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A Versatile Approach to the Enantiospecific Syntheses of Sugar-Linked Oxapolyquinanes *via* IPKR

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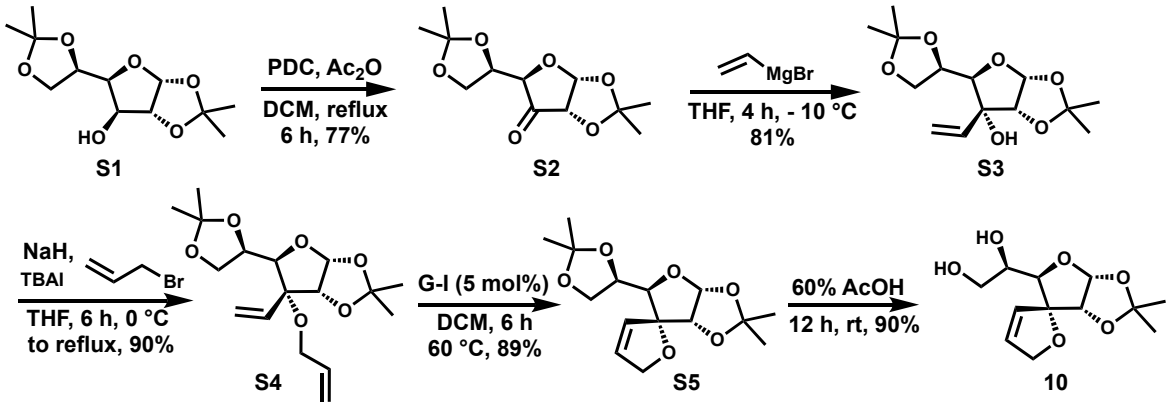
1. Preparation of Starting Material:



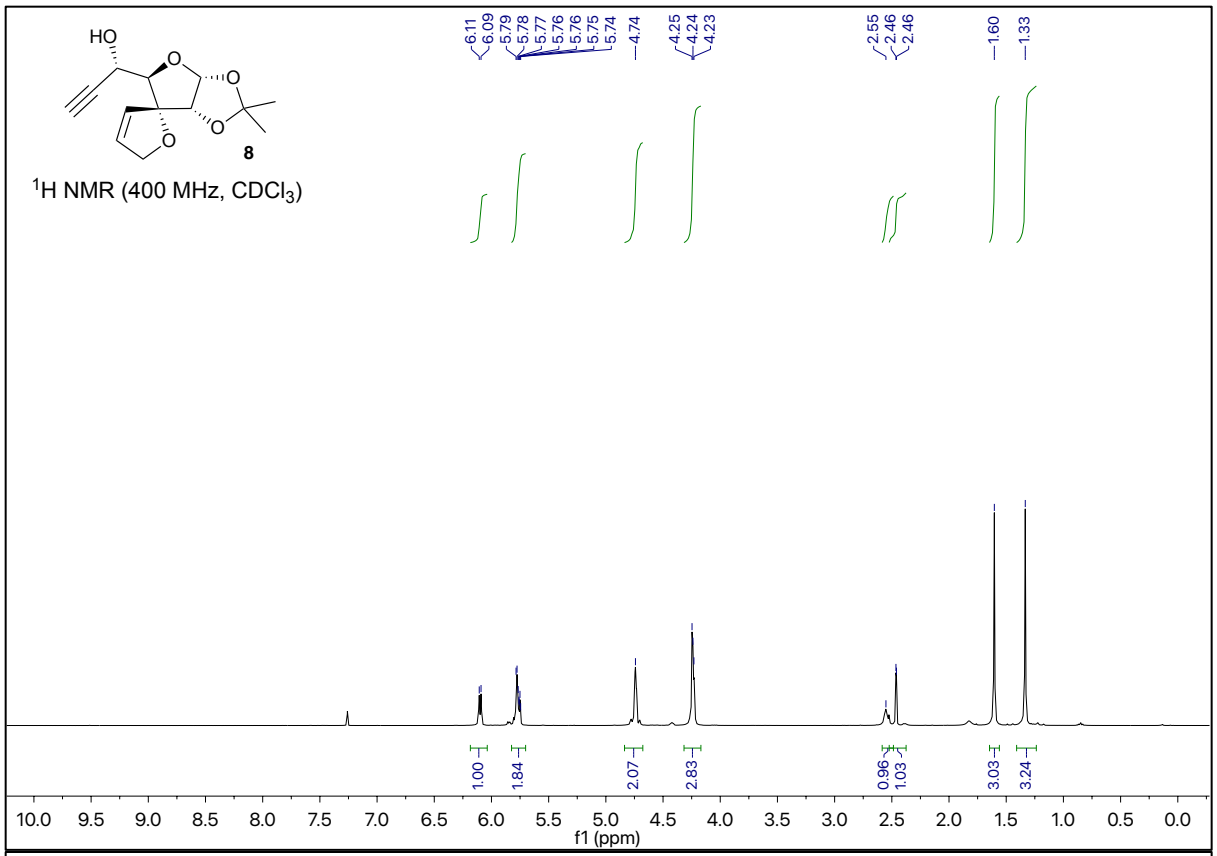
Scheme S1: Preparation of Diol **10**[1,2]

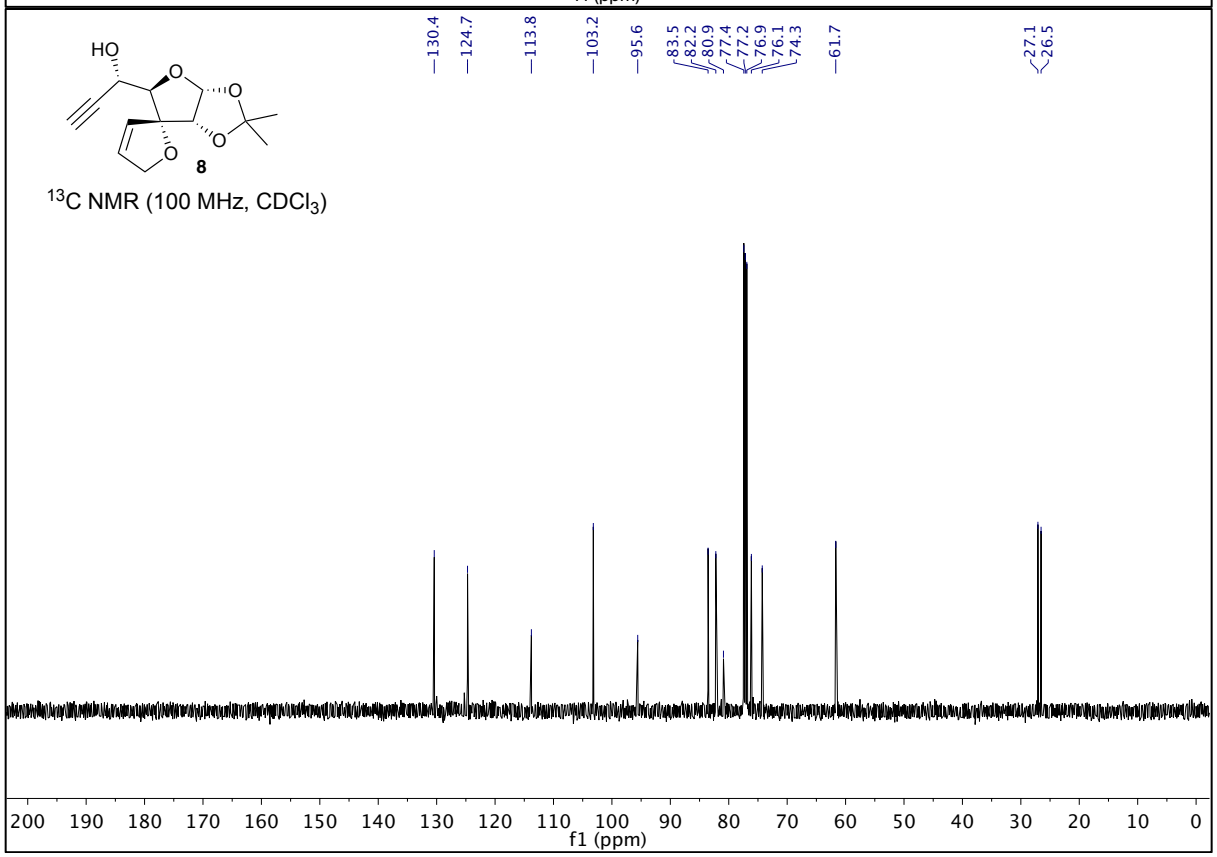
(*R*)-1-((2*R*,3a'*R*,5'*R*,6a'*R*)-2',2'-dimethyl-3a',6a'-dihydro-5*H*,5'*H*-spiro[furan-2,6'-furo[2,3-*d*][1,3]dioxol]-5'-yl)ethane-1,2-diol (10):[1,2]

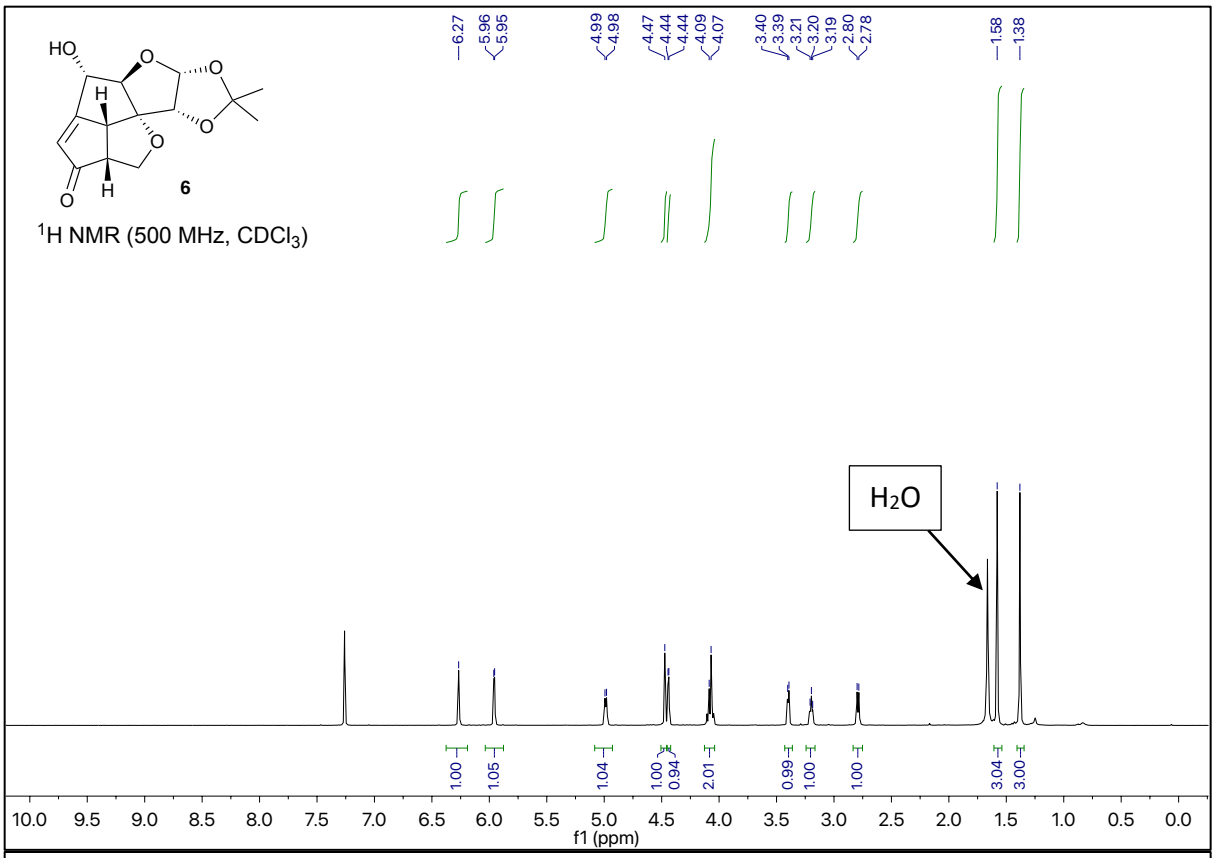
To the compound **S5** (100 mg, 0.38 mmol) was added 60% aq. AcOH (5 mL) and allowed to stir at room temperature for 12 h. The acetic acid was evaporated by azeotrope formation with toluene and concentrated to get a crude product, which upon 100-200 mesh silica gel column chromatography using EtOAc/petroleum ether (1:1) as the eluent to obtain the diol **10** (78 mg, 90% yield) as a colourless sticky solid. $\mathbf{R}_f$ = 0.3, (100% EA)

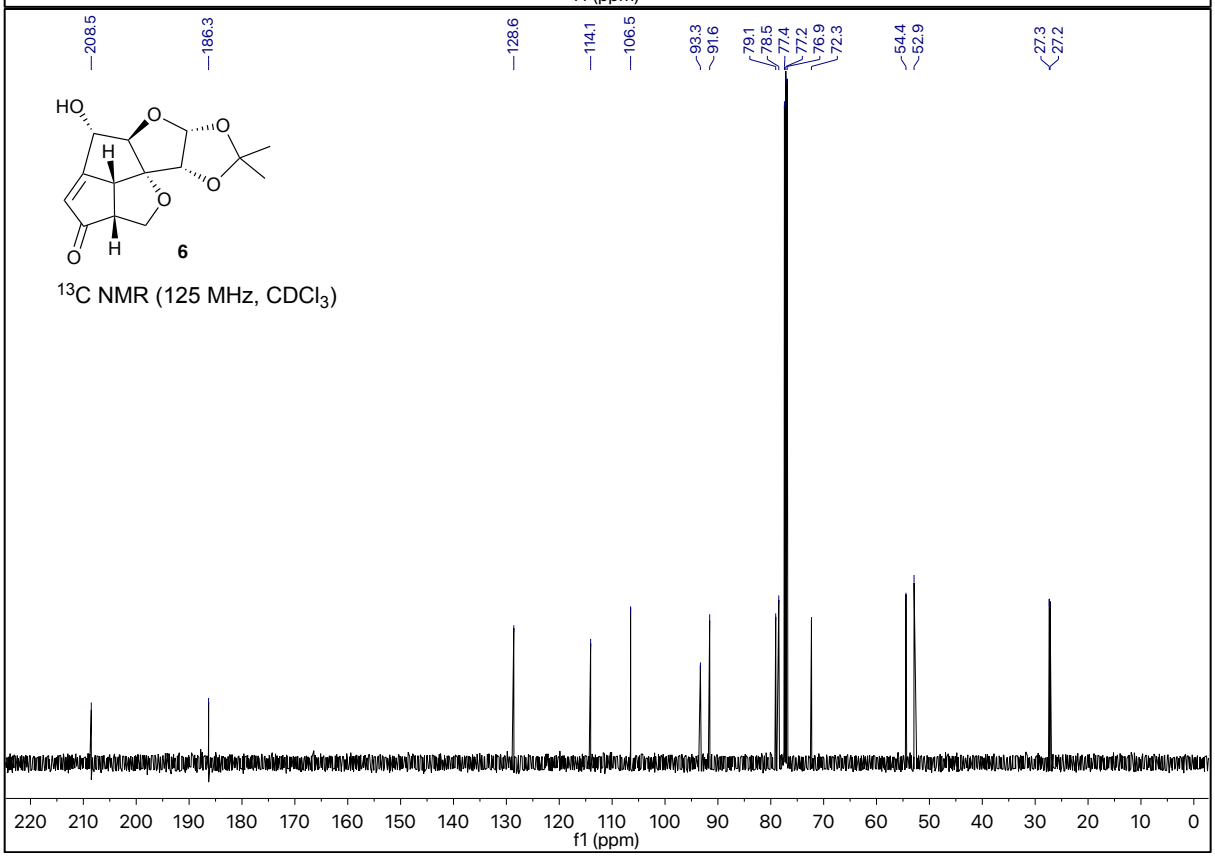
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (d, *J* = 6.2 Hz, 1H), 5.81 (dt, *J* = 6.2, 2.4 Hz, 1H), 5.74 (d, *J* = 3.5 Hz, 1H), 4.75 (s, 2H), 4.23 (d, *J* = 3.5 Hz, 1H), 4.11 (d, *J* = 7.2 Hz, 1H), 3.78 – 3.57 (m, 3H), 2.34 (s, 2H), 1.61 (s, 3H), 1.34 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 130.2, 125.4, 113.5, 103.0, 96.3, 83.1, 77.5, 75.7, 70.9, 64.2, 26.8, 26.4.

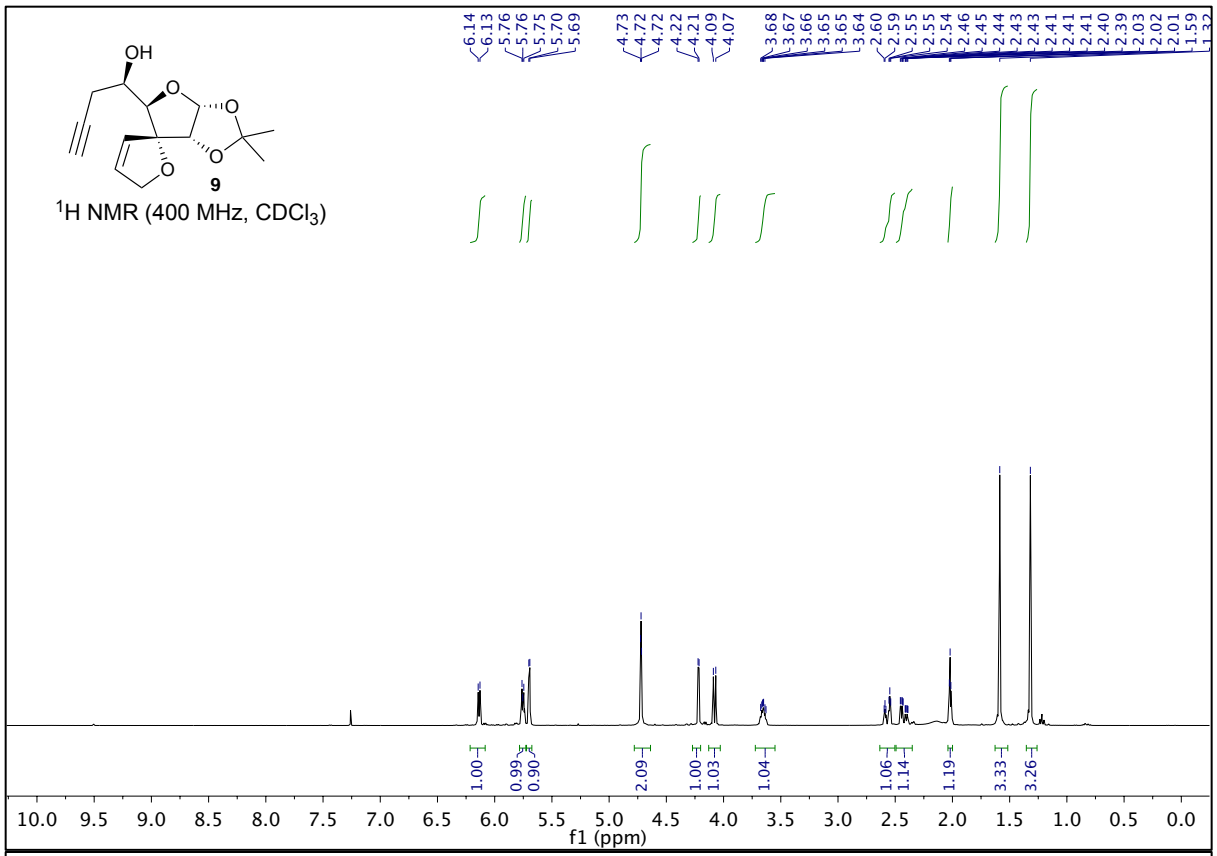
2. NMR Data:

