Supporting Information for

Collective Synthesis of Several 2,7′-Cyclolignans and Their Chemical Correlation by Chemical Transformations

Yu Peng*, Zhen-Biao Luo, Jian-Jian Zhang, Long Luo and Ya-Wen Wang

State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

pengyu@lzu.edu.cn

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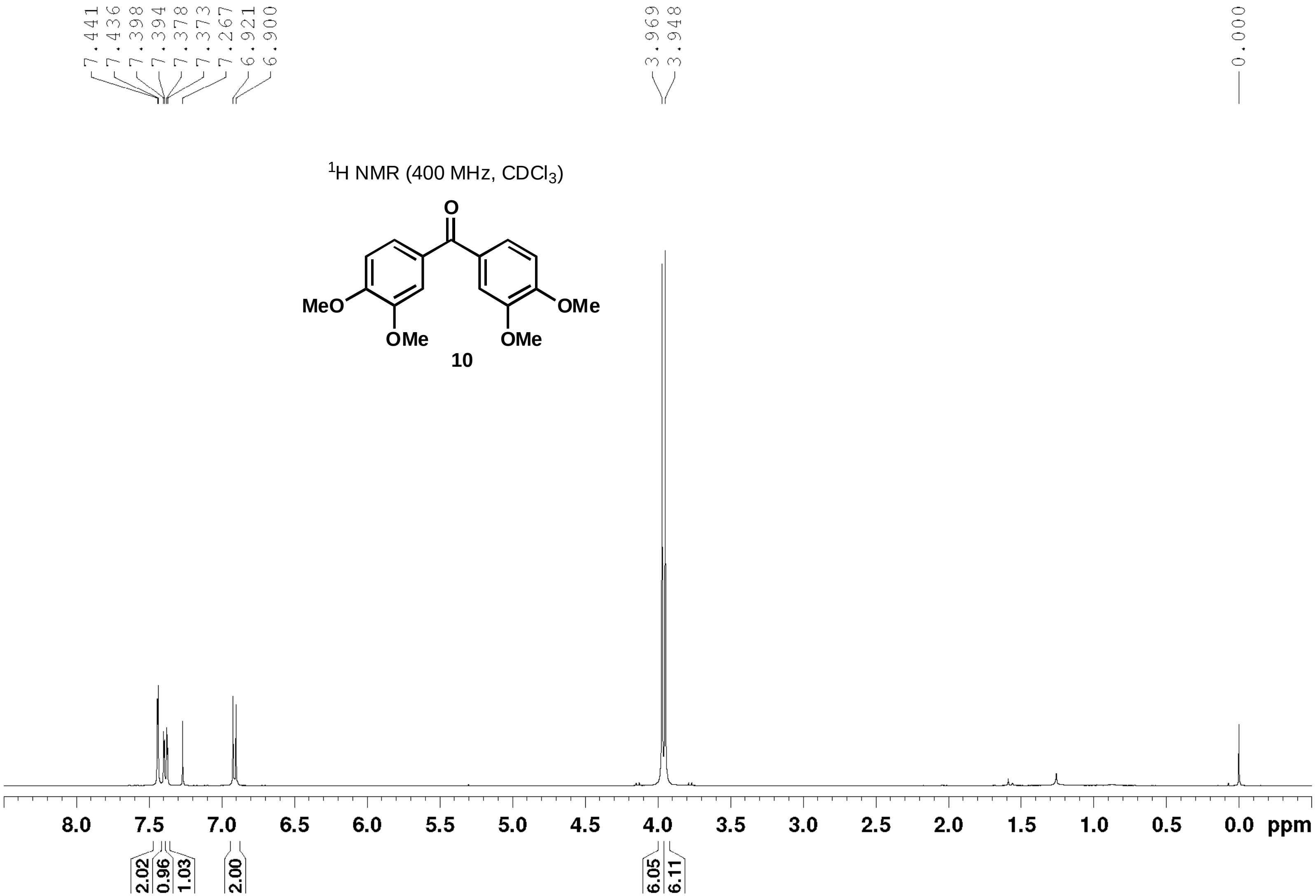

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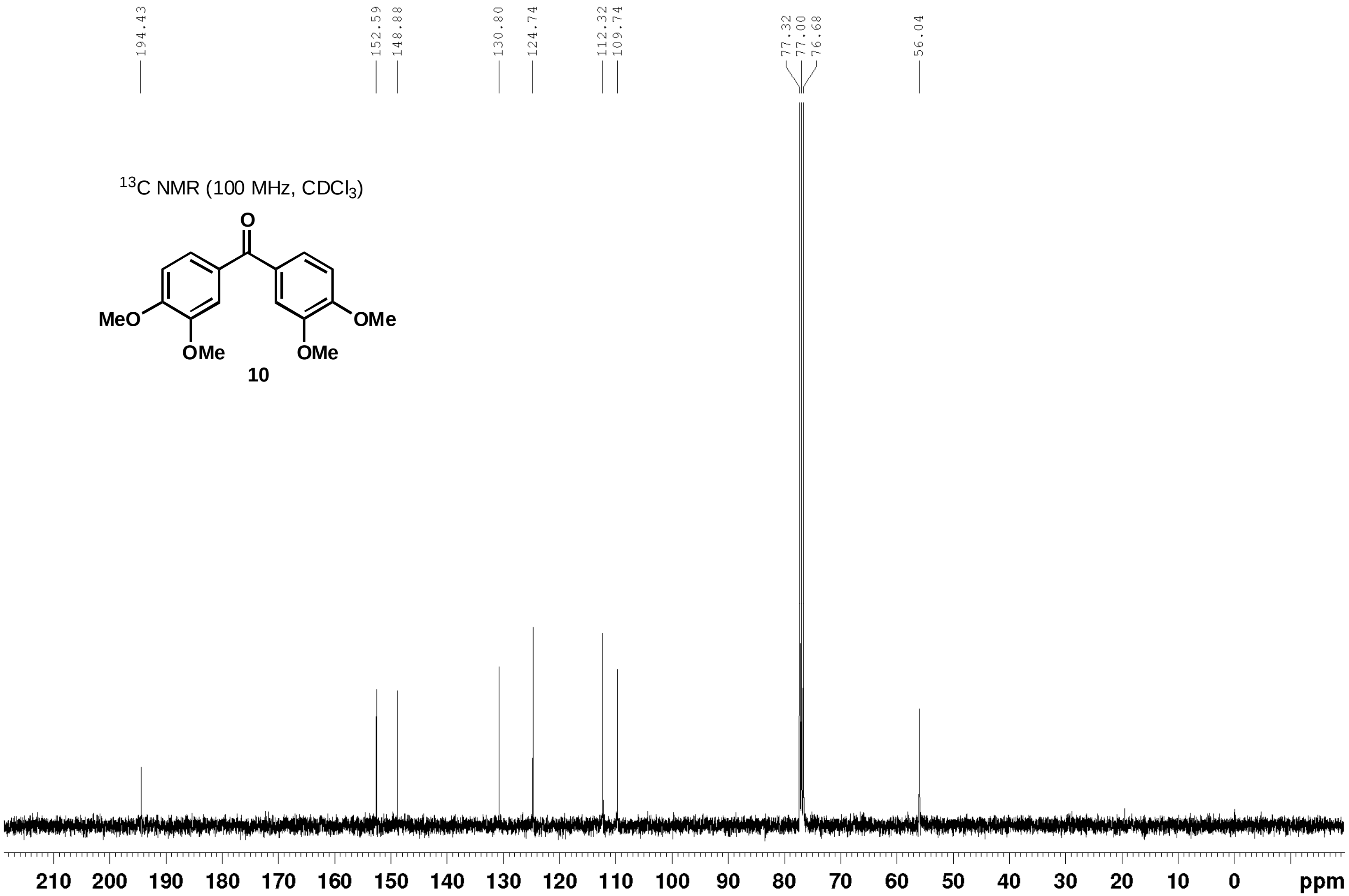
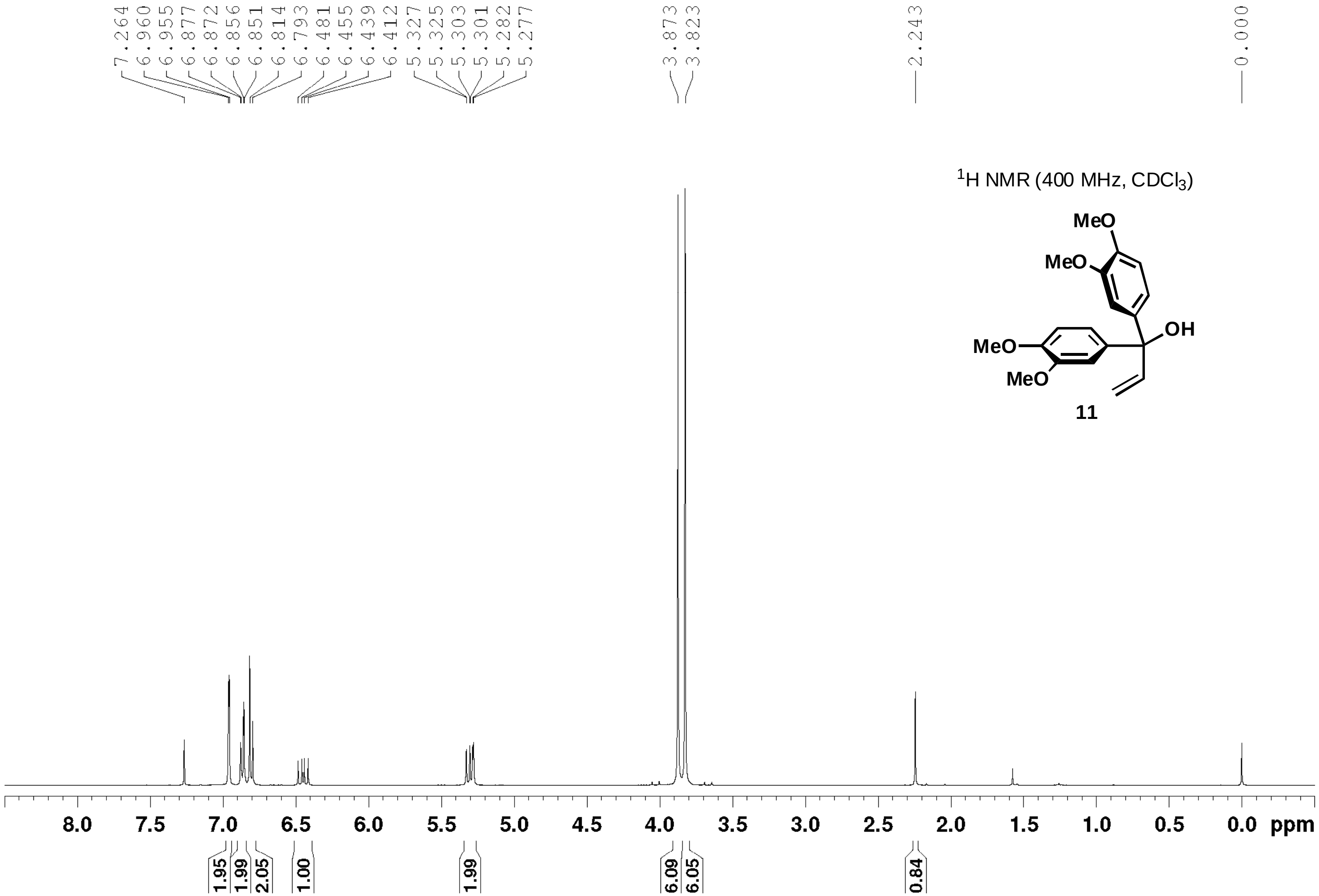
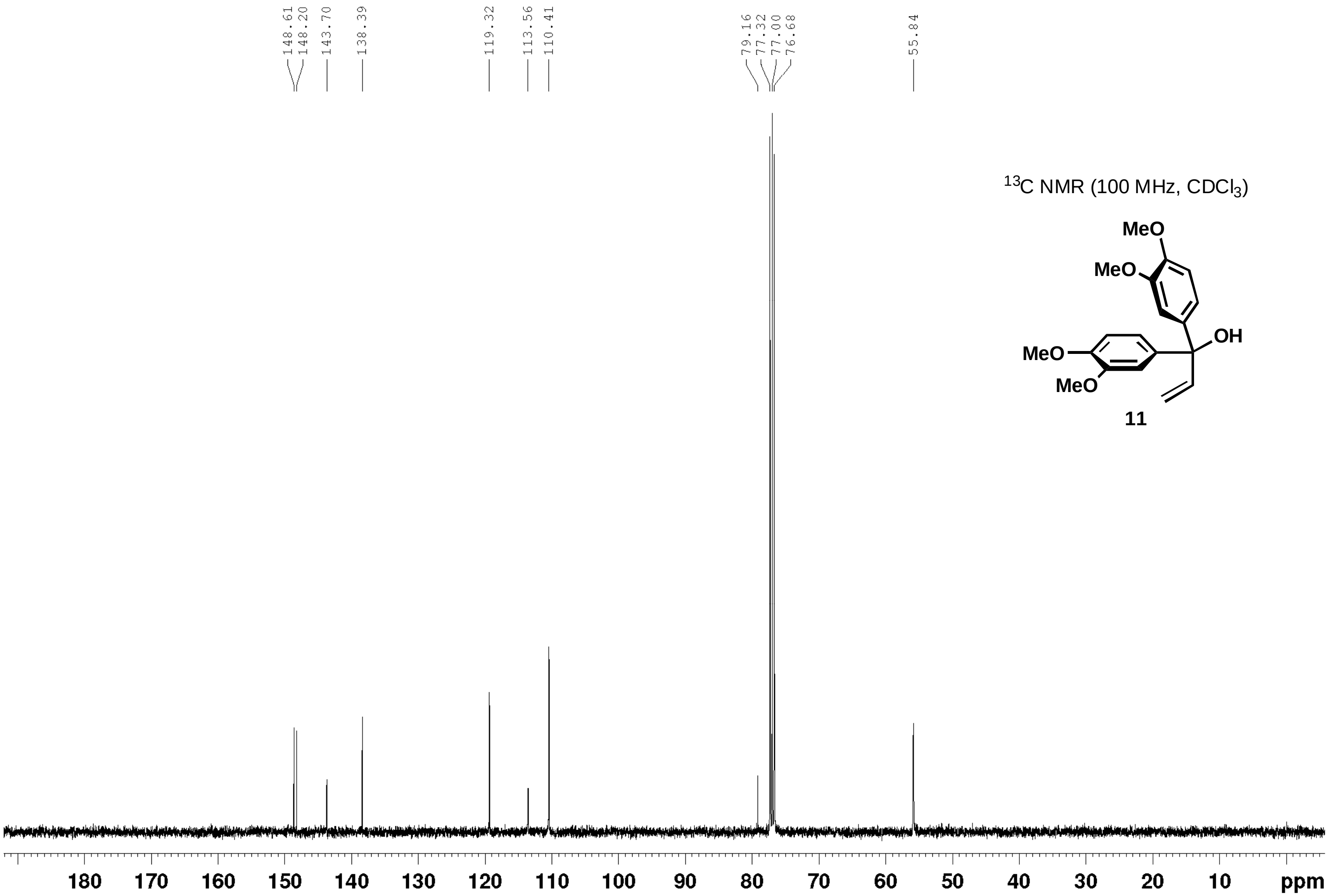
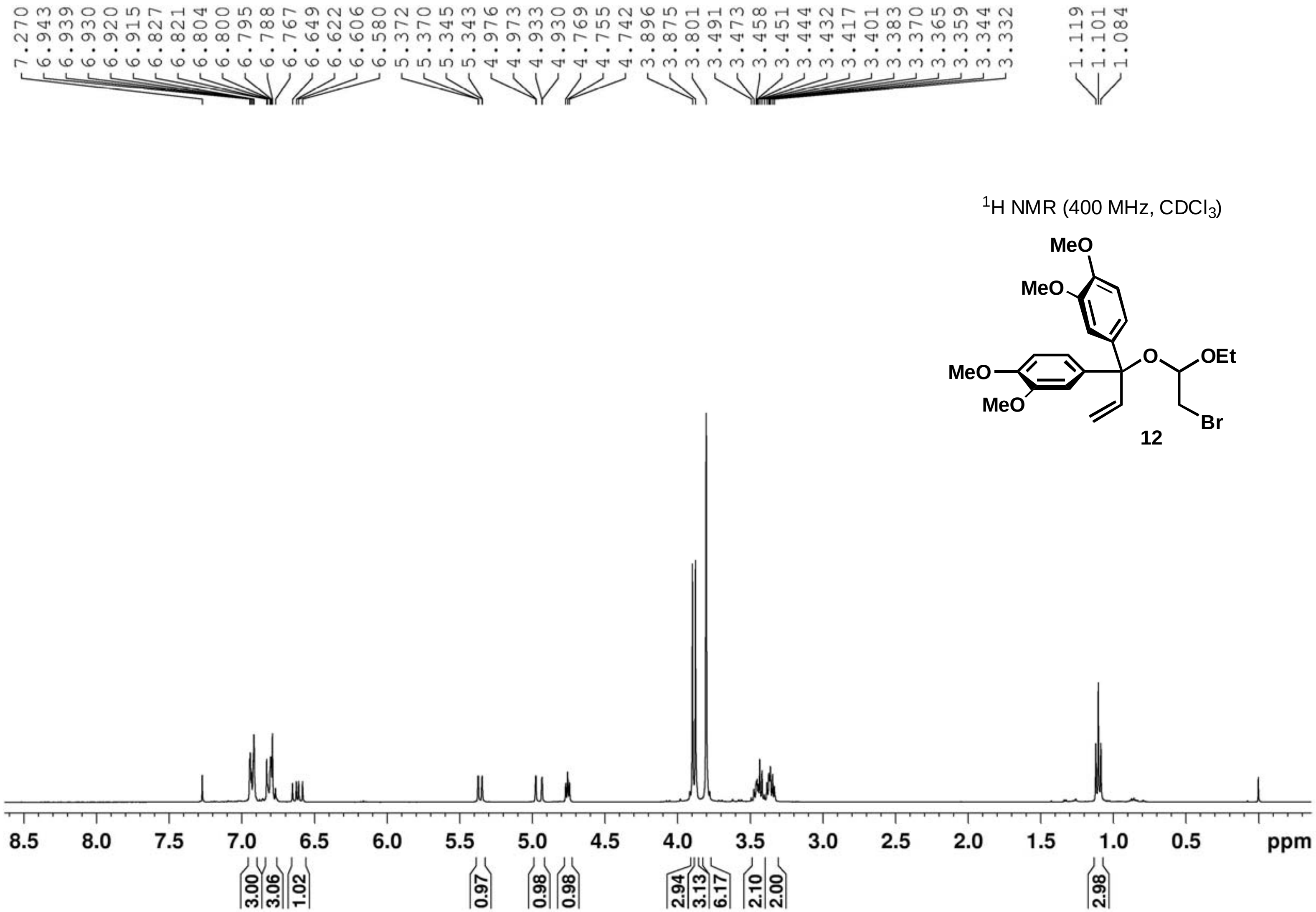
7.436
7.398
7.394
7.378
7.373
7.267
6.921
6.900
3.969
3.948
0.000
1H NMR (400 MHz, CDCl3)
O
MeO
OMe
OMe
OMe
10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
0.96
1.03
2.00
6.05
6.11


194.43
152.59
148.88
130.80
124.74
112.32
109.74
77.32
77.00
76.68
56.04
13C NMR (100 MHz, CDCl3)
O
MeO
OMe
OMe
OMe
10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

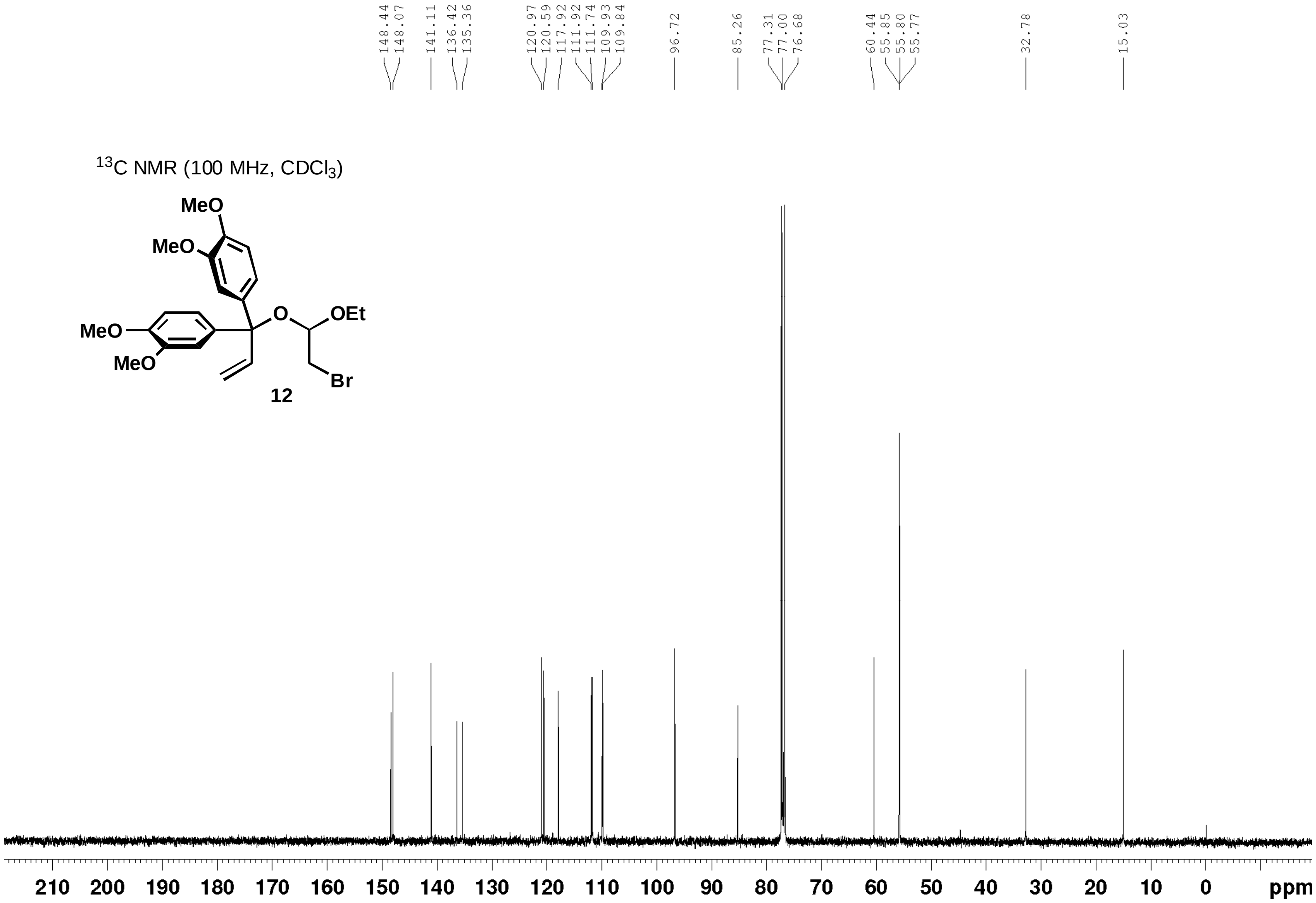

7.264
6.960
6.955
6.877
6.872
6.856
6.851
6.814
6.793
6.481
6.455
6.439
6.412
5.327
5.325
5.303
5.301
5.282
5.277
3.873
3.823
2.243
0.000
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
MeO
OH
MeO
MeO
11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.95
1.99
2.05
1.00
1.99
6.09
6.05
0.84

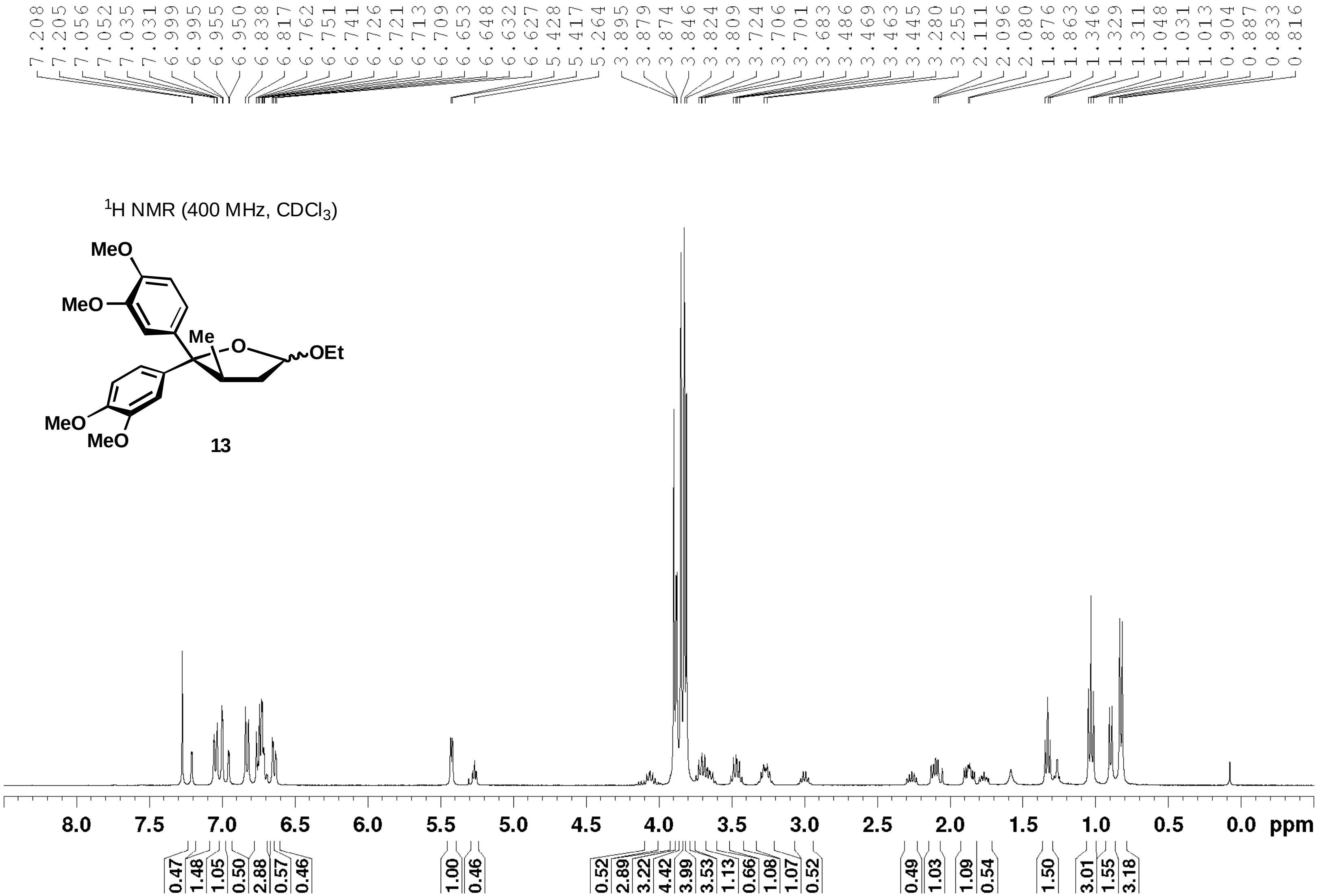

148.61
148.20
143.70
138.39
119.32
113.56
110.41
79.16
77.32
77.00
76.68
55.84
^{13}C NMR (100 MHz, CDCl$_3$)
MeO
MeO
OH
MeO
MeO
11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

