SUPPORTING INFORMATION

Synthesis and Absolute Configuration of Both Enantiomers of 4,5-Dihydroxy-3-(formyl)cyclopent-2-enone Acetonide as a New Chiral Building Block for Prostanoid Synthesis

Beata Łukasik, Marian Mikołajczyk, Grzegorz Bujacz, and Remigiusz Żurawiński*

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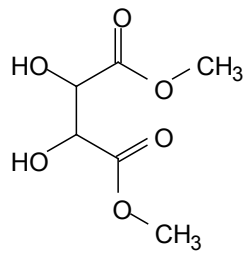
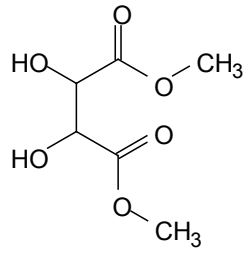

HO
O
CH3
O
HO
O
O
CH3

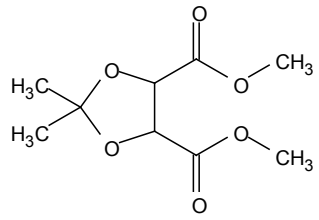
7

1.00
3.29
0.92
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
O
CH3
O
HO
O
O
CH3

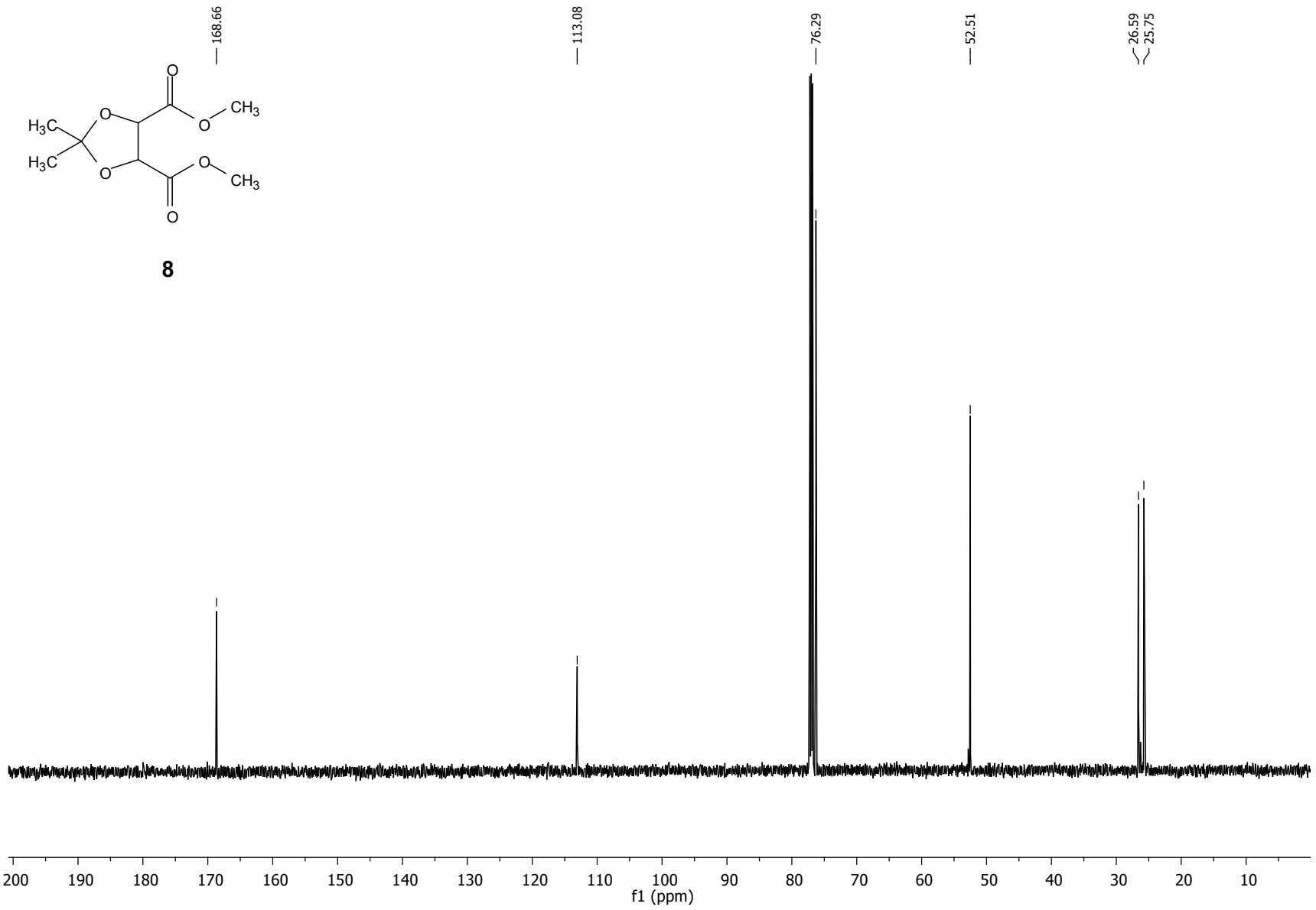
7

171.36
72.91
52.92
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

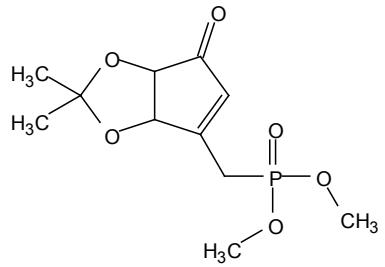

O
O
CH3
H3C
O
H3C
O
O
CH3
O

8

2.00
6.26
3.22
3.19
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
f1 (ppm)

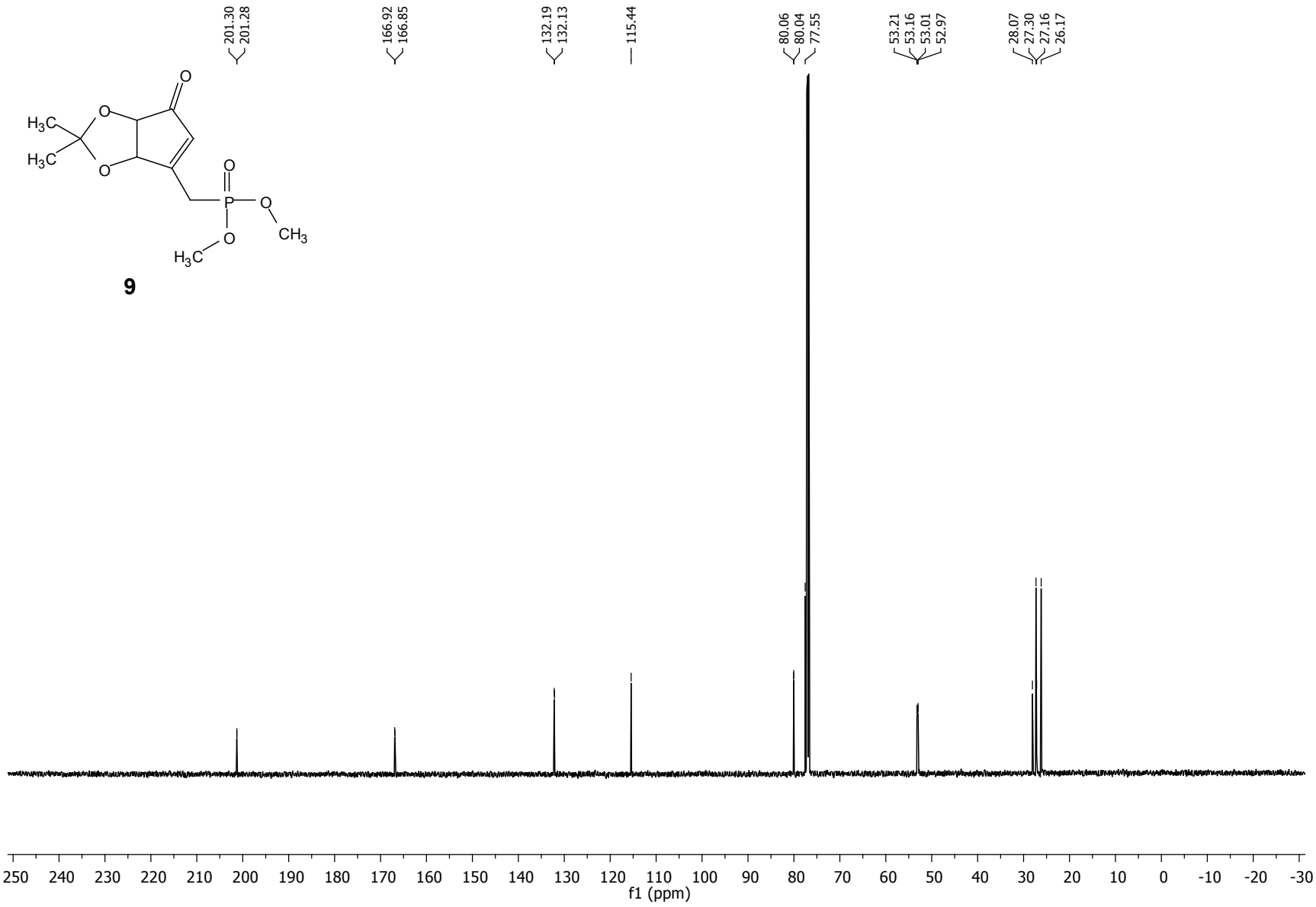

168.66
113.08
76.29
52.51
26.59
25.75
O
O
O
O
O
O
H_3C
H_3C
CH_3
CH_3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

