Supporting Information for

^{t}BuOK-Promoted Cyclization of Imines with Aryl Halides

Ya-Wei Li,[†] [§]Hong-Xing Zheng,[‡] [§]Bo Yang,[‡] Xiang-Huan Shan,[‡] Jian-Ping Qu,*[,†] Yan-Biao Kang*[,‡]

[†] Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China, E-mail: ias_jpqu@njtech.edu.cn

[‡] Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China, E-mail: ybkang@ustc.edu.cn

Contents

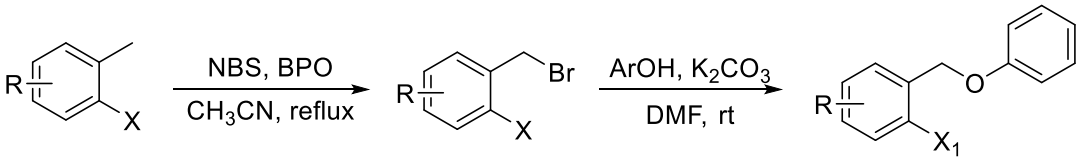
1. General Information

Solvents were predried over activated 4 Å molecular sieves and further dried by refluxing and distilling over sodium (1,4-dioxane), CaH_2 (toluene, DMSO, DMF, and DMA) or P_2O_5 (PhCl) under argon atmosphere. ^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].

2. Experimental Details for Table 1

The weighed base was added to a dry Schlenk reaction tube, dried under vacuum for 15 min. Then solvent (1 mL), **1a** (0.5 mmol, 132 mg) and **2a** (0.6 mmol, 109 mg) was added. The reaction was stirred at 50 °C and was monitored by TLC. After the reaction was completed, the reaction was quenched with H_2O and extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The conversion and yield were determined by ^1H NMR analysis of the crude mixture using CH_3NO_2 (18 μL) and MeO^{t}Bu (40 μL) as internal standards.

3. Preparation of 1

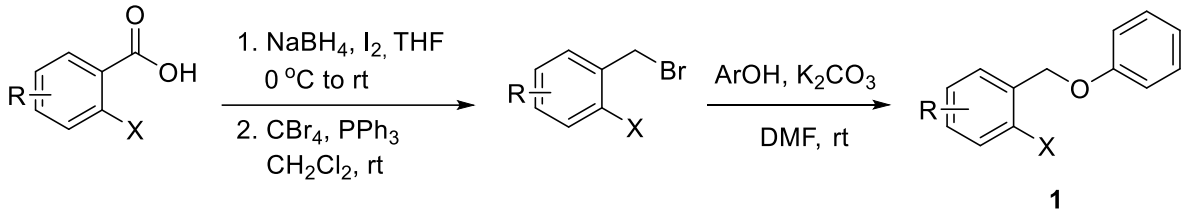


1

General procedure 1 (GP1): Under argon atmosphere, toluenes (10 mmol), *N*-bromosuccinimide (11 mmol), benzoyl peroxide (0.5 mmol) and acetonitrile (30 mL) were added to a glass flask (100 mL) in an oil bath. The mixture was heated at 80 °C and was monitored by TLC nanlysis. The reaction mixture was cooled to room temperature, filtered, and concentrated *in vacuo*. The crude residues were purified by silica gel flash column chromatography affording the corresponding benzyl bromide.[1]

In a 100 mL round-bottomed flask was added potassium carbonate (18 mmol) and phenol (7.2 mmol); then N, N-dimethylformamide (15 mL) was added. After stirring for 10 minutes, benzyl bromide or benzyl chloride (6 mmol) was added. The reaction was stirred at room temperature and monitored by TLC. After the reaction was completed, the reaction was quenched with H_2O and extracted 3 times

with ethyl acetate. The organic phases were combined and washed by saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo and purified by column chromatography to give the corresponding product.[2]

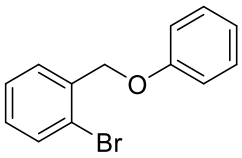


1

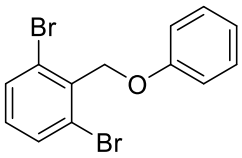
General procedure 2 (GP2): Benzoic acid (10 mmol) and THF (30 mL) were added to a 100 mL round bottom flask. When the mixture was cooled to 0 °C, $NaBH_4$ (25 mmol) was slowly added. I_2 (10 mmol) was dissolved in THF (15 mL), and the solution was added dropwise with vigorous releasing of hydrogen. The mixture was then heated to reflux and was monitored by TLC analysis. After the complete consumption of the starting materilas, the mixture is cooled to room temperature and quenched with methanol. The solution was concentrated, washed with 20% aqueous NaOH (25 mL) and extracted 3 times with ethyl acetate. The organic phases were combined and washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The concentrated benzyl alcohol was directly used in the next step without purification.[2]

Under an argon atmosphere, benzyl alcohol (10 mmol) and triphenylphosphine (11 mmol) were dissolved in dry dichloromethane (30 mL), carbon tetrabromide (11 mmol) was then added slowly. The mixture was stirred and monitored by TLC. The solution were concentrated *in vacuo*. After the complete consumption of the starting materilas, the crude residues were purified by flash column chromatography on silica gel affording the corresponding benzyl bromide.[3]

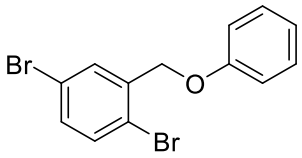
In a 100 mL round-bottomed flask was added potassium carbonate (18 mmol), phenol (7.2 mmol), and *N, N*-dimethylformamide (15 mL). After stirring for 10 minutes, benzyl bromide or benzyl chloride (6 mmol) was added. The reaction was stirred at room temperature and monitored by TLC. After the reaction was completed, the reaction was quenched with H_2O and extracted 3 times with ethyl acetate. The organic phases were combined and washed with saturated NaCl solution, dried over anhydrous Na_2SO_4, filtered, concentrated in vacuo and purified by column chromatography to gave the corresponding product.[2]



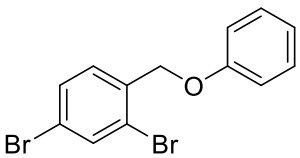
1-Bromo-2-(phenoxymethyl)benzene (1a) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.33 g, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (t, *J* = 8.8 Hz, 2H), 7.37-7.32 (m, 3H), 7.20 (t, *J* = 7.8 Hz ,1H), 7.01 (t, *J* = 7.7 Hz, 3H), 5.16 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.6, 136.5, 132.7, 129.7, 129.3, 129.0, 127.7, 122.4, 121.3, 115.0, 69.4.[2]



1,3-Dibromo-2-(phenoxymethyl)benzene (1b) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.04 g, 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.04 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.11-7.04 (m, 4H), 5.36 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.9, 135.1, 132.6, 131.3, 129.6, 126.8, 121.4, 115.0, 70.3.[2]

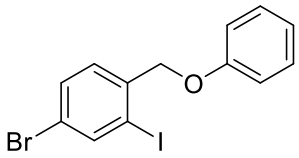


1,4-Dibromo-2-(phenoxymethyl)benzene (1c) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.56 g, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.35-7.31 (m, 3H), 7.03-7.0 (m, 3H),5.08 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 138.6, 134.0, 132.2, 131.7, 129.8, 121.8, 121.6, 120.6, 115.0, 68.8.[2]

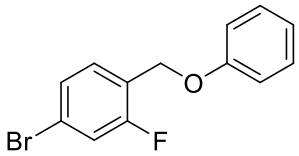


2,4-Dibromo-1-(phenoxymethyl)benzene (1d) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.87 g, 91%. ^{1}H NMR (400 MHz,

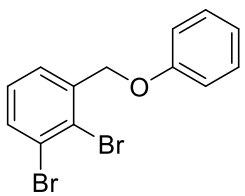
$CDCl_3$) δ 7.76 (d, *J* = 1.7 Hz, 1H), 7.49-7.43 (m, 2H), 7.34 -7.30 (m, 2H), 7.01-6.97 (m, 3H), 5.08 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 135.7, 135.0, 130.9, 130.3, 129.7, 122.7, 122.0, 121.5, 114.9, 68.9.[2]



4-Bromo-2-iodo-1-(phenoxymethyl)benzene (1dB) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.82 g, 78%. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.50 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.32 (td, *J* = 7.5, 1.6 Hz, 2H), 7.02-6.96 (m, 3H), 4.99 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 141.2, 138.5, 131.7, 129.7(4), 129.7(1), 122.2, 121.6, 115.0, 97.3, 73.3. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{10}BrINaO^+$ 410.8857, found 410.8846.

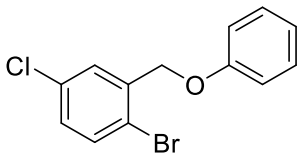


4-Bromo-2-fluoro-1-(phenoxymethyl)benzene (1dC) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 860 mg, 51%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.9 Hz, 1H), 7.34-7.28 (m, 4H), 7.02-6.97 (m, 3H), 5.09 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2 (d, *J* = 249.9 Hz), 158.4, 130.8 (d, *J* = 47.9 Hz), 129.7, 127.8 (d, *J* = 36.3 Hz), 123.7 (d, *J* = 14.4 Hz), 122.1 (d, *J* = 9.4 Hz), 121.5, 119.2 (d, *J* = 24.2 Hz) , 114.9, 63.2 (d, *J* = 4.2 Hz). HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{11}BrFO^+$ 280.9977, found 280.9972.

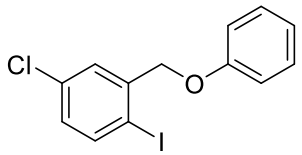


1,2-Dibromo-3-(phenoxymethyl)benzene (1e) was prepared according to GP2, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.23 g, 60%. ^1H NMR (400 MHz,

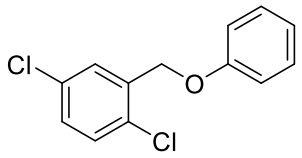
$CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 8.0 Hz , 2H), 7.21 (t, *J* = 7.8 Hz, 1H),7.03 - 6.97(m, 3H), 5.16 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 139.4, 132.9, 129.7, 128.6, 127.2, 125.9, 124.2, 121.5, 115.0, 70.3.[2]



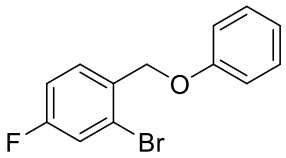
1-Bromo-4-chloro-2-(phenoxymethyl)benzene (1f) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), light yellow solid, 1.70 g, 95%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.5 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.03-6.99 (m, 3H), 5.08 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.2, 138.4, 134.0, 133.7, 129.8, 129.3, 128.8, 121.6, 119.7, 115.0, 68.9.[2]



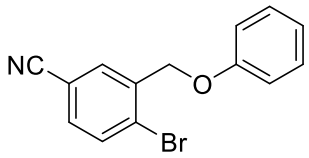
4-Chloro-1-iodo-2-(phenoxymethyl)benzene (1fB) was prepared according to GP2, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.49 g, 72%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.55 (s, 1H), 7.35 - 7.31 (m, 2H), 7.04 - 7.01 (m, 4H), 4.99 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 141.2, 140.2, 135.2, 129.8, 129.7, 128.7, 121.7, 115.0, 93.7, 73.4. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{11}ClIO^+$ 344.9543, found 344.9538.



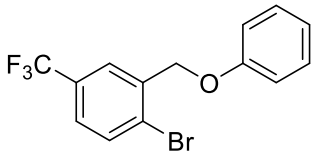
1,4-Dichloro-2-(phenoxymethyl)benzene (1fC) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 896 mg, 59%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.36-7.32 (m, 3H), 7.26-7.23 (m, 1H), 7.04 -7.00 (m, 3H), 5.13 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.3, 136.8, 133.2, 130.5, 130.0, 129.8, 129.0, 128.6, 121.6, 114.9, 66.6. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{11}Cl_2O^+$ 253.0187, found 253.0181.



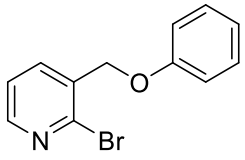
2-Bromo-4-fluoro-1-(phenoxymethyl)benzene (1g) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.23 g, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.53 (m, 1H), 7.37-7.31 (m, 3H), 7.13-6.98 (m, 4H), 5.1 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.0 (d, J = 249.2 Hz), 158.4, 132.4 (d, J = 3.5 Hz), 130.2(d, J = 8.5 Hz), 129.7, 122.5 (d, J = 9.5 Hz), 121.5, 120.0 (d, J = 24.4 Hz), 115.0, 114.8 (d, J = 20.7 Hz), 68.9.[2]



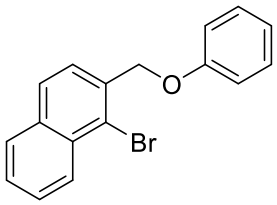
4-Bromo-3-(phenoxymethyl)benzonitrile (1h) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM/EA = 20/1/1), white solid, 1.19 g, 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, J = 0.9 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.47 (dd, J = 8.2, 2.0Hz, 1H), 7.34-7.32 (m, 2H), 7.05-6.99 (m, 3H), 5.11 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.9, 138.6, 133.6, 132.2, 131.8, 129.8, 127.1, 121.9, 118.2, 114.9, 111.9, 68.5.[2]



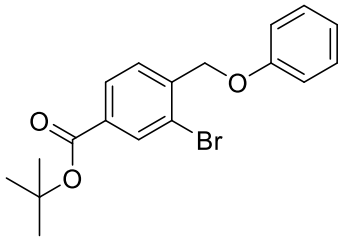
1-Bromo-2-(phenoxymethyl)-4-(trifluoromethyl)benzene (1i) was prepared according to GP2, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.73 g, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.72 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 8.3 Hz , 1H), 7.34 (t, J = 8.0 Hz, 2H),7.04-7.01 (m, 3H), 5.14 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.2, 137.8, 133.2, 130.6 (q, J = 33 Hz), 129.8, 125.9 (q, J = 3.6 Hz), 125.6 (q, J = 3.7 Hz),123.9 (q, J = 270.6 Hz), 121.8, 115.0, 68.9.[2]



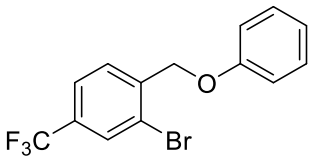
2-Bromo-3-(phenoxymethyl)pyridine (1j) was prepared according to GP2, and purified by flash column chromatography on silica gel (PE/DCM/EA = 10/1/1), white solid, 934 mg, 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.4 Hz 1H), 7.88 (d, *J* = 7.4 Hz, 1H), 7.34-7.29 (m, 3H), 7.02-6.98 (m, 3H), 5.11(s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.0, 149.1, 141.4, 136.9, 134.2, 129.8, 123.1, 121.7, 114.9, 67.9.[2]



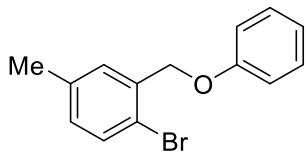
1-Bromo-2-(phenoxymethyl)naphthalene (1k) was prepared according to GP2, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), brown yellow solid, 1.28 g, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.5 Hz, 1H), 7.85-7.82 (m, 2H), 7.70-7.61 (m, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.05-6.99 (m, 3H), 5.40 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.6, 134.8, 134.2, 132.3, 129.7, 128.3, 128.0, 127.7, 127.0, 126.8, 125.6, 122.2, 121.3, 115.0, 70.2.[2]



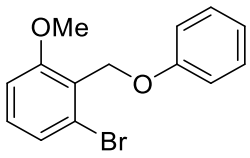
***tert*-Butyl 3-bromo-4-(phenoxymethyl)benzoate (1l)** was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.35 g, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.1, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.01-6.97 (m, 3H), 5.17 (s, 2H), 1.60(s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.3, 158.3, 141.0, 133.6, 133.0, 129.7, 128.6, 128.2, 121.6, 121.5, 115.0, 81.9, 69.1, 28.3. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}BrO_3^+$ 363.0590, found 363.0596.