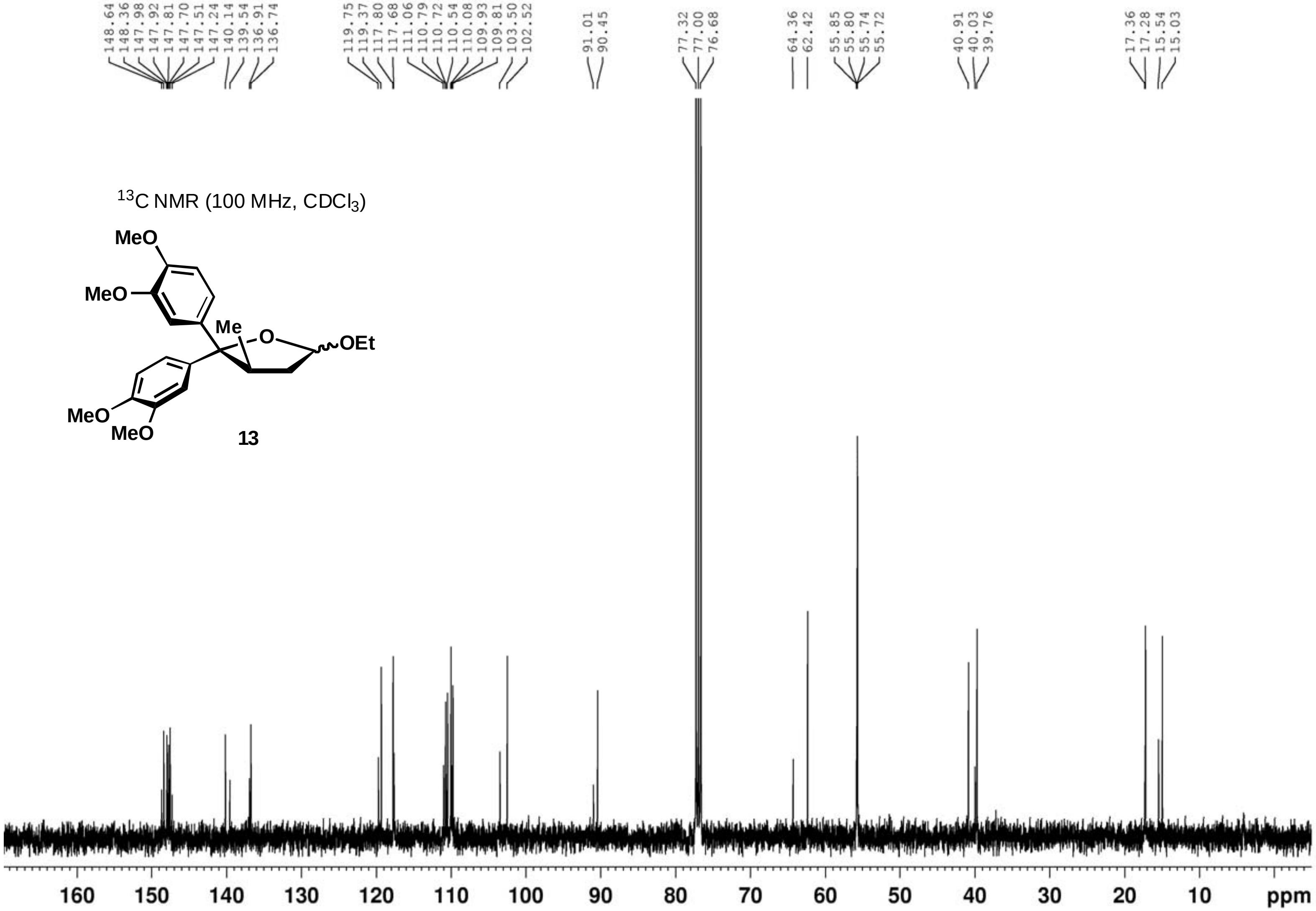

7.270
6.943
6.939
6.930
6.920
6.915
6.827
6.821
6.804
6.800
6.795
6.788
6.767
6.649
6.622
6.606
6.580
5.372
5.370
5.345
5.343
4.976
4.973
4.933
4.930
4.769
4.755
4.742
3.896
3.875
3.801
3.491
3.473
3.458
3.451
3.444
3.432
3.417
3.401
3.383
3.370
3.365
3.359
3.344
3.332
1.119
1.101
1.084
^{1}H NMR (400 MHz, CDCl$_3$)
MeO
MeO
MeO
MeO
O
OEt
Br
12
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
ppm
3.00
3.06
1.02
0.97
0.98
0.98
2.94
3.13
6.17
2.10
2.00
2.98

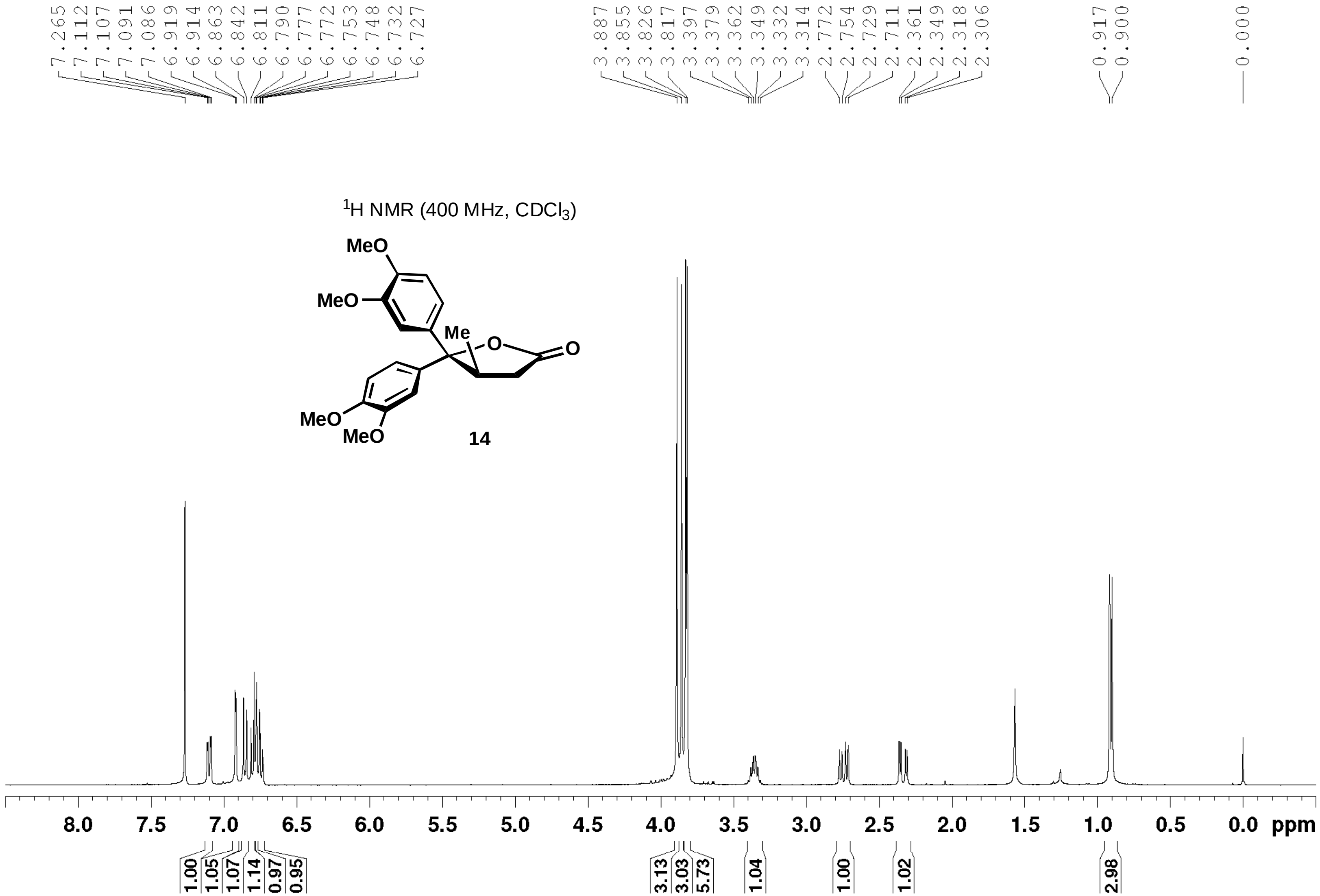
^{13}C NMR (100 MHz, $CDCl_3$)

12



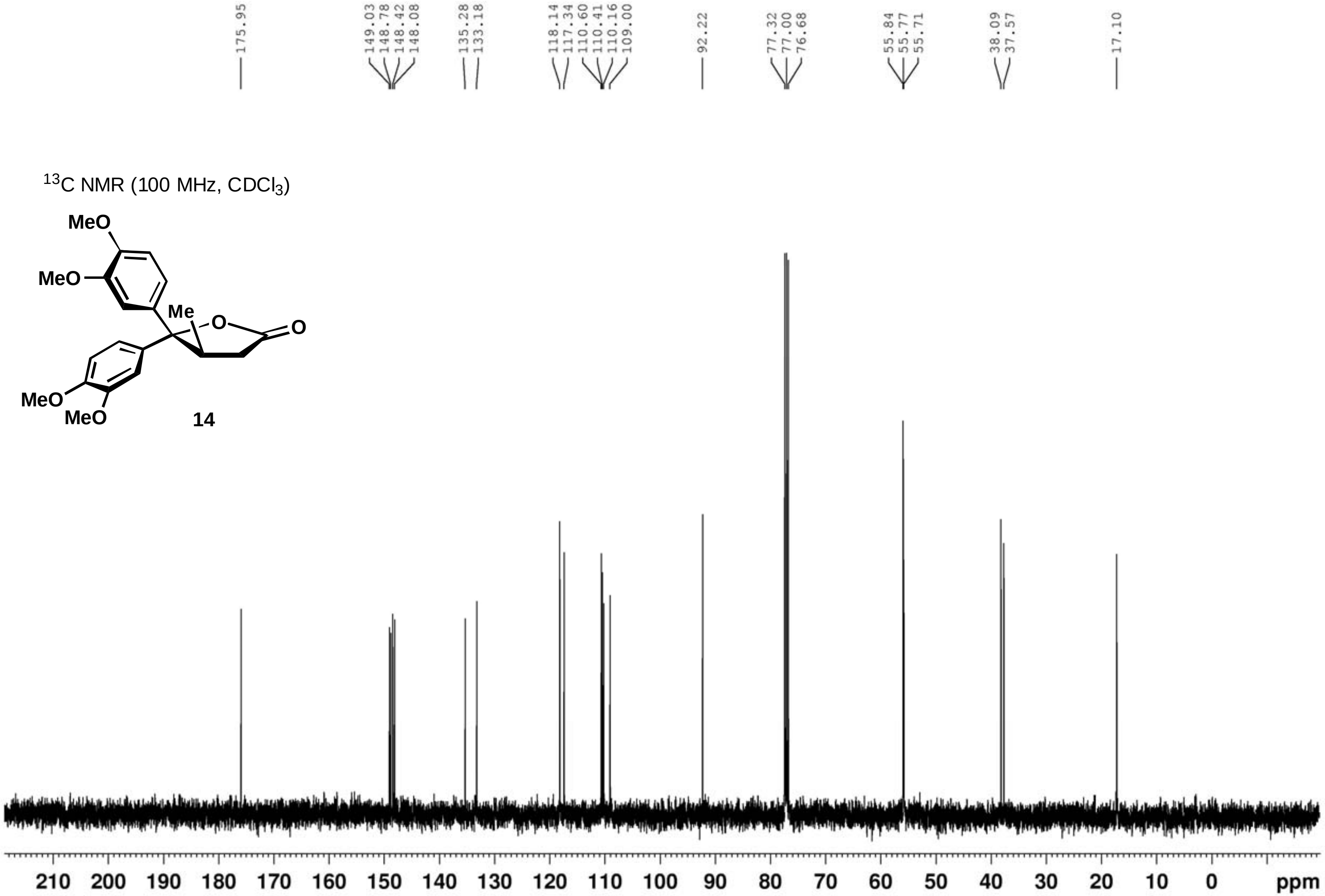

7.208 7.205 7.056 7.052 7.035 7.031 6.999 6.995 6.955 6.950 6.838 6.817 6.762 6.751 6.741 6.726 6.721 6.713 6.709 6.653 6.648 6.632 6.627 5.428 5.417 5.264 3.895 3.879 3.874 3.846 3.824 3.809 3.724 3.706 3.701 3.683 3.486 3.469 3.463 3.445 3.280 3.255 2.111 2.096 2.080 1.876 1.863 1.346 1.329 1.311 1.048 1.031 1.013 0.904 0.887 0.833 0.816
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
MeO
Me
O
OEt
MeO
MeO
13
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 ppm
0.47 1.48 1.05 0.50 2.88 0.57 0.46 1.00 0.46 0.52 2.89 3.22 4.42 3.99 3.53 1.13 0.66 1.08 1.07 0.52 0.49 1.03 1.09 0.54 1.50 3.01 1.55 3.18

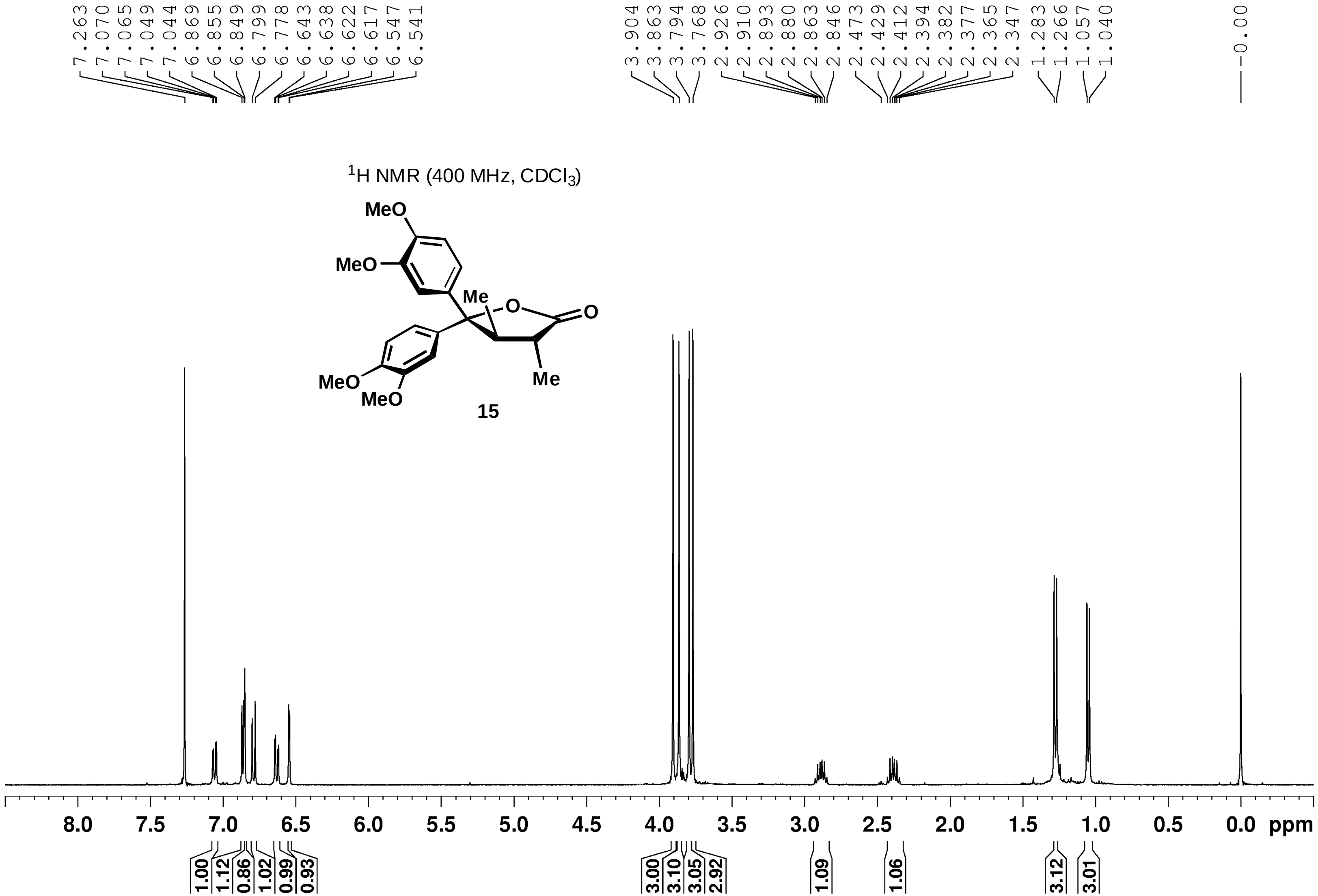

148.64
148.36
147.98
147.92
147.81
147.70
147.51
147.24
140.14
139.54
136.91
136.74
119.75
119.37
117.80
117.68
111.06
110.79
110.72
110.54
110.08
109.93
109.81
103.50
102.52
91.01
90.45
77.32
77.00
76.68
64.36
62.42
55.85
55.80
55.74
55.72
40.91
40.03
39.76
17.36
17.28
15.54
15.03
^{13}C NMR (100 MHz, CDCl$_3$)
MeO
MeO
Me
O
OEt
MeO
MeO
13
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

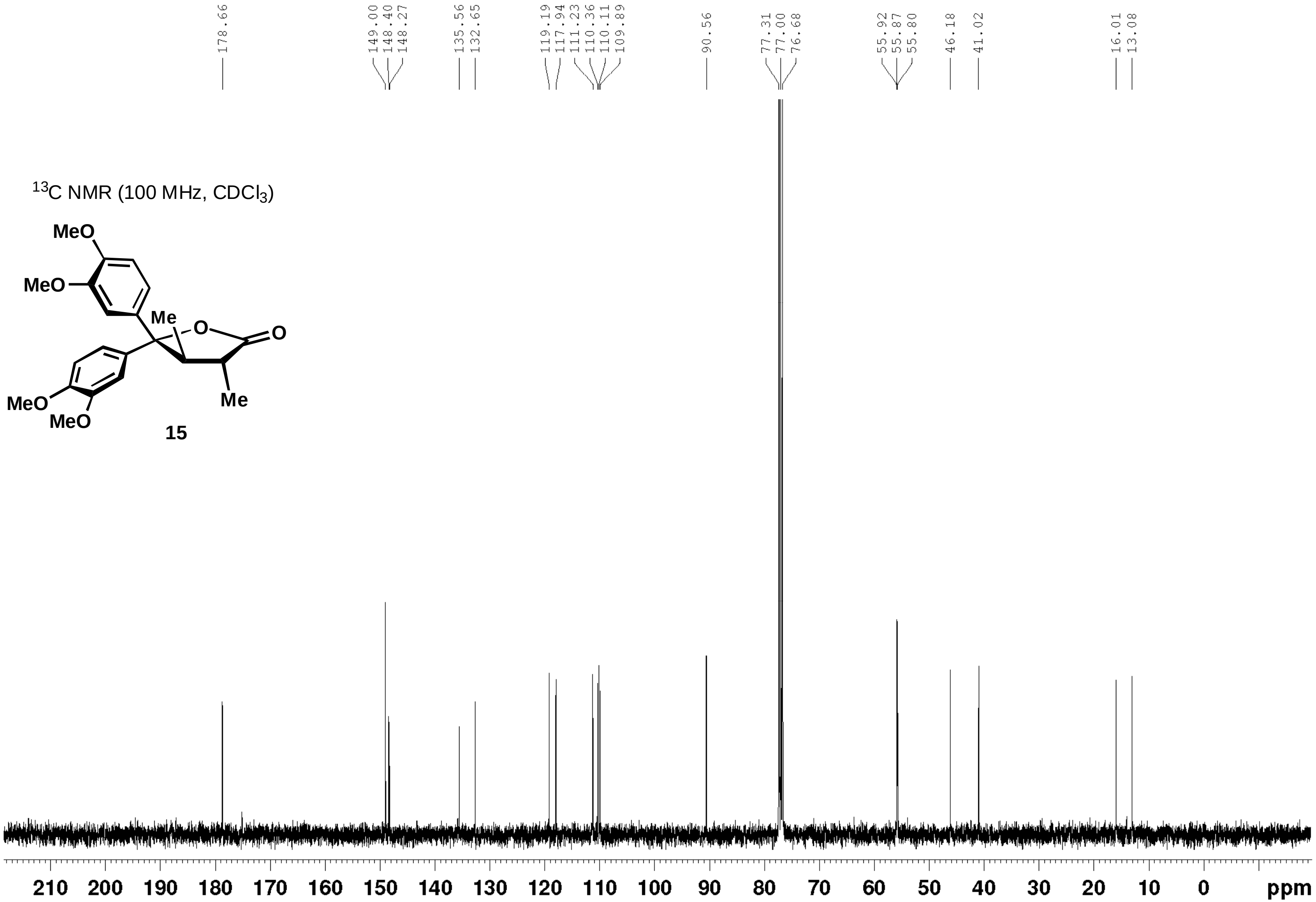

1H NMR (400 MHz, CDCl3)
MeO
MeO
Me
O
O
MeO
MeO
14
ppm

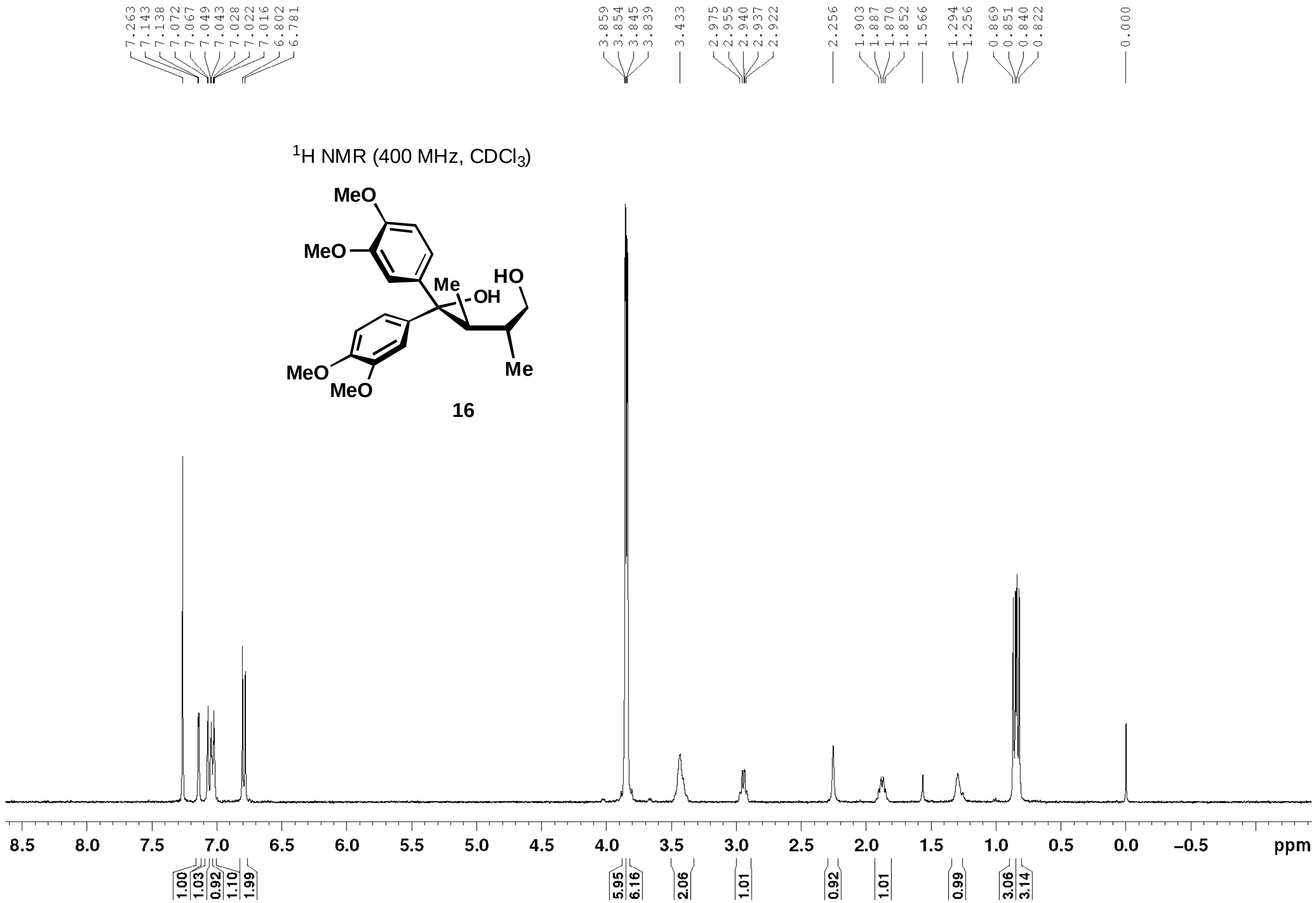
^{13}C NMR (100 MHz, $CDCl_3$)

