

Supporting Information

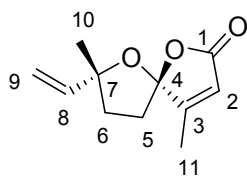
**Asymmetric Total Synthesis of Naturally Occurring Spirocyclic
Tetranorsesquiterpenoid Lanceolactone A**

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India

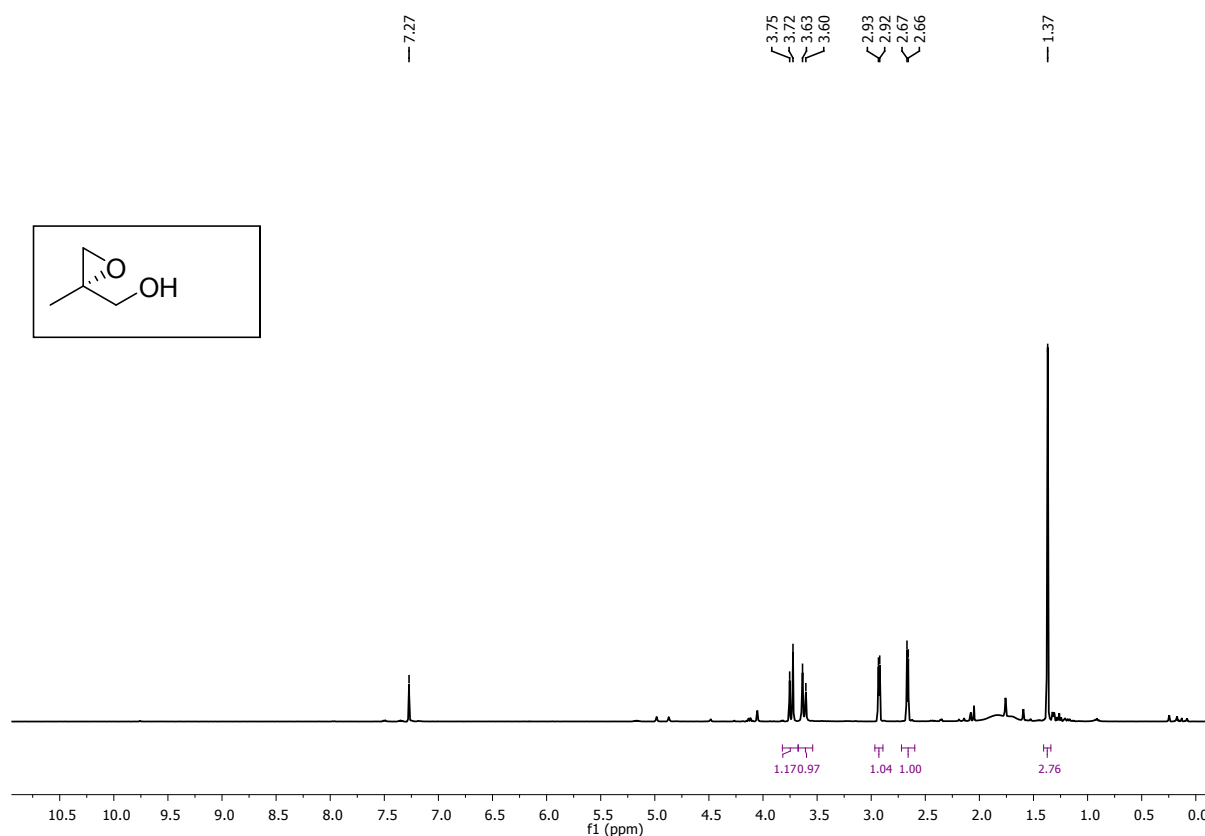
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2. NMR data for all compounds	S3-S21
3. Crystal data for compound 2	S22

Table SI-1: NMR comparison table of natural and synthetic Lanceolactone A

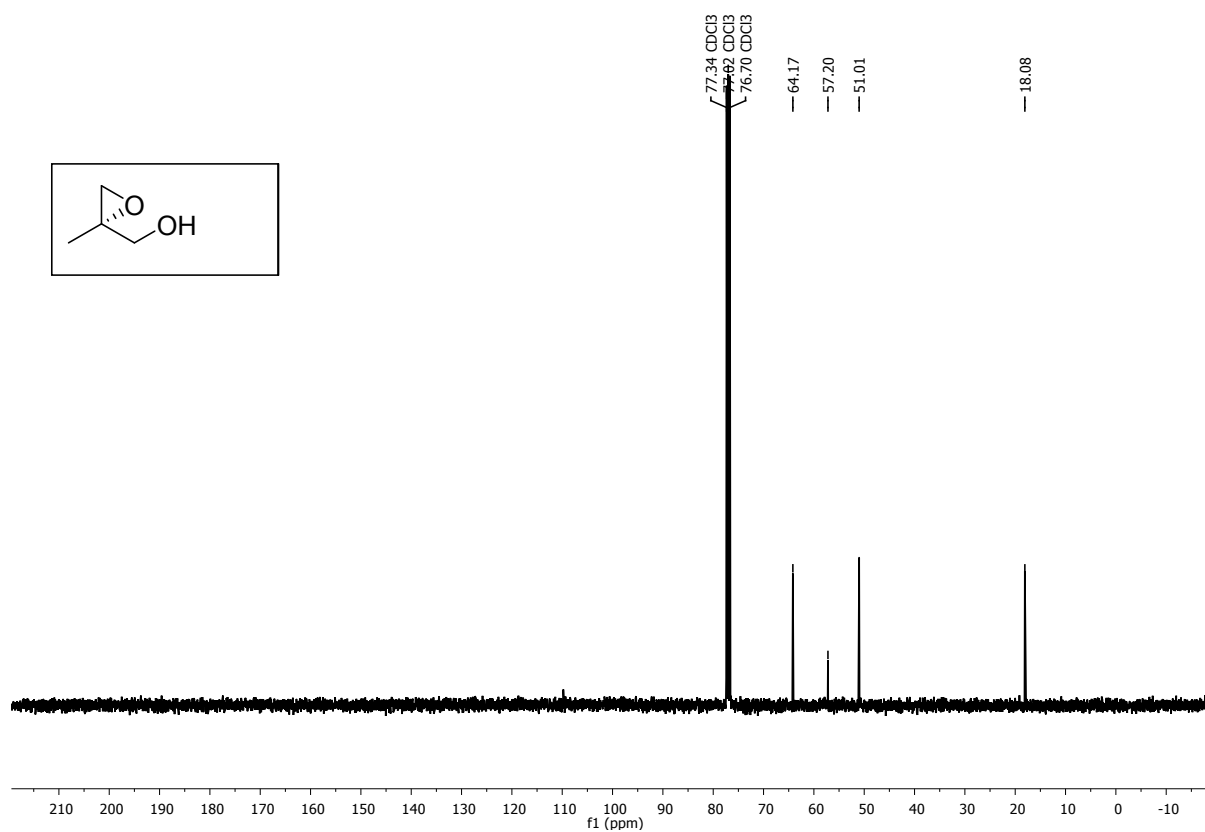


Position	Reported ^1H δ (ppm); J (Hz)	Observed ^1H δ (ppm); J (Hz)	$\Delta\delta$ (ppm)	Reported ^{13}C δ (ppm)	Observed ^{13}C δ (ppm)	$\Delta\delta$ (ppm)
1				170.0	169.9	0.1
2	5.86, q, (1.4)	5.87, q, (1.6)	0.01	119.4	119.4	0.0
3				163.9	163.8	0.1
4				115.2	115.1	0.1
5	2.08, m; 2.21, m	2.09, m; 2.22, m		34.3	34.3	0.0
6	2.18, m; 2.25, m	2.18, m; 2.24, m		36.1	36.0	0.1
7				87.5	87.4	0.1
8	5.92, dd, (10.7, 1.1)	5.93, dd, (10.8, 1.2)	0.01	142.2	142.2	0.0
9	5.06, dd, (10.7, 1.1) 5.27, dd, (17.3, 1.2)	5.09, dd, (10.8, 1.2), 5.27, dd, (17.3, 1.2)		112.2	112.2	0.0
10	1.52, s	1.54, s	0.02	27.7	27.7	0.0
11	2.05, d, (1.4)	2.07, d, (1.6)	0.02	12.6	12.5	0.1

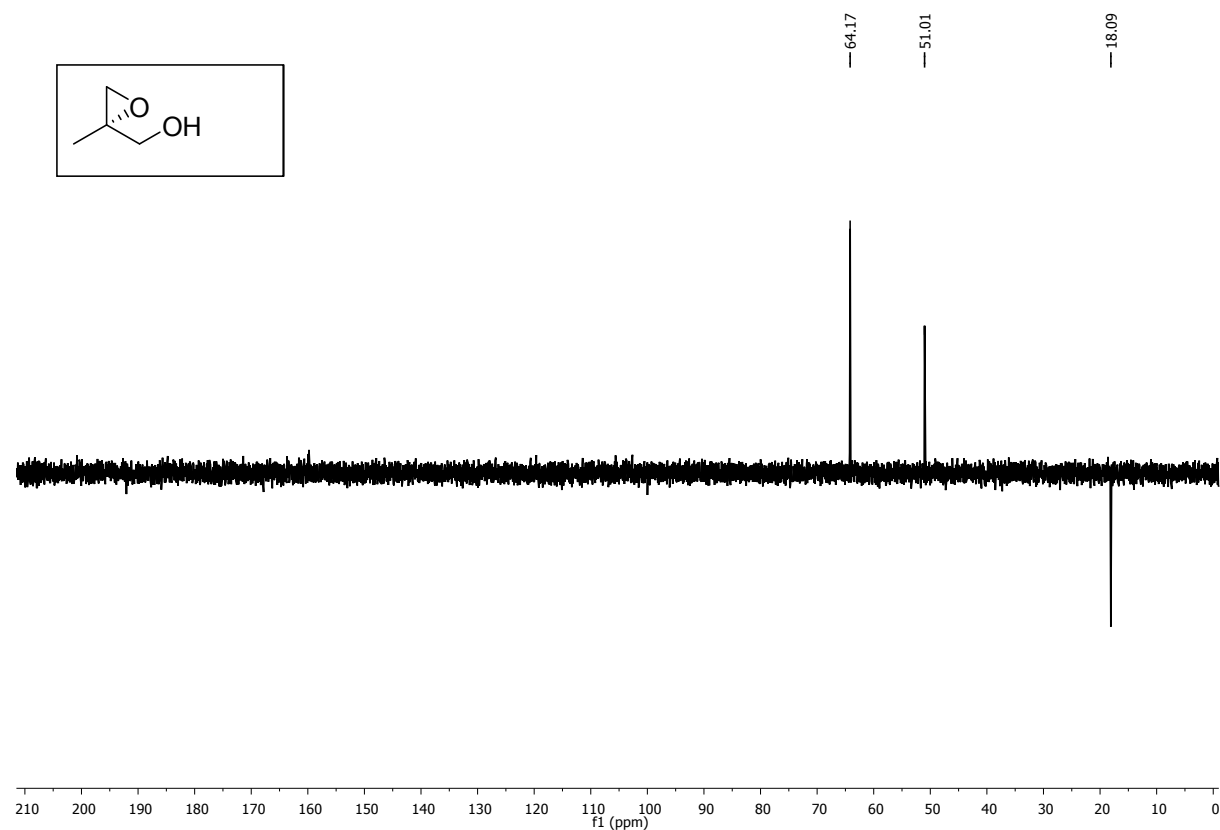
¹H NMR of compound 6 (400 MHz, CDCl₃)



