

Stereocontrolled First Total Syntheses of Amarouciaxanthin A and B

Yumiko Yamano, Mahankhali Venu Chary, and Akimori Wada*

*Department of Organic Chemistry for Life Science, Kobe Pharmaceutical University,
4-19-1, Motoyamakita-machi, Higashinada-ku, Kobe 658-8558, Japan*

E-mail: y-yamano@kobepharm-u.ac.jp

NMR and CD spectra



14

^1H NMR

4.2 3.2 1.9 1.7 1.3 1.1 0.6

1.00 1.00 1.99 1.99 3.00 1.00 1.00

4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm



14

^{13}C NMR

217.860

77.410
77.000
76.575

66.376

48.013
44.886
43.854

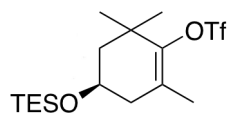
35.295

28.415
26.371

14.548

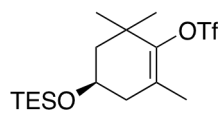
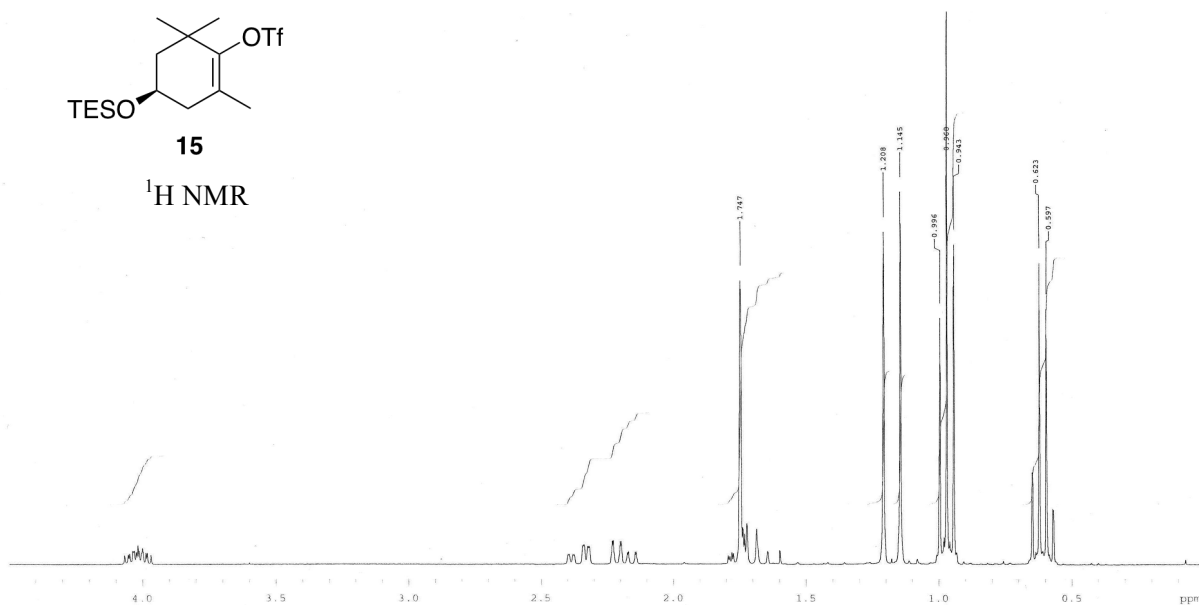
4.854
0.778

ppm



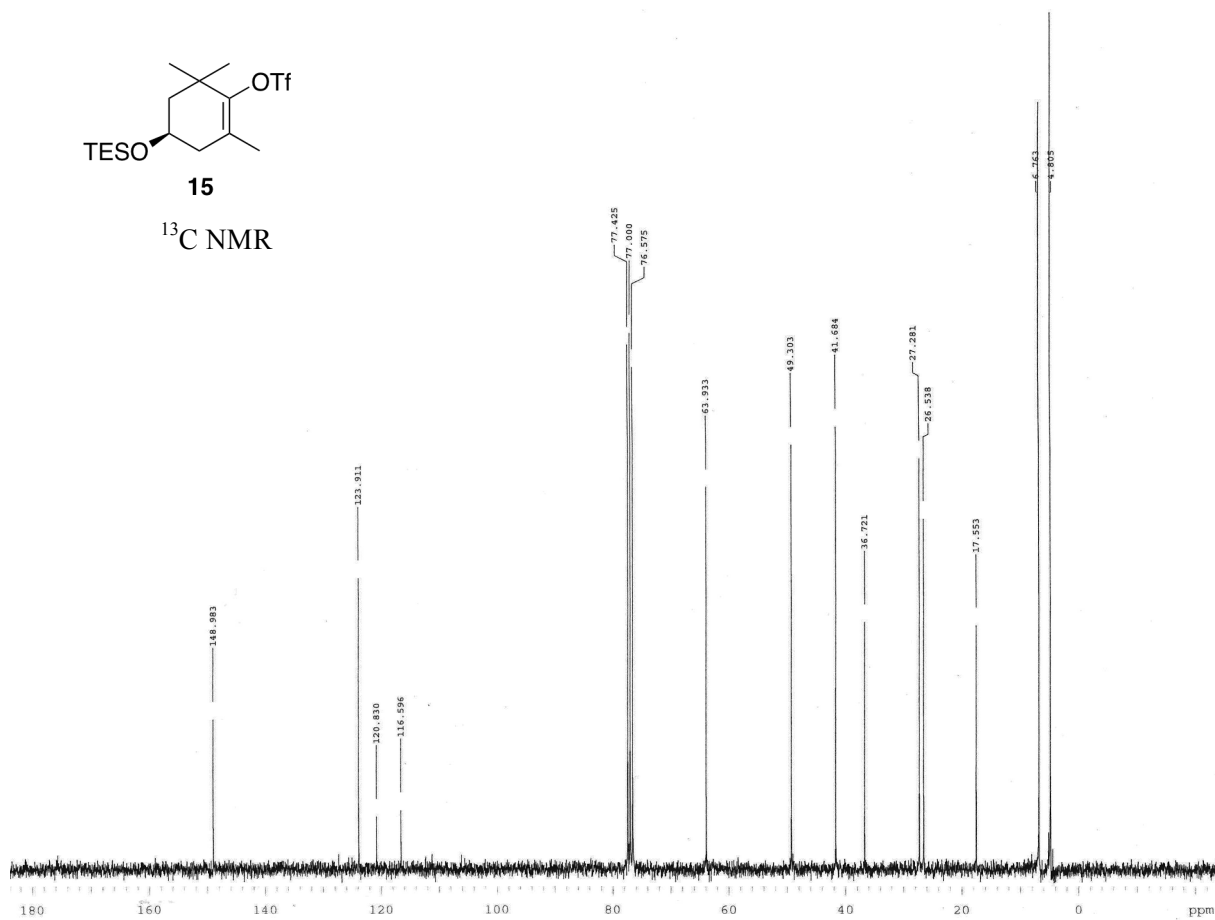
15

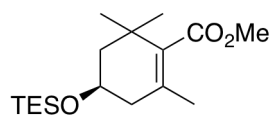
¹H NMR



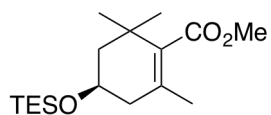
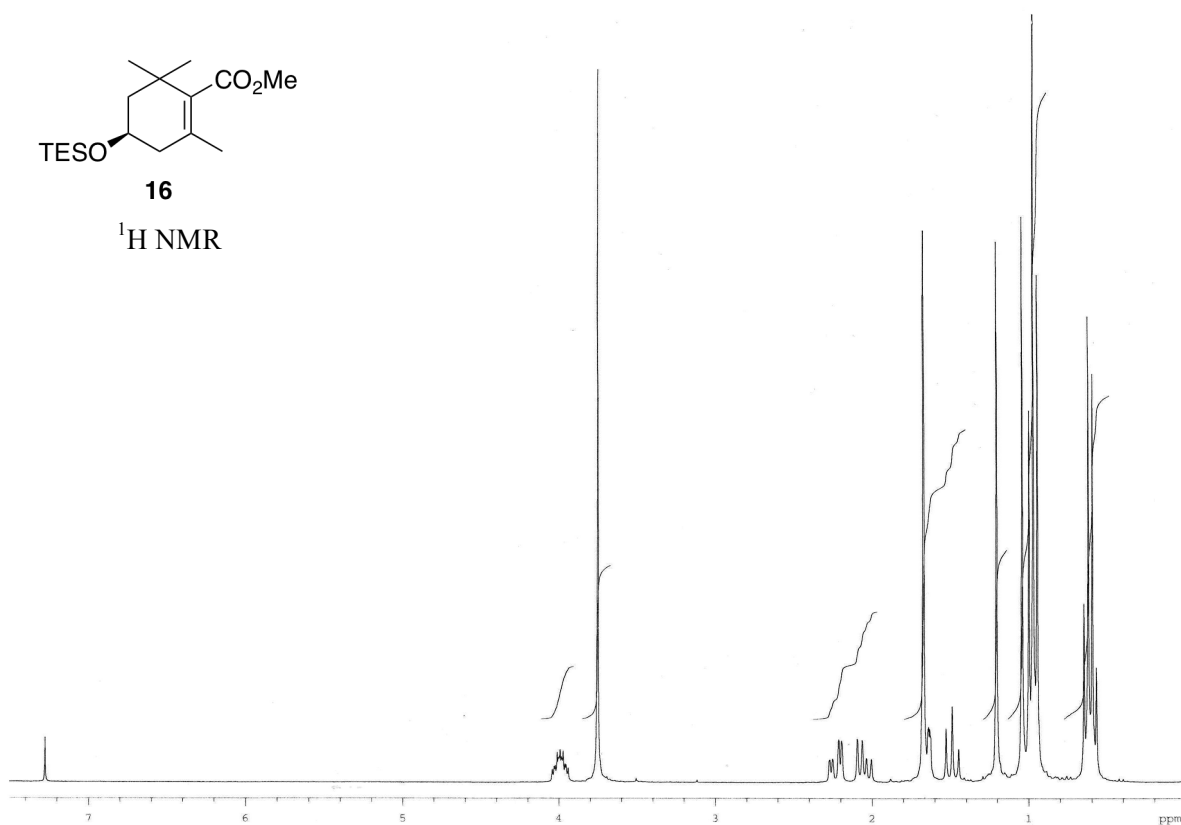
15

¹³C NMR

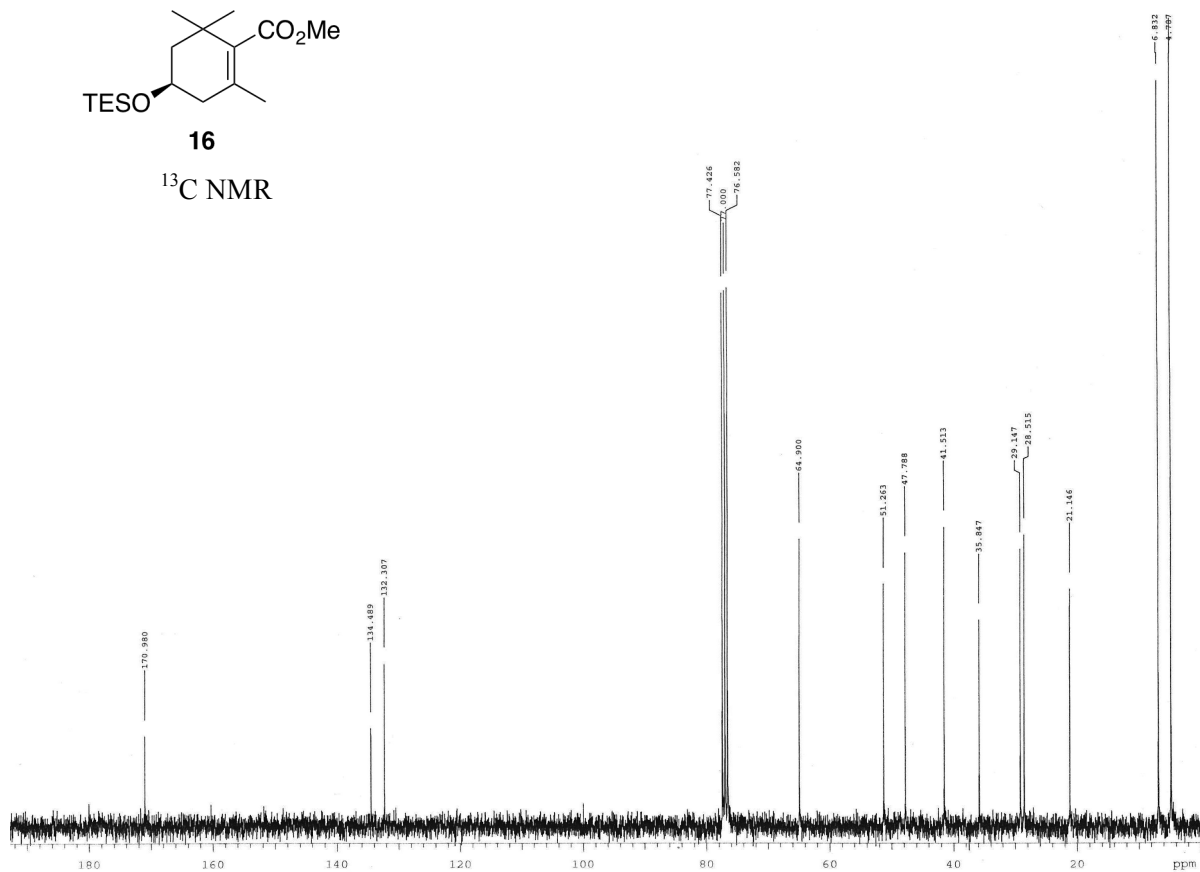


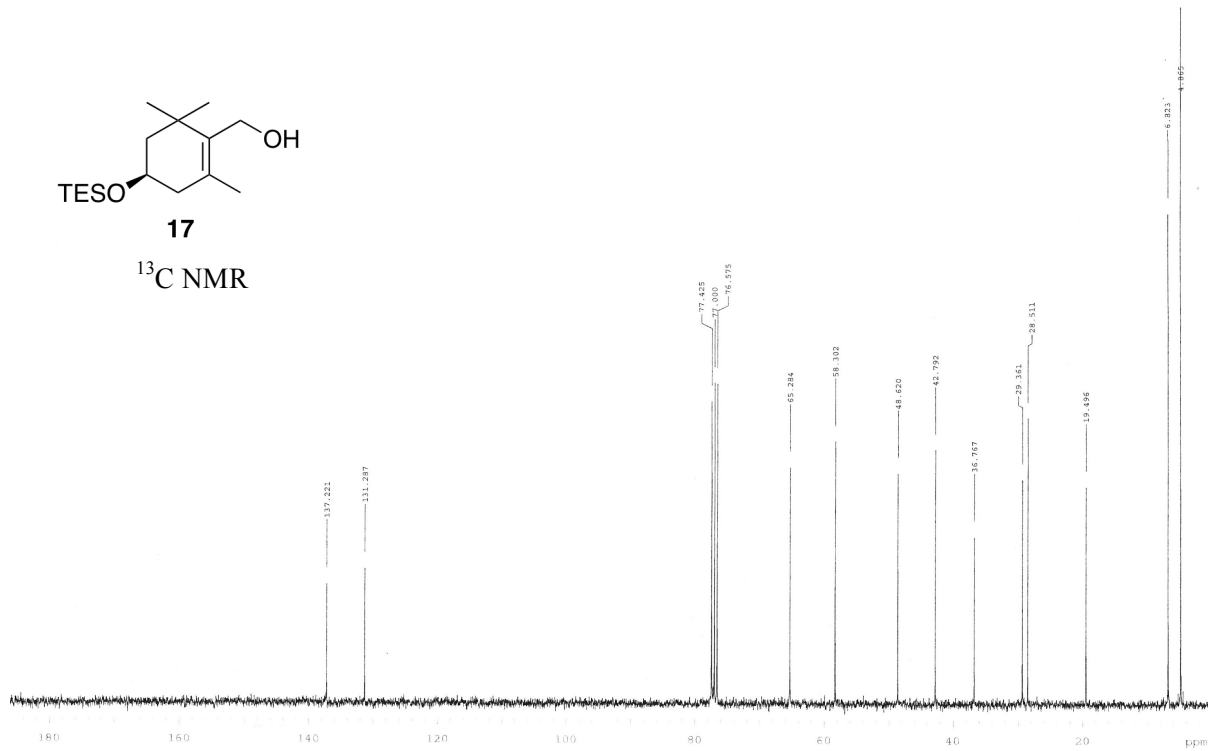
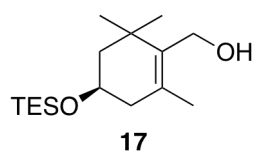


