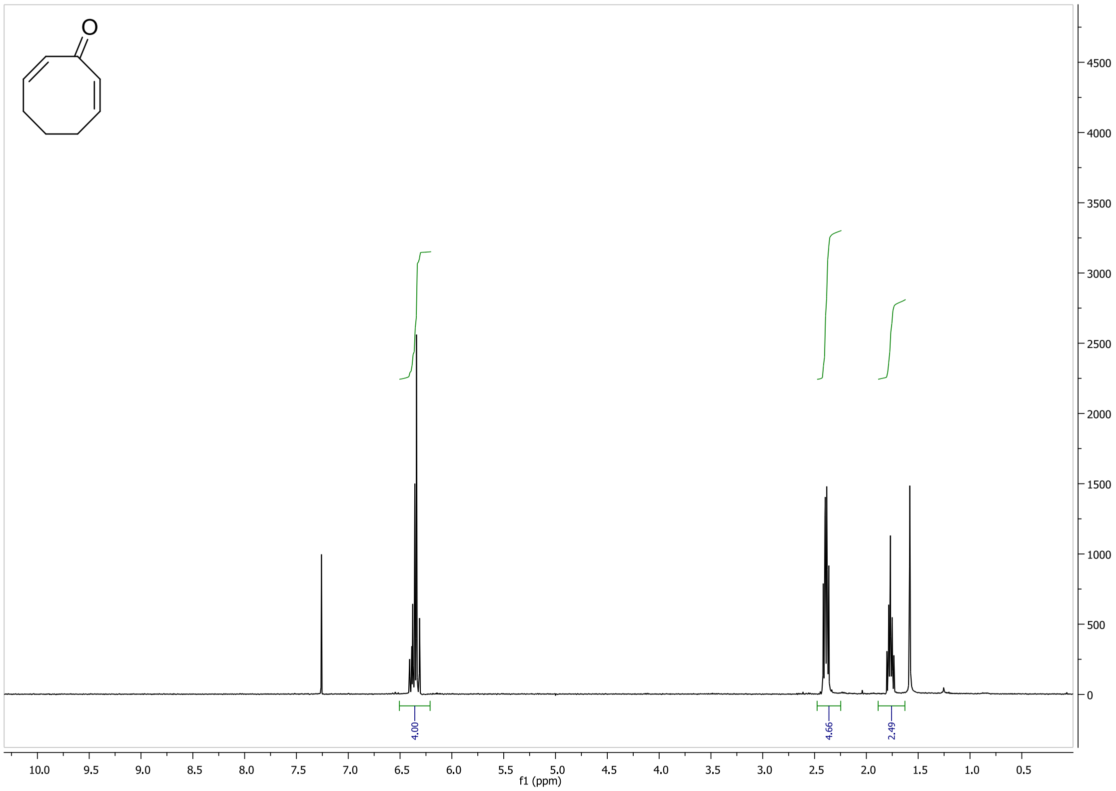
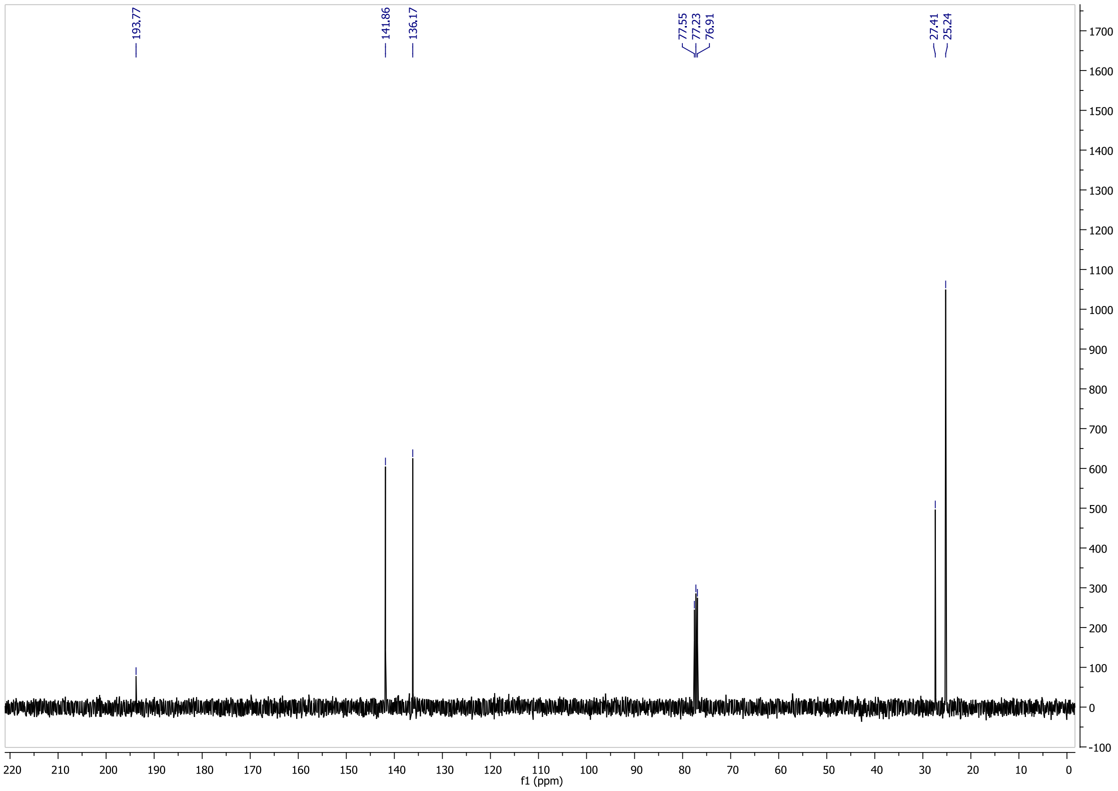
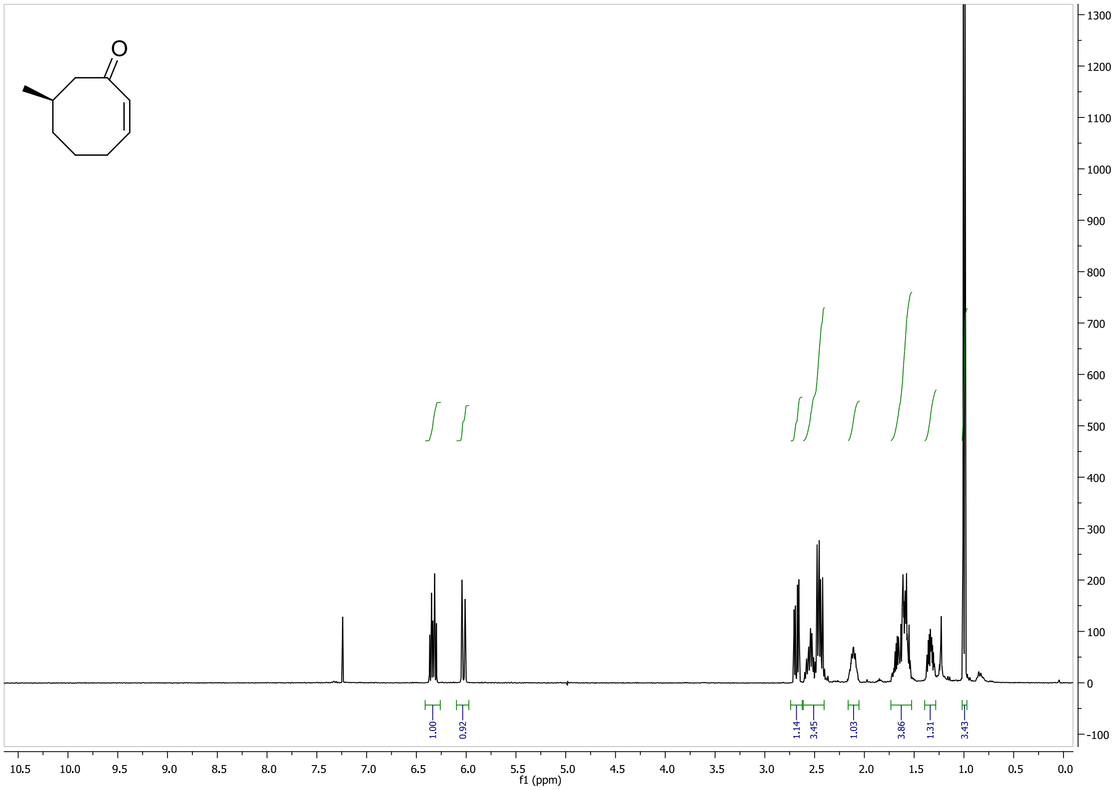
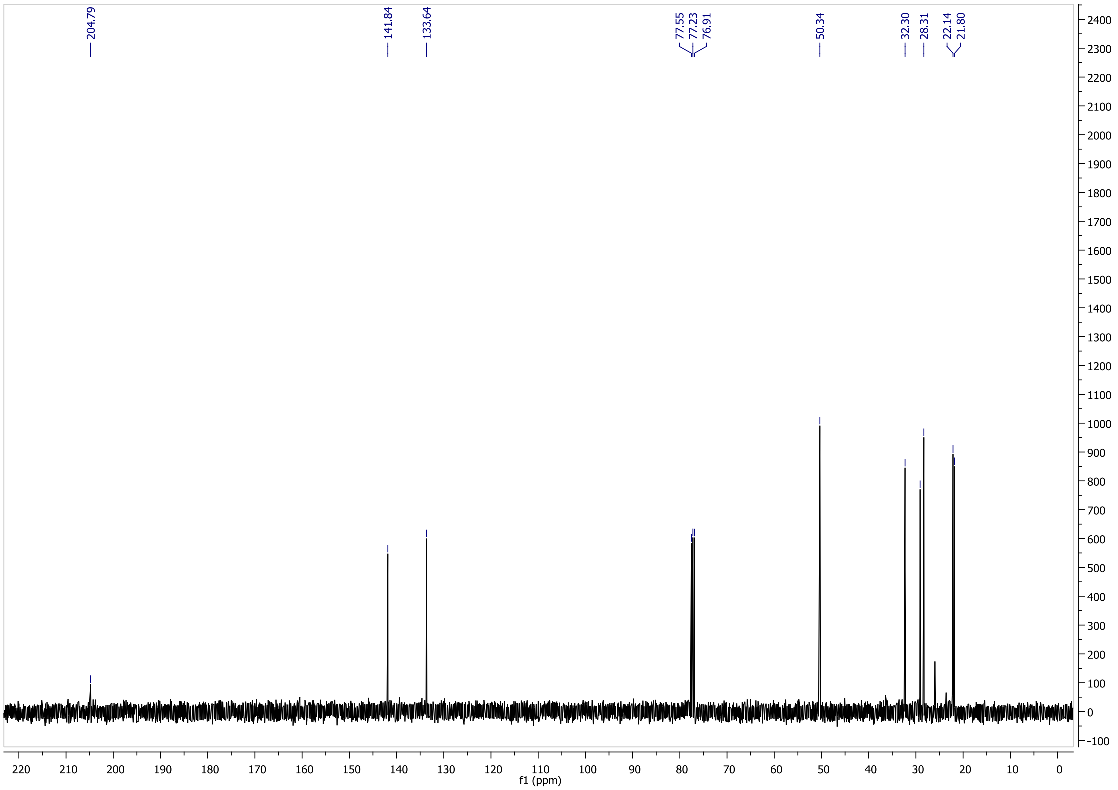
(2*Z*,7*Z*)-Cycloocta-2,7-dienone 4



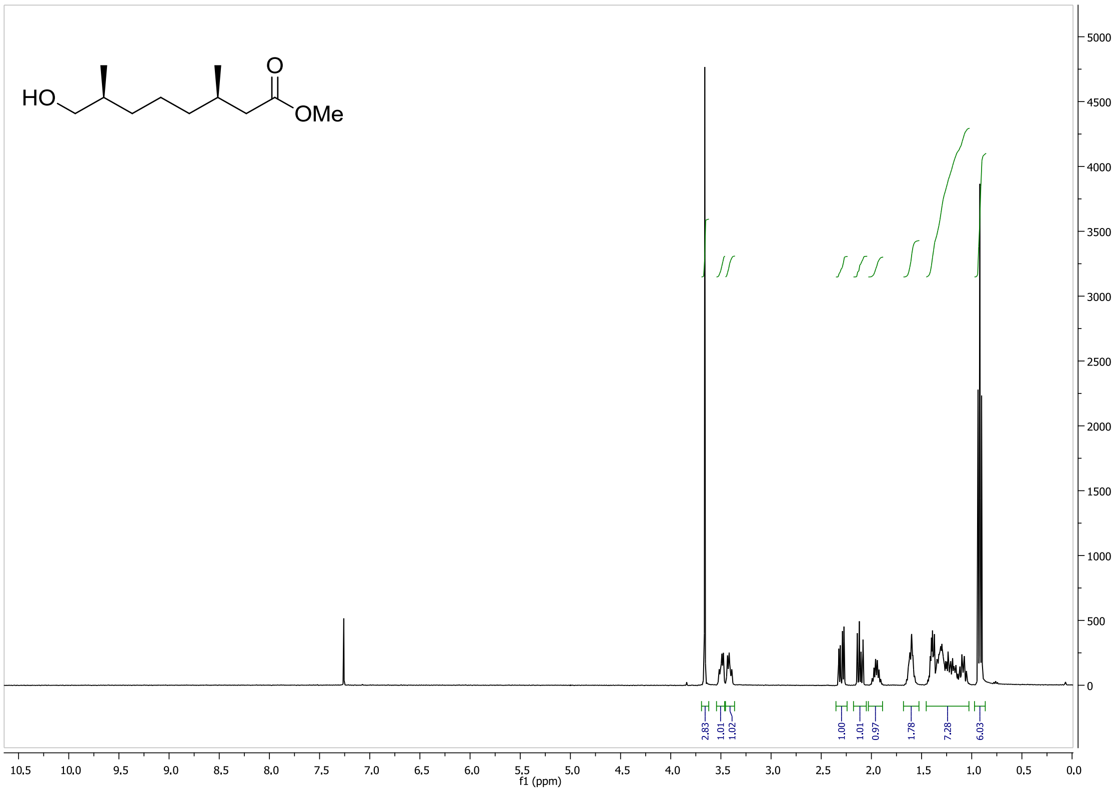

193.77
141.86
136.17
77.55
77.23
76.91
27.41
25.24
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

