

A Chiral Auxiliary-Based Synthesis of the C5-C17 *trans*-Decalin Framework of Anthracimycin

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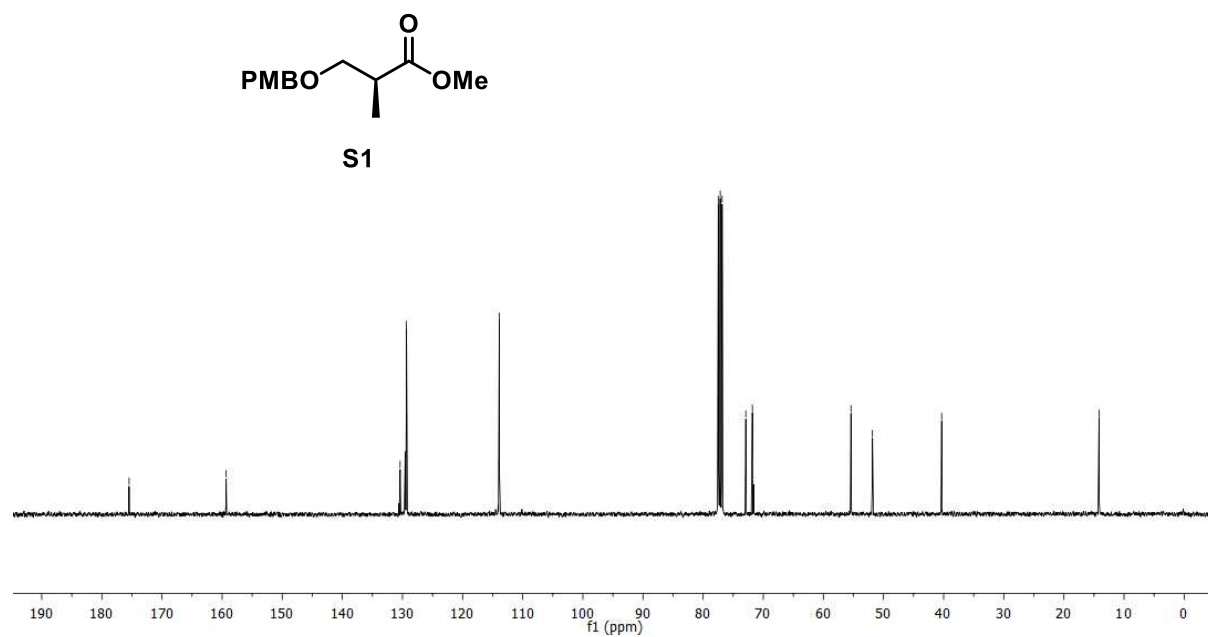
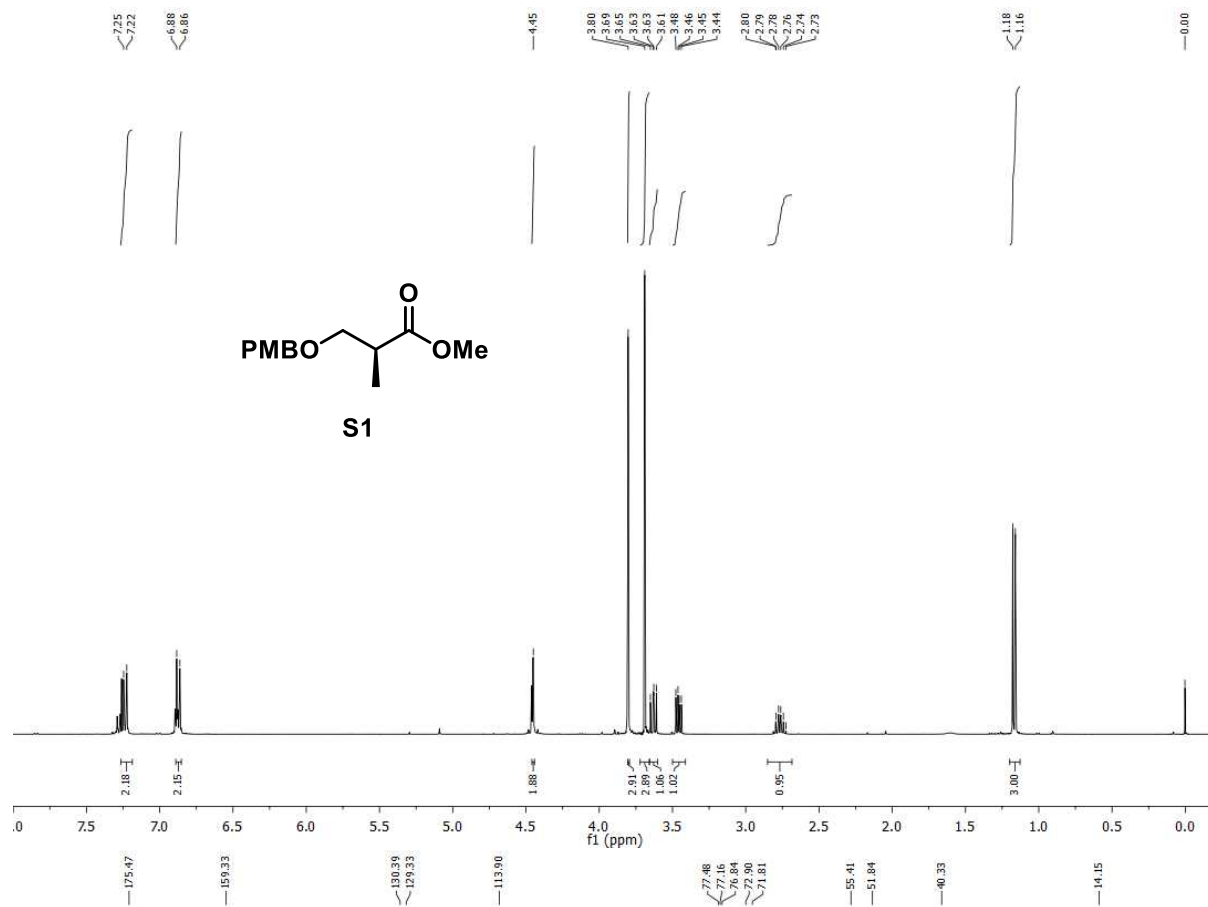
Supporting Information

S2	General Information
S3	¹ H and ¹³ C NMR Spectra
S21	NOESY Spectra for 17 + 18
S22	X-ray structure for 22

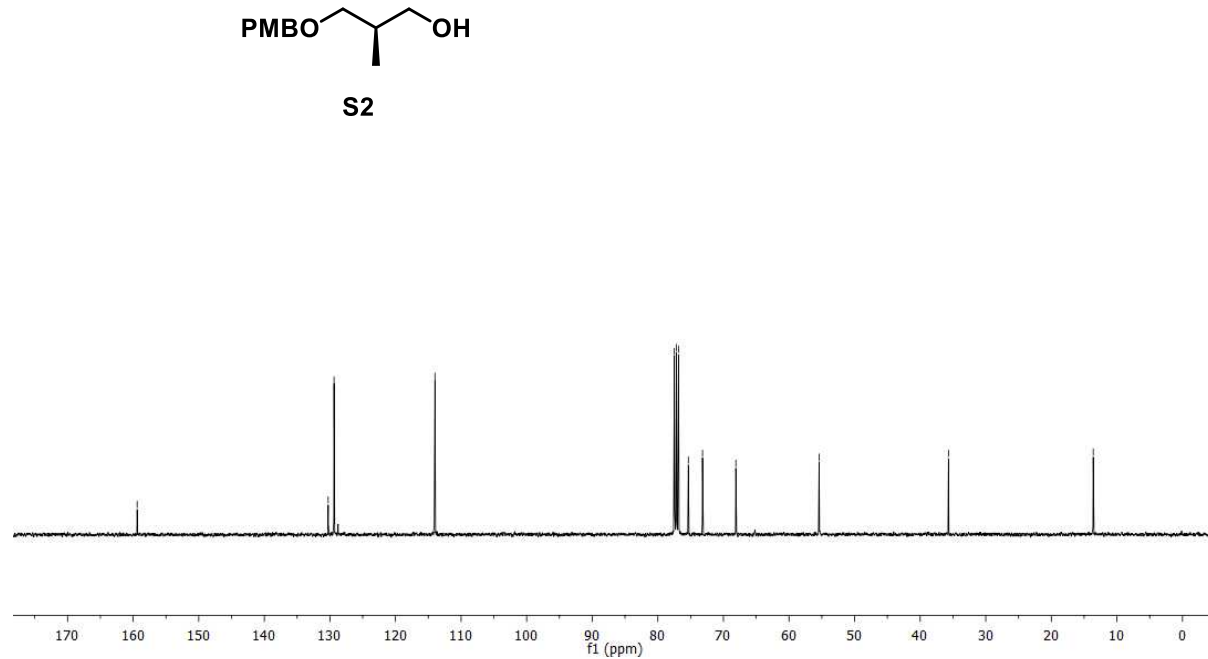
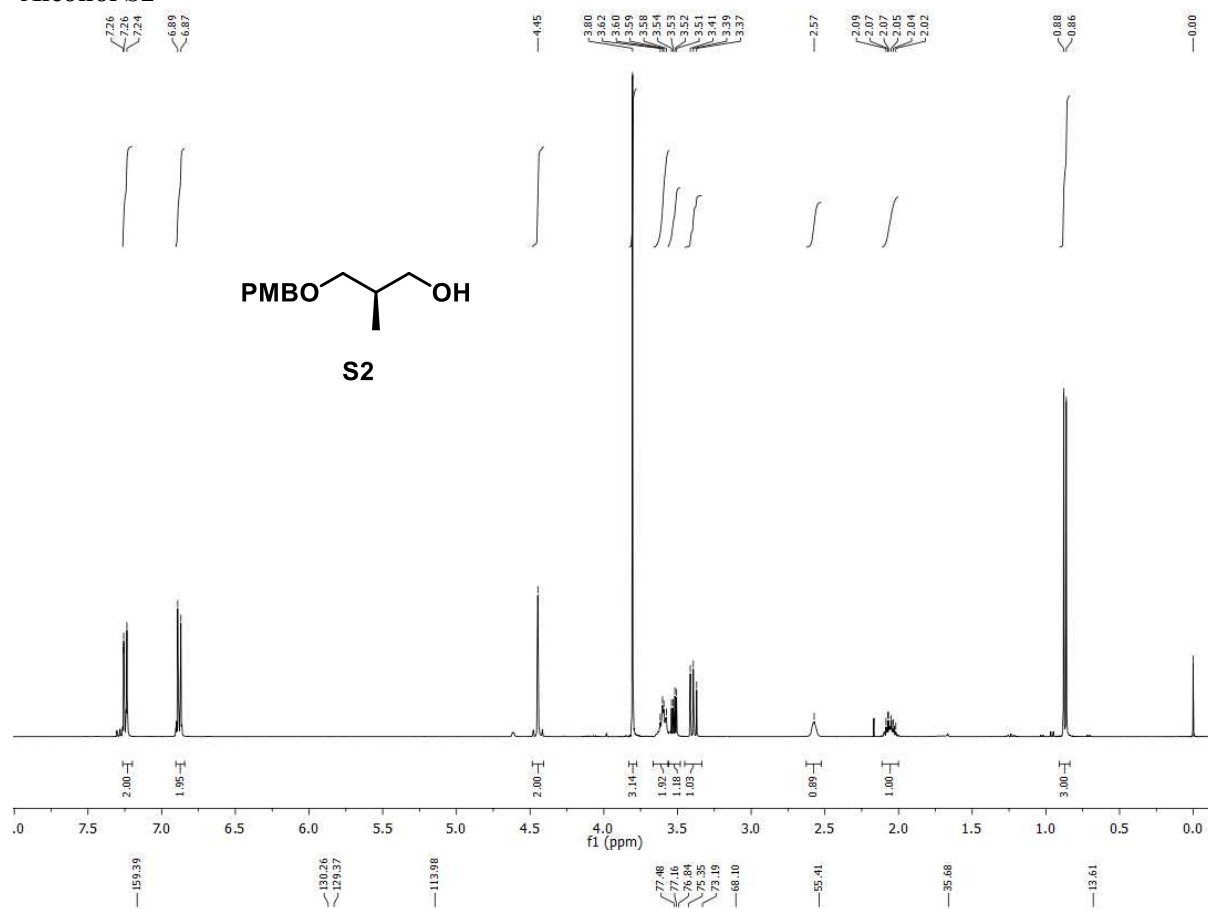
General Information

All reactions were carried out in flame- or oven-dried glassware under a dry nitrogen atmosphere unless otherwise stated. CH_2Cl_2 , $(\text{CH}_3)_2\text{CO}$, DMF, THF CH_3CN and Et_2O were obtained from a solvent purifier from LC Technology Systems. Triethylamine was distilled from calcium hydride. All other reagents were used as received unless otherwise noted. Yields refer to chromatographically and spectroscopically (^1H NMR) homogenous materials, unless otherwise stated. Reactions performed at low temperature were either cooled with an acetone/dry ice bath to reach $-78\text{ }^\circ\text{C}$, or acetone/brine/dry ice bath to reach $-30\text{ }^\circ\text{C}$, or a water ice bath to reach $0\text{ }^\circ\text{C}$. Flash chromatography was carried out using 0.063-0.1 mm silica gel with the required solvent system. TLC was carried out using 0.2 mm Kieselgel F254 (Merck) silica plates and compounds were visualised using UV irradiation at 365 nm and/or staining with vanillin in methanolic sulphuric acid or potassium permanganate and potassium carbonate in aqueous sodium hydroxide. Melting points were measured with a Kofler hot-stage apparatus and are uncorrected. NMR spectra were recorded as indicated on the Bruker DRX-400 spectrometer operating at 400 MHz for ^1H nuclei, 100 MHz for ^{13}C nuclei and 282 MHz for ^{19}F nuclei. All chemical shifts are reported in ppm relative to tetramethylsilane ($\delta = 0$ for ^1H NMR) and CDCl_3 ($\delta = 77.0$ for ^{13}C NMR). ^1H NMR data is reported as chemical shift, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; m, multiplet), coupling constant (J , Hz), and assignment. Assignments were made with the aid of COSY, NOESY and HSQC experiments where required. High resolution mass spectra were recorded using a VG-70SE spectrometer at a nominal accelerating voltage of 70 eV or on a Bruker micrOTOF-Q II mass spectrometer.

