Supporting Information

Asymmetric Hydroformylation-Initiated Tandem Sequences for Syntheses of (+)-Patulolide C, (-)-Pyrenophorol, (+)-Decarestrictine L and (+)-Prelog-Djerassi Lactone

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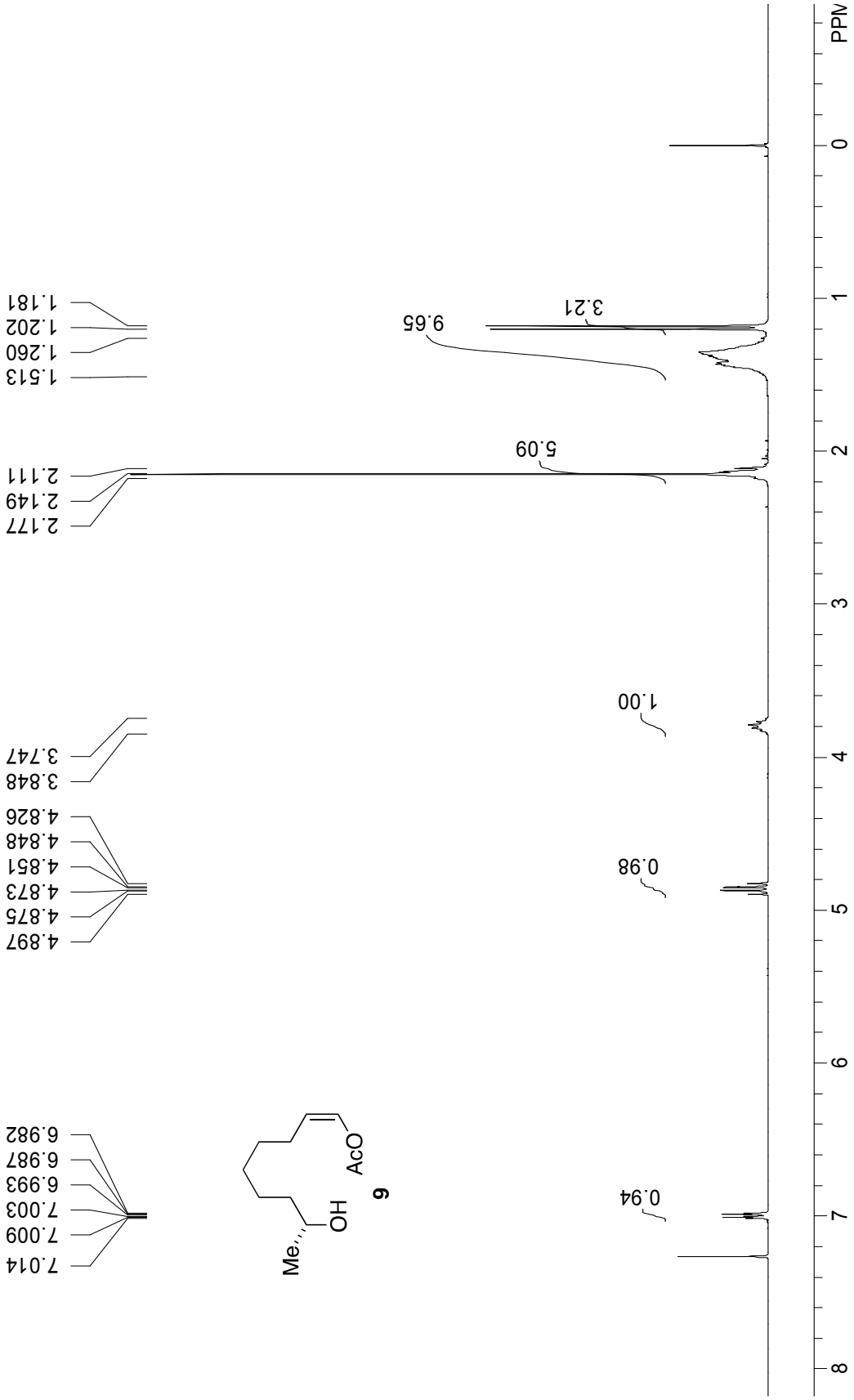
1. ^{1}H and ^{13}C NMR spectra **S2**

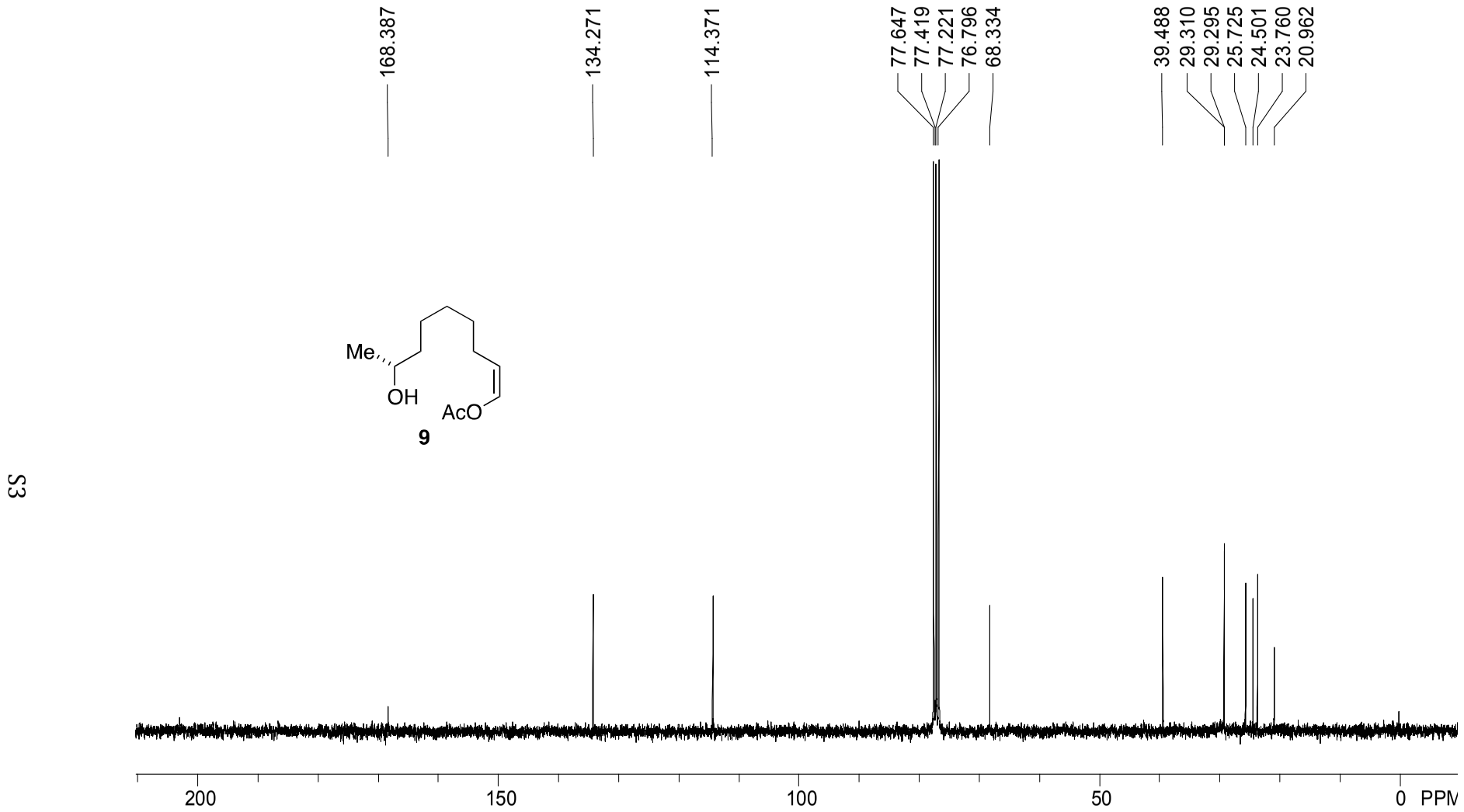
2. HPLC/ SFC Data **S40**

3. NMR Comparison Tables **S46**

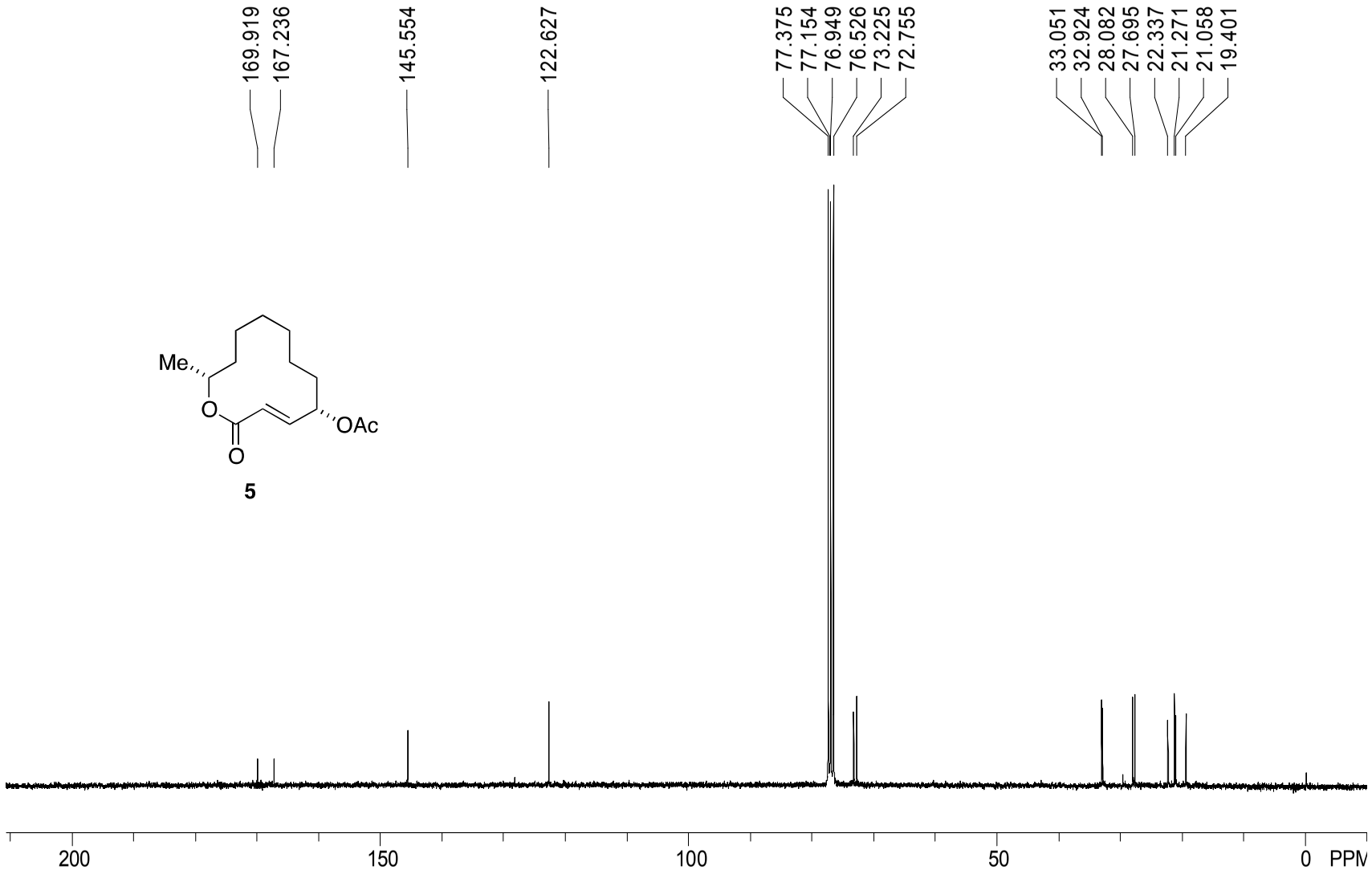
4. X-ray Crystallographic Data for SI-1 **S51**

