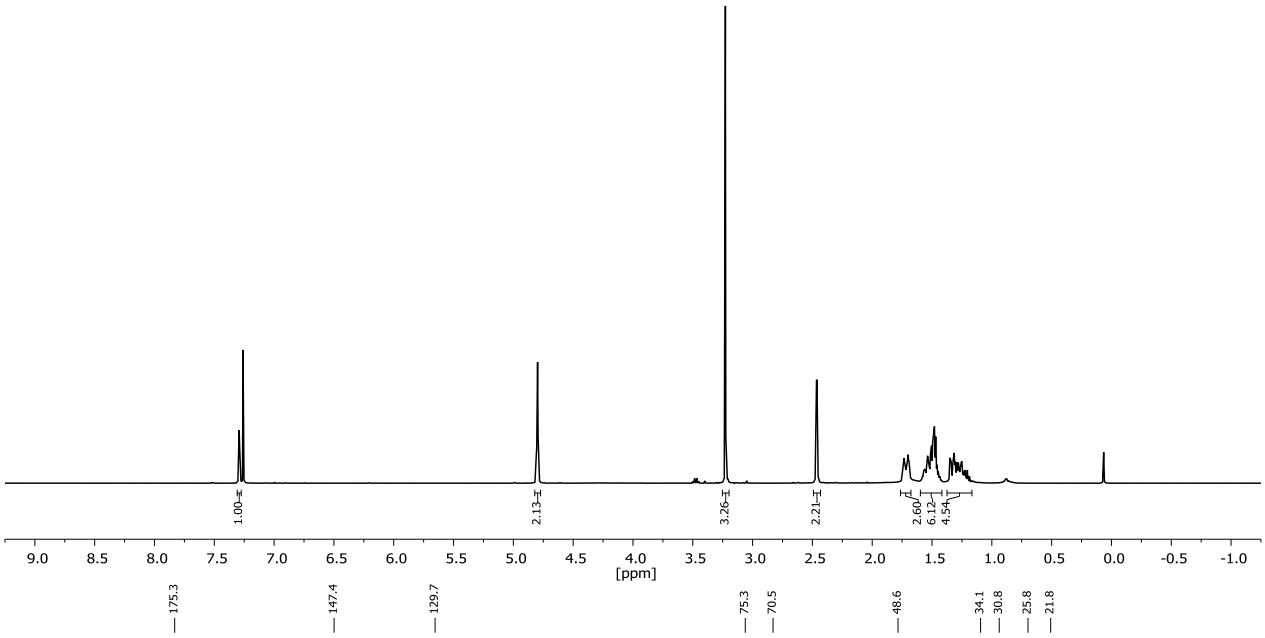
11h

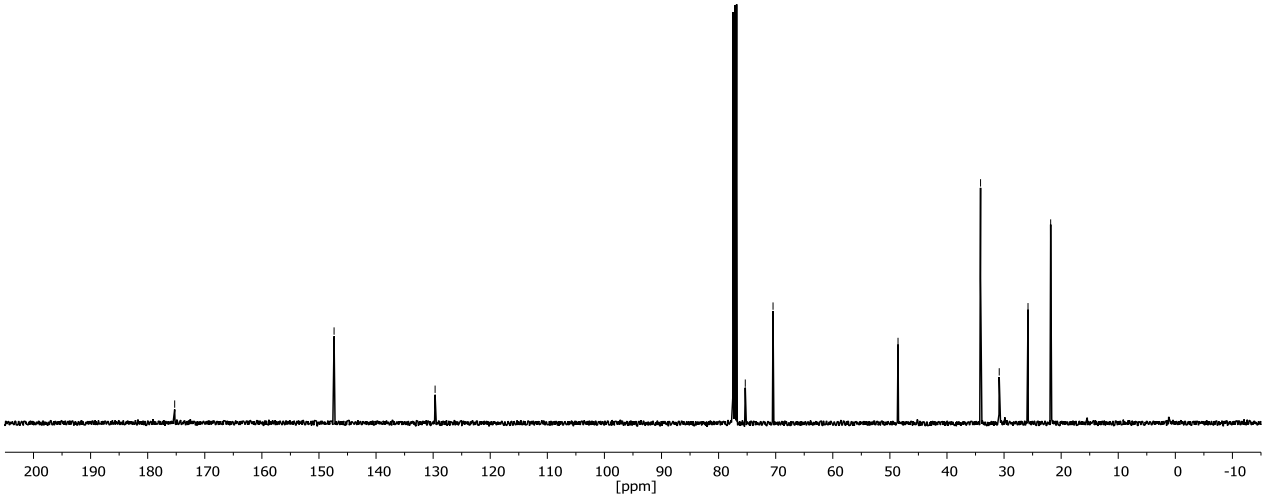

1.00
3.18
2.15
2.14
2.10
2.35
1.83
3.78
3.51
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
160.8
141.9
75.4
48.5
34.2
34.0
30.1
26.9
25.9
21.9

