$CuSO_4$-Catalyzed Dual Annulation to Synthesize O, S or N-Containing Tetracyclic Heteroacenes

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Contents

1. General information

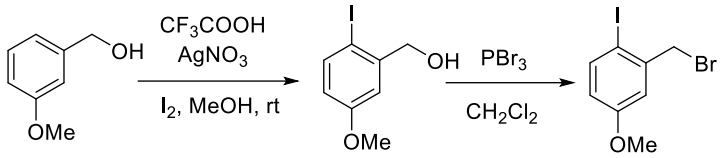
Solvents were predried over activated 4 Å molecular sieves and further dried by refluxing and distilling over sodium (1,4-dioxane), CaH_2 (toluene, octane, CH_3CN, CH_2Cl_2, DMSO and DMF) or P_2O_5 (PhCl) under argon atmosphere. $CuSO_4$ (>98%) was purchased from J&K. ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are reported in δ units relative to $CDCl_3$ [^1H δ = 7.26, ^{13}C δ = 77.16], DMSO-d_6 [^1H δ = 2.50, ^{13}C δ = 39.52].

2. General procedures

2.1. Screening reaction conditions (Table 1)

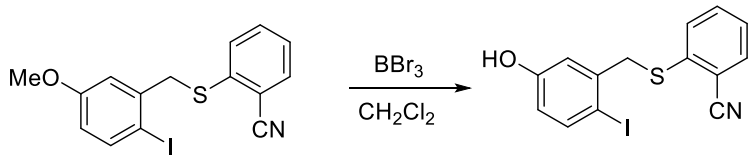
To a Schlenk tube charged with $CuSO_4$ (0.025 mmol, 4 mg) and ^{t}BuOK (1.1 mmol, 124 mg) was added **3a** (0.5 mmol, 167.5 mg) and solvent (10 mL) and the resulting reaction mixture was stirred at 90 °C (oil bath). The reaction mixture was directly prified by silica gel column to give the desired product.

2.2. Preparation of Starting Materials



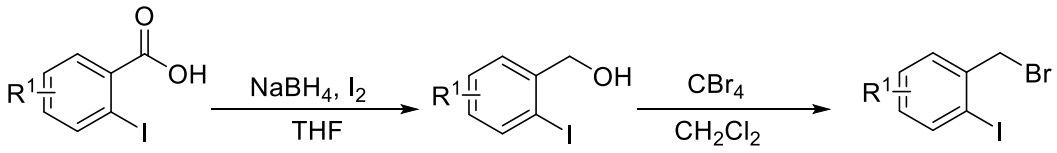
1b-1 **1b-2**

A 100 mL round-bottom flask was charged with benzyl alcohol (10 mmol), CF_3COOH (13 mmol) and $AgNO_3$ (13 mmol). Then MeOH (15 mL) was added and cooled by ice bath. A solution of I_2 (1.0 equiv) in MeOH (25 mL) was added dropwise over 30 min. The resulting reaction mixture was monitored by TLC. Then filtered and concentrated under vacuum. The residue benzyl alcohol **1b-1** was used in the next step without purification. PBr_3 (1.0 mL, 16 mmol) was added over a solution of **1b-1** (8 mmol) in dry CH_2Cl_2 (100 mL), and the reaction mixture was stirred at rt for 5 h. After rotary evaporation of solvent, the resulting oil was washed with saturated $NaHCO_3$. The resulting aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried Na_2SO_4, concentrated and purified on silica gel chromatography (EtOAc/petroleum ether as eluent) to afford **1b-2** as white solid.(2.22 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 6.59 (dd, J = 8.8, 3.2 Hz, 1H), 4.54 (s, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.3, 141.1, 140.6, 116.5, 116.3, 88.5, 55.6, 38.9.[1]

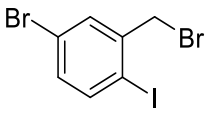


5h

5b (10 mmol)was dissolved in 50 mL of DCM. BBr_3 (25 mmol) was added to the mixture and the mixture stirred at -78 ºC. The reaction was stirred at room temperature. The resulting reaction mixture was monitored by TLC. The mixture was diluted with water and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated by rotary evaporation. Purification by silica gel chromatography (EtOAc/petroleum ether as eluent) to obtain **5h** as white solid, 3.60 g, 98%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 9.77-9.76 (m, 1H), 7.83-7.78 (m, 1H), 7.68-7.54 (m, 3H), 7.41-7.35 (m, 1H), 6.90-6.88 (m, 1H), 6.54-6.50 (m, 1H), 4.31 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 157.9, 140.4, 139.9, 139.1, 133.8, 133.6, 129.1, 126.7, 117.7, 117.4, 116.9, 111.7, 87.1, 42.2. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{10}NOISNa$ 389.9420; found 389.9429.

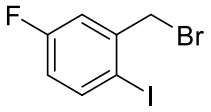


A 100 mL round-bottom flask was charged with benzoic acid (8 mmol) and THF (20 mL, pre-dried over sodium). $NaBH_4$ (2.5 equiv) was added and cooled in an ice bath. A solution of I_2 (1.0 equiv) in THF (10 mL) was added dropwise over 30 min with vigorous evolution of hydrogen. After H_2 evolution had ceased, the flask was heated to reflux for 12 h and then cooled to room temperature, diluted with methanol until the solid disappeared. After stirring 30 min, the solvent was removed by rotary evaporation leaving a white paste which was dissolved by addition of 20% aqueous KOH (20 mL). The solution was stirred for 4 h and extracted with ethyl acetate (30 mL × 2). The combined organic extracts were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. This was purified by flash chromatography.



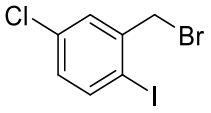
4-bromo-2-(bromomethyl)-1-iodobenzene (1c)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.51 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.3, 141.4, 133.4, 133.2, 122.9, 98.0, 37.6.[2]



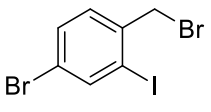
2-(bromomethyl)-4-fluoro-1-iodobenzene (1f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.21 (dd, *J* = 9.2, 3.2 Hz, 1H), 6.76 (ddd, *J* = 10.8, 8.0, 2.8 Hz, 1H), 4.53 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.6 Hz), 142.3 (d, *J* = 7.3 Hz), 141.3 (d, *J* = 7.8 Hz), 117.8 (d, *J* = 6.6 Hz), 117.6 (d, *J* = 5.6 Hz), 92.9 (d, *J* = 3.0 Hz), 37.8.[3]



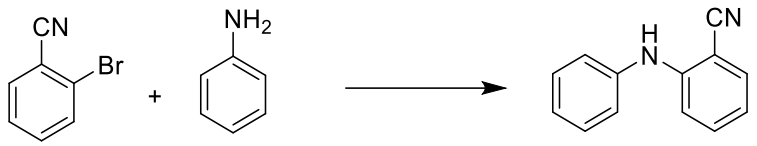
2-(bromomethyl)-4-chloro-1-iodobenzene (1e)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.52 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.0, 141.1, 135.1, 130.5, 130.3, 97.1, 37.7.[2]



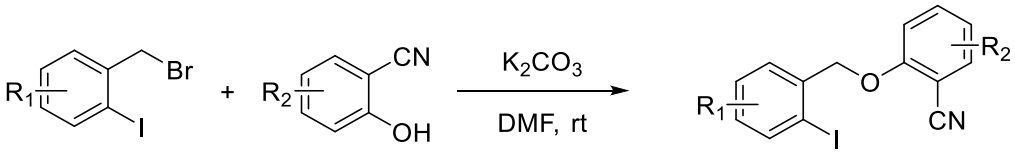
4-bromo-1-(bromomethyl)-2-iodobenzene (1j)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 1.6 Hz, 1H), 7.48-7.45 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 4.54 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.1, 139.4, 132.2, 131.4, 123.0, 100.5, 37.8.[4]

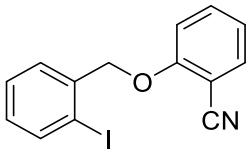


13g

Under nitrogen, a mixture of 2-bromobenzonitrile (10 mmol), aniline (15 mmol), Pd(dppf)Cl_2 (0.5 mmol), PPh_3 (3 mmol) and Cs_2CO_3 (20 mmol) in 1,4-dioxane (40 mL) was heated at 95 ºC for 24 h. The reaction was quenched with water and extracted with EtOAc. After concentration of the organic solution in vacuum. Purification by silica gel chromatography (EtOAc/petroleum ether as eluent) to obtain **13g** as yellow solid, 1.61 g, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.40-7.35 (m, 3H), 7.22-7.18 (m, 3H), 7.16-7.12 (m, 1H), 6.84 (td, *J* = 8.0, 1.2 Hz, 1H), 6.40 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.4, 140.0, 134.0, 133.1, 129.7, 124.3, 121.8, 119.3, 117.7, 114.2, 98.6.[5]

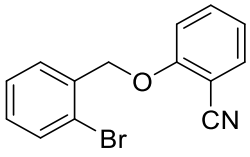


To a solution of Phenyl nitrile (10 mmol) in DMF(30 mL) was added K_2CO_3 (30 mmol) under stirring. After 10 min, Benzyl bromide (12 mmol) was added. The resulting reaction mixture was monitored by TLC. The reaction was quebched by H_2O and extracted with EtOAc. The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated and purified on silica gel chromatography (EtOAc/CH_2Cl_2/petroleum ether as eluent) to give the product.



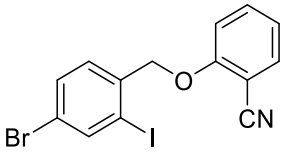
2-((2-iodobenzyl)oxy)benzonitrile (3aA)

This compound was prepared according to the general procedure, white solid, 3.18 g, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.62-7.58 (m, 2H), 7.53 (ddd, *J* = 9.2, 7.6, 1.6 Hz, 1H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 7.06-6.99 (m, 3H), 5.13 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.9, 139.3, 137.8, 134.6, 134.0, 129.8, 128.8, 128.3, 121.5, 116.5, 112.9, 102.4, 96.5, 74.4. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}INO$ 335.9880; found 335.9880.



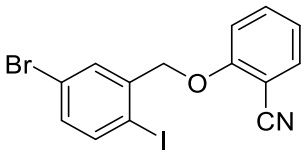
2-((2-bromobenzyl)oxy)benzonitrile (3aB)

This compound was prepared according to the general procedure, white solid, 2.19 g, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 1H), 7.60-7.50 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.05-7.00 (m, 2H), 5.22 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 135.0, 134.5, 133.9, 132.6, 129.5, 128.5, 127.9, 121.7, 121.4, 116.4, 112.8, 102.4, 69.8. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{10}NOBrNa$ 309.9838; found 309.9845.



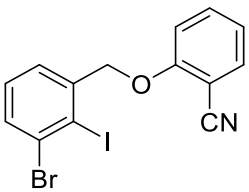
2-((4-bromo-2-iodobenzyl)oxy)benzonitrile (3b)

This compound was prepared according to the general procedure, white solid, 3.64 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 1.6 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.57-7.48 (m, 3H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 5.08 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 141.2, 137.0, 134.6, 134.1, 132.0, 129.4, 122.6, 121.7, 116.4, 112.9, 102.6, 96.6, 73.9. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9BrINONa$ 435.8804; found 435.8807.



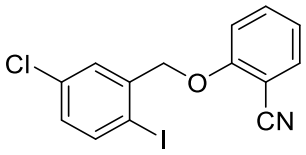
2-((5-bromo-2-iodobenzyl)oxy)benzonitrile (3c)

This compound was prepared according to the general procedure, white solid, 3.39 g, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 2.4 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.55 (td, *J* = 7.6, 1.6 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.08 (td, *J* = 7.6, 0.8 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 5.10 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 140.5, 139.9, 134.6, 134.1, 133.0, 131.4, 123.3, 121.8, 116.3, 112.9, 102.6, 94.2, 74.0. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9BrINONa$ 435.8804; found 435.8811.



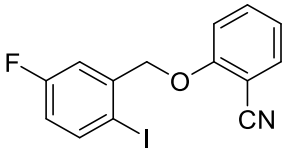
2-((3-bromo-2-iodobenzyl)oxy)benzonitrile (3d)

This compound was prepared according to the general procedure, white solid, 3.65 g, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 2H), 7.57-7.53 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.17 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 141.2, 134.6, 134.0, 132.2, 131.1, 129.9, 126.2, 121.6, 116.4, 112.8, 103.2, 102.4, 76.0. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9BrINONa$ 435.8804; found 435.8807.



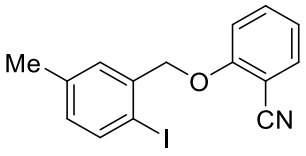
2-((5-chloro-2-iodobenzyl)oxy)benzonitrile (3e)

This compound was prepared according to the general procedure, white solid, 3.07 g, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.59-7.53 (m, 2H), 7.10-7.04 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 5.10 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 140.3, 139.6, 135.4, 134.6, 134.1, 130.1, 128.5, 121.8, 116.3, 112.9, 102.6, 93.2, 74.1. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9ClINONa$ 391.9310; found 391.9308.



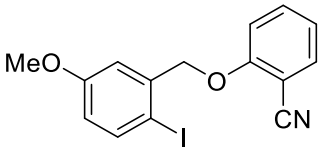
2-((2-fluoro-6-iodobenzyl)oxy)benzonitrile (3f)

This compound was prepared according to the general procedure, white solid, 3.00 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 6.4, 2.0 Hz, 1H), 7.59-7.55 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.13-7.04 (m, 3H), 5.26 (d, *J* = 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1 (d, *J* = 252.3 Hz), 160.2, 135.8 (d, *J* = 3.6 Hz), 134.4, 134.2, 132.3 (d, *J* = 9.2 Hz), 125.8 (d, *J* = 15.5 Hz), 121.5, 116.3, 116.0 (d, *J* = 22.7 Hz), 113.0, 102.7, 101.6 (d, *J* = 2.3 Hz), 68.0 (d, *J* = 4.0 Hz). HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}FINO$ 353.9786; found 353.9783.



2-((2-iodo-5-methylbenzyl)oxy)benzonitrile (3g)

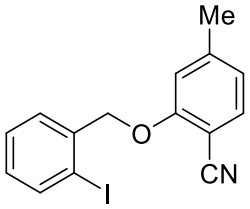
This compound was prepared according to the general procedure, white solid, 2.97 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.60 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.53 (ddd, *J* = 8.4, 7.6, 1.6 Hz, 1H), 7.41 (d, *J* = 1.6 Hz, 1H), 7.04 (td, *J* = 7.6, 0.8 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.87 (dt, *J* = 8.0, 0.8 Hz, 1H), 5.12 (s, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.1, 139.1, 139.0, 137.5, 134.5, 134.0, 130.9, 129.3, 121.4, 116.5, 113.1, 102.5, 92.5, 74.6, 21.3. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{12}NOINa$ 371.9856; found 371.9867.



2-((2-iodo-5-methoxybenzyl)oxy)benzonitrile (3h)

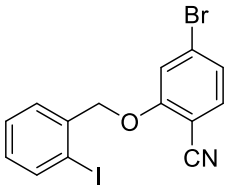
This compound was prepared according to the general procedure, white solid, 3.25 g, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.57-7.53 (m, 1H), 7.28 (d, *J* = 2.8 Hz, 1H), 7.06 (td, *J* = 7.6, 0.8 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.65 (dd, *J* =

8.8, 3.2 Hz, 1H), 5.11 (s, 2H), 3.82 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.5, 160.0, 139.7, 138.9, 134.6, 133.9, 121.6, 116.7, 116.5, 113.6, 113.0, 102.6, 84.1, 74.3, 55.6. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{12}INO_2Na$ 387.9805; found 387.9805.



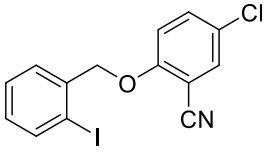
2-((2-iodobenzyl)oxy)-4-methylbenzonitrile (3i)

This compound was prepared according to the general procedure, white solid, 2.79 g, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.86 (dd, *J* = 7.6, 0.4 Hz, 1H), 6.82 (s, 1H), 5.12 (s, 2H), 2.41 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.0, 146.0, 139.3, 138.0, 133.7, 129.8, 128.8, 128.4, 122.4, 116.8, 113.6, 99.5, 96.5, 74.4, 22.5. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{12}INONa$ 371.9856; found 371.9852.



4-bromo-2-((2-iodobenzyl)oxy)benzonitrile (3j)

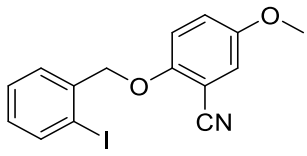
This compound was prepared according to the general procedure, white solid, 4.10 g, 99%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 7.95 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.59 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.48 (td, *J* = 7.2, 1.2 Hz, 1H), 7.36 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.17 (td, *J* = 7.6, 1.6 Hz, 1H), 5.24 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–d_6) δ 160.2, 139.4, 137.6, 135.1, 130.7, 130.2, 128.6 (two peaks), 124.7, 116.9, 115.7, 100.1, 99.6, 74.7. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9BrINONa$ 435.8810; found 435.8806.



5-chloro-2-((2-iodobenzyl)oxy)benzonitrile (3k)

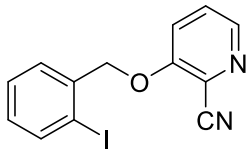
This compound was prepared according to the general procedure, white solid, 2.92 g, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.58-7.56 (m, 2H), 7.49 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.41 (td, *J* = 7.6, 0.8 Hz, 1H), 7.06 (td, *J* = 8.0, 1.6 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 5.15 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.7, 139.4, 137.4, 134.5, 133.3, 130.1, 128.9, 128.4,

126.4, 115.1, 114.4, 103.9, 96.6, 75.0. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9ClINONa$ 391.9310; found 391.9308.



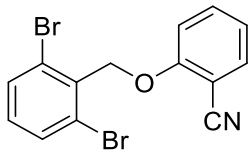
2-((2-iodobenzyl)oxy)-5-methoxybenzonitrile (3l)

This compound was prepared according to the general procedure, light red solid, 2.74 g, 75%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.41 (td, *J* = 7.6, 0.8 Hz, 1H), 7.05 (td, *J* = 7.6, 1.6 Hz, 1H), 6.55 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 5.12 (s, 2H), 3.84 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.6, 161.5, 139.3, 137.8, 135.1, 129.9, 128.9, 128.5, 116.9, 106.5, 100.1, 96.5, 94.6, 74.5, 55.9. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{12}INO_2Na$ 387.9805; found 387.9804.



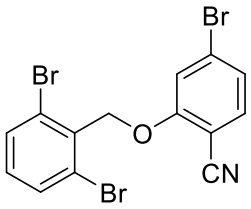
3-((2-iodobenzyl)oxy)picolinonitrile (3m)

This compound was prepared according to the general procedure, white solid, 3.06 g, 91%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.48 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.44-7.37 (m, 2H), 7.08 (t, *J* = 8.0 Hz, 1H), 5.20 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5, 143.4, 139.5, 137.0, 130.3, 129.0, 128.5, 128.0, 124.3, 120.8, 115.1, 96.7, 74.8. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_9IN_2ONa$ 358.9652; found 358.9653.



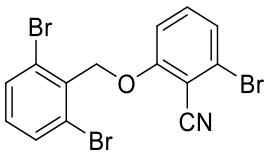
2-((2,6-dibromobenzyl)oxy)benzonitrile (3n)

This compound was prepared according to the general procedure, white solid, 1.87 g, 51%. ^1H NMR (400 MHz, DMSO–d_6) δ 7.79-7.71 (m, 4H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 5.41 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO–d_6) δ 159.8, 135.2, 133.9, 133.5, 132.8, 132.7, 126.3, 121.8, 116.1, 113.3, 100.7, 71.2. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9Br_2NONa$ 387.8943; found 387.8936.



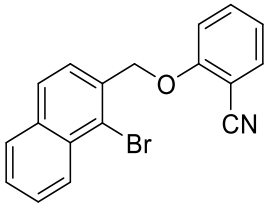
4-bromo-2-((2,6-dibromobenzyl)oxy)benzonitrile (3o)

This compound was prepared according to the general procedure, white solid, 3.21 g, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.60 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 1.6 Hz, 1H), 7.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 5.42 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.6, 134.7, 133.2, 132.7, 131.8, 128.7, 126.8, 124.8, 116.8, 115.5, 101.7, 71.5. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9Br_3NO$ 443.8229; found 443.8236.



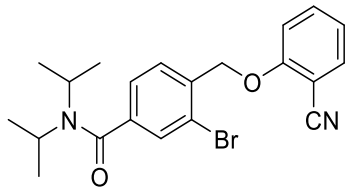
2-bromo-6-((2,6-dibromobenzyl)oxy)benzonitrile (3p)

This compound was prepared according to the general procedure, white solid, 2.19 g, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.14-7.10 (m, 2H), 5.43 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 134.5, 133.4, 132.8, 131.9, 126.9, 125.6, 114.6, 111.5, 106.4, 71.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9Br_3NO$ 443.8229; found 443.8239.



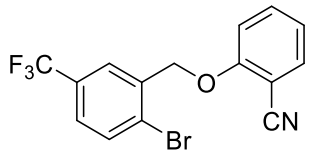
2-((1-bromonaphthalen-2-yl)methoxy)benzonitrile (3q)

This compound was prepared according to the general procedure, white solid, 3.15 g, 93%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 8.28 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.76-7.65 (m, 4H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.15 (td, *J* = 7.6, 0.8 Hz, 1H), 5.55 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 159.6, 135.2, 133.9, 133.8, 133.4, 131.4, 128.5, 128.3, 127.3, 126.4, 126.3, 122.7, 121.6, 116.3, 113.4, 100.8, 70.7. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{12}NOBrNa$ 359.9994; found 359.9995.



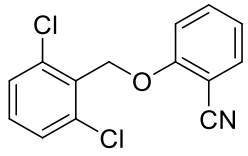
3-bromo-4-((2-cyanophenoxy)methyl)-N,N-diisopropylbenzamide (3r)

This compound was prepared according to the general procedure, white solid, 3.41 g, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.58-7.53 (m, 2H), 7.30 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.09-7.02 (m, 2H), 5.24 (s, 2H), 3.82 (s, 1H), 3.55 (s, 1H), 1.51 (s, 6H), 1.19 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.9, 159.9, 140.2, 135.5, 134.6, 134.0, 130.1, 128.5, 125.0, 121.9, 121.6, 116.4, 112.8, 102.4, 69.7, 51.0, 46.2, 20.8. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{23}N_2O_2BrNa$ 437.0835; found 437.0824.



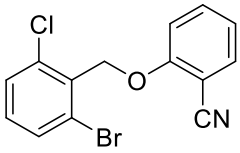
2-((2-bromo-5-(trifluoromethyl)benzyl)oxy)benzonitrile (3s)

This compound was prepared according to the general procedure, white solid, 3.45g, 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.56 (ddd, *J* = 9.2, 7.6, 1.6 Hz, 1H), 7.48 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.09 (td, *J* = 7.2, 0.8 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.25 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 136.3, 134.6, 134.1, 133.4, 130.6 (q, *J* = 32.9 Hz), 126.4 (q, *J* = 3.6 Hz), 125.7, 125.5 (q, *J* = 3.9 Hz), 123.7 (d, *J* = 271.0 Hz), 121.9, 116.2, 112.8, 102.8, 69.7. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_9NOBrF_3Na$ 377.9712; found 377.9702.



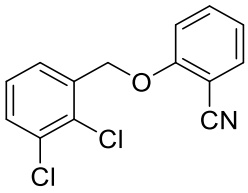
2-((2,6-dichlorobenzyl)oxy)benzonitrile (3t)

This compound was prepared according to the general procedure, white solid, 2.40 g, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.39-7.37 (m, 2H), 7.27 (dd, *J* = 8.8, 7.2 Hz, 1H), 7.17 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.06 (td, *J* = 7.2, 0.8 Hz, 1H), 5.39 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 137.2, 134.4, 134.2, 131.0 (two peaks), 128.7, 121.5, 116.3, 113.2, 102.8, 66.2. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9Cl_2NONa$ 299.9953; found 299.9946.



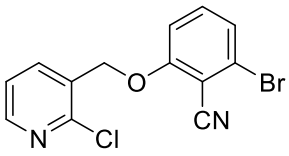
2-((2-bromo-6-chlorobenzyl)oxy)benzonitrile (3t')

This compound was prepared according to the general procedure, white solid, 2.74 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 3H), 7.41 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.21-7.16 (m, 2H), 7.06 (td, *J* = 7.6, 0.8 Hz, 1H), 5.41 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 136.9, 134.4, 134.1, 132.4, 132.0, 131.3, 129.3, 127.1, 121.5, 116.3, 113.2, 102.7, 68.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}BrClNO$ 321.9629; found 321.9625.



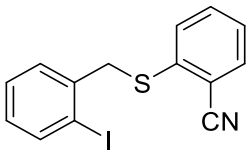
2-((2,3-dichlorobenzyl)oxy)benzonitrile (3u)

This compound was prepared according to the general procedure, white solid, 2.59 g, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.61 (m, 2H), 7.55 (ddd, *J* = 9.2, 7.2, 1.6 Hz, 1H), 7.45 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.28 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.9, 135.9, 134.6, 134.1, 133.2, 130.1, 129.9, 128.0, 126.3, 121.7, 116.4, 112.7, 102.6, 67.8. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9Cl_2NONa$ 299.9953; found 299.9958.



2-bromo-6-((2-chloropyridin-3-yl)methoxy)benzonitrile (3v)

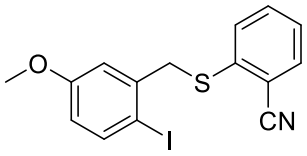
This compound was prepared according to the general procedure, white solid, 2.65 g, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 3.6 Hz, 1H), 8.09-8.07 (m, 1H), 7.42 (t, *J* = 8.4 Hz, 1H), 7.36 (dd, *J* = 8.0, 3.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.4 Hz, 1H), 5.24 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1, 149.2, 148.5, 136.9, 134.8, 130.1, 126.8, 125.9, 123.3, 114.7, 111.2, 106.3. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_9BrClN_2O$ 322.9581; found 322.9575.



2-((2-iodobenzyl)thio)benzonitrile (5a)

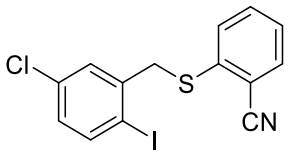
This compound was prepared according to the general procedure, white solid, 2.77 g, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.61 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.47-7.43 (m,

1H), 7.36 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.30 (td, *J* = 7.2, 1.2 Hz, 1H), 7.25-7.20 (m, 2H), 6.95-6.91 (m, 1H), 4.28 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 139.9, 139.8, 138.6, 133.7, 132.9, 131.7, 130.1, 129.4, 128.5, 127.2, 117.2, 115.3, 100.7, 44.4. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{10}INSNa$ 373.9471; found 373.9472.



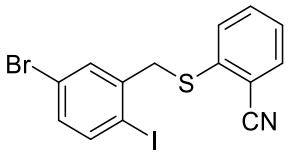
2-((2-iodo-5-methoxybenzyl)thio)benzonitrile (5b)

This compound was prepared according to the general procedure, white solid, 3.01 g, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 1H), 7.63 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.49-7.44 (m, 1H), 7.38 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.31 (td, *J* = 7.6, 1.6 Hz, 1H), 6.84 (d, *J* = 3.2 Hz, 1H), 6.55 (dd, *J* = 8.8, 3.2 Hz, 1H), 4.25 (s, 2H), 3.71 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 140.3, 140.0, 139.7, 133.8, 133.0, 131.9, 127.3, 117.3, 115.9, 115.8, 115.4, 89.0, 55.5, 44.4. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{15}H_{12}INOSNa$ 403.9576; found 403.9564.



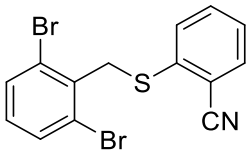
2-((5-chloro-2-iodobenzyl)thio)benzonitrile (5c)

This compound was prepared according to the general procedure, white solid, 2.04 g, 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 1H), 7.66 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.48 (td, *J* = 7.2, 1.2 Hz, 1H), 7.37-7.33 (m, 2H), 7.16 (d, *J* = 2.8 Hz, 1H), 6.94 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.23 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.8, 140.7, 139.1, 134.7, 133.9, 133.0, 132.4, 130.1, 129.5, 127.8, 117.1, 115.9, 97.6, 44.3. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9INClSNa$ 407.9081; found 407.9072.



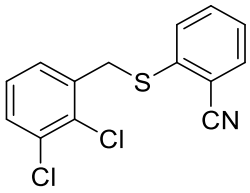
2-((5-bromo-2-iodobenzyl)thio)benzonitrile (5d)

This compound was prepared according to the general procedure, white solid, 2.84 g, 66%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.68 (t, *J* = 6.8 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.22 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.37 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–d_6) δ 141.3, 141.2, 139.2, 133.9, 133.7, 132.8, 132.3, 130.4, 127.4, 121.6, 116.8, 112.8. 99.8, 42.1. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9INBrSNa$ 451.8576; found 451.8561.



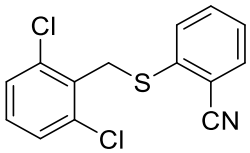
2-((2,6-dibromobenzyl)thio)benzonitrile (5e)

This compound was prepared according to the general procedure, white solid, 1.80 g, 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.51-7.48 (m, 4H), 7.40-7.34 (m, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 4.53 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.4, 135.9, 134.0, 133.9, 133.0, 132.9, 132.7, 130.2, 128.1, 125.9, 117.3, 41.3. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9Br_2NSNa$ 403.8715; found 403.8719.



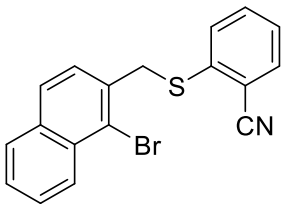
2-((2,3-dichlorobenzyl)thio)benzonitrile (5f)

This compound was prepared according to the general procedure, white solid, 2.09 g, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.46 (td, *J* = 8.0, 1.6 Hz, 1H), 7.39-7.31 (m, 3H), 7.15 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 4.34 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.6, 136.5, 133.9, 133.7, 133.0, 132.7, 132.2, 129.9, 128.9, 127.6, 127.4, 117.2, 115.8, 37.7. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9SNCl_2Na$ 315.9725; found 315.9717.



2-((2,6-dichlorobenzyl)thio)benzonitrile (5g)

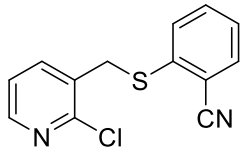
This compound was prepared according to the general procedure, white solid, 1.77 g, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.49-7.47 (m, 2H), 7.39-7.35 (m, 1H), 7.29-7.27 (m, 2H), 7.15 (dd, *J* = 8.4, 7.2 Hz, 1H), 4.47 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.2, 136.0, 133.9, 133.8, 133.0, 132.9, 129.3, 128.5, 128.1, 117.2 (two peaks), 35.5. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_9Cl_2NSNa$ 315.9725; found 315.9734.



2-(((1-bromonaphthalen-2-yl)methyl)thio)benzonitrile (5i)

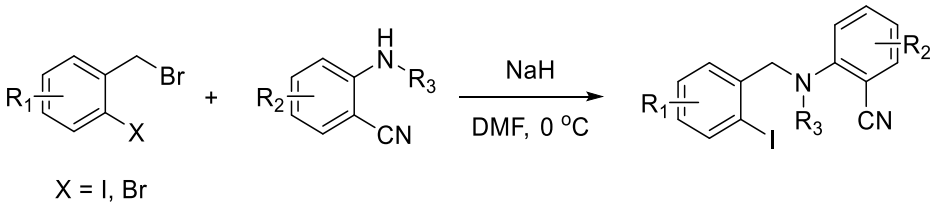
This compound was prepared according to the general procedure, light yellow solid, 1.64 g, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.4

Hz, 1H), 7.62 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.58 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.51 (td, *J* = 8.0, 1.2 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.40-7.36 (m, 2H), 7.30-7.26 (m, 1H), 4.58 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.1, 133.9 (two peaks), 133.8, 132.9, 132.5, 132.0, 128.3, 128.1, 127.8, 127.7, 127.3, 126.9, 124.9, 117.3, 115.6, 40.6. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{18}H_{12}NSBrNa$ 375.9766; found 375.9762.

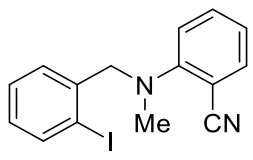


2-(((2-chloropyridin-3-yl)methyl)thio)benzonitrile (5l)

This compound was prepared according to the general procedure, yellow solid, 2.19 g, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.65-7.62 (m, 2H), 7.46 (td, *J* = 8.0, 1.2 Hz, 1H), 7.36-7.31 (m, 2H), 7.08 (dd, *J* = 7.6, 4.8 Hz, 1H), 4.29 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 151.2, 148.8, 139.3, 138.9, 134.0, 132.2, 131.2, 127.8, 122.8, 117.1, 115.8, 36.2. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{10}ClN_2S$ 261.0248; found 261.0241.

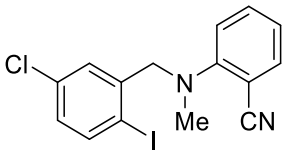


In a 100 mL round bottom flask equipped with a Teflon-coated stir bar and charged with a solution of aniline (5.5 mmol) in DMF (20 mL) was added NaH (5.5 mmol) in one portion at 0 °C. The resulting mixture was stirred vigorously under nitrogen atmosphere until the evolution of gas ceased. Subsequently, a solution of Benzyl bromide (5.0 mmol) in DMF (8 mL) was added dropwise at 0 °C. The resulting reaction mixture was monitored by TLC. The reaction was quenched with cold water (40 mL), and then transferred to a separatory funnel with EtOAc (100 mL). The aqueous layer was separated and extracted with EtOAc (2 x 100 mL). The combined organic extract was washed with brine, dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crued material was purified by silica gel chromatography ((EtOAc/CH_2Cl_2/petroleum ether as eluent) to give the product.



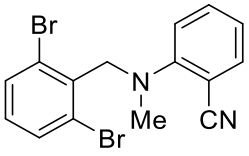
2-((2-iodobenzyl)(methyl)amino)benzonitrile (7a)

This compound was prepared according to the general procedure, light yellow solid, 2.02 g, 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.84 (m, 1H), 7.53 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.41-7.31 (m, 3H), 7.00-6.96 (m, 1H), 6.89-6.85 (m, 2H), 4.48 (s, 2H), 3.07 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.4, 139.7, 139.1, 135.2, 133.6, 129.2, 128.6, 128.5, 119.8, 119.4, 117.9, 101.5, 98.7, 64.1, 40.8. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}N_2I$ 349.0196; found 349.0193.



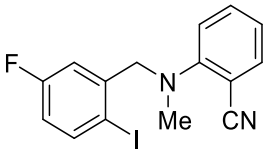
2-((5-chloro-2-iodobenzyl)(methyl)amino)benzonitrile (7b)

This compound was prepared according to the general procedure, white solid, 497 mg, 26%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.57-7.54 (m, 1H), 7.45-7.41 (m, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.94-6.90 (m, 2H), 4.44 (s, 2H), 3.05 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.2, 141.3, 140.7, 135.3, 135.2, 133.8, 129.5, 128.6, 120.3, 119.2, 117.8, 101.7, 95.4, 64.4, 40.6. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}N_2ClI$ 382.9806; found 382.9805.



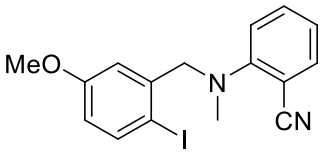
2-((2,6-dibromobenzyl)(methyl)amino)benzonitrile (7c)

This compound was prepared according to the general procedure, yellow solid, 1.46 g, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.52 (m, 3H), 7.47-7.42 (m, 1H), 7.04-7.00 (m, 2H), 6.91 (td, *J* = 7.6, 1.2 Hz, 1H), 4.81 (s, 2H), 2.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.0, 135.4, 134.8, 133.4, 132.8, 130.3, 126.9, 120.2, 119.4, 118.9, 102.9, 57.5, 39.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}Br_2N_2$ 378.9440; found 378.9445.



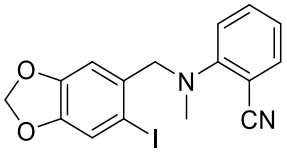
2-((5-fluoro-2-iodobenzyl)(methyl)amino)benzonitrile (7d)

This compound was prepared according to the general procedure, white solid, 1.39 g, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45-7.40 (m, 1H), 7.16 (dd, *J* = 10.0, 3.2 Hz, 1H), 6.93-6.90 (m, 2H), 6.77 (td, *J* = 8.4, 3.2 Hz, 1H), 4.44 (s, 2H), 3.06 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.0 (d, *J* = 246.3 Hz), 154.2, 141.8 (d, *J* = 6.7 Hz), 140.7 (d, *J* = 7.6 Hz), 135.3, 133.8, 120.3, 119.2, 117.8, 116.6 (d, *J* = 21.9 Hz), 115.9 (d, *J* = 23.5 Hz), 101.7, 90.8 (d, *J* = 2.0 Hz), 64.4, 40.6. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}FIN_2$ 367.0102; found 367.0107.



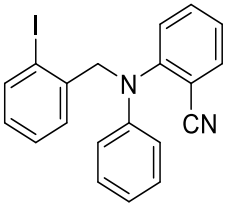
2-((2-iodo-5-methoxybenzyl)(methyl)amino)benzonitrile (7e)

This compound was prepared according to the general procedure, white solid, 1.44 g, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.43-7.39 (m, 1H), 7.05 (d, *J* = 3.2 Hz, 1H), 6.93-6.88 (m, 2H), 6.60 (dd, *J* = 8.4, 2.8 Hz, 1H), 4.44 (s, 2H), 3.76 (s, 3H), 3.06 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 154.6, 140.2, 140.1, 135.2, 133.7, 120.1, 119.4, 118.1, 115.3, 114.6, 101.9, 86.8, 64.2, 55.5, 40.9. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{16}H_{15}IN_2NaO$ 401.0121; found 401.0127.



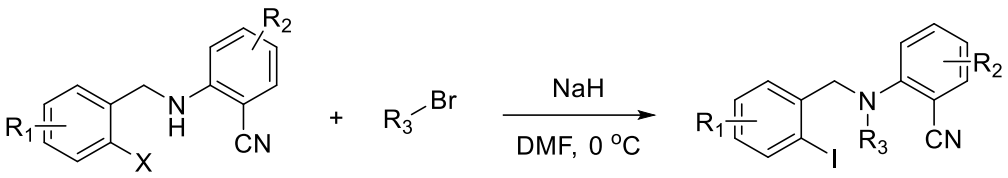
2-(((6-iodobenzo[d][1,3]dioxol-5-yl)methyl)(methyl)amino)benzonitrile (7f)

This compound was prepared according to the general procedure, white solid, 1.04 g, 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.41 (ddd, *J* = 8.8, 7.6, 1.6 Hz, 1H), 7.27 (s, 1H), 6.93 (s, 1H), 6.92-6.88 (m, 2H), 5.97 (s, 2H), 4.40 (s, 2H), 3.02 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.5, 148.9, 148.0, 135.2, 133.7, 132.7, 120.1, 119.4, 118.9, 118.0, 108.9, 101.9, 101.8, 86.3, 64.2, 40.5. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{14}N_2O_2I$ 393.0100; found 393.0096.



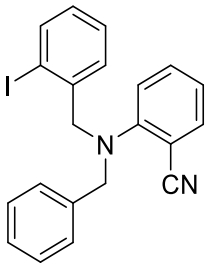
2-((2-iodobenzyl)(phenyl)amino)benzonitrile (7g)

This compound was prepared according to the general procedure, white solid, 1.66 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.55-7.50 (m, 2H), 7.30-7.14 (m, 5H), 6.96-6.93 (m, 2H), 6.81 (dd, *J* = 7.6, 0.8 Hz, 2H), 4.96 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.8, 147.8, 139.5, 139.1, 134.9, 134.3, 129.5, 129.1, 128.6, 128.3, 126.1, 124.5, 121.8, 118.6, 117.5, 109.8, 97.5, 62.9. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{16}IN_2$ 411.0353; found 411.0358.



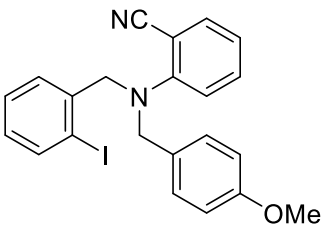
X = I, Br

In a 100 mL round bottom flask equipped with a Teflon-coated stir bar and charged with a solution of aniline (5.5 mmol) in DMF (20 mL) was added NaH (5.5 mmol) in one portion at 0 °C. The resulting mixture was stirred vigorously under nitrogen atmosphere until the evolution of gas ceased. Subsequently, a solution of Benzyl bromide (5.0 mmol) in DMF (8 mL) was added dropwise at 0 °C. Upon the completion of S_N2 reaction as judged by TLC analysis, which was ~1 h. The reaction was quenched with cold water (40 mL), and then transferred to a separatory funnel with EtOAc (100 mL). The aqueous layer was separated and extracted with EtOAc (2 x 100 mL). The combined organic extract was washed with brine, dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crued material was purified by silica gel chromatography ((EtOAc/CH_2Cl_2/petroleum ether as eluent) to give the product.



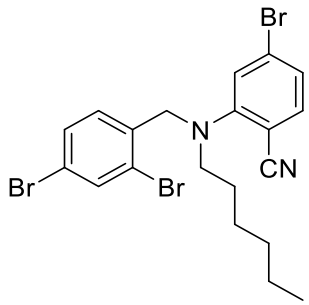
2-(benzyl(2-iodobenzyl)amino)benzonitrile (7h)

This compound was prepared according to the general procedure, white solid, 1.63 g, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.57 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46-7.44 (m, 1H), 7.37-7.33 (m, 1H), 7.32-7.24 (m, 6H), 6.96-6.91 (m, 3H), 4.56 (s, 2H), 4.43 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.5, 139.7, 139.2, 137.0, 135.1, 133.5, 129.3, 129.2, 128.7, 128.5, 128.2, 127.6, 121.5, 120.8, 119.0, 104.9, 99.1, 60.6, 57.6. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{17}IN_2Na$ 447.0329; found 447.0334.



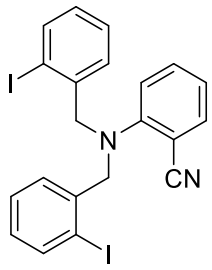
2-((2-iodobenzyl)(4-methoxybenzyl)amino)benzonitrile (7i)

This compound was prepared according to the general procedure, light green oil, 1.82 g, 80%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 7.84 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 8.0, 1.6 Hz, 1H), 7.46 (td, J = 8.4, 1.6 Hz, 1H), 7.41-7.34 (m, 2H), 7.19 (d, J = 8.8 Hz, 2H), 7.04-6.99 (m, 3H), 6.87 (d, J = 8.8 Hz, 2H), 4.48 (s, 2H), 4.39 (s, 2H), 3.71 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.5, 152.6, 139.4, 139.2, 134.8, 133.8, 129.2 (two peaks), 128.9, 128.8, 121.6, 120.8, 118.7, 113.8, 104.0, 99.4, 59.9, 56.3, 55.0. HRMS (ESI–TOF) m/z: [M+Na]$^{+}$ calcd for $C_{22}H_{19}IN_2ONa$ 477.0434; found 477.0441.



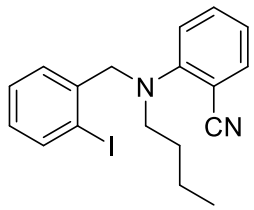
4-bromo-2-((2,4-dibromobenzyl)(hexyl)amino)benzonitrile (7j)

This compound was prepared according to the general procedure, white solid, 0.93 g, 35%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 2.0 Hz, 1H), 7.41 (dd, J = 8.4, 2.0 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 8.4 Hz, 1H), 7.03-7.00 (m, 2H), 4.50 (s, 2H), 3.38-3.34 (m, 2H), 1.65-1.60 (m, 2H), 1.33-1.27 (m, 6H), 0.90-0.83 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.7, 136.3, 135.5, 135.4, 131.0, 130.3, 128.7, 123.9, 123.5, 122.1, 121.8, 101.2, 55.9, 53.2, 31.6, 27.5, 26.5, 22.7, 14.1. HRMS (ESI–TOF) m/z: [M+H]$^{+}$ calcd for $C_{20}H_{22}N_2Br_3$ 526.9333; found 526.9340.



2-(bis(2-iodobenzyl)amino)benzonitrile (7k)

This compound was prepared according to the general procedure, white solid, 1.98 g, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 7.6, 0.8 Hz, 2H), 7.57 (dd, J = 8.0, 1.6 Hz, 1H), 7.42-7.28 (m, 5H), 7.00-6.91 (m, 3H), 6.87 (d, J = 8.4 Hz, 1H), 4.56 (s, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.8, 139.8, 138.9, 135.4, 133.7, 129.3, 128.6, 128.1, 121.0, 119.6, 119.0, 102.9, 98.8, 61.7. HRMS (ESI–TOF) m/z: [M+H]$^{+}$ calcd for $C_{21}H_{17}I_2N_2$ 550.9476; found 550.9481.



2-(butyl(2-iodobenzyl)amino)benzonitrile (7l)

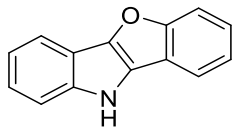
This compound was prepared according to the general procedure, yellow oil, 1.6 g, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.38-7.28 (m, 3H), 6.96 (td, *J* = 8.0, 2.0 Hz, 1H), 6.88-6.83 (m, 2H), 4.46 (s, 2H), 3.43 (t, *J* = 8.0 Hz, 2H), 1.67-1.62 (m, 2H), 136-1.30 (m, 2H), 0.91 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.1, 139.7, 139.3, 135.4, 133.5, 129.1, 128.8, 128.5, 120.0, 119.5, 119.2, 102.5, 98.7, 61.2, 53.2, 29.9, 20.1, 14.1. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}IN_2$ 391.0666; found 391.0682.

2.3. General Procedure for Synthesis of Indoles

procedure 1: The Schlenk tube charged with **3/5/7** (0.5 mmol), ^{t}BuOK (1.1 mmol, 124 mg) and $CuSO_4$ (0.025 mmol, 4 mg) was dried under high vacuum for 15 min. PhCl (10 mL) was added under argon and stirred at 90 °C. The resulting reaction mixture was monitored by TLC. Upon completion of astarting materials, the reaction mixture was directly prified by silica gel column to give the desired product.

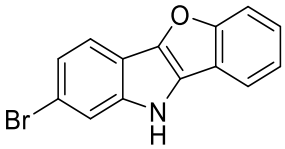
procedure 2: The Schlenk tube charged with **12/13** (0.6 mmol), K_2CO_3 (0.5 mmol) and $CuSO_4$ (0.05 mmol, 8 mg) was dried under high vacuum for 15 min. **1** (0.5 mmol) and DMF (10 mL) were added under argon. 10 min later, ^{t}BuOK (1.1 mmol, 124 mg) was added under argon and stirred at 90 °C. The resulting reaction mixture was monitored by TLC. Upon completion of astarting materials, the reaction mixture was directly prified by silica gel column to give the desired product.

procedure 3: The Schlenk tube charged with **14** (0.6 mmol) and $CuSO_4$ (0.05 mmol, 8 mg) was dried under high vacuum for 15 min. **1** and DMF (10 mL) were added under argon at 0 °C. Then KHMDS (0.6 mmol) was added. 1h later, ^{t}BuOK (1.1 mmol, 124 mg) was added under argon and stirred at 90 °C. The resulting reaction mixture was monitored by TLC. Upon completion of astarting materials, the reaction mixture was directly prified by silica gel column to give the desired product.



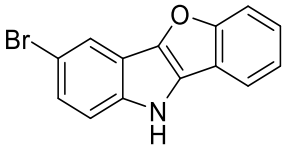
10*H*-benzofuro[3,2-b]indole (4a)

This compound was prepared according to the general procedure 1, white solid, X = Br, 79.6 mg, 77%. X = I, 101.6 mg, 98%. The general procedure 2, 85.8 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.66-7.61 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.34-7.21 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 143.8, 139.8, 125.3, 124.0, 123.0, 122.8, 120.5, 118.8, 118.0, 117.3, 114.4, 112.9, 112.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}NO$ 208.0757; found 208.0757.



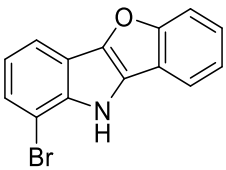
2-bromo-10*H*-benzofuro[3,2-b]indole (4b)

This compound was prepared according to the general procedure 1, white solid, 114.3 mg, 80%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.70 (s, 1H), 7.84-7.81 (m, 1H), 7.78 (d, *J* = 1.6 Hz, 1H), 7.74-7.70 (m, 2H), 7.40-7.35 (m, 2H), 7.28 (dd, *J* = 8.4, 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.8, 141.5, 139.8, 126.2, 124.4, 123.1, 122.4, 118.6, 118.3, 118.0, 115.6, 114.8, 112.7, 111.7. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_8NONaBr$ 307.9681; found 307.9679.



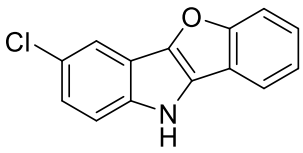
3-bromo-10*H*-benzofuro[3,2-b]indole (4c)

This compound was prepared according to the general procedure 1, yellow solid, 118.7 mg, 83%. The general procedure 2, 114.2 mg, 80% ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.95-7.94 (m, 1H), 7.68-7.66 (m, 1H), 7.63-7.61 (m, 1H), 7.37-7.29 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.5, 142.6, 138.2, 126.5, 125.8, 124.6, 123.0, 119.9, 118.5, 118.2, 115.7, 114.0, 113.5, 113.0. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9BrNO$ 285.9862; found 285.9852.



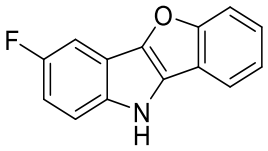
1-bromo-10*H*-benzofuro[3,2-b]indole (4d)

This compound was prepared according to the general procedure 1, white solid, 129.9 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.70-7.67 (m, 1H), 7.64-7.62 (m, 1H), 7.44 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.38-7.31 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 143.7, 137.5, 125.6, 125.1, 124.5, 123.0, 121.3, 118.4, 118.2, 116.4, 115.5, 112.9, 105.9. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9NOBr$ 285.9862; found 285.9852.



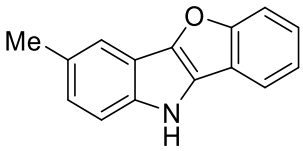
3-chloro-10*H*-benzofuro[3,2-b]indole (4e)

This compound was prepared according to the general procedure 1, light yellow solid, 102.8 mg, 86%. The general procedure 2, 92.8 mg, 77% ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.79 (d, *J* = 2.0 Hz, 1H), 7.67 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.62 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.35-7.29 (m, 2H), 7.21 (dd, *J* = 8.8, 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.5, 142.8, 138.0, 126.7, 126.2, 124.6, 123.2, 123.0, 118.5, 118.2, 116.8, 115.1, 113.6, 113.0. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9NOCl$ 242.0373; found 242.0365.



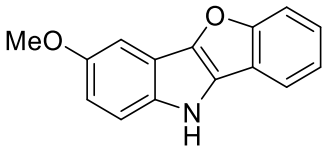
3-fluoro-10*H*-benzofuro[3,2-b]indole (4f)

This compound was prepared according to the general procedure 1, yellow solid, 101.2 mg, 90%. The general procedure 2, 78.8 mg, 70% ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.67 (s, 1H), 7.89-7.84 (m, 1H), 7.77-7.71 (m, 1H), 7.62-7.58 (m, 2H), 7.44-7.37 (m, 2H), 7.12 (td, *J* = 9.2, 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.8, 156.9 (d, *J* = 231.5 Hz), 141.7 (d, *J* = 4.4 Hz), 135.9, 127.3, 124.5, 123.0, 118.6, 118.3, 114.1 (d, *J* = 9.6 Hz), 112.6, 112.4 (d, *J* = 10.9 Hz), 110.3 (d, *J* = 26.0 Hz), 101.5 (d, *J* = 25.1 Hz). HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9NOF$ 226.0663; found 226.0663.



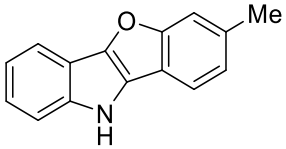
3-methyl-10*H*-benzofuro[3,2-b]indole (4g)

This compound was prepared according to the general procedure 1, white solid, 79.8 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.67-7.59 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.33-7.27 (m, 2H), 7.10 (ddd, *J* = 8.4, 1.6, 0.4 Hz, 1H), 2.51 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 143.7, 138.3, 129.9, 125.5, 124.6, 123.8, 122.7, 119.0, 117.9, 117.0, 114.6, 112.8, 112.3, 21.6. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NO$ 222.0913; found 222.0908.



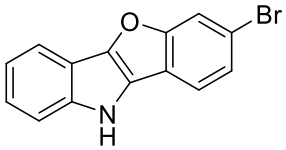
3-methoxy-10*H*-benzofuro[3,2-b]indole (4h)

This compound was prepared according to the general procedure 1, white solid, 101.5 mg, 86%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.33 (s, 1H), 7.79-7.78 (m, 1H), 7.71-7.68 (m, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.38-7.33 (m, 2H), 7.27 (d, J = 2.4 Hz, 1H), 6.89 (dd, J = 8.8, 2.4 Hz, 1H), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.6, 153.5, 142.0, 134.5, 126.0, 123.9, 122.9, 118.6, 118.3, 113.8, 112.7, 112.5, 112.4, 98.3, 55.5. HRMS (ESI–TOF) m/z: [M+H]+ calcd for $C_{15}H_{12}NO_2$ 238.0863; found 238.0869.



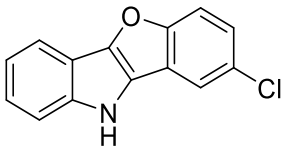
7-methyl-10*H*-benzofuro[3,2-b]indole (4i)

This compound was prepared according to the general procedure 1, white solid, 107.6 mg, 97%. The general procedure 2, 94.0 mg, 85% ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.46-7.43 (m, 2H), 7.28-7.20 (m, 2H), 7.12 (d, J = 7.6 Hz, 1H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.8, 143.4, 139.5, 134.4, 125.4, 124.0, 122.6, 120.4, 117.5, 117.0, 116.4, 114.6, 113.2, 112.6, 21.9. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NO$ 222.0913; found 222.0909



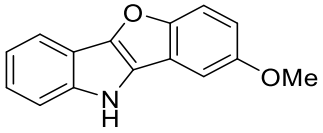
7-bromo-10*H*-benzofuro[3,2-b]indole (4j)

This compound was prepared according to the general procedure 1, white solid, 97.4 mg, 68%. The general procedure 2, 94.4 mg, 66% ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.56 (s, 1H), 7.99 (d, J = 1.6 Hz, 1H), 7.78-7.73 (m, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.52 (dd, J = 8.4, 1.6 Hz, 1H), 7.26 (t, J = 7.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.7, 142.7, 139.5, 126.0, 124.7, 122.8, 119.7, 119.5, 117.8, 116.5, 116.0, 115.7, 113.2, 112.5. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9BrNO$ 285.9862; found 285.9855.



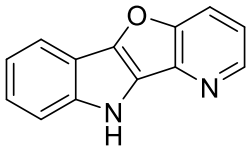
8-chloro-10*H*-benzofuro[3,2-b]indole (4k)

This compound was prepared according to the general procedure 1, white solid, 84.4 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 2.0 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.33-7.22 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 145.2, 140.1, 128.3, 124.3, 123.8, 123.7, 120.7, 119.9, 117.7, 117.5, 114.2, 113.7, 112.8. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9ClNO$ 242.0367; found 242.0361.



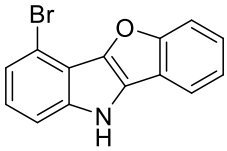
8-methoxy-10*H*-benzofuro[3,2-b]indole (4l)

This compound was prepared according to the general procedure 1, white solid, 99.9 mg, 84%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.39 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 2.4 Hz, 1H), 7.18 (td, J = 6.8, 1.2 Hz, 1H), 7.12 (t, J = 6.8 Hz, 1H), 6.98 (dd, J = 8.4, 2.0 Hz, 1H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 159.8, 157.3, 141.3, 138.6, 125.5, 121.5, 119.4, 118.5, 115.7, 113.1, 112.9, 112.1, 111.0, 98.2, 55.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NO_2$ 238.0863; found 238.0858.



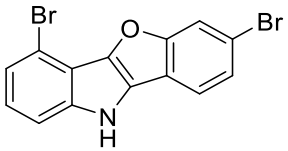
10*H*-pyrido[2',3':4,5]furo[3,2-b]indole (4m)

This compound was prepared according to the general procedure 1, light orange solid, 62.5 g, 60%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.90 (s, 1H), 8.53 (dd, J = 4.8, 1.2 Hz, 1H), 8.11 (dd, J = 8.4, 1.2 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.37 (dd, J = 8.4, 5.2 Hz, 1H), 7.32 (td, J = 6.8, 1.2 Hz, 1H), 7.22-7.18 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 152.2, 145.5, 144.8, 140.3, 137.6, 123.9, 123.8, 119.8, 119.3, 118.5, 116.9, 113.3, 112.4. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_9N_2O$ 209.0709; found 209.0711.



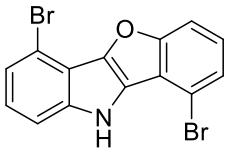
4-bromo-10*H*-benzofuro[3,2-b]indole (4n)

This compound was prepared according to the general procedure 1, brown solid, 114.3mg, 80%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.89 (s, 1H), 7.85-7.83 (m, 1H), 7.79-7.77 (m, 1H), 7.58 (dd, J = 8.0, 0.4 Hz, 1H), 7.43-7.37 (m, 2H), 7.34 (dd, J = 7.2, 0.4 Hz, 1H), 7.15 (dd, J = 8.0, 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.8, 140.8, 139.7, 126.5, 124.7, 123.3, 123.1, 122.3, 118.6, 117.9, 113.8, 112.8, 112.3, 109.5. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9NOBr$ 285.9862; found 285.9864.



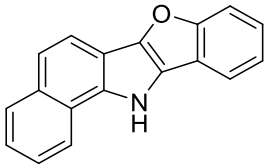
4,7-dibromo-10*H*-benzofuro[3,2-b]indole (4o)

This compound was prepared according to the general procedure 1, yellow solid, 121.7 mg, 66%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.93 (s, 1H), 8.09 (d, J = 1.6 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.55 (dd, J = 8.0, 1.6 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.9, 141.4, 139.9, 126.3, 125.8, 123.7, 122.5, 119.9, 117.2, 116.8, 116.0, 113.7, 112.5, 109.5. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_7Br_2NONa$ 385.8792; found 385.8790.



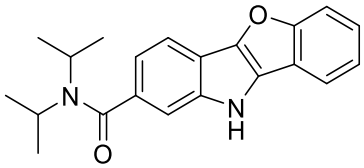
4,9-dibromo-10*H*-benzofuro[3,2-b]indole (4p)

This compound was prepared according to the general procedure 1, white solid, 164.3 mg, 90%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.03 (s, 1H), 7.79 (dd, J = 8.4, 0.8 Hz, 1H), 7.60 (dd, J = 8.4, 0.8 Hz, 1H), 7.55 (dd, J = 8.0, 0.8 Hz, 1H), 7.35 (dd, J = 7.6, 0.4 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.17 (dd, J = 8.4, 0.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.4, 141.4, 140.4, 125.9, 125.8, 125.0, 124.0, 122.6, 119.7, 113.3, 112.7, 112.1, 110.7, 109.6. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_8Br_2NO$ 363.8967; found 363.8973.



12*H*-benzo[g]benzofuro[3,2-b]indole (4q)

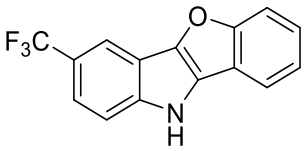
This compound was prepared according to the general procedure 1, white solid, 87.0 mg, 68%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.51 (s, 1H), 8.47 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.66-7.60 (m, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.38 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.7, 143.4, 133.7, 130.0, 128.8, 126.1, 124.4, 123.7, 123.6, 123.1, 122.7, 120.7, 120.4, 118.8, 117.9, 116.6, 112.6, 108.0. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{12}NO$ 258.0913; found 258.0914.



N,N-diisopropyl-10*H*-benzofuro[3,2-b]indole-2-carboxamide (4r)

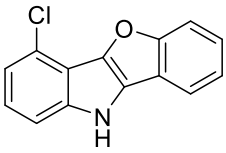
This compound was prepared according to the general procedure 1, white solid, 115.2 mg, 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.53-7.48 (m, 2H), 7.23-7.14

(m, 3H), 7.03 (d, J = 8.0 Hz, 1H), 1.51 (s, 12H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 172.5, 159.5, 143.0, 139.5, 132.5, 127.3, 124.0, 122.6, 118.9, 118.5, 117.2, 116.6, 114.2, 112.6, 111.1, 20.9. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{22}N_2O_2Na$ 357.1573; found 357.1561.



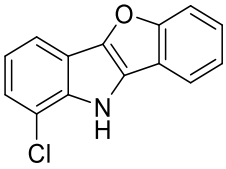
3-(trifluoromethyl)-10*H*-benzofuro[3,2-b]indole (4s)

This compound was prepared according to the general procedure 1, white solid, 78.1 mg, 56%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.07 (s, 1H), 8.16 (t, J = 0.8 Hz, 1H), 7.87-7.85 (m, 1H), 7.77-7.74 (m, 2H), 7.52 (dd, J = 8.8, 2.0 Hz, 1H), 7.44-7.37 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–d_6) δ 158.9, 141.7, 140.4, 129.4, 127.4, 126.7 (d, J = 269.8 Hz), 124.9, 123.2, 120.8 (q, J = 31.2 Hz), 118.8, 118.5 (d, J = 3.5 Hz), 118.1, 114.1 (d, J = 4.2 Hz) , 113.8, 112.8, 111.9. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_9NOF_3$ 276.0631; found 276.0626.



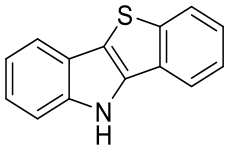
4-chloro-10*H*-benzofuro[3,2-b]indole (4t)

This compound was prepared according to the general procedure 1, white solid, 118.5 mg, 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.69-7.64 (m, 2H), 7.85-7.83 (m, 1H), 7.38-7.29 (m, 3H), 7.22-7.14 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 142.3, 140.2, 126.0, 124.6, 123.7, 123.4, 123.0, 120.5, 118.2, 118.1, 113.7, 113.2, 111.0. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9NOCl$ 242.0367; found 242.0365.



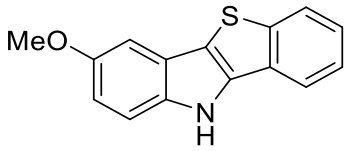
1-chloro-10*H*-benzofuro[3,2-b]indole (4u)

This compound was prepared according to the general procedure 1, white solid, 93.9 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.76-7.73 (m, 2H), 7.65-7.62 (m, 1H), 7.39-7.32 (m, 2H), 7.29 (dd, J = 7.6, 0.8 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 143.5, 136.2, 125.7, 124.4, 122.9, 122.2, 120.9, 118.4, 118.1, 117.6, 115.8, 115.6, 112.8. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9NOCl$ 242.0367; found 242.0361.



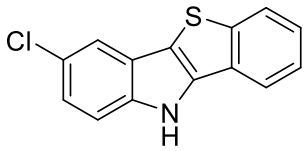
10*H*-benzo[4,5]thieno[3,2-b]indole (6a)

This compound was prepared according to the general procedure 1, white solid, 109.4 mg, 98%. The general procedure 2, 100.5 mg, 90%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.12 (s, 1H), 8.07 (d, J = 7.6 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.2 Hz, 1H), 7.29 (td, J = 7.2, 1.2 Hz, 1H), 7.15 (t, J = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 142.0, 140.6, 137.5, 126.7, 124.5, 124.4, 124.3, 122.8, 121.5, 120.2, 119.4, 118.8, 113.8, 112.6. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}NS$ 224.0528; found 224.0527.



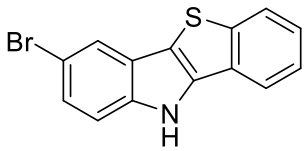
3-methoxy-10*H*-benzo[4,5]thieno[3,2-b]indole (6b)

This compound was prepared according to the general procedure 1, white solid, 114.1 mg, 90%. The general procedure 2, 101.1 mg, 80%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.93 (s, 1H), 8.04-7.99 (m, 2H), 7.49-7.45 (m, 2H), 7.36 (td, J = 8.0, 1.2 Hz, 1H), 7.30 (d, J = 2.4 Hz, 1H), 6.91 (dd, J = 8.8, 2.4 Hz, 1H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 153.5, 141.9, 138.1, 135.5, 126.8, 124.5, 124.4, 124.2, 121.8, 120.1, 113.5, 113.3, 113.0, 100.7, 55.5. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}NOS$ 254.0634; found 254.0623.



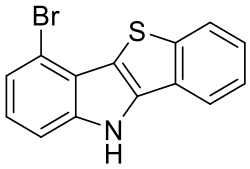
3-chloro-10*H*-benzo[4,5]thieno[3,2-b]indole (6c)

This compound was prepared according to the general procedure 1, yellow solid, 126.2 mg, 98%. The general procedure 2, 117.1 mg, 91%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.34 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 8.8 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.27 (dd, J = 8.4, 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 142.4, 139.0, 138.9, 126.3, 124.9, 124.7, 124.5, 123.8, 122.7, 122.5, 120.5, 118.3, 114.1, 113.3.[6]



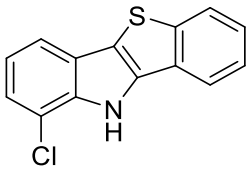
3-bromo-10*H*-benzo[4,5]thieno[3,2-b]indole (6d)

This compound was prepared according to the general procedure 1, yellow solid, 148.6 mg, 98%. The general procedure 2, 132.6 mg, 88%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.36 (s, 1H), 8.09 (s, 1H), 8.05-8.02 (m, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.42-7.37 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 142.4, 139.3, 138.7, 126.3, 125.2, 124.8, 124.6, 124.5, 123.2, 121.2, 120.5, 114.5, 113.2, 111.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9NSBr$ 301.9634; found 301.9628.



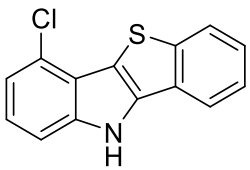
4-bromo-10*H*-benzo[4,5]thieno[3,2-b]indole (6e)

This compound was prepared according to the general procedure 1, yellow solid, 142.7 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.94-7.91 (m, 1H), 7.85-7.83 (m, 1H), 7.46-7.36 (m, 4H), 7.15 (t, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.6, 140.7, 137.2, 126.2, 124.6, 124.5, 124.4, 124.3, 124.0, 123.0, 119.6, 117.0, 113.8, 111.2. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_8BrNSNa$ 323.9453; found 323.9459.



1-chloro-10*H*-benzo[4,5]thieno[3,2-b]indole (6f)

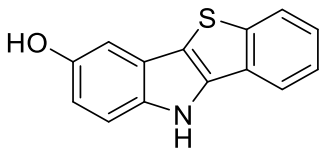
This compound was prepared according to the general procedure 1, white solid, 98.9 mg, 77%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.4 (s, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.51 (t, J = 8.0 Hz, 1H), 7.44-7.40 (m, 1H), 7.36 (dd, J = 8.0, 1.2 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 142.3, 138.3, 137.2, 126.5, 124.9, 124.7, 124.4, 123.3, 122.2, 121.0, 120.4, 117.9, 116.5, 114.7. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_8ClNSNa$ 279.9958; found 279.9962.



4-chloro-10*H*-benzo[4,5]thieno[3,2-b]indole (6g)

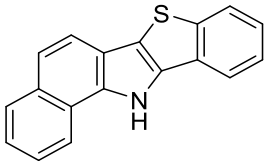
This compound was prepared according to the general procedure 1, white solid, 118.1 mg, 92%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.5 (s, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.29-7.22 (m, 2H). ^{13}C{^{1}H}

NMR (100 MHz, DMSO–d_6) δ 142.6, 141.2, 138.0, 126.1, 124.8, 124.7, 124.5, 123.8, 123.4, 120.5, 120.4, 118.8, 112.5, 111.6. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_8ClNSNa$ 279.9958; found 279.9976.



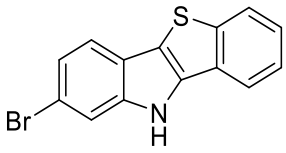
10*H*-benzo[4,5]thieno[3,2-b]indol-3-ol (6h)

This compound was prepared according to the general procedure 1, white solid, 100.0 mg, 84%. ^1H NMR (400 MHz, DMSO–d_6) δ 11.77 (s, 1H), 8.98 (s, 1H), 8.01-7.97 (m, 2H), 7.46 (td, J = 7.2, 1.2 Hz, 1H), 7.39-7.33 (m, 2H), 7.02 (d, J = 2.4 Hz, 1H), 6.79 (dd, J = 8.8, 2.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO–d_6) δ 151.0, 141.8, 138.0, 135.0, 126.8, 124.5, 124.4, 124.1, 122.1, 120.0, 113.1, 113.0, 112.9, 102.8. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{10}NOS$ 240.0478; found 240.0472.



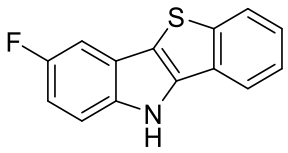
12*H*-benzo[g]benzo[4,5]thieno[3,2-b]indole (6i)

This compound was prepared according to the general procedure 1, white solid, 92.9 mg, 68%. ^1H NMR (400 MHz, DMSO–d_6) δ 12.94 (s, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.05-8.00 (m, 2H), 7.90 (d, J = 8.8 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.61 (d, J = 8.8 Hz, 1H), 7.55-7.49 (m, 2H), 7.39 (t, J = 8.0 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO–d_6) δ 141.6, 136.0, 135.3, 130.3, 128.7, 126.9, 125.8, 124.7, 124.5, 124.0, 122.5, 120.8, 120.2, 119.8, 118.9, 117.1, 115.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{12}NS$ 274.0685; found 274.0685.



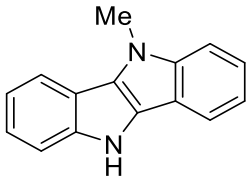
2-bromo-10*H*-benzo[4,5]thieno[3,2-b]indole (6j)

This compound was prepared according to the general procedure 2, yellow solid, 113.1 mg, 75%. ^1H NMR (400 MHz, DMSO–d_6) δ 12.33 (s, 1H), 8.10 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO–d_6) δ 142.2, 141.3, 138.2, 126.4, 124.7, 124.5, 122.2, 120.6, 120.4, 115.4, 115.1, 113.9. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_8NNaS$ 323.9453; found 323.9441.



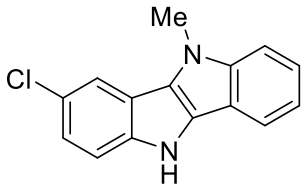
3-fluoro-10*H*-benzo[4,5]thieno[3,2-b]indole (6k)

This compound was prepared according to the general procedure 2, yellow solid, 102.4 mg, 85%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 12.23 (s, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.65 (dd, J = 9.6, 2.0 Hz, 1H), 7.61 (dd, J = 9.2, 4.8 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.14 (td, J = 9.2, 2.4 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 156.8 (d, J = 231.3 Hz), 142.3, 139.2, 137.2, 126.5, 124.7, 124.6, 124.5, 121.6 (d, J = 11.0 Hz), 126.4, 113.7 (d, J = 4.4 Hz), 113.5 (d, J = 9.8 Hz), 110.8 (d, J = 25.7 Hz), 104.0 (d, J = 24.5 Hz). HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_9FNS$ 242.0434; found 242.0424.



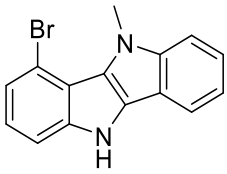
5-methyl-5,10-dihydroindolo[3,2-b]indole (8a)

This compound was prepared according to the general procedure 1, white solid, 107.9 mg, 98%. The general procedure 3, 94.3 mg, 86%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.20 (s, 1H), 7.96 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.26-7.18 (m, 2H), 7.13-7.07 (m, 2H), 4.10 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 140.8, 140.3, 126.8, 124.1, 121.6, 121.4, 118.0, 117.9, 117.7, 117.3, 114.5, 114.3, 112.2, 109.9, 31.4. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{13}N_2$ 221.1073; found 221.1067.



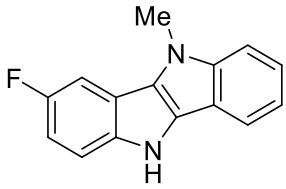
3-chloro-5-methyl-5,10-dihydroindolo[3,2-b]indole (8b)

This compound was prepared according to the general procedure 1, yellow solid, 125.7 mg, 99%. The general procedure 3, 108.1 mg, 85%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.43 (s, 1H), 8.03 (d, J = 2.4 Hz, 1H), 7.79-7.76 (m, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.52 (dd, J = 8.8, 0.4 Hz, 1H), 7.29-7.25 (m, 1H), 7.18 (dd, J = 8.8, 2.0 Hz, 1H), 7.14-7.10 (m, 1H), 4.09 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 141.2, 138.5, 126.0, 125.6, 122.4, 122.2, 121.2, 118.1, 118.0, 116.6, 115.1, 113.9, 113.5, 110.1, 31.4. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{12}ClN_2$ 255.0684; found 255.0689.



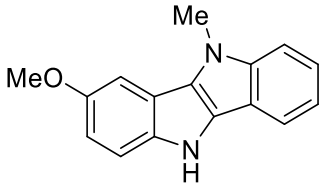
4-bromo-5-methyl-5,10-dihydroindolo[3,2-b]indole (8c)

This compound was prepared according to the general procedure 1, yellow solid, 119.4 mg, 80%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.80 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 8.4, 0.8 Hz, 1H), 7.35-7.30 (m, 2H), 7.17-7.09 (m, 2H), 4.31 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 142.0, 141.2, 126.5, 124.9, 122.8, 122.3, 122.2, 118.3, 117.9, 115.5, 113.3, 111.6, 110.5, 109.8, 34.6. HRMS (ESI–TOF) m/z: [M+H]$^{+}$ calcd for $C_{15}H_{12}BrN_2$ 299.0178; found 299.0184.



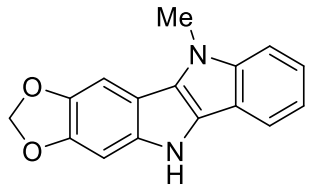
3-fluoro-5-methyl-5,10-dihydroindolo[3,2-b]indole (8d)

This compound was prepared according to the general procedure 1, yellow solid, 119.4 mg, 99%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.32 (s, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.56-7.50 (m, 2H), 7.27 (t, J = 7.2 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.06 (td, J = 9.2, 2.8 Hz, 1H), 4.08 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 156.3 (d, J = 229.4 Hz), 141.3, 137.0, 126.8 (d, J = 4.0 Hz), 126.2, 122.2, 118.1, 114.2, 114.0 (d, J = 10.5 Hz), 113.0 (d, J = 9.8 Hz), 110.7, 109.3 (d, J = 25.6 Hz), 102.5 (d, J = 24.5 Hz), 31.3. HRMS (ESI–TOF) m/z: [M+H]$^{+}$ calcd for $C_{15}H_{12}FN_2$ 239.0979; found 239.0985.



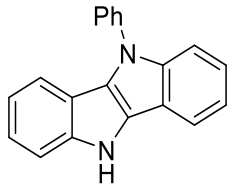
3-methoxy-5-methyl-5,10-dihydroindolo[3,2-b]indole (8e)

This compound was prepared according to the general procedure 1, white solid, 103.7 mg, 83%. The general procedure 3, 88.6 mg, 71%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 10.96 (s, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 2.4 Hz, 1H), 7.39 (d, J = 7.2 Hz, 1H), 7.25-7.21 (m, 1H), 7.09 (t, J =7.2 Hz, 1H), 6.85 (dd, J = 8.8, 2.4 Hz, 1H), 4.09 (s, 3H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 152.7, 141.0, 135.6, 126.9, 125.2, 121.5, 117.8, 117.7, 114.4 (two peaks), 112.8, 111.2, 109.9, 100.0, 55.7, 31.4. HRMS (ESI–TOF) m/z: [M+H]$^{+}$ calcd for $C_{16}H_{15}N_2O$ 251.1179; found 251.1184.



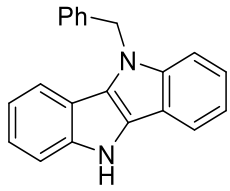
5-methyl-5,10-dihydro-[1,3]dioxolo[4,5-f]indolo[3,2-b]indole (8f)

This compound was prepared according to the general procedure 1, white solid, 106.7 mg, 81%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.00 (s, 1H), 7.67 (m, 1H), 7.50-7.47 (m, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.06-7.04 (m, 2H), 6.00 (s, 2H), 4.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 144.0, 141.2, 140.4, 135.6, 127.4, 123.4, 120.7, 117.8, 117.0, 114.7, 109.7, 107.7, 100.3, 96.6, 93.4, 31.2. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{13}N_2O_2$ 265.0972; found 265.0977.



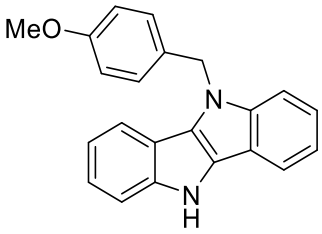
5-phenyl-5,10-dihydroindolo[3,2-b]indole (8g)

This compound was prepared according to the general procedure 1, yellow solid, 134.1 mg, 95%. The general procedure 3, 105.9 mg, 75%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.51 (s, 1H), 7.90-7.87 (m, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.50-7.43 (m, 2H), 7.29-7.20 (m, 3H), 7.04 (t, J = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 140.4, 139.9, 138.5, 129.9, 126.4, 126.0, 125.1, 124.8, 122.7, 121.8, 119.7, 118.3, 118.2, 117.5, 115.7, 114.1, 112.5, 110.6. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}N_2$ 283.1230; found 283.1235.



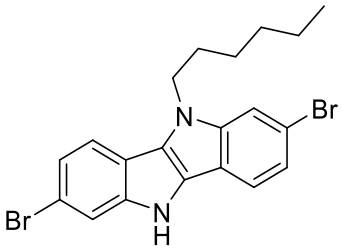
5-benzyl-5,10-dihydroindolo[3,2-b]indole (8h)

This compound was prepared according to the general procedure 1, white solid, 109.4 mg, 74%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.27 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.26-7.10 (m, 8H), 7.04-7.00 (m, 1H), 5.78 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 140.6, 140.3, 138.7, 128.5, 127.2, 126.7, 126.1, 127.7, 121.7, 121.6, 118.3, 118.1, 117.8, 117.4, 114.6, 114.4, 112.2, 110.4, 47.8. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}N_2$ 297.1386; found 297.1392.



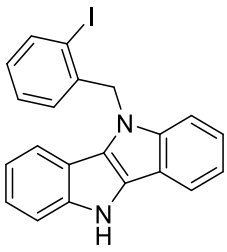
5-(4-methoxybenzyl)-5,10-dihydroindolo[3,2-b]indole (8i)

This compound was prepared according to the general procedure 1, white solid, 141.1 mg, 86%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.25 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 7.18-7.15 (m, 3H), 7.12-7.09 (m, 1H), 7.05-7.01 (m, 1H), 6.81-6.78 (m, 2H), 5.70 (s, 2H), 3.64 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO–d_6) δ 158.4, 140.5, 140.3, 130.6, 128.0, 126.1, 124.7, 121.6, 121.5, 118.2, 118.1, 117.8, 117.5, 114.6, 114.4, 113.9, 112.2, 110.4, 55.0, 47.3. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{22}H_{18}N_2ONa$ 349.1311; found 349.1320.



2,7-dibromo-5-hexyl-5,10-dihydroindolo[3,2-*b*]indole (8j)

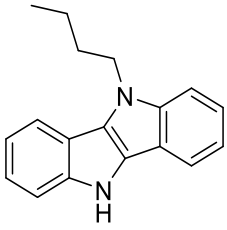
This compound was prepared according to the general procedure 1, white solid, 174.5 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 5.6, 1.6 Hz, 2H), 7.54 (d, J = 8.4 Hz, 1H), 7.31 (dd, J = 8.4, 1.6 Hz, 1H), 7.26-7.24 (m, 1H), 4.35 (t, J = 7.2 Hz, 2H), 1.92-1.86 (m, 2H), 1.39-1.24 (m, 6H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.4, 142.2, 127.3, 124.2, 122.8, 121.7, 119.0, 118.6, 115.9, 115.7, 115.3, 114.3, 113.2, 113.0, 45.6, 31.6, 30.3, 26.8, 22.6, 14.1. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}N_2Br_2$ 447.0066; found 447.0051.



5-(2-iodobenzyl)-5,10-dihydroindolo[3,2-b]indole (8k)

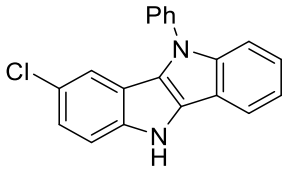
This compound was prepared according to the general procedure 1, yellow solid, 137.1 mg, 65%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.36 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.55-7.50 (m, 2H), 7.45 (d, J = 7.6 Hz, 1H), 7.24-7.21 (m, 1H), 7.18-7.13 (m, 2H), 7.09 (t, J = 7.6

Hz, 1H), 7.00-6.95 (m, 2H), 6.28 (d, *J* = 7.6 Hz, 1H), 5.73 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–d_6) δ 140.6, 140.3, 139.9, 139.3, 129.4, 128.4, 126.6, 125.9, 124.8, 122.0, 121.7, 118.6, 118.3, 118.0, 116.9, 114.6, 114.2, 112.4, 110.2, 97.4, 53.2. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}IN_2$ 423.0353; found 423.0343.



5-butyl-5,10-dihydroindolo[3,2-b]indole (8l)

This compound was prepared according to the general procedure 1, yellow solid, 114.5 mg, 85%. The general procedure 3, 104.8 mg, 80%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.21 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.24-7.18 (m, 2H), 7.12-7.07 (m, 2H), 4.52 (t, *J* = 7.2 Hz, 2H), 1.86-1.79 (m, 2H), 1.32-1.24 (m, 2H), 0.85 (t, *J* = 7.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–d_6) δ 140.3, 140.2, 126.1, 124.3, 121.5, 121.4, 118.1, 117.7, 114.4, 114.2, 112.2, 110.0, 44.2, 32.2, 19.6, 13.8. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{19}N_2$ 263.1543; found 263.1541.



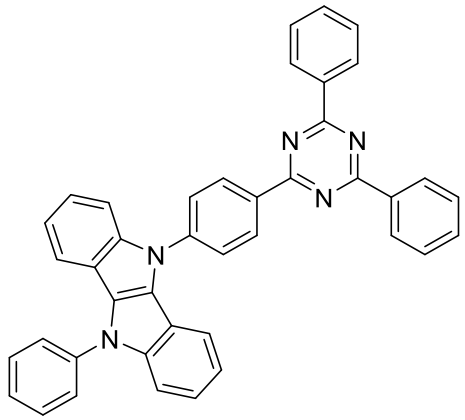
3-chloro-5-phenyl-5,10-dihydroindolo[3,2-b]indole (8m)

This compound was prepared according to the general procedure 3, yellow solid, 105.9 mg, 67%. ^{1}H NMR (400 MHz, DMSO–d_6) δ 11.74 (s, 1H), 7.90-7.88 (m, 1H), 7.78-7.70 (m, 4H), 7.62-7.58 (m, 2H), 7.53-7.48 (m, 1H), 7.33-7.23 (m, 3H), 7.21 (dd, *J* = 8.8, 2.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO–d_6) δ 140.3, 138.6, 138.2, 130.0, 127.5, 126.7, 124.8, 124.2, 123.4, 122.4, 121.5, 119.9, 118.5, 116.3, 115.3, 114.7, 114.0, 110.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{14}ClN_2$ 317.0840; found 4317.0827.

Synthesis of 10

^{t}BuOK (99 mmol, 11.1 g), **7g** (45 mmol, 18.5 g) and $CuSO_4$ (2.25 mmol, 359 mg) were weighed directly into a 2000 mL round bottom flask and dried under high vacuum for 15 min. PhCl (900 mL) was added under argon and stirred at 90 °C until the disappearance of **7b**. The resulting mixture was cooled to RT, filtered through a silica gel pad and washed with EtOAc. The filtrate was concentrated and purified by chromatography on silica gel (PE/EA = 200/1 to PE/EA = 30/1) to

afford the corresponding product **8g** as a yellow solid (11.8 g, 93%). To **8g** (41.8 mmol, 11.8 g) in 350 mL DMF was added in an ice bath. Then NaH was added. After stirring for 30 min, **9** (54.3 mmol, 17.8 g) was added. The reaction mixture was stirred at 60 ºC. The resulting reaction mixture was monitored by TLC. Upon completion of astarting materials, the reaction was cooled to RT. EtOAc (1 L) was added. Filtered get **10** as a yellow solid (20.7 g, 84%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10-9.06 (m, 2H), 8.87-8.84 (m, 4H), 8.02-7.99 (m, 2H), 7.80-7.75 (m, 1H), 7.69-7.57 (m, 10H), 7.52-7.48 (m, 1H), 7.34-7.29 (m, 2H), 7.20-7.15 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.0, 171.2, 142.8, 141.2, 140.8, 138.8, 136.4, 134.2, 132.8, 130.7, 129.9, 129.2, 128.9, 127.5, 127.1, 126.3, 126.1, 125.4, 123.3, 123.0, 120.3, 119.9, 118.9, 118.8, 116.4, 115.8, 111.2, 111.1. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{41}H_{28}N_5$ 590.2345; found 590.2336.

3. X-Ray Crystallographic Data

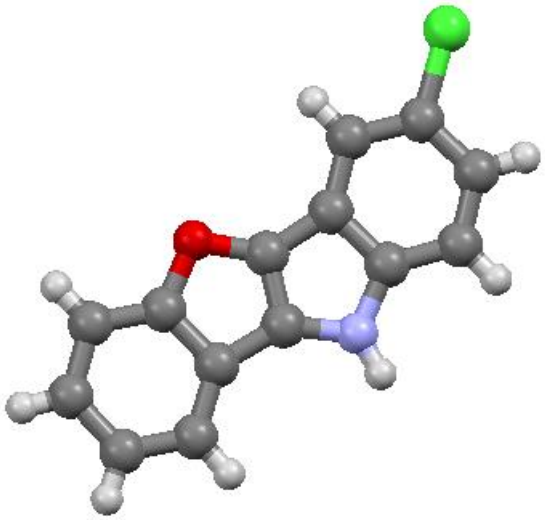


Table S1 Crystal data and structure refinement for 3-chloro-10*H*-benzofuro[3,2-b]indole

Empirical formula	$C_{14}H_8ClNO$
Formula weight	241.66
Temperature/K	291(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	14.7356(3)
b/Å	5.75805(13)
c/Å	24.9630(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2118.07(7)
Z	8
ρcalcg/cm^3	1.516
μ/mm^{-1}	3.014
F(000)	992.0
Crystal size/mm^3	0.23 × 0.22 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.082 to 147.156

Index ranges	$-11 \leq h \leq 17, -4 \leq k \leq 6, -30 \leq l \leq 30$
Reflections collected	4814
Independent reflections	2073 [R_{int} = 0.0201, R_{sigma} = 0.0198]
Data/restraints/parameters	2073/0/155
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1= 0.0379, wR_2= 0.0996
Final R indexes [all data]	R_1= 0.0398, wR_2 = 0.1019
Largest diff. peak/hole / e $Å^{-3}$	0.29/-0.27

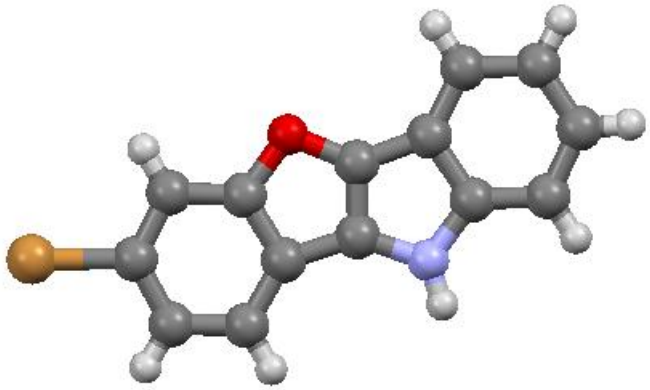


Table S2 Crystal data and structure refinement for 7-bromo-10*H*-benzofuro[3,2-b]indole

Empirical formula	$C_{14}H_8BrNO$
Formula weight	286.12
Temperature/K	291(2)
Crystal system	orthorhombic
Space group	Pca21
a/Å	8.28779(11)
b/Å	5.59996(10)
c/Å	24.2843(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1127.07(3)
Z	4

ρcalcg/cm^3	1.686
μ/mm^{-1}	4.806
F(000)	568.0
Crystal size/mm^3	0.2 × 0.2 × 0.17
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.28 to 147.562
Index ranges	-10 ≤ h ≤ 10, -5 ≤ k ≤ 6, -29 ≤ l ≤ 29
Reflections collected	9432
Independent reflections	2233 [R_{int} = 0.0332, R_{sigma} = 0.0189]
Data/restraints/parameters	2233/1/155
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0305, wR_2 = 0.0831
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0833
Largest diff. peak/hole / e Å^{-3}	0.33/-0.30
Flack parameter	0.00(2)

4. Reference

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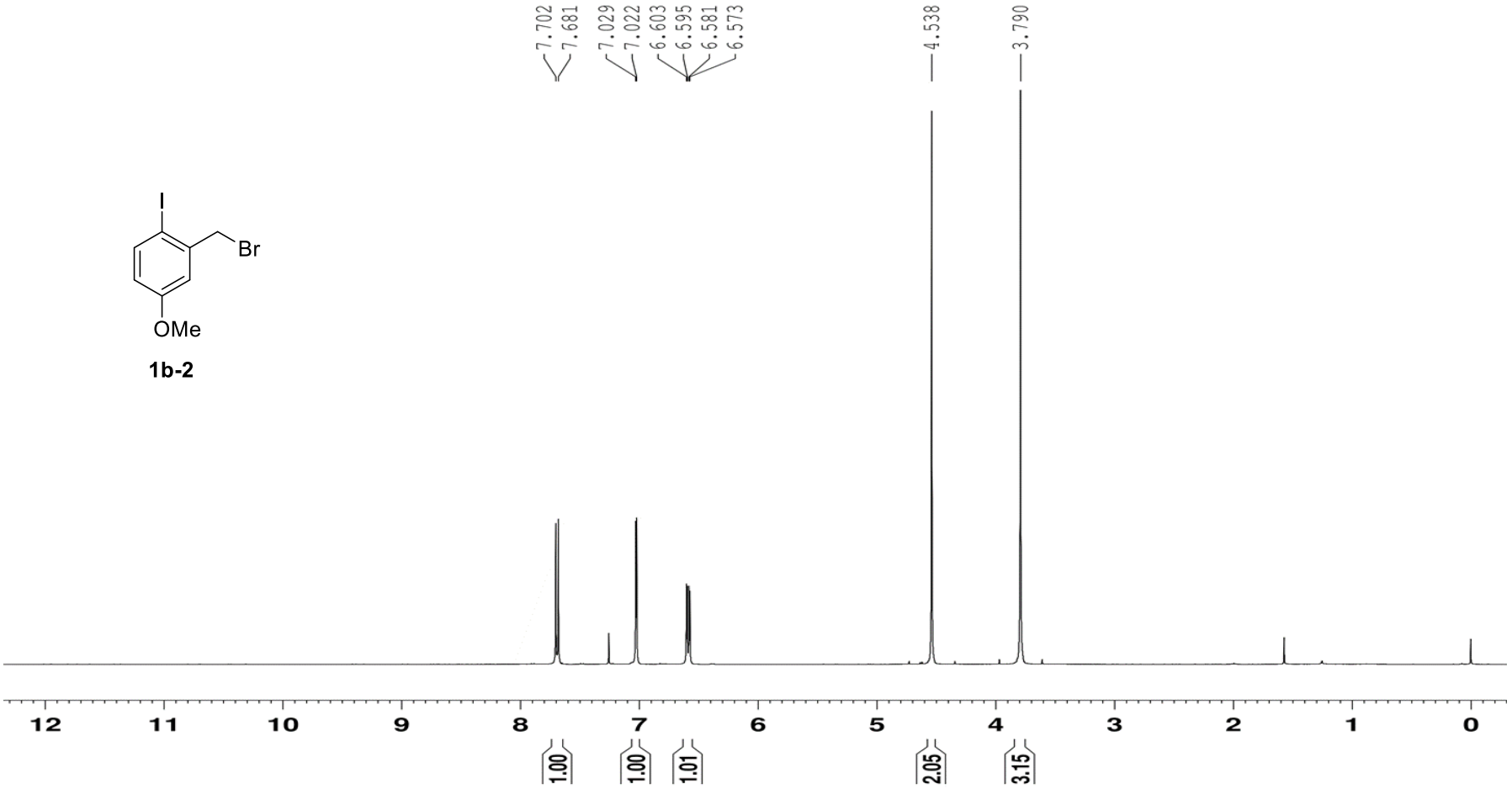
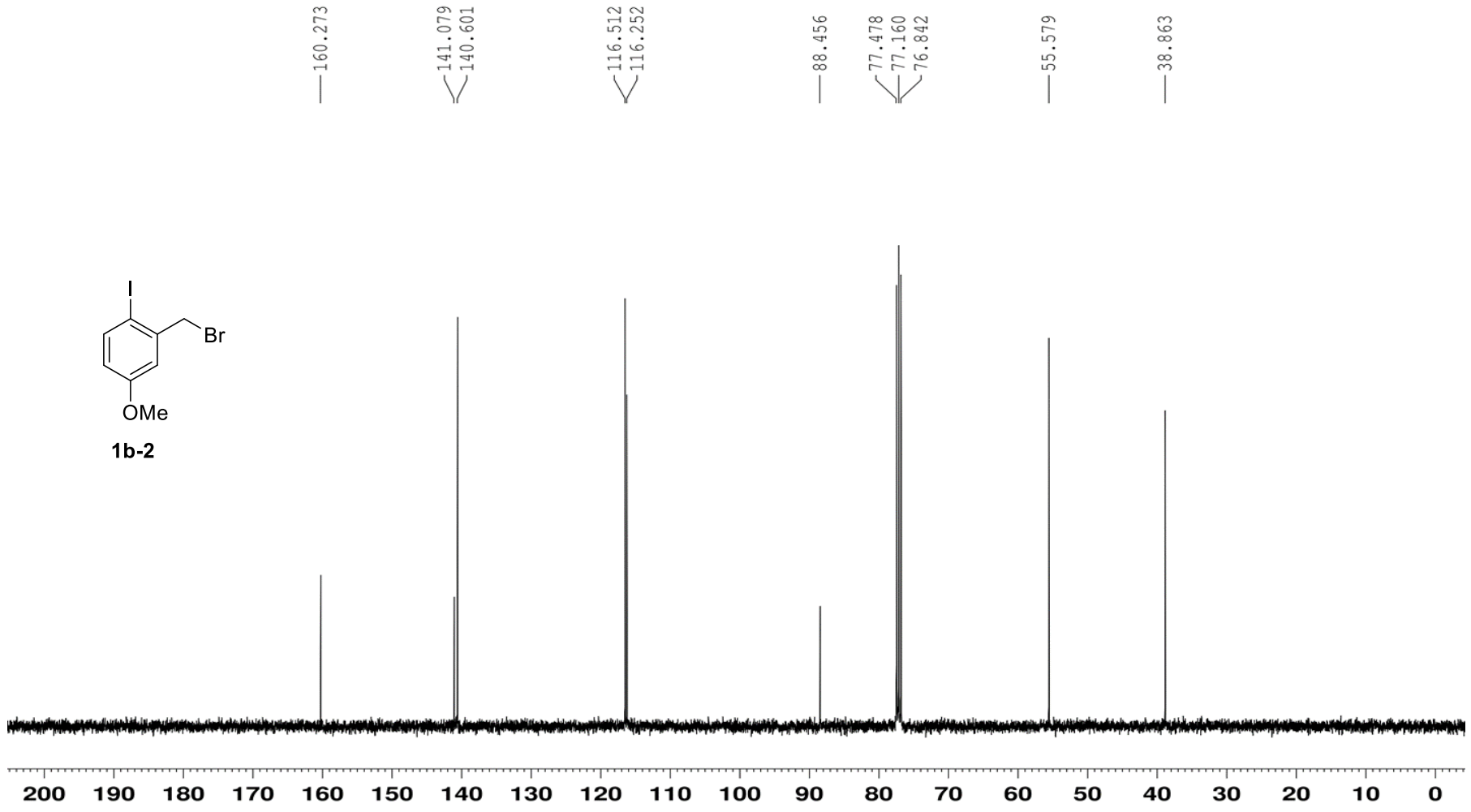
5. NMR spectra




