Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Synergetic catalytic effect of ionic liquids and ZnO nanoparticles on the selective synthesis of 1,2-disubstituted benzimidazoles using a ball-milling technique

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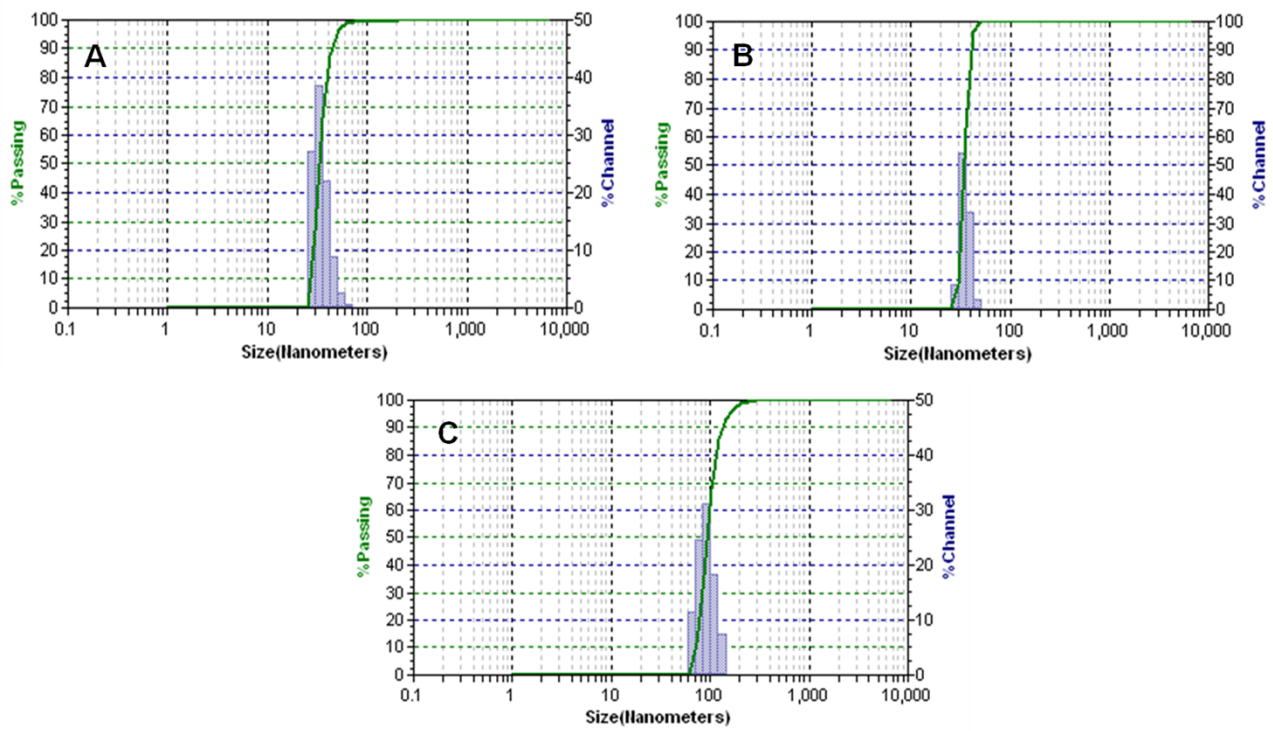


Figure S1. DLS studies of catalyst (A) **3** (30 nm), (B) **4** (34 nm) and (C) **5** (90 nm), representing d_{50} values in parentheses.

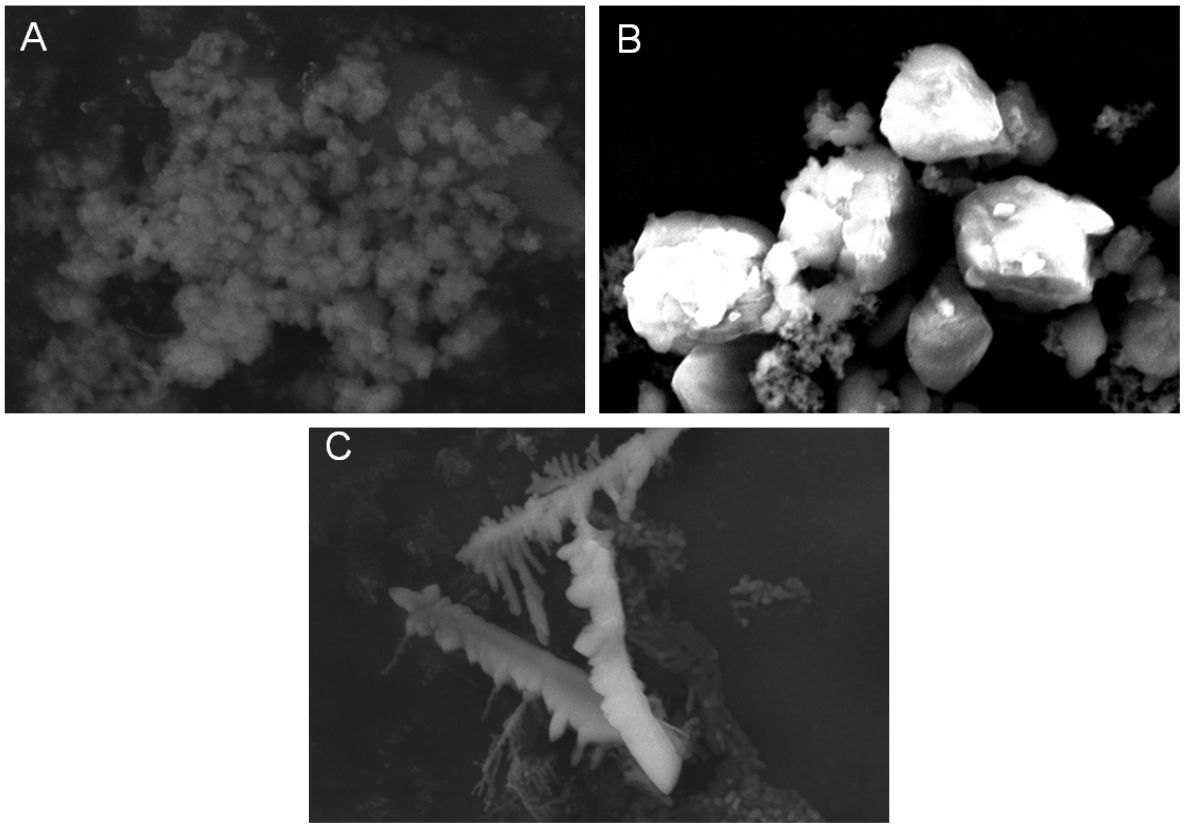


Figure S2. SEM images representing the morphology of catalyst (A) **3**, (B) **4** and (C) **5**.

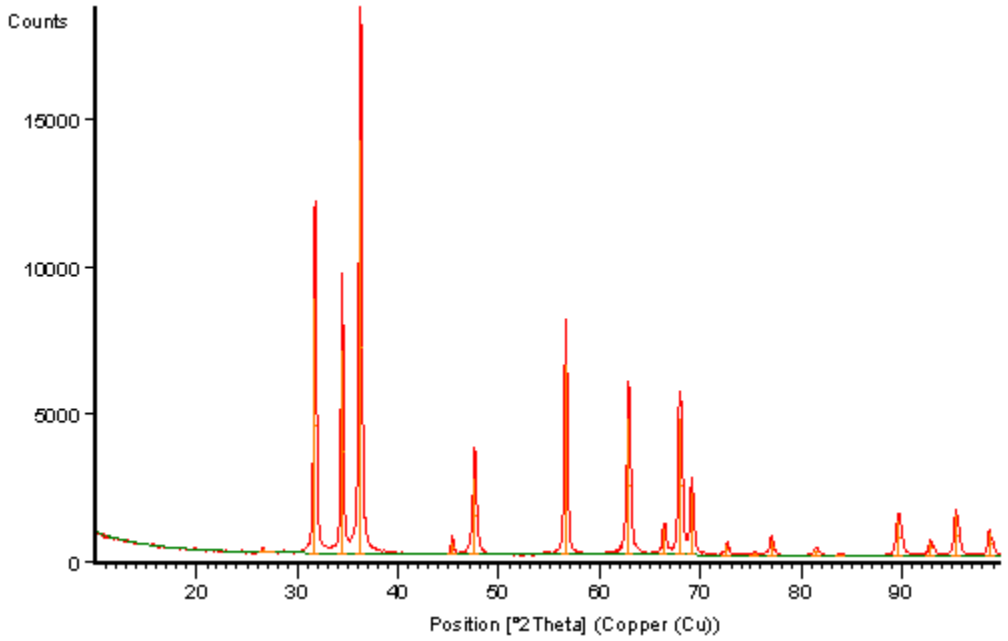


Figure S3. XRD pattern of catalyst **5**.

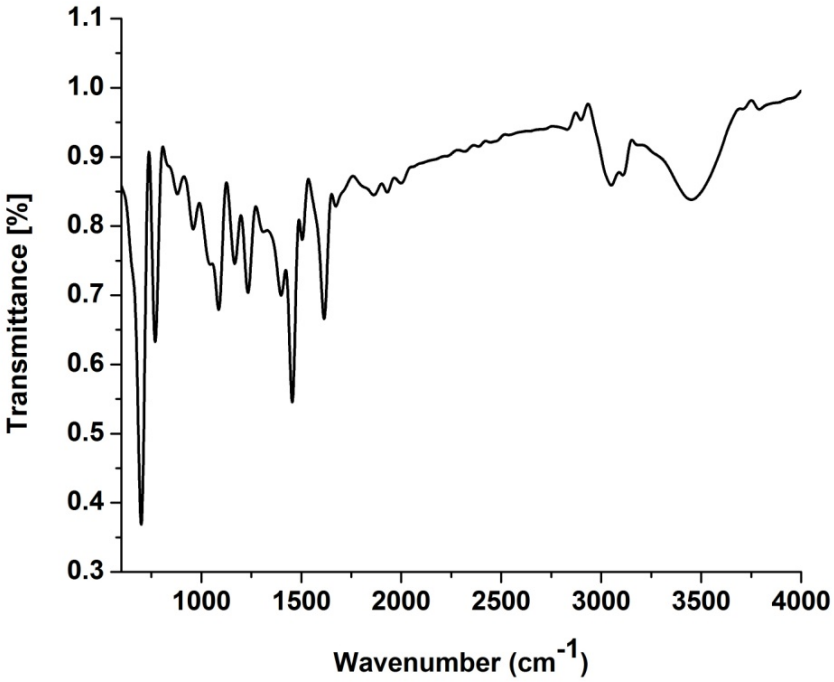


Figure S4. FT-IR spectra of catalyst 5.

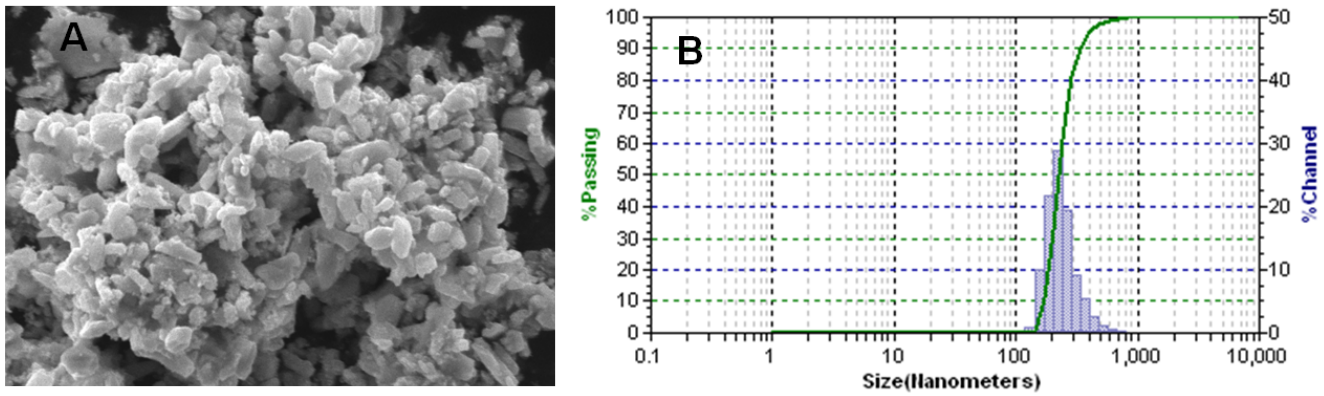


Figure S5. (A) SEM image and (B) DLS analysis (d_{50} = 260 nm) of catalyst **5** after the seventh run.

