A Facile Phenol Driven Intramolecular Diastereoselective Thermal/Base Catalyzed Dipolar [2+2] Annulation Reactions: An Easy Access to Complex Bioactive Natural and Unnatural Benzopyran Congeners

Mukulesh Mondal,[a] Vedavati G. Puranik[b] and Narshinha P. Argade[a,*]

[a]*Division of Organic Chemistry (Synthesis),*
[b]*Centre for Materials and Characterization,*
National Chemical Laboratory,
Pune 411 008, India
np.argade@ncl.res.in

SI-1

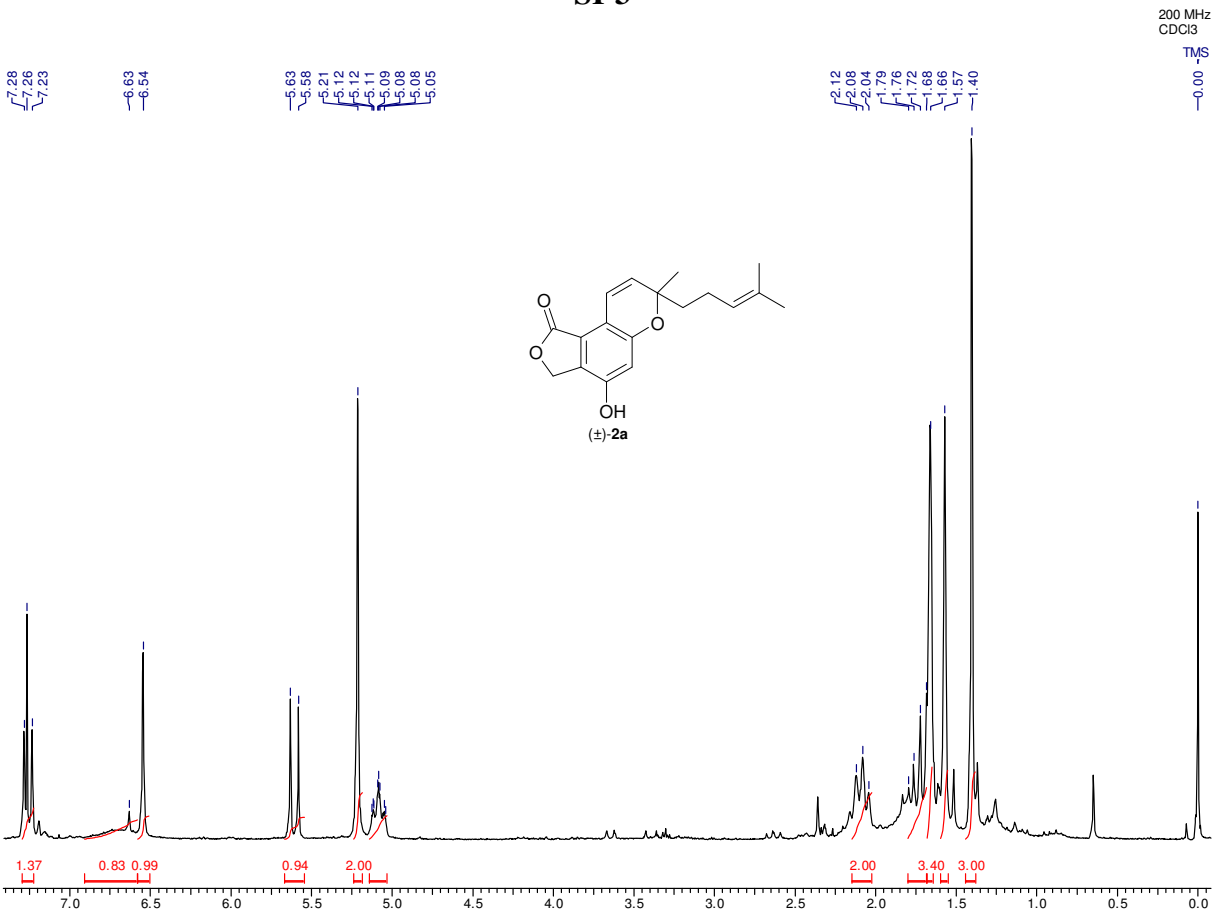
Table of contents in Supporting Information

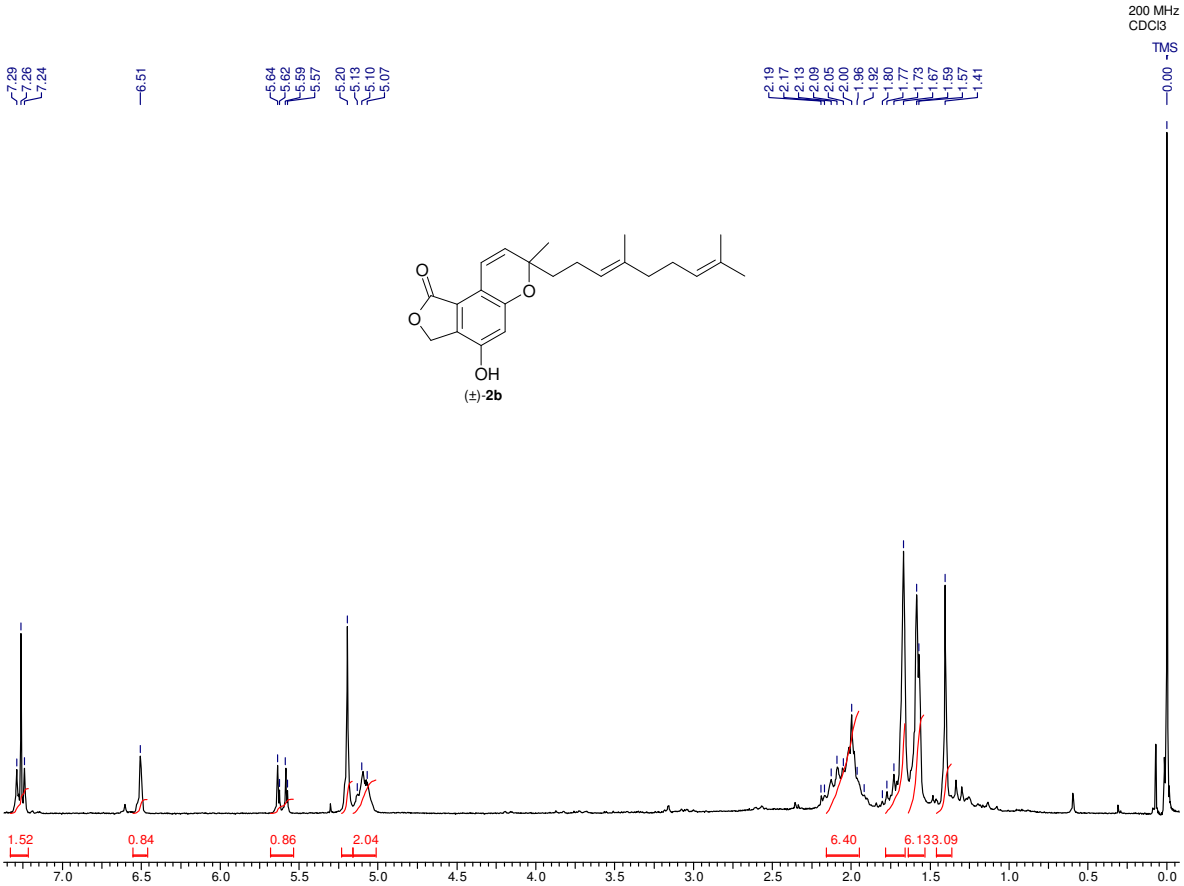
Sr. No	Contents
SI-2	Experimental: General Description
SI-3	^{1}H spectra of compounds **2a** and **2b**
SI-4	^{1}H and ^{13}C spectra of compound **4a**
SI-5	DEPT spectra of compound **4a** and ^{1}H spectra of compound **5**
SI-6	Expanded ^{1}H and ^{13}C spectra of compound **5**
SI-7	DEPT spectra of compound **5** and ^{1}H spectra of compound **7a**
SI-8	^{13}C and DEPT spectra of compound **7a**
SI-9	^{1}H spectra of compounds **7b** and **8**
SI-10	^{13}C and DEPT spectra of compound **8**
SI-11	^{1}H and Expanded ^{1}H spectra of compound **10**
SI-12	^{13}C and DEPT spectra of compound **10**
SI-13	^{1}H and ^{13}C spectra of compound **16**
SI-14	DEPT spectra of compound **16** and ^{1}H spectra of compound **17a**
SI-15	^{13}C and DEPT spectra of compound **17a**
SI-16	^{1}H and ^{13}C spectra of compound **17b**
SI-17	DEPT spectra of compound **17b** and ^{1}H spectra of compound **18a**
SI-18	^{13}C and DEPT spectra of compound **18a**

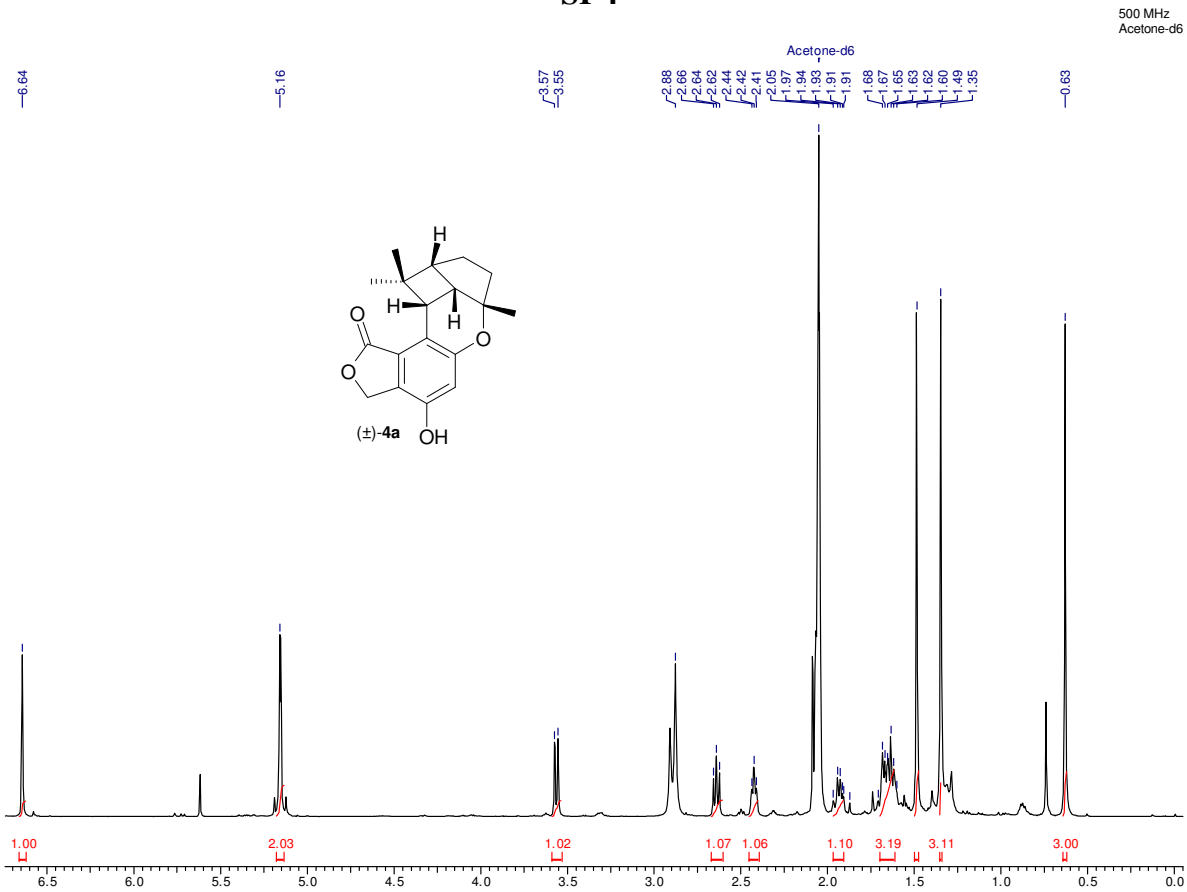
SI-19	^{1}H and Expanded ^{1}H spectra of compound **18b**
SI-20	^{13}C and DEPT spectra of compound **18b**
SI-21	^{1}H and ^{13}C spectra of compound **19**
SI-22	DEPT spectra of compound **19** and ^{1}H spectra of compound **21**
SI-23	^{13}C and DEPT spectra of compound **21**
SI-24	^{1}H and ^{13}C spectra of compound **25**
SI-25	DEPT spectra of compound **25** and ^{1}H spectra of compound **26**
SI-26	^{13}C and DEPT spectra of compound **26**
SI-27	^{1}H and ^{13}C spectra of compound **27**
SI-28	DEPT spectra of compound **27** and ^{1}H spectra of compound **28**
SI-29	^{13}C and DEPT spectra of compound **28**
SI-30	^{1}H and ^{13}C spectra of compound **29**
SI-31	Expanded ^{13}C spectra of compound **29**
SI-32	Expanded ^{13}C and DEPT spectra of compound **29**
SI-33	Expanded DEPT spectra of compound **29**
SI-34	^{1}H and ^{13}C spectra of compound **30**
SI-35	DEPT spectra of compound **30** and ^{1}H spectra of compound **31**
SI-36	Expanded ^{1}H and ^{13}C spectra of compound **31**
SI-37	Expanded ^{13}C and DEPT spectra of compound **31**
SI-38	Experimental section of single crystal X-ray crystallographic studies of compound **4a**
SI-39	ORTEP Diagram of compound **4a** and experimental section of single crystal X-ray crystallographic studies of compound **5**
SI-40	ORTEP Diagram of compound **5**

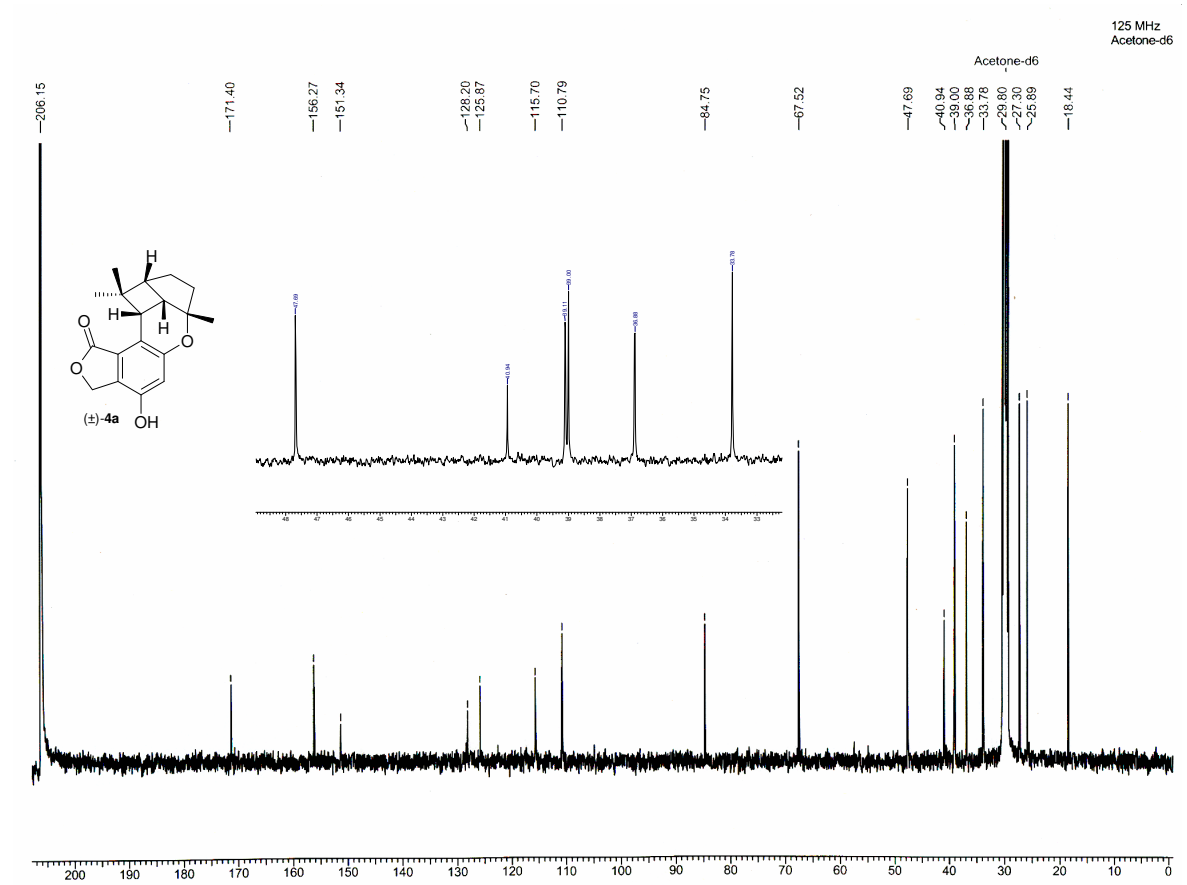
Experimental: General Description

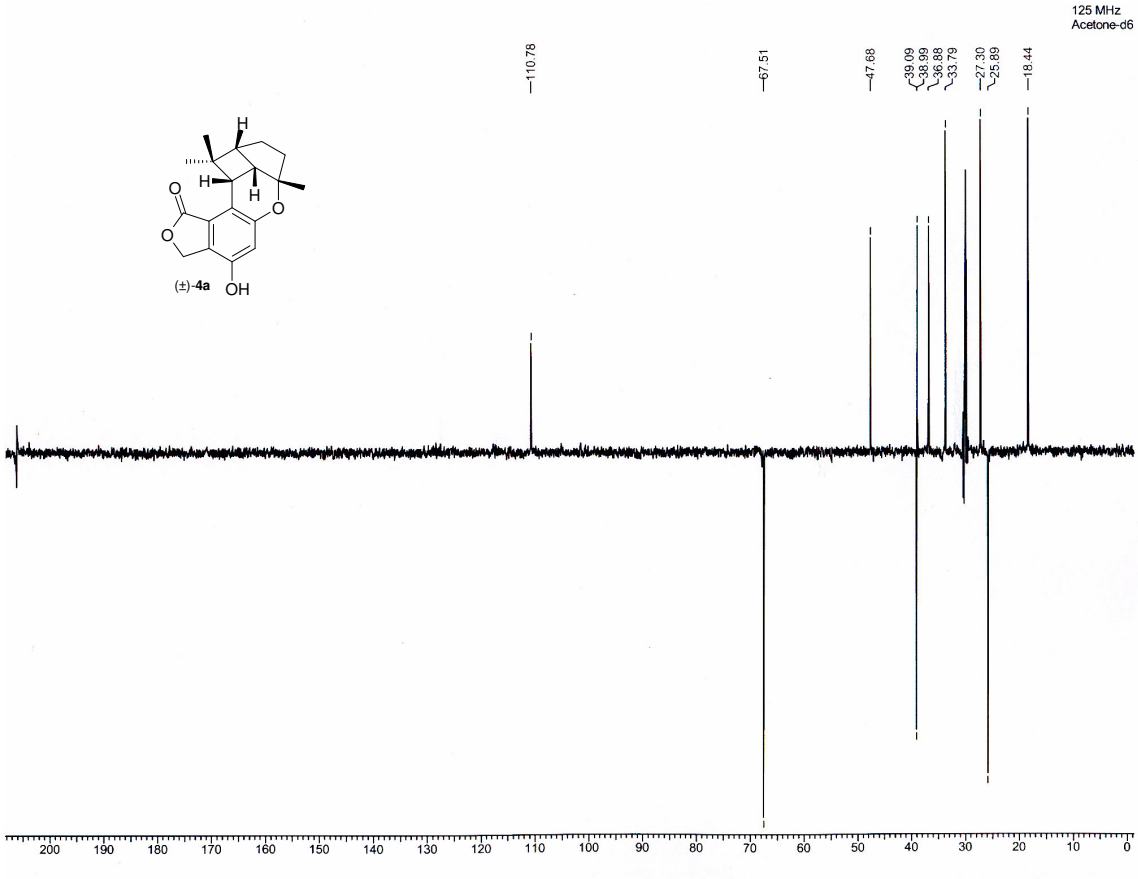
Commercially available methyl 3,5-dimethoxybenzoate, $Ca(OH)_2$, DBU, orcinol monohydrate, methyl iodide, NBS, *n*-BuLi (1.5 M), methyl chloroformate, anhydrous aluminum chloride, 1,3,5-trimethoxybenzene, BBr_3, 3-methyl-2-butenal, citral and farnesol were used. Melting points are uncorrected. Dichloromethane was distilled from phosphorous pentoxide under argon. Tetrahydrofuran was freshly distilled from benzophenone ketyl radical under argon prior to use. Column chromatographic separations were carried out on silica gel (60-120 mesh). All yields given refer to as isolated yields. IR spectra were recorded on FT-IR spectrometer. MS experiments were performed on a low resolution magnetic sector mass spectrometer.

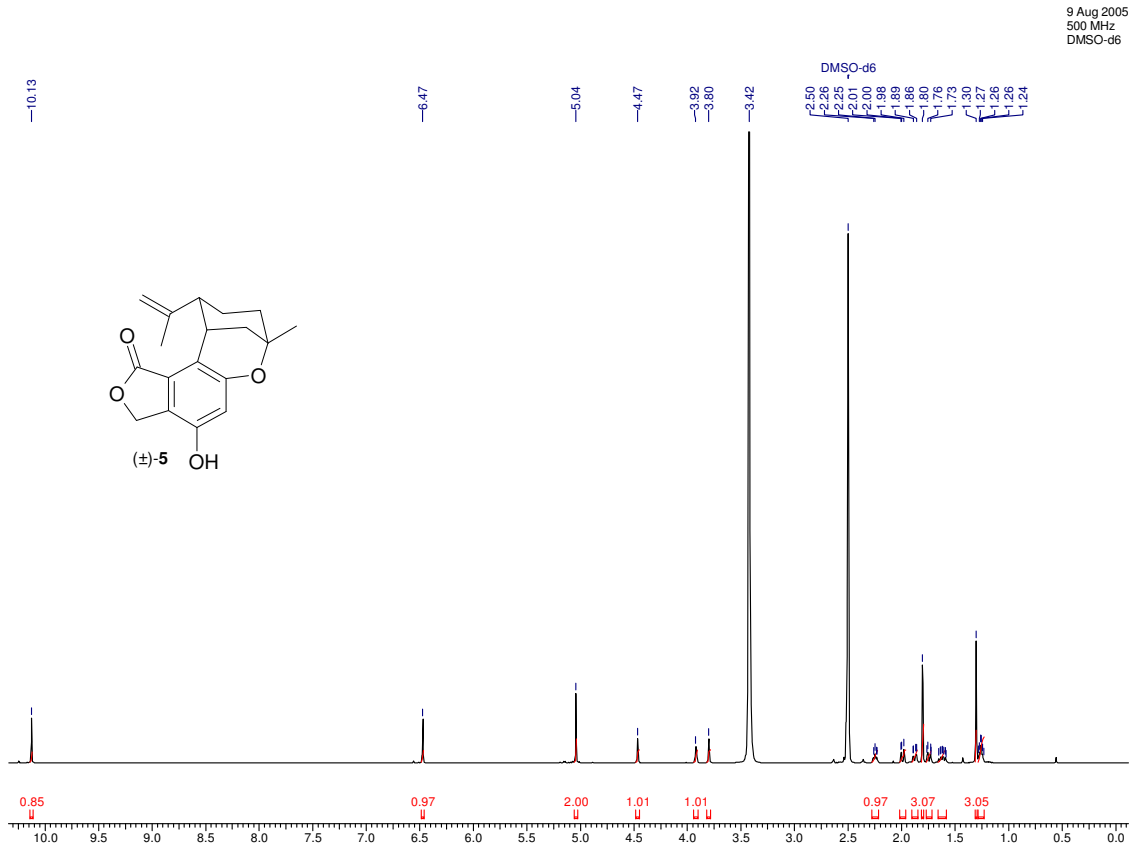

200 MHz
CDCl3
TMS
7.28
7.26
7.23
6.63
6.54
5.63
5.58
5.21
5.12
5.12
5.11
5.09
5.08
5.08
5.05
2.12
2.08
2.04
1.79
1.76
1.72
1.68
1.66
1.57
1.40
0.00
O
O
O
OH
(±)-2a
1.37
0.83
0.99
0.94
2.00
2.00
3.40
3.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

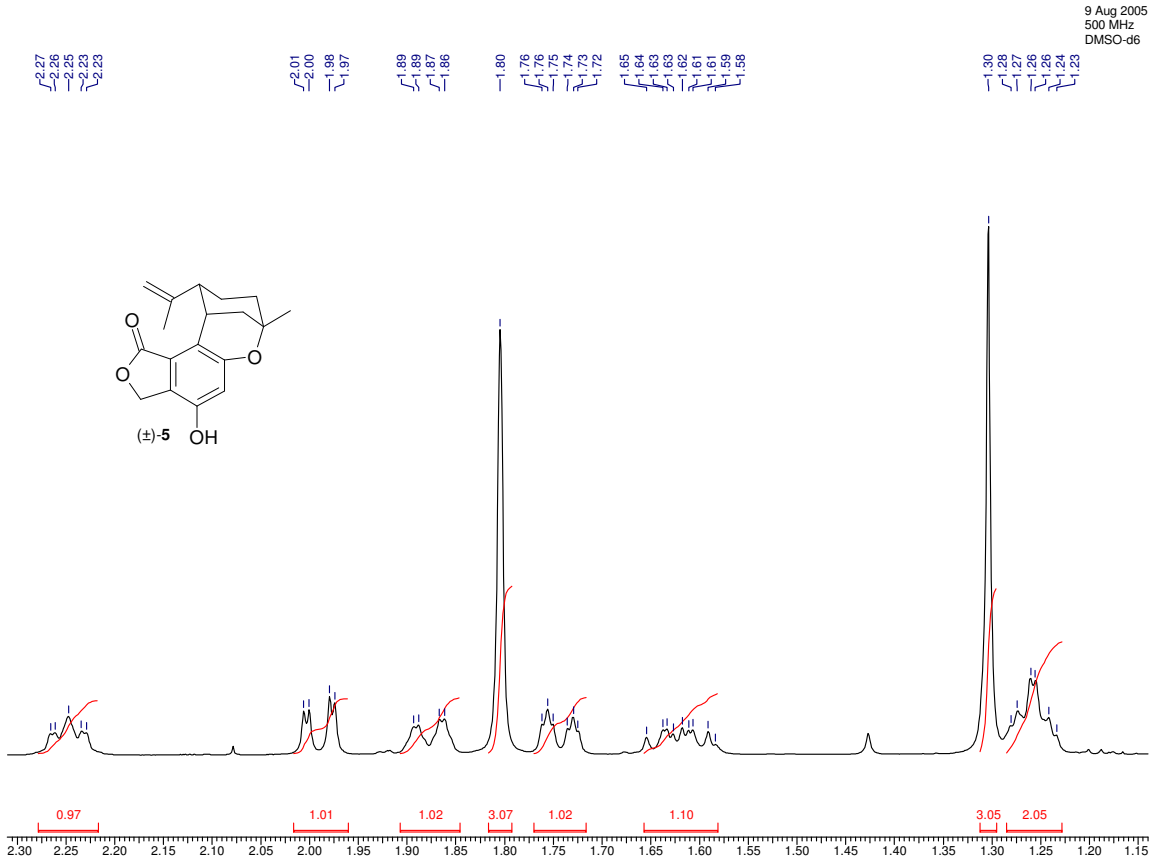

200 MHz
CDCl3
TMS
7.29
7.26
7.24
6.51
5.64
5.62
5.59
5.57
5.20
5.13
5.10
5.07
2.19
2.17
2.13
2.09
2.05
2.00
1.96
1.92
1.80
1.77
1.73
1.67
1.59
1.57
1.41
0.00
O
O
O
OH
(±)-2b
1.52
0.84
0.86
2.04
6.40
6.13
3.09
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

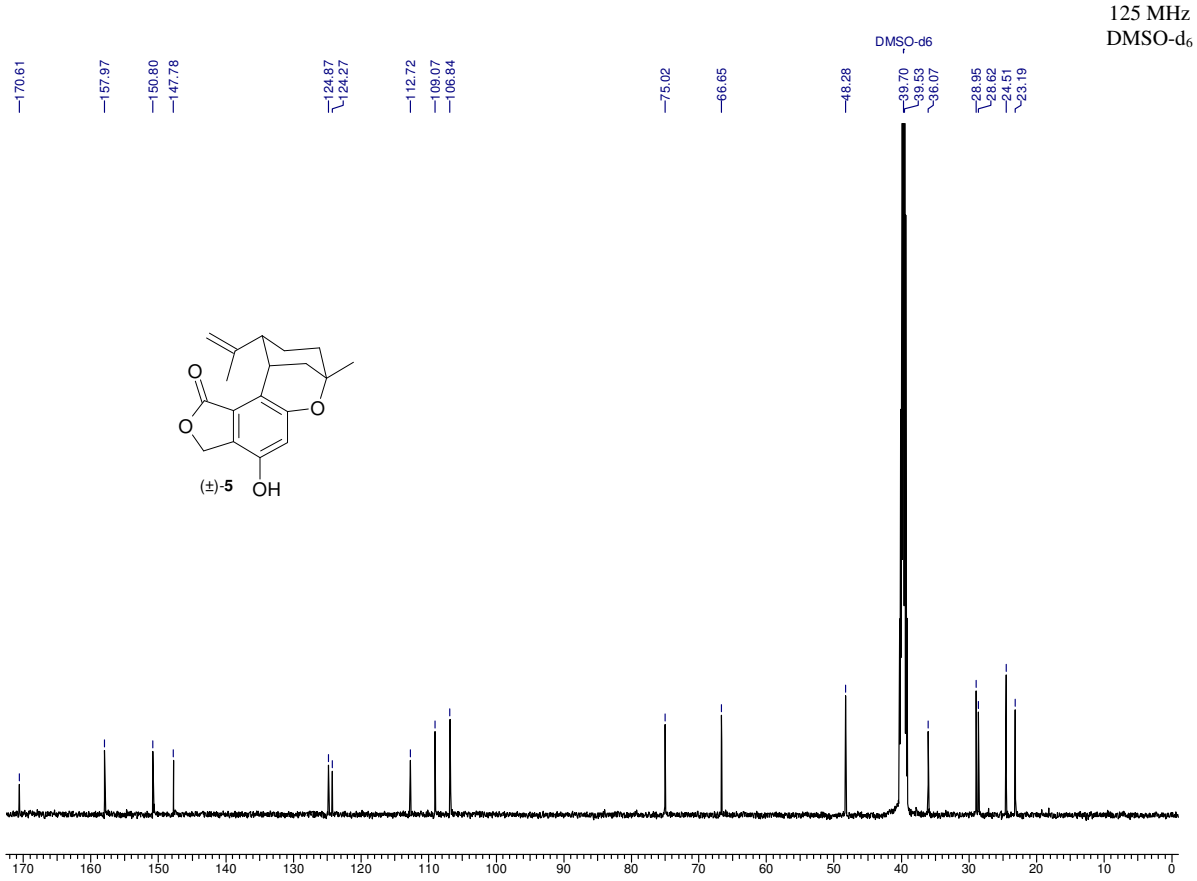

500 MHz
Acetone-d6
6.64
5.16
3.57
3.55
2.88
2.86
2.64
2.62
2.44
2.42
2.41
2.05
1.97
1.94
1.93
1.91
1.91
1.68
1.67
1.65
1.63
1.62
1.60
1.49
1.35
0.63
1.00
2.03
1.02
1.07
1.06
1.10
3.19
3.11
3.00
(±)-4a