Copies of ^{1}H and ^{13}C NMR spectra

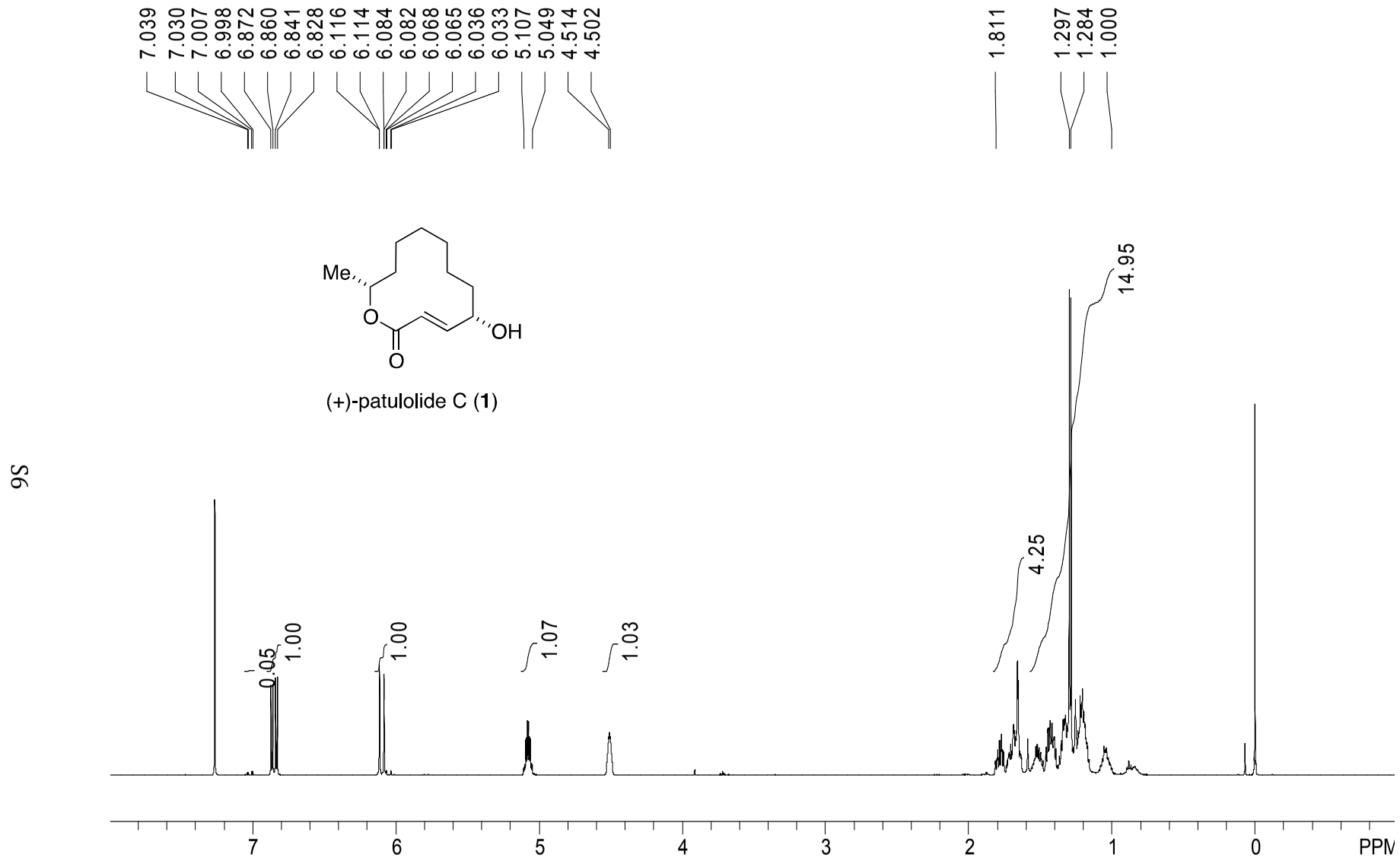


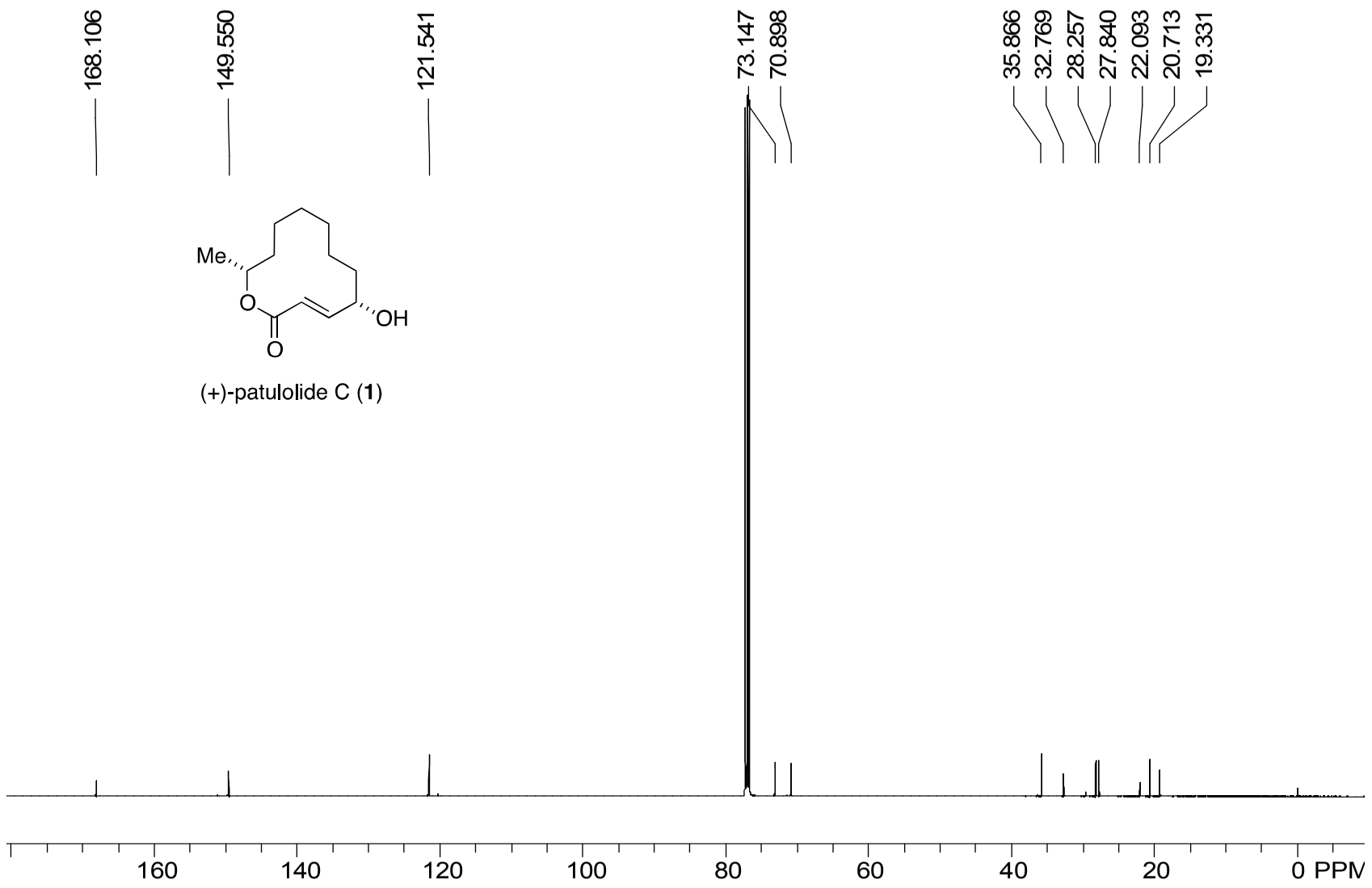

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77.647
77.419
77.221
76.796
68.334
39.488
29.310
29.295
25.725
24.501
23.760
20.962
Me
OH
AcO
9
200
150
100
50
0
PPM

PPM
0
1
2
3
4
5
6
7
8
0.92
0.90
0.95
0.99
3.00
17.99
2.083
1.910
1.306
1.283
1.027
6.864
6.840
6.810
6.787
6.088
6.034
5.435
5.413
5.400
5.378
5.124
5.081
5.071
5.015
OAc
Me
O
O
5


169.919
167.236
145.554
122.627
77.375
77.154
76.949
76.526
73.225
72.755
33.051
32.924
28.082
27.695
22.337
21.271
21.058
19.401
Me
O
O
OAc
O
200
150
100
50
0
PPM

5


7.039
7.030
7.007
6.998
6.872
6.860
6.841
6.828
6.116
6.114
6.084
6.082
6.068
6.065
6.036
6.033
5.107
5.049
4.514
4.502
1.811
1.297
1.284
1.000
Me
O
O
OH
(+)-patulolide C (1)
14.95
4.25
1.07
1.03
1.00
1.00
0.05
7
6
5
4
3
2
1
0
PPM



(+)-patulolide C (**1**)

7.080
7.064
4.953
4.938
4.924
4.909
3.878
3.866
3.854
3.842
3.829
3.817
2.334
2.220
2.140
1.143
1.131
0.888
0.058
0.054
OAc
Me
OTBS
13
0.94
0.93
0.97
1.96
3.02
3.00
9.39
5.99
PPM

-4.641
-4.430
18.284
20.882
23.548
25.982
34.747
68.179
110.577
135.168
168.201
OAc
Me
OTBS
13
PPM
0
50
100
150

6.743
6.732
6.712
6.701
5.868
5.866
5.837
5.834
5.395
5.383
5.372
5.360
3.825
3.813
3.801
3.789
3.777
3.765
2.095
1.816
1.744
1.674
1.600
1.486
1.466
1.421
1.130
1.118
0.882
0.046
0.041
5.96
9.31
3.07
11.12
1.11
1.03
2.87
1.00
0.98
0.95
0.96
OAc
Me
OTBS
O
t-BuO
12
PPM
0
2
4
6
8

-4.628
-4.267
18.228
21.188
23.804
25.992
28.215
30.040
34.784
68.186
72.730
80.834
123.589
144.191
165.479
170.252
PPM
0
50
100
150
OAc
Me
OTBS
O
t-BuO
12

9.515
5.000
4.991
4.984
4.974
3.853
3.840
3.828
3.816
3.805
3.793
2.178
2.010
1.939
1.747
1.670
1.541
1.495
1.146
1.134
0.884
0.052
0.044
7.02
10.85
3.24
2.12
4.06
0.98
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Me
OTBS
O
15
PPM
0
2
4
6
8
10

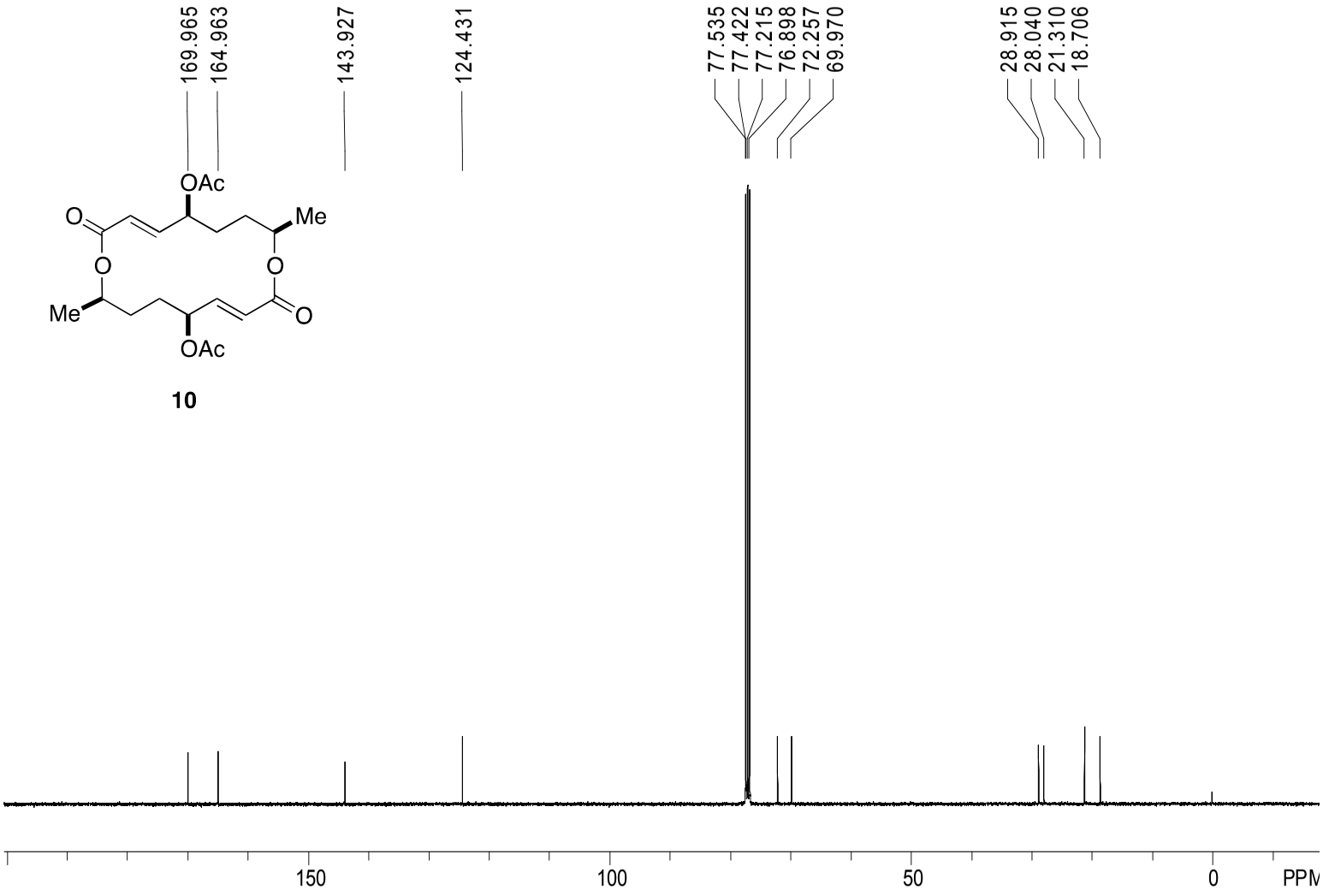
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18.236
-4.211
-4.640
OAc
Me
OTBS
15
PPM
0
50
100
150
200

6.871
6.858
6.832
6.819
5.935
5.932
5.896
5.893
5.428
5.414
5.401
5.383
3.758
3.743
3.727
3.712
3.696
3.681
2.097
1.900
1.811
1.738
1.645
1.533
1.410
1.166
1.150
OAc
Me
OH
HO
O
11
0.93
0.93
0.93
1.00
2.71
0.96
1.01
1.99
3.02
PPM

20.988
23.629
31.341
35.452
48.510
48.725
48.938
49.150
49.364
49.574
49.789
68.339
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169.396
171.993
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OAc
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HO
11
0 PPM
50
100
150

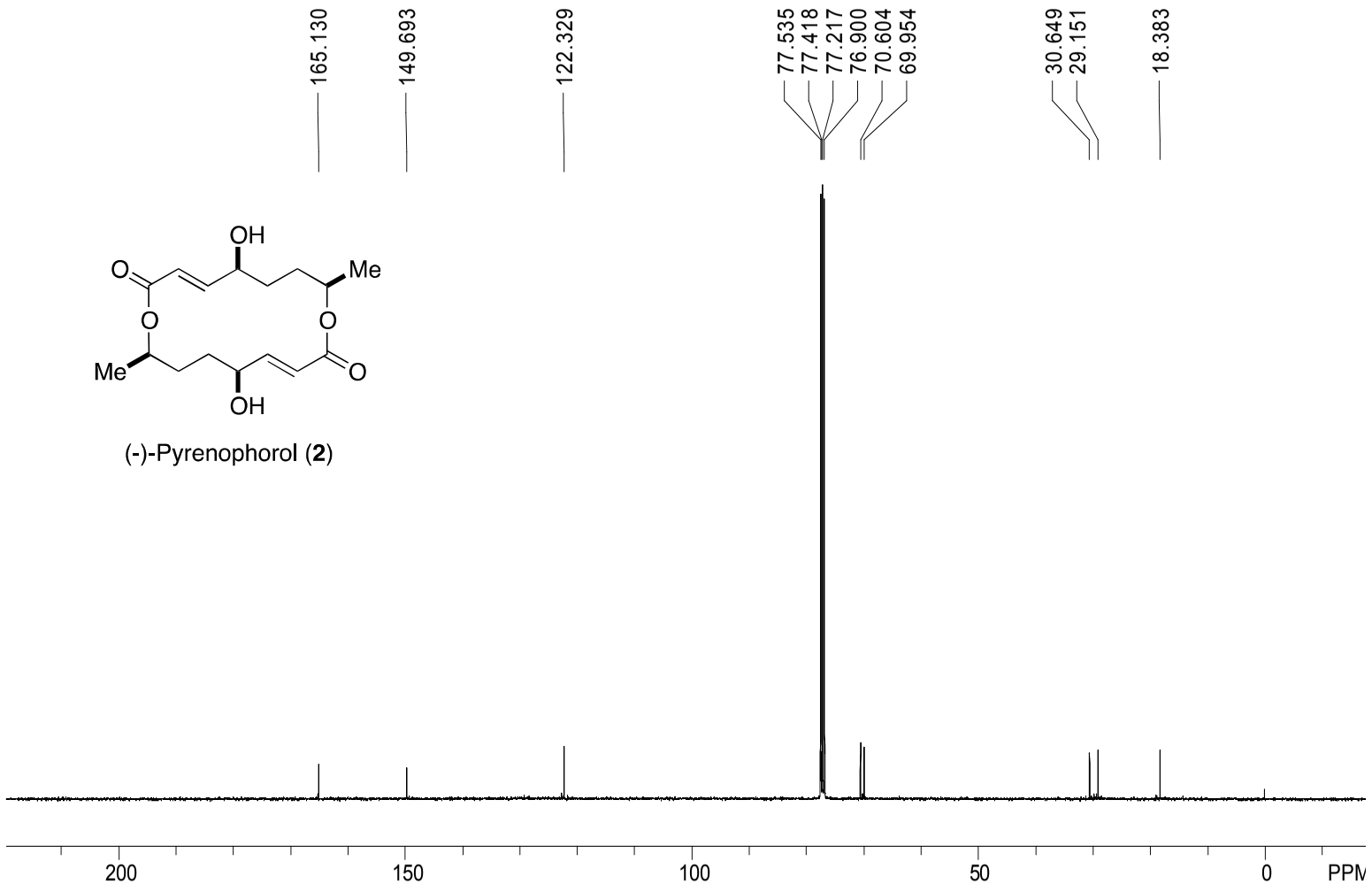
6.811
6.794
6.771
6.754
5.998
5.995
5.958
5.956
5.246
5.195
5.127
5.058
2.084
1.891
1.829
1.780
1.690
1.654
1.575
1.264
1.247
1.00
1.01
1.00
2.98
2.02
1.05
1.20
3.13
PPM
0
1
2
3
4
5
6
7
8
Me
OAc
OAc
Me
O
O
O
O

10

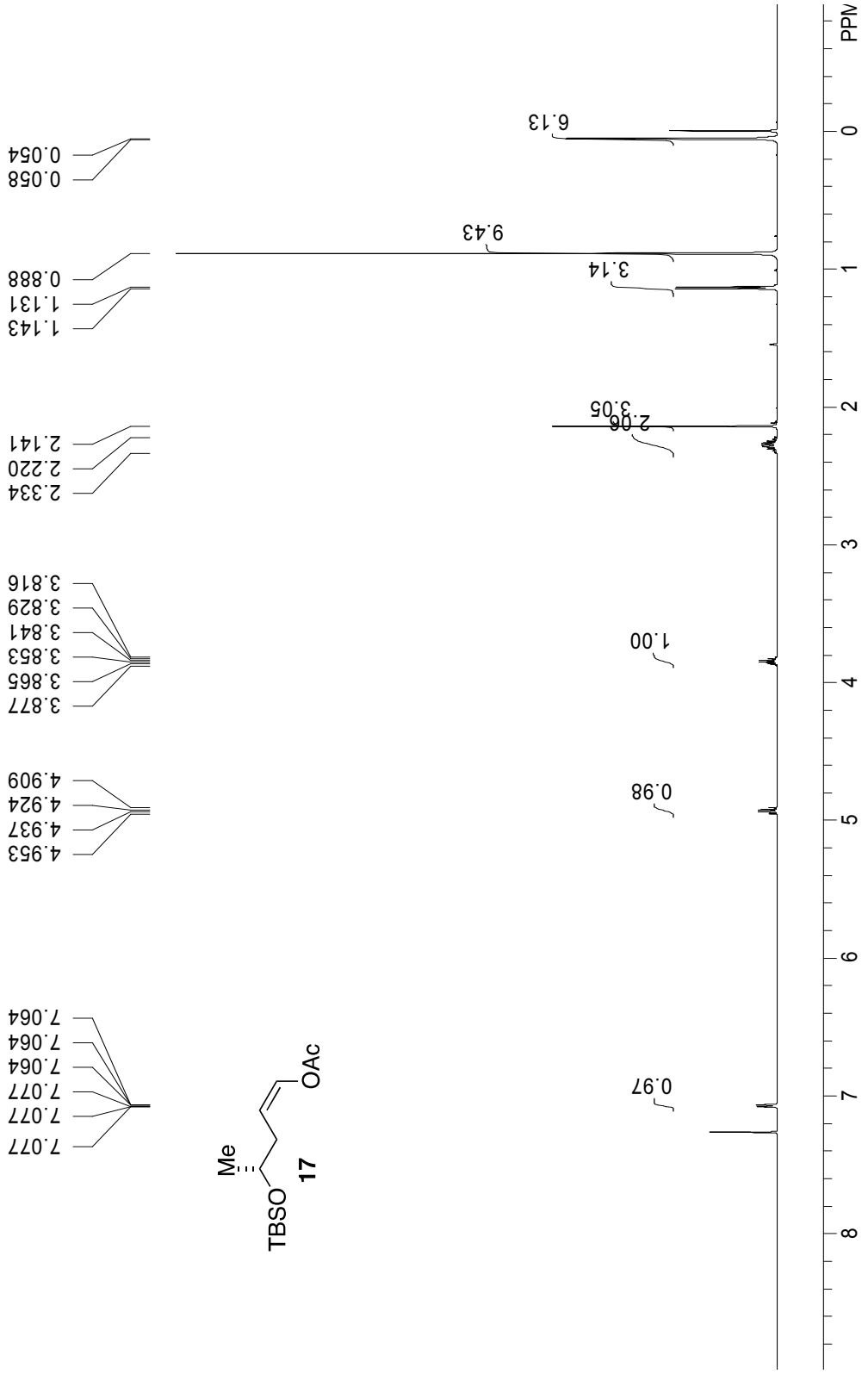

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143.927
124.431
77.535
77.422
77.215
76.898
72.257
69.970
28.915
28.040
21.310
18.706
OAc
Me
O
O
O
Me
O
OAc
150
100
50
0
PPM

