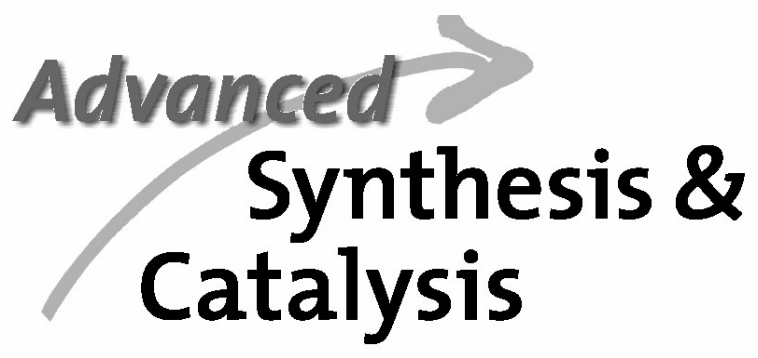

Supporting Information

Supporting Information

Zeolite NaY-promoted monocyclization of epoxy polyene terpenes: A unique route for the direct synthesis of incompletely cyclized naturally occurring terpenols

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General method for the synthesis of epoxy terpenoids

To a solution of a polyene terpene (10 mmol) dissolved in a 50 mL solvent system of THF/H_2O=5/1, were added over a period of 15 minutes, 11 mmol of *N*-bromosuccinimide (NBS). After 30 minutes (disappearance of the reactant and formation of the bromohydrin by TLC), 50 mL of ether were added and the organic layer was washed with brine. The organic layer was dried over anhydrous $MgSO_4$, and then concentrated under reduced pressure to afford quantitatively the crude bromohydrin. The bromohydrin was dissolved in a slurry containing 12 mmol of K_2CO_3 in 30 mL of methanol. Typically, after 20 minutes formation of the epoxide was complete. Most of the methanol was removed under reduced pressure and the residue was extracted with diethyl ether to afford after evaporation of the solvents the crude epoxide. Purification by flash column chromatography can be accomplished either at the stage of the formation of bromohydrin, or at the second step (formation of the epoxide). All epoxides were isolated in pure form, in yields ranging from 50-80%.

(*E*)-8-(3,3-Dimethyloxiran-2-yl)-6-methyloct-5-en-2-yl acetate (5c). It was prepared in 56% yield as an equimolar mixture of two diastereomers from the epoxidation of (*E*)-6,10-dimethylundeca-5,9-dien-2-yl acetate.[1] ^{1}H NMR: 5.15 (t, *J* = 7.0 Hz, 1H), 4.88 (m, 1H), 2.70 (t, *J* = 6.0 Hz, 1H), 2.18-2.07 (m, 2H), 2.05-2.00 (m, 2H), 2.03 (s, 3H), 1.68-1.58 (m, 3H), 1.60 (s, 3H), 1.51 (m, 1H), 1.30 (s, 3H), 1.26 (s, 3H), 1.21 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR: 170.7, 134.9, 124.0, 70.6, 64.1, 58.3, 36.6, 35.9, 27.4, 24.9, 23.9, 21.4, 20.0, 18.8, 15.9. Note that the absorptions of the two diastereomers overlap even in the ^{13}C NMR spectrum. The equimolar presence of the 2 diastereomers was seen by GC analysis.

2,2-Dimethyl-3-(3-methylenepent-4-enyl)oxirane (14). It was prepared in 79% isolated yield by m-CPBA addition to myrcene.[2] ^{1}H NMR: 6.38 (dd, J_1 = 11.0 Hz, J_2 = 17.5 Hz, 1H), 5.25 (dd, J_1 = 17.5 Hz, J_2 = 0.5 Hz, 1H), 5.09 (dd, J_1 = 11.0 Hz, J_2 = 0.5 Hz, 1H), 5.05 (s, 1H), 5.03 (s, 1H), 2.75 (t, *J* = 6.0 Hz, 1H), 2.42 (m, 1H), 2.33 (m, 1H), 1.73 (m, 2H), 1.30 (s, 3H), 1.25 (s, 3H). ^{13}C NMR: 145.5, 138.6, 116.1, 113.4, 64.1, 58.5, 28.1, 27.6, 24.9, 18.8.

(5*E*,9*E*)-12-(3,3-Dimethyloxiran-2-yl)-6,10-dimethyldodeca-5,9-dien-2-one (32).[3] It was prepared in 64% yield from *trans*,*trans*-farnesylacetone. ^{1}H NMR: 5.13 (t, *J* = 7.0 Hz, 1H), 5.07 (t, *J* = 7.0 Hz, 1H), 2.70 (t, *J* = 6.5 Hz, 1H), 2.45 (t, *J* = 7.0 Hz, 2H), 1.89-2.27 (m, 6H), 2.13 (s, 3H), 1.60-1.68 (m, 4H), 1.61 (br. s, 6H), 1.29 (s, 3H), 1.25 (s, 3H). ^{13}C NMR: 190.6, 136.1, 133.9, 124.5, 122.4, 64.0, 58.1, 43.5, 40.0, 39.3, 36.1, 29.7, 27.2, 26.3, 24.7, 22.2, 18.5, 15.8.

2,3-Epoxysqualene (37). It was prepared in 62% yield from the commercially available squalene. In the addition of NBS to squalene, approximately 15% of bromohydrin was formed in the internal C6-C7 and C10-C11 double bonds. The terminal C2-C3 bromohydrin was easily isolated from the internal regioisomers by column chromatography and then transformed to the epoxide. ^{1}H NMR: 5.12 (m, 5H), 2.70 (t, *J* = 6.5 Hz, 1H), 1.97-2.14 (m, 18H), 1.67 (br. s, 3H), 1.65 (br. s, 3H), 1.61 (br. s, 12H), 1.29 (s, 3H), 1.25 (s, 3H). ^{13}C NMR: 135.1, 135.0, 134.9, 134.0, 131.2, 125.0, 124.4, 124.3, 64.2, 58.3, 39.8, 36.3, 28.3, 27.5, 26.8, 26.7, 25.7, 24.9, 18.7, 17.7, 16.0.

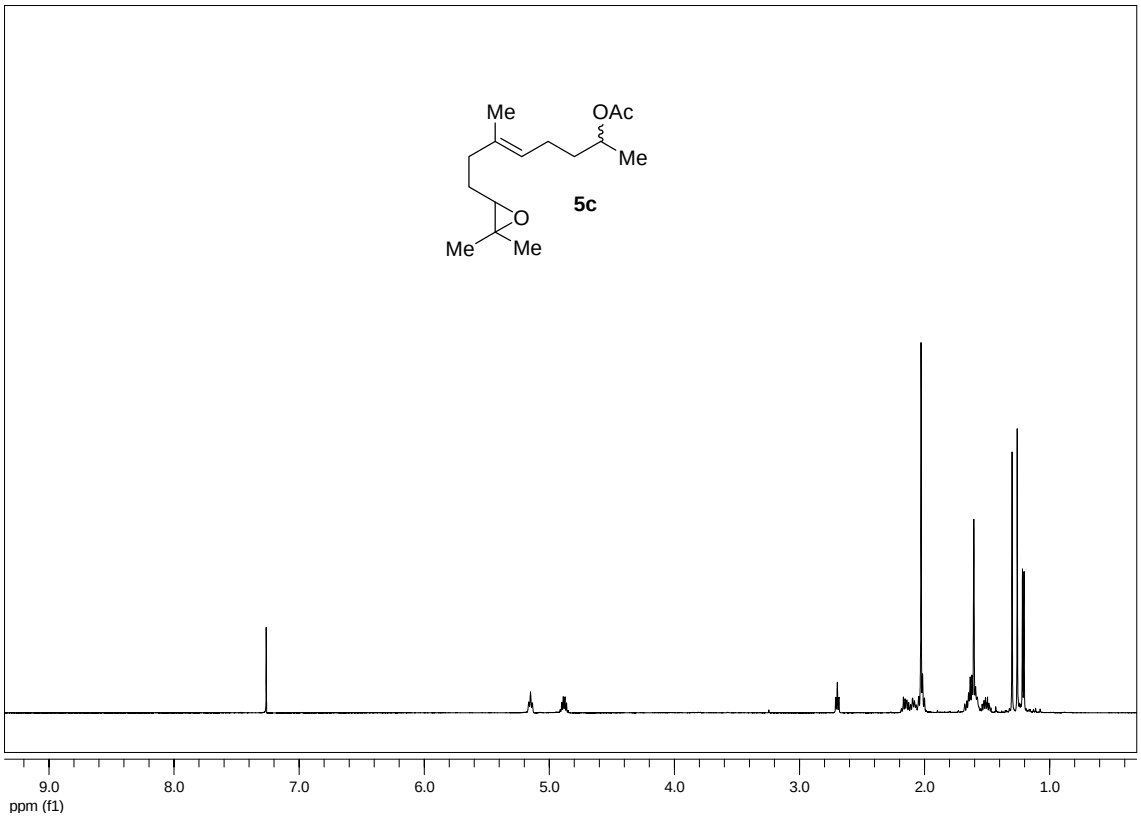
References

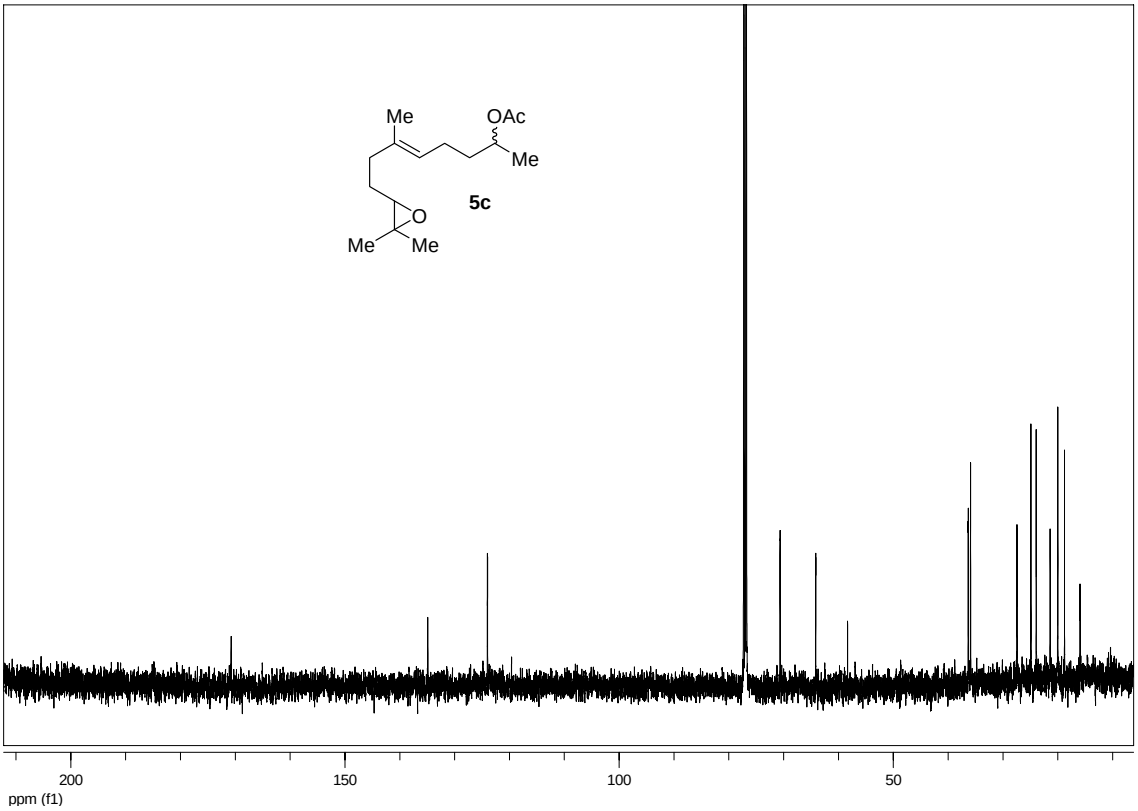
[1] Y. Li, B. Lu, C. Li, Y. Li, *Synth. Commun.* **2003**, *33*, 1417.

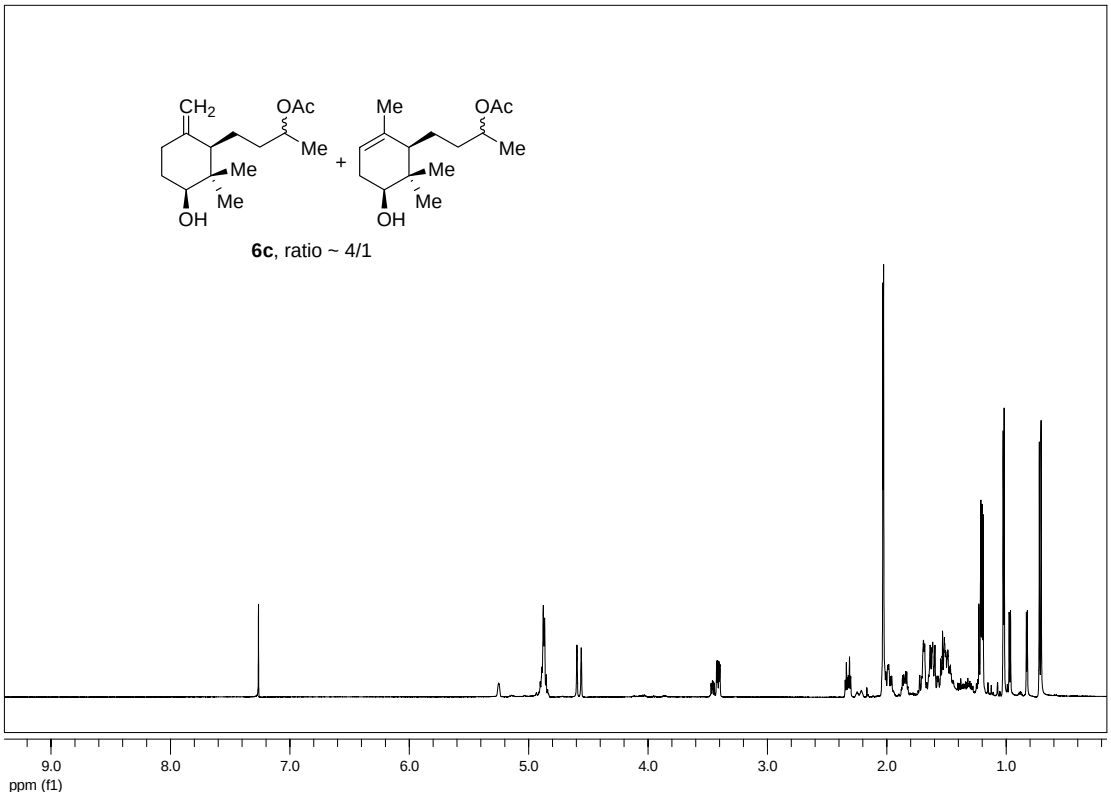
[2] H. Hioki, H. Ooi, M. Hamano, Y. Mimura, S. Yoshio, M. Kodama, S. Ohta, M. Yanai, S. Ikegami, *Tetrahedron* **2001**, *57*, 1235.

[3] B. N. Ravi, P. T. Murphy, R. O. Lidgard, R. G. Warren, R. J. Wells, *Aust. J. Chem*. **1982**, *35*, 171.