2-Bromo-1-(phenoxymethyl)-4-(trifluoromethyl)benzene (1m) was prepared according to GP2, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.61 g, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.36-7.32 (m, 2H), 7.04-6.99 (m, 3H), 5.17 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 140.8, 131.4 (q, *J* = 32.9 Hz), 129.8, 129.6 (q, *J* = 3.8 Hz), 128.9, 124.6 (q, *J* = 3.6 Hz), 123.3 (q, *J* = 270.9 Hz), 122.0, 121.7, 115.0, 68.9. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}BrF_3O^+$ 330.9945, found 330.9945.

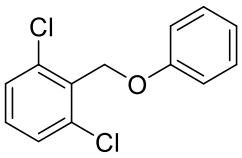


1-Bromo-4-methyl-2-(phenoxymethyl)benzene (1q) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 3.30 g, 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.33 (dd, *J* = 8.8, 7.2 Hz, 2H), 7.03-7.01 (m, 4H), 5.11 (s, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.7, 137.7, 136.0, 132.5, 130.2, 129.8, 129.7, 121.3, 119.1, 115.0, 69.5, 21.2. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}BrO^+$ 277.0228, found 277.0223.

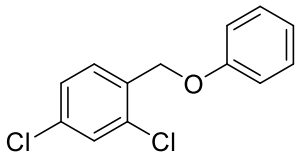


1-Bromo-3-methoxy-2-(phenoxymethyl)benzene (1r) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 2.63 g, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.4, 7.2 Hz, 2H), 7.23 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.20 (s, 2H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.5, 159.4, 130.9, 129.5, 127.3, 125.3, 124.8, 121.0, 115.1, 110.3, 64.4, 56.2. HRMS (ESI–TOF) m/z: $[M+Na]^+$ calcd for $C_{14}H_{13}BrNaO_2^+$ 314.9998,

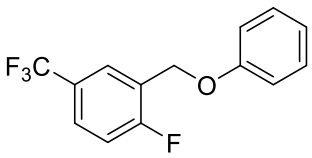
found 314.9997.



1,3-Dichloro-2-(phenoxymethyl)benzene (1t) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.15 g, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 4H), 7.15-7.10 (m, 1H), 7.00-6.93 (m, 3H), 5.21 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.0, 137.2, 132.3, 130.5, 129.6, 128.6, 121.4, 115.1, 65.3.[4]



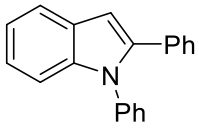
2,4-Dichloro-1-(phenoxymethyl)benzene (1u) was prepared according to GP1, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 714 mg, 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.32 Hz, 1H), 7.38 (d, J = 2.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.24-7.20 (m, 1H), 6.98-6.94 (m, 3H), 5.08 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4, 134.2, 133.6, 133.2, 129.7(3), 129.7(0), 129.3, 127.4, 121.5, 114.9, 66.6. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{11}Cl_2O^+$ 253.0187, found 253.0181.



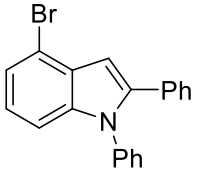
1-Fluoro-2-(phenoxymethyl)-4-(trifluoromethyl)benzene (1iB) was prepared according to GP2, and purified by flash column chromatography on silica gel (PE/DCM = 10/1), white solid, 1.04 g, 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 6.3 Hz, 1H), 7.63 (s, 1H), 7.39-7.35 (m, 2H), 7.22 (t, J = 9.0 Hz, 1H), 7.07-7.04 (m, 3H), 5.18 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.1 (d, J = 251.3 Hz), 158.3, 129.8, 128.9, 127.9, 127.3, 127.2, 127.1(4), 127.1(0), 127.0, 126,9, 125.7, 125.5, 125.2, 122.5, 122.0, 121.7, 116.1 (d, J = 22.3 Hz), 114.9, 63.1 (d, J = 4.1 Hz). HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{11}F_4O^+$ 271.0746, found 271.0741.

4. Synthesis of 3

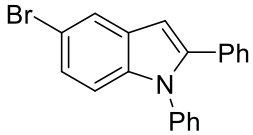
General procedures for the synthesis of 3 (**GP3**): ^{t}BuOK (1.2 mmol, 135 mg) was directly weighted to a dry Schlenk tube and was then subjected to vacuum for 15 min. DMF (1 mL), **1a** (0.5 mmol, 1.0 equiv), and **2a** (0.6 mmol, 1.2 equiv) were added under argon atmosphere. The reaction mixture was stirred at 50 °C and monitored by TLC. When reaction was completed, the reaction mixture was purified by flash column chromatography on silica gel to give the product **3**.



1,2-Diphenyl-1H-indole (3a) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 113 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 5.9, 3.0 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.35–7.17 (m, 11H), 6.81 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 140.9, 139.1, 138.6, 132.6, 129.4, 129.0, 128.4, 128.3, 128.2, 127.4, 127.3, 122.5, 120.8, 120.7, 110.8, 103.8.[5]

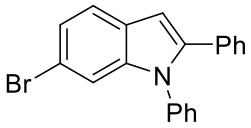


4-Bromo-1,2-diphenyl-indole (3b) was prepared according to GP3 , and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 163 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.35 (m, 4H), 7.29–7.21 (m, 8H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.88 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 139.3, 138.3, 132.0, 129.5, 129.1, 129.0, 128.4, 128.1, 127.8 (two peaks), 123.6, 123.2, 114.5, 110.0, 103.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}BrN^+$ 348.0388, found 348.0381.

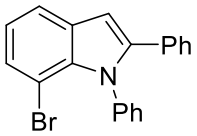


5-Bromo-1,2-diphenyl-indole (3c) was prepared according to GP3, and purified by flash column

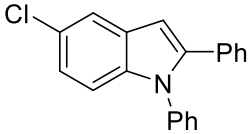
chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 153 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.45–7.36 (m, 3H), 7.26–7.23 (m, 8H), 7.15 (d, *J* = 8.7 Hz, 1H), 6.74 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0, 138.2, 137.8, 132.1, 130.0, 129.5, 129.0, 128.4, 128.0, 127.8, 127.7, 125.2, 123.0, 113.9, 112.2, 103.0.[6]



6-Bromo-1,2-diphenyl-indole (3d) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 146 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.46–7.37 (m, 4H), 7.31–7.24 (m, 8H), 6.78 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 139.9, 138.0, 132.1, 129.6, 129.0, 128.4, 128.1, 127.8, 127.7, 127.2, 124.1, 121.8, 115.9, 113.7, 103.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}BrN^+$ 348.0388, found 348.0380.

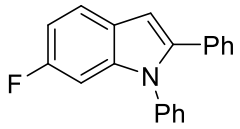


7-Bromo-1,2-diphenyl-indole (3e) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 127 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.38–7.30 (m, 6H), 7.26–7.23 (m, 5H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.75 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 138.4, 135.0, 132.4, 131.3, 131.1, 129.7, 128.6, 128.2, 128.1, 127.8, 121.5, 120.0, 104.5, 103.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}BrN^+$ 348.0388, found 348.0381.

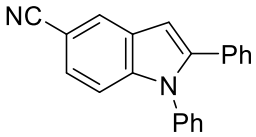


5-Chloro-1,2-diphenyl-1H-indole (3f) was prepared from bromide according to GP3 at 90 ºC, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 122 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.8 Hz, 1H), 7.45–7.35 (m, 3H), 7.26–7.19

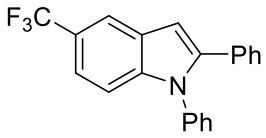
(m, 8H), 7.13 (dd, J = 8.7, 1.9 Hz, 1H), 6.75 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.1, 138.2, 137.5, 132.1, 129.5, 129.3, 129.0, 128.4, 128.0, 127.8, 127.7, 126.3, 122.6, 119.9, 111.8, 103.2.[7]



6-Fluoro-1,2-diphenyl-indole (3g) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 89 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.6, 5.4 Hz, 1H), 7.46–7.43 (m, 2H), 7.40–7.36 (m, 1H), 7.27–7.24 (m, 7H), 7.01–6.93 (m, 2H), 6.79 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3 (d, J = 236.9 Hz), 141.4 , 139.3, 139.2, 138.3, 132.4, 129.6, 128.9, 128.3, 127.9, 127.6, 127.5, 124.8, 121.4 (d, J = 10.0 Hz), 109.6, 109.4, 103.6, 97.3 (d, J = 26.9 Hz).[8]



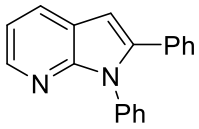
1,2-Diphenyl-1H-indole-5-carbonitrile (3h) was prepared according to GP3 at 90 ºC, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 122 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.43-7.34 (m, 4H), 7.24-7.18 (m, 8H), 6.80 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 143.3, 140.5, 137.5, 131.5, 129.7, 129.1, 128.5, 128.2, 128.1, 128.0, 126.1, 125.3, 120.8, 111.6, 103.8.[9]



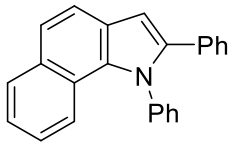
1,2-Diphenyl-5-(trifluoromethyl)-indole (3i) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 155 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.46–7.39 (m, 4H), 7.33 (d, J = 8.7 Hz, 1H), 7.26–7.23 (m, 7H), 6.87 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.7, 140.3, 138.0, 131.9, 129.6, 129.1, 128.4, 128.1, 128.0, 127.9, 127.7, 125.4 (q, J = 269.6 Hz), 123.2 (q, J = 32.1 Hz), 119.1 (q, J = 3.4 Hz), 118.4 (q, J = 4.2 Hz), 110.9, 104.1. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{15}F_3N^+$ 338.1157, found

338.1151.

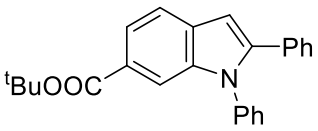
142.7, 140.3, 138.0, 131.9, 129.6, 129.1, 128.4, 128.1, 128.0, 127.9, 127.7, ,125.4 (q, J = 269.6 Hz), 123.2 (q, J = 32.1 Hz), 119.1 (q, J = 3.4 Hz), 118.4 (q, J = 4.2 Hz), 111.0, 104.2.



1,2-Diphenyl-1H-pyrrolo[2,3-b]pyridine (3j) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), yellow solid, 130 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 4.7 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.33 (t, J = 7.4 Hz, 3H), 7.26–7.24 (m, 5H), 7.14-7.11 (m, 1H), 6.72 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.1, 143.8, 141.2, 137.2, 132.3, 129.2, 129.1, 128.5, 128.4, 127.9, 127.5, 121.0, 117.2, 101.5.[10]

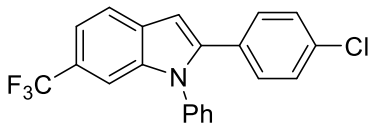


1,2-Diphenyl-1H-benzo[g]indole (3k) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), yellow solid, 111 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.48–7.40 (m, 5H), 7.32–7.10 (m, 8H), 6.88 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.8, 140.6, 133.0, 132.0, 131.8, 130.0, 129.6 (two peaks), 129.2, 128.9, 128.1, 127.3, 125.2, 125.0, 123.5,122.9, 122.1, 120.9, 120.6, 104.8.[11]

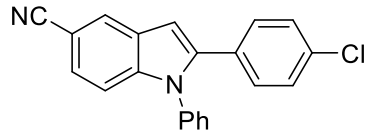


***tert*-Butyl 1,2-diphenyl-1H-indole-6-carboxylate (3l)** was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 85 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (s, 1H), 7.82 (dd, J = 8.3, 1.4 Hz, 1H), 7.66 (dd, J = 8.3 Hz, 1H), 7.44-7.34 (m, 3H), 7.26-7.24 (m, 7H), 6.82 (s, 1H),1.59 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.0, 143.7, 138.6, 138.0, 132.1, 131.7, 129.6, 129.1, 128.4, 128.2, 127.9, 127.7, 125.9, 121.8, 119.9,

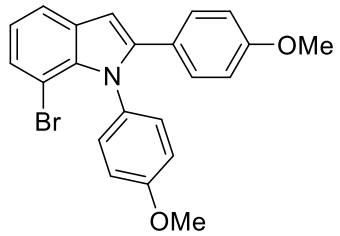
113.0, 103.8, 80.7, 28.4.[12]



2-(4-Chlorophenyl)-1-phenyl-6-(trifluoromethyl)-1H-indole (3m) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 74 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76(d, *J* = 8.3 Hz, 1H), 7.52–7.42 (m, 5H), 7.26-7.19 (m, 6H), 6.85 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.2, 138.2, 137.6, 134.2, 130.5, 130.4, 130.3, 129.9, 128.7, 128.2, 128.1, 126.6, 124.8, 124.5, 123.9, 121.1, 117.6 (q, *J* = 3.5 Hz), 108.4 (q, *J* = 4.4 Hz), 103.9. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{14}ClF_3N^+$ 372.0763, found 372.0767.

