Supplementary Information

Transannular dipolar cycloaddition as an approach towards the synthesis of the core ring system of the sarain alkaloids

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Contents

1. Experimental procedures and compound characterization data for the OBn analogs of the OPMB compounds 15–18 and the cycloadduct from 19 + hydroxylamine

We provide here, procedures and spectroscopic data for the compounds (not drawn in the main manuscript) from the oxazolidinone **9** to the aldehyde **21**. These are the OBn analogs of the OPMB compounds **15**–**18**.

(*S*)-4-[(*R*)-1-(Benzyloxy)pent-4-en-2-yl]-3-(but-3-enyl)oxazolidin-2-one (OBn analog of the OPMB compound **15**). NaOH (1.76 g, 44 mmol), K_2CO_3 (1.78 g, 12.9 mmol) and *n*-Bu_4NHSO_4 (0.21 g, 0.6 mmol) were added to the oxazolidinone **9** (1.53 g, 5.86 mmol) in PhMe (31 mL). To this mixture was added 4-bromo-1-butene (1.84 mL, 17.6 mmol) and the mixture was heated under reflux. After 1 h, water (50 mL) was added and the mixture was extracted with Et_2O (3 × 100 mL). The organic layers were dried ($MgSO_4$) and evaporated to give the diene (OBn analog of the OPMB compound **15**) (1.5 g, 82%) as an oil; $[\alpha]^{20}_D$ 9.4 (3.5, CH_2Cl_2); ν_{max}/cm^{-1} 1740, 1640; ^{1}H NMR (500 MHz, C_6D_6) δ = 7.20–7.11 (m, 5H), 5.66 (ddt, 1H, *J* 17, 10, 7 Hz), 5.52–5.44 (m, 1H), 5.02–4.89 (m, 4H), 4.15 (d, 1H, *J* 12 Hz), 4.09 (d, 1H, *J* 12 Hz), 3.86–3.78 (m, 2H), 3.65 (ddd, 1H, *J* 9, 6, 3.5 Hz), 3.49 (dt, 1H, *J* 14, 8 Hz), 3.05 (dd, 1H, *J* 10, 4 Hz), 2.98 (dd, 1H, *J* 10, 6 Hz) 2.78 (ddd, 1H, *J* 14, 8, 6 Hz), 2.17–2.14

(m, 2H), 1.94–1.90 (m, 1H), 1.78–1.72 (m, 1H), 1.64–1.58 (m, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ = 158.2, 138.4, 136.1, 135.4, 128.6, 128.2, 127.7, 116.9, 116.8, 73.3, 69.1, 63.6, 56.4, 41.5, 38.9, 32.1, 28.9; HRMS (ES) found 338.1746, $C_{19}H_{25}NO_3Na$ requires (MNa) 338.1732; *m/z* (ES) 338 (100%), 316 (5).

(10*R*,10a*S*,*Z*)-10-(Benzyloxy)methyl-5,6,10,10a-tetrahydro-1*H*-oxazolo[3,4-a]azocin-3(9*H*)-one (OBn analog of the OPMB compound **16**). The diene above (OBn analog of the OPMB compound **15**) (543 mg, 1.72 mmol) was added to de–gassed dry PhMe (400 mL) at room temperature. Grubbs 2nd generation ruthenium catalyst (48 mg, 0.057 mmol, 3.3 mol%) was added at 40 °C. After 1 h, further catalyst (48 mg, 0.057 mmol, 3.3 mol%) was added. After 1 h, further catalyst (48 mg, 0.057 mmol, 3.3 mol%) was added. After a further 1 h, DMSO (~ 0.5 mL) was added and the mixture was allowed to cool to room temperature. After 18 h, the solvent was evaporated, and the residue was purified by column chromatography on silica, eluting with EtOAc–petrol (1:4 to 2:5), to give the alkene (OBn analog of the OPMB compound **16**) (290 mg, 59%) as an oil; $[\alpha]^{20}_D$ 1.0 (6.0, CH_2Cl_2); ν_{max}/cm^{-1} 1740, 1670; ^{1}H NMR (500 MHz, C_6D_6) δ = 7.29–7.18 (m, 5H), 5.56–5.47 (m, 2H), 4.44 (d, 1H, *J* 12 Hz), 4.41 (d, 1H, *J* 12 Hz), 4.13–4.04 (m, 3H), 3.70 (ddd, 1H, *J* 14, 12, 5 Hz), 3.31 (dd, 1H, *J* 9.5, 6 Hz), 3.26 (dd, 1H, *J* 9.5, 7.5 Hz), 3.13 (ddd, 1H, *J* 14, 5, 4 Hz), 2.73–2.67 (m, 1H), 2.61–2.53 (m, 1H), 2.32–2.24 (m, 2H), 2.19–2.14 (m, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ = 159.4, 137.8, 129.6, 128.5, 127.9, 127.6, 125.7, 73.6, 70.7, 63.8, 57.5, 43.1, 39.7, 27.7, 26.7; HRMS (ES) found 288.1589, $C_{17}H_{22}NO_3$ requires (MH) 288.1600.

[(2*S*,3*R*,*Z*)-3-(Benzyloxy)methyl)-1,2,3,4,7,8-hexahydroazocin-2-yl]methanol (OBn analog of the OPMB compound **17**). NaOH (225 mg, 5.63 mmol) in ethanol (3.4 mL) and water (1.1 mL) was added to oxazolidinone above (OBn analog of the OPMB compound **16**) (260 mg, 0.9 mmol) and the mixture was heated under reflux. After 16 h, CH_2Cl_2 (10 mL) was added and the mixture was washed with brine (3 × 10 mL). The organic layer was dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica, eluting with CH_2Cl_2–MeOH–NH_3 (95:5:1), gave the amine (OBn analog of the OPMB compound **17**) (216 mg, 92%) as an oil; $[\alpha]^{20}_D$ –8.8 (1.7, CH_2Cl_2); ν_{max}/cm^{-1} 3325, 3215; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38–7.29 (m, 5H), 5.83–5.77 (m, 1H), 5.73–5.68 (m, 1H), 4.49 (s, 2H), 3.5 (dd, 1H, *J* 9.5, 5 Hz), 3.46 (dd, 1H, *J* 9.5, 4, Hz), 3.40 (d, 2H, *J* 7 Hz), 3.06 (ddd, 1H, *J* 14, 6, 3.5 Hz), 2.89 (td, 1H, *J* 7, 4 Hz), 2.61–2.52 (m, 2H), 2.27–2.20 (m, 1H), 2.15–2.09 (m, 1H), 2.03–1.92 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 137.9, 130.4, 129.8, 128.5, 127.8, 127.7, 73.6, 71.5, 64.8, 59.6, 49.4, 41.9, 30.4, 28.5; HRMS (ES) found 262.1814, $C_{16}H_{24}NO_2$ requires (MH) 262.1807; *m/z* (ES) 284 (15%), 262 (100).

(2*S*,3*R*,*Z*)-*tert*-Butyl 3-[(Benzyloxy)methyl]-2-(hydroxymethyl)-3,4,7,8-tetrahydroazocine-1(2*H*)-carboxylate (OBn analog of the OPMB compound **18**). $NaHCO_3$ (174 mg, 2.07 mmol) in water (3 mL) was added to the amine above (OBn analog of the OPMB compound **17**) (540 mg, 2.07 mmol) in dioxane (6.4 mL) at room temperature. After 10 min, further $NaHCO_3$ was added until the pH of the solution reached 10. To the mixture was added di–*tert*–butyldicarbonate (0.48 mL, 2.07 mmol). After 18 h, water (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 15 mL). The organic layers were dried ($MgSO_4$), evaporated and purified by column chromatography on silica, eluting with EtOAc–petrol (1:4 to 2:5), to give the carbamate (OBn analog of the OPMB compound **18**) (648 mg, 87%) as an oil; $[\alpha]^{20}_D$ 5.4 (3.8, CH_2Cl_2); ν_{max}/cm^{-1} 3430, 2925, 1690, 1665; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.33–7.34 (m, 5H), 5.86–5.65 (m, 2H), 4.61–4.57 (m, 1H), 4.50–4.45 (m, 1H), 4.13–3.87 (m, 4H), 3.52–3.37 (m, 2H), 2.74–2.00 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.8, 138.5, 130.7, 129.3, 128.4, 127.8, 127.6, 79.5, 73.1, 72.3, 63.6, 61.9, 51.0, 43.6, 28.5, 28.5, 27.2; HRMS (ES) found 362.2334, $C_{21}H_{32}NO_4$ requires (MH) 362.2331; *m/z* (ES) 384 (100%) 362 (20).

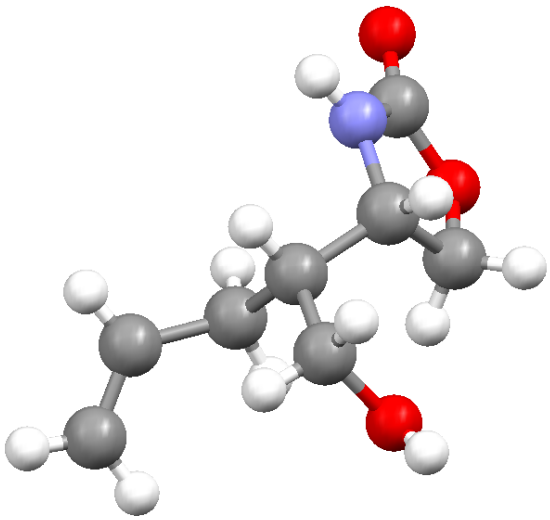
Cycloadduct from 19 + hydroxylamine

$NaHCO_3$ (74 mg, 0.86 mmol) was added to the aldehyde **19** (73 mg, 0.19 mmol), and N-methylhydroxylamine·HCl (49 mg, 0.57 mmol) in EtOH (2 mL) and the mixture was heated in a sealed tube at 125 °C. After 4.5 h, the solvent was evaporated, H_2O (10 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography on silica, eluting with EtOAc–petrol (1:4), gave the cycloadduct (OPMB analog of the OBn compound **22a**) (51 mg, 65%) as an oil; $[\alpha]^{22}_D$ 3.8 (4.0, CH_2Cl_2); ν_{max}/cm^{-1} 2930, 2845, 1679; ^1H NMR (500 MHz, $CDCl_3$, mixture of rotamers) δ = 7.23 (d, 2H, *J* 8 Hz), 6.86 (d, 2H, *J* 8 Hz), 4.49–4.36 (m, 3.5H), 4.20–4.19 (m, 0.5H), 3.83–3.73 (m, 1H), 3.79 (s, 1.5H), 3.78 (s, 1.5H), 3.66–3.61 (m, 0.5H), 3.51–3.34 (m, 3.5H), 3.18–3.11 (m, 1H), 2.70 (s, 1.5H), 2.68 (s, 1.5H), 2.34–2.28 (m, 1H), 1.96–1.84 (m, 2H), 1.71–1.60 (m, 2H), 1.45 (s, 4.5H), 1.41 (s, 4.5H); ^{13}C NMR (125 MHz, $CDCl_3$, mixture of rotamers) δ = 159.1, 159.0, 156.0, 155.6, 130.4, 130.2, 129.1, 129.0, 113.7, 113.6, 79.1, 79.0, 77.6, 77.3, 74.0, 73.6, 72.8, 72.7, 72.6, 71.6, 59.6, 59.1, 55.2, 55.1, 49.2, 49.0, 48.5, 48.4, 47.4, 46.8, 39.4, 38.3, 29.0, 28.7, 28.4, 28.37, 25.5, 25.1; HRMS (ES) found 419.2544, $C_{23}H_{35}N_2O_5$ requires (MH) 419.2546; *m/z* (ES) 441 (15%), 419 (98), 363 (100).

2. X-ray structure analysis for compounds 8 and 23

X-ray data for oxazolidinone **8**.

Ball-and-stick representation of **8**:



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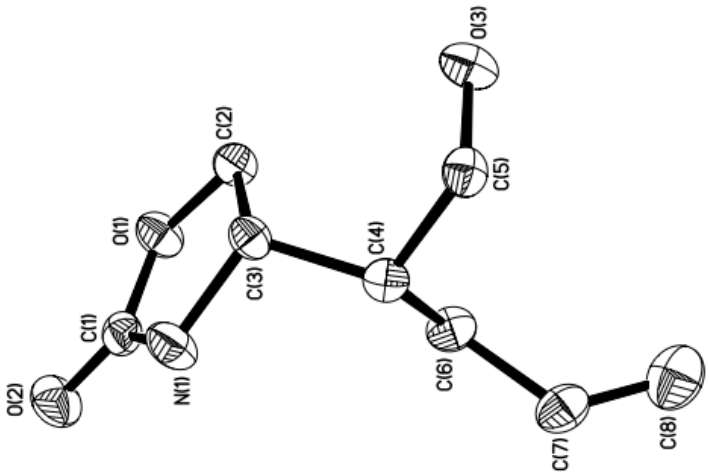
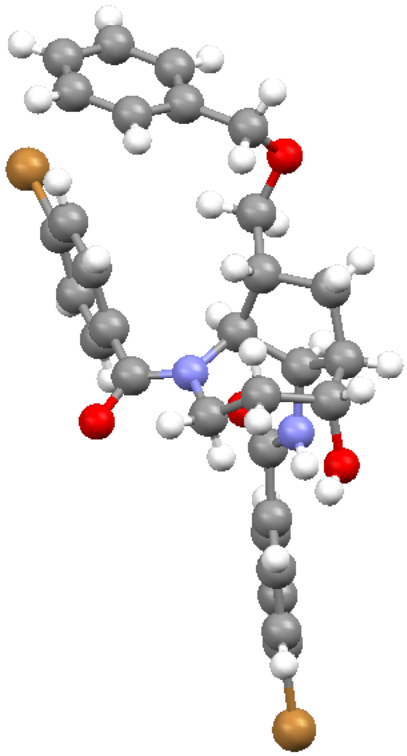


Empirical formula	C8 H13 N O3	
Formula weight	171.19	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.0046(14) Å	α= 90°.
	b = 6.1040(14) Å	β= 103.144(4)°.
	c = 12.099(3) Å	γ = 90°.
Volume	431.83(17) $Å^3$	
Z	2	
Density (calculated)	1.317 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	184	
Crystal size	0.32 x 0.21 x 0.20 mm^3	
Theta range for data collection	1.73 to 27.53°.	
Index ranges	-7<=h<=7, -7<=k<=7, -15<=l<=15	
Reflections collected	4884	
Independent reflections	1080 [R(int) = 0.0246]	
Completeness to theta = 27.53°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9802 and 0.9685	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1080 / 1 / 109	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0319, wR2 = 0.0832	
R indices (all data)	R1 = 0.0360, wR2 = 0.0855	
Absolute structure parameter	0(10)	
Largest diff. peak and hole	0.228 and -0.146 $e.Å^{-3}$	

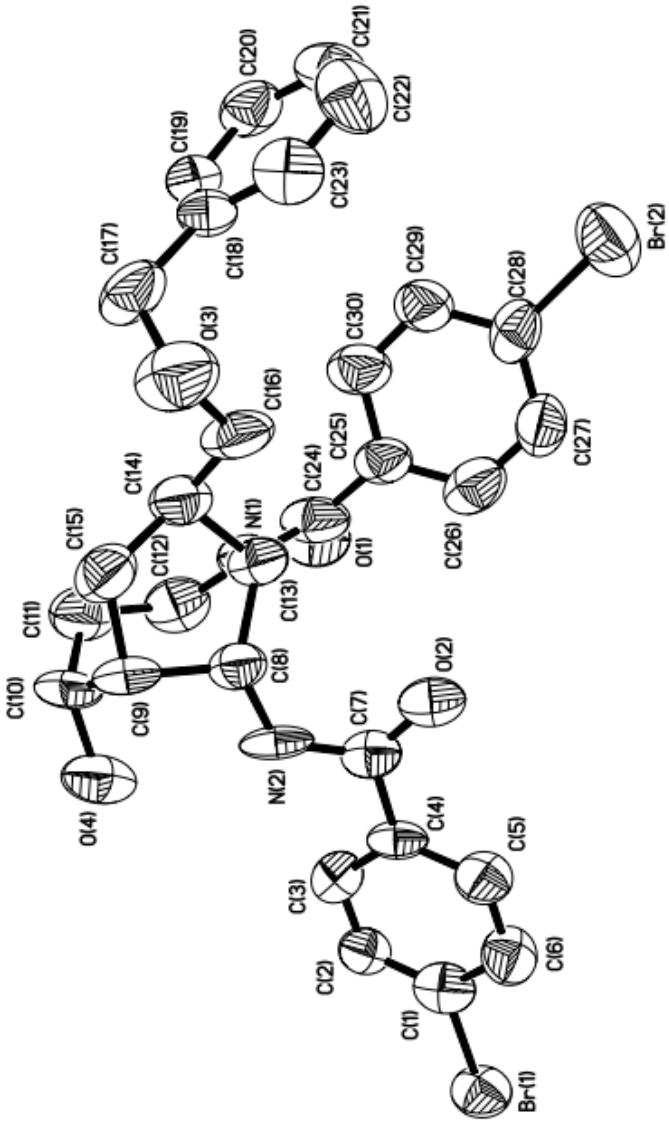
For atomic coordinates, bond lengths and angles and displacement parameters, see data deposited at the Cambridge Crystallographic Data Centre. Structure number CCDC-791948.

X-ray data for amide **23**.