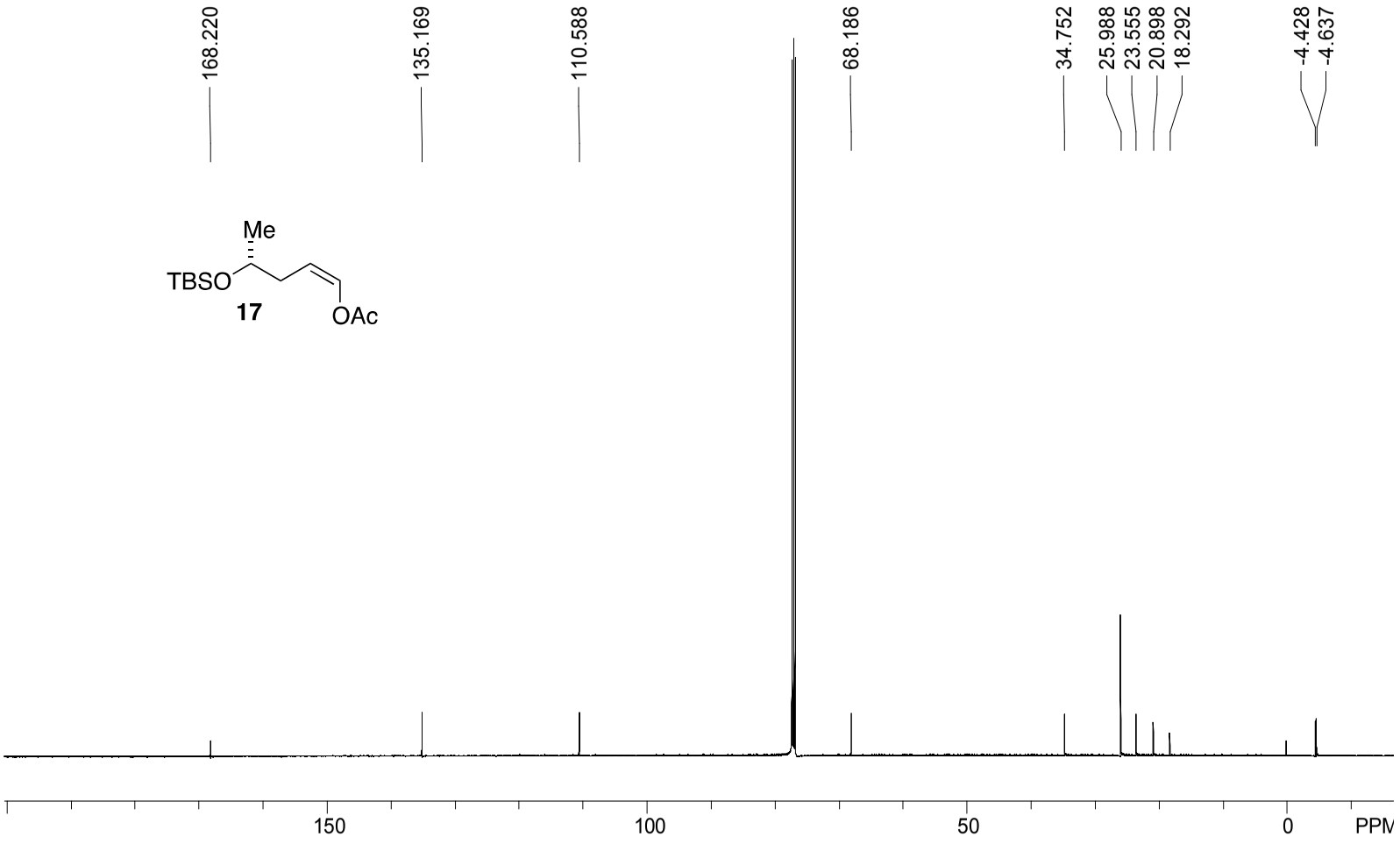
10

(-)-Pyrenophorol (**2**)

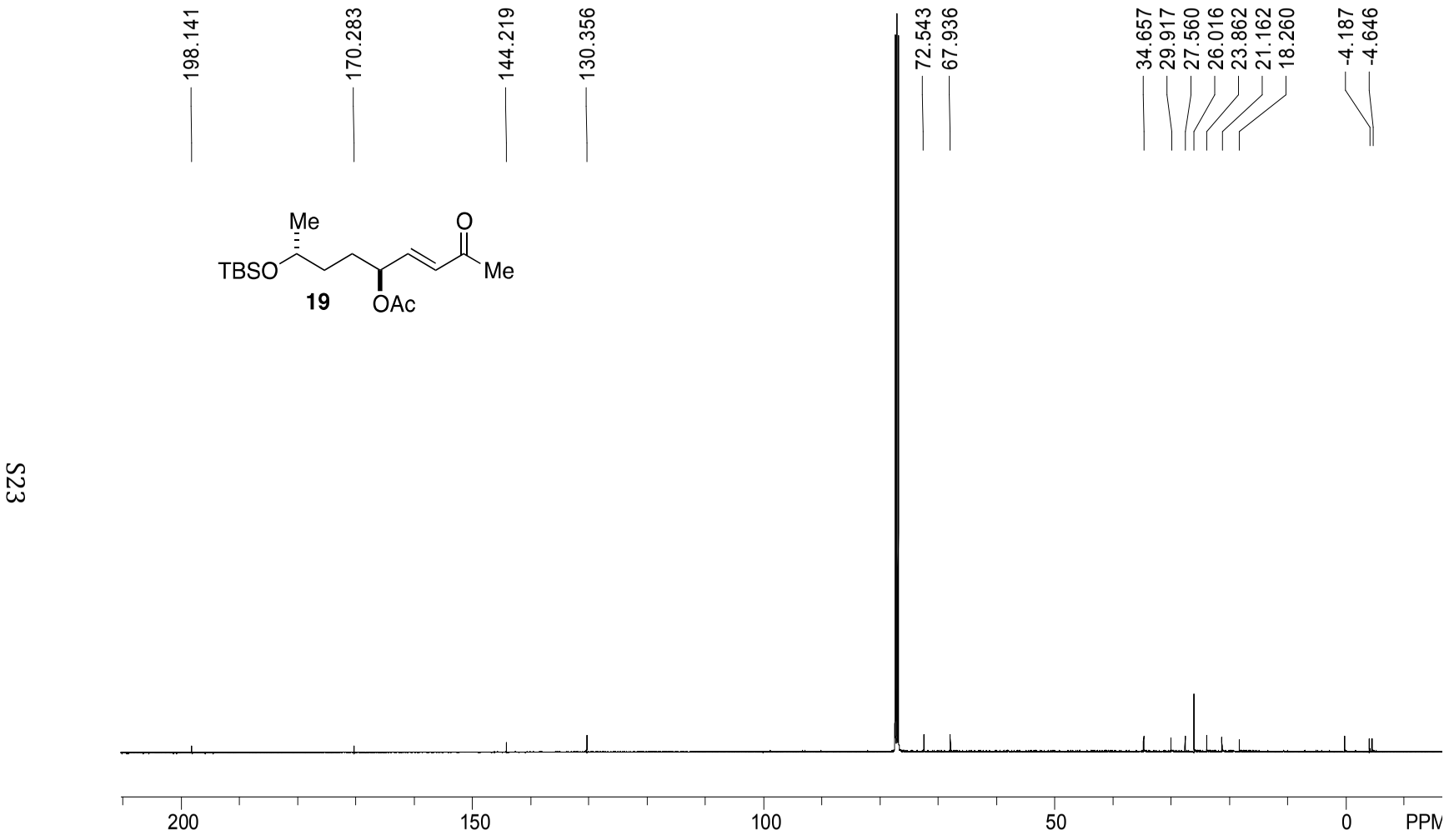


(-)-Pyrenophorol (**2**)

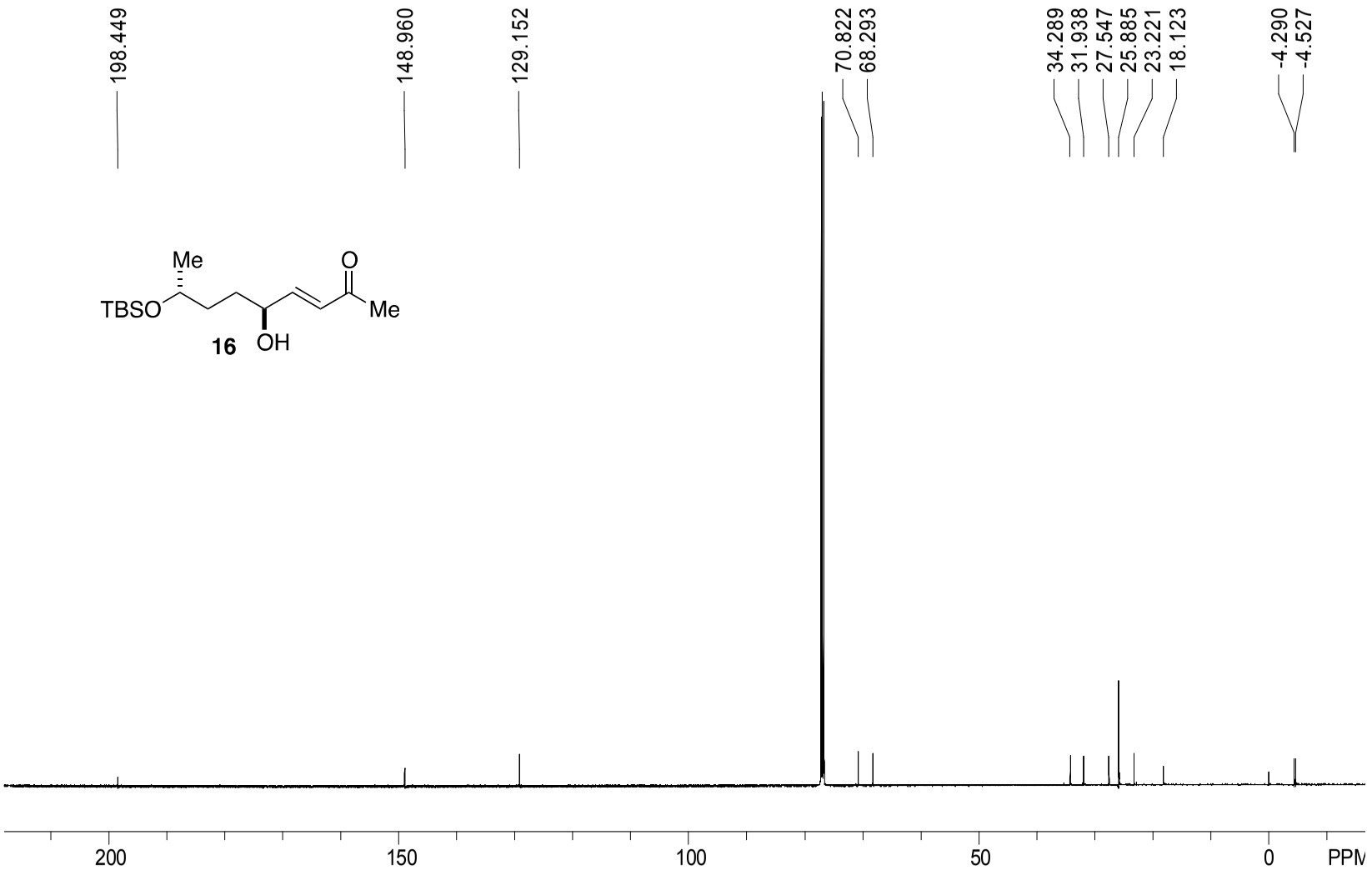

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2
3
4
5
6
7
8
6.13
9.43
3.14
2.06
3.05
1.00
0.98
0.97
0.058
0.054
0.888
1.131
1.143
2.141
2.220
2.334
3.816
3.829
3.841
3.853
3.865
3.877
4.909
4.924
4.937
4.953
7.064
7.064
7.064
7.077
7.077
7.077
Me
TBSO
OAc
17


168.220
135.169
110.588
68.186
34.752
25.988
23.555
20.898
18.292
-4.428
-4.637
Me
TBSO
17
OAc
150
100
50
0
PPM

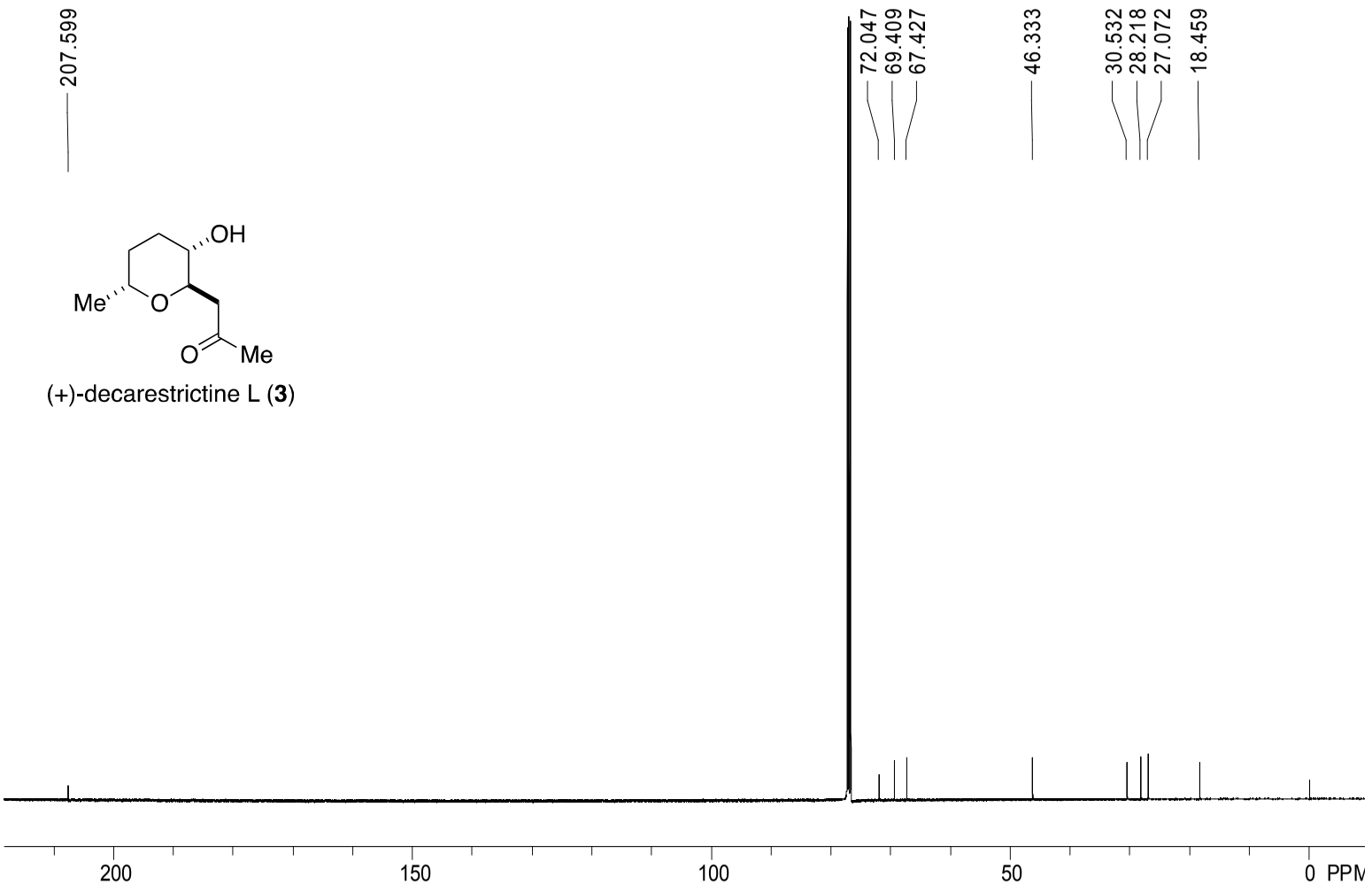
6.675
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6.642
6.632
6.186
6.184
6.154
6.151
5.436
5.425
5.414
5.400
3.844
3.832
3.819
3.809
3.797
3.784
2.275
2.106
1.825
1.751
1.733
1.662
1.489
1.396
1.130
1.117
0.883
0.050
0.042
6.09
9.41
3.05
2.11
1.02
1.05
2.99
2.94
1.00
0.98
0.96
0.98
TBSO
Me
OAc
Me
O
19
0
2
4
6
8
PPM