8


O
H3C
H3C
O
O
O
P
O
O
CH3
H3C

9

1.00
1.04
1.03
3.16
3.20
2.24
3.29
3.29
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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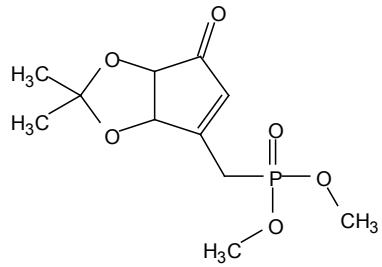
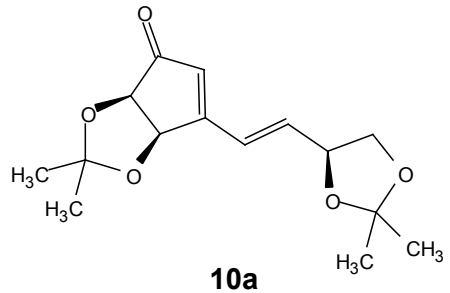
201.28
166.92
166.85
132.19
132.13
115.44
80.06
80.04
77.55
53.21
53.16
53.01
52.97
28.07
27.30
27.16
26.17
O
H3C
H3C
O
O
O
P
O
CH3
O
H3C
9
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

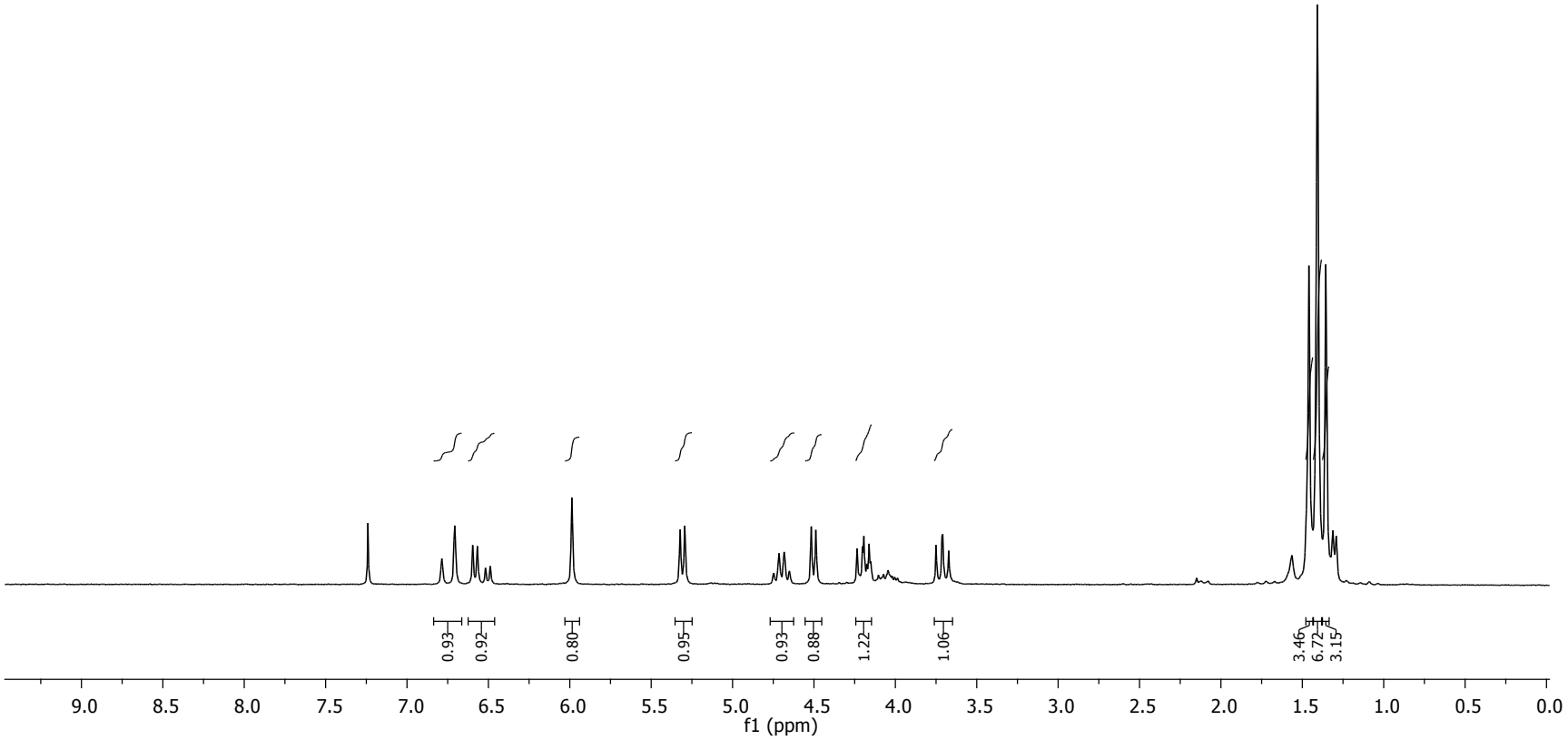

O
H3C
H3C
O
O
O
P
O
O
CH3
H3C

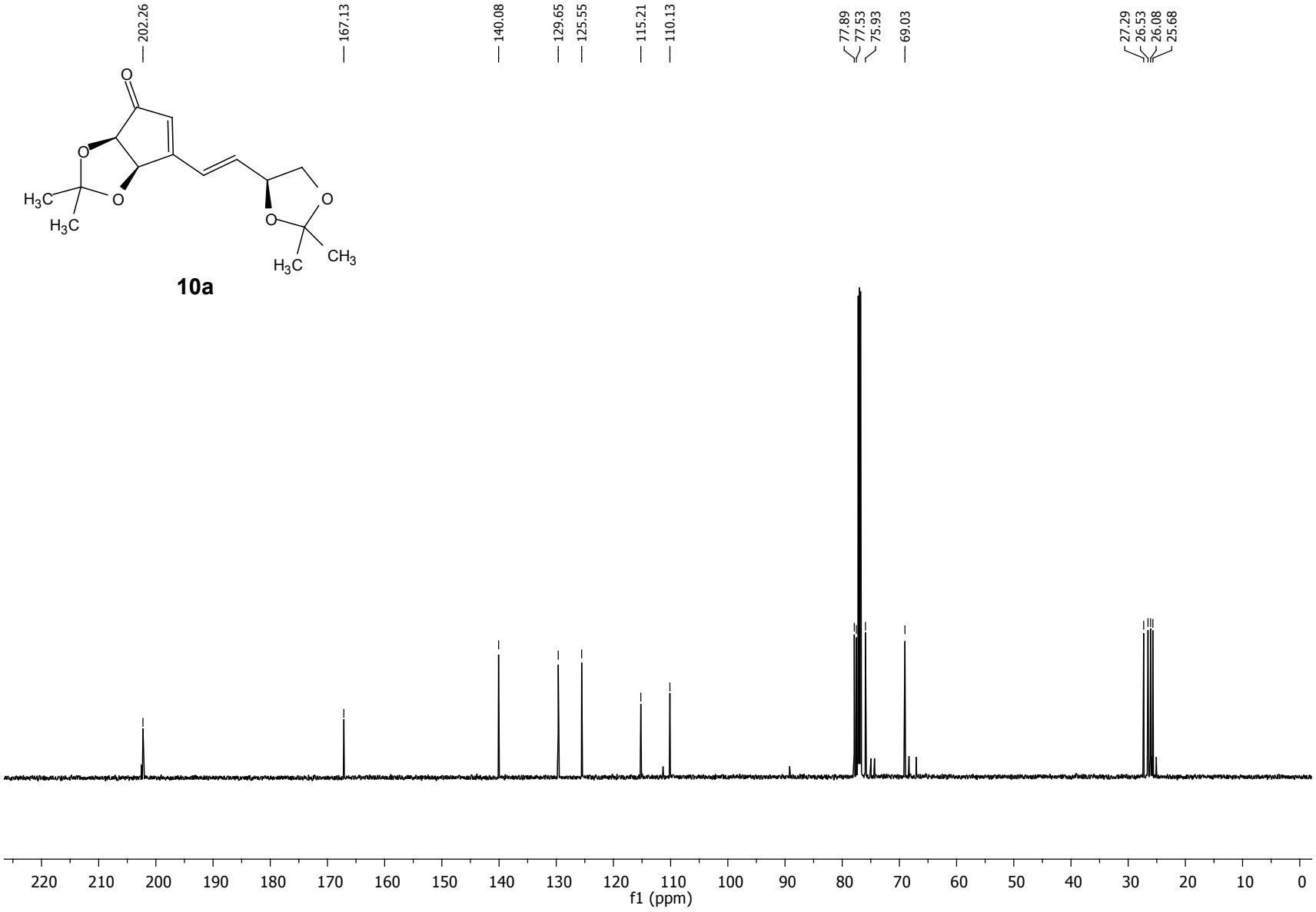
9

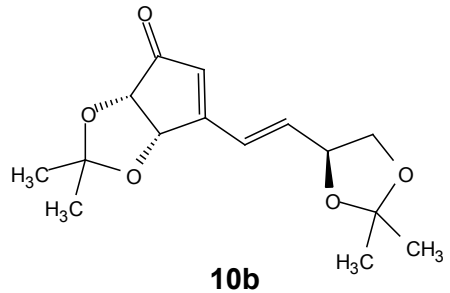
24.72
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


