Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

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

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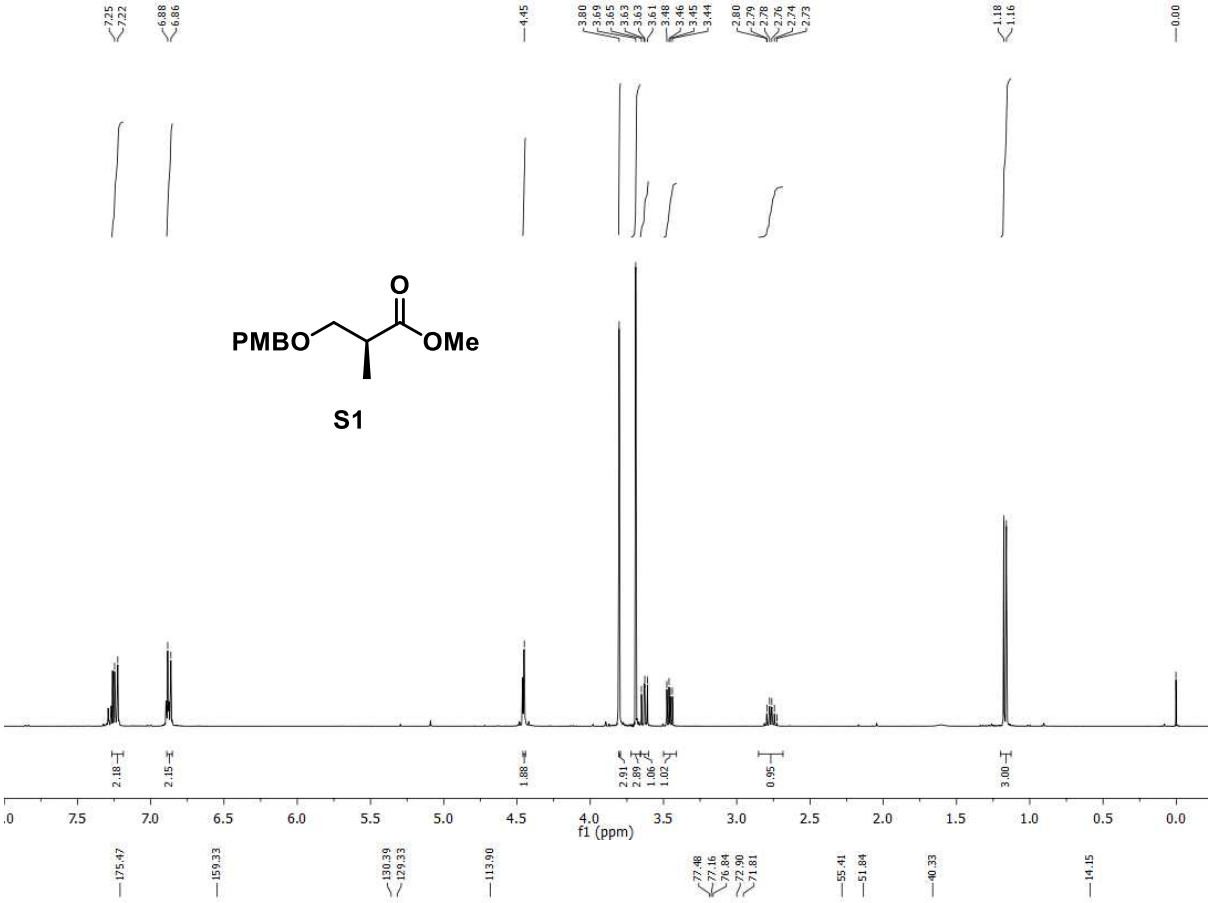
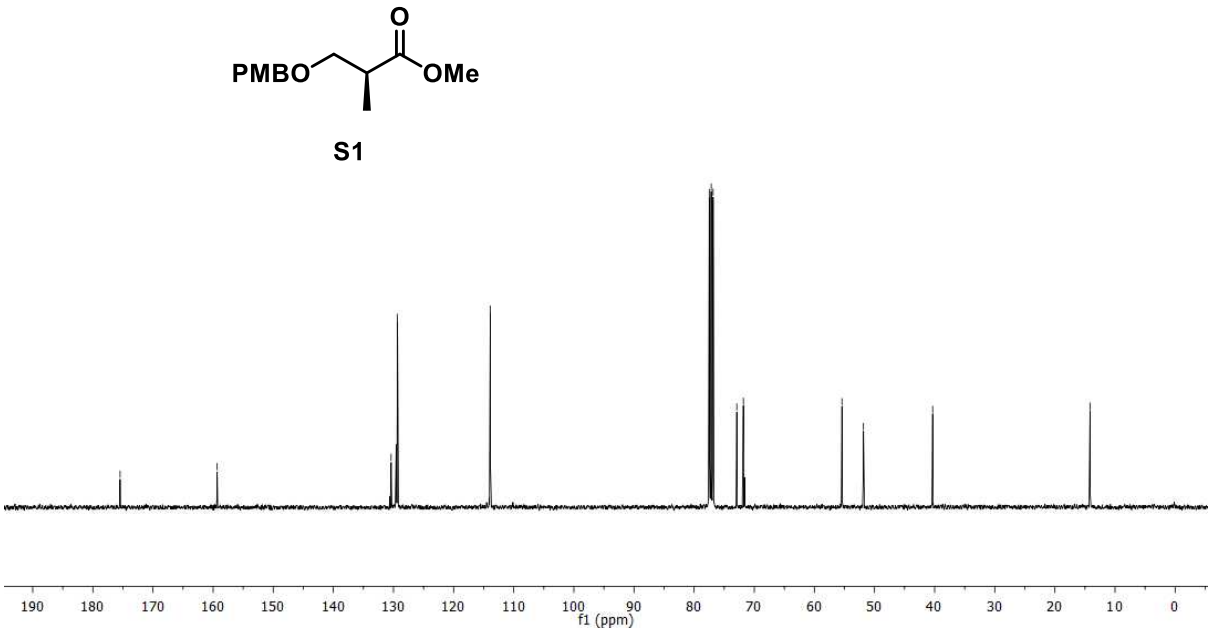
Supporting Information

General Information

All reactions were carried out in flame- or oven-dried glassware under a dry nitrogen atmosphere unless otherwise stated. CH_2Cl_2, $(CH_3)_2CO$, 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 (^{1}H NMR) homogenous materials, unless otherwise stated. Reactions performed at low temperature were either cooled with an acetone/dry ice bath to reach -78 °C, or acetone/brine/dry ice bath to reach -30 °C, or a water ice bath to reach 0 °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 ^{1}H 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 ^{1}H NMR) and $CDCl_3$ ($\delta = 77.0$ for ^{13}C NMR). ^{1}H 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





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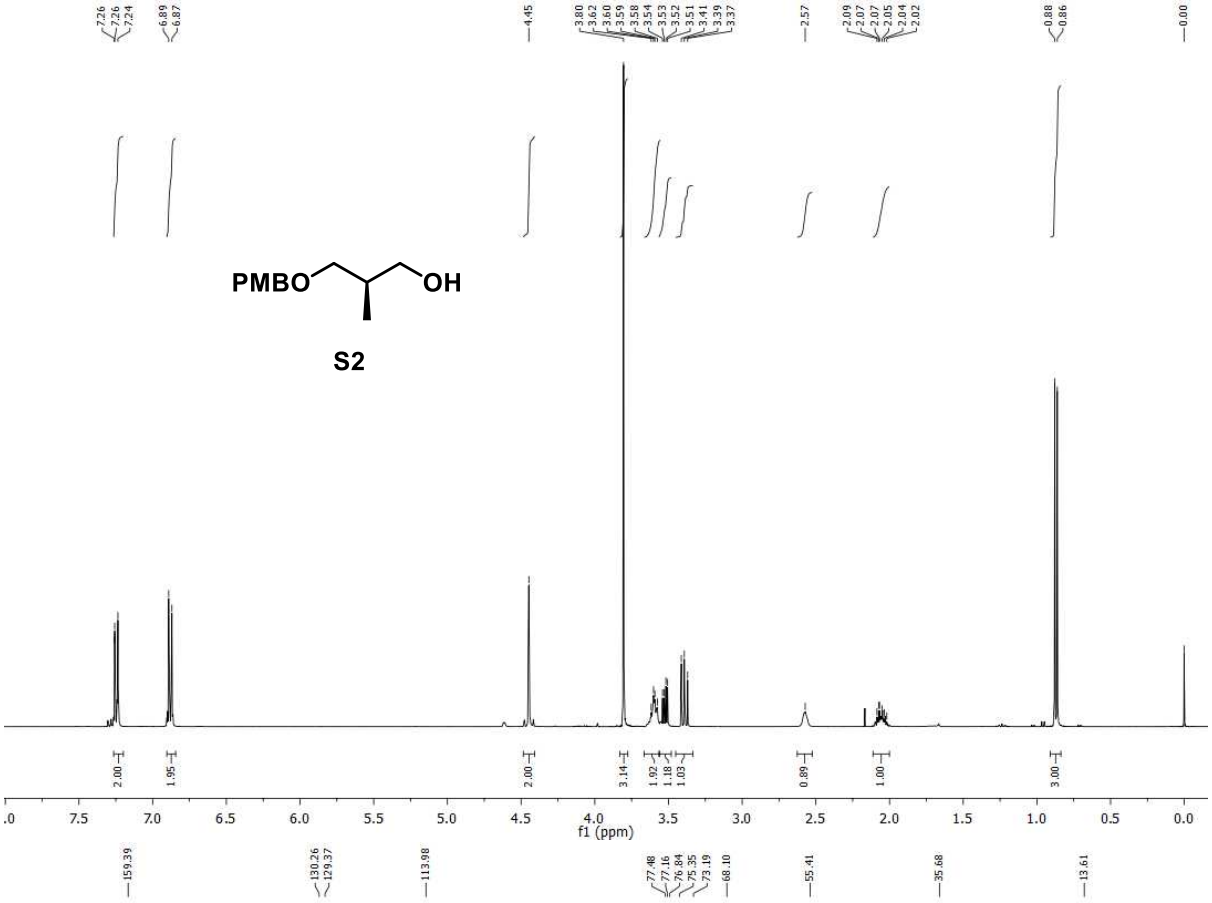
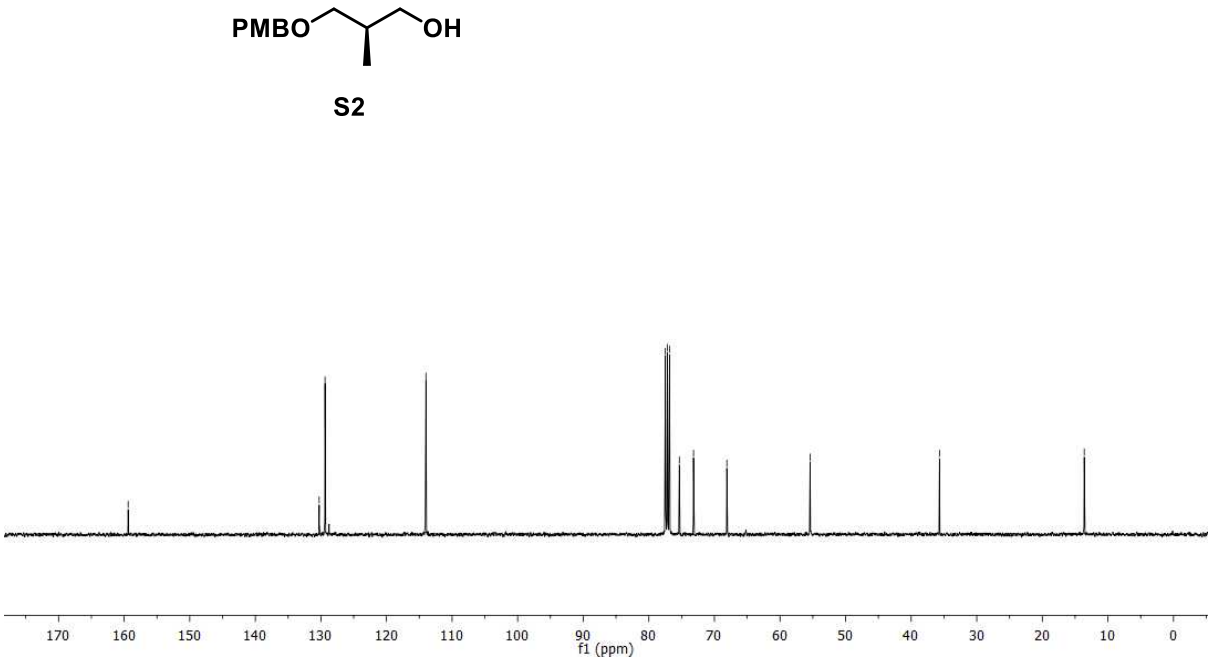
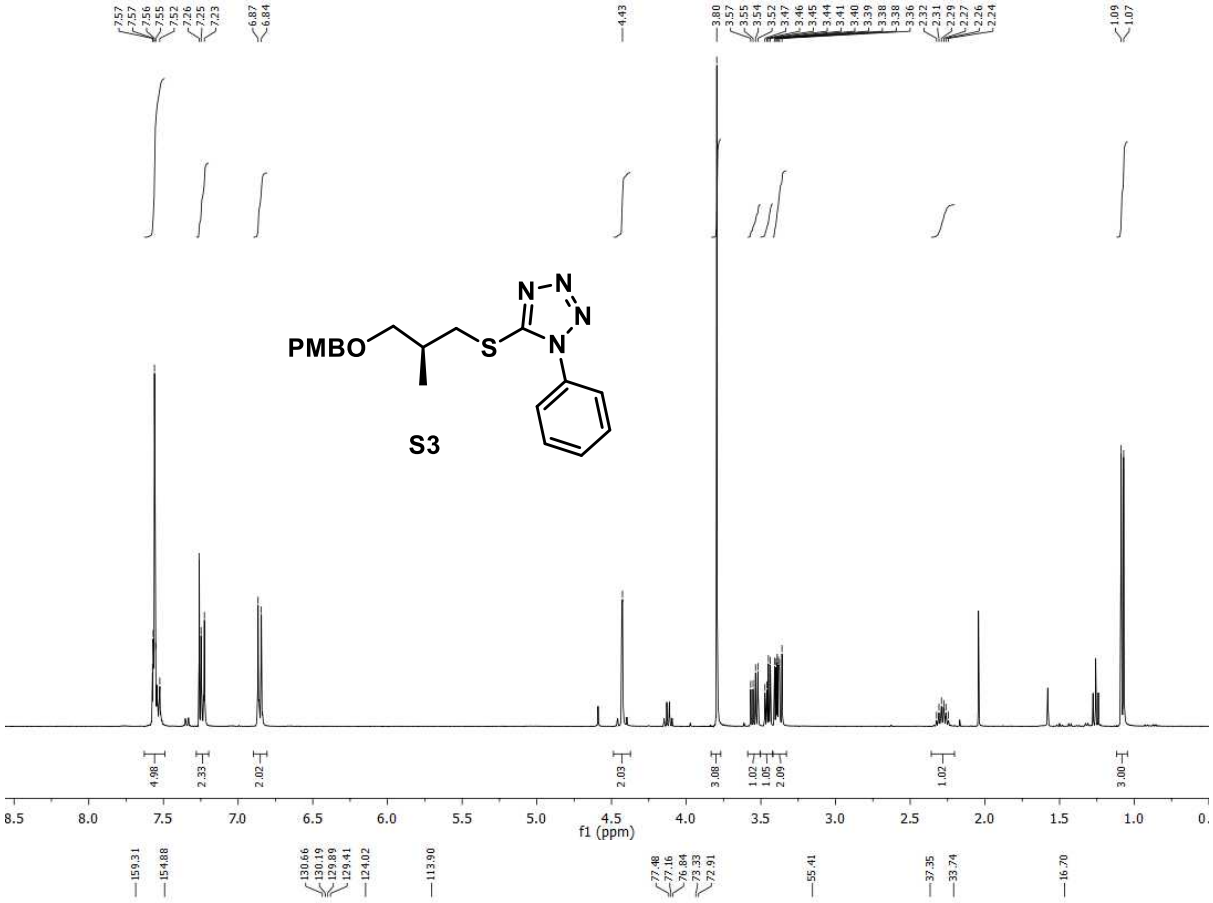
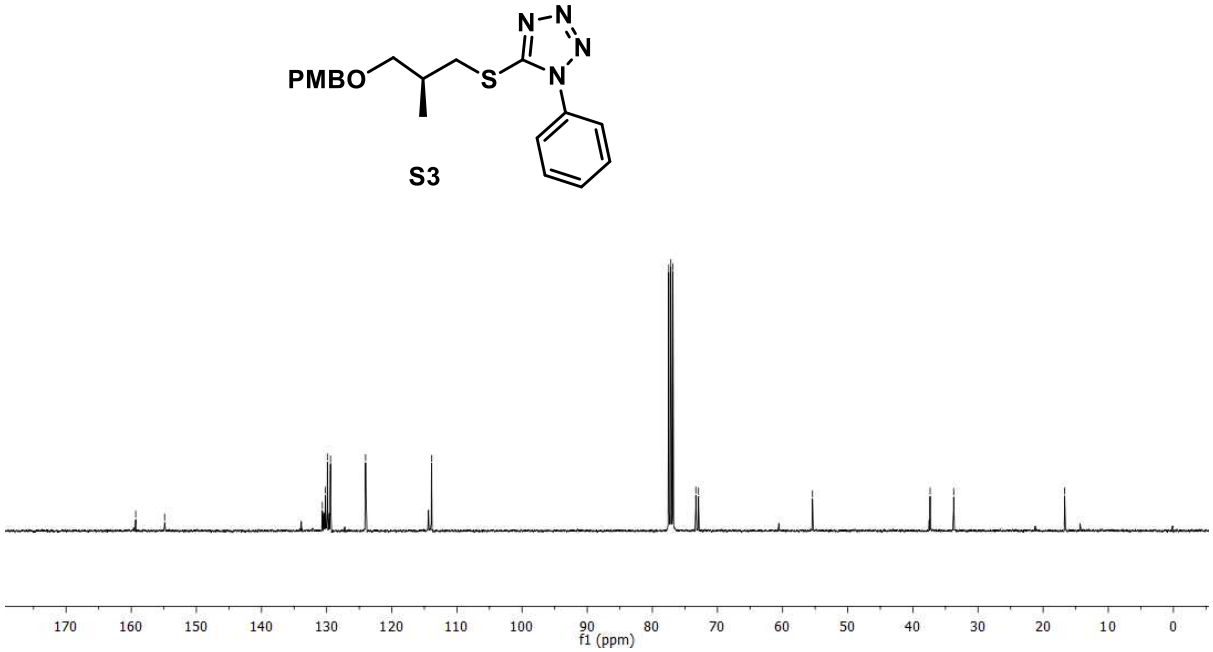