^{1}H and ^{13}C NMR spectra of key compounds and reaction products



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4.0
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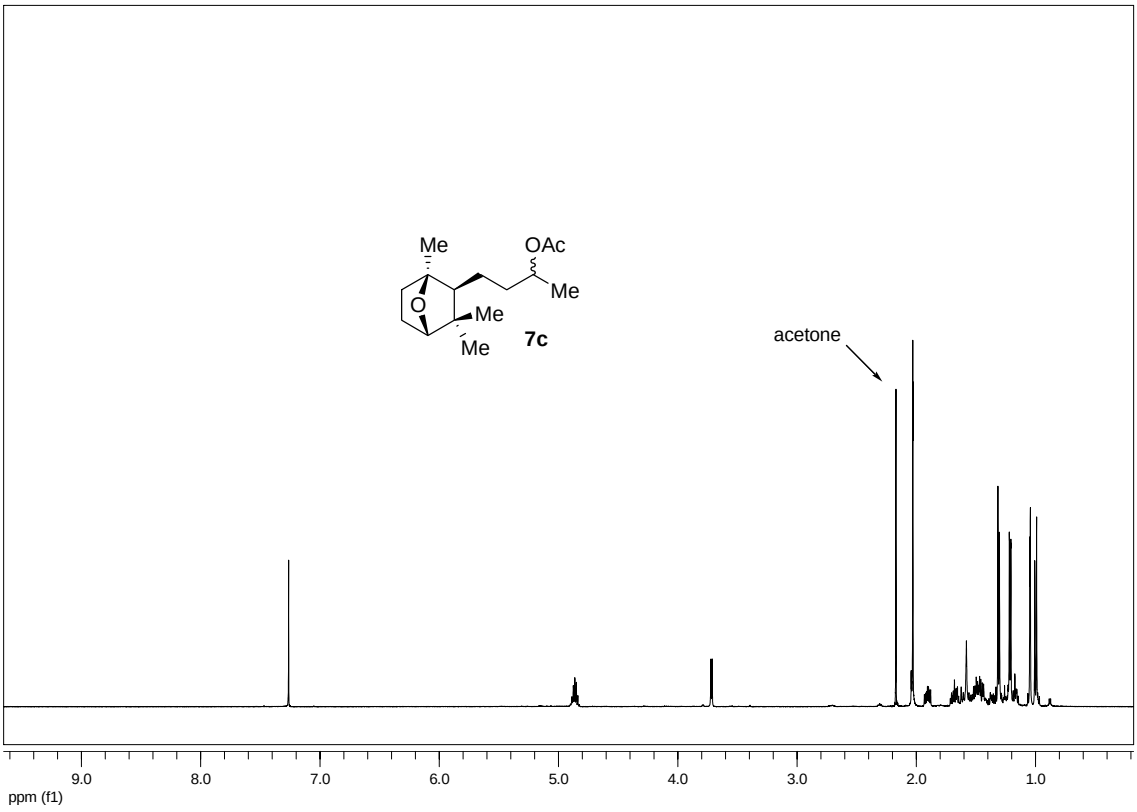
1.0
ppm (f1)