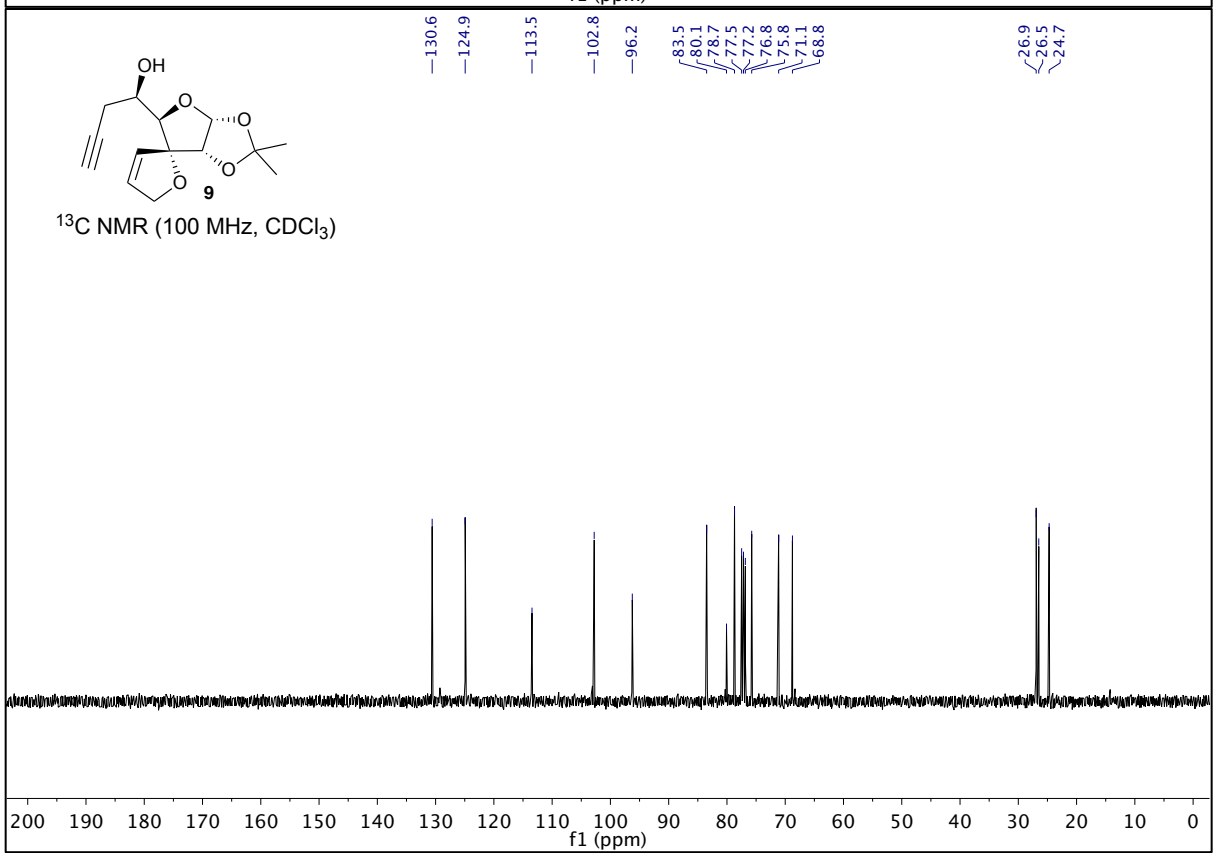

HO
O
O
O
O
8
^{1}H NMR (400 MHz, $CDCl_3$)
6.11
6.09
5.79
5.78
5.77
5.76
5.76
5.75
5.74
4.74
4.25
4.24
4.23
2.55
2.46
2.46
1.60
1.33
1.00
1.84
2.07
2.83
0.96
1.03
3.03
3.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

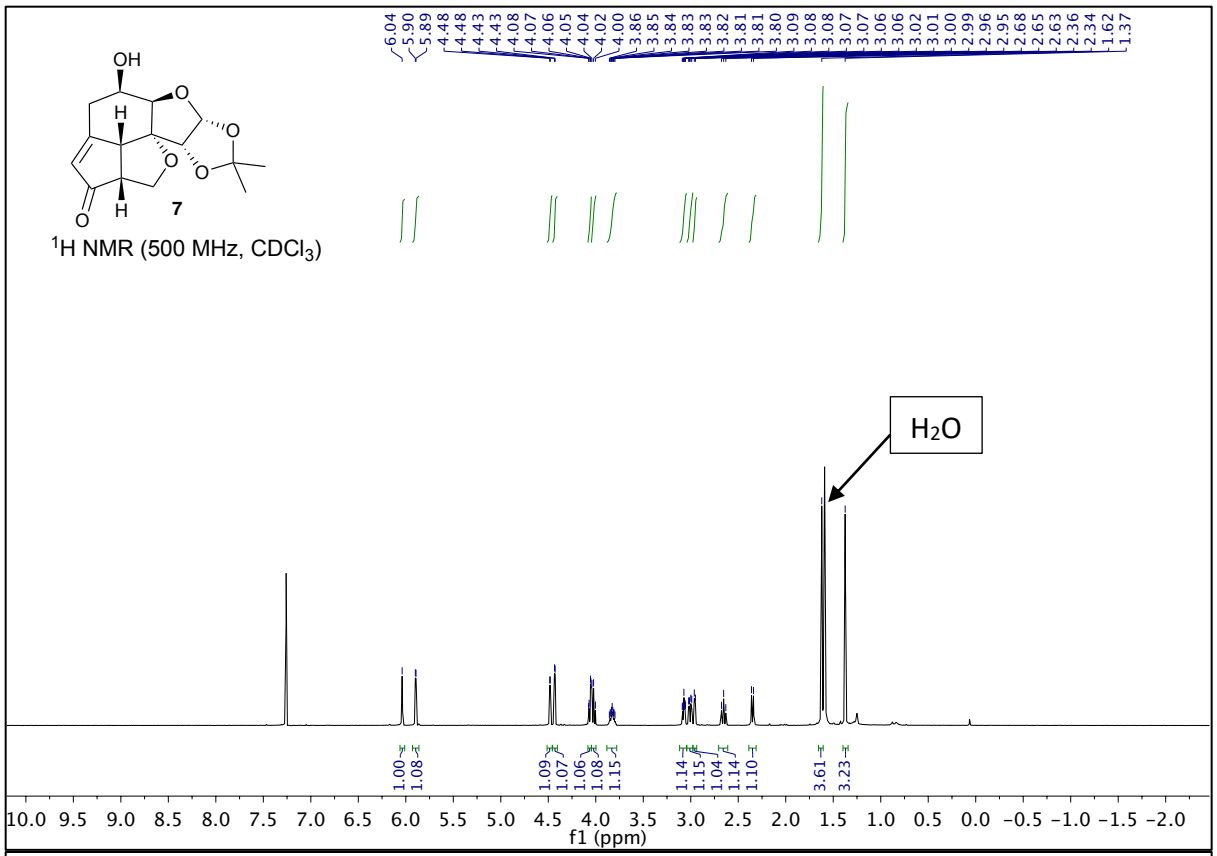

HO
O
O
O
O
8
^{13}C NMR (100 MHz, $CDCl_3$)
130.4
124.7
113.8
103.2
95.6
83.5
82.2
80.9
77.4
77.2
76.9
76.1
74.3
61.7
27.1
26.5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

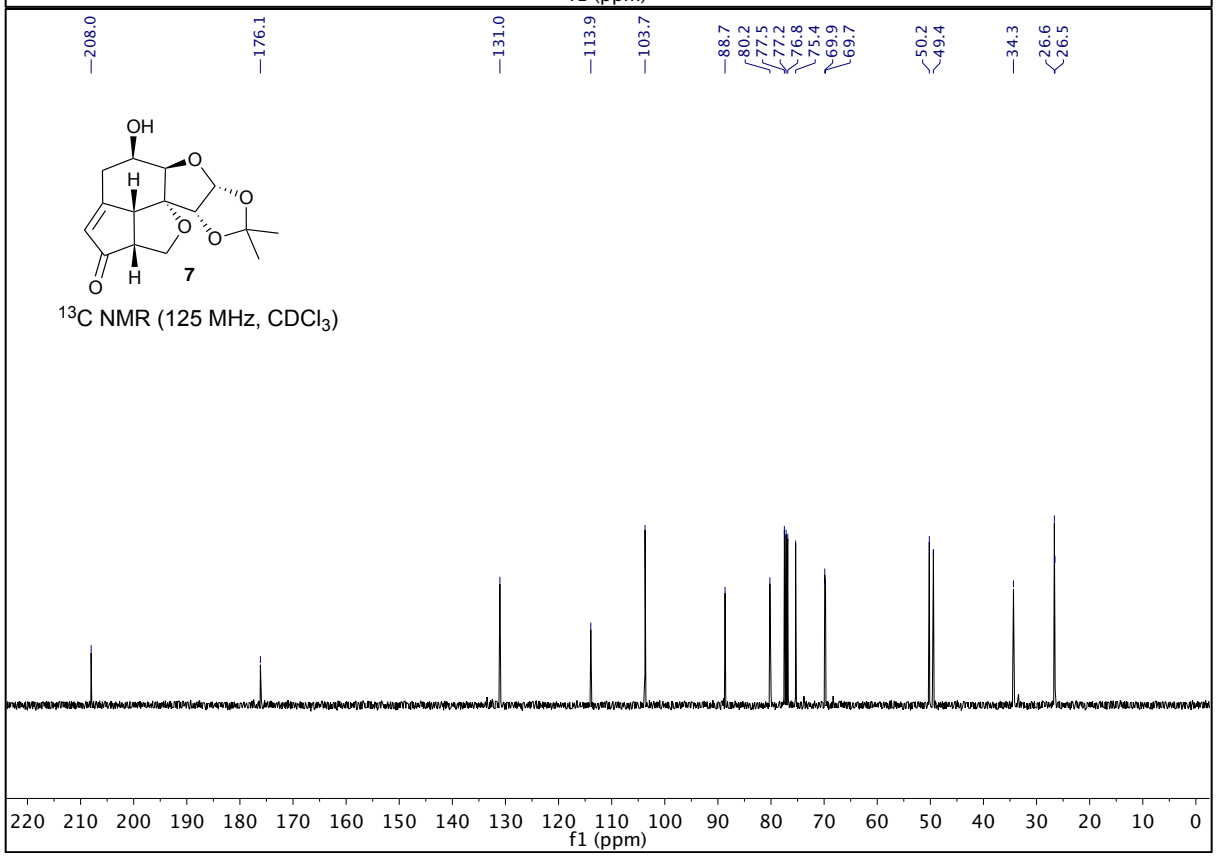

HO
O
O
O
O
H
H
O
6
^{1}H NMR (500 MHz, $CDCl_3$)
6.27
5.96
5.95
4.99
4.98
4.47
4.44
4.44
4.09
4.07
3.40
3.39
3.21
3.20
3.19
2.80
2.78
1.58
1.38
H_2O
1.00
1.05
1.04
1.00
0.94
2.01
0.99
1.00
1.00
3.04
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

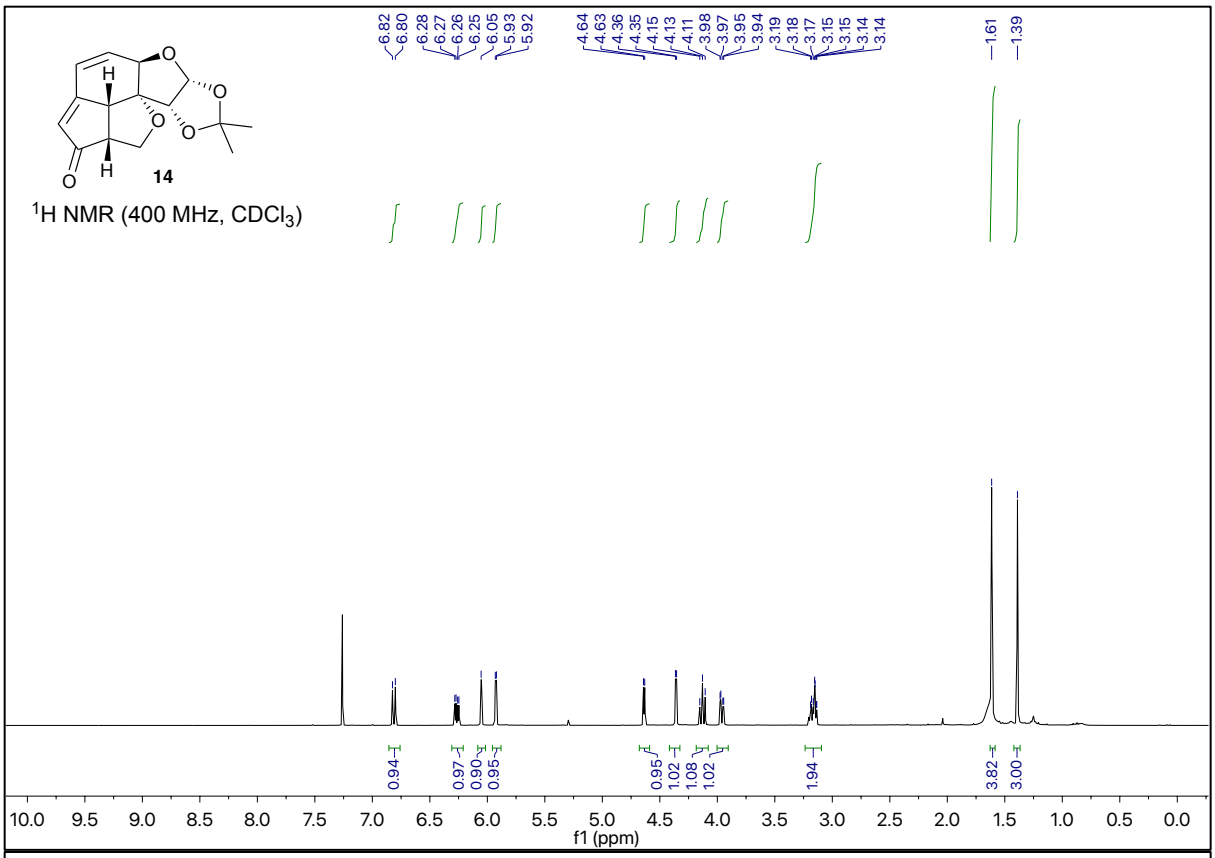

208.5
186.3
128.6
114.1
106.5
93.3
91.6
79.1
78.5
77.4
77.2
76.9
72.3
54.4
52.9
27.3
27.2
HO
O
O
O
O
H
H
O
6
^{13}C NMR (125 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

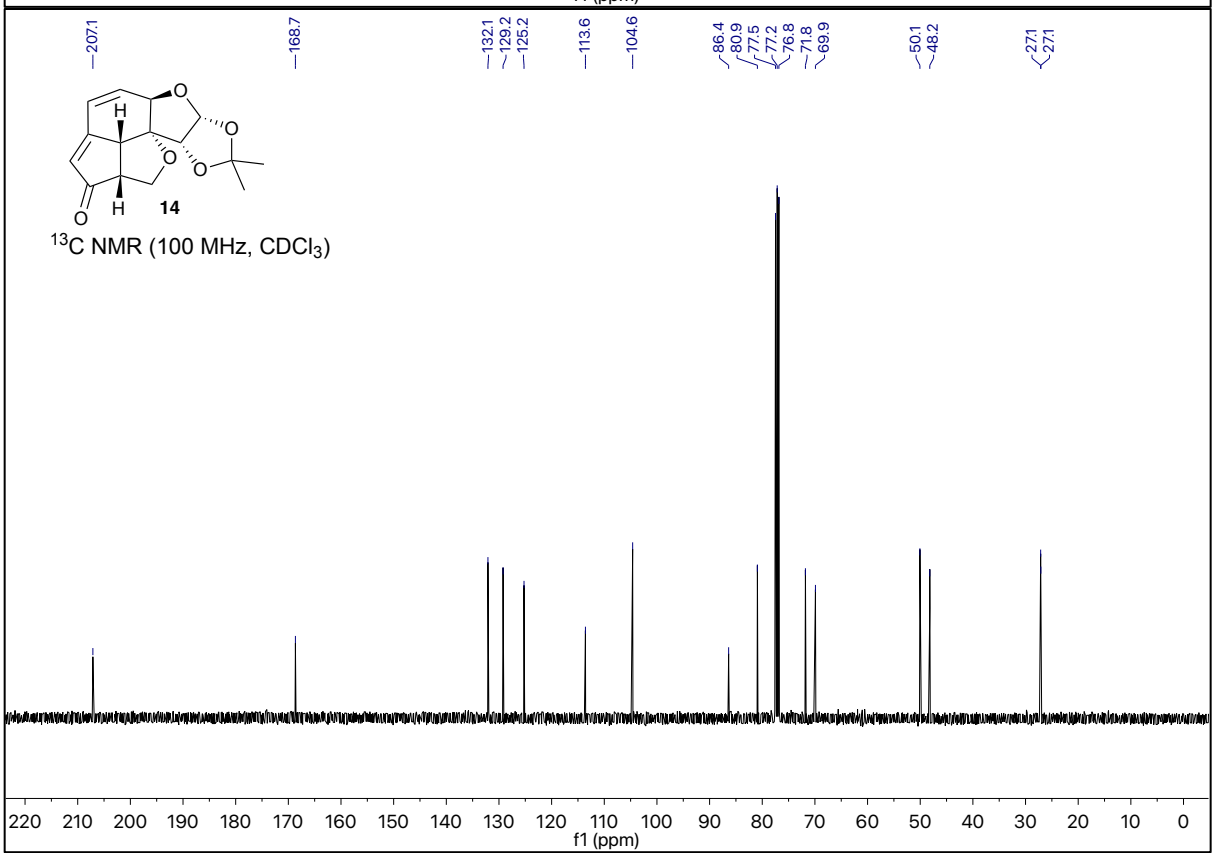

OH
O
O
O
O
9
^{1}H NMR (400 MHz, $CDCl_3$)
6.14
6.13
5.76
5.76
5.75
5.70
5.69
4.73
4.72
4.72
4.22
4.21
4.09
4.07
3.68
3.67
3.66
3.65
3.65
3.64
2.60
2.59
2.55
2.55
2.54
2.46
2.45
2.44
2.43
2.43
2.41
2.41
2.41
2.40
2.39
2.03
2.02
2.01
1.59
1.32
1.00
0.99
0.90
2.09
1.00
1.03
1.04
1.06
1.14
1.19
3.33
3.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

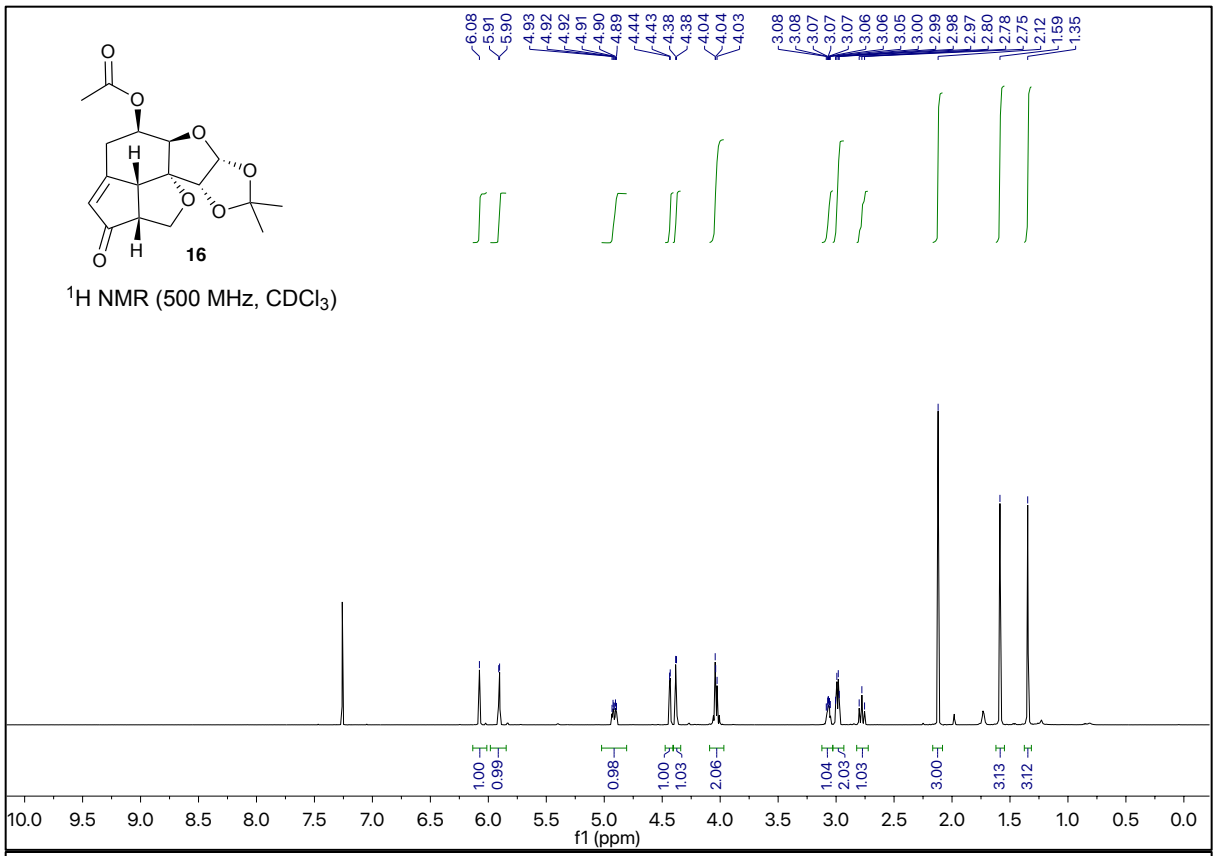

OH
O
O
O
O
9
^{13}C NMR (100 MHz, $CDCl_3$)
130.6
124.9
113.5
102.8
96.2
83.5
80.1
78.7
77.5
77.2
76.8
75.8
71.1
68.8
26.9
26.5
24.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