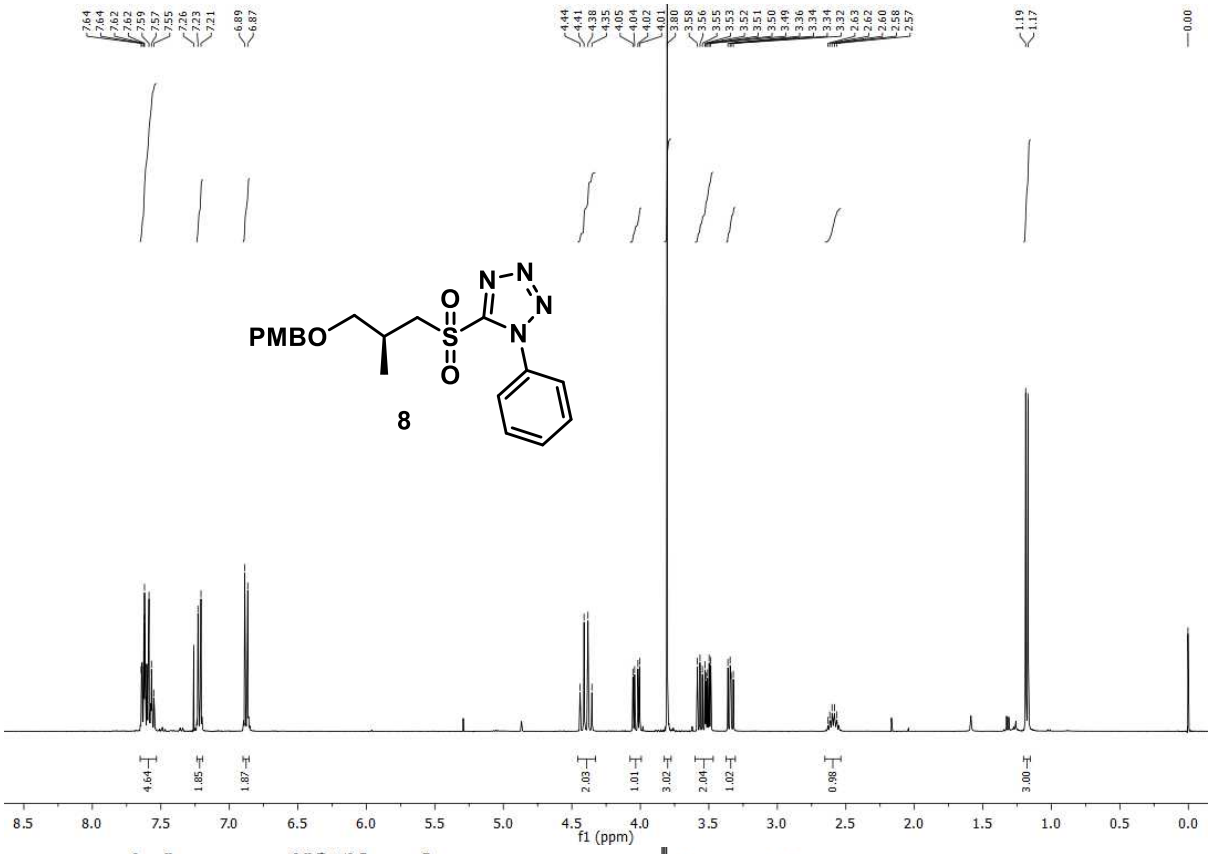


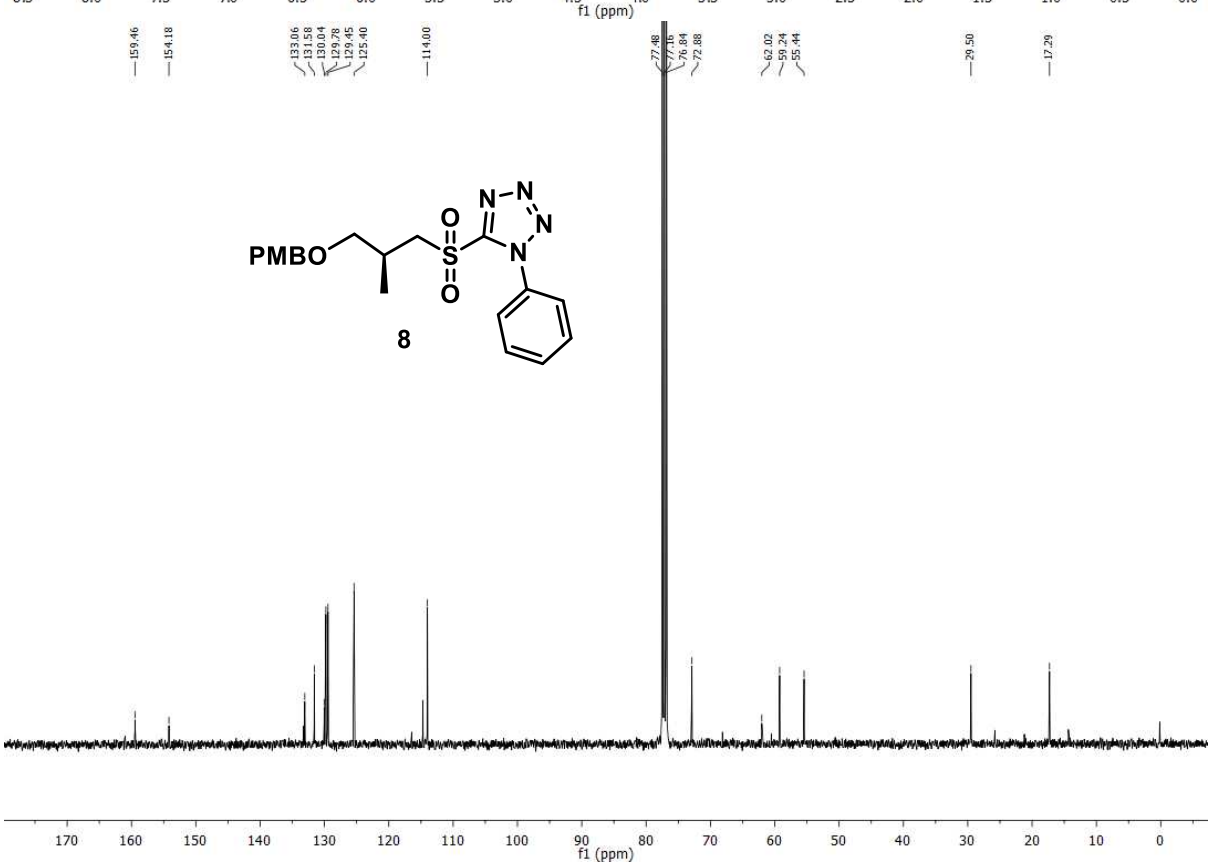
Sulfide S3





Sulfone 8





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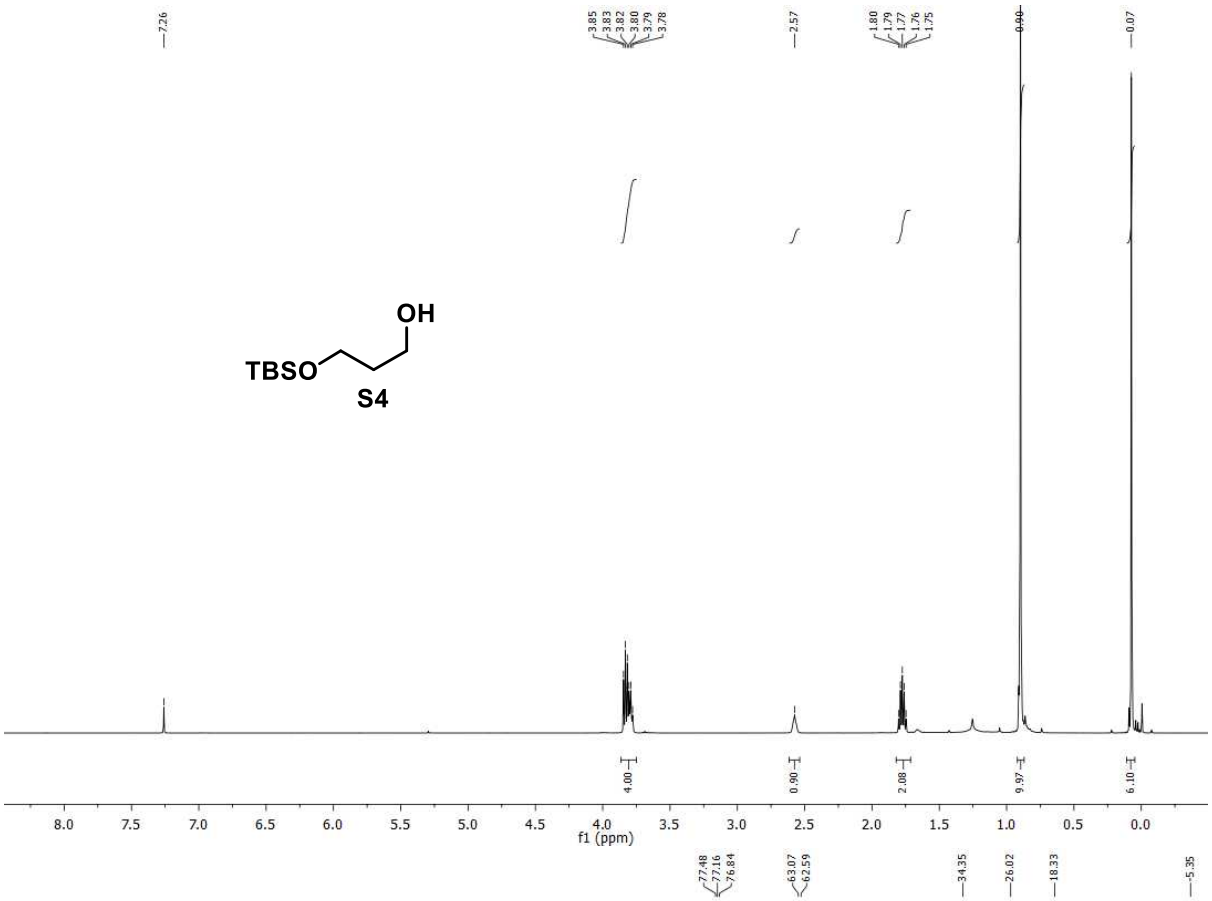
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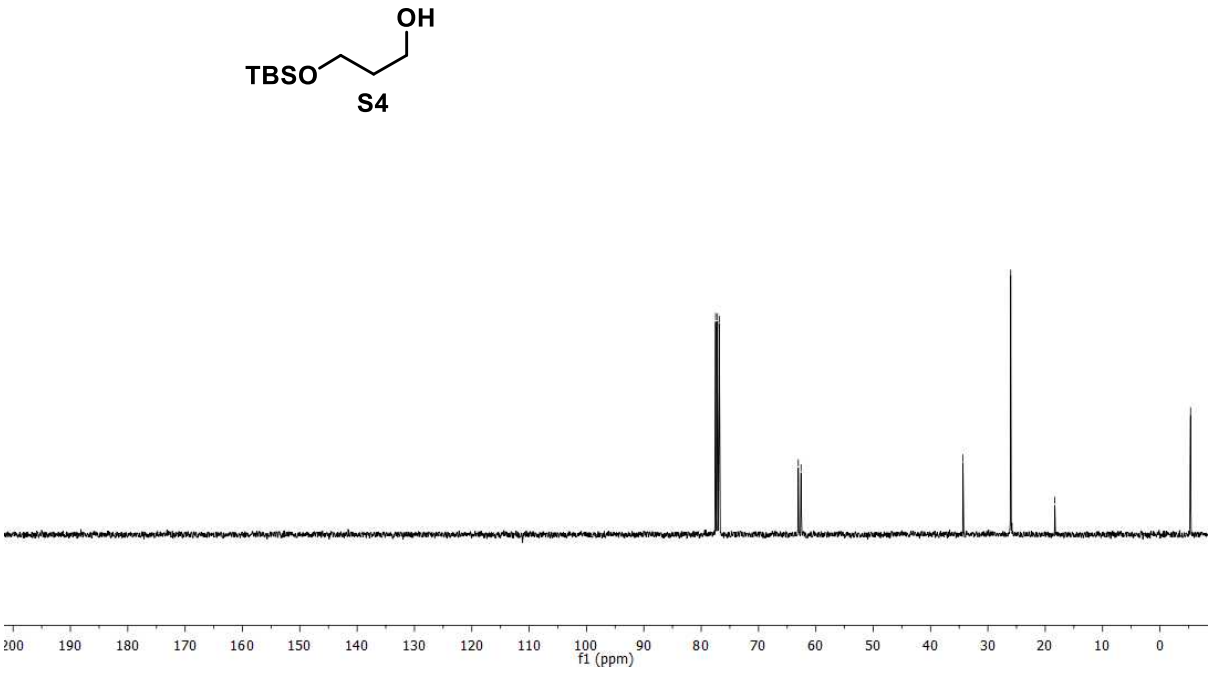
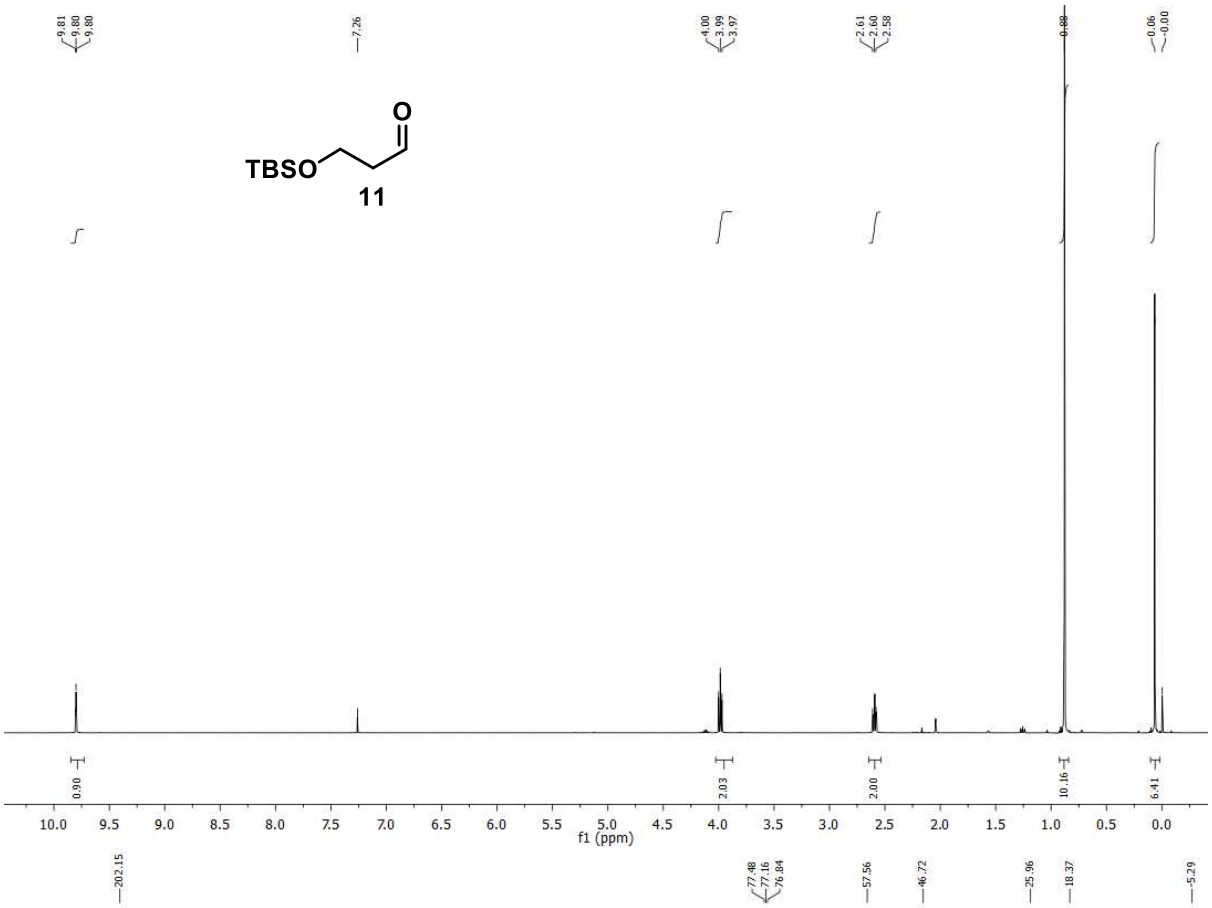
3.85
3.83
3.82
3.80
3.79
3.78
2.57
1.80
1.79
1.77
1.76
1.75
0.90
0.07
OH
TBSO
S4
4.00
0.90
2.08