Ball-and-stick representation of **23**:



Thermal ellipsoid plot for **23**:



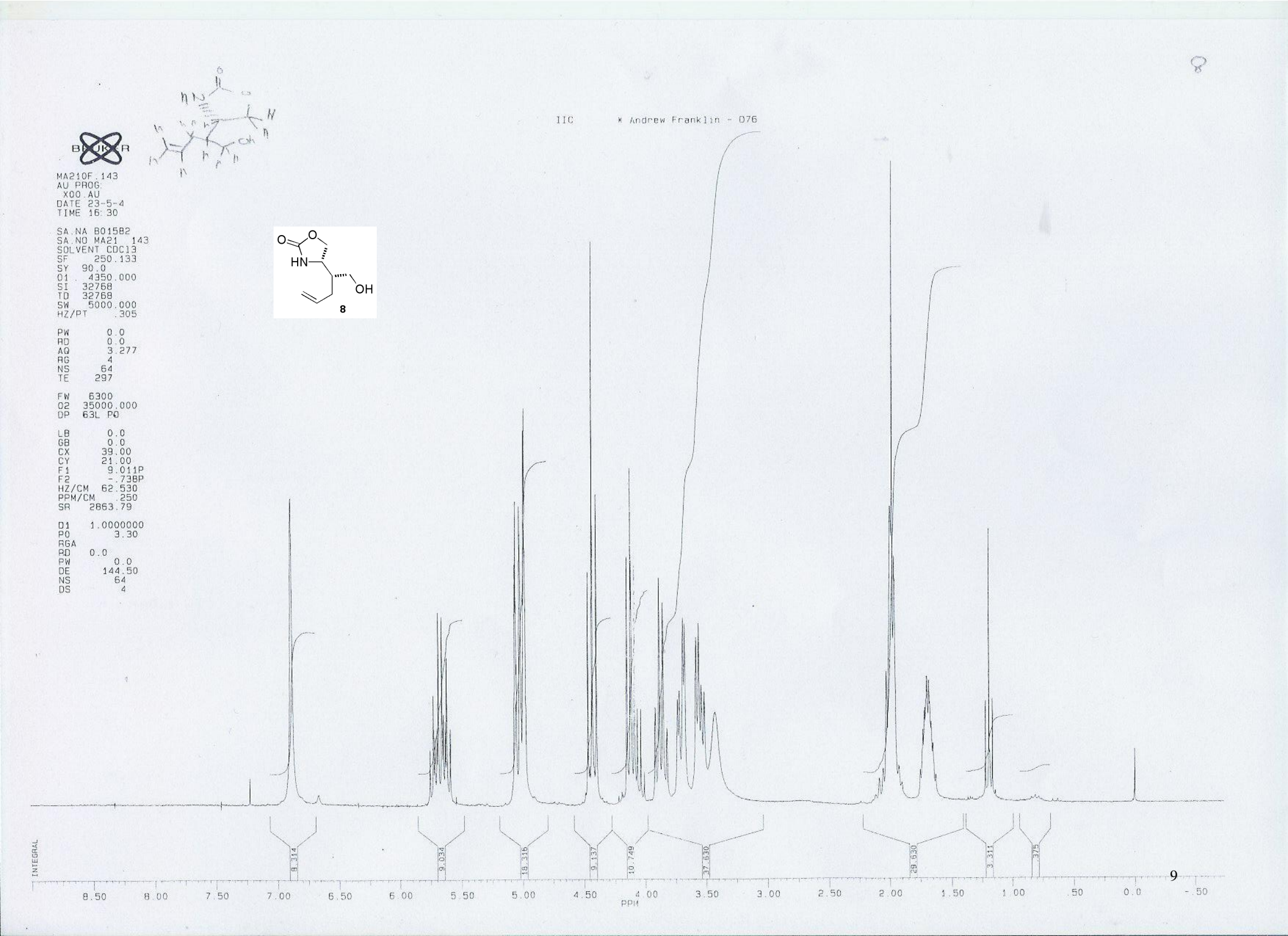
Empirical formula	C30 H30 Br2 N2 O4
Formula weight	642.38
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$

Unit cell dimensions	a = 9.5861(10) Å	α= 90°.
	b = 14.7570(15) Å	β= 90°.
	c = 19.402(2) Å	γ = 90°.
Volume	2744.7(5) $Å^3$	
Z	4	
Density (calculated)	1.555 Mg/m^3	
Absorption coefficient	2.992 mm^{-1}	
F(000)	1304	
Crystal size	0.26 x 0.11 x 0.09 mm^3	
Theta range for data collection	1.73 to 22.94°.	
Index ranges	-10<=h<=10, -16<=k<=14, -14<=l<=21	
Reflections collected	29383	
Independent reflections	3759 [R(int) = 0.1242]	
Completeness to theta = 22.94°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7745 and 0.5100	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3759 / 0 / 344	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0665, wR2 = 0.1502	
R indices (all data)	R1 = 0.1246, wR2 = 0.1843	
Absolute structure parameter	0.02(3)	
Largest diff. peak and hole	0.784 and -0.593 $e.Å^{-3}$	

The crystal was a poor diffractor and during data collection it decomposed; however the overall structure is clearly visible, sufficient to assign the regiochemistry in the cycloaddition reaction.

For atomic coordinates, bond lengths and angles and displacement parameters, see data deposited at the Cambridge Crystallographic Data Centre. Structure number CCDC-791949.

