Supplementary Material

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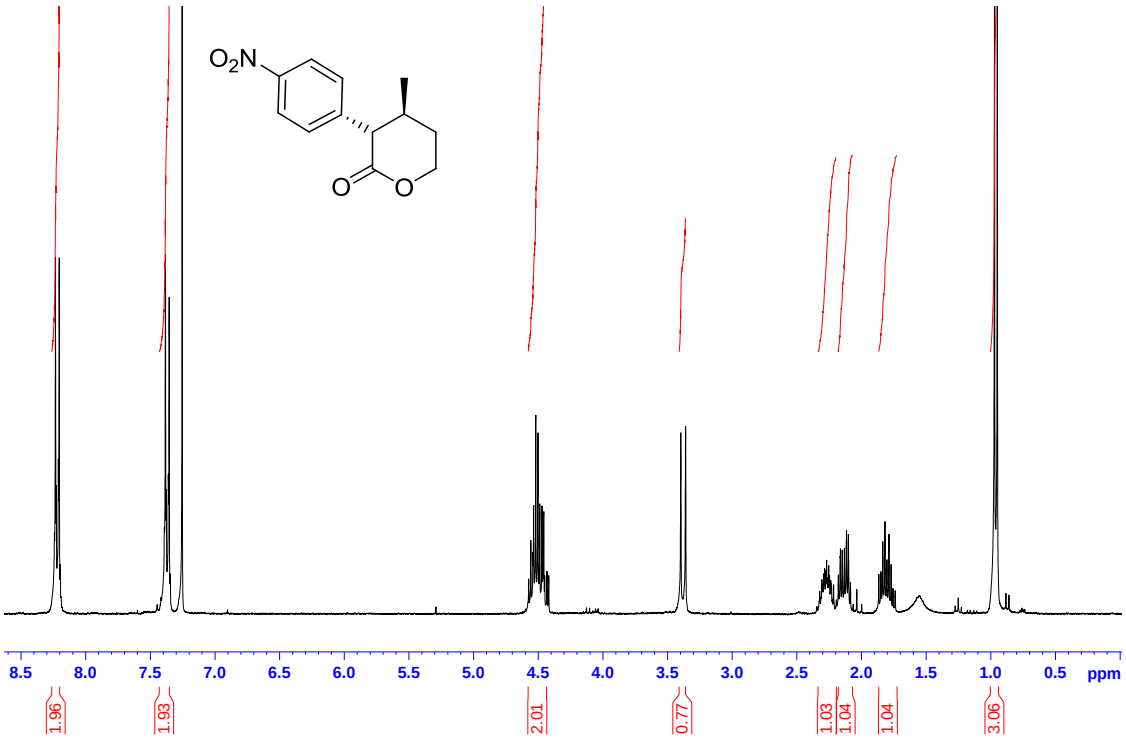
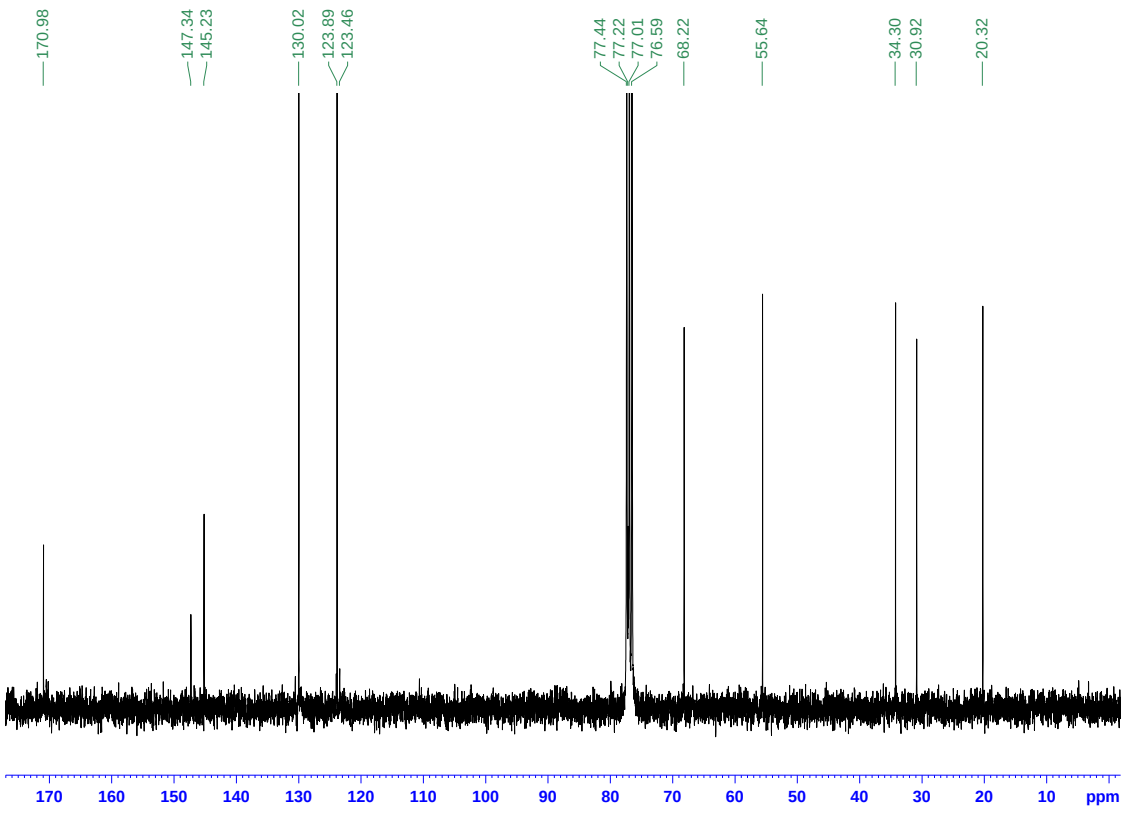
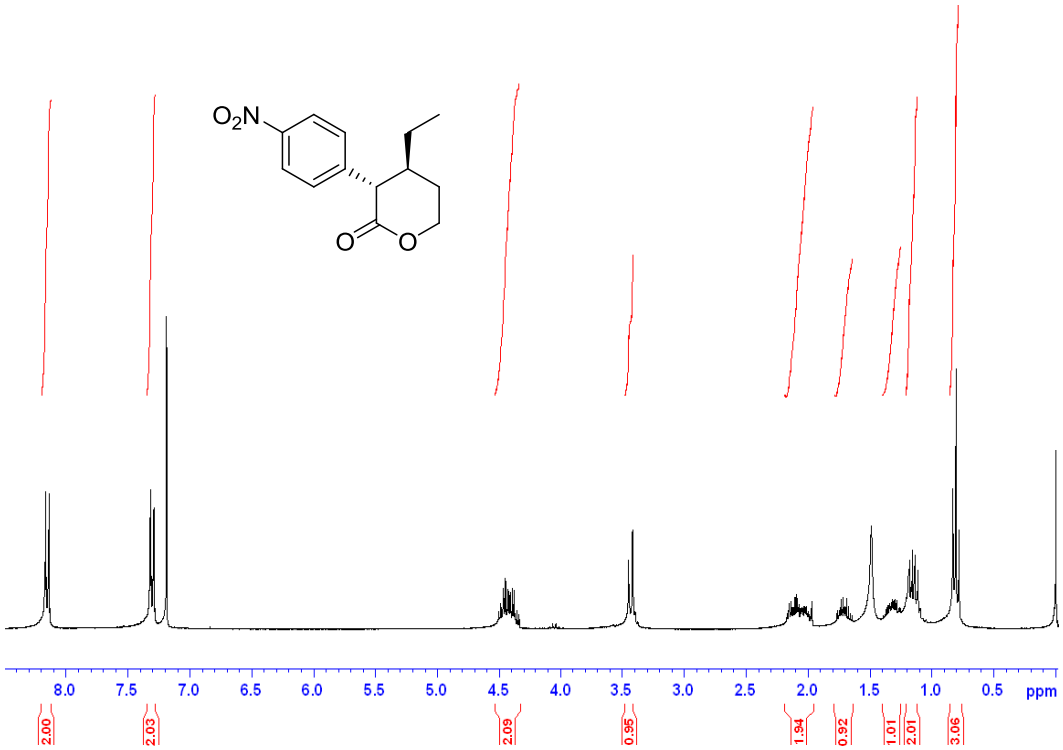
^{1}H and ^{13}C NMR spectra



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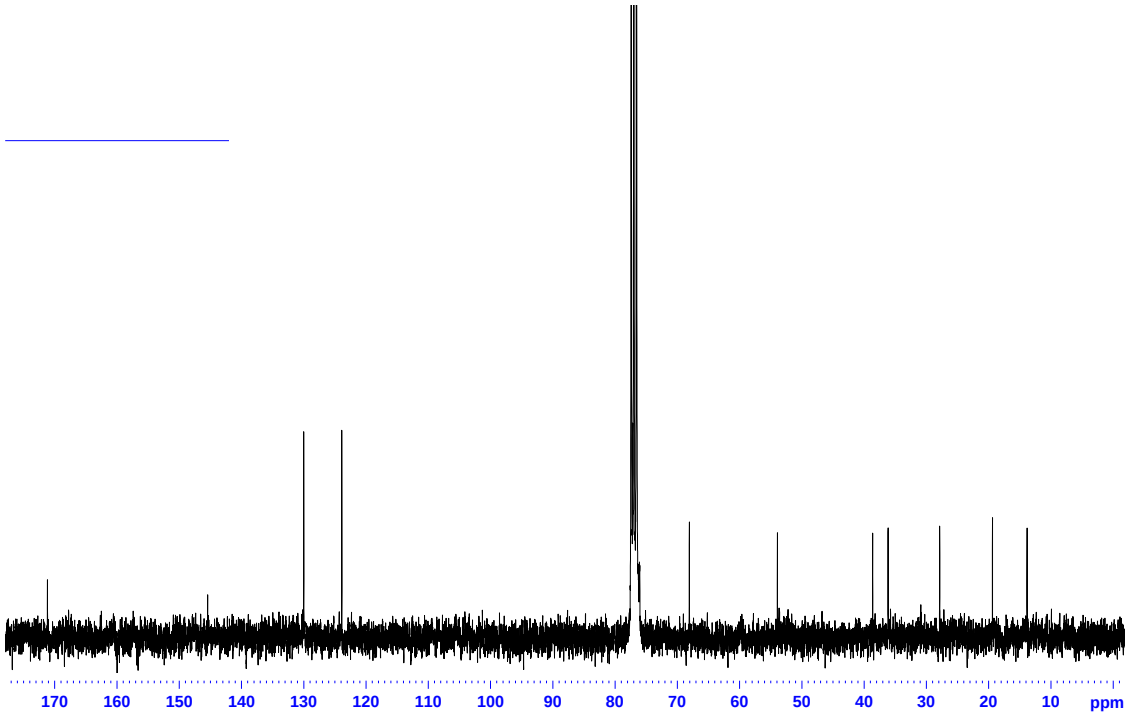
1.01
2.01
3.06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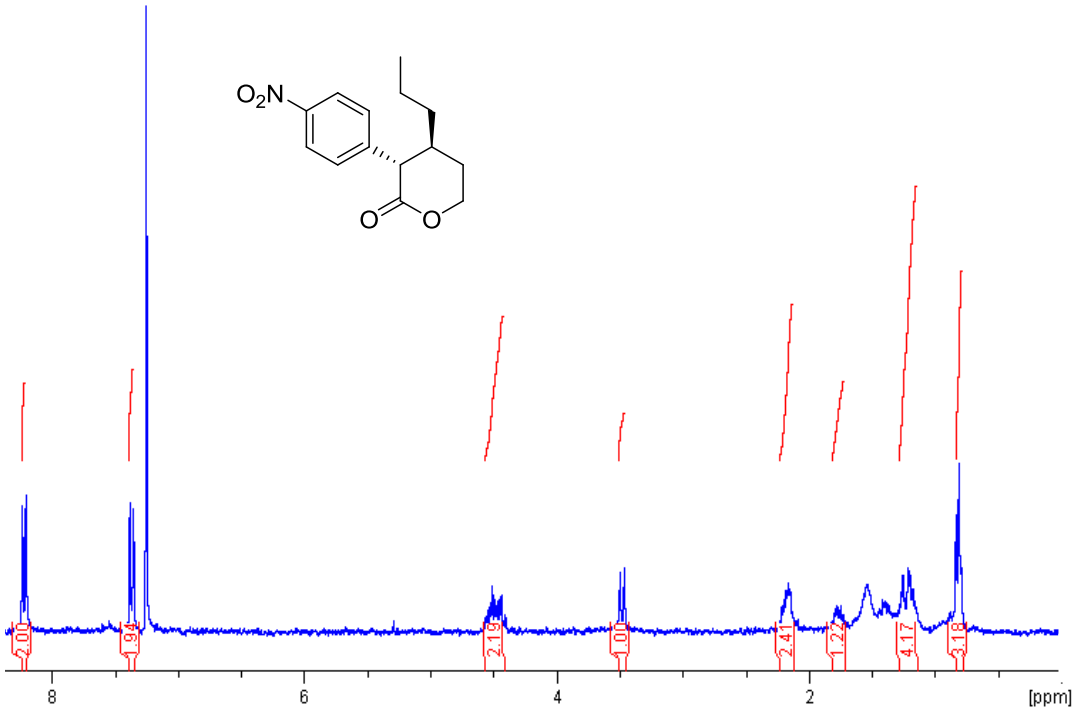
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4
2
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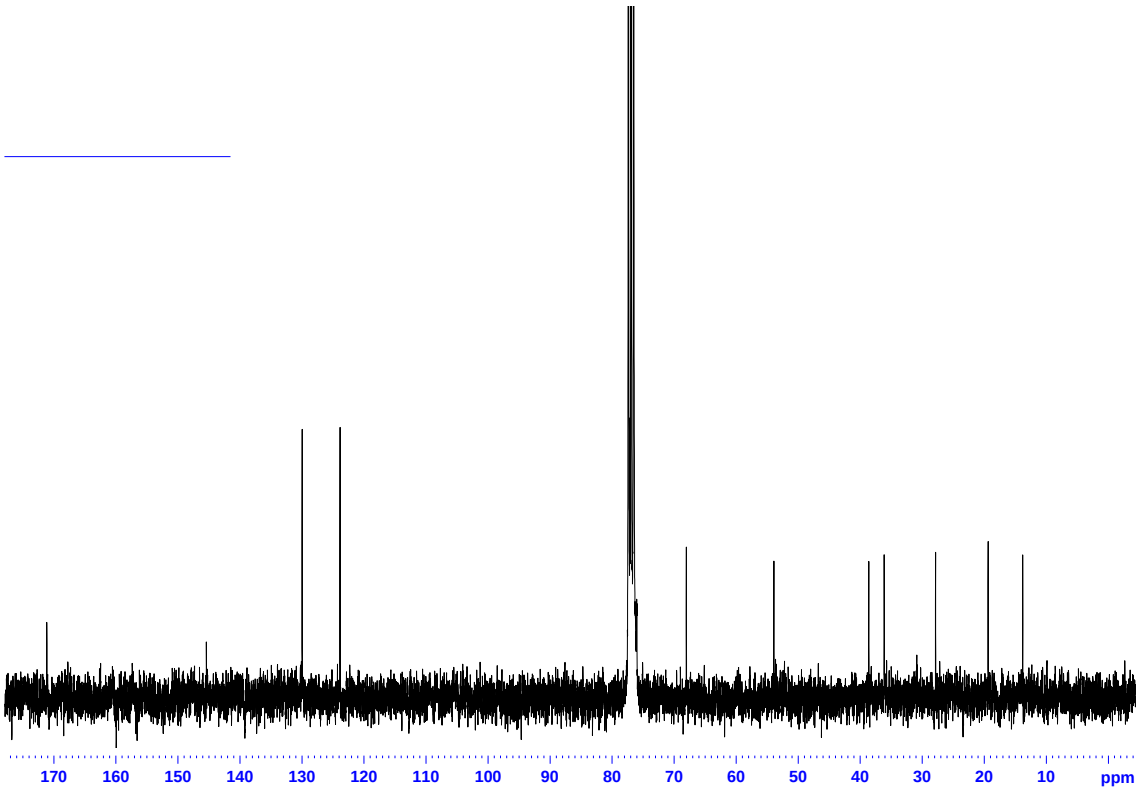
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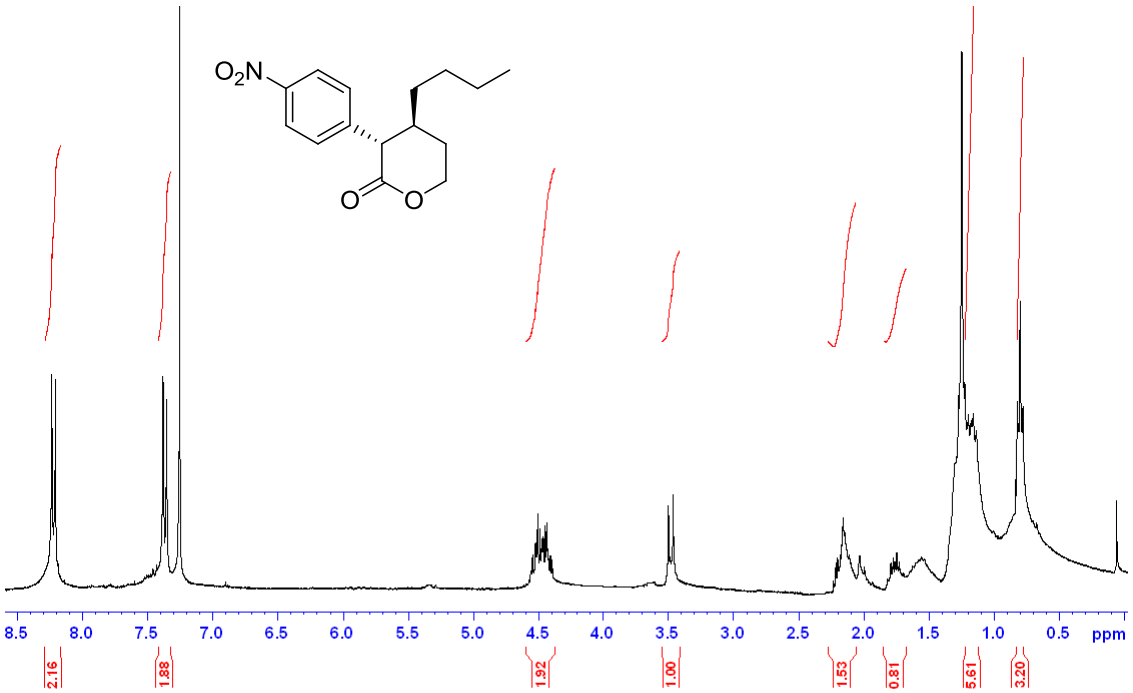
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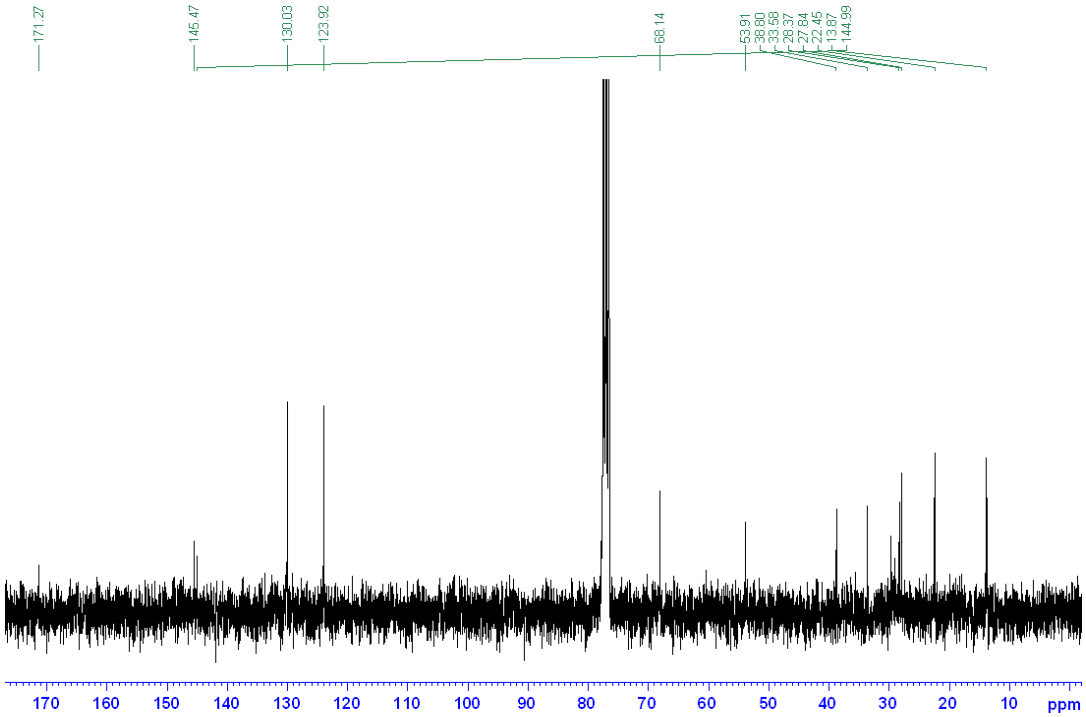
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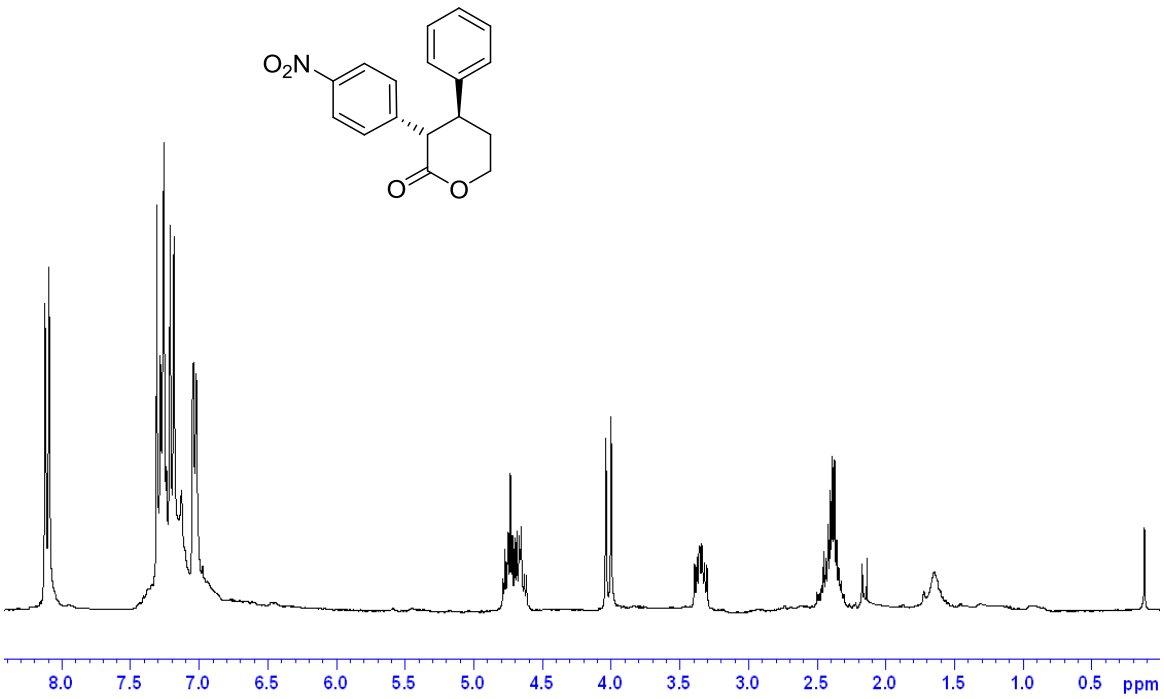
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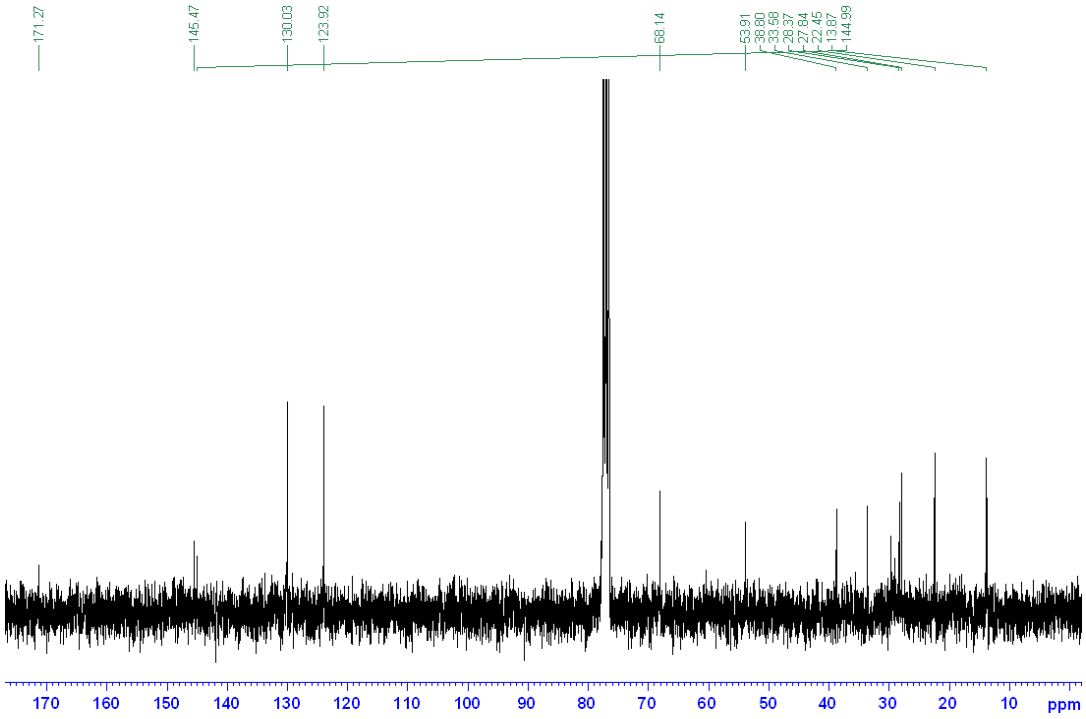
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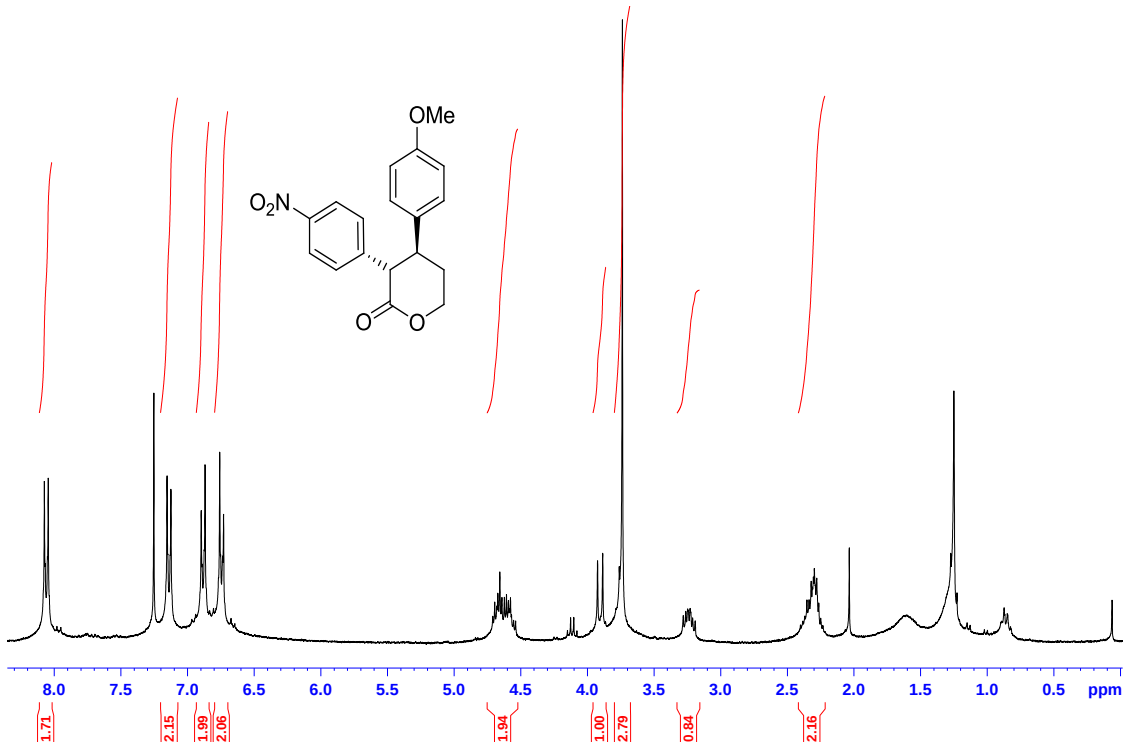
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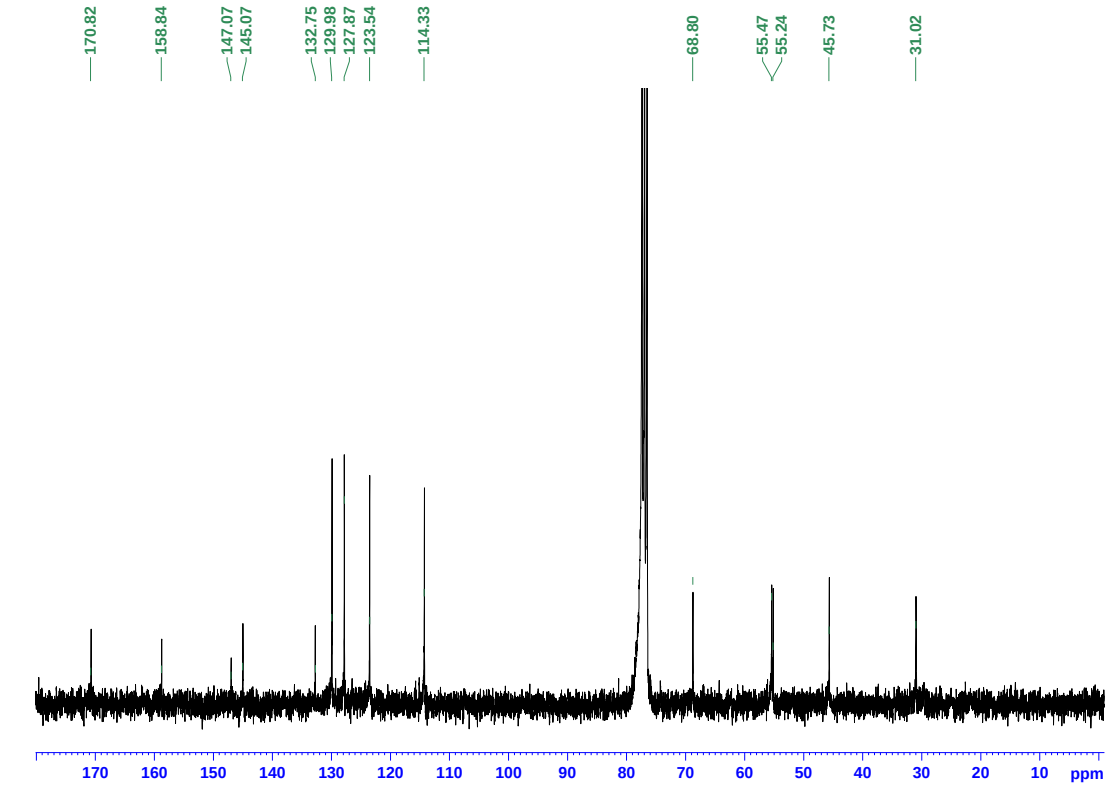
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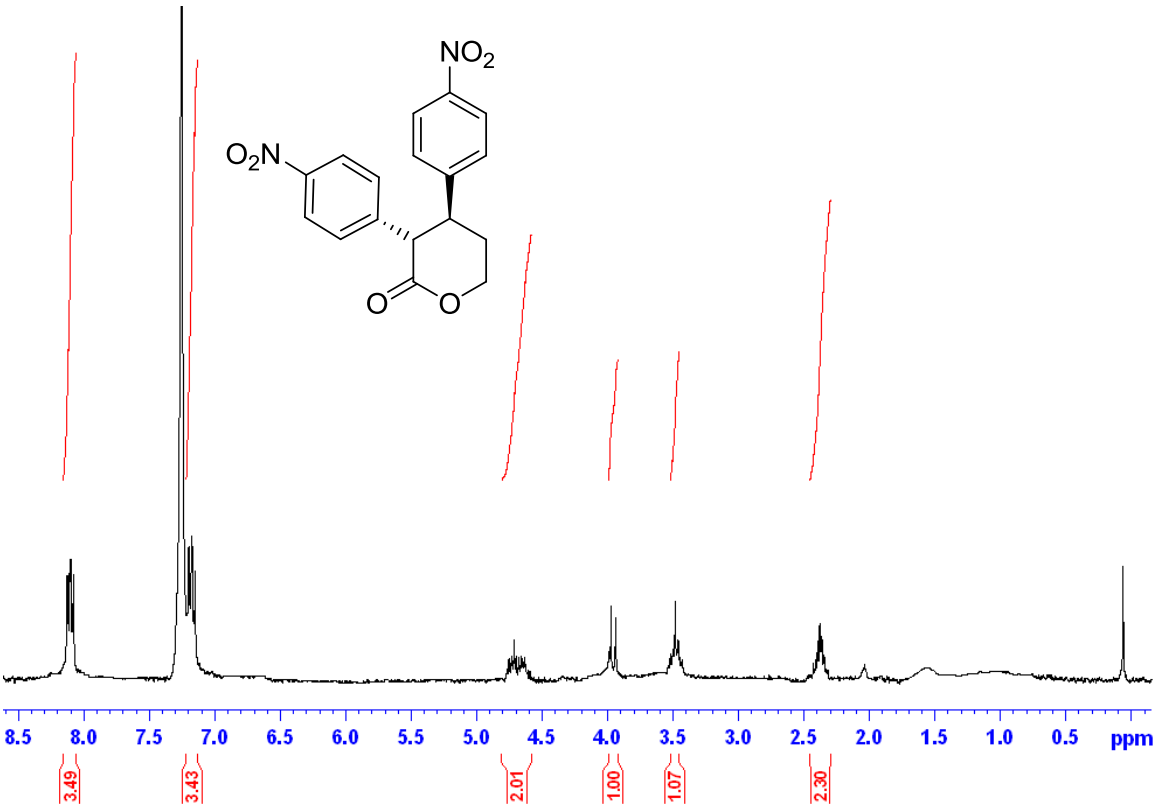
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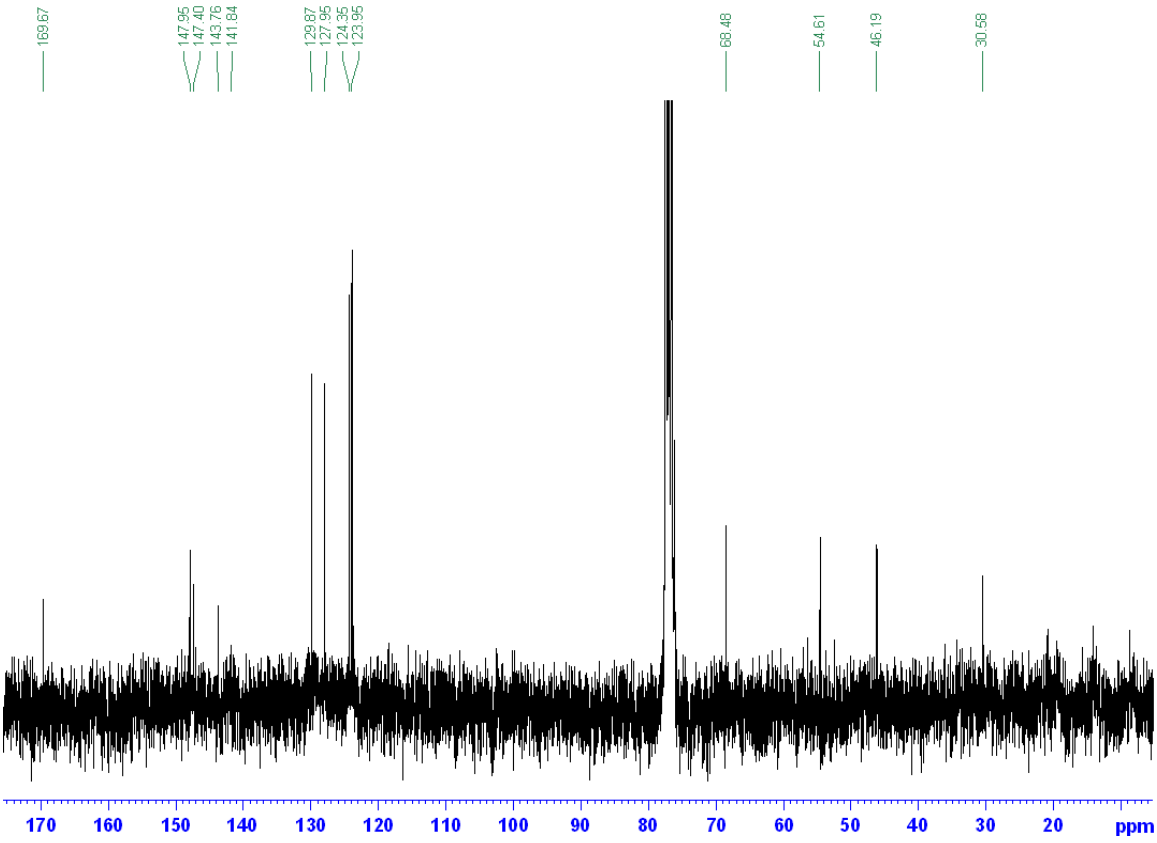
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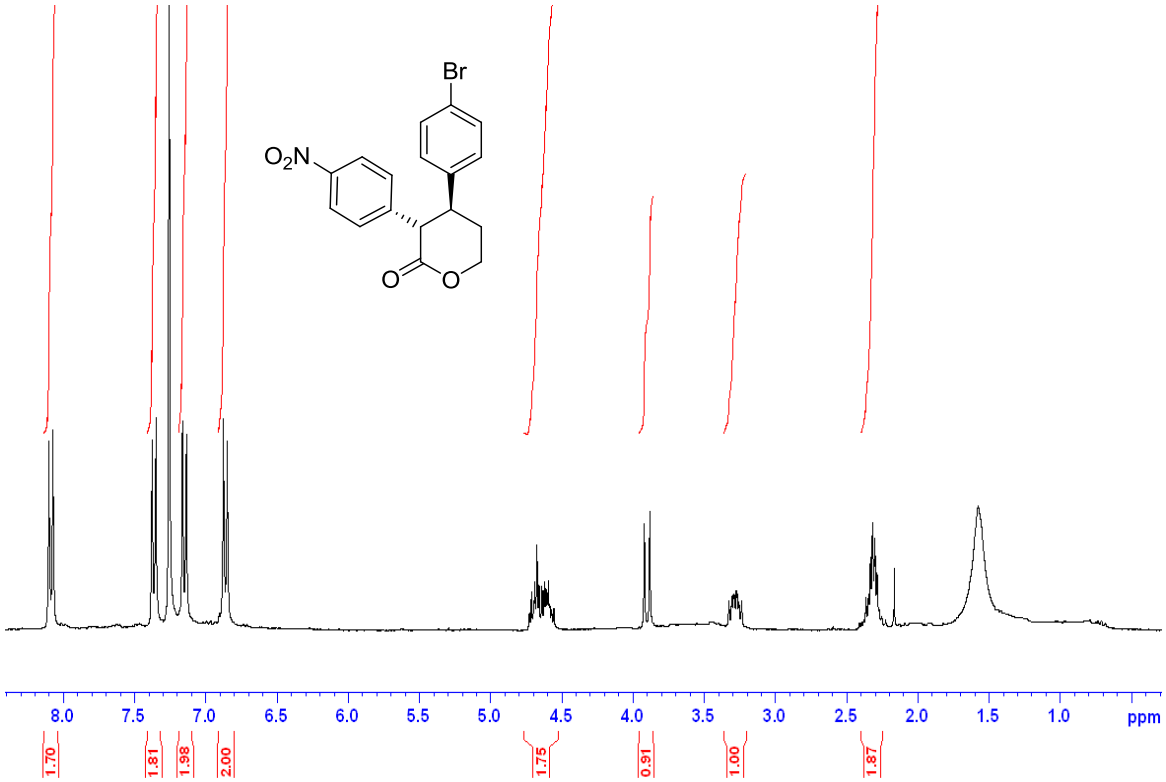
30
20
ppm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4.5
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3.0
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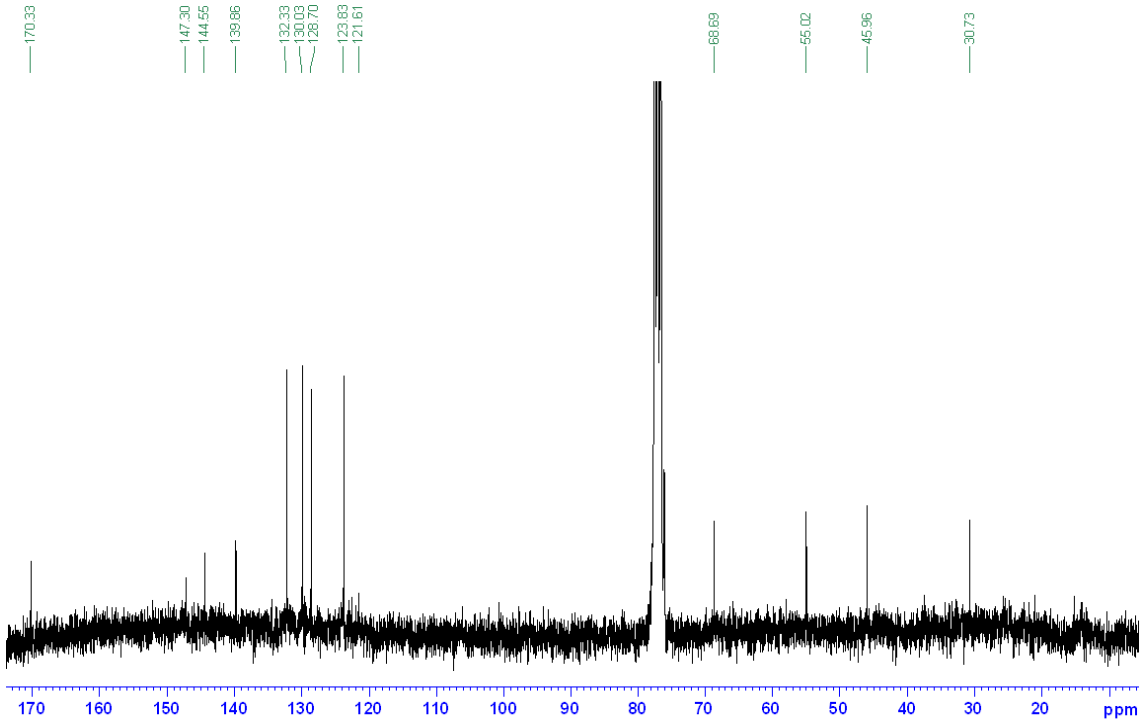
1.87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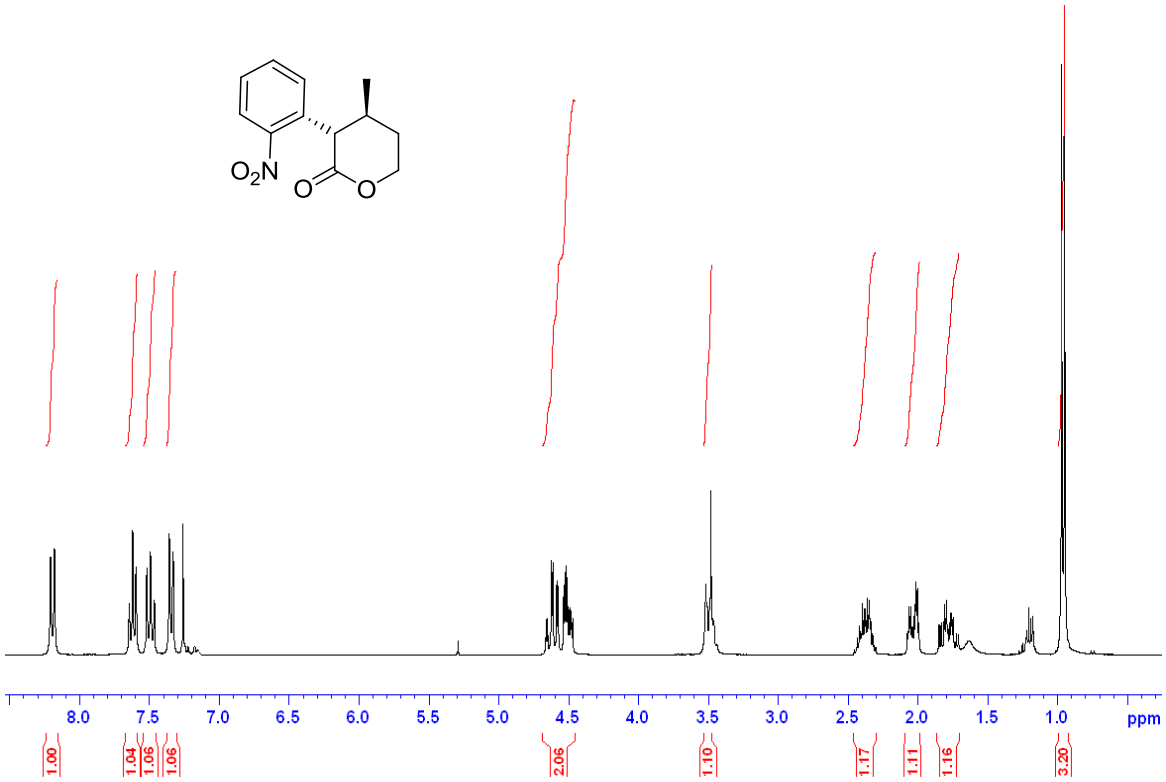
ppm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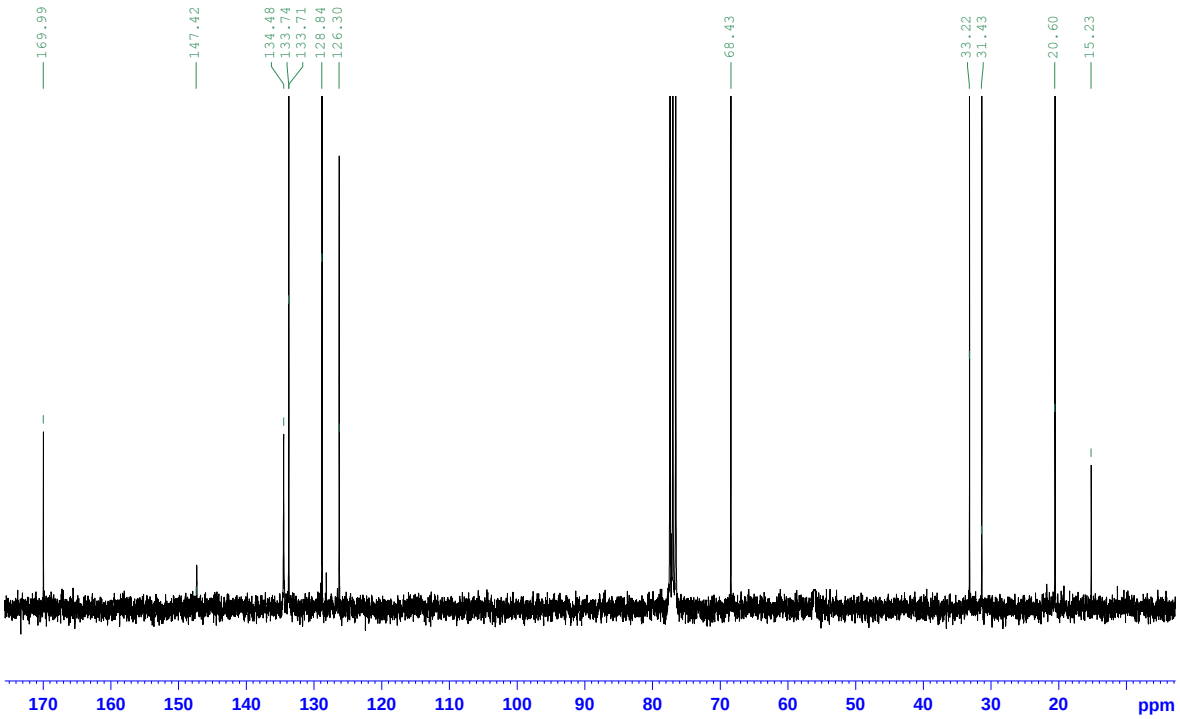
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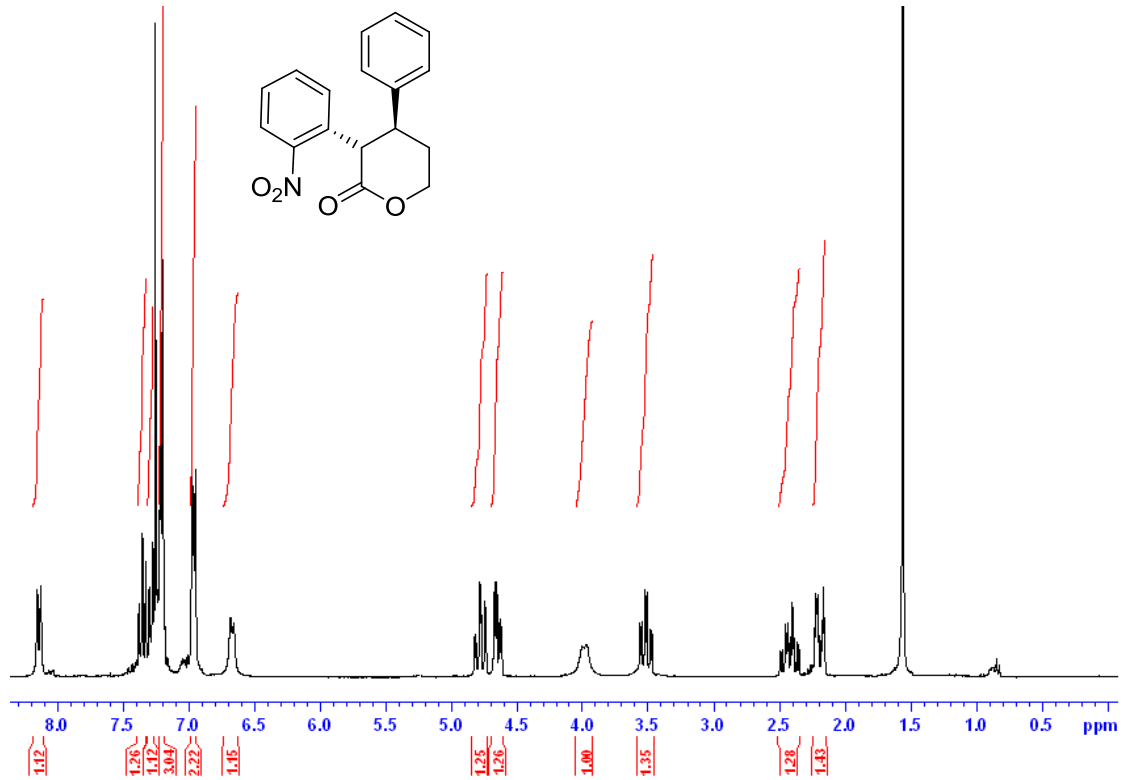
50
40
30
20
ppm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3.5
3.0
2.5
2.0
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1.0
0.5
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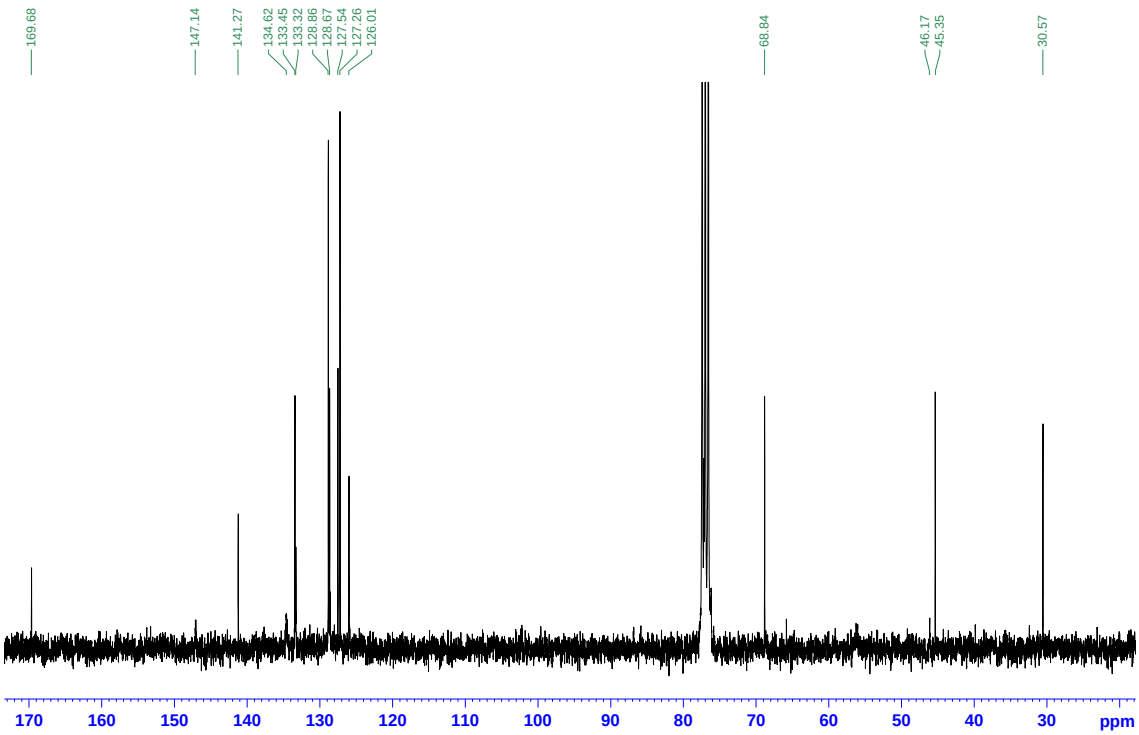
1.28
1.43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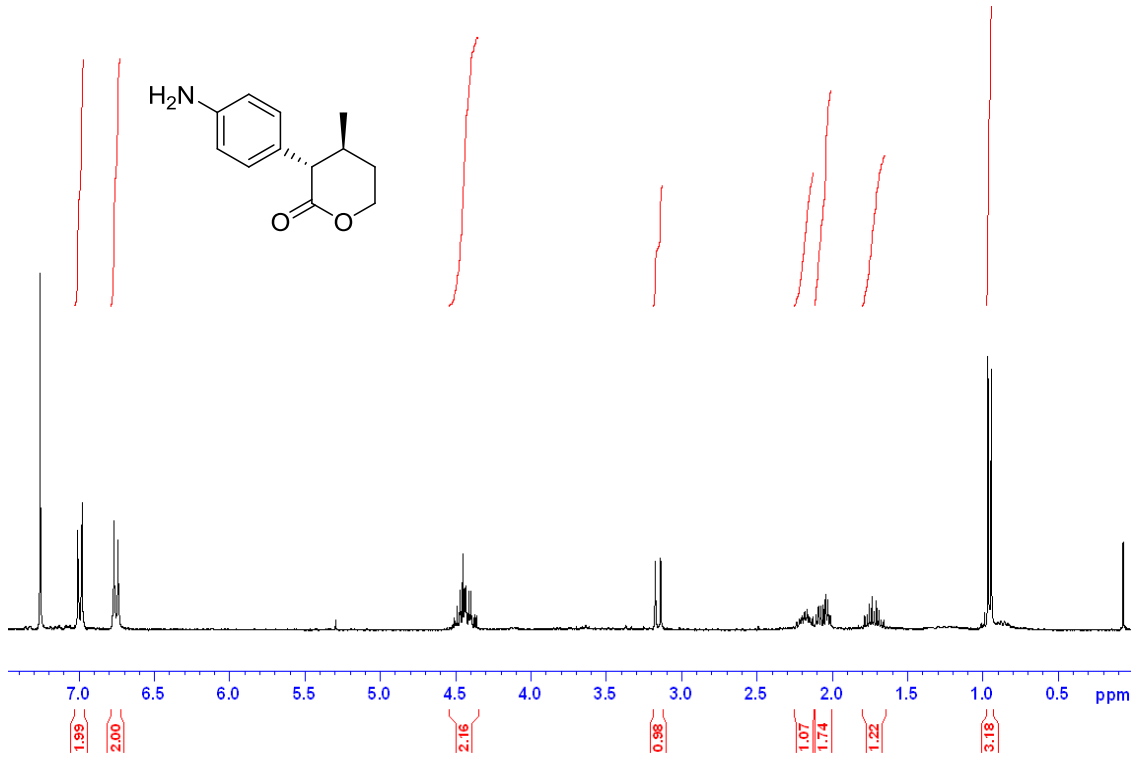
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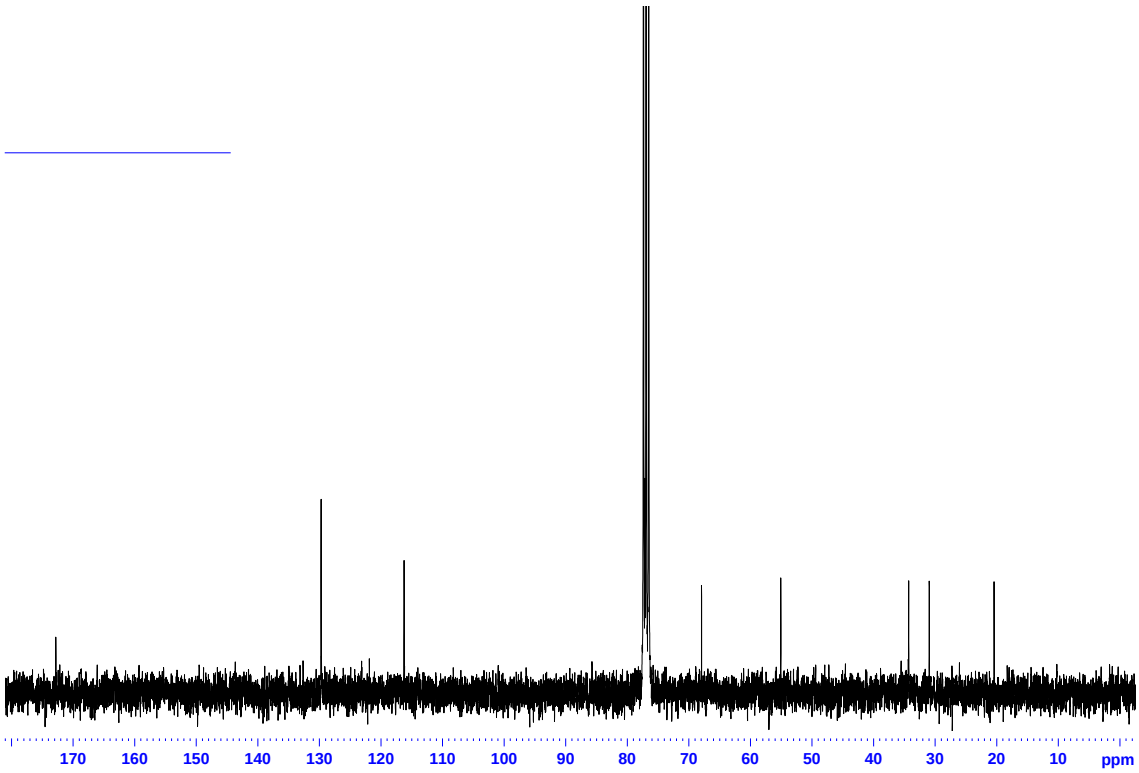
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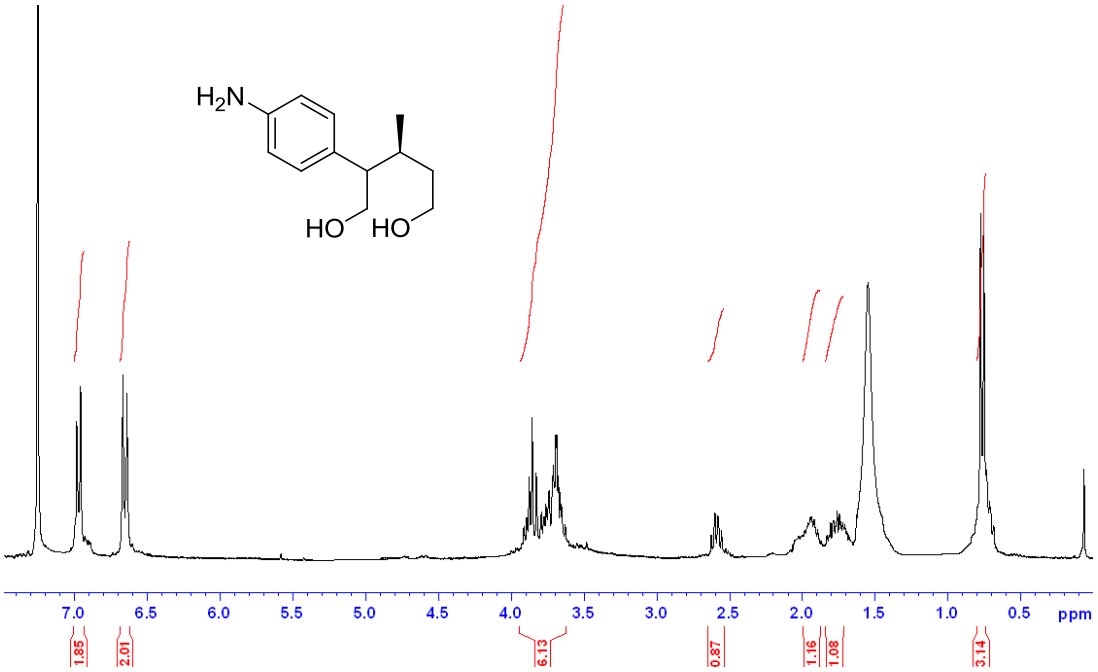
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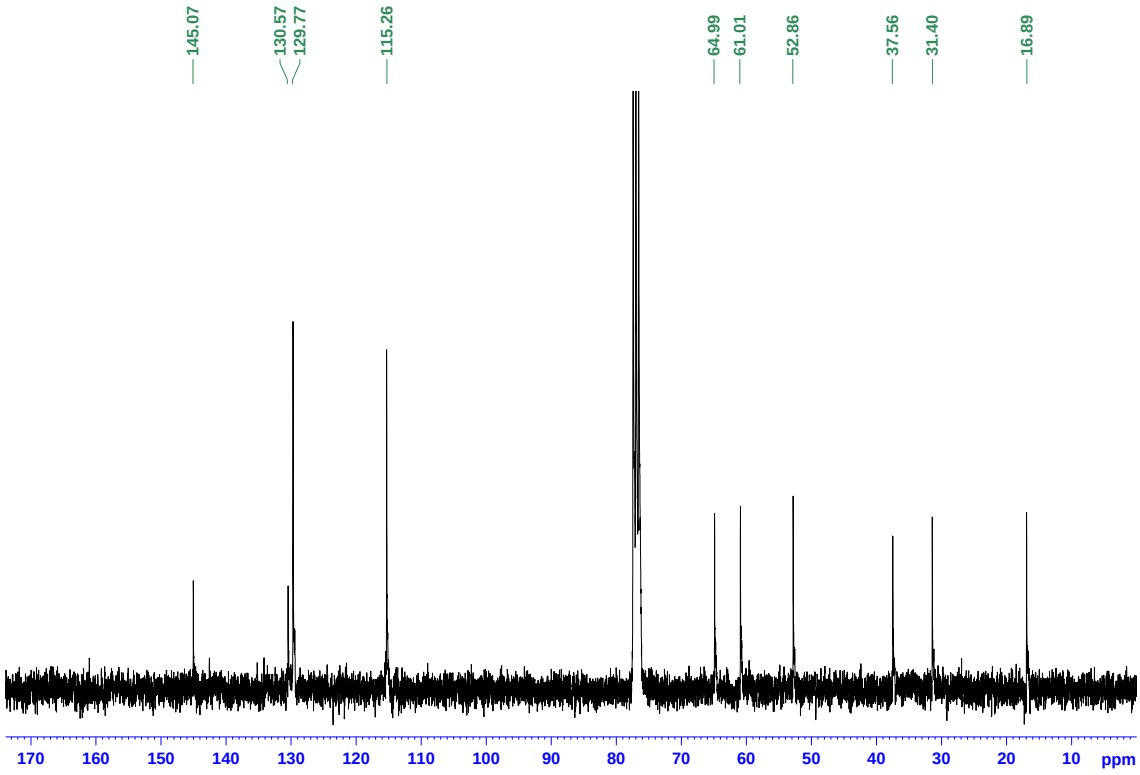
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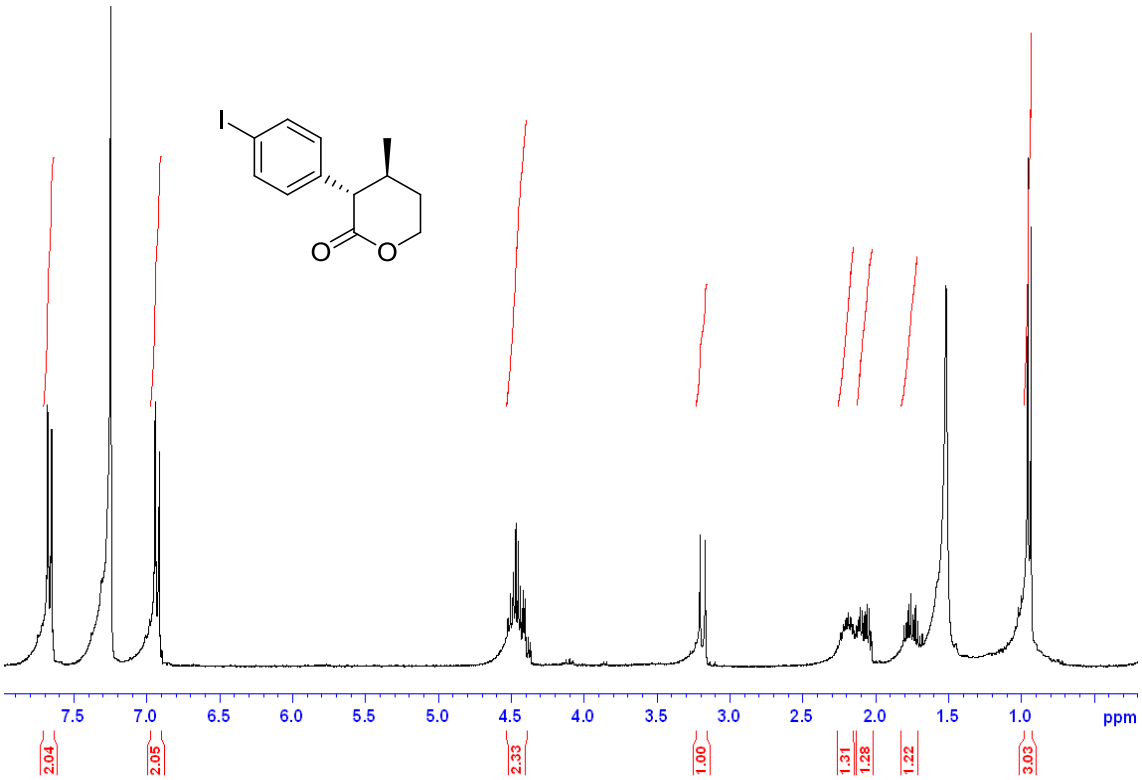
ppm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O
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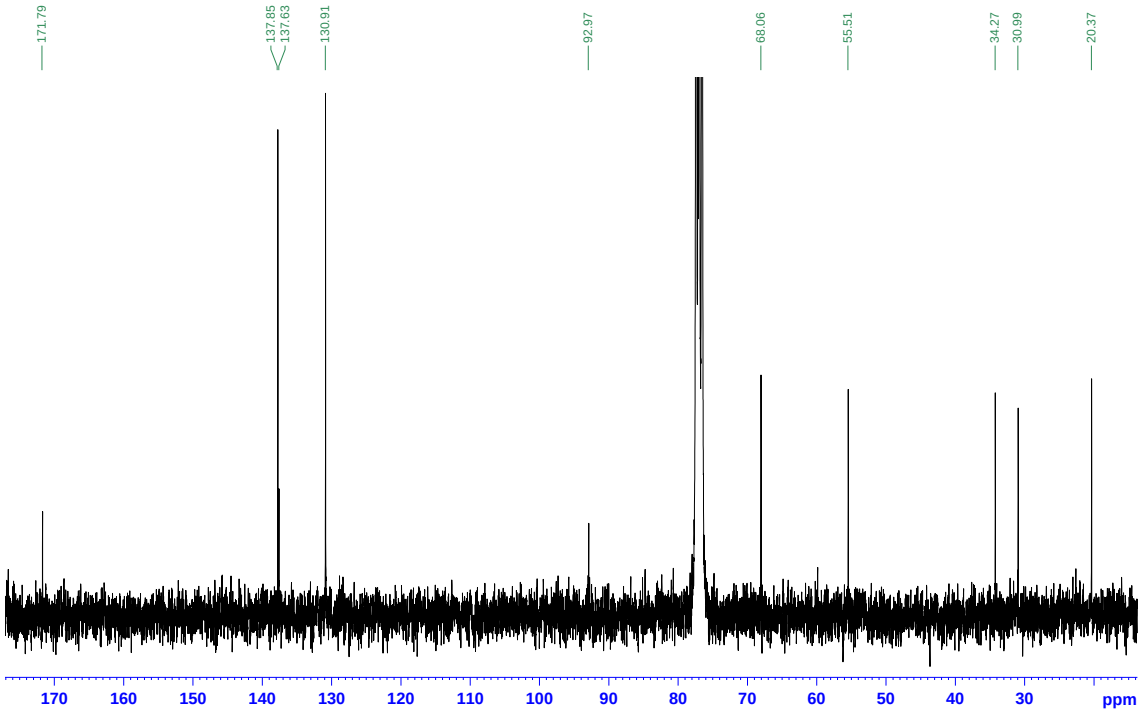
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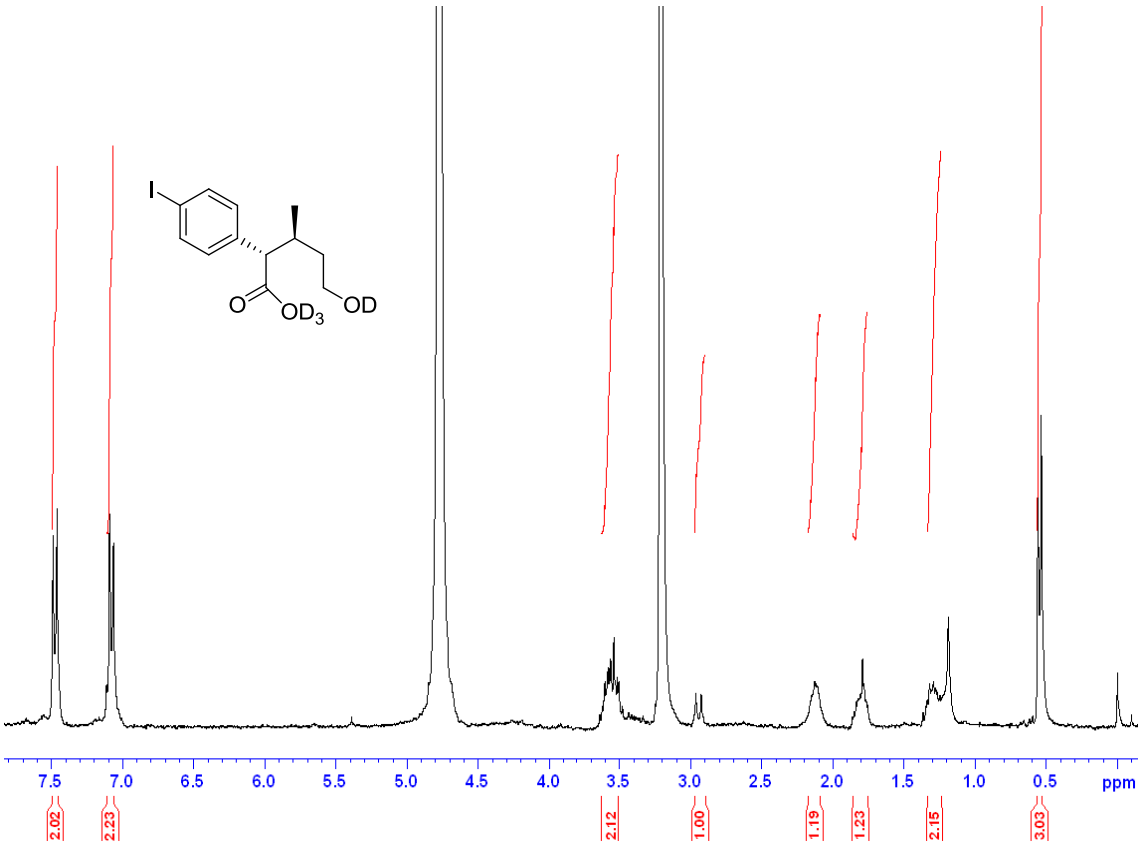
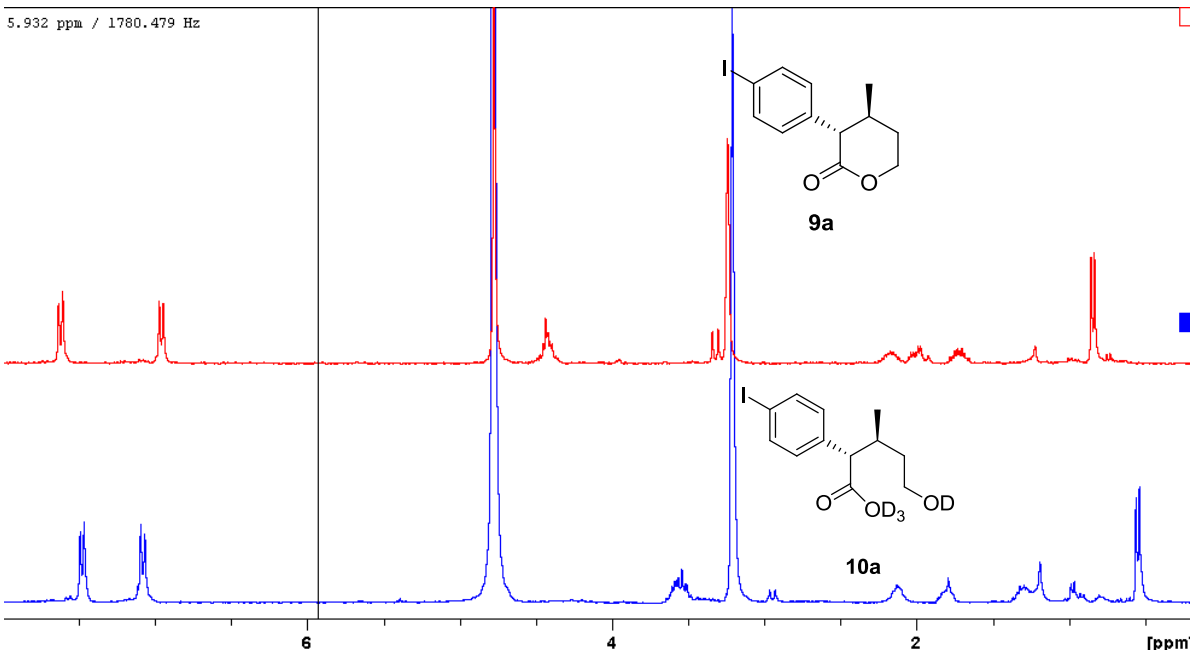
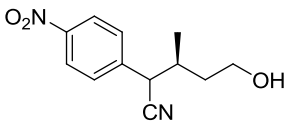
ppm