9.97
6.10
f1 (ppm)
77.48
77.16
76.84
63.07
62.59
34.35
26.02
18.33
5.35


OH
TBSO
S4
f1 (ppm)

Aldehyde 11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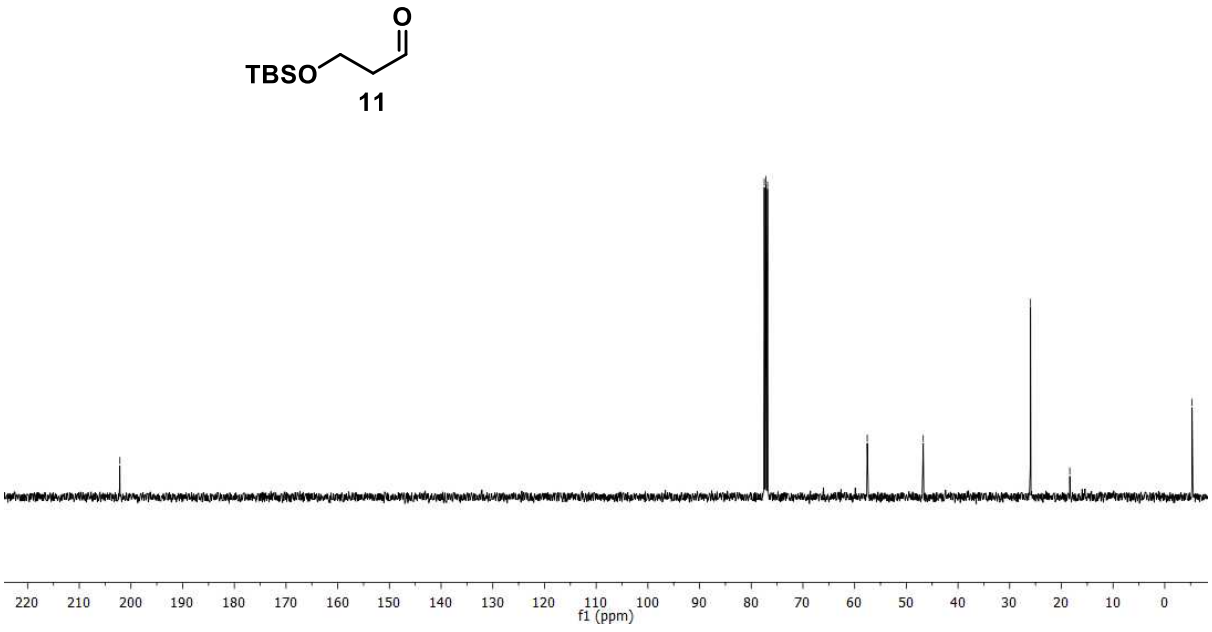
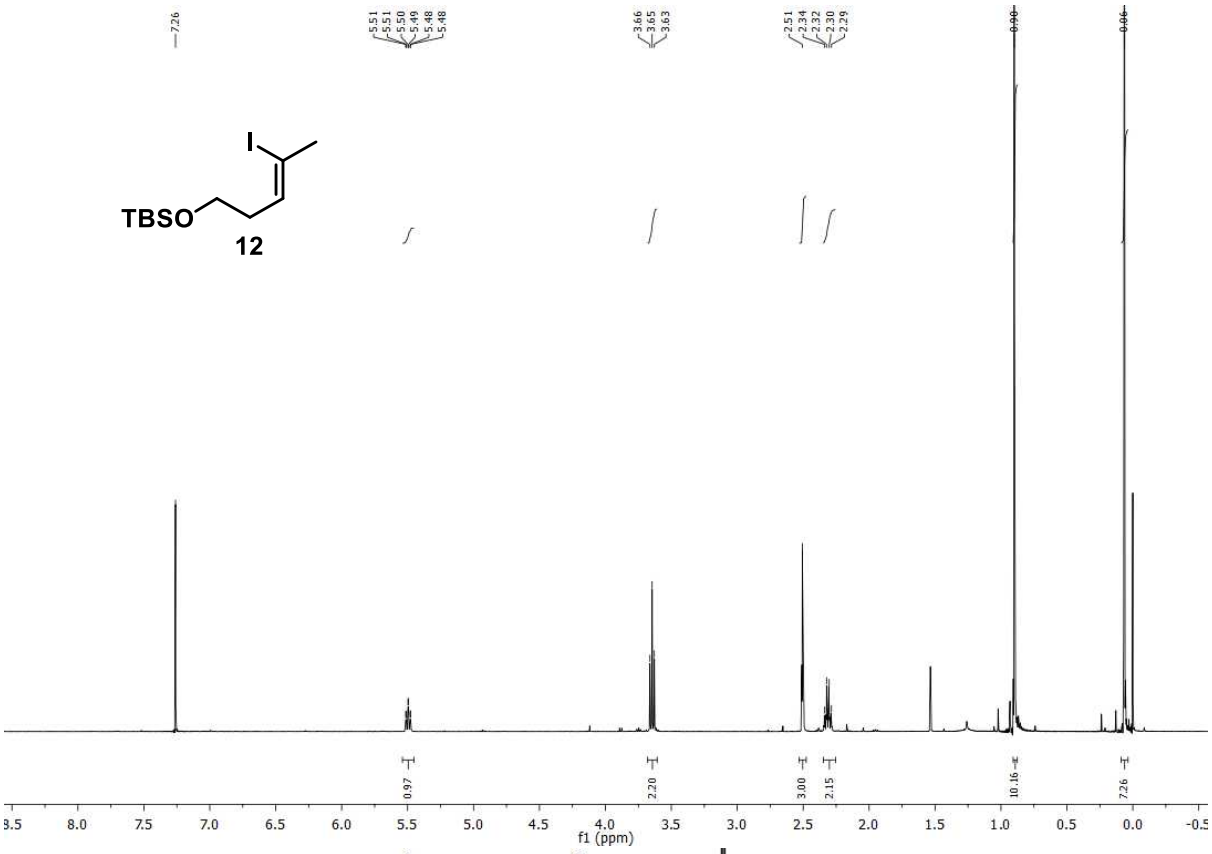
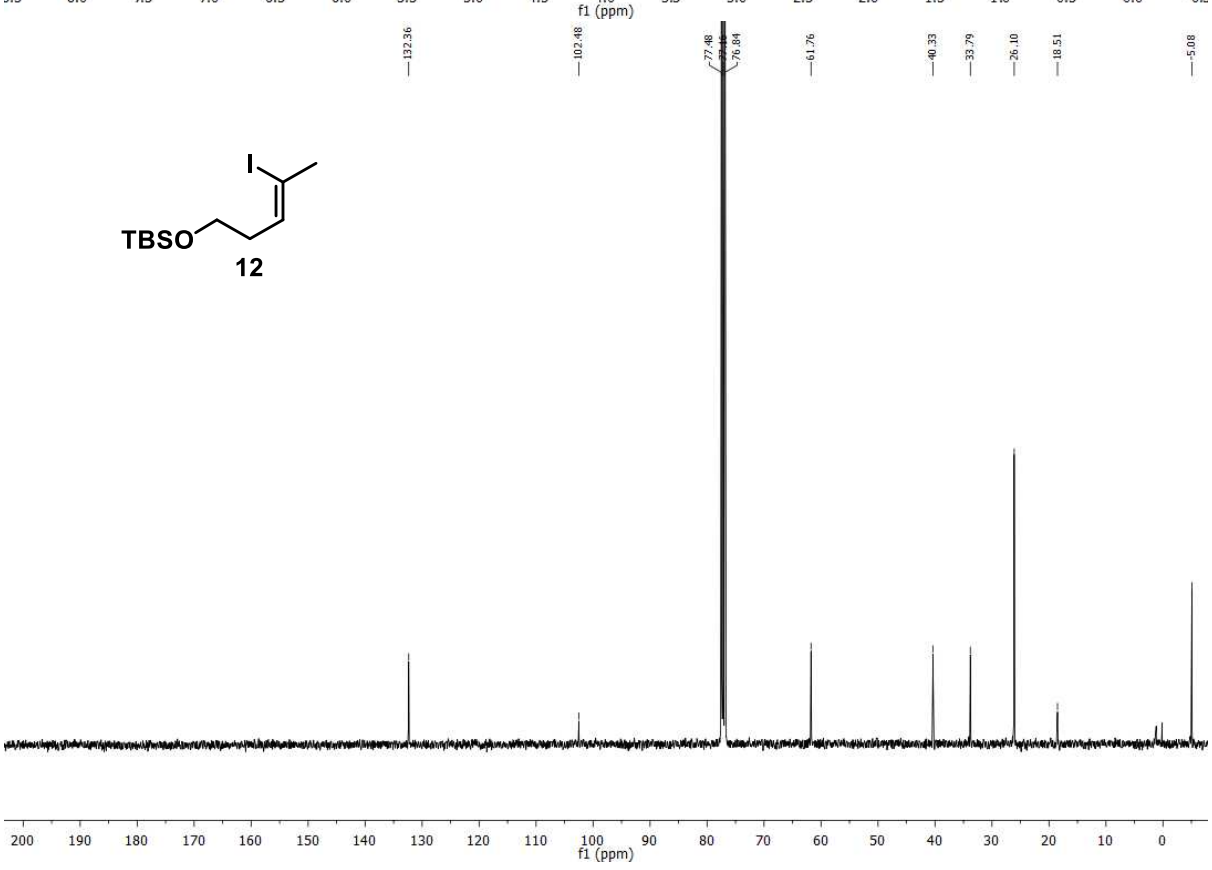
9.80
9.80
7.26
4.00
3.99
3.97
2.61
2.60
2.58
0.88
0.06
0.00
TBSO
O
11
0.90
2.03
2.00
10.16
6.41
f1 (ppm)
202.15
77.48
77.16
76.84
57.56
46.72
25.96
18.37
-5.29