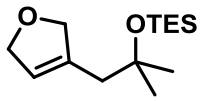

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


O
O
OMe

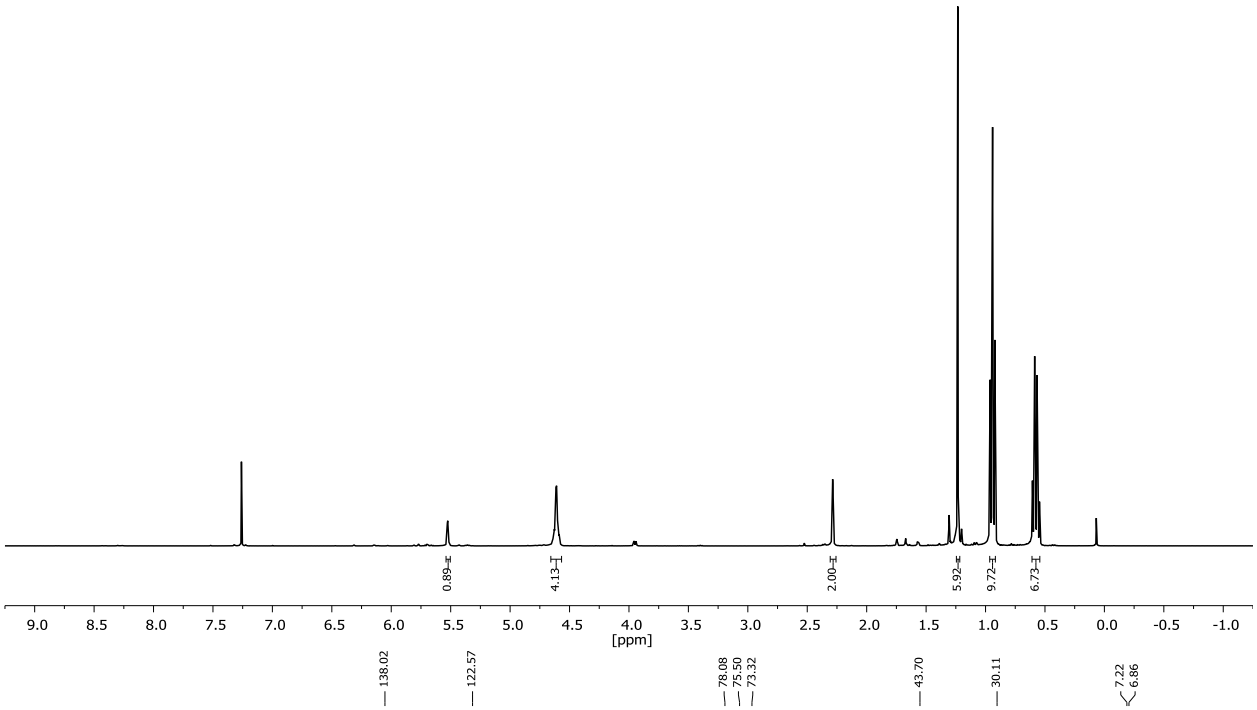
11i

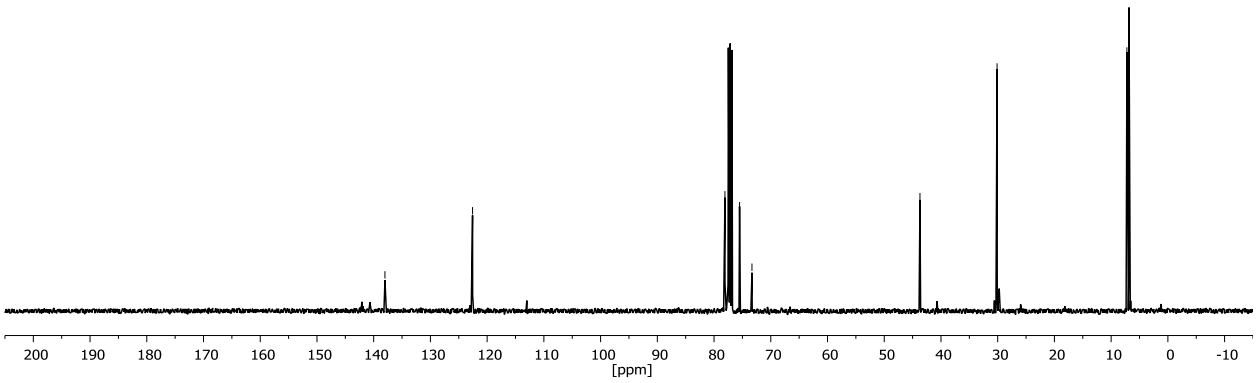

1.00
2.13
3.26
2.21
2.60
6.12
4.54
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
175.3
147.4
129.7
75.3
70.5
48.6
34.1
30.8
25.8
21.8

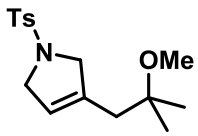

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


O
OTES

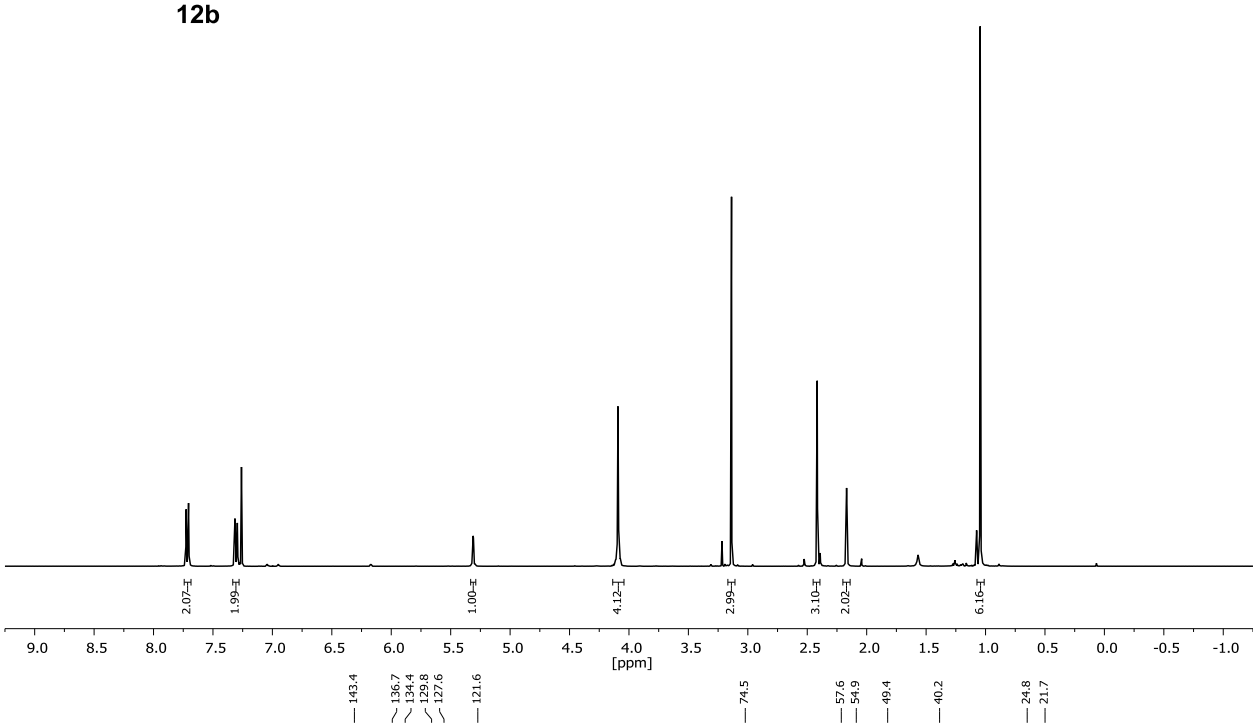
12a

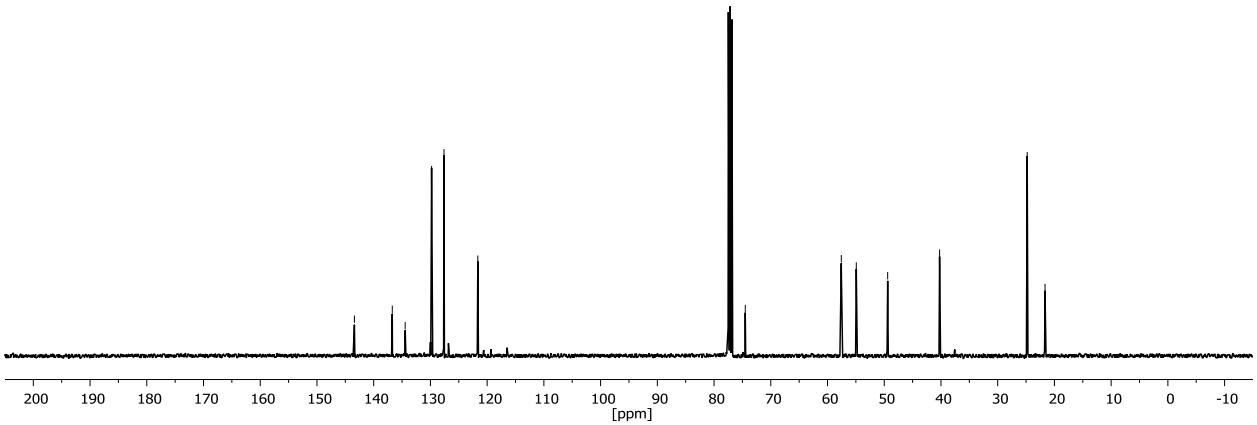

0.89
4.13
2.00
5.92
9.72
6.73
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
138.02
122.57
78.08
75.50
73.32
43.70
30.11
7.22
6.86