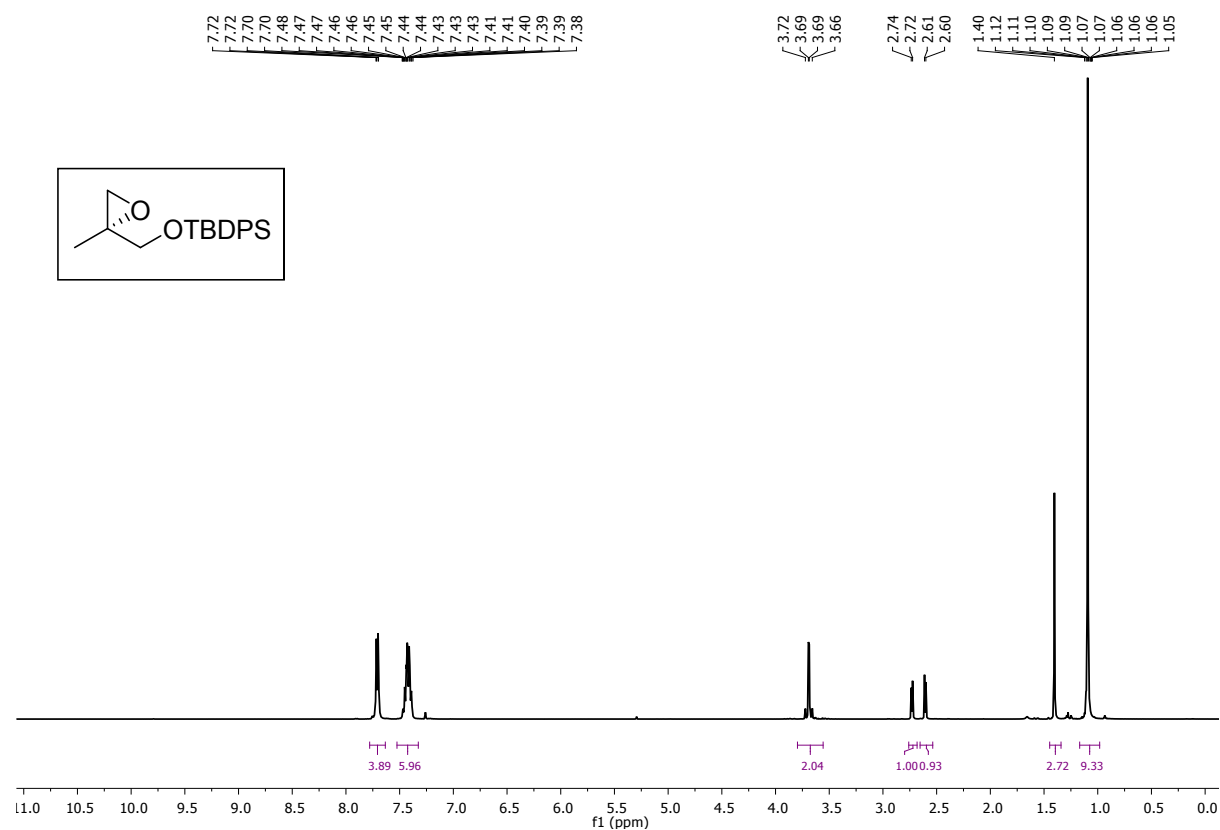
¹³C NMR of compound 6 (101 MHz, CDCl₃)



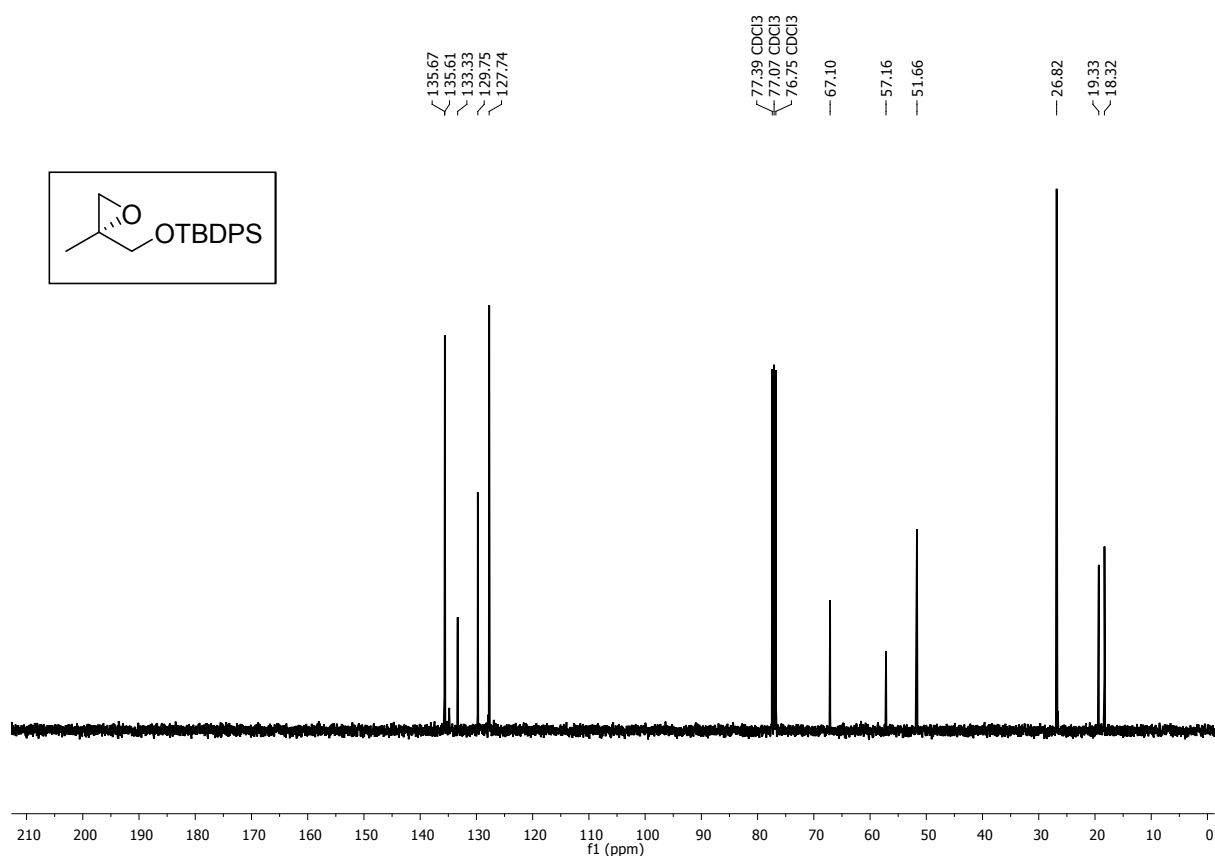
DEPT-135- NMR of compound 6 (101 MHz, CDCl₃)



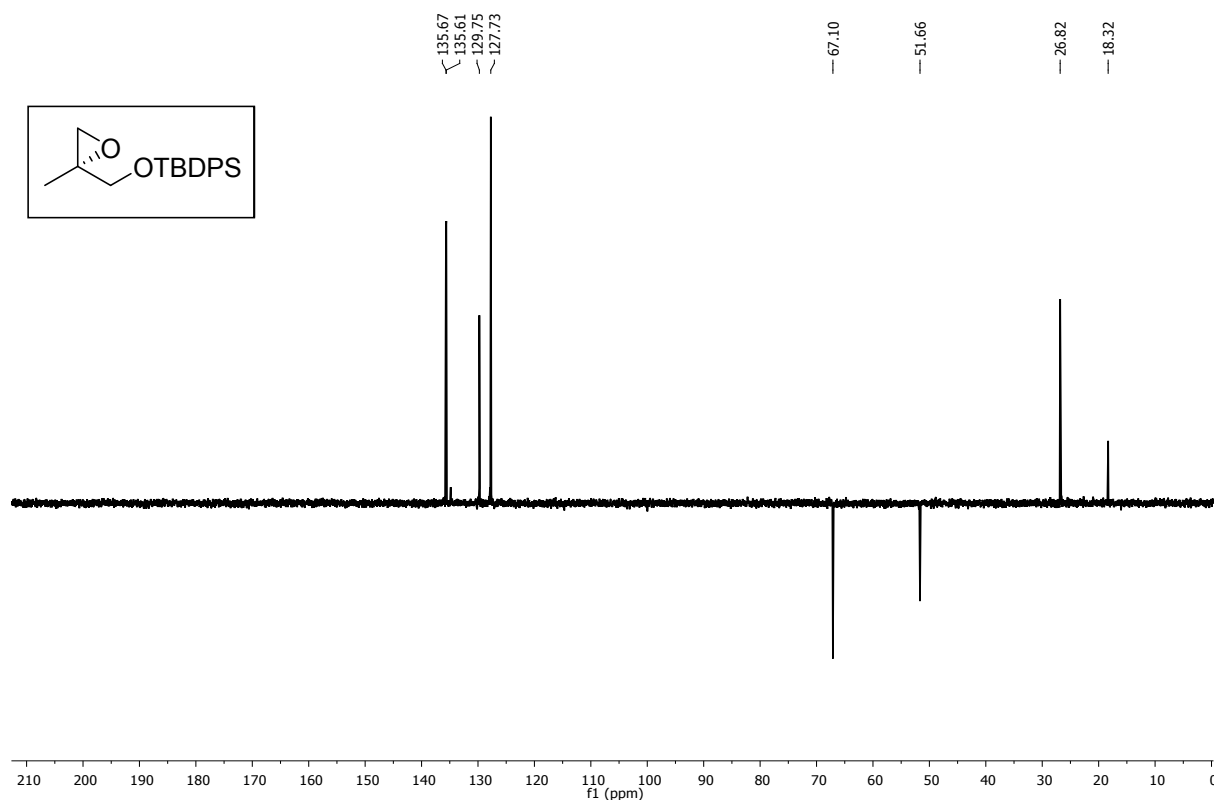
¹H NMR of compound 7 (400 MHz, CDCl₃)