198.141
170.283
144.219
130.356
72.543
67.936
34.657
29.917
27.560
26.016
23.862
21.162
18.260
-4.187
-4.646
Me
O
TBSO
Me
19
OAc
200
150
100
50
0
PPM

6.785
6.776
6.753
6.744
6.320
6.317
6.288
6.285
4.379
4.332
3.934
3.876
2.691
2.681
2.278
1.822
1.754
1.697
1.626
1.607
1.535
1.171
1.158
0.902
0.080
0.074
6.23
9.81
3.13
1.90
1.49
1.07
3.13
0.91
0.98
1.00
1.00
1.05
O
Me
OH
16
Me
TBSO
PPM
0
2
4
6
8

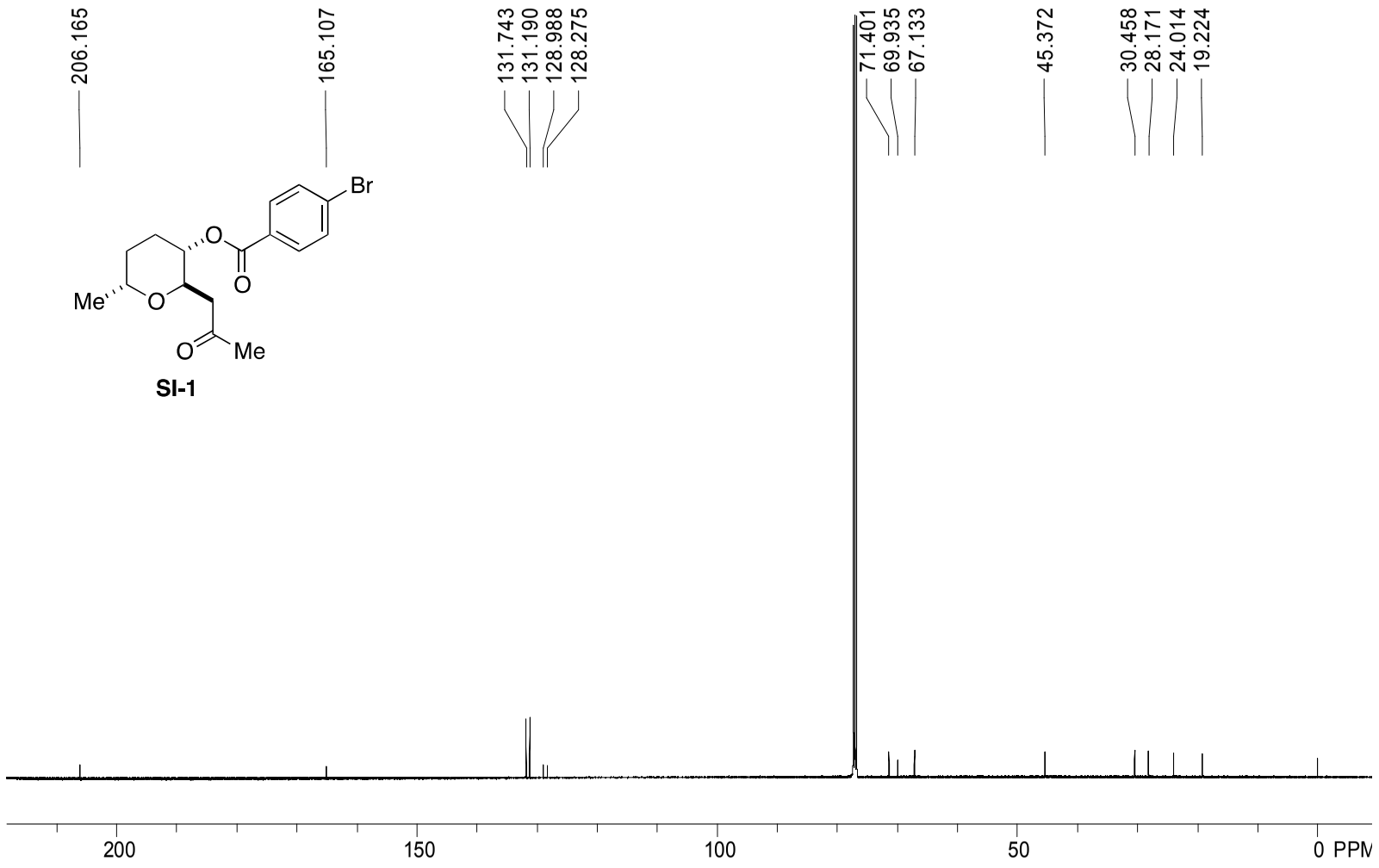

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148.960
129.152
70.822
68.293
34.289
31.938
27.547
25.885
23.221
18.123
-4.290
-4.527
Me
O
TBSO
Me
16
OH
200
150
100
50
0
PPM

(+)-decarestrictine L (3)
OH
O
Me
Me
O
PPM
0
2
4
6
8
3.15
1.18
2.10
1.06
1.02
3.03
2.04
1.00
1.00
1.01
4.041
4.028
4.015
4.002
3.980
3.923
3.439
3.390
2.743
2.730
2.004
2.212
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1.853
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1.676
1.595
1.546
1.229
1.216



(+)-decarestrictine L (**3**)

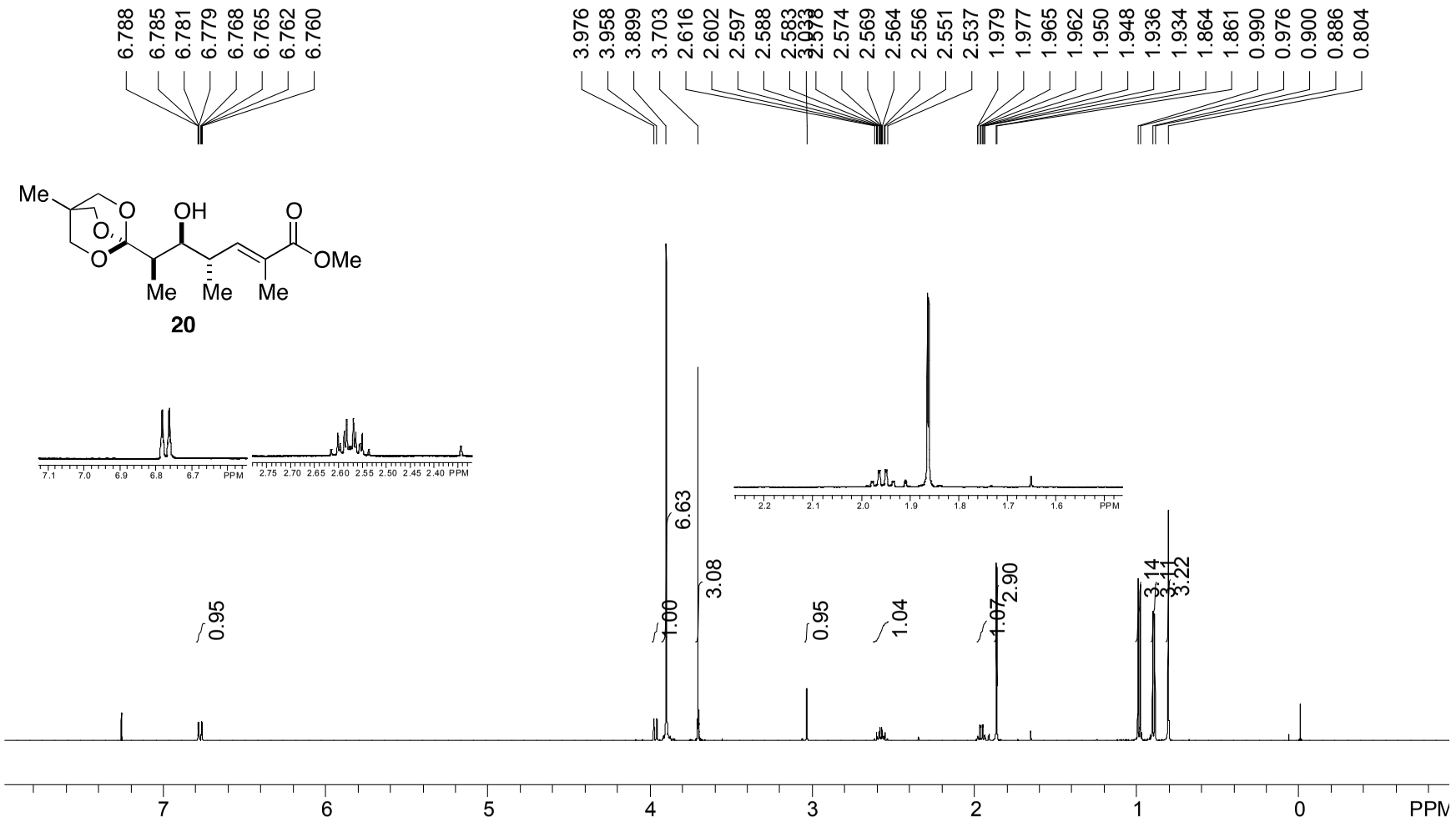
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7.600
7.583
4.838
4.826
4.825
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4.806
4.436
4.426
4.417
4.408
4.398
3.996
3.936
2.836
2.817
2.805
2.787
2.627
2.618
2.597
2.587
2.194
2.065
1.999
1.957
1.892
1.799
1.739
1.670
1.604
1.263
1.250
Br
O
O
O
Me
O
Me
SI-1
1.94
1.94
0.98
0.98
1.00
1.00
1.01
2.04
2.02
2.03
1.03
2.91
3.14
0
2
4
6
8
PPM


206.165
165.107
131.743
131.190
128.988
128.275
71.401
69.935
67.133
45.372
30.458
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SI-1

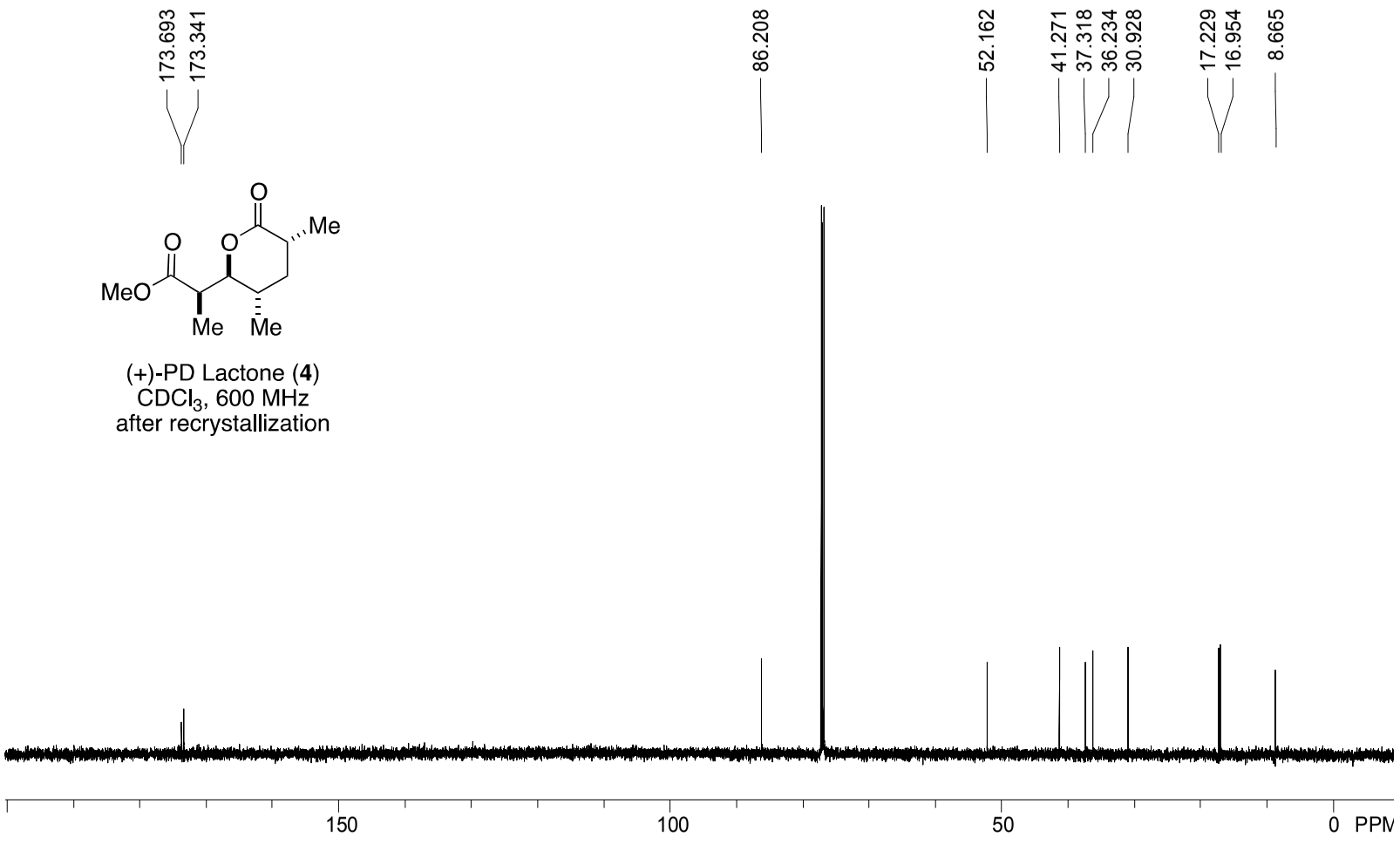
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5.099
5.070
5.068
5.067
5.065
5.047
5.045
5.043
5.042
5.026
5.025
5.023
5.021
3.915
3.854
3.835
3.063
2.270
2.256
2.241
2.224
2.208
2.195
1.985
1.983
1.971
1.969
1.957
1.955
1.943
1.940
0.995
0.981
0.923
0.909
0.815
Me
O
O
O
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1.04
1.00
0.95
3.02
PPM

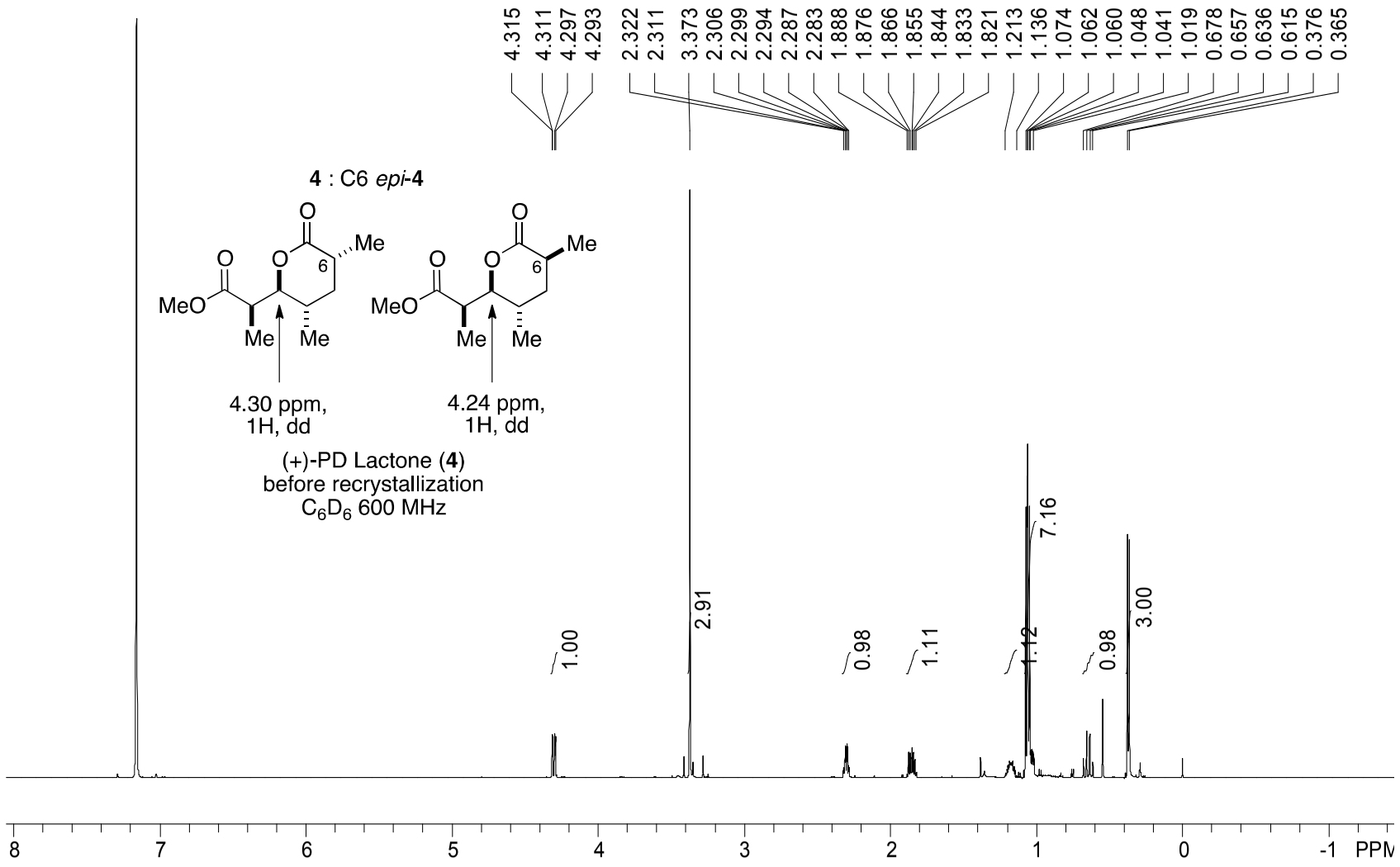
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30.538
40.838
41.017
72.851
73.393
76.800
77.226
77.644
110.892
114.096
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PPM
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100
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Me
O
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O
Me
OH
Me
21