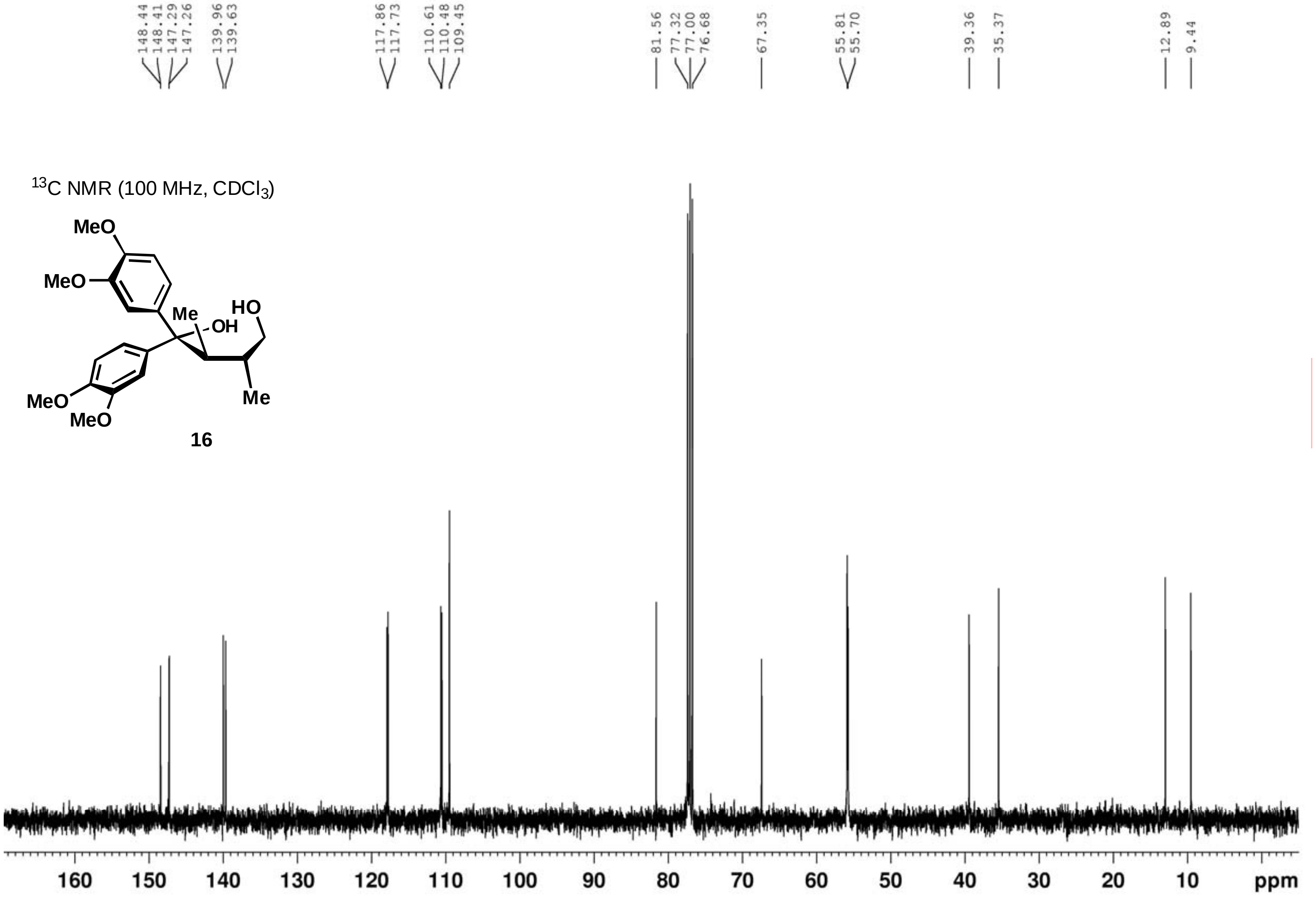
14



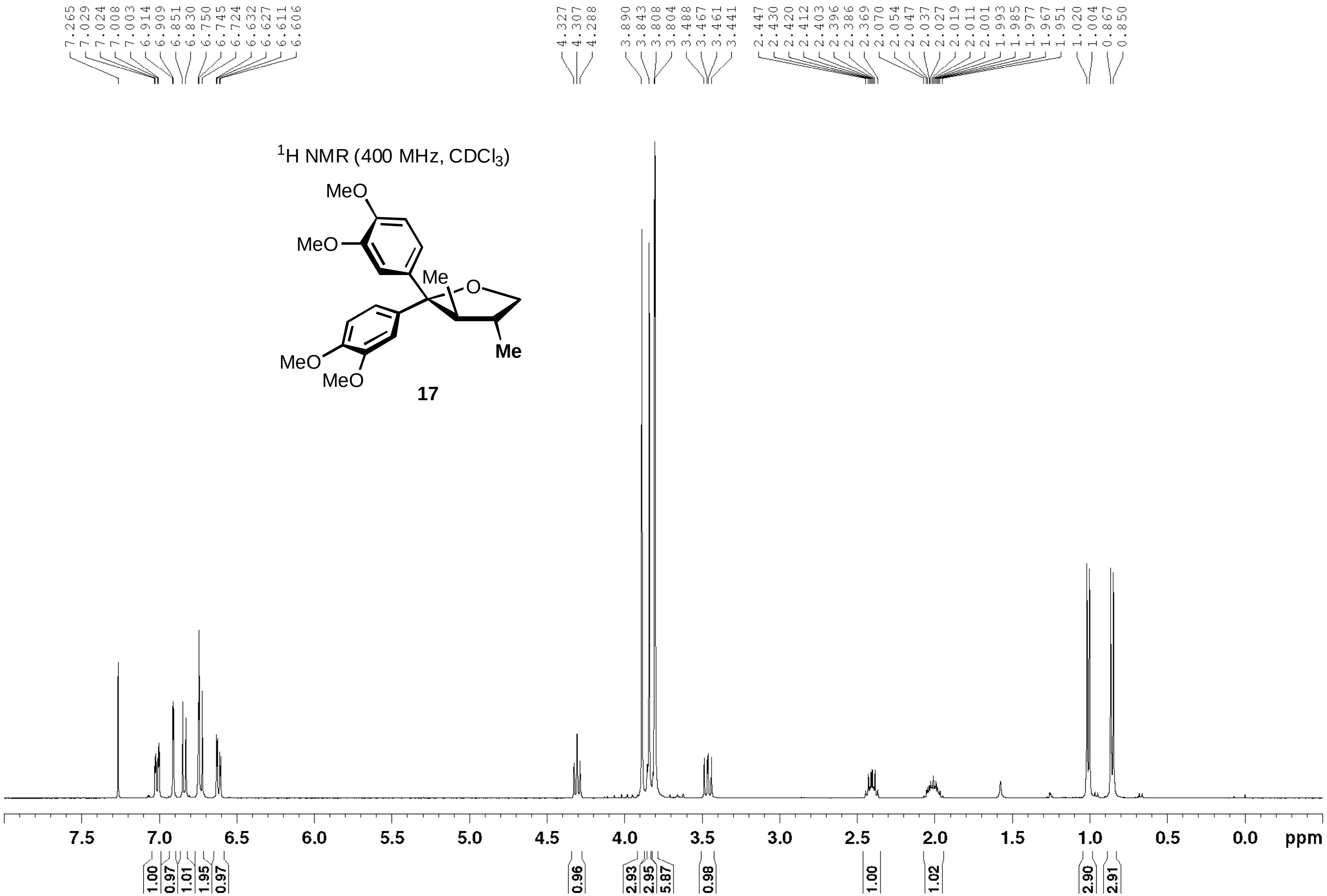

7.263 7.070 7.065 7.049 7.044 6.869 6.855 6.849 6.799 6.778 6.643 6.638 6.622 6.617 6.547 6.541
3.904 3.863 3.794 3.768 2.926 2.910 2.893 2.880 2.863 2.846 2.473 2.429 2.412 2.394 2.382 2.377 2.365 2.347 1.283 1.266 1.057 1.040
0.00
1H NMR (400 MHz, CDCl3)
MeO
MeO
Me
O
O
MeO
MeO
Me
15
8.0 7.5 7.0 6.5 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 ppm
1.00 1.12 0.86 1.02 0.99 0.93 3.00 3.10 3.05 2.92 1.09 1.06 3.12 3.01

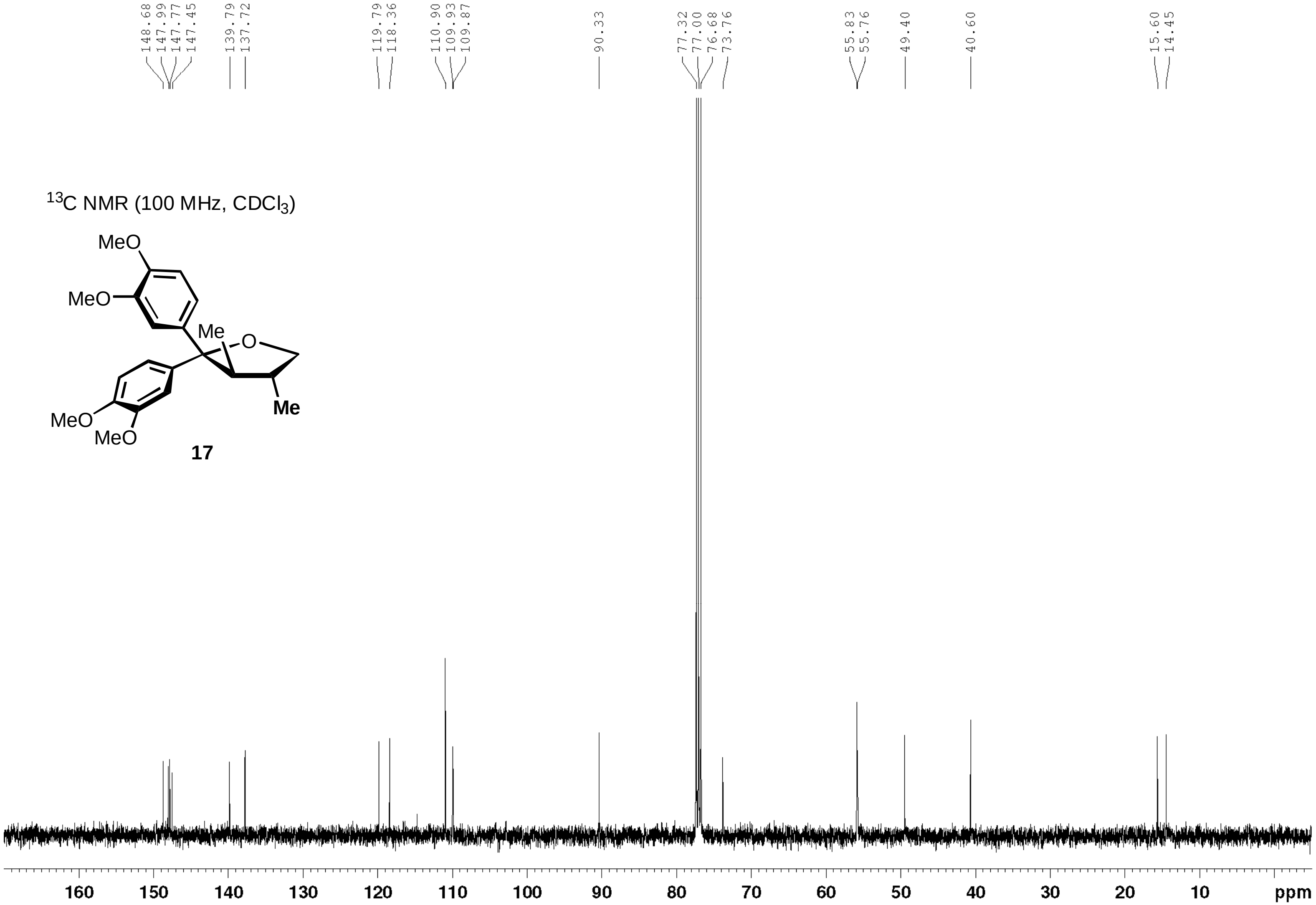

178.66
149.00
148.40
148.27
135.56
132.65
119.19
117.94
111.23
110.36
110.11
109.89
90.56
77.31
77.00
76.68
55.92
55.87
55.80
46.18
41.02
16.01
13.08
13C NMR (100 MHz, CDCl3)
MeO
MeO
Me
O
O
Me
MeO
MeO
15
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

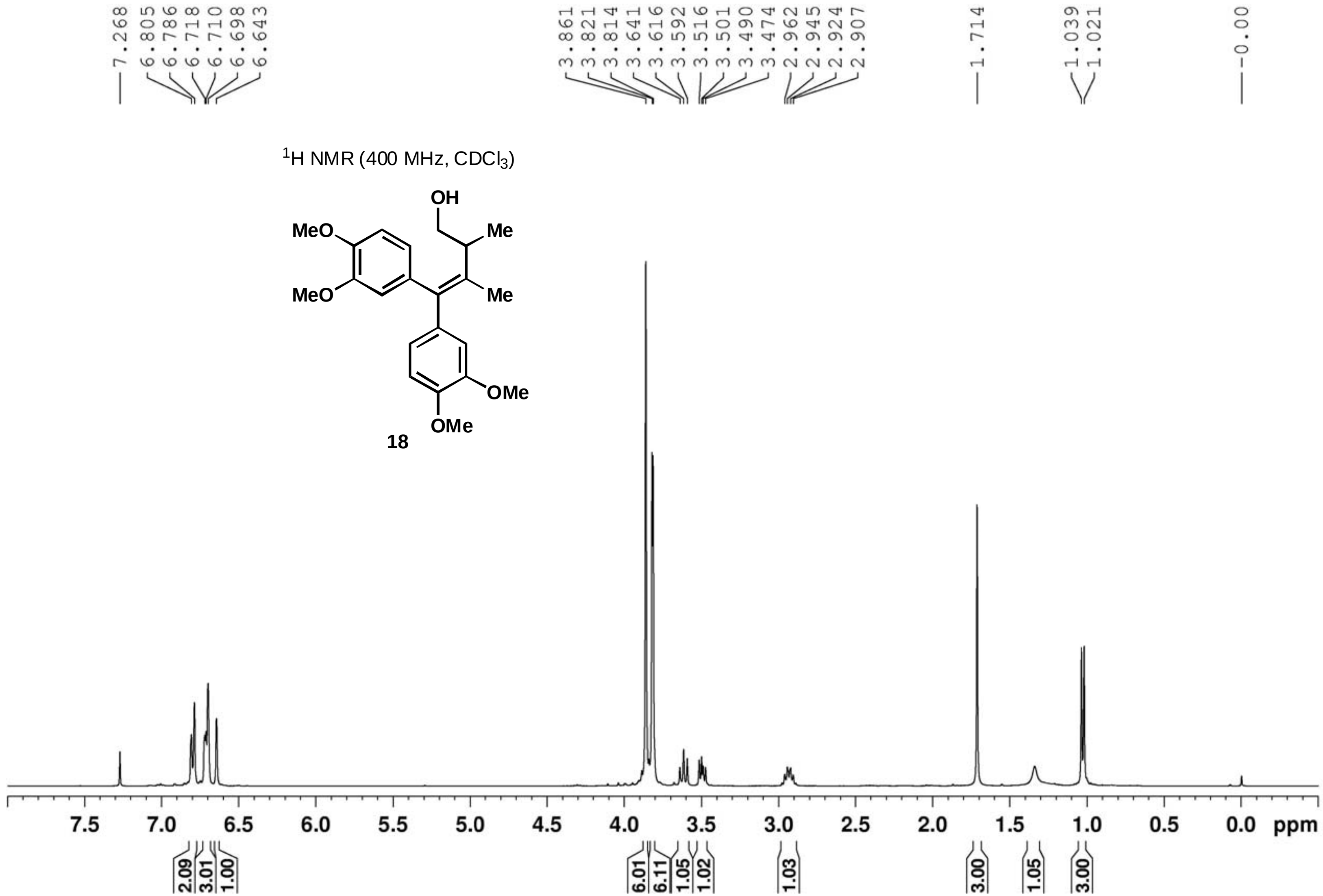

7.263 7.143 7.138 7.072 7.067 7.049 7.043 7.028 7.022 7.016 6.802 6.781
3.859 3.854 3.845 3.839
3.433
2.975 2.955 2.940 2.937 2.922
2.256
1.903 1.887 1.870 1.852
1.566
1.294 1.256
0.869 0.851 0.840 0.822
0.000
1H NMR (400 MHz, CDCl3)
MeO
MeO
Me
HO
OH
MeO
MeO
Me
16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 –0.5 ppm
1.00 1.03 0.92 1.10 1.99
5.95 6.16
2.06
1.01
0.92
1.01
0.99
3.06 3.14

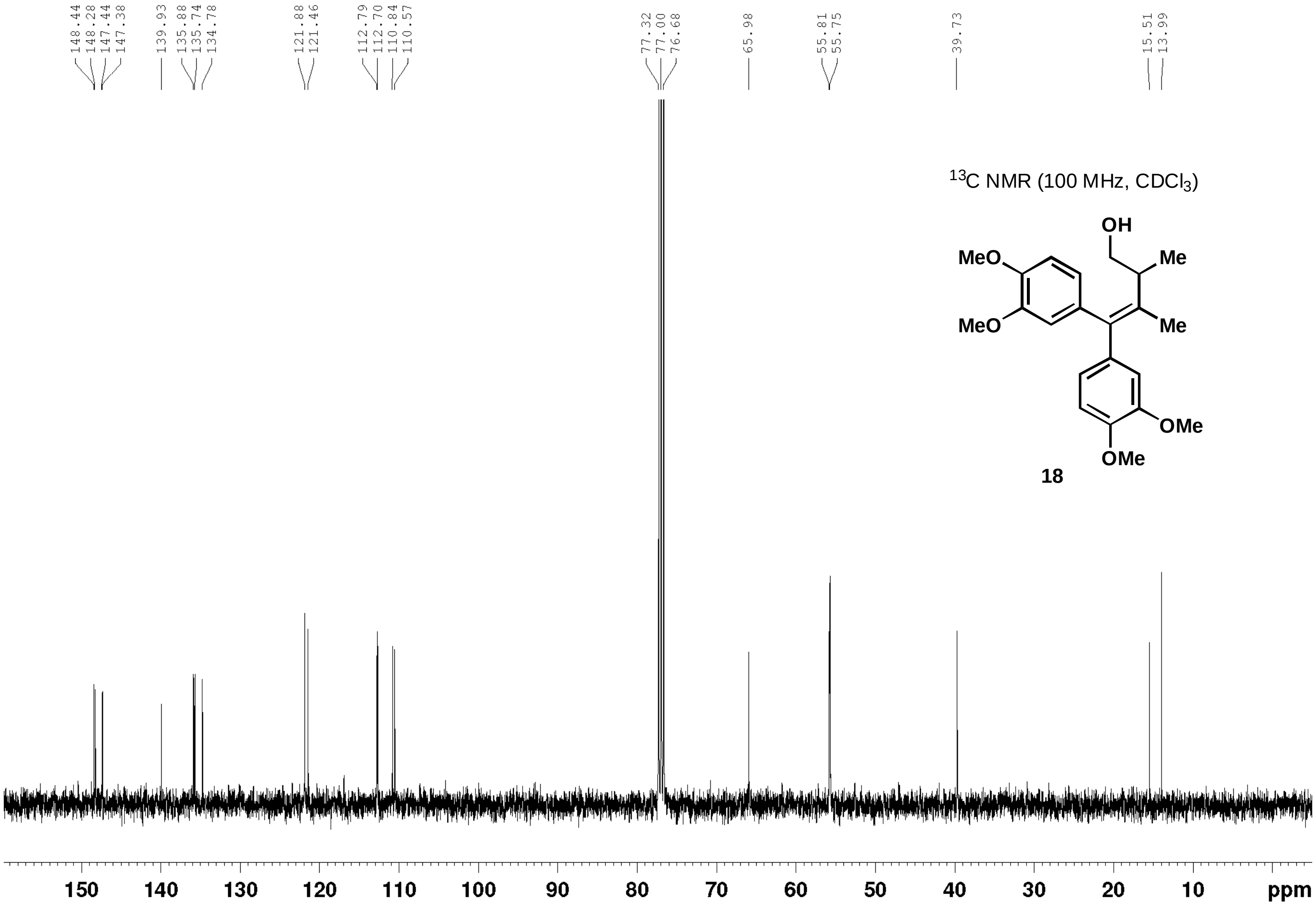

148.44
148.41
147.29
147.26
139.96
139.63
117.86
117.73
110.61
110.48
109.45
81.56
77.32
77.00
76.68
67.35
55.81
55.70
39.36
35.37
12.89
9.44
13C NMR (100 MHz, CDCl3)
MeO
MeO
Me
OH
HO
MeO
MeO
Me
16
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

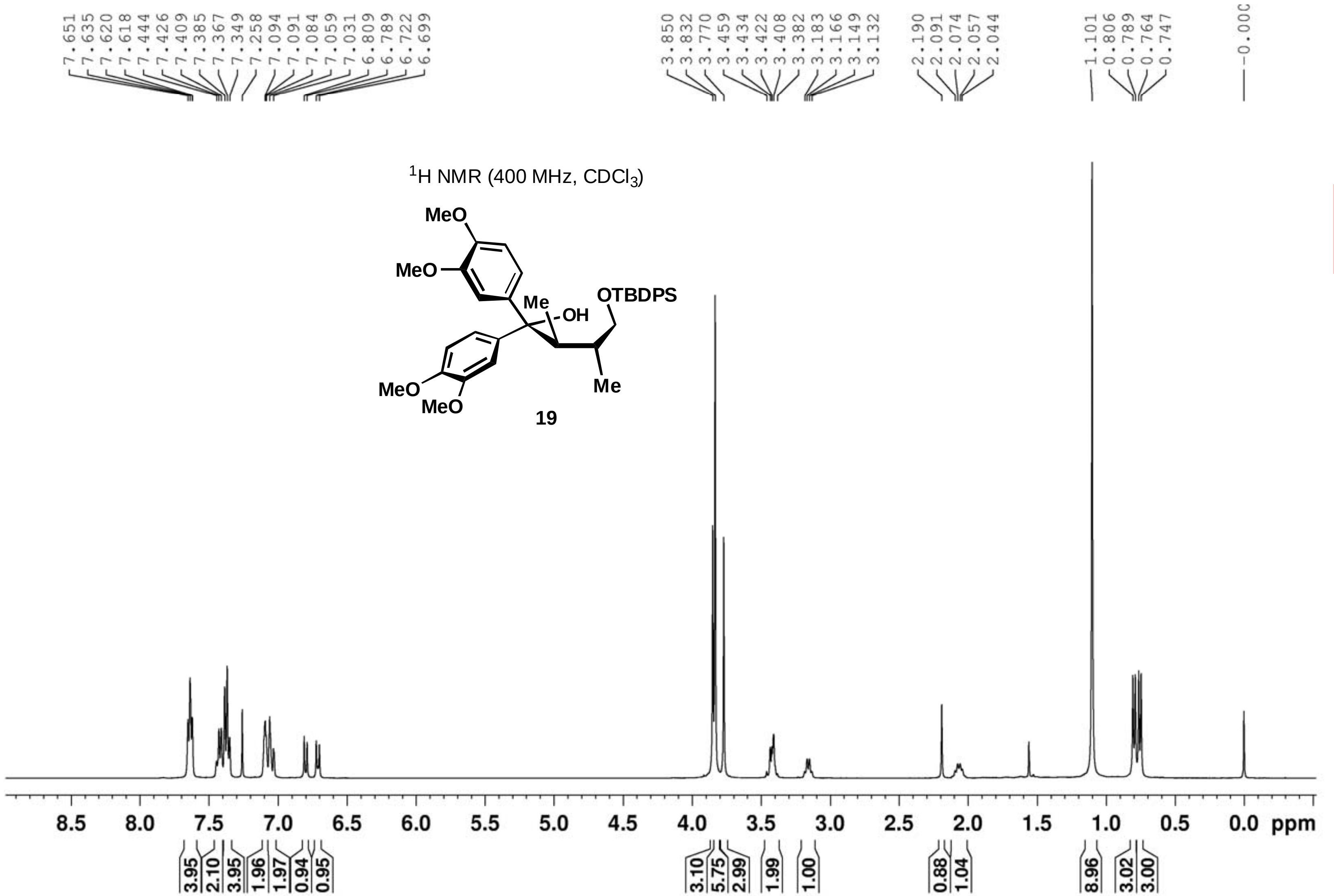
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

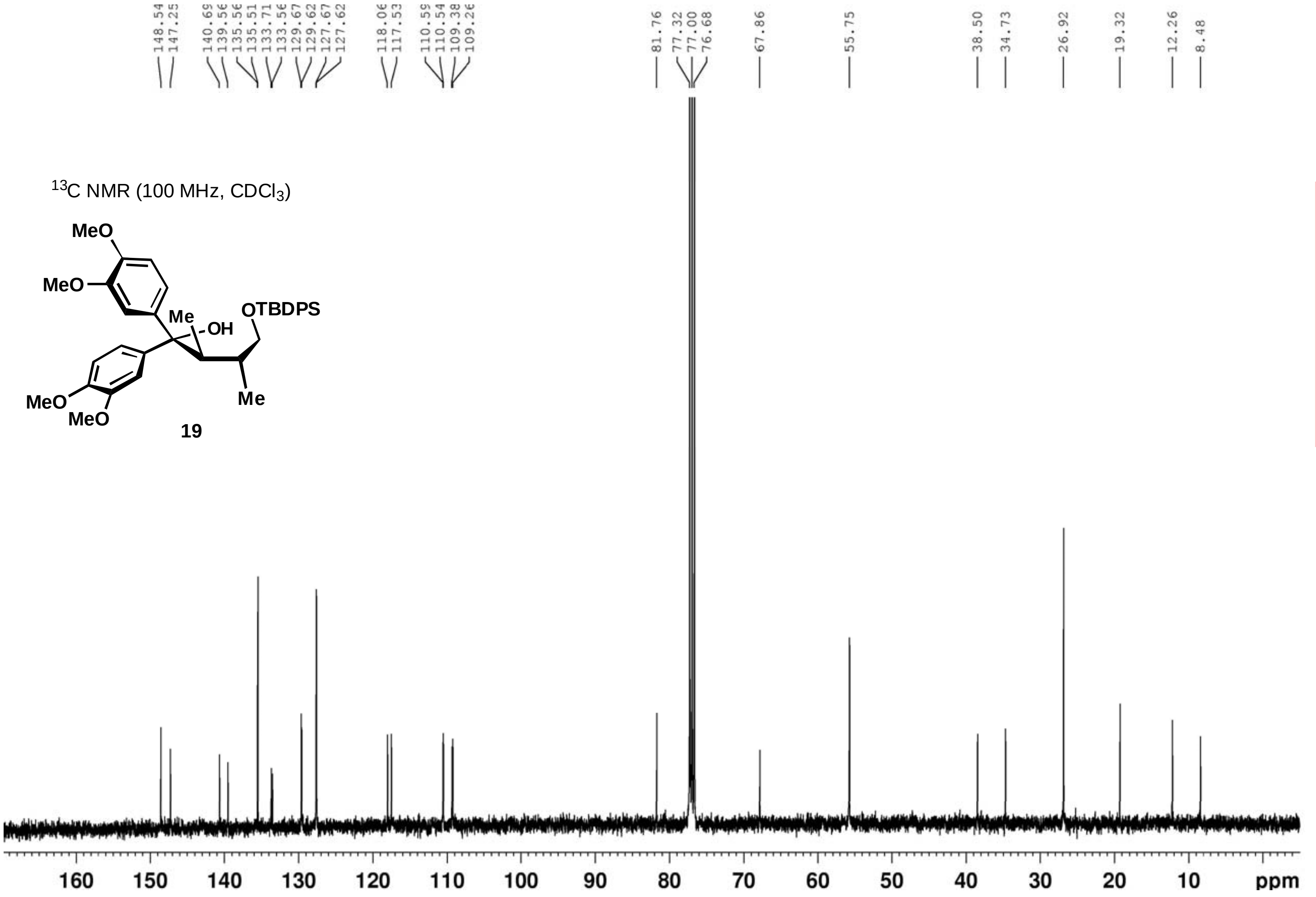


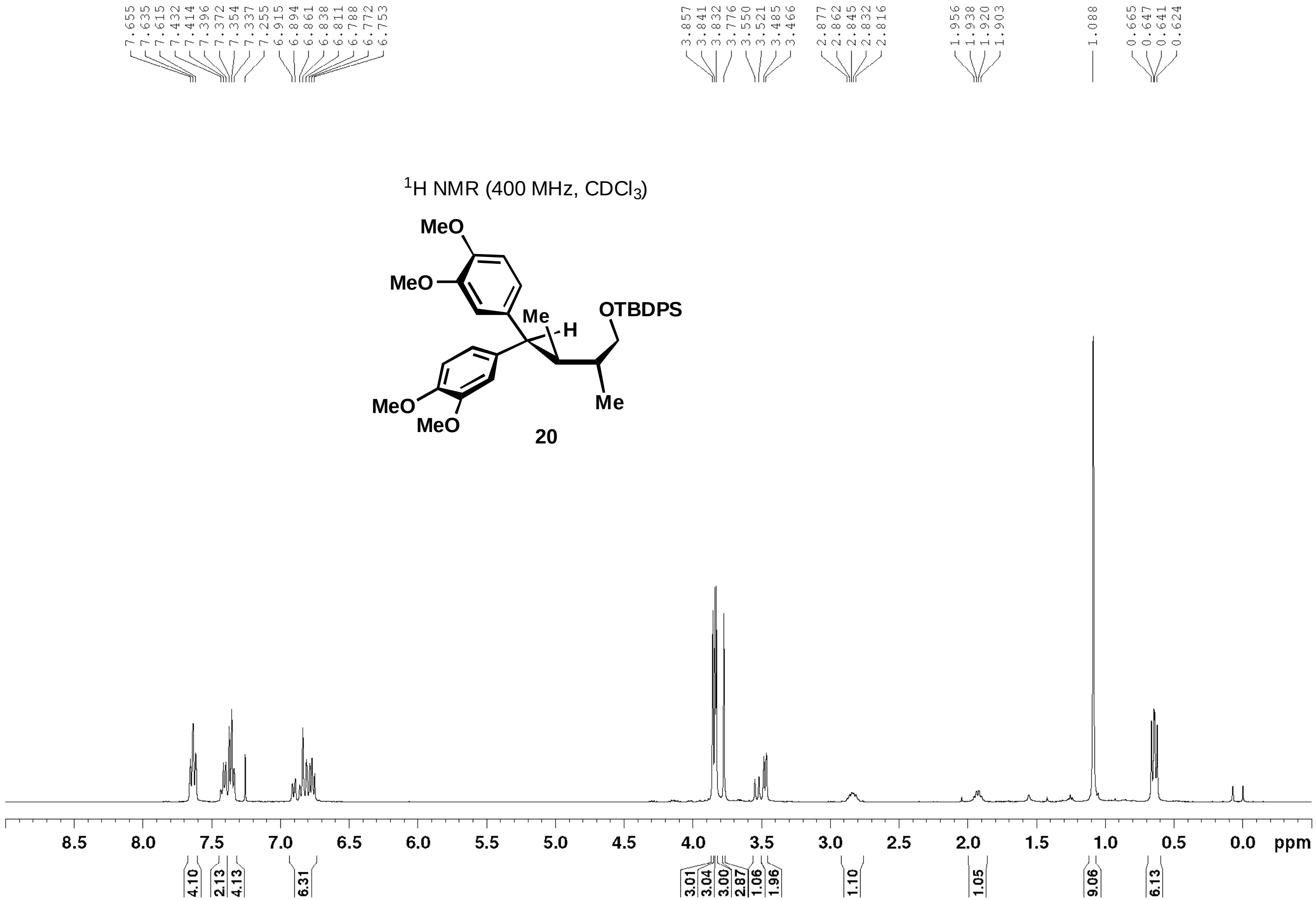

148.68
147.99
147.77
147.45
139.79
137.72
119.79
118.36
110.90
109.93
109.87
90.33
77.32
77.00
76.68
73.76
55.83
55.76
49.40
40.60
15.60
14.45
13C NMR (100 MHz, CDCl3)
MeO
MeO
Me
O
MeO
MeO
Me
17
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.268
6.805
6.786
6.718
6.710
6.698
6.643
3.861
3.821
3.814
3.641
3.616
3.592
3.516
3.501
3.490
3.474
2.962
2.945
2.924
2.907
1.714
1.039
1.021
0.00
1H NMR (400 MHz, CDCl3)
OH
MeO
Me
MeO
Me
OMe
OMe
18
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
ppm
2.09
3.01
1.00
6.01
6.11
1.05
1.02
1.03
3.00
1.05
3.00