O
O
O
H3C
H3C
O
O
O
H3C
CH3

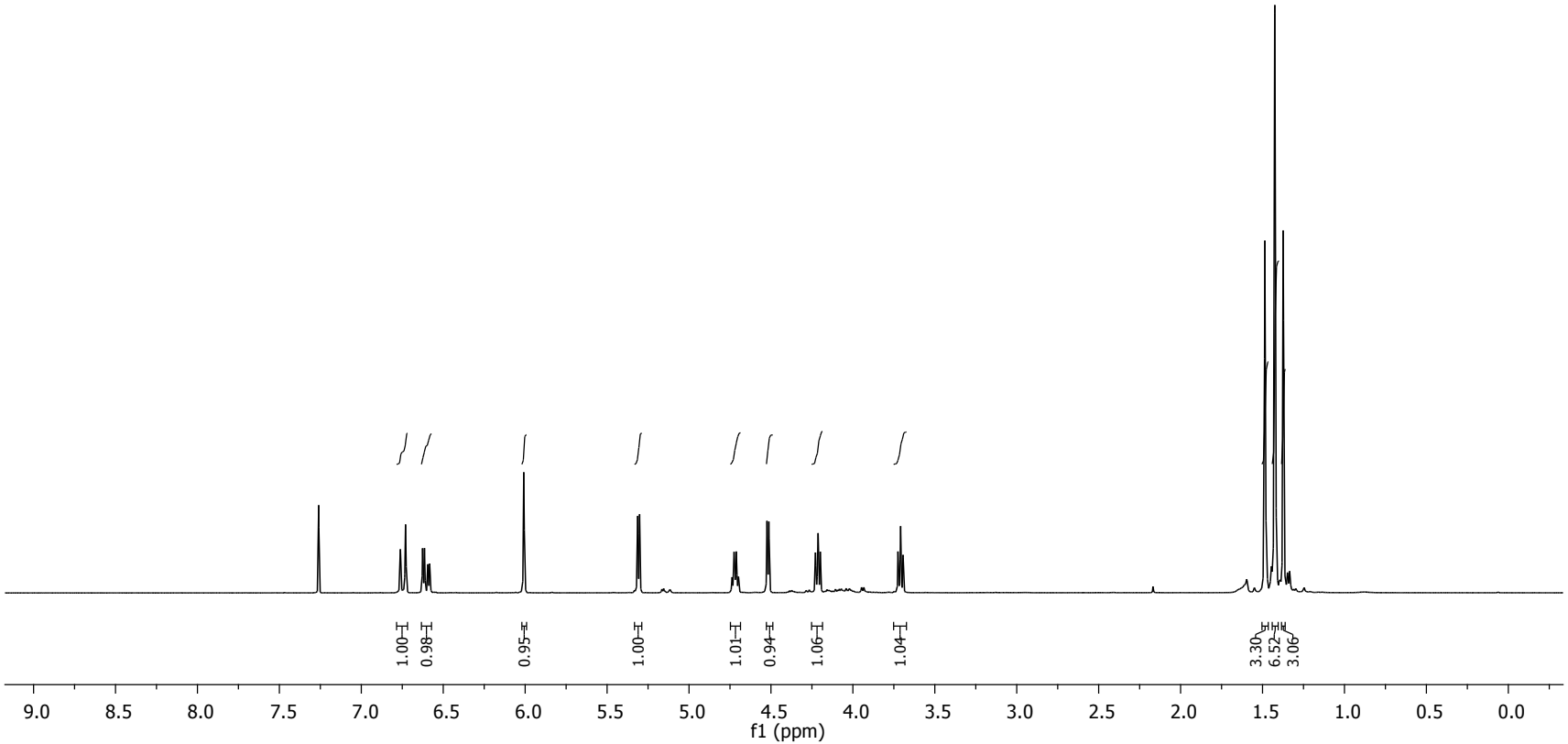
10a

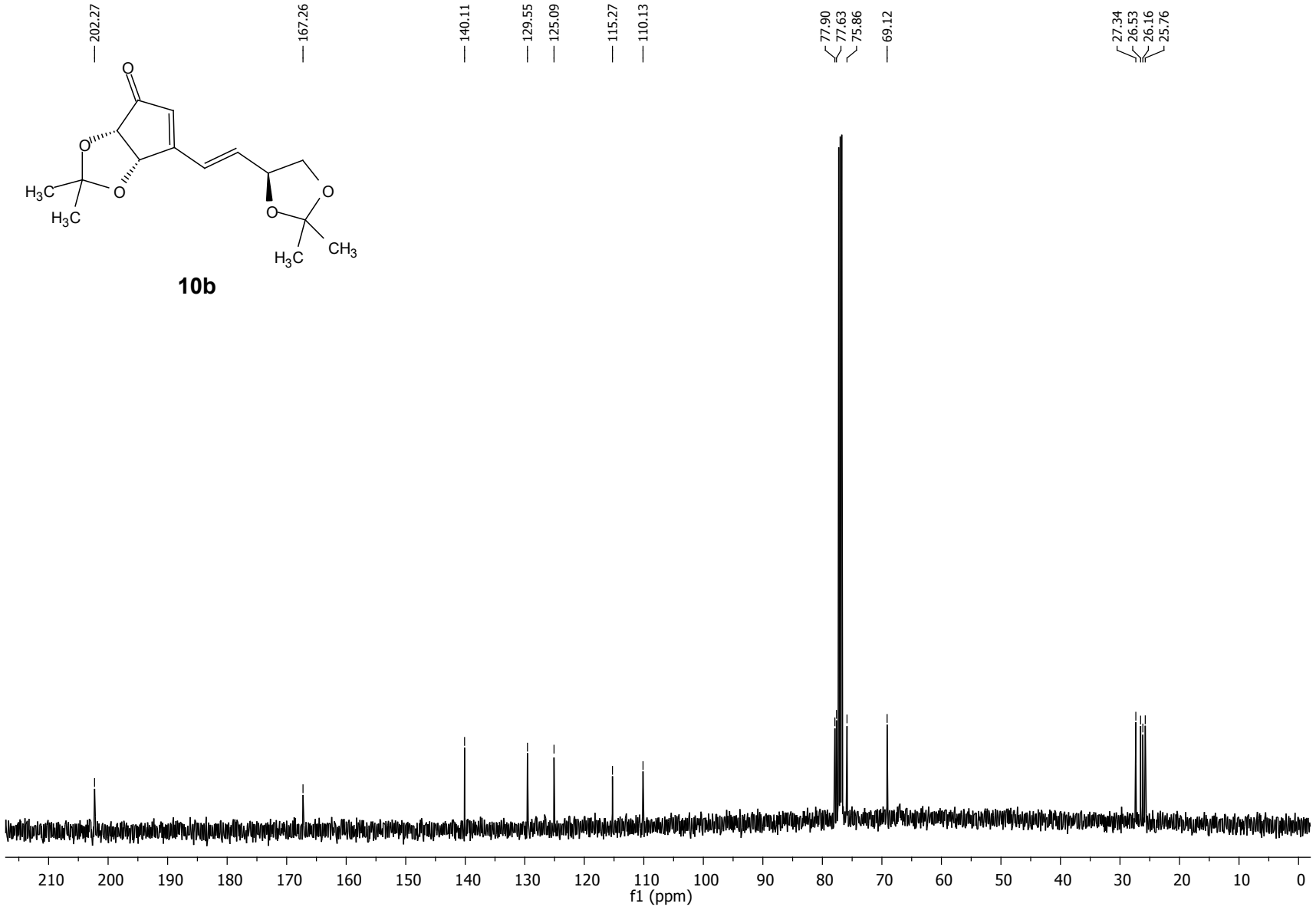

0.93
0.92
0.80
0.95
0.93
0.88
1.22
1.06
3.46
6.72
3.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

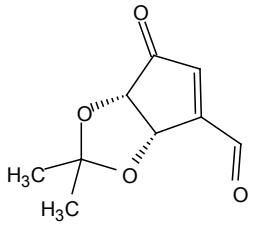

202.26
167.13
140.08
129.65
125.55
115.21
110.13
77.89
77.53
75.93
69.03
27.29
26.53
26.08
25.68
O
O
O
O
O
H3C
H3C
H3C
CH3
10a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O
H3C
H3C
O
O
O
H3C
CH3