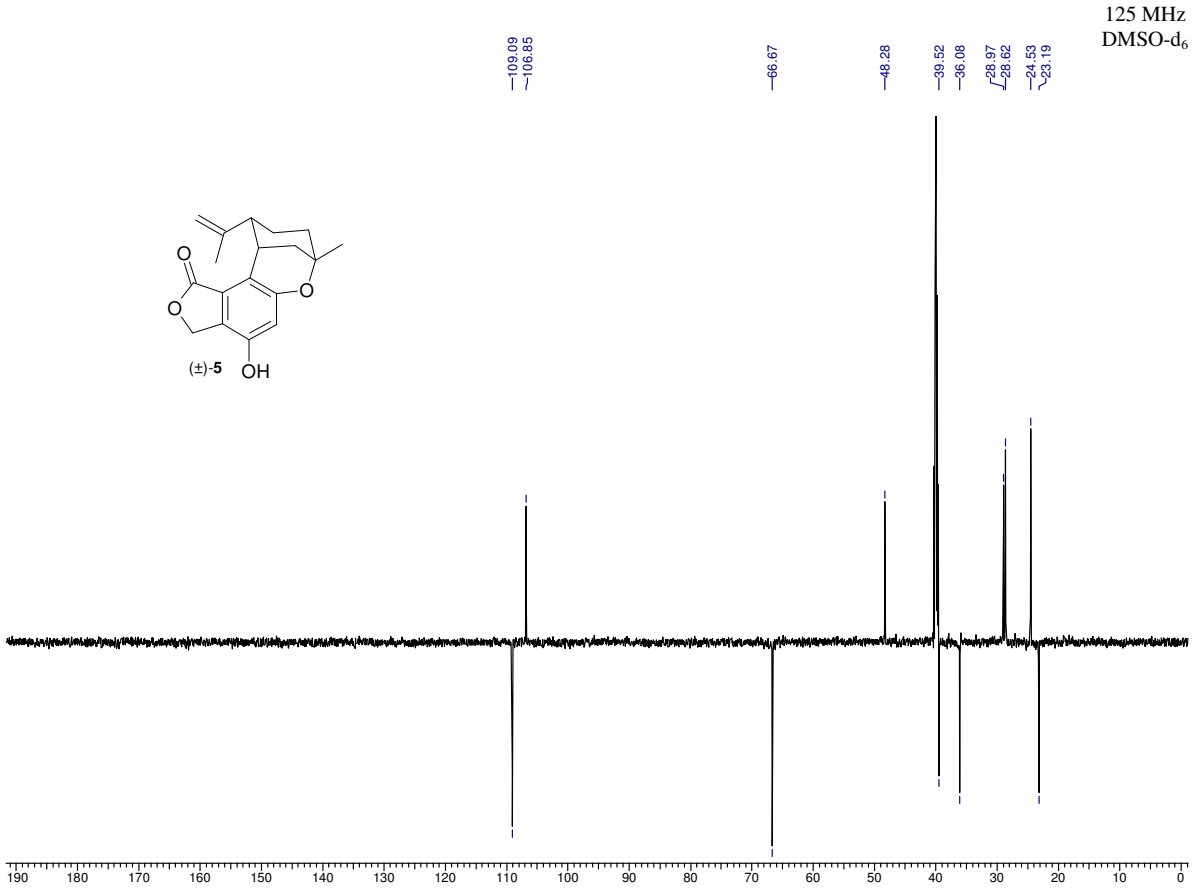

125 MHz
Acetone-d6
206.15
171.40
156.27
151.34
128.20
125.87
115.70
110.79
84.75
67.52
47.69
40.94
39.00
36.88
33.78
29.80
27.30
25.89
18.44
(±)-4a

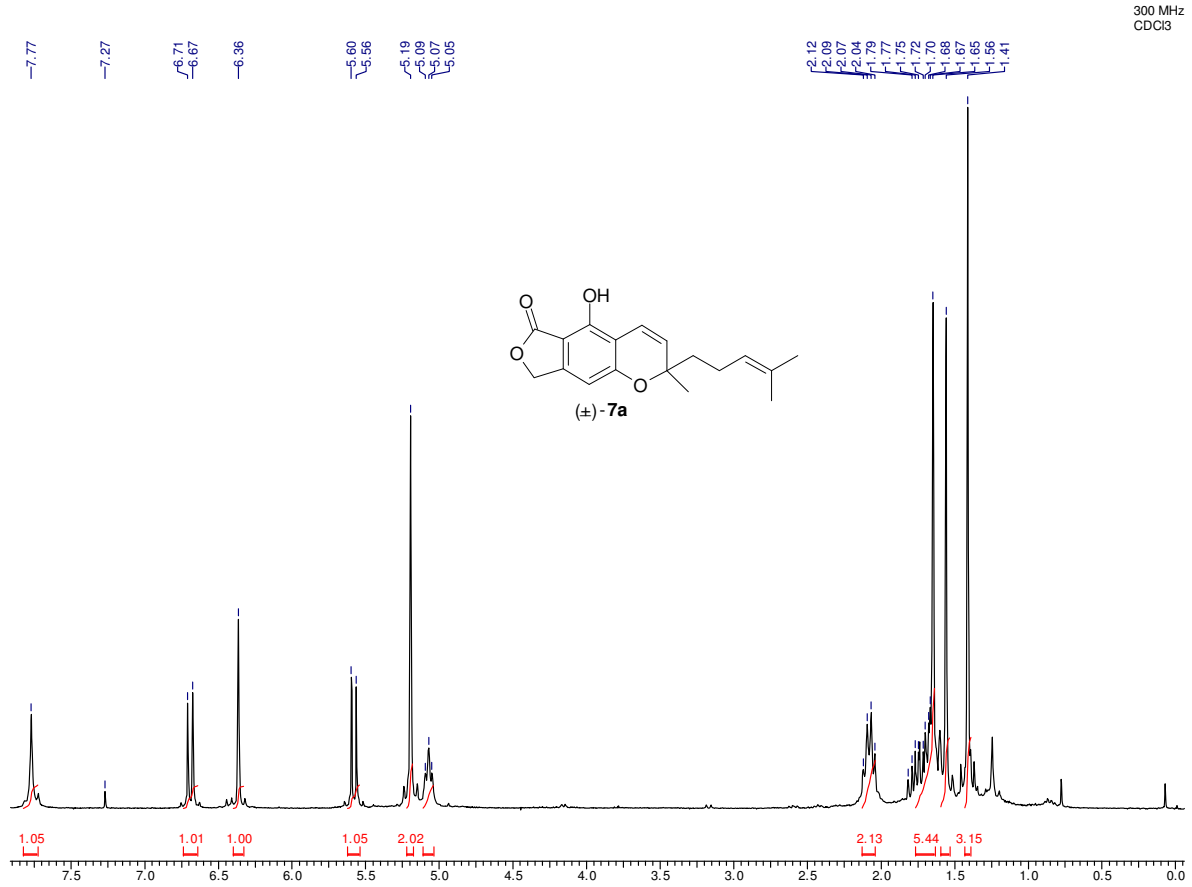

125 MHz
Acetone-d6
110.78
67.51
47.68
39.09
38.89
36.88
33.79
27.30
25.89
18.44
(±)-4a
OH

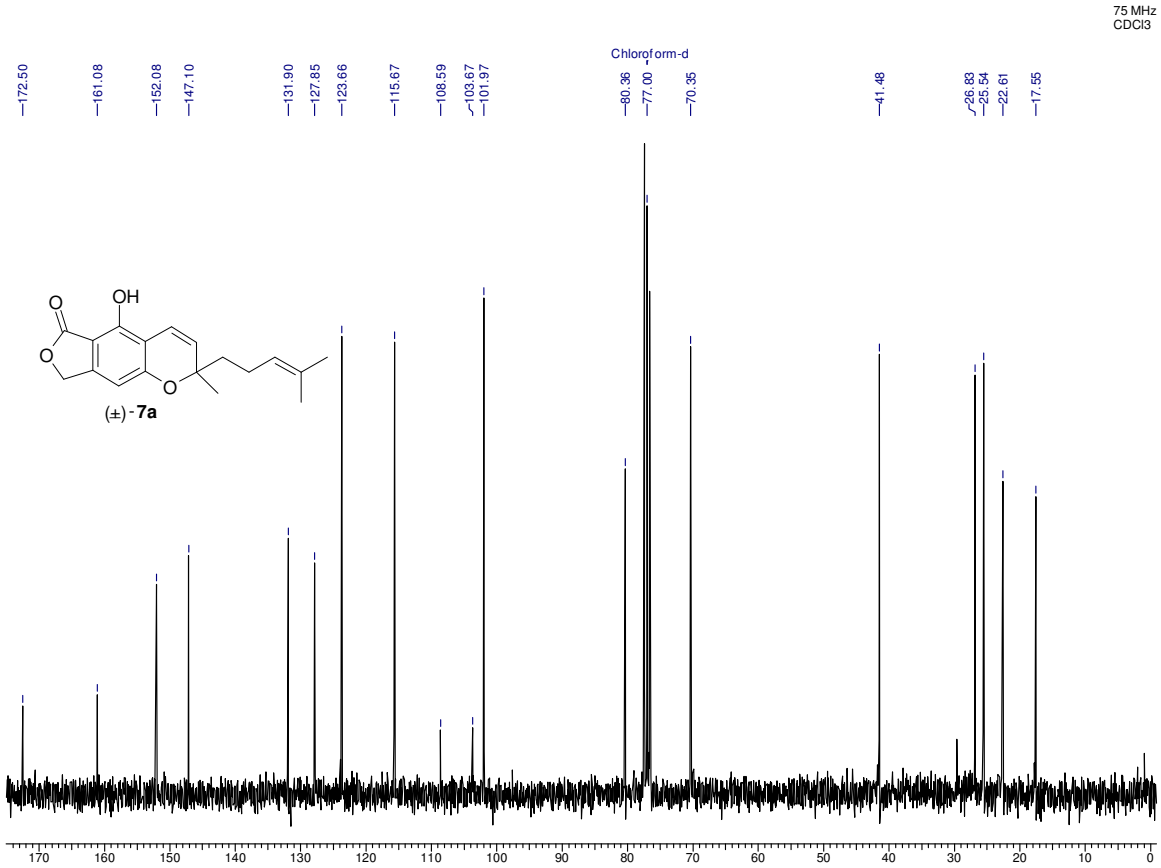

9 Aug 2005
500 MHz
DMSO-d6
10.13
6.47
5.04
4.47
3.92
3.80
3.42
2.50
2.26
2.25
2.01
2.00
1.98
1.89
1.86
1.80
1.76
1.73
1.30
1.27
1.26
1.26
1.24
(±)-5
OH
0.85
0.97
2.00
1.01
1.01
0.97
3.07
3.05

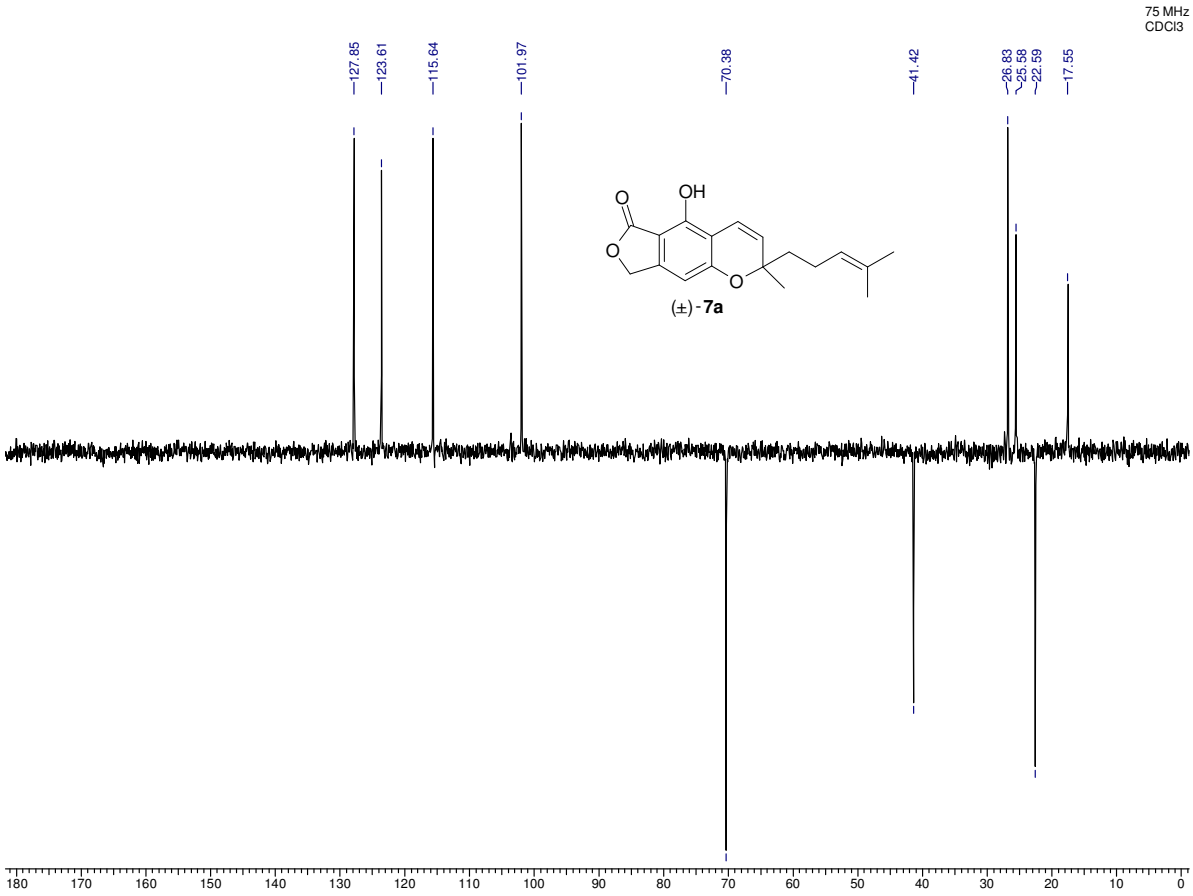

9 Aug 2005
500 MHz
DMSO-d6
2.27
2.26
2.25
2.23
2.23
2.01
2.00
1.98
1.97
1.89
1.89
1.87
1.86
1.80
1.76
1.76
1.75
1.74
1.73
1.72
1.65
1.64
1.63
1.63
1.62
1.61
1.61
1.59
1.58
1.30
1.28
1.27
1.26
1.26
1.24
1.23
O
O
O
OH
(±)-5
0.97
1.01
1.02
3.07
1.02
1.10
3.05
2.05
2.30 2.25 2.20 2.15 2.10 2.05 2.00 1.95 1.90 1.85 1.80 1.75 1.70 1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15

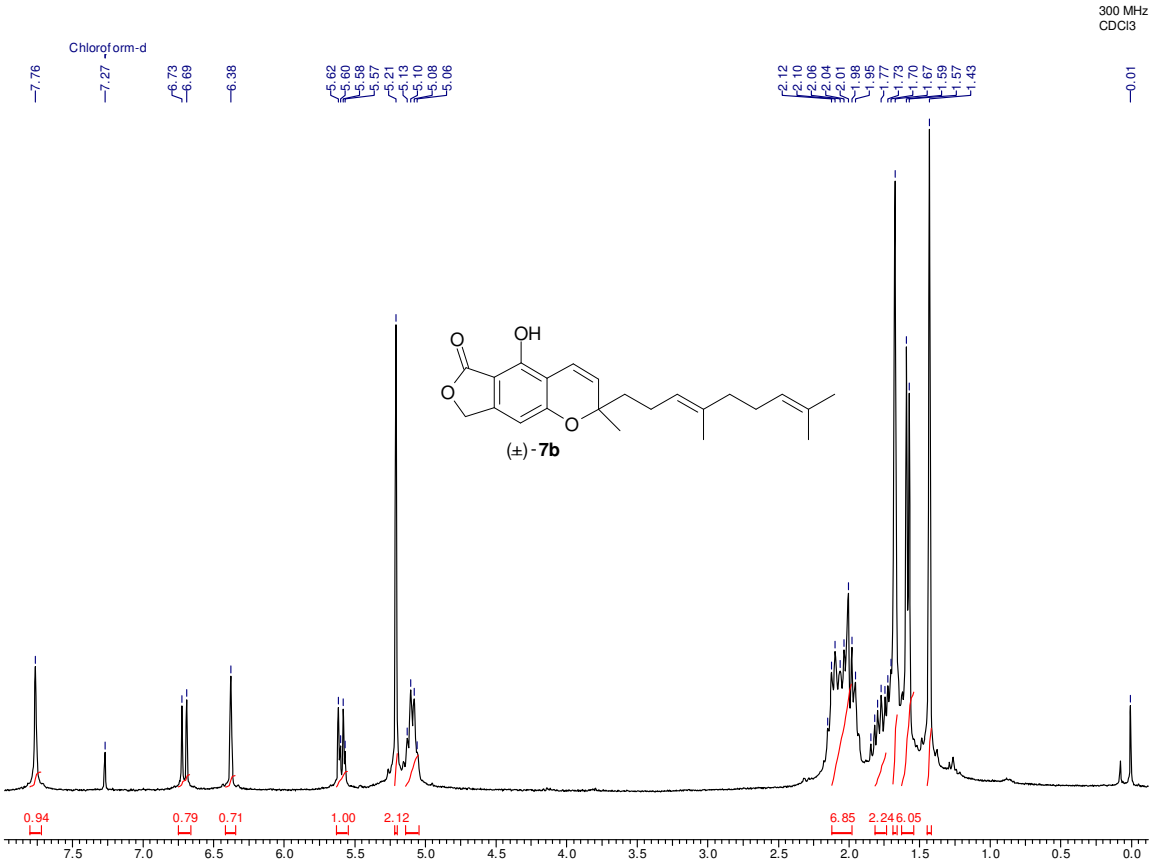

125 MHz
DMSO-d6
DMSO-d6
170.61
157.97
150.80
147.78
124.87
124.27
112.72
109.07
106.84
75.02
66.65
48.28
39.70
39.53
36.07
28.95
28.62
24.51
23.19
O
O
O
OH
(±)-5
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

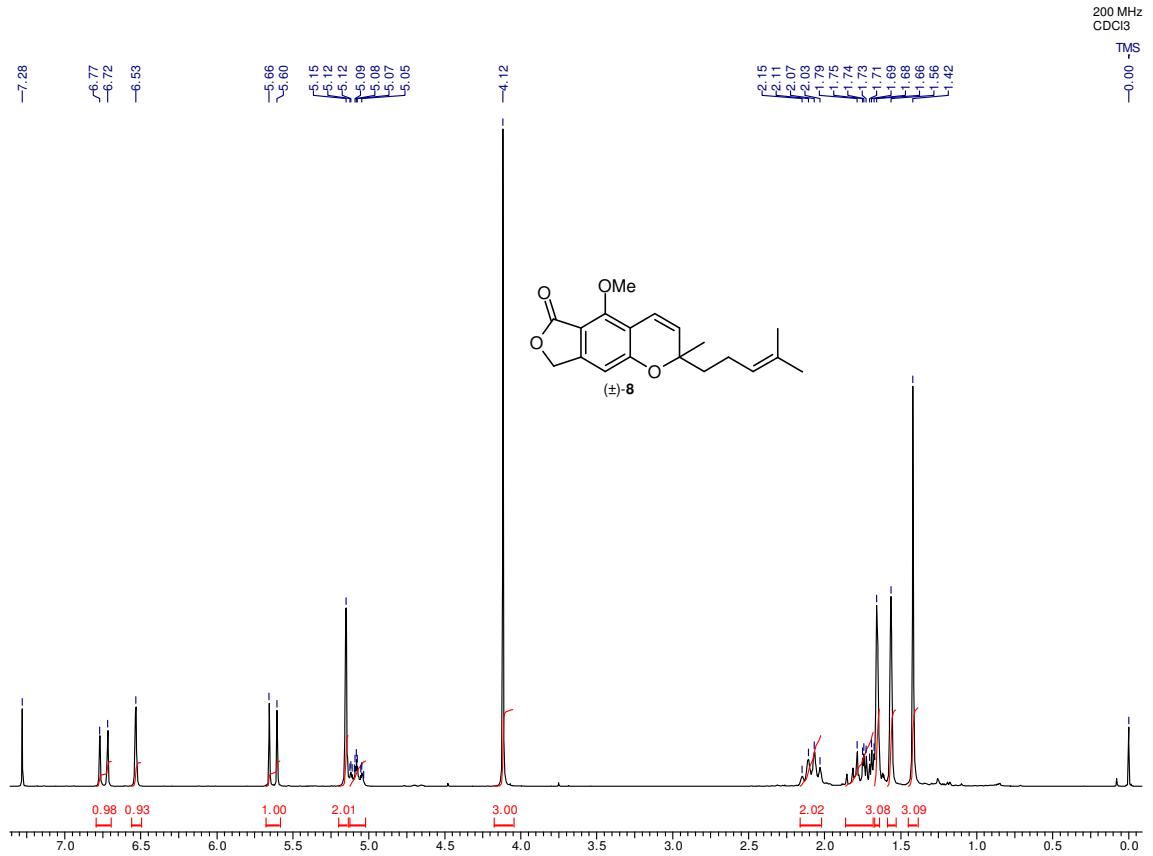

125 MHz
DMSO-d6
109.09
106.85
66.67
48.28
39.52
36.08
28.97
28.62
24.53
23.19
(±)-5
OH
O
O
O

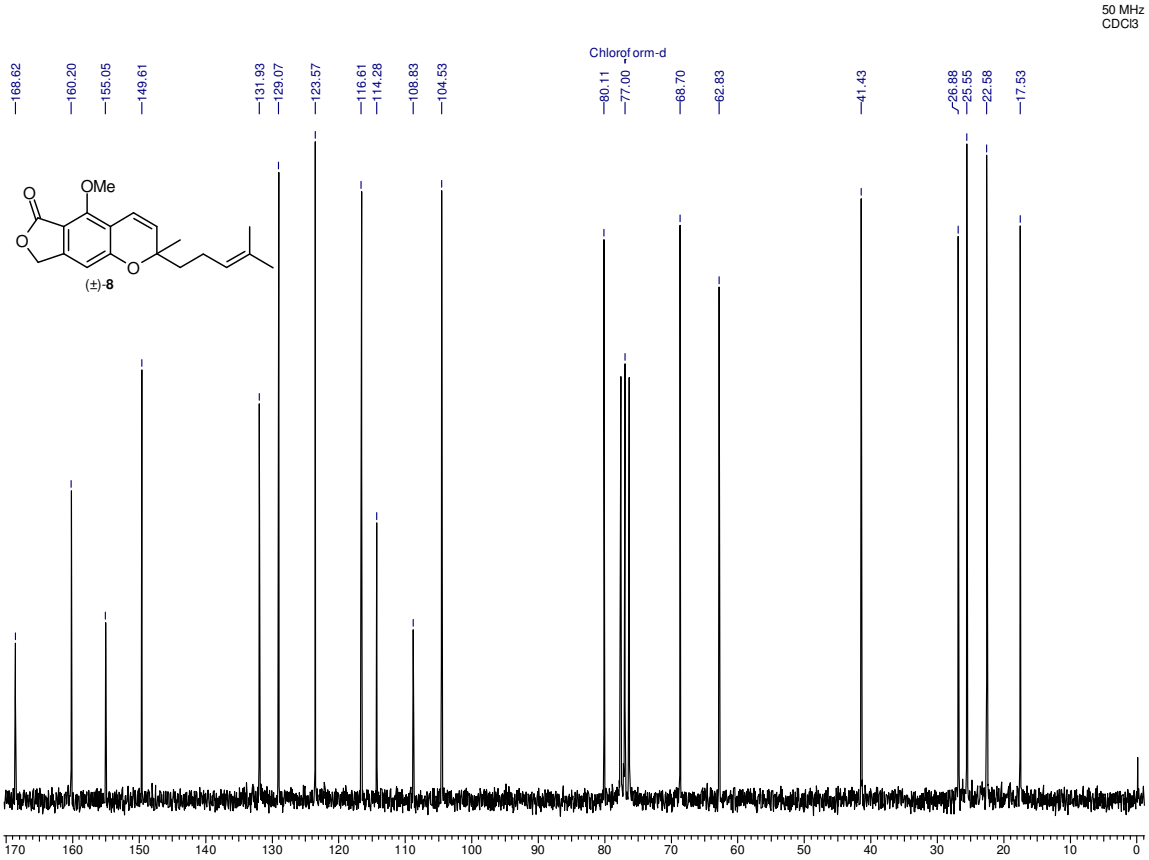

300 MHz
CDCl3
7.77
7.27
6.71
6.67
6.36
5.60
5.56
5.19
5.09
5.07
5.05
2.12
2.09
2.07
2.04
1.79
1.77
1.75
1.72
1.70
1.68
1.67
1.65
1.56
1.41
(±)-7a
OH
O
O
O
1.05
1.01
1.00
1.05
2.02
2.13
5.44
3.15

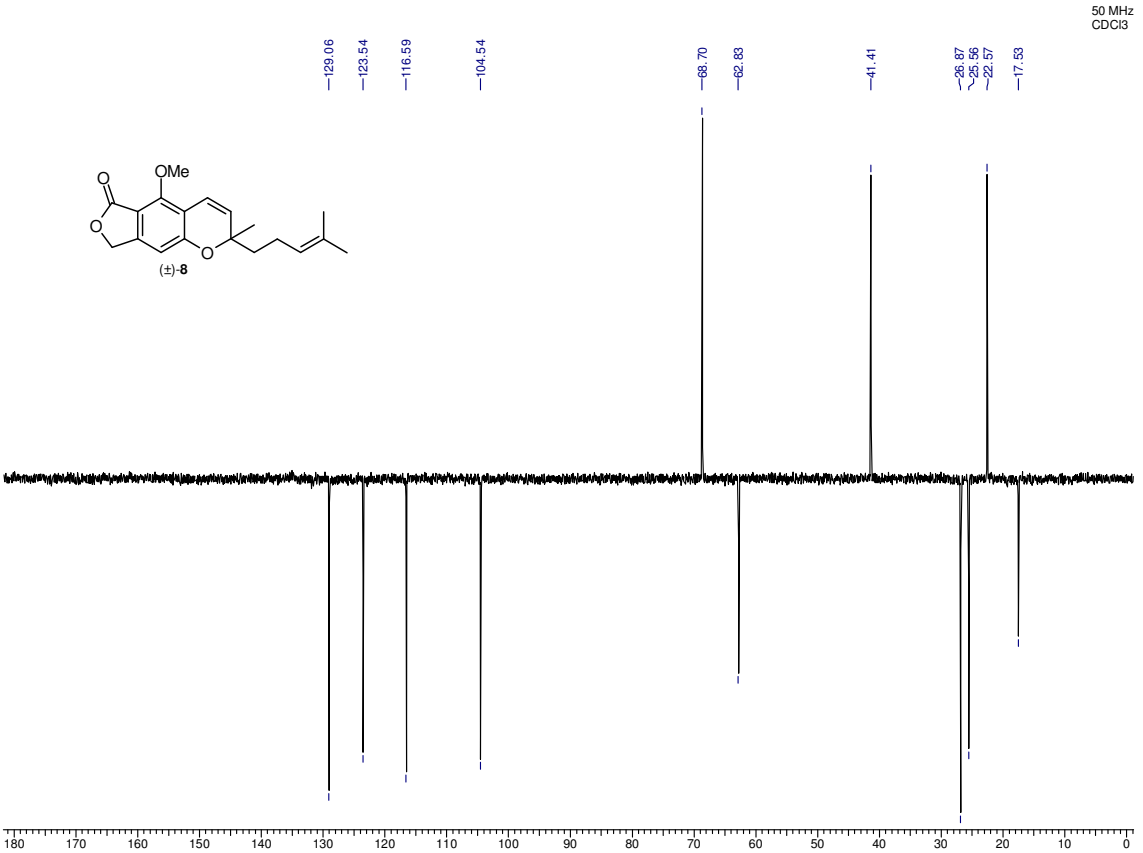

75 MHz
CDCl3
Chloroform-d
172.50
161.08
152.08
147.10
131.90
127.85
123.66
115.67
108.59
103.67
101.97
80.36
77.00
70.35
41.48
26.83
25.54
22.61
17.55
OH
O
O
O
(±)-7a