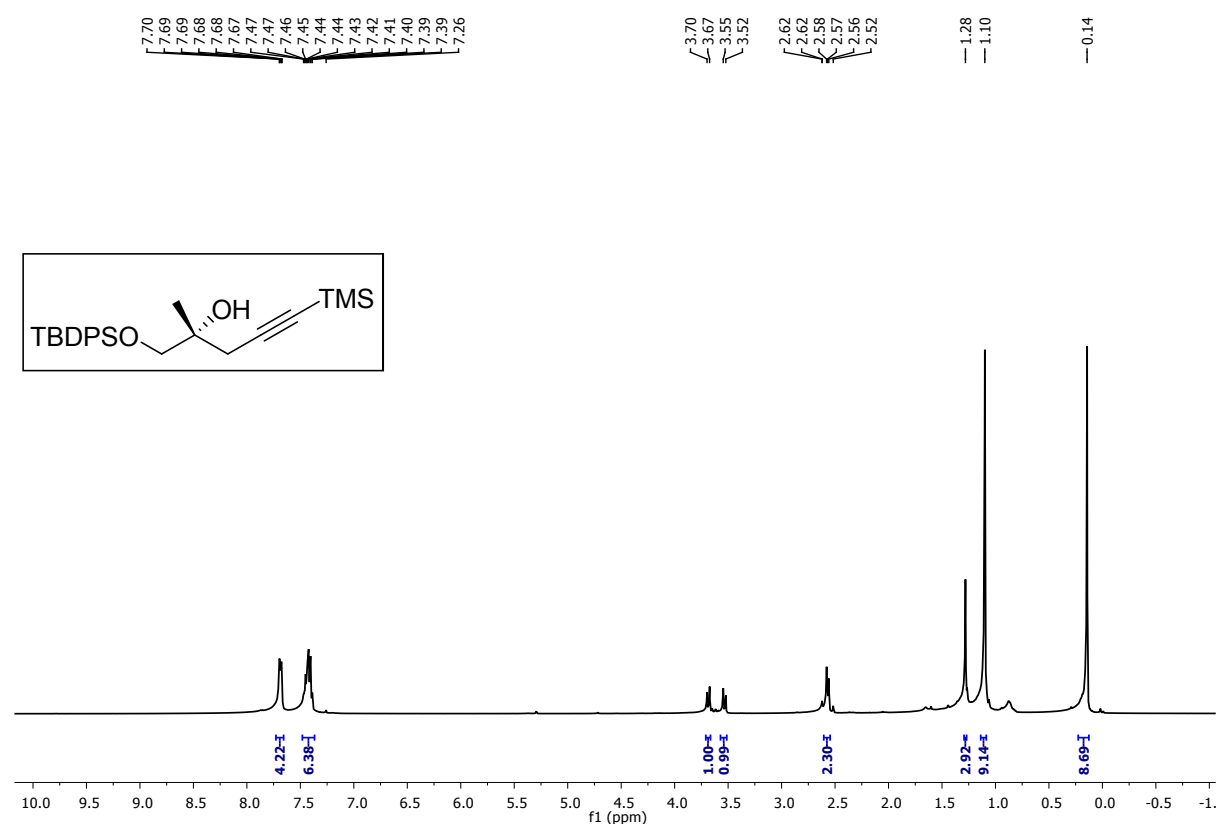
¹³C NMR of compound 7 (101 MHz, CDCl₃)



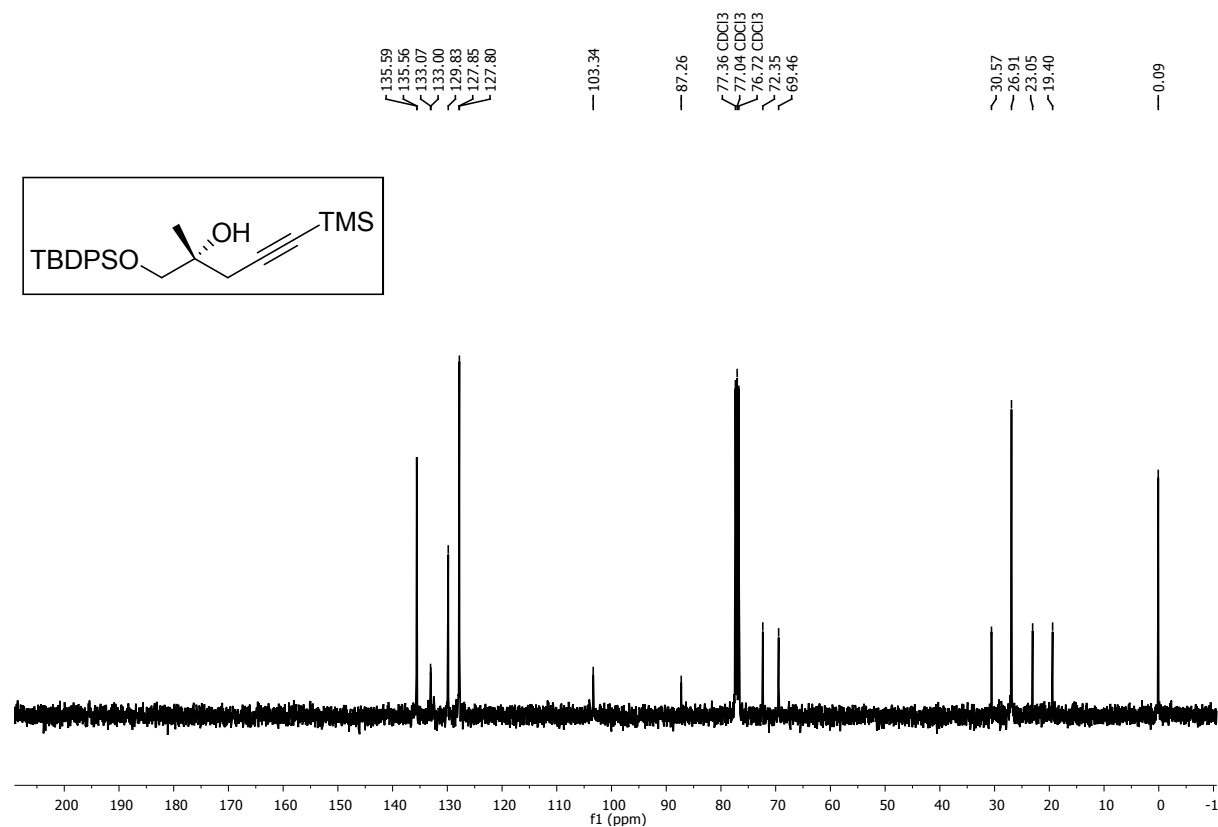
DEPT-135- NMR of compound 7 (101 MHz, CDCl₃)



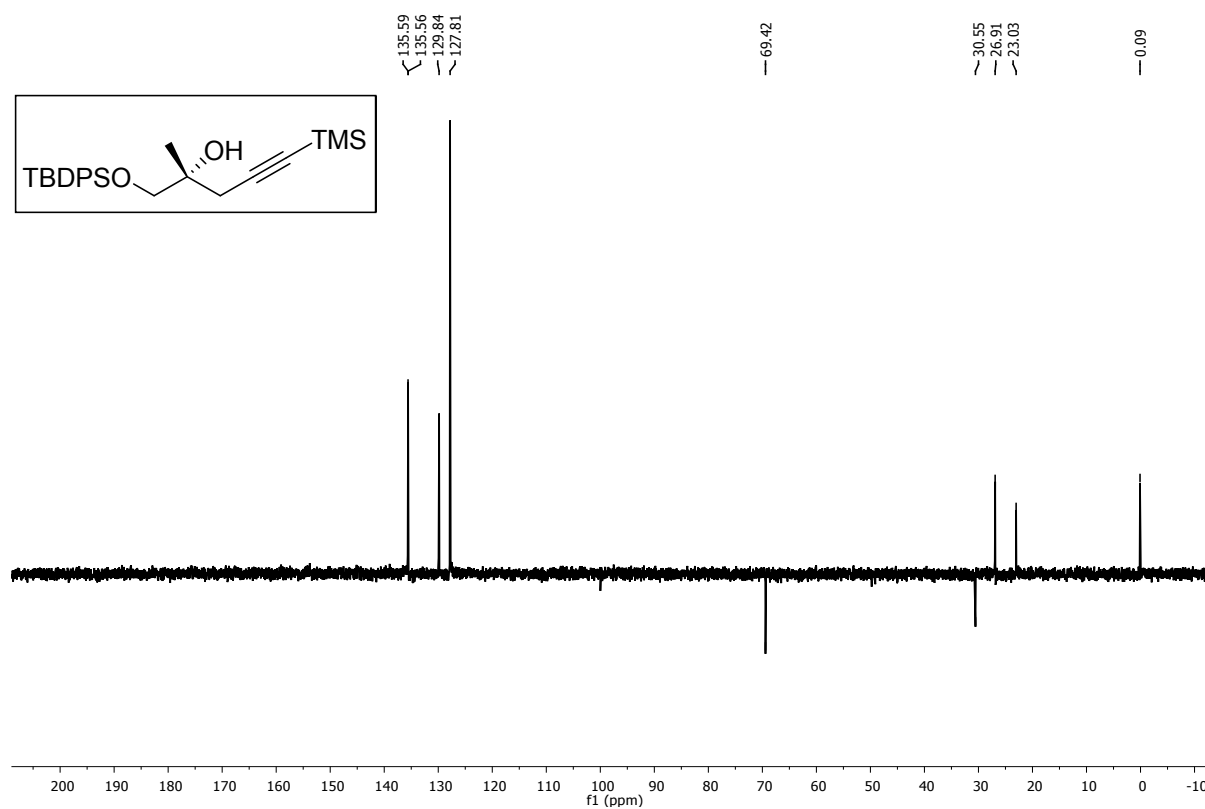
¹H NMR of compound 8 (400 MHz, CDCl₃)



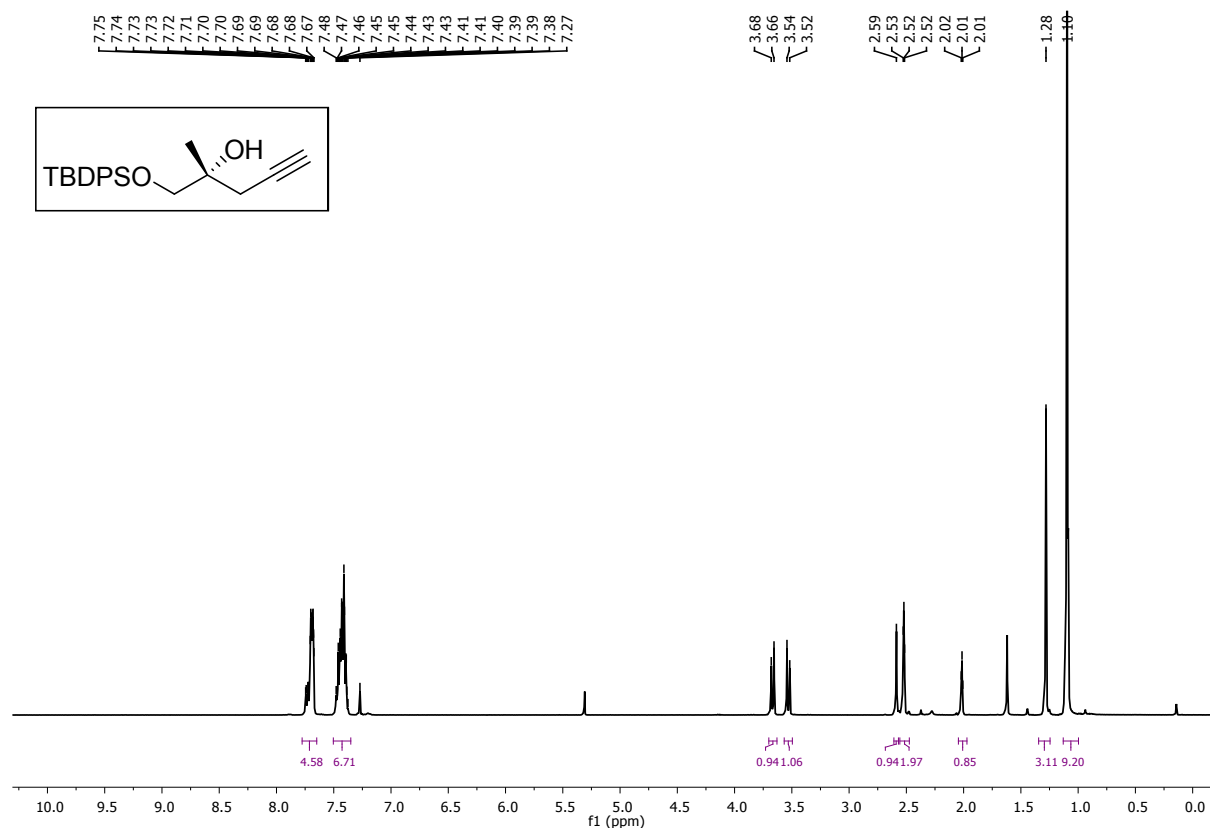
¹³C NMR of compound 8 (101 MHz, CDCl₃)