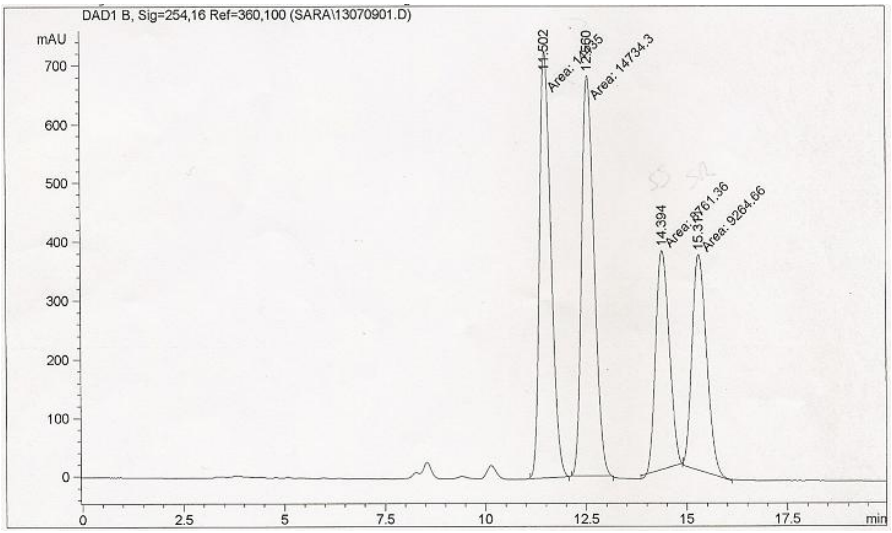
^{1}H-NMR of **9a** and **10a** in d_4-MeOH .



HPLC of compounds (racemic and non-racemic)

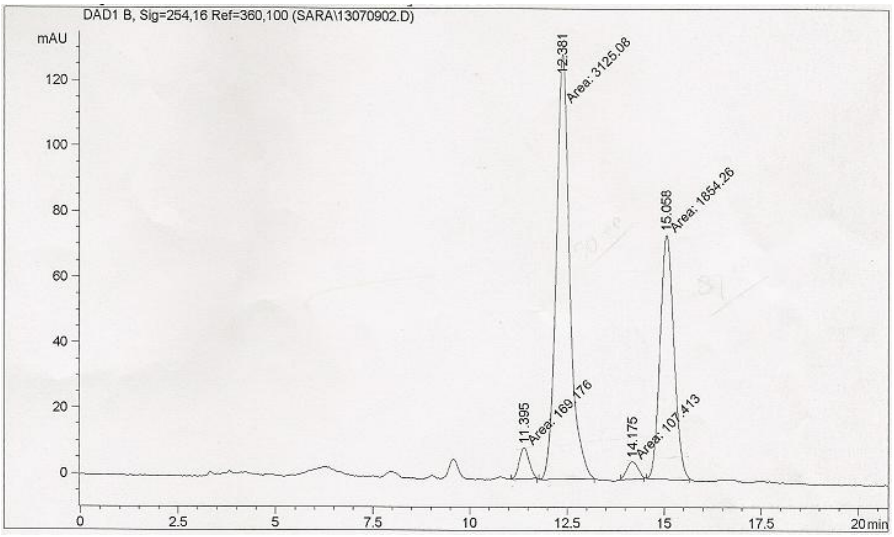


rac - 3a and 3'a

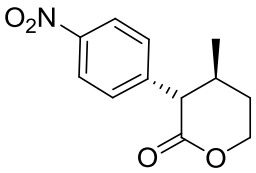


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.502	MM	0.3311	1.44350e4	726.62903	30.5857
2	12.560	MM	0.3603	1.47343e4	681.60809	31.2198
3	14.394	MM	0.3921	8761.35742	372.40762	18.5640
4	15.311	MM	0.4200	9264.65918	367.68707	19.6304

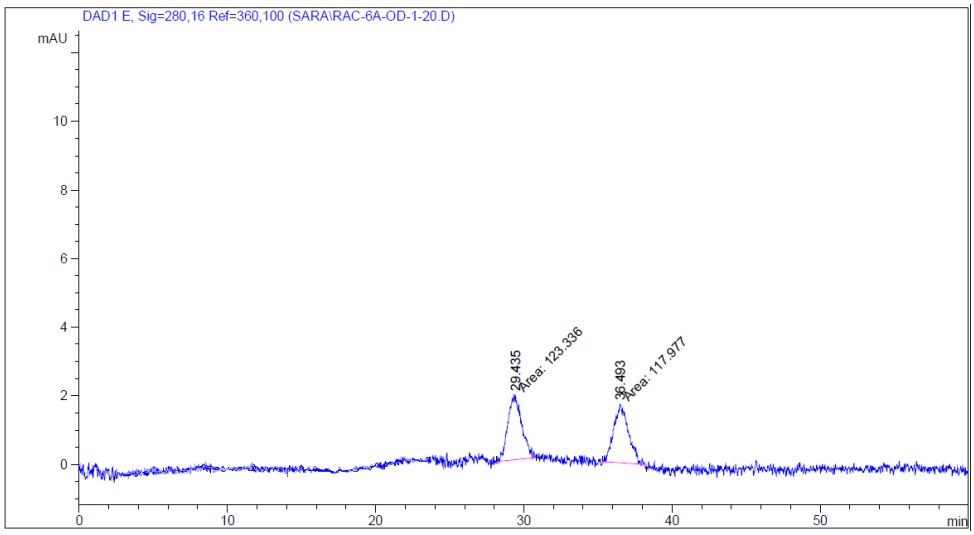
3a and 3'a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.395	MM	0.2981	169.17580	9.45984	3.2188
2	12.381	MM	0.4014	3125.08423	129.76886	59.4582
3	14.175	MM	0.3346	107.41296	5.34986	2.0437
4	15.058	MM	0.4148	1854.25903	74.50969	35.2794

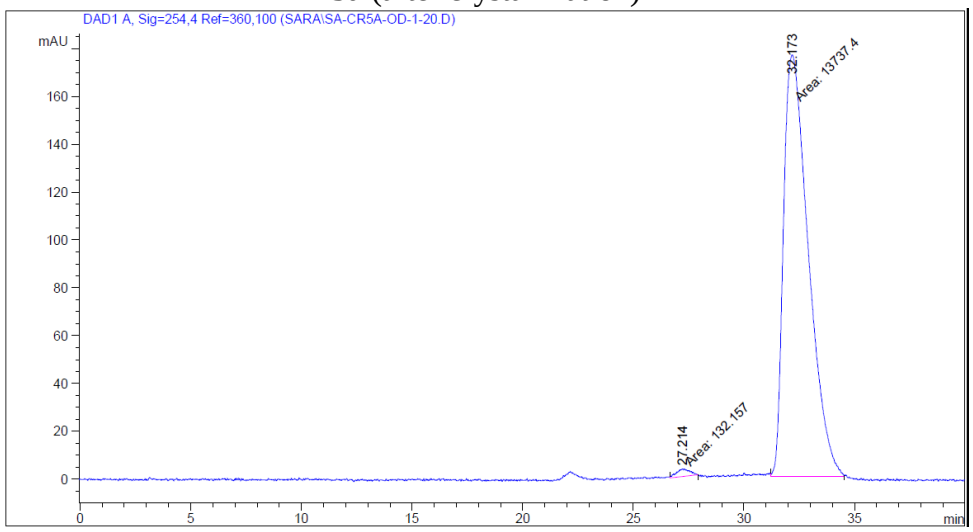


***rac*-5a**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.435	MM	1.0773	123.33630	1.90808	51.1105
2	36.493	MM	1.1451	117.97697	1.71717	48.8895

5a (after crystallization)



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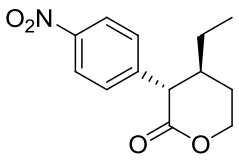
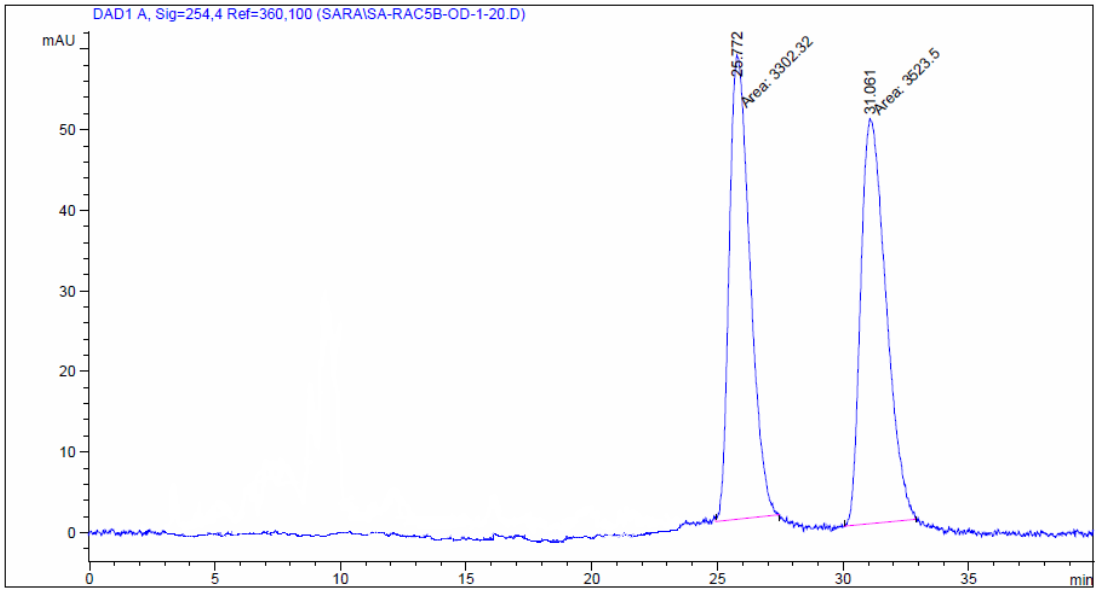
1	27.214	MM	0.6930	132.15701	3.17855	0.9529
2	32.173	MM	1.2992	1.37374e4	176.22203	99.0471

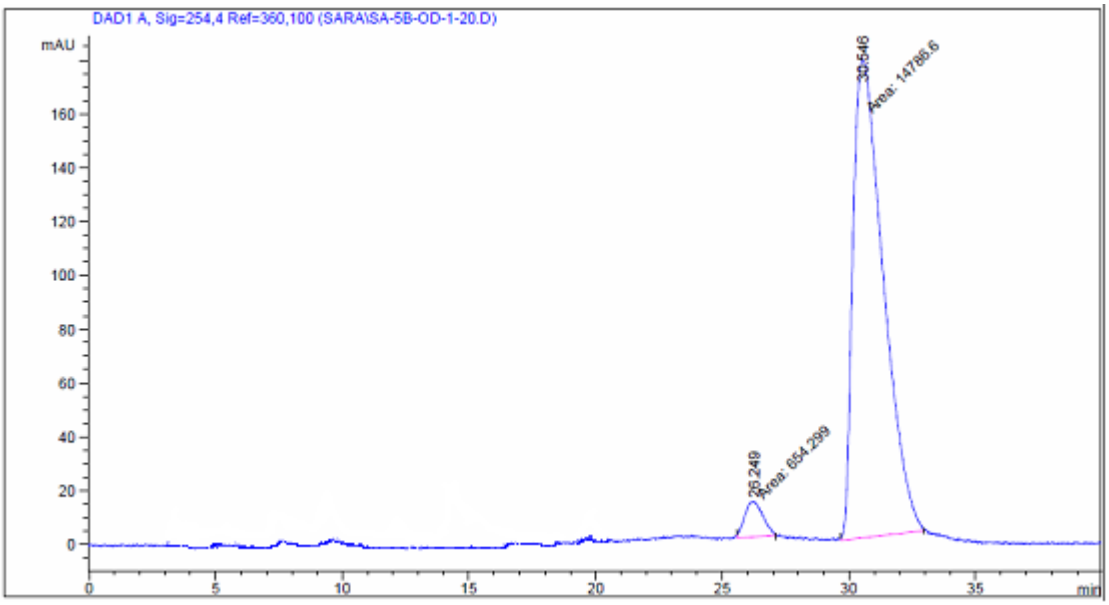


***rac*-5b**

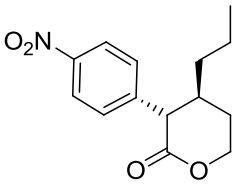


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.772	MM	0.9559	3302.32153	57.57564	48.3798
2	31.061	MM	1.1671	3523.50269	50.31555	51.6202

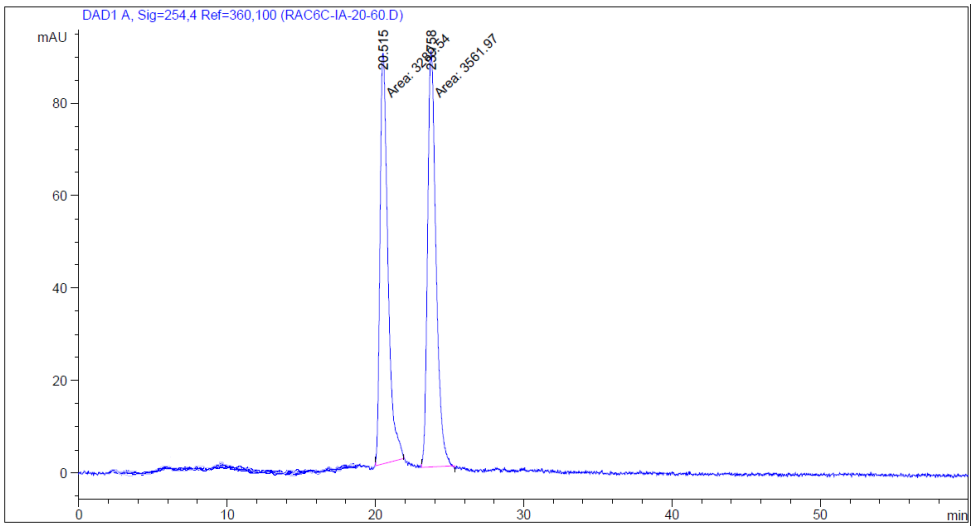
5b



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.249	MM	0.8369	654.29877	13.03057	4.2374
2	30.546	MM	1.3883	1.47866e4	177.50902	95.7626

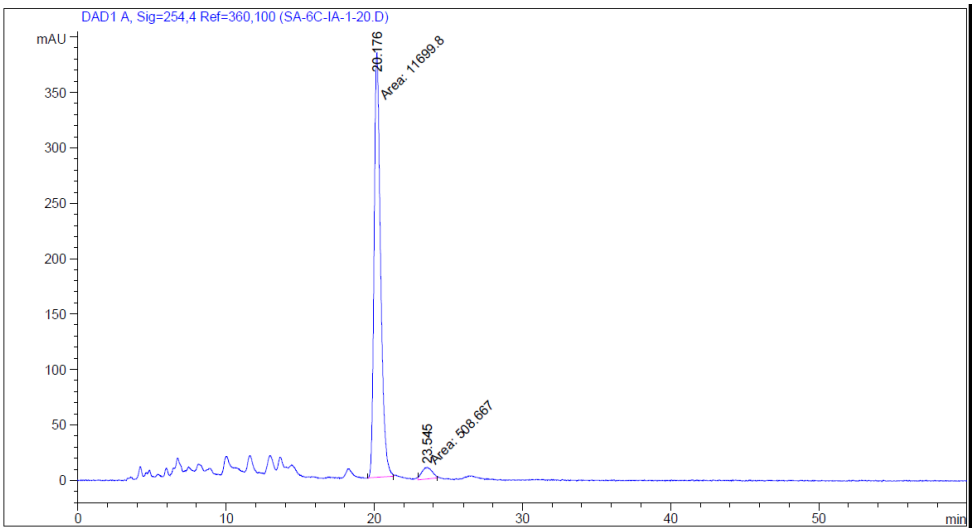


rac-5c

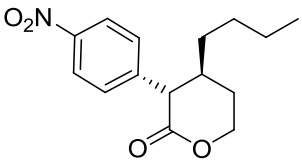


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.515	MM	0.6166	3289.53711	88.92082	48.0118
2	23.758	MM	0.6596	3561.97485	89.99939	51.9882

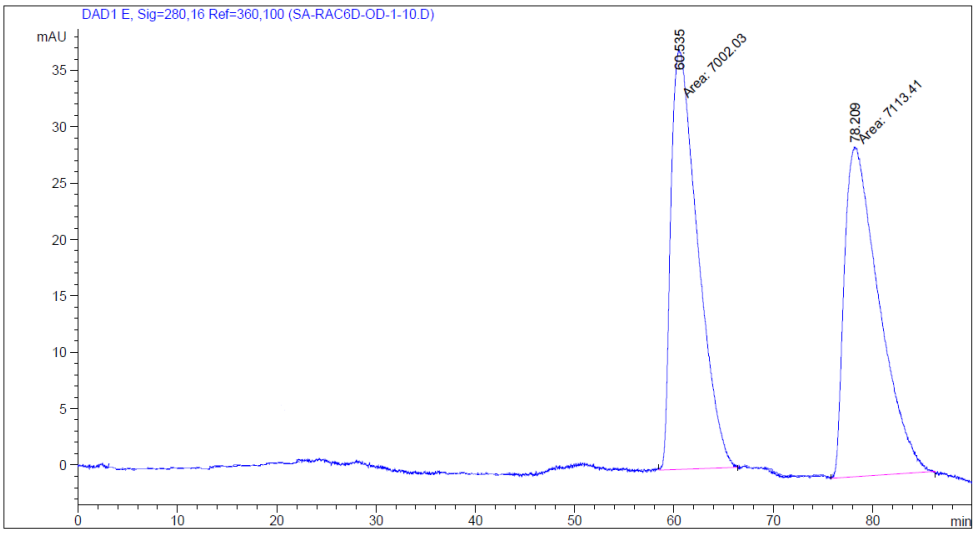
5c



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.176	MM	0.5090	1.16998e4	383.06992	95.8335
2	23.545	MM	0.8152	508.66653	10.39938	4.1665

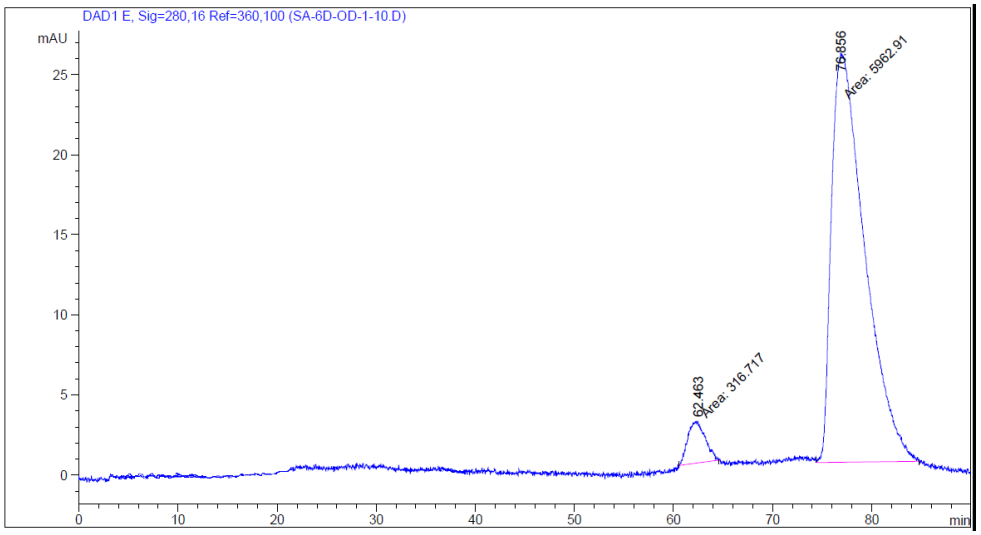


rac-5d

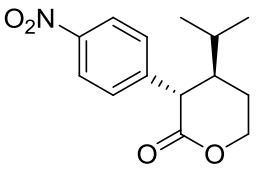


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	60.535	MM	3.1422	7002.03271	37.13992	49.6055
2	78.209	MM	4.0509	7113.40527	29.26648	50.3945

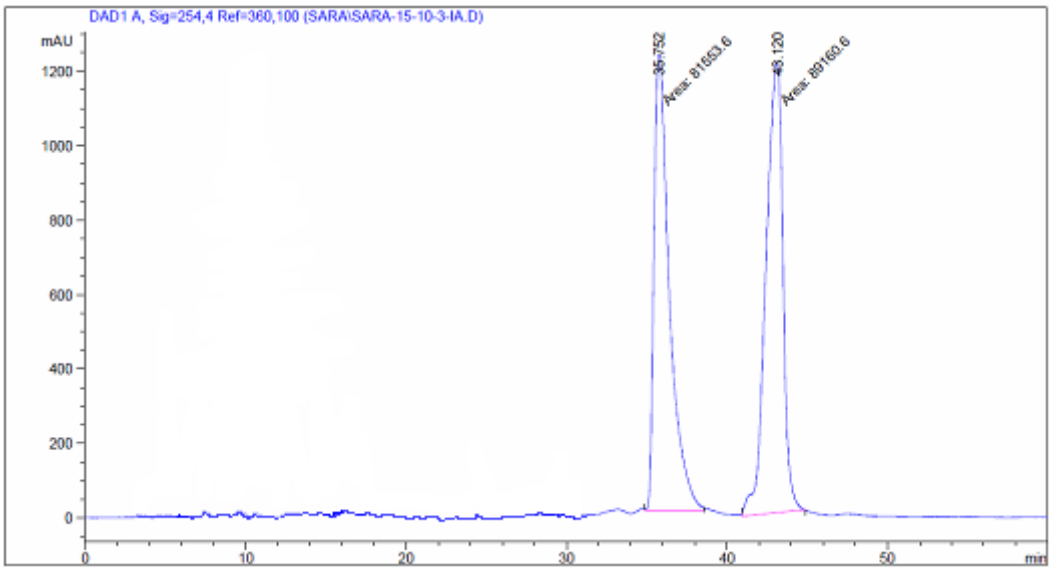
5d



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	62.463	MM	2.0116	316.71747	2.62412	5.0436
2	76.856	MM	3.8832	5962.91064	25.59270	94.9564

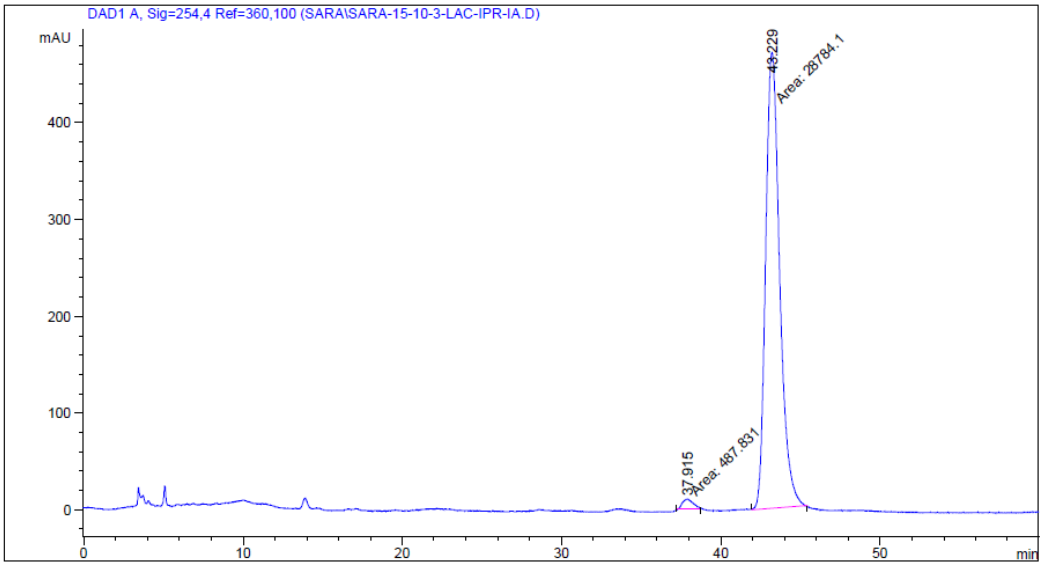


rac-5e

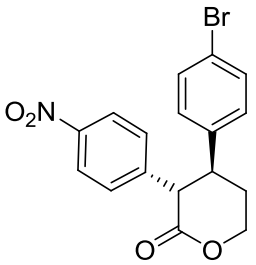


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.752	MM	1.1134	8.15536e4	1220.82397	47.7720
2	43.120	MM	1.2290	8.91606e4	1209.13794	52.2280

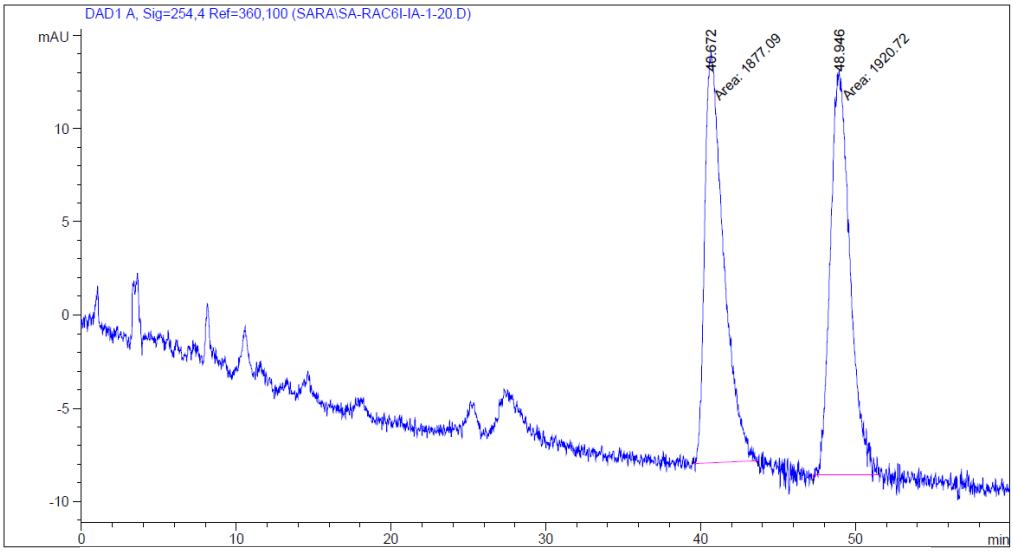
5e



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.915	MM	0.7767	487.83090	10.46805	1.6665
2	43.229	MM	1.0185	2.87841e4	471.02887	98.3335

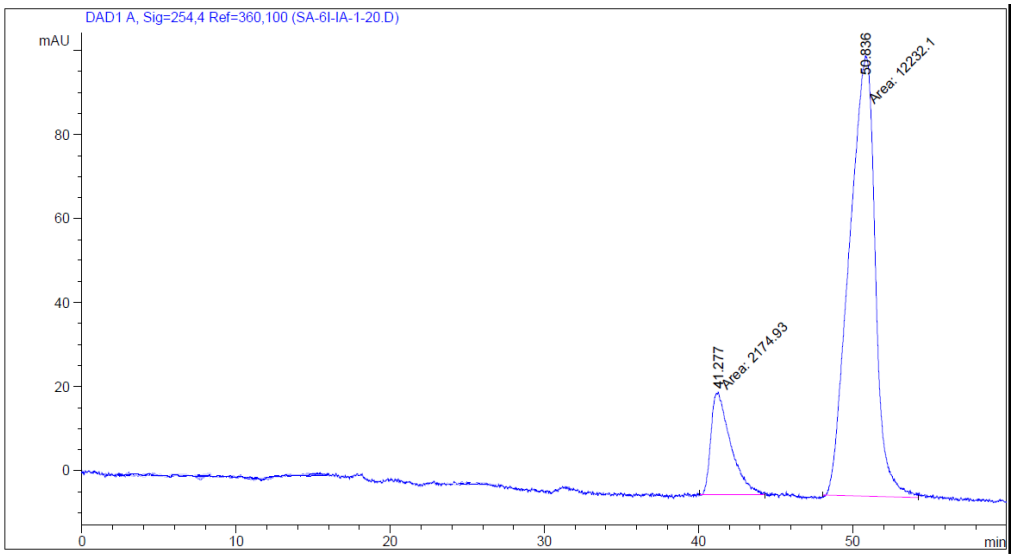


rac-5i

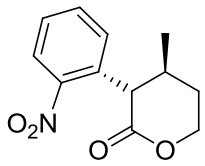


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.672	MM	1.4180	1877.09485	22.06268	49.4256
2	48.946	MM	1.4732	1920.72351	21.72904	50.5744

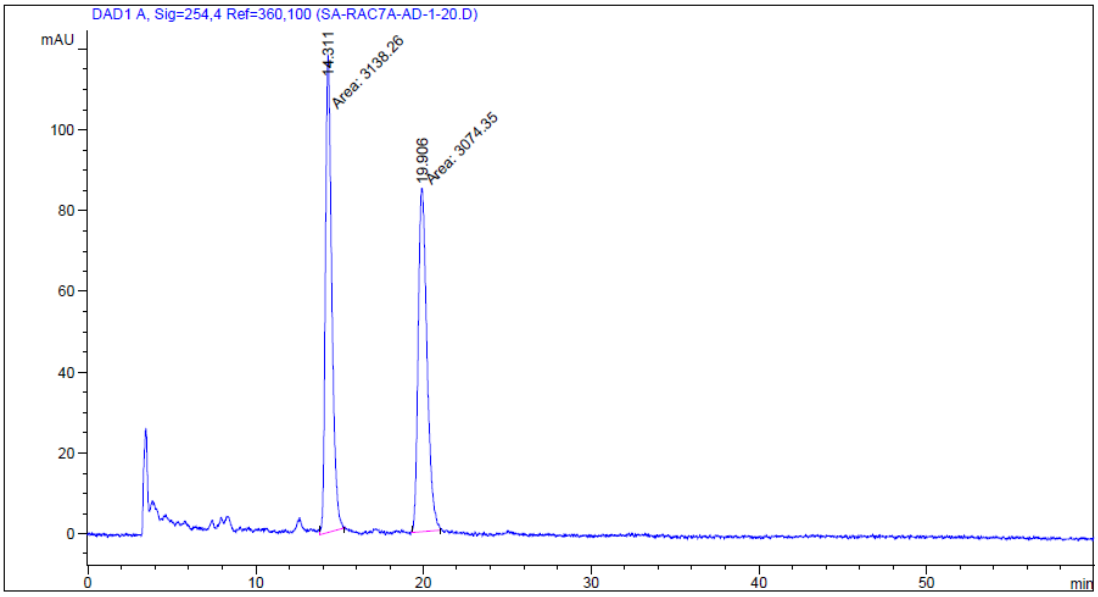
5i



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.277	MM	1.4819	2174.93433	24.46160	15.0964
2	50.836	MM	1.9416	1.22321e4	105.00189	84.9036

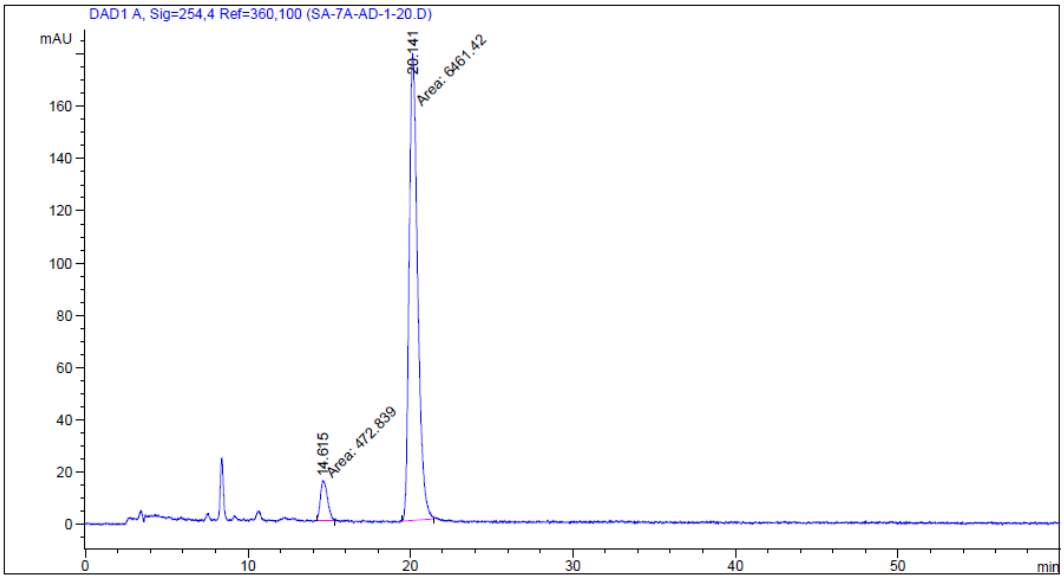


***rac*-6a**

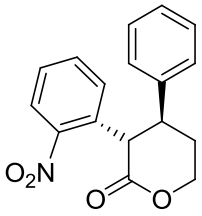


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.311	MM	0.4423	3138.26318	118.24985	50.5144
2	19.906	MM	0.6015	3074.34692	85.18885	49.4856

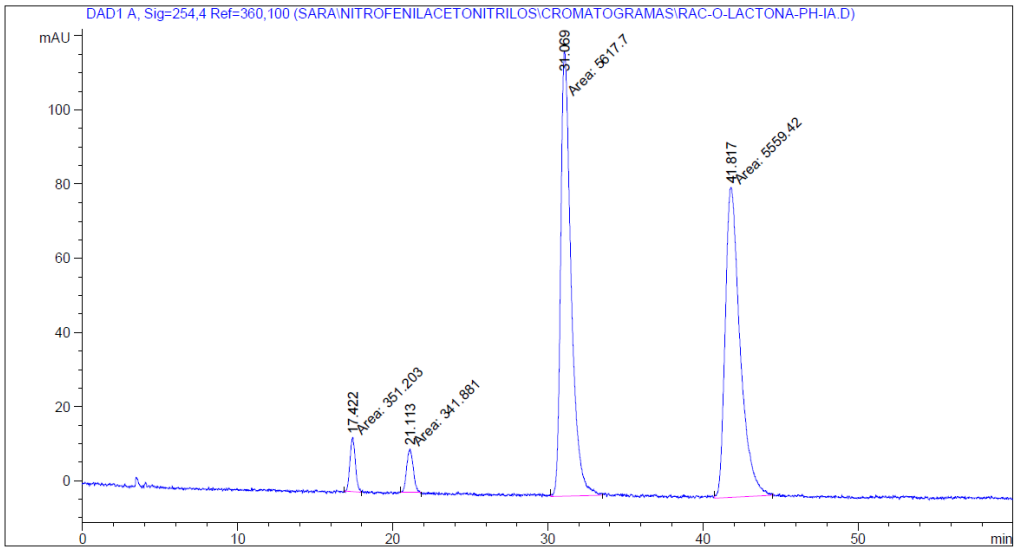
6a



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.615	MM	0.5099	472.83893	15.45513	6.8189
2	20.141	MM	0.6033	6461.41553	178.50308	93.1811

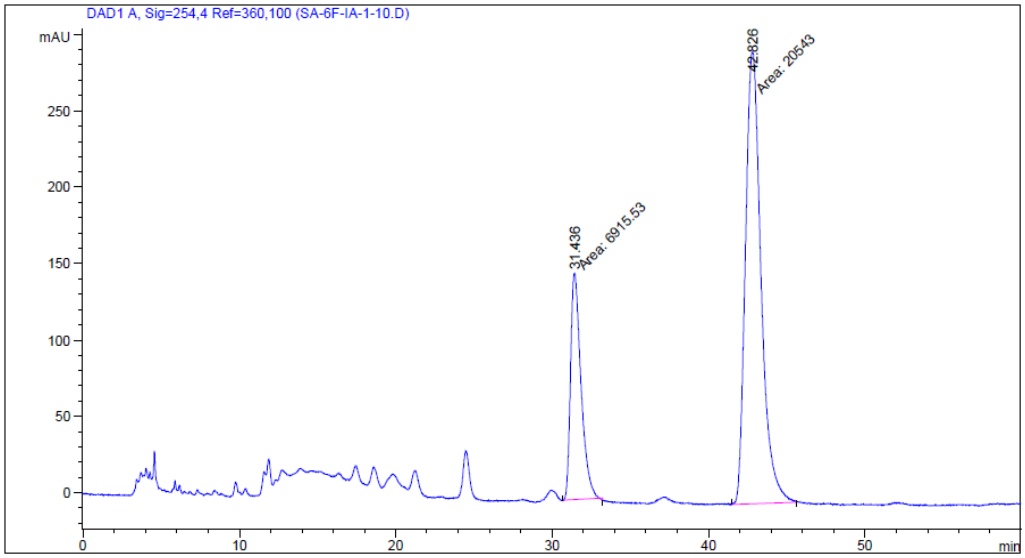


rac-6f

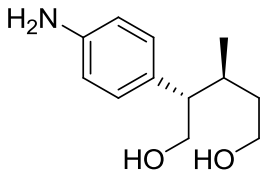


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.422	MM	0.3970	351.20303	14.74298	2.9587
2	21.113	MM	0.4859	341.88055	11.72698	2.8802
3	31.069	MM	0.7812	5617.69531	119.85349	47.3260
4	41.817	MM	1.1083	5559.42480	83.60614	46.8351

