Supporting Information for:

Nickel-catalysed aromatic Finkelstein reaction of aryl and heteroaryl bromides

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1. General Experimental

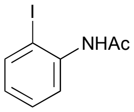
All reagents and starting materials were obtained from commercial sources and used as received. All dry solvents were purified using a PureSolv 500 MD solvent purification system. All reactions were performed under an atmosphere of argon unless otherwise mentioned. Brine refers to a saturated solution of sodium chloride. Flash column chromatography was carried out using Fisher matrix silica 60. Macherey-Nagel aluminium-backed plates pre-coated with silica gel 60 (UV_{254}) were used for thin layer chromatography and were visualised by staining with $KMnO_4$. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 400 spectrometer with chemical shift values in ppm relative to TMS (δ_H 0.00 and δ_C 0.0) or residual chloroform (δ_H 7.28 and δ_C 77.2) as standard. Proton and carbon assignments are based on two-dimensional COSY and DEPT experiments, respectively. Mass spectra were obtained using a JEOL JMS-700 spectrometer. Infrared spectra were obtained neat using a Shimadzu IRPrestige-21 spectrometer. Melting points were determined on a Reichert platform melting point apparatus. Microwave reactions were conducted using a CEM Discover^{TM} Synthesis Unit (CEM Corp., Matthews, NC) and performed in glass vessels (capacity 10 mL) sealed with a septum.

2. Experimental Procedures and Spectroscopic Data for All Compounds

General Procedure for the Conversion of Aryl Bromides to Aryl Iodides

Aryl bromide (0.3 mmol, 1 equiv.), sodium iodide (0.27 g, 1.8 mmol, 6 equiv.), nickel(II) bromide (6 mg, 0.03 mmol, 10 mol%), tri-*n*-butylphosphine (20 µL, 0.075 mmol, 25 mol%), *N*-methyl pyrrolidinone (0.3 mL) and 4Å molecular sieves were placed in a sealed tube and heated to X °C for Y h. The reaction was then allowed to cool and ethyl acetate (5 mL) and water (5 mL) were added. The aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were washed with brine (5 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was then purified using column chromatography eluting with 5% ethyl acetate in petroleum ether.

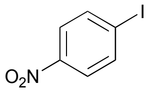
2-Iodoacetanilide[1]



Reaction was heated to 180 °C for 3 h and product was isolated as an orange oil. Yield 65%. δ_H (400 MHz, $CDCl_3$) 2.23 (3H, s, $COCH_3$), 6.84 (1H, t, *J* 7.6 Hz, 5-H), 7.33 (1H, td, *J* 7.6, 1.4 Hz, 4-

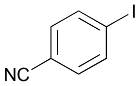
H), 7.43 (1H, br s, NH), 7.77 (1H, d, *J* 7.6 Hz, 3-H), 8.21 (1H, br d, *J* 7.6 Hz, 6-H); δ_C (100 MHz, $CDCl_3$) 24.8 (CH_3), 89.9 (C), 122.0 (CH), 126.0 (CH), 129.3 (CH), 138.2 (C), 138.7 (CH), 168.2 (C); *m/z* (CI) 262 (MH^+, 100%), 218 (5), 176 (6), 136 (27), 85 (9). Spectroscopic data was in agreement with previously published data.[1]

4-Iodonitrobenzene[2]



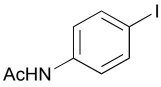
Reaction was heated to 180 °C for 3 h and product was isolated as a light yellow solid. Yield 87%. Mp 169–171 °C; δ_H (400 MHz, $CDCl_3$) 7.80–7.90 (4H, m, ArH); δ_C (100 MHz, $CDCl_3$) 102.7 (C), 124.9 (2 × CH), 138.7 (2 × CH), 147.8 (C); *m/z* (CI) 250 (MH^+, 39%), 220 (41), 187 (9), 124 (58), 113 (31), 85 (72). Spectroscopic data was in agreement with previously published data.[2]

4-Iodobenzonitrile[3]



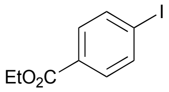
Reaction was heated to 180 °C for 3 h and product was isolated as an off-white solid. Yield 84%. Mp 122–123 °C; δ_H (400 MHz, $CDCl_3$) 7.36 (2H, d, *J* 8.5 Hz, 3-H and 5-H), 7.85 (2H, d, *J* 8.5 Hz, 2-H and 6-H); δ_C (100 MHz, $CDCl_3$) 100.3 (C), 111.7 (C), 118.2 (C), 133.1 (2 × CH), 138.5 (2 × CH); *m/z* (EI) 229 (M^+, 42%), 203 (18), 149 (9), 121 (34), 102 (26). Spectroscopic data was in agreement with previously published data.[3]

4-Iodoacetanilide[4]



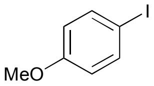
Reaction was heated to 180 °C for 16 h and product was isolated as an off-white solid. Yield 83%. Mp 178–180 °C; δ_H (400 MHz, $CDCl_3$) 2.17 (3H, s, $COCH_3$), 7.19 (1H, br, NH), 7.29 (2H, d, *J* 8.7 Hz, 3-H and 5-H), 7.61 (2H, d, *J* 8.7 Hz, 2-H and 6-H); δ_C (100 MHz, $CDCl_3$) 24.7 (CH_3), 87.4 (C), 121.6 (2 × CH), 137.6 (C), 137.9 (2 × CH), 168.3 (C); *m/z* (CI) 262 (MH^+, 100%), 214 (4), 136 (54), 85 (12). Spectroscopic data was in agreement with previously published data.[4]

Ethyl 4-iodobenzoate[5]



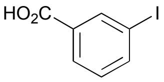
Reaction was heated to 180 °C for 3 h and product was isolated as a clear oil. Yield 57%. δ_H (400 MHz, $CDCl_3$) 1.38 (3H, t, *J* 7.1 Hz, OCH_2CH_3), 4.36 (2H, q, *J* 7.1 Hz, OCH_2CH_3), 7.72–7.81 (4H, m, ArH); δ_C (100 MHz, $CDCl_3$) 14.3 (CH_3), 61.2 (CH_2), 100.6 (C), 130.0 (C), 131.0 (2 × CH), 137.7 (2 × CH), 166.1 (C). *m/z* (EI) 276 (M^+, 88%), 248 (66), 231 (100), 203 (27), 149 (10), 149 (10), 76 (28). Spectroscopic data was in agreement with previously published data.[5]

4-Iodoanisole[3]



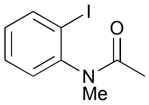
Reaction was heated to 160 °C for 3 h and product was isolated as an off-white waxy solid. Yield 67%. Mp 49–50 °C; δ_H (400 MHz, $CDCl_3$) 3.78 (3H, s, OCH_3), 6.68 (2H, dt, *J* 9.0, 3.2 Hz, 2-H and 6-H), 7.56 (2H, dt, *J* 9.0, 3.2 Hz, 3-H and 5-H); δ_C (100 MHz, $CDCl_3$) 55.3 (CH_3), 82.7 (C), 116.4 (2 × CH), 138.2 (2 × CH), 159.5 (C); *m/z* (EI) 235 (M^+, 100%), 219 (71), 191 (66), 127 (16), 107 (15), 92 (42), 77 (37). Spectroscopic data was in agreement with previously published data.[3]

3-Iodobenzoic acid[5]



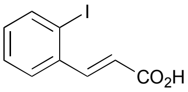
Reaction was heated to 180 °C for 3 h and product was isolated as an off-white solid. Yield 77%. Mp 178–179 °C; δ_H (400 MHz, DMSO-d_6) 7.34 (1H, t, *J* 7.8 Hz, 5-H), 7.98 (1H, dt, *J* 7.8, 1.6 Hz, 4-H), 8.01 (1H, ddd, *J* 7.8, 1.6, 1.6 Hz, 6-H), 8.26 (1H, t, *J* 1.6 Hz, 2-H), 13.28 (1H, br, NH); δ_C (100 MHz, DMSO-d_6) 94.6 (C), 128.6 (CH), 130.8 (CH), 132.8 (C), 137.6 (CH), 141.3 (CH), 165.9 (C); *m/z* (CI) 249 (MH^+, 100%), 231 (31), 169 (72), 125 (33), 84 (66). Spectroscopic data was in agreement with previously published data.[5]

N-(2-Iodophenyl)-*N*-methylacetamide[6]



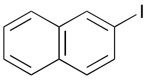
Reaction was heated to 190 °C for 7 h and product was isolated as an orange oil. Yield 70%. δ_H (400 MHz, $CDCl_3$) 1.80 (3H, s, $COCH_3$), 3.18 (3H, s, NCH_3), 7.09 (1H, td, *J* 7.9, 1.6 Hz, 5-H), 7.26 (1H, dd, *J* 7.9, 1.6 Hz, 3-H), 7.41 (1H, td, *J* 7.9, 1.3 Hz, 4-H), 7.92 (1H, dd, *J* 7.9, 1.3 Hz, 6-H); δ_C (100 MHz, $CDCl_3$) 22.4 (CH_3), 35.7 (CH_3), 99.4 (C), 128.7 (CH), 129.8 (CH), 130.0 (CH), 140.1 (CH), 146.5 (C), 170.2 (C); *m/z* (CI) 276 (MH^+, 26%), 233 (8), 181 (5), 148 (93), 101 (100), 85 (42). Spectroscopic data was in agreement with previously published data.[6]

2-Iodocinnamic acid[7]



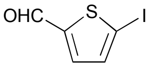
Reaction was heated to 140 °C for 16 h and product was isolated as a white solid. Yield 86%. Mp 212–213 °C; δ_H (400 MHz, DMSO-d_6) 3.48 (1H, br s, CO_2H), 6.51 (1H, d, *J* 15.8 Hz, $C\mathit{H}CO_2H$), 7.18 (1H, td, *J* 7.8, 1.5 Hz, 4-H), 7.46 (1H, br t, *J* 7.8 Hz, 5-H), 7.74 (1H, d, *J* 15.8 Hz, $C\mathit{H}{=}CHCO_2H$), 7.85 (1H, dd, *J* 7.8, 1.5 Hz, 3-H), 7.98 (1H, dd, *J* 7.8, 1.5 Hz, 6-H); δ_C (100 MHz, DMSO-d_6) 102.9 (C), 123.1 (CH), 128.7 (CH), 129.8 (CH), 132.7 (CH), 137.7 (C), 140.6 (CH), 147.4 (CH), 168.0 (C); *m/z* (CI) 275 (MH^+, 20%), 250 (34), 220 (22), 149 (18), 124 (21), 85 (100). Spectroscopic data was in agreement with previously published data.[7]

2-Iodonaphthalene[5]



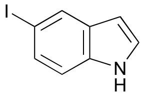
Reaction was heated to 180 °C for 16 h and product was isolated as a brown solid. Yield 74%. Mp 50–52 °C; δ_H (400 MHz, $CDCl_3$) 7.46–7.52 (2H, m, 6-H and 7-H), 7.58 (1H, d, *J* 8.7 Hz, 5-H), 7.70-7.74 (2H, m, 4-H and 8-H), 7.83–7.78 (1H, m, 3-H), 8.25 (1H, s, 1-H); δ_C (100 MHz, $CDCl_3$) 91.6 (C), 126.5 (CH), 126.7 (CH), 126.8 (CH), 127.9 (CH), 129.5 (CH), 132.1 (C), 134.4 (CH), 135.0 (C), 136.7 (CH); *m/z* (EI) 254 (M^+, 100%), 248 (23), 149 (11), 127 (72), 100 (58), 77 (59). Spectroscopic data was in agreement with previously published data.[5]

5-Iodo-2-thiophenecarboxaldehyde[8]



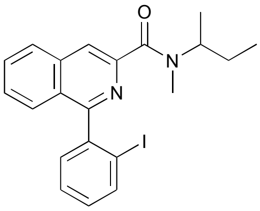
Reaction was heated to 160 °C for 3 h and product was isolated as a clear oil. Yield 65%. δ_H (400 MHz, $CDCl_3$) 7.39 (2H, s, ArH), 9.77 (1H, s, CHO); δ_C (100 MHz, $CDCl_3$) 87.9 (C), 137.1 (CH), 138.3 (CH), 149.6 (C), 181.2 (CH); *m/z* (EI) 238 (M^+, 100%), 209 (4), 165 (3), 127 (10), 82 (18). Spectroscopic data was in agreement with previously published data.[8]

5-Iodoindole[9]



Reaction was heated to 160 °C for 16 h and product was isolated as an off-white solid. Yield 64%. Mp 97–98 °C; δ_H (400 MHz, $CDCl_3$) 6.49 (1H, dd, *J* 3.1, 2.0 Hz, 2-H), 7.16–7.19 (2H, m, 3-H and 7-H), 7.44 (1H, dd, *J* 8.5, 1.7 Hz, 6-H), 7.98–8.00 (1H, m, 4-H), 8.18 (1H, br s, NH); δ_C (100 MHz, $CDCl_3$) 83.2 (C), 101.9 (CH), 112.9 (CH), 124.9 (CH), 129.5 (CH), 130.2 (CH), 130.4 (C), 134.8 (C); *m/z* (CI) 244 (MH^+, 100%), 196 (7), 173 (21), 159 (22), 118 (23), 85 (18). Spectroscopic data was in agreement with previously published data.[9]

1-(2-Iodophenyl)isoquinoline-3-*N*-methyl-3-*N*-*sec*-butylcarboxamide (I-PK11195)

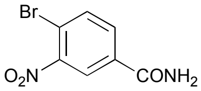


2

Reaction was heated to 160 °C for 16 h and product was isolated as a yellow oil. Yield 75%. ν_{max}/cm^{-1} (neat) 2926 (CH), 2360, 1620 (CO), 1464, 1403, 1091, 824. Compound exists as a mixture of rotomers. NMR spectroscopic data presented is for the major rotomer: δ_H (400 MHz, $CDCl_3$) 0.74–0.84 (3H, m, CH_2CH_3), 1.23 (3H, d, *J* 6.4 Hz, $NCHCH_3$), 1.49–1.68 (2H, m, CH_2CH_3), 2.98 (3H, s, NCH_3), 3.91–4.04 (1H, m, $NCHCH_3$), 7.18–7.22 (1H, m, ArH), 7.33–7.42

(1H, m, ArH), 7.47–7.57 (3H, m, ArH), 7.71–7.74 (1H, m, ArH), 7.94–8.06 (3H, m, ArH); δ_C (100 MHz, $CDCl_3$) 11.1 (CH_3), 18.6 (CH_3), 26.3 (CH_3), 27.4 (CH_2), 55.8 (CH), 97.5 (C), 120.0 (CH), 120.5 (CH), 127.1 (CH), 127.4 (CH), 128.1 (CH), 128.2 (CH), 130.1 (CH), 130.2 (C), 130.8 (CH), 136.7 (C), 139.0 (CH), 143.8 (C), 148.2 (C), 161.6 (C), 170.1 (C); *m/z* (CI) 445.0779 (MH^+. $C_{21}H_{22}IN_2O$ requires 445.0777), 347 (10%), 319 (48), 257 (7), 181 (5), 113 (15), 81 (58).

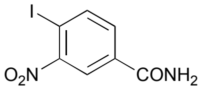
4-Bromo-3-nitrobenzamide 4



4

Potassium nitrate (0.92 g, 9.1 mmol, 1 equiv.) was added to a stirred solution of 4-bromobenzonitrile (1.66 g, 9.1 mmol, 1 equiv) in sulfuric acid (10 mL) and the solution was stirred at room temperature for 16 h. The reaction was then poured onto ice and extracted with ethyl acetate (20 mL). The organic layer was washed with water (20 mL) and then 10% sodium carbonate solution (20 mL). The organic layer was dried ($MgSO_4$), filtered and evaporated to dryness. The resulting residue was dissolved in a minimum amount of hot ethanol and allowed to cool. The addition of hexane resulted in the formation of a pale yellow precipitate which was filtered under vacuum to give 4-bromo-3-nitrobenzamide as a pale yellow solid (1.65 g, 74%). Mp 153–154 °C; δ_H (400 MHz, DMSO-d_6) 7.80 (1H, br s, 6-H), 8.07–8.12 (2H, m, $CONH_2$), 8.32 (1H, br s, 5-H), 8.46–8.50 (1H, m, 2-H); δ_C (100 MHz, DMSO-d_6) 117.2 (C), 125.3 (CH), 133.3 (CH), 135.8 (C), 135.9 (CH), 150.4 (C), 165.9 (C); *m/z* (CI) 244.9557 (MH^+, $C_7H_6{}^{79}BrN_2O_3$ requires 244.9562), 216 (6%), 167 (7), 157 (22), 119 (9), 79 (100).