Table S1. A relationship between milling time and temperature of milling jar.[a]

Time (min)	Temp (ºC)
0	25.2
4	26.6
8	28.2
15	29.1
22	30.0
30	33.4
40	37.2
60	42.8

[a]Reaction conditions: *o*-phenylenediamine (9.2 mmol), 4-hydroxy-3-nitrobenzaldehyde (18.5 mmol), catalyst **5** (0.2 mol%), 20 milling balls (5 mm) in a milling jar (80 mL).

Table S2. A ratio of ball to powder for each product .

Product	Ratio of ball to powder[a,b]
6	20:4
8	20:3
9	20:3.2
10	20:3.2
11	20:3.2
12	20:3.5
13	20:3.5
14	20:4
15	20:3
16	20:3

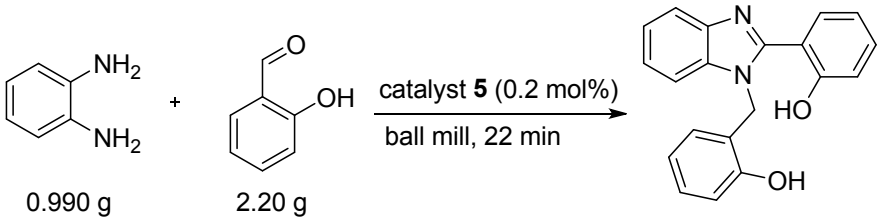
[a]Weight of milling balls is 20g (1×20). [b]Maximum temperature was 30 ºC.

Table S3. Eco-scale calculation for the reaction of *o*-phenylenediamine with 2-hydroxybenzaldehyde.[a]

	Detail of parameters	Penalty points[b]
1. Yield	94%	3
2. Cost of reactants to obtain 10 mmol of product		
	o-phenylenediamine	0
	2-hydroxybenzaldehyde	0
	ZnO-NPs	0
	MeOH	0
3. Safety		
	o-phenylenediamine	10 (T, N)
	2-hydroxybenzaldehyde	5 (T)
	ZnO-NPs	5 (N)
	MeOH	10 (F, T)
4. Technical setup		
	ball-mill	2
5. Temperature / Time		
	room temperature / < 1 h	0
6. Work-up and purification		
	adding solvent	0
	simple filtration	0

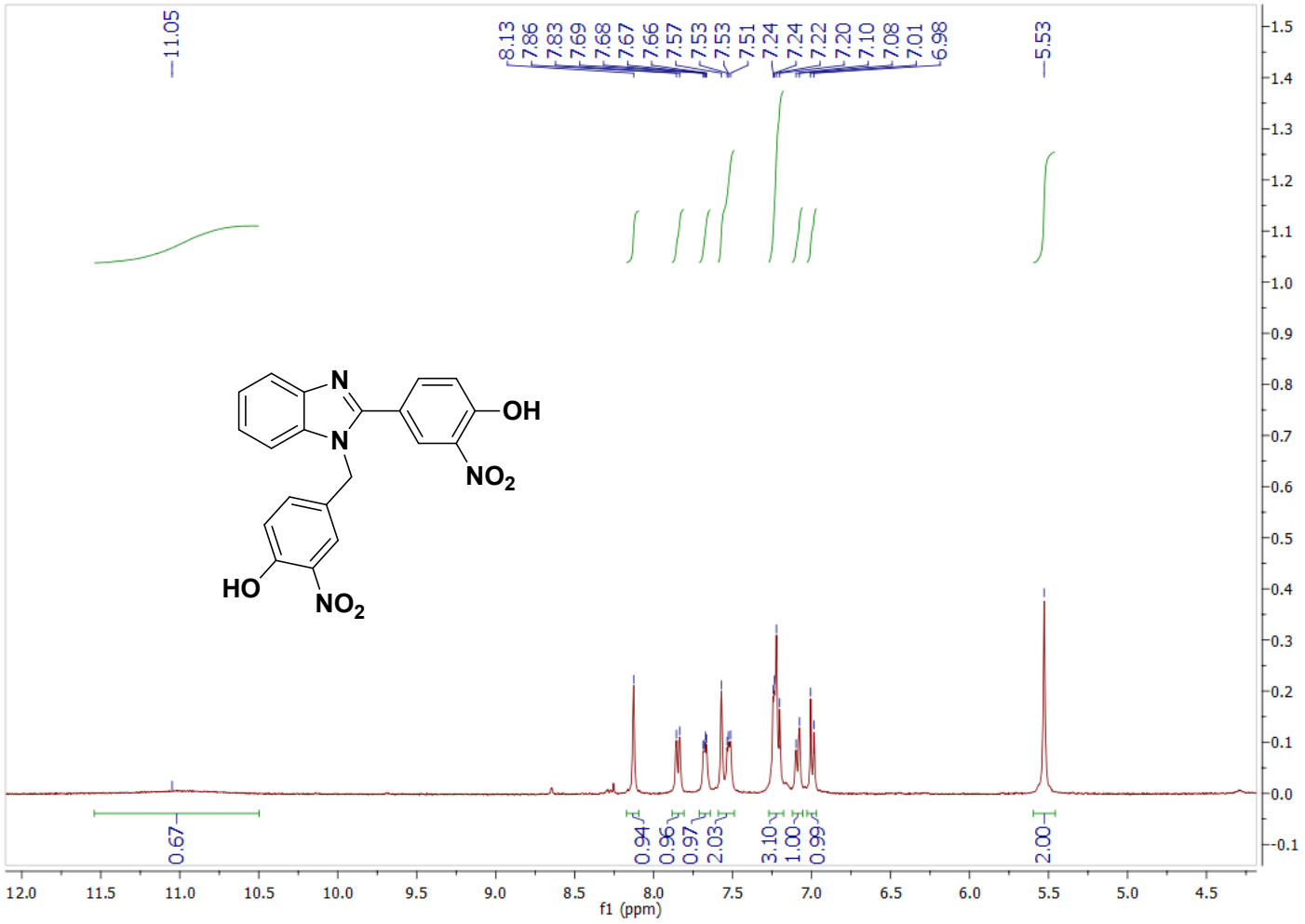
[a]The reaction was performed on a 10 mmol scale. [b]The total of all penalties was 35 that produced an eco-scale score of 65 (100-35), which is indicative of an acceptable synthesis.

Table S4. Calculation of the E-factor and mass intensity for the reaction of *o*-phenylenediamine with 2-hydroxybenzaldehyde**.**