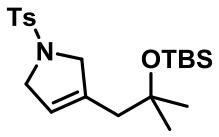

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


Ts
N
OMe

12b

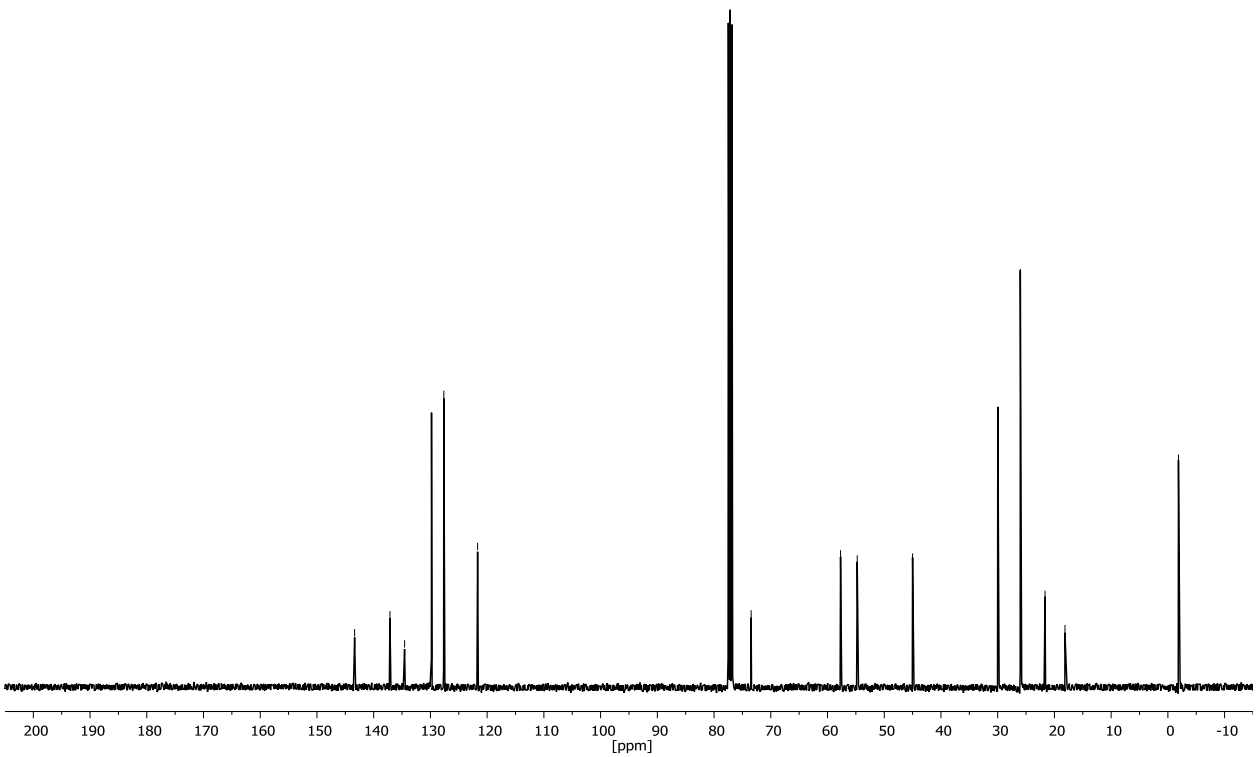

2.07
1.99
1.00
4.12
2.99
3.10
2.02
6.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.4
136.7
134.4
129.8
127.6
121.6
74.5
57.6
54.9
49.4
40.2
24.8
21.7

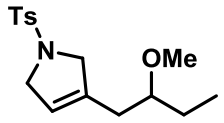

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


Ts
N
OTBS

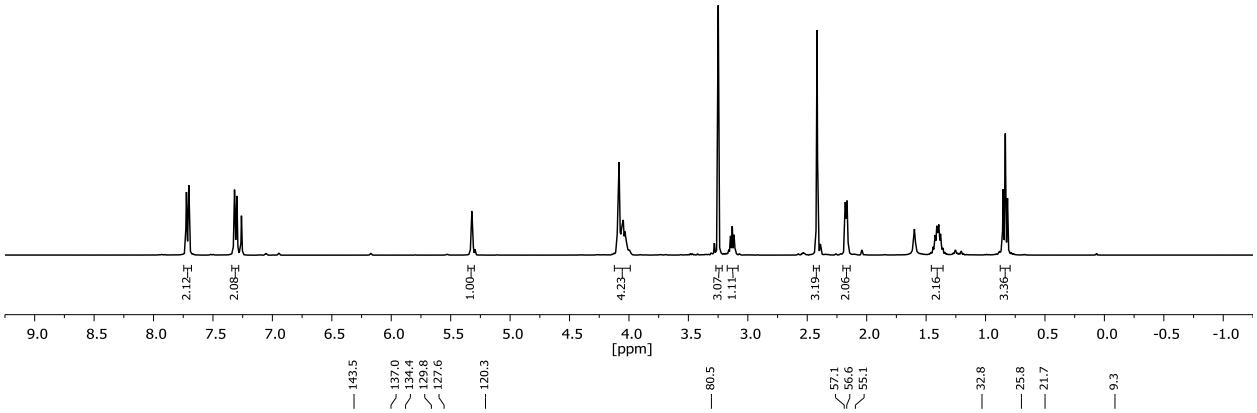
12c

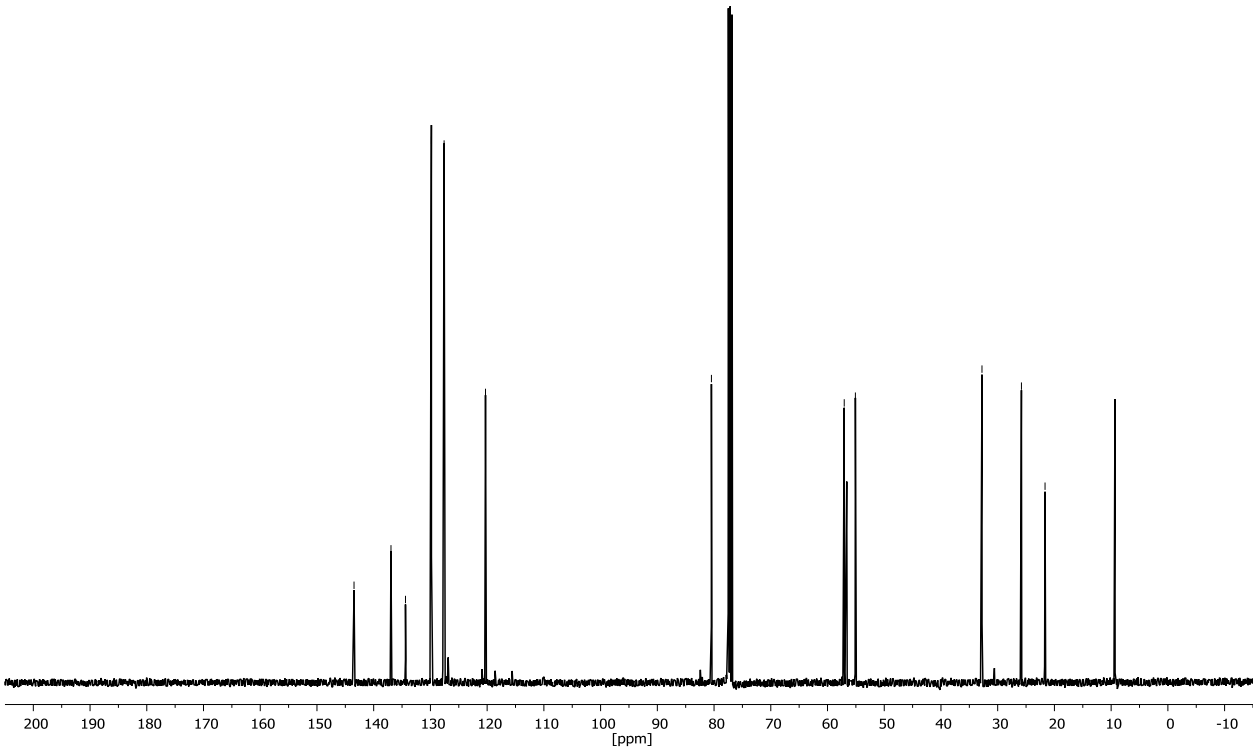
2.01
2.05
1.00
4.25
3.14
2.08
6.28
9.43
6.23
[ppm]
143.4
137.1
134.6
129.8
127.6
121.7
73.5
57.7
54.8
45.0
30.0
26.0
21.7
18.1
-1.9

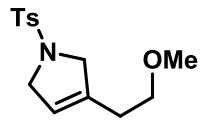

[ppm]