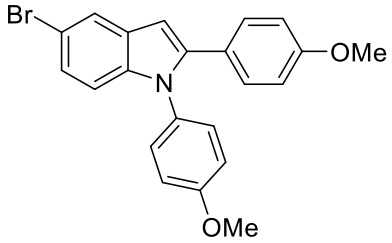


2-(4-Chlorophenyl)-1-phenyl-1H-indole-5-carbonitrile (3n) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 44 mg, 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.53-7.46 (m, 3H), 7.43 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.33-7.28 (m, 4H), 7.24-7.19 (m, 3H), 6.87 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.0, 140.6, 137.2, 134.4, 130.2, 130.0, 129.9, 128.8, 128.5, 128.0 (two peaks), 126.2, 125.5, 120.6, 111.7, 104.1, 104.0. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{14}ClN_2^+$ 329.0846, found 329.0839.

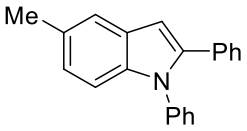


7-Bromo-1,2-bis(4-methoxyphenyl)-1H-indole (3o) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 139 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.34 (dd, *J* = 7.6, 0.7 Hz, 1H), 7.22-7.16

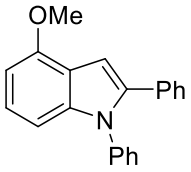
(m, 4H), 6.99 (t, J = 7.7 Hz, 1H), 6.88-6.84 (m, 2H), 6.78-6.75 (m, 2H), 6.66 (s, 1H), 3.84 (s, 3H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 159.2, 143.6, 135.0, 132.2, 131.2, 131.1, 130.9, 127.4, 124.9, 121.3, 119.7, 113.6, 113.3, 104.4, 102.7, 55.5, 55.3.HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}BrNO_2^+$ 408.0599, found 408.0593.



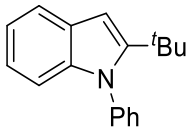
5-Bromo-1,2-bis(4-methoxyphenyl)-1H-indole (3p) was prepared according to GP3 at 90 ºC, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 143 mg, 70%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 1.9 Hz, 1H), 7.22-7.17 (m, 3H), 7.16-7.12 (m, 2H), 7.05 (d, J = 8.7 Hz, 1H), 6.96-6.92 (m, 2H), 6.81-6.77 (m, 2H), 6.63 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.2, 158.8, 142.1, 138.0, 131.0, 130.3, 129.9, 129.2, 124.7, 122.7, 114.7, 113.9, 113.7, 112.1, 101.6, 55.6, 55.3. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{18}BrNNaO_2^+$ 430.0419, found 430.0422.



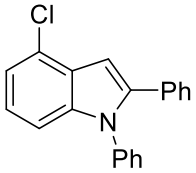
5-methyl-1,2-diphenyl-1H-indole (3q) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 65.2 mg, 46%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.42-7.38 (m, 2H), 7.35-7.30 (m, 1H), 7.27-7.18 (m, 8H), 7.00 (dd, J = 8.4, 1.6 Hz, 1H), 6.72 (s, 1H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.9, 138.8, 137.6, 132.8, 130.1, 129.4, 129.0, 128.6, 128.3, 128.1, 127.3, 127.2, 124.0, 120.3, 110.4, 103.4, 21.5.[13]



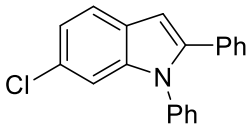
4-methoxy-1,2-diphenyl-1H-indole (3r) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 95.4 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.25-7.21 (m, 7H), 7.10 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 1H), 4.00 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.4, 140.5, 139.5, 138.8, 132.7, 129.4, 128.9, 128.3, 128.2, 127.4, 127.2, 123.2, 119.0, 104.2, 101.0, 100.6, 55.6.[14]



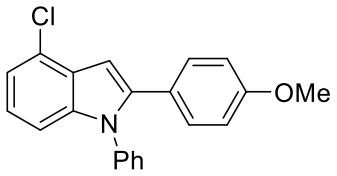
2-(tert-butyl)-1-phenyl-1H-indole (3s) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 62.9 mg, 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.50-7.49 (m, 3H), 7.38-7.36 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.47 (s, 1H), 1.26 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.8, 141.0, 140.4, 130.9, 129.1, 128.7, 127.0, 121.3, 119.9, 119.7, 110.3, 99.3, 33.4, 31.2.[13]



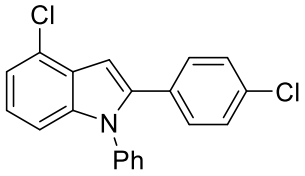
4-Chloro-1,2-diphenyl-1H-indole (3t) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 128 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.36 (m, 4H), 7.31–7.27 (m, 5H), 7.25 (d, *J* = 2.7 Hz, 1H), 7.20-7.17 (m, 2H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.92 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.5, 139.7, 138.3, 132.1, 129.5, 129.1, 128.4, 128.1, 127.8 (two peaks), 127.2, 125.9, 122.9, 120.5, 109.4, 102.1. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}ClN^+$ 304.0893, found 304.0891.



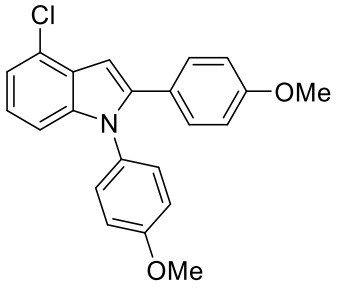
6-Chloro-1,2-diphenyl-1H-indole (3u) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 108 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.4 Hz, 1H), 7.47–7.36 (m, 4H), 7.27 (d, *J* = 1.9 Hz, 1H), 7.25-7.23 (m, 6H), 7.15 (dd, *J* = 8.4,1.8 Hz, 1H), 6.78 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.6, 139.5, 138.1, 132.2, 129.6, 129.0, 128.4, 128.3, 128.1, 127.7 (two peaks), 126.9, 121.5, 110.8, 103.6.HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{15}ClN^+$ 304.0888, found 304.0893.



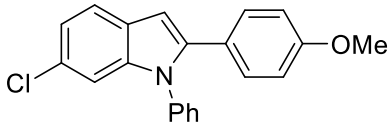
4-Chloro-2-(4-methoxyphenyl)-1-phenyl-1H-indole (3v) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 129 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 –7.36 (m, 3H), 7.26 –7.15 (m, 6H), 7.07 (t, *J* = 7.9 Hz, 1H), 6.85 (s, 1H), 6.82-6.78 (m, 2H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 141.5, 139.6, 138.4, 130.3, 129.5, 128.2, 127.7, 127.2, 125.6, 124.5, 122.6, 120.4, 113.9, 109.3, 101.1, 55.3. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}ClNO^+$ 334.0999, found 334.0993.



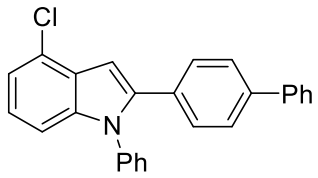
4-Chloro-2-(4-chlorophenyl)-1-phenyl-1H-indole (3w) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 161 mg, 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 –7.38 (m, 3H), 7.24 –7.15 (m, 8H), 7.10 (t, *J* = 7.8 Hz, 1H), 6.91 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 140.2, 139.8, 138.0, 133.9, 130.6, 130.2, 129.7, 128.7, 128.1, 128.0, 127.1, 126.0, 123.2, 120.6, 109.5, 102.3. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{14}Cl_2N^+$ 338.0503, found 338.0497.



4-Chloro-1,2-bis(4-methoxyphenyl)-1H-indole (3x) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 107 mg, 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.17 –7.15 (m, 3H), 7.10-7.03 (m, 2H), 6.96-6.93 (m, 2H), 6.80 (d, *J* = 8.5 Hz, 3H), 3.86 (s, 3H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.3, 158.9, 141.6, 139.9, 131.1, 130.3, 129.3, 127.1, 125.6, 124.6, 122.4, 120.2, 114.7, 113.9, 109.3, 100.6, 55.6, 55.3. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}ClNO_2^+$ 364.1104, found 364.1100.

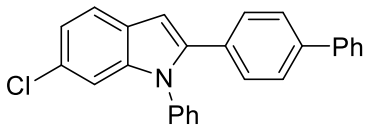


6-Chloro-2-(4-methoxyphenyl)-1-phenyl-1H-indole (3y) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 107 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.4 Hz, 1H), 7.46 –7.36 (m, 3H), 7.24-7.22 (m, 3H), 7.19-7.15 (m, 2H), 7.13 (dd, *J* = 8.4, 1.4 Hz, 1H), 6.80 - 6.76 (m, 2H), 6.69 (s, 1H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.2, 141.6, 139.3, 138.2, 130.2, 129.6, 128.1, 127.9, 127.7, 127.0, 124.7, 121.4, 121.2, 113.9, 110.6, 102.7, 55.3. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}ClNO^+$ 334.0999, found 334.0991.

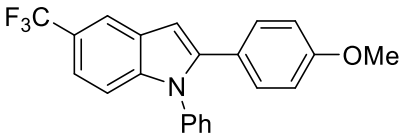


2-([1,1'-Biphenyl]-4-yl)-4-chloro-1-phenyl-1H-indole (3z) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 169 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.57 (m, 2H), 7.52–7.40 (m, 7H), 7.39-7.28 (m, 5H), 7.22-7.18 (m, 2H), 7.12-7.09 (m, 1H), 6.99 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.1,

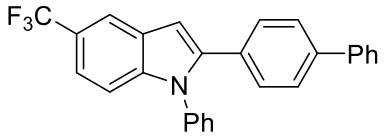
140.4 (two peaks), 139.9, 138.3, 130.9, 129.6, 129.4, 128.9, 128.2, 127.8, 127.6, 127.2, 127.1, 127.0, 125.9, 123.0, 120.5, 109.4, 102.1. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{19}ClN^+$ 380.1206, found 380.1191.



2-([1,1'-Biphenyl]-4-yl)-6-chloro-1-phenyl-1H-indole (3Za) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), yellow solid, 129 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (m, 3H), 7.51–7.39 (m, 7H), 7.36-7.28 (m, 6H), 7.16 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.83 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.2, 140.4, 140.3, 139.7, 138.2, 131.1, 129.7, 129.2, 128.9, 128.4, 128.1, 127.8, 127.6, 127.1, 127.0, 126.9, 121.5 (two peaks), 110.8, 103.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{19}ClN^+$ 380.1206, found 380.1194.

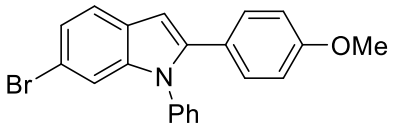


2-(4-Methoxyphenyl)-1-phenyl-5-(trifluoromethyl)-1H-indole (3Zb) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 165 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.48–7.38 (m, 4H), 7.31 (d, *J* = 8.6 Hz, 1H), 7.26–7.18 (m, 4H), 6.82–6.79 (m, 3H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.4, 142.6, 140.1, 138.1, 130.4, 129.6, 128.1, 127.9, 127.8, 126.8, 124.4, 124.1, 123.1 (q, *J* = 31.5 Hz), 118.7 (q, *J* = 2.6 Hz), 118.1 (q, *J* = 3.2 Hz), 113.9, 110.9, 103.3, 55.4. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}F_3NO^+$ 368.1262, found 368.1263.

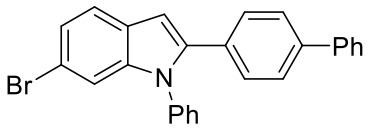


2-([1,1'-Biphenyl]-4-yl)-1-phenyl-5-(trifluoromethyl)-1H-indole (3Zc) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1),

white solid, 182 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.59 –7.57 (m, 2H), 7.52–7.41 (m, 8H), 7.37– 7.29(m, 6H), 6.93 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 142.3, 140.4(5), 140.4(4), 140.4(0), 130.8, 129.7, 129.4, 129.0, 128.1, 128.0, 127.7(4), 127.7(0), 127.1, 124.3 (q, J = 123.1 Hz), 119.1 (q, J = 3.3 Hz), 118.4 (q, J = 4.0 Hz), 111.0, 104.2. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{19}F_3N^+$ 414.1470, found 414.1470.



6-Bromo-2-(4-methoxyphenyl)-1-phenyl-1H-indole (3Zd) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), white solid, 138 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.4 Hz, 1H), 7.46 –7.36 (m, 4H), 7.28-7.22 (m, 3H), 7.17 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.69 (s, 1H), 3.78 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 159.2, 141.5, 139.7, 138.1, 130.2, 129.6, 128.1, 127.7, 127.3, 124.6, 123.9, 121.6, 115.5, 113.9, 113.6, 102.7, 55.3. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}BrNO^+$ 378.0494, found 378.0489.



2-([1,1'-Biphenyl]-4-yl)-6-bromo-1-phenyl-1H-indole (3Ze) was prepared according to GP3, and purified by flash column chromatography on silica gel (PE/DCM/EA = 200/1/1~50/1/1), yellow solid, 174 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, J = 7.5 Hz, 3H), 7.51 –7.39 (m, 8H), 7.36 –7.28 (m, 6H), 6.83 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 141.2, 140.4, 140.3, 140.0, 138.1, 131.0, 129.7, 129.2, 128.9, 128.1, 127.9, 127.6, 127.2, 127.0 (two peaks), 124.1, 121.9, 116.0, 113.7, 103.7. HRMS (ESI–TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{19}BrN^+$ 424.0701, found 424.0699.

5. References

[1] Makhija, M.-T.; Kasliwal, R.-T.; Kulkarni, V.-M.; Neamati, N. *Bioorgan. Med. C**hem***. **2004**, *12*, 2317.

[2] Zheng, H.-X.; Shan, X.–H.; Qu, J.-P.; Kang, Y.–B. *Org. Lett.* **2018**, *20*, 3310.

[3] Courchay, F.-C.; Sworen, J.-C.; Ghiviriga, I.; Abboud, K.-A.; Wagener, K.-B. *Organometallics*, **2006**, *25*, 6074.

[4] Forrester, J.; Jones, R.-V.-H.; Newton, L.; Preston, P.-N. T*etrahedron*, **2001**, *57*, 2871.

[5] Tussing, S.; Ohland, M.; Wicker, G.; Flörke, U.; Paradies, J. Dalto*n T*. **2017**, *46*, 1539.

[6] Sharma, U.; Kancherla, R.; Naveen, T.; Agasti, S.; Maiti, D. *Angew. Chem., Int. Ed*. **2014**, *53*, 11895.

[7] Li, P.-F.; Weng, Y.-X.; Xu, X.-X.; Cui, X.-L. *J. Org. Chem.* **2016**, *81*, 3994.

[8] Crawford, S.-M.; Lavery, C.-B.; Stradiotto, M. *Chem.-Eur. J*. **2013**, *19*, 16760.

[9] Gao, J.-L.; Shao, Y.-Y.; Zhu, J.-Y.; Zhu, J.-Q.; Mao, H.; Wang, X.-X.; Lv X. *J. Org. Chem.* **2014**, *79*, 9000.