3. NMR spectra for 8–23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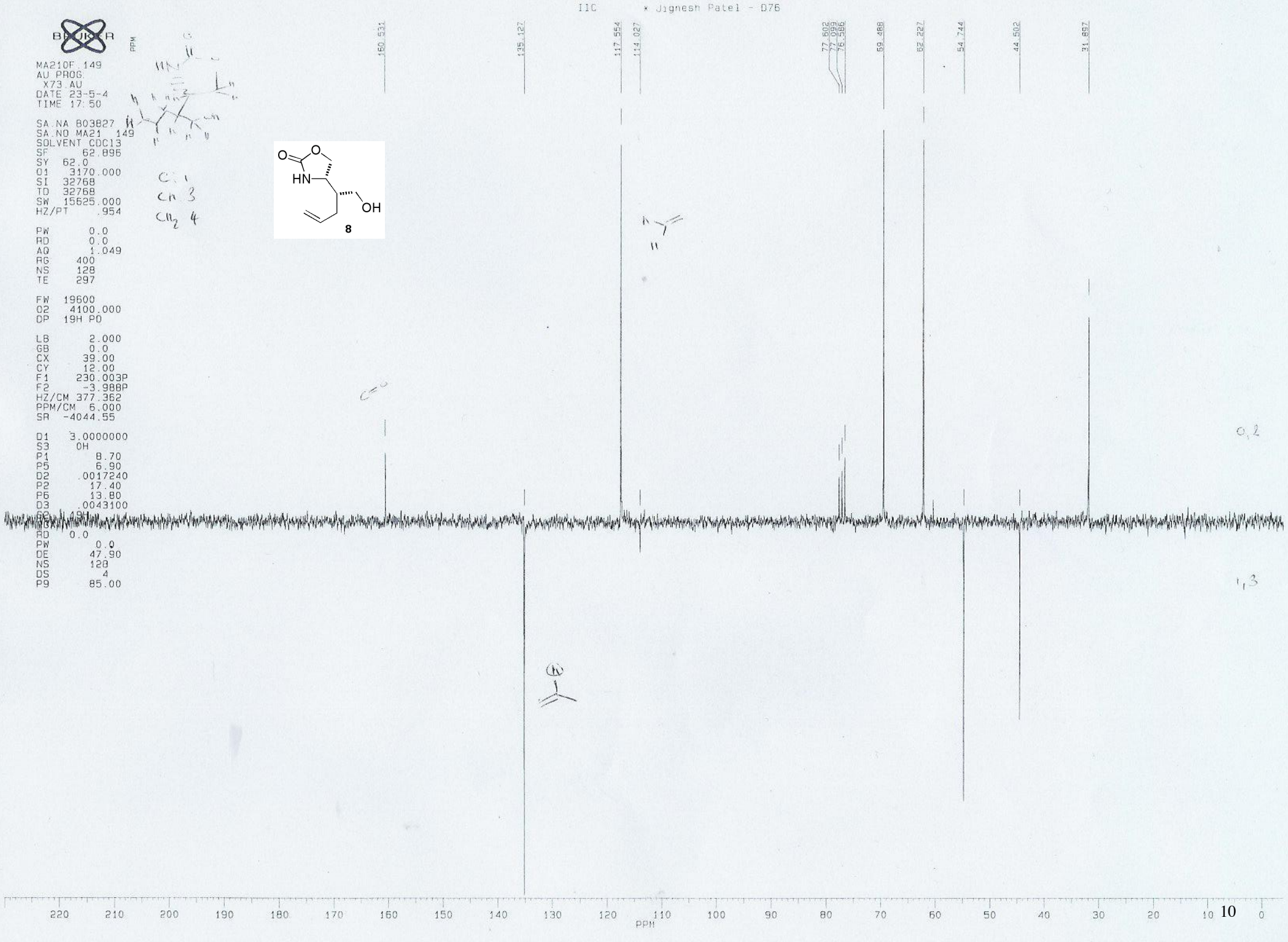
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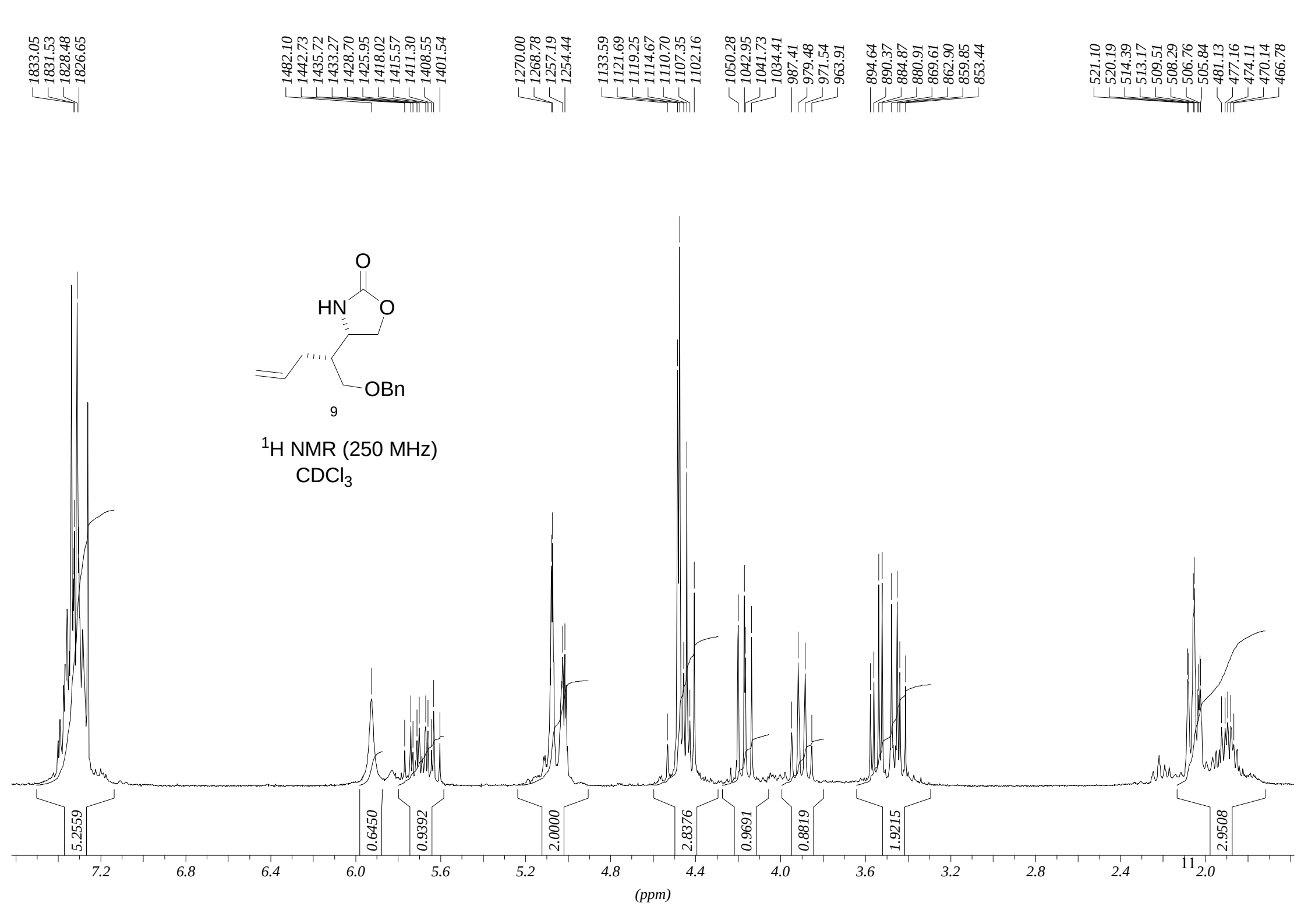
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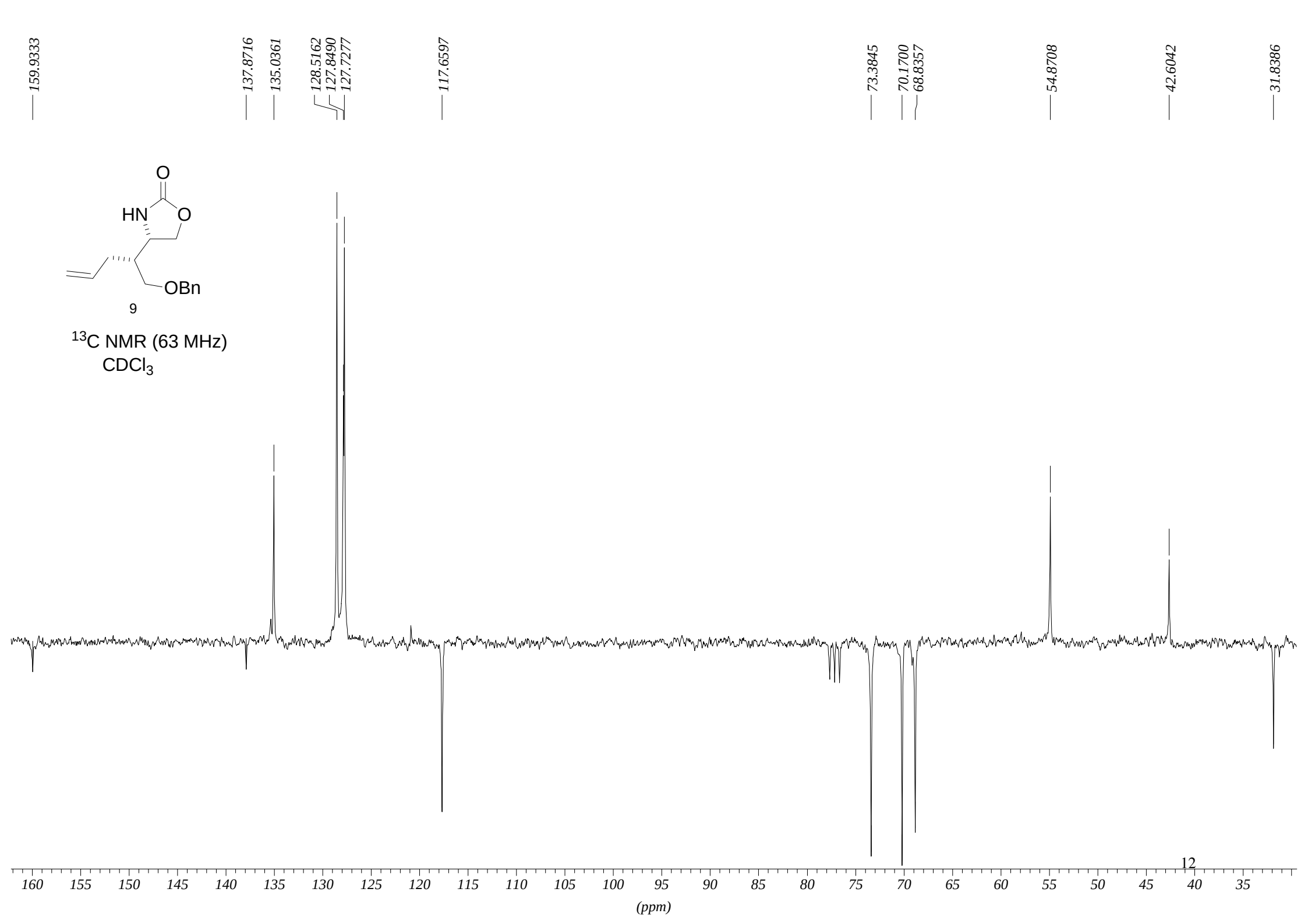
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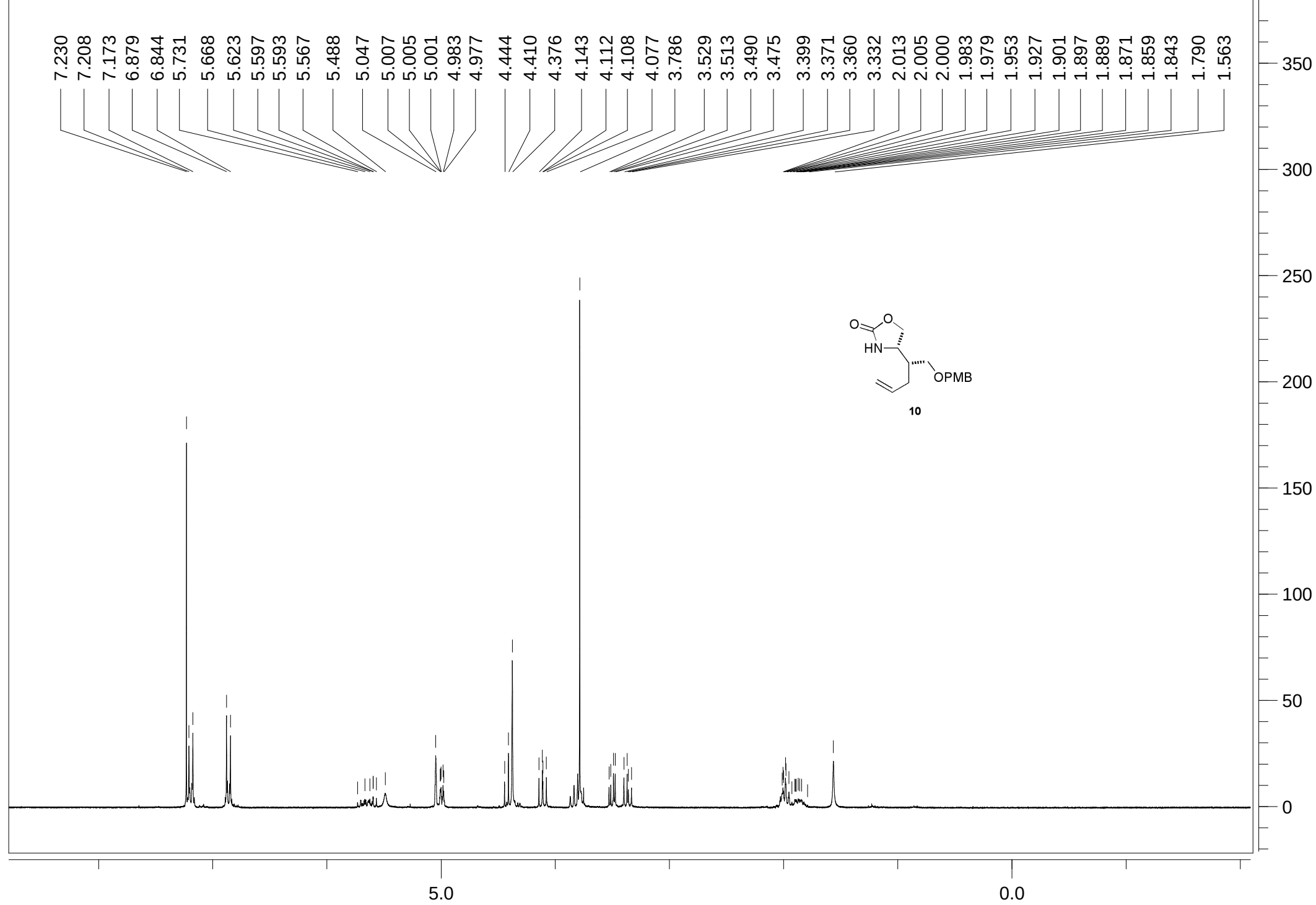
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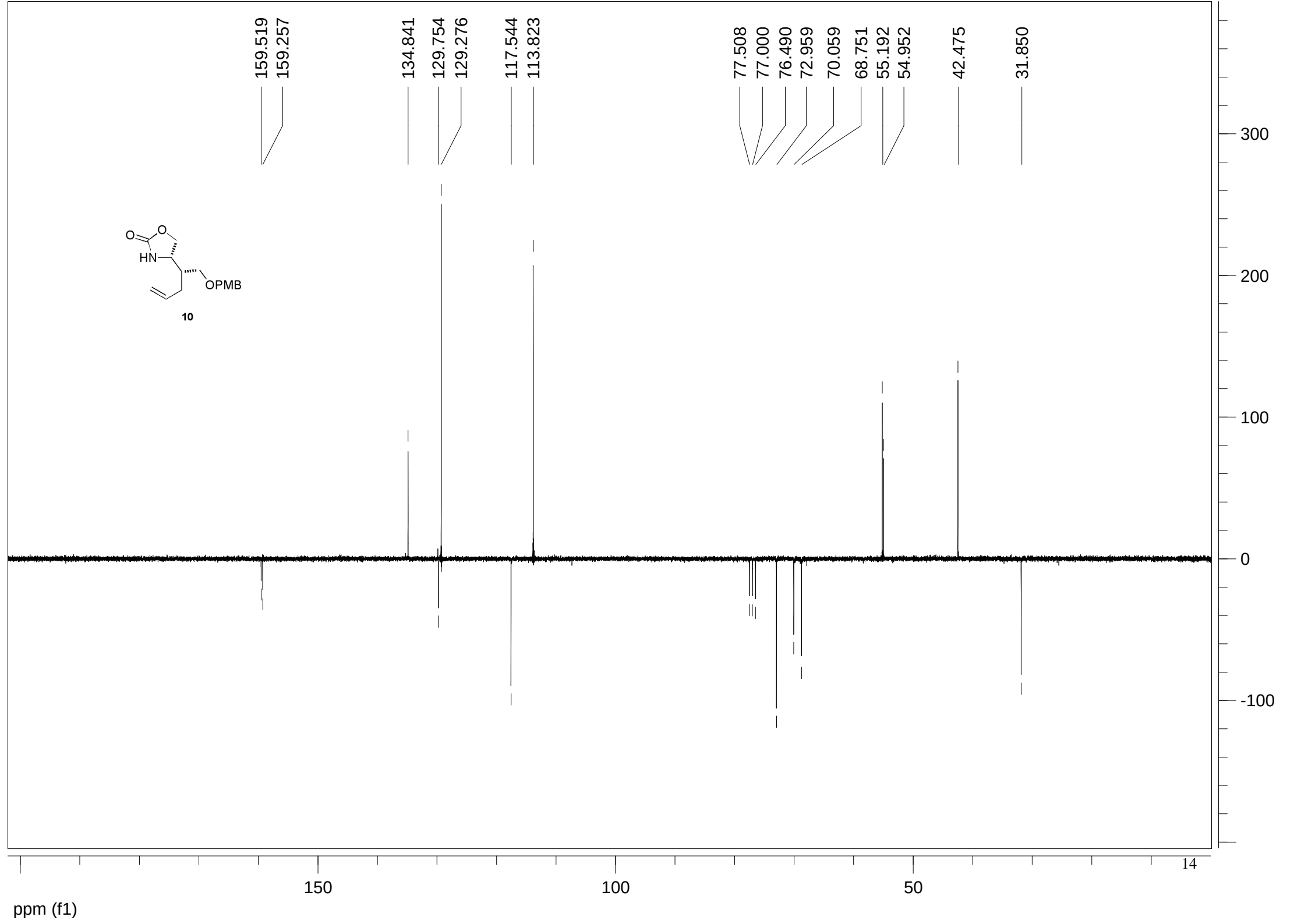
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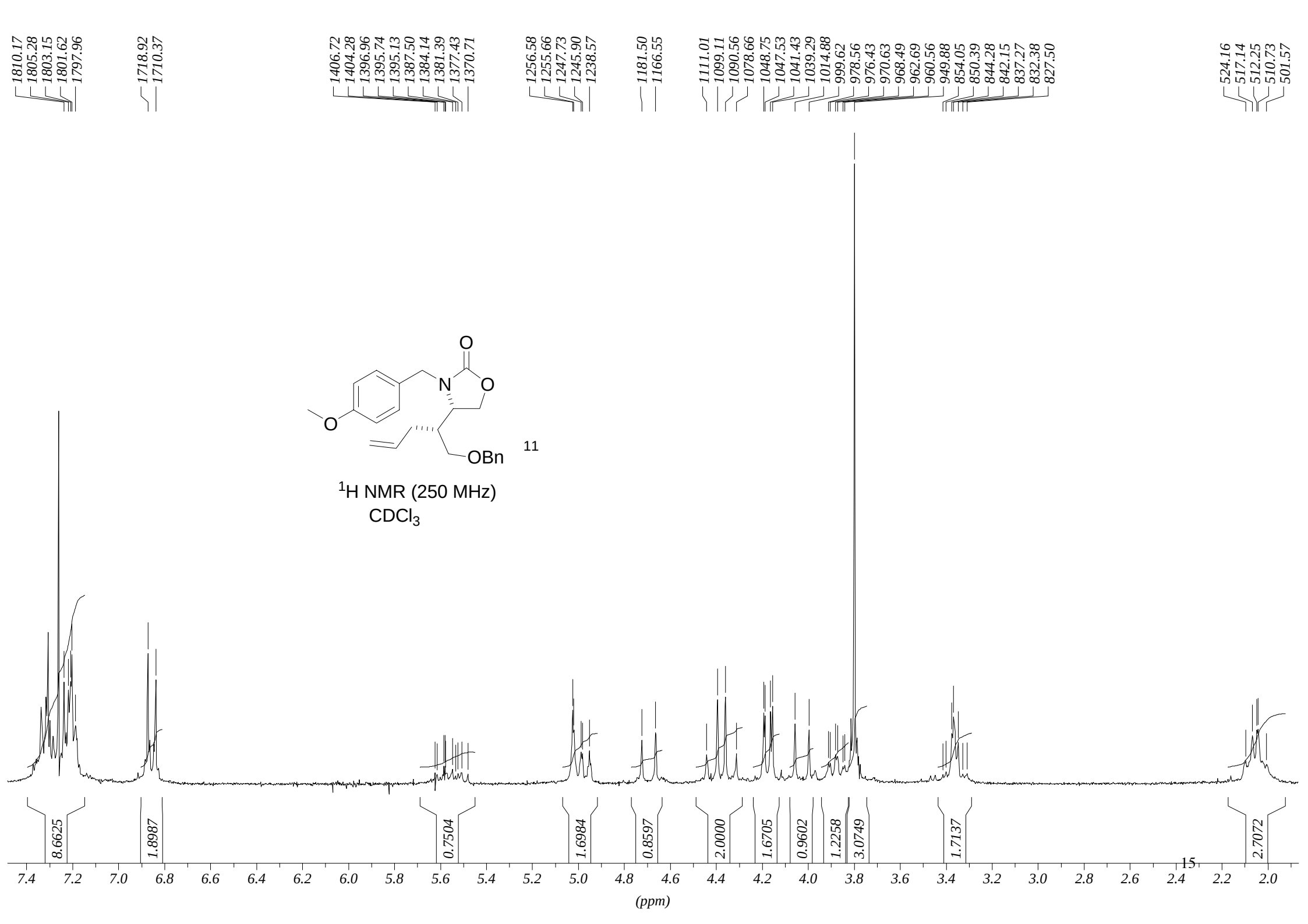
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968.49
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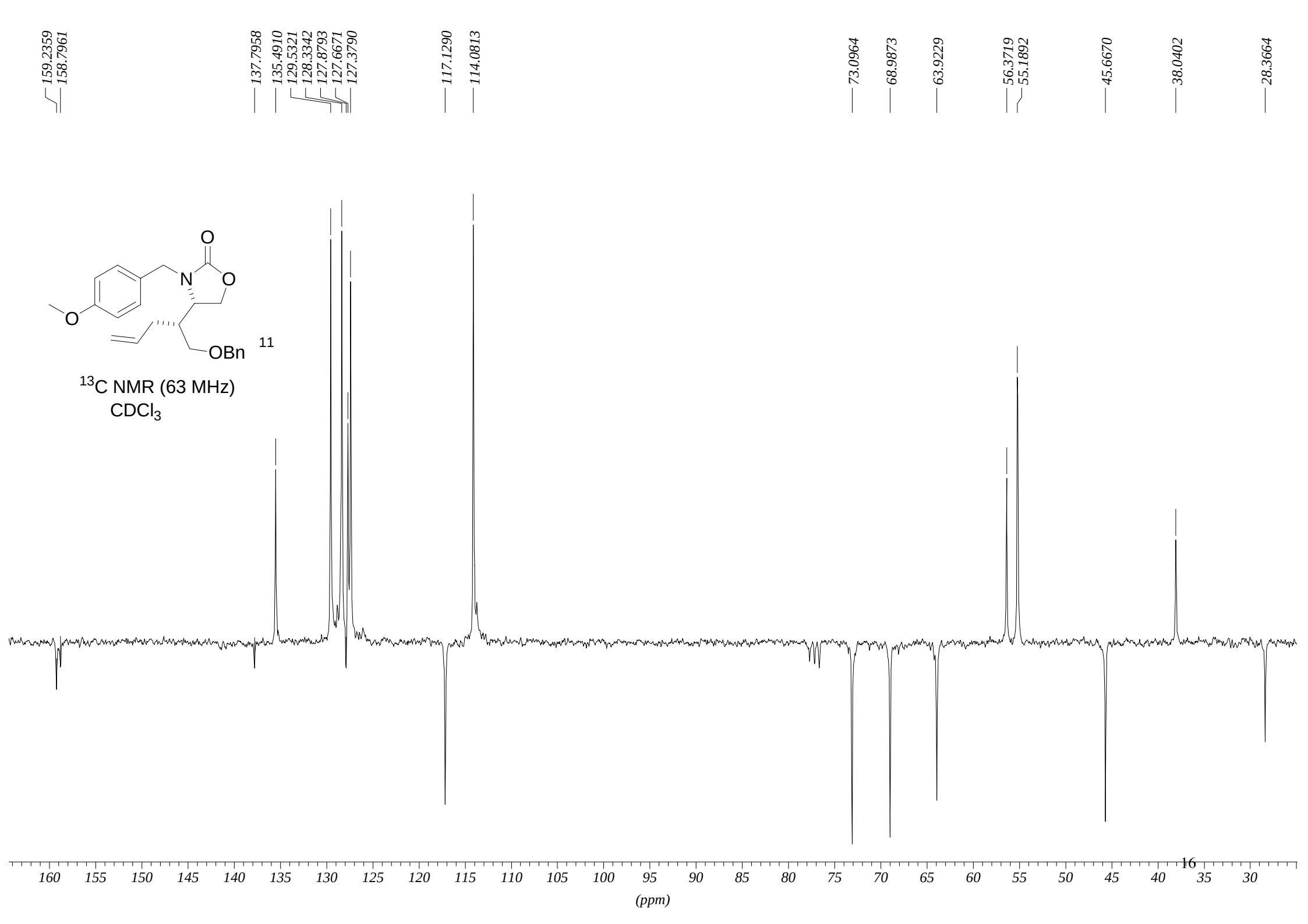
960.56
949.88
854.05
850.39
844.28
842.15
837.27
832.38
827.50
524.16
517.14
512.25
510.73
501.57
O
N
O
O
OBn
11
1H NMR (250 MHz)
CDCl3
8.6625
1.8987
0.7504
1.6984
0.8597
2.0000
1.6705
0.9602
1.2258
3.0749
1.7137
2.7072
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
(ppm)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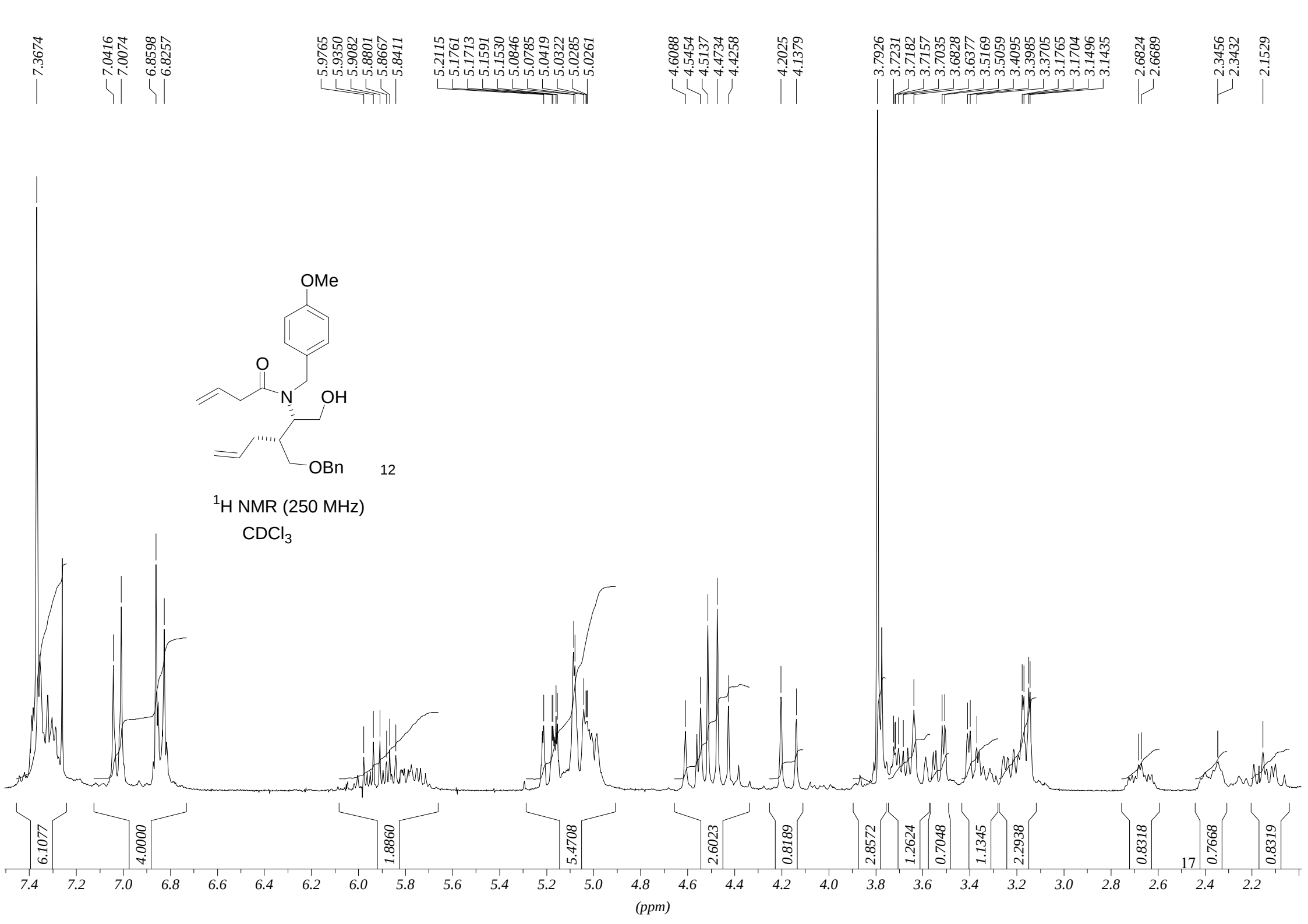
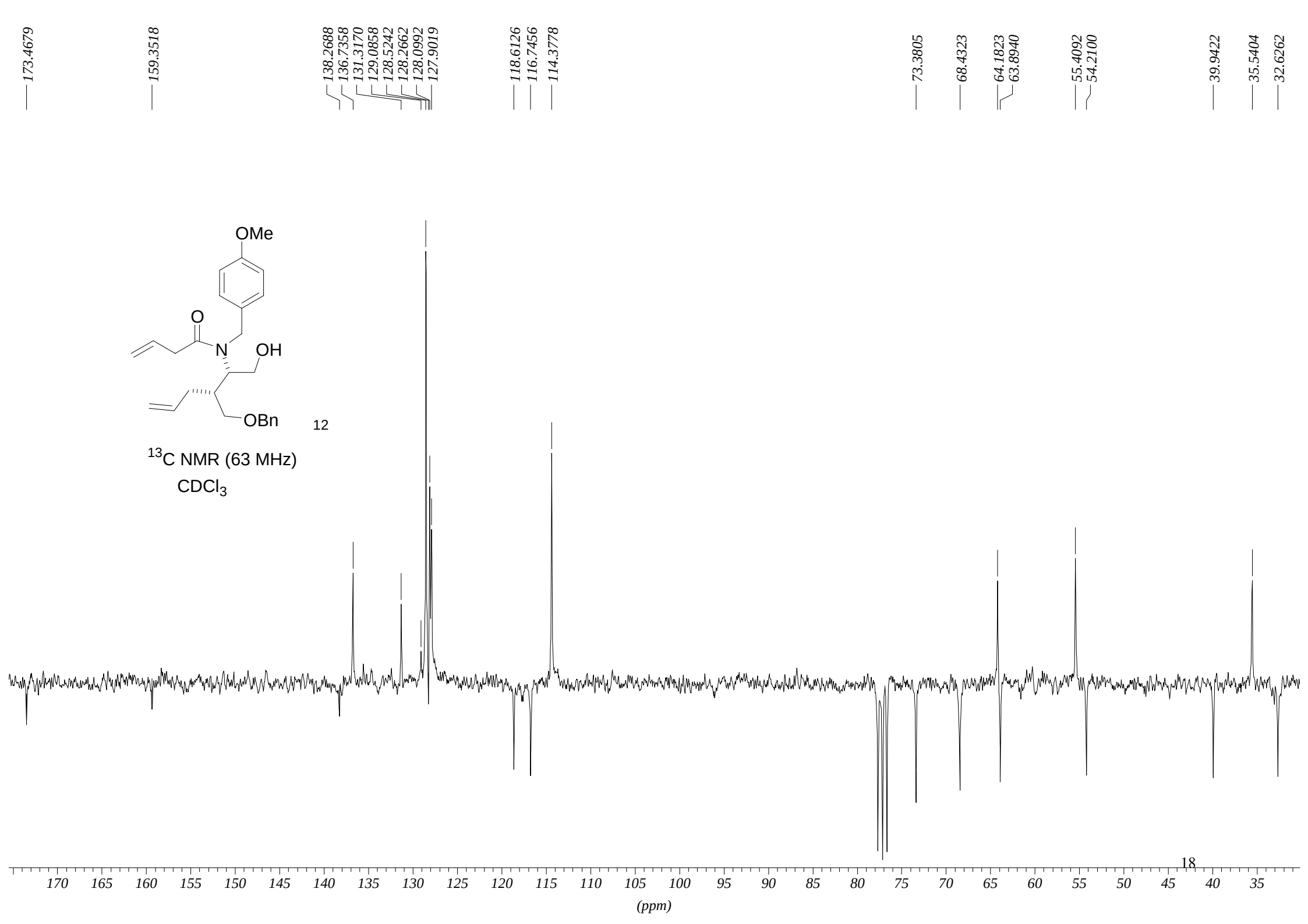
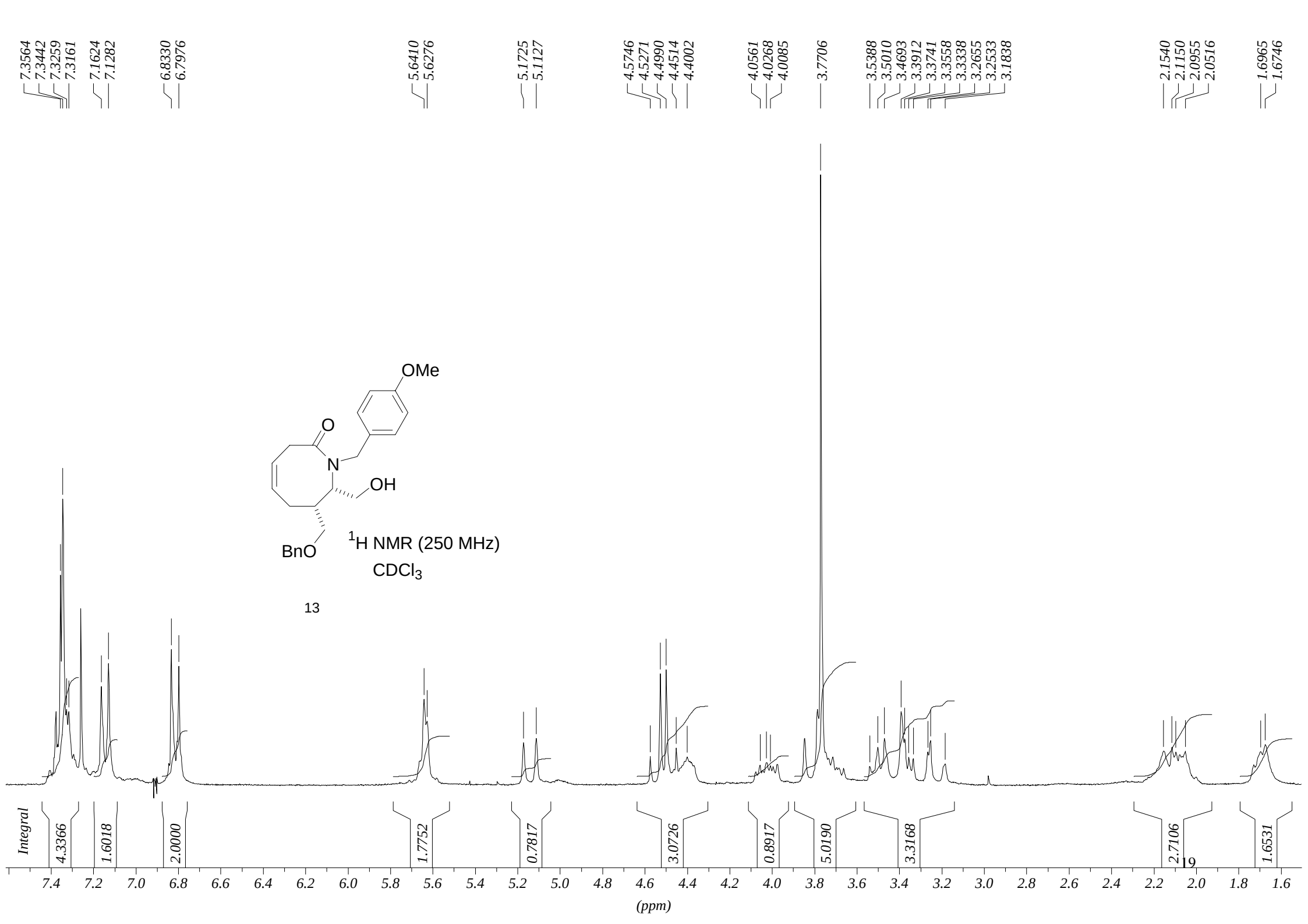
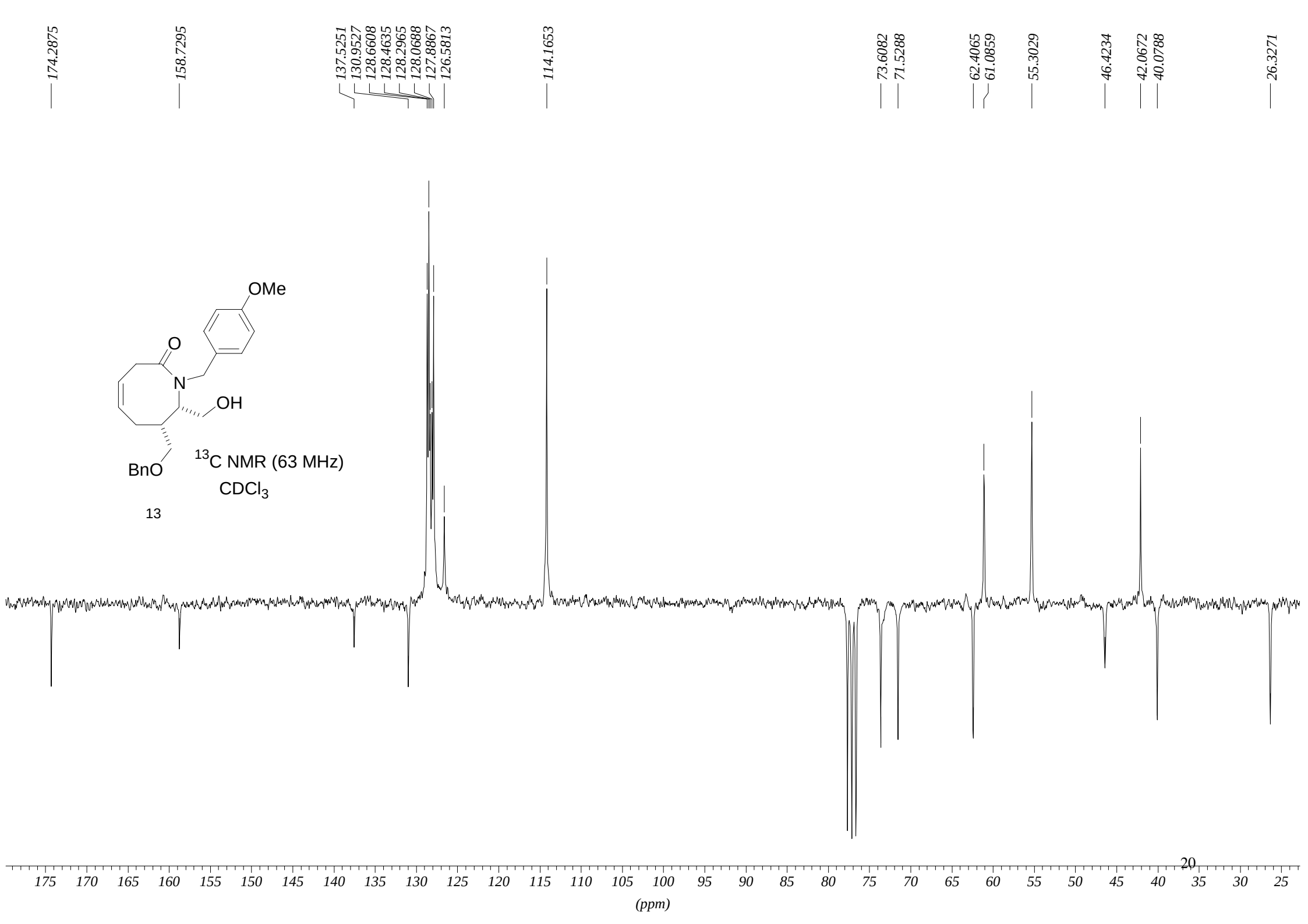
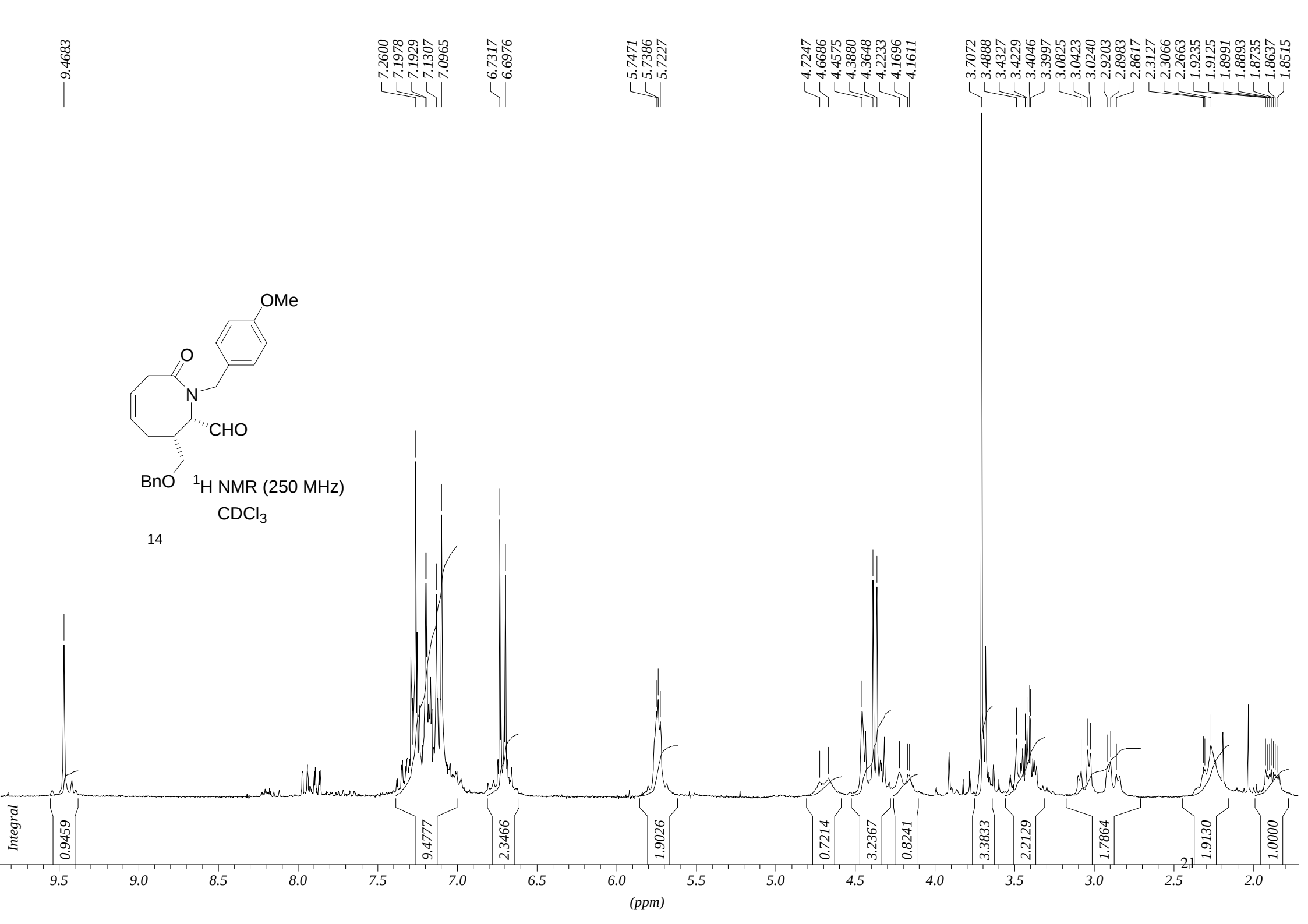
158.7961
137.7958
135.4910
129.5321
128.3342
127.8793
127.6671
127.3790
117.1290
114.0813
73.0964
68.9873
63.9229
56.3719
55.1892
45.6670
38.0402
28.3664
O
N
O
O
OBn
11
13C NMR (63 MHz)
CDCl3
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
(ppm)