0.990 g 2.20 g 2.73 g, 94%

Total amount of reactants: 0.990 g + 2.20 g + 0.013= 3.20 g
Amount of final product: 2.73 g
Amount of waste: (3.20 g - 2.73 g) = 0.47 g
E-Factor = amount of waste/amount of product = 0.47/2.73 = 0.17
Mass intensity (MI) = 1.17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7.66
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7.53
7.53
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7.24
7.22
7.20
7.10
7.08
7.01
6.98
5.53
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HO
NO2
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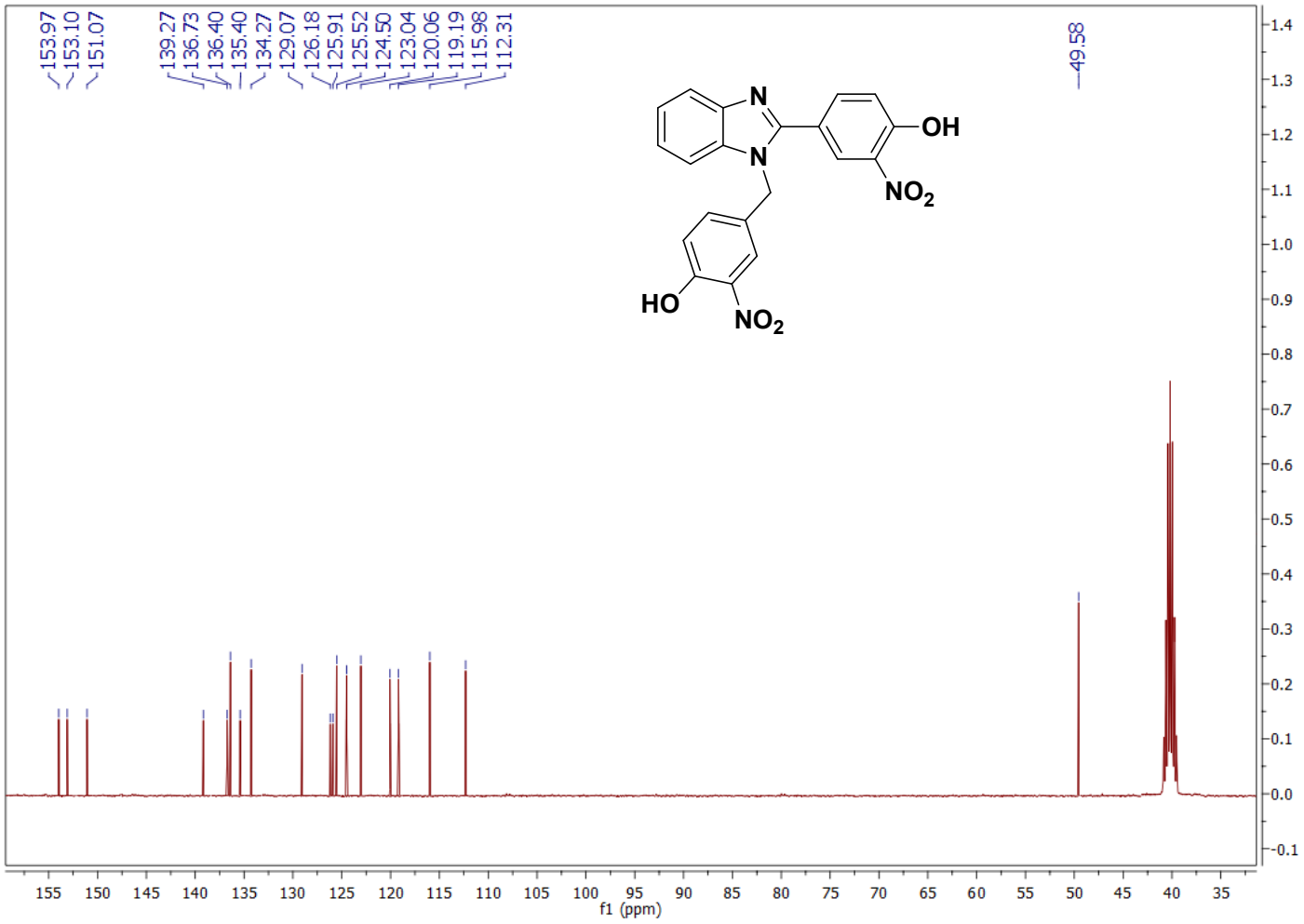
1.00
0.99
2.00