[10] Chesnokov, G.-A.; Ageshina, A.-A.; Topchiy, M.-A.; Nechaev, M.-S.; Asachenko, A.-F. *Eur. J. Org. Chem*. **2019**, *2019*, 4844.

[11] Barluenga, J.; Jiménez-Aquino, A.; Aznar, F.; Valdes, C. Ch*em.-Eur. J*. **2010**, *16*, 11707.

[12] Barluenga, J.; Jimenez-Aquino, A.; Aznar, F.; Valdes, C. *J. Am. Chem. Soc.* **2009**, *131*, 4031.

[13] José, B; Agustín, J.-A.; Fernando, A; Carlos, V. *J. Am. Chem. Soc.* **2009**, *131*, 4031.

[14] Gleb, A.-C.; Alexandra, A.-A.; Maxim, A.-T.; Mikhail, S.-N.; Andrey, F.-A. *Eur. J. Org. Chem.* **2019**, *30*, 4844.

6. NMR spectra

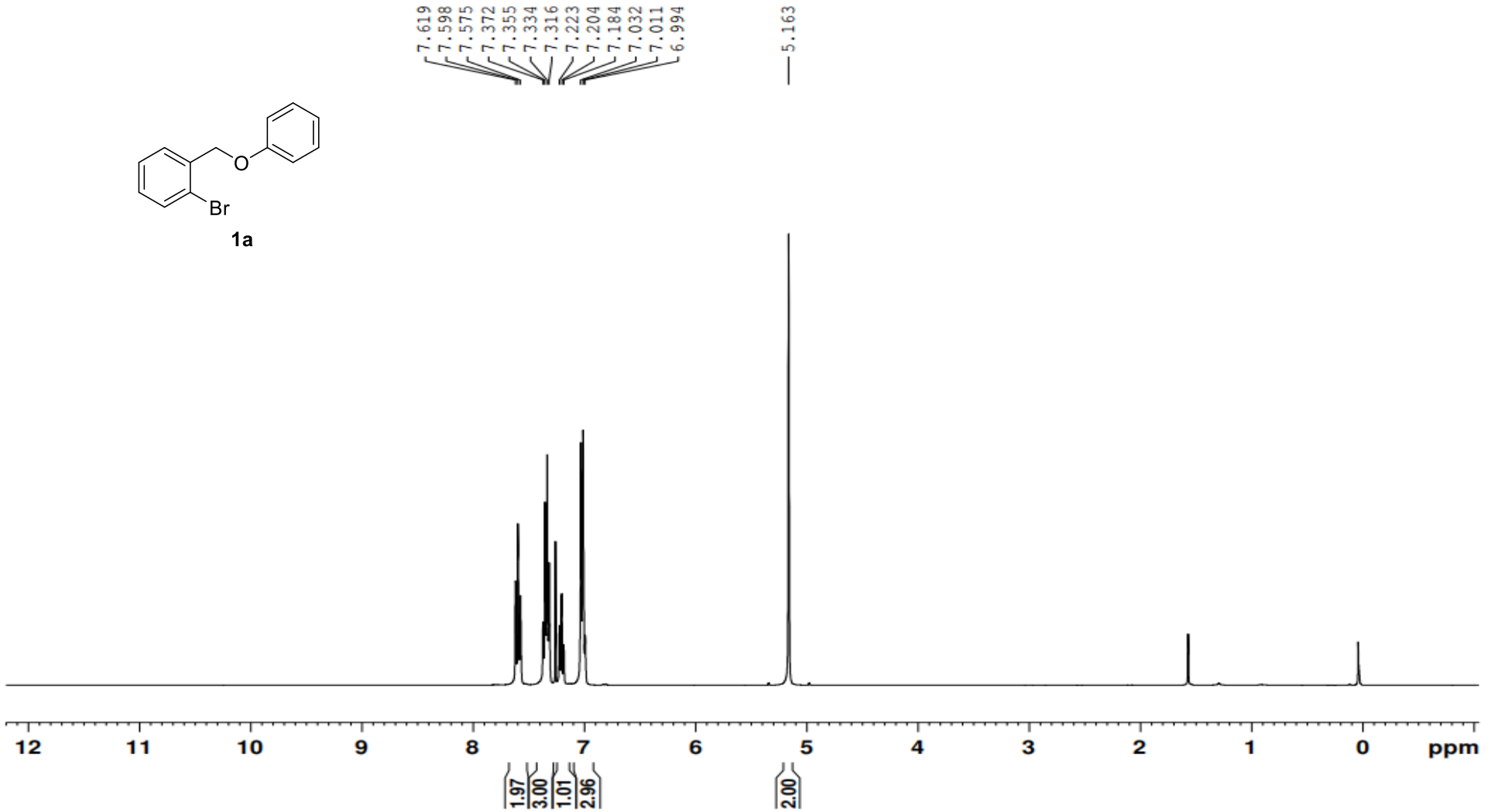


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1a.**

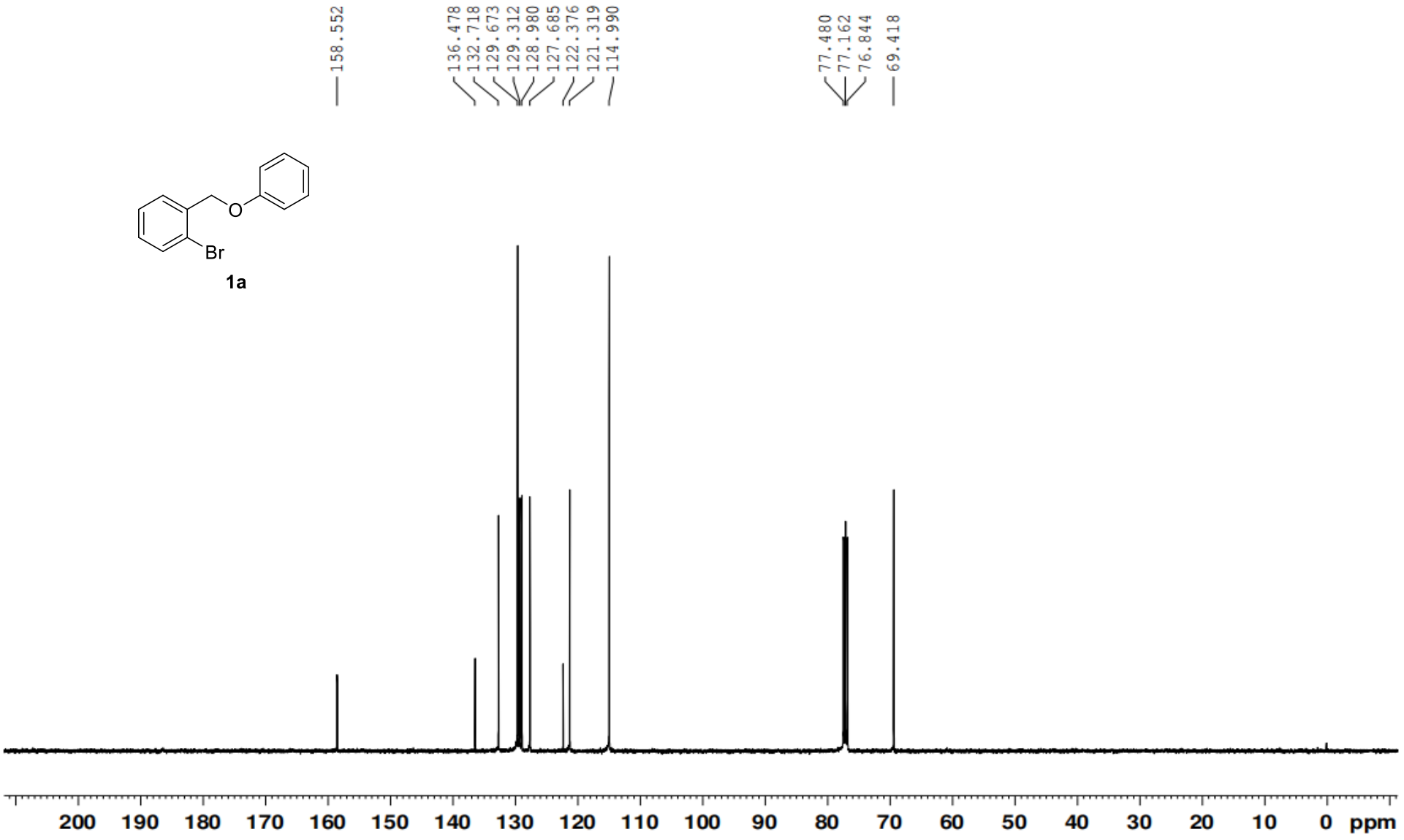


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1a.**

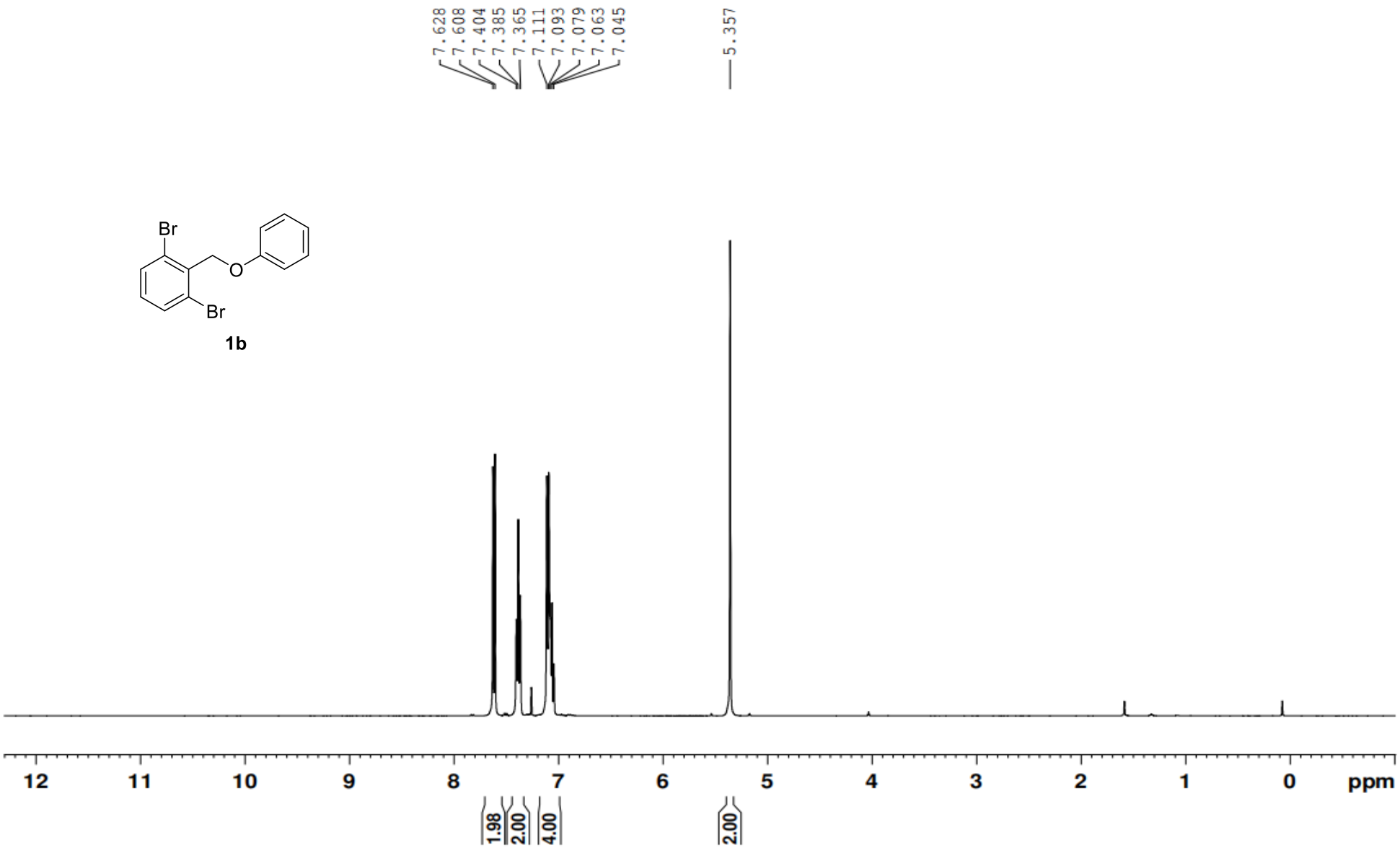


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1b.**

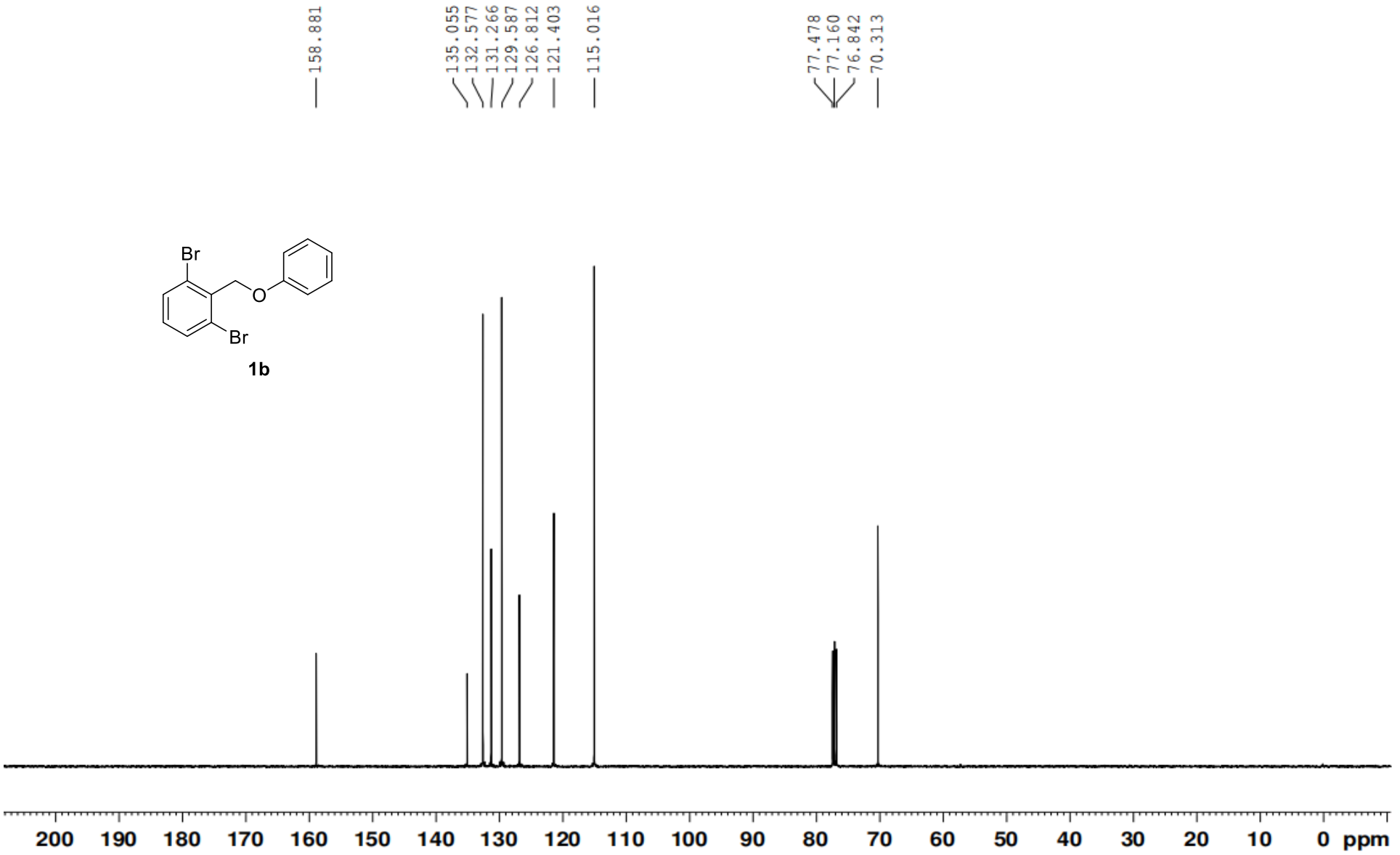


Figure S4. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1b.**

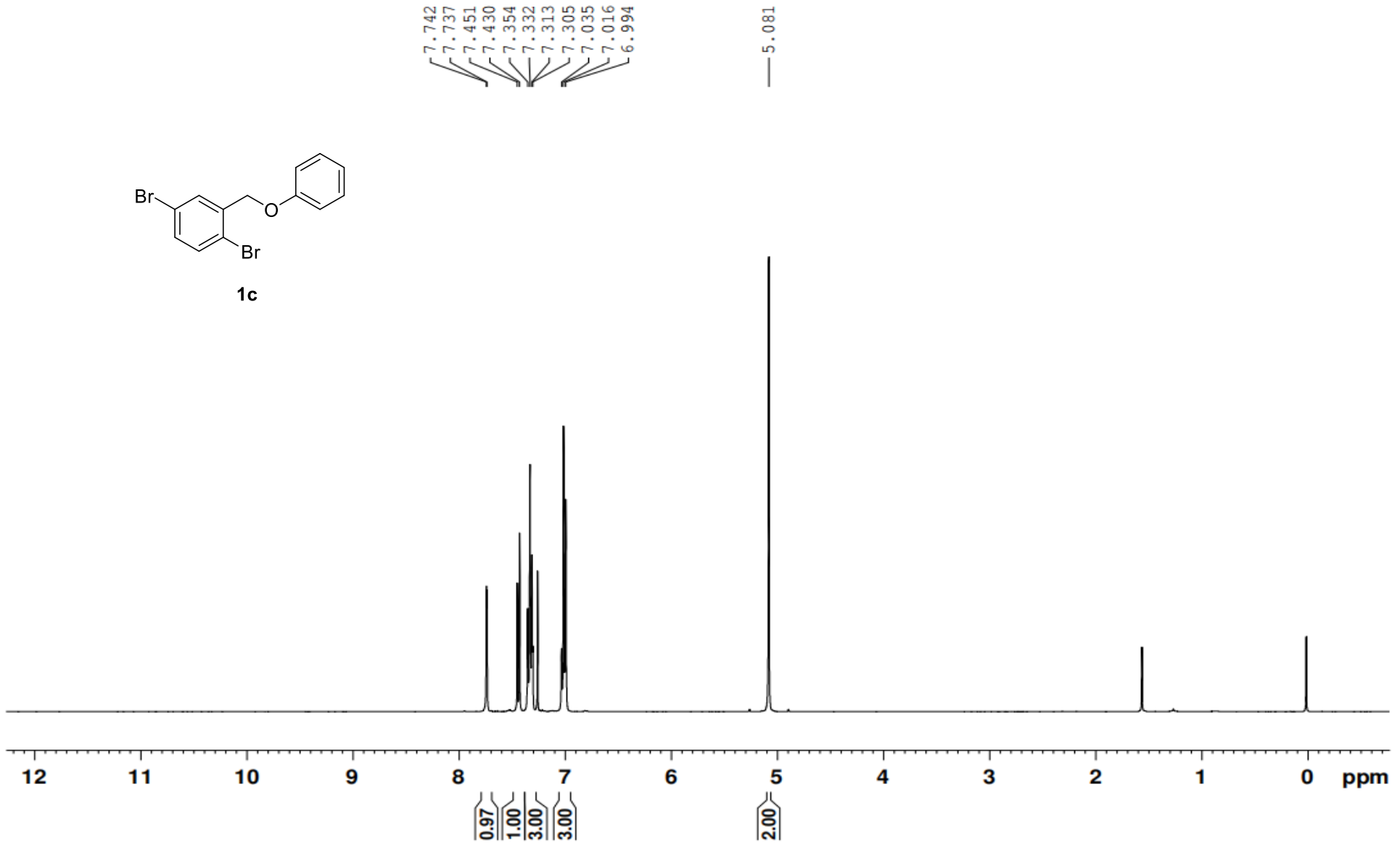


