Supplementary Information

Synthesis of 6-hydroxyceramide using ruthenium-catalyzed hydrosilylation-protodesilylation. Unexpected formation of a long periodicity lamellar phase in skin lipid membranes†

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1. Determination of enantiomeric purity (*ee*) of compounds (*R*)-5 and (*S*)-5

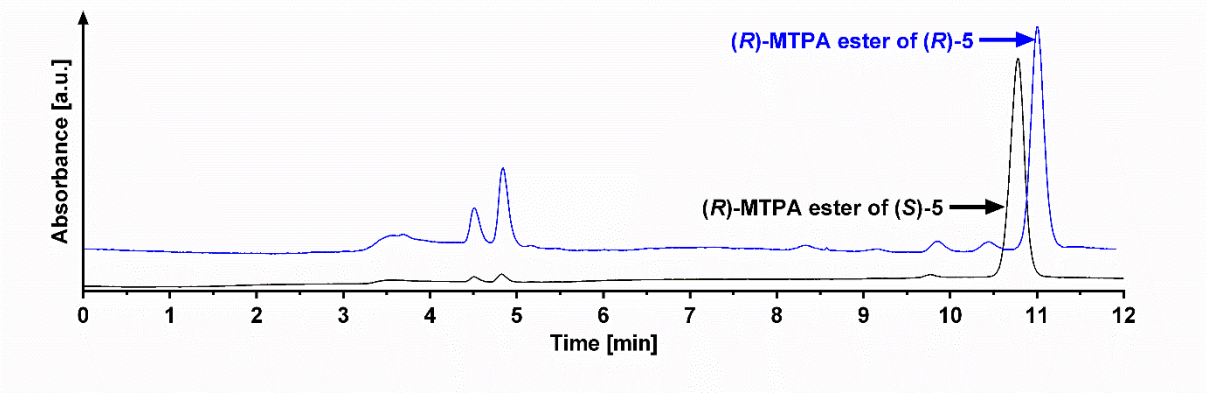
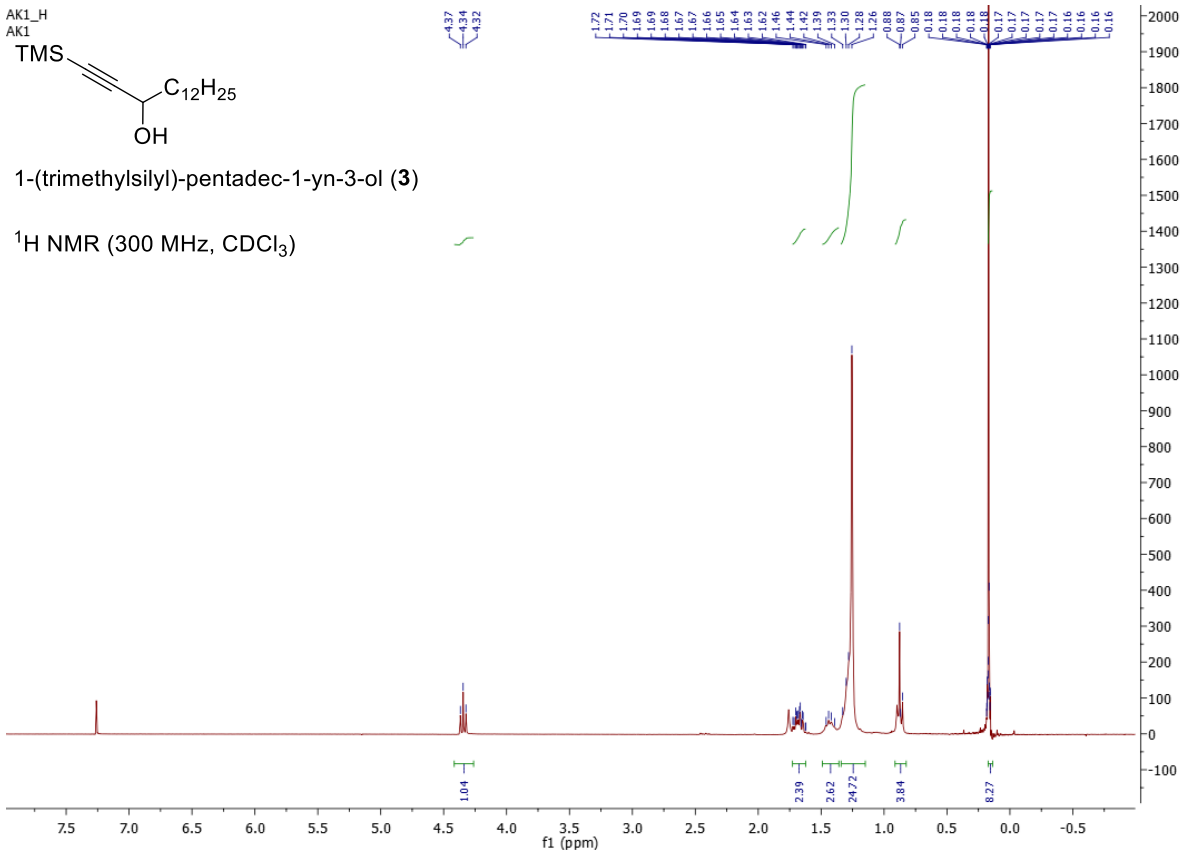
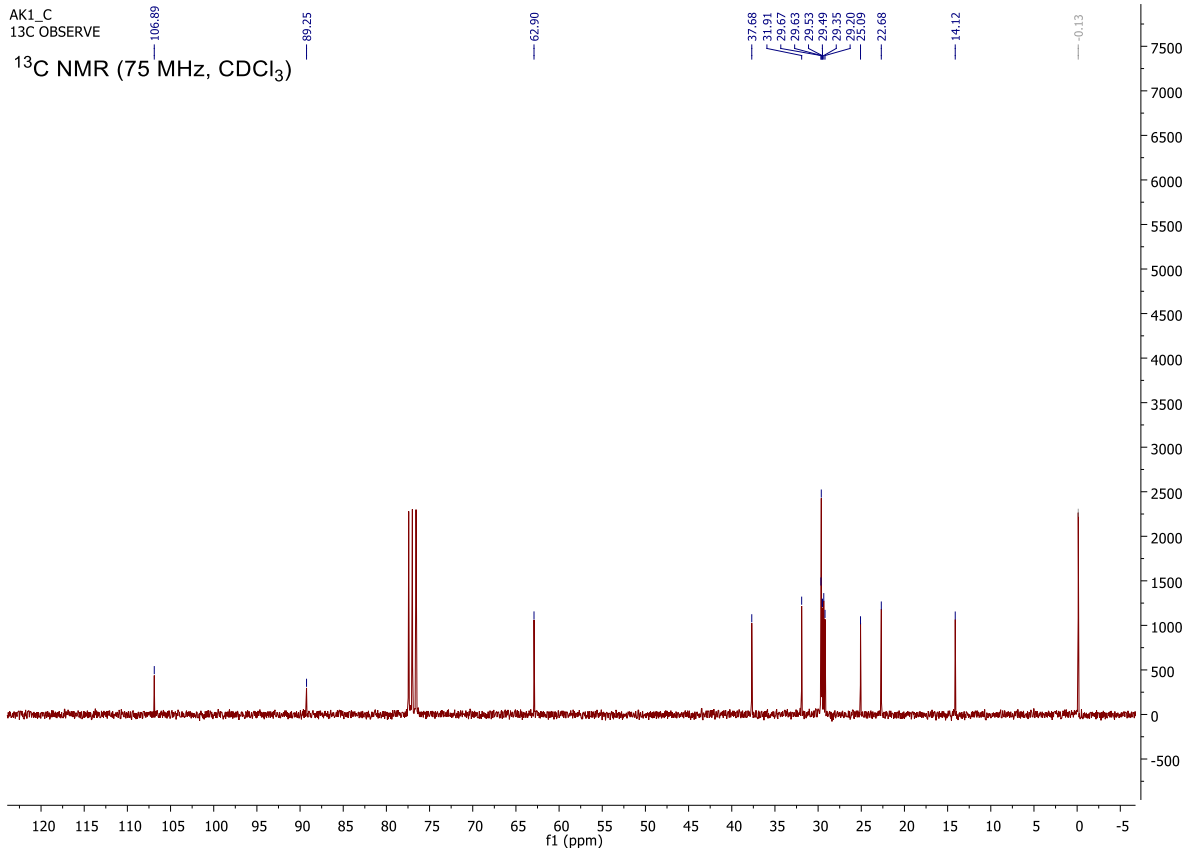
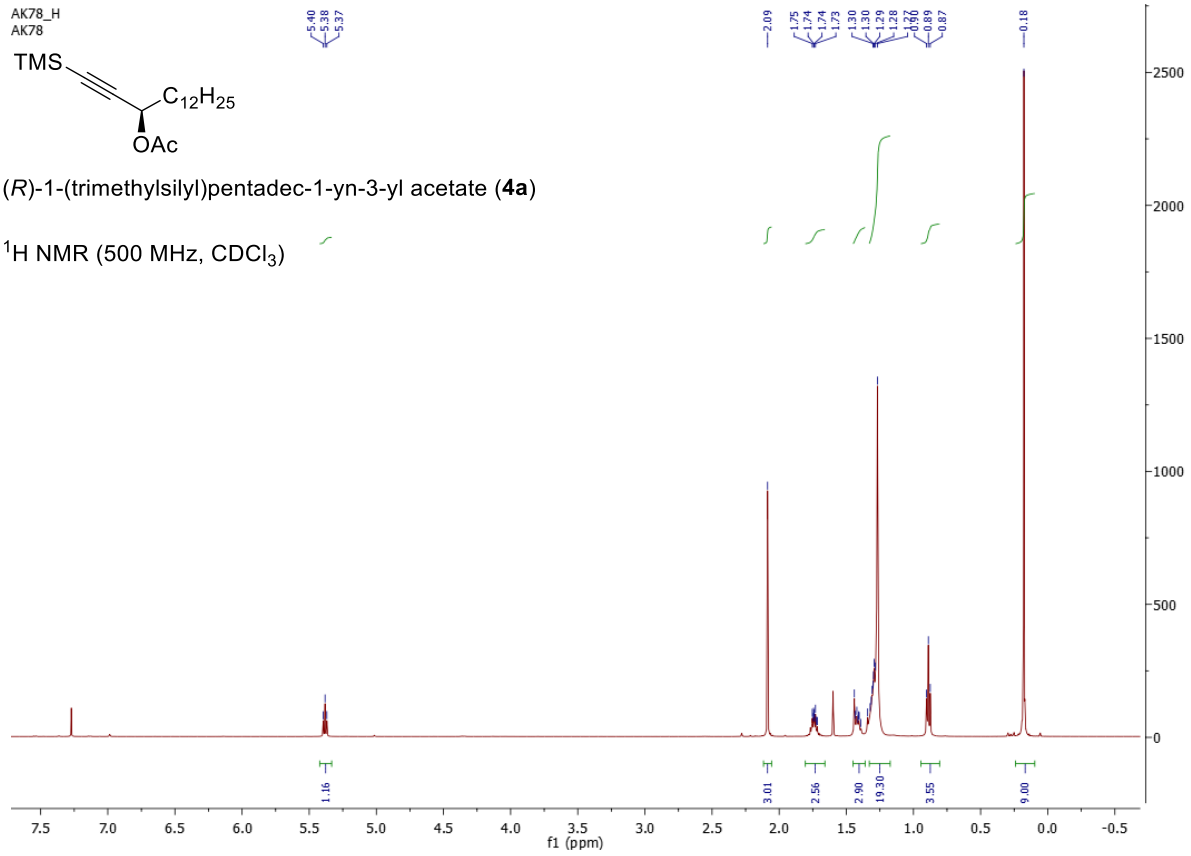


Figure 1. The chromatograms of (*R*)-MTPA ester of (*R*)-**5** (blue) and (*R*)-MTPA ester of (*S*)-**5** (black).