4-Iodo-3-nitrobenzamide 5



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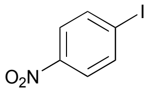
Reaction was heated to 140 °C for 18 h using 19 mol% of tri-*n*-butylphosphine and product was isolated as a light yellow solid. Yield 54%. Mp 155–156 °C; ν_{max}/cm^{-1} (neat) 3462 (NH), 3184 (CH), 2360, 1684 (CO), 1528, 1351, 1021, 668; δ_H (400 MHz, DMSO-d_6) 7.74 (1H, br s, NH), 7.88 (1H, dd, *J* 8.2, 2.1 Hz, 6-H), 8.27 (1H, d, *J* 8.2 Hz, 5-H), 8.29 (1H, br s, NH), 8.39 (1H, d, *J* 2.1 Hz, 2-H); δ_C (100 MHz, DMSO-d_6) 92.0 (C), 123.7 (CH), 132.1 (CH), 135.4 (C), 141.5 (CH), 153.2

(C), 165.2 (C); *m/z* (CI) 292.9425 (MH^+, $C_7H_6IN_2O_3$ requires 292.9423), 263 (12%), 245 (8), 201 (5), 167 (8), 85 (9).

General Procedure for the Conversion of Aryl Bromides to Aryl Iodides using Microwave Heating

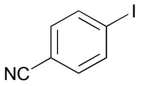
Aryl bromide (1.2 mmol, 1 equiv.), sodium iodide (1.08 g, 7.2 mmol, 6 equiv.), nickel(II) bromide (24 mg, 0.12 mmol, 10 mol%), tri-*n*-butylphosphine (80 µL, 0.3 mmol, 25 mol%), *N*-methyl pyrrolidinone (1.2 mL) and 4Å molecular sieves were placed into a sealed tube and heated to X °C for Y minutes in the microwave reactor. The reaction was then allowed to cool and ethyl acetate (5 mL) and water (5 mL) were added. The aqueous layer was extracted with ethyl acetate (3 × 5 mL) and the combined organic layers were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was then purified using column chromatography eluting with 5% ethyl acetate in petroleum ether.

4-Iodonitrobenzene



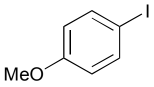
Reaction was heated to 200 °C for 30 minutes and product was isolated as a light yellow solid. Yield 74%. Spectroscopic data was in agreement with that described above.

4-Iodobenzonitrile



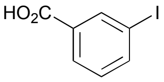
Reaction was heated to 200 °C for 10 minutes and product was isolated as an off-white solid. Yield 67%. Spectroscopic data was in agreement with that described above.

4-Iodoanisole



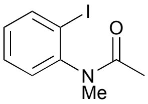
Reaction was heated to 160 °C for 10 minutes and product was isolated as an off-white waxy solid. Yield 49%. Spectroscopic data was in agreement with that described above.

3-Iodobenzoic acid



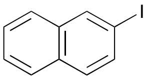
Reaction was heated to 160 °C for 10 minutes and product was isolated as an off-white solid. Yield 72%. Spectroscopic data was in agreement with that described above.

N-(2-Iodophenyl)-*N*-methylacetamide



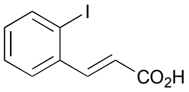
Reaction was heated to 200 °C for 30 minutes and product was isolated as an orange oil. Yield 51%. Spectroscopic data was in agreement with that described above.

2-Iodonaphthalene



Reaction was heated to 180 °C for 10 minutes and product was isolated as a brown solid. Yield 68%. Spectroscopic data was in agreement with that described above.

2-Iodocinnamic acid



Reaction was heated to 160 °C for 60 minutes and product was isolated as a white solid. Yield 30%. Spectroscopic data was in agreement with that described above.