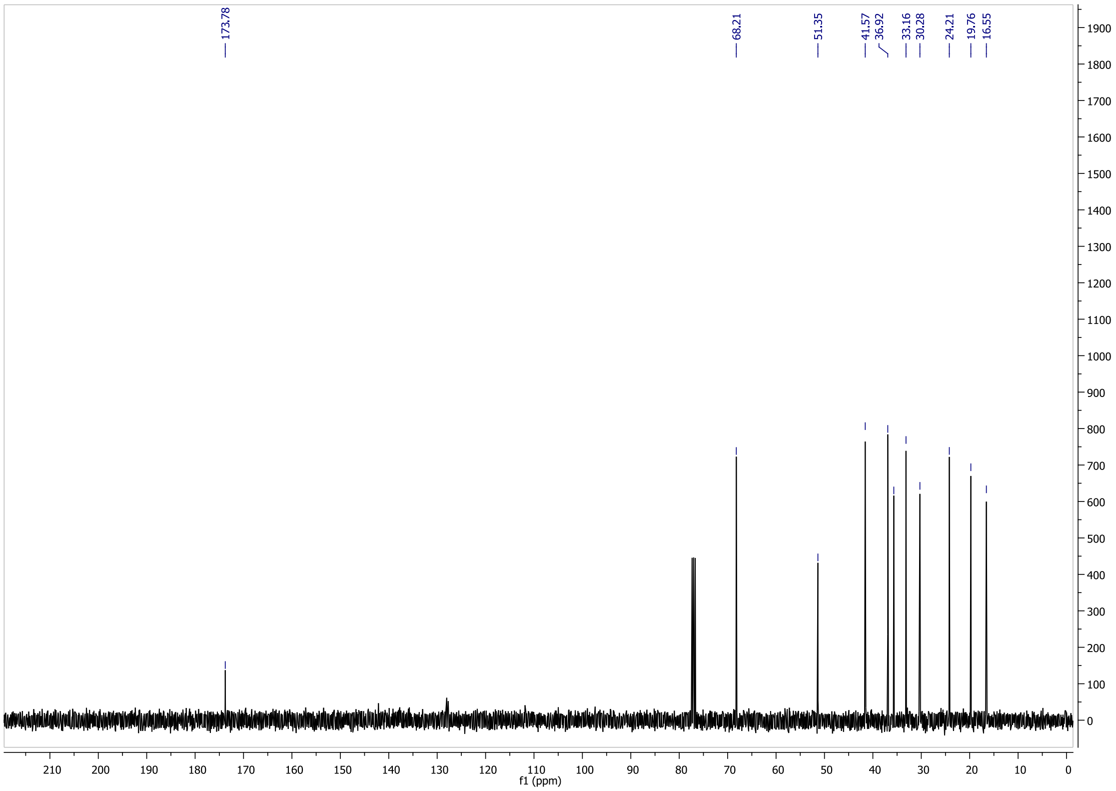
(*R*,*Z*)-7-Methylcyclooct-2-enone 5



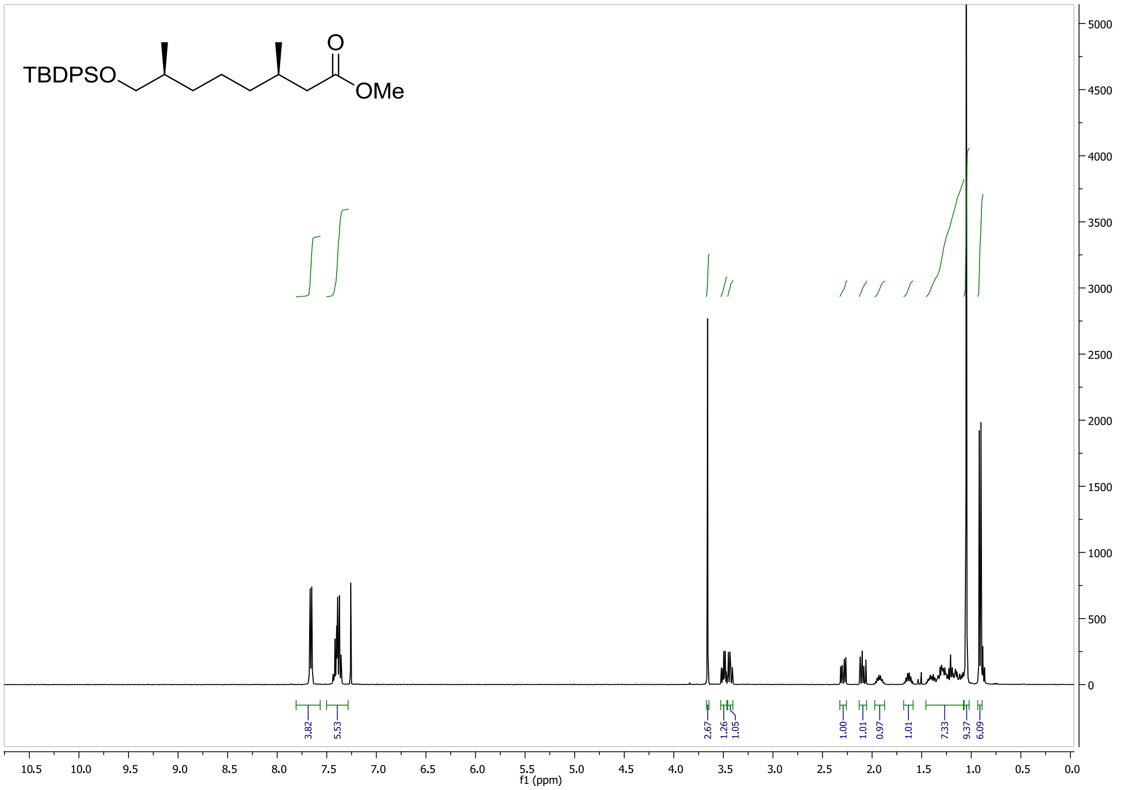


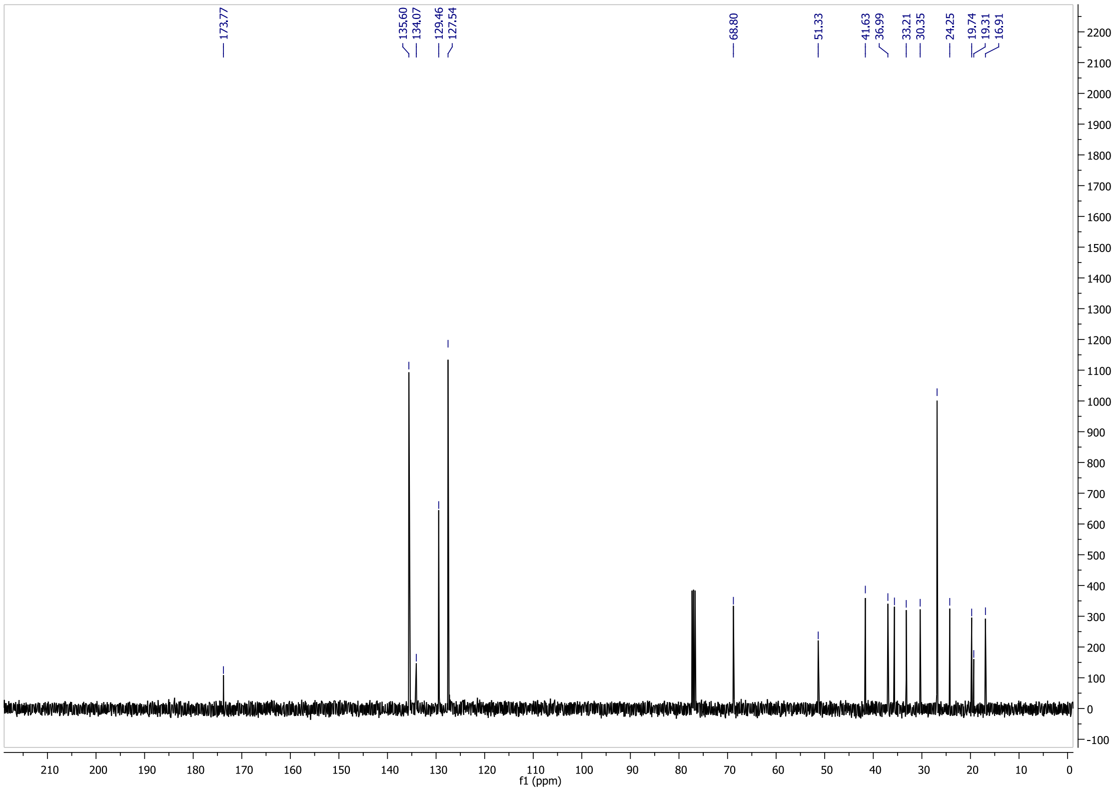
(3*R*,7*S*)-Methyl 8-hydroxy-3,7-dimethyloctanoate 3



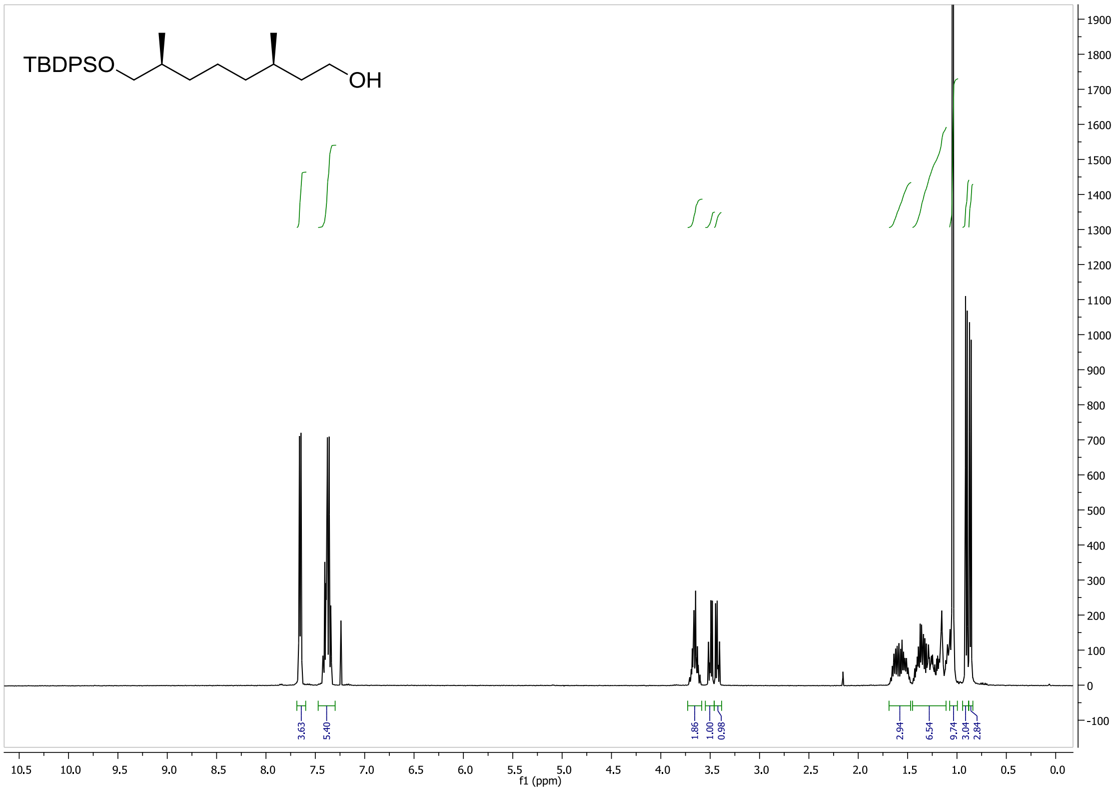


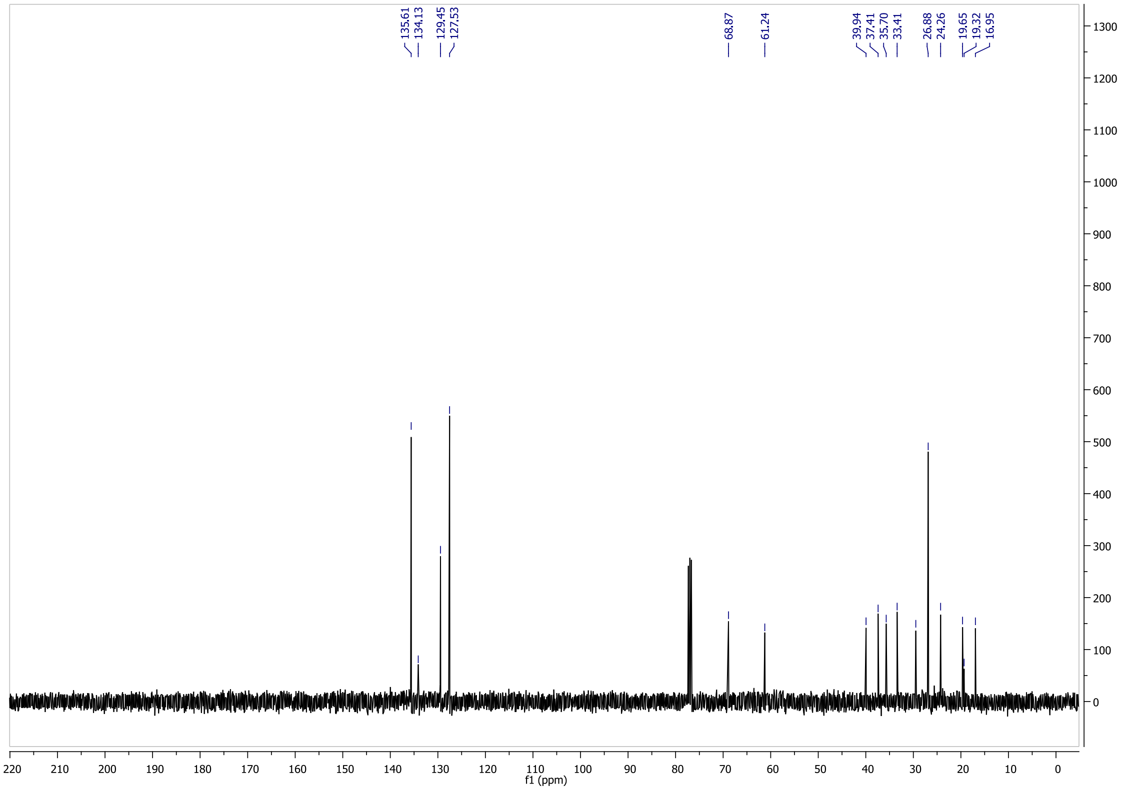
(3*R*,7*S*)-Methyl 8-((*tert*-butyldiphenylsilyl)oxy)-3,7-dimethyloctanoate 7



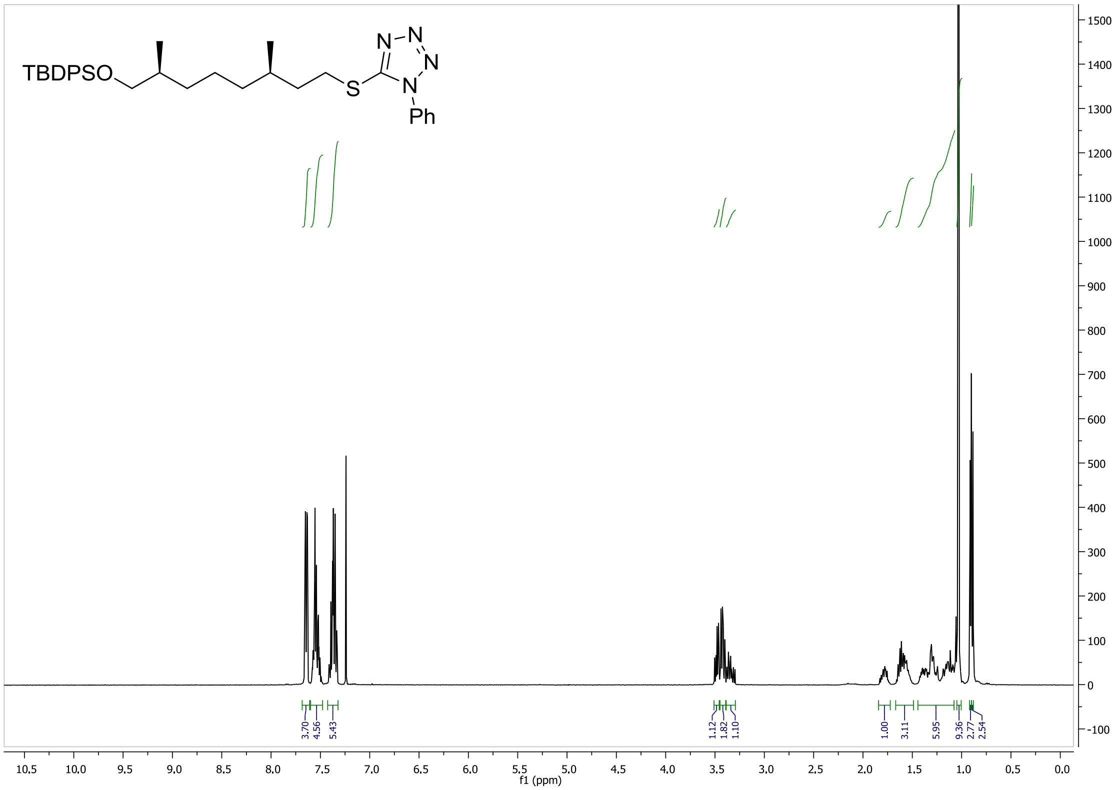


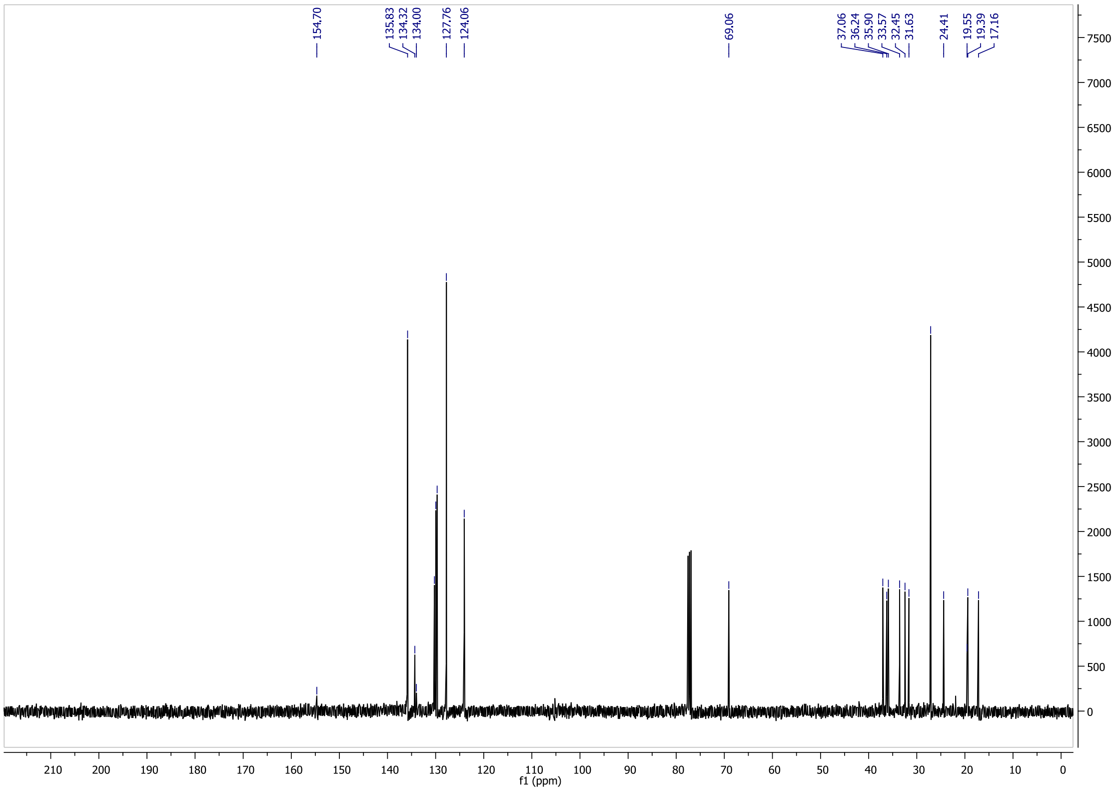
(3*R*,7*S*)-8-((*tert*-Butyldiphenylsilyl)oxy)-3,7-dimethyloctan-1-ol 8



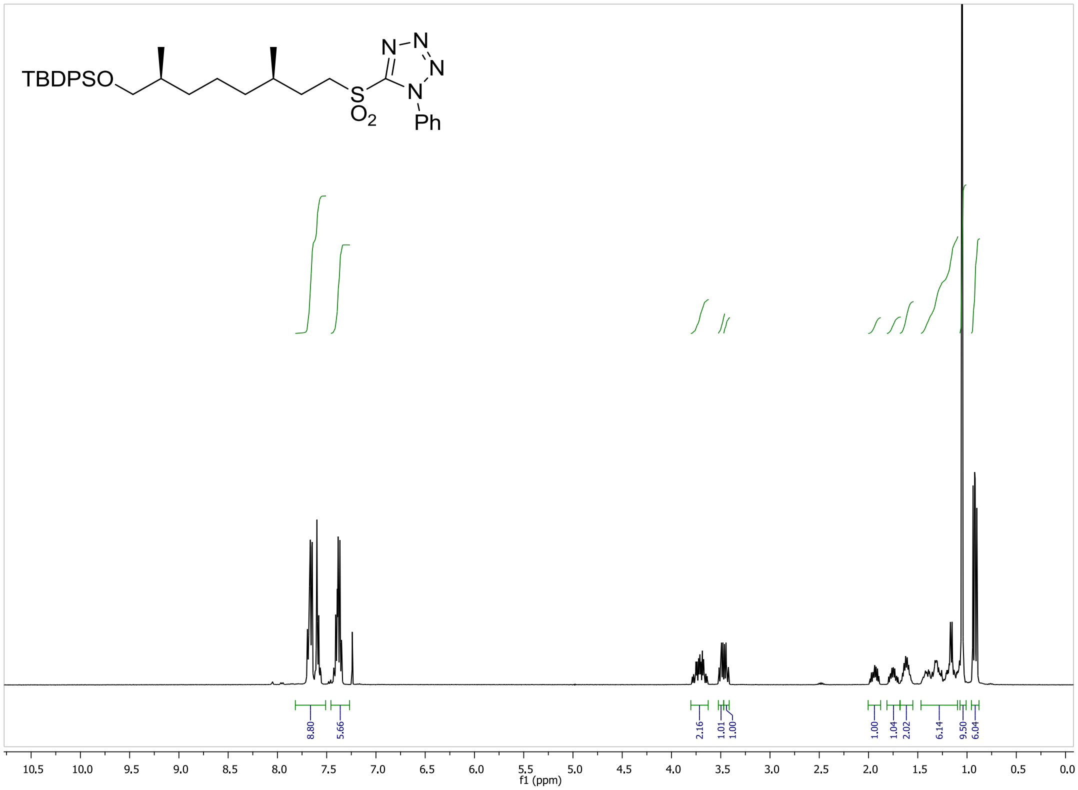

135.61
134.13
129.45
127.53
68.87
61.24
39.94
37.41
35.70
33.41
26.88
24.26
19.65
19.32
16.95
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