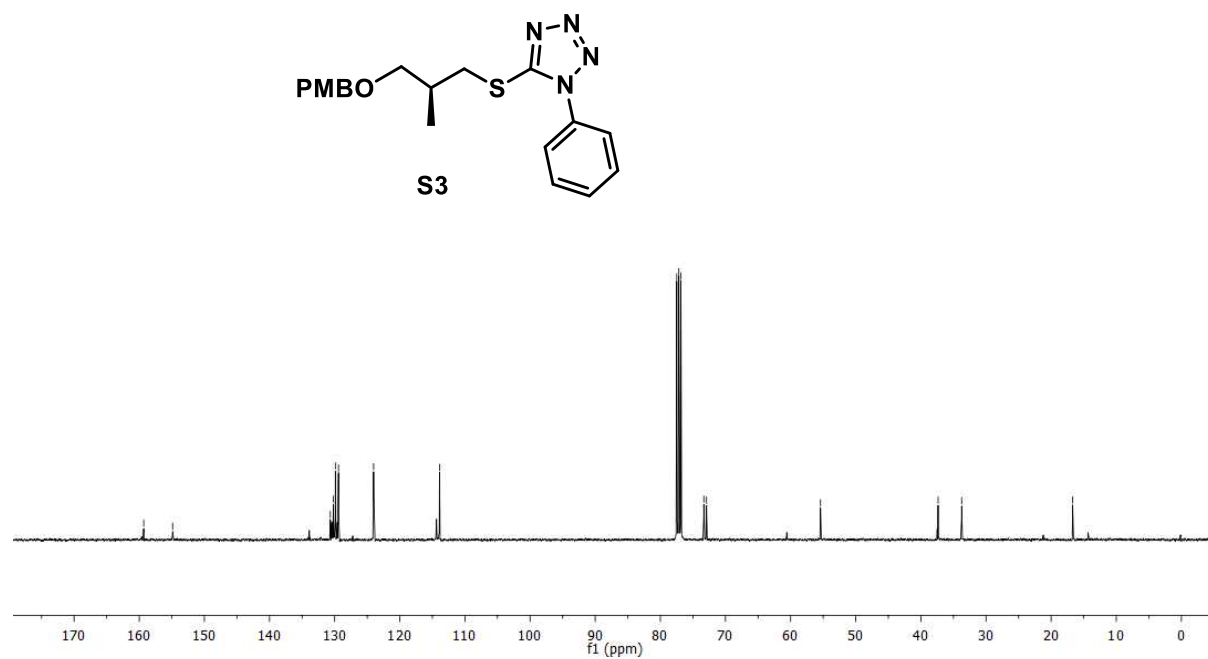
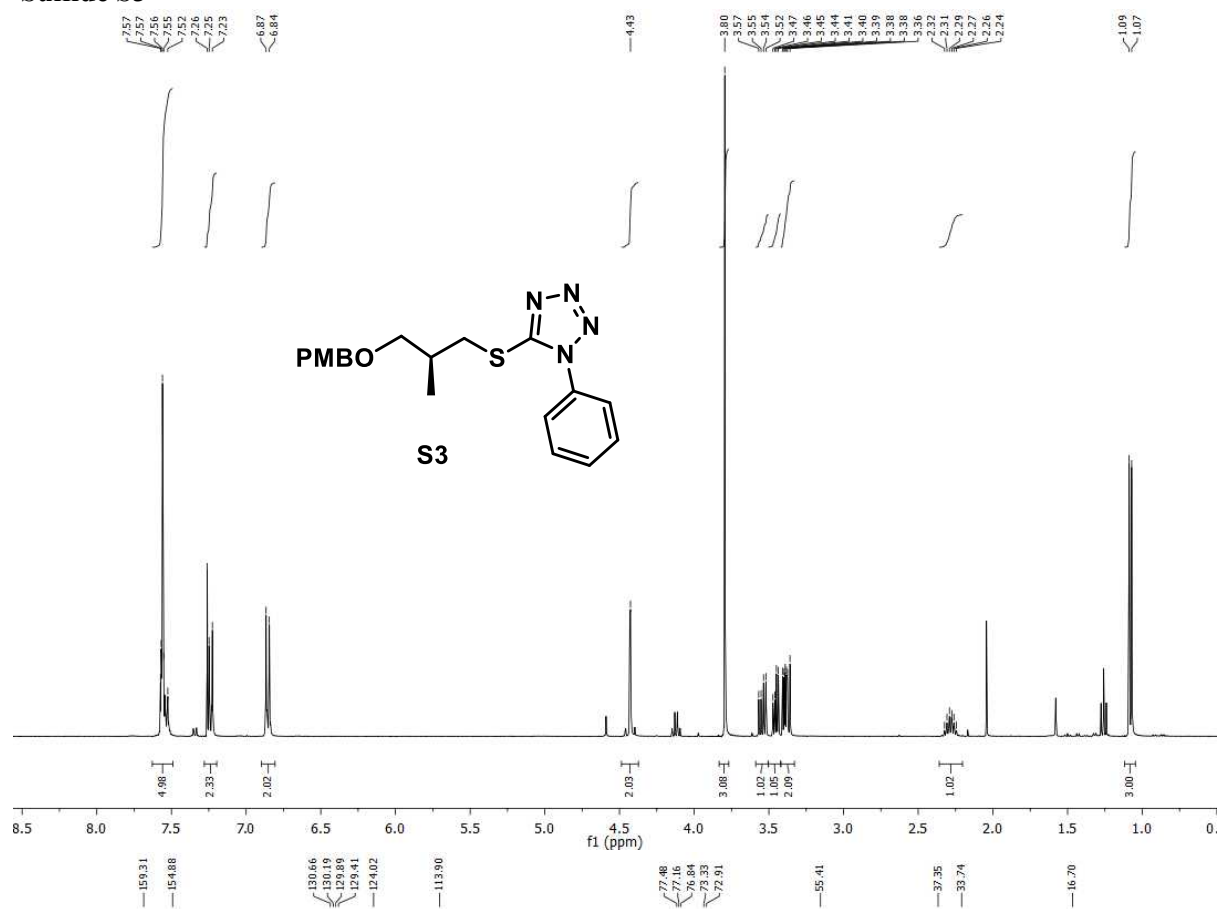
Ester S1



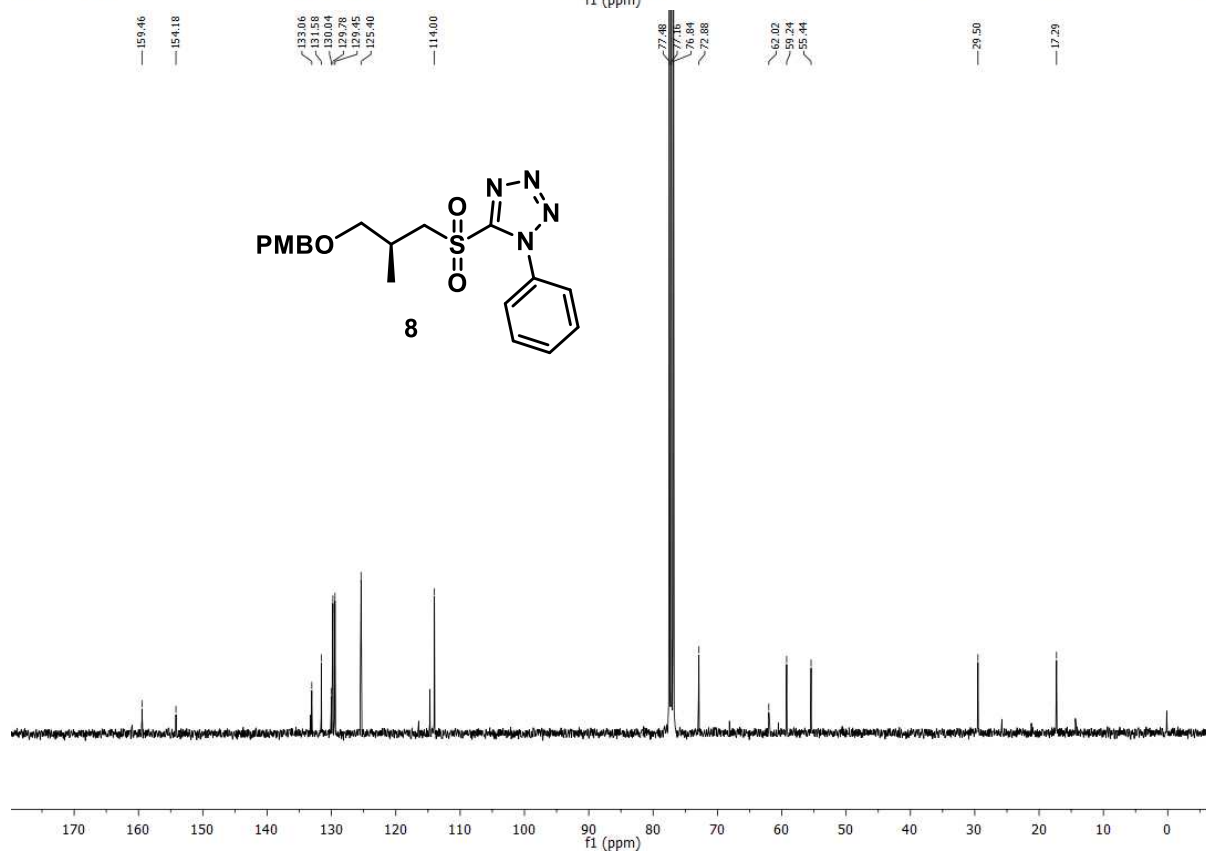
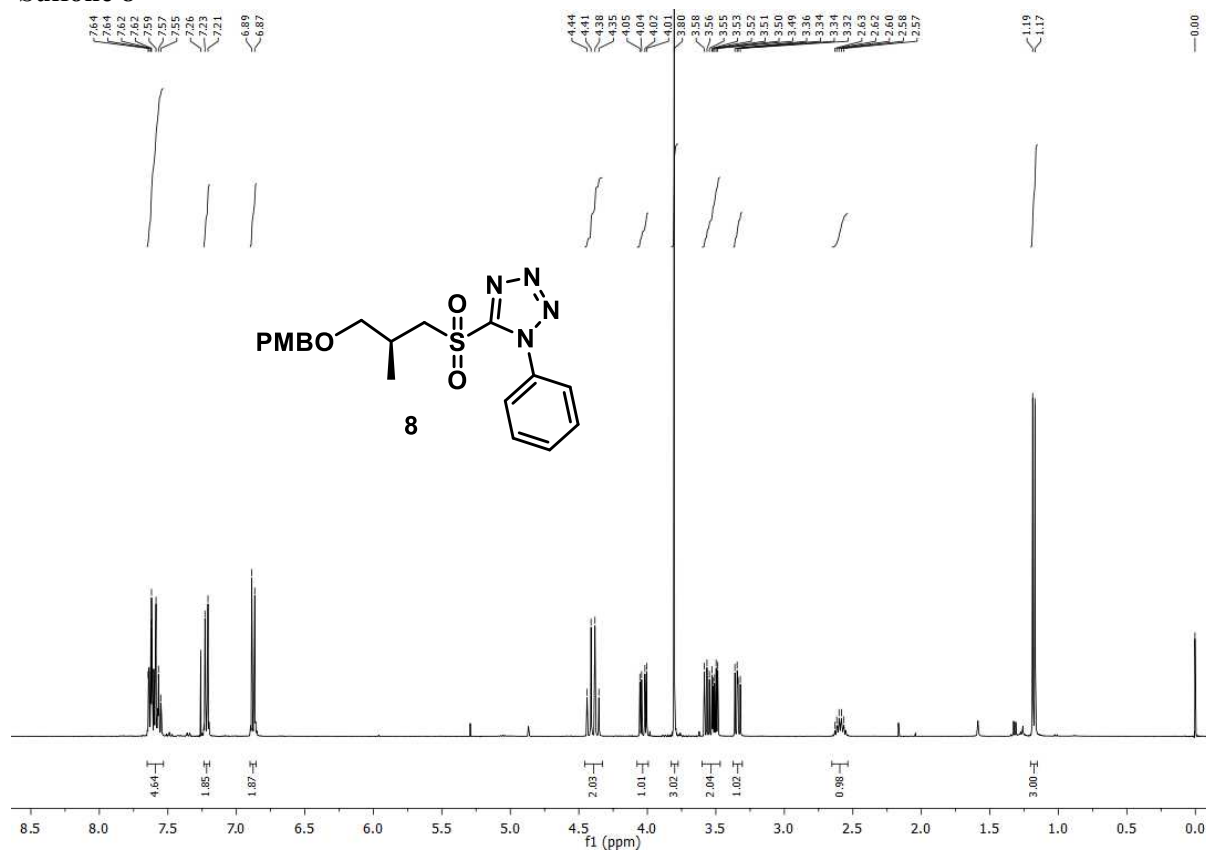
Alcohol S2