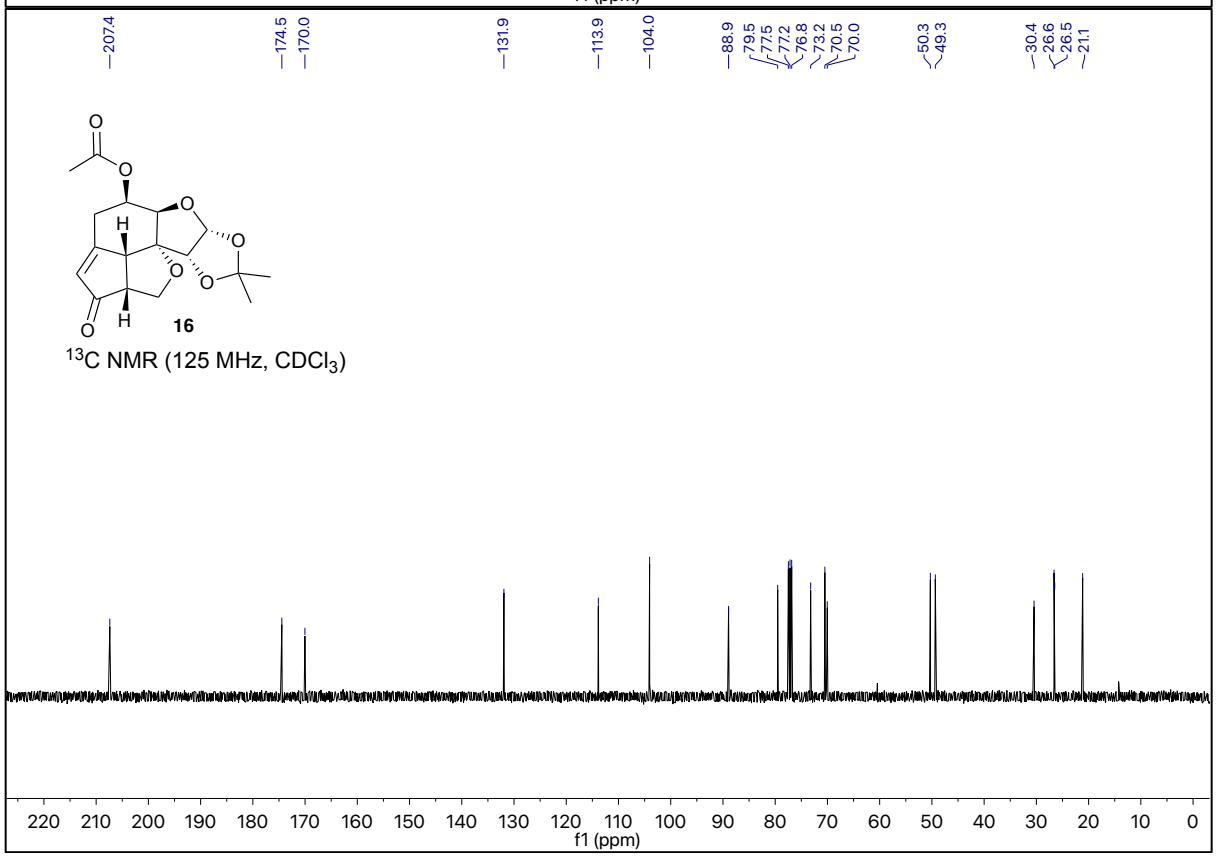

OH
H
O
O
O
O
H
O
7
^{1}H NMR (500 MHz, $CDCl_3$)
6.04
5.90
5.89
4.48
4.48
4.43
4.43
4.08
4.07
4.06
4.05
4.04
4.02
4.00
3.86
3.85
3.84
3.83
3.83
3.82
3.81
3.81
3.80
3.09
3.08
3.08
3.07
3.07
3.06
3.06
3.02
3.01
3.00
2.99
2.96
2.95
2.68
2.65
2.63
2.36
2.34
1.62
1.37
H_2O
1.00
1.08
1.09
1.07
1.06
1.08
1.15
1.14
1.15
1.04
1.14
1.10
3.61
3.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5 −2.0
f1 (ppm)

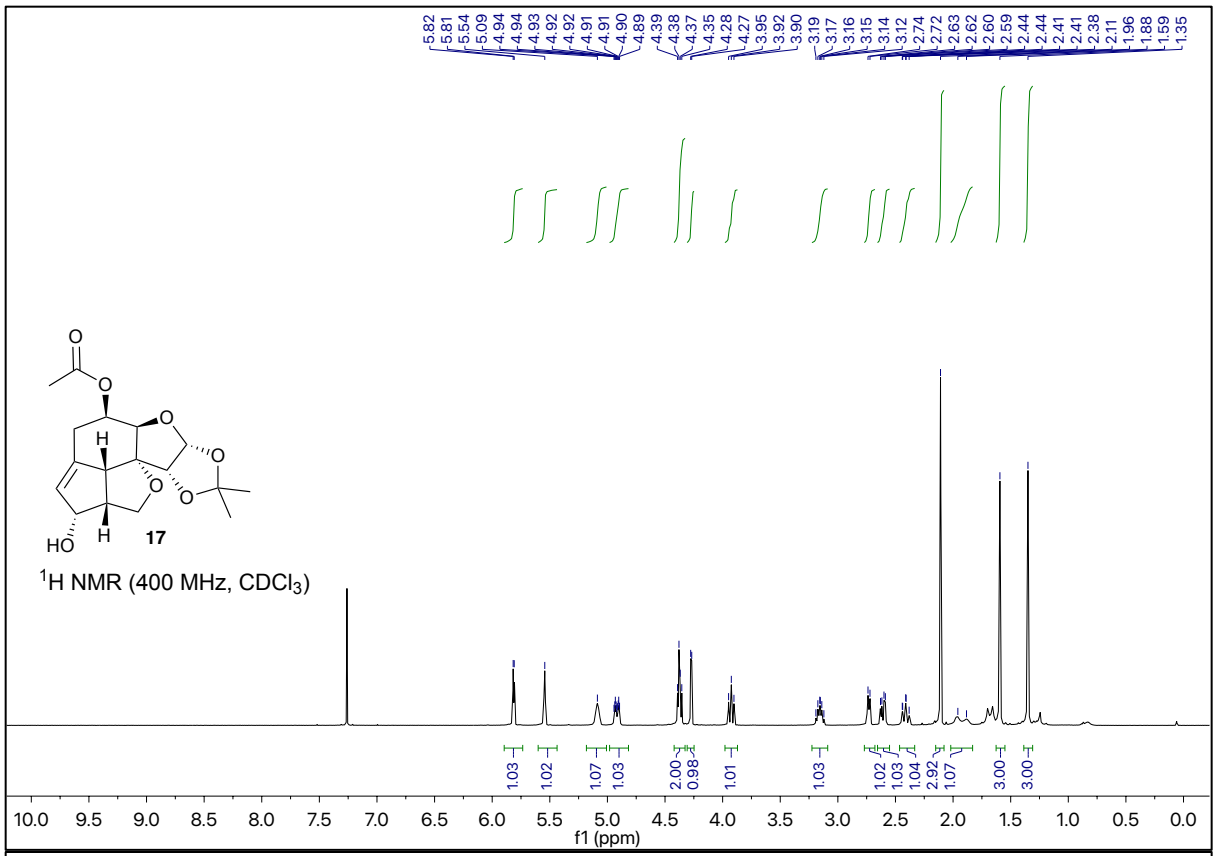

208.0
176.1
131.0
113.9
103.7
88.7
80.2
77.5
77.2
76.8
75.4
69.9
69.7
50.2
49.4
34.3
26.6
26.5
OH
H
O
O
O
O
H
O
7
^{13}C NMR (125 MHz, $CDCl_3$)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


14
^{1}H NMR (400 MHz, $CDCl_3$)
6.82
6.80
6.28
6.27
6.26
6.25
6.05
5.93
5.92
4.64
4.63
4.36
4.35
4.15
4.13
4.11
3.98
3.97
3.95
3.94
3.19
3.18
3.17
3.15
3.15
3.14
3.14
1.61
1.39
0.94
0.97
0.90
0.95
0.95
1.02
1.08
1.02
1.94
3.82
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


14
^{13}C NMR (100 MHz, $CDCl_3$)
207.1
168.7
132.1
129.2
125.2
113.6
104.6
86.4
80.9
77.5
77.2
76.8
71.8
69.9
50.1
48.2
27.1
27.1
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)


16
1H NMR (500 MHz, CDCl3)
f1 (ppm)


16
13C NMR (125 MHz, CDCl3)
f1 (ppm)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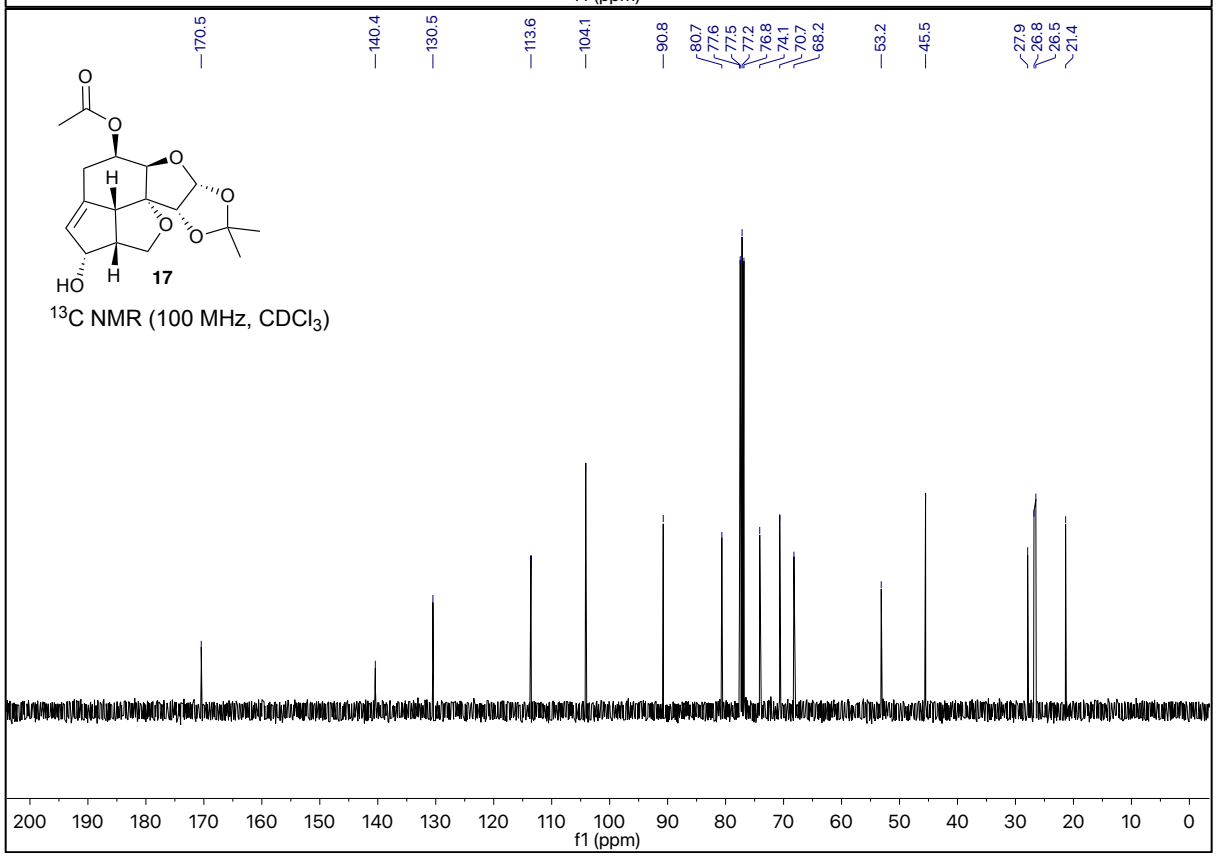
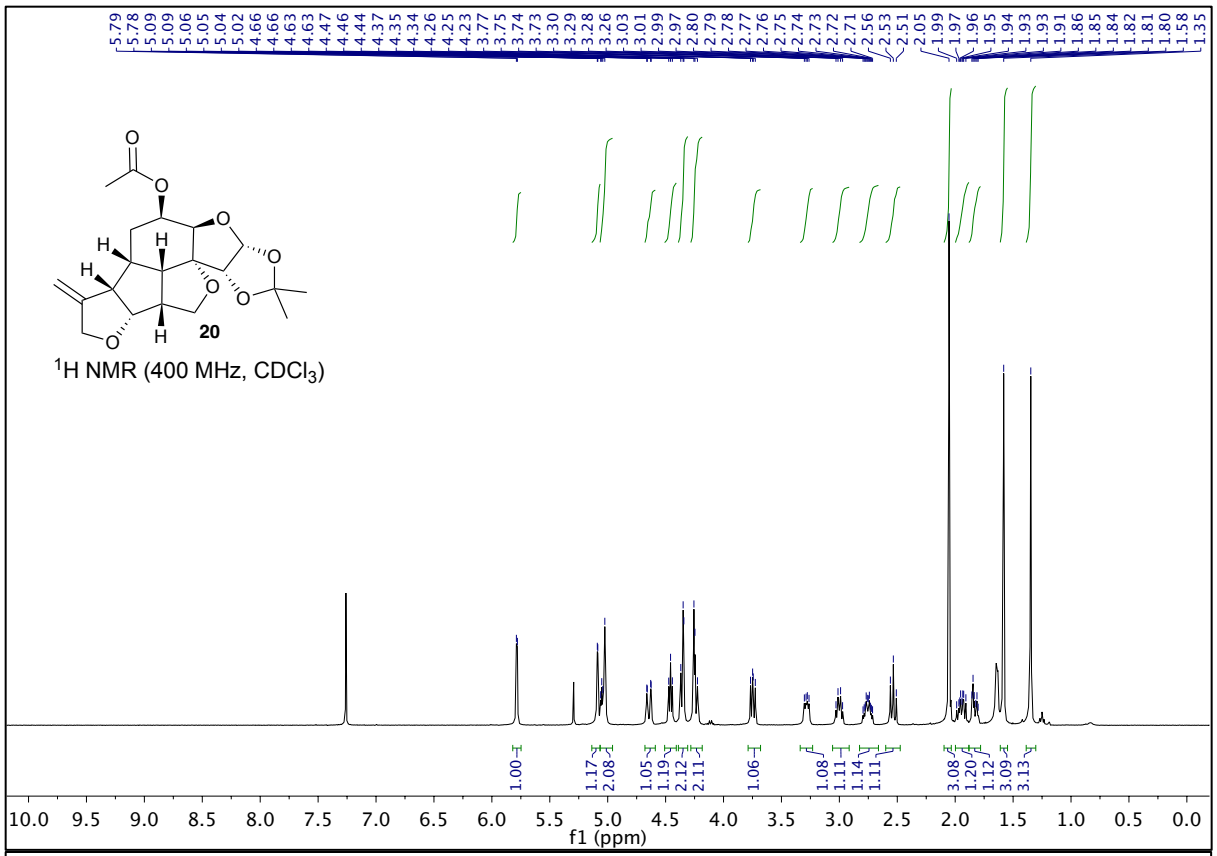
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