Ts
N
OMe

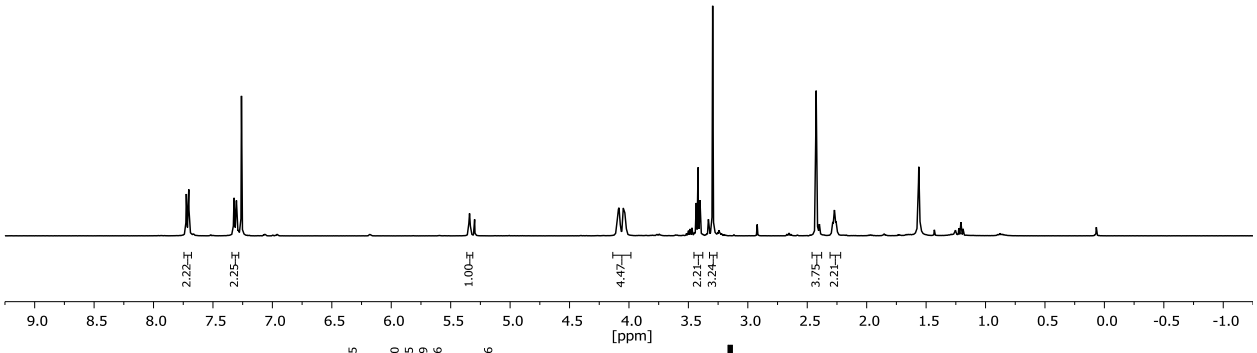
12d

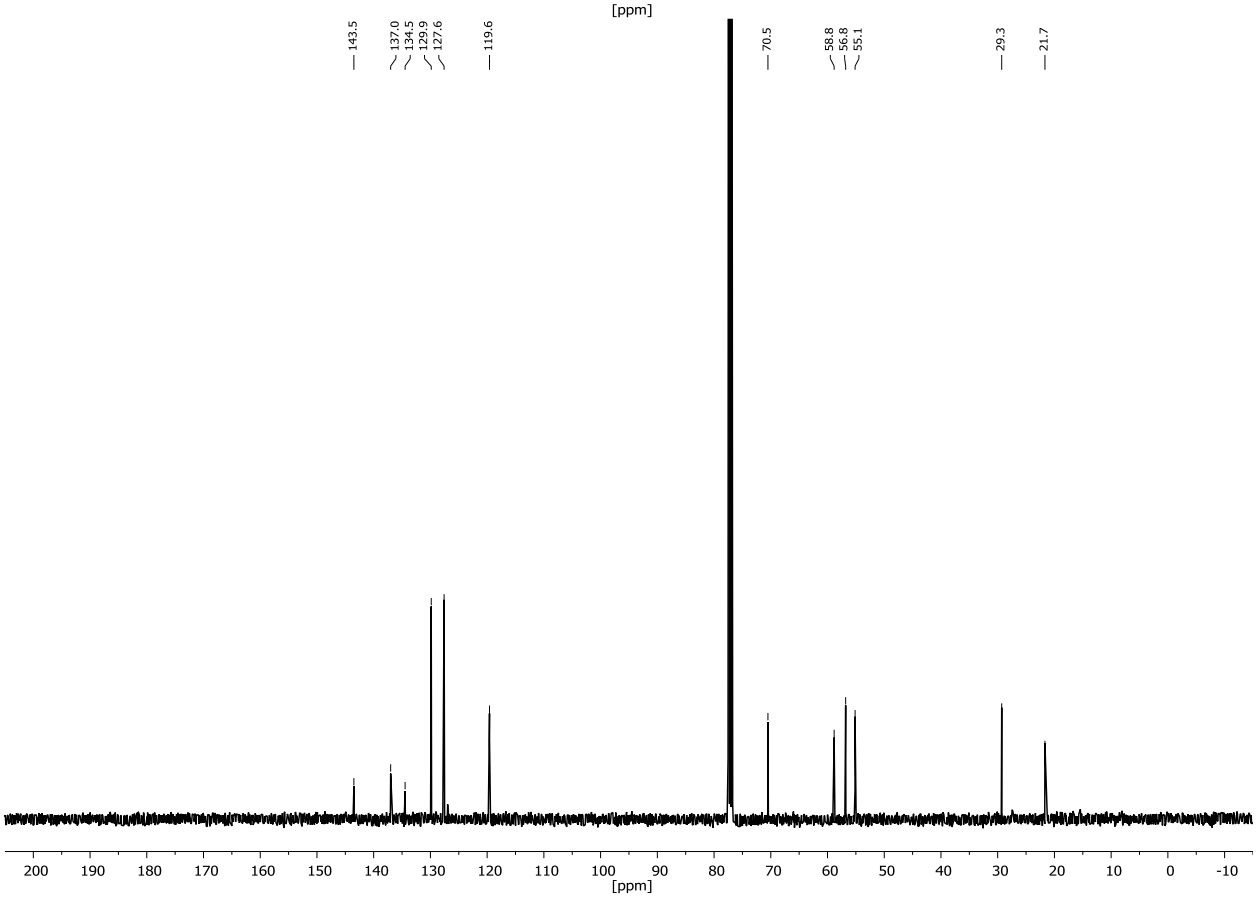

2.12
2.08
1.00
4.23
3.07
1.11
3.19
2.06
2.16
3.36
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.5
137.0
134.4
129.8
127.6
120.3
80.5
57.1
56.6
55.1
32.8
25.8
21.7
9.3