160.273
141.079
140.601
116.512
116.252
88.456
77.478
77.160
76.842
55.579
38.863
I
Br
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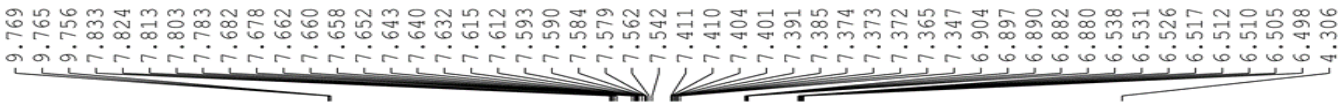
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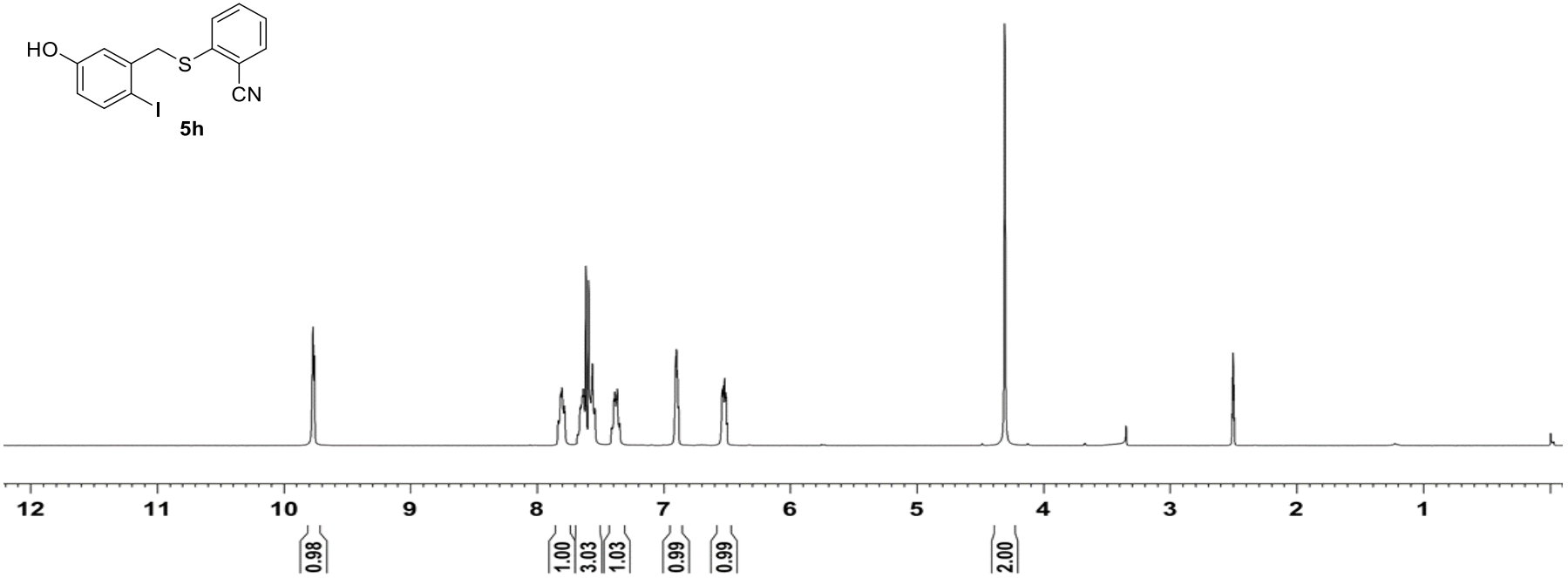
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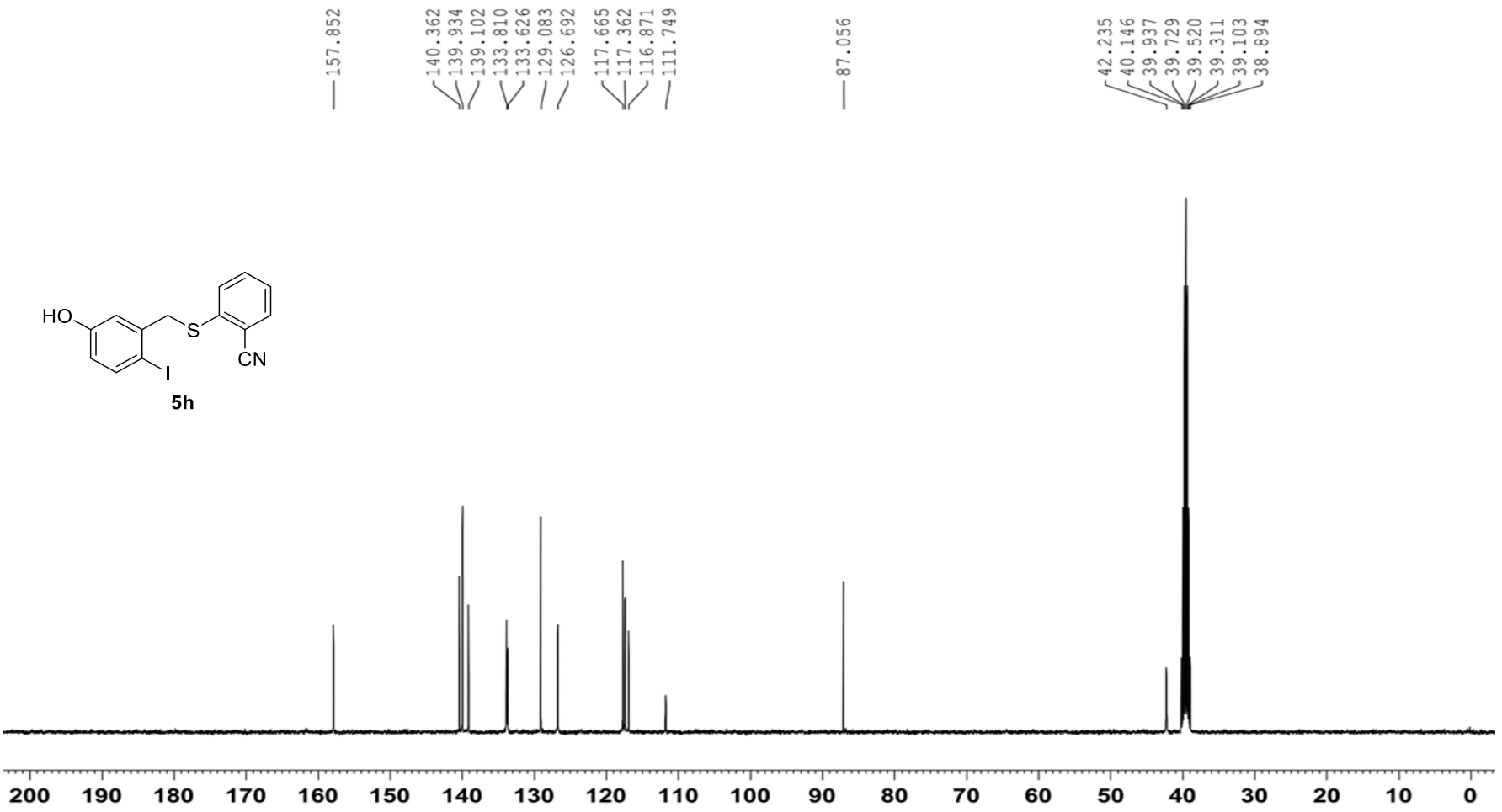
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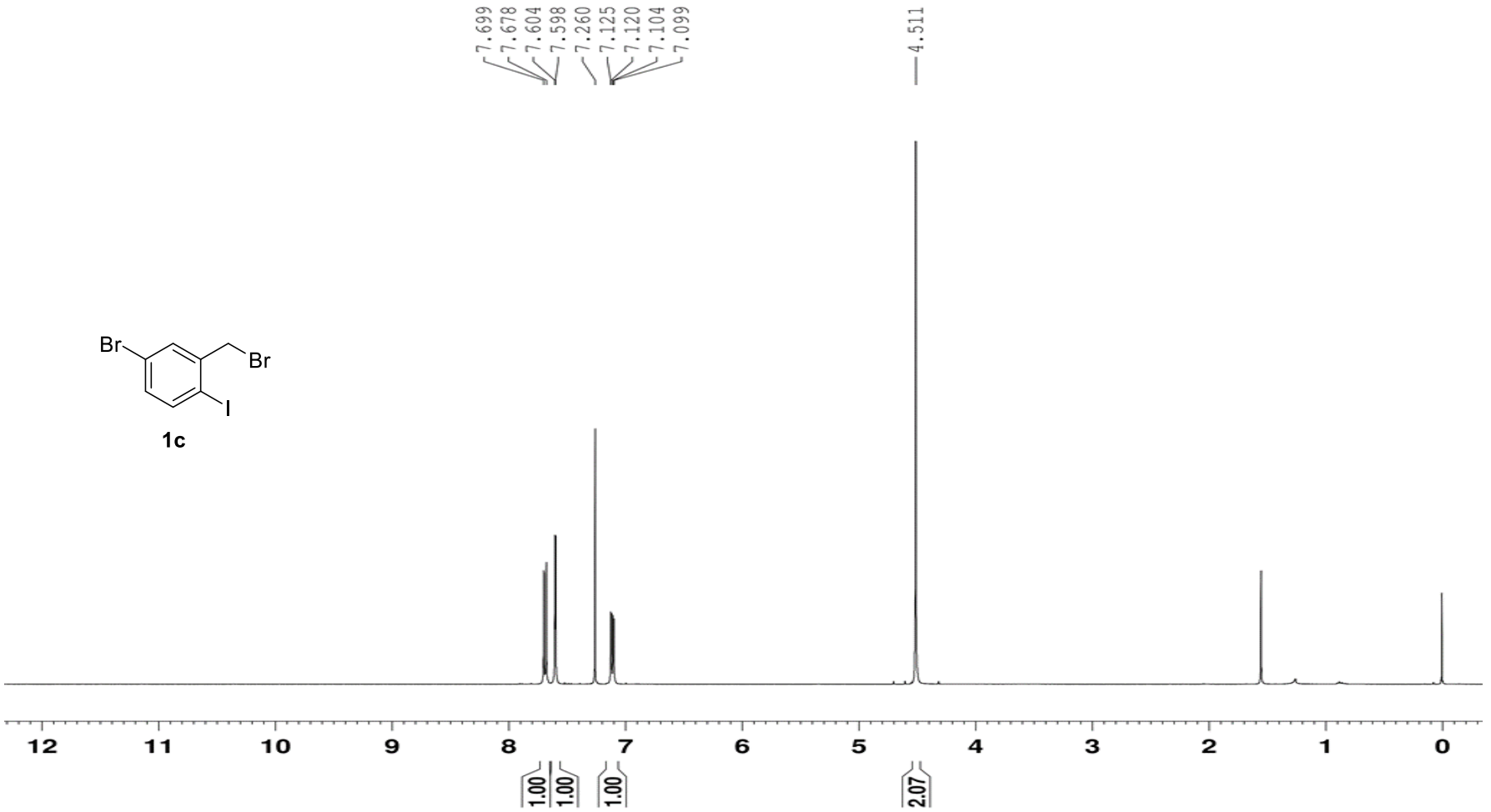
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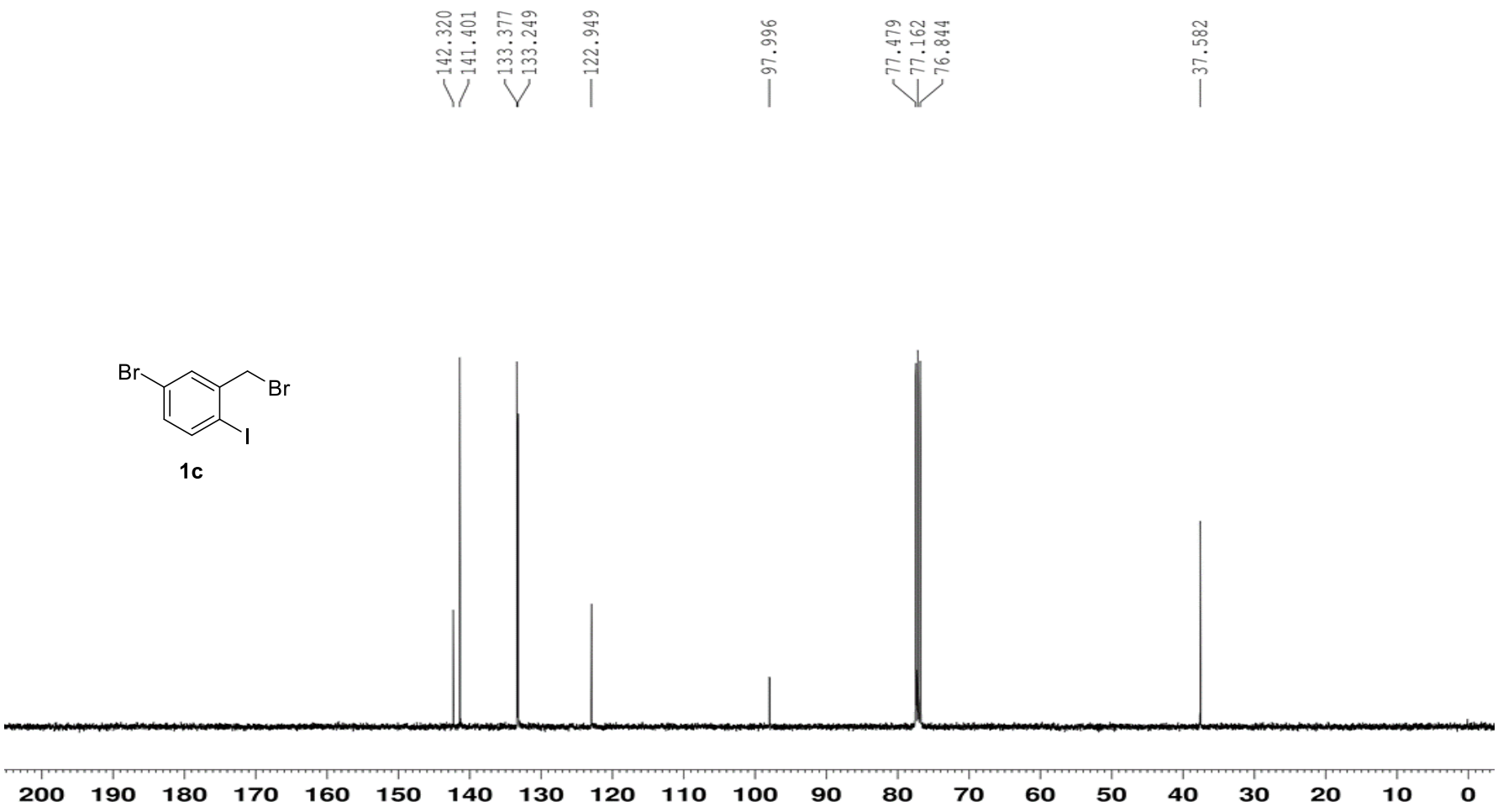
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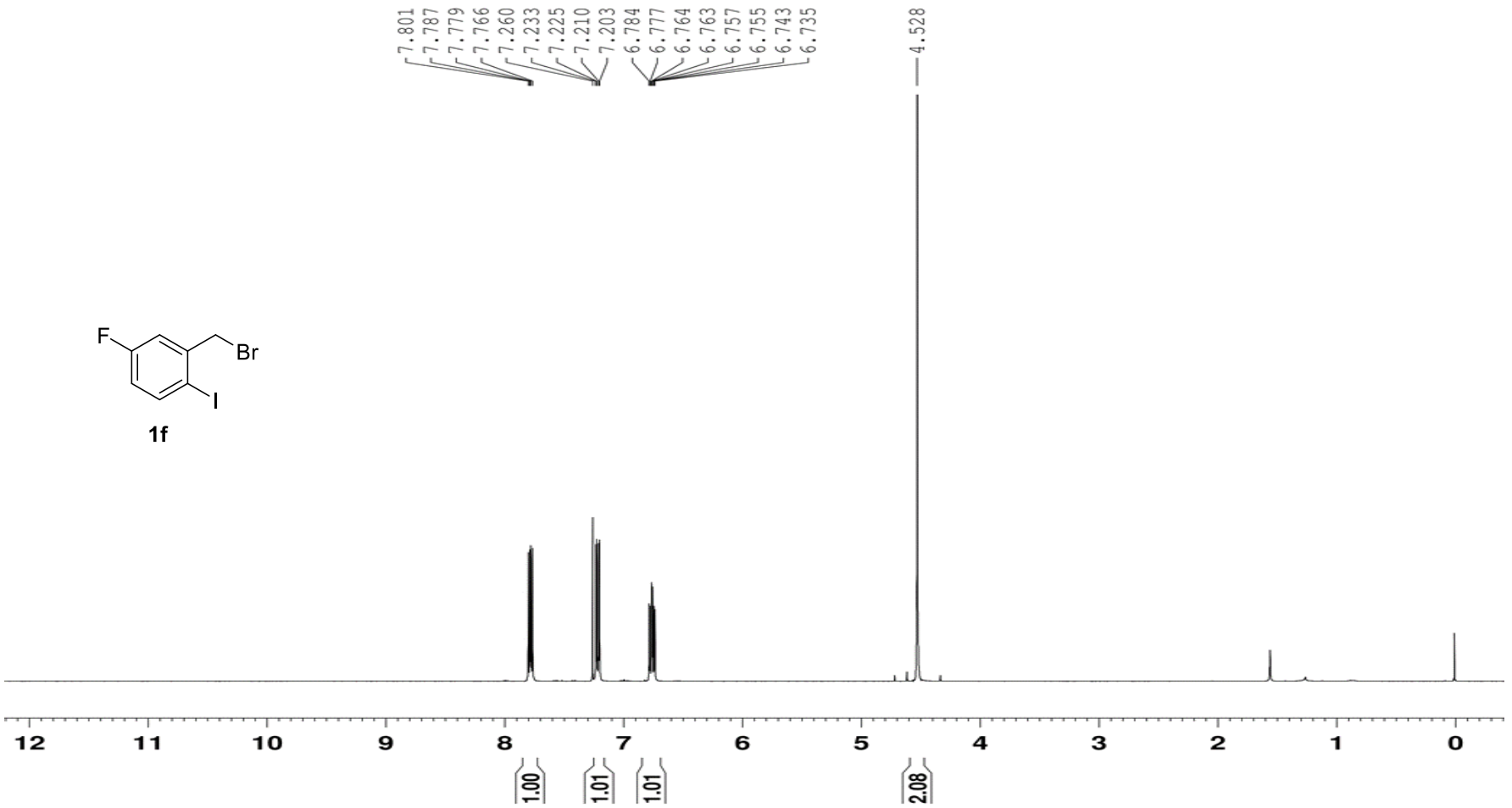
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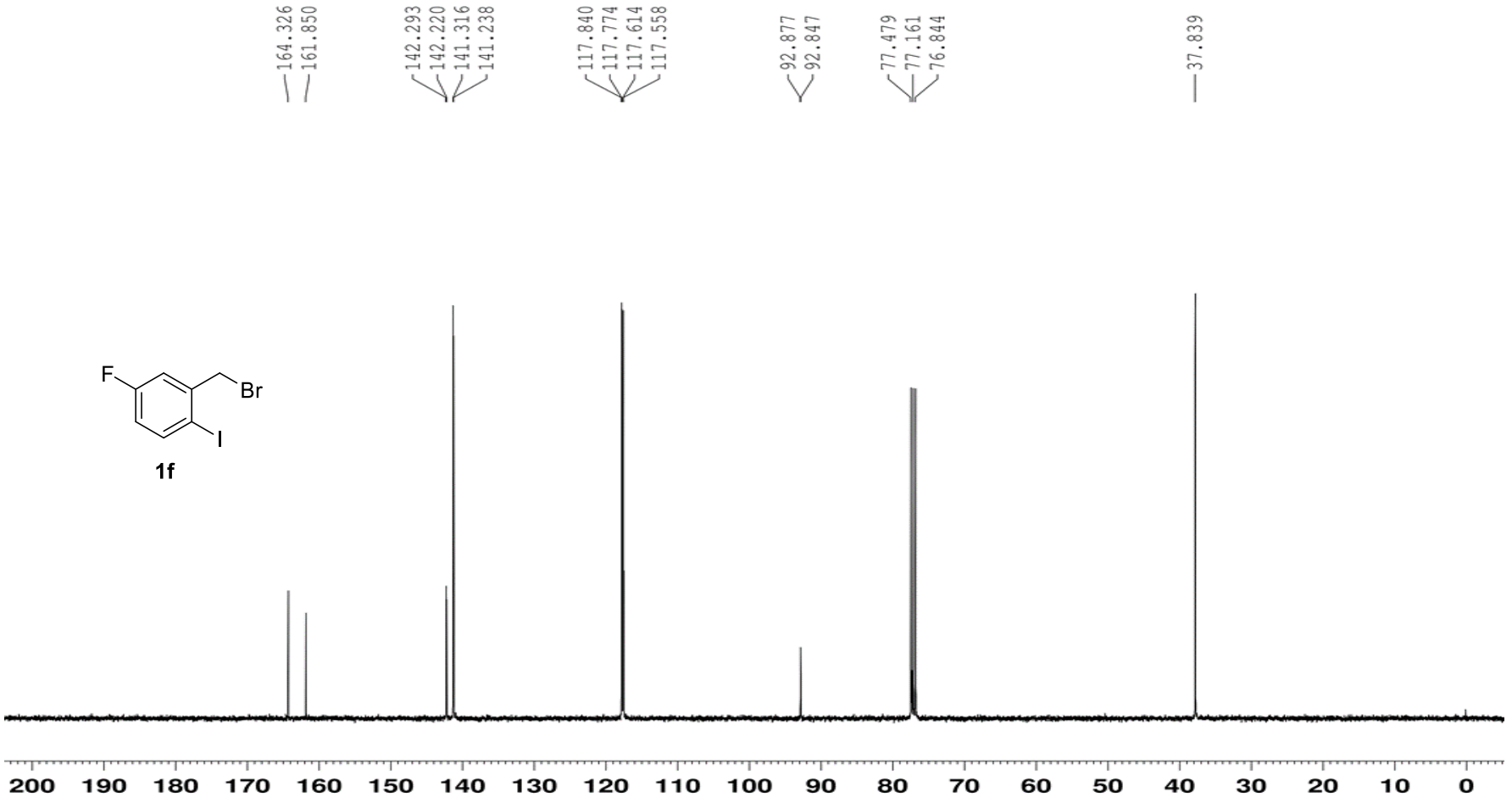
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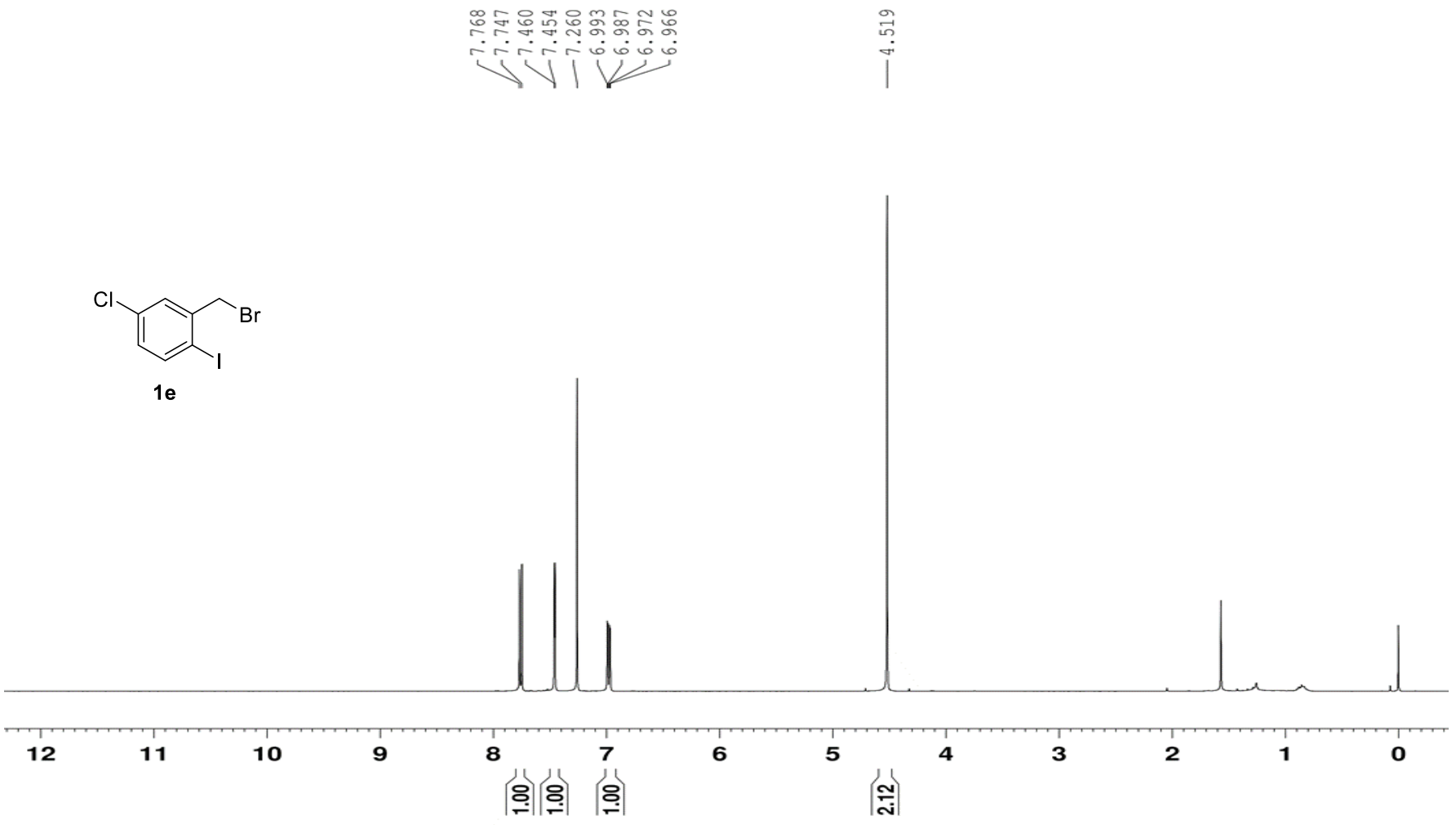
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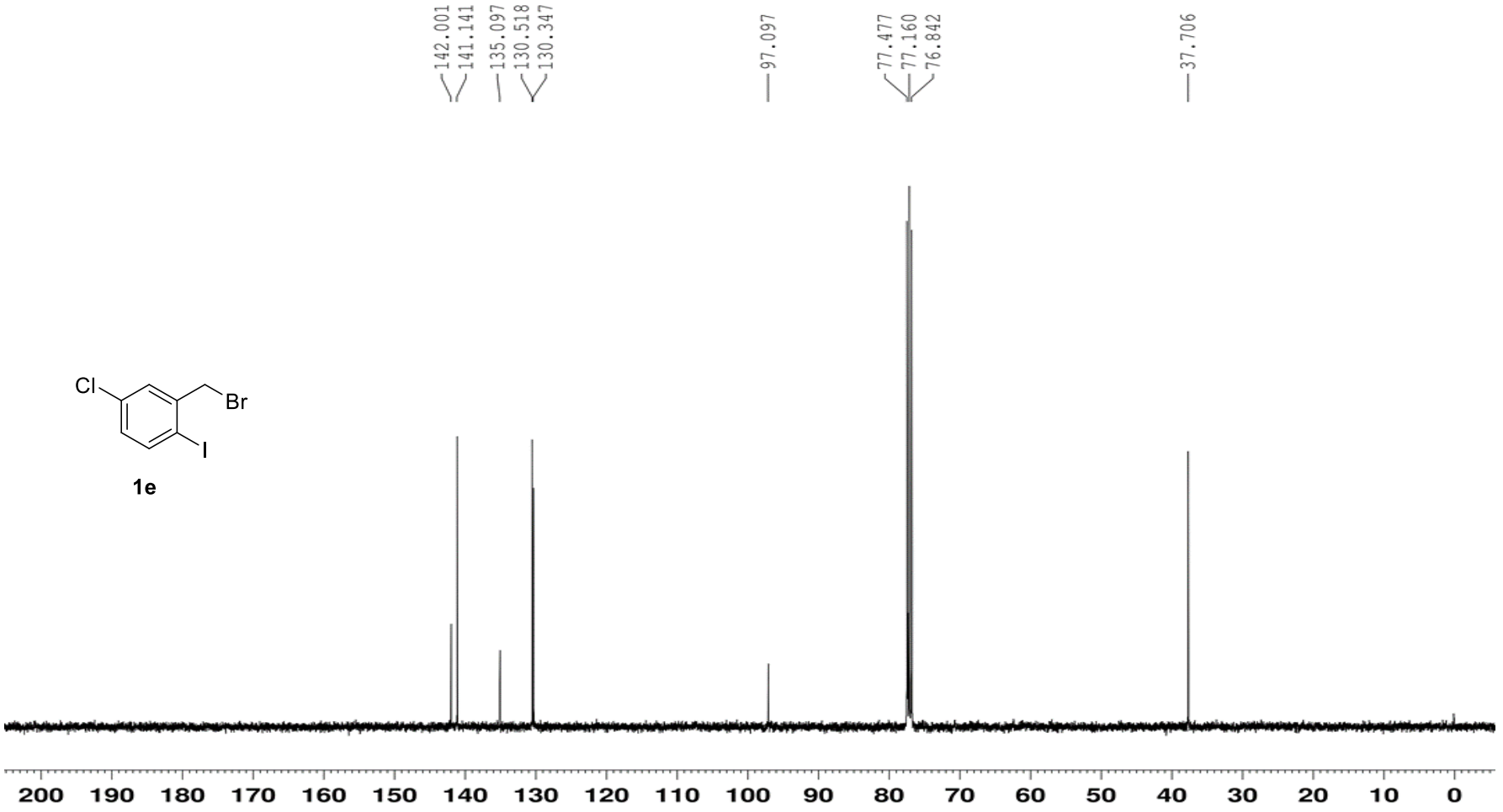
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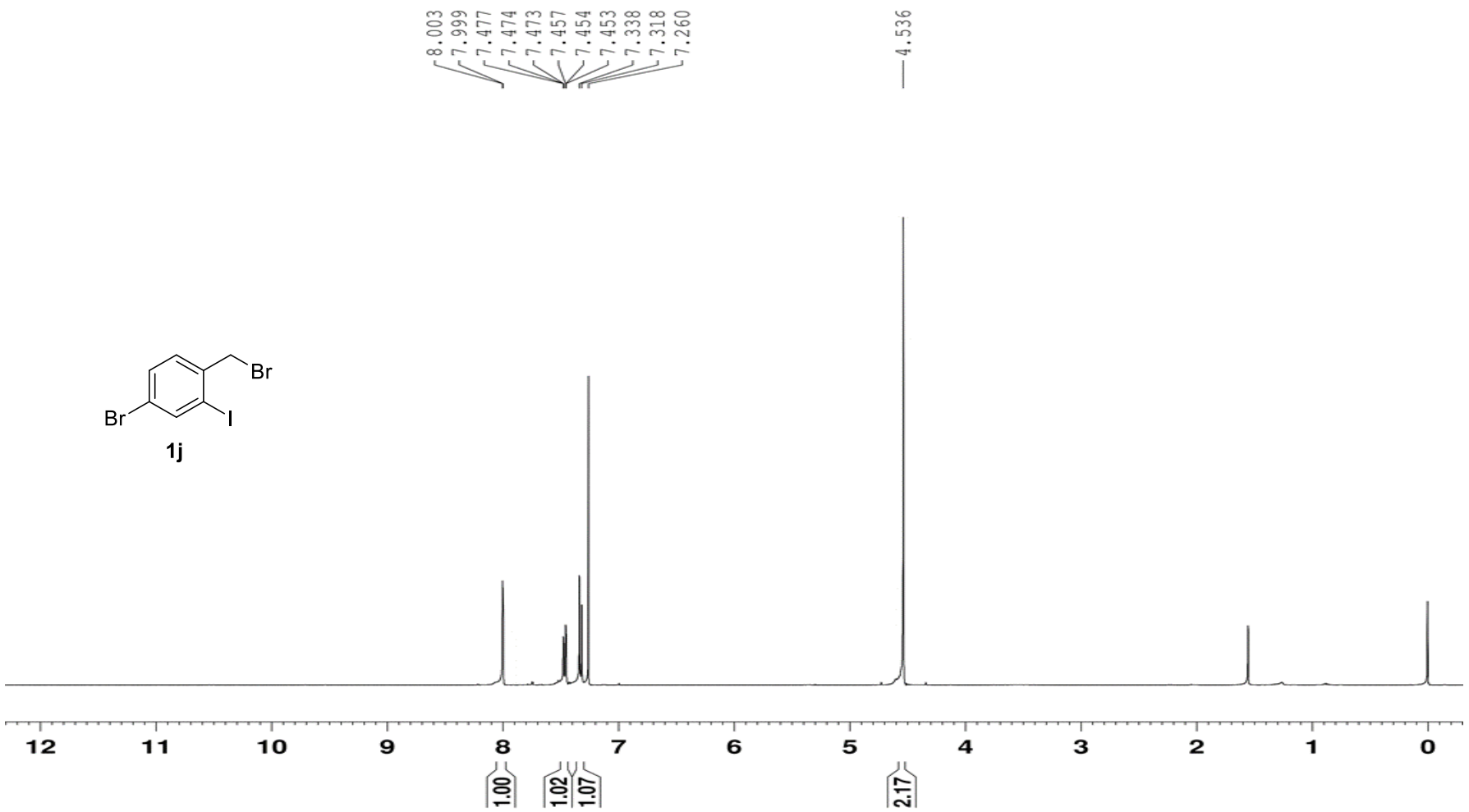
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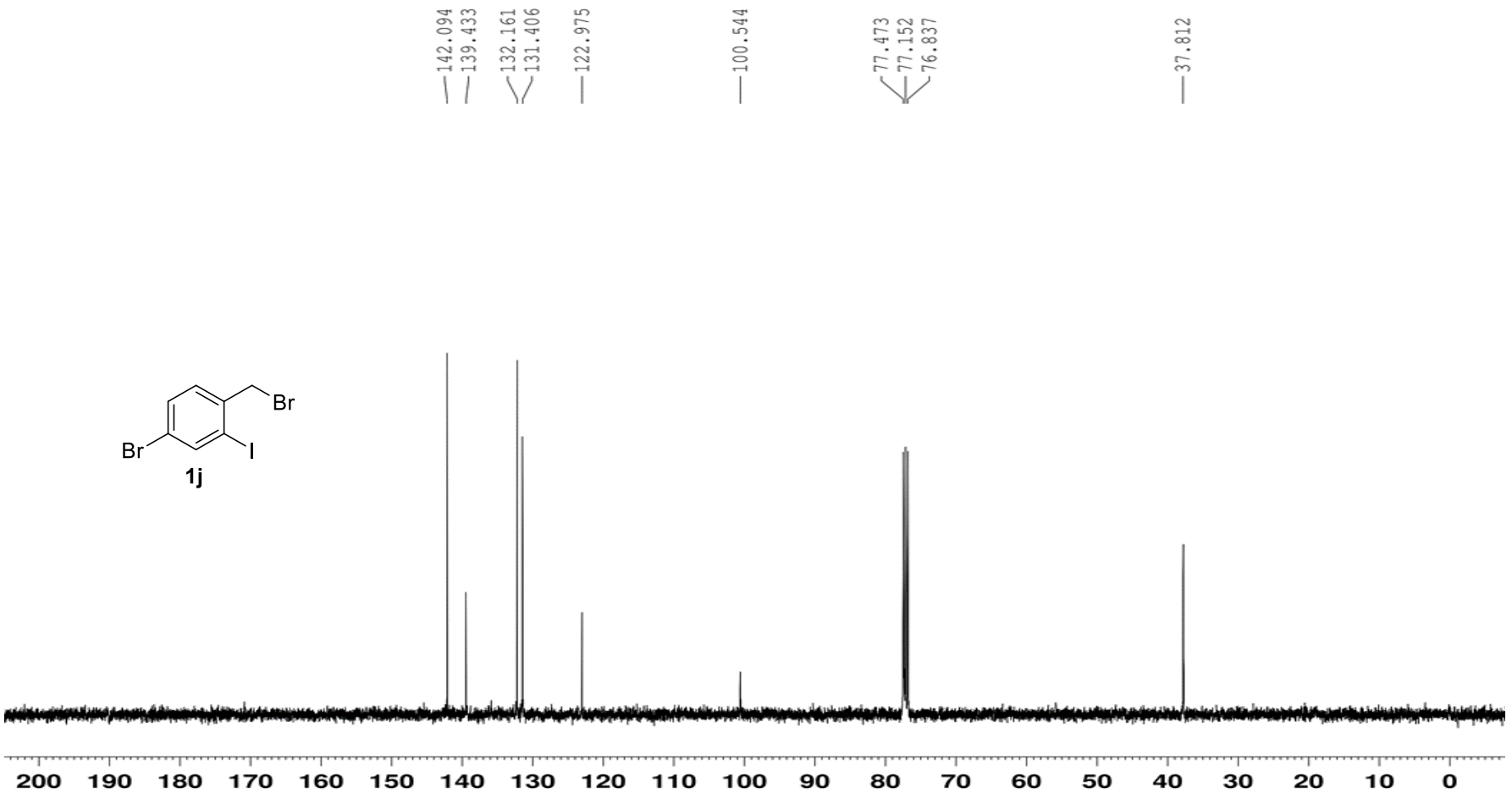
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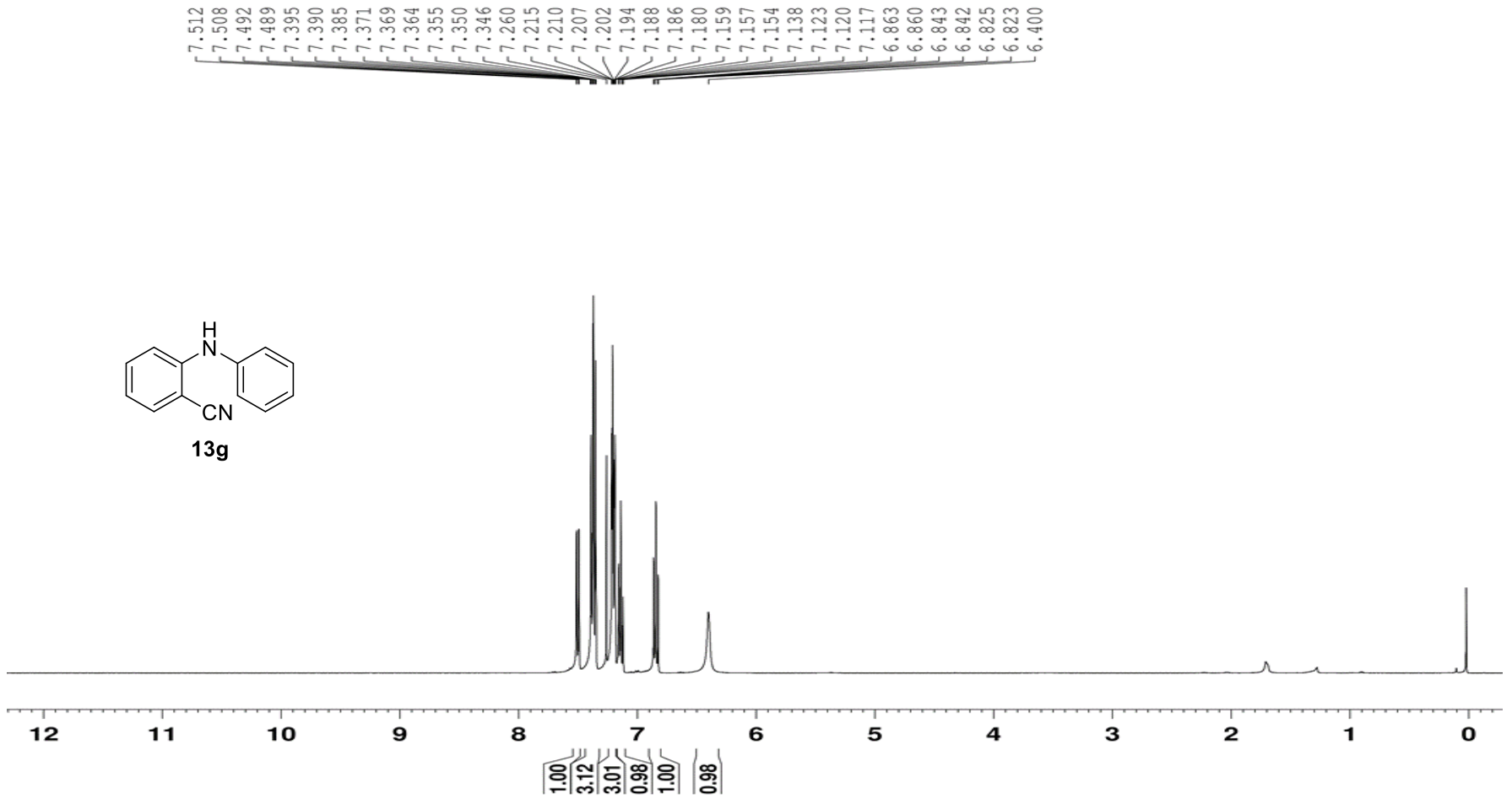
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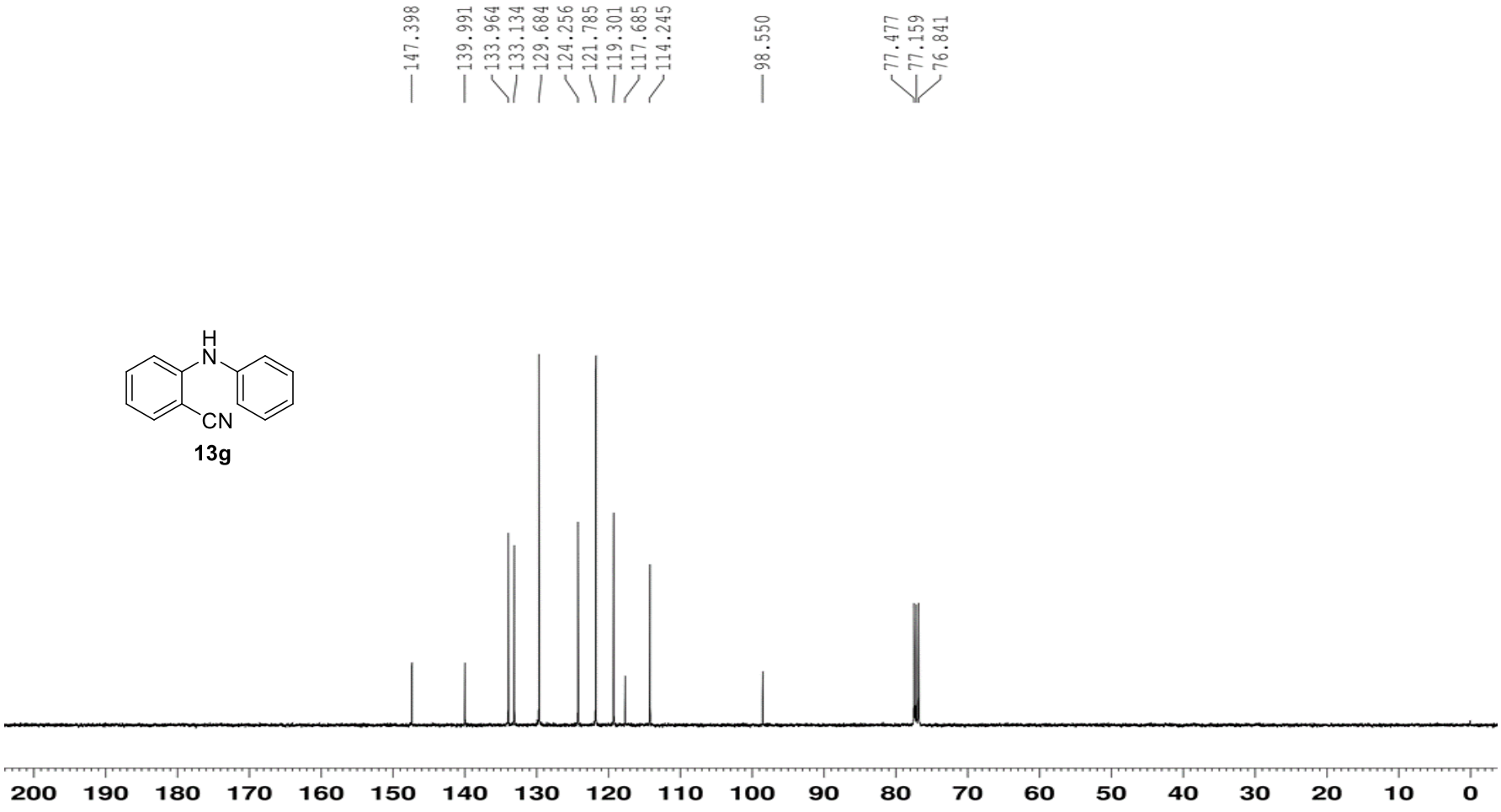
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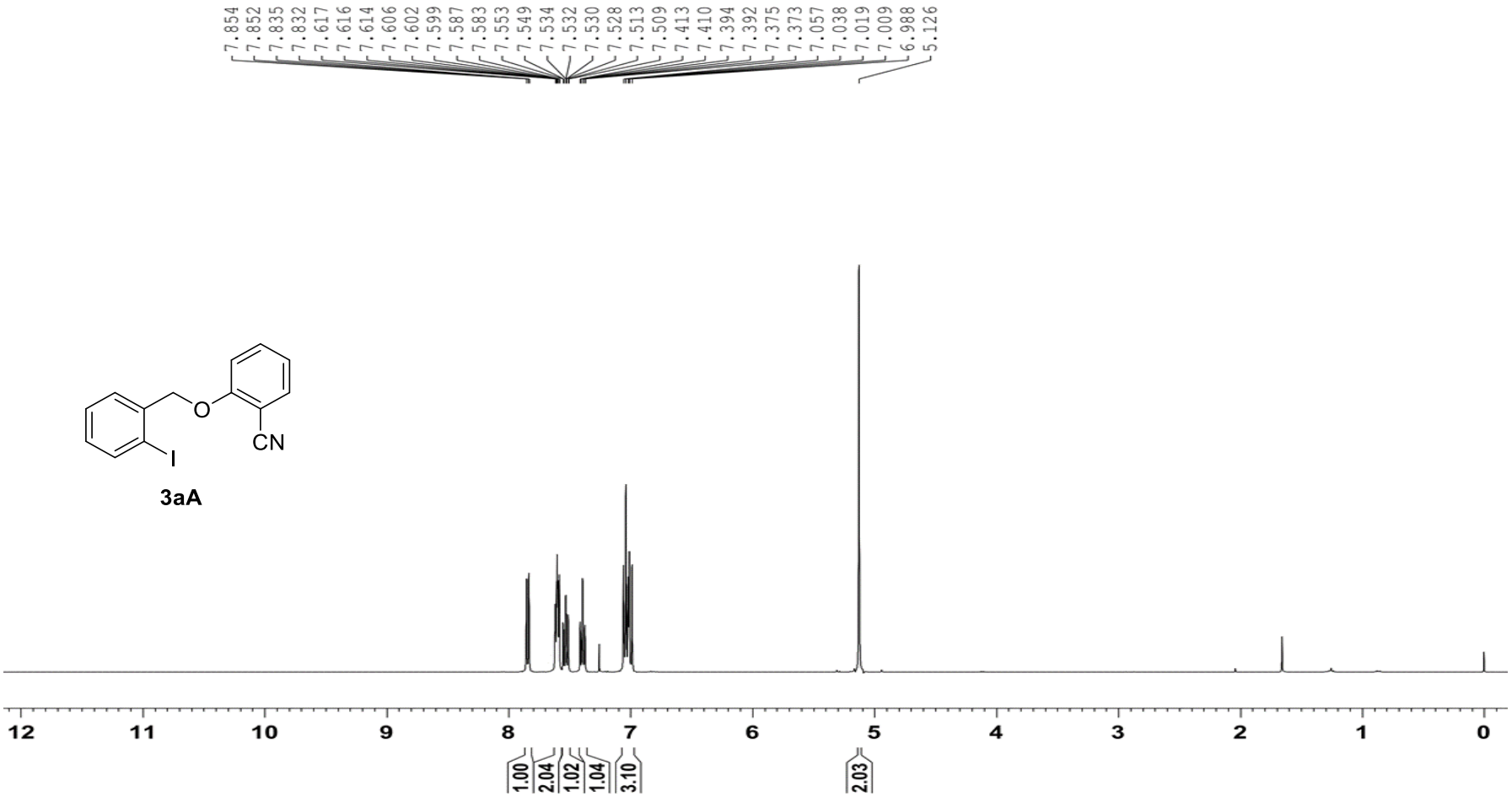
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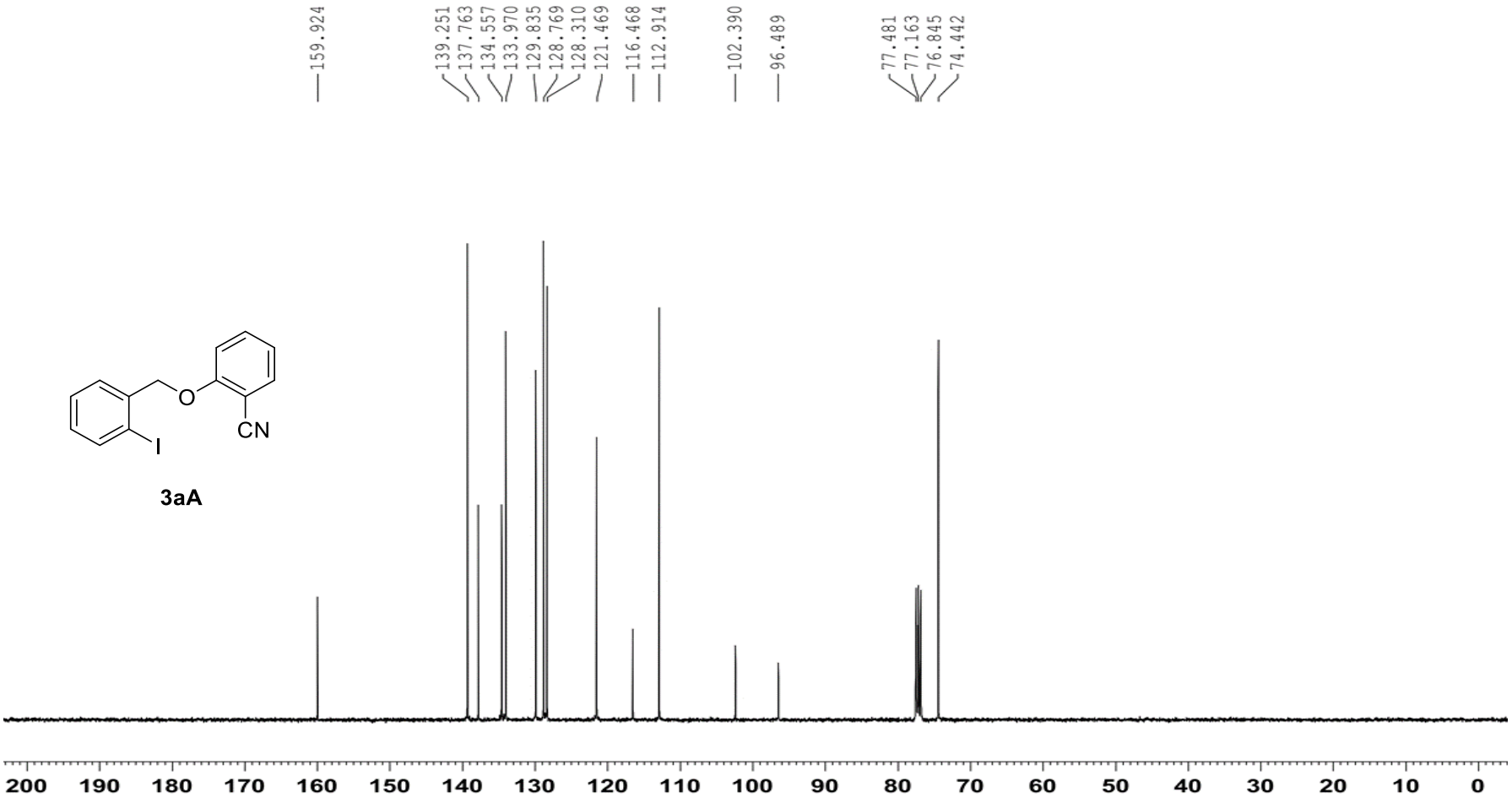
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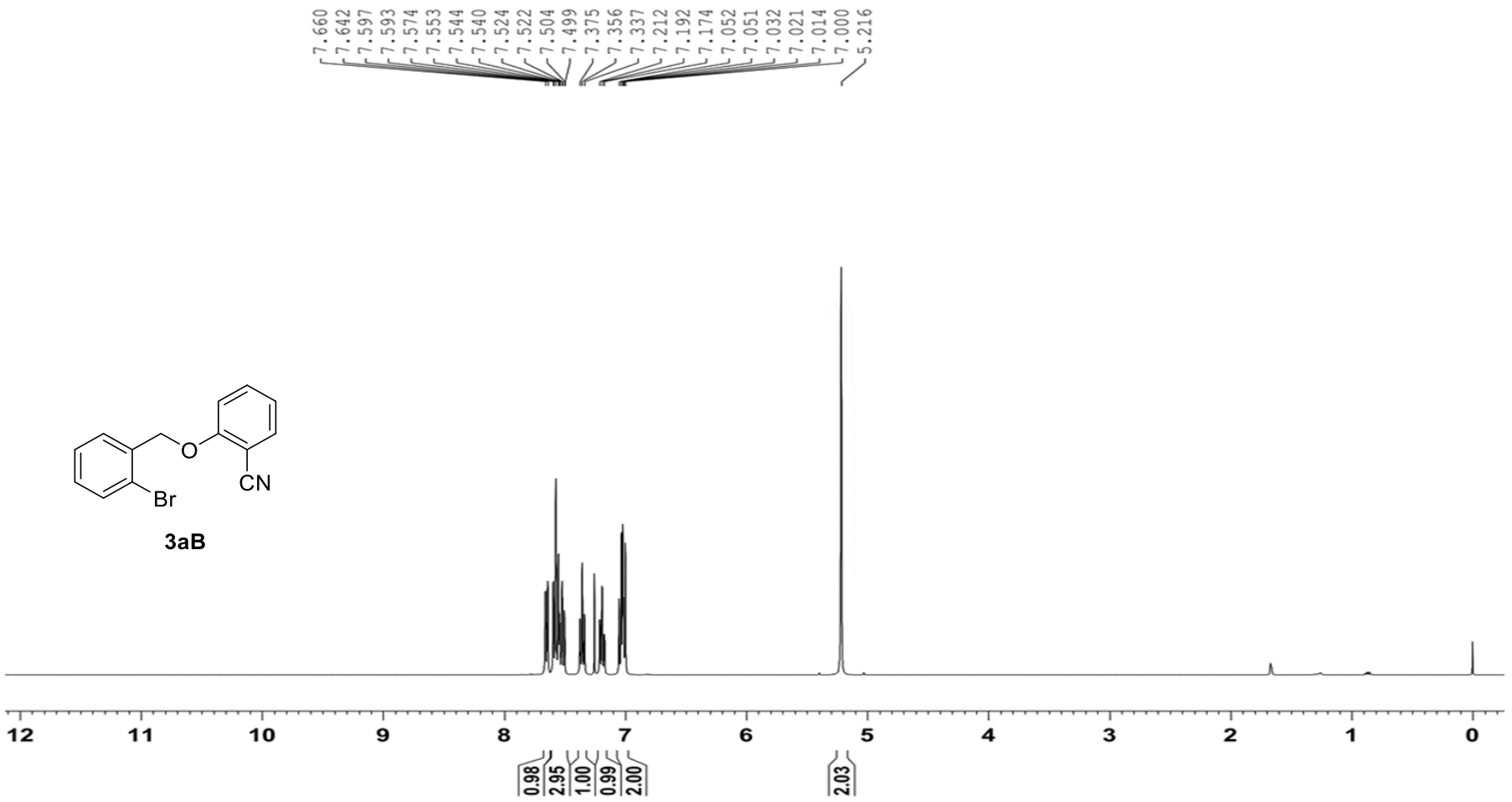
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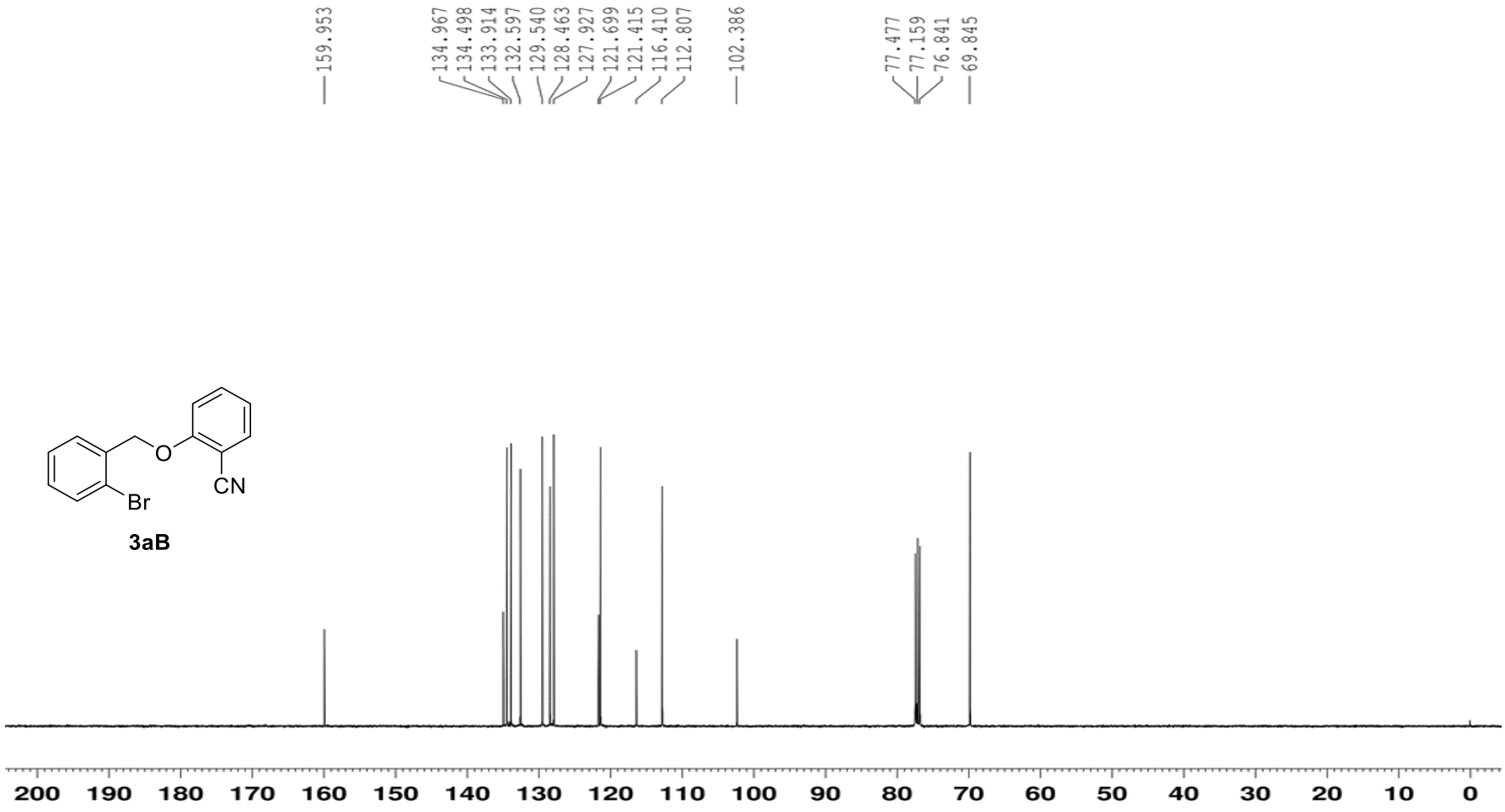
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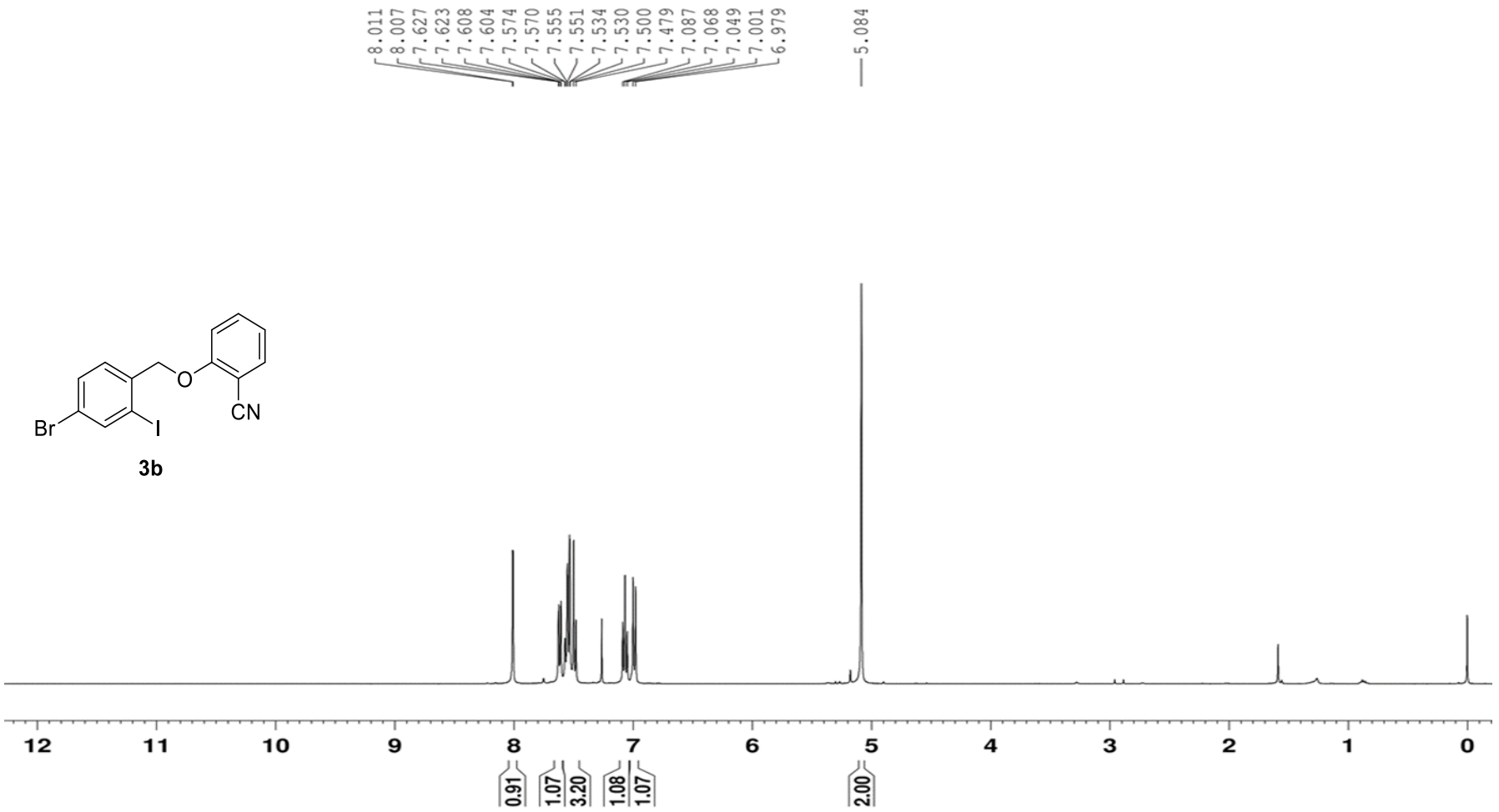
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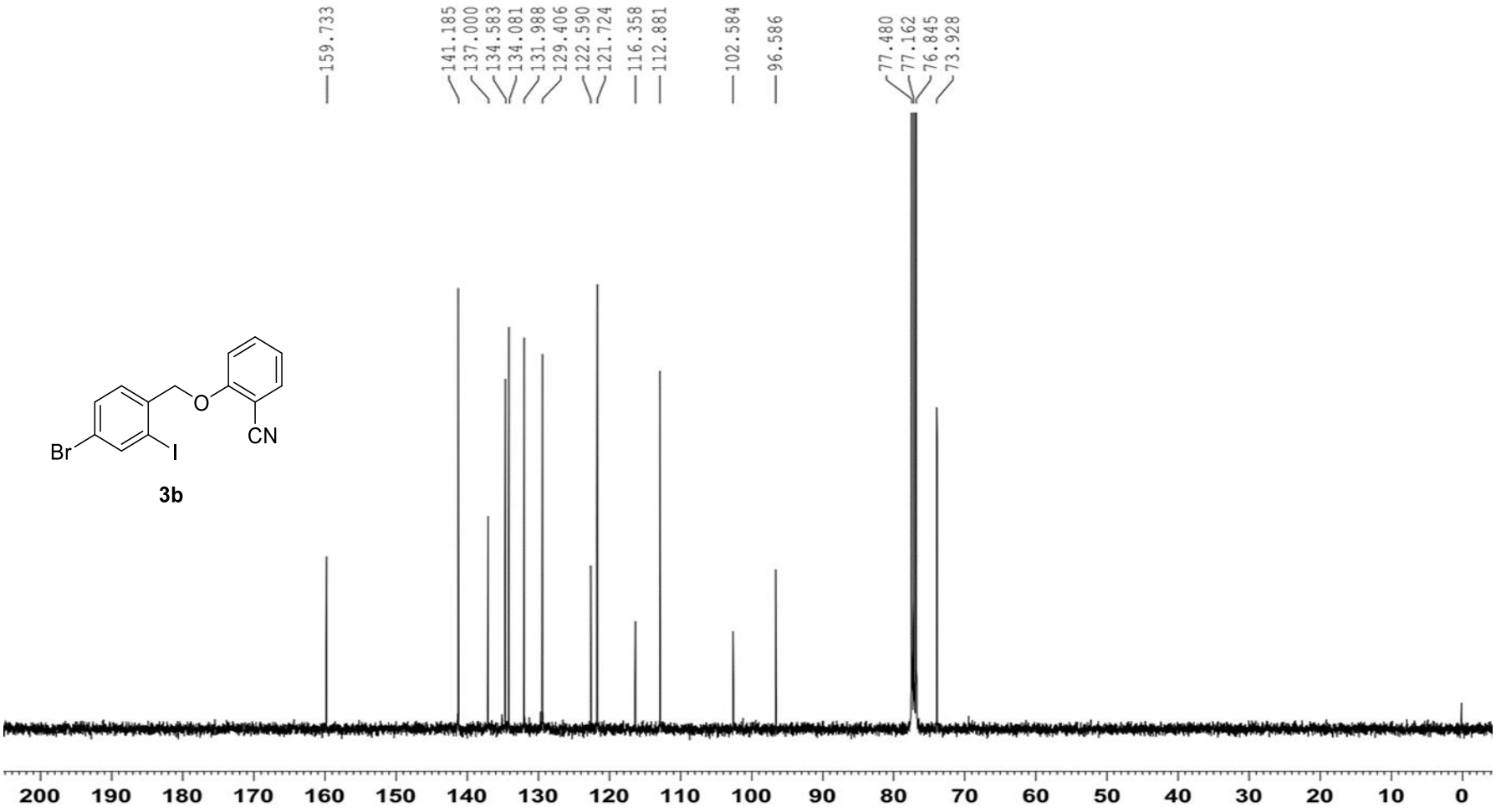
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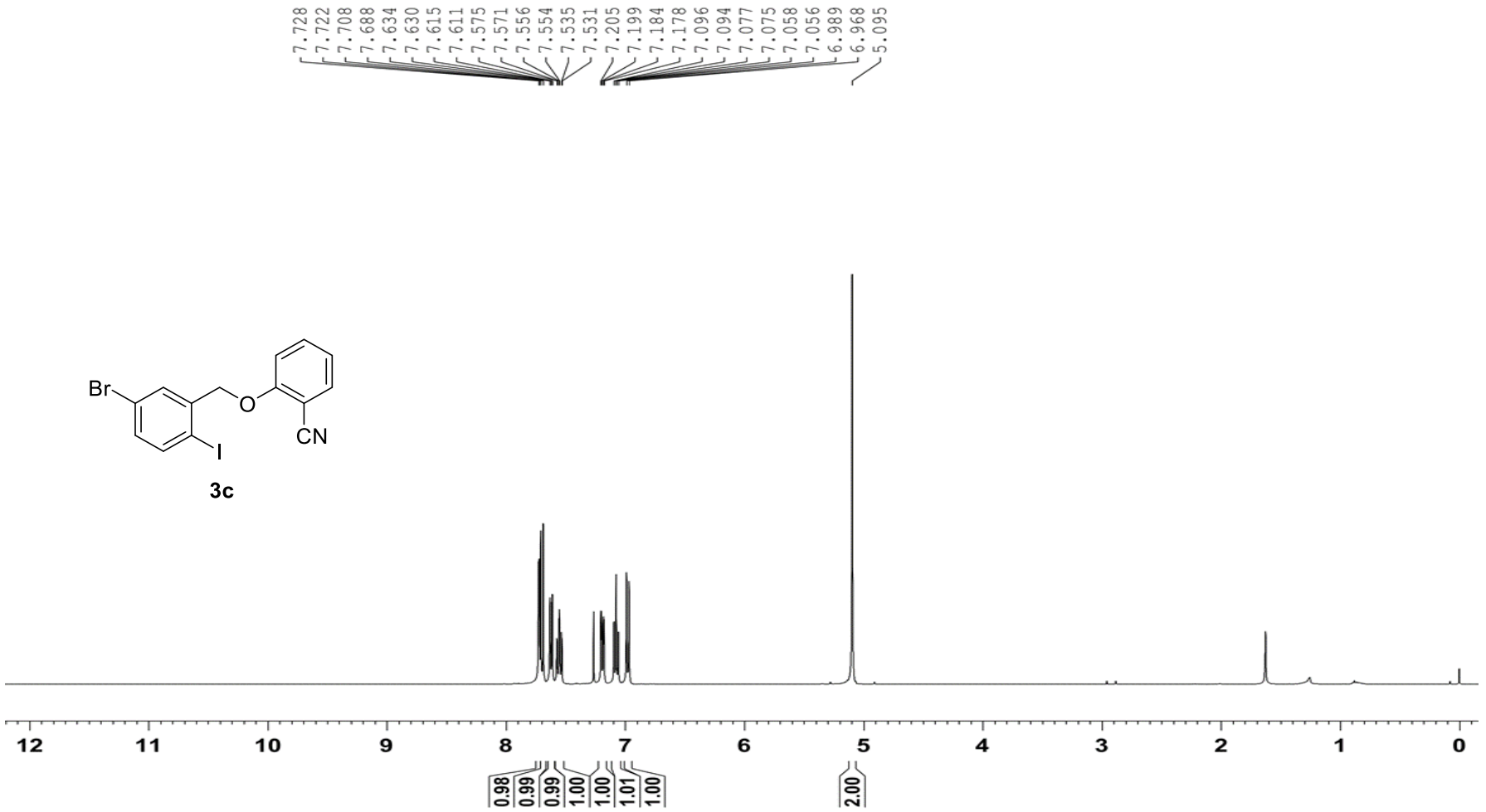
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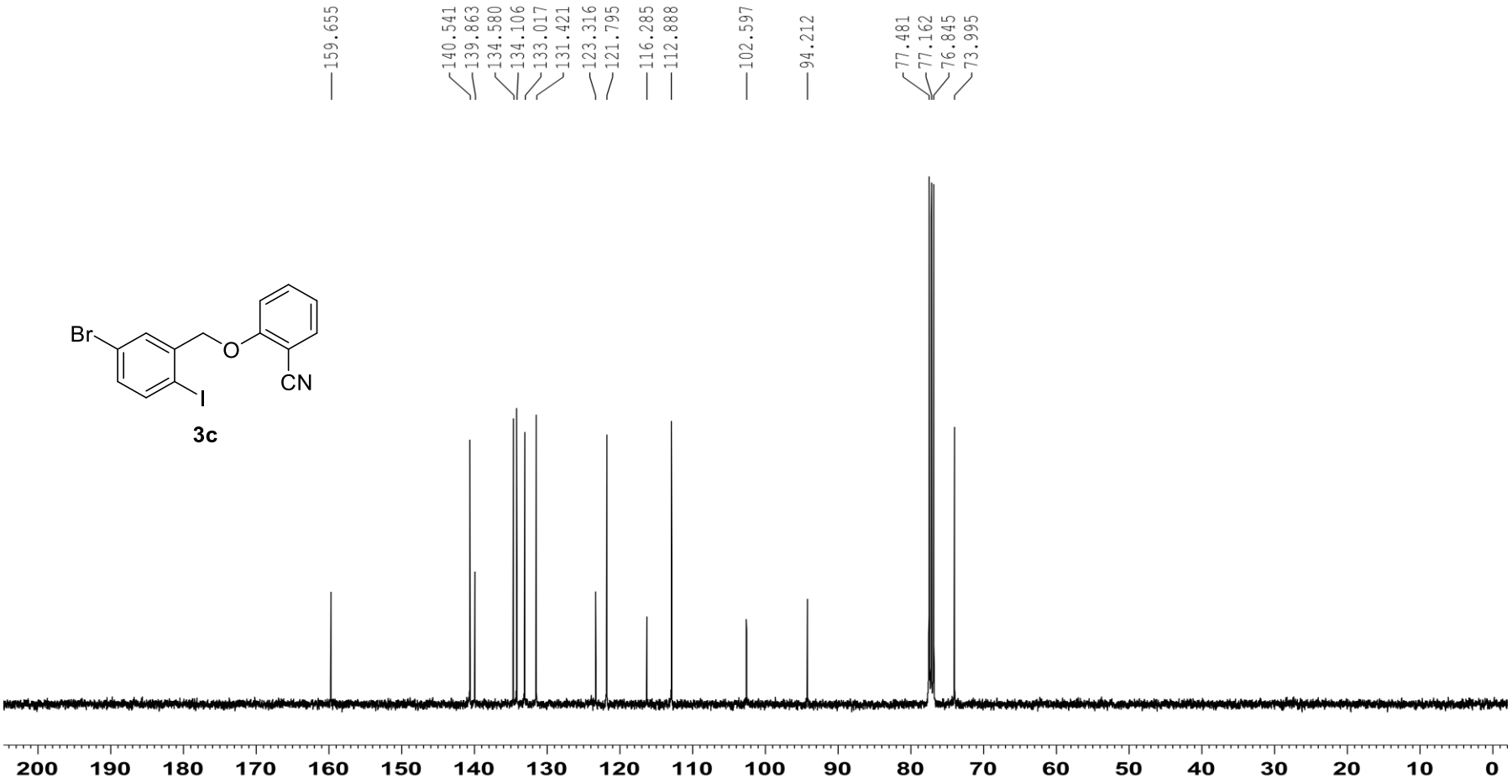
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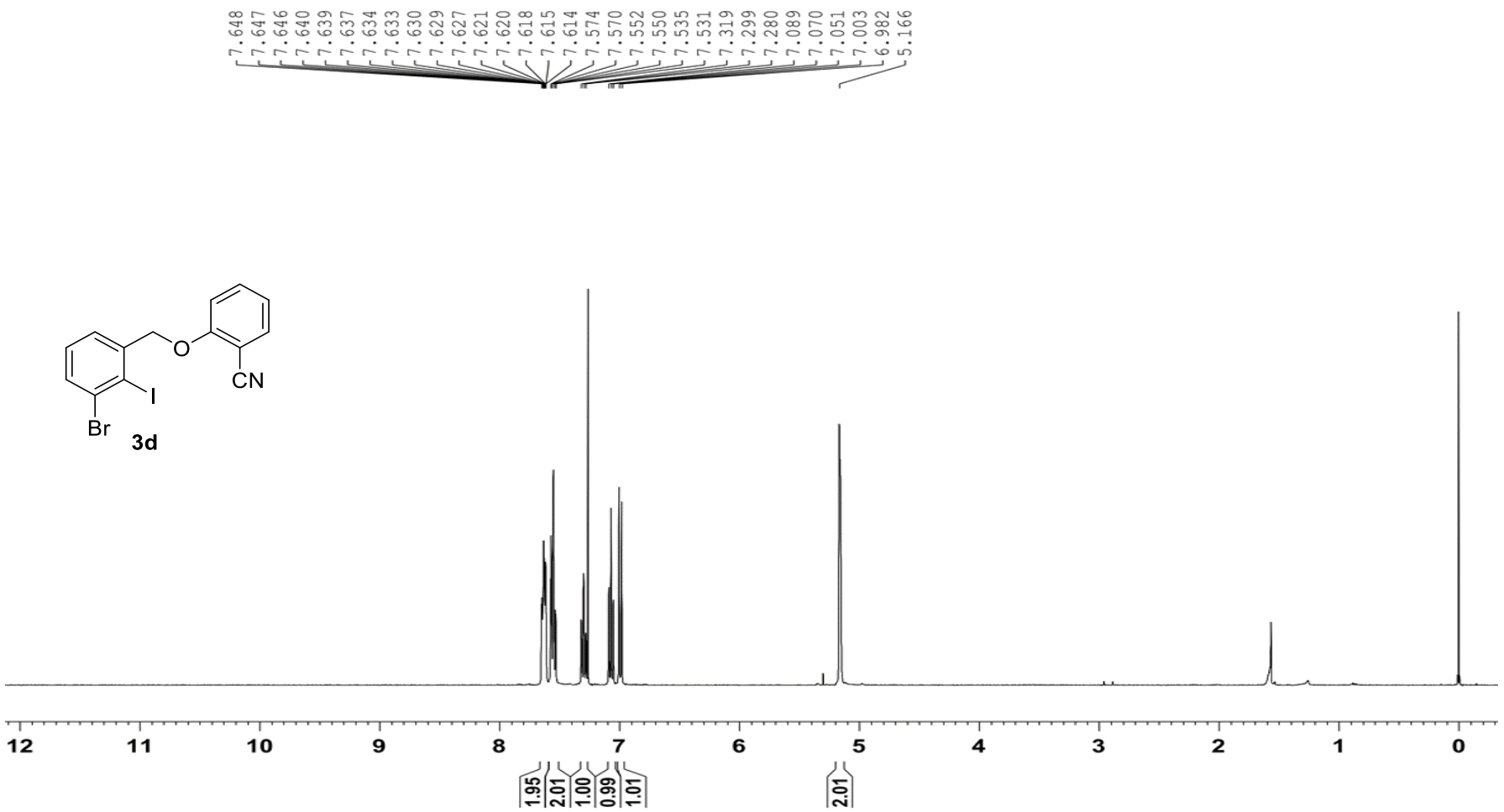
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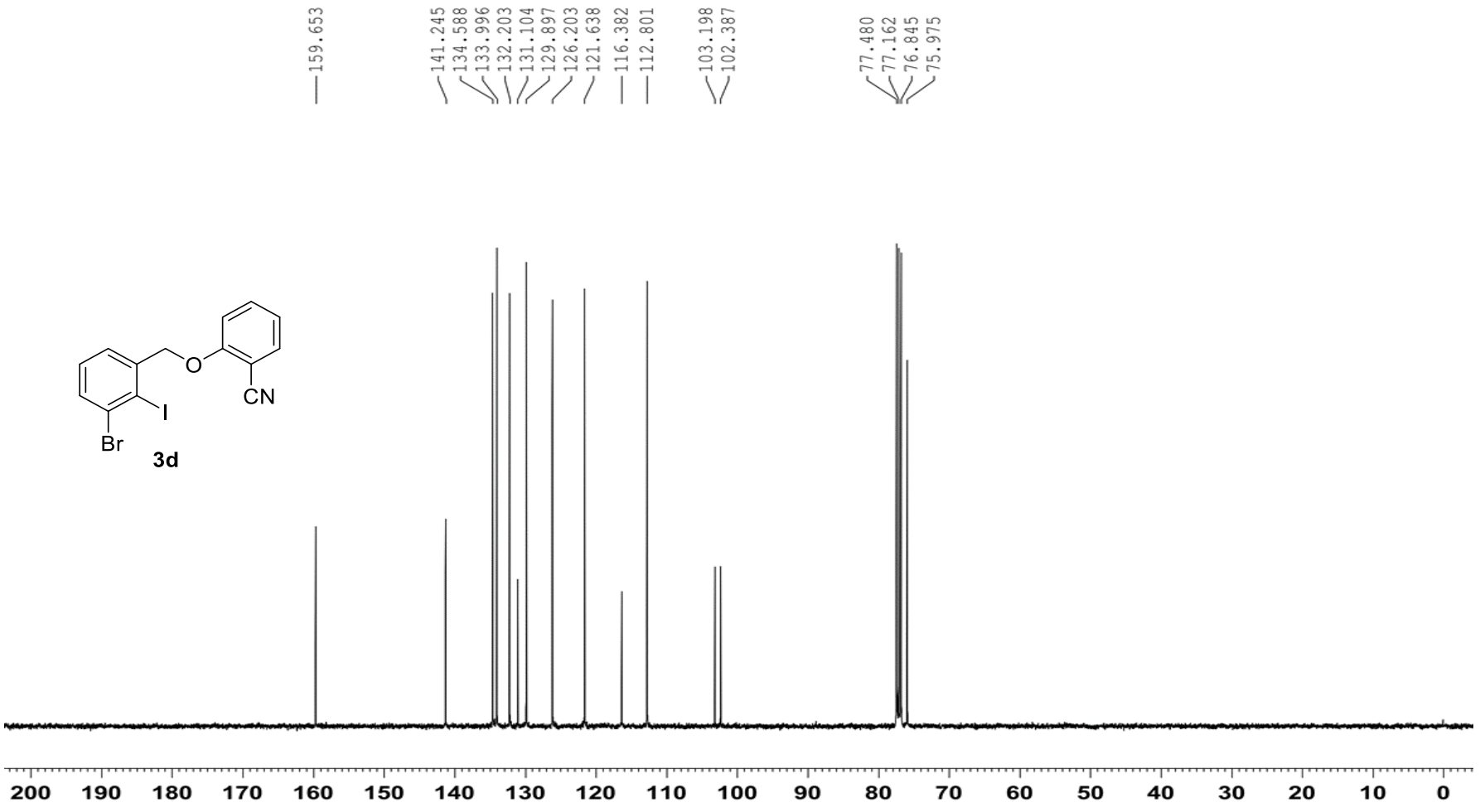
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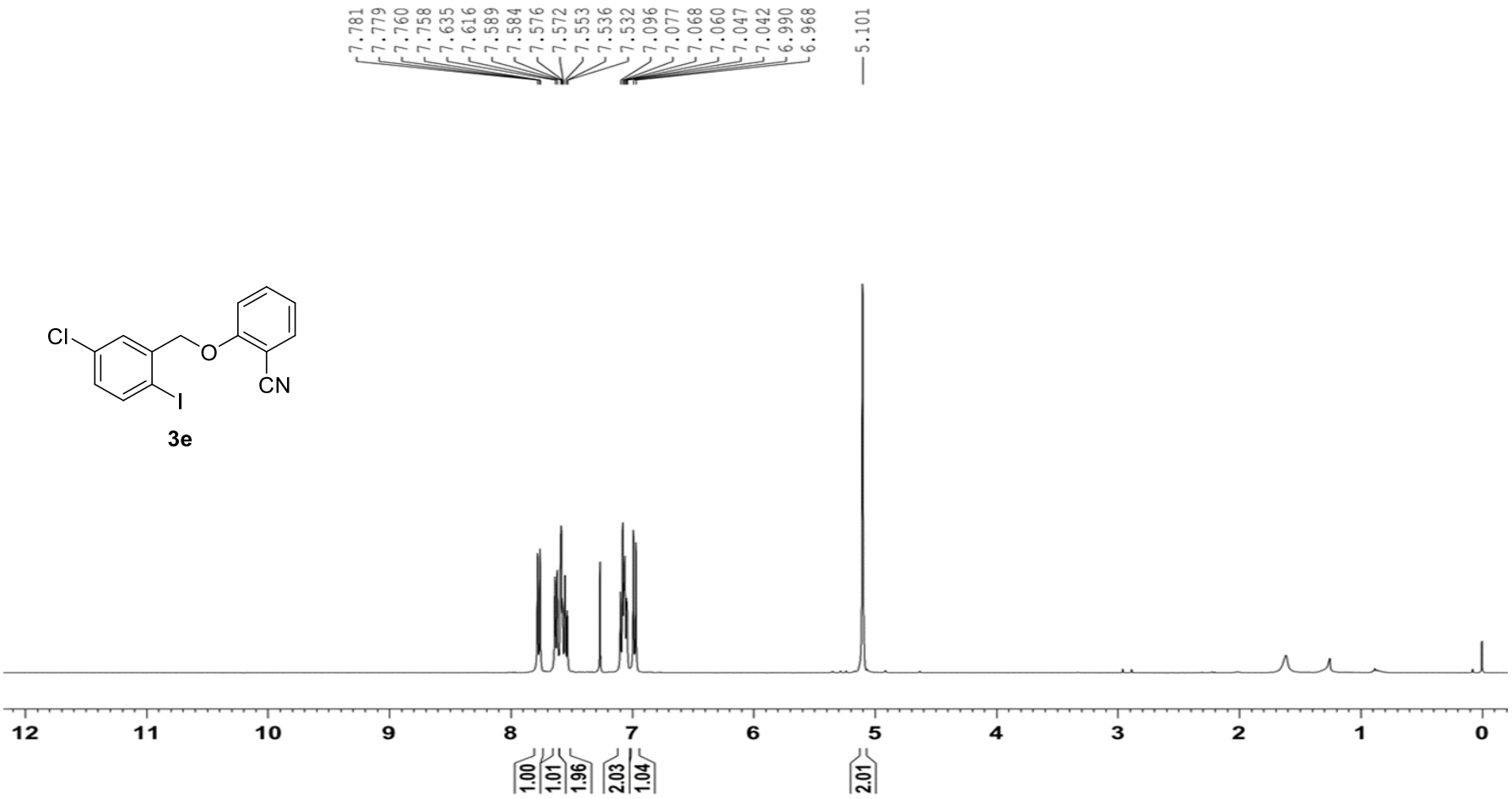
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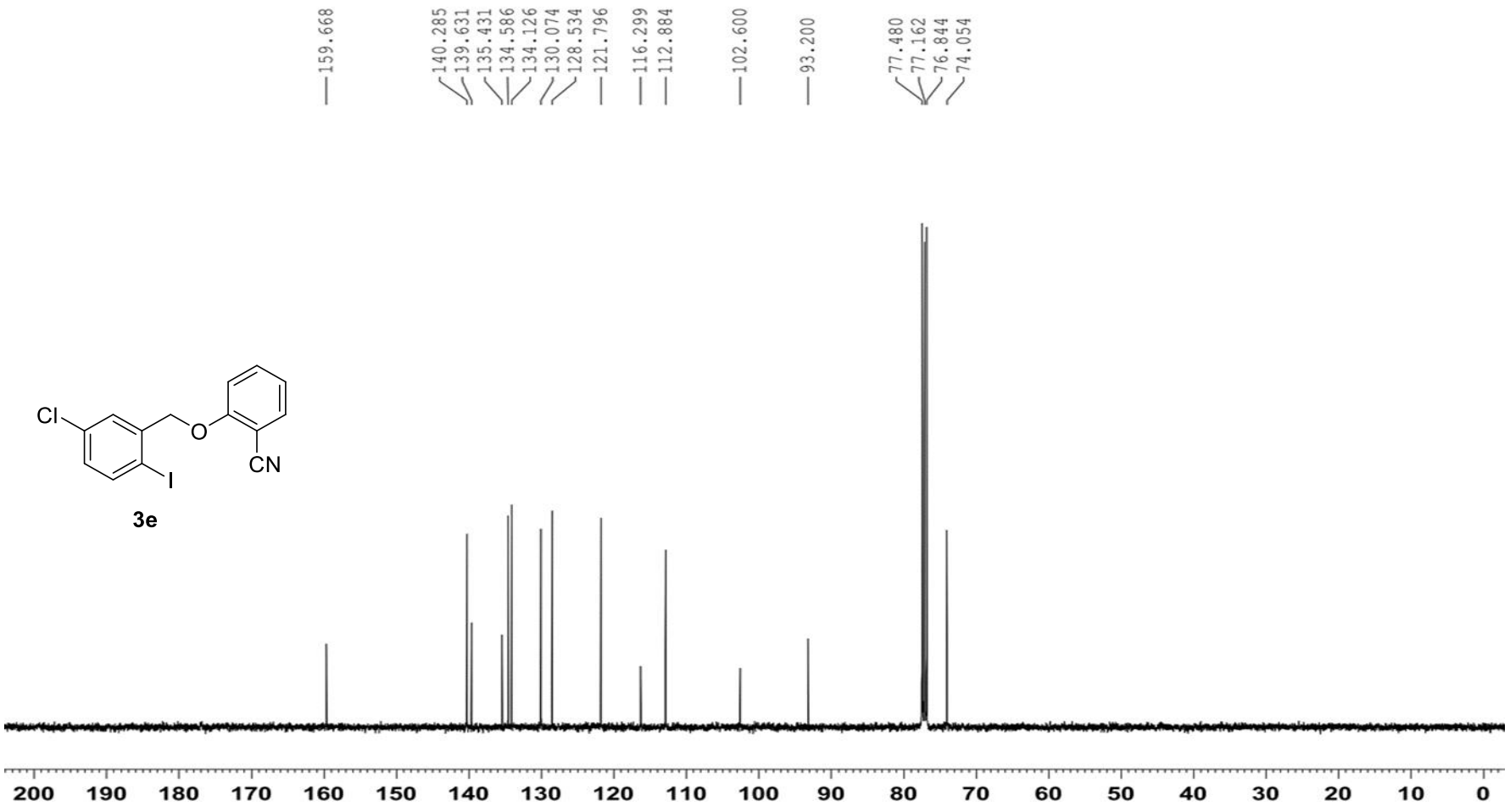
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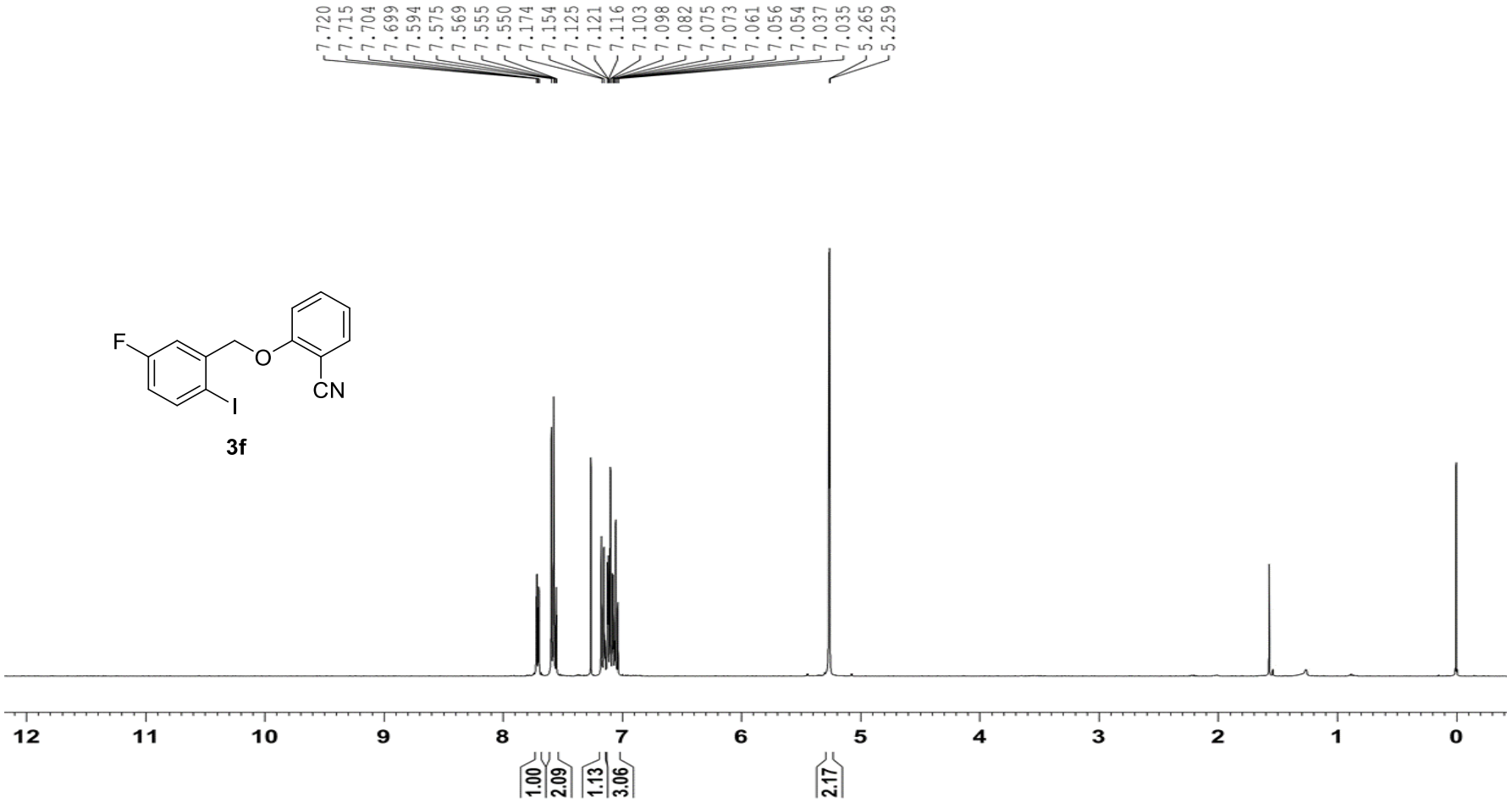
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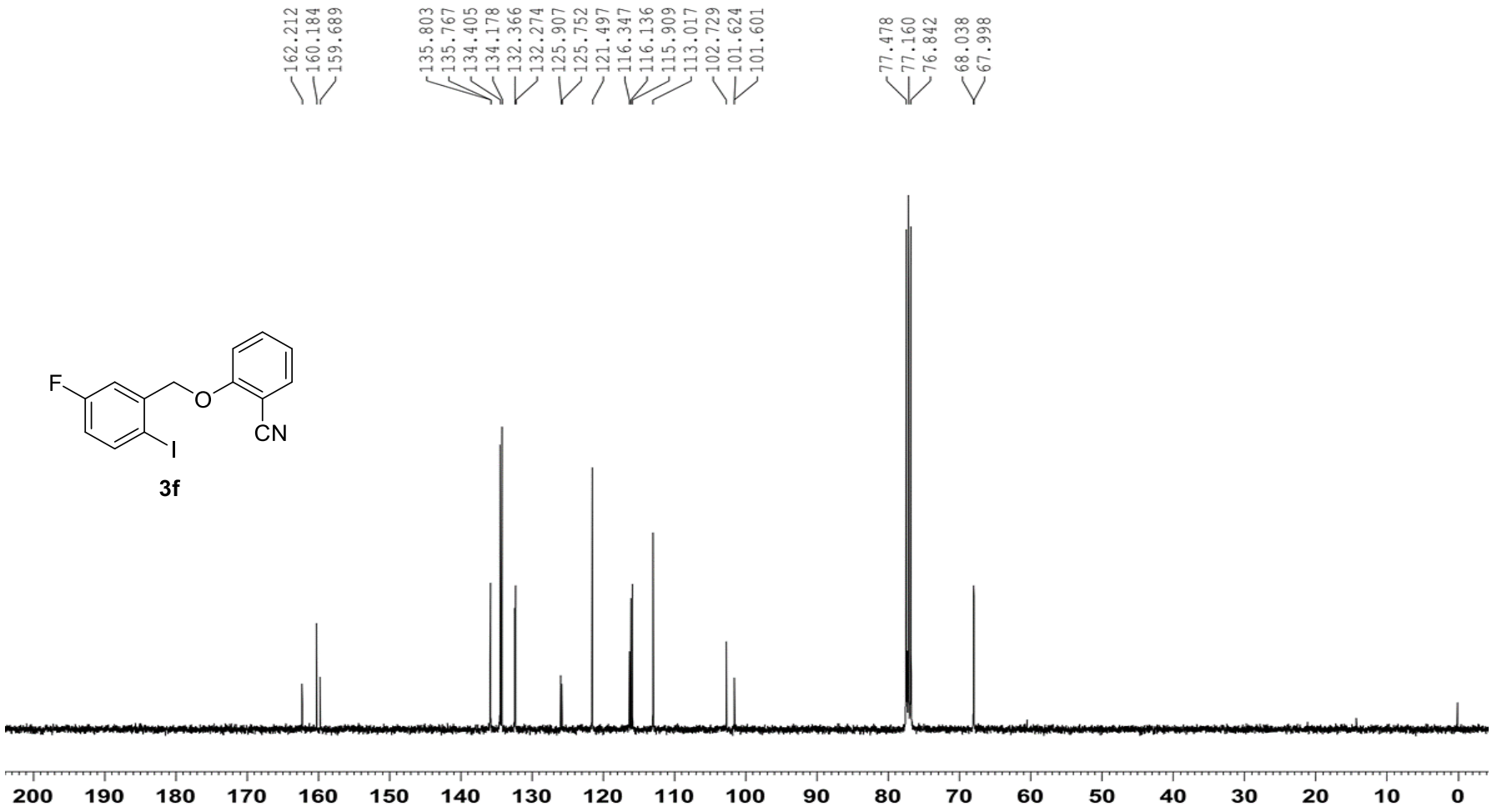
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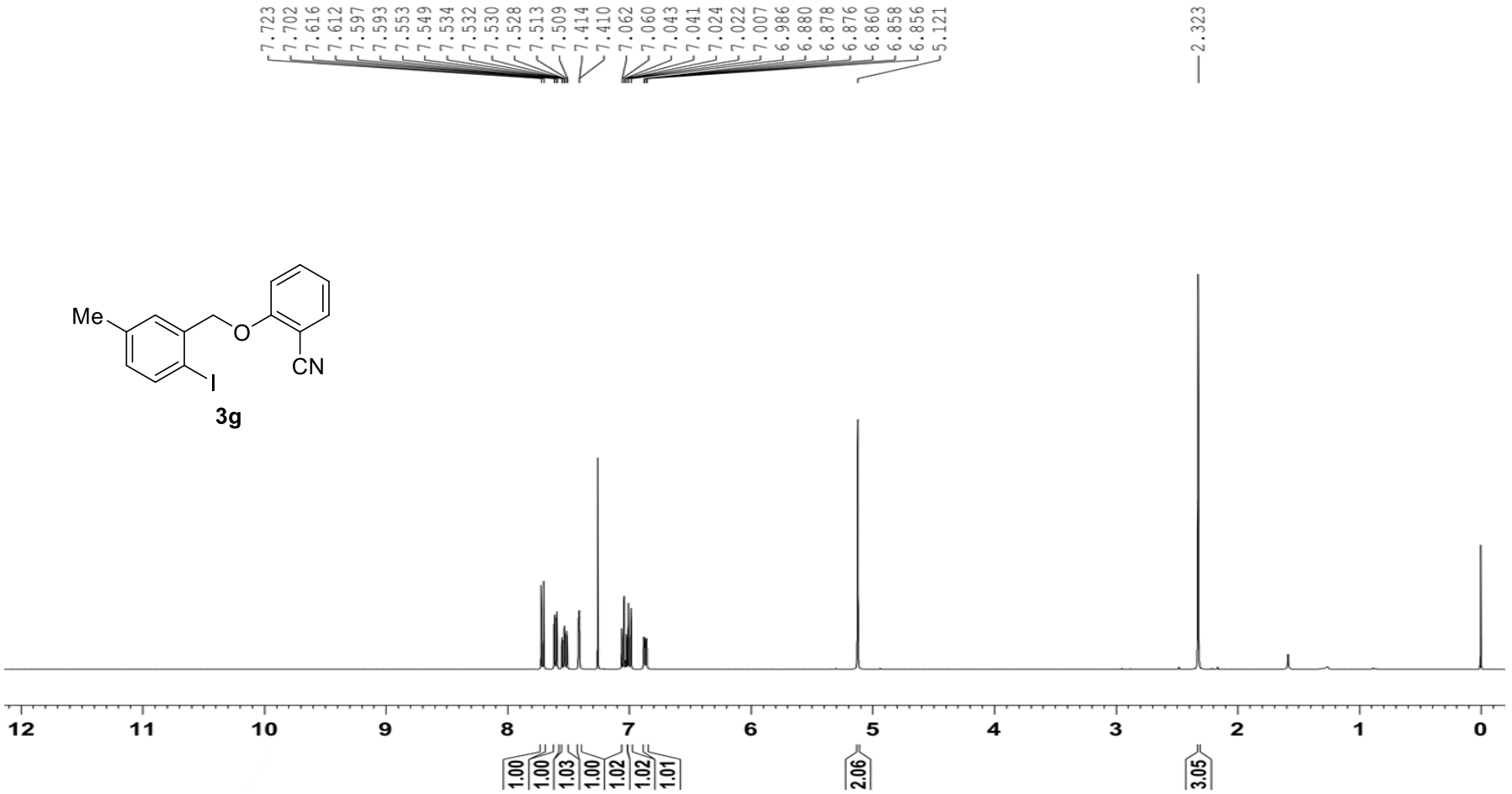