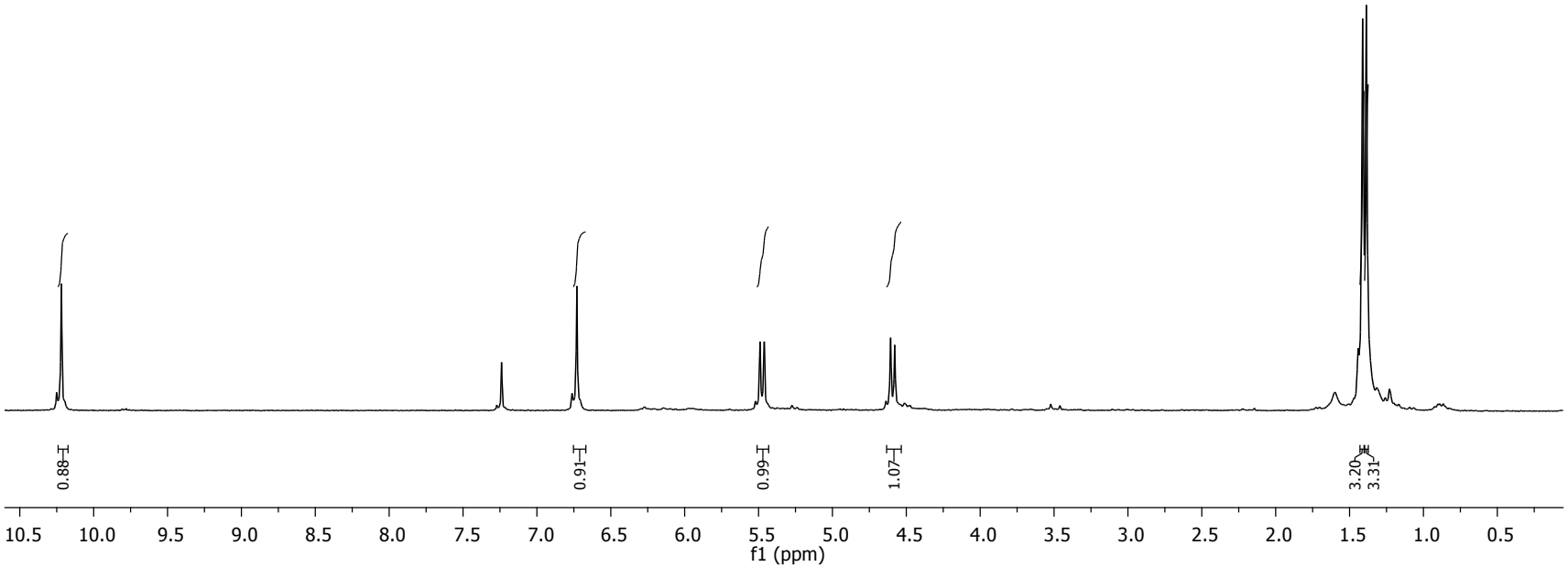
10b


1.00
0.98
0.95
1.00
1.01
0.94
1.06
1.04
3.30
6.52
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


202.27
167.26
140.11
129.55
125.09
115.27
110.13
77.90
77.63
75.86
69.12
27.34
26.53
26.16
25.76
O
O
O
O
O
O
H3C
H3C
H3C
CH3
10b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
H3C
O
H3C
O

(*S*,*S*)-**5**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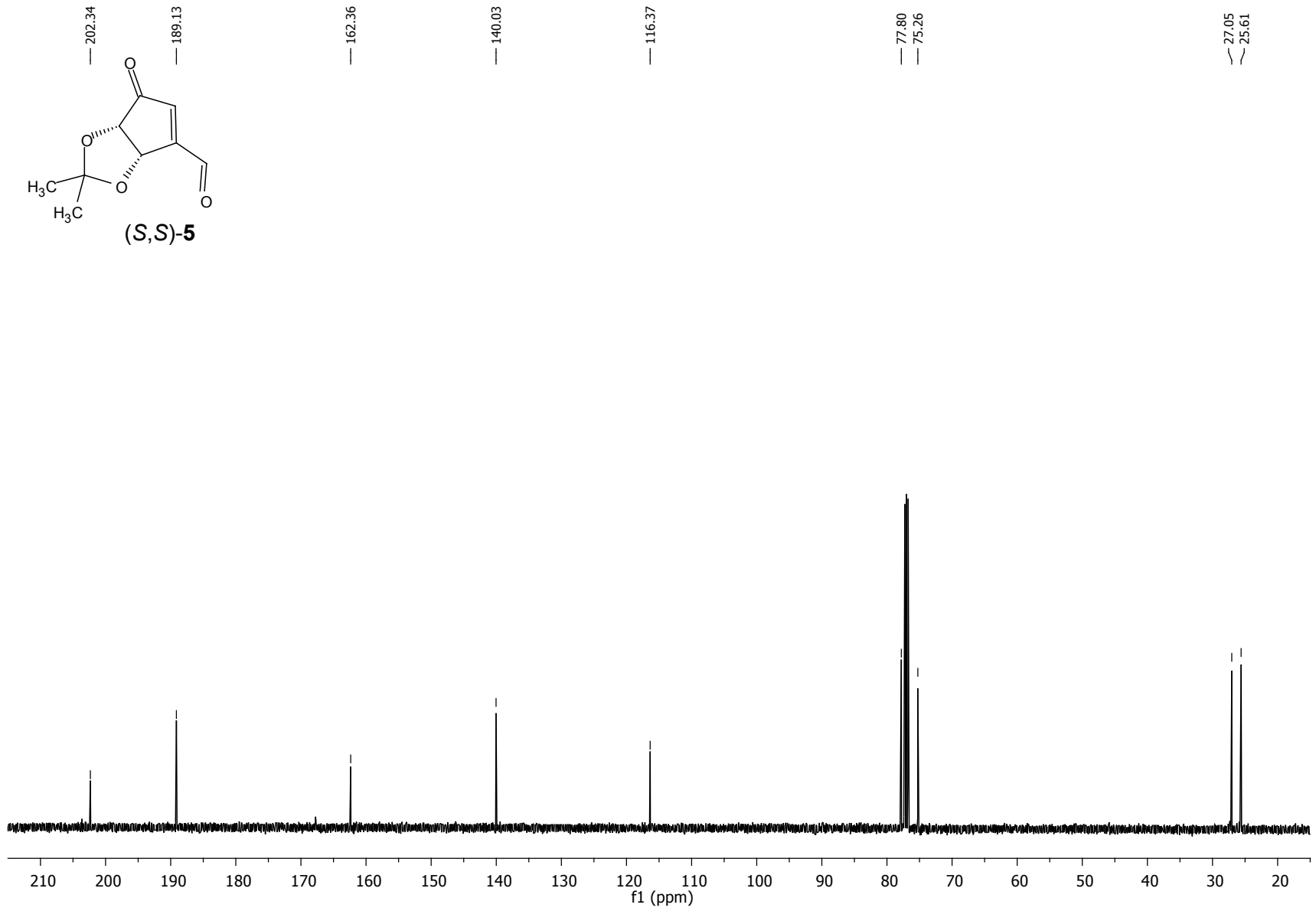
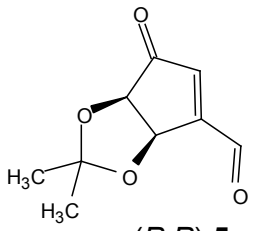
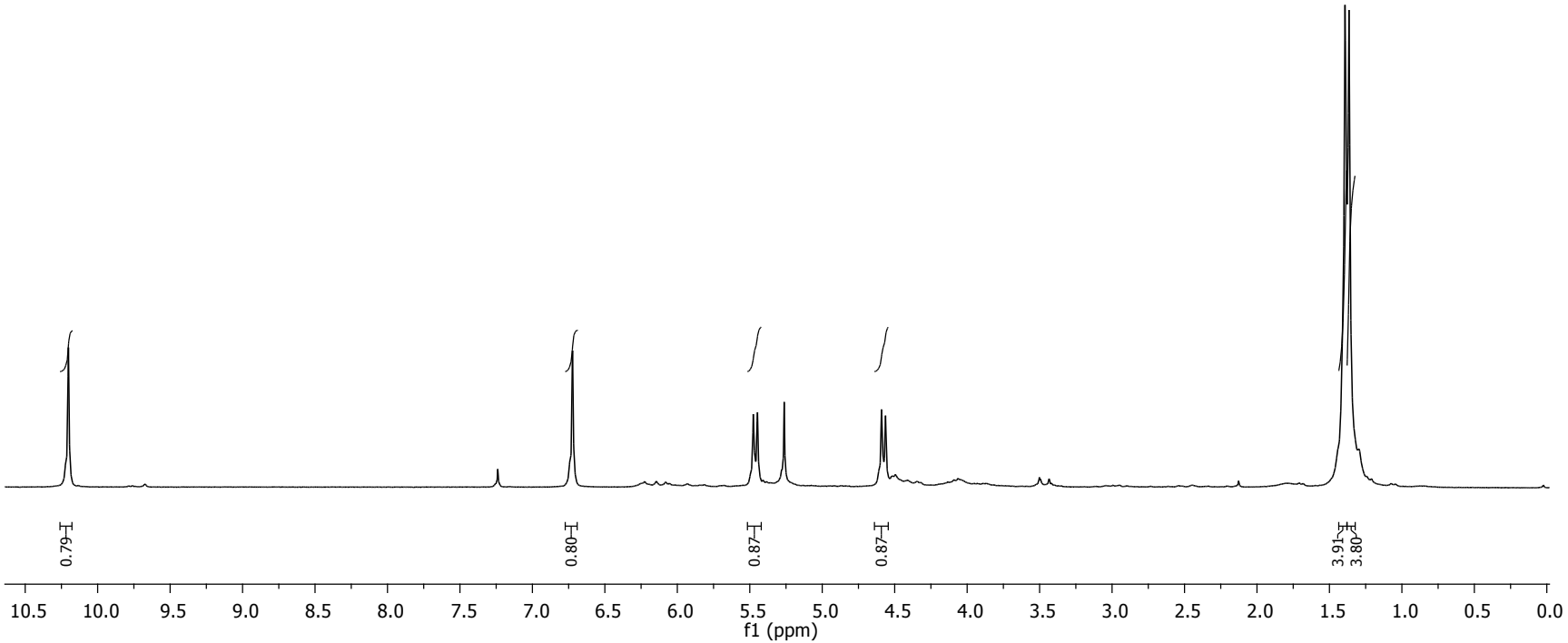
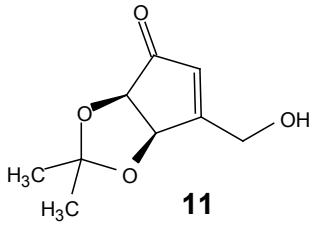
0.99
1.07
3.20
3.31
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