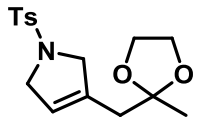

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


Ts
N
OMe

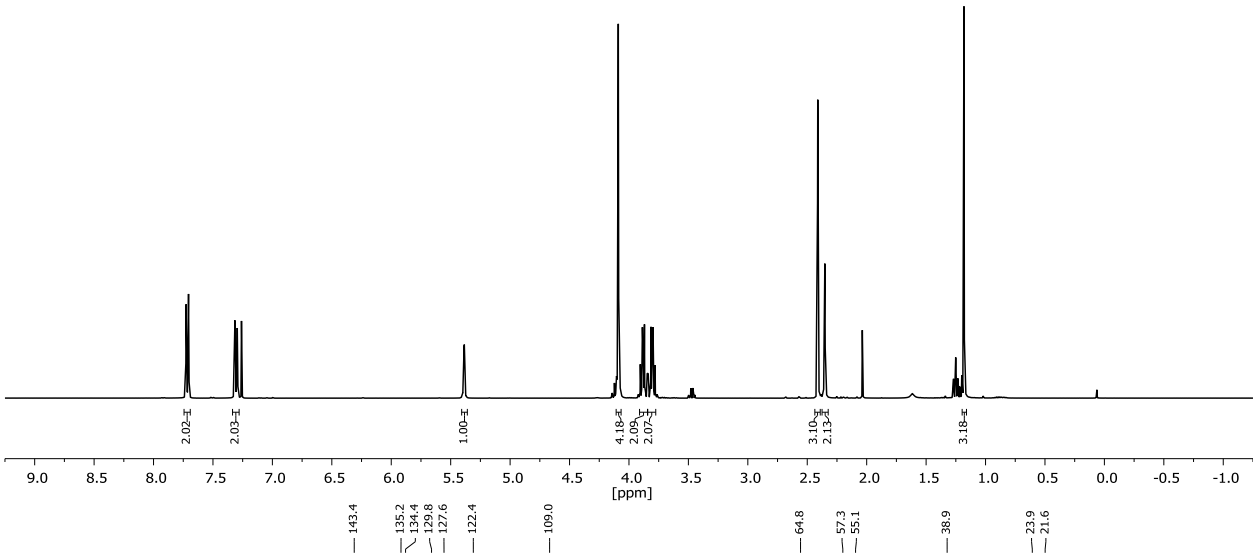
12e

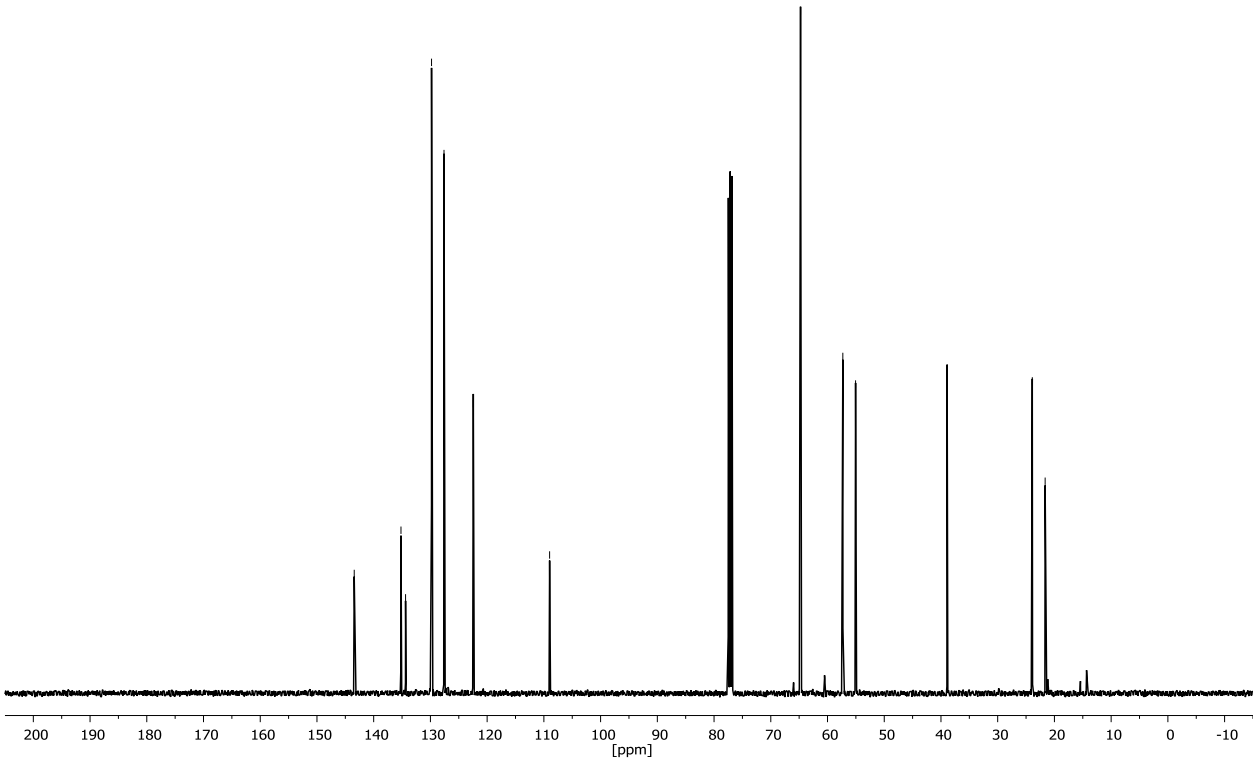

2.22
2.25
1.00
4.47
2.21
3.24
3.75
2.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

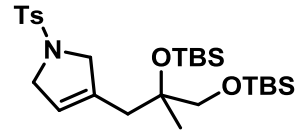

143.5
137.0
134.5
129.9
127.6
119.6
70.5
58.8
56.8
55.1
29.3
21.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


Ts
N
O
O

13

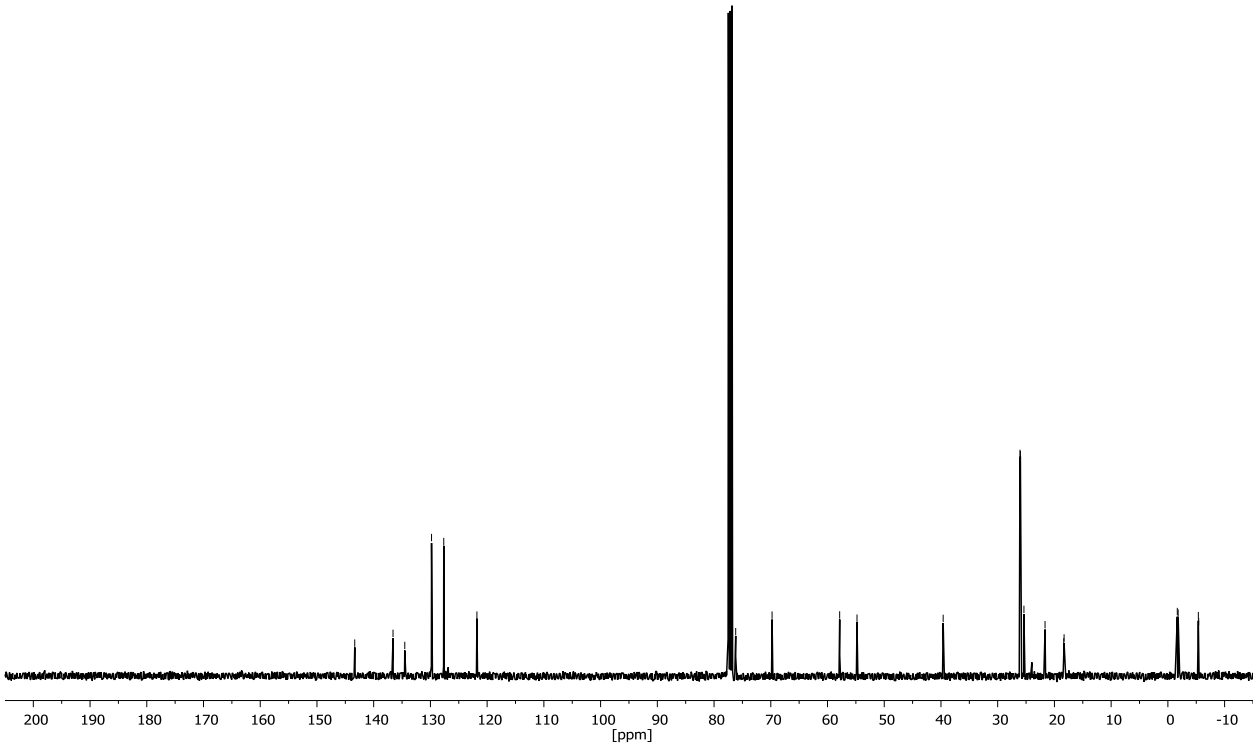

2.02
2.03
1.00
4.18
2.09
2.07
3.10
2.13
3.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.4
135.2
134.4
129.8
127.6
122.4
109.0
64.8
57.3
55.1
38.9
23.9
21.6

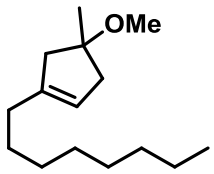

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


Ts
N
OTBS
OTBS

14

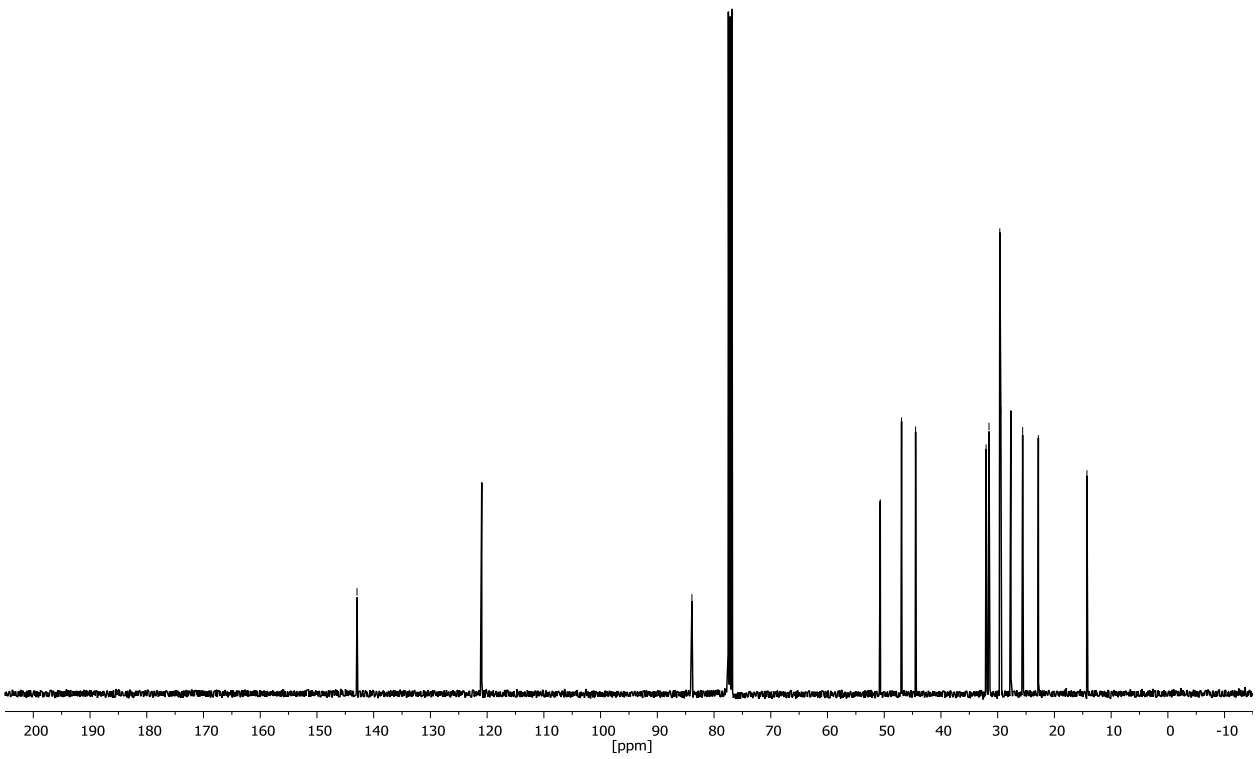
2.15
2.14
1.00
4.13
2.18
3.27
1.07
1.11
3.27
10.07
10.01
2.86
2.95
2.95
2.78
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.3
136.6
134.5
129.8
127.6
121.8
76.2
69.8
57.9
54.8
39.6
26.1
26.0
25.4
21.7
18.4
18.3
-1.7
-1.8
-5.4
-5.4