2. NMR spectra

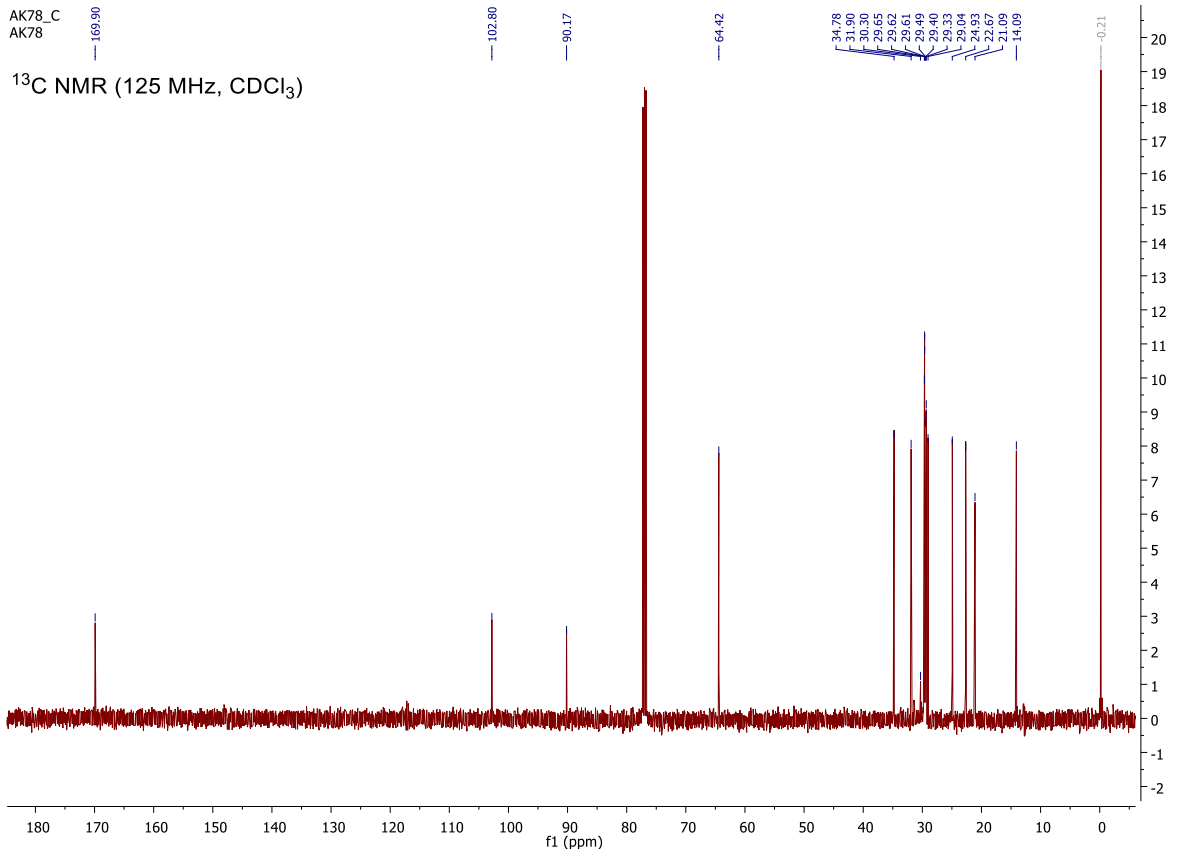






(*R*)-1-(trimethylsilyl)pentadec-1-yn-3-yl acetate (**4a**)

^{1}H NMR (500 MHz, $CDCl_3$)

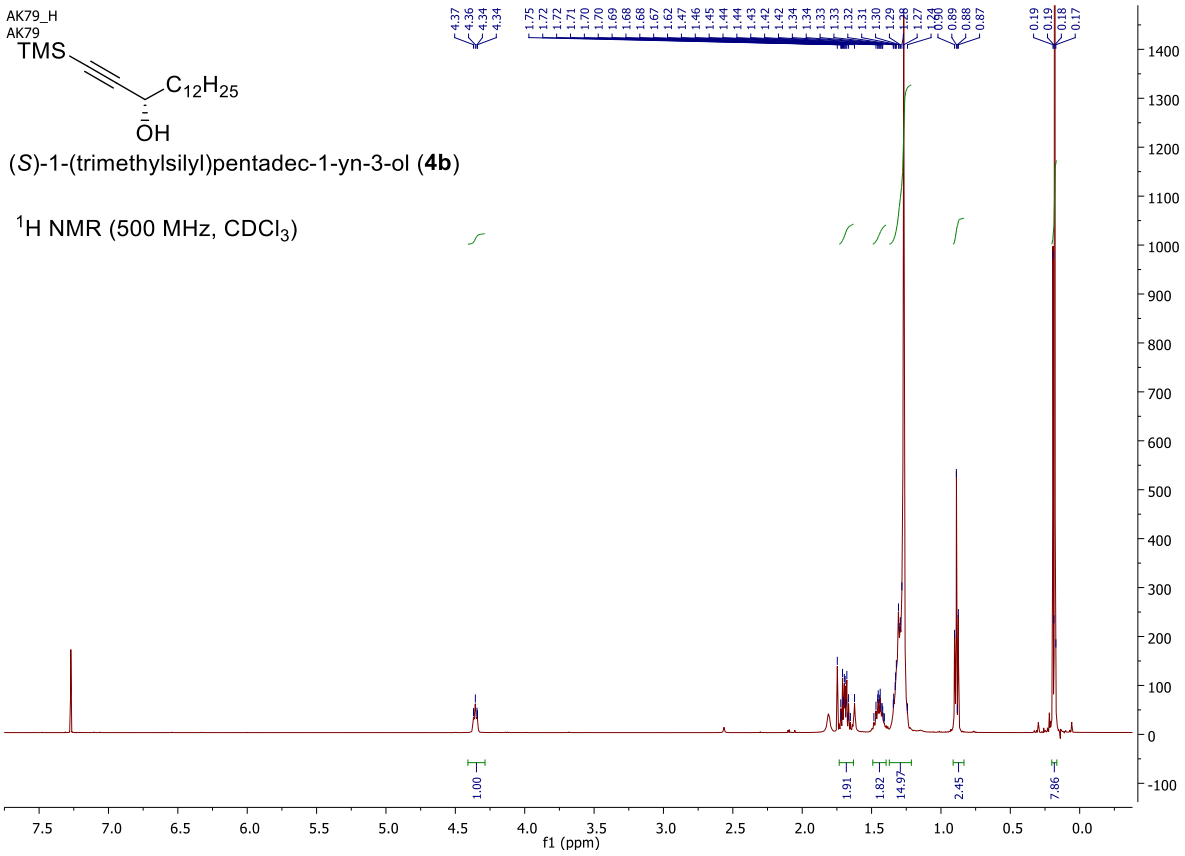


^{13}C NMR (125 MHz, $CDCl_3$)

AK79_H
AK79

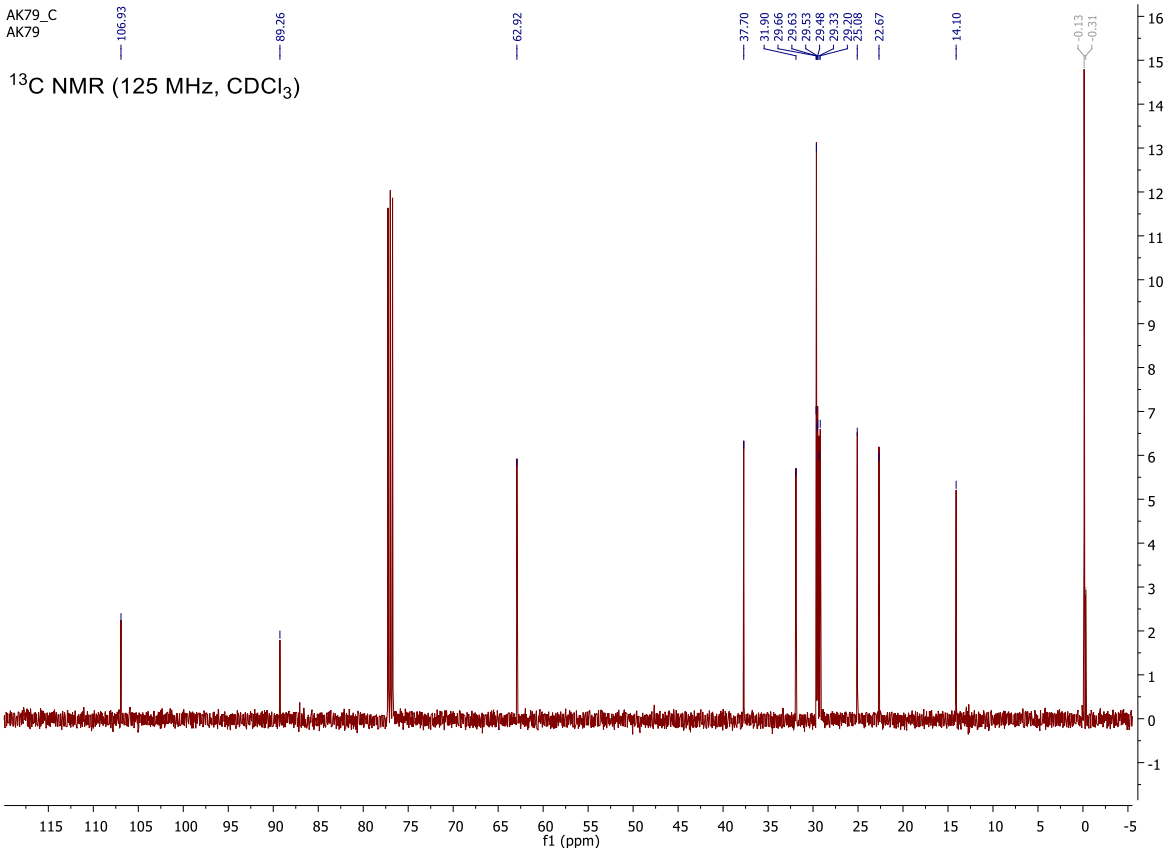
(*S*)-1-(trimethylsilyl)pentadec-1-yn-3-ol (**4b**)