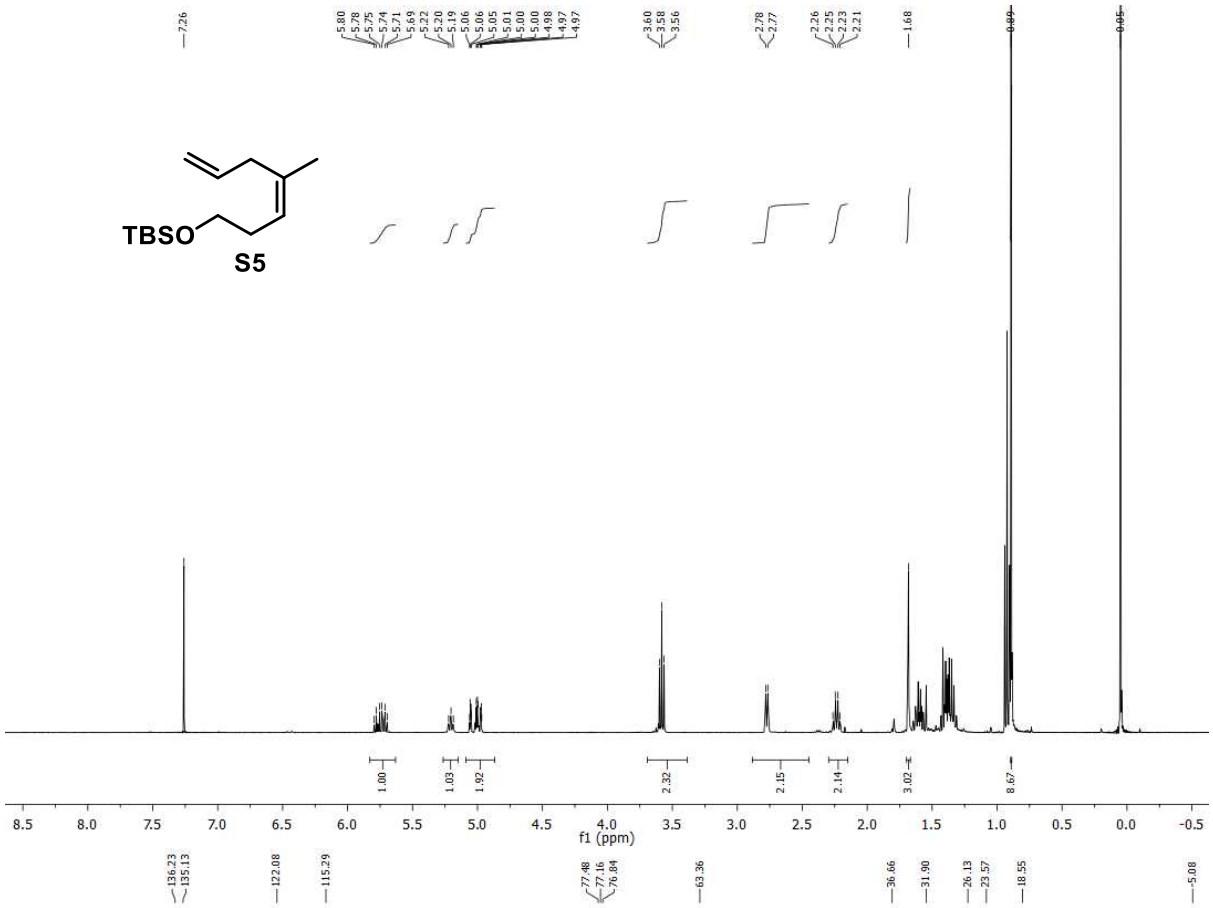

TBSO
O
11
f1 (ppm)

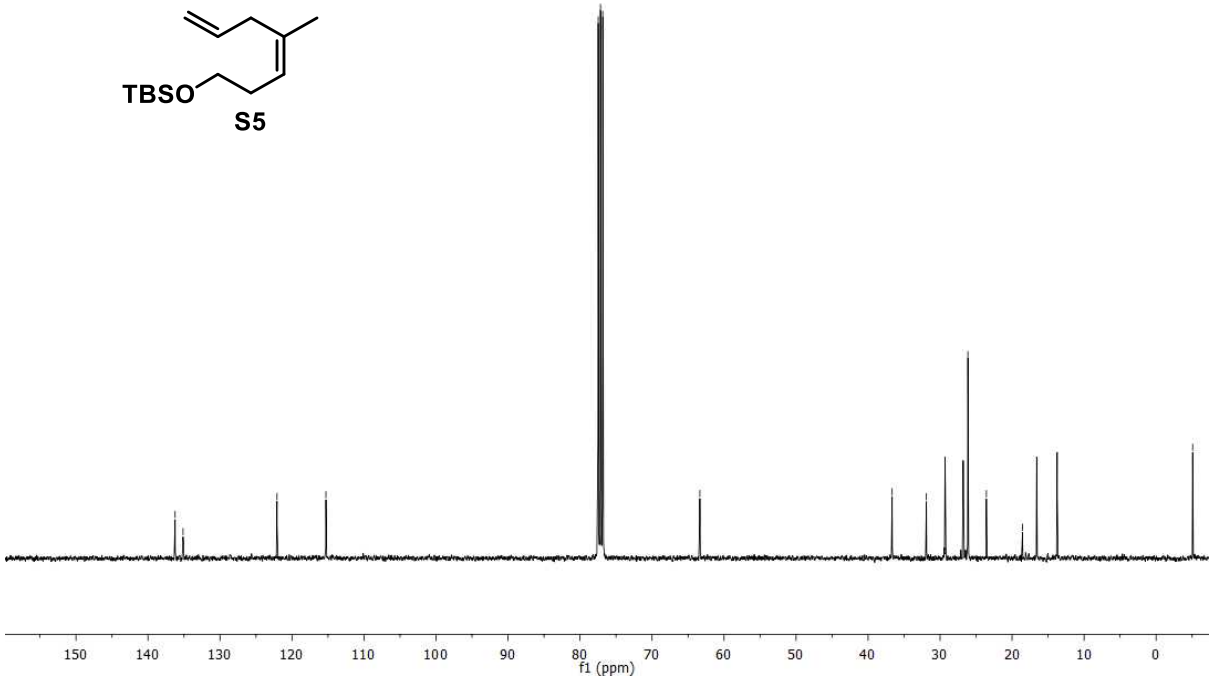
Iodide 12


7.26
5.51
5.51
5.50
5.49
5.48
5.48
3.66
3.65
3.63
2.51
2.34
2.32
2.30
2.29
0.00
0.06
I
TBSO
12
0.97
2.20
3.00
2.15
10.16
7.26
f1 (ppm)

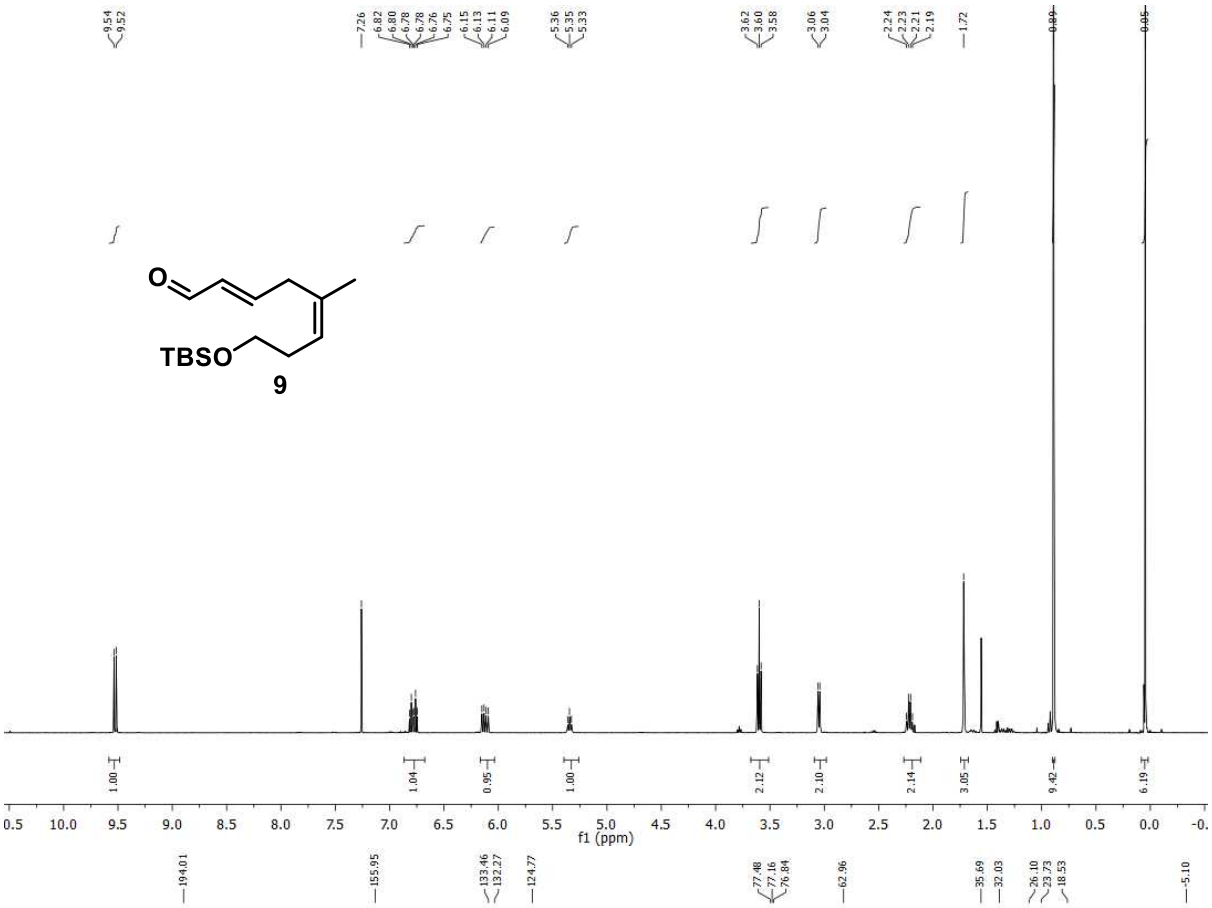

132.36
102.48
77.48
76.84
61.76
40.33
33.79
26.10
18.51
-5.08
I
TBSO
12
f1 (ppm)