148.44
148.28
147.44
147.38
139.93
135.88
135.74
134.78
121.88
121.46
112.79
112.70
110.84
110.57
77.32
77.00
76.68
65.98
55.81
55.75
39.73
15.51
13.99
^{13}C NMR (100 MHz, $CDCl_3$)
OH
MeO
Me
MeO
Me
OMe
OMe
18
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

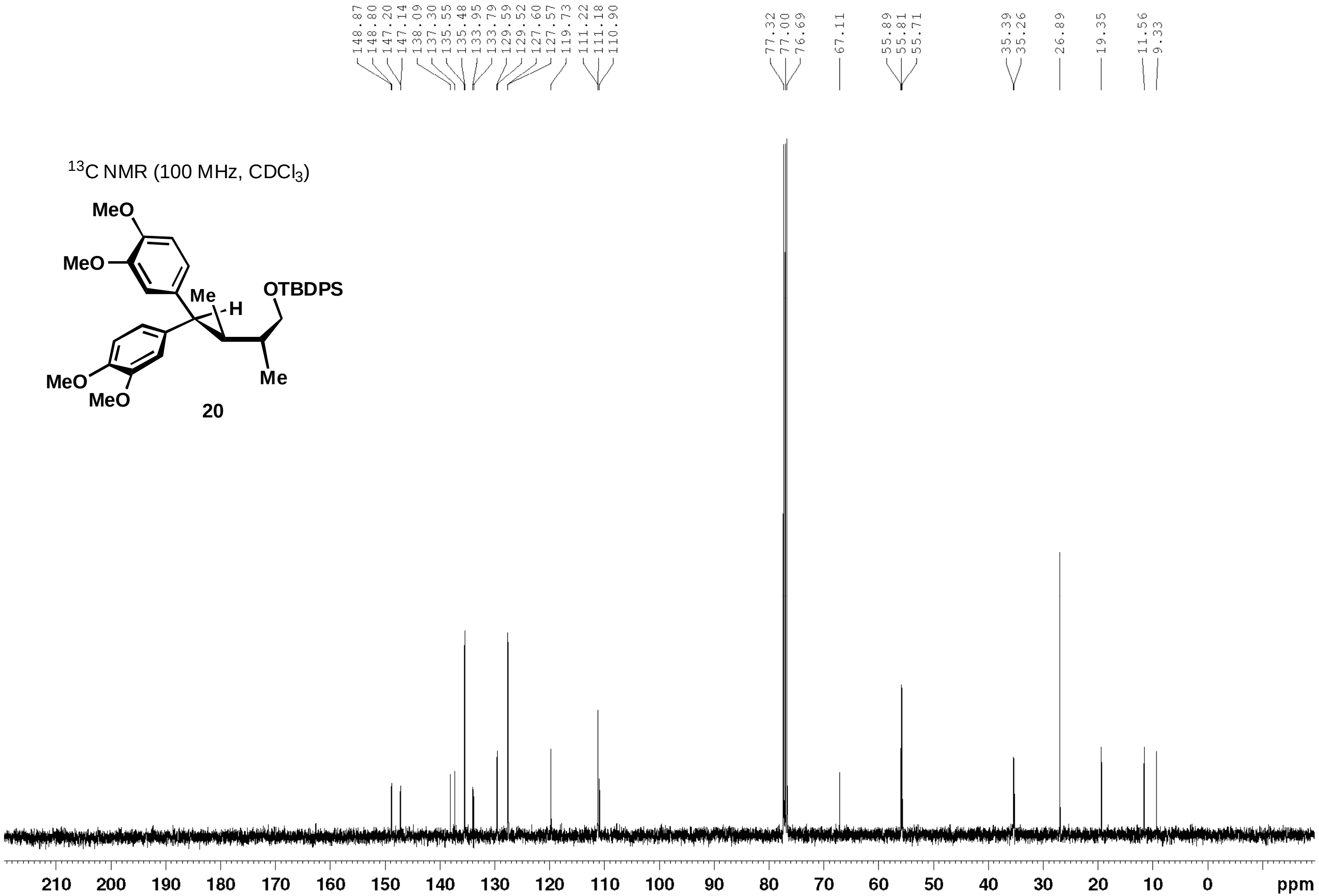

7.651
7.635
7.620
7.618
7.444
7.426
7.409
7.385
7.367
7.349
7.258
7.094
7.091
7.084
7.059
7.031
6.809
6.789
6.722
6.699
3.850
3.832
3.770
3.459
3.434
3.422
3.408
3.382
3.183
3.166
3.149
3.132
2.190
2.091
2.074
2.057
2.044
1.101
0.806
0.789
0.764
0.747
-0.000
1H NMR (400 MHz, CDCl3)
MeO
MeO
Me
OH
OTBDPS
MeO
MeO
Me
19
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 ppm
3.95
2.10
3.95
1.96
1.97
0.94
0.95
3.10
5.75
2.99
1.99
1.00
0.88
1.04
8.96
3.02
3.00


148.54
147.25
140.69
139.56
135.56
135.51
133.71
133.56
129.67
129.62
127.67
127.62
118.06
117.53
110.59
110.54
109.38
109.26
81.76
77.32
77.00
76.68
67.86
55.75
38.50
34.73
26.92
19.32
12.26
8.48
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
MeO
Me
OH
OTBDPS
MeO
MeO
Me
19
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



^{1}H NMR (400 MHz, CDCl$_3$)
MeO
MeO
Me
H
OTBDPS
MeO
MeO
Me
20
7.655
7.635
7.615
7.432
7.414
7.396
7.372
7.354
7.337
7.255
6.915
6.894
6.861
6.838
6.811
6.788
6.772
6.753
3.857
3.841
3.832
3.776
3.550
3.521
3.485
3.466
2.877
2.862
2.845
2.832
2.816
1.956
1.938
1.920
1.903
1.088
0.665
0.647
0.641
0.624
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
ppm
4.10
2.13
4.13
6.31
3.01
3.04
3.00
2.87
1.06
1.96
1.10
1.05
9.06
6.13

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



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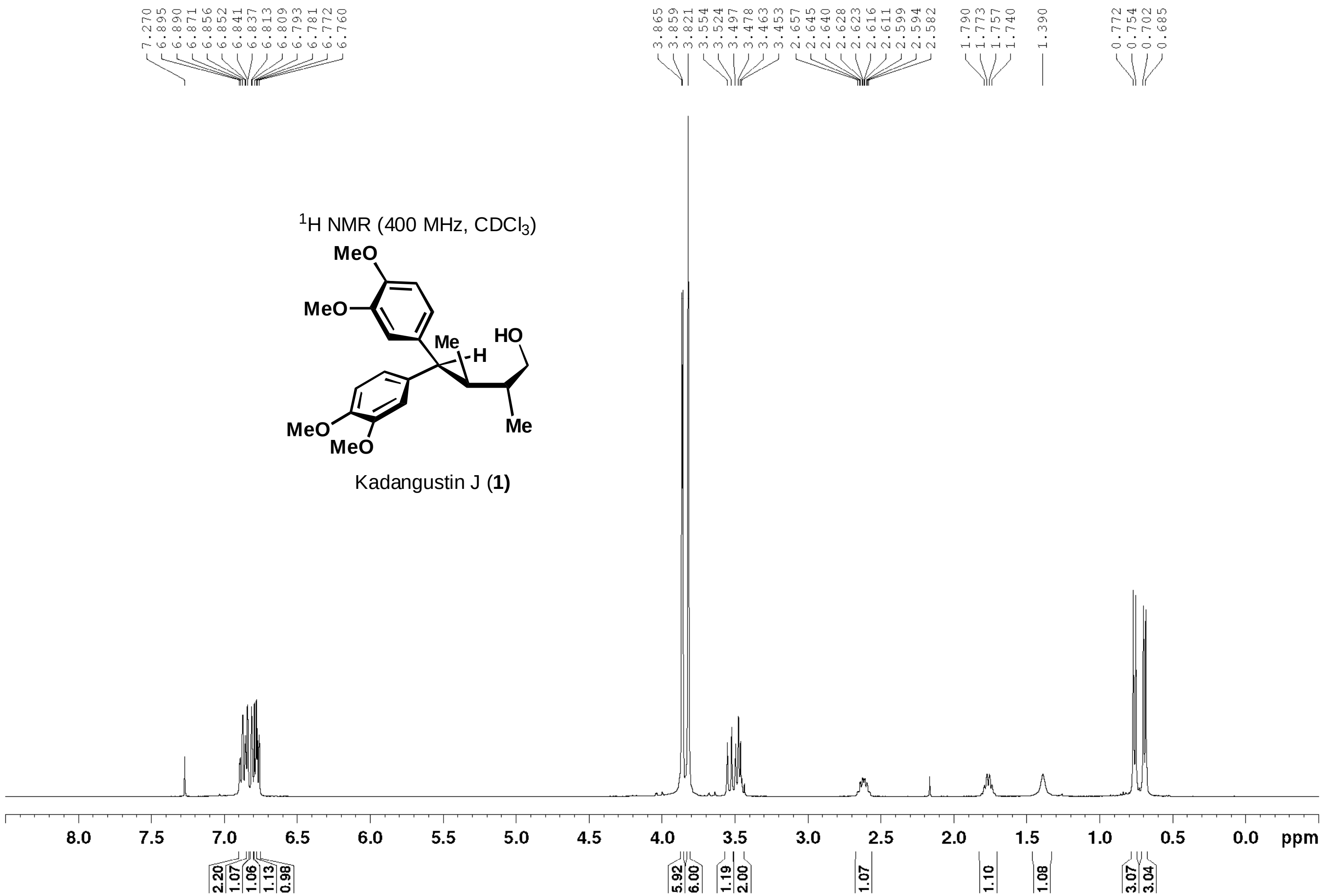
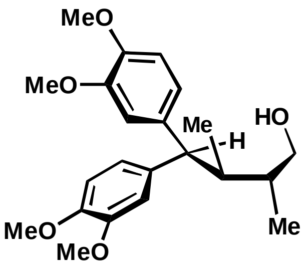
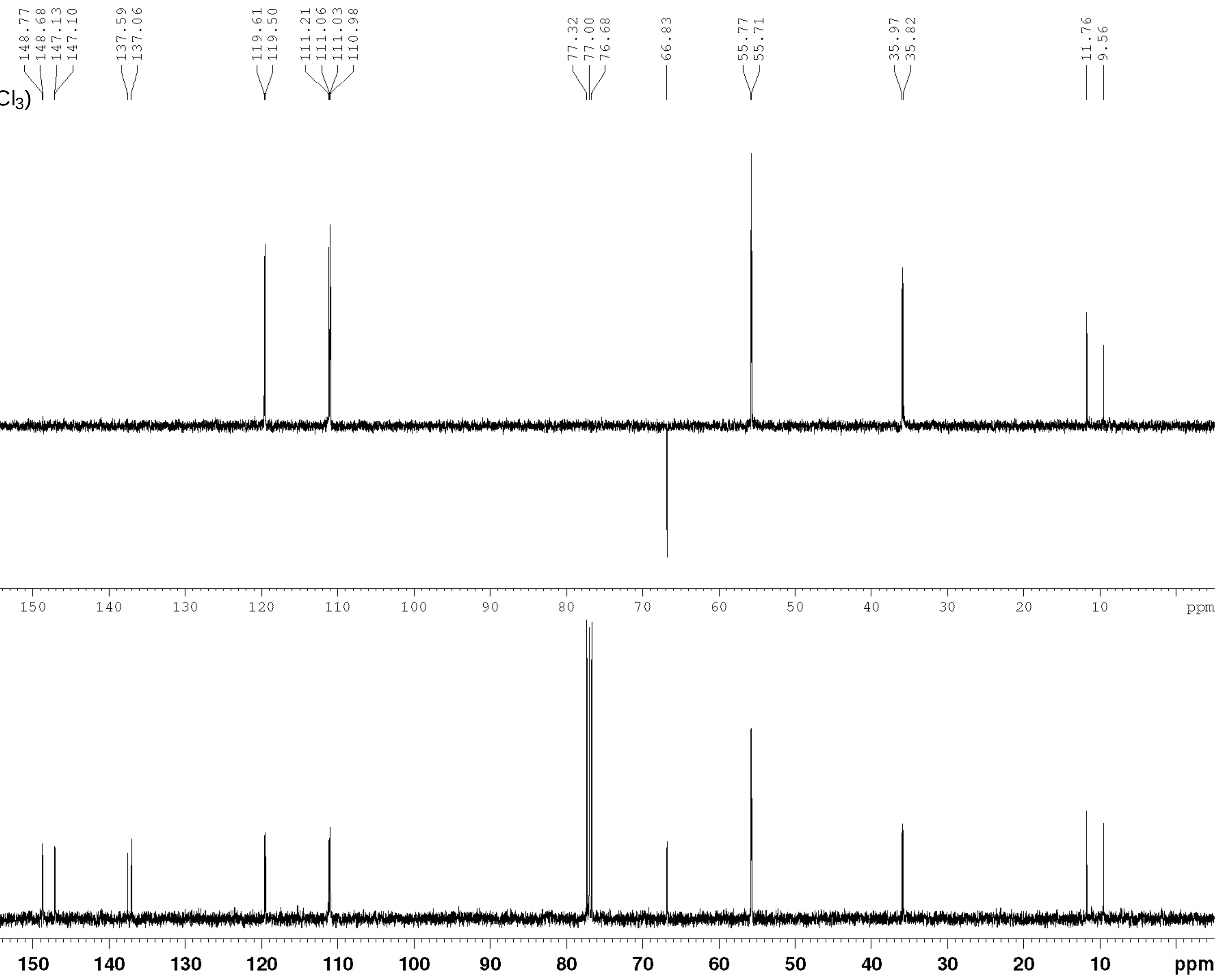

1H NMR (400 MHz, CDCl3)
MeO
MeO
Me
H
HO
MeO
MeO
Me
Kadangustin J (1)
7.270 6.895 6.890 6.871 6.856 6.852 6.841 6.837 6.813 6.809 6.793 6.781 6.772 6.760
3.865 3.859 3.821 3.554 3.524 3.497 3.478 3.463 3.453 2.657 2.645 2.640 2.628 2.623 2.616 2.611 2.599 2.594 2.582
1.790 1.773 1.757 1.740
1.390
0.772 0.754 0.702 0.685
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 ppm
2.20 1.07 1.06 1.13 0.98
5.92 6.00
1.19 2.00
1.07
1.10
1.08
3.07 3.04

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

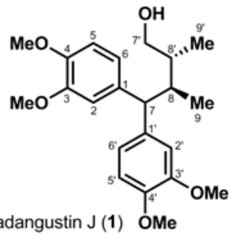


Kadangustin J (**1**)



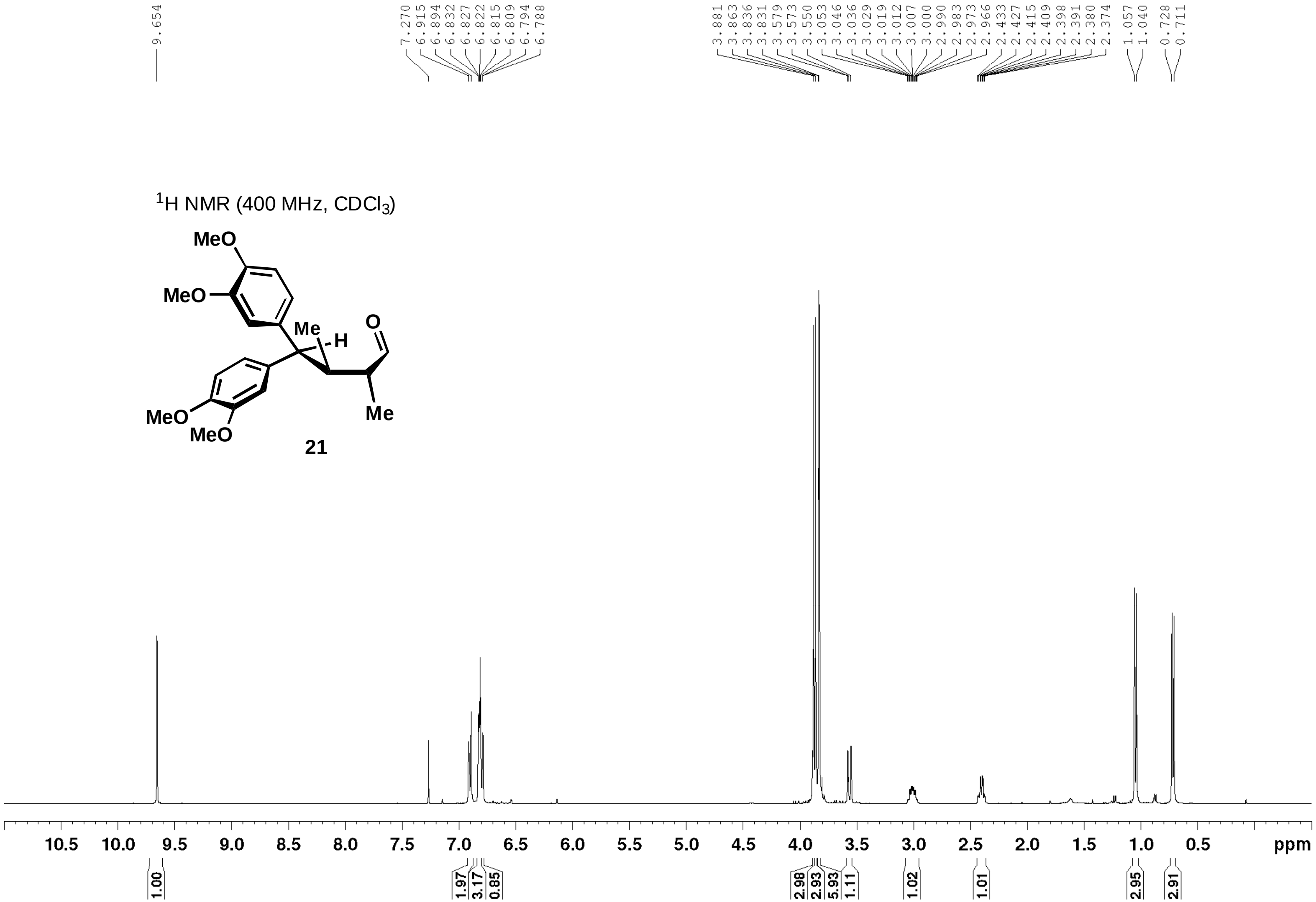
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Table S1: ^{1}H and ^{13}C Chemical Shift (*ppm*) Comparison of Synthetic and Natural Kadangustin **1**

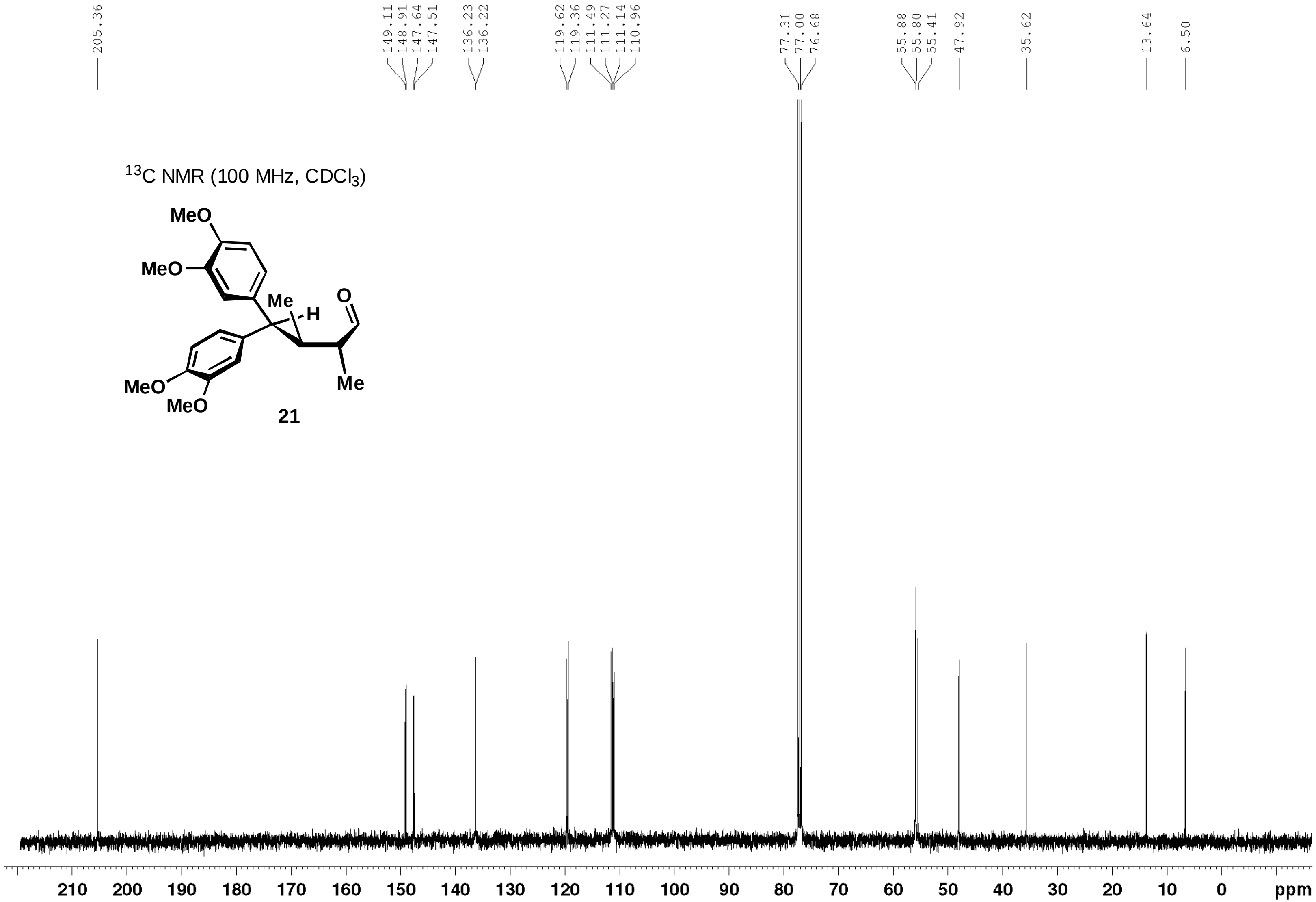
No.	Synthetic **1** by us ($CDCl_3$, 400 MHz)	Natural **1**[1] ($CDCl_3$, 500 MHz)	Synthetic **1** by others[2] ($CDCl_3$, 400 MHz)	Synthetic **1** by us ($CDCl_3$, 100 MHz)	Natural **1**[1] ($CDCl_3$, 126 MHz)	Synthetic **1** by others[2] ($CDCl_3$, 100 MHz)
	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_c	δ_c	δ_c
2	6.84 *d* (1.6)	6.83–6.80 *overlap*	6.88–6.74 *m*	111.2	111.5	111.3
5	6.78 *d* (8.0)	6.80–6.78 *overlap*	6.88–6.74 *m*	111.1	111.4	111.2
6	6.88 *dd* (1.6, 8.0)	6.78–6.76 *overlap*	6.88–6.74 *m*	119.5	119.7	119.5
7	3.54 *d* (12.0)	3.53 *d* (11.8)	3.52 *d* (12.0)	55.8	55.9	77.2
8	2.66–2.58 *m*	2.63–2.59 *m*	2.60 *m*	35.9	36.0	35.8
9	0.69 *d* (6.8)	0.68 *d* (7.0)	0.68 *d* (8.0)	11.8	11.8	11.7
2′	6.81 *d* (1.6)	6.83–6.80 *overlap*	6.88–6.74 *m*	111.0	111.3	111.1
5′	6.77 *d* (8.0)	6.80–6.78 *overlap*	6.88–6.74 *m*	111.0	111.3	111.1
6′	6.86 *dd* (1.6, 8.0)	6.78–6.76 *overlap*	6.88–6.74 *m*	119.6	119.8	119.6
7′	3.50–3.43 *m*	3.50–3.46 *m*	3.45*m*	66.9	67.0	66.8
8′	1.81–1.72 *m*	1.78–1.74 *m*	1.75 *m*	36.0	36.1	35.9
9′	0.76 *d* (7.2)	0.75 *d* (7.0)	0.74 *d* (4.0)	9.6	9.6	9.5
4 × OCH_3	3.82 *s*, 3.82 *s*, 3.86 *s*, 3.87 *s*	3.82 *s*, 3.82 *s*, 3.86 *s*, 3.86 *s*	3.80 *s*, 3.80 *s*, 3.84 *s*, 3.85 *s*	55.7 (2C), 55.8 (2C)	55.8 (2C), 55.9 (2C)	55.7 (4C)
1				137.1	137.2	137.1
3				148.7	148.9	148.7
4				147.1	147.3	147.1
1′				137.6	137.7	137.6
3′				148.8	149.0	148.8
4′		Kadangustin J (**1**)		147.1	147.3	147.1

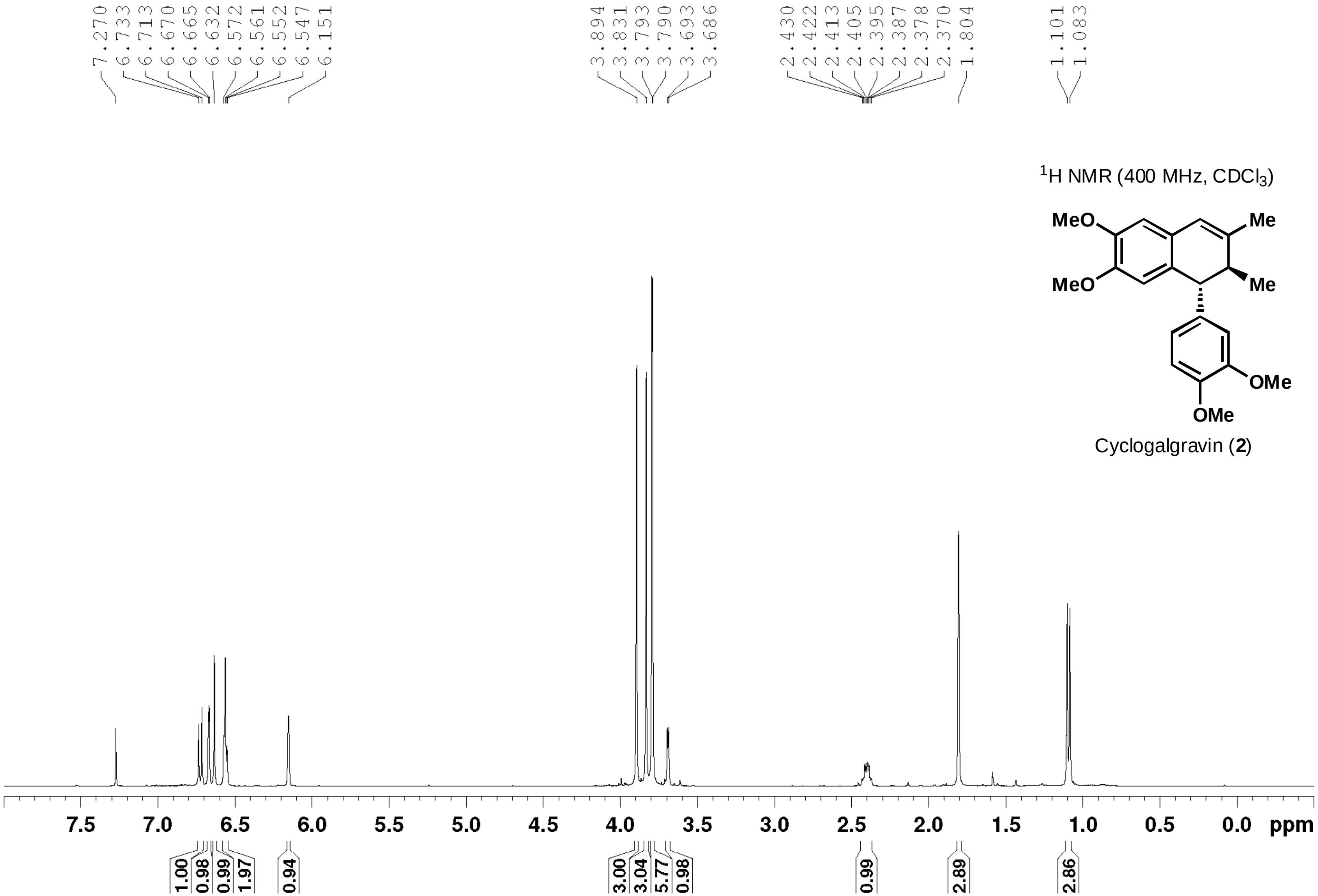
(1) Gao, X.-M.; Pu, J.-X.; Huang, S.-X.; Yang, L.-M.; Huang, H.; Xiao, W.-L.; Zheng, Y.-T.; Sun, H.-D. *J. Nat. Prod.* **2008**, *71*, 558–563. (2) Rye, C. E.; Barker, D. *J. Org. Chem.* **2011**, *76*, 6636–6648.