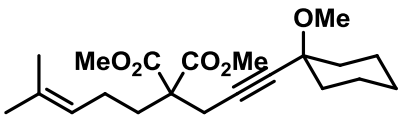

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

15

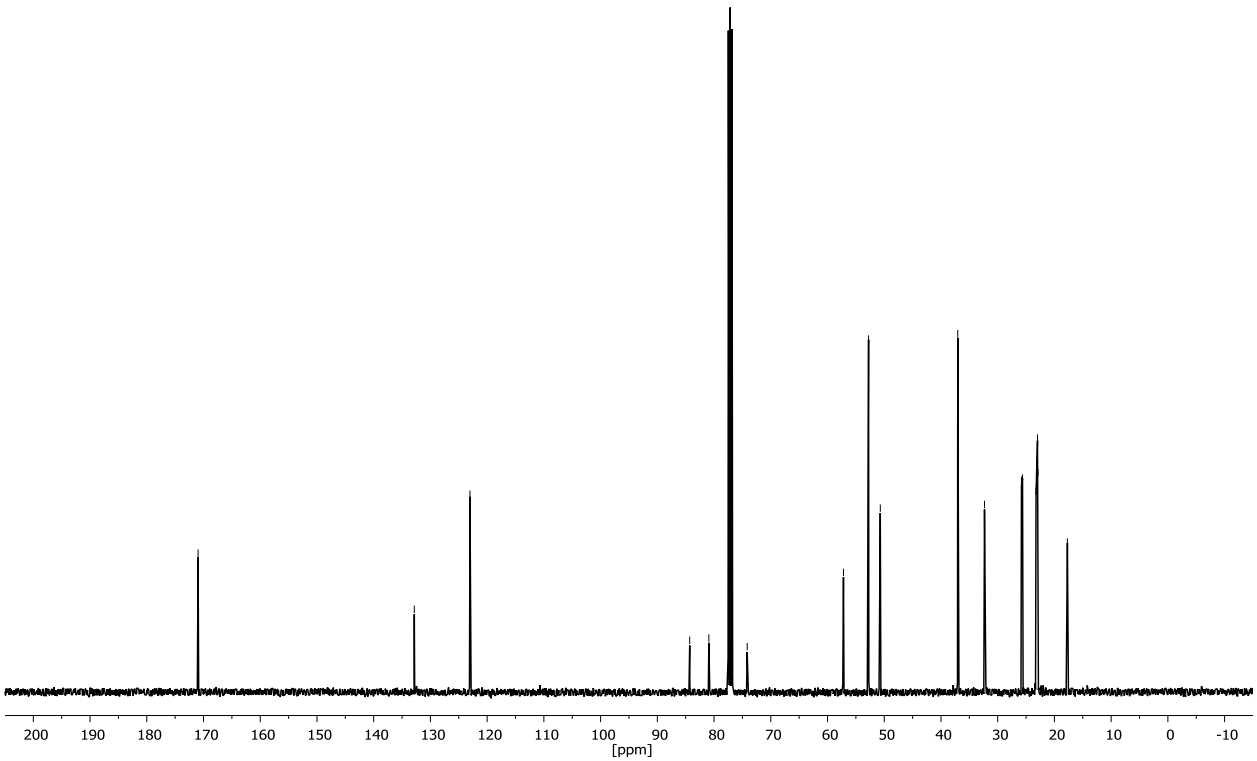
1.00
3.06
2.12
2.13
2.10
2.26
3.03
10.41
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
142.9
121.0
83.9
50.7
46.9
44.5
32.0
31.5
29.6
29.4
27.7
25.6
22.8
14.3

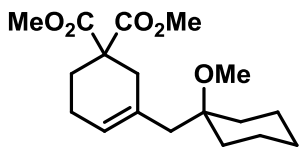

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe
MeO2C
CO2Me

17

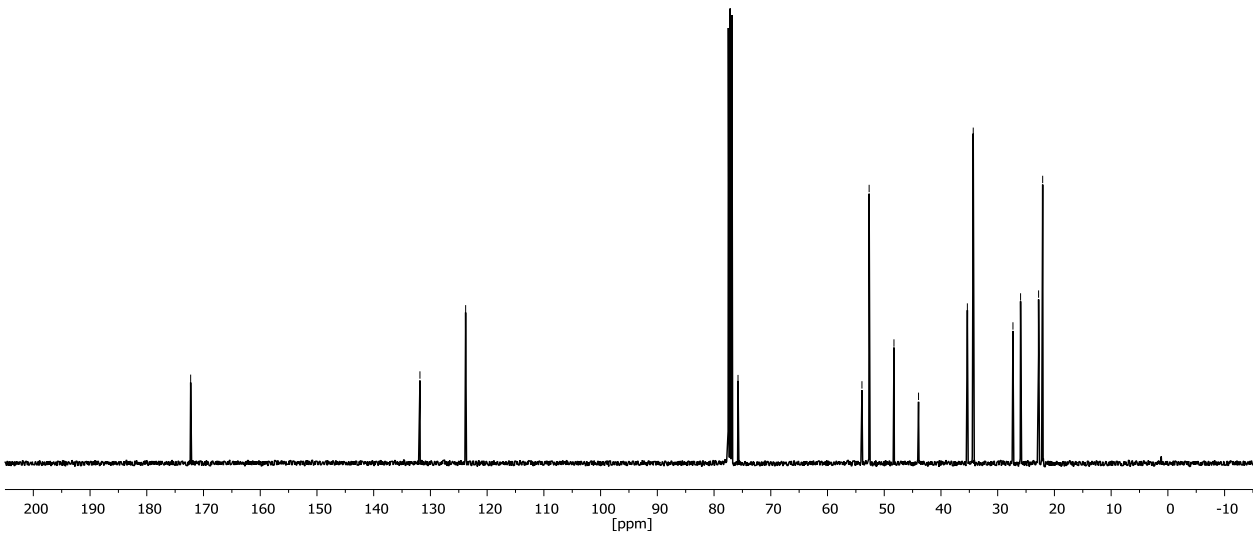
1.00
6.16
3.17
1.97
2.06
4.31
9.14
5.64
1.23
[ppm]
171.0
132.8
123.0
84.3
80.9
74.2
57.2
52.8
50.7
37.0
32.3
25.8
25.6
23.2
23.0
22.9
17.7

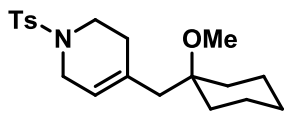

[ppm]


MeO2C
CO2Me
OMe

18

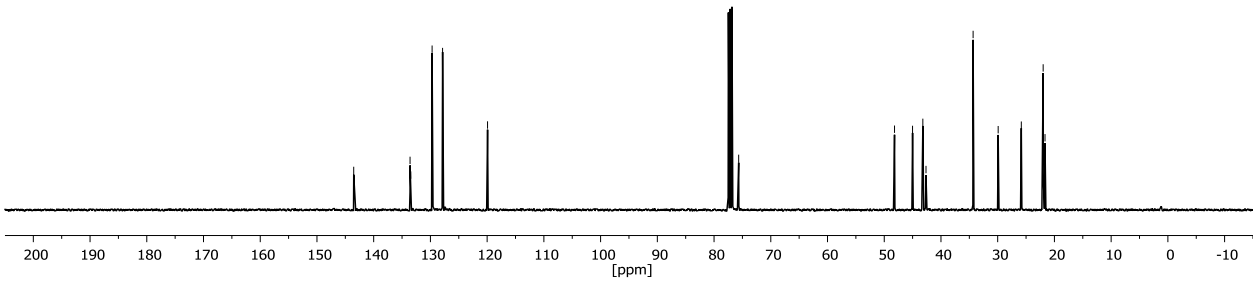
1.00
6.29
3.03
1.99
1.99
3.99
2.36
5.62
3.32
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
172.3
131.8
123.8
75.8
53.9
52.7
48.3
44.0
35.3
34.3
27.3
26.0
22.8
22.1