^{1}H NMR (500 MHz, $CDCl_3$)



AK79_C
AK79

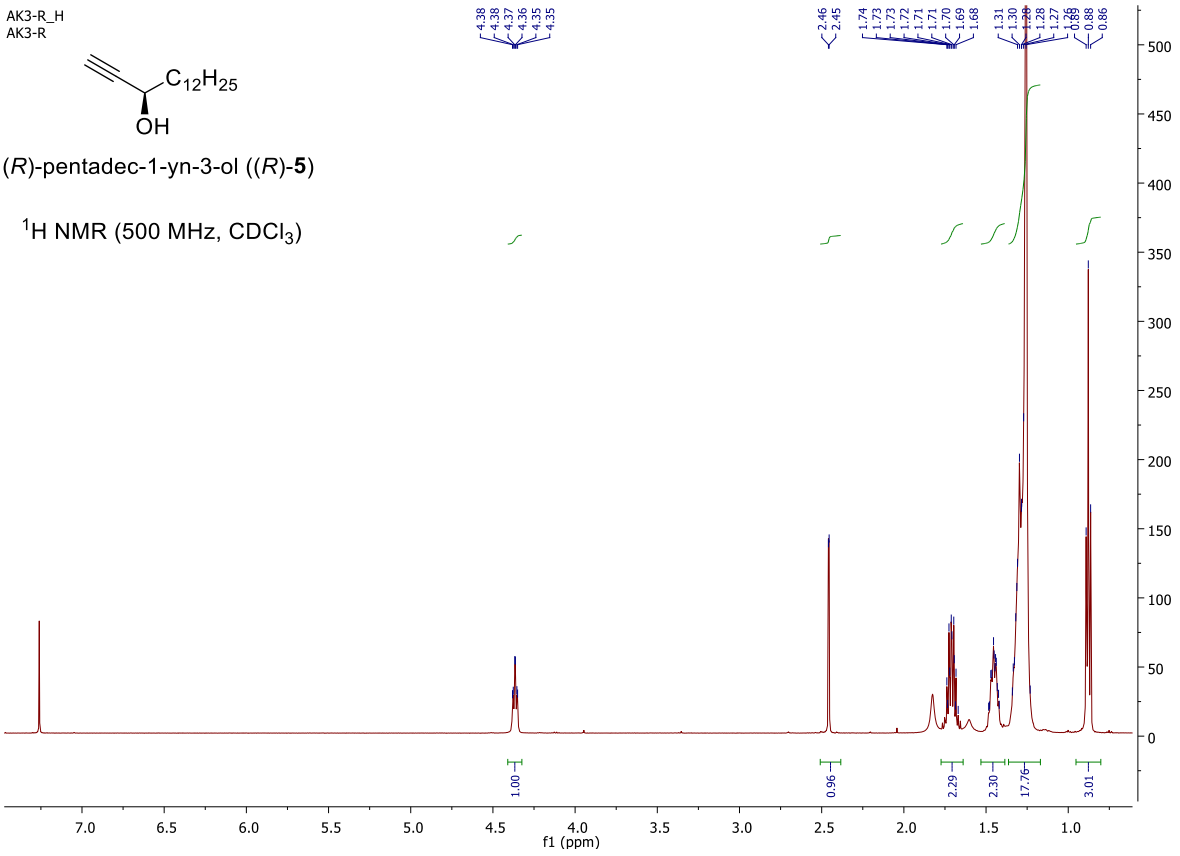
^{13}C NMR (125 MHz, $CDCl_3$)



AK3-R_H
AK3-R

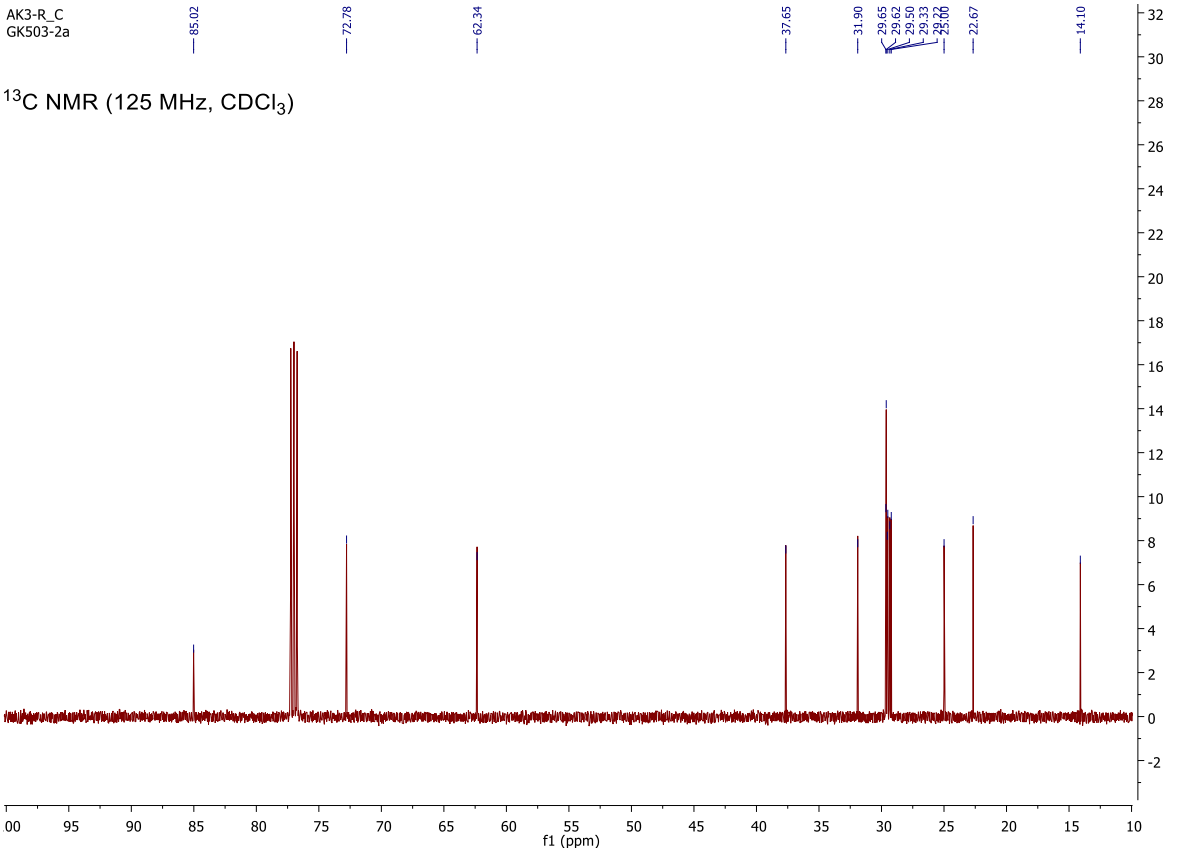
(*R*)-pentadec-1-yn-3-ol ((*R*)-**5**)

^{1}H NMR (500 MHz, $CDCl_3$)



AK3-R_C
GK503-2a

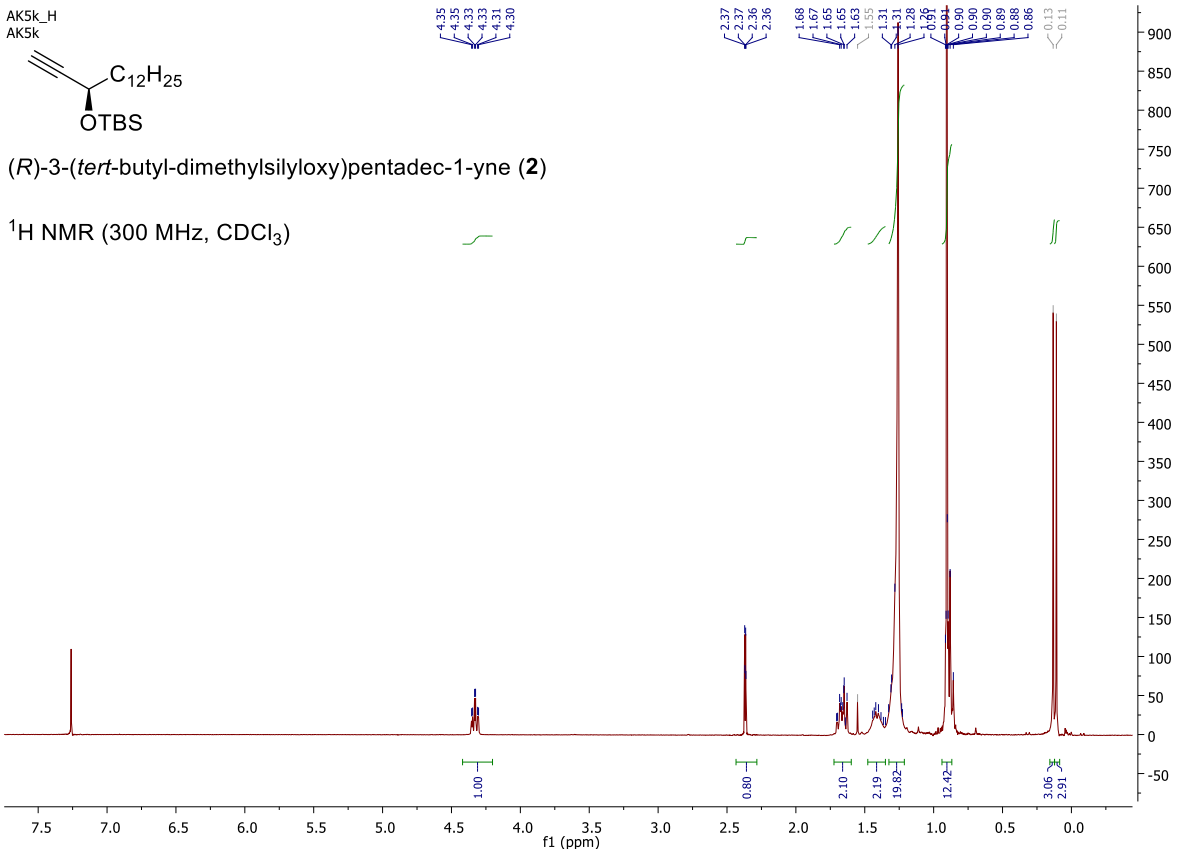
^{13}C NMR (125 MHz, $CDCl_3$)