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

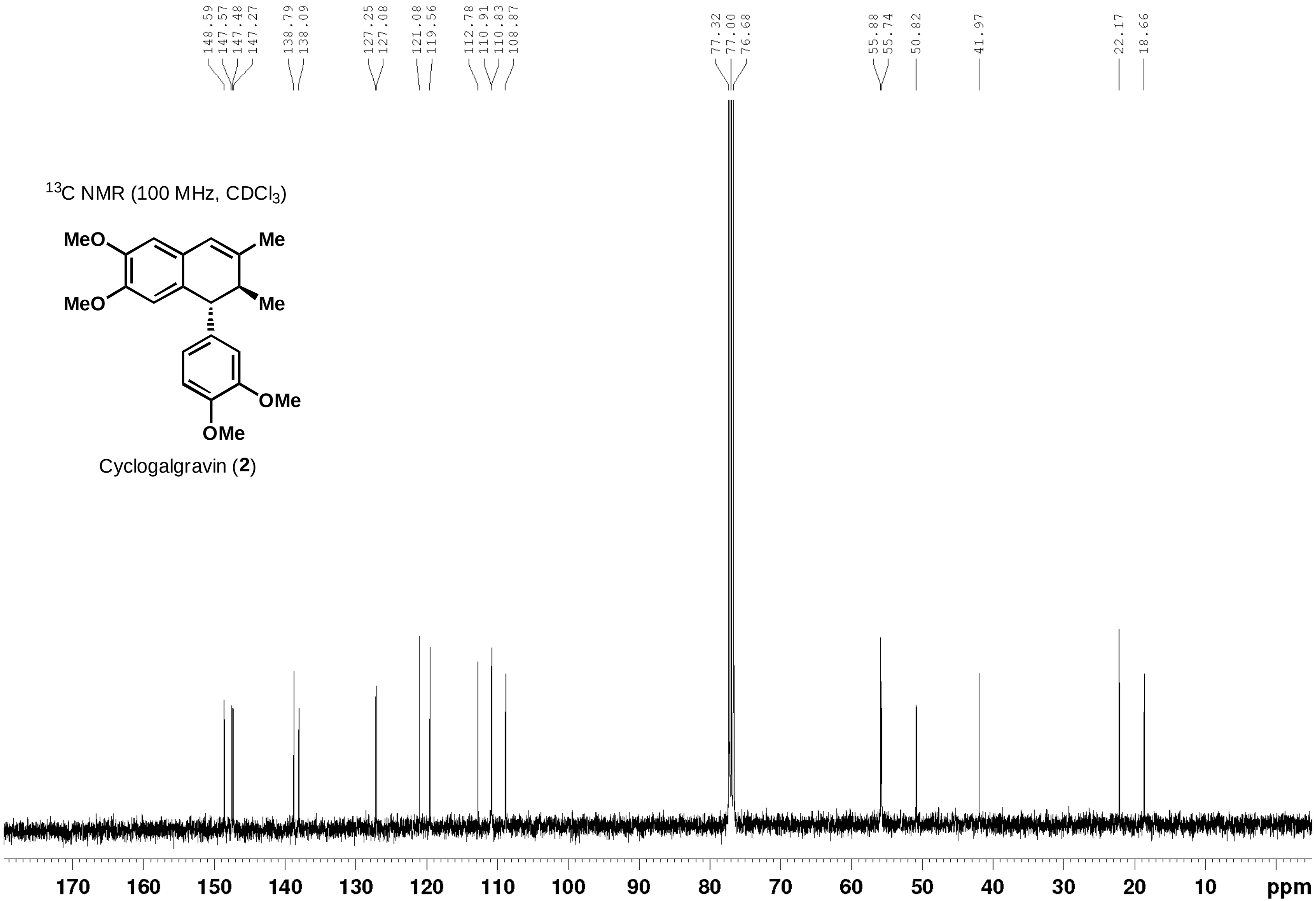


21


205.36
149.11
148.91
147.64
147.51
136.23
136.22
119.62
119.36
111.49
111.27
111.14
110.96
77.31
77.00
76.68
55.88
55.80
55.41
47.92
35.62
13.64
6.50
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
MeO
Me
H
O
MeO
MeO
Me
21
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



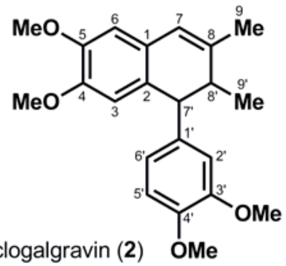
Cyclogalgravin (**2**)



Cyclogalgravin (**2**)

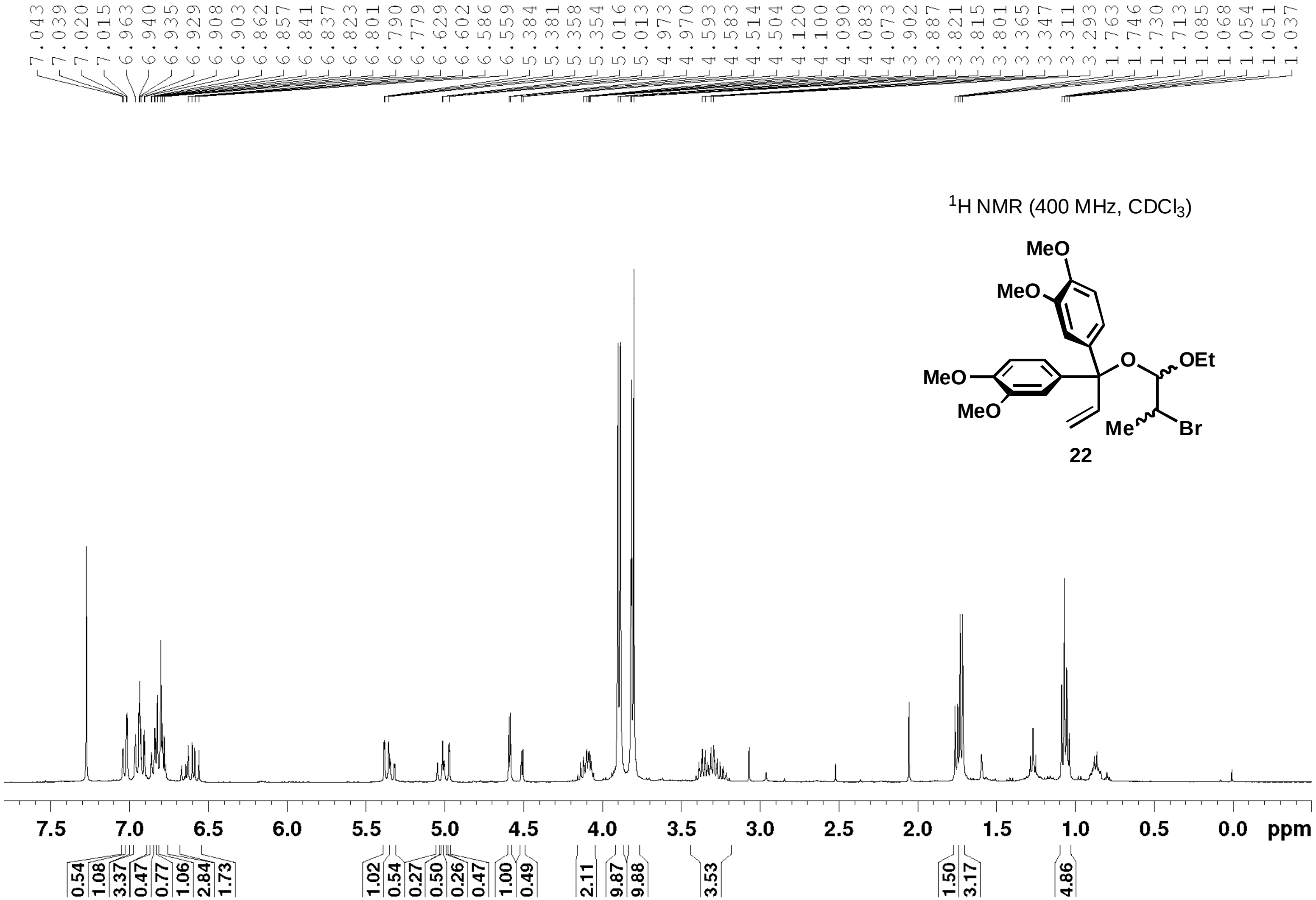
Table S2: ^{1}H and ^{13}C Chemical Shift (*ppm*) Comparison of Synthetic and Natural Cyclogalgravin **2**

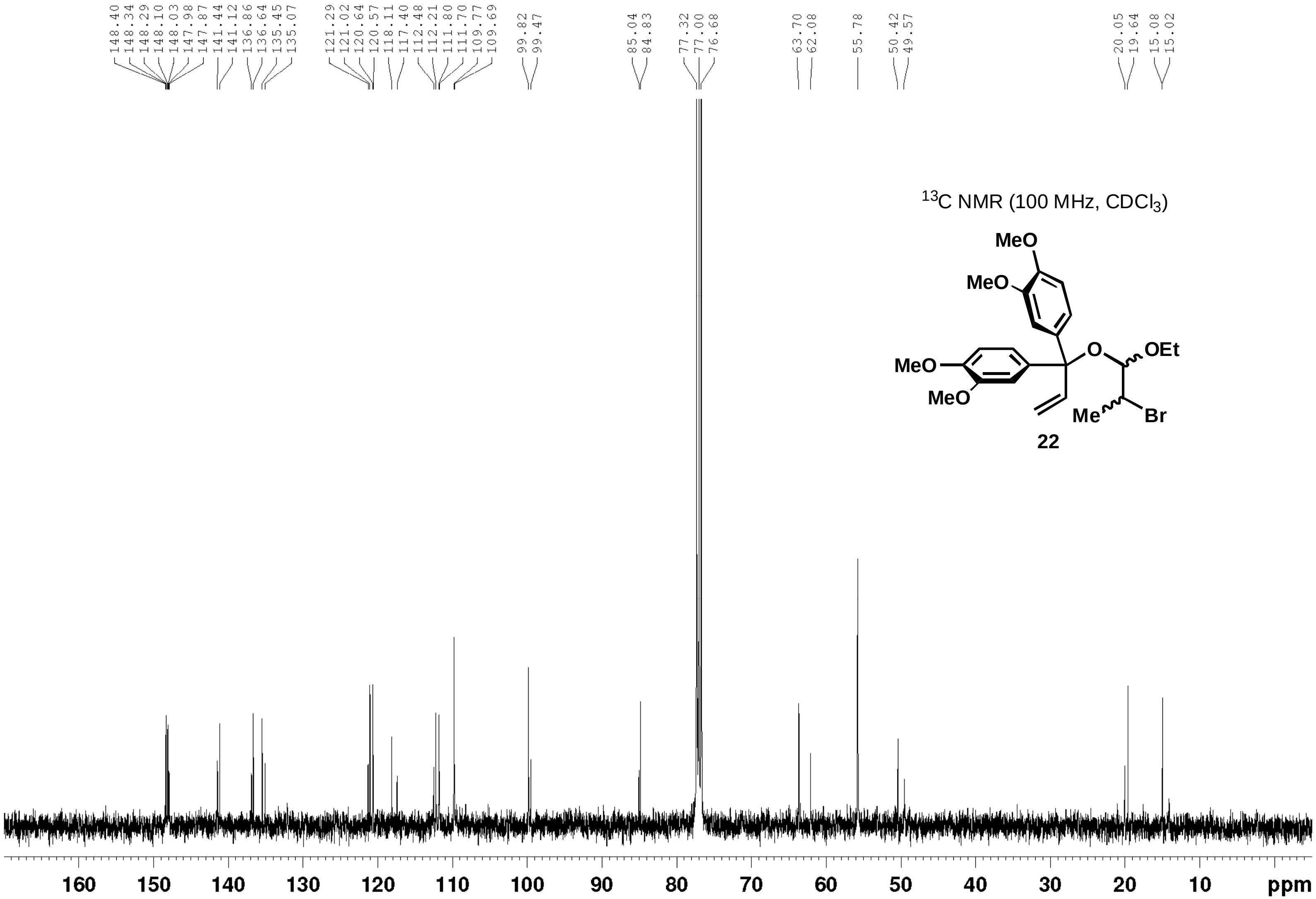
No.	Synthetic **2** by us (CDCl$_3$, 400 MHz)	Natural **2**[3] (CDCl$_3$, 500 MHz)	Synthetic **2** by others[2] (CDCl$_3$, 300 MHz)	Synthetic **2** by us (CDCl$_3$, 100 MHz)	Natural **2**[3] (CDCl$_3$, 126 MHz)	Synthetic **2** by others[2] (CDCl$_3$, 75 MHz)
	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_c	δ_c	δ_c
3	6.56 *s*	6.48 *s*	6.54–6.57 *m*	112.8	113.0	112.8
6	6.63 *s*	6.55 *s*	6.62 *s*	108.9	109.1	108.9
7	6.15 br *s*	6.11 br *s*	6.14 *s*	121.1	121.1	121.1
9	1.80 *s*	1.73 *d* (1.0)	1.79 *d* (3.0)	22.2	22.1	22.1
2′	6.67 *d* (2.0)	6.59 *d* (2.0)	6.66 *d* (3.0)	110.9	111.1	111.0
5′	6.72 *d* (8.0)	6.64 *d* (8.5)	6.72 *d* (9.0)	110.8	111.0	110.9
6′	6.56 *dd* (2.0, 8.0)	6.49 *dd* (2.0, 8.5)	6.54–6.57 *m*	119.6	119.6	119.6
7′	3.69 *d* (2.8)	3.60 *d* (3.5)	3.67 *d* (3.0)	50.8	50.9	50.8
8′	2.40 *dq* (3.2, 6.8)	2.32 *dq* (3.5, 7.0)	2.40 *m*	42.0	42.0	42.0
9′	1.09 *d* (7.2)	1.01 *d* (7.0)	1.08 *d* (9.0)	18.7	18.7	18.6
4 × OCH$_3$	3.79 *s*, 3.79 *s*, 3.83 *s*, 3.89 *s*	3.71 *s*, 3.71 *s*, 3.75 *s*, 3.81 *s*	3.78 *s*, 3.78 *s*, 3.82 *s*, 3.88 *s*	55.7 (2C), 55.9 (2C)	55.8 (2C), 55.9 (2C)	55.7, 55.8, 55.9 (2C)
1				127.1	127.3	127.1
2				127.3	127.4	127.3
4				147.5	147.6	147.5
5				147.6	147.5	147.6
8				138.8	138.8	138.8
1′				138.1	138.2	138.1
3′				148.6	148.7	148.6
4′				147.3	147.8	147.3

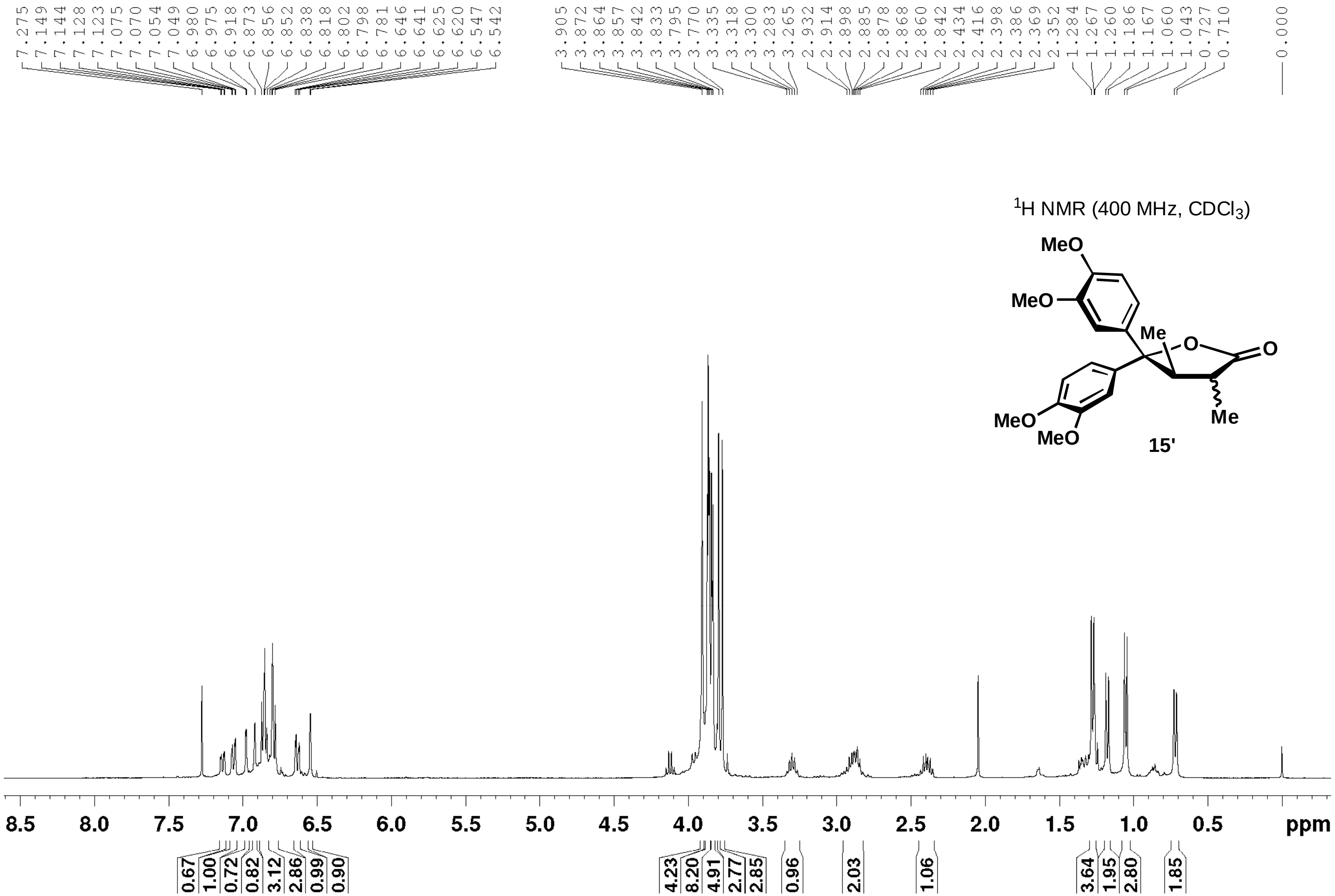


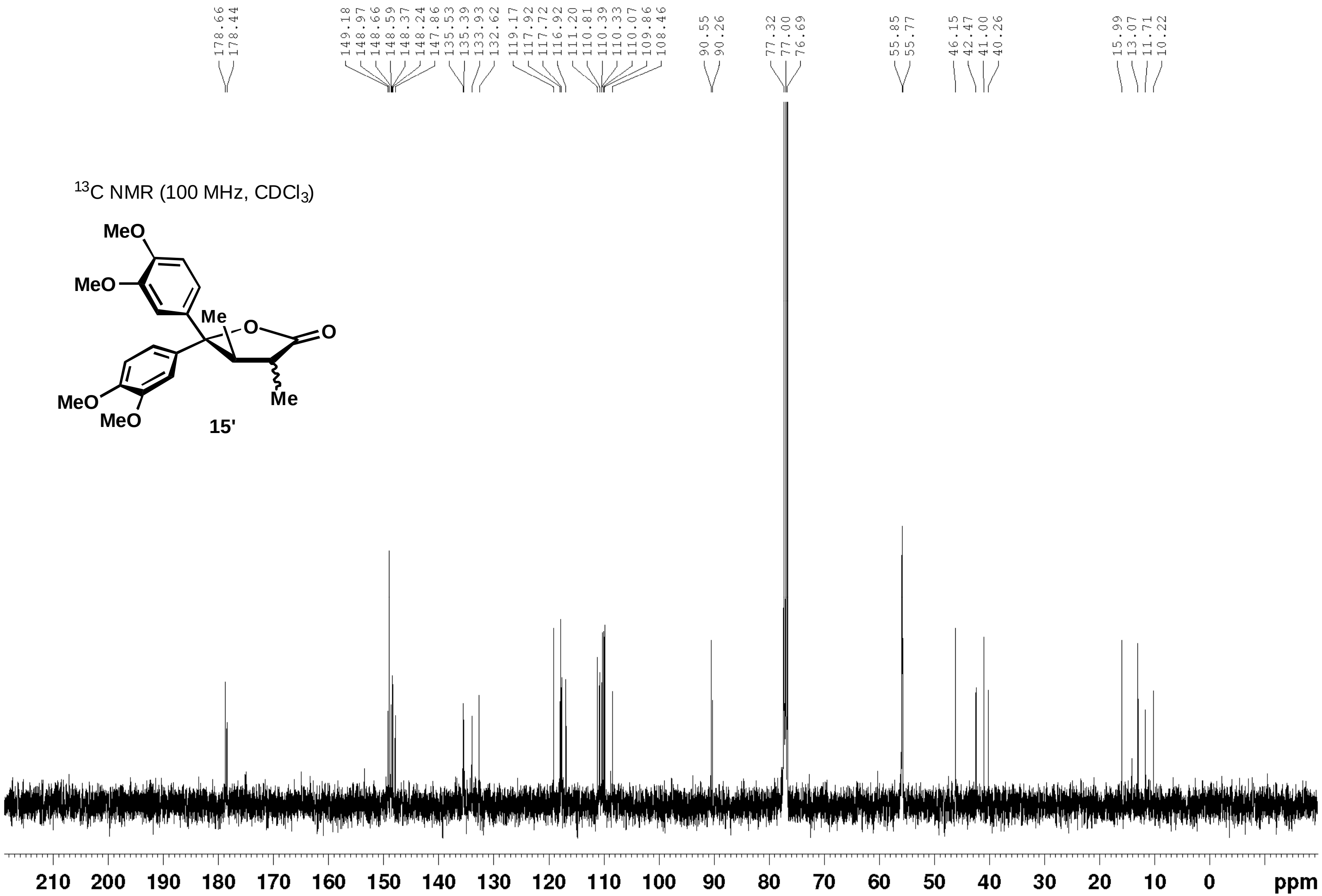
Cyclogalgravin (**2**)

(3) da Silva, T.; Lopes, L. M. X. *Phytochemistry* **2006**, *67*, 929–937.