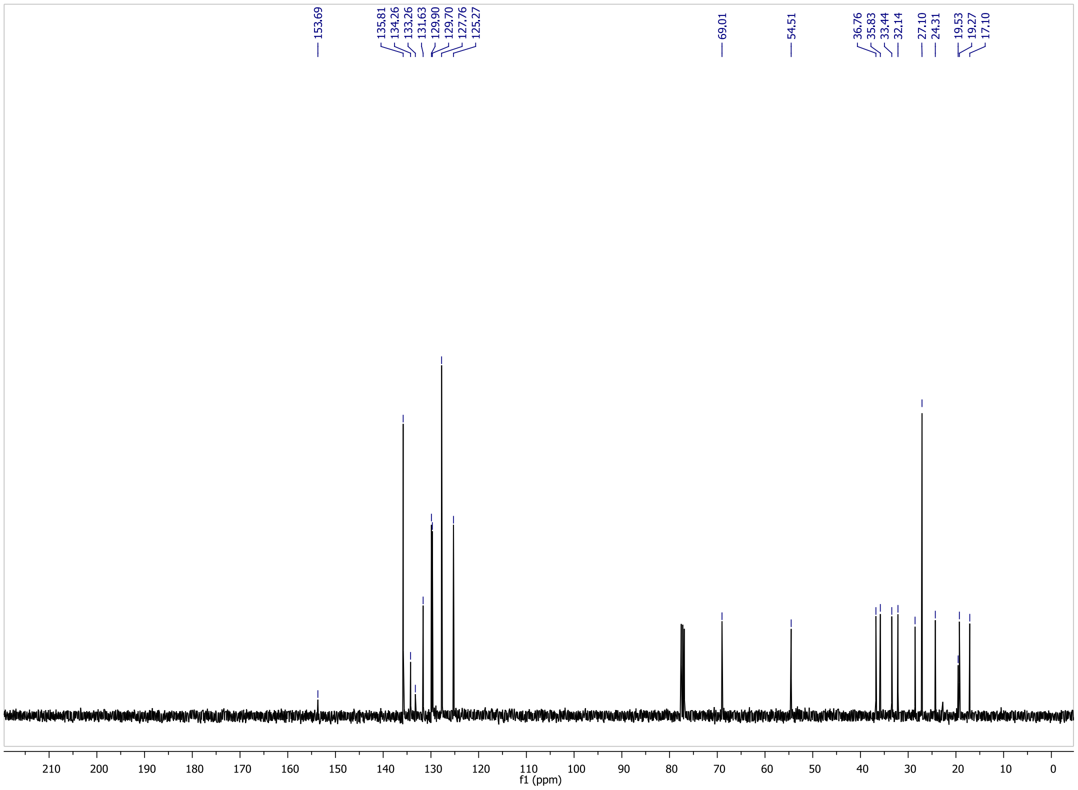
5-(((3*R*,7*S*)-8-((*tert*-Butyldiphenylsilyl)oxy)-3,7-dimethyloctyl)thio)-1-phenyl-1H-tetrazole



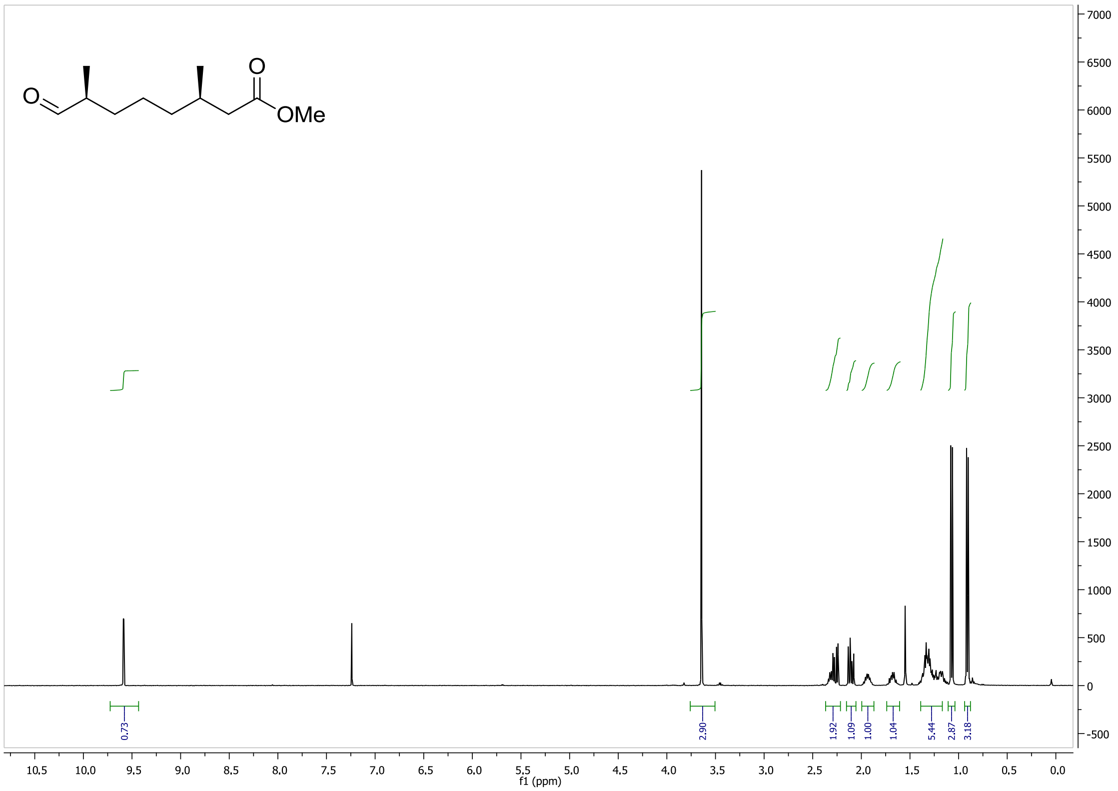


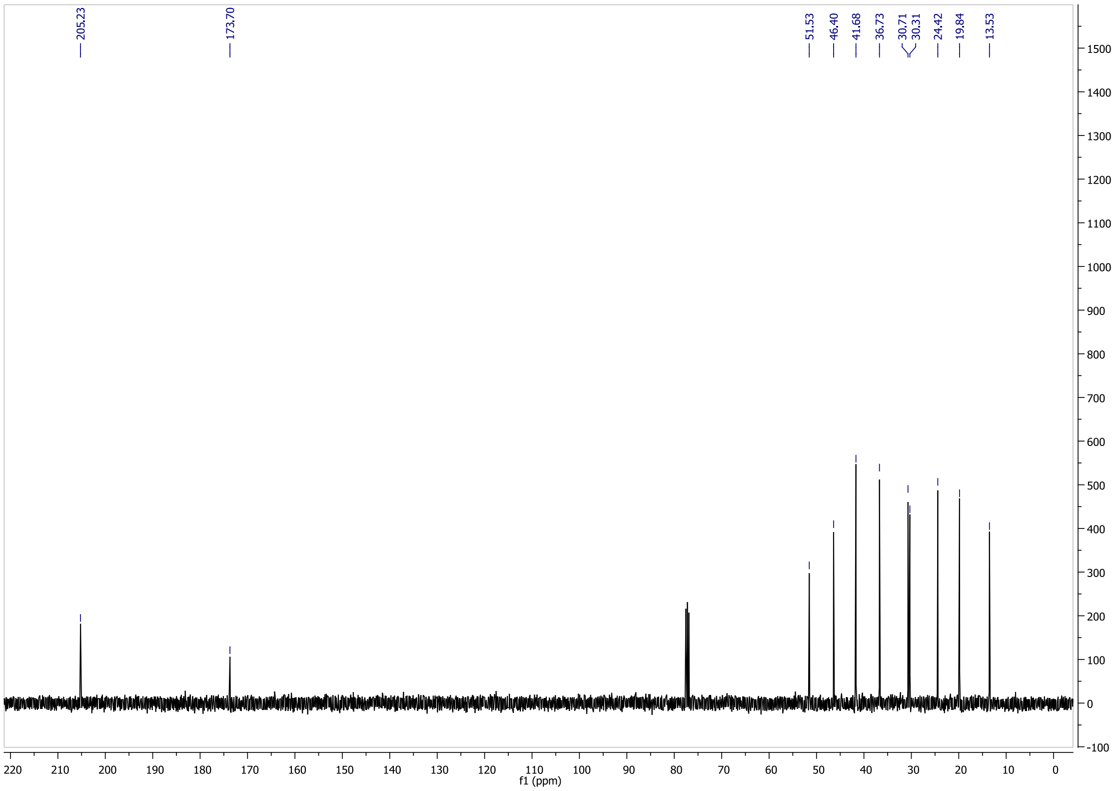
5-(((3*R*,7*S*)-8-((*tert*-Butyldiphenylsilyl)oxy)-3,7-dimethyloctyl)sulfonyl)-1-phenyl-1H-tetrazole 9



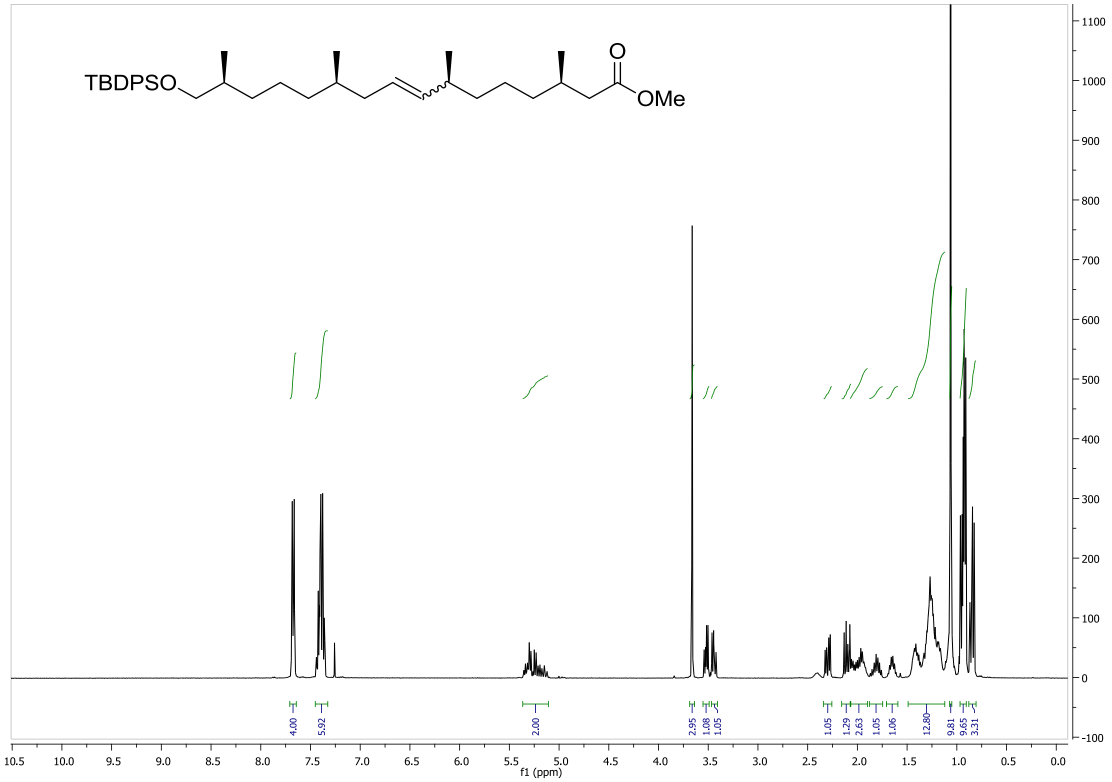


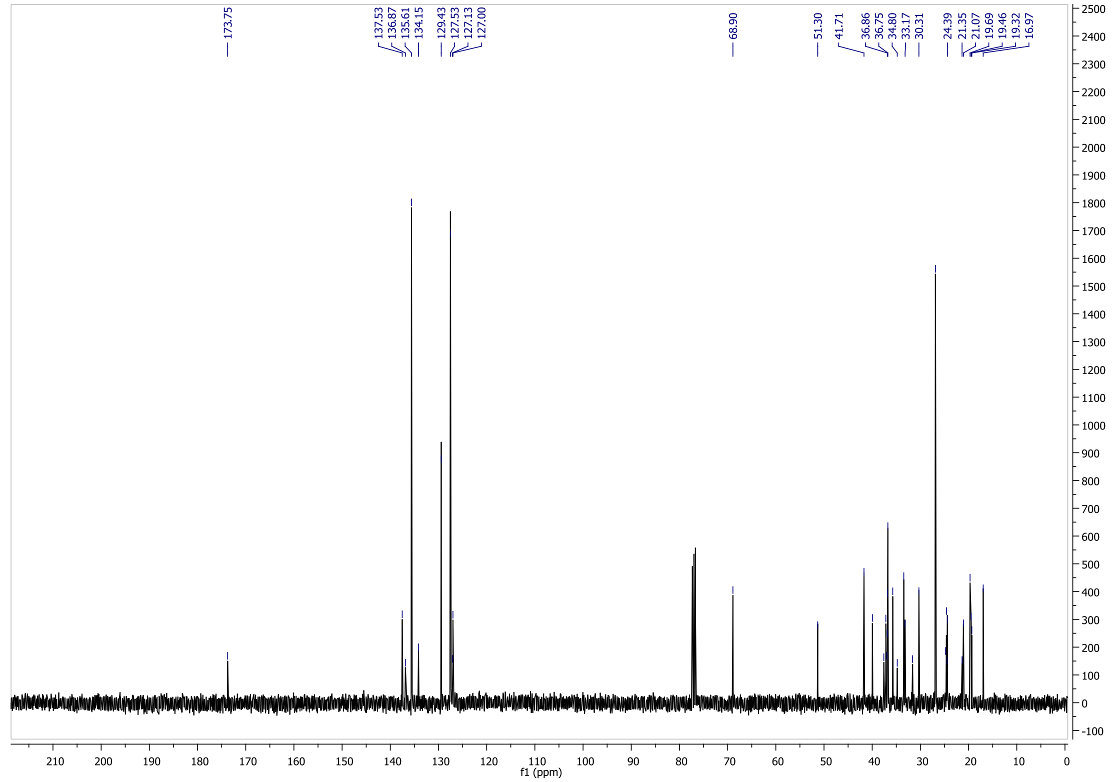
(3*R*,7*S*)-Methyl 3,7-dimethyl-8-oxooctanoate 10



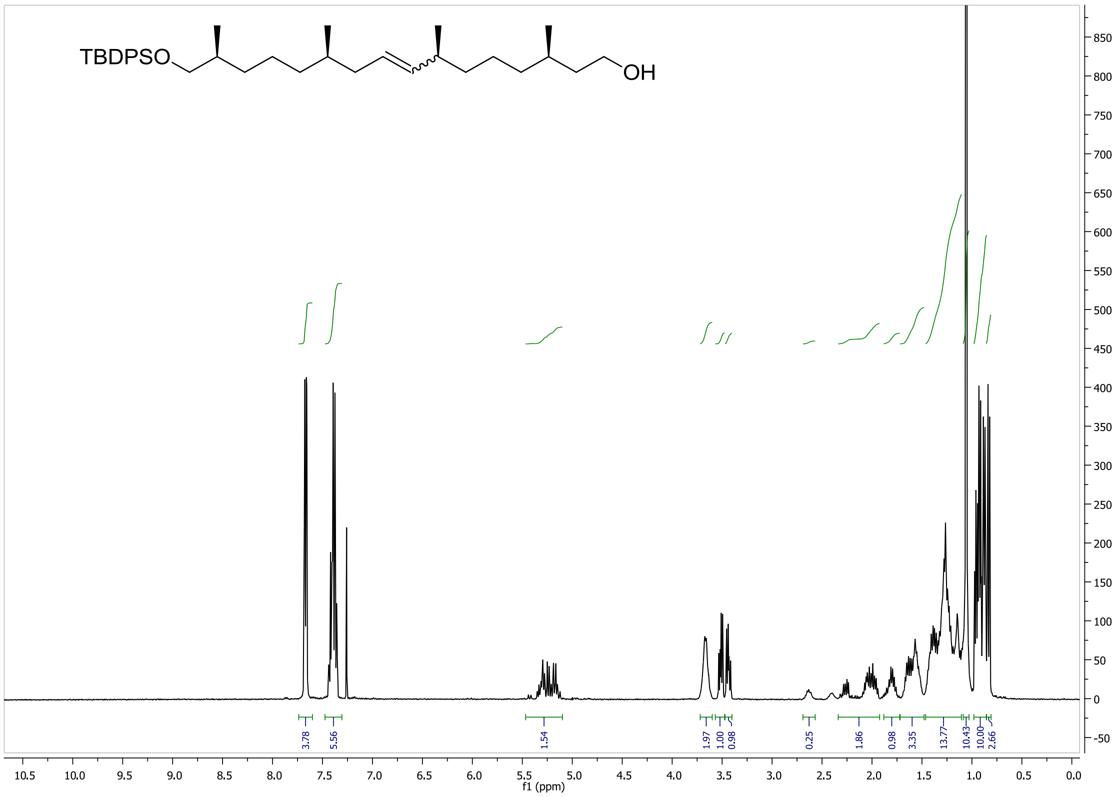


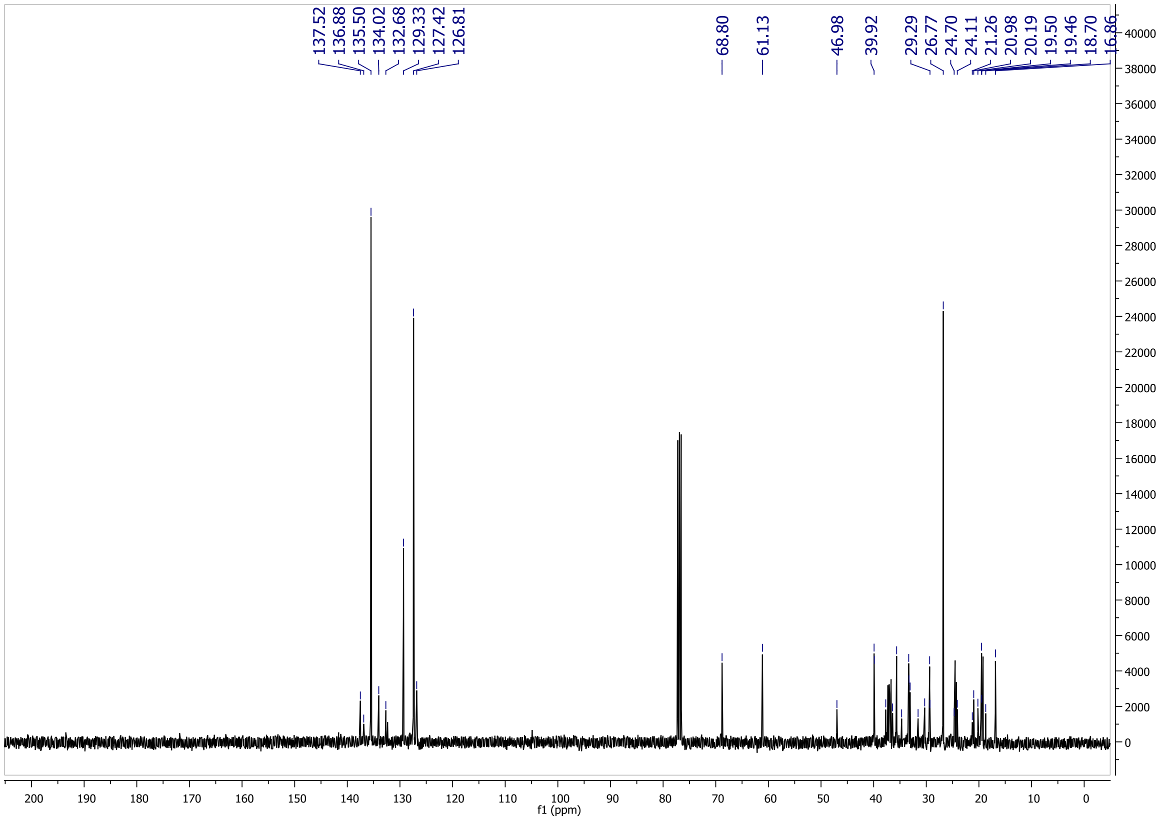
(3*R*,7*S*,11*R*,15*S*)-Methyl 16-((*tert*-butyldiphenylsilyl)oxy)-3,7,11,15-tetramethylhexadec-8-enoate 11