6c, ratio ~ 4/1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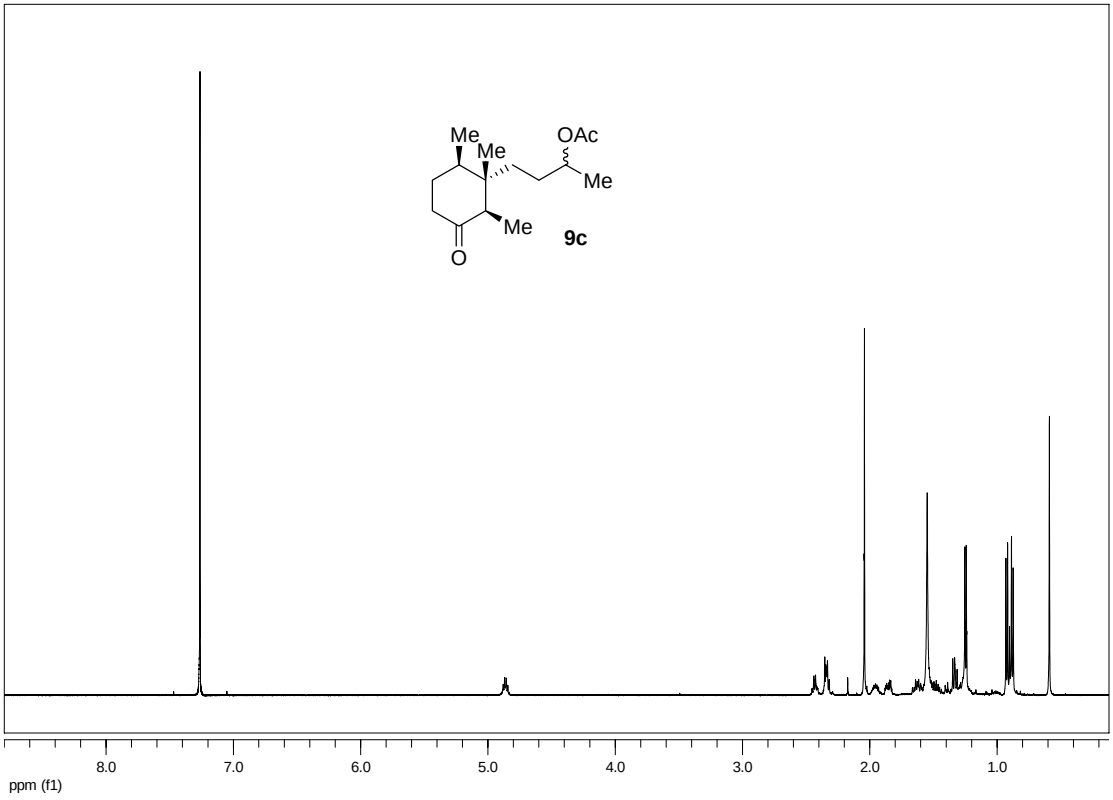
ppm (f1)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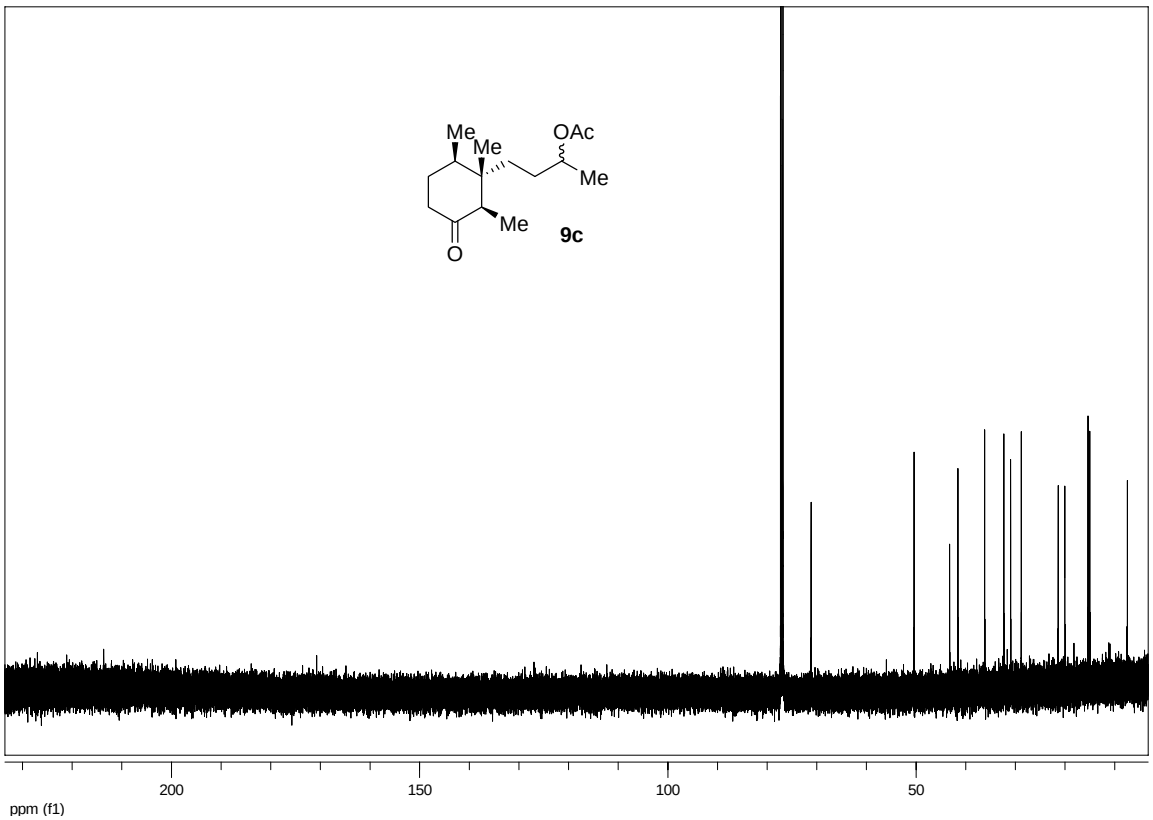
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O
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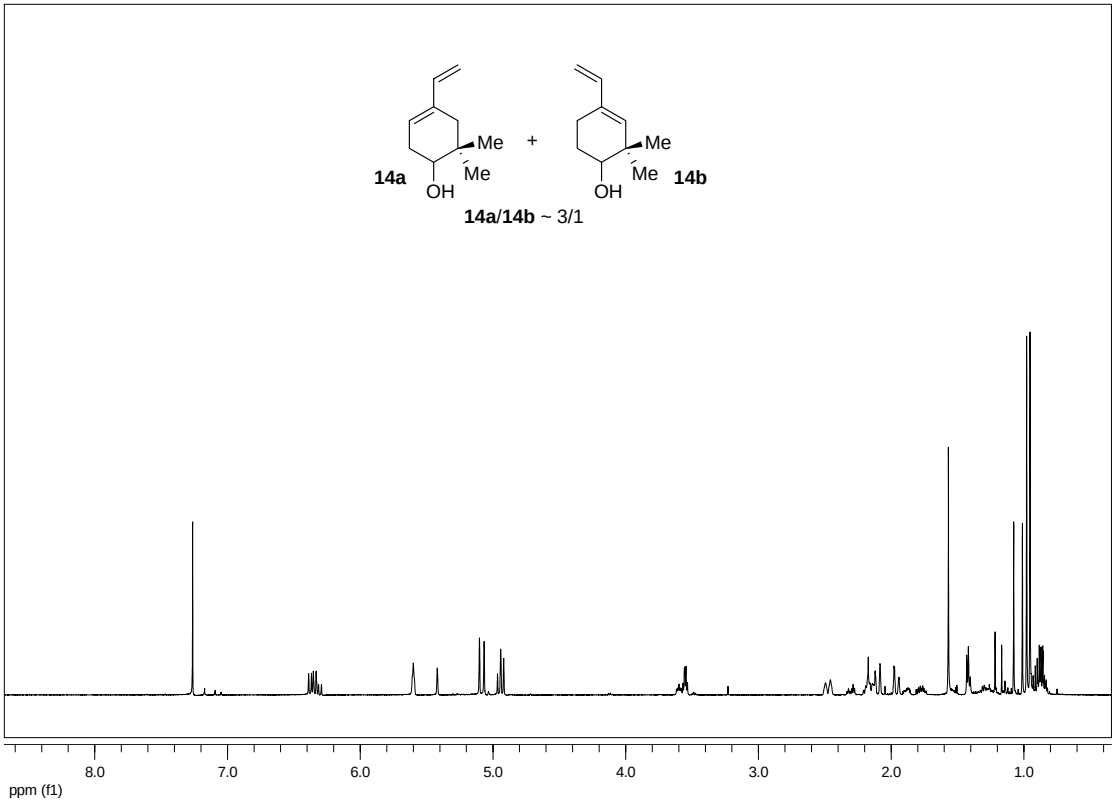
100
50
ppm (f1)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Me
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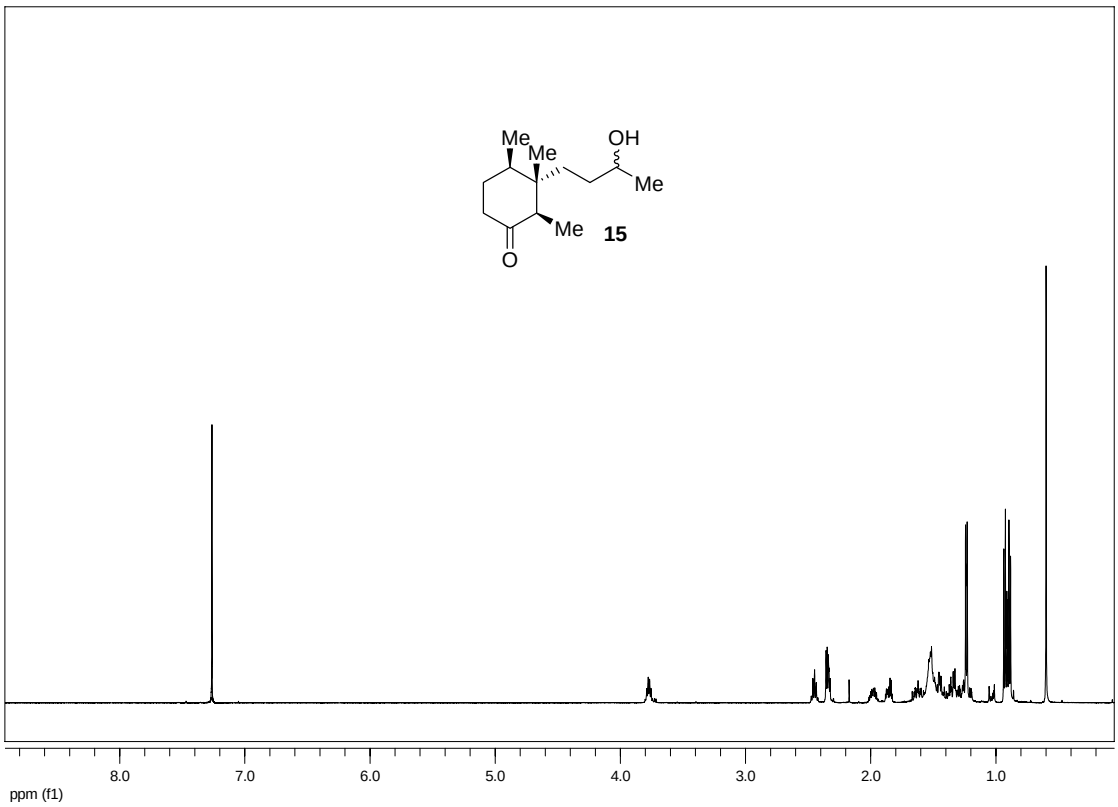
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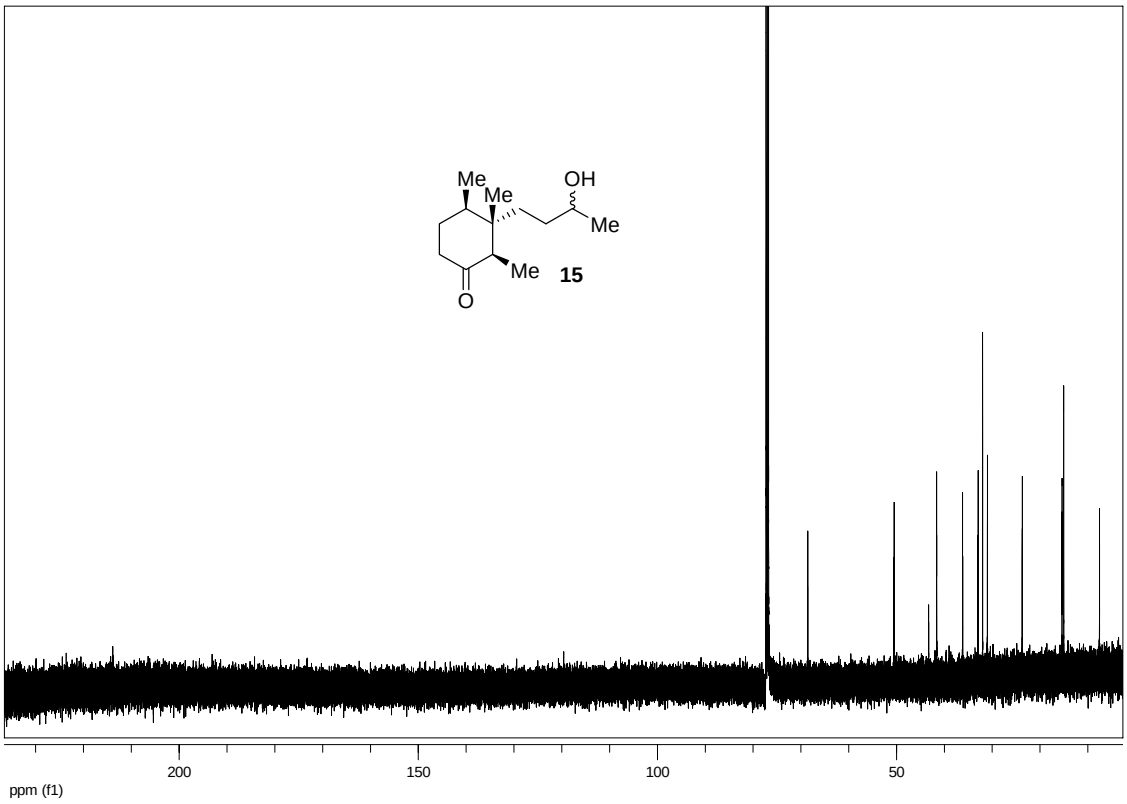
ppm (f1)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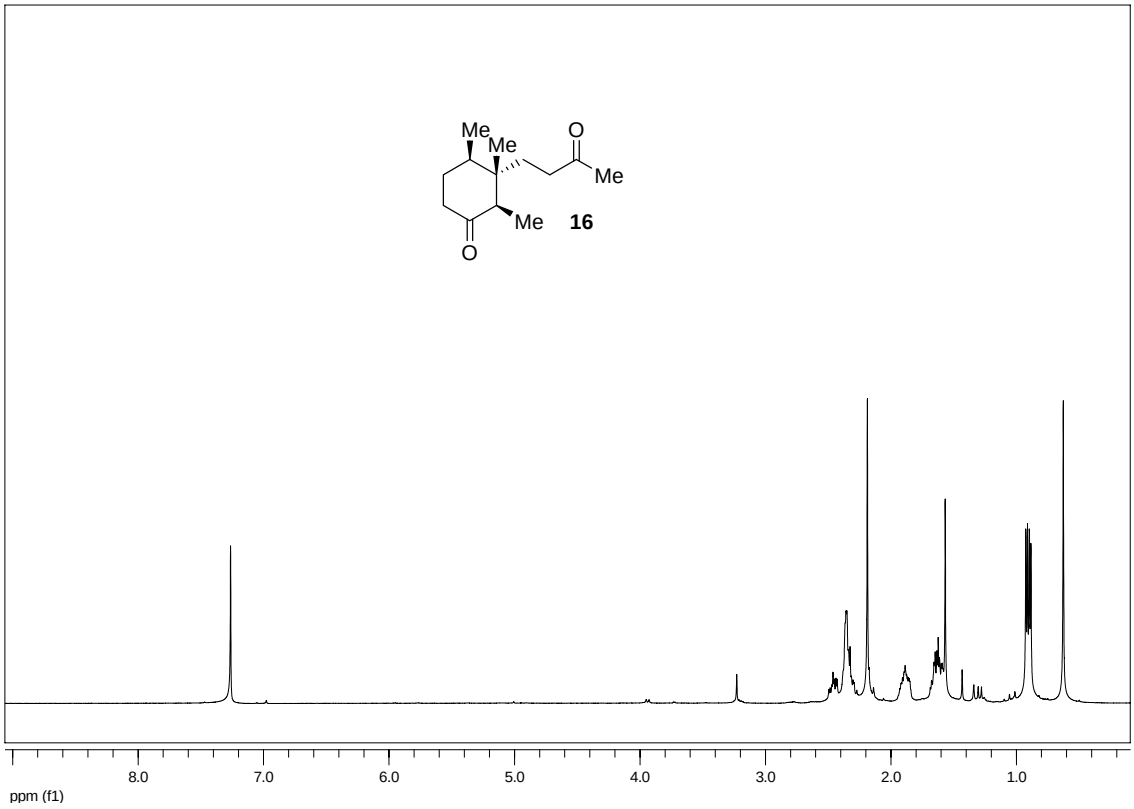
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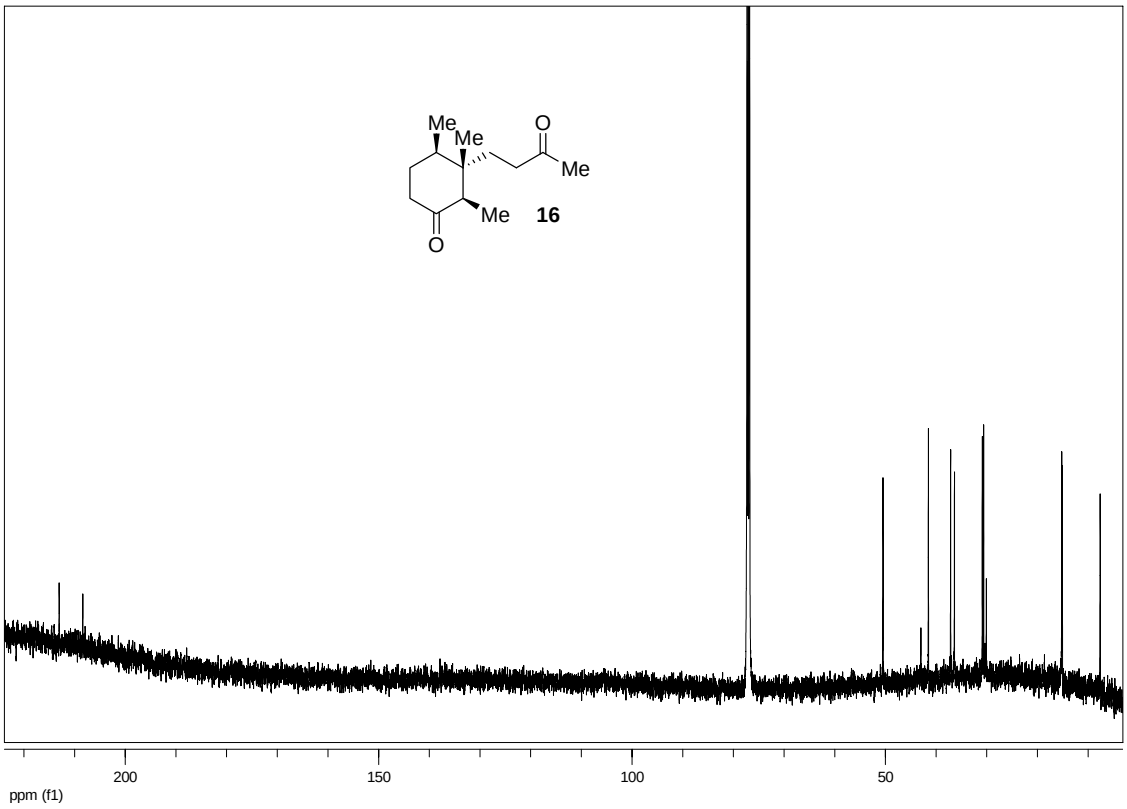
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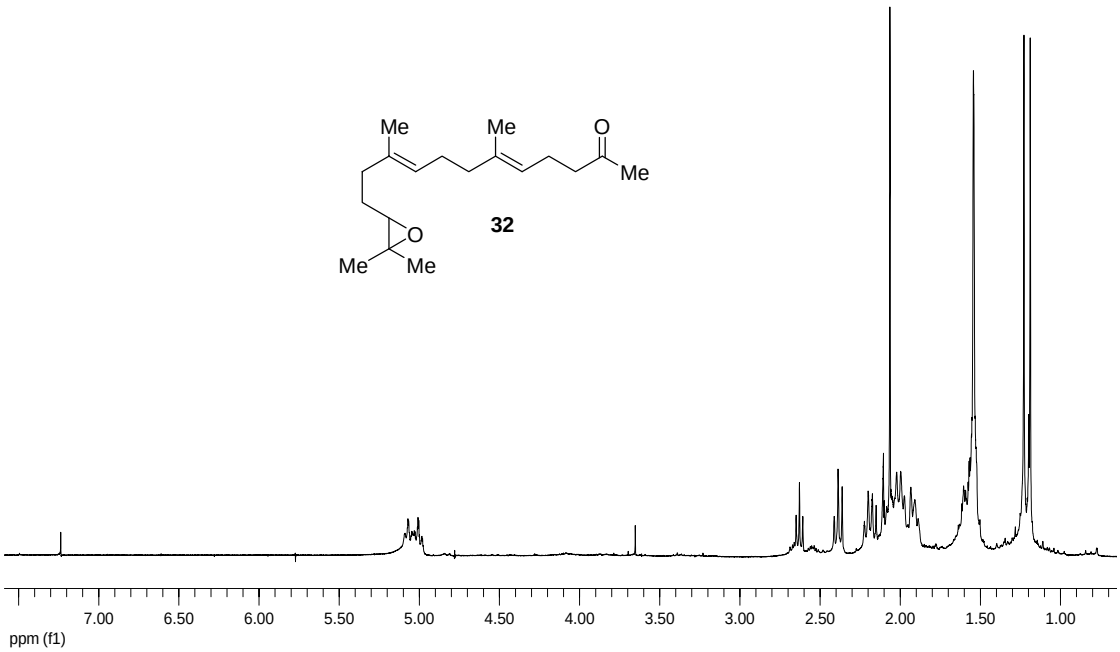
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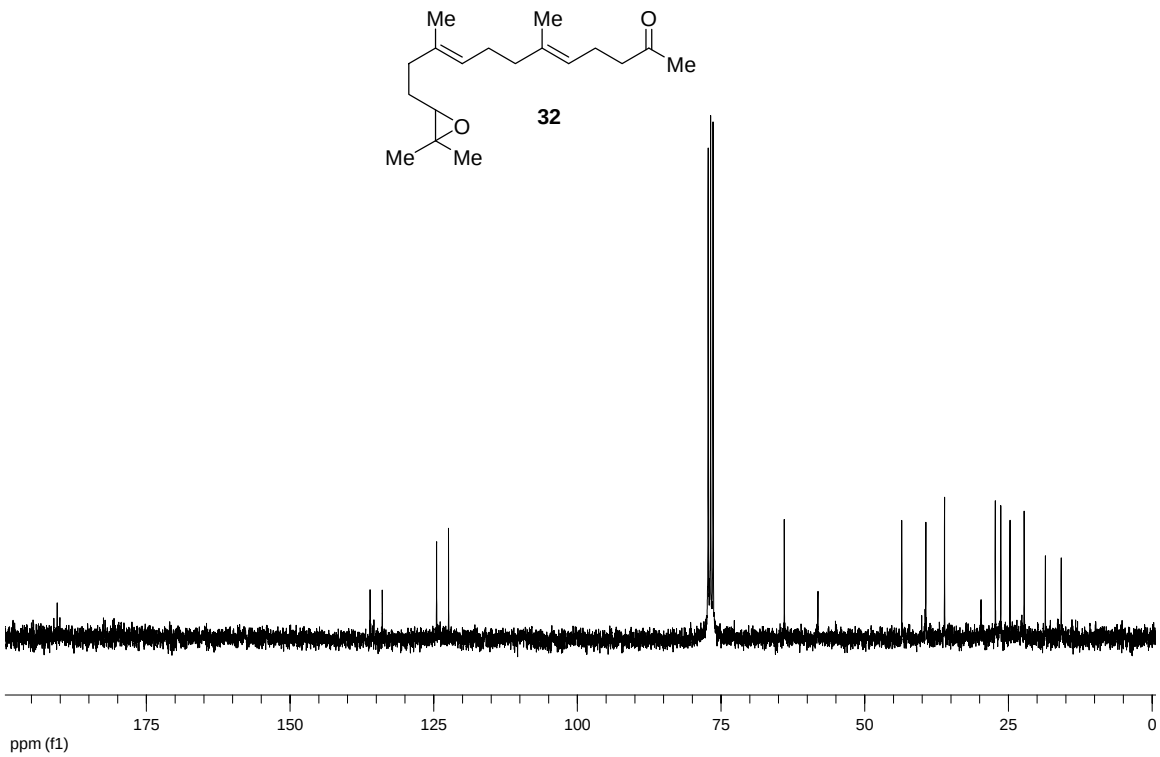
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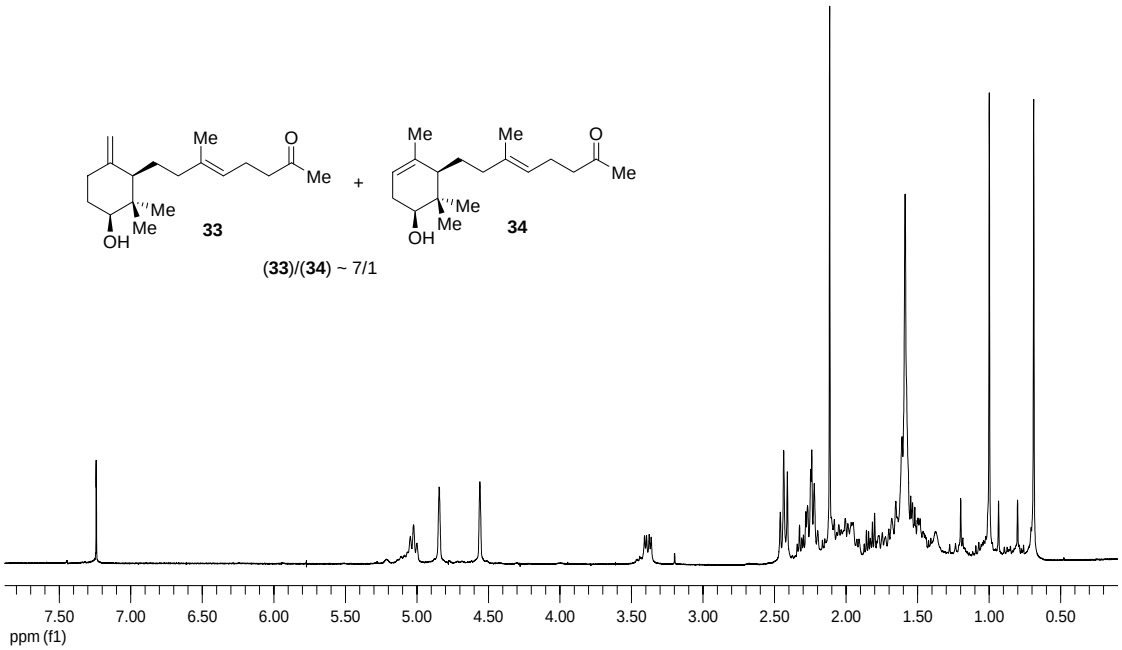
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Me
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+
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Me
O
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Me
Me
OH