202.34
189.13
162.36
140.03
116.37
77.80
75.26
27.05
25.61
O
O
O
O
H_3C
H_3C
(*S*,*S*)-**5**
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


O
O
H3C
O
H3C
O

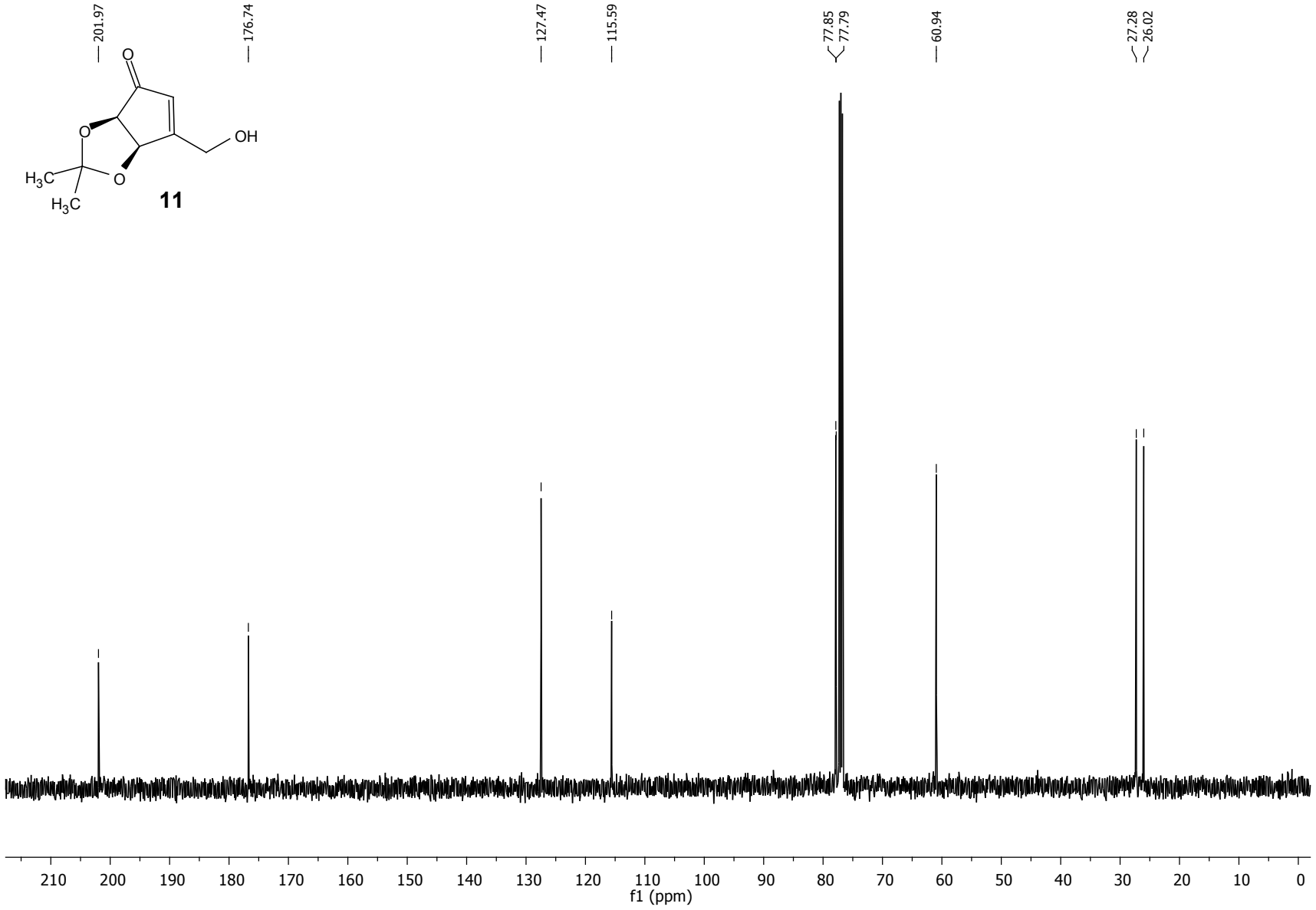
(*R*,*R*)-**5**

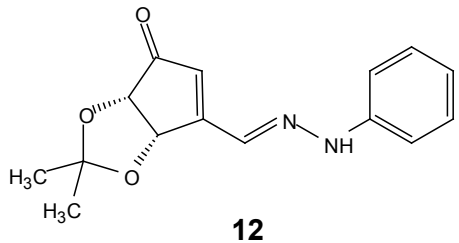

0.79
0.80
0.87
0.87
3.91
3.80
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
O
OH
H3C
O
H3C