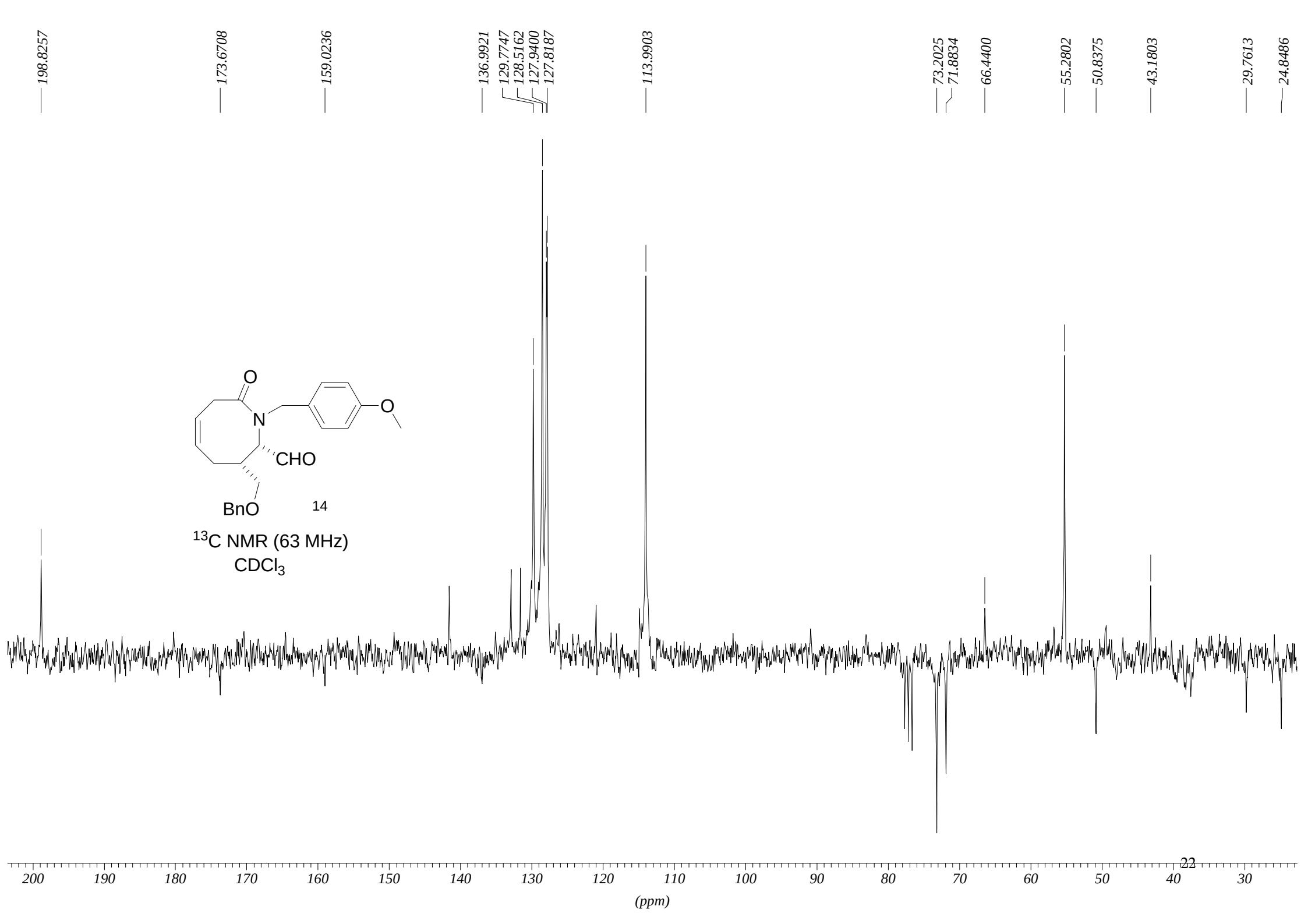

7.3674
7.0416
7.0074
6.8598
6.8257
5.9765
5.9350
5.9082
5.8801
5.8667
5.8411
5.2115
5.1761
5.1713
5.1591
5.1530
5.0846
5.0785
5.0419
5.0322
5.0285
5.0261
4.6088
4.5454
4.5137
4.4734
4.4258
4.2025
4.1379
3.7926
3.7231
3.7182
3.7157
3.7035
3.6828
3.6377
3.5169
3.5059
3.4095
3.3985
3.3705
3.1765
3.1704
3.1496
3.1435
2.6824
2.6689
2.3456
2.3432
2.1529
OMe
O
N
OH
OBn
12
1H NMR (250 MHz)
CDCl3
6.1077
4.0000
1.8860
5.4708
2.6023
0.8189
2.8572
1.2624
0.7048
1.1345
2.2938
0.8318
0.7668
0.8319
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
(ppm)
17