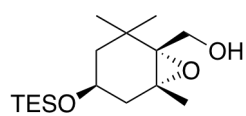
16
¹H NMR



16
¹³C NMR



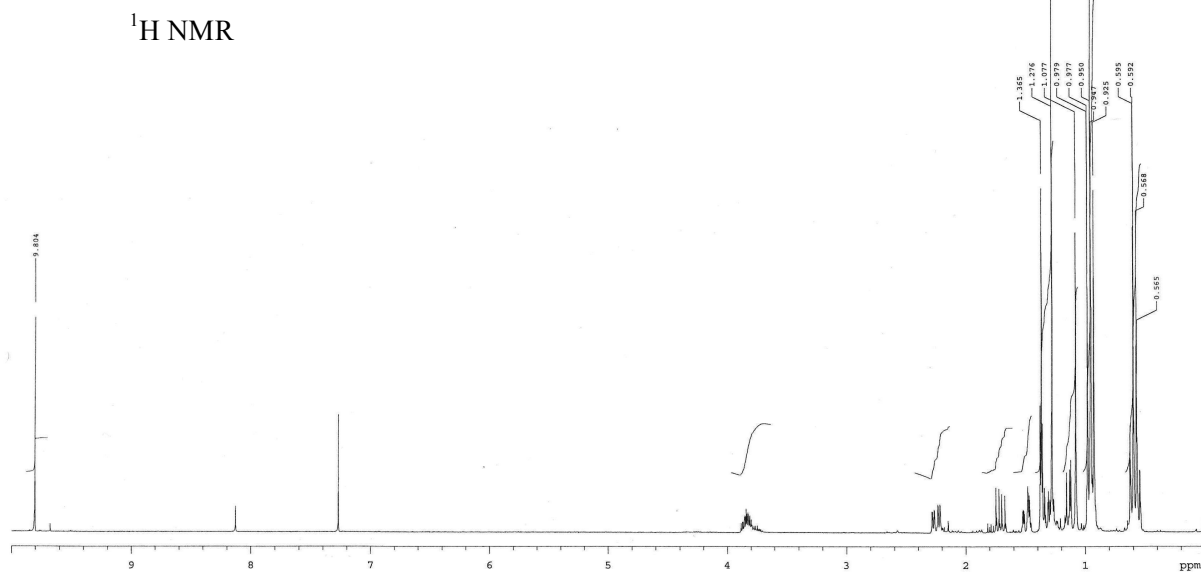


¹H NMR

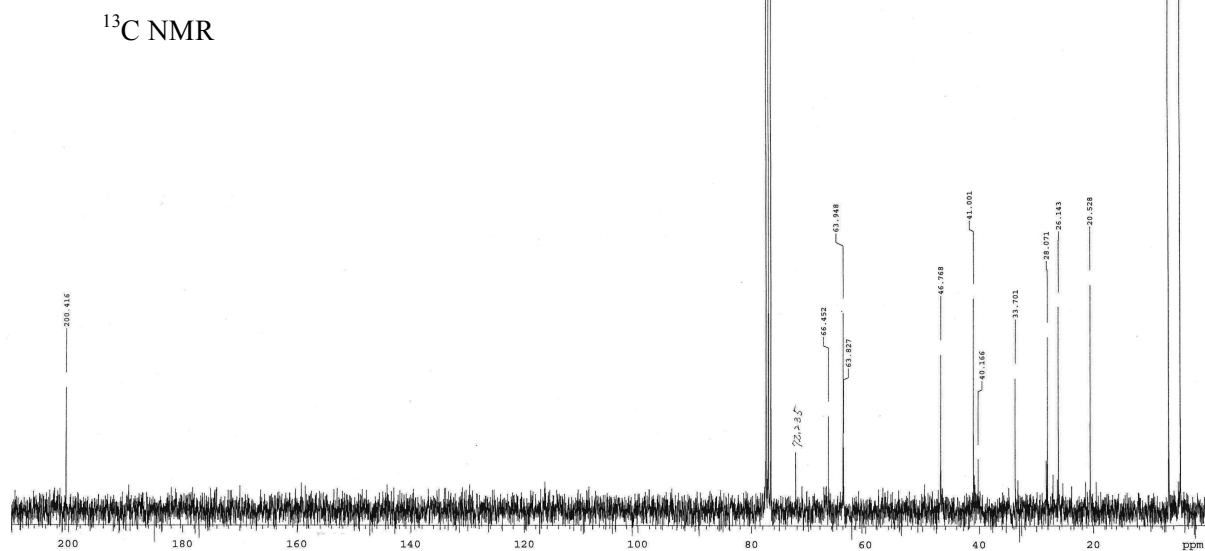
18
¹³C NMR

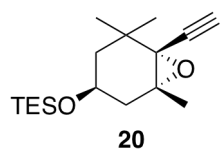


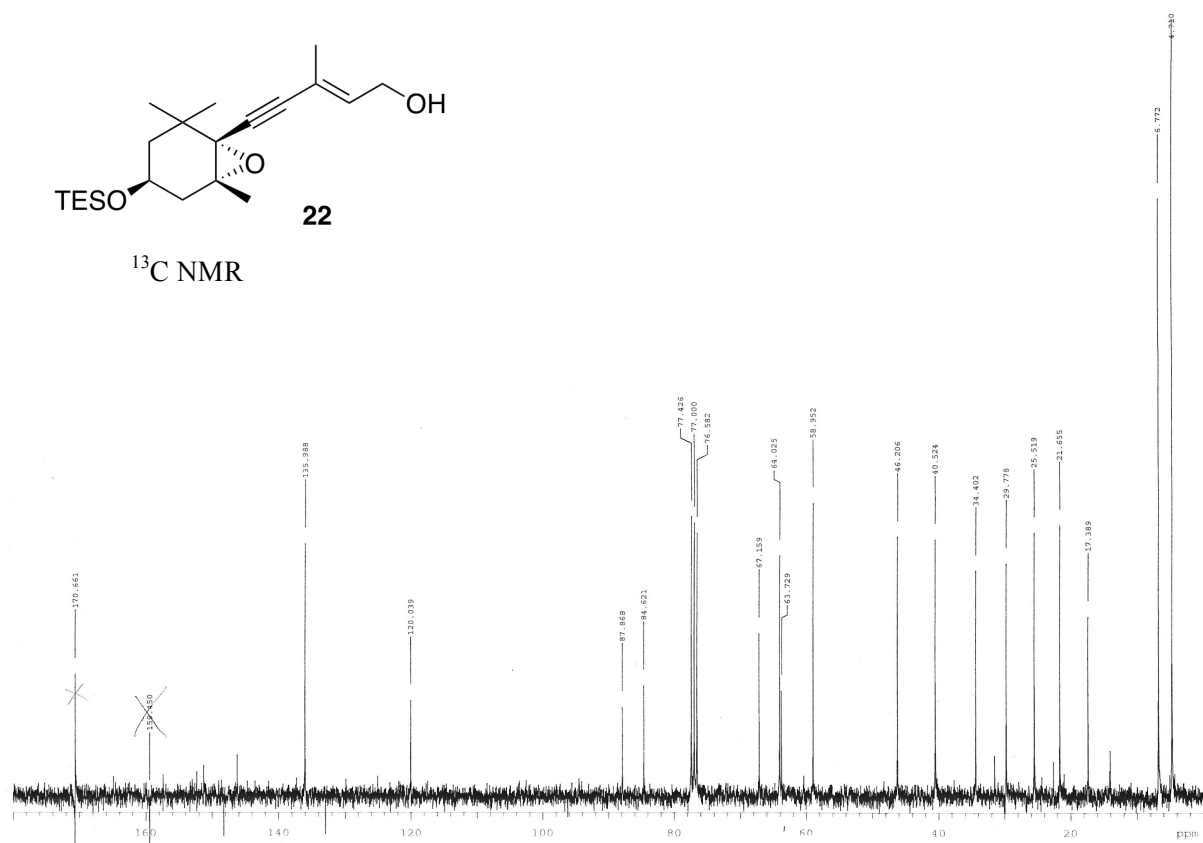
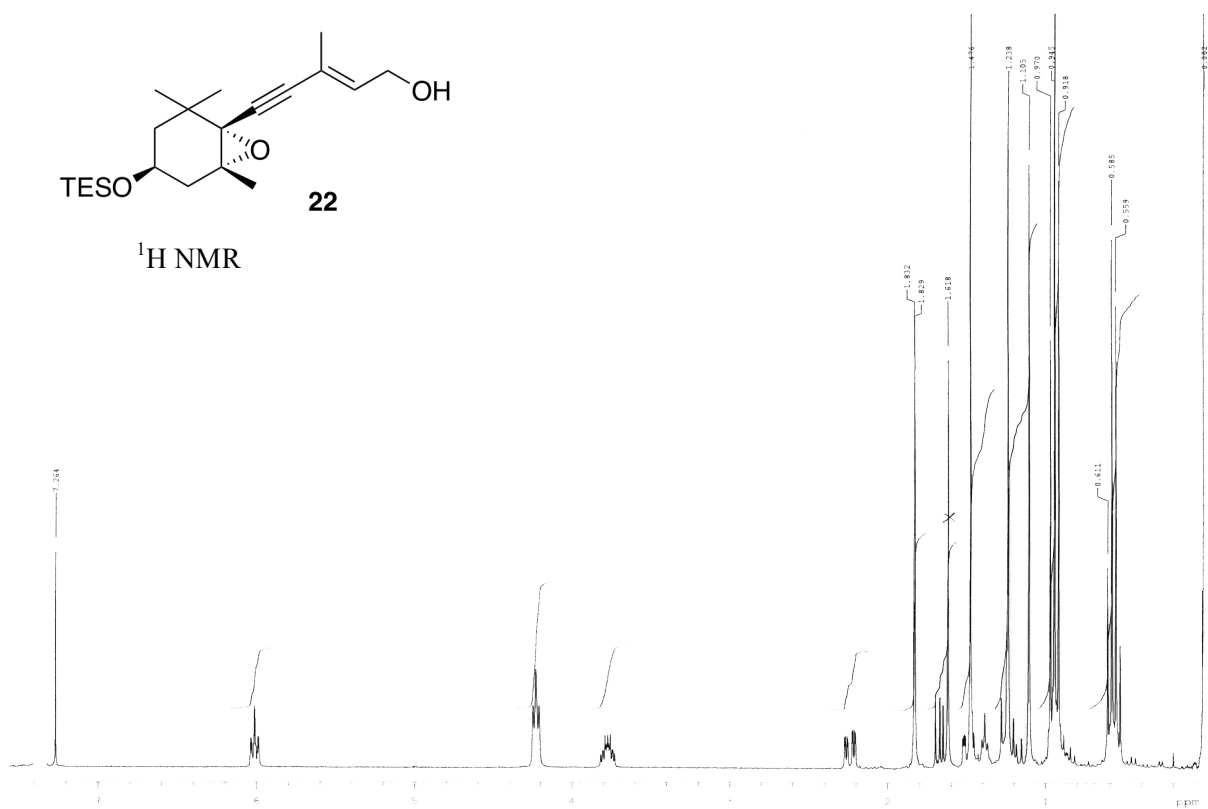
19

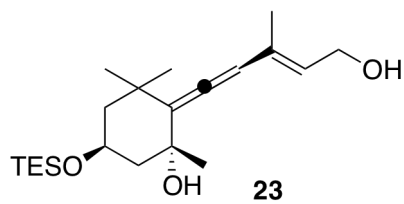


19

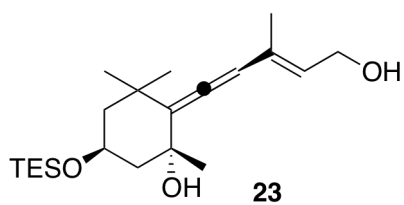
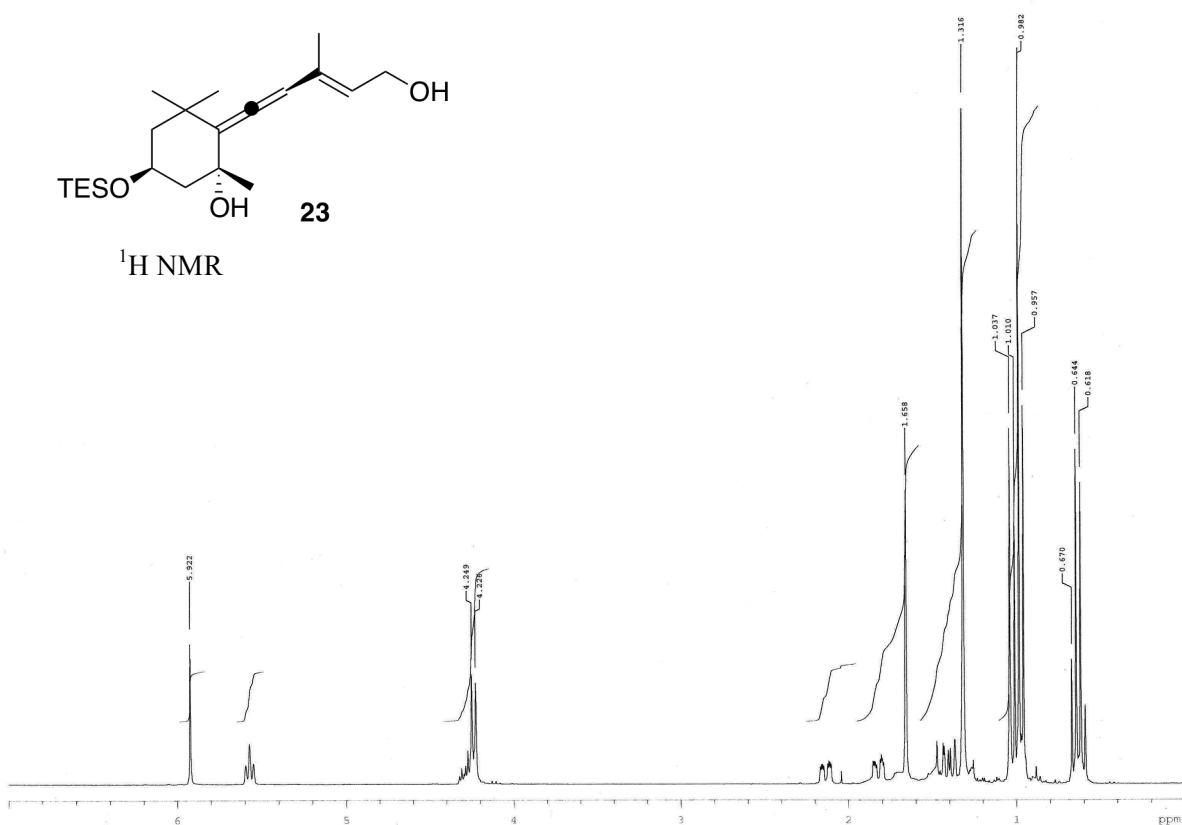