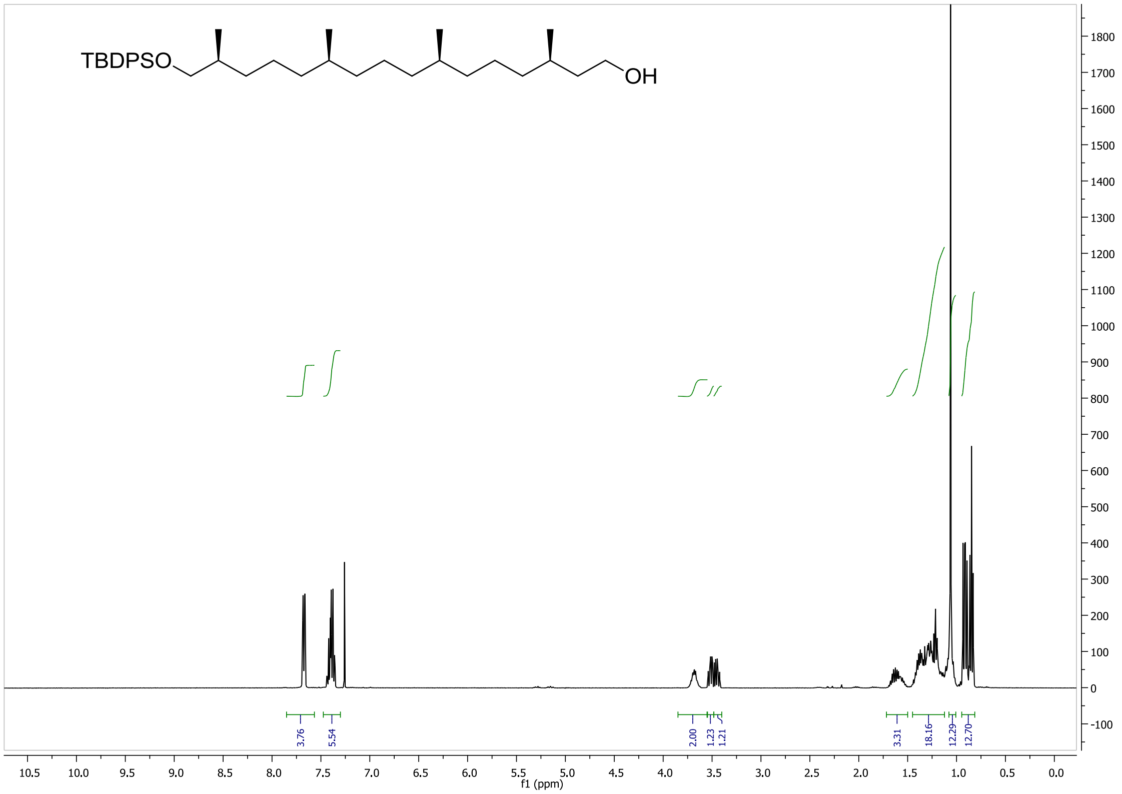


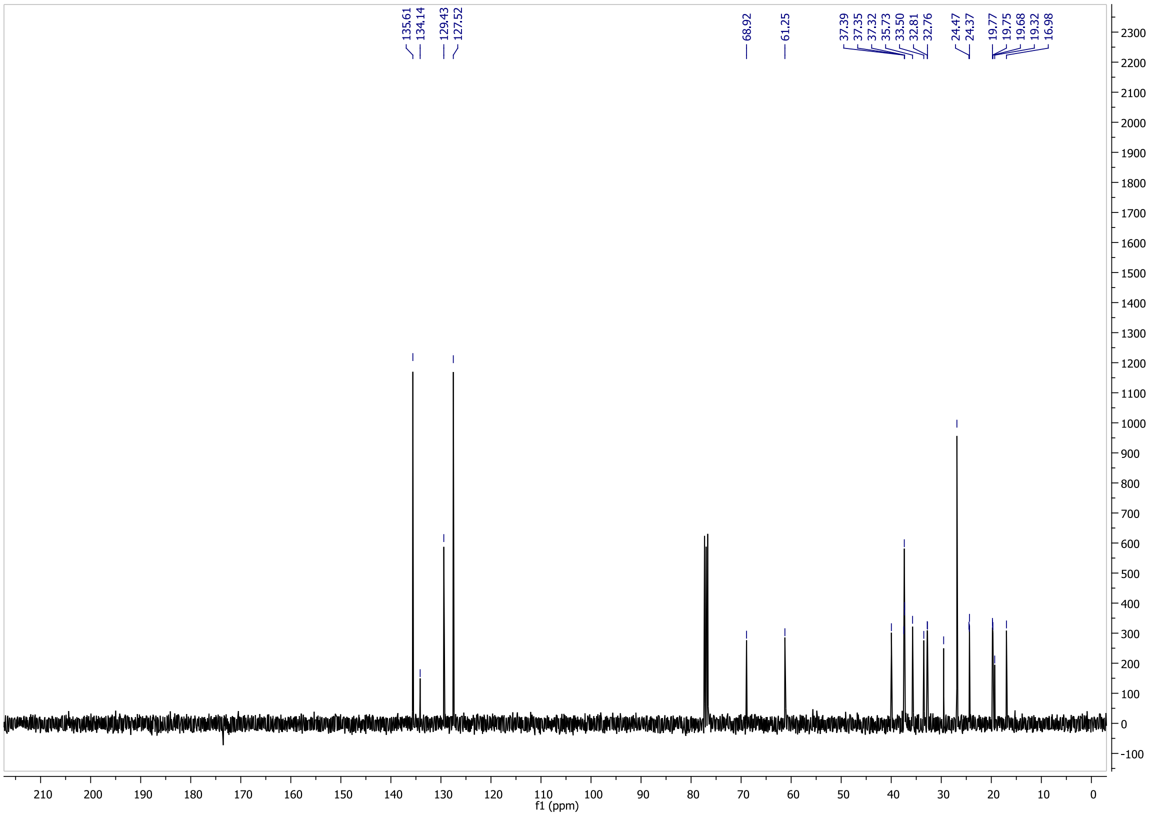
(3*R*,7*S*,11*R*,15*S*)-16-((*tert*-Butyldiphenylsilyl)oxy)-3,7,11,15-tetramethylhexadec-8-en-1-ol 12



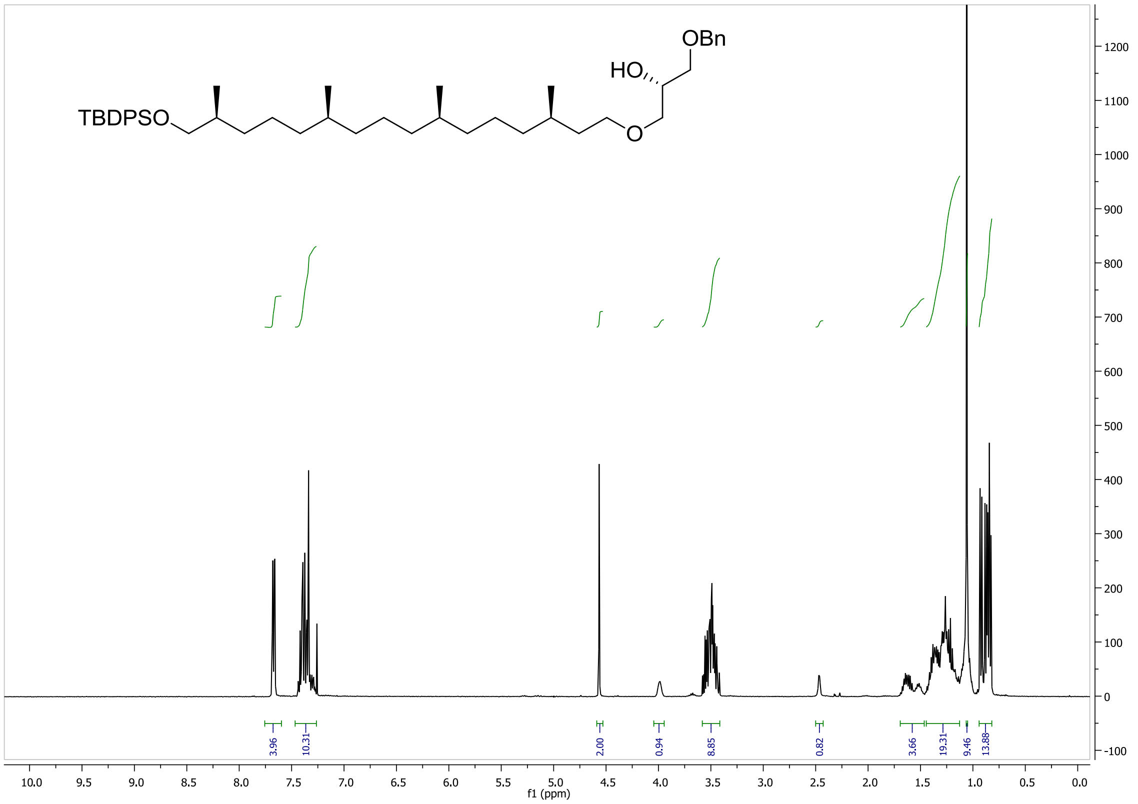


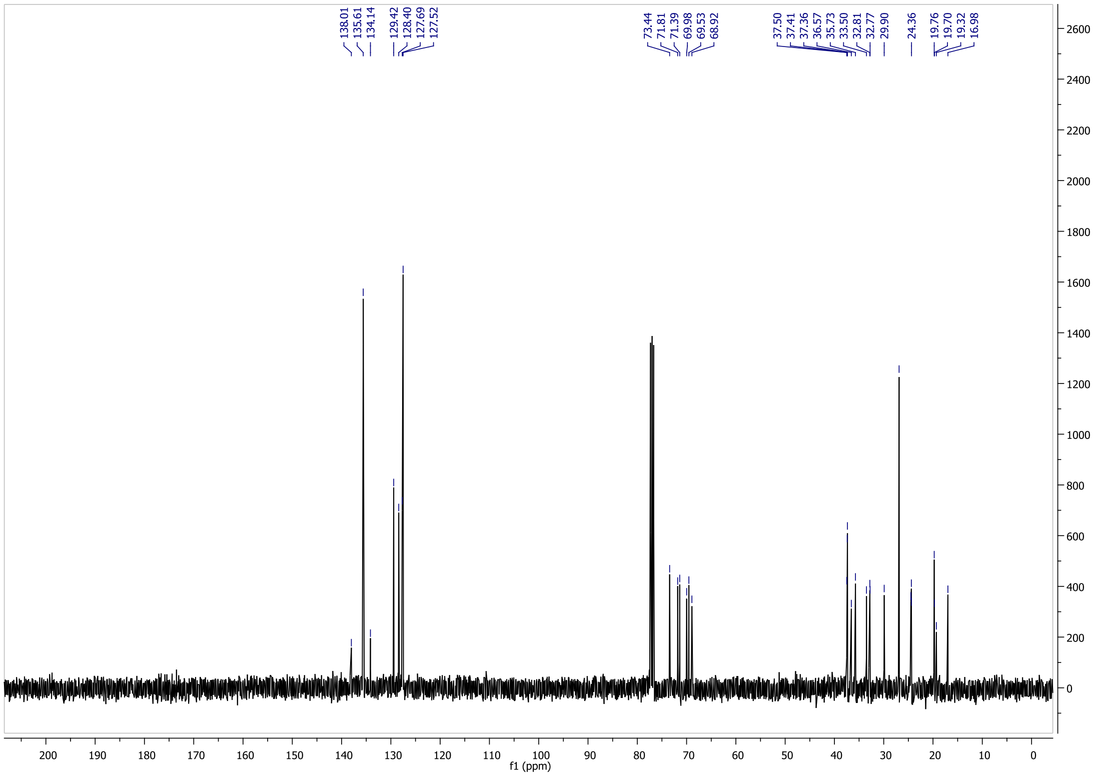
(3*R*,7*R*,11*S*,15*S*)-16-((*tert*-Butyldiphenylsilyl)oxy)-3,7,11,15-tetramethylhexadecan-1-ol 13



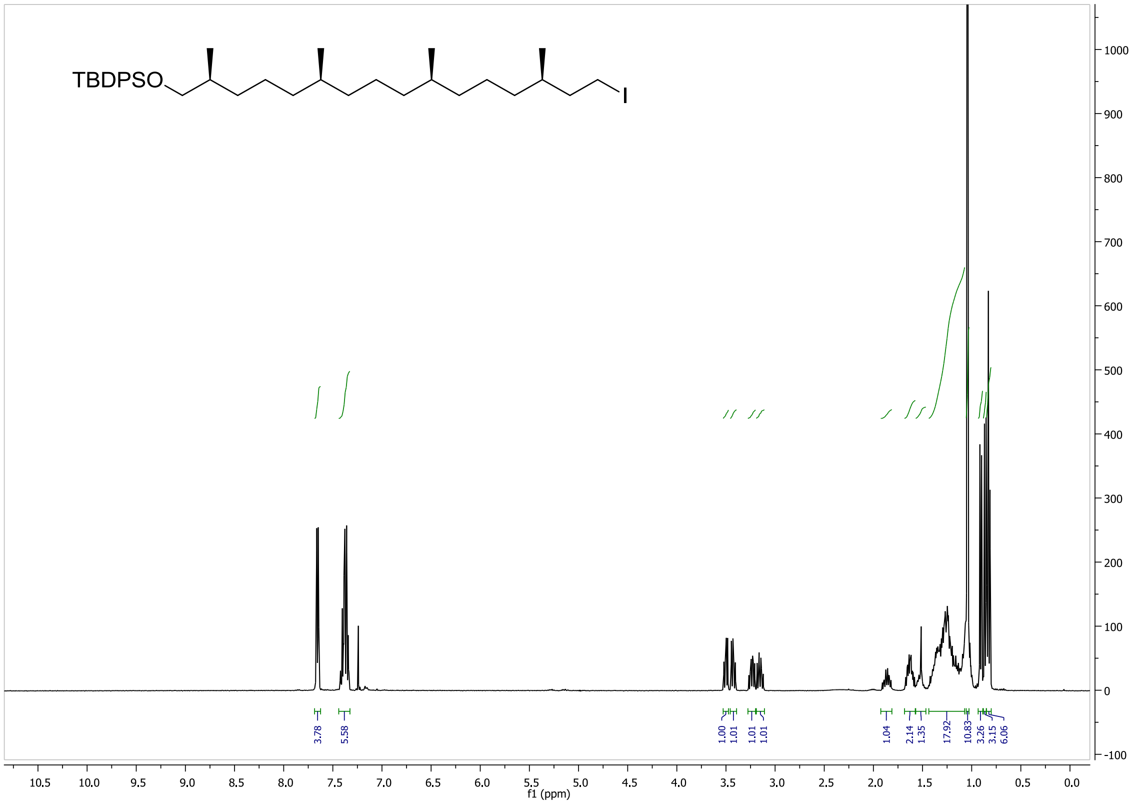


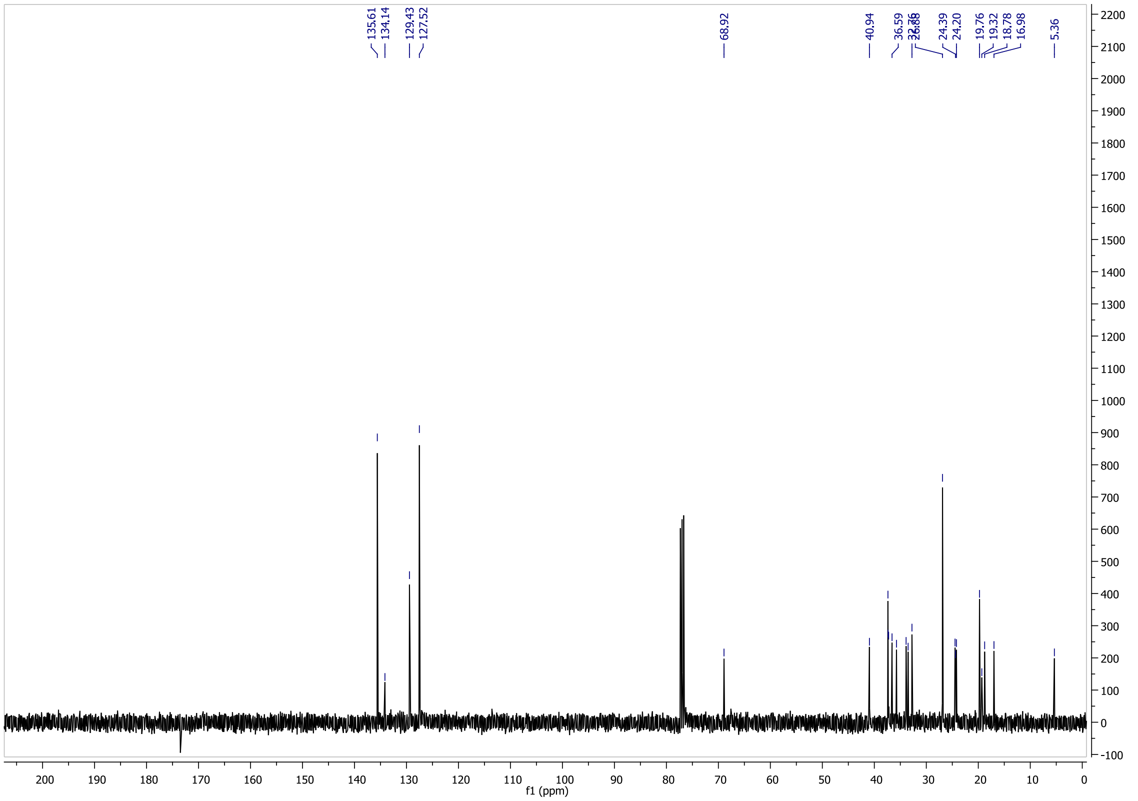
(4*S*,9*R*,13*R*,17*S*,21*S*)-9,13,17,21,25,25-Hexamethyl-1,24,24-triphenyl-2,6,23-trioxa-24-silahexacosan-4-ol 14