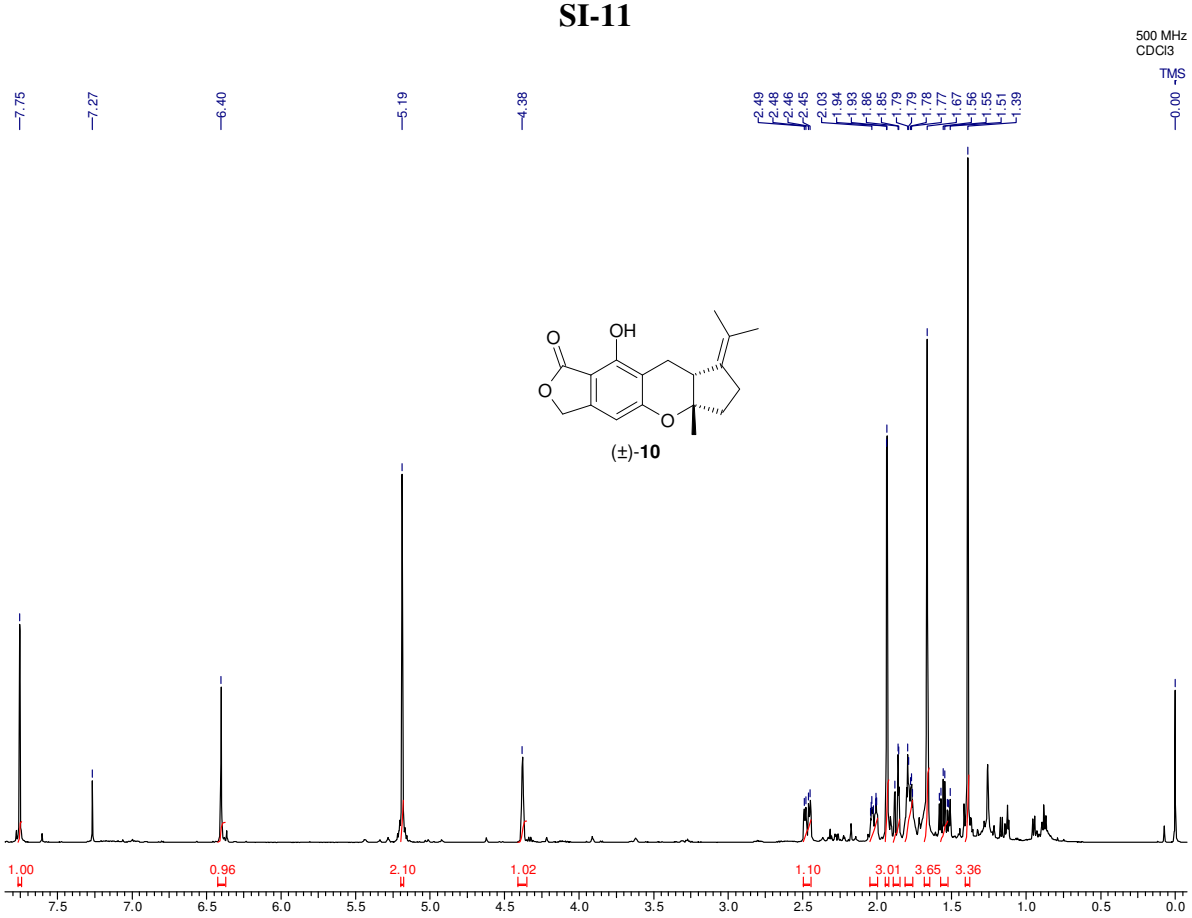

75 MHz
CDCl3
127.85
123.61
115.64
101.97
70.38
41.42
26.83
25.58
22.59
17.55
OH
O
O
O
(±)-7a

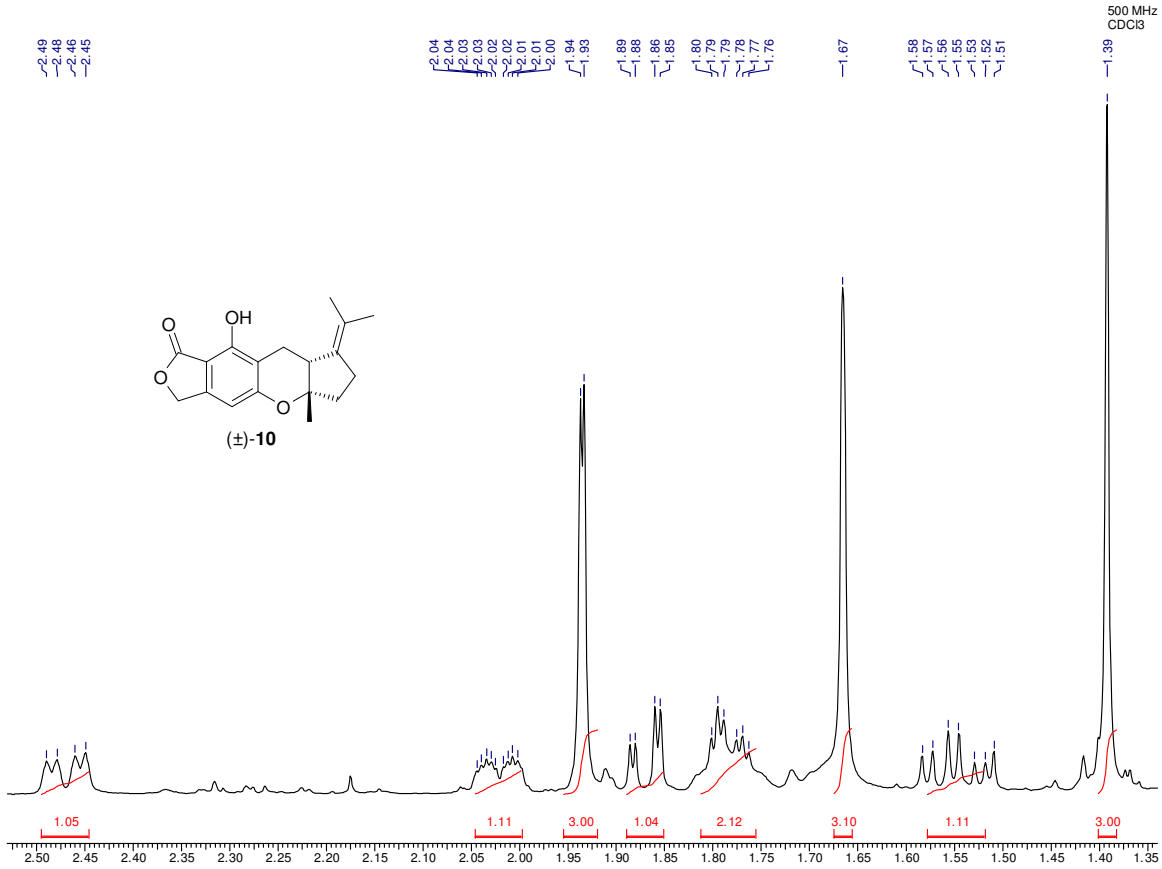

300 MHz
CDCl3
Chloroform-d
7.76
7.27
6.73
6.69
6.38
5.62
5.60
5.58
5.57
5.21
5.13
5.10
5.08
5.06
2.12
2.10
2.06
2.04
2.01
1.98
1.95
1.77
1.73
1.70
1.67
1.59
1.57
1.43
0.01
OH
O
O
O
(±)-7b
0.94
0.79
0.71
1.00
2.12
6.85
2.24
6.05

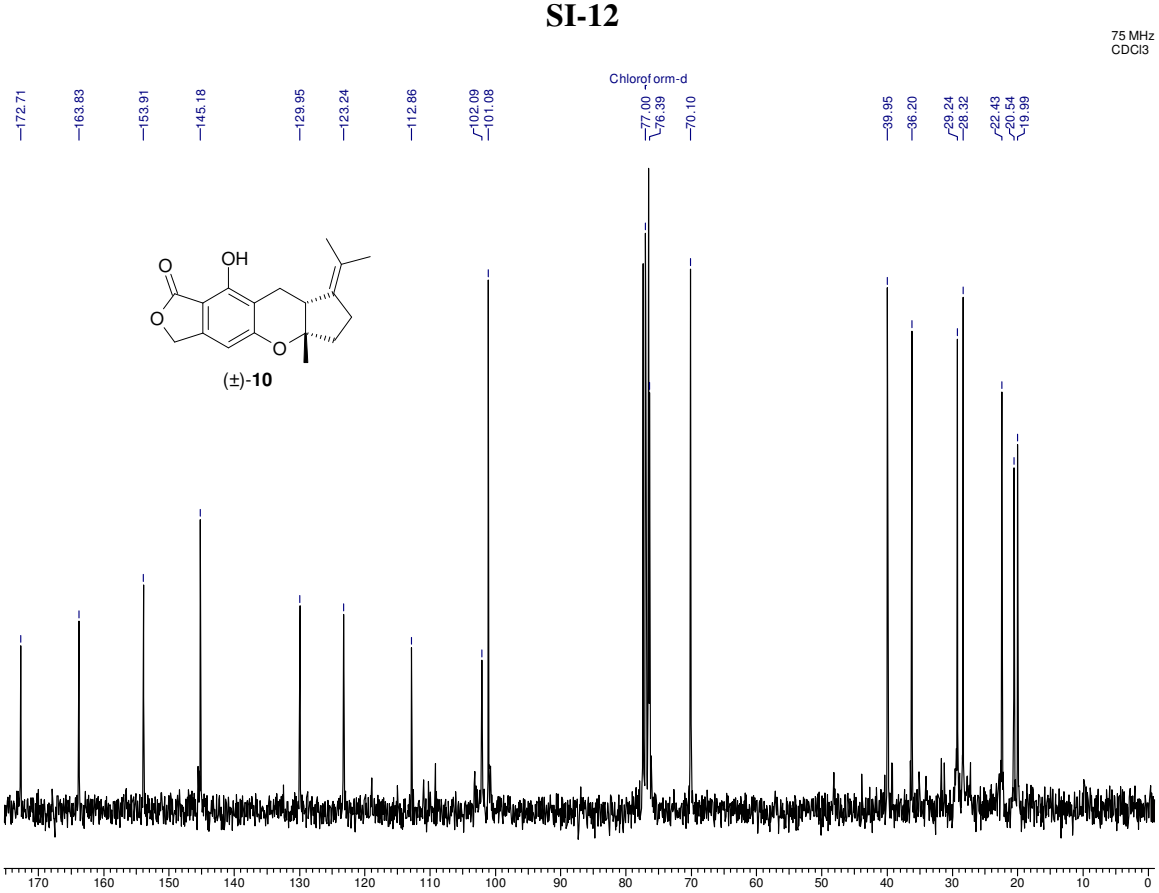

200 MHz
CDCl3
TMS
7.28
6.77
6.72
6.53
5.66
5.60
5.15
5.12
5.12
5.09
5.08
5.07
5.05
4.12
2.15
2.11
2.07
2.03
1.79
1.75
1.74
1.73
1.71
1.69
1.68
1.66
1.56
1.42
0.00
OMe
O
O
O
(±)-8
0.98
0.93
1.00
2.01
3.00
2.02
3.08
3.09

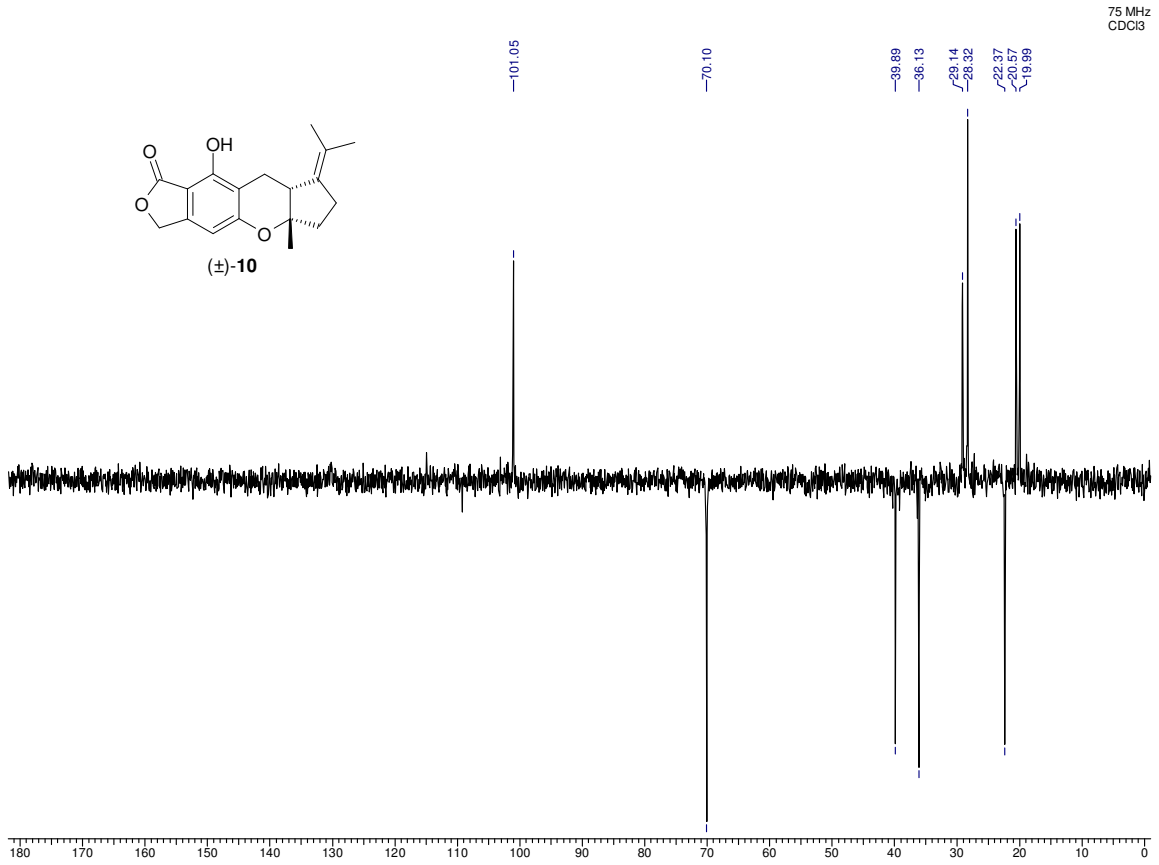

50 MHz
CDCl3
Chloroform-d
168.62
160.20
155.05
149.61
131.93
129.07
123.57
116.61
114.28
108.83
104.53
80.11
77.00
68.70
62.83
41.43
26.88
25.55
22.58
17.53
OMe
O
O
O
(±)-8
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

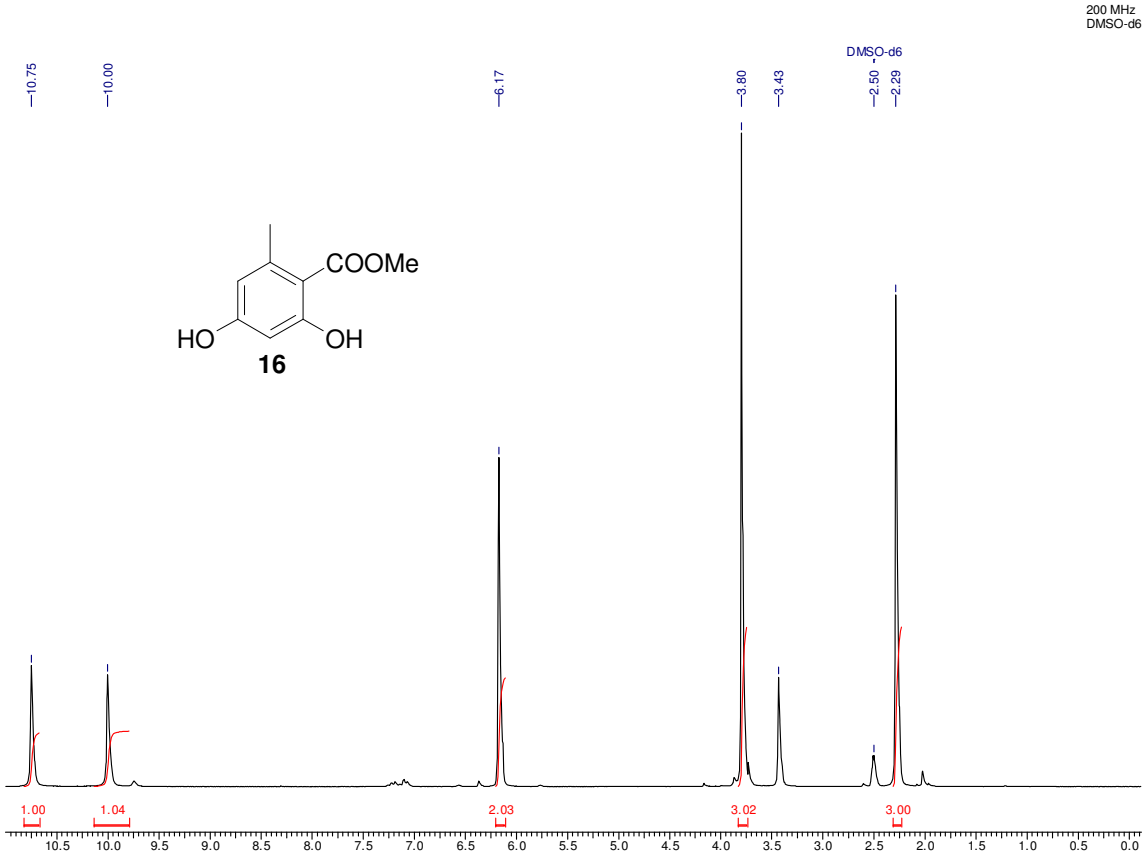

50 MHz
CDCl3
129.06
123.54
116.59
104.54
68.70
62.83
41.41
26.87
25.56
22.57
17.53
OMe
O
O
O
(±)-8
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

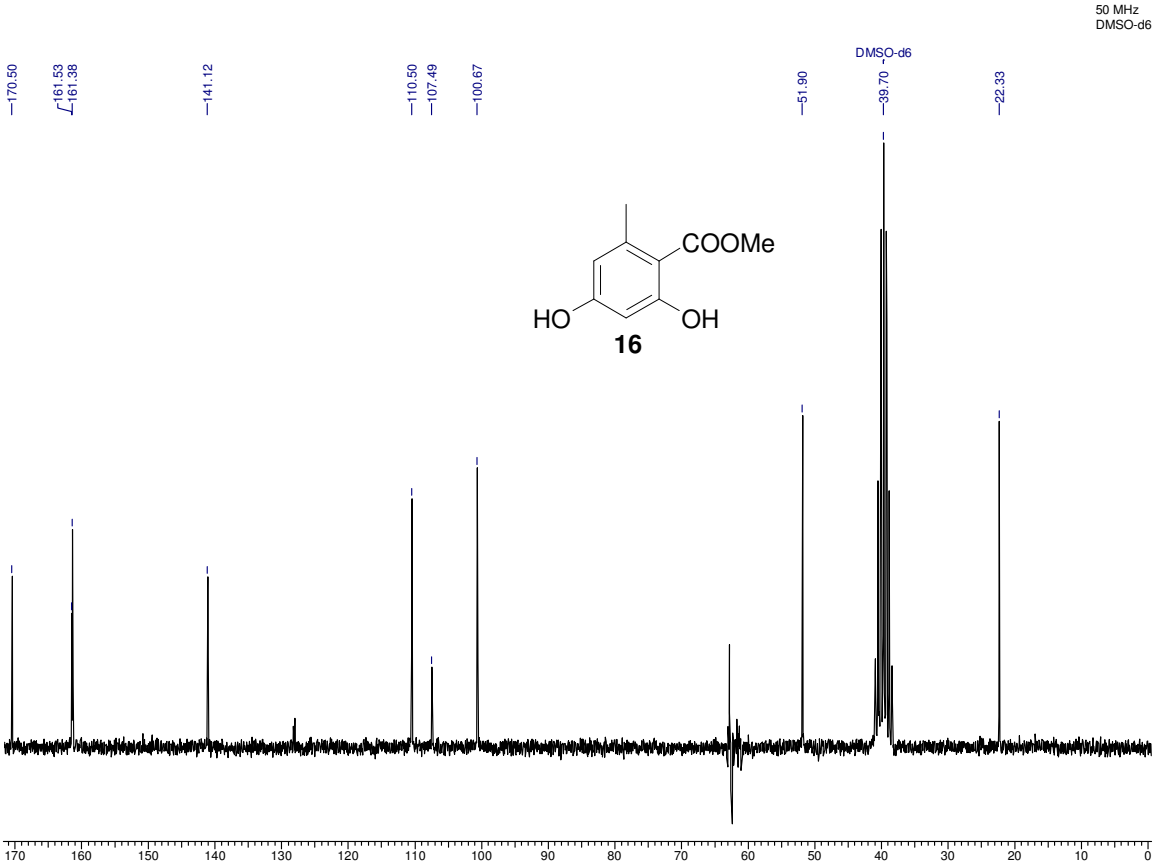

500 MHz
CDCl3
TMS
7.75
7.27
6.40
5.19
4.38
2.49
2.48
2.46
2.45
2.03
1.94
1.93
1.86
1.85
1.79
1.78
1.77
1.67
1.56
1.55
1.51
1.39
0.00
OH
O
O
O
(±)-10
1.00
0.96
2.10
1.02
1.10
3.01
3.65
3.36

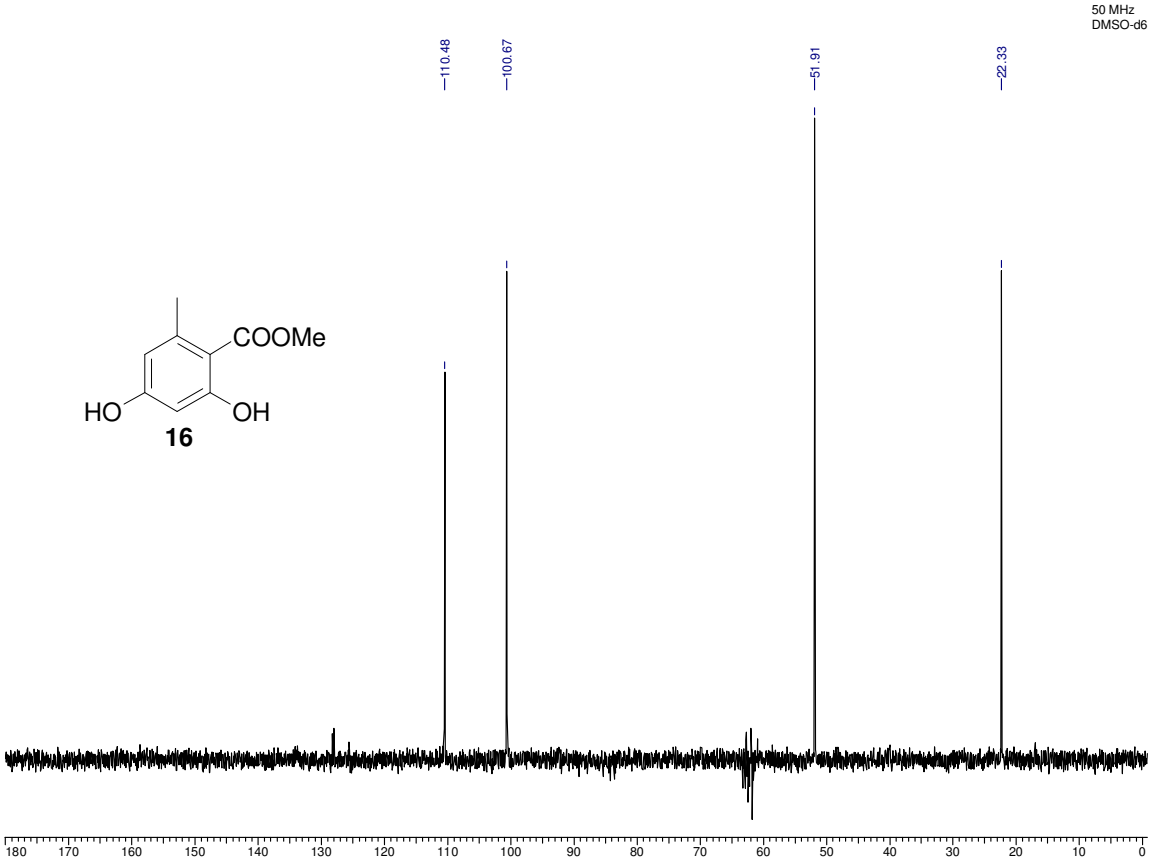

500 MHz
CDCl3
2.49
2.48
2.46
2.45
2.04
2.04
2.03
2.03
2.02
2.02
2.01
2.01
2.00
1.94
1.93
1.89
1.88
1.86
1.85
1.80
1.79
1.79
1.78
1.77
1.76
1.67
1.58
1.57
1.56
1.55
1.53
1.52
1.51
1.39
OH
O
O
O
(±)-10
1.05
1.11
3.00
1.04
2.12
3.10
1.11
3.00

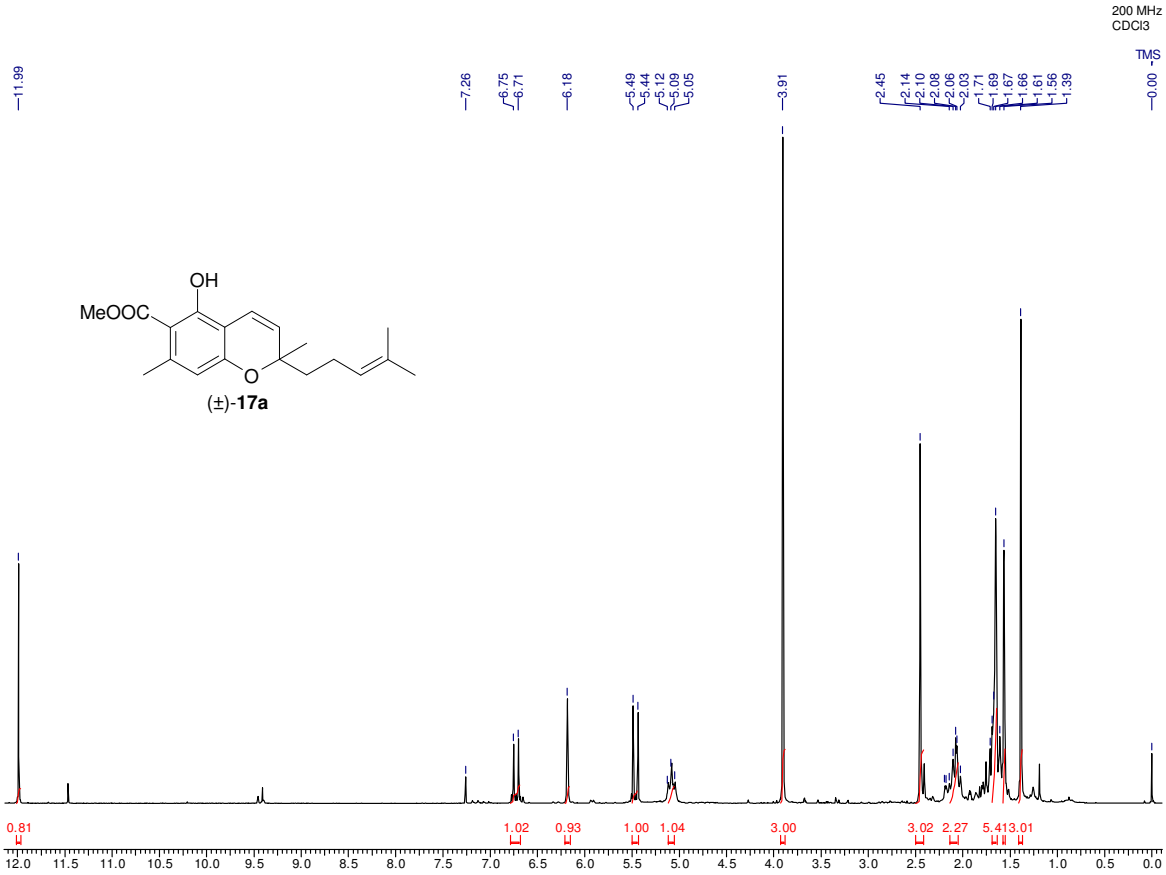

75 MHz
CDCl3
Chloroform-d
172.71
163.83
153.91
145.18
129.95
123.24
112.86
102.09
101.08
77.00
76.39
70.10
39.95
36.20
29.24
28.32
22.43
20.54
19.99
OH
O
O
O
(±)-10

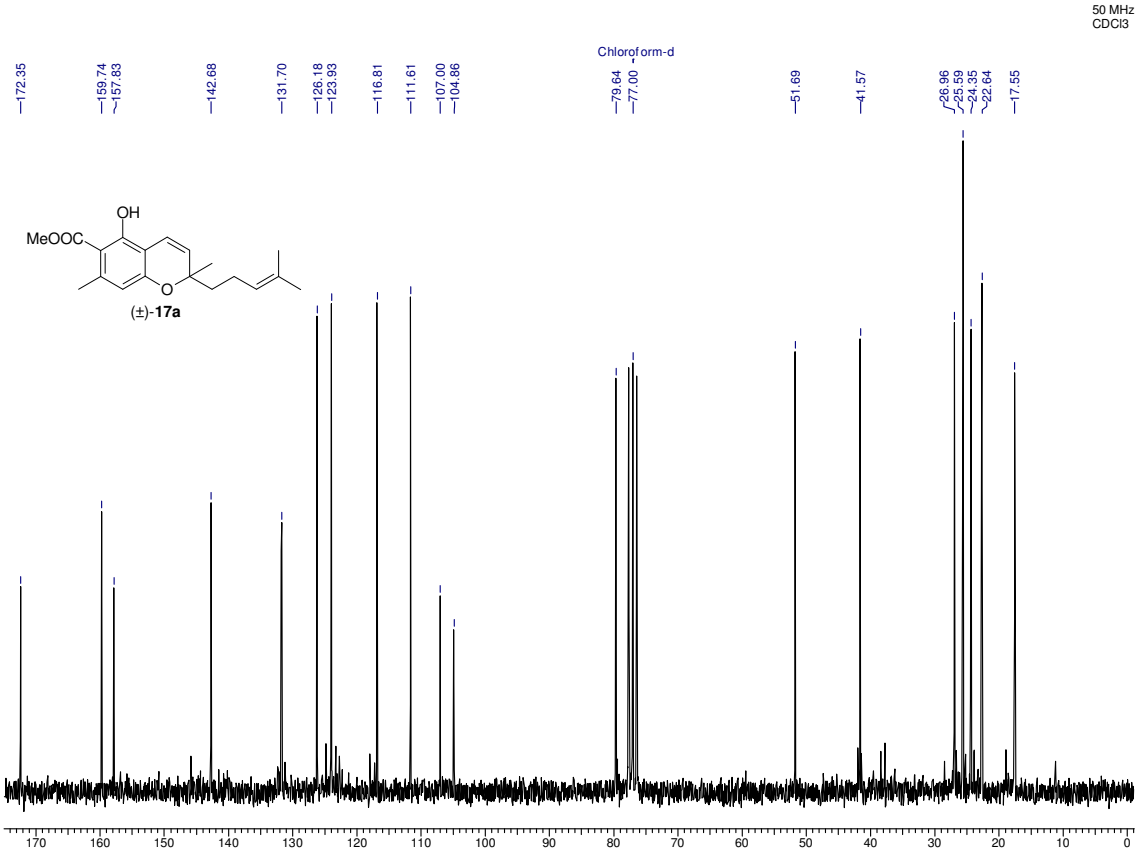

75 MHz
CDCl3
101.05
70.10
39.89
36.13
29.14
28.32
22.37
20.57
19.99
OH
O
O
O
(±)-10

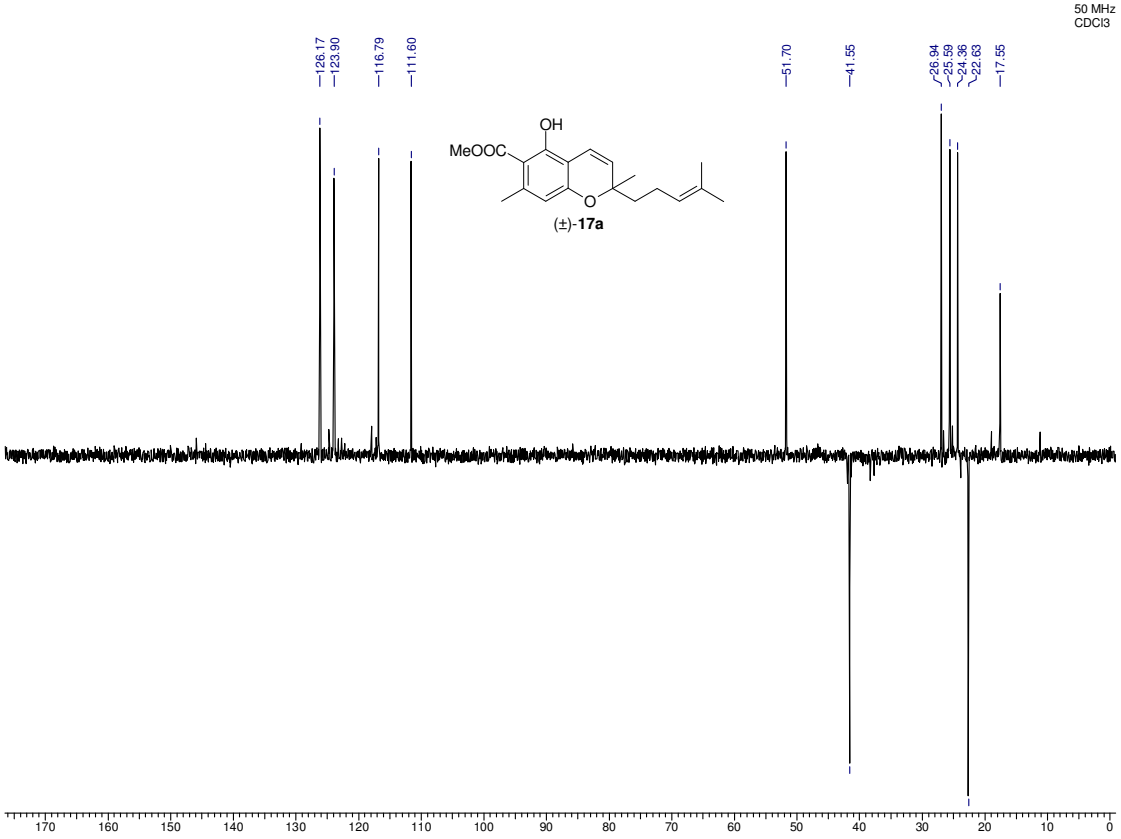

200 MHz
DMSO-d6
10.75
10.00
6.17
3.80
3.43
DMSO-d6
2.50
2.29
COOMe
HO
OH
16
1.00
1.04
2.03
3.02
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