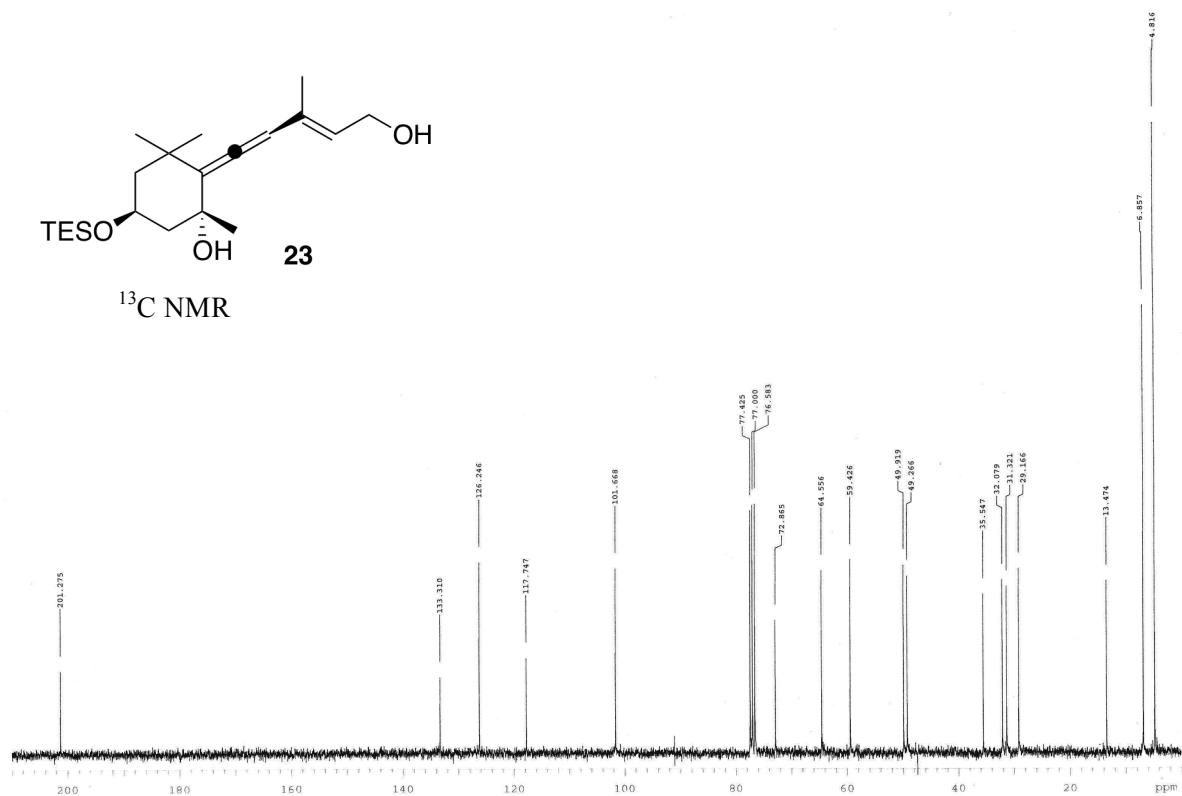


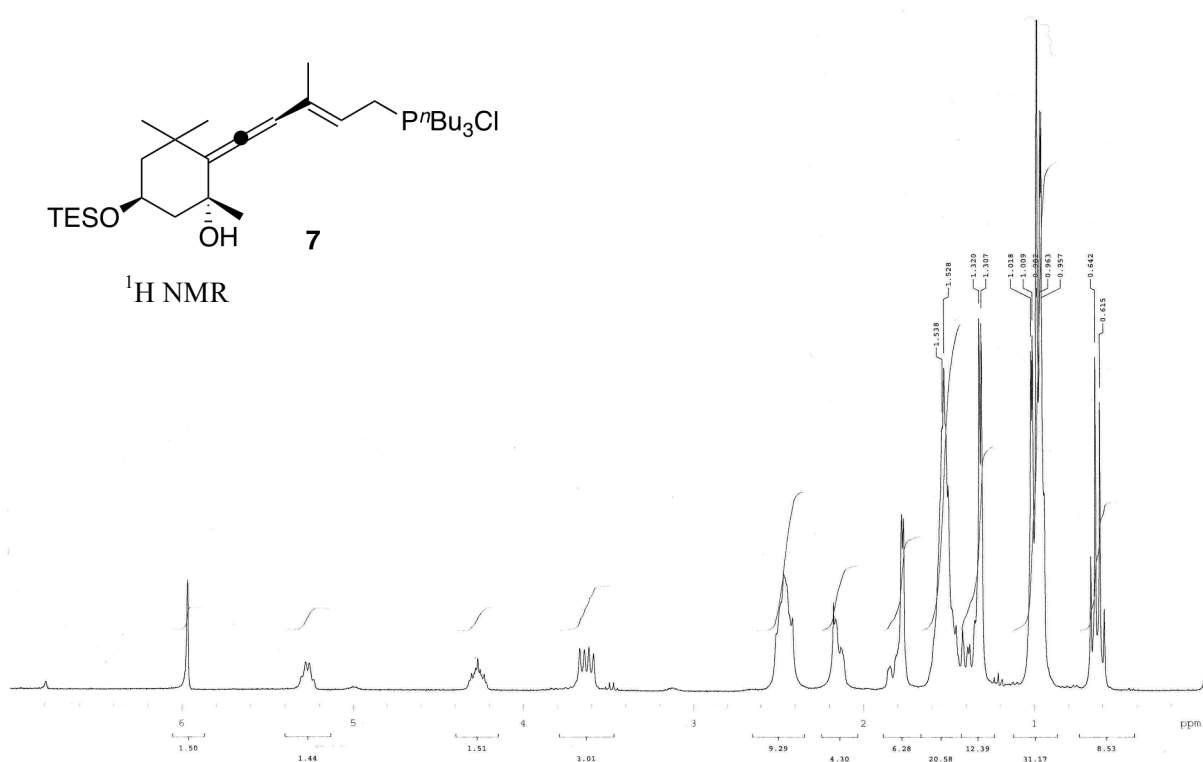


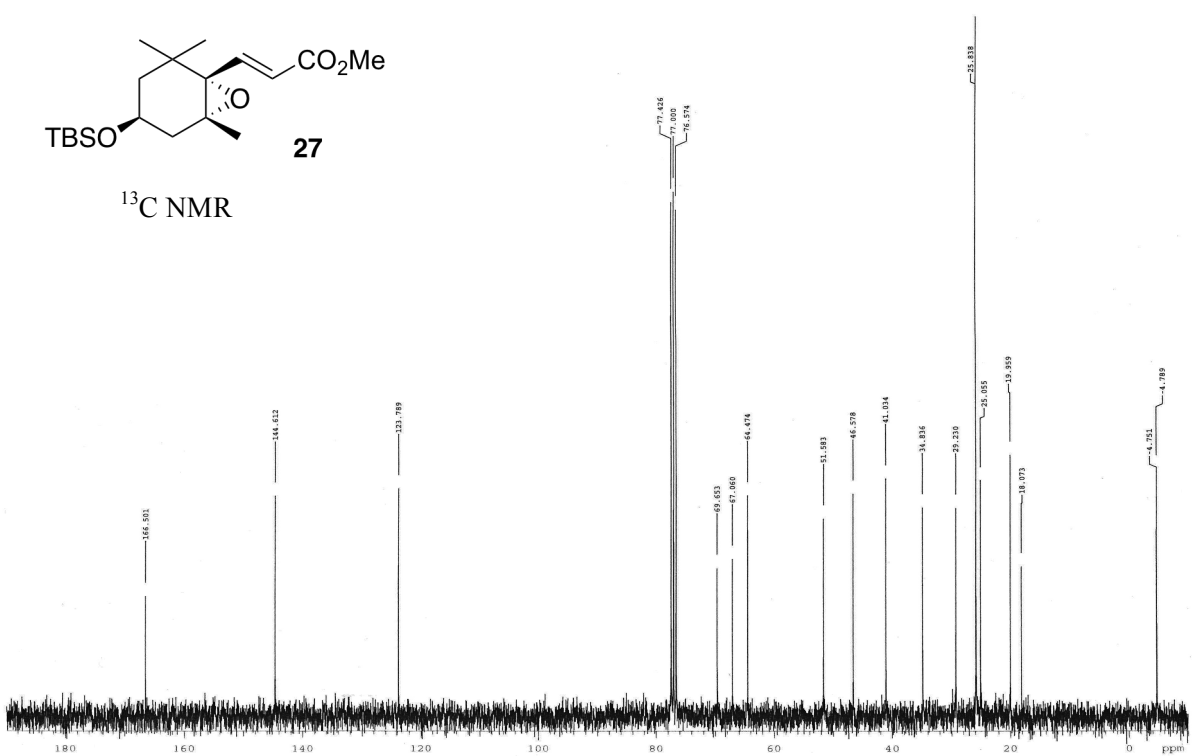
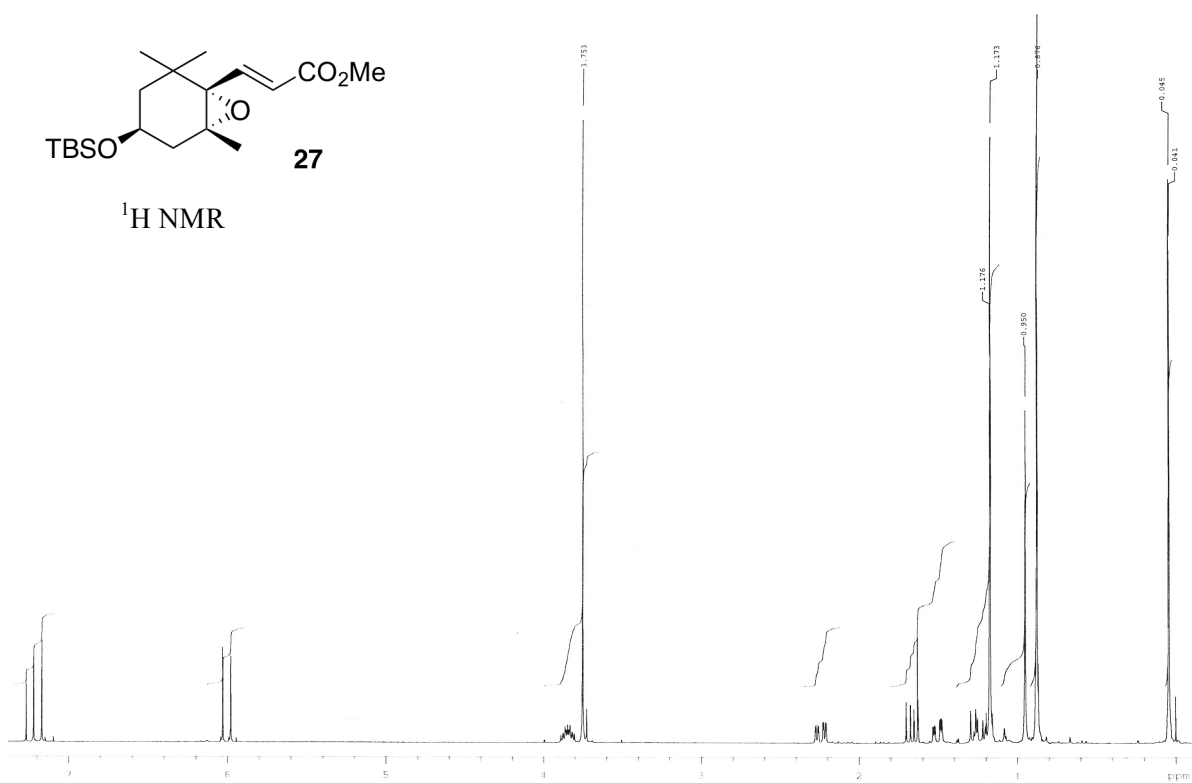
^1H NMR

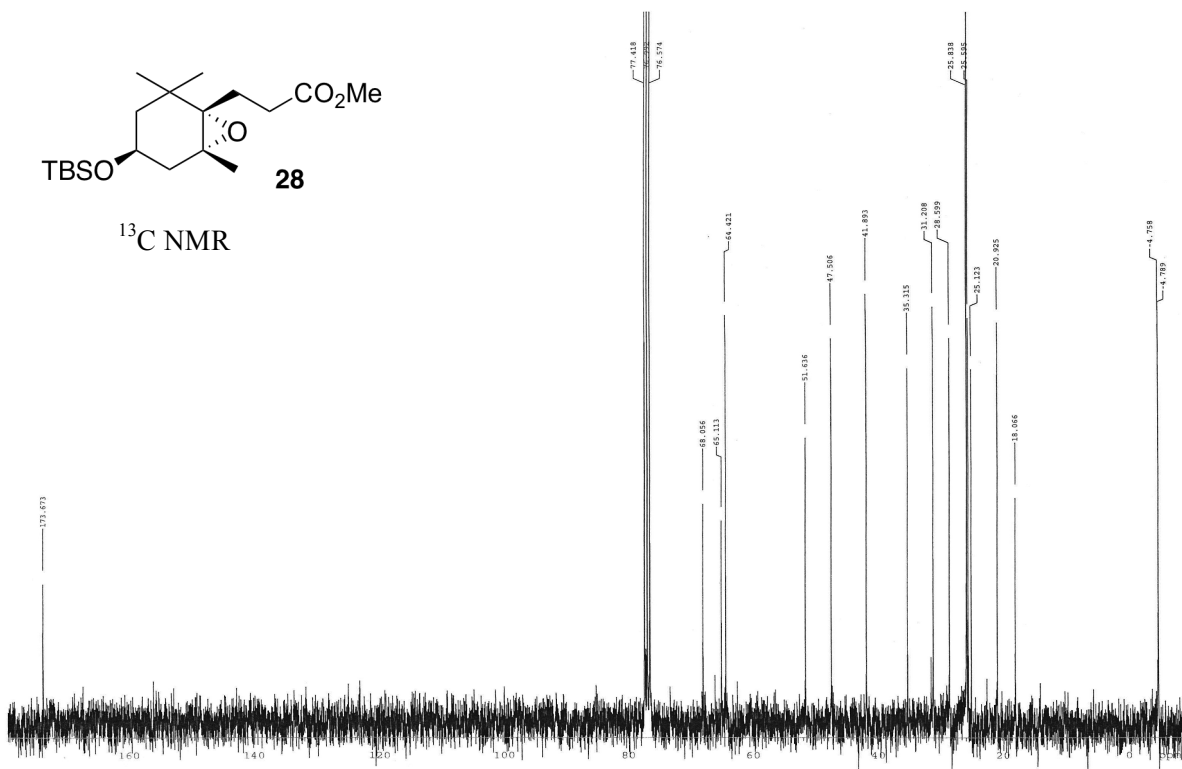
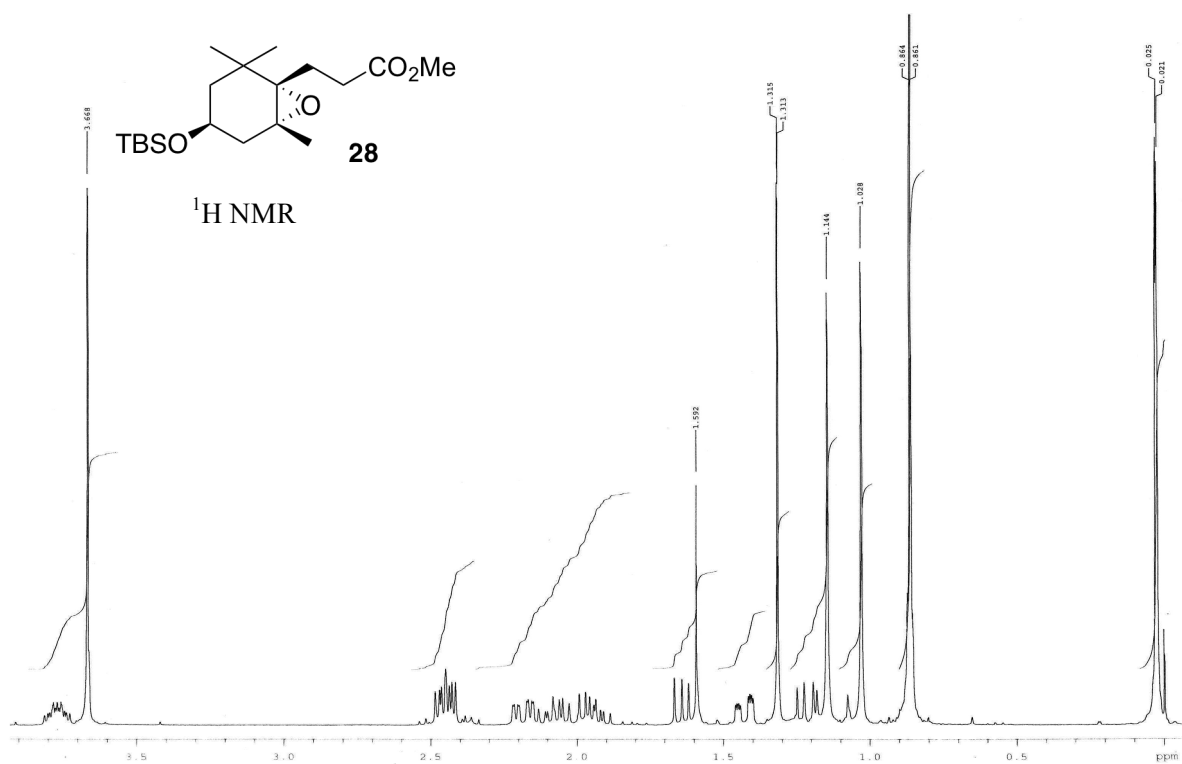