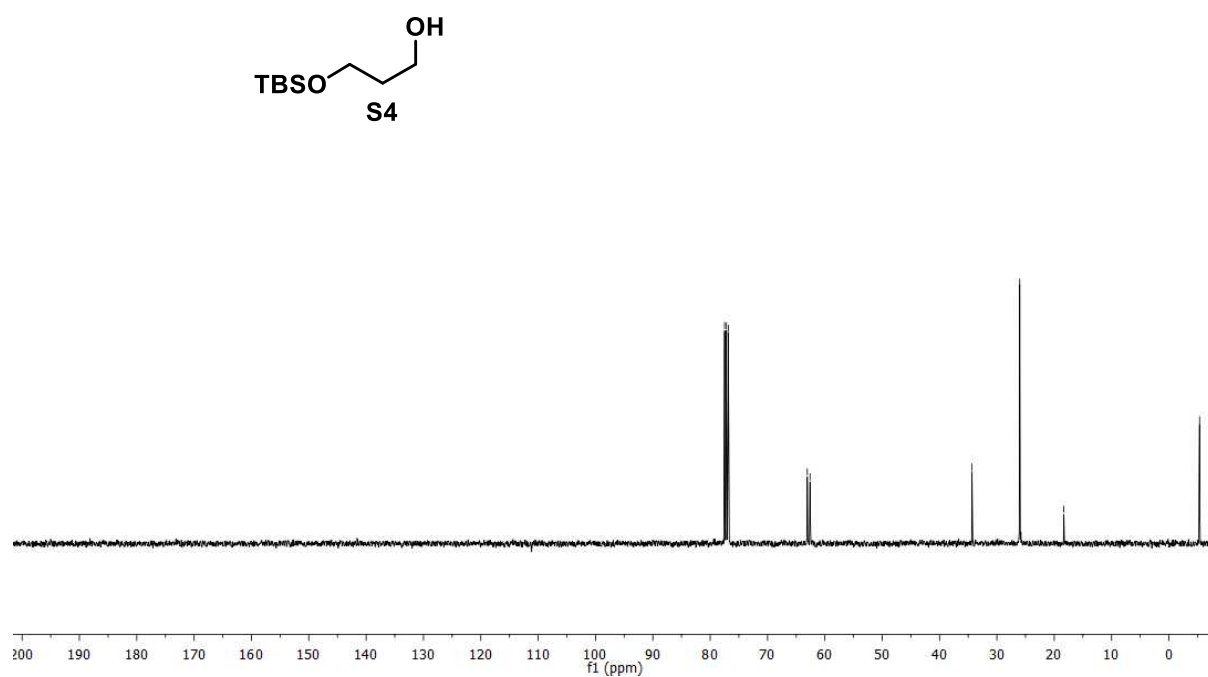
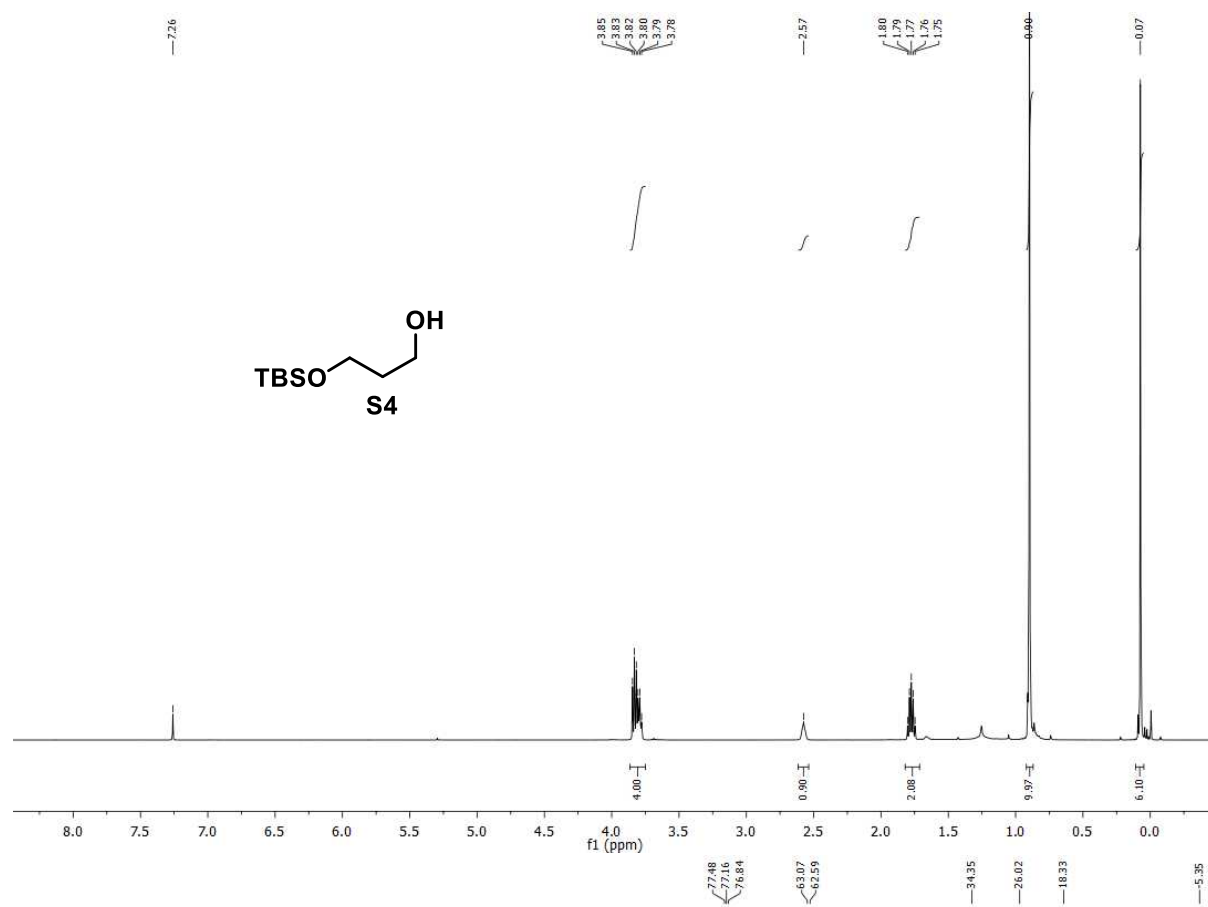
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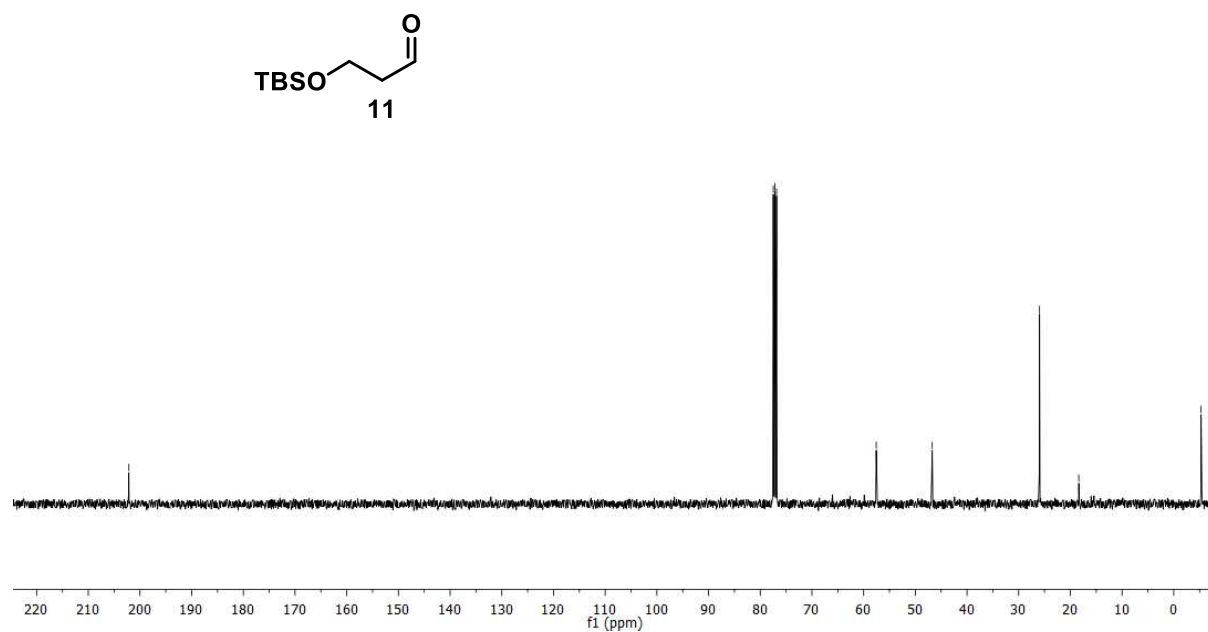
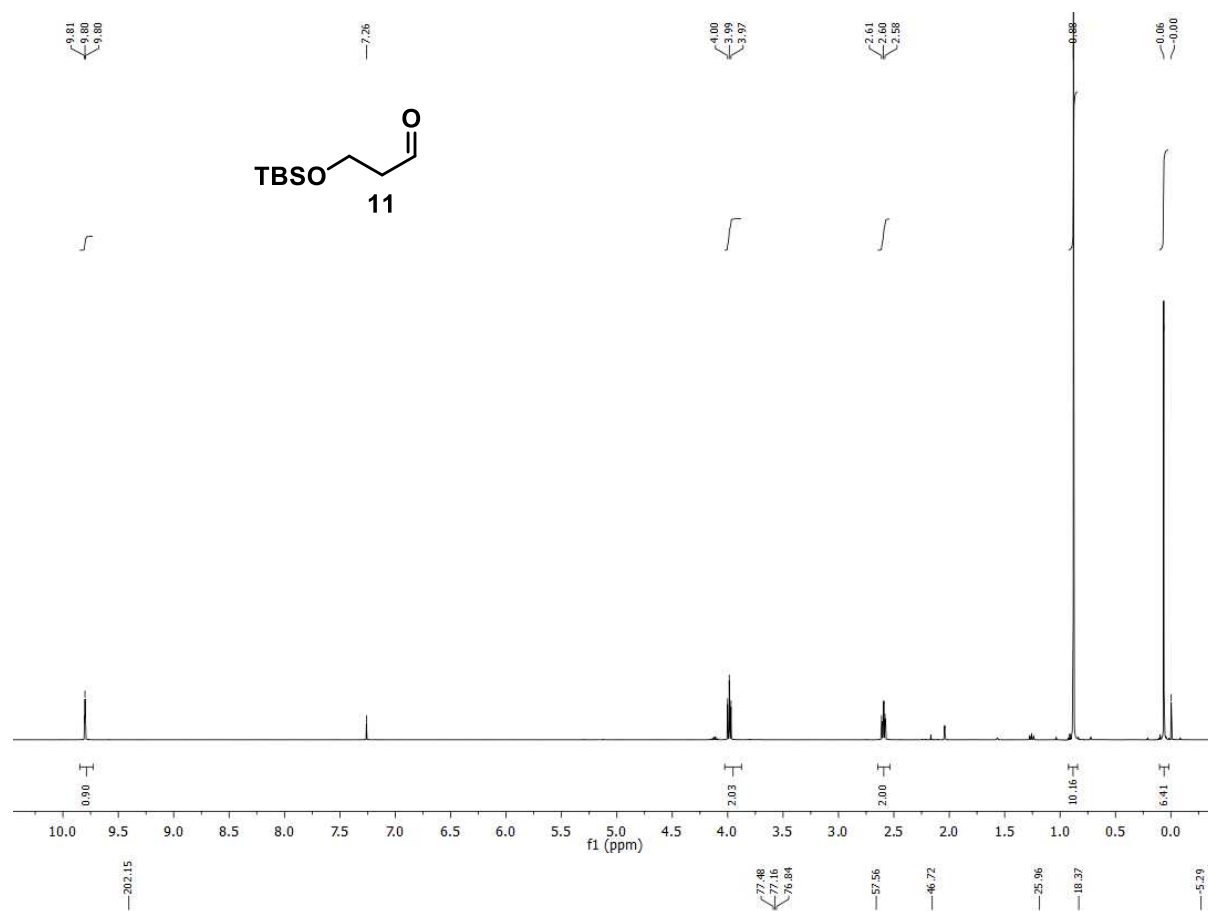
Sulfone 8