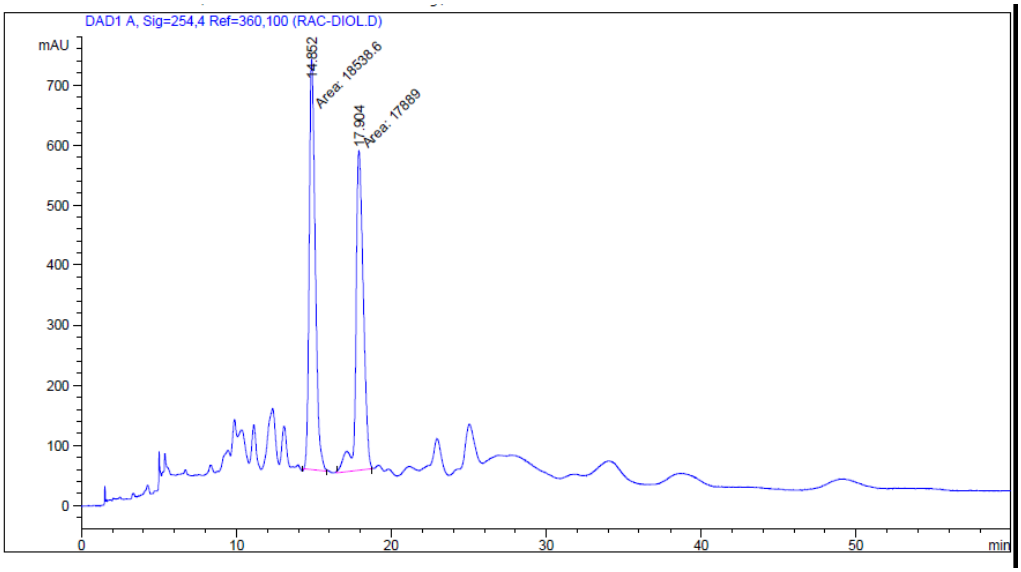
6f



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.436	MM	0.7782	6915.52637	148.10838	25.1853
2	42.826	MM	1.1566	2.05430e4	296.02289	74.8147

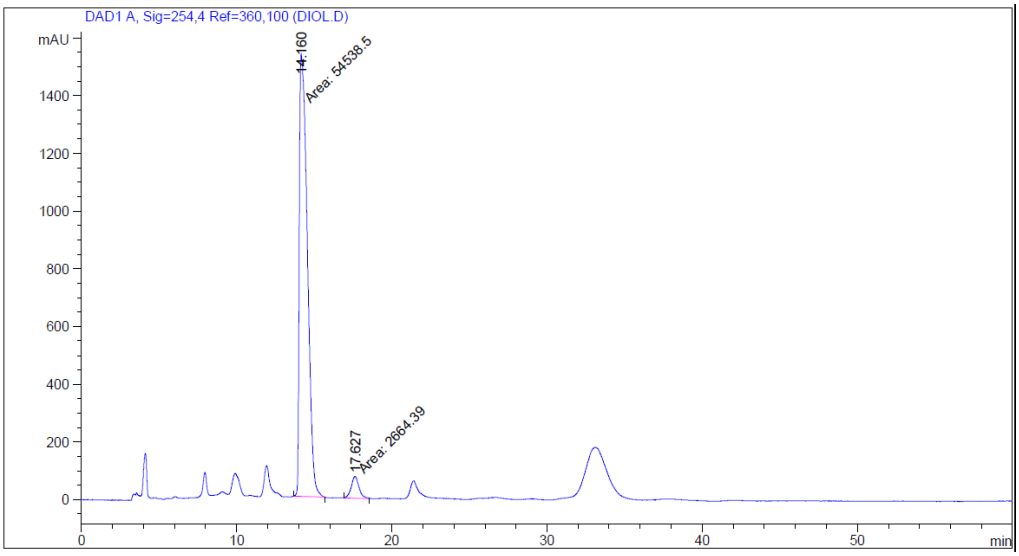


8a rac



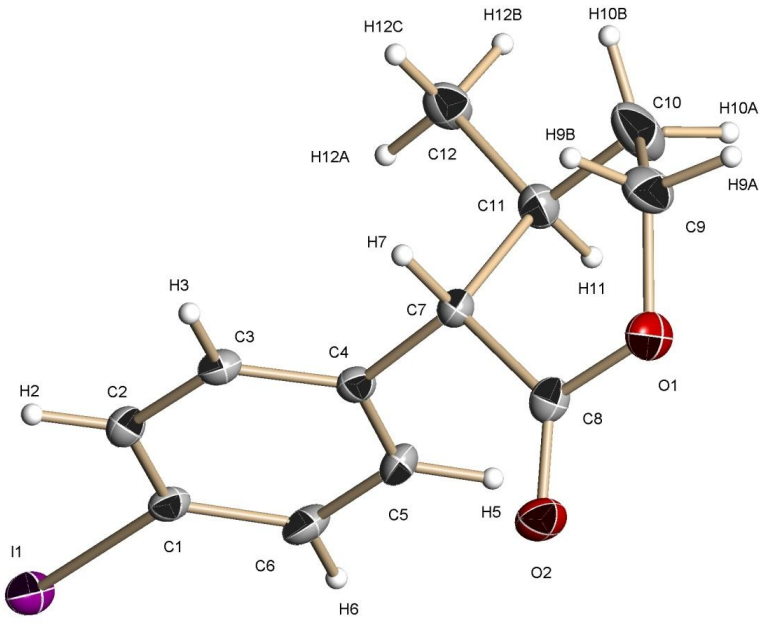
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.852	MM	0.4521	1.85386e4	683.41864	50.8917
2	17.904	MM	0.5607	1.78890e4	531.71362	49.1083

8a

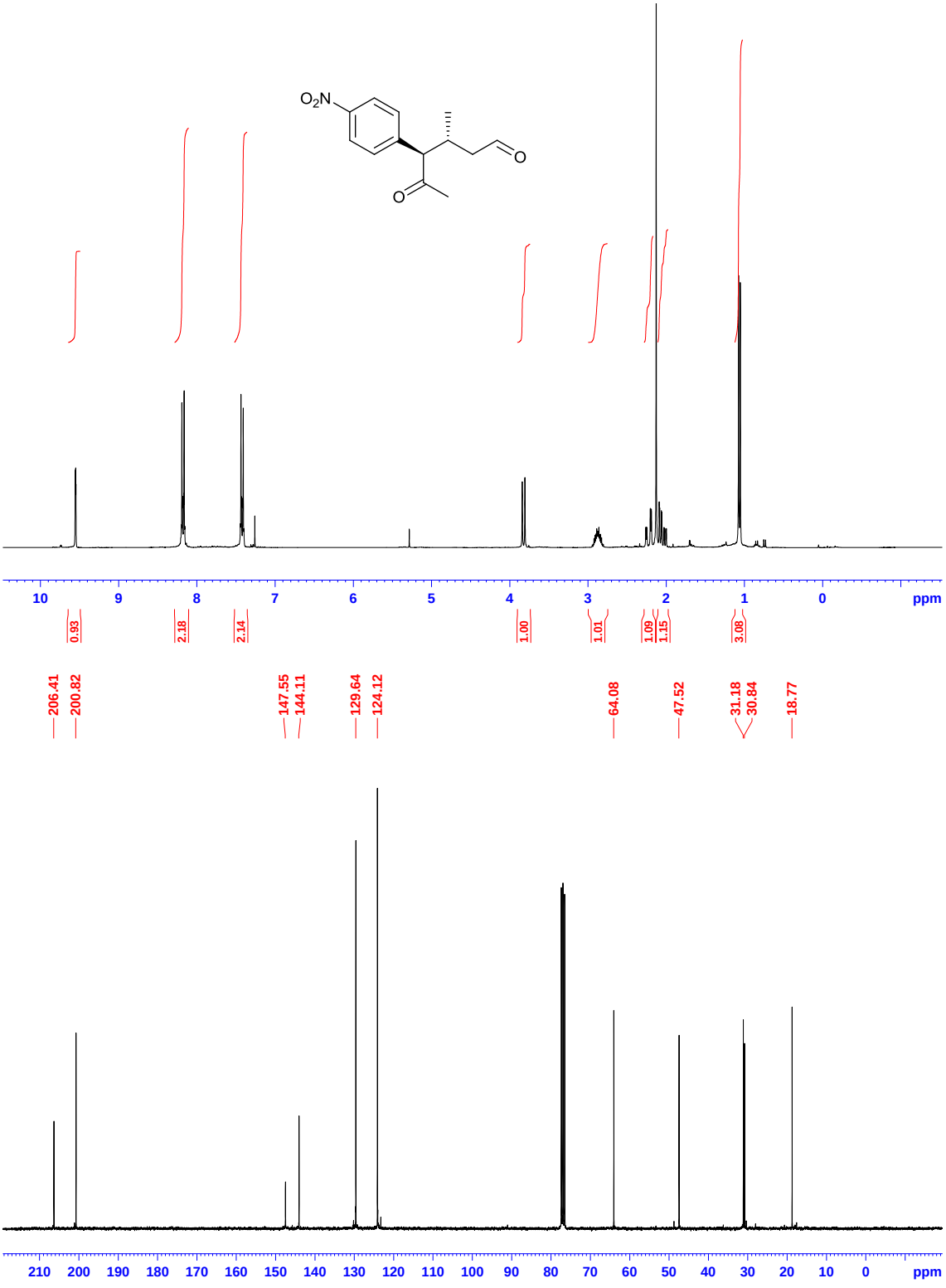


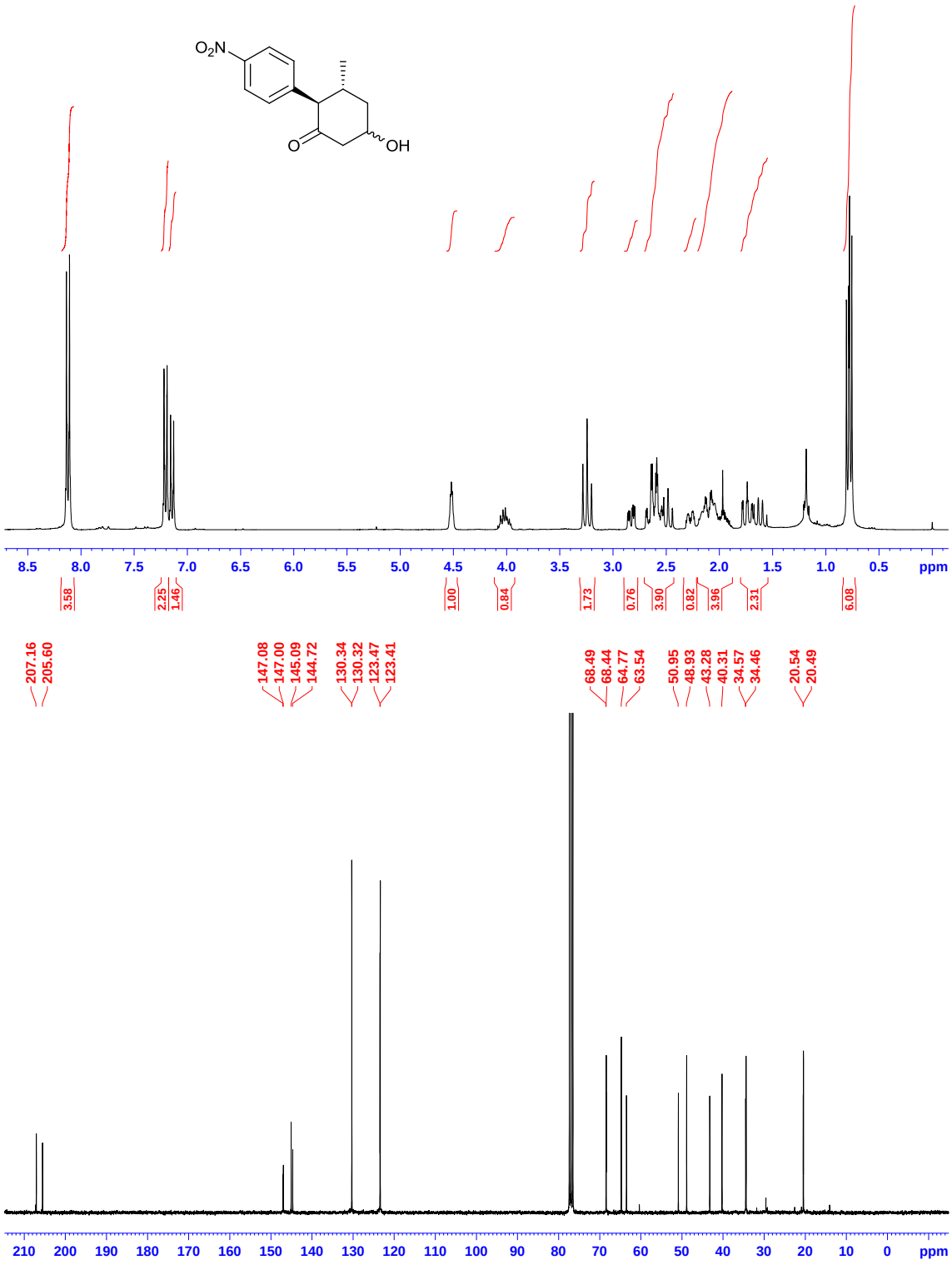
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.160	MM	0.5929	5.45385e4	1533.04272	95.3422
2	17.627	MM	0.5859	2664.39453	75.79018	4.6578

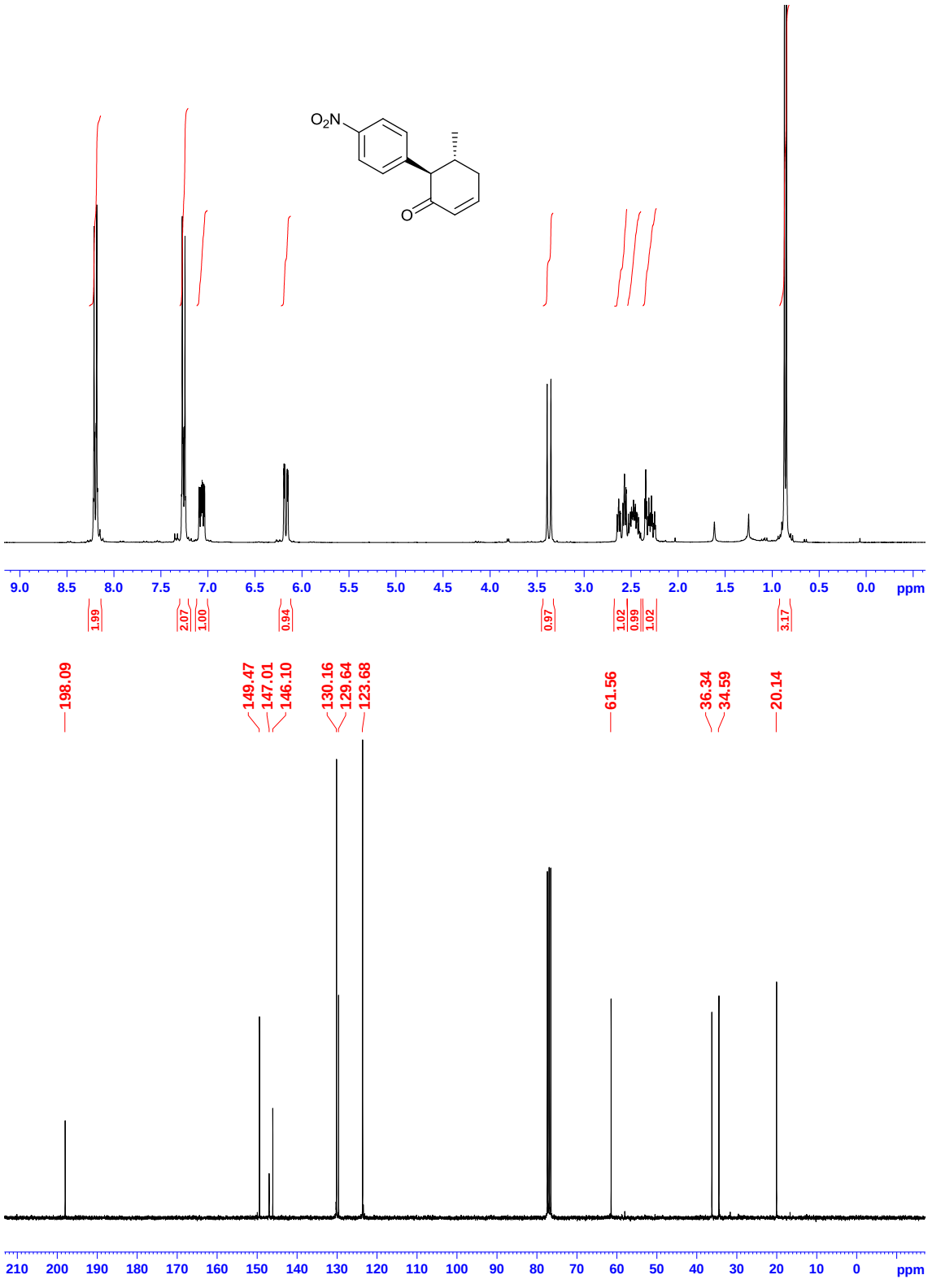
ORTEP DRAWING FOR COMPOUND (3*S*,4*S*)-9a

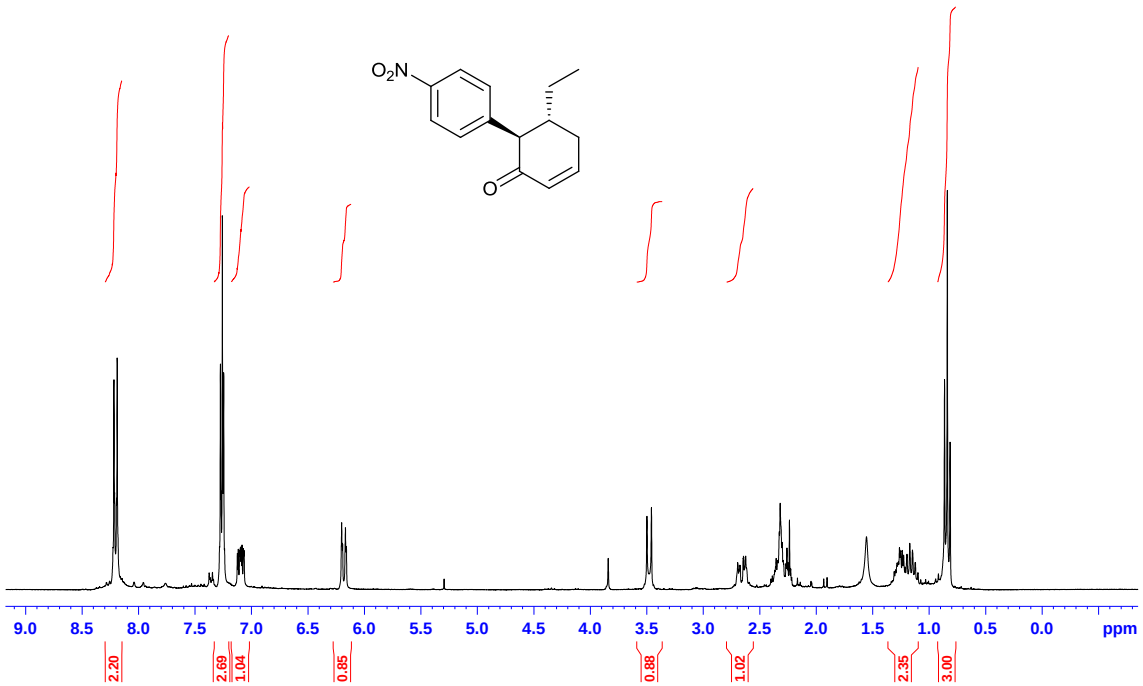


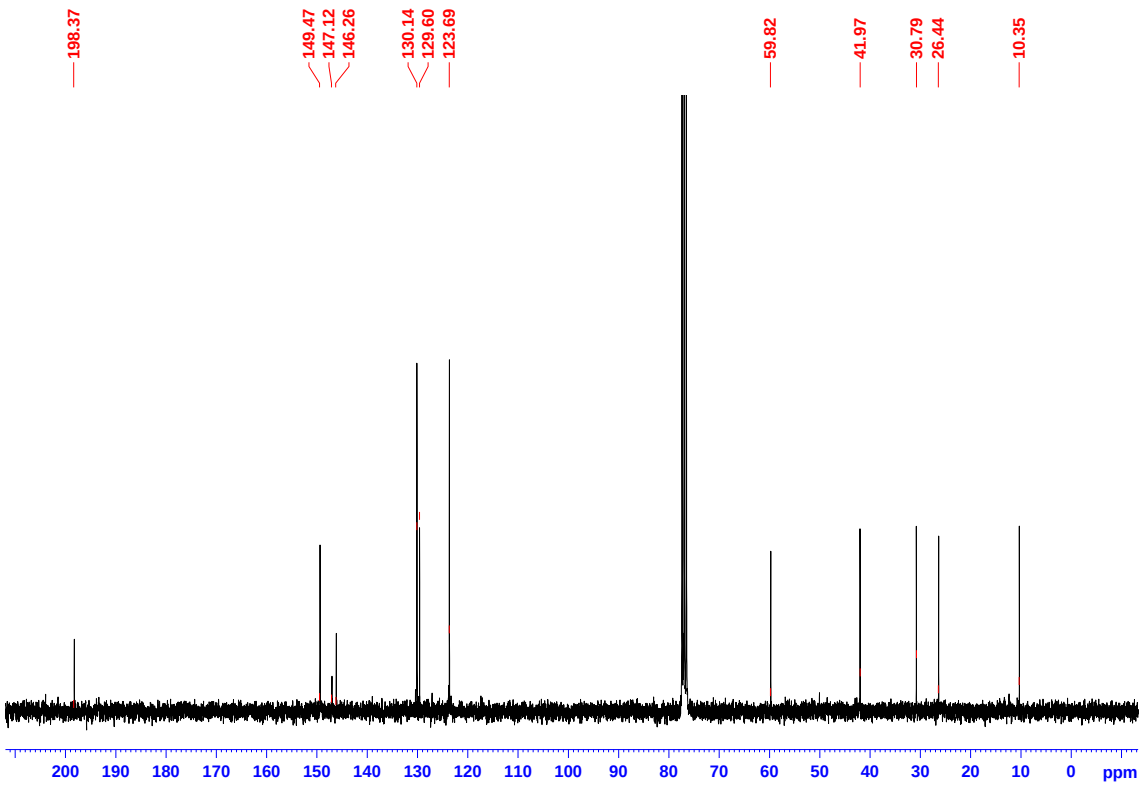
^{1}H and ^{13}C NMR spectra

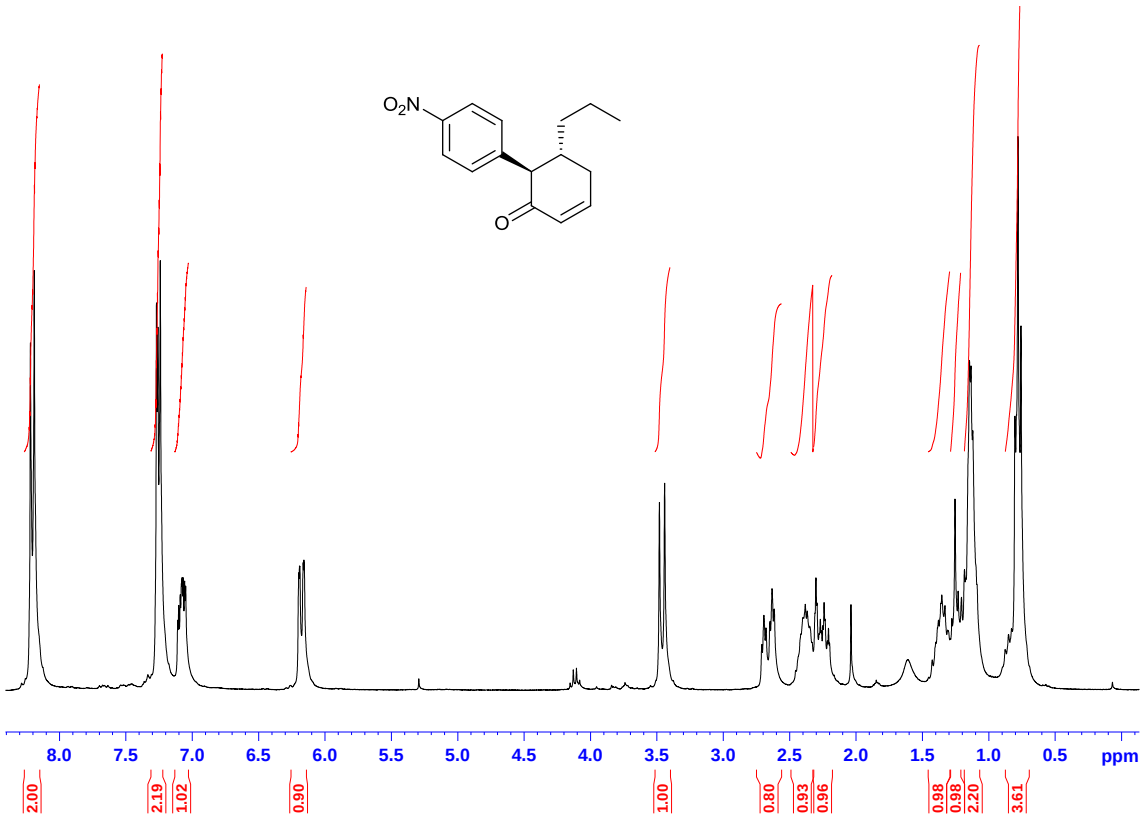


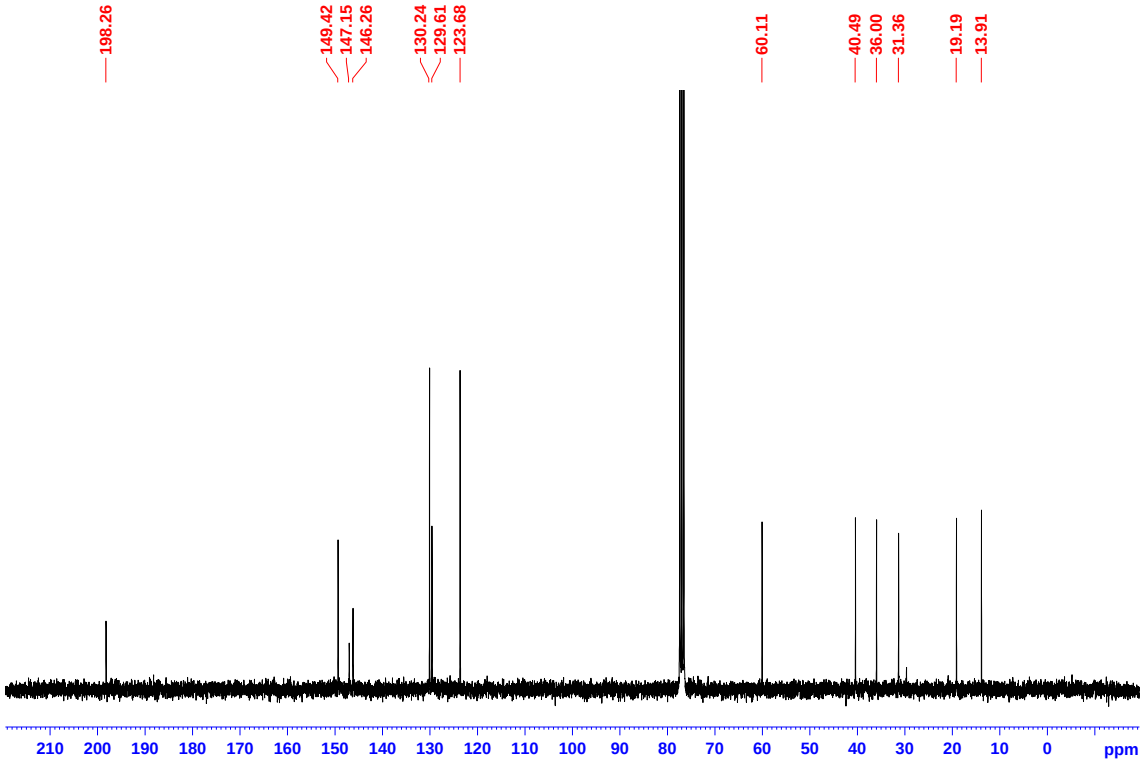

O2N
O
OH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.58 2.25 1.46 1.00 0.84 1.73 0.76 3.90 0.82 3.96 2.31 6.08
207.16 205.60 147.08 147.00 145.09 144.72 130.34 130.32 123.47 123.41 68.49 68.44 64.77 63.54 50.95 48.93 43.28 40.31 34.57 34.46 20.54 20.49
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

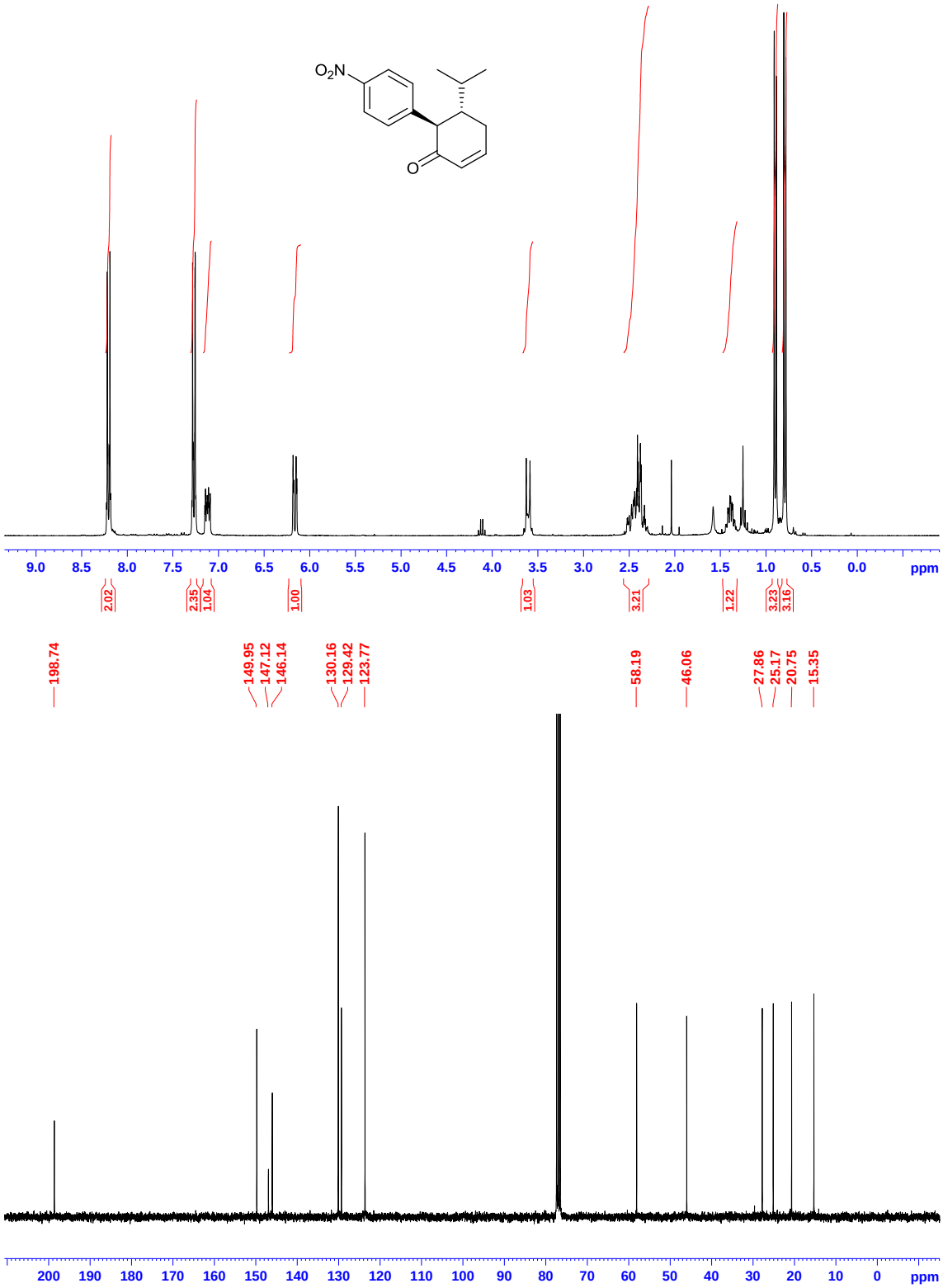

O2N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.99
2.07
1.00
0.94
0.97
1.02
0.99
1.02
3.17
198.09
149.47
147.01
146.10
130.16
129.64
123.68
61.56
36.34
34.59
20.14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

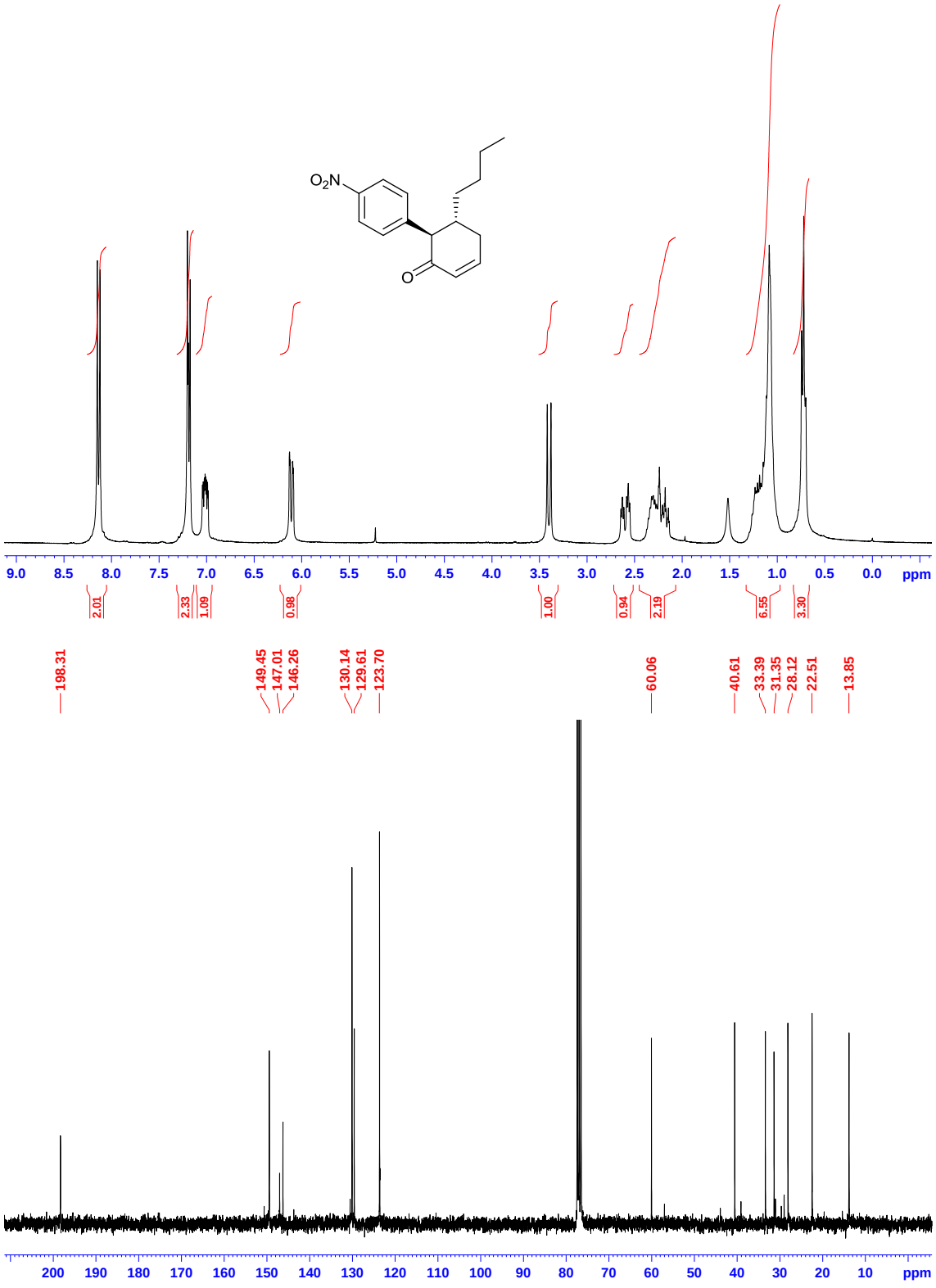

O2N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.20
2.69
1.04
0.85
0.88
1.02
2.35
3.00

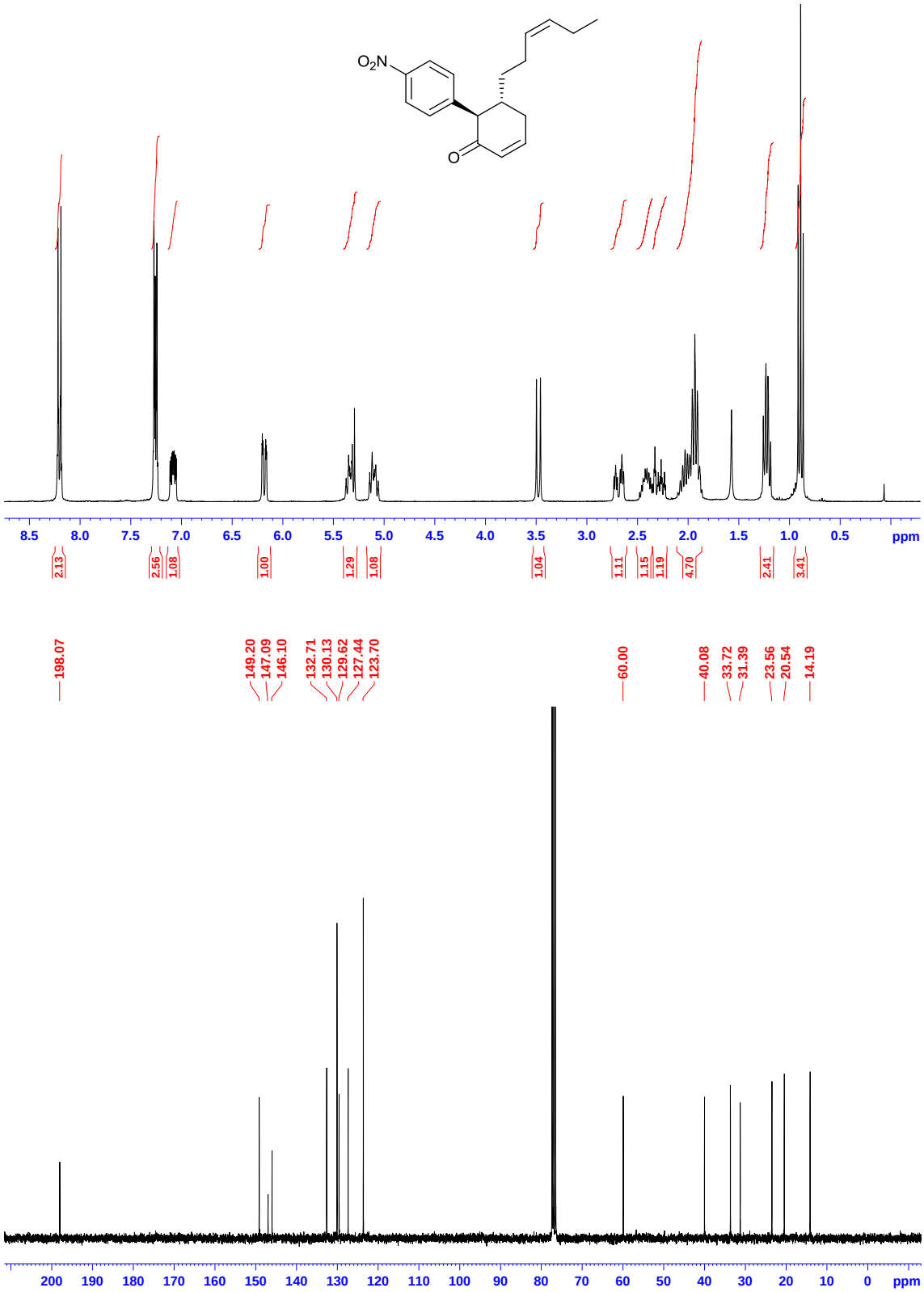

198.37
149.47
147.12
146.26
130.14
129.60
123.69
59.82
41.97
30.79
26.44
10.35
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

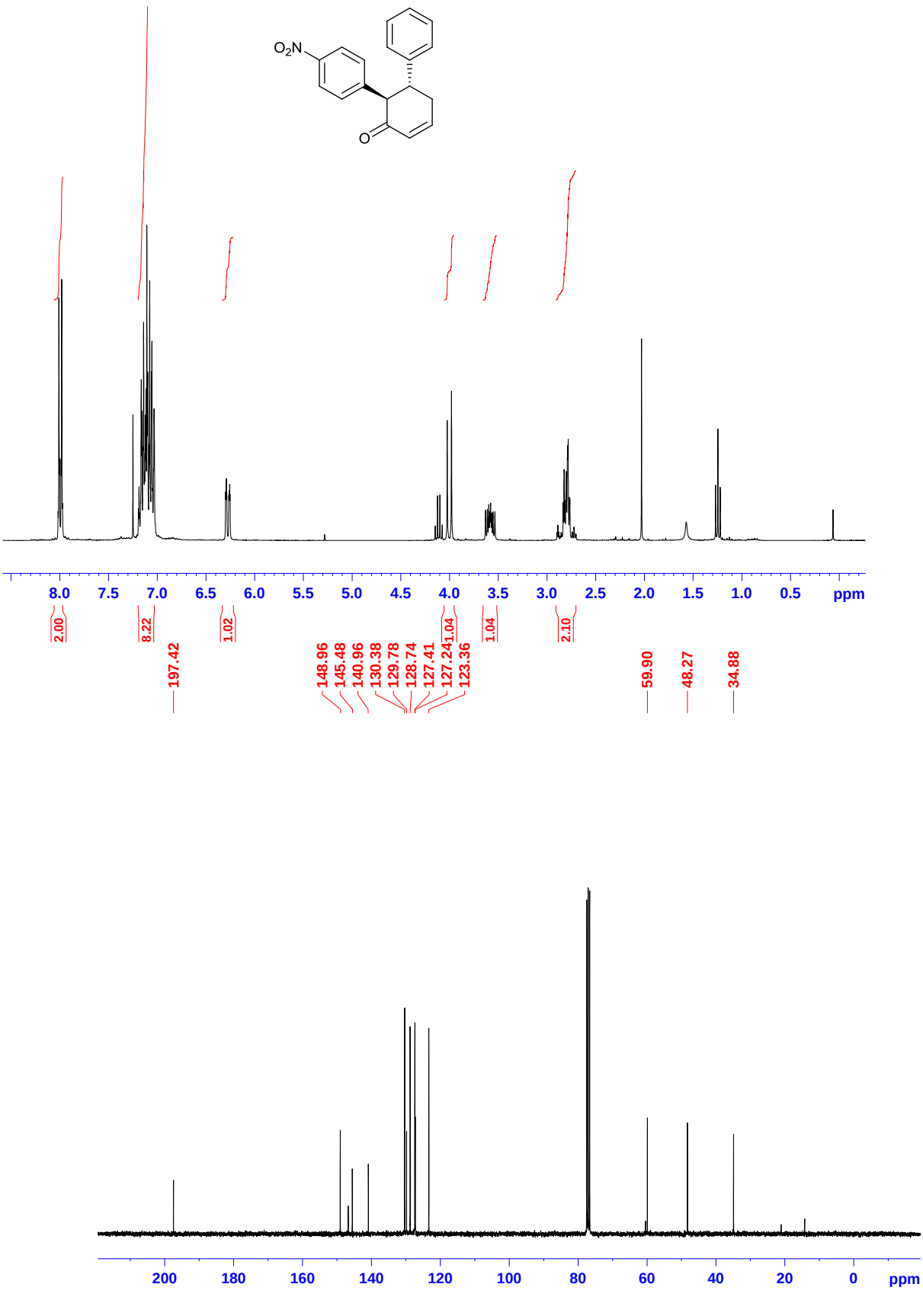

O2N
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.19
1.02
0.90
1.00
0.80
0.93
0.96
0.98
0.98
2.20
3.61

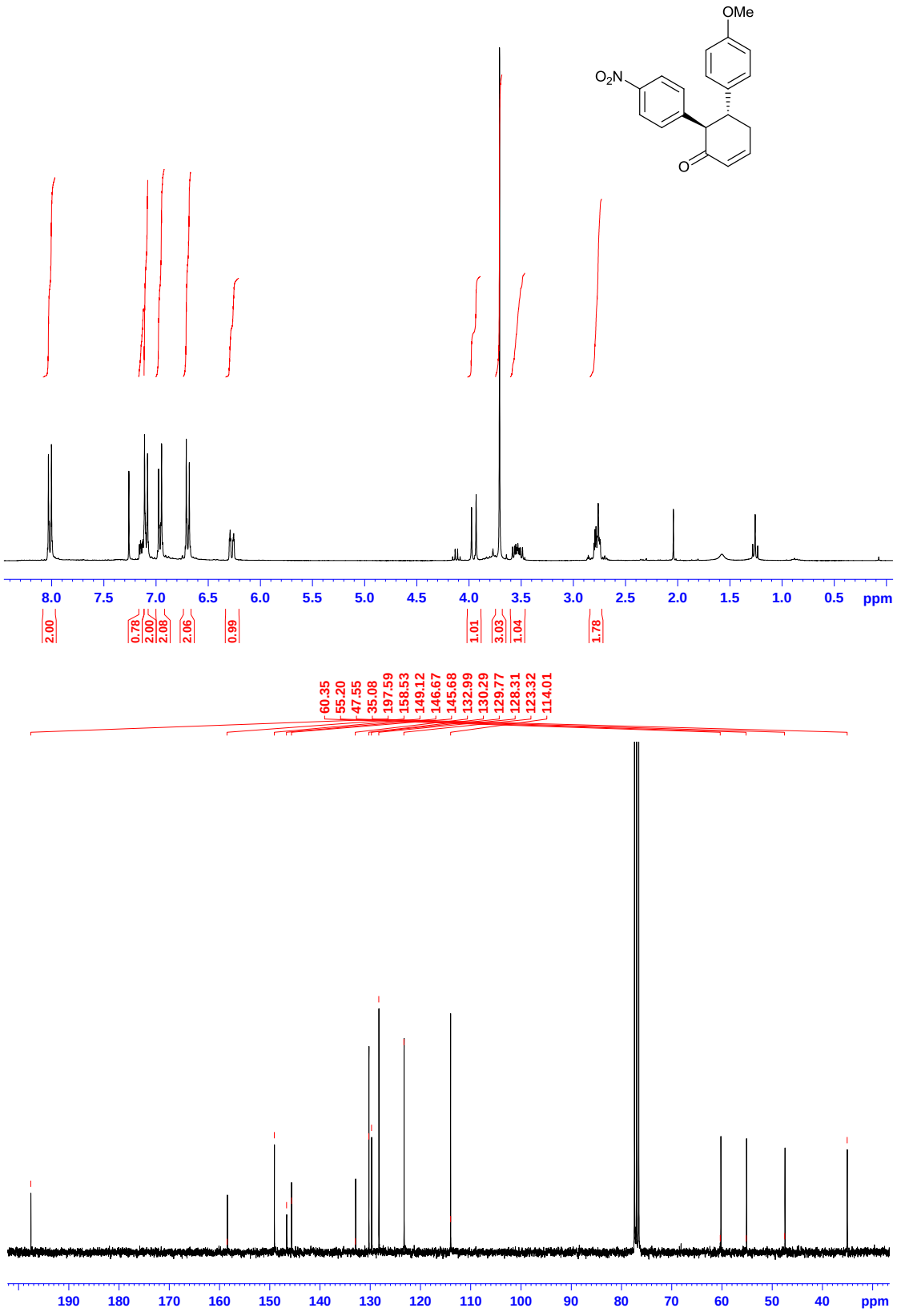

198.26
149.42
147.15
146.26
130.24
129.61
123.68
60.11
40.49
36.00
31.36
19.19
13.91
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

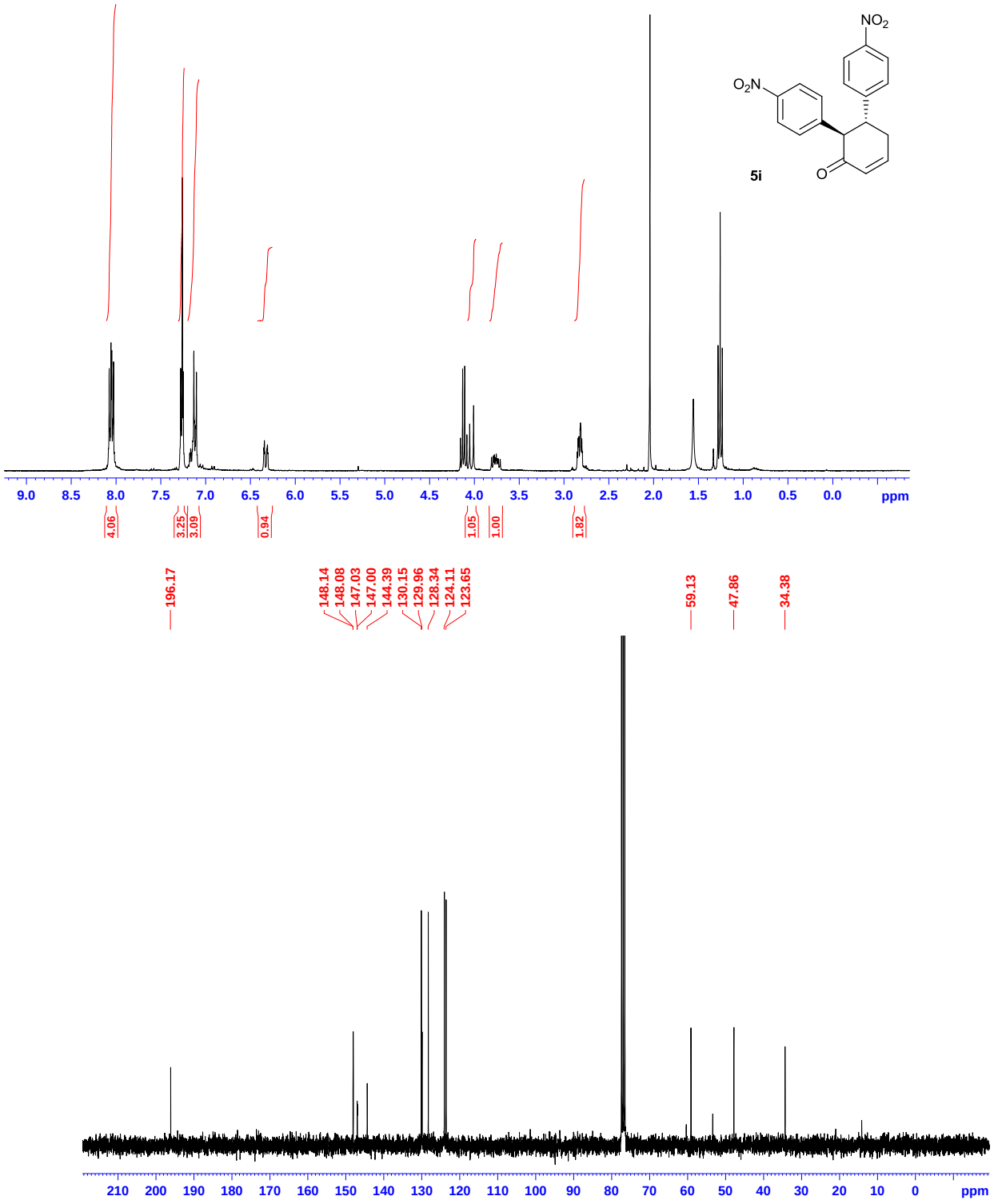

O2N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.02
2.35
1.04
1.00
1.03
3.21
1.22
3.23
3.16
198.74
149.95
147.12
146.14
130.16
129.42
123.77
58.19
46.06
27.86
25.17
20.75
15.35
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

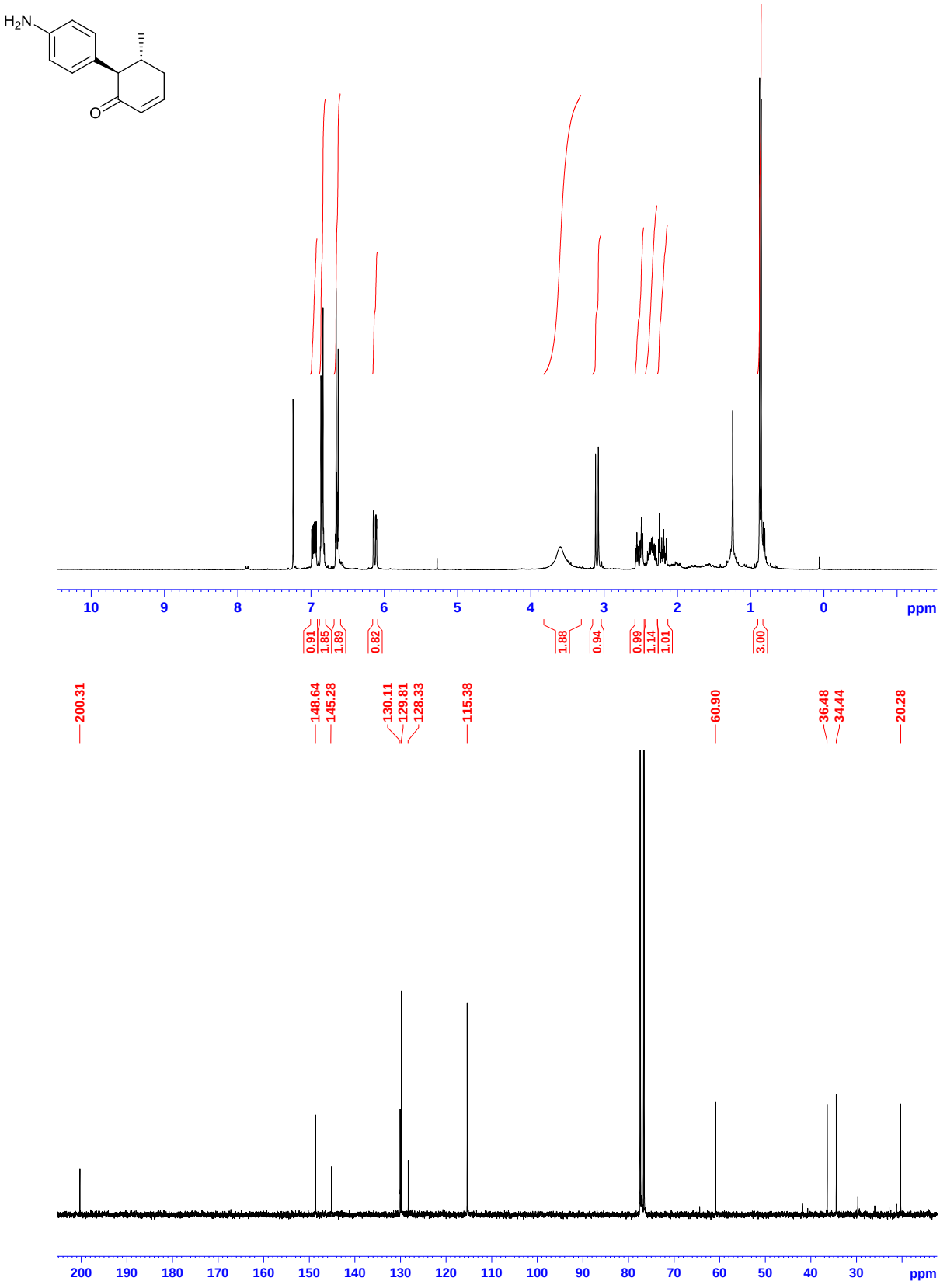

O2N
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
2.33
1.09
0.98
1.00
0.94
2.19
6.55
3.30
198.31
149.45
147.01
146.26
130.14
129.61
123.70
60.06
40.61
33.39
31.35
28.12
22.51
13.85
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