^{13}C NMR



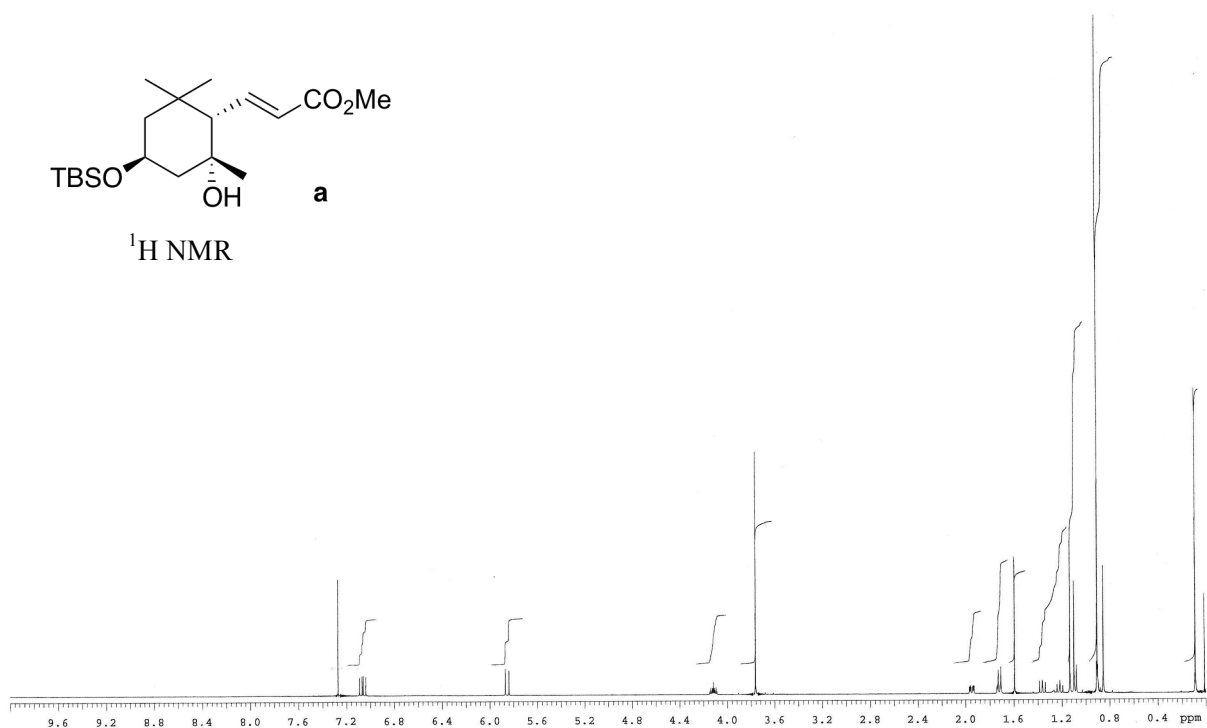




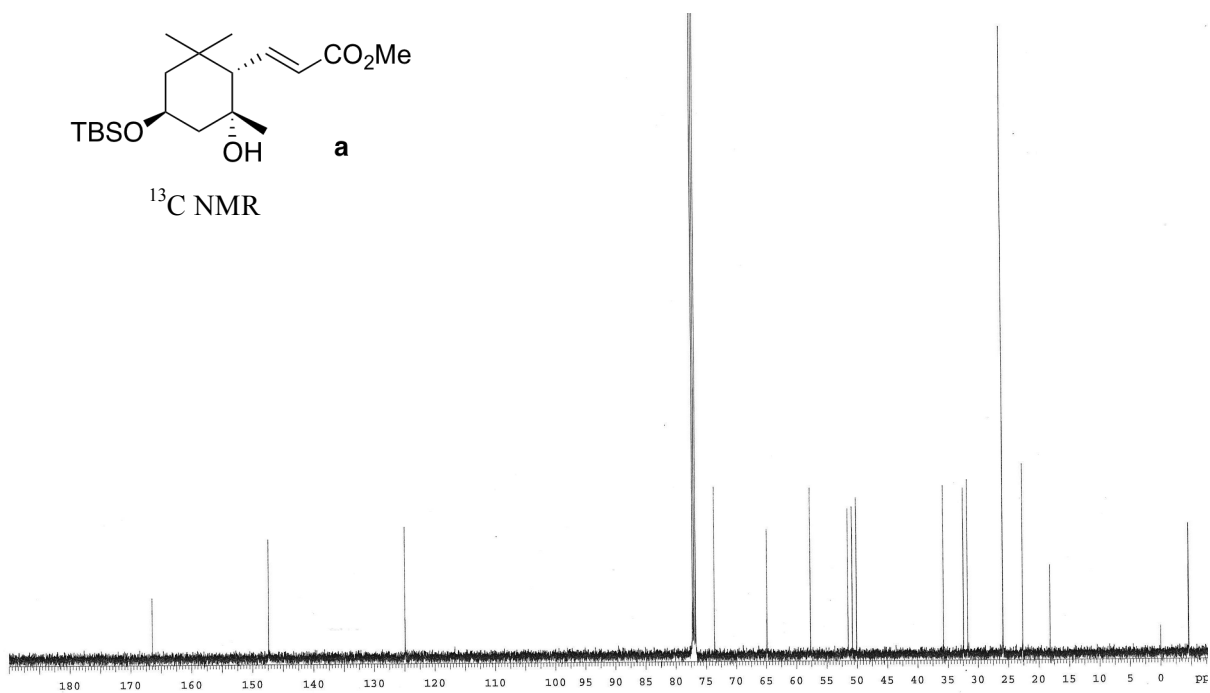




a

¹H NMR

a

¹³C NMR



b

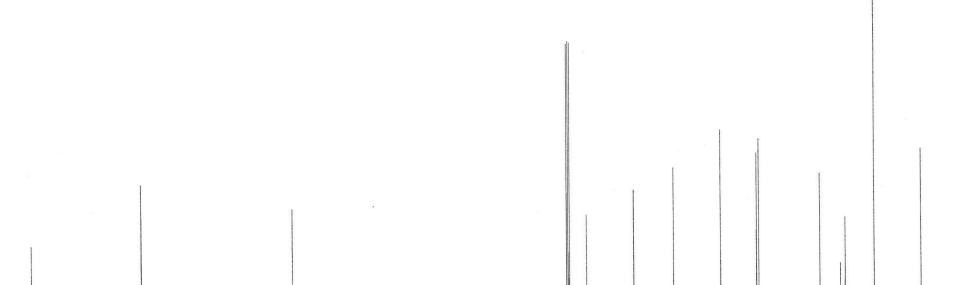
$^1\text{H NMR}$

9.6 9.2 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 ppm

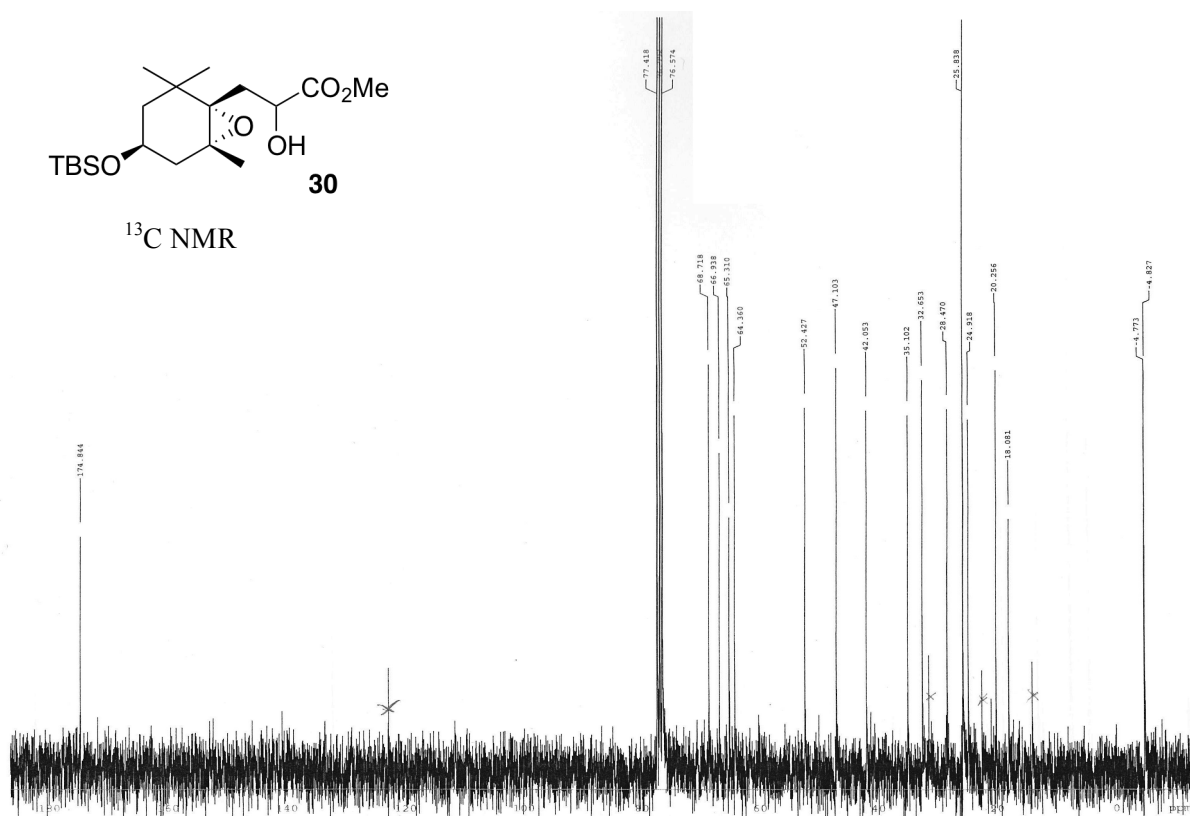
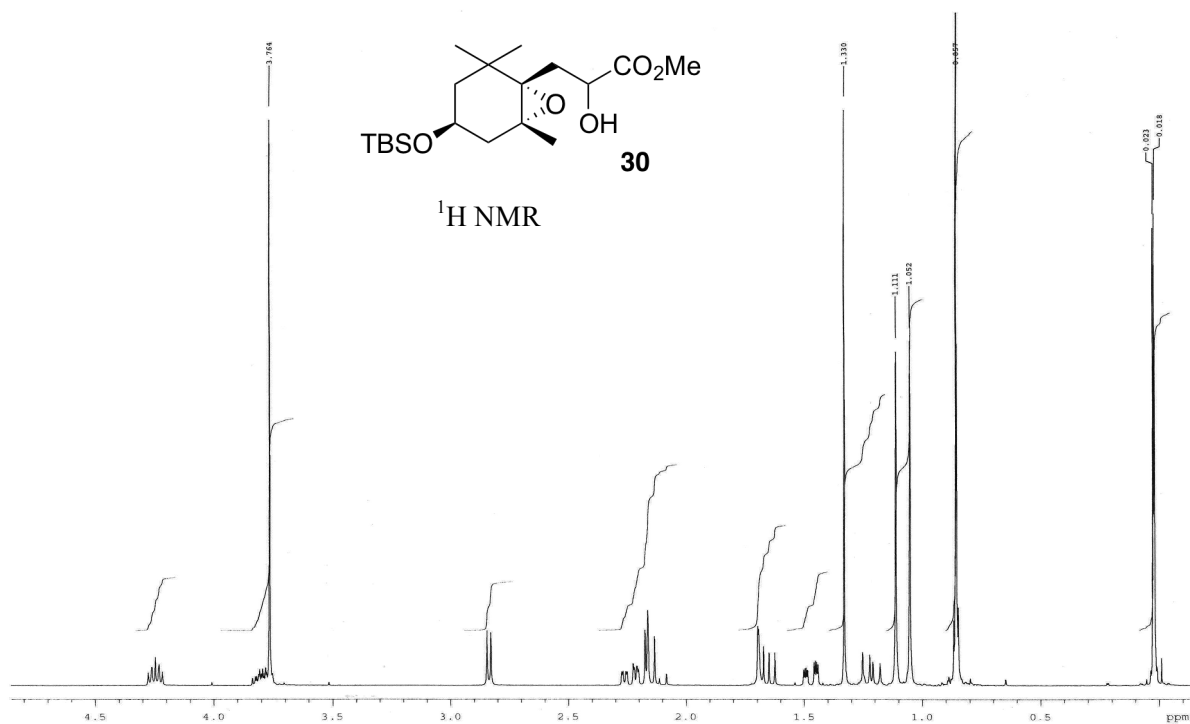


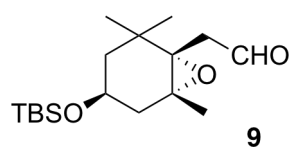
b

^{13}C NMR

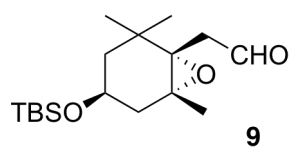
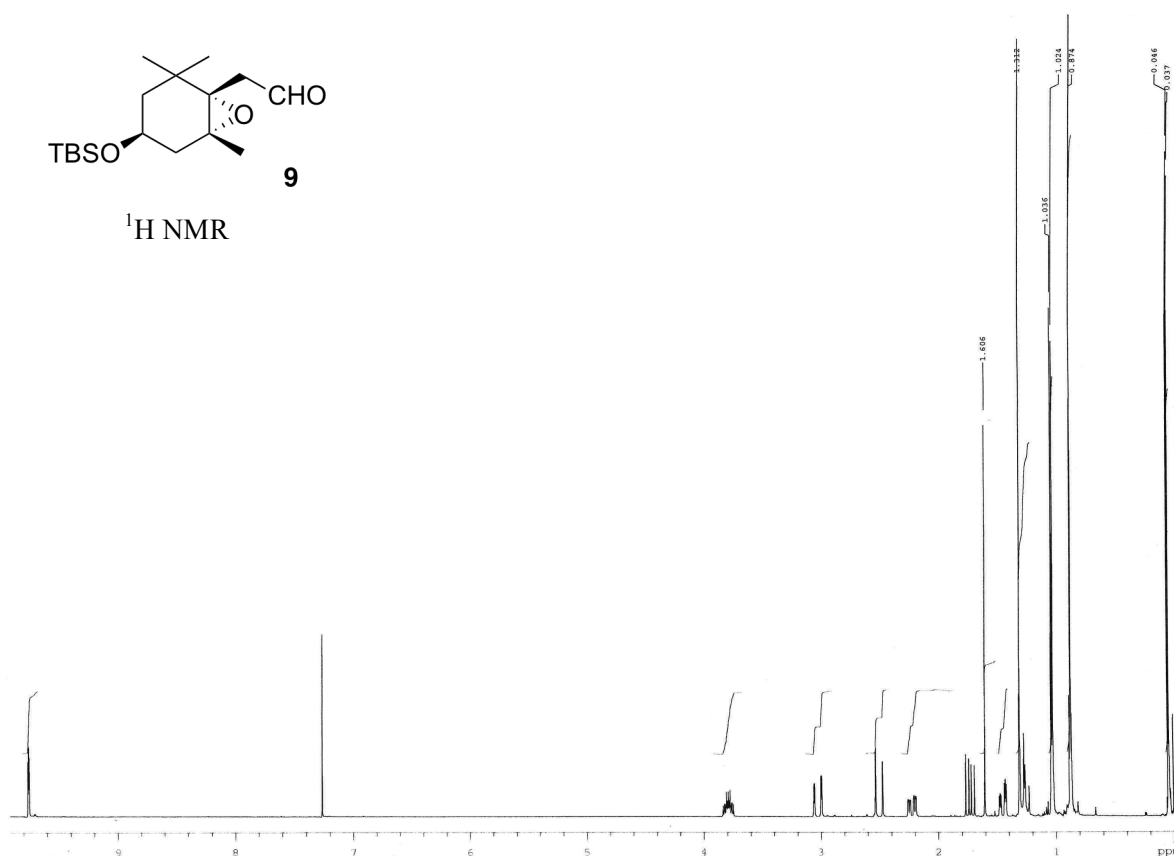


The ^{13}C NMR spectrum of compound **b** shows several peaks in the aliphatic region (20-60 ppm) and a prominent peak at 25 ppm, likely corresponding to the TBSO group. The x-axis is labeled from 180 to 0 ppm.