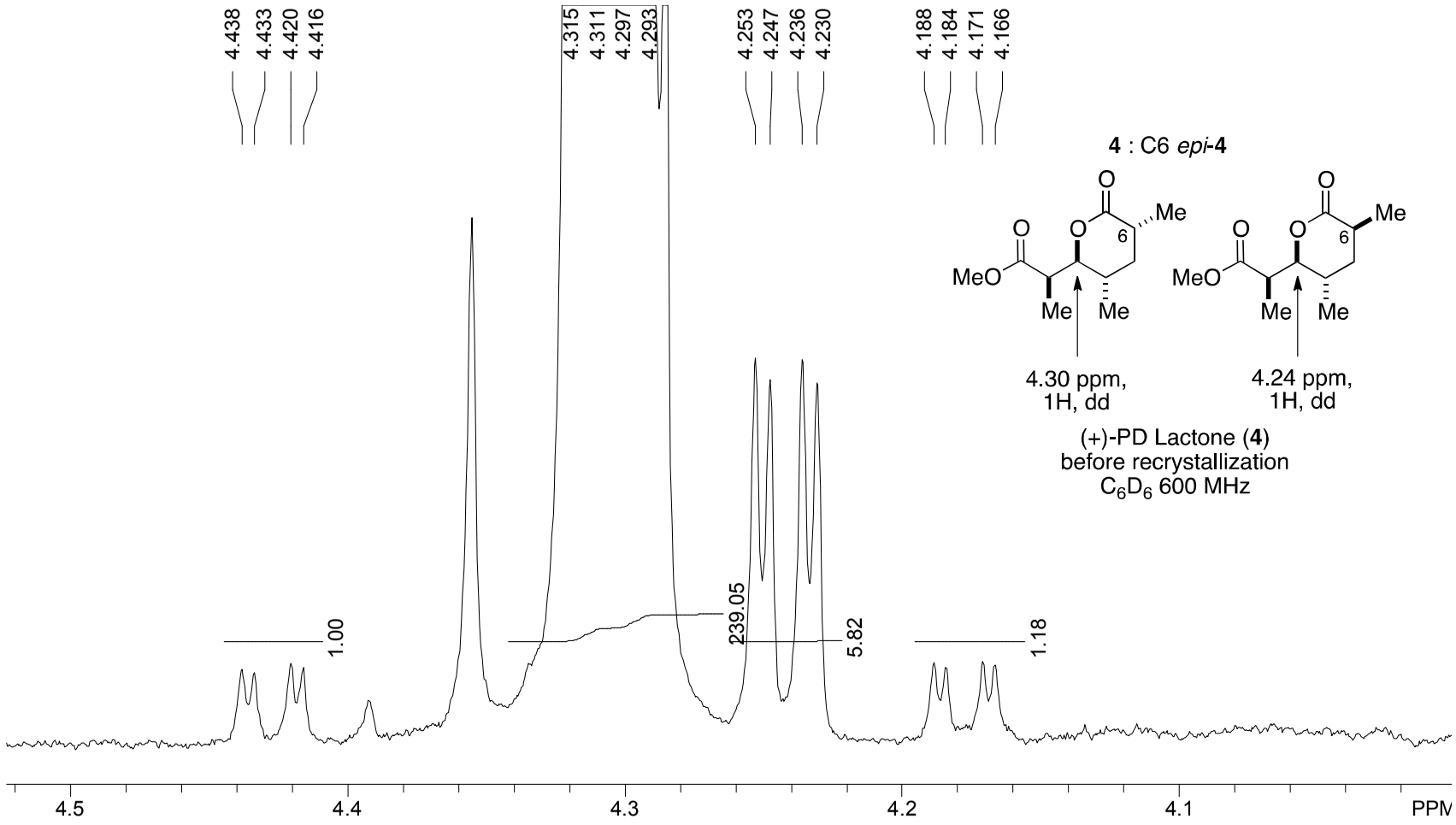

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6.785
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6.779
6.768
6.765
6.762
6.760
3.976
3.958
3.899
3.703
2.616
2.602
2.597
2.588
2.583
2.574
2.569
2.564
2.556
2.551
2.537
1.979
1.977
1.965
1.962
1.950
1.948
1.936
1.934
1.864
1.861
0.990
0.976
0.900
0.886
0.804
Me
O
OH
O
O
O
OMe
Me
Me
Me
20
0.95
1.00
6.63
3.08
0.95
1.04
1.07
2.90
3.14
3.11
3.22
PPM

168.718
146.230
127.171
110.540
77.251
76.996
76.741
73.518
72.612
51.574
40.589
36.266
30.303
16.015
14.385
12.656
6.250
PPM
0
20
40
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80
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120
140
160
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O
OH
Me
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Me
O
OMe
Me
20

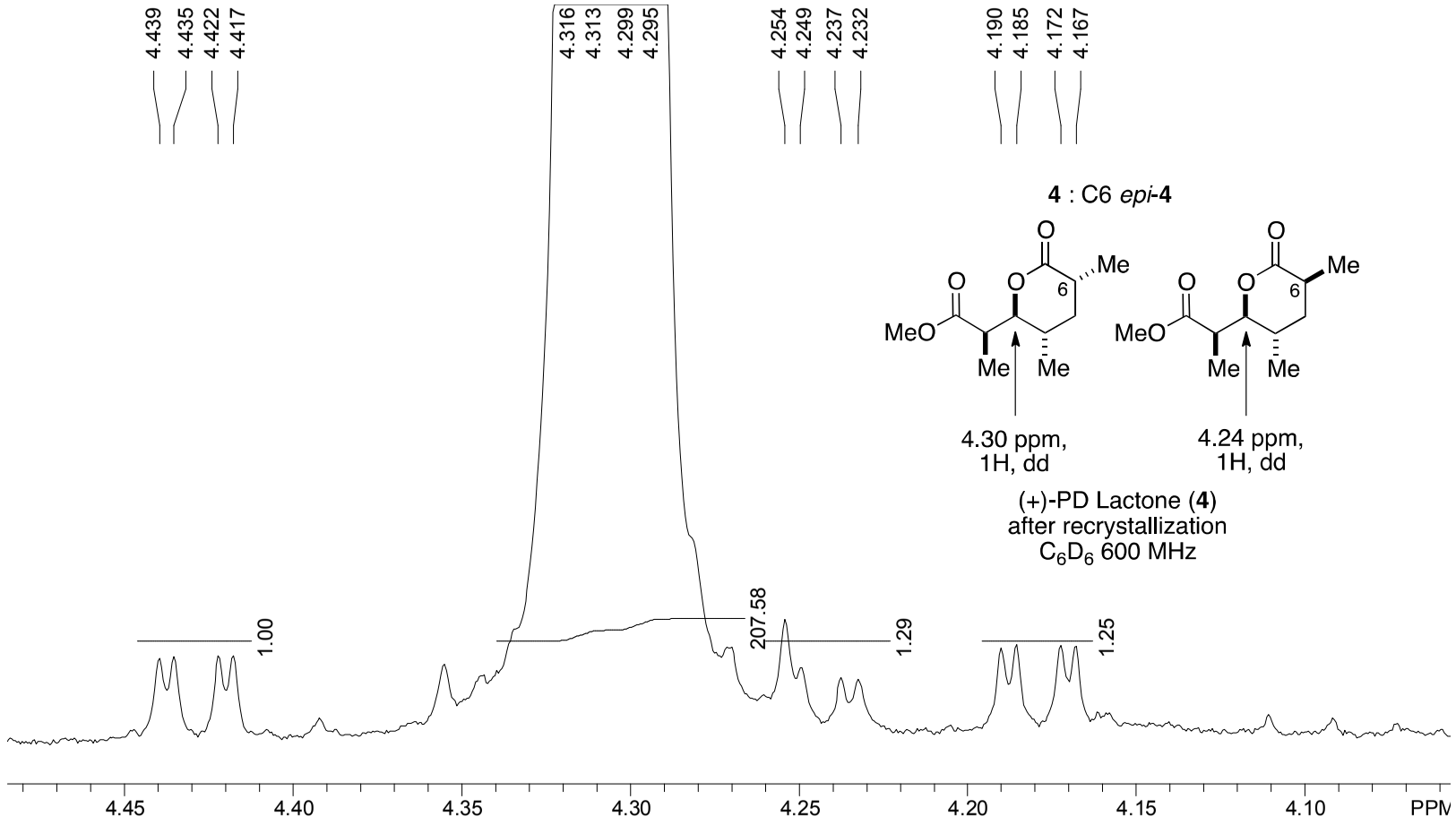
(+)-PD Lactone (4)
CDCl3, 600 MHz
after recrystallization
MeO
Me
Me
Me
4.555
4.550
4.537
4.533
2.747
2.743
3.732
2.735
2.731
2.723
2.719
2.711
2.707
2.537
2.525
2.514
2.505
2.493
2.482
2.471
1.972
1.866
1.454
1.433
1.412
1.391
1.290
1.278
1.207
1.196
1.011
1.000
1.00
2.98
1.00
0.99
1.99
0.98
3.00
3.02
3.02
PPM


173.693
173.341
86.208
52.162
41.271
37.318
36.234
30.928
17.229
16.954
8.665
O
O
O
Me
MeO
Me
Me
(+)-PD Lactone (4)
CDCl3, 600 MHz
after recrystallization
150
100
50
0 PPM


4.315
4.311
4.297
4.293
2.322
2.311
3.373
2.306
2.299
2.294
2.287
2.283
1.888
1.876
1.866
1.855
1.844
1.833
1.821
1.213
1.136
1.074
1.062
1.060
1.048
1.041
1.019
0.678
0.657
0.636
0.615
0.376
0.365
4 : C6 epi-4
MeO
Me
Me
Me
6
4.30 ppm,
1H, dd
4.24 ppm,
1H, dd
(+)-PD Lactone (4)
before recrystallization
C6D6 600 MHz
1.00
2.91
0.98
1.11
1.12
7.16
0.98
3.00
8
7
6
5
4
3
2
1
0
-1
PPM


4.438
4.433
4.420
4.416
4.315
4.311
4.297
4.293
4.253
4.247
4.236
4.230
4.188
4.184
4.171
4.166
1.00
239.05
5.82
1.18
4.5
4.4
4.3
4.2
4.1
PPM
4 : C6 epi-4
MeO
Me
Me
Me
4.30 ppm,
1H, dd
4.24 ppm,
1H, dd
(+)-PD Lactone (4)
before recrystallization
C6D6 600 MHz

4.316
4.313
4.299
4.295
2.325
2.320
2.313
3.374
2.309
2.301
2.297
2.289
2.285
1.891
1.880
1.869
1.858
1.847
1.836
1.825
1.215
1.140
1.075
1.063
1.061
1.050
1.038
1.032
1.028
1.022
0.681
0.659
0.639
0.618
0.329
2.99
1.00
1.00
1.00
7.02
2.98
1.16
PPM
0
1
2
3
4
5
6
7
(+)-PD Lactone (4)
after recrystallization
C6D6 600 MHz
4.30 ppm,
1H, dd
4.24 ppm,
1H, dd
4 : C6 epi-4
MeO
Me
Me
Me
Me
Me
Me
MeO
Me
Me
Me
Me
Me
Me



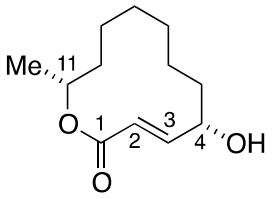
4 : C6 *epi*-**4**

4.30 ppm,
1H, dd

4.24 ppm,
1H, dd

(+)-PD Lactone (**4**)
after recrystallization
C_6D_6 600 MHz

HPLC or SFC data



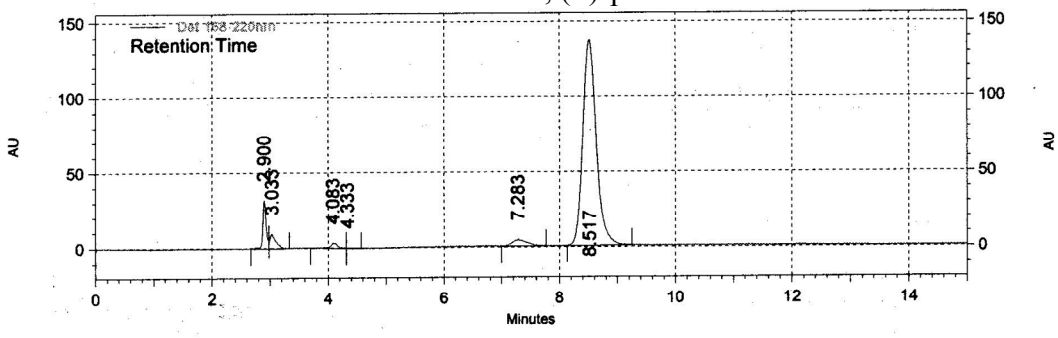
(+)-patulolide C (**1**)

SFC data for (+)-patulolide C (**1**)

Area % Report

Data File: D:\32Karat\Projects\Rob\Data\RR8282 pat C 410-10-2011 1-34-06 PMRR8280 5% ipa .met
Method: D:\32Karat\Projects\Rob\Method\RR8280 5% ipa data extraction.met
Acquired: 10/10/2011 1:35:30 PM
Printed: 12/9/2011 10:00:24 AM

minor diast. = 7.283, (+)-patulolide C = 8.517



Det 168-220nm
Results

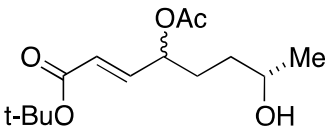
Time	Area	Area %	Height	Height %
2.900	127158	5.07	32054	17.13
3.033	67315	2.68	9611	5.14
4.083	31564	1.26	3354	1.79
4.333	3548	0.14	572	0.31
7.283	78193	3.11	4276	2.29
8.517	2202629	87.74	137259	73.35
Totals	2510407	100.00	187126	100.00

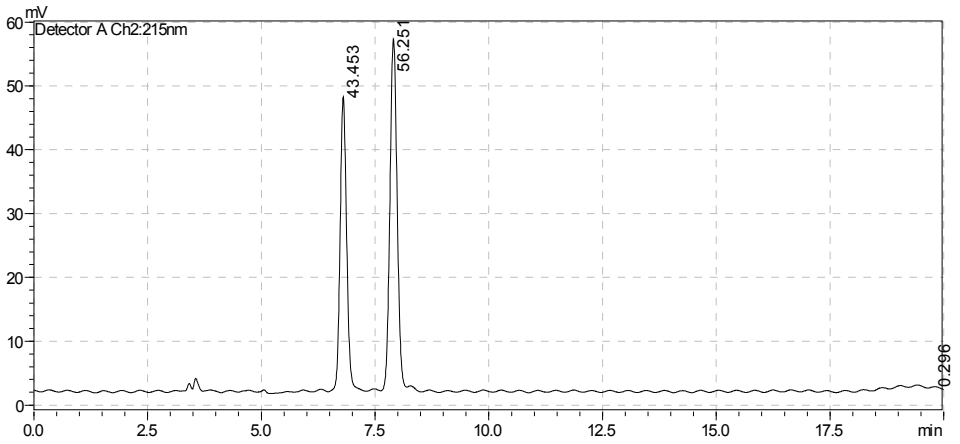
HPLC data for (-)-Pyrenophorol (2)

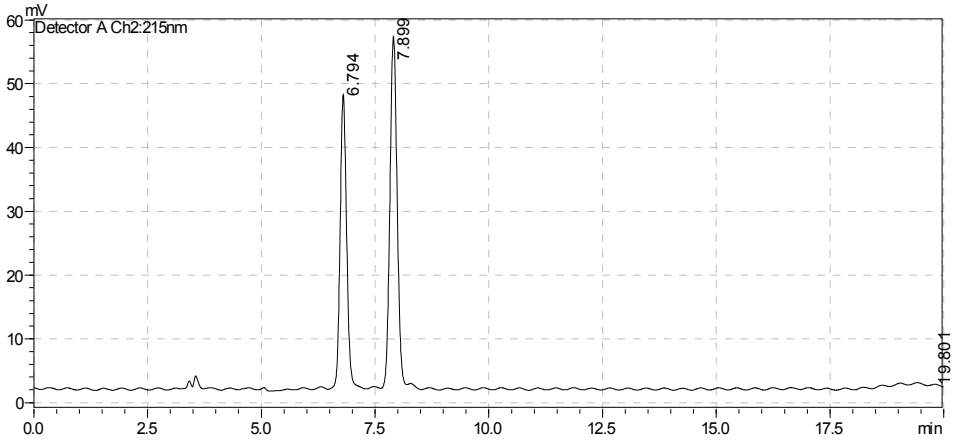
The following HPLC data was obtained on the AHF/Wittig product following desilylation ($AcOH/H_2O/THF$) to measure the diastereoselectivity of the AHF and to determine if any erosion of the newly formed stereocenter occurred during any of the following reactions.