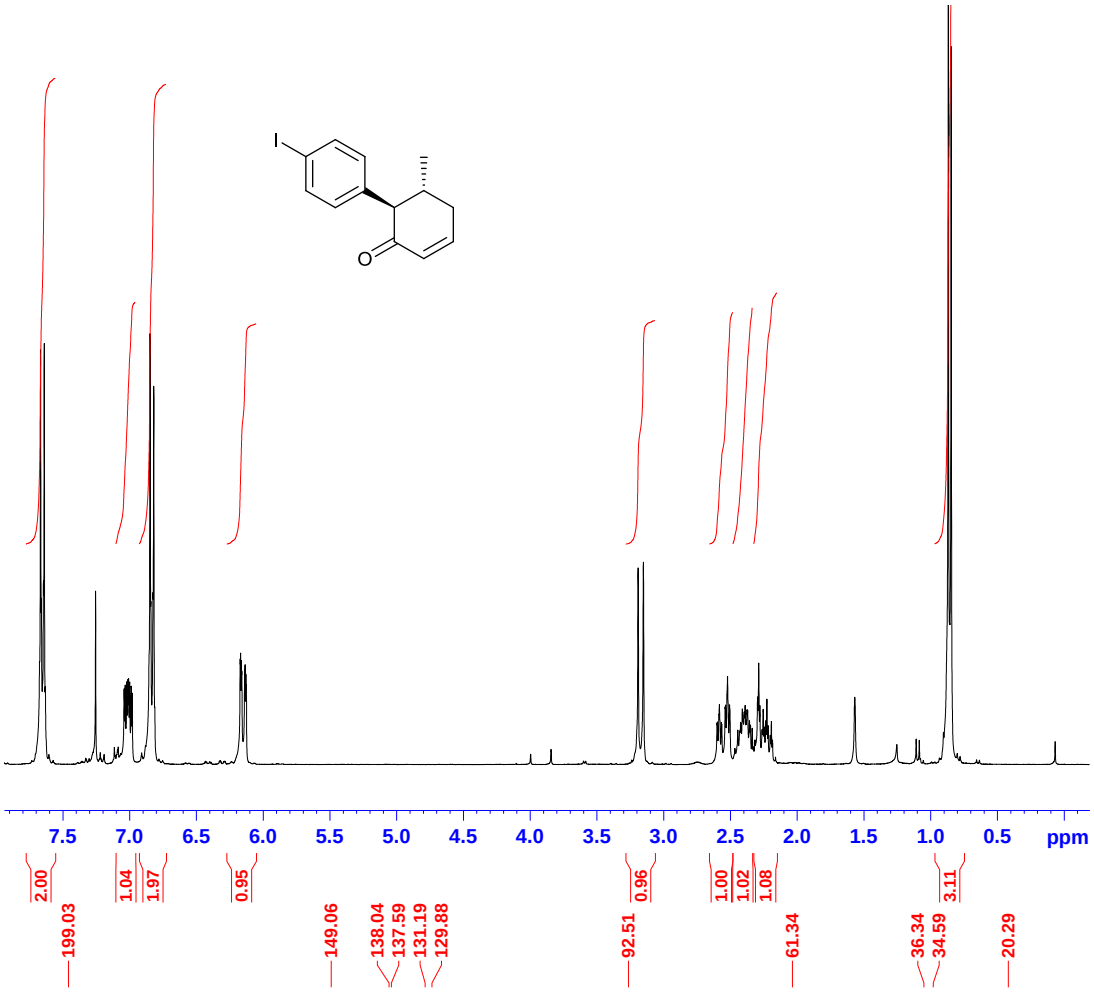

O2N
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.13 2.56 1.08 1.00 1.29 1.08 1.04 1.11 1.15 1.19 4.70 2.41 3.41
198.07 149.20 147.09 146.10 132.71 130.13 129.62 127.44 123.70 60.00 40.08 33.72 31.39 23.56 20.54 14.19
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

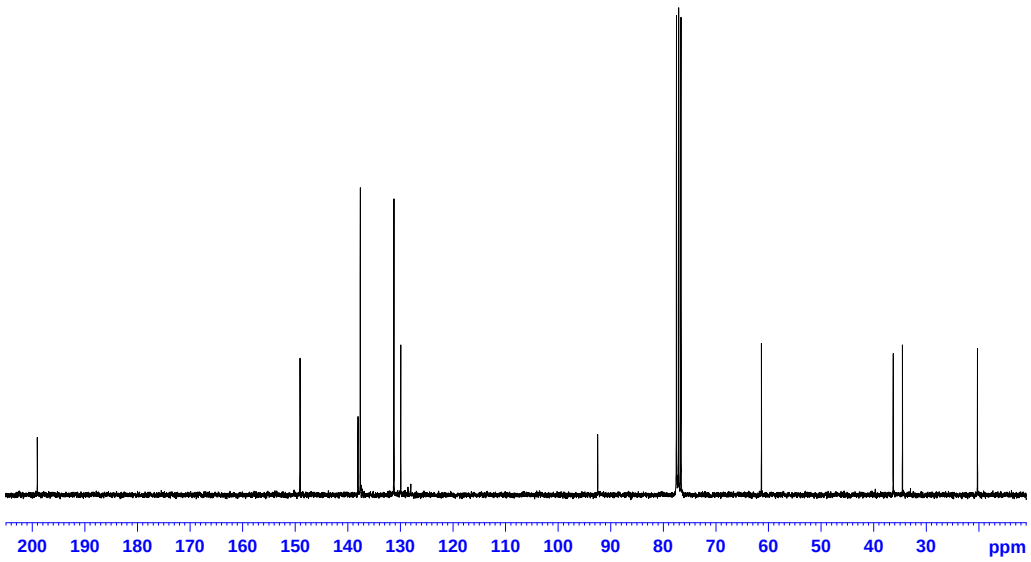

O2N
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
8.22
1.02
1.04
1.04
2.10
197.42
148.96
145.48
140.96
130.38
129.78
128.74
127.41
127.24
123.36
59.90
48.27
34.88
200
180
160
140
120
100
80
60
40
20
0
ppm

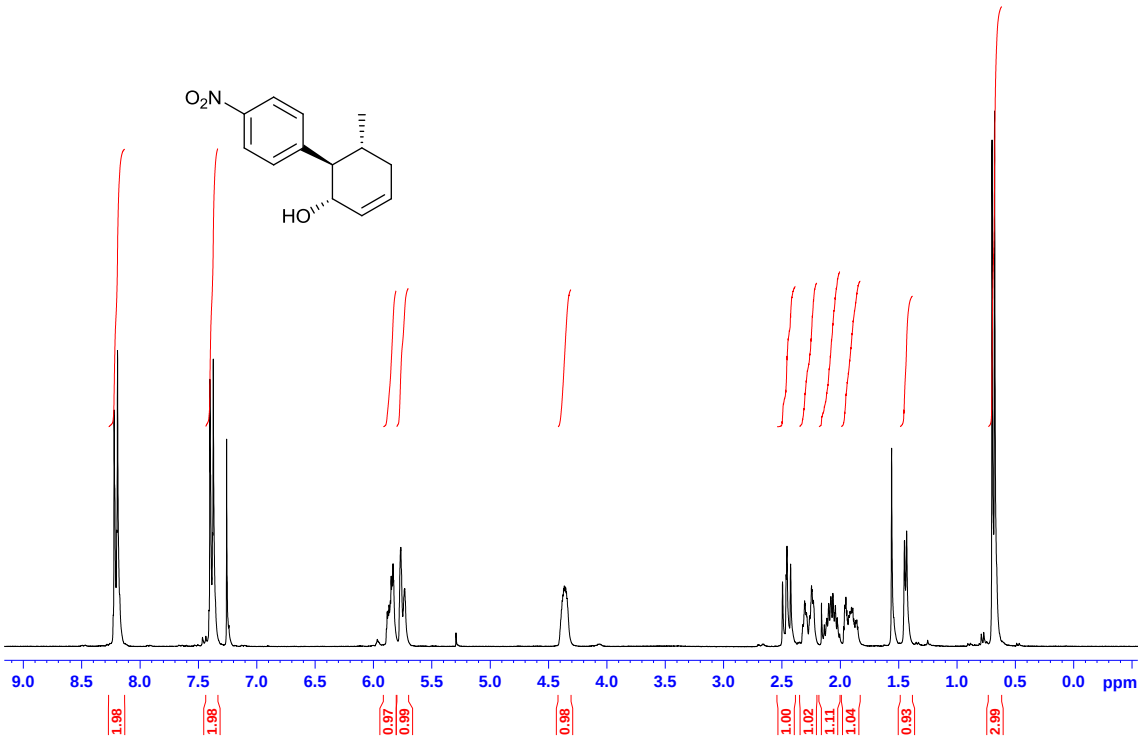

OMe
O2N
O
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 0.78 2.00 2.08 2.06 0.99 1.01 3.03 1.04 1.78
60.35 55.20 47.55 35.08 197.59 158.53 149.12 146.67 145.68 132.99 130.29 129.77 128.31 123.32 114.01
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

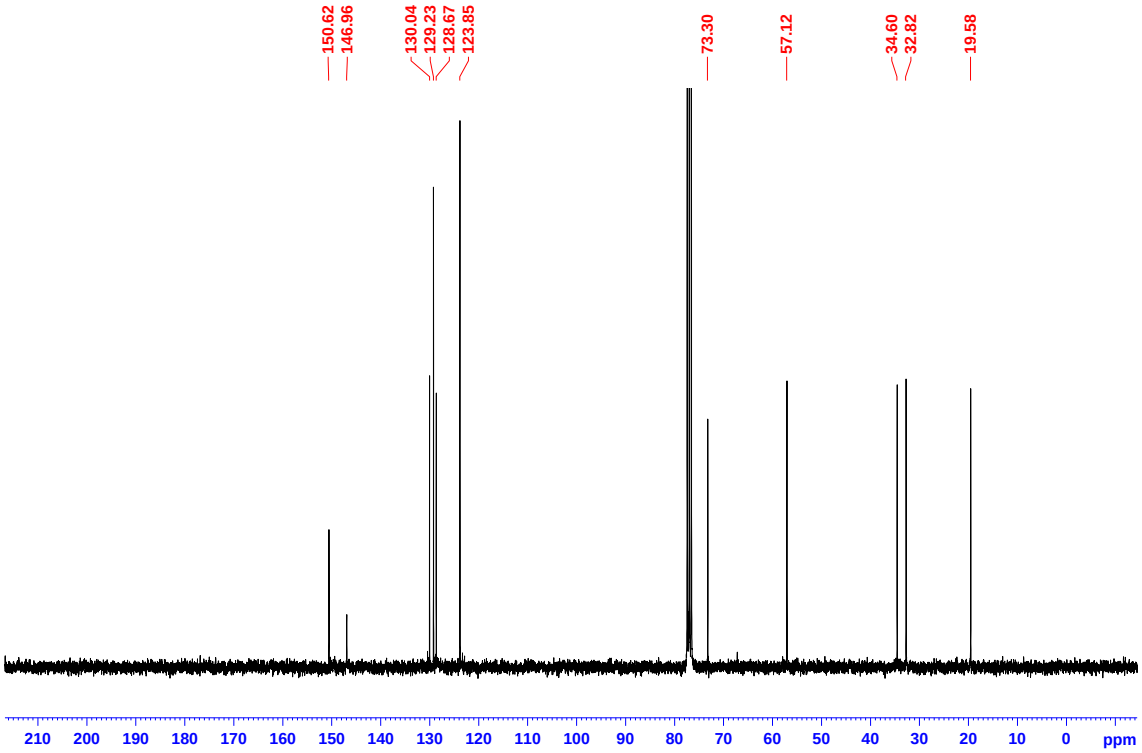

NO2
O2N
O
5i
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.06
3.25
3.09
0.94
1.05
1.00
1.82
196.17
148.14
148.08
147.03
147.00
144.39
130.15
129.96
128.34
124.11
123.65
59.13
47.86
34.38
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

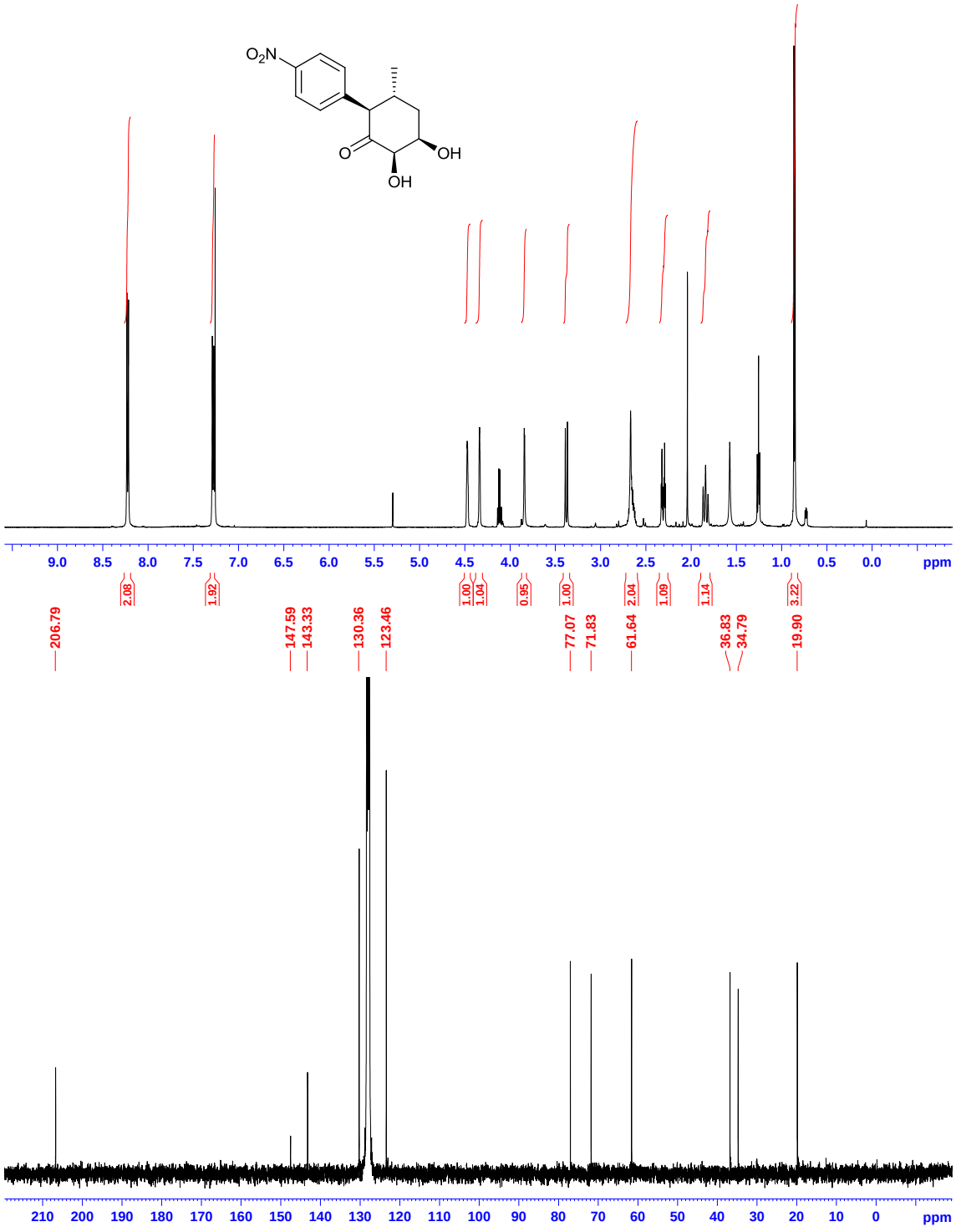

H2N
O
10
9
8
7
6
5
4
3
2
1
0
ppm
0.91
1.85
1.89
0.82
1.88
0.94
0.99
1.14
1.01
3.00
200.31
148.64
145.28
130.11
129.81
128.33
115.38
60.90
36.48
34.44
20.28
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

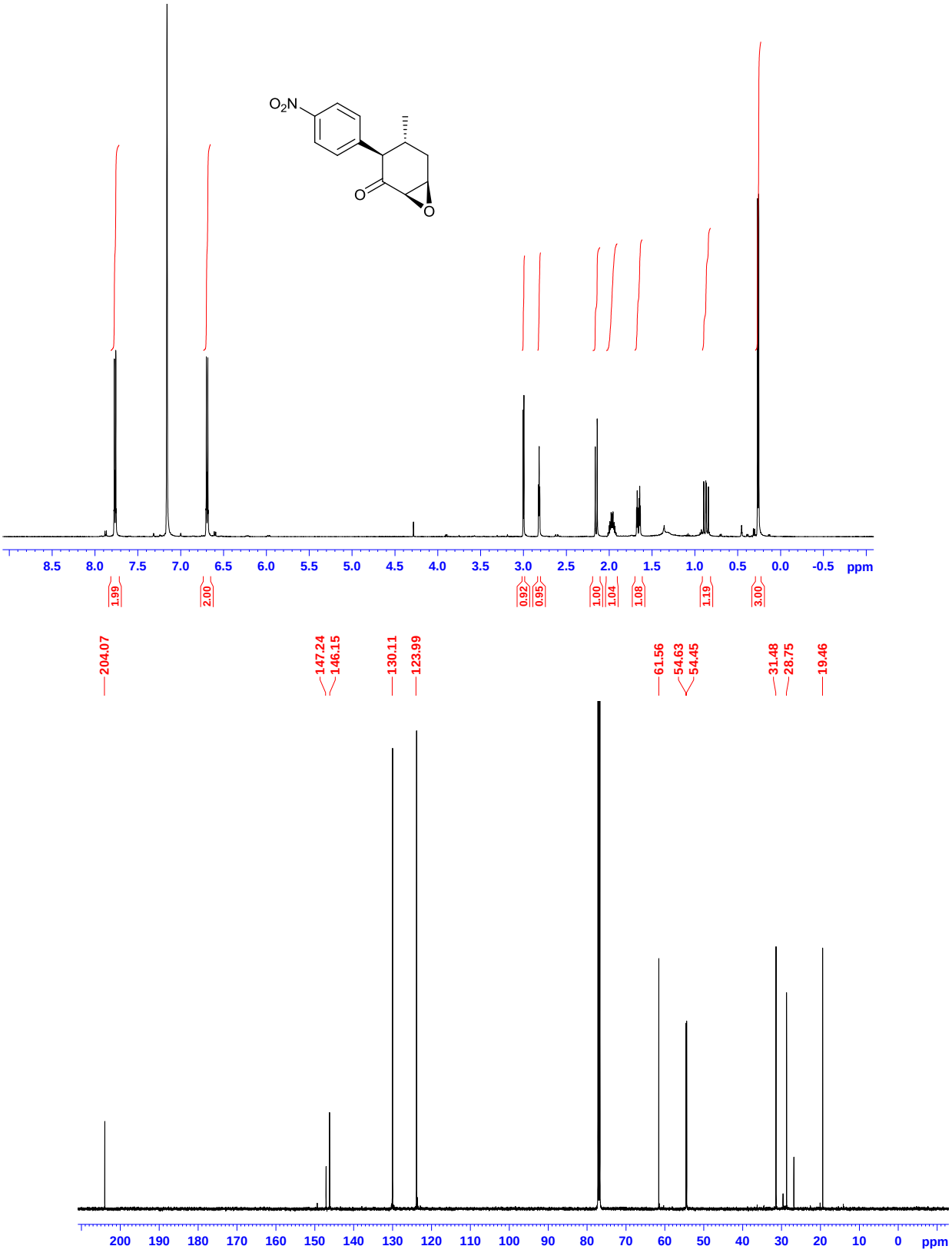

I
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
1.04
1.97
0.95
0.96
1.00
1.02
1.08
3.11
199.03
149.06
138.04
137.59
131.19
129.88
92.51
61.34
36.34
34.59
20.29


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


O2N
HO
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 ppm
1.98
1.98
0.97
0.99
0.98
1.00
1.02
1.11
1.04
0.93
2.99

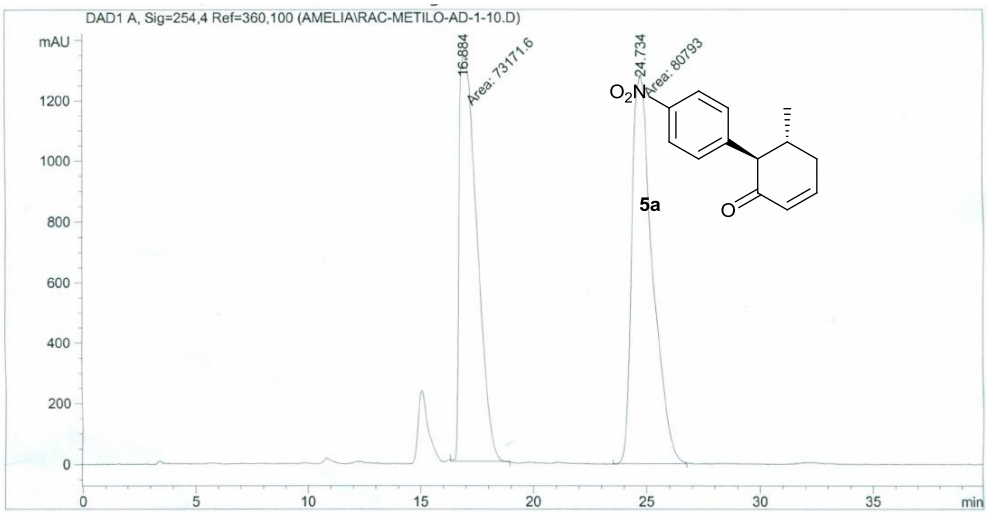

150.62
146.96
130.04
129.23
128.67
123.85
73.30
57.12
34.60
32.82
19.58
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O2N
O
OH
OH
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 ppm
2.08
1.92
1.00
1.04
0.95
1.00
2.04
1.09
1.14
3.22
206.79
147.59
143.33
130.36
123.46
77.07
71.83
61.64
36.83
34.79
19.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


O2N
O
O
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
1.99
2.00
0.92
0.95
1.00
1.04
1.08
1.19
3.00
204.07
147.24
146.15
130.11
123.99
61.56
54.63
54.45
31.48
28.75
19.46
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

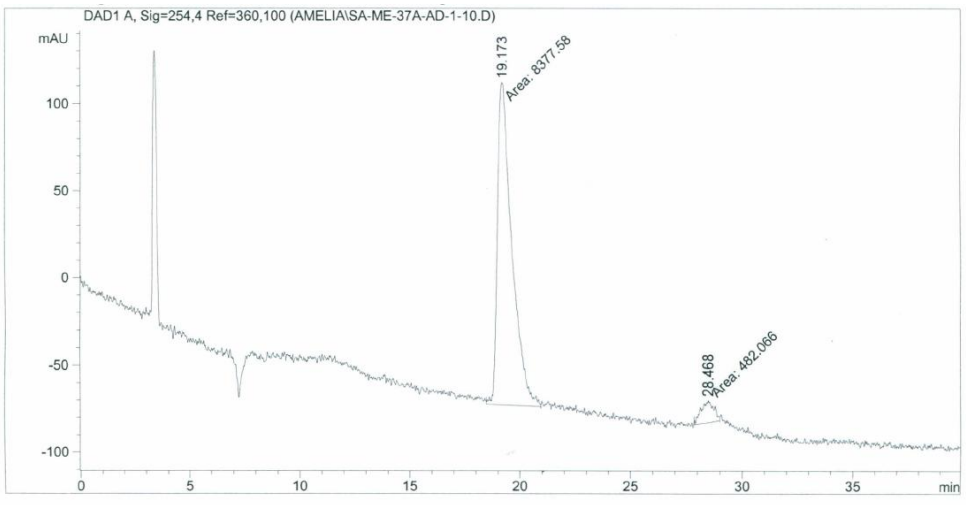
HPLC of compounds (racemic and non-racemic)

rac-**13a**



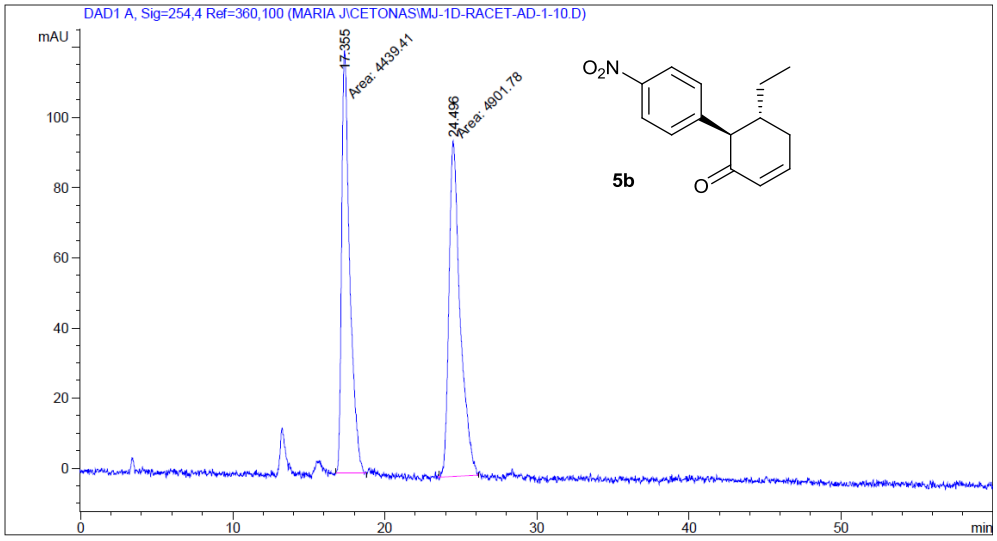
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.884	MM	0.9071	7.31716e4	1344.43909	47.5249
2	24.734	MM	1.0484	8.07930e4	1284.43176	52.4751

513a



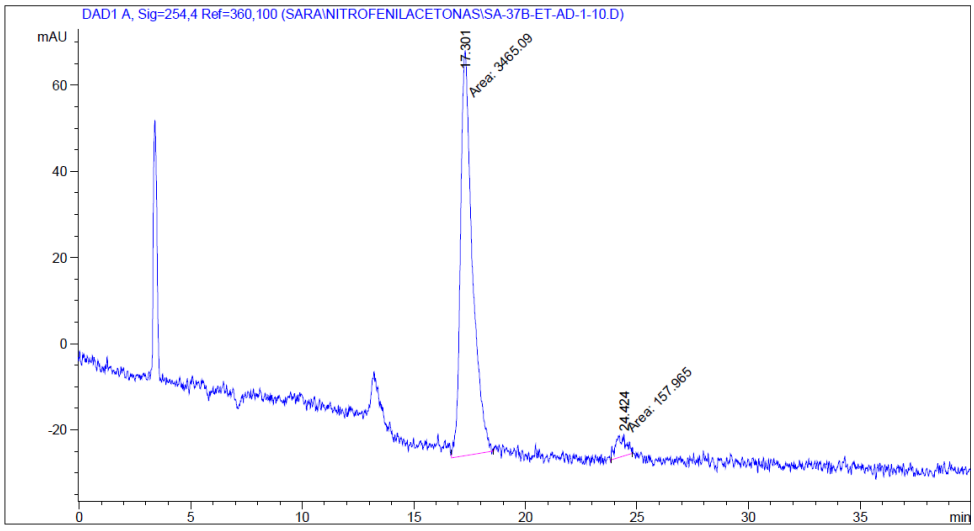
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.173	MM	0.7556	8377.57520	184.79465	94.5589
2	28.468	MM	0.6203	482.06573	12.95344	5.4411

rac-**13b**



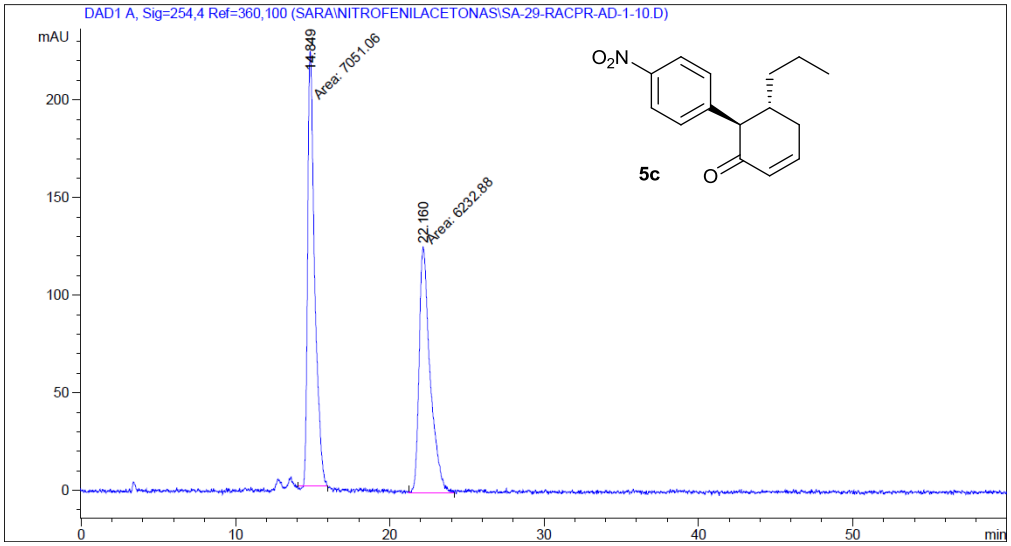
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.355	MM	0.6151	4439.40820	120.28900	47.5251
2	24.496	MM	0.8541	4901.77979	95.65139	52.4749

13b



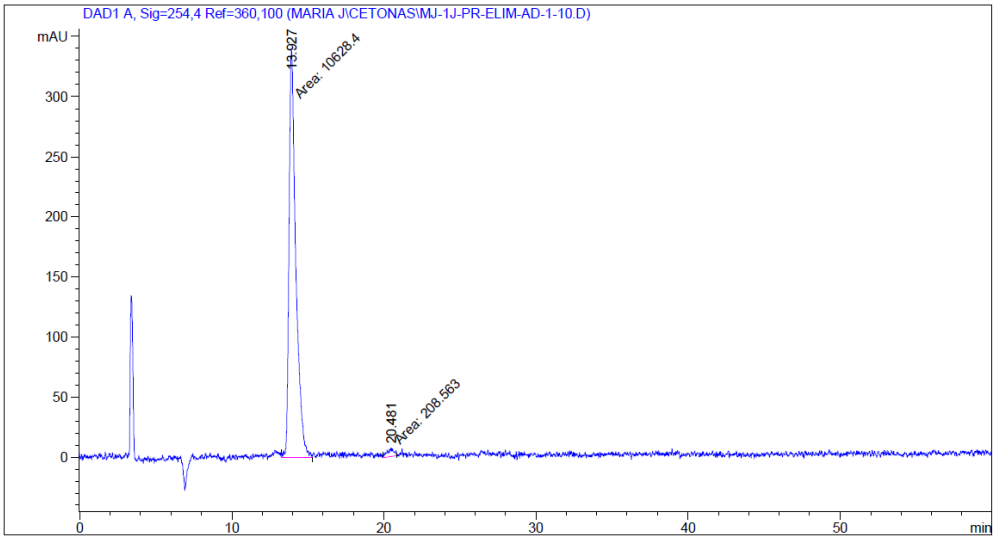
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.301	MM	0.6137	3465.08789	94.10890	95.6400
2	24.424	MM	0.5342	157.96533	4.92841	4.3600

rac-**13c**



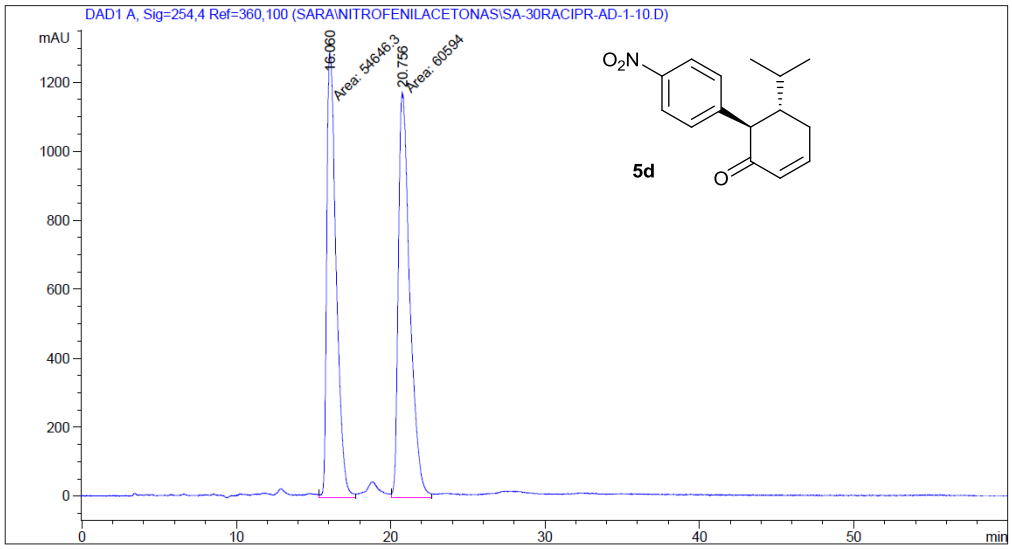
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.849	MM	0.5278	7051.05957	222.64926	53.0796
2	22.160	MM	0.8267	6232.87793	125.65984	46.9204

13c



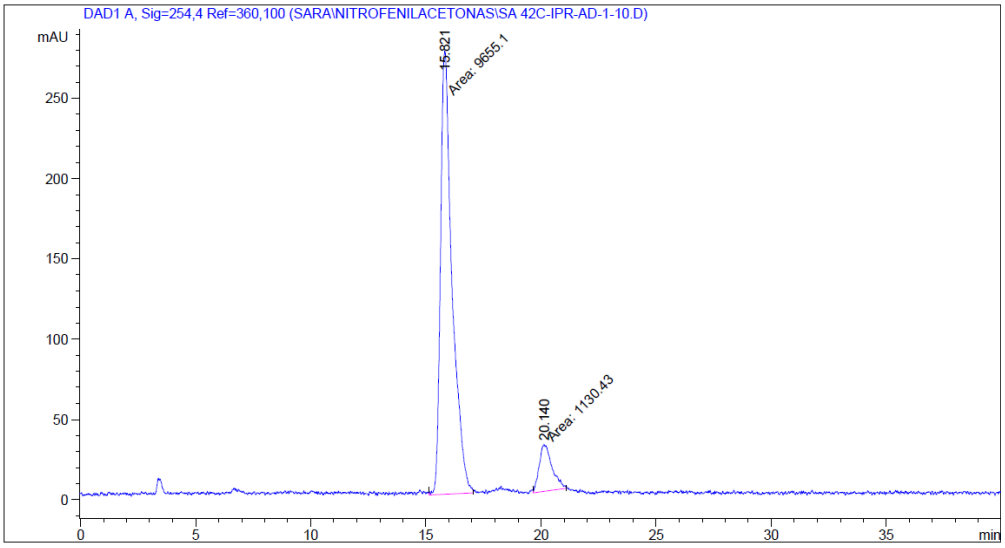
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.927	MM	0.5225	1.06284e4	339.03641	98.0754
2	20.481	MM	0.4630	208.56314	7.50715	1.9246

rac-**13e**



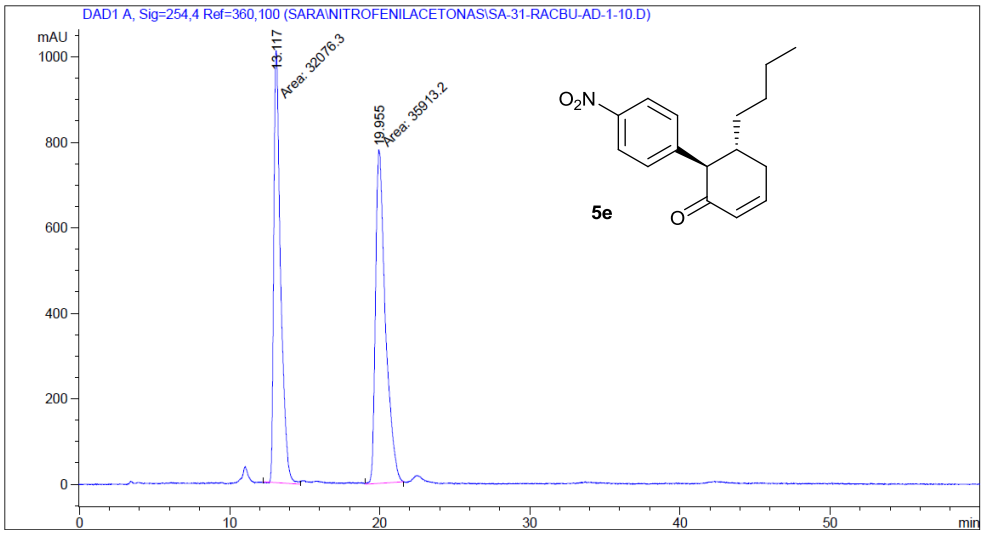
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.060	MM	0.7054	5.46463e4	1291.18250	47.4195
2	20.756	MM	0.8574	6.05940e4	1177.92542	52.5805

13e



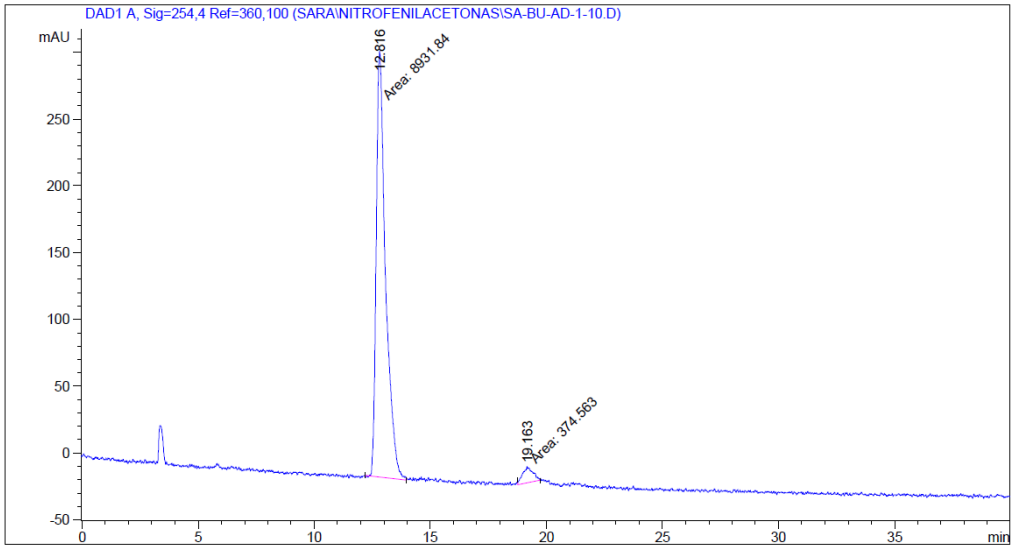
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.821	MM	0.5831	9655.09668	275.99304	89.5190
2	20.140	MM	0.6485	1130.43457	29.05090	10.4810

rac-**13d**



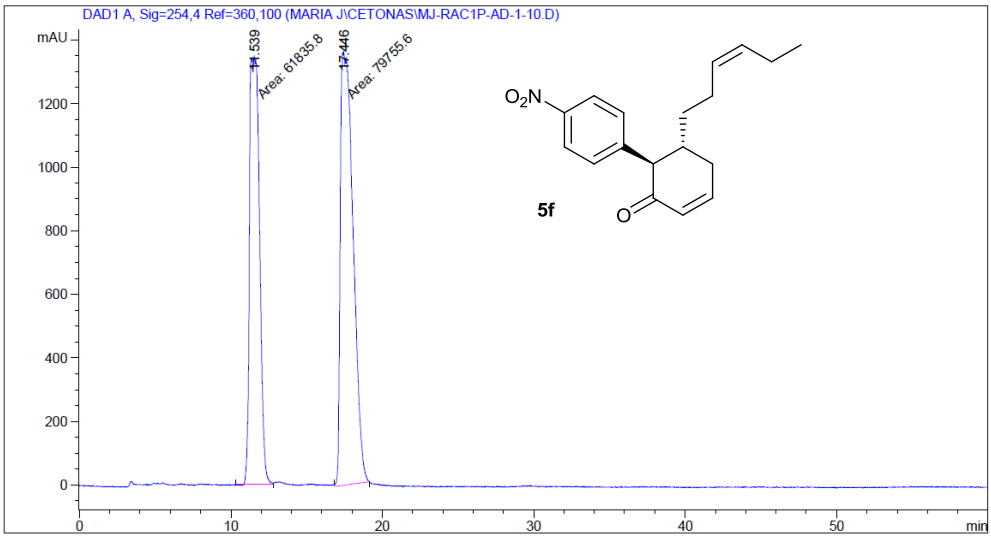
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.117	MM	0.5289	3.20763e4	1010.87885	47.1783
2	19.955	MM	0.7661	3.59132e4	781.26788	52.8217

13d



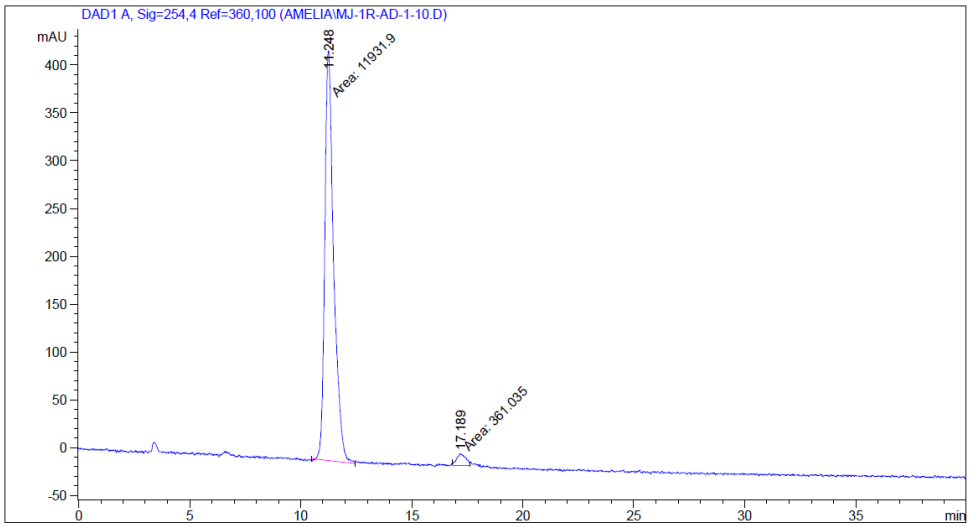
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.816	MM	0.4669	8931.83594	318.81171	95.9752
2	19.163	MM	0.5095	374.56265	12.25285	4.0248

rac-**13j**



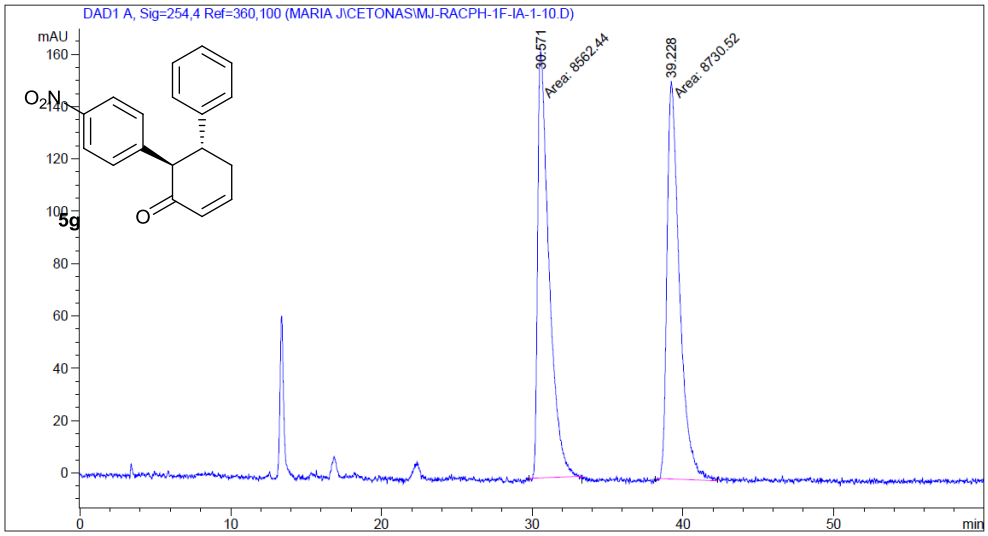
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.539	MM	0.7662	6.18358e4	1345.16016	43.6720
2	17.446	MM	0.9735	7.97556e4	1365.50452	56.3280

13j



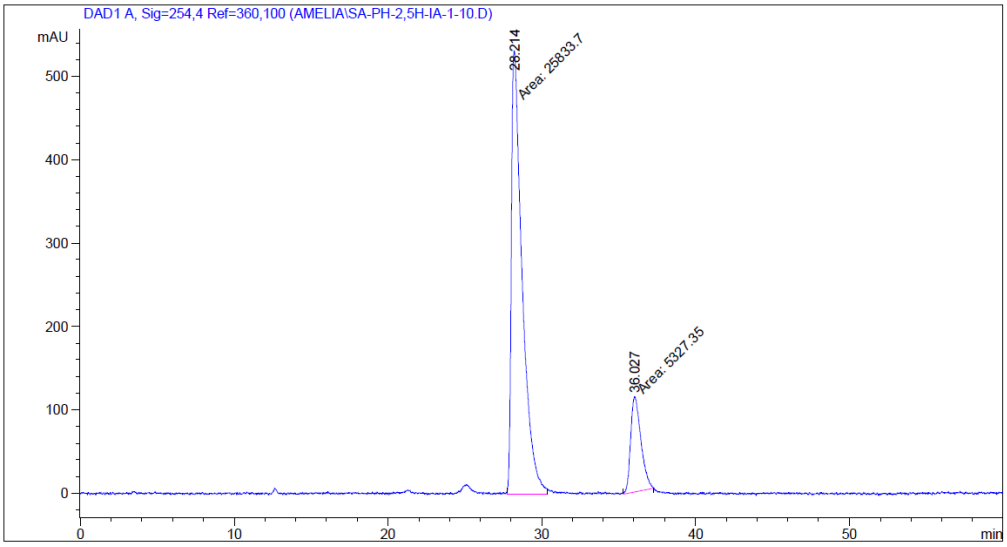
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.248	MM	0.4639	1.19319e4	428.72336	97.0631
2	17.189	MM	0.4895	361.03494	12.29385	2.9369

rac-**13f**



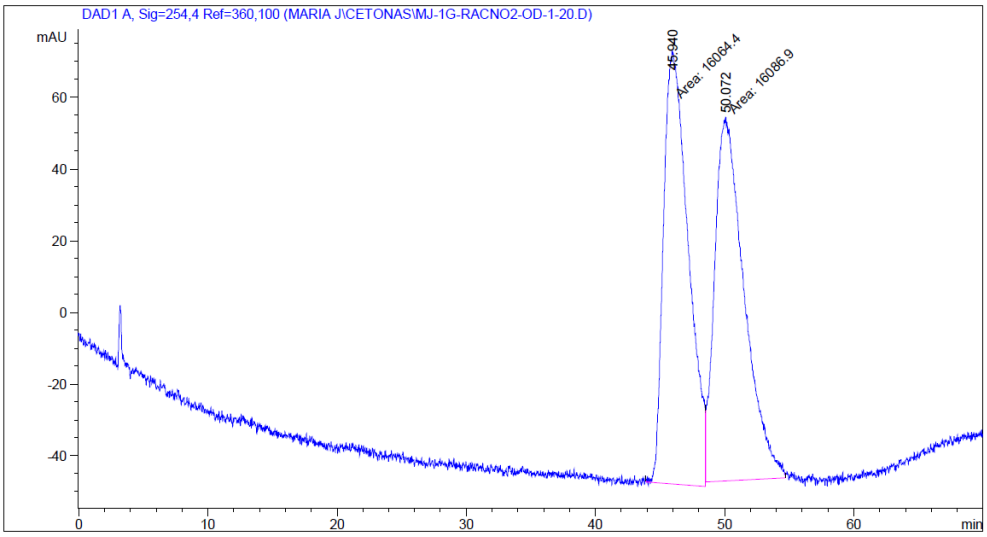
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.571	MM	0.8734	8562.43555	163.39560	49.5140
2	39.228	MM	0.9580	8730.51758	151.89227	50.4860

13f



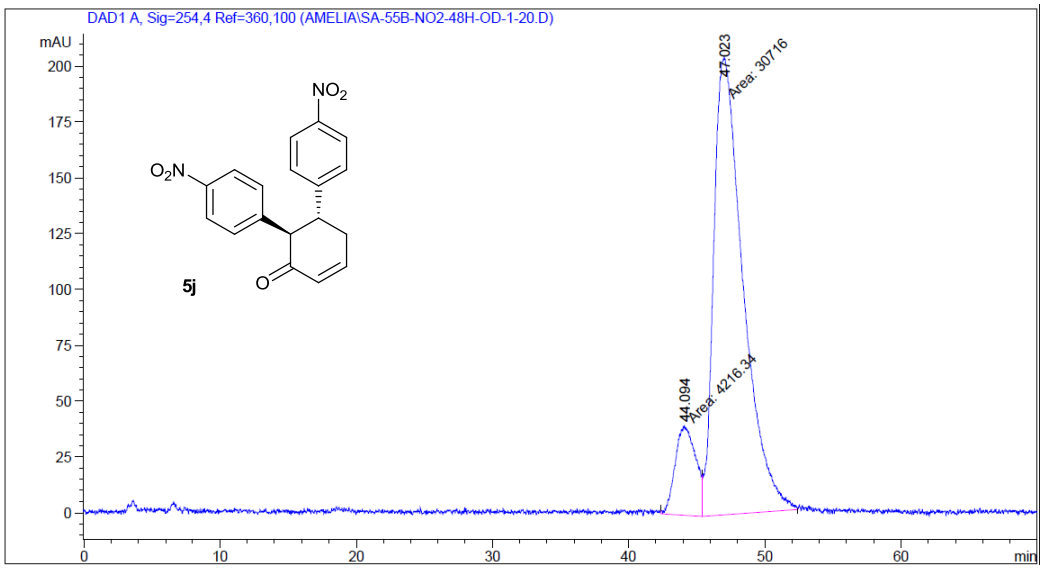
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.214	MM	0.8111	2.58337e4	530.83289	82.9038
2	36.027	MM	0.7743	5327.35107	114.66869	17.0962

rac-**13h**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	45.940	MM	2.2167	1.60644e4	120.78139	49.9650
2	50.072	MM	2.6399	1.60869e4	101.56200	50.0350

13h



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.094	MM	1.7445	4216.33643	40.28169	12.0700
2	47.023	MM	2.4955	3.07160e4	205.14651	87.9300

X-ray crystallographic data of (*R*,*R*)-15a

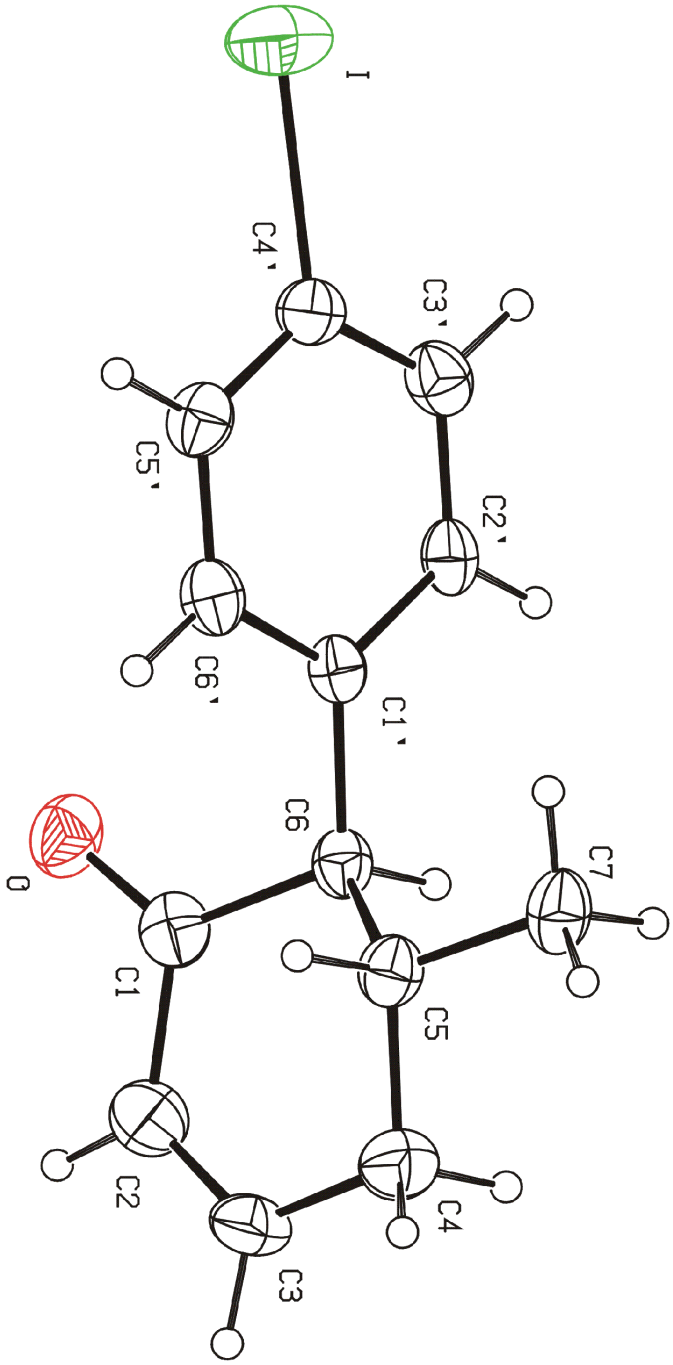


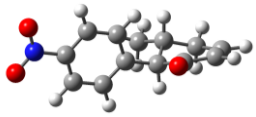
Table 1. Crystal data and structure refinement for jg10551s.

Identification code	jg10551s	
Empirical formula	C13 H13 I O	
Formula weight	312.13	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 5.4376(7) Å	a= 90°.
	b = 9.7637(12) Å	b= 90°.
	c = 22.815(3) Å	g = 90°.
Volume	1211.3(3) $Å^3$	
Z	4	
Density (calculated)	1.712 Mg/m^3	
Absorption coefficient	2.615 mm^{-1}	
F(000)	608	
Crystal size	0.47 x 0.31 x 0.22 mm^3	
Theta range for data collection	1.79 to 25.03°.	
Index ranges	-6<=h<=6, -11<=k<=11, -26<=l<=27	
Reflections collected	9292	
Independent reflections	2156 [R(int) = 0.0299]	
Completeness to theta = 25.03°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.5494	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2156 / 0 / 138	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0586	
R indices (all data)	R1 = 0.0393, wR2 = 0.0640	
Absolute structure parameter	0.00(3)	
Largest diff. peak and hole	0.597 and -0.556 $e.Å^{-3}$	

Theoretical calculations

Geometries have been fully optimized using the standard 6-31G(d) basis set for all the atoms: (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. Frequencies, zero-point energy (ZPE) and NMR spectra were also computed at the same level of theory.

Cartesian coordinates (Å) and energies (hartrees) of all the optimized structures.