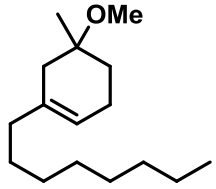

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


Ts
N
OMe

19

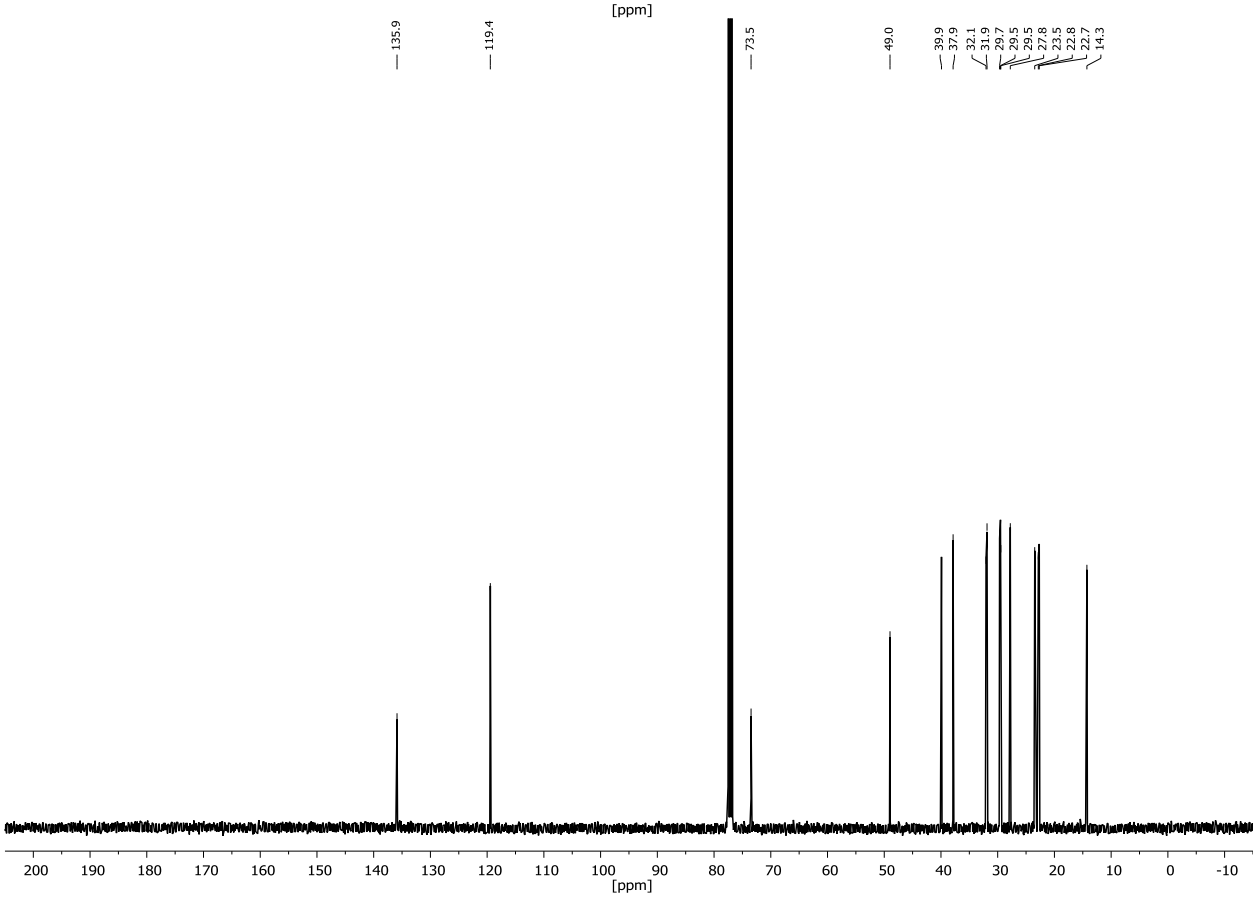
2.00
2.04
1.00
2.03
5.14
3.14
2.08
2.12
2.42
5.81
3.46
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]
143.5
133.6
133.5
129.7
127.9
119.9
75.7
48.2
45.0
43.2
42.6
34.3
29.9
25.8
22.0
21.7

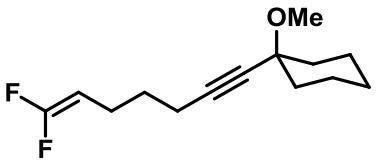

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


OMe

20

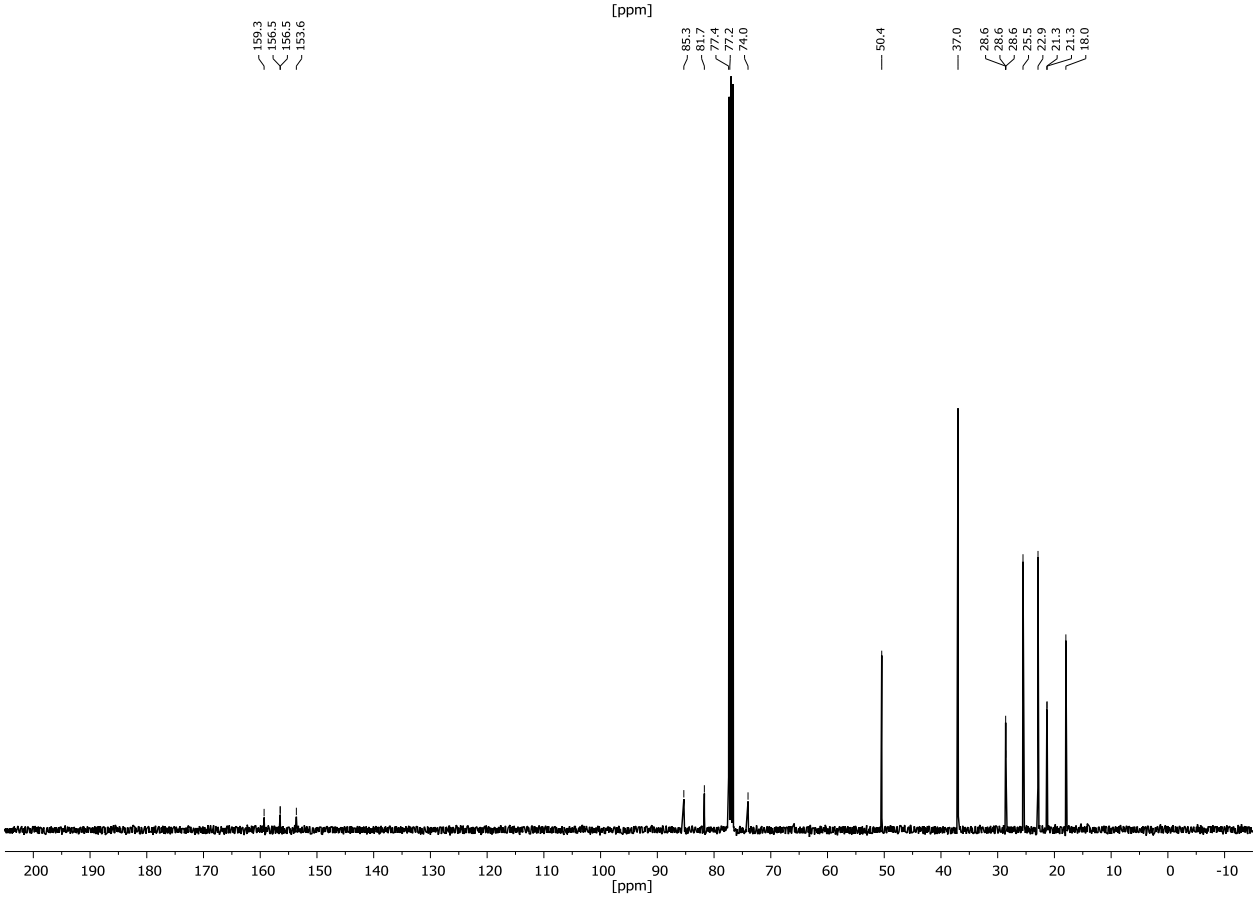
1.00
3.08
2.16
4.16
1.19
1.13
2.18
10.29
3.04
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
[ppm]