173.4679
159.3518
138.2688
136.7358
131.3170
129.0858
128.5242
128.2662
128.0992
127.9019
118.6126
116.7456
114.3778
73.3805
68.4323
64.1823
63.8940
55.4092
54.2100
39.9422
35.5404
32.6262
OMe
O
N
OH
OBn
12
13C NMR (63 MHz)
CDCl3
18
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
(ppm)


7.3564
7.3442
7.3259
7.3161
7.1624
7.1282
6.8330
6.7976
5.6410
5.6276
5.1725
5.1127
4.5746
4.5271
4.4990
4.4514
4.4002
4.0561
4.0268
4.0085
3.7706
3.5388
3.5010
3.4693
3.3912
3.3741
3.3558
3.3338
3.2655
3.2533
3.1838
2.1540
2.1150
2.0955
2.0516
1.6965
1.6746
OMe
O
N
OH
BnO
1H NMR (250 MHz)
CDCl3
13
Integral
4.3366
1.6018
2.0000
1.7752
0.7817
3.0726
0.8917
5.0190
3.3168
2.7106
1.6531
7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
(ppm)


174.2875
158.7295
137.5251
130.9527
128.6608
128.4635
128.2965
128.0688
127.8867
126.5813
114.1653
73.6082
71.5288
62.4065
61.0859
55.3029
46.4234
42.0672
40.0788
26.3271
OMe
O
N
OH
BnO
13C NMR (63 MHz)
CDCl3
13
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
(ppm)


9.4683
7.2600
7.1978
7.1929
7.1307
7.0965
6.7317
6.6976
5.7471
5.7386
5.7227
4.7247
4.6686
4.4575
4.3880
4.3648
4.2233
4.1696
4.1611
3.7072
3.4888
3.4327
3.4229
3.4046
3.3997
3.0825
3.0423
3.0240
2.9203
2.8983
2.8617
2.3127
2.3066
2.2663
1.9235
1.9125
1.8991
1.8893
1.8735
1.8637
1.8515
OMe
O
N
CHO
BnO
1H NMR (250 MHz)
CDCl3
14
Integral
0.9459
9.4777
2.3466
1.9026
0.7214
3.2367
0.8241
3.3833
2.2129
1.7864
1.9130
1.0000
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
(ppm)
21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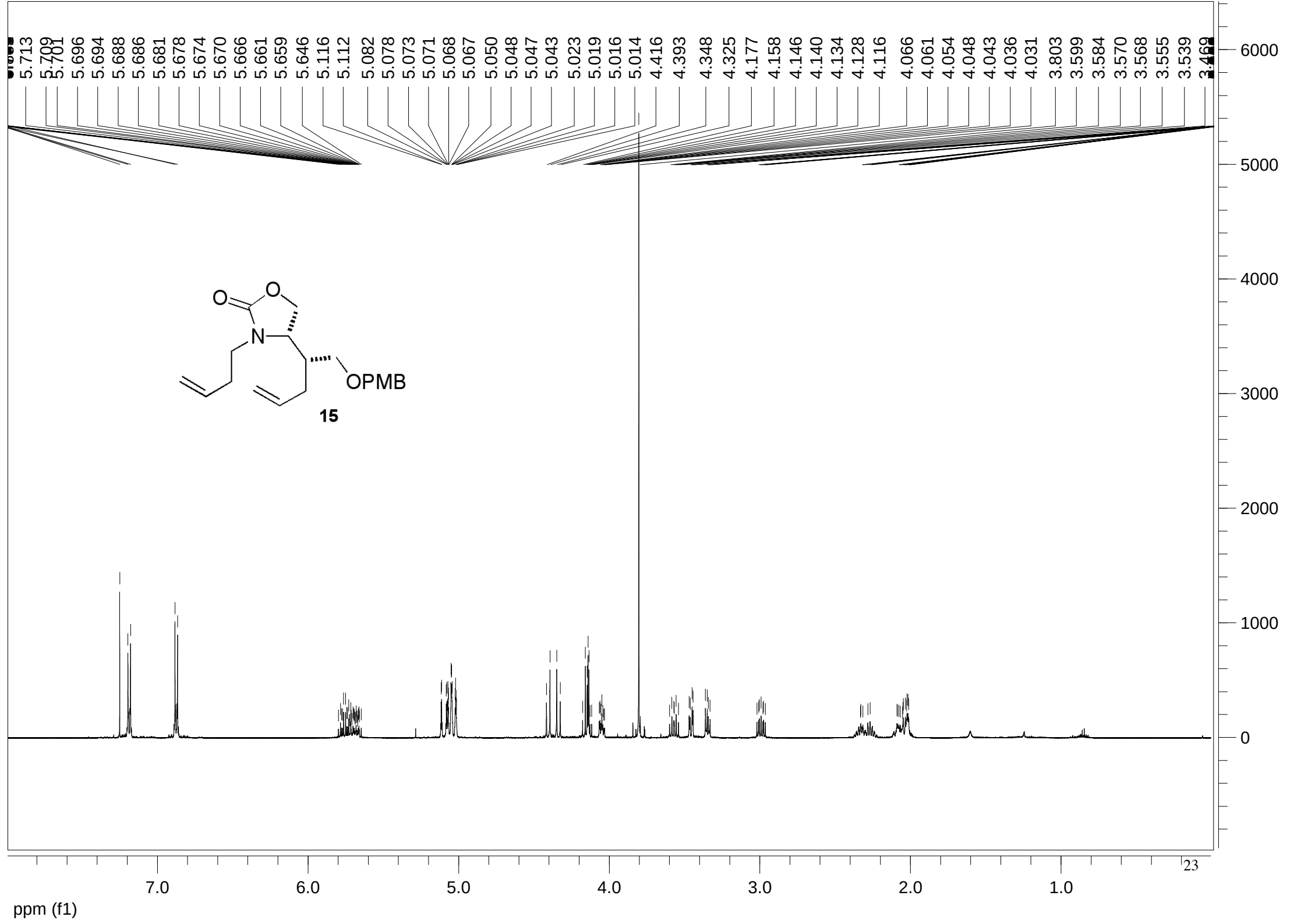
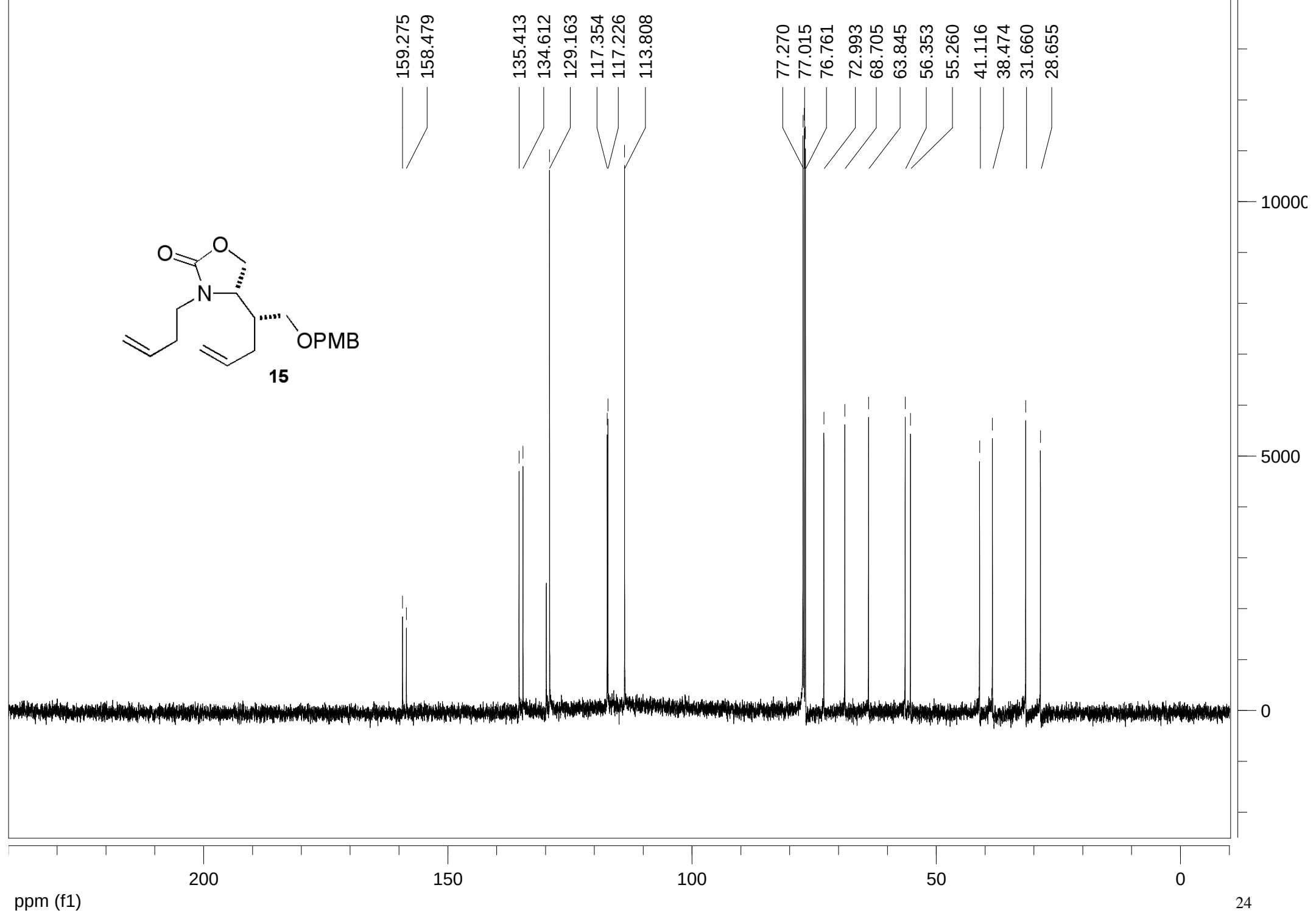
173.6708
159.0236
136.9921
129.7747
128.5162
127.9400
127.8187
113.9903
73.2025
71.8834
66.4400
55.2802
50.8375
43.1803
29.7613
24.8486
O
N
O
CHO
BnO
14
13C NMR (63 MHz)
CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
(ppm)


5.713
5.709
5.701
5.696
5.694
5.688
5.686
5.681
5.678
5.674
5.670
5.666
5.661
5.659
5.646
5.116
5.112
5.082
5.078
5.073
5.071
5.068
5.067
5.050
5.048
5.047
5.043
5.023
5.019
5.016
5.014
4.416
4.393
4.348
4.325
4.177
4.158
4.146
4.140
4.134
4.128
4.116
4.066
4.061
4.054
4.048
4.043
4.036
4.031
3.803
3.599
3.584
3.570
3.568
3.555
3.539
O
O
N
OPMB
15
6000
5000
4000
3000
2000
1000
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)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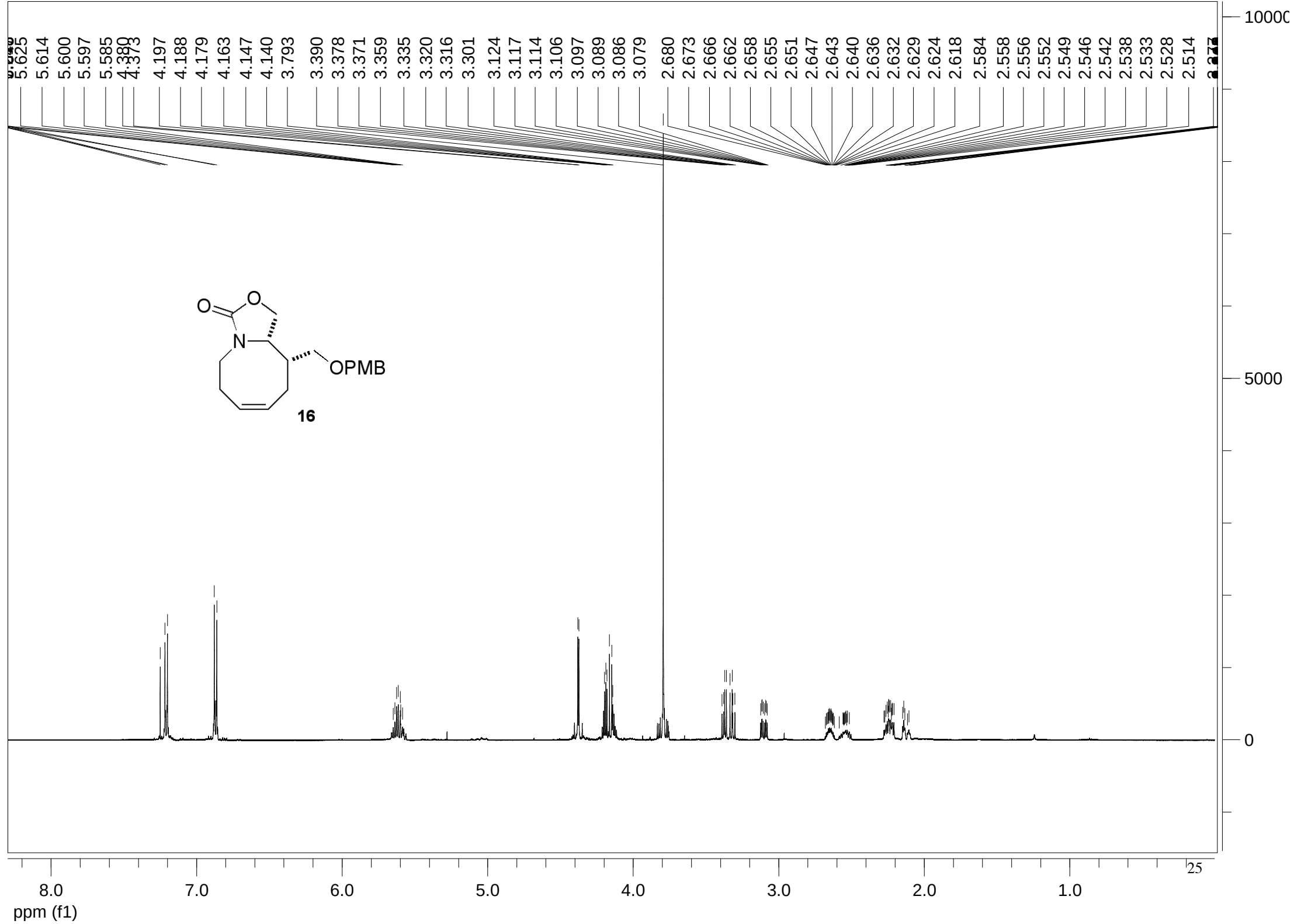
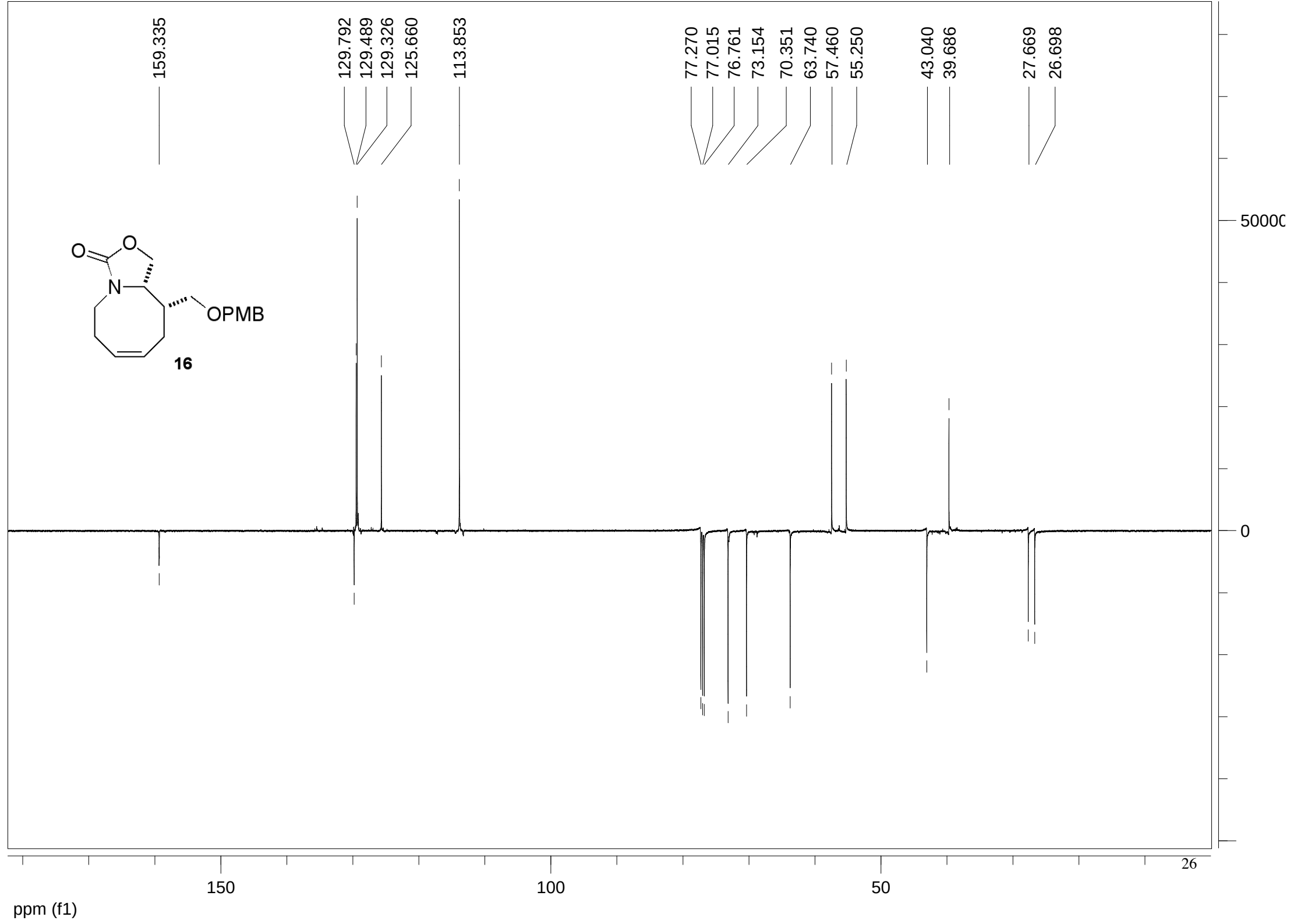
158.479
135.413
134.612
129.163
117.354
117.226
113.808
77.270
77.015
76.761
72.993
68.705
63.845
56.353
55.260
41.116
38.474
31.660
28.655
O
O
N
OPMB
15
10000
5000
0
200
150
100
50
0
ppm (f1)