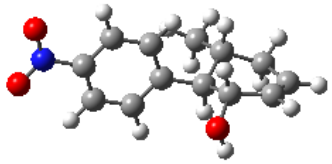
Ciclohexenone **13a**

E(B3LYP 6-31G*) = -783.530748686

Zero-point correction= 0.239643

Number of imaginary frequencies: 0

6	-3.68703	-1.38418	0.08775
6	-1.59024	0.05823	0.44111
6	-3.79822	1.09214	-0.2515
6	-2.28223	1.06997	-0.51888
6	-4.40669	-0.2772	-0.1532
6	-2.22775	-1.3439	0.3125
1	-4.00098	1.64009	0.68451
1	-2.13448	0.70321	-1.54536
1	-4.30492	1.66664	-1.03832
1	-4.14159	-2.37022	0.13325
8	-1.57403	-2.36757	0.43268
1	-1.82109	0.38642	1.46798
1	-5.48512	-0.35532	-0.28538
6	-0.08329	0.00815	0.29211
6	2.6877	-0.02532	0.002
6	0.75028	0.48919	1.31031
6	0.50917	-0.49888	-0.87596
6	1.89032	-0.5182	-1.03047
6	2.13644	0.47778	1.17692
1	0.30983	0.87755	2.2248
1	-0.11547	-0.89841	-1.66909
1	2.35728	-0.90991	-1.92562
1	2.78795	0.84735	1.95904
6	-1.69244	2.48139	-0.42208
1	-1.77633	2.8753	0.5989
1	-2.22749	3.16744	-1.08908
1	-0.63524	2.49791	-0.70153
7	4.14911	-0.03903	-0.15321
8	4.82803	0.39917	0.77599
8	4.60947	-0.48533	-1.20433



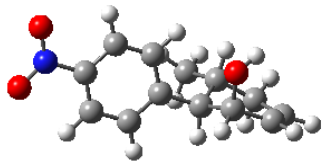
Alcohol **16a**

E(B3LYP 6-31G*) = -784.722884376

Zero-point correction= 0.263012

Number of imaginary frequencies: 0

6	-3.65469	-1.24201	-0.46436
6	-1.55943	-0.03911	0.31261
6	-3.76548	1.18706	0.11374
6	-2.25548	1.25715	-0.18569
6	-4.37876	-0.14789	-0.21452
6	-2.14847	-1.28458	-0.40168
1	-3.94145	1.41976	1.1771
1	-2.13938	1.30129	-1.27894
1	-4.28303	1.98047	-0.44359
1	-4.13427	-2.18613	-0.71821
1	-1.80808	-0.14566	1.38011
1	-5.46623	-0.20085	-0.24956
6	-0.04649	-0.0173	0.19189
6	2.73669	-0.00804	-0.01943
6	0.7624	-0.22308	1.31829
6	0.58177	0.19041	-1.04801
6	1.96745	0.19808	-1.16376
6	2.15127	-0.22127	1.2259
1	0.29658	-0.3912	2.28545
1	-0.01791	0.34959	-1.93998
1	2.45867	0.35876	-2.11552
1	2.7806	-0.3812	2.09268
6	-1.64907	2.53162	0.41498
1	-1.70311	2.51211	1.51116
1	-2.19803	3.41649	0.07186
1	-0.59947	2.65762	0.13386
7	4.2013	0.00129	-0.1305
8	4.85553	-0.18153	0.89668
8	4.69043	0.19288	-1.24442
1	-1.7383	-1.33804	-1.41895
8	-1.69844	-2.49654	0.20766
1	-2.14607	-2.56682	1.06688



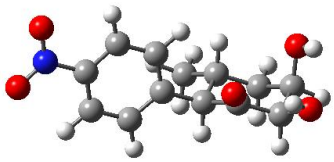
Alcohol **16a'**

E(B3LYP 6-31G*) = -784.722705804

Zero-point correction= 0.263272

Number of imaginary frequencies: 0

6	-3.66405	-1.23371	0.65627
6	-1.53474	0.1149	0.44496
6	-3.75178	1.12582	-0.18668
6	-2.27552	0.98099	-0.6075
6	-4.37134	-0.15039	0.31805
6	-2.16545	-1.30643	0.51071
1	-3.82963	1.89437	0.60046
1	-2.249	0.43984	-1.56553
1	-4.34049	1.51652	-1.02844
1	-4.16371	-2.13657	1.0025
1	-1.73636	0.56951	1.42642
1	-5.45588	-0.16311	0.42165
6	-0.02602	0.06244	0.28489
6	2.75689	-0.01949	0.06139
6	0.79821	0.46605	1.34739
6	0.58853	-0.38723	-0.89745
6	1.97372	-0.4297	-1.01655
6	2.18618	0.42849	1.24969
1	0.34438	0.81794	2.27039
1	-0.0231	-0.72655	-1.72409
1	2.45412	-0.77633	-1.92324
1	2.82466	0.73948	2.06732
6	-1.64207	2.36085	-0.82227
1	-1.5918	2.92128	0.12007
1	-2.23719	2.95204	-1.52845
1	-0.62601	2.28564	-1.22018
7	4.22035	-0.05934	-0.05859
8	4.88555	0.30311	0.91273
8	4.6985	-0.45229	-1.12331
1	-1.72865	-1.83041	1.36869
8	-1.82488	-2.12689	-0.61862
1	-2.49255	-1.95536	-1.30132



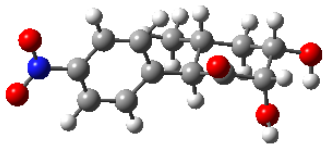
Diol **17a-up**

E(B3LYP 6-31G*) =-935.184687368

Zero-point correction= 0.272823

Number of imaginary frequencies: 0

6	3.2728	-0.79992	-0.76202
6	0.97882	0.40812	-0.58296
6	3.1367	1.57482	0.11261
6	1.62841	1.45177	0.39211
6	3.88048	0.24451	0.19598
6	1.76624	-0.89862	-0.51683
1	3.29747	2.01176	-0.88391
1	1.50943	1.06872	1.4126
1	3.58296	2.26625	0.83651
8	1.27875	-1.98773	-0.27012
1	1.13483	0.80216	-1.5999
6	-0.50708	0.20664	-0.36912
6	-3.2442	-0.12099	0.02001
6	-1.42077	0.56914	-1.36778
6	-0.99869	-0.33116	0.83134
6	-2.36429	-0.49672	1.03405
6	-2.79205	0.41035	-1.18438
1	-1.05683	0.98307	-2.30464
1	-0.30764	-0.6348	1.6107
1	-2.75566	-0.91224	1.95432
1	-3.50609	0.68867	-1.9495
6	0.94025	2.81795	0.29417
1	1.02259	3.23103	-0.71975
1	1.40977	3.52942	0.98259
1	-0.12217	2.75734	0.54754
7	-4.69036	-0.2912	0.22743
8	-5.44277	0.04302	-0.68788
8	-5.06289	-0.75647	1.30425
1	3.43623	-0.47989	-1.80537
1	4.93772	0.38815	-0.07826
8	3.77463	-0.24952	1.52209
1	4.05962	-1.18012	1.46539
8	3.87728	-2.05155	-0.52078
1	3.13056	-2.6784	-0.42377



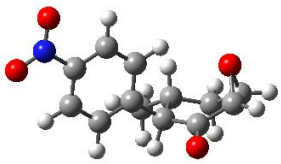
Diol-down 17a‘

E(B3LYP 6-31G*) = -935.174255784

Zero-point correction= 0.272344

Number of imaginary frequencies: 0

6	-3.16404	-1.17882	0.15129
6	-0.94869	0.12385	0.31596
6	-3.12788	1.31094	-0.29499
6	-1.60147	1.29128	-0.50835
6	-3.8176	-0.02138	-0.62636
6	-1.65206	-1.1764	-0.09361
1	-3.34267	1.56656	0.75141
1	-1.40138	1.09507	-1.57252
1	-3.57946	2.09608	-0.91181
8	-1.10341	-2.11528	-0.63578
1	-1.21883	0.30375	1.36527
6	0.55709	0.0461	0.20359
6	3.3361	-0.06325	0.03319
6	1.35582	0.27139	1.33399
6	1.18856	-0.24227	-1.01768
6	2.57509	-0.29666	-1.11125
6	2.74519	0.21977	1.26153
1	0.88334	0.49163	2.2878
1	0.59242	-0.44037	-1.90142
1	3.07258	-0.51996	-2.04689
1	3.36885	0.39379	2.12956
6	-0.98781	2.6505	-0.14957
1	-1.13866	2.87929	0.91292
1	-1.46202	3.44762	-0.733
1	0.08677	2.67743	-0.35189
7	4.80262	-0.11831	-0.05836
8	5.44848	0.08593	0.96987
8	5.29899	-0.36399	-1.1577
1	-3.5723	-2.13797	-0.18708
1	-3.71279	-0.23371	-1.69736
8	-3.47356	-0.94422	1.53346
1	-3.35277	-1.77611	2.01607
8	-5.20799	0.01432	-0.36511
1	-5.29115	-0.03918	0.60313



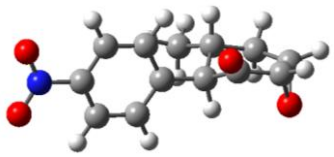
Epoxide **18a**

E(B3LYP 6-31G*) = -858.724339987

Zero-point correction= 0.244886

Number of imaginary frequencies: 0

6	-3.00671	-1.51012	0.27963
6	-1.36982	0.50836	0.61192
6	-3.5985	0.83624	-0.63013
6	-2.09488	1.16122	-0.6039
6	-3.84945	-0.65728	-0.58964
6	-1.97177	-0.82315	1.11813
1	-4.11994	1.30473	0.21767
1	-1.66804	0.73491	-1.51689
1	-4.04221	1.2591	-1.54041
8	-1.67244	-1.27071	2.2077
1	-1.48236	1.17639	1.47657
6	0.12119	0.31851	0.36923
6	2.84514	-0.04611	-0.06826
6	1.06629	0.94432	1.19294
6	0.57275	-0.50611	-0.67551
6	1.93227	-0.6925	-0.90065
6	2.43158	0.77072	0.98056
1	0.73111	1.57358	2.01237
1	-0.14812	-1.01322	-1.31084
1	2.29425	-1.32639	-1.70067
1	3.17138	1.25197	1.60819
6	-1.85056	2.67541	-0.62778
1	-2.28754	3.16298	0.25307
1	-2.29794	3.13072	-1.51858
1	-0.77895	2.90218	-0.64007
7	4.28453	-0.23392	-0.303
8	5.06766	0.34722	0.44841
8	4.6217	-0.95999	-1.23822
1	-3.38725	-2.44318	0.69123
1	-4.8639	-1.00189	-0.79396
8	-2.82659	-1.48546	-1.14989



Epoxide-down 18a’

E(B3LYP 6-31G*) = -858.724239712

Zero-point correction= 0.244910

Number of imaginary frequencies: 0

6	-3.48706	-1.30048	0.16568
6	-1.33238	0.06765	0.27812
6	-3.5073	1.25293	-0.42209
6	-1.989	1.11904	-0.68691
6	-4.22824	-0.03304	-0.06087
6	-1.99808	-1.28309	-0.02014
1	-3.67469	1.95839	0.40347
1	-1.85788	0.73864	-1.71029
1	-3.98297	1.69342	-1.30683
8	-1.41963	-2.26265	-0.4486
1	-1.6219	0.34777	1.2992
6	0.17667	0.00873	0.19379
6	2.95939	-0.04476	0.07271
6	0.95092	0.38198	1.30146
6	0.83408	-0.40134	-0.9781
6	2.22289	-0.42865	-1.04694
6	2.34212	0.35983	1.25306
1	0.45786	0.69454	2.2182
1	0.25739	-0.71572	-1.84074
1	2.74074	-0.74447	-1.94407
1	2.94737	0.64764	2.10368
6	-1.31765	2.49517	-0.60266
1	-1.36353	2.8918	0.41923
1	-1.82806	3.20794	-1.26089
1	-0.26707	2.45377	-0.90211
7	4.42813	-0.06748	0.00597
8	5.05218	0.27571	1.01034
8	4.94791	-0.42623	-1.05072
1	-3.96402	-2.26539	0.00053
1	-5.26752	-0.11876	-0.38189
8	-3.99682	-0.52196	1.26123

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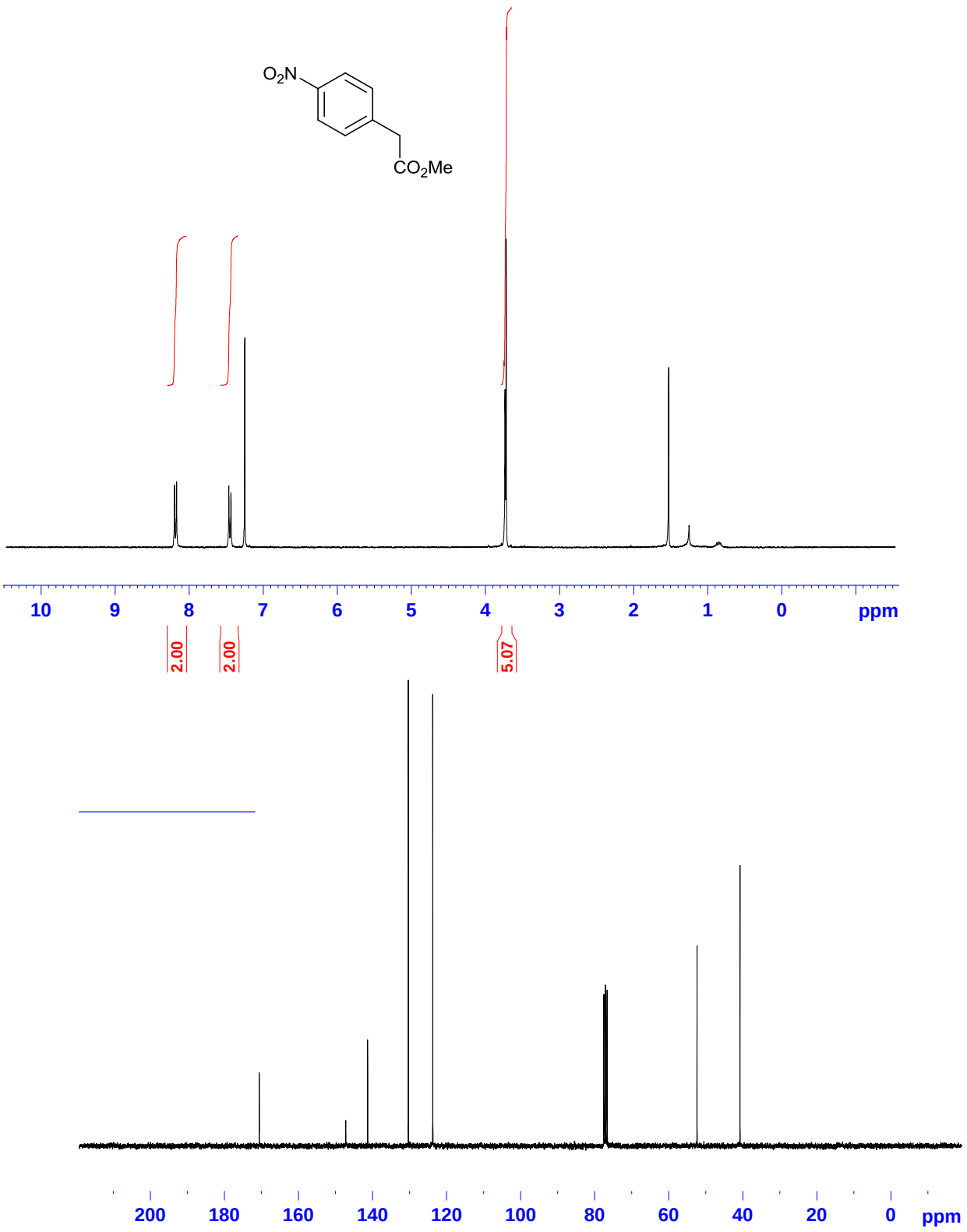
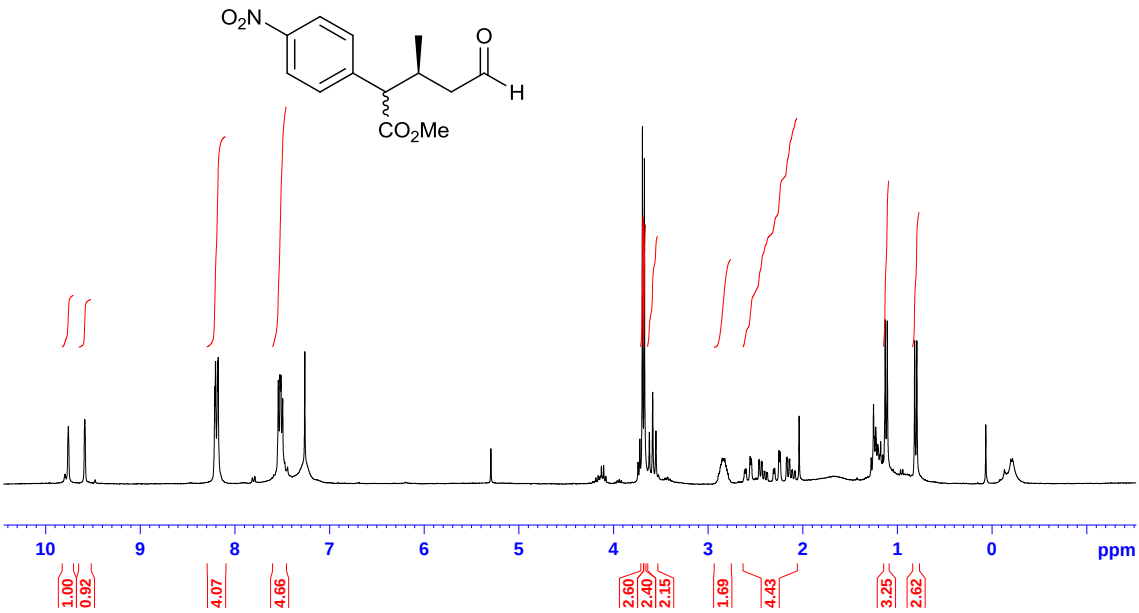
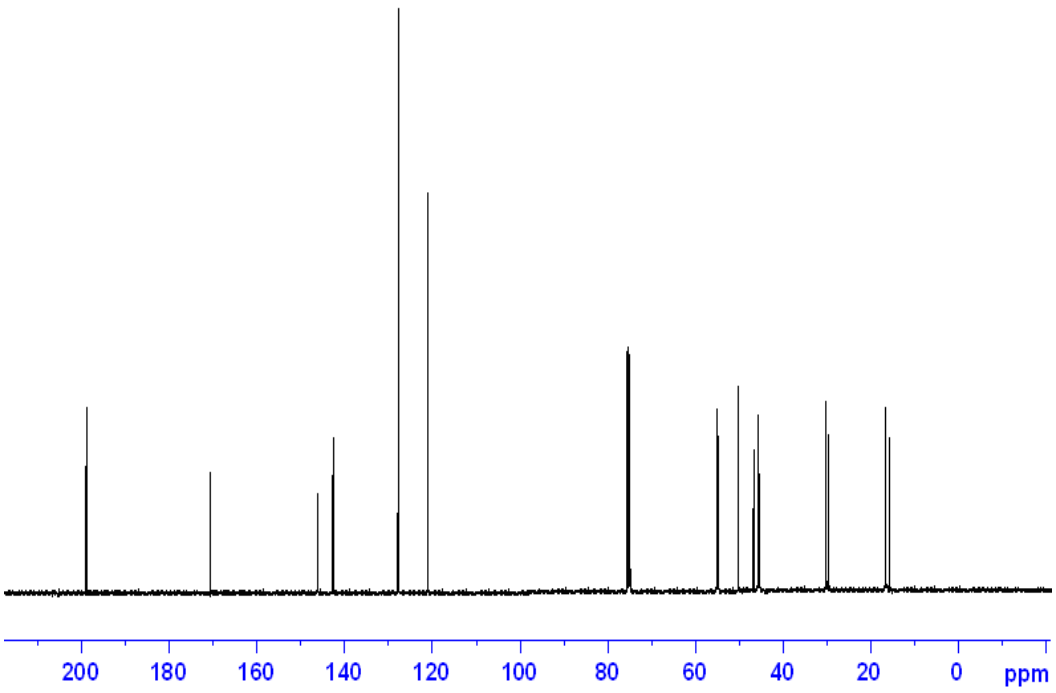
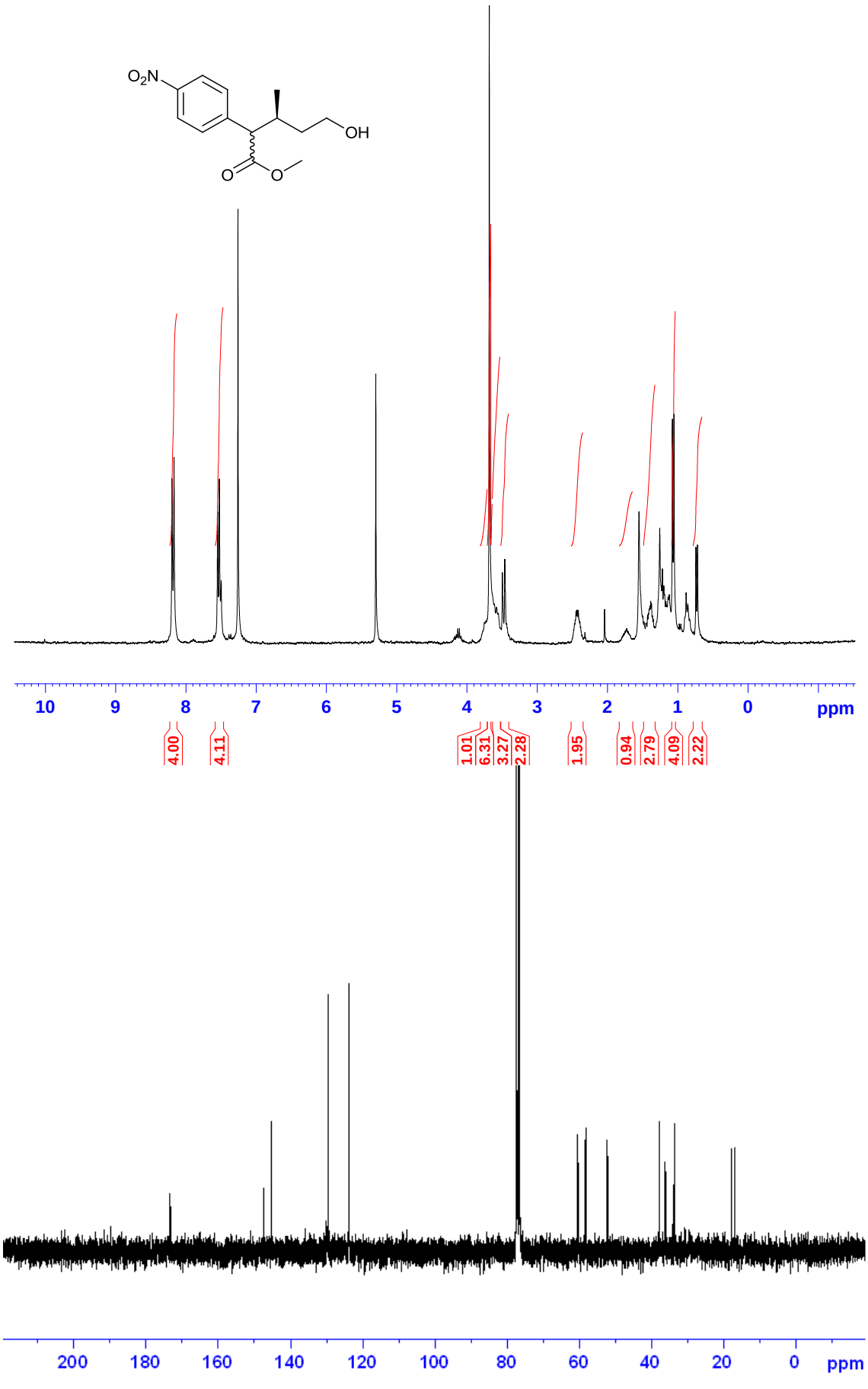
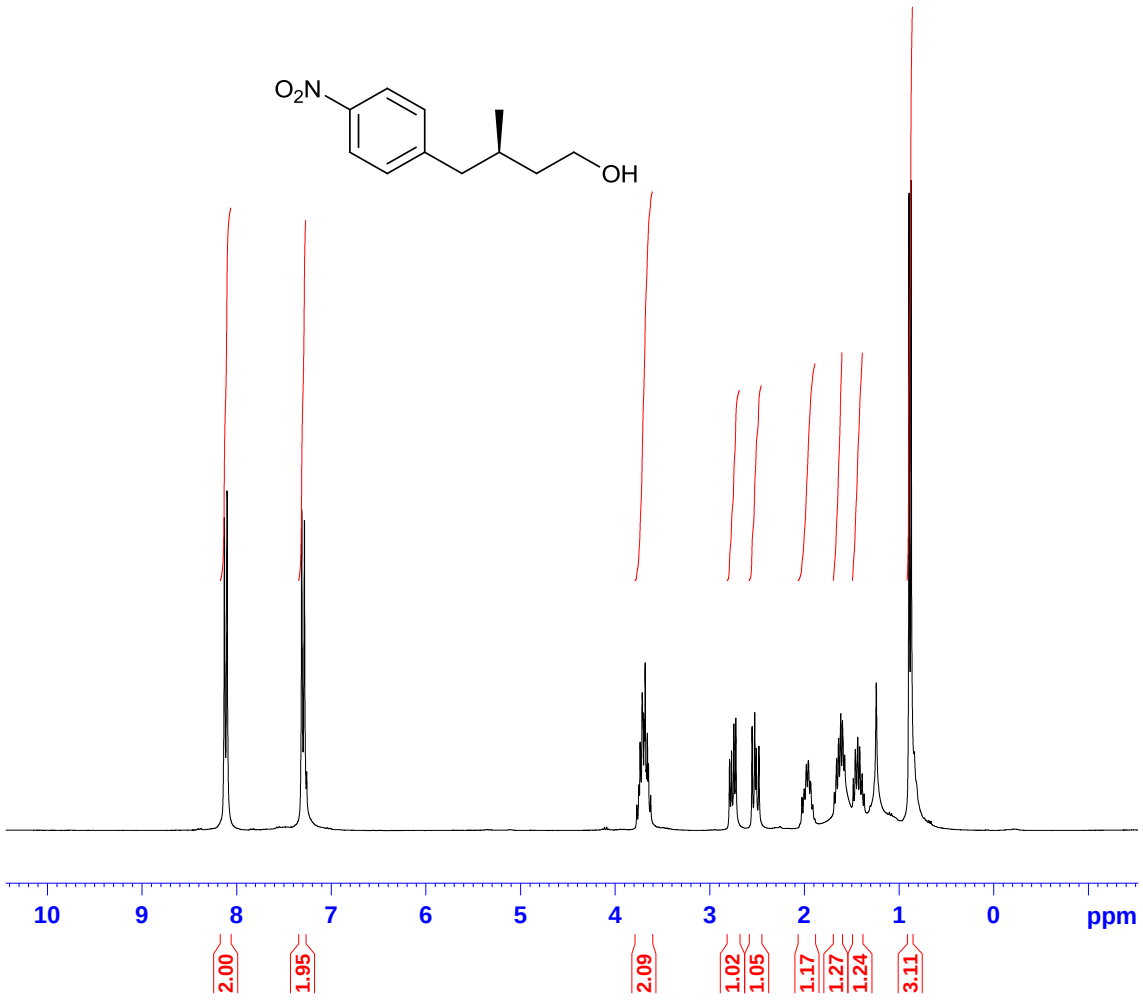
^{1}H and ^{13}C NMR spectra

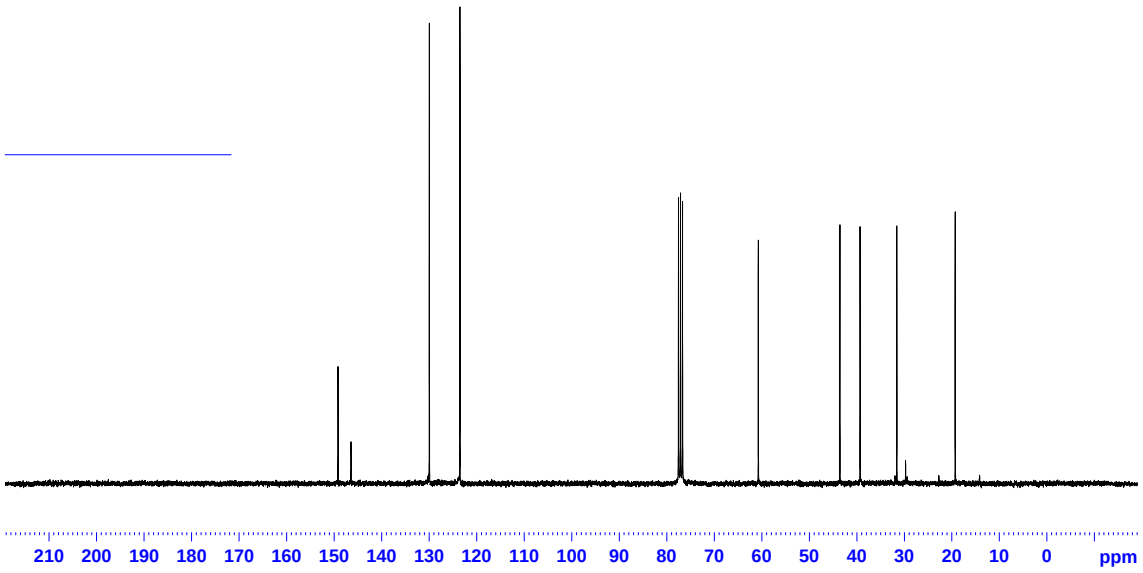


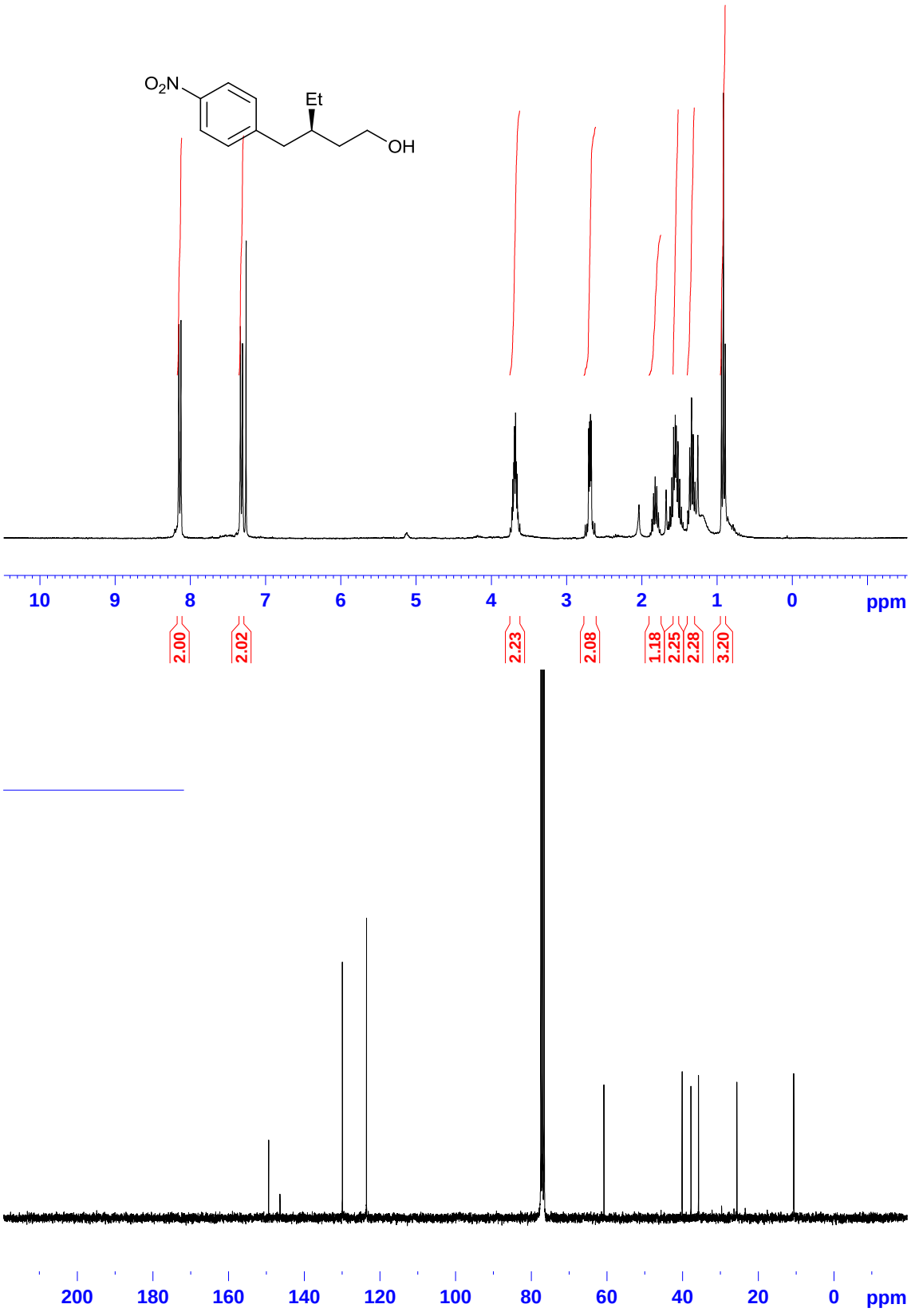

O2N
O
H
CO2Me
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.92
4.07
4.66
2.60
2.40
2.15
1.69
4.43
3.25
2.62

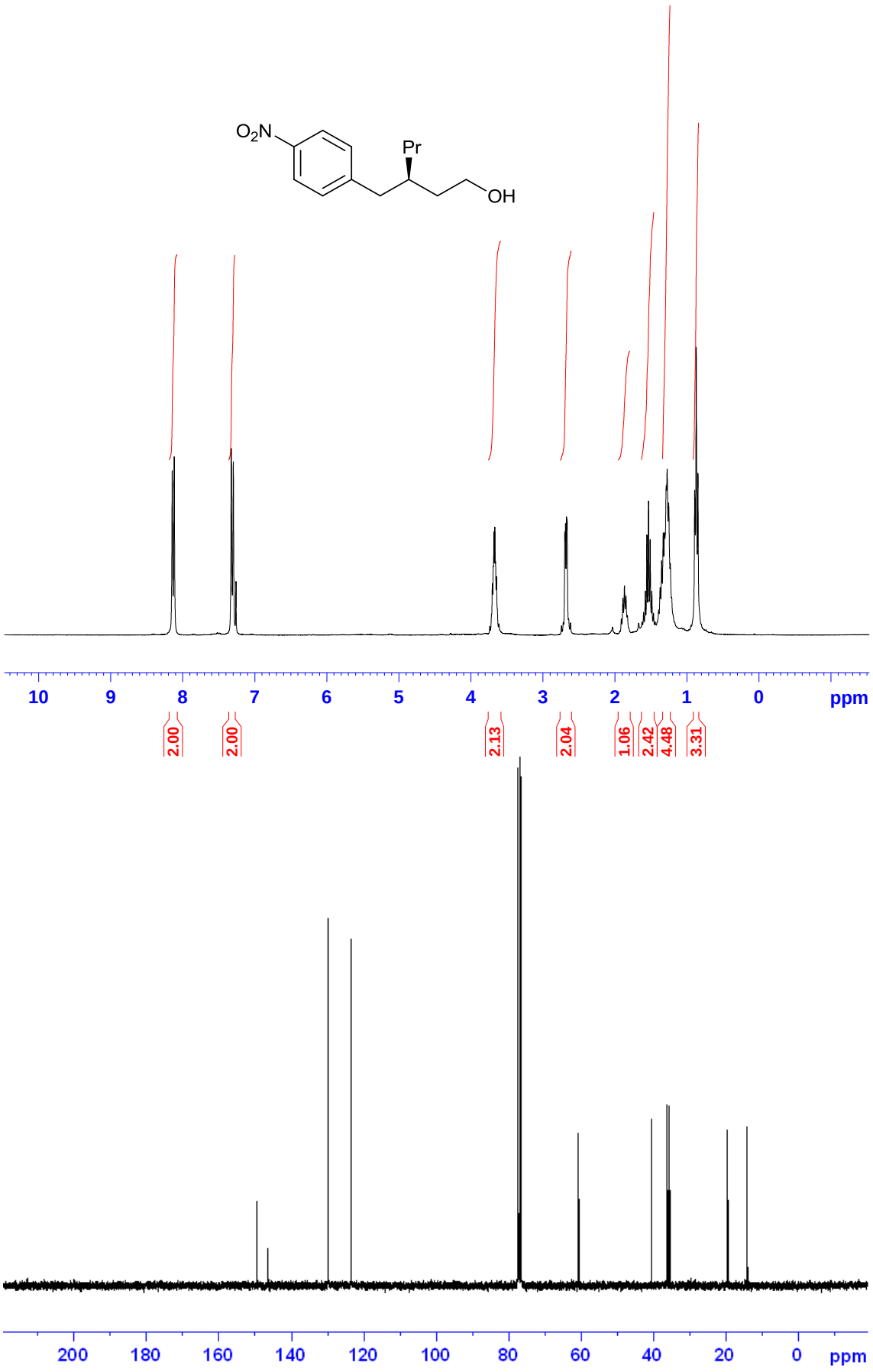

200
180
160
140
120
100
80
60
40
20
0
ppm

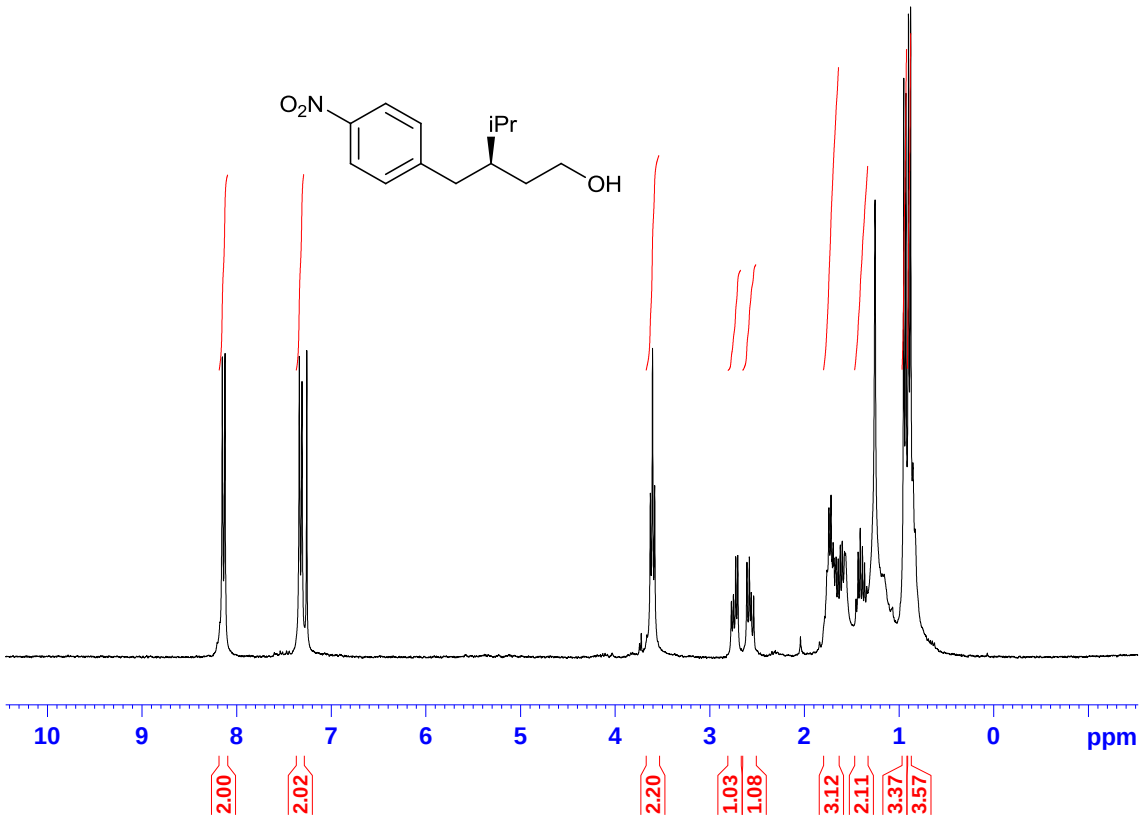

O2N
OH
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
4.11
1.01
6.31
3.27
2.28
1.95
0.94
2.79
4.09
2.22
200
180
160
140
120
100
80
60
40
20
0
ppm

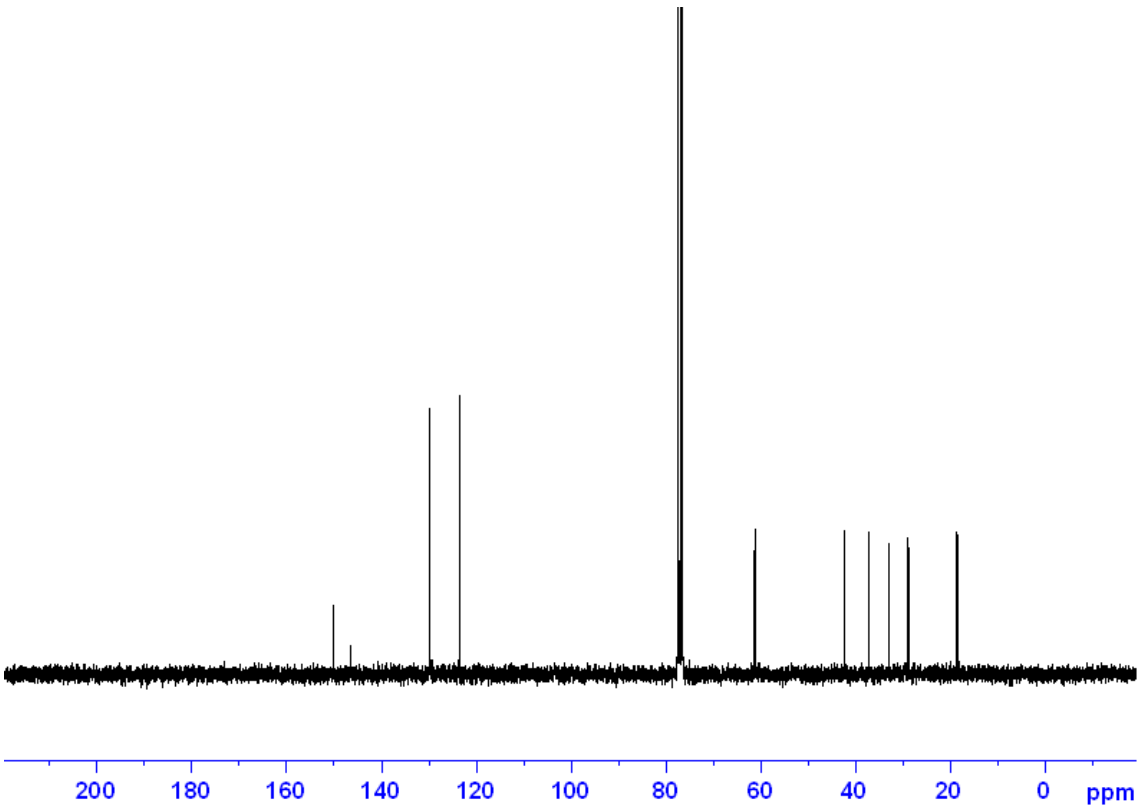

O2N
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.95
2.09
1.02
1.05
1.17
1.27
1.24
3.11


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O2N
Et
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
2.23
2.08
1.18
2.25
2.28
3.20
200
180
160
140
120
100
80
60
40
20
0
ppm


O2N
Pr
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
2.13
2.04
1.06
2.42
4.48
3.31
200
180
160
140
120
100
80
60
40
20
0
ppm


O2N
iPr
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.02
2.20
1.03
1.08
3.12
2.11
3.37
3.57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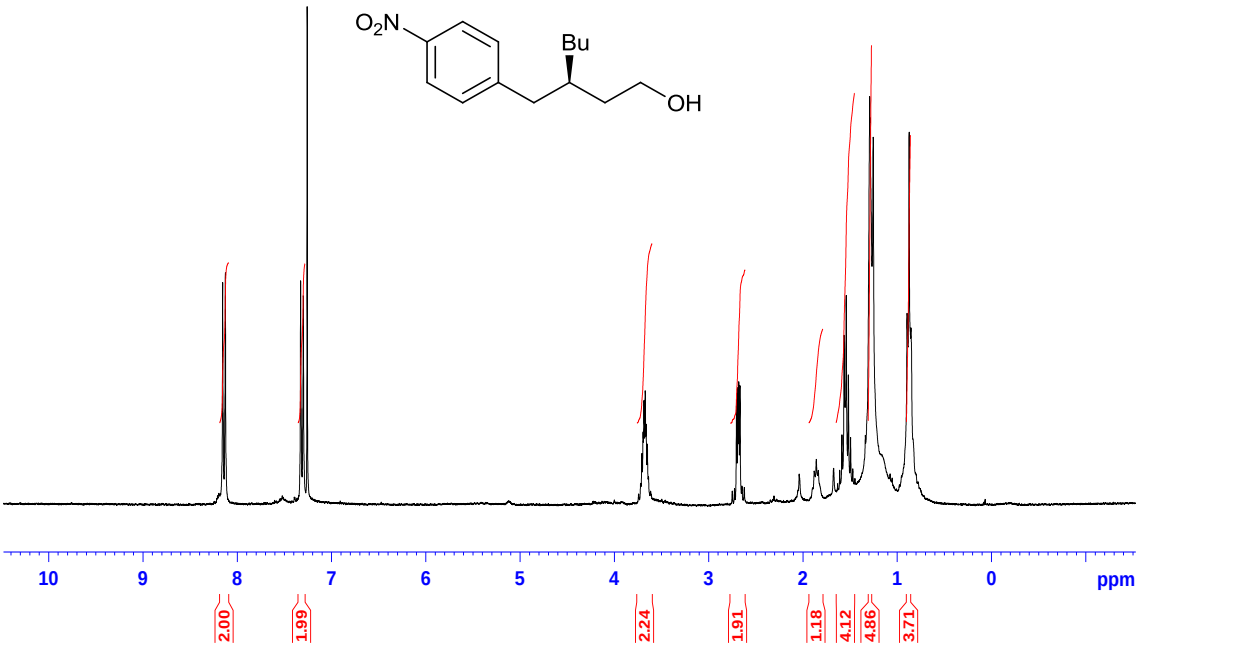
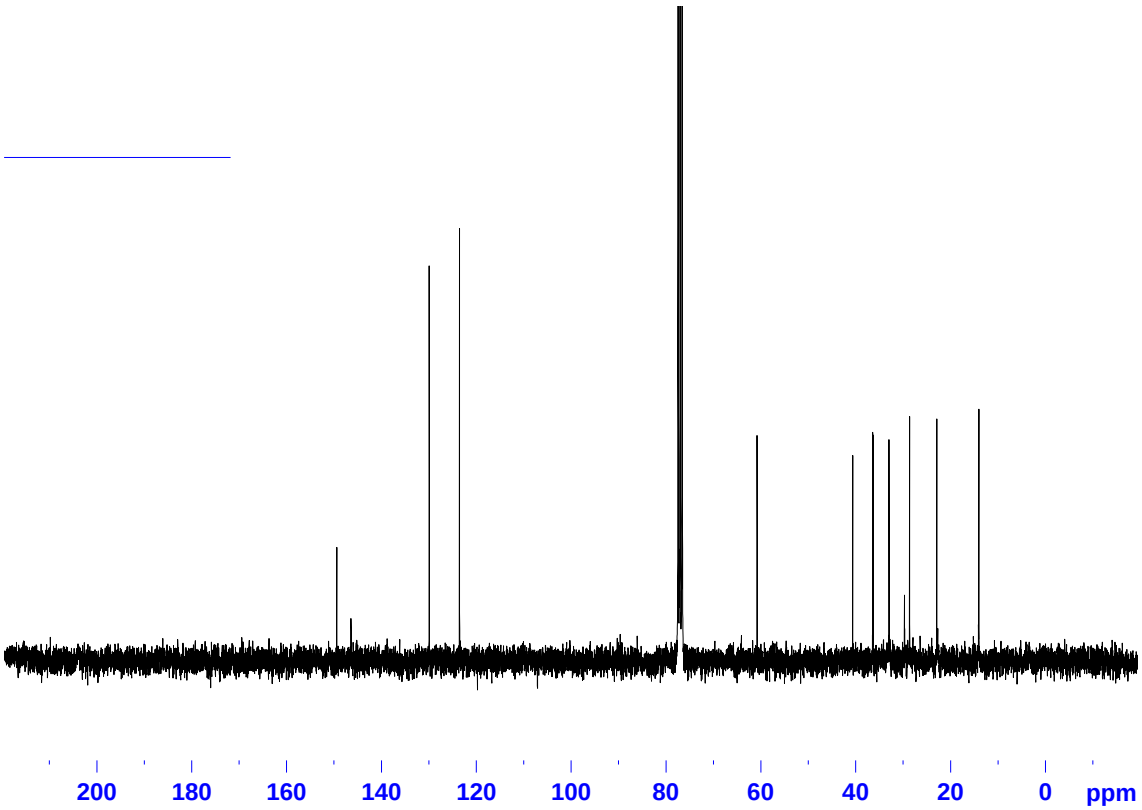
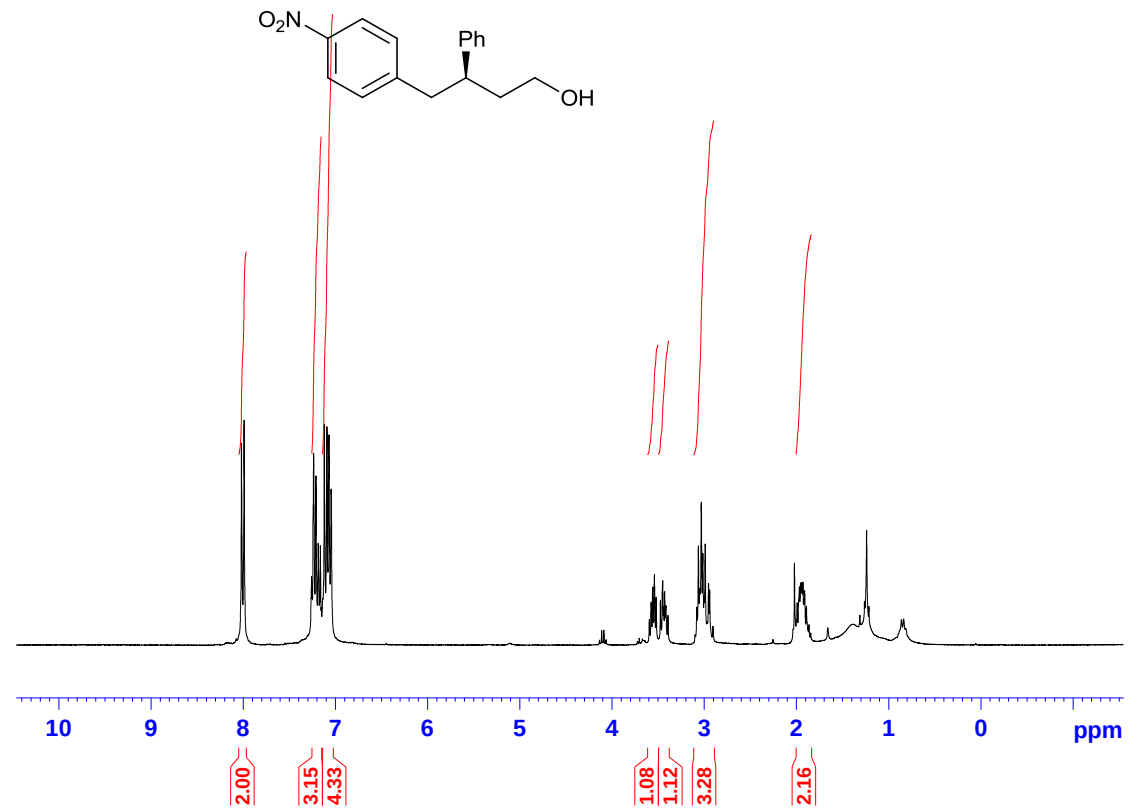
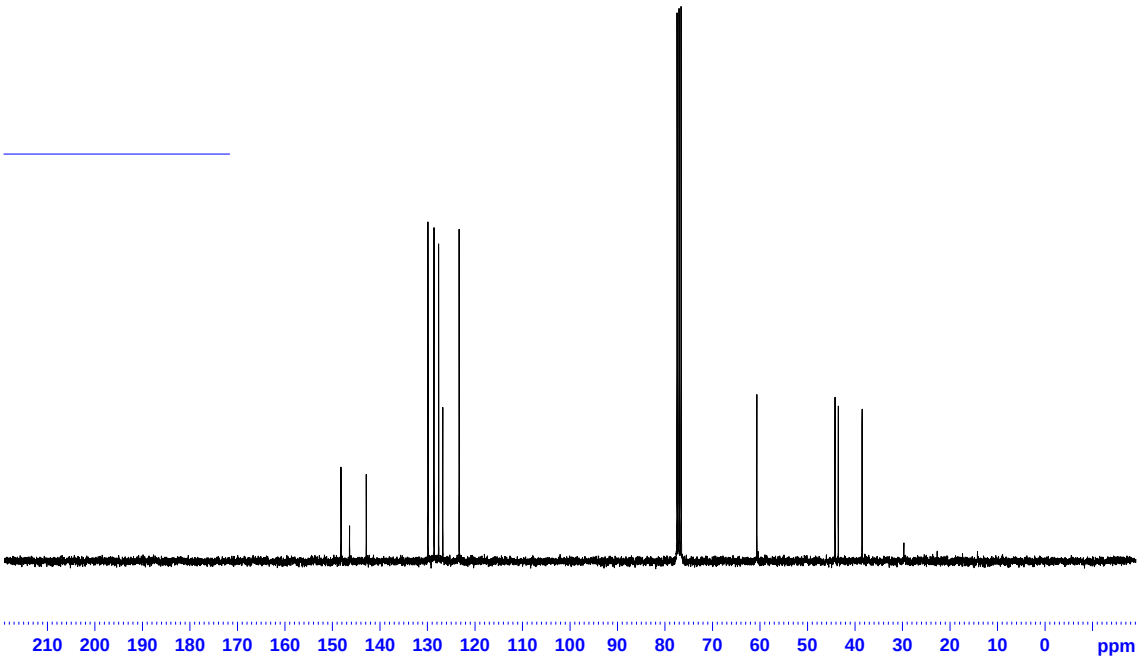
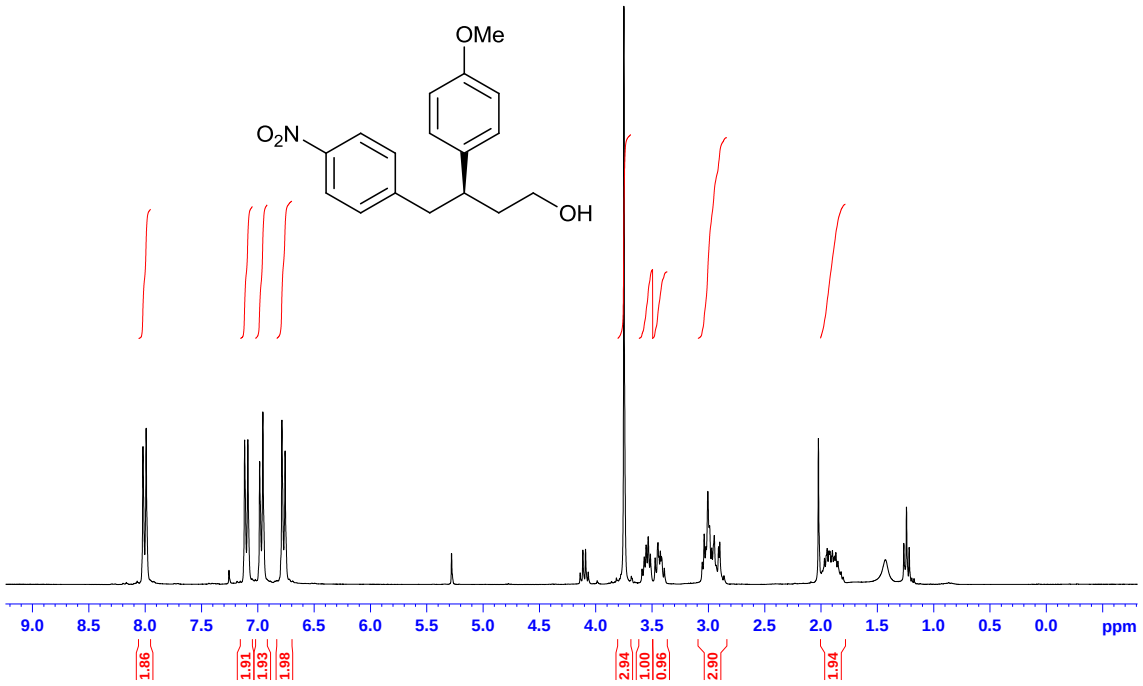
180
160
140
120
100
80
60
40
20
0
ppm