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6.50
6.00
5.50
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4.00
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3.00
2.50
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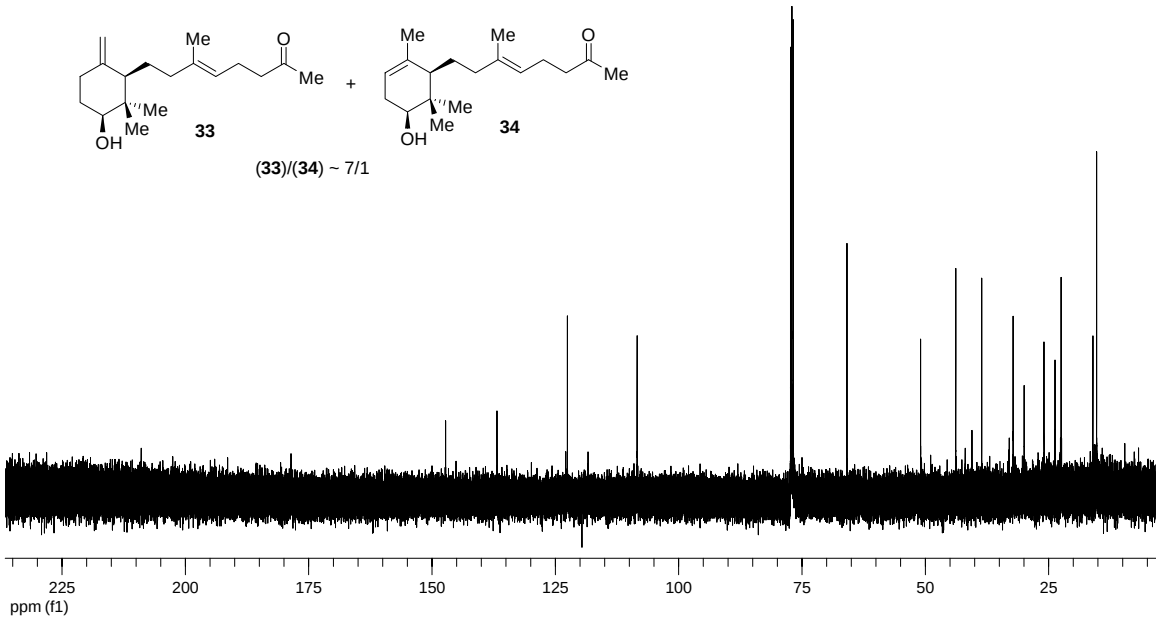
ppm (f1)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Me
Me
OH
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+
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Me
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Me
Me
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175
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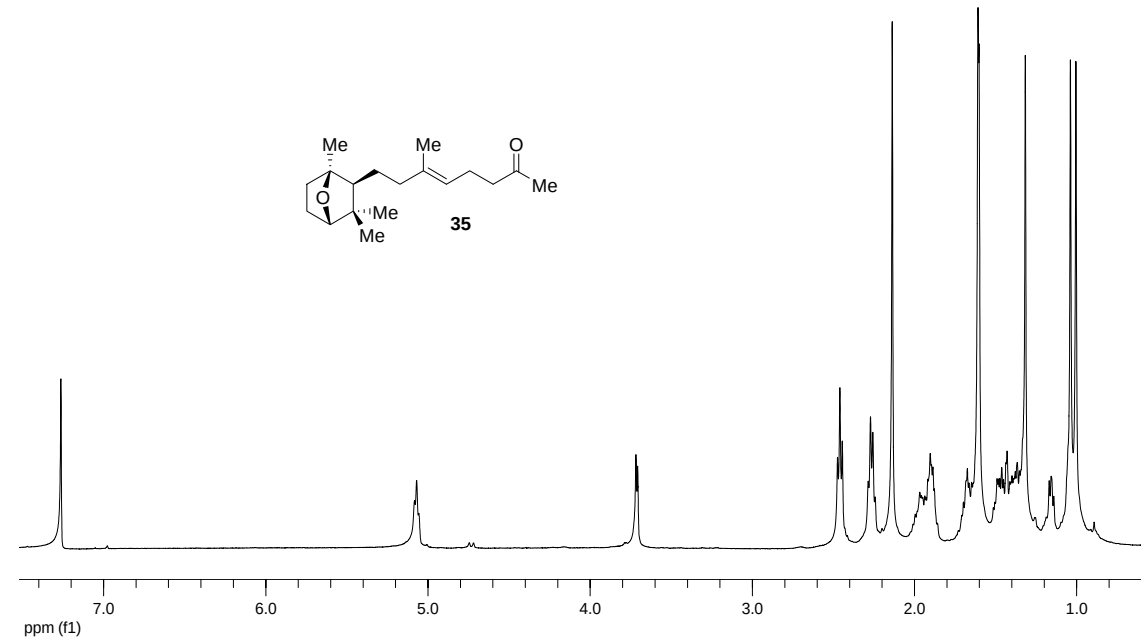
125
100
75
50
25
ppm (f1)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Me
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Me
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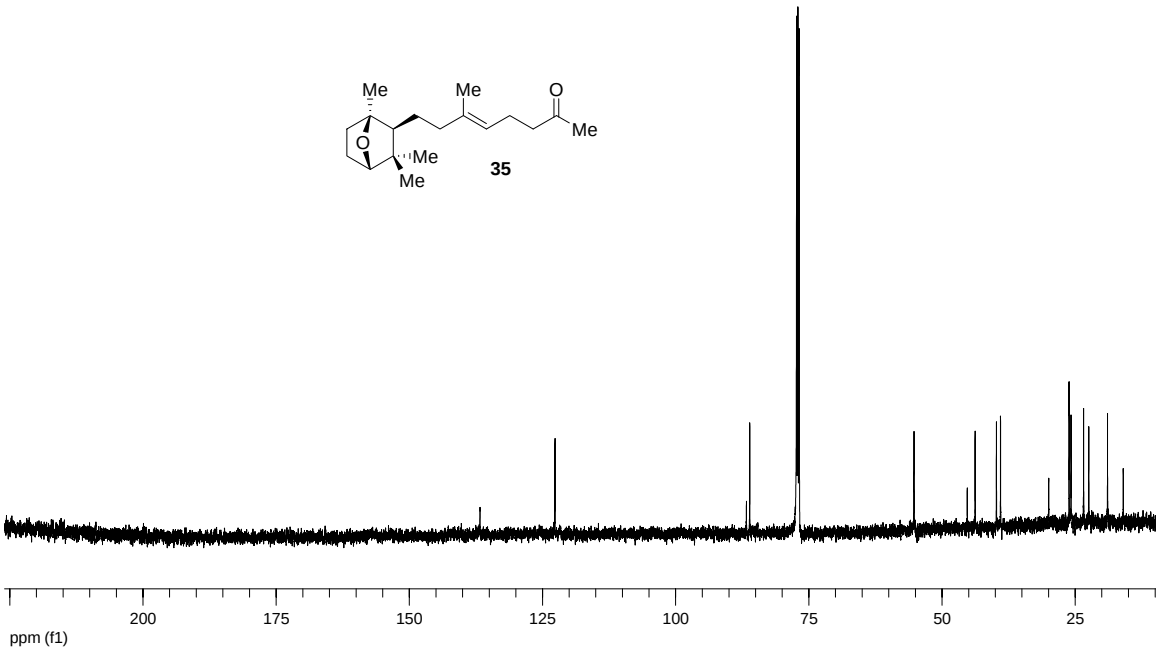
ppm (f1)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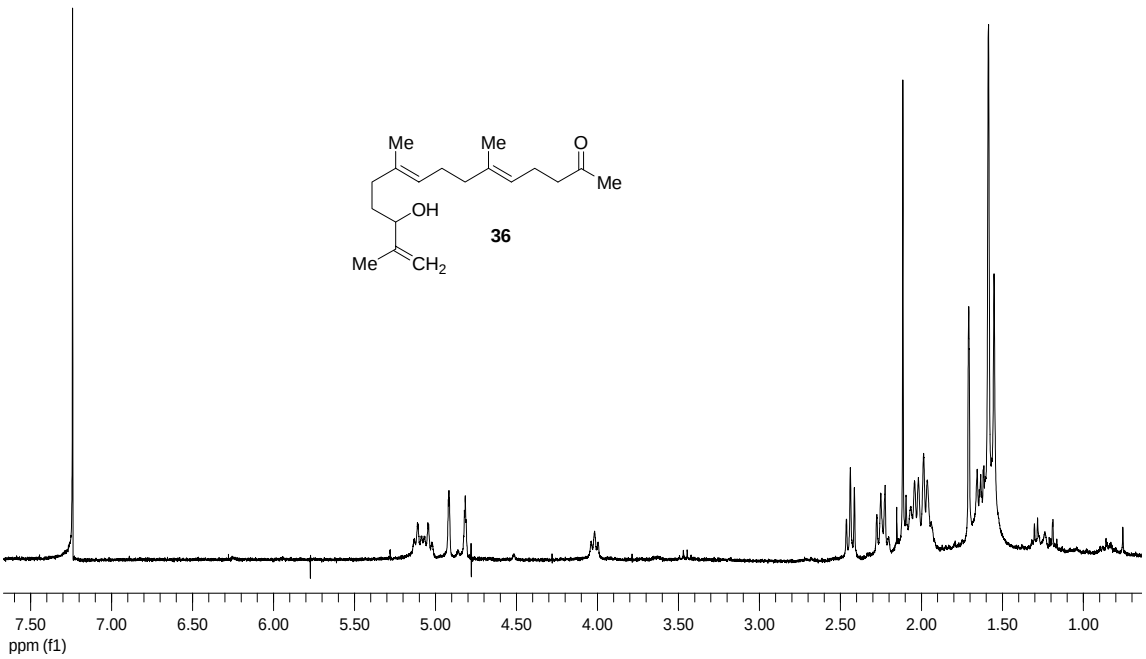
ppm (f1)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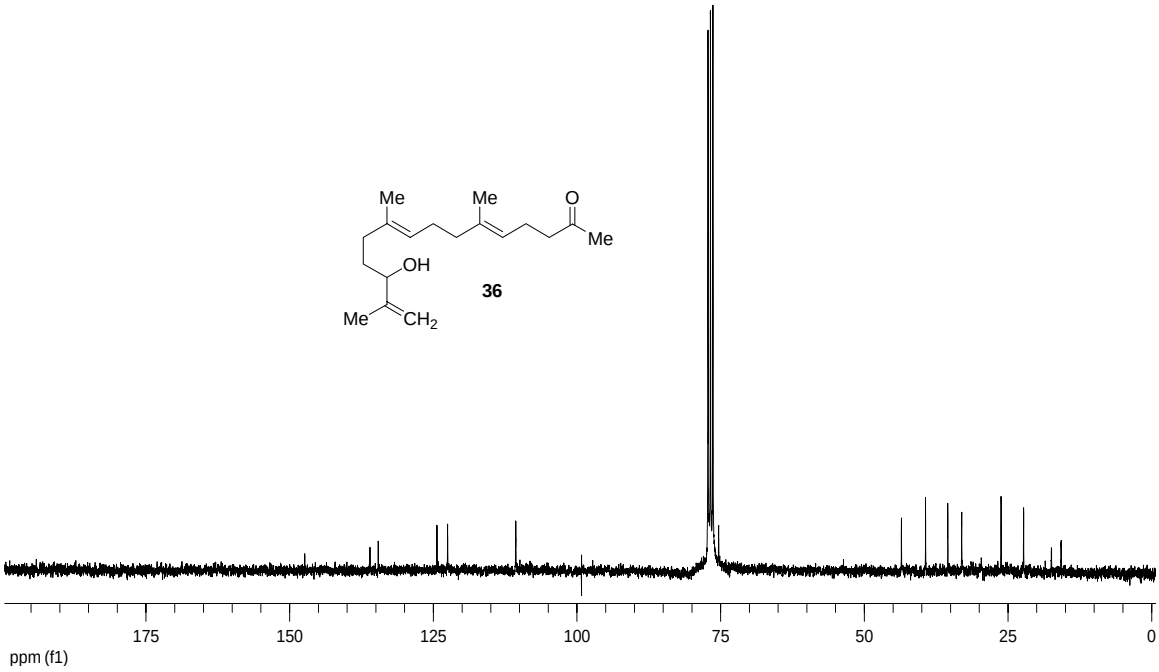
ppm (f1)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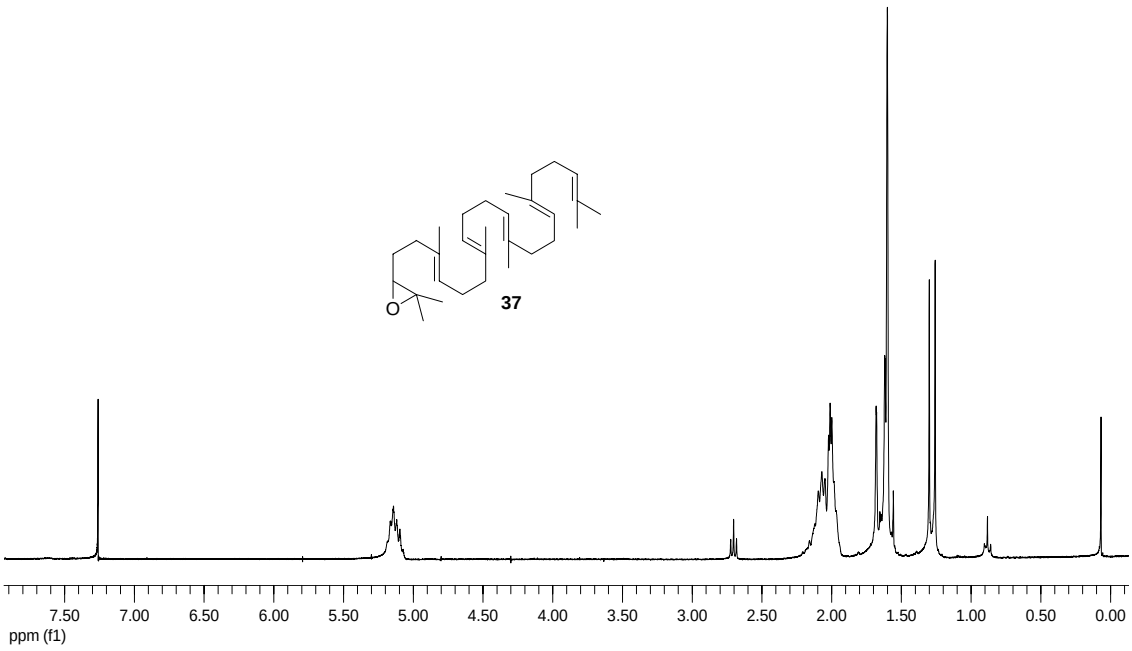
36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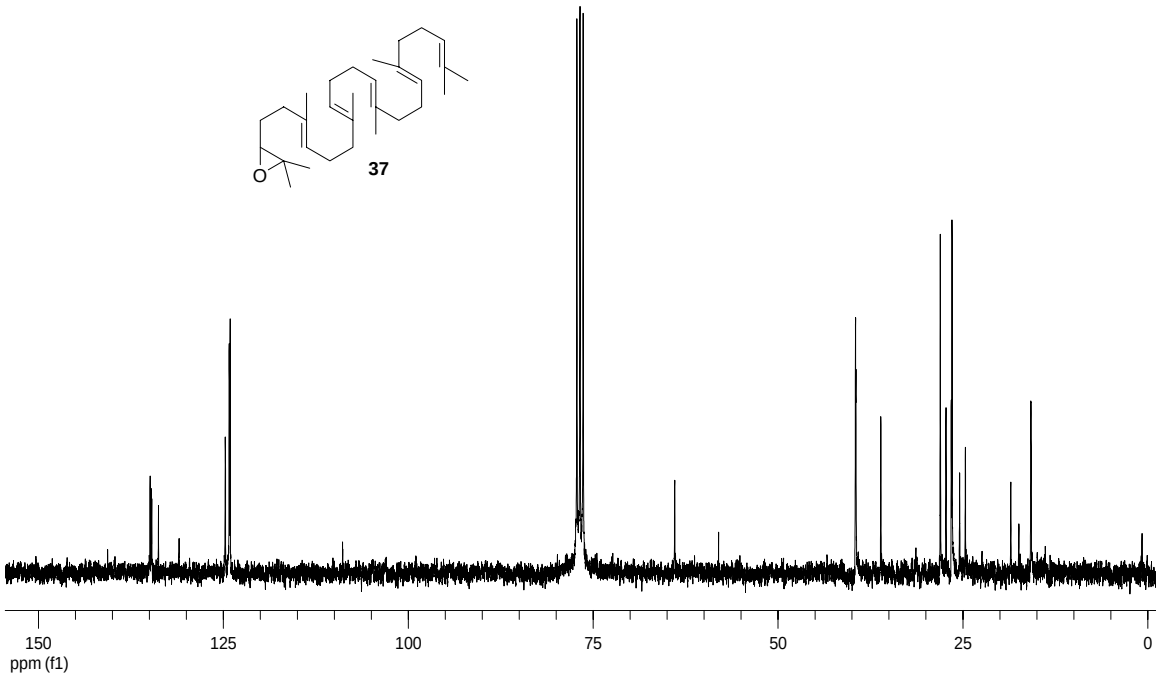
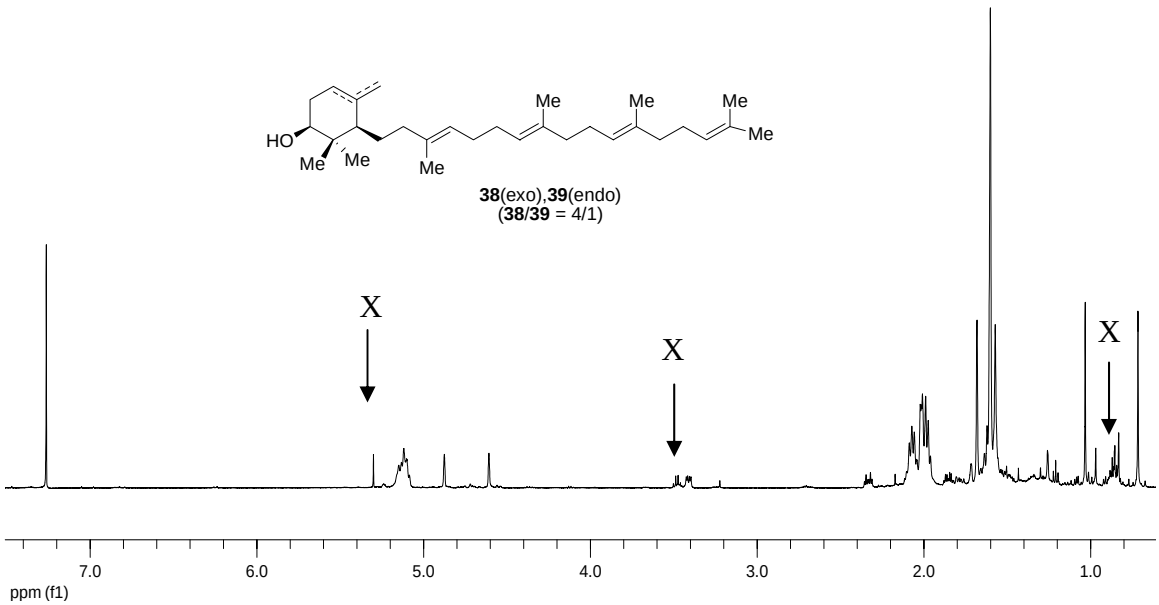
ppm (f1)