f1 (ppm)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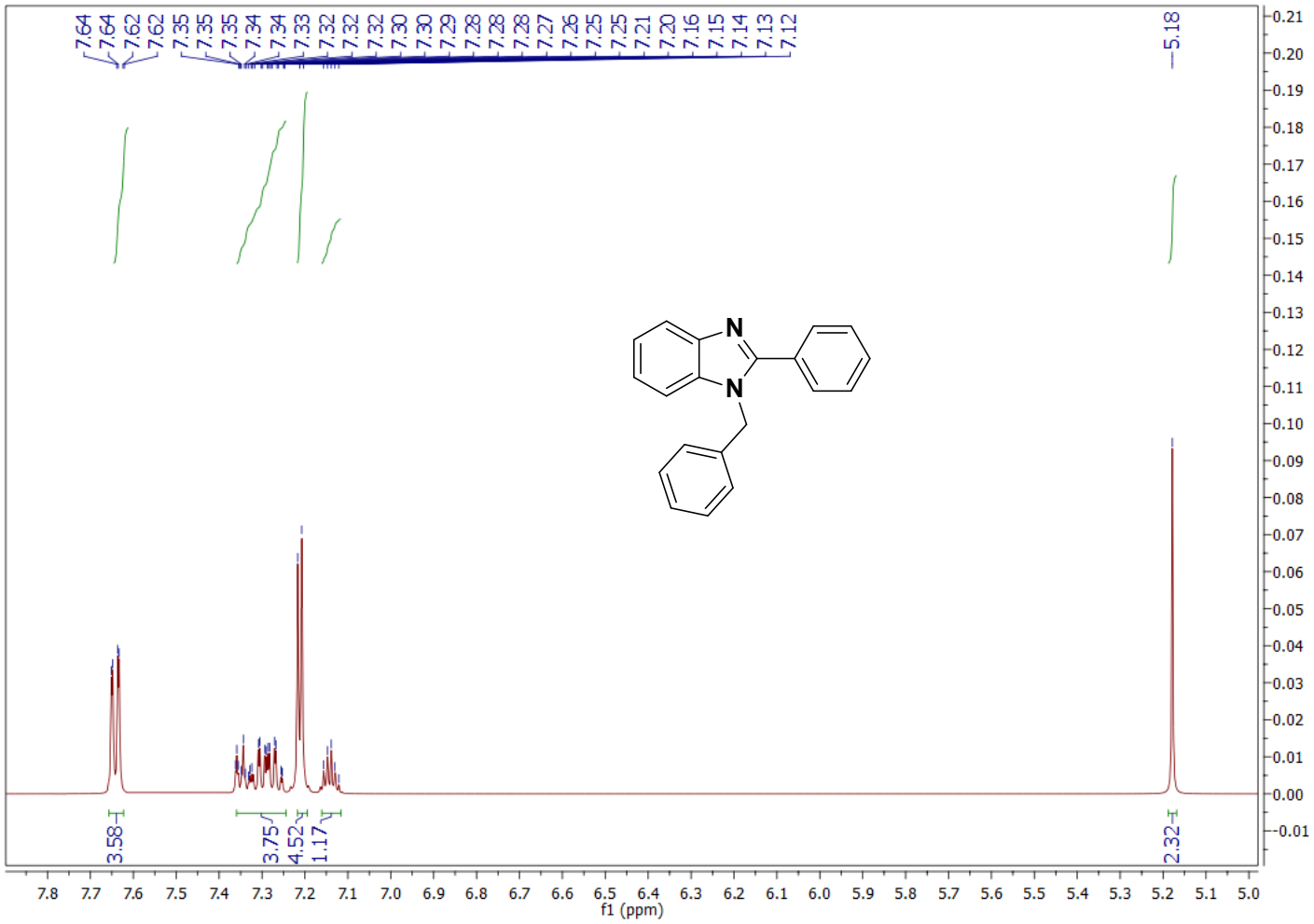
N
OH
NO2
HO
NO2
f1 (ppm)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7.27
7.26
7.25
7.25
7.21
7.20
7.16
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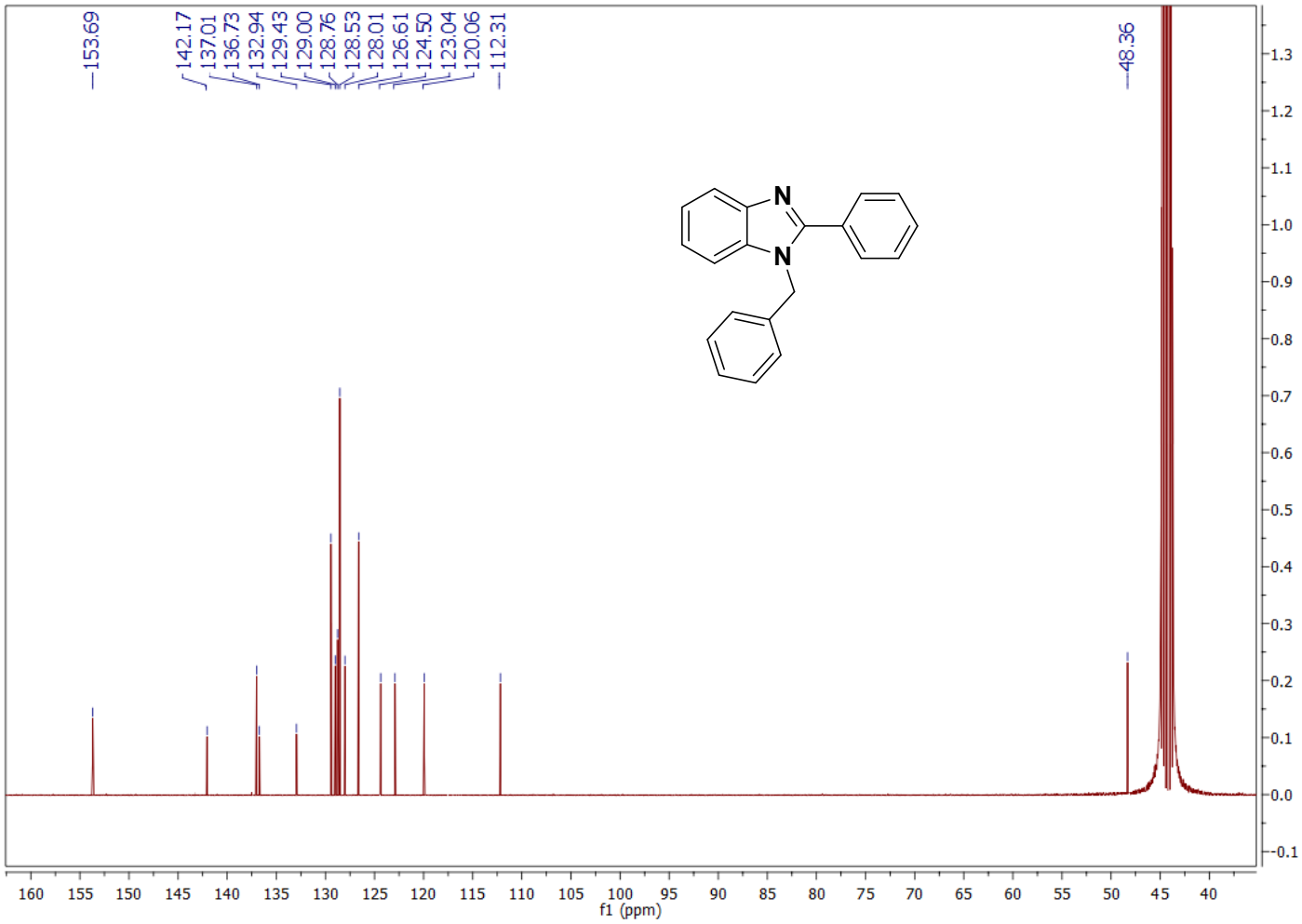
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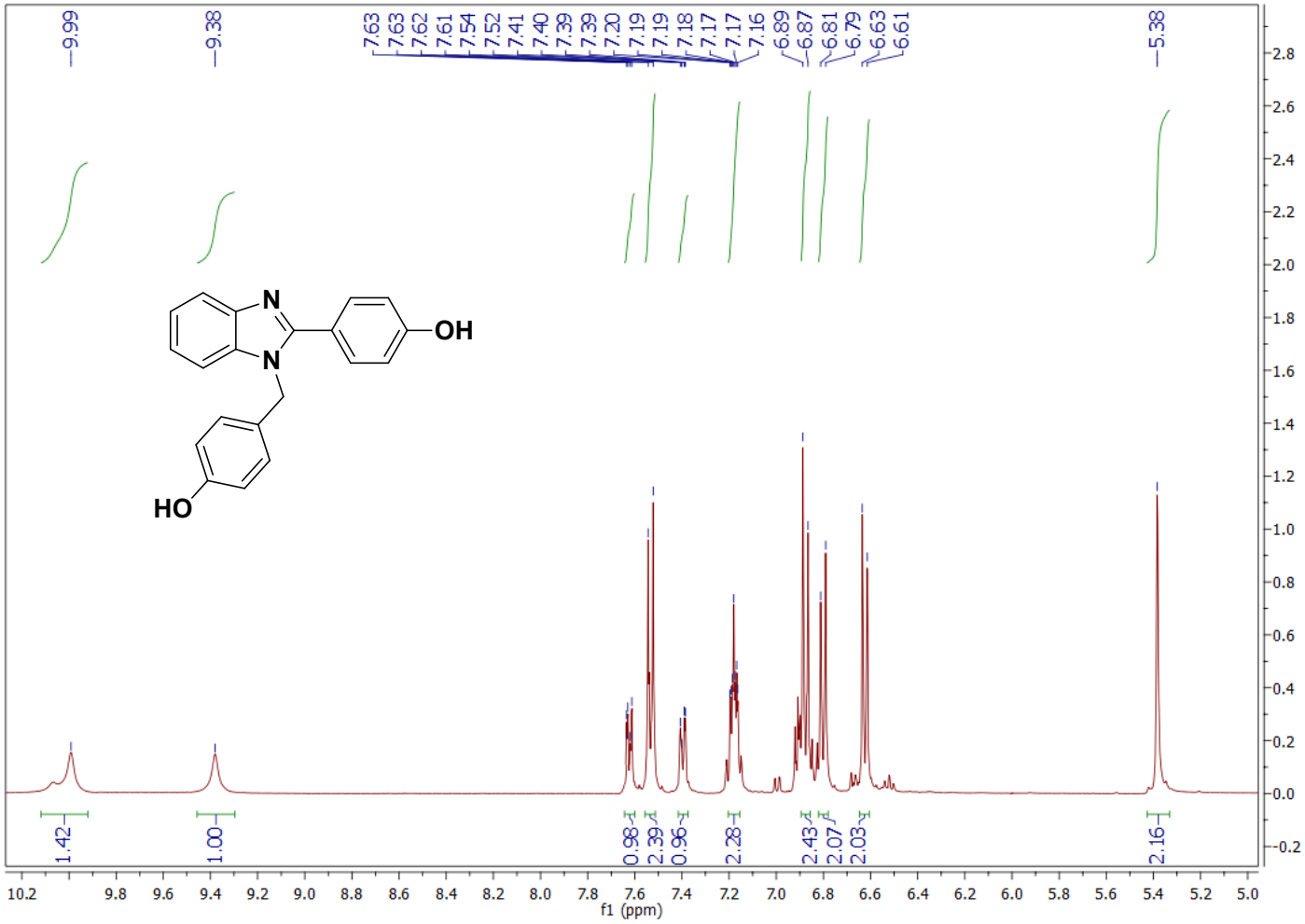
N
f1 (ppm)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7.19
7.19
7.18
7.17
7.17
7.16
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6.87
6.81
6.79
6.63
6.61
5.38
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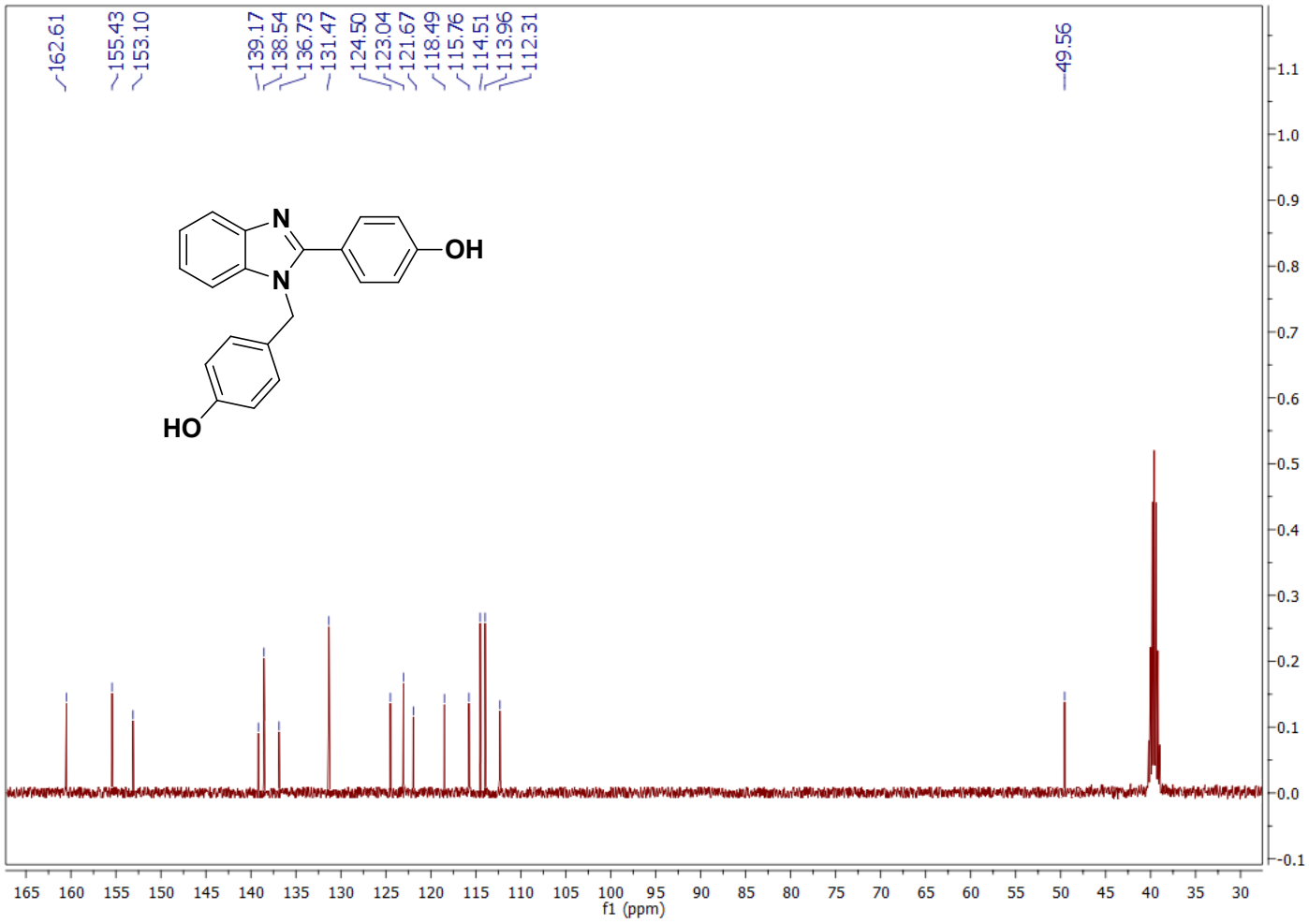
f1 (ppm)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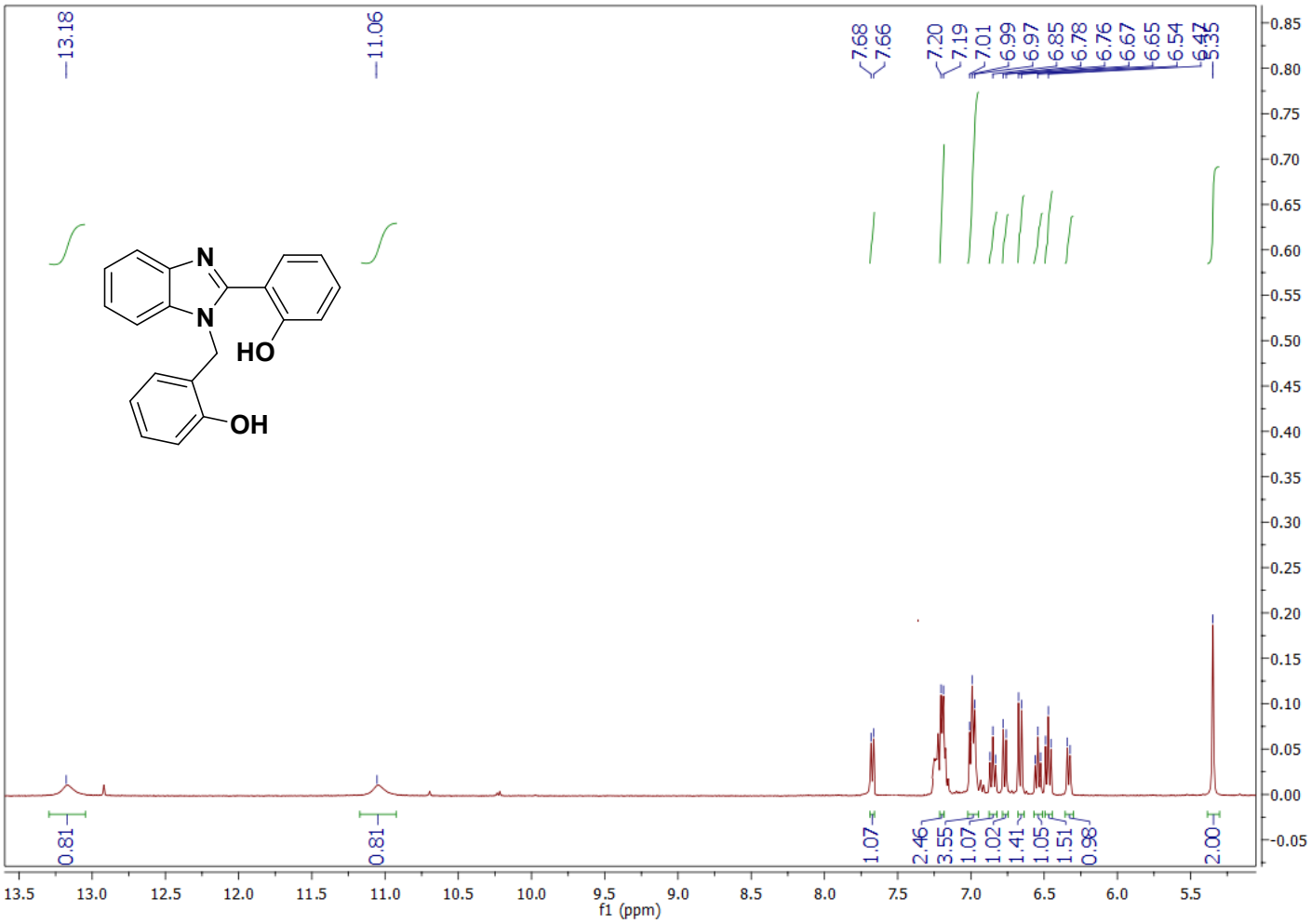