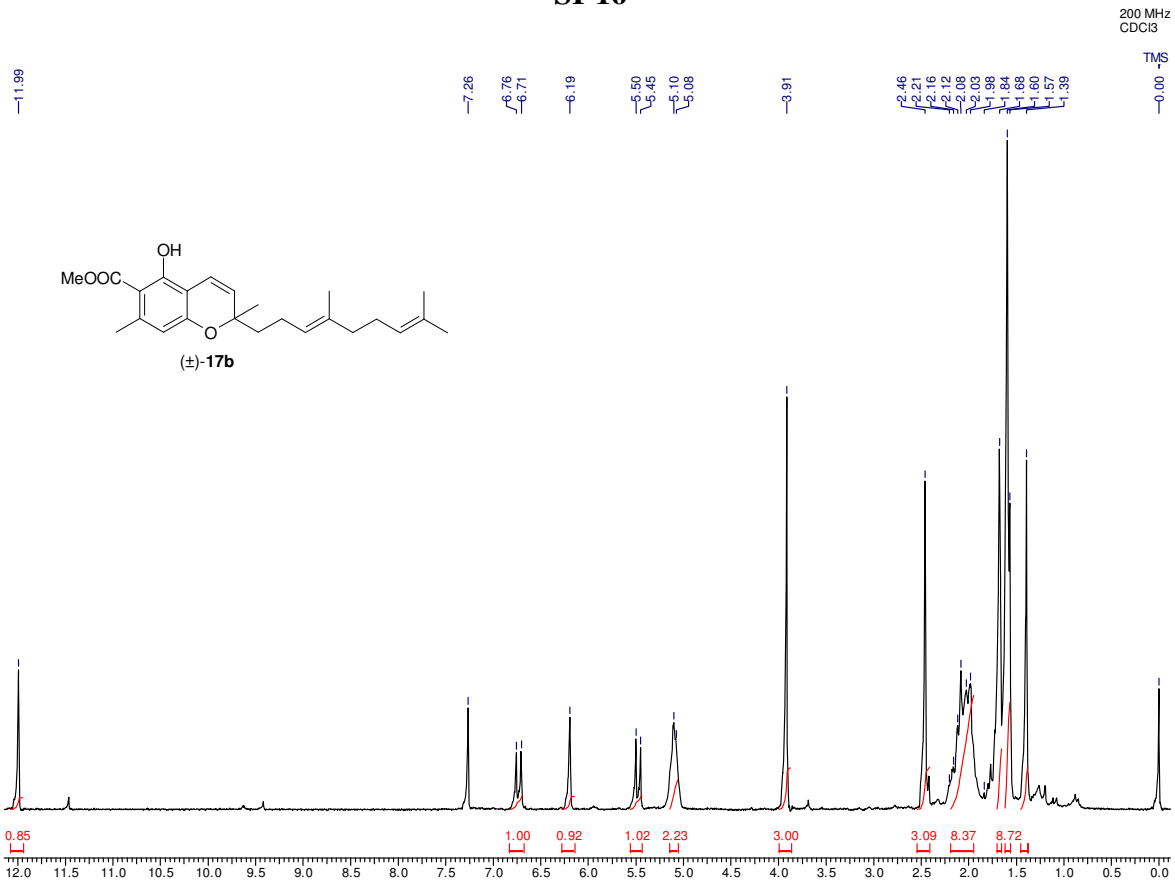

50 MHz
DMSO-d6
170.50
161.53
161.38
141.12
110.50
107.49
100.67
51.90
DMSO-d6
39.70
22.33
COOMe
HO
OH
16
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

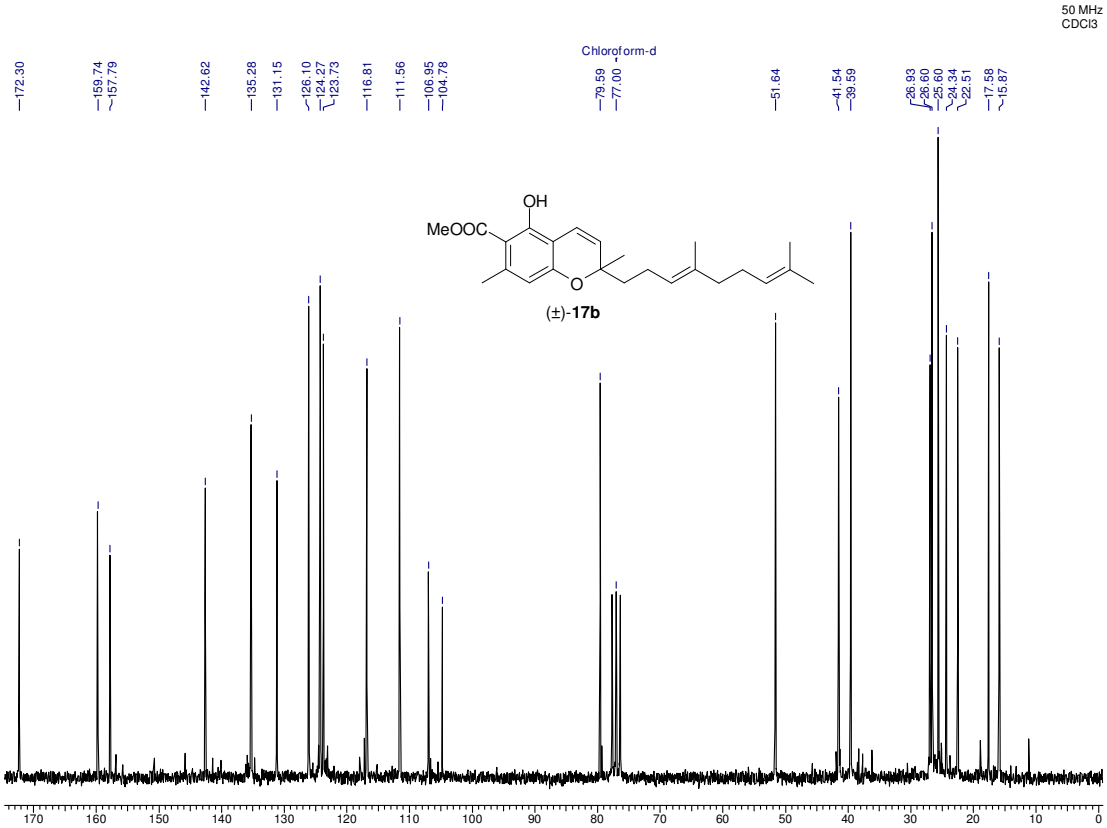

50 MHz
DMSO-d6
110.48
100.67
51.91
22.33
COOMe
HO
OH
16
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

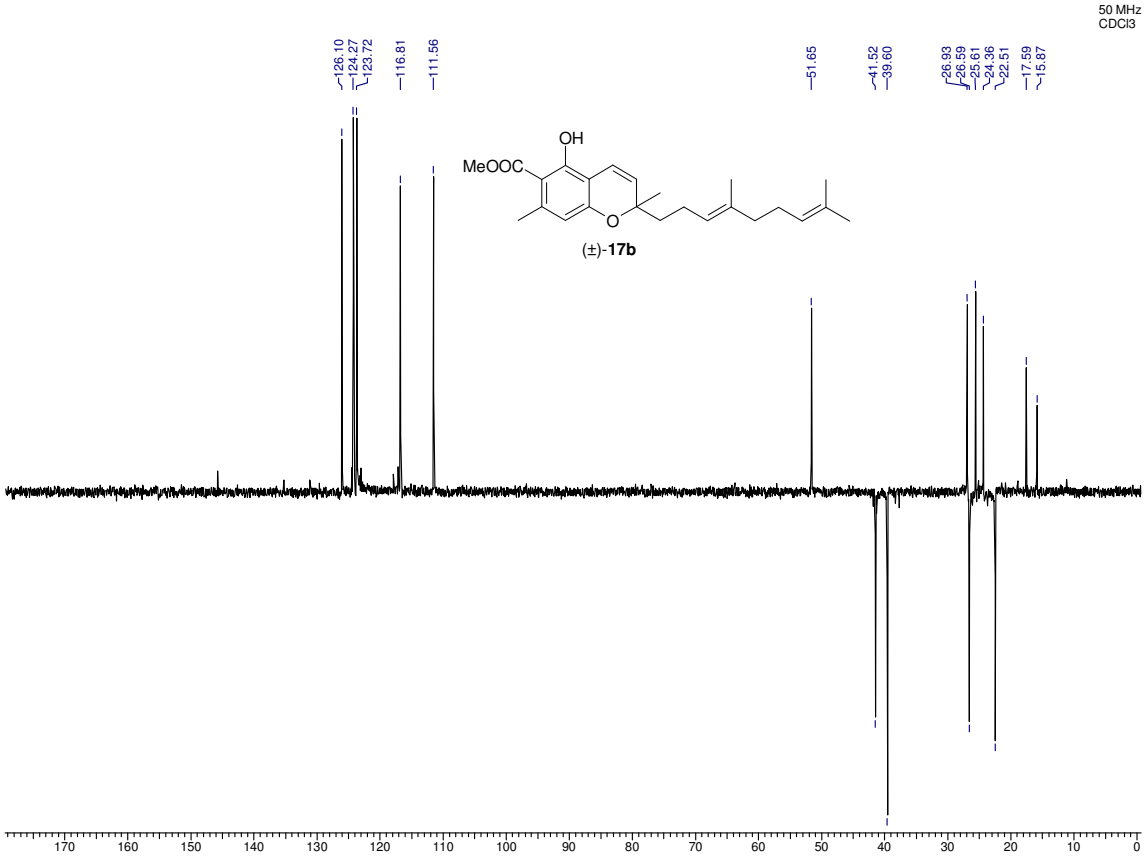

200 MHz
CDCl3
TMS
11.99
7.26
6.75
6.71
6.18
5.49
5.44
5.12
5.09
5.05
3.91
2.45
2.14
2.10
2.08
2.06
2.03
1.71
1.69
1.67
1.66
1.61
1.56
1.39
0.00
OH
MeOOC
O
(±)-17a
0.81
1.02
0.93
1.00
1.04
3.00
3.02
2.27
5.41
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

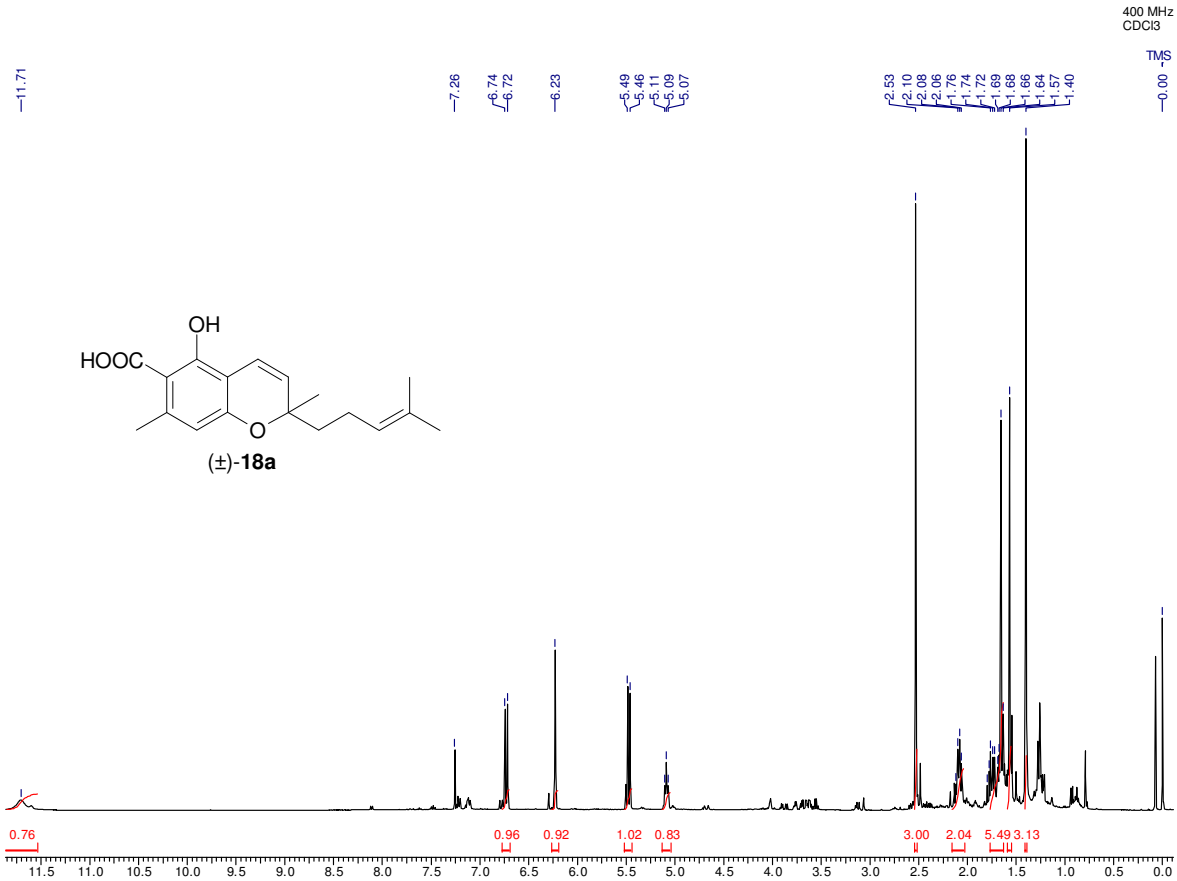

50 MHz
CDCl3
Chloroform-d
172.35
159.74
157.83
142.68
131.70
126.18
123.93
116.81
111.61
107.00
104.86
79.64
77.00
51.69
41.57
26.96
25.59
24.35
22.64
17.55
OH
MeOOC
O
(±)-17a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

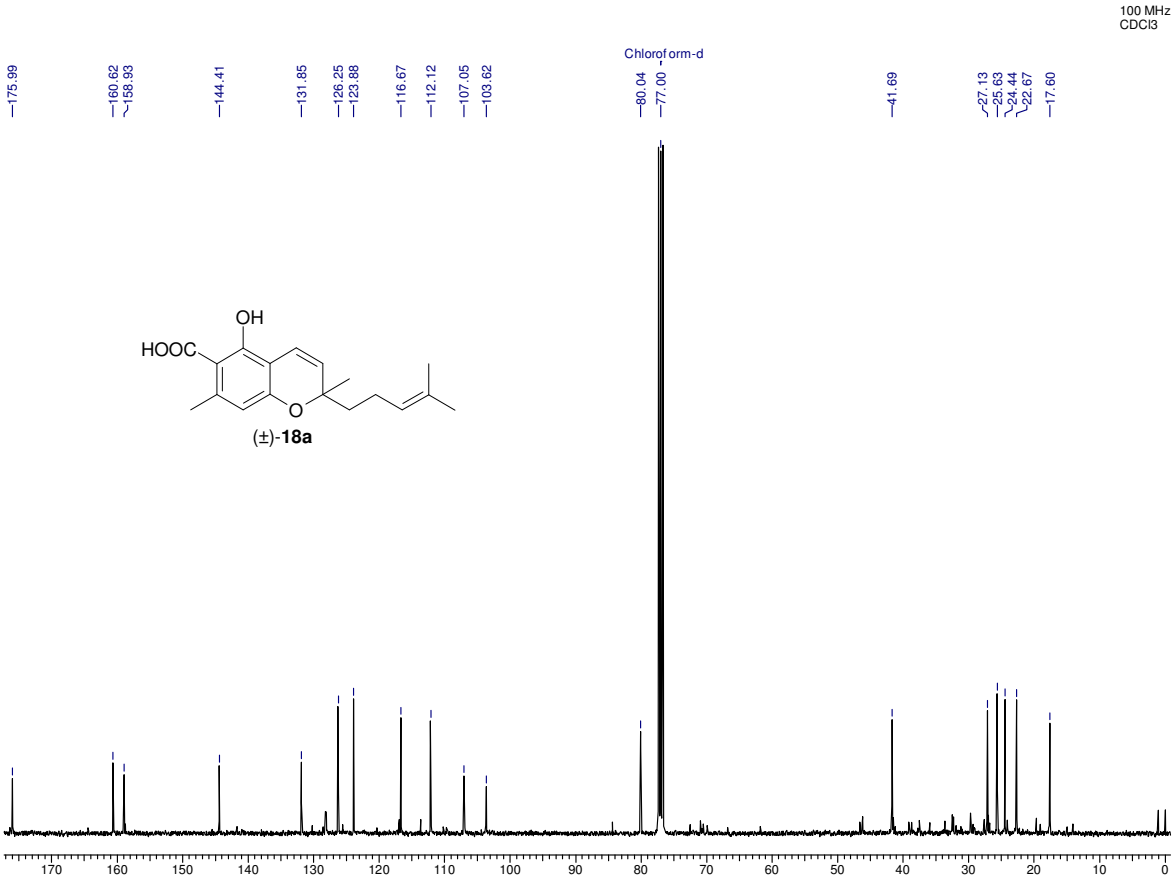

50 MHz
CDCl3
126.17
123.90
116.79
111.60
51.70
41.55
26.94
25.59
24.36
22.63
17.55
OH
MeOOC
O
(±)-17a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

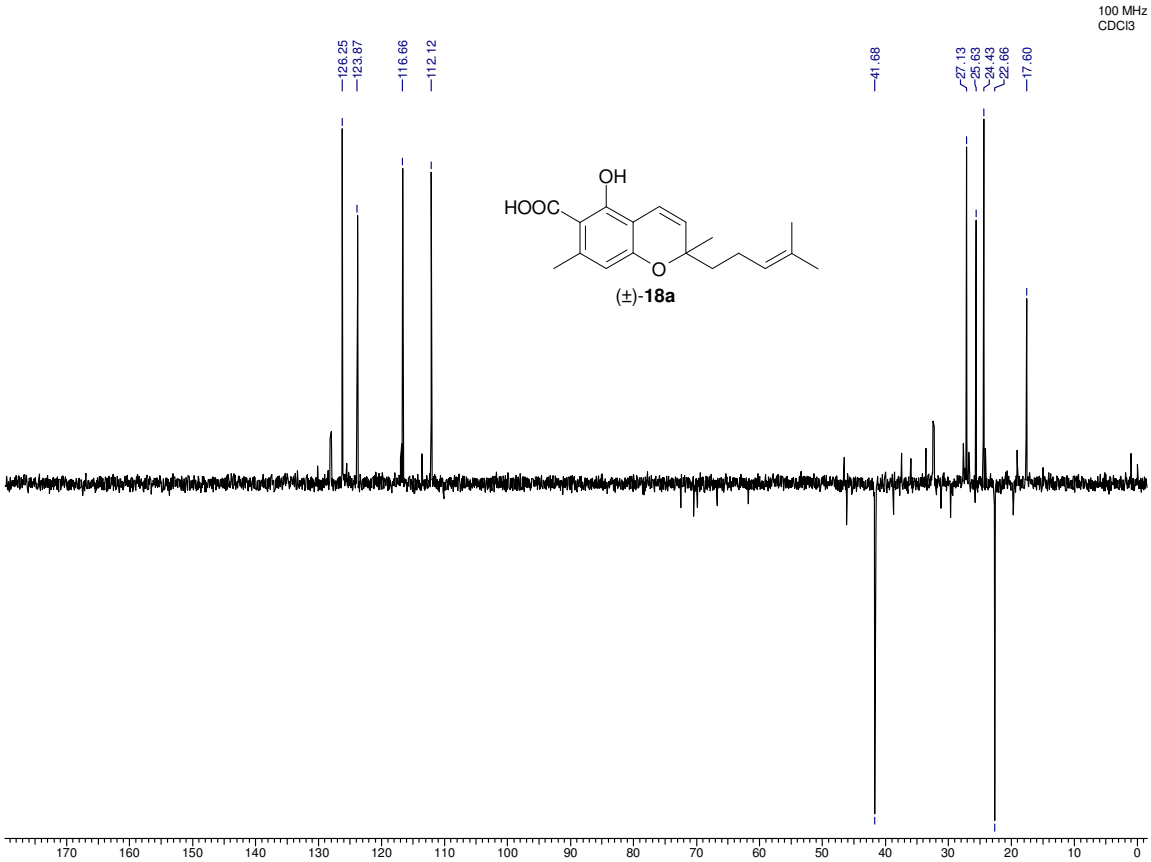

200 MHz
CDCl3
TMS
11.99
7.26
6.76
6.71
6.19
5.50
5.45
5.10
5.08
3.91
2.46
2.21
2.16
2.12
2.08
2.03
1.98
1.84
1.68
1.60
1.57
1.39
0.00
OH
MeOOC
O
(±)-17b
0.85
1.00
0.92
1.02
2.23
3.00
3.09
8.37
8.72

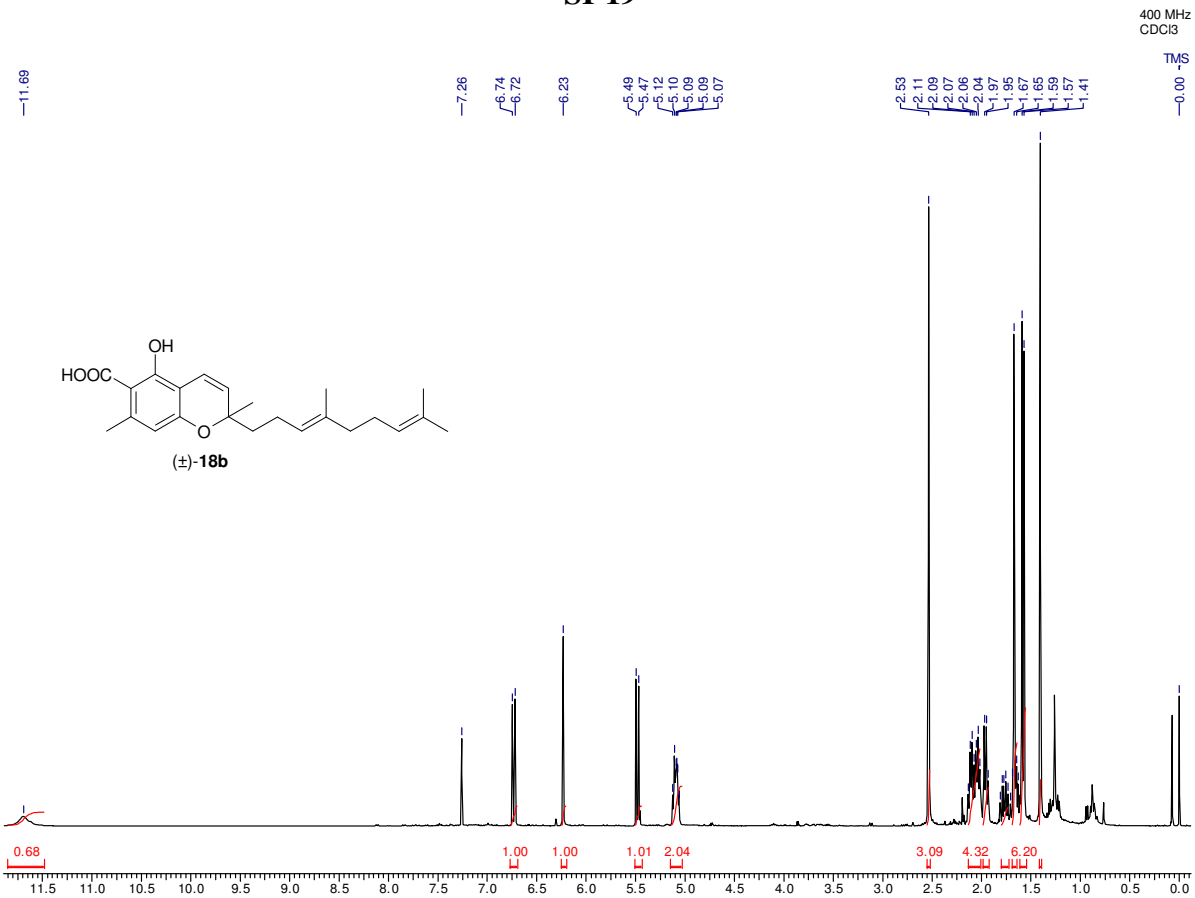

50 MHz
CDCl3
Chloroform-d
172.30
159.74
157.79
142.62
135.28
131.15
126.10
124.27
123.73
116.81
111.56
106.95
104.78
79.59
77.00
51.64
41.54
39.59
26.93
26.60
25.60
24.34
22.51
17.58
15.87
OH
MeOOC
O
(±)-17b

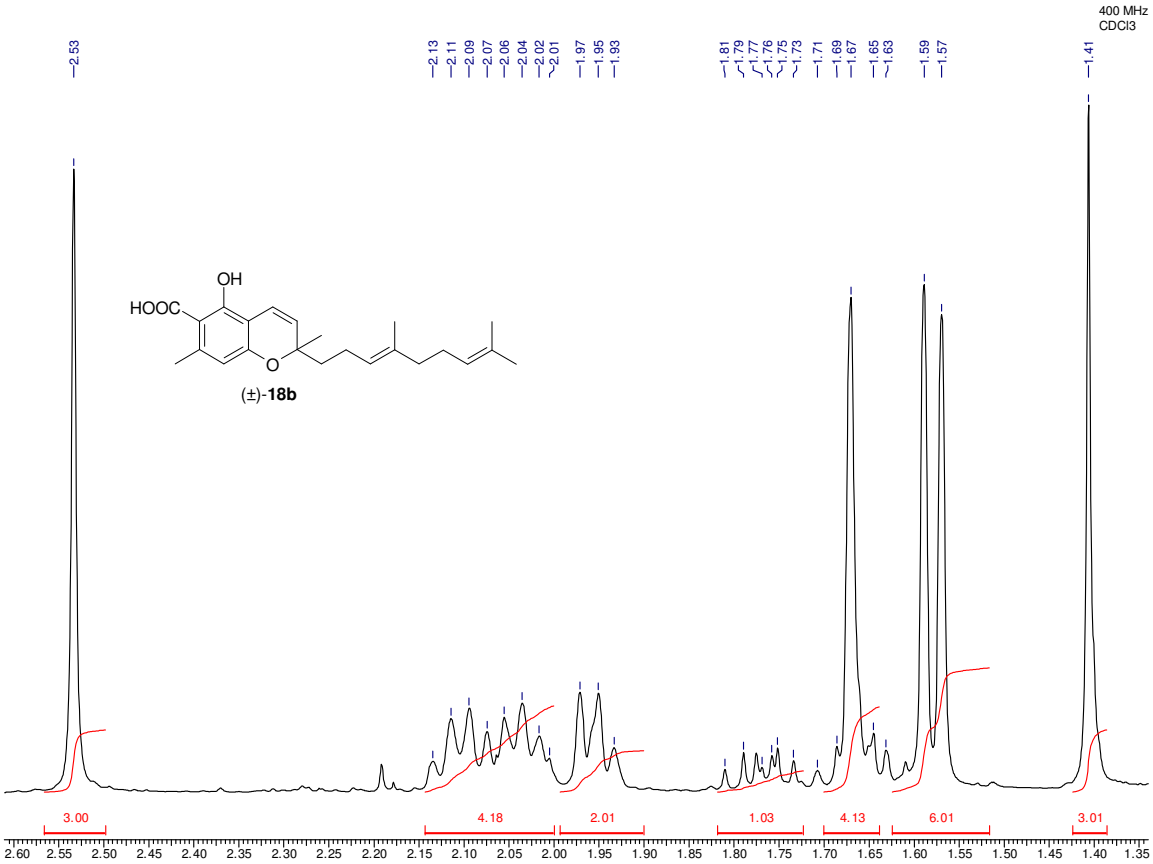

50 MHz
CDCl3
126.10
124.27
123.72
116.81
111.56
51.65
41.52
39.60
26.93
26.59
25.61
24.36
22.51
17.59
15.87
OH
MeOOC
O
(±)-17b
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

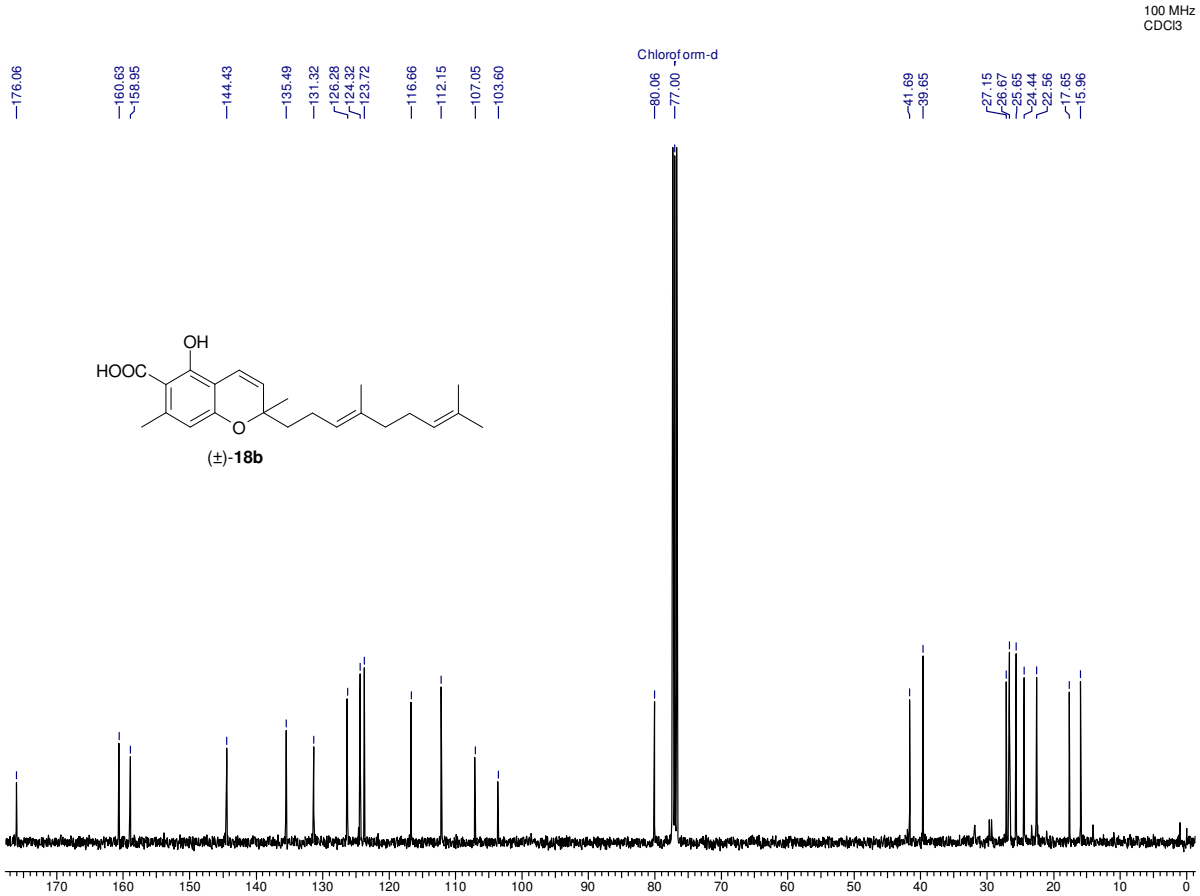

400 MHz
CDCl3
TMS
11.71
7.26
6.74
6.72
6.23
5.49
5.46
5.11
5.09
5.07
2.53
2.10
2.08
2.06
1.76
1.74
1.72
1.69
1.68
1.66
1.64
1.57
1.40
0.00
OH
HOOC
O
(±)-18a
0.76
0.96
0.92
1.02
0.83
3.00
2.04
5.49
3.13
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