DEPT-135- NMR of compound 8 (101 MHz, CDCl₃)



¹H NMR of compound 4 (400 MHz, CDCl₃)



Chemical structure of the compound is shown in the inset:

CC(C)(O)C#C

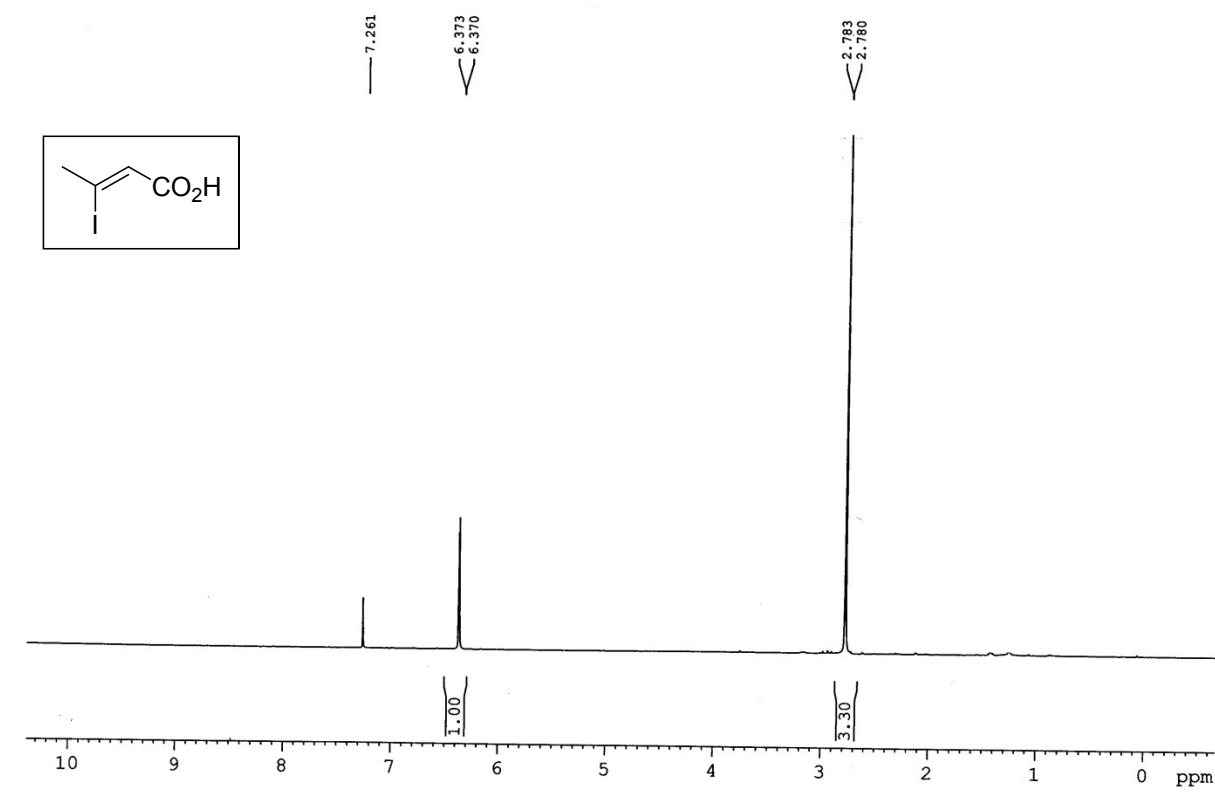
The ¹³C NMR spectrum (CDCl₃) shows the following chemical shifts (ppm):

- 135.64, 135.60, 134.81, 132.90, 132.84, 129.86, 129.65, 127.81, 127.78, 127.73
- 80.78, 77.35, 77.03, 76.72, 72.26, 70.67, 69.41
- 29.09, 26.87, 22.97, 19.33

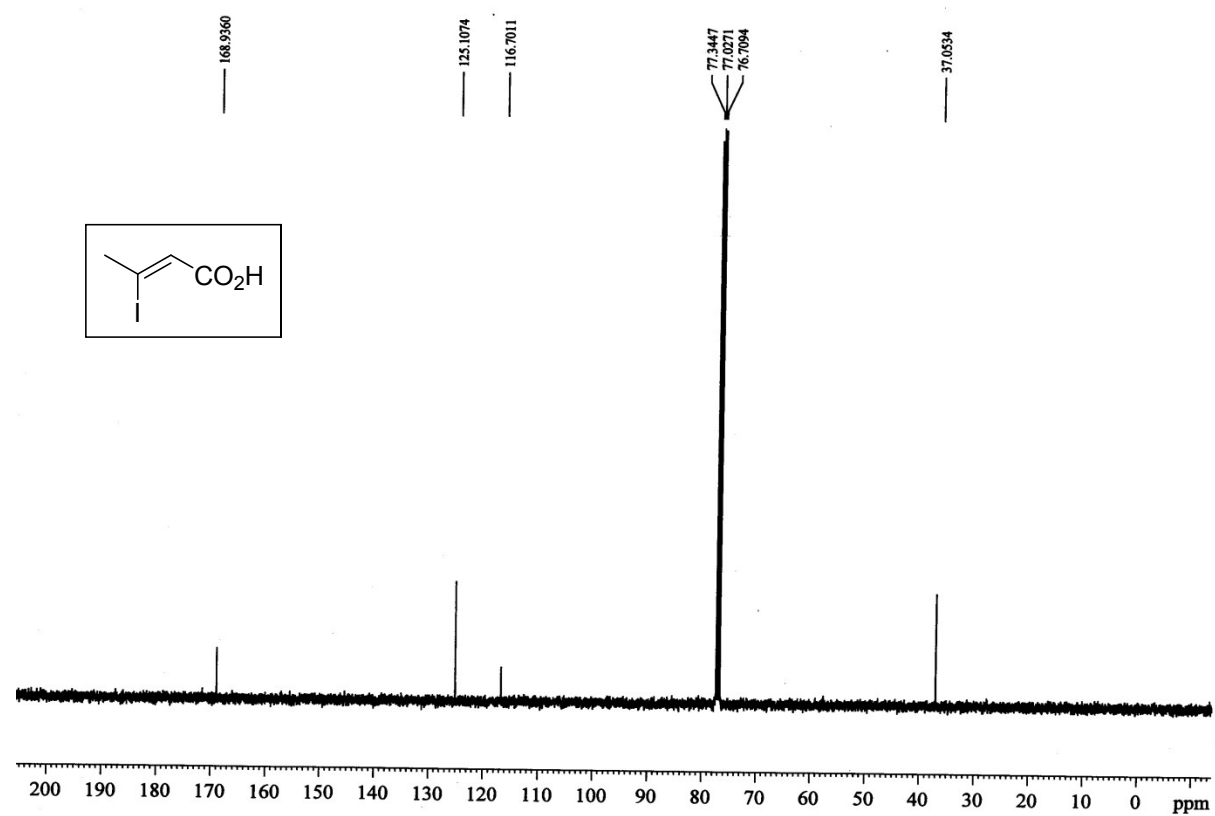
The spectrum displays several peaks corresponding to these chemical shifts, with the solvent peak (CDCl₃) visible at 77.03 ppm.

[illegible]

^1H NMR of compound 5 (400 MHz, CDCl_3)



^{13}C NMR of compound 5 (101 MHz, CDCl_3)



Chemical structure of 3-methylcrotonic acid (isobut-3-enoic acid) is shown in the top left corner:

CC(=C)C(=O)O

The spectrum displays two main peaks:

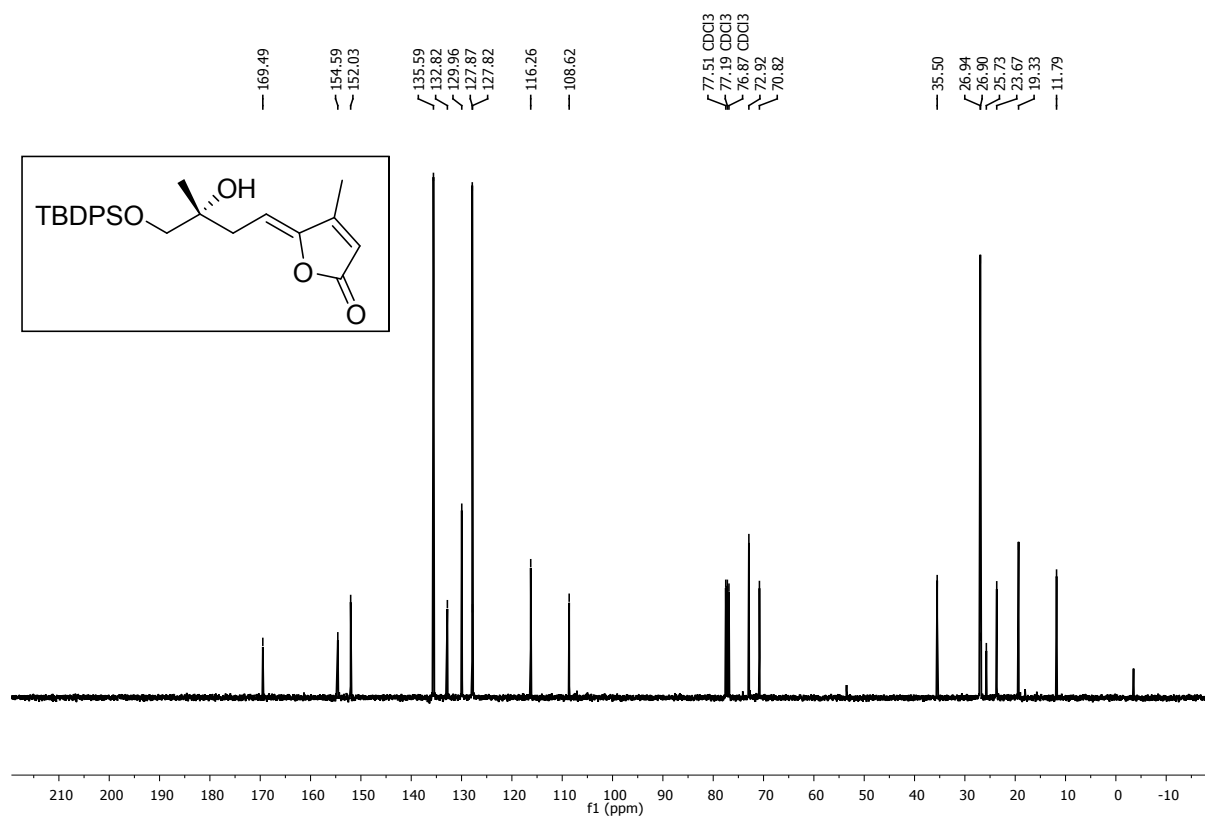
- A peak at 125.1067 ppm, corresponding to the carbonyl carbon (C=O).
- A peak at 37.0544 ppm, corresponding to the methyl carbon (CH₃).