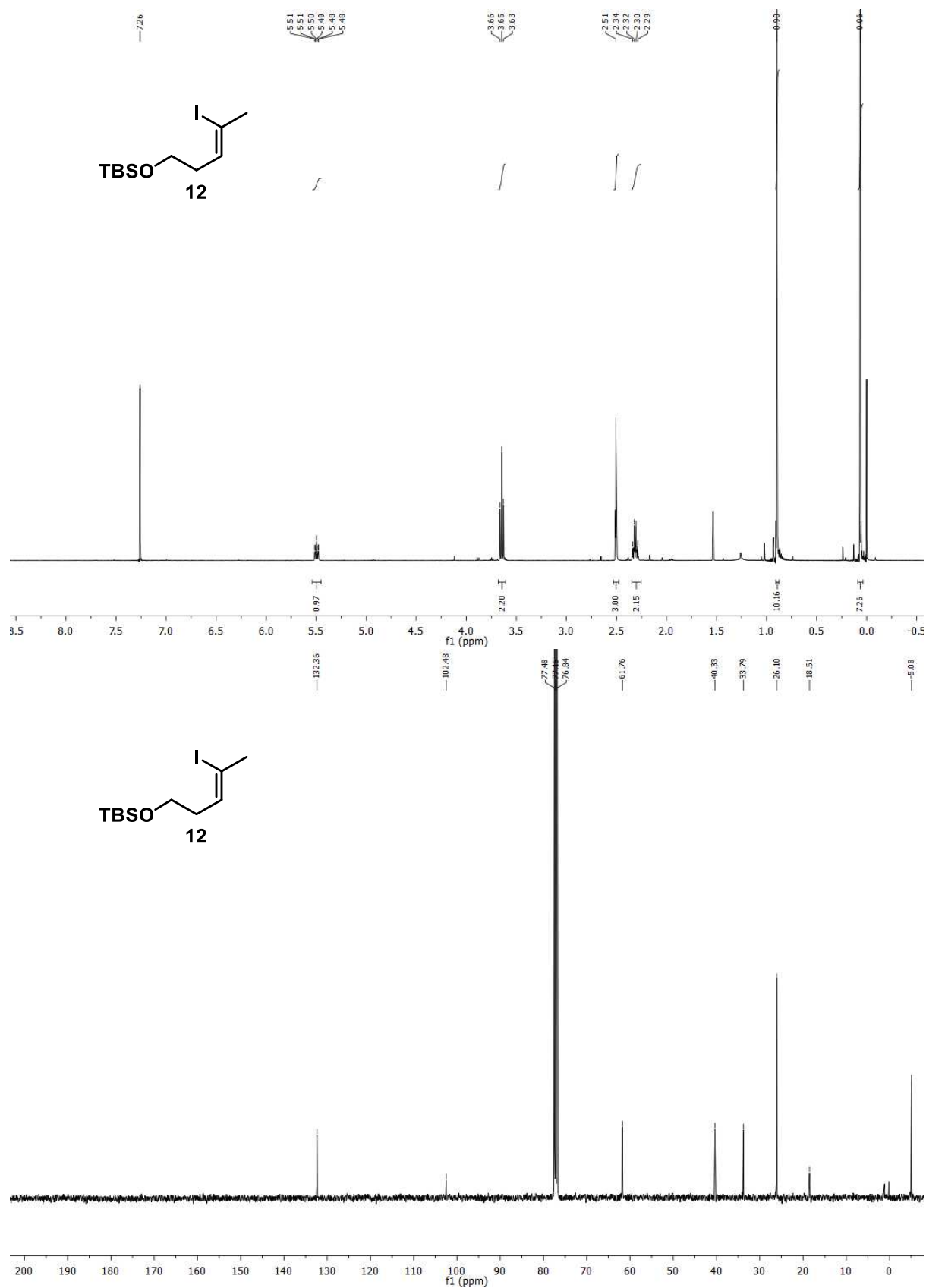
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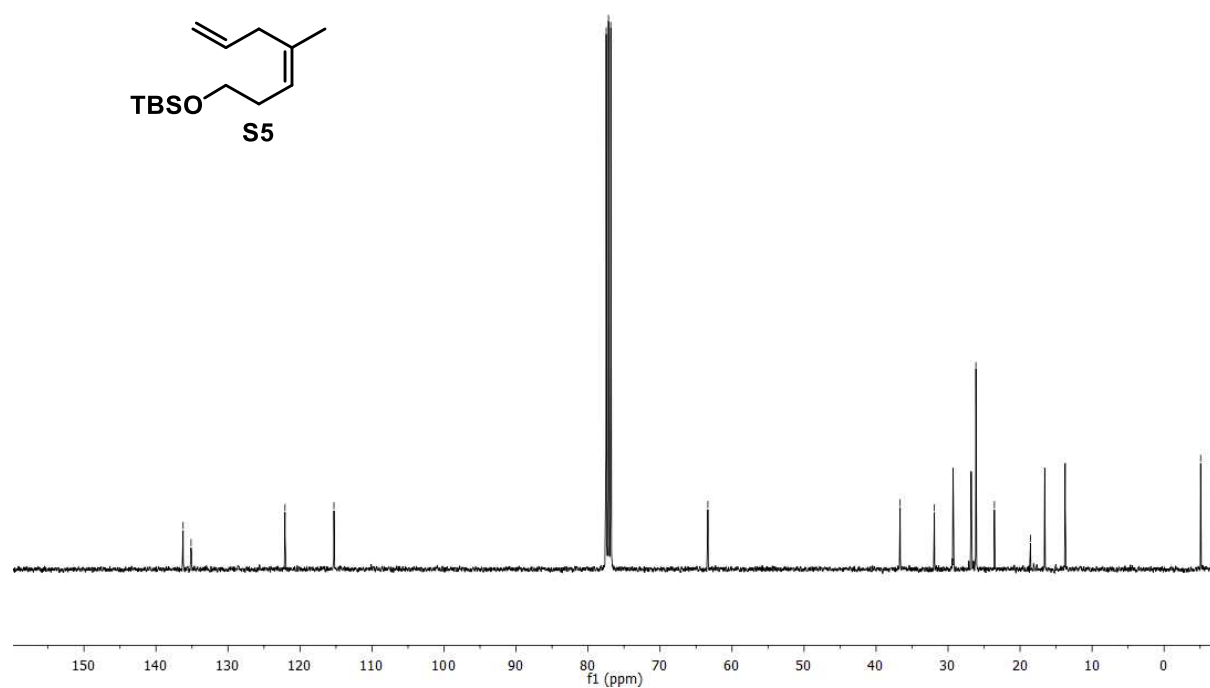
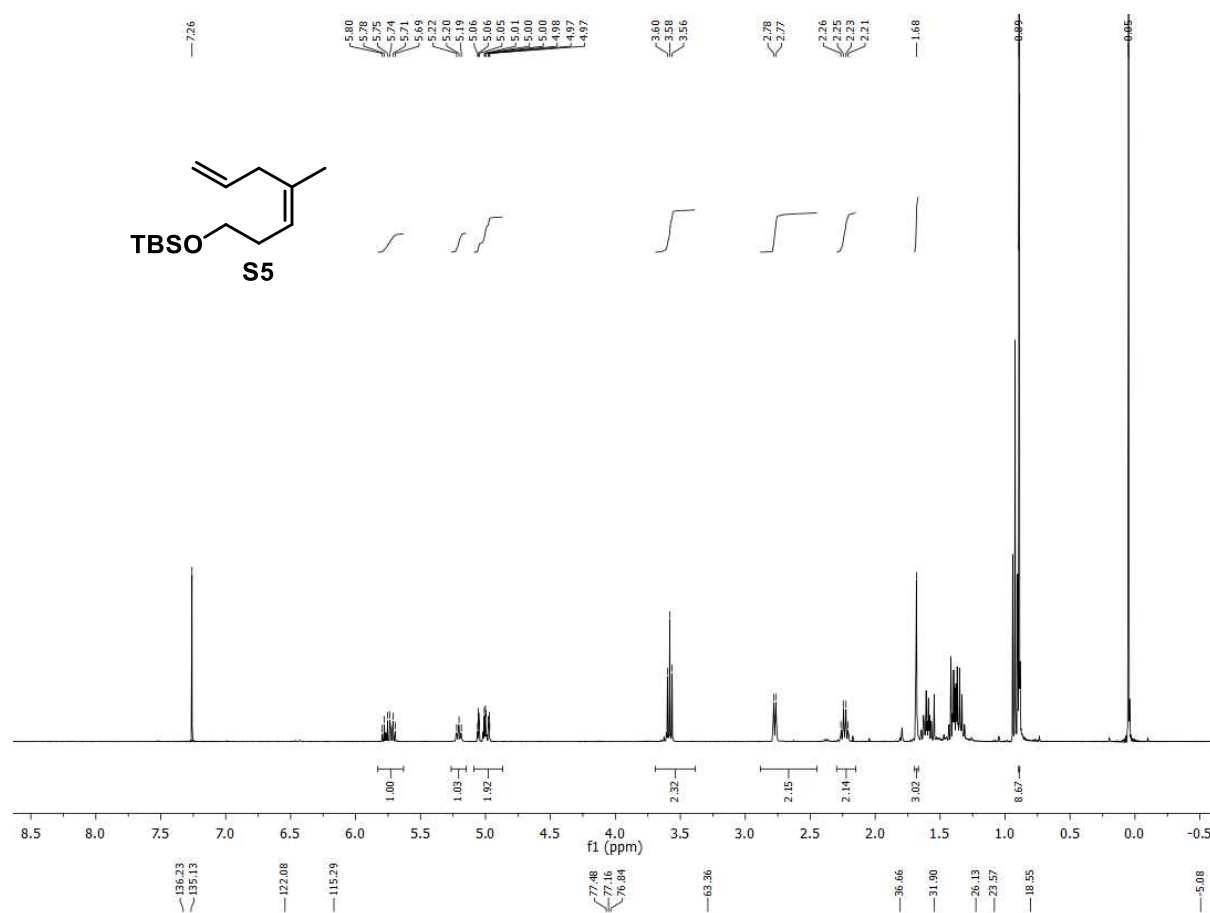
Aldehyde 11