3. References

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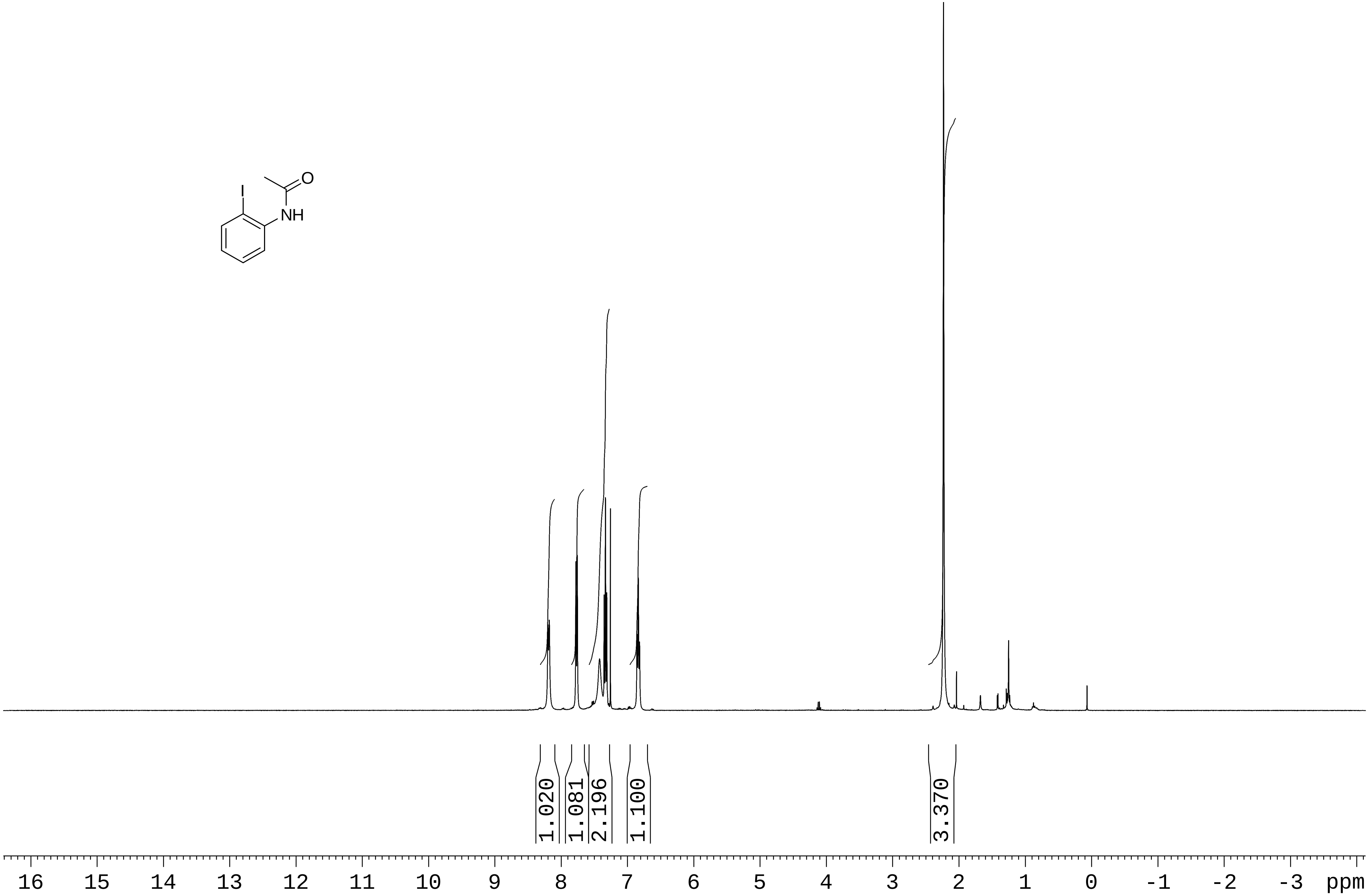
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O
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1.100
3.370
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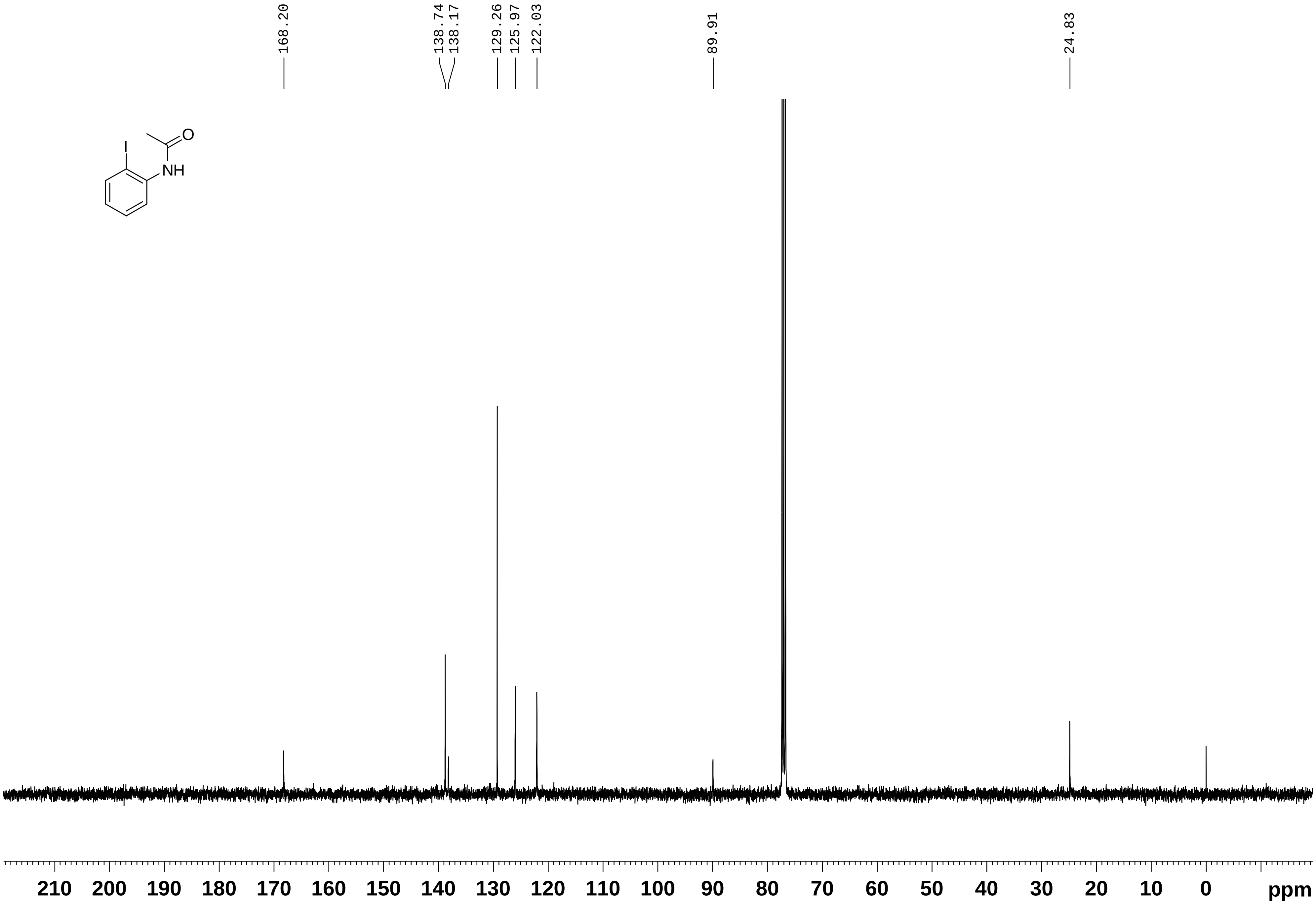
-2
-3
ppm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125.97
122.03
89.91
24.83
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O
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140
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120
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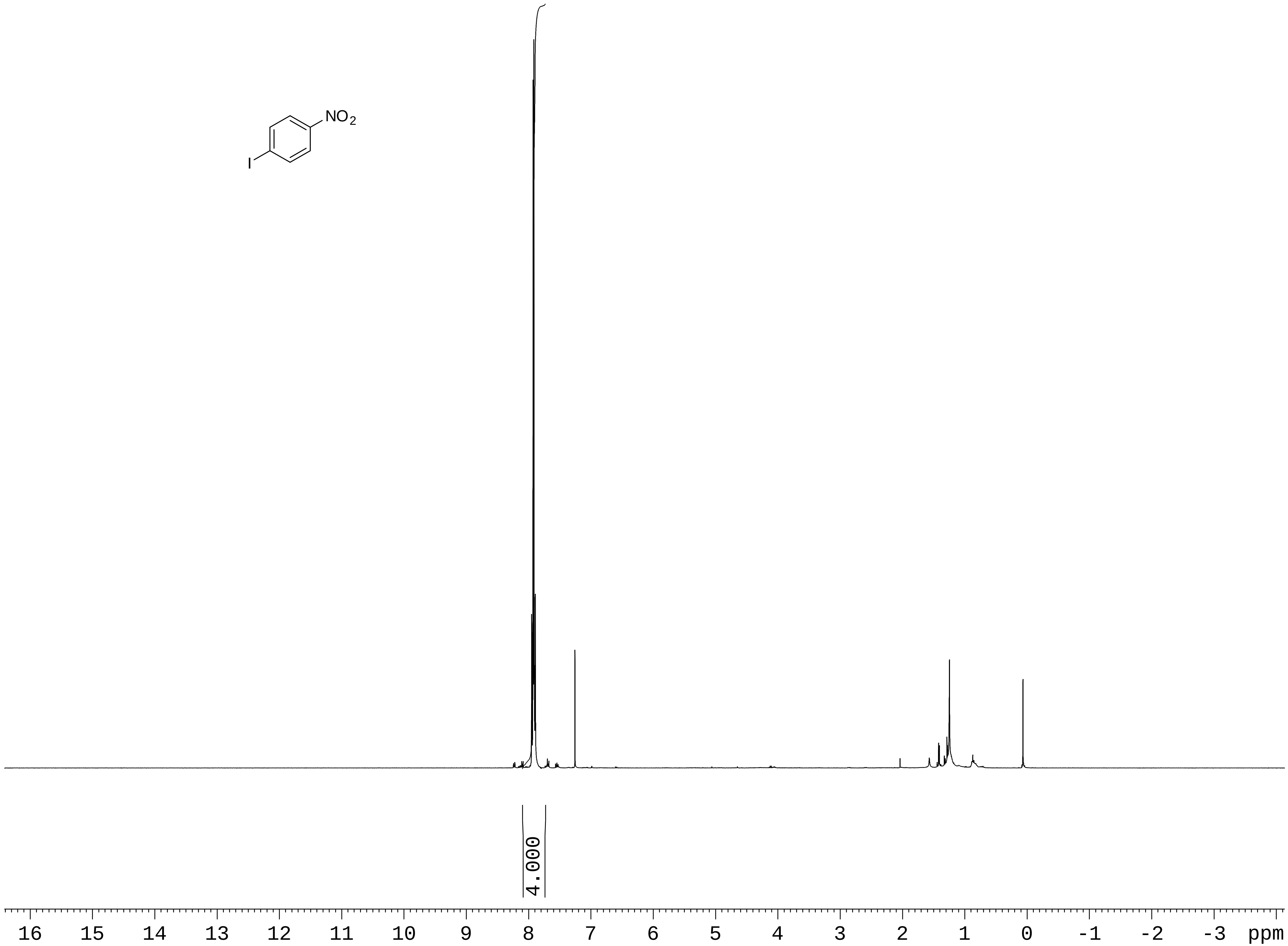
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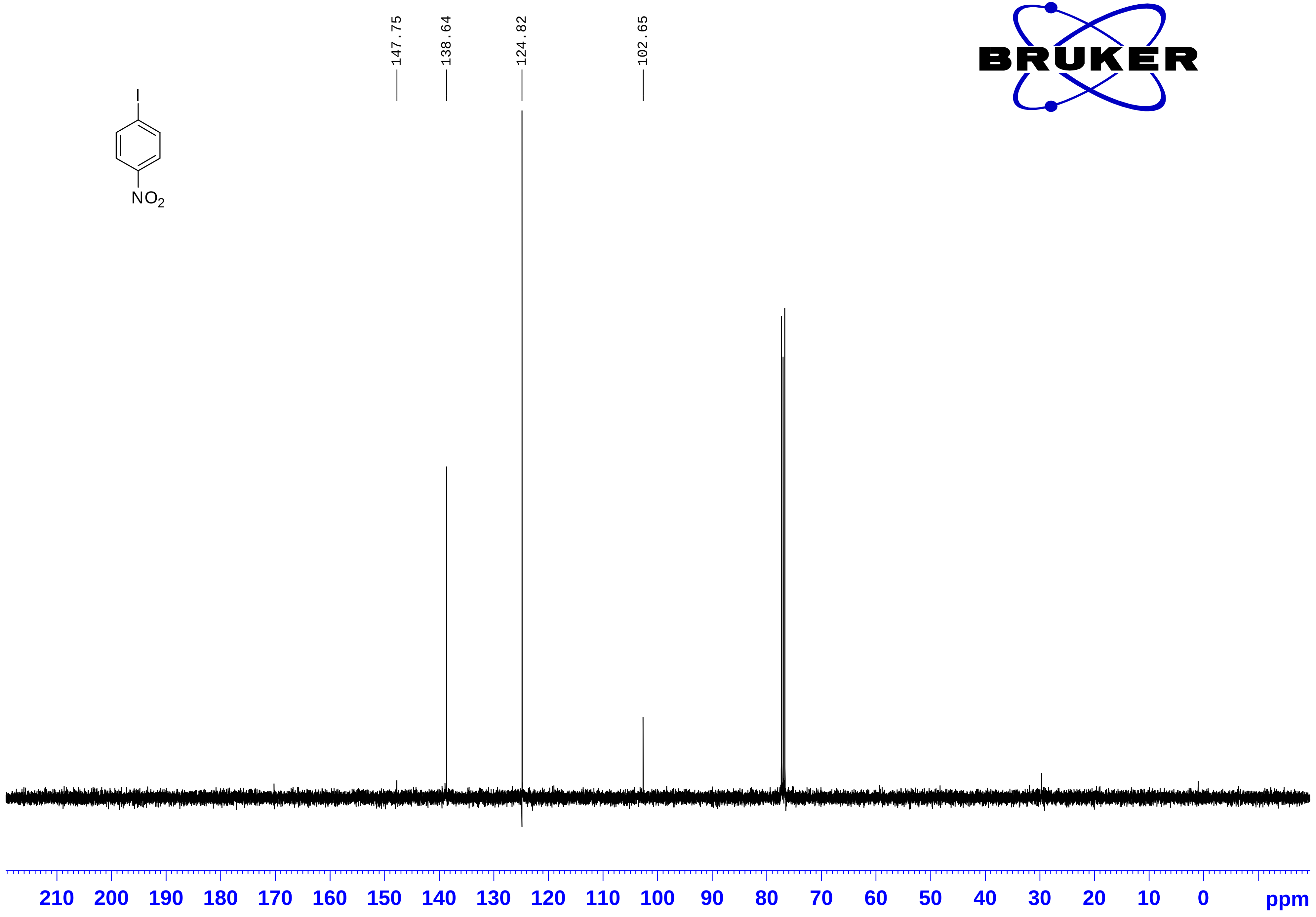