HO
f1 (ppm)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6.47
6.35
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HO
OH
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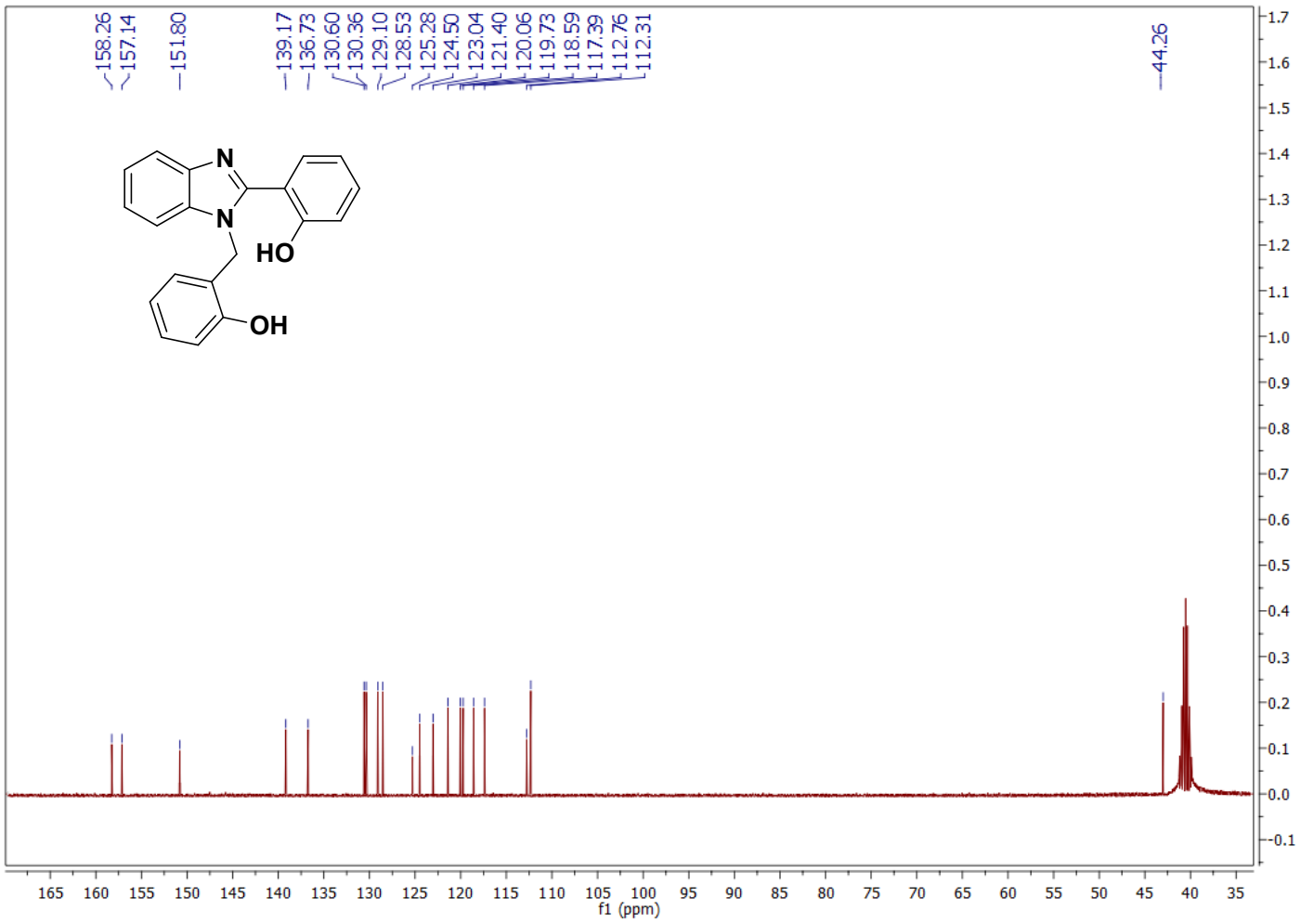
f1 (ppm)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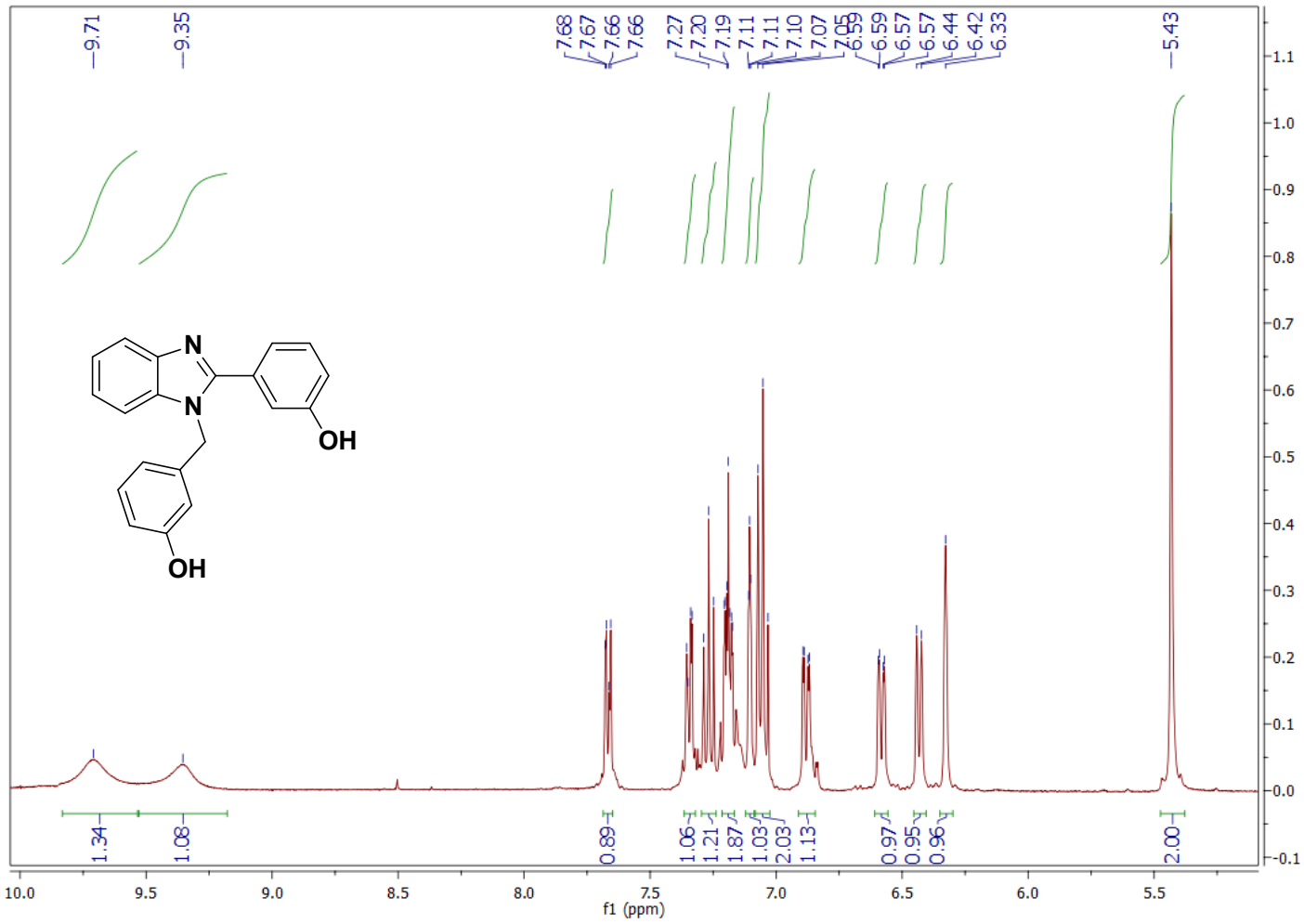
HO
OH
f1 (ppm)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7.05
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6.59
6.57
6.57
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6.33
5.43
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OH
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0.89