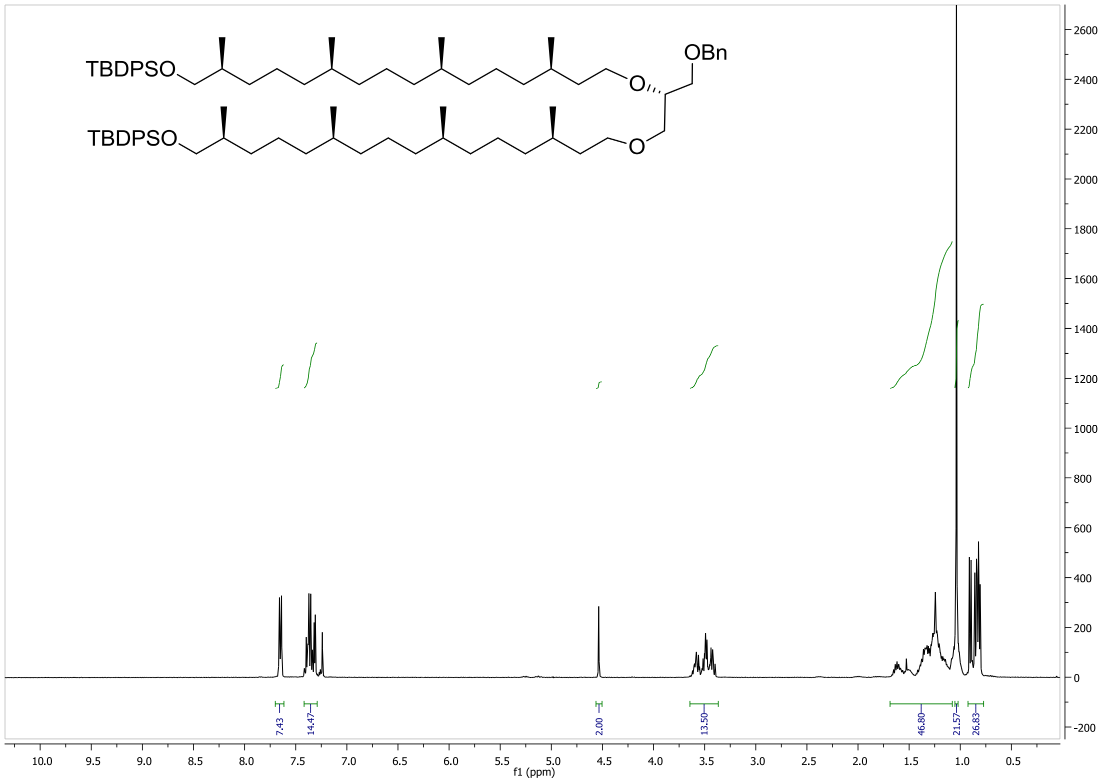


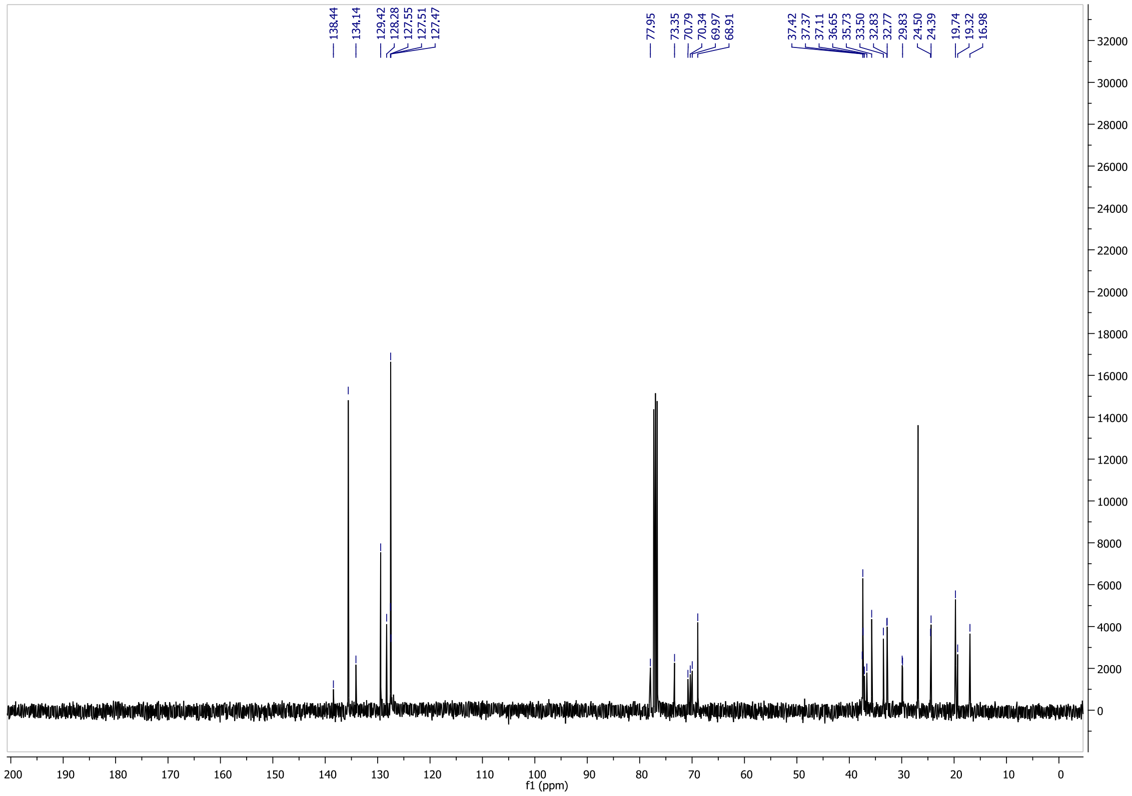
***tert*-Butyl(((2*S*,6*S*,10*R*,14*R*)-16-iodo-2,6,10,14-tetramethylhexadecyl)oxy)diphenylsilane 15**



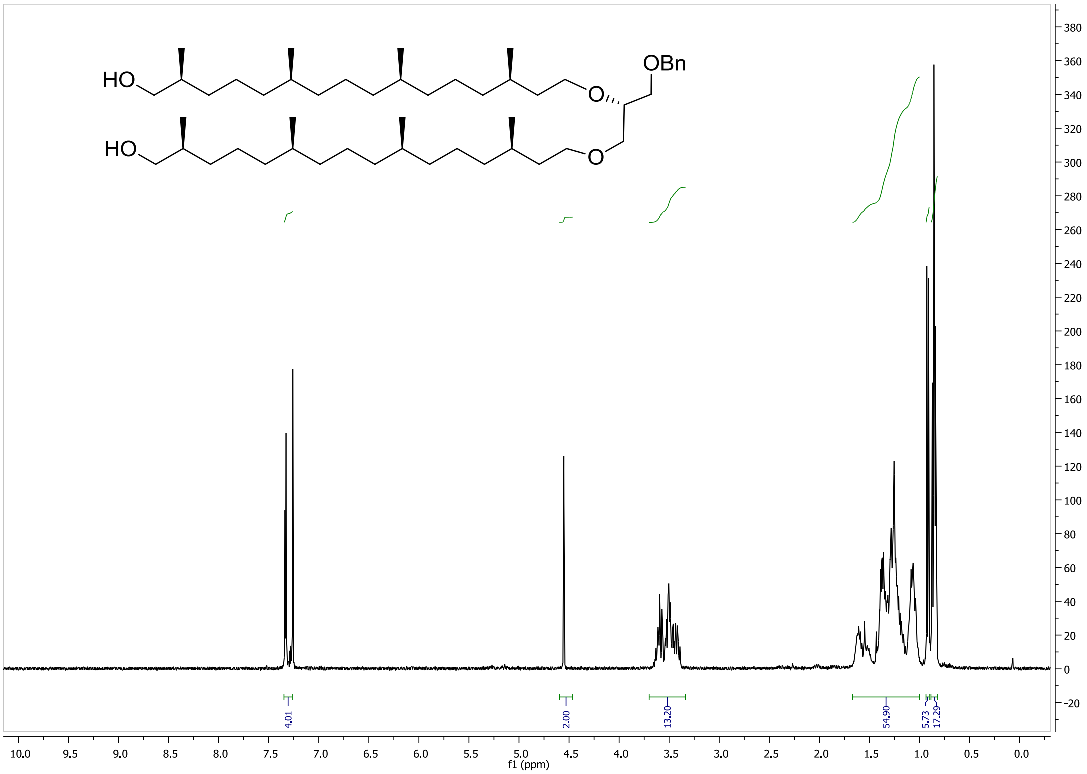


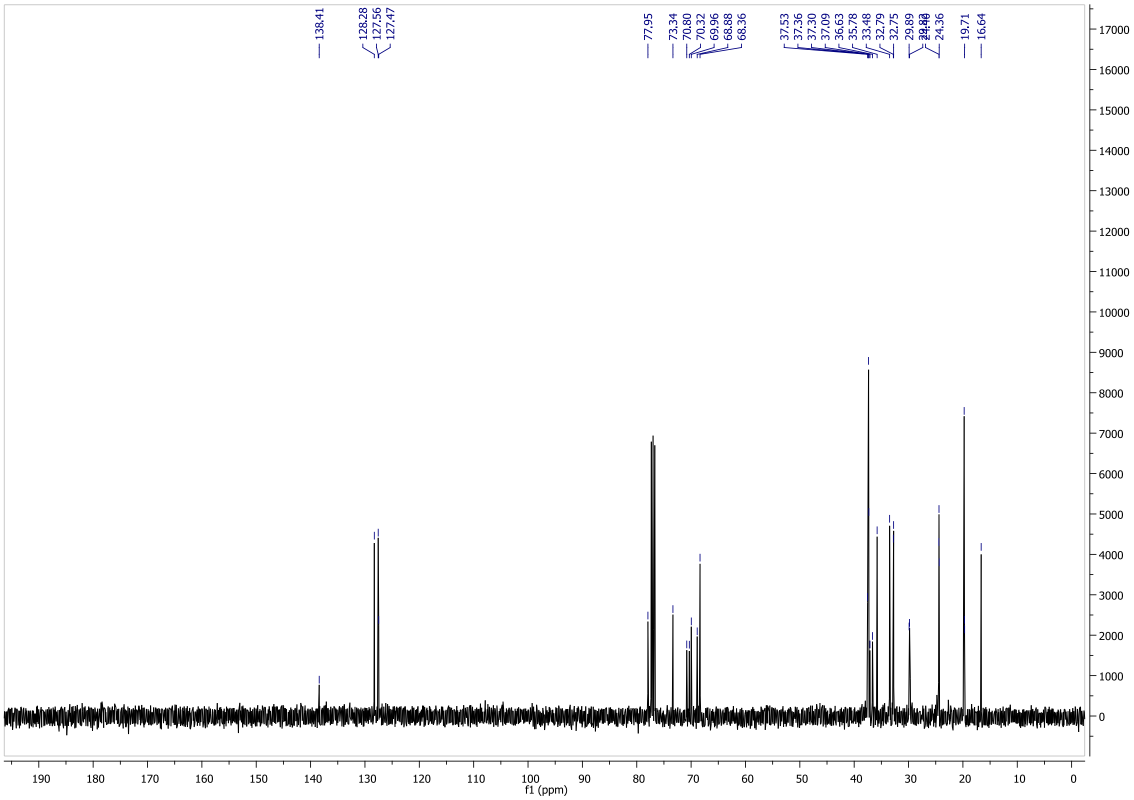
1-*O*-Benzyl-2,3-bis-*O*-[(3*R*,7*R*,11*S*,15*S*)-16-((*tert*-butyldiphenylsilyl)oxy)-3,7,11,15-tetramethylhexadecanyl]-*sn*-glycerol 16



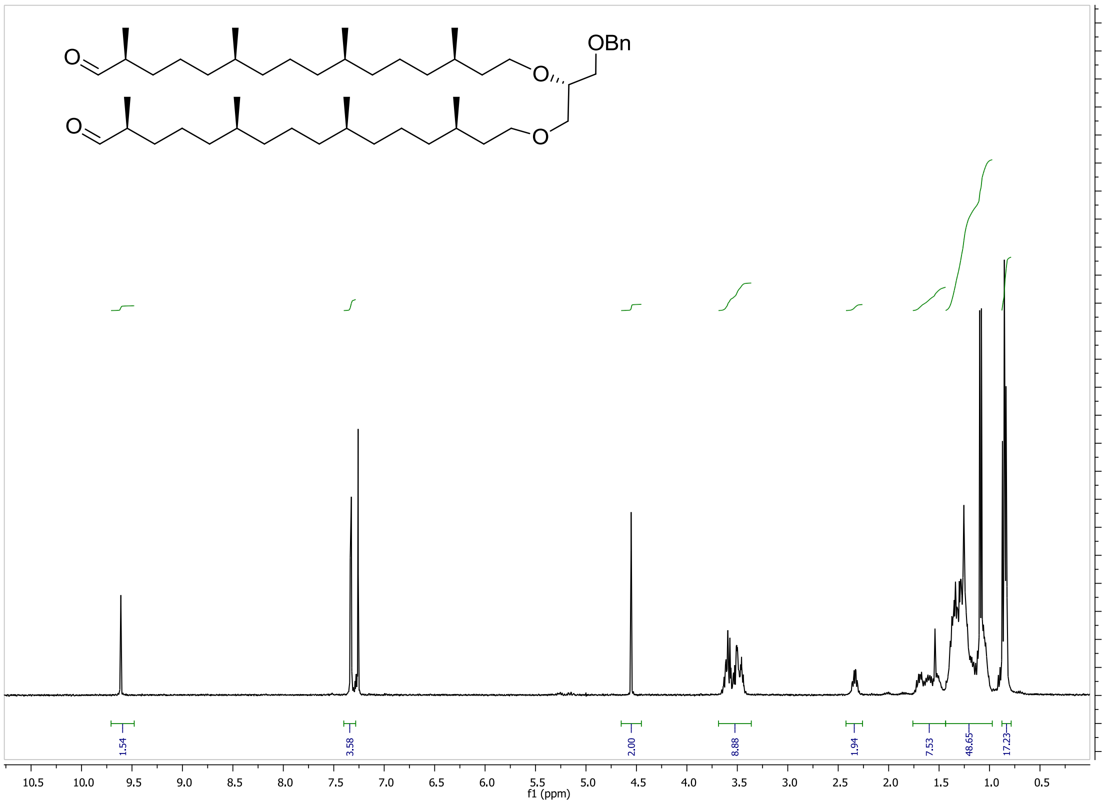


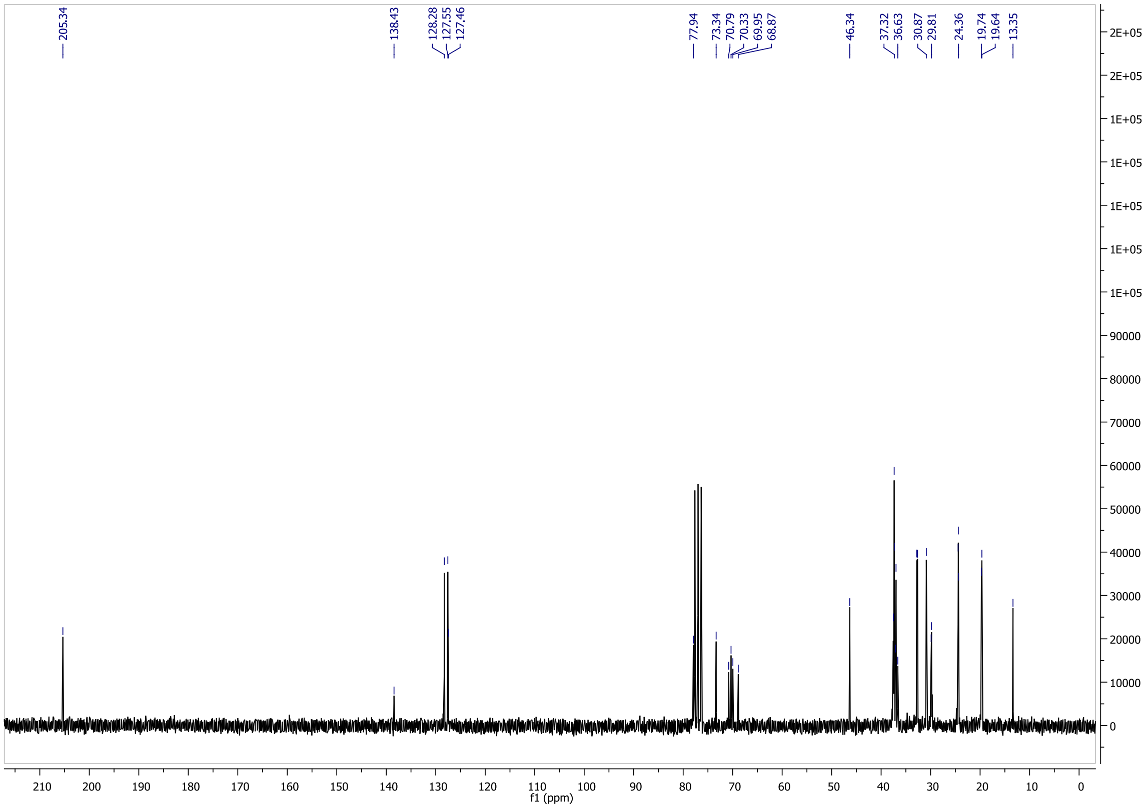
1-*O*-Benzyl-2,3-bis-*O*-[(3*R*,7*R*,11*S*,15*S*)-16-hydroxy-3,7,11,15-tetramethylhexadecanyl]-*sn*-glycerol 17