-2
-3
ppm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NO$_2$
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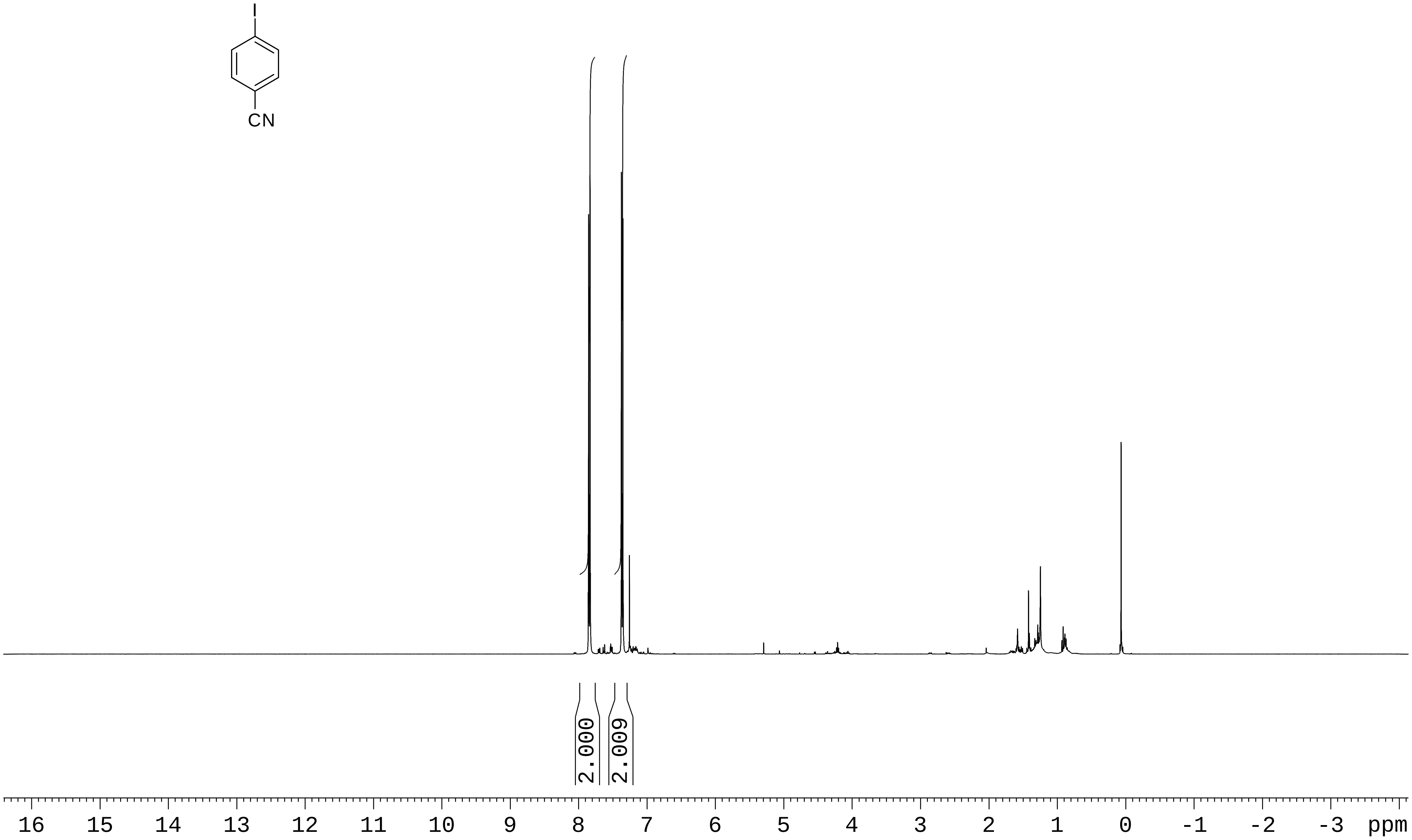
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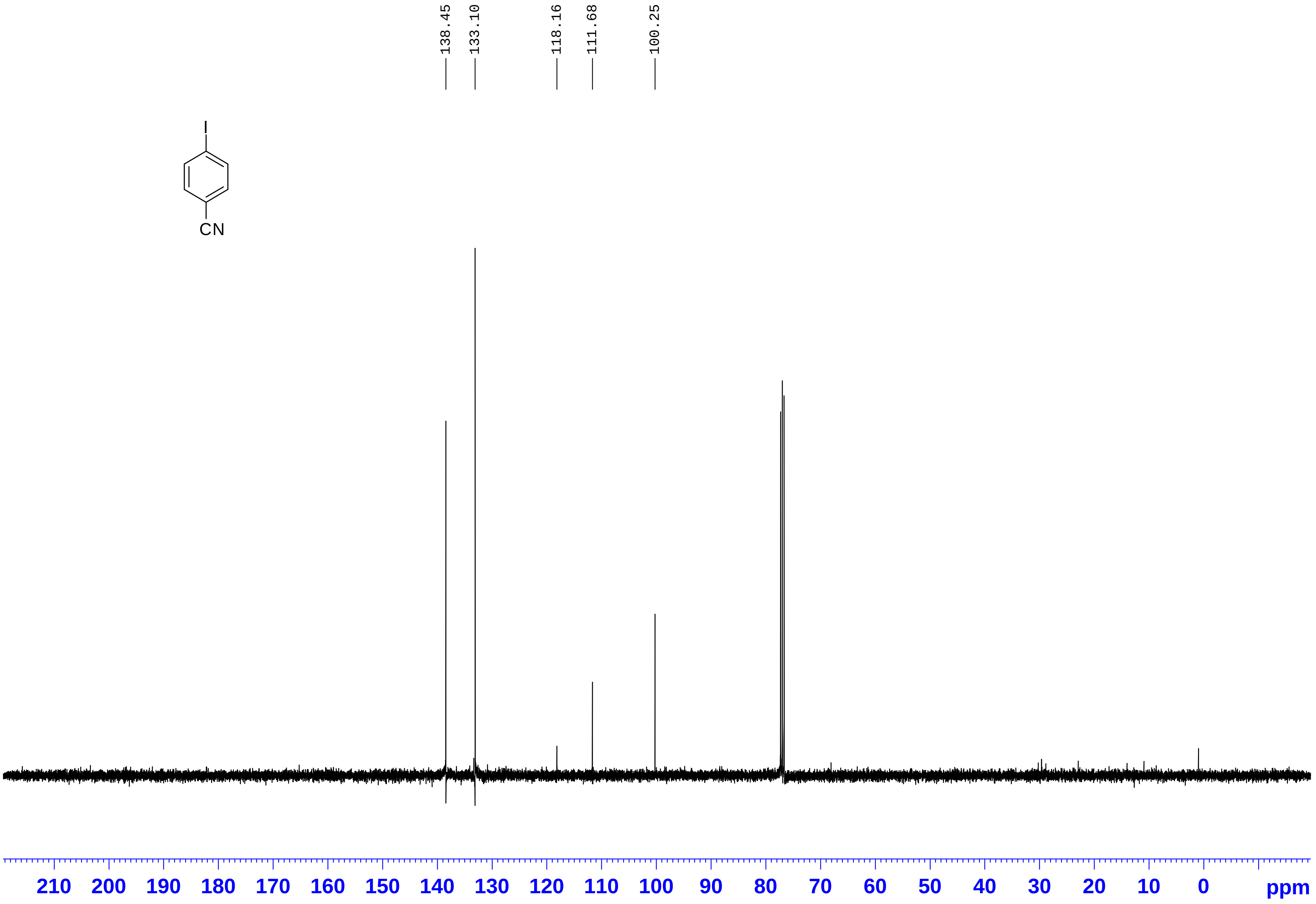
-2
-3
ppm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CN
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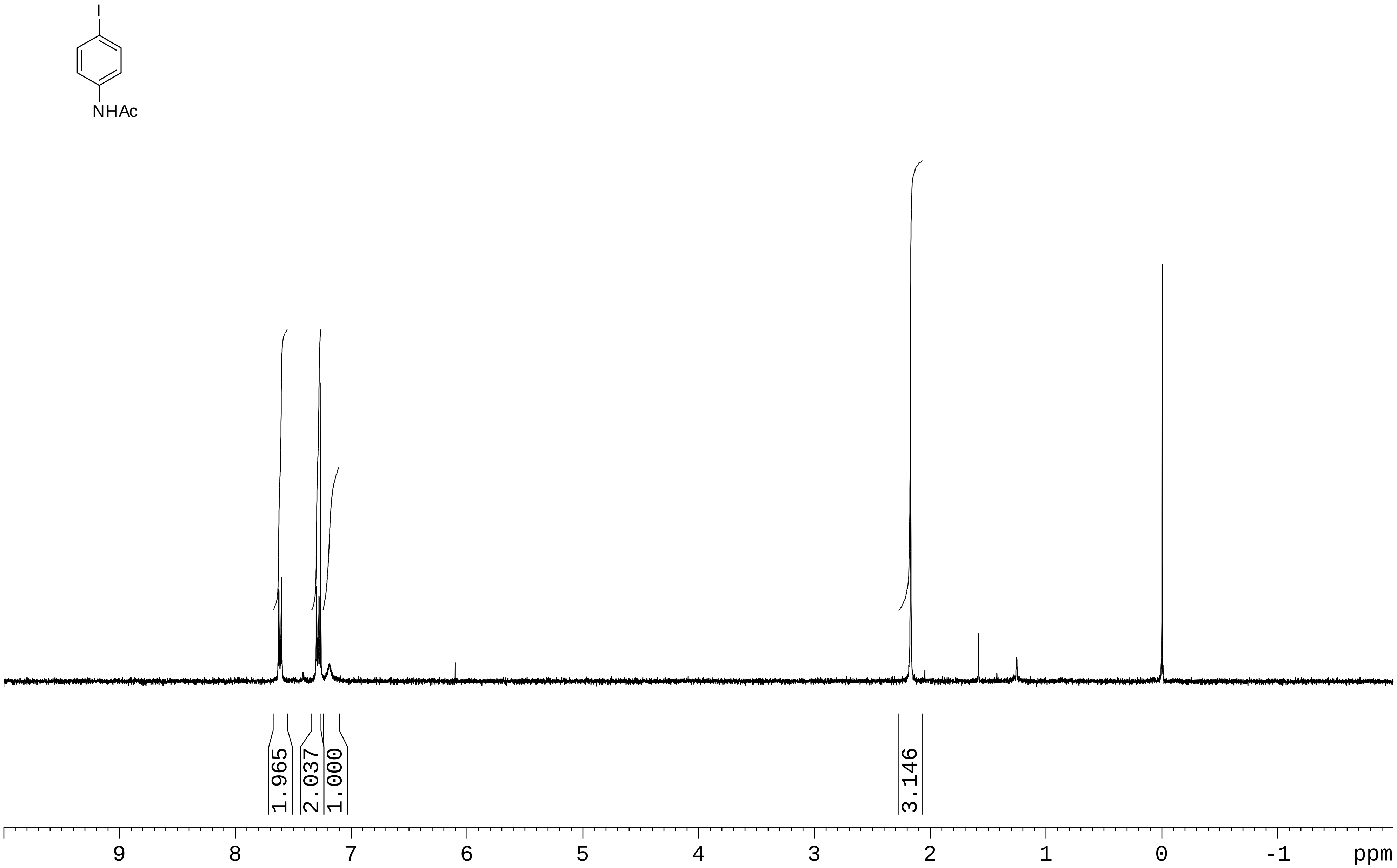
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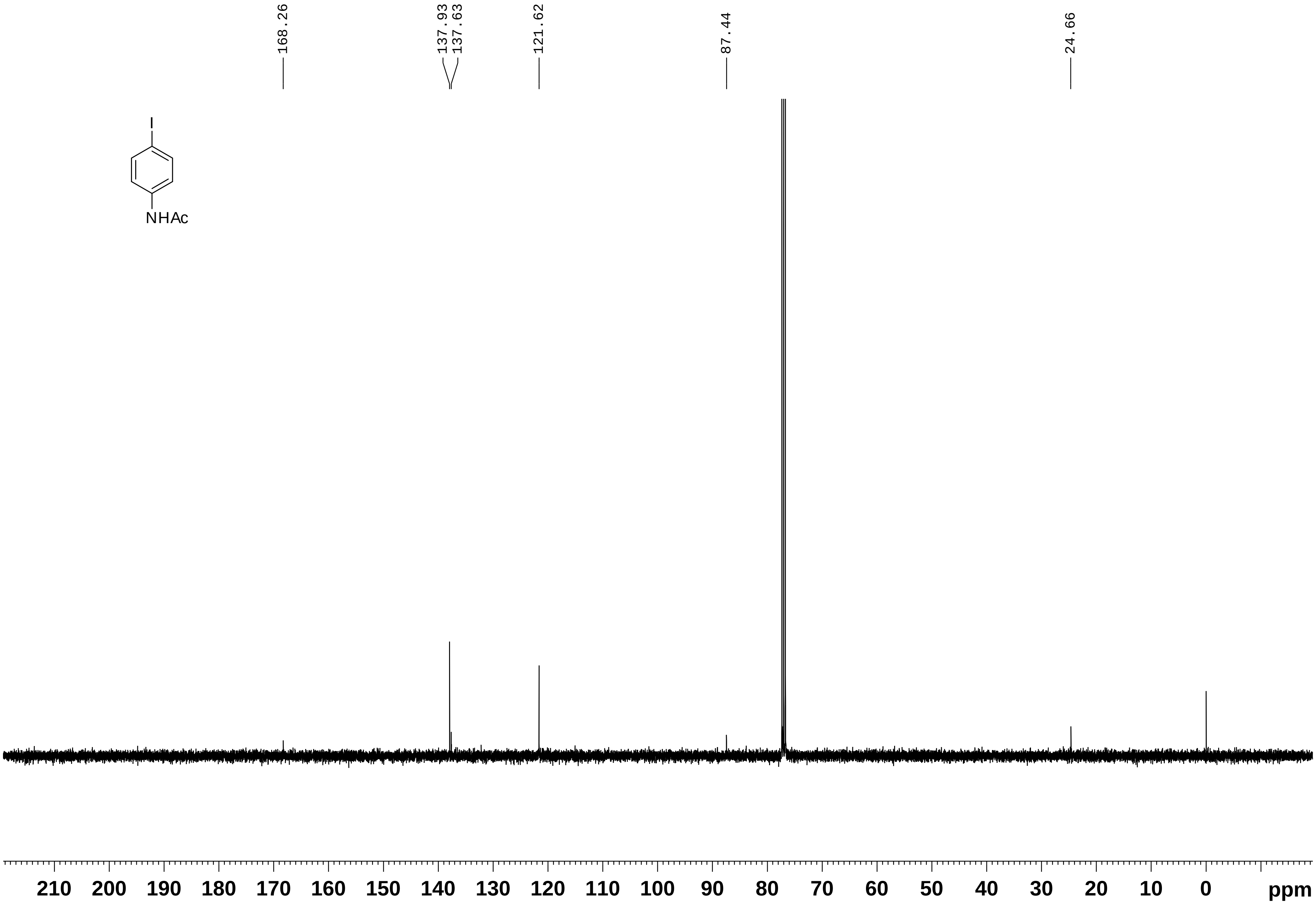
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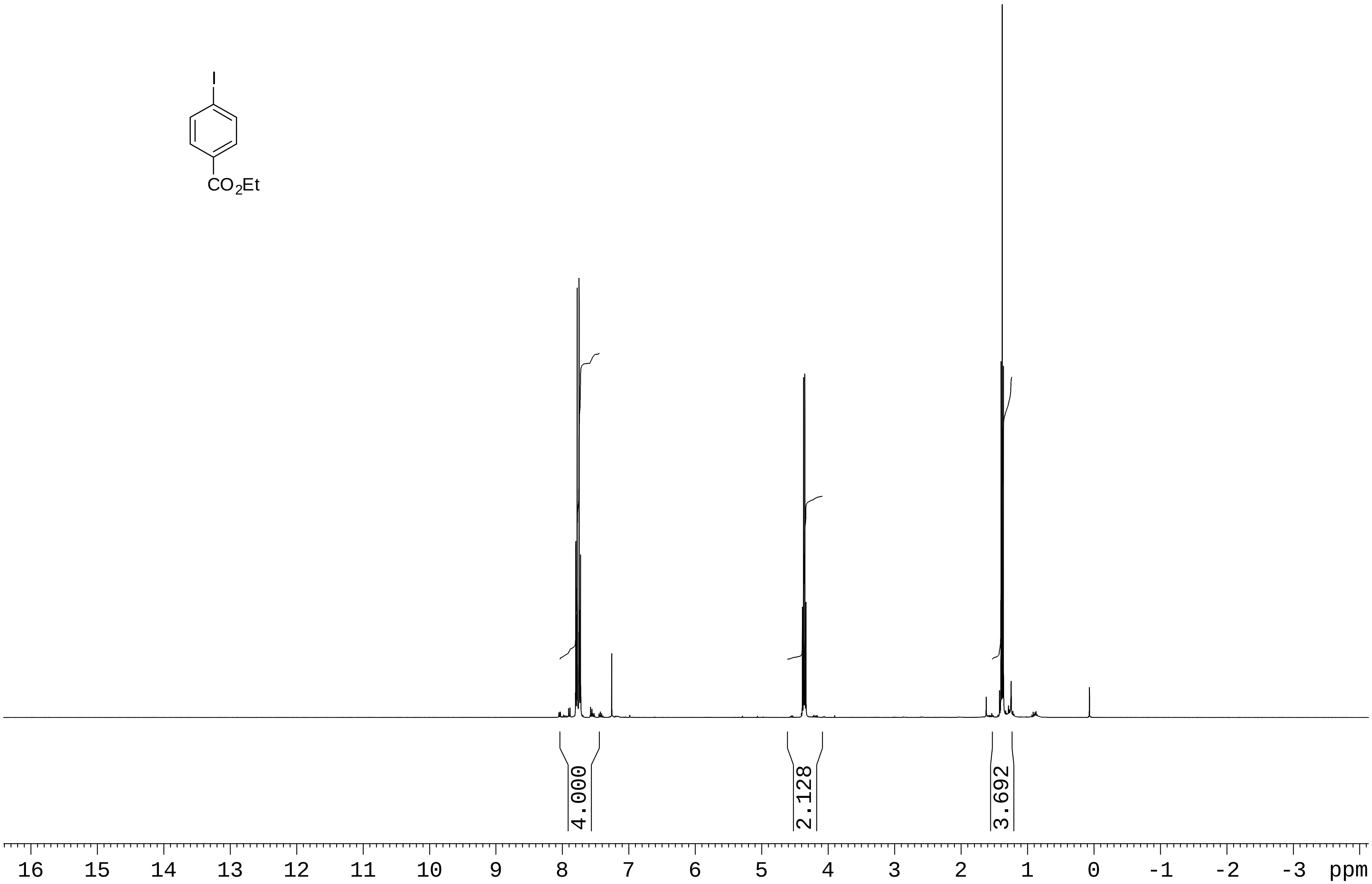
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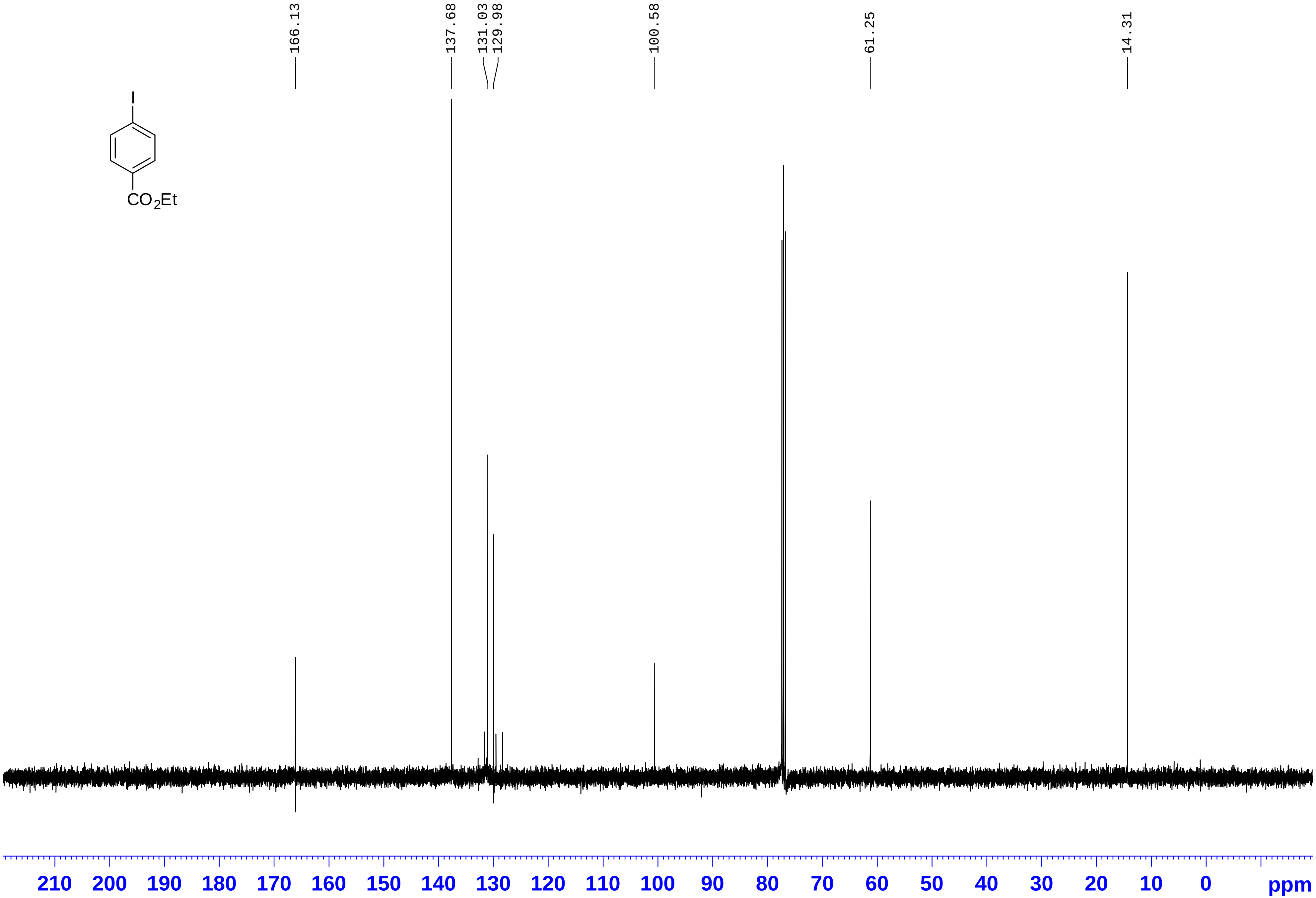
-2
-3
ppm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61.25