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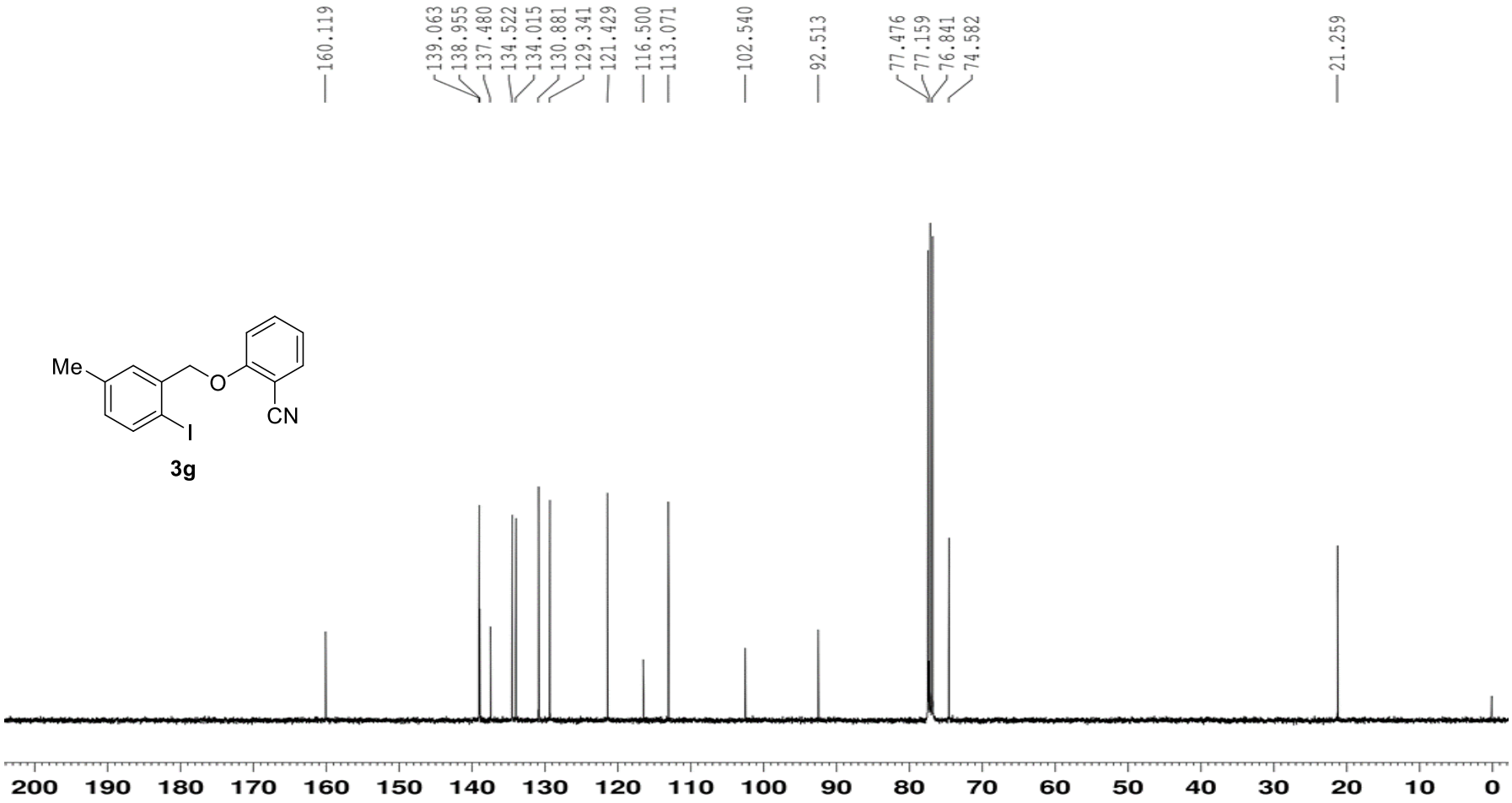
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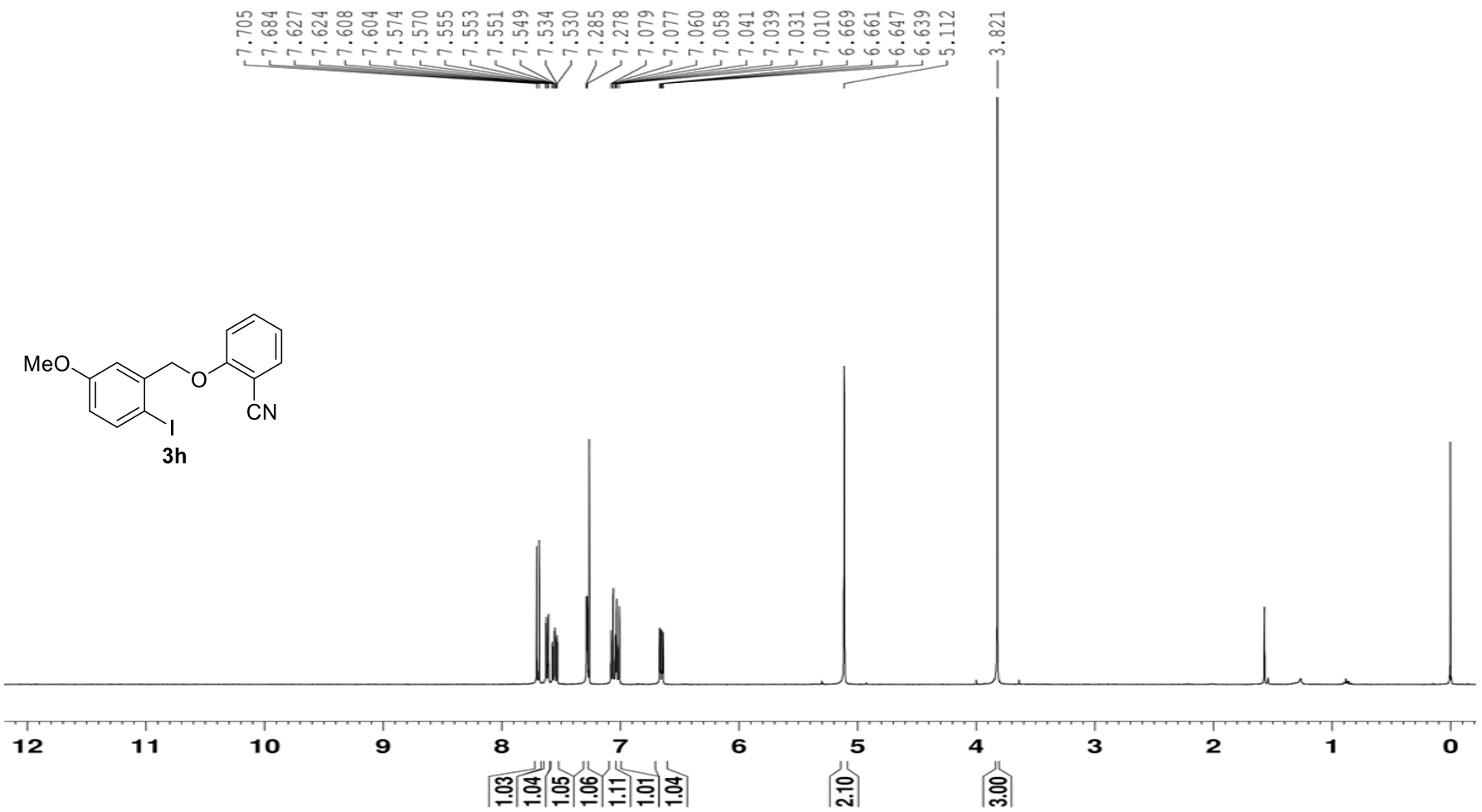
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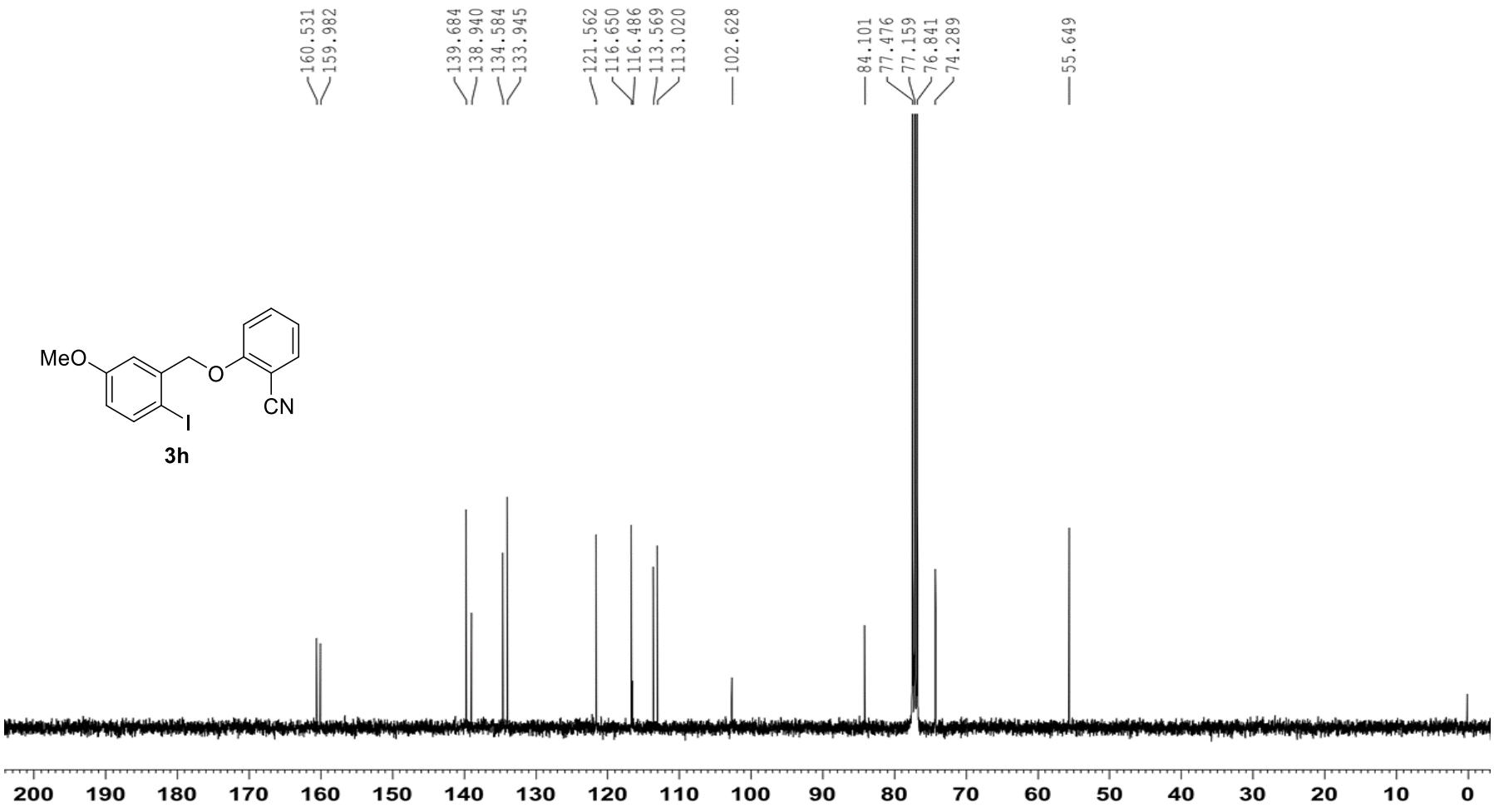
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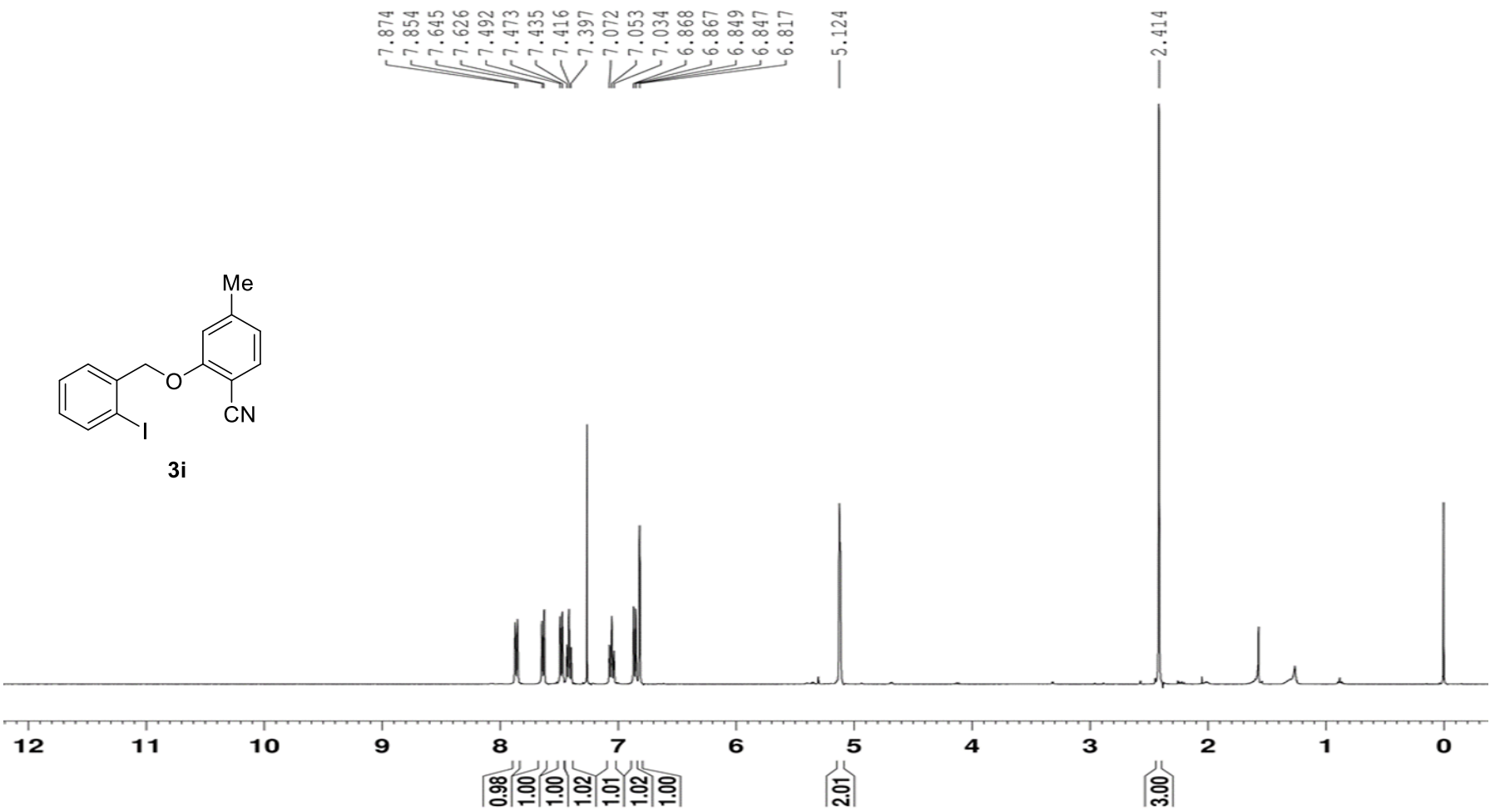
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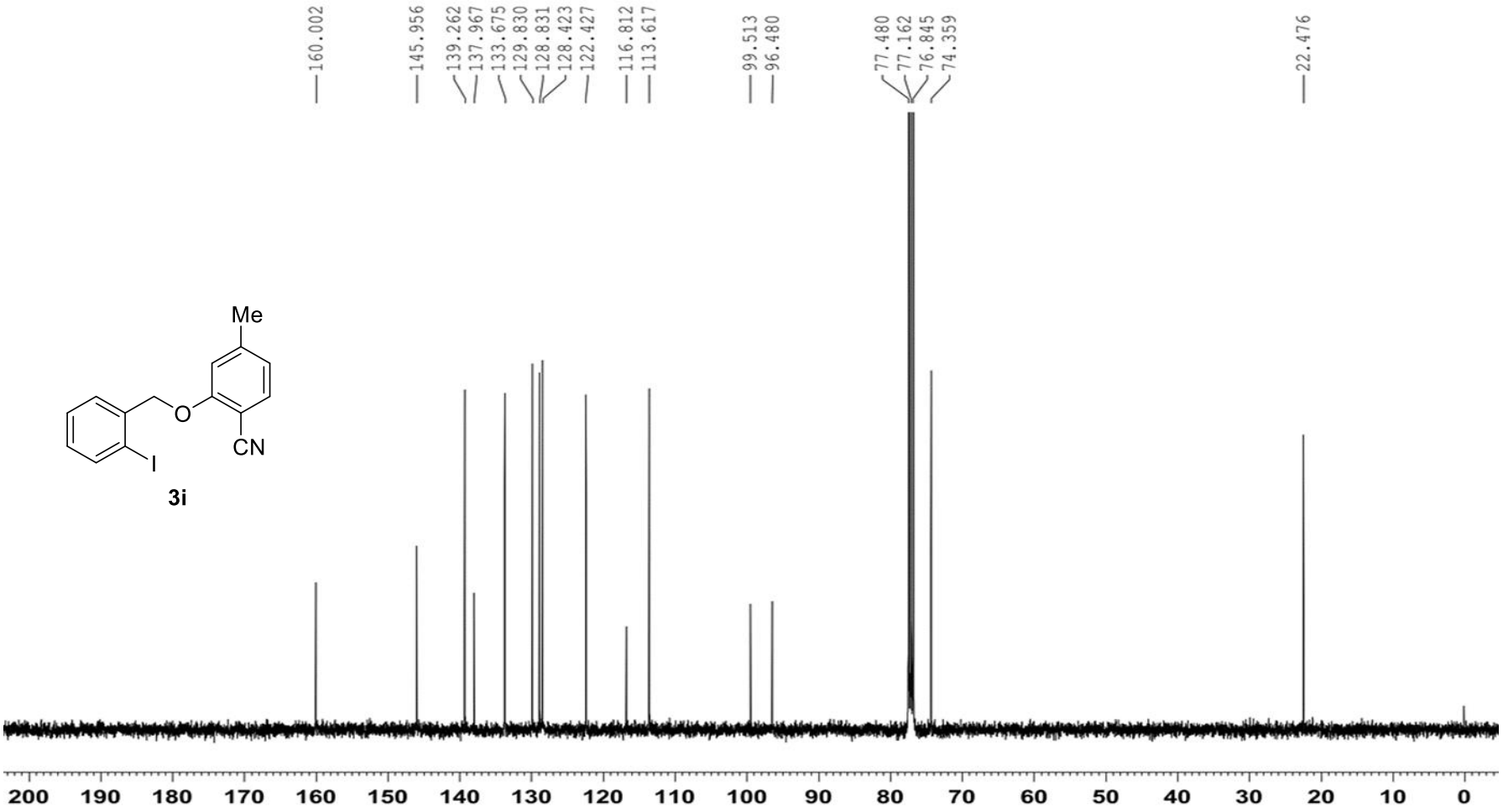
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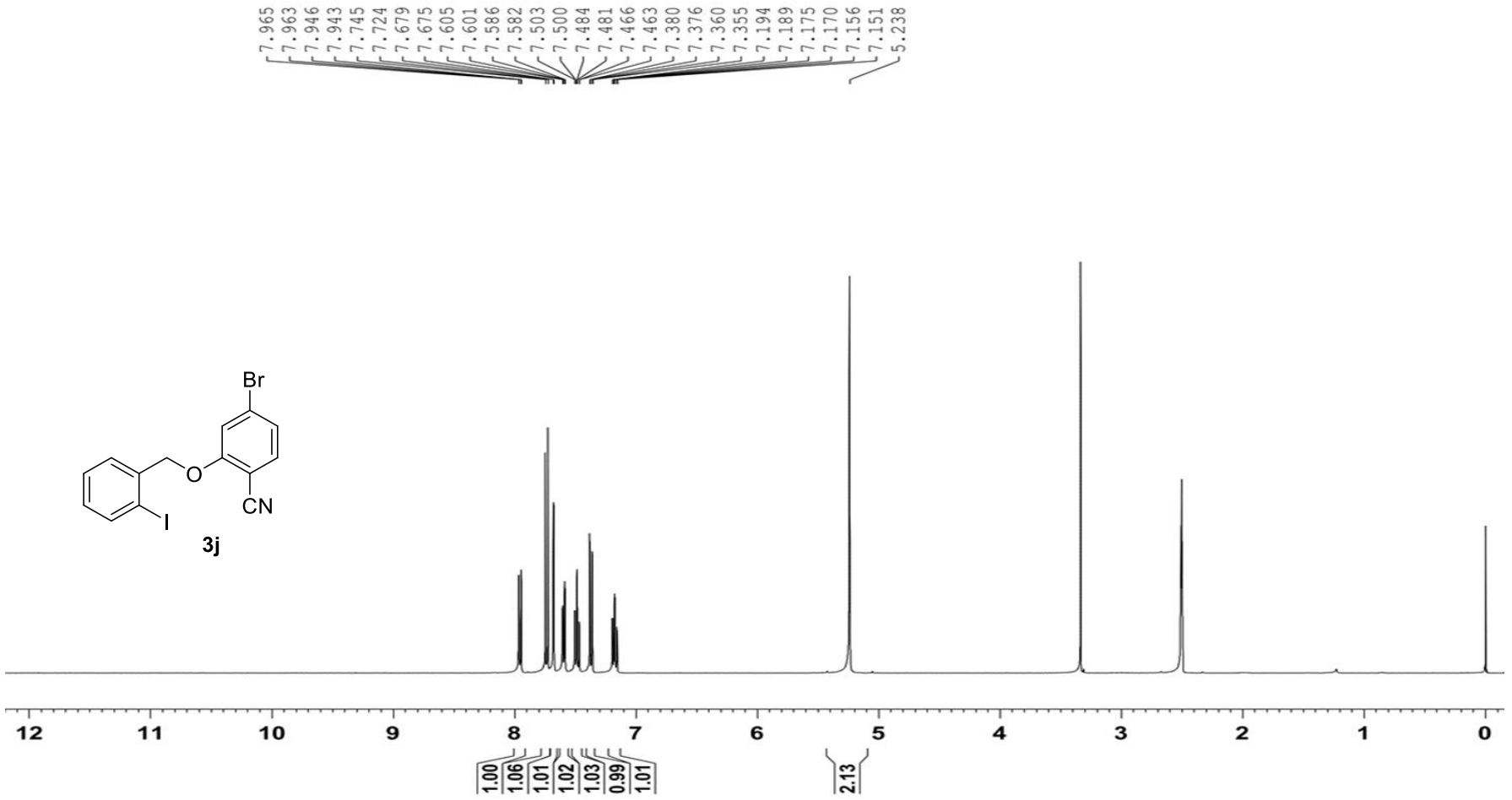
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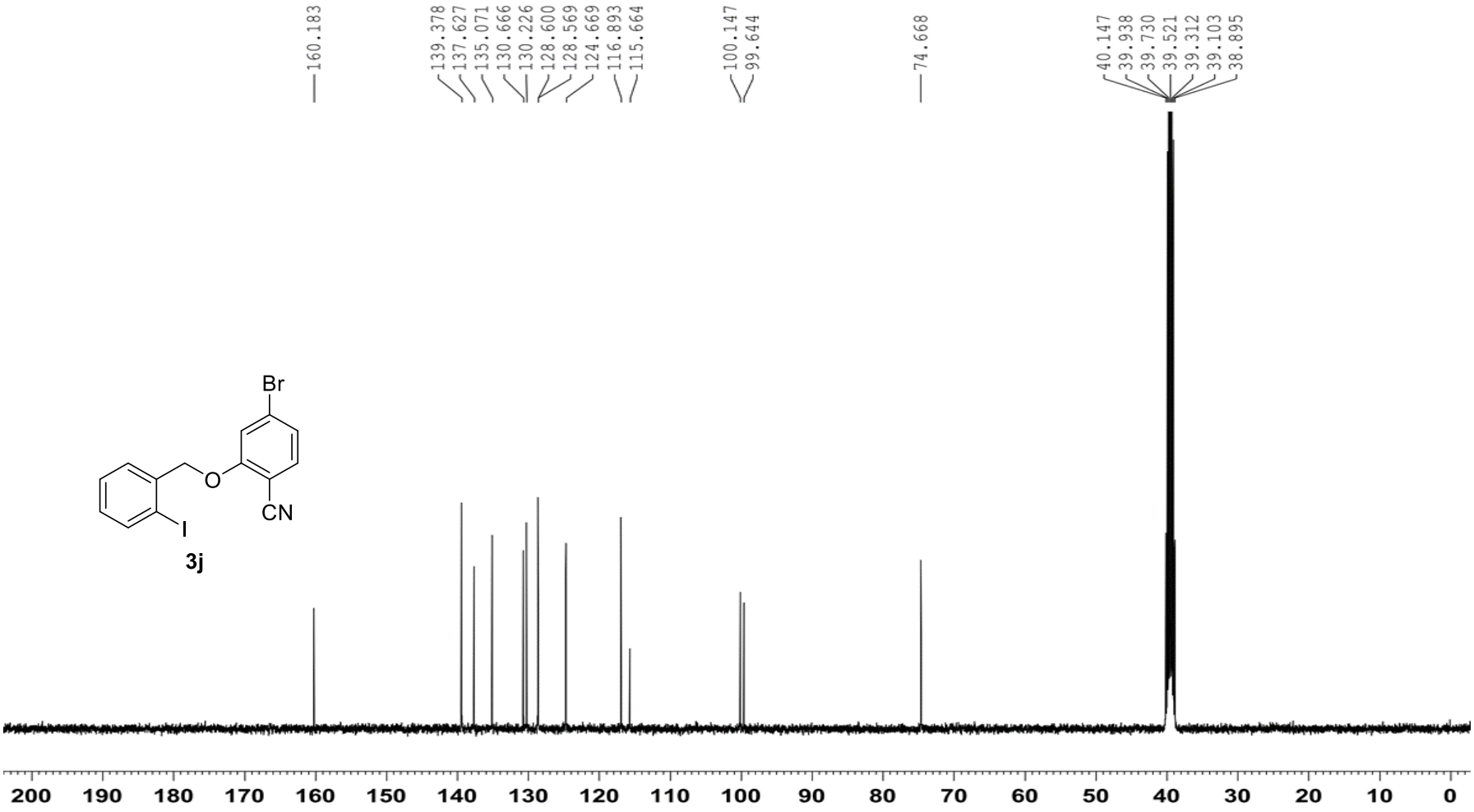
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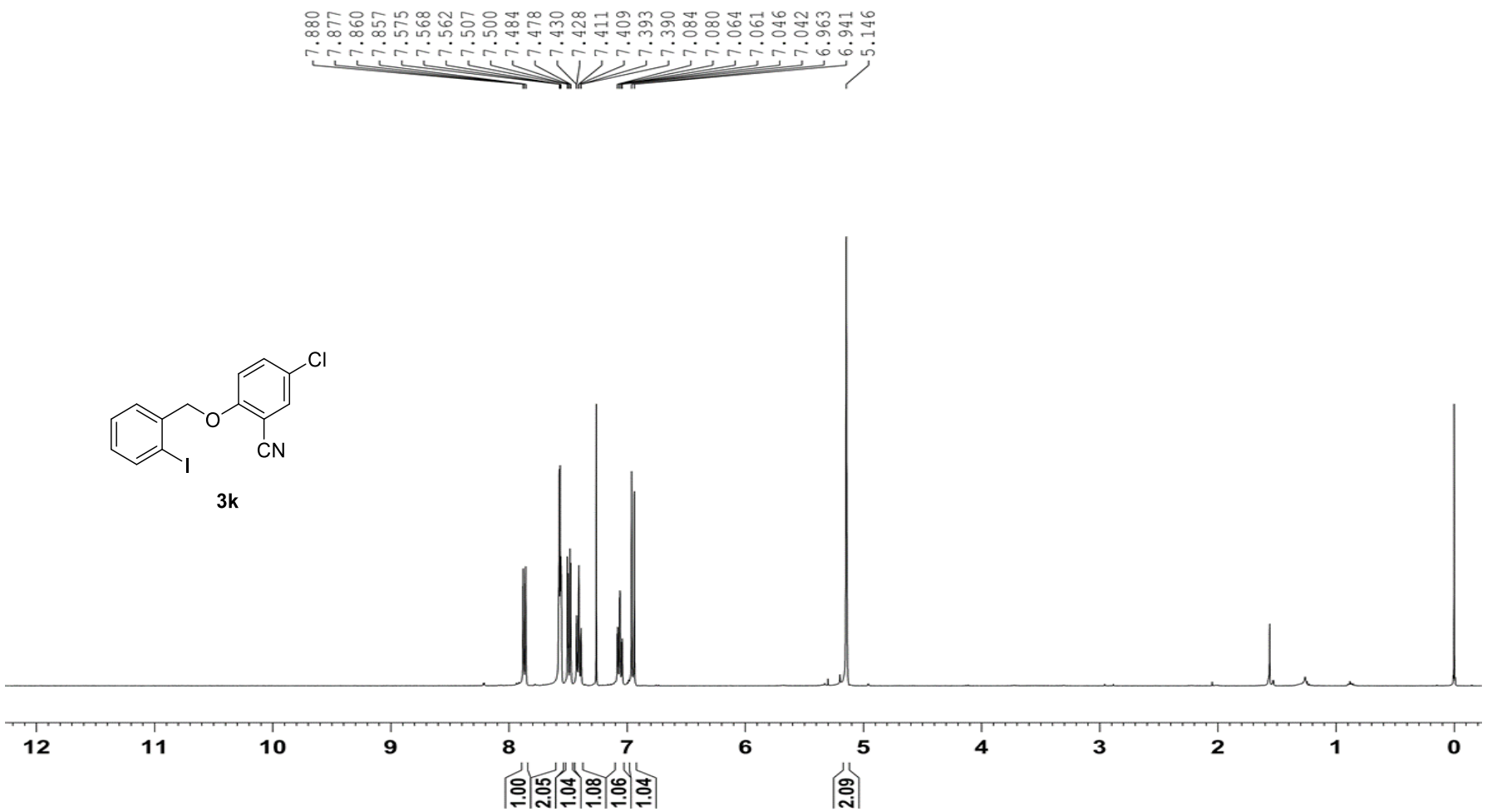
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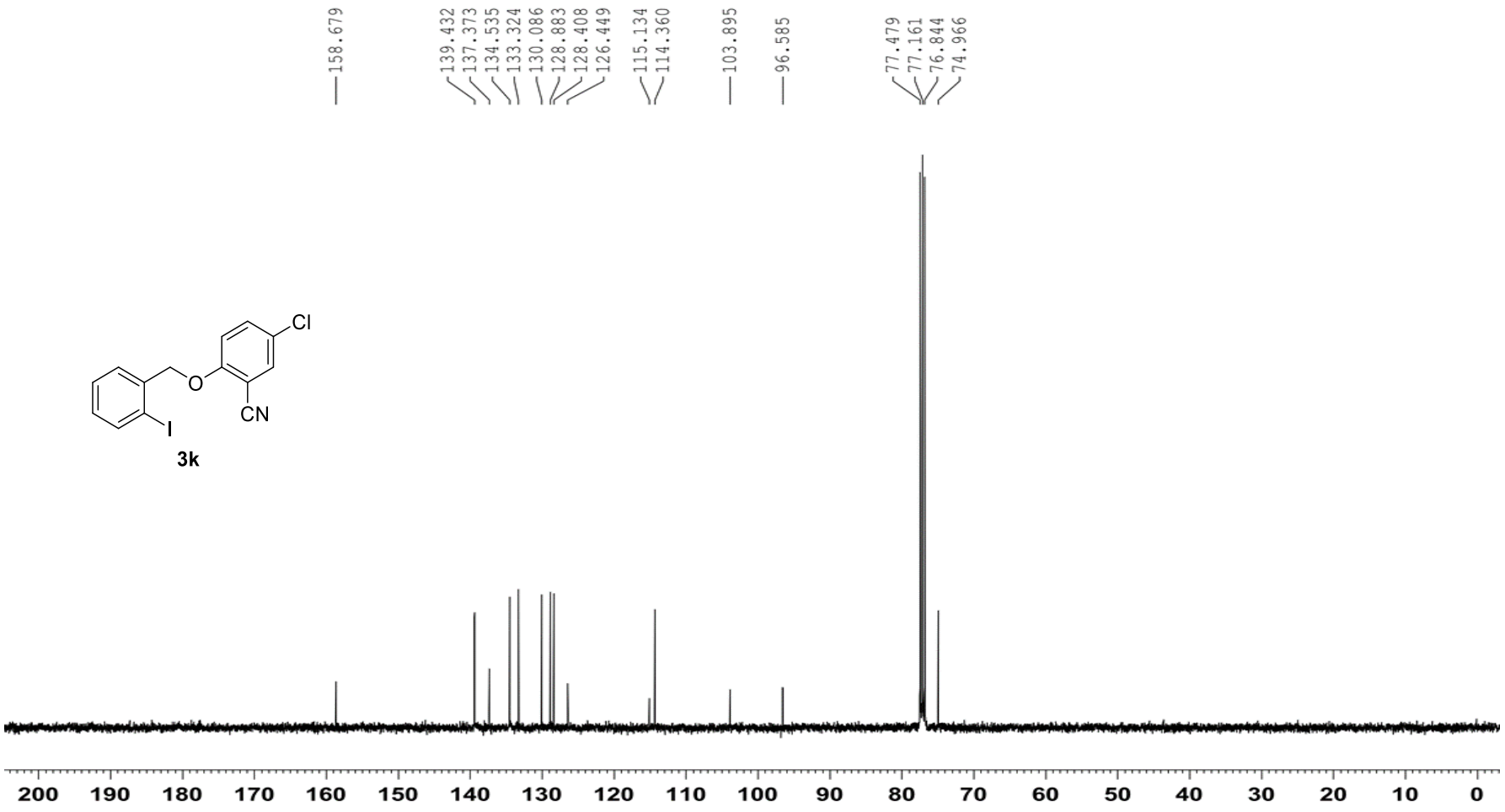
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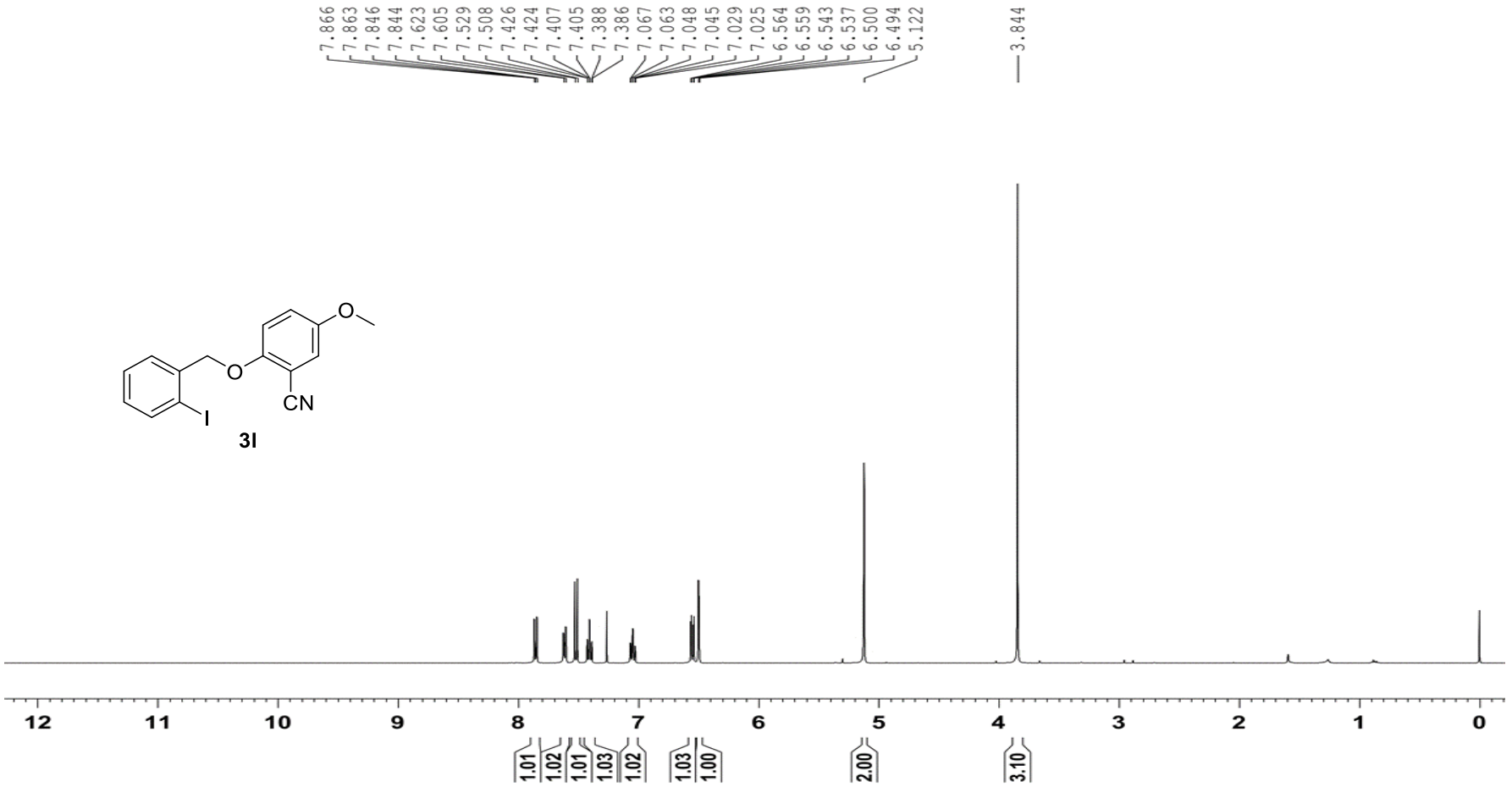
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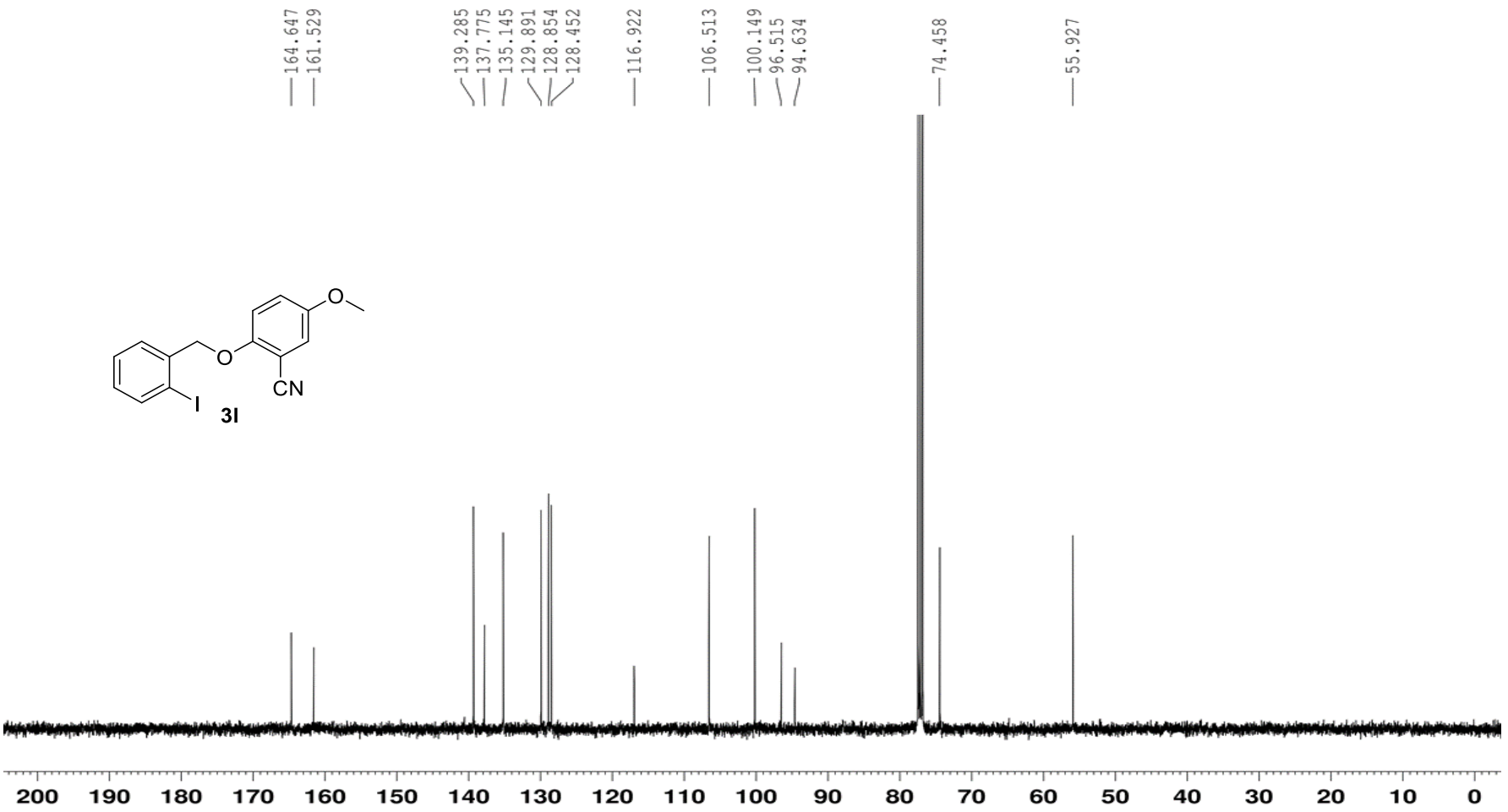
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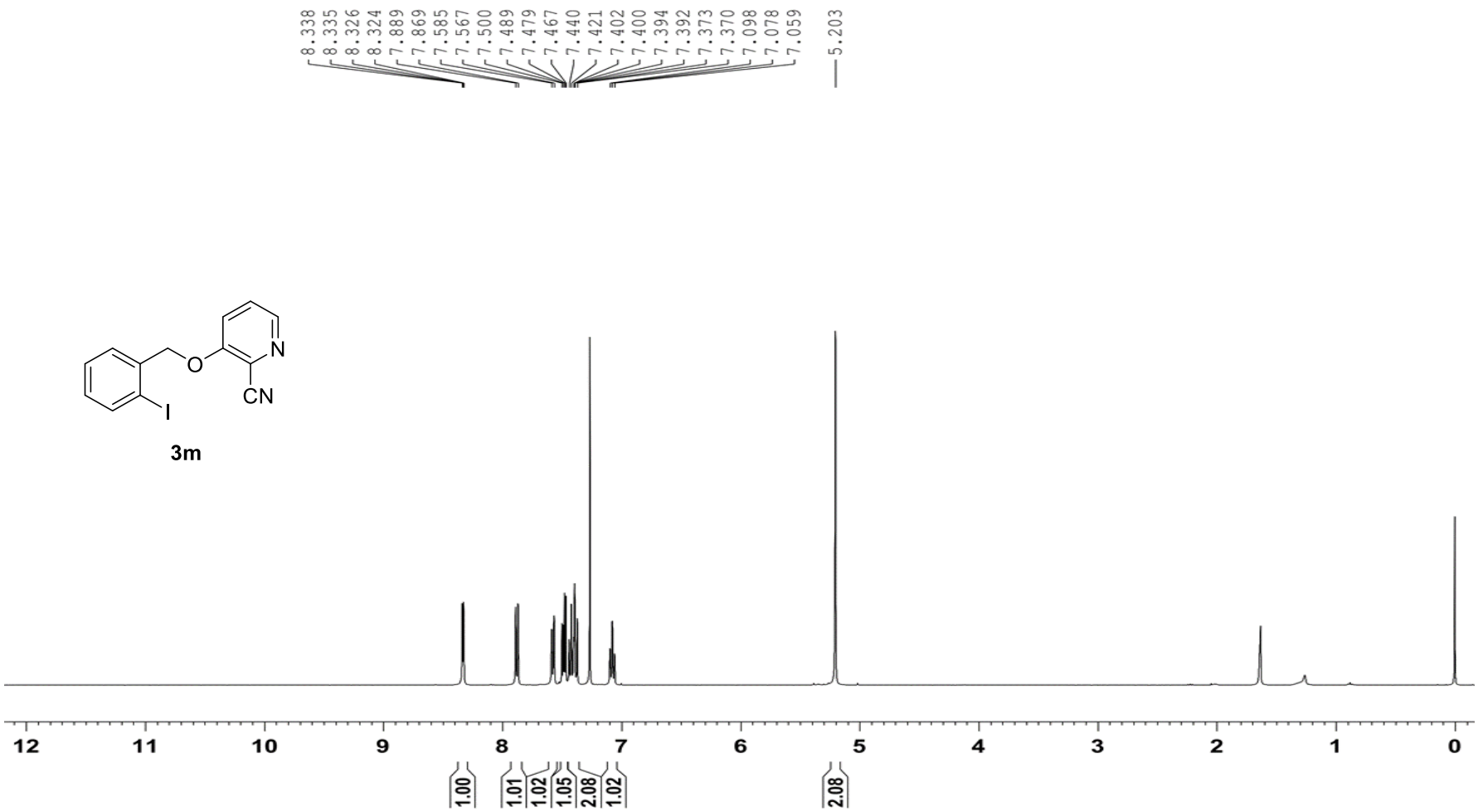
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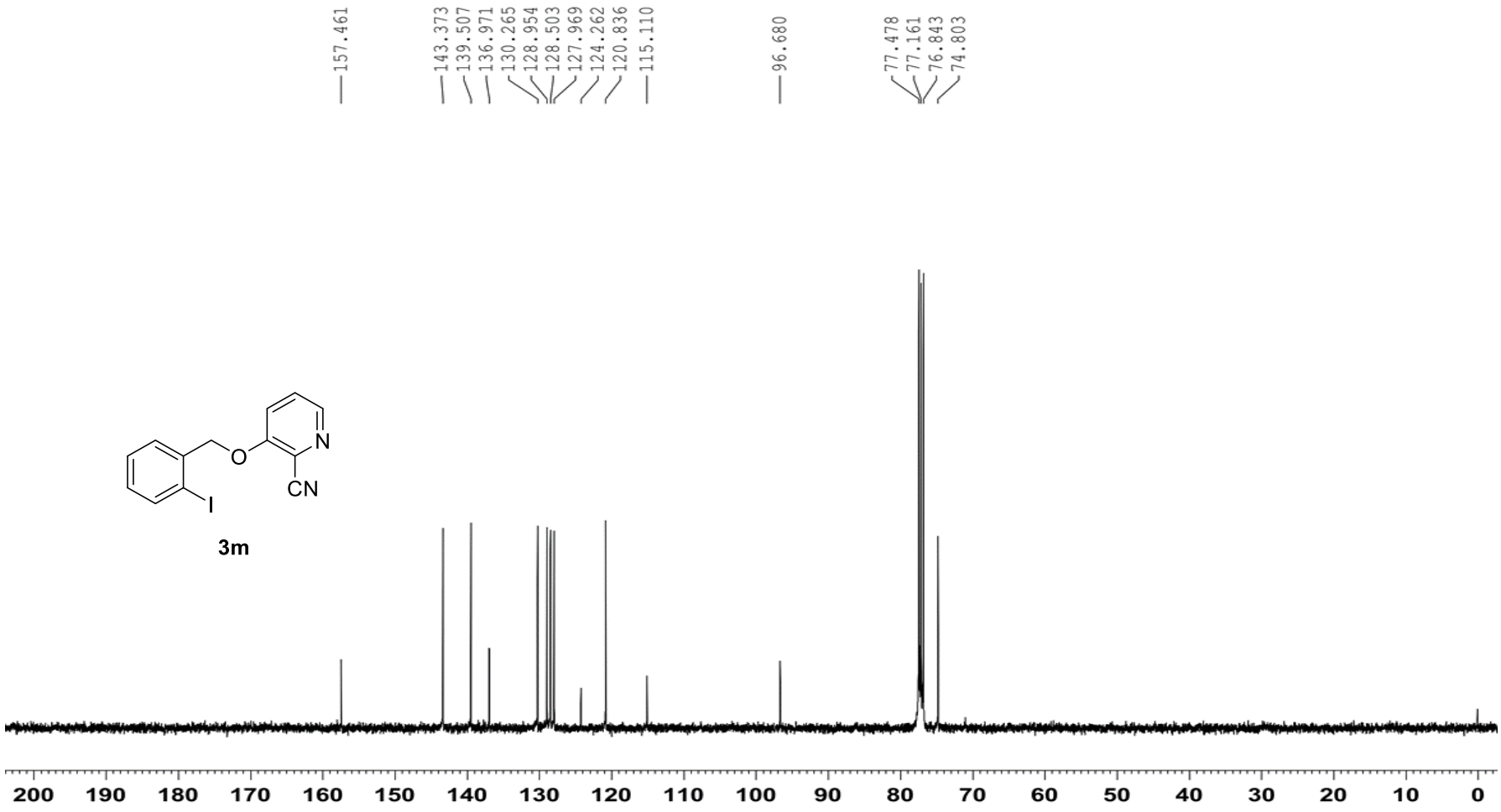
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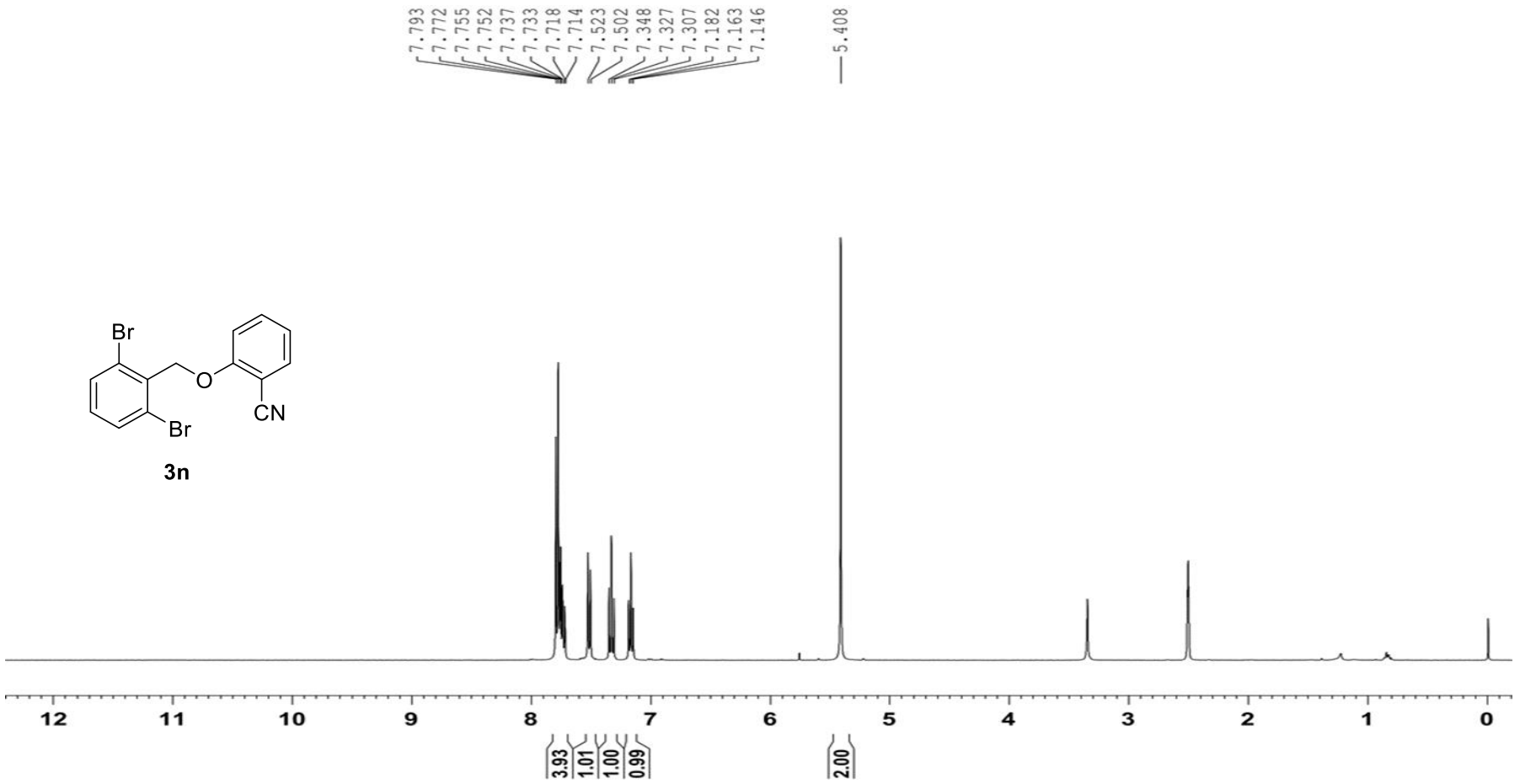
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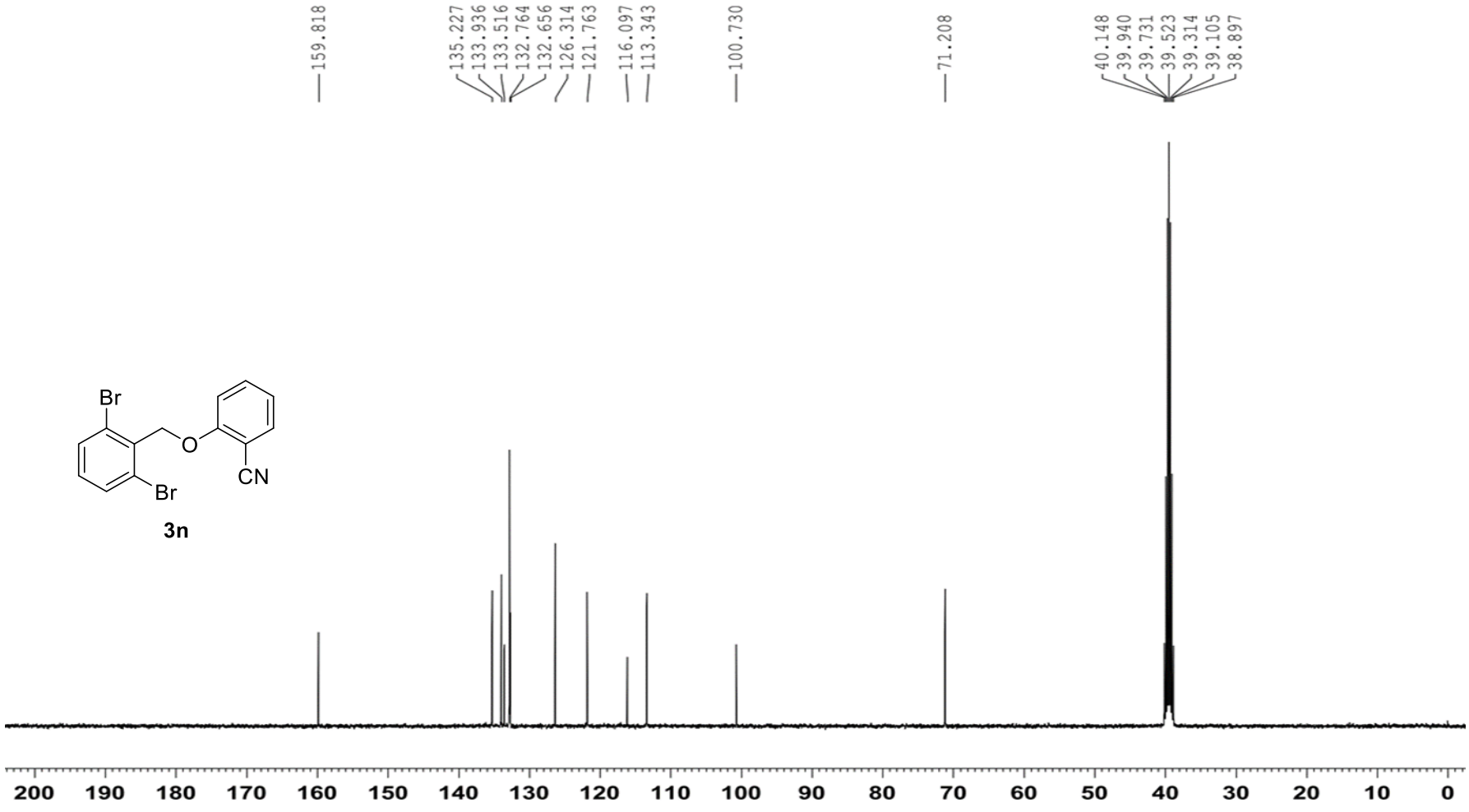
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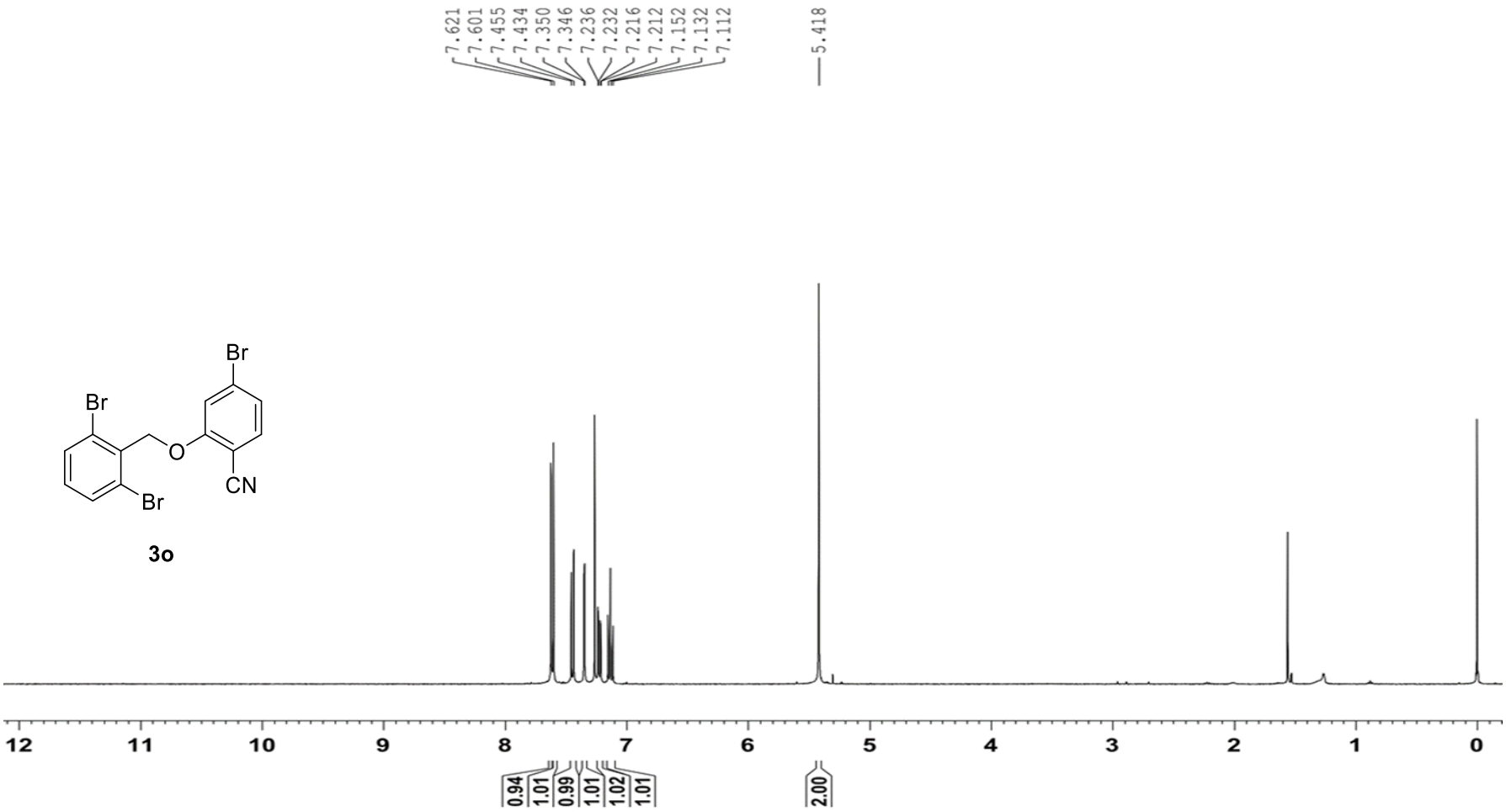
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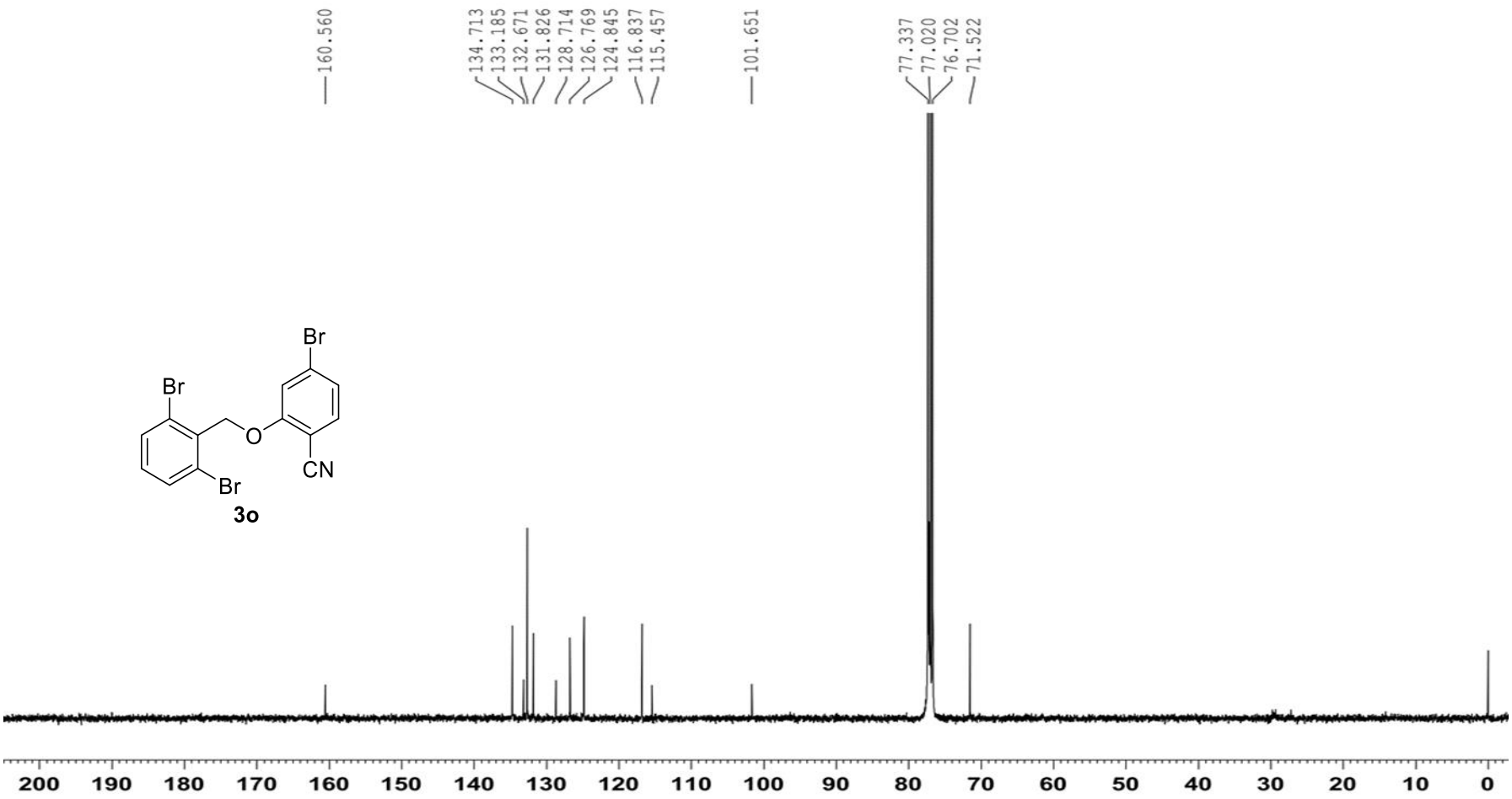
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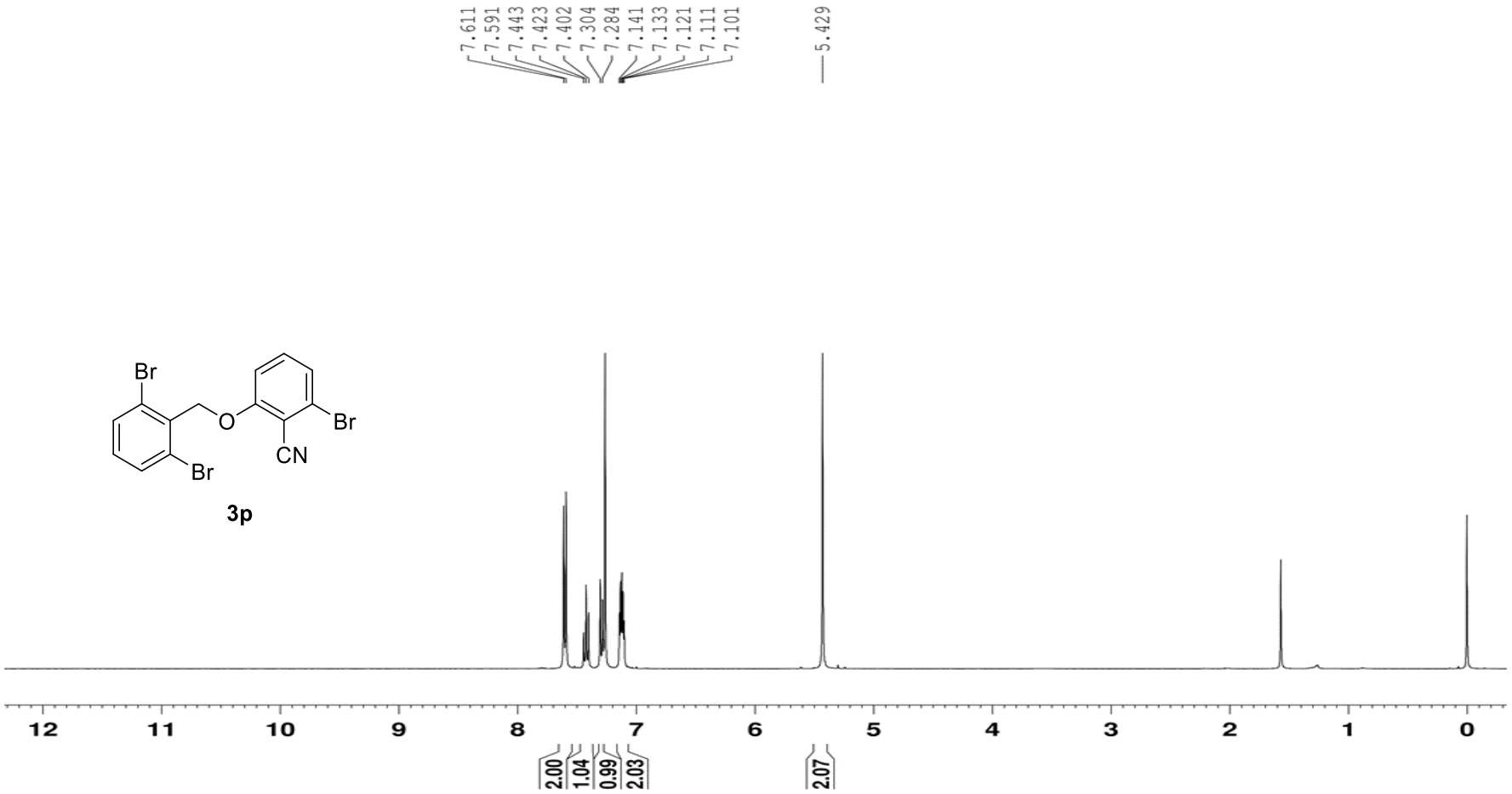
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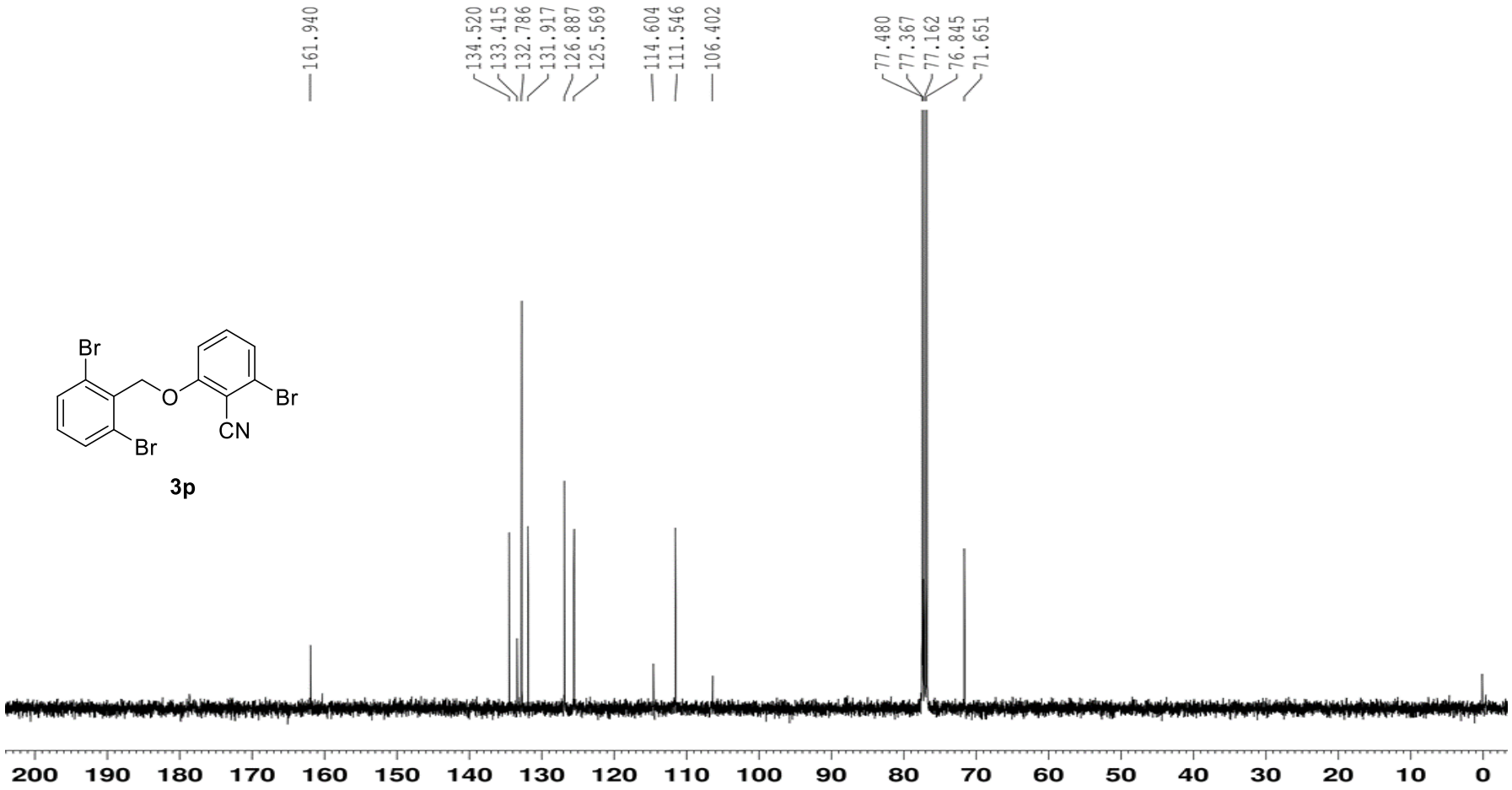
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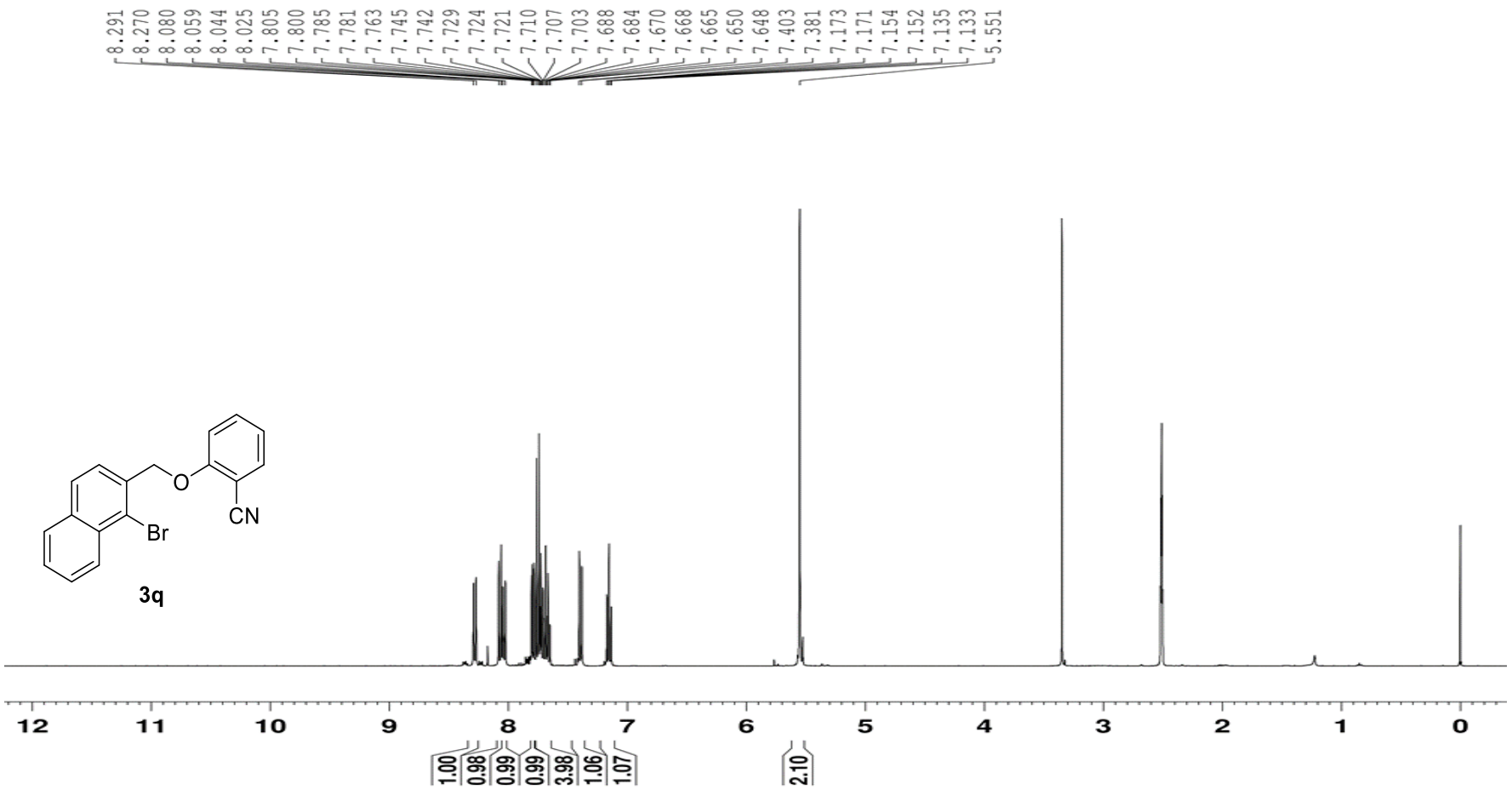
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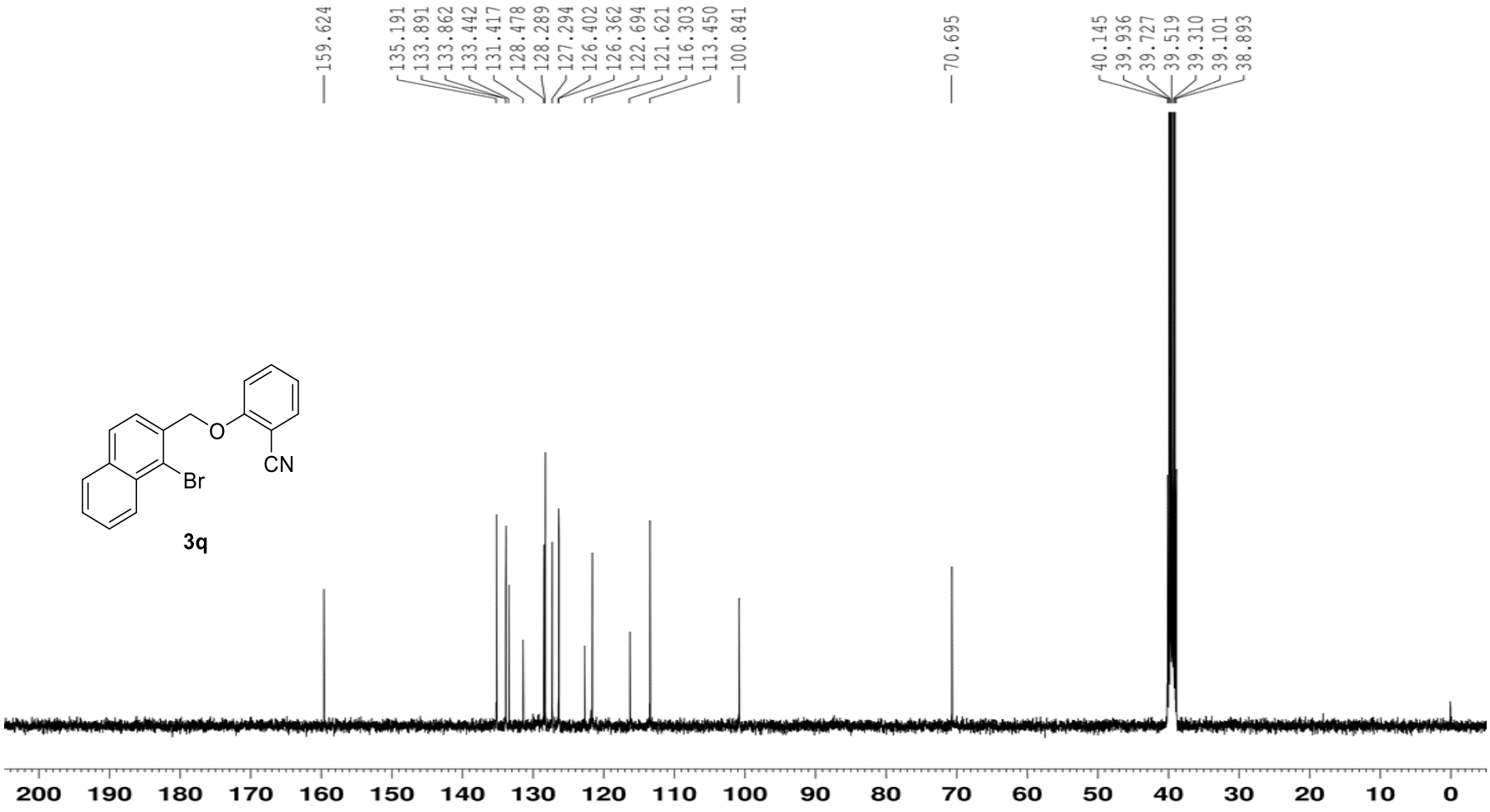
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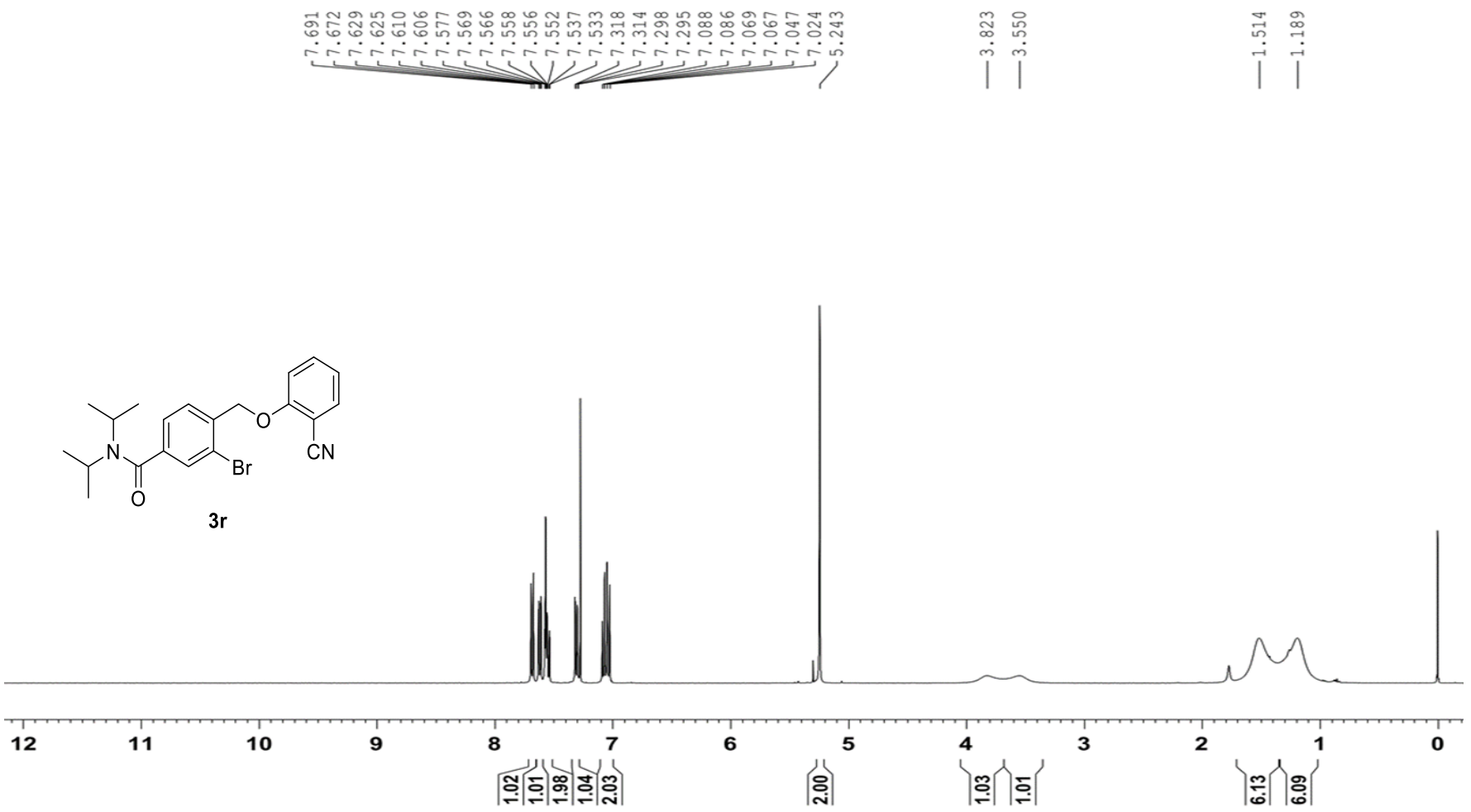
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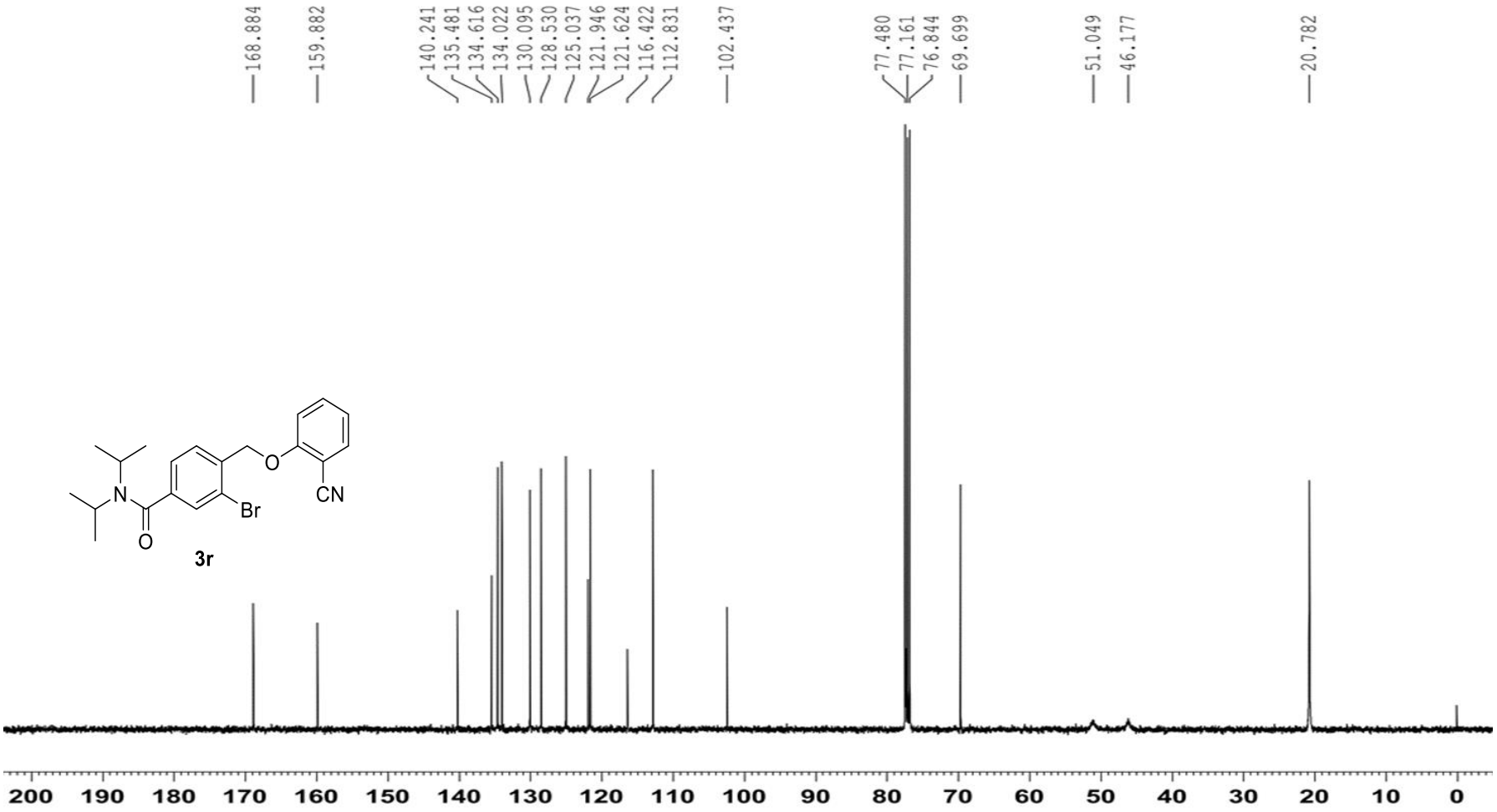
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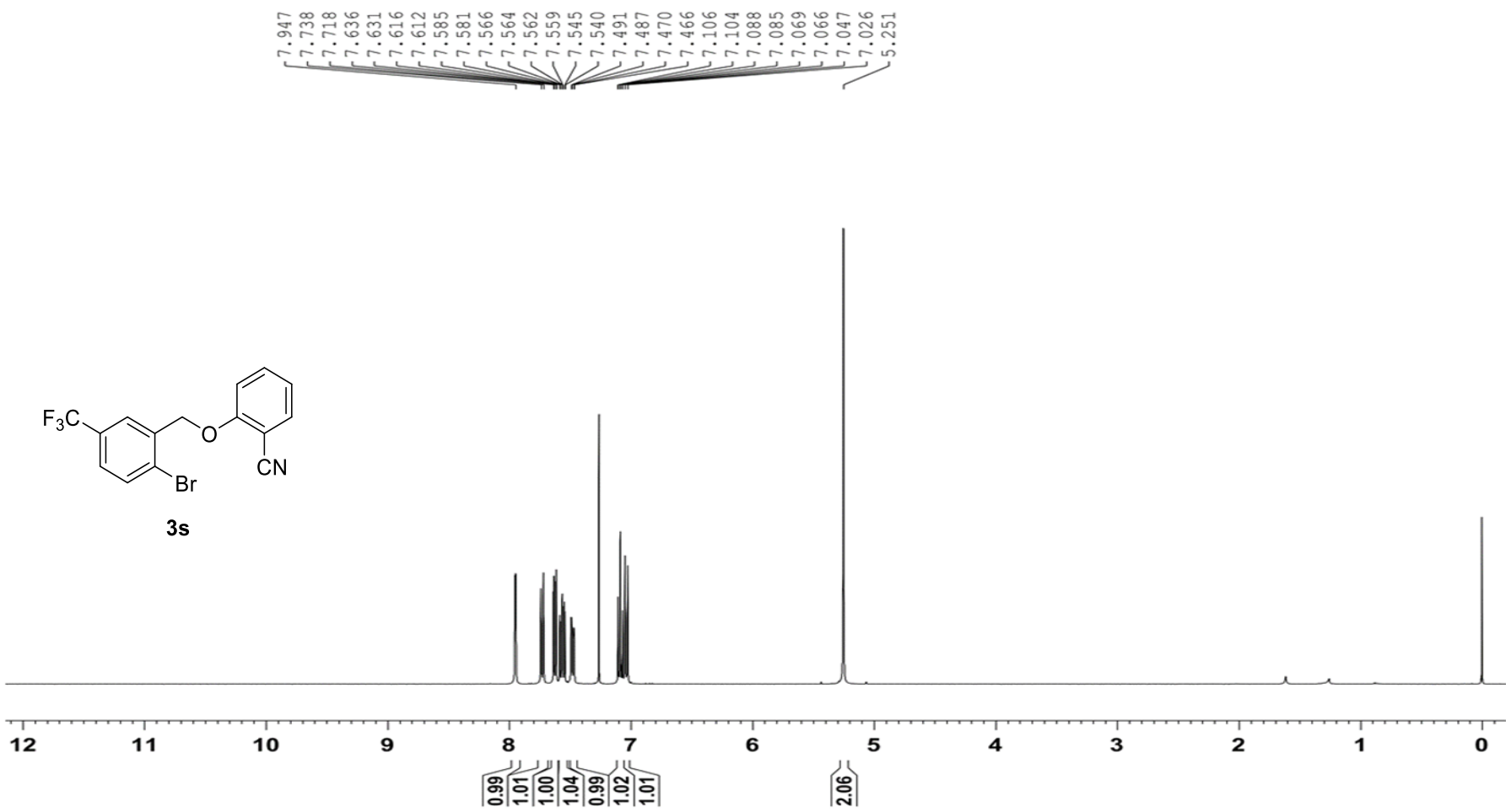
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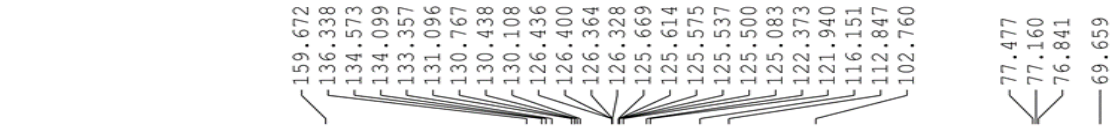
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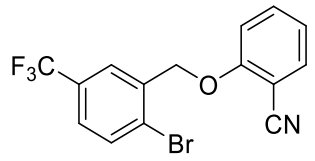
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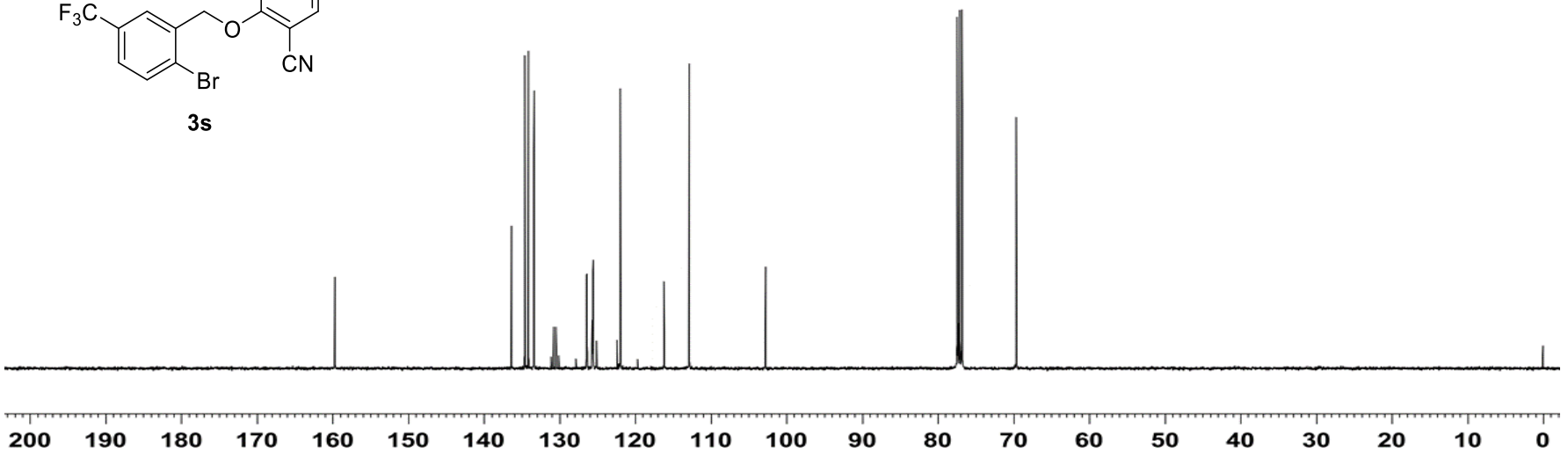
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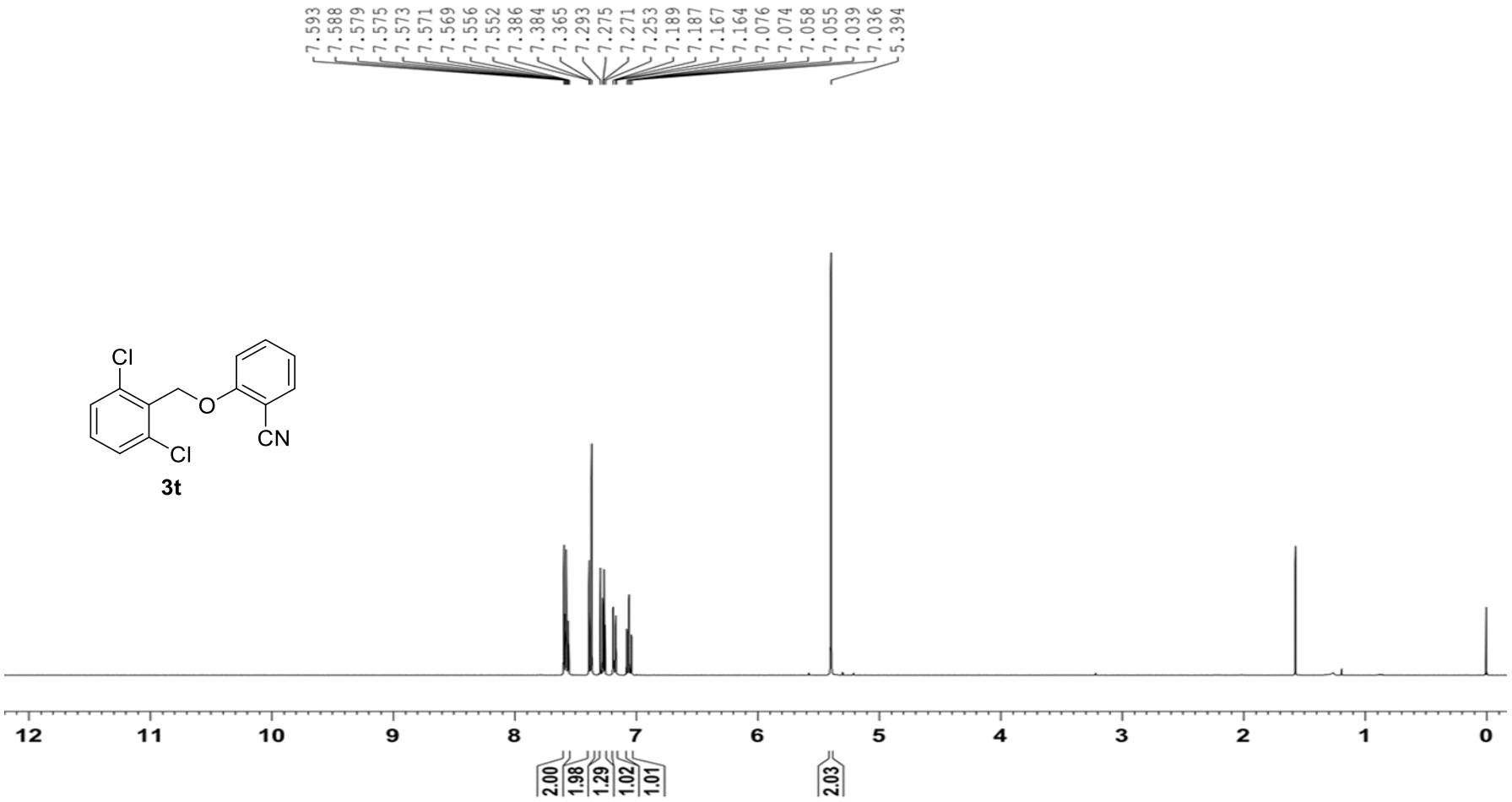