AK5k_H
AK5k

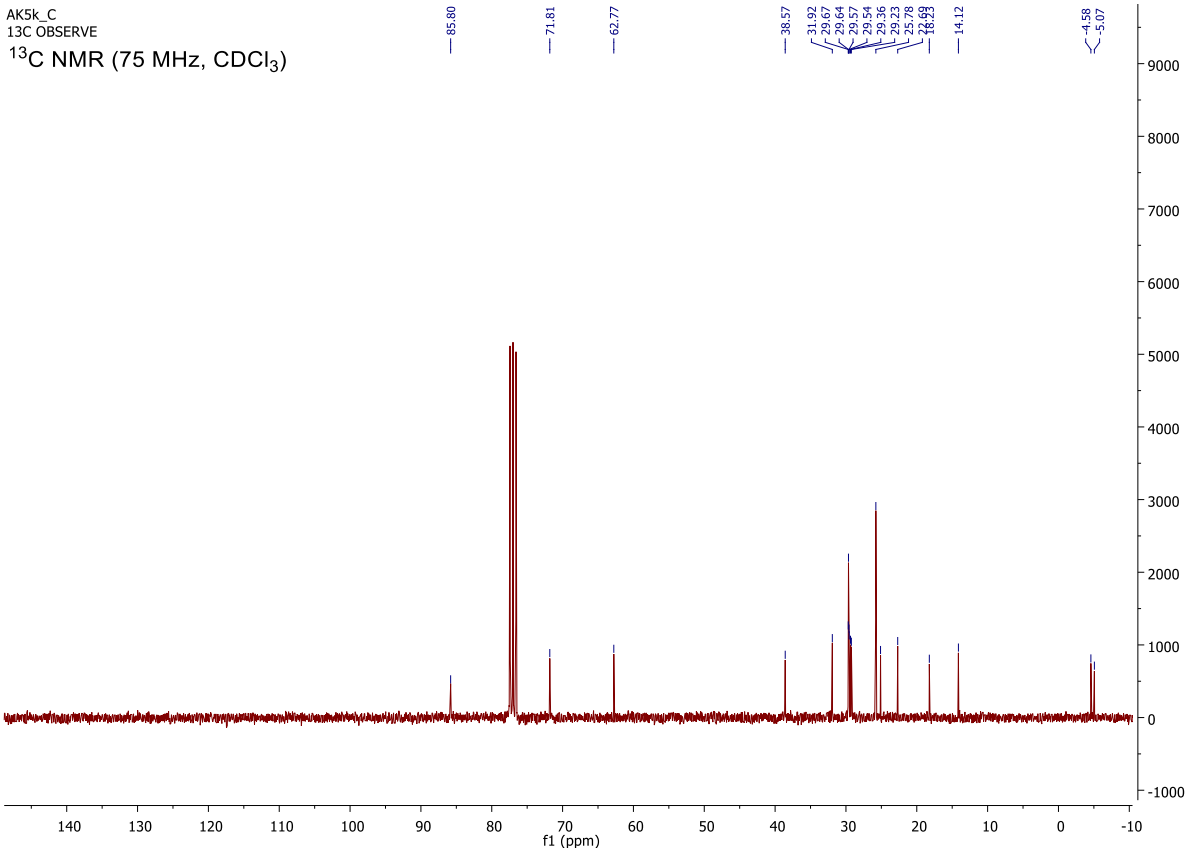
(*R*)-3-(*tert*-butyl-dimethylsilyloxy)pentadec-1-yne (**2**)

^{1}H NMR (300 MHz, $CDCl_3$)



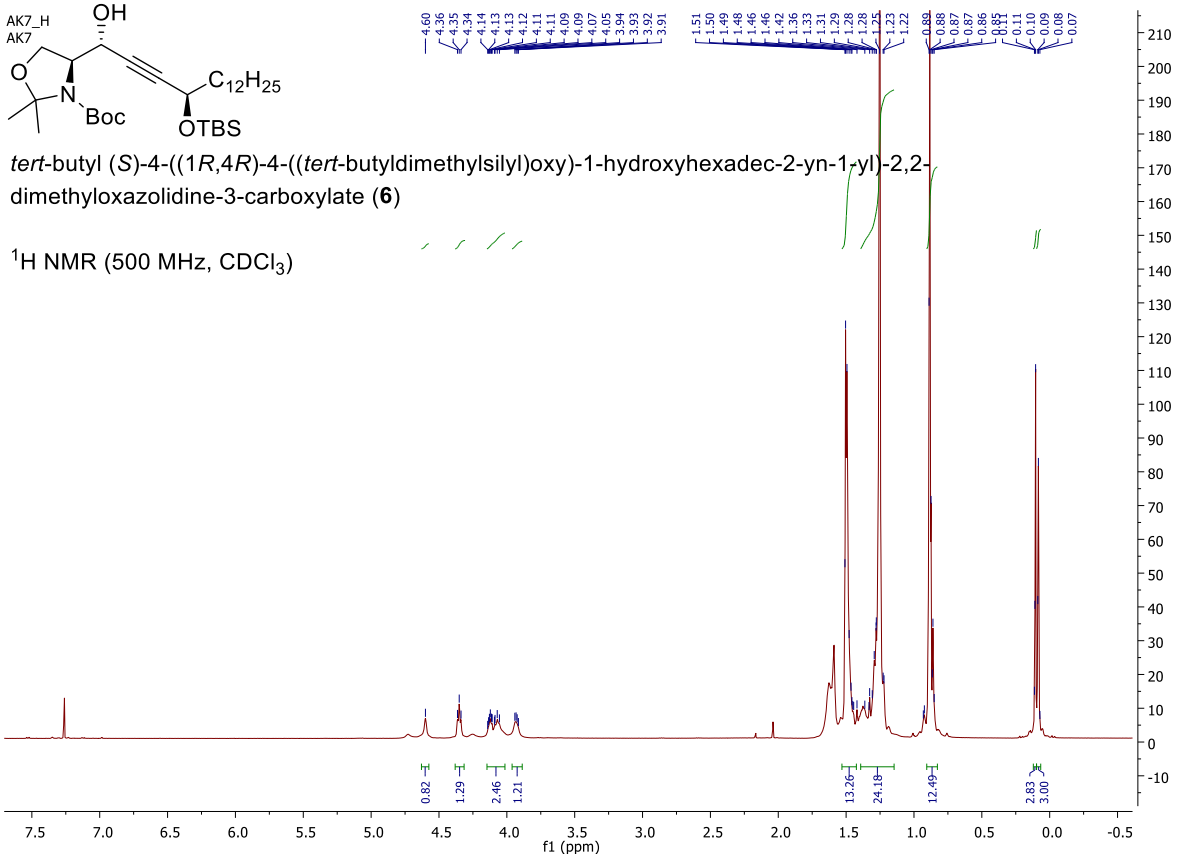
AK5k_C
13C OBSERVE

^{13}C NMR (75 MHz, $CDCl_3$)