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CO2Et
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200
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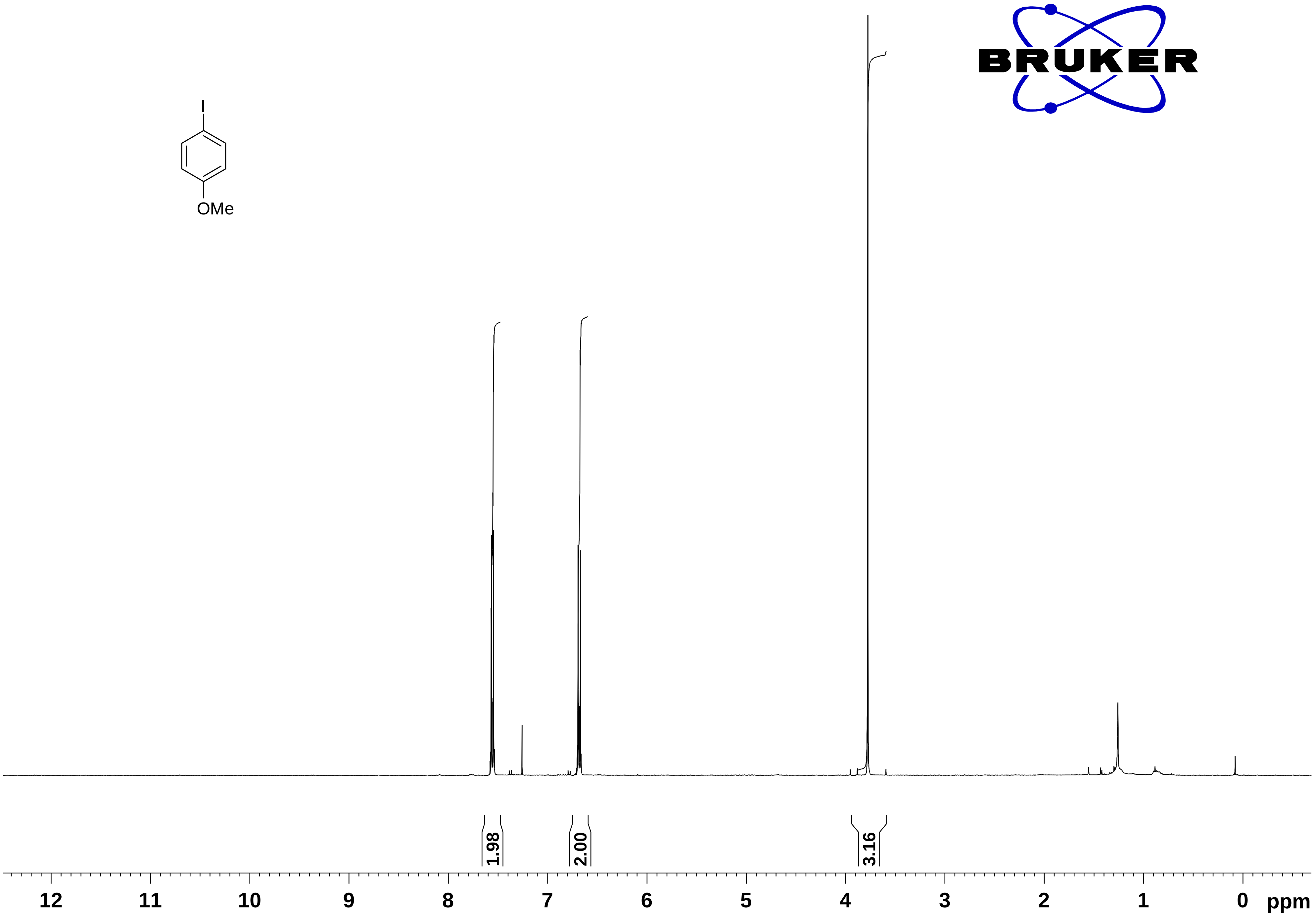
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8
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2
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0
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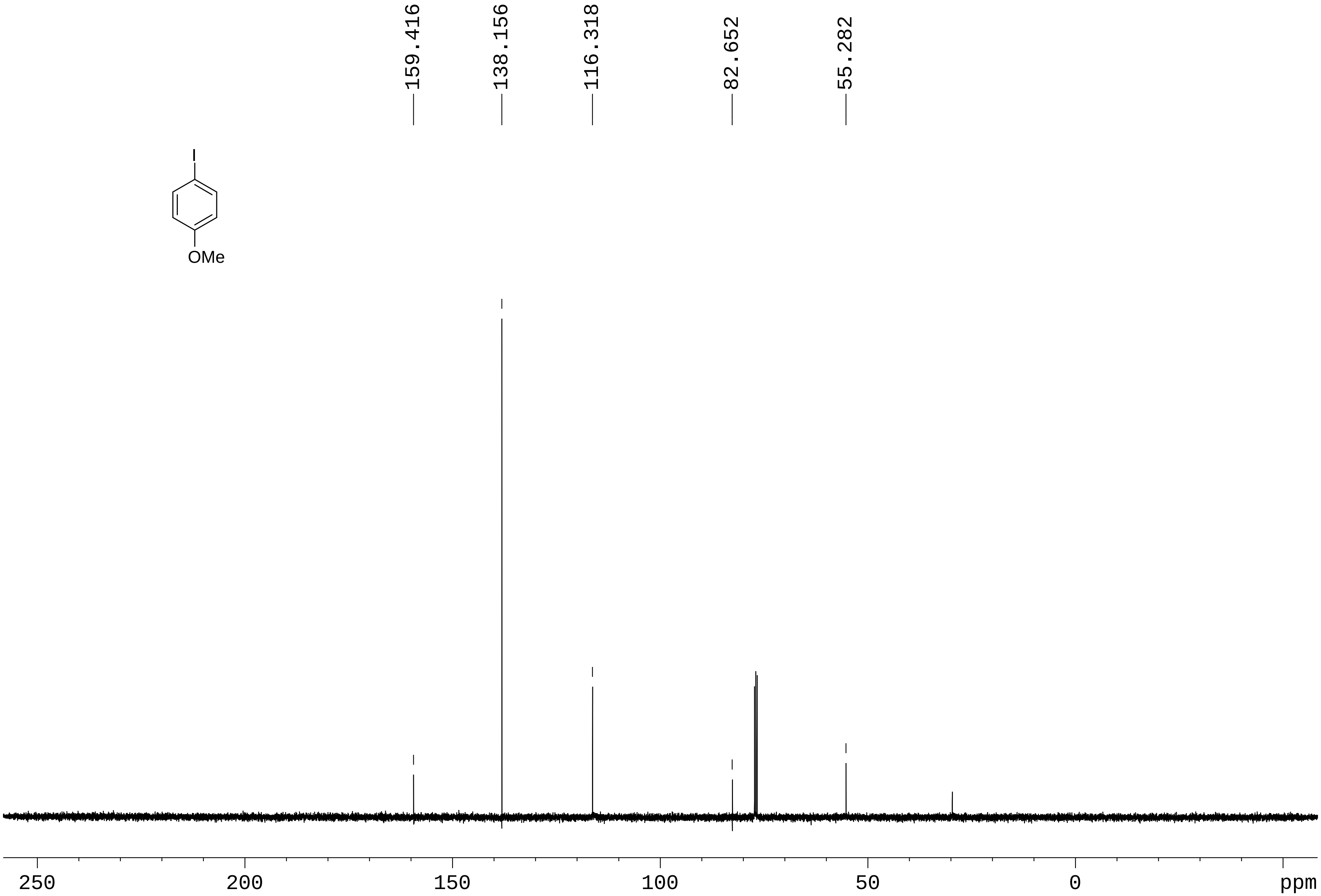
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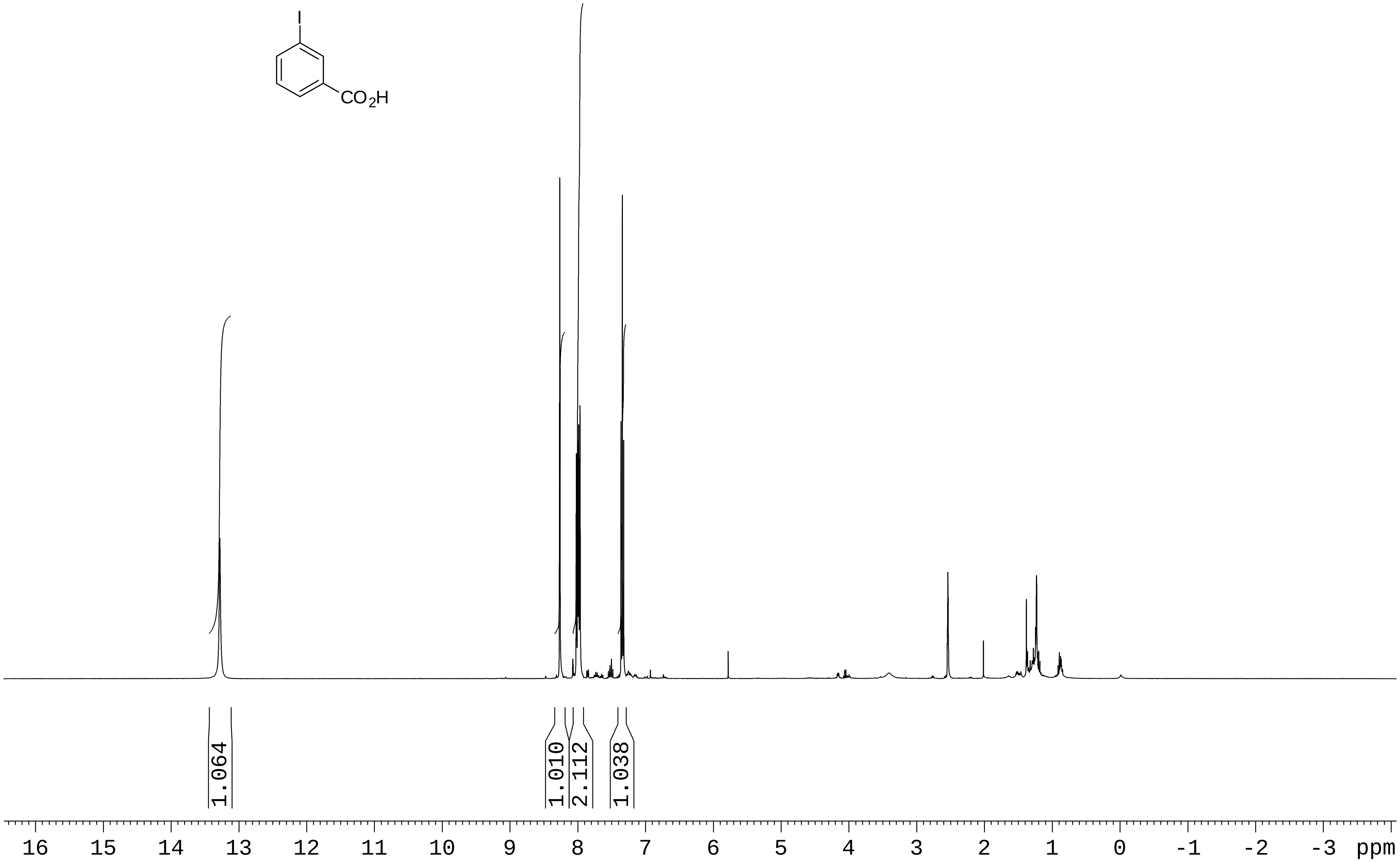
ppm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-2
-3
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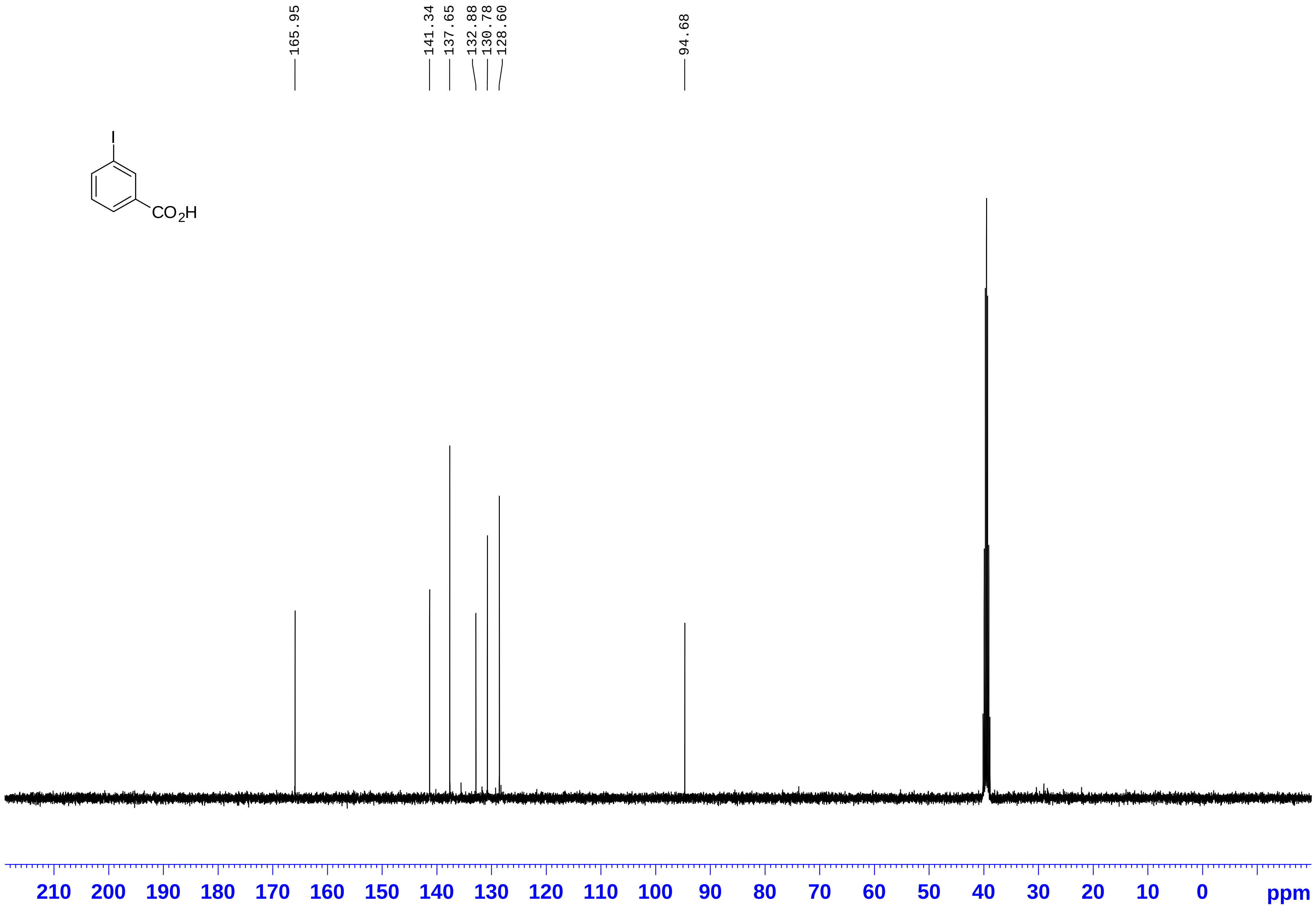
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94.68