The x-axis is labeled "ppm" and ranges from 0 to 200.

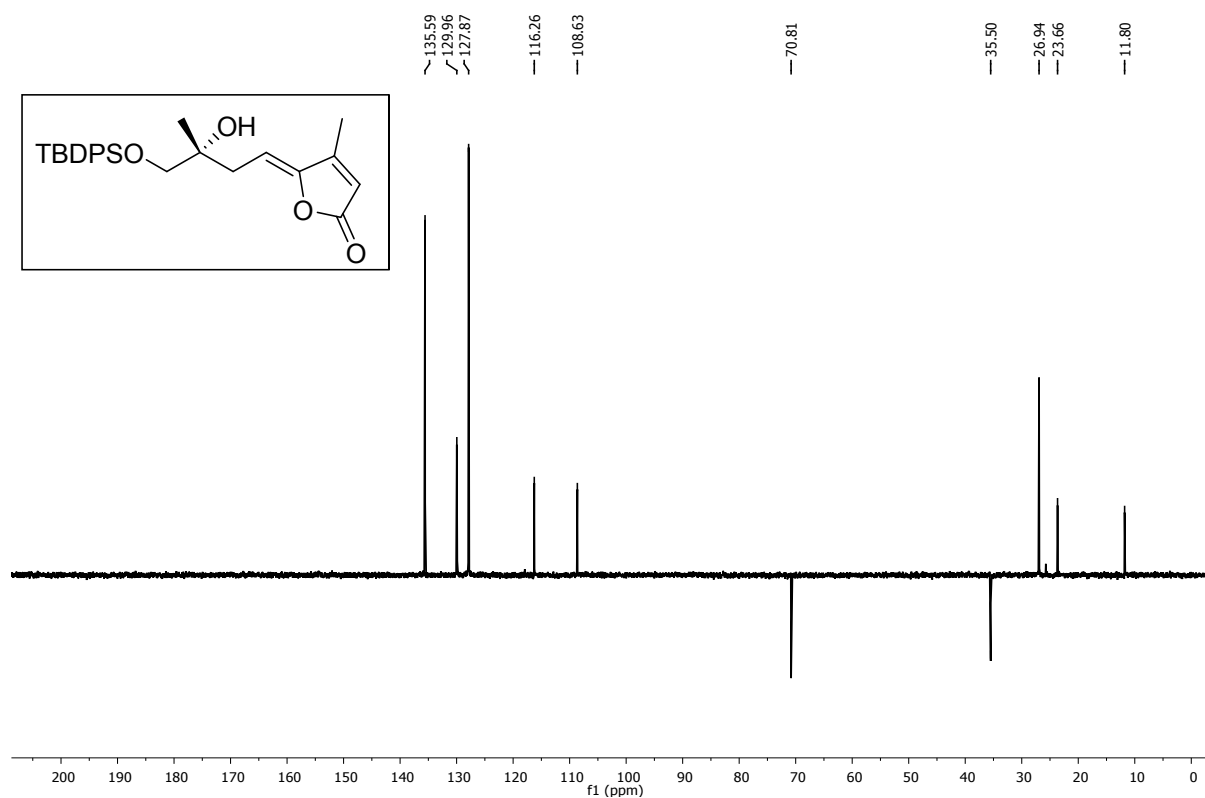
Chemical structure: CC1=CC(=C(C=C1)OC(=O)C=C[C@H](O)[C@@H](C)COP(=O)(C1=CC=CC=C1)C2=CC=CC=C2C3(C)C(C)C(C)C3

¹H NMR spectrum (CDCl₃) showing peaks from 0.0 to 11.0 ppm. The spectrum includes a broad singlet at 7.6 ppm (OH), aromatic signals between 7.2-7.7 ppm, a singlet at 5.9 ppm (CH), a doublet at 3.5 ppm (CH₂), a multiplet at 2.6 ppm (CH₃), and aliphatic signals between 1.1-1.3 ppm. Integration values are shown below the peaks: 4.66, 6.87, 1.00, 1.06, 2.30, 1.35, 1.20, 3.26, 2.87, 8.96.

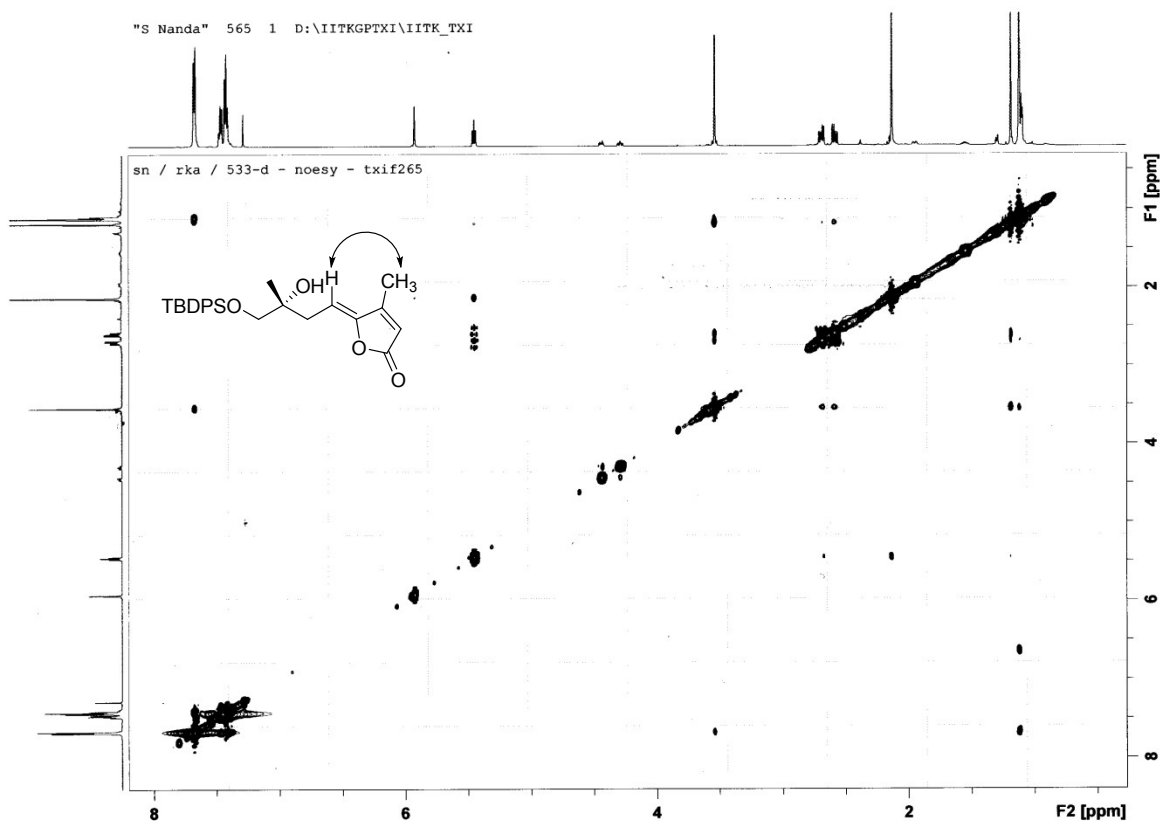
¹³C NMR of compound 3 (101 MHz, CDCl₃)



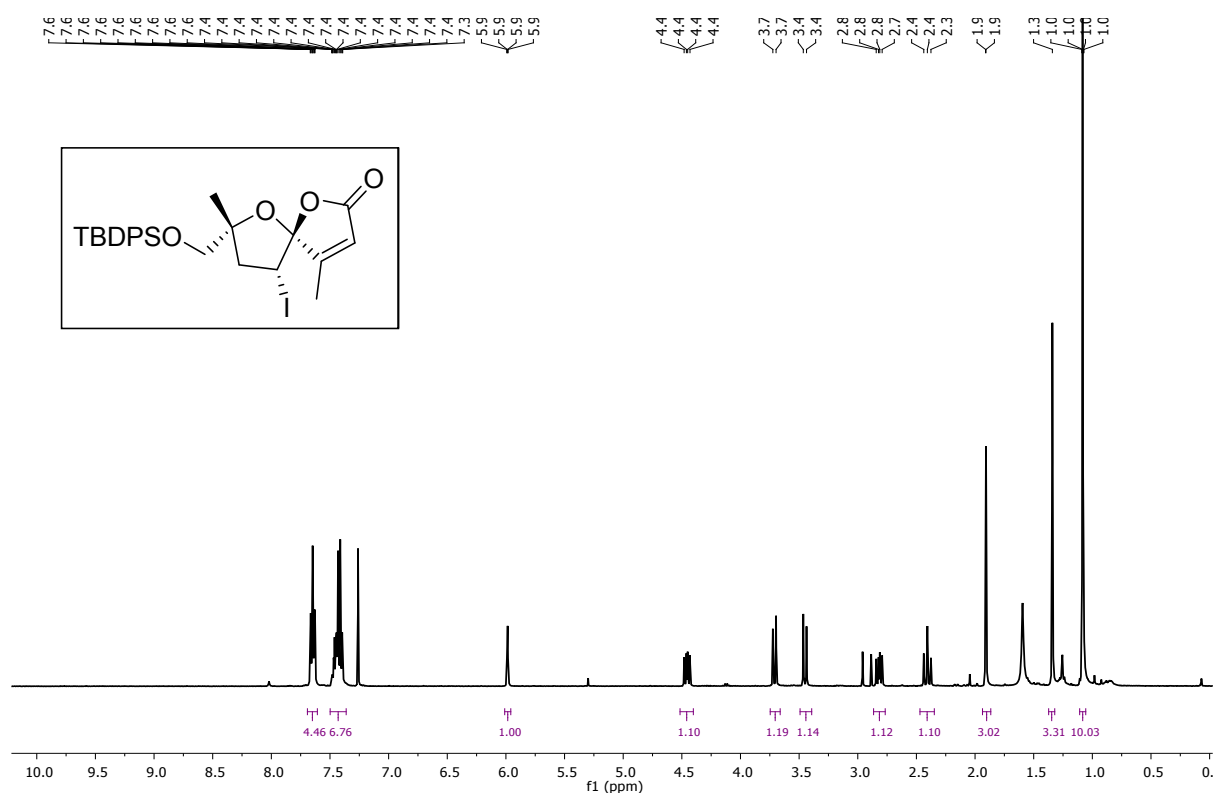
DEPT-135- NMR of compound 3 (101 MHz, CDCl₃)