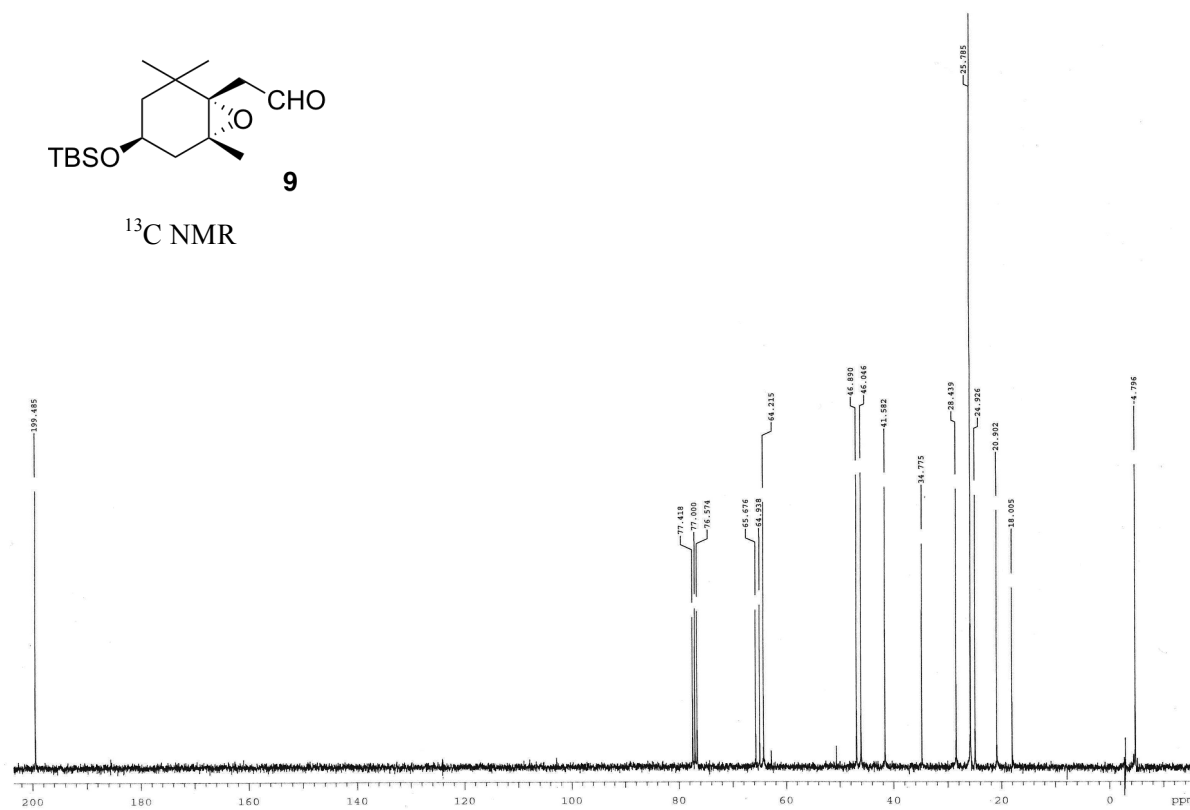


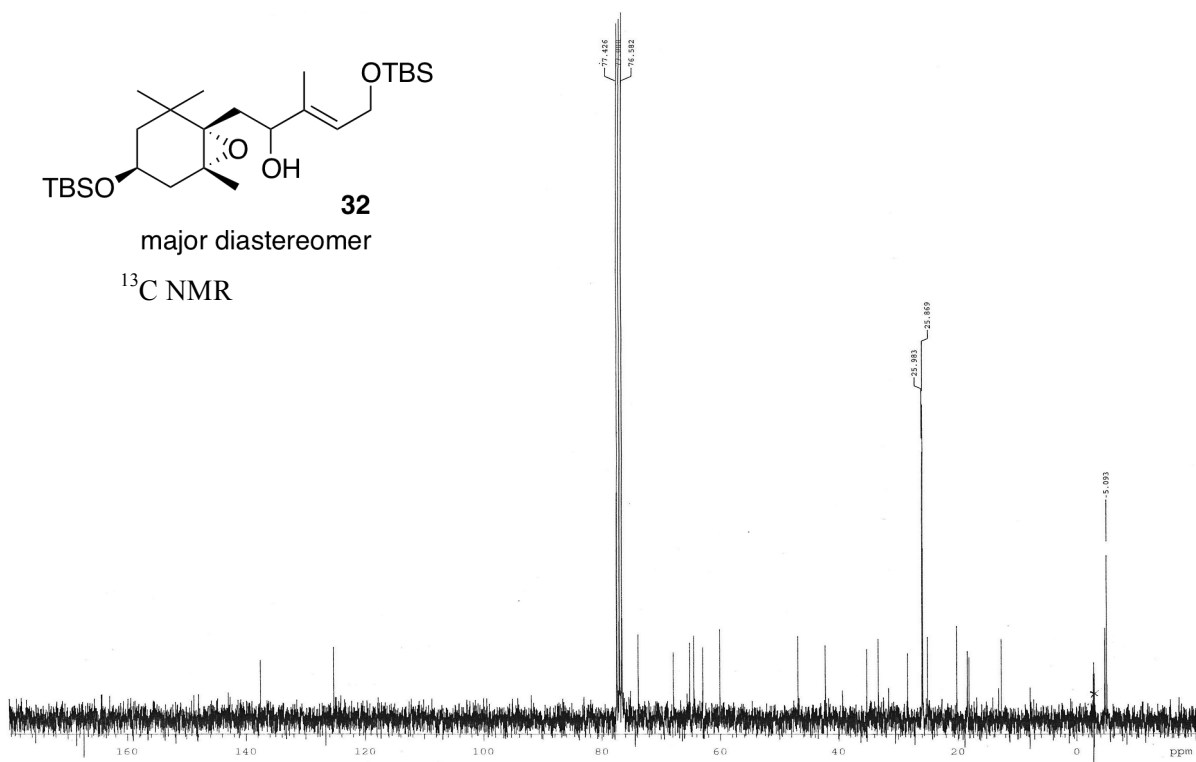
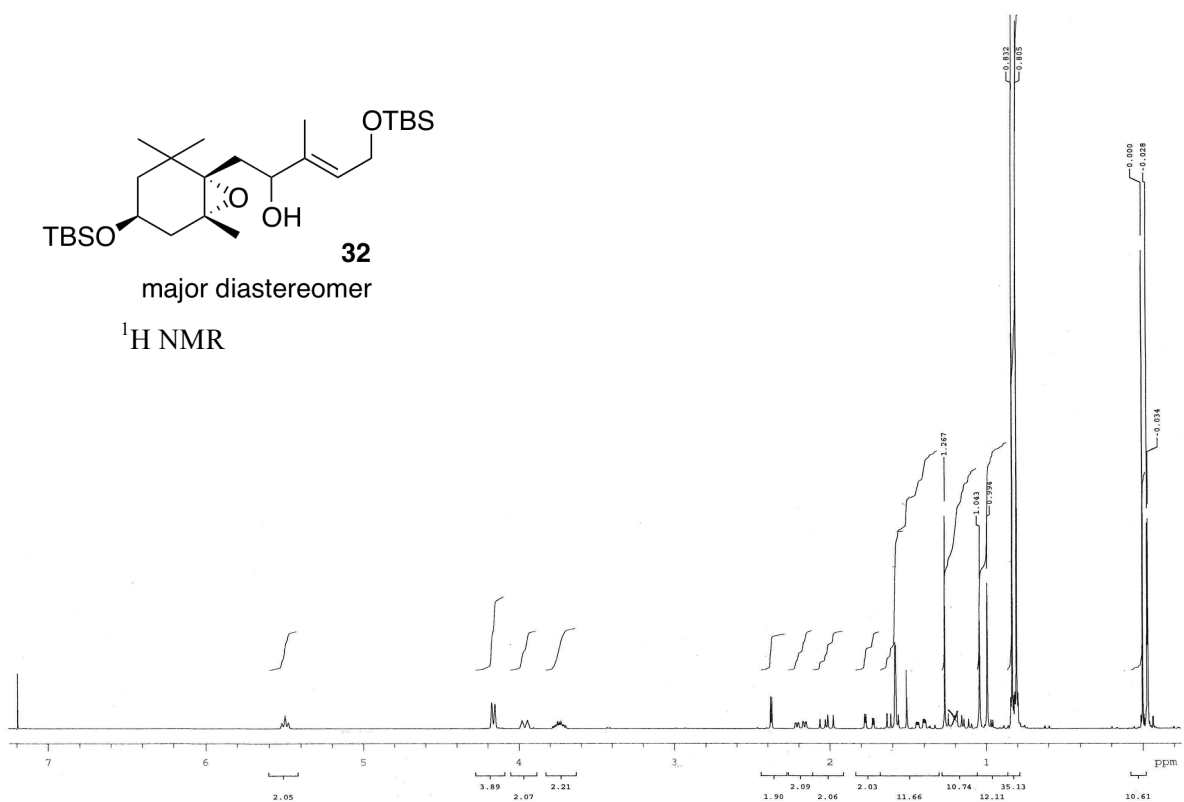


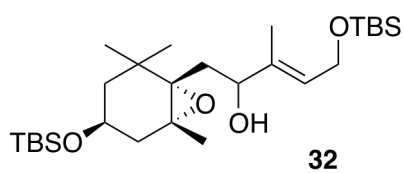
^1H NMR



^{13}C NMR

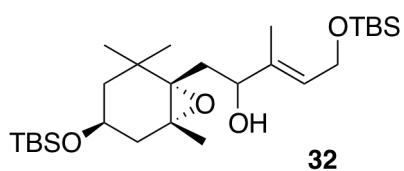
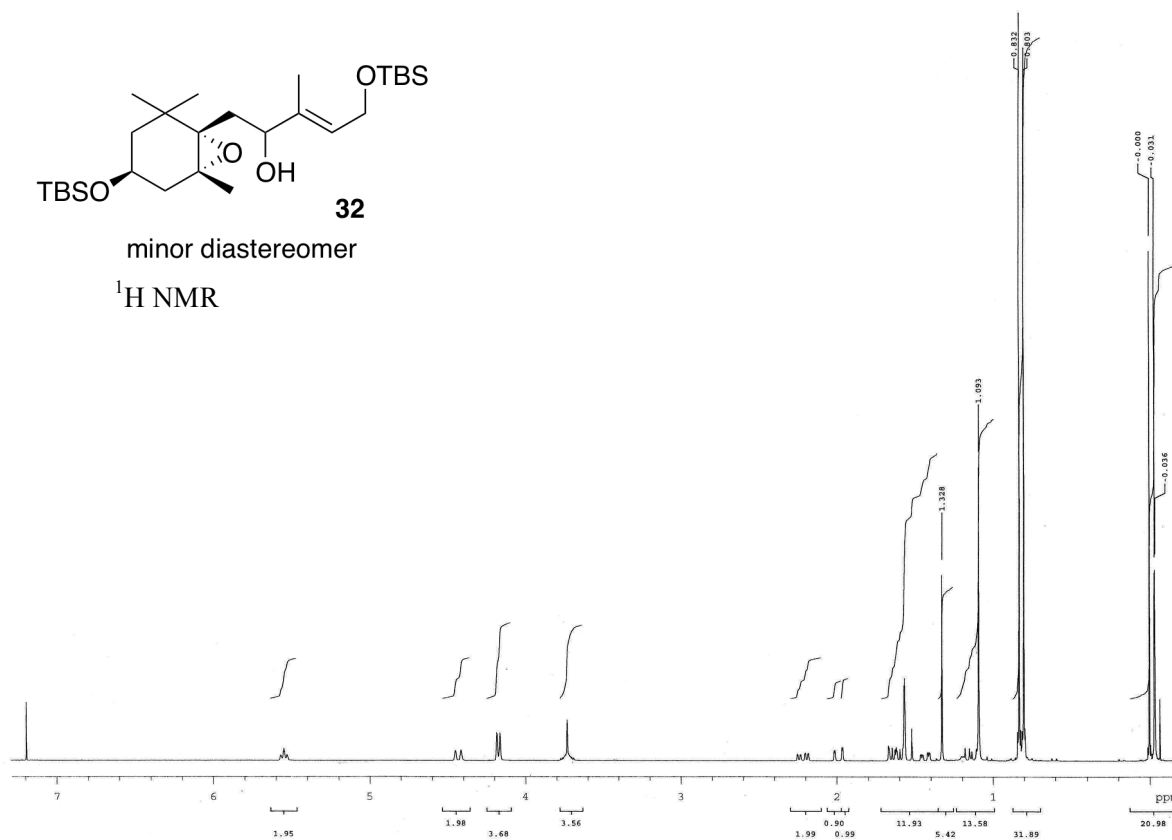






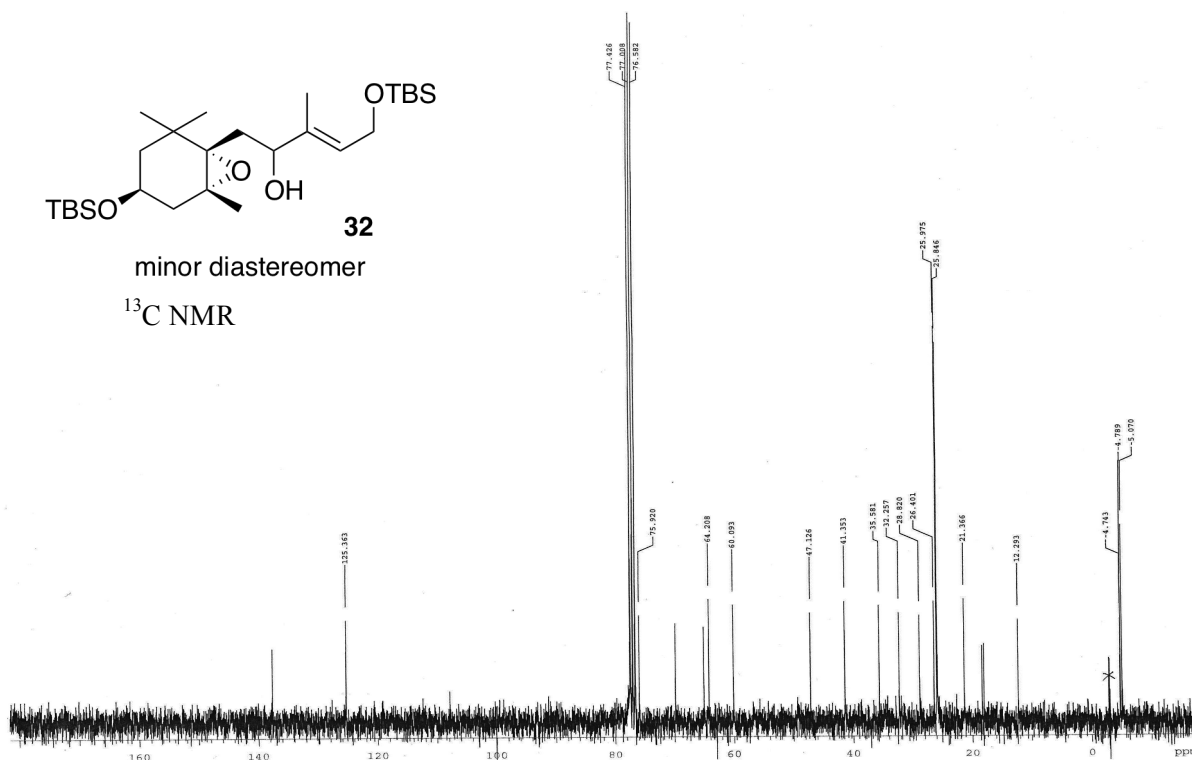
minor diastereomer

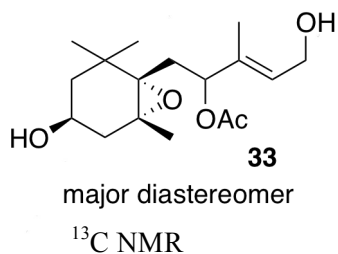
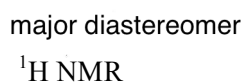
^1H NMR

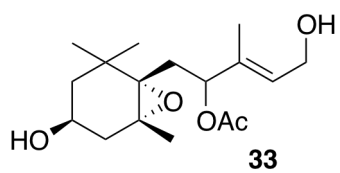


minor diastereomer

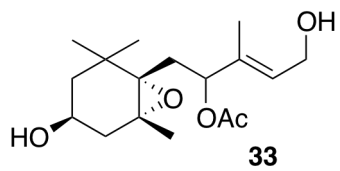
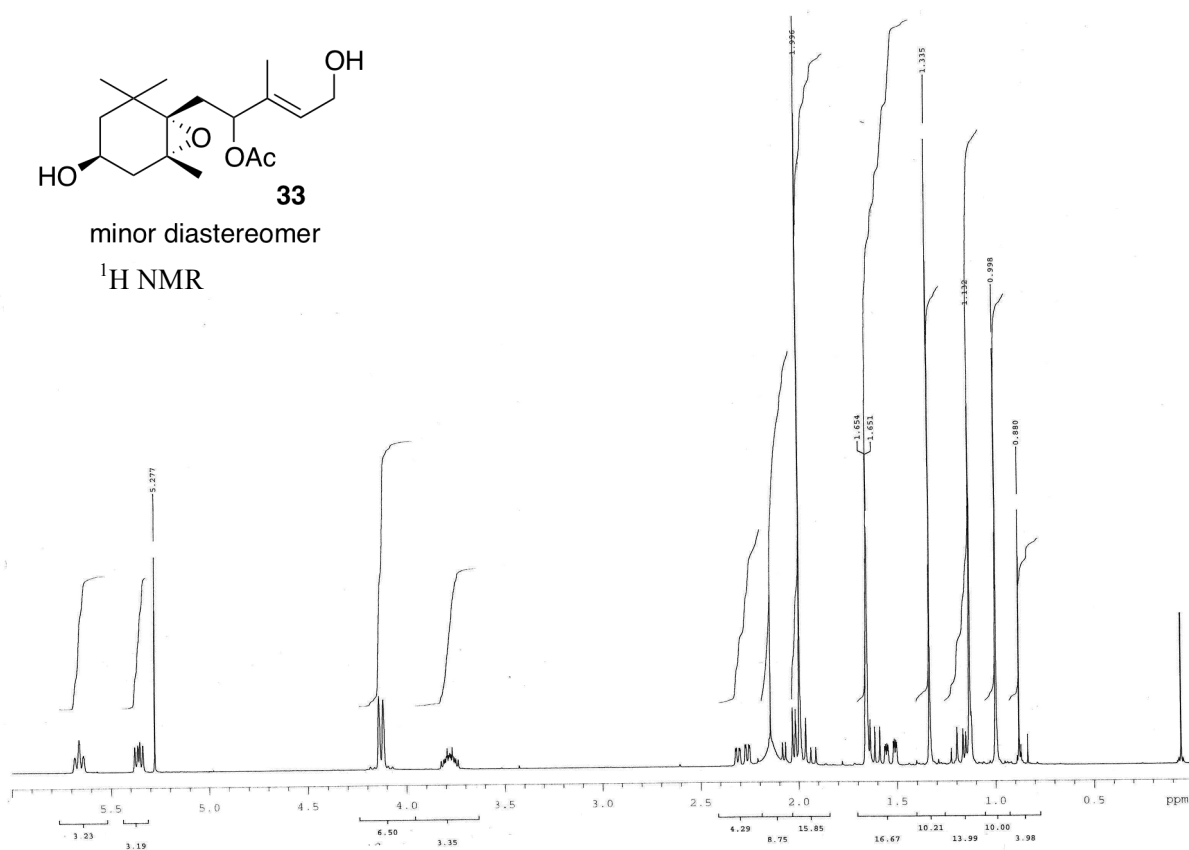
^{13}C NMR