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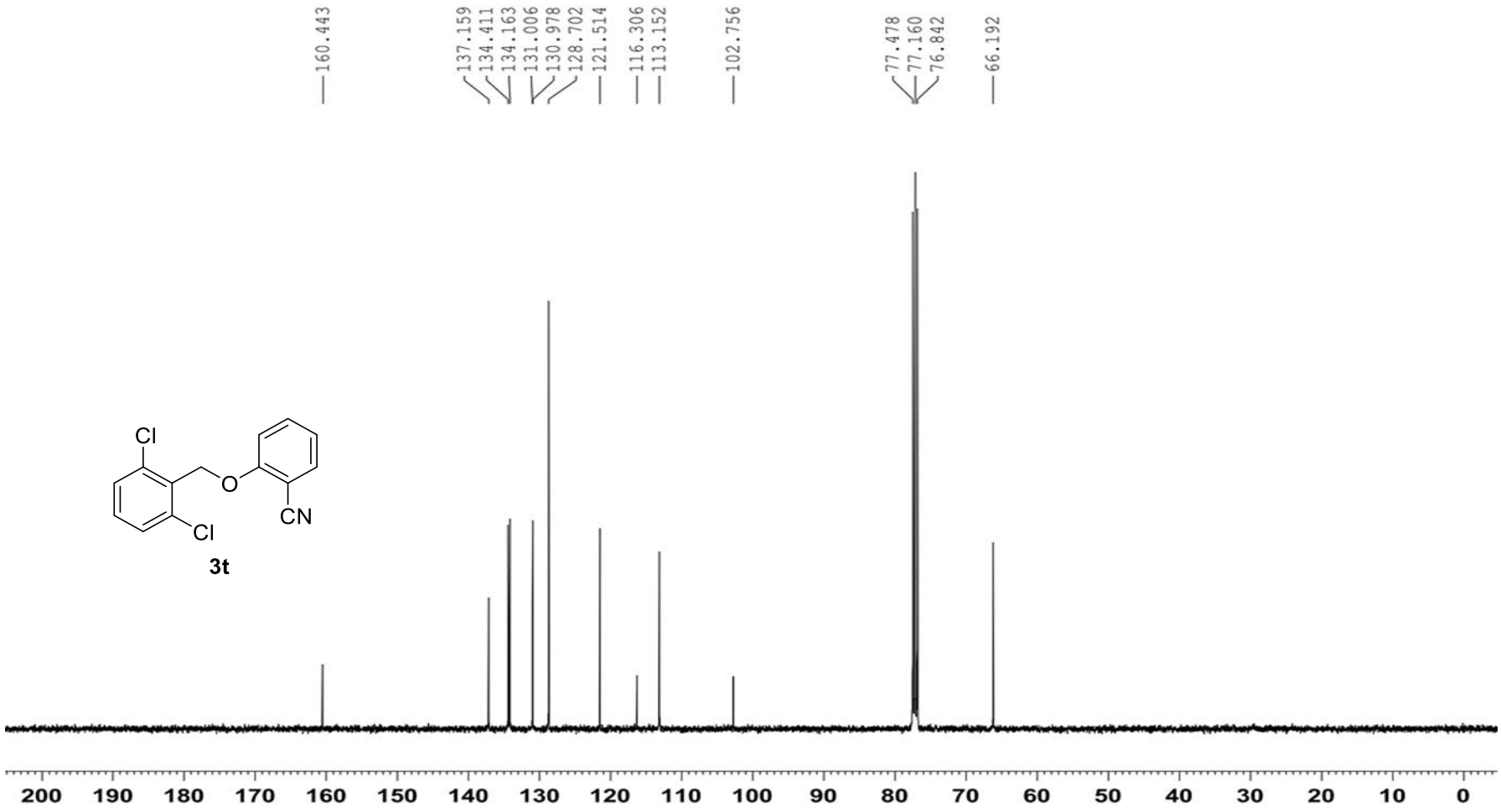
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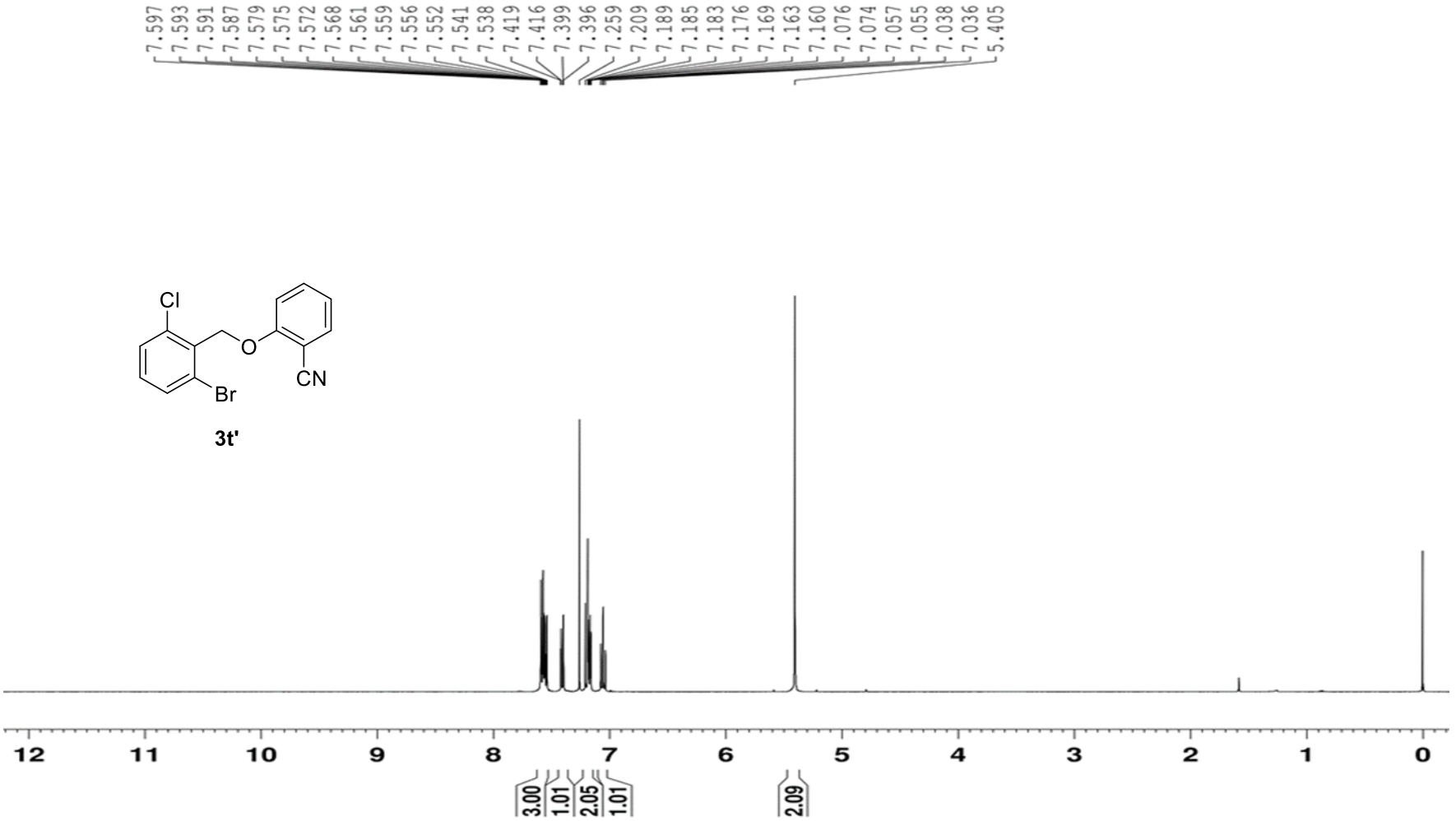
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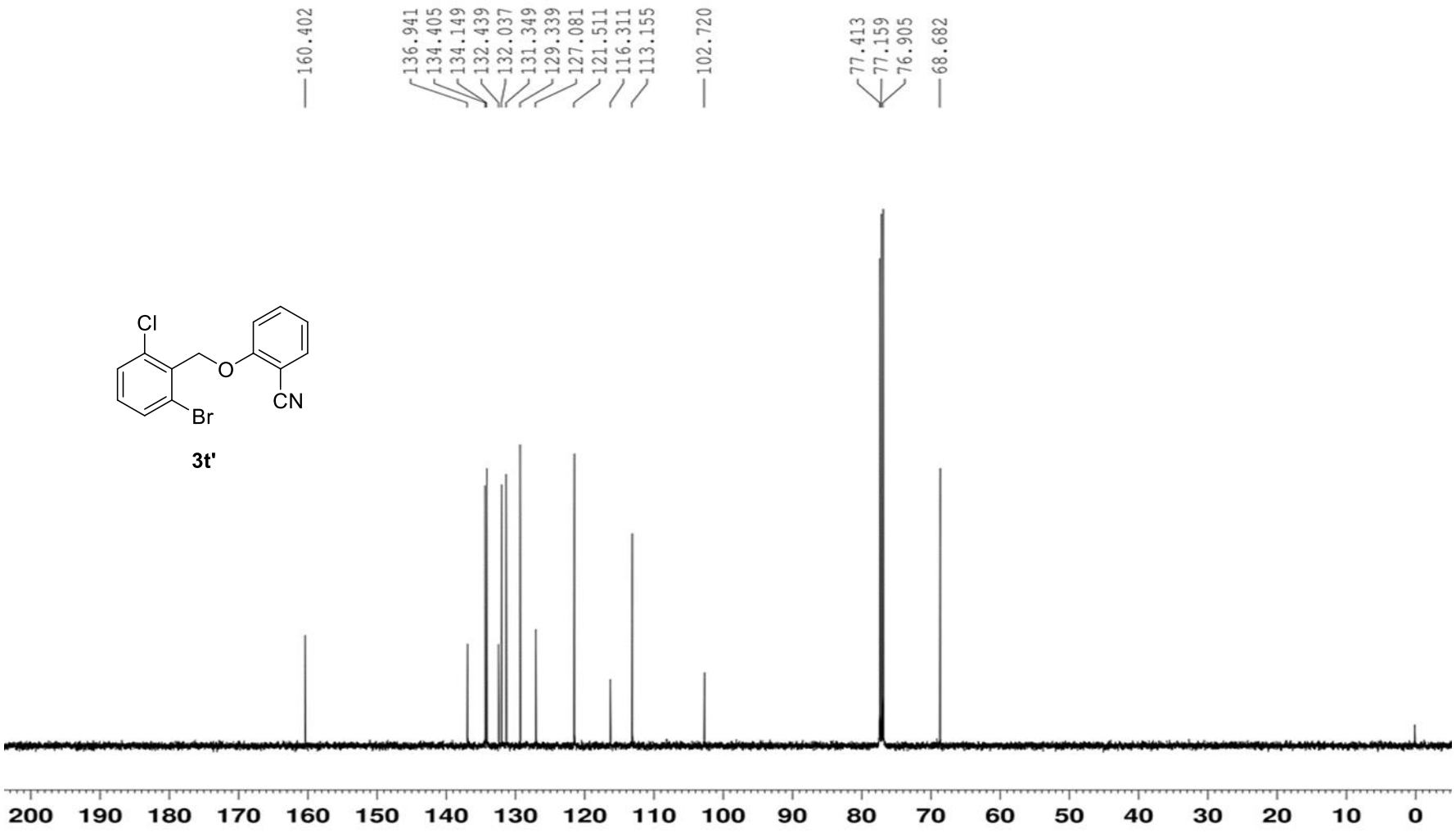
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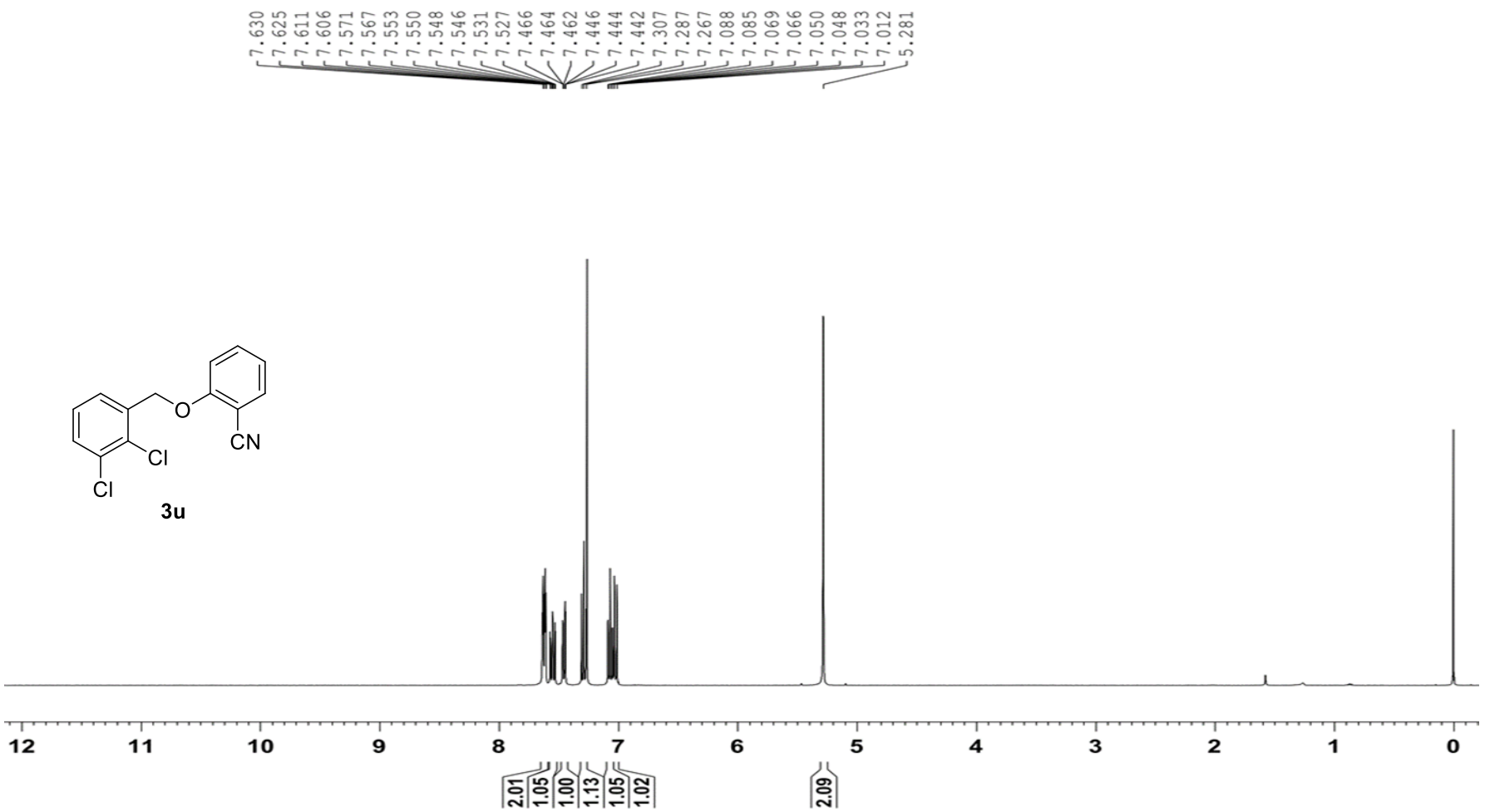
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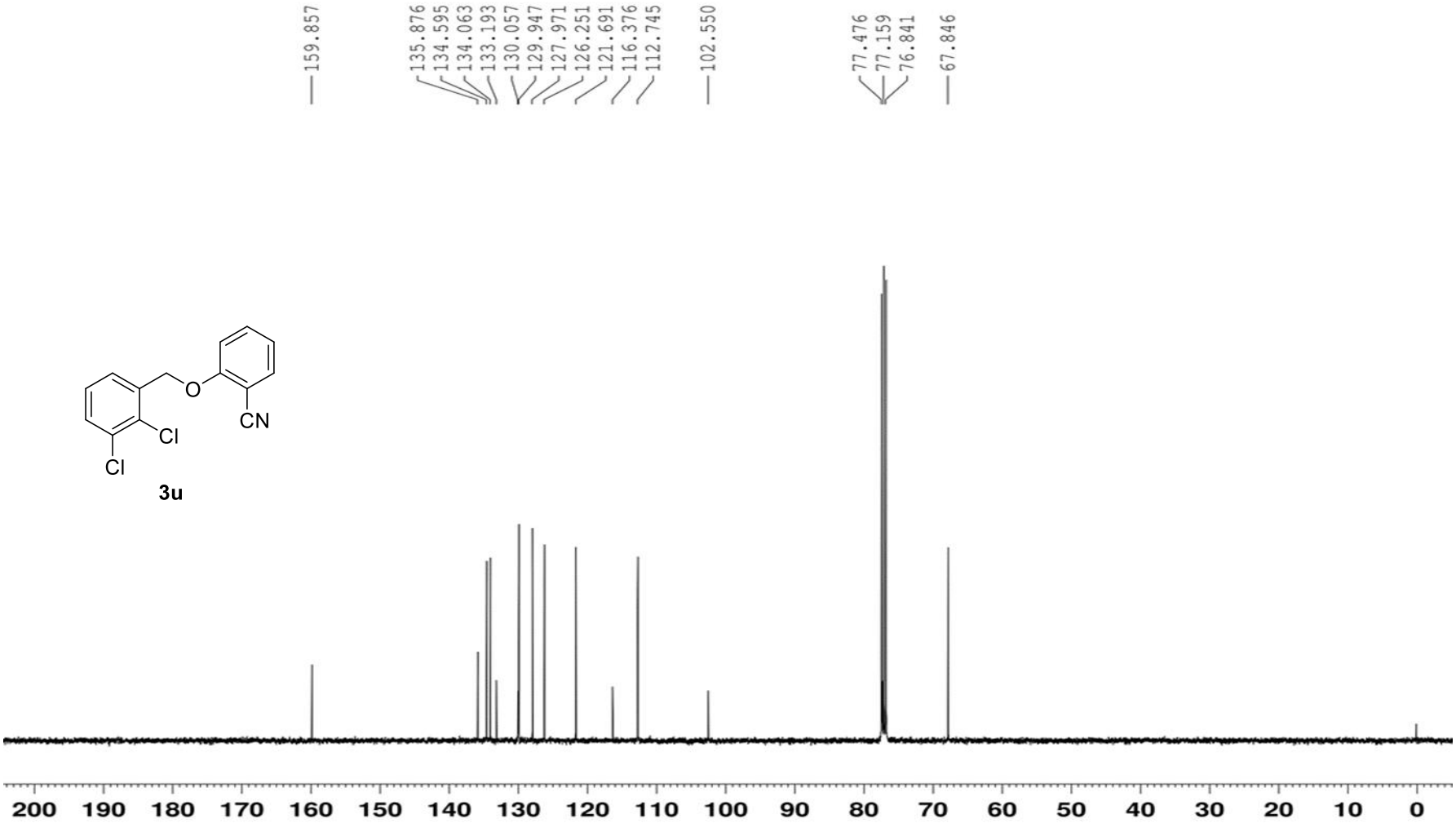
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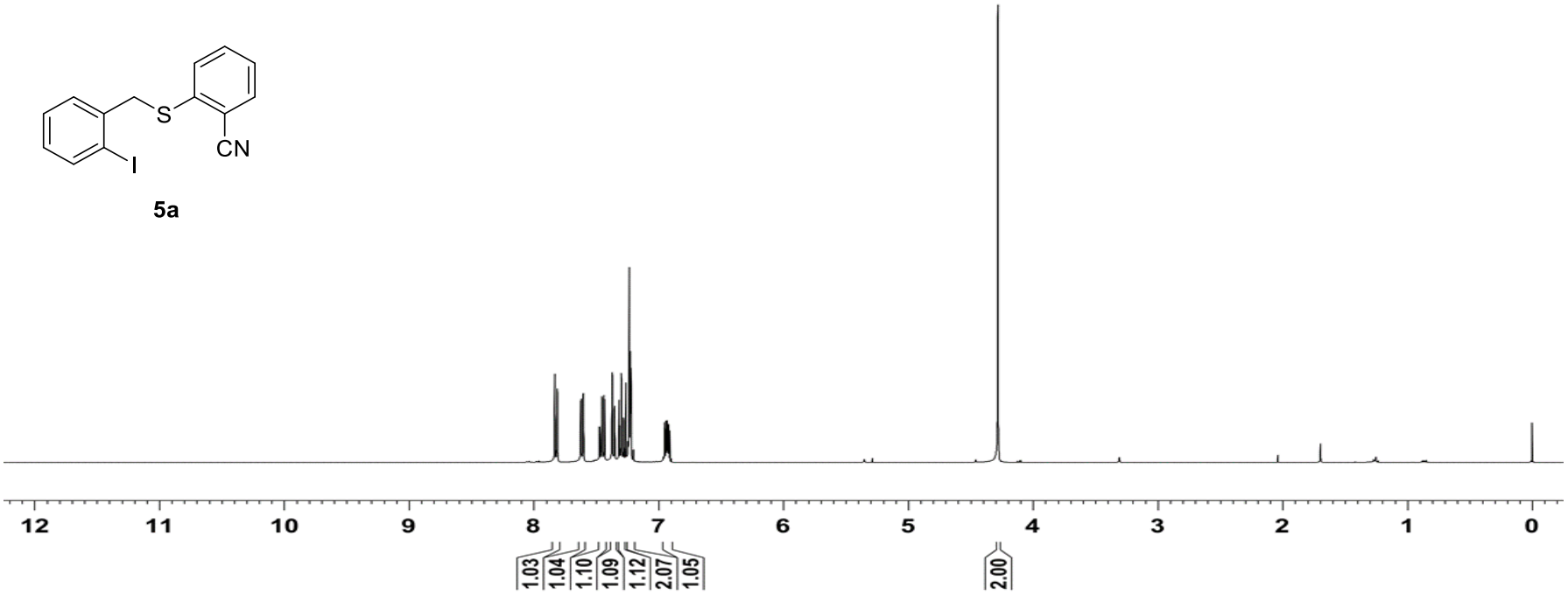
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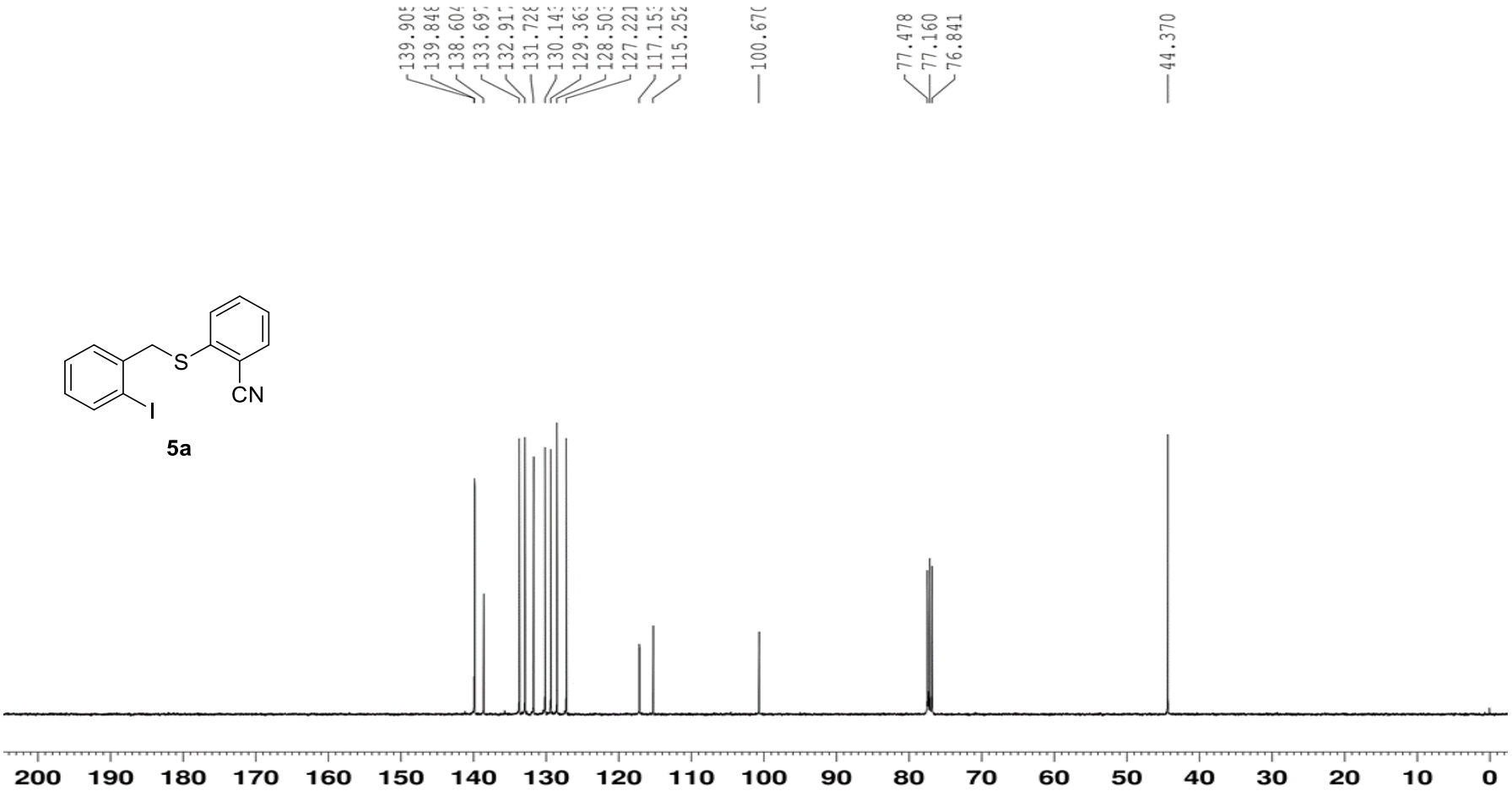
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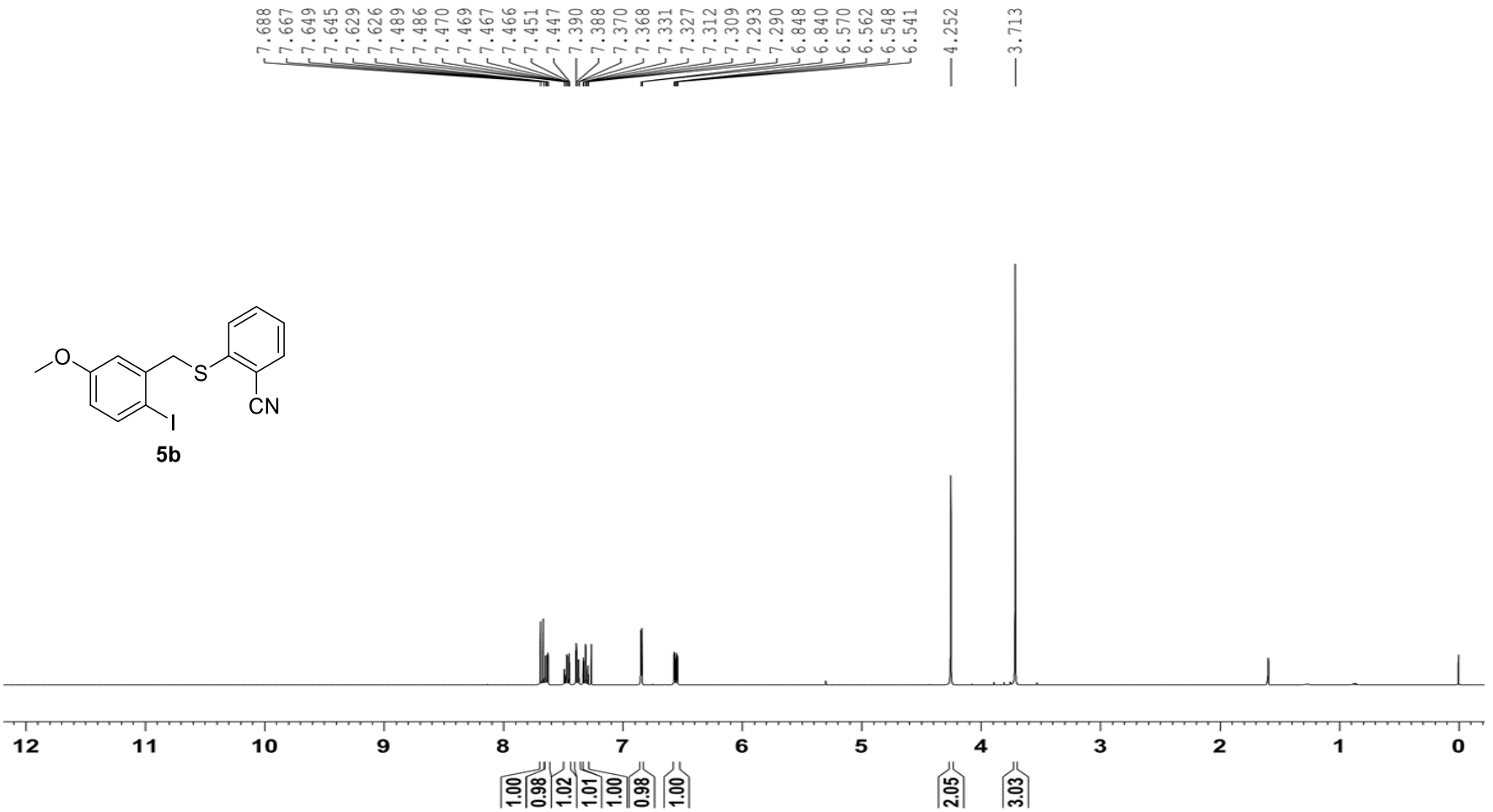
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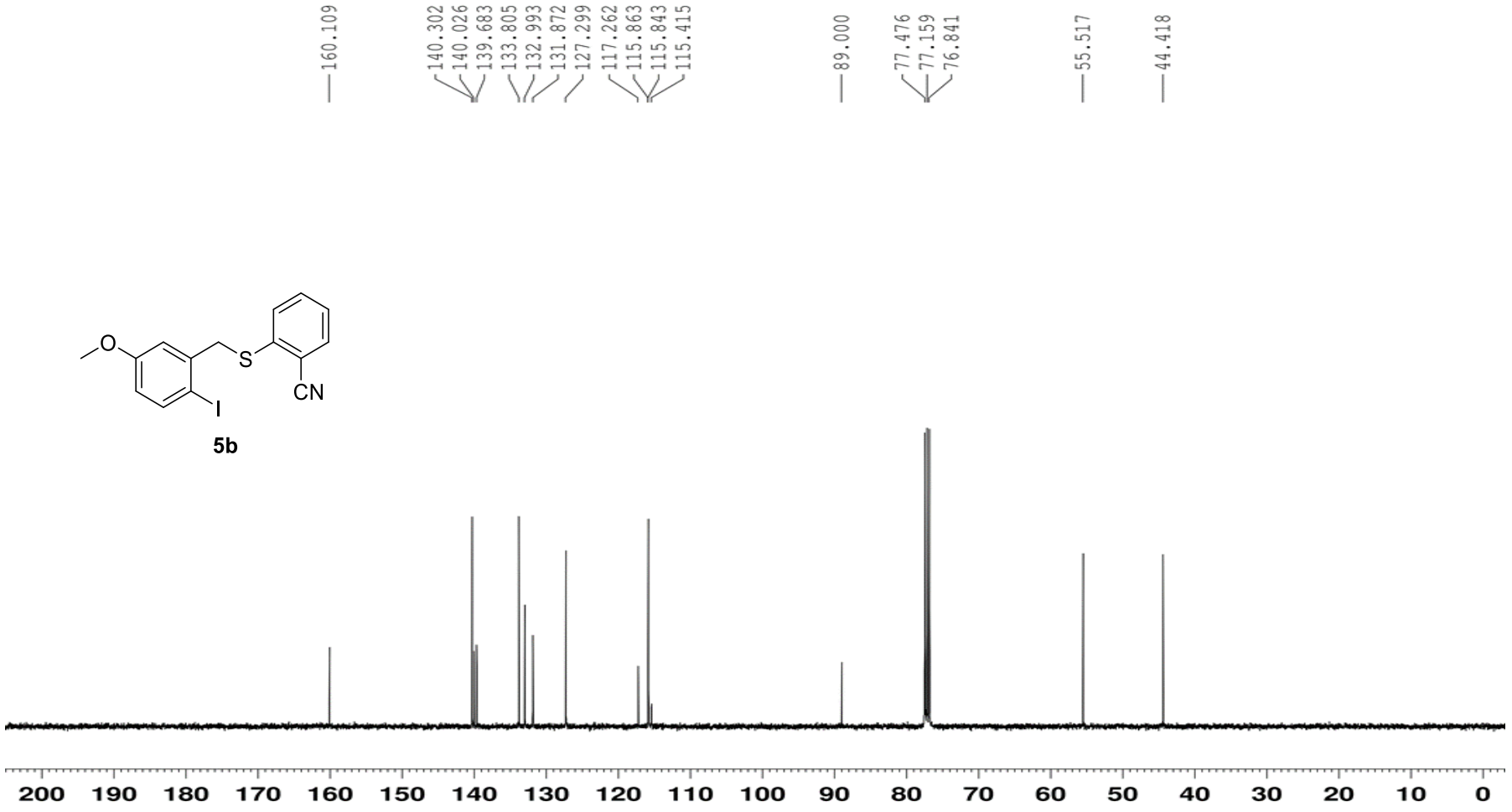
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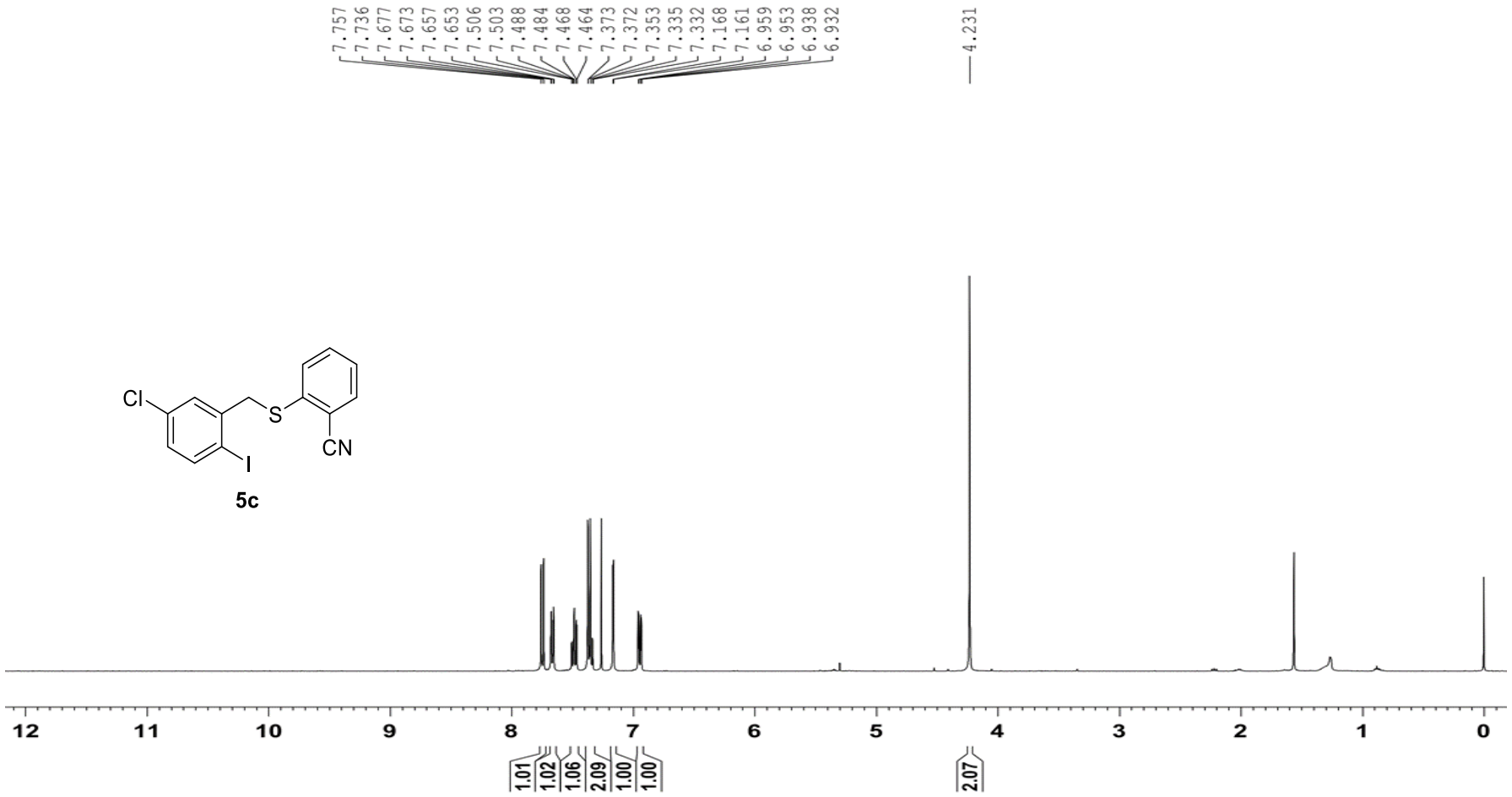
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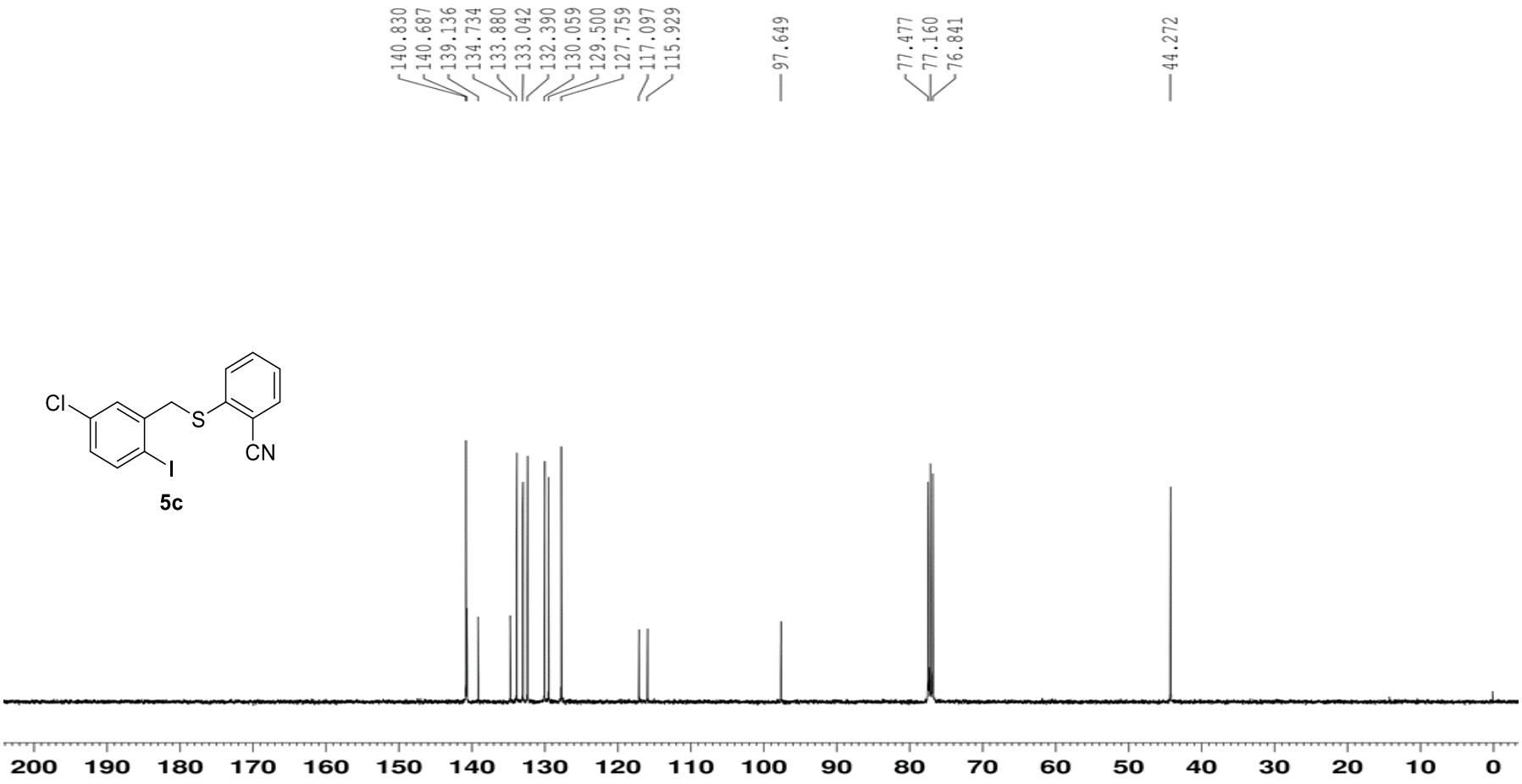
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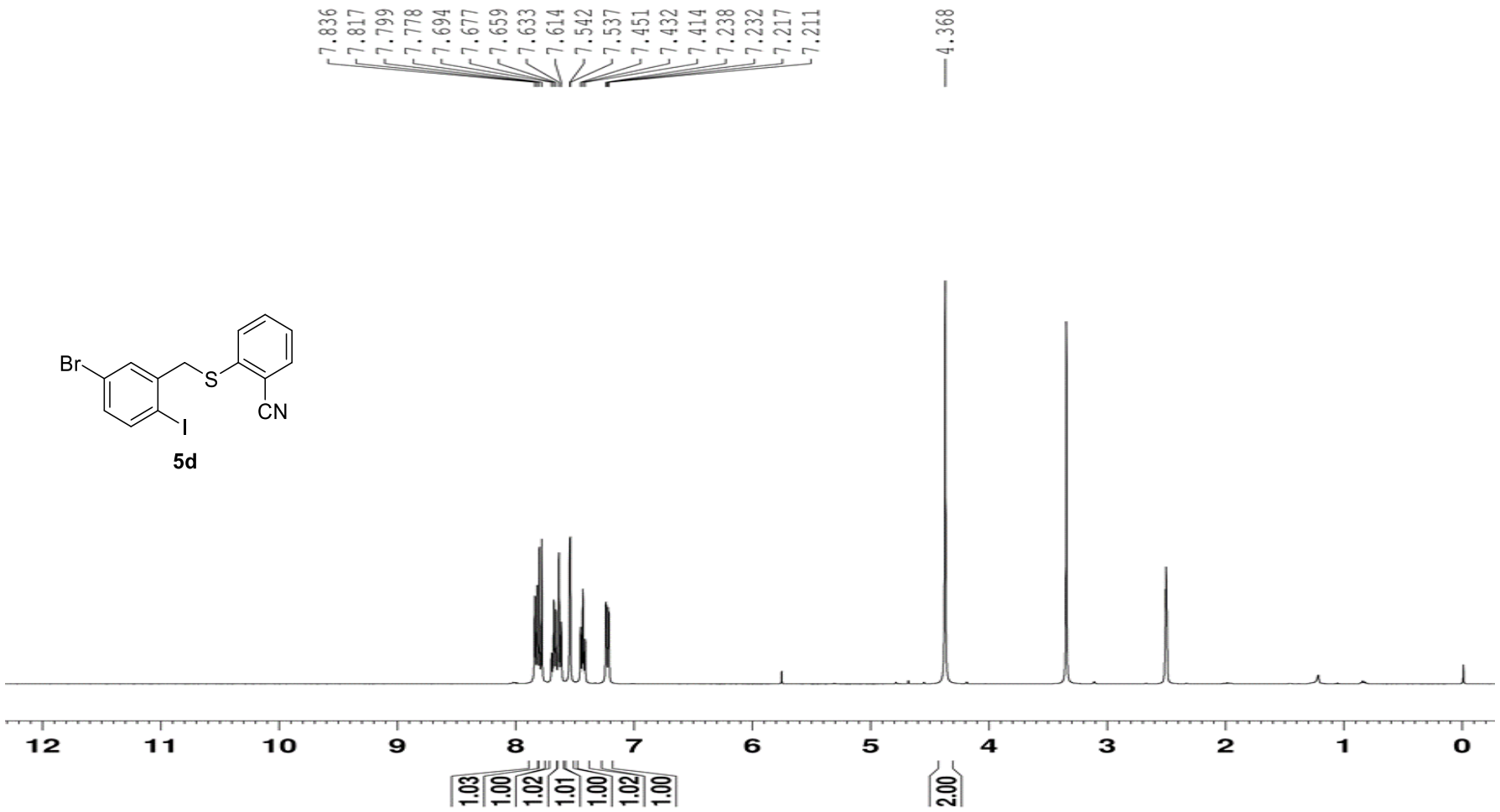
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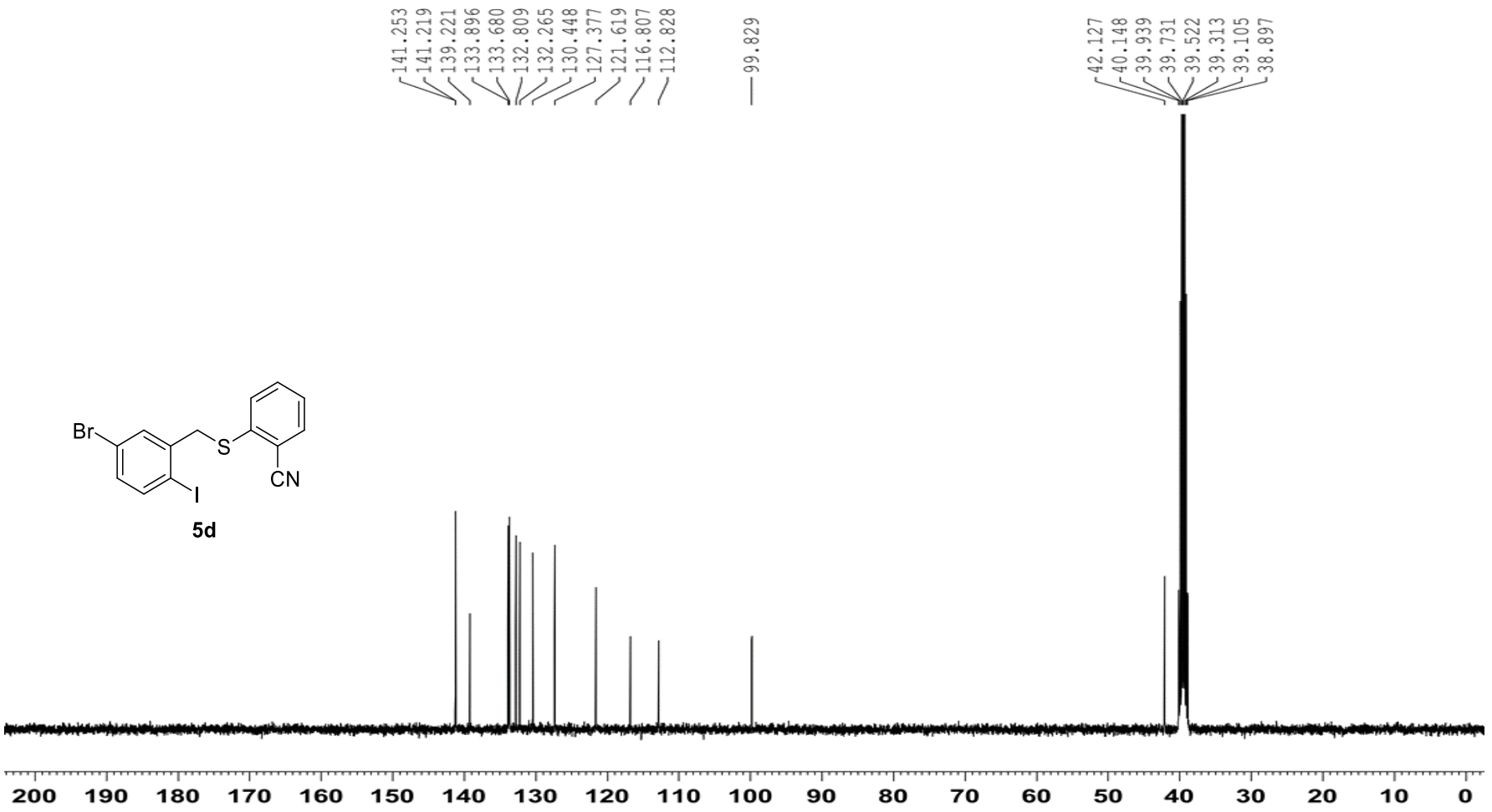
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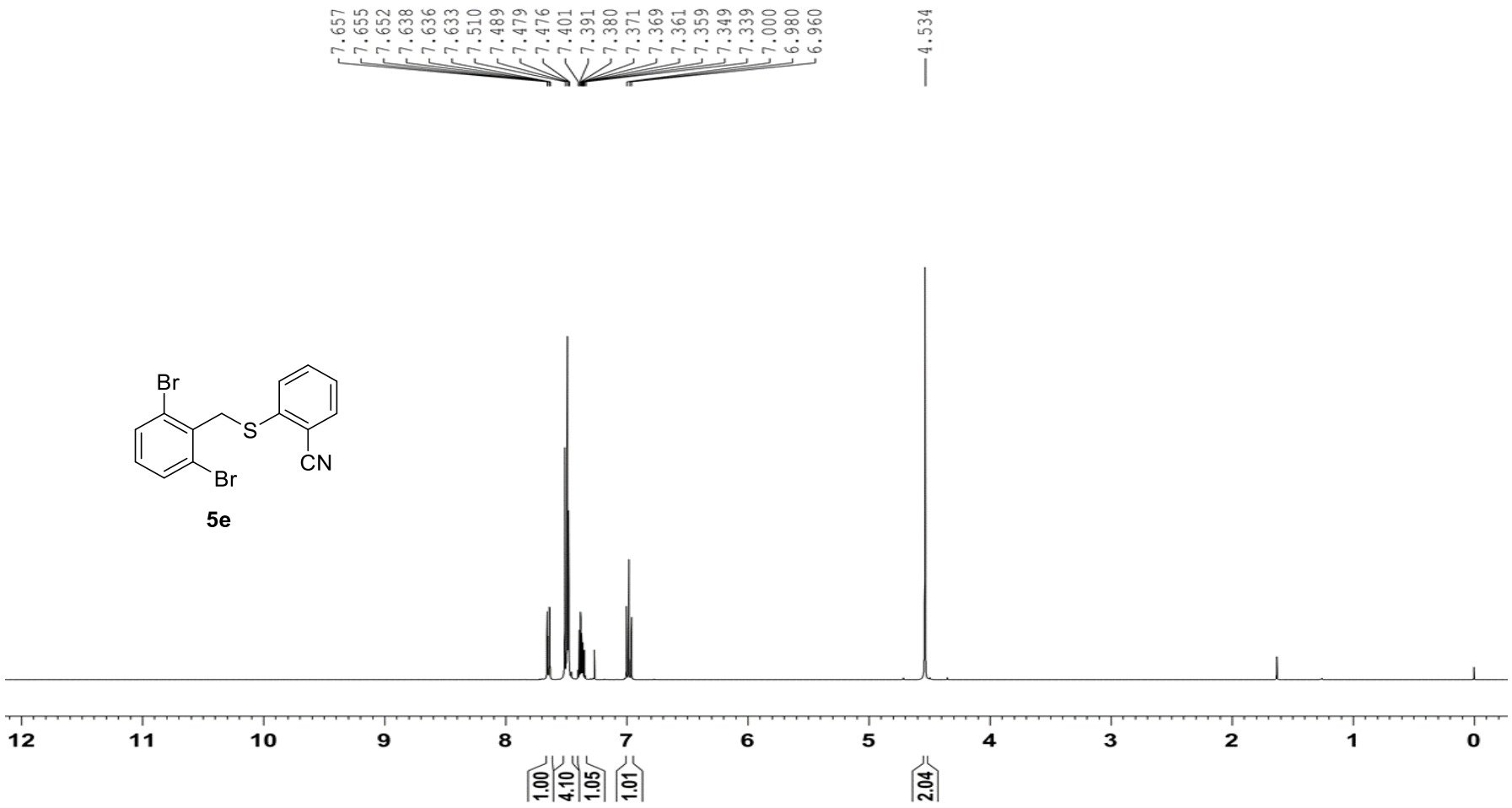
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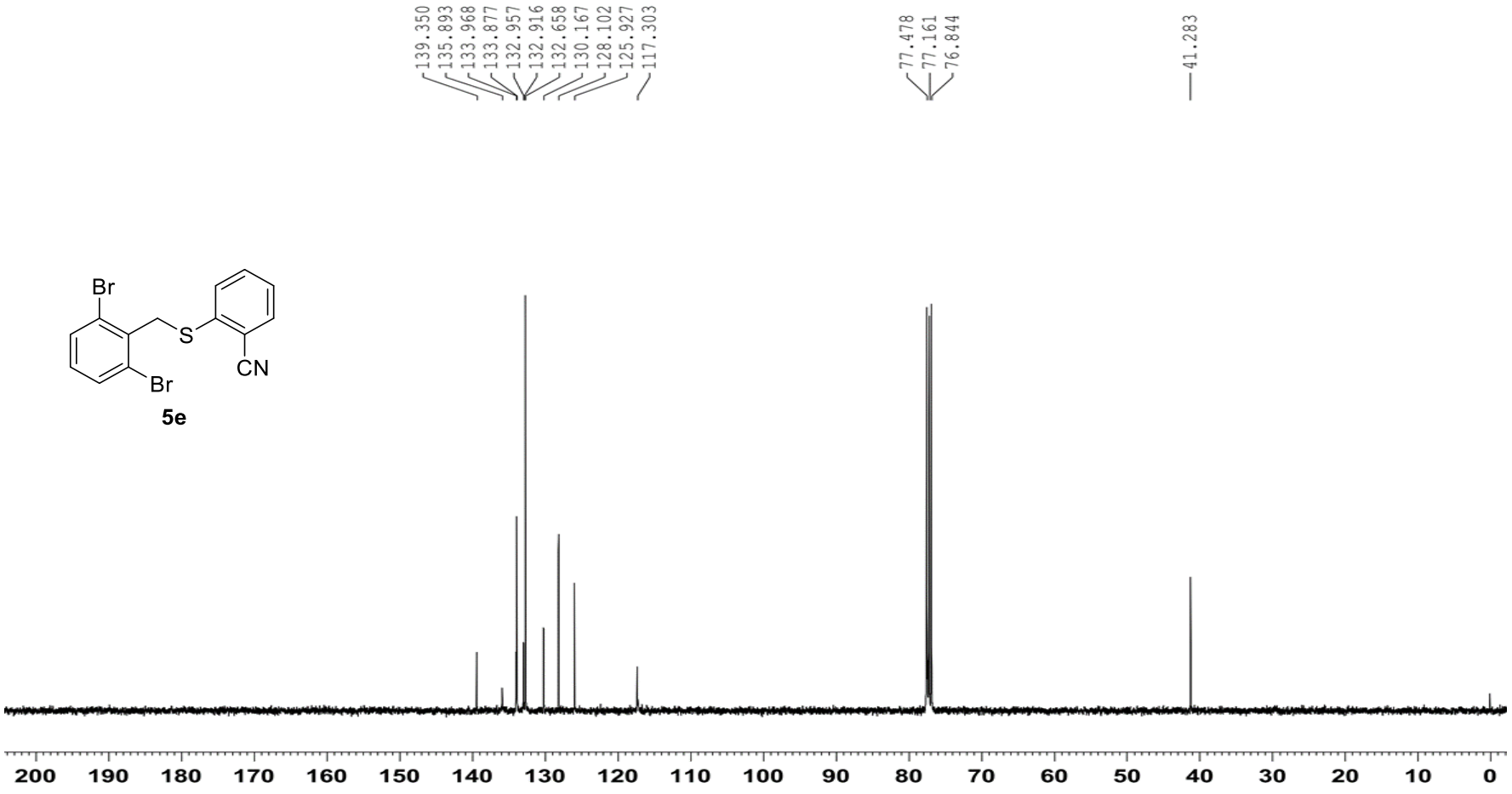
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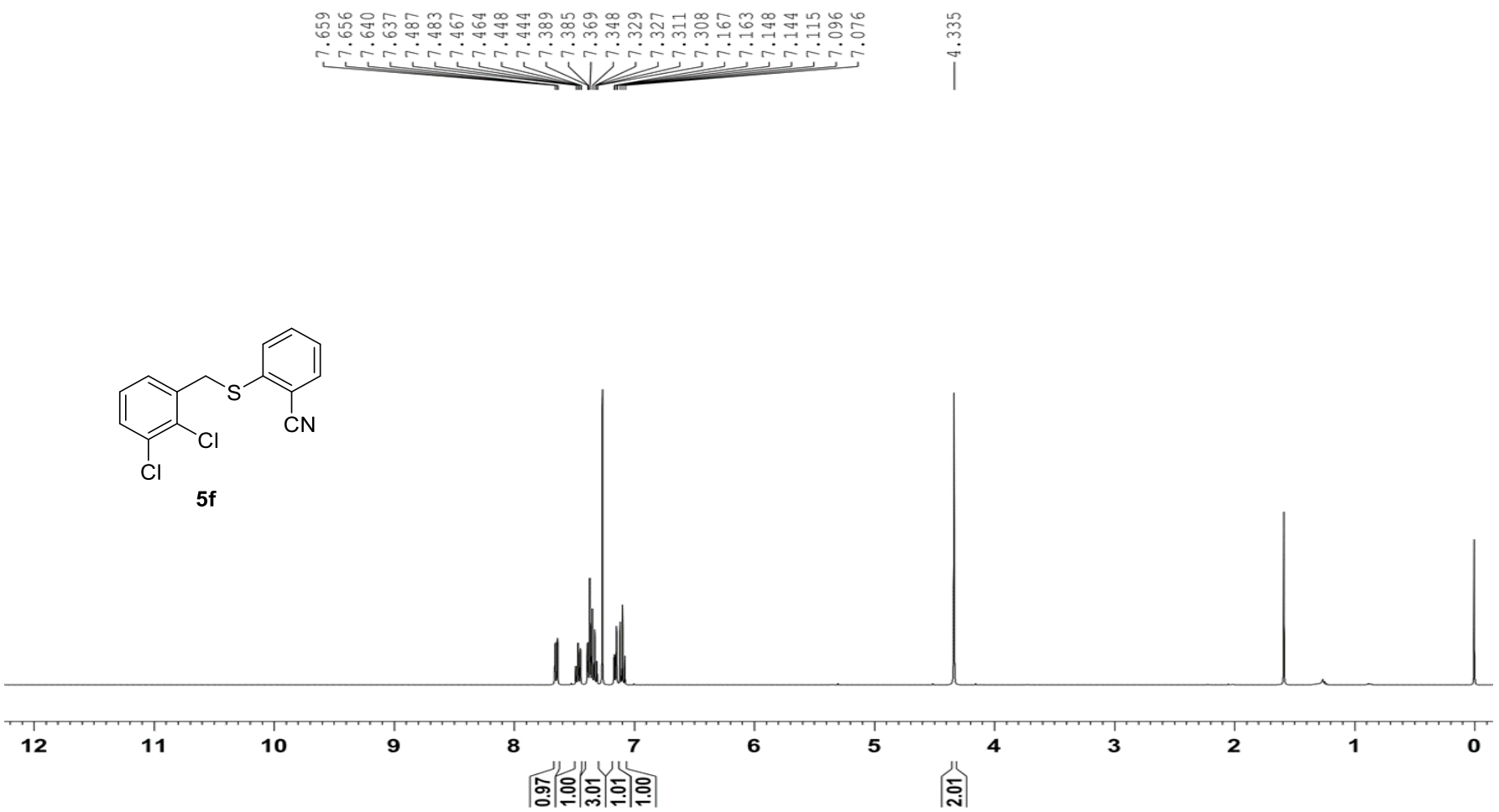
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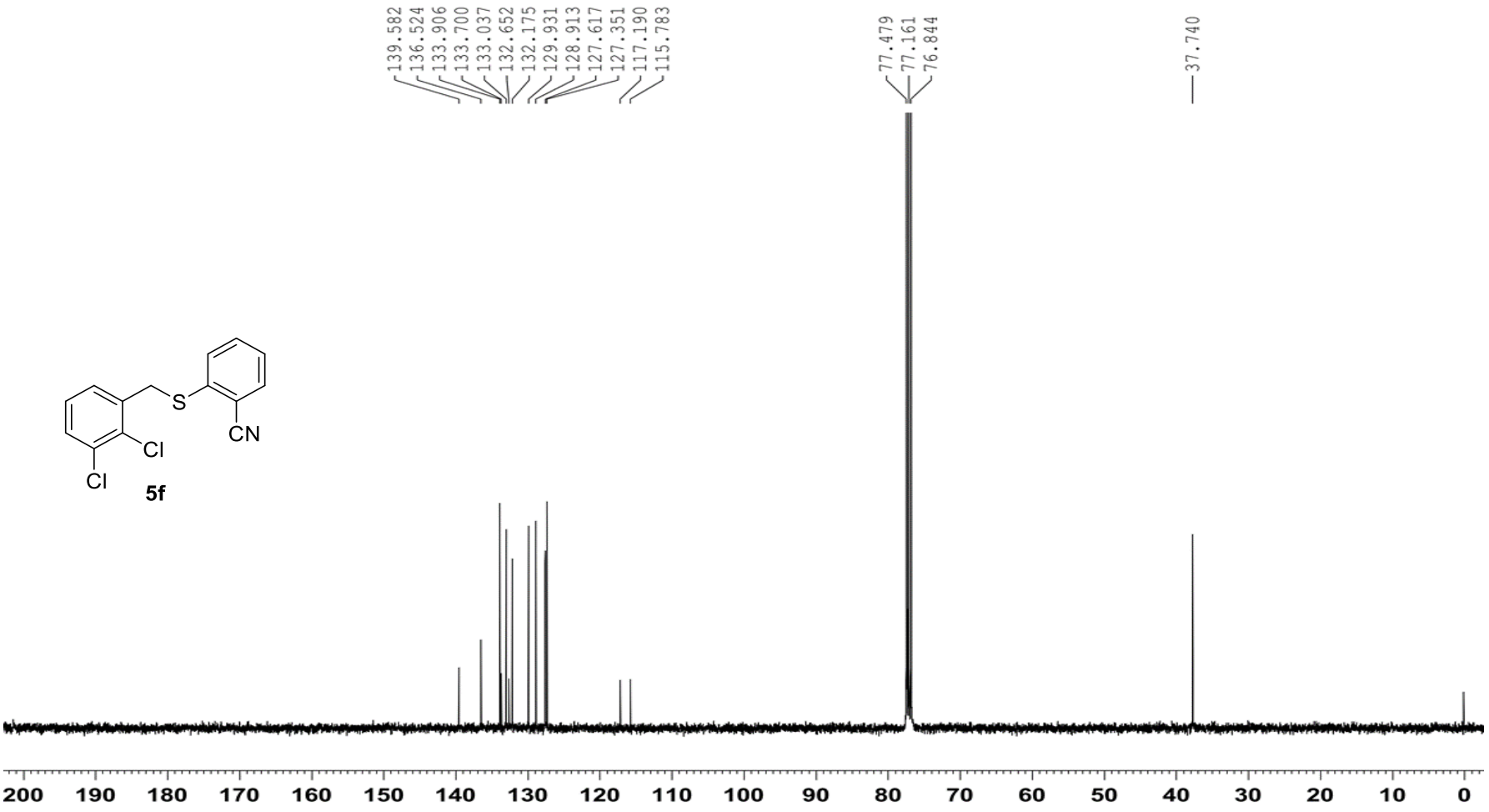
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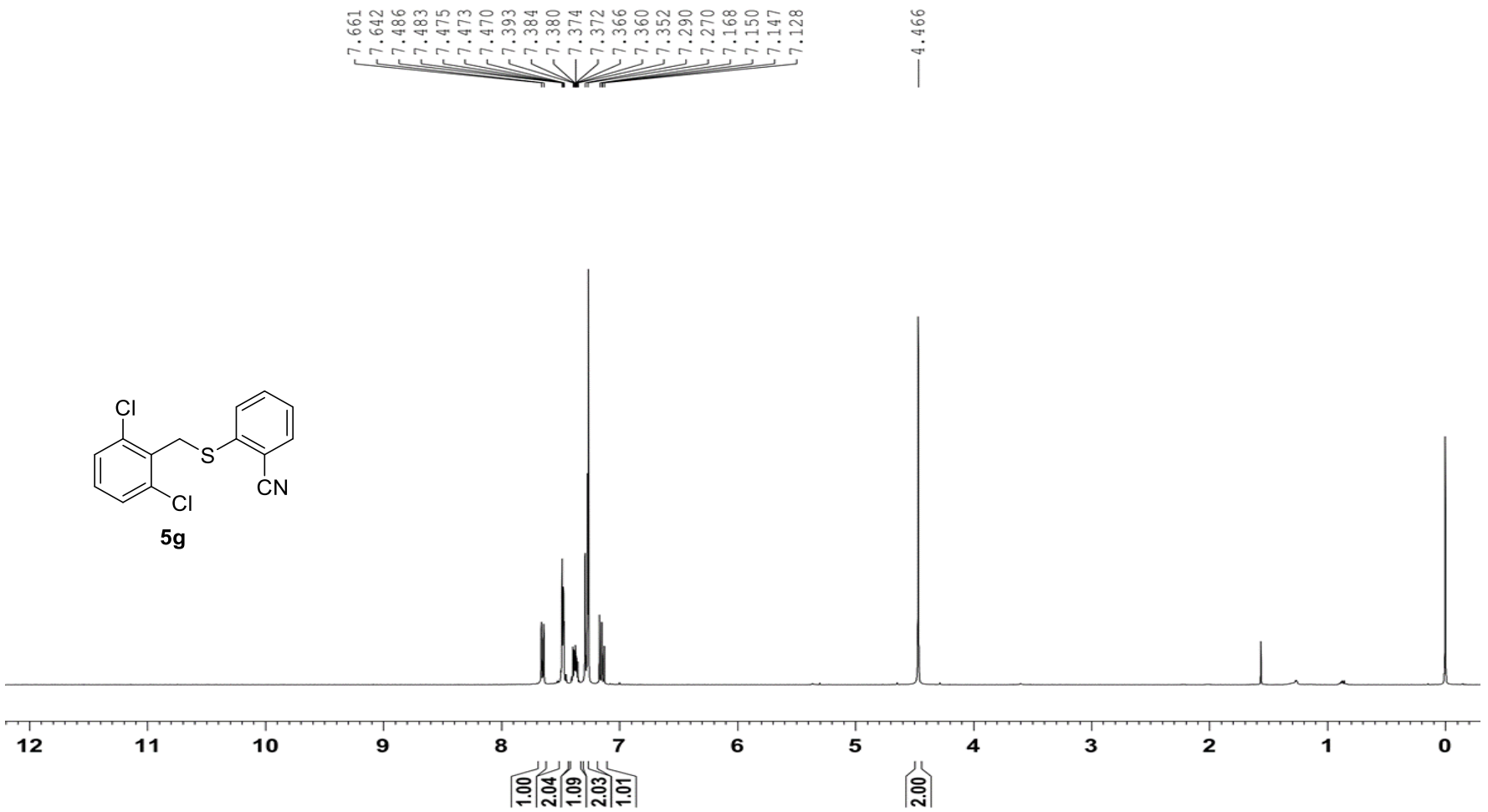
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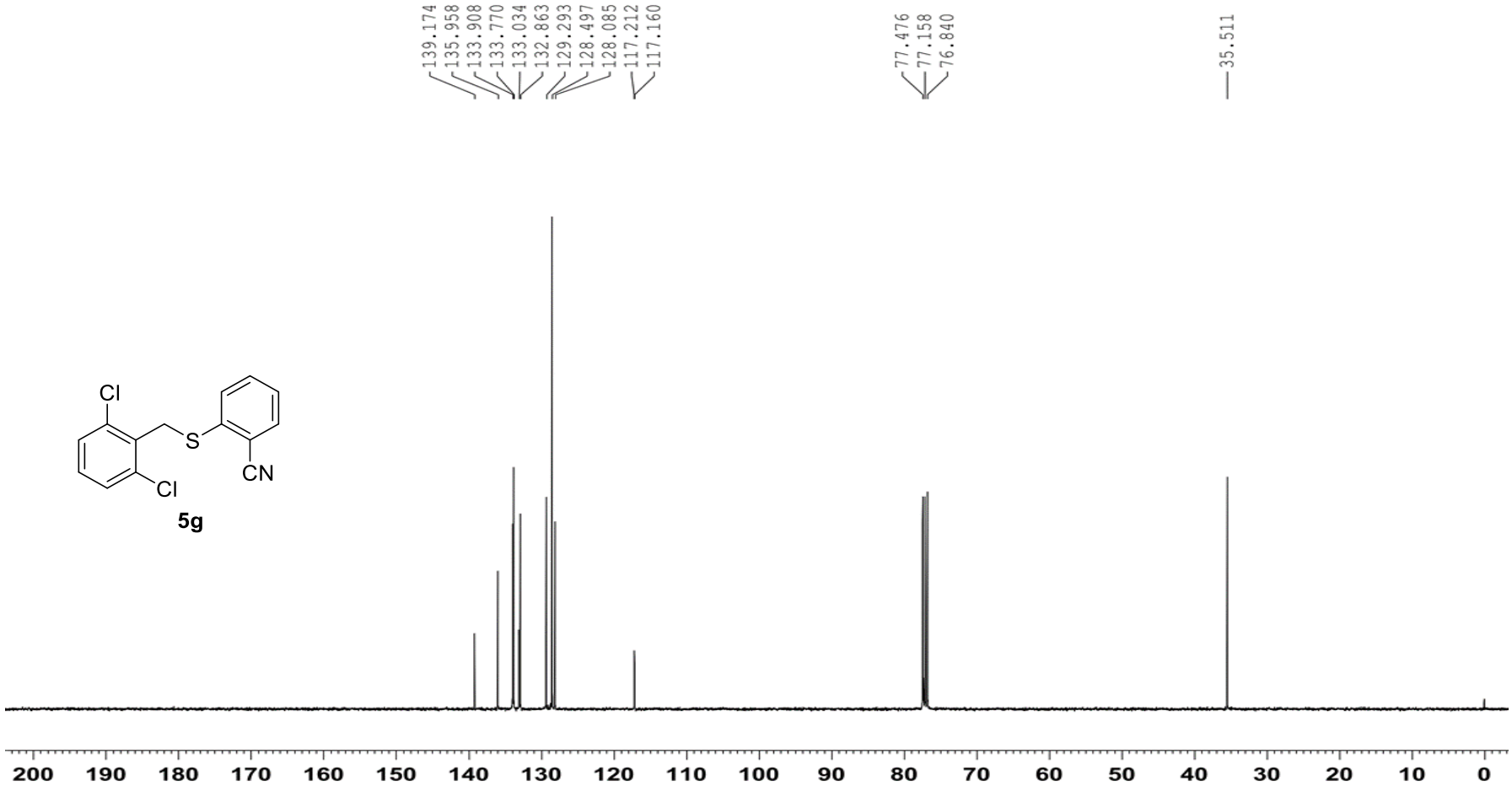
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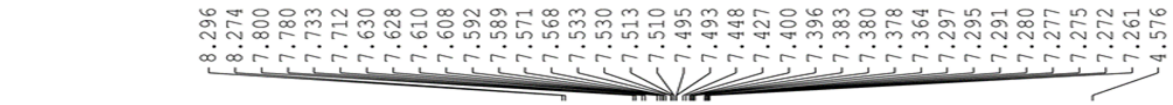
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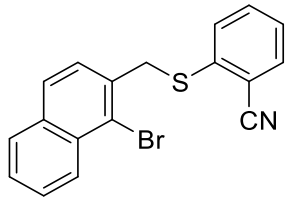
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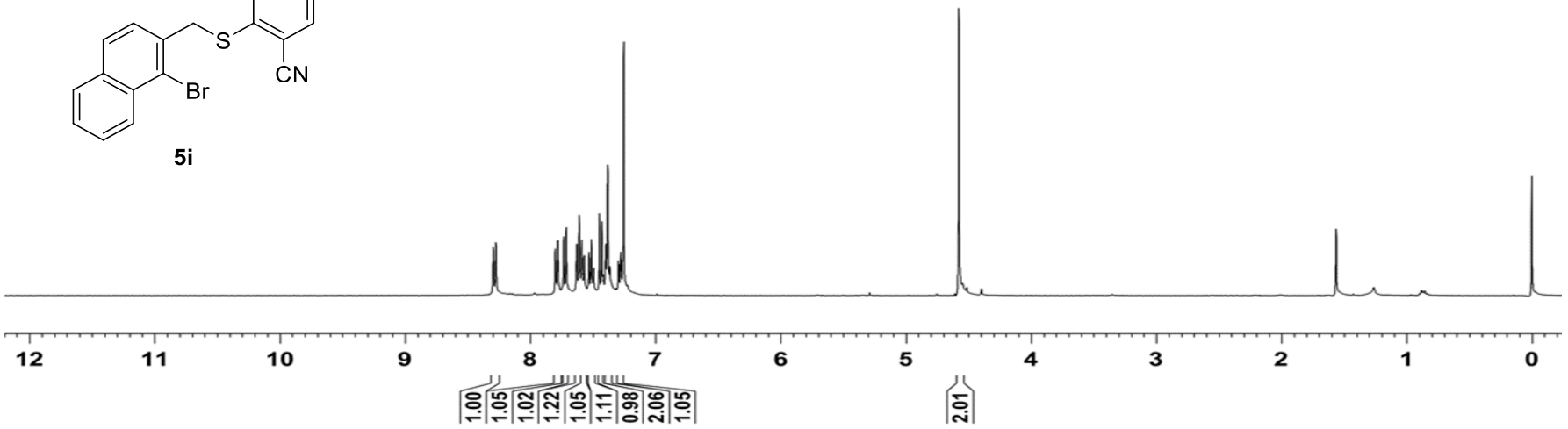
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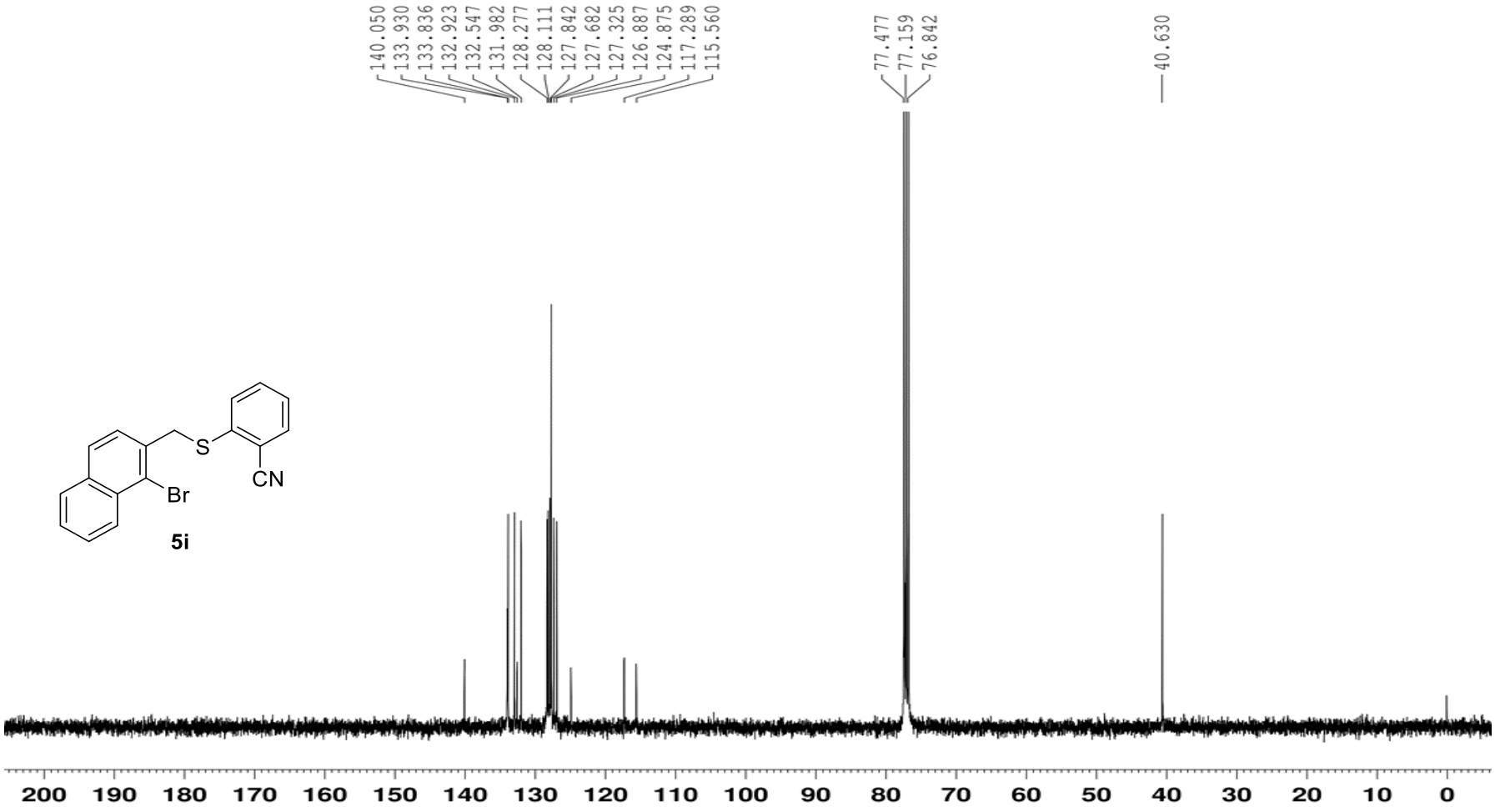
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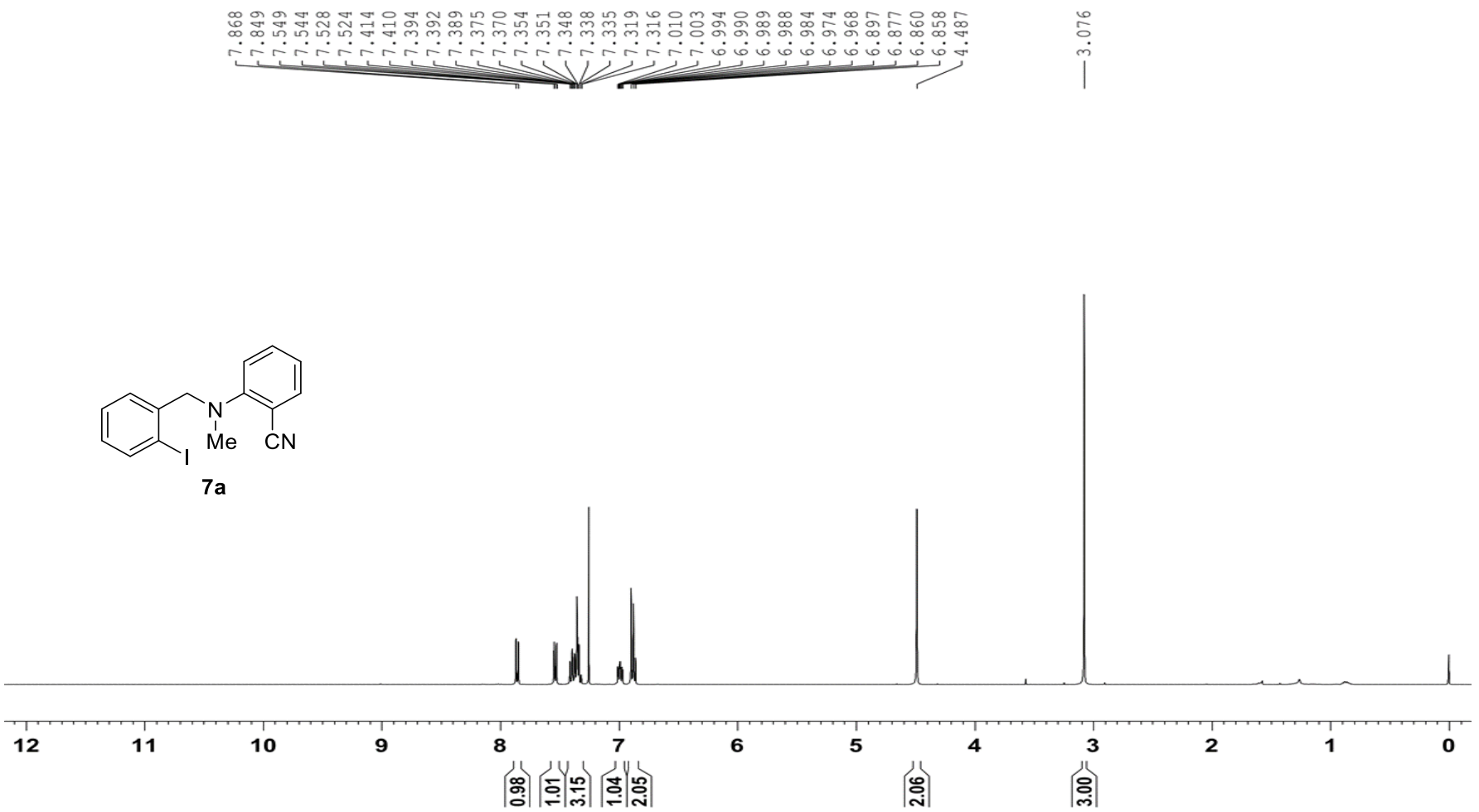
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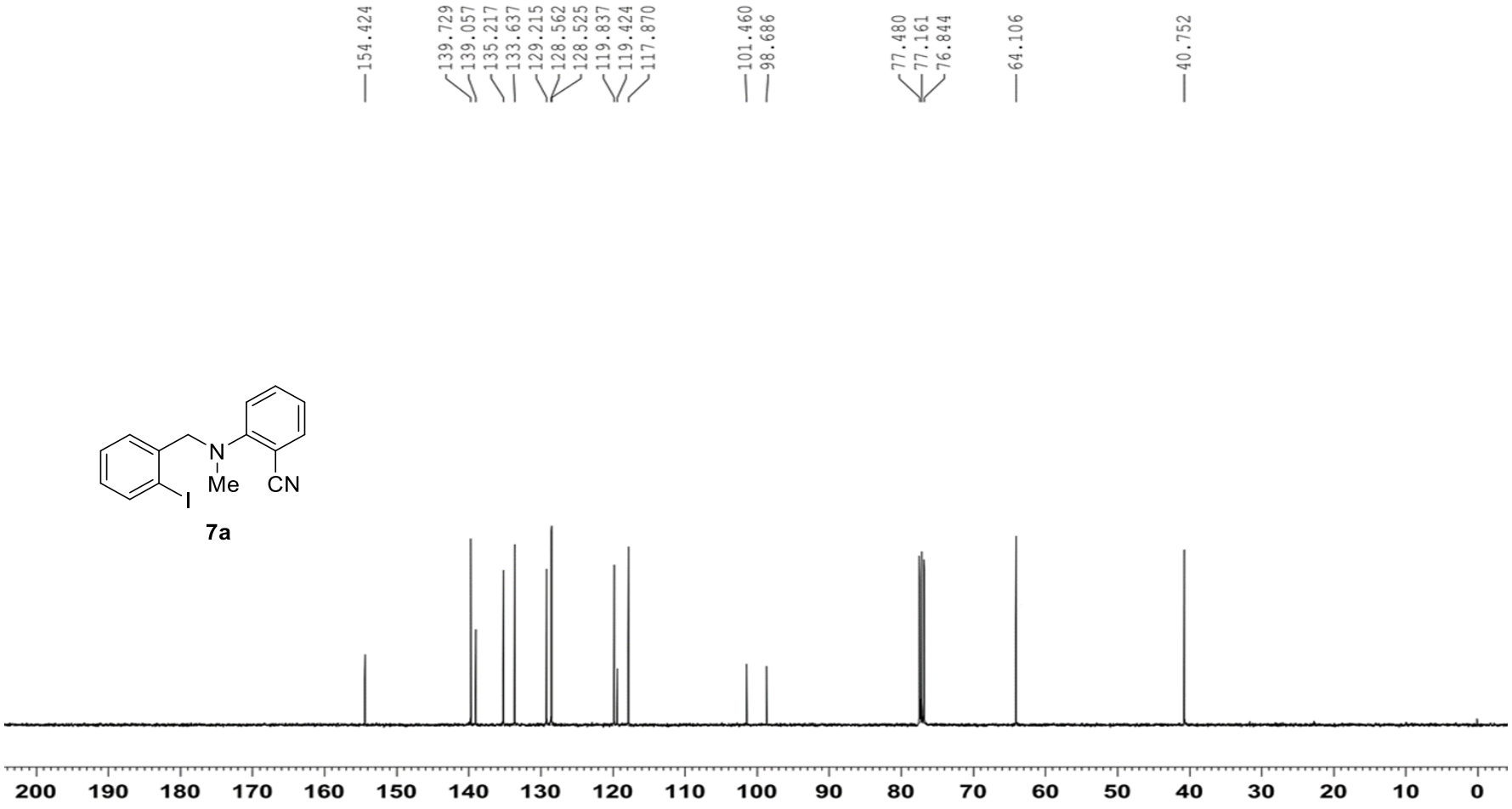
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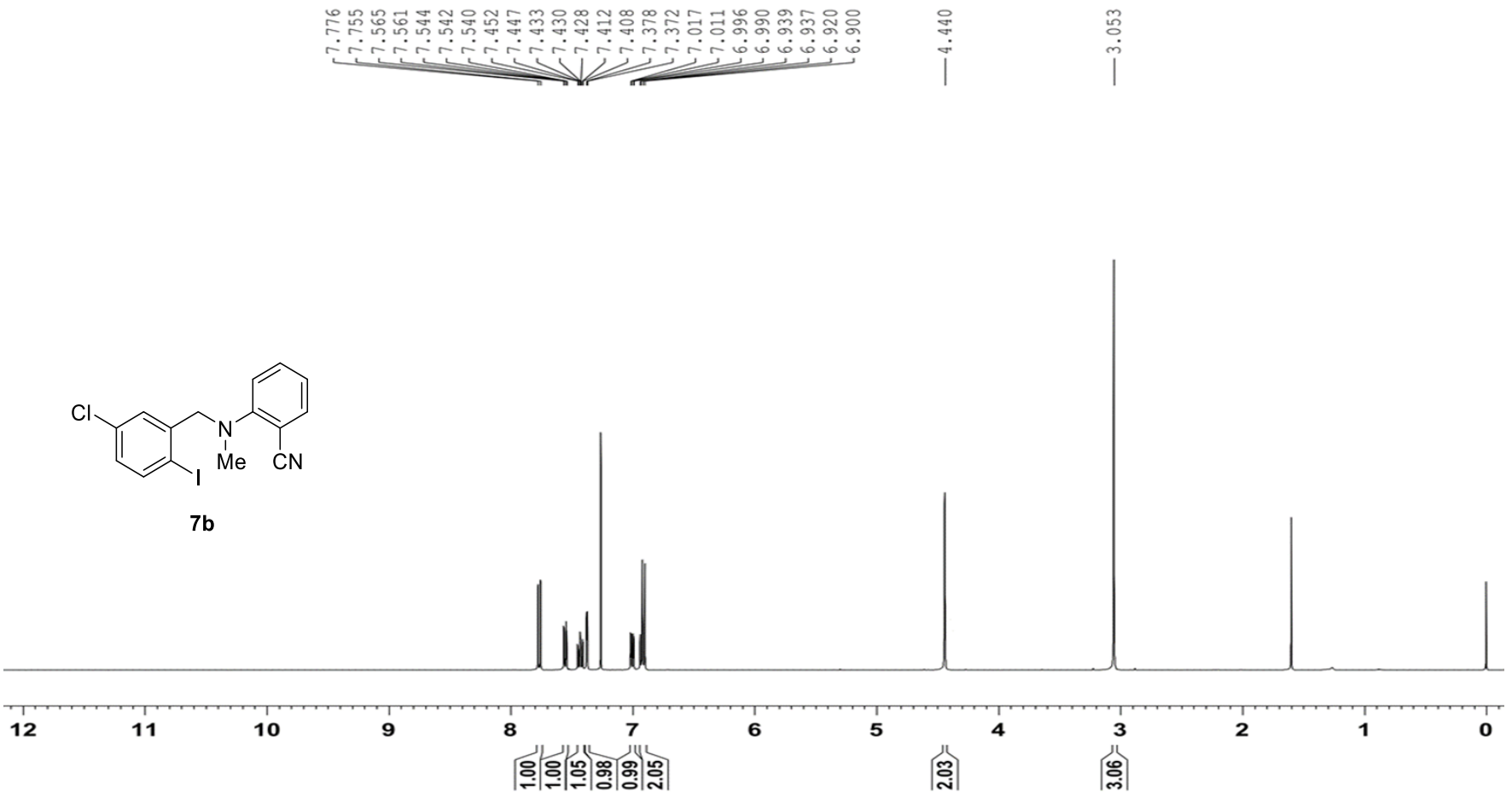
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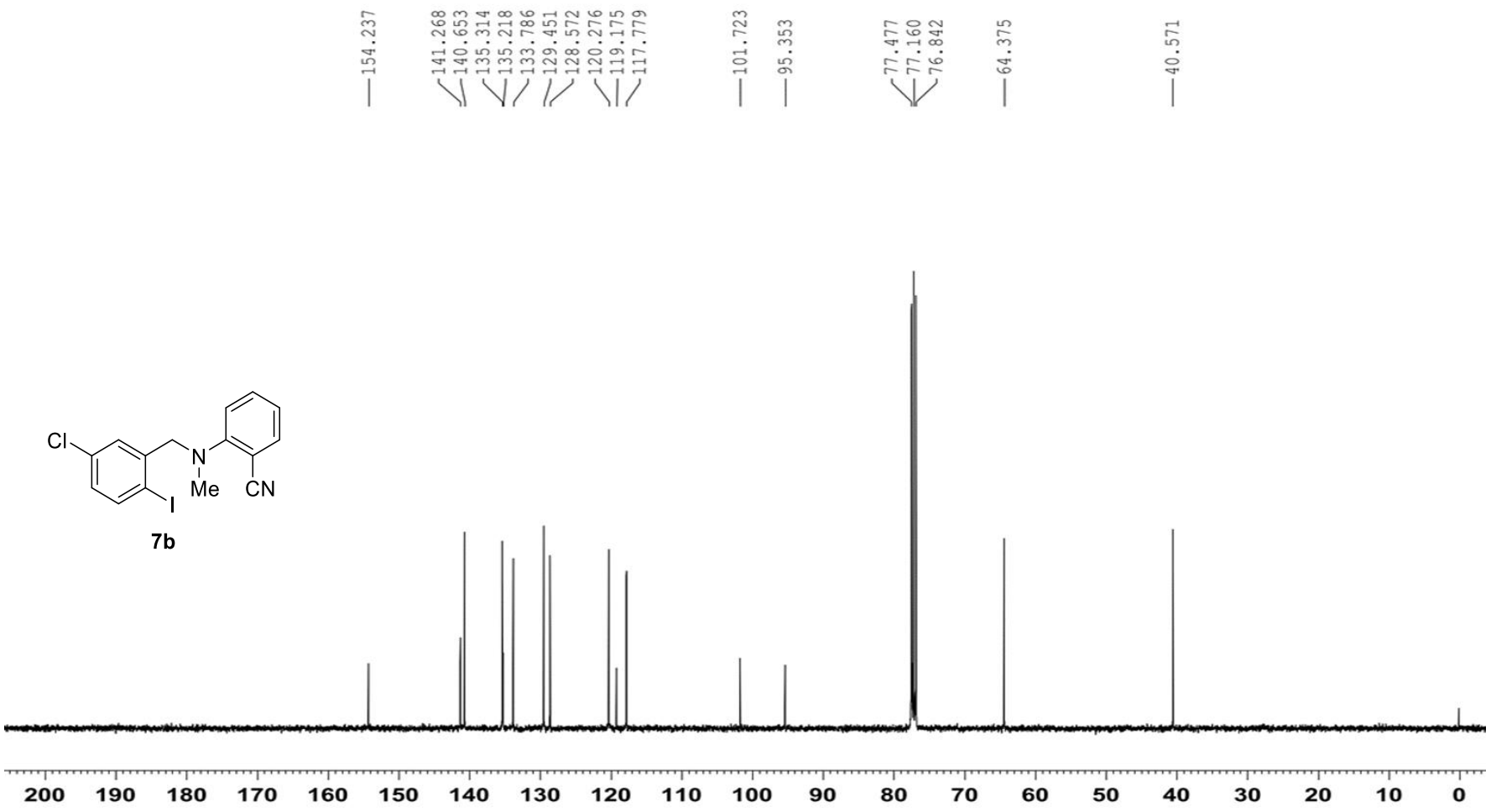
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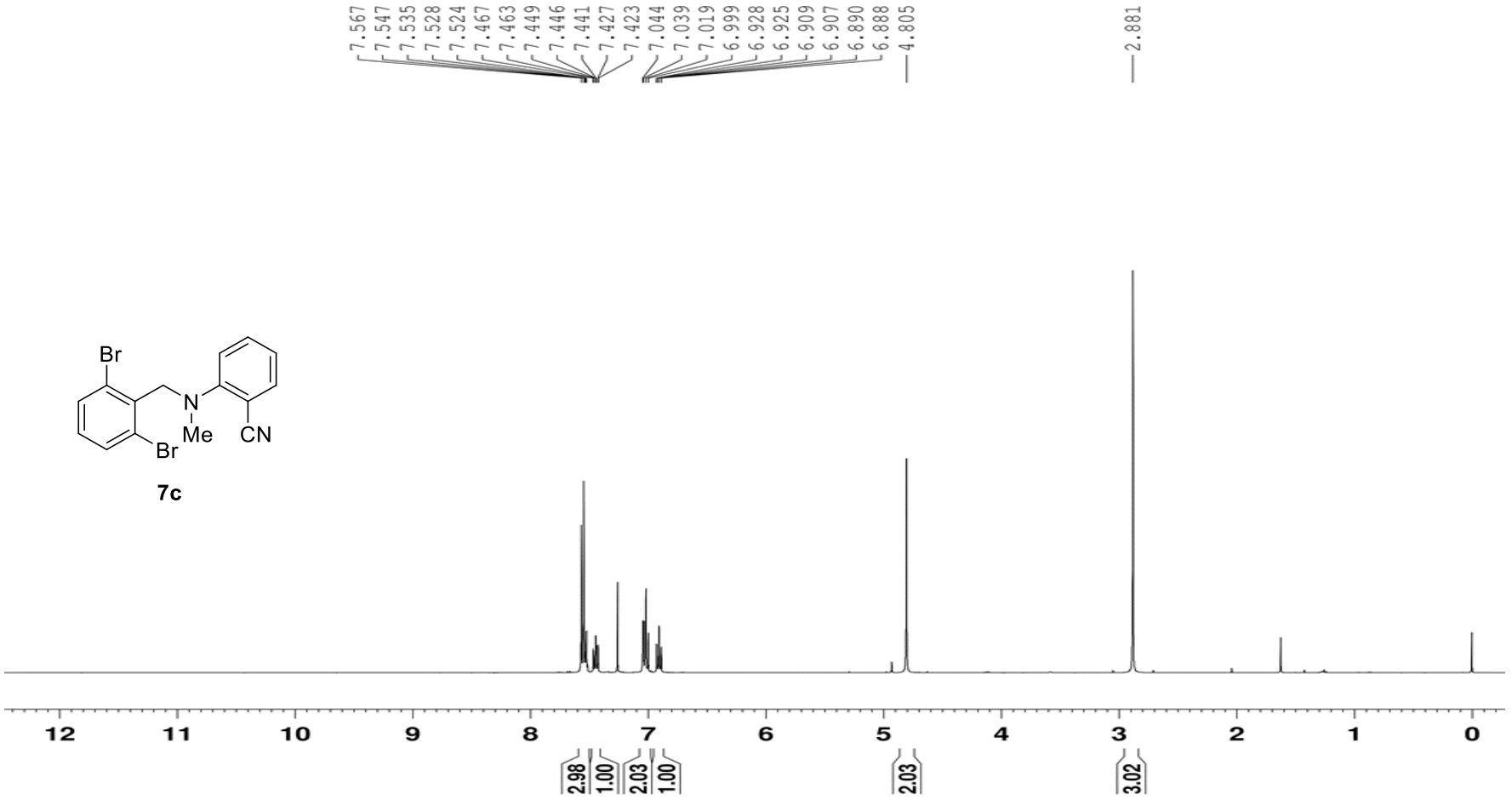
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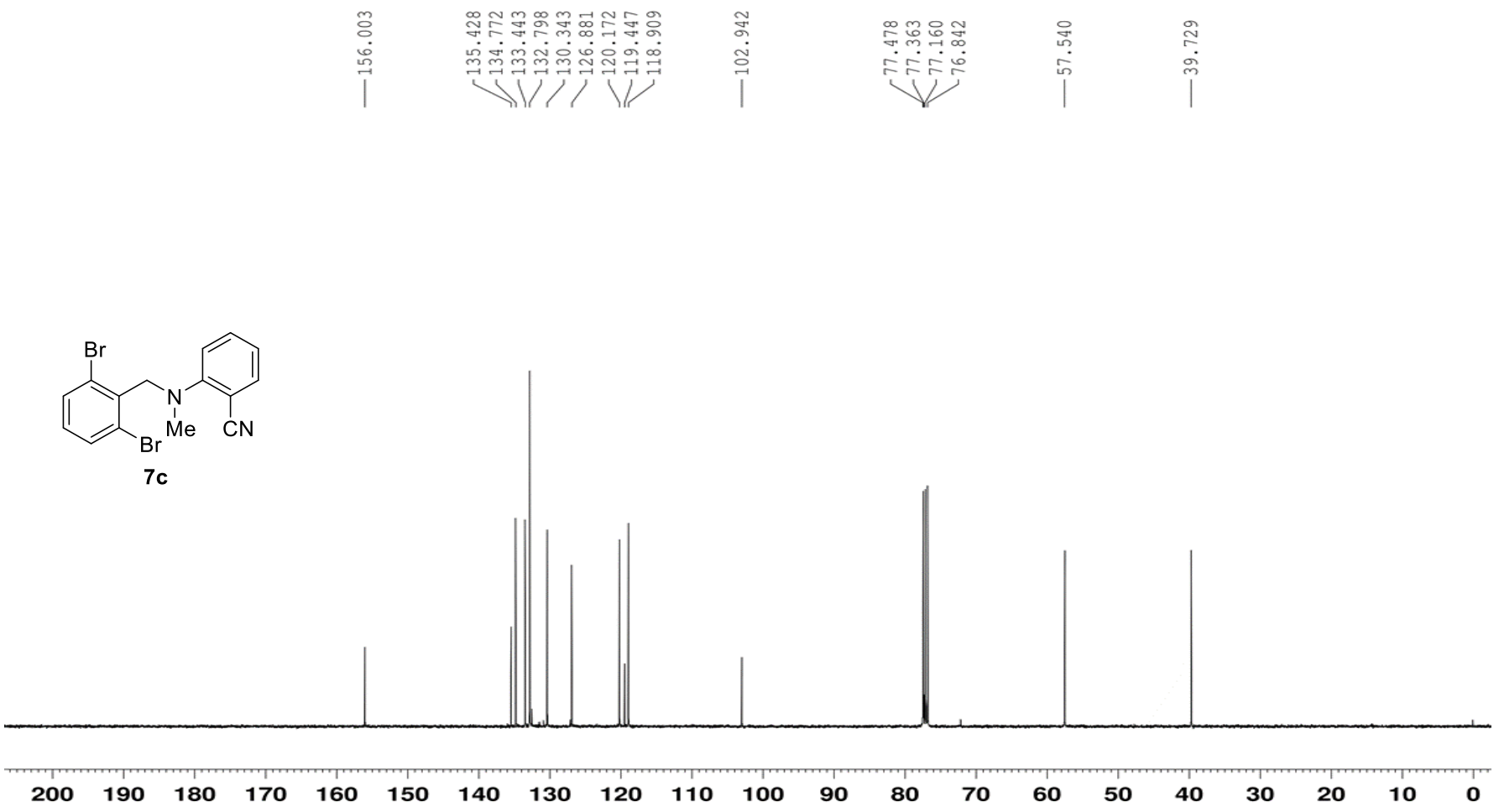