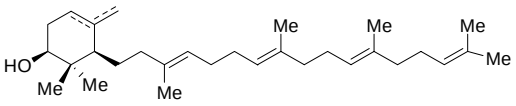
37



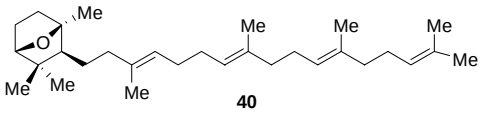


38(exo),**39**(endo)
(**38**/**39** = 4/1)

X = solvent



38(exo),**39**(endo)
(**38**/**39** = 4/1)



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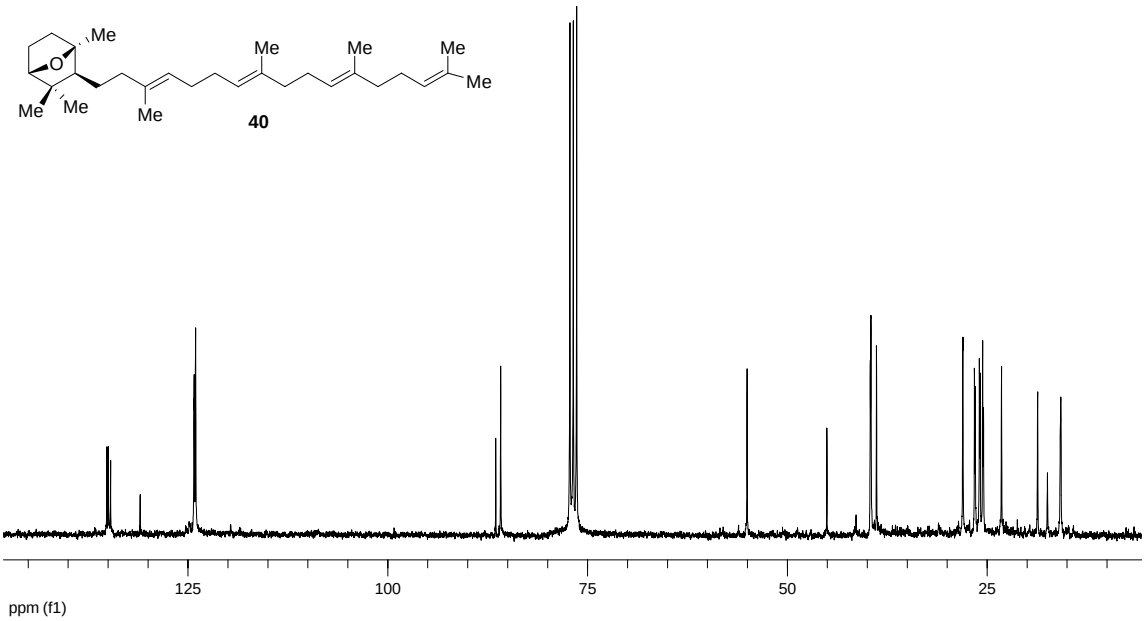
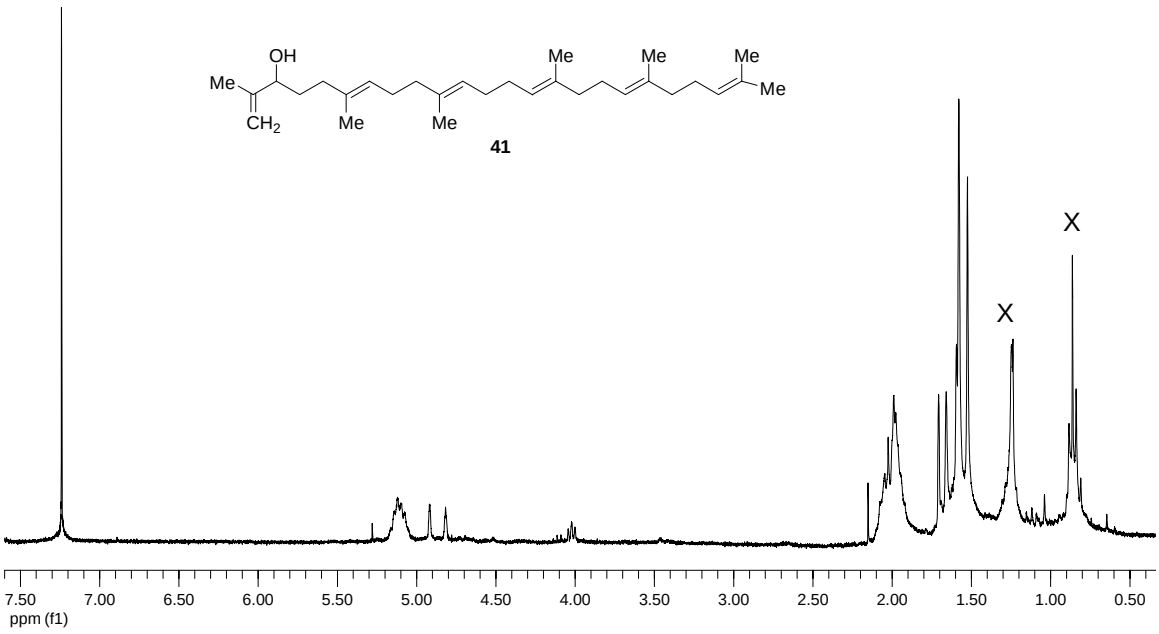
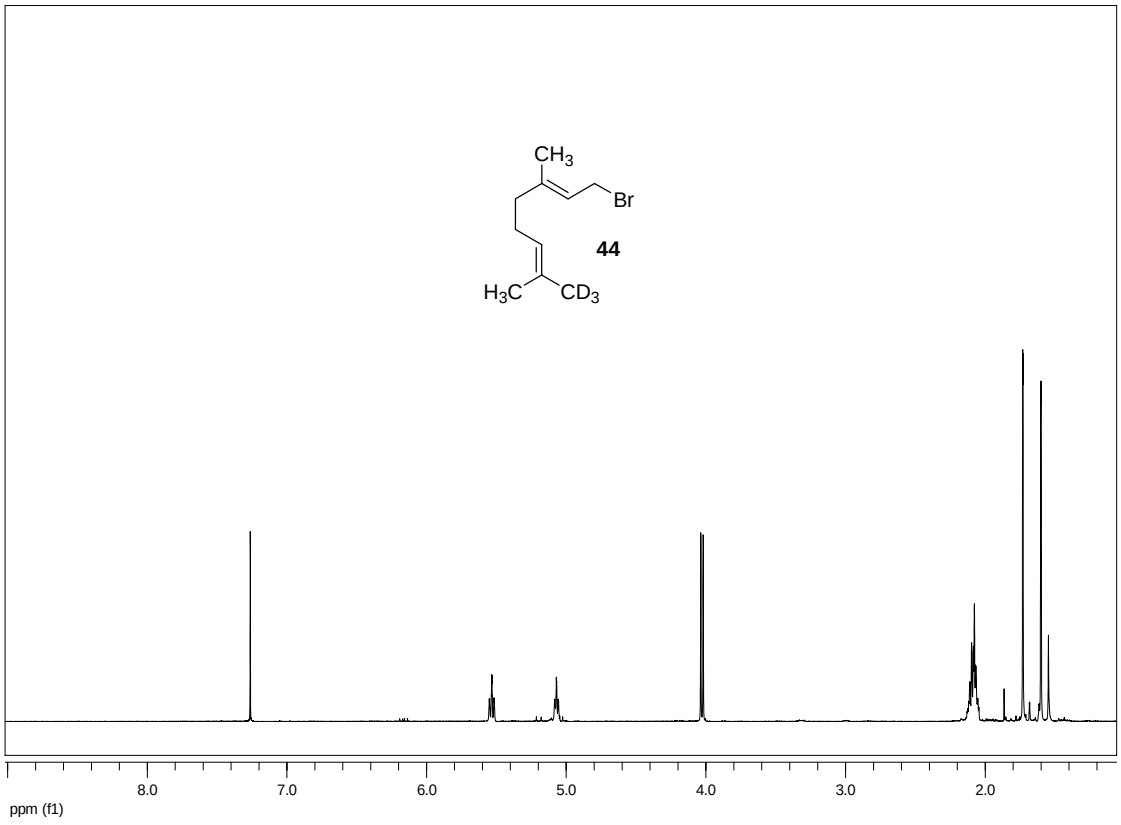




X = solvent (hexane)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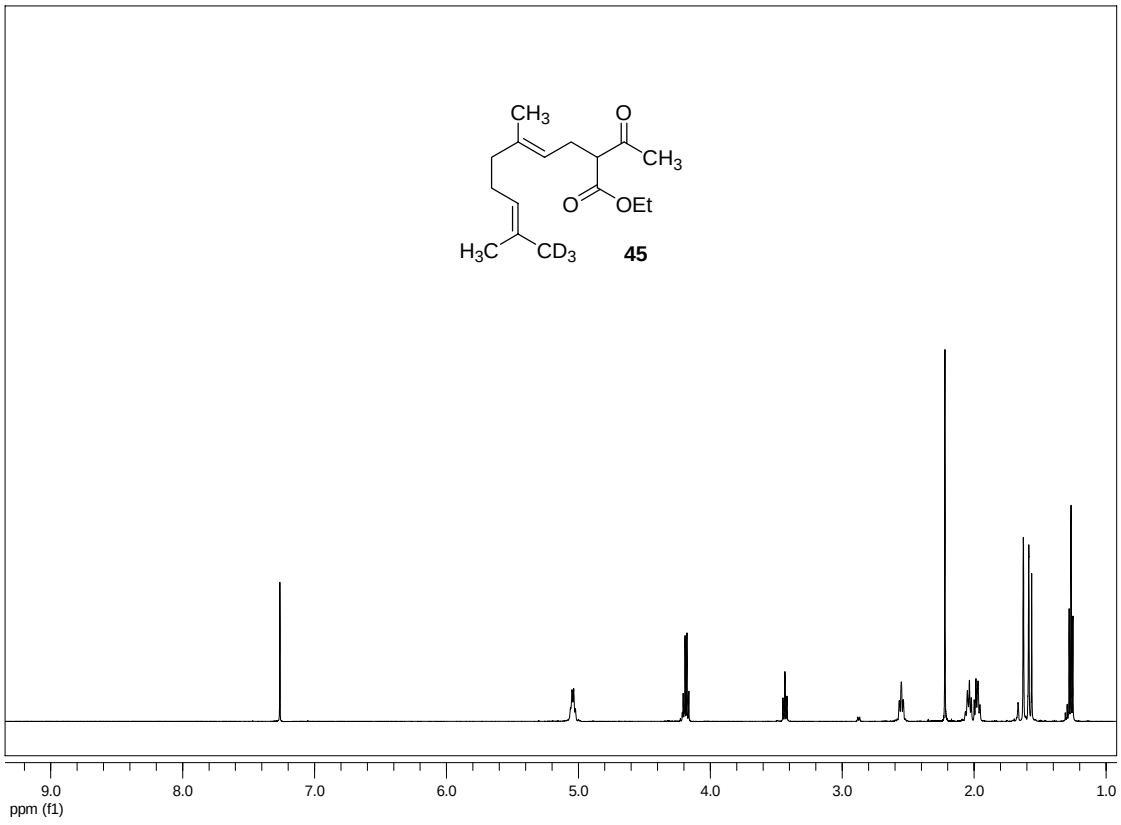
ppm (f1)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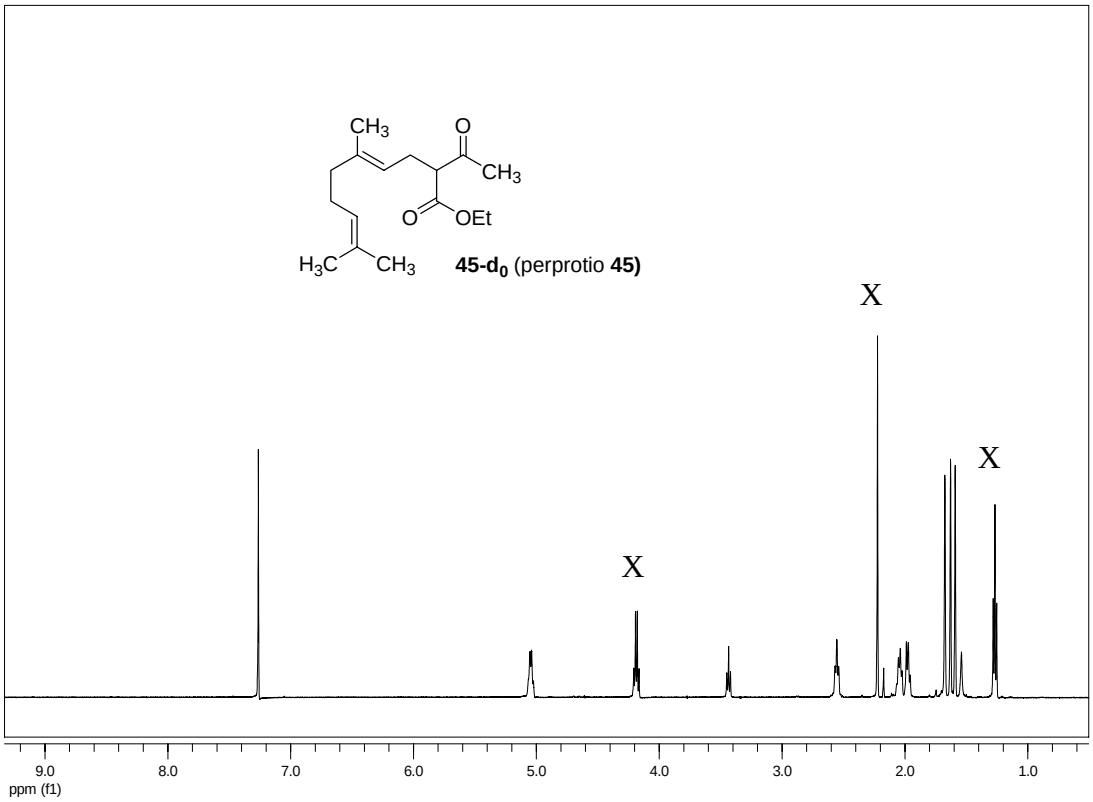