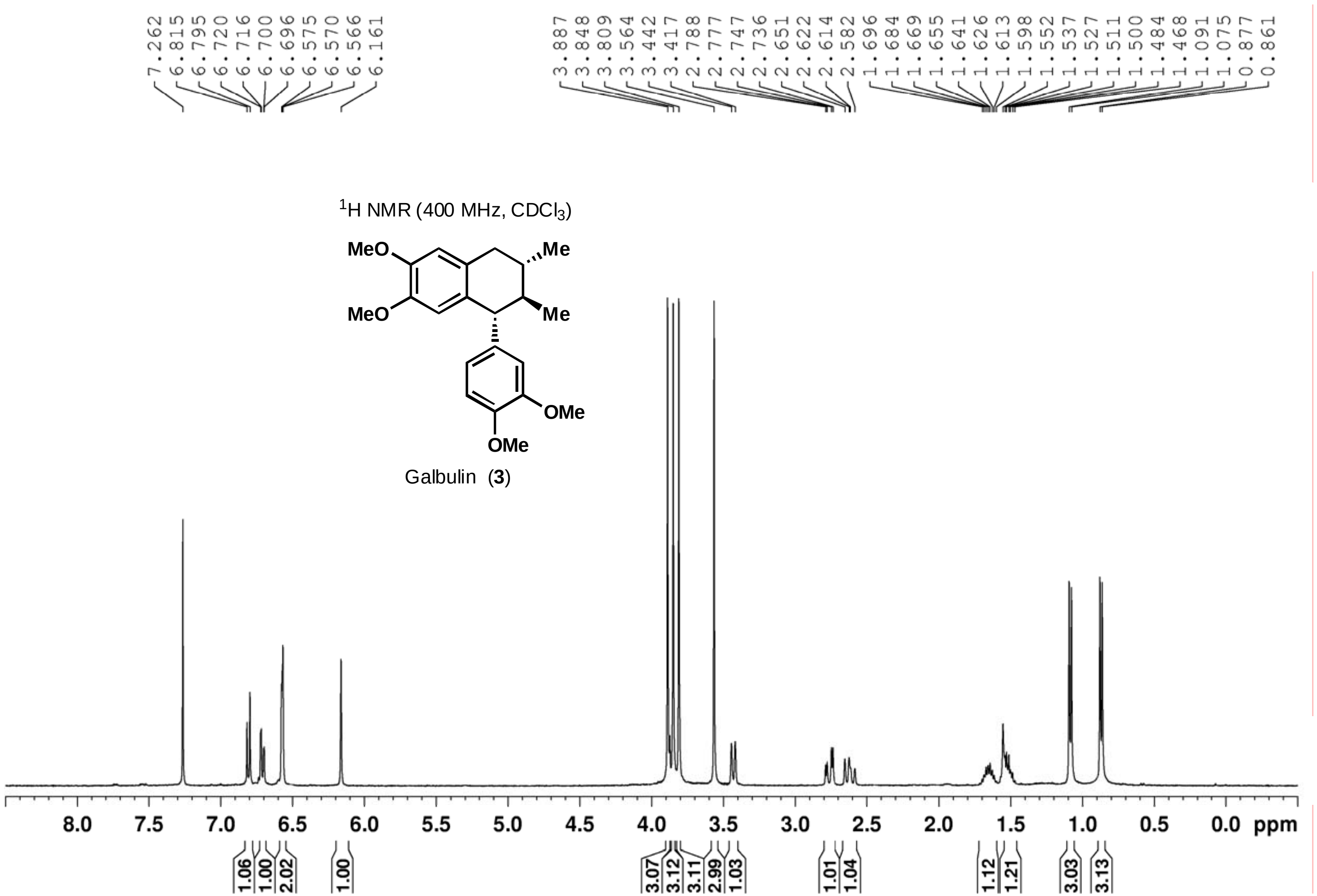

7.043
7.039
7.020
7.015
6.963
6.940
6.935
6.929
6.908
6.903
6.862
6.857
6.841
6.837
6.823
6.801
6.790
6.779
6.629
6.602
6.586
6.559
5.384
5.381
5.358
5.354
5.016
5.013
4.973
4.970
4.593
4.583
4.514
4.504
4.120
4.100
4.090
4.083
4.073
3.902
3.887
3.821
3.815
3.801
3.365
3.347
3.311
3.293
1.763
1.746
1.730
1.713
1.085
1.068
1.054
1.051
1.037
^{1}H NMR (400 MHz, $CDCl_3$)
MeO
MeO
MeO
MeO
O
OEt
Me
Br
22
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
ppm
0.54
1.08
3.37
0.47
0.77
1.06
2.84
1.73
1.02
0.54
0.27
0.50
0.26
0.47
1.00
0.49
2.11
9.87
9.88
3.53
1.50
3.17
4.86


148.40
148.34
148.29
148.10
148.03
147.98
147.87
141.44
141.12
136.86
136.64
135.45
135.07
121.29
121.02
120.64
120.57
118.11
117.40
112.48
112.21
111.80
111.70
109.77
109.69
99.82
99.47
85.04
84.83
77.32
77.00
76.68
63.70
62.08
55.78
50.42
49.57
20.05
19.64
15.08
15.02
13C NMR (100 MHz, CDCl3)
MeO
MeO
O
OEt
MeO
MeO
Me
Br
22
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

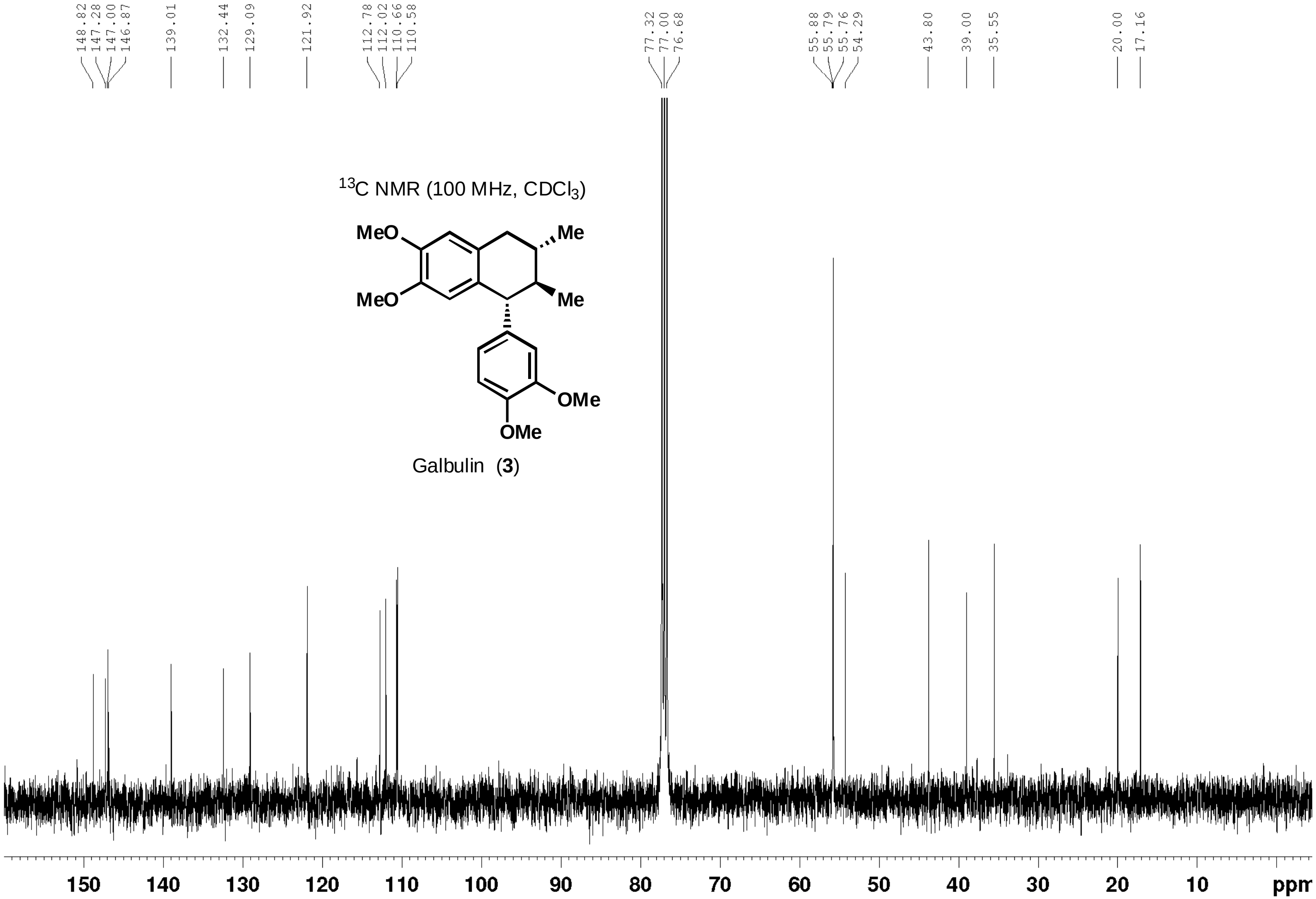

7.275 7.149 7.144 7.128 7.123 7.075 7.070 7.054 7.049 6.980 6.975 6.918 6.873 6.856 6.852 6.838 6.818 6.802 6.798 6.781 6.646 6.641 6.625 6.620 6.547 6.542
3.905 3.872 3.864 3.857 3.842 3.833 3.795 3.770 3.335 3.318 3.300 3.283 3.265 2.932 2.914 2.898 2.885 2.878 2.868 2.860 2.842 2.434 2.416 2.398 2.386 2.369 2.352 1.284 1.267 1.260 1.186 1.167 1.060 1.043 0.727 0.710
0.000
1H NMR (400 MHz, CDCl3)
MeO
MeO
Me
O
O
MeO
MeO
Me
15'
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 ppm
0.67 1.00 0.72 0.82 3.12 2.86 0.99 0.90
4.23 8.20 4.91 2.77 2.85
0.96
2.03
1.06
3.64 1.95 2.80
1.85


178.66
178.44
149.18
148.97
148.66
148.59
148.37
148.24
147.86
135.53
135.39
133.93
132.62
119.17
117.92
117.72
116.92
111.20
110.81
110.39
110.33
110.07
109.86
108.46
90.55
90.26
77.32
77.00
76.69
55.85
55.77
46.15
42.47
41.00
40.26
15.99
13.07
11.71
10.22
^{13}C NMR (100 MHz, $CDCl_3$)
MeO
MeO
Me
O
O
MeO
MeO
Me
15'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

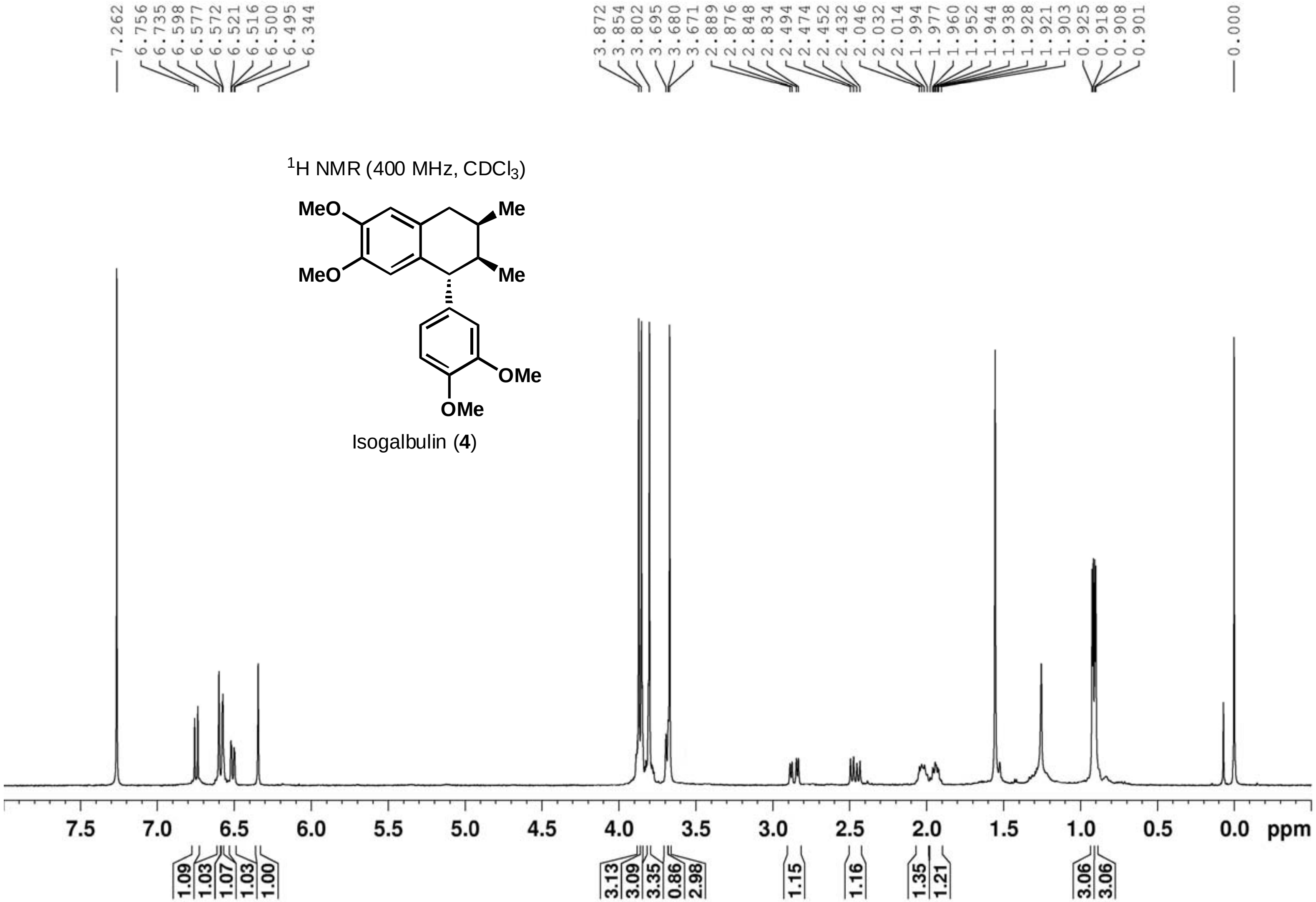


Galbulin (**3**)

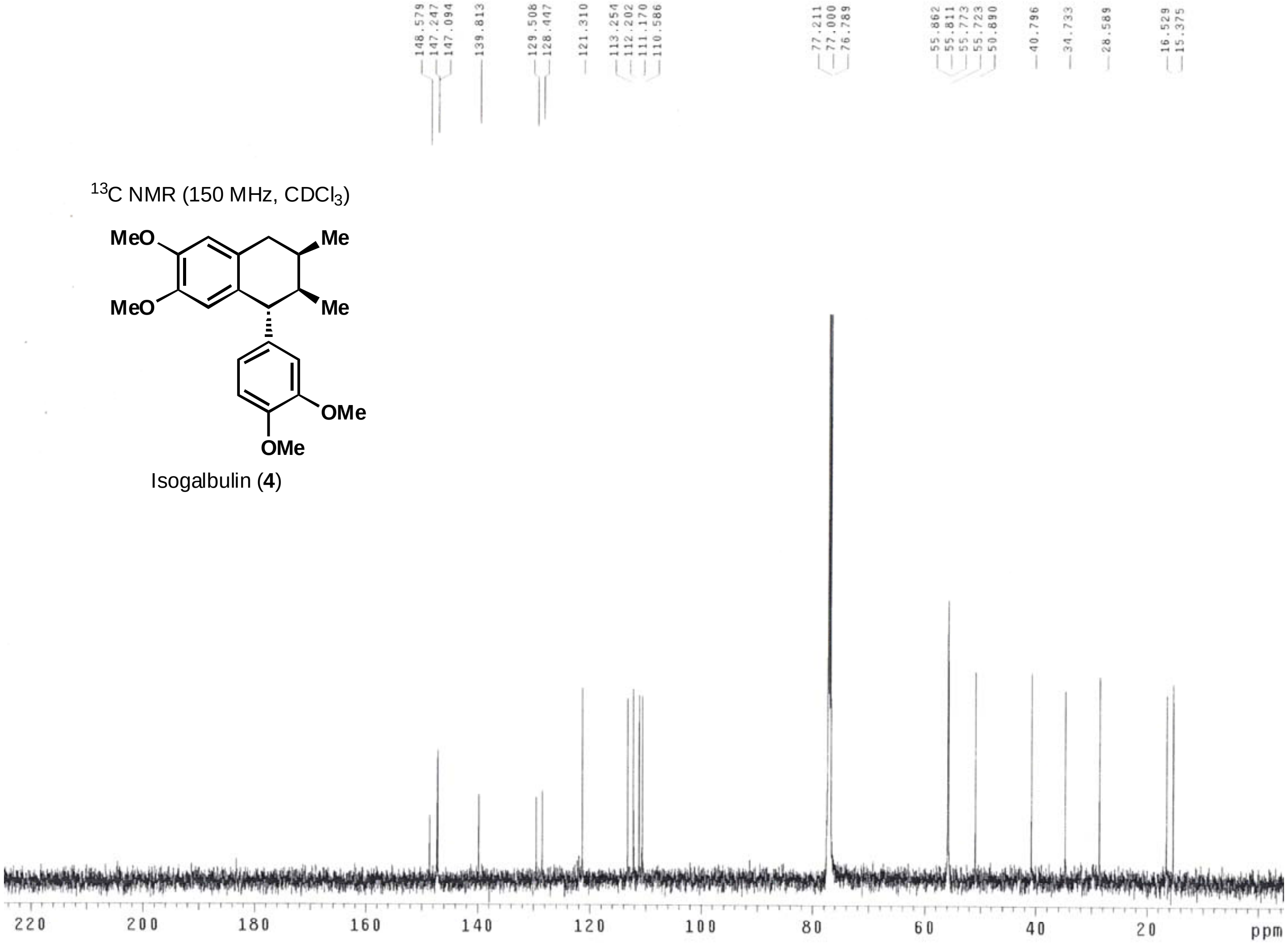


^{13}C NMR (100 MHz, $CDCl_3$)

Galbulin (**3**)



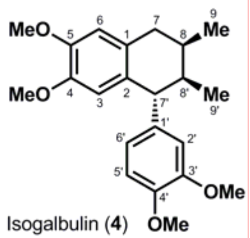
Isogalbulin (**4**)



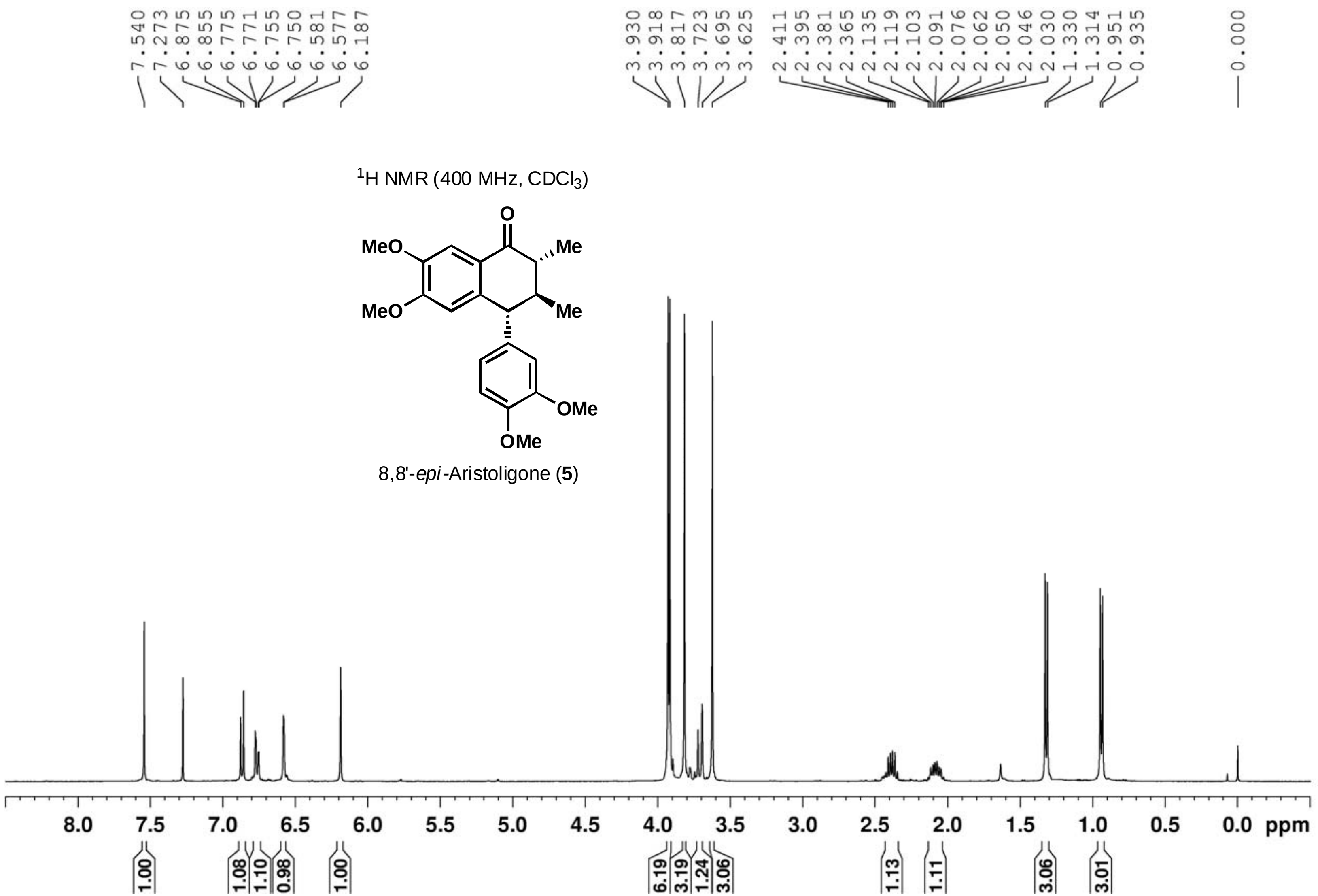
^{13}C NMR (150 MHz, $CDCl_3$)

Isogalbulin (**4**)

Table S3: ^{1}H and ^{13}C Chemical Shift (*ppm*) Comparison of Synthetic and Natural Isogalbulin **4**

No.	Synthetic **4** by us ($CDCl_3$, 400 MHz)	Natural **4**[4] ($CDCl_3$, 90 MHz)	Synthetic **4** by us ($CDCl_3$, 150 MHz)	Synthetic **4** by others[5] ($CDCl_3$, 75 MHz)
	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_c	δ_c
3	6.34 *s*	6.37 *s*	113.3	113.4
6	6.60 *s*	6.64 *s*	110.6	110.7
7	2.46 *dd* (8.0, 16.8) 2.86 *dd* (5.2, 16.8)	2.48 *dd* (7.0, 18.0) 2.88 *dd* (5.0, 18.0)	40.8	41.0
8	1.97–1.90 *m*	2.00 *m*	28.6	28.7
9	0.92 *d* (6.8)	0.92 *d* (7.0)	15.4	15.5
2′	6.58 *d* (2.0)	6.60 *d* (2.0)	112.2	112.3
5′	6.75 *d* (8.4)	6.80 *d* (8.0)	111.2	111.3
6′	6.51 *dd* (2.0, 8.4)	6.52 *dd* (2.0, 8.0)	121.3	121.5
7′	3.69 *d* (6.0)	3.63 *d* (6.0)	50.9	51.0
8′	2.07–1.98 *m*	2.00 *m*	34.7	34.9
9′	0.91 *d* (6.8)	0.92 *d* (7.0)	16.5	16.7
4 × OCH_3	3.67 *s*, 3.80 *s*, 3.85 *s*, 3.87 *s*	3.70 *s*, 3.83 *s*, 3.88 *s*, 3.90 *s*	55.72, 55.77, 55.81, 55.86	55.87, 55.91, 55.95, 56.00
1	 Isogalbulin (**4**)		128.5	128.6
2			129.5	129.6
4			147.1	147.2
5			147.3	147.4
1′			139.8	140.0
3′			148.6	148.7
4′			147.1	147.2

(4) Li, L.-n.; Xue, H. *Planta Med.* **1985**, *51*, 217–219. (5) Kasatkin, A. N.; Checksfield, G.; Whitby, R. J. *J. Org. Chem.* **2000**, *65*, 3236–3238.



8,8'-*epi*-Aristoligone (**5**)

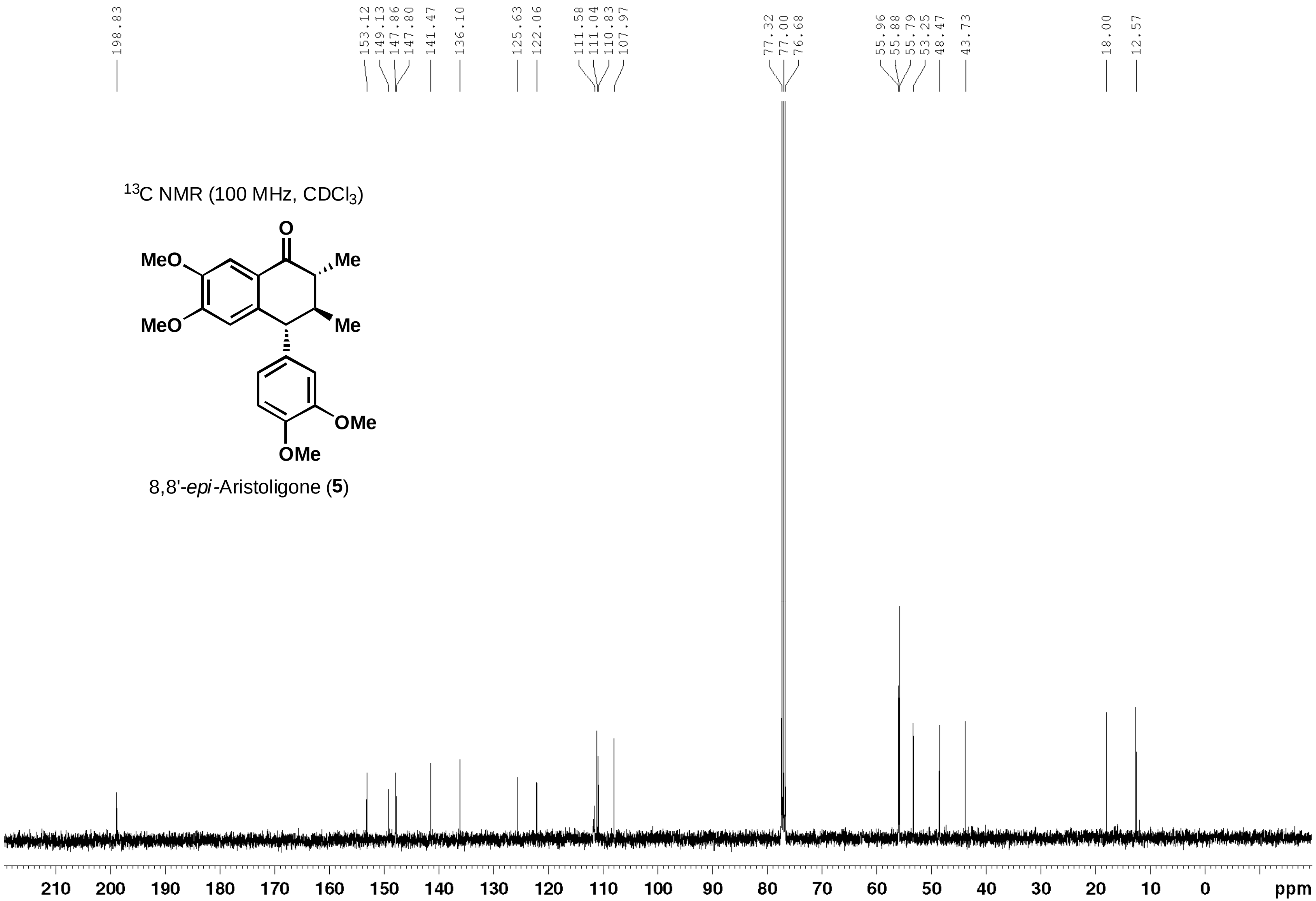
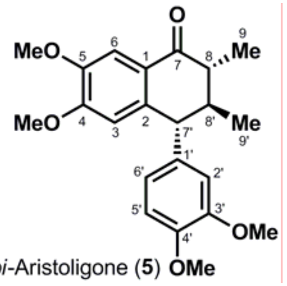

198.83
153.12
149.13
147.86
147.80
141.47
136.10
125.63
122.06
111.58
111.04
110.83
107.97
77.32
77.00
76.68
55.96
55.88
55.79
53.25
48.47
43.73
18.00
12.57
^{13}C NMR (100 MHz, $CDCl_3$)
O
MeO
Me
MeO
Me
OMe
OMe
8,8'-*epi*-Aristoligone (**5**)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