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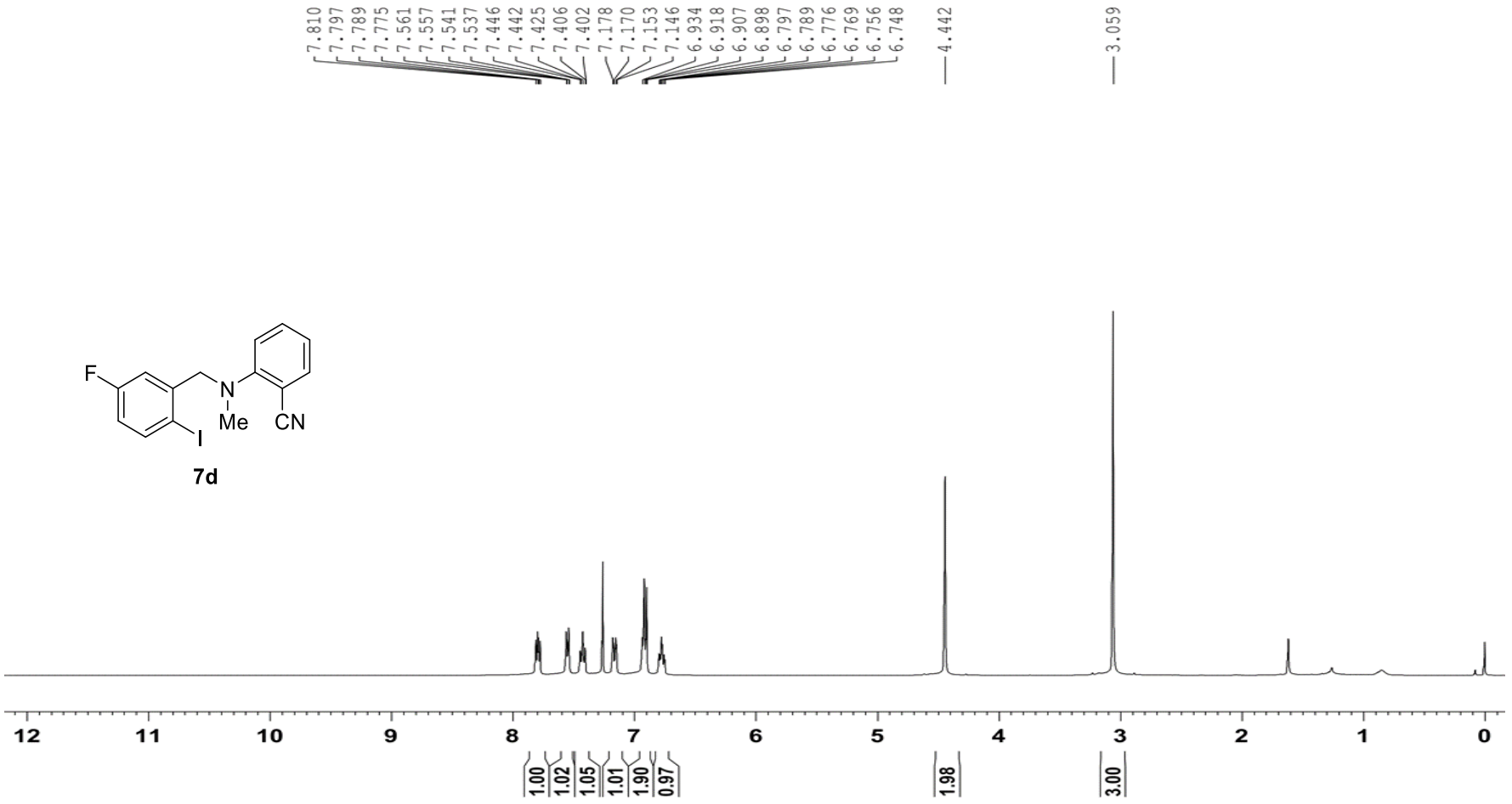
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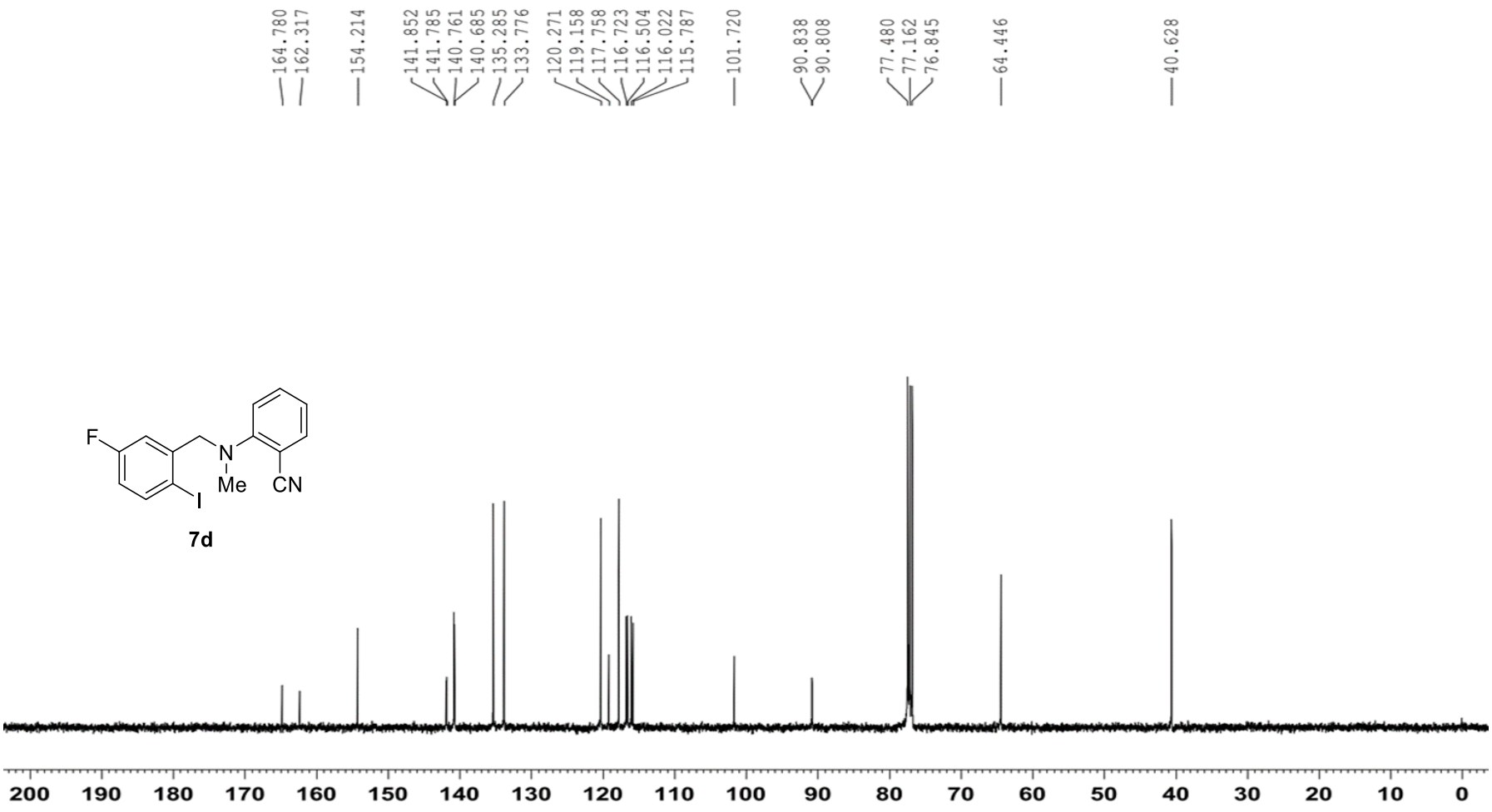
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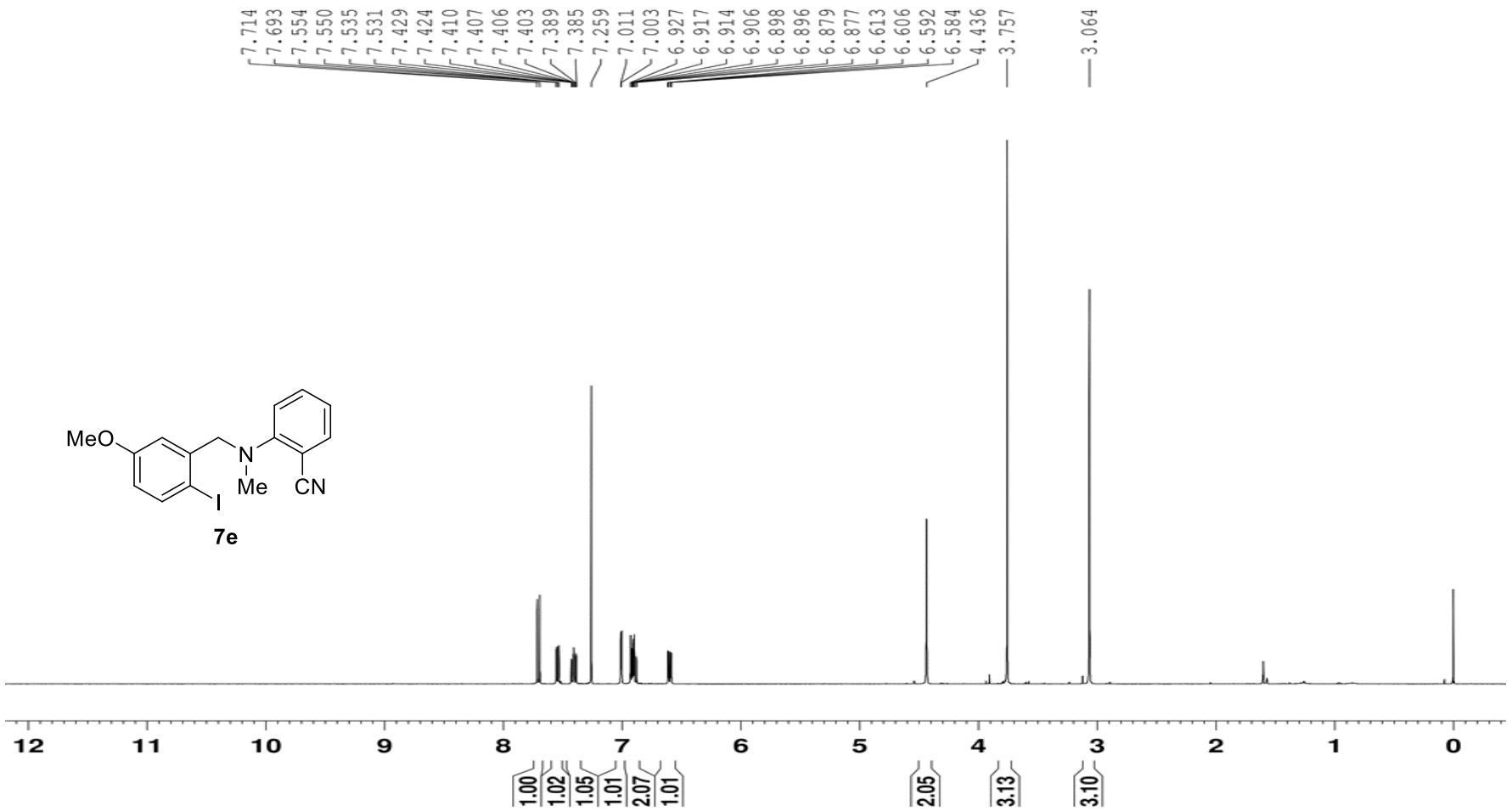
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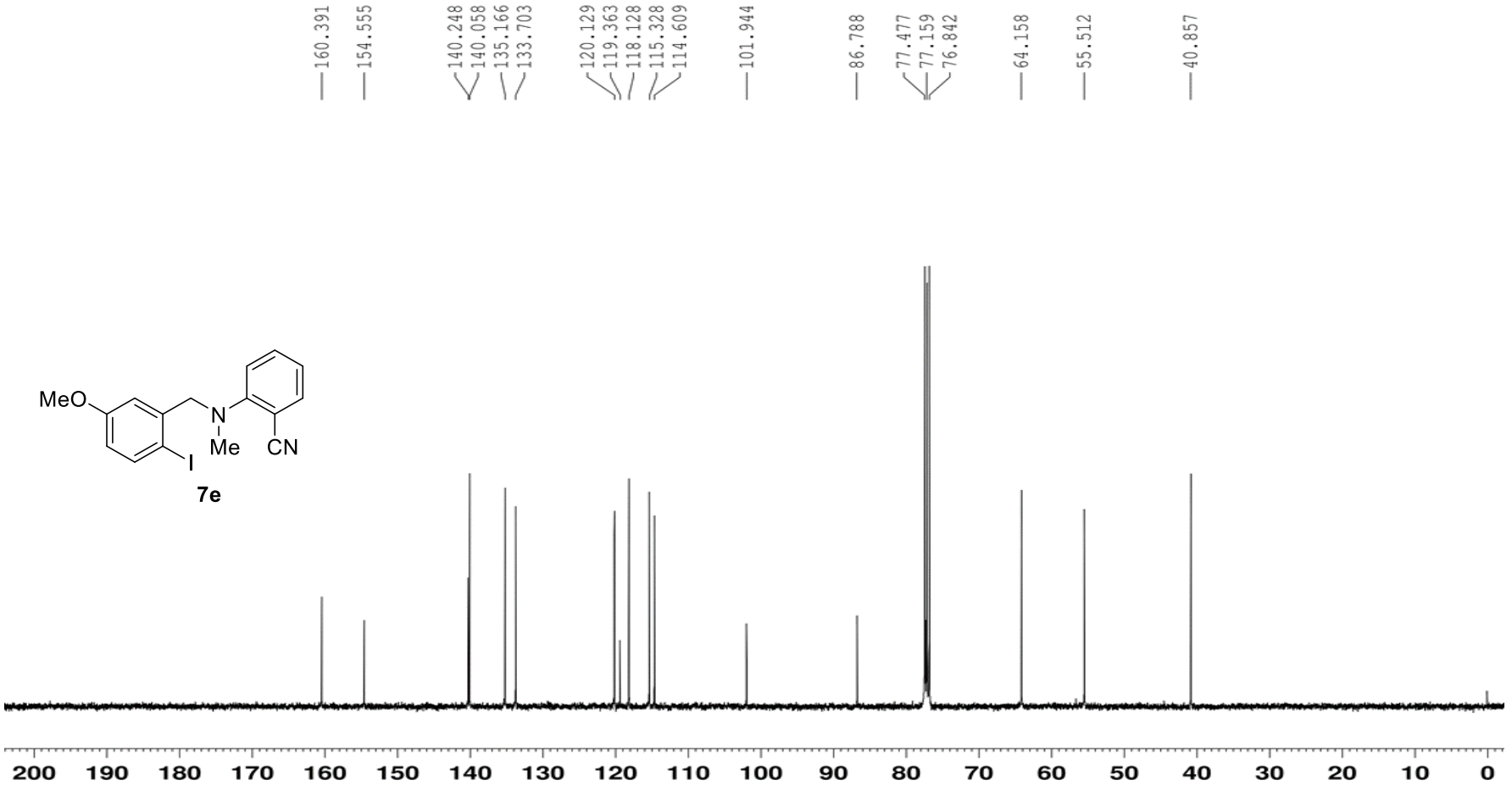
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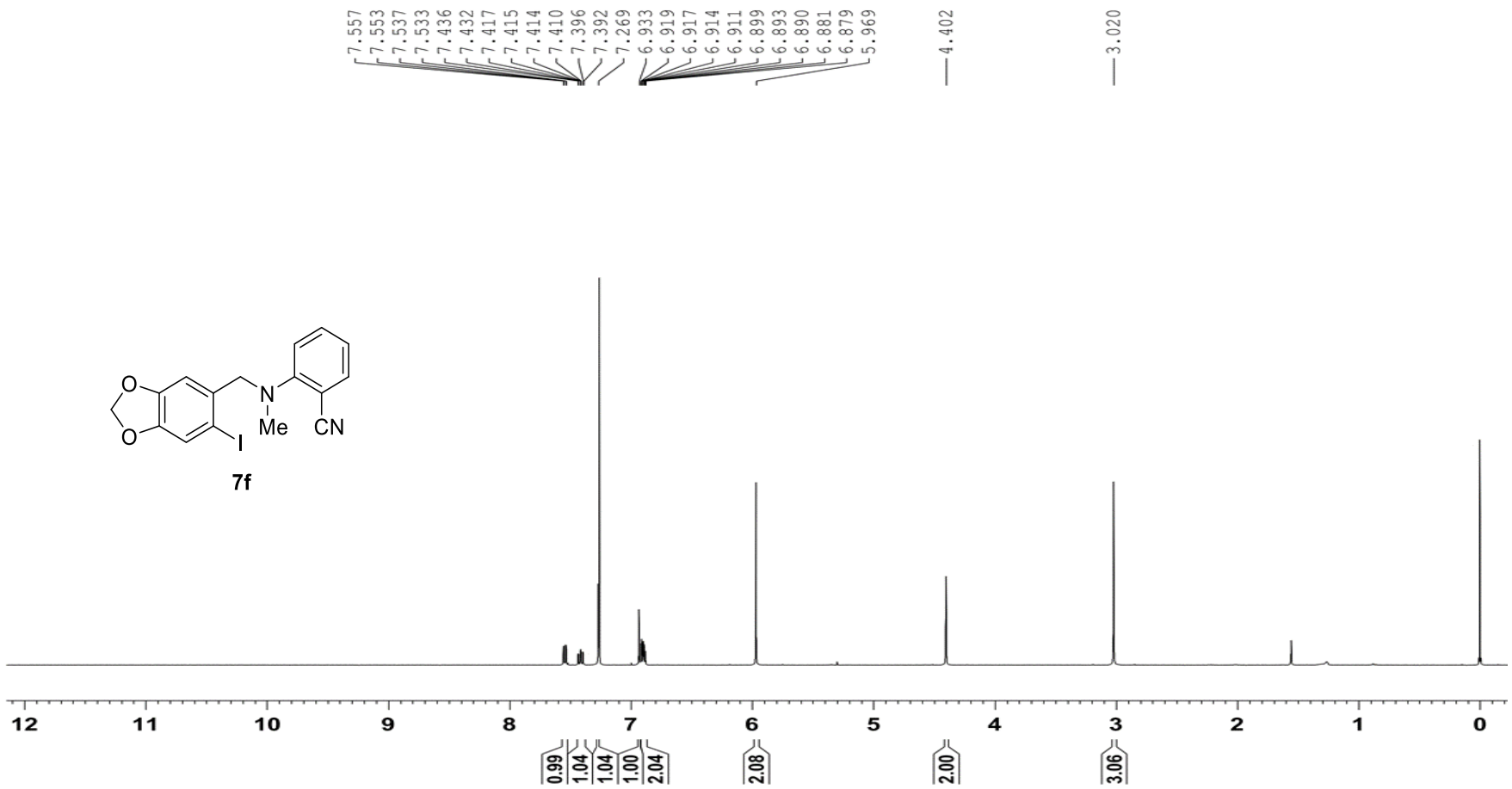
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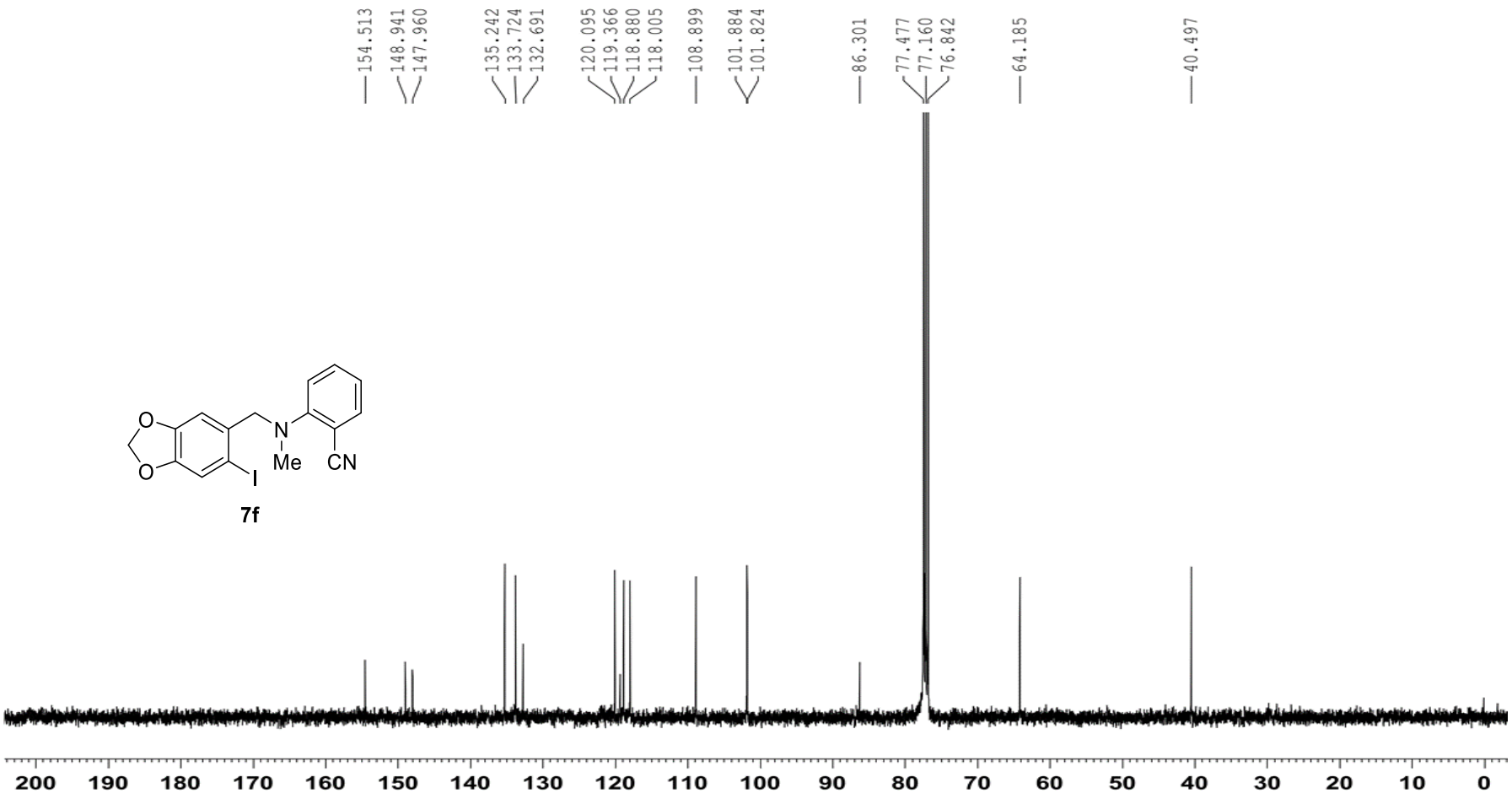
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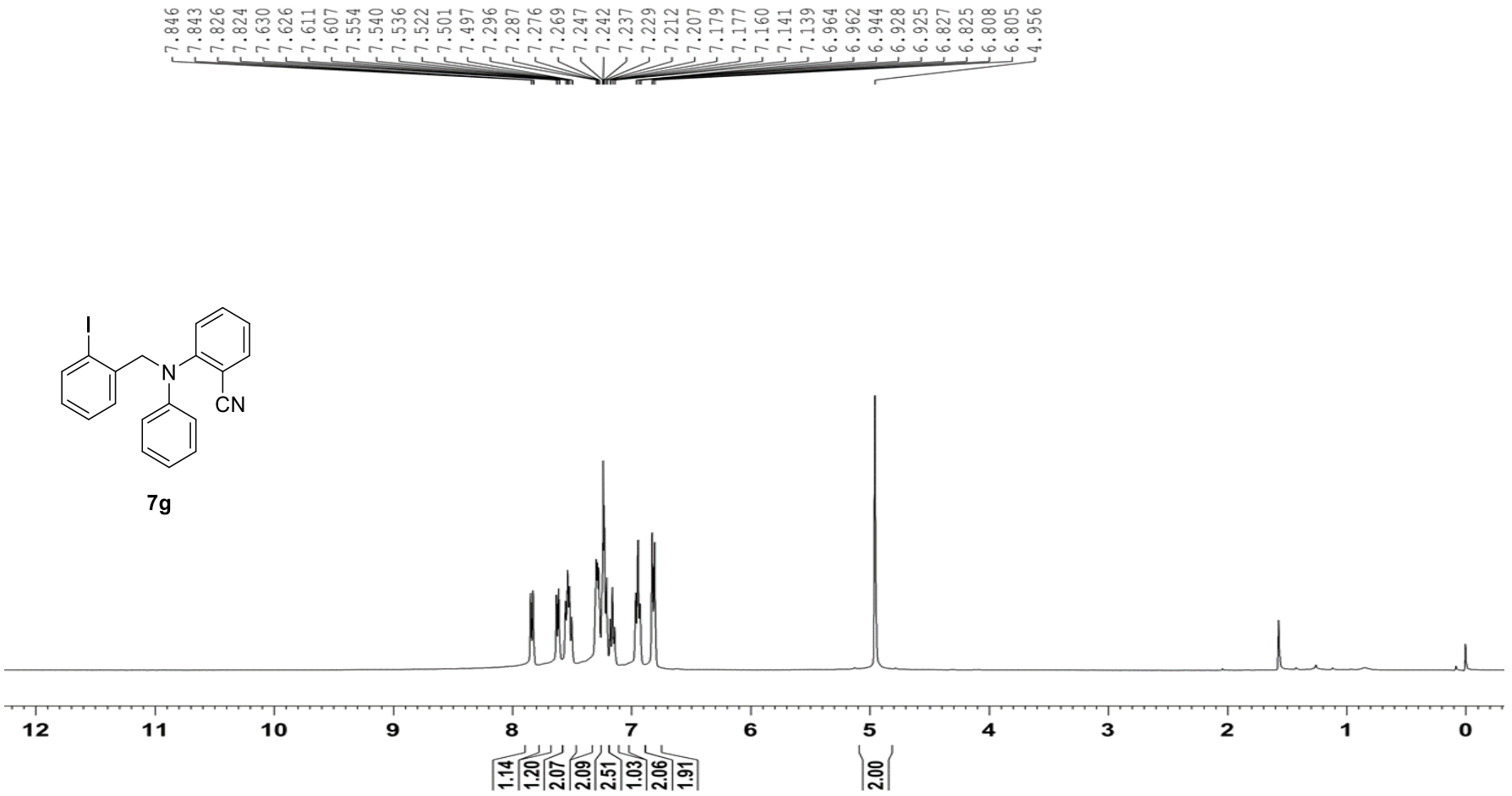
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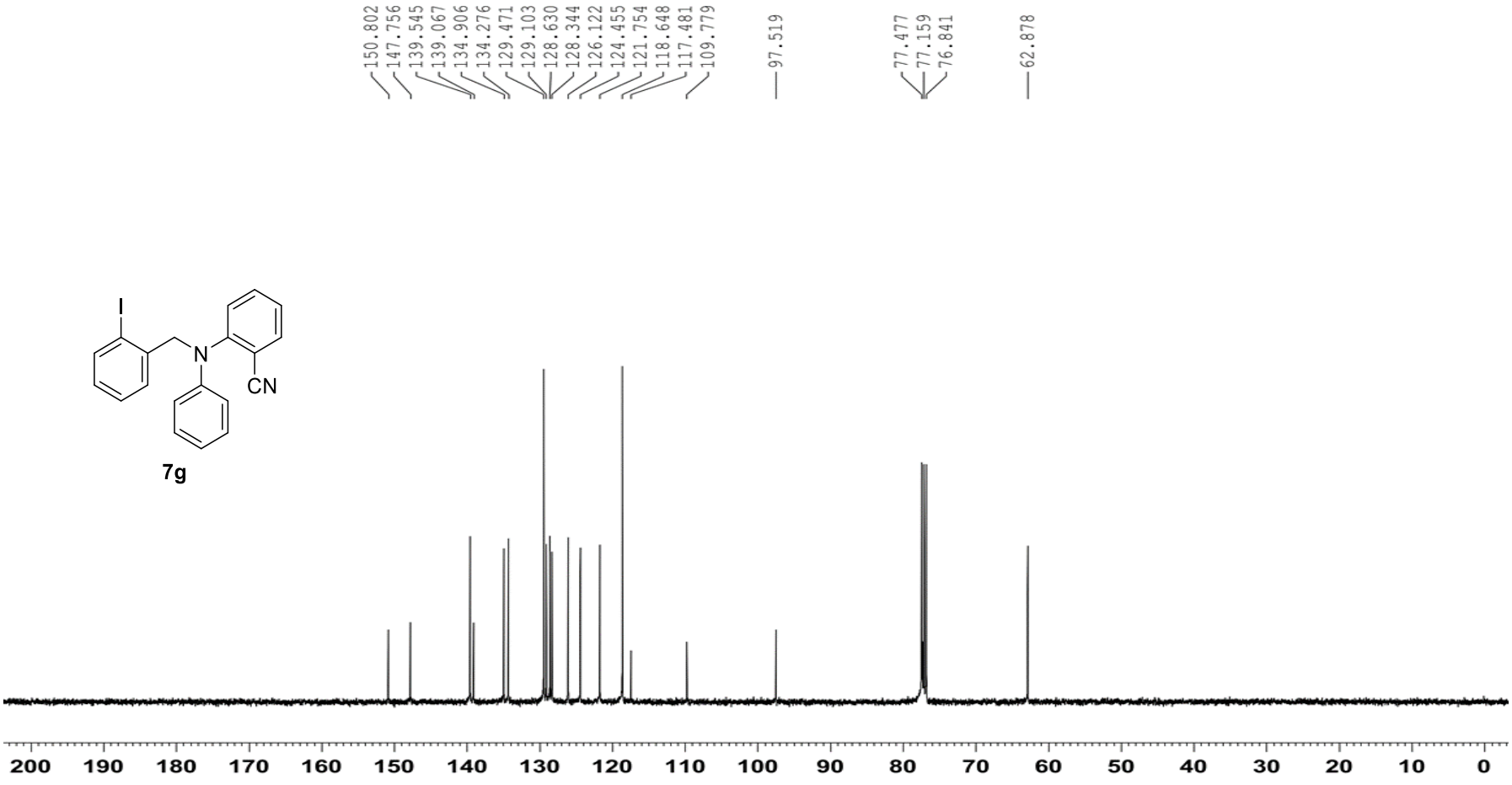
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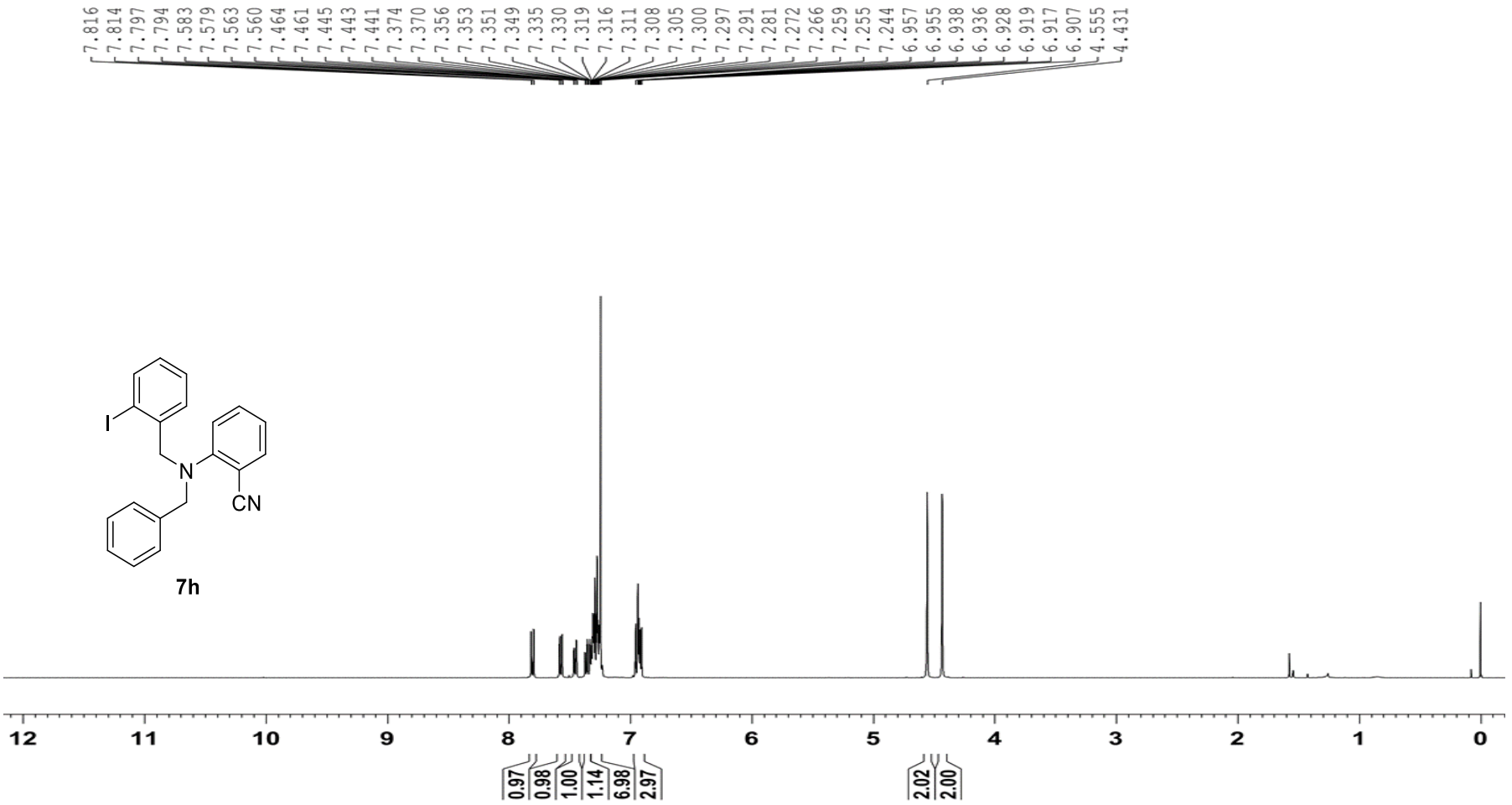
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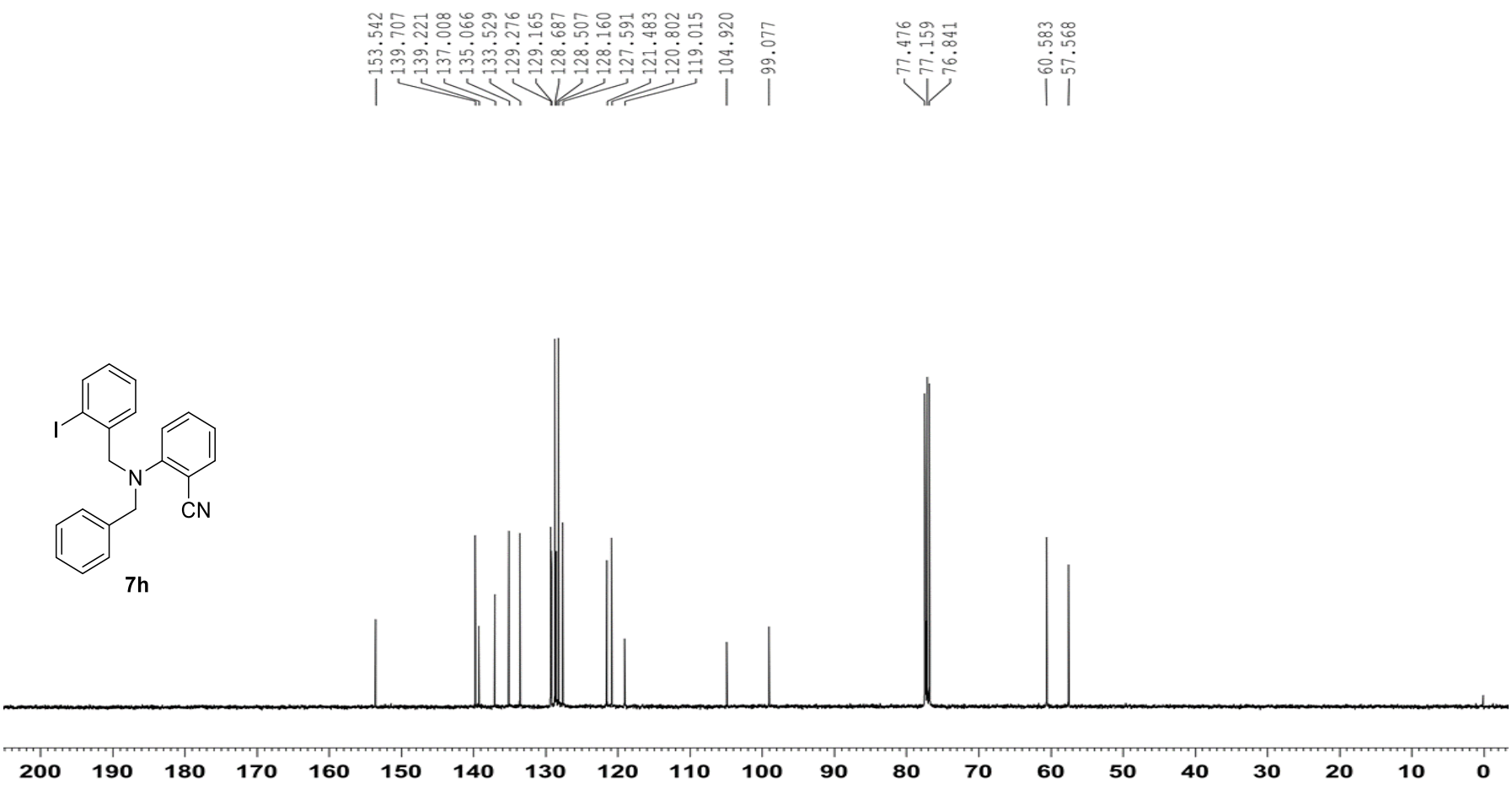
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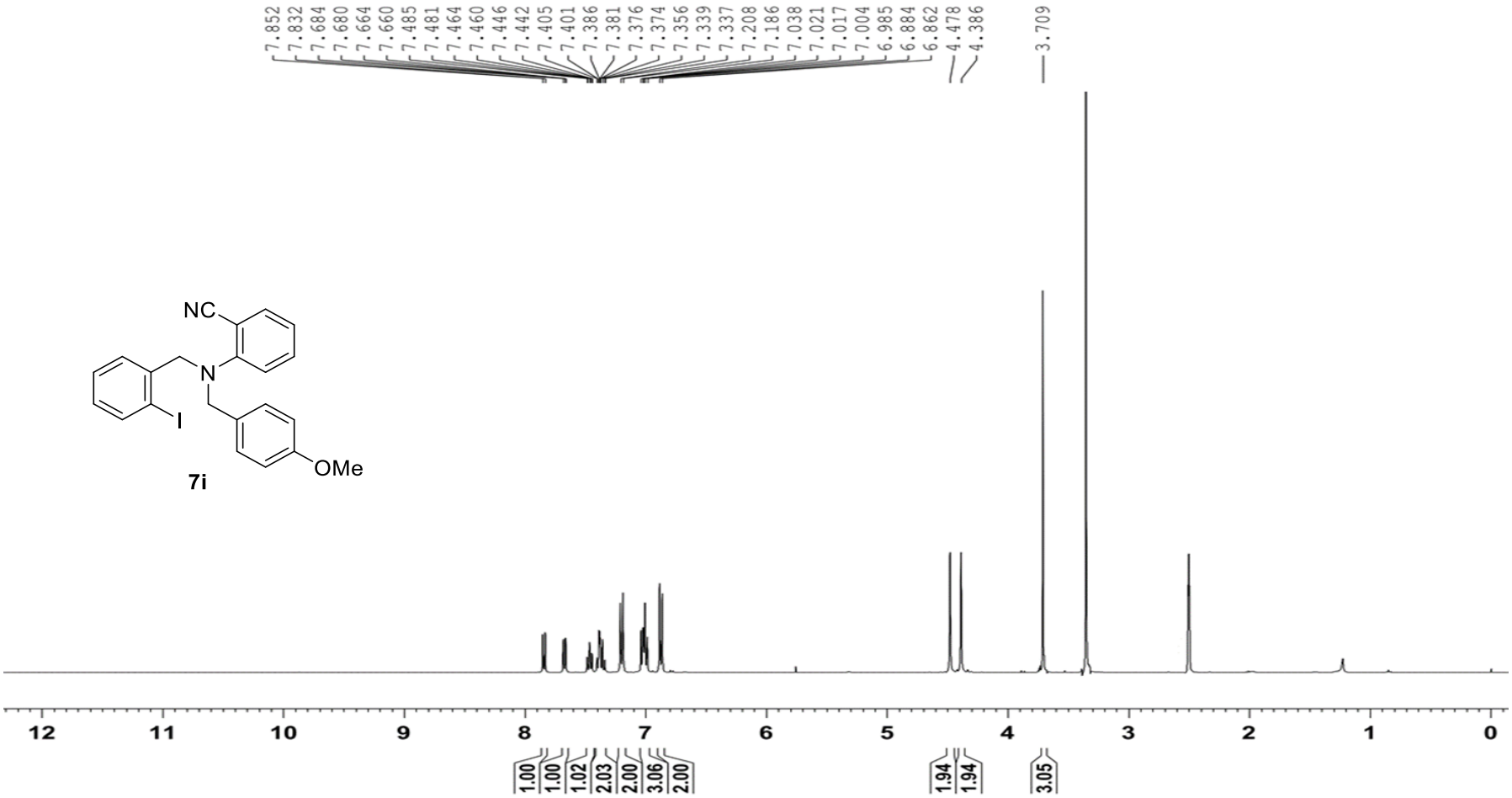
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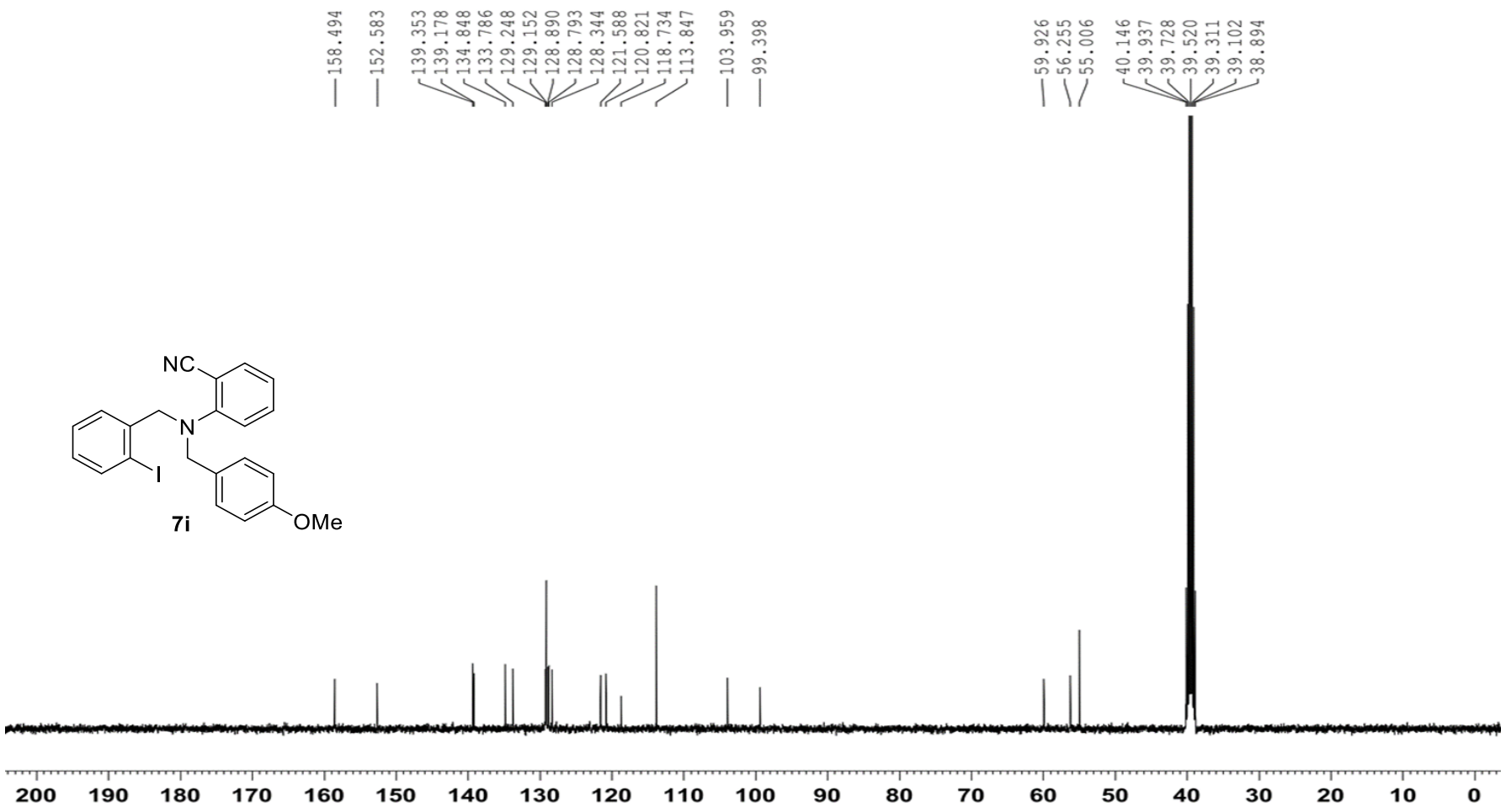
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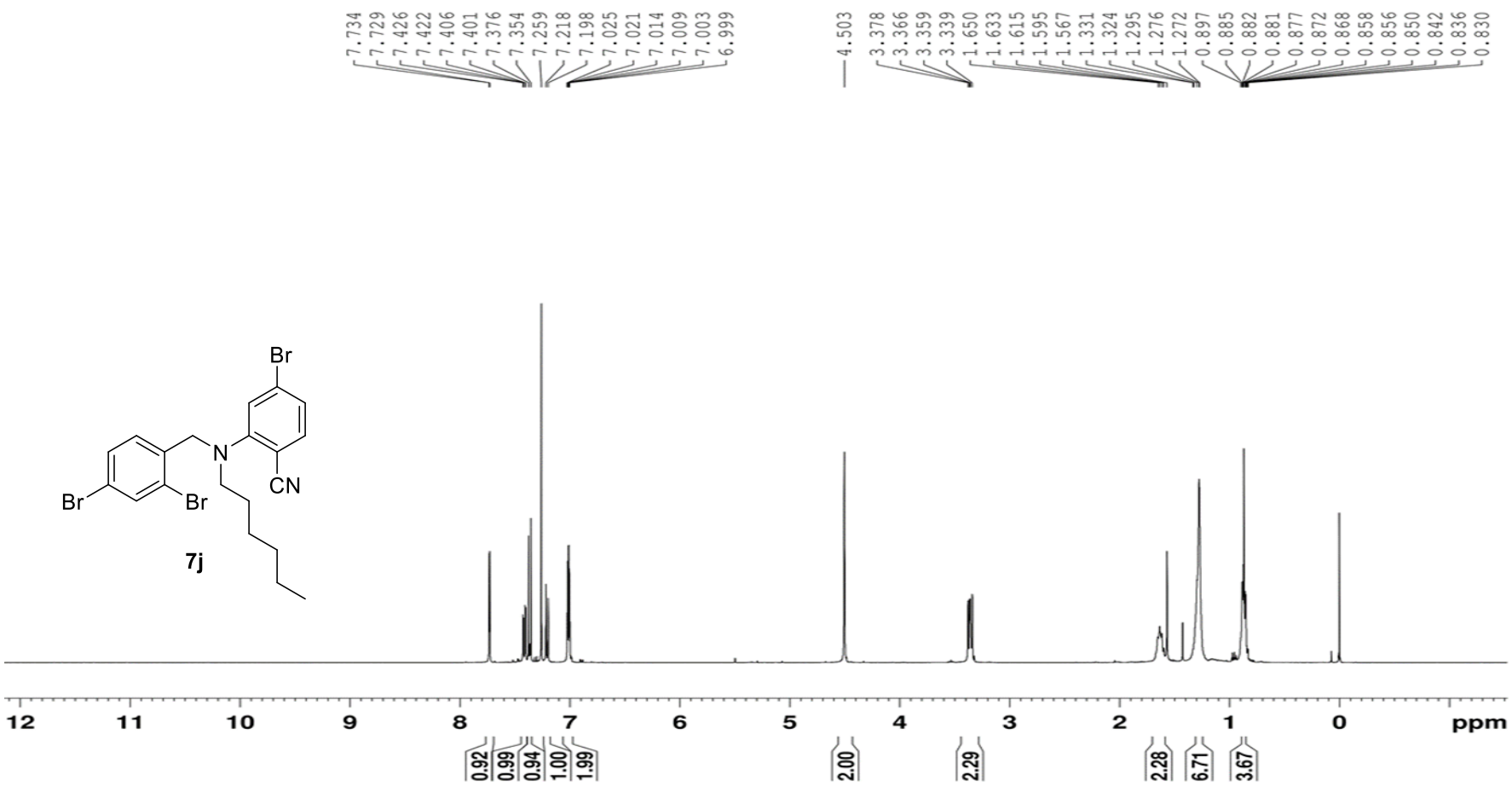
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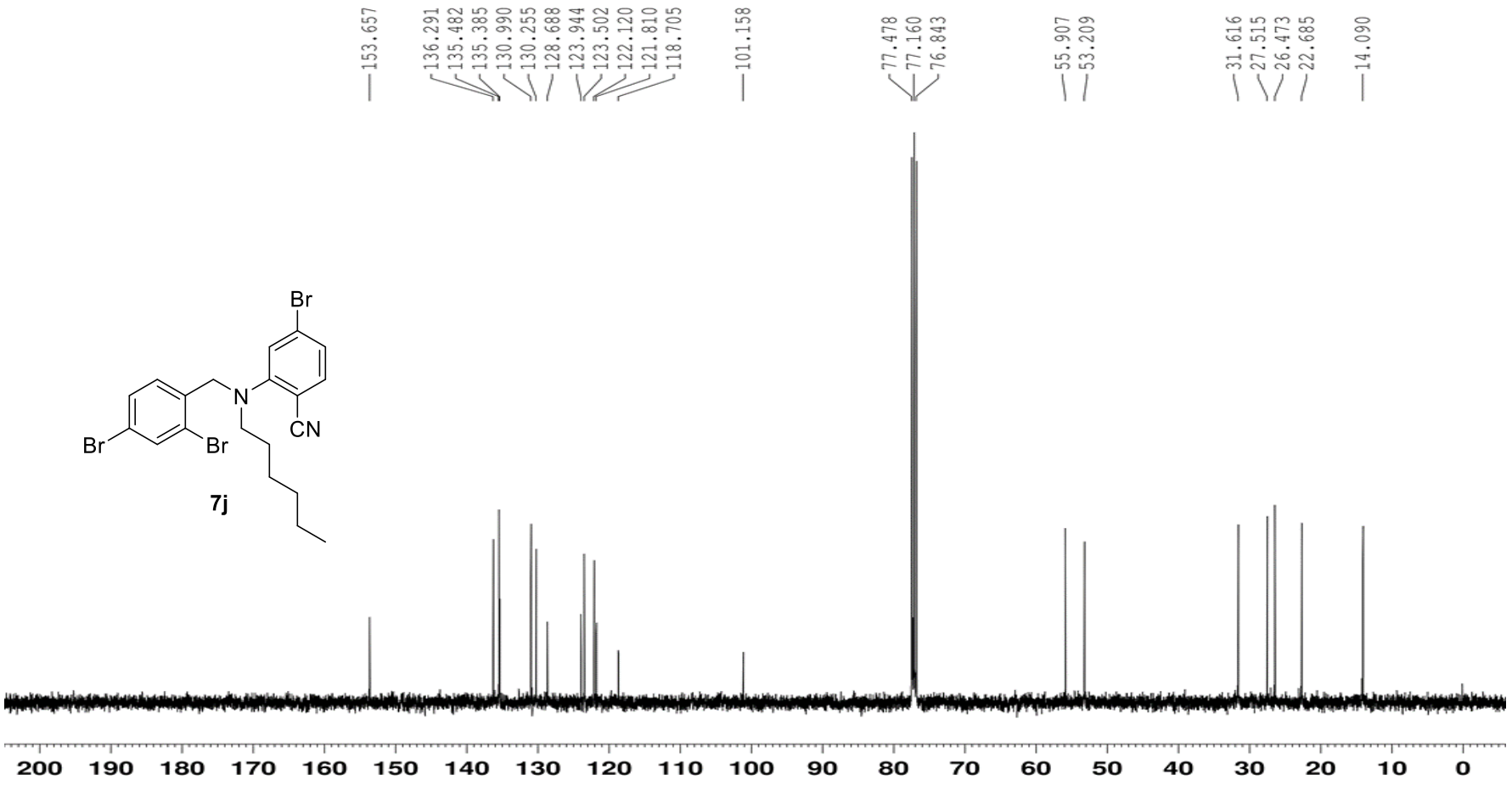
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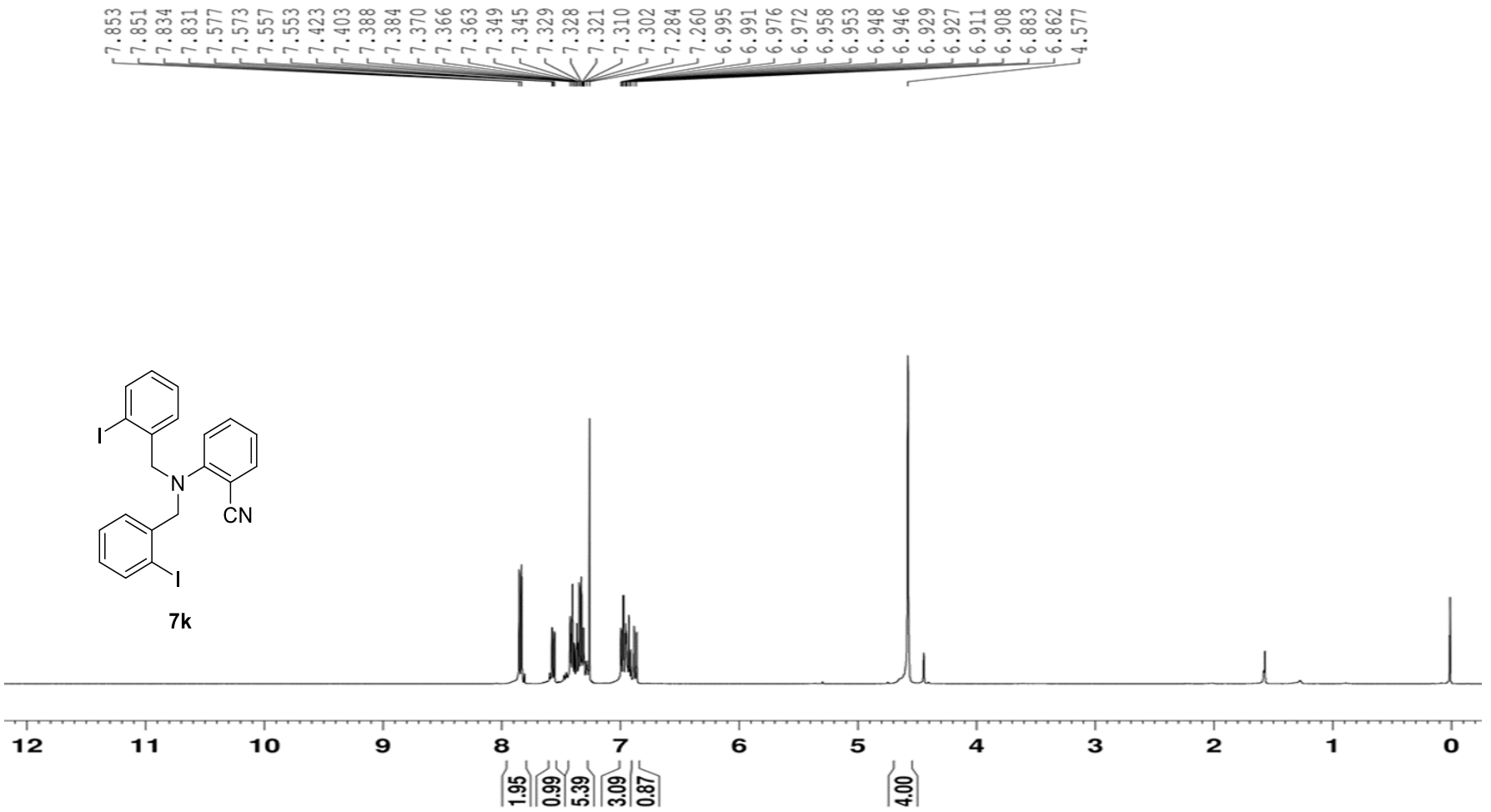
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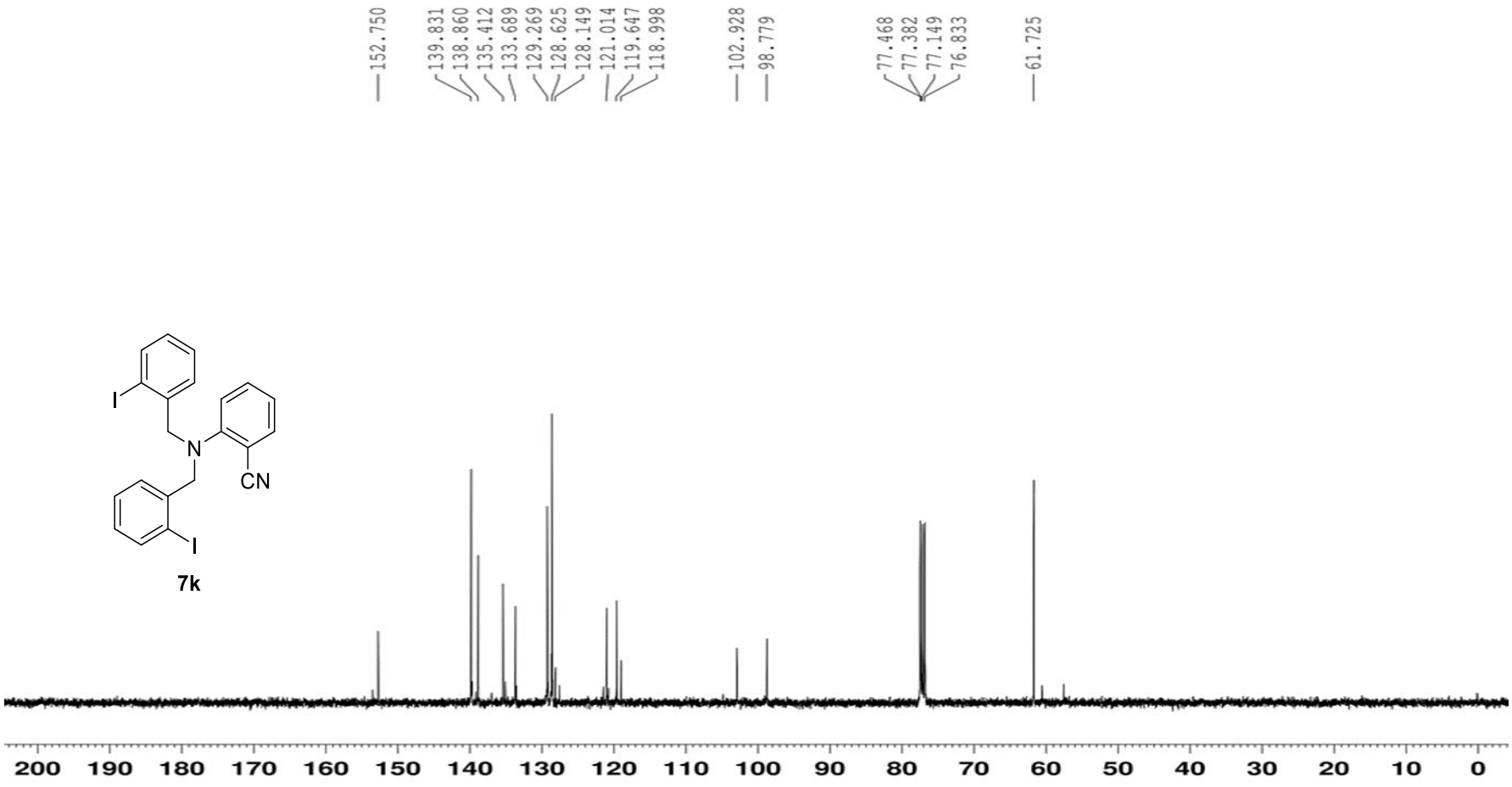
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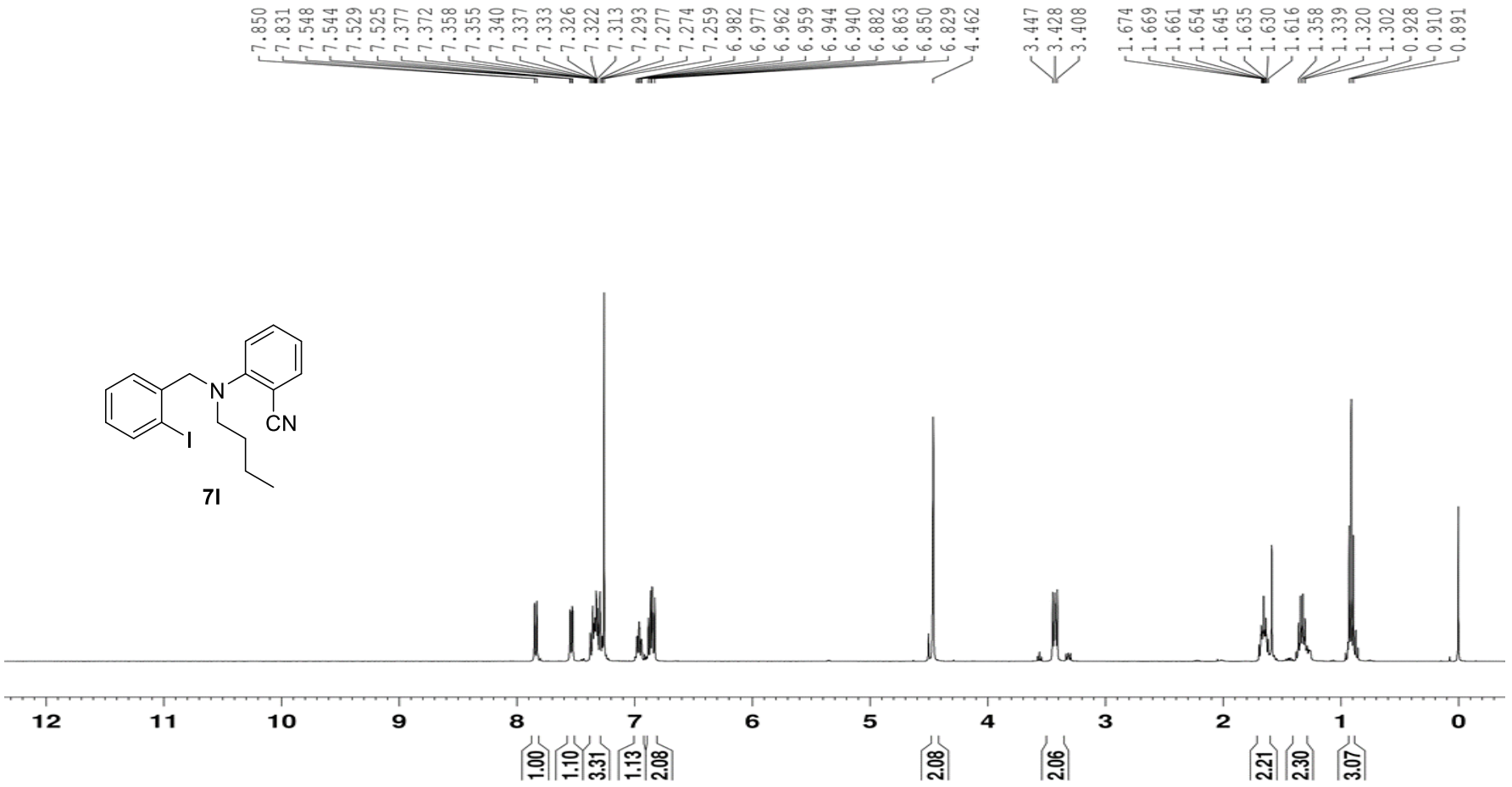
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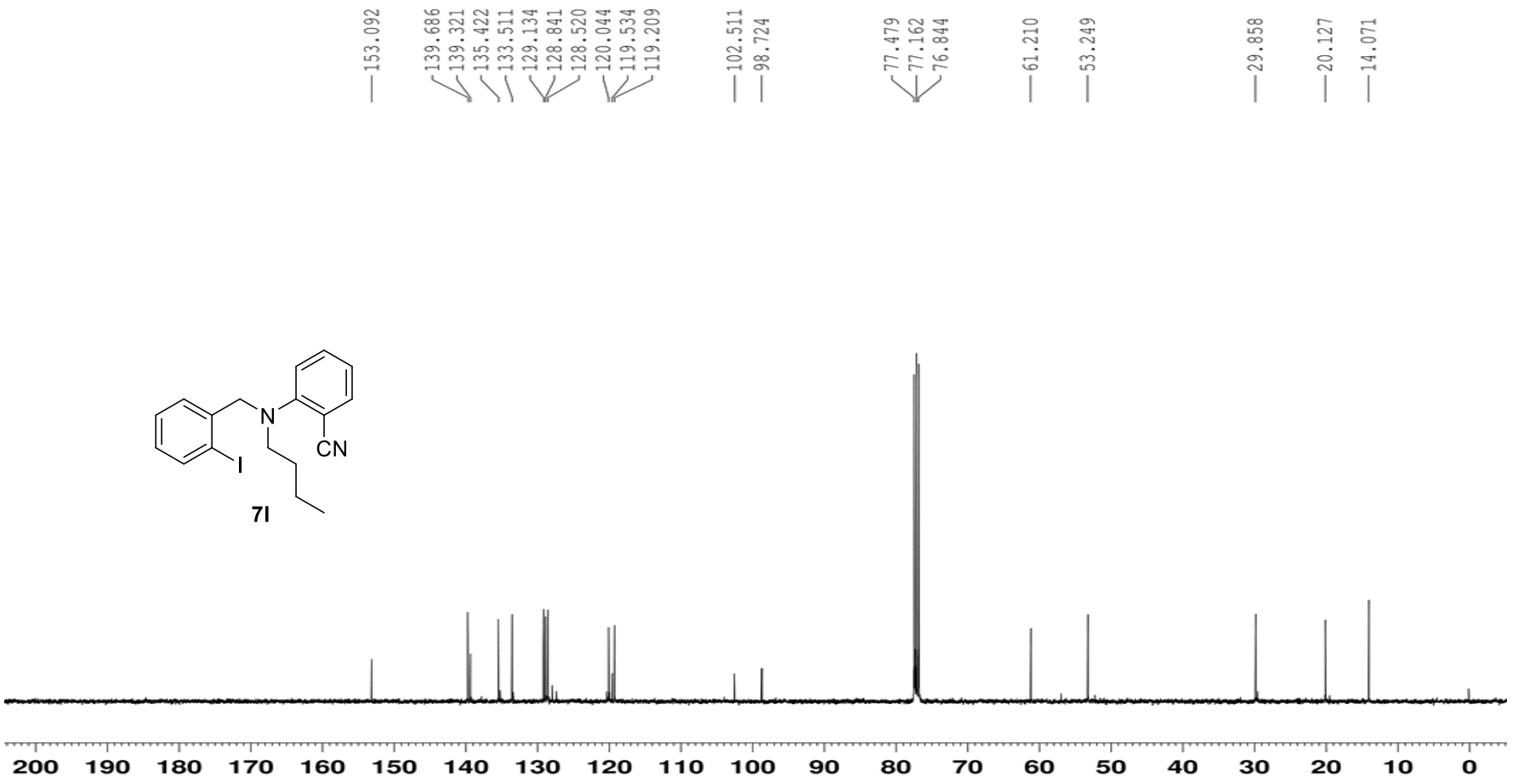
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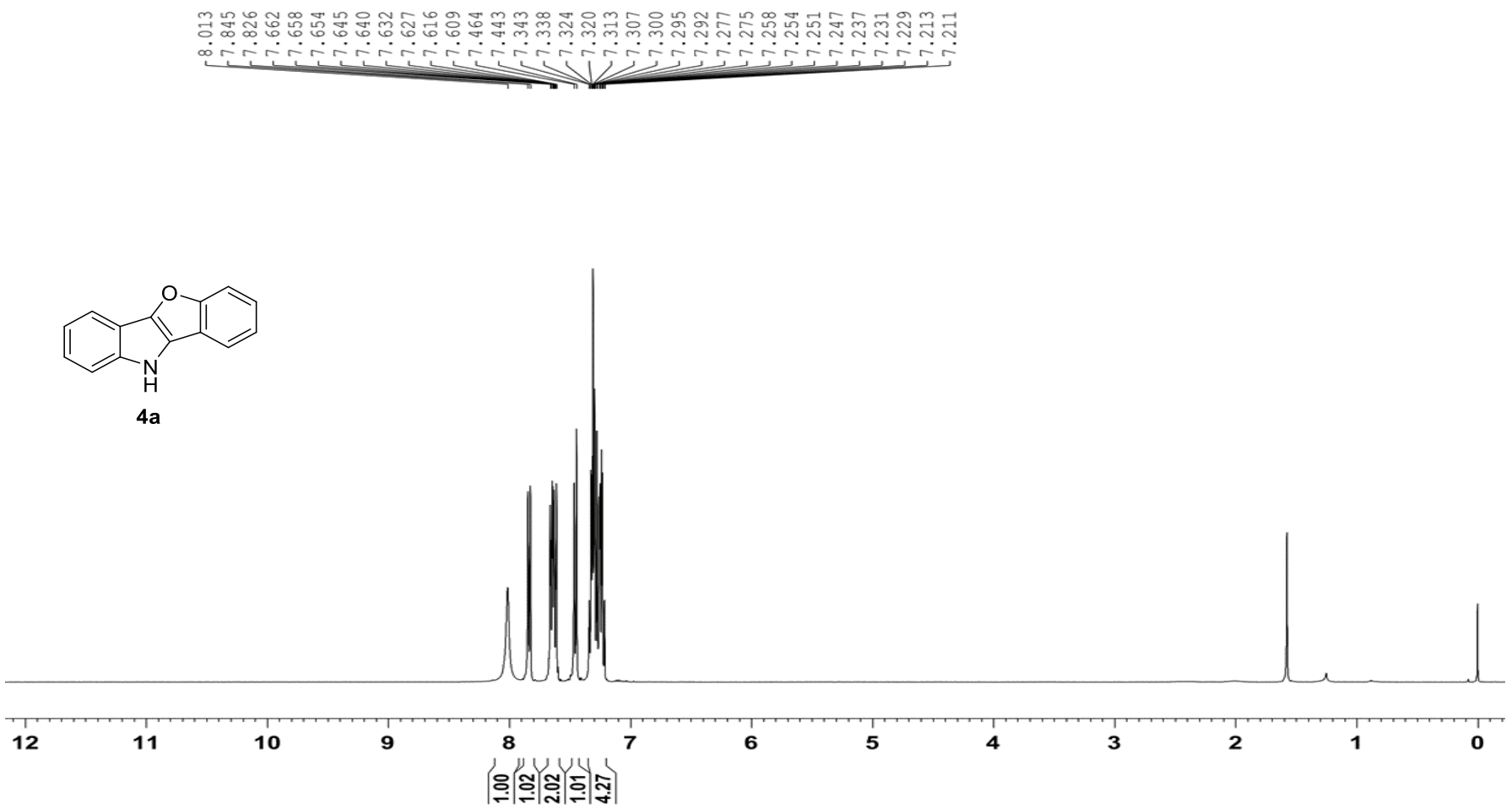
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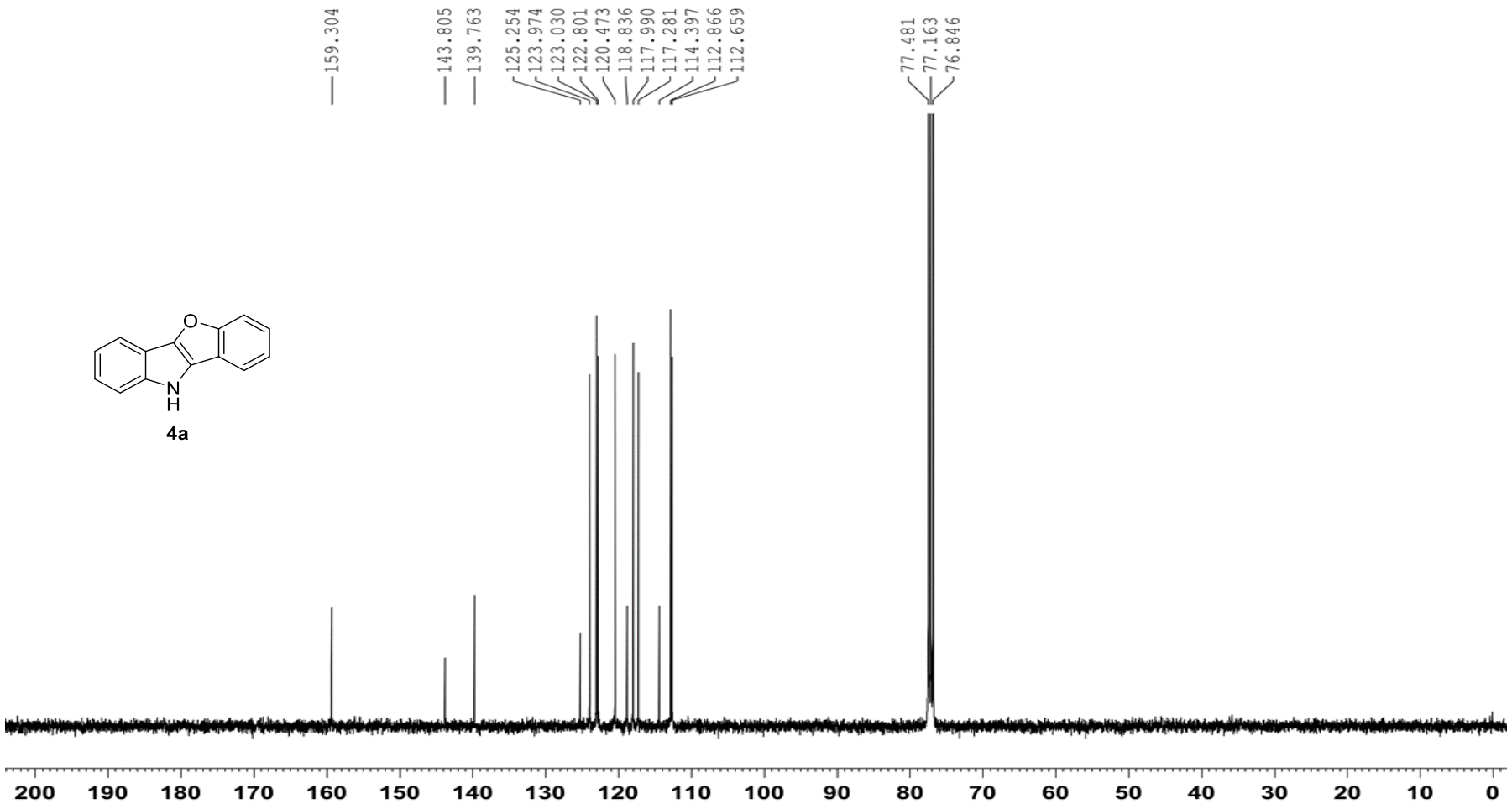
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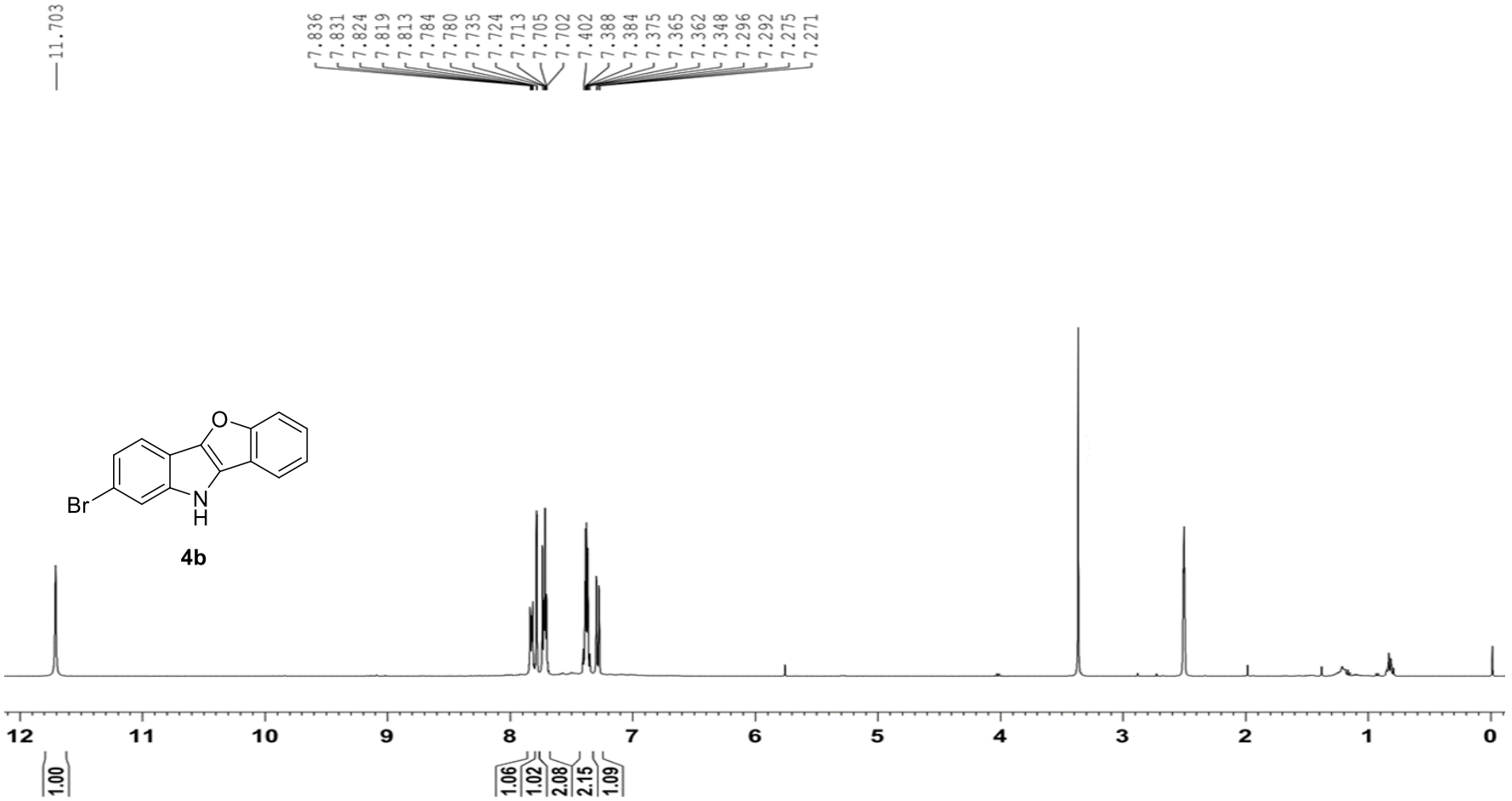
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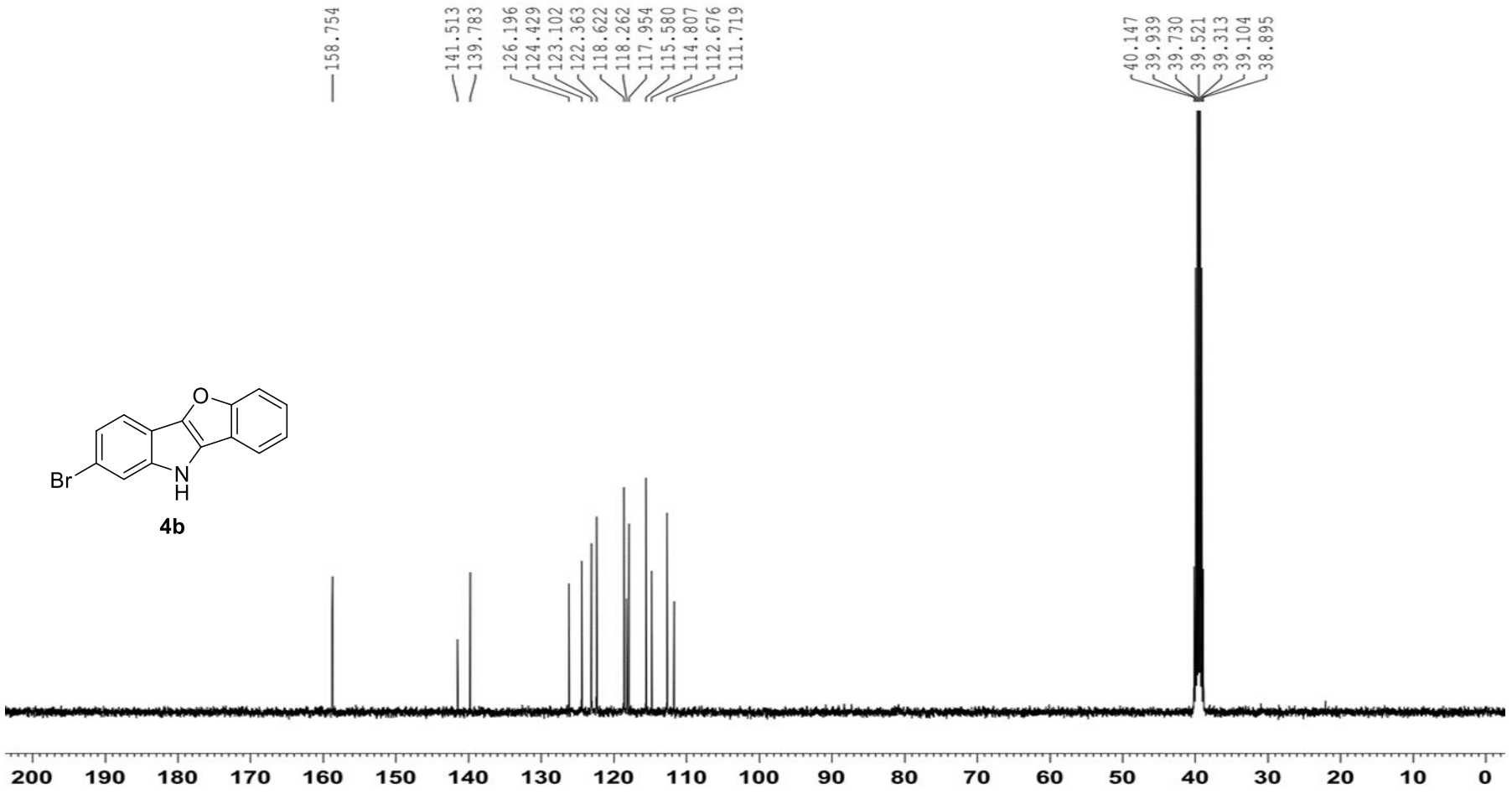
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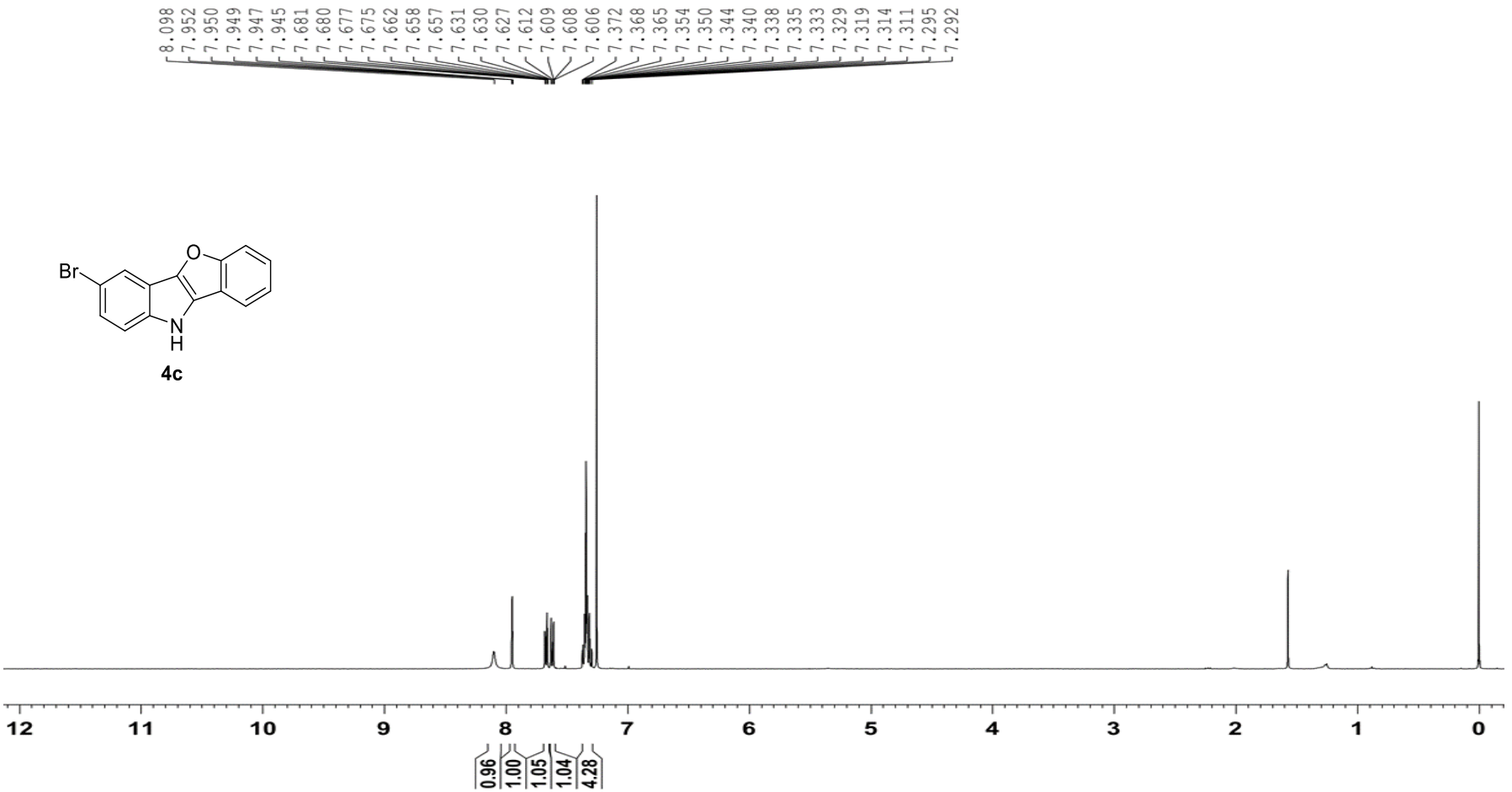
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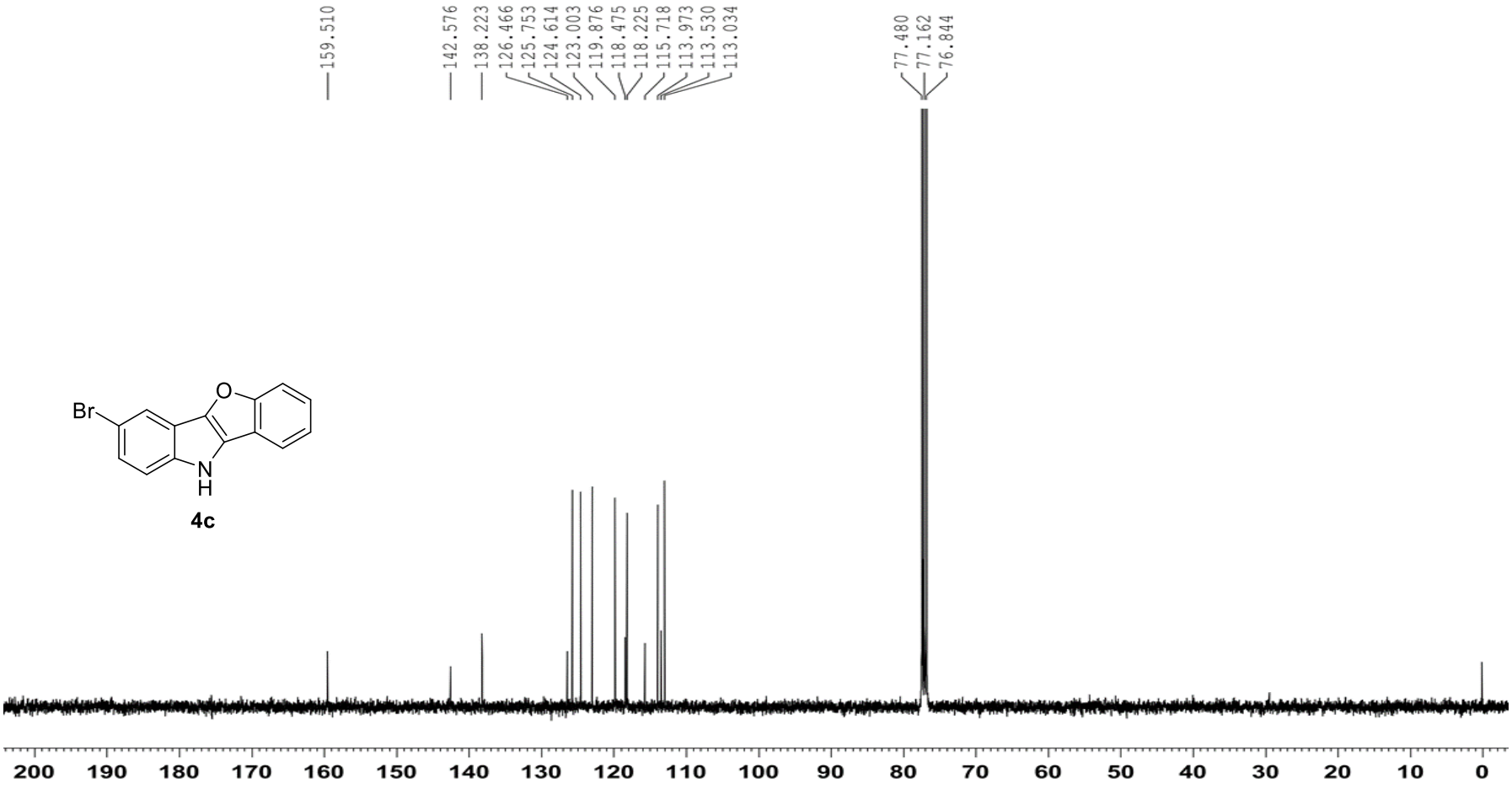
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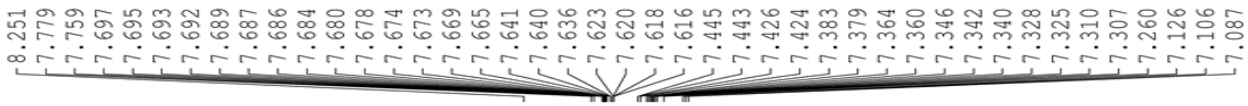
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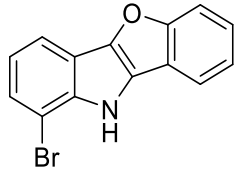
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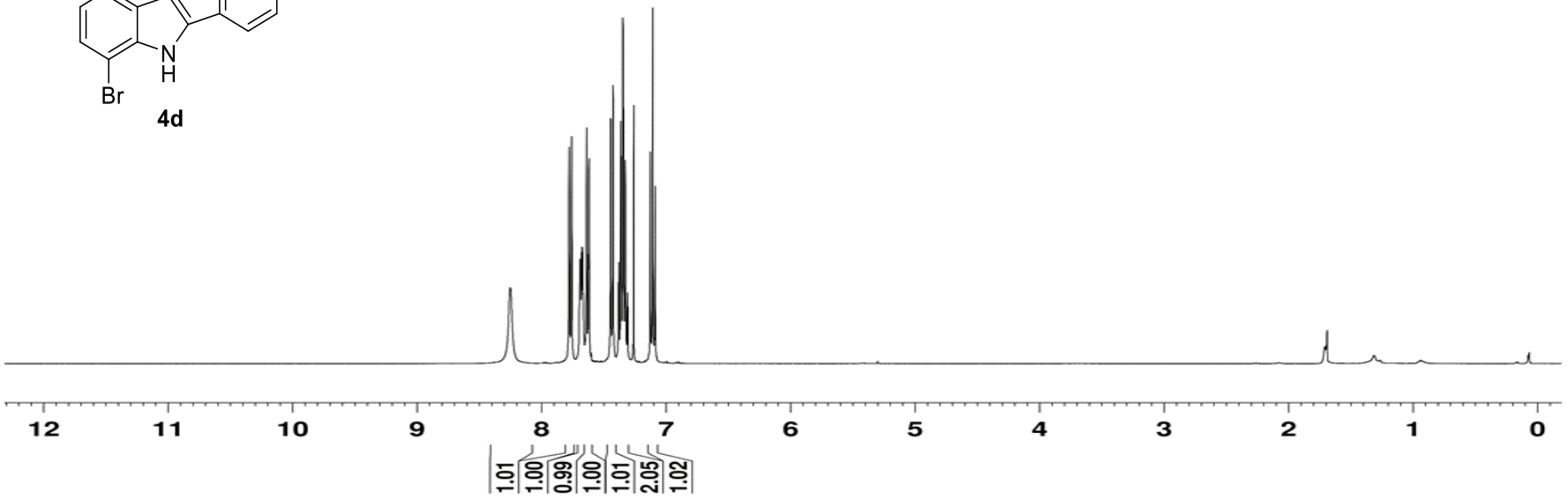
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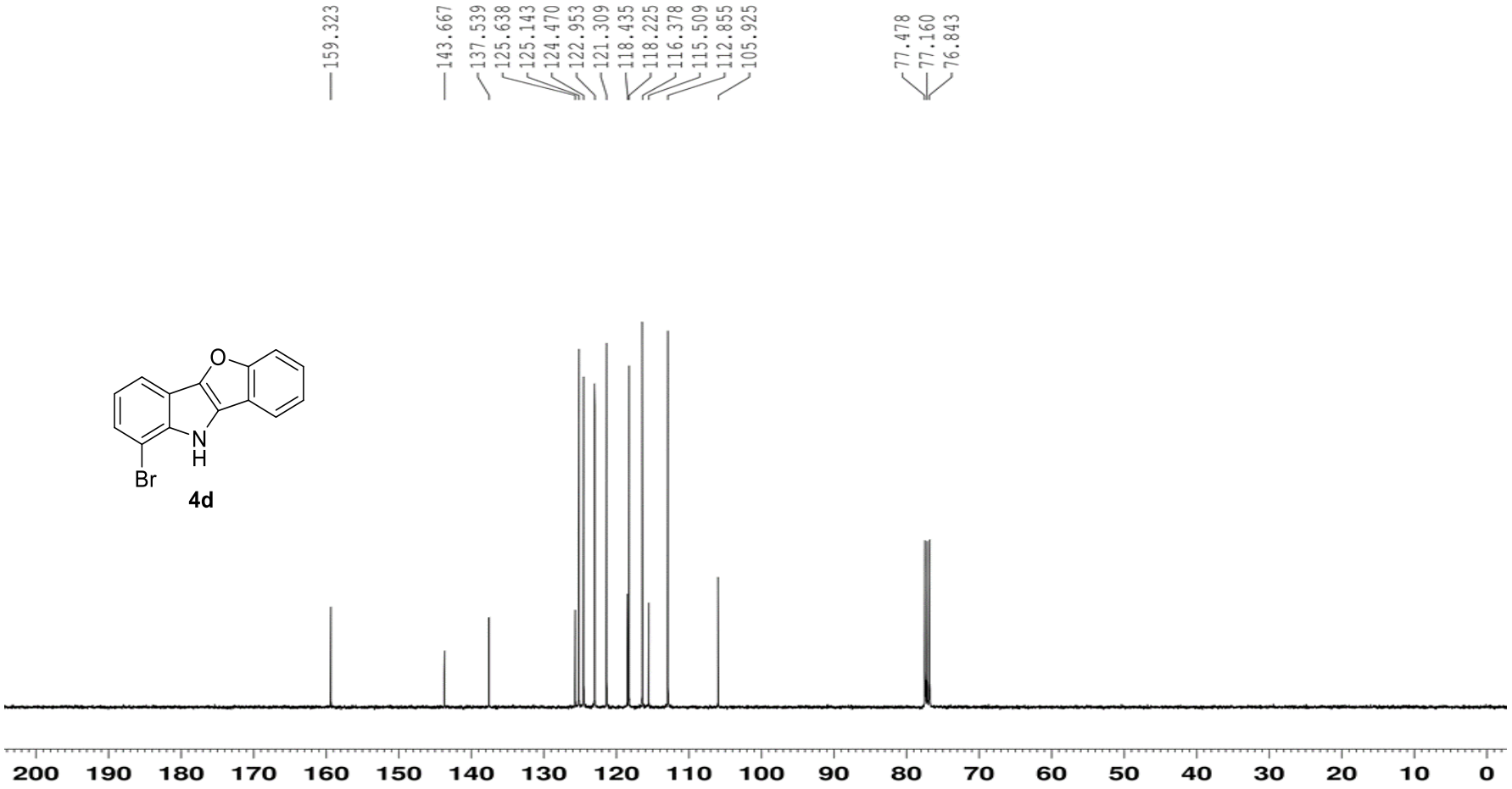
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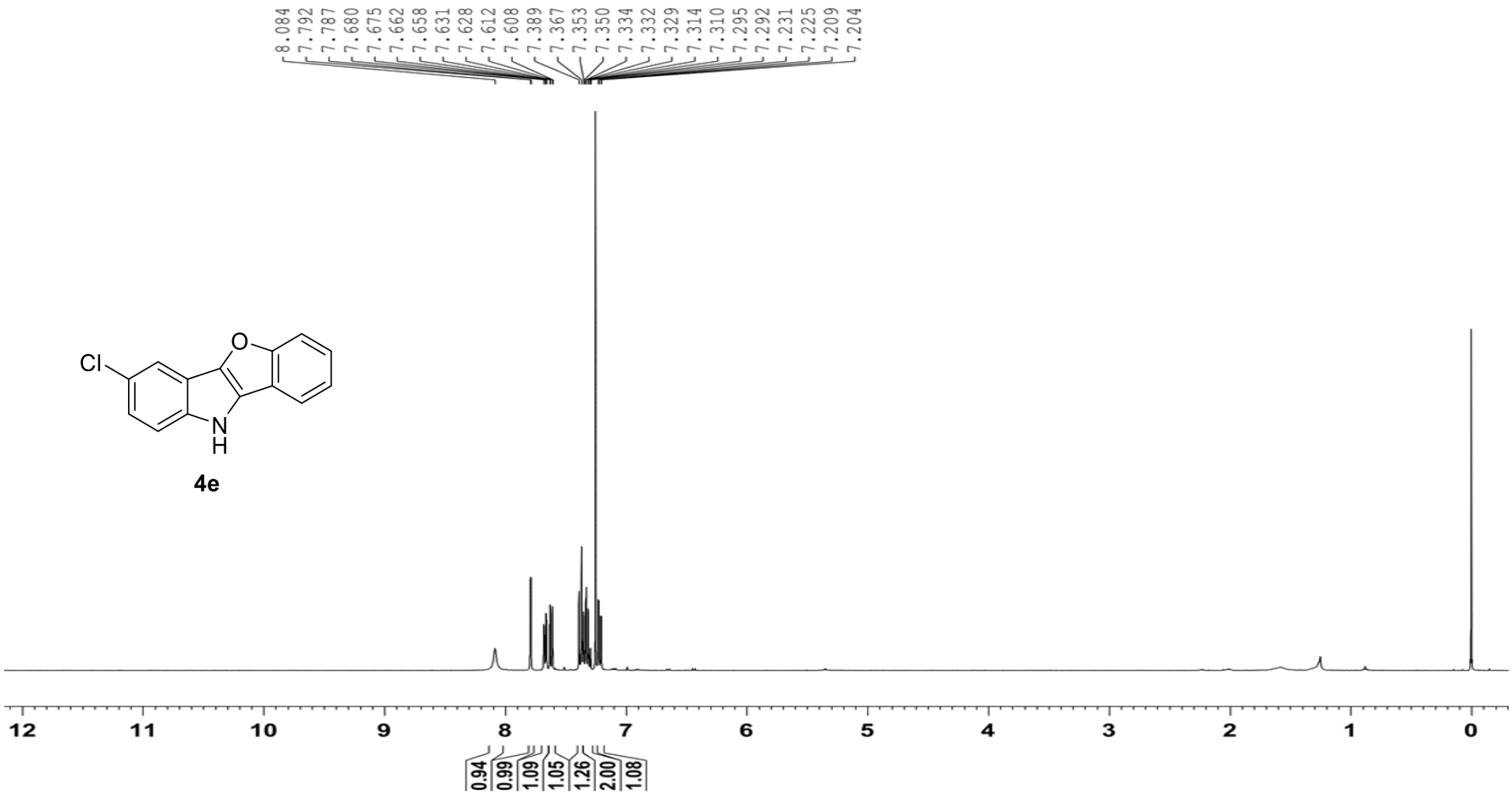