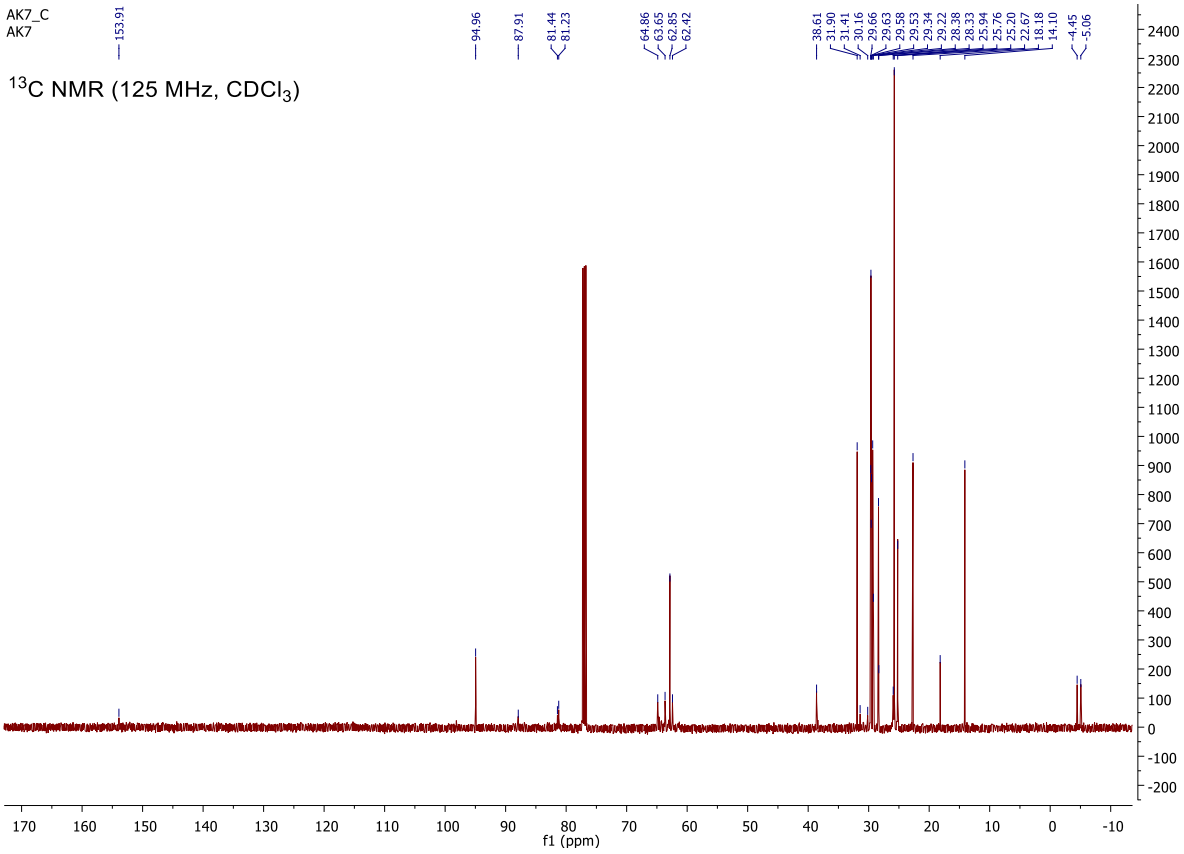


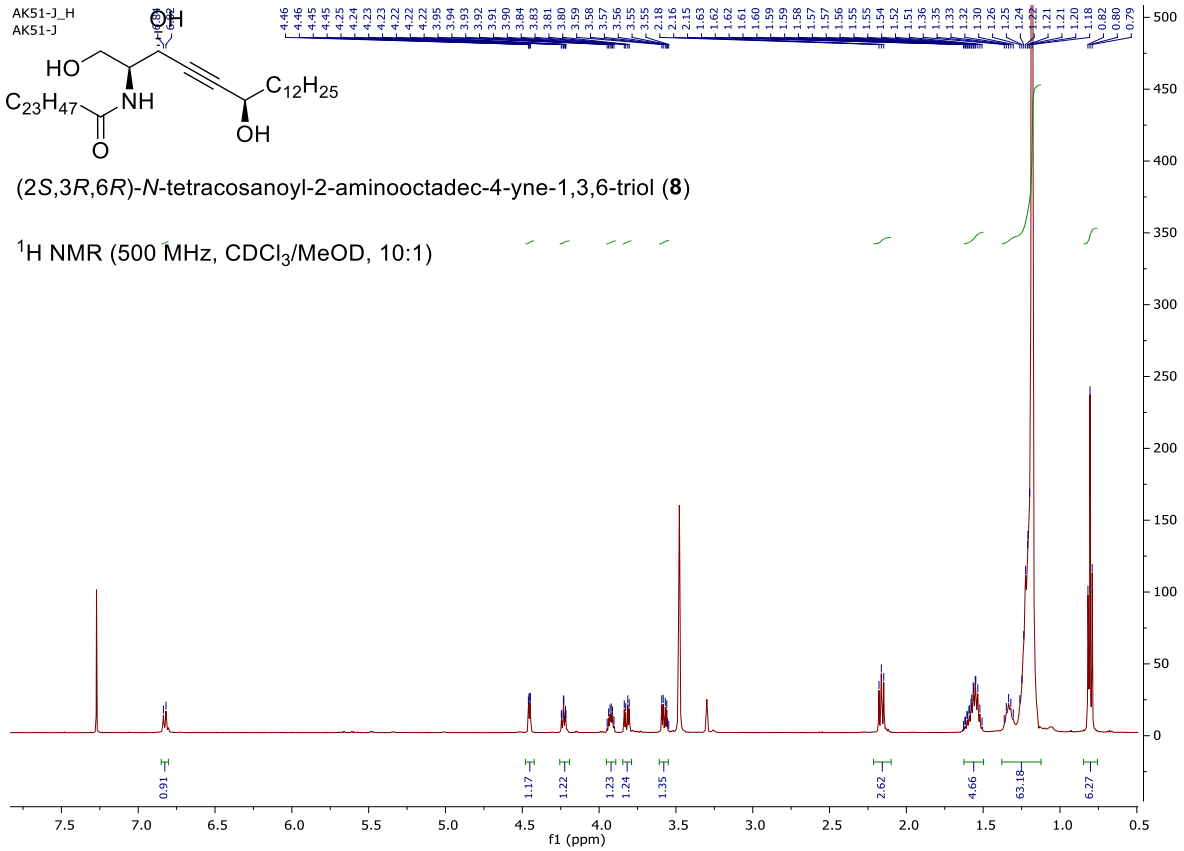
tert-butyl (*S*)-4-((1*R*,4*R*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxyhexadec-2-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (**6**)

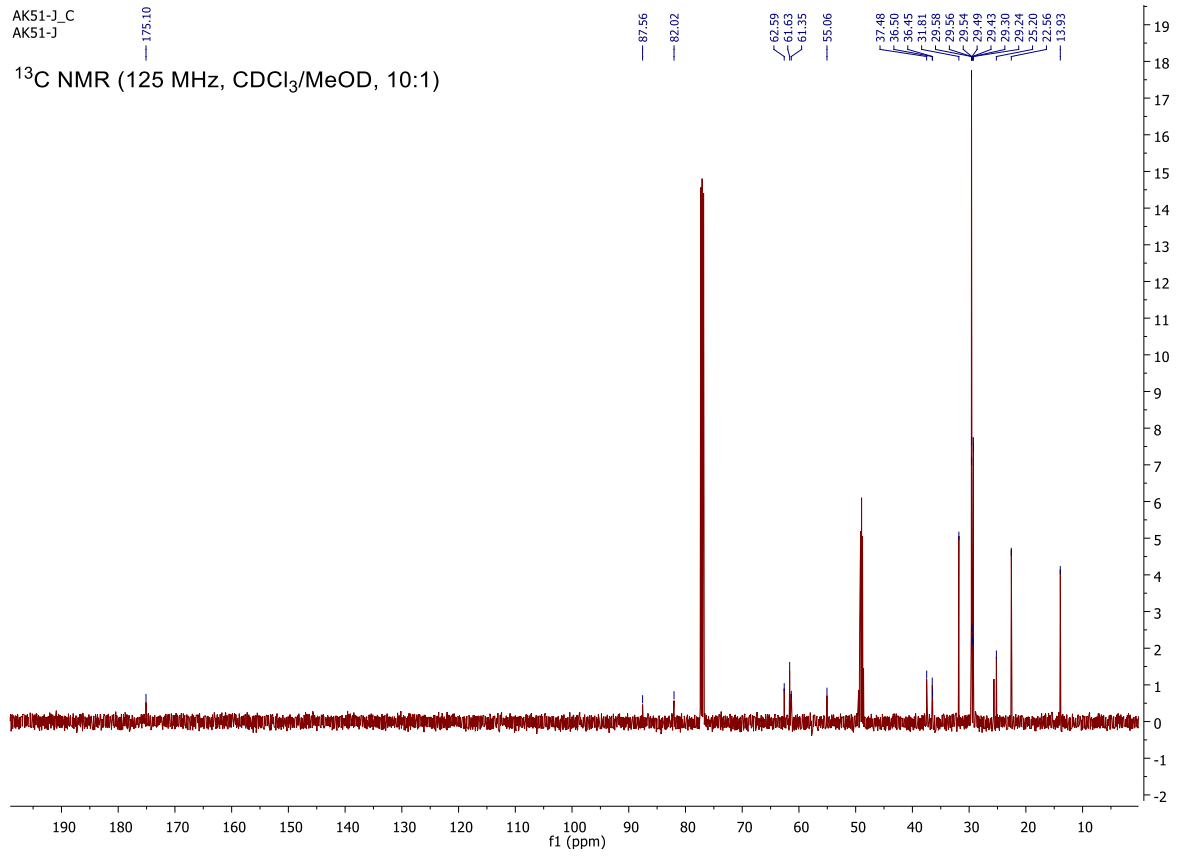
^{1}H NMR (500 MHz, $CDCl_3$)

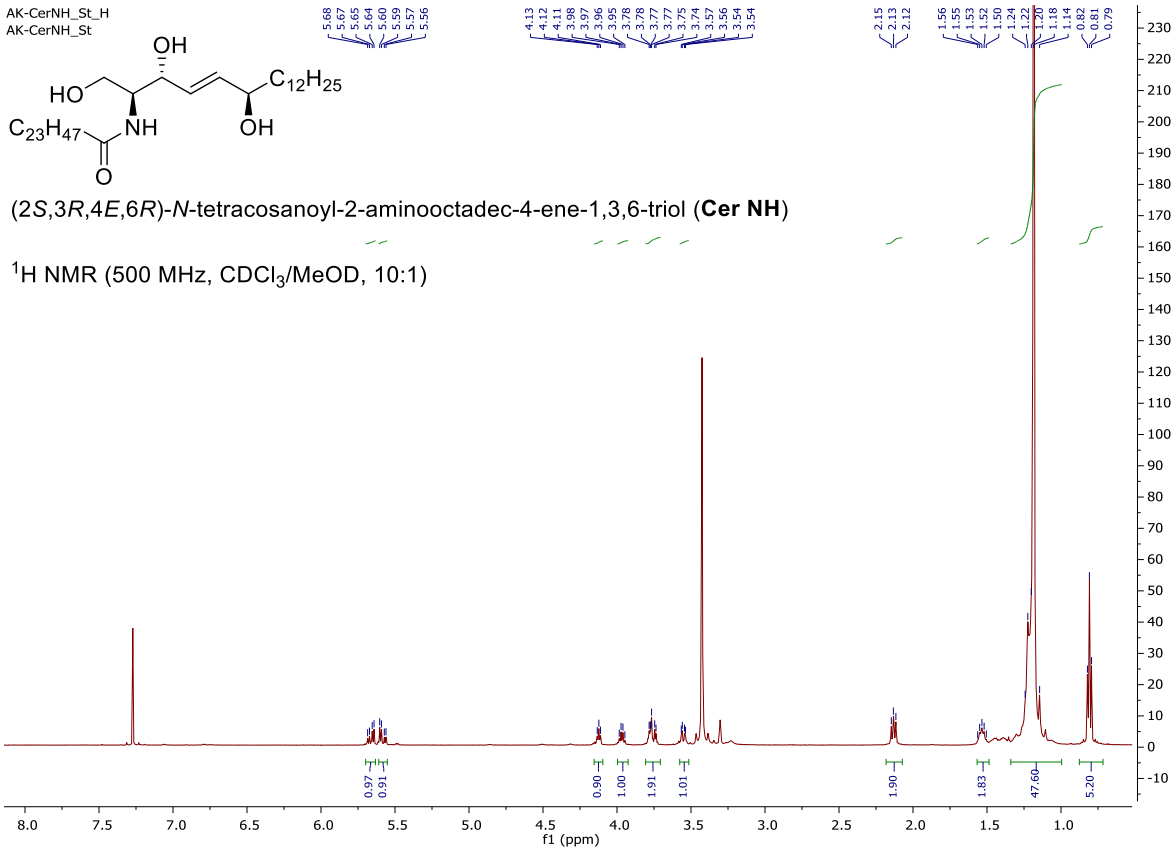


^{13}C NMR (125 MHz, $CDCl_3$)