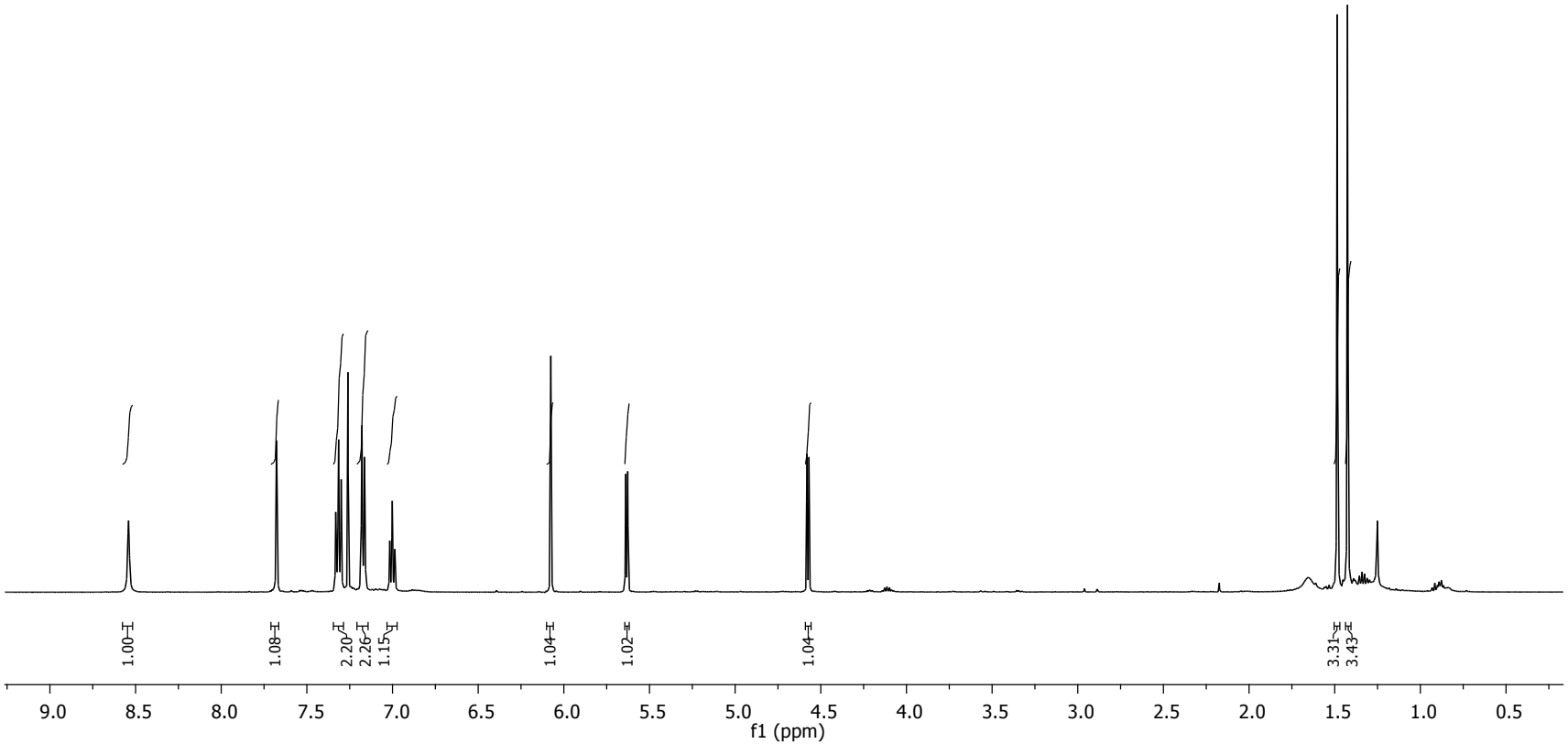
11

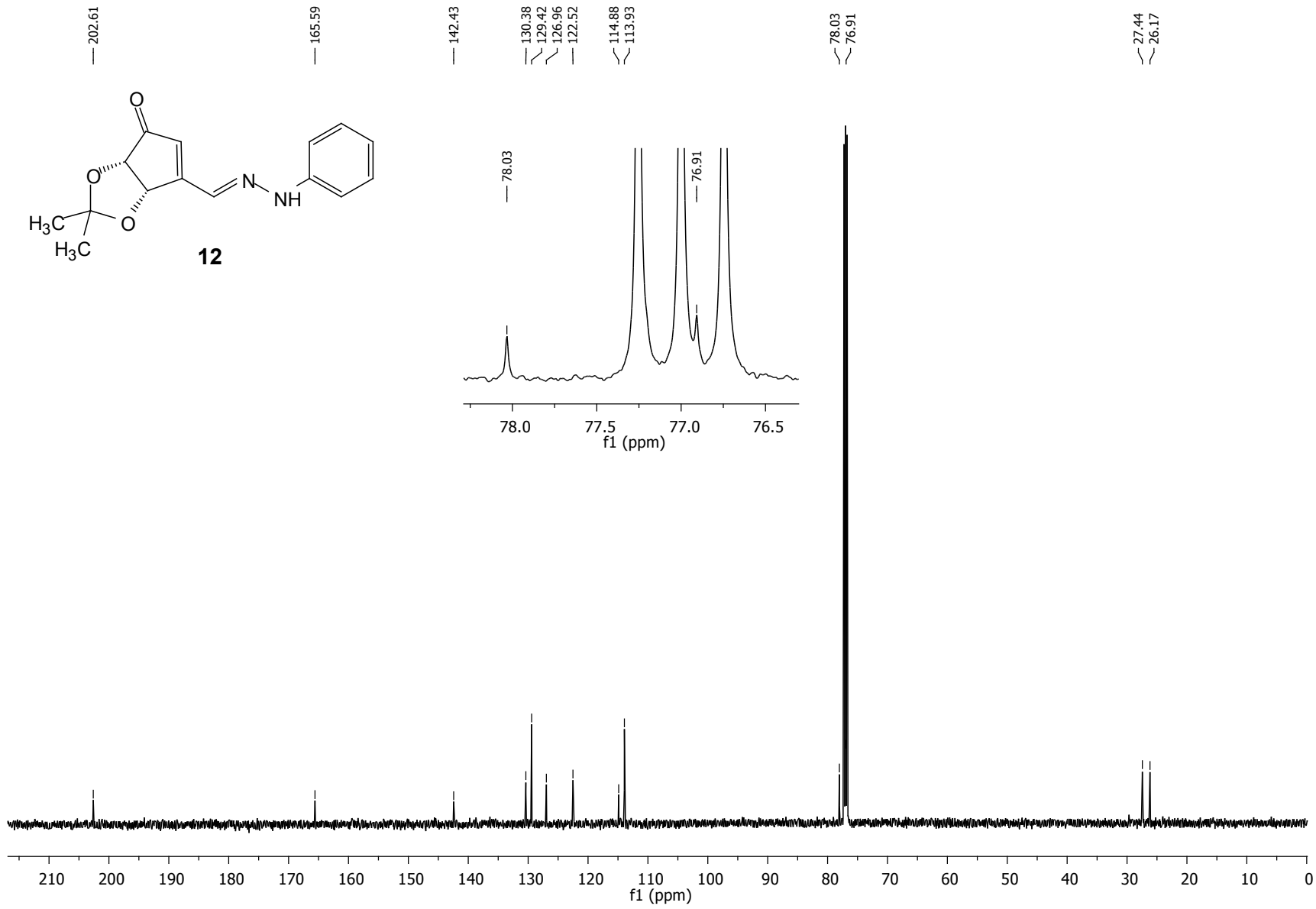
1.00
1.04
1.06
2.11
0.98
6.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

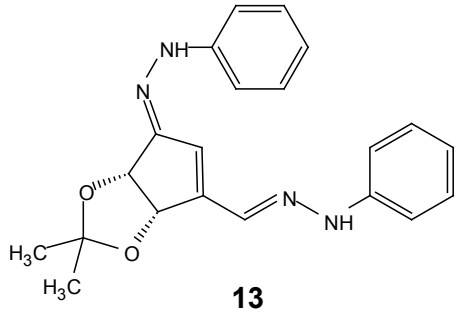

201.97
176.74
127.47
115.59
77.85
77.79
60.94
27.28
26.02
O
O
OH
H3C
O
H3C
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
N
NH
H_3C
O
H_3C