17
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)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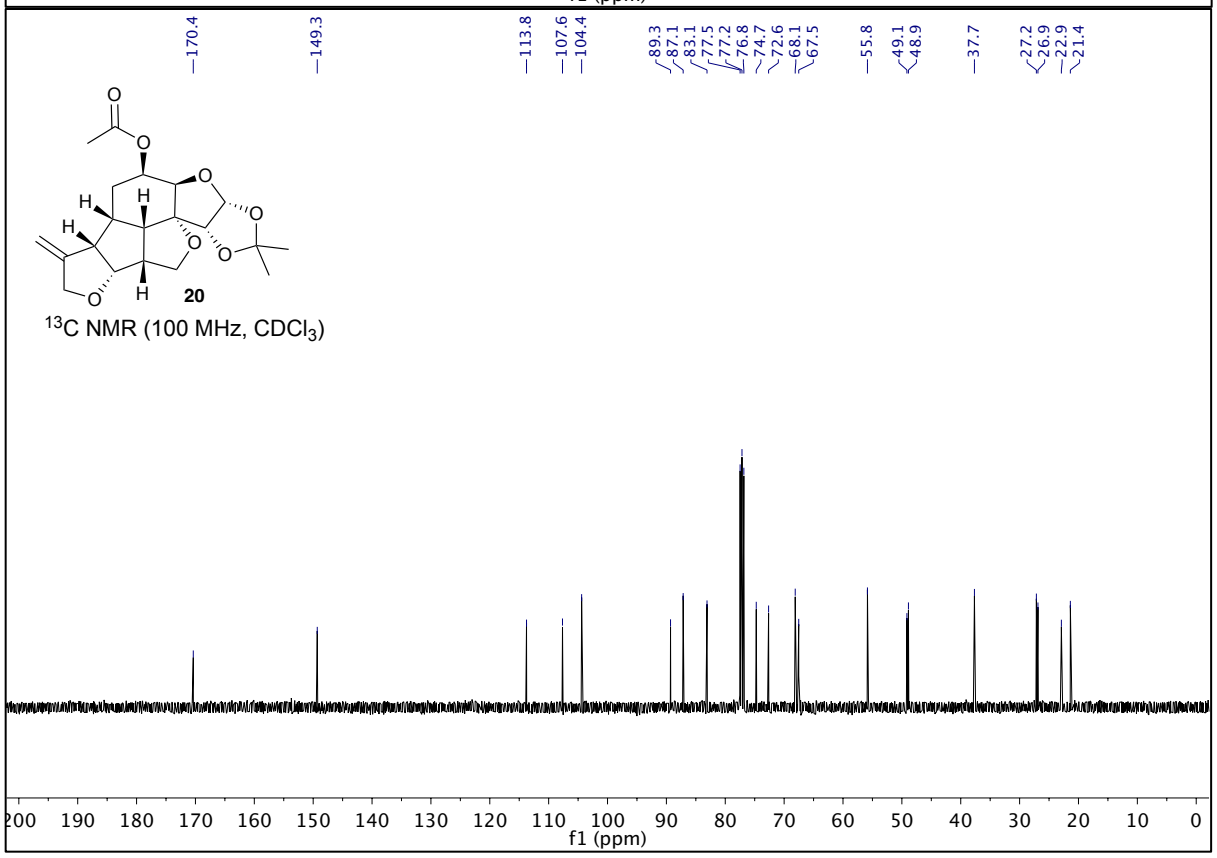
1H NMR (400 MHz, CDCl3)
f1 (ppm)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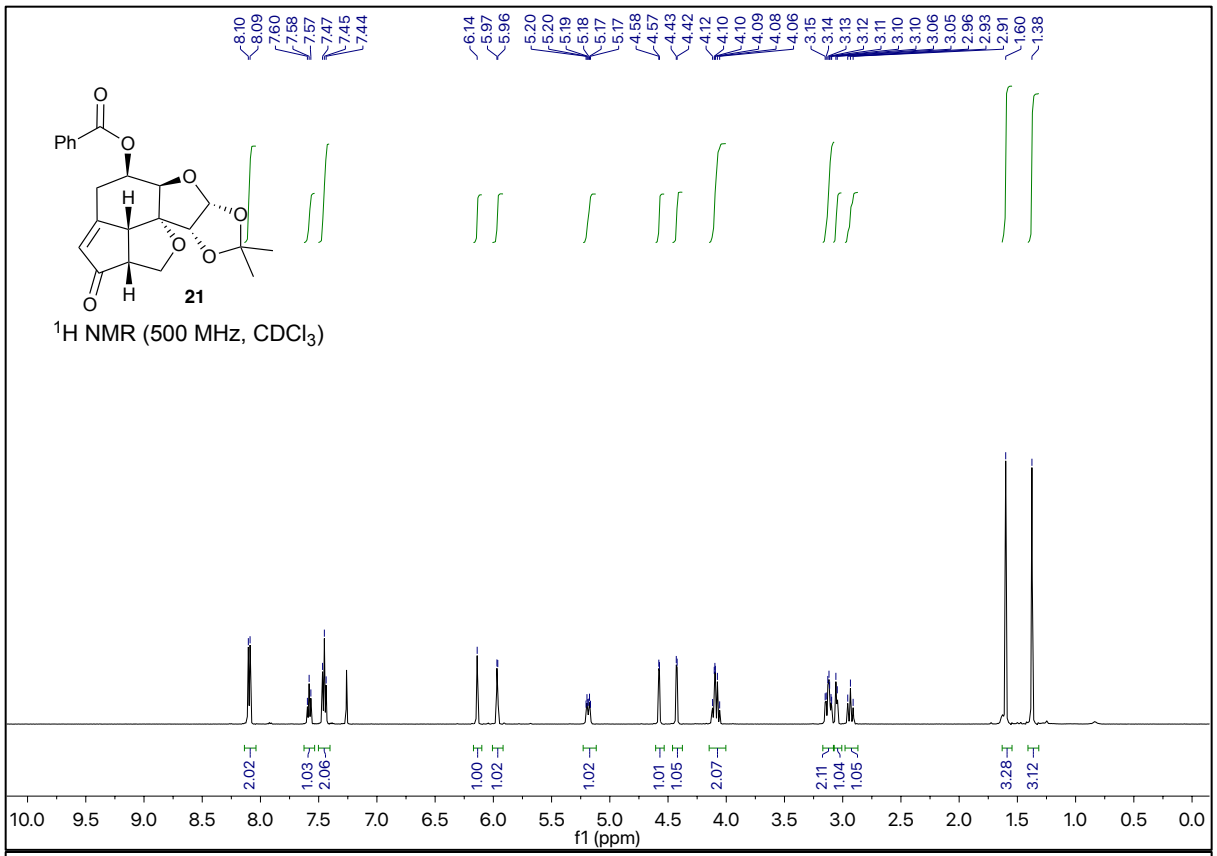
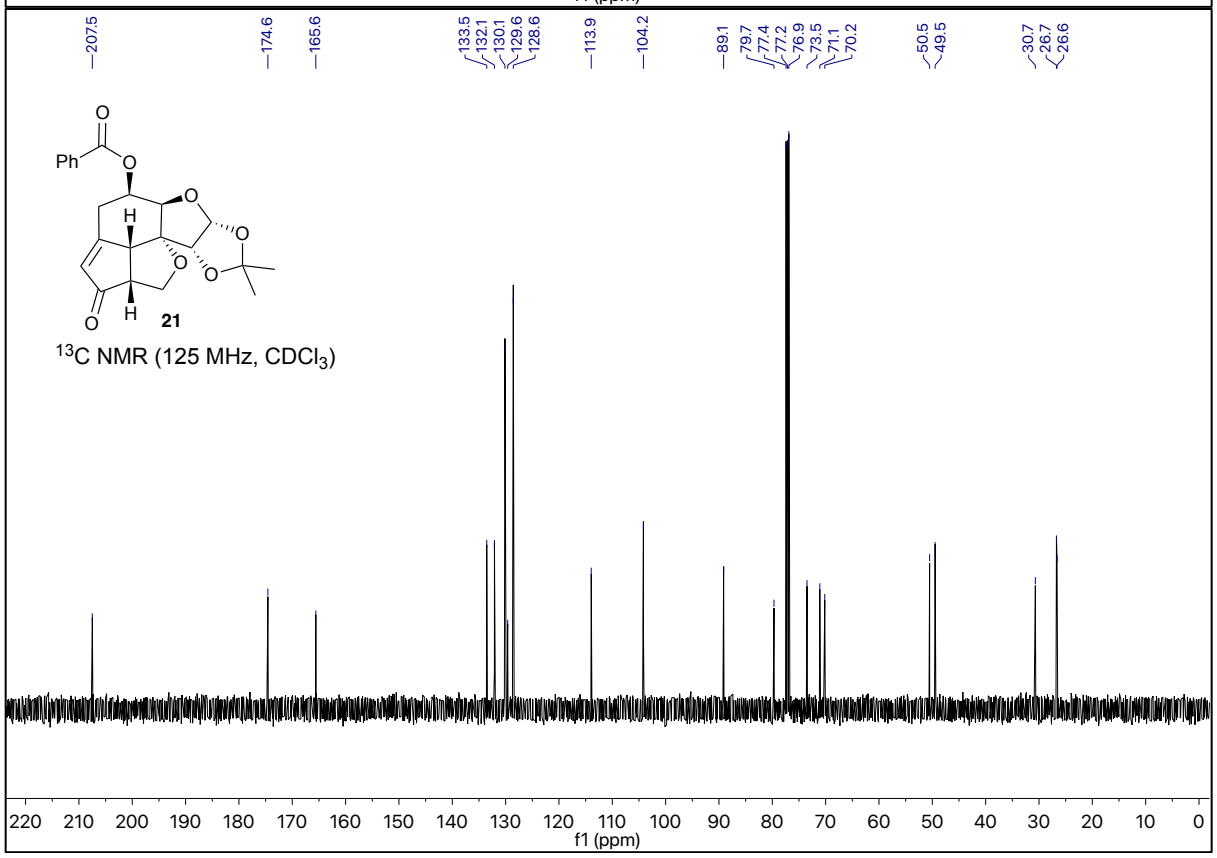
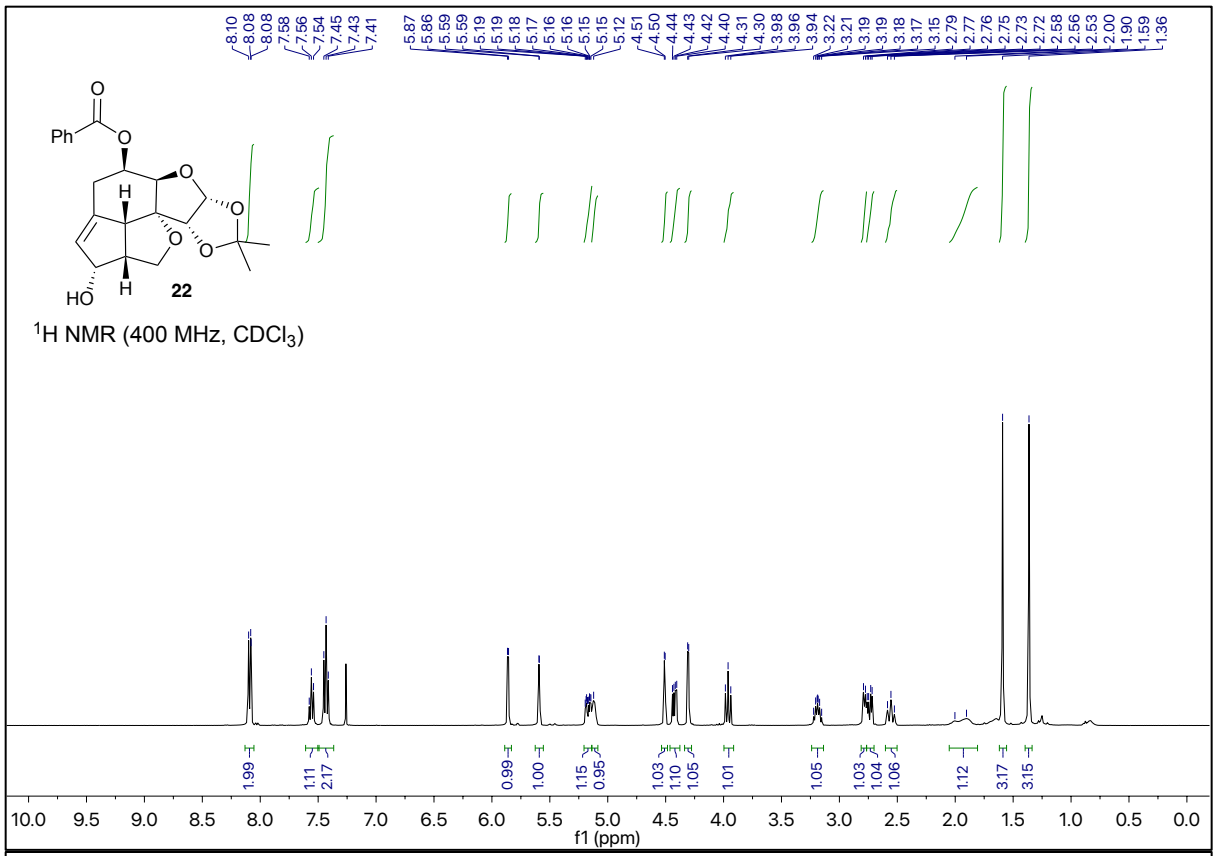
13C NMR (100 MHz, CDCl3)
f1 (ppm)



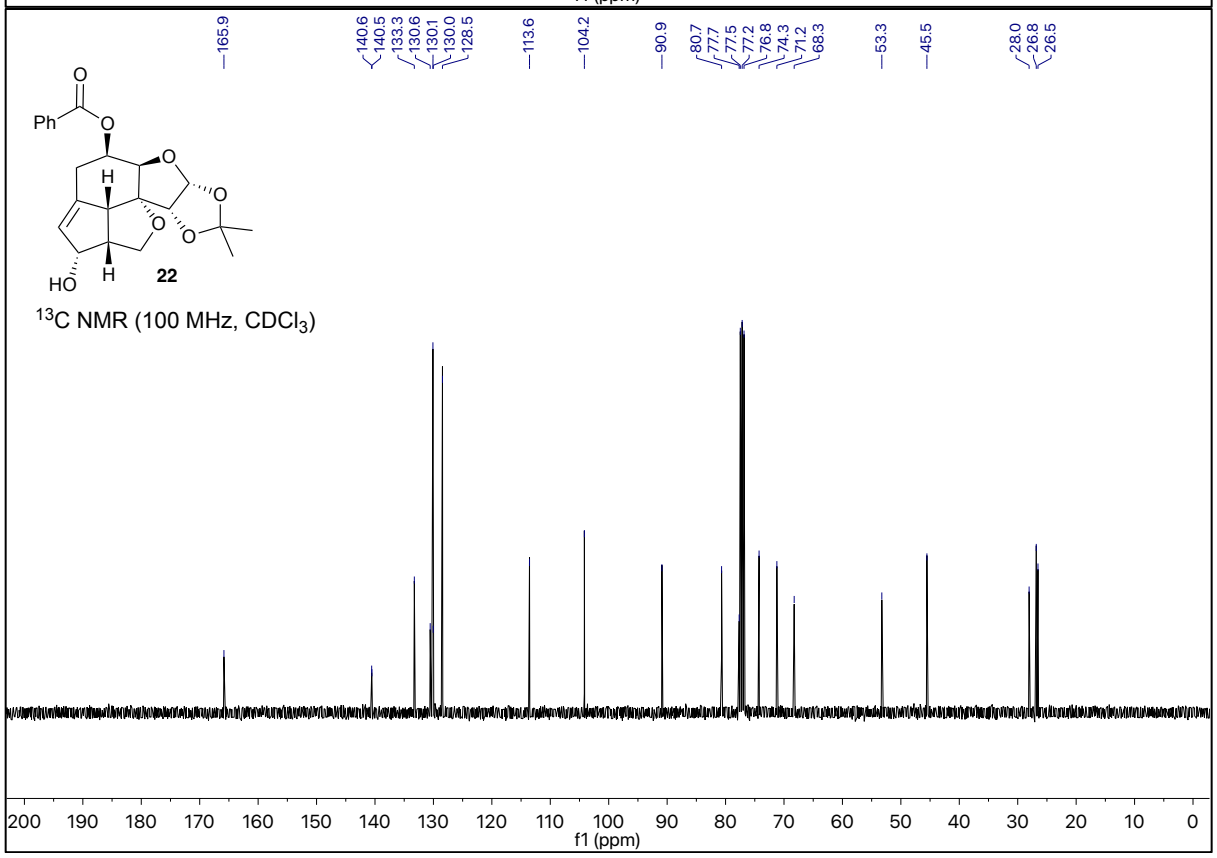
^{1}H NMR (500 MHz, $CDCl_3$)



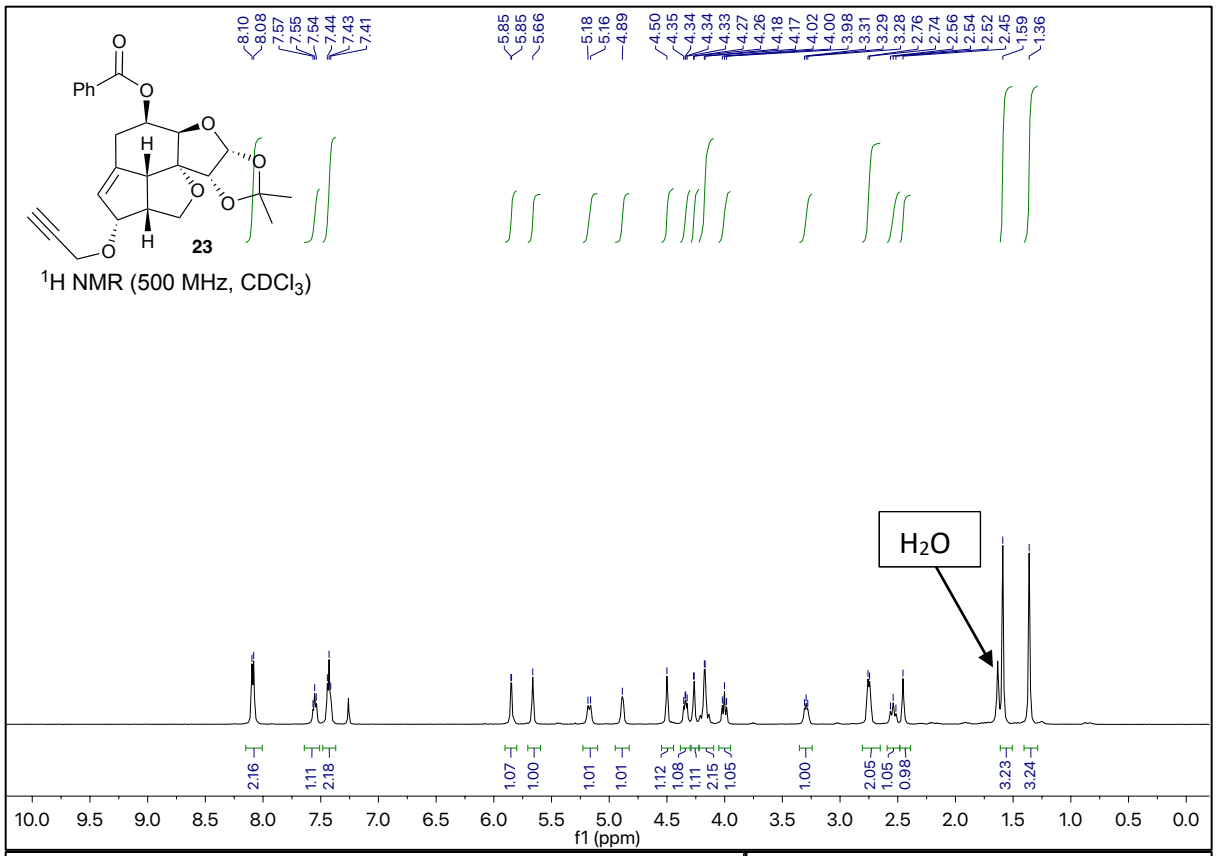
^{13}C NMR (125 MHz, $CDCl_3$)

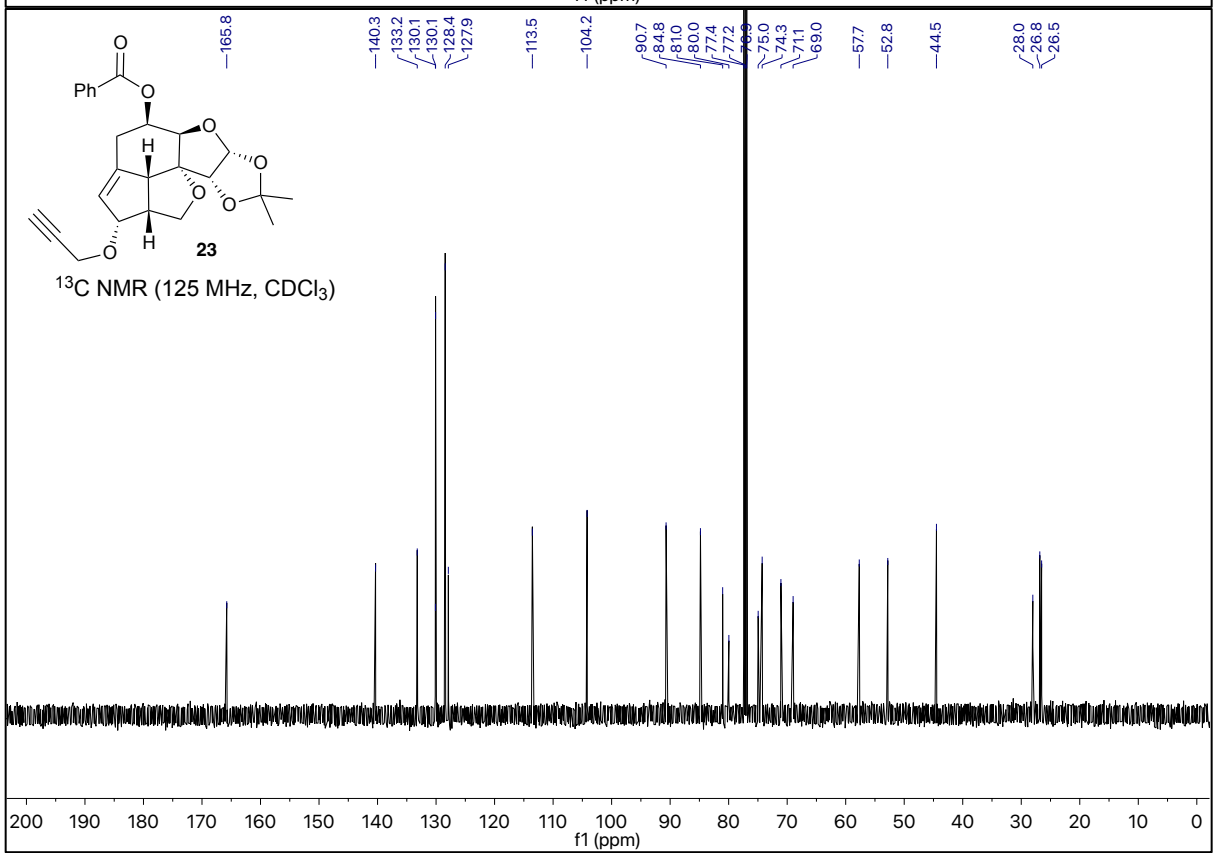


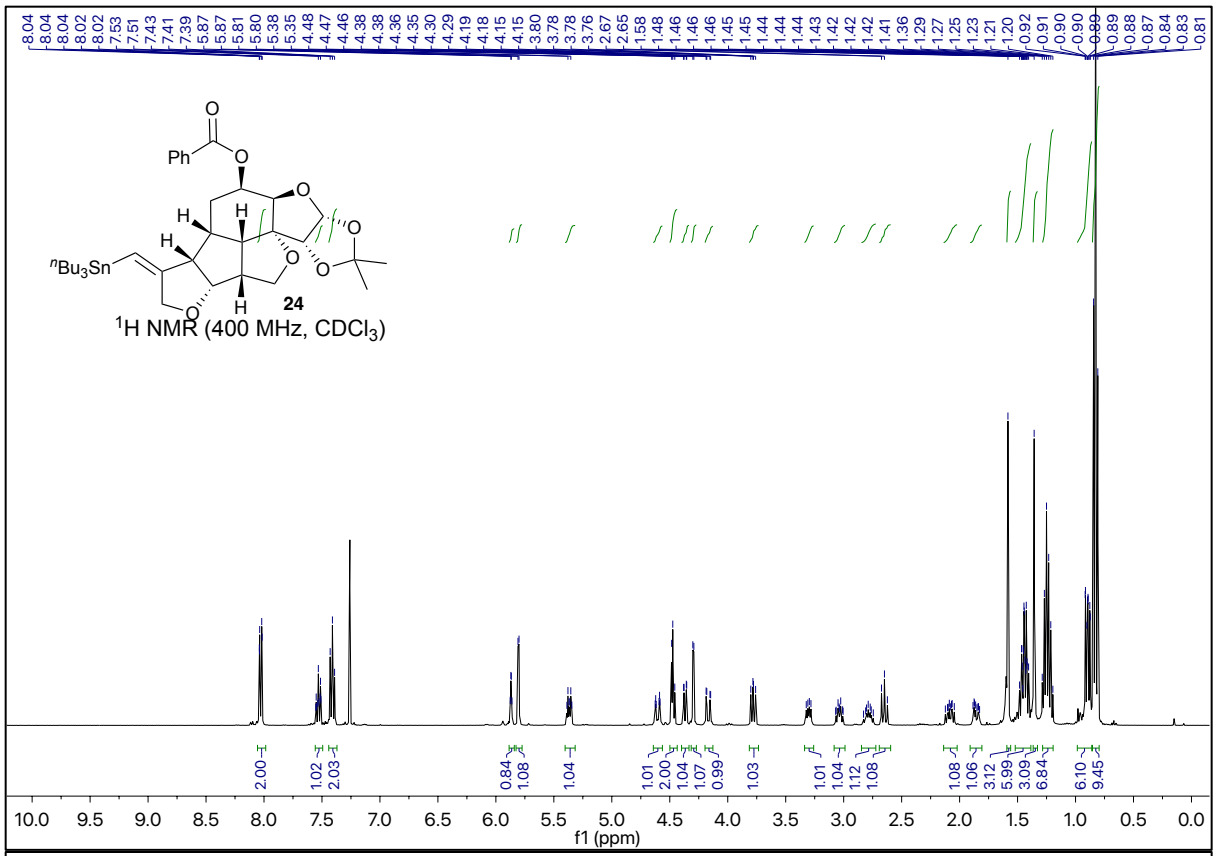
^{1}H NMR (400 MHz, $CDCl_3$)