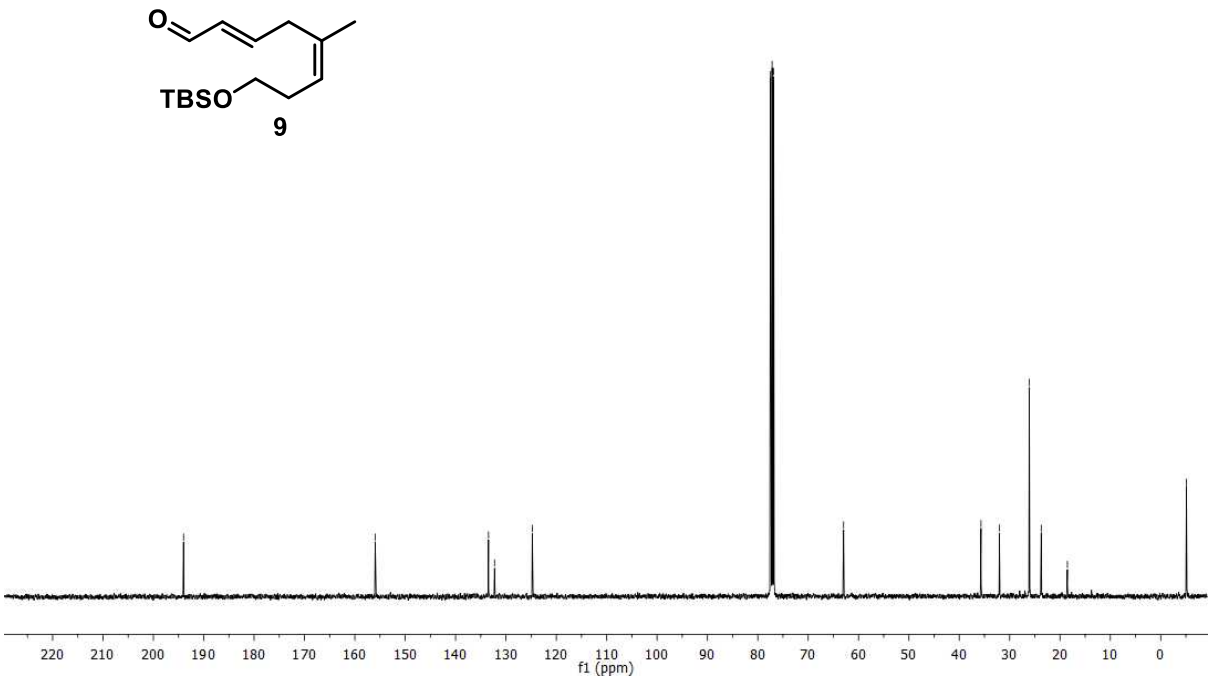
Alkene S5



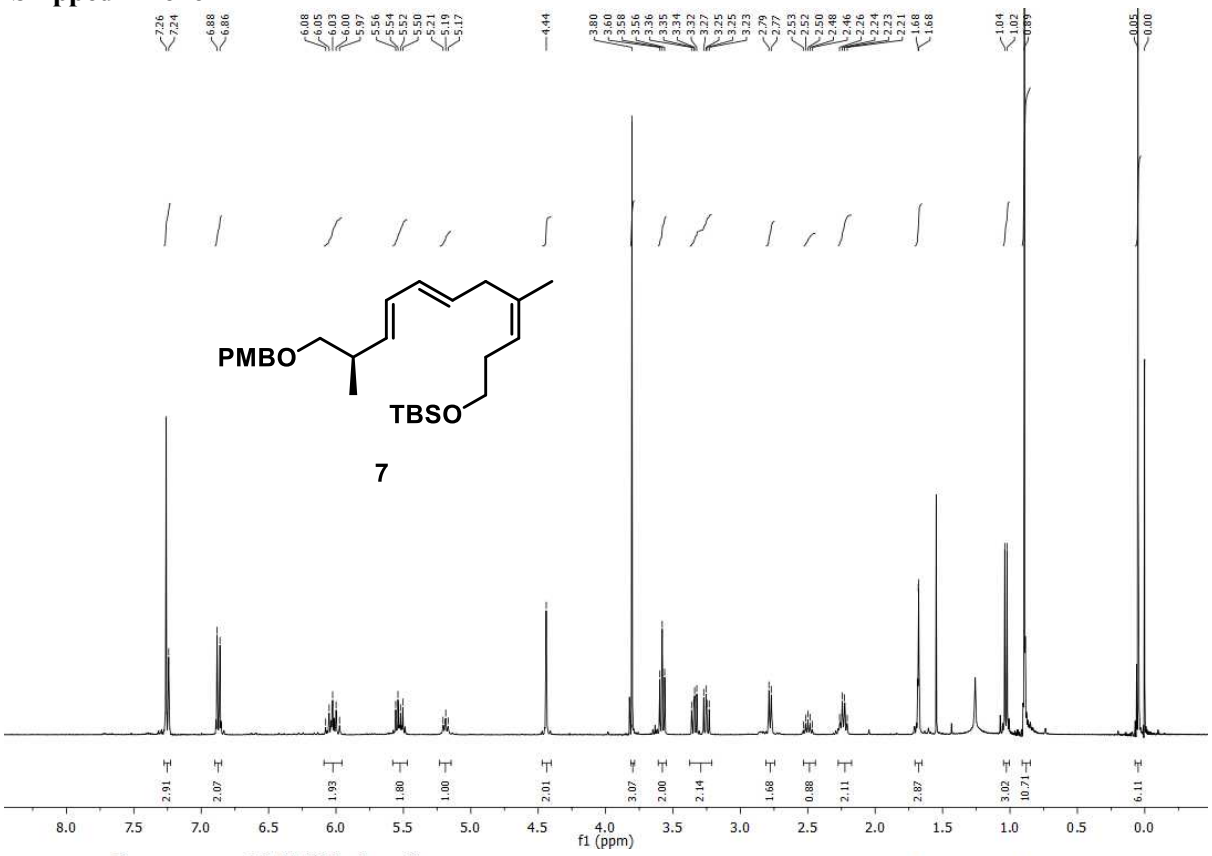


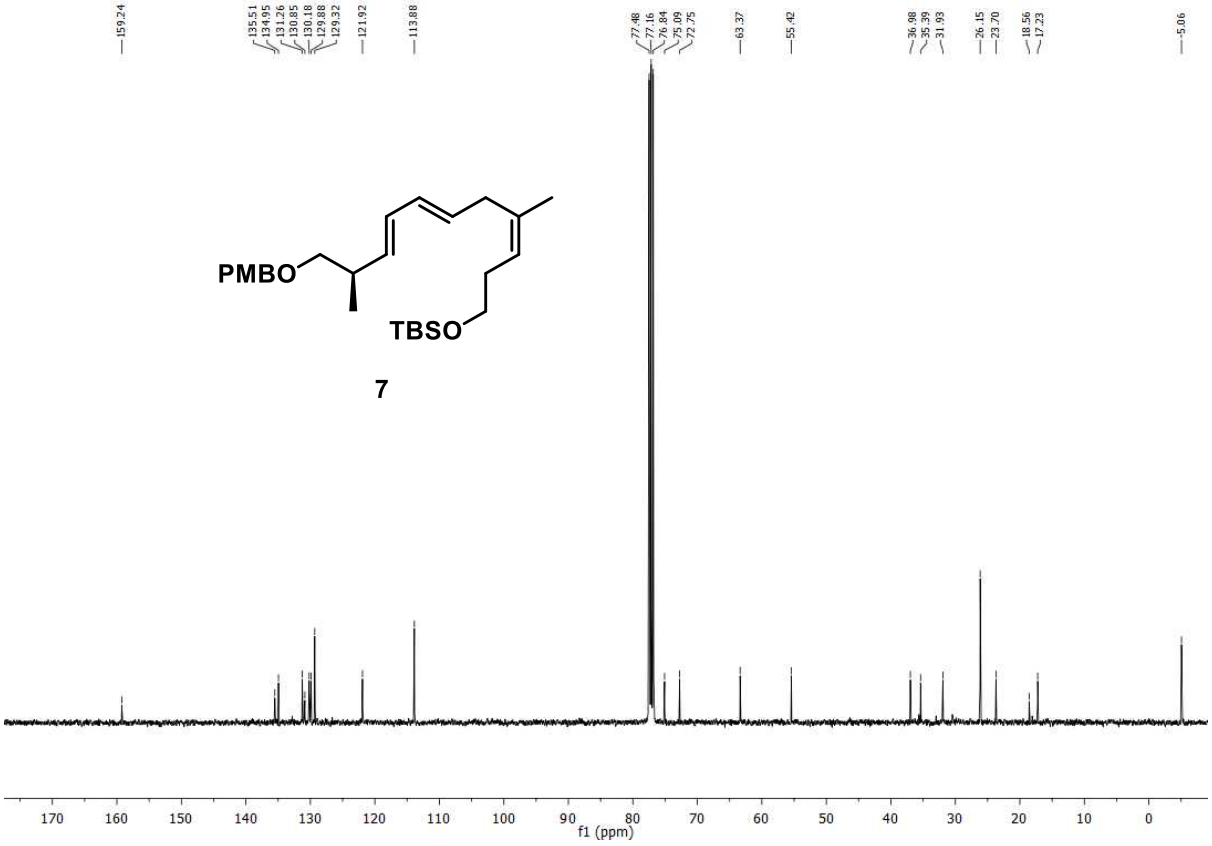
Aldehyde 9



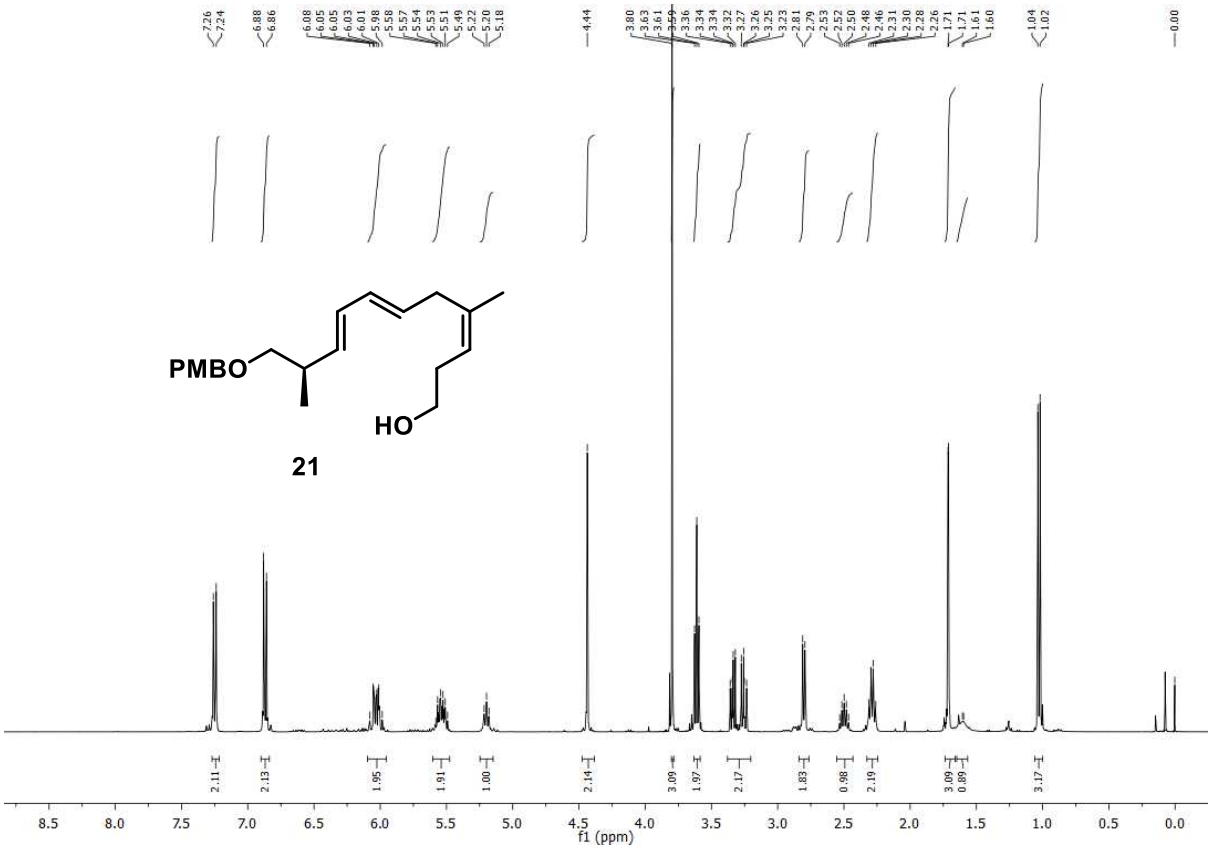


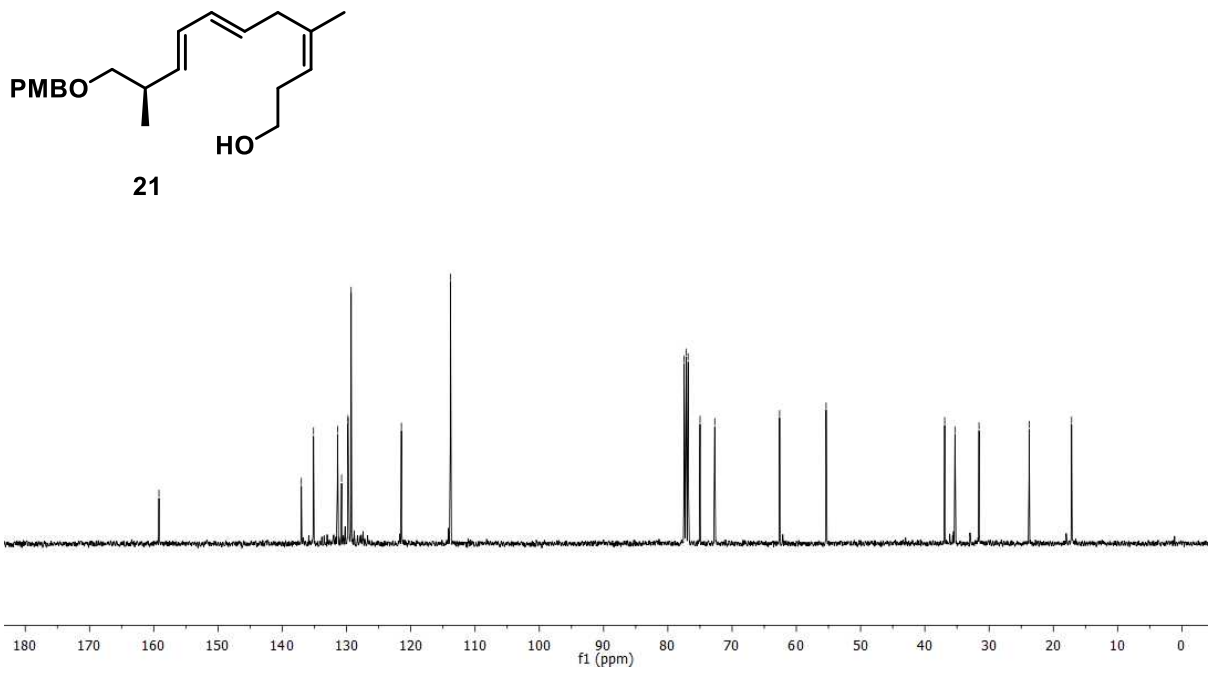
Skipped Triene 7



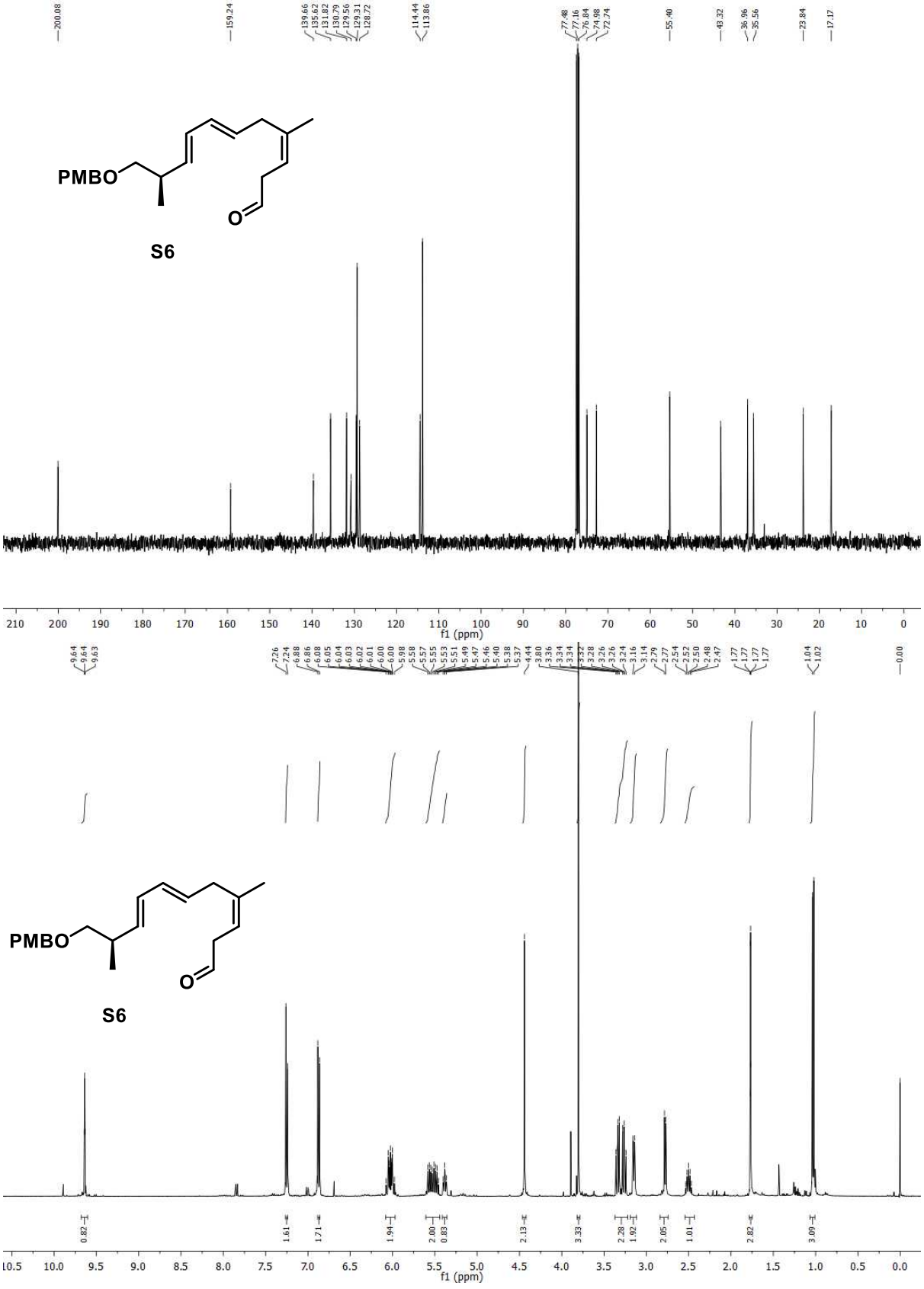


Alcohol 21

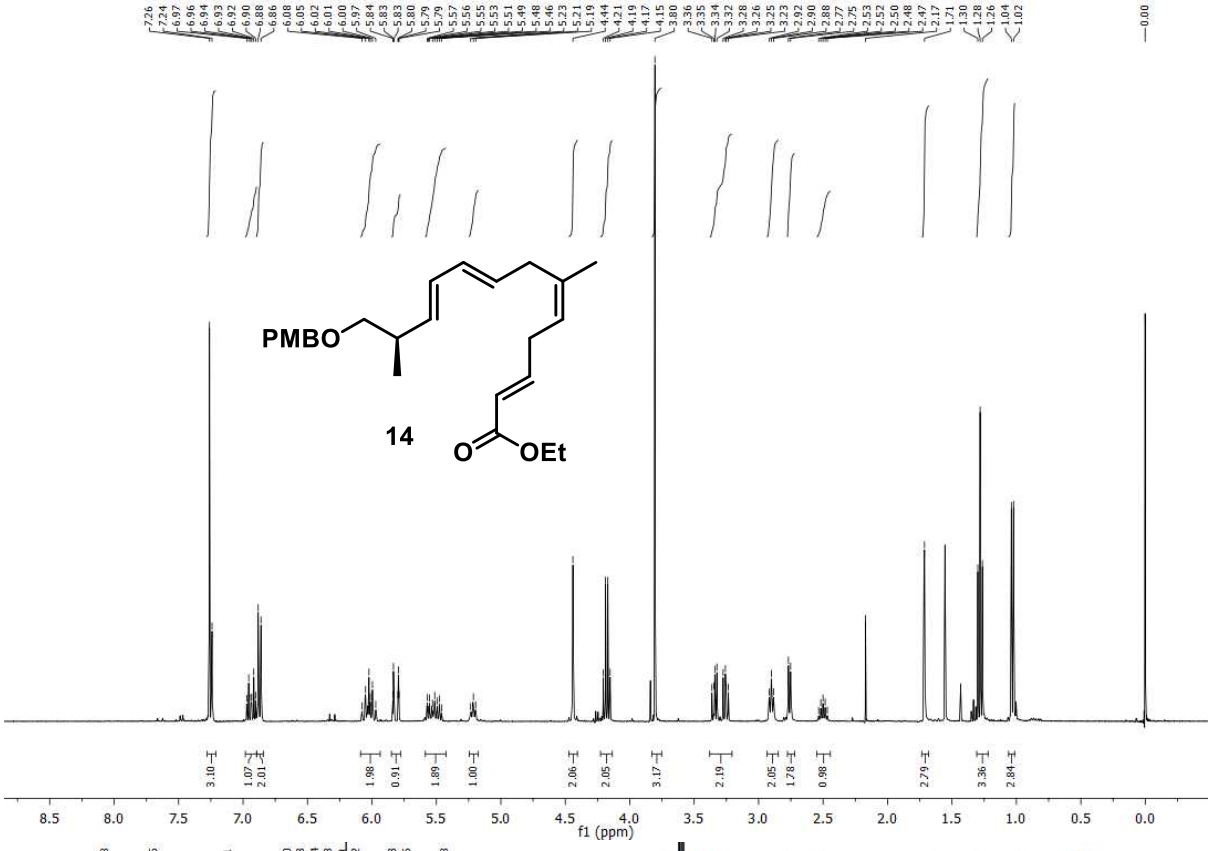