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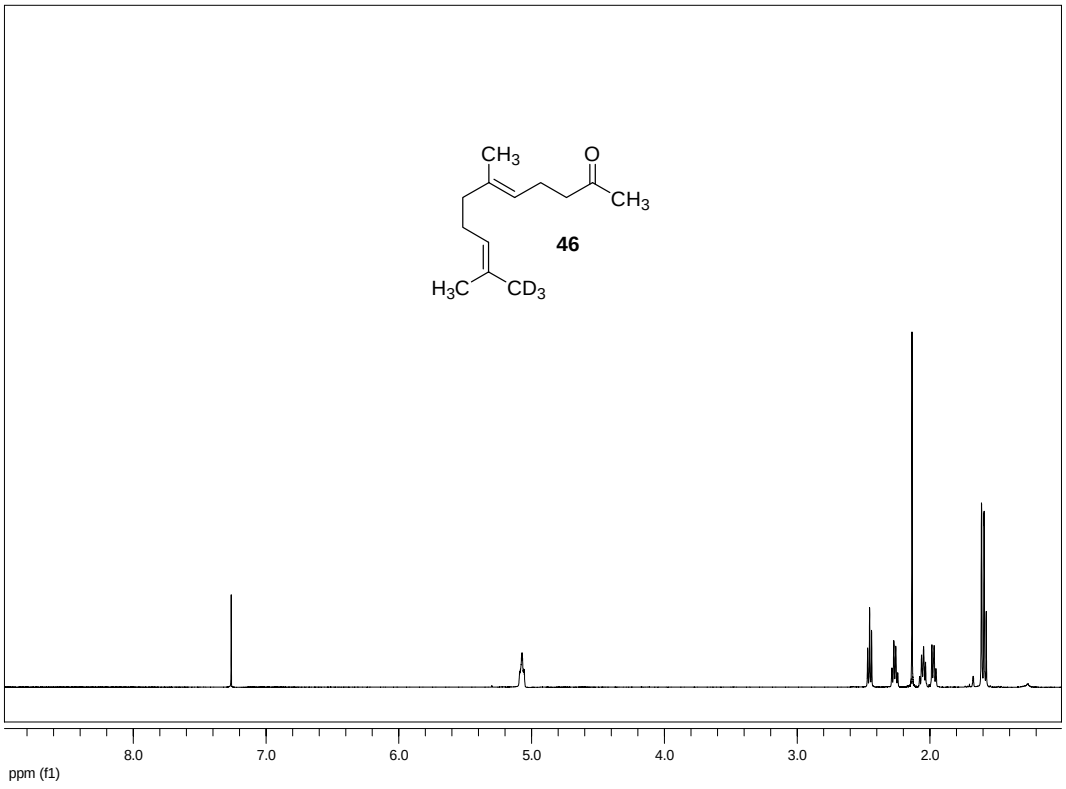

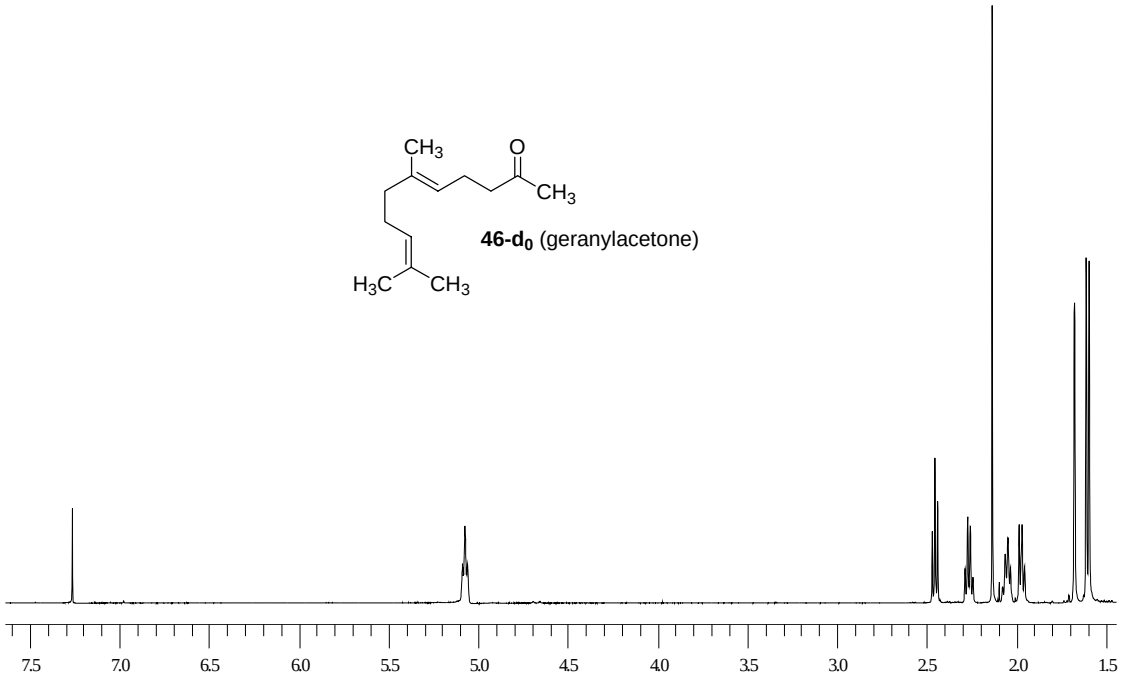

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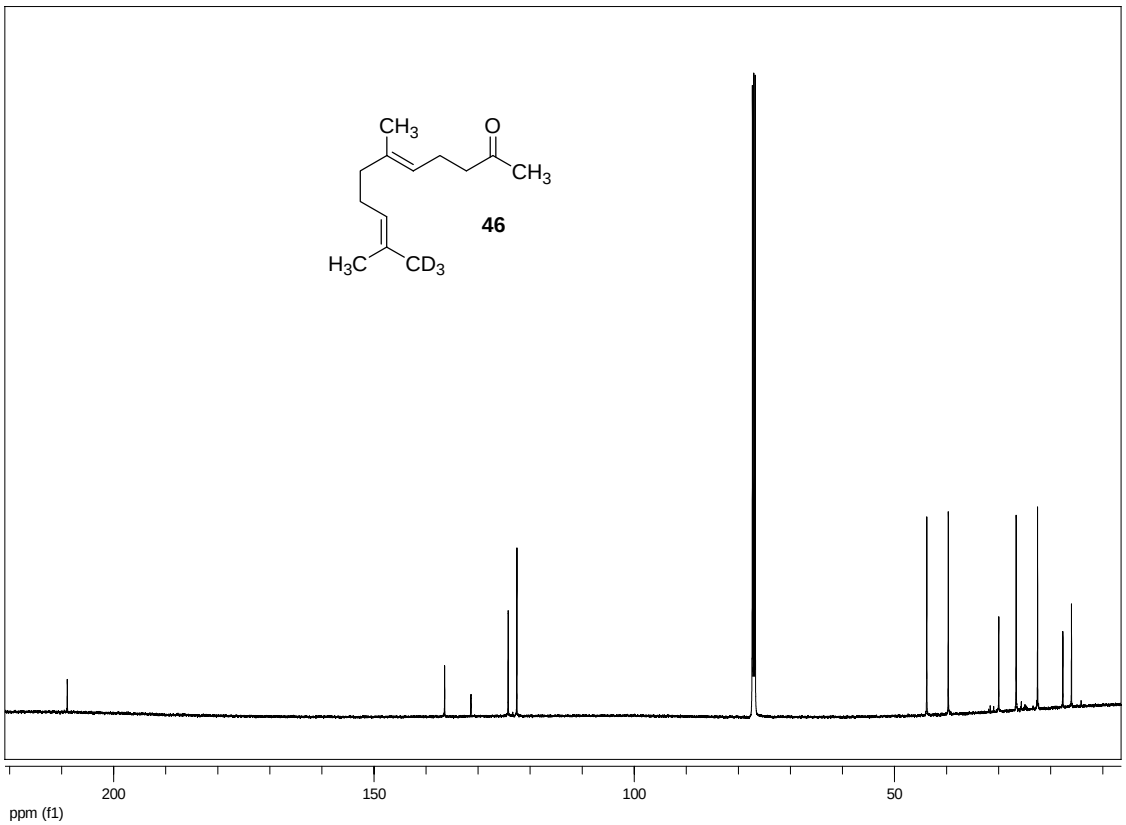

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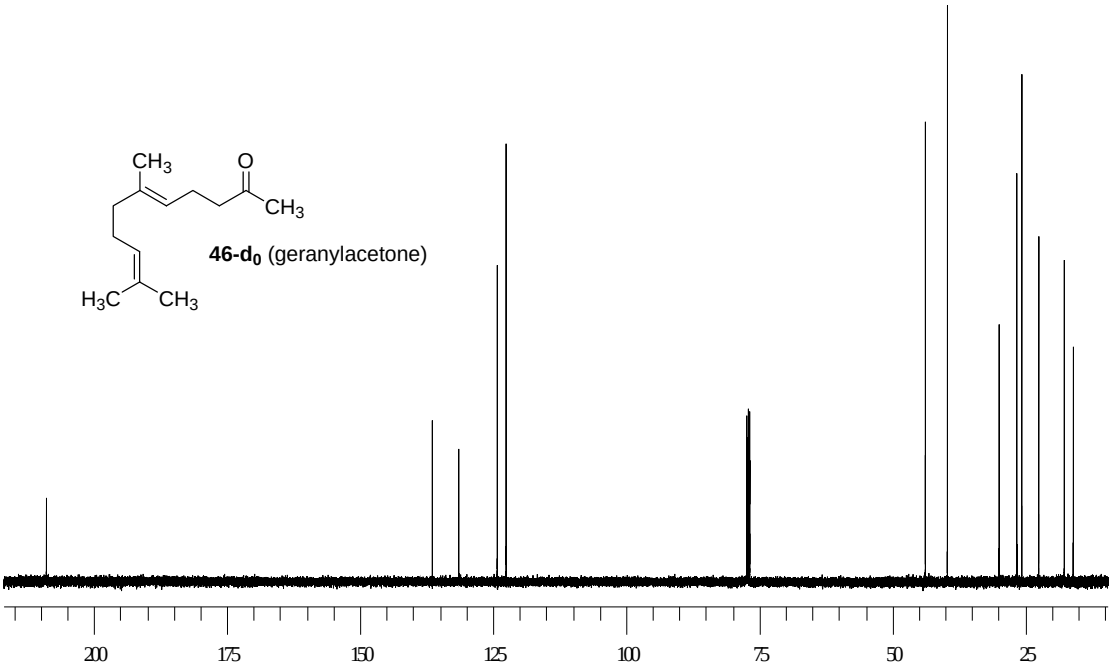

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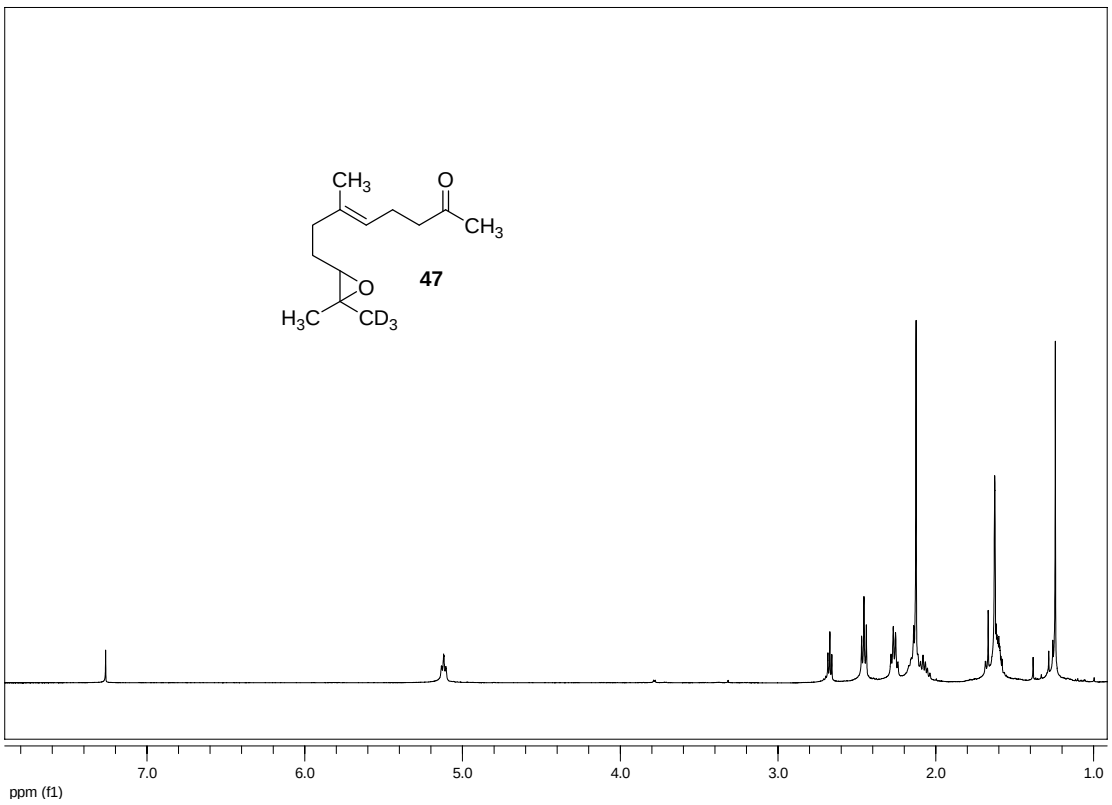