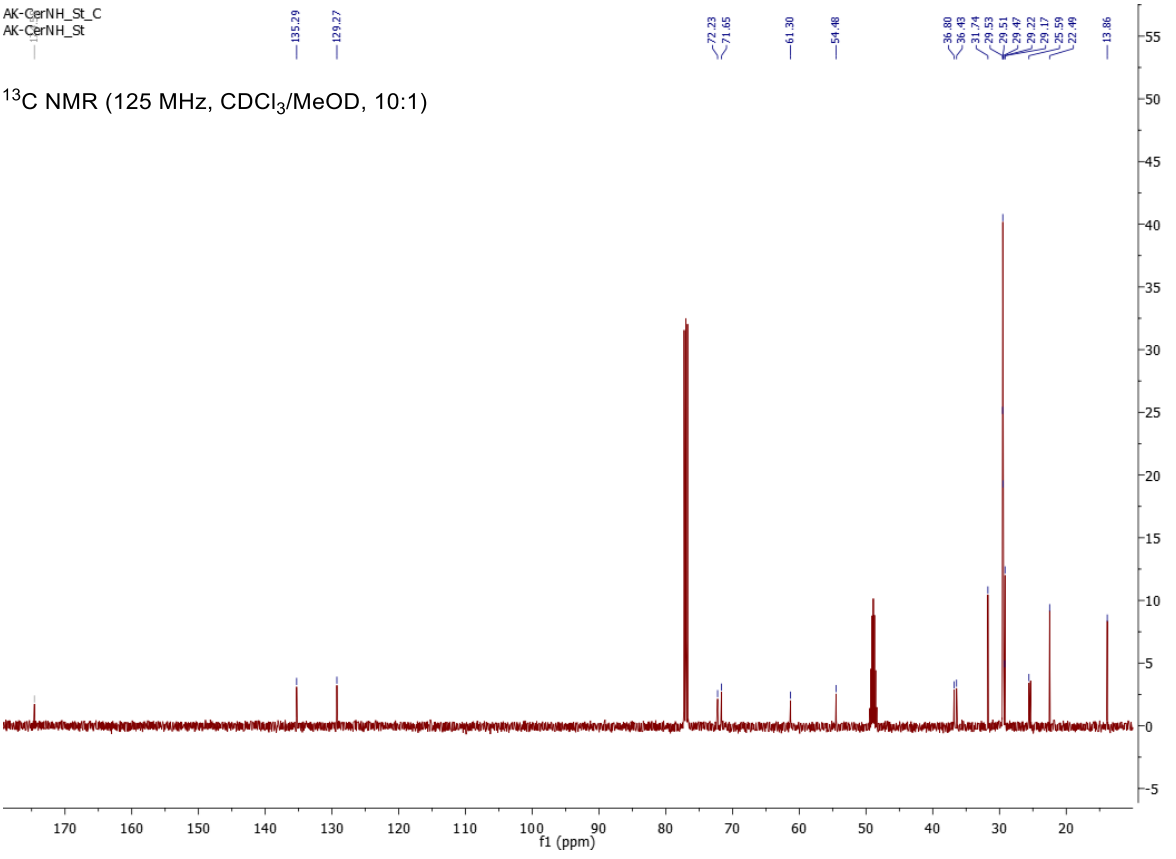

AK51-J_H
AK51-J
HO
OH
NH
O
OH
$C_{23}H_{47}$
$C_{12}H_{25}$
(2*S*,3*R*,6*R*)-*N*-tetracosanoyl-2-aminooctadec-4-yne-1,3,6-triol (**8**)
^{1}H NMR (500 MHz, $CDCl_3$/MeOD, 10:1)
f1 (ppm)


AK51-J_C
AK51-J
^{13}C NMR (125 MHz, $CDCl_3$/MeOD, 10:1)
f1 (ppm)



(2*S*,3*R*,4*E*,6*R*)-*N*-tetracosanoyl-2-aminooctadec-4-ene-1,3,6-triol (**Cer NH**)

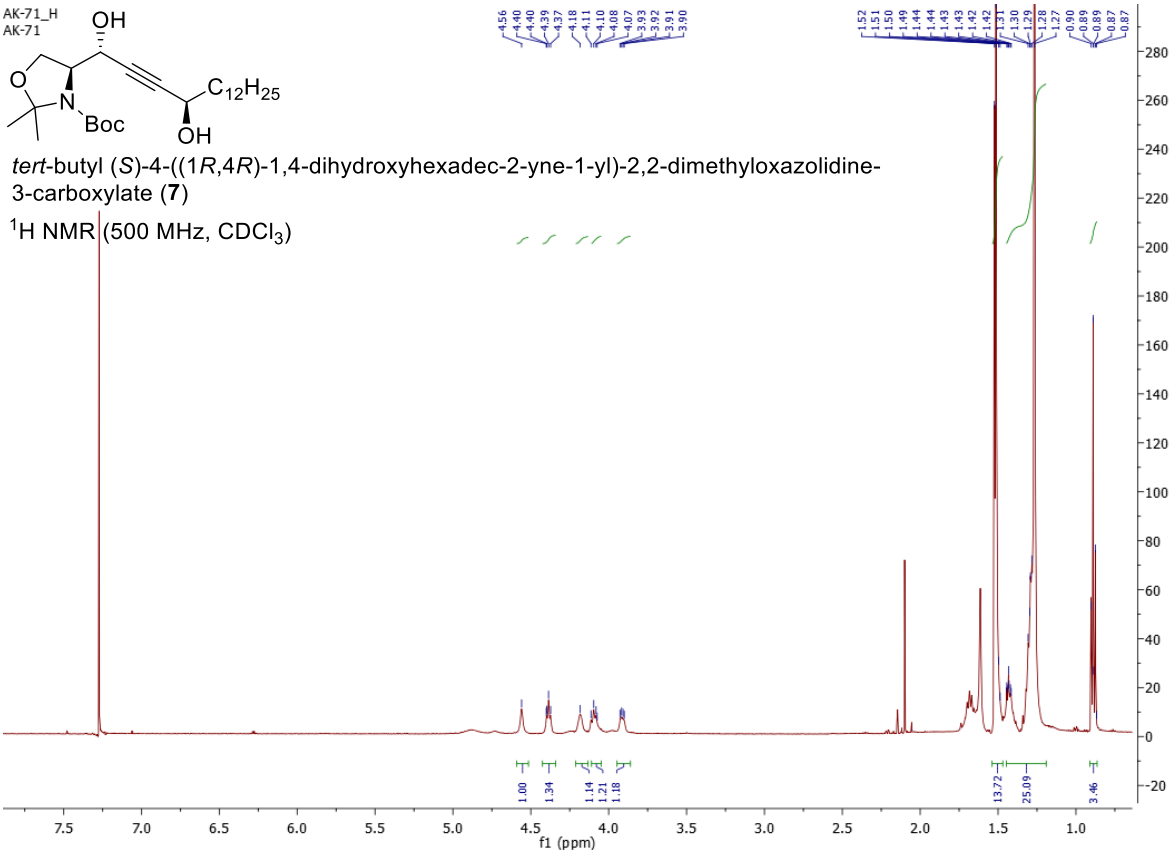
^{1}H NMR (500 MHz, $CDCl_3$/MeOD, 10:1)



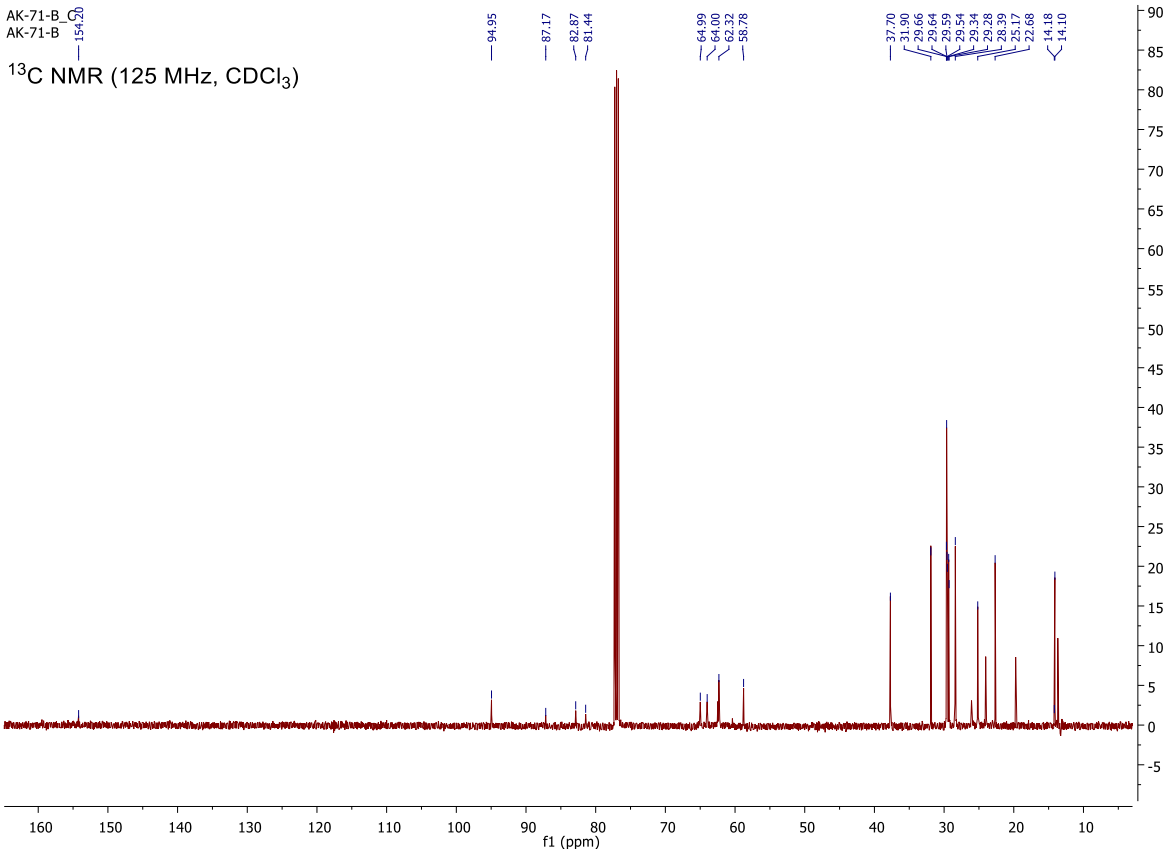
^{13}C NMR (125 MHz, $CDCl_3$/MeOD, 10:1)

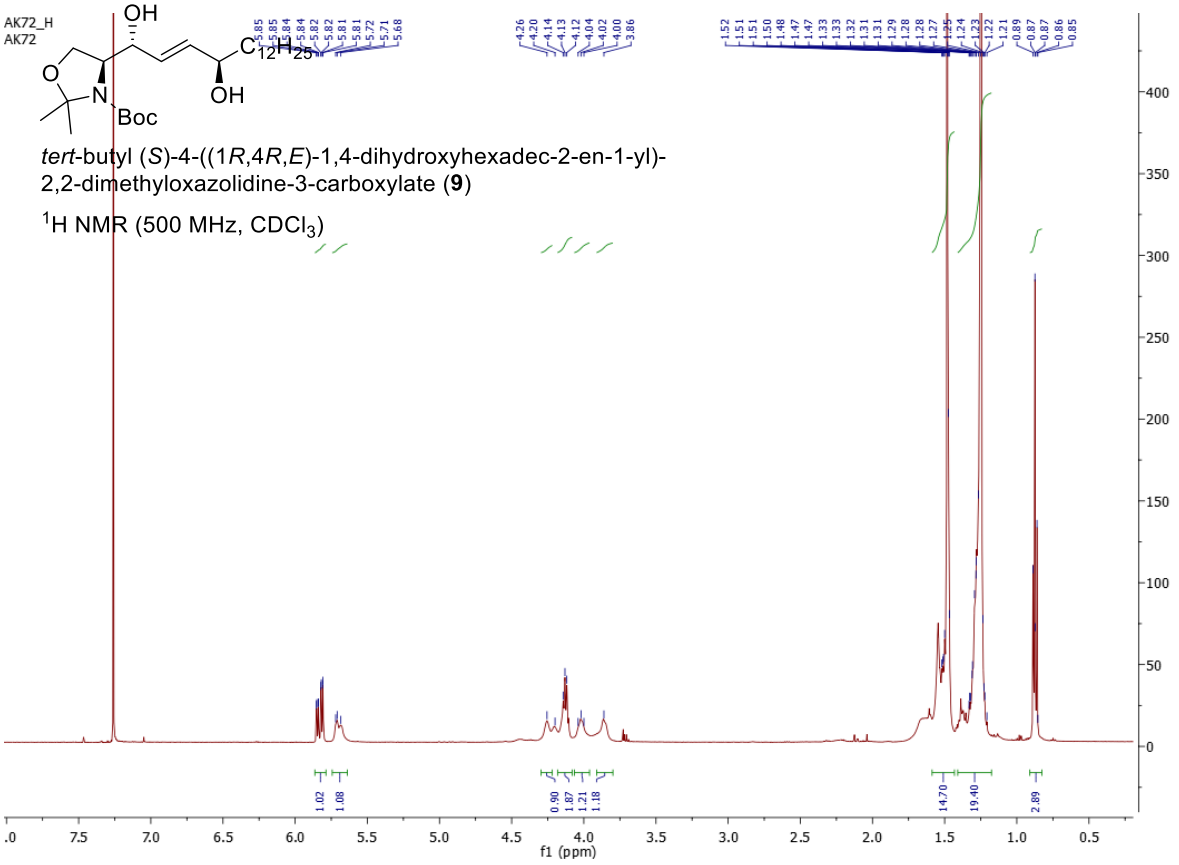
tert-butyl (*S*)-4-((1*R*,4*R*)-1,4-dihydroxyhexadec-2-yne-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (**7**)