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1c.**

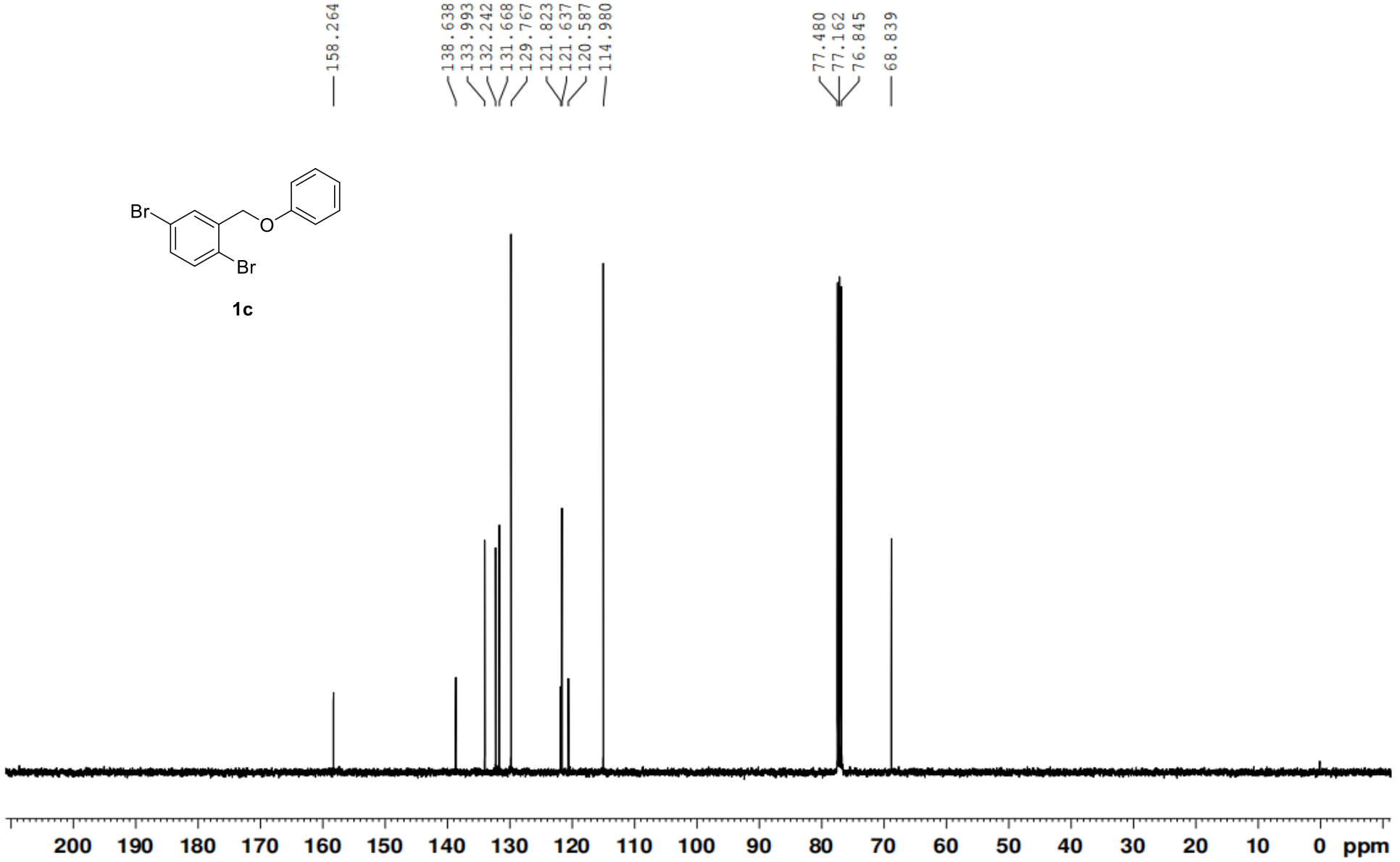


Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1c.**

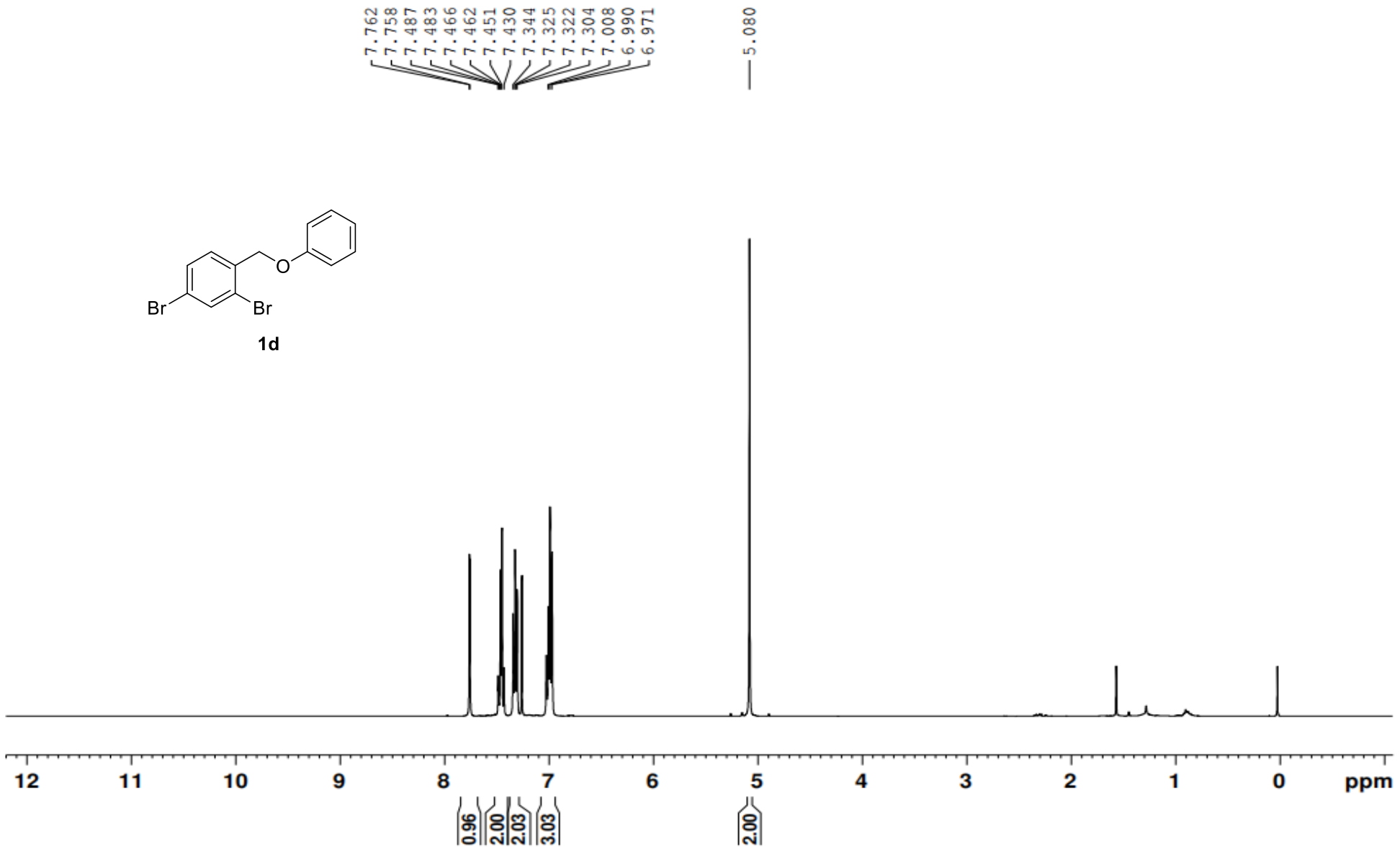


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1d.**

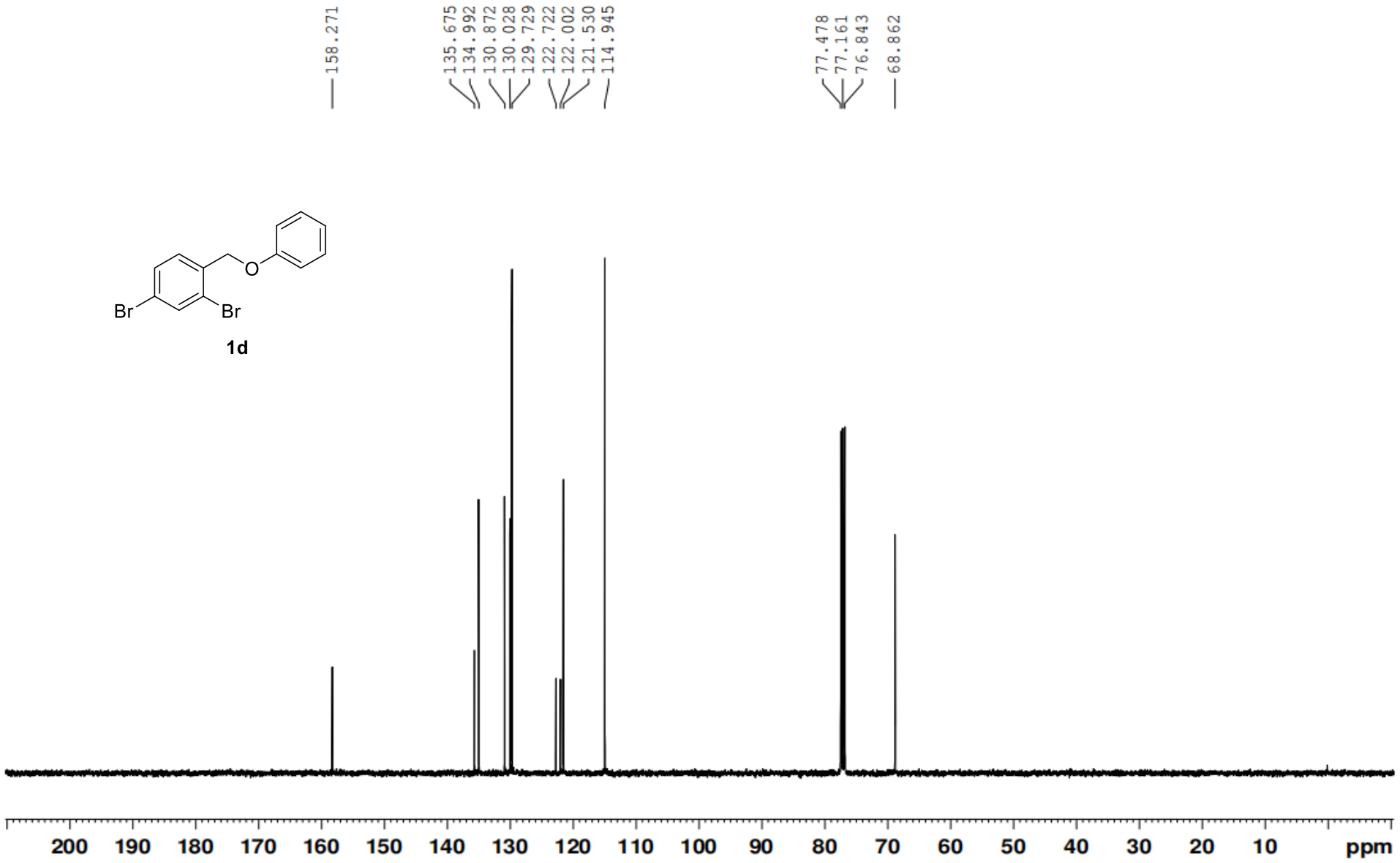


Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1d.**

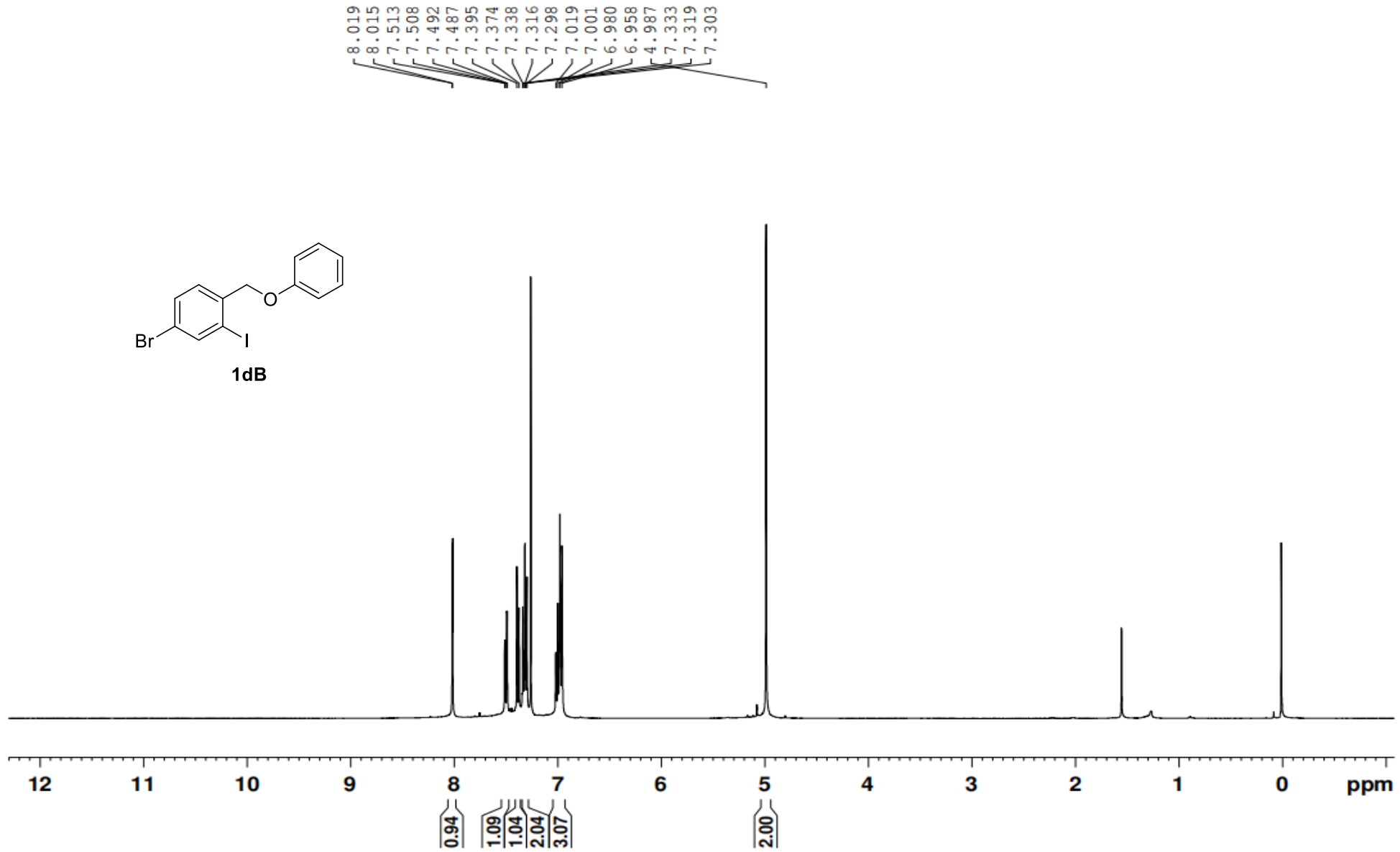


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1dB.**

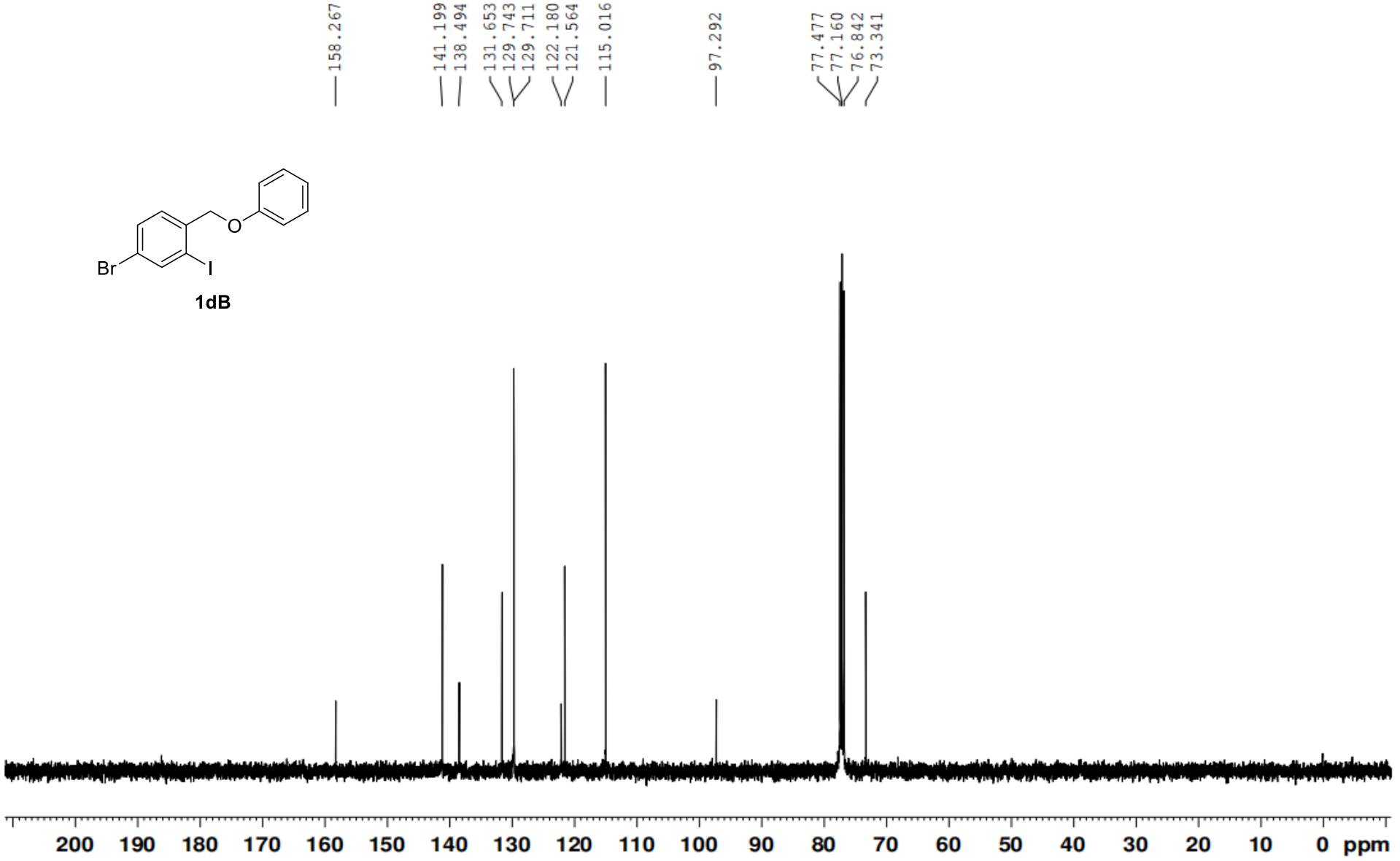