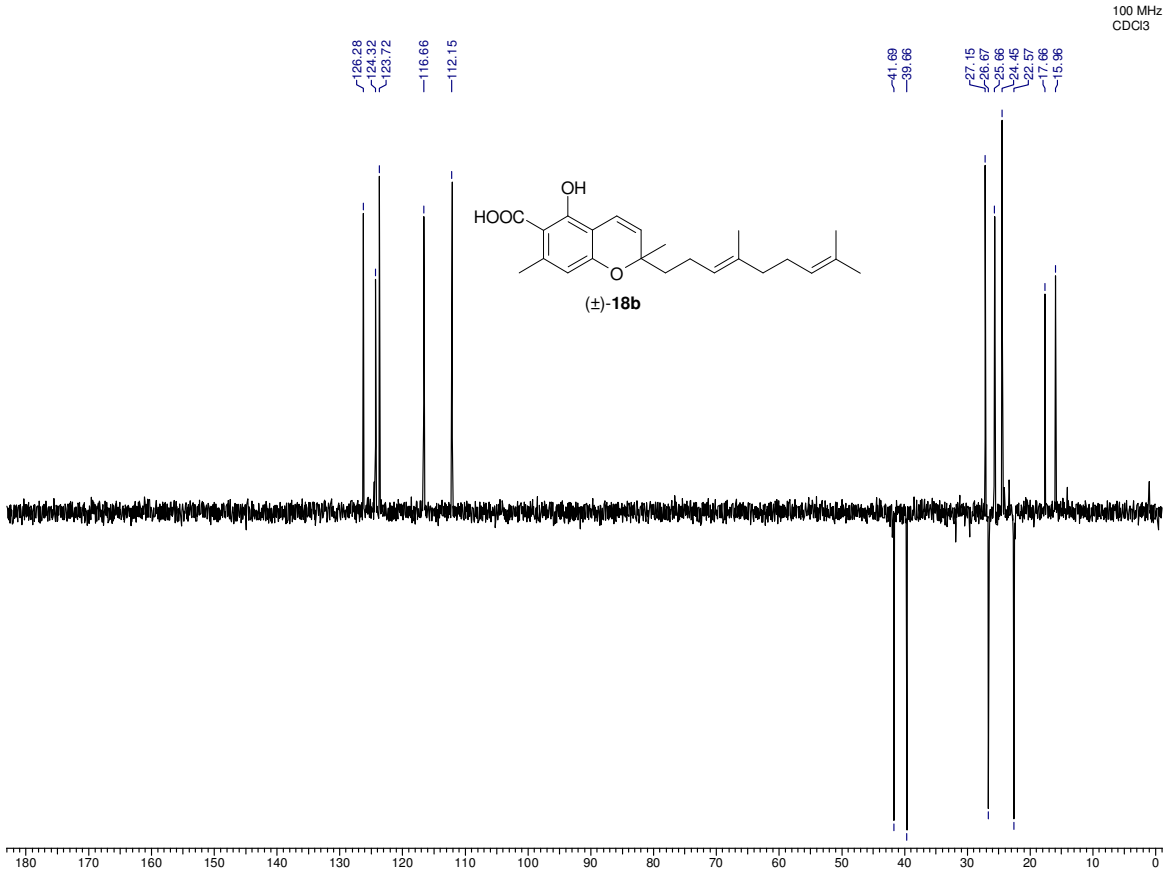

100 MHz
CDCl3
Chloroform-d
175.99
160.62
158.93
144.41
131.85
126.25
123.88
116.67
112.12
107.05
103.62
80.04
77.00
41.69
27.13
25.63
24.44
22.67
17.60
OH
HOOC
O
(±)-18a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

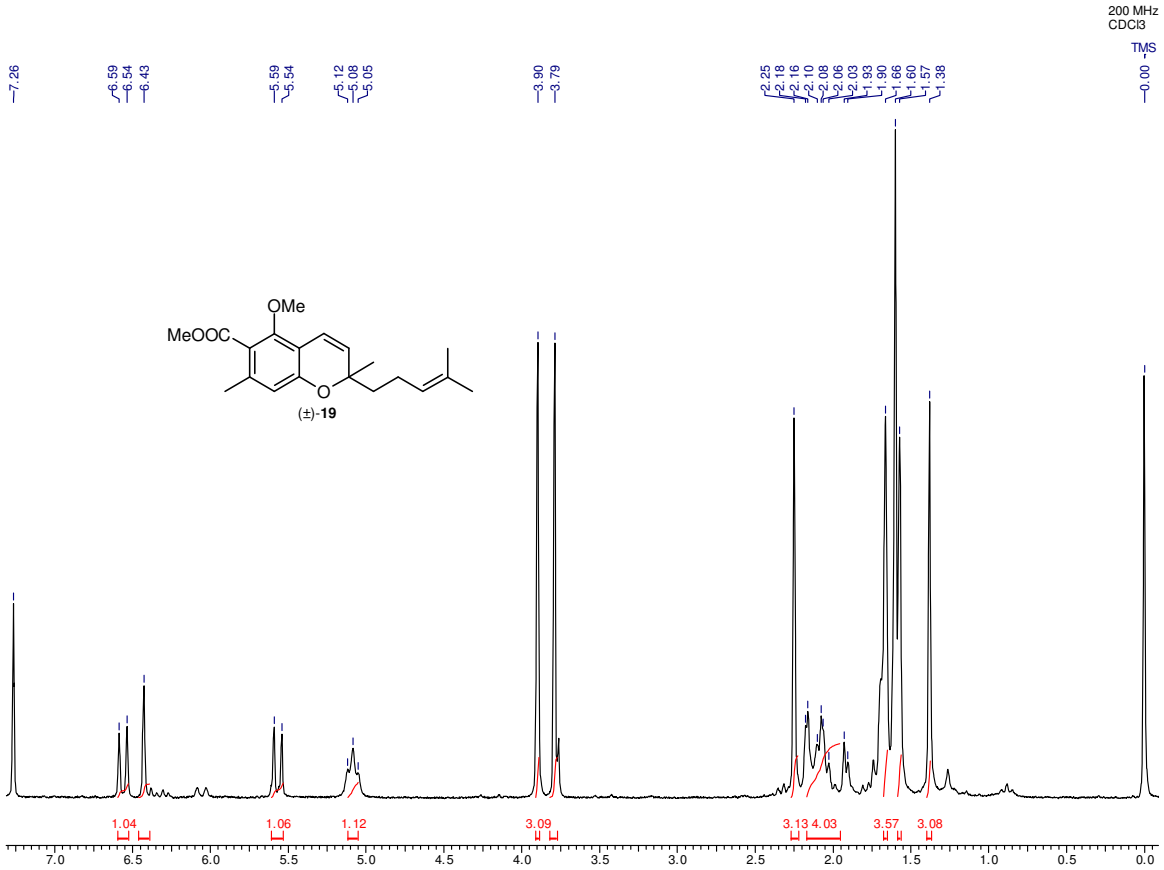

100 MHz
CDCl3
126.25
123.87
116.66
112.12
41.68
27.13
25.63
24.43
22.66
17.60
OH
HOOC
O
(±)-18a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

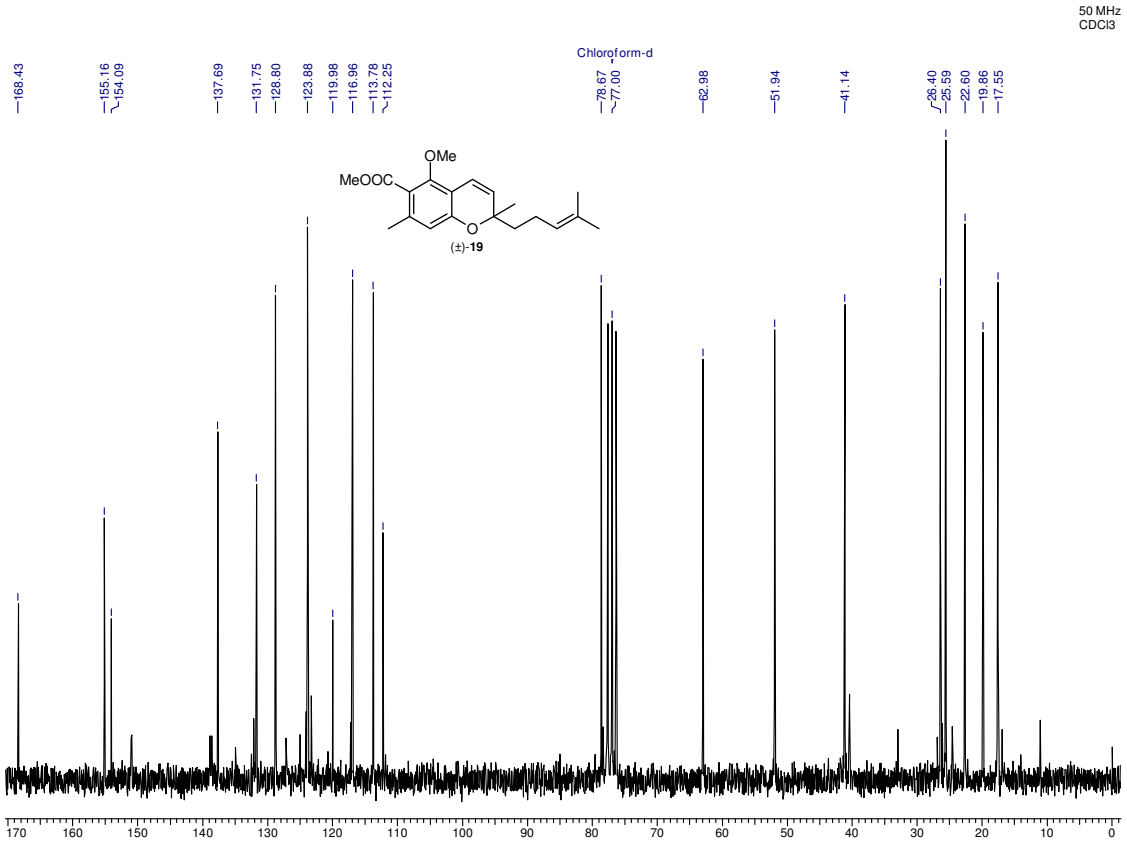

400 MHz
CDCl3
TMS
11.69
7.26
6.74
6.72
6.23
5.49
5.47
5.12
5.10
5.09
5.09
5.07
2.53
2.11
2.09
2.07
2.06
2.04
1.97
1.95
1.67
1.65
1.59
1.57
1.41
0.00
OH
HOOC
O
(±)-18b
0.68
1.00
1.00
1.01
2.04
3.09
4.32
6.20

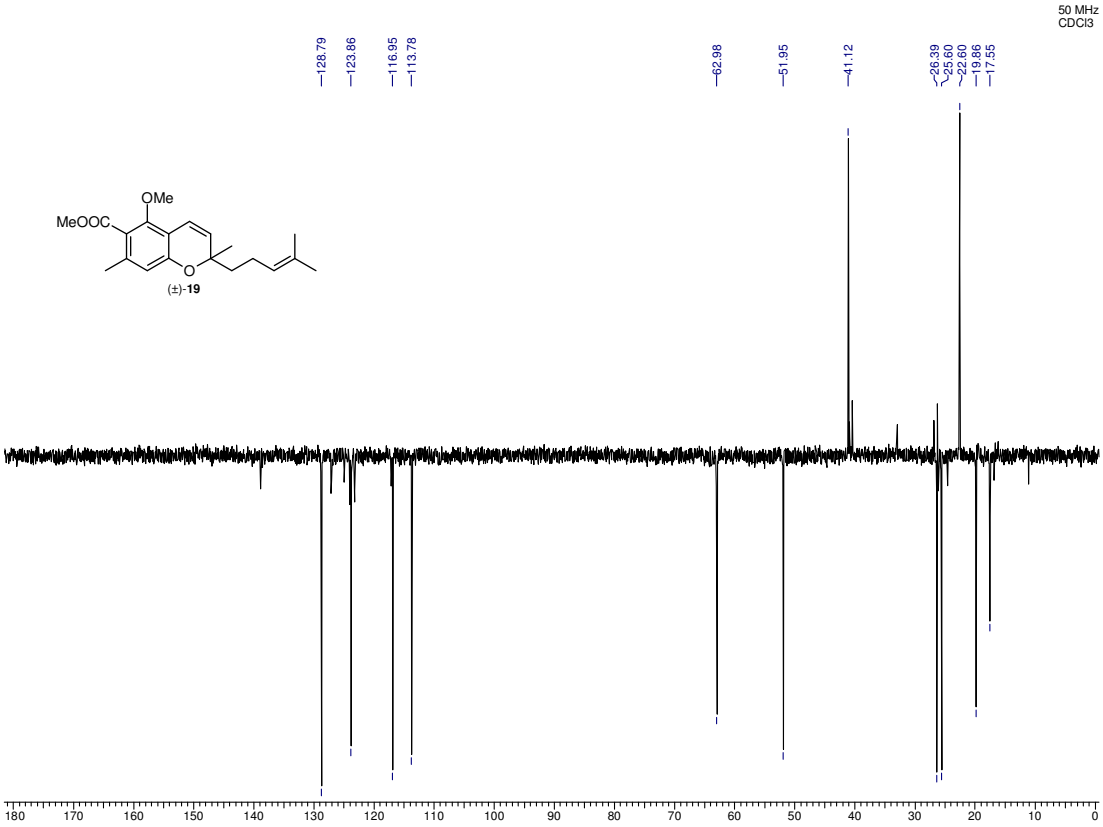

400 MHz
CDCl3
2.53
2.13
2.11
2.09
2.07
2.06
2.04
2.02
2.01
1.97
1.95
1.93
1.81
1.79
1.77
1.76
1.75
1.73
1.71
1.69
1.67
1.65
1.63
1.59
1.57
1.41
OH
HOOC
O
(±)-18b
3.00
4.18
2.01
1.03
4.13
6.01
3.01

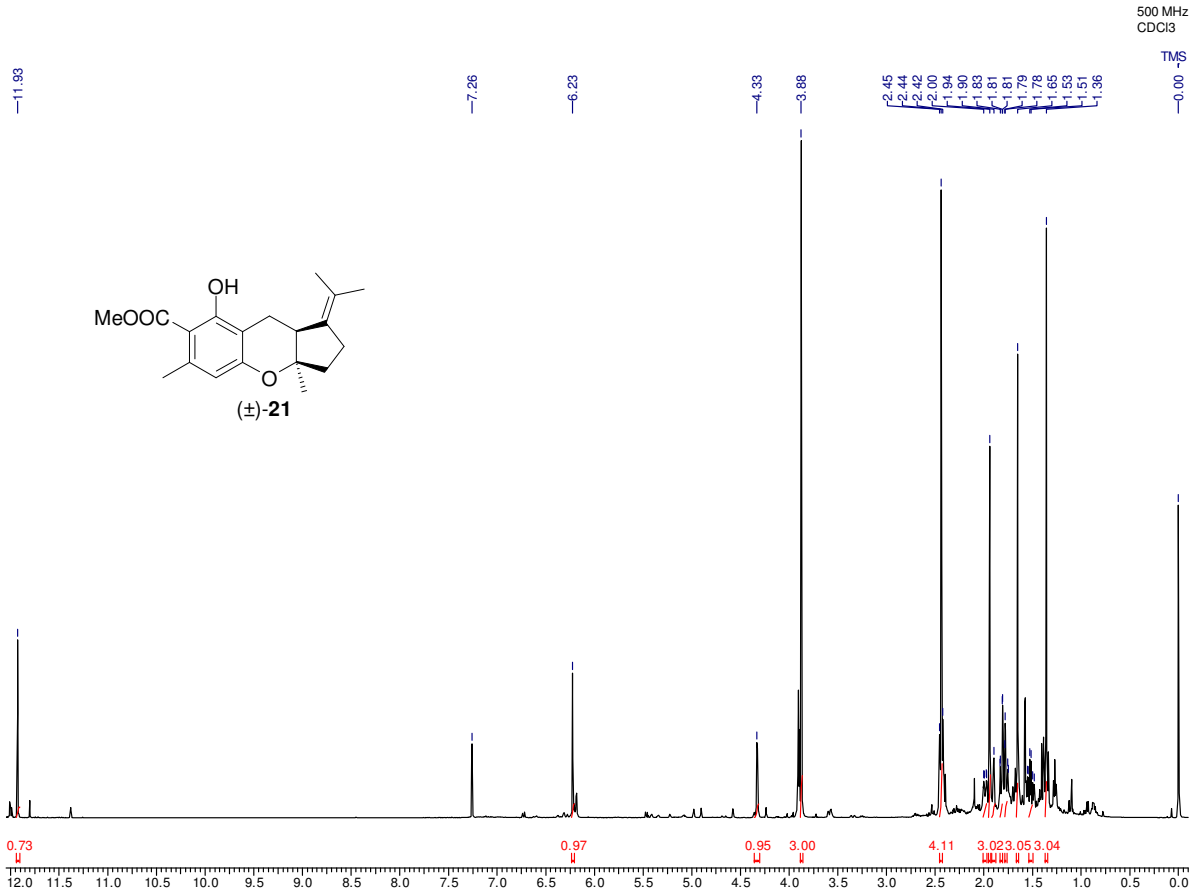

100 MHz
CDCl3
Chloroform-d
176.06
160.63
158.95
144.43
135.49
131.32
126.28
124.32
123.72
116.66
112.15
107.05
103.60
80.06
77.00
41.69
39.65
27.15
26.67
25.65
24.44
22.56
17.65
15.96
OH
HOOC
O
(±)-18b

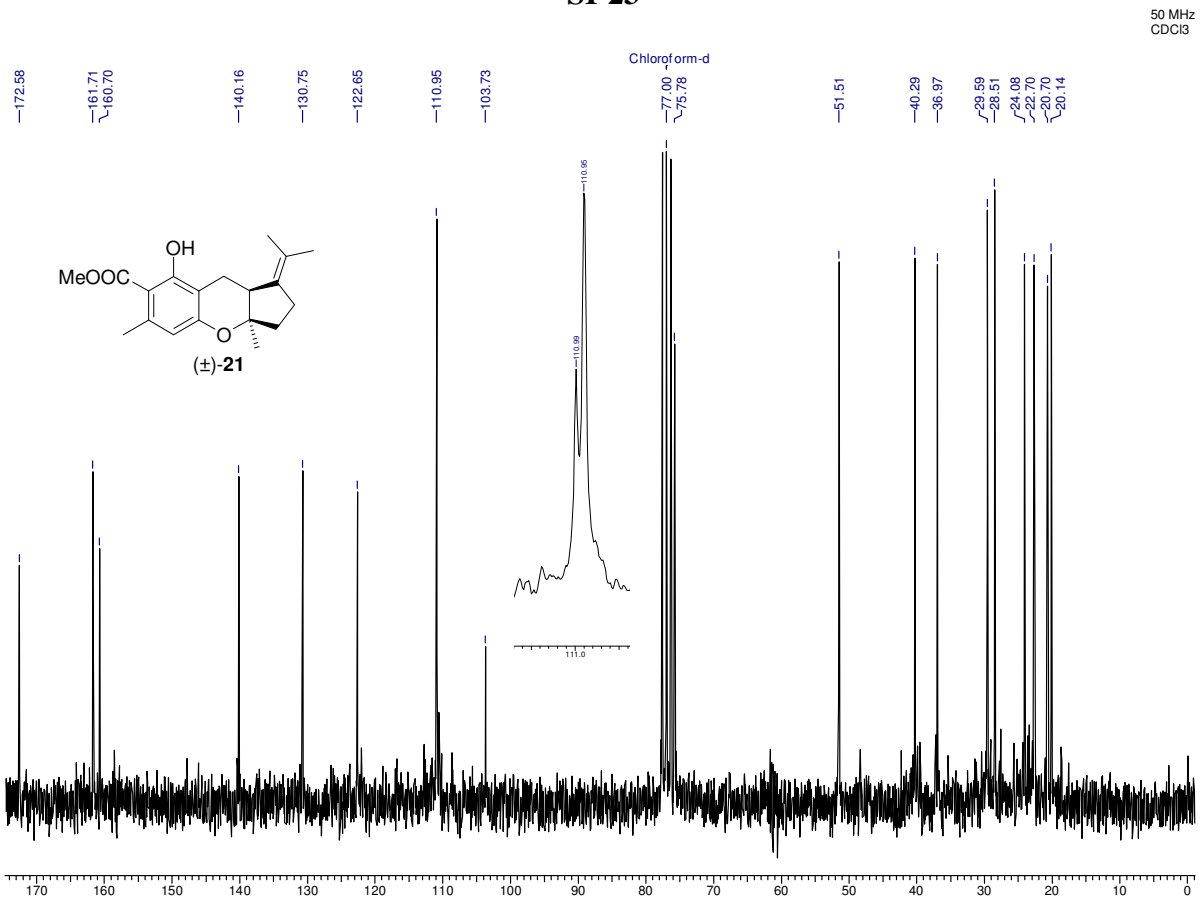

100 MHz
CDCl3
126.28
124.32
123.72
116.66
112.15
41.69
39.66
27.15
26.67
25.66
24.45
22.57
17.66
15.96
OH
HOOC
O
(±)-18b

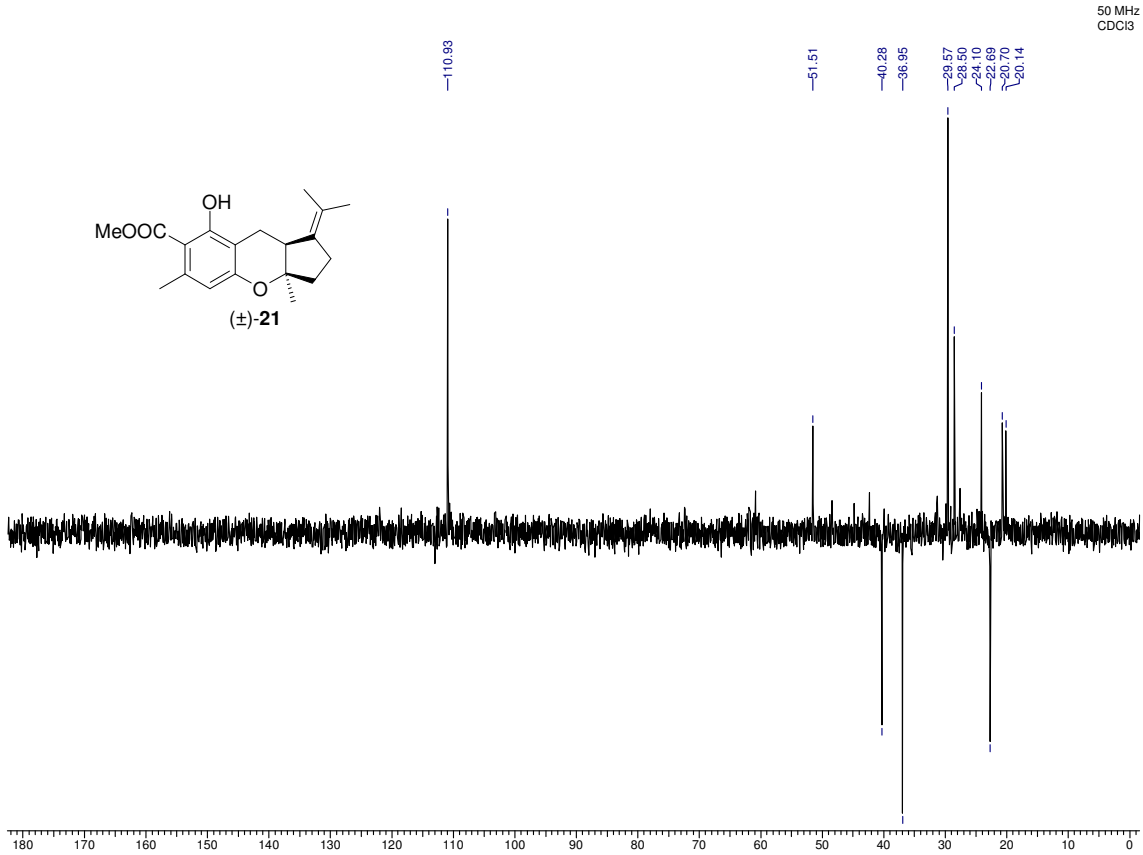

200 MHz
CDCl3
TMS
7.26
6.59
6.54
6.43
5.59
5.54
5.12
5.08
5.05
3.90
3.79
2.25
2.18
2.16
2.10
2.08
2.06
2.03
1.93
1.90
1.66
1.60
1.57
1.38
0.00
OMe
MeOOC
O
(±)-19
1.04
1.06
1.12
3.09
3.13
4.03
3.57
3.08
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

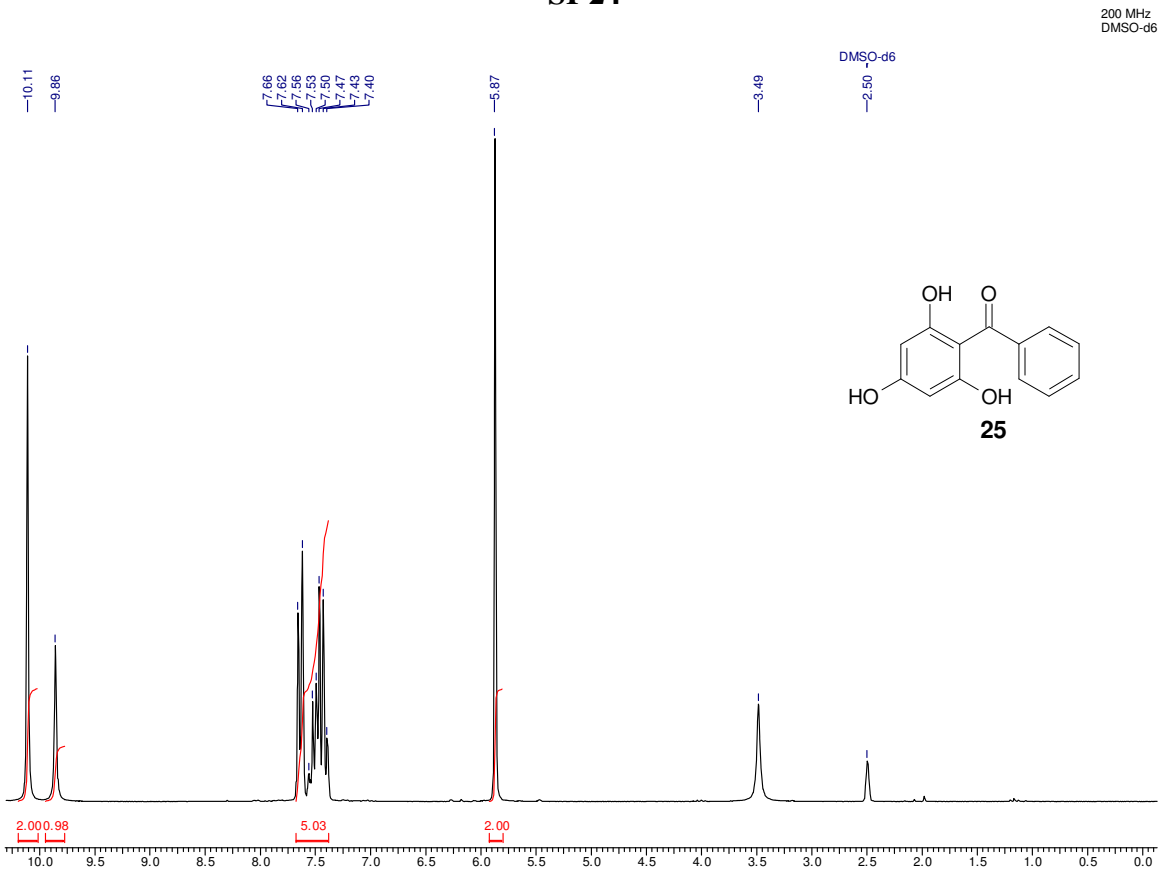

50 MHz
CDCl3
Chloroform-d
168.43
155.16
154.09
137.69
131.75
128.80
123.88
119.98
116.96
113.78
112.25
78.67
77.00
62.98
51.94
41.14
26.40
25.59
22.60
19.86
17.55
OMe
MeOOC
O
(±)-19
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

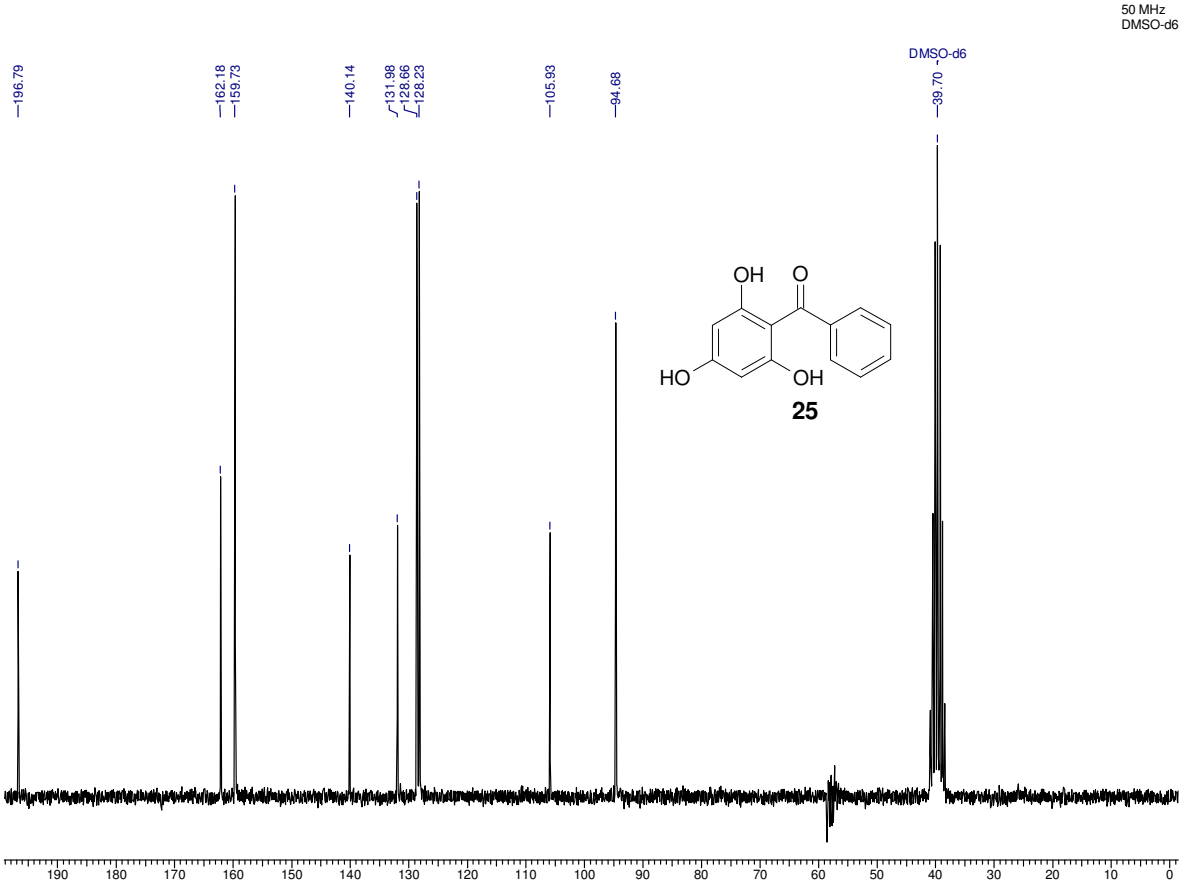

50 MHz
CDCl3
128.79
123.86
116.95
113.78
62.98
51.95
41.12
26.39
25.60
22.60
19.86
17.55
OMe
MeOOC
O
(±)-19
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