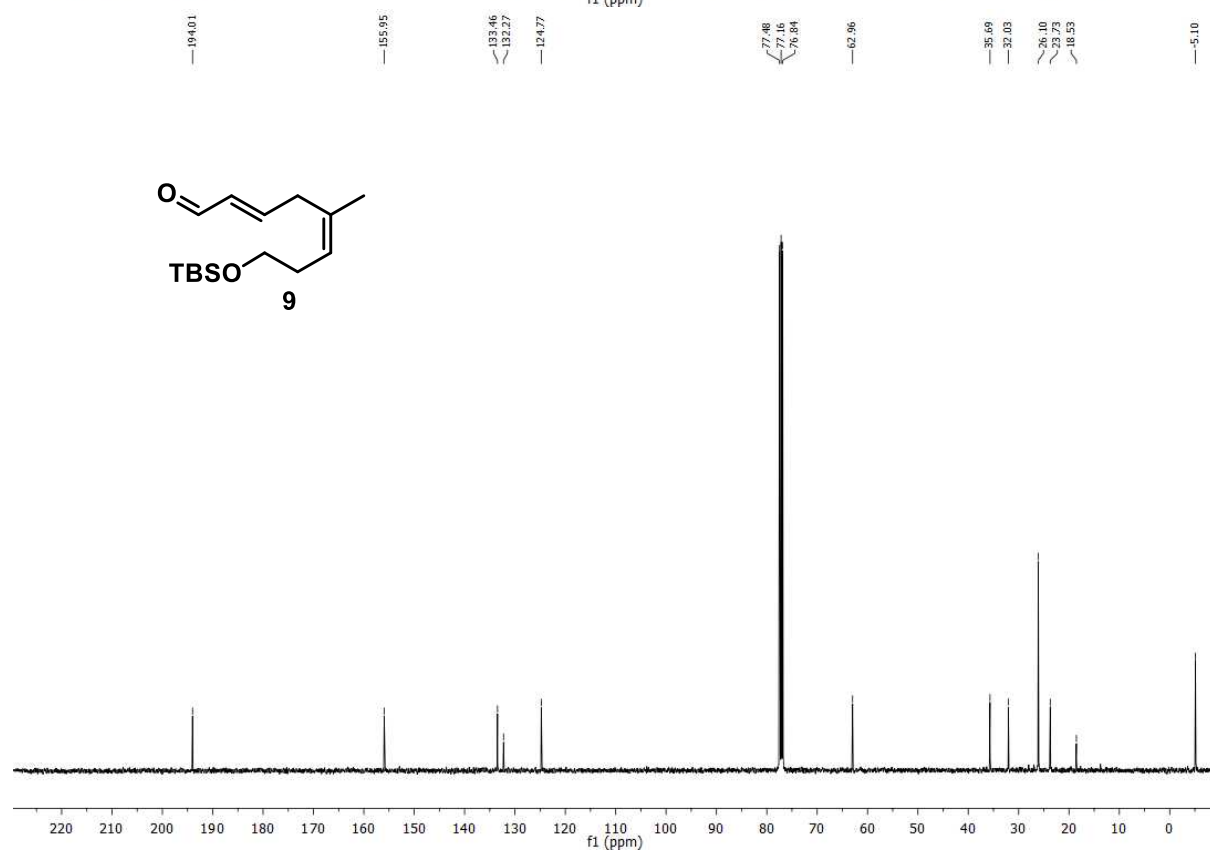
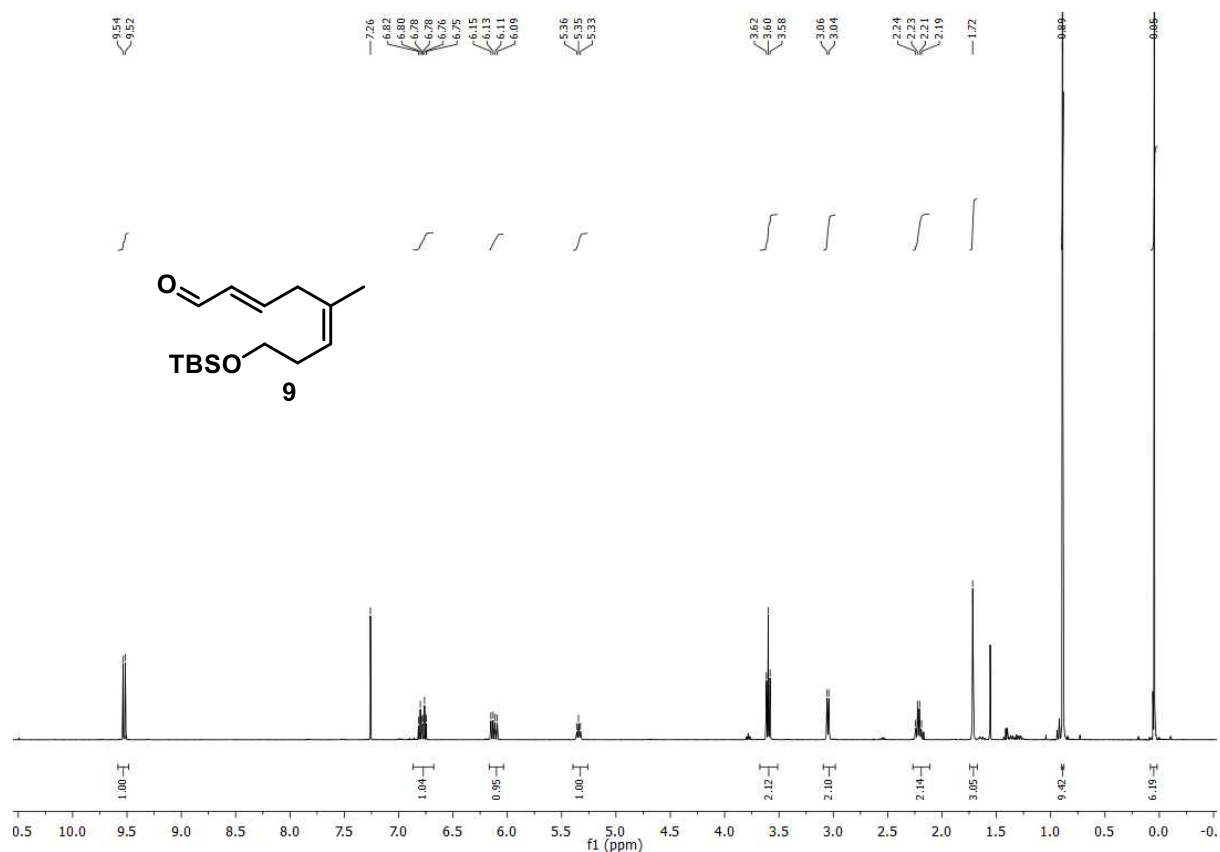
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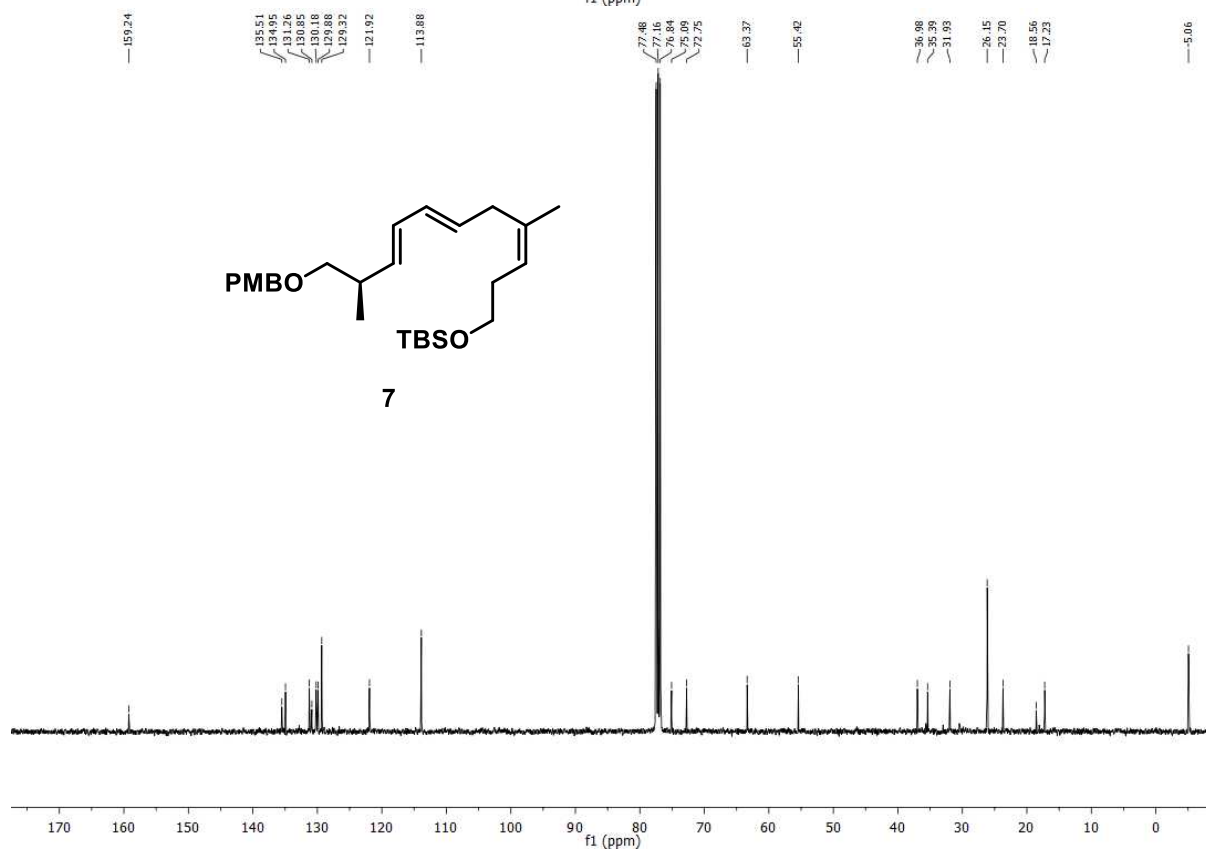
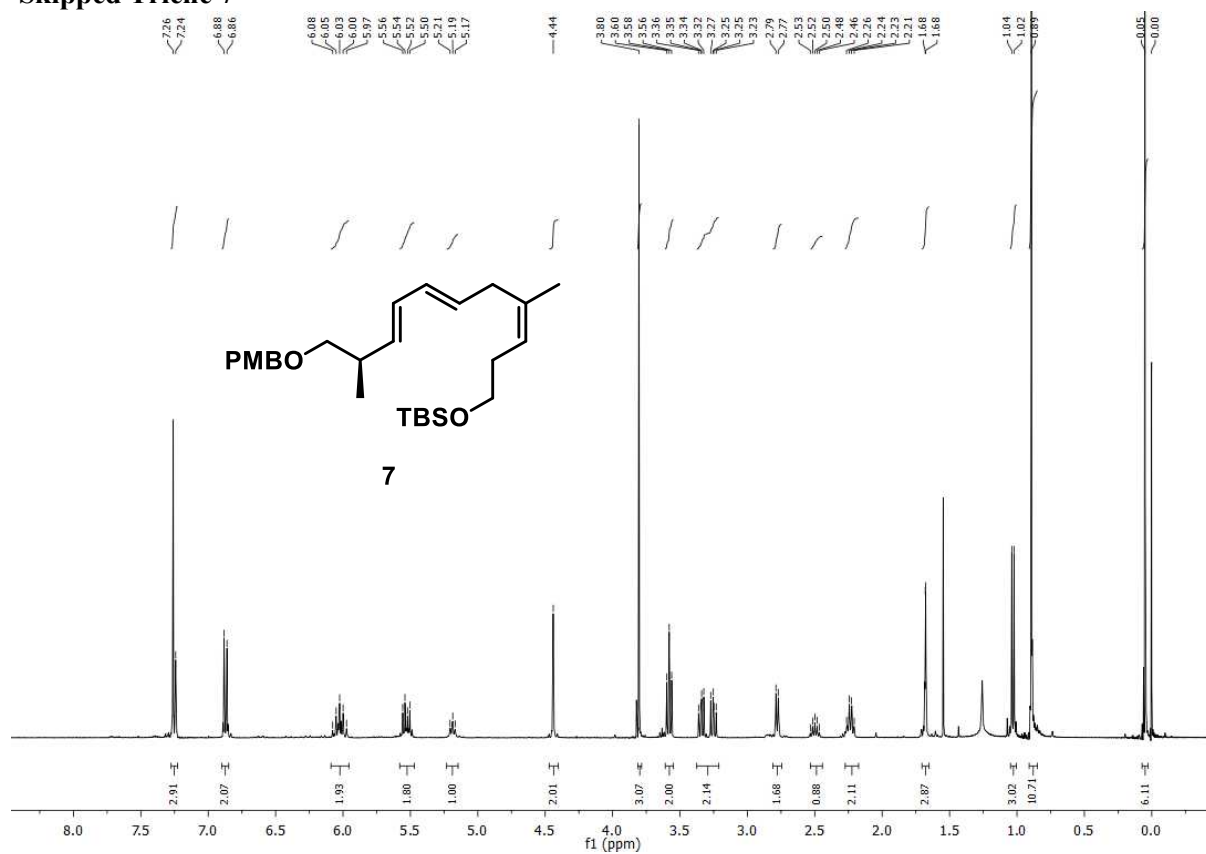
Alkene S5