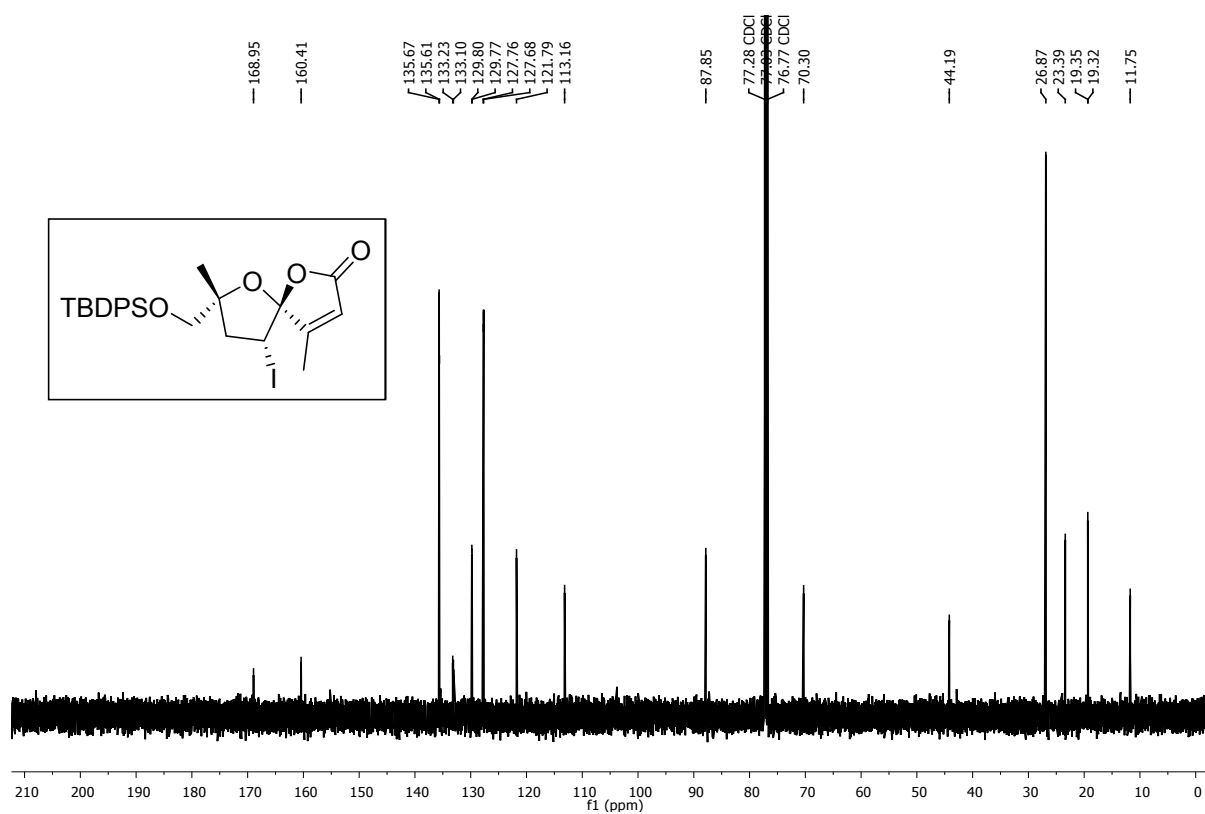
NOESY Spectrum of compound 3 (600 MHz, CDCl₃)



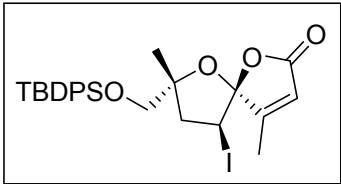
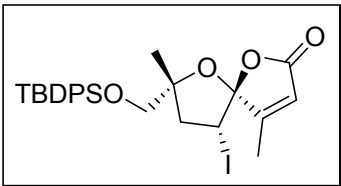
¹H NMR of compound 9 (400 MHz, CDCl₃)

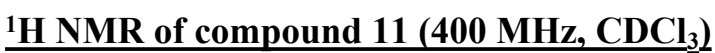


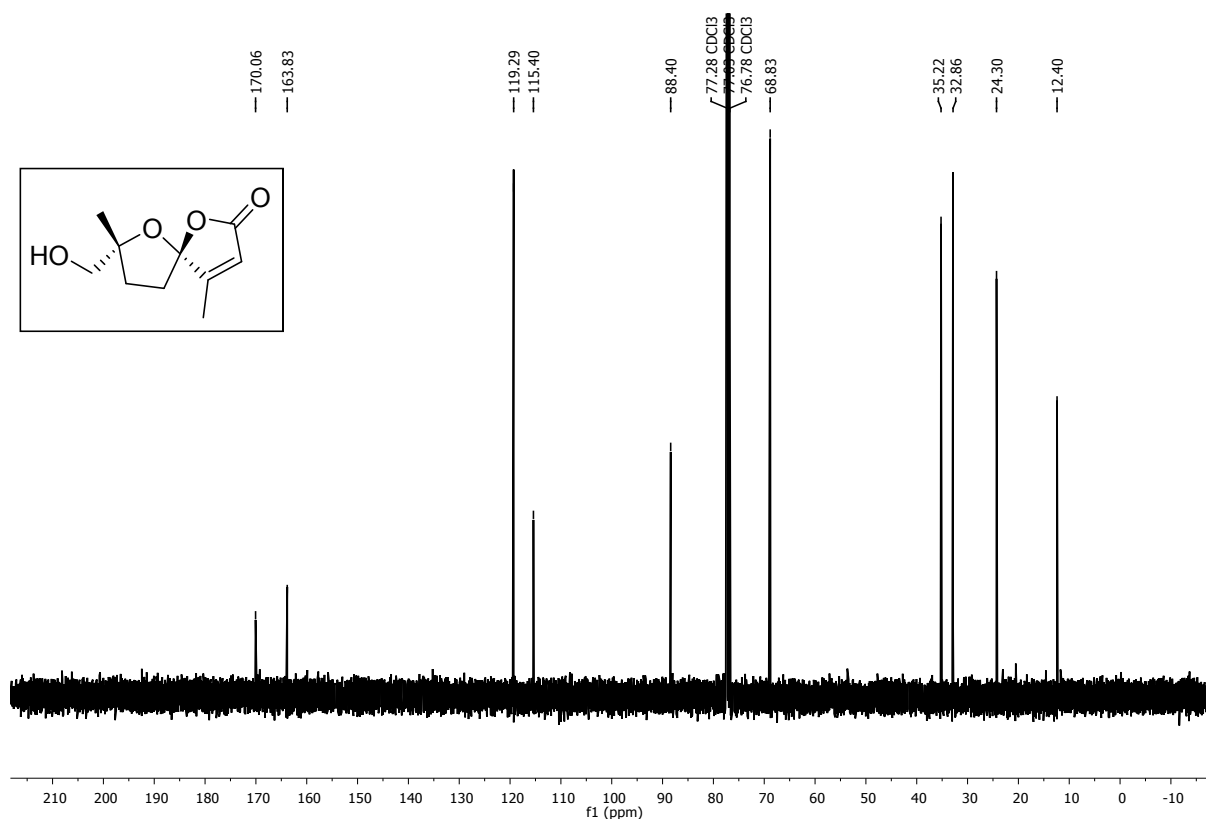
¹³C NMR of compound 9 (126 MHz, CDCl₃)



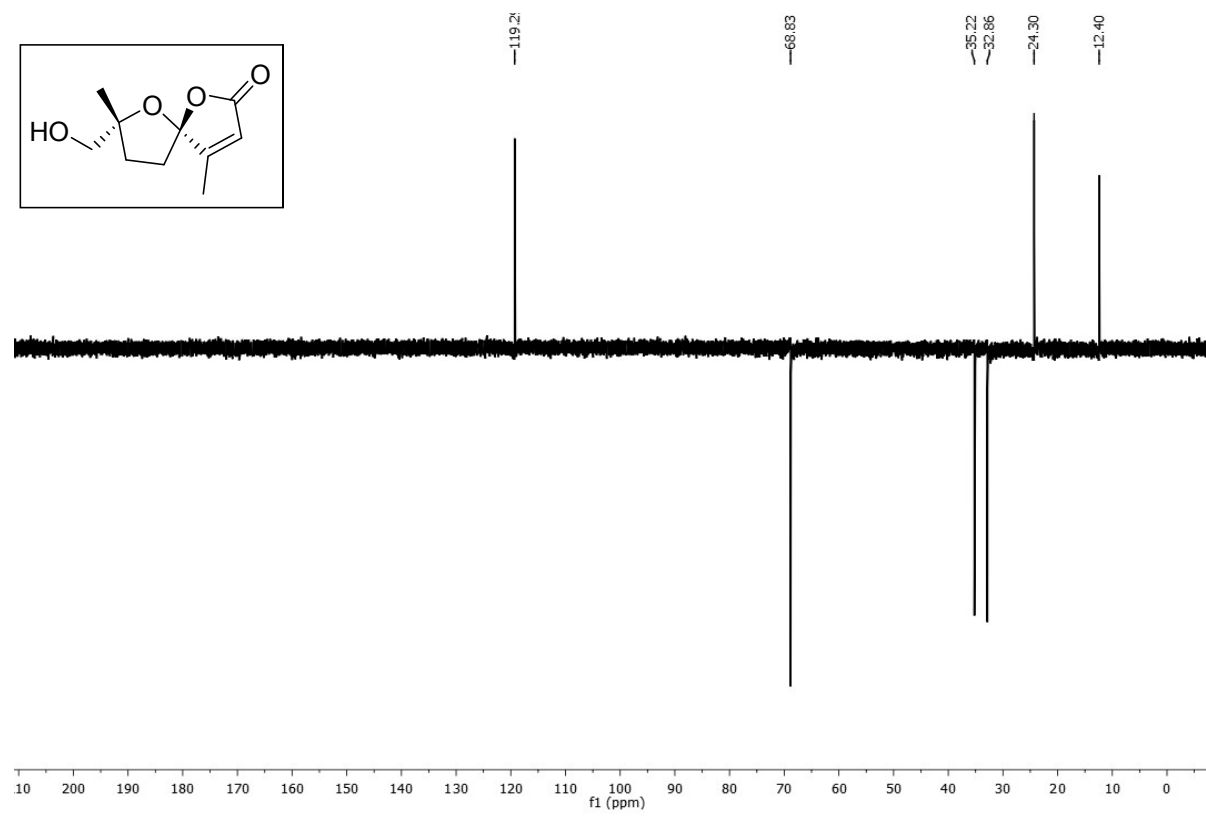
DEPT-135- NMR of compound 9 (126 MHz, CDCl₃)