^{1}H NMR (500 MHz, $CDCl_3$)



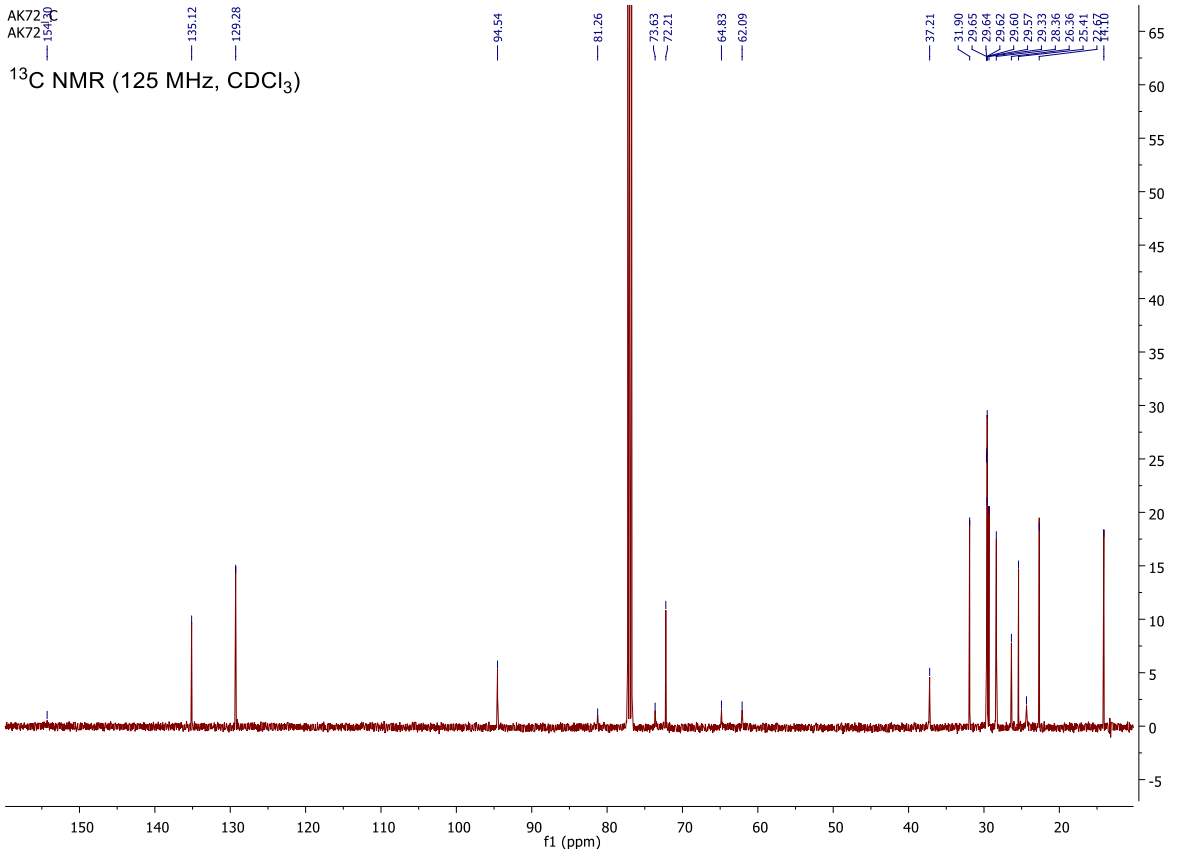
^{13}C NMR (125 MHz, $CDCl_3$)



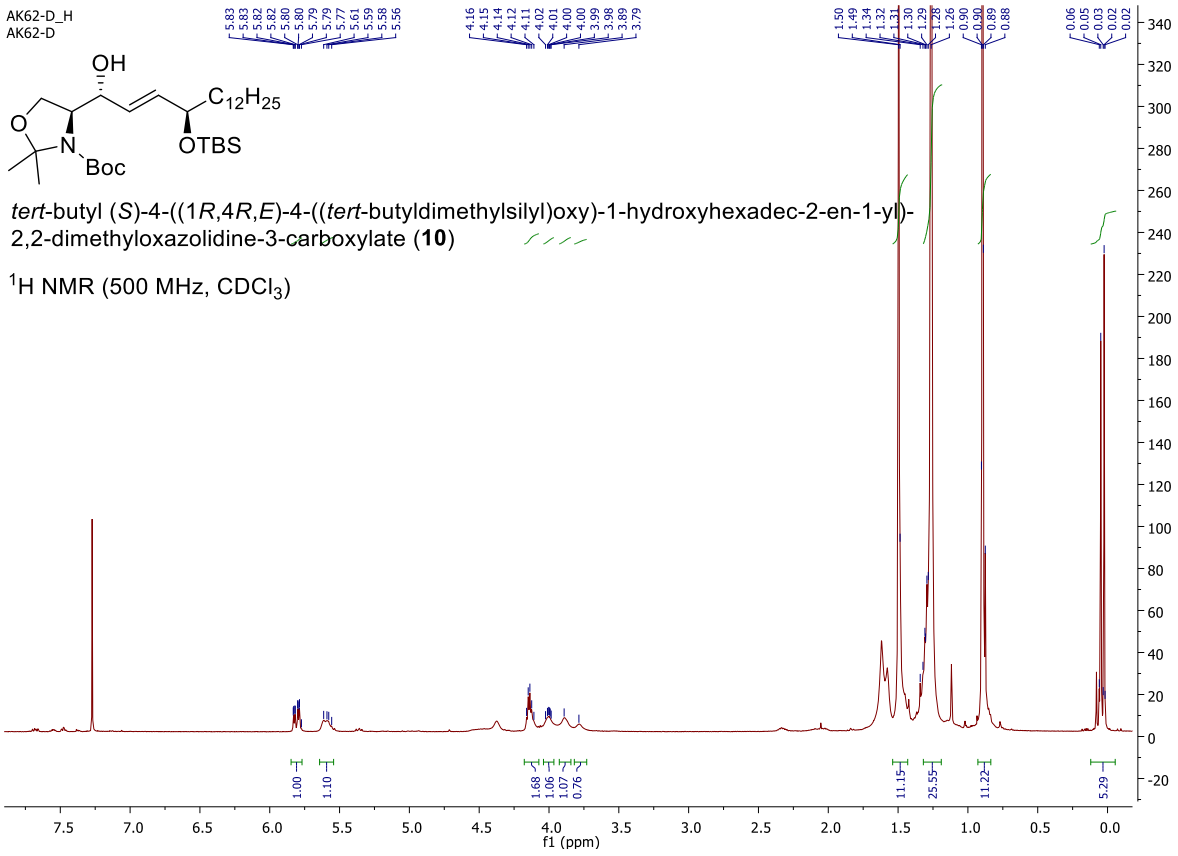


tert-butyl (*S*)-4-((1*R*,4*R*,*E*)-1,4-dihydroxyhexadec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (**9**)

^{1}H NMR (500 MHz, $CDCl_3$)

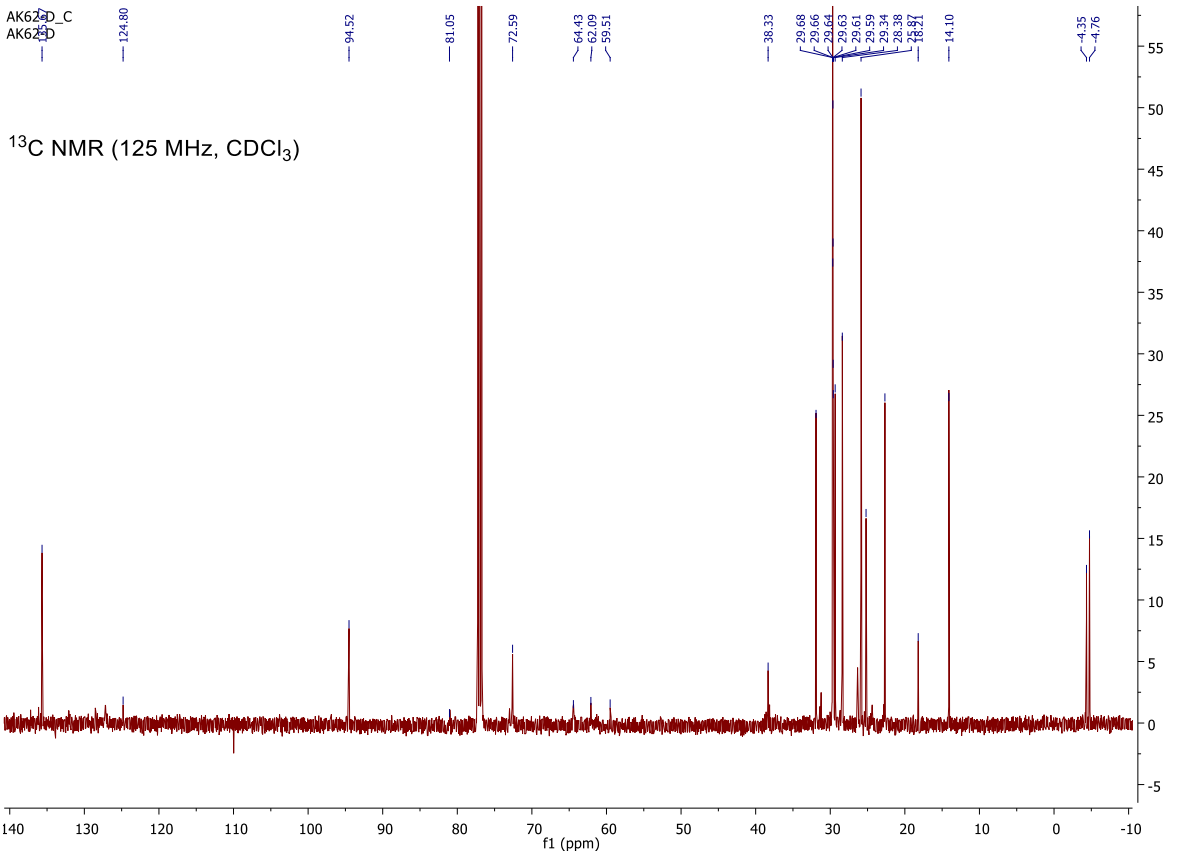


^{13}C NMR (125 MHz, $CDCl_3$)