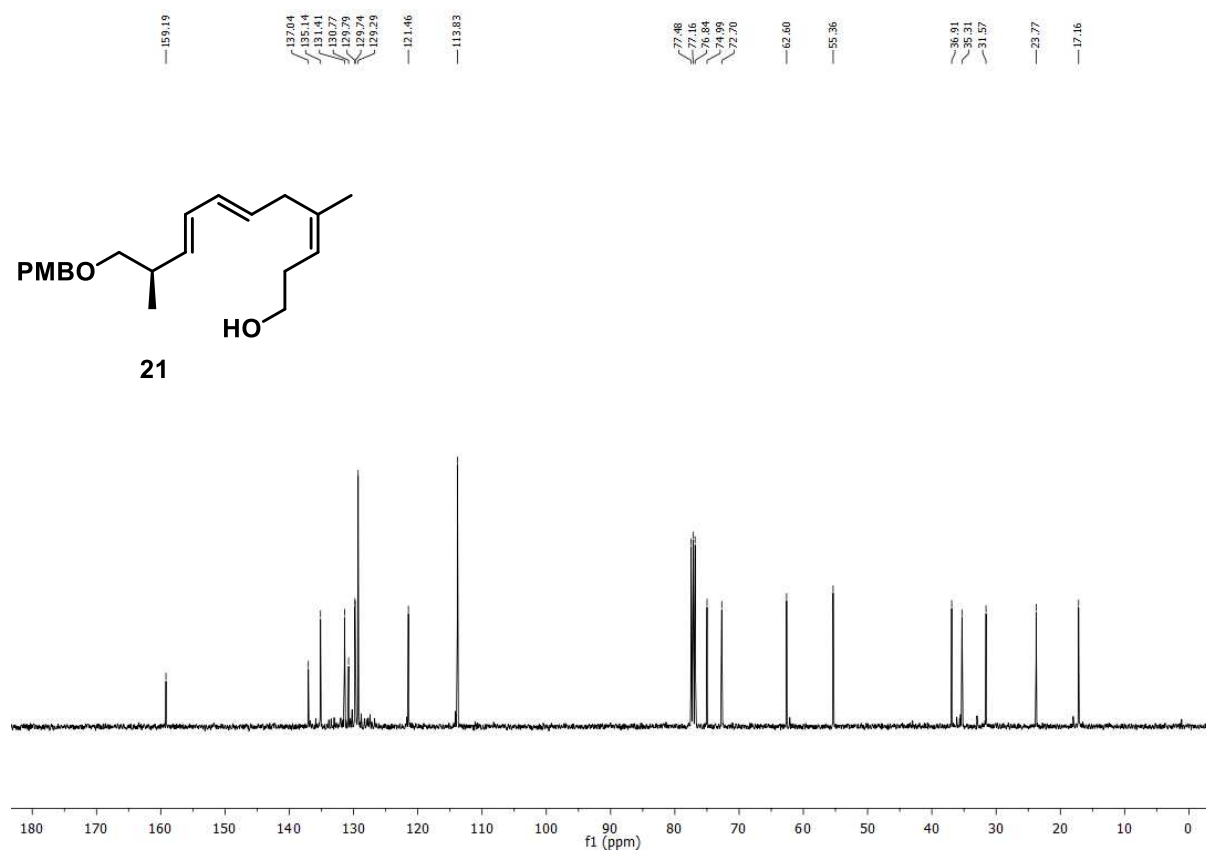
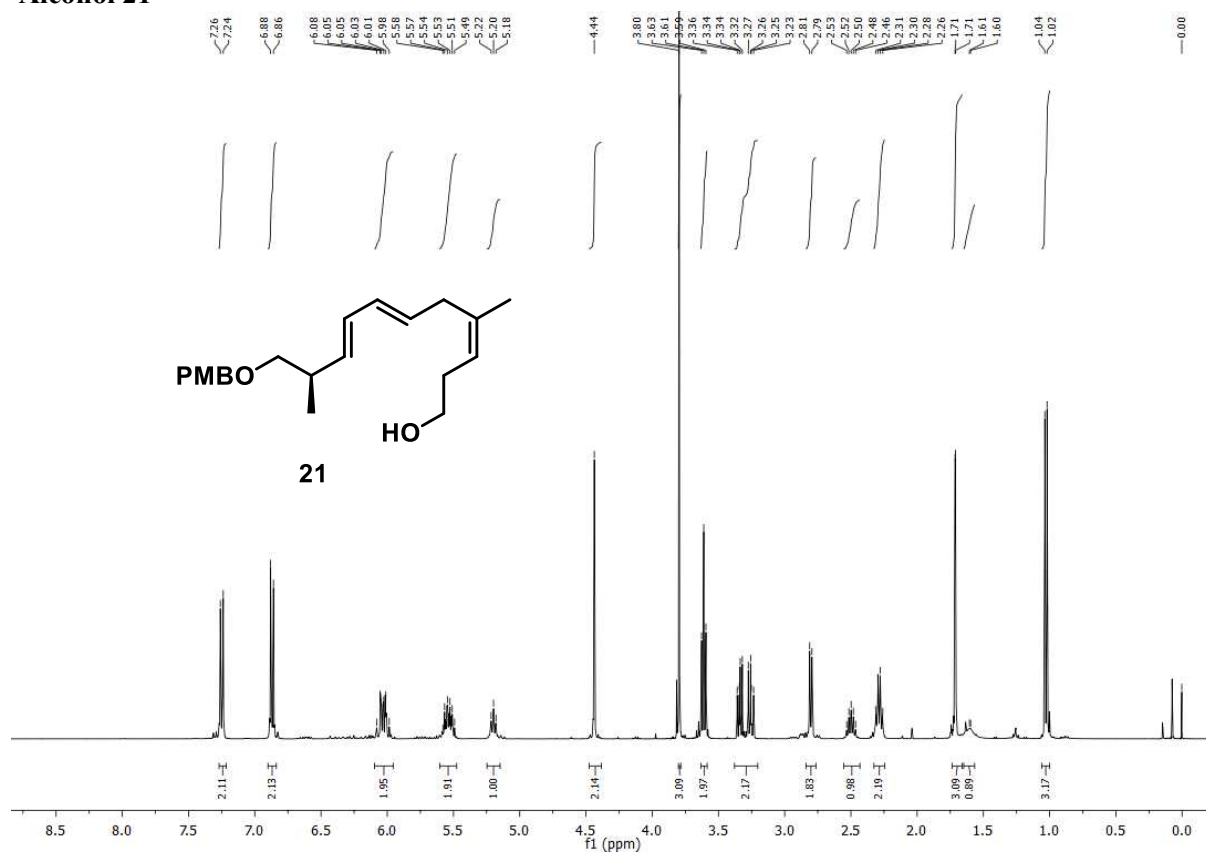
Aldehyde 9



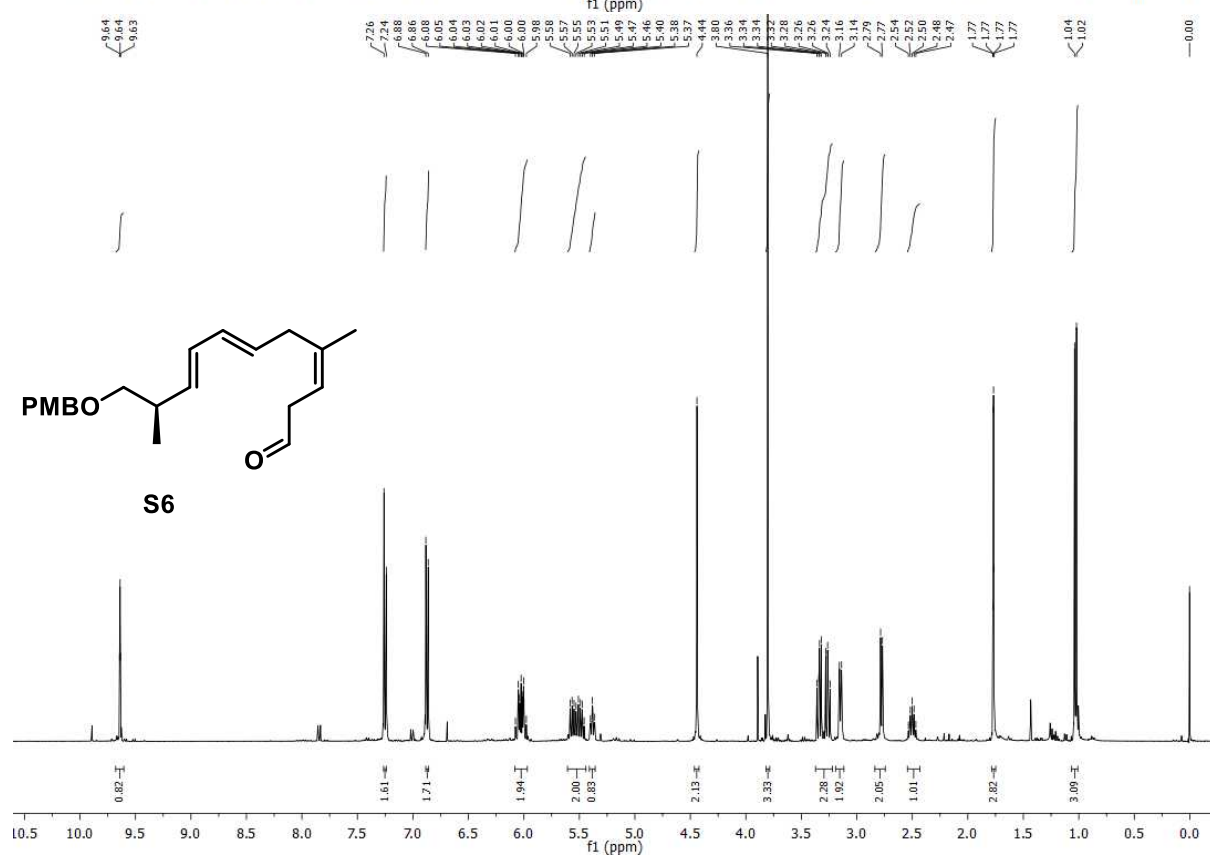
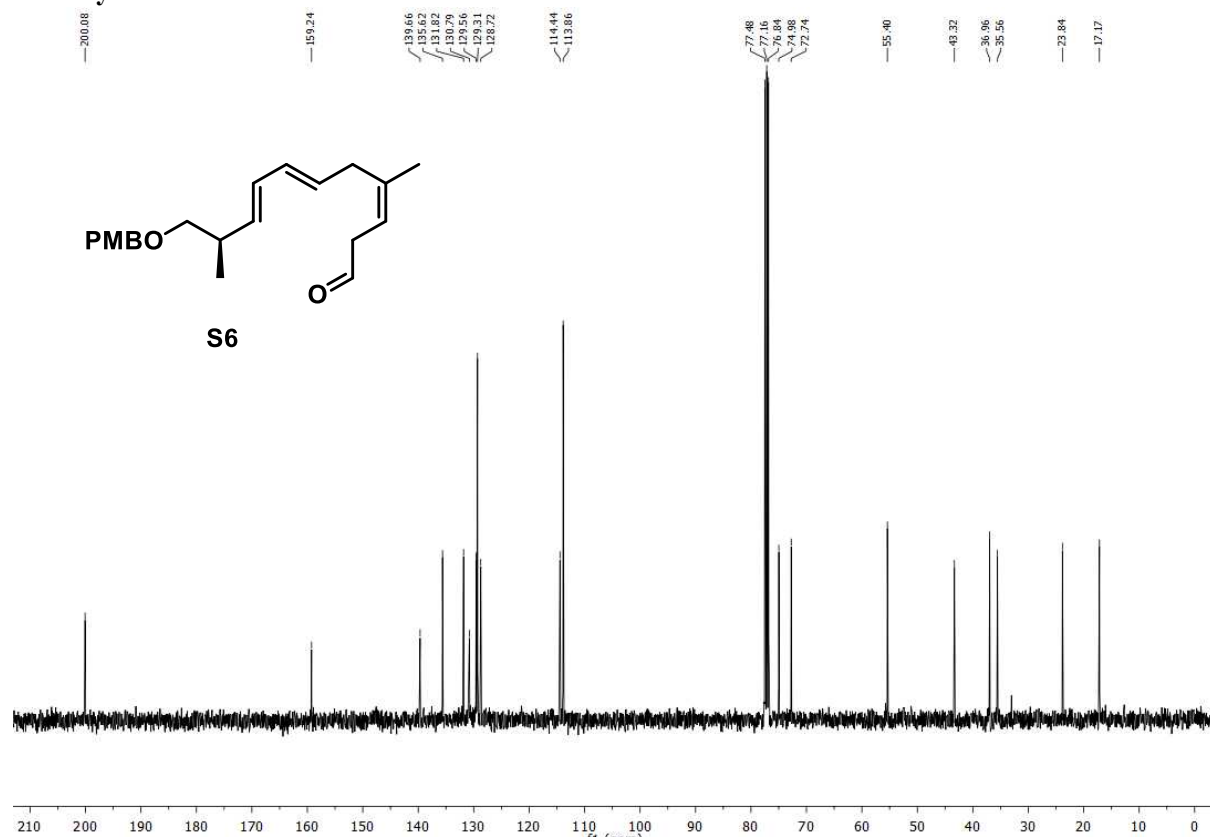
Skipped Triene 7



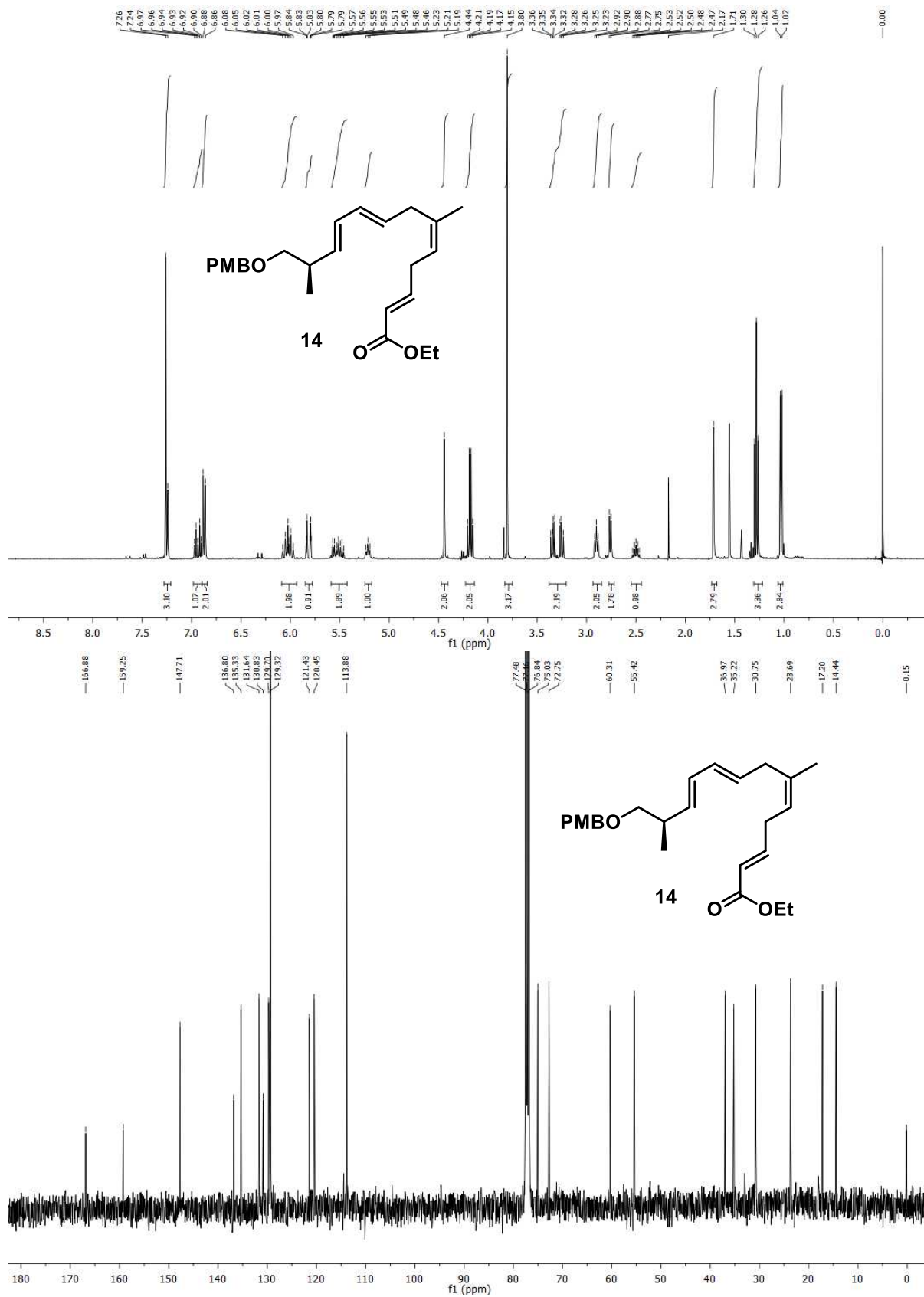
Alcohol 21



Aldehyde S6



Ester 14



The figure displays the ^1H and ^{13}C NMR spectra of compound **15**, which is a long-chain unsaturated aldehyde with a PMBO group and a chiral center. The chemical structure of **15** is shown in the top left corner of each spectrum.