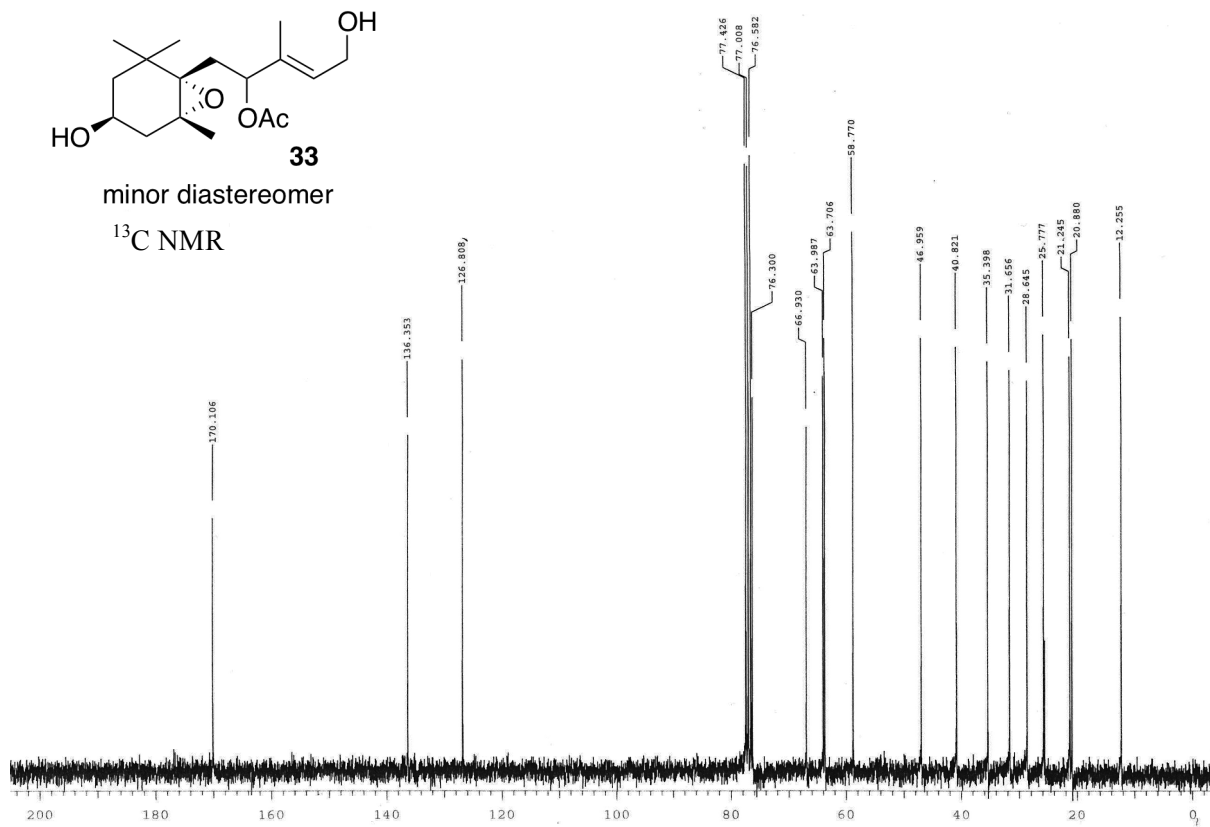


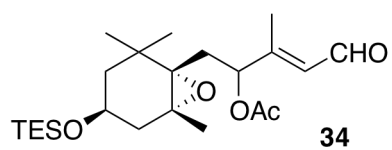


^1H NMR



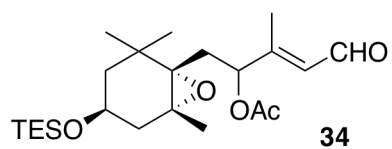
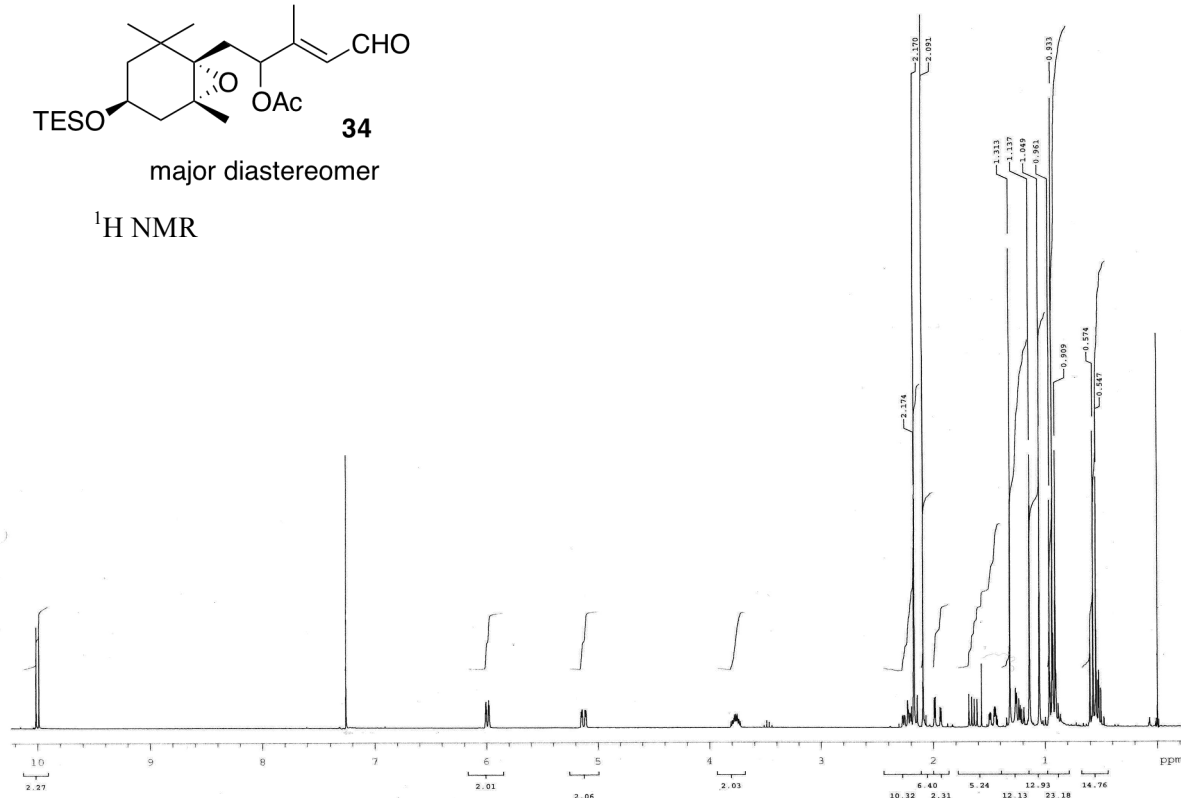
^{13}C NMR





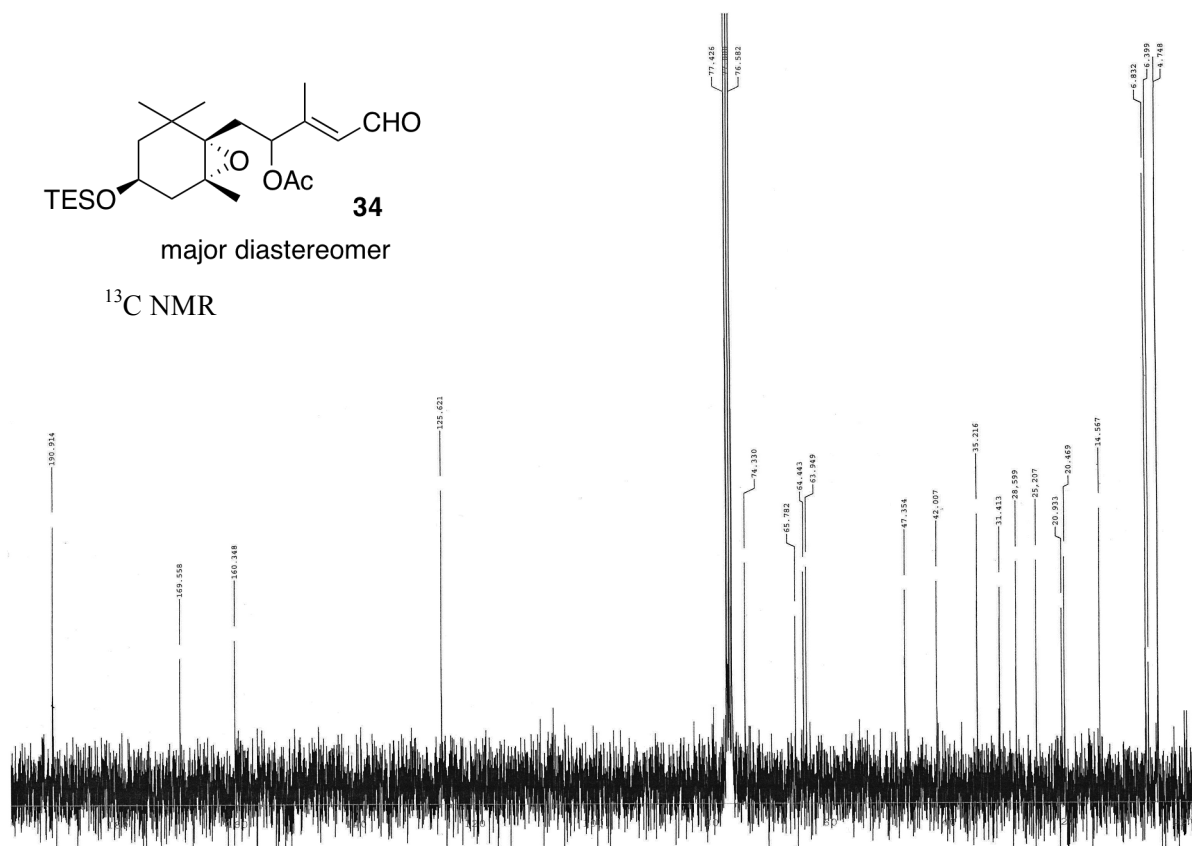
major diastereomer

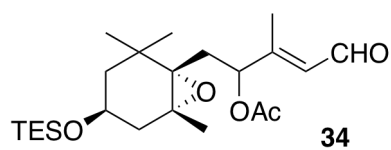
^1H NMR



major diastereomer

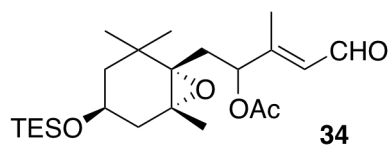
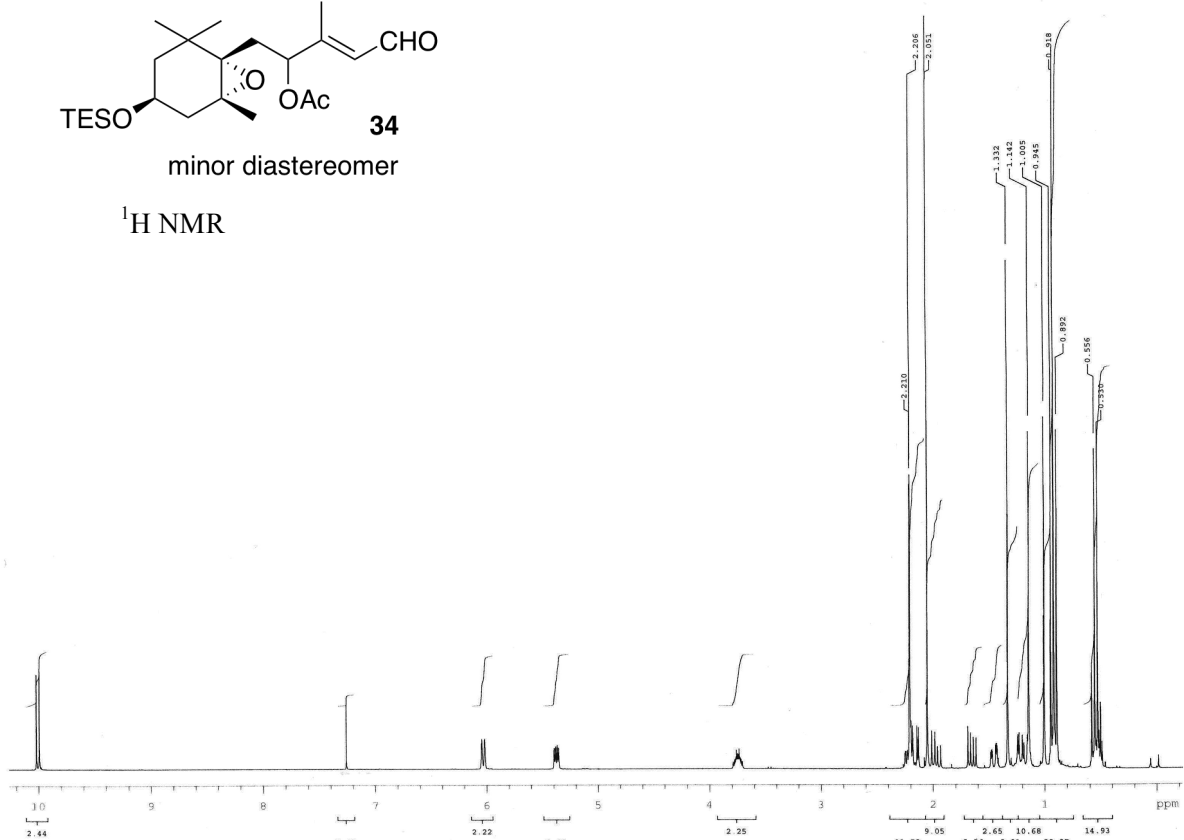
^{13}C NMR





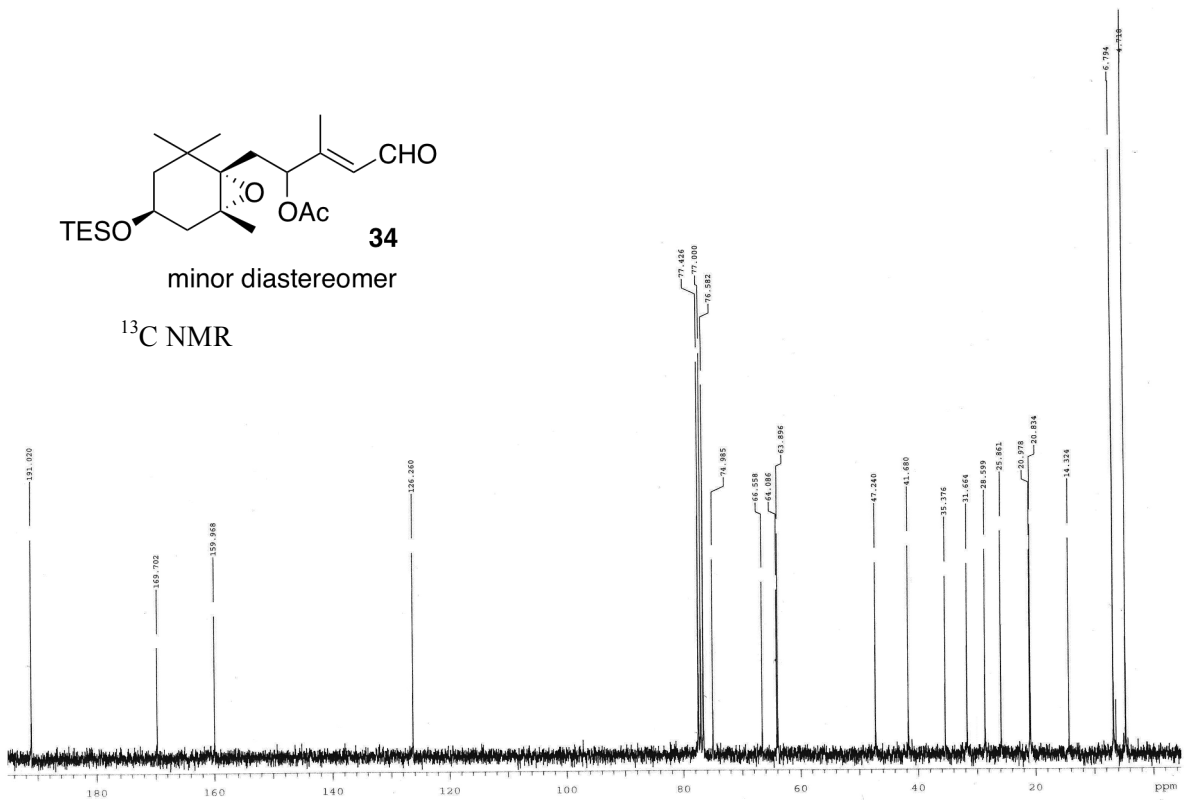
minor diastereomer

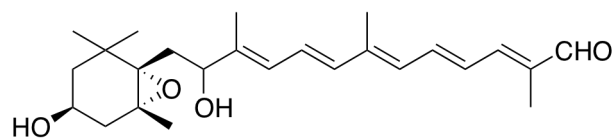
^1H NMR



minor diastereomer

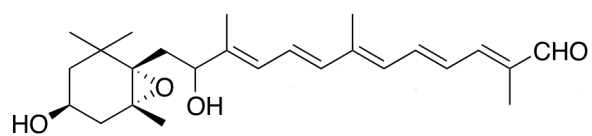
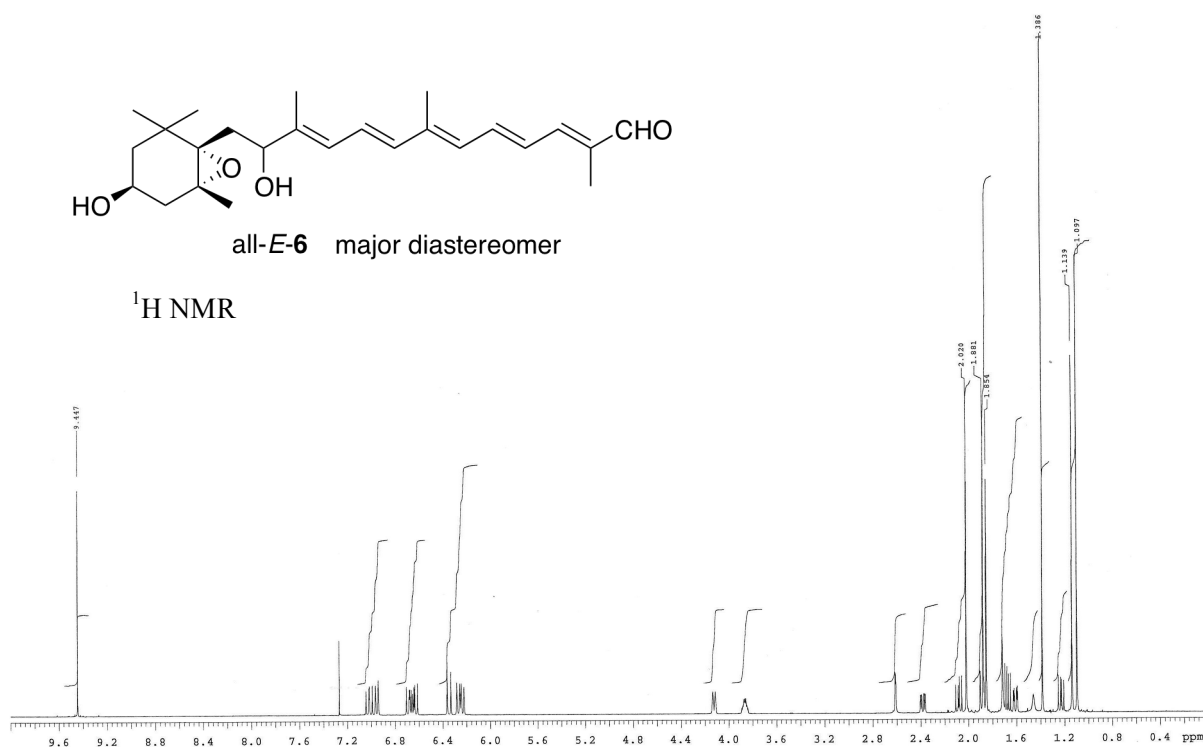
^{13}C NMR