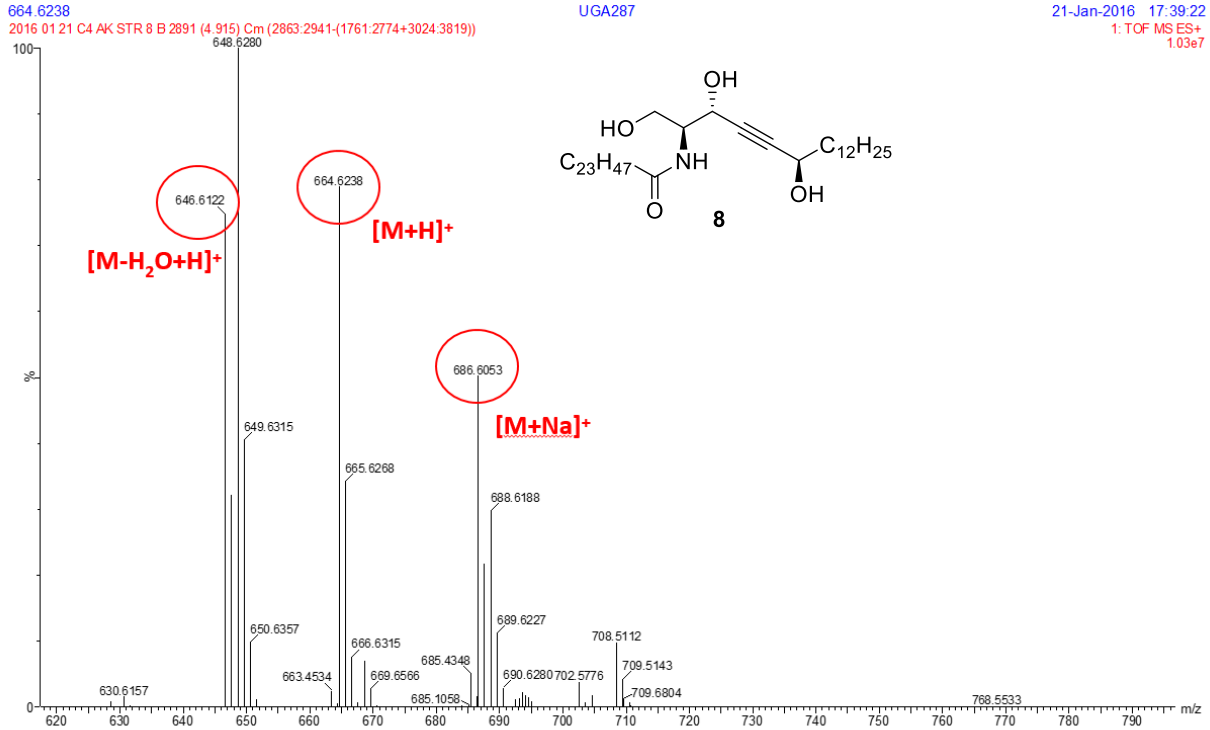
tert-butyl (*S*)-4-((1*R*,4*R*,*E*)-4-((*tert*-butyldimethylsilyl)oxy)-1-hydroxyhexadec-2-en-1-yl)-2,2-dimethyloxazolidine-3-carboxylate (**10**)

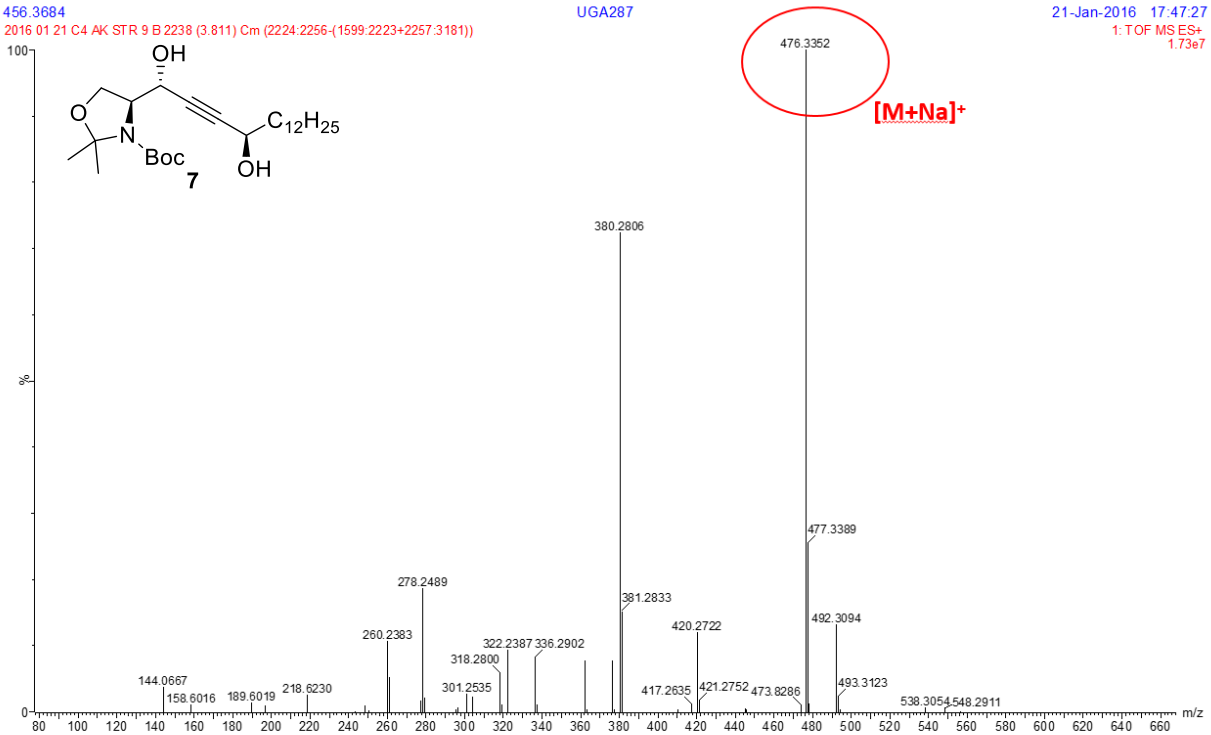
^{1}H NMR (500 MHz, $CDCl_3$)

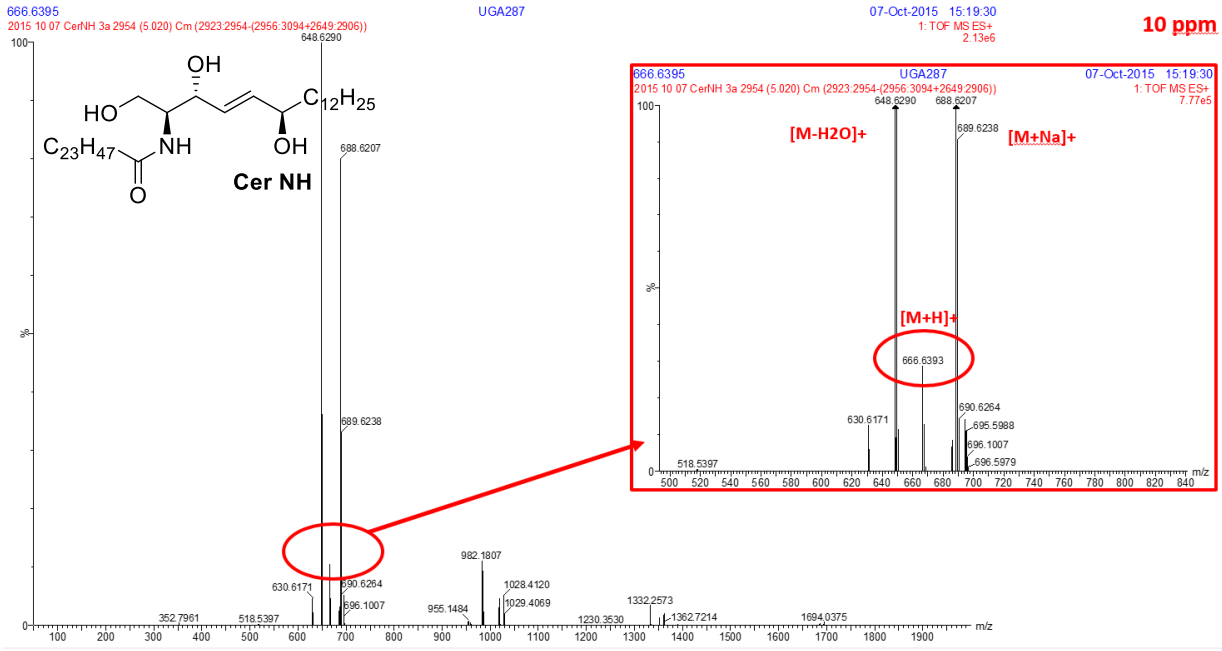


^{13}C NMR (125 MHz, $CDCl_3$)

3. HRMS spectra






666.6395
2015 10 07 CerNH 3a 2954 (5.020) Cm (2923:2954-(2956:3094+2649:2906))
UGA287
07-Oct-2015 15:19:30
1: TOF MS ES+
2.13e6
10 ppm
OH
HO
C12H25
C23H47
NH
OH
O
Cer NH
[M-H2O]+
[M+Na]+
[M+H]+
m/z
%

4. X-Ray powder diffraction measurements

A		B		C	
n	Q [nm]	*n*	Q [nm]	*n*	Q [nm]
2	1.237	1	1.698	1	1.870
4	2.403	2	3.355	2	3.703
5	2.992	3	5.002	6	11.028
6	3.589	4	6.661		
7	4.171	6	9.970		
8	4.767	7	11.626		
12	7.128	8	13.277		
14	8.310				

Table 1. Sections **A, B and C** show values for the long periodicity phase (*d* = 10.6 nm), second lamellar phase (*d* = 3.8 nm) and crystalline cholesterol (*d* = 3.4 nm), respectively. Q [nm^{-1}] is the scattering vector – a function of the scattered intensity, which is proportional to the scattering angle θ.