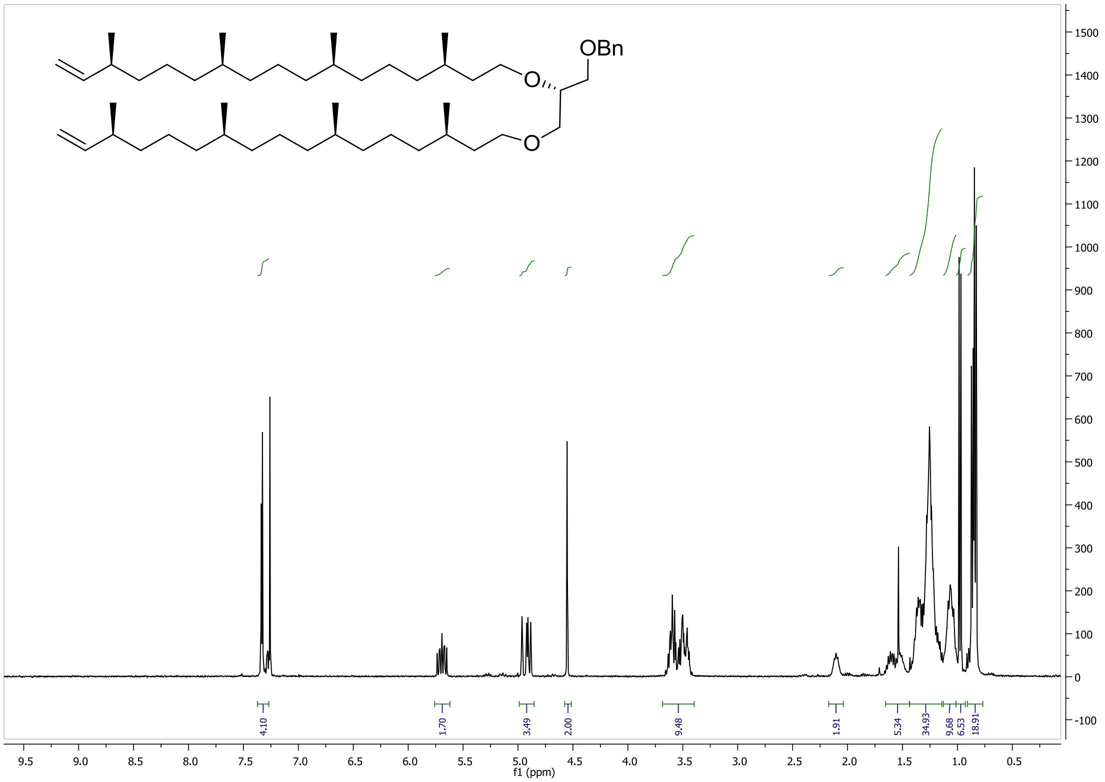
1-*O*-Benzyl-2,3-bis-*O*-[(3*R*,7*R*,11*S*,15*S*)-16-formyl-3,7,11,15-tetramethylhexadecanyl]-*sn*-glycerol 18

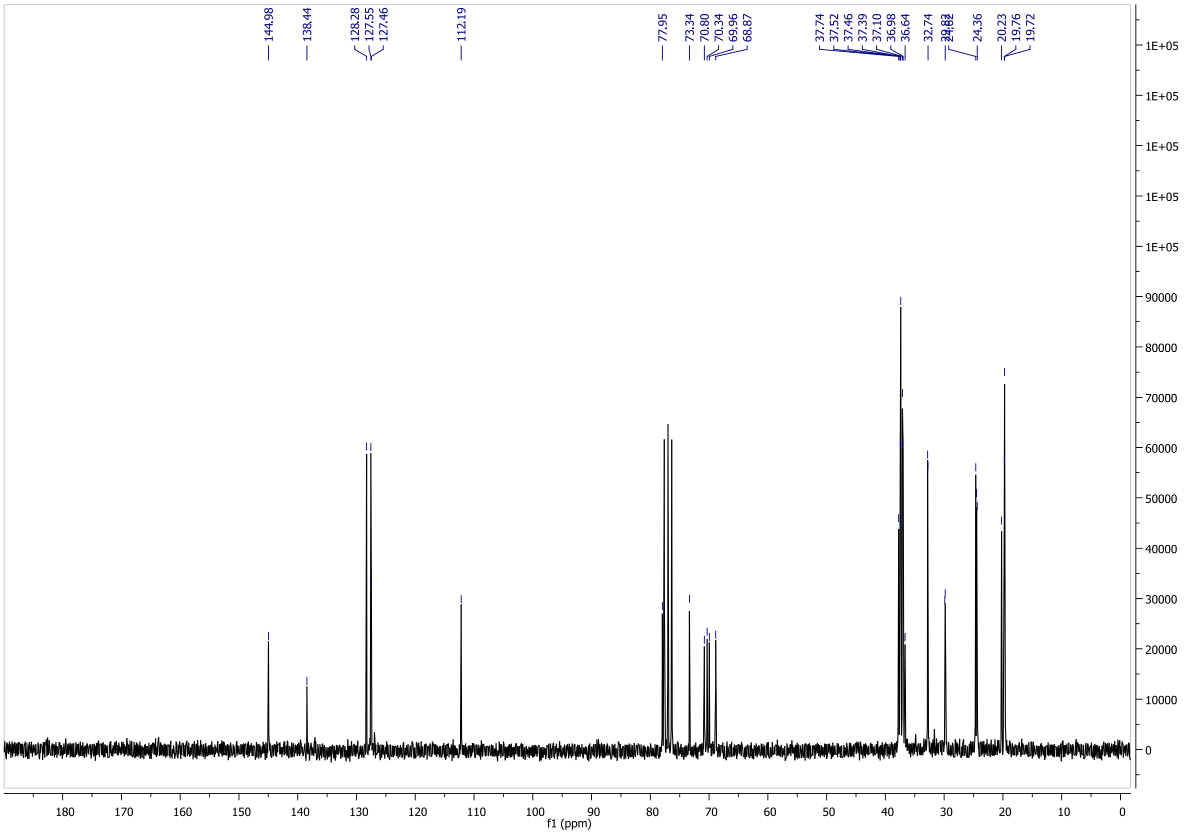




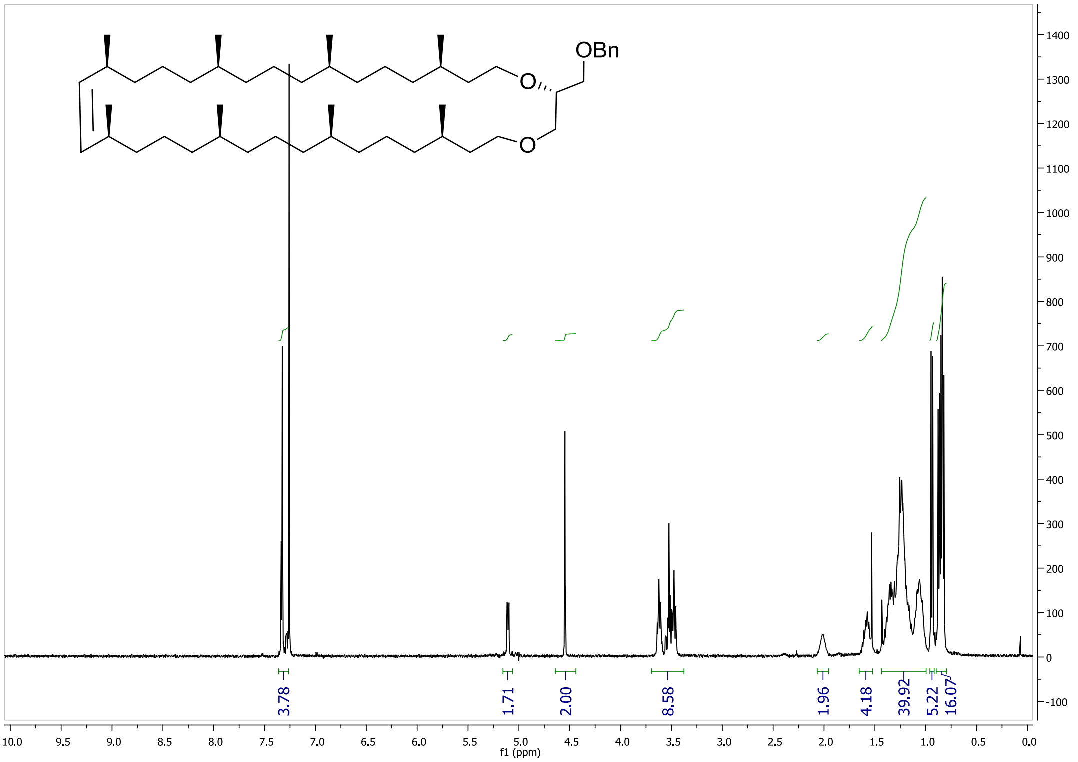
1-*O*-Benzyl-2,3-bis-*O*-[(3*R*,7*R*,11*S*,15*S*)-3,7,11,15-tetramethylheptadec-16-enyl]-*sn*-glycerol

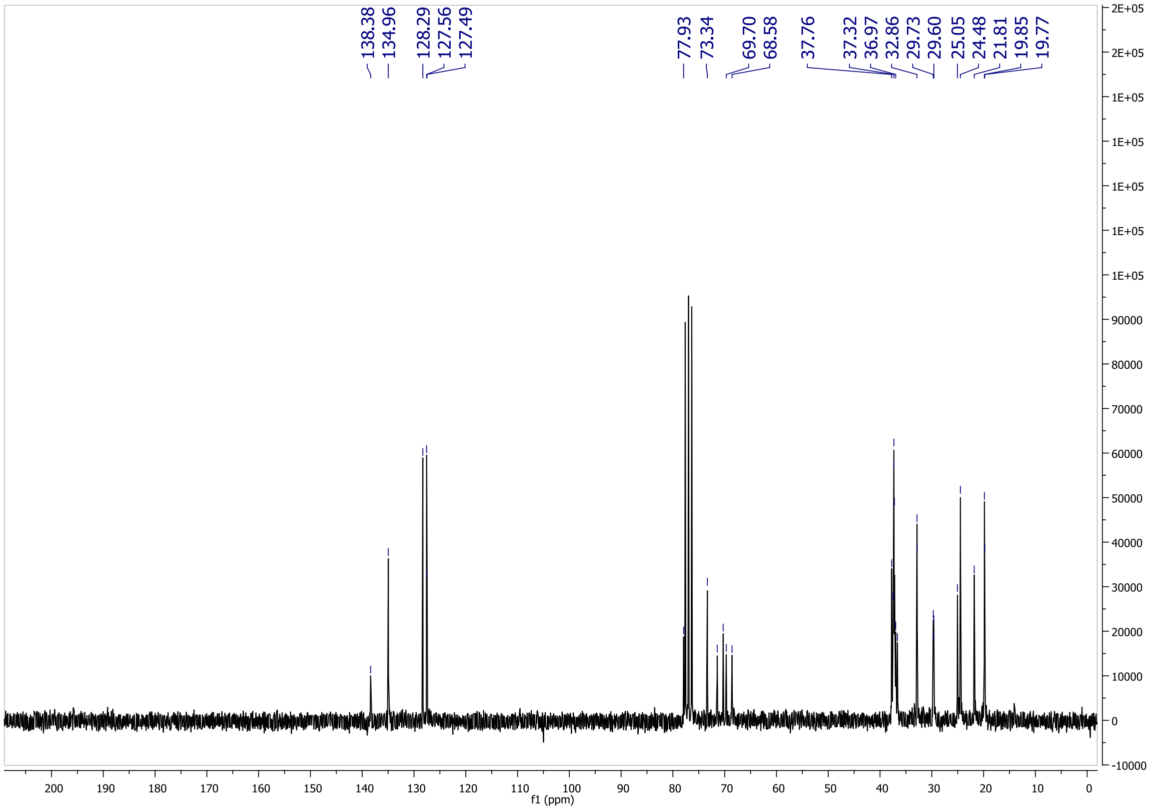
19



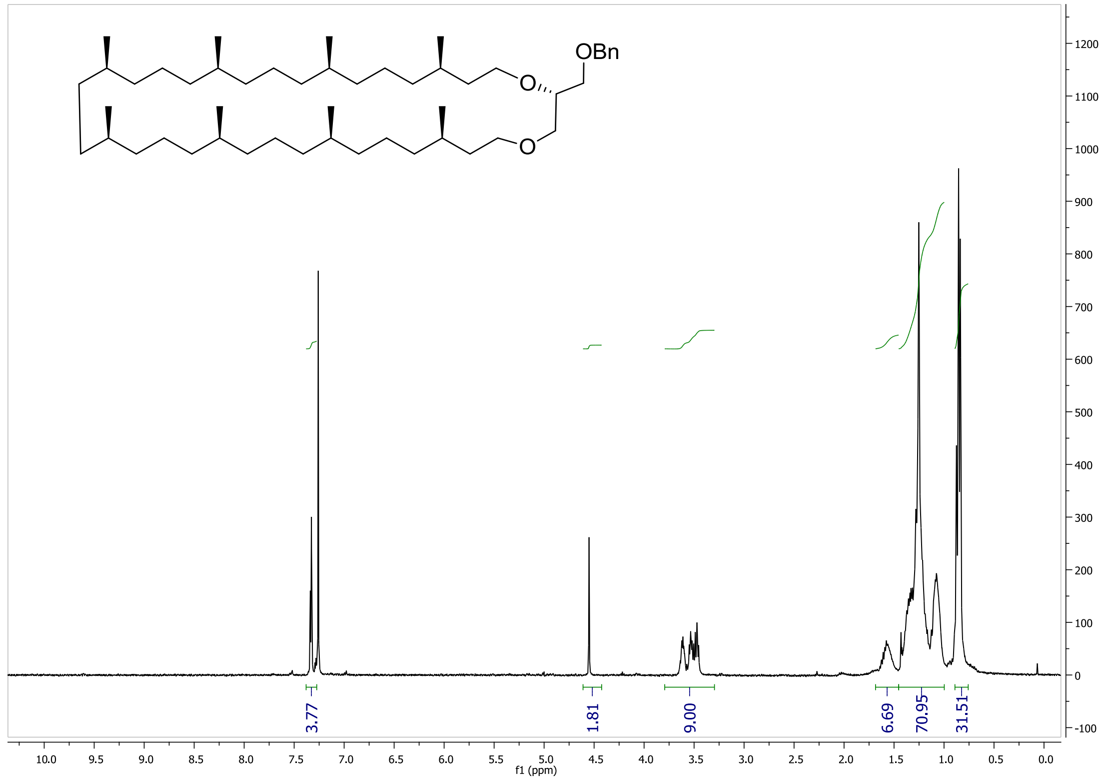

144.98
138.44
128.28
127.55
127.46
112.19
77.95
73.34
70.80
70.34
69.96
68.87
37.74
37.52
37.46
37.39
37.10
36.98
36.64
32.74
29.83
24.62
24.36
20.23
19.76
19.72
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

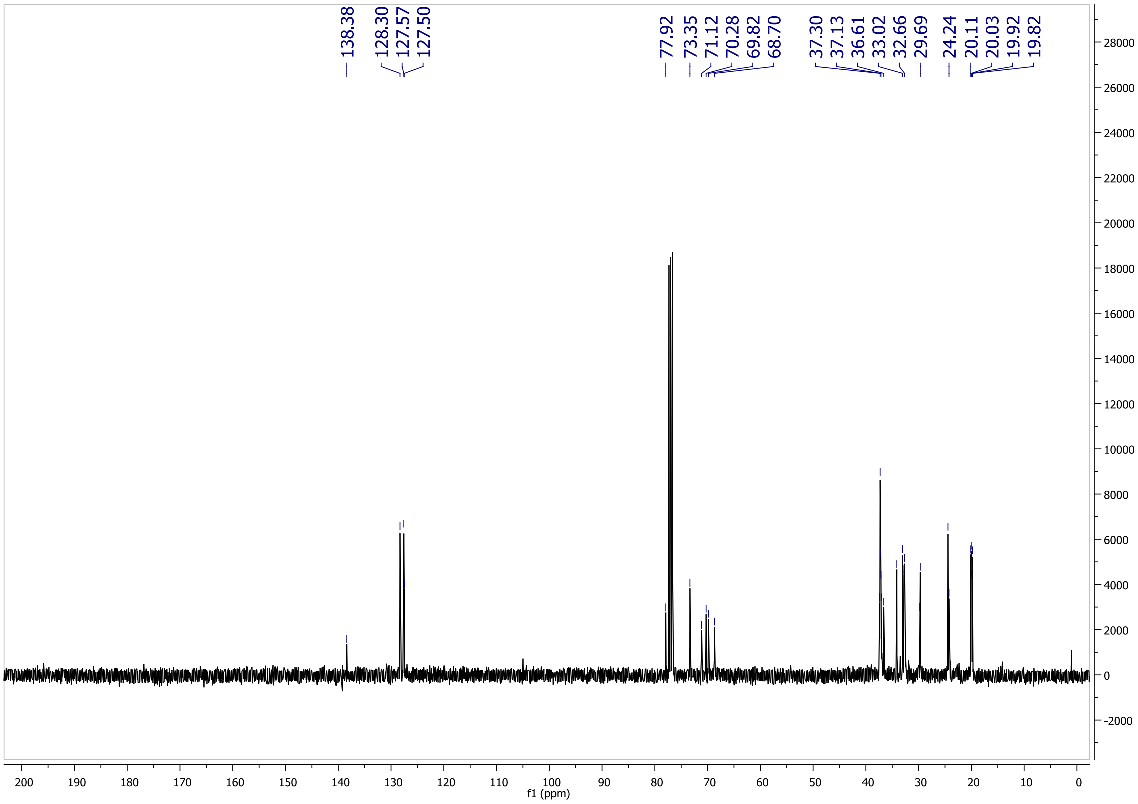
(2*S*,7*R*,11*R*,15*S*,19*S*,22*S*,26*S*,30*R*,34*R*,*E*)-2-((Benzyloxy)methyl)-7,11,15,19,22,26,30,34-octamethyl-1,4-dioxacyclohexatriacont-20-ene 20