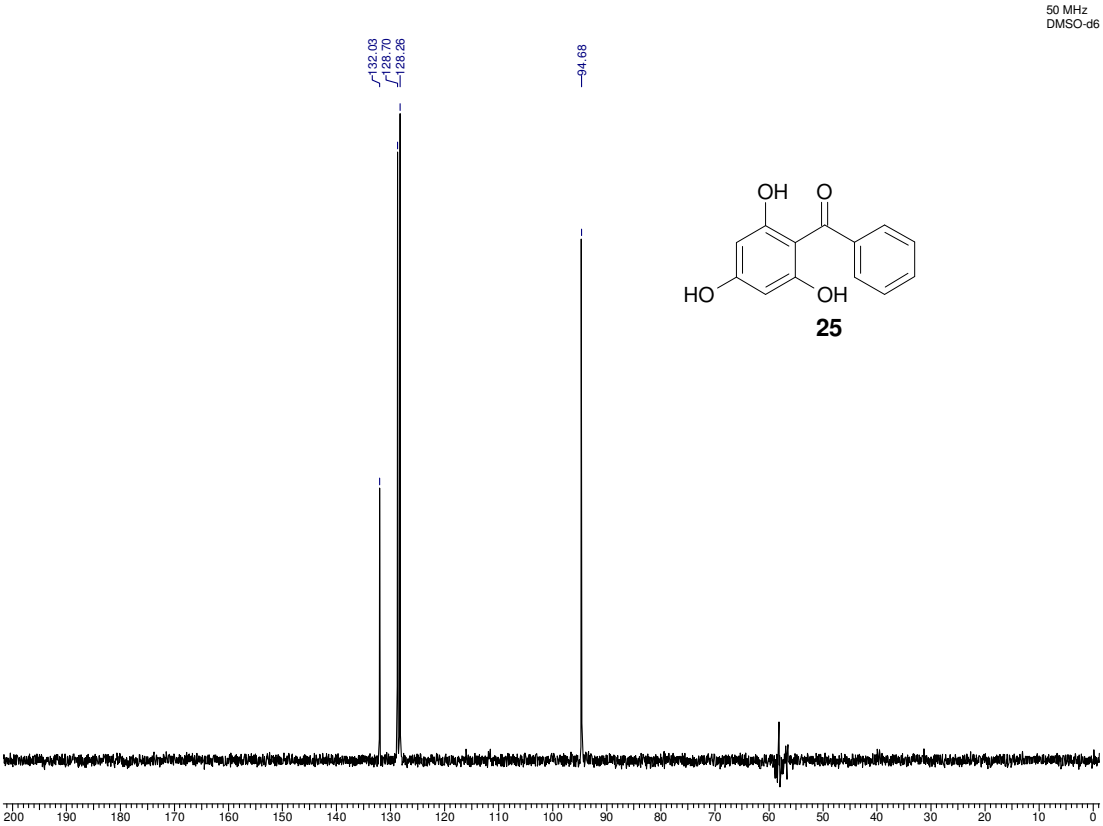

500 MHz
CDCl3
TMS
11.93
7.26
6.23
4.33
3.88
2.45
2.44
2.42
2.00
1.94
1.90
1.83
1.81
1.81
1.79
1.78
1.65
1.53
1.51
1.36
0.00
OH
MeOOC
O
(±)-21
0.73
0.97
0.95
3.00
4.11
3.02
3.05
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

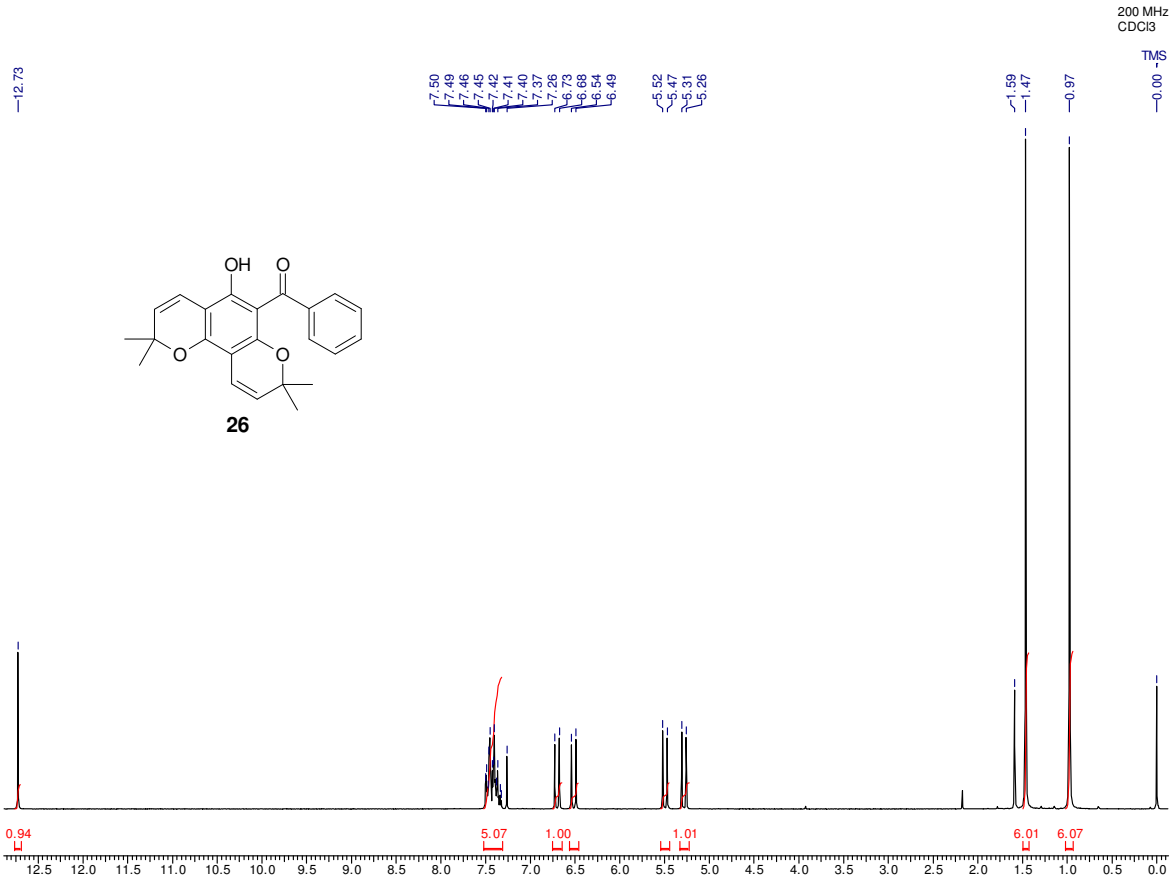

50 MHz
CDCl3
Chloroform-d
172.58
161.71
160.70
140.16
130.75
122.65
110.95
103.73
77.00
75.78
51.51
40.29
36.97
29.59
28.51
24.08
22.70
20.70
20.14
110.95
110.99
111.0
OH
MeOOC
O
(±)-21
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

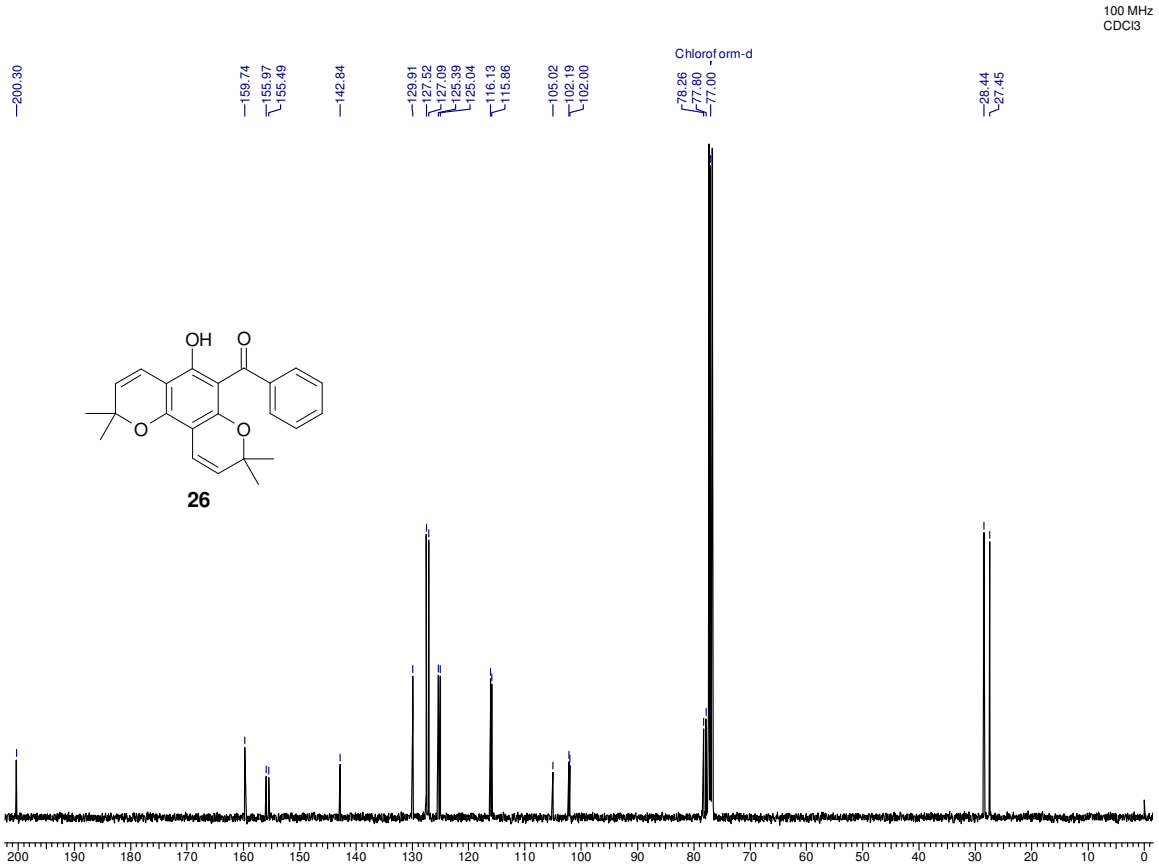

50 MHz
CDCl3
110.93
51.51
40.28
36.95
29.57
28.50
24.10
22.69
20.70
20.14
OH
MeOOC
O
(±)-21
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

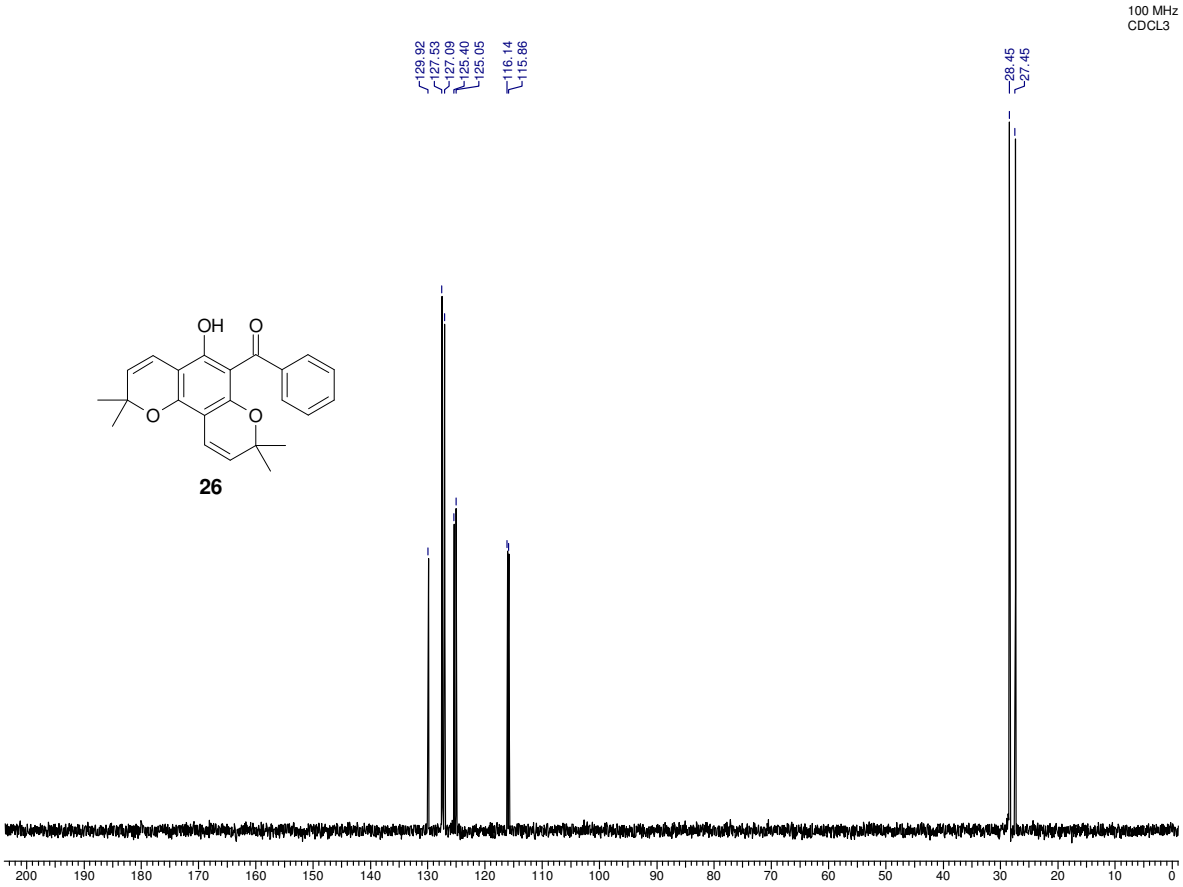

200 MHz
DMSO-d6
10.11
9.86
7.66
7.62
7.56
7.53
7.50
7.47
7.43
7.40
5.87
3.49
DMSO-d6
2.50
OH
O
HO
OH
25
2.00
0.98
5.03
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


50 MHz
DMSO-d6
196.79
162.18
159.73
140.14
131.98
128.66
128.23
105.93
94.68
DMSO-d6
39.70
OH
O
HO
OH
25
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

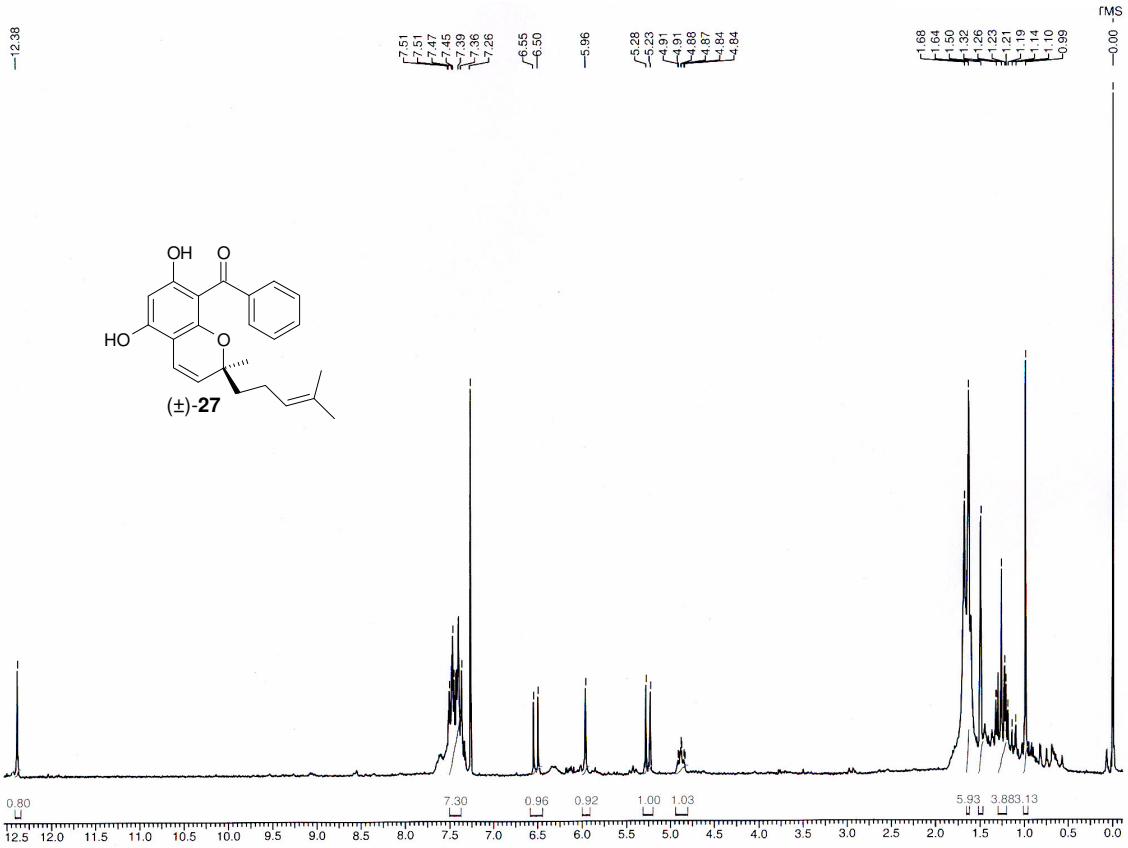

50 MHz
DMSO-d6
132.03
128.70
128.26
94.68
OH
O
HO
OH
25
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


200 MHz
CDCl3
TMS
12.73
7.50
7.49
7.46
7.45
7.42
7.41
7.40
7.37
7.26
6.73
6.68
6.54
6.49
5.52
5.47
5.31
5.26
1.59
1.47
0.97
0.00
OH
O
O
O
26
0.94
5.07
1.00
1.01
6.01
6.07
12.5 12.0 11.5 11.0 10.5 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

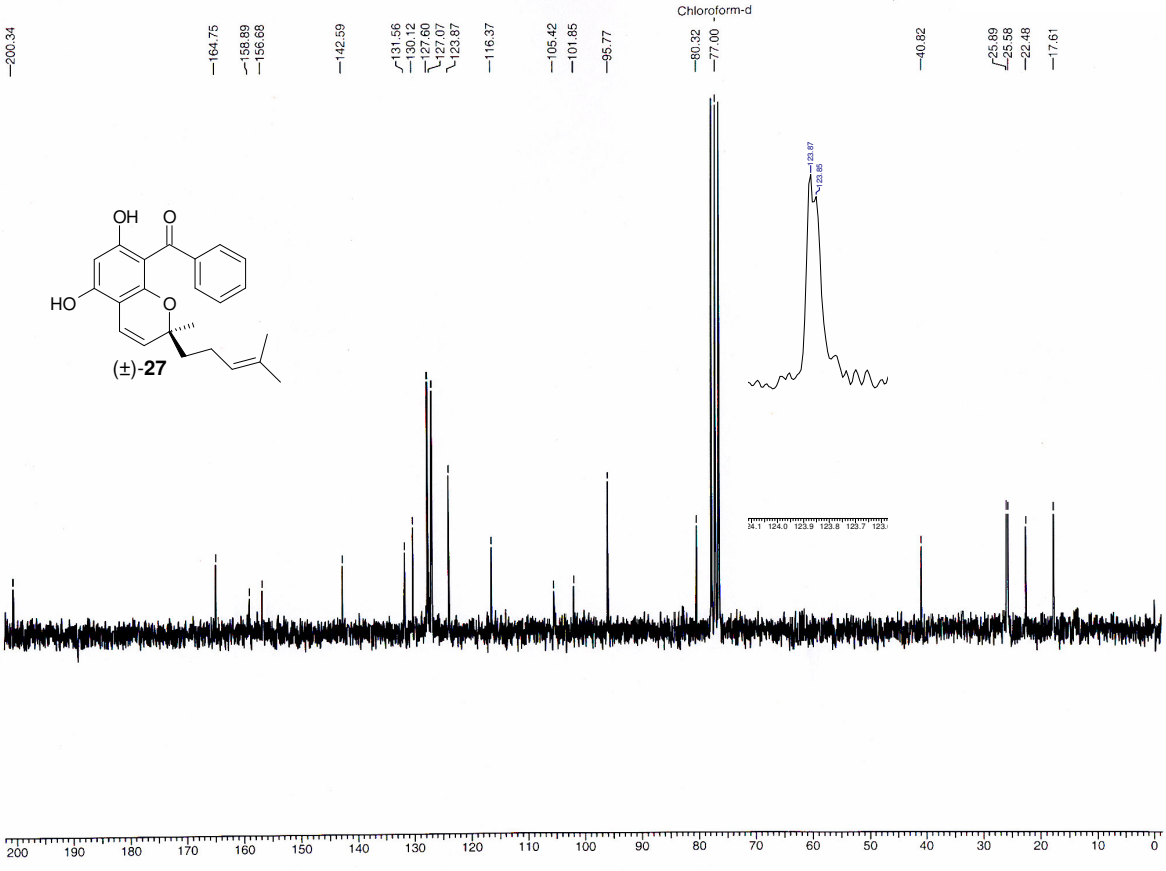

100 MHz
CDCl3
Chloroform-d
200.30
159.74
155.97
155.49
142.84
129.91
127.52
127.09
125.39
125.04
116.13
115.86
105.02
102.19
102.00
78.26
77.80
77.00
28.44
27.45
OH
O
O
O
26