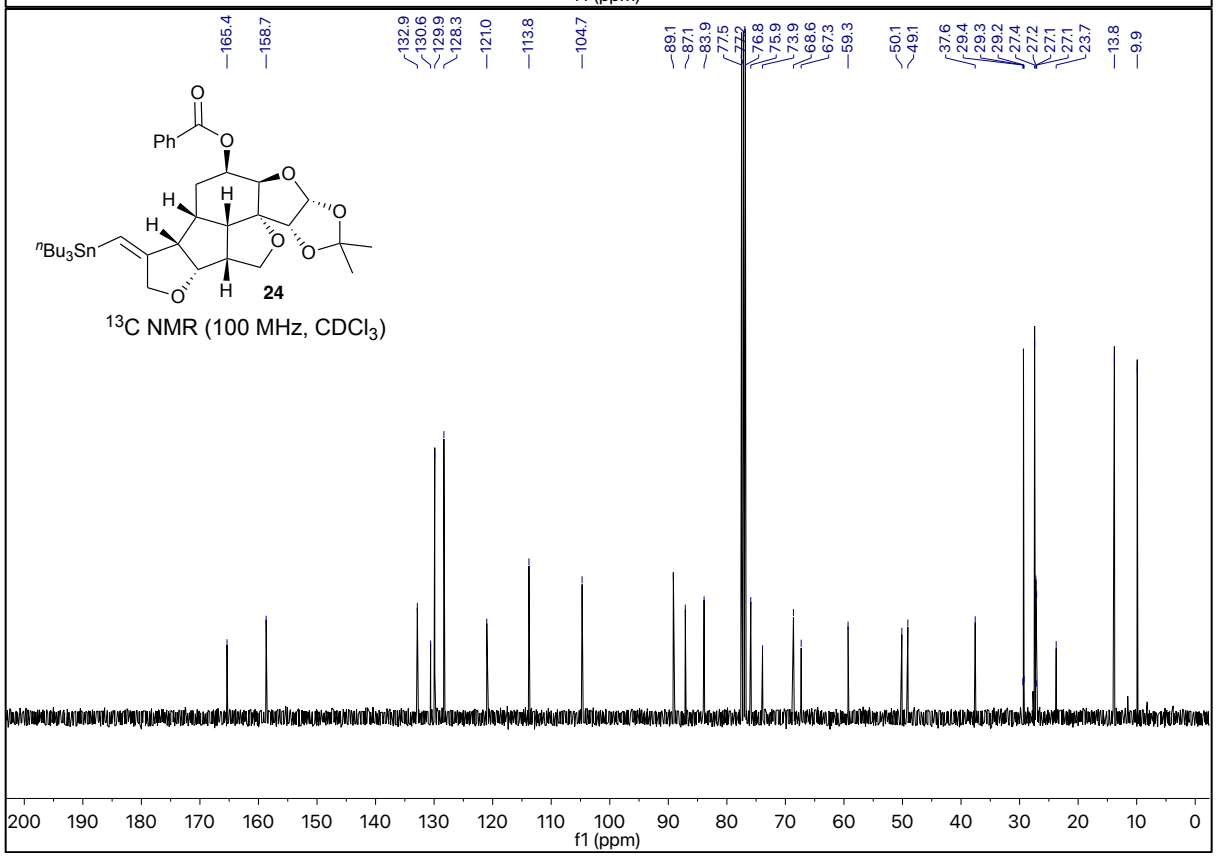


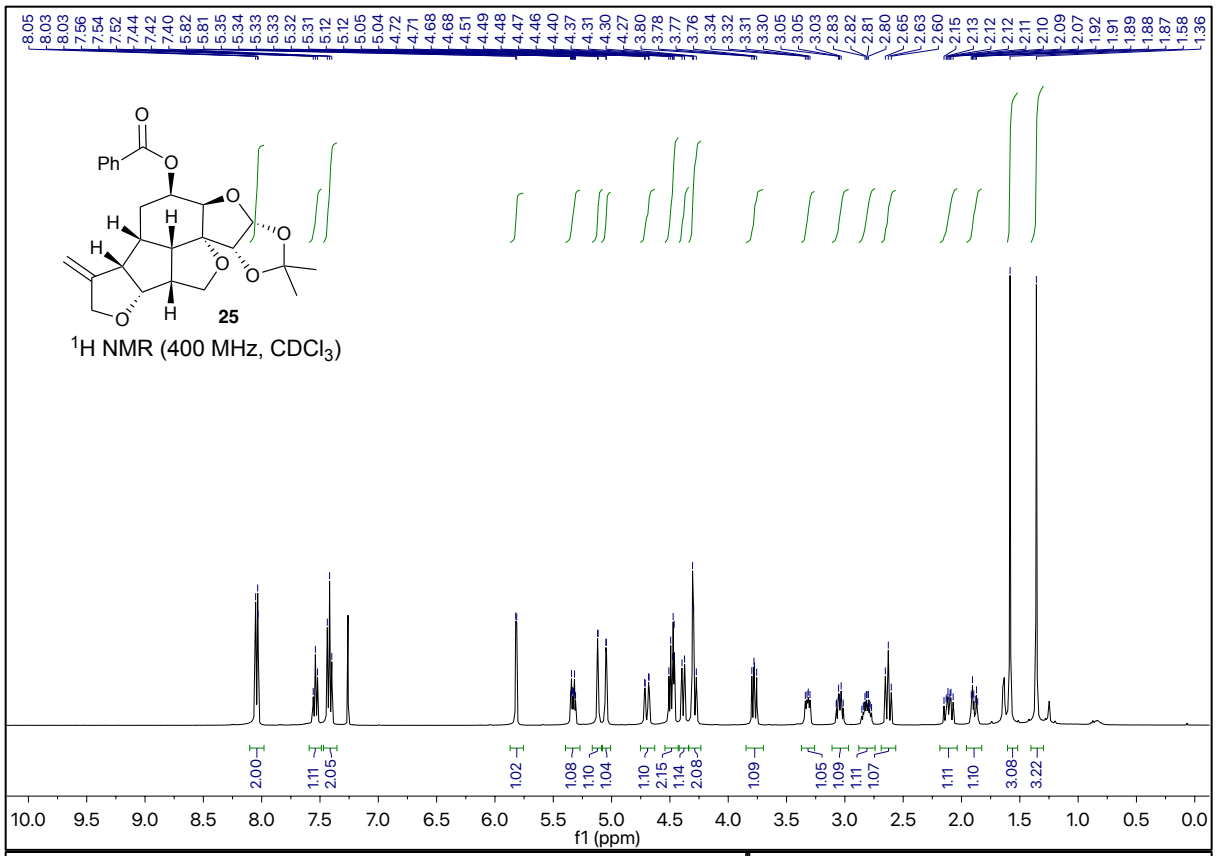
^{13}C NMR (100 MHz, $CDCl_3$)

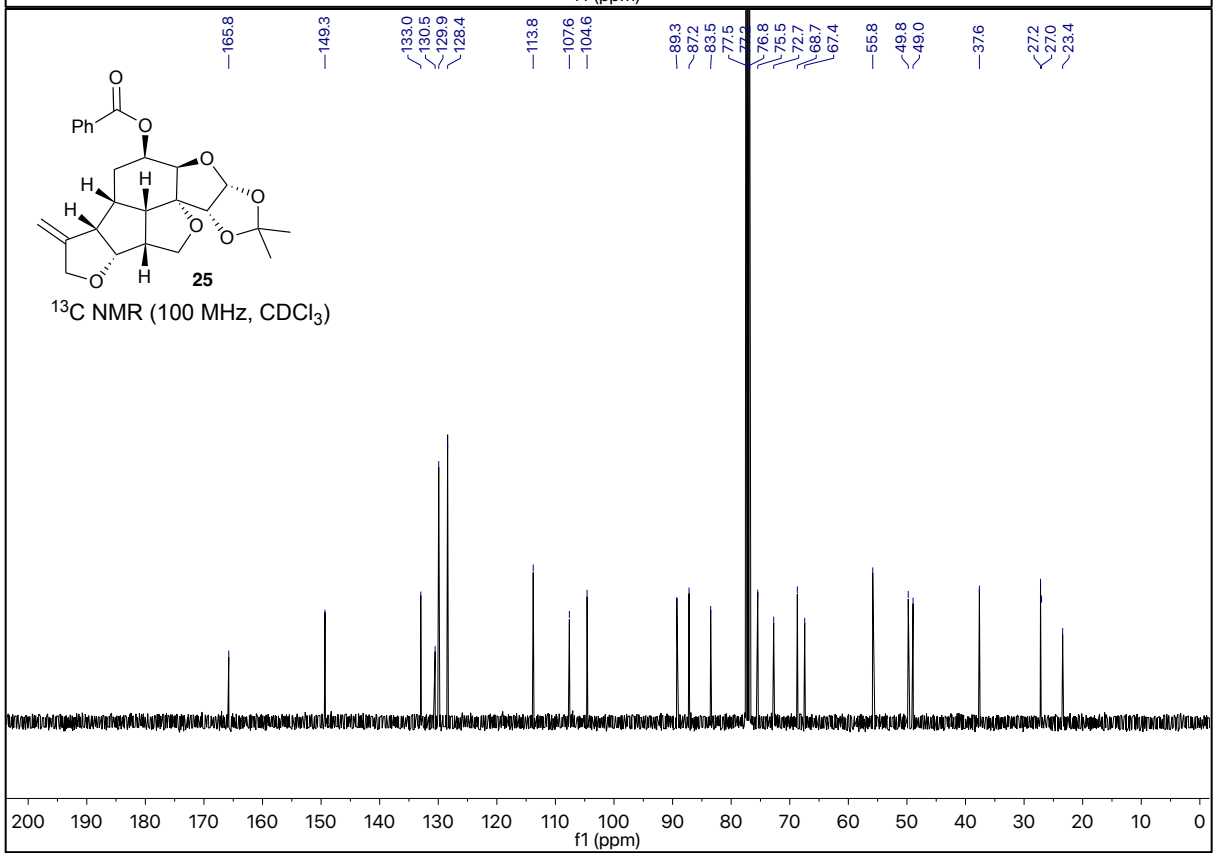

23
^{1}H NMR (500 MHz, $CDCl_3$)
H_2O
f1 (ppm)

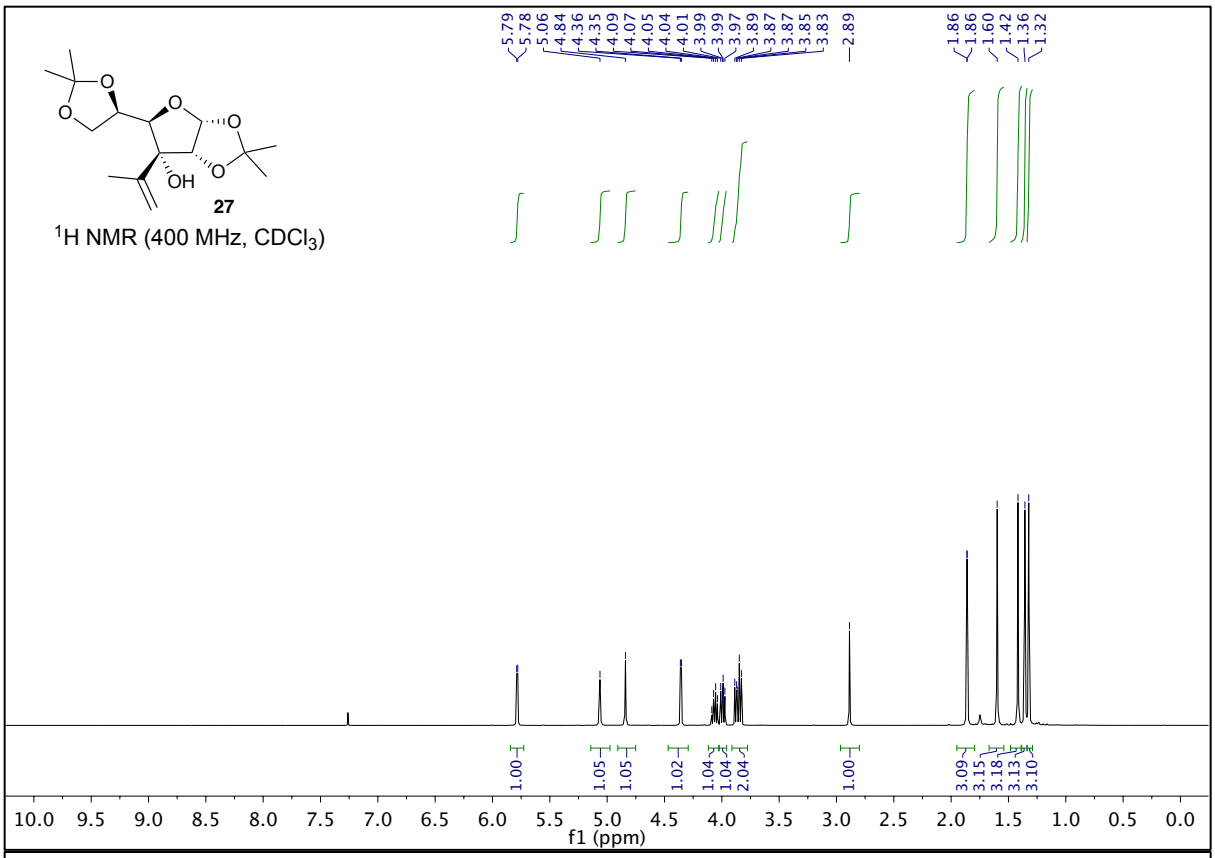

23
^{13}C NMR (125 MHz, $CDCl_3$)
f1 (ppm)

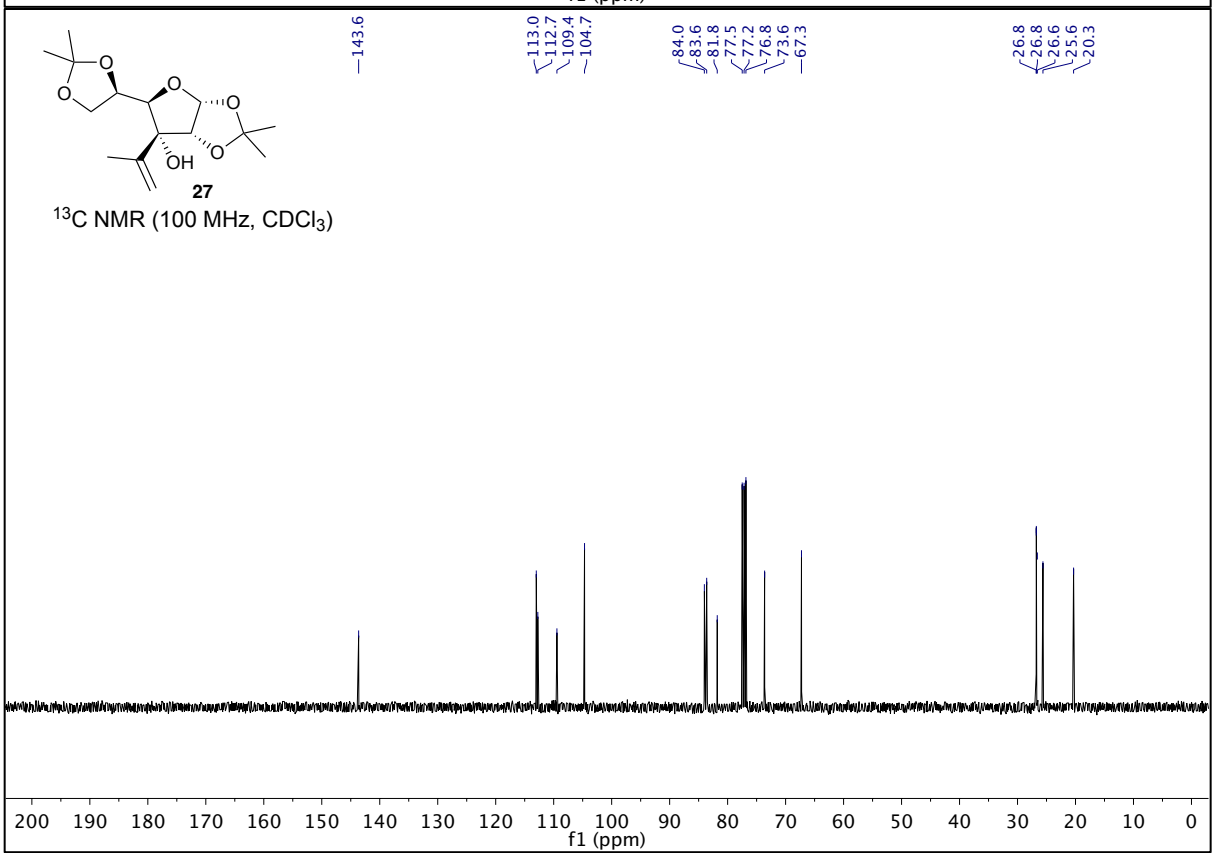

24
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

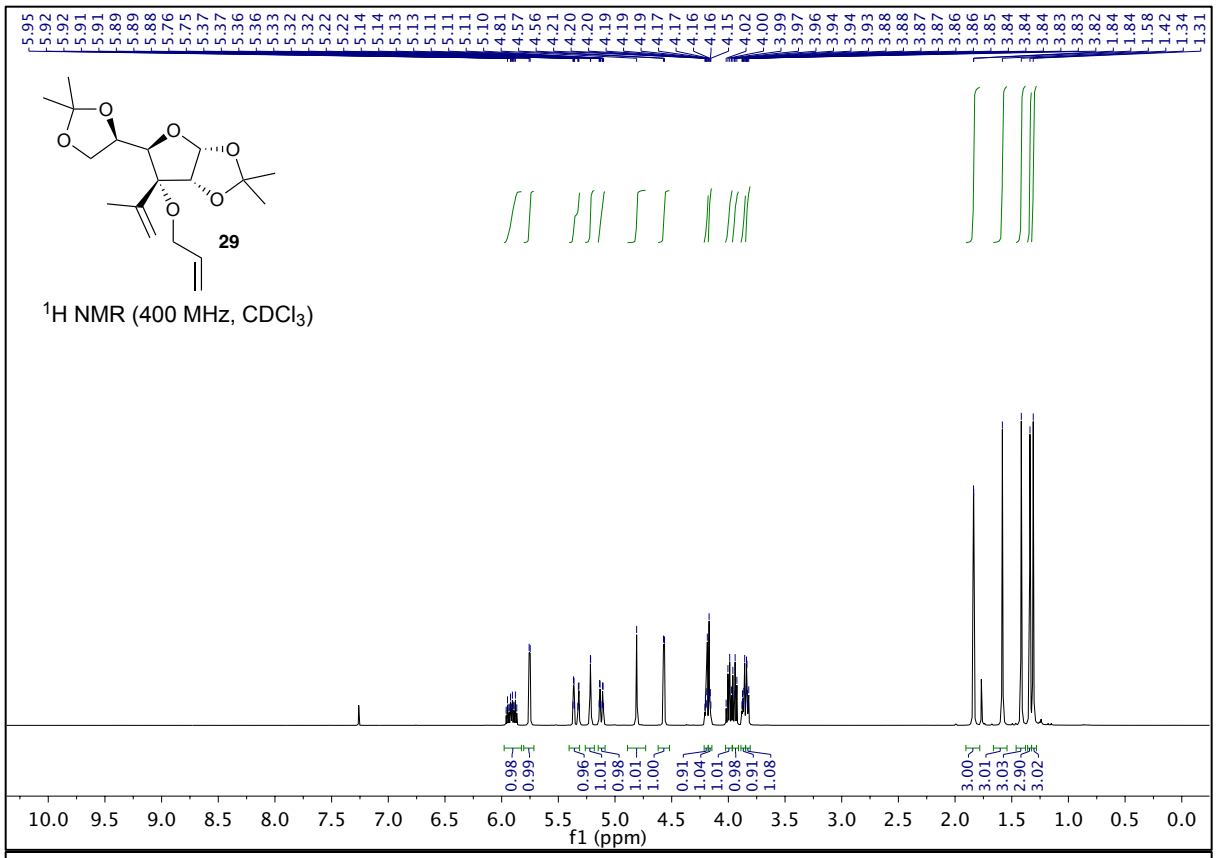

24
^{13}C NMR (100 MHz, CDCl$_3$)
f1 (ppm)