5.625
5.614
5.600
5.597
5.585
4.197
4.188
4.179
4.163
4.147
4.140
3.793
3.390
3.378
3.371
3.359
3.335
3.320
3.316
3.301
3.124
3.117
3.114
3.106
3.097
3.089
3.086
3.079
2.680
2.673
2.666
2.662
2.658
2.655
2.651
2.647
2.643
2.640
2.636
2.632
2.629
2.624
2.618
2.584
2.558
2.556
2.552
2.549
2.546
2.542
2.538
2.533
2.528
2.514
O
O
N
OPMB
16
10000
5000
0
25
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)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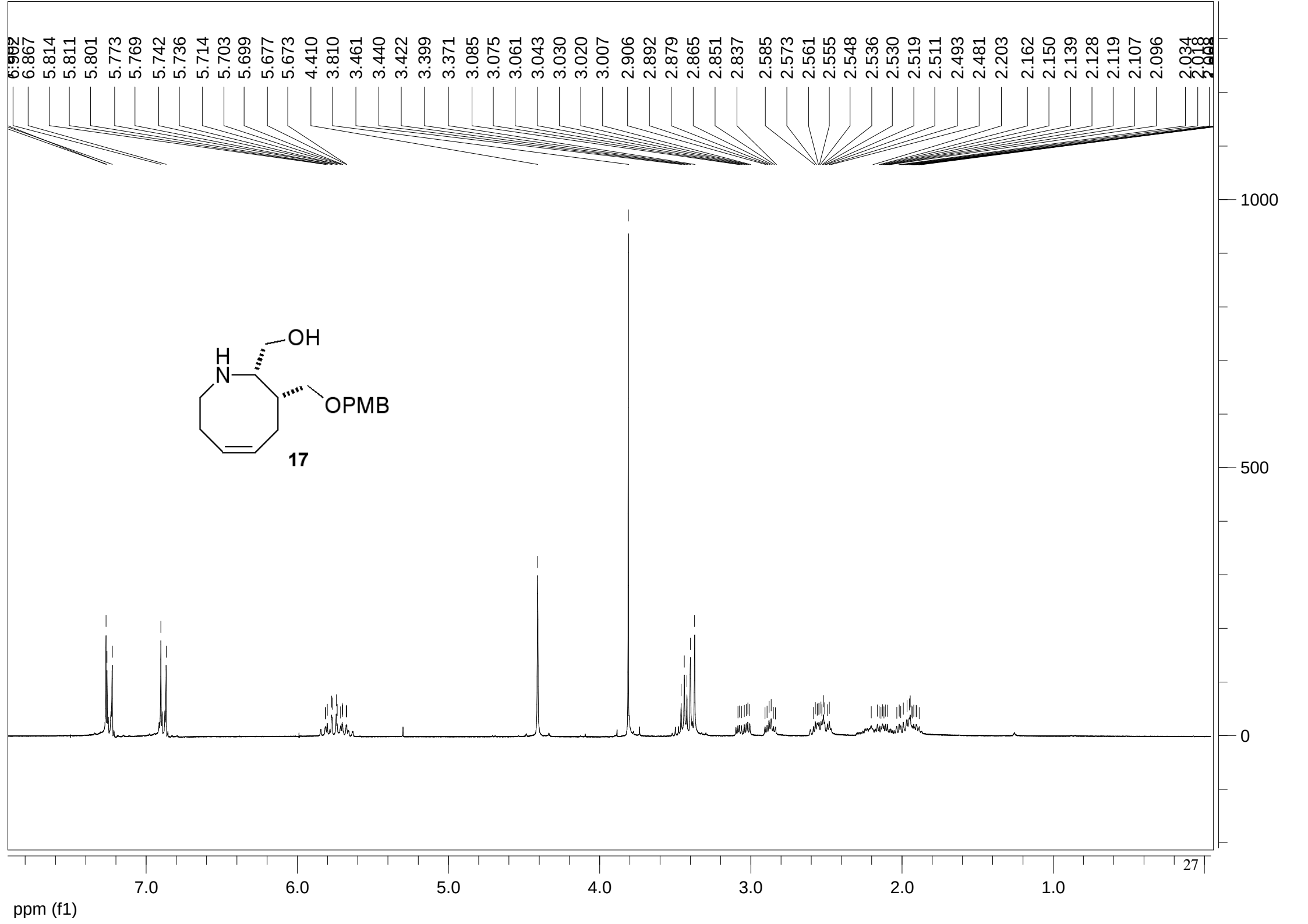
129.792
129.489
129.326
125.660
113.853
77.270
77.015
76.761
73.154
70.351
63.740
57.460
55.250
43.040
39.686
27.669
26.698
O
O
N
OPMB
16
50000
0
150
100
50
26
ppm (f1)


6.867
5.814
5.811
5.801
5.773
5.769
5.742
5.736
5.714
5.703
5.699
5.677
5.673
4.410
3.810
3.461
3.440
3.422
3.399
3.371
3.085
3.075
3.061
3.043
3.030
3.020
3.007
2.906
2.892
2.879
2.865
2.851
2.837
2.585
2.573
2.561
2.555
2.548
2.536
2.530
2.519
2.511
2.493
2.481
2.203
2.162
2.150
2.139
2.128
2.119
2.107
2.096
2.034
OH
H
N
OPMB
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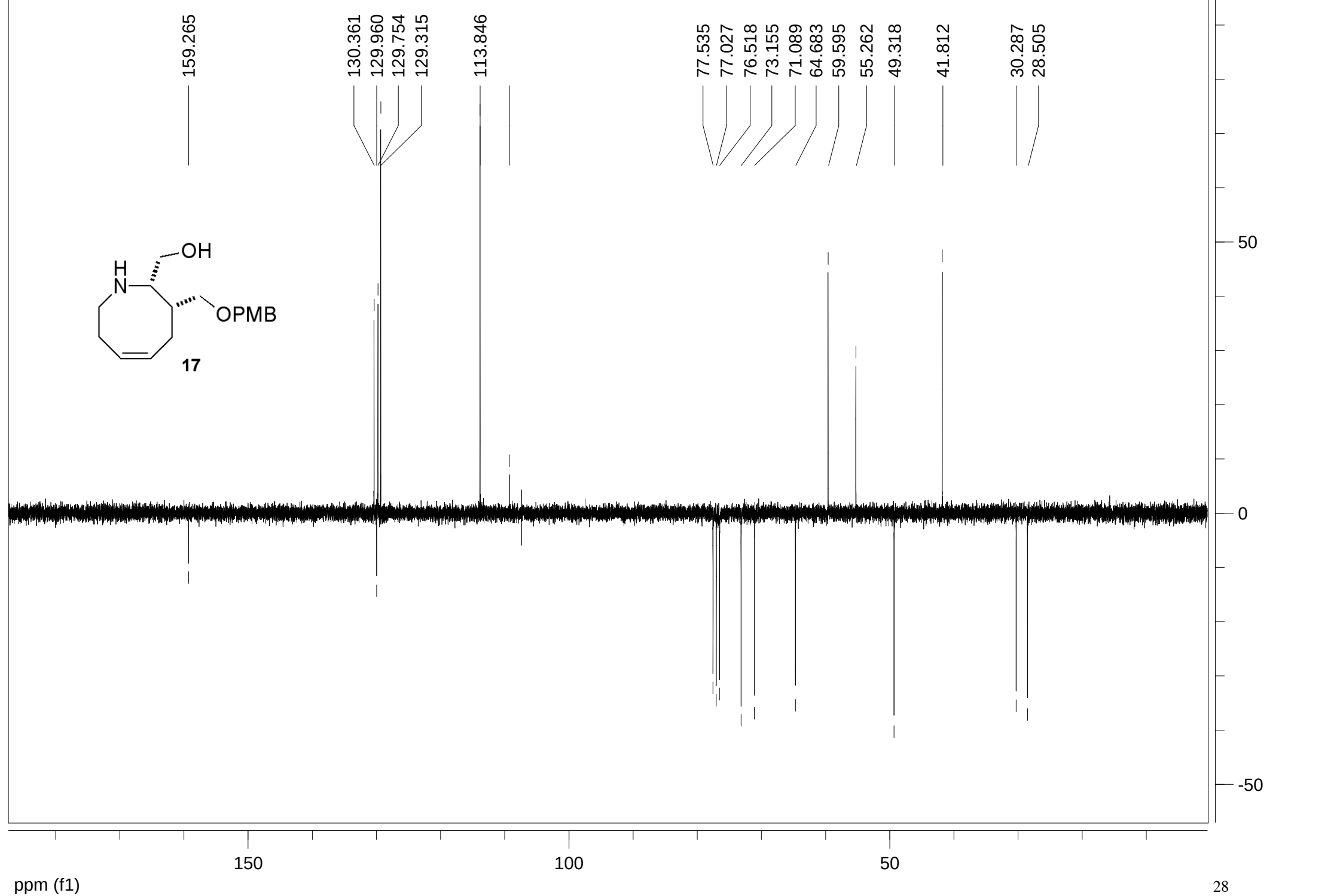
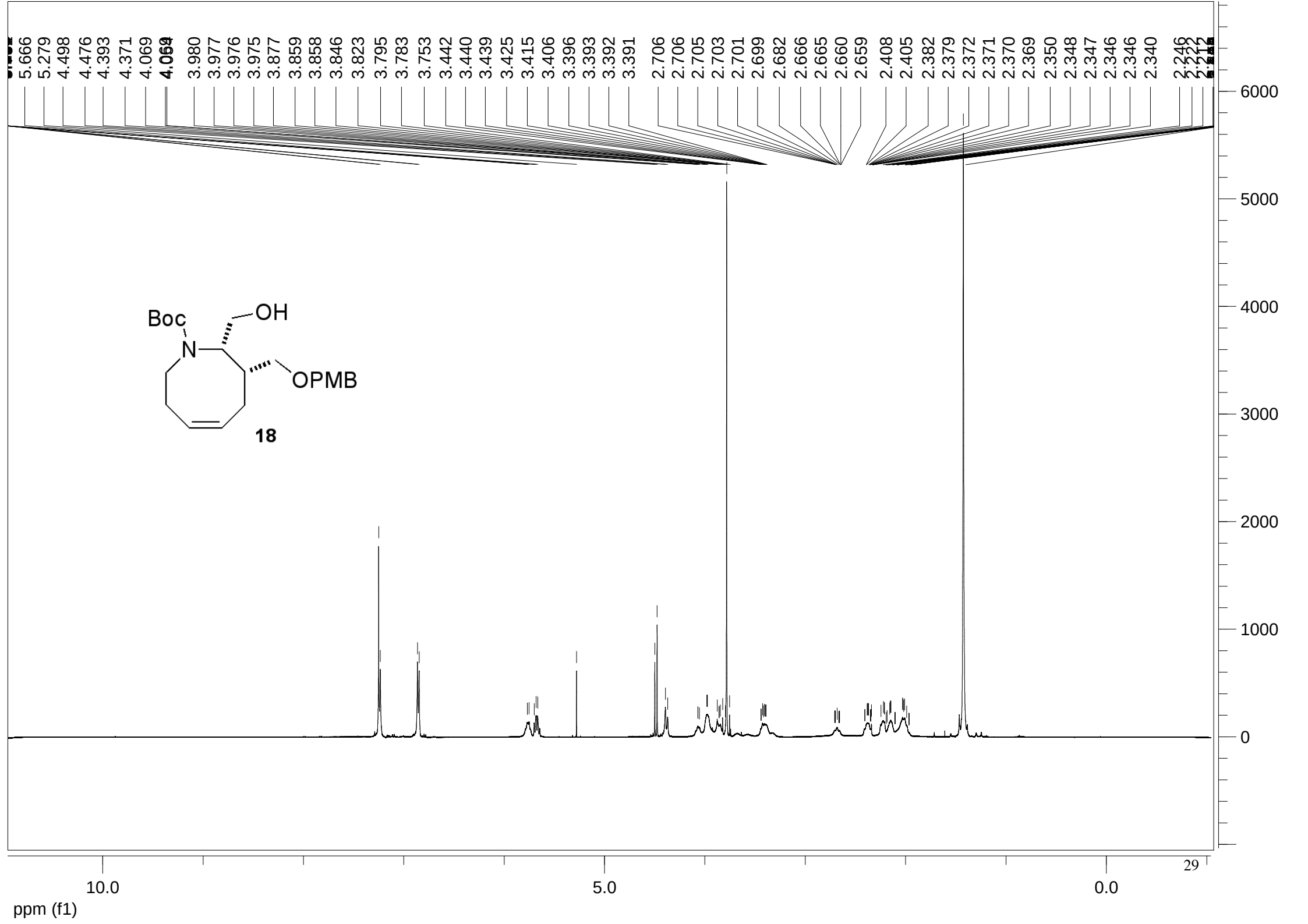
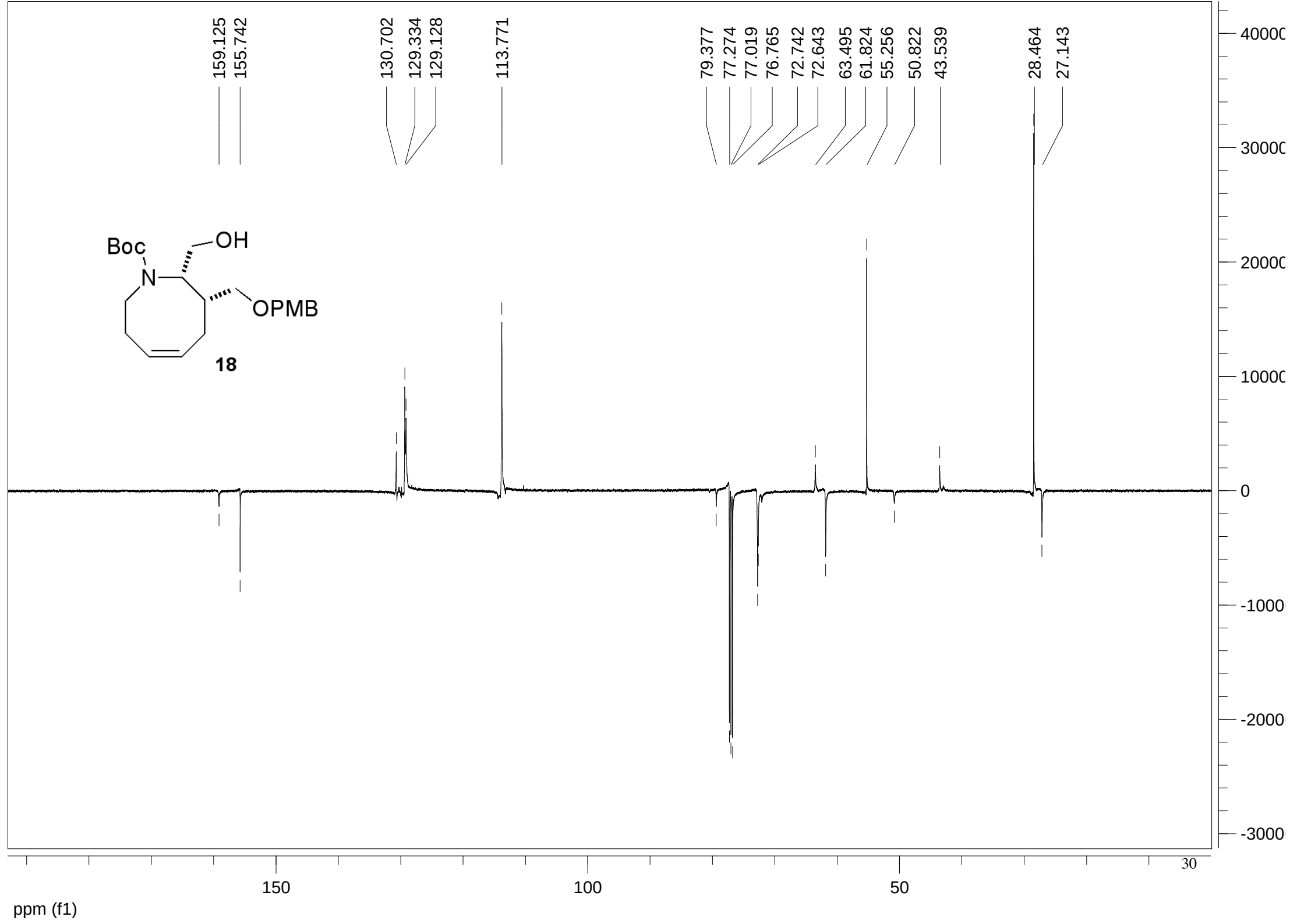
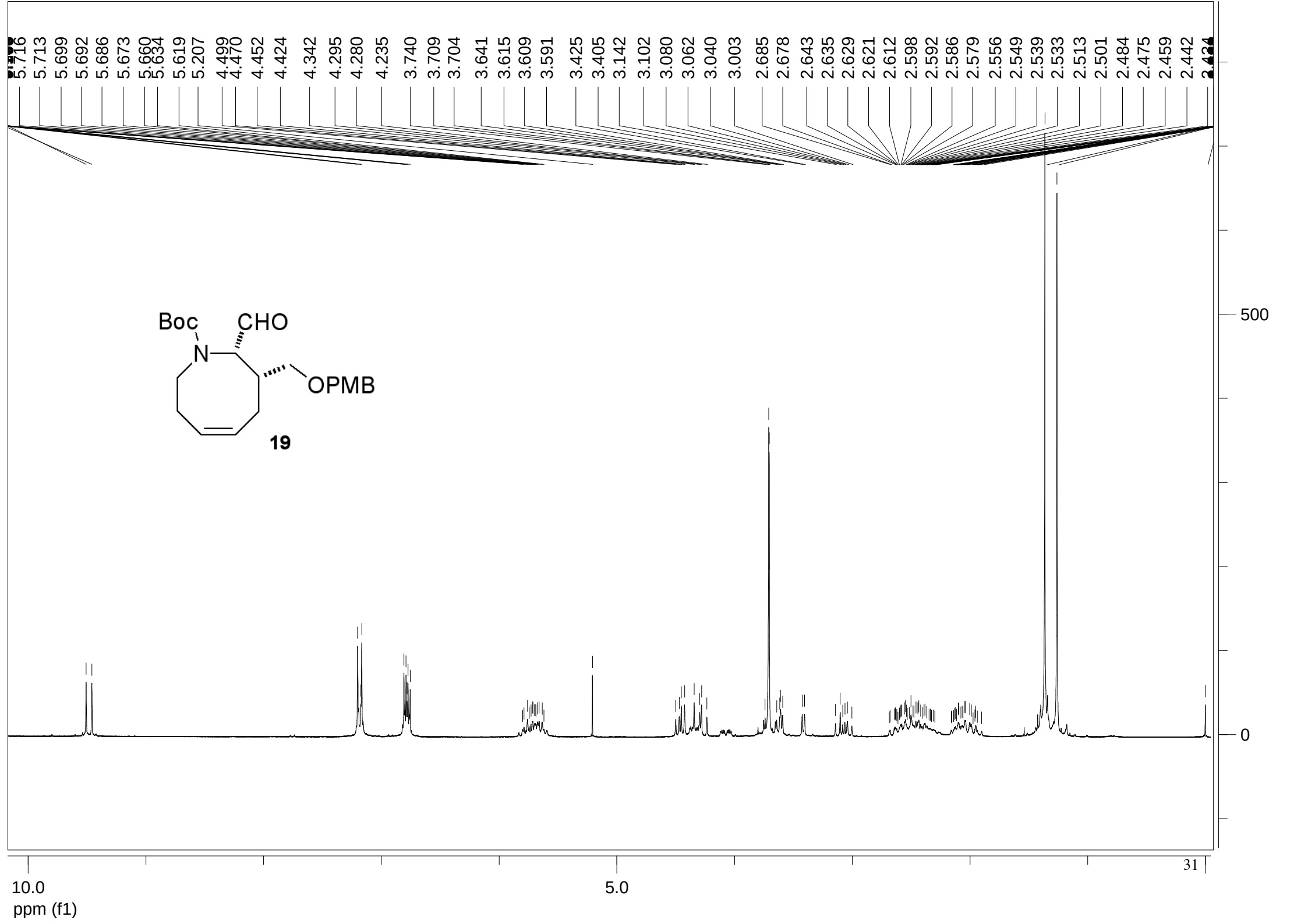
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