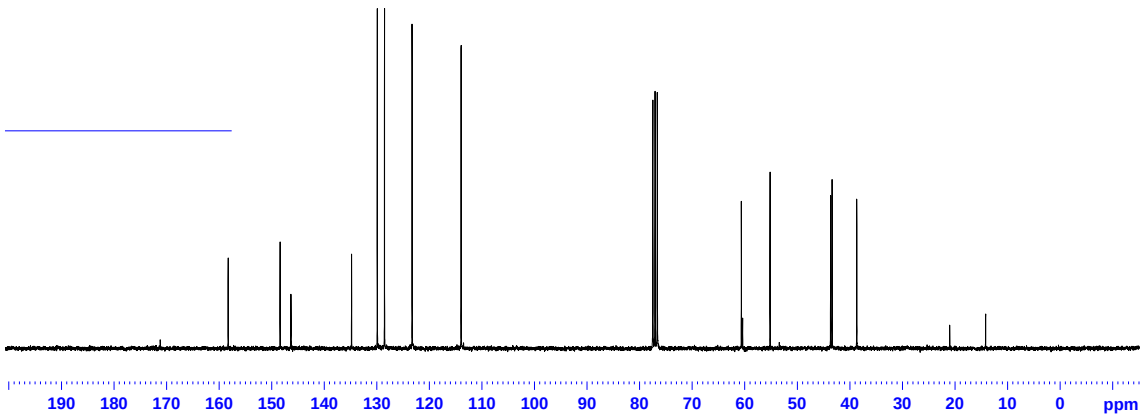

O2N
Bu
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.99
2.24
1.91
1.18
4.12
4.86
3.71

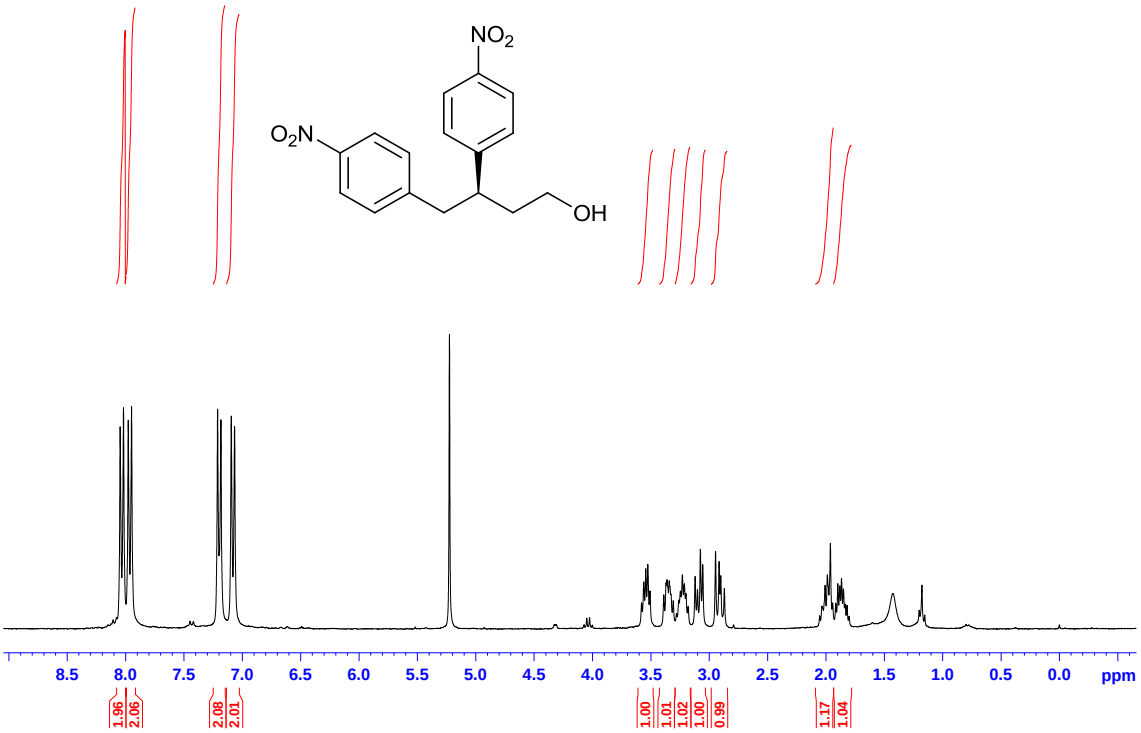

200
180
160
140
120
100
80
60
40
20
0
ppm

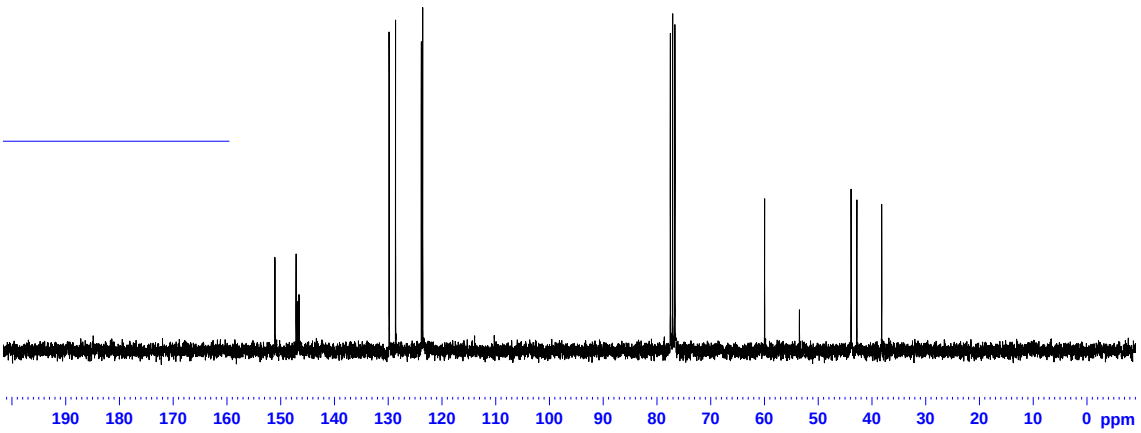

O2N
Ph
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
3.15
4.33
1.08
1.12
3.28
2.16

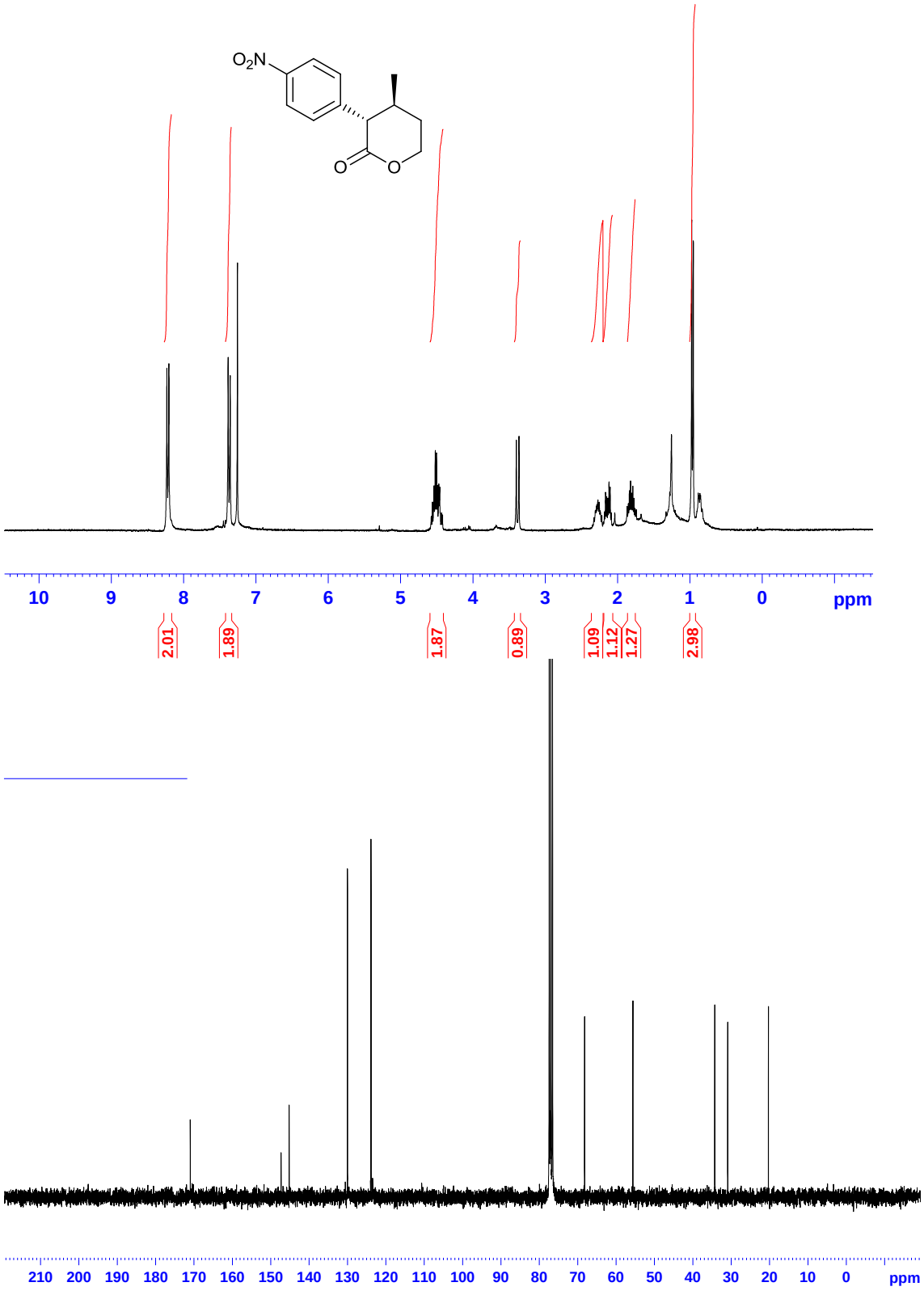

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

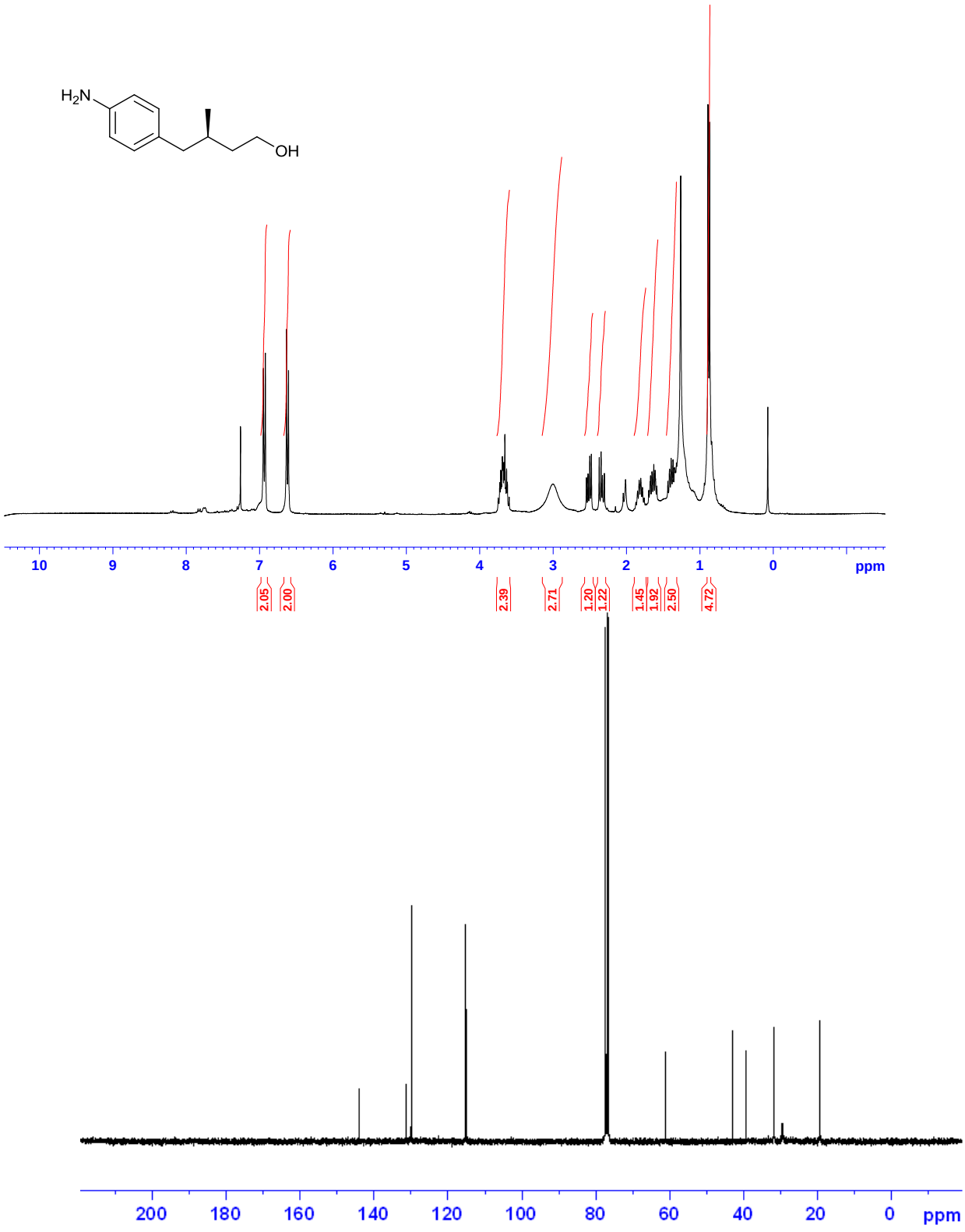

OMe
O2N
OH
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.86
1.91
1.93
1.98
2.94
1.00
0.96
2.90
1.94

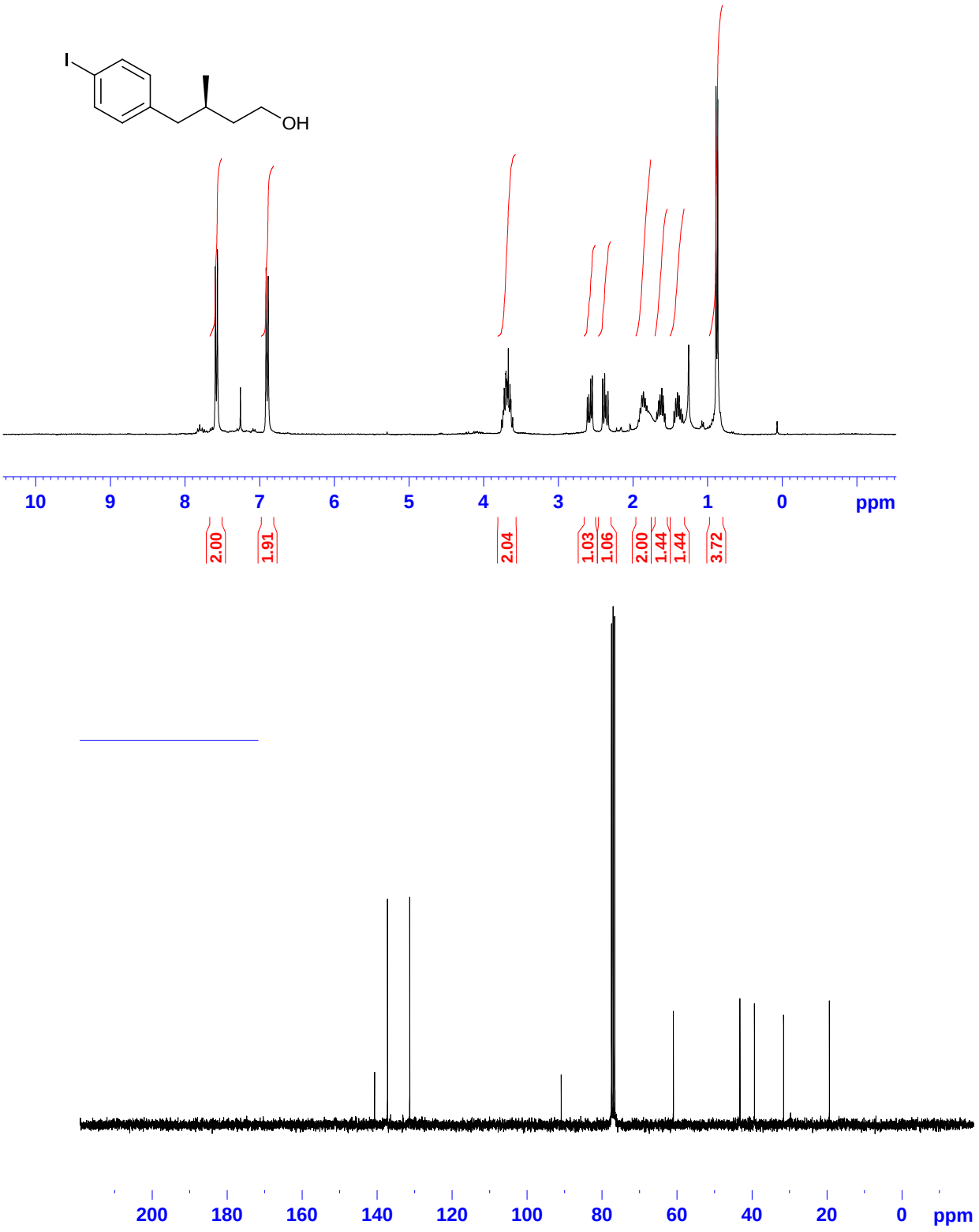

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


NO2
O2N
OH
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
1.96
2.06
2.08
2.01
1.00
1.01
1.02
1.00
0.99
1.17
1.04


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O2N
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.89
1.87
0.89
1.09
1.12
1.27
2.98
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


H2N
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.05
2.00
2.39
2.71
1.20
1.22
1.45
1.92
2.50
4.72
200
180
160
140
120
100
80
60
40
20
0
ppm


I
OH
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.91
2.04
1.03
1.06
2.00
1.44
1.44
3.72
200
180
160
140
120
100
80
60
40
20
0
ppm

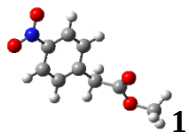
Theoretical calculations.

Geometries have been fully optimized at the DFT (B3LYP)[1] level, in the solvent-phase (CH_2CL_2) with the CPCM model,[2] by using the Gaussian09 program.[3] The standard 6-31G(d)[4] basis set was used for all the atoms. Frequencies and zero-point energy (ZPE) were also computed at the same level of theory. Final energies were obtained using the more extended 6-311G(d,p)[5] basis set for all atoms. Relative free energies (in kcal/mol) were evaluated at the B3LYP/6-311G(d,p) level with ZPE and entropy corrections evaluated at 298 K using the frequencies previously calculated at B3LYP/6-31G(d) level. For the study of the deprotonation step, Me_4N^+ ion has been used as a simplified model for the corresponding tBu$_4$N$^+$ one.

Several conformations and orientations of the nucleophilic enol were studied being the approach through *Re*-faces of both iminium ion (the less hindered face of iminium) and enol the less energy demanding. From this approach the corresponding TSs with enolate were studied as well as the corresponding TSs through *si*-faces of both enol and enolate. In the case of the study of the Michael addition, the enantiomer of the catalyst, (*S*)-**II**, was used in all the calculations.

Cartesian coordinates (Å) and energies (hartrees) of all the optimized structures.

1 (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B***1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.***1993**, *98*, 5648.
2 (a) Barone, V.; Cossi, M. *J. Phys. Chem*. A **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. J*. Comput. Chem.***2003**, *24*, 669.
3 Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
4(a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
5 Krishnan, R.; Binkley, J.S.; Seeger, R.; Pople, J.A. *J. Chem. Phys.***1980**, *72*, 650. The inclusion of diffuse functions in the basis sets are avoided in the PCM single-point energy calculations, as this could lead to electron density tails going beyond the solute cavities generated by the molecularly shaped interlocking spheres. It has also been reported that the use of more extended basis sets often worsen the results obtained using the continuum models. See: (a) Patil, M. P.; Sunoj, R. B. *Chem. Asian J*. **2009**, *4*, 714. (b) Sadlej-Sosnowska, N. *Theor. Chem. Acc*. **2007**, *118*, 281.



1

E(B3LYP 6-31G*) = -703.949193189
Zero-point correction= 0.174659
Thermal correction to Gibbs Free Energy= 0.132691
E(B3LYP 6-311G**) = -704.136649816
Number of imaginary frequencies: 0

6	0	0.41869	0.38284	0.61906
6	0	-2.27386	0.02779	0.02188
6	0	-0.19056	-0.86994	0.79377
6	0	-0.35117	1.45087	0.13805
6	0	-1.69997	1.28443	-0.16358
6	0	-1.53591	-1.05699	0.49838
1	0	0.39364	-1.70552	1.16531
1	0	0.10712	2.42563	-0.00074
1	0	-2.30076	2.10552	-0.53362
1	0	-2.01431	-2.0188	0.63313
7	0	-3.6925	-0.15856	-0.28802
8	0	-4.18395	-1.2768	-0.11604
8	0	-4.32952	0.81134	-0.70664
6	0	1.87853	0.58193	0.94717
1	0	2.1013	0.19093	1.94947
1	0	2.1395	1.6434	0.96676
6	0	2.825	-0.13379	-0.01184
8	0	2.5371	-1.07347	-0.72368
8	0	4.05518	0.40245	0.06326
6	0	5.06666	-0.2239	-0.75301
1	0	4.79526	-0.16041	-1.80929
1	0	5.98225	0.33376	-0.55907
1	0	5.18835	-1.27222	-0.47035

Me_4NOH

E(B3LYP 6-31G*) = -290.141006113
Zero-point correction= 0.17487711
Thermal correction to Gibbs Free Energy= 0.14241111
E(B3LYP 6-311G**) = -290.244499533
Number of imaginary frequencies: 0

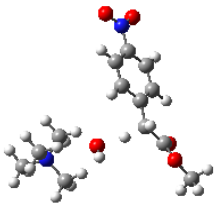
7	0	0.57889	-0.00692	-0.00003
6	0	-0.02707	-0.65923	-1.22124
1	0	0.37943	-0.16801	-2.10817
1	0	0.25337	-1.71483	-1.21712
1	0	-1.12235	-0.50009	-1.09035
6	0	0.1674	1.44233	-0.00032

1	0	0.57417	1.9195	0.89328
1	0	-0.92582	1.43863	0.00086
1	0	0.57223	1.91863	-0.89527
6	0	-0.02677	-0.65836	1.22175
1	0	-1.12195	-0.49906	1.09086
1	0	0.2535	-1.71399	1.21829
1	0	0.37993	-0.16656	2.10827
6	0	2.06797	-0.13339	-0.00014
1	0	2.33144	-1.19215	0.00012
1	0	2.46587	0.3493	-0.89463
1	0	2.46598	0.34974	0.89408
8	0	-2.587	0.10902	-0.00044
1	0	-2.95125	-0.79299	0.00312

Br^-

E(B3LYP 6-31G*) = -13.3363474535
Zero-point correction= 0.000000
Thermal correction to Gibbs Free Energy= -0.016176
E(B3LYP 6-311G**) = -13.5525490616
Number of imaginary frequencies: 0

35	0	-1.99367	3.10365	-0.82681

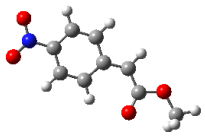


$TS_{deprotonation}$

E(B3LYP 6-31G*) = -994.107756861
Zero-point correction= 0.34901486
Thermal correction to Gibbs Free Energy= -0.29296786
E(B3LYP 6-311G**) = -994.395176
Number of imaginary frequencies: 1 (-112.6552)

6	0	-1.23725	0.95144	0.46948
6	0	-3.24982	-0.94998	0.0352
6	0	-1.42955	-0.12767	1.36123
6	0	-2.0747	1.03053	-0.66007
6	0	-3.07827	0.09346	-0.87754
6	0	-2.42432	-1.07085	1.15891
1	0	-0.75654	-0.22776	2.20717
1	0	-1.93169	1.83524	-1.37007
1	0	-3.72929	0.16355	-1.74043
1	0	-2.56751	-1.89599	1.84568
7	0	-4.2967	-1.93006	-0.18912
8	0	-4.43827	-2.84134	0.63678

8	0	-5.00624	-1.81635	-1.19689
6	0	-0.13434	1.90608	0.79242
1	0	0.86287	1.22798	0.88416
1	0	-0.23922	2.2826	1.81555
6	0	0.15006	3.03106	-0.13046
8	0	0.01399	3.05111	-1.34634
8	0	0.7022	4.0773	0.54363
6	0	1.134	5.18229	-0.2645
1	0	0.29244	5.61632	-0.81134
1	0	1.54762	5.91216	0.43229
1	0	1.89857	4.86646	-0.97987
7	0	3.74349	-2.07539	-0.30535
6	0	3.66689	-2.32274	1.18147
1	0	3.25956	-3.32231	1.3439
1	0	4.67574	-2.25932	1.59322
1	0	3.00992	-1.5371	1.58013
6	0	2.34761	-2.14238	-0.86953
1	0	2.39615	-1.93822	-1.94021
1	0	1.76216	-1.38555	-0.34541
1	0	1.95057	-3.14396	-0.69747
6	0	4.28161	-0.68266	-0.53269
1	0	3.5777	-0.00789	-0.02001
1	0	5.28554	-0.62986	-0.10758
1	0	4.32153	-0.50172	-1.60831
6	0	4.62114	-3.09534	-0.96392
1	0	5.62263	-3.02572	-0.53735
1	0	4.20661	-4.08827	-0.78358
1	0	4.65613	-2.89246	-2.03519
8	0	1.96177	0.21039	1.198
1	0	2.465	0.7215	1.85448



Enolate

E(B3LYP 6-31G*) = -703.4555885

Zero-point correction= 0.16123648

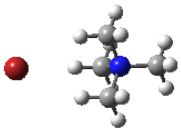
Thermal correction to Gibbs Free Energy= -0.12158348

E(B3LYP 6-311G**) = -703.64982

Number of imaginary frequencies: 0

6	0	-0.44959	0.51487	-0.00003
6	0	2.35953	0.00407	-0.00002
6	0	0.08182	-0.82454	-0.00004
6	0	0.52614	1.57504	-0.00001
6	0	1.87692	1.33451	0.
6	0	1.4342	-1.06621	-0.00004
1	0	-0.61951	-1.64953	-0.00005

1	0	0.16875	2.60249	0.
1	0	2.58971	2.151	0.00003
1	0	1.81371	-2.08177	-0.00005
7	0	3.7448	-0.24962	0.00001
8	0	4.15386	-1.43726	0.00003
8	0	4.54709	0.71724	0.00005
6	0	-1.81618	0.83334	-0.00003
1	0	-2.09126	1.88411	-0.00001
6	0	-2.90123	-0.09389	-0.00002
8	0	-2.87755	-1.33171	-0.00001
8	0	-4.11943	0.57296	-0.00002
6	0	-5.27282	-0.26507	0.00008
1	0	-5.30371	-0.90533	0.88822
1	0	-6.13207	0.40923	0.00005
1	0	-5.30376	-0.90546	-0.88797



Me_4NBr

E(B3LYP 6-31G*) = -227.5922744

Zero-point correction= 0.1652184

Thermal correction to Gibbs Free Energy= 0.1301644

E(B3LYP 6-311G**) = -227.870466

Number of imaginary frequencies: 0

7	0	1.83393	-0.00061	-0.00009
6	0	1.32266	-0.68572	1.24251
1	0	1.69323	-1.71158	1.24955
1	0	1.69551	-0.14588	2.11387
1	0	0.2303	-0.66648	1.21106
6	0	1.31952	-0.73372	-1.21372
1	0	1.6893	-0.22784	-2.10649
1	0	0.22723	-0.71372	-1.17929
1	0	1.691	-1.75878	-1.18182
6	0	1.322	1.41784	-0.02712
1	0	0.2297	1.37981	-0.02623
1	0	1.69432	1.93669	0.8572
1	0	1.69408	1.90273	-0.93062
6	0	3.33636	0.00072	-0.00172
1	0	3.68784	0.53538	0.88147
1	0	3.69002	-1.03071	0.01742
1	0	3.68611	0.50073	-0.90564
35	0	-2.24427	0.00026	0.00001

H_2O

E(B3LYP 6-31G*) = -76.41554103

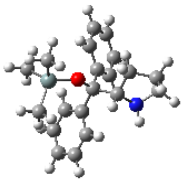
Zero-point correction= 0.02113403

Thermal correction to Gibbs Free Energy= 0.00346303

E(B3LYP 6-311G**) = -76.4538219

Number of imaginary frequencies: 0

8	0	0.	0.	0.12062
1	0	0.	0.75912	-0.48249
1	0	0.	-0.75912	-0.48249



(*S*)-II

E(B3LYP 6-31G*) = -1197.920984

Zero-point correction= 0.42692963

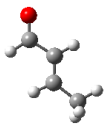
Thermal correction to Gibbs Free Energy= 0.37231063

E(B3LYP 6-311G**) = -1198.1832

Number of imaginary frequencies: 0

14	0	-2.10449	-1.6684	-0.54433
8	0	-0.57236	-1.01041	-0.77061
7	0	1.85316	1.75185	-1.29324
6	0	1.91834	-0.50902	-2.16896
1	0	2.3123	-1.17262	-1.39247
1	0	1.38752	-1.12973	-2.89515
6	0	0.99305	0.57115	-1.55283
1	0	0.23098	0.81687	-2.30083
6	0	3.2218	1.4413	-1.76158
1	0	3.69866	2.34131	-2.16277
1	0	3.82713	1.09719	-0.9118
6	0	3.06454	0.30786	-2.78524
1	0	2.76731	0.71727	-3.75948
1	0	3.97931	-0.27764	-2.92957
6	0	0.19696	0.10056	-0.28507
6	0	-0.74051	1.20877	0.24688
6	0	-1.24717	2.2237	-0.57992
1	0	-0.95054	2.28897	-1.62069
6	0	-2.15059	3.17168	-0.09442
6	0	-2.5782	3.12509	1.23312
1	0	-3.28055	3.86308	1.61103
6	0	-2.08835	2.12095	2.06993
6	0	-1.17907	1.18133	1.58117
1	0	-0.79896	0.41849	2.25211
6	0	1.16877	-0.37886	0.80746

6	0	1.35246	-1.74231	1.06989
1	0	0.7794	-2.47057	0.50829
6	0	2.26666	-2.17421	2.03604
6	0	3.02181	-1.24719	2.75407
1	0	3.73228	-1.58048	3.50599
6	0	2.85303	0.11619	2.49691
6	0	1.9356	0.54564	1.53716
1	0	1.8153	1.60435	1.34108
6	0	-3.48123	-0.52666	-1.1468
1	0	-4.43702	-1.06679	-1.13424
1	0	-3.30129	-0.19667	-2.17693
1	0	-3.59116	0.36536	-0.52232
6	0	-2.4378	-2.18501	1.24232
1	0	-3.37262	-2.75901	1.28691
1	0	-2.54423	-1.32601	1.91267
1	0	-1.63723	-2.82275	1.63442
6	0	-2.05496	-3.20513	-1.63639
1	0	-3.01782	-3.73028	-1.61076
1	0	-1.28233	-3.90925	-1.30555
1	0	-1.84452	-2.94381	-2.68023
1	0	3.43371	0.85073	3.04935
1	0	2.38622	-3.2385	2.22268
1	0	-2.40692	2.06965	3.10778
1	0	-2.51948	3.94781	-0.75984
1	0	1.49328	2.54604	-1.81387



2a

E(B3LYP 6-31G*) = -231.2399495

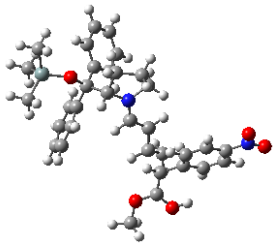
Zero-point correction= 0.09003648

Thermal correction to Gibbs Free Energy= 0.06140948

E(B3LYP 6-311G**) = -231.306412

Number of imaginary frequencies: 0

6	0	1.39859	0.33278	-0.0002
1	0	1.35794	1.44385	-0.00057
6	0	0.0936	-0.32853	-0.00056
1	0	0.08606	-1.41696	-0.00095
6	0	-1.04278	0.39052	-0.00011
1	0	-0.96135	1.47913	0.00025
6	0	-2.42887	-0.16598	0.00024
1	0	-2.43285	-1.25967	-0.00173
1	0	-2.98294	0.18693	0.88013
1	0	-2.98492	0.19027	-0.87702
8	0	2.47435	-0.24953	0.00046



TSiminium-*re*-enol

E(B3LYP 6-31G*) = -2057.08267

Zero-point correction= 0.68327587

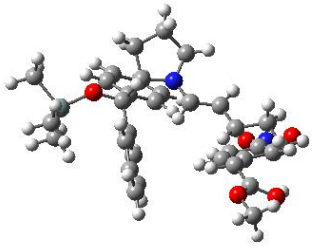
Thermal correction to Gibbs Free Energy= 0.60399287

E(B3LYP 6-311G**) = -2057.564

Number of imaginary frequencies: 1 (-351.2546)

14	0	-5.49686	-0.01298	-1.47741
8	0	-3.97533	-0.66875	-1.11882
7	0	-0.40818	-1.04247	-0.14938
6	0	-1.86435	-2.49595	-1.35127
1	0	-2.60504	-2.9779	-0.70876
1	0	-2.22483	-2.56392	-2.37907
6	0	-1.67068	-1.02068	-0.92629
1	0	-1.51388	-0.40005	-1.81189
6	0	0.09755	-2.41193	0.04253
1	0	1.19009	-2.40259	0.05189
1	0	-0.25776	-2.81841	0.99739
6	0	-0.49075	-3.15815	-1.15766
1	0	0.14555	-2.99827	-2.03515
1	0	-0.56236	-4.23491	-0.98185
6	0	-2.93716	-0.42545	-0.17067
6	0	-2.80131	1.09977	0.06083
6	0	-2.40605	1.92978	-1.00499
1	0	-2.17559	1.501	-1.97498
6	0	-2.3195	3.31406	-0.85559
6	0	-2.64171	3.91092	0.36559
1	0	-2.57529	4.98864	0.4849
6	0	-3.06044	3.10705	1.42457
6	0	-3.14093	1.71963	1.27233
1	0	-3.47981	1.12336	2.11062
6	0	-3.18639	-1.2237	1.12318
6	0	-4.23403	-2.15094	1.20194
1	0	-4.89168	-2.28399	0.35198
6	0	-4.43526	-2.92146	2.35066
6	0	-3.5836	-2.78769	3.44629
1	0	-3.73755	-3.38595	4.34
6	0	-2.52876	-1.87455	3.38095
6	0	-2.33262	-1.10275	2.23466
1	0	-1.51229	-0.39366	2.21928
6	0	-5.34308	1.33367	-2.78854
1	0	-6.34133	1.62385	-3.14076

1	0	-4.77631	0.9773	-3.65712
1	0	-4.84692	2.2314	-2.4066
6	0	-6.40047	0.65517	0.0377
1	0	-7.4193	0.94317	-0.25204
1	0	-5.90972	1.54038	0.45458
1	0	-6.47942	-0.09444	0.83257
6	0	-6.43402	-1.47256	-2.21381
1	0	-7.4239	-1.15454	-2.56373
1	0	-6.58218	-2.27778	-1.48496
1	0	-5.89724	-1.89269	-3.07255
6	0	0.28997	0.05365	0.17096
1	0	-0.12615	0.98116	-0.21344
6	0	1.43052	0.11672	0.94836
1	0	1.84814	-0.78121	1.39363
6	0	2.08969	1.36017	1.183
1	0	1.5189	2.24643	0.90626
6	0	2.87205	1.50711	2.46737
1	0	3.53303	0.65223	2.63958
1	0	3.46099	2.42787	2.5073
1	0	2.15888	1.53776	3.30088
1	0	-1.85599	-1.75567	4.22603
1	0	-5.25859	-3.63	2.3811
1	0	-3.33026	3.55464	2.37717
1	0	-2.00599	3.92487	-1.69773
6	0	3.42874	1.62025	-0.32283
1	0	2.66248	1.60623	-1.0906
6	0	3.91506	2.94337	-0.14079
8	0	5.10737	3.28719	0.29957
1	0	5.72169	2.52624	0.28141
6	0	4.35749	0.47006	-0.38118
6	0	6.02019	-1.76881	-0.57034
6	0	4.15887	-0.49789	-1.38633
6	0	5.39968	0.25949	0.54788
6	0	6.2378	-0.84717	0.45092
6	0	4.97999	-1.61297	-1.48744
1	0	3.35725	-0.36247	-2.10537
1	0	5.54033	0.92205	1.39734
1	0	7.03792	-1.0057	1.16268
1	0	4.83083	-2.35054	-2.26593
7	0	6.8976	-2.93516	-0.67639
8	0	7.8181	-3.04371	0.13679
8	0	6.6716	-3.74988	-1.57375
8	0	3.08271	3.92731	-0.34229
6	0	3.51462	5.30295	-0.12944
1	0	2.64999	5.90323	-0.40266
1	0	4.36555	5.52534	-0.77405
1	0	3.77552	5.44834	0.9195



TSiminium-*si*-enol

E(B3LYP 6-31G*) = -2057.082768

Zero-point correction= 0.6832711

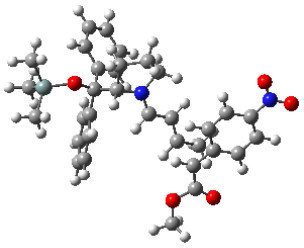
Thermal correction to Gibbs Free Energy= 0.6043321

E(B3LYP 6-311G**) = -2057.56332

Number of imaginary frequencies: 1 (-348.2244)

14	0	-5.24728	-0.59769	-0.76446
8	0	-4.03614	-0.19004	0.34942
7	0	-0.80572	-0.08873	2.17515
6	0	-2.9968	0.56792	2.85903
1	0	-3.3513	1.48834	2.38881
1	0	-3.86999	0.03746	3.24284
6	0	-2.23132	-0.29787	1.82869
1	0	-2.46763	-1.35349	1.98286
6	0	-0.64184	0.95803	3.19991
1	0	0.2228	0.729	3.82616
1	0	-0.48376	1.93307	2.72463
6	0	-1.97138	0.89551	3.95742
1	0	-1.92919	0.09256	4.70153
1	0	-2.19504	1.83028	4.47878
6	0	-2.62853	0.03598	0.32613
6	0	-1.96111	-0.9496	-0.66323
6	0	-2.07477	-2.3332	-0.43313
1	0	-2.61813	-2.69781	0.43279
6	0	-1.51675	-3.26476	-1.30877
6	0	-0.83849	-2.83624	-2.45252
1	0	-0.40389	-3.55928	-3.13688
6	0	-0.74169	-1.46949	-2.7124
6	0	-1.29887	-0.53865	-1.82899
1	0	-1.22085	0.51528	-2.06639
6	0	-2.32217	1.5152	0.02045
6	0	-3.35806	2.4478	-0.11906
1	0	-4.38532	2.1184	-0.03076
6	0	-3.0909	3.80061	-0.34796
6	0	-1.7755	4.25434	-0.43243
1	0	-1.56504	5.30539	-0.60904
6	0	-0.73015	3.33992	-0.28444
6	0	-1.00007	1.98873	-0.06168
1	0	-0.16751	1.30198	0.04187
6	0	-5.56242	-2.45727	-0.73788
1	0	-6.47205	-2.68585	-1.30794

1	0	-5.71567	-2.8175	0.28655
1	0	-4.73917	-3.0287	-1.17827
6	0	-4.87086	-0.02178	-2.52032
1	0	-5.74686	-0.21001	-3.15428
1	0	-4.02064	-0.55415	-2.95853
1	0	-4.65546	1.05161	-2.56039
6	0	-6.77709	0.27778	-0.09662
1	0	-7.65807	0.01647	-0.69594
1	0	-6.674	1.36885	-0.11747
1	0	-6.98043	-0.01936	0.93899
6	0	0.16869	-0.93834	1.82245
1	0	-0.17248	-1.79657	1.24918
6	0	1.51374	-0.83746	2.1192
1	0	1.90632	0.04841	2.60915
6	0	2.42562	-1.88438	1.78873
1	0	1.97074	-2.84118	1.53597
6	0	3.66947	-2.00355	2.64025
1	0	3.36871	-2.33864	3.64103
1	0	4.38806	-2.73192	2.25482
1	0	4.1707	-1.03829	2.76264
1	0	0.30163	3.67597	-0.34394
1	0	-3.91782	4.49758	-0.45386
1	0	-0.23898	-1.11774	-3.60923
1	0	-1.6183	-4.32576	-1.09801
6	0	3.05841	-1.59981	-0.12609
1	0	2.08334	-1.81627	-0.55151
6	0	3.94892	-2.68111	-0.35974
8	0	5.26078	-2.60834	-0.45127
1	0	5.55519	-1.68051	-0.54901
6	0	3.50712	-0.20445	-0.33537
6	0	4.23173	2.45974	-0.7635
6	0	2.69323	0.65312	-1.10185
6	0	4.68669	0.32507	0.22965
6	0	5.05741	1.64901	0.01132
6	0	3.04616	1.97824	-1.3202
1	0	1.78079	0.26658	-1.54487
1	0	5.30724	-0.27062	0.89272
1	0	5.96185	2.05459	0.44668
1	0	2.42496	2.63239	-1.91893
7	0	4.61045	3.85554	-0.98873
8	0	5.67835	4.2498	-0.51554
8	0	3.84077	4.5659	-1.63921
8	0	3.44563	-3.884	-0.40586
6	0	4.31889	-5.03258	-0.61072
1	0	3.64346	-5.88441	-0.6387
1	0	5.0195	-5.11689	0.22079
1	0	4.85229	-4.92458	-1.55572

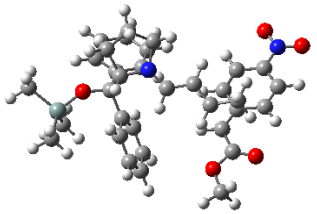


TSiminium-*re*-enolate

E(B3LYP 6-31G*) = -2056.662218
Zero-point correction= 0.6690149
Thermal correction to Gibbs Free Energy= 0.5884069
E(B3LYP 6-311G**) = -2057.14554
Number of imaginary frequencies: 1 (-83.1914)

14	0	-5.36685	0.06144	-1.54615
8	0	-3.86464	-0.61452	-1.14356
7	0	-0.32894	-1.01168	-0.07142
6	0	-1.73954	-2.4167	-1.38878
1	0	-2.49123	-2.93472	-0.78852
1	0	-2.07283	-2.43777	-2.42746
6	0	-1.57132	-0.96234	-0.89223
1	0	-1.38006	-0.3035	-1.74131
6	0	0.18072	-2.39214	0.06357
1	0	1.27123	-2.37844	0.11085
1	0	-0.21156	-2.84112	0.98321
6	0	-0.36452	-3.07377	-1.19265
1	0	0.29531	-2.86013	-2.04053
1	0	-0.42768	-4.15871	-1.07572
6	0	-2.8621	-0.40256	-0.1521
6	0	-2.74076	1.11202	0.14535
6	0	-2.304	1.98569	-0.86824
1	0	-2.02887	1.59911	-1.84436
6	0	-2.2287	3.36268	-0.65849
6	0	-2.60488	3.90795	0.57129
1	0	-2.54566	4.9797	0.73793
6	0	-3.06571	3.0606	1.57757
6	0	-3.13428	1.68055	1.36579
1	0	-3.50548	1.04988	2.16423
6	0	-3.15098	-1.2561	1.09854
6	0	-4.19071	-2.19574	1.09554
1	0	-4.81236	-2.29803	0.21485
6	0	-4.42954	-3.01578	2.20184
6	0	-3.62467	-2.92032	3.33614
1	0	-3.80784	-3.55732	4.1969
6	0	-2.57895	-1.99477	3.35272
6	0	-2.34577	-1.17299	2.24886
1	0	-1.53666	-0.4529	2.30109
6	0	-5.15172	1.44872	-2.80451
1	0	-6.13152	1.7456	-3.20016

1	0	-4.53717	1.1222	-3.65199
1	0	-4.68206	2.33595	-2.36857
6	0	-6.32866	0.68068	-0.04651
1	0	-7.33772	0.97413	-0.36361
1	0	-5.85721	1.55359	0.41606
1	0	-6.43257	-0.09463	0.72053
6	0	-6.2764	-1.37091	-2.36481
1	0	-7.24907	-1.03772	-2.74738
1	0	-6.45944	-2.19518	-1.66575
1	0	-5.70523	-1.76998	-3.2113
6	0	0.33215	0.06089	0.33613
1	0	-0.08544	1.01112	0.01625
6	0	1.47732	0.07864	1.14528
1	0	1.88553	-0.84942	1.5326
6	0	2.10068	1.27206	1.46035
1	0	1.64148	2.2012	1.13242
6	0	3.15931	1.36822	2.50949
1	0	3.67827	0.41483	2.64768
1	0	3.89389	2.14584	2.28251
1	0	2.68729	1.63581	3.46717
1	0	-1.94283	-1.90396	4.22894
1	0	-5.24551	-3.73265	2.16879
1	0	-3.37642	3.46813	2.53561
1	0	-1.87987	4.00774	-1.46
6	0	3.60555	1.77573	-0.62409
1	0	2.69928	1.75344	-1.21924
6	0	4.00548	3.07351	-0.16252
8	0	5.01106	3.38391	0.48554
6	0	4.40826	0.60412	-0.62292
6	0	5.85797	-1.82938	-0.61658
6	0	3.90914	-0.57412	-1.26307
6	0	5.68478	0.49618	0.01348
6	0	6.39016	-0.6891	0.01478
6	0	4.60912	-1.76232	-1.2601
1	0	2.95238	-0.5225	-1.77578
1	0	6.09518	1.3743	0.49521
1	0	7.35746	-0.75812	0.49826
1	0	4.21743	-2.64466	-1.75188
7	0	6.58792	-3.05679	-0.60834
8	0	7.69159	-3.09768	-0.03058
8	0	6.09854	-4.05251	-1.17746
8	0	3.05818	4.02325	-0.48317
6	0	3.34371	5.35296	-0.03885
1	0	2.49705	5.96078	-0.36244
1	0	4.26758	5.72953	-0.48869
1	0	3.44145	5.39514	1.05015



TSiminium-*si*-enolate

E(B3LYP 6-31G*) = -2056.661692

Zero-point correction= 0.66952145

Thermal correction to Gibbs Free Energy= 0.59155645

E(B3LYP 6-311G**) = -2057.14477

Number of imaginary frequencies: 1 (-99.1676)

14	0	5.41324	0.32044	-0.60155
8	0	4.14469	-0.22592	0.38328
7	0	0.86001	-0.46508	2.10473
6	0	2.97918	-1.4314	2.64556
1	0	3.26793	-2.25582	1.9896
1	0	3.88253	-1.07082	3.14023
6	0	2.31386	-0.30333	1.82152
1	0	2.61751	0.66964	2.21229
6	0	0.59637	-1.69973	2.87285
1	0	-0.27062	-1.55876	3.51926
1	0	0.39371	-2.52461	2.18108
6	0	1.9046	-1.89918	3.64063
1	0	1.90211	-1.27033	4.5375
1	0	2.04221	-2.93759	3.95329
6	0	2.72556	-0.32513	0.28743
6	0	2.16722	0.90783	-0.46274
6	0	2.37603	2.19047	0.07825
1	0	2.91044	2.30722	1.0156
6	0	1.92332	3.3371	-0.57388
6	0	1.2571	3.233	-1.79731
1	0	0.89958	4.1237	-2.3057
6	0	1.0653	1.97253	-2.36113
6	0	1.51749	0.82455	-1.7023
1	0	1.36376	-0.13886	-2.17239
6	0	2.32052	-1.67095	-0.3455
6	0	3.28788	-2.63548	-0.65732
1	0	4.33232	-2.42257	-0.46836
6	0	2.92817	-3.87771	-1.1877
6	0	1.58718	-4.18809	-1.40852
1	0	1.30514	-5.15304	-1.82019
6	0	0.60904	-3.24351	-1.09027
6	0	0.97147	-2.00181	-0.56611
1	0	0.18938	-1.28632	-0.33805
6	0	5.84799	2.1059	-0.17848
1	0	6.78473	2.38678	-0.67681
1	0	5.9971	2.23111	0.90075
1	0	5.07404	2.81112	-0.49726

6	0	5.05646	0.14944	-2.44538
1	0	5.96251	0.4075	-3.00879
1	0	4.255	0.8164	-2.77857
1	0	4.77829	-0.87554	-2.71443
6	0	6.8582	-0.78488	-0.10847
1	0	7.77649	-0.4588	-0.61242
1	0	6.68788	-1.83391	-0.37719
1	0	7.03869	-0.74042	0.97201
6	0	-0.03417	0.49411	1.9083
1	0	0.36382	1.41094	1.48265
6	0	-1.40386	0.44561	2.20049
1	0	-1.85811	-0.47451	2.55462
6	0	-2.192	1.5756	2.05653
1	0	-1.70992	2.50682	1.7715
6	0	-3.56469	1.66728	2.6388
1	0	-3.48641	2.02798	3.67589
1	0	-4.19517	2.37408	2.09365
1	0	-4.05739	0.69034	2.6643
1	0	-0.44147	-3.46789	-1.25377
1	0	3.70306	-4.60279	-1.42133
1	0	0.56396	1.87297	-3.31978
1	0	2.09517	4.31146	-0.12511
6	0	-2.91656	1.69165	-0.44102
1	0	-1.87438	1.57215	-0.71555
6	0	-3.37223	3.04817	-0.3309
8	0	-4.51381	3.46	-0.09815
6	0	-3.74967	0.54361	-0.54098
6	0	-5.27646	-1.83754	-0.69145
6	0	-3.15135	-0.71987	-0.84176
6	0	-5.16445	0.5482	-0.33208
6	0	-5.90688	-0.61257	-0.40607
6	0	-3.88786	-1.88267	-0.91263
1	0	-2.08254	-0.75537	-1.03393
1	0	-5.65059	1.4918	-0.12112
1	0	-6.97875	-0.5961	-0.24806
1	0	-3.41792	-2.83153	-1.14238
7	0	-6.04722	-3.03805	-0.76362
8	0	-7.2761	-2.97799	-0.56497
8	0	-5.4672	-4.11104	-1.02169
8	0	-2.32279	3.9337	-0.46369
6	0	-2.66465	5.31768	-0.33921
1	0	-1.7282	5.86485	-0.45978
1	0	-3.10105	5.53186	0.641
1	0	-3.3766	5.6193	-1.11364

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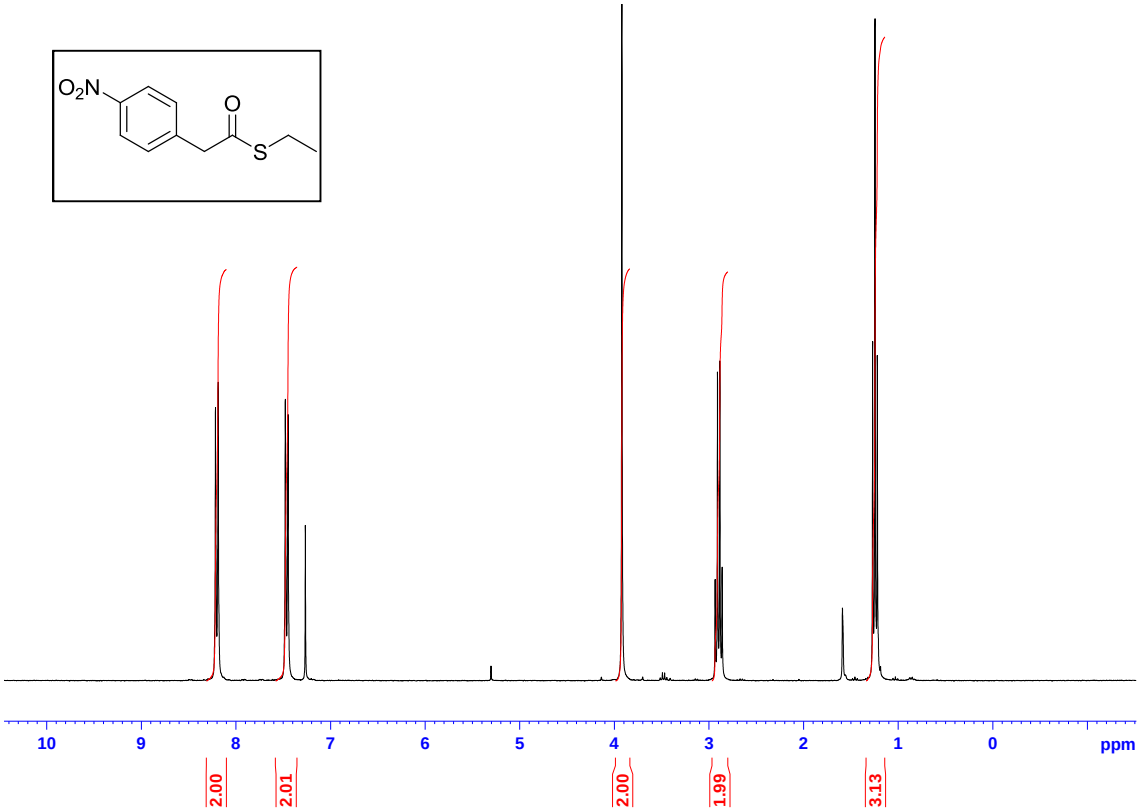
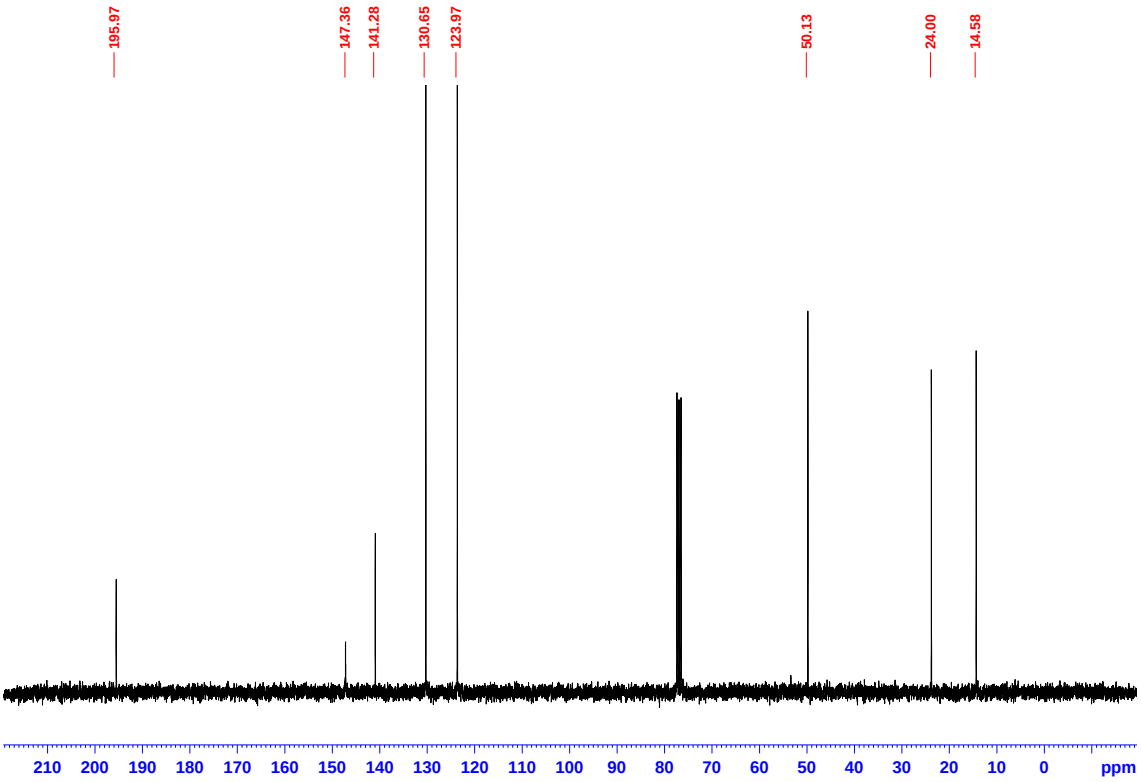
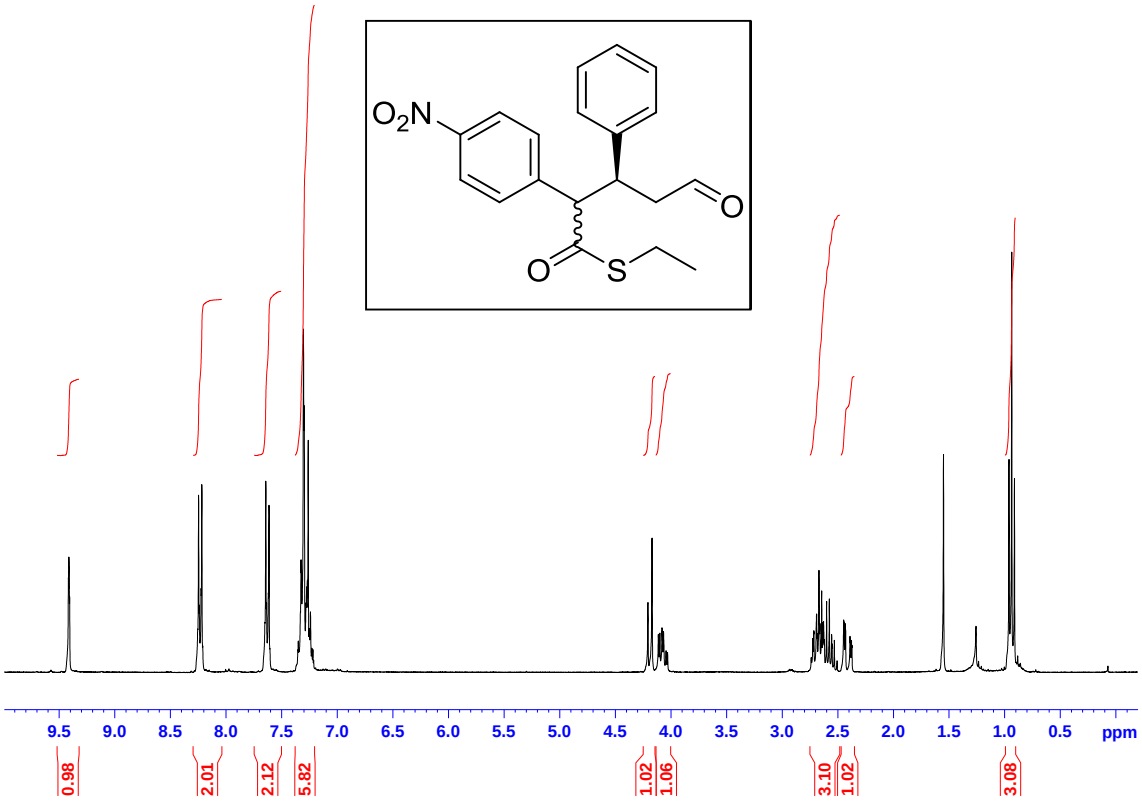
^{1}H and ^{13}C spectra