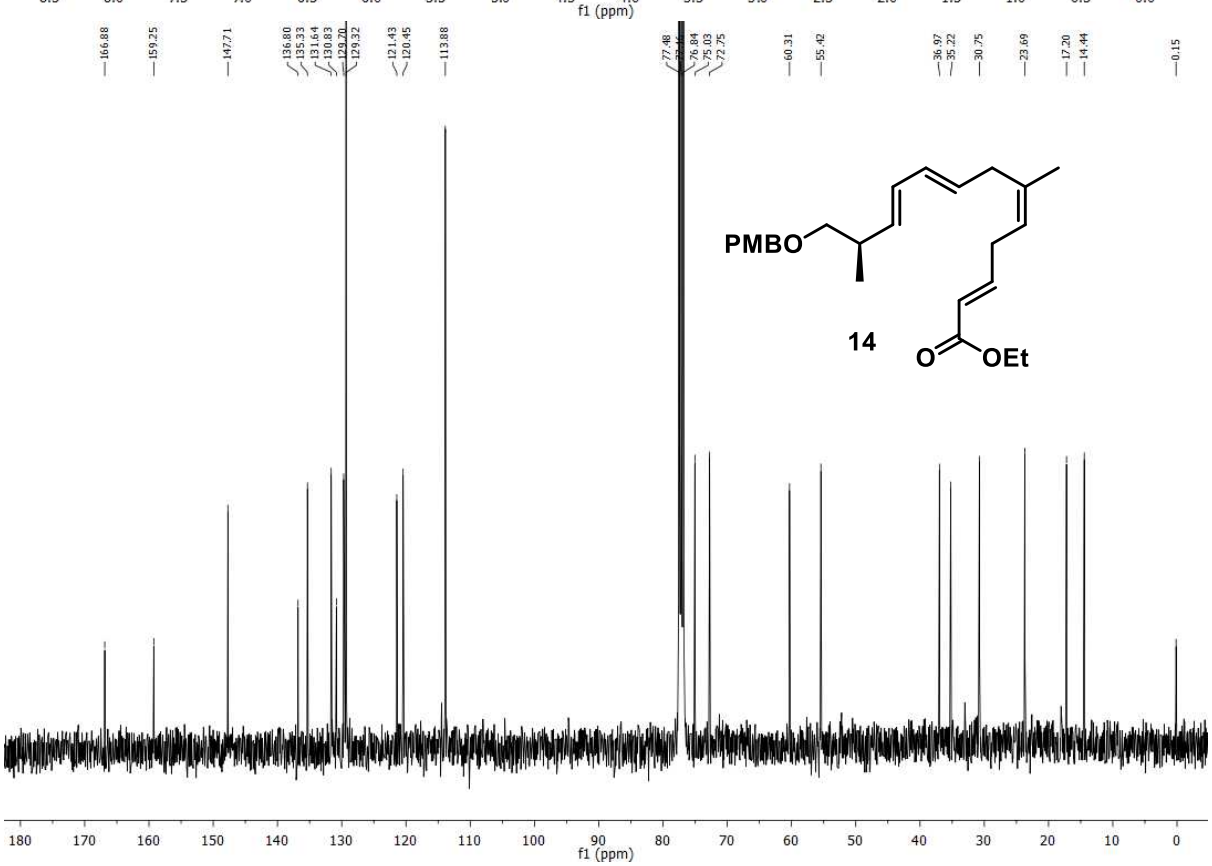


Aldehyde S6

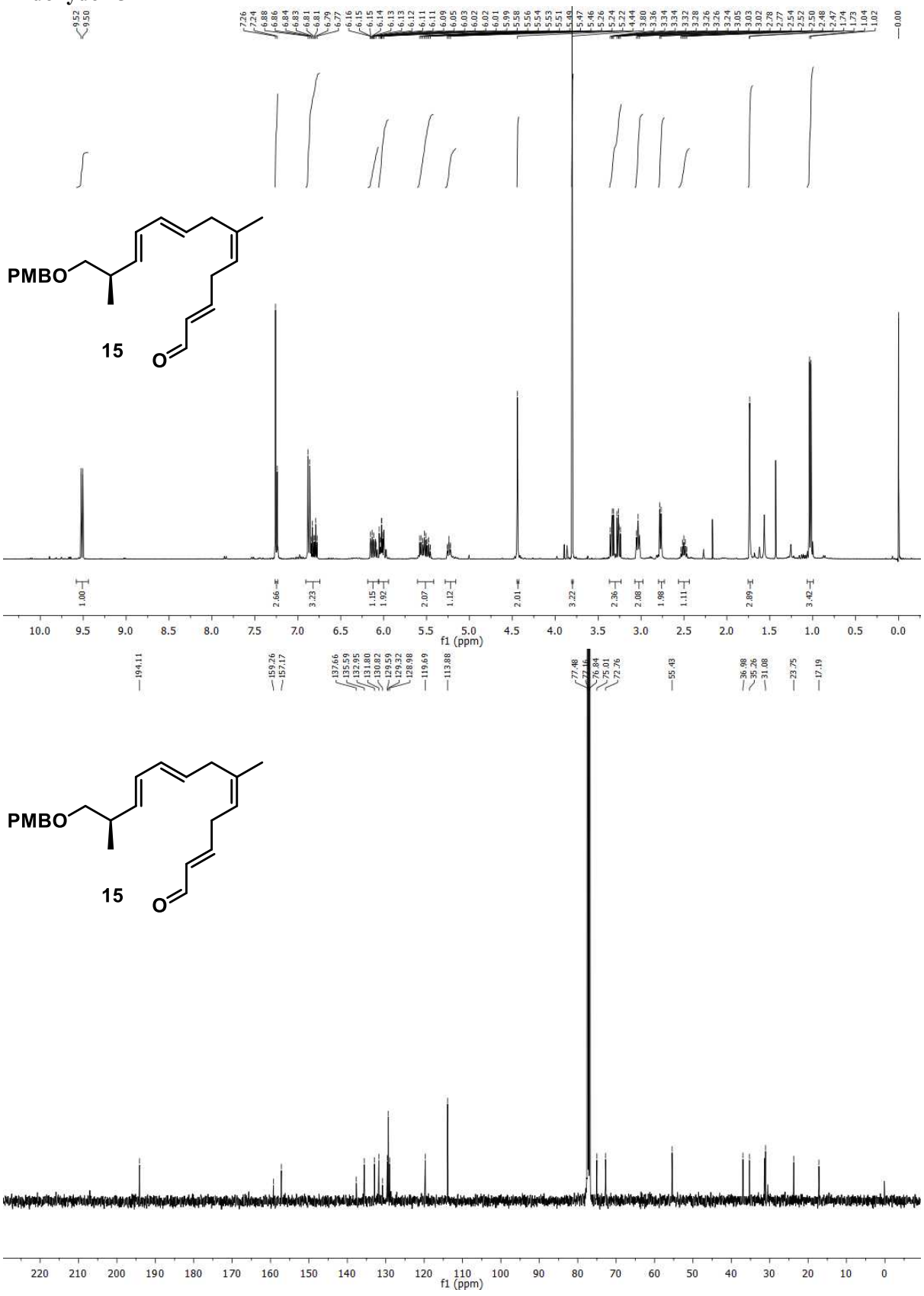


Ester 14

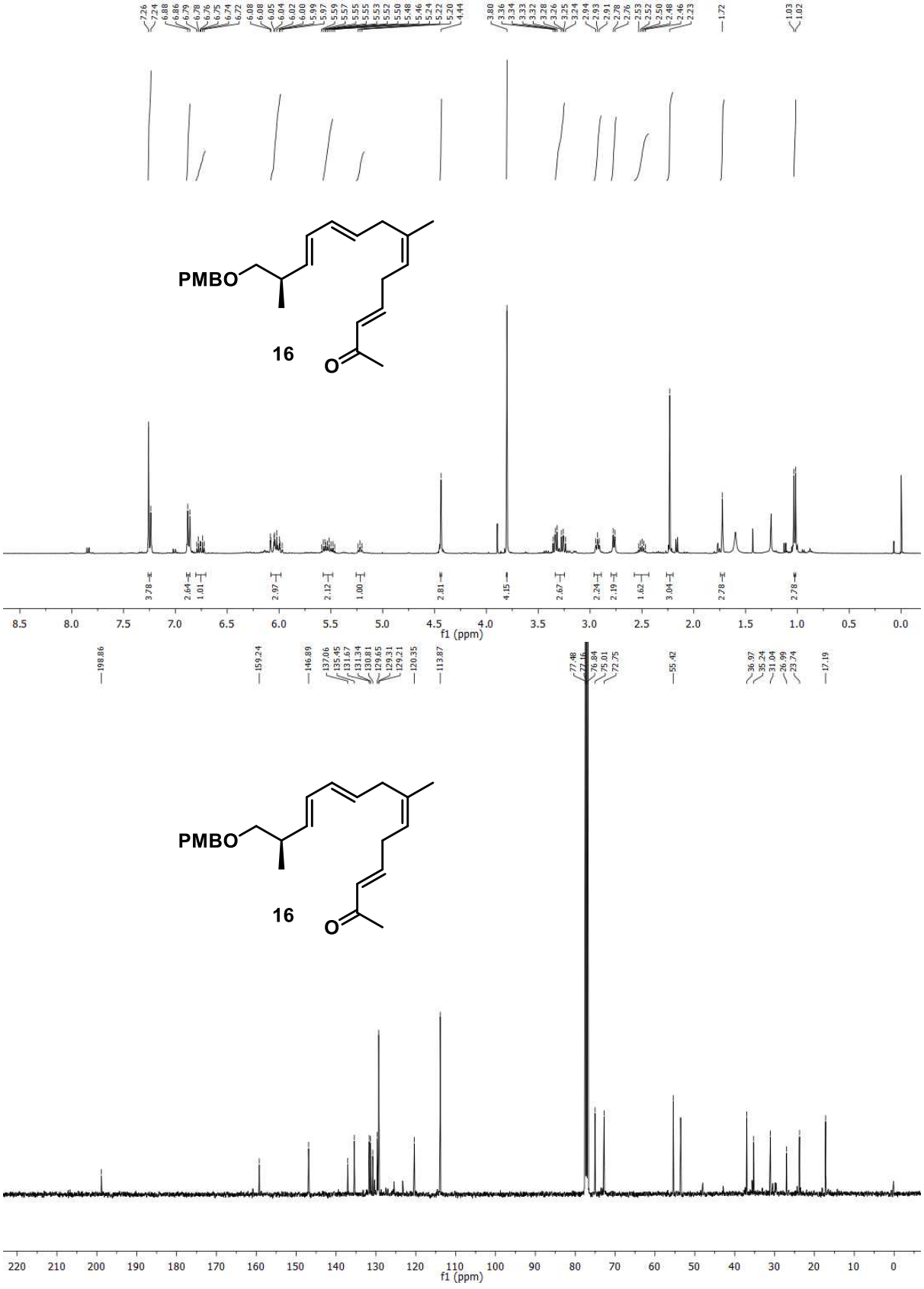




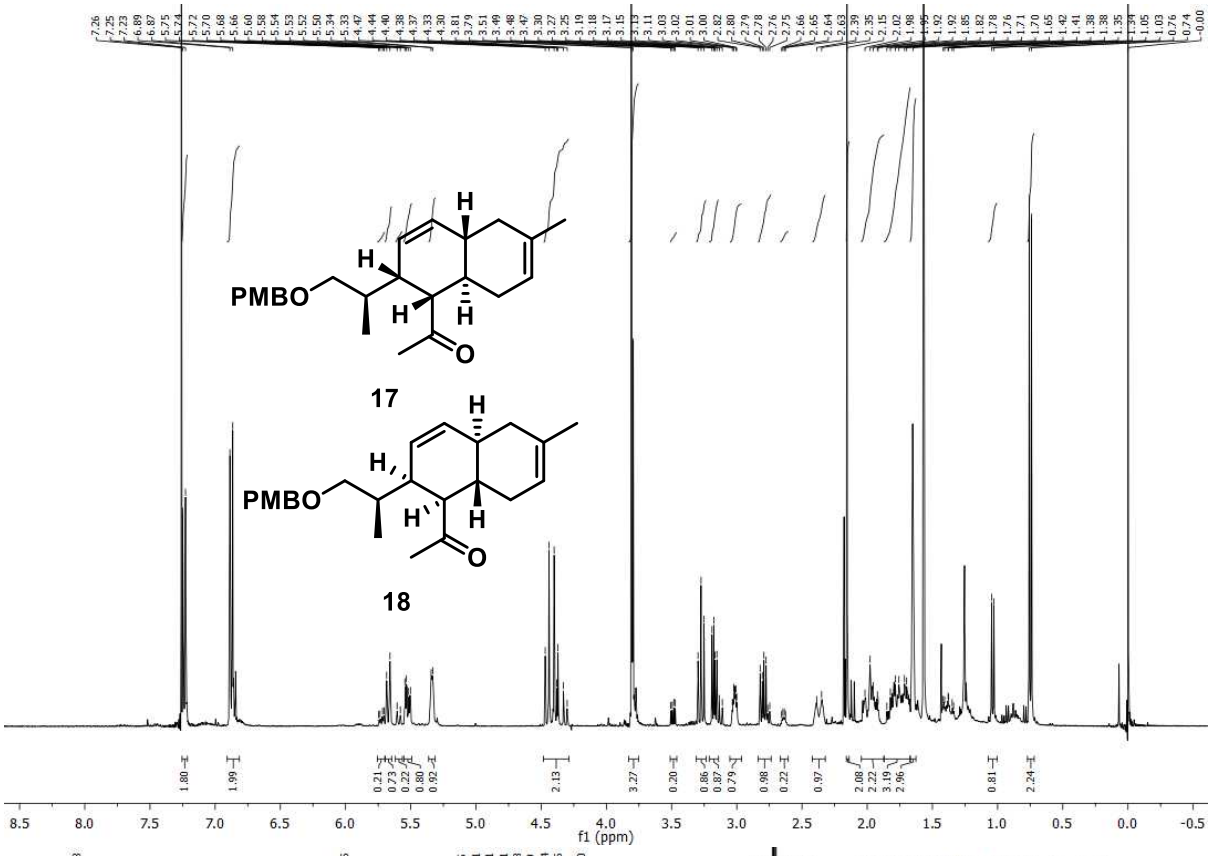
Aldehyde 15

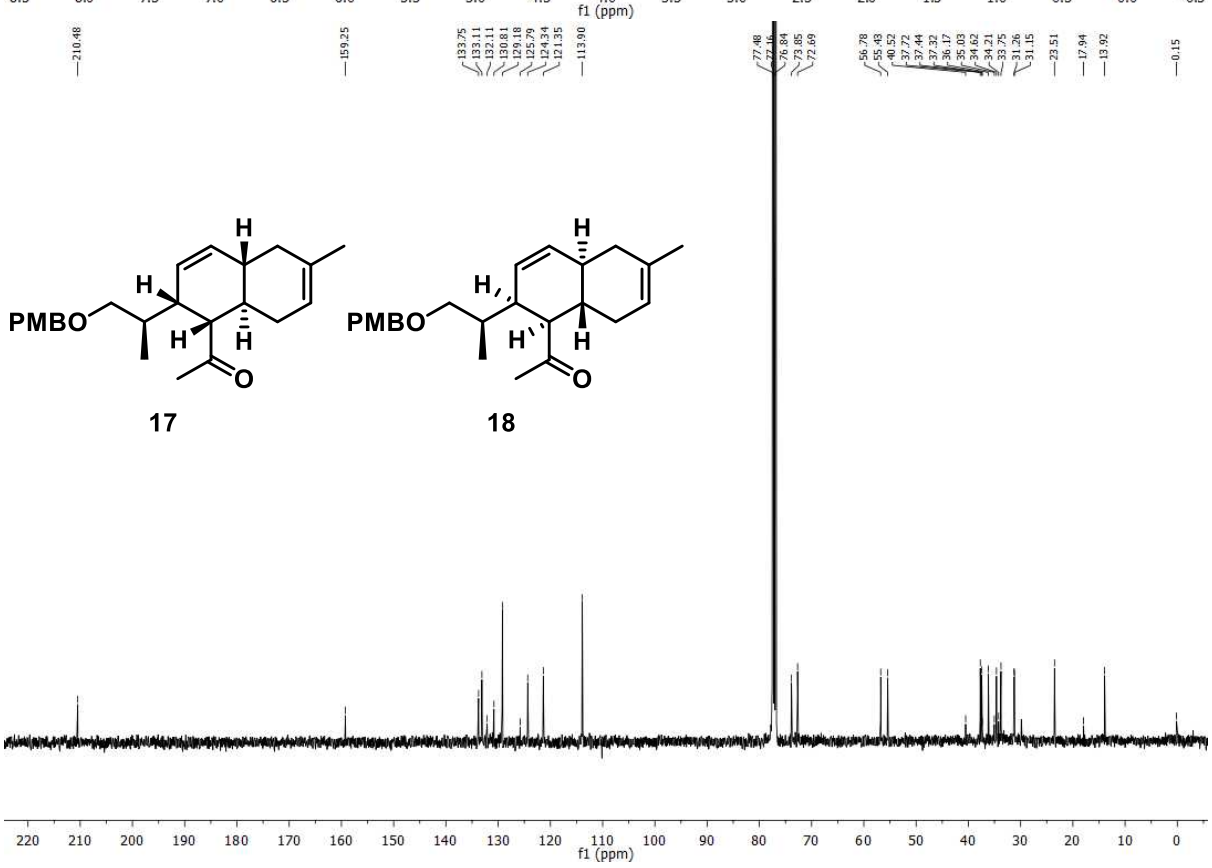


Enone 16

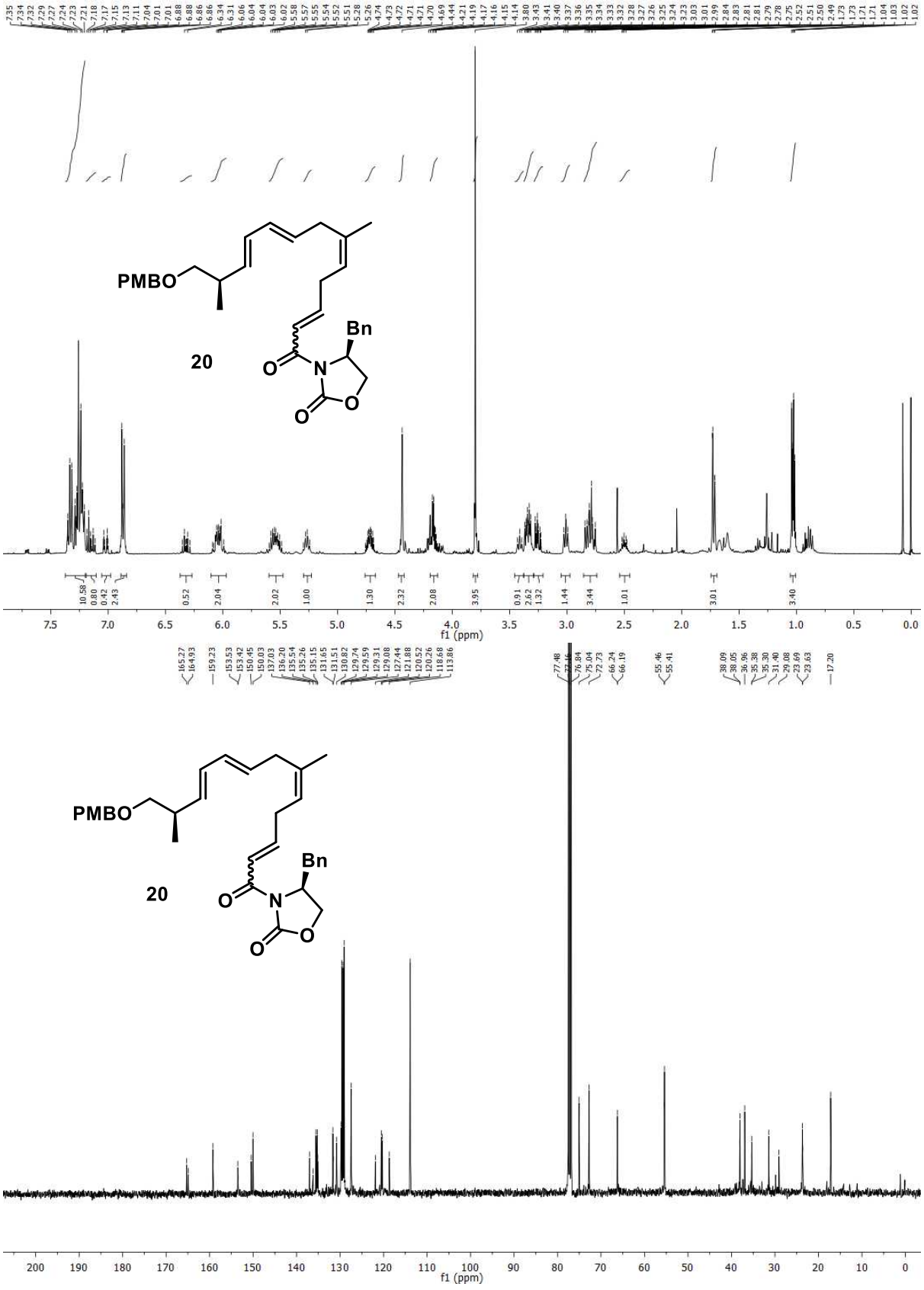


Adducts 17 and 18