100 MHz
CDCL3
129.92
127.53
127.09
125.40
125.05
116.14
115.86
28.45
27.45
OH
O
O
O
26

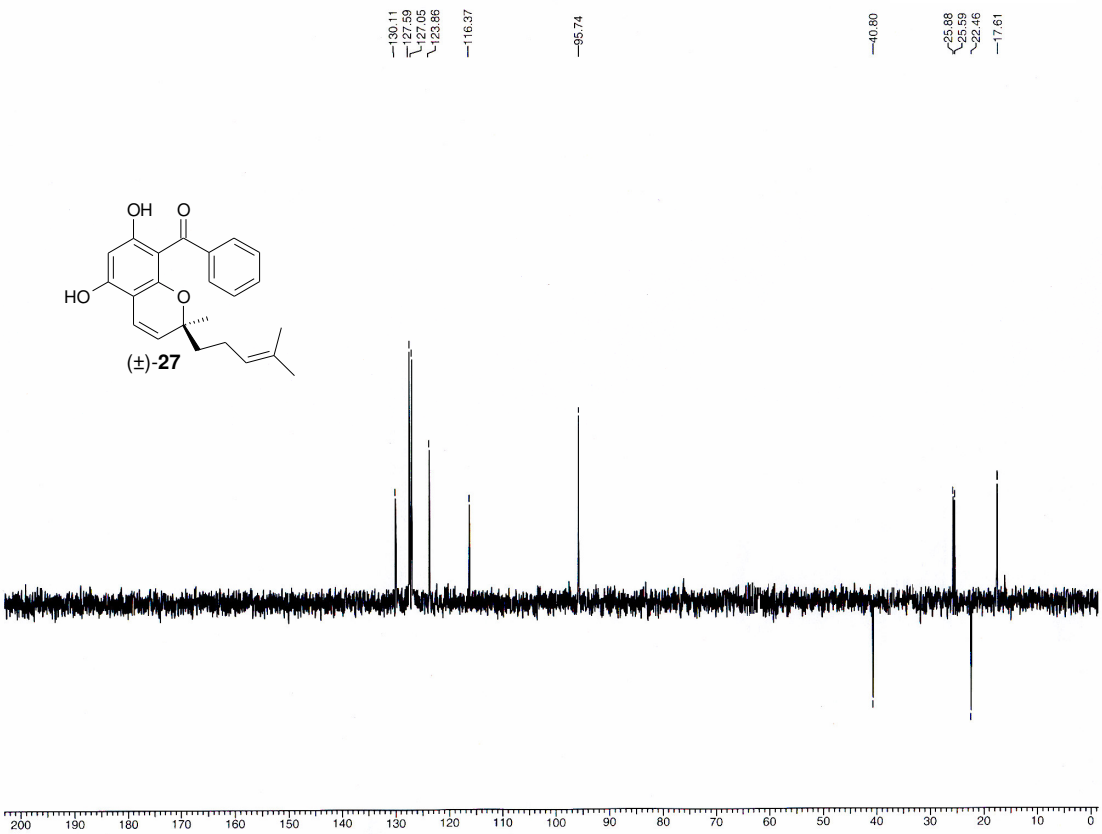
CDCl3/200 MHZ



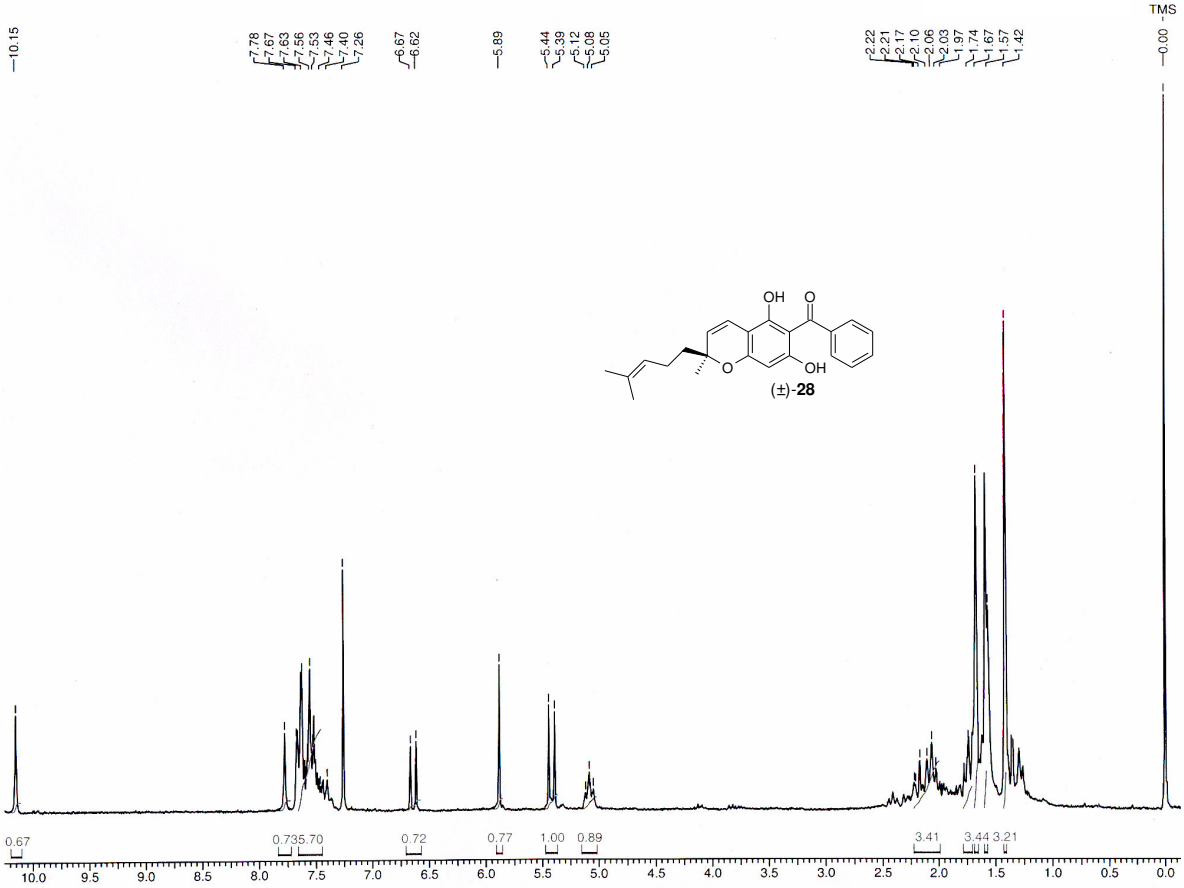
CDCl3/50 MHZ

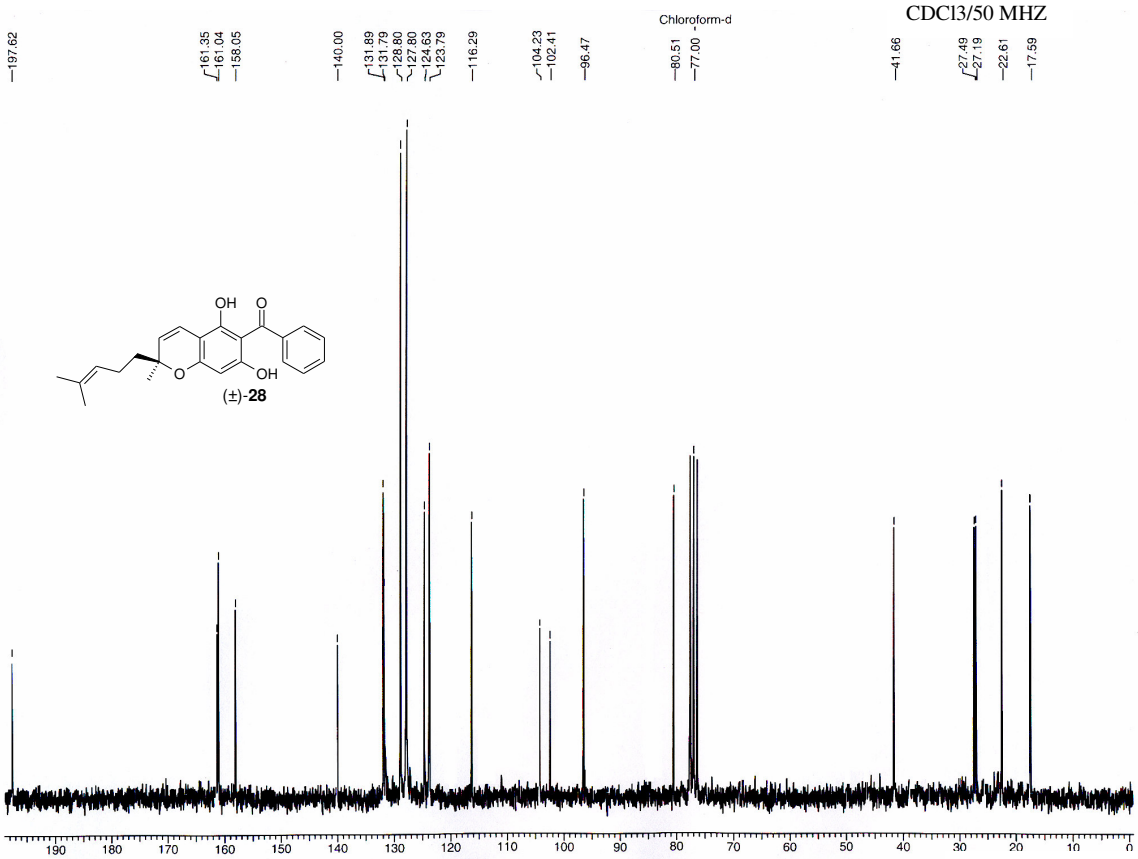


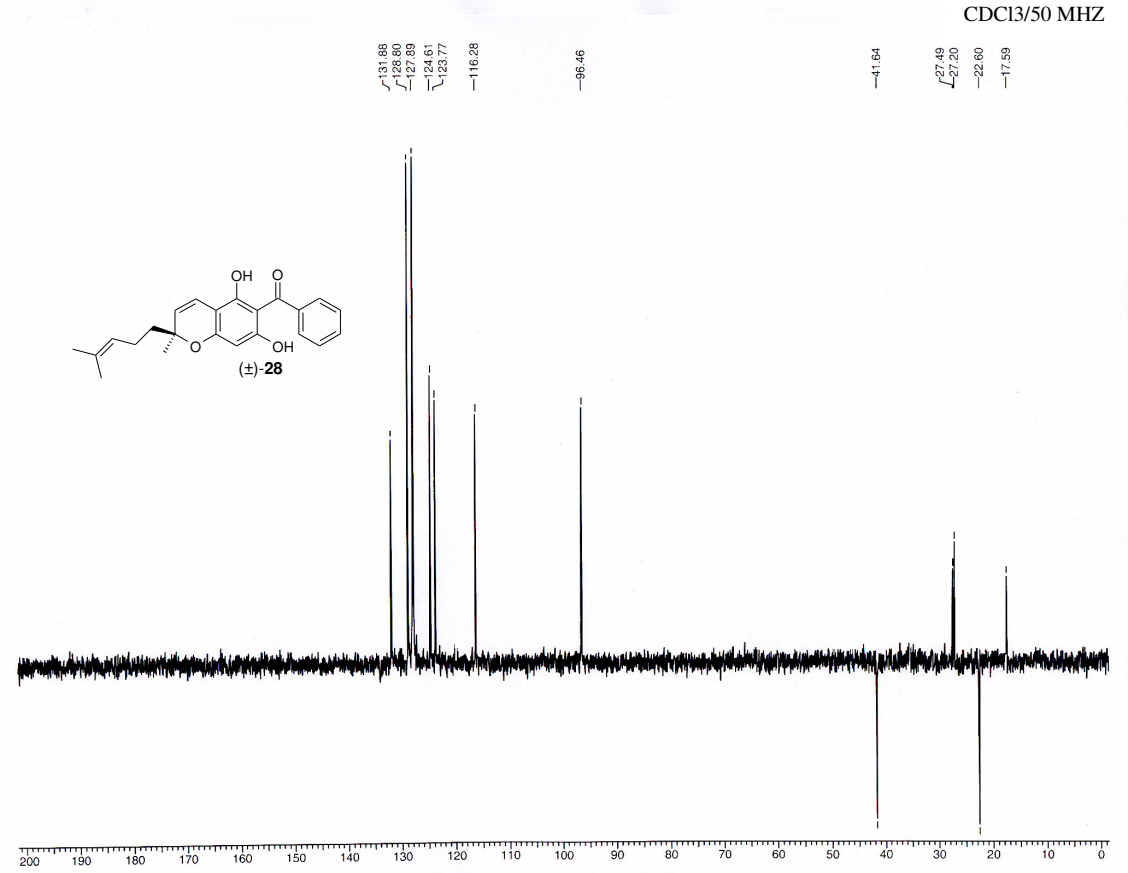
CDCl3/50 MHZ

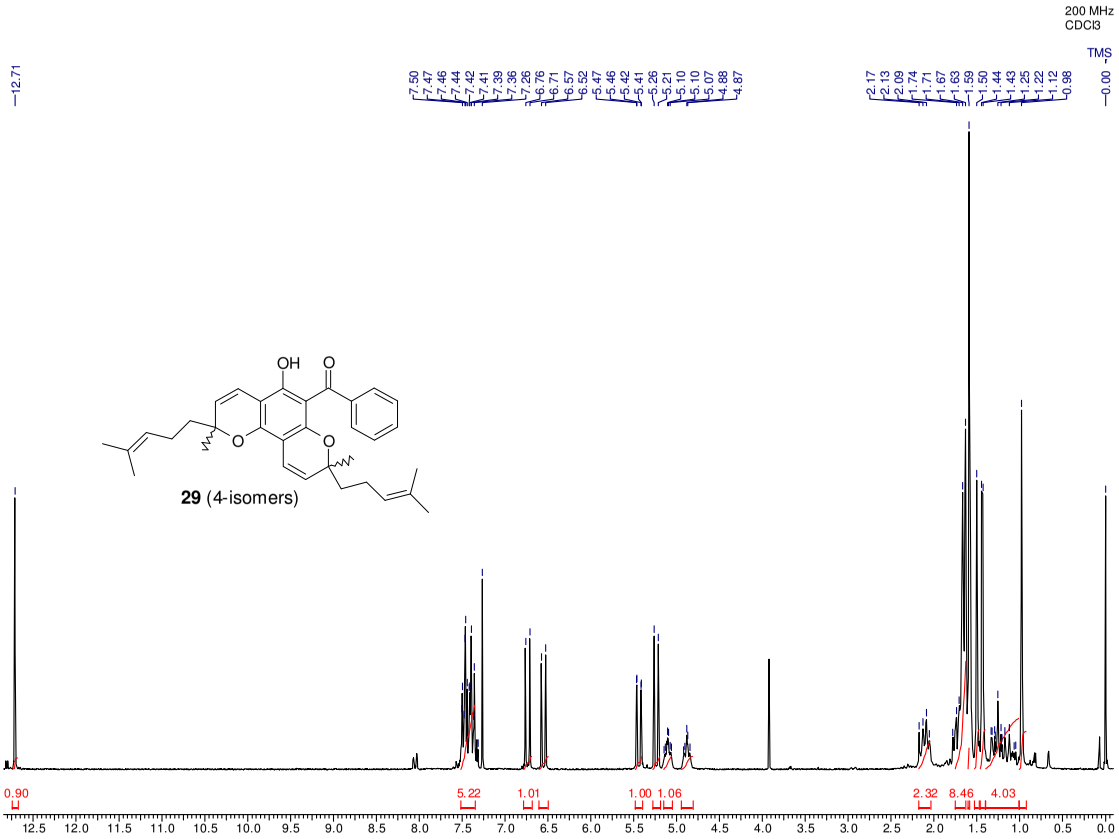


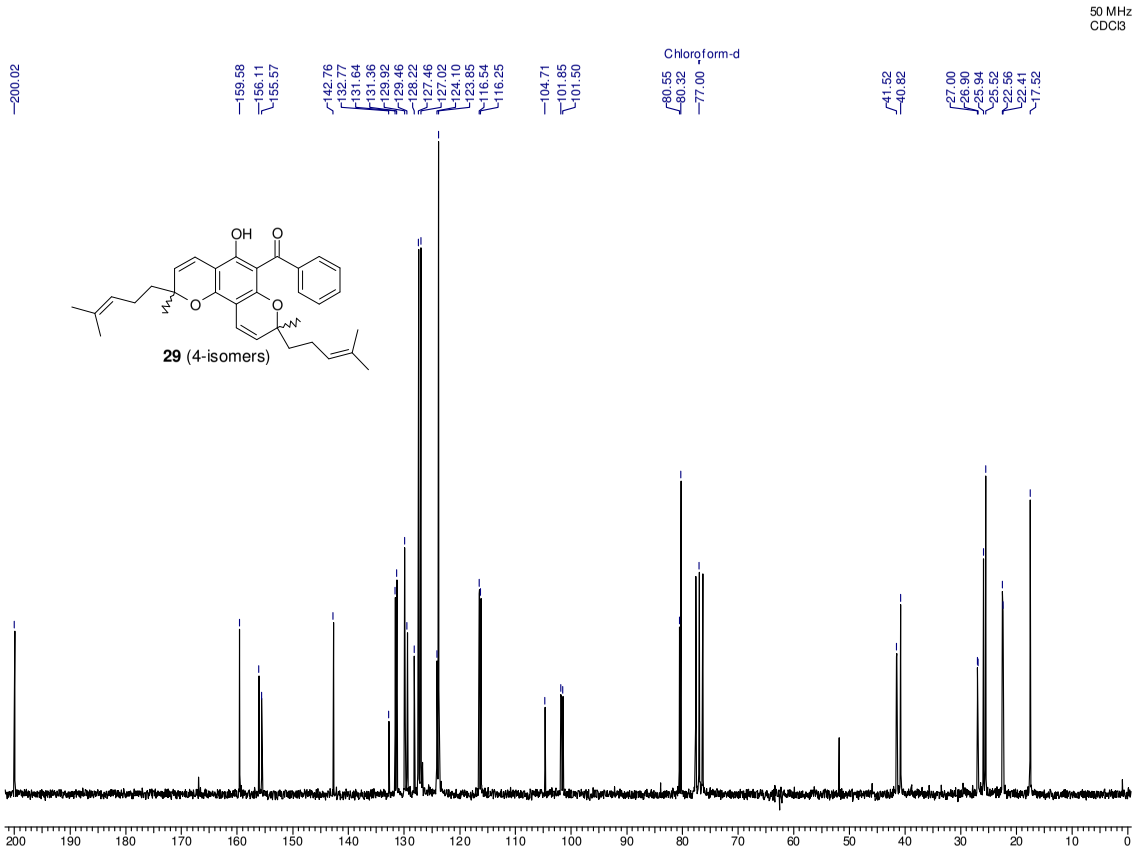
CDCl3/200 MHZ

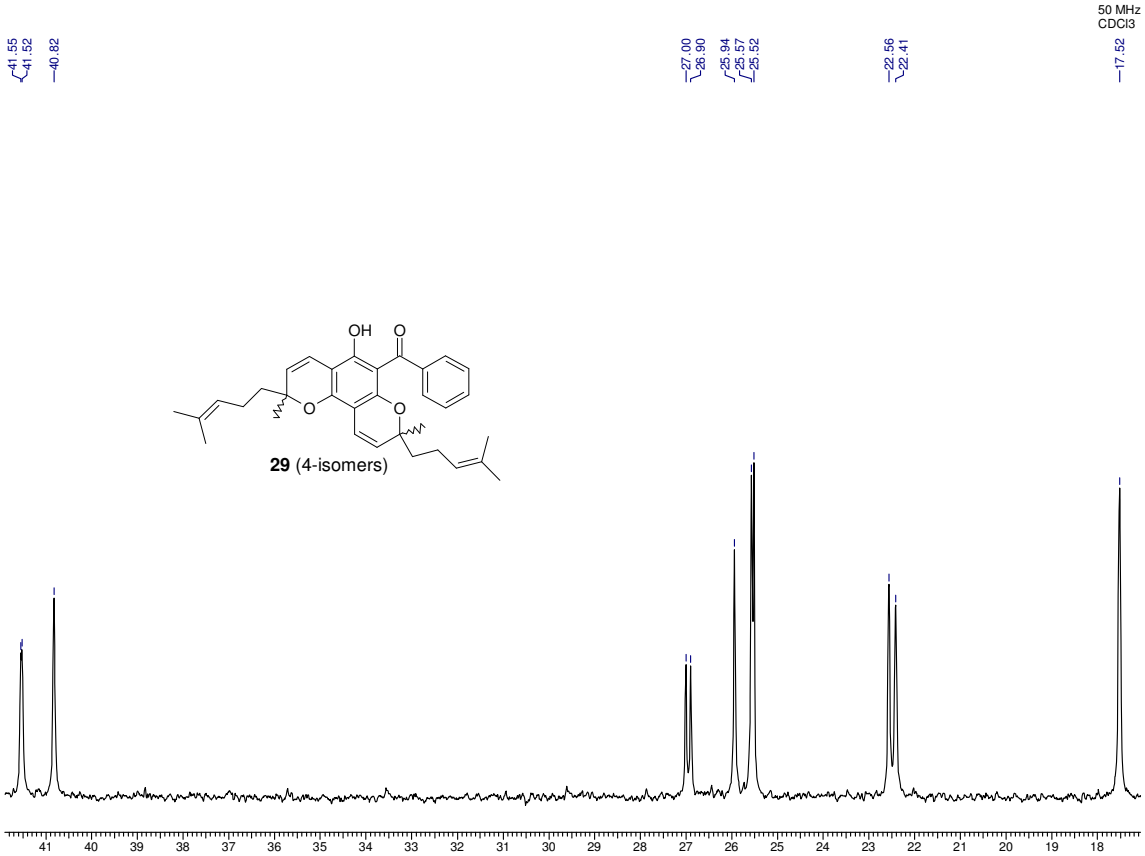


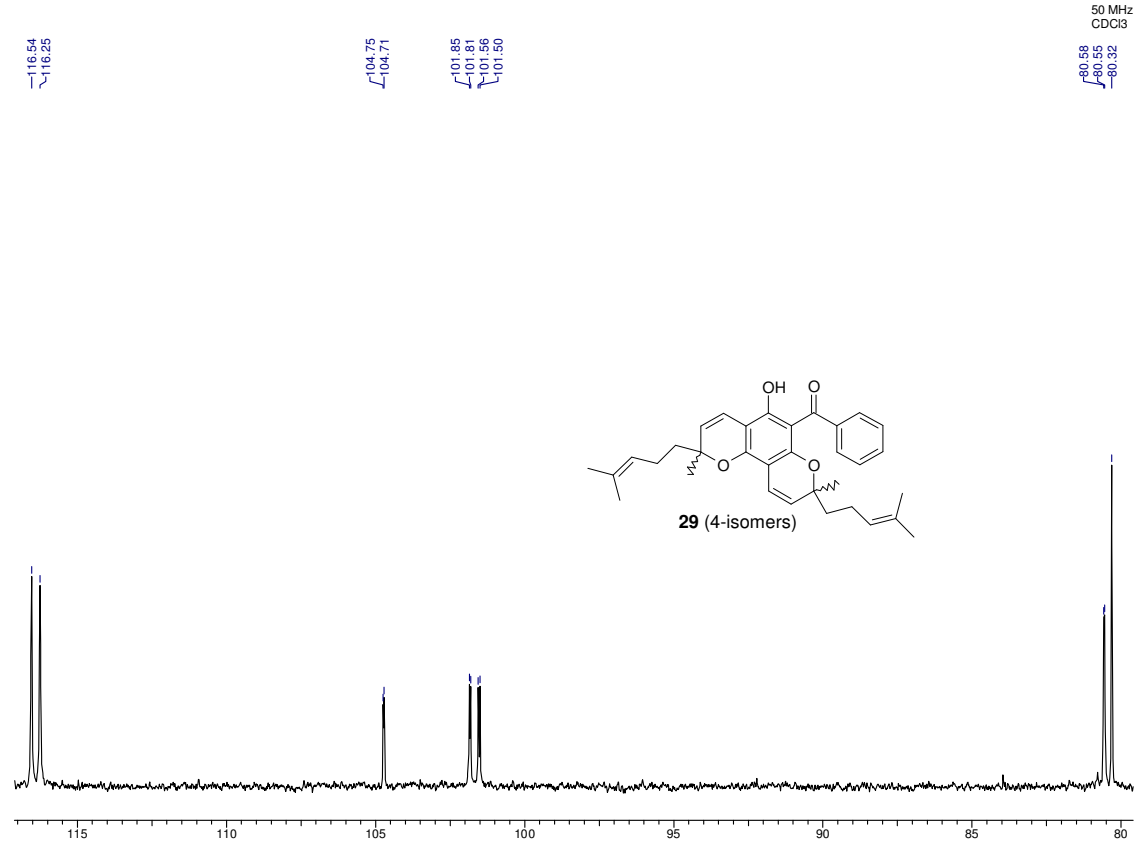

CDCl3/50 MHZ
Chloroform-d
197.62
161.35
161.04
158.05
140.00
131.89
131.79
128.80
127.80
124.63
123.79
116.29
104.23
102.41
96.47
80.51
77.00
41.66
27.49
27.19
22.61
17.59
OH
O
OH
O
(±)-28

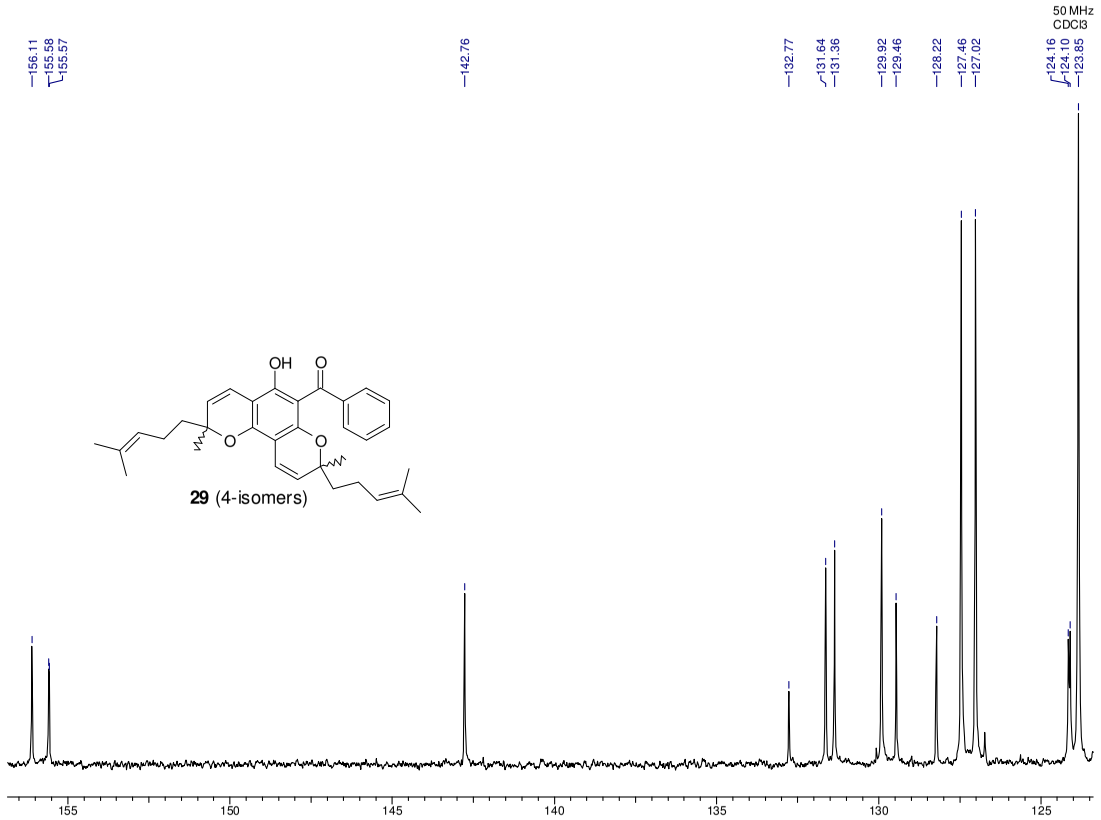

CDCl3/50 MHZ
131.88
128.80
127.89
124.61
123.77
116.28
96.46
41.64
27.49
27.20
22.60
17.59
OH
O
OH
O
(±)-28

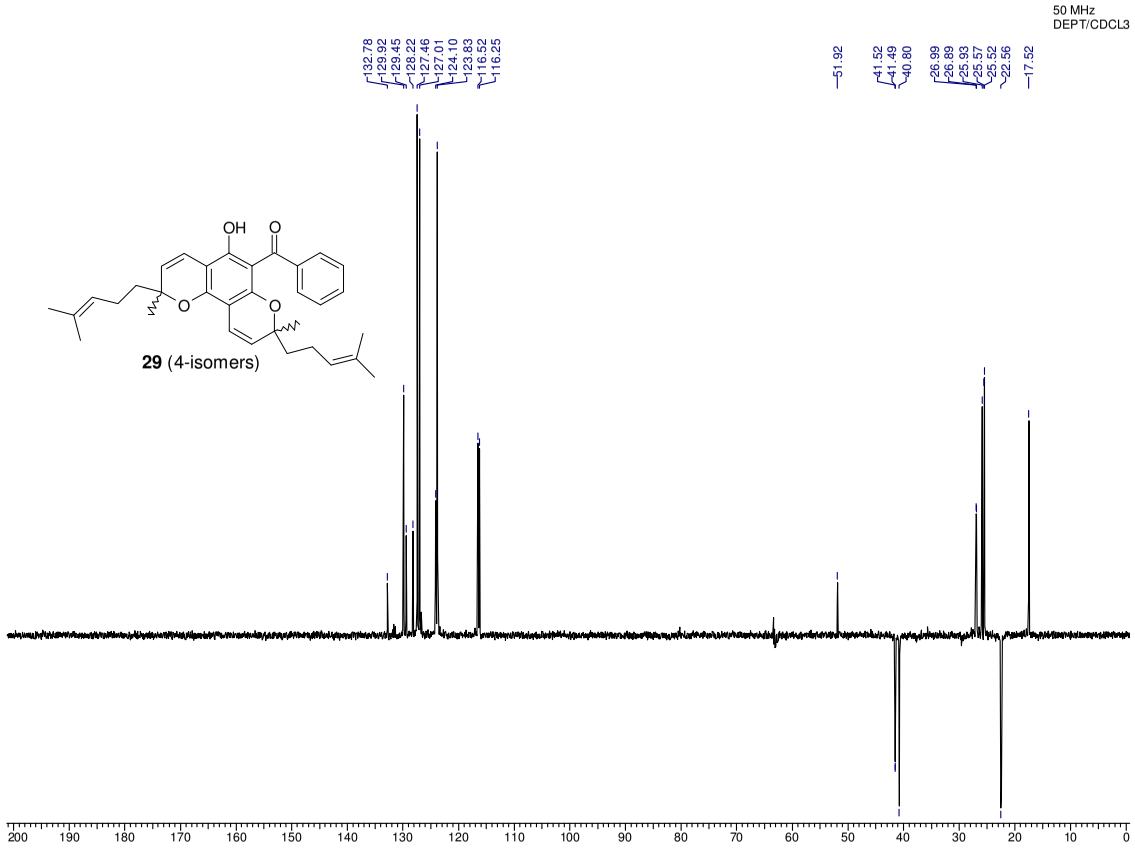

200 MHz
CDCl3
TMS
12.71
7.50
7.47
7.46
7.44
7.42
7.41
7.39
7.36
7.26
6.76
6.71
6.57
6.52
5.47
5.46
5.42
5.41
5.26
5.21
5.10
5.10
5.07
4.88
4.87
2.17
2.13
2.09
1.74
1.71
1.67
1.63
1.59
1.50
1.44
1.43
1.25
1.22
1.12
0.98
0.00
OH
O
O
O
29 (4-isomers)
0.90
5.22
1.01
1.00
1.06
2.32
8.46
4.03
12.5 12.0 11.5 11.0 10.5 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

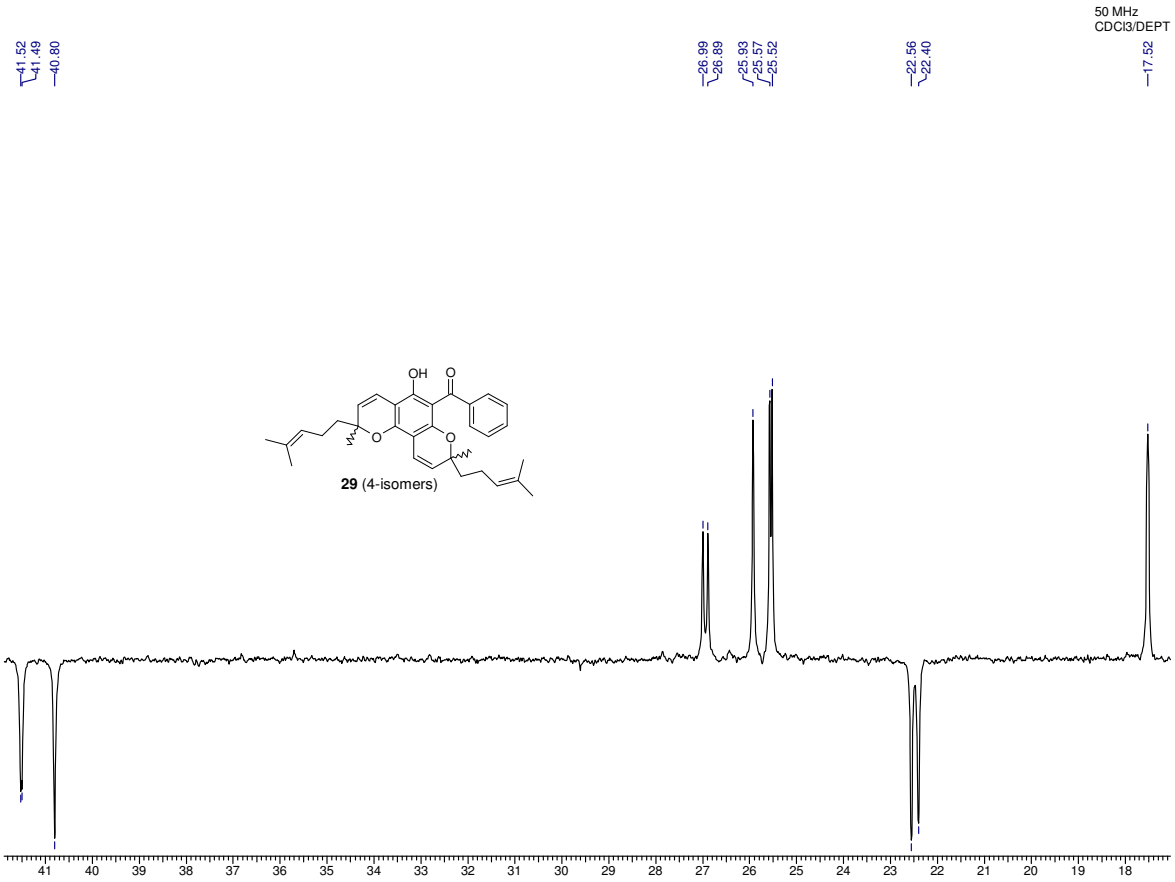

50 MHz
CDCl3
Chloroform-d
200.02
159.58
156.11
155.57
142.76
132.77
131.64
131.36
129.92
129.46
128.22
127.46
127.02
124.10
123.85
116.54
116.25
104.71
101.85
101.50
80.55
80.32
77.00
41.52
40.82
27.00
26.90
25.94
25.52
22.56
22.41
17.52
OH
O
O
O
29 (4-isomers)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

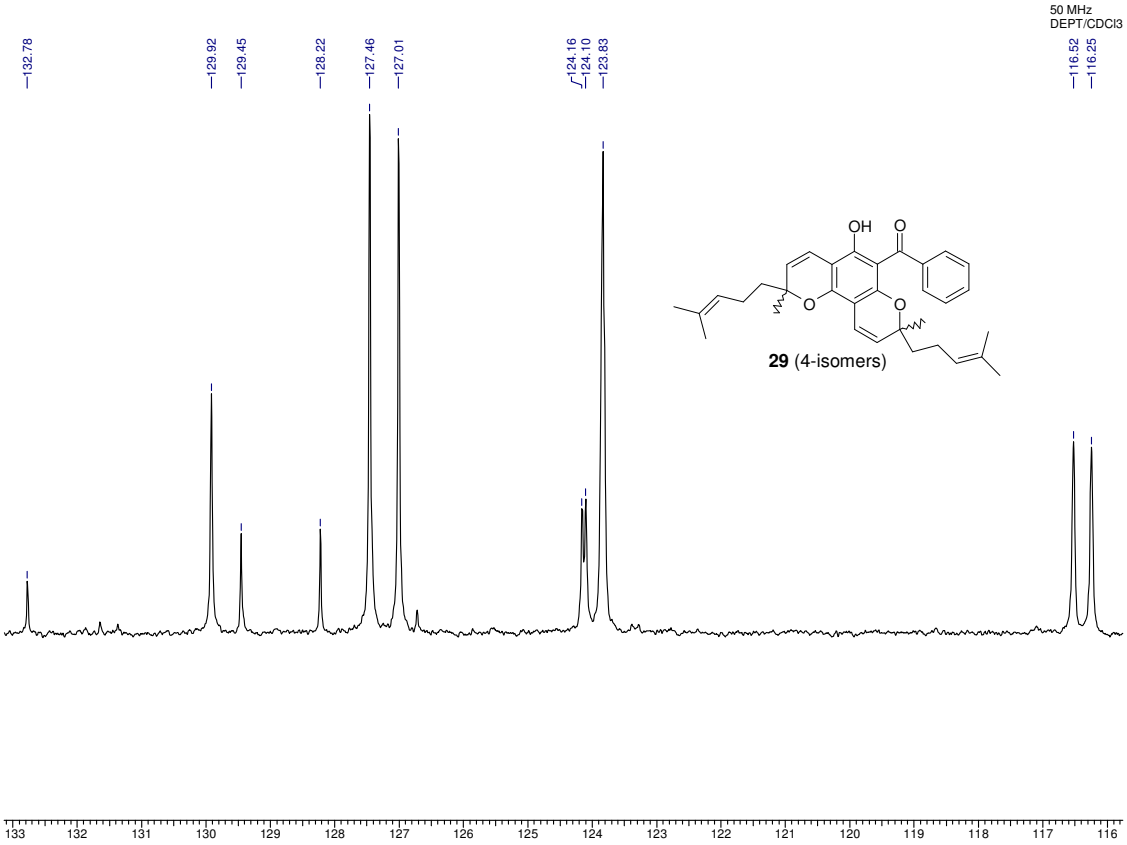

50 MHz
CDCl3
41.55
41.52
40.82
27.00
26.90
25.94
25.57
25.52
22.56
22.41
17.52
OH
O
O
O
29 (4-isomers)
41
40
39
38
37
36
35
34
33
32
31
30
29
28
27
26
25
24
23
22
21
20
19
18

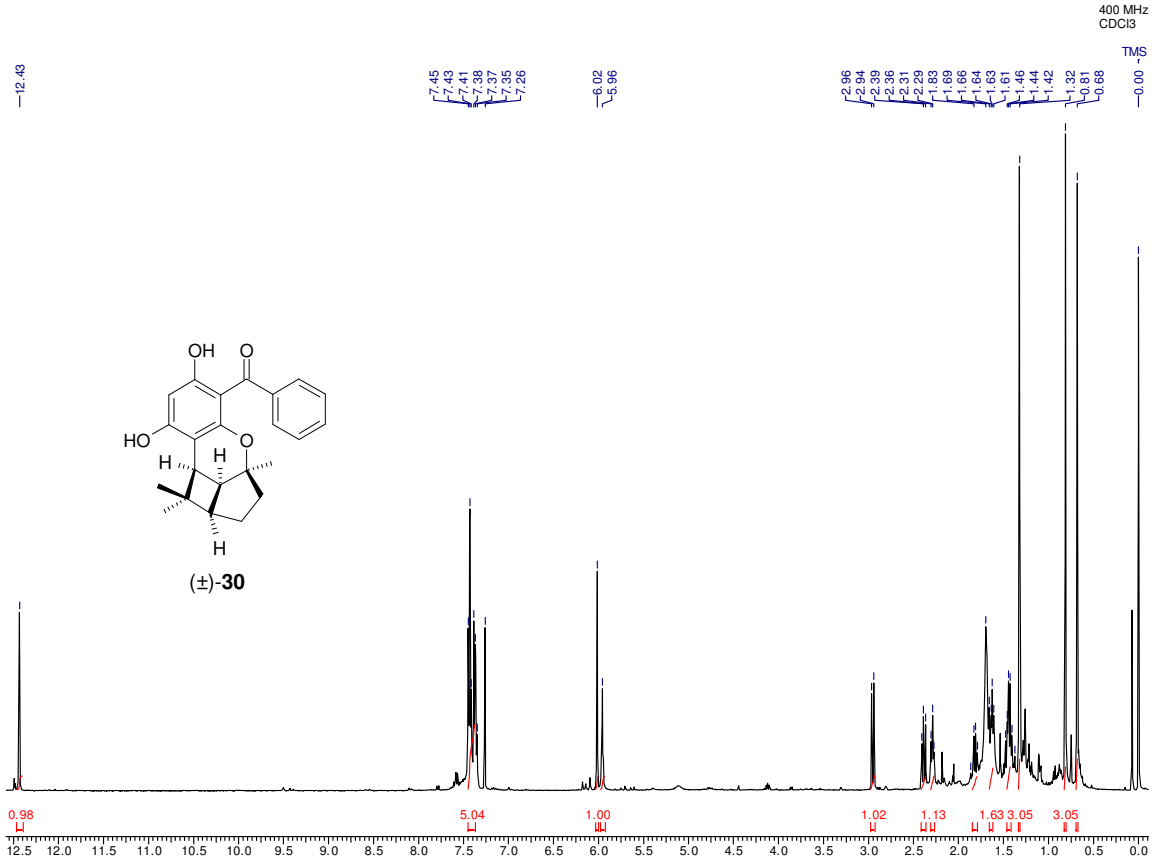

50 MHz
CDCl3
116.54
116.25
104.75
104.71
101.85
101.81
101.56
101.50
80.58
80.55
80.32
OH
O
O
O
29 (4-isomers)
115
110
105
100
95
90
85
80