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1dB.**

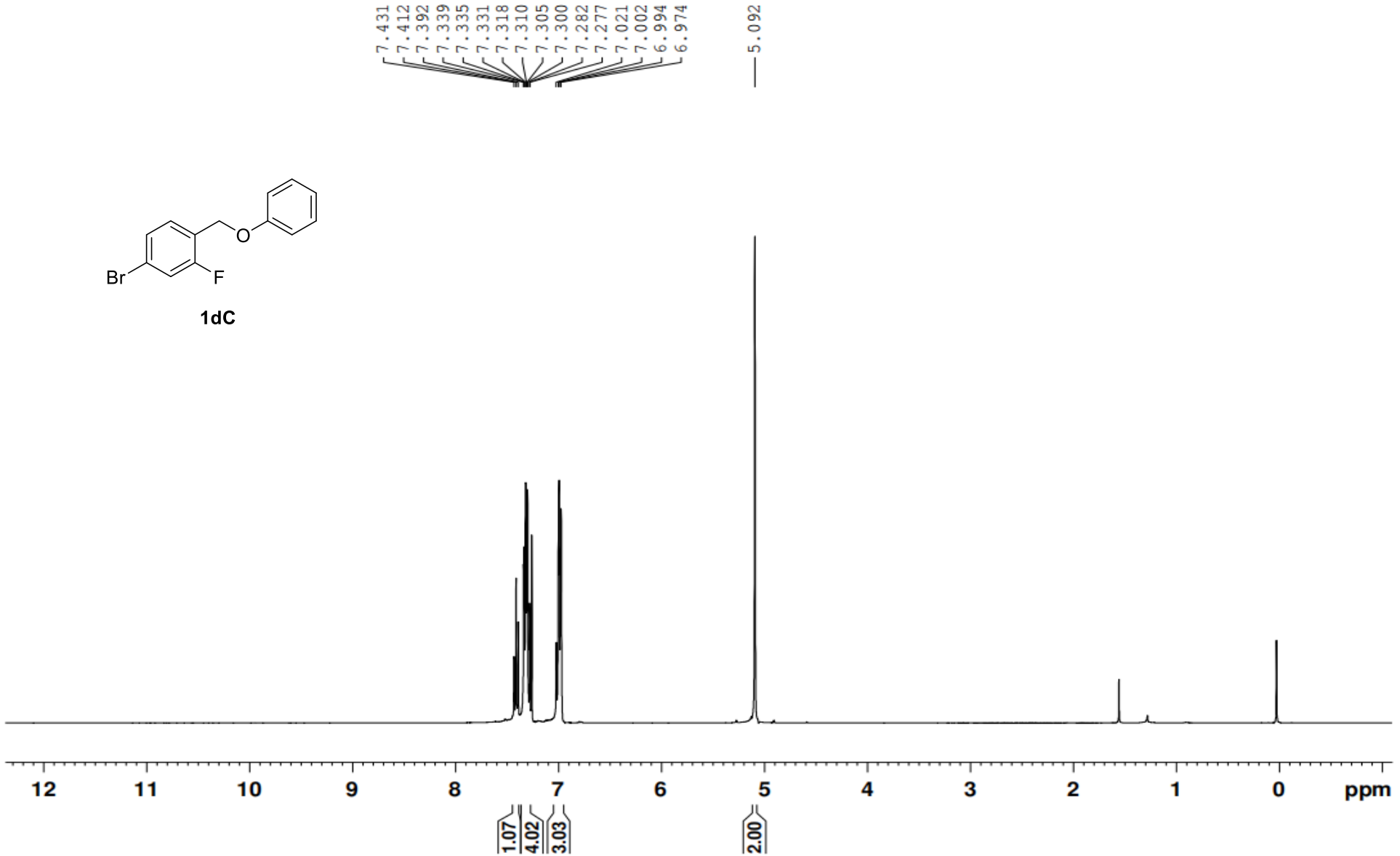


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1dC.**

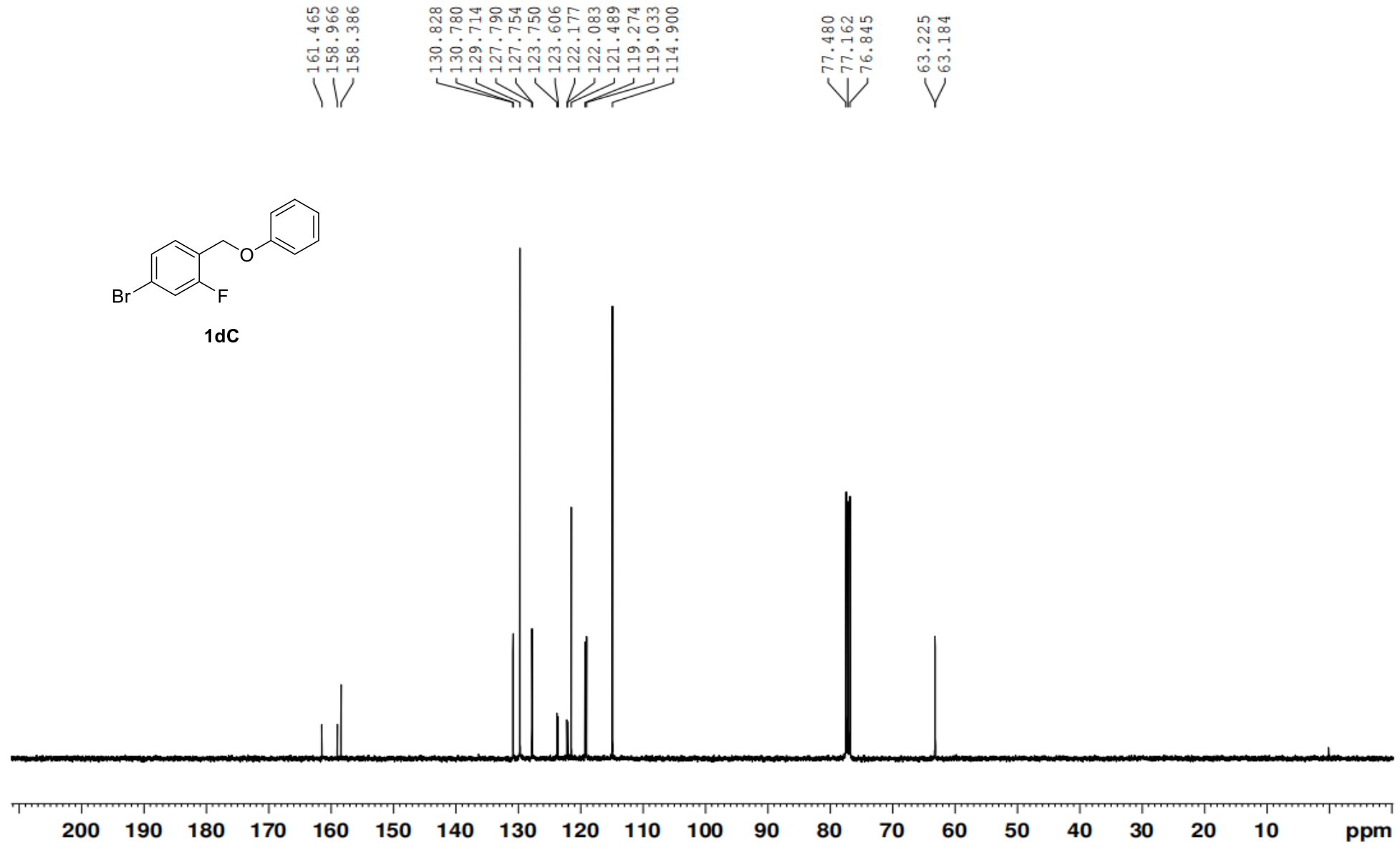


Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1dC.**

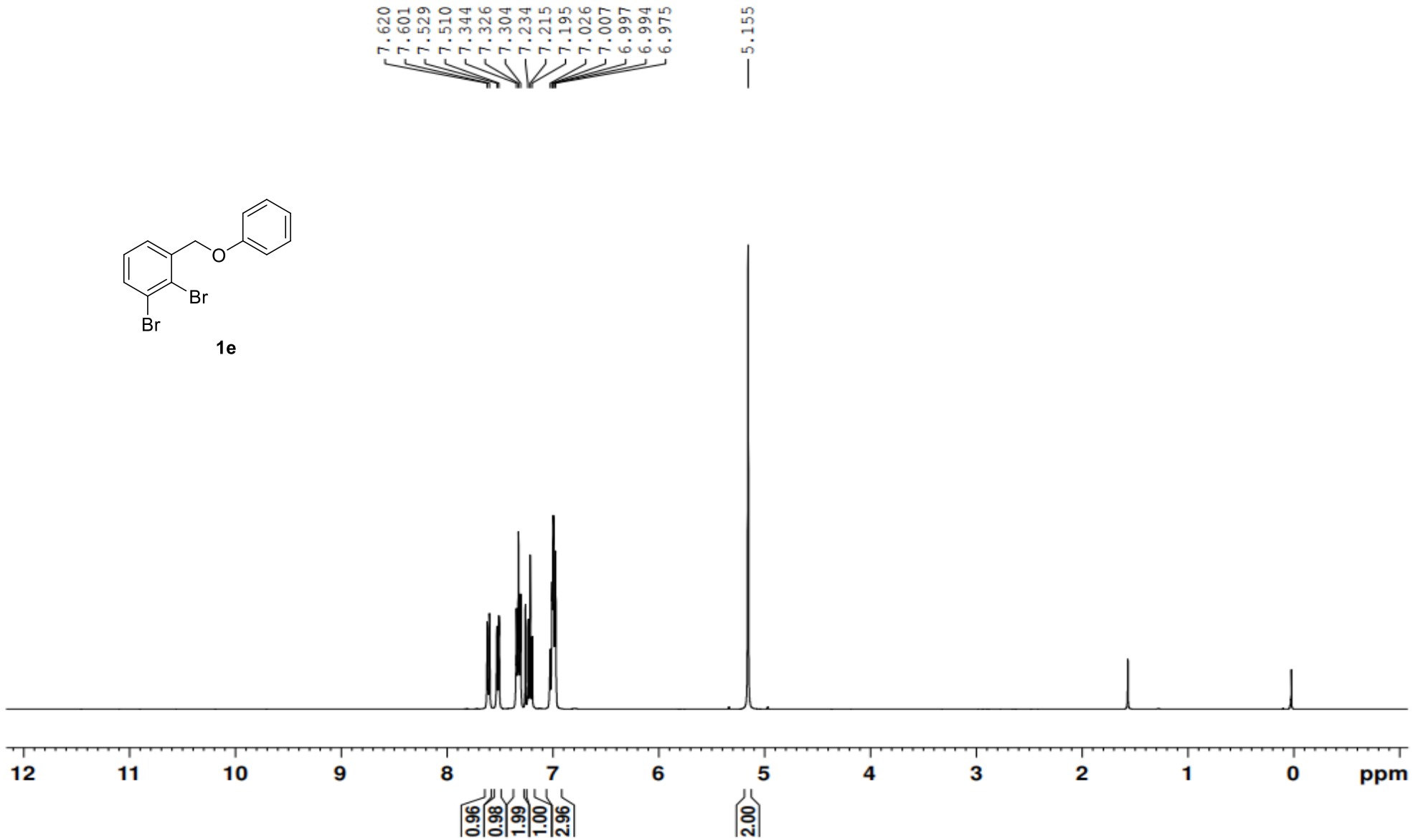


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1e.**

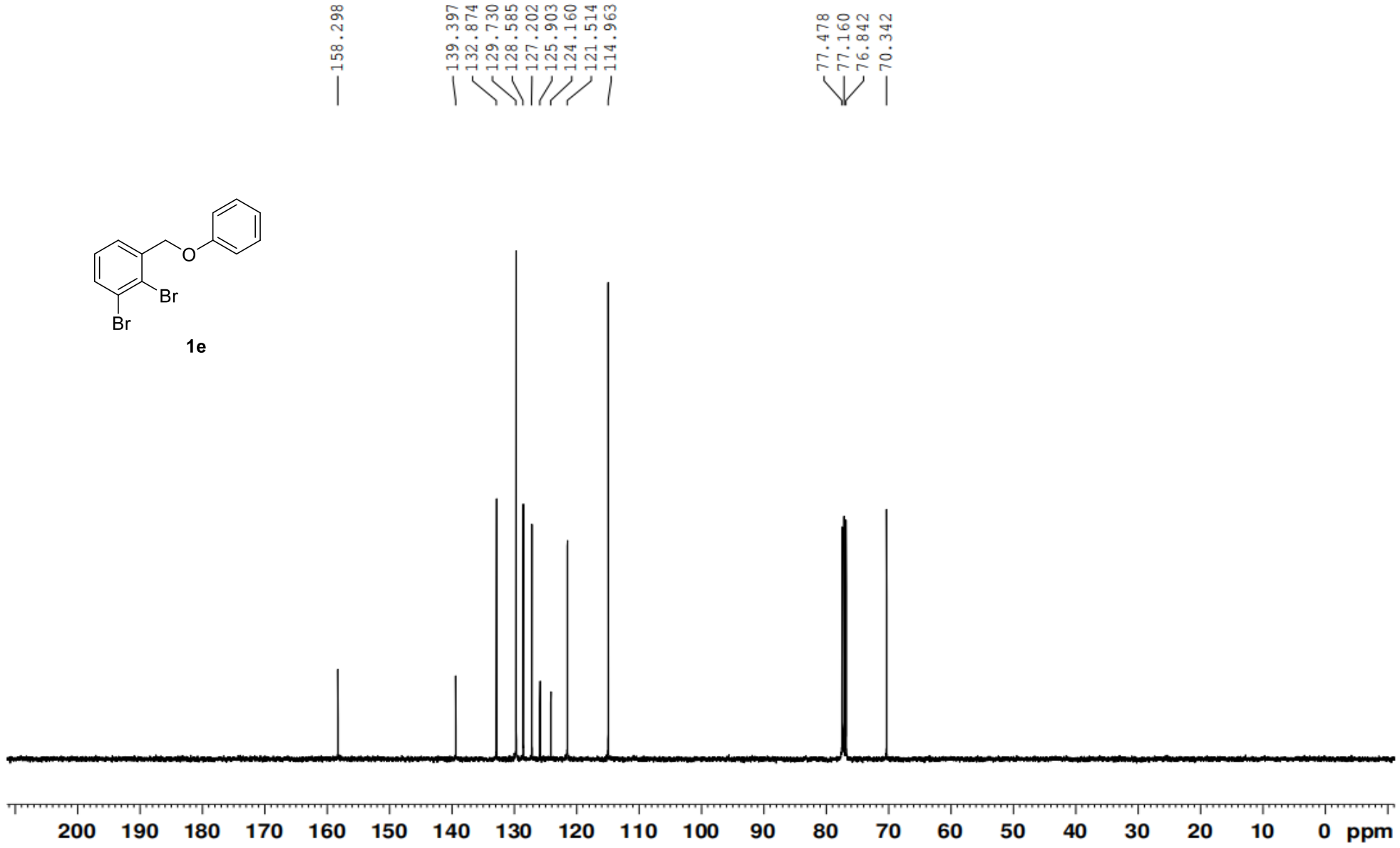


Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1e.**

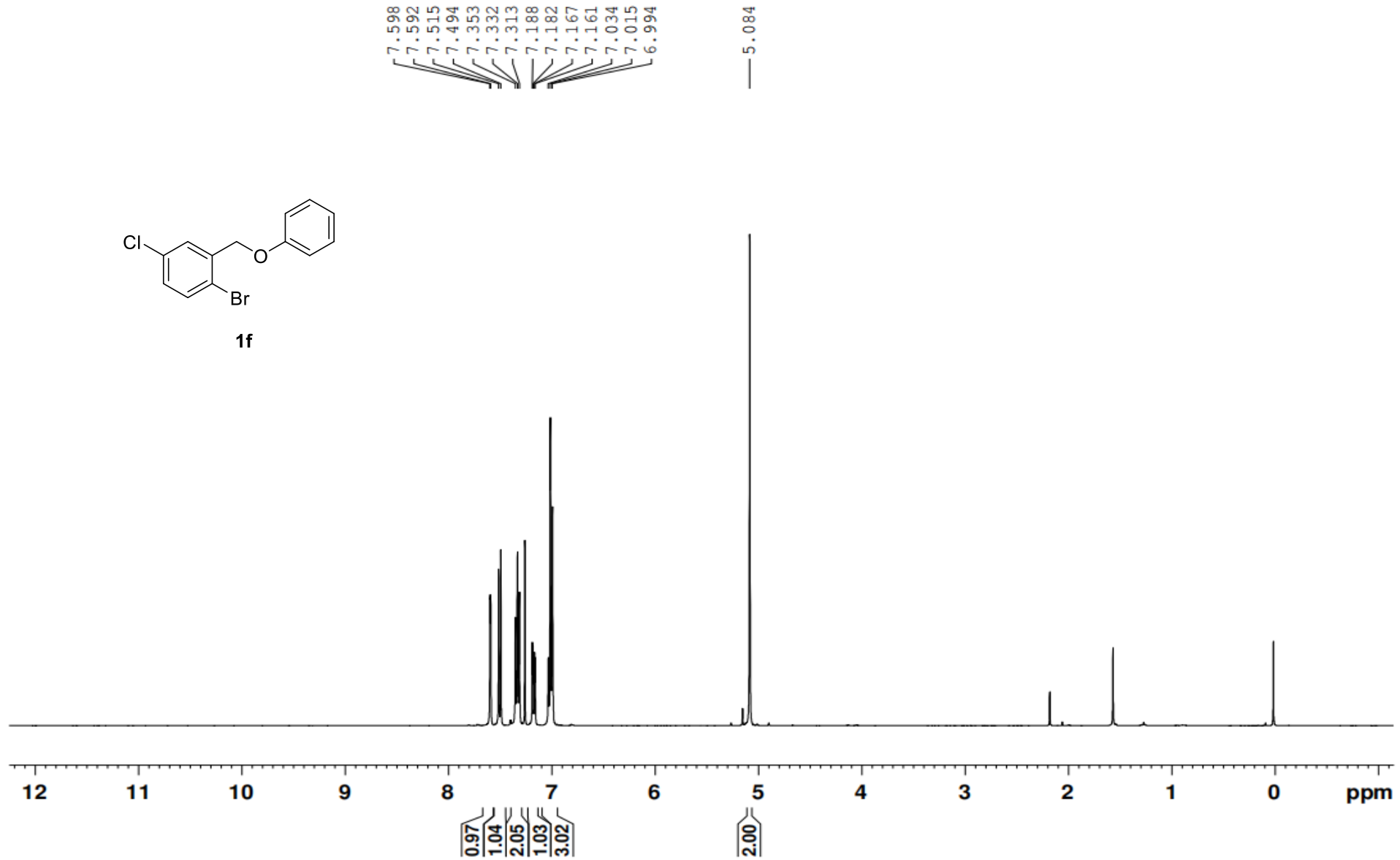