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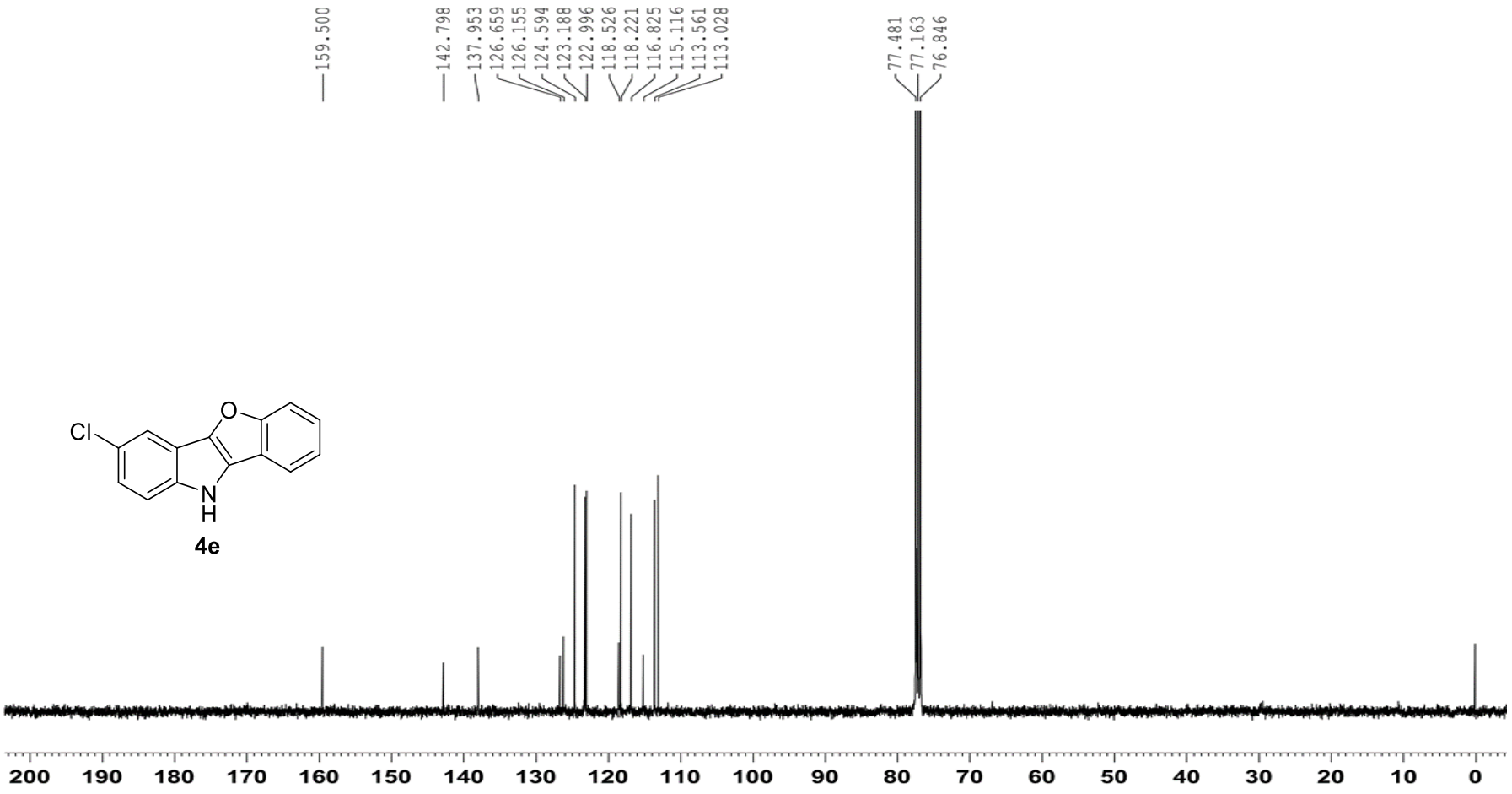
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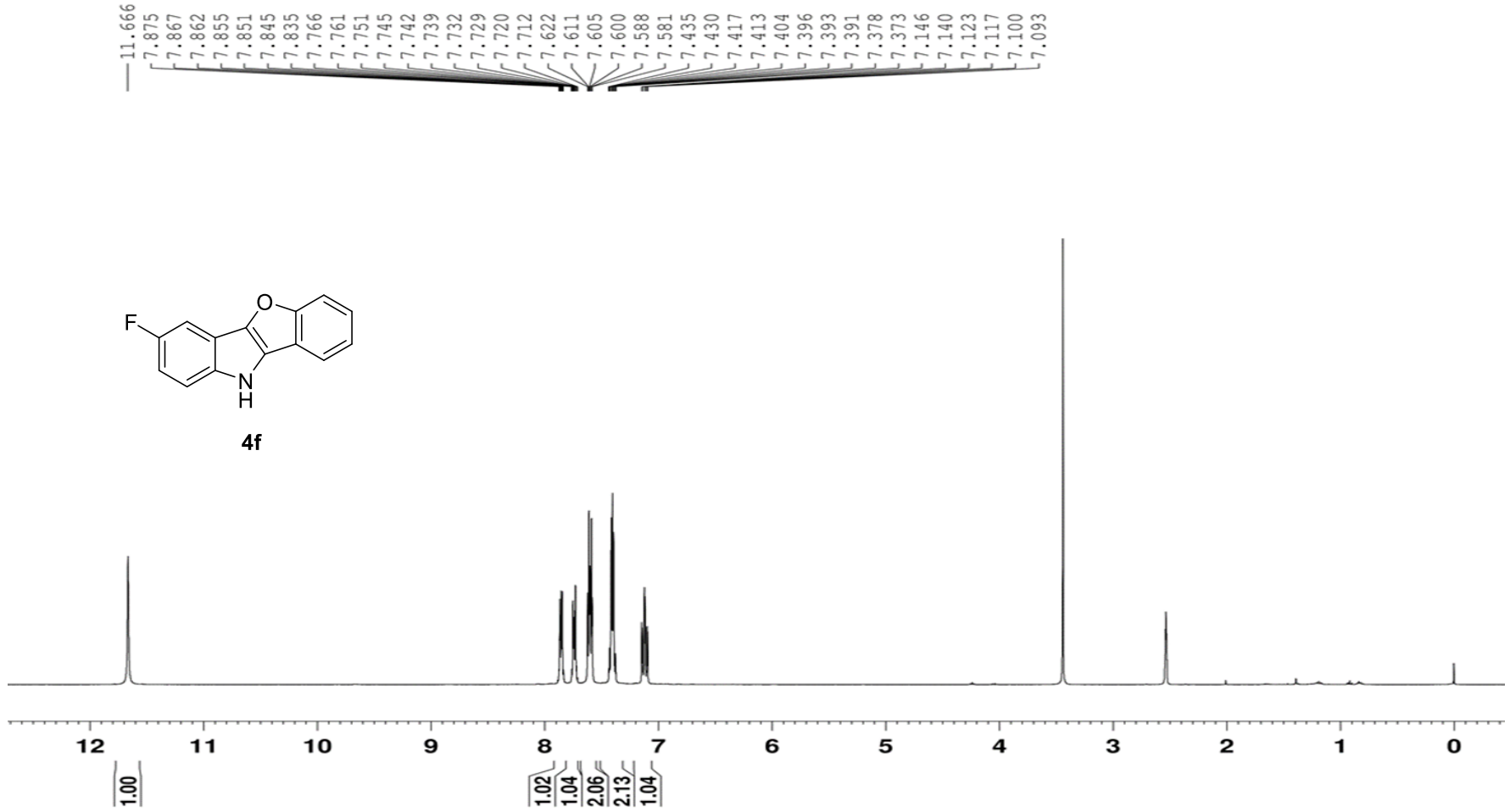
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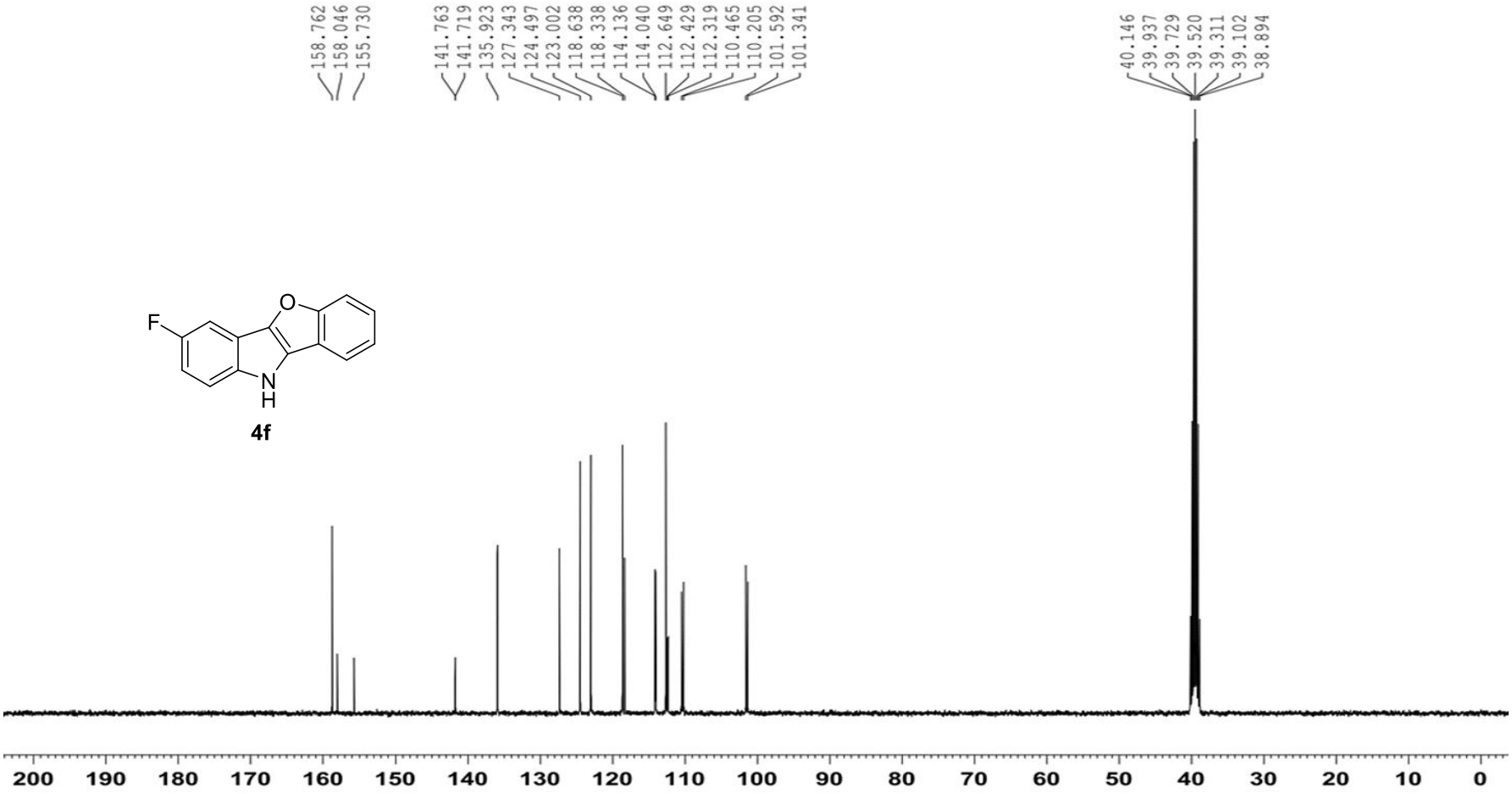
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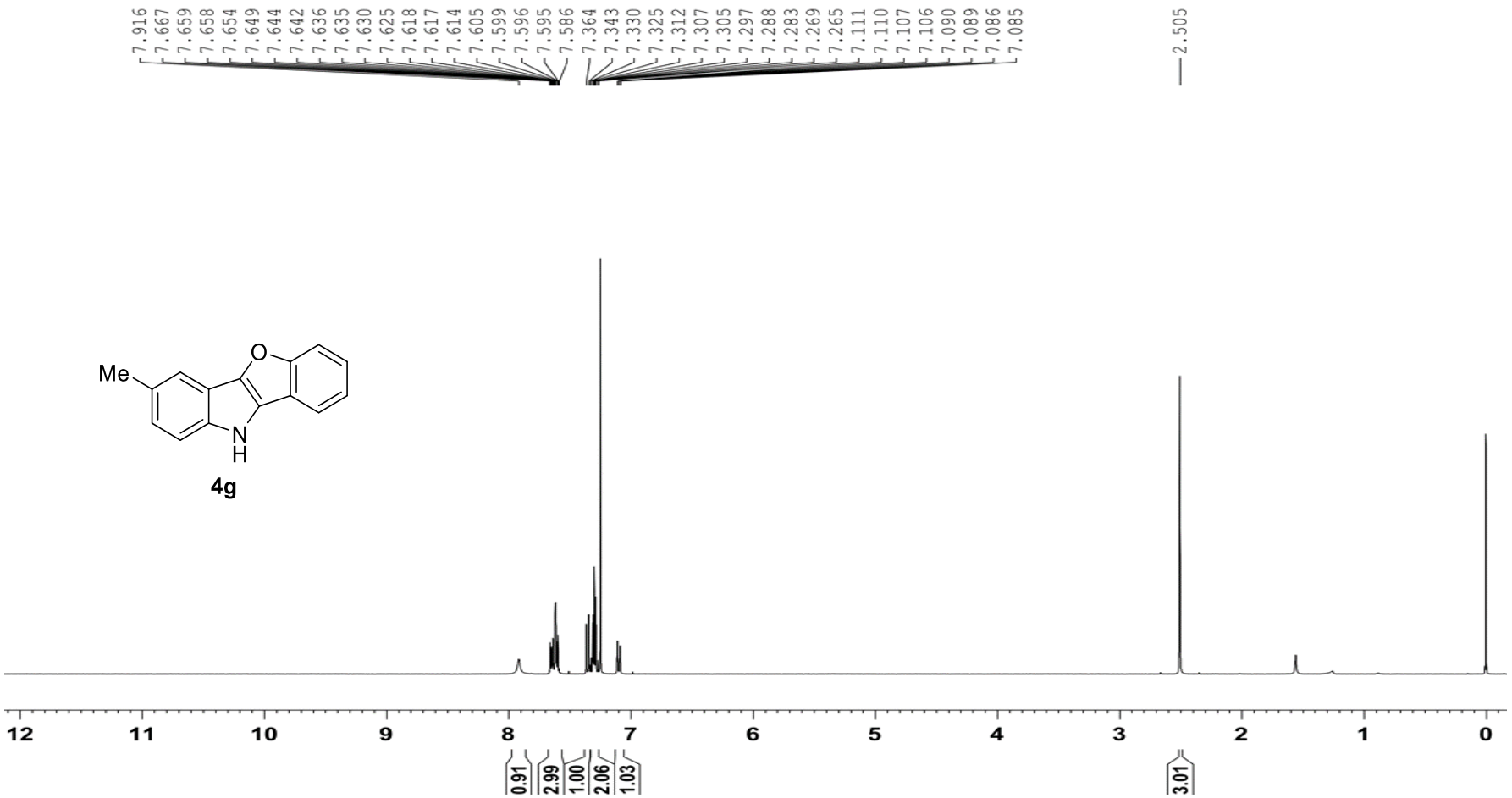
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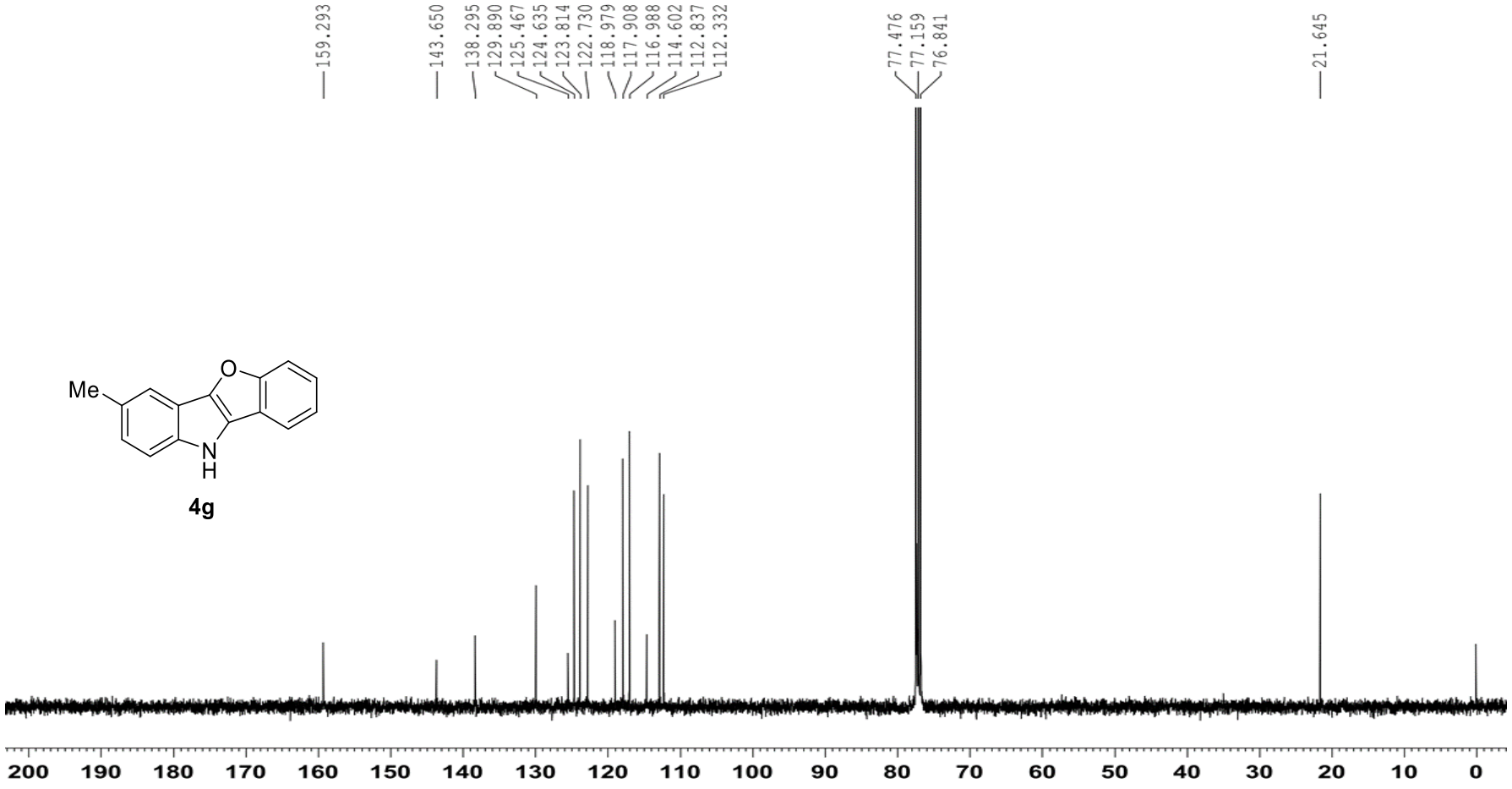
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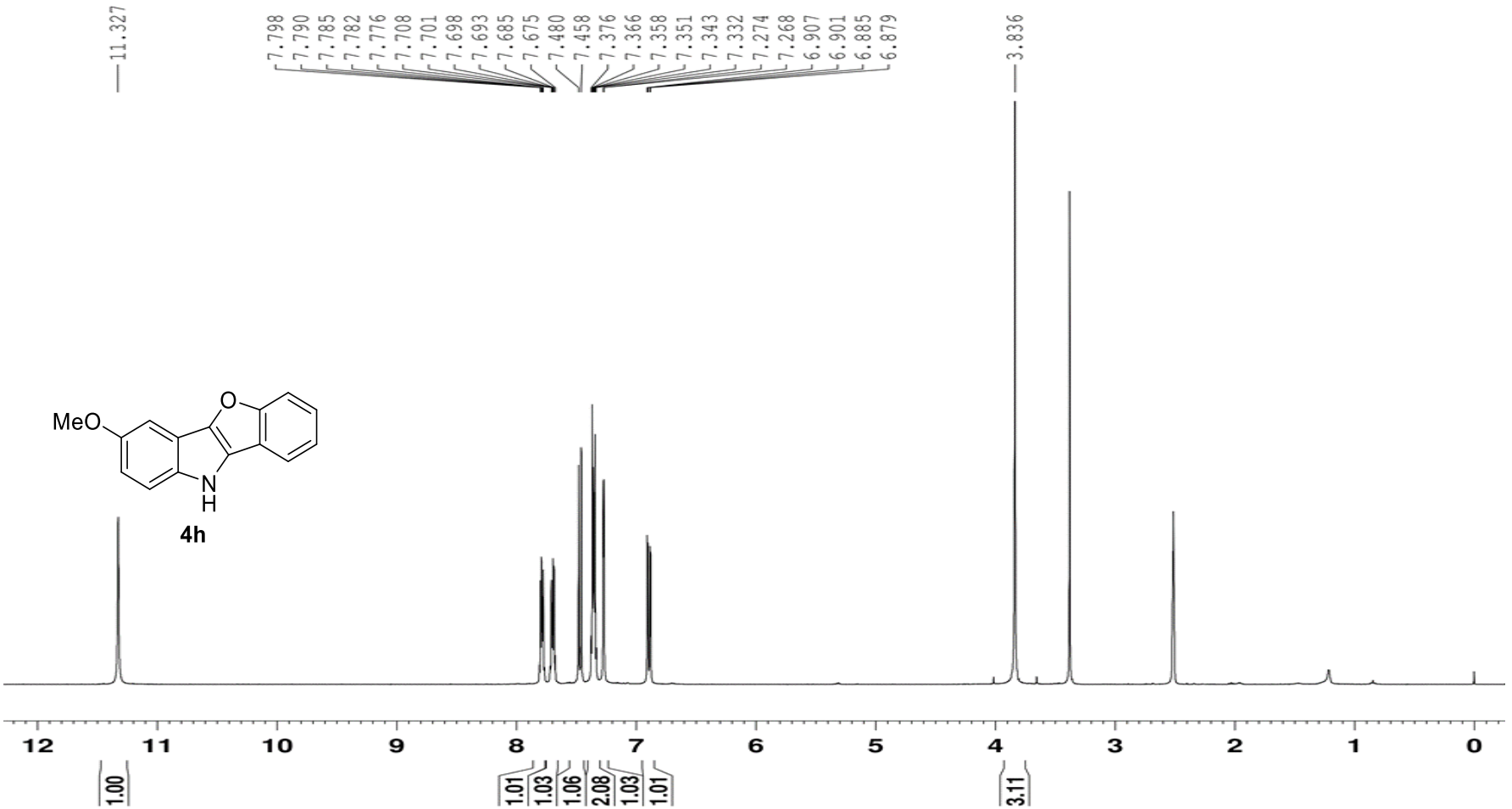
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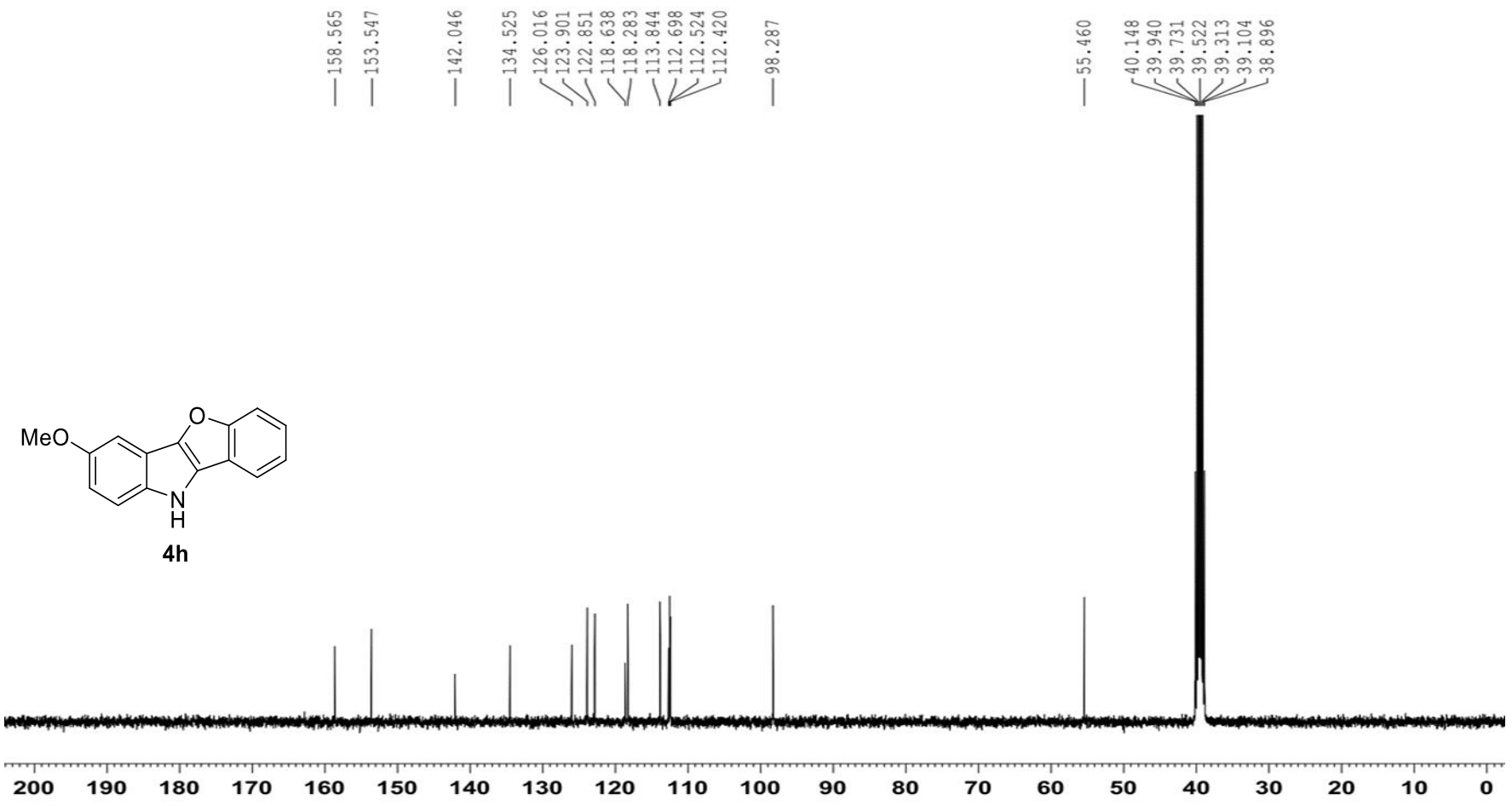
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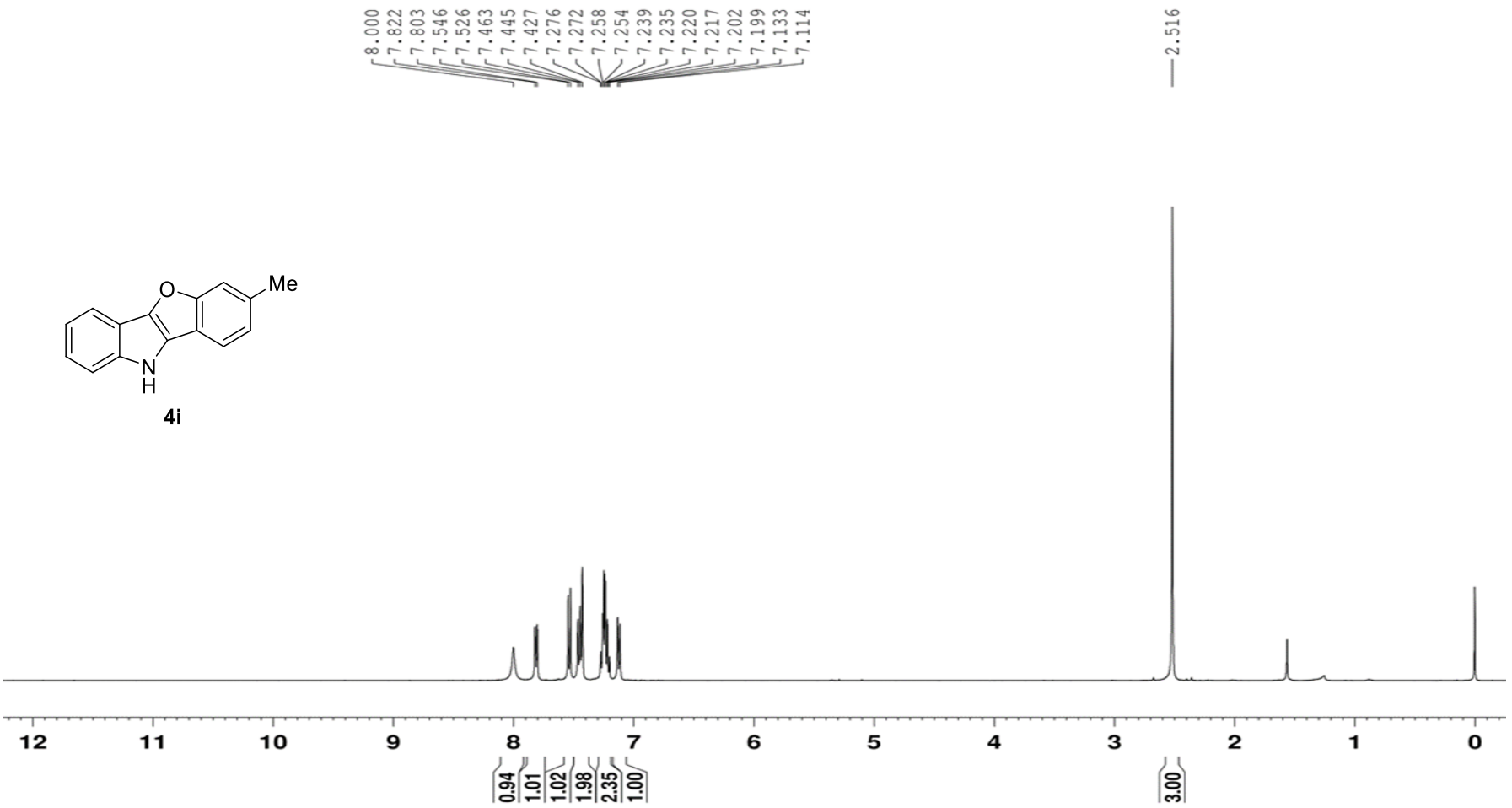
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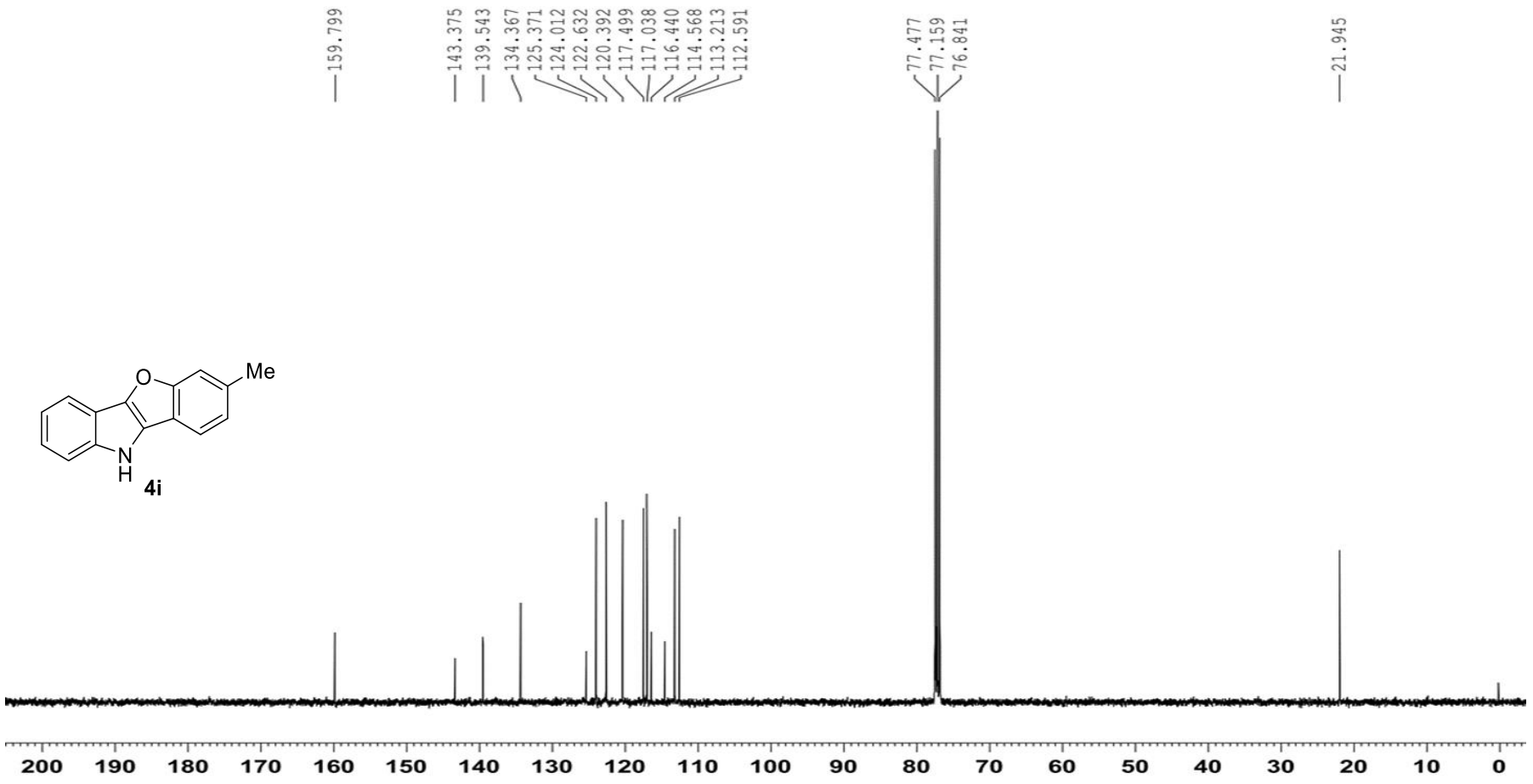
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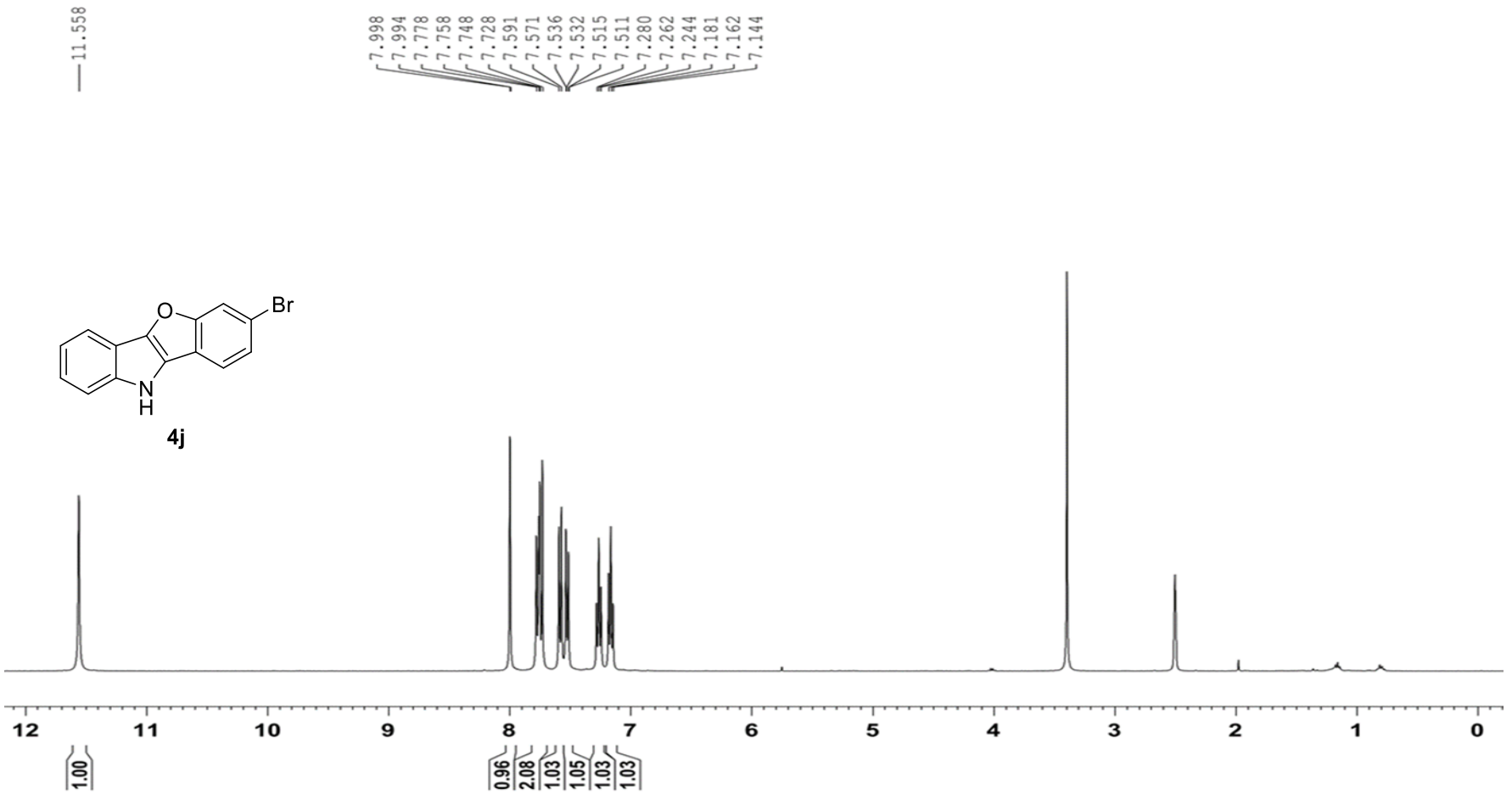
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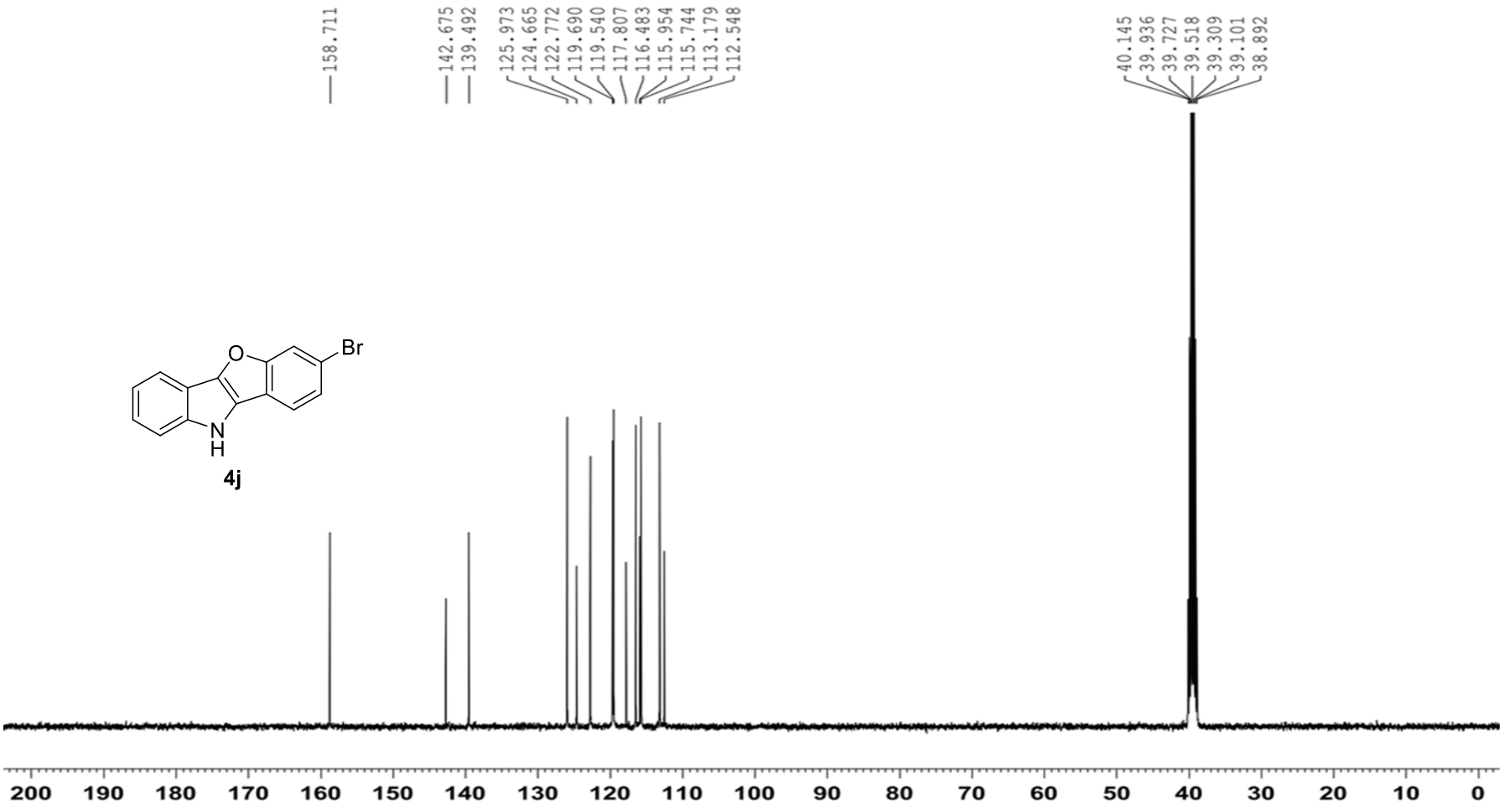
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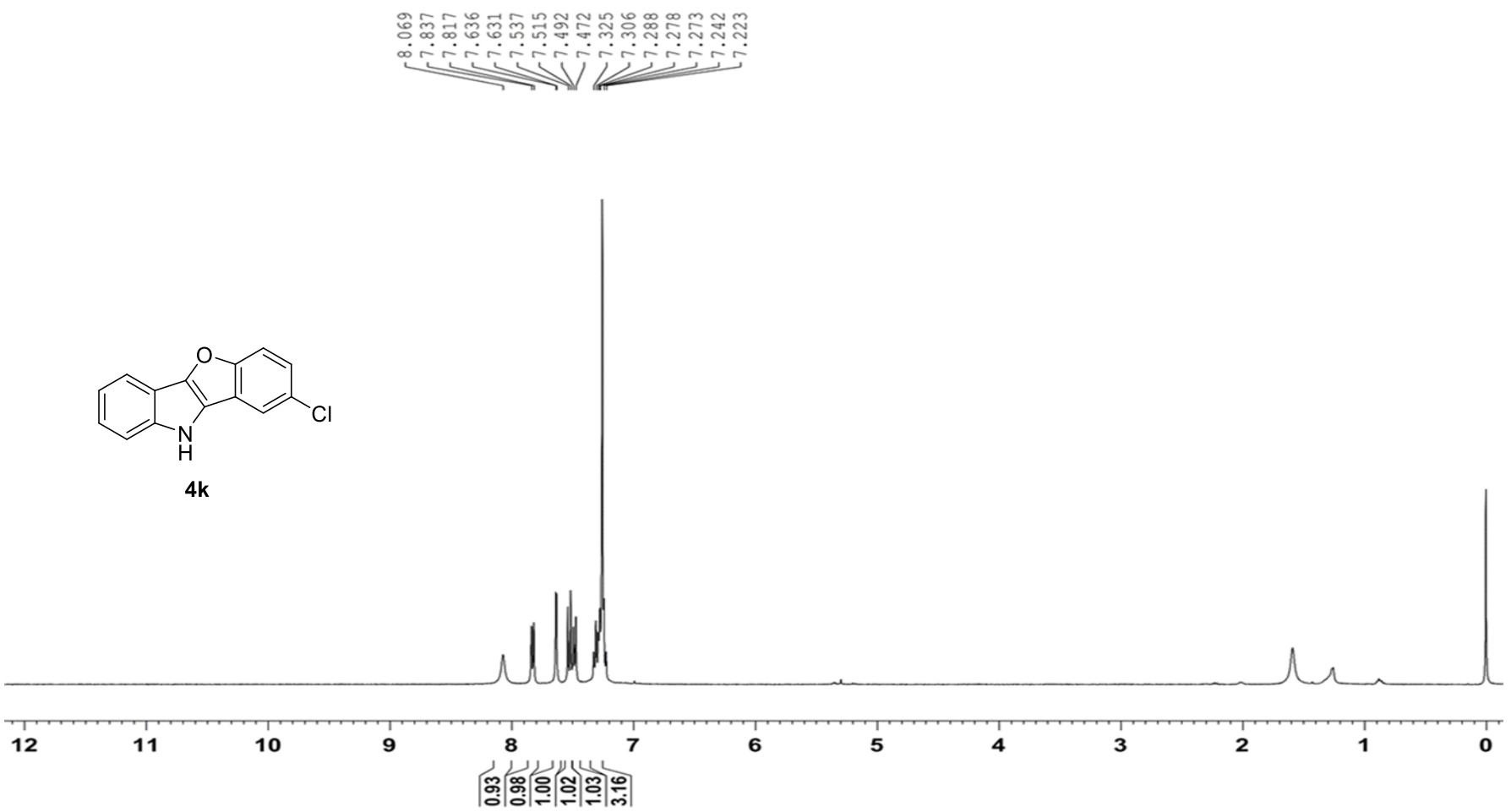
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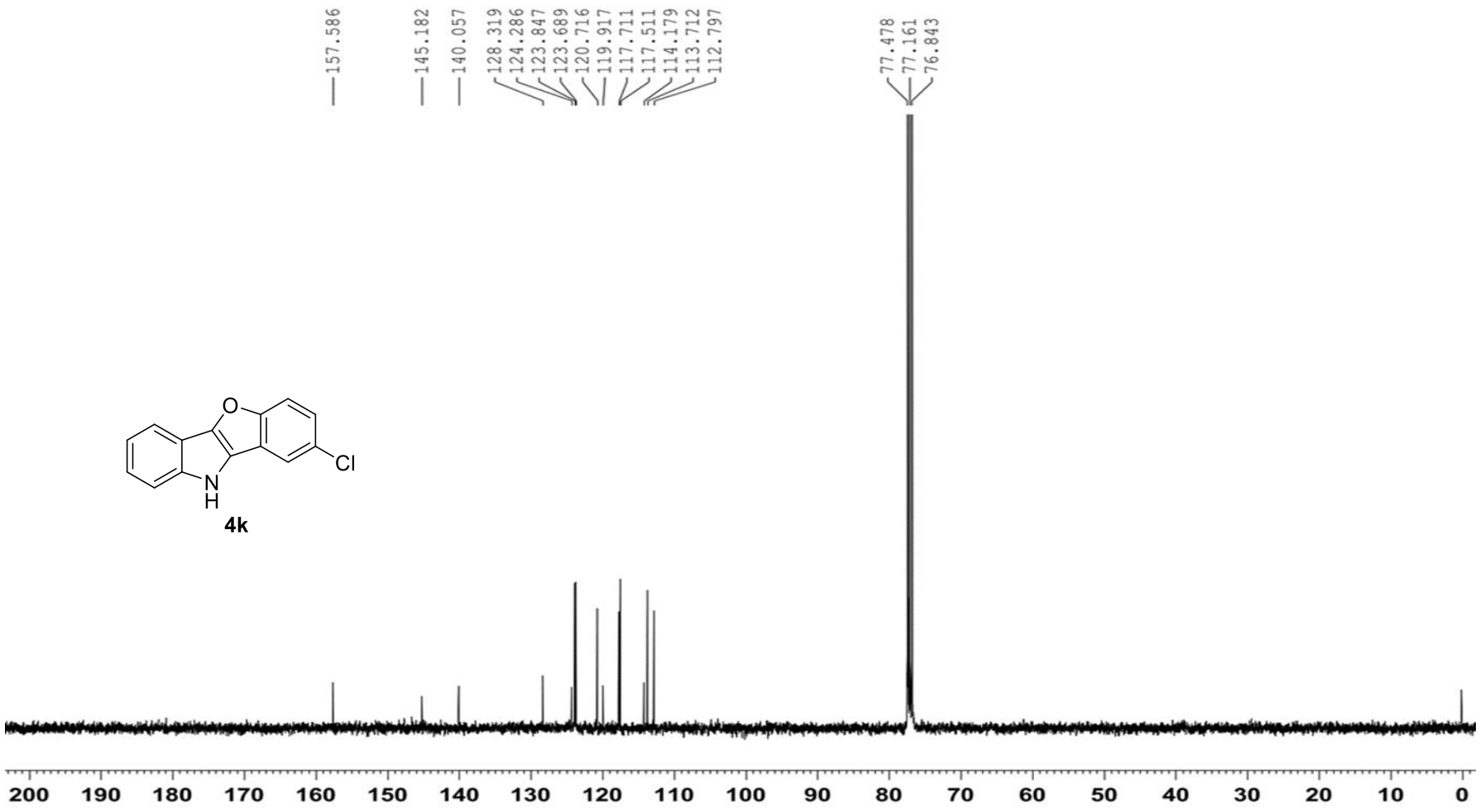
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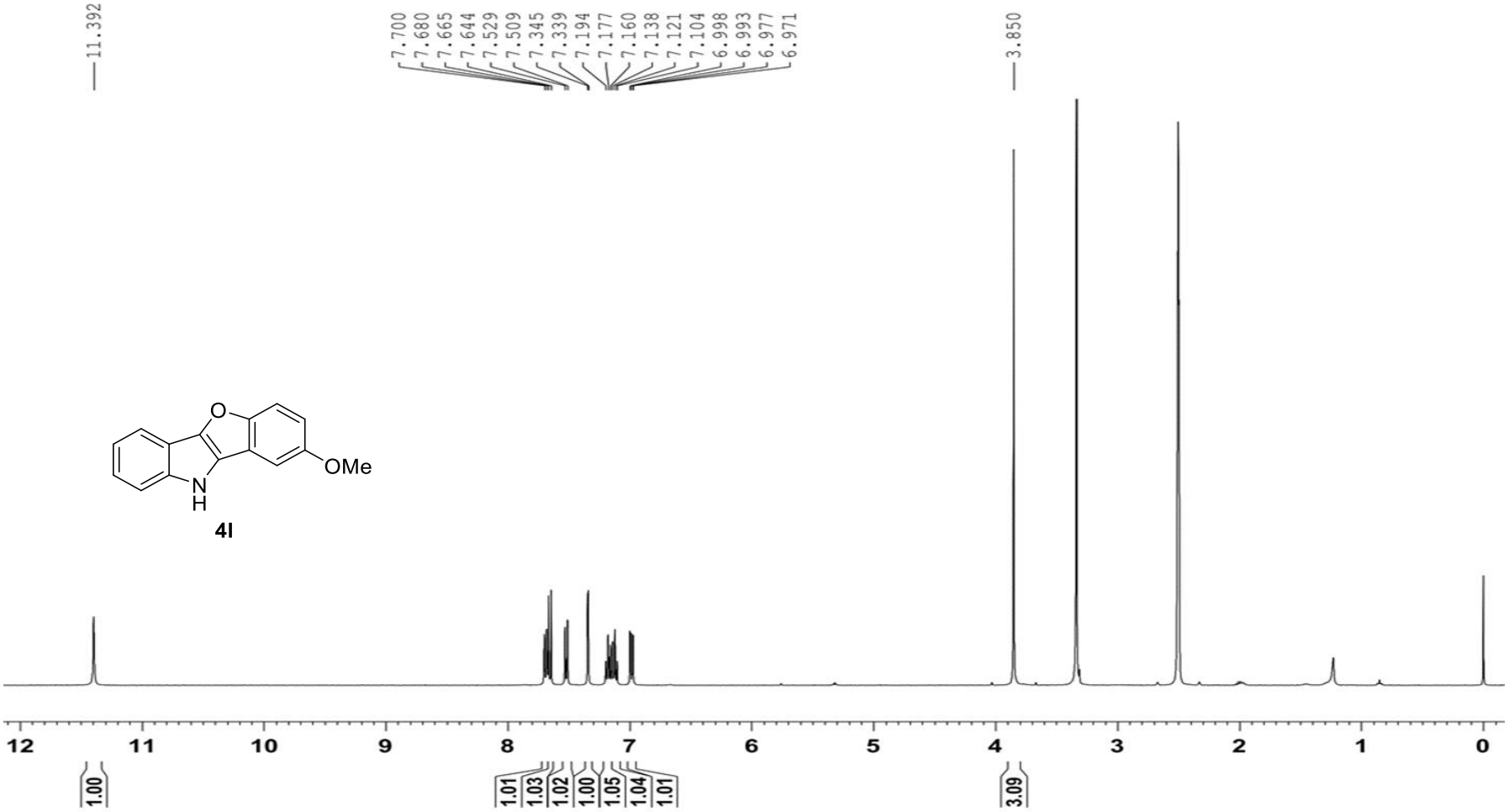
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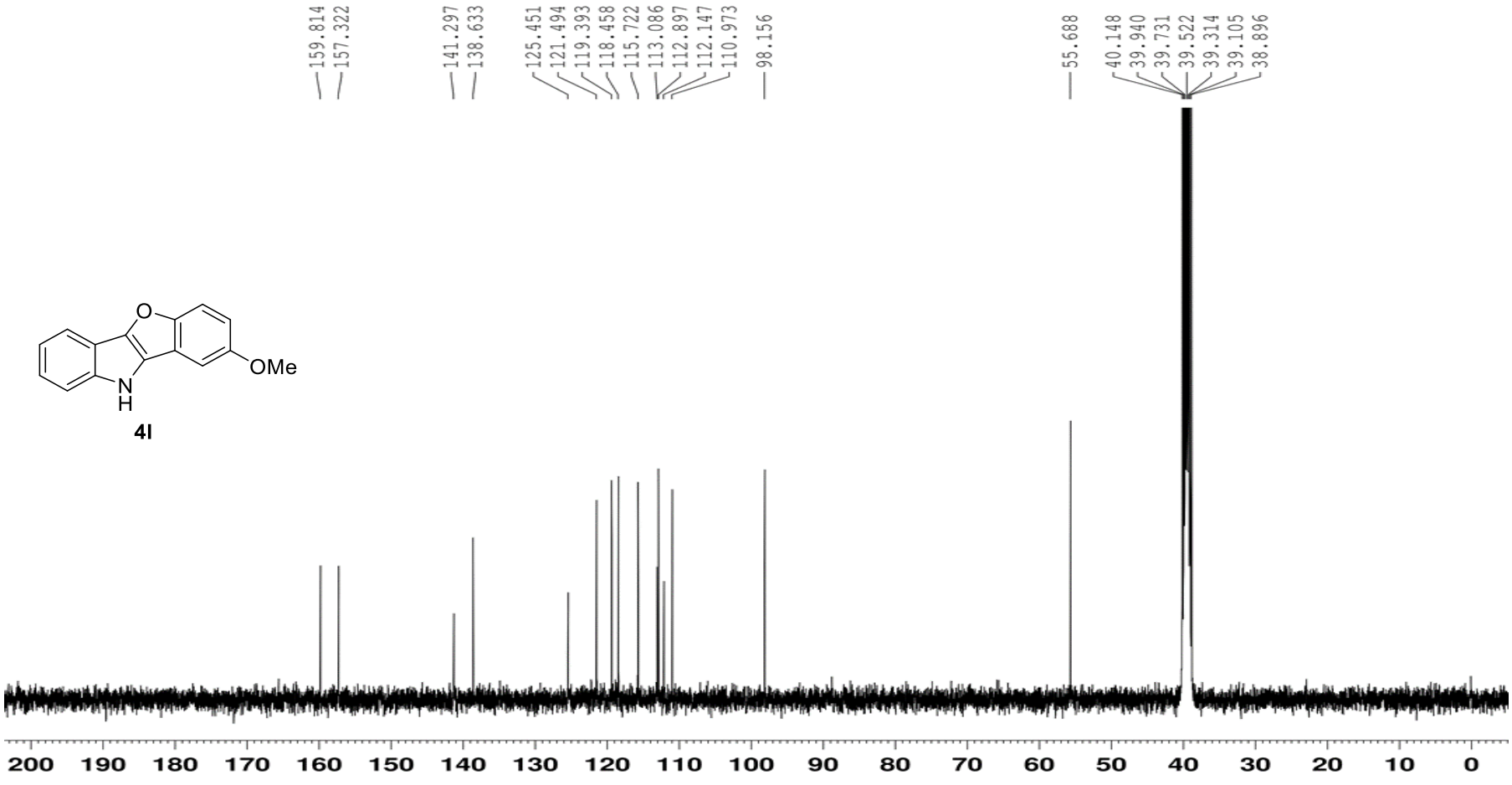
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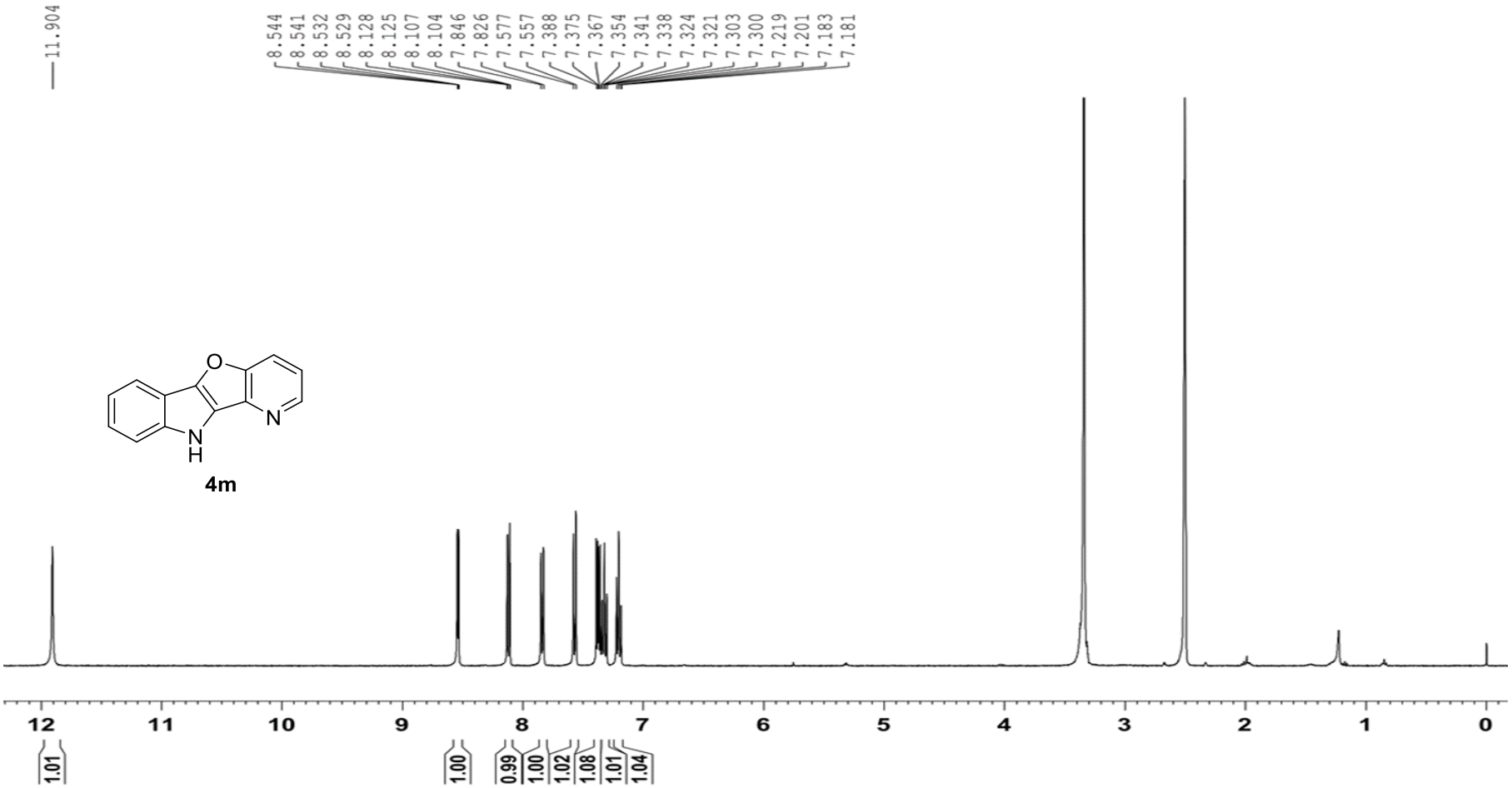
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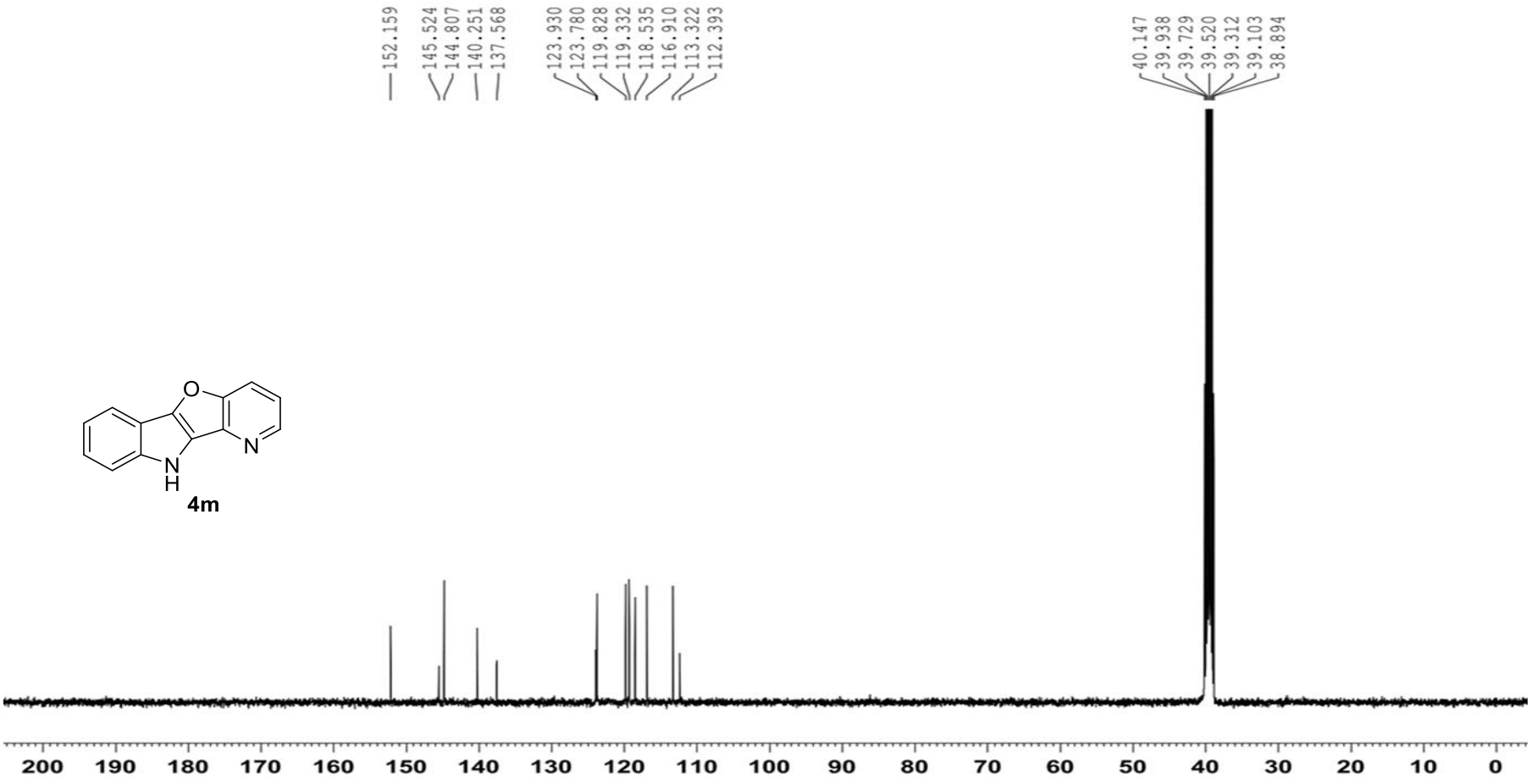
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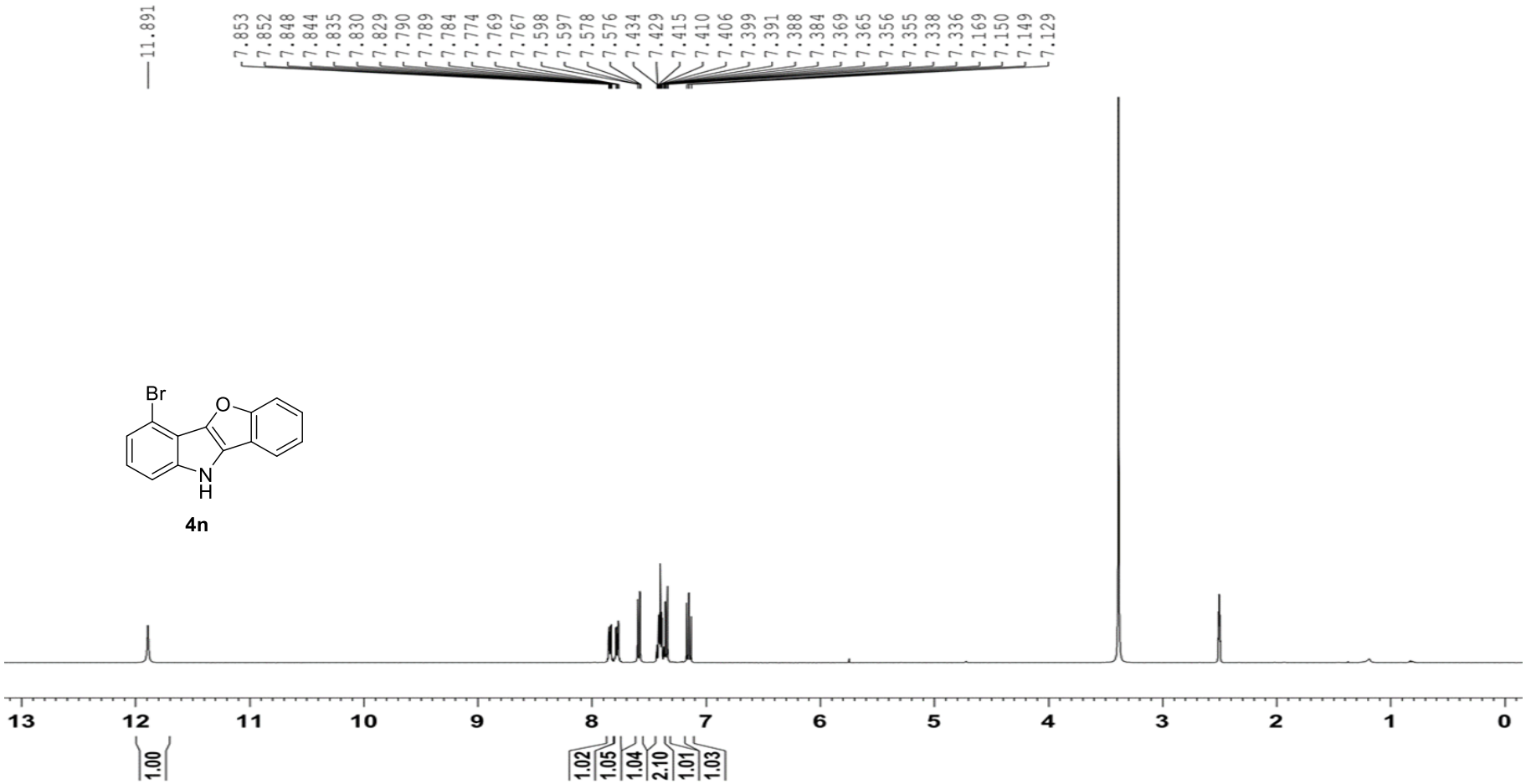
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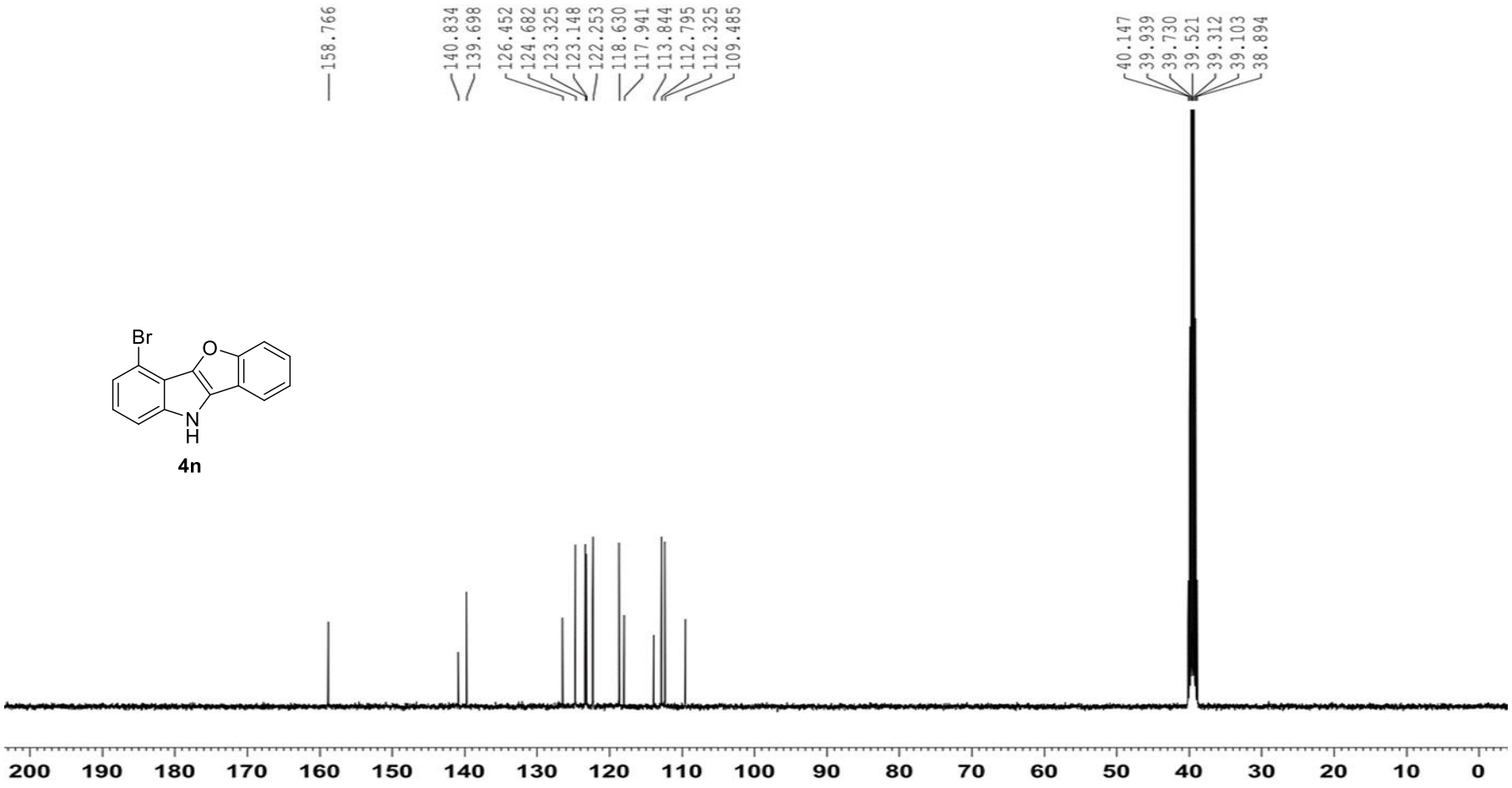
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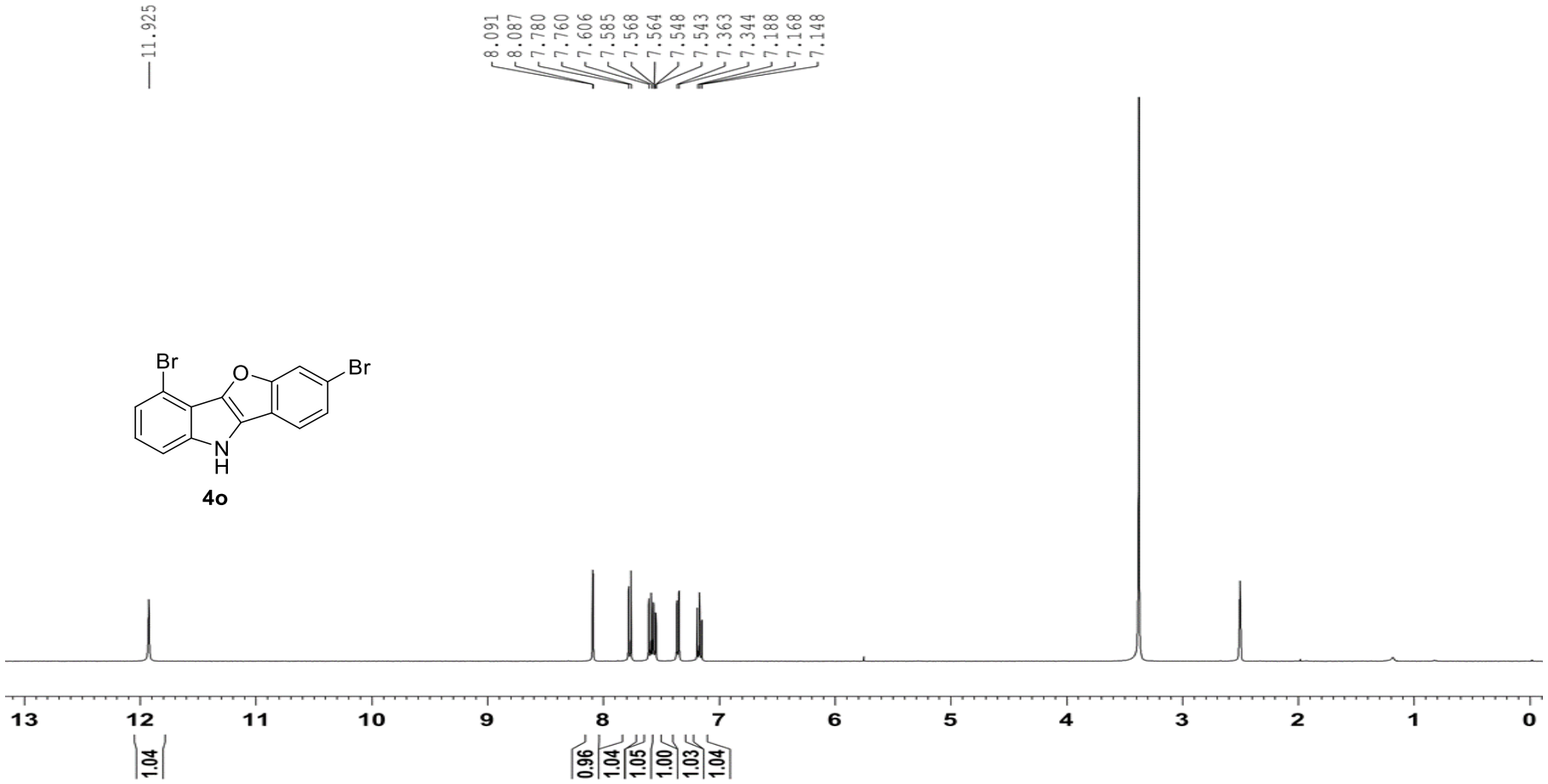
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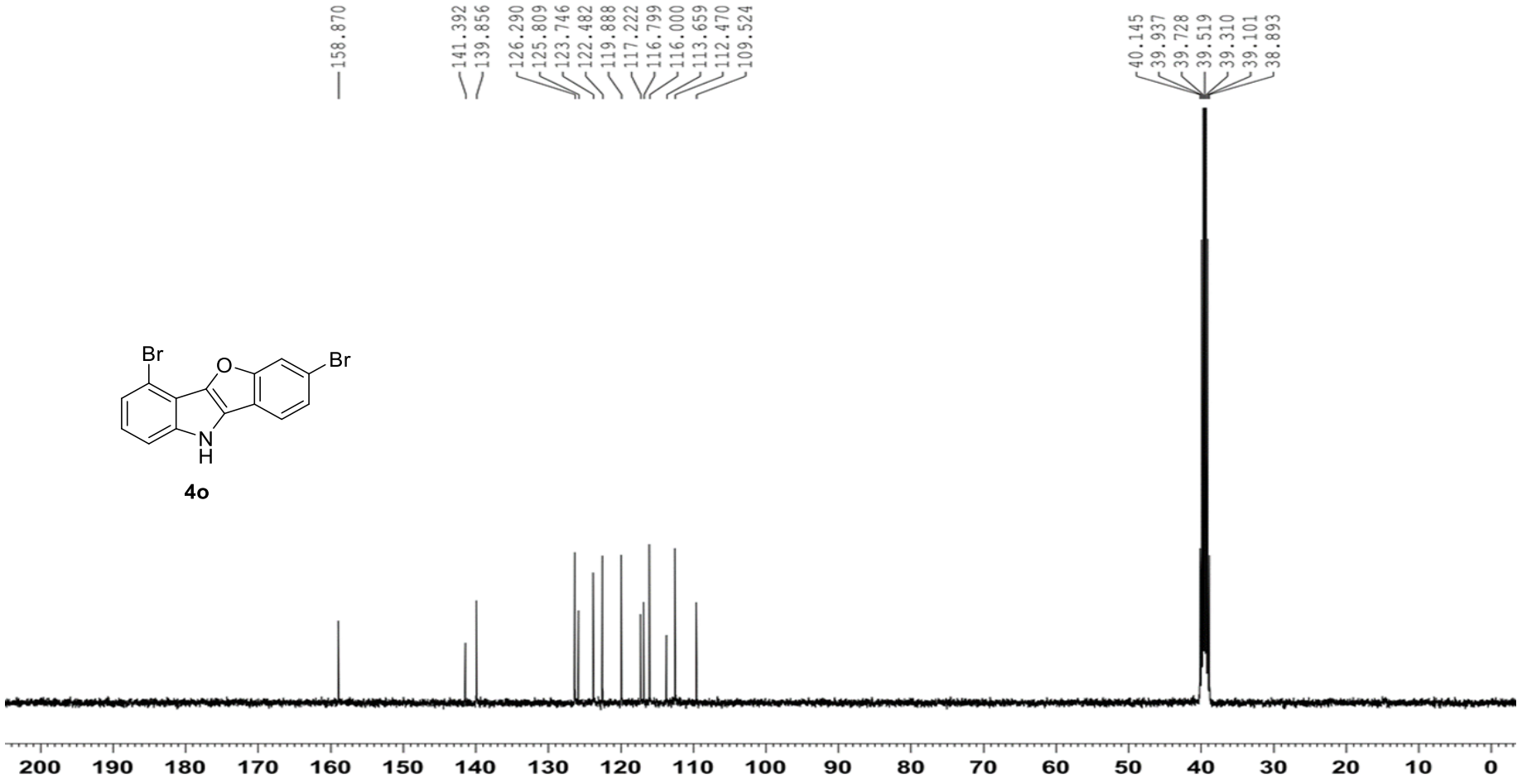
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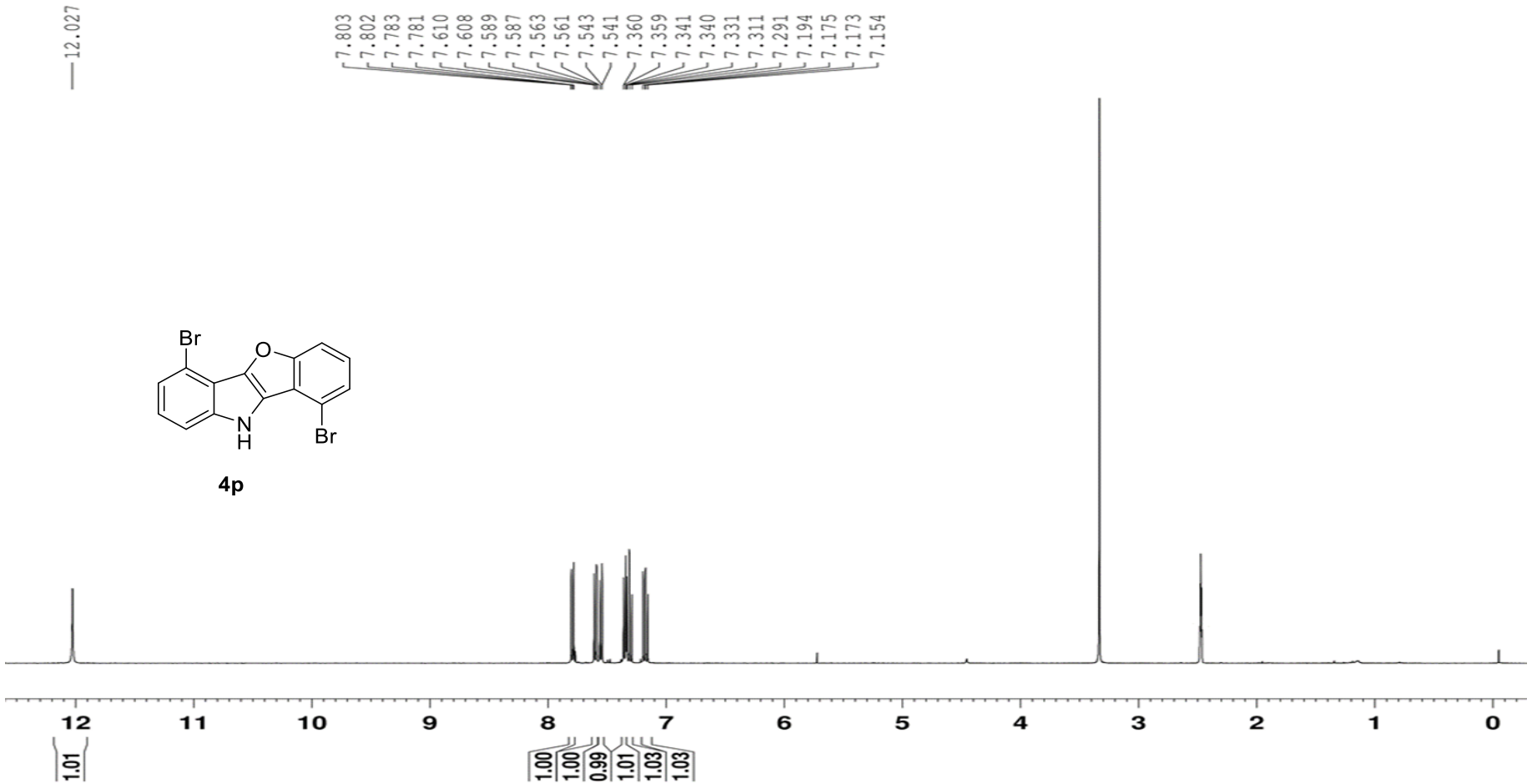
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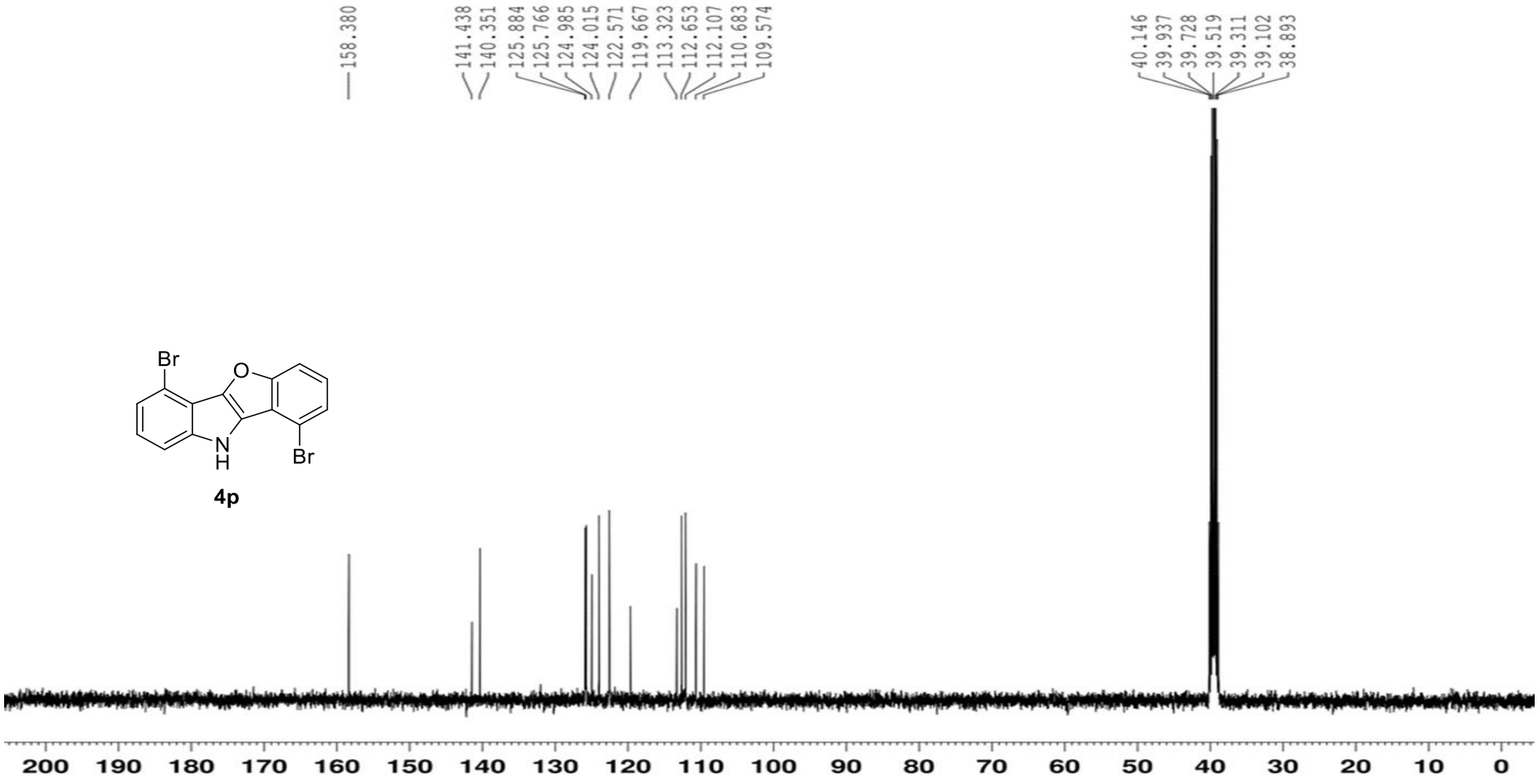
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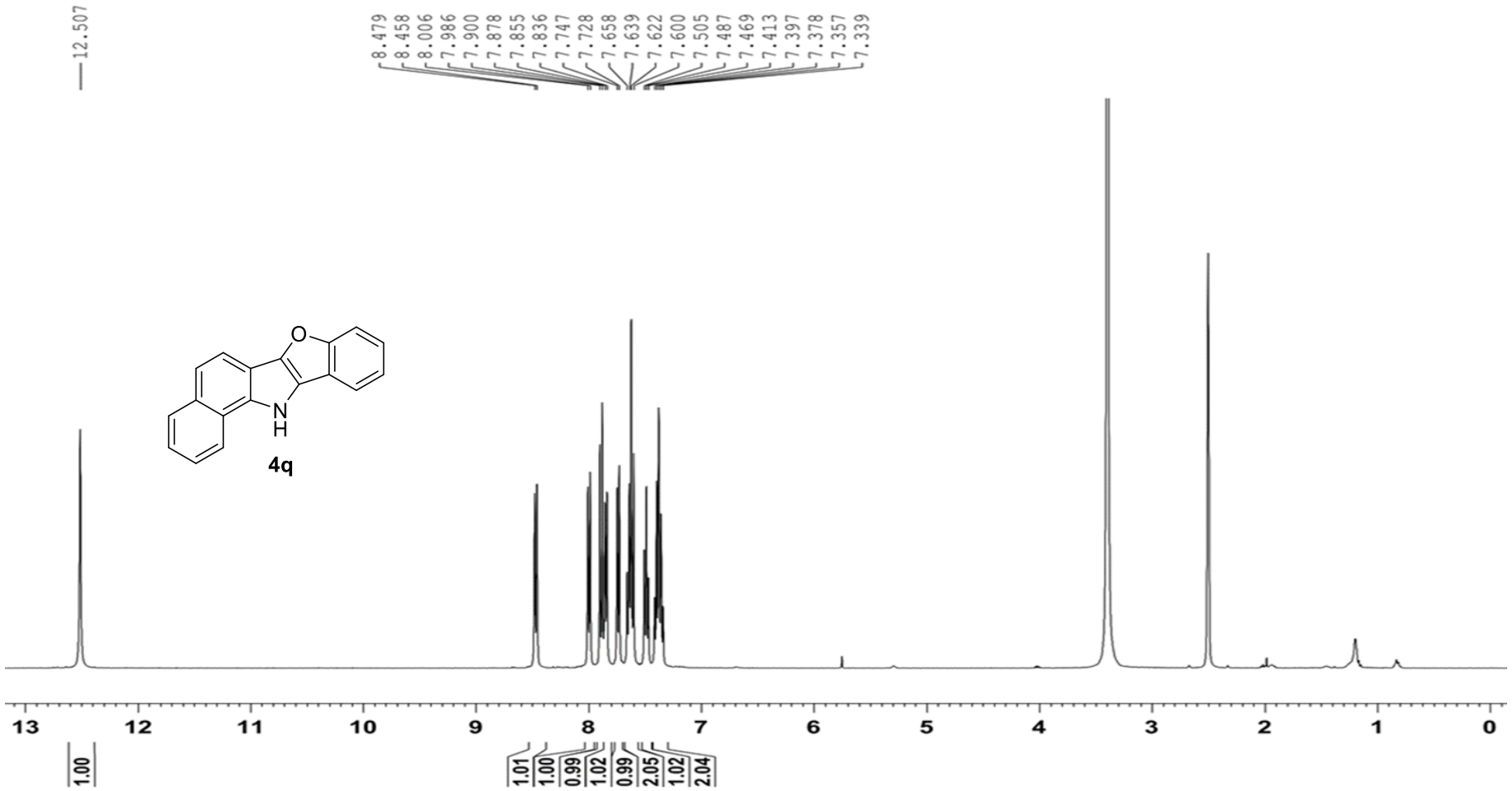
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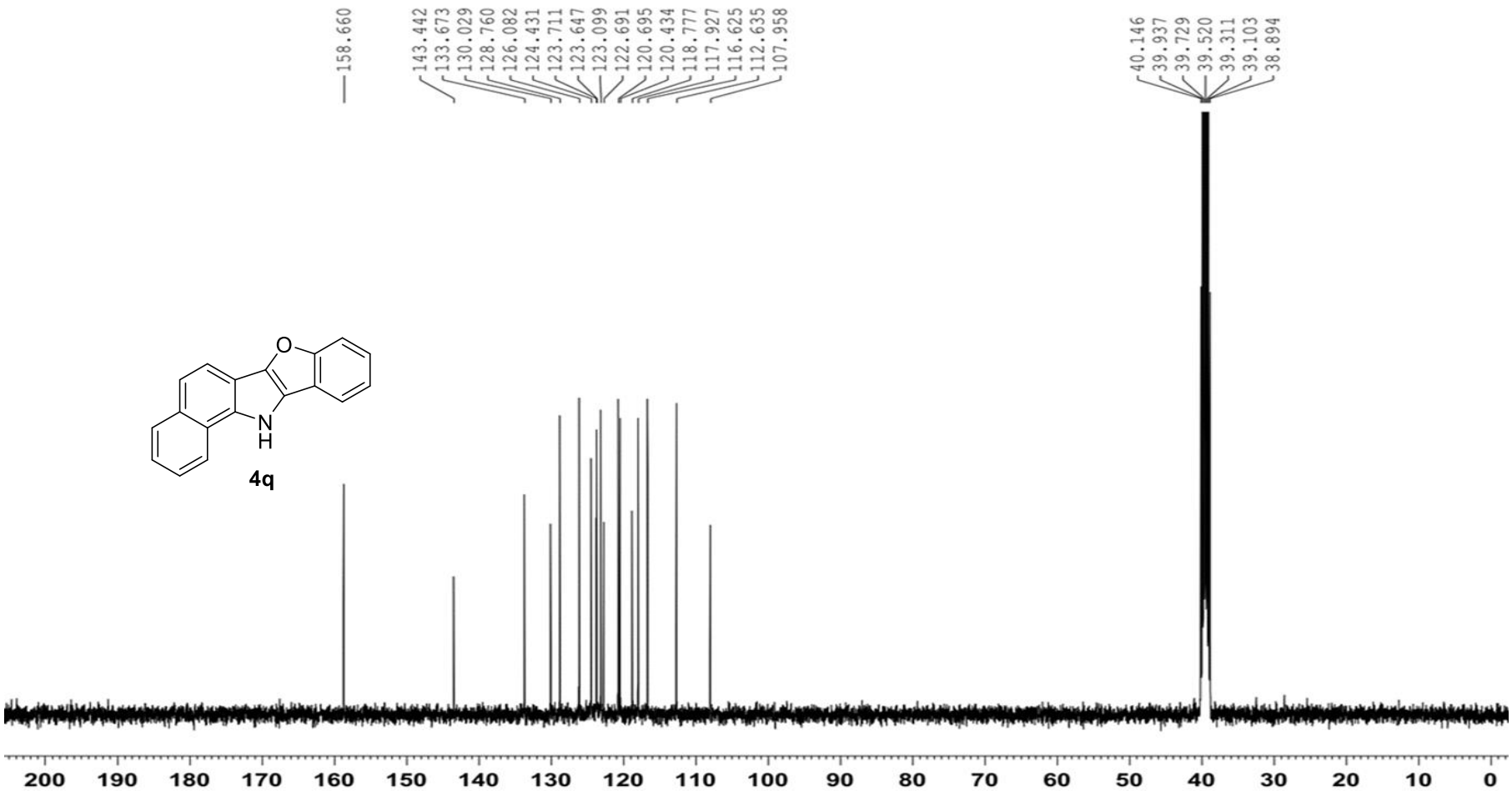
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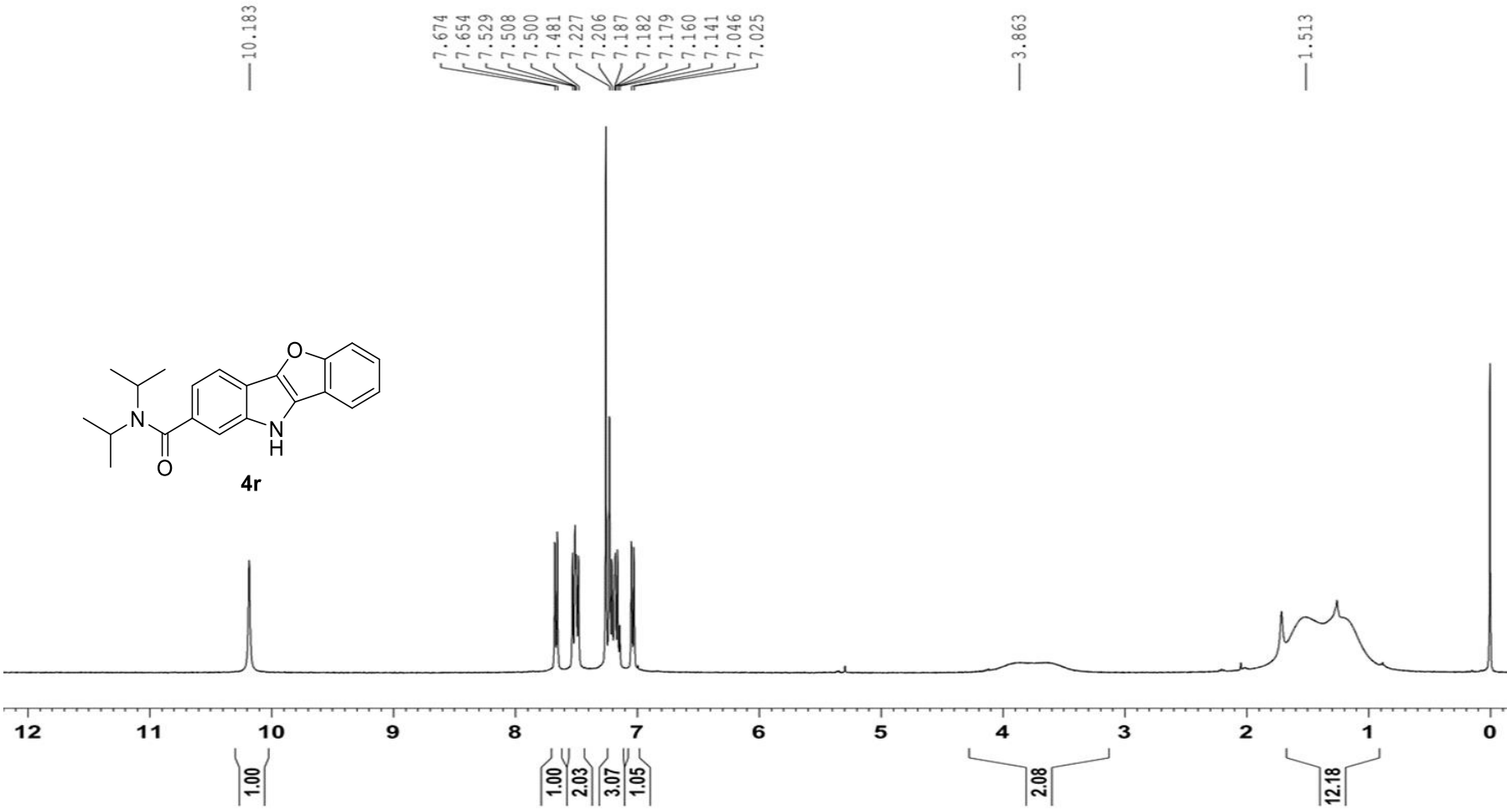
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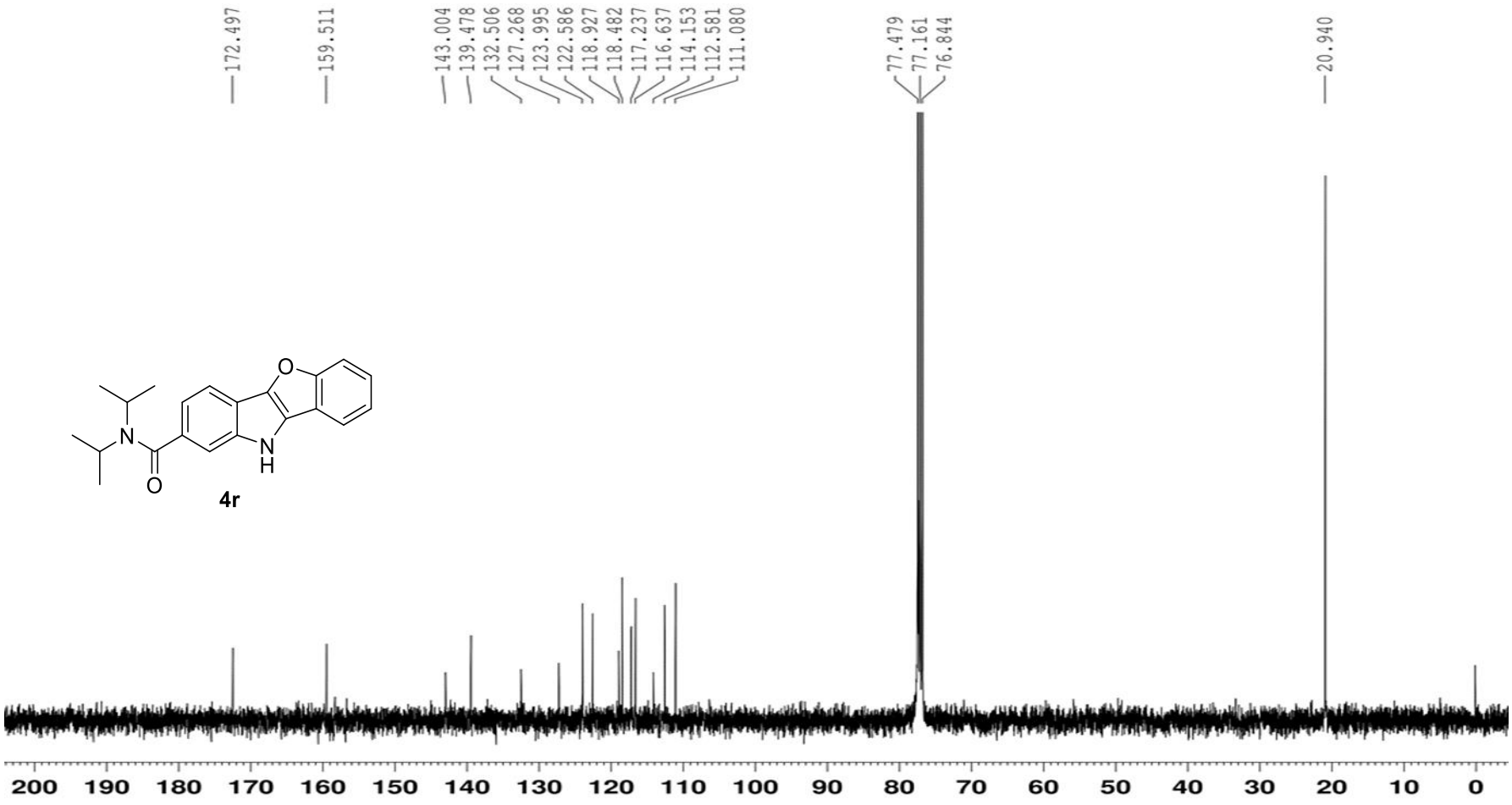
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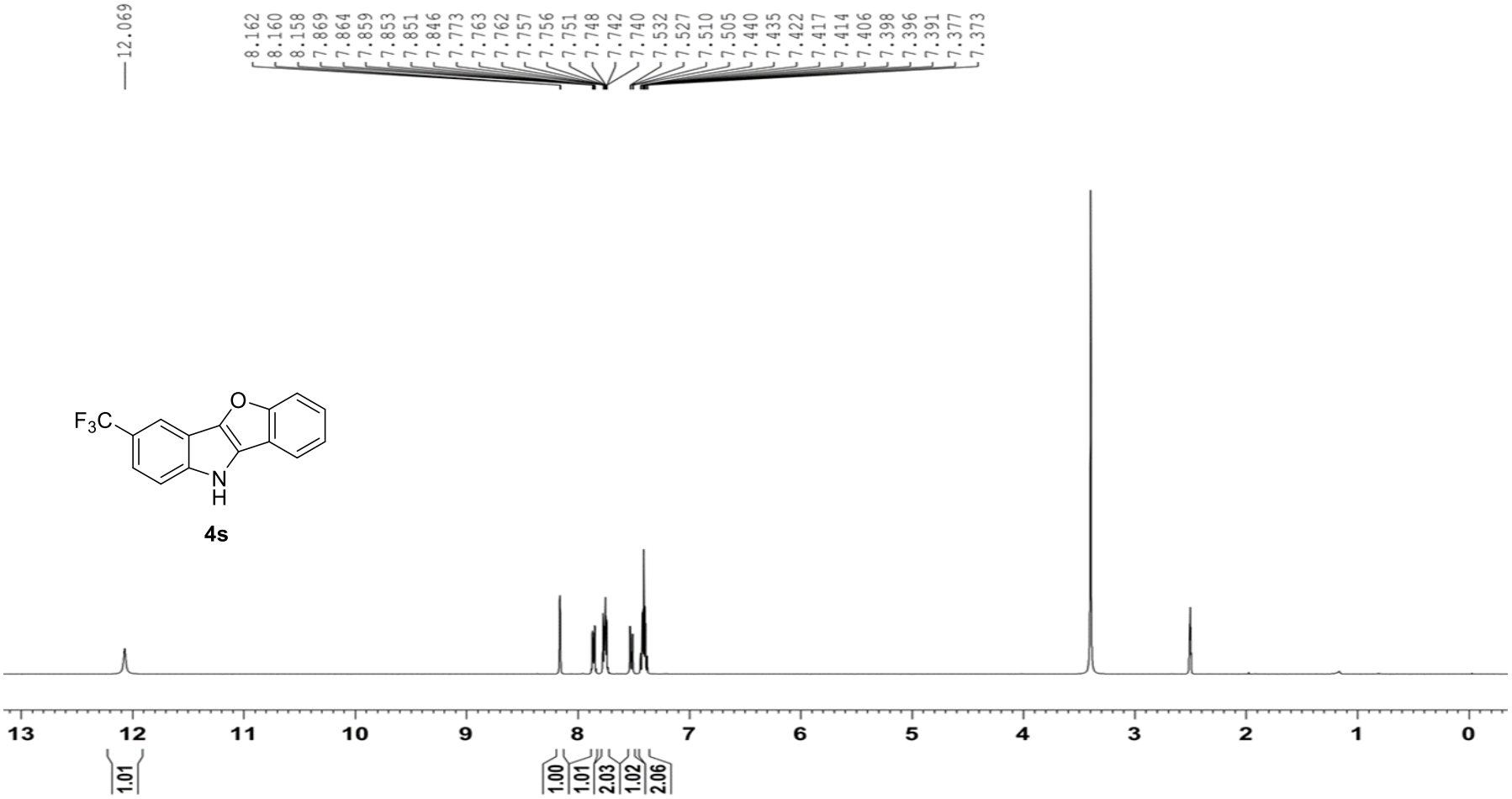
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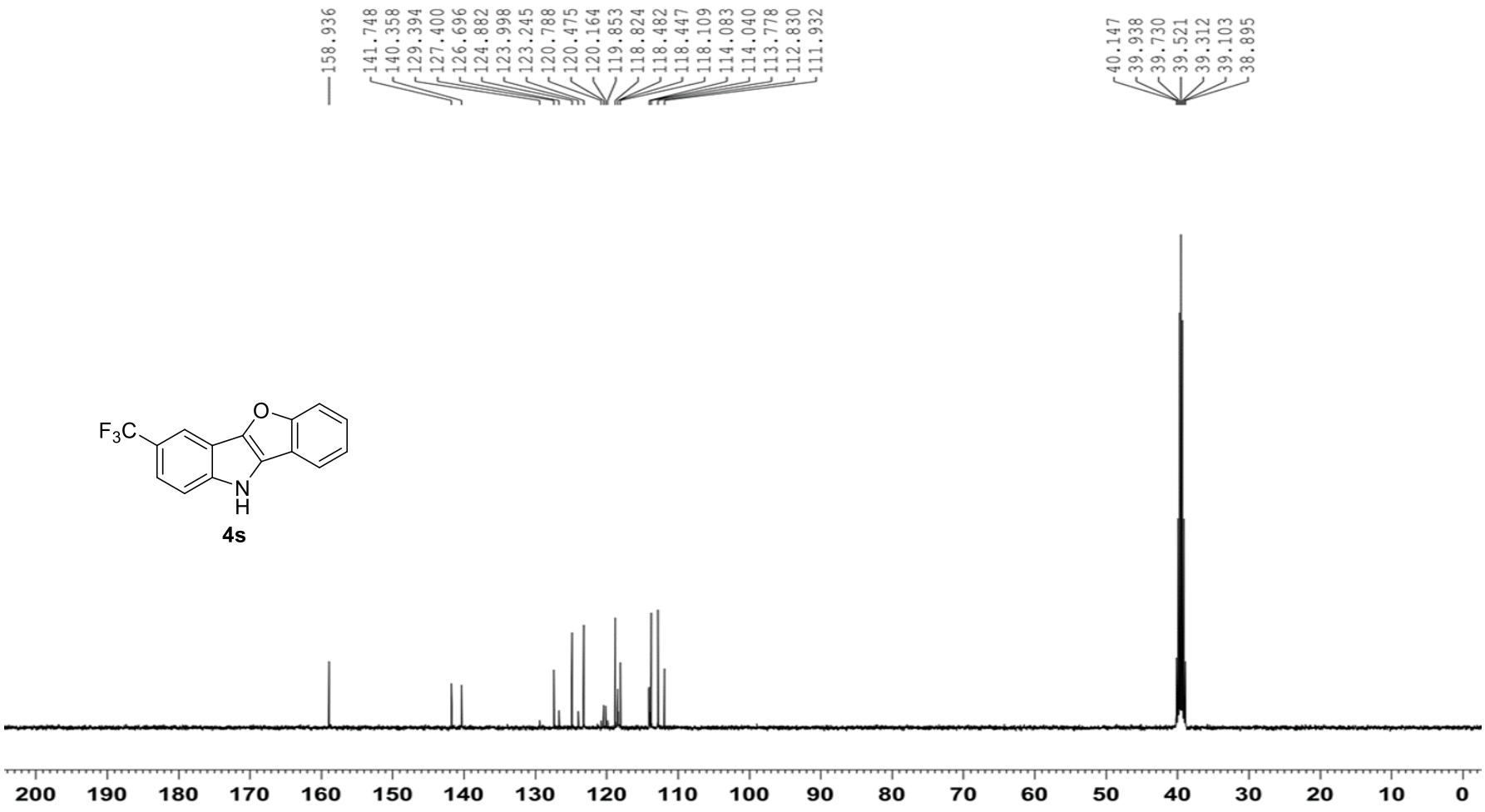