HPLC 5% isopropanol/hexane Chiracel OJ-H

Racemic AHF/Wittig for pyrenophorol

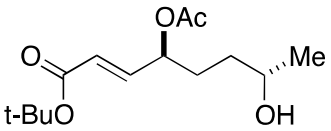


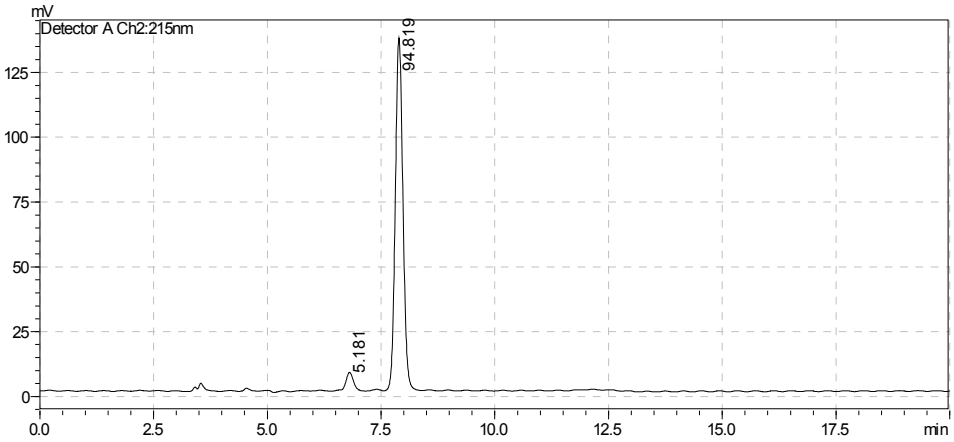


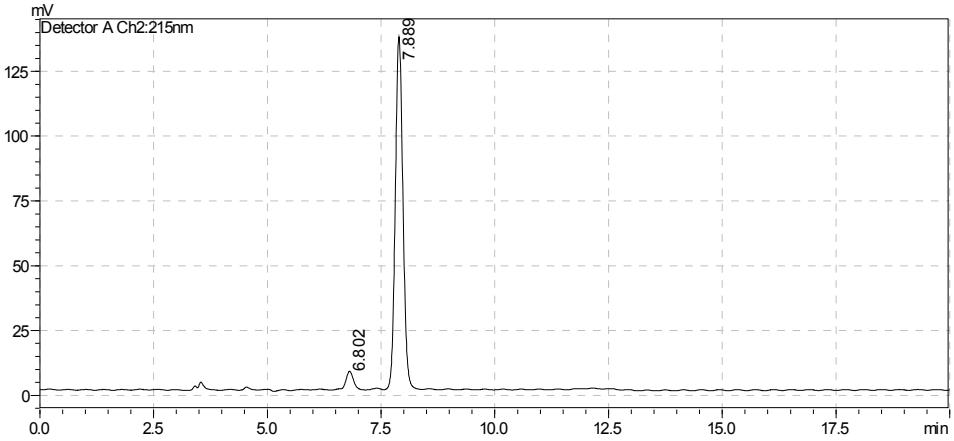


AHF/ Wittig with (*S,S,S*)-BDP

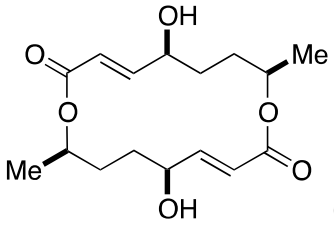
HPLC 5% isopropanol/hexane Chiracel OJ-H



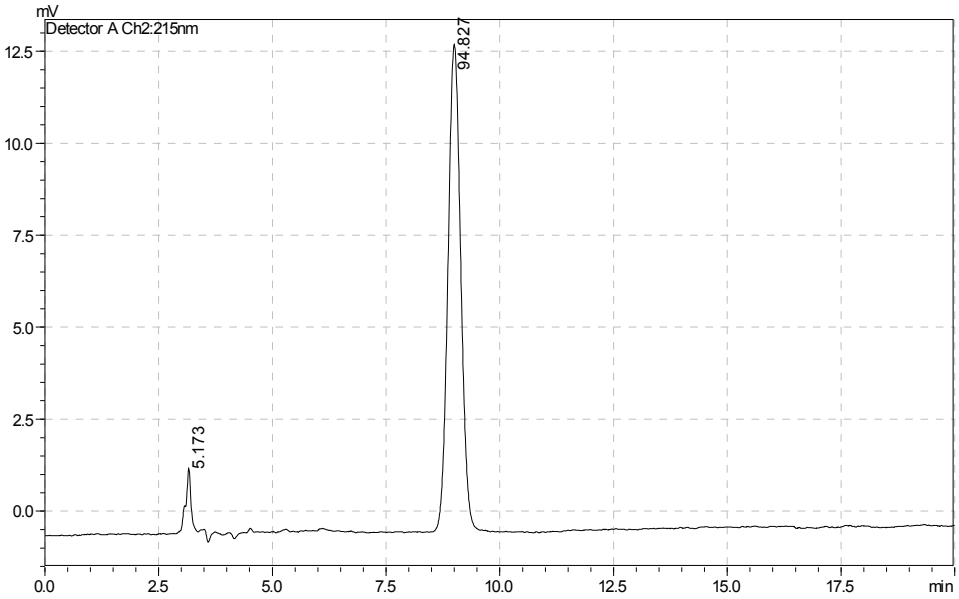


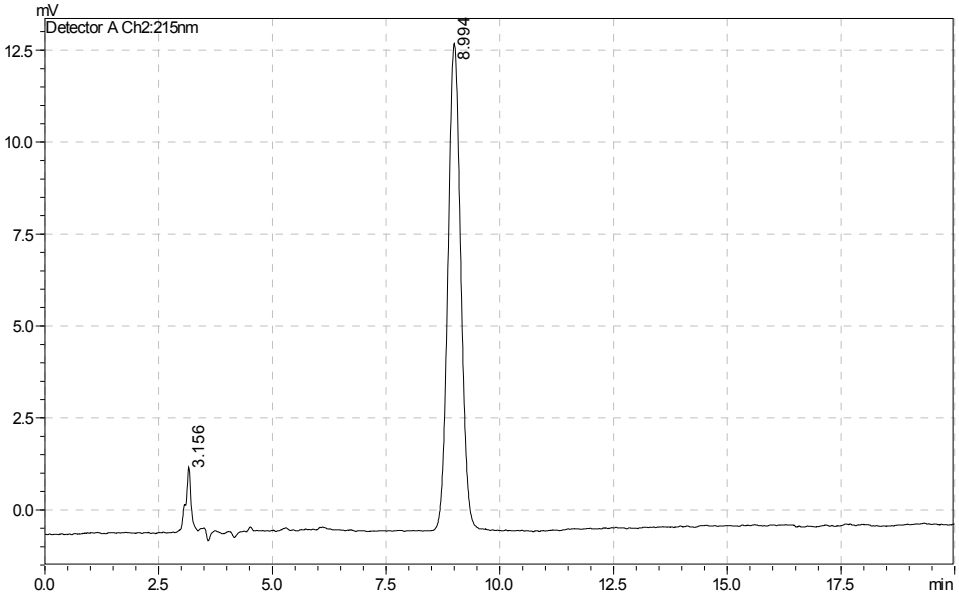


(-)-pyrenophorol (**2**)

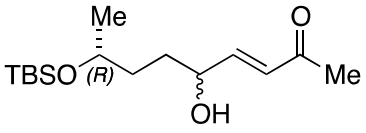


Chiracel OJ-H 20% isopropanol/hexane



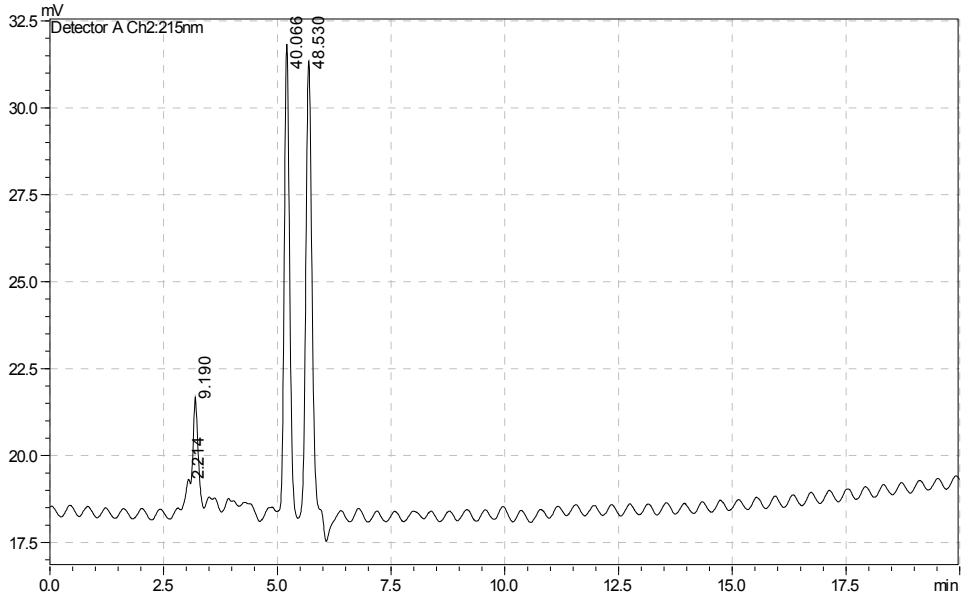


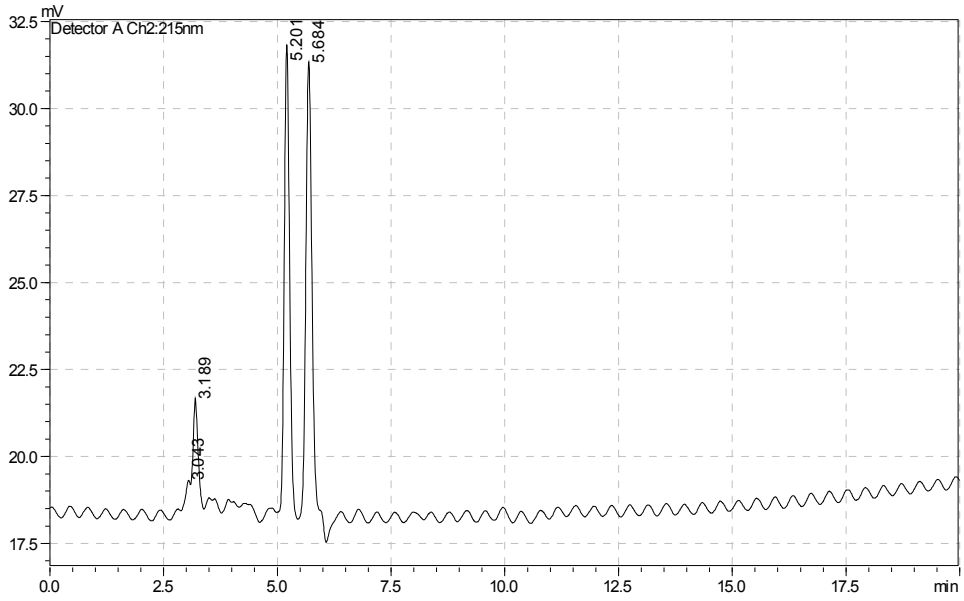
HPLC data for ketone 16

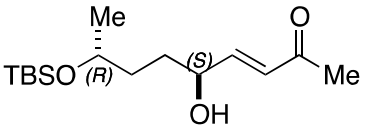


racemic AHF/ Wittig

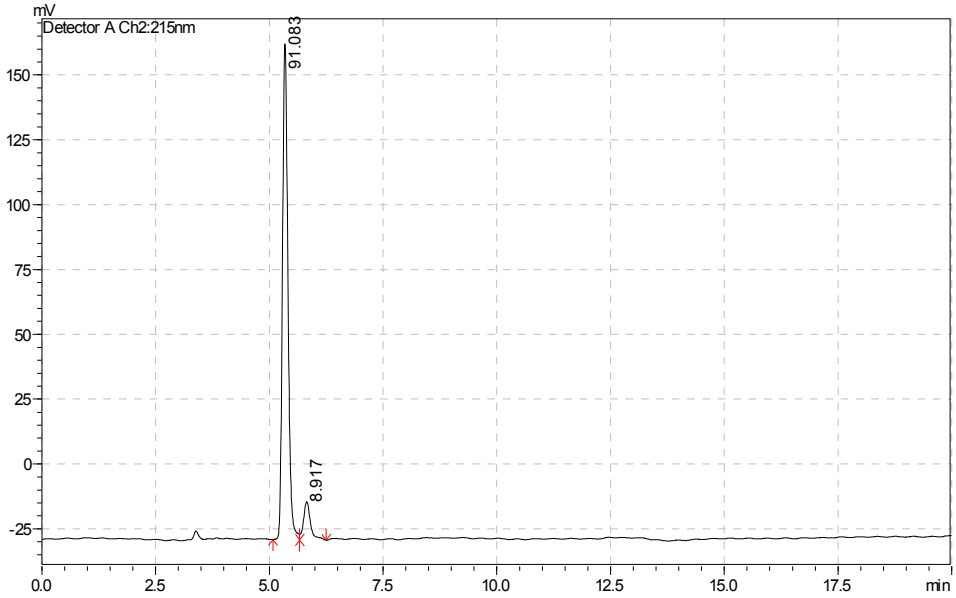
5 % isopropanol: hexane Chiracel AJ-H

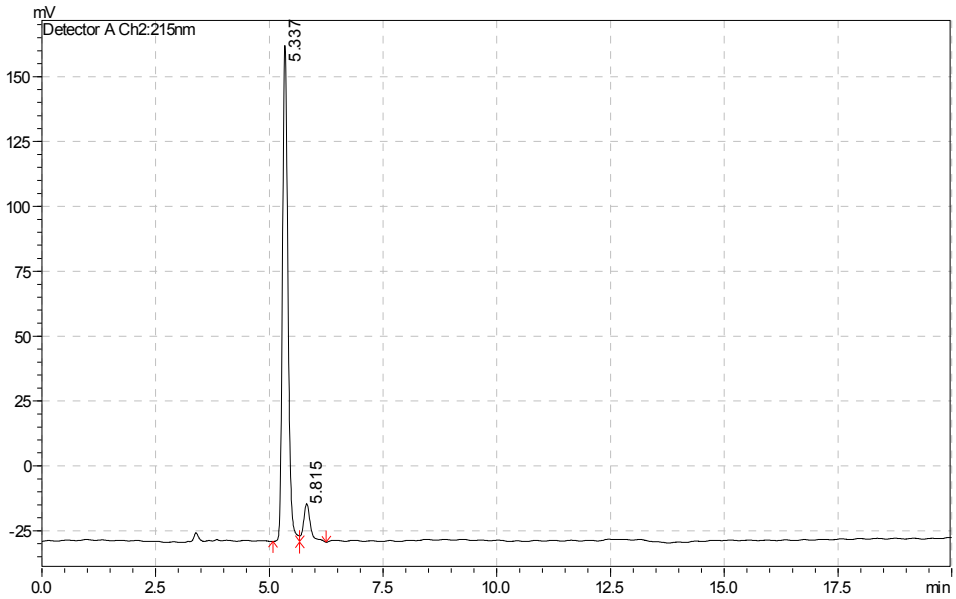





Me
O
TBSO
(R)
(S)
Me
OH

16

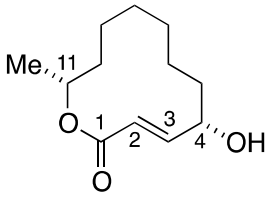

mV
Detector A Ch2:215nm
91.083
8.917
150
125
100
75
50
25
0
-25
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
min


mV
Detector A Ch2:215nm
5.337
5.815
150
125
100
75
50
25
0
-25
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
min

NMR Comparison Tables

NMR data for (+)-patulolide C (1)