^1H NMR Spectrum (Top): The spectrum shows peaks in the aromatic region (6.8–7.3 ppm), alkene region (5.5–6.2 ppm), aliphatic region (1.0–2.8 ppm), and a TMS peak at 0.00 ppm. Integration values are provided below the baseline.

Chemical Shift (ppm)	Integration
~9.52	1.00
~7.26	2.66
~6.88	3.23
~6.15	1.15
~6.02	1.92
~5.58	2.07
~4.50	1.12
~4.50	2.01
~3.22	3.22
~2.36	2.36
~2.08	2.08
~1.98	1.98
~1.11	1.11
~1.59	2.89
~1.04	3.42

^{13}C NMR Spectrum (Bottom): The spectrum shows peaks from 17 to 159 ppm. The TMS peak is at 0 ppm.

Chemical Shift (ppm)
159.26
157.17
137.66
135.59
132.95
131.80
130.82
129.59
128.98
128.96
119.69
113.88
77.48
77.16
76.84
75.01
72.76
55.43
36.98
35.26
31.08
23.75
17.19

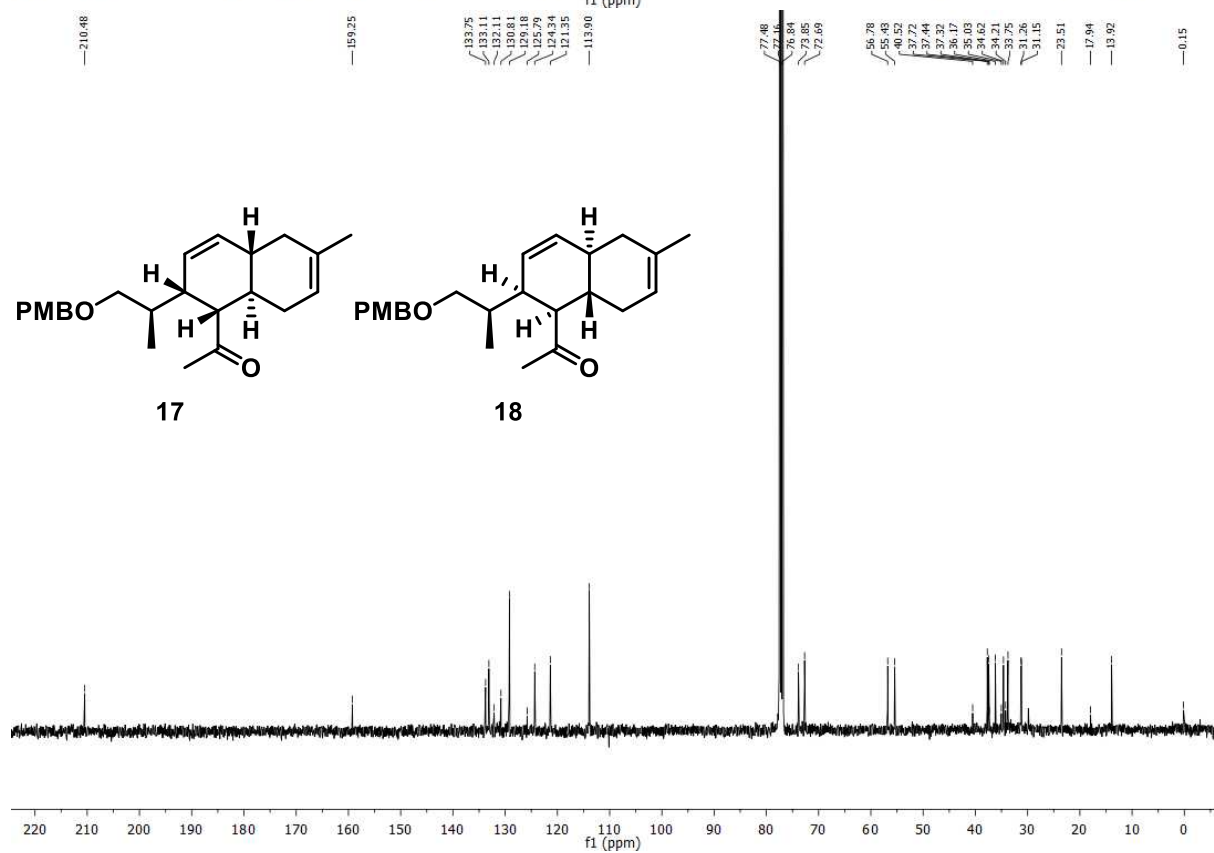
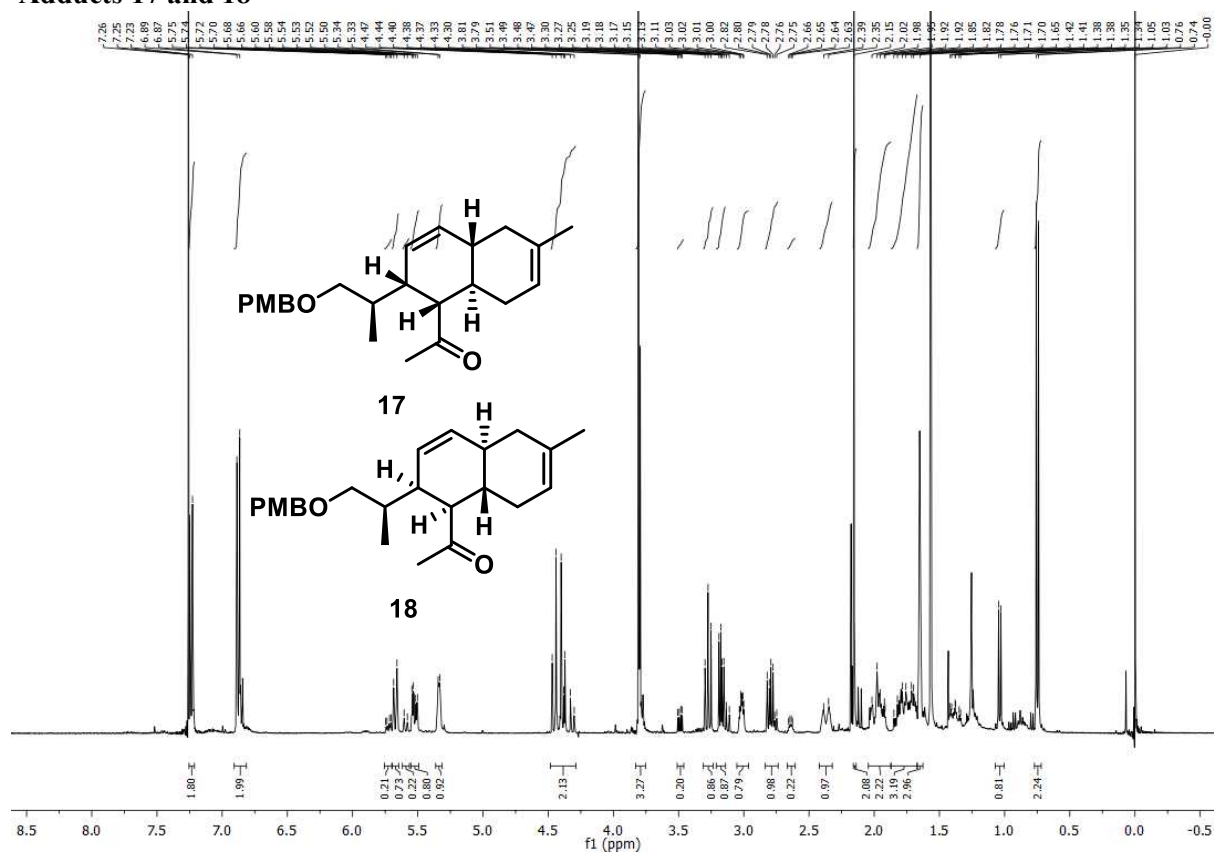
The figure displays the ¹H and ¹³C NMR spectra of compound 16, along with its chemical structure.

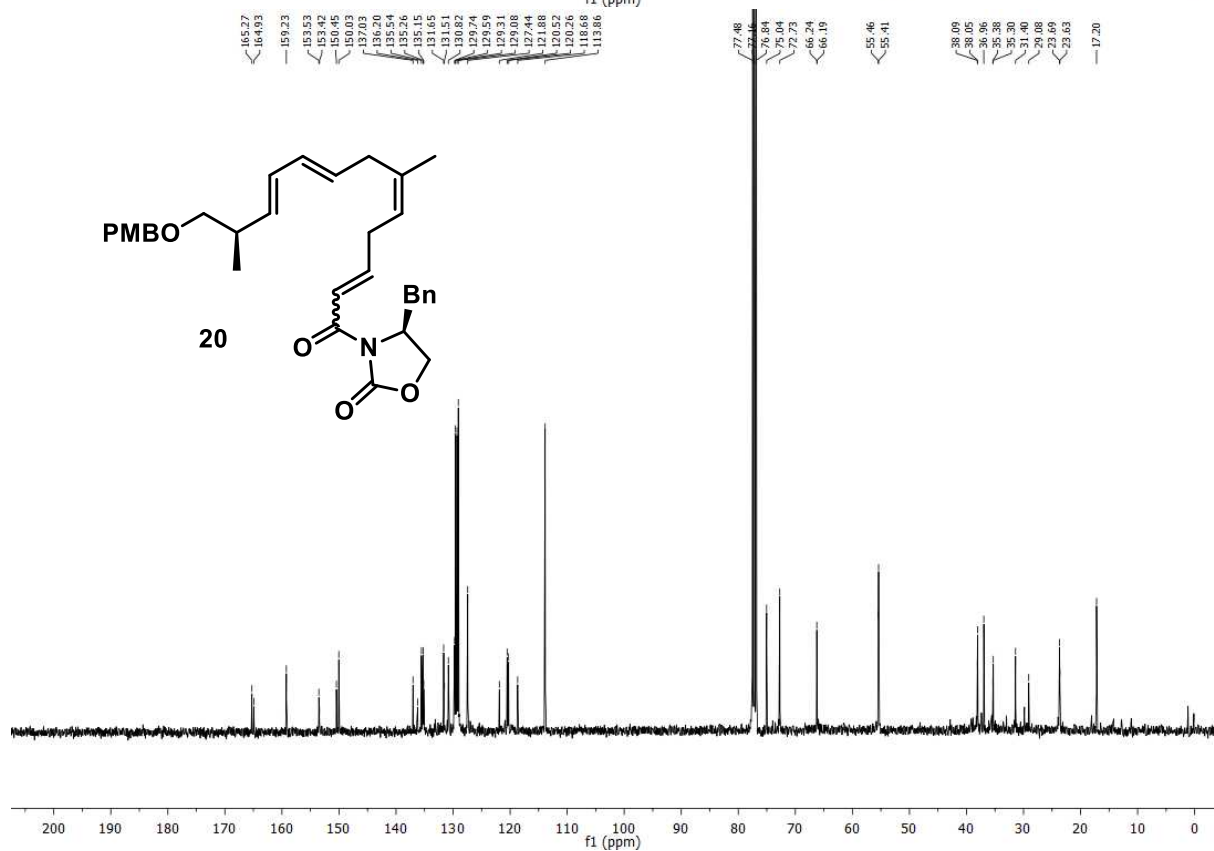
Chemical Structure of 16: The structure shows a 4-methoxyphenyl group attached to a 1-methyl-4-(3-methyl-5-oxopent-1-en-1-yl)but-1-en-3-yl chain. The structure is labeled **16**.