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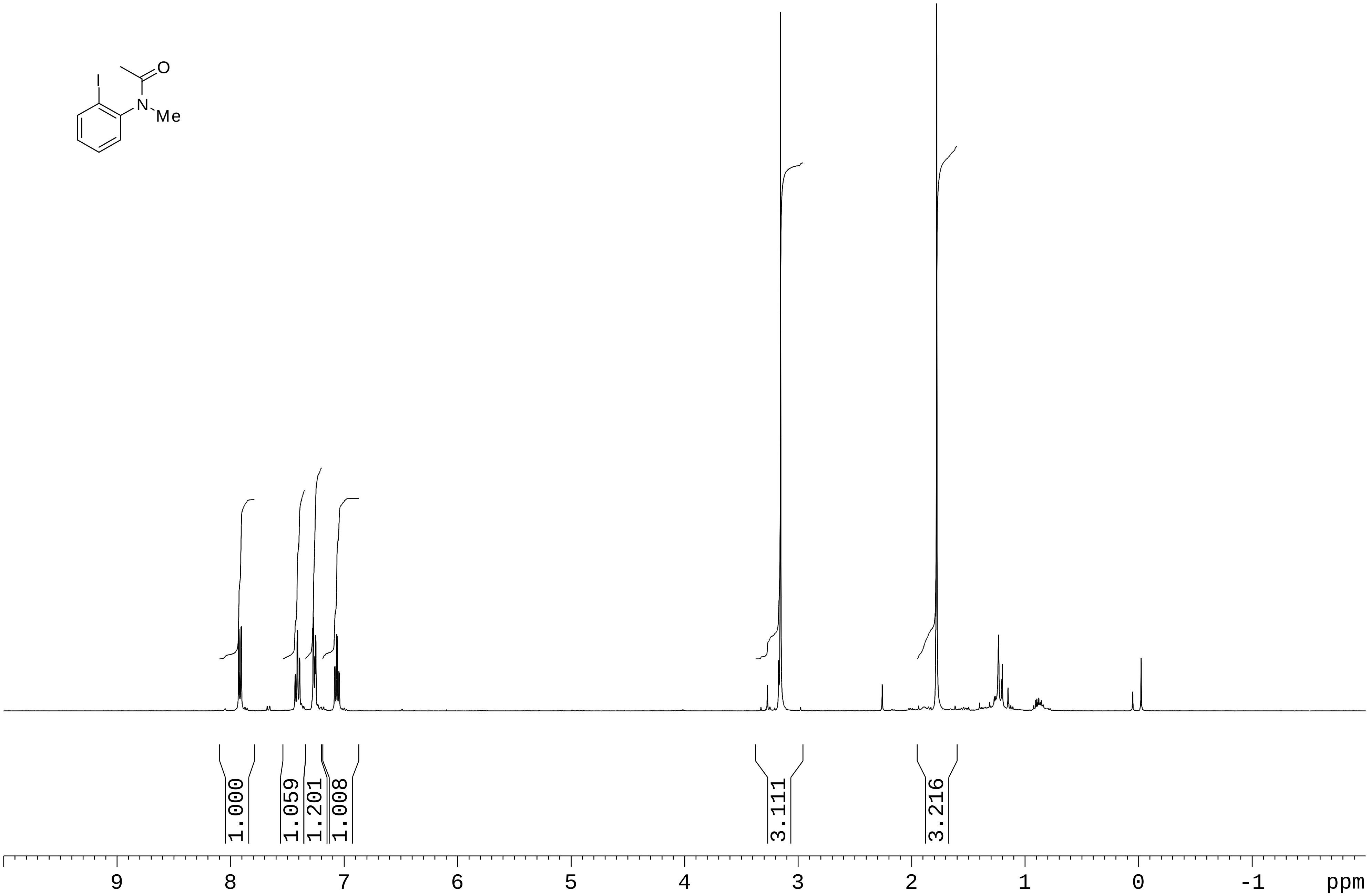
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8
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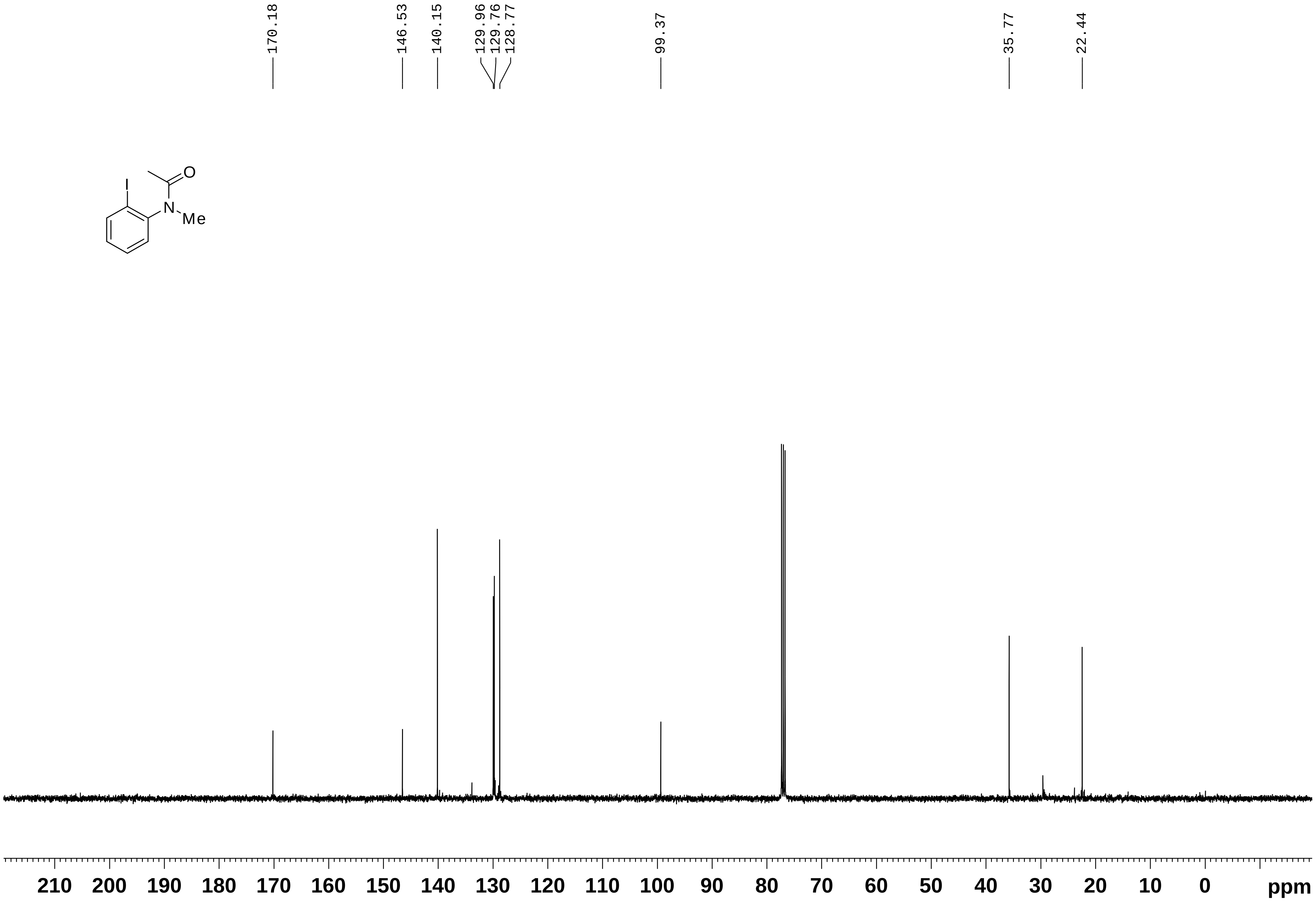
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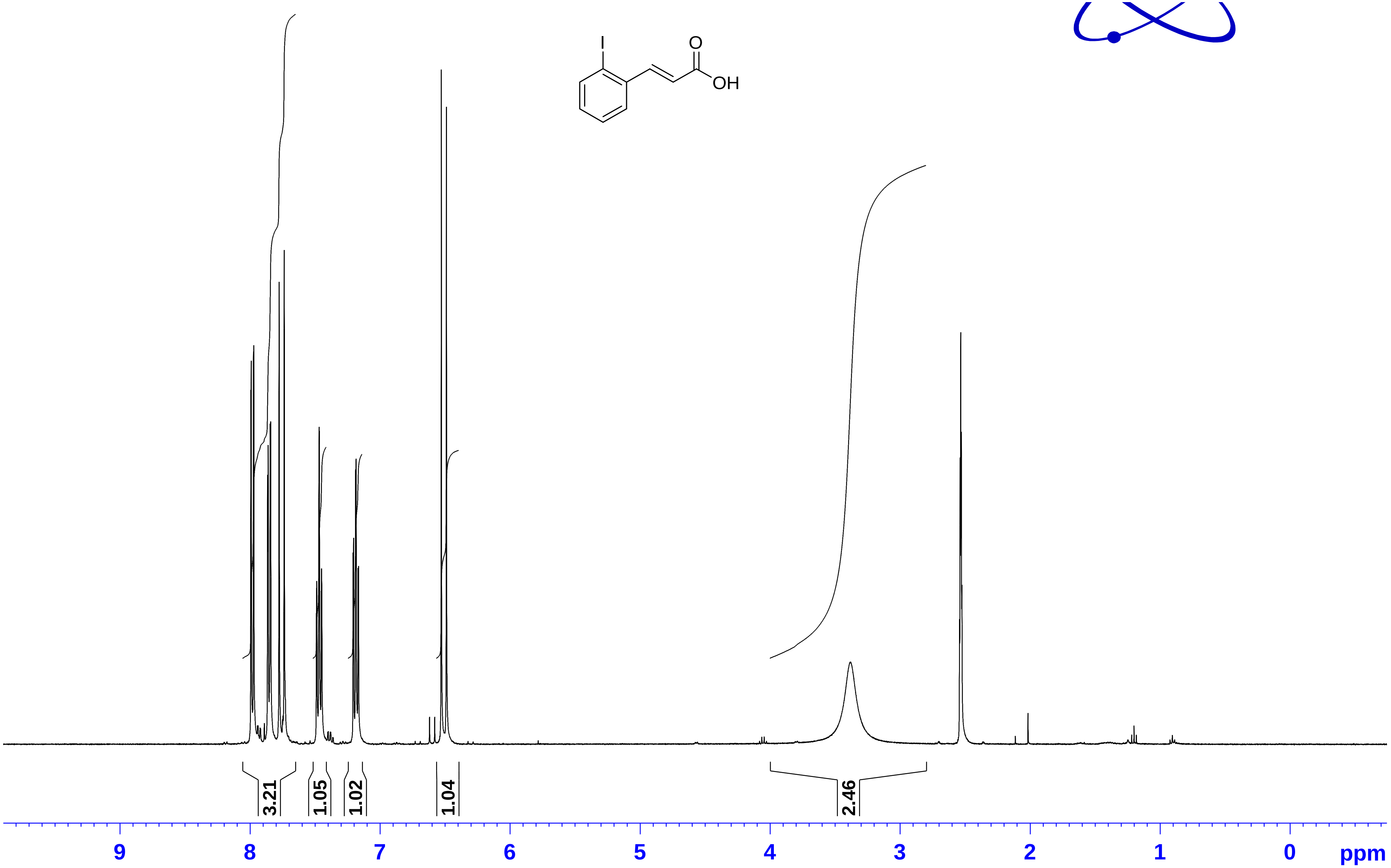
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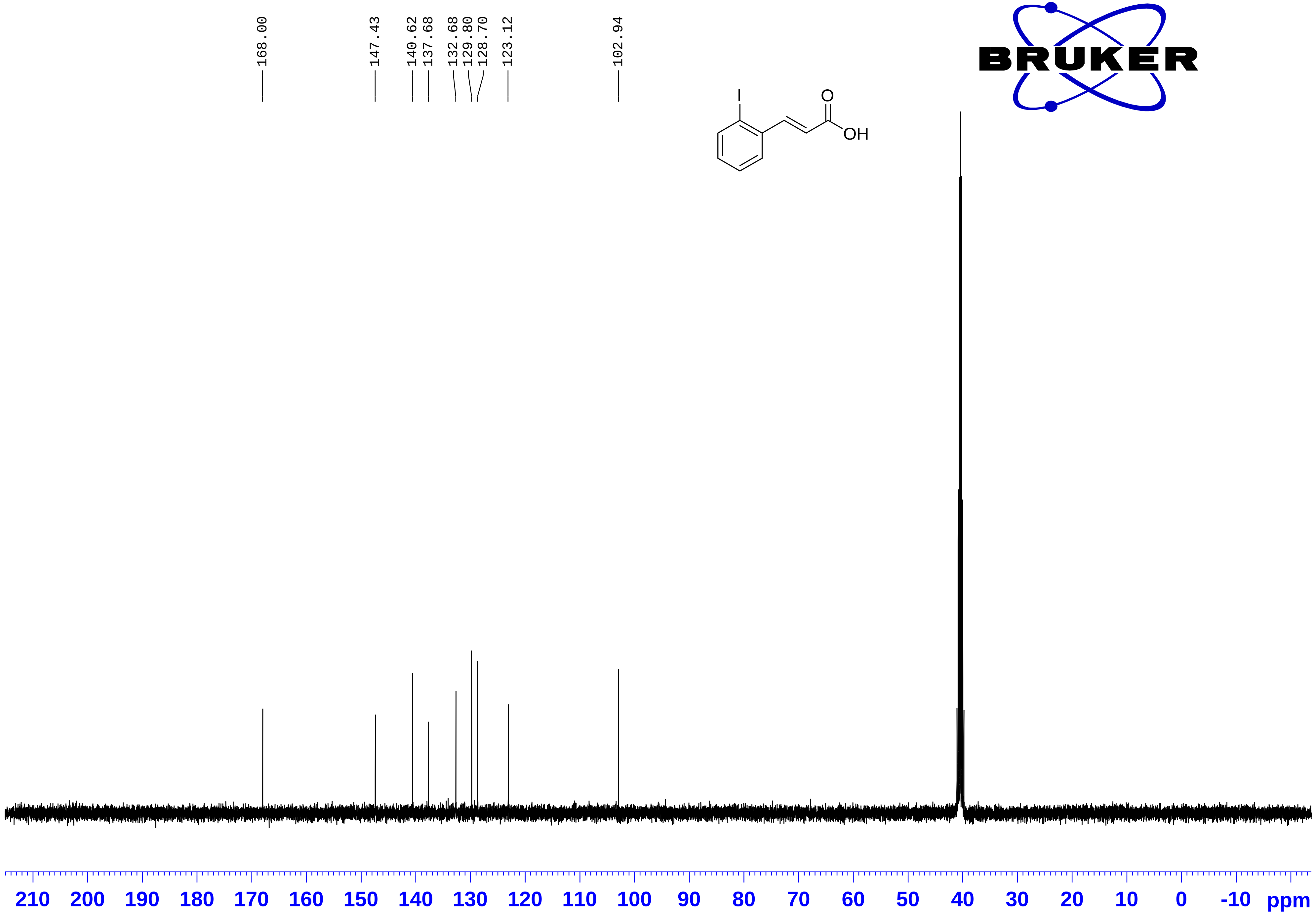
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O
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200
190
180
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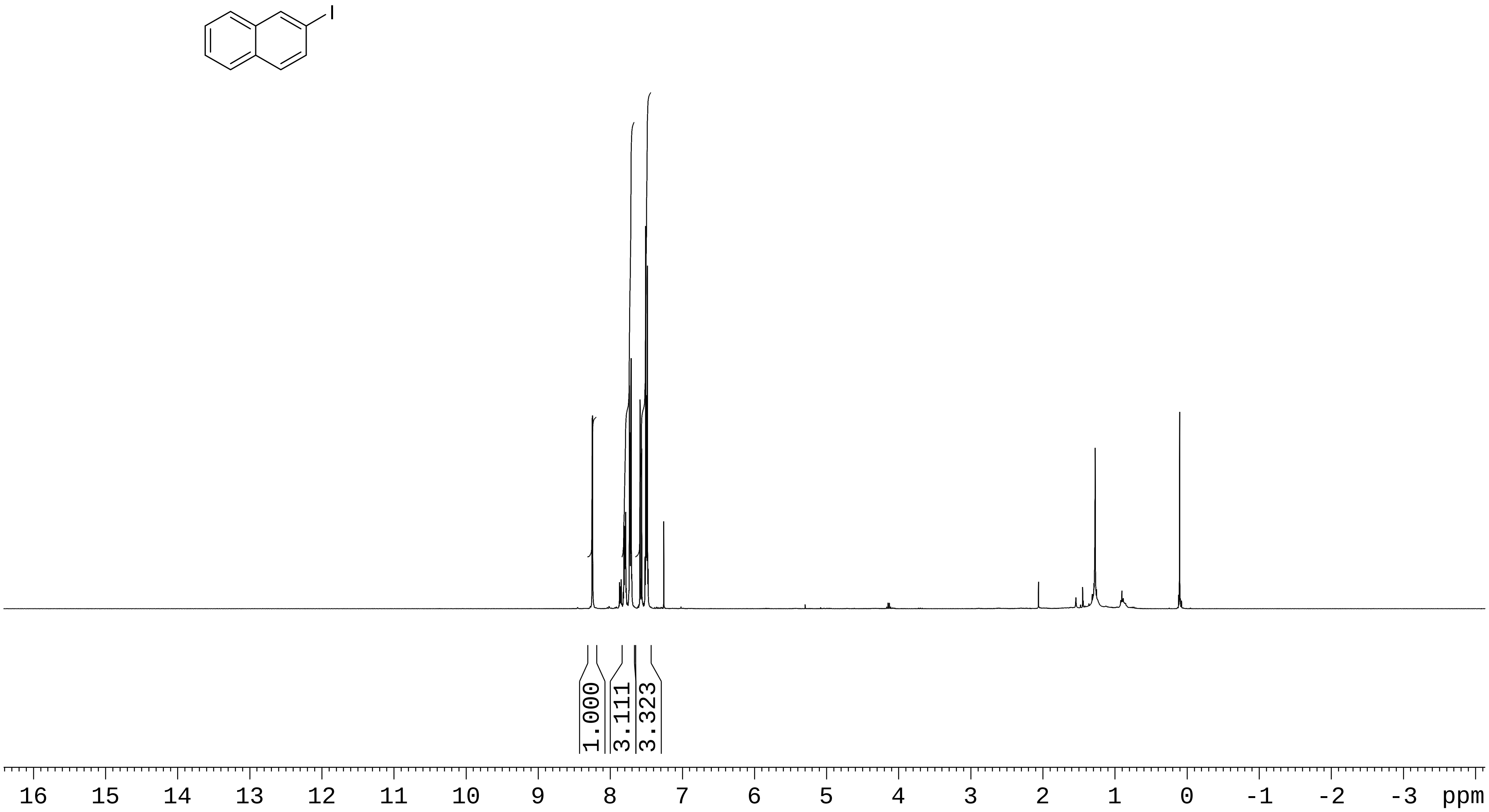
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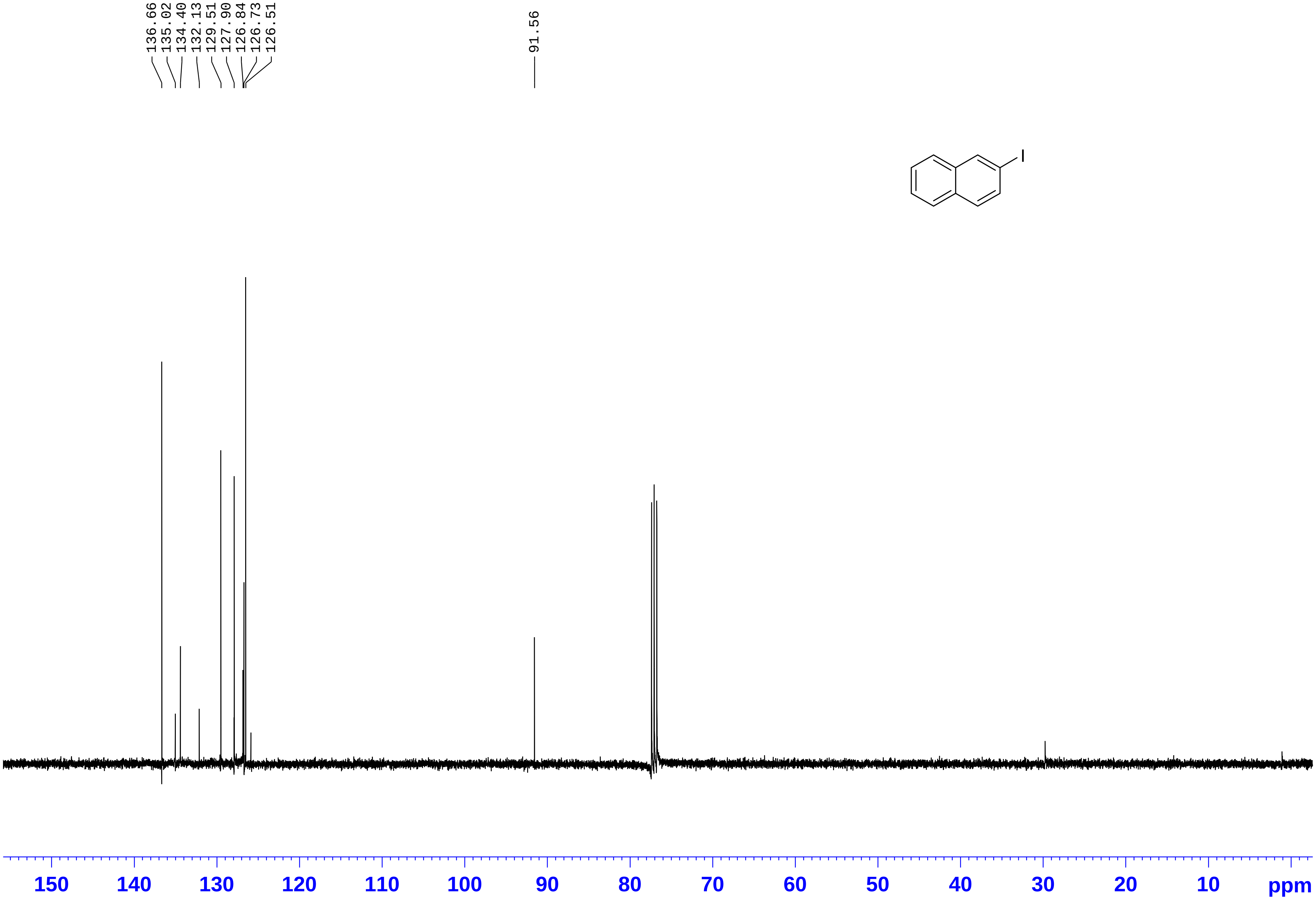