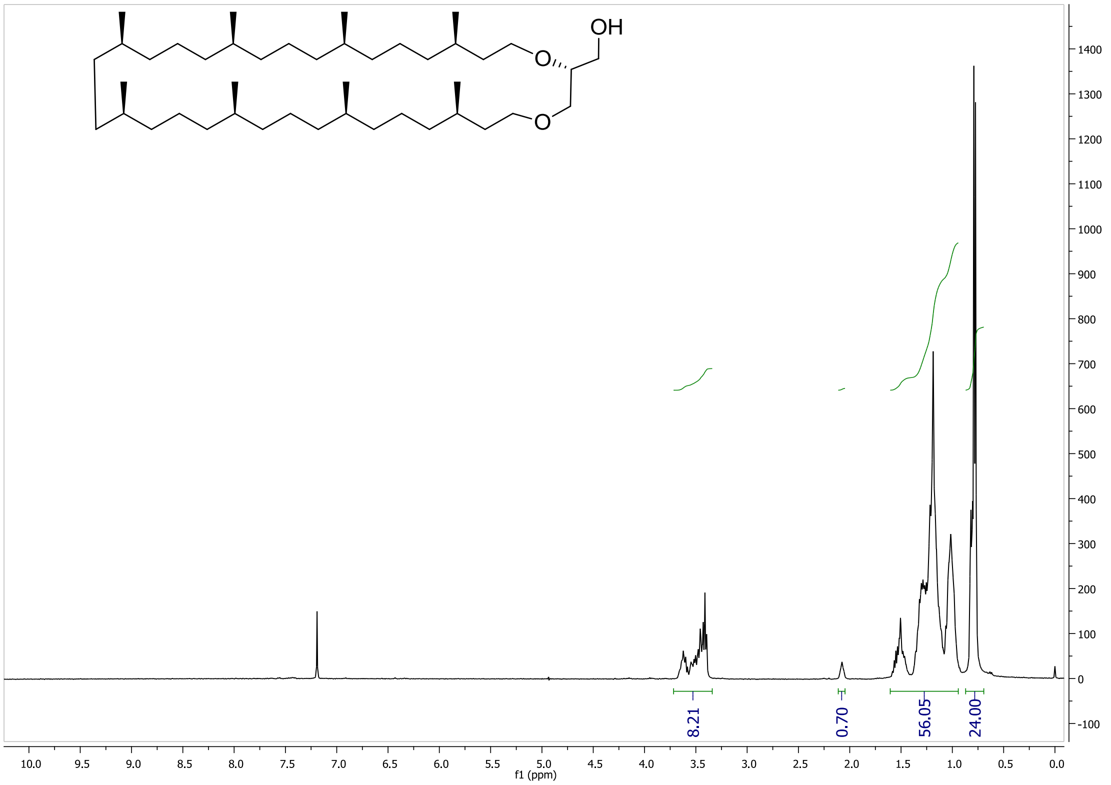


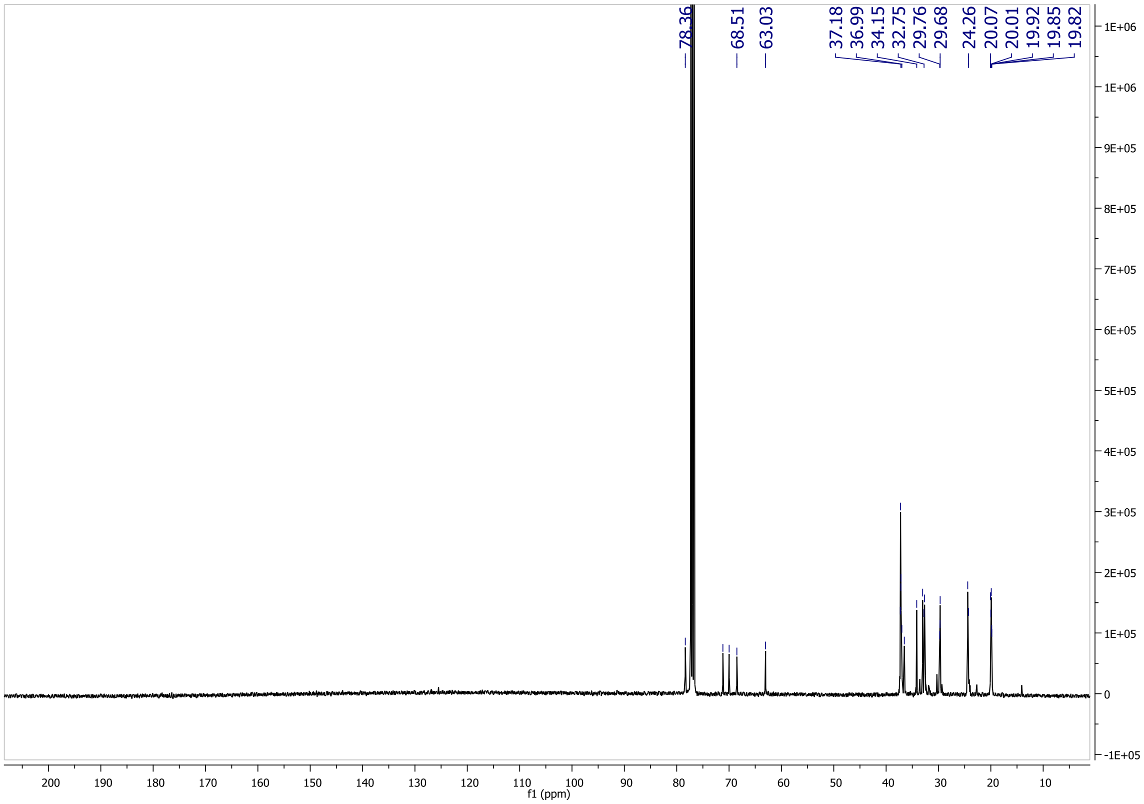
(2*S*,7*R*,11*R*,15*S*,19*S*,22*S*,26*S*,30*R*,34*R*)-2-((Benzyloxy)methyl)-7,11,15,19,22,26,30,34-octamethyl-1,4-dioxacyclohexatriacontane 21

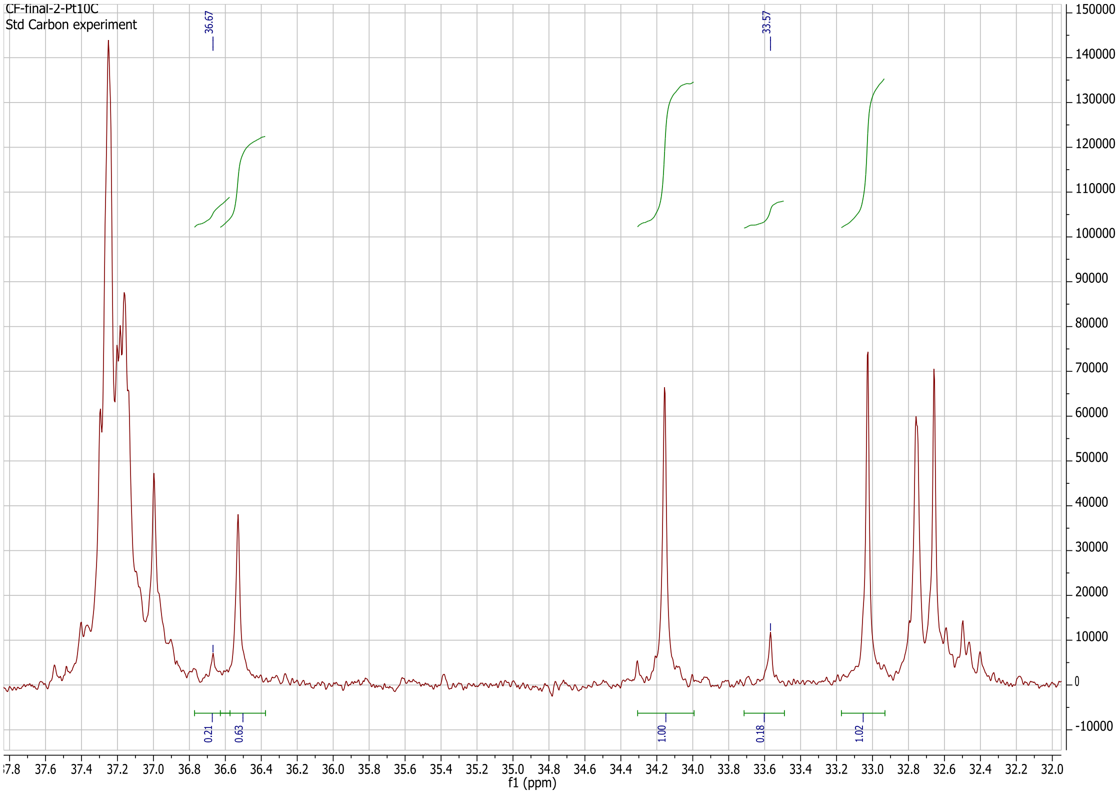


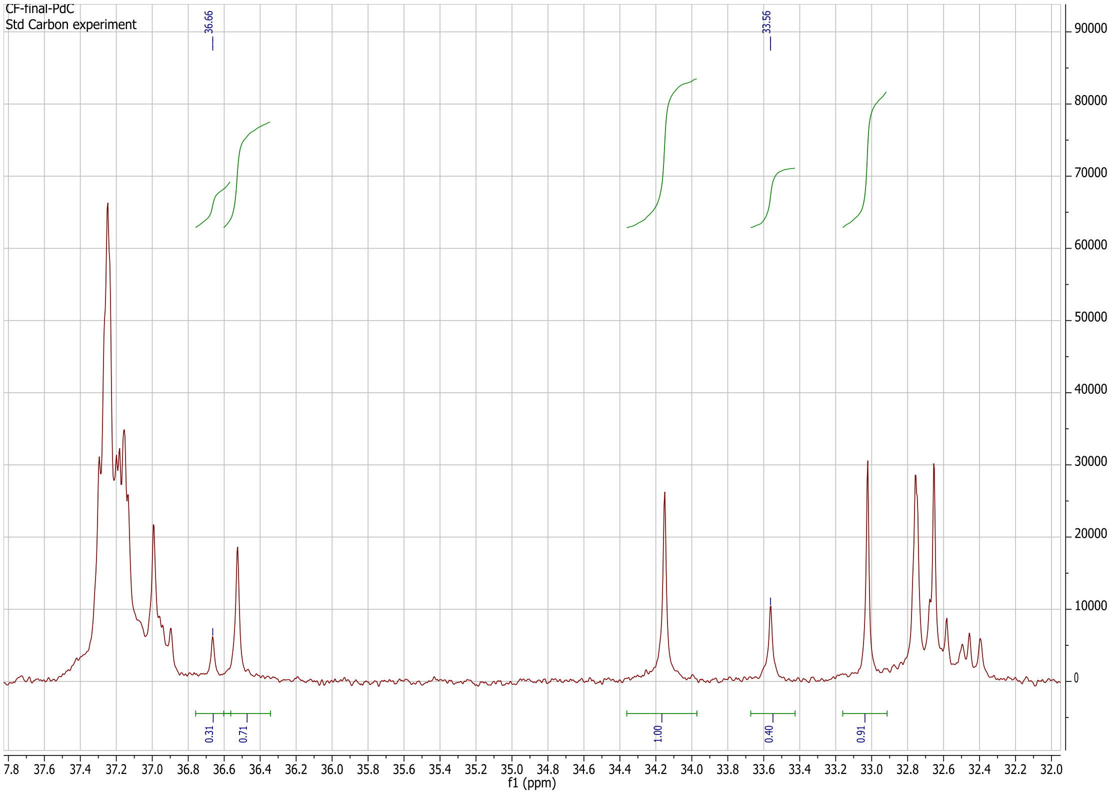


((2*R*,7*R*,11*R*,15*S*,19*S*,22*S*,26*S*,30*R*,34*R*)-7,11,15,19,22,26,30,34-Octamethyl-1,4-dioxacyclohexatriacontan-2-yl)methanol 2

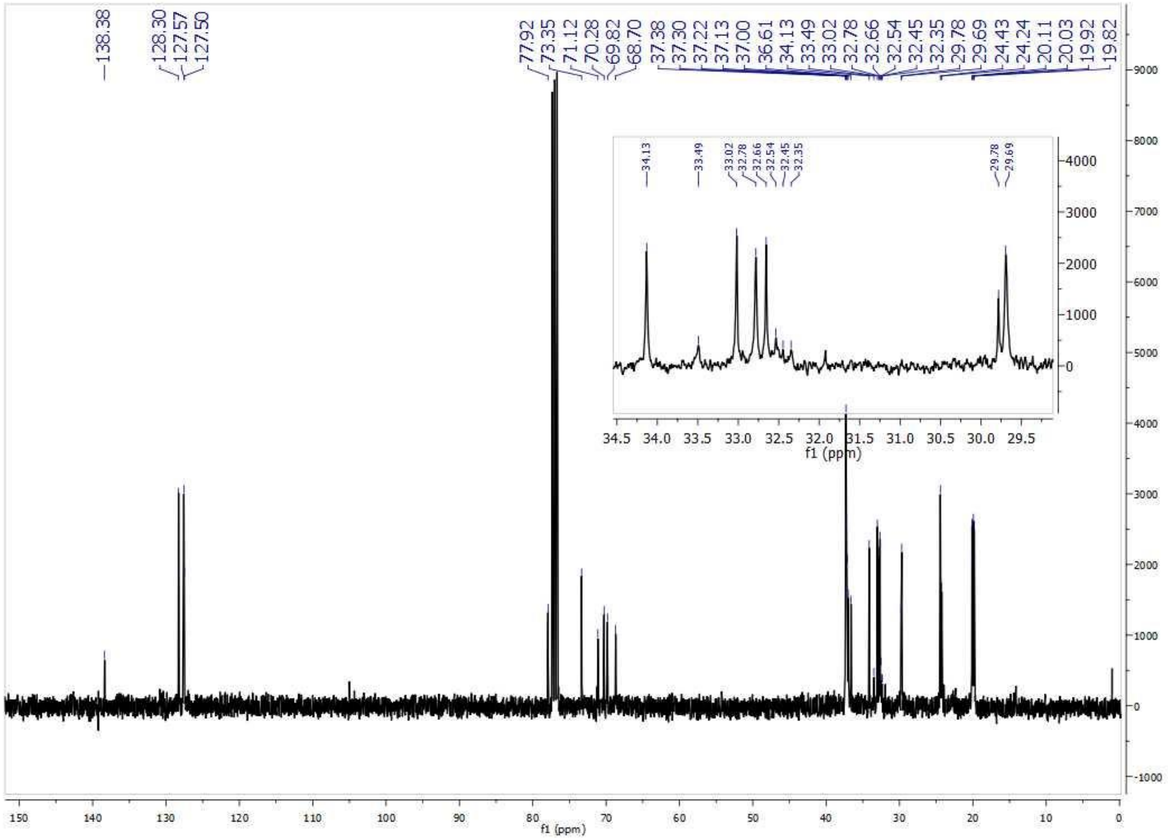




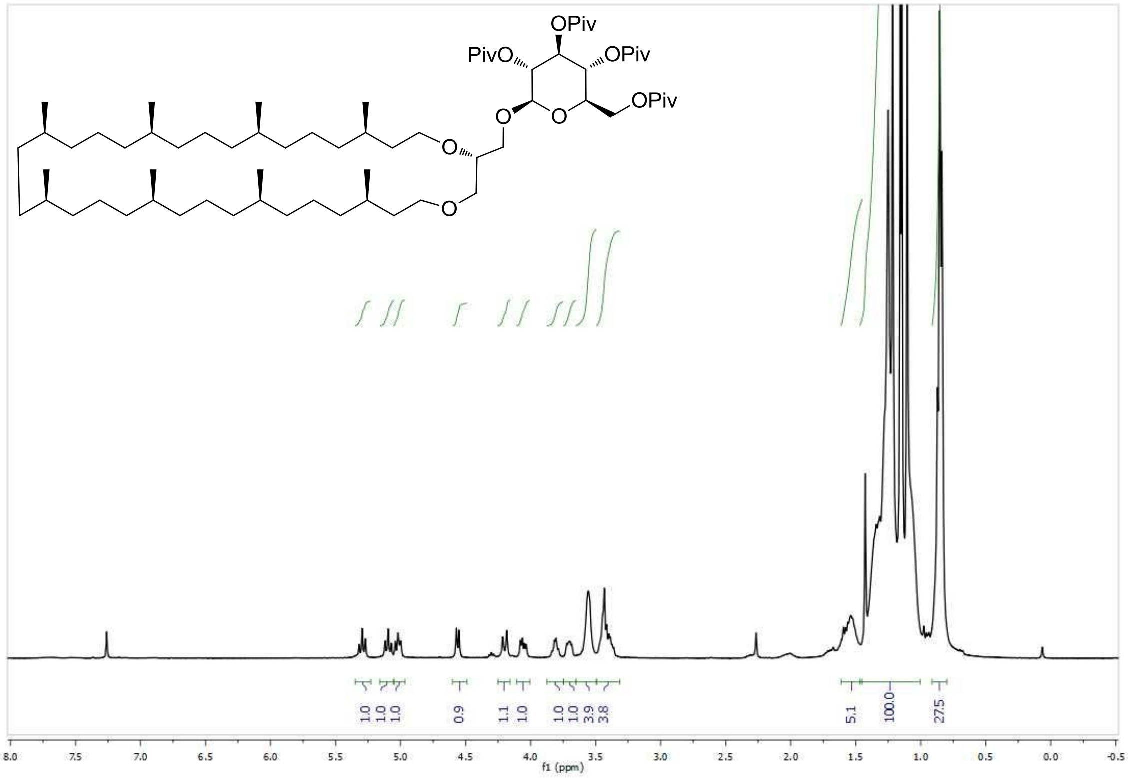

CF-final-2-Pt10C
Std Carbon experiment
36.67
33.57
0.21
0.63
1.00
0.18
1.02
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
37.8 37.6 37.4 37.2 37.0 36.8 36.6 36.4 36.2 36.0 35.8 35.6 35.4 35.2 35.0 34.8 34.6 34.4 34.2 34.0 33.8 33.6 33.4 33.2 33.0 32.8 32.6 32.4 32.2 32.0
f1 (ppm)

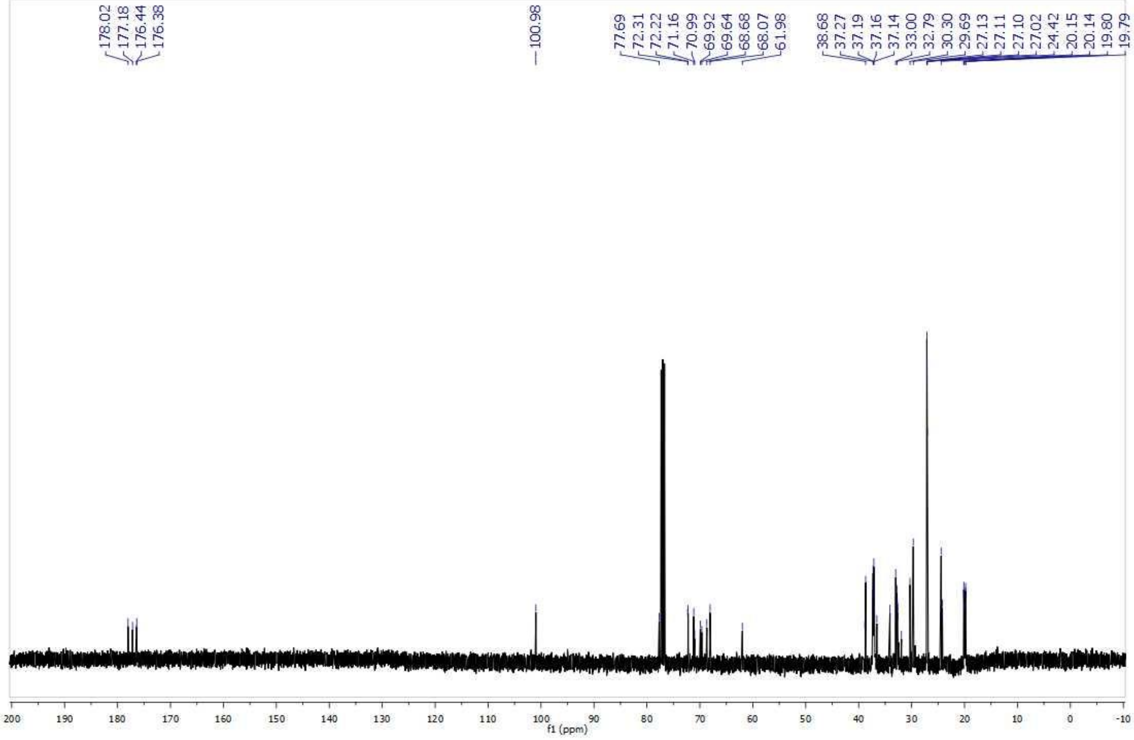

CF-final-PdC
Std Carbon experiment
36.66
33.56
0.31
0.71
1.00
0.40
0.91
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
37.8 37.6 37.4 37.2 37.0 36.8 36.6 36.4 36.2 36.0 35.8 35.6 35.4 35.2 35.0 34.8 34.6 34.4 34.2 34.0 33.8 33.6 33.4 33.2 33.0 32.8 32.6 32.4 32.2 32.0
f1 (ppm)