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O
O
S
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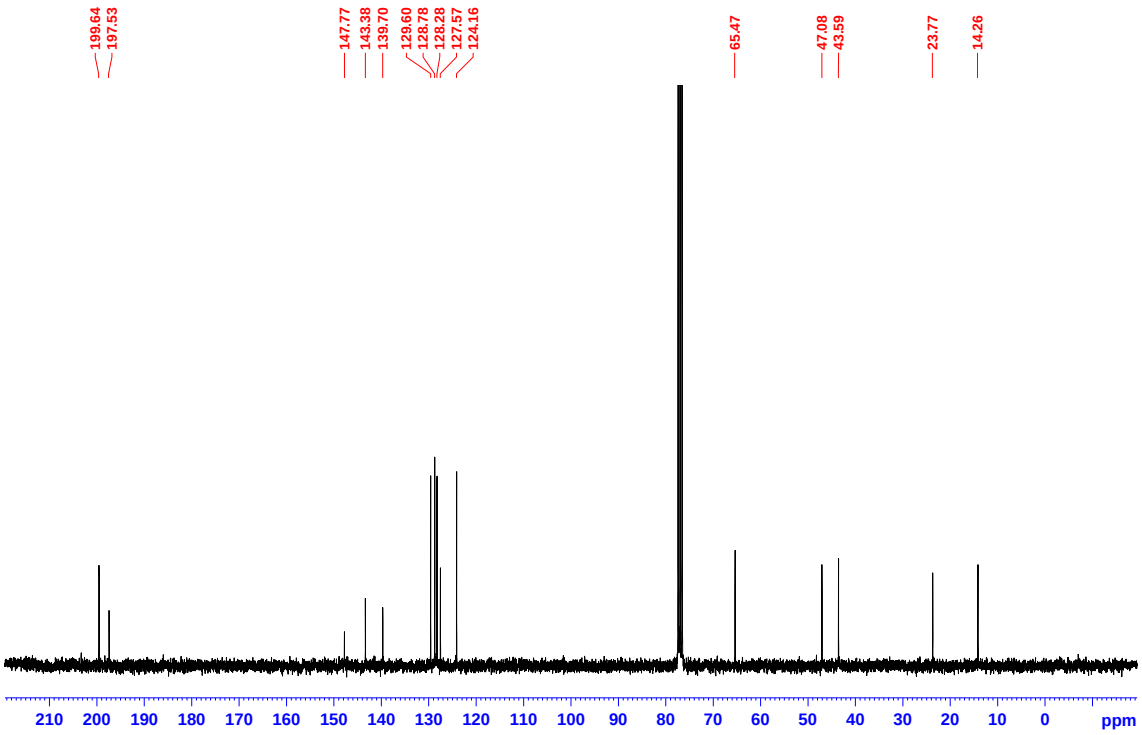
2.01
2.12
5.82
1.02
1.06
3.10
1.02
3.08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128.28
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124.16
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47.08
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23.77
14.26
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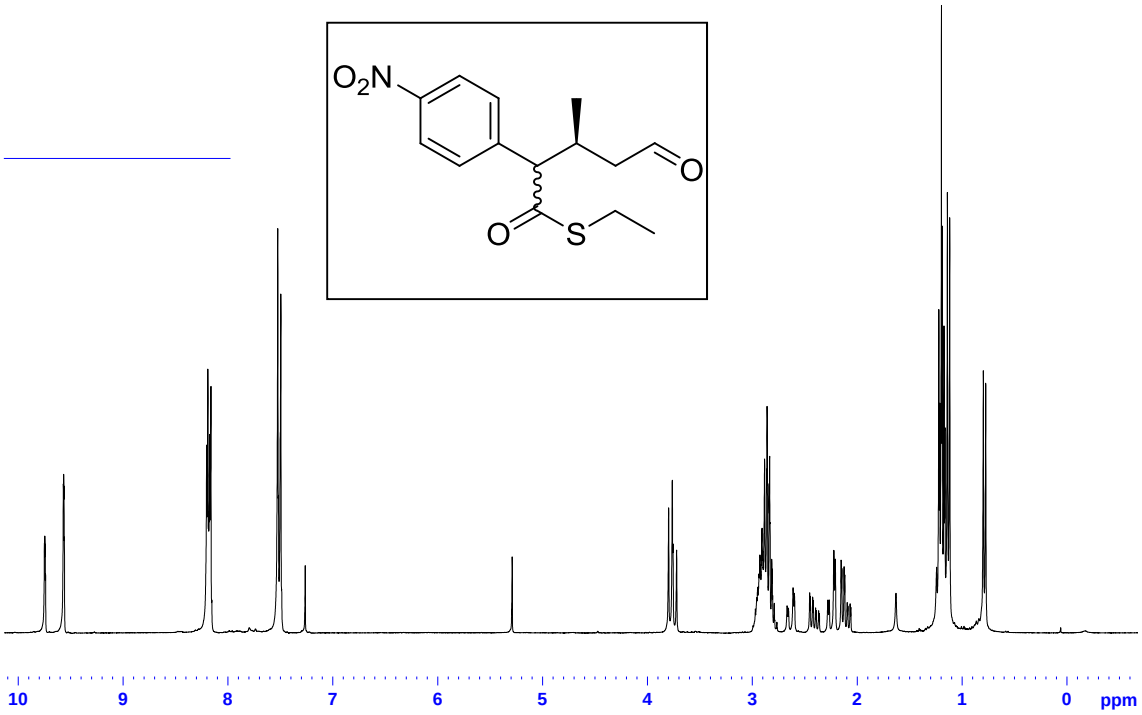
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O
S
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9
8
7
6
5
4
3
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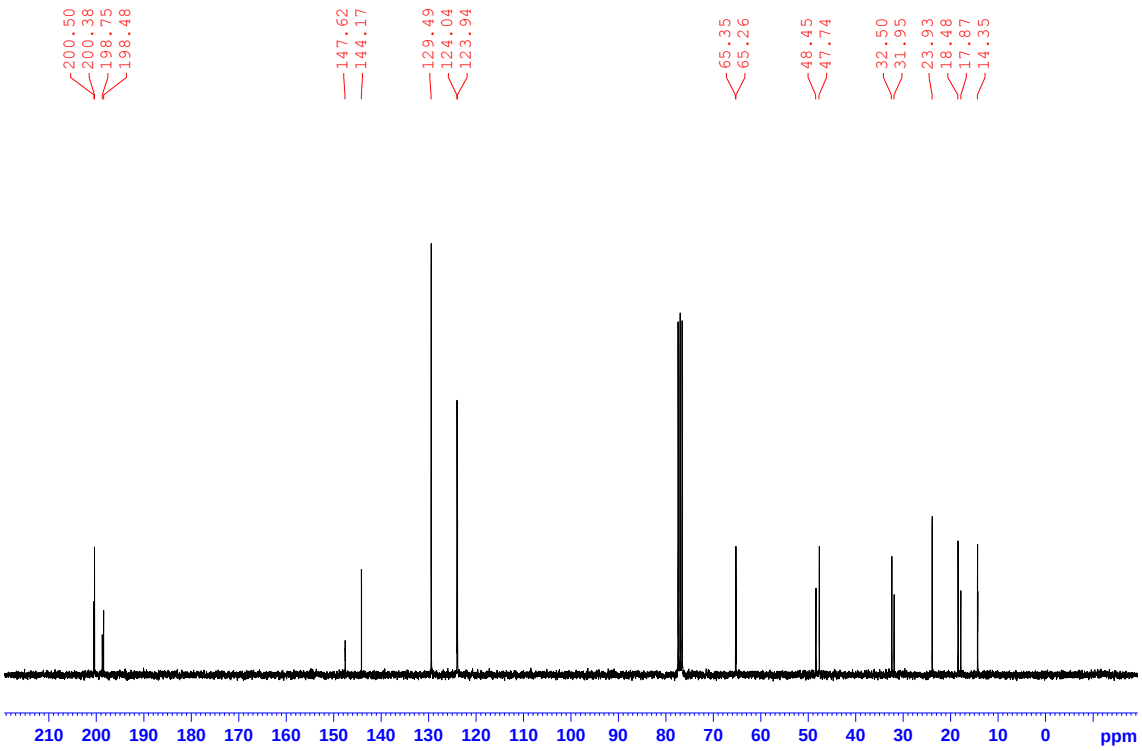
1
0
ppm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32.50
31.95
23.93
18.48
17.87
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200
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180
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120
110
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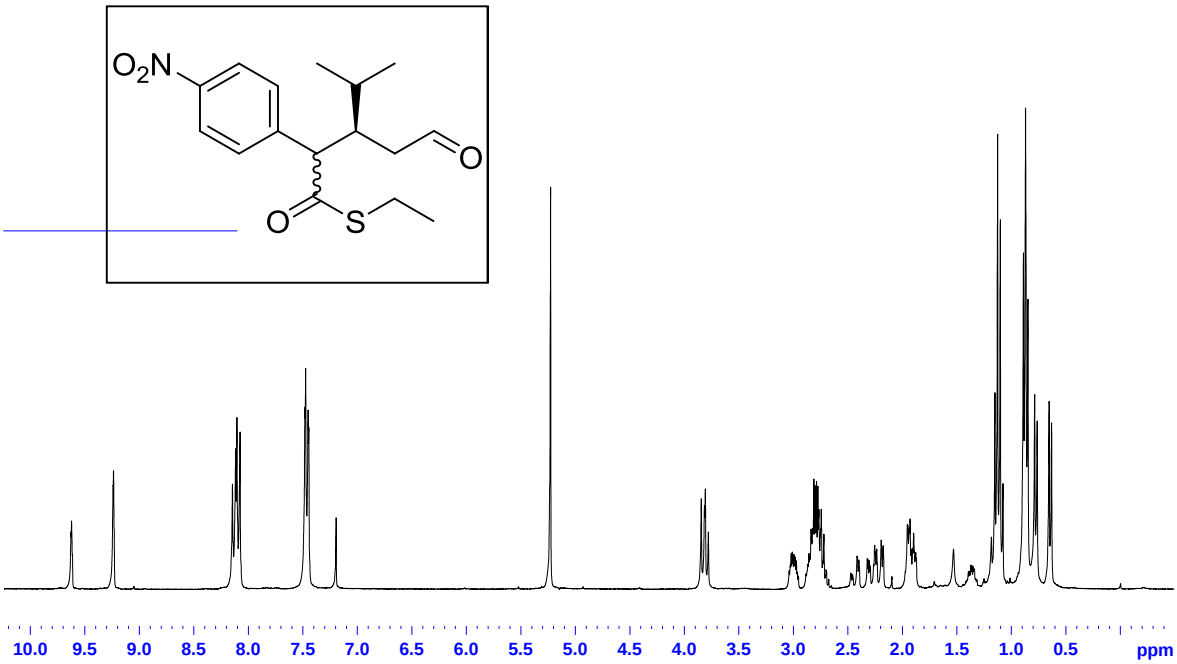
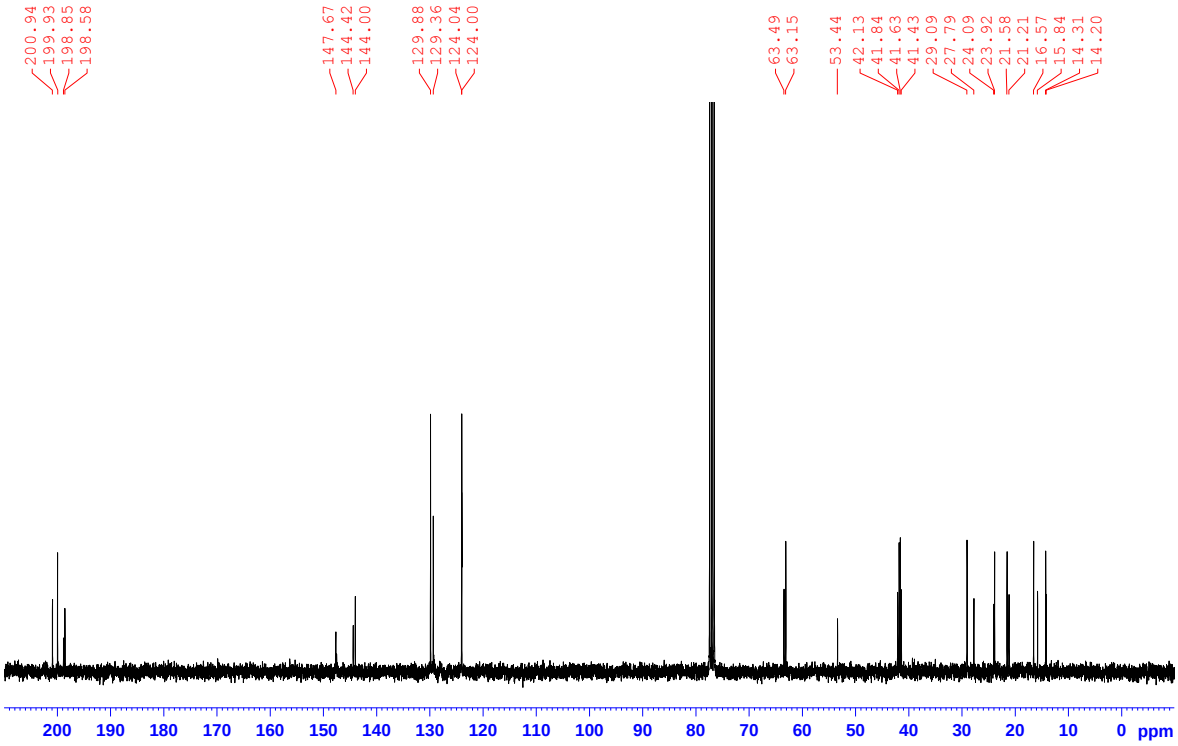
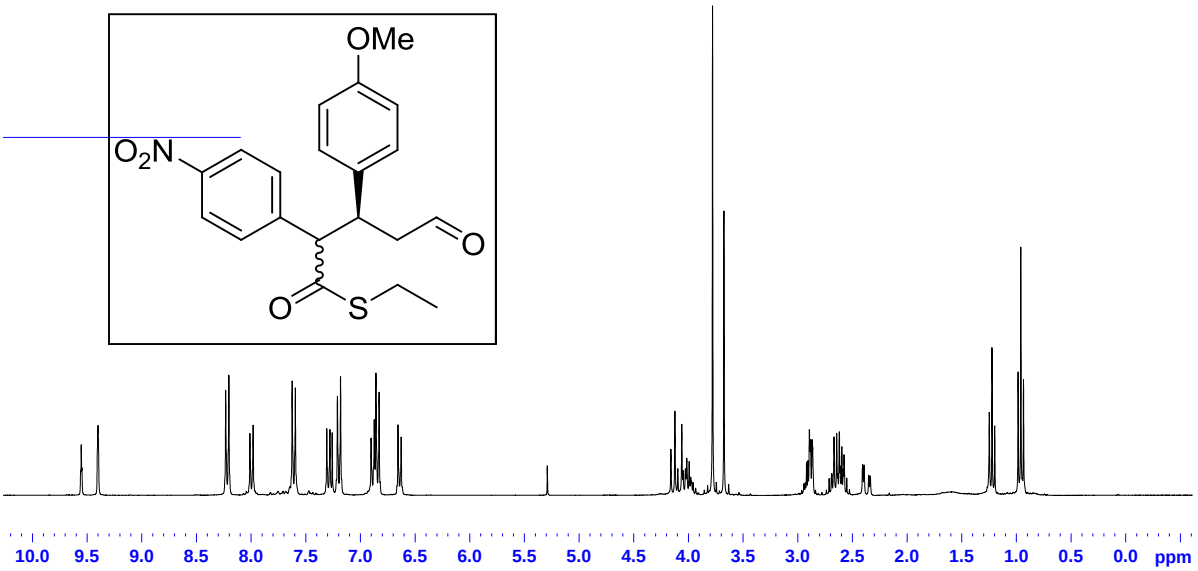
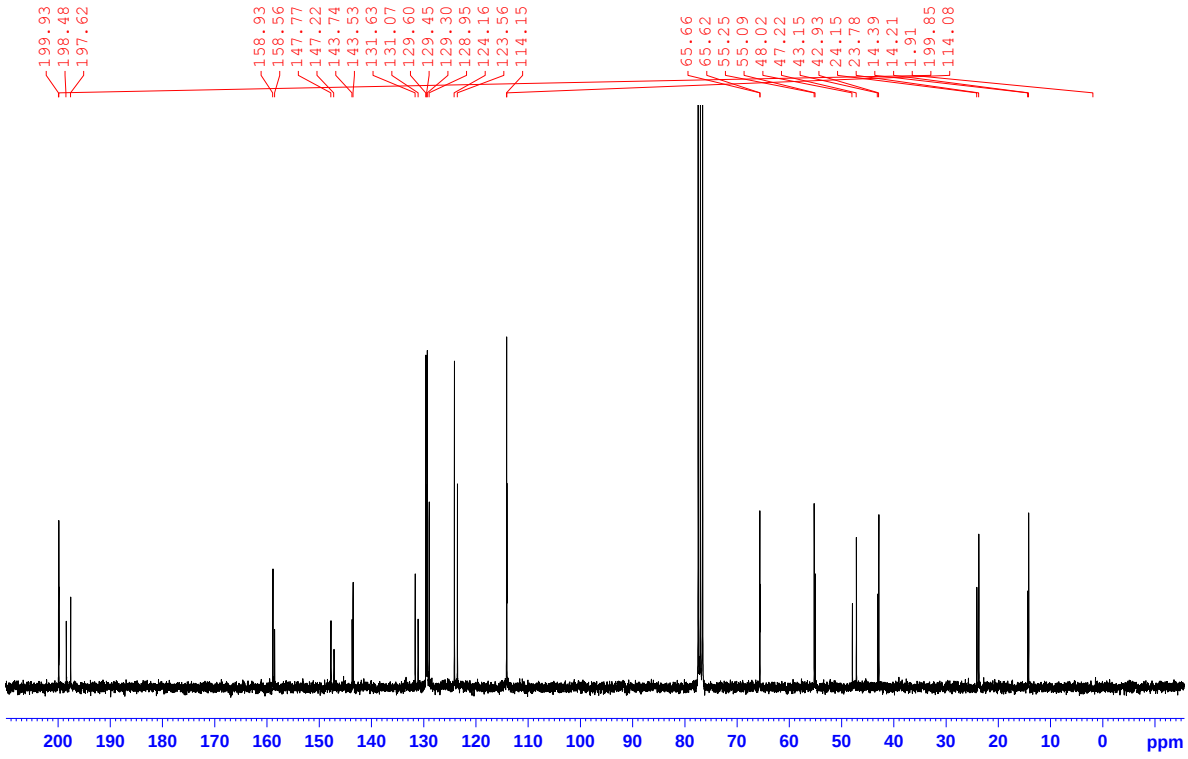
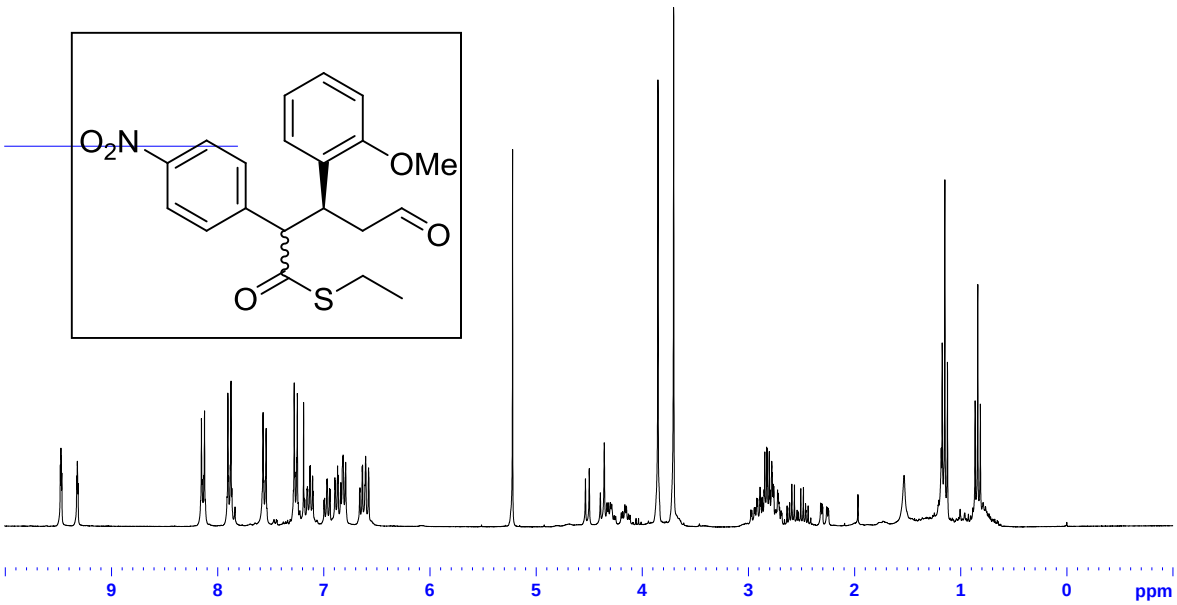
60
50
40
30
20
10
0
ppm

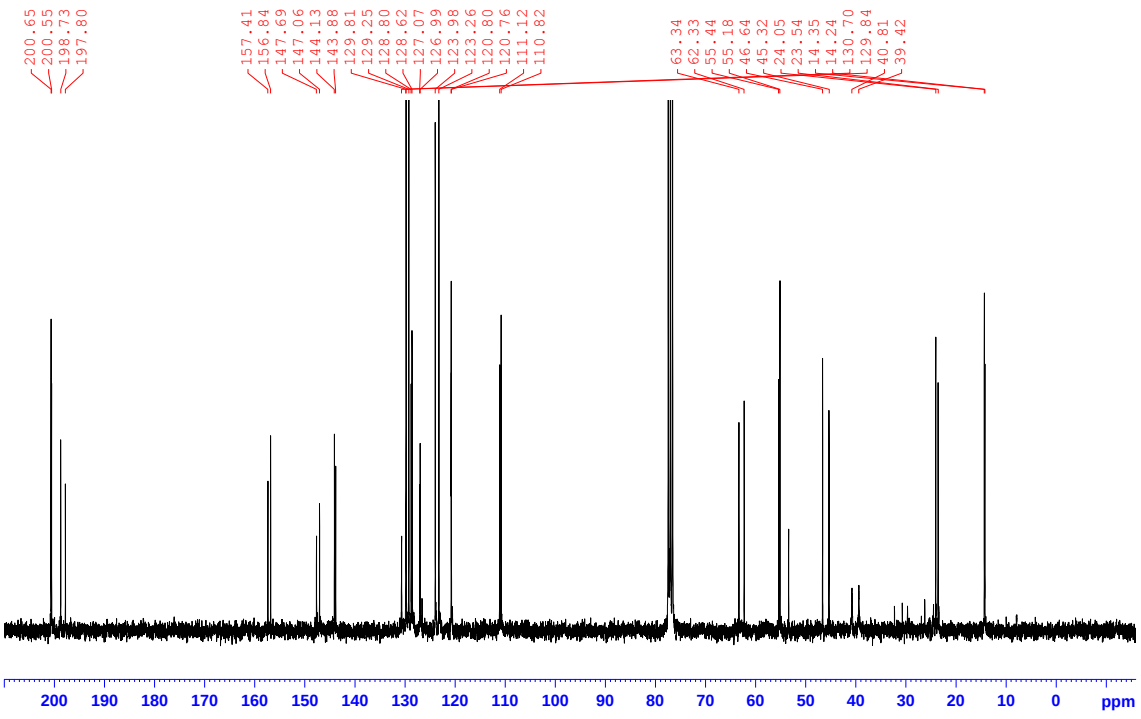

O2N
O
O
S
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

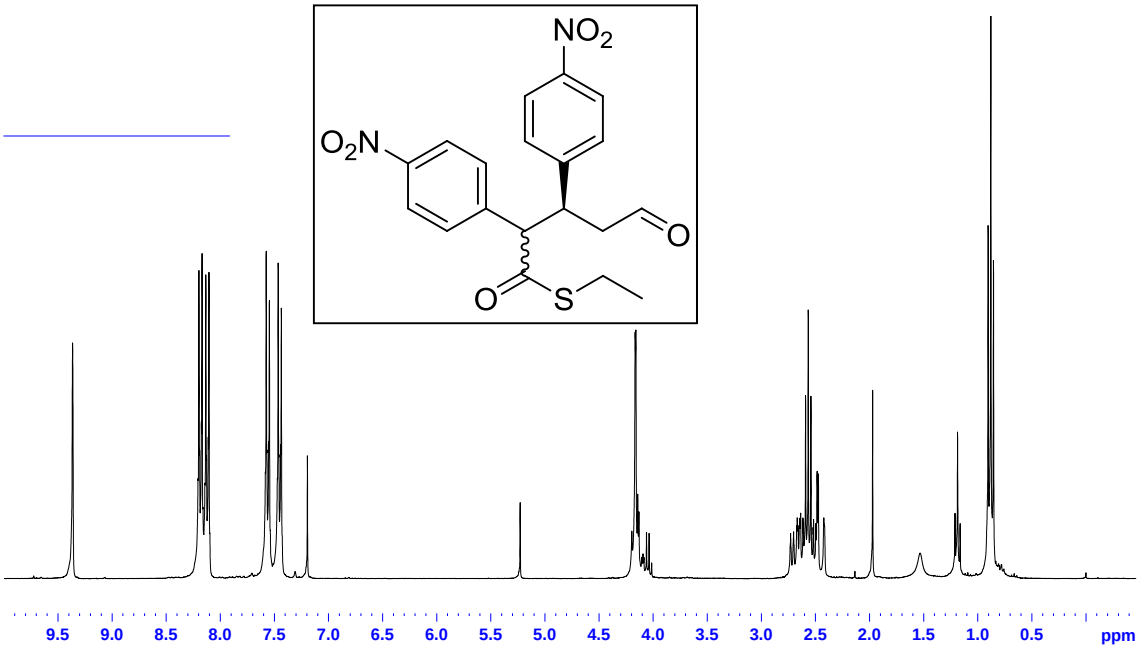

200.94
199.93
198.85
198.58
147.67
144.42
144.00
129.88
129.36
124.04
124.00
63.49
63.15
53.44
42.13
41.84
41.63
41.43
29.09
27.79
24.09
23.92
21.58
21.21
16.57
15.84
14.31
14.20
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

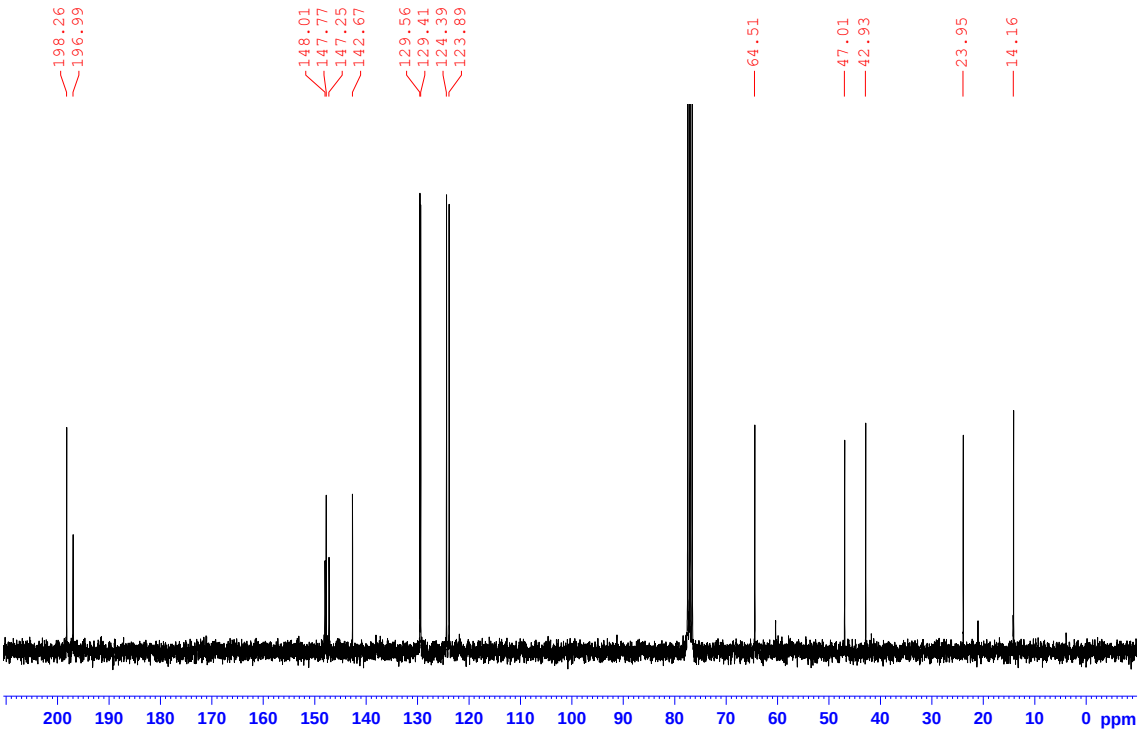

OMe
O2N
O
O
S
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

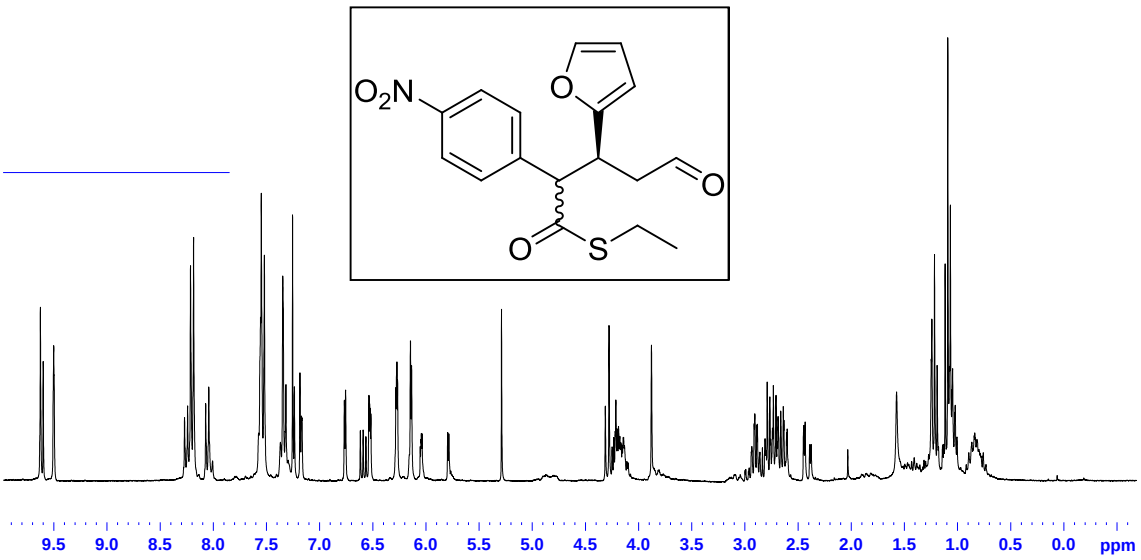

199.93
198.48
197.62
158.93
158.56
147.77
147.22
143.74
143.53
131.63
131.07
129.60
129.45
129.30
128.95
124.16
123.56
114.15
65.66
65.62
55.25
55.09
48.02
47.22
43.15
42.93
24.15
23.78
14.39
14.21
1.91
199.85
114.08
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

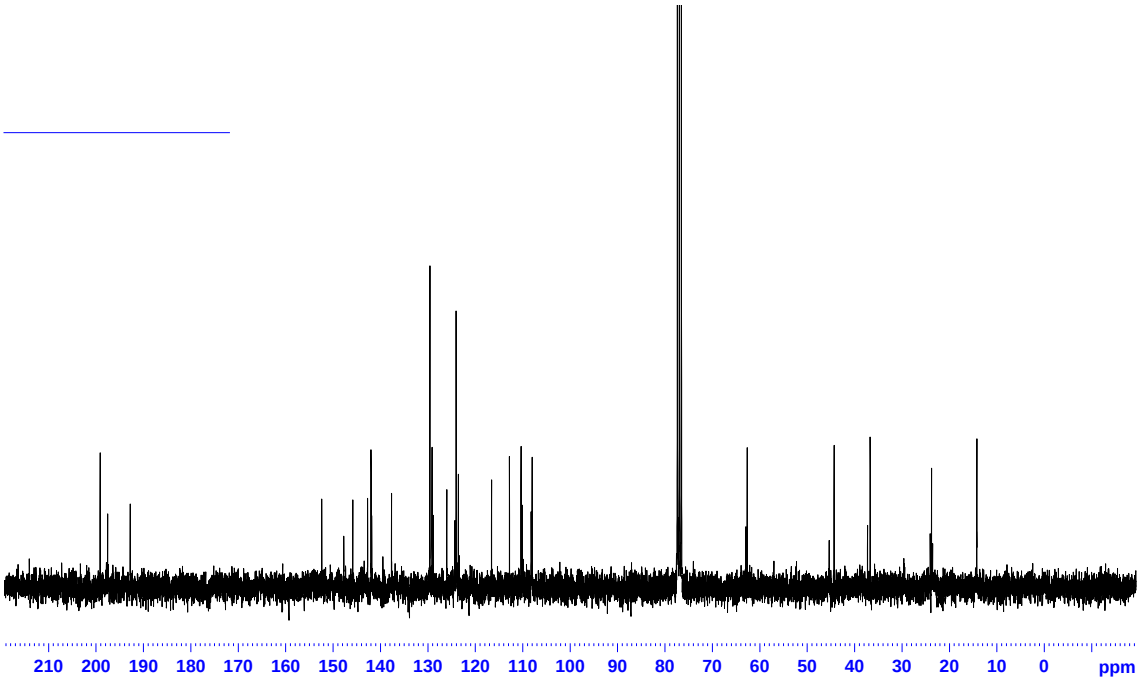

O2N
OMe
O
O
S
9
8
7
6
5
4
3
2
1
0
ppm

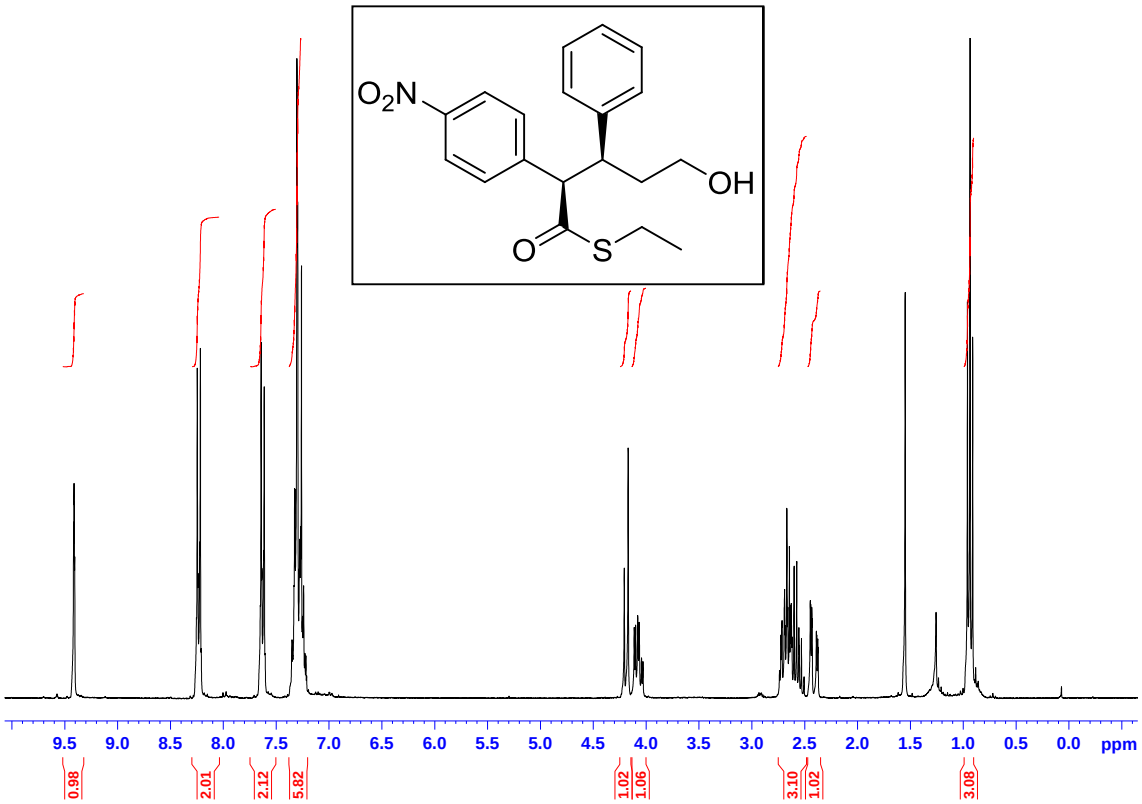

200.65
200.55
198.73
197.80
157.41
156.84
147.69
147.06
144.13
143.88
129.81
129.25
128.80
128.62
127.07
126.99
123.98
123.26
120.80
120.76
111.12
110.82
63.34
62.33
55.44
55.18
46.64
45.32
24.05
23.54
14.35
14.24
130.70
129.84
40.81
39.42
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

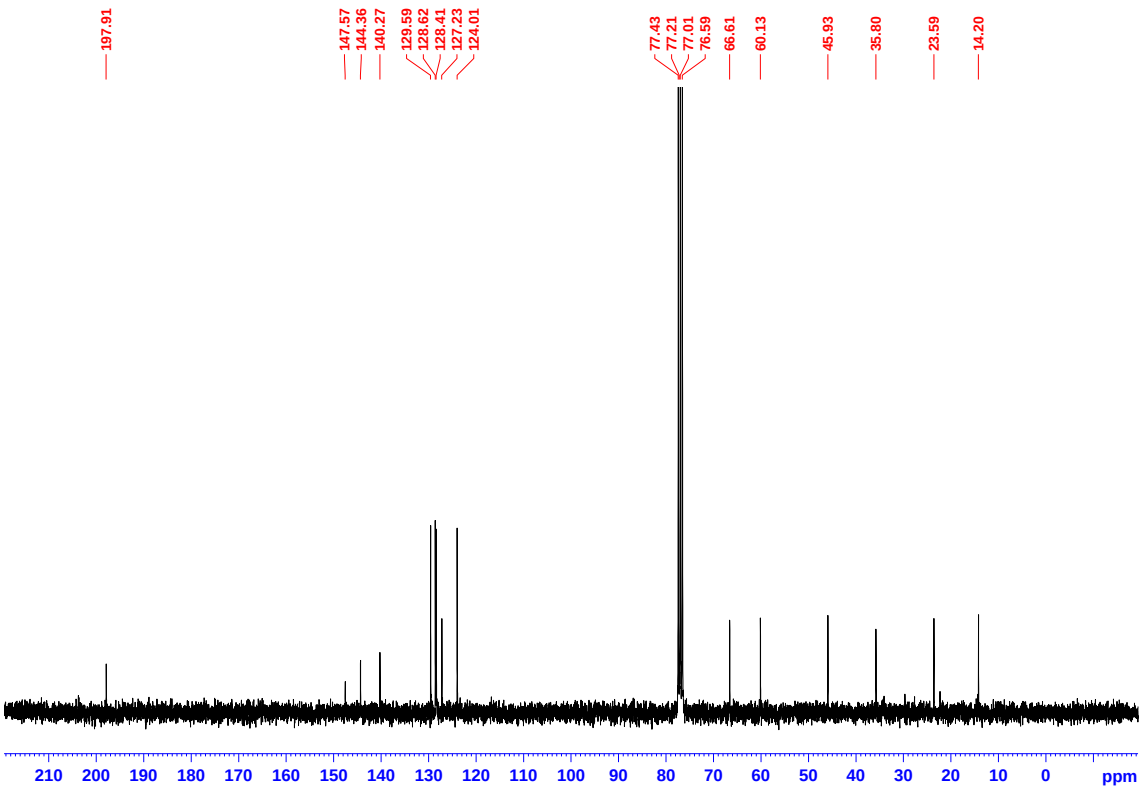

NO2
O2N
O
O
S
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

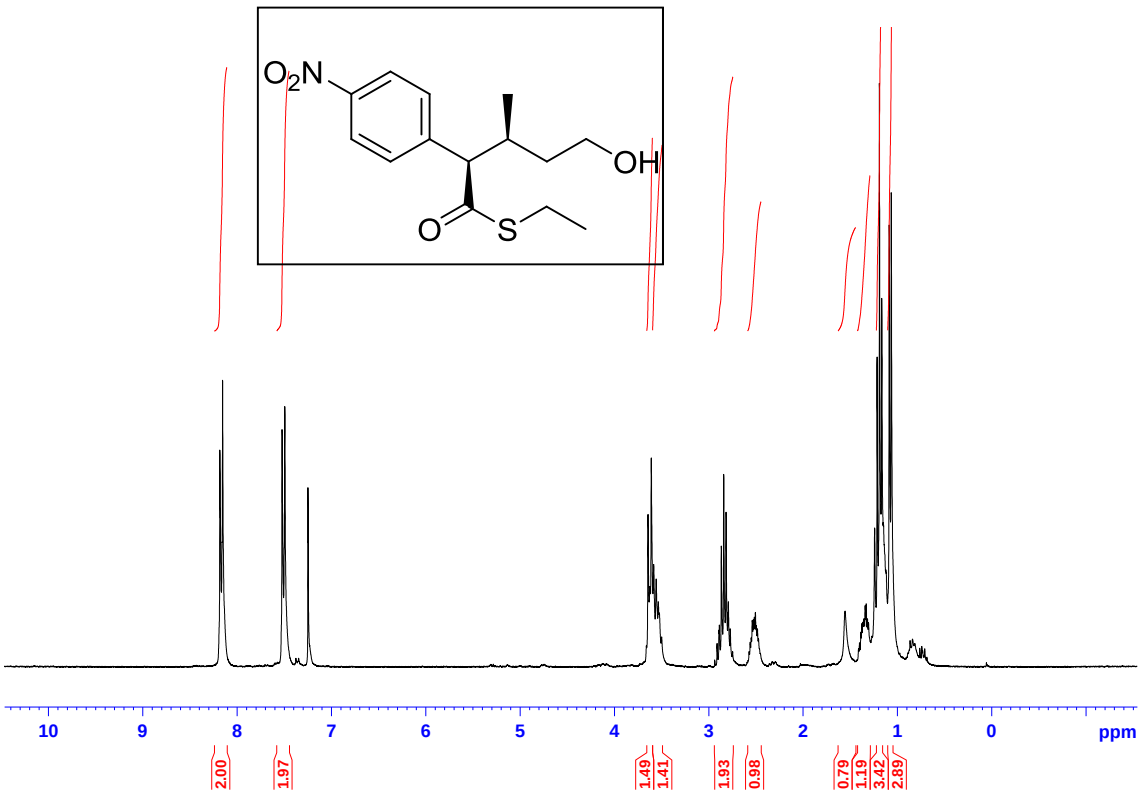

198.26
196.99
148.01
147.77
147.25
142.67
129.56
129.41
124.39
123.89
64.51
47.01
42.93
23.95
14.16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

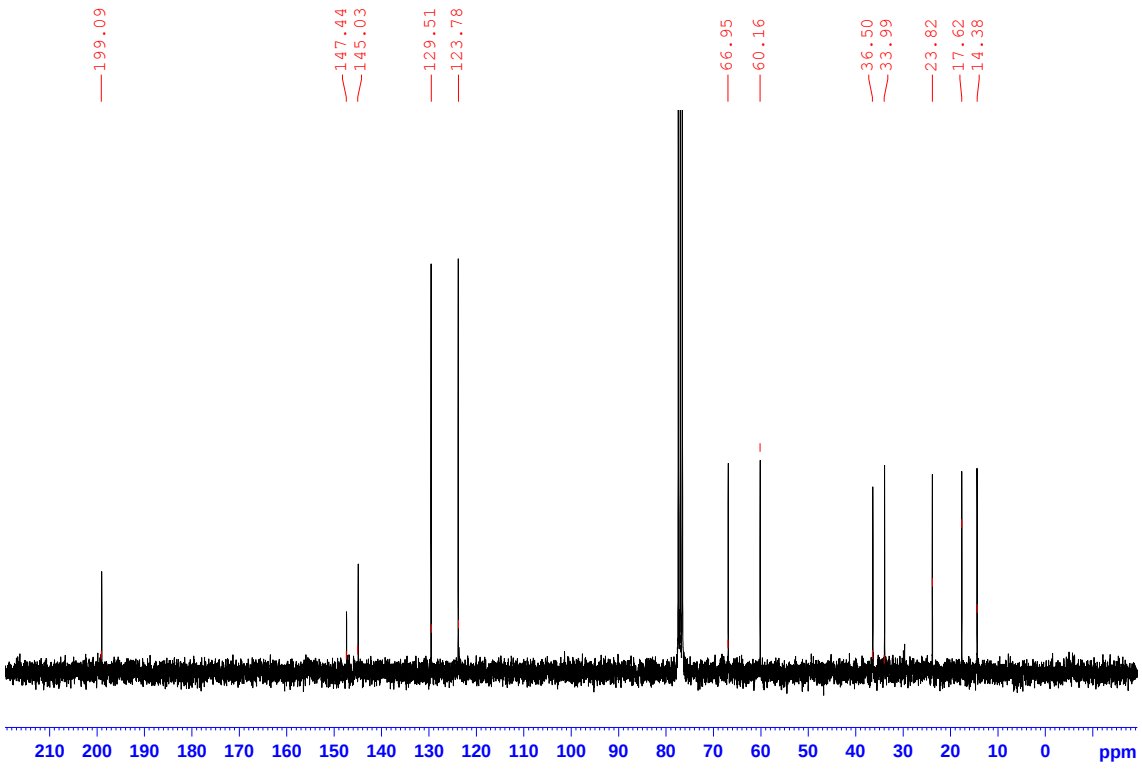

O2N
O
O
O
S
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

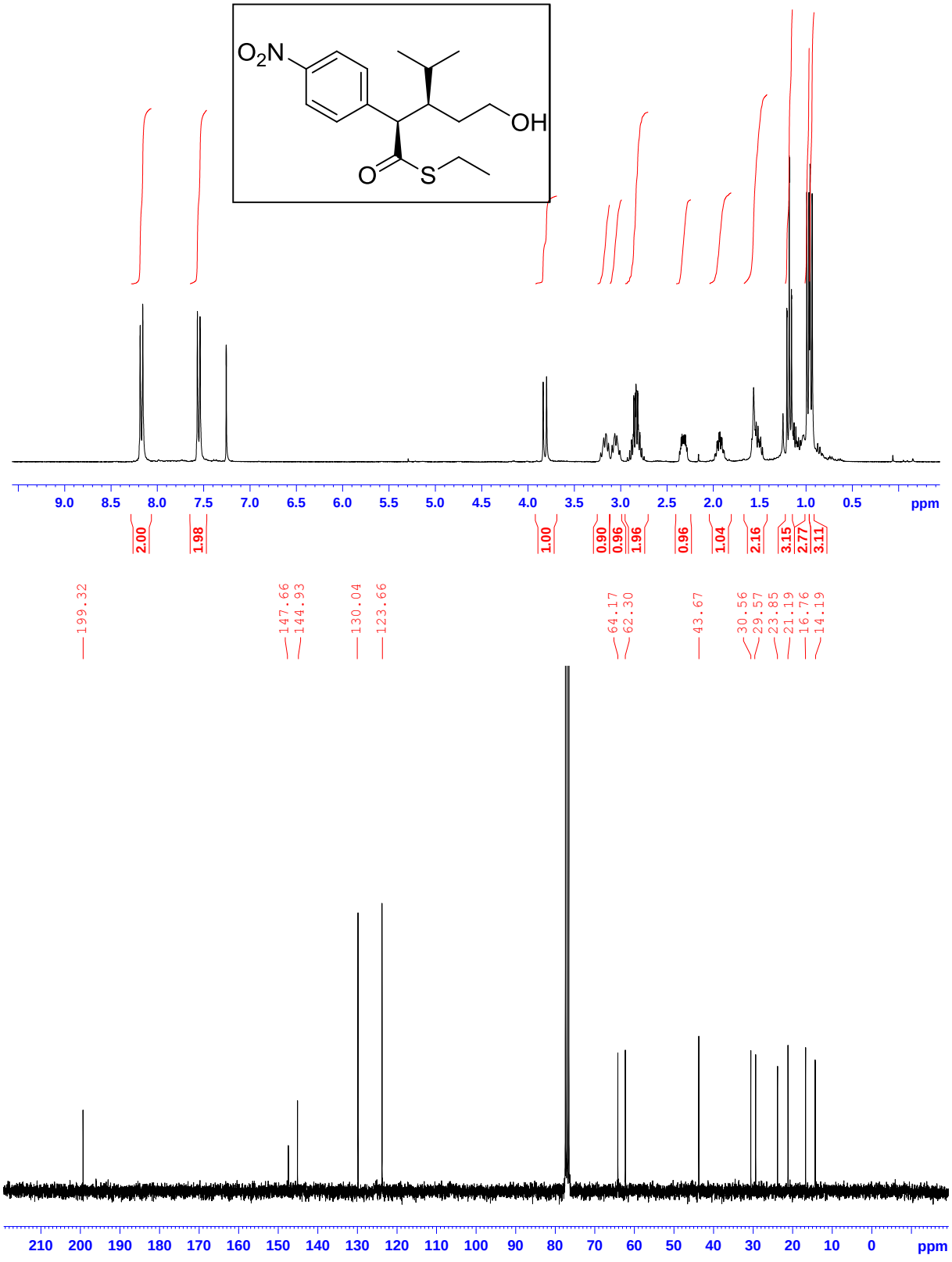

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

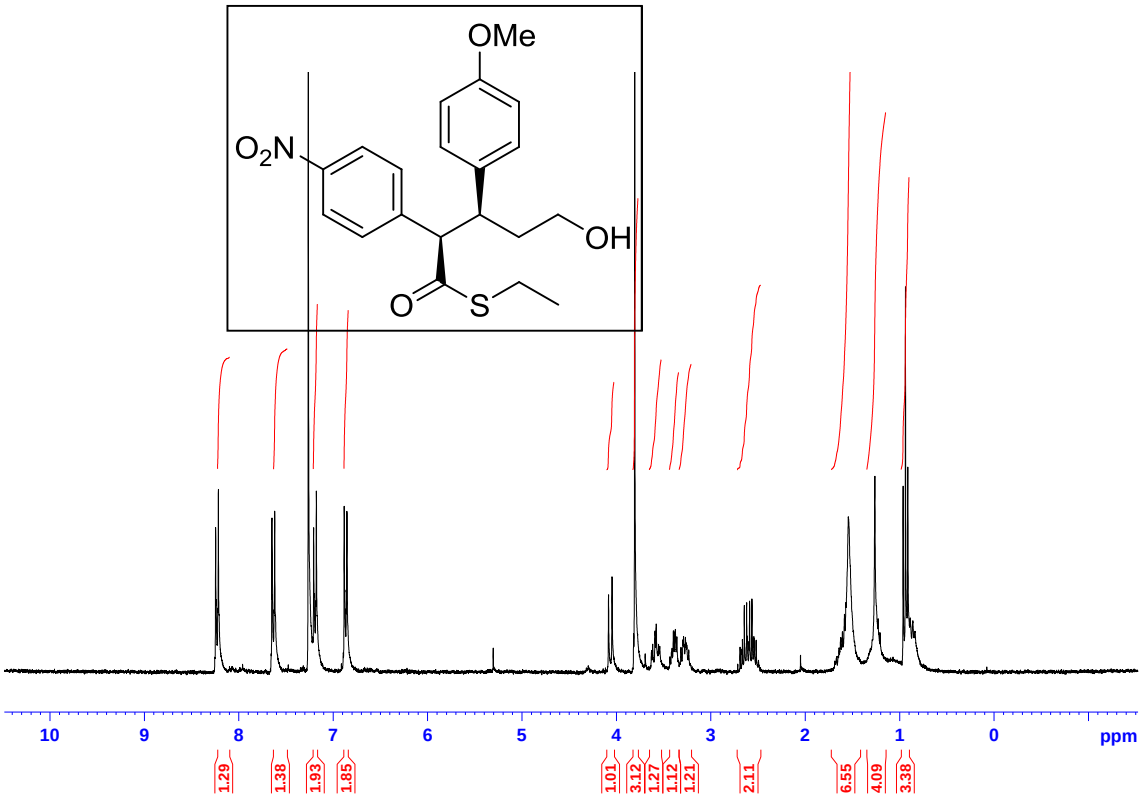

O2N
OH
O
S
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98
2.01
2.12
5.82
1.02
1.06
3.10
1.02
3.08