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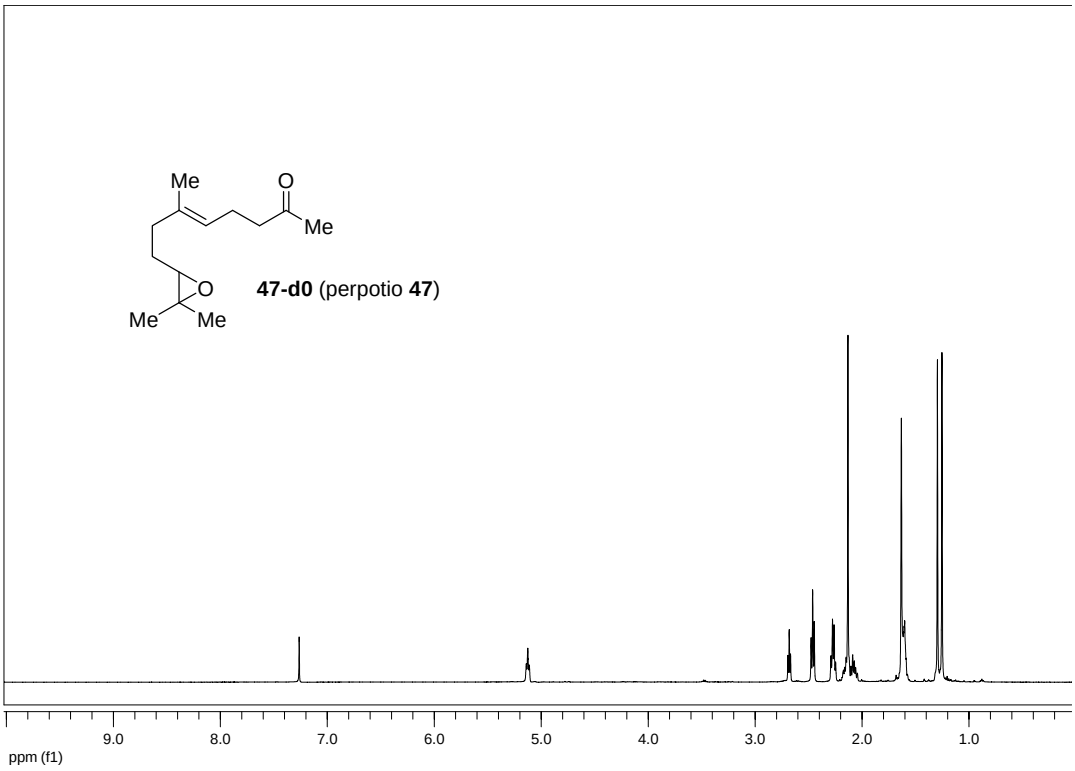
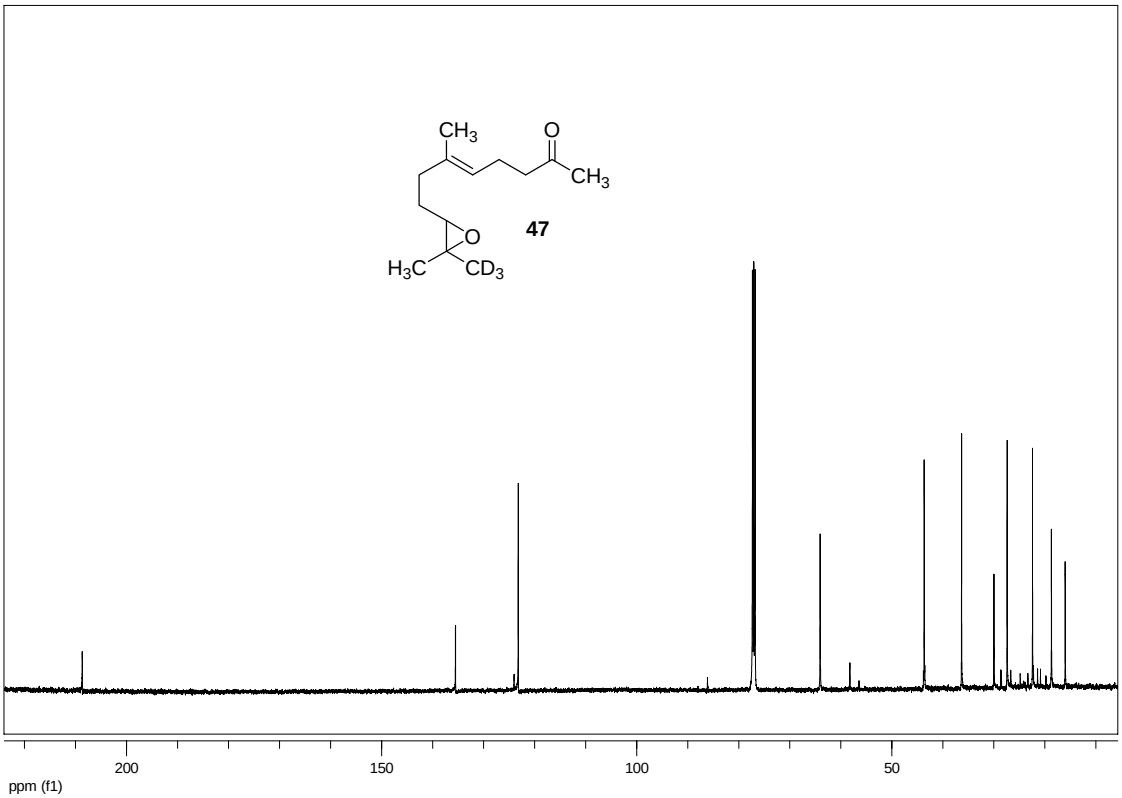
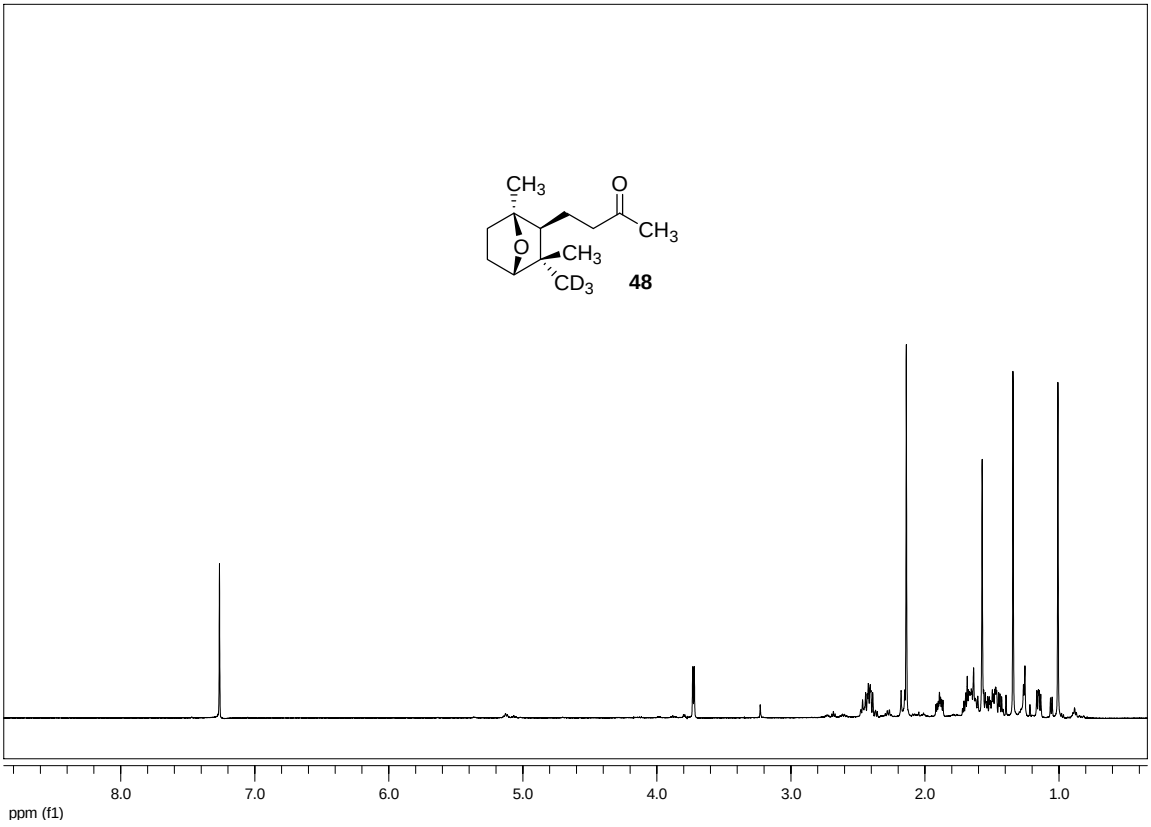
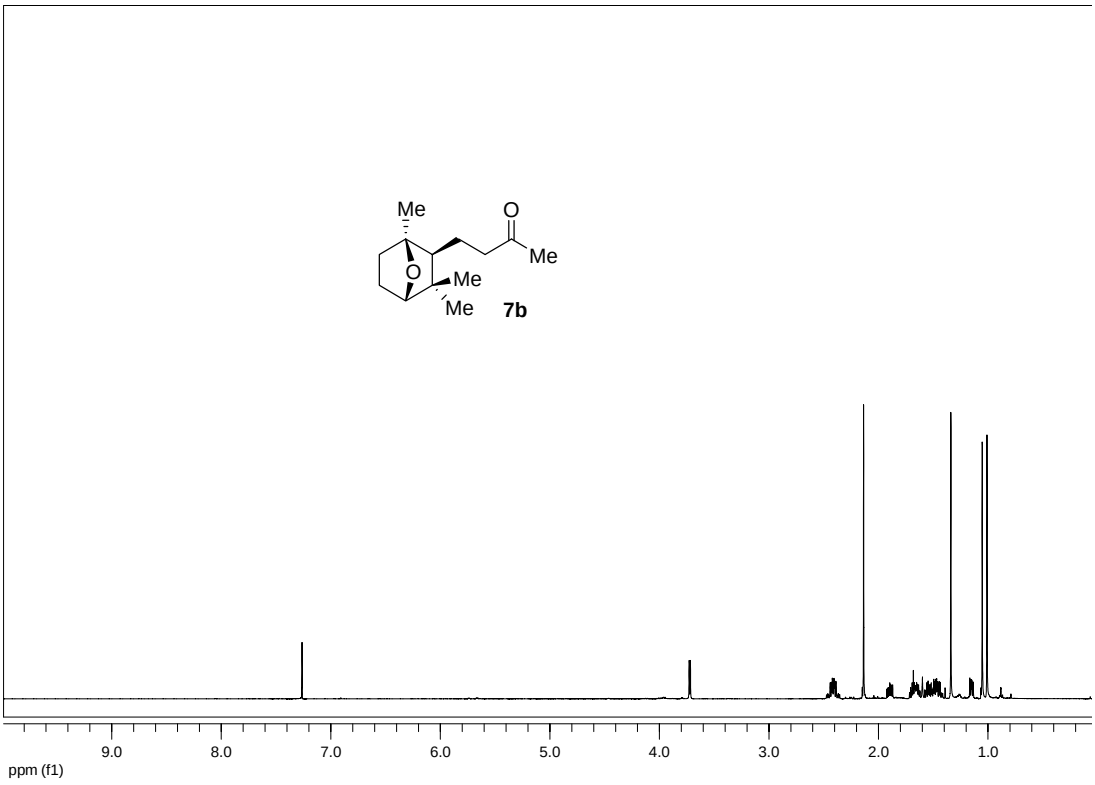


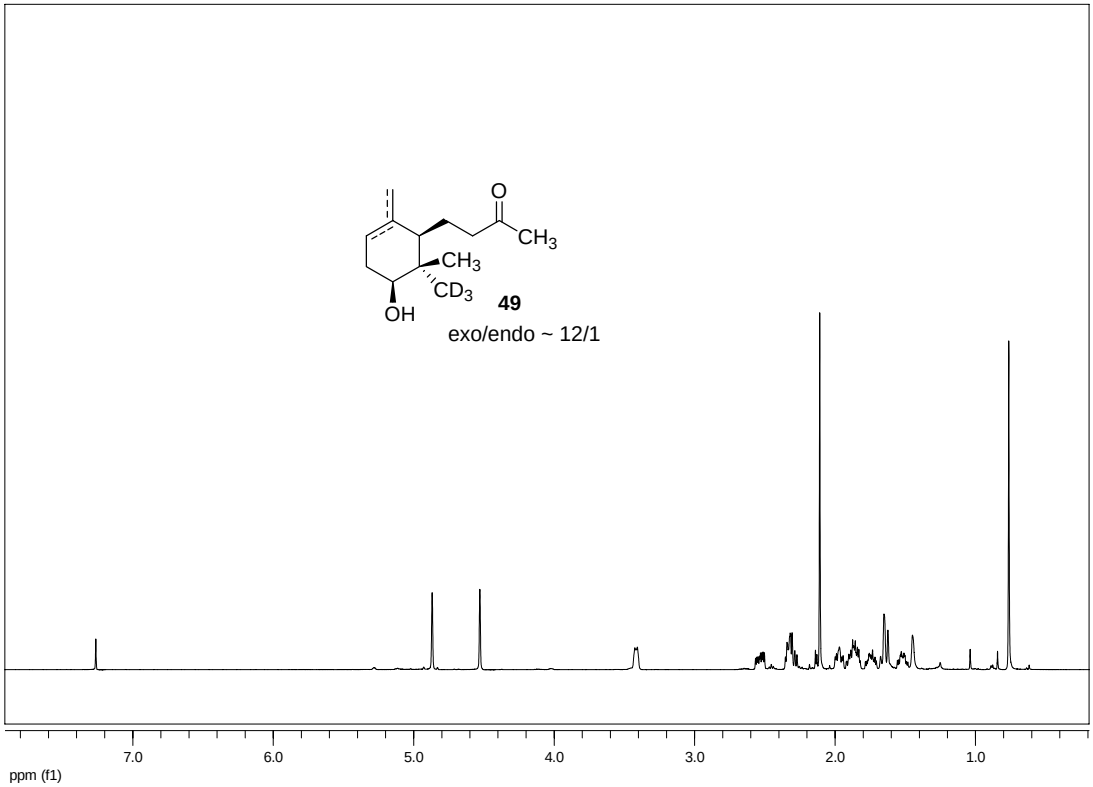
47-d0 (perpotio **47**)