159.265
130.361
129.960
129.754
129.315
113.846
77.535
77.027
76.518
73.155
71.089
64.683
59.595
55.262
49.318
41.812
30.287
28.505
OH
H
N
OPMB
17
50
0
-50
150
100
50
ppm (f1)


5.666
5.279
4.498
4.476
4.393
4.371
4.069
3.980
3.977
3.976
3.975
3.877
3.859
3.858
3.846
3.823
3.795
3.783
3.753
3.442
3.440
3.439
3.425
3.415
3.406
3.396
3.393
3.392
3.391
2.706
2.706
2.705
2.703
2.701
2.699
2.682
2.666
2.665
2.660
2.659
2.408
2.405
2.382
2.379
2.372
2.371
2.370
2.369
2.350
2.348
2.347
2.346
2.346
2.340
2.246
Boc
N
OH
OPMB
18
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)


159.125
155.742
130.702
129.334
129.128
113.771
79.377
77.274
77.019
76.765
72.742
72.643
63.495
61.824
55.256
50.822
43.539
28.464
27.143
Boc
N
OH
OPMB
18
40000
30000
20000
10000
0
-10000
-20000
-30000
150
100
50
30
ppm (f1)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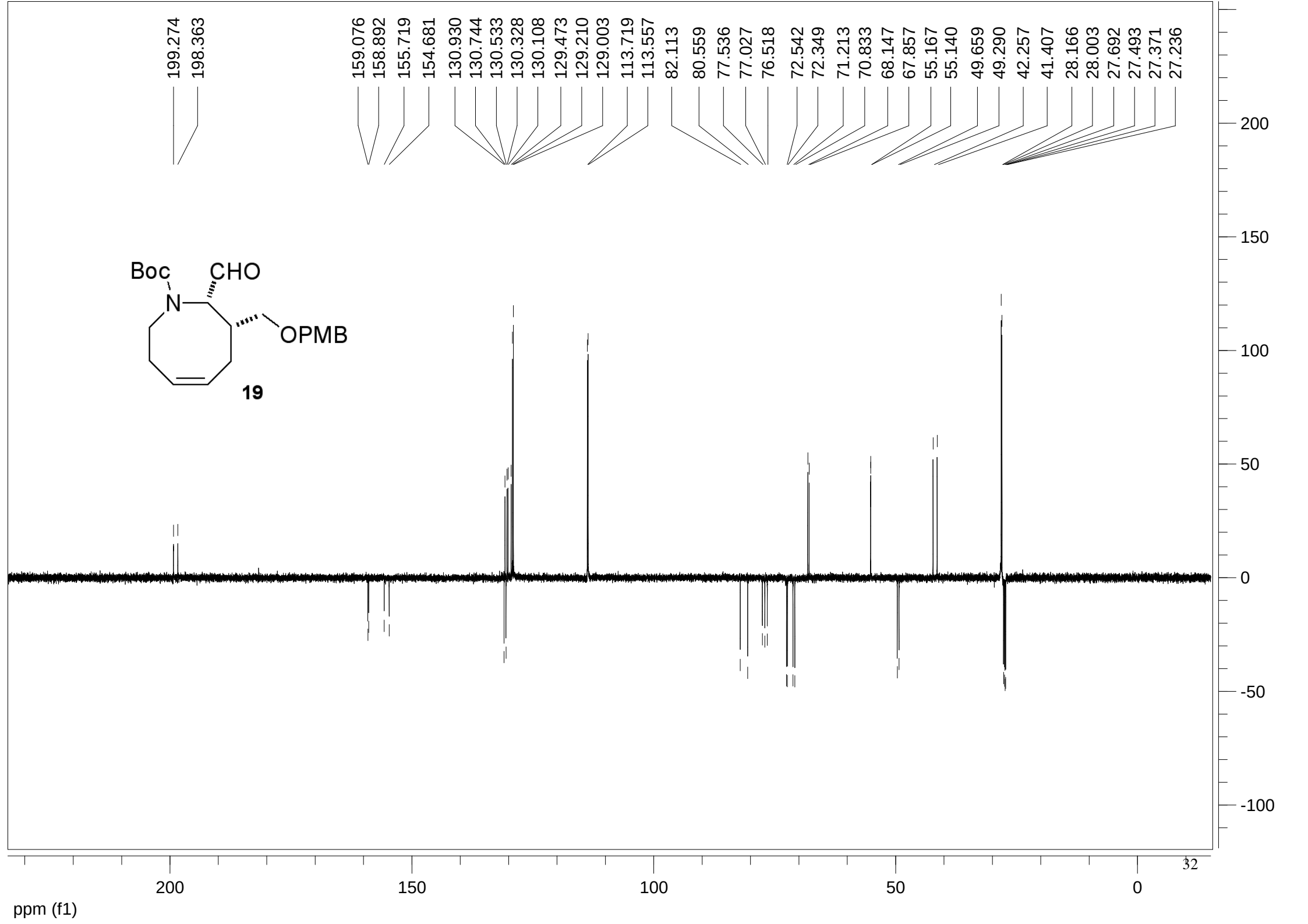
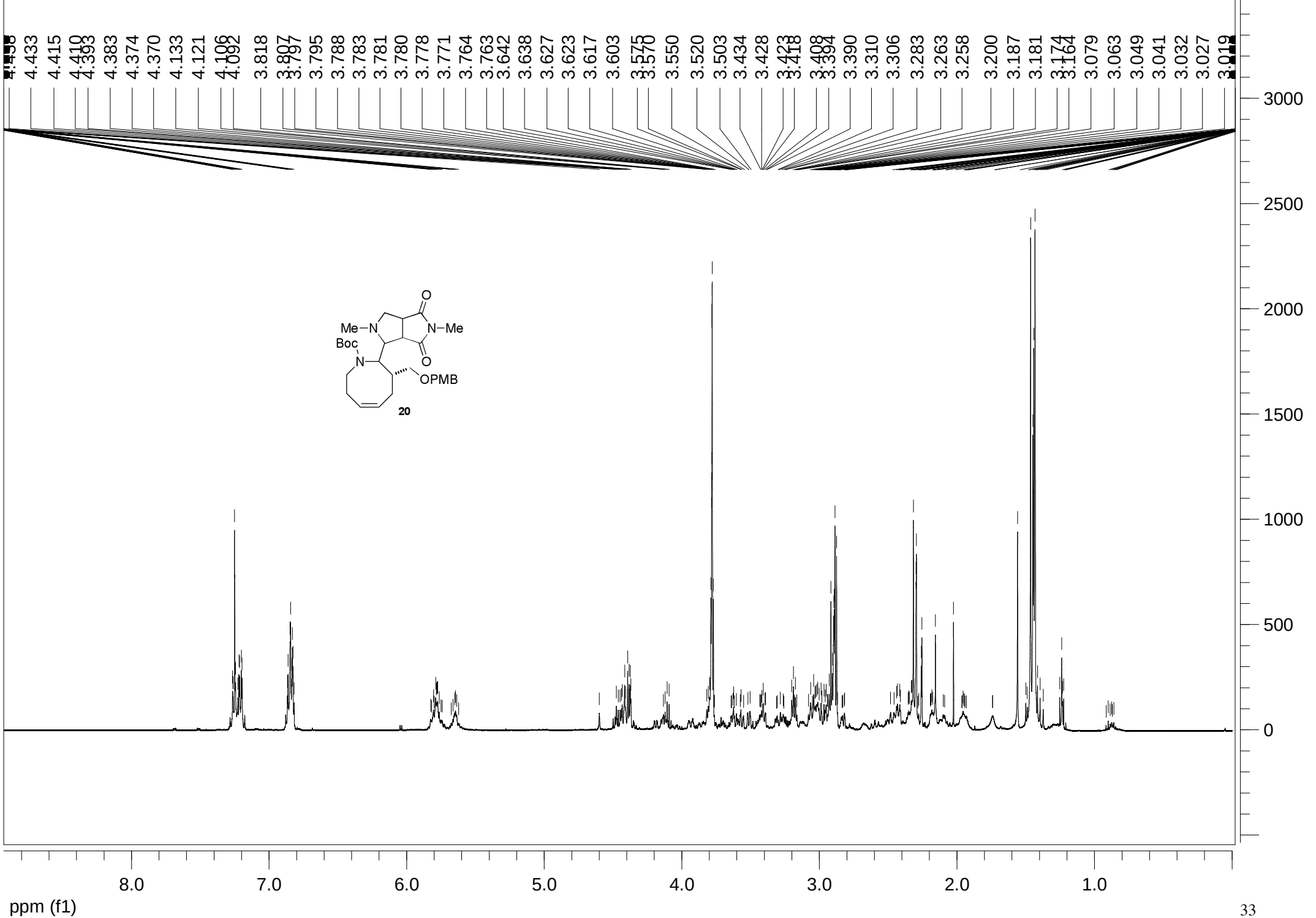
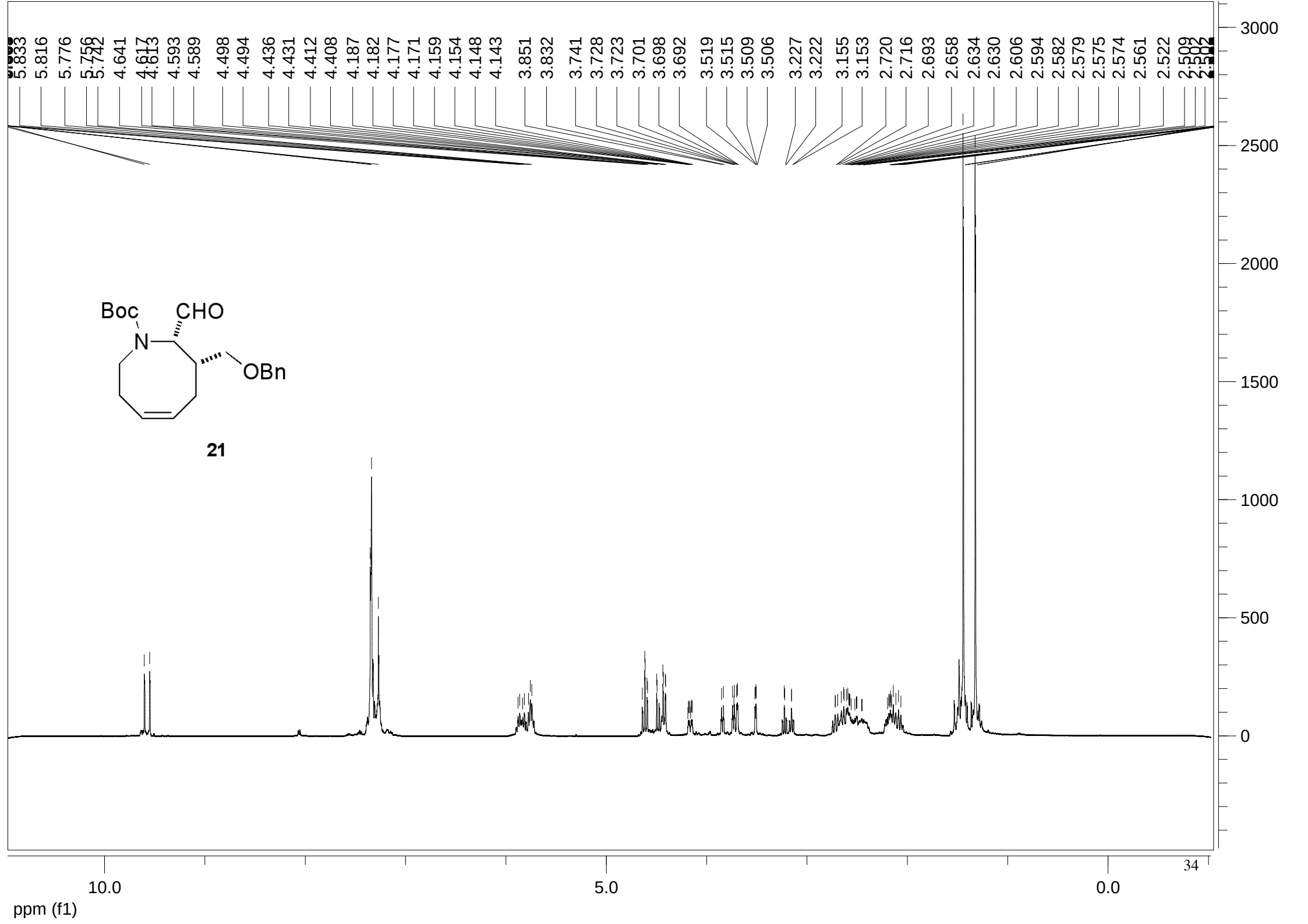
5.699
5.692
5.686
5.673
5.660
5.634
5.619
5.207
4.499
4.470
4.452
4.424
4.342
4.295
4.280
4.235
3.740
3.709
3.704
3.641
3.615
3.609
3.591
3.425
3.405
3.142
3.102
3.080
3.062
3.040
3.003
2.685
2.678
2.643
2.635
2.629
2.621
2.612
2.598
2.592
2.586
2.579
2.556
2.549
2.539
2.533
2.513
2.501
2.484
2.475
2.459
2.442
Boc
CHO
N
OPMB
19
500
0
31
10.0
5.0
ppm (f1)