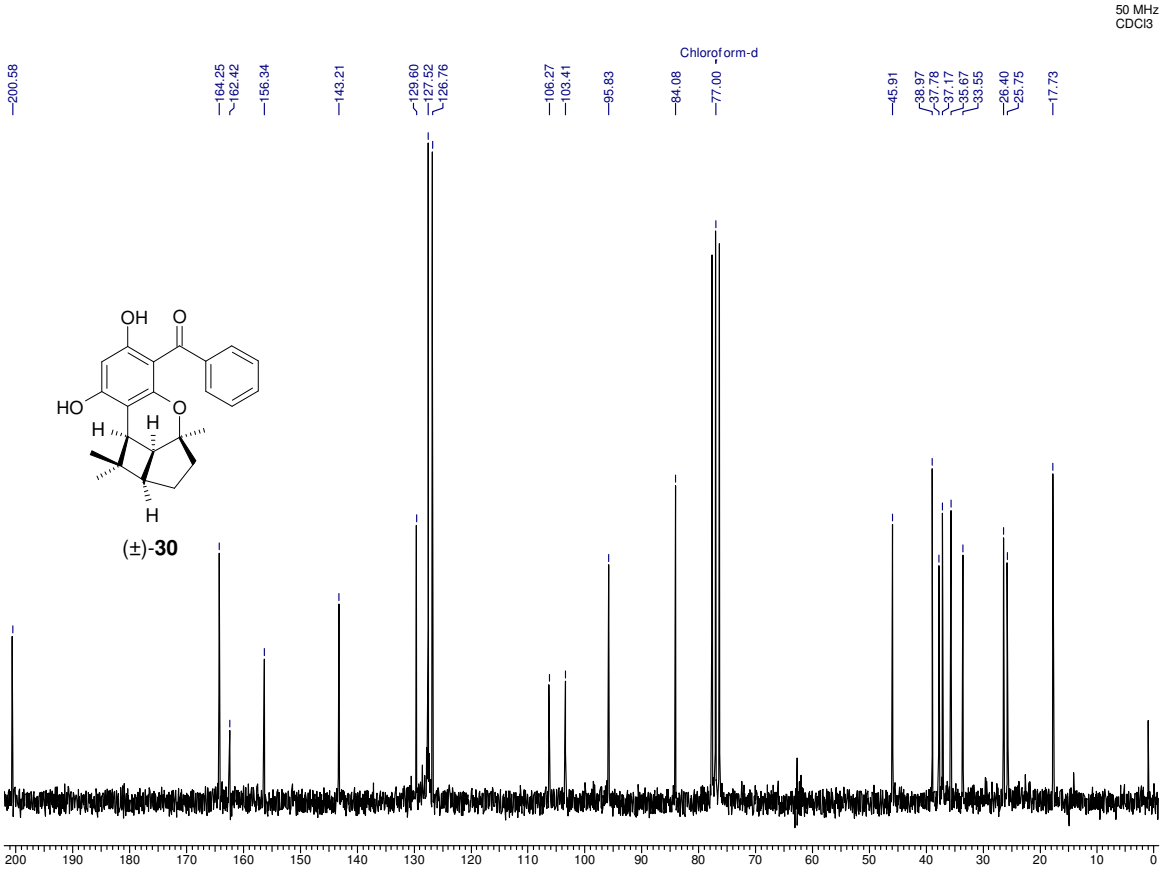

50 MHz
CDCl3
156.11
155.58
155.57
142.76
132.77
131.64
131.36
129.92
129.46
128.22
127.46
127.02
124.16
124.10
123.85
OH
O
O
O
29 (4-isomers)
155
150
145
140
135
130
125

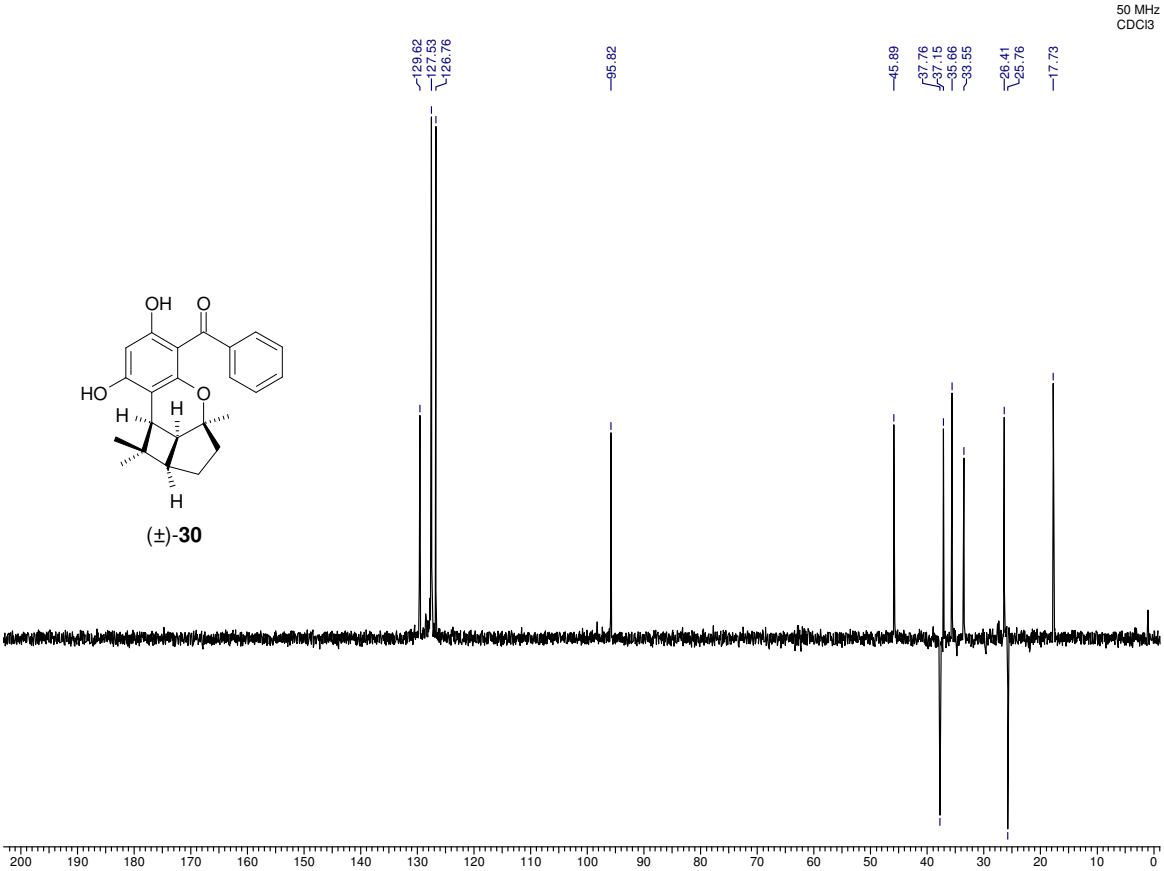

50 MHz
DEPT/CDCL3
132.78
129.92
129.45
128.22
127.46
127.01
124.10
123.83
116.52
116.25
51.92
41.52
41.49
40.80
26.99
26.89
25.93
25.57
25.52
22.56
17.52
OH
O
O
O
29 (4-isomers)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

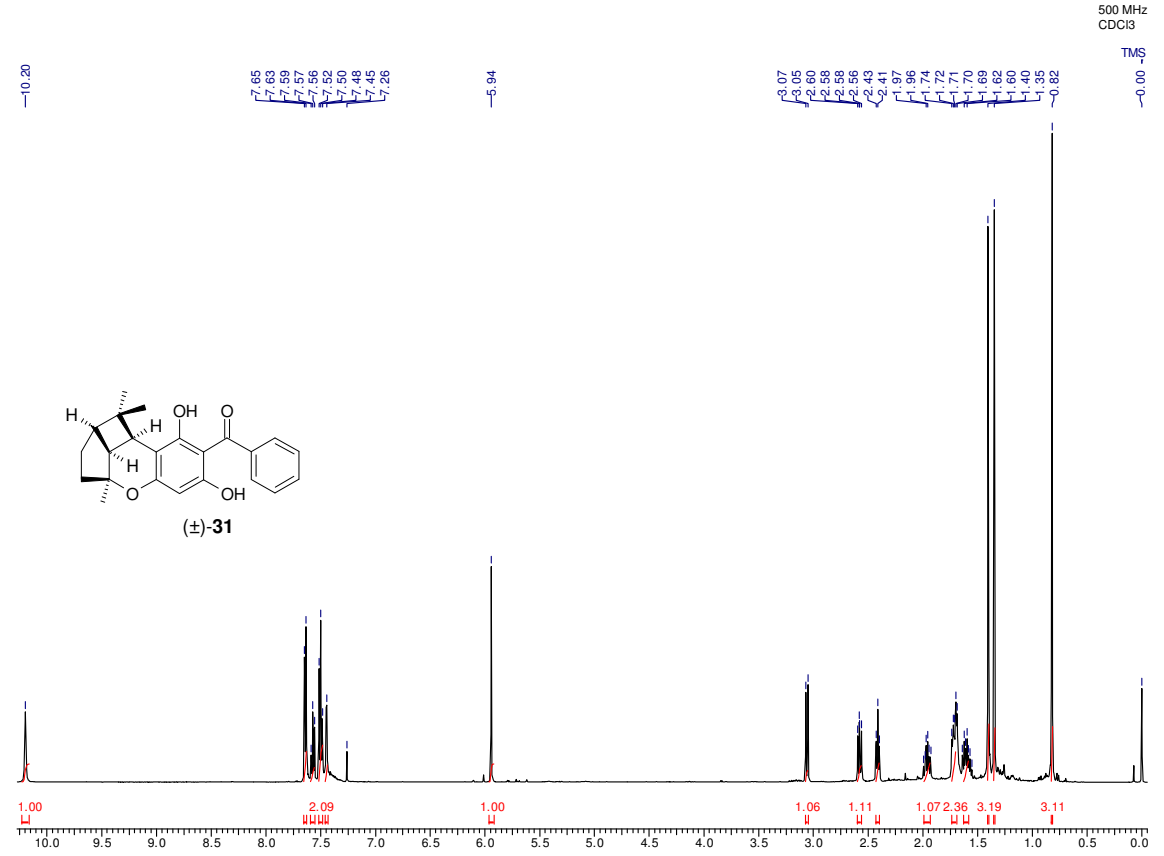

50 MHz
CDCl3/DEPT
41.52
41.49
40.80
26.99
26.89
25.93
25.57
25.52
22.56
22.40
17.52
OH
O
O
O
29 (4-isomers)
41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18

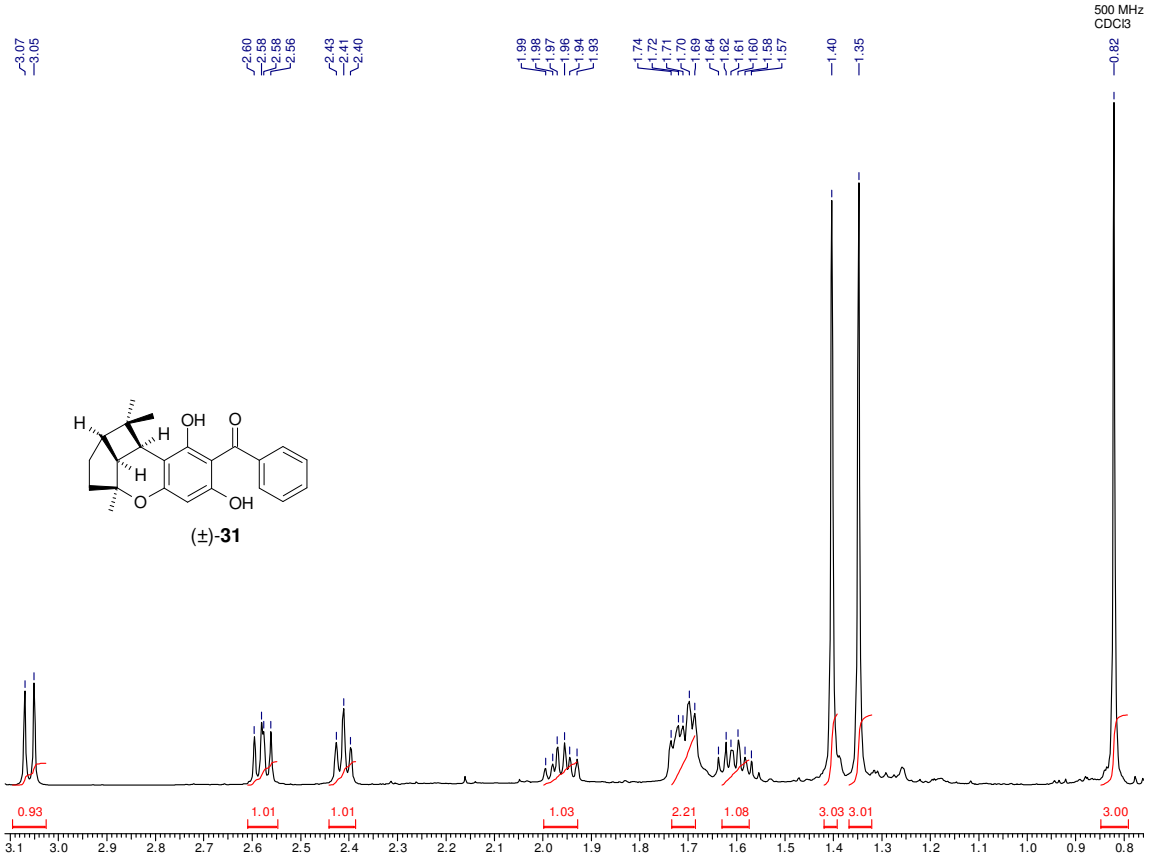

50 MHz
DEPT/CDCl3
132.78
129.92
129.45
128.22
127.46
127.01
124.16
124.10
123.83
116.52
116.25
OH
O
O
O
29 (4-isomers)
133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116

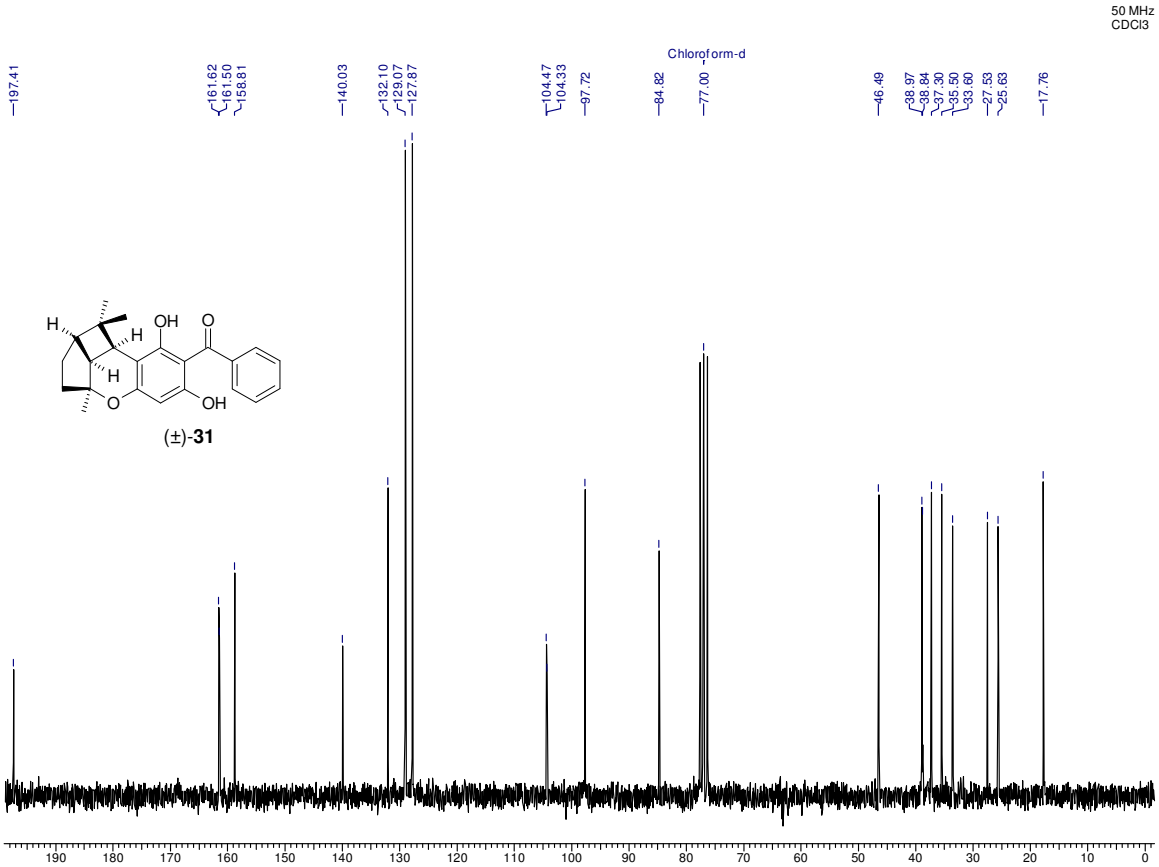

400 MHz
CDCl3
TMS
12.43
7.45
7.43
7.41
7.39
7.37
7.35
7.26
6.02
5.96
2.96
2.94
2.39
2.36
2.31
2.29
1.83
1.69
1.66
1.64
1.63
1.61
1.46
1.44
1.42
1.32
0.81
0.68
0.00
OH
O
HO
O
H
H
H
(±)-30
0.98
5.04
1.00
1.02
1.13
1.63
3.05
3.05
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

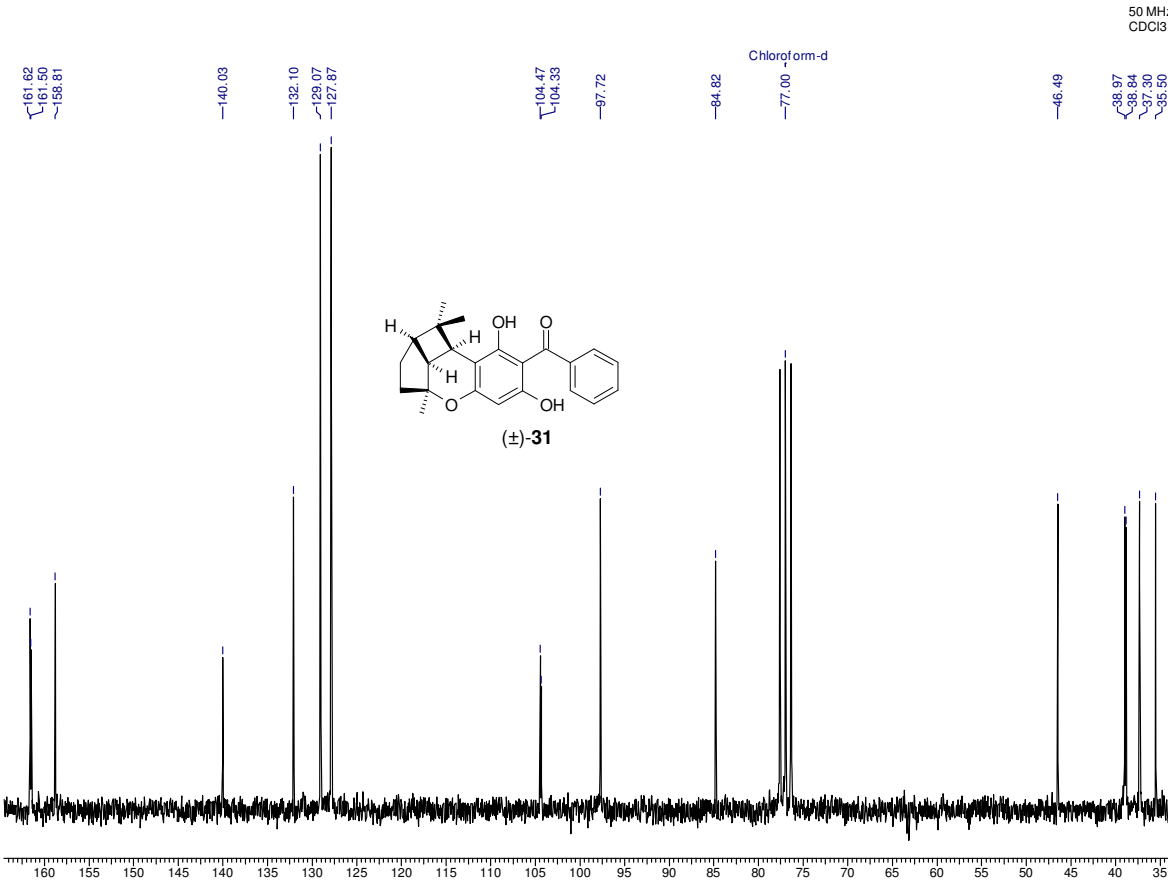

50 MHz
CDCl3
Chloroform-d
200.58
164.25
162.42
156.34
143.21
129.60
127.52
126.76
106.27
103.41
95.83
84.08
77.00
45.91
38.97
37.78
37.17
35.67
33.55
26.40
25.75
17.73
OH
O
HO
O
H
H
H
(±)-30
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

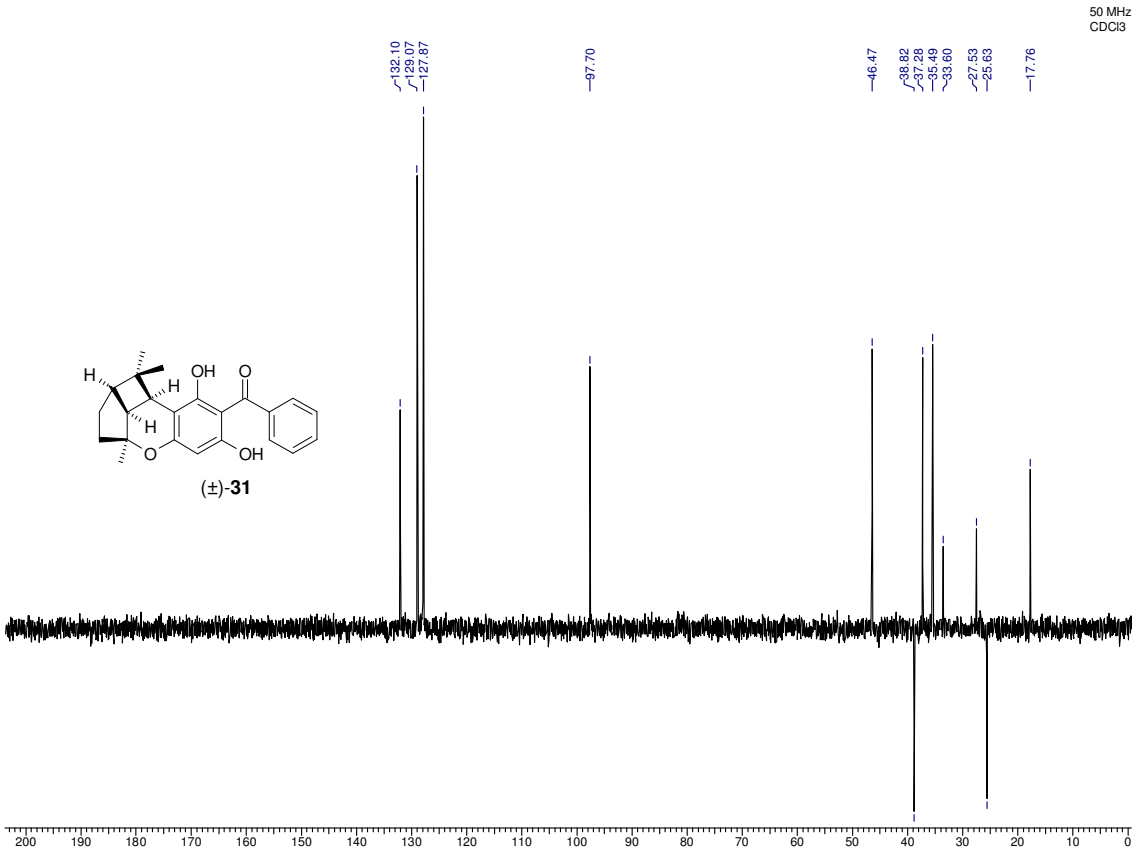

50 MHz
CDCl3
129.62
127.53
126.76
95.82
45.89
37.76
37.15
35.66
33.55
26.41
25.76
17.73
OH
O
HO
O
H
H
H
(±)-30


500 MHz
CDCl3
TMS
10.20
7.65
7.63
7.59
7.57
7.56
7.52
7.50
7.48
7.45
7.26
5.94
3.07
3.05
2.60
2.58
2.58
2.56
2.43
2.41
1.97
1.96
1.74
1.72
1.71
1.70
1.69
1.62
1.60
1.40
1.35
0.82
0.00
H
H
H
OH
O
O
OH
(±)-31
1.00
2.09
1.00
1.06
1.11
1.07
2.36
3.19
3.11


500 MHz
CDCl3
3.07
3.05
2.60
2.58
2.58
2.56
2.43
2.41
2.40
1.99
1.98
1.97
1.96
1.94
1.93
1.74
1.72
1.71
1.70
1.69
1.64
1.62
1.61
1.60
1.58
1.57
1.40
1.35
0.82
H
H
H
OH
O
O
OH
(±)-31
0.93
1.01
1.01
1.03
2.21
1.08
3.03
3.01
3.00
3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8


50 MHz
CDCl3
Chloroform-d
197.41
161.62
161.50
158.81
140.03
132.10
129.07
127.87
104.47
104.33
97.72
84.82
77.00
46.49
38.97
38.84
37.30
35.50
33.60
27.53
25.63
17.76
H
H
H
OH
O
O
OH
(±)-31
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

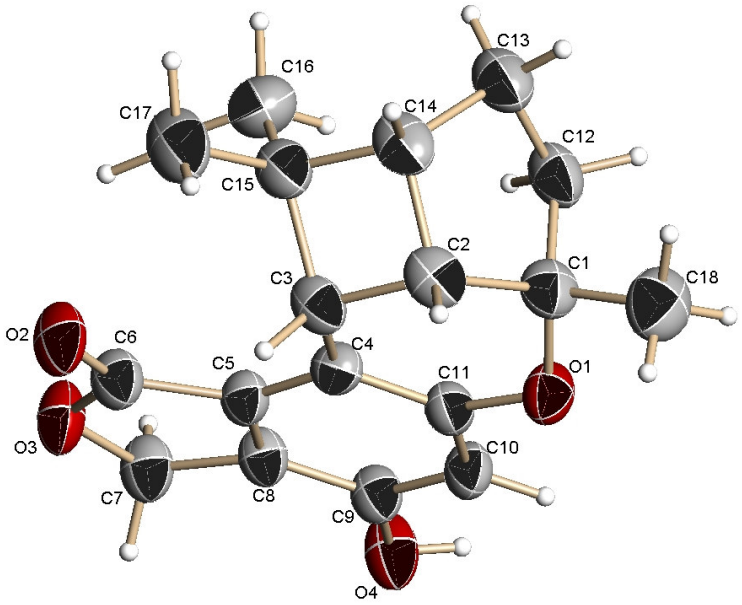

50 MH:
CDCl3
Chloroform-d
161.62
161.50
158.81
140.03
132.10
129.07
127.87
104.47
104.33
97.72
84.82
77.00
46.49
38.97
38.84
37.30
35.50
H
H
H
OH
O
O
OH
(±)-31


50 MHz
CDCl3
132.10
129.07
127.87
97.70
46.47
38.82
37.28
35.49
33.60
27.53
25.63
17.76
H
H
H
OH
O
O
OH
(±)-31

Single Crystal X-ray Crystallographic Studies:

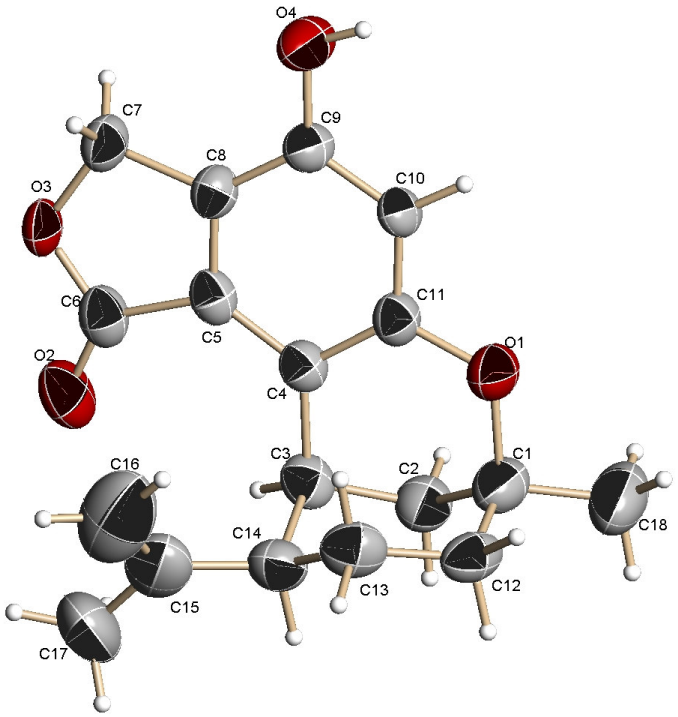
The X-ray data of **4a** and **5** were collected on a SMART APEX CCD single crystal X-ray diffractometer with omega and phi scan mode and different number of scans and exposure times for different crystals using λ MoK$_\alpha$ = 0.71073 Å radiation, at T = 293(2) K with Oscillation / frame -0.3º, maximum detector swing angle = –30.0º, beam center = (260.2, 252.5), in plane spot width = 1.24. All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs. The crystal structures were solved by direct method using SHELXS-97 and the refinement was performed by full matrix least squares of F^2 using SHELXL-97 (G. M. Sheldrick, SHELX-97 program for crystal structure solution and refinement, University of Göttingen, Germany, 1997).

Crystal Data for 4a: Single crystals of the compound **4a** were grown by slow evaporation of the solution in acetone colourless rectangular crystal of approximate size 0.27 x 0.17 x 0.06 mm, was used for data collection on *Bruker SMART APEX* CCD diffractometer using Mo K$_\alpha$ radiation with fine focus tube with 50kV and 30mA. Crystal to detector distance 6.05 cm, 512 x 512 pixels / frame, Quadrant data acquisition. Total scans = 4, total frames = 2424, Oscillation / frame -0.3º, exposure / frame = 20.0 sec / frame, maximum detector swing angle = –30.0º, beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration, θ range = 1.53 to 25.0 º, completeness to θ of 25.0º is 99.9 %. SADABS correction applied, C_{18} H_{20} O_4, M = 300.34. Crystals belong to monoclinic, space group P2$_1$/c, a = *13.3486 (15)*, b = *7.9630 (9)*, c = *13.8757 (15)* Å, β = 93.676 (2)°, V = 1471.9 (3) Å^3, Z = 4, 1.355 mg m^{-3}, μ (MoK$_\alpha$) = 0.095 mm^{-1}, T = 293(2) K, 9215 reflections measured, 2594 unique [I>2σ(I)], R value 0.0501, wR2 = 0.1043. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL) was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model. Data collection and refinement parameters are listed in table 1.



ORTEP diagram of **4a** (ellipsoids are drawn at 40% probability)

<u>Crystal Data for 5:</u> Single crystals of the compound **5** were grown by slow evaporation of the solution in acetone colorless rectangular crystal of approximate size 0.37 x 0.14 x 0.07 mm, was used for data collection on *Bruker SMART APEX* CCD diffractometer using Mo K_α radiation with fine focus tube with 50kV and 30mA. Crystal to detector distance 6.05 cm, 512 x 512 pixels / frame, Quadrant data acquisition. Total scans = 3, total frames = 1818, Oscillation / frame -0.3º, exposure / frame = 15.0 sec / frame, maximum detector swing angle = –30.0º, beam center = (260.2, 252.5), in plane spot width = 1.24, SAINT integration, θ range = 2.32 to 24.99 º, completeness to θ of 24.99 º is 100.0 %. SADABS correction applied, C_{18} H_{20} O_4, M = 300.34. Crystals belong to monoclinic, space group $P2_1/c$, $a = 10.1385(7)$, $b = 11.8567(8)$, $c = 13.1736(9)$ Å, β = 97.779(1) °, V = 569.01(19) Å^3, Z = 4, 1.271 mg m^{-3}, μ (MoK_α) = 0.089 mm^{-1}, T = 293(2) K, 9714 reflections measured, 2758 unique [I>2σ(I)], R value 0.0398, wR2 = 0.1027. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL) was used for structure solution and full matrix least squares refinement on F^2. Hydrogen atoms were included in the refinement as per the riding model. Data collection and refinement parameters are listed in table 1.



ORTEP diagram of **5** (ellipsoids are drawn at 50% probability)