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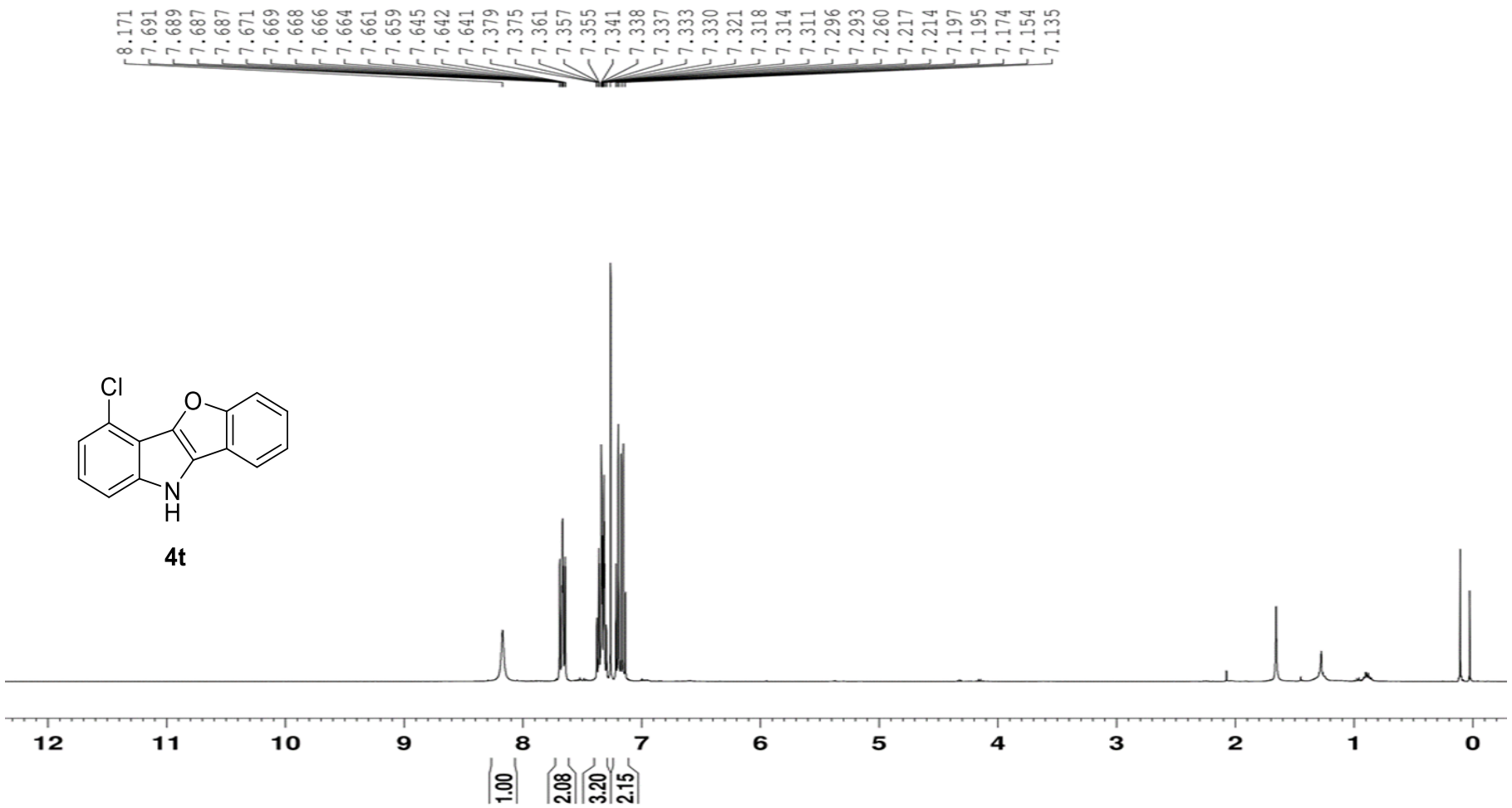
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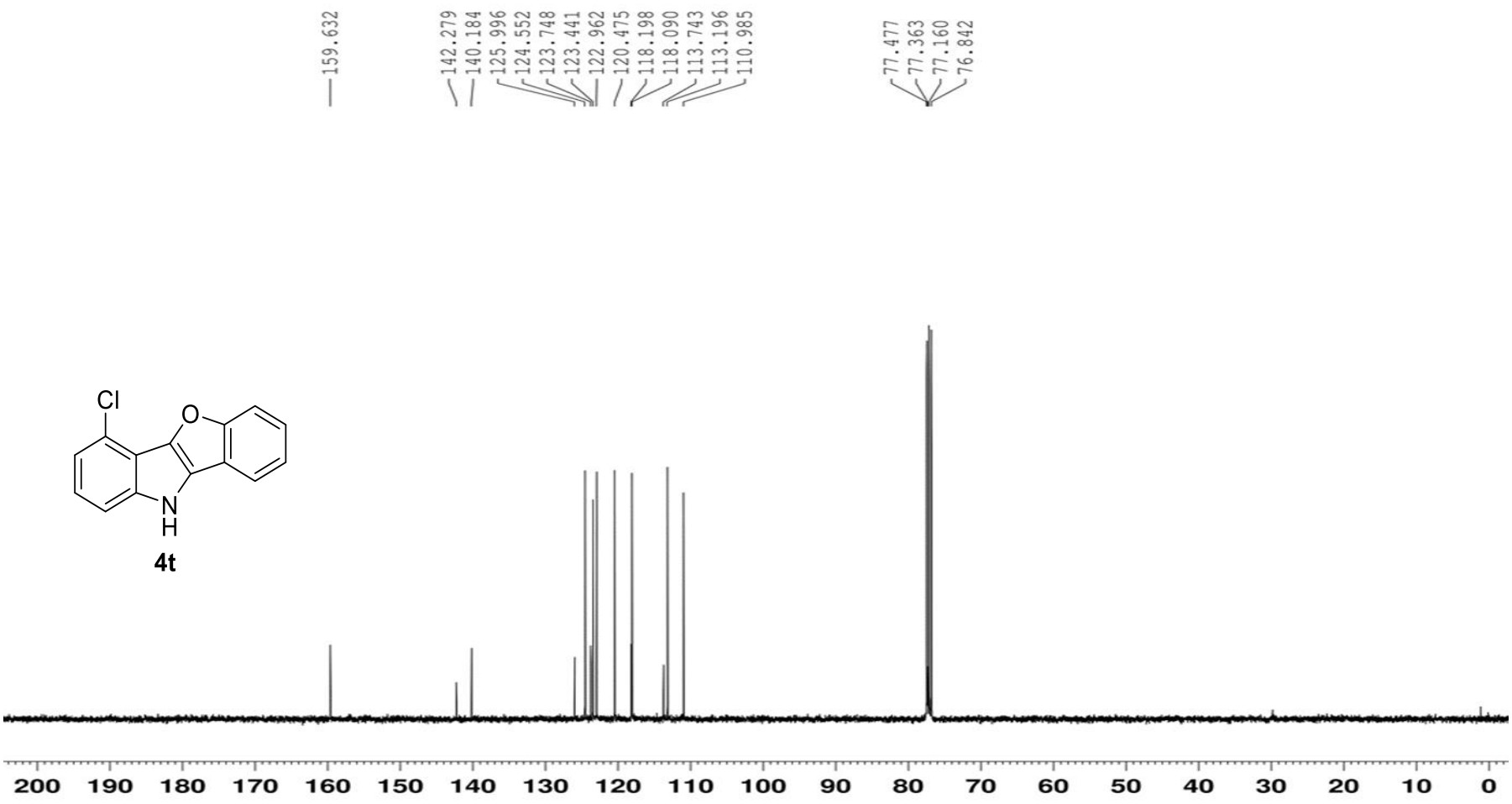
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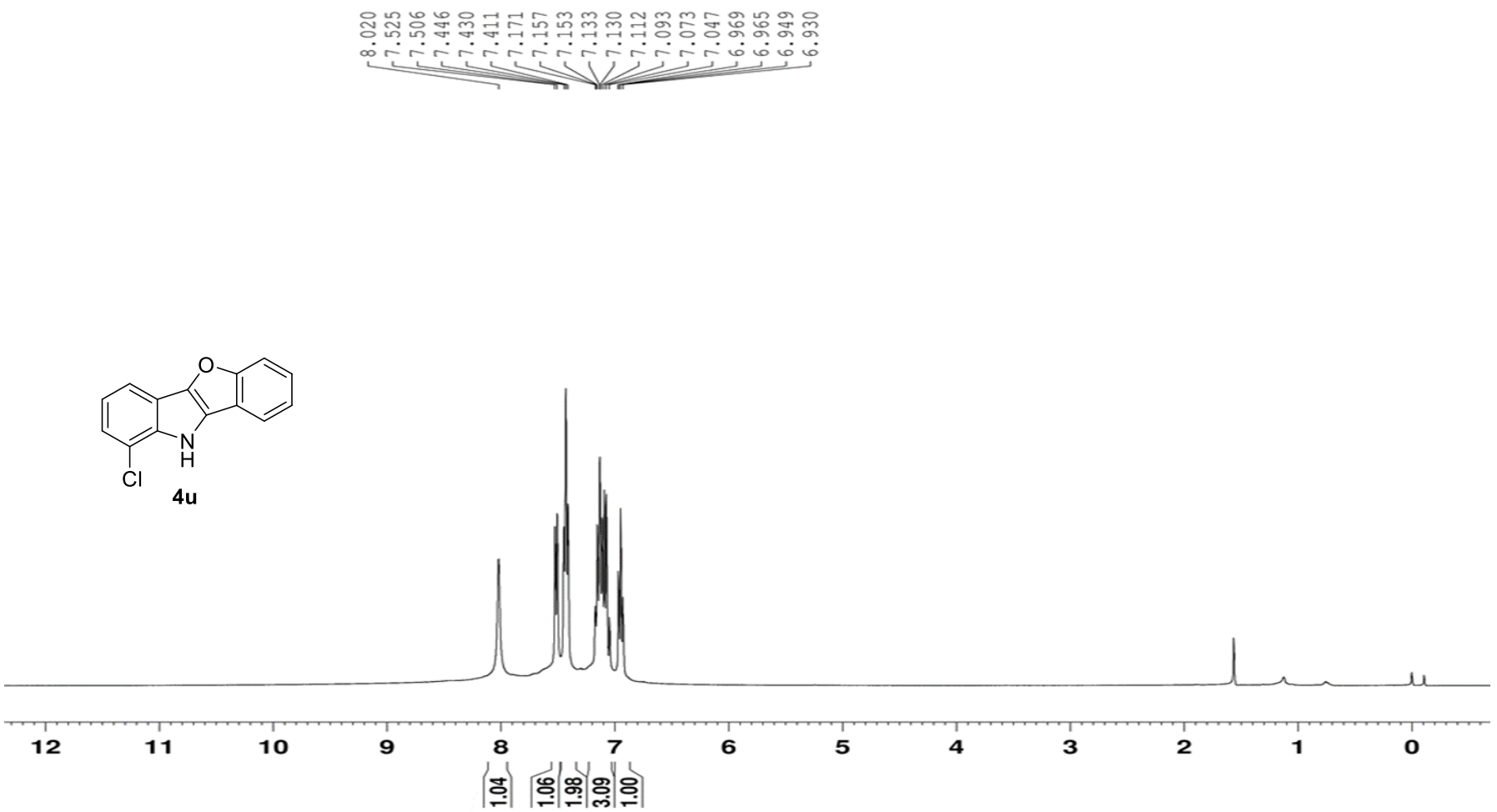
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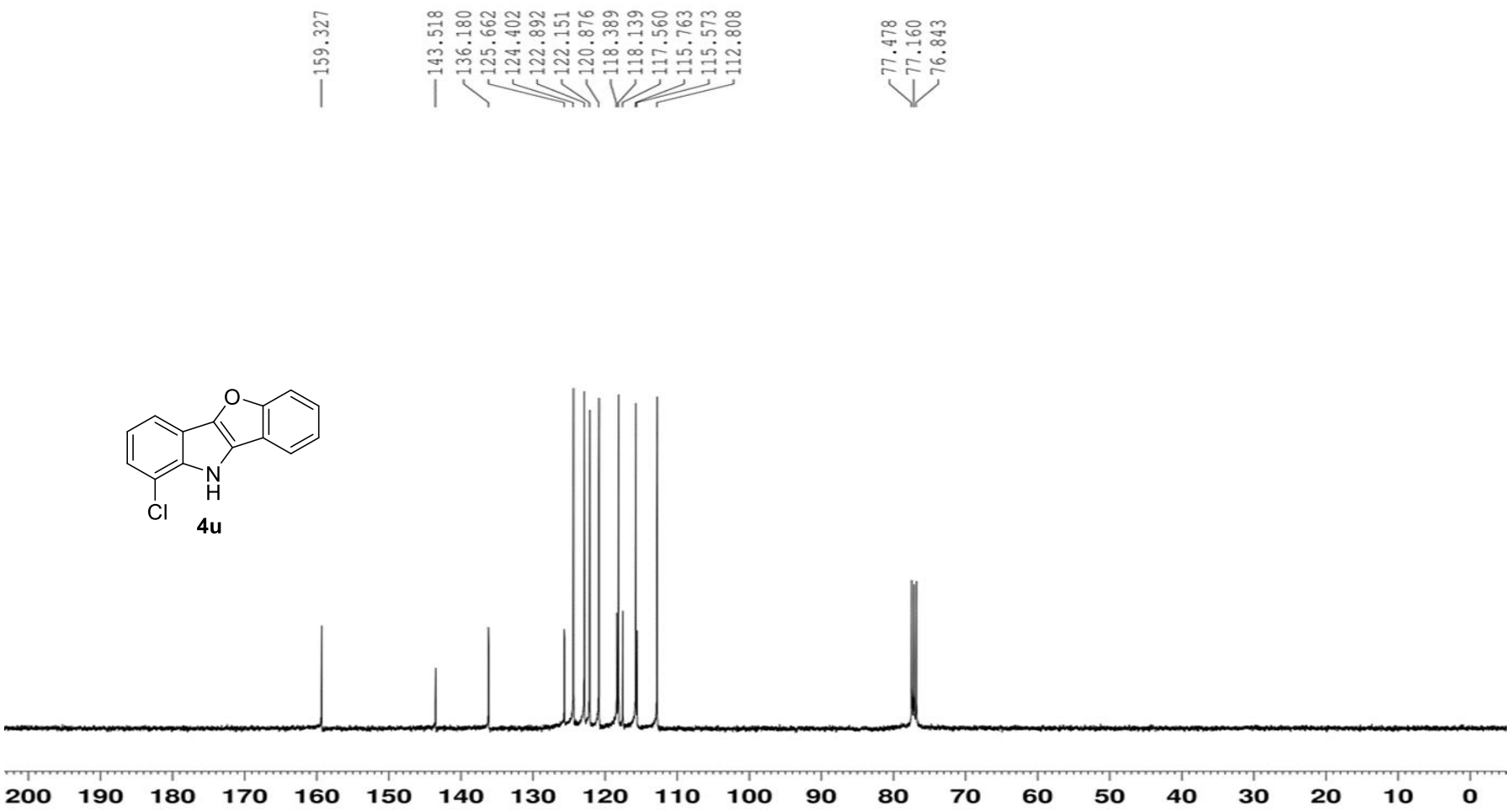
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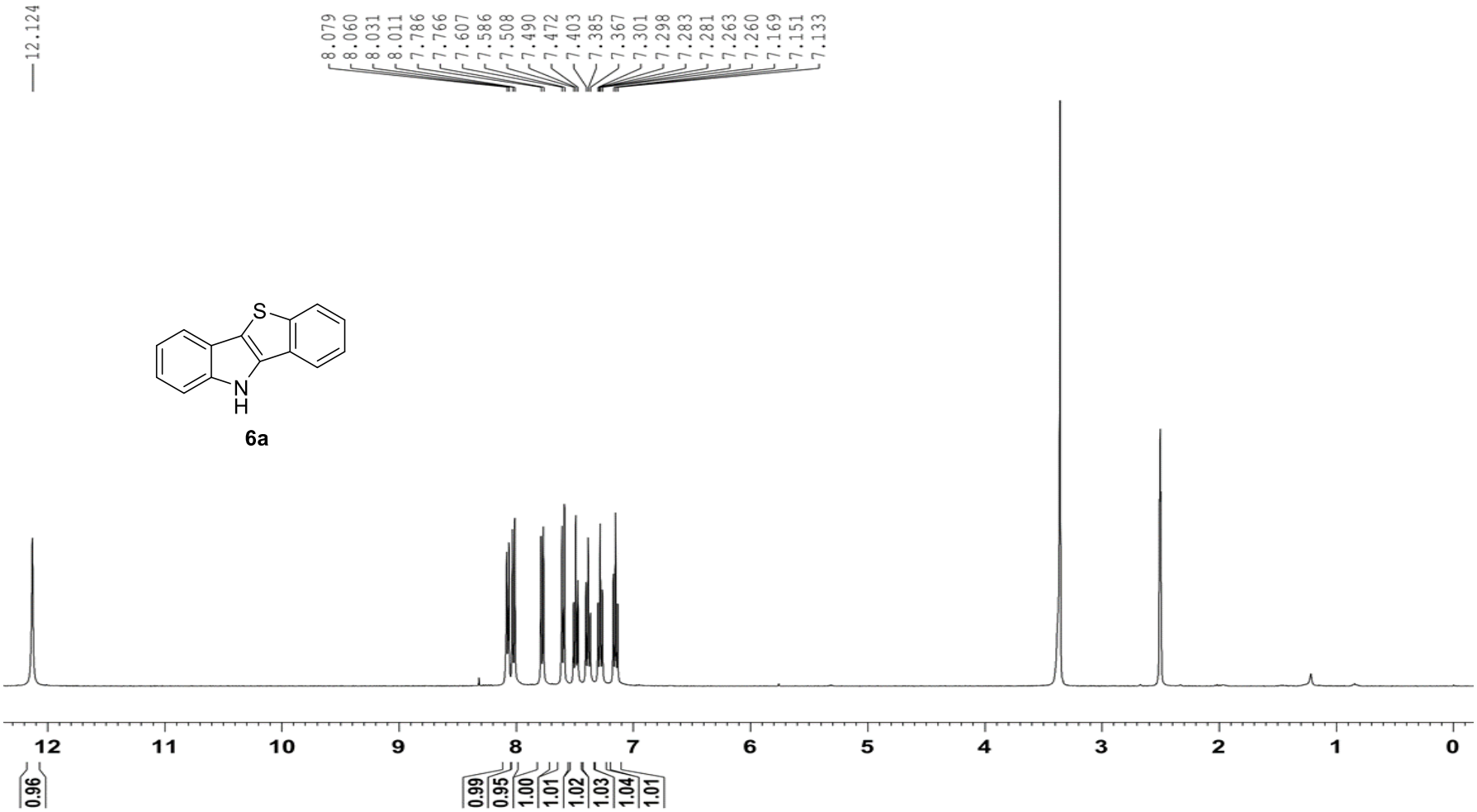
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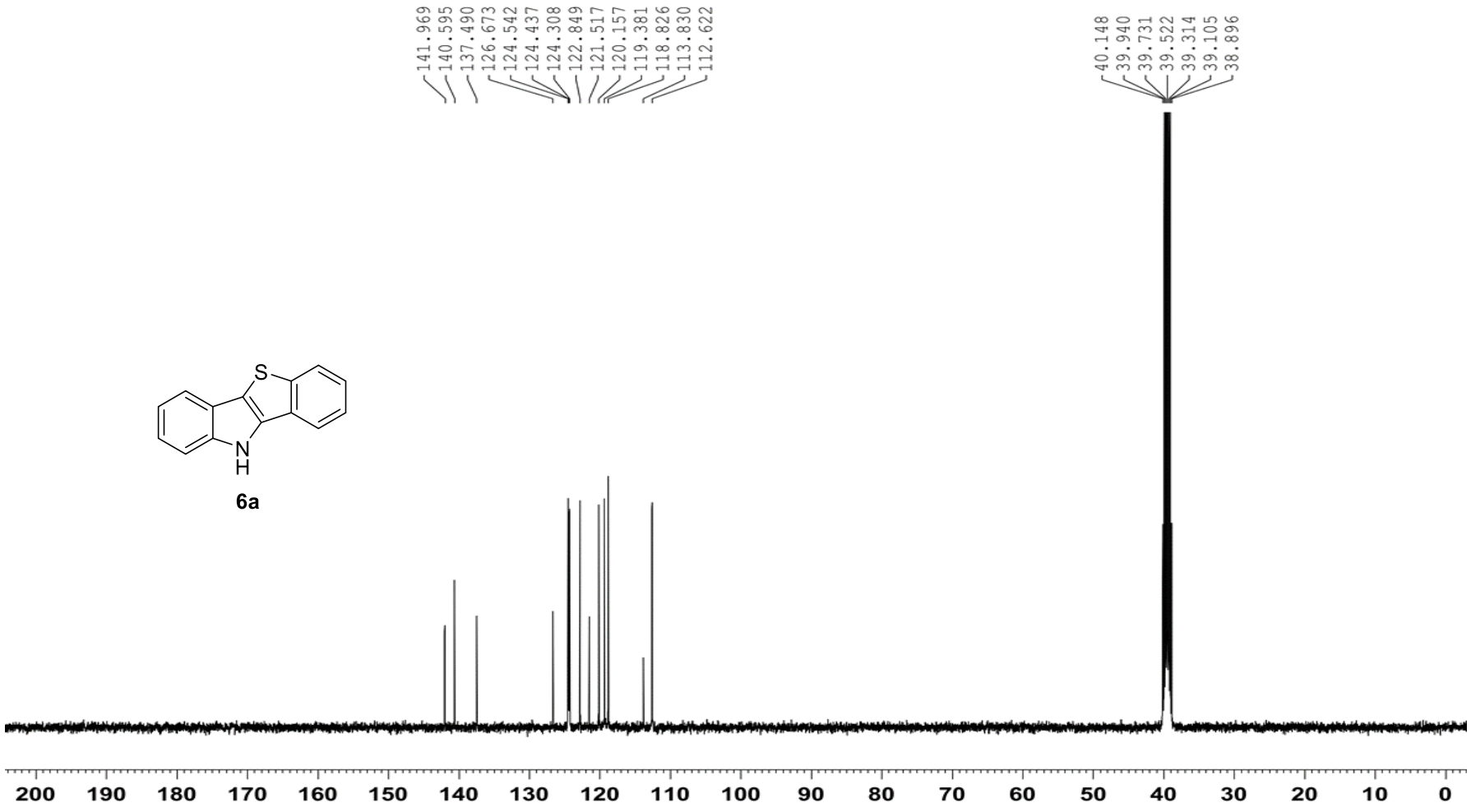
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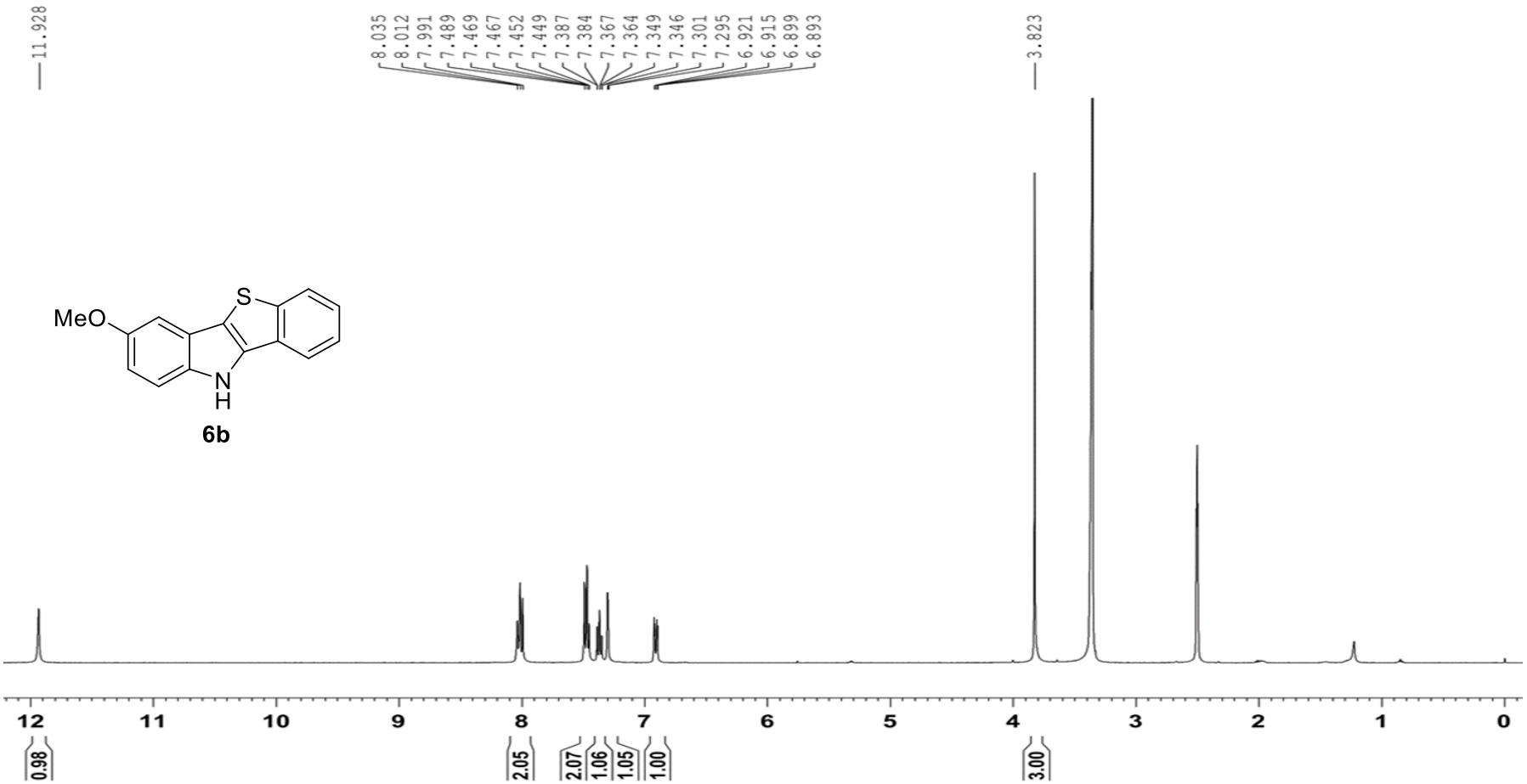
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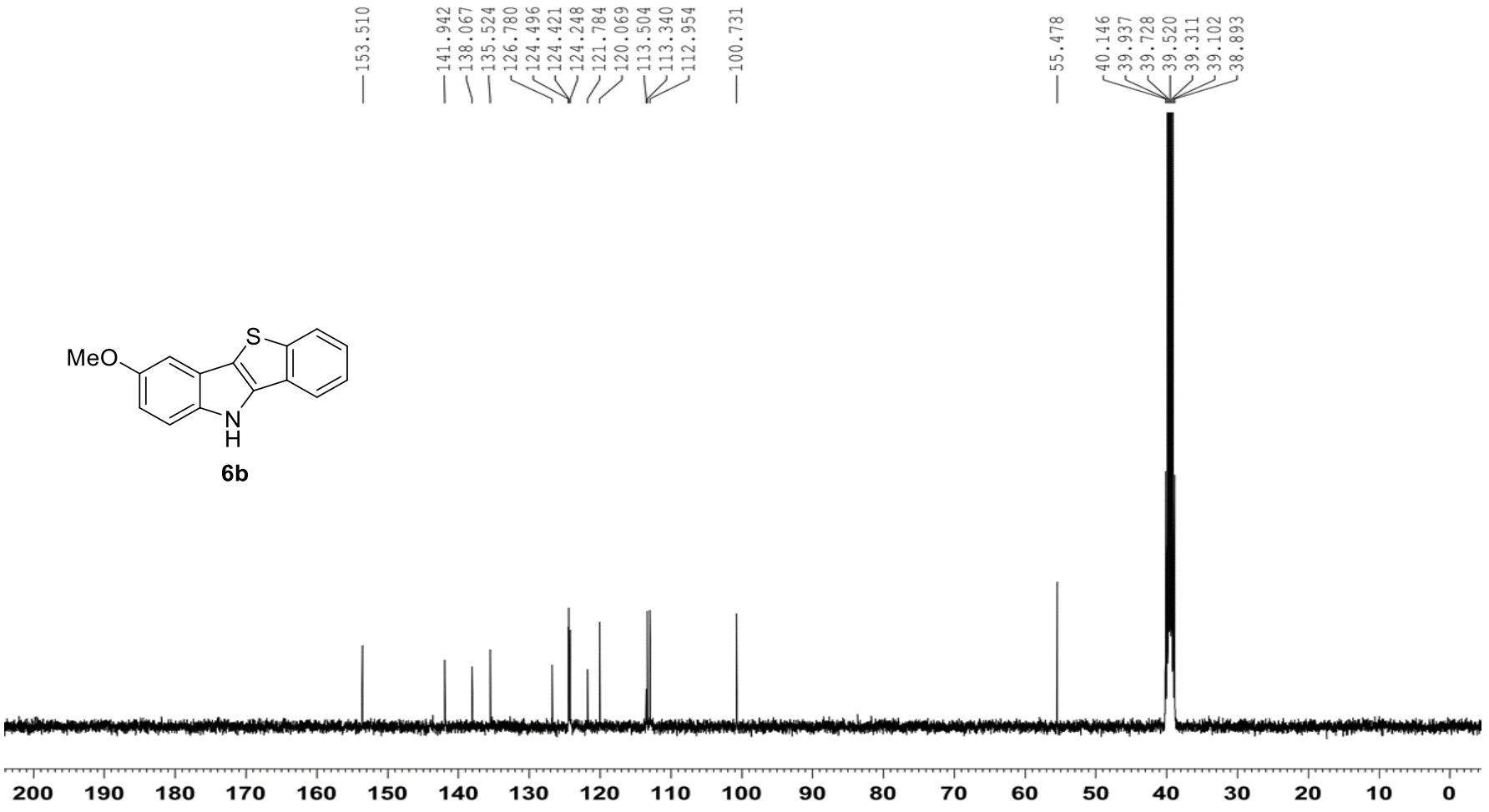
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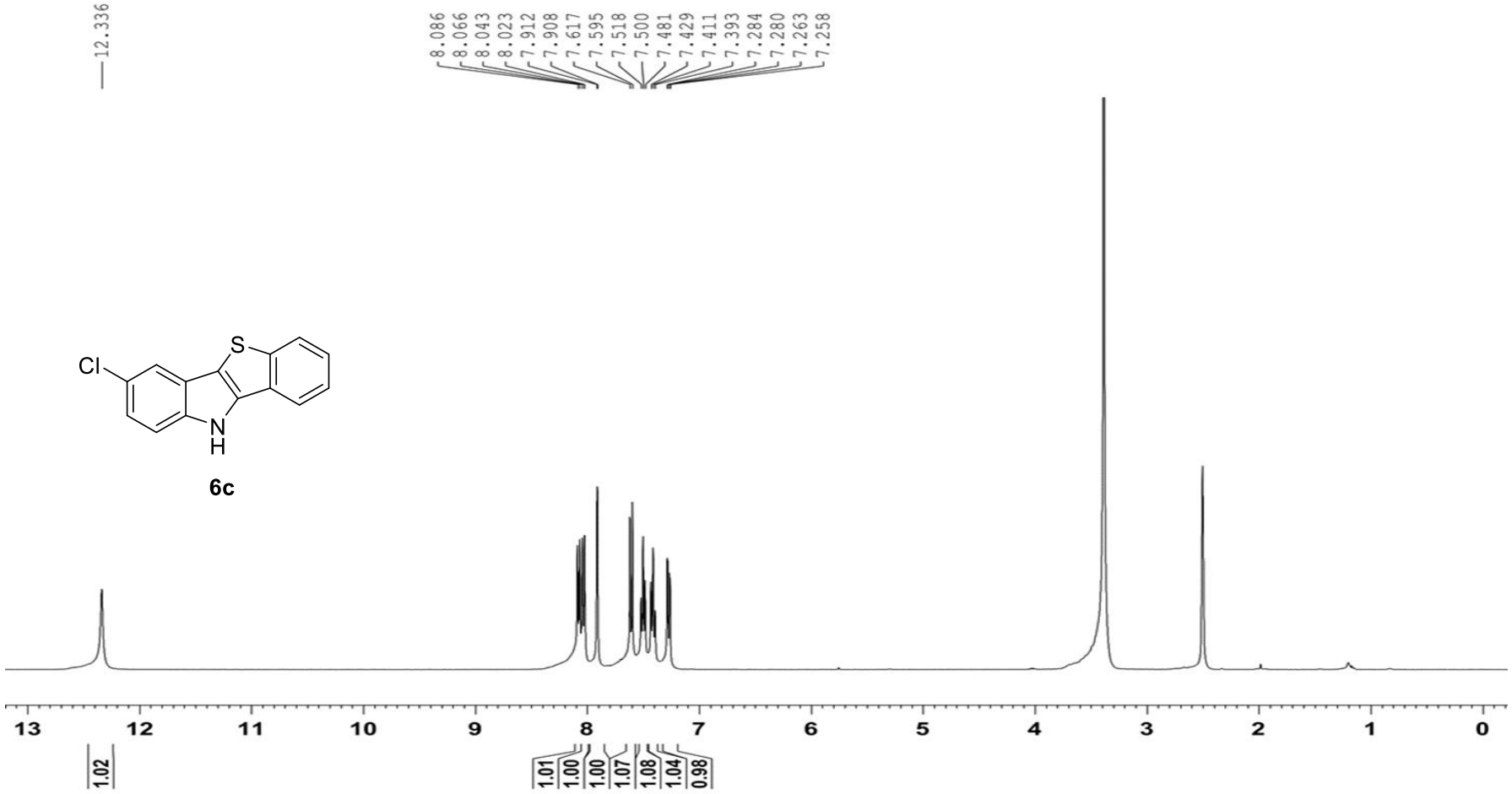
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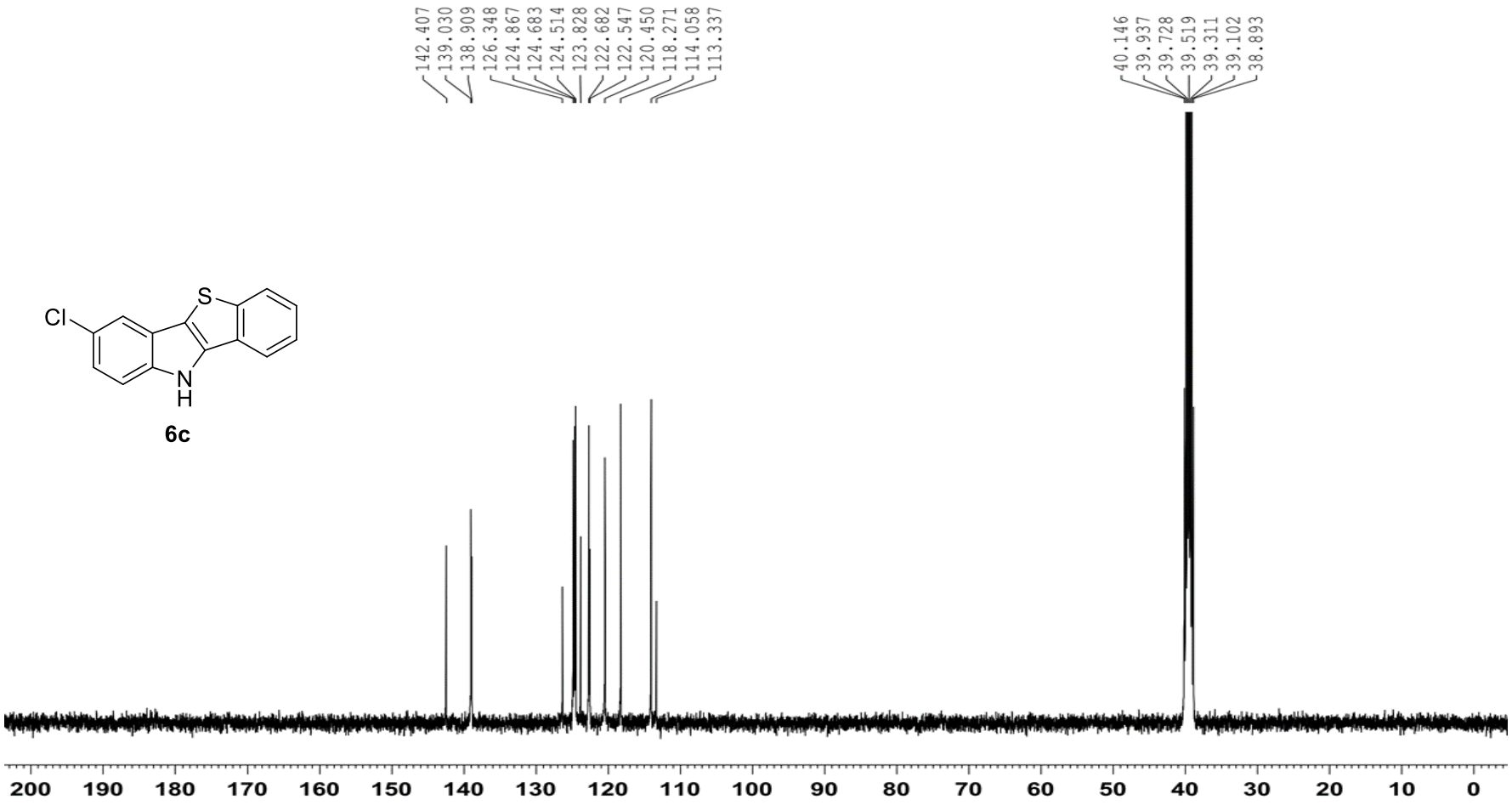
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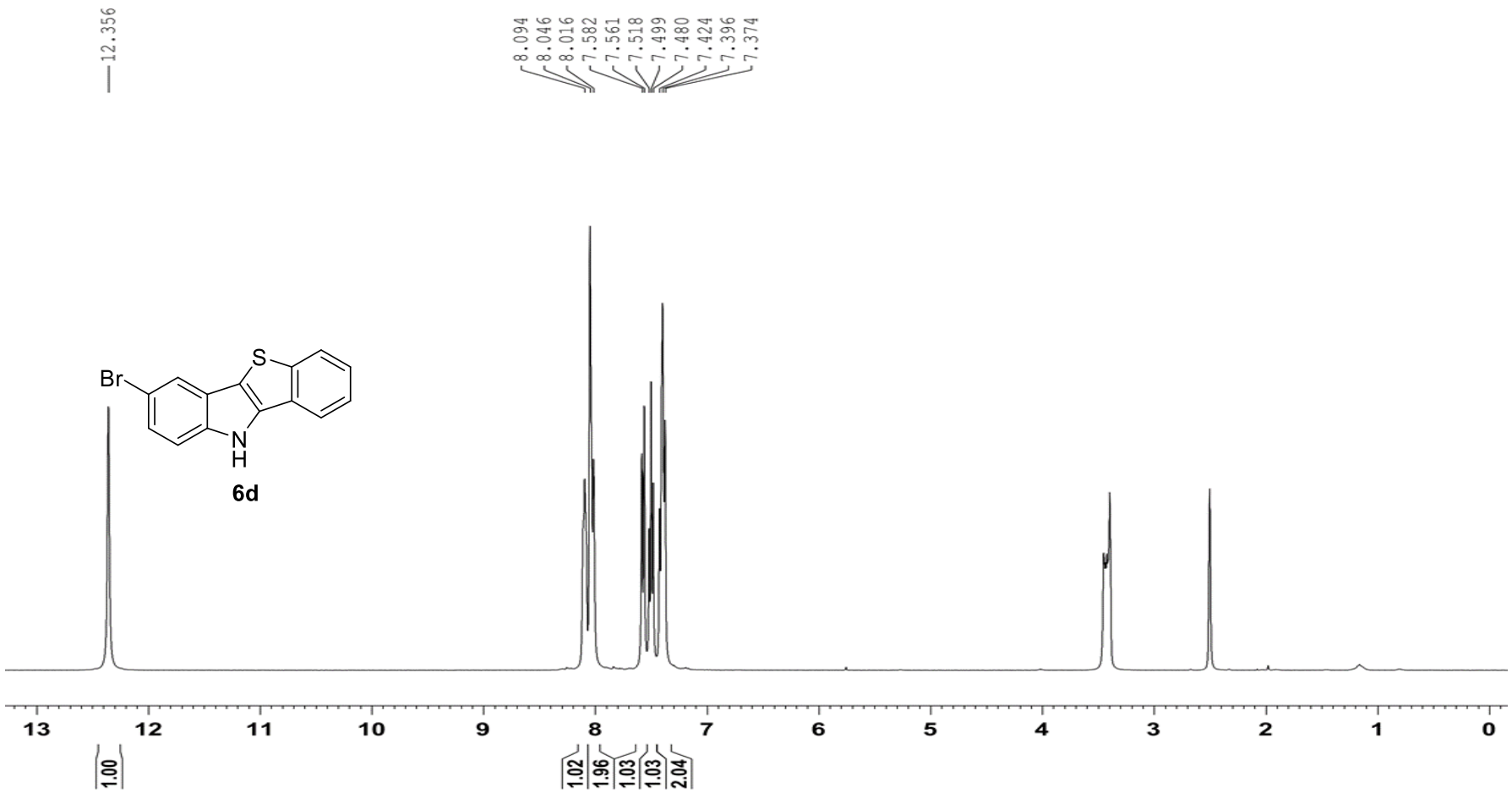
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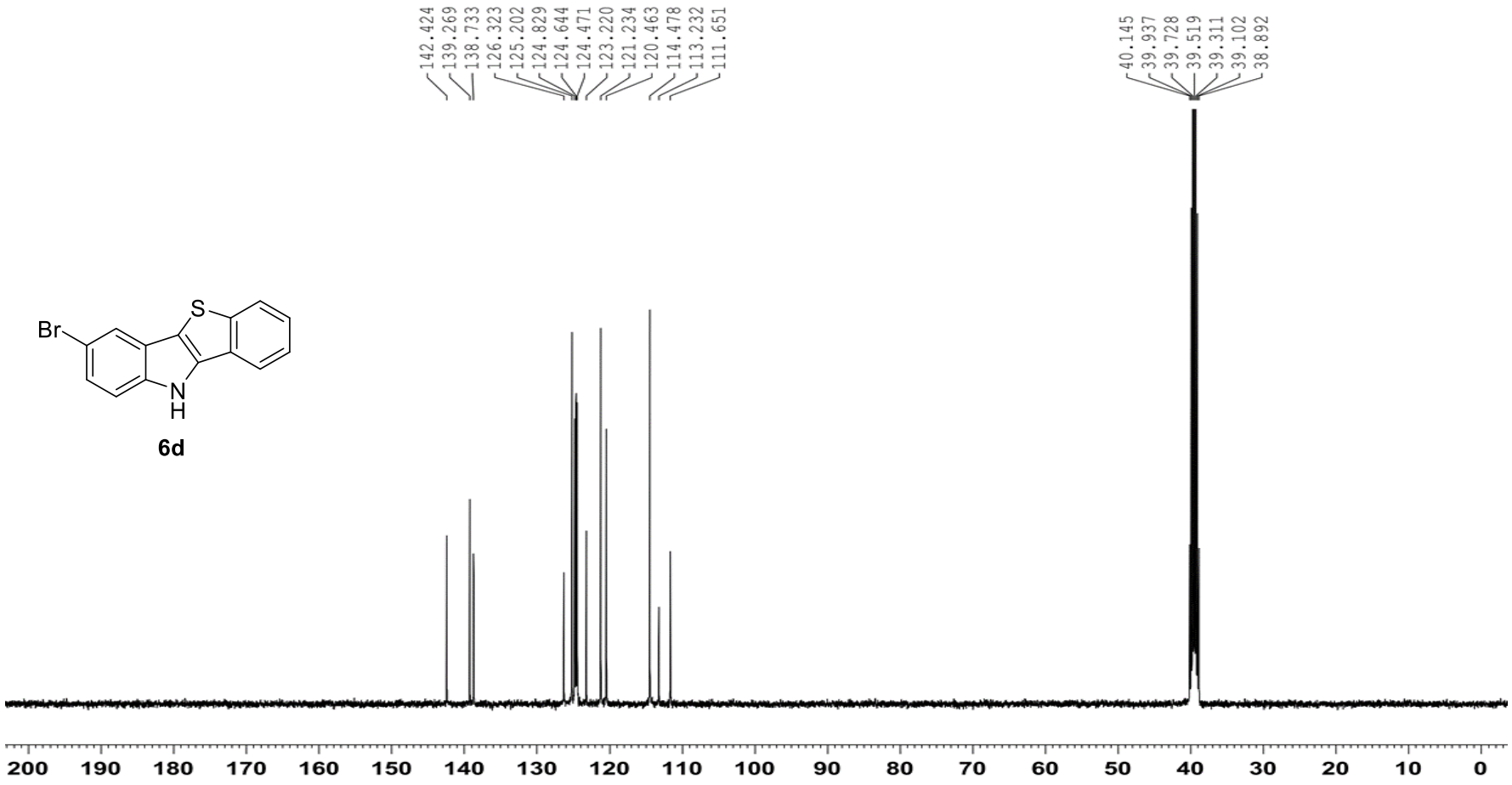
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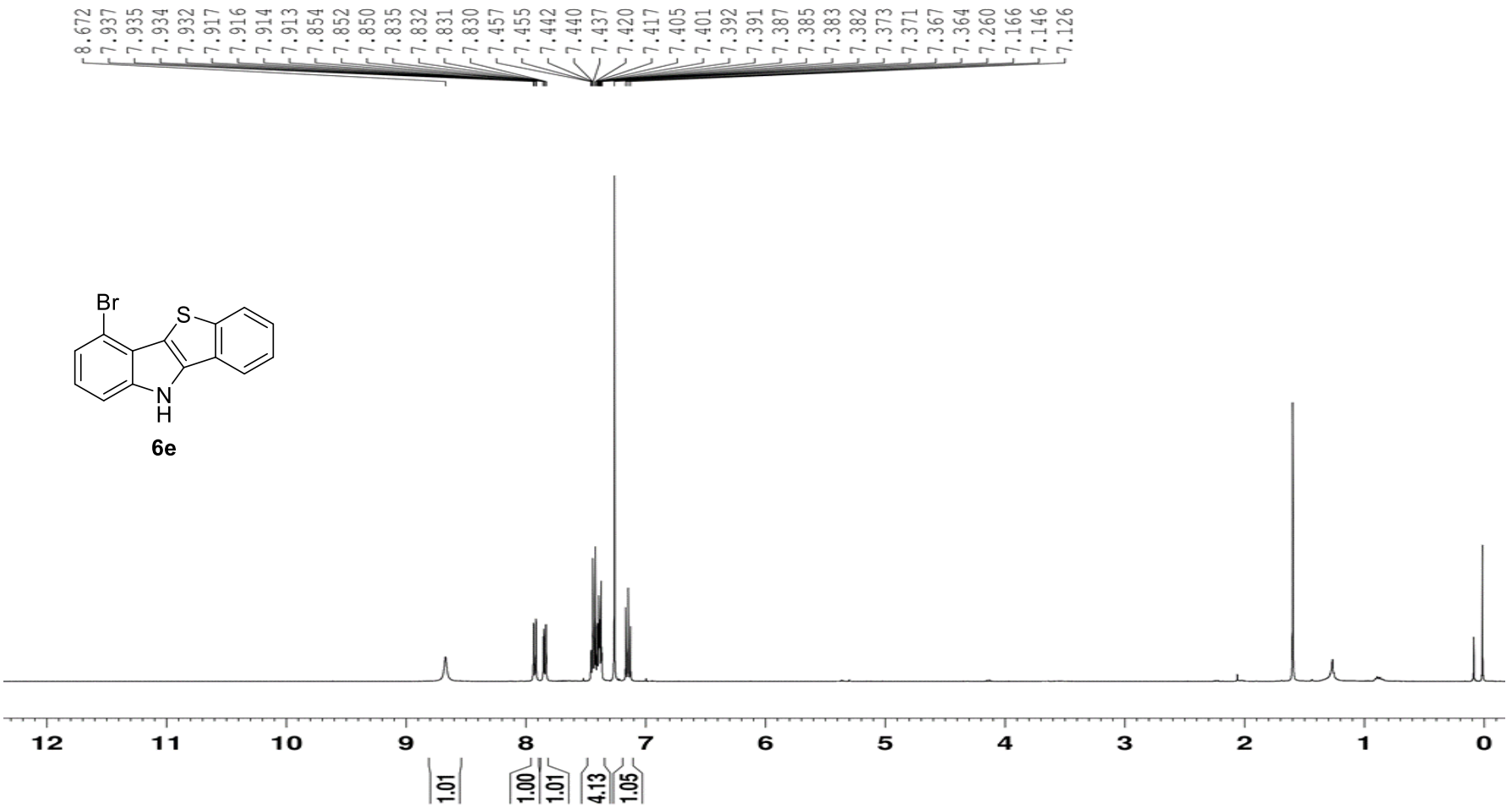
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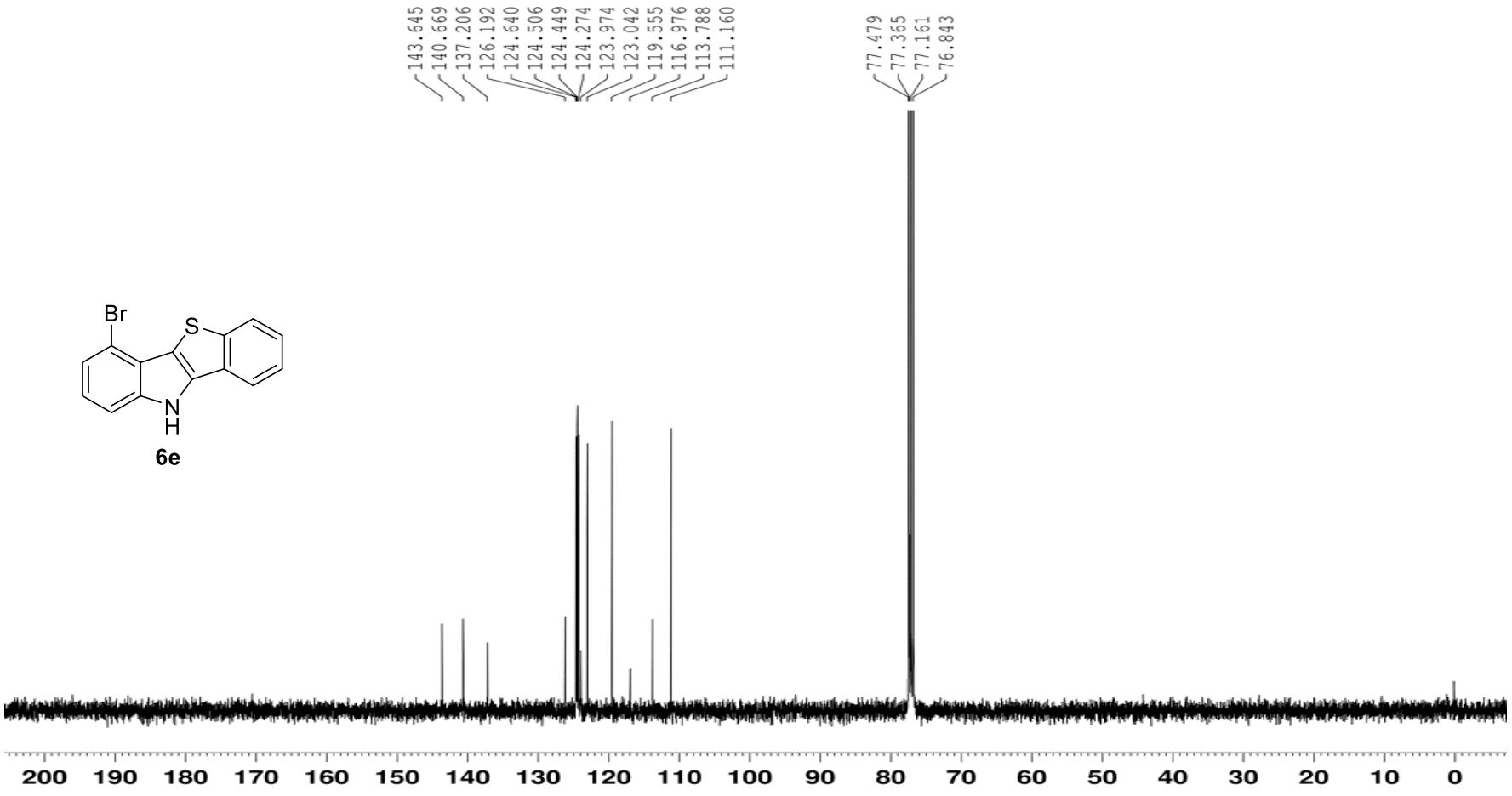
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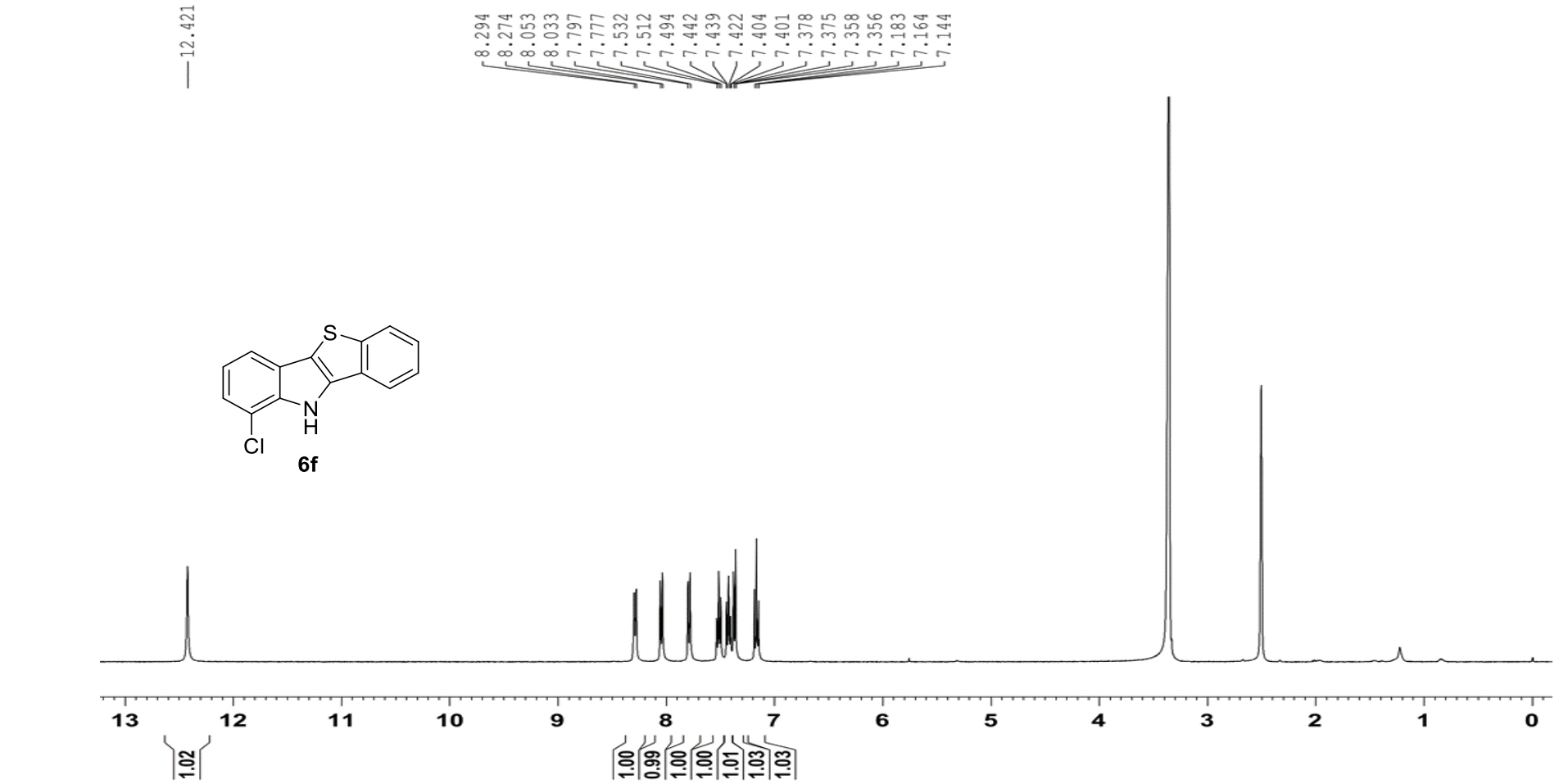
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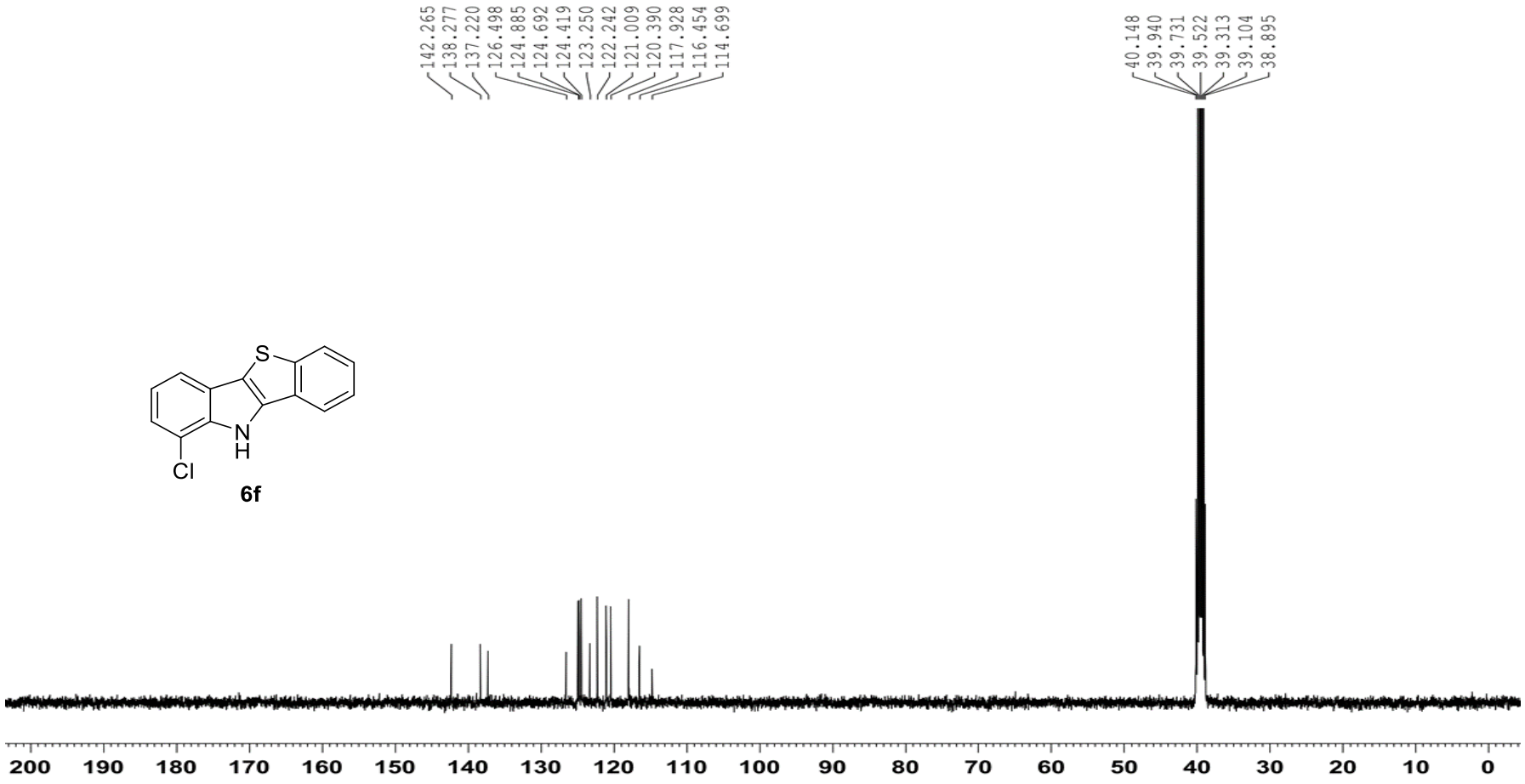
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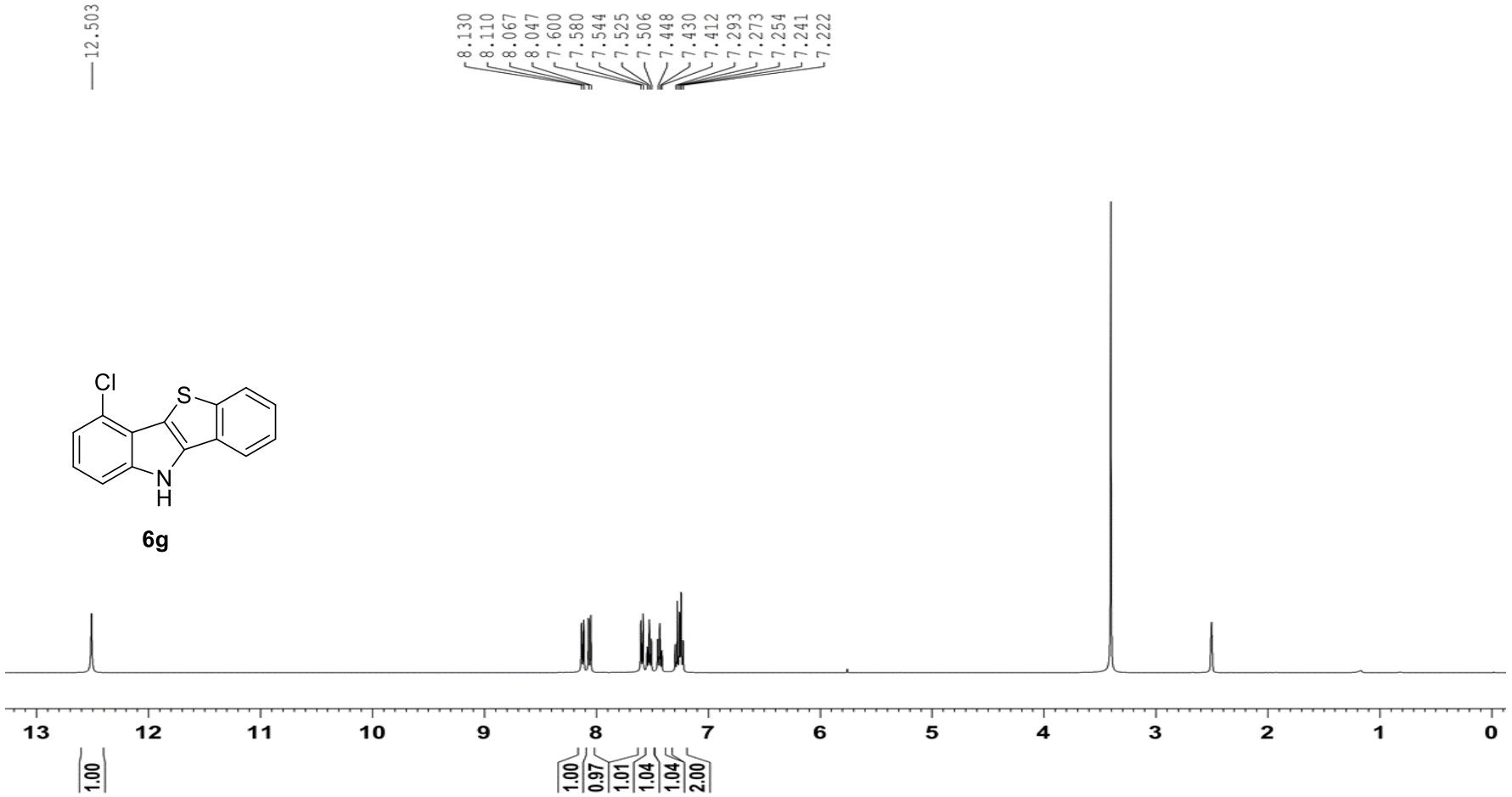
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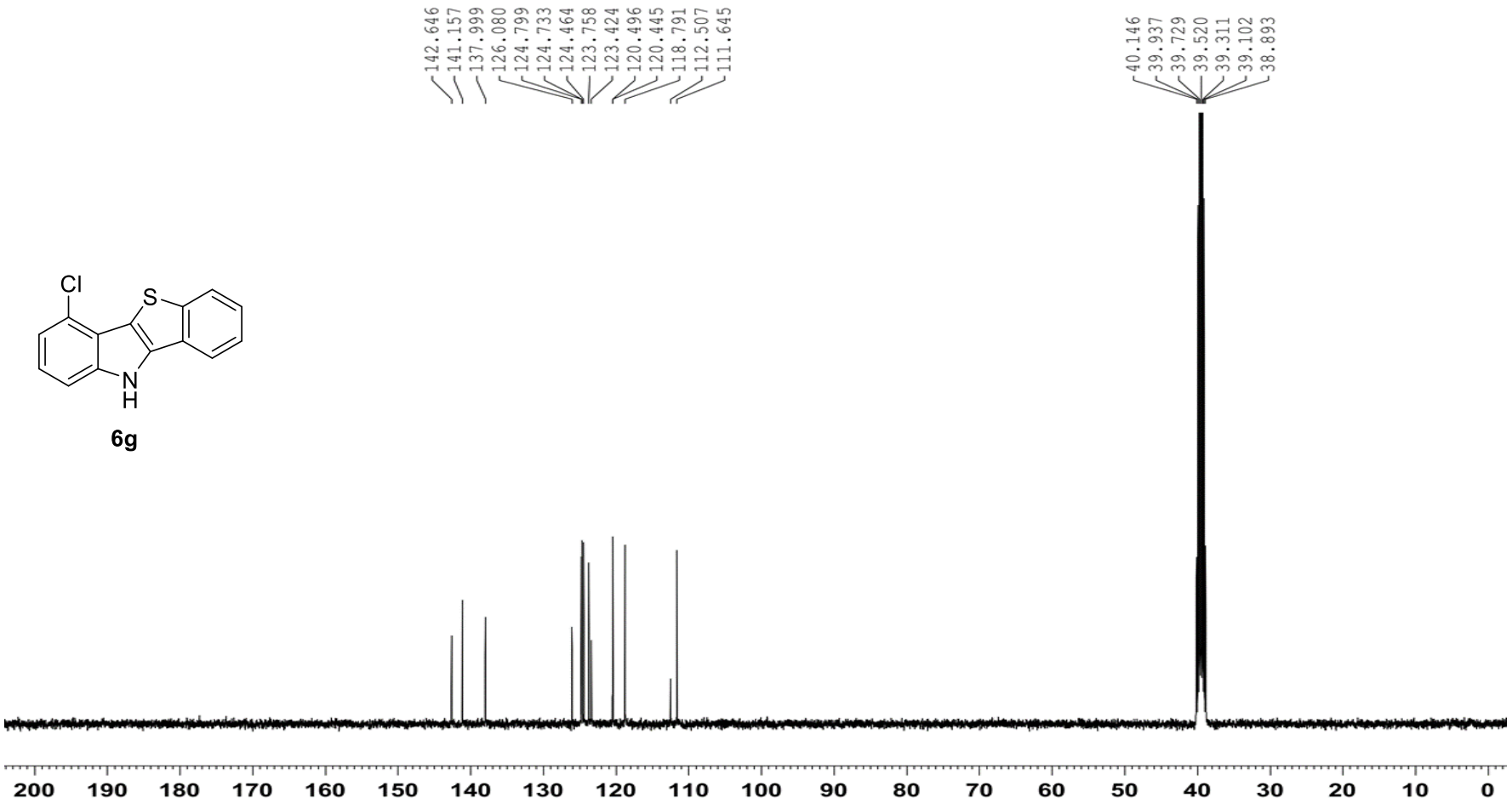
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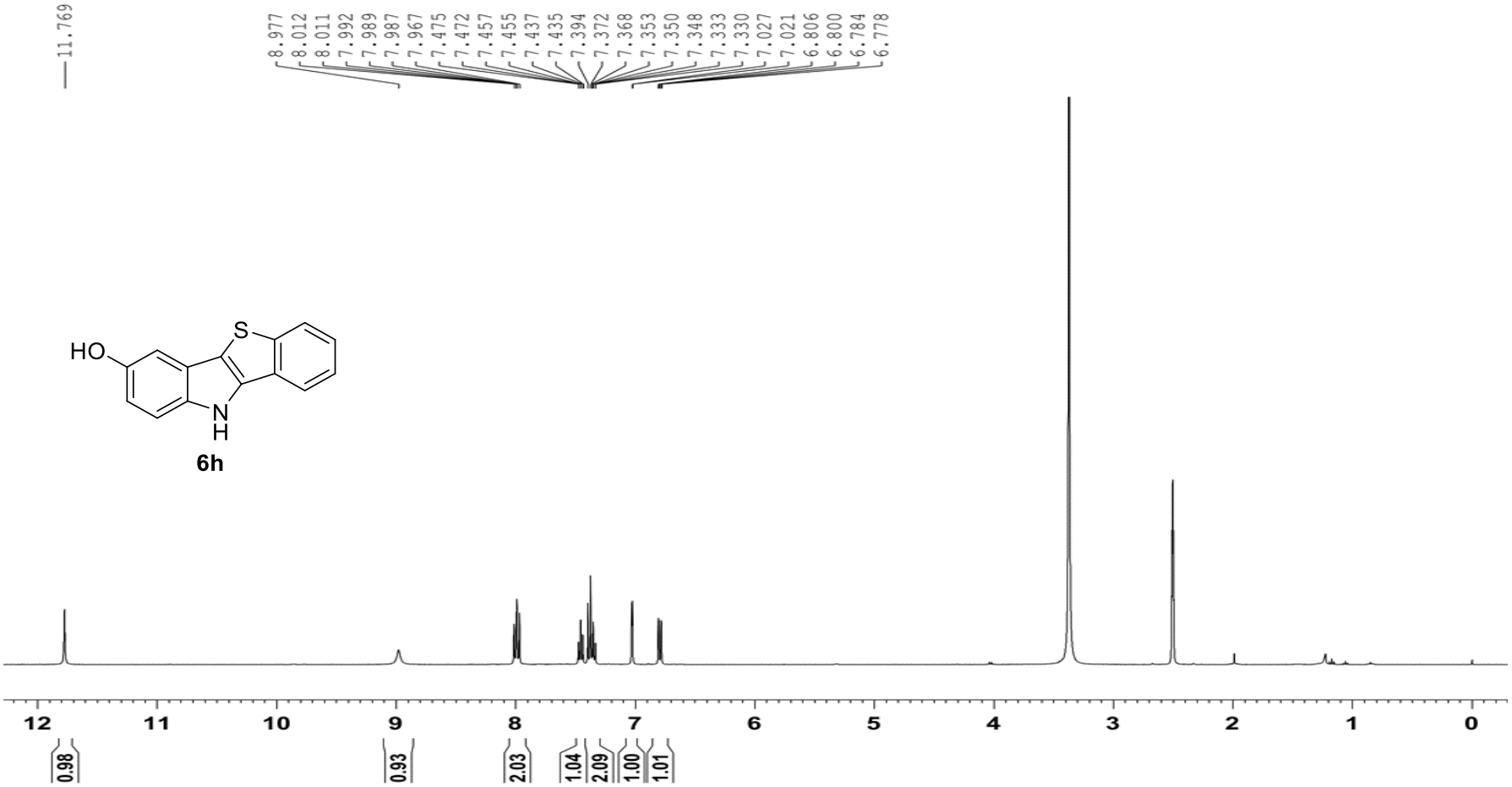
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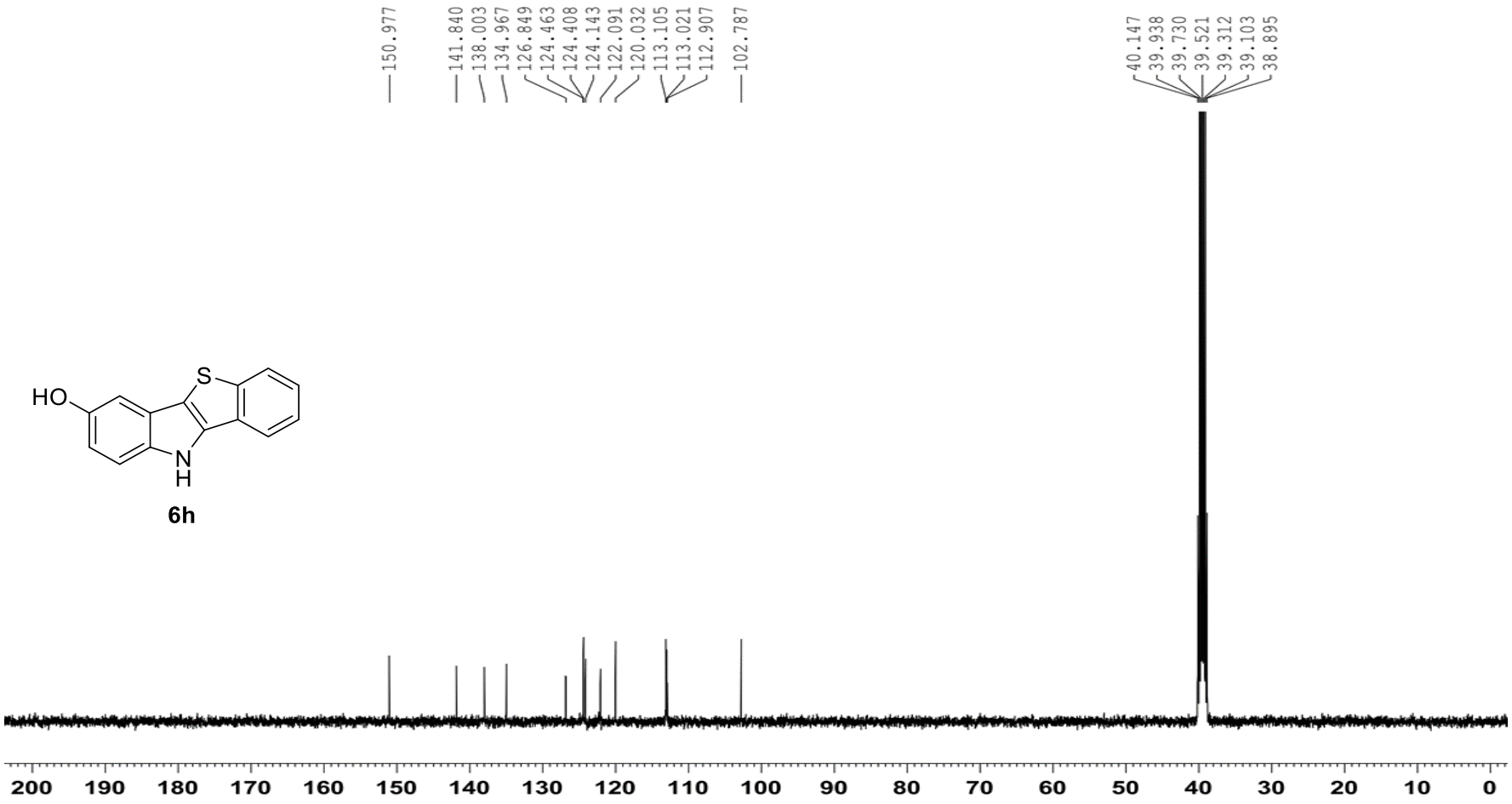
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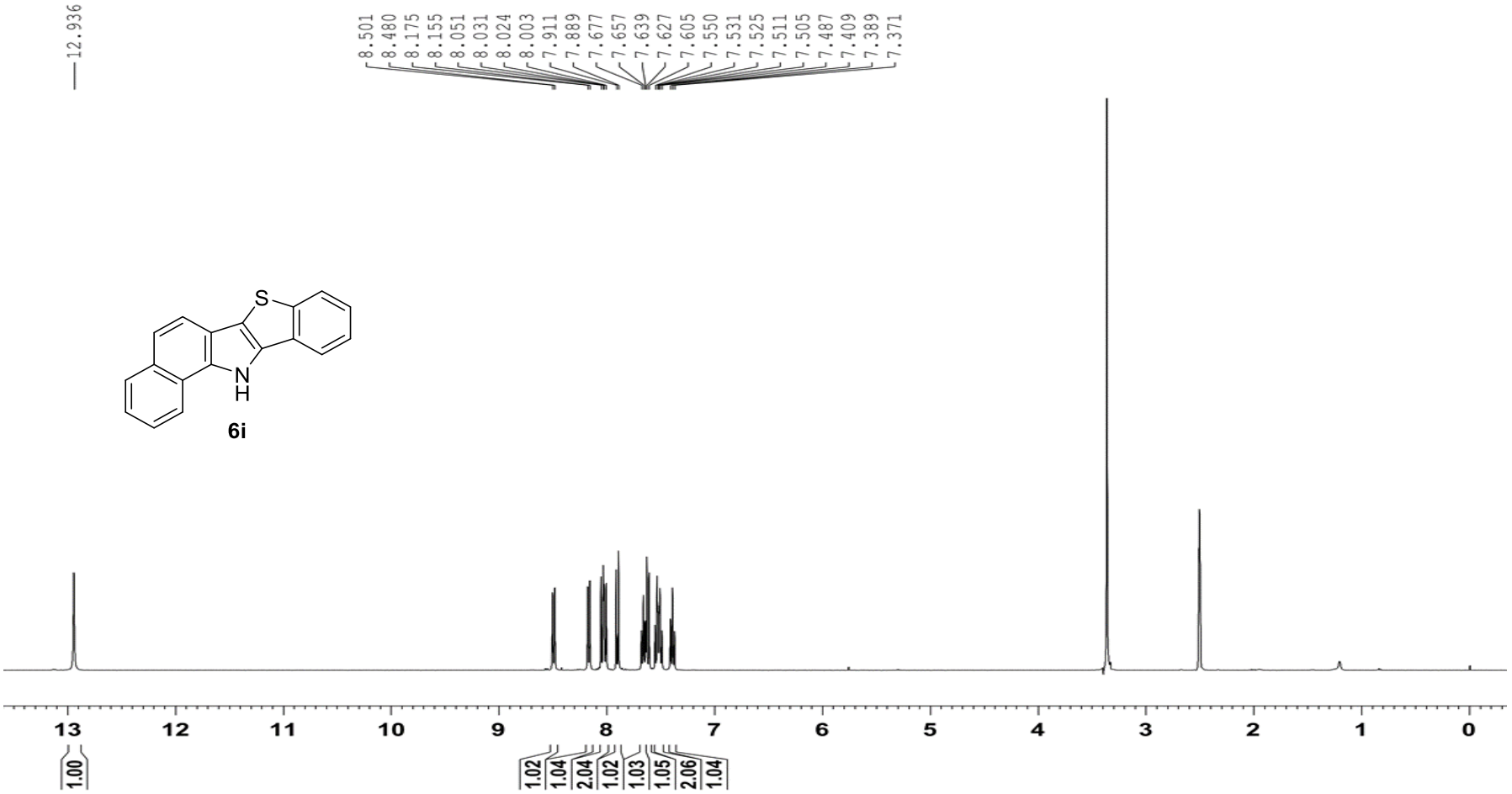
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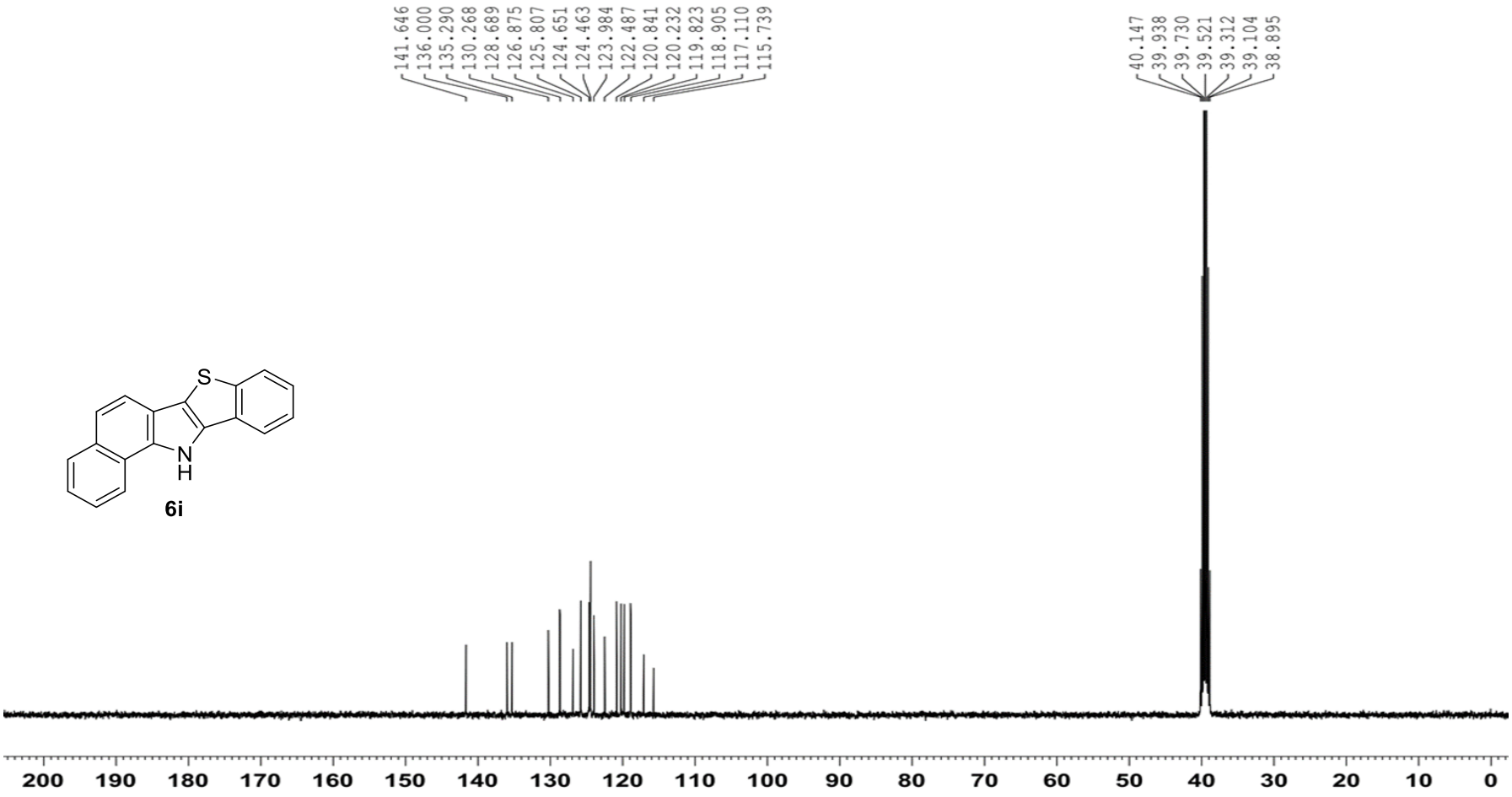
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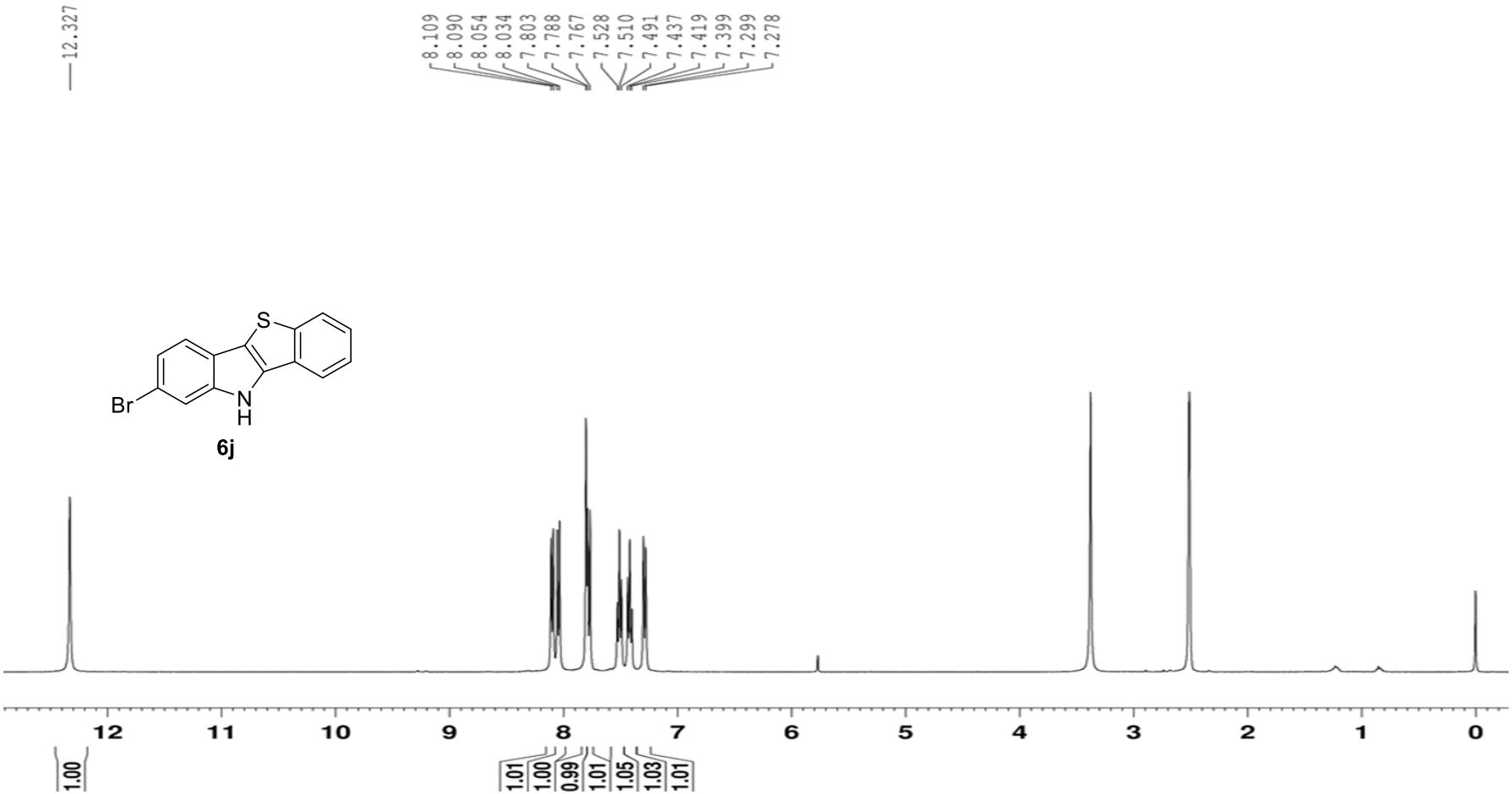
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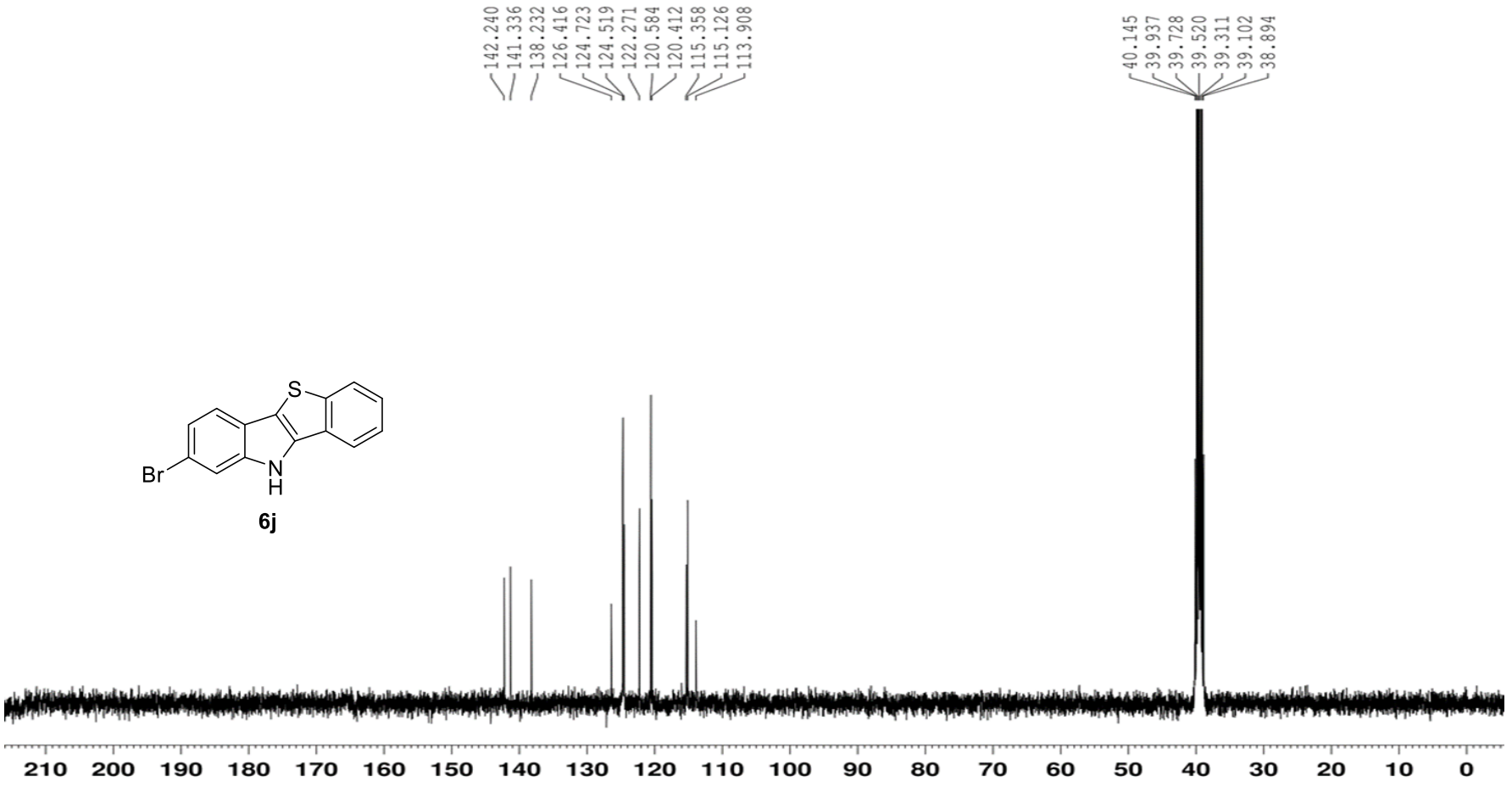
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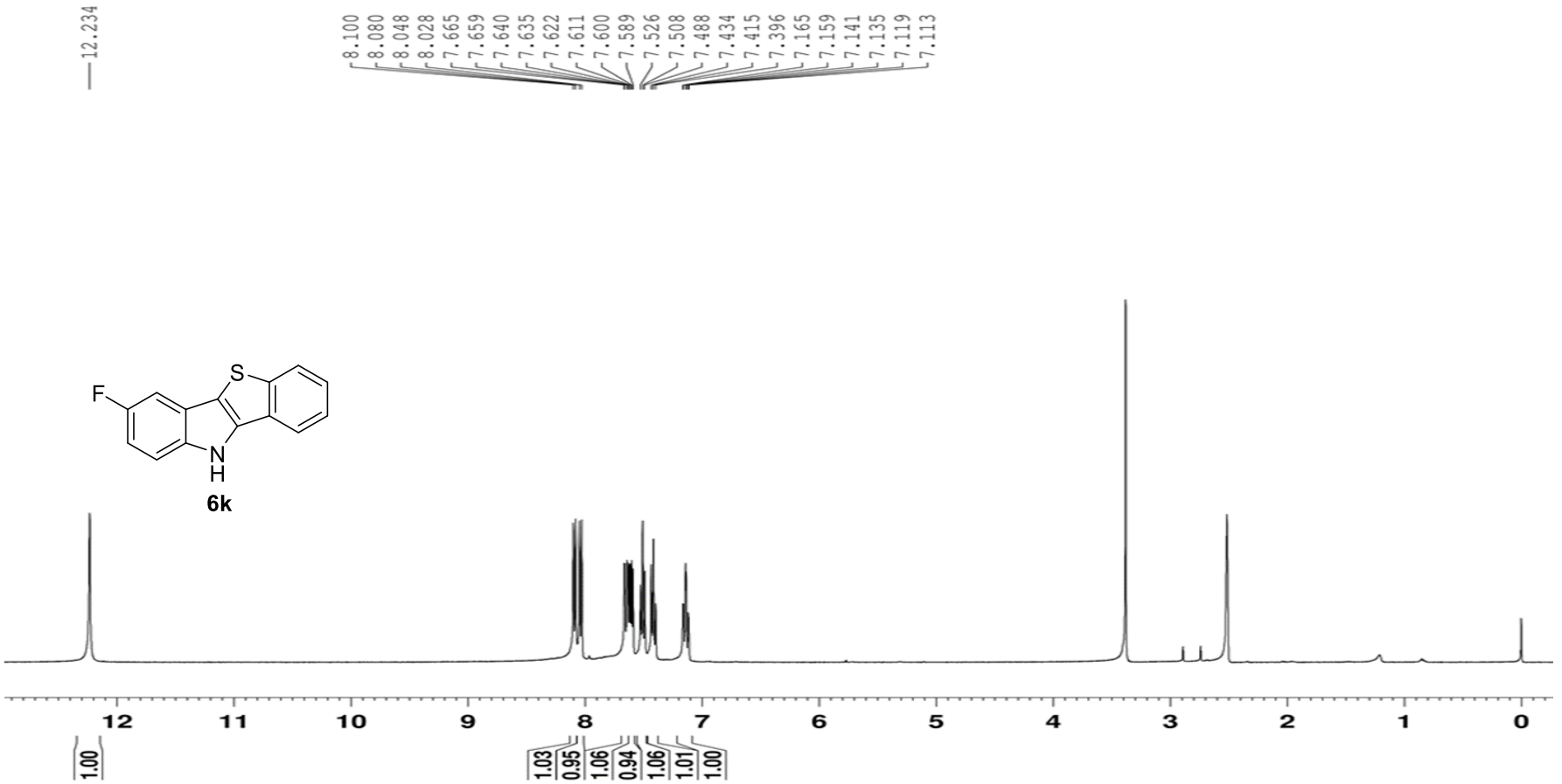
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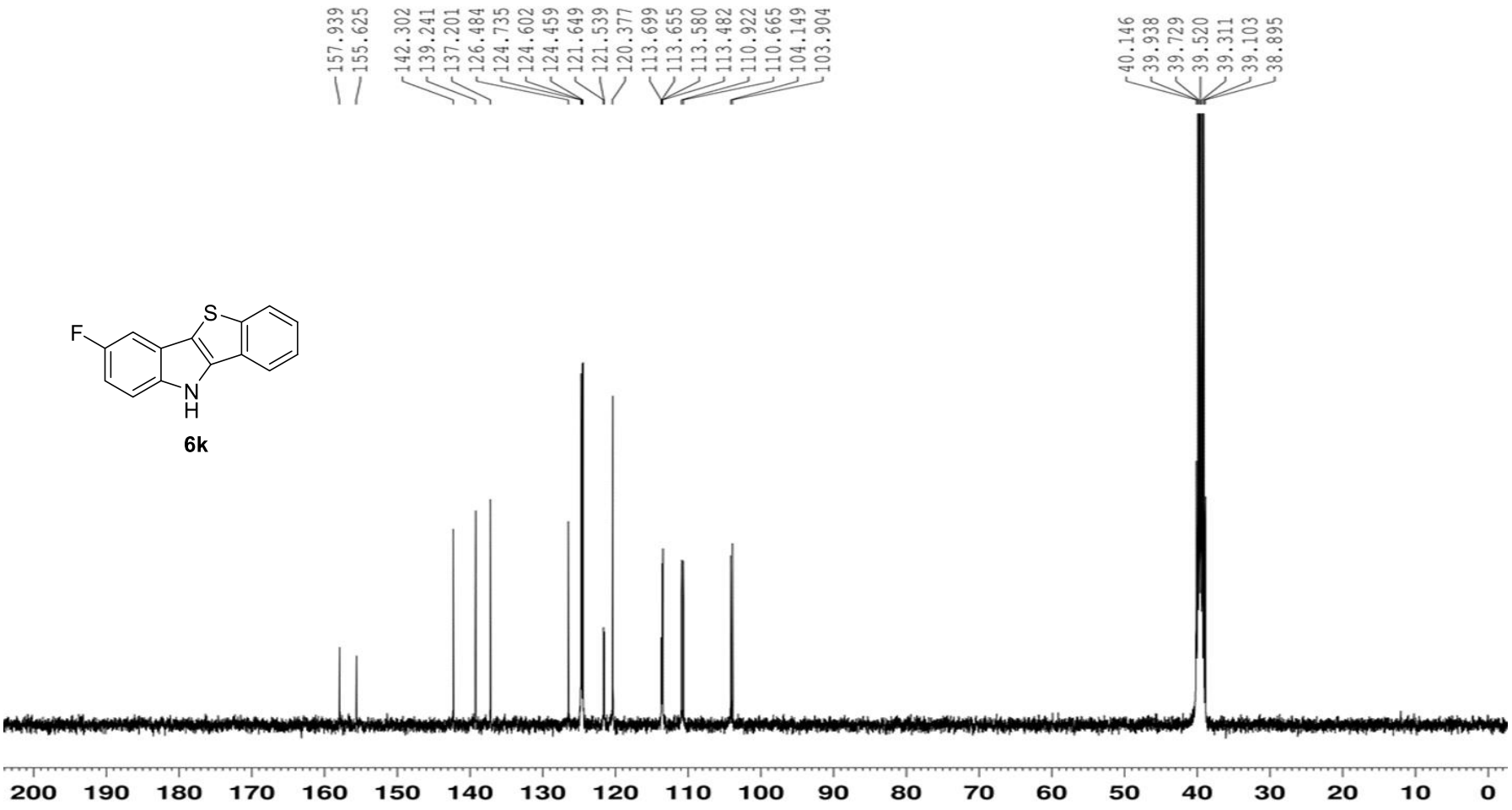
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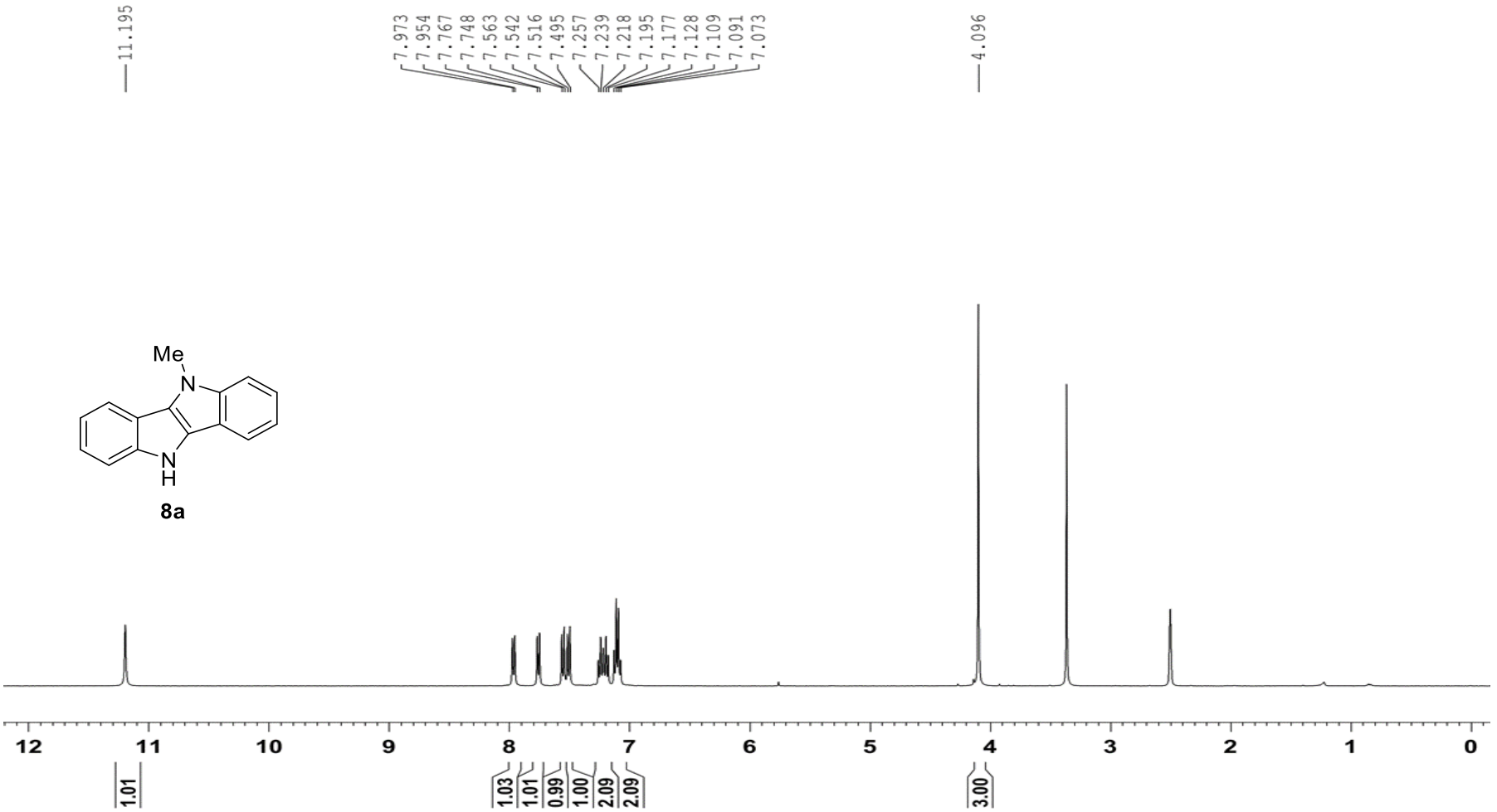
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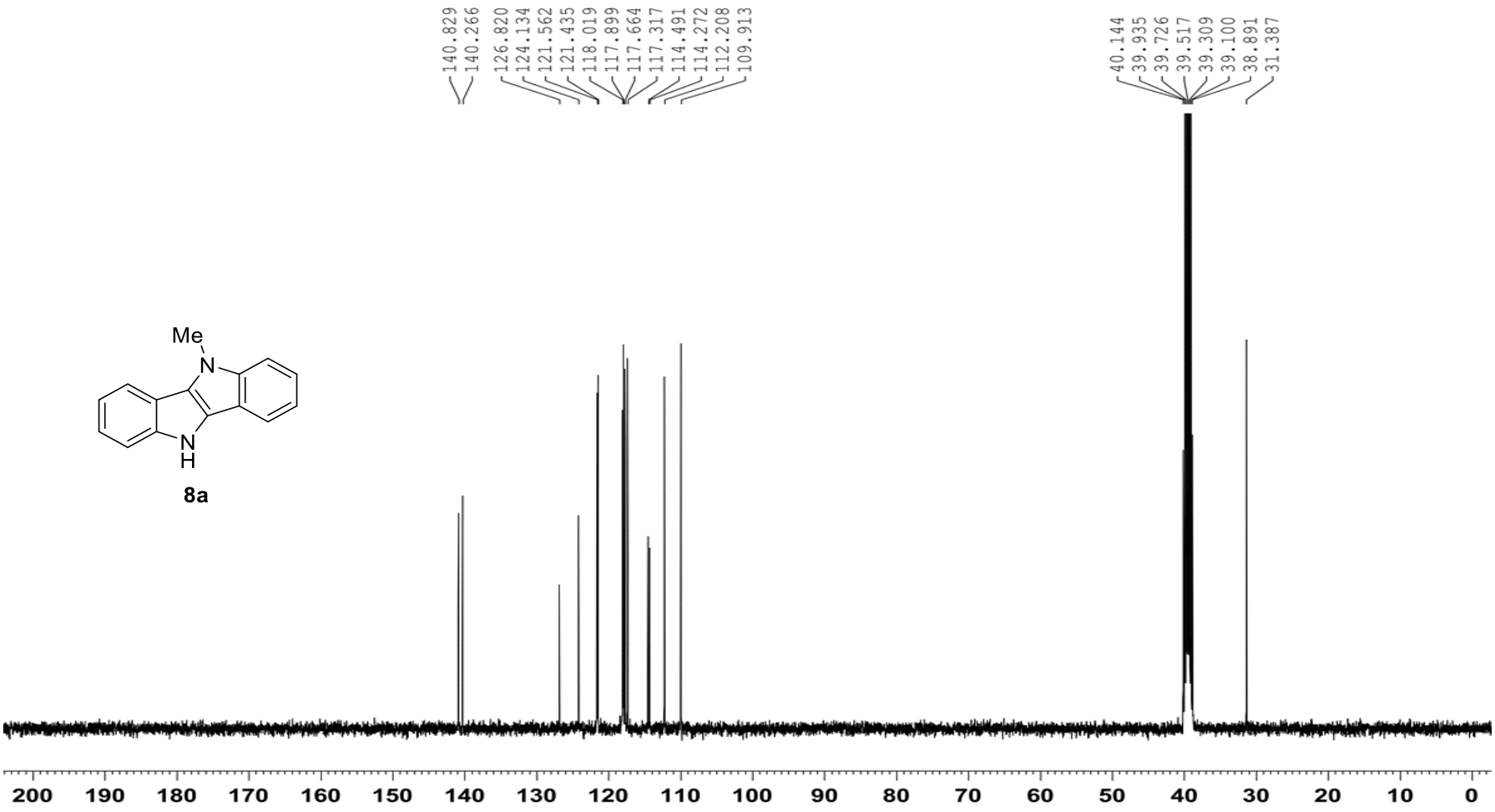