199.274
198.363
159.076
158.892
155.719
154.681
130.930
130.744
130.533
130.328
130.108
129.473
129.210
129.003
113.719
113.557
82.113
80.559
77.536
77.027
76.518
72.542
72.349
71.213
70.833
68.147
67.857
55.167
55.140
49.659
49.290
42.257
41.407
28.166
28.003
27.692
27.493
27.371
27.236
Boc
CHO
N
OPMB
19
200
150
100
50
0
-50
-100
200
150
100
50
0
ppm (f1)


4.433
4.415
4.410
4.393
4.383
4.374
4.370
4.133
4.121
4.106
4.092
3.818
3.807
3.797
3.795
3.788
3.783
3.781
3.780
3.778
3.771
3.764
3.763
3.642
3.638
3.627
3.623
3.617
3.603
3.575
3.570
3.550
3.520
3.503
3.434
3.428
3.423
3.418
3.408
3.394
3.390
3.310
3.306
3.283
3.263
3.258
3.200
3.187
3.181
3.174
3.164
3.079
3.063
3.049
3.041
3.032
3.027
3.019
Me–N
Boc
N
N–Me
O
O
OPMB
20
3000
2500
2000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


5.833
5.816
5.776
5.756
5.742
4.641
4.617
4.613
4.593
4.589
4.498
4.494
4.436
4.431
4.412
4.408
4.187
4.182
4.177
4.171
4.159
4.154
4.148
4.143
3.851
3.832
3.741
3.728
3.723
3.701
3.698
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3.153
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2.630
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2.575
2.574
2.561
2.522
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CHO
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OBn
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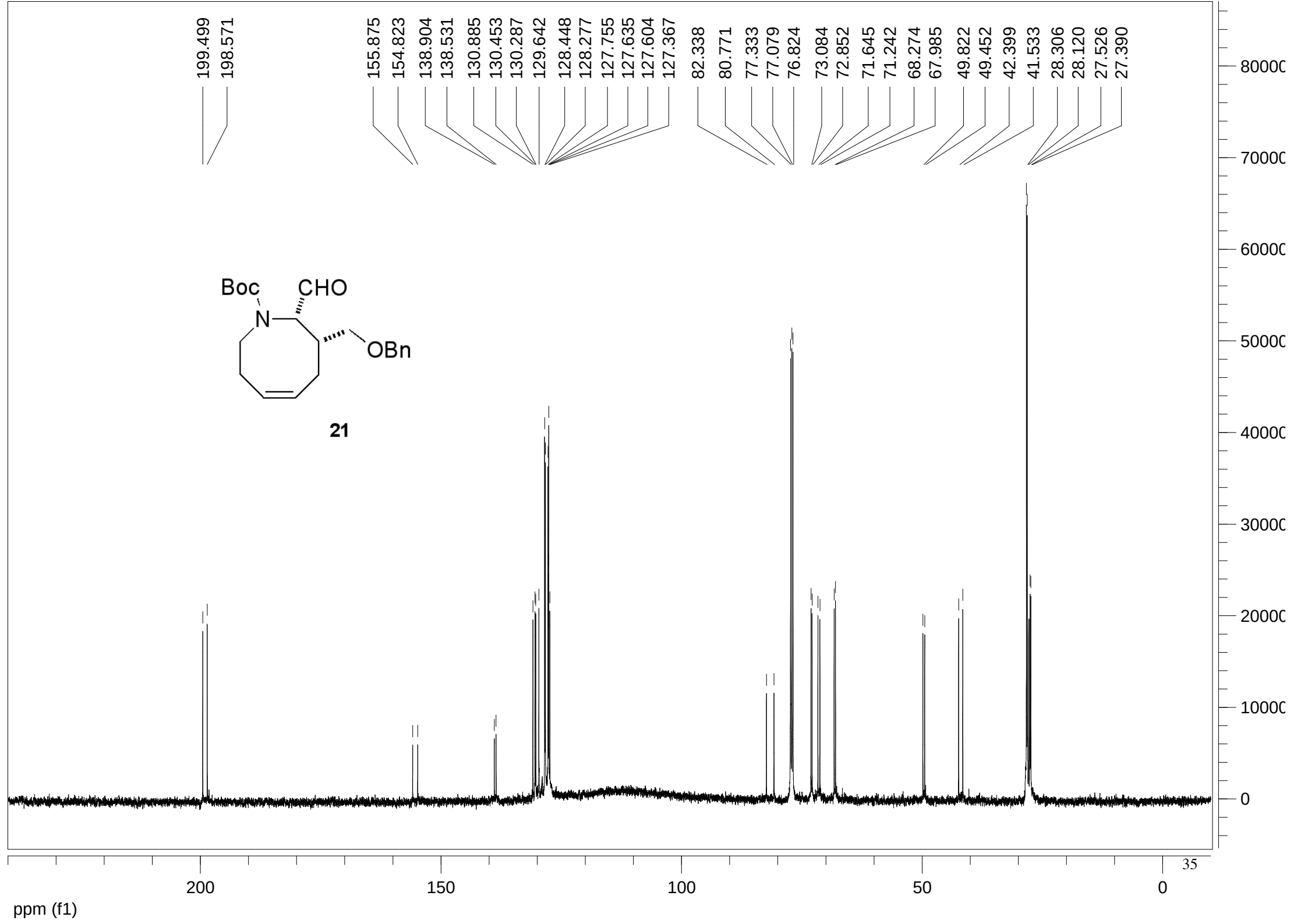
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80.771
77.333
77.079
76.824
73.084
72.852
71.645
71.242
68.274
67.985
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41.533
28.306
28.120
27.526
27.390
Boc
CHO
N
OBn
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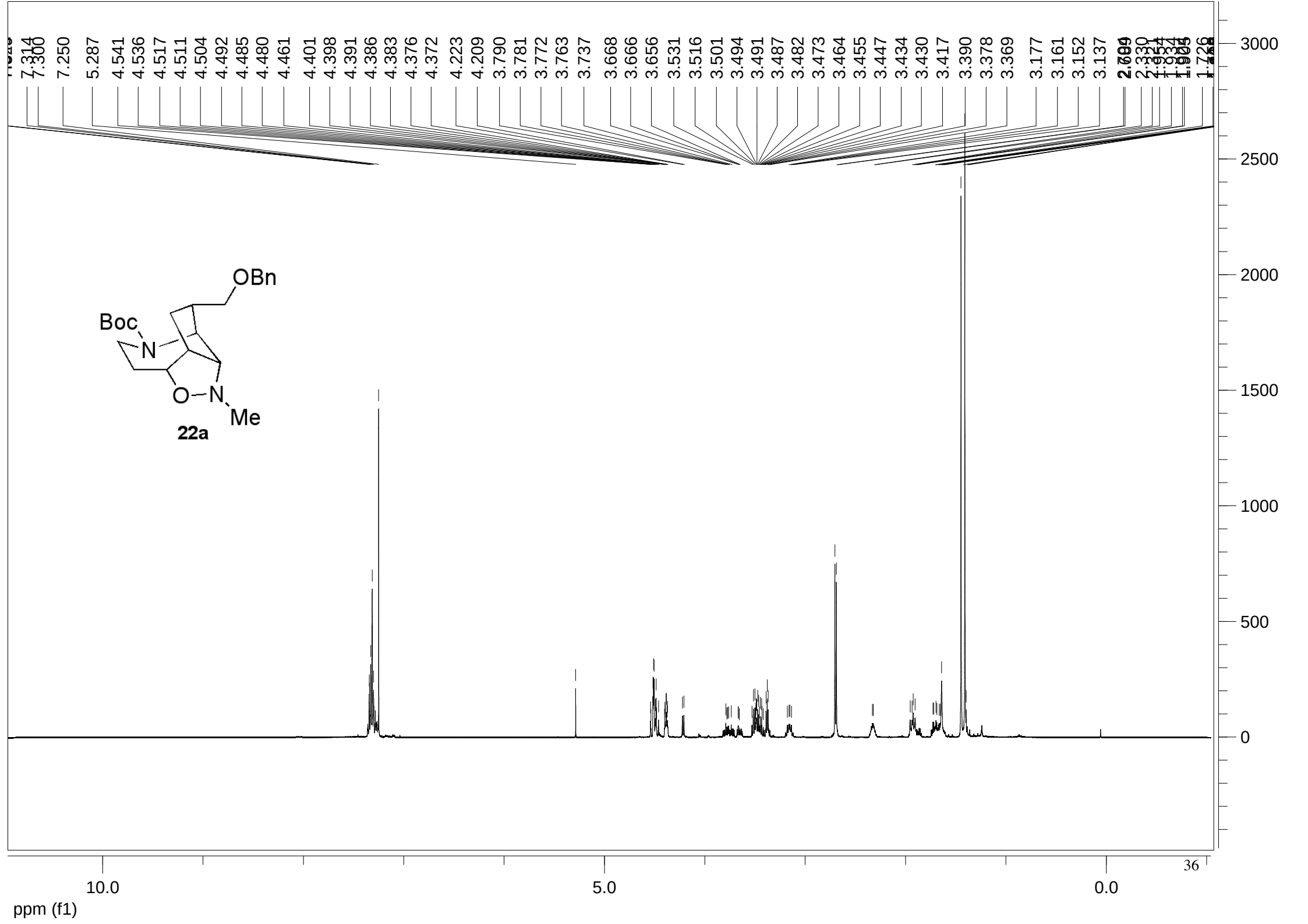
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4.398
4.391
4.386
4.383
4.376
4.372
4.223
4.209
3.790
3.781
3.772
3.763
3.737
3.668
3.666
3.656
3.531
3.516
3.501
3.494
3.491
3.487
3.482
3.473
3.464
3.455
3.447
3.434
3.430
3.417
3.390
3.378
3.369
3.177
3.161
3.152
3.137
OBn
Boc
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O
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Me
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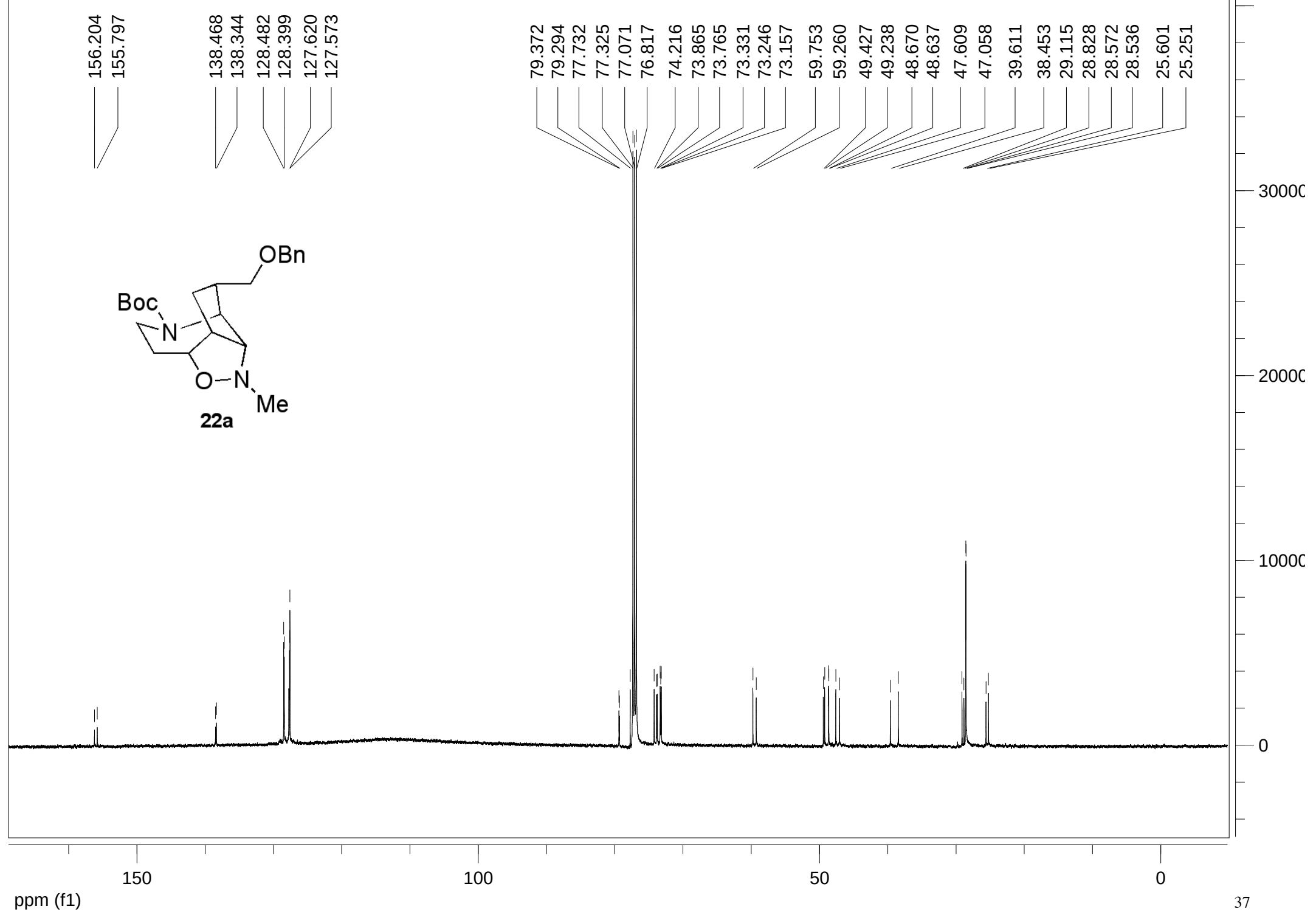
ppm (f1)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74.216
73.865
73.765
73.331
73.246
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49.427
49.238
48.670
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47.609
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39.611
38.453
29.115
28.828
28.572
28.536
25.601
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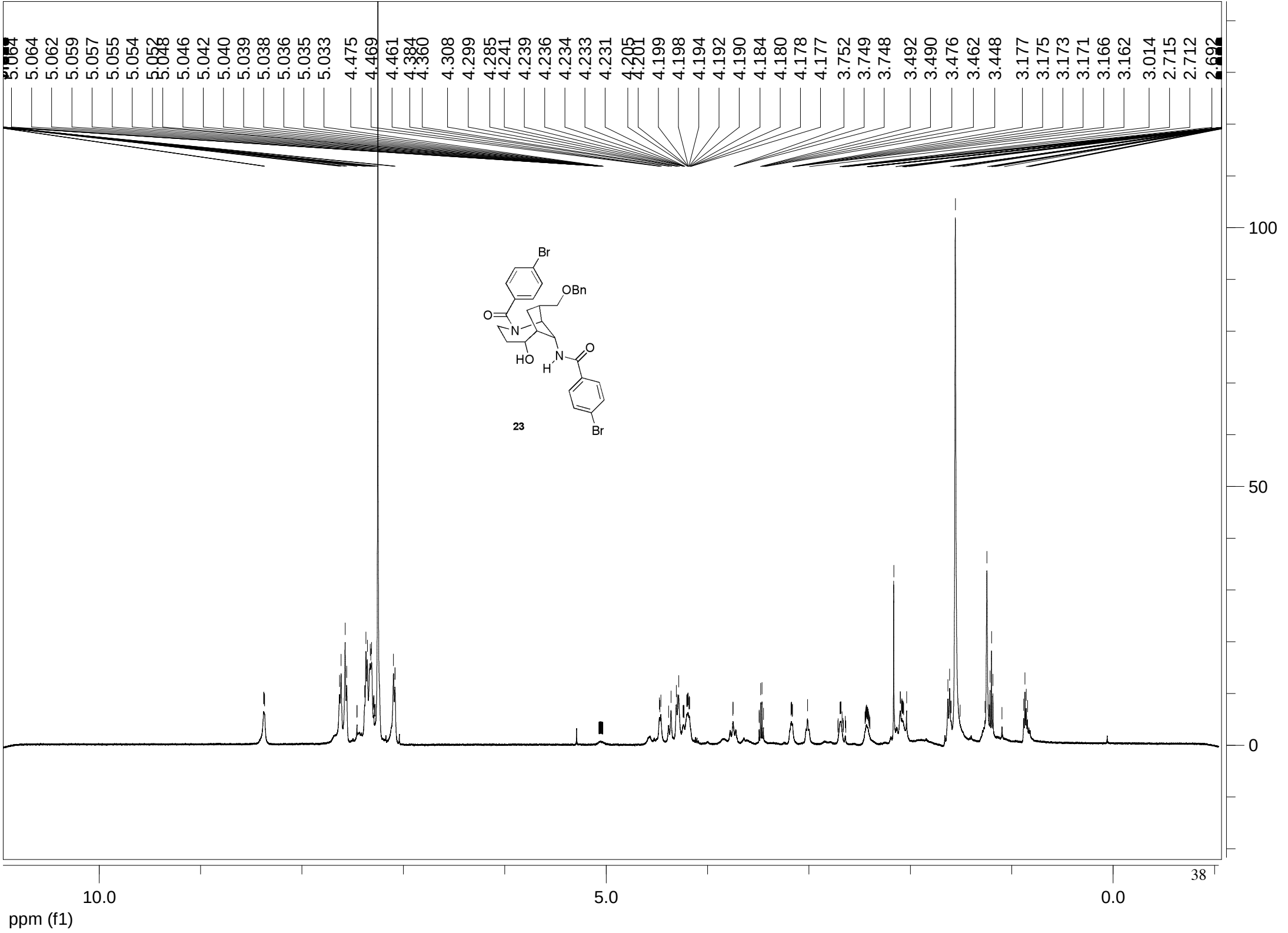
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5.033
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4.285
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4.234
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4.190
4.184
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4.177
3.752
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3.748
3.492
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3.476
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3.448
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3.175
3.173
3.171
3.166
3.162
3.014
2.715
2.712
Br
OBn
O
N
HO
H
N
O
Br
23
100
50
0
10.0
5.0
0.0
ppm (f1)