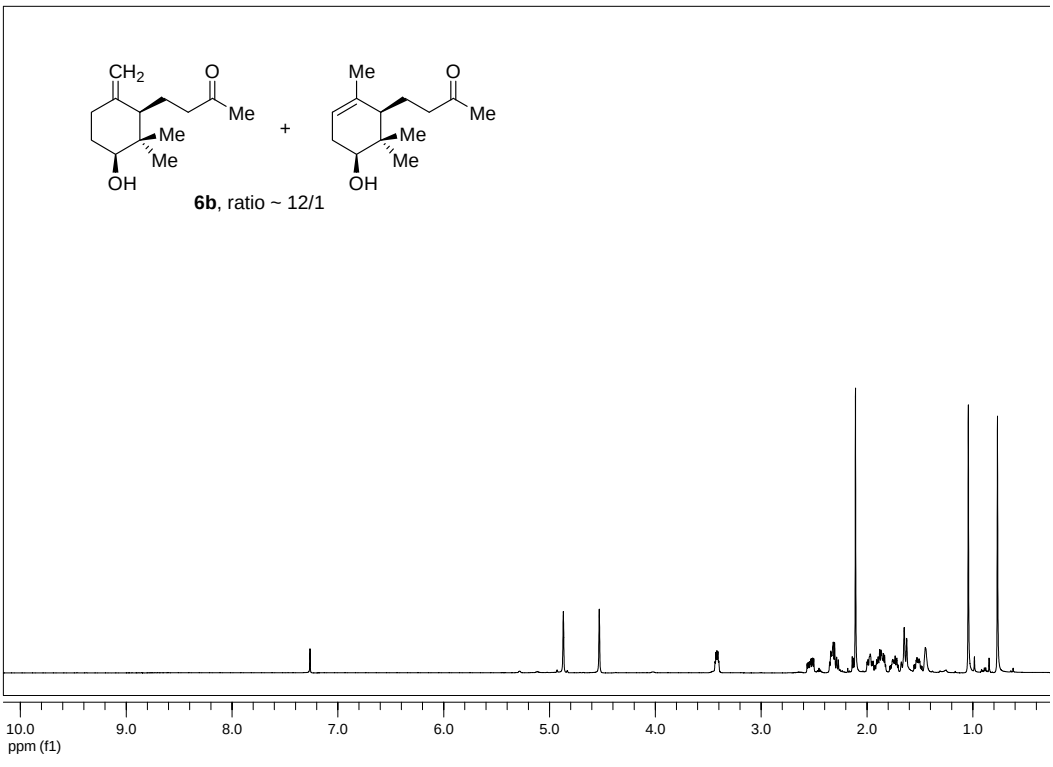
47


CH3
O
CH3
O
CH3
CD3
48
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

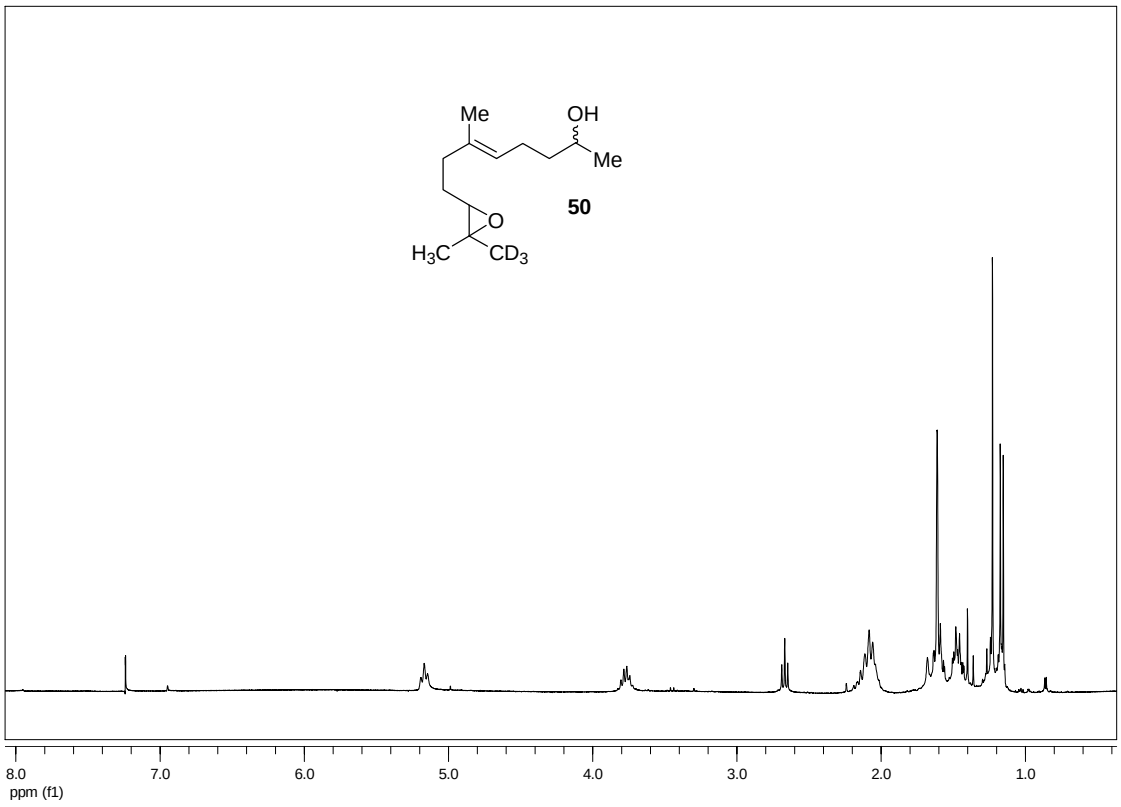

Me
O
Me
O
Me
Me
7b
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

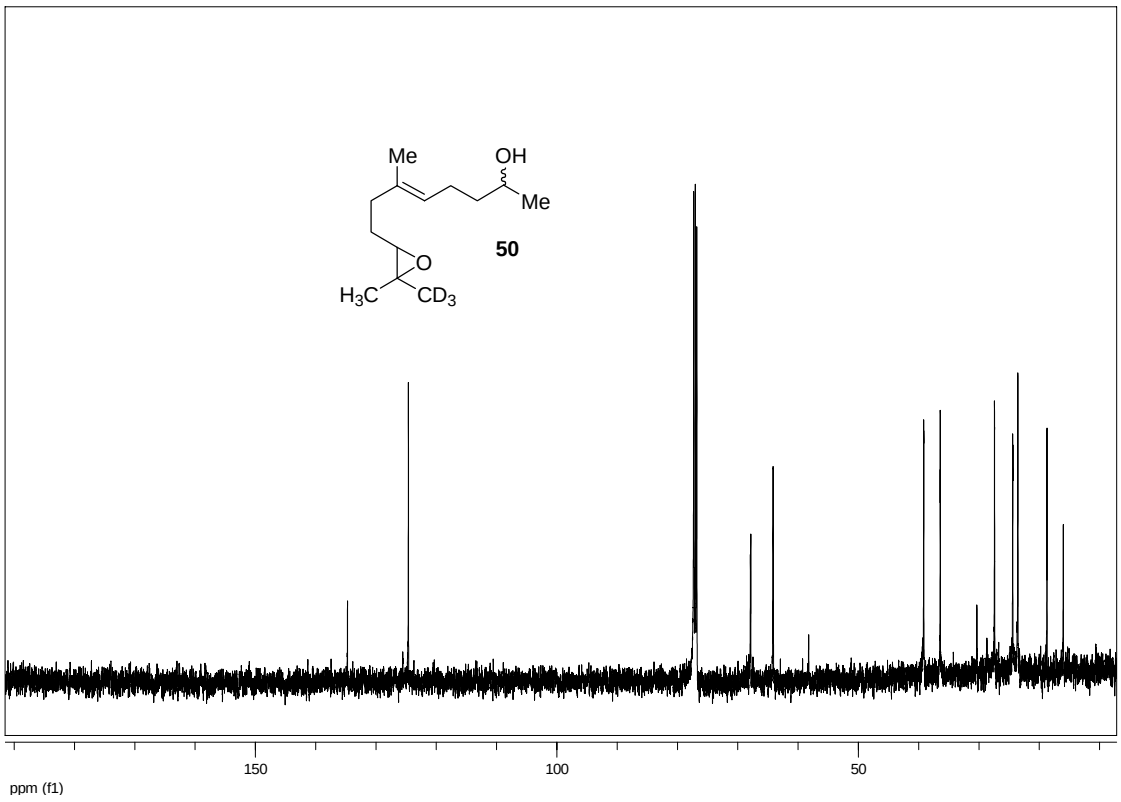


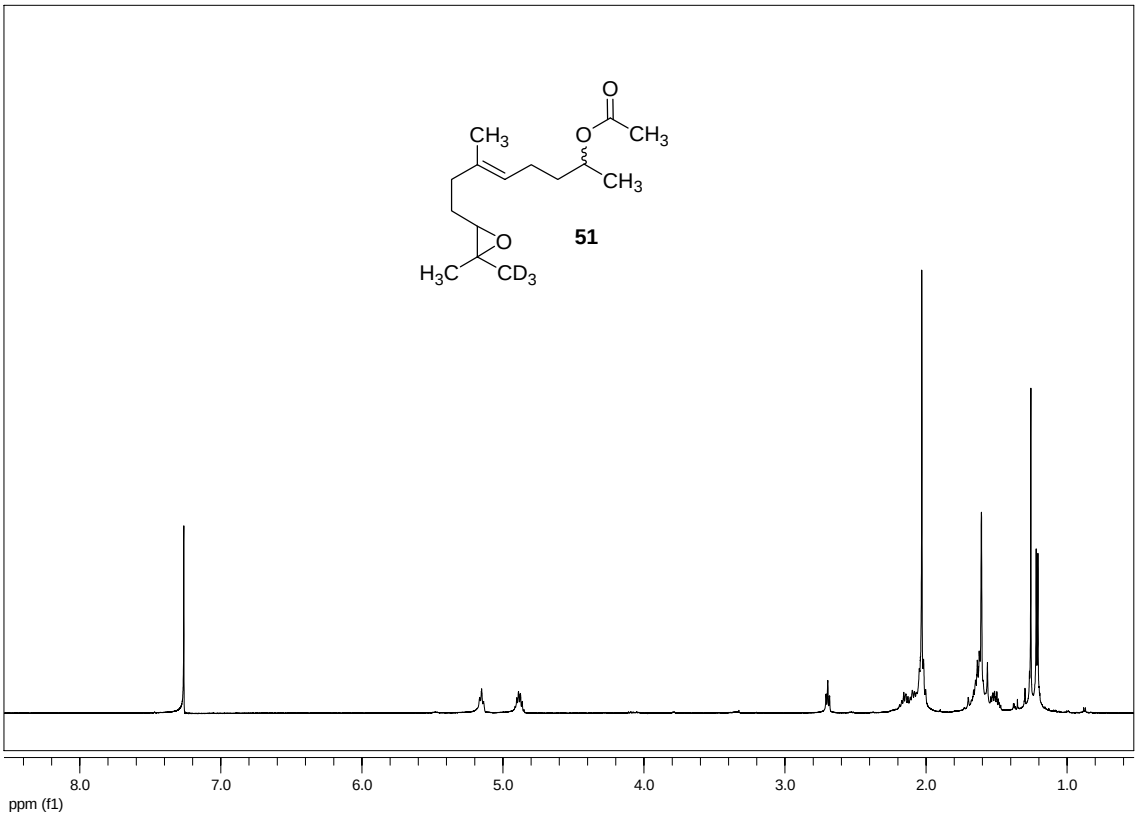
49
exo/endo ~ 12/1

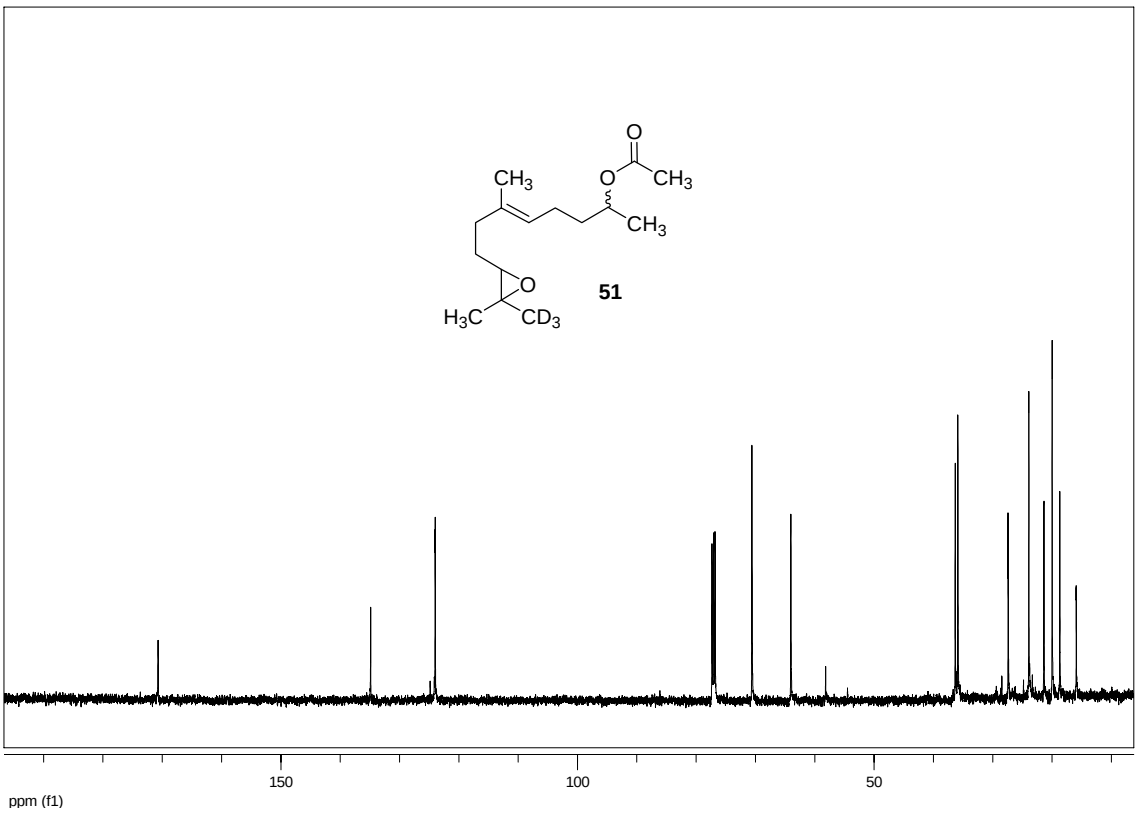


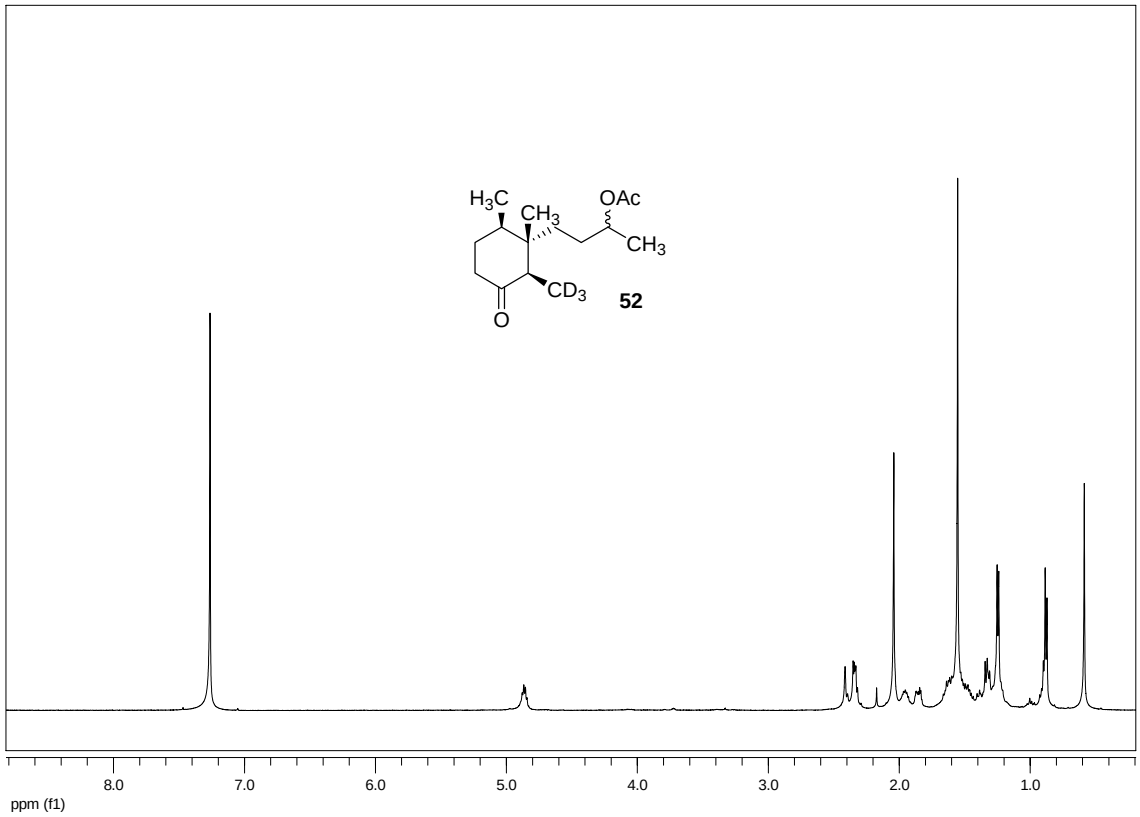
6b, ratio ~ 12/1


Me
OH
Me
50
O
H3C
CD3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


Me
OH
Me
50
O
H3C
CD3
150
100
50
ppm (f1)


O
CH3
O
CH3
CH3
O
51
H3C
CD3
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


O
CH3
O
CH3
CH3
O
51
H3C
CD3
150
100
50
ppm (f1)



^{1}H NMR spectra of **9c** and **52** in the region 0.5-1.5 ppm