1.06
1.21
1.87
1.03
2.03
1.13
0.97
0.95
0.96
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
f1 (ppm)
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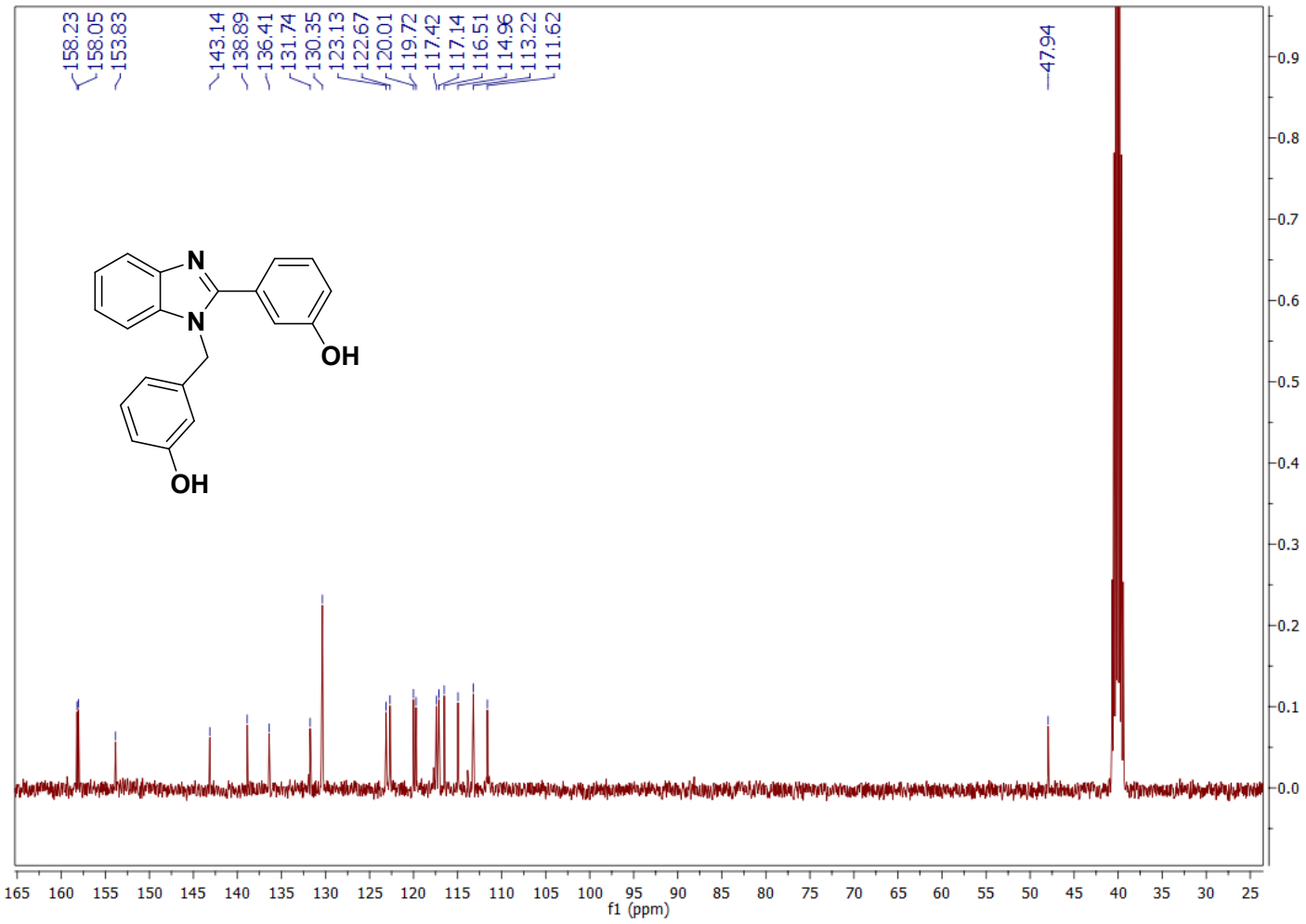
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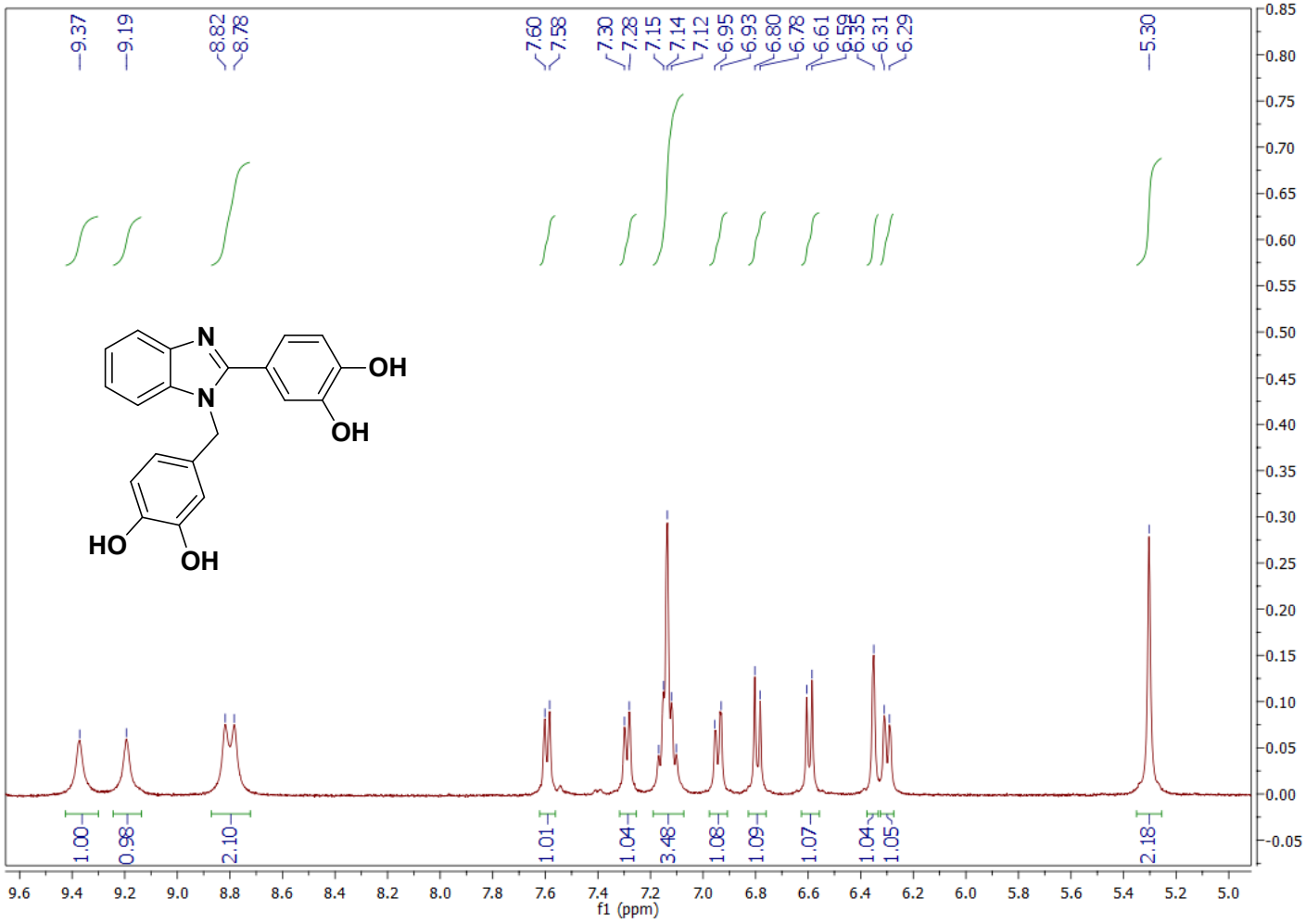
OH
OH
f1 (ppm)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6.35
6.31
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OH
HO
OH
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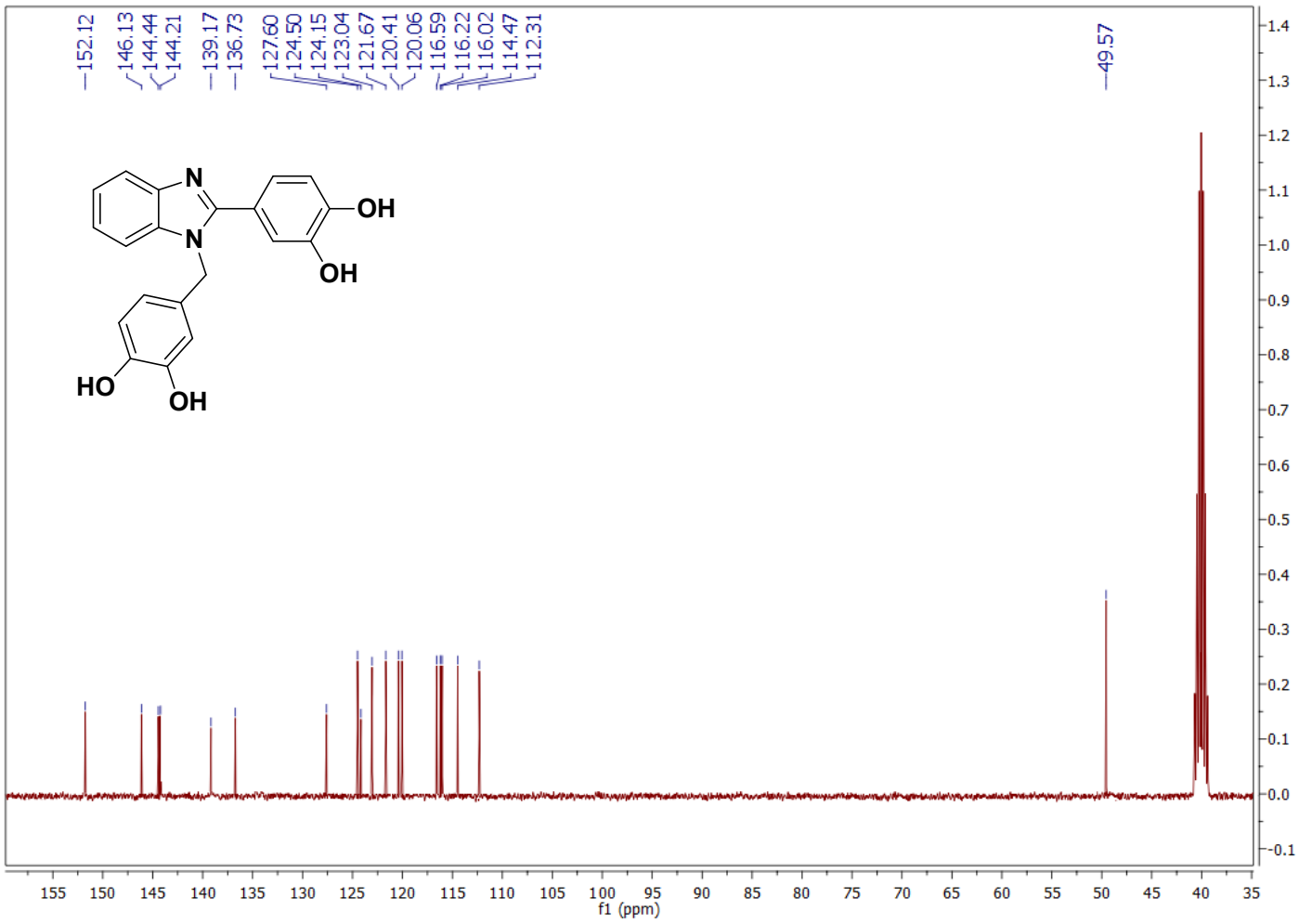
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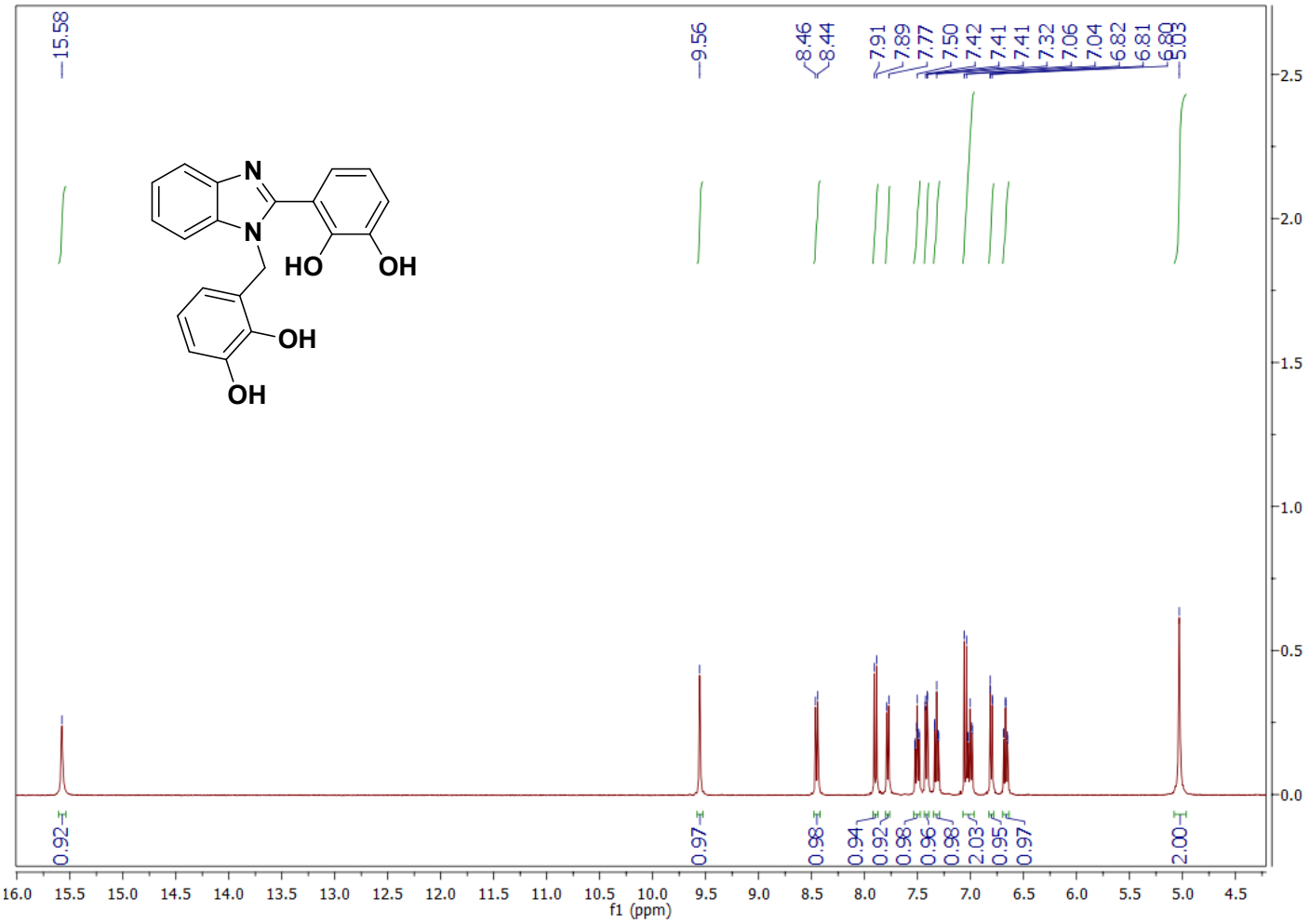
OH
HO
OH