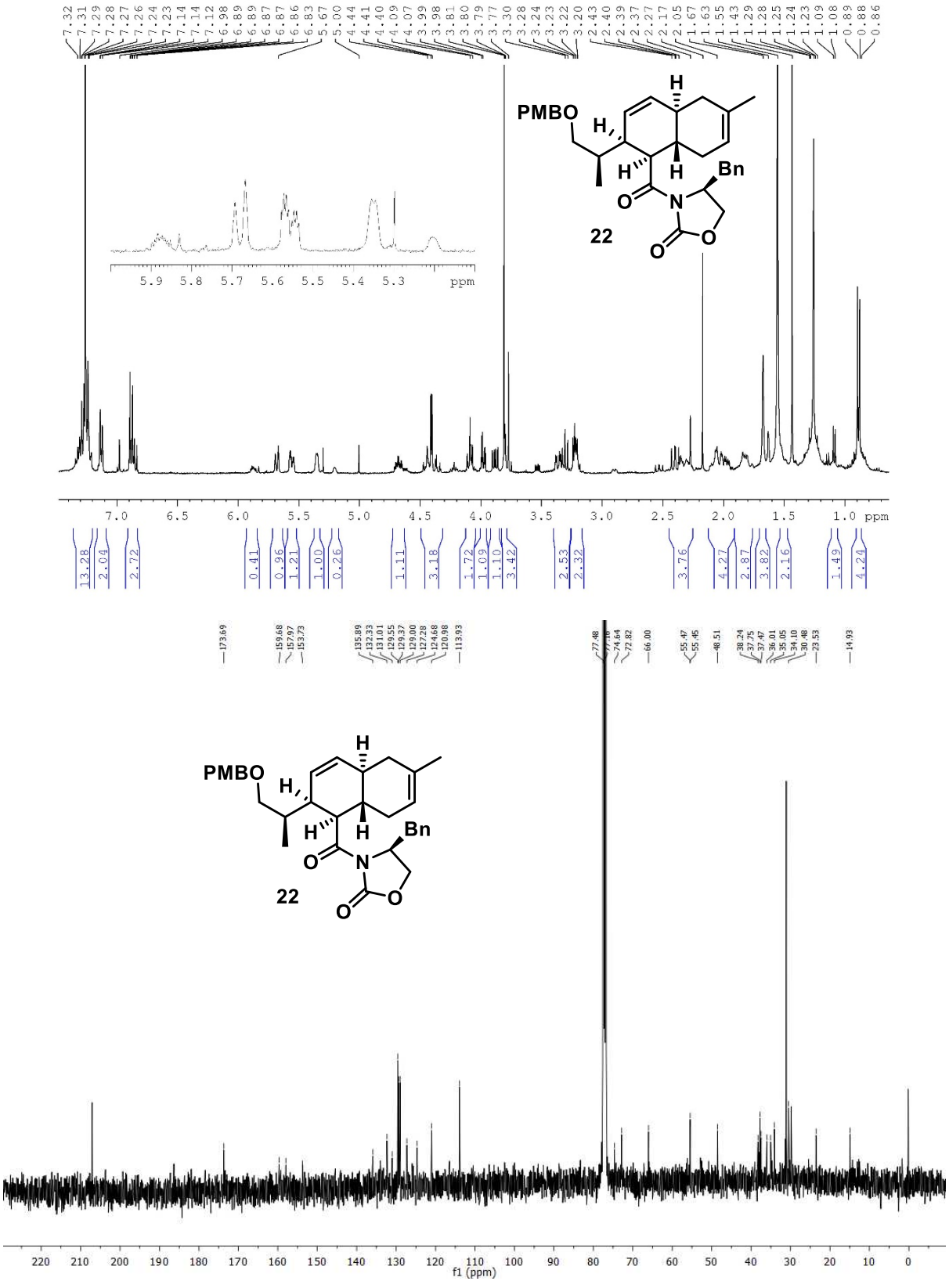




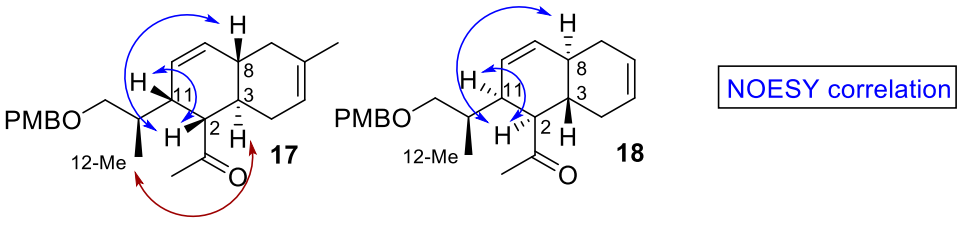
Imide 20

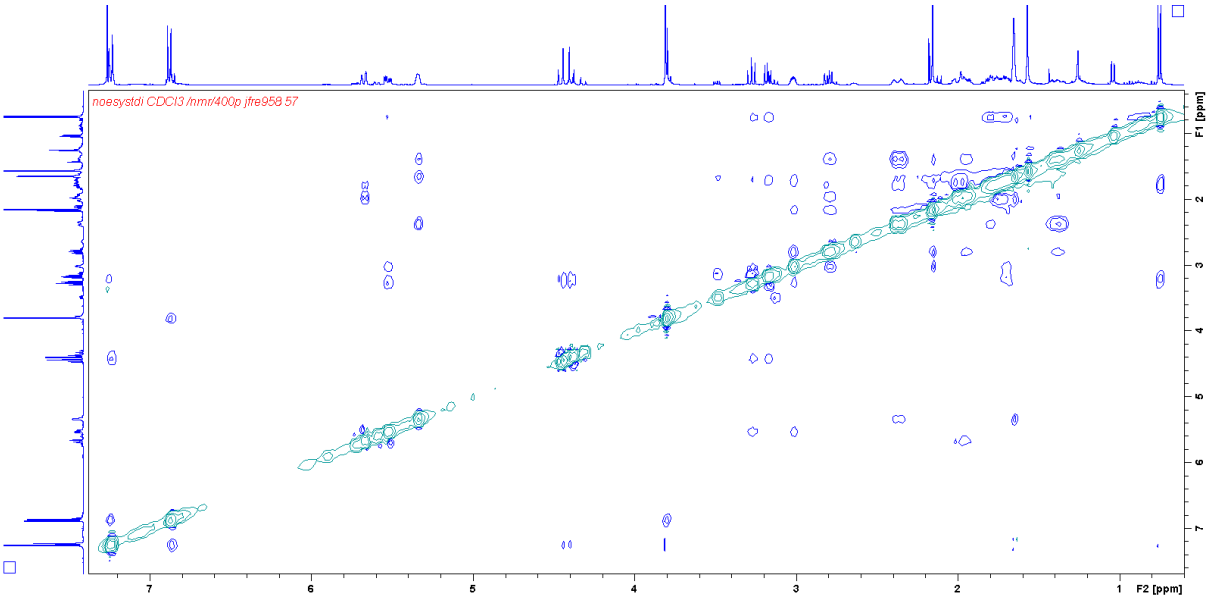


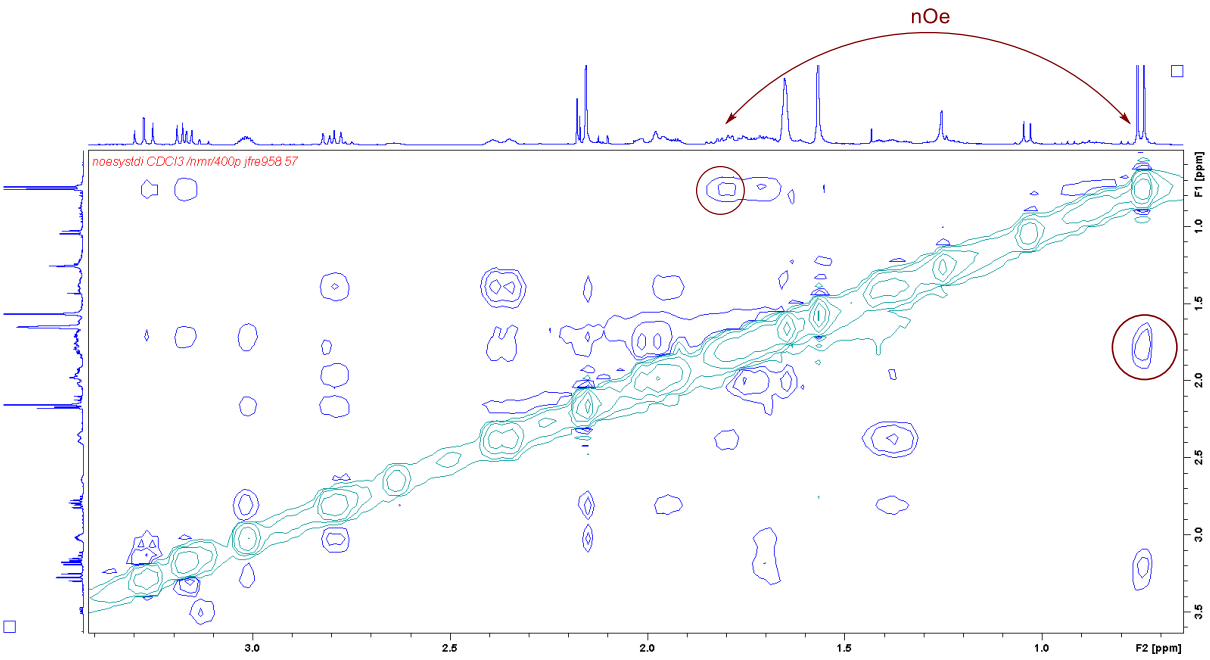
Adduct 22



Adducts 17-18







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

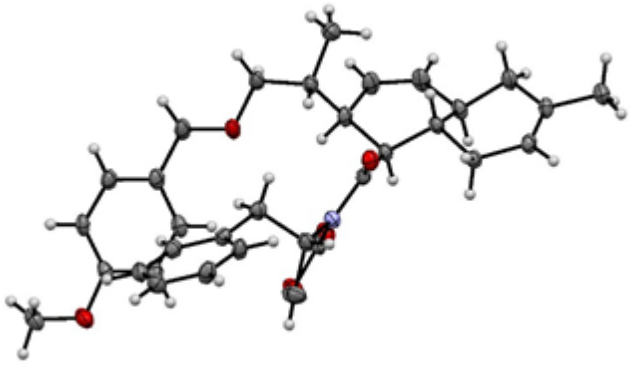


Figure S1. ORTEP diagram drawn with 50% ellipsoid probability of the crystal structure of Adduct **22**.

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 (A)	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 [$I > 2\sigma(I)$]]	0.0595
Parameters	356
R_{int}	0.0595
Goodness-of-fit	1.054
R [$F_2 > 2\sigma(F_2)$]	0.0448
wR (F2, all data)	0.1169