Ref.[12] ^{1}H-NMR 90 MHz	Synthetic ^{1}H-NMR 500MHz	Δδ	Ref.[25] ^{13}C-NMR 100MHz	Synthetic ^{13}C-NMR 125MHz	Δδ
0.93-2.03ppm, 12H, m	1.0-1.81ppm, 12H, m	0.07	168.1	168.1	0
1.32ppm, 3H, d,J=6.6Hz	1.29ppm,3H, d,J=7Hz	0.03	121.5	121.5	0
4.33-4.58ppm, 1H, m	4.51ppm, 1H,m	0.05	149.7	149.6	0.1
4.85-5.23ppm, 1H, m	5.08ppm,1H,m	0.04	70.9	70.9	0
6.07ppm, 1H, d,J=16.5Hz	6.10ppm, 1H,dd, J=16,1Hz	0.03	35.9	35.9	0
6.82ppm, 1H, dd,J=16.5, 6.3Hz	6.85ppm, 1H,dd, J=16,7Hz	0.03	20.7	20.7	0
			28.3	28.3	0
			27.8	27.8	0
			22.2	22.1	0.1
			32.8	32.8	0
			73.2	73.1	0.1
			19.3	19.3	0

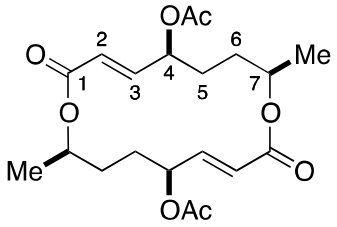


(+)-patulolide C (**1**)

NMR data for diacetylpyrenophorol 10

^{1}H Assignment (#H)	Synthetic δ (ppm)/ J (Hz)	Ref.[84] δ (ppm)/J (Hz)	$\Delta\delta=\delta_{exp}-\delta_{ref}$
C_1 ,C_1' (0)	x	x	x
C_2,C_2' (2)	5.97, d/ 15.6	5.98, dd/ 15.7, 0.7	0.01
C_3,C_3' (2)	6.79, dd/ 15.6, 6.9	6.77, dd/ 15.7, 6.7	0.02
C_4,C_4' (2)	5.23, m	5.22, m	0.01
C_5,C_5' (4)	1.86, m	1.86, m	0
C_6,C_6' (4)	1.62, m & 1.74, m	1.62, m & 1.74, m	0
C_7,C_7' (2)	5.10, m	5.09, m	0.01
C_{Me},C_{Me}' (6)	1.26, d/ 6.3	1.26, d/ 6.5	0
C_{OAc},C_{OAc}' (6)	2.09, s	2.08, s	0.01

^{13}C Assignment	Synthetic δ (ppm)/ J (Hz)	Ref.[84] δ (ppm)/J (Hz)	$\Delta\delta=\delta_{exp}-\delta_{ref}$
C_1	164.8	164.7	0.1
C_2	124.2	124.1	0.1
C_3	143.7	143.7	0
C_4	72.1	72.0	0.1
C_5	27.8	27.9	0.1
C_6	28.7	28.8	0.1
C_7	69.8	69.8	0
C_{Me}	18.5	18.5	0
C_{OAc}	169.8	169.7	0.1
C_{OAc}	21.1	21.0	0.1

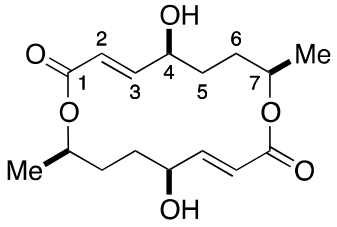


diacetylpyrenophorol **10**

NMR data for pyrenophorol 2

^{1}H Assignment (#H)	Synthetic δ (ppm)/ J (Hz)	Ref.[36] δ (ppm)/J (Hz)	Ref.[84] δ (ppm)/J (Hz)	$\Delta\delta=\delta_{exp}-\delta_{ref}$ (Ref[36]/Ref[84])
C_1 ,C_1' (0)	x	x	x	x
C_2,C_2' (1)	5.99, dd/ 15.7, 1.4	5.97, dd/ 15.7, 1.7	5.98, dd/15.3, 1.5	0.02/0.01
C_3,C_3' (1)	6.92, dd/ 15.8,5.2	6.89, dd/ 15.7, 5.5	6.90, dd/15.3, 5.0	0.03/0.02
C_4,C_4' (1)	4.32, m	4.29, m	4.30, m	0.02/0.01
C_5,C_5' (2)	1.92, m	1.88, m	1.84, m & 1.91, m	0.04/0.01
C_6,C_6' (2)	1.74, m	1.69, m	1.65, m & 1.74, m	0.05/0
C_7,C_7' (1)	5.16, m	5.12, m	5.13, m	0.04/0.03
C_{Me},C_{Me}' (3)	1.29, d/ 6.6	1.27, d/ 6.5	1.28, d/6.5	0.02/0.01

^{13}C Assignment	Synthetic δ (ppm)/ J (Hz)	Ref.[36] δ (ppm)/J (Hz)	Ref.[84] δ (ppm)/J (Hz)	$\Delta\delta=\delta_{exp}-\delta_{ref}$ (Ref[36]/Ref[84])
C_1	164.9	164.9	165.0	0/0.1
C_2	122.1	122.1	122.2	0/0.1
C_3	149.5	149.5	149.4	0/0.1
C_4	70.4	70.4	69.8	0/0.6
C_5	30.5	30.4	30.5	0.1/0
C_6	29.0	28.9	29.0	0.1/0
C_7	69.8	69.7	70.4	0.1/0.6
C_{Me}	18.2	18.1	18.3	0.1/0.1

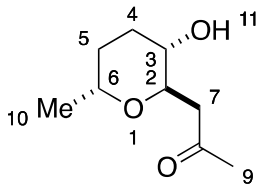


(-)-Pyrenophorol (**2**)

NMR data for decarestrictine L 3

^{1}H Assignment (#H)	Synthetic δ (ppm)/ J (Hz)	Ref.[52] δ (ppm)/J (Hz)	$\Delta\delta=\delta_{exp}-\delta_{ref}$
C_2 (1)	4.02/ q 6.4	4.01/ ddd 6.6, 8.2, 4.9	0.01
C_3 (1)	3.41/ m	3.39/ m	0.02
C_4 (2)	1.56/ m; 1.72/ m	1.58/ m; 1.72/m	0.02
C_5 (2)	1.72/ m; 1.88/ m	1.73/ m; 1.87/ m	0.01
C_6 (1)	3.95/ m	3.95/ qdd 4.3, 4.3, 6.6	0
C_7 (2)	2.74/ d	2.69/ 8.2 -15.5; 2.76/ -15.5, 4.9	0.05
C_9 (3)	2.21/ s	2.21/ s	0
C_{Me} (3)	1.22/ d 6.6	1.22/ d 6.6	0
C_{OH} (1)	2.00/ d 6.6	x	X

^{13}C Assignment	Synthetic δ (ppm)/ J (Hz)	Ref.[52] δ (ppm)/J (Hz)	$\Delta\delta=\delta_{exp}-\delta_{ref}$
C_2	72.0	72.0	0
C_3	69.4	69.1	0.3
C_4	28.2	28.2	0
C_5	27.1	26.9	0.2
C_6	67.4	67.4	0
C_7	46.3	46.2	0.1
C_8	207.6	207.9	0.3
C_9	30.5	30.5	0
C_{Me}	18.5	18.1	0.3



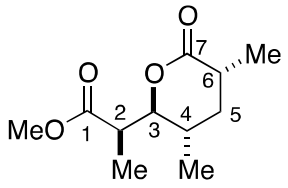
(+)-Decarestrictine L (**3**)

^{1}H NMR Data Comparison Table for (+)-PD Lactone 4

Carbon	Ref.[82] (200 MHz)	Synthetic (600 MHz)	Δδ	Ref.[82] mult/J(Hz)	Synth. mult/J(Hz)
MeO	3.73	3.73	0.00	s/none	s/none
C1	-	-	-	-	-
C2	2.73	2.73	0.00	qd/7.1,2.6	qd/7.1,2.6
C3	4.54	4.54	0.00	dd/2.6,10.4	dd/2.9,10.5
C4	1.80-2.05	1.86-1.97	-	-	-
C5(eq)	1.80-2.05	1.86-1.97	-	-	-
C5(ax)	1.45	1.42	0.03	dd/12.0,12.0	dt/12.1, 13.1(ap. q)
C6	2.49	2.50	-0.01	ddq/12.0,6.0,7.1	ddq/13.6,7.0,7.0 (ap. sept)
C7	-	-	-	-	-
C2-Me	1.20	1.20	0.00	d/7.1	d/7.0
C4-Me	1.00	1.01	-0.01	d/6.4	d/6.5
C6-Me	1.29	1.29	0.00	d/7.1	d/6.8

^{13}C NMR Data Comparison Table for (+)-PD Lactone 4

Carbon	Ref.[82]	Synthetic	Δδ
1	173.6	173.7	-0.1
2	173.3	173.3	0.0
3	86.2	86.2	0.0
4	52.2	52.2	0.0
5	41.4	41.3	0.1
6	37.4	37.3	0.1
7	36.3	36.2	0.1
8	31.0	30.9	0.1
9	17.3	17.2	0.1
10	17.0	17.0	0.0
11	8.8	8.7	0.1



(+)-Prelog-Djerassi lactone (**4**)

MOLECULAR STRUCTURE LABORATORY

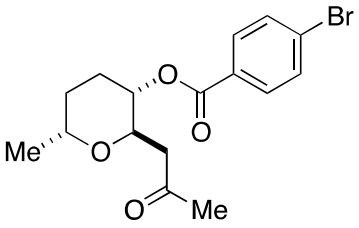
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2124 Chemistry Department
1101 University Ave
Madison, WI 53706

☎ 608-263-4694
Fax 608-262-0381

E-mail: iguzei@chem.wisc.edu

Structural report on **SI-1**



SI-1

MARCH 18, 2013

Crystallographic Experimental Section

Data Collection

A colorless crystal with approximate dimensions 0.395 × 0.041 × 0.04 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 30 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 9917 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.70 Å. A total of 35047 data were harvested by collecting 5 sets of frames with 0.5º scans in ω and φ with exposure times of 90 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [6]

Structure Solution and Refinement

The systematic absences in the diffraction data and the *E*-statistics were consistent for the space groups *C*2 and *C*m. Only the chiral space group *C*2 was consistent with the proposed structure. It was chosen for the refinement and yielded chemically reasonable and computationally stable results of refinement [7-9].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic

displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

There are two chemically equivalent molecules with the same handedness but slightly different conformations in the asymmetric unit. The molecules can be superimposed with a rms of 0.214 Å. The absolute configuration was unequivocally established by anomalous dispersion as C8(S), C11(R), C13(R).

The final least-squares refinement of 384 parameters against 8541 data resulted in residuals R (based on F^2 for $I \geq 2\sigma$) and wR (based on F^2 for all data) of 0.0305 and 0.0616, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{16}H_{19}O_4Br$ (M =355.22): monoclinic, space group C2 (no. 5), a = 28.650(11) Å, b = 4.9547(18) Å, c = 22.409(8) Å, β = 97.901(13)°, V = 3151(2) Å^3, Z = 8, T = 100.0 K, μ(Mo Kα) = 2.622 mm^{-1}, *Dcalc* = 1.498 g/mm^3, 35047 reflections measured ($2.87 \leq 2\Theta \leq 58.572$), 8541 unique ($R_{int}$ = 0.0430) which were used in all calculations. The final R_1 was 0.0305 ($I > 2\sigma(I)$) and wR_2 was 0.0616 (all data).

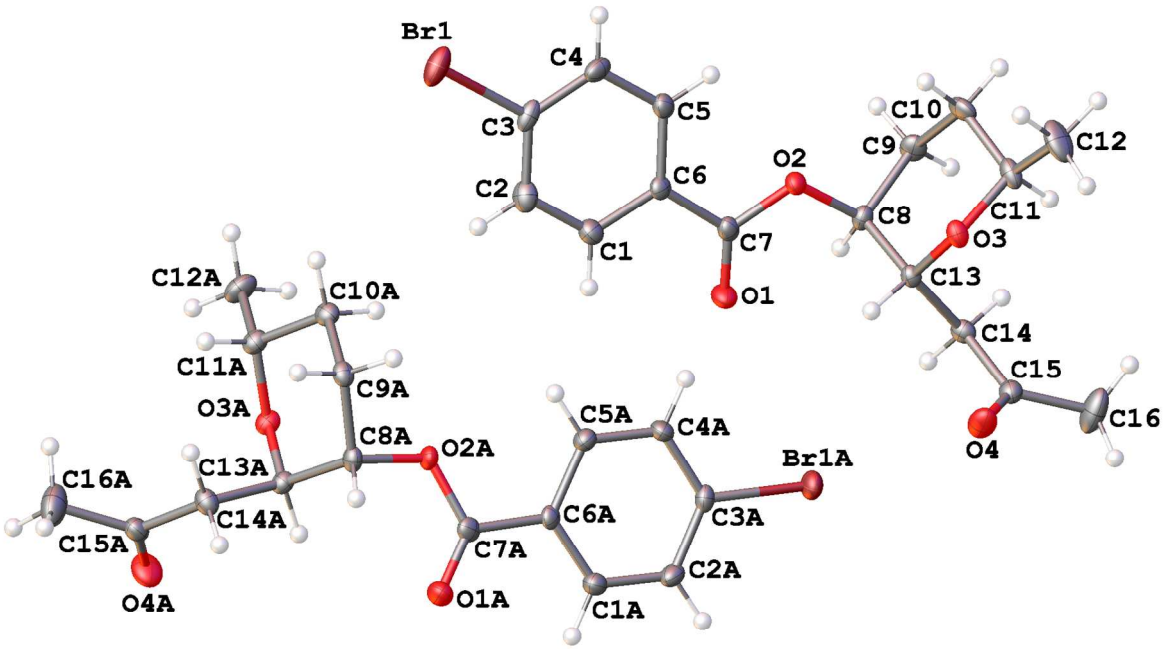


Figure 1. A molecular drawing of SI-1 shown with 50% probability ellipsoids.

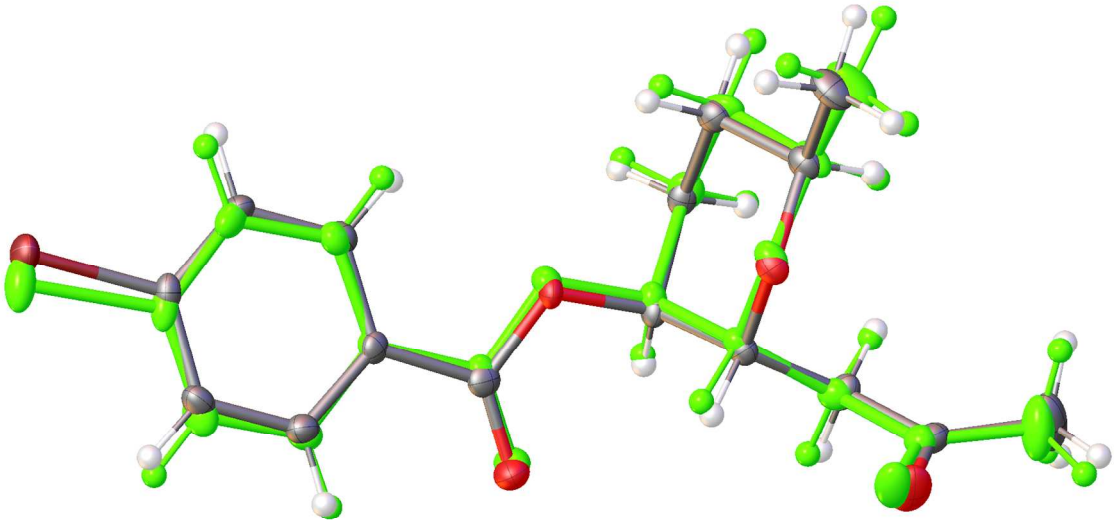


Figure 2. The two molecules of SI-1 superimposed. Shown with 50% probability ellipsoids.