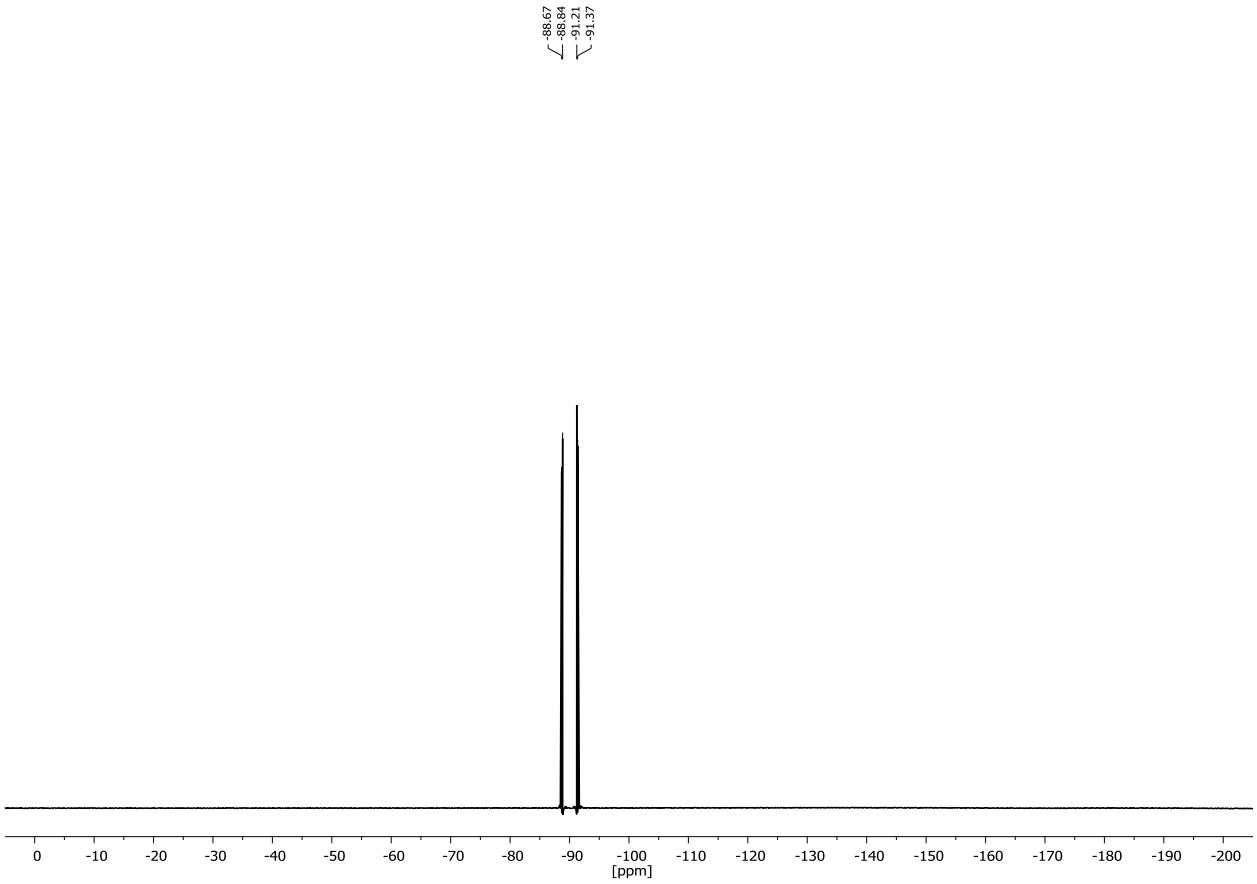

135.9
119.4
73.5
49.0
39.9
37.9
32.1
31.9
29.7
29.5
29.5
27.8
23.5
22.8
22.7
14.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

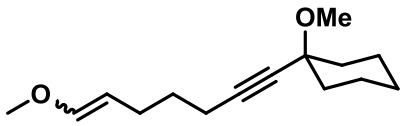

OMe
F
F

22

1.00
2.87
1.99
1.98
2.02
9.28
1.21
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 -0.5 -1.0
[ppm]

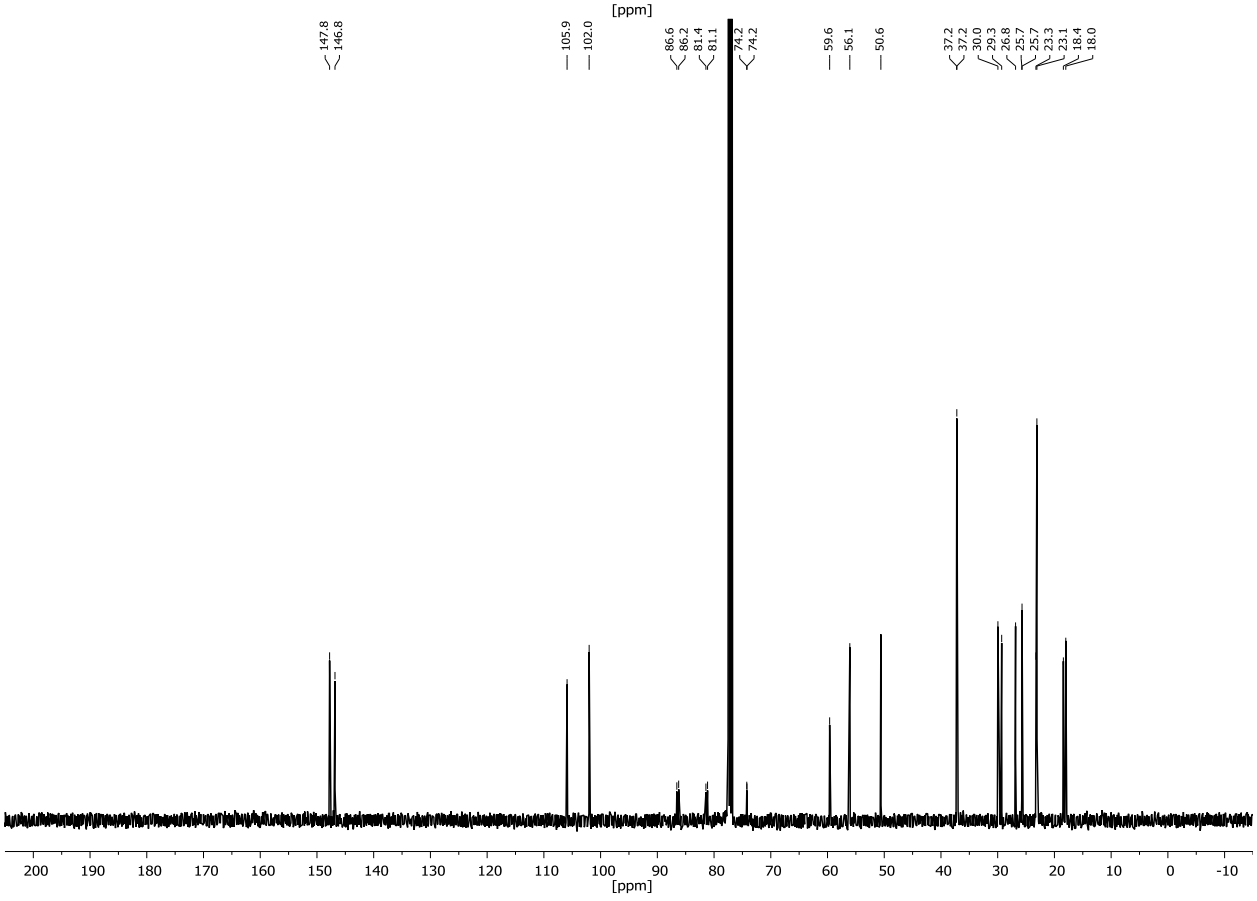

159.3
156.5
156.5
153.6
85.3
81.7
77.4
77.2
74.0
50.4
37.0
28.6
28.6
28.6
25.5
22.9
21.3
21.3
18.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]


-88.67
-88.84
-91.21
-91.37
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
[ppm]


OMe
O

23

0.54
0.46
0.55
0.47
1.40
1.70
3.13
2.17
1.03
1.19
2.04
10.55
1.47
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 -0.5 -1.0
[ppm]


147.8
146.8
105.9
102.0
86.6
86.2
81.4
81.1
74.2
74.2
59.6
56.1
50.6
37.2
37.2
30.0
29.3
26.8
25.7
25.7
23.3
23.1
18.4
18.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
[ppm]

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