f1 (ppm)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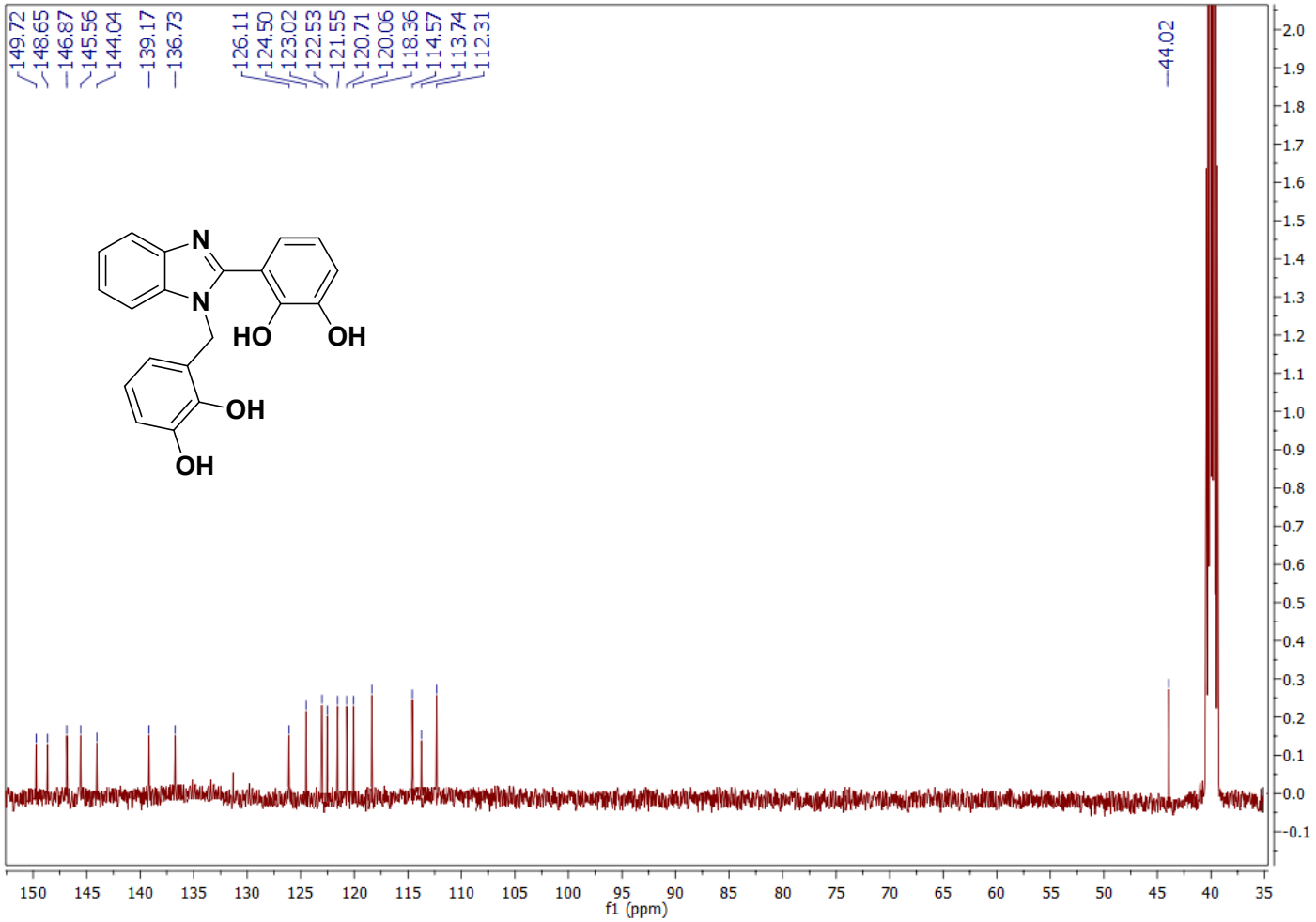
f1 (ppm)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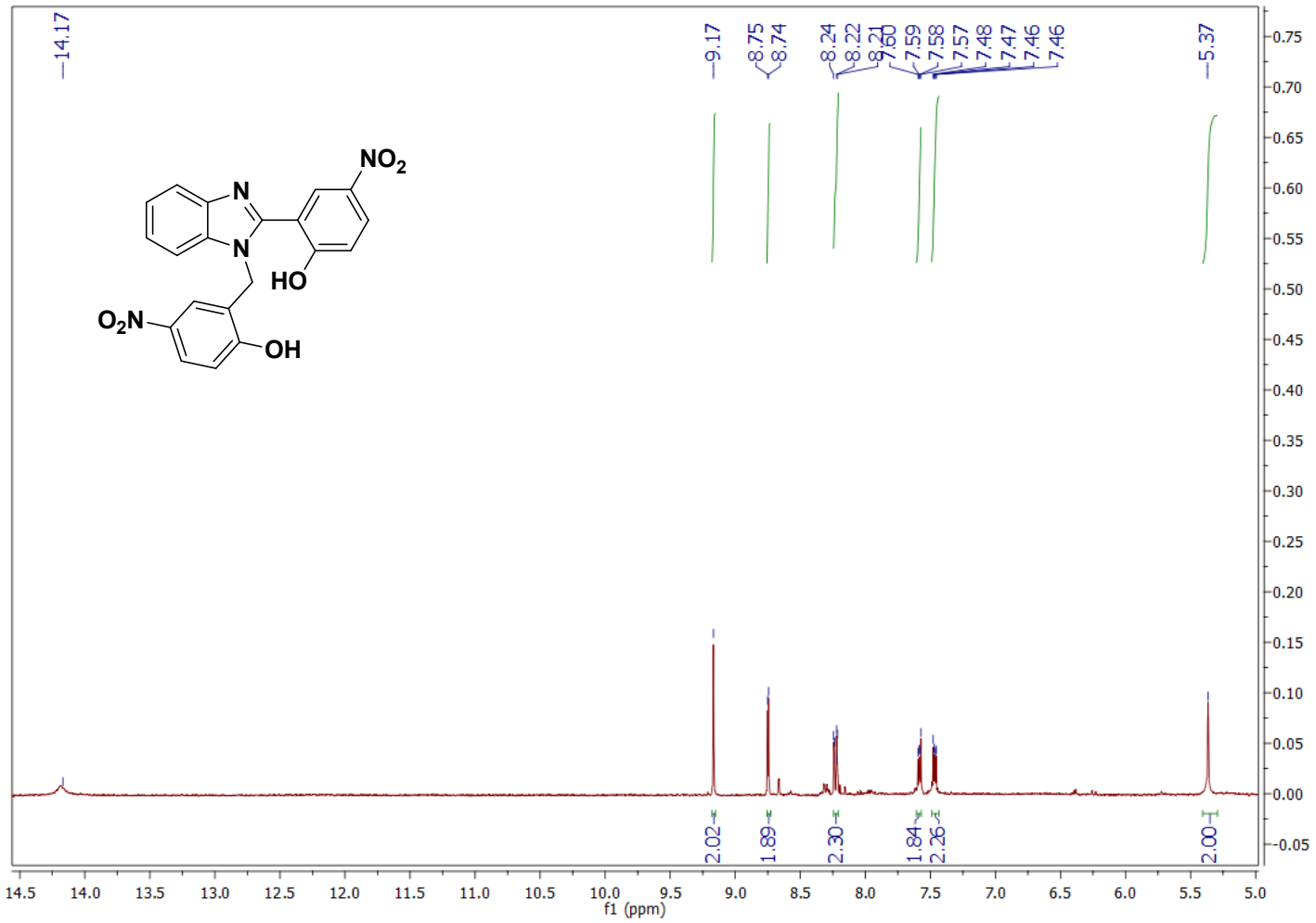
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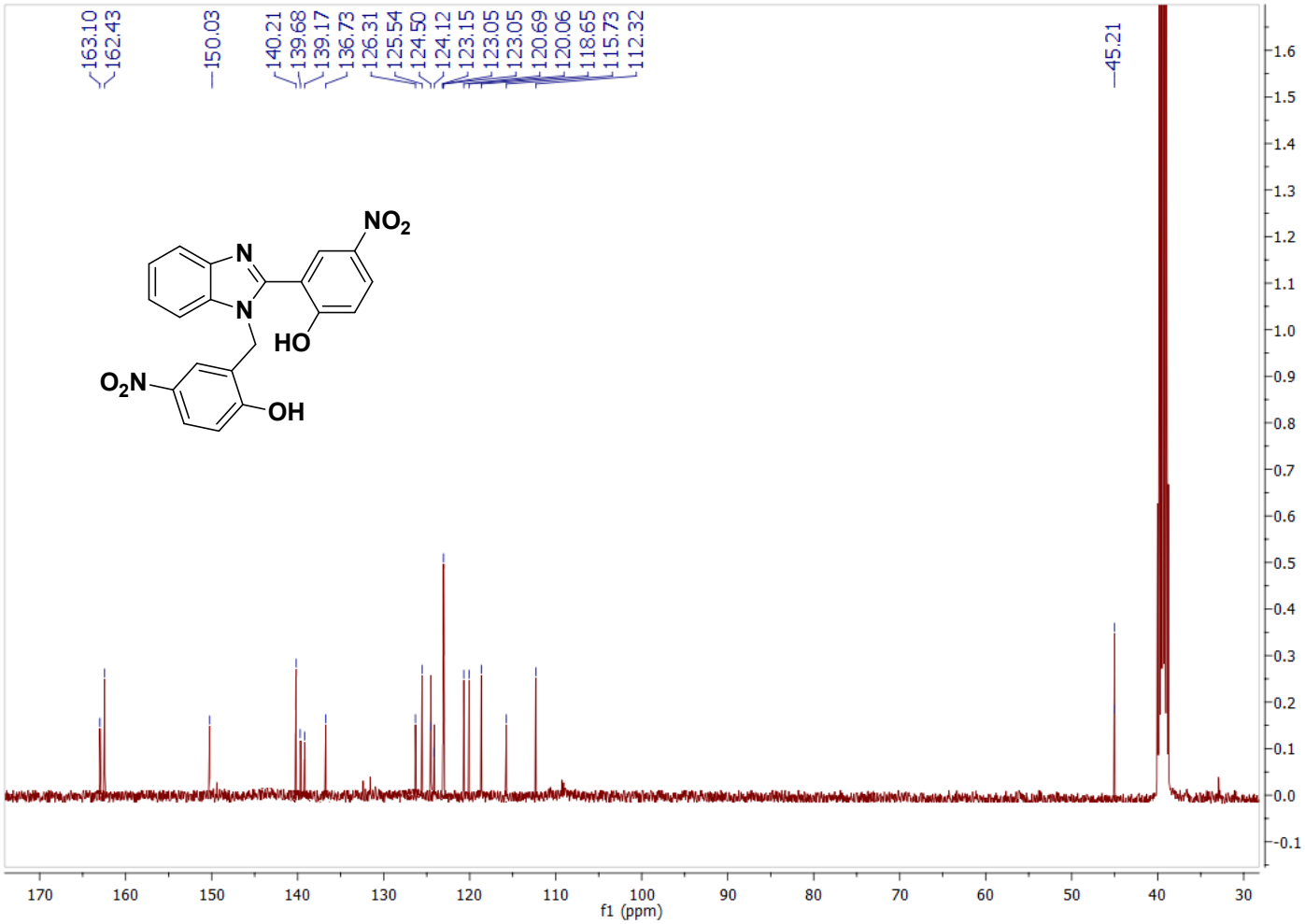
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OH
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0.2
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140
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120
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80
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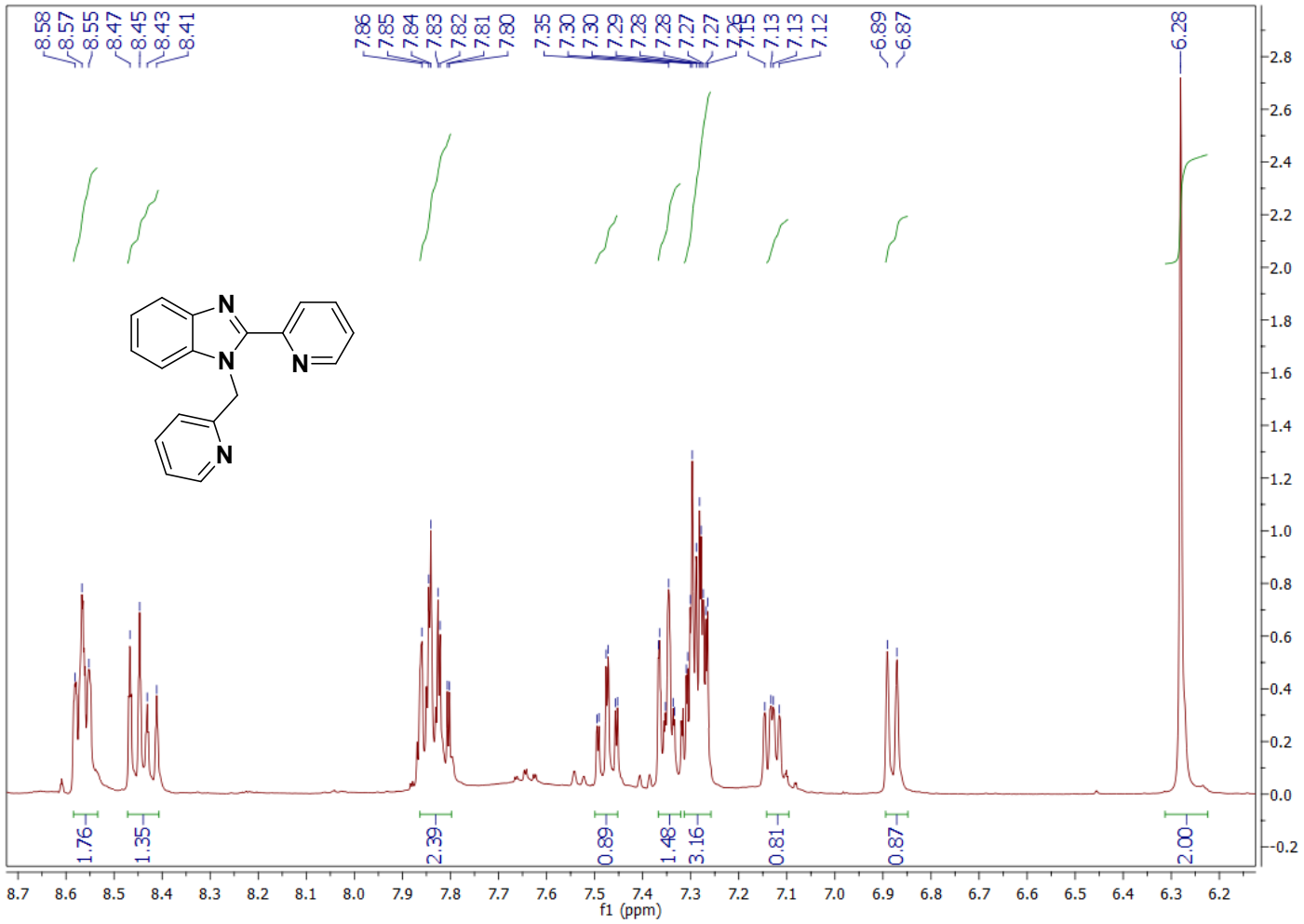
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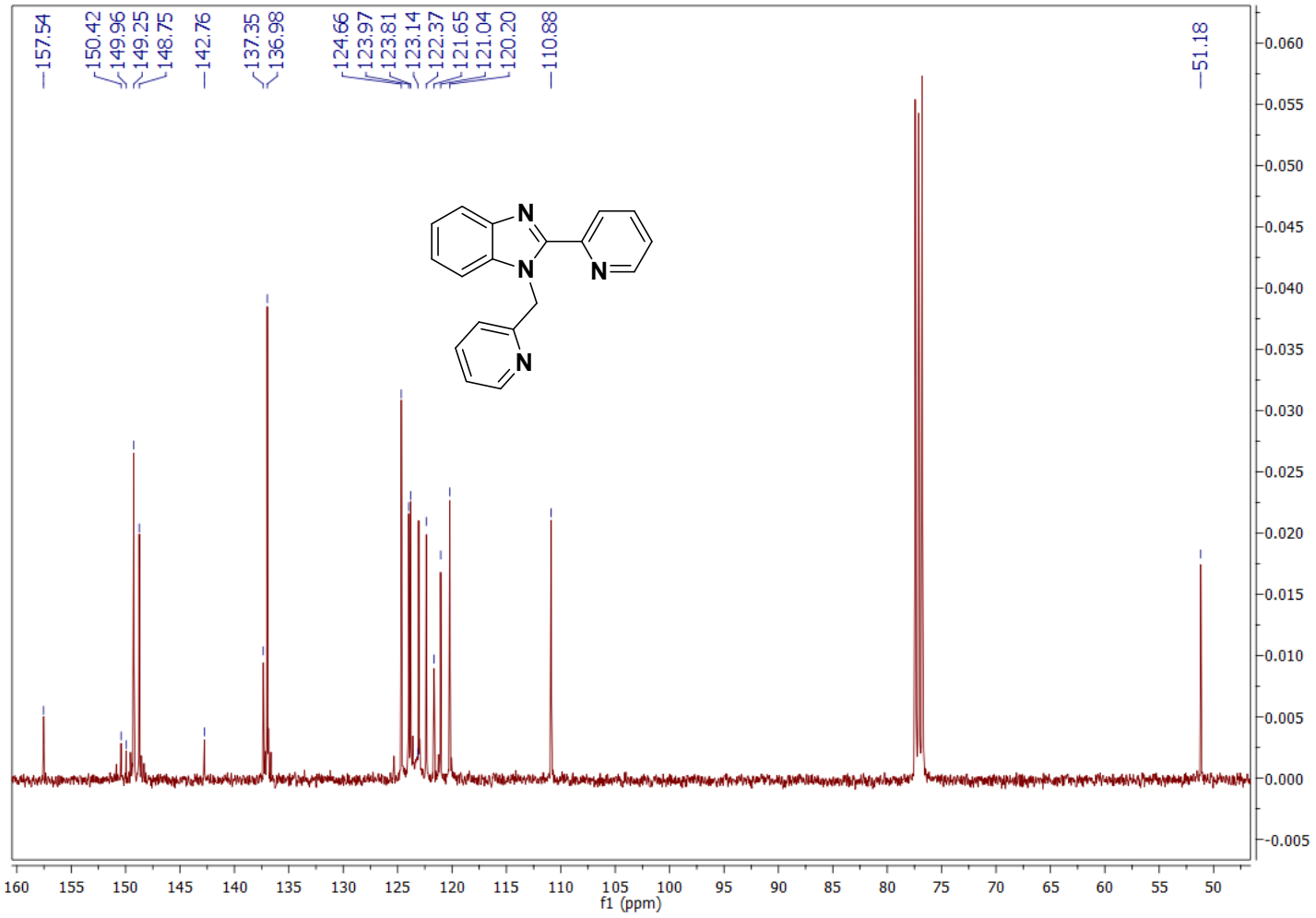