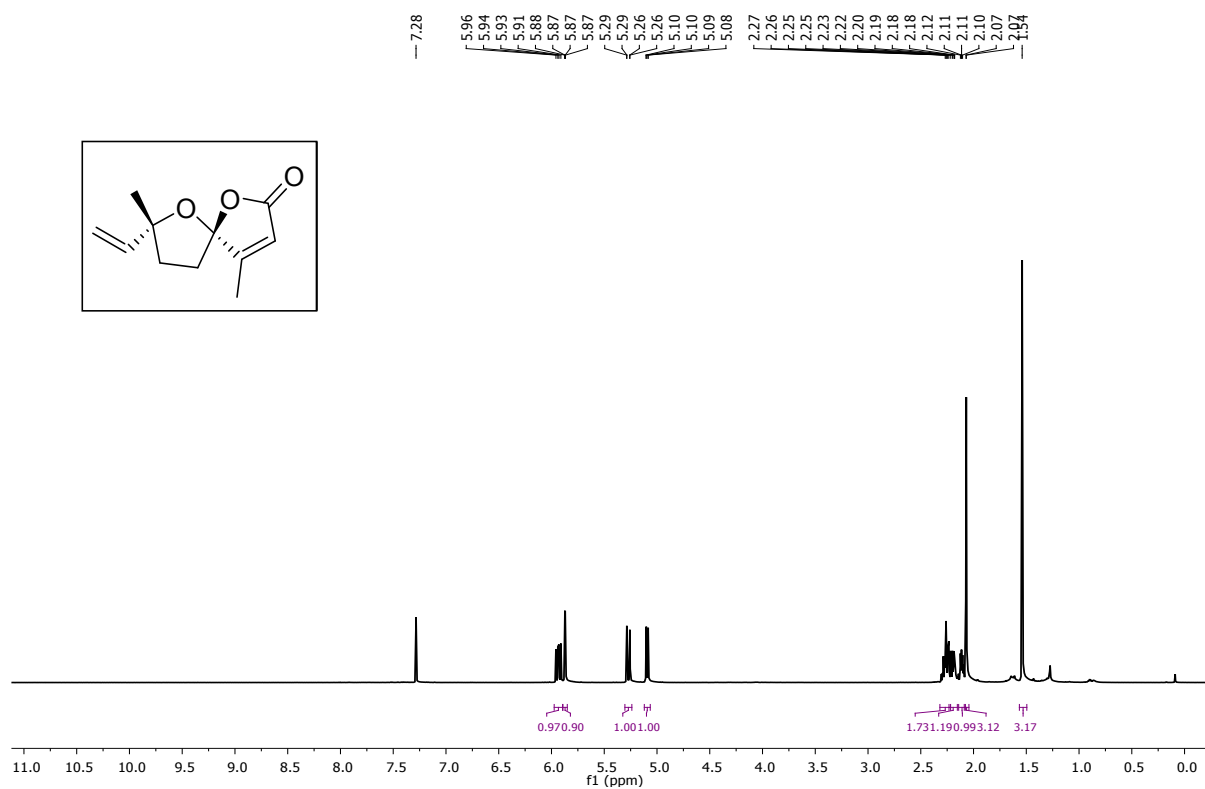




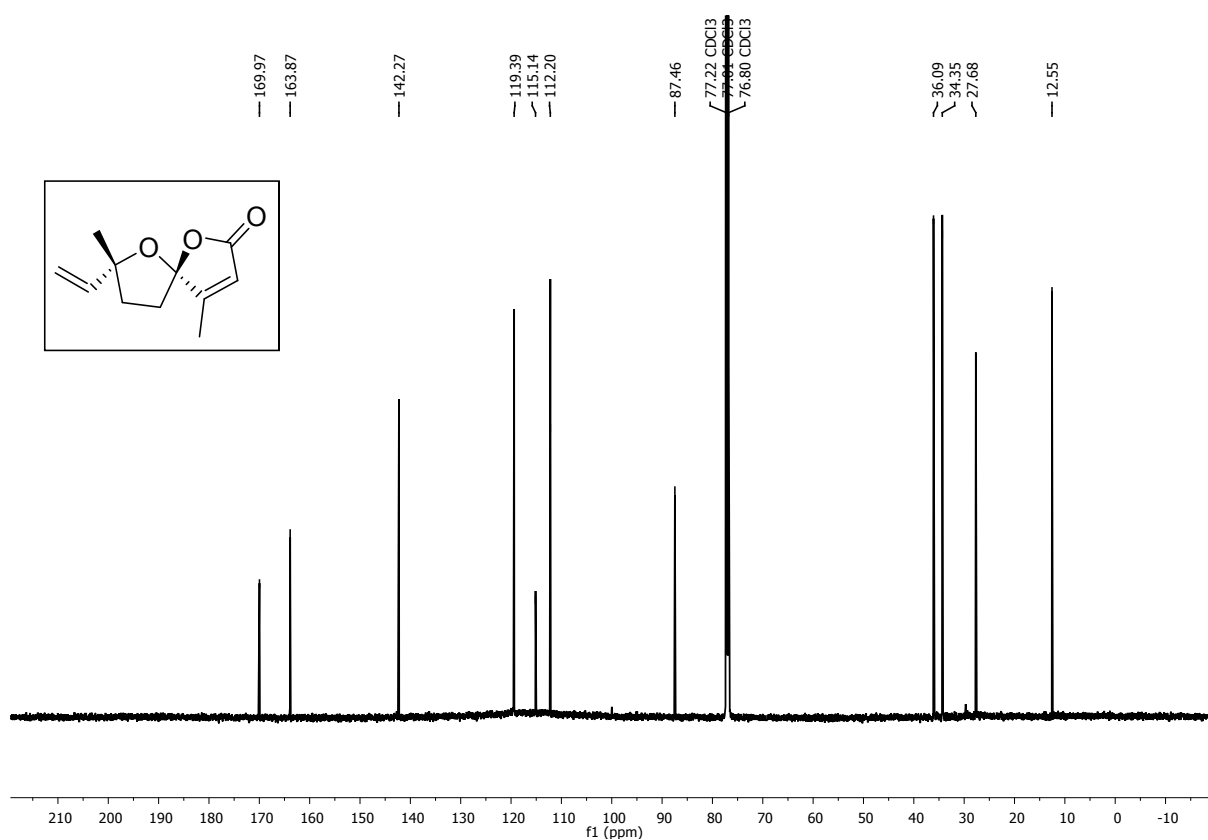
DEPT-135- NMR of compound 11 (151 MHz, CDCl₃)



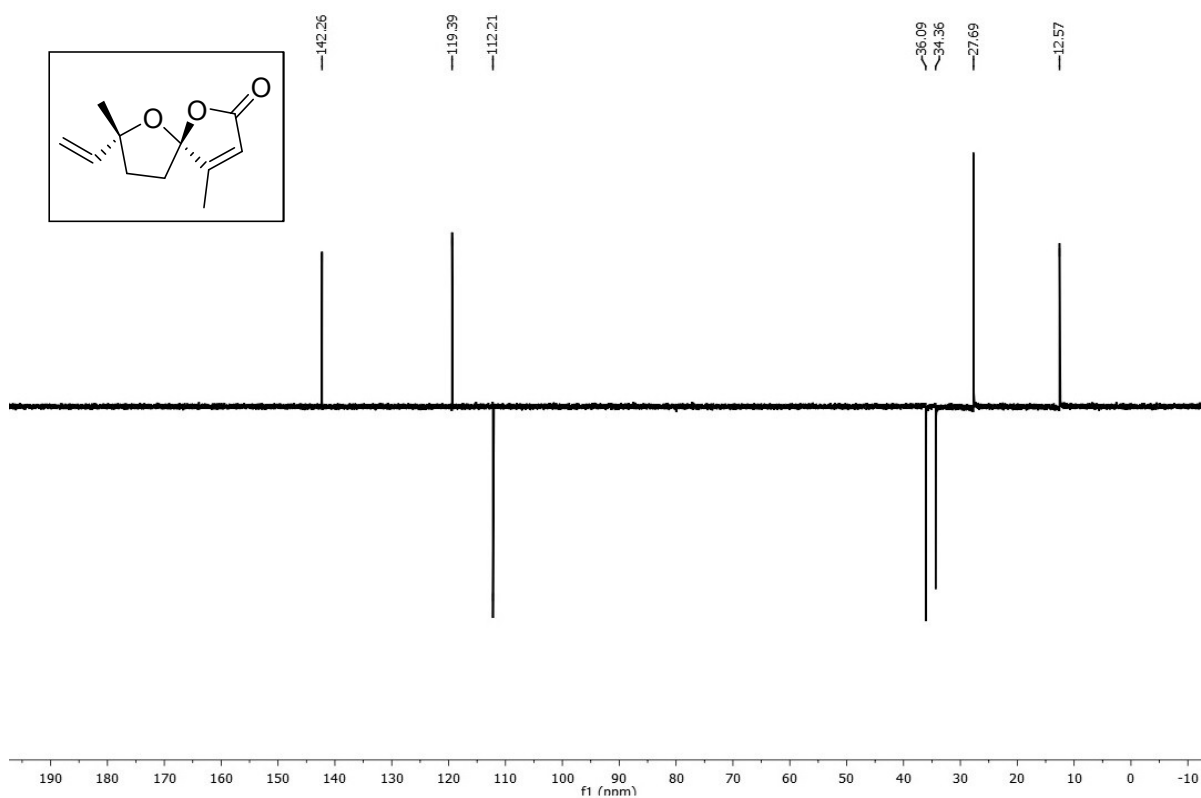
¹H NMR of compound 1; Lanceolactone A (600 MHz, CDCl₃)



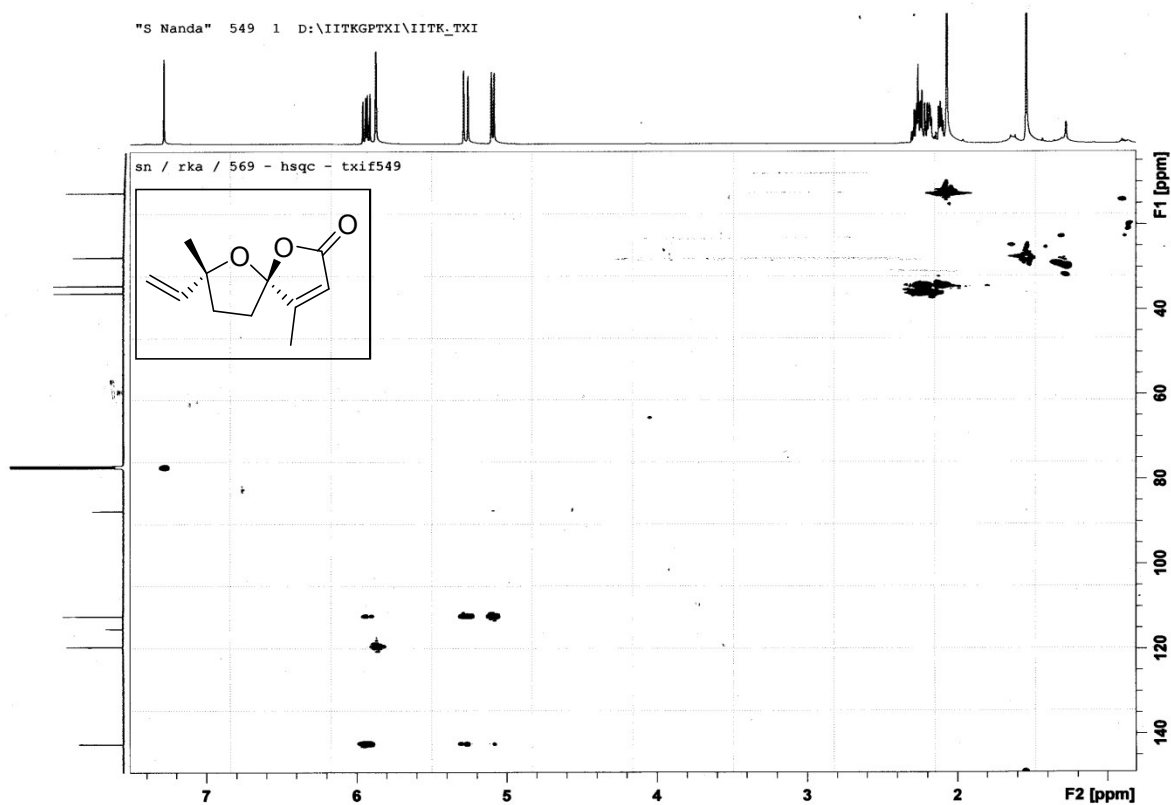
¹³C NMR of compound 1; Lanceolactone A (151 MHz, CDCl₃)