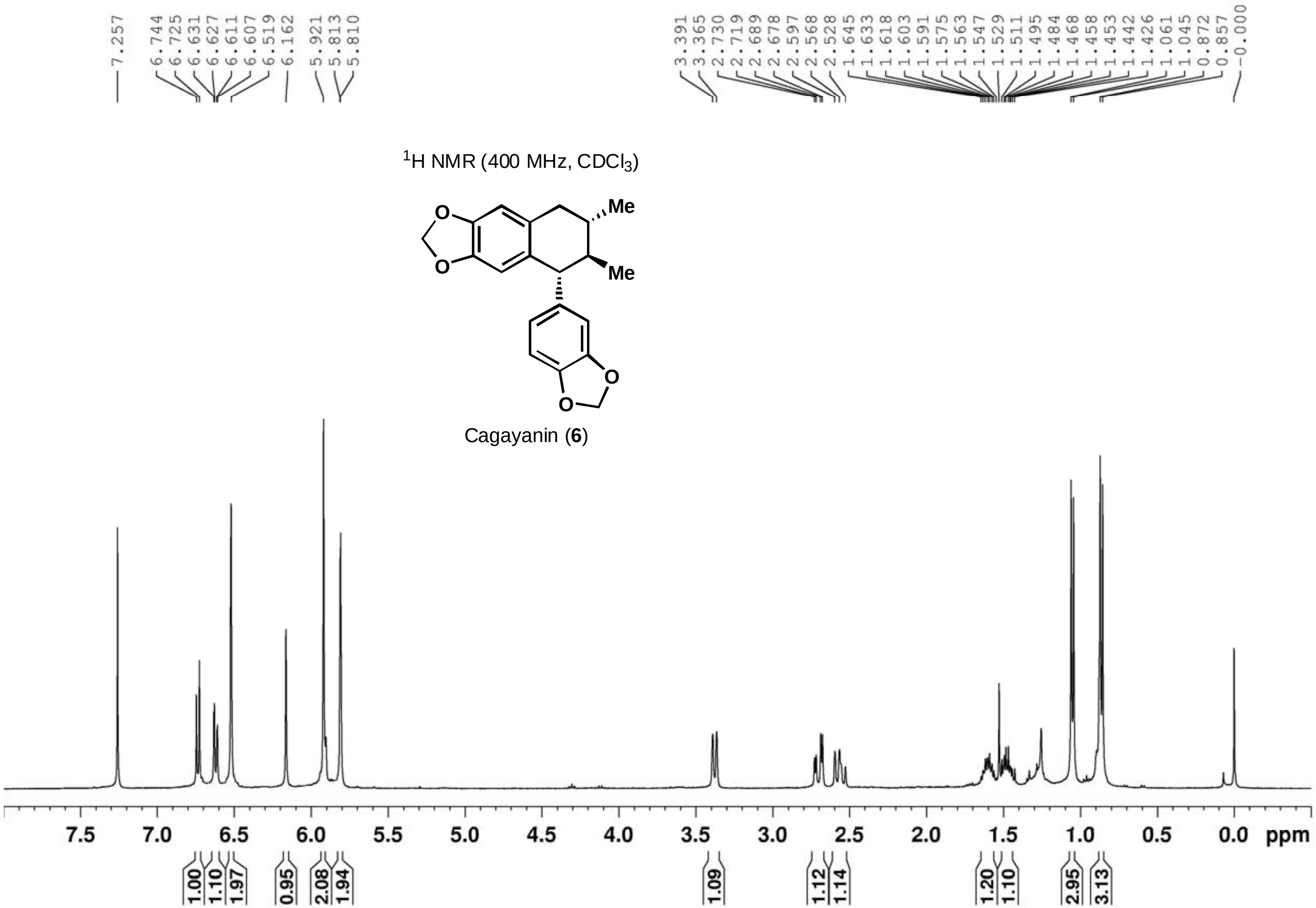
Table S4: ^{1}H and ^{13}C Chemical Shift (*ppm*) Comparison of Synthetic and Natural 8,8′-*epi*-aristoligone **5**

No.	Synthetic **5** by us ($CDCl_3$, 400 MHz)	Natural **5**[6] ($CDCl_3$, 500 MHz)	Synthetic **5** by us ($CDCl_3$, 100 MHz)	Natural **5**[6] ($CDCl_3$, 126 MHz)
	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_c	δ_c
3	6.19 *s*	6.13 *s*	111.0	111.2
6	7.54 *s*	7.48 *s*	108.0	108.1
8	2.39 *dq* (6.4, 12.0)	2.33 *dq* (6.5, 12.5)	48.5	48.5
9	1.32 *d* (6.4)	1.27 *d* (6.5)	12.6	12.6
2′	6.58 *d* (1.6)	6.53 *d* (2.0)	111.6	111.8
5′	6.87 *d* (8.0)	6.81 *d* (8.0)	110.8	111.0
6′	6.76 *dd* (1.6, 8.0)	6.70 *dd* (2.0, 8.0)	122.1	122.2
7′	3.71 *d* (11.2)	3.65 *d* (11.5)	53.3	53.3
8′	2.14–2.00 *m*	2.03 *ddq* (6.0, 11.5, 12.5)	43.7	43.8
9′	0.94 *d* (6.4)	0.89 *d* (6.0)	18.0	18.0
4 × OCH_3	3.63 *s*, 3.82 *s*, 3.92 *s*, 3.93 *s*	3.57 *s*, 3.76 *s*, 3.86 *s*, 3.87 *s*	55.8 (2C), 55.9, 56.0	55.8, 55.9, 56.0 (2C)
1			125.6	125.7
2			141.5	141.5
4			153.1	153.2
5			147.9	148.0
7			198.8	198.8
1′			136.1	136.1
3′			149.1	149.3
4′			147.8	147.9



8,8'-*epi*-Aristoligone (**5**)

(6) da Silva, T.; Lopes, L. M. X. *Phytochemistry* **2004**, *65*, 751–759.


7.257
6.744
6.725
6.631
6.627
6.611
6.607
6.519
6.162
5.921
5.813
5.810
3.391
3.365
2.730
2.719
2.689
2.678
2.597
2.568
2.528
1.645
1.633
1.618
1.603
1.591
1.575
1.563
1.547
1.529
1.511
1.495
1.484
1.468
1.458
1.453
1.442
1.426
1.061
1.045
0.872
0.857
-0.000
1H NMR (400 MHz, CDCl3)
Me
Me
O
O
O
O
Cagayanin (6)
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
ppm
1.00
1.10
1.97
0.95
2.08
1.94
1.09
1.12
1.14
1.20
1.10
2.95
3.13

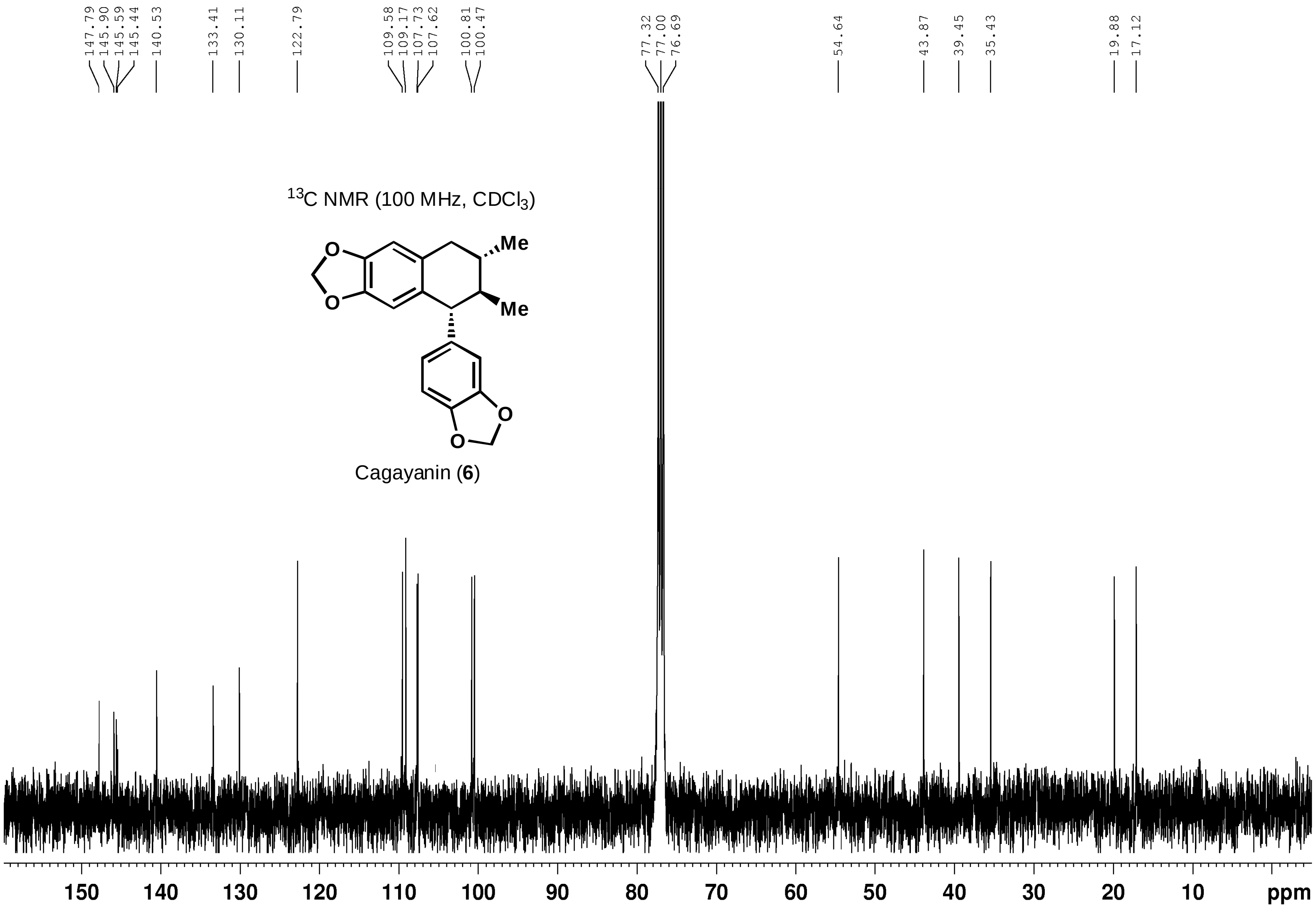
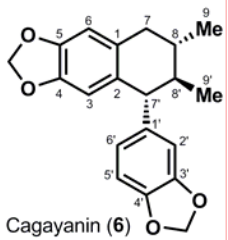
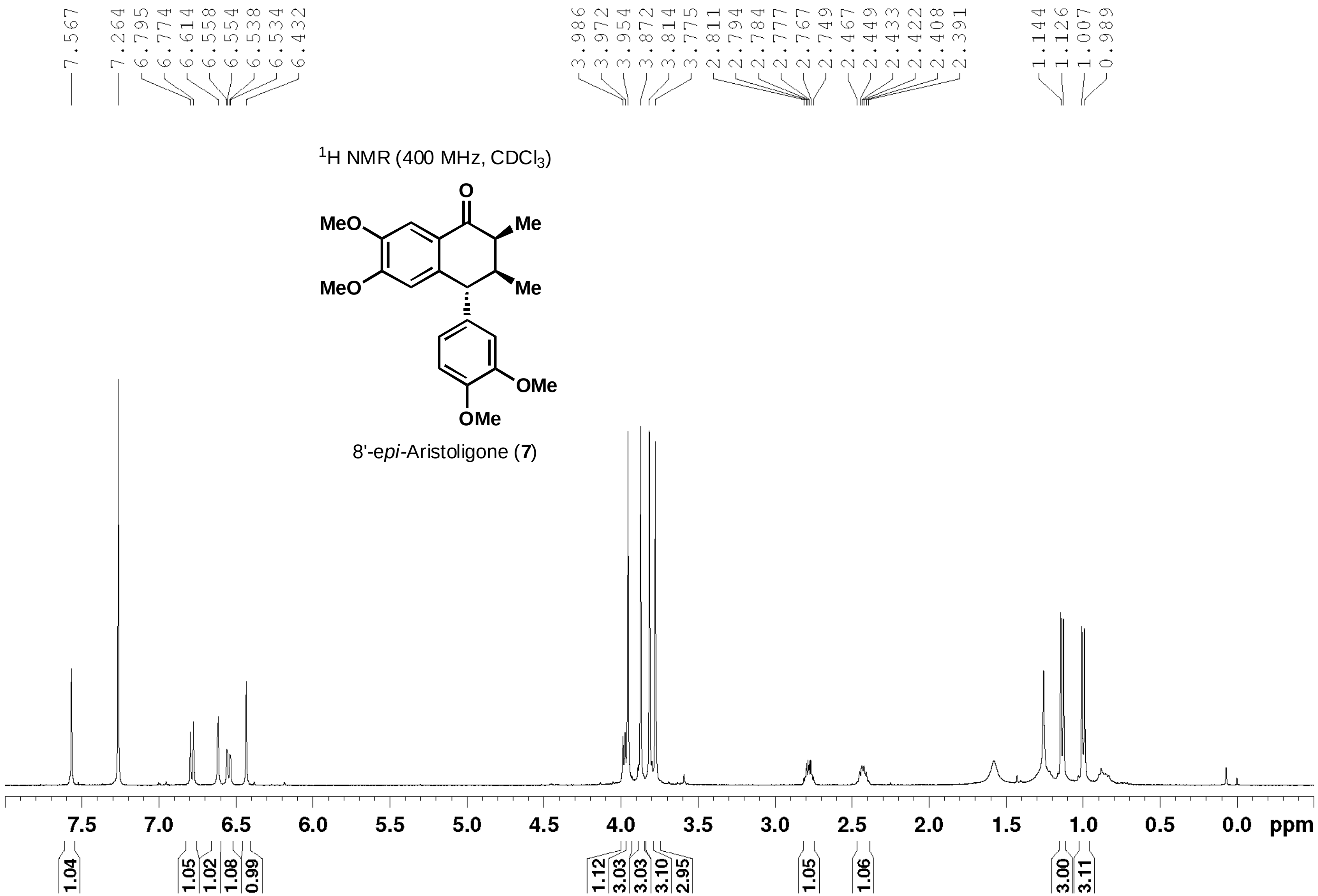

147.79
145.90
145.59
145.44
140.53
133.41
130.11
122.79
109.58
109.17
107.73
107.62
100.81
100.47
77.32
77.00
76.69
54.64
43.87
39.45
35.43
19.88
17.12
^{13}C NMR (100 MHz, $CDCl_3$)
O
O
Me
Me
O
O
Cagayanin (**6**)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

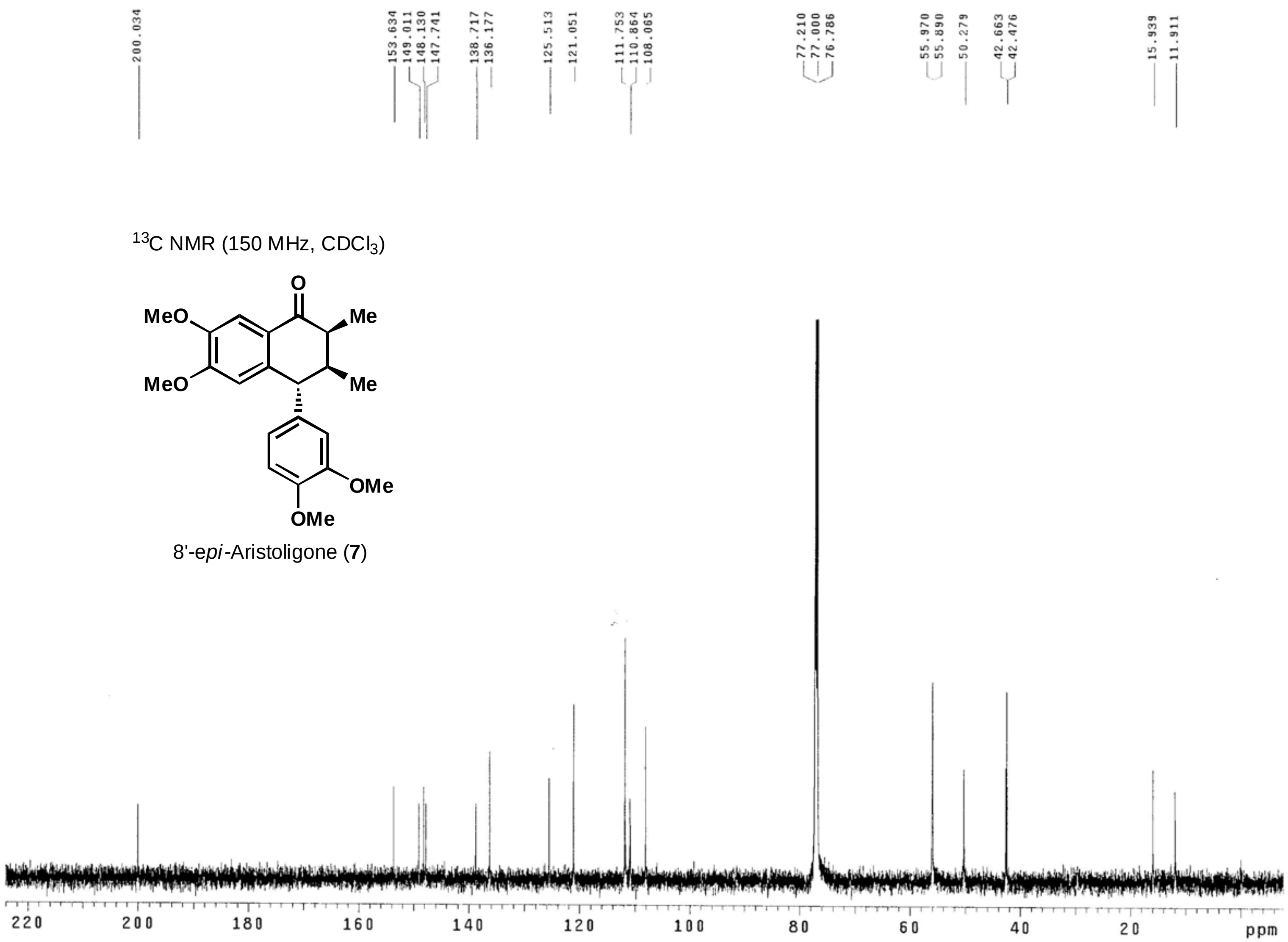
Table S5: ^{1}H and ^{13}C Chemical Shift (*ppm*) Comparison of Synthetic and Natural Cagayanin **6** (^{a} in 300 MHz)

No.	Synthetic **6** by us (CDCl$_3$, 400 MHz)	Natural **6**[7] (CDCl$_3$, 60 MHz)	Synthetic **6** by us (CDCl$_3$, 100 MHz)	Synthetic **6** by others[8] (CDCl$_3$, 75 MHz)
	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_c	δ_c
3	6.16 *s*	6.15 *s*	109.2	109.1
6	6.52 *s*	6.68 *s*	107.6	107.6
7	2.57 *dd* (11.6, 16.0) 2.70 *dd* (4.4, 16.4)	2.53 *dd* (7.2, 10.6)^{a} 2.71 *dd* (4.5, 10.6)^{a}	43.9	43.8
8	1.51–1.42 *m*	1.52–1.44 *m*	35.4	35.4
9	1.05 *d* (6.4)	1.03 *d* (6.0)	17.1	17.1
2′	6.52 *s*	6.50 *s*	107.7	107.7
5′	6.74 *d* (7.6)	6.70 *d* (8.0)	109.6	109.6
6′	6.62 *dd* (1.6, 8.0)	6.55 *d* (8.0)	122.8	122.8
7′	3.38 *d* (10.4)	3.38 *d* (10.0)	54.6	54.6
8′	1.65–1.53 *m*	1.65–1.52 *m*	39.5	39.4
9′	0.87 *d* (6.0)	0.85 *d* (6.0)	19.9	19.9
2 × –OCH$_2$O–	5.81 *d* (1.2), 5.92 *s*	5.79 *s*, 5.88 *s*	100.5, 100.8	100.5, 100.8
1			130.1	130.1
2			133.4	133.4
4			147.8	147.8
5			145.9	145.9
1′			140.5	140.5
3′			145.6	145.6
4′	Cagayanin (**6**)		145.4	Not observed

(7) Kuo, Y.-H.; Lin, S.-T.; Wu, R.-E. *Chem. Pharm. Bull.* **1989**, *37*, 2310–2312. (8) Datta, P. K.; Yau, C.; Hooper, T. S.; Yvon, B. L.; Charlton, J. L. *J. Org. Chem.* **2001**, *66*, 8606–8611.

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



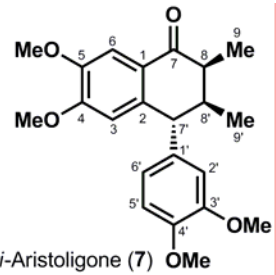


^{13}C NMR (150 MHz, $CDCl_3$)

8'-*epi*-Aristoligone (**7**)

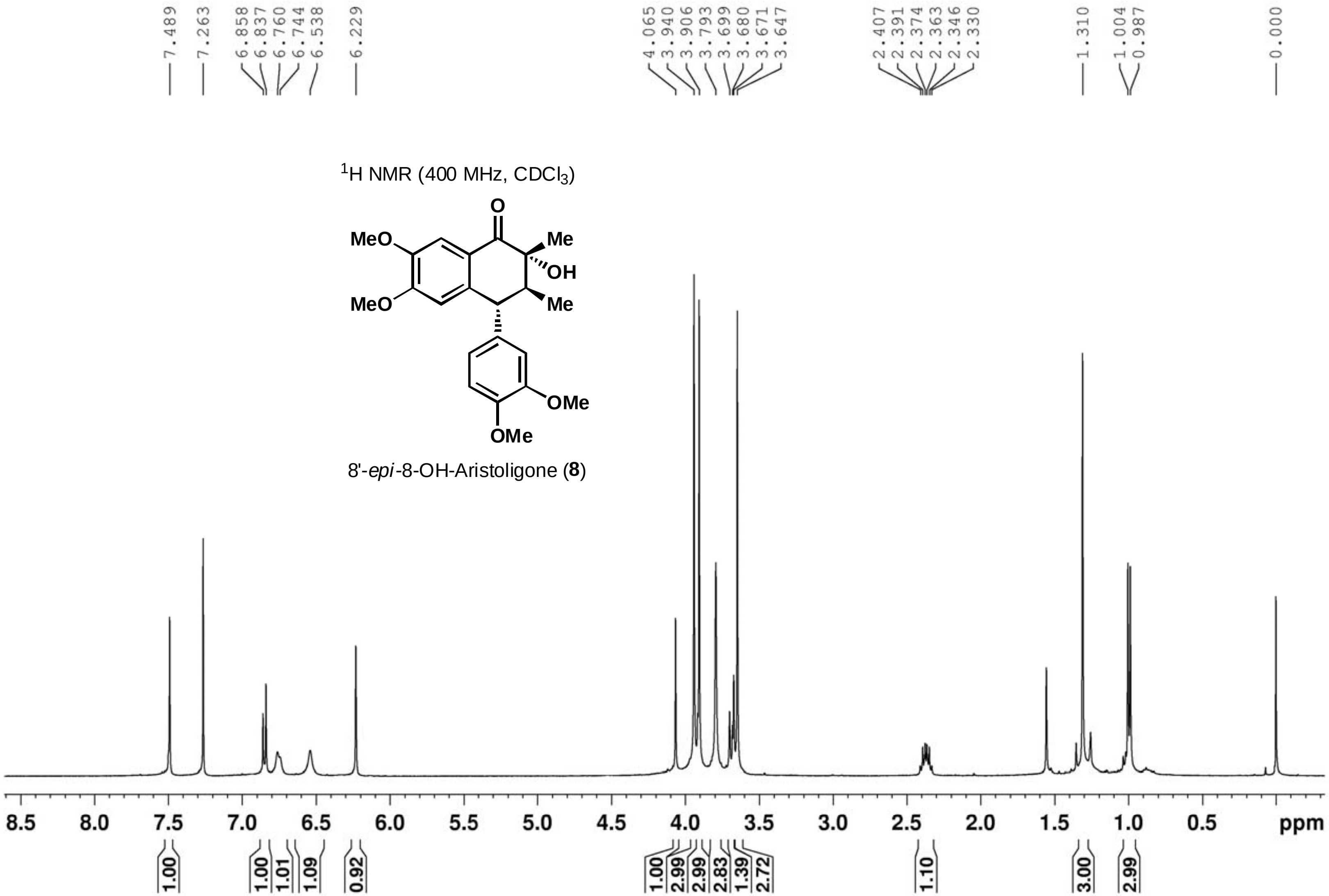
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Table S6: ^{1}H and ^{13}C Chemical Shift (*ppm*) Comparison of Synthetic and Natural 8′-*epi*-aristoligone **7**

No.	Synthetic **7** by us ($CDCl_3$, 400 MHz)	Natural **7**[6] ($CDCl_3$, 500 MHz)	Synthetic **7** by us ($CDCl_3$, 150 MHz)	Natural **7**[6] ($CDCl_3$, 126 MHz)
	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_c	δ_c
3	6.43 *s*	6.36 *s*	111.8	111.7
6	7.57 *s*	7.49 *s*	108.1	108.2
8	2.82–2.74 *m*	2.70 *dq* (6.5, 12.5)	42.7	42.7
9	1.14 *d* (6.8)	1.06 *d* (6.9)	11.9	11.9
2′	6.62 *d* (1.6)	6.54 *d* (1.8)	111.8	111.9
5′	6.78 *d* (8.4)	6.71 *d* (8.4)	110.9	111.0
6′	6.55 *dd* (1.6, 8.0)	6.47 *dd* (1.8, 8.4)	121.1	121.1
7′	3.98 *d* (5.2)	3.91 *d* (5.4)	50.3	50.3
8′	2.46–2.40 *m*	2.35 *ddq* (4.2, 5.4, 6.9)	42.5	42.5
9′	0.99 *d* (6.8)	0.92 *d* (6.9)	15.9	15.9
4 × OCH_3	3.78 *s*, 3.81 *s*, 3.87 *s*, 3.95 *s*	3.70 *s*, 3.75 *s*, 3.79 *s*, 3.88 *s*	55.9 (2C), 56.0 (2C)	55.8, 55.9, 56.0 (2C)
1			125.5	125.6
2			138.7	138.7
4			153.6	153.7
5			148.1	148.0
7			200.0	200.0
1′			136.2	136.2
3′			149.0	149.1
4′			147.7	147.9

8'-*epi*-Aristoligone (**7**)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



^{13}C NMR (150 MHz, $CDCl_3$)

8'-*epi*-8-OH-Aristoligone (**8**)