25
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

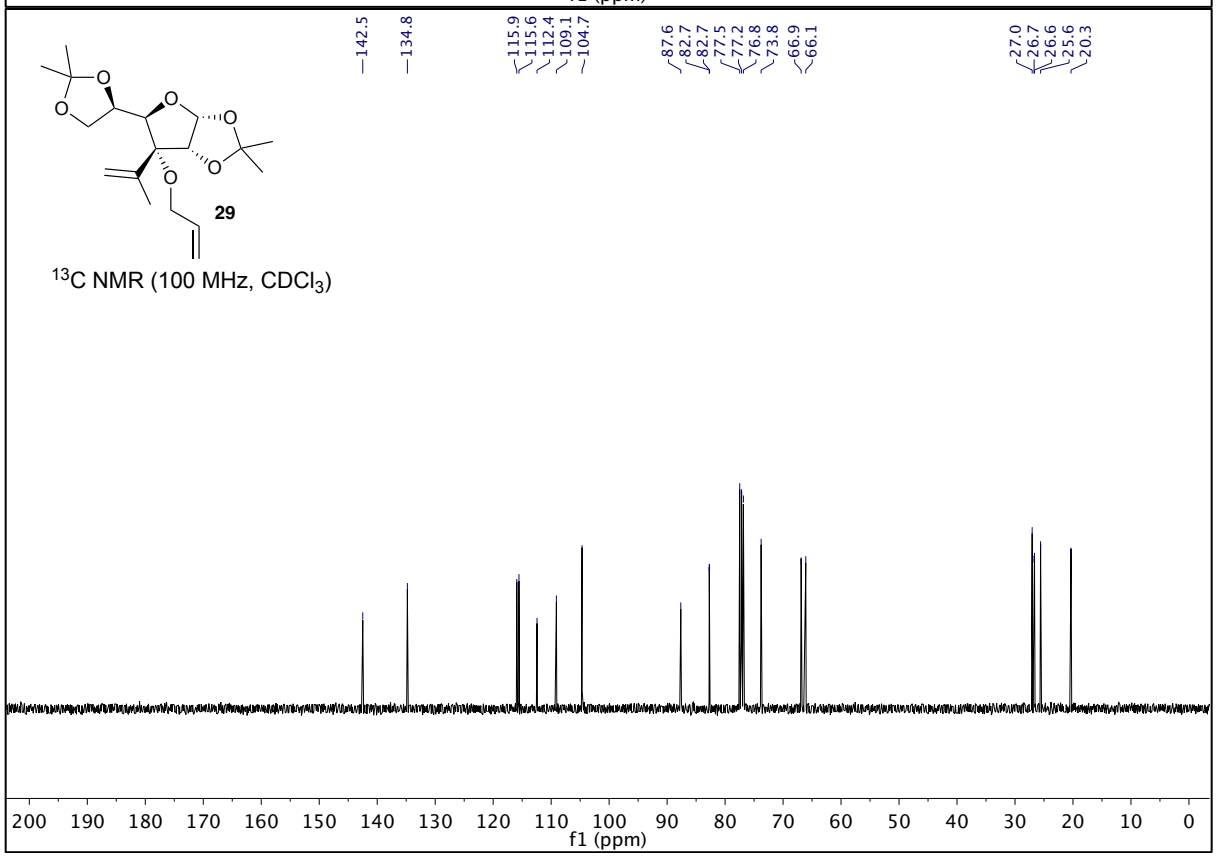

25
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)


27
^{1}H NMR (400 MHz, $CDCl_3$)
5.79
5.78
5.06
4.84
4.36
4.35
4.09
4.07
4.05
4.04
4.01
3.99
3.99
3.97
3.89
3.87
3.87
3.85
3.83
2.89
1.86
1.86
1.60
1.42
1.36
1.32
1.00
1.05
1.05
1.02
1.04
1.04
2.04
1.00
3.09
3.15
3.18
3.13
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

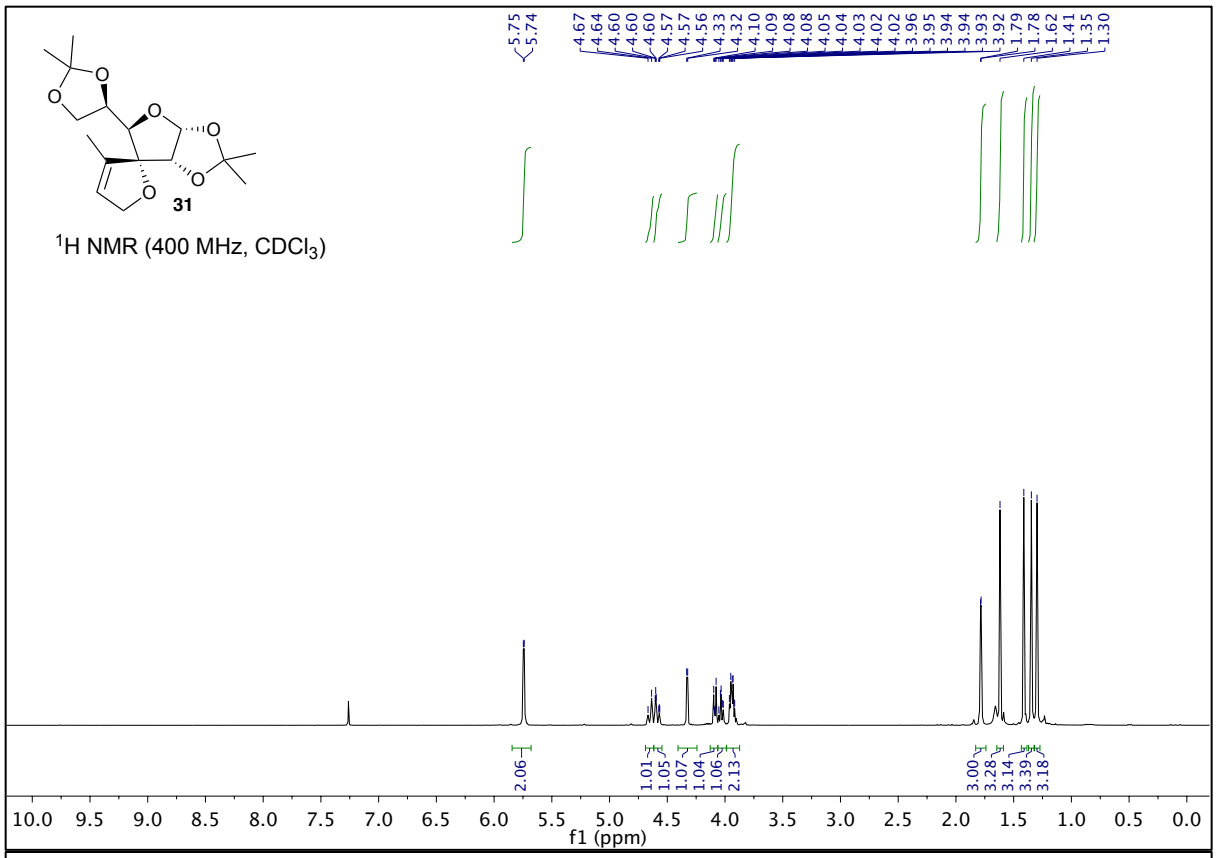

27
^{13}C NMR (100 MHz, $CDCl_3$)
143.6
113.0
112.7
109.4
104.7
84.0
83.6
81.8
77.5
77.2
76.8
73.6
67.3
26.8
26.8
26.6
25.6
20.3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

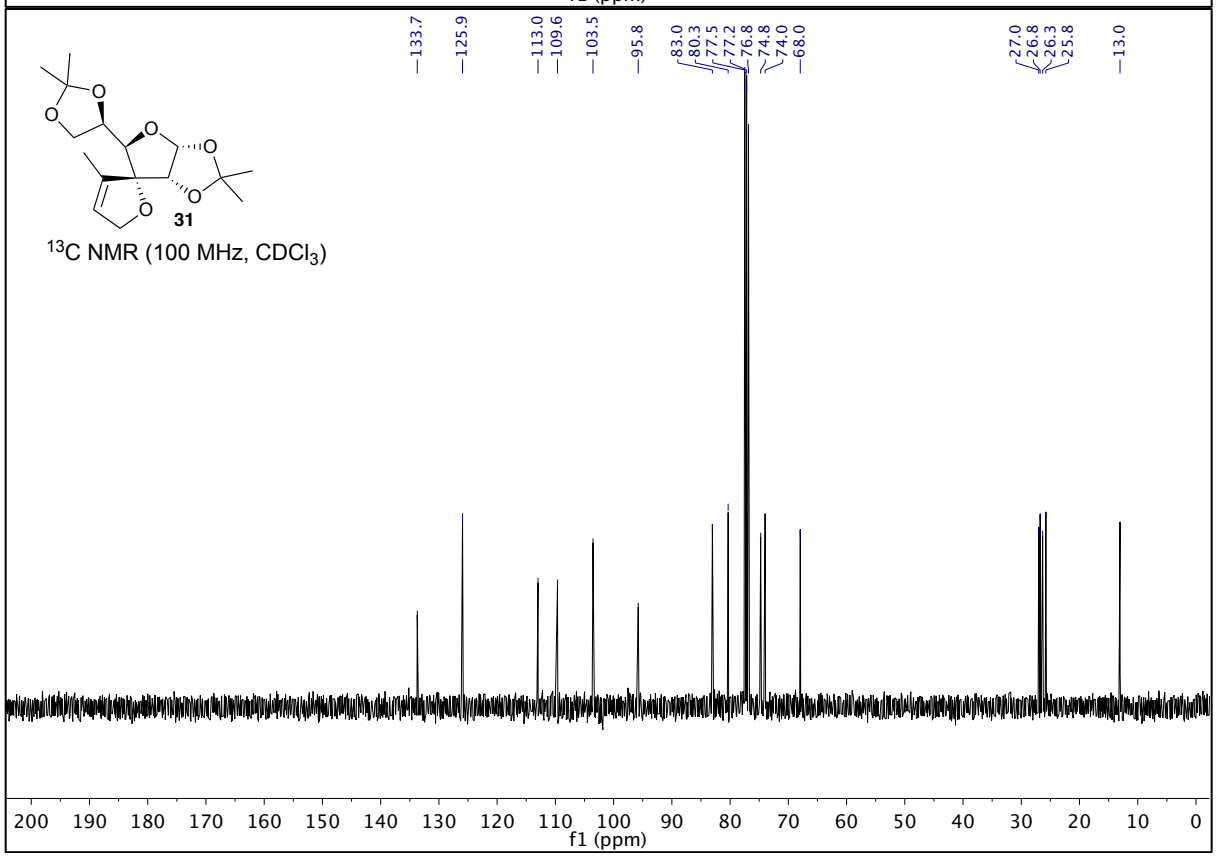


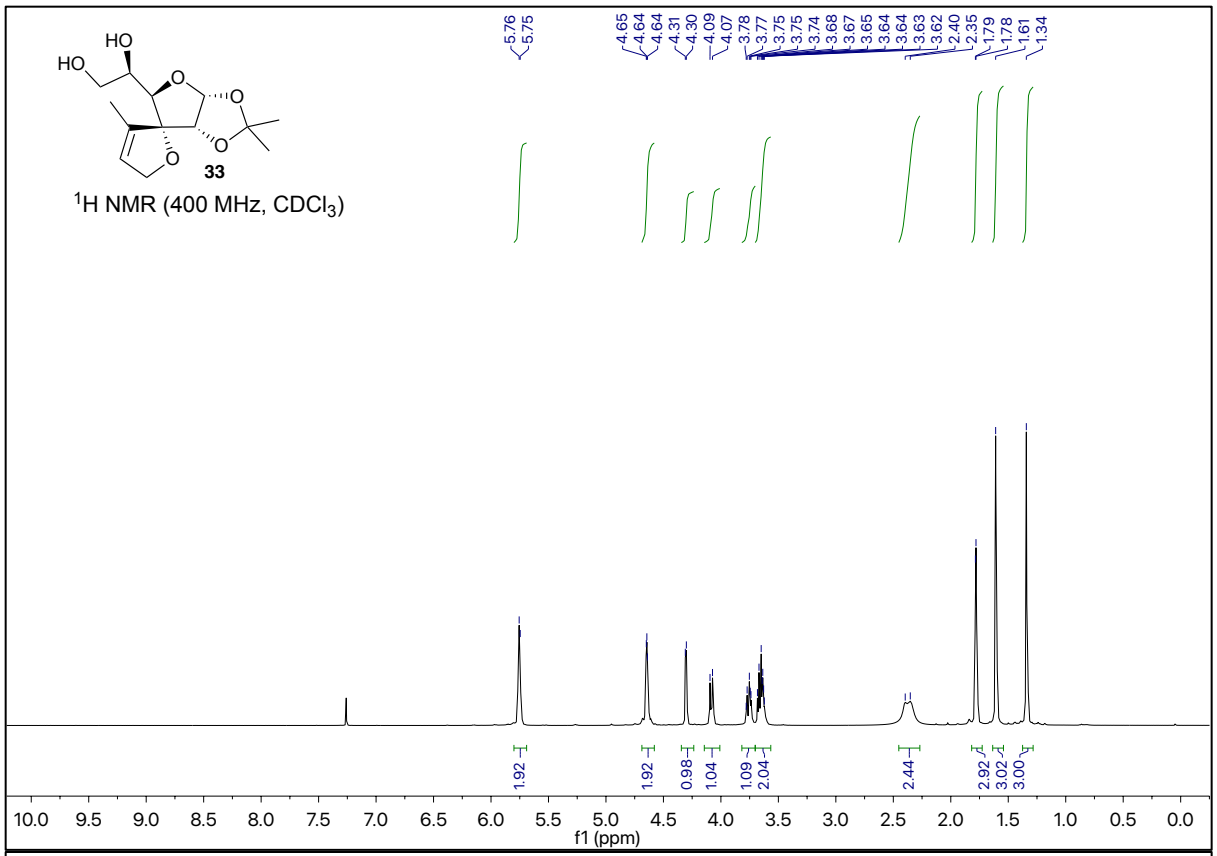
^{1}H NMR (400 MHz, $CDCl_3$)

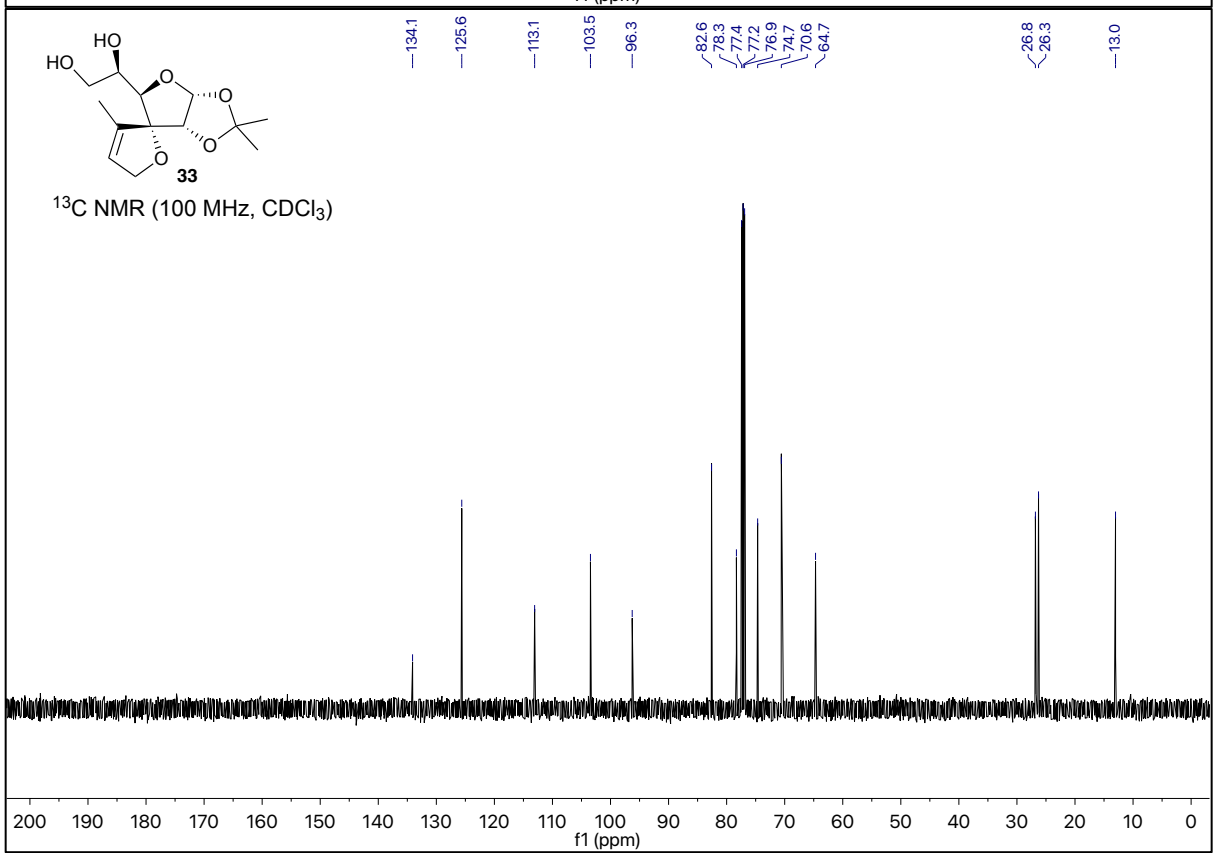


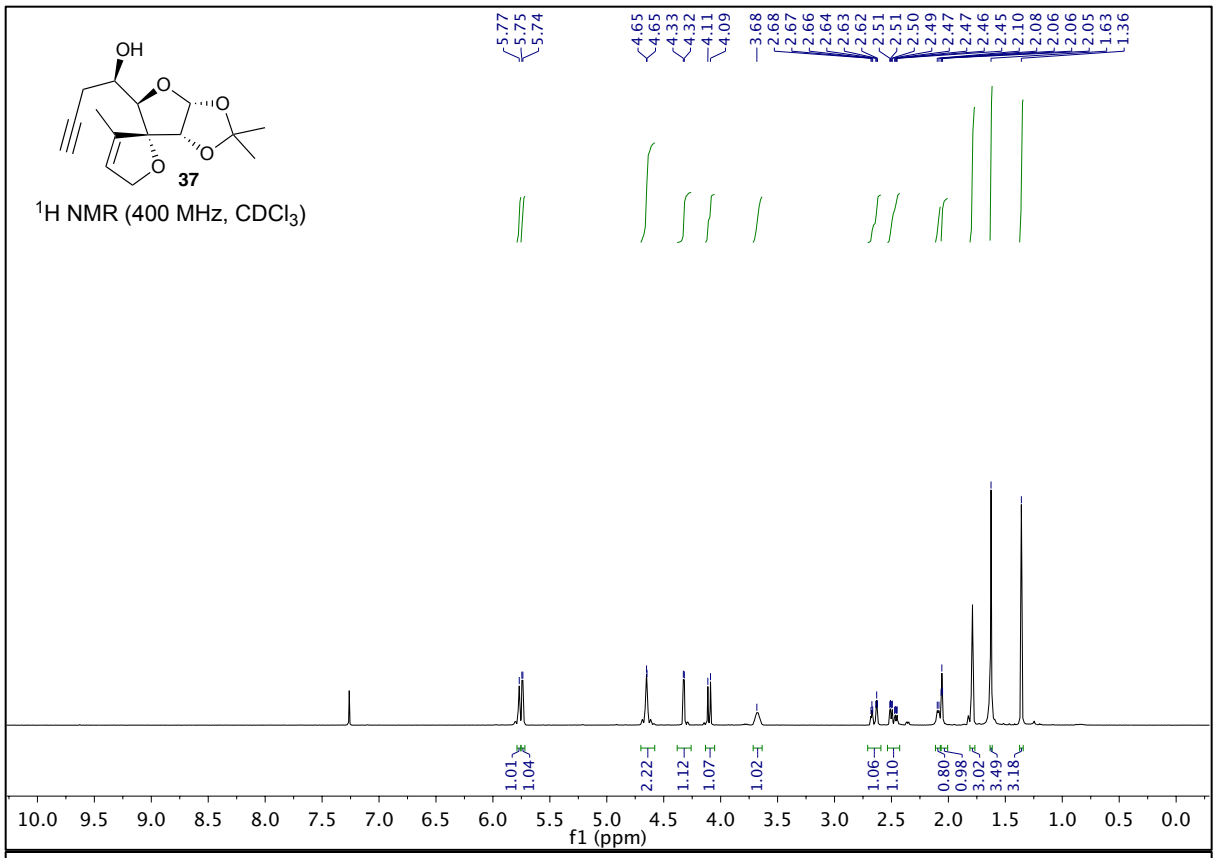
^{13}C NMR (100 MHz, $CDCl_3$)