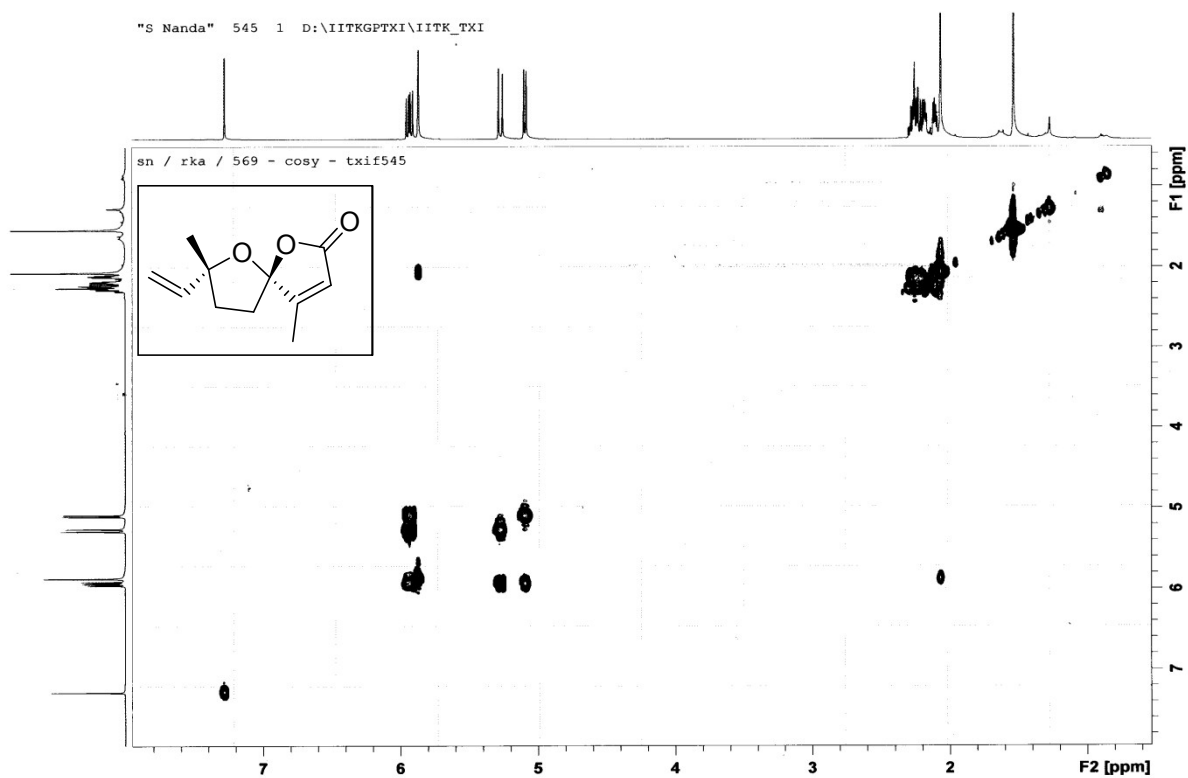
DEPT-135- NMR of compound 1; Lanceolactone A (151 MHz, CDCl₃)



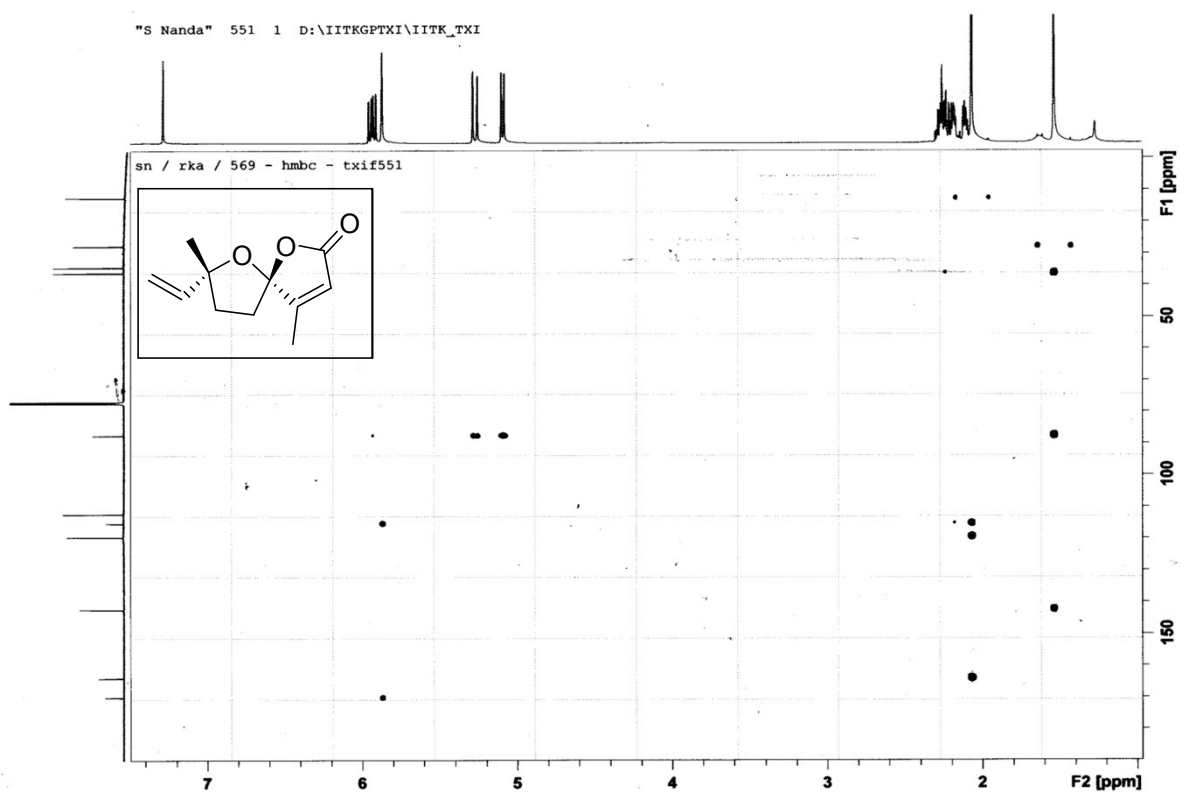
HSQC spectrum of compound 1; Lanceolactone A (600 MHz, CDCl₃)



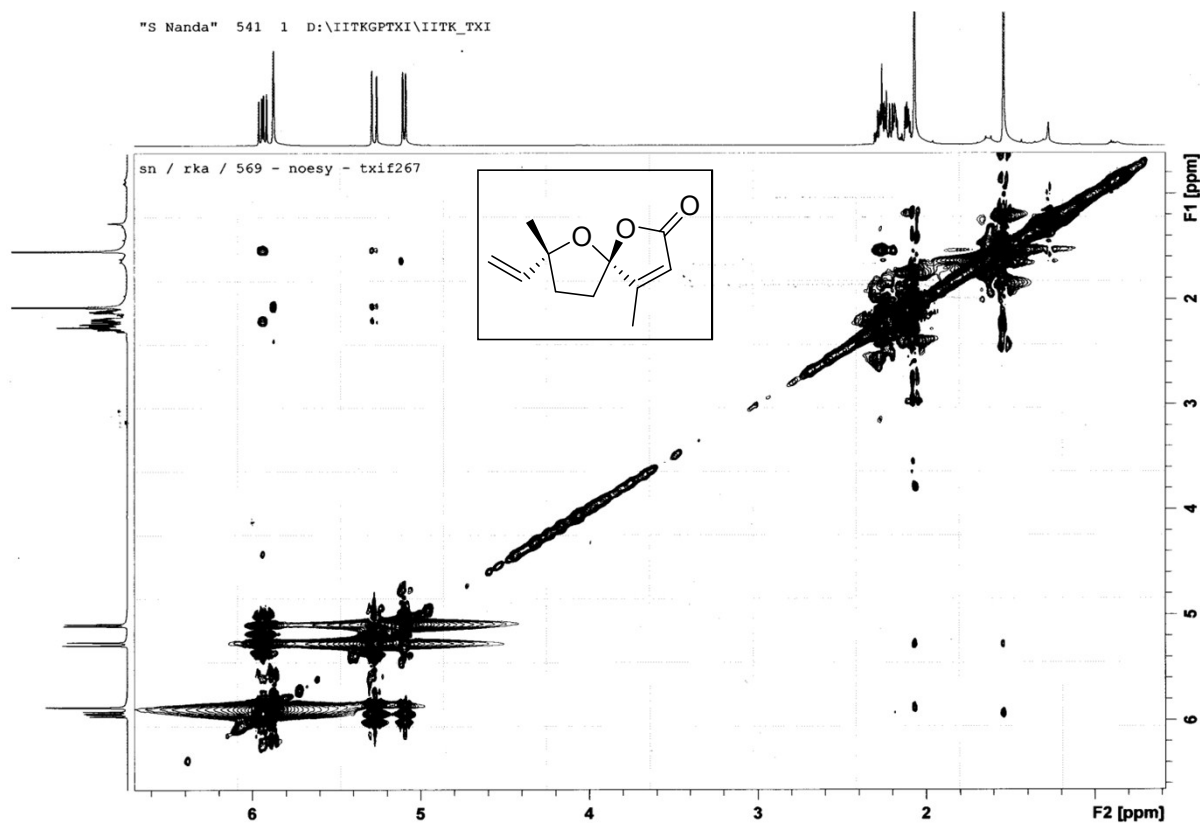
COSY Spectrum of compound 1; Lanceolactone A (600 MHz, CDCl₃)



HMBC Spectrum of compound 1; Lanceolactone A (600 MHz, CDCl₃)

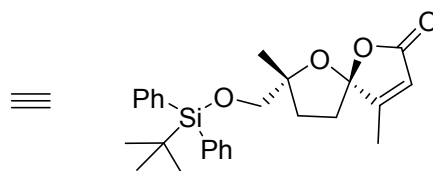
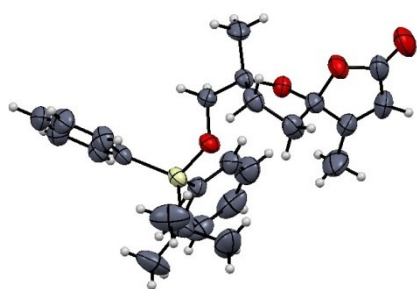


NOESY Spectrum of compound 1; Lanceolactone A (600 MHz, CDCl₃)



Crystal data and structure refinement for compound 2

X-ray crystal data of compound **2** (the following crystal has been deposited at the Cambridge Crystallographic Data Centre and has the deposition number CCDC NO: 1834617



CCDC NO: 1834617

ORTEP presentation (drawn at 50% probability)

Bond precision: C-C = 0.0050 Å

Wavelength=0.71073

Cell: a=11.660(14) b=12.070(9) c=18.027(13)

alpha=90

beta=100.58(7)

gamma=90

Temperature: 290 K

	Calculated	Reported
Volume	2494(4)	2494(4)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H32 O4 Si	?
Sum formula	C26 H32 O4 Si	C26 H32 O4 Si
Mr	436.61	436.60
Dx, g cm ⁻³	1.163	1.163
Z	4	4
Mu (mm ⁻¹)	0.122	0.122
F000	936.0	936.0
F000'	936.73	
h,k,lmax	13,14,21	13,14,21
Nref	4325	4284
Tmin,Tmax	0.978,0.984	
Tmin'	0.978	

Correction method= Not given

Data completeness= 0.991

Theta(max)= 24.860

R(reflections)= 0.0499(2513)

wR2(reflections)= 0.1623(4284)

S = 0.894

Npar= 285