Carbon NMR after Pt reduction of the double bond but still with the benzyl group on:

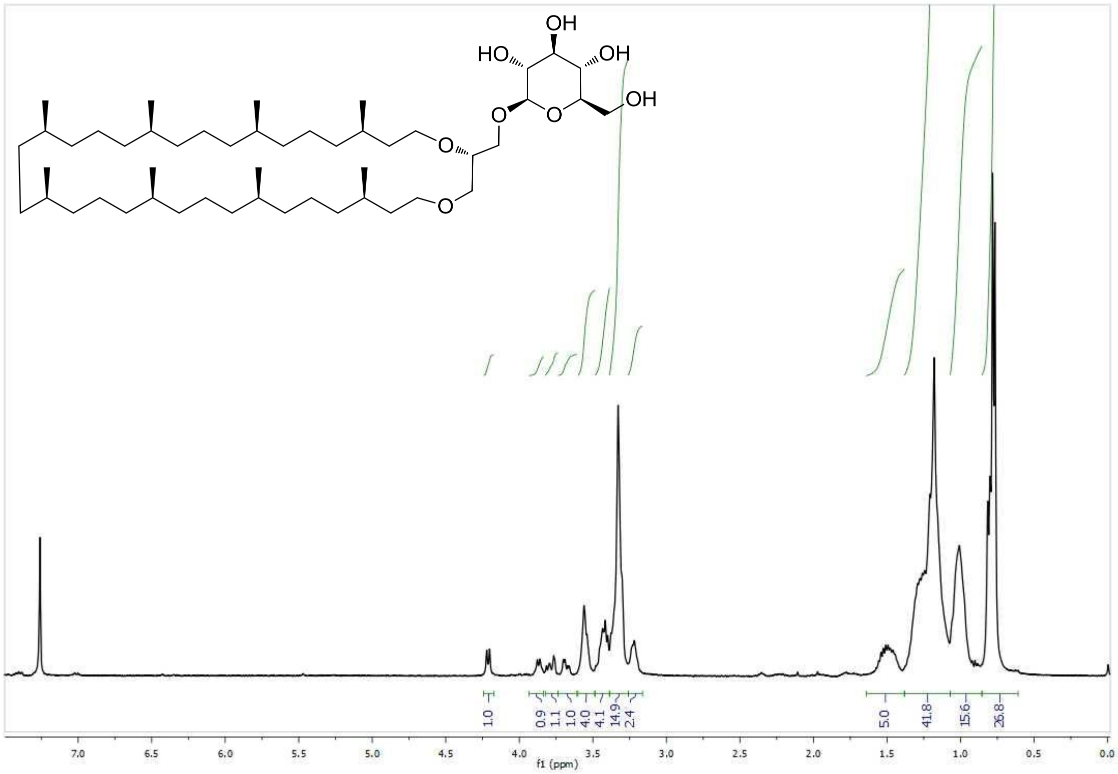


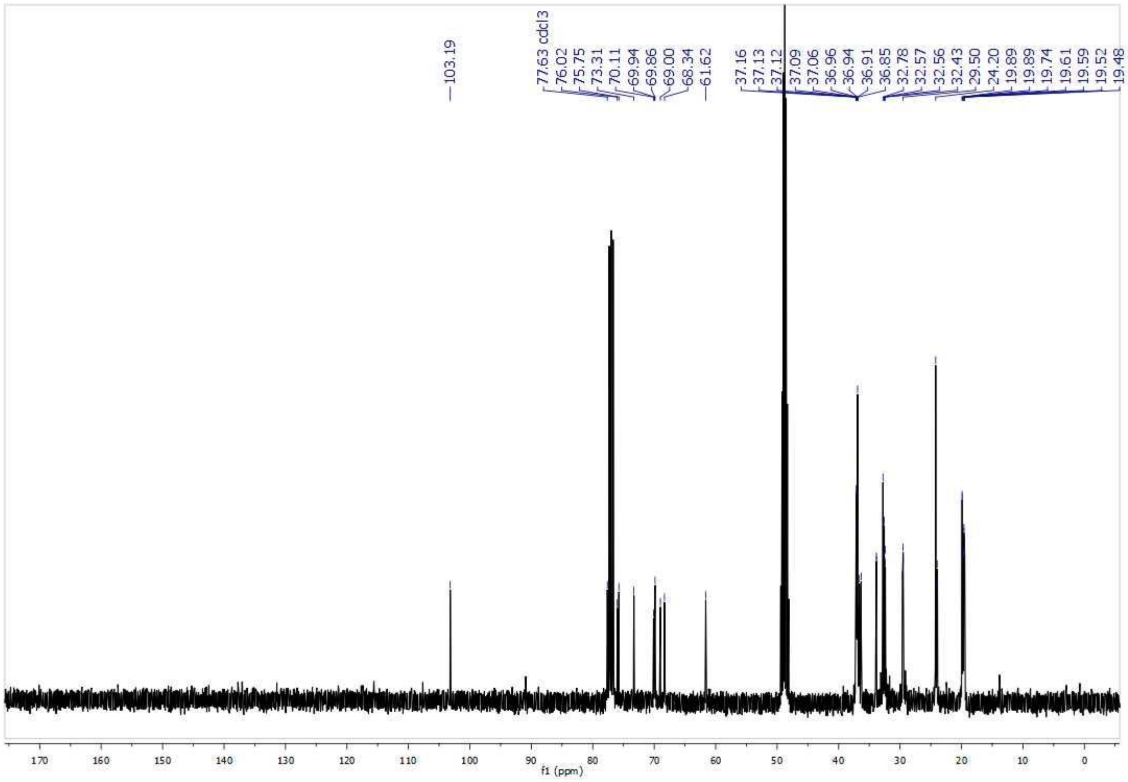
(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(((7*R*,11*R*,15*S*,19*S*,22*S*,26*S*,30*R*,34*R*)-7,11,15,19,22,26,30,34-Octamethyl-1,4-dioxacyclohexatriacontan-2-yl)methoxy)-6-((pivaloyloxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tris(2,2-dimethylpropanoate) 22





(2*R*,3*S*,4*S*,5*R*,6*R*)-2-(Hydroxymethyl)-6-(((2*S*,7*R*,11*R*,15*S*,19*S*,22*S*,26*S*,30*R*,34*R*)-7,11,15,19,22,26,30,34-octamethyl-1,4-dioxacyclohexatriacontan-2-yl)methoxy)tetrahydro-2H-pyran-3,4,5-triol 23





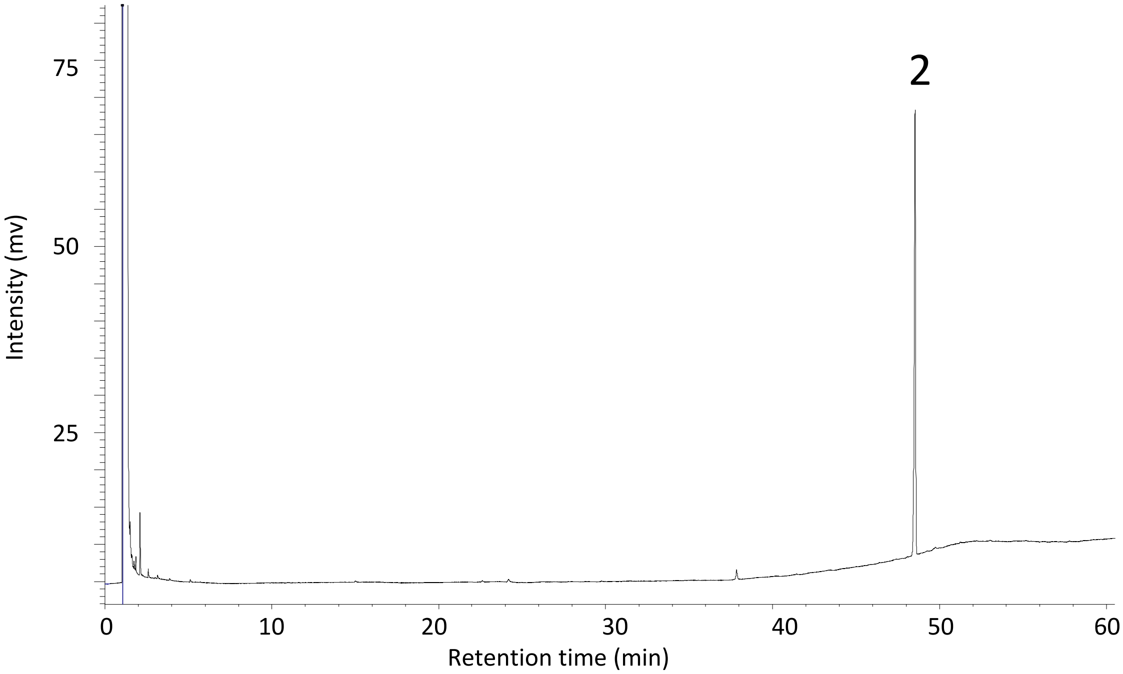
Sample description and analysis for the comparison with natural **2** and **23**

The sample was collected from the Rainbow hydrothermal vent field (RHF) located on the Mid-Atlantic Ridge. RHF has been characterized as an ultra-mafic hydrothermal system with fluids that are known to reach up to 360^{o}C and contain abundant H_2, CH_4 and CO_2.[1] Samples were collected during a sampling campaign in 2008 using the ROV Jason.

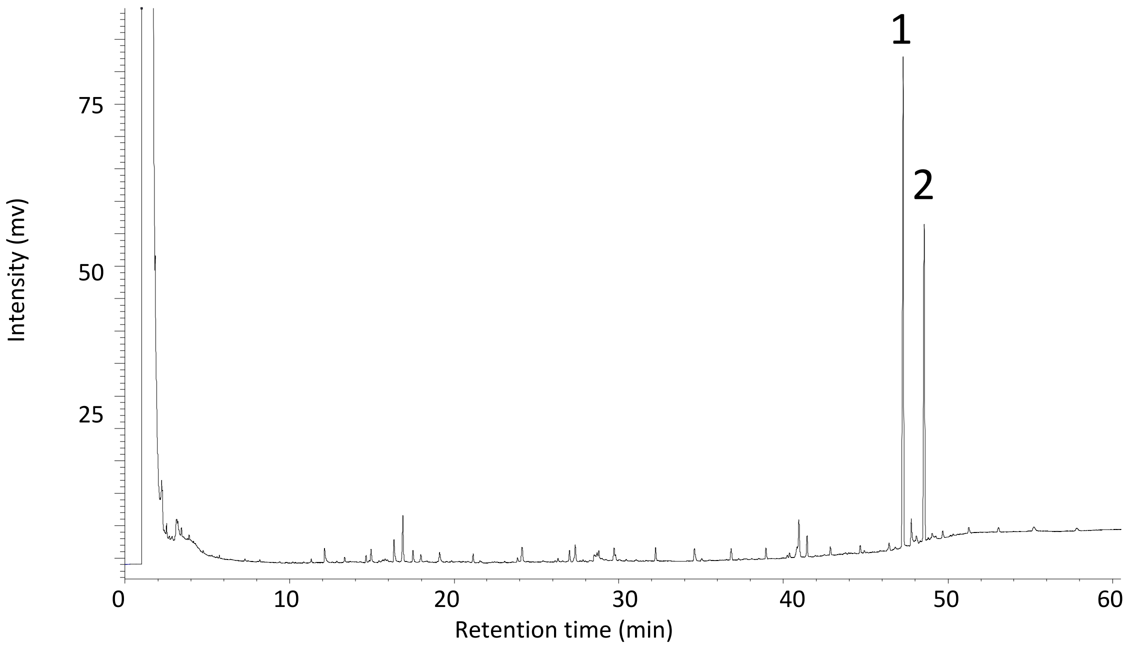
The sample analysed is composed of material from the interior of a vent chimney collected at a depth of 2293 m below sea level. The location of the vent is 57^{o}39'N, 32^{o}65'W.

Intact Polar Lipids were extracted from freeze-dried, powdered (approximately 5 g) vent deposit using a modified Bligh and Dyer method described by Pitcher *et al*..[2] The extract was analysed by high performance liquid chromatography electrospray ionisation mass spectrometry (HPLC-ESI-MS^{n}) using modified literature methods.[3] The analysis was conducted on an Agilent 1200 series LC equipped with a Lichrosphere diol column (250 x 2.1 µm, 5 µm particles; Alltech Associates Inc.) coupled to a Thermo LTQ XL linear ion trap with Ion Max source with electrospray ionization (ESI) probe (Thermo Scientific, Waltham, MA).

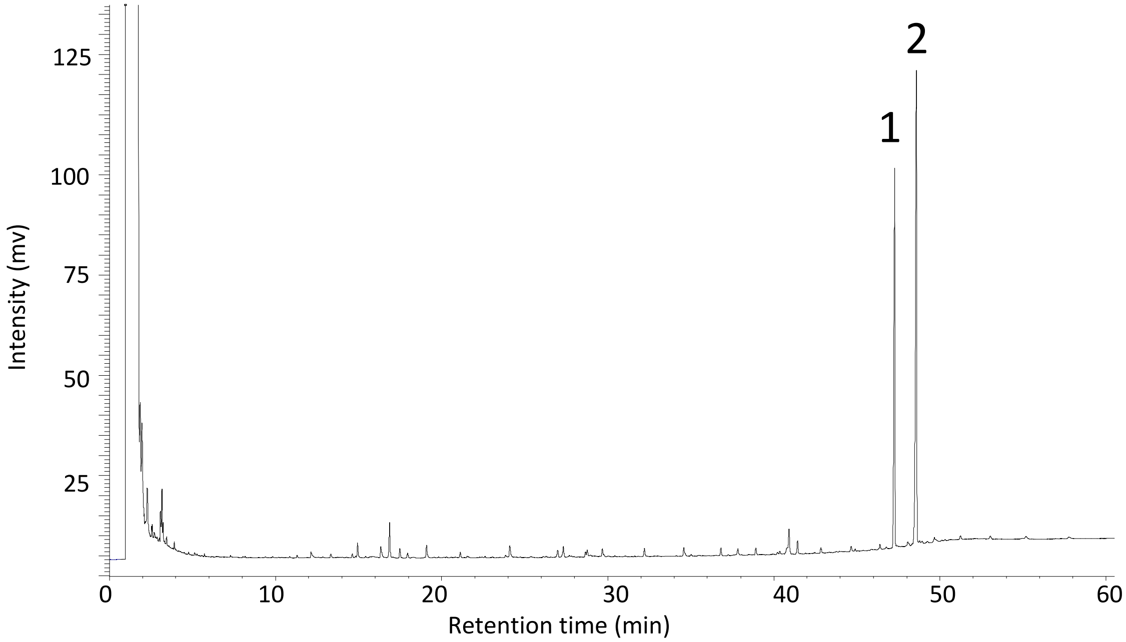
The extract was acid hydrolysed to release **2**.[4] The hydrolyzed extract was reacted with diazomethane to convert free acids to methyl esters then separated over a short Al_2O_3 column using hexane/DCM (9:1; v/v) and DCM/methanol (1:1; v/v). Part of the latter fraction was subsequently silylated using bis(trimethylsilyl)trifluoroacetamide (BSTFA) in pyridine at 60˚C for 15 min. The fatty acid methyl ester and silylated alcohol fraction were analyzed by gas chromatography (GC) and GC-mass spectrometry (MS). GC was performed on a Hewlett-Packard 6890 series GC system with an on-column injector and flame ionization detector. A fused silica capillary column (length 25 m, internal diameter 0.32 µm) coated with CP Sil-5 (film thickness, df = 0.12 µm) was used with helium as the carrier gas. Samples were injected at 70 ˚C and oven temperature was increased to 130 ˚C at 20˚C/min and then increased to 320˚C at a rate of 4˚C/min, where it remained stable for 10 min. GC-MS was performed on a Thermo Trace DSQ mass spectrometer fitted with a Thermo Trace GC Ultra. The mass spectrometer was operated at 70 eV with a mass range of m/z 50 – 800 and a cycle time of 0.33 s. The GC was equipped with a fused silica capillary column as described for GC analysis above and the same temperature program was used.



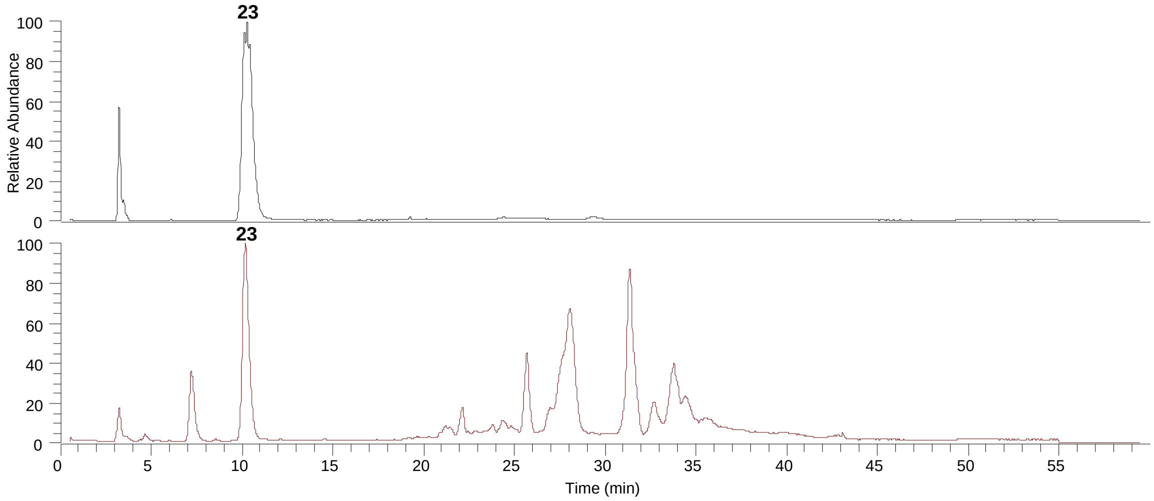
Gas chromatogram of synthetic **2**, R_t = 48.54 min



Gas chromatogram of TMSi-derivatized acid hydrolysed extract of the hydrothermal vent sample,. First peak corresponds to archaeol (**1**), second peak corresponds to **2** with R_t = 48.56 min.



Co-injection of the vent sample with synthetic **2**, showing the same R_t = 48.56 min



HPLC/MS selected ion chromatograms of mass m/z 830.5, the NH_4^+ ion of the molecular mass of **23.** *Top* chromatogram shows synthetic **23** the *lower* chromatogram shows the hydrothermal vent sample at Rainbow hydrothermal field with natural **23**, both eluting at 10.2 min.

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