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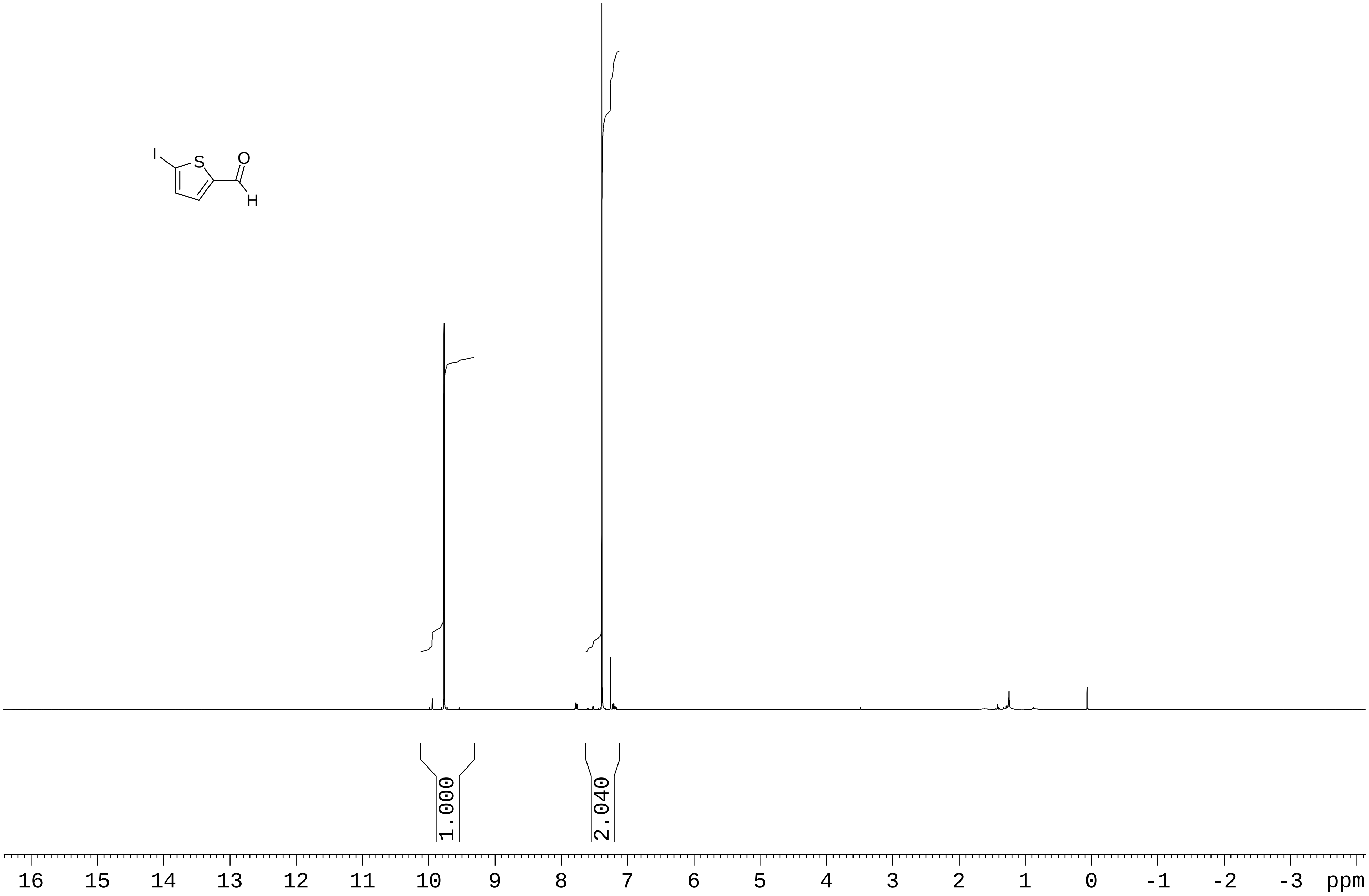
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S
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H
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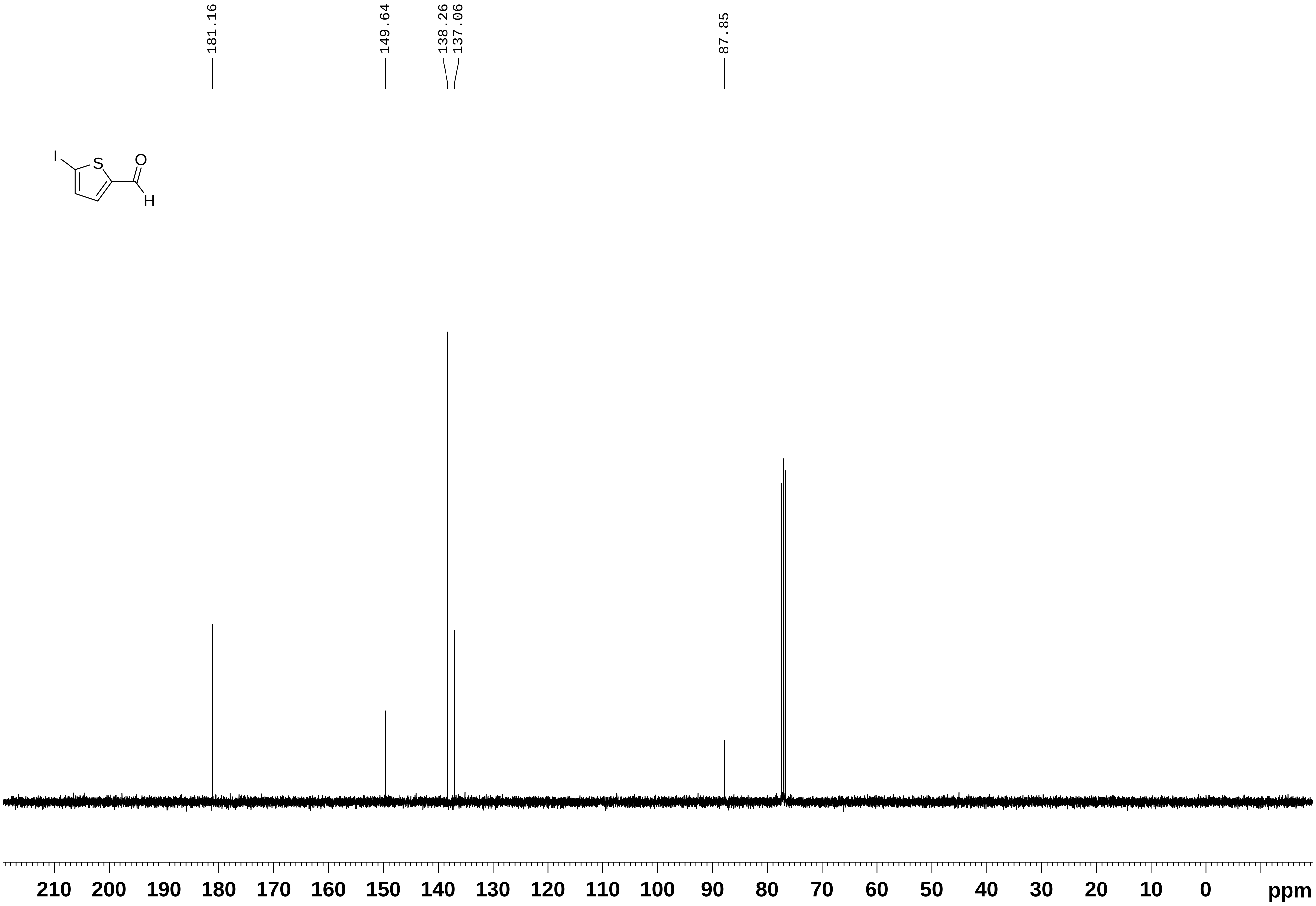
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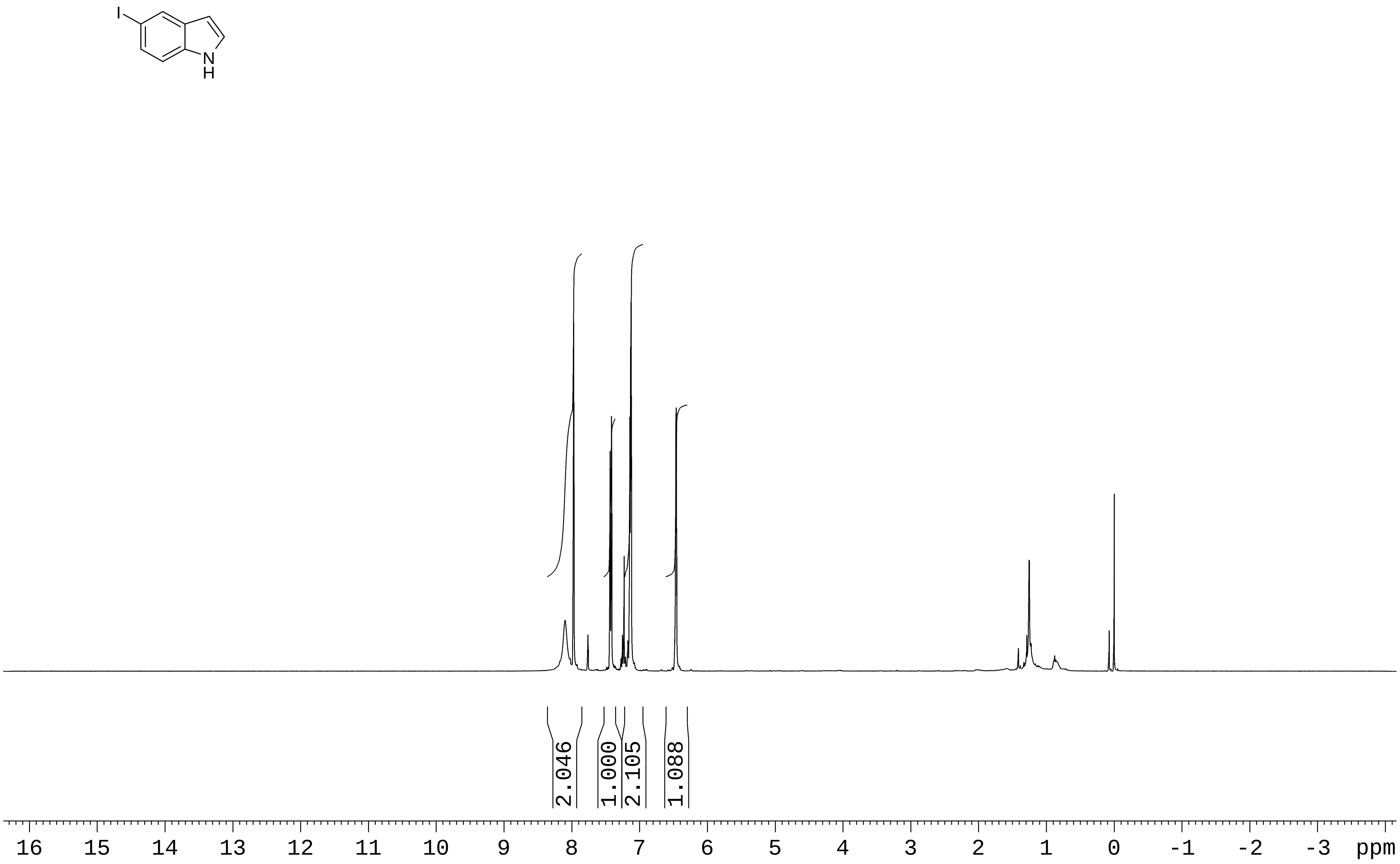
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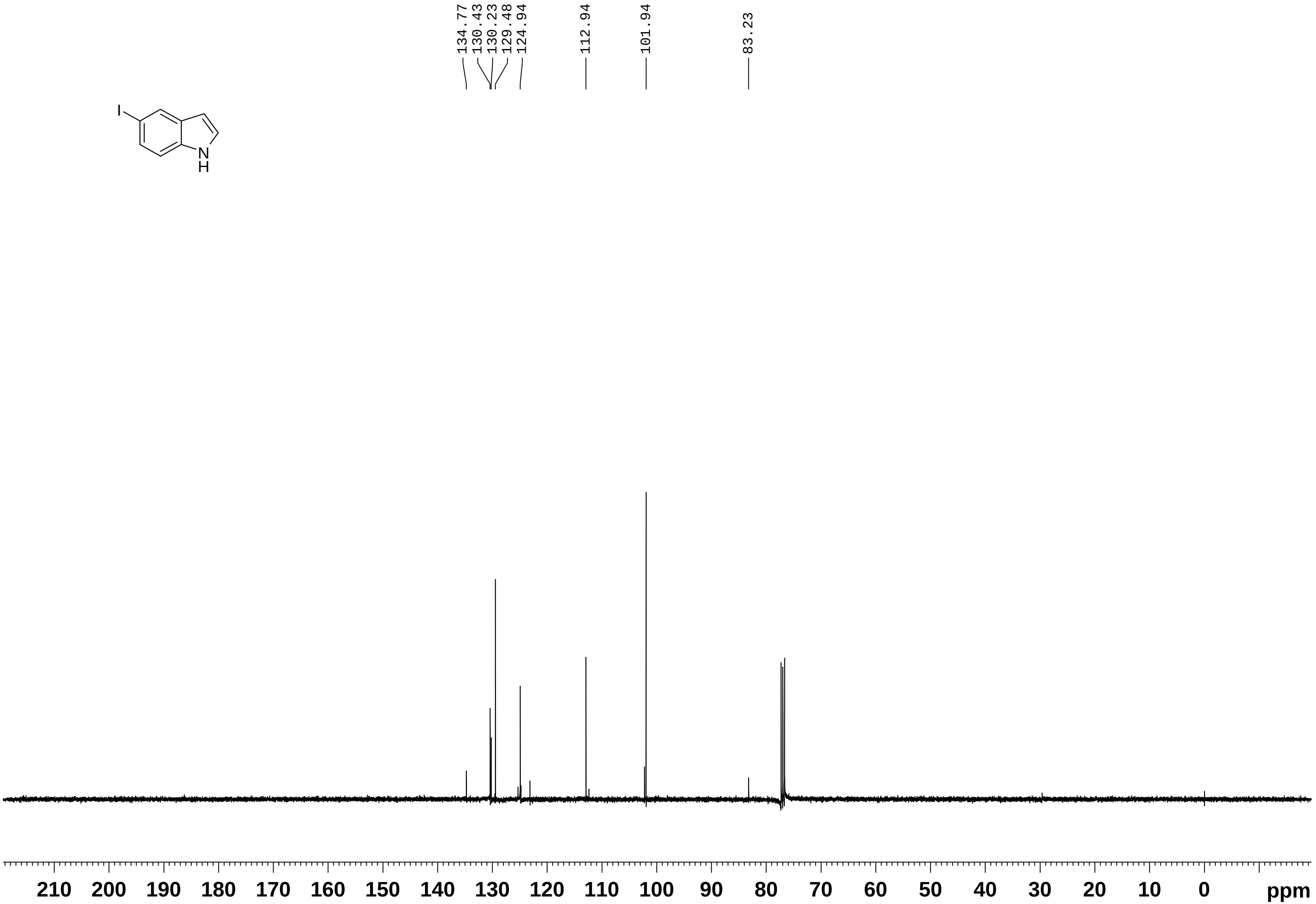
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112.94
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H
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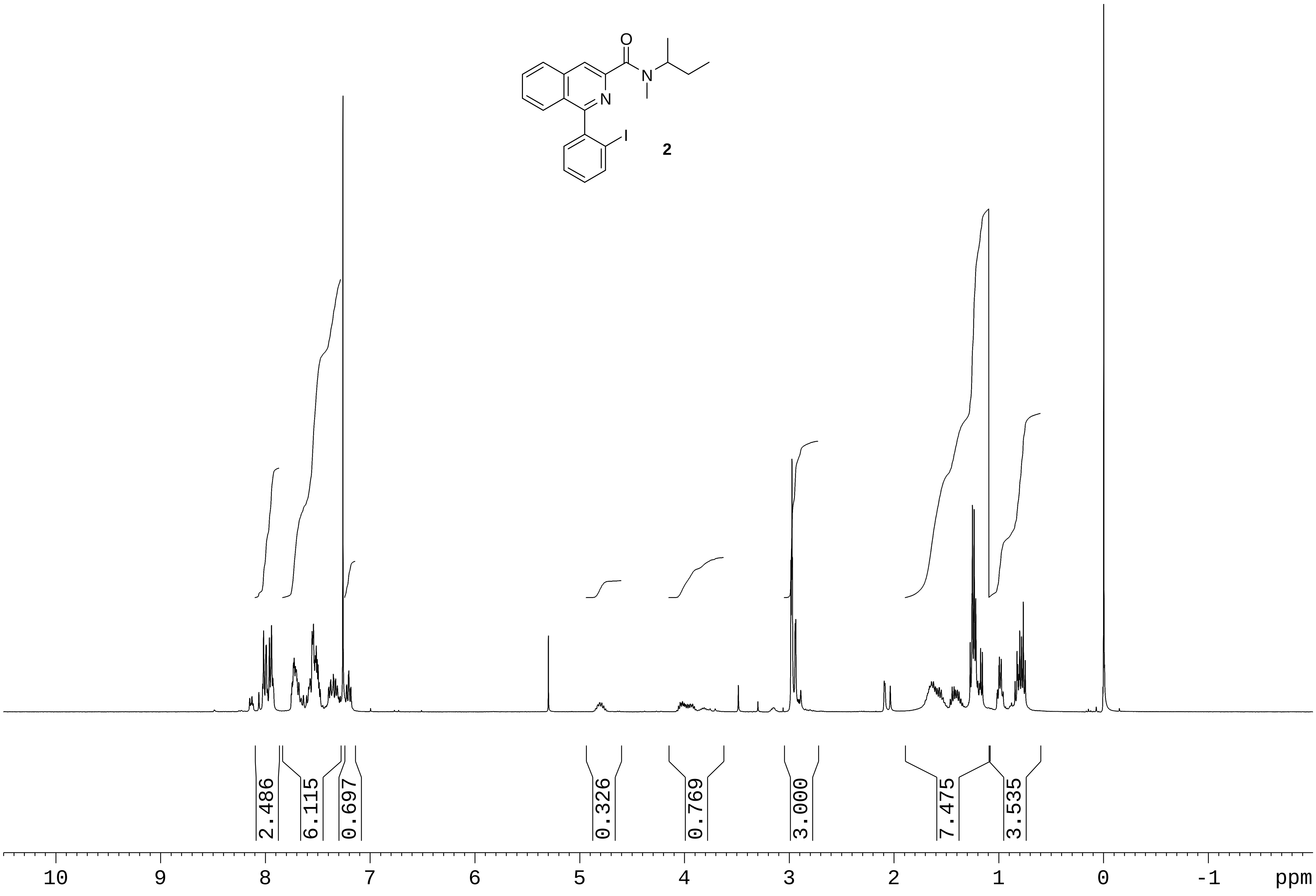
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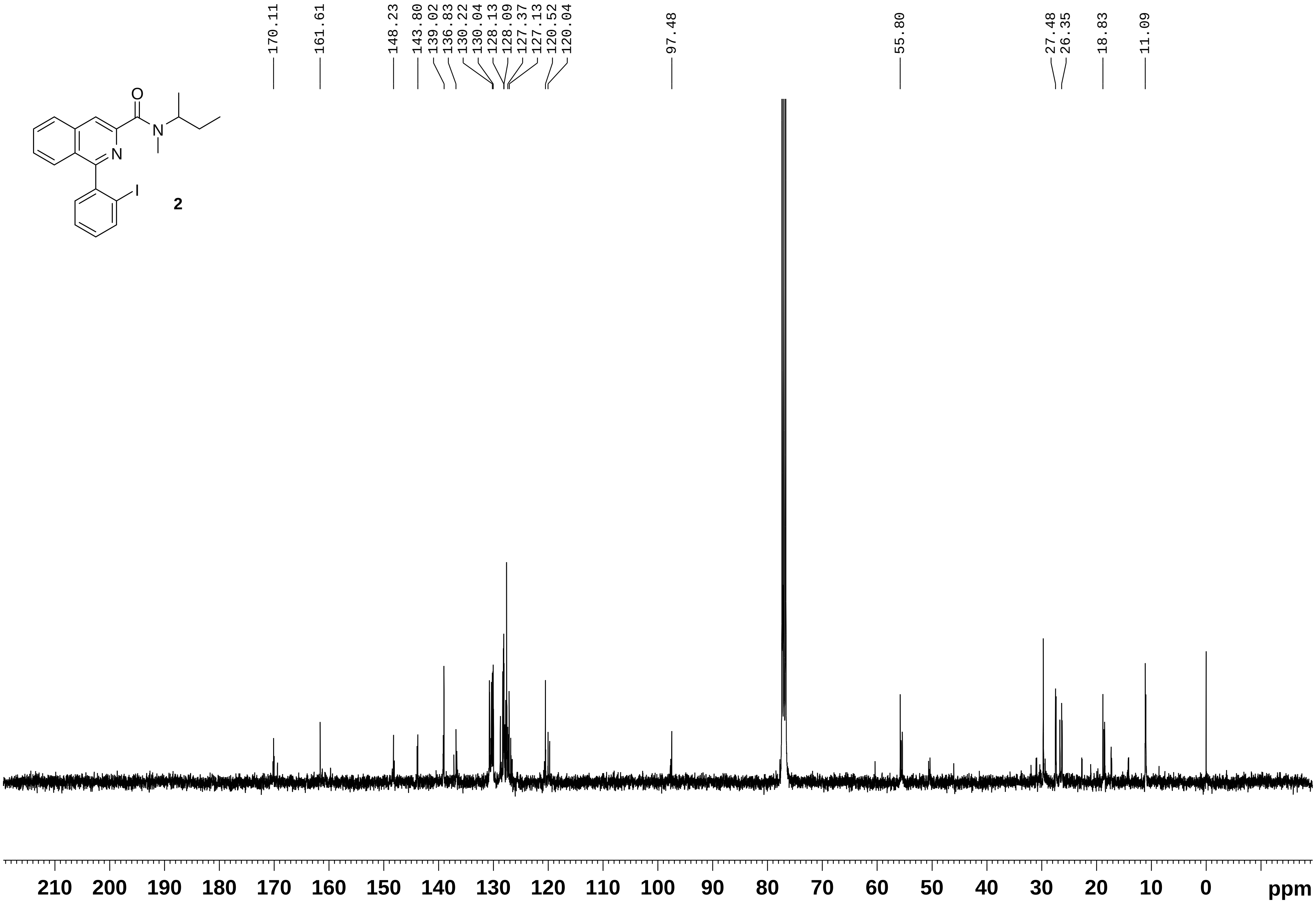