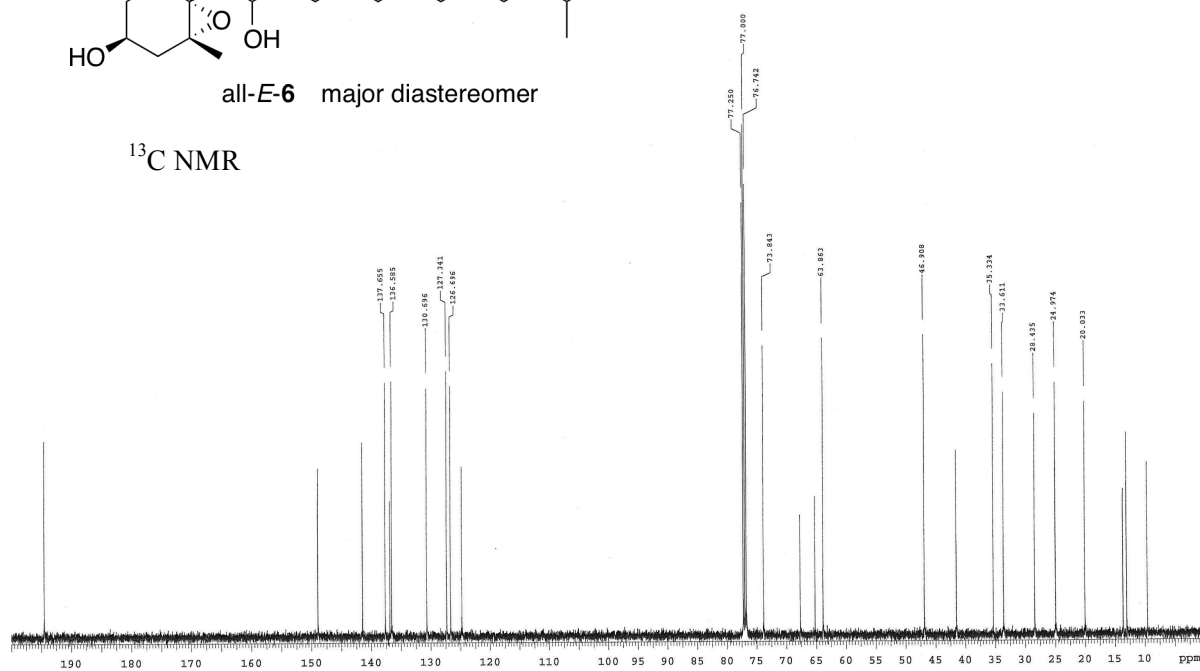
all-*E*-6 major diastereomer

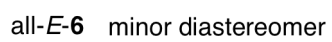
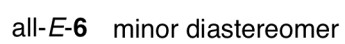
^1H NMR



all-*E*-6 major diastereomer

^{13}C NMR

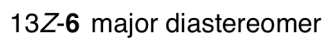




all-*E*-6 minor diastereomer

^{13}C NMR

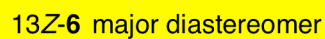
Chemical shifts (ppm): 194.619, 141.619, 136.469, 127.140, 126.787, 124.714, 77.278, 77.025, 76.760, 75.960, 61.587, 61.650, 47.118, 40.651, 35.684, 32.655, 28.893, 26.422, 21.212, 11.936.



CC(C)C=CC=CC(=C)C(O)[C@H]1C[C@@H](O)C(C)(C)[C@H]1O
 13Z-6 major diastereomer
¹H NMR

The ¹H NMR spectrum displays the following peak regions and integration:

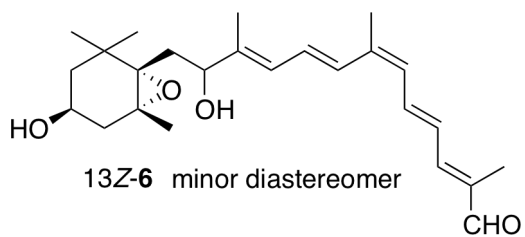
- 9.4 ppm: sharp singlet (aldehyde H, integration ~1.0)
- 7.2 ppm: sharp singlet (TMS, integration ~0.0)
- 6.8 ppm: multiplet (alkene H, integration ~1.0)
- 6.4 ppm: multiplet (alkene H, integration ~1.0)
- 6.0 ppm: multiplet (alkene H, integration ~1.0)
- 3.9 ppm: doublet (OH, integration ~1.0)
- 2.0 ppm: multiplet (aliphatic H, integration ~2.0)
- 1.6 ppm: multiplet (aliphatic H, integration ~2.0)
- 1.2 ppm: multiplet (aliphatic H, integration ~2.0)
- 0.8 ppm: multiplet (aliphatic H, integration ~2.0)



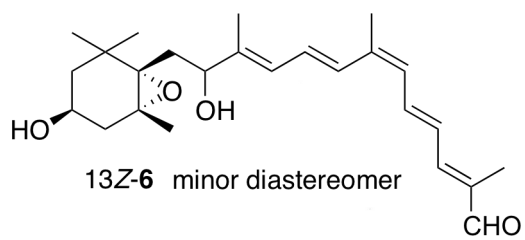
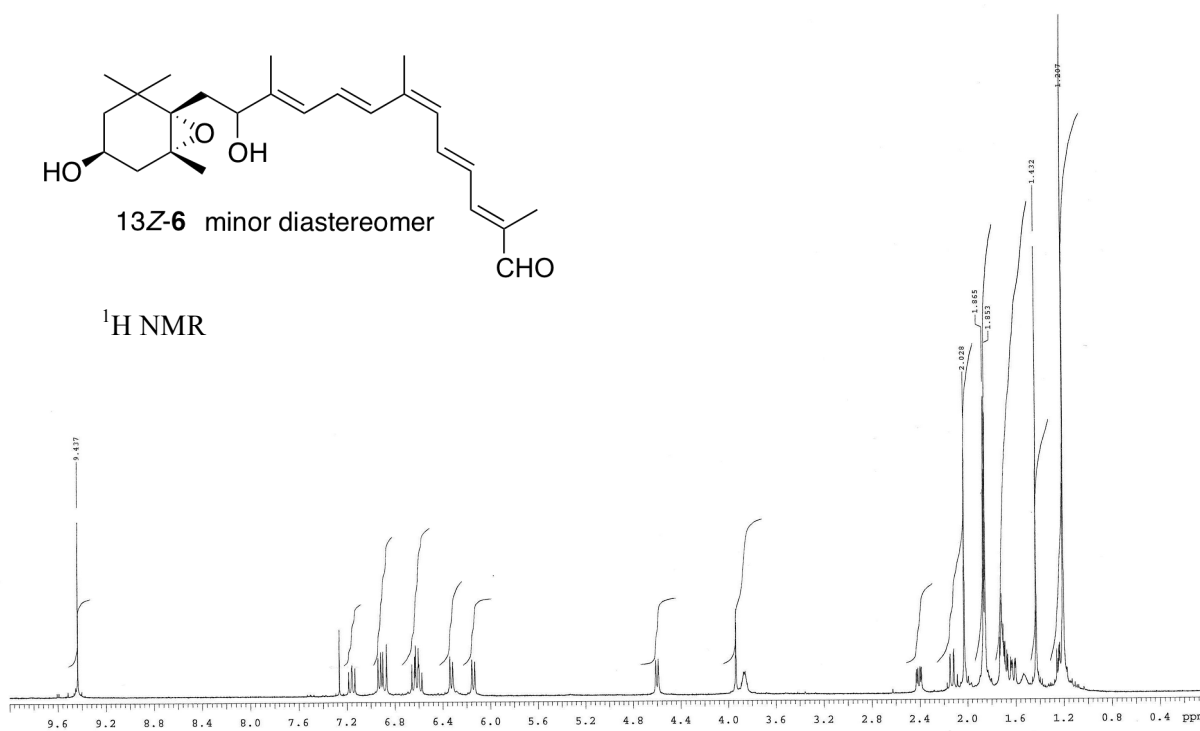
13Z-6 major diastereomer

¹³C NMR

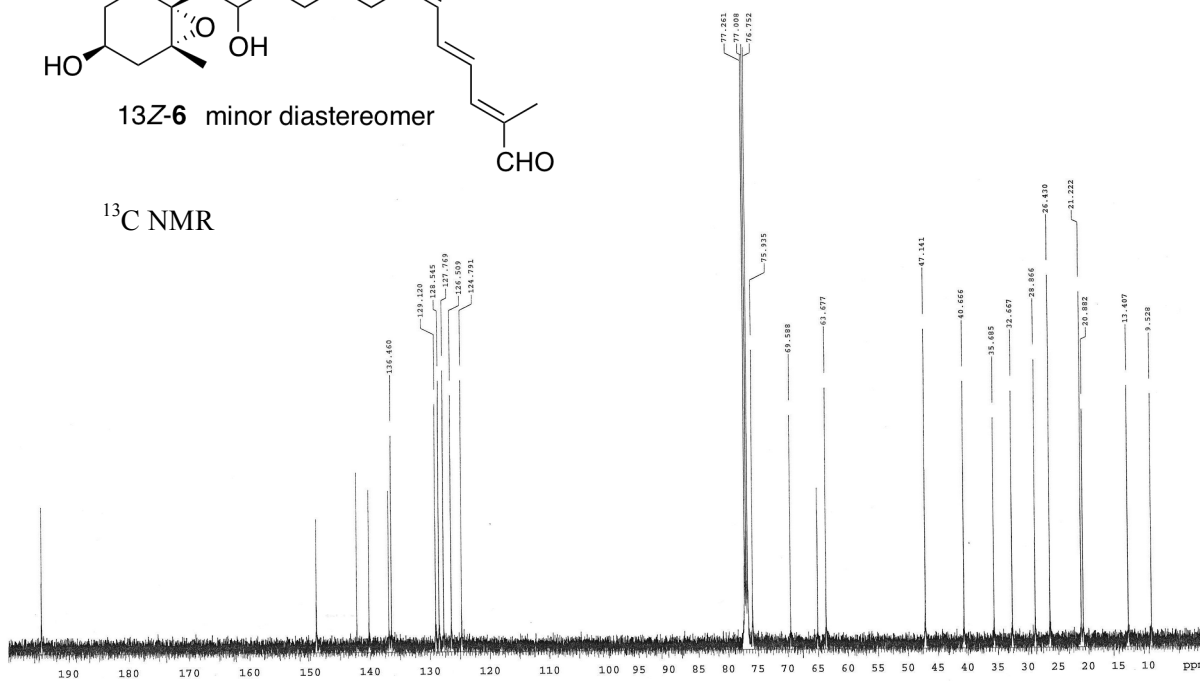
Chemical structure of 13Z-6 major diastereomer is shown above the spectrum. The structure is a complex molecule with a long chain, multiple double bonds, and a terminal aldehyde group (CHO). The spectrum shows peaks corresponding to the carbons in the molecule, with a large solvent peak at 77 ppm.

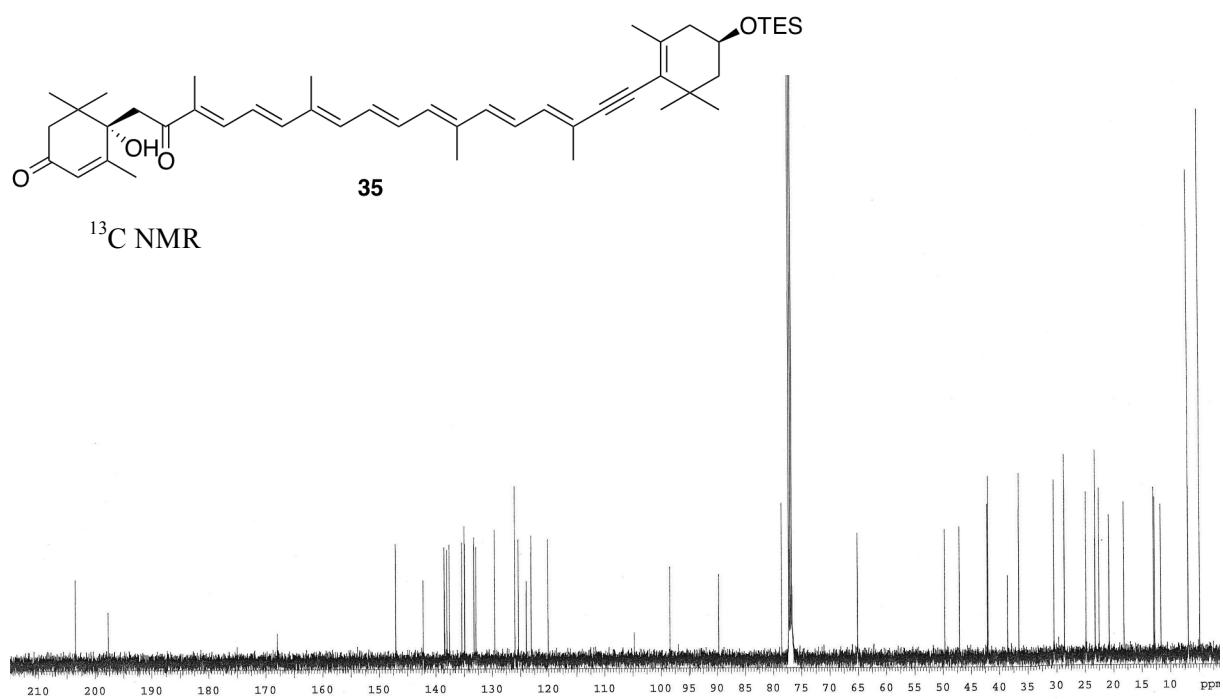
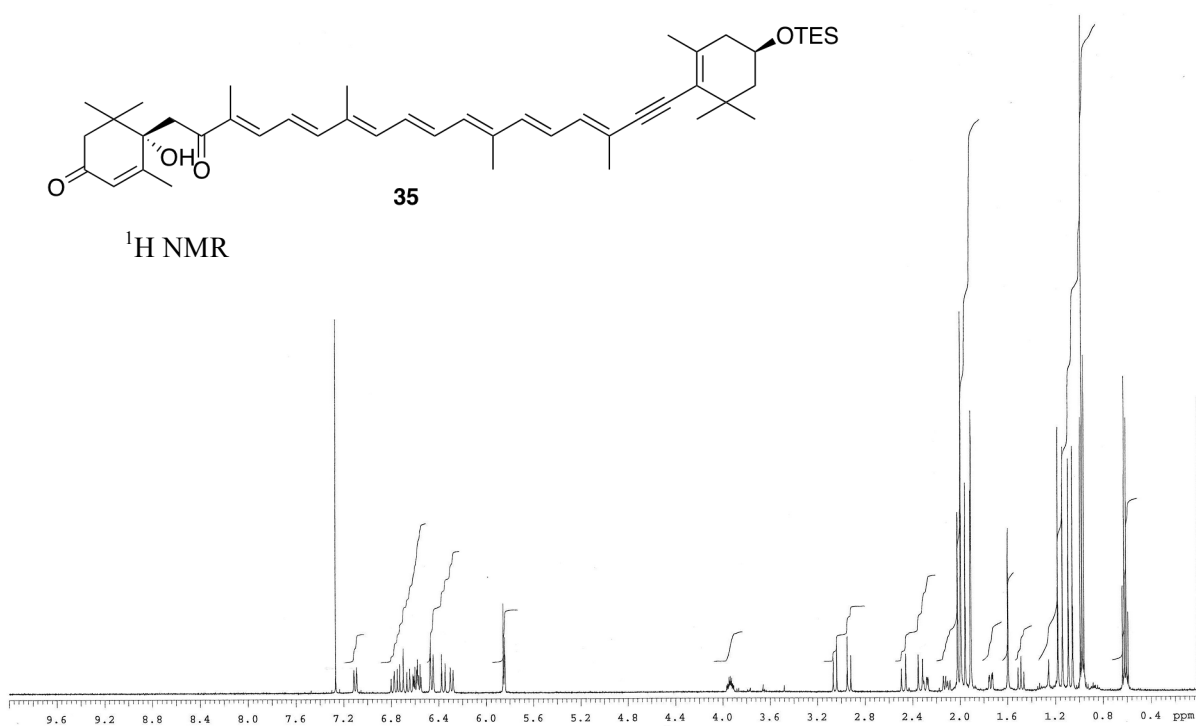