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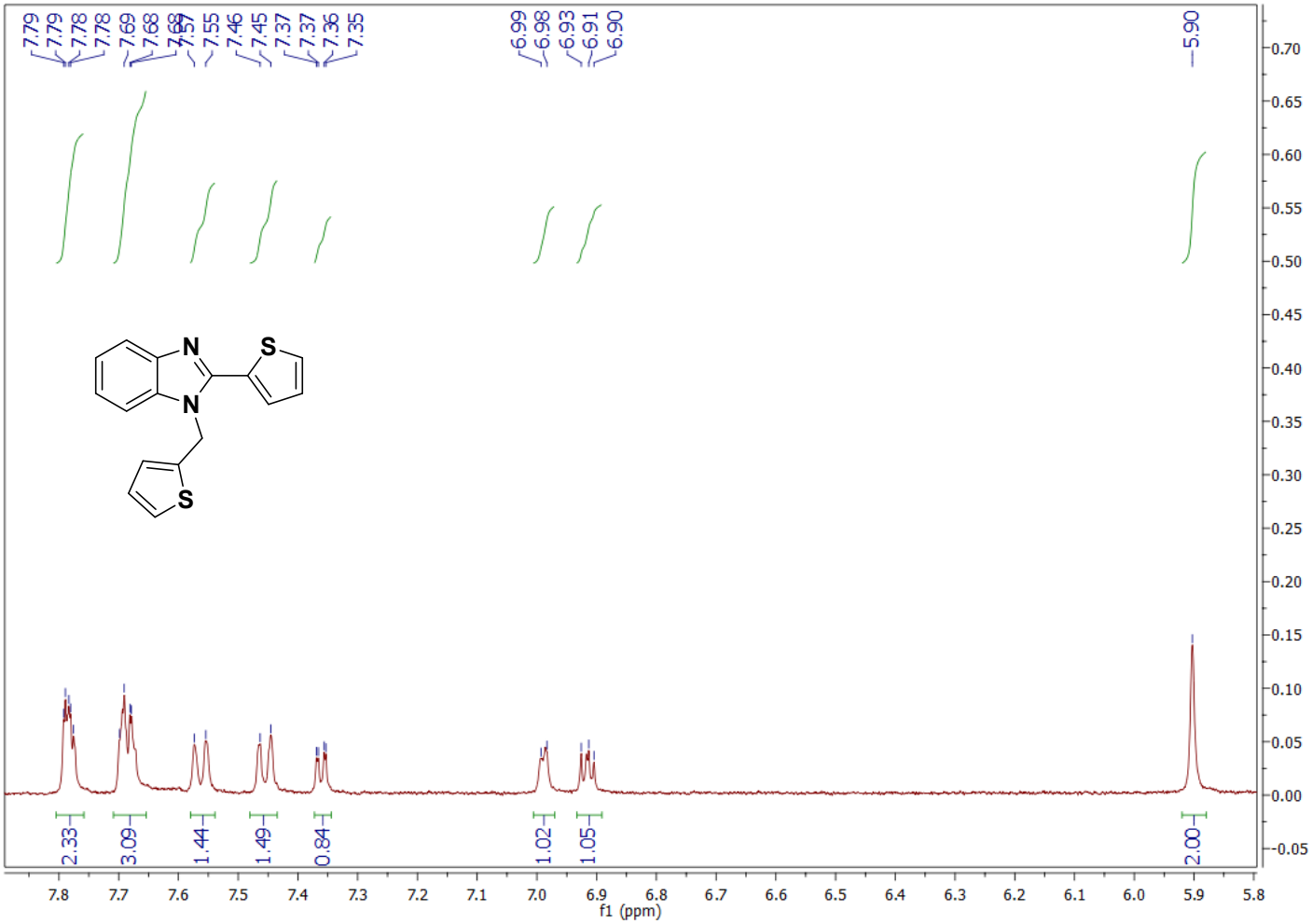
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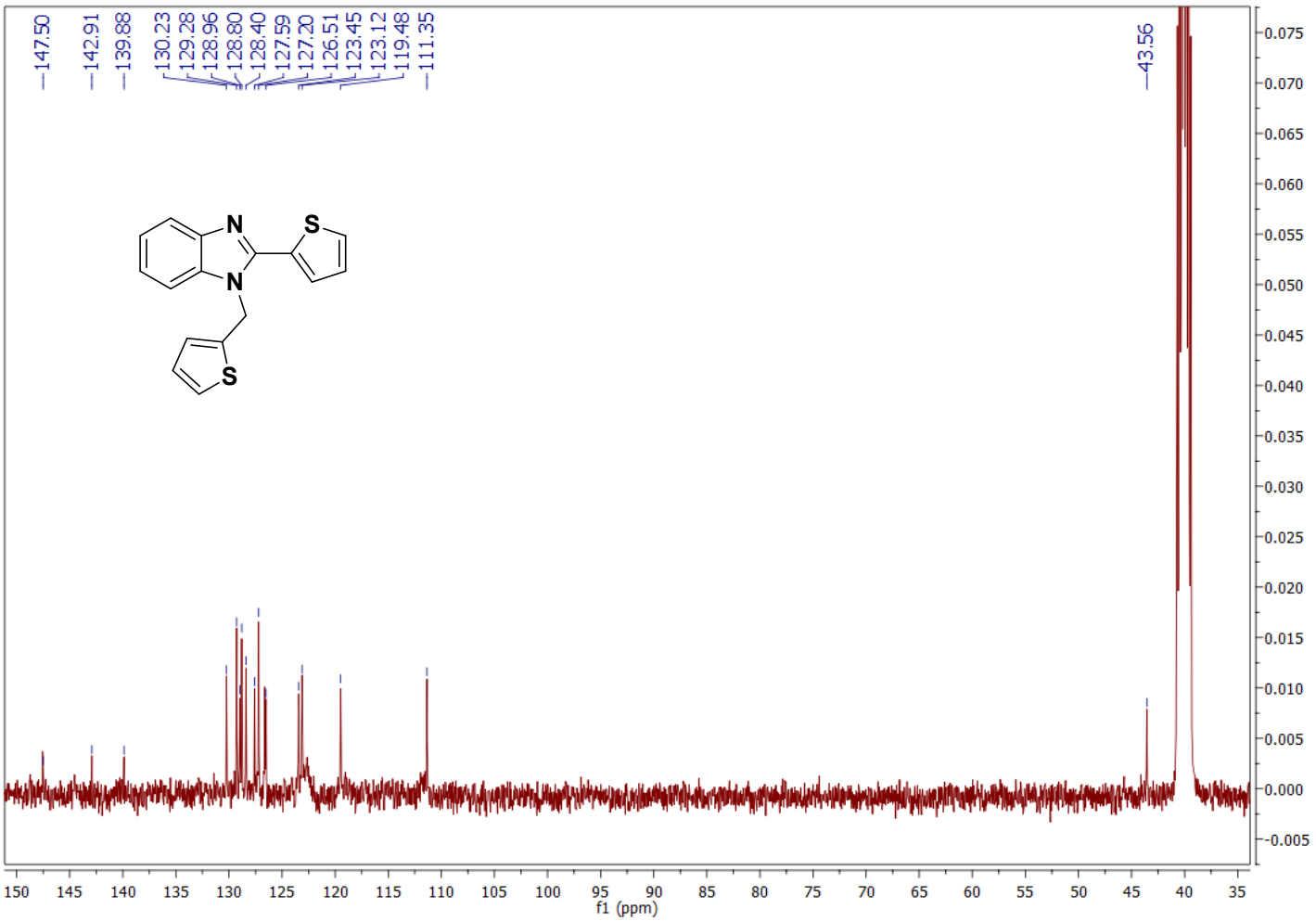
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S
N
S
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0.070
0.065
0.060
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
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0.005
0.000
-0.005
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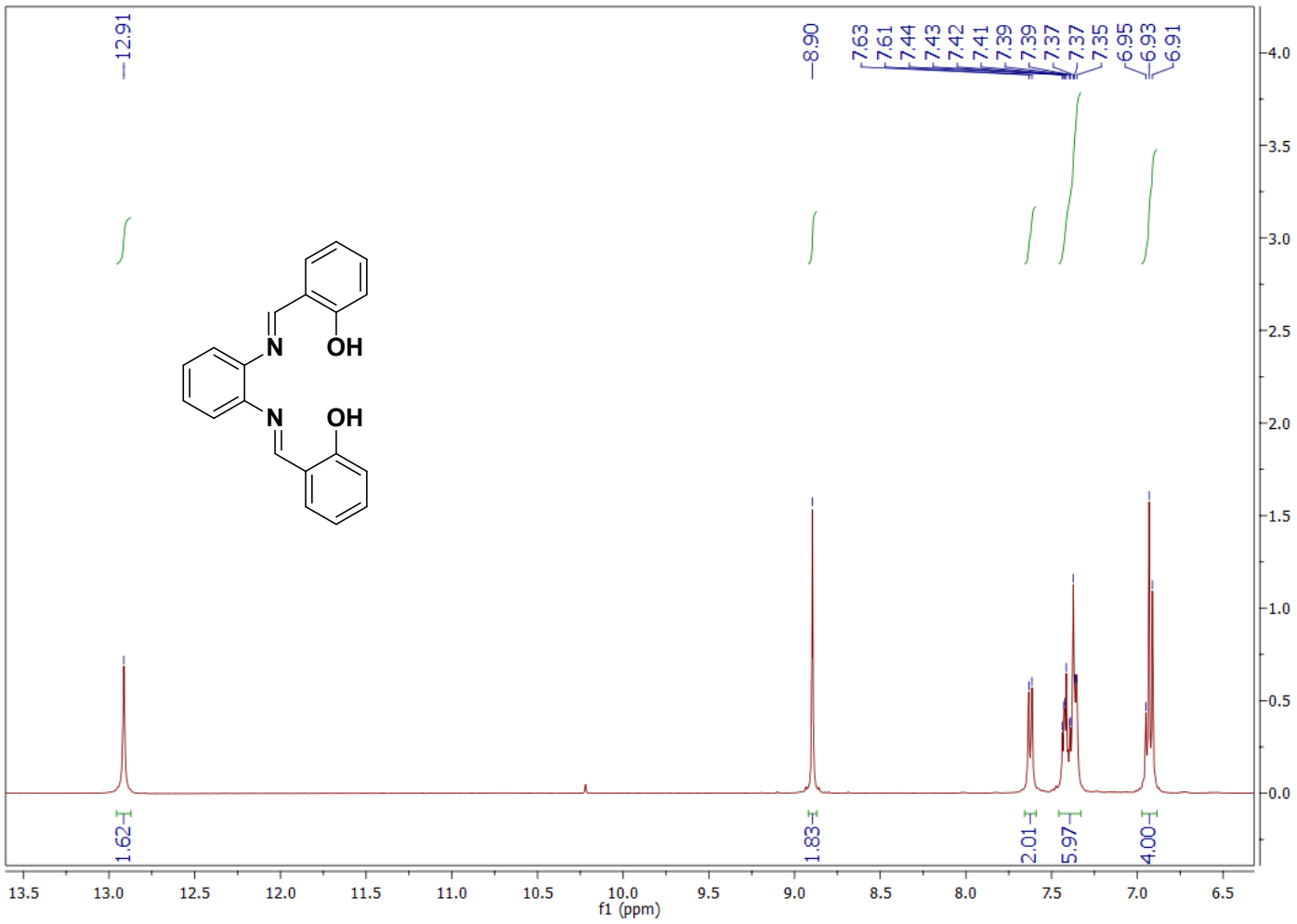
f1 (ppm)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N
OH
1.62
1.83
2.01
5.97
4.00
f1 (ppm)