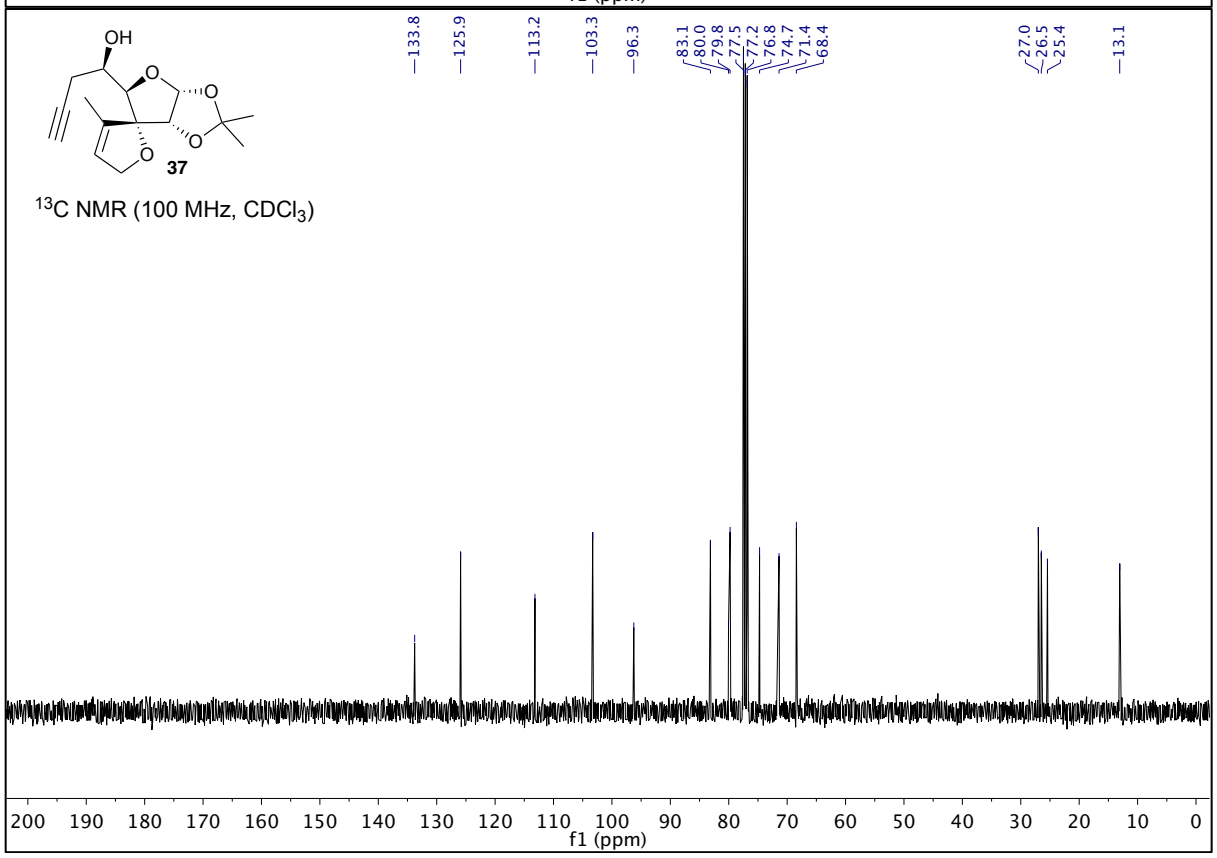

31
^{1}H NMR (400 MHz, $CDCl_3$)
5.75
5.74
4.67
4.64
4.60
4.60
4.60
4.57
4.57
4.56
4.33
4.32
4.10
4.09
4.08
4.08
4.05
4.04
4.03
4.02
4.02
3.96
3.95
3.94
3.94
3.93
3.92
1.79
1.78
1.62
1.41
1.35
1.30
2.06
1.01
1.05
1.07
1.04
1.06
2.13
3.00
3.28
3.14
3.39
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

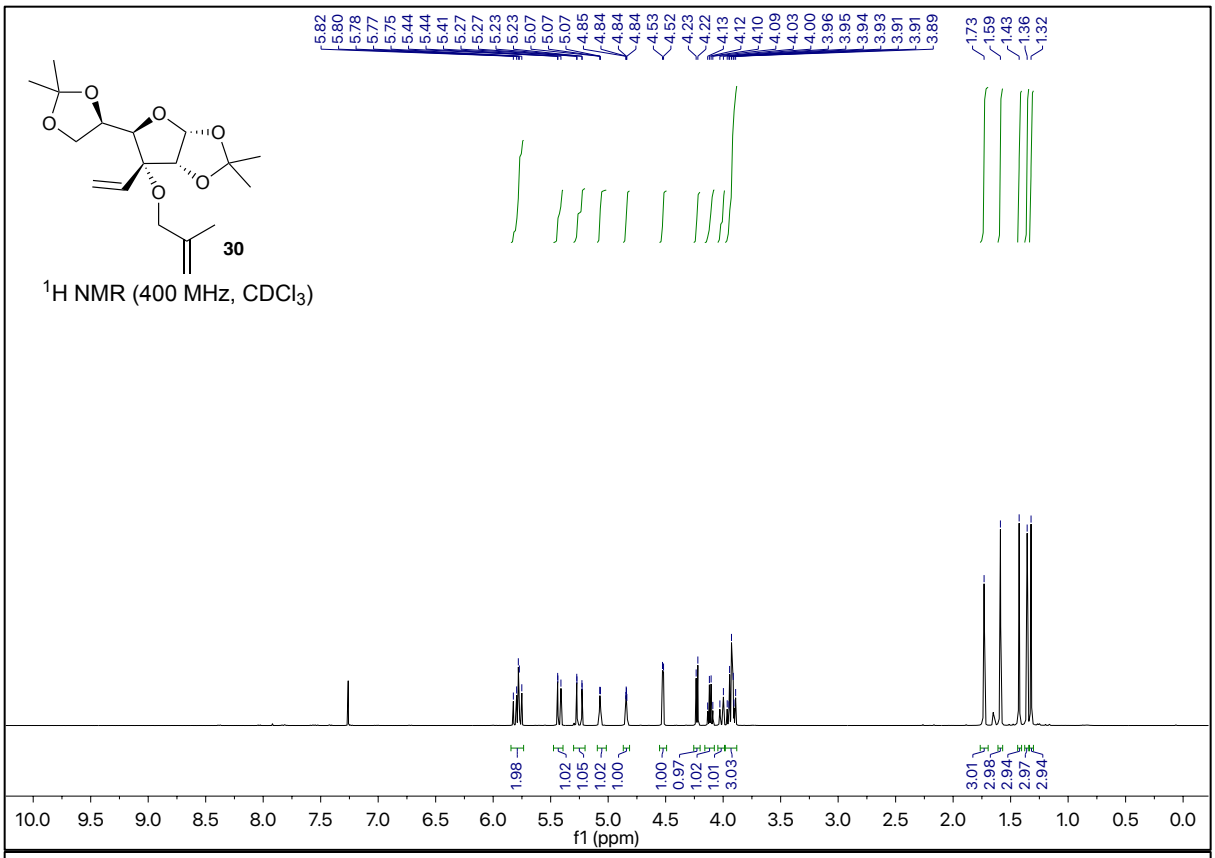

31
^{13}C NMR (100 MHz, $CDCl_3$)
133.7
125.9
113.0
109.6
103.5
95.8
83.0
80.3
77.5
77.2
76.8
74.8
74.0
68.0
27.0
26.8
26.3
25.8
13.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

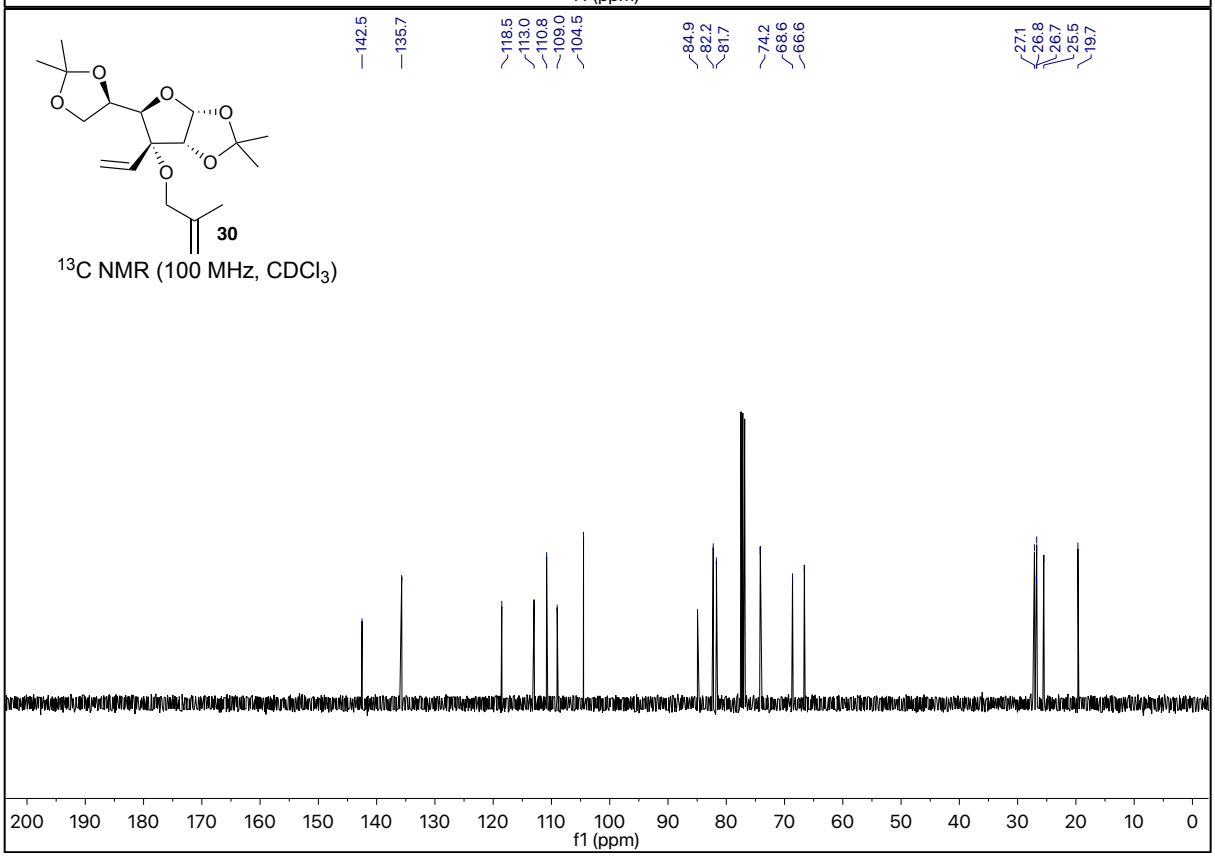

HO
HO
O
O
O
O
33
^{1}H NMR (400 MHz, $CDCl_3$)
5.76
5.75
4.65
4.64
4.64
4.31
4.30
4.09
4.07
3.78
3.77
3.75
3.75
3.74
3.68
3.67
3.65
3.64
3.64
3.63
3.62
2.40
2.35
1.79
1.78
1.61
1.34
1.92
1.92
0.98
1.04
1.09
2.04
2.44
2.92
3.02
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

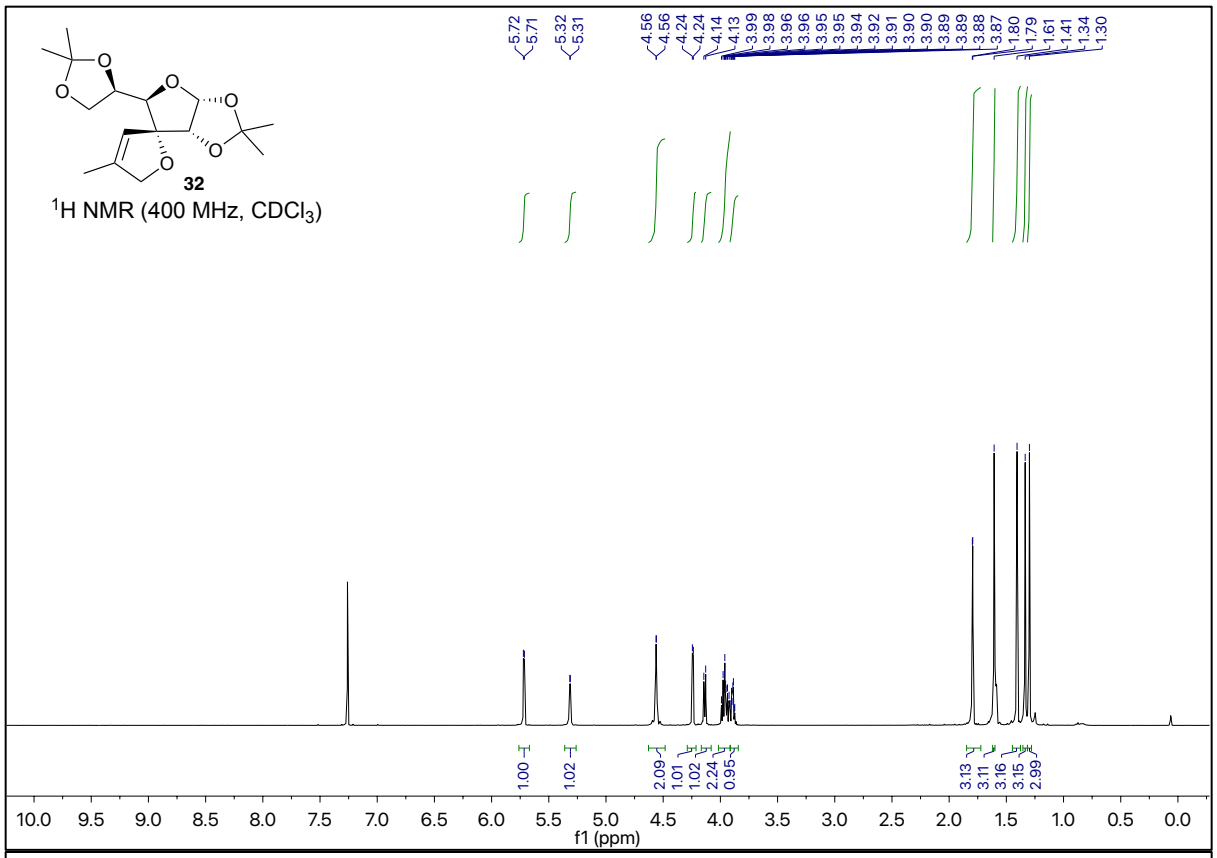

HO
HO
O
O
O
O
33
^{13}C NMR (100 MHz, $CDCl_3$)
134.1
125.6
113.1
103.5
96.3
82.6
78.3
77.4
77.2
76.9
74.7
70.6
64.7
26.8
26.3
13.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

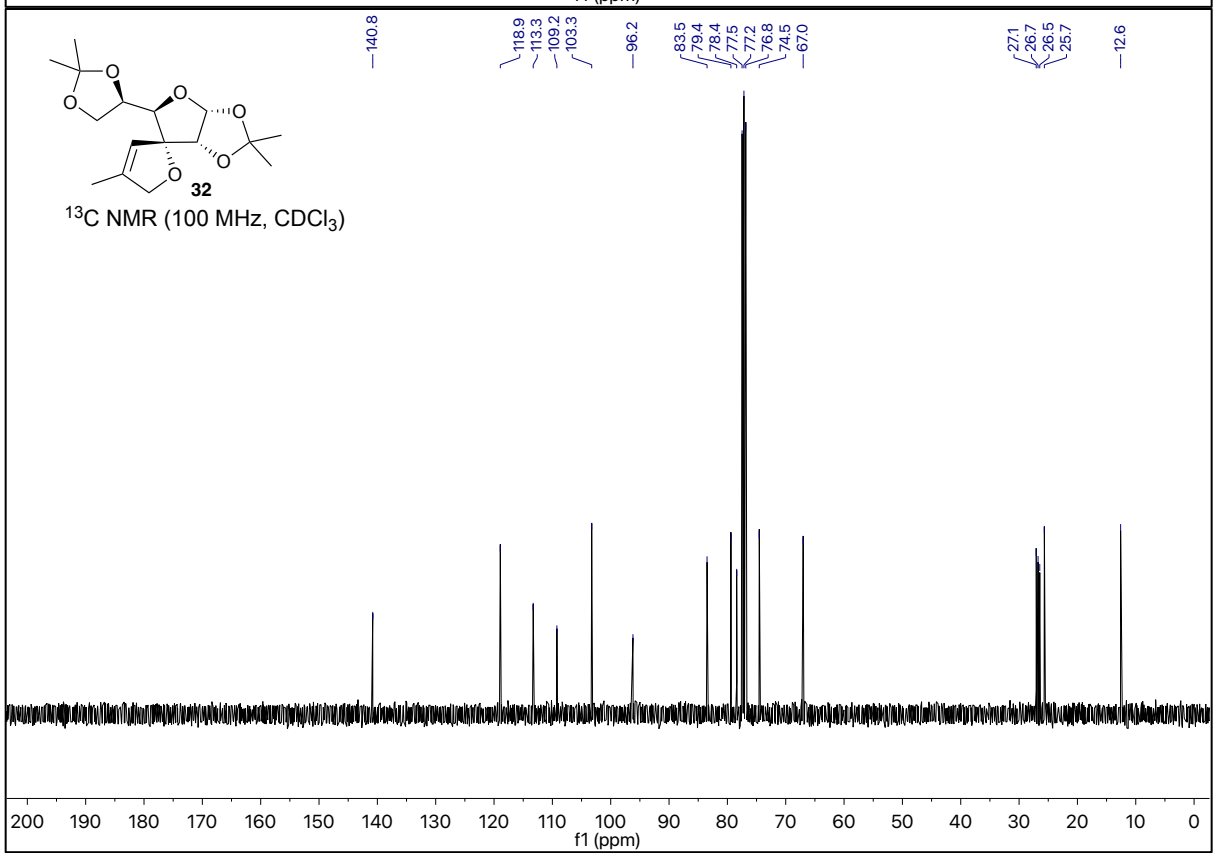

OH
O
O
O
O
37
^{1}H NMR (400 MHz, $CDCl_3$)
5.77
5.75
5.74
4.65
4.65
4.33
4.32
4.11
4.09
3.68
2.68
2.67
2.66
2.64
2.63
2.62
2.51
2.51
2.50
2.49
2.47
2.47
2.46
2.45
2.10
2.08
2.06
2.06
2.05
1.63
1.36
1.01
1.04
2.22
1.12
1.07
1.02
1.06
1.10
0.80
0.98
3.02
3.49
3.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

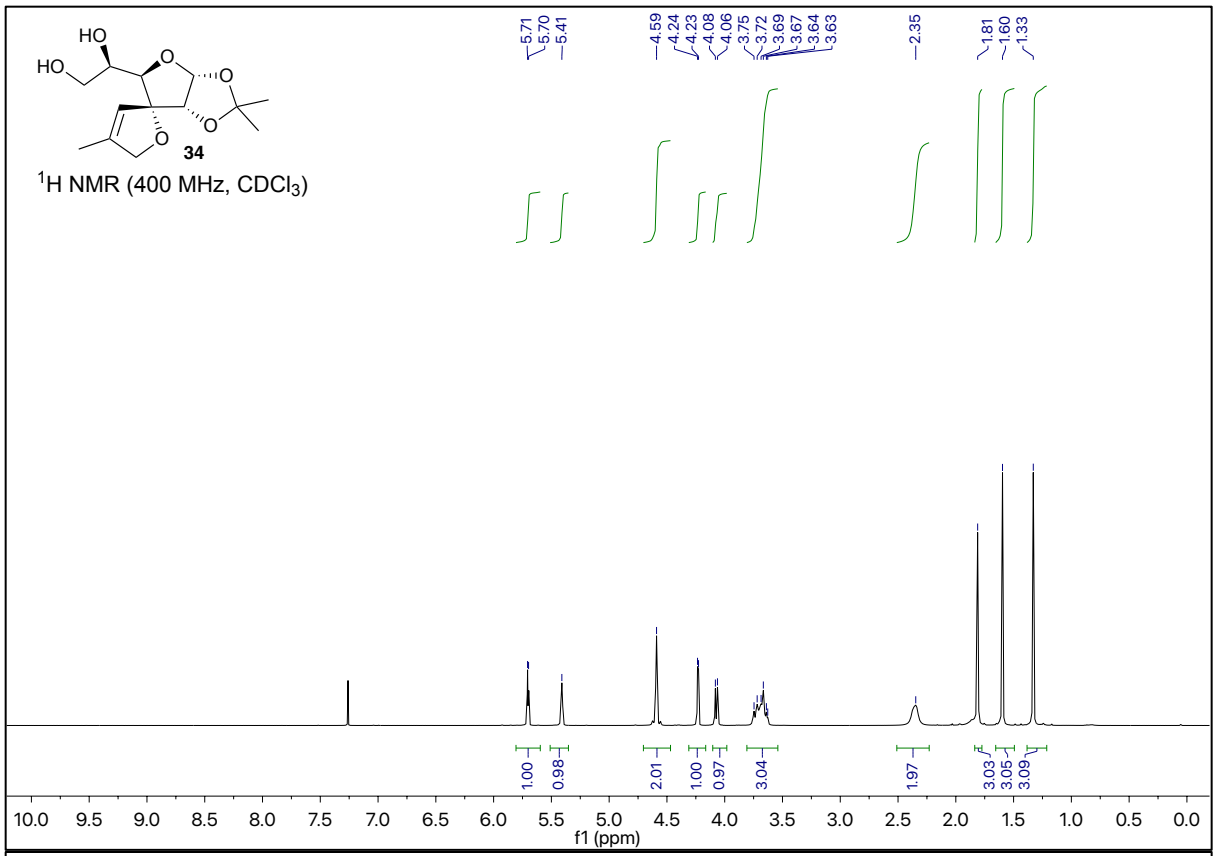

OH
O
O
O
O
37
^{13}C NMR (100 MHz, $CDCl_3$)
133.8
125.9
113.2
103.3
96.3
83.1
80.0
79.8
77.5
77.2
76.8
74.7
71.4
68.4
27.0
26.5
25.4
13.1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