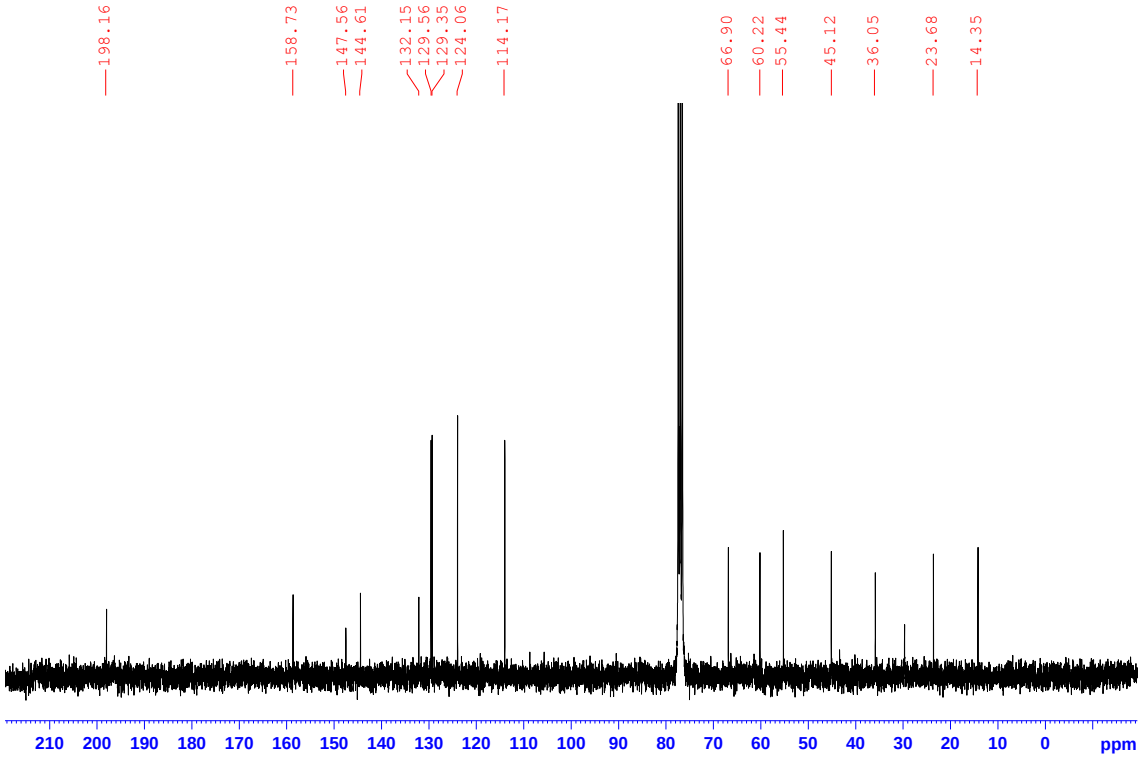

197.91
147.57
144.36
140.27
129.59
128.62
128.41
127.23
124.01
77.43
77.21
77.01
76.59
66.61
60.13
45.93
35.80
23.59
14.20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

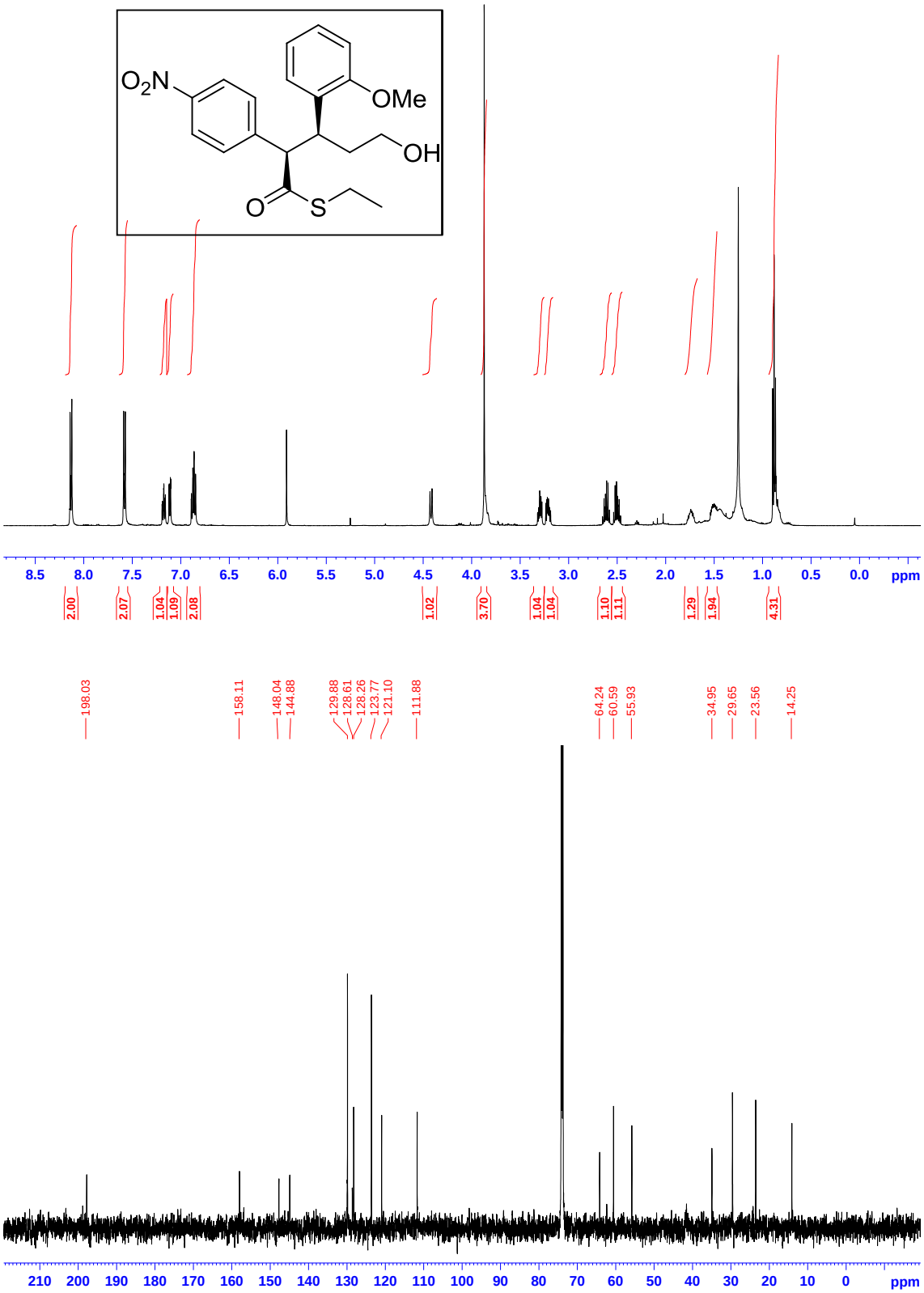

O2N
OH
O
S
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.97
1.49
1.41
1.93
0.98
0.79
1.19
3.42
2.89

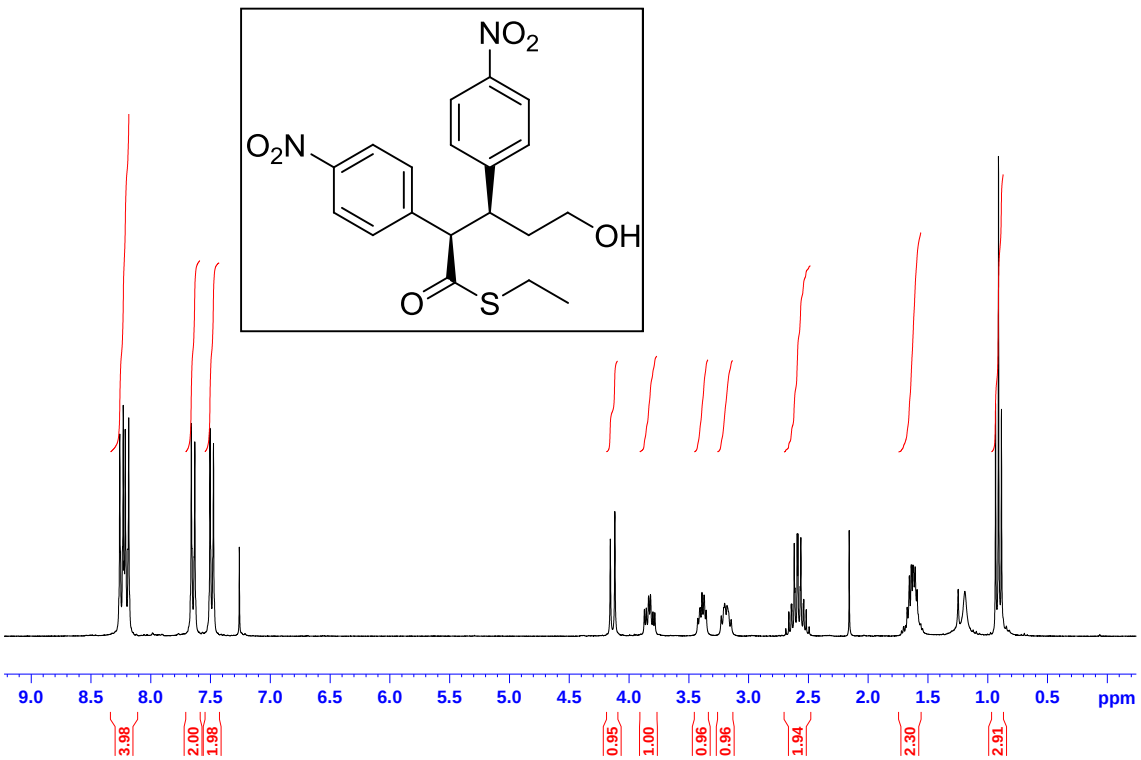

199.09
147.44
145.03
129.51
123.78
66.95
60.16
36.50
33.99
23.82
17.62
14.38
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

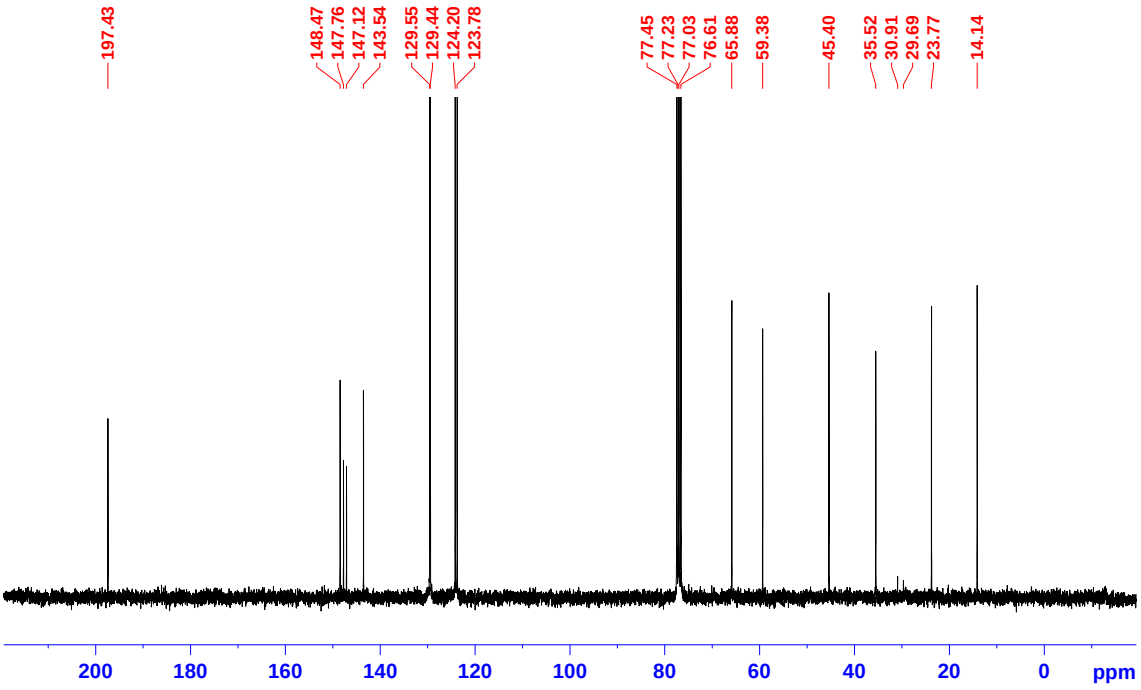

O2N
OH
O
S
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00 1.98 1.00 0.90 0.96 1.96 0.96 1.04 2.16 3.15 2.77 3.11
199.32 147.66 144.93 130.04 123.66 64.17 62.30 43.67 30.56 29.57 23.85 21.19 16.76 14.19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

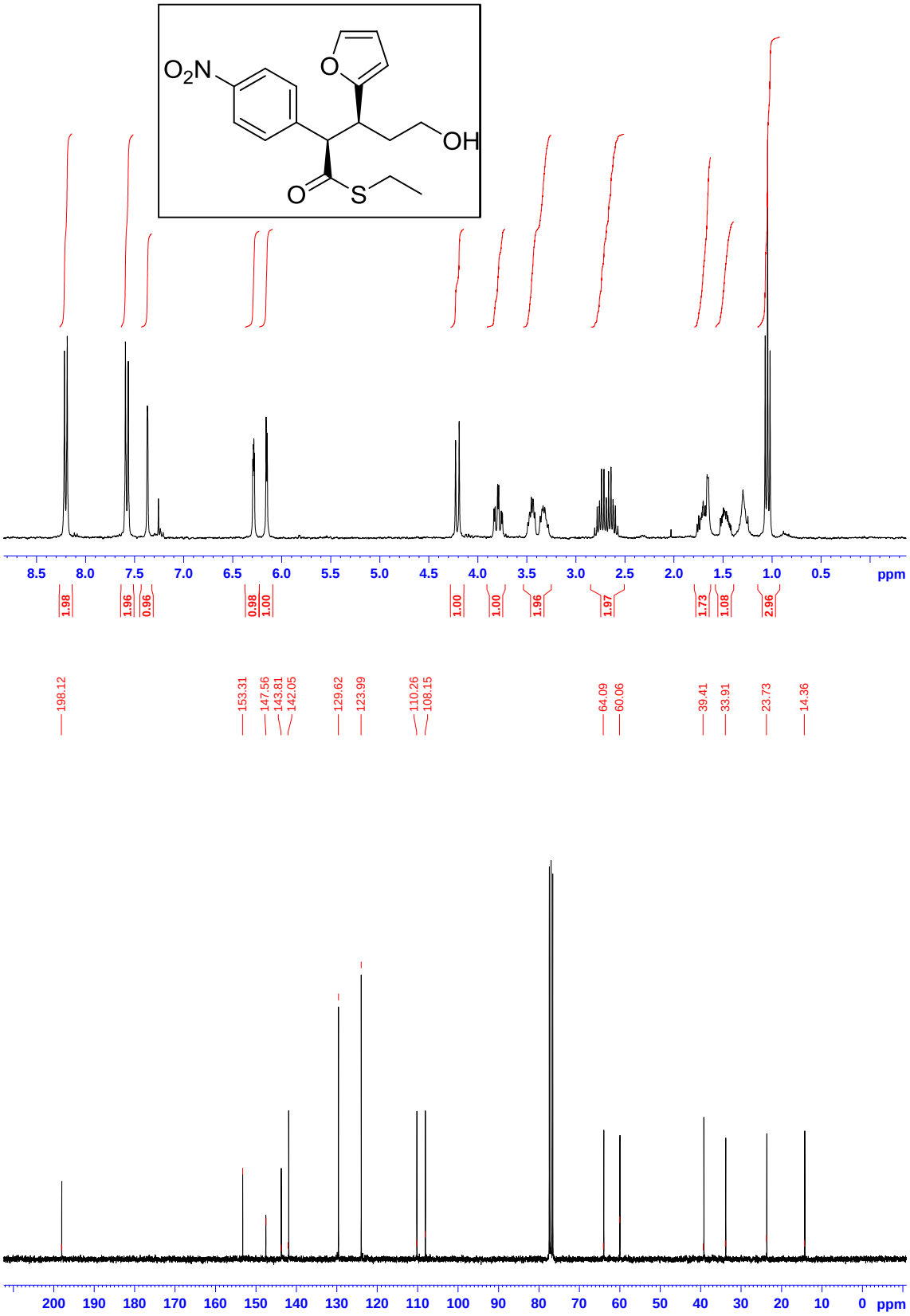

OMe
O2N
OH
O
S
10
9
8
7
6
5
4
3
2
1
0
ppm
1.29
1.38
1.93
1.85
1.01
3.12
1.27
1.12
1.21
2.11
6.55
4.09
3.38

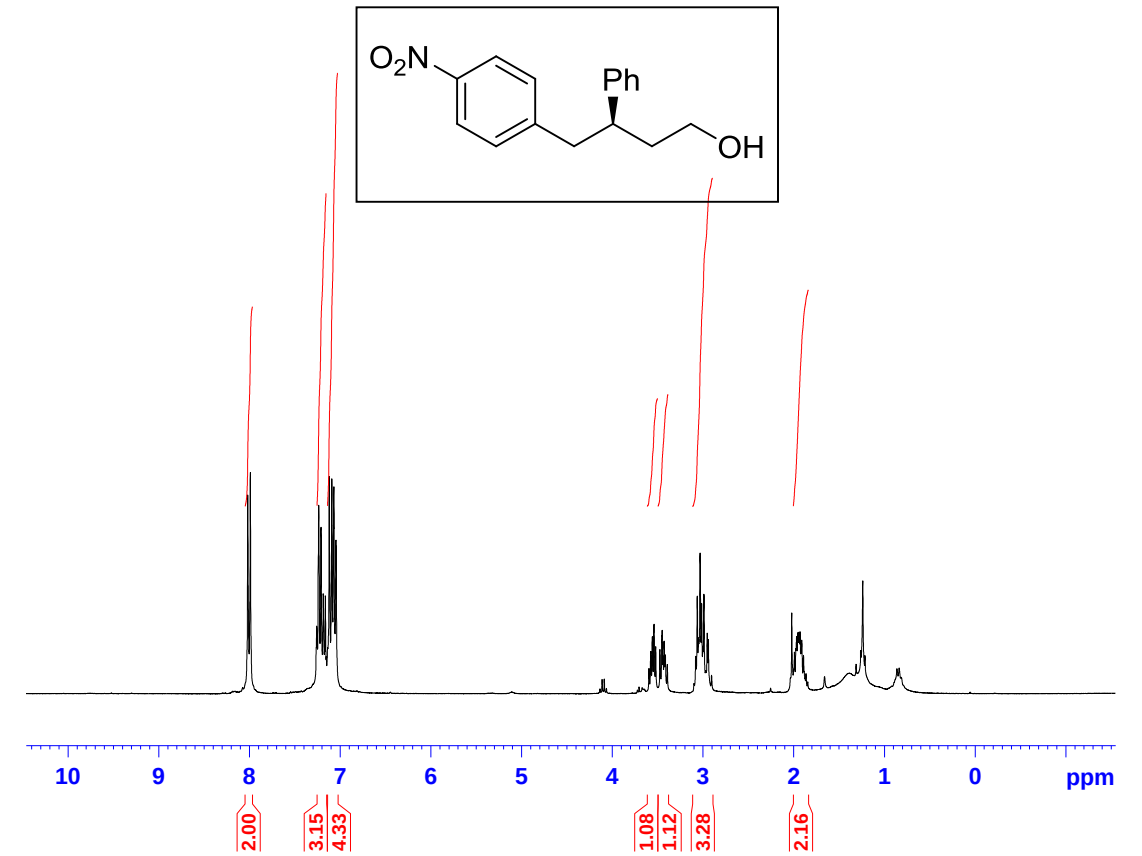

198.16
158.73
147.56
144.61
132.15
129.56
129.35
124.06
114.17
66.90
60.22
55.44
45.12
36.05
23.68
14.35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

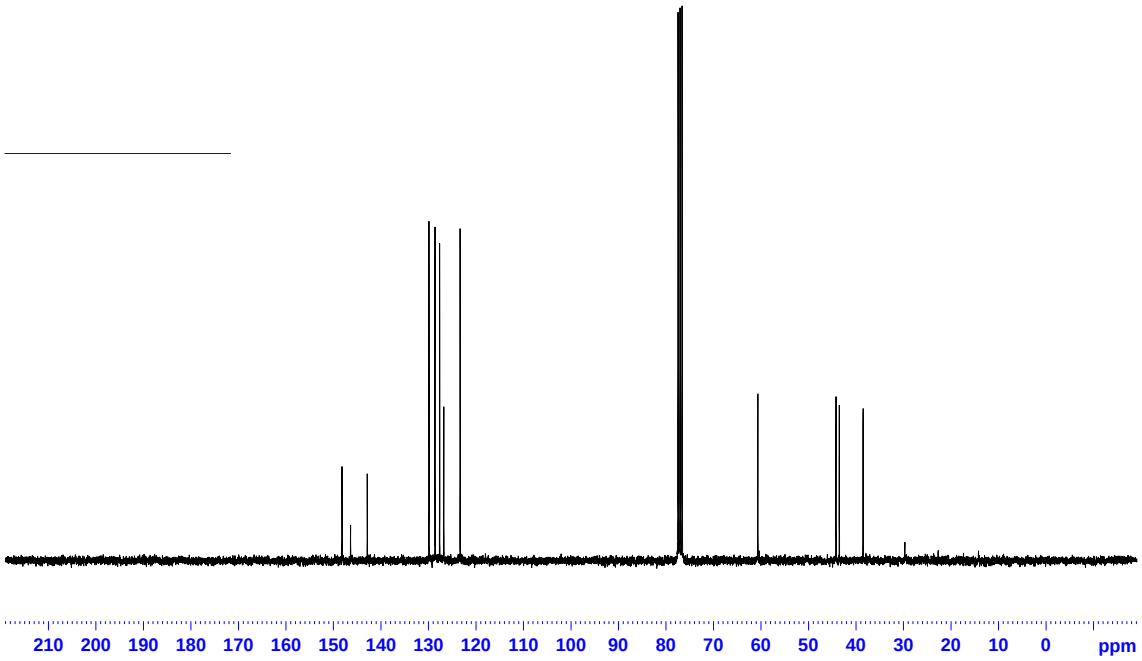

O2N
OMe
OH
O
S
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00 2.07 1.04 1.09 2.08 1.02 3.70 1.04 1.04 1.10 1.11 1.29 1.94 4.31
198.03 158.11 148.04 144.88 129.88 128.61 128.26 123.77 121.10 111.88 64.24 60.59 55.93 34.95 29.65 23.56 14.25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

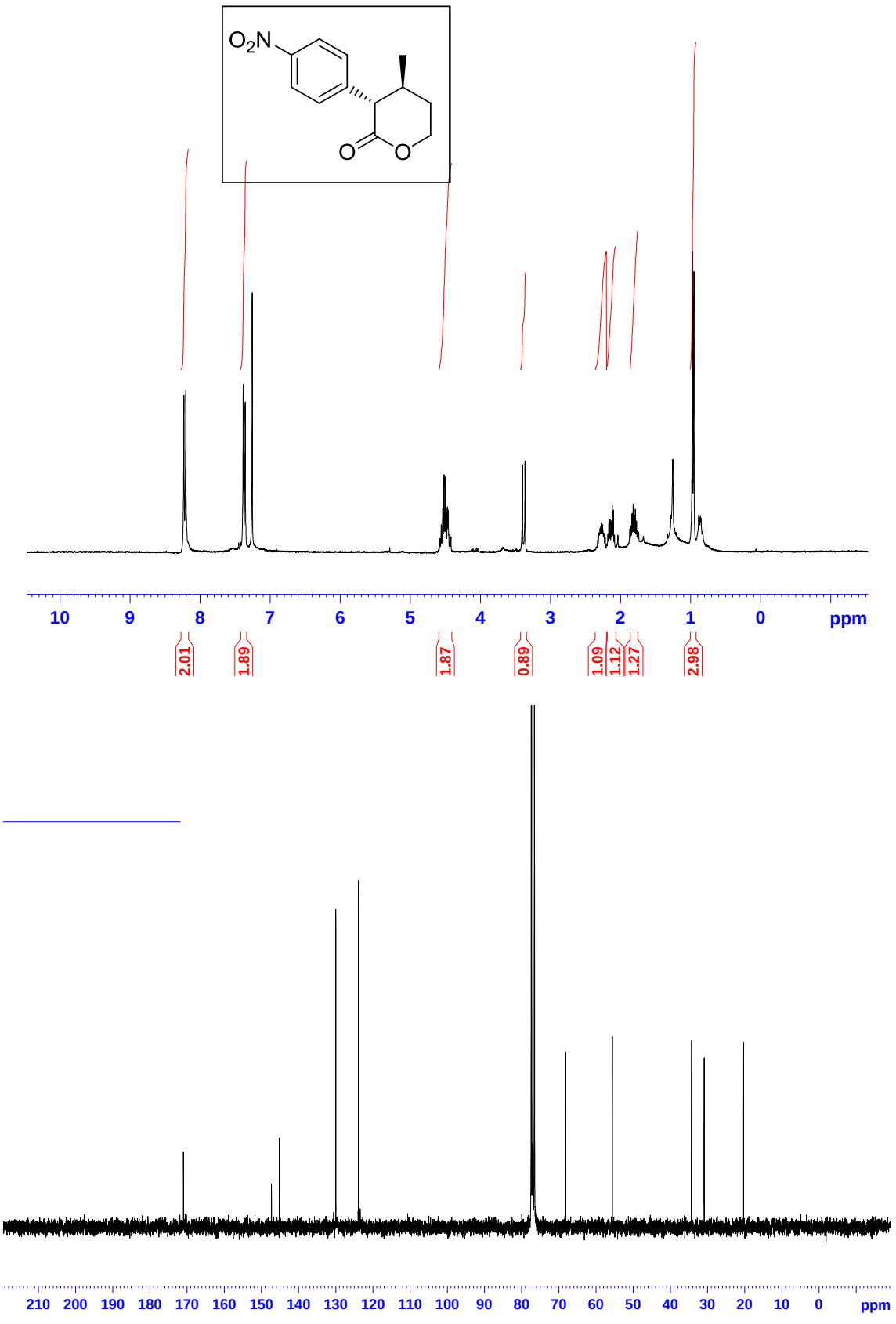

NO2
O2N
OH
O
S
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.98
2.00
1.98
0.95
1.00
0.96
0.96
1.94
2.30
2.91

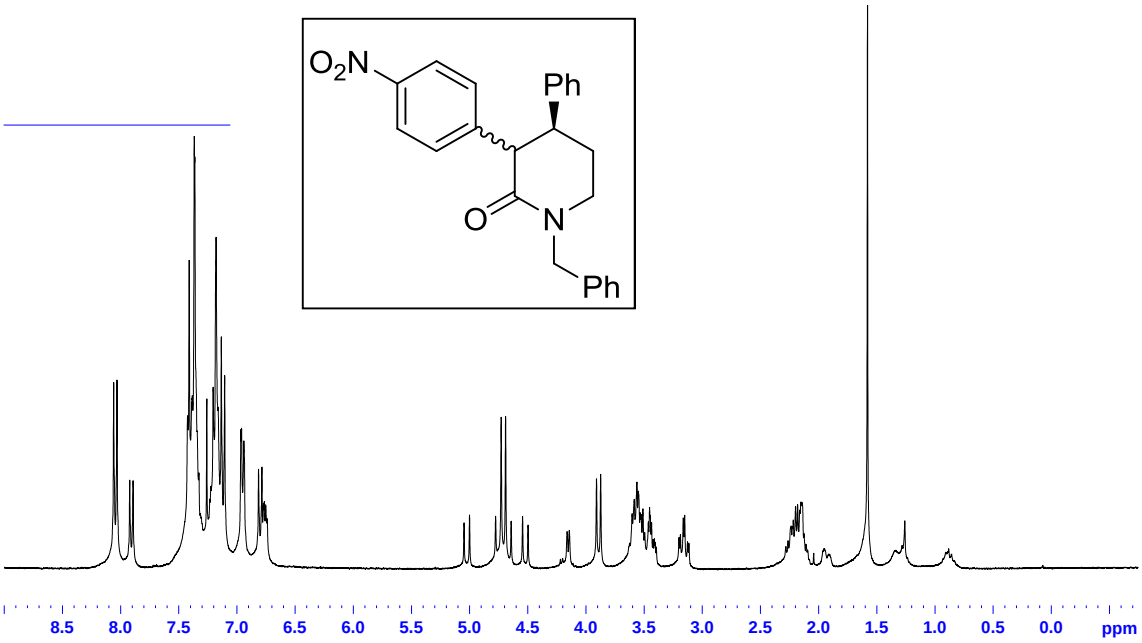

197.43
148.47
147.76
147.12
143.54
129.55
129.44
124.20
123.78
77.45
77.23
77.03
76.61
65.88
59.38
45.40
35.52
30.91
29.69
23.77
14.14
200
180
160
140
120
100
80
60
40
20
0
ppm

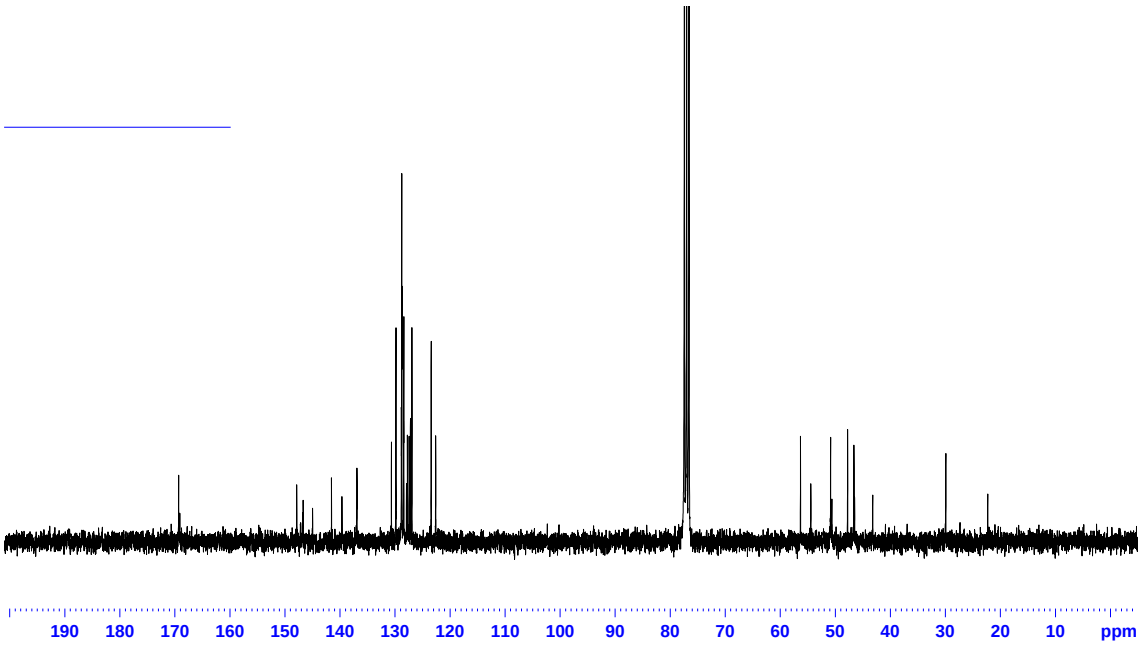

O2N
O
OH
O
S
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.98 1.96 0.96 0.98 1.00 1.00 1.00 1.96 1.97 1.73 1.08 2.96
198.12 153.31 147.56 143.81 142.05 129.62 123.99 110.26 108.15 64.09 60.06 39.41 33.91 23.73 14.36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

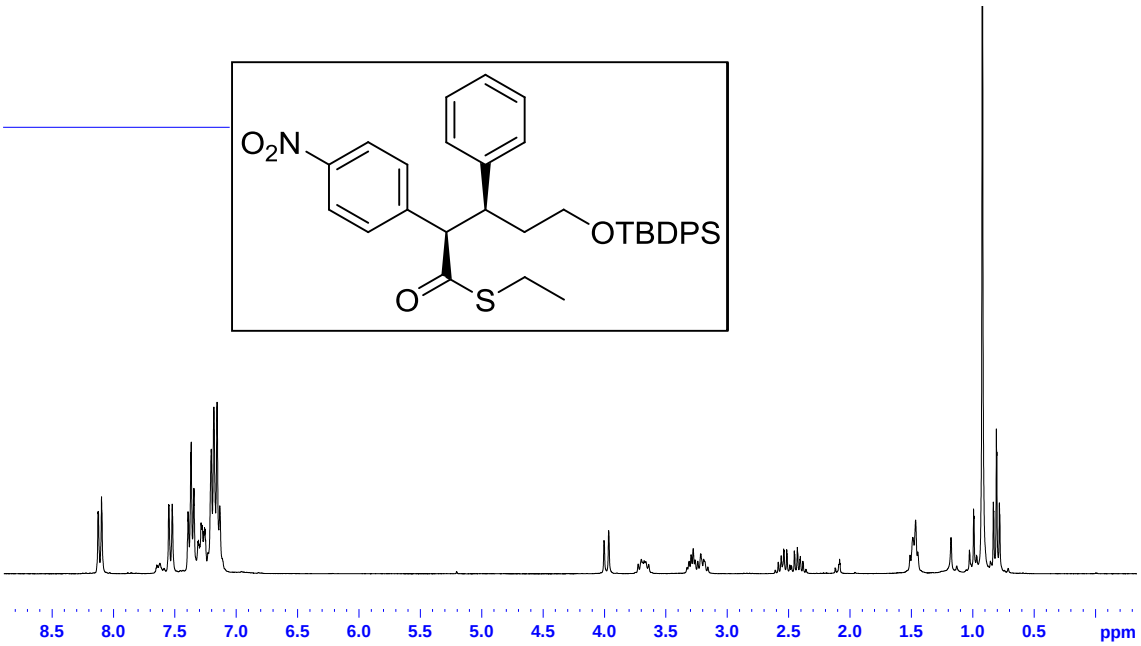

O2N
Ph
OH
10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
3.15
4.33
1.08
1.12
3.28
2.16

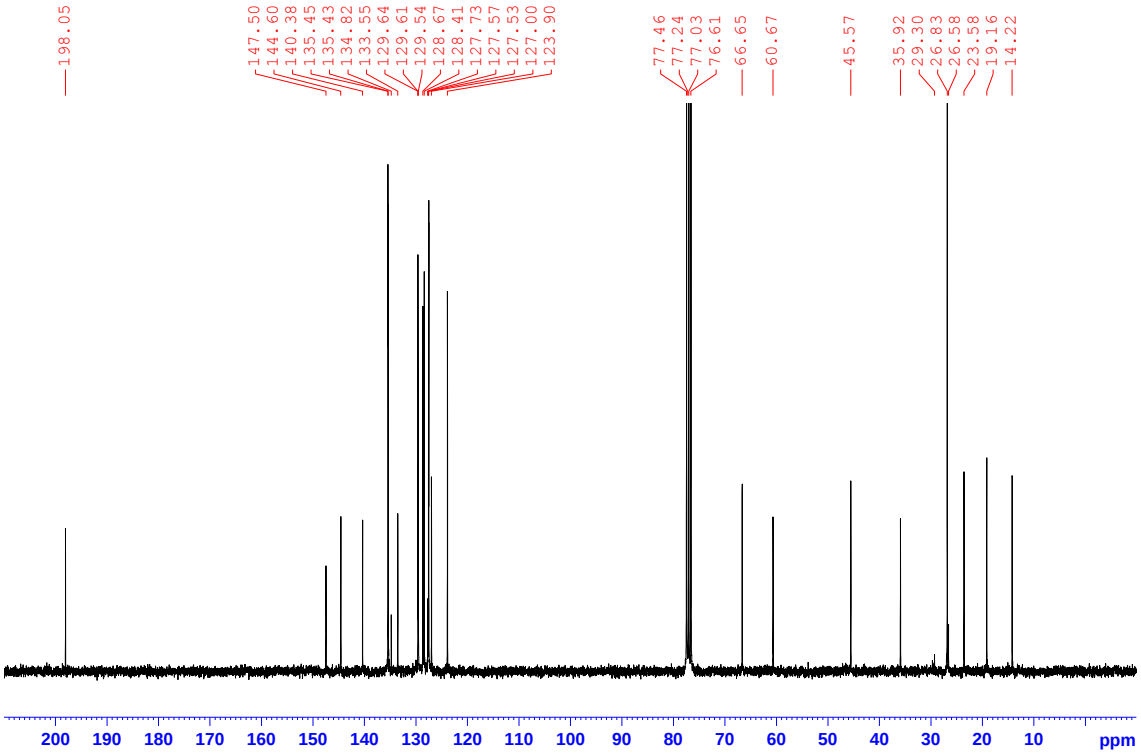

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

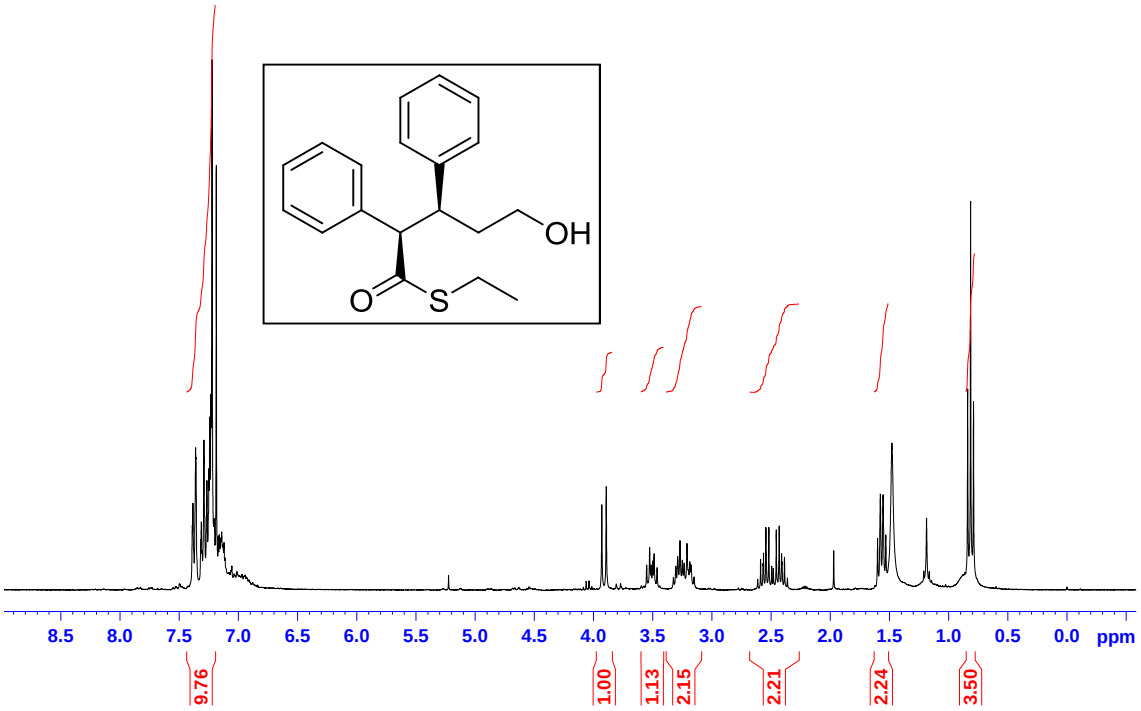

O2N
O
O
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
1.89
1.87
0.89
1.09
1.12
1.27
2.98
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

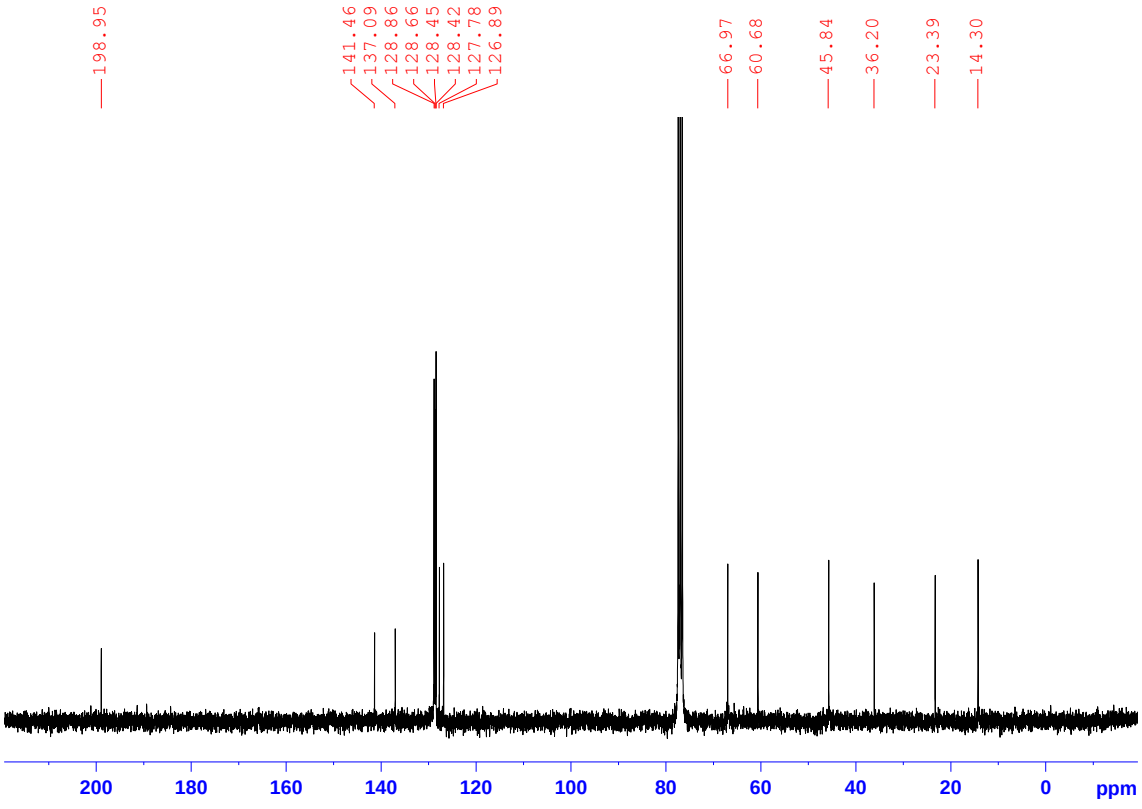

O2N
Ph
O
N
Ph
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

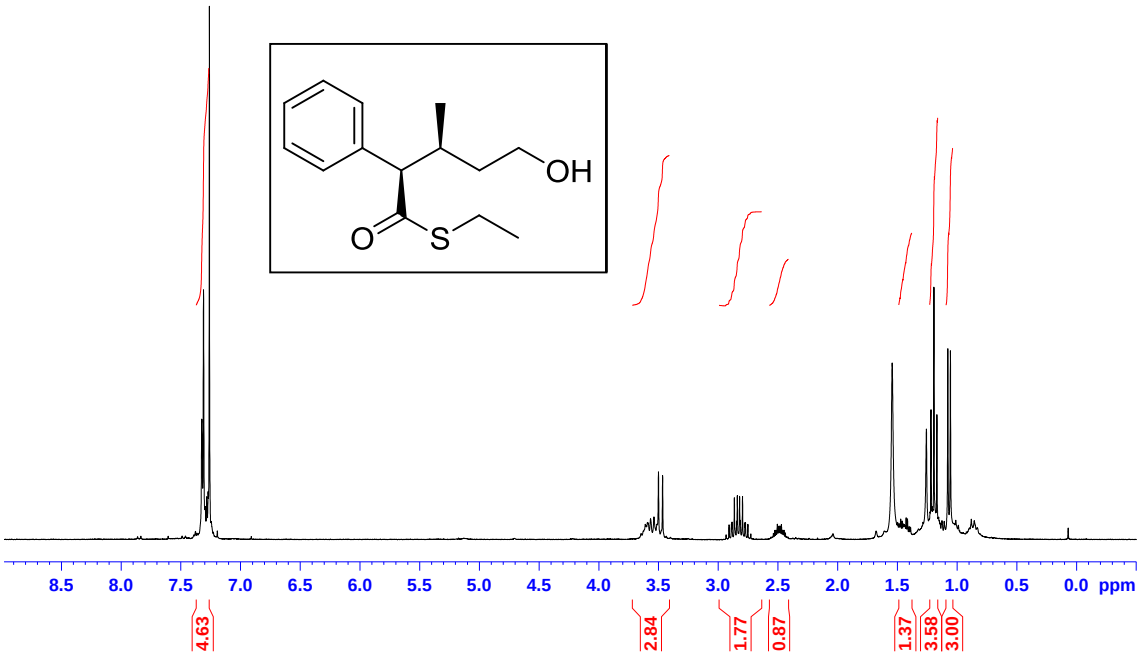

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

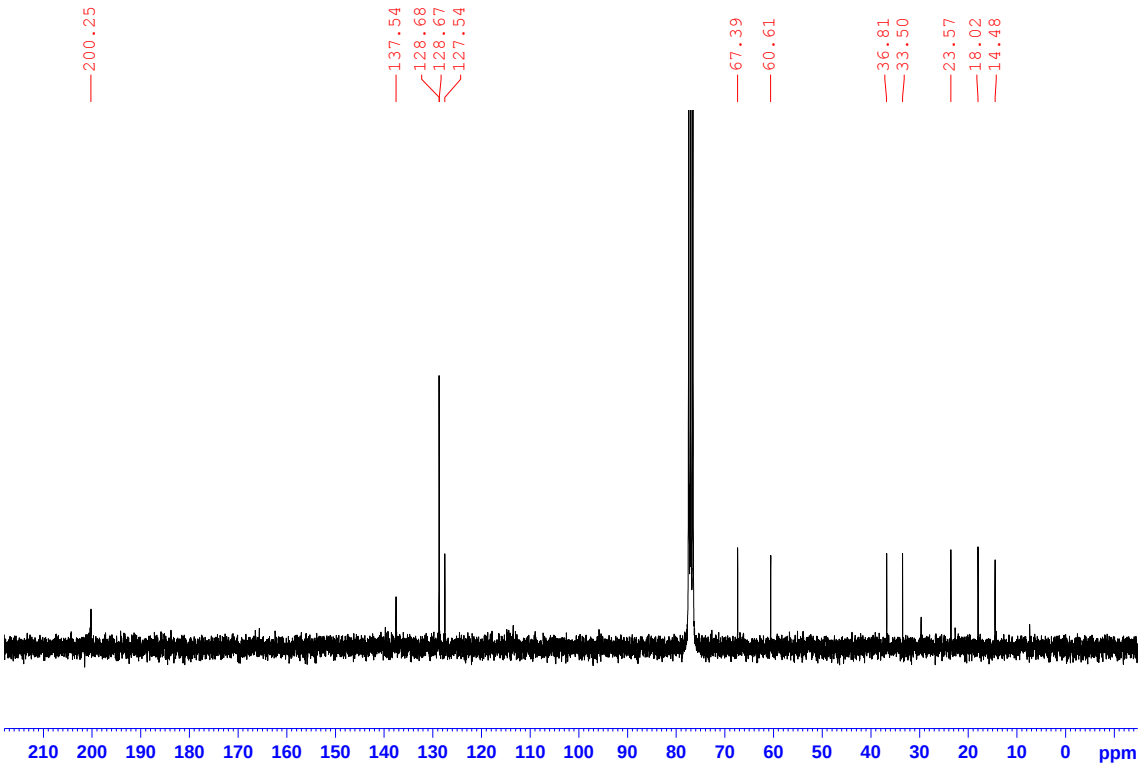

O2N
OTBDPS
O
S
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


198.05
147.50
144.60
140.38
135.45
135.43
134.82
133.55
129.64
129.61
129.54
128.67
128.41
127.73
127.57
127.53
127.00
123.90
77.46
77.24
77.03
76.61
66.65
60.67
45.57
35.92
29.30
26.83
26.58
23.58
19.16
14.22
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OH
O
S
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
9.76
1.00
1.13
2.15
2.21
2.24
3.50

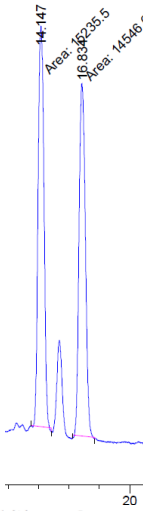

198.95
141.46
137.09
128.86
128.66
128.45
128.42
127.78
126.89
66.97
60.68
45.84
36.20
23.39
14.30
200
180
160
140
120
100
80
60
40
20
0
ppm

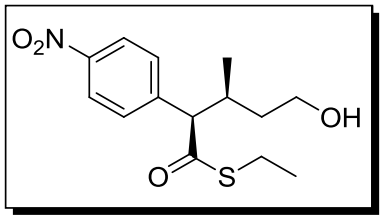

OH
O
S
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
4.63
2.84
1.77
0.87
1.37
3.58
3.00


200.25
137.54
128.68
128.67
127.54
67.39
60.61
36.81
33.50
23.57
18.02
14.48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

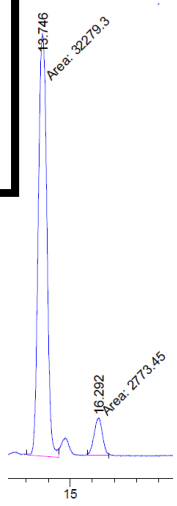
HPLC of compounds (racemic and non-racemic)

***rac*- 26a**





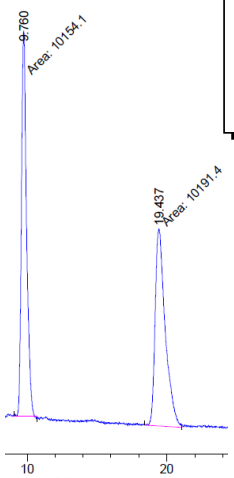
26a

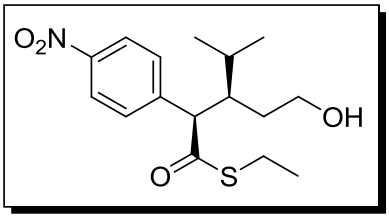


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.147	MM	0.4443	1.52355e4	571.49420	51.1566
2	16.834	MM	0.4819	1.45466e4	503.06580	48.8434

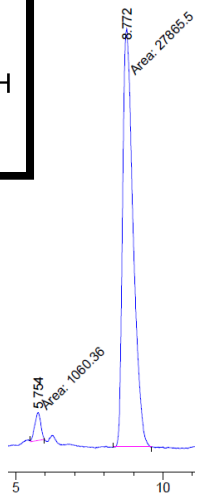
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.746	MM	0.4454	3.22793e4	1207.82397	92.0878
2	16.292	MM	0.4371	2773.45288	105.75397	7.9122

***rac*- 26e**





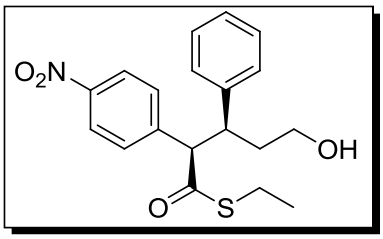
26e

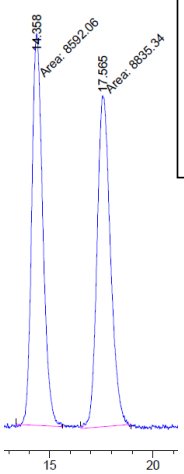


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.147	MM	0.4443	1.52355e4	571.49420	51.1566
2	16.834	MM	0.4819	1.45466e4	503.06580	48.8434

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.754	MM	0.2357	1060.36047	74.99189	3.6658
2	8.772	MM	0.4135	2.78655e4	1123.19531	96.3342

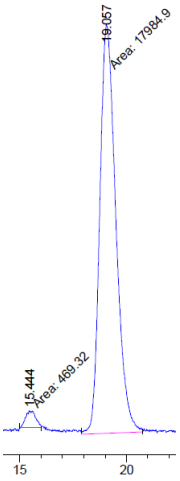
***rac*- 26f**





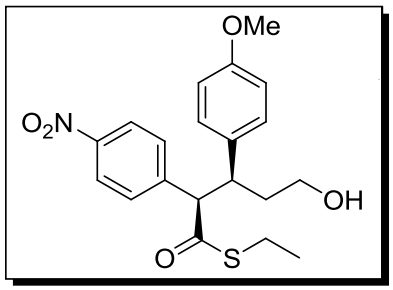
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.358	MM	0.6200	8592.06445	230.96307	49.3020
2	17.565	MM	0.7538	8835.33984	195.35493	50.6980

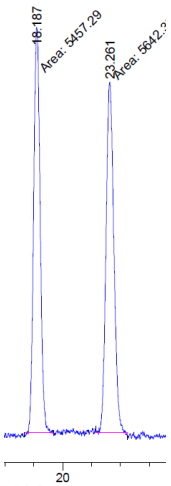
26f



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.444	MM	0.5504	469.31985	14.21098	2.5432
2	19.057	MM	0.8720	1.79849e4	343.74048	97.4568

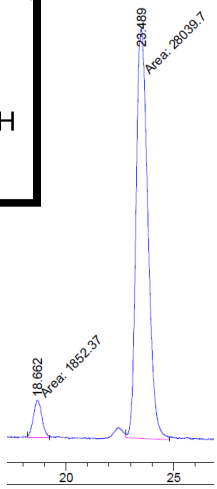
***rac*- 26g**





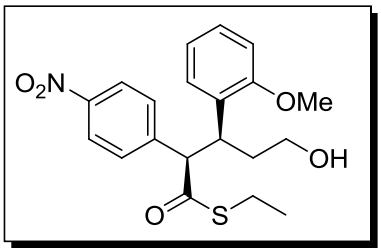
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.187	MM	0.5249	5457.29346	173.29254	49.1665
2	23.261	MM	0.6284	5642.33398	149.65248	50.8335

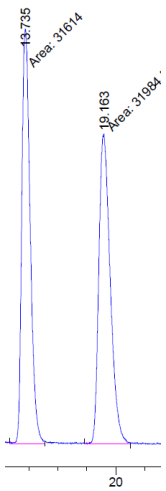
26g



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.662	MM	0.4597	1852.36597	67.15166	6.1969
2	23.489	MM	0.6347	2.80397e4	736.26782	93.8031

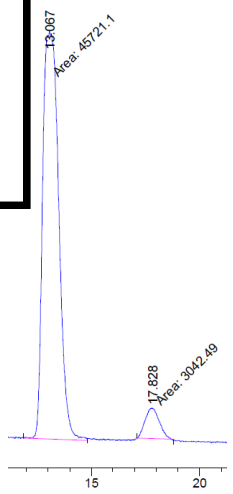
***rac*- 26k**





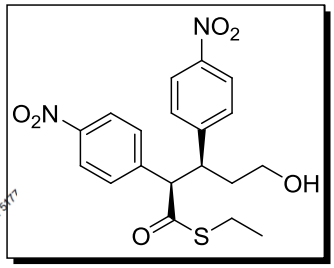
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.735	MM	0.6716	3.16140e4	784.57953	49.7087
2	19.163	MM	0.9104	3.19845e4	585.54767	50.2913

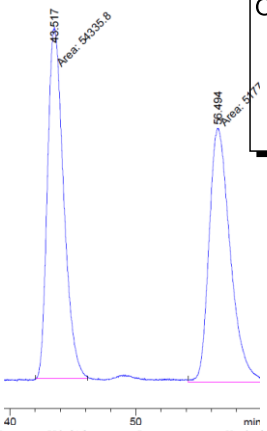
26k



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.067	MM	0.8550	4.57211e4	891.21277	93.7607
2	17.828	MM	0.7619	3042.48828	66.55432	6.2393

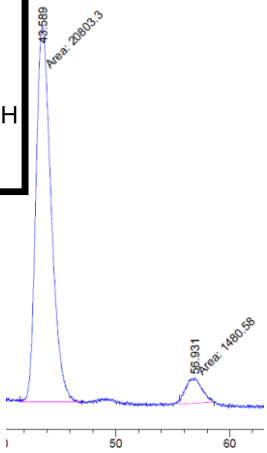
***rac*- 26h**





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.517	MM	1.4813	5.43358e4	611.34503	51.2083
2	56.494	MM	1.9522	5.17717e4	441.98657	48.7917

26h



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.589	MM	1.5446	2.08032e4	224.47452	93.3558
2	56.931	MM	1.5966	1480.58484	15.45603	6.6442