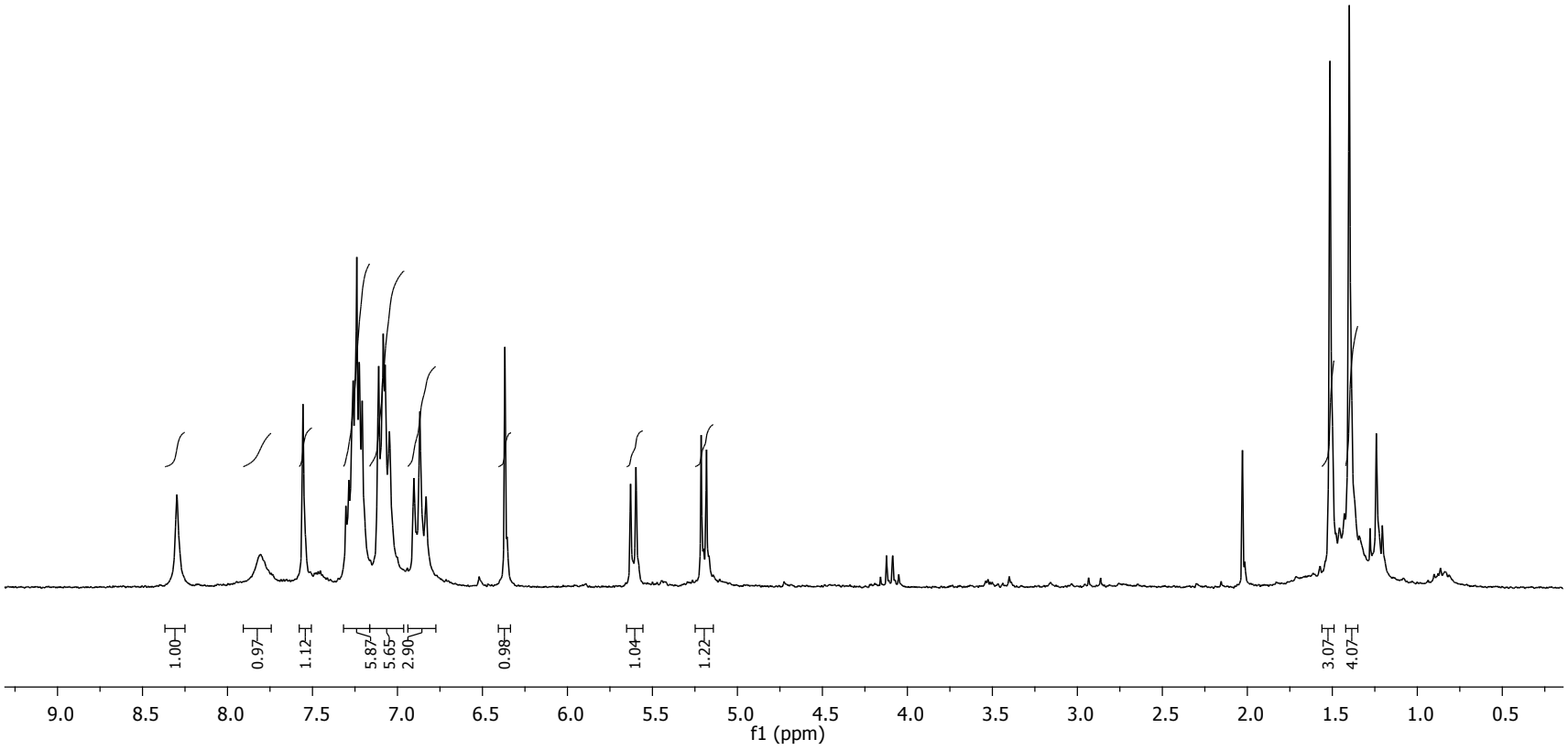
12

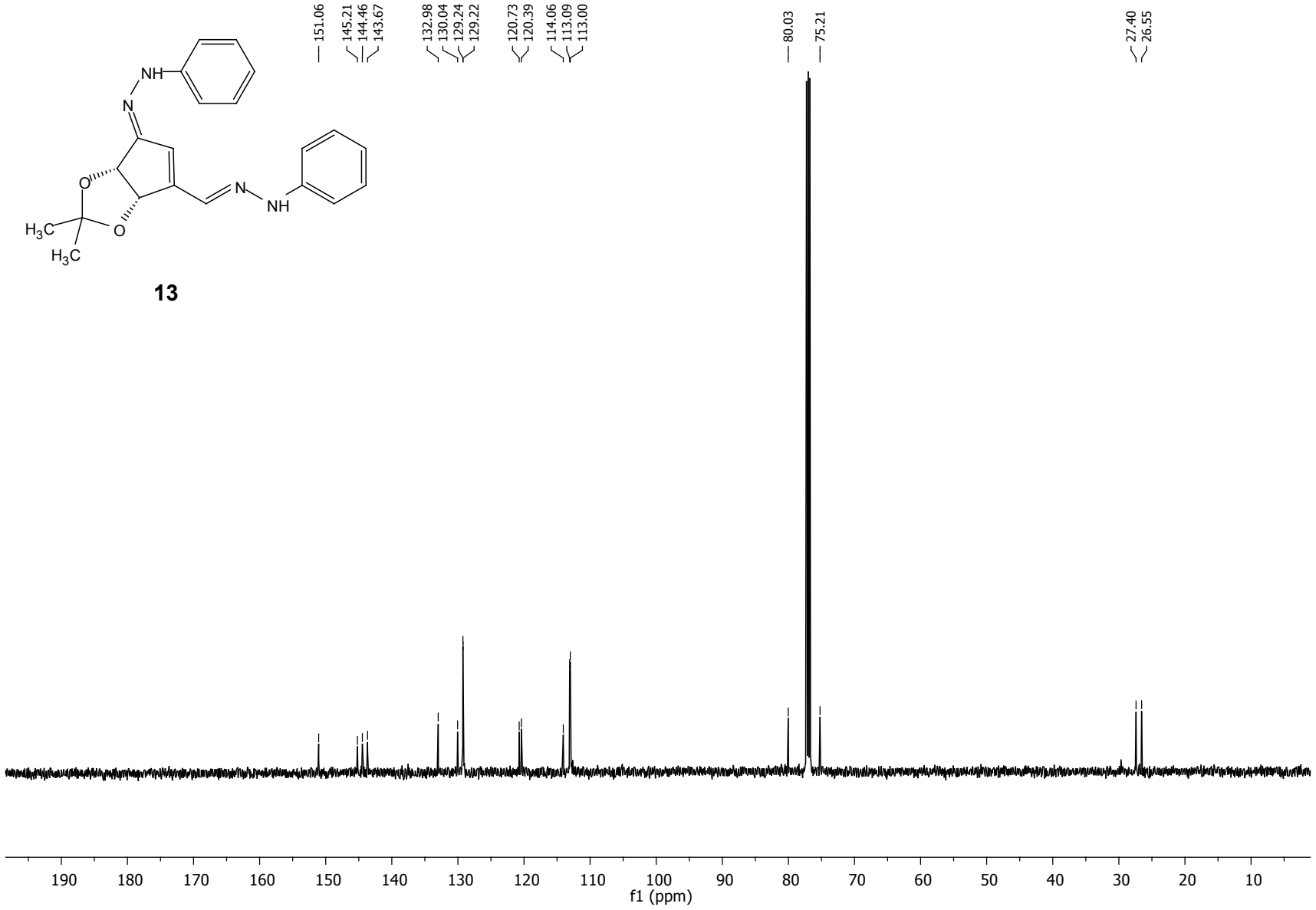

1.00
1.08
2.20
2.26
1.15
1.04
1.02
1.04
3.31
3.43
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


202.61
165.59
142.43
130.38
129.42
126.96
122.52
114.88
113.93
78.03
76.91
27.44
26.17
O
O
O
N
NH
H3C
H3C
12
78.03
76.91
78.0
77.5
77.0
76.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NH
N
O
O
H_3C
H_3C
N
NH

13


1.00
0.97
1.12
5.87
5.65
2.90
0.98
1.04
1.22
3.07
4.07
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
f1 (ppm)


151.06
145.21
144.46
143.67
132.98
130.04
129.24
129.22
120.73
120.39
114.06
113.09
113.00
80.03
75.21
27.40
26.55
NH
N
O
O
H_3C
H_3C
N
NH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

13

Energy, thermodynamic properties and geometry of **5a** optimized at the B3LYP-6-311++G(2d,2p)level in CH_2Cl_2 (IEFPCM)

Energy: E(RB3LYP)=-650.0484757

Zero-point correction=	0.178210 (Hartree/Particle)
Thermal correction to Energy=	0.190123
Thermal correction to Enthalpy=	0.191067
Thermal correction to Gibbs Free Energy=	0.139778
Sum of electronic and zero-point Energies=	-649.870265
Sum of electronic and thermal Energies=	-649.858353
Sum of electronic and thermal Enthalpies=	-649.857409
Sum of electronic and thermal Free Energies=	-649.908698

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.347783	-0.396381	-0.675053
2	6	0	-0.244694	1.026573	-0.712919
3	1	0	0.469432	-0.849673	-1.658696
4	1	0	-0.437060	1.399191	-1.720070
5	6	0	1.916632	1.034439	0.402507
6	1	0	2.789208	1.397802	0.925448
7	6	0	1.676430	-0.233044	0.033630
8	6	0	0.794055	1.911381	0.000217
9	8	0	0.697283	3.102013	0.191048
10	8	0	-1.434062	0.954420	0.059798
11	8	0	-0.567316	-1.148275	0.120489
12	6	0	-1.810021	-0.431585	0.159283
13	6	0	-2.696361	-0.827440	-1.016570
14	1	0	-2.944144	-1.885986	-0.955602
15	1	0	-3.618678	-0.248843	-0.999076
16	1	0	-2.192255	-0.645338	-1.964917
17	6	0	-2.462419	-0.659585	1.505392
18	1	0	-3.381223	-0.080046	1.576564
19	1	0	-2.707925	-1.713308	1.625822
20	1	0	-1.785077	-0.356377	2.300703
21	6	0	2.615234	-1.349671	0.254026
22	8	0	2.431972	-2.464862	-0.184496
23	1	0	3.516151	-1.106624	0.840261

Energy, thermodynamic properties and geometry of **5b** optimized at the B3LYP-6-311++G(2d,2p)level in CH_2Cl_2 (IEFPCM)

Energy: E(RB3LYP)=-650.0457425

Zero-point correction=	0.177862 (Hartree/Particle)
Thermal correction to Energy=	0.189971
Thermal correction to Enthalpy=	0.190916
Thermal correction to Gibbs Free Energy=	0.138703
Sum of electronic and zero-point Energies=	-649.867880
Sum of electronic and thermal Energies=	-649.855771
Sum of electronic and thermal Enthalpies=	-649.854827
Sum of electronic and thermal Free Energies=	-649.907040

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.163920	-0.330342	-0.881219
2	6	0	-0.356897	1.088341	-0.588444
3	1	0	0.188739	-0.573207	-1.944626
4	1	0	-0.690943	1.636748	-1.469851
5	6	0	1.906368	0.820623	0.260465
6	1	0	2.841673	1.043865	0.750469
7	6	0	1.547453	-0.360635	-0.263024
8	6	0	0.818758	1.808019	0.097335
9	8	0	0.830974	2.969374	0.437636
10	8	0	-1.409352	0.895837	0.348075
11	8	0	-0.723590	-1.207457	-0.189205
12	6	0	-1.884395	-0.452838	0.202942
13	6	0	-2.955558	-0.530278	-0.878792
14	1	0	-2.574299	-0.163612	-1.831039
15	1	0	-3.277177	-1.562177	-1.010724
16	1	0	-3.816704	0.072716	-0.594815
17	6	0	-2.356108	-0.946123	1.553287
18	1	0	-2.666692	-1.986958	1.480468
19	1	0	-1.550694	-0.862492	2.279545
20	1	0	-3.205749	-0.354706	1.890146
21	6	0	2.383131	-1.587678	-0.267392
22	8	0	3.463010	-1.660987	0.276860
23	1	0	1.962505	-2.451804	-0.805738

Energy, thermodynamic properties and geometry of **5c** optimized at the B3LYP-6-311++G(2d,2p)level in CH_2Cl_2 (IEFPCM)

Energy: E(RB3LYP)=-650.0473986

Zero-point correction=	0.178173	(Hartree/Particle)
Thermal correction to Energy=	0.190093	
Thermal correction to Enthalpy=	0.191037	
Thermal correction to Gibbs Free Energy=	0.139831	
Sum of electronic and zero-point Energies=	-649.869226	
Sum of electronic and thermal Energies=	-649.857306	
Sum of electronic and thermal Enthalpies=	-649.856362	
Sum of electronic and thermal Free Energies=	-649.907567	

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.348911	0.905445	-1.006853
2	6	0	0.370131	1.934673	-0.104376
3	6	0	1.580149	1.275257	0.437048
4	6	0	1.625506	-0.007354	0.044649
5	6	0	0.460449	-0.394124	-0.850277
6	8	0	-1.662648	0.588224	-0.591589
7	8	0	-0.442216	-1.318533	-0.252036
8	6	0	-1.637647	-0.635217	0.167049
9	6	0	-1.602692	-0.349017	1.664427
10	6	0	-2.837257	-1.469105	-0.238660
11	8	0	0.001250	3.066514	0.112667
12	6	0	2.712485	-0.941019	0.398101
13	8	0	2.793365	-2.063320	-0.052776
14	1	0	3.468139	-0.550965	1.099140
15	1	0	-0.384889	1.286647	-2.026411
16	1	0	2.294514	1.780348	1.071074
17	1	0	0.810396	-0.820055	-1.788149
18	1	0	-1.550403	-1.286027	2.217135
19	1	0	-0.740324	0.256037	1.935153
20	1	0	-2.505869	0.181791	1.961597
21	1	0	-2.820341	-2.424674	0.282836
22	1	0	-3.758085	-0.949089	0.020887
23	1	0	-2.816936	-1.647151	-1.311671

Energy, thermodynamic properties and geometry of **5d** optimized at the B3LYP-6-311++G(2d,2p)level in CH_2Cl_2 (IEFPCM)

Energy: E(RB3LYP)=-650.044841

Zero-point correction=	0.177934 (Hartree/Particle)
Thermal correction to Energy=	0.190009
Thermal correction to Enthalpy=	0.190953
Thermal correction to Gibbs Free Energy=	0.138967
Sum of electronic and zero-point Energies=	-649.866907
Sum of electronic and thermal Energies=	-649.854832
Sum of electronic and thermal Enthalpies=	-649.853888
Sum of electronic and thermal Free Energies=	-649.905874