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1f.**

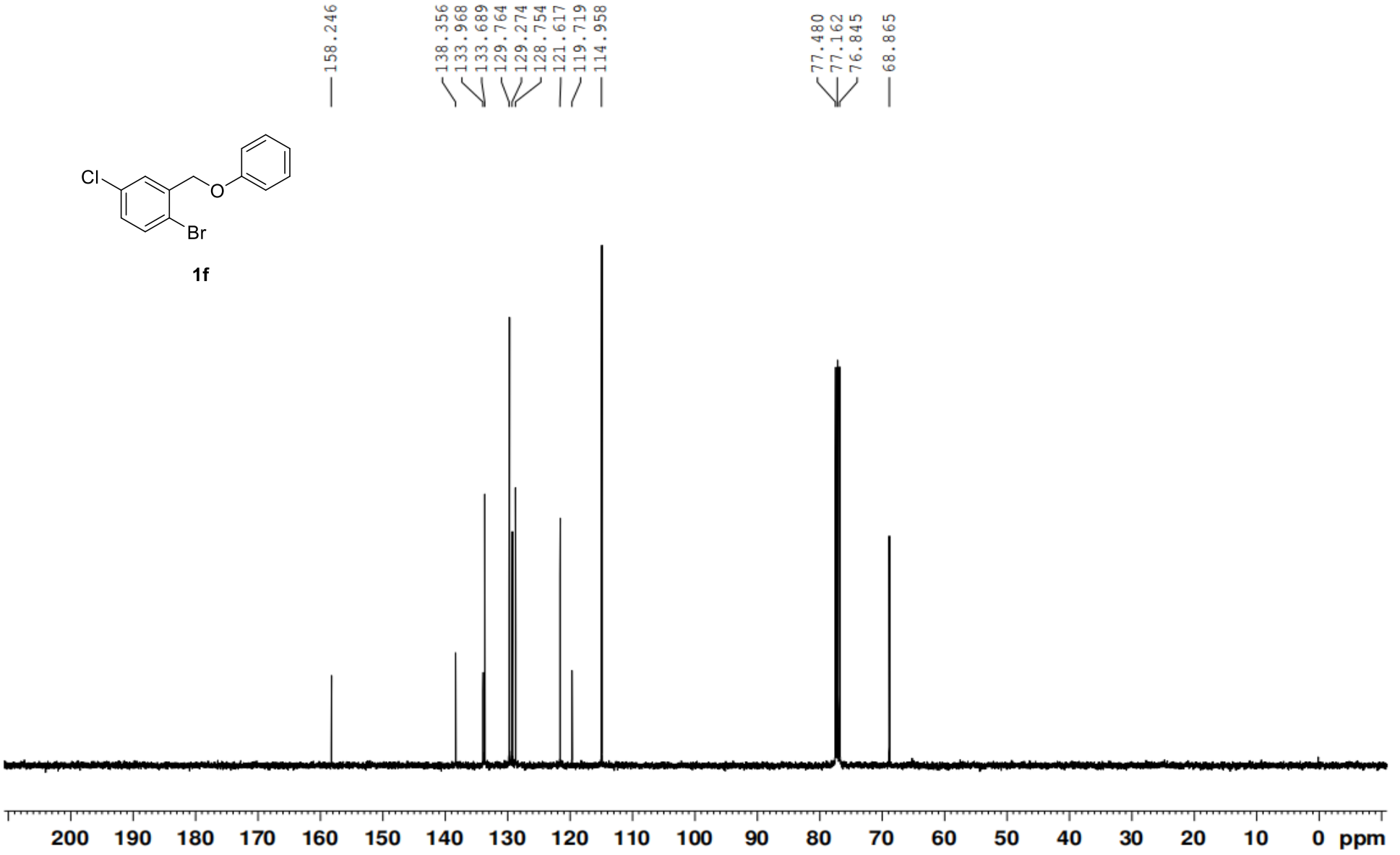


Figure S16. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1f.**

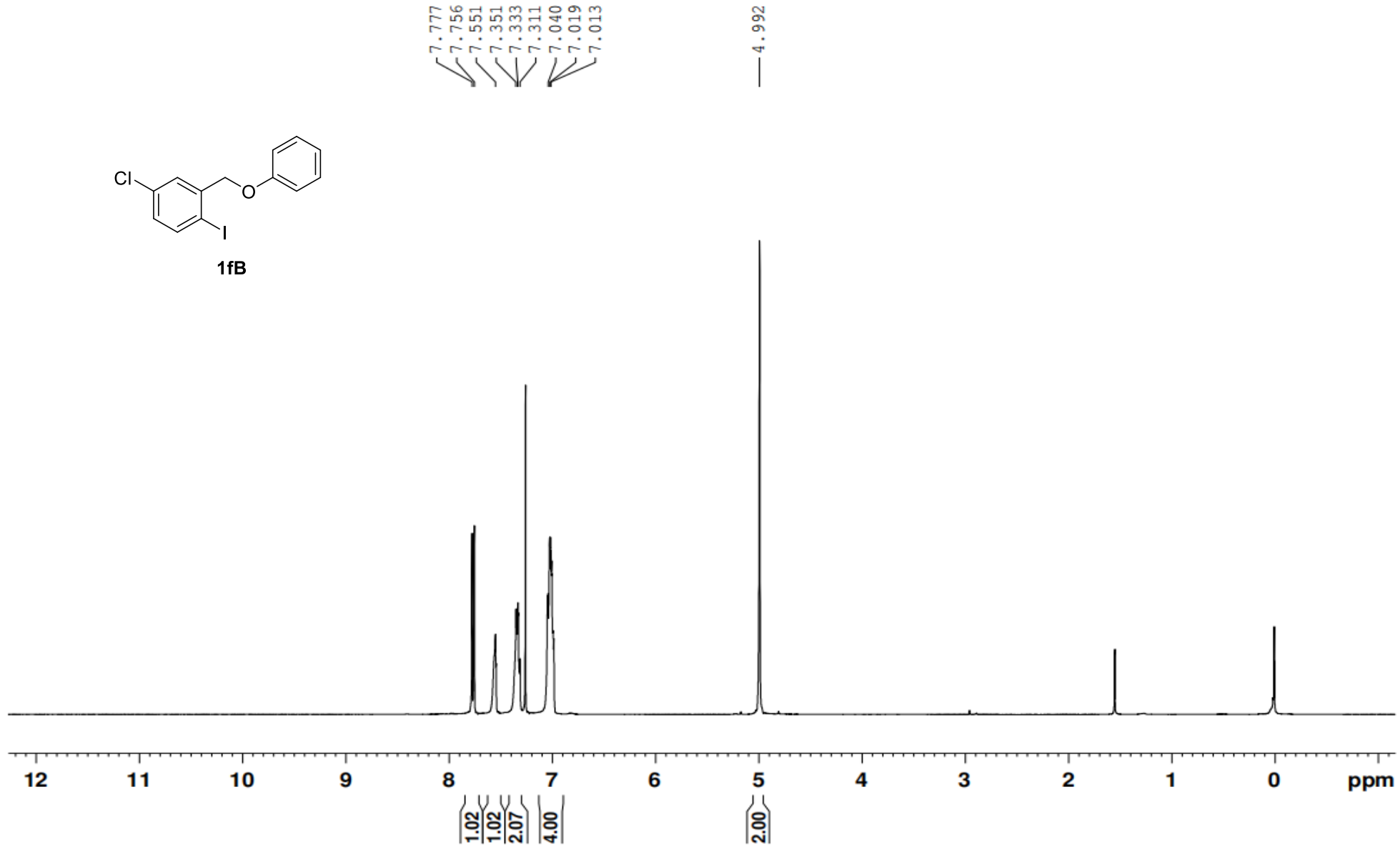


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1fB.**

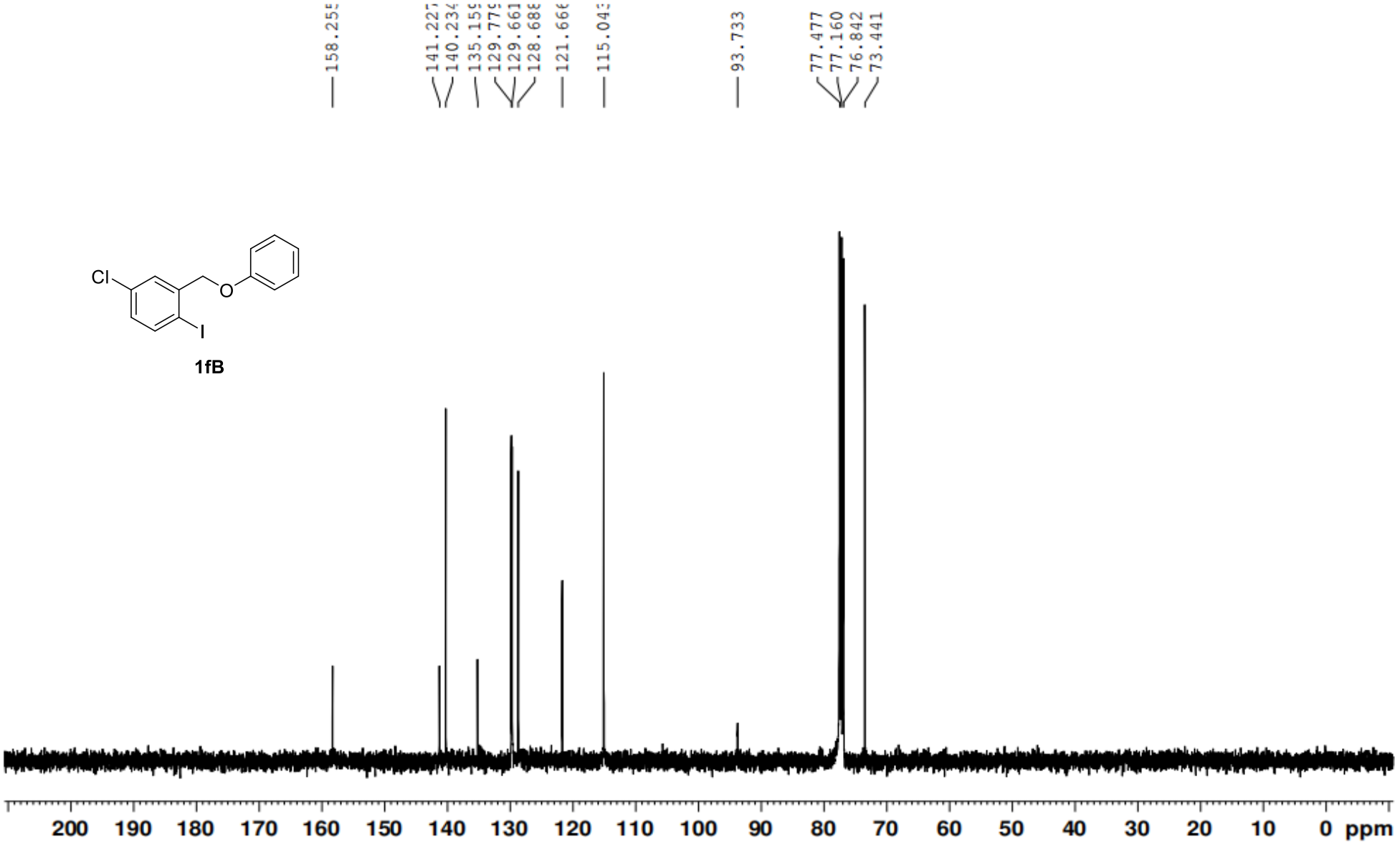


Figure S18. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1fB.**

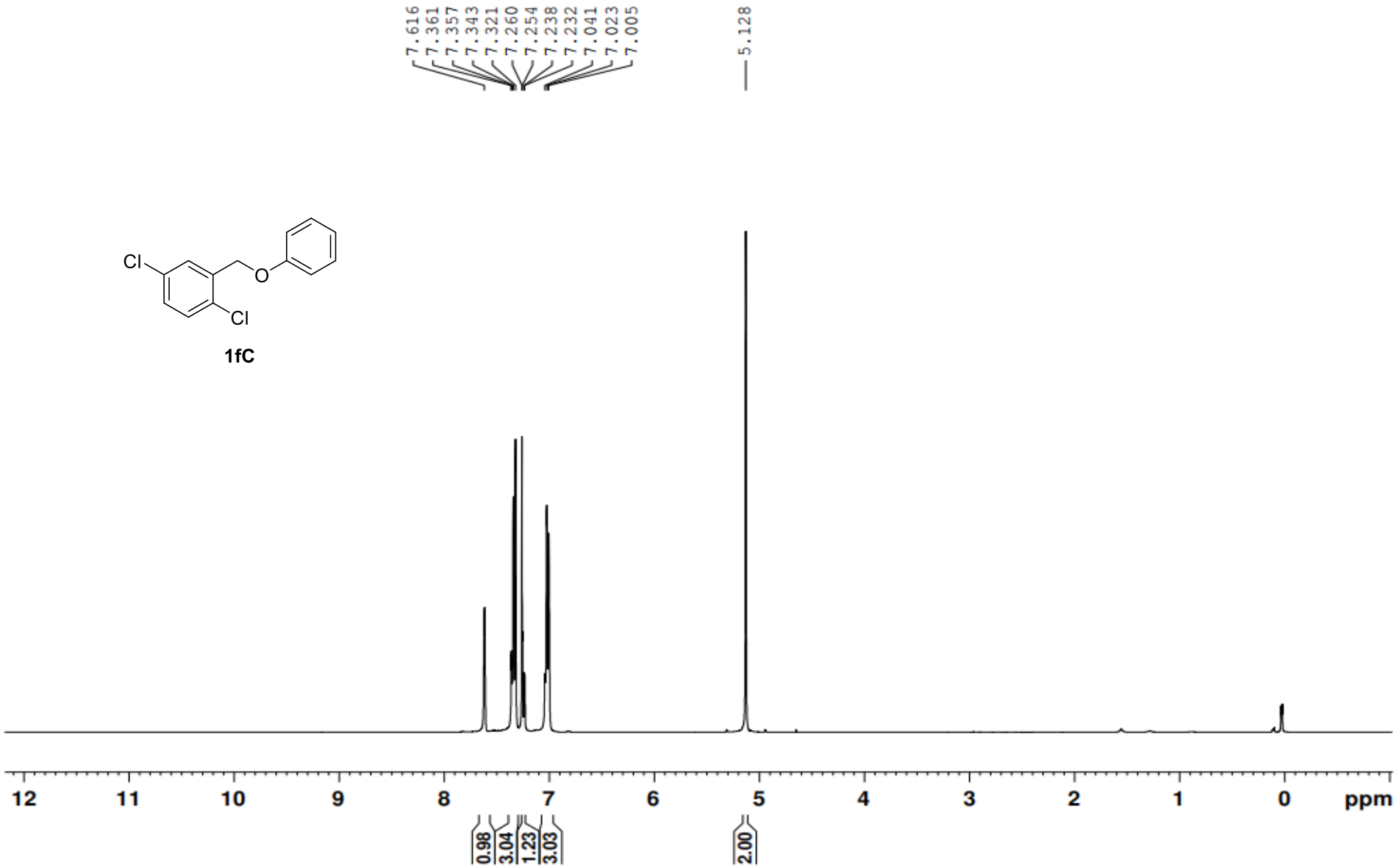


Figure S19. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1fC.**