2

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130.22
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128.09
127.37
127.13
120.52
120.04
97.48
55.80
27.48
26.35
18.83
11.09
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200
190
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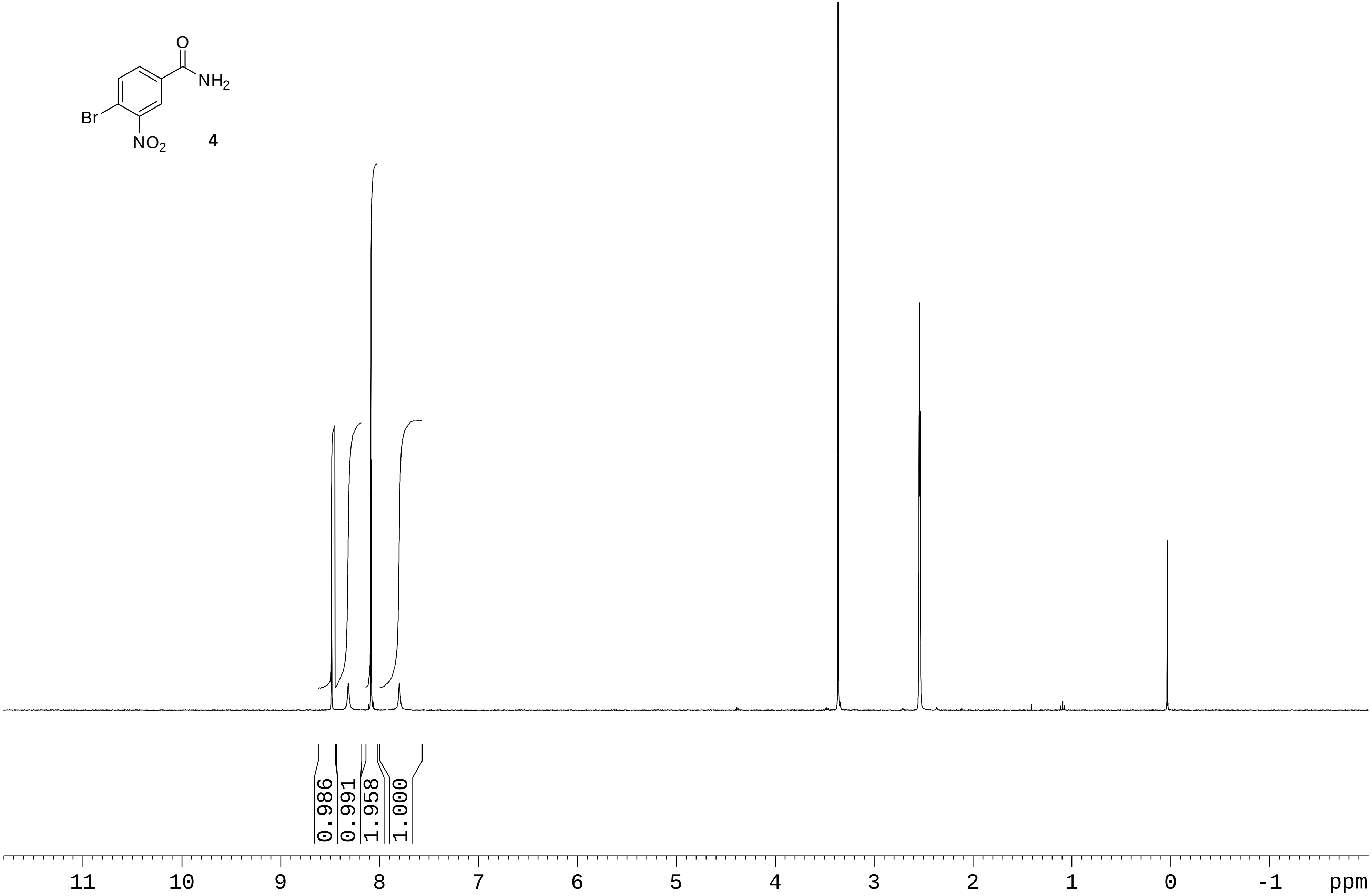
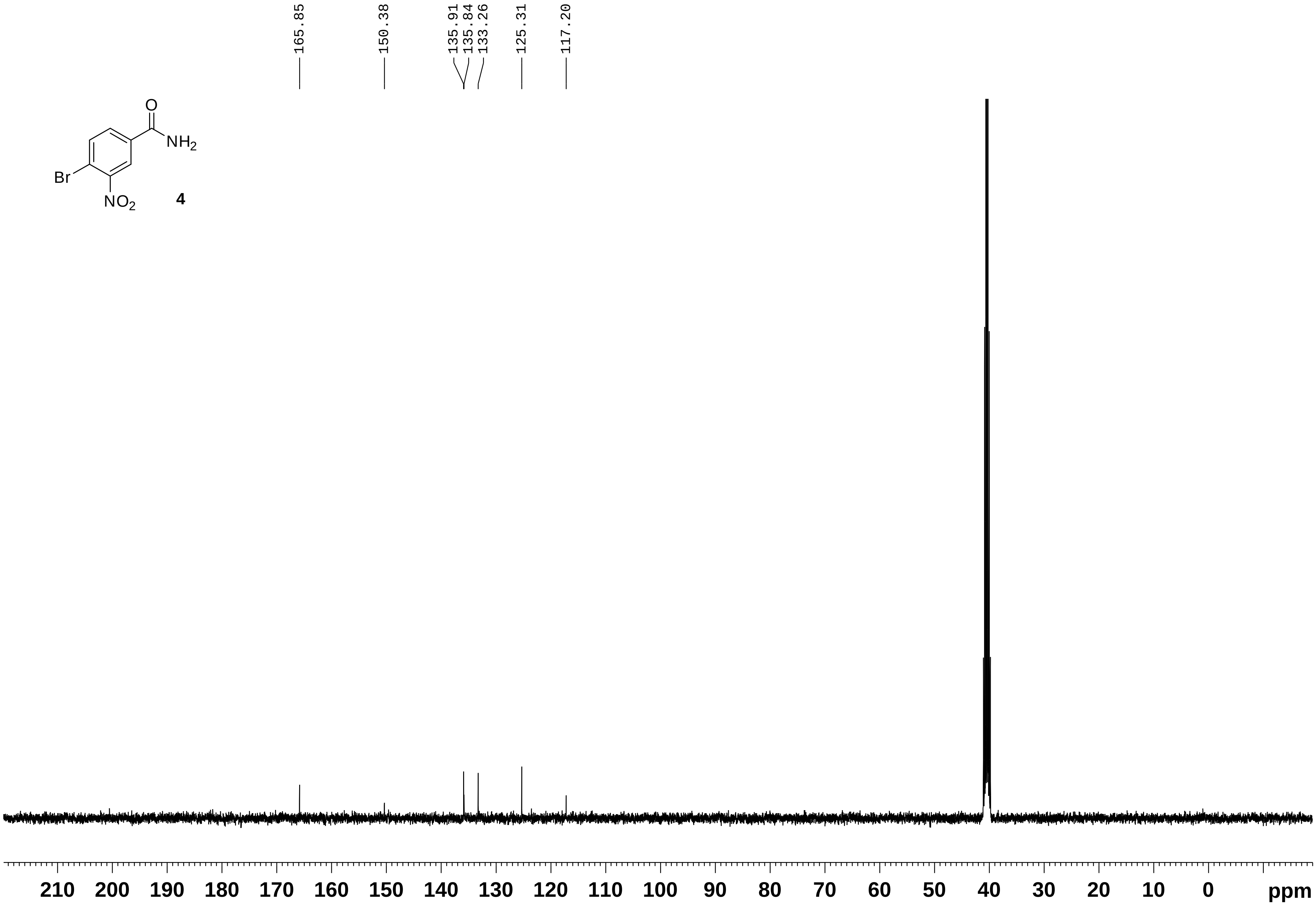
ppm

4

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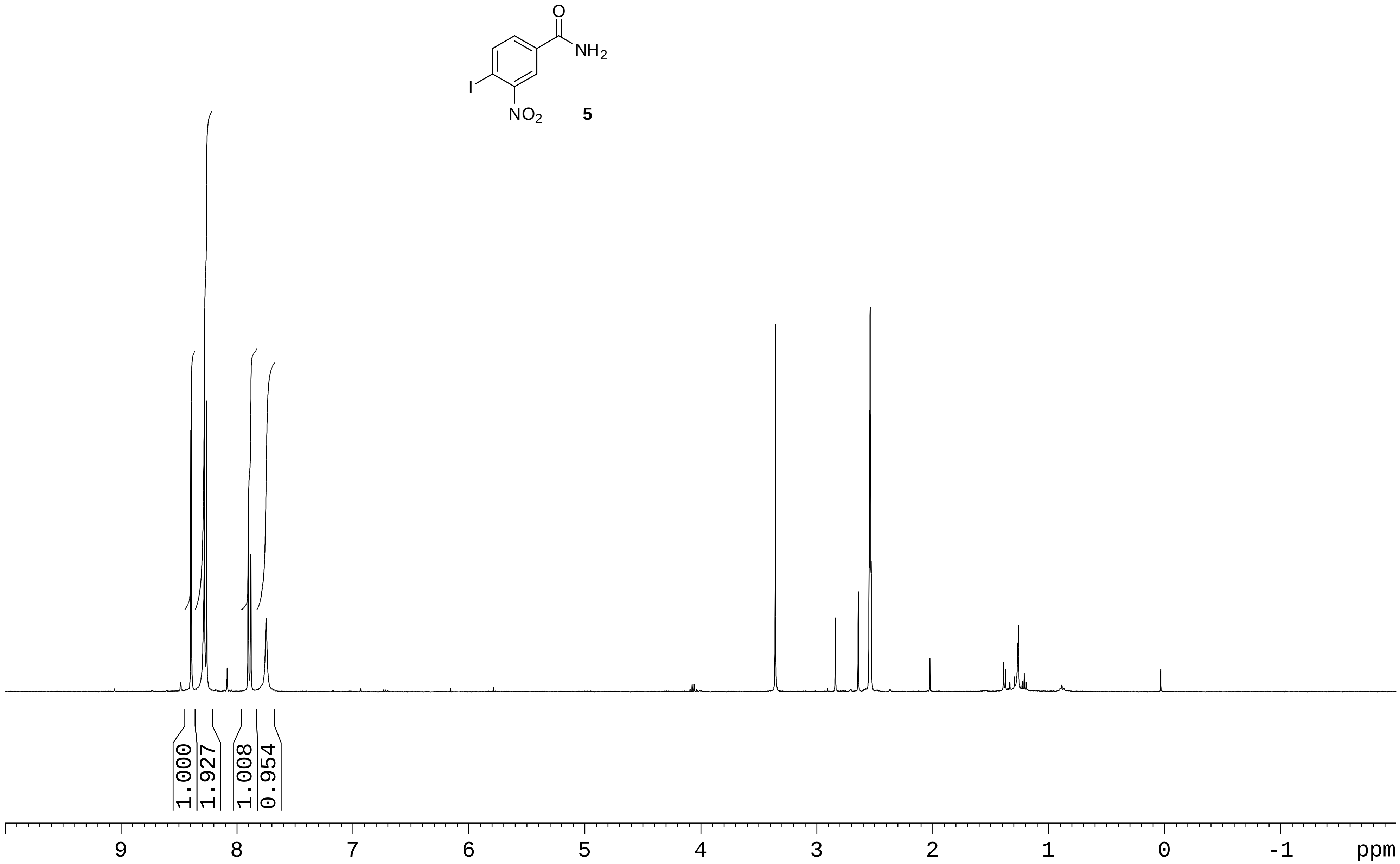
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NO$_2$
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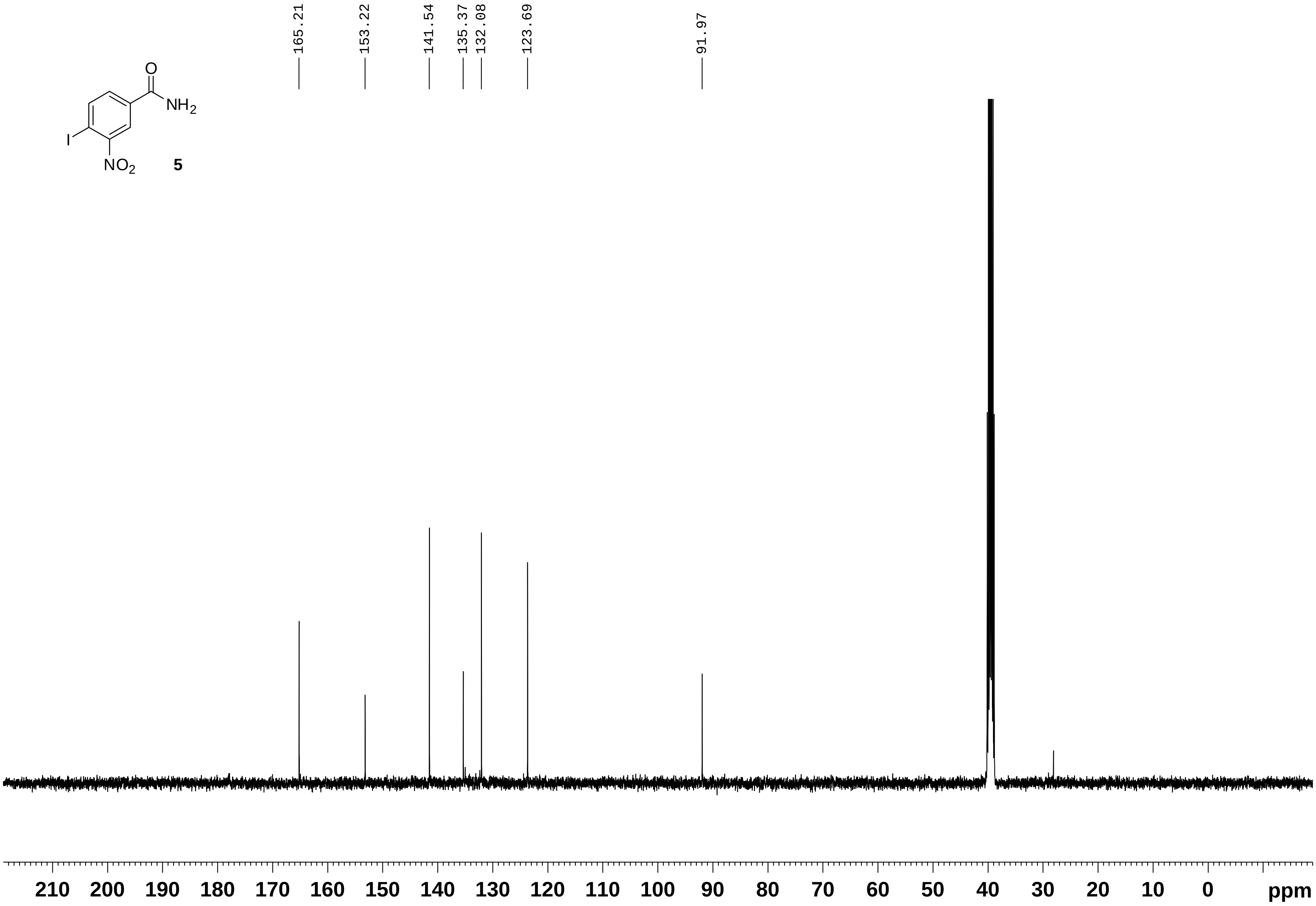
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100
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30
20
10
0
ppm