Table 1 Crystal data and structure refinement for SI-1

Identification code	SI-1
Empirical formula	$C_{16}H_{19}O_4Br$
Formula weight	355.22
Temperature/K	100.0
Crystal system	monoclinic
Space group	C2
a/Å	28.650(11)
b/Å	4.9547(18)
c/Å	22.409(8)
α/°	90
β/°	97.901(13)
γ/°	90
Volume/Å^3	3151(2)
Z	8
ρ_{calc}mg/mm^3	1.498
m/mm^{-1}	2.622
F(000)	1456.0
Crystal size/mm^3	0.395 × 0.041 × 0.04
2Θ range for data collection	2.87 to 58.572°
Index ranges	-38 ≤ h ≤ 38, -6 ≤ k ≤ 6, -30 ≤ l ≤ 30
Reflections collected	35047
Independent reflections	8541[R(int) = 0.0430]
Data/restraints/parameters	8541/1/384
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0595
Final R indexes [all data]	R_1 = 0.0379, wR_2 = 0.0616
Largest diff. peak/hole / e Å^{-3}	0.49/-0.32
Flack parameter	0.004(6)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Burke25. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Br1	2116.2(2)	9856.8(6)	9542.8(2)	29.20(9)
O1	1968.0(7)	124(5)	7354.5(10)	24.1(5)
O2	1203.4(7)	493(4)	7472.5(9)	16.3(4)
O3	650.4(7)	791(4)	6229.7(9)	16.4(4)

O4	1278.4(8)	-201(6)	5200.5(10)	29.6(5)
C1	2203.9(10)	4375(6)	8176.5(14)	20.3(7)
C2	2309.6(12)	6333(6)	8612.1(15)	23.5(7)
C3	1964.1(10)	7207(6)	8935.2(13)	18.8(6)
C4	1509.9(11)	6201(7)	8825.5(13)	20.6(7)
C5	1403.9(10)	4226(6)	8389.1(13)	18.3(7)
C6	1752.7(10)	3290(6)	8062.1(13)	15.4(6)
C7	1663.3(10)	1166(6)	7595.6(13)	17.2(6)
C8	1096.9(10)	-1757(6)	7055.2(13)	16.4(6)
C9	639(1)	-2992(6)	7191.7(14)	20.4(7)
C10	216.9(10)	-1208(7)	6966.9(15)	21.9(7)
C11	216.3(10)	-533(6)	6308.4(14)	19.8(6)
C12	-176.6(11)	1362(7)	6056.8(19)	34.8(9)
C13	1066.6(9)	-772(5)	6403.2(13)	13.4(6)
C14	1108(1)	-3143(6)	5979.9(13)	16.9(6)
C15	1093.3(9)	-2268(7)	5332.0(13)	18.2(6)
C16	839.8(15)	-4091(8)	4866.8(17)	38.2(10)
Br1A	2207.3(2)	2581.1(6)	5710.8(2)	23.12(8)
O1A	4059.3(8)	10852(5)	6808(1)	25.1(5)
O2A	3593.8(7)	11098(4)	7539.1(9)	17.2(4)
O3A	4207.4(7)	10562(4)	8716.3(9)	16.3(4)
O4A	5295.2(8)	11222(5)	8649.0(12)	32.6(6)
C1A	3438(1)	6865(6)	6210.5(13)	19.0(6)
C2A	3104.7(10)	5112(7)	5914.9(13)	19.9(6)
C3A	2676.1(10)	4848(7)	6124.2(12)	17.0(5)
C4A	2572.6(10)	6273(6)	6620.7(14)	18.5(6)
C5A	2906.3(10)	8001(6)	6915.7(13)	17.6(6)
C6A	3344.9(10)	8308(6)	6711.3(13)	14.9(6)
C7A	3706.6(10)	10184(6)	7007.2(13)	17.2(6)
C8A	3880(1)	13253(6)	7837.6(13)	16.3(6)
C9A	3557.7(10)	14686(7)	8222.0(13)	16.6(6)
C10A	3462.3(9)	12869(6)	8743.8(13)	17.5(6)
C11A	3921.4(10)	11928(6)	9102.7(13)	17.7(6)
C12A	3847.6(12)	9930(8)	9595.0(13)	26.8(7)
C13A	4320.6(9)	12118(6)	8214.6(12)	15.3(6)
C14A	4670.6(10)	14383(6)	8415.4(14)	18.4(6)
C15A	5124.5(10)	13345(6)	8769.1(14)	19.8(7)
C16A	5356.7(13)	15146(9)	9255.8(17)	39.1(9)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for SI-1.
The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	46.5(2)	18.13(15)	19.32(16)	-2.42(14)	-8.47(14)	3.28(15)
O1	16.1(10)	29.5(13)	26.9(12)	-9.0(11)	3.9(9)	2.7(10)
O2	13.1(9)	18.6(11)	16.7(10)	-1.5(8)	0.3(8)	0.9(8)
O3	15(1)	12.5(9)	20.6(11)	2.5(8)	-1.6(8)	-0.8(8)
O4	35.1(12)	34.0(13)	20.7(11)	1.4(12)	7.1(9)	-15.8(12)
C1	16.6(14)	22.5(18)	21.8(15)	0.0(13)	1.9(12)	0.9(12)
C2	25.0(16)	17.2(16)	26.6(17)	-1.5(13)	-2.4(14)	-0.9(13)
C3	30.1(15)	11.0(14)	13.2(13)	-0.1(11)	-4.6(11)	2.3(12)
C4	23.0(15)	26.4(17)	11.9(14)	0.5(13)	1.1(12)	7.7(13)
C5	15.1(14)	23.0(18)	15.9(15)	1.3(12)	-0.7(11)	-0.2(12)
C6	14.3(13)	17.0(15)	13.8(14)	2.0(11)	-1.3(11)	2.8(10)
C7	15.6(14)	20.5(16)	14.8(14)	2.5(12)	-0.3(11)	-1.1(11)
C8	18.7(14)	15.9(15)	13.9(14)	-0.1(11)	-0.2(11)	-1.6(11)
C9	23.7(15)	18.6(17)	19.5(15)	4.3(12)	4.9(12)	-6.0(12)
C10	15.1(14)	21.0(15)	31.0(18)	-2.9(14)	8.2(13)	-6.4(12)
C11	13.8(13)	13.8(15)	30.1(16)	-1.3(13)	-3.2(12)	-0.6(11)
C12	19.1(16)	25.5(18)	56(2)	1.3(18)	-9.3(16)	5.8(14)
C13	12.9(13)	12.2(14)	14.9(14)	1.5(11)	0.7(11)	-1.1(10)
C14	16.3(13)	14.3(14)	20.5(15)	1.2(11)	4.0(11)	-1(1)
C15	16.5(12)	19.2(14)	19.0(14)	-3.3(14)	2.5(10)	0.7(13)
C16	60(3)	26.1(19)	24.2(19)	-3.0(15)	-8.5(18)	-10.1(18)
Br1A	20.91(14)	24.43(16)	23.12(16)	-7.52(14)	-0.14(11)	-4.33(13)
O1A	19.5(11)	34.0(13)	22.4(12)	-3.4(10)	5.5(9)	-6.5(10)
O2A	16.7(10)	20.0(11)	14.6(10)	-3.9(9)	0.2(8)	-5.2(8)
O3A	20.2(10)	12.4(10)	16.2(10)	-0.2(8)	2.0(8)	2.4(8)
O4A	21.9(12)	32.3(14)	42.3(15)	-7.6(12)	0.1(11)	9.8(10)
C1A	15.8(13)	24.1(17)	17.4(15)	-0.3(12)	3.4(11)	0.5(11)
C2A	19.0(14)	25.5(17)	15.3(14)	-3.6(14)	2.3(11)	5.1(13)
C3A	17.7(13)	16.2(13)	15.8(13)	-0.9(14)	-3.1(10)	-0.8(12)
C4A	12.3(13)	24.2(16)	19.4(15)	-2.5(13)	3.8(12)	-0.2(11)
C5A	17.6(13)	19.8(17)	15.4(14)	-2.7(13)	2.5(11)	0.6(12)
C6A	12.6(13)	17.5(15)	13.3(14)	1.1(11)	-2.5(11)	2(1)
C7A	15.6(13)	21.0(16)	14.3(13)	4.5(12)	-0.7(11)	2.3(12)
C8A	17.4(13)	14.4(14)	16.0(14)	-0.1(11)	-1.4(11)	-3.3(10)

C9A	14.7(12)	14.1(13)	20.0(14)	-0.8(13)	-1.5(11)	1.8(12)
C10A	18.4(13)	15.6(14)	18.8(14)	-3.4(13)	3.8(11)	0.1(12)
C11A	21.6(14)	15.1(15)	16.5(14)	-1.8(11)	3.3(12)	0.9(11)
C12A	39.6(18)	25.5(16)	15.9(14)	2.0(15)	6.0(13)	1.8(16)
C13A	17.2(12)	14.1(15)	14.4(13)	-1.5(11)	2.2(10)	0.7(11)
C14A	15.7(13)	15.2(16)	23.9(16)	-0.4(12)	0.8(12)	-0.3(11)
C15A	14.9(14)	24.6(17)	19.9(16)	1.5(12)	2.8(12)	-0.9(11)
C16A	35(2)	42(2)	35.2(19)	-11.1(19)	-13.6(16)	10.6(18)

Table 4 Bond Lengths for SI-1.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Br1	C3	1.898(3)	Br1A	C3A	1.893(3)
O1	C7	1.204(4)	O1A	C7A	1.206(4)
O2	C7	1.350(3)	O2A	C7A	1.355(4)
O2	C8	1.460(3)	O2A	C8A	1.452(3)
O3	C11	1.438(3)	O3A	C11A	1.440(3)
O3	C13	1.430(3)	O3A	C13A	1.436(3)
O4	C15	1.208(4)	O4A	C15A	1.206(4)
C1	C2	1.380(4)	C1A	C2A	1.390(4)
C1	C6	1.391(4)	C1A	C6A	1.387(4)
C2	C3	1.374(4)	C2A	C3A	1.380(4)
C3	C4	1.383(4)	C3A	C4A	1.384(4)
C4	C5	1.387(4)	C4A	C5A	1.382(4)
C5	C6	1.397(4)	C5A	C6A	1.404(4)
C6	C7	1.480(4)	C6A	C7A	1.479(4)
C8	C9	1.517(4)	C8A	C9A	1.522(4)
C8	C13	1.532(4)	C8A	C13A	1.526(4)
C9	C10	1.526(4)	C9A	C10A	1.530(4)
C10	C11	1.513(4)	C10A	C11A	1.518(4)
C11	C12	1.514(4)	C11A	C12A	1.518(4)
C13	C14	1.525(4)	C13A	C14A	1.531(4)
C14	C15	1.510(4)	C14A	C15A	1.517(4)
C15	C16	1.491(4)	C15A	C16A	1.493(5)

Table 5 Bond Angles for SI-1.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C7	O2	C8	115.6(2)	C7A	O2A	C8A	117.6(2)
C13	O3	C11	115.0(2)	C13A	O3A	C11A	115.3(2)

C2	C1	C6	120.7(3)	C6A	C1A	C2A	120.8(3)
C3	C2	C1	119.4(3)	C3A	C2A	C1A	118.8(3)
C2	C3	Br1	119.0(2)	C2A	C3A	Br1A	119.6(2)
C2	C3	C4	121.4(3)	C2A	C3A	C4A	121.6(3)
C4	C3	Br1	119.6(2)	C4A	C3A	Br1A	118.7(2)
C3	C4	C5	119.3(3)	C5A	C4A	C3A	119.3(3)
C4	C5	C6	120.1(3)	C4A	C5A	C6A	120.2(3)
C1	C6	C5	119.2(3)	C1A	C6A	C5A	119.2(3)
C1	C6	C7	118.1(3)	C1A	C6A	C7A	119.1(3)
C5	C6	C7	122.6(3)	C5A	C6A	C7A	121.7(3)
O1	C7	O2	123.3(3)	O1A	C7A	O2A	123.2(3)
O1	C7	C6	123.8(3)	O1A	C7A	C6A	125.3(3)
O2	C7	C6	112.9(2)	O2A	C7A	C6A	111.5(2)
O2	C8	C9	106.8(2)	O2A	C8A	C9A	104.8(2)
O2	C8	C13	110.3(2)	O2A	C8A	C13A	110.8(2)
C9	C8	C13	112.6(2)	C9A	C8A	C13A	112.2(2)
C8	C9	C10	111.6(2)	C8A	C9A	C10A	110.1(3)
C11	C10	C9	110.1(2)	C11A	C10A	C9A	110.7(2)
O3	C11	C10	109.6(2)	O3A	C11A	C10A	110.4(2)
O3	C11	C12	106.4(3)	O3A	C11A	C12A	106.1(2)
C10	C11	C12	113.7(3)	C10A	C11A	C12A	112.8(3)
O3	C13	C8	111.6(2)	O3A	C13A	C8A	111.9(2)
O3	C13	C14	112.4(2)	O3A	C13A	C14A	111.9(2)
C14	C13	C8	110.4(2)	C8A	C13A	C14A	110.5(2)
C15	C14	C13	112.5(2)	C15A	C14A	C13A	112.6(2)
O4	C15	C14	121.5(3)	O4A	C15A	C14A	121.6(3)
O4	C15	C16	122.1(3)	O4A	C15A	C16A	122.1(3)
C16	C15	C14	116.4(3)	C16A	C15A	C14A	116.3(3)

Table 6 Torsion Angles for SI-1.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
Br1	C3	C4	C5	-178.7(2)	Br1A	C3A	C4A	C5A	-178.0(2)
O2	C8	C9	C10	73.6(3)	O2A	C8A	C9A	C10A	69.5(3)
O2	C8	C13	O3	-71.7(3)	O2A	C8A	C13A	O3A	-66.9(3)
O2	C8	C13	C14	162.5(2)	O2A	C8A	C13A	C14A	167.7(2)
O3	C13	C14	C15	56.2(3)	O3A	C13A	C14A	C15A	57.1(3)
C1	C2	C3	Br1	178.9(2)	C1A	C2A	C3A	Br1A	177.6(2)
C1	C2	C3	C4	-1.2(5)	C1A	C2A	C3A	C4A	-0.3(5)

C1	C6	C7	O1	8.1(4)	C1A	C6A	C7A	O1A	10.0(5)
C1	C6	C7	O2	-172.6(3)	C1A	C6A	C7A	O2A	-170.2(3)
C2	C1	C6	C5	0.7(4)	C2A	C1A	C6A	C5A	-0.6(5)
C2	C1	C6	C7	-179.1(3)	C2A	C1A	C6A	C7A	-179.1(3)
C2	C3	C4	C5	1.4(5)	C2A	C3A	C4A	C5A	-0.1(5)
C3	C4	C5	C6	-0.6(4)	C3A	C4A	C5A	C6A	0.2(5)
C4	C5	C6	C1	-0.5(4)	C4A	C5A	C6A	C1A	0.1(4)
C4	C5	C6	C7	179.3(3)	C4A	C5A	C6A	C7A	178.6(3)
C5	C6	C7	O1	-171.7(3)	C5A	C6A	C7A	O1A	-168.5(3)
C5	C6	C7	O2	7.6(4)	C5A	C6A	C7A	O2A	11.3(4)
C6	C1	C2	C3	0.1(5)	C6A	C1A	C2A	C3A	0.6(5)
C7	O2	C8	C9	154.7(2)	C7A	O2A	C8A	C9A	154.3(2)
C7	O2	C8	C13	-82.7(3)	C7A	O2A	C8A	C13A	-84.5(3)
C8	O2	C7	O1	4.5(4)	C8A	O2A	C7A	O1A	8.6(4)
C8	O2	C7	C6	-174.8(2)	C8A	O2A	C7A	C6A	-171.2(2)
C8	C9	C10	C11	52.8(3)	C8A	C9A	C10A	C11A	54.2(3)
C8	C13	C14	C15	-178.4(2)	C8A	C13A	C14A	C15A	-177.5(2)
C9	C8	C13	O3	47.5(3)	C9A	C8A	C13A	O3A	49.9(3)
C9	C8	C13	C14	-78.3(3)	C9A	C8A	C13A	C14A	-75.5(3)
C9	C10	C11	O3	-57.9(3)	C9A	C10A	C11A	O3A	-56.6(3)
C9	C10	C11	C12	-176.8(3)	C9A	C10A	C11A	C12A	-175.2(3)
C11	O3	C13	C8	-55.2(3)	C11A	O3A	C13A	C8A	-53.9(3)
C11	O3	C13	C14	69.5(3)	C11A	O3A	C13A	C14A	70.8(3)
C13	O3	C11	C10	60.9(3)	C13A	O3A	C11A	C10A	57.5(3)
C13	O3	C11	C12	-175.8(3)	C13A	O3A	C11A	C12A	-179.9(2)
C13	C8	C9	C10	-47.6(3)	C13A	C8A	C9A	C10A	-50.8(3)
C13	C14	C15	O4	37.2(4)	C13A	C14A	C15A	O4A	35.8(4)
C13	C14	C15	C16	-142.9(3)	C13A	C14A	C15A	C16A	-146.6(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for SI-1.

Atom	***x***	***y***	***z***	**U(eq)**
H1	2442	3763	7952	24
H2	2618	7070	8688	28
H4	1273	6856	9047	25
H5	1094	3510	8313	22
H8	1354	-3133	7132	20
H9A	655	-3253	7632	24

H9B	596	-4786	6997	24
H10A	-78	-2159	7020	26
H10B	232	477	7206	26
H11	189	-2243	6069	24
H12A	-153	3038	6291	52
H12B	-482	504	6081	52
H12C	-149	1769	5635	52
H13	1343	435	6380	16
H14A	1408	-4104	6109	20
H14B	847	-4423	6010	20
H16A	500	-3963	4878	57
H16B	944	-5955	4949	57
H16C	909	-3553	4467	57
H1A	3733	7077	6068	23
H2A	3171	4113	5574	24
H4A	2275	6066	6757	22
H5A	2839	8982	7258	21
H8A	3974	14532	7530	20
H9AA	3256	15148	7971	20
H9AB	3708	16385	8383	20
H10C	3276	13875	9011	21
H10D	3276	11282	8583	21
H11A	4097	13530	9289	21
H12D	3688	8320	9414	40
H12E	3654	10764	9872	40
H12F	4154	9416	9817	40
H13A	4475	10874	7950	18
H14C	4745	15364	8055	22
H14D	4522	15677	8668	22
H16D	5649	14303	9447	59
H16E	5144	15431	9557	59
H16F	5429	16886	9082	59