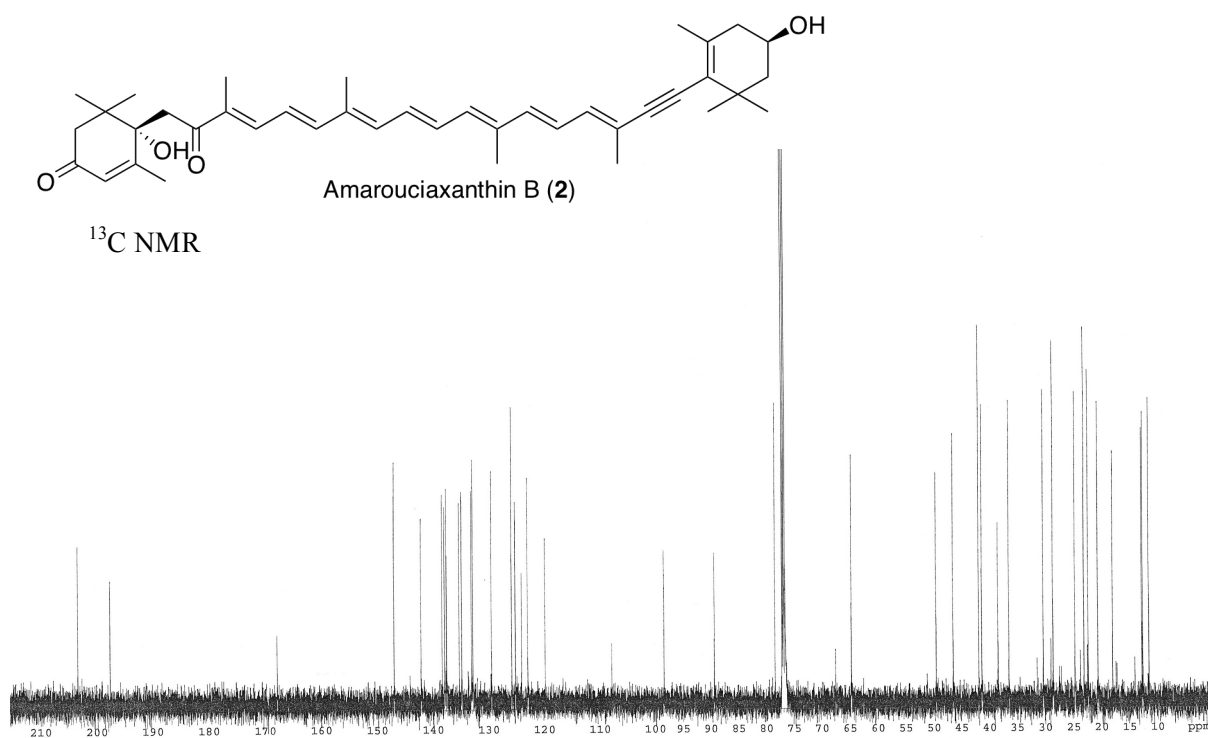
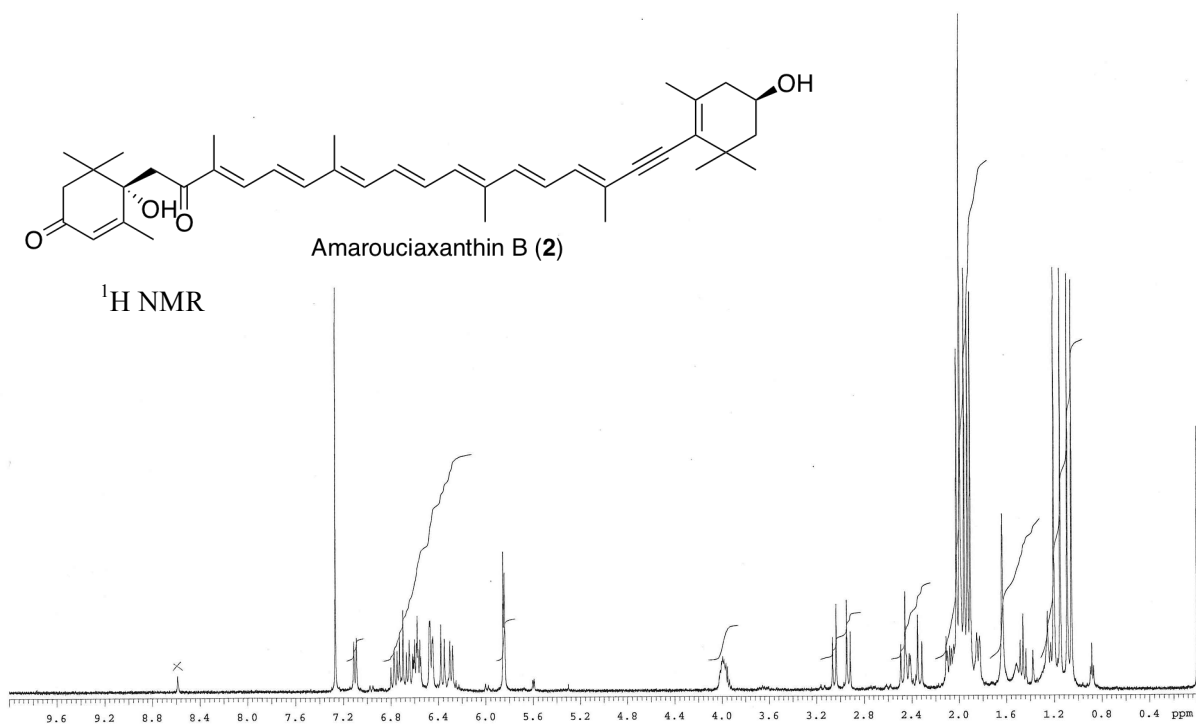
^1H NMR



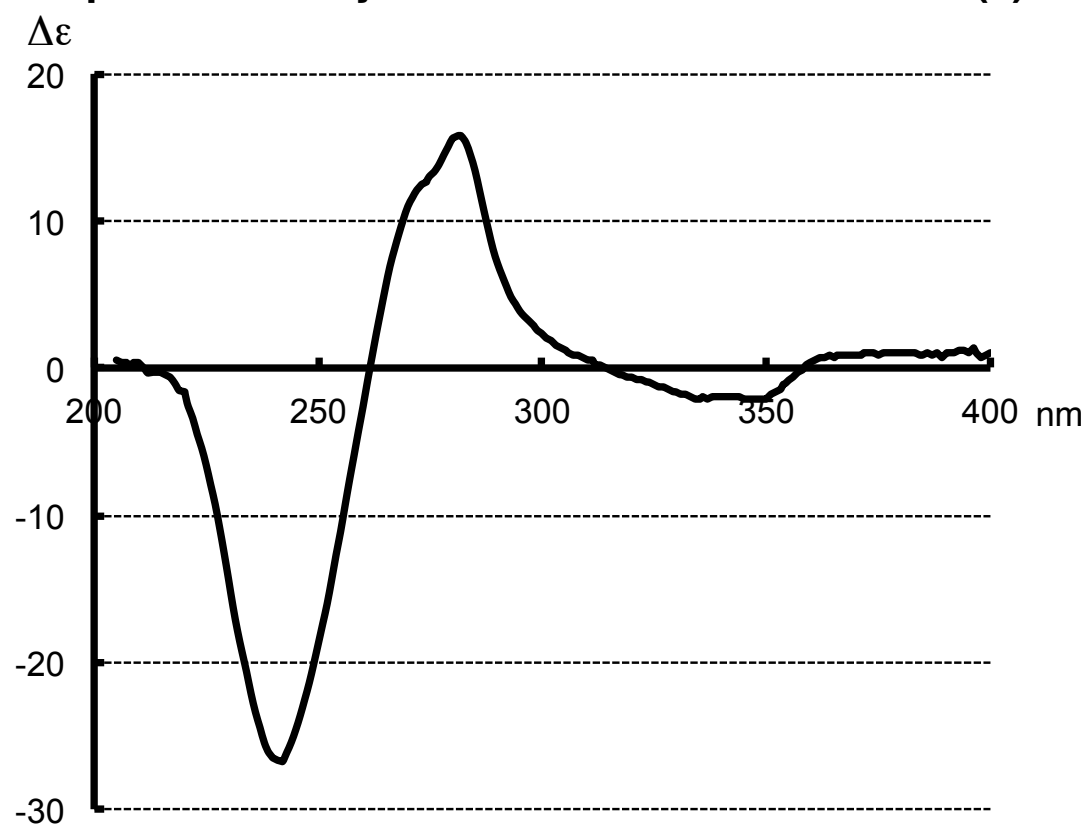
^{13}C NMR

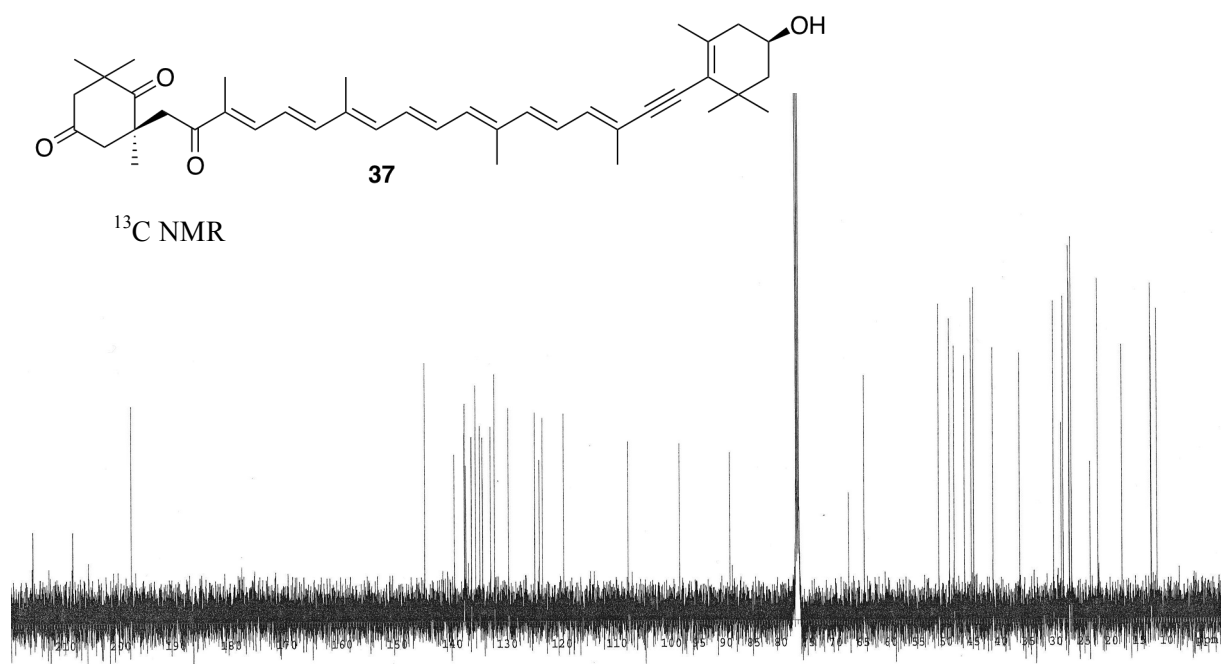
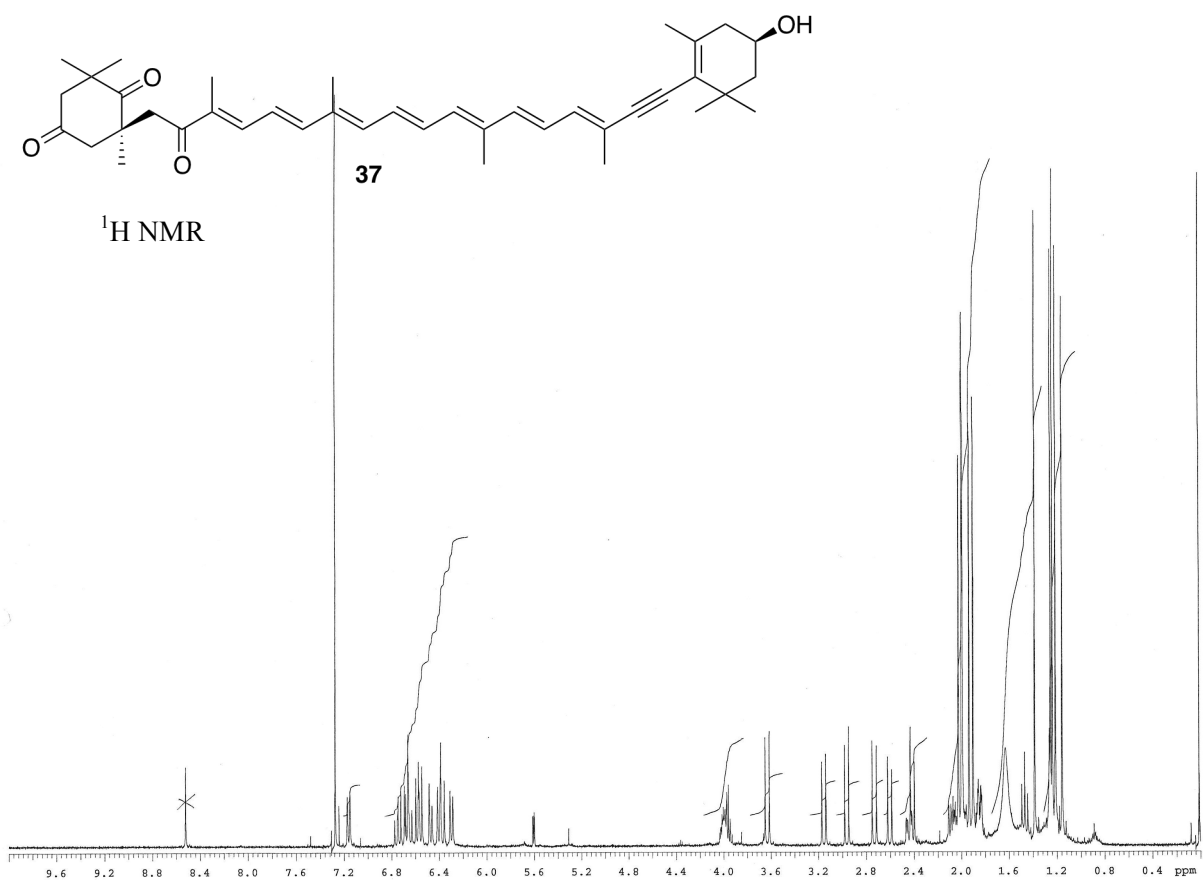


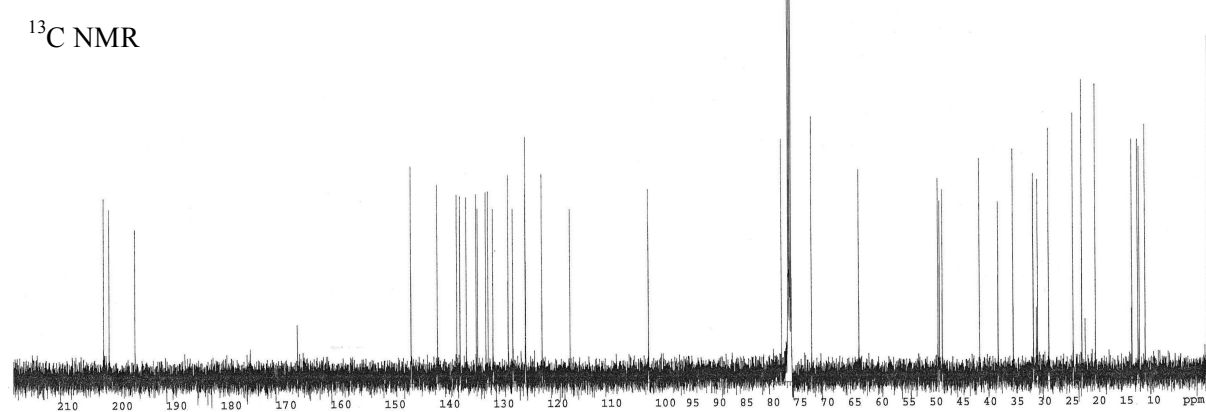
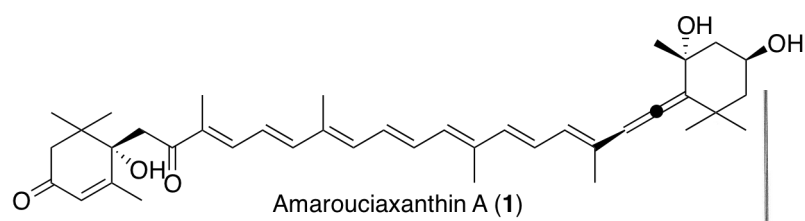




CD spectrum of Synthetic Amarouciaxanthin B (2) in EPA







CD spectrum of Synthetic Amarouciaxanthin A (1) in EPA