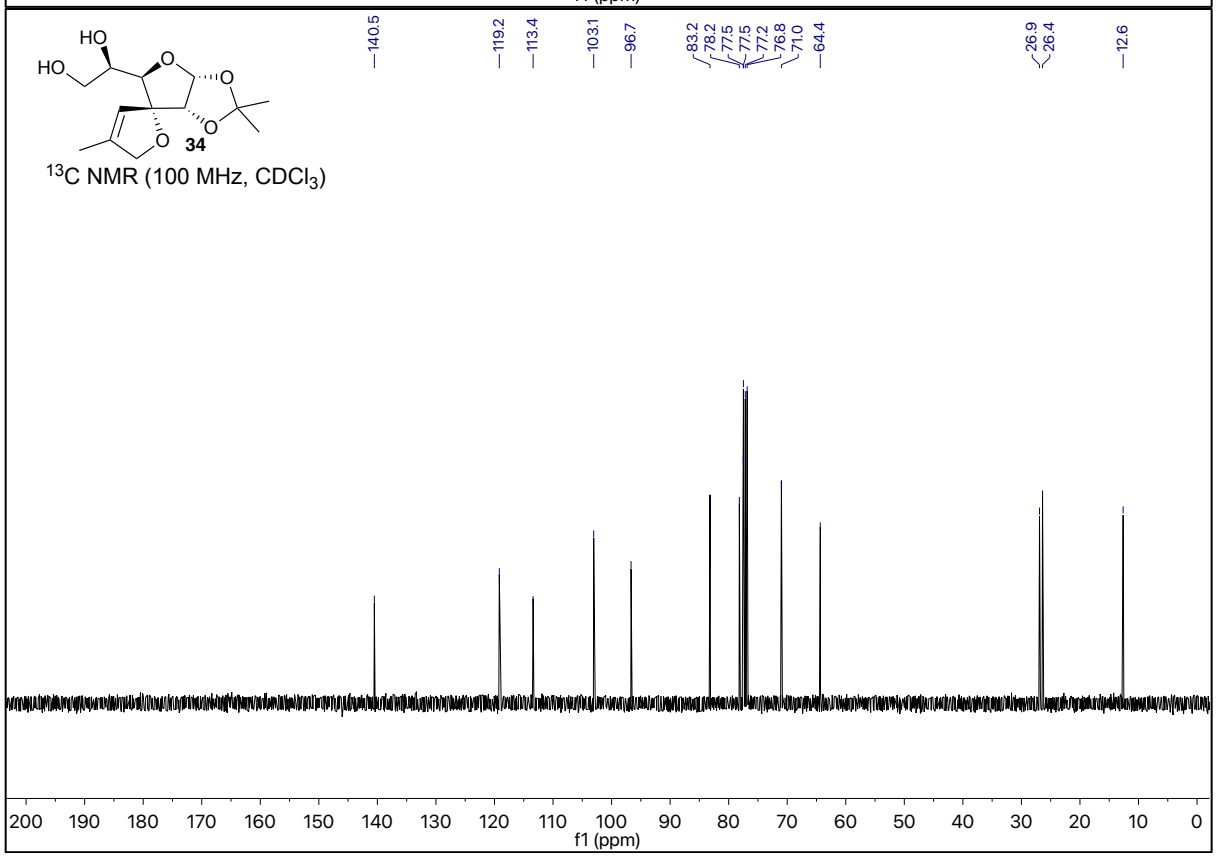

30
^{1}H NMR (400 MHz, $CDCl_3$)
5.82 5.80 5.78 5.77 5.75 5.44 5.44 5.41 5.27 5.27 5.23 5.07 5.07 5.07 4.85 4.84 4.84 4.84 4.53 4.52 4.23 4.22 4.13 4.12 4.10 4.09 4.03 4.00 3.96 3.95 3.94 3.93 3.91 3.91 3.89
1.73 1.59 1.43 1.36 1.32
1.98 1.02 1.05 1.02 1.00 1.00 0.97 1.02 1.01 3.03 3.01 2.98 2.94 2.97 2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

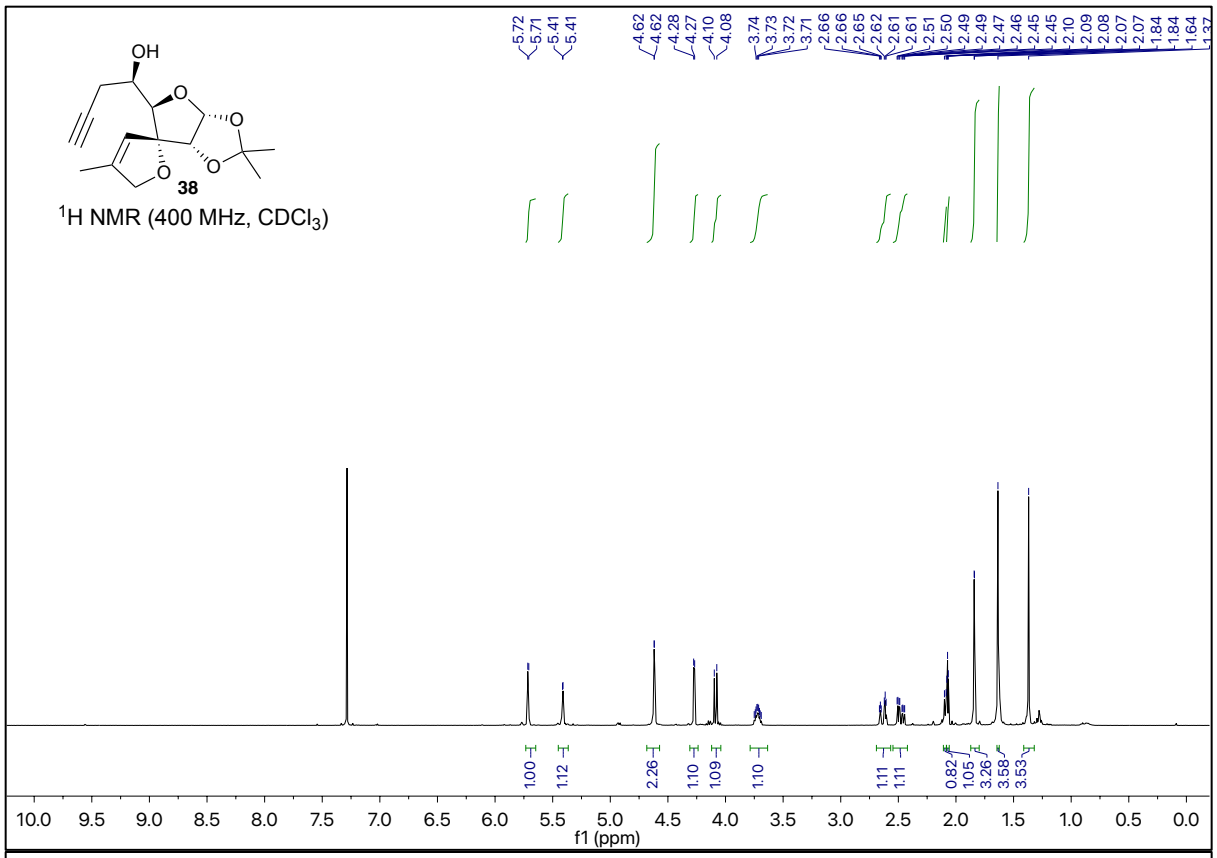

30
^{13}C NMR (100 MHz, $CDCl_3$)
142.5 135.7 118.5 113.0 110.8 109.0 104.5 84.9 82.2 81.7 74.2 68.6 66.6 27.1 26.8 26.7 25.5 19.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

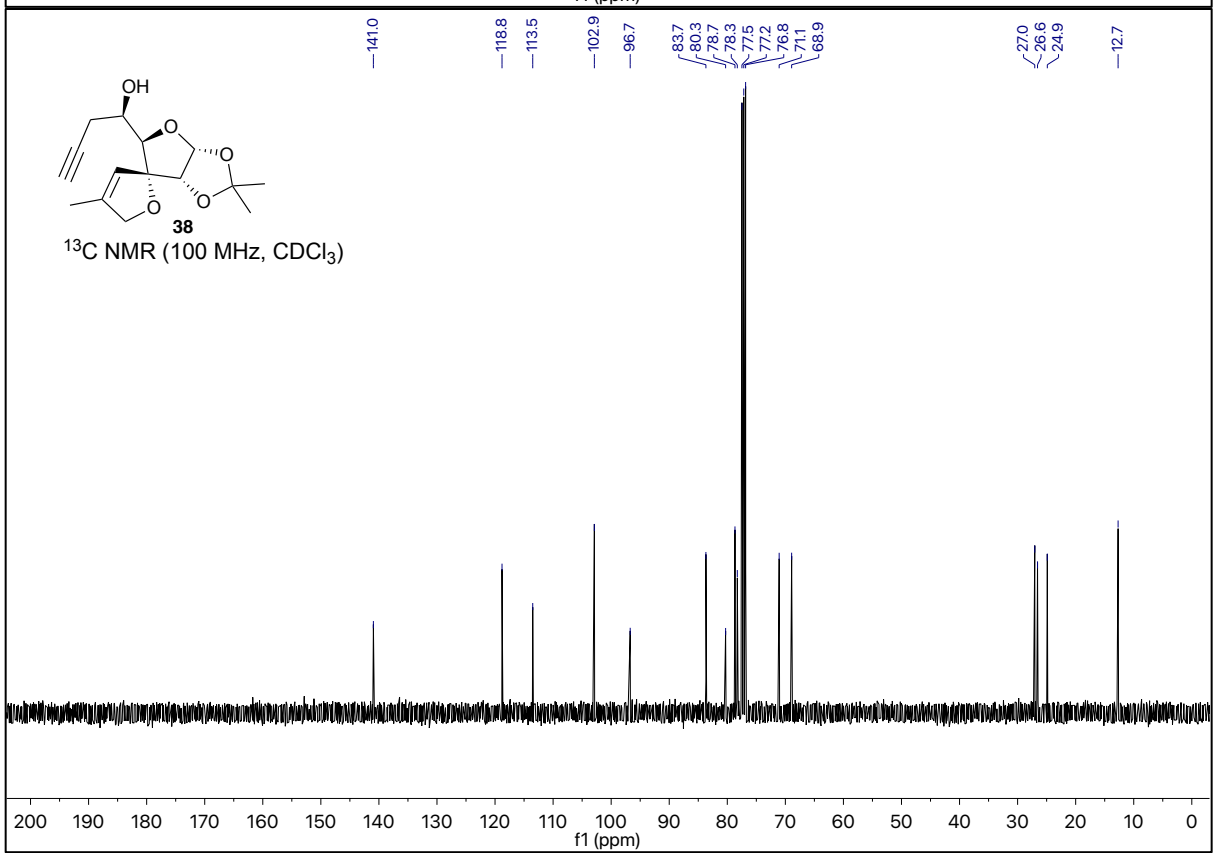

32
^{1}H NMR (400 MHz, $CDCl_3$)
5.72
5.71
5.32
5.31
4.56
4.56
4.24
4.24
4.14
4.13
3.99
3.98
3.96
3.96
3.95
3.95
3.94
3.92
3.91
3.90
3.90
3.89
3.89
3.88
3.87
1.80
1.79
1.61
1.41
1.34
1.30
1.00
1.02
2.09
1.01
1.02
2.24
0.95
3.13
3.11
3.16
3.15
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


32
^{13}C NMR (100 MHz, $CDCl_3$)
140.8
118.9
113.3
109.2
103.3
96.2
83.5
79.4
78.4
77.5
77.2
76.8
74.5
67.0
27.1
26.7
26.5
25.7
12.6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


34
^{1}H NMR (400 MHz, $CDCl_3$)
5.71
5.70
5.41
4.59
4.24
4.23
4.08
4.06
3.75
3.72
3.69
3.67
3.64
3.63
2.35
1.81
1.60
1.33
1.00
0.98
2.01
1.00
0.97
3.04
1.97
3.03
3.05
3.09
f1 (ppm)


34
^{13}C NMR (100 MHz, $CDCl_3$)
140.5
119.2
113.4
103.1
96.7
83.2
78.2
77.5
77.5
77.2
76.8
71.0
64.4
26.9
26.4
12.6
f1 (ppm)

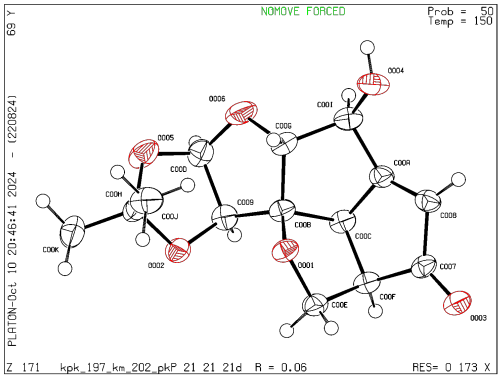

OH
O
O
O
O
38
^{1}H NMR (400 MHz, $CDCl_3$)
5.72
5.71
5.41
5.41
4.62
4.62
4.28
4.27
4.10
4.08
3.74
3.73
3.72
3.71
2.66
2.66
2.65
2.62
2.61
2.61
2.51
2.50
2.49
2.49
2.47
2.46
2.45
2.45
2.10
2.09
2.08
2.07
2.07
1.84
1.84
1.64
1.37
1.00
1.12
2.26
1.10
1.09
1.10
1.11
1.11
0.82
1.05
3.26
3.58
3.53
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


OH
O
O
O
O
38
^{13}C NMR (100 MHz, $CDCl_3$)
141.0
118.8
113.5
102.9
96.7
83.7
80.3
78.7
78.3
77.5
77.2
76.8
71.1
68.9
27.0
26.6
24.9
12.7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3. XRD Data:

X-Ray crystallographic analysis

Crystal data and structure refinement for 6 (ellipsoid is drawn at the 50% probability level):



Identification code		**6**
Solvent		**CH_2Cl_2**
CCDC	**2363008**	

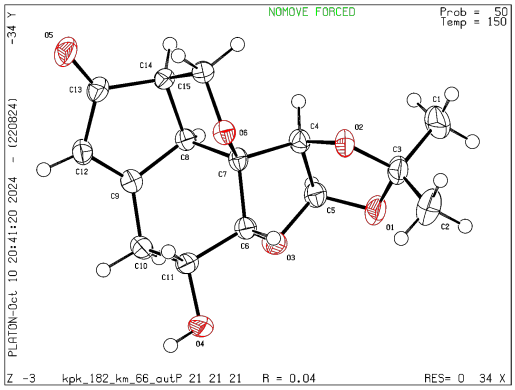
Bond precision:		**C-C = 0.0060 A**	**Wavelength=0.71073**
Cell:	**a=7.2184(4)**	**b=7.8161(5)**	**c=22.5614(14)**
	alpha=90	**beta=90**	**gamma=90**
Temperature:	**150 K**		

	Calculated	**Reported**
Volume	**1272.91(13)**	**1272.91(13)**
Space group	**P 21 21 21**	**P 21 21 21**
Hall group	**P 2ac 2ab**	**P 2ac 2ab**
Moiety formula	**C14 H16 O6**	**C14 H16 O6**
Sum formula	**C14 H16 O6**	**C14 H16 O6**
Mr	**280.27**	**280.27**
Dx,g cm-3	**1.462**	**1.462**
Z	**4**	**4**
Mu (mm-1)	**0.115**	**0.115**
F000	**592.0**	**592.0**
F000'	**592.38**	
h,k,lmax	**8,9,26**	**8,9,26**
Nref	**2257[1338]**	**2252**
Tmin,Tmax	**0.984,0.995**	**0.714,1.000**
Tmin'	**0.977**	

Correction method= # Reported T Limits: Tmin=0.714 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.68/1.00	**Theta(max)= 24.987**
R(reflections)= 0.0591(1910)	**wR2(reflections)= 0.1682(2252)**
S = 1.049	**Npar= 184**

X-Ray crystallographic analysis
Crystal data and structure refinement for 7 (ellipsoid is drawn at the 50% probability level):



Identification code		**7**
Solvent		**CH_2Cl_2**
CCDC	**2363005**	

Bond precision:		**C-C = 0.0045 A**	**Wavelength=0.71073**
Cell:	**a=8.5016(4)**	**b=11.7104(5)**	**c=14.3897(6)**
	alpha=90	**beta=90**	**gamma=90**
Temperature:	**150 K**		

	Calculated	**Reported**
Volume	**1432.60(11)**	**1432.60(11)**
Space group	**P 21 21 21**	**P 21 21 21**
Hall group	**P 2ac 2ab**	**P 2ac 2ab**
Moiety formula	**C15 H18 O6**	**C15 H18 O6**
Sum formula	**C15 H18 O6**	**C15 H18 O6**
Mr	**294.29**	**294.29**
Dx,g cm-3	**1.365**	**1.364**
Z	**4**	**4**
Mu (mm-1)	**0.106**	**0.106**
F000	**624.0**	**624.0**
F000'	**624.39**	
h,k,lmax	**10,13,17**	**10,13,17**
Nref	**2516[1464]**	**2516**
Tmin,Tmax	**0.980,0.996**	**0.113,1.000**
Tmin'	**0.980**	

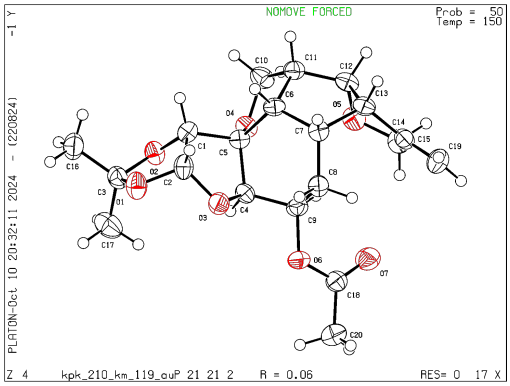
Correction method= # Reported T Limits: Tmin=0.113 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.72/1.00 **Theta(max)= 24.990**

R(reflections)= 0.0397(2121) **wR2(reflections)= 0.0972(2516)**

S = 1.025 **Npar= 193**

X-Ray crystallographic analysis
Crystal data and structure refinement for 20 (ellipsoid is drawn at the 50% probability level):



Identification code		**20**	
Solvent		**CH_2Cl_2**	
CCDC	**2363006**		
Bond precision:		**C-C = 0.0066 A**	**Wavelength=0.71073**
Cell:	**a=22.6546(7)**	**b=14.3623(4)**	**c=5.6230(1)**
	alpha=90	**beta=90**	**gamma=90**
Temperature:	**150 K**		

	Calculated	**Reported**
Volume	**1829.57(8)**	**1829.57(8)**
Space group	**P 21 21 2**	**P 21 21 2**
Hall group	**P 2 2ab**	**P 2 2ab**
Moiety formula	**C20 H26 O7**	**C20 H26 O7**
Sum formula	**C20 H26 O7**	**C20 H26 O7**
Mr	**378.41**	**378.41**
Dx,g cm-3	**1.374**	**1.374**
Z	**4**	**4**
Mu (mm-1)	**0.104**	**0.104**
F000	**808.0**	**808.0**
F000'	**808.47**	
h,k,lmax	**26,17,6**	**26,17,6**
Nref	**3231[1899]**	**3228**
Tmin,Tmax	**0.985,0.991**	**0.045,1.000**
Tmin'	**0.979**	

Correction method= # Reported T Limits: Tmin=0.045 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 1.70/1.00 **Theta(max)= 24.997**

R(reflections)= 0.0588(2435) **wR2(reflections)= 0.1565(3228)**

S = 1.025 **Npar= 247**

4. References:

1 K. Ramakrishna, K. P. Kaliappan, A One-Pot Deprotection and Intramolecular Oxa-Michael Addition to Access Angular Trioxatriquinanes, *Synlett.*, 2011, **17**, 2580–2584.

2 M. F. Hossain, K. Matcha, S. Ghosh, Synthetic Studies Toward Nortriterpenoids of Schisandraceae Family. Approach to the Construction of Functionalised C/D and A/B Ring Units of Micrandilactone C and Rubrifloradilactone B, *Tetrahedron Lett.*, 2011, **52**, 6473–6476.