¹H NMR Spectrum (Top): The spectrum shows peaks in the aromatic region (6.7-7.3 ppm), a methoxy singlet (3.8 ppm), and aliphatic/methine signals (1.0-5.6 ppm). Integration values are provided below the peaks: 3.78, 2.64, 1.01, 2.97, 2.12, 1.00, 2.81, 4.15, 2.67, 2.24, 2.19, 1.62, 3.04, 2.78, and 2.78.

¹³C NMR Spectrum (Bottom): The spectrum shows peaks from 17.2 to 198.9 ppm. Key peaks include the carbonyl carbon at 198.86 ppm, aromatic carbons between 120-147 ppm, the methoxy carbon at 55.42 ppm, and aliphatic carbons from 17.19 to 36.97 ppm. The solvent peak for CDCl₃ is visible at 77.0 ppm.

Adducts 17 and 18



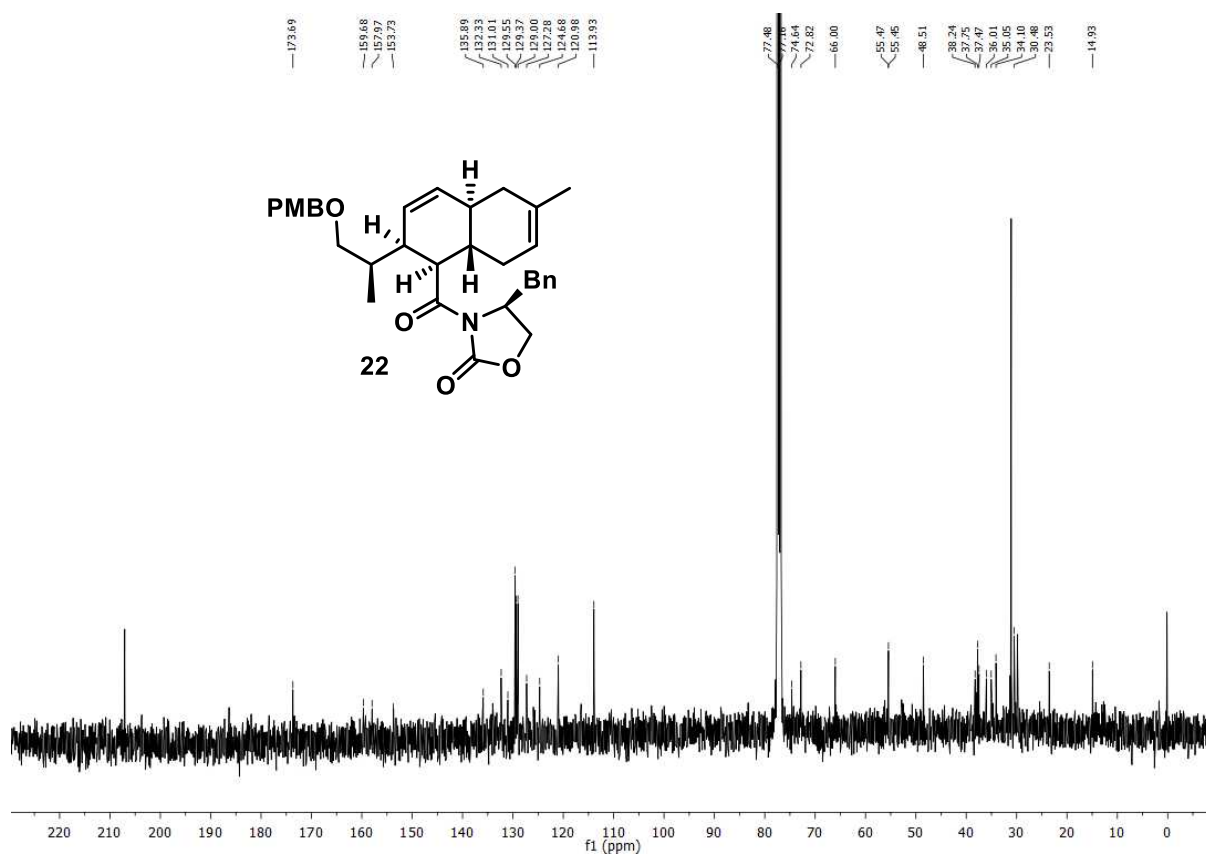
[illegible]

Chemical structure of 22: CC1=C(C)C[C@H]2C[C@@H](C[C@H](C1)C[C@@H](C2)C(=O)N(C[C@H](C3CCOC3=O)C)C)C(=O)C[C@H](C)C

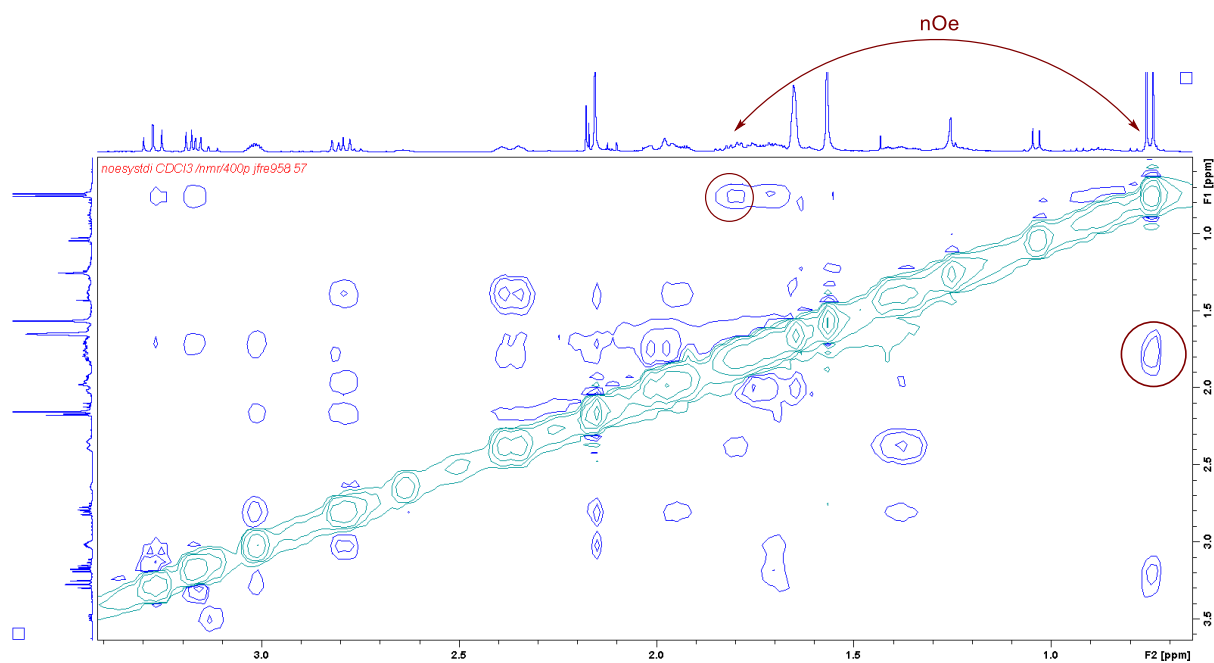
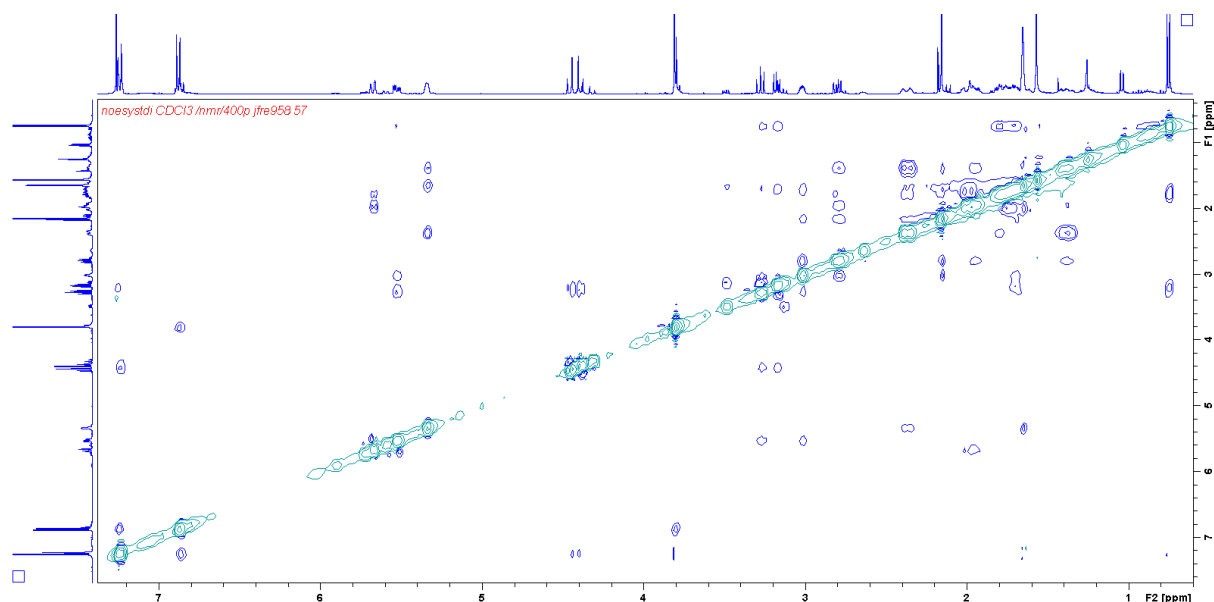
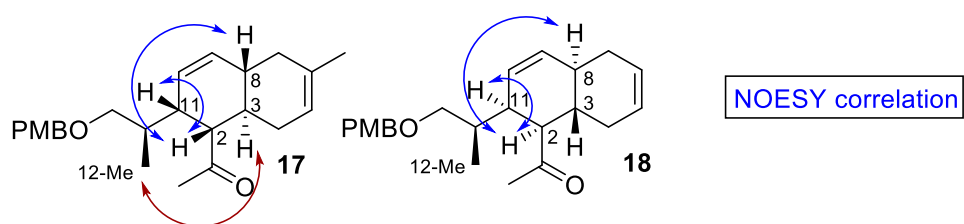
¹H NMR spectrum (CDCl₃):

Chemical shift (ppm): 7.32, 7.31, 7.29, 7.28, 7.27, 7.26, 7.24, 7.23, 7.14, 7.12, 7.12, 6.98, 6.89, 6.87, 6.87, 6.86, 6.83, 5.67, 5.00, 4.44, 4.41, 4.40, 4.09, 4.07, 3.99, 3.98, 3.81, 3.80, 3.79, 3.77, 3.30, 3.28, 3.24, 3.23, 3.22, 3.20, 2.43, 2.40, 2.39, 2.37, 2.27, 2.27, 2.17, 2.05, 1.67, 1.63, 1.55, 1.43, 1.29, 1.28, 1.25, 1.24, 1.23, 1.09, 1.08, 0.89, 0.88, 0.86.

Integration values: 13.28, 2.04, 2.72, 0.41, 0.96, 1.21, 1.00, 0.26, 1.11, 3.18, 1.72, 1.09, 1.10, 3.42, 2.53, 2.32, 3.76, 4.27, 2.87, 3.82, 2.16, 1.49, 4.24.



Adducts 17-18



Crystallization. Single crystals of Adduct **22** were obtained by slow recrystallization of a solution of the compound in ethyl acetate.

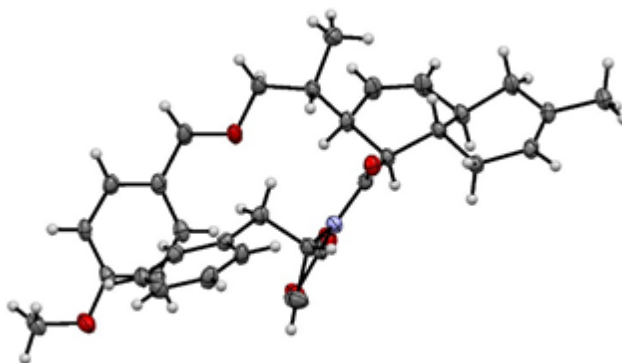


Figure S1. ORTEP diagram drawn with 50% ellipsoid probability of the crystal structure of Adduct **22**.

Table S1. Crystal data and structure refinement details for *N*-Ts bicyclic ketone **20**.

Empirical formula	C ₃₃ H ₃₈ NO ₅
Formula weight	528.64
Temperature (K)	100
Wavelength (Å)	1.54184
Crystal system	Triclinic
Space group	P 1
a (Å)	9.1302(3)
b (Å)	9.1578(5)
c (Å)	10.2260(4)
α (°)	108.986(4)
β (°)	98.417(3)
γ (°)	114.037
V (Å ³)	698.83(6)
Z	1
D _c (Mg/m ³)	1.256
F(000)	283
μ (mm ⁻¹)	0.670
θ _{max} (°)	68.241
Total reflections	16713
Unique reflections	4896
Reflections [<i>I</i> > 2σ(<i>I</i>)]	0.0595
Parameters	356
<i>R</i> _{int}	0.0595
Goodness-of-fit	1.054
<i>R</i> [<i>F</i> ₂ > 2σ(<i>F</i> ₂)]	0.0448
<i>wR</i> (<i>F</i> ₂ , all data)	0.1169