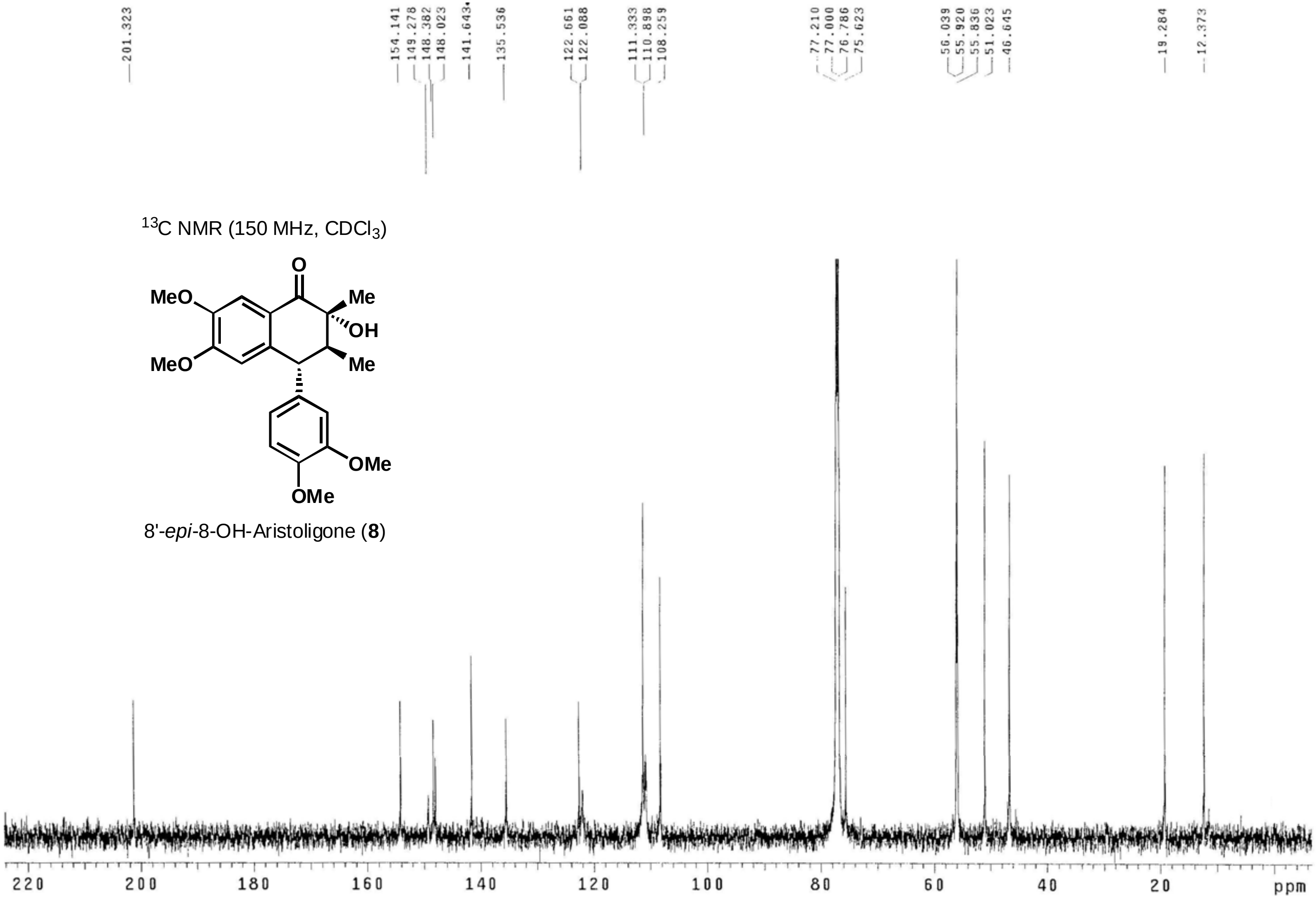
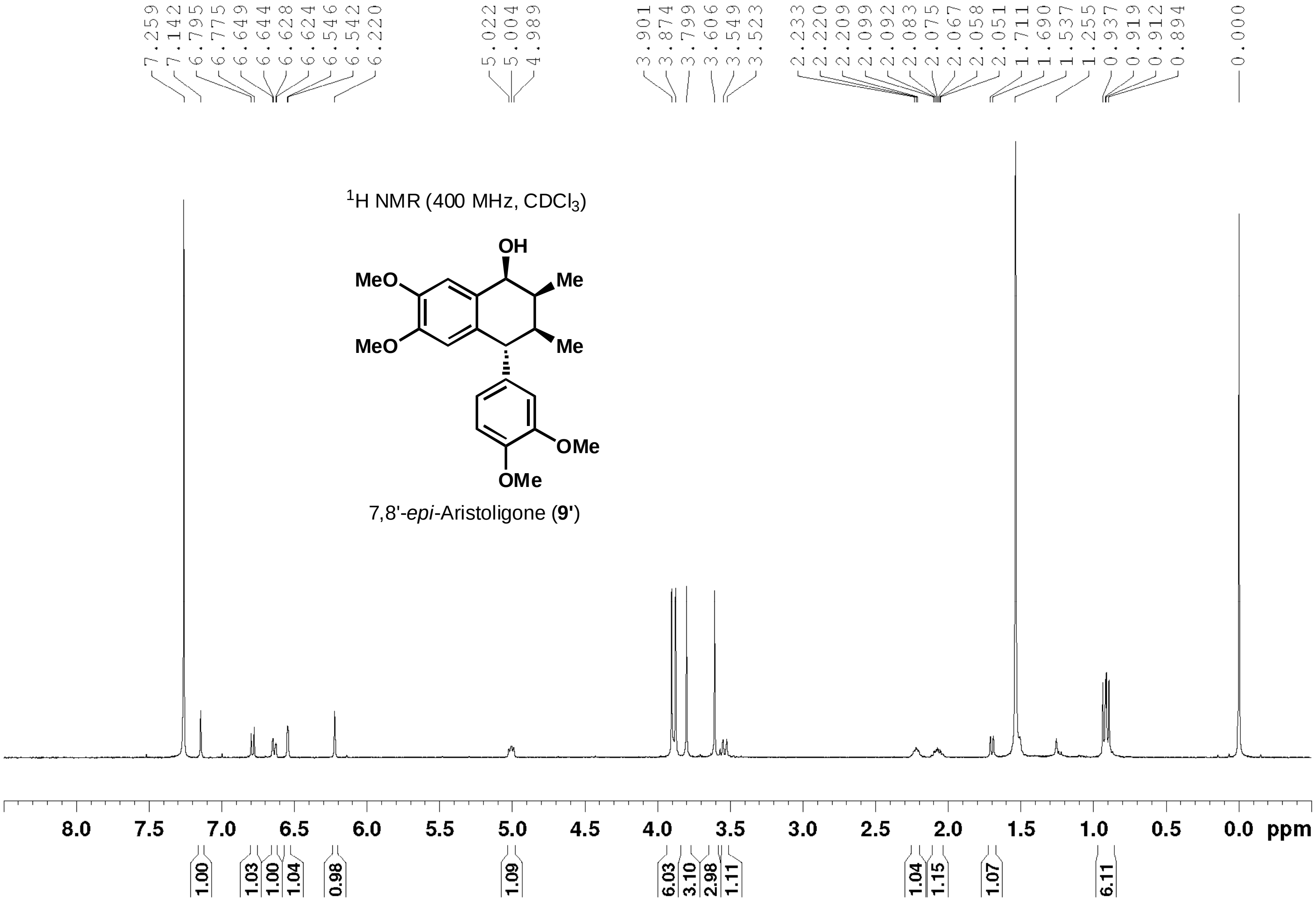


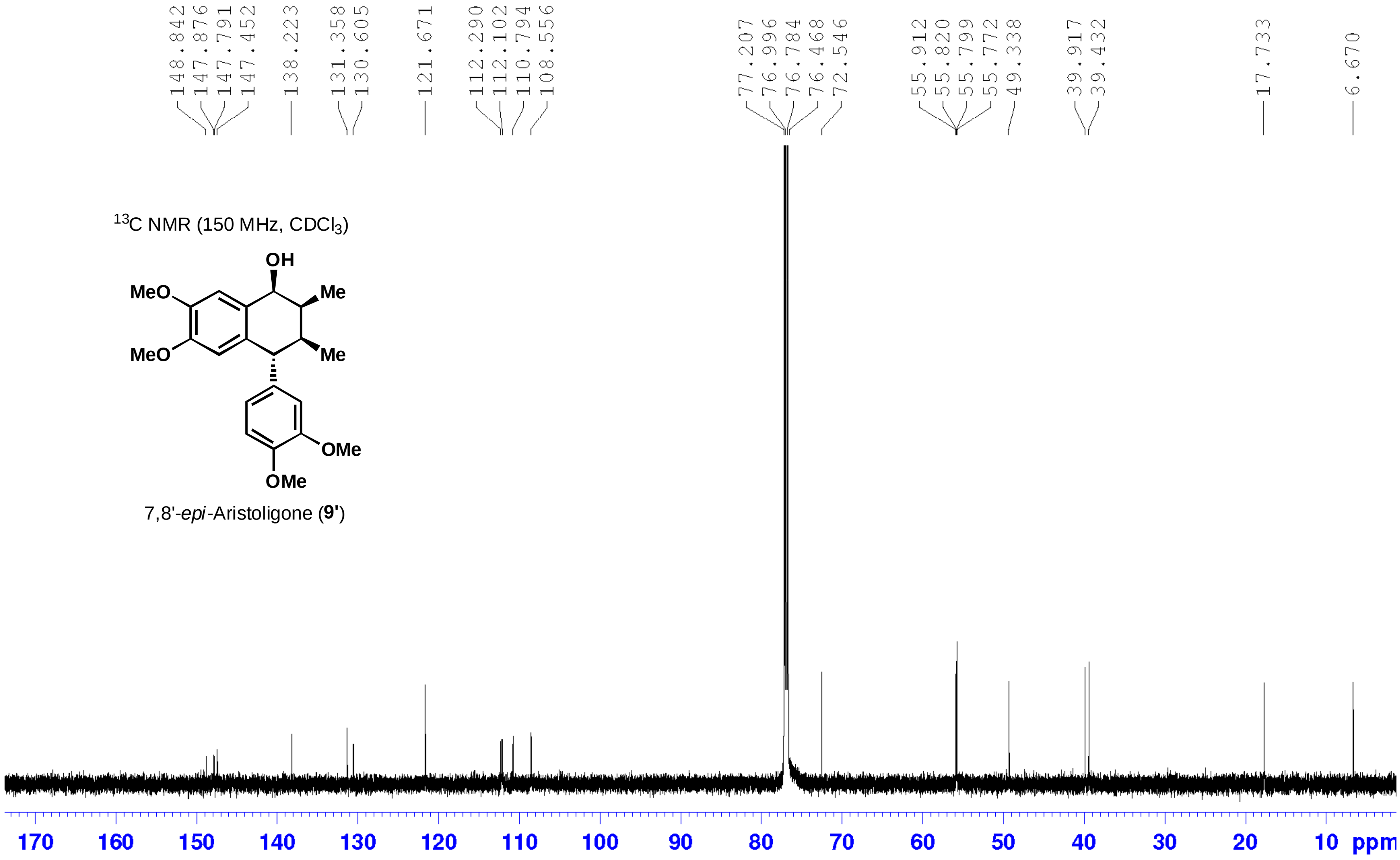
Table S7: ^{1}H and ^{13}C Chemical Shift (*ppm*) Comparison of Synthetic and Natural 8′-*epi*-8-OH-aristoligone **8**

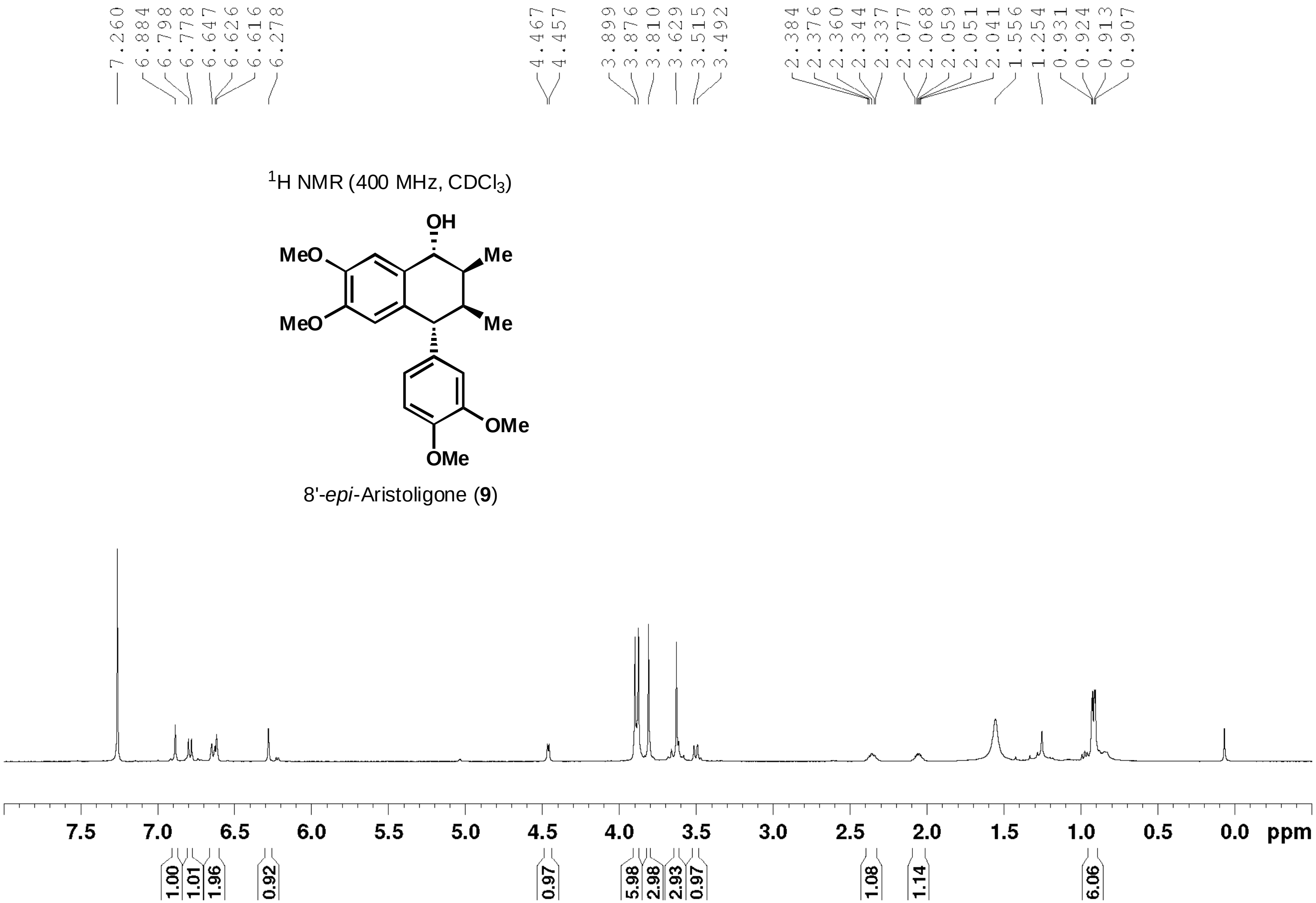
No.	Synthetic **8** by us[a] (CDCl$_3$, 400 MHz)	Natural **8**[3] (CDCl$_3$, 500 MHz)[b]	Synthetic **8** by us (CDCl$_3$, 150 MHz)	Natural **8**[3] (CDCl$_3$, 126 MHz)
	δ_H, J (Hz)	δ_H, J (Hz)	δ_c	δ_c
3	6.23 *s*	6.17 *s*	110.9	111.9
6	7.49 *s*	7.43 *s*	108.3	108.4
9	1.31 *s*	1.25 *s*	19.3	19.3
2′	6.54 *br s*	6.48 *br s*	111.3	Not observed
5′	6.85 *d* (8.4)	6.79 *d* (8.0)	111.3	111.4
6′	6.76 *br d* (6.4)	6.69 *br d* (8.0)	122.1	122.0
7′	3.69 *d* (11.2)	3.62 *br d* (11.0)	51.0	51.0
8′	2.37 *dq* (6.4, 11.2)	2.31 *dq* (6.5, 11.0)	46.6	46.7
9′	0.99 *d* (6.8)	0.94 *d* (6.5)	12.4	12.4
4 × OCH$_3$	3.65 *s*, 3.79 br *s*, 3.91 *s*, 3.94 *s*	3.58 *s*, 3.73 br *s*, 3.84 *s*, 3.88 *s*	55.8 (2C), 55.9, 56.0	55.8, 55.9, 56.0, 56.1
1			122.7	122.7
2			141.6	141.7
4			154.1	154.2
5			148.0	148.2
7			201.3	201.3
8			75.6	75.6
1′			135.5	135.6
3′			148.4	148.5
4′			149.3	149.4

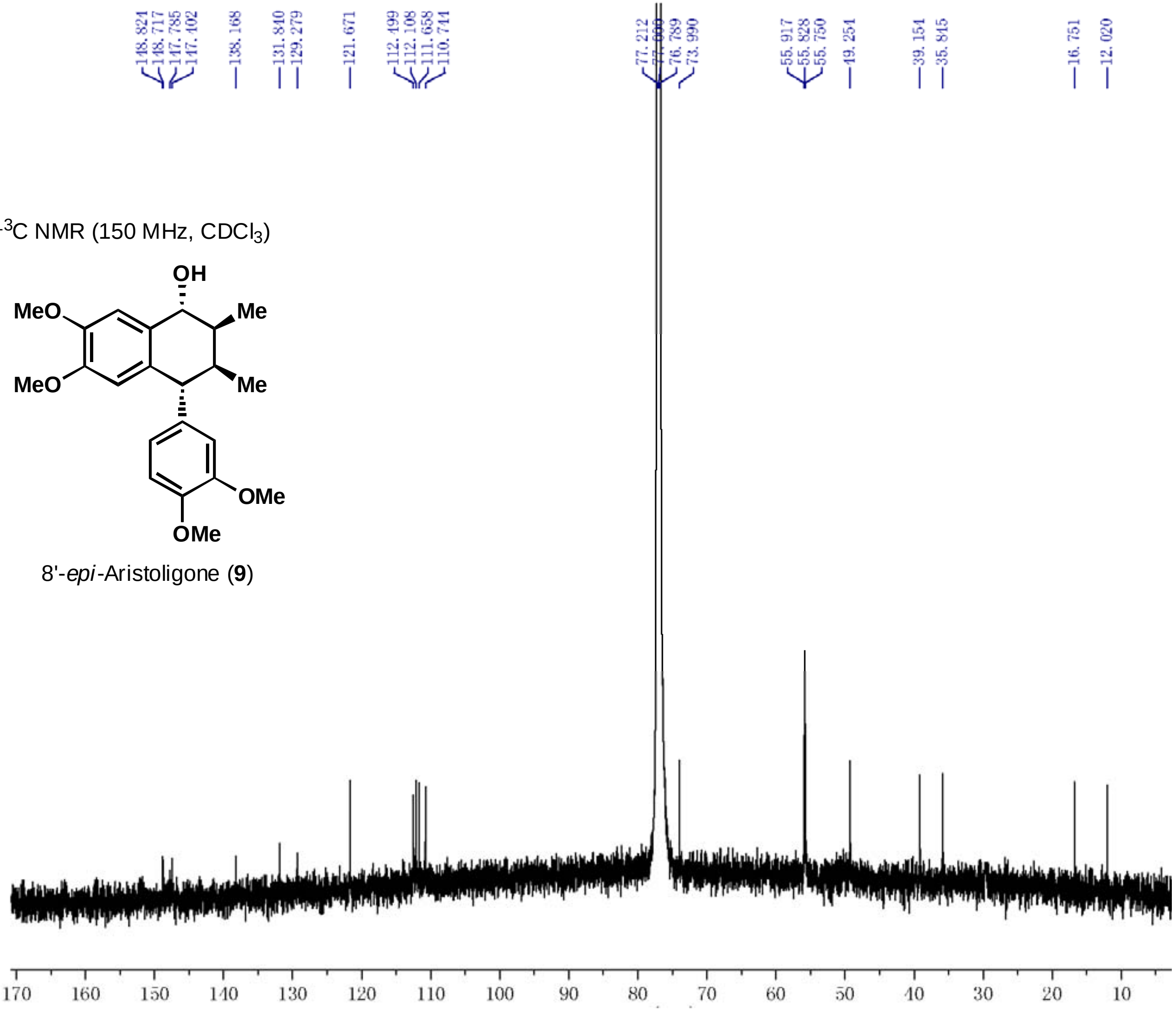
8'-*epi*-8-OH-Aristoligone (**8**)

[a] 4.07 (s, 1H, –O*H*). [b] 4.00 (s, 1H, –O*H*).


7.259
7.142
6.795
6.775
6.649
6.644
6.628
6.624
6.546
6.542
6.220
5.022
5.004
4.989
3.901
3.874
3.799
3.606
3.549
3.523
2.233
2.220
2.209
2.099
2.092
2.083
2.075
2.067
2.058
2.051
1.711
1.690
1.537
1.255
0.937
0.919
0.912
0.894
0.000
^{1}H NMR (400 MHz, $CDCl_3$)
OH
MeO
Me
MeO
Me
OMe
OMe
7,8'-*epi*-Aristoligone (**9'**)
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
ppm
1.00
1.03
1.00
1.04
0.98
1.09
6.03
3.10
2.98
1.11
1.04
1.15
1.07
6.11


148.842
147.876
147.791
147.452
138.223
131.358
130.605
121.671
112.290
112.102
110.794
108.556
77.207
76.996
76.784
76.468
72.546
55.912
55.820
55.799
55.772
49.338
39.917
39.432
17.733
6.670
13C NMR (150 MHz, CDCl3)
OH
MeO
Me
MeO
Me
OMe
OMe
7,8'-epi-Aristoligone (9')
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

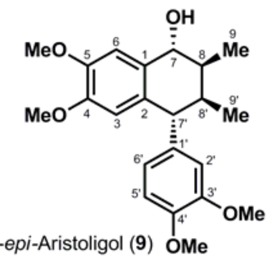

7.260
6.884
6.798
6.778
6.647
6.626
6.616
6.278
4.467
4.457
3.899
3.876
3.810
3.629
3.515
3.492
2.384
2.376
2.360
2.344
2.337
2.077
2.068
2.059
2.051
2.041
1.556
1.254
0.931
0.924
0.913
0.907
^{1}H NMR (400 MHz, $CDCl_3$)
OH
MeO
MeO
Me
Me
OMe
OMe
8'-*epi*-Aristoligone (**9**)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.01
1.96
0.92
0.97
5.98
2.98
2.93
0.97
1.08
1.14
6.06



^{13}C NMR (150 MHz, $CDCl_3$)

8'-*epi*-Aristoligone (**9**)

Table S8: ^{1}H and ^{13}C Chemical Shift (*ppm*) Comparison of Synthetic and Natural 8′-*epi*-Aristoligol **9**

No.	Synthetic **9** by us (CDCl$_3$, 400 MHz)	Natural **9**[3] (CDCl$_3$, 500 MHz)	Synthetic **9** by us (CDCl$_3$, 150 MHz)	Natural **9**[3] (CDCl$_3$, 126 MHz)
	δ_H, *J* (Hz)	δ_H, *J* (Hz)	δ_c	δ_c
3	6.28 *s*	6.22 *s*	112.5	112.6
6	6.88 *s*	6.83 *s*	111.7	111.8
7	4.46 *d* (4.0)	4.40 *d* (4.5)	74.0	74.0
8	2.10–2.02 *m*	2.00 *ddq* (4.5, 3.1, 7.0)	39.2	39.2
9	0.92 *d* (6.8)	0.87 *d* (7.0)	12.0	12.0
2′	6.62 *d* (2.4)	6.56 *d* (2.0)	112.1	112.3
5′	6.79 *d* (8.0)	6.73 *d* (8.0)	110.7	110.9
6′	6.64 *dd* (1.8, 8.4)	6.58 *dd* (2.0, 8.0)	121.7	121.7
7′	3.50 *d* (9.2)	3.45 *d* (9.0)	49.3	49.3
8′	2.41–2.32 *m*	2.30 *ddq* (3.1, 7.0, 9.0)	35.8	35.9
9′	0.93 *d* (7.2)	0.86 *d* (7.0)	16.8	16.7
4 × OCH$_3$	3.63 *s*, 3.81 *s*, 3.88 *s*, 3.90 *s*	3.57 *s*, 3.75 *s*, 3.82 *s*, 3.84 *s*	55.9, 55.83 (2C), 55.75	56.0, 55.9 (2C), 55.8
1			129.3	129.4
2			131.8	131.9
4			148.8	148.9
5			147.8	147.9
1′			138.2	138.2
3′			148.7	148.8
4′	8′-*epi*-Aristoligol (**9**)		147.4	147.5

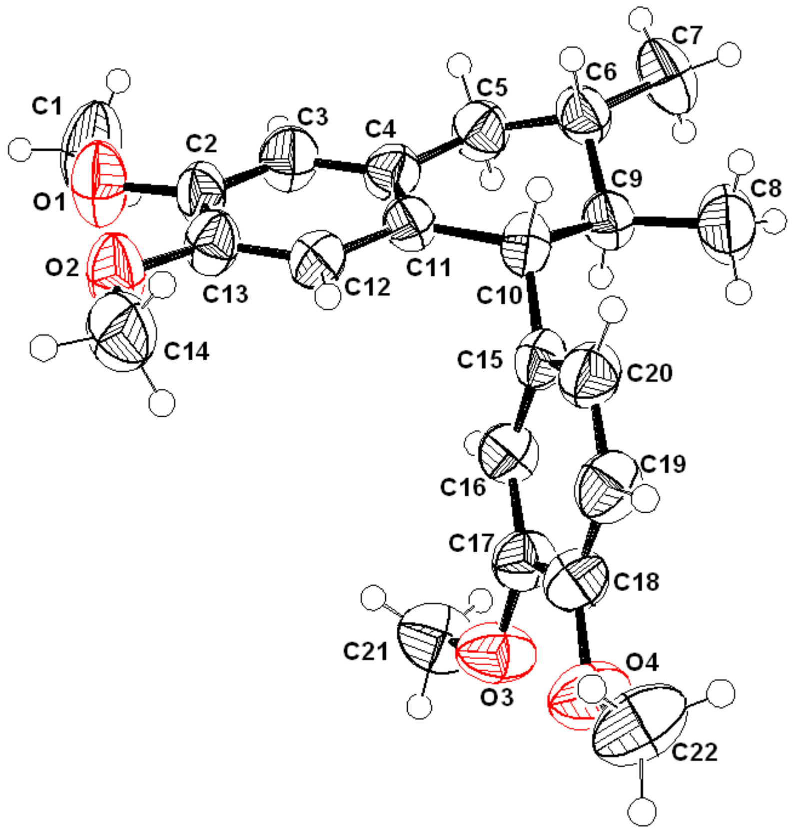


Figure S1. The X-ray structure of **(±)-Galbulin (3)** with thermal ellipsoids at 50% probability.

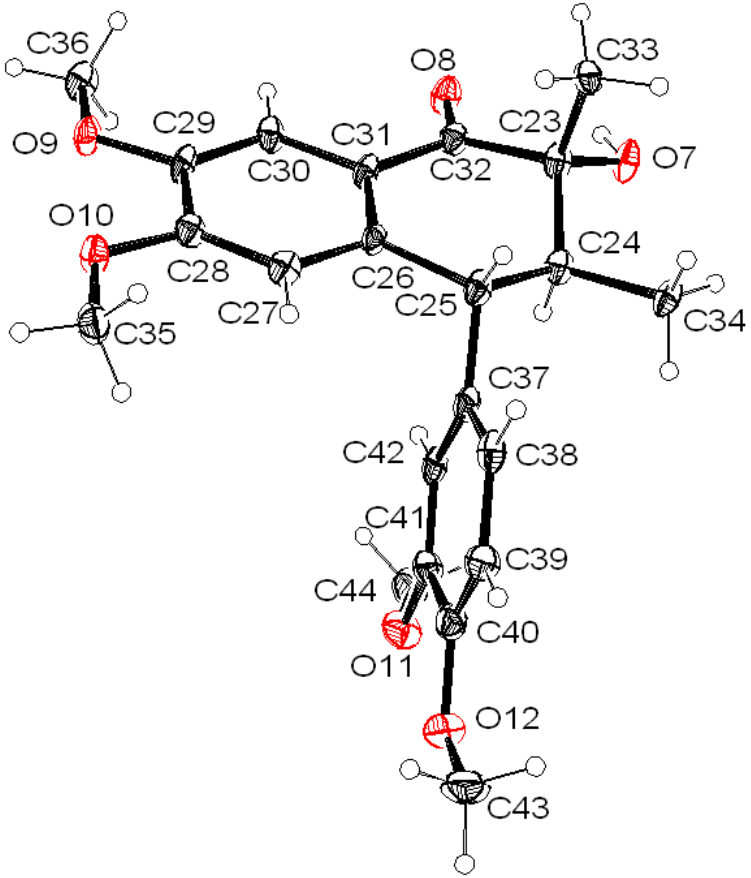


Figure S2. The X-ray structure of **8'-*epi*-8-OH-Aristoligone (8)** with thermal ellipsoids at 30% probability.