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.422596	1.036932	-0.900435
2	6	0	0.560554	1.818053	0.001156
3	6	0	1.707244	0.928567	0.283714
4	6	0	1.509529	-0.275057	-0.274108
5	6	0	0.214710	-0.352471	-1.065212
6	8	0	-1.686565	0.804640	-0.305630
7	8	0	-0.734085	-1.265429	-0.523794
8	6	0	-1.741125	-0.539980	0.207155
9	6	0	-1.454277	-0.564731	1.704214
10	6	0	-3.097120	-1.125221	-0.136194
11	8	0	0.404138	2.950726	0.399007
12	6	0	2.435716	-1.431014	-0.173197
13	8	0	3.441654	-1.423431	0.501862
14	1	0	2.155860	-2.320372	-0.759987
15	1	0	-0.567578	1.578220	-1.834076
16	1	0	2.555318	1.223475	0.882881
17	1	0	0.397983	-0.635662	-2.100976
18	1	0	-0.481947	-0.134079	1.931283
19	1	0	-2.217354	0.001865	2.235692
20	1	0	-1.468233	-1.592236	2.065190
21	1	0	-3.152321	-2.159901	0.198217
22	1	0	-3.883543	-0.558740	0.359996
23	1	0	-3.253914	-1.087875	-1.212056

Energy, thermodynamic properties and geometry of **5a** optimized at the B3LYP-6-311++G(2d,2p)level in MeOH (IEFPCM)

Energy: E(RB3LYP)=-650.0505711

Zero-point correction=	0.178246	(Hartree/Particle)
Thermal correction to Energy=	0.190141	
Thermal correction to Enthalpy=	0.191085	
Thermal correction to Gibbs Free Energy=	0.139869	
Sum of electronic and zero-point Energies=	-649.872325	
Sum of electronic and thermal Energies=	-649.860430	
Sum of electronic and thermal Enthalpies=	-649.859486	
Sum of electronic and thermal Free Energies=	-649.910702	

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.347068	-0.396036	-0.671620
2	6	0	-0.243913	1.027108	-0.709606
3	1	0	0.463019	-0.850777	-1.655043
4	1	0	-0.431503	1.400122	-1.717339
5	6	0	1.921284	1.034924	0.398049
6	1	0	2.797046	1.397977	0.915599
7	6	0	1.679156	-0.232587	0.030022
8	6	0	0.793726	1.909420	0.007089
9	8	0	0.690123	3.098028	0.211208
10	8	0	-1.437036	0.956108	0.058530
11	8	0	-0.566872	-1.144713	0.129847
12	6	0	-1.811667	-0.430791	0.160784
13	6	0	-2.691864	-0.831231	-1.017880
14	1	0	-2.938913	-1.889833	-0.954518
15	1	0	-3.615308	-0.254282	-1.005876
16	1	0	-2.183750	-0.650974	-1.964380
17	6	0	-2.469253	-0.655852	1.504754
18	1	0	-3.389006	-0.077194	1.570557
19	1	0	-2.715268	-1.709294	1.626538
20	1	0	-1.795510	-0.350507	2.302408
21	6	0	2.618611	-1.348841	0.247389
22	8	0	2.423542	-2.469168	-0.174762
23	1	0	3.529234	-1.102823	0.816040

Energy, thermodynamic properties and geometry of **5b** optimized at the B3LYP-6-311++G(2d,2p)level in MeOH (IEFPCM)

Energy: E(RB3LYP)=-650.0476113

Zero-point correction=	0.177882	(Hartree/Particle)
Thermal correction to Energy=	0.189985	
Thermal correction to Enthalpy=	0.190929	
Thermal correction to Gibbs Free Energy=	0.138715	
Sum of electronic and zero-point Energies=	-649.869730	
Sum of electronic and thermal Energies=	-649.857626	
Sum of electronic and thermal Enthalpies=	-649.856682	
Sum of electronic and thermal Free Energies=	-649.908897	

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.161414	-0.333725	-0.872263
2	6	0	-0.355129	1.087075	-0.582815
3	1	0	0.175167	-0.584021	-1.933877
4	1	0	-0.676667	1.636238	-1.468239
5	6	0	1.911593	0.818076	0.256433
6	1	0	2.851678	1.043031	0.736346
7	6	0	1.550692	-0.362285	-0.267982
8	6	0	0.818486	1.801142	0.110872
9	8	0	0.824018	2.956874	0.472735
10	8	0	-1.418581	0.902770	0.343387
11	8	0	-0.720633	-1.203646	-0.162877
12	6	0	-1.888224	-0.450217	0.208232
13	6	0	-2.948930	-0.541727	-0.882498
14	1	0	-2.560257	-0.184774	-1.835401
15	1	0	-3.267515	-1.575680	-1.005333
16	1	0	-3.814025	0.062112	-0.612581
17	6	0	-2.371041	-0.930687	1.559249
18	1	0	-2.678102	-1.973081	1.494477
19	1	0	-1.572812	-0.837123	2.292333
20	1	0	-3.226020	-0.338937	1.881692
21	6	0	2.392748	-1.584589	-0.290777
22	8	0	3.461974	-1.668079	0.273736
23	1	0	1.988540	-2.434519	-0.862491

Energy, thermodynamic properties and geometry of **5c** optimized at the B3LYP-6-311++G(2d,2p)level in MeOH (IEFPCM)

Energy: E(RB3LYP)=-650.0494763

Zero-point correction=	0.178161 (Hartree/Particle)
Thermal correction to Energy=	0.190078
Thermal correction to Enthalpy=	0.191022
Thermal correction to Gibbs Free Energy=	0.139823
Sum of electronic and zero-point Energies=	-649.871315
Sum of electronic and thermal Energies=	-649.859398
Sum of electronic and thermal Enthalpies=	-649.858454
Sum of electronic and thermal Free Energies=	-649.909653

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.348256	0.906012	-1.007511
2	6	0	0.370714	1.934866	-0.105701
3	6	0	1.581621	1.277663	0.434285
4	6	0	1.625502	-0.005815	0.044224
5	6	0	0.461103	-0.393047	-0.851144
6	8	0	-1.662167	0.589491	-0.589954
7	8	0	-0.442758	-1.318992	-0.255473
8	6	0	-1.637407	-0.635941	0.166830
9	6	0	-1.600373	-0.352360	1.664429
10	6	0	-2.837964	-1.468134	-0.239405
11	8	0	-0.002033	3.065805	0.113391
12	6	0	2.710248	-0.939757	0.402044
13	8	0	2.781542	-2.068962	-0.035109
14	1	0	3.471970	-0.545618	1.093152
15	1	0	-0.384585	1.286299	-2.027264
16	1	0	2.296984	1.782927	1.066825
17	1	0	0.811750	-0.816876	-1.789592
18	1	0	-1.550094	-1.290423	2.215499
19	1	0	-0.736276	0.249960	1.935656
20	1	0	-2.502538	0.179237	1.963352
21	1	0	-2.821390	-2.424595	0.280472
22	1	0	-3.758246	-0.948511	0.022839
23	1	0	-2.819180	-1.643943	-1.312880

Energy, thermodynamic properties and geometry of **5d** optimized at the B3LYP-6-311++G(2d,2p)level in MeOH (IEFPCM)

Energy: E(RB3LYP)=-650.046653

Zero-point correction=	0.177924	(Hartree/Particle)
Thermal correction to Energy=	0.189999	
Thermal correction to Enthalpy=	0.190944	
Thermal correction to Gibbs Free Energy=	0.138986	
Sum of electronic and zero-point Energies=	-649.868729	
Sum of electronic and thermal Energies=	-649.856654	
Sum of electronic and thermal Enthalpies=	-649.855709	
Sum of electronic and thermal Free Energies=	-649.907667	

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.420876	1.034171	-0.899904
2	6	0	0.559350	1.812620	0.006005
3	6	0	1.709088	0.926560	0.282586
4	6	0	1.511412	-0.277015	-0.275613
5	6	0	0.214930	-0.355578	-1.063647
6	8	0	-1.687914	0.804206	-0.310118
7	8	0	-0.734320	-1.266584	-0.518055
8	6	0	-1.743061	-0.539215	0.208150
9	6	0	-1.458904	-0.557991	1.705707
10	6	0	-3.098295	-1.125727	-0.135743
11	8	0	0.396576	2.941848	0.413409
12	6	0	2.441869	-1.429935	-0.180985
13	8	0	3.440199	-1.426916	0.506177
14	1	0	2.173766	-2.311755	-0.783541
15	1	0	-0.560071	1.575677	-1.834198
16	1	0	2.558861	1.223109	0.878428
17	1	0	0.396142	-0.640507	-2.098930
18	1	0	-0.486952	-0.126490	1.932931
19	1	0	-2.223568	0.009521	2.234004
20	1	0	-1.473140	-1.584180	2.070309
21	1	0	-3.154084	-2.159126	0.202448
22	1	0	-3.885905	-0.558159	0.357368
23	1	0	-3.253054	-1.092259	-1.212086

Single Point Energy:

B2PLYPD/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) in MeOH (IEFPCM)

5a: Energy: (B2PLYPD)=-649,6174147
5b: Energy: (B2PLYPD)=-649,6143193
5c: Energy: (B2PLYPD)=-649,6170058
5d: Energy: (B2PLYPD)=-649,6140124

B2PLYPD/aug-cc-pVTZ//B3LYP/6-311++G(2d,2p) in DCM (IEFPCM)

5a: Energy: (B2PLYPD)=-649,6153791
5b: Energy: (B2PLYPD)=-649,6125289
5c: Energy: (B2PLYPD)=-649,6149982
5d: Energy: (B2PLYPD)=-649,6122666