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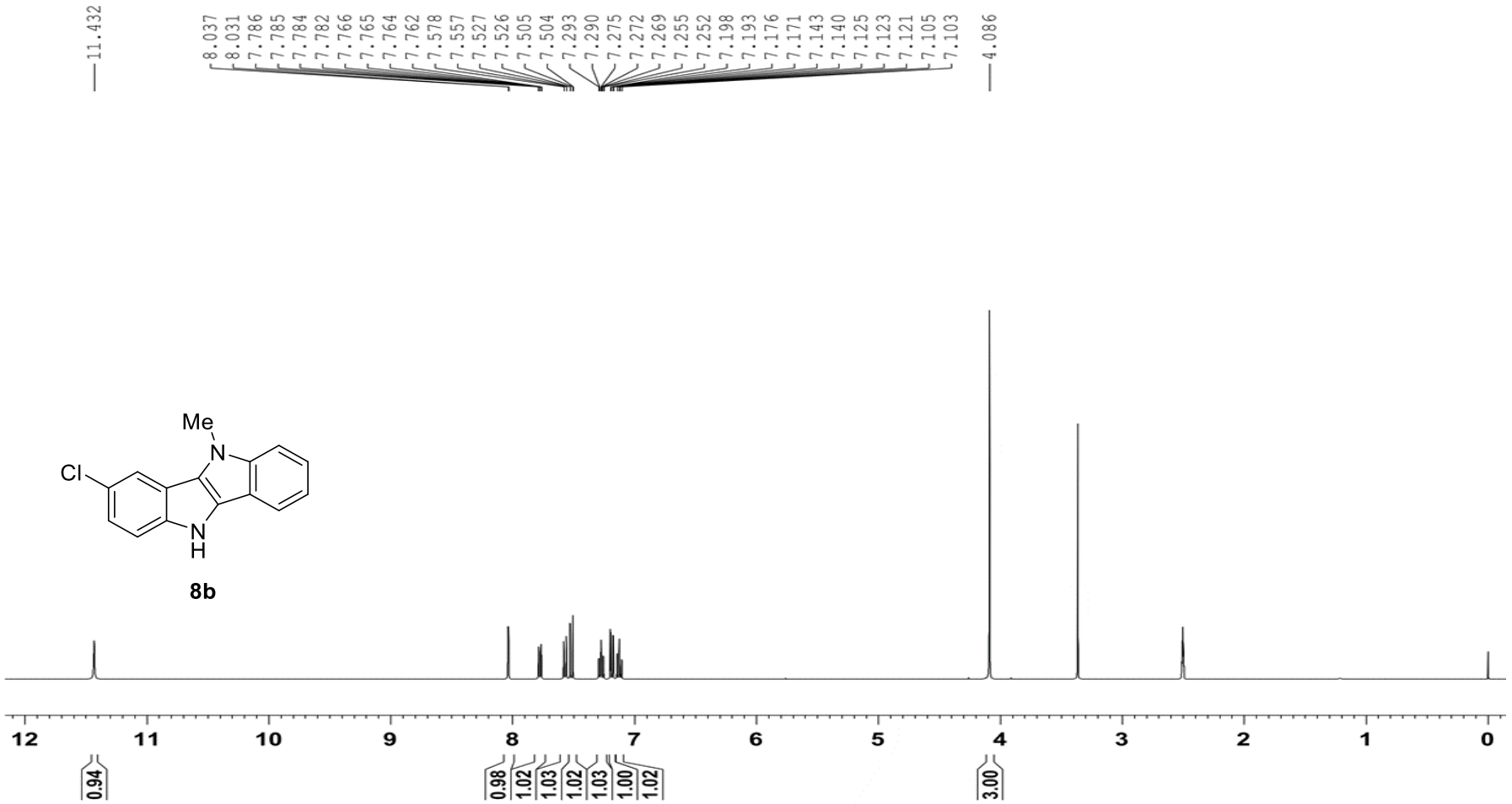
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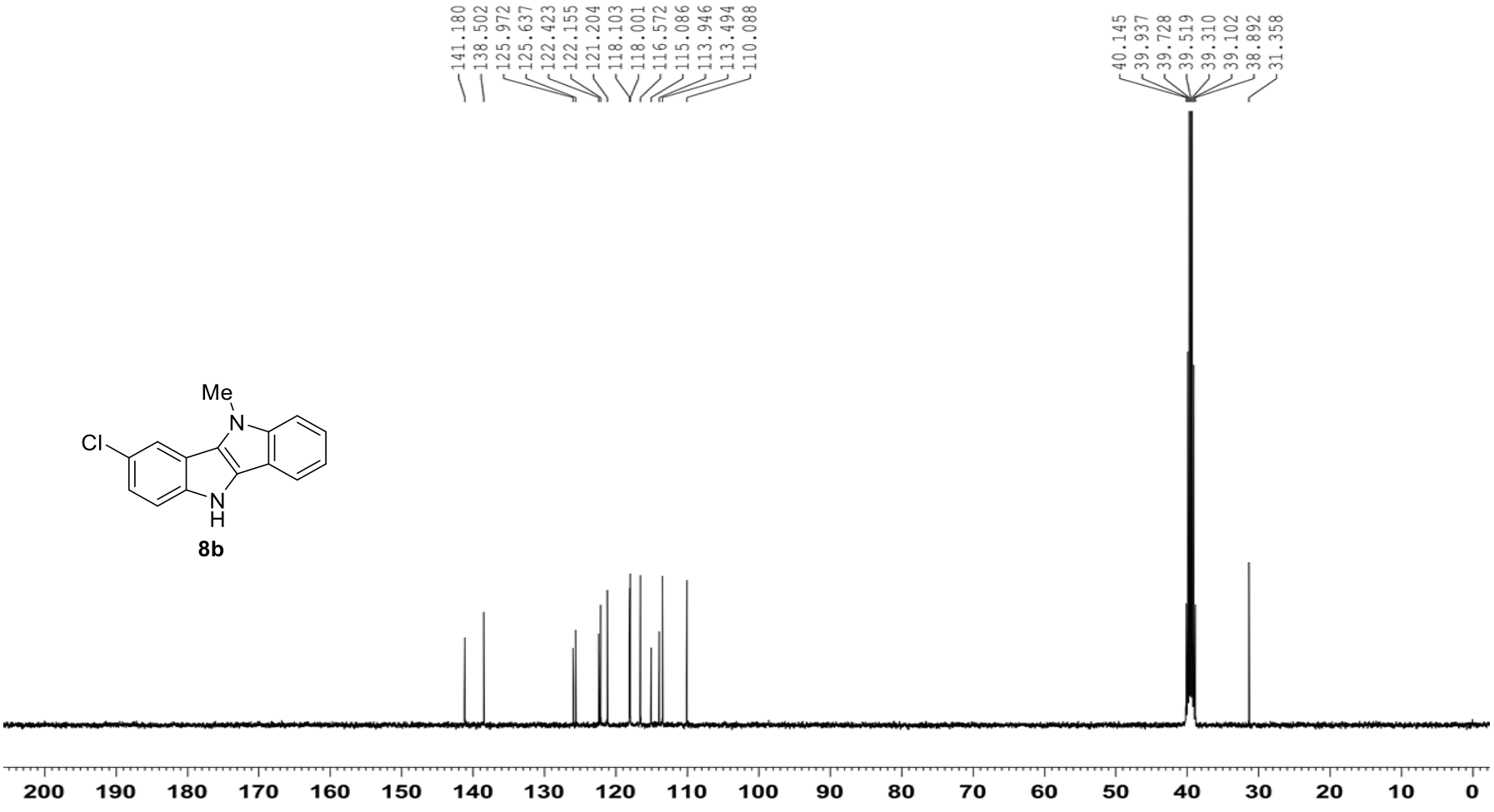
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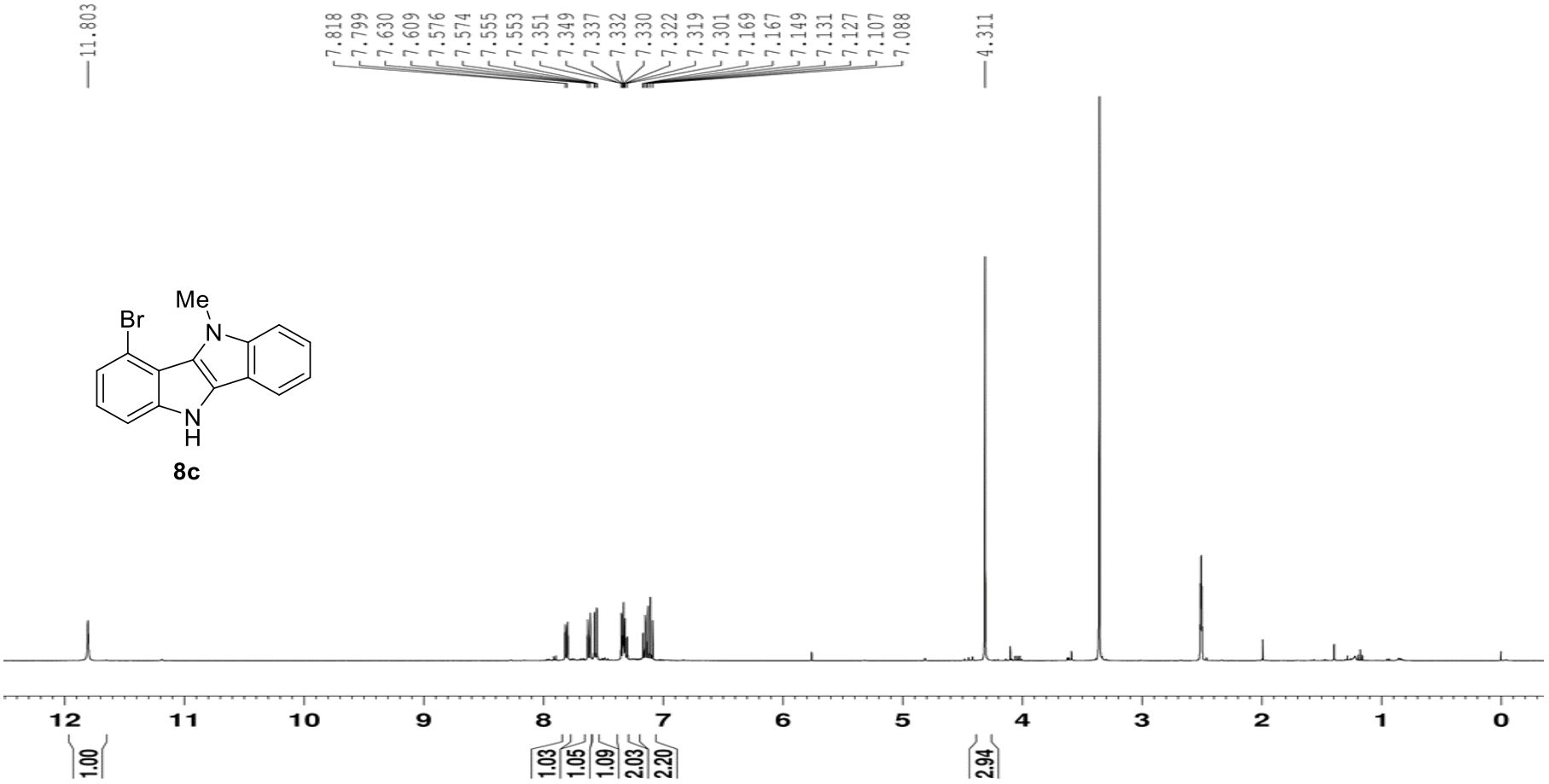
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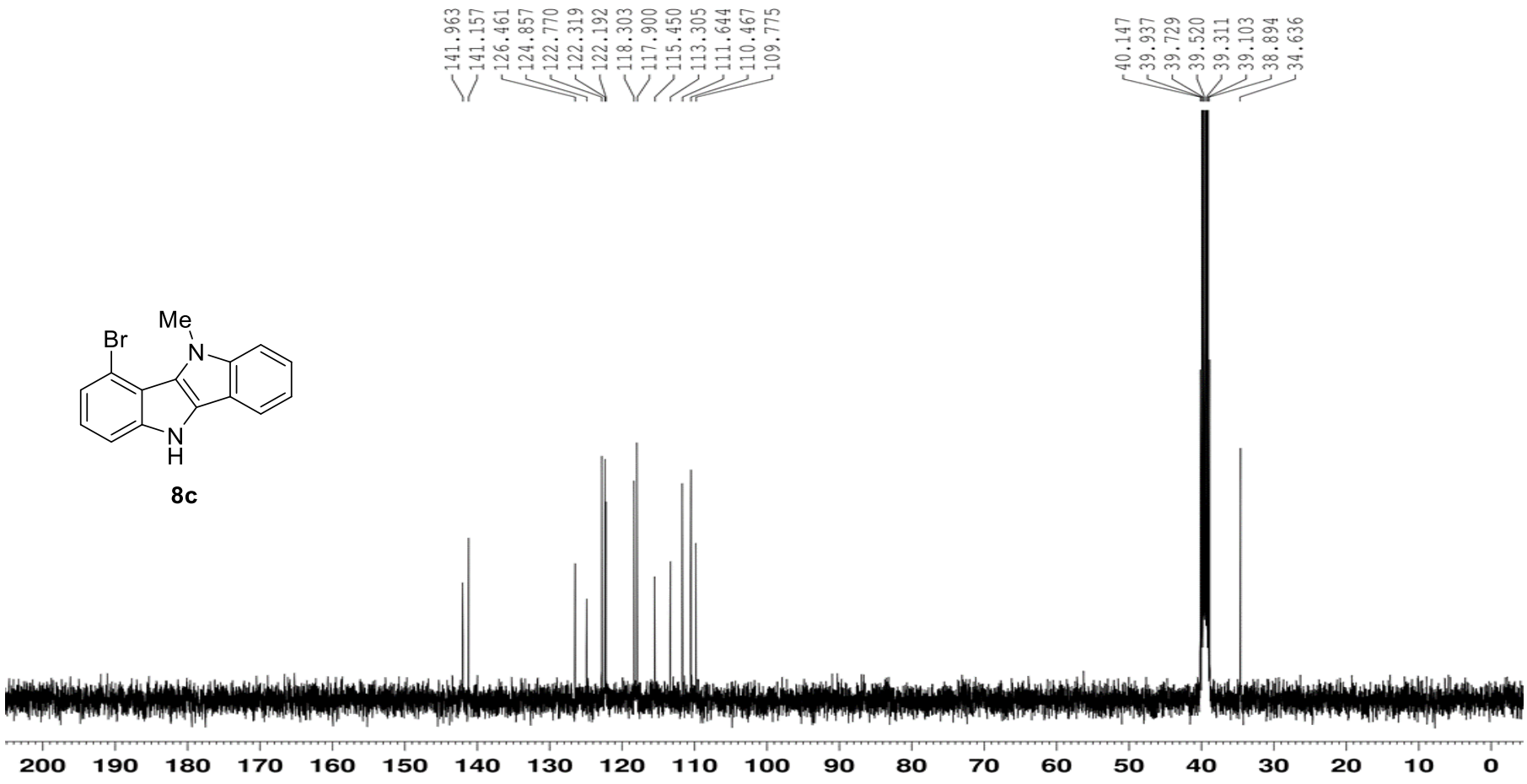
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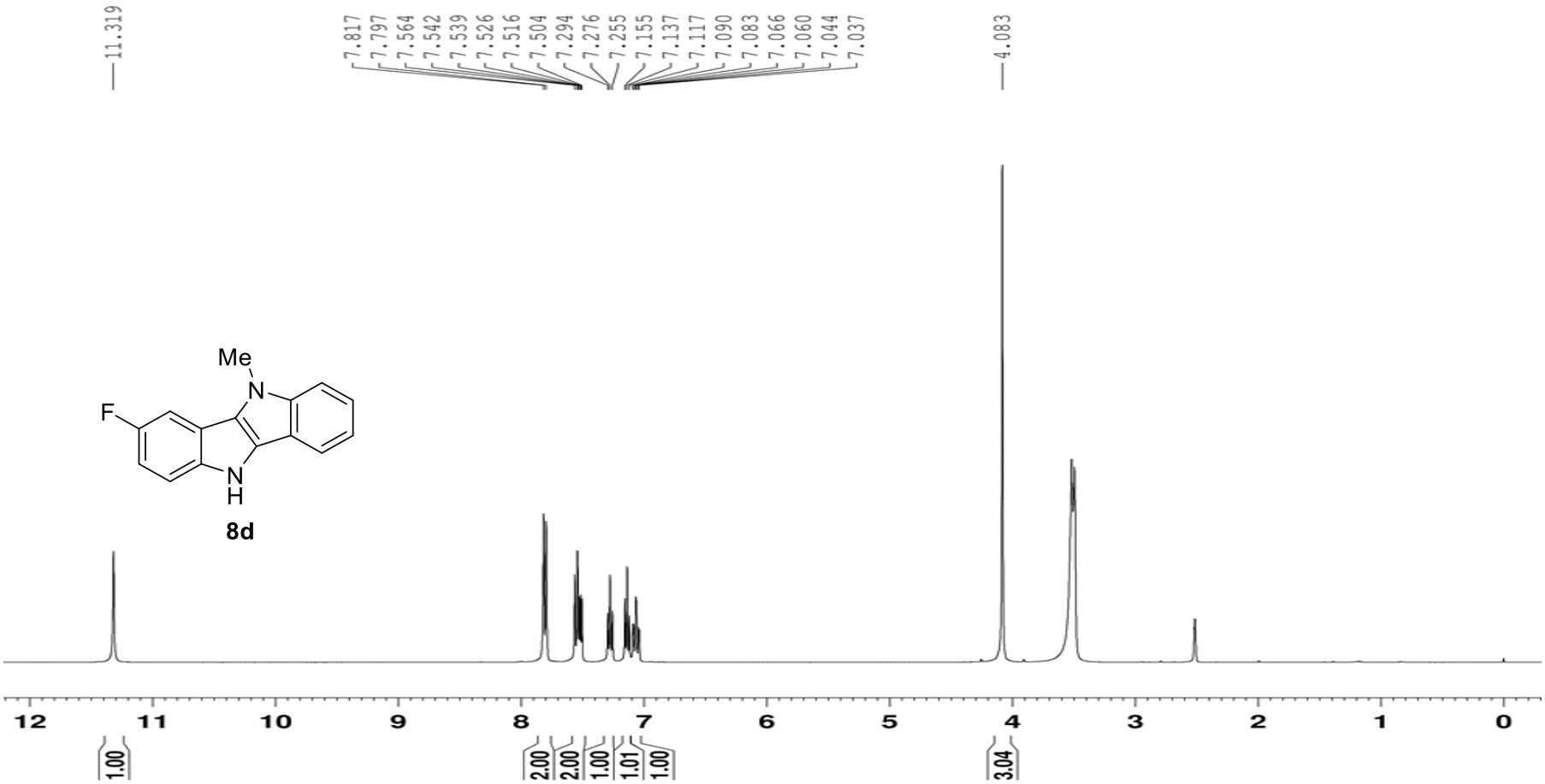
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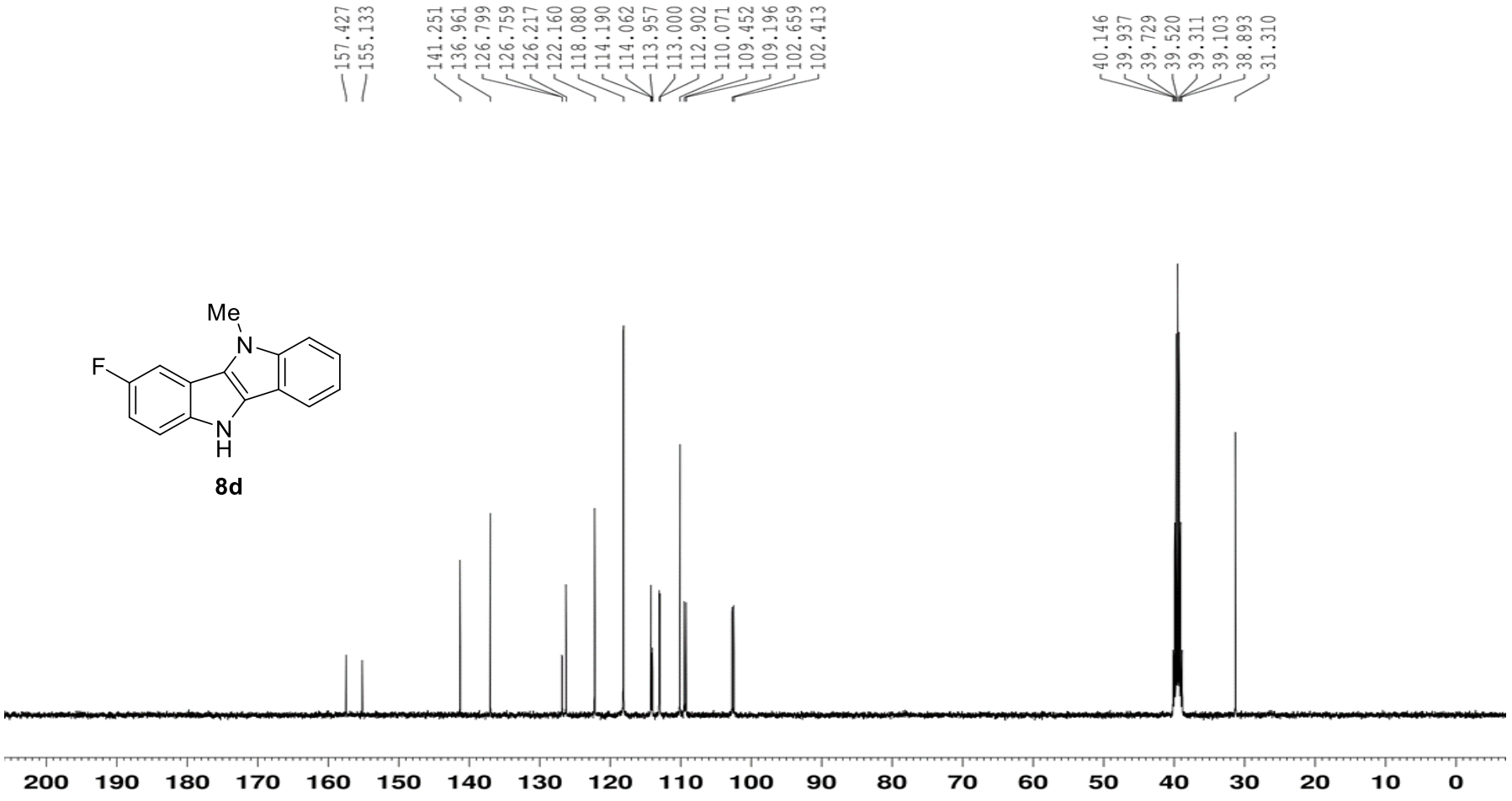
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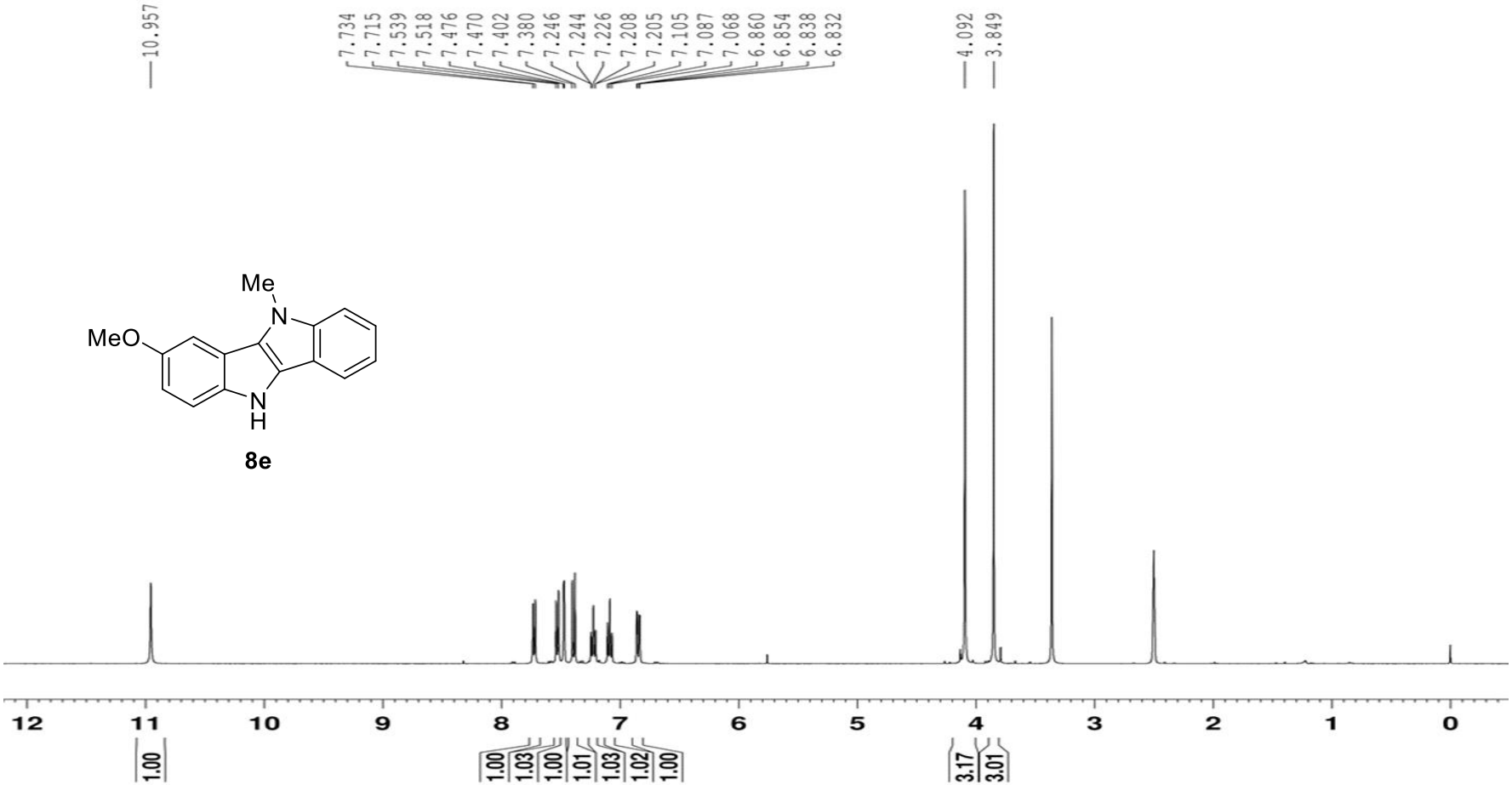
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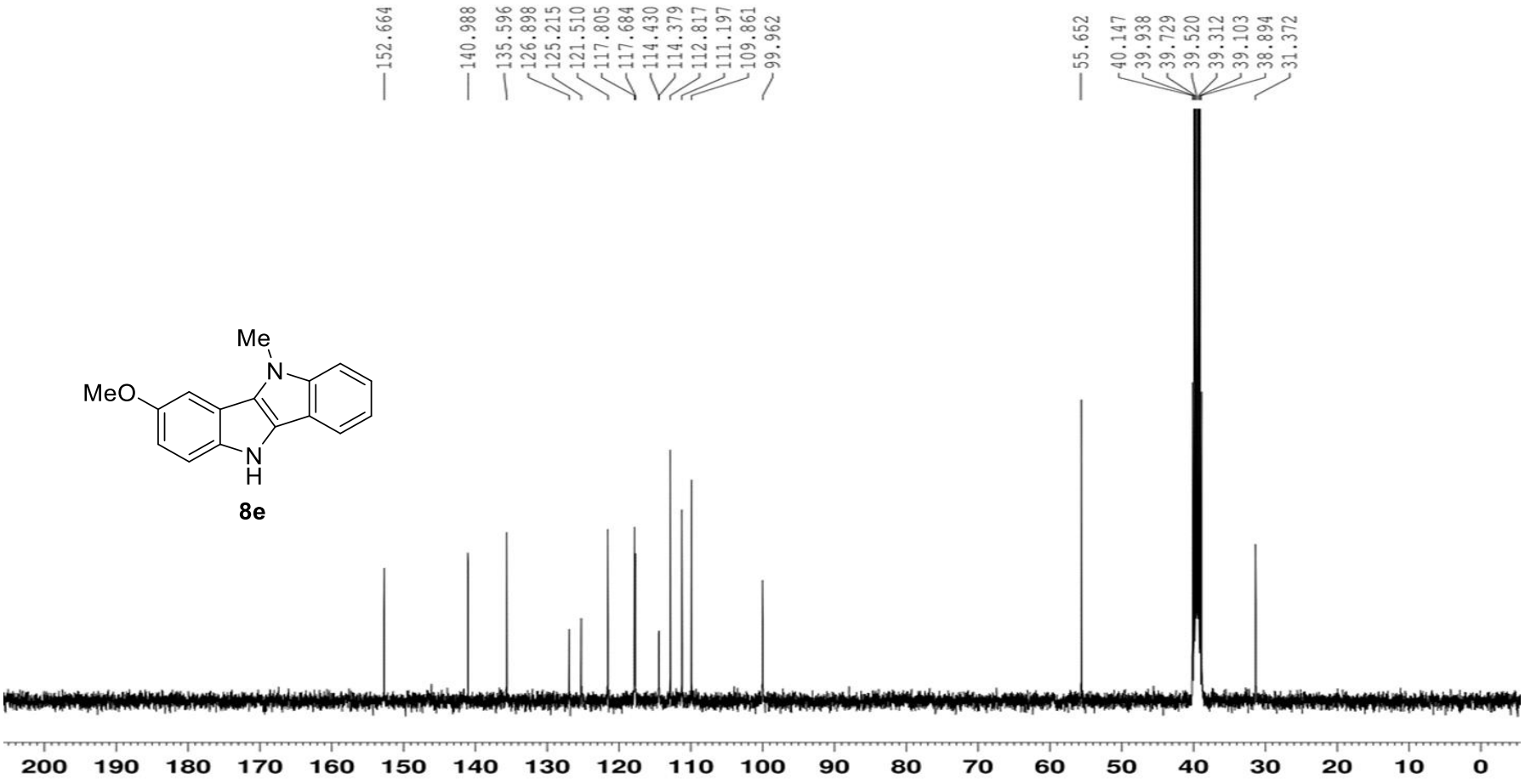
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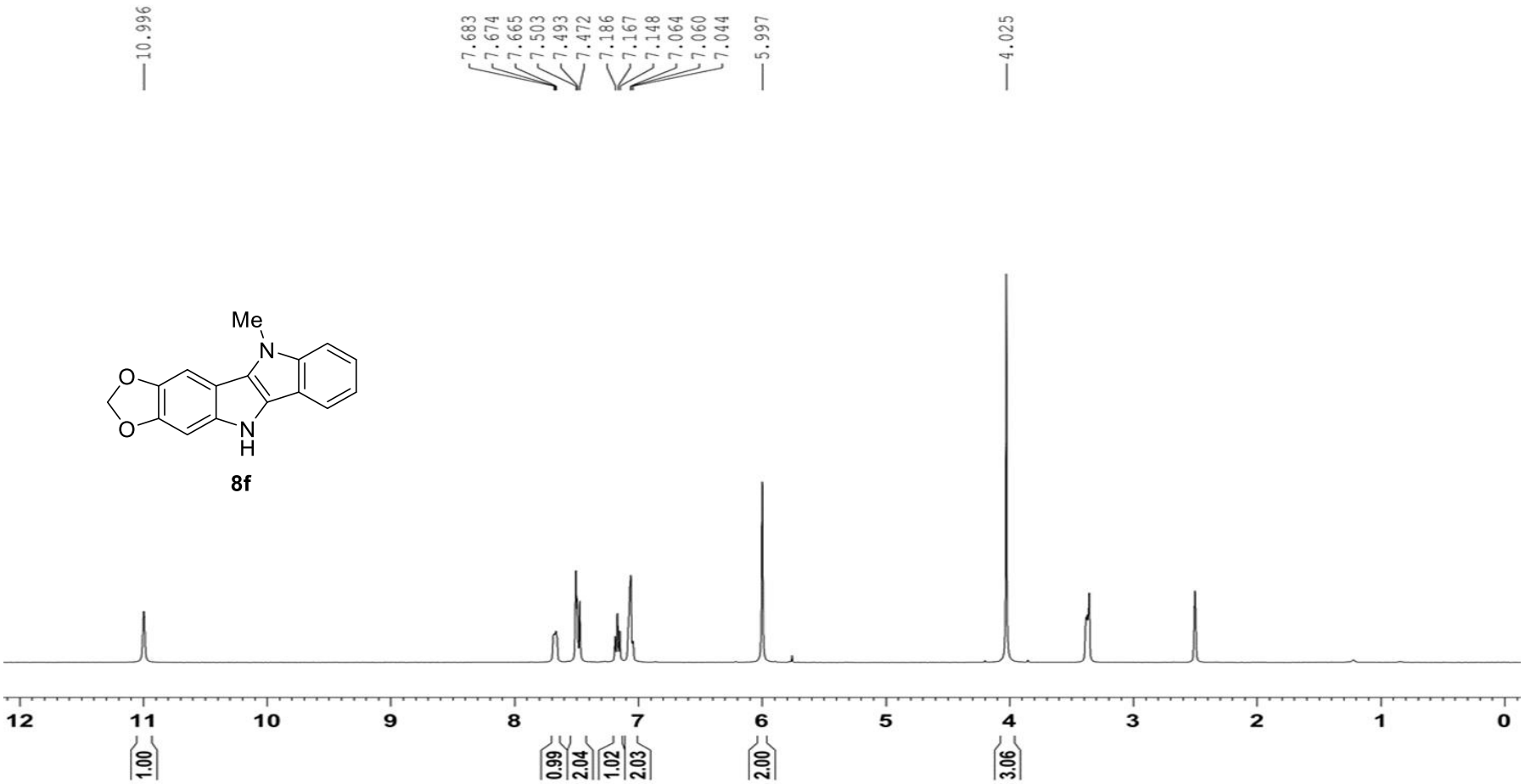
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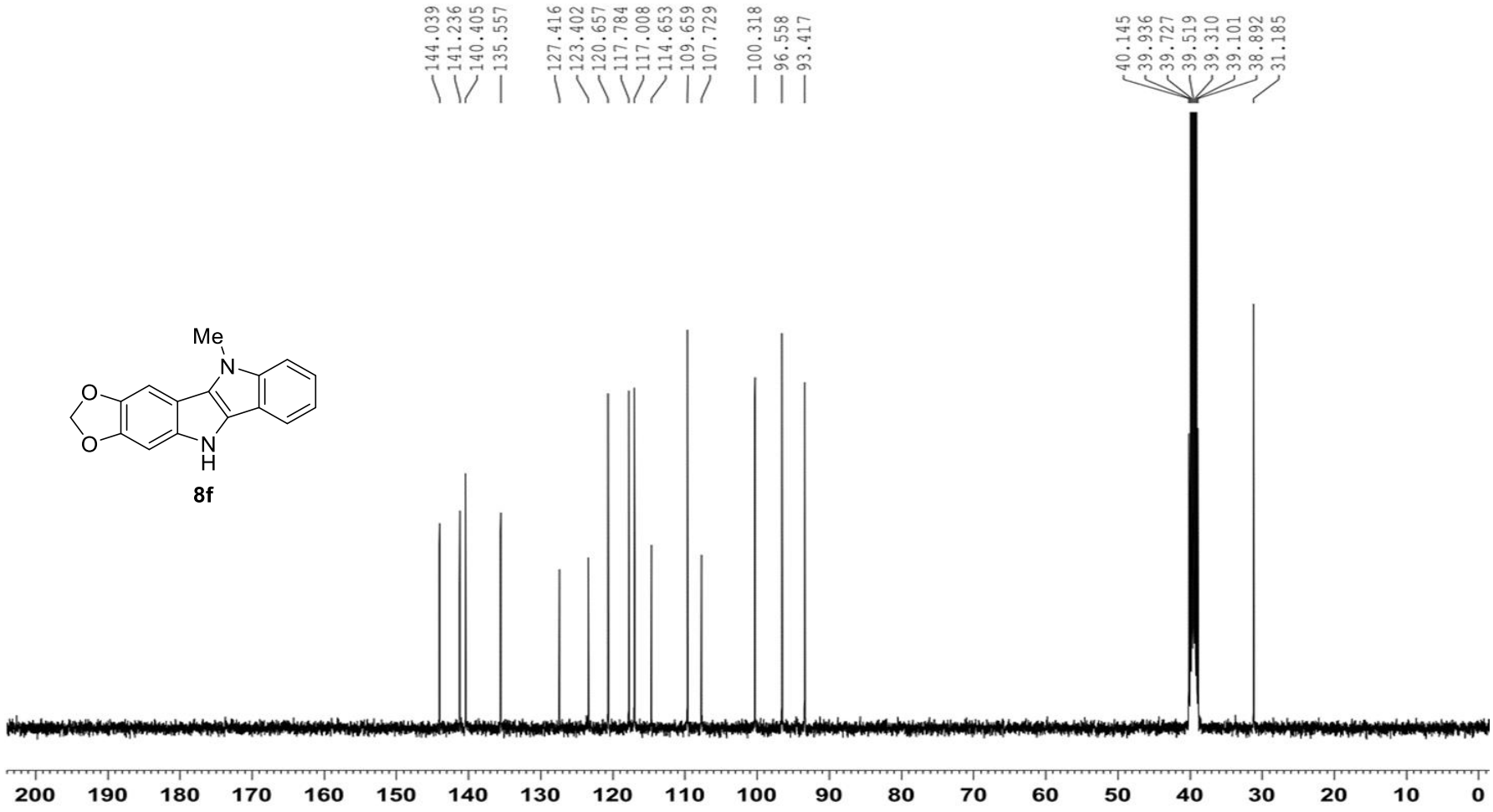
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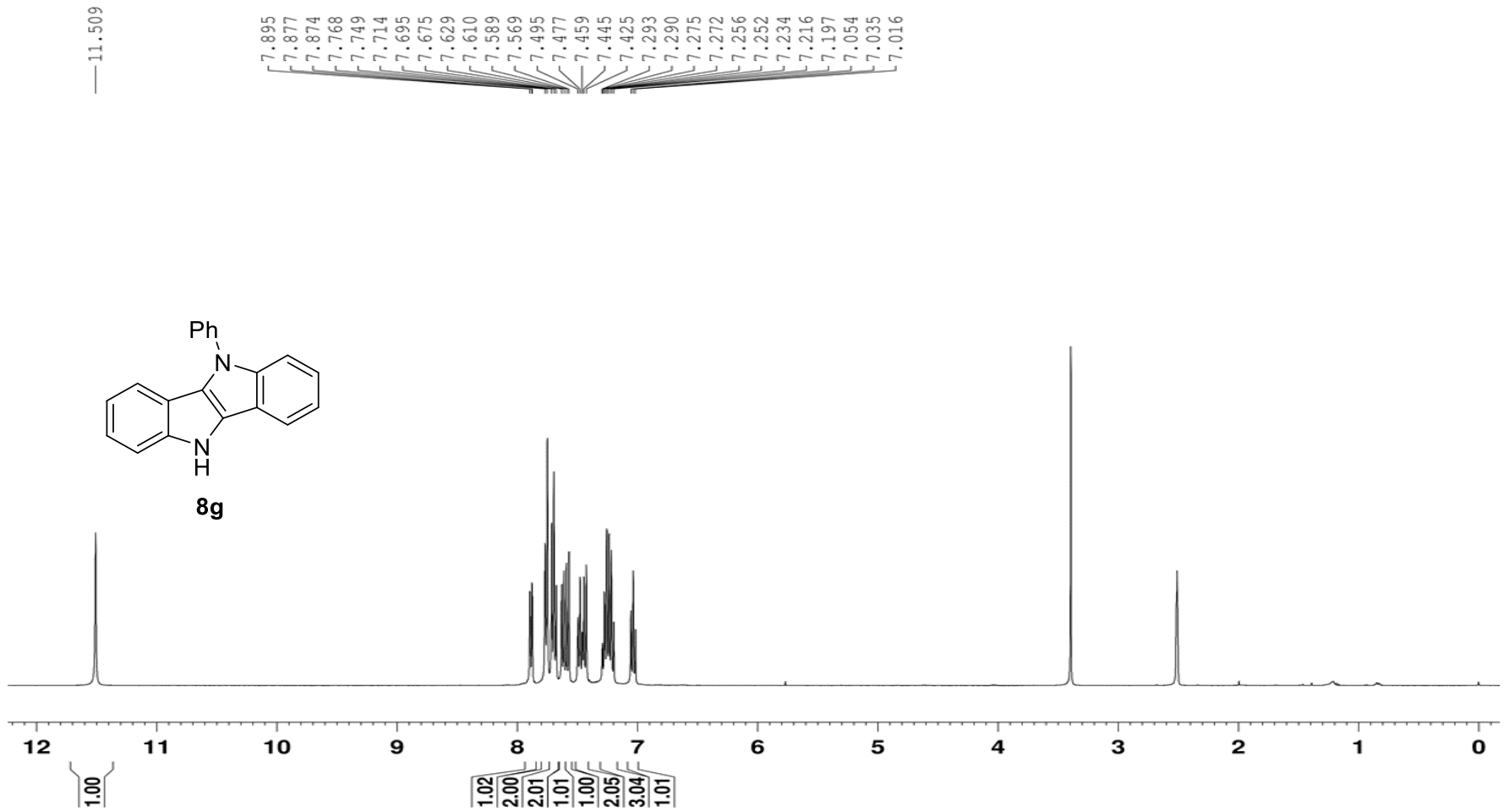
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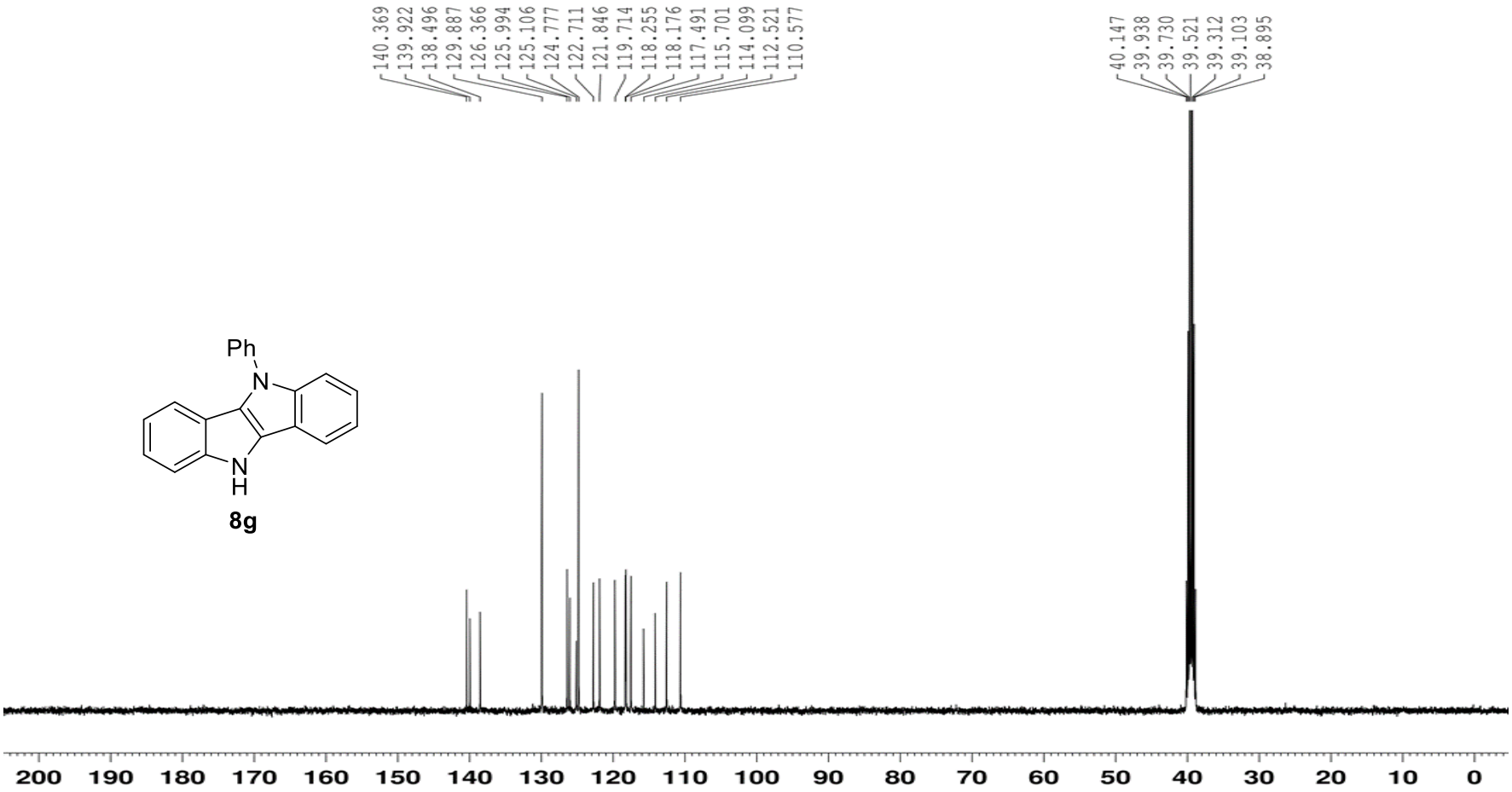
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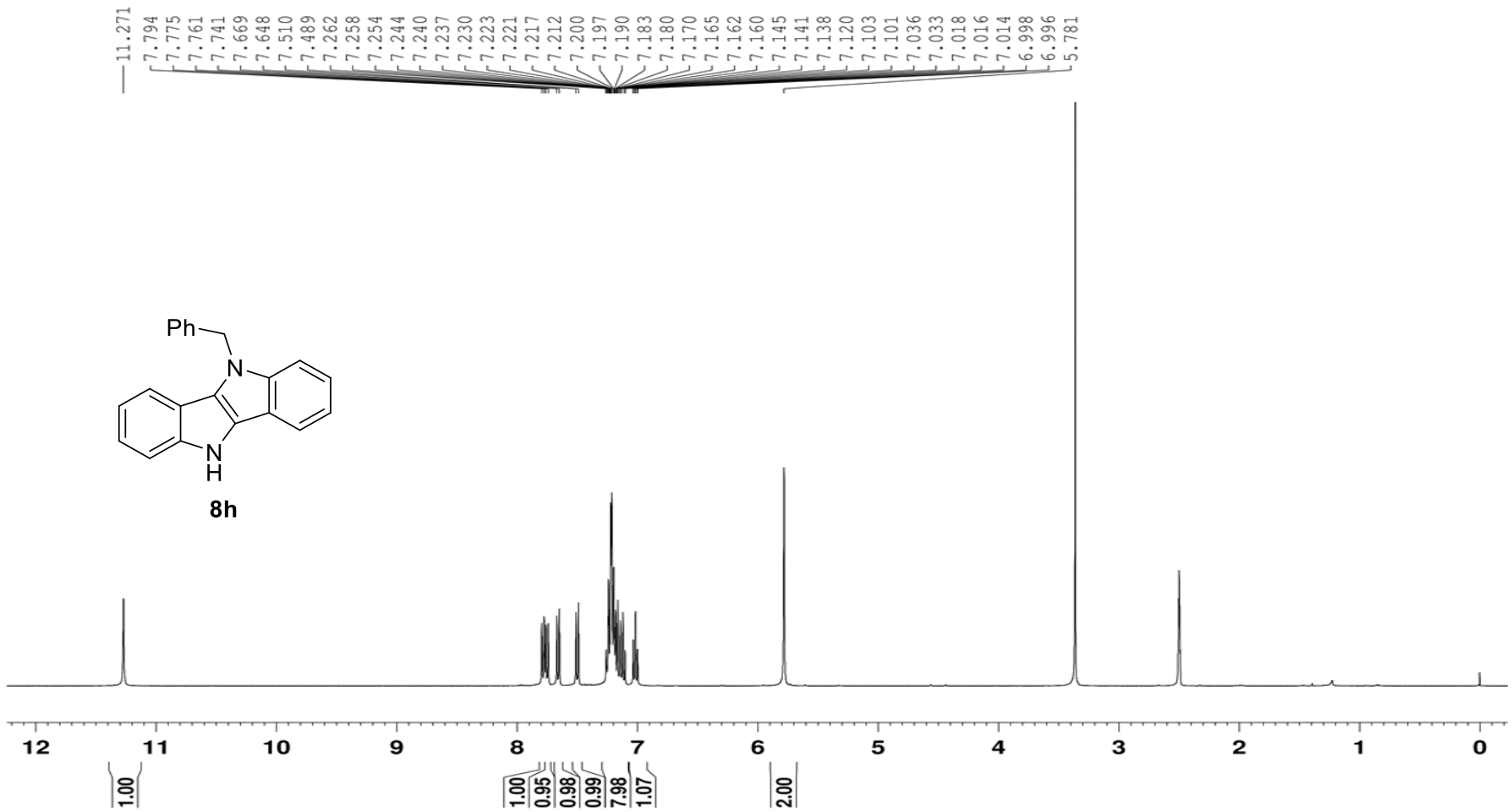
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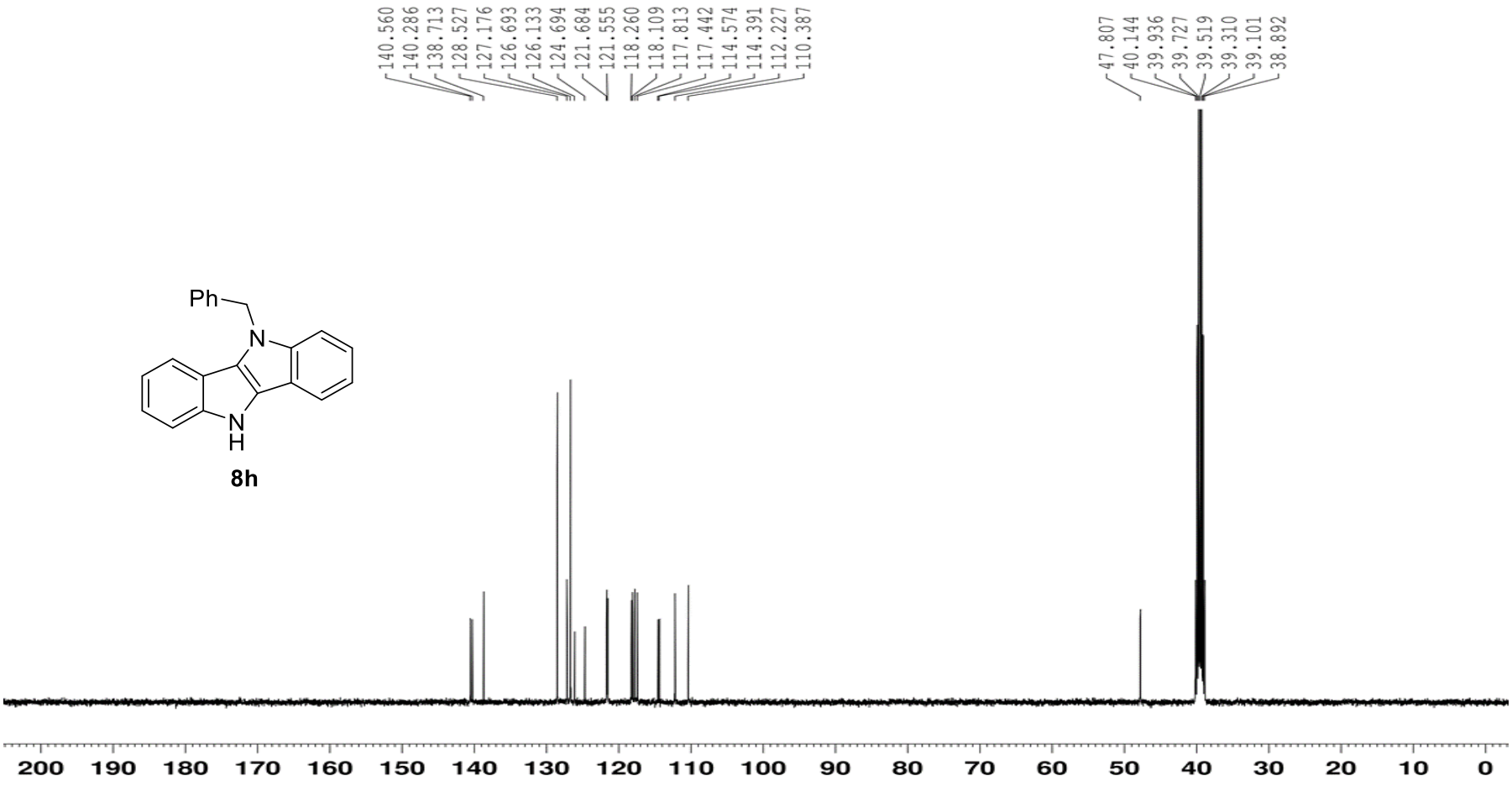
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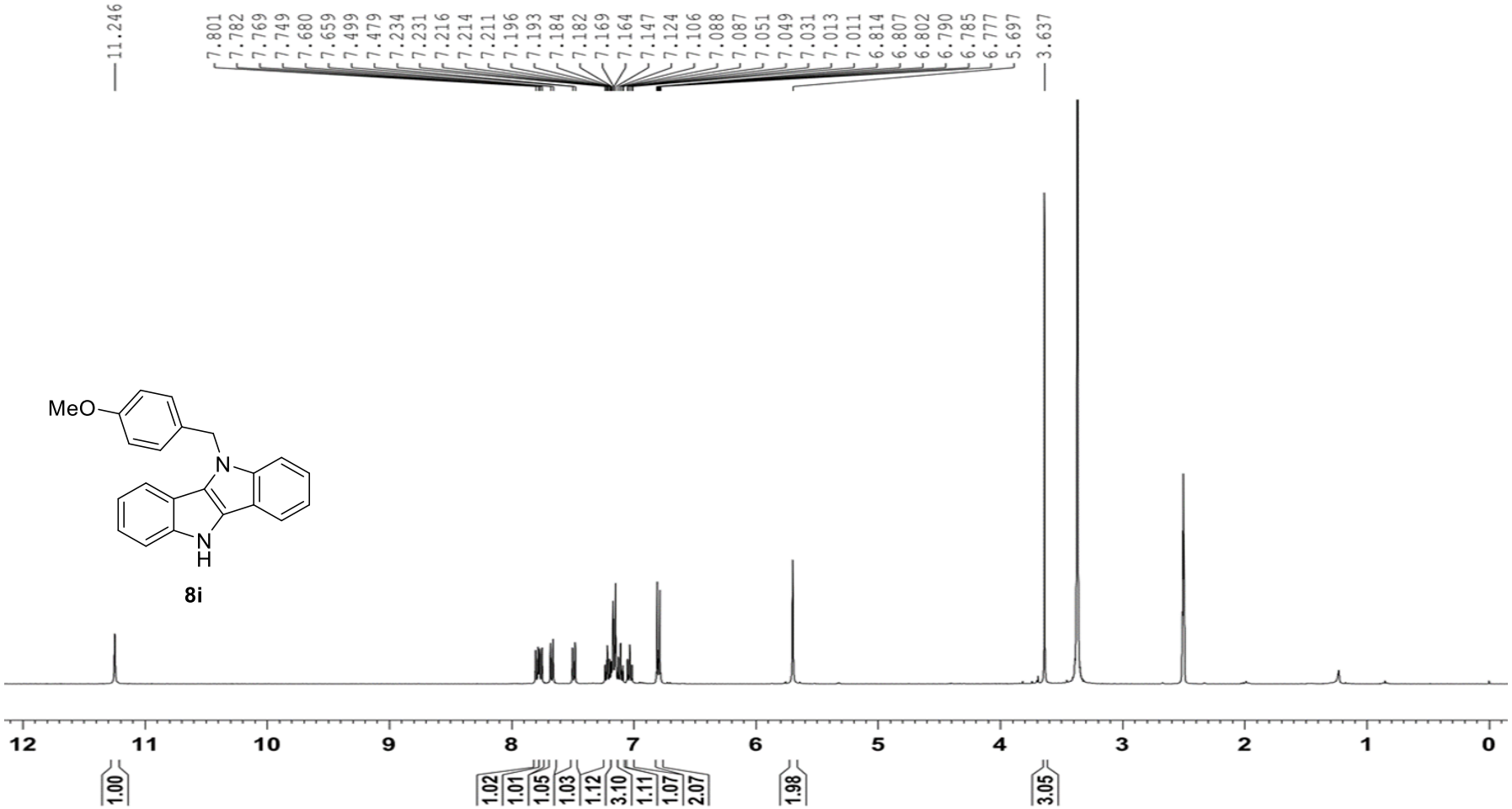
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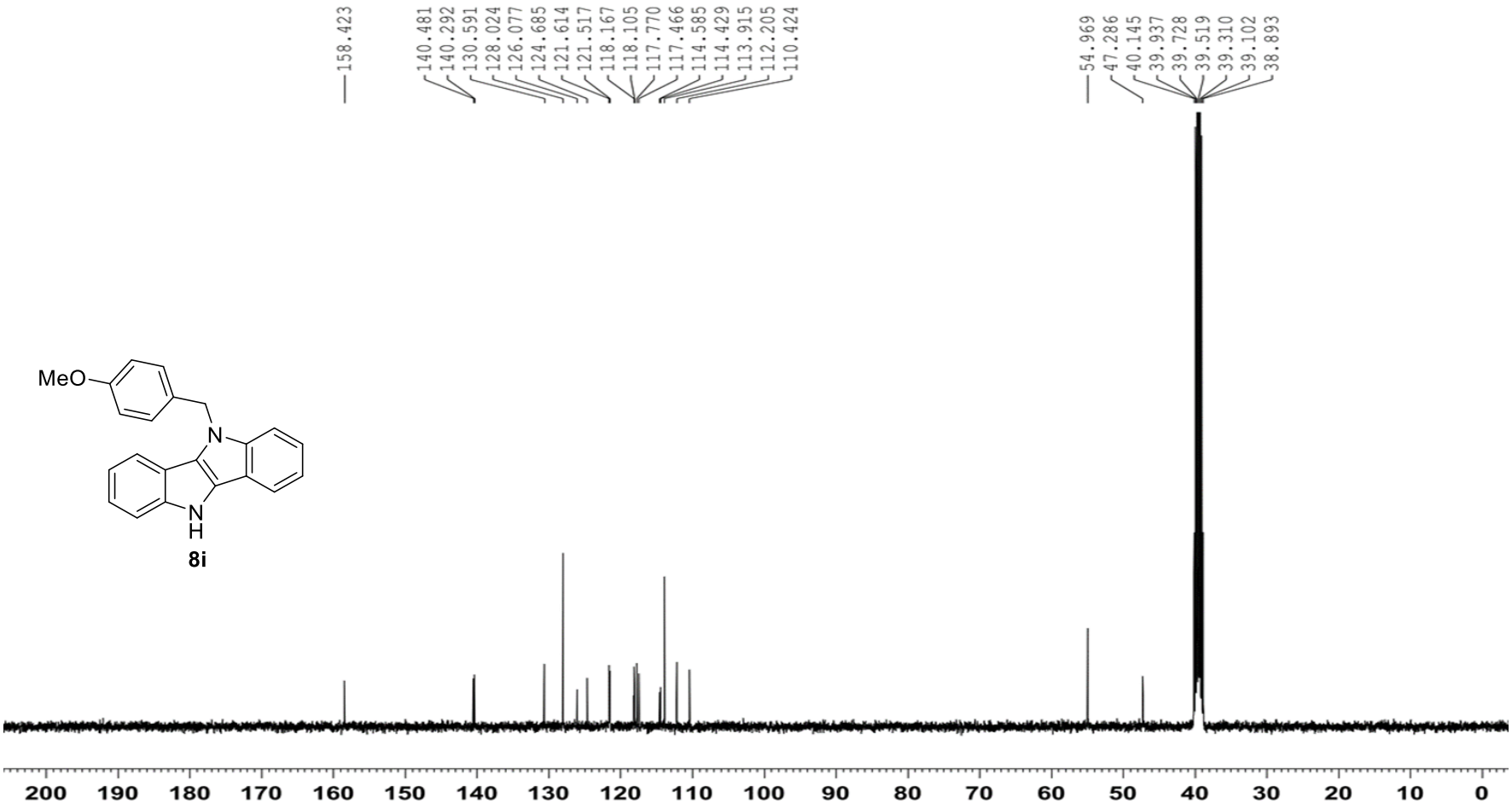
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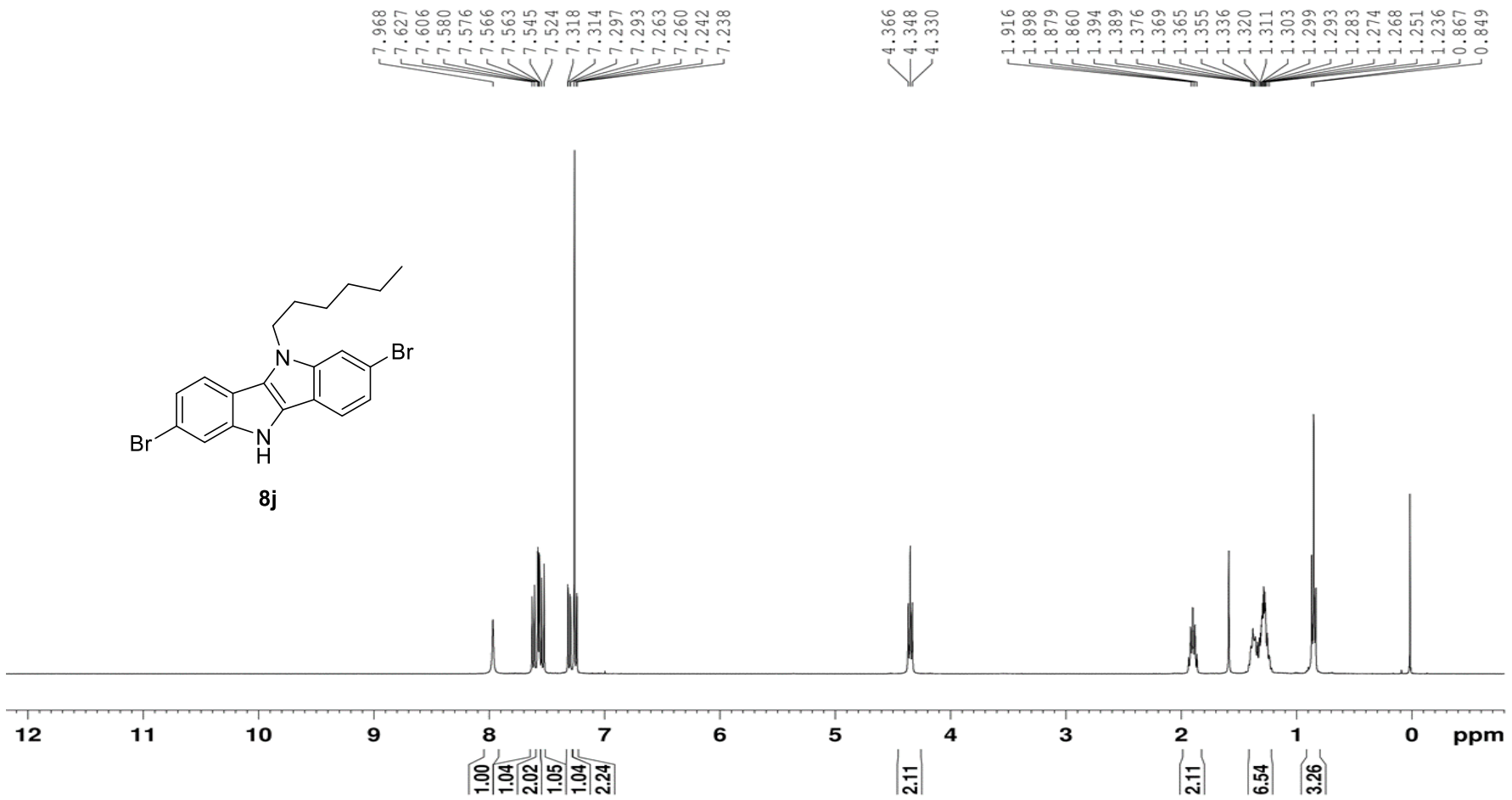
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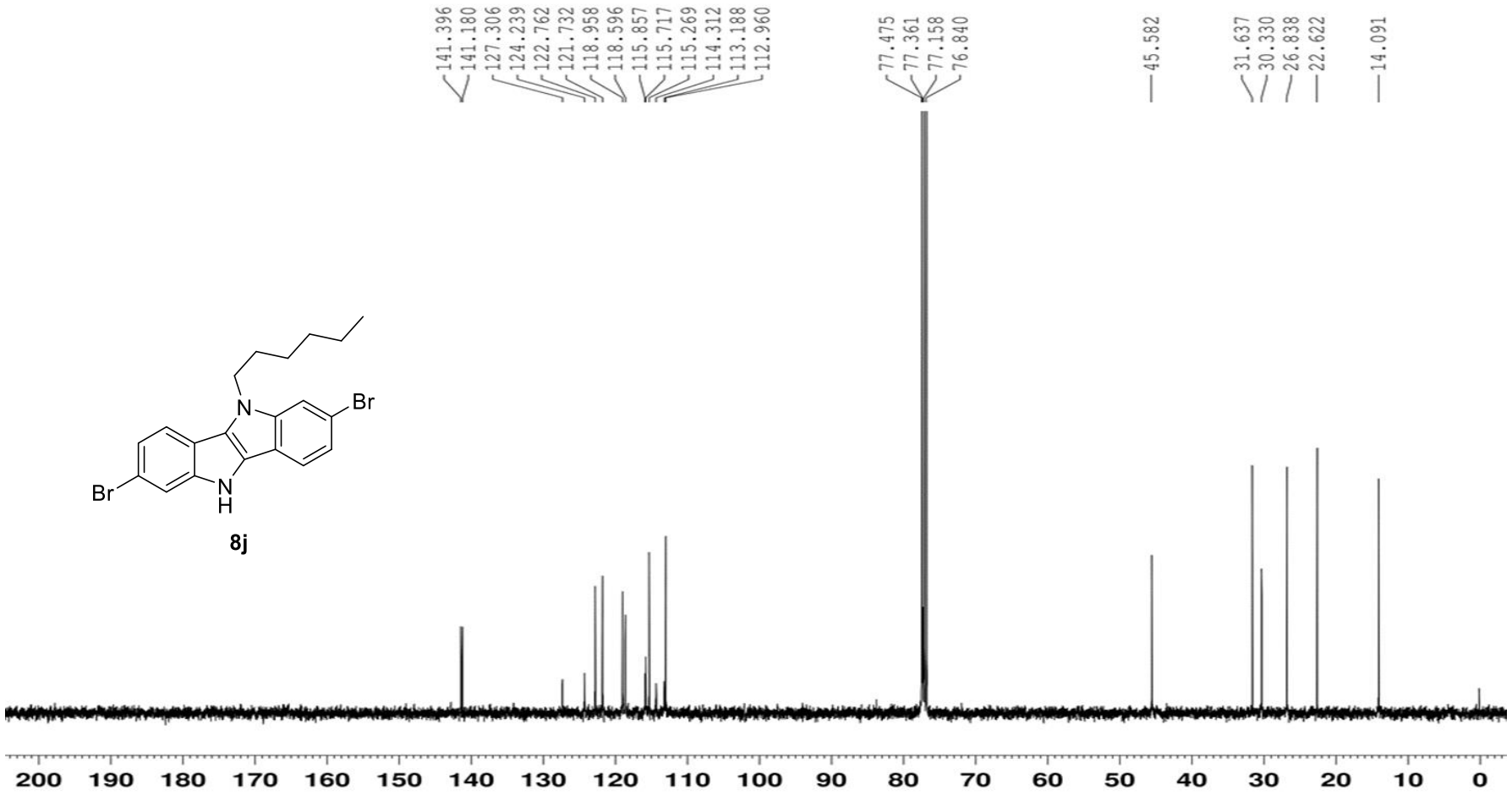
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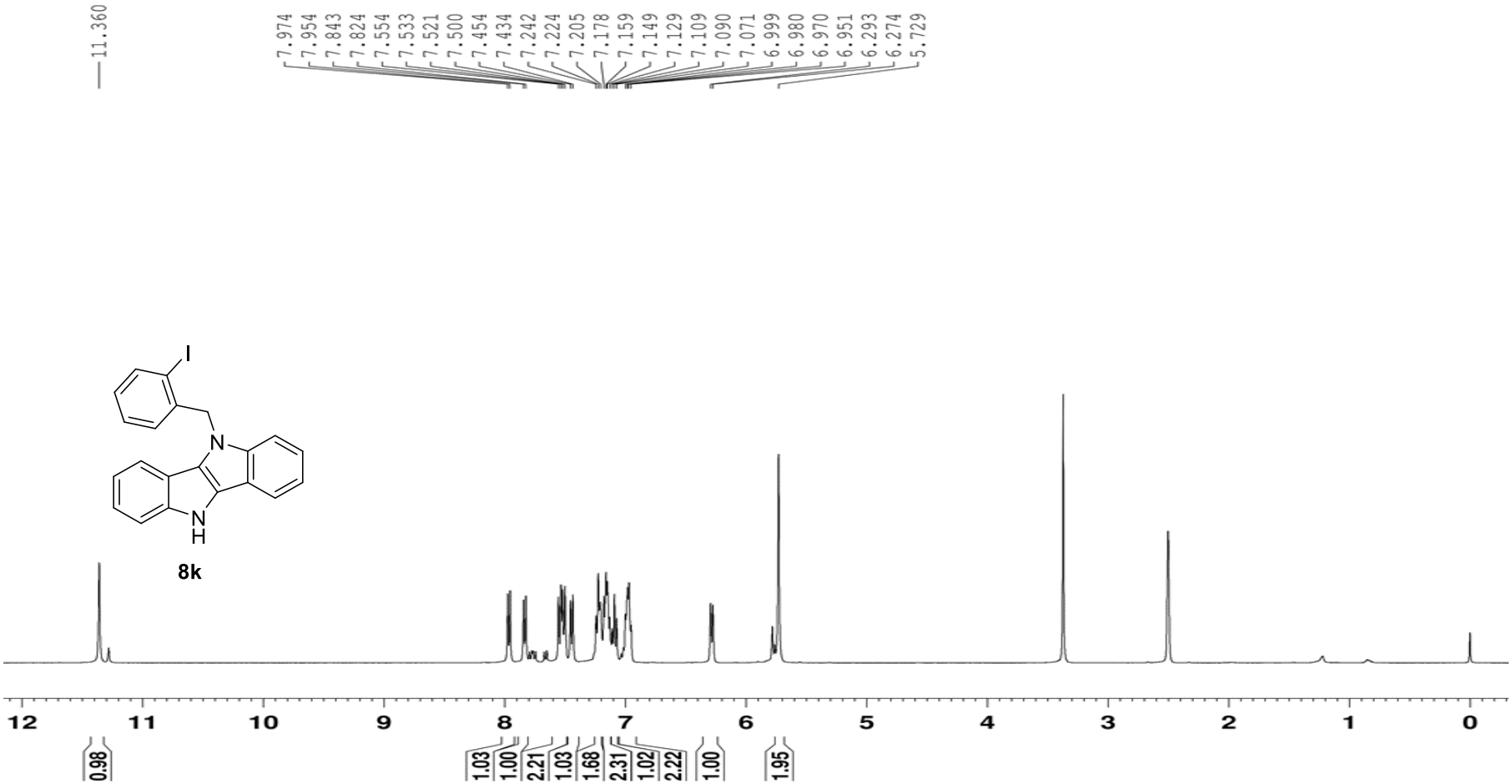
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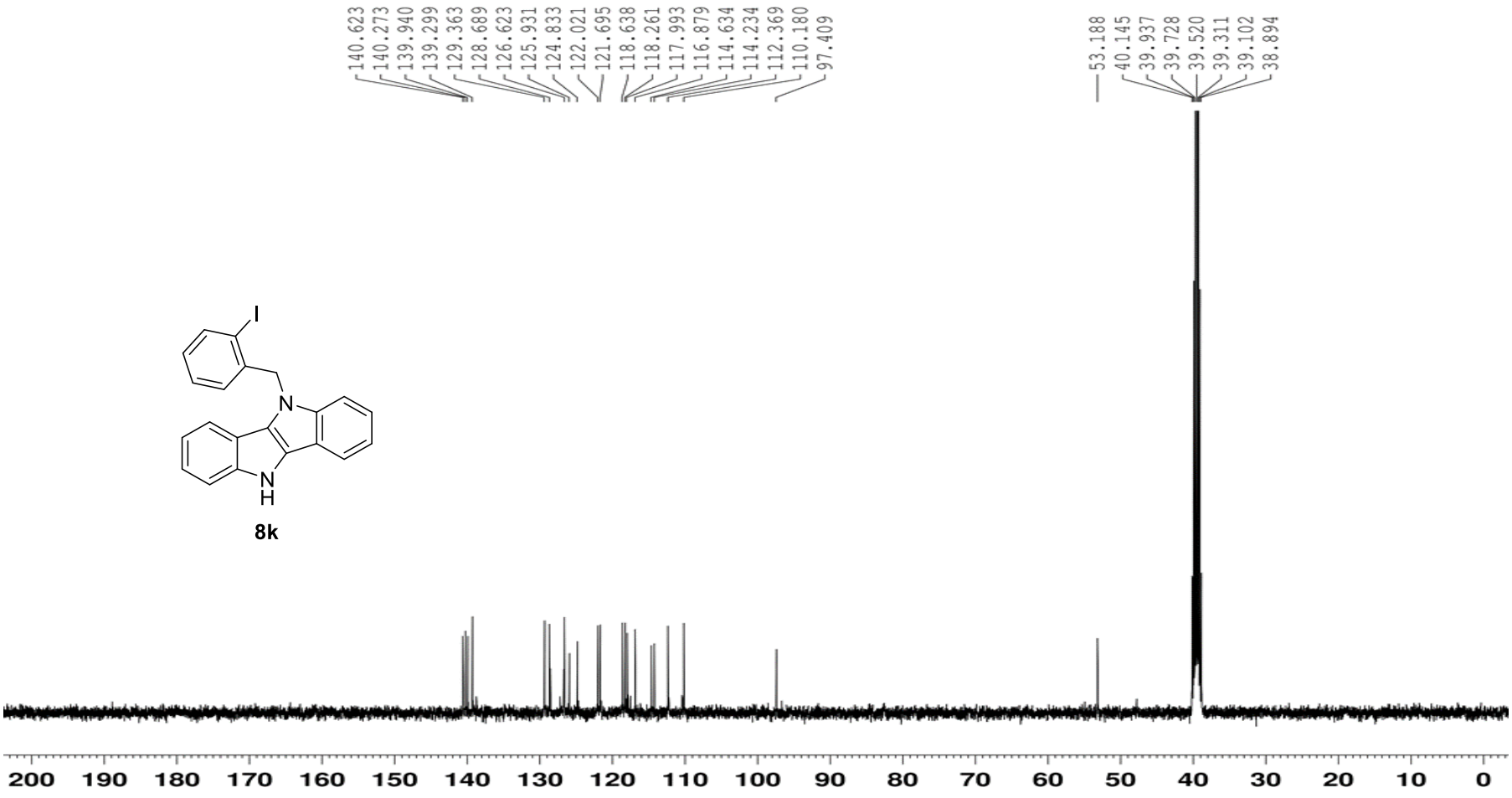
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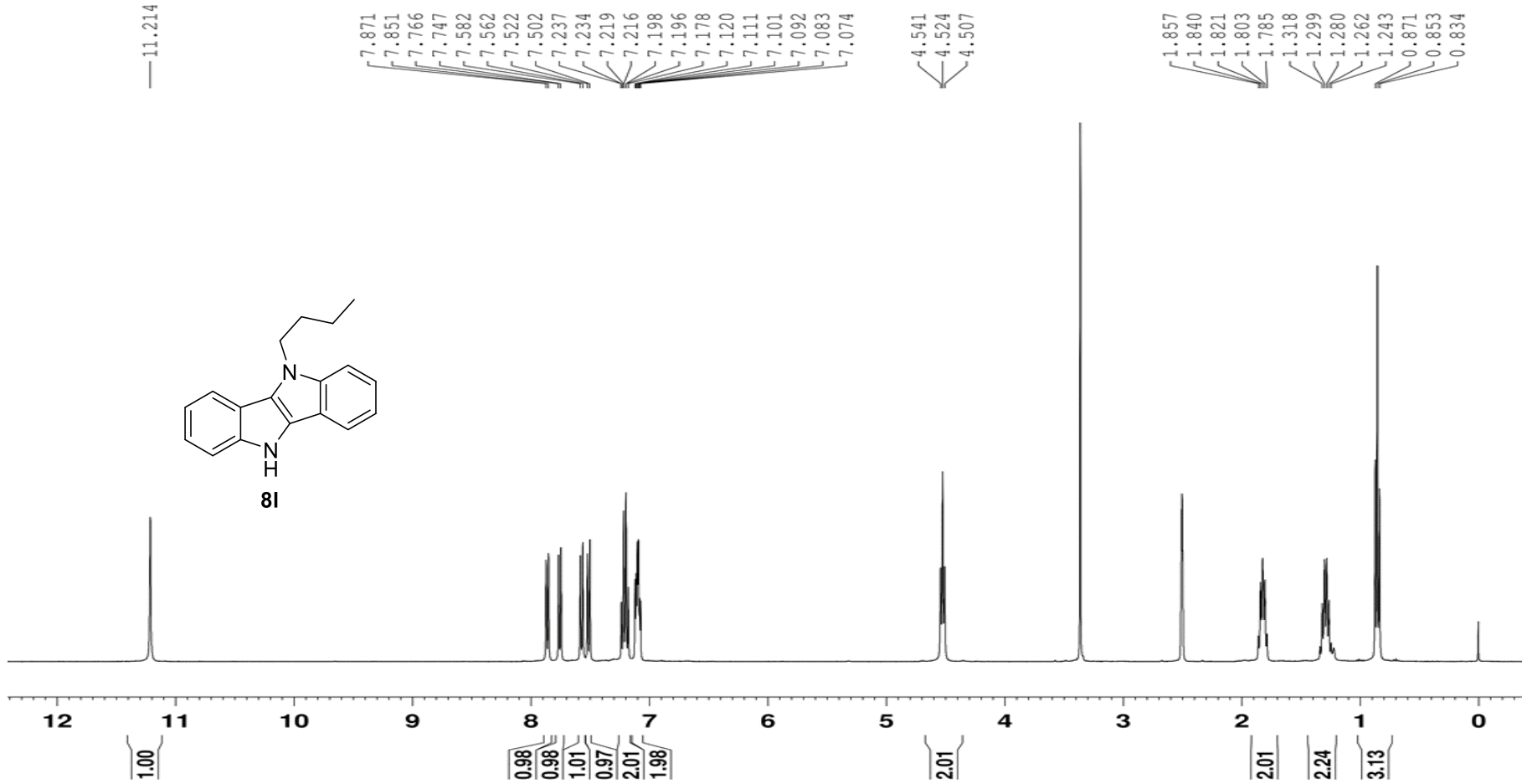
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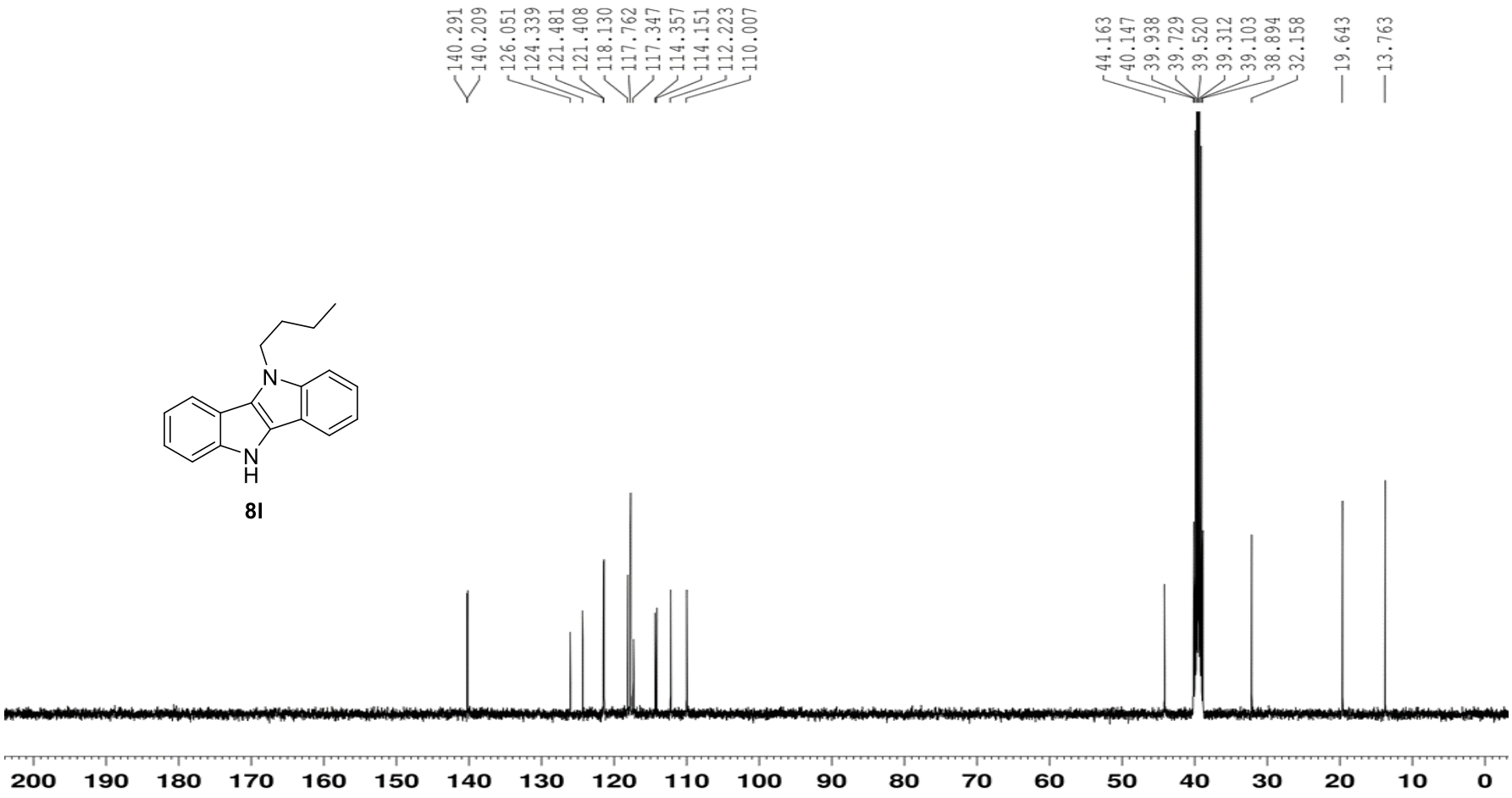
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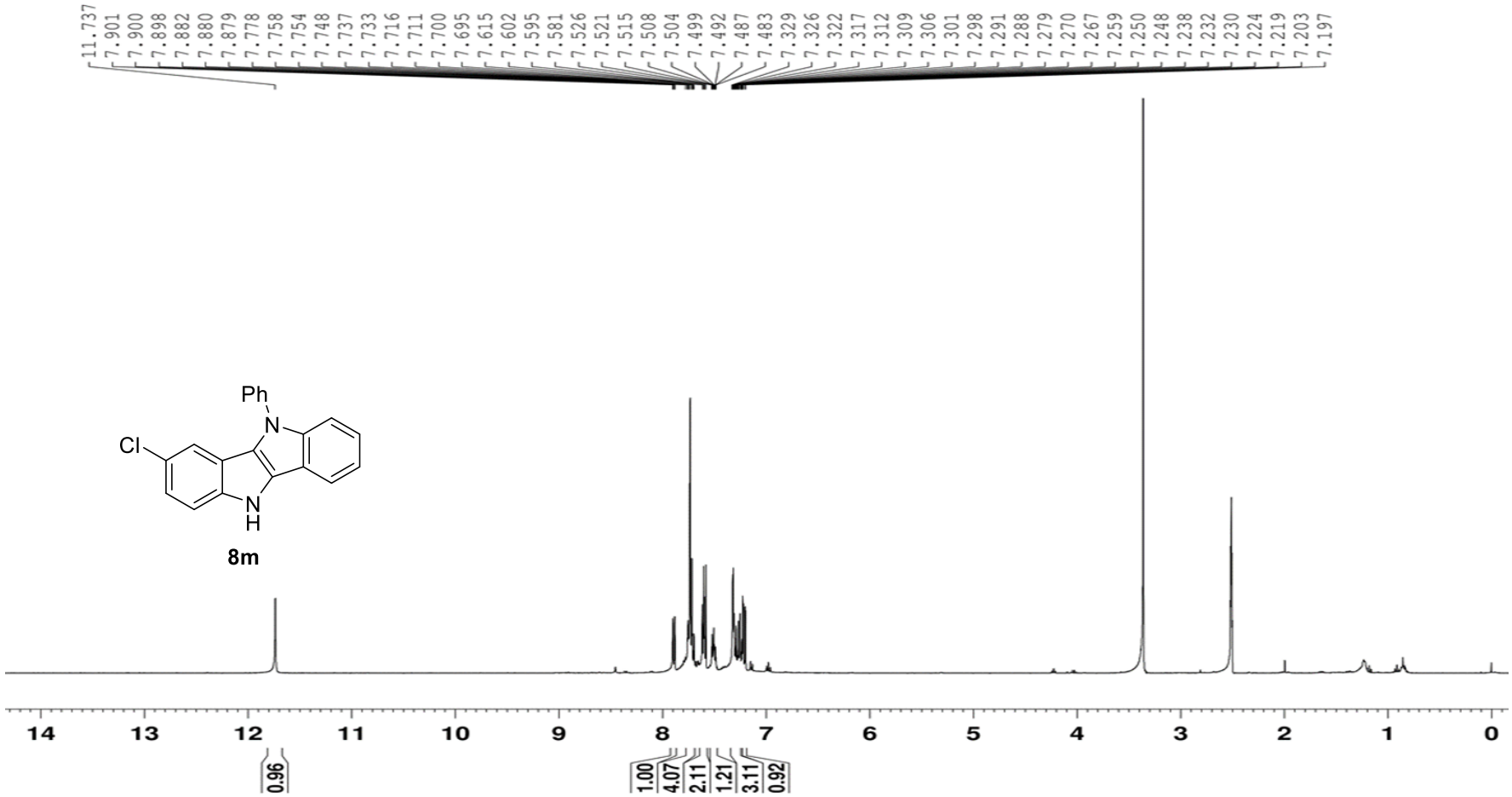
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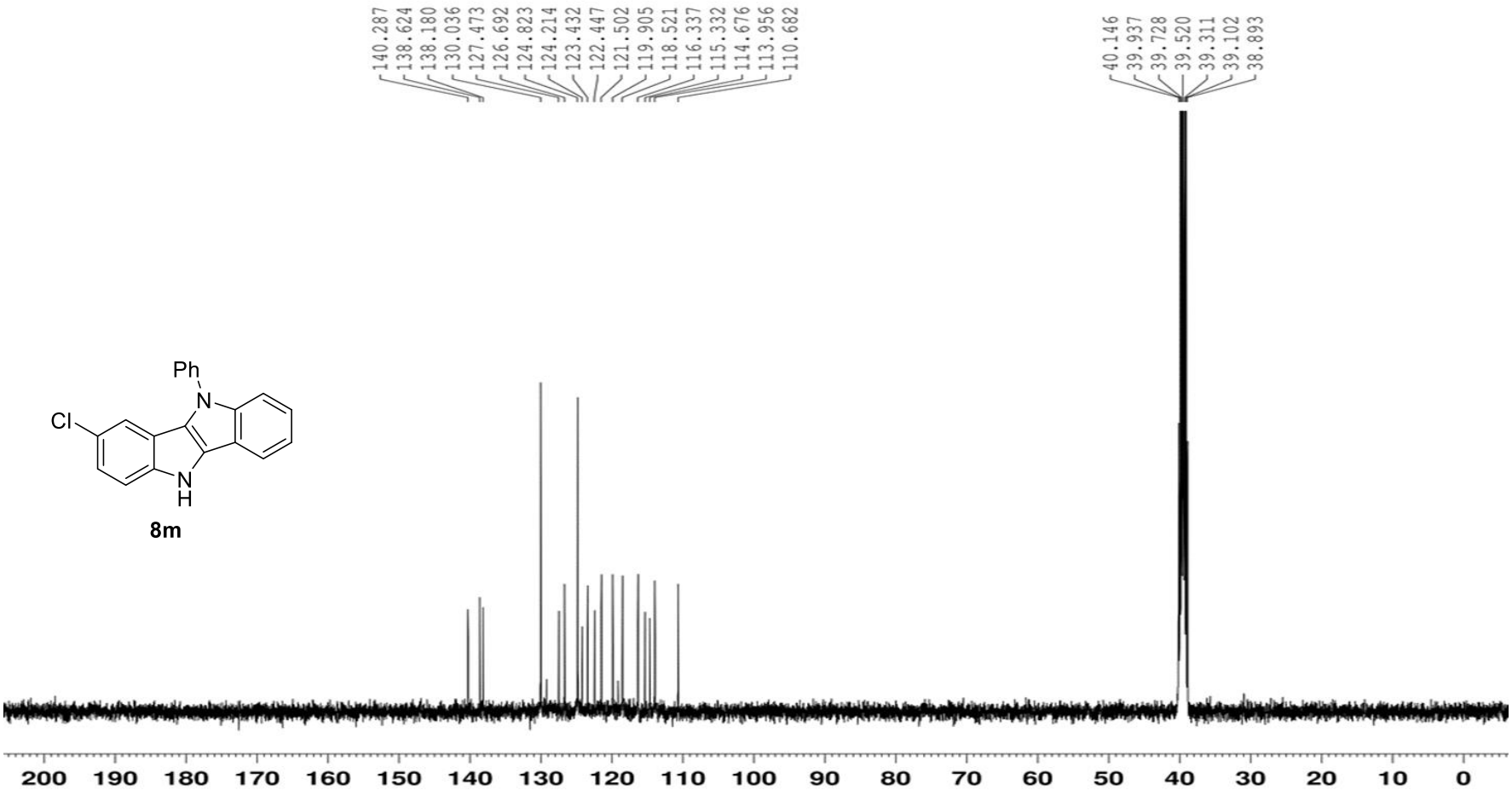
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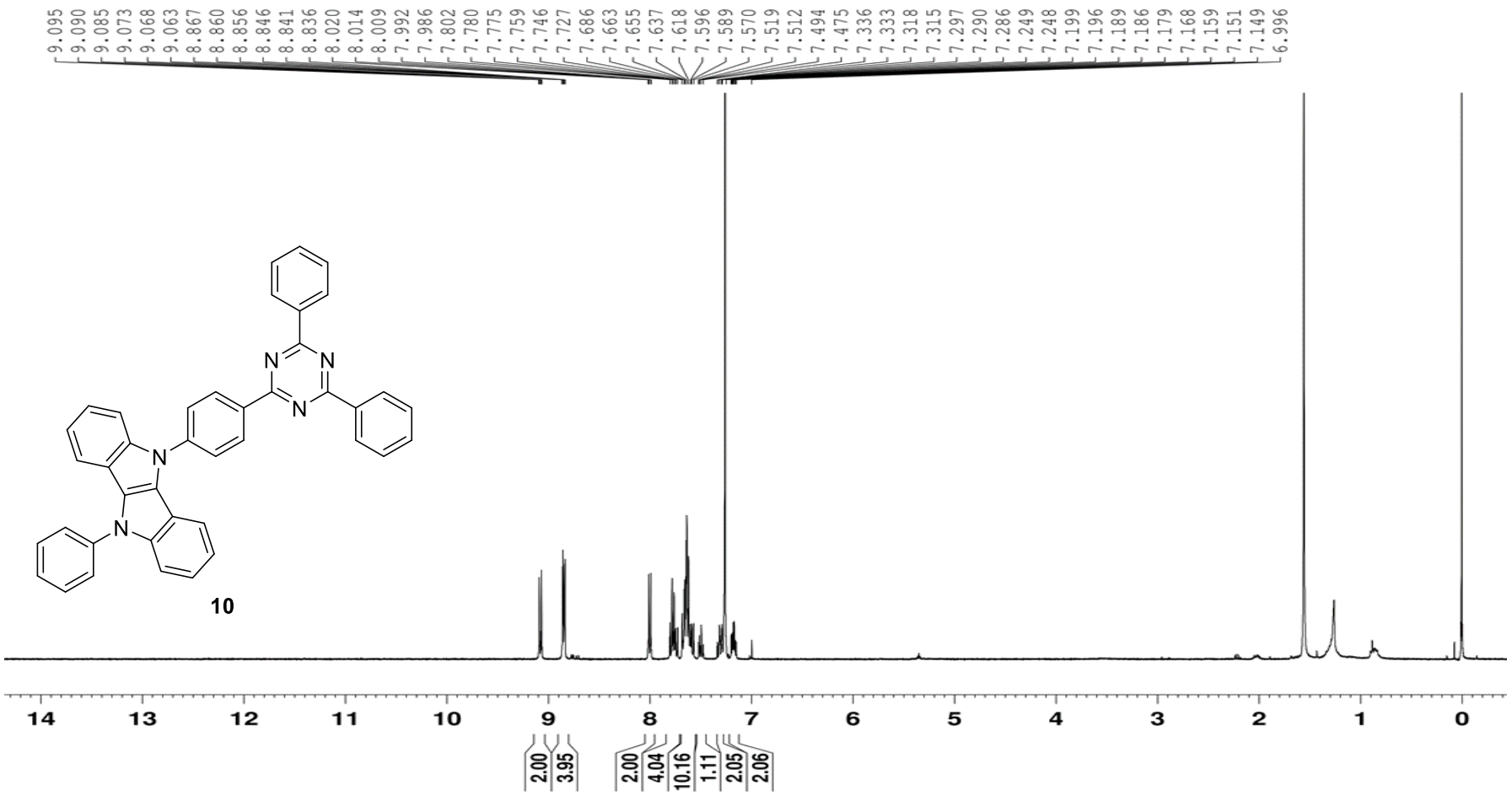
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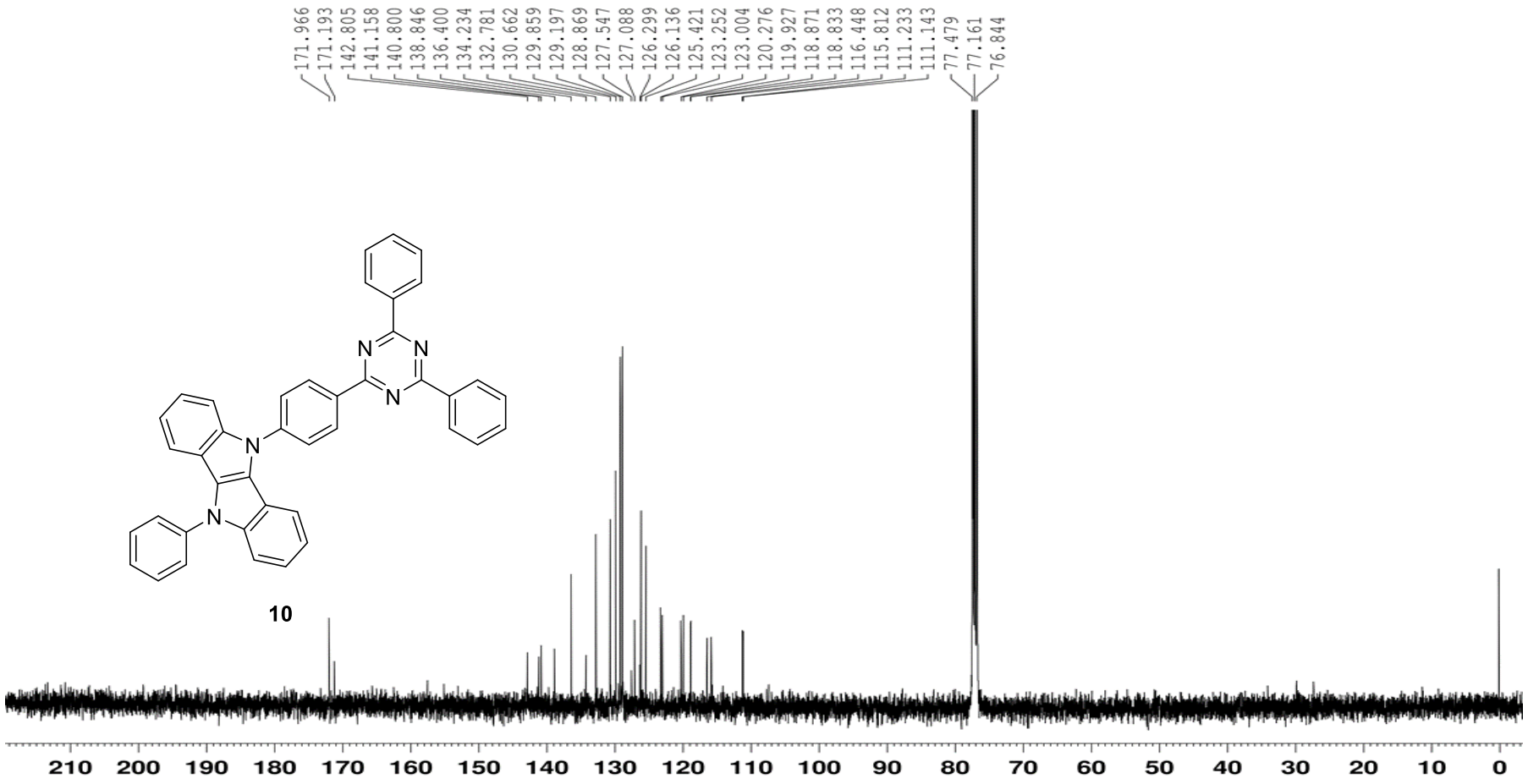
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116.448
115.812
111.233
111.143
77.479
77.161
76.844
N
N
N
N
10
210
200
190
180
170
160
150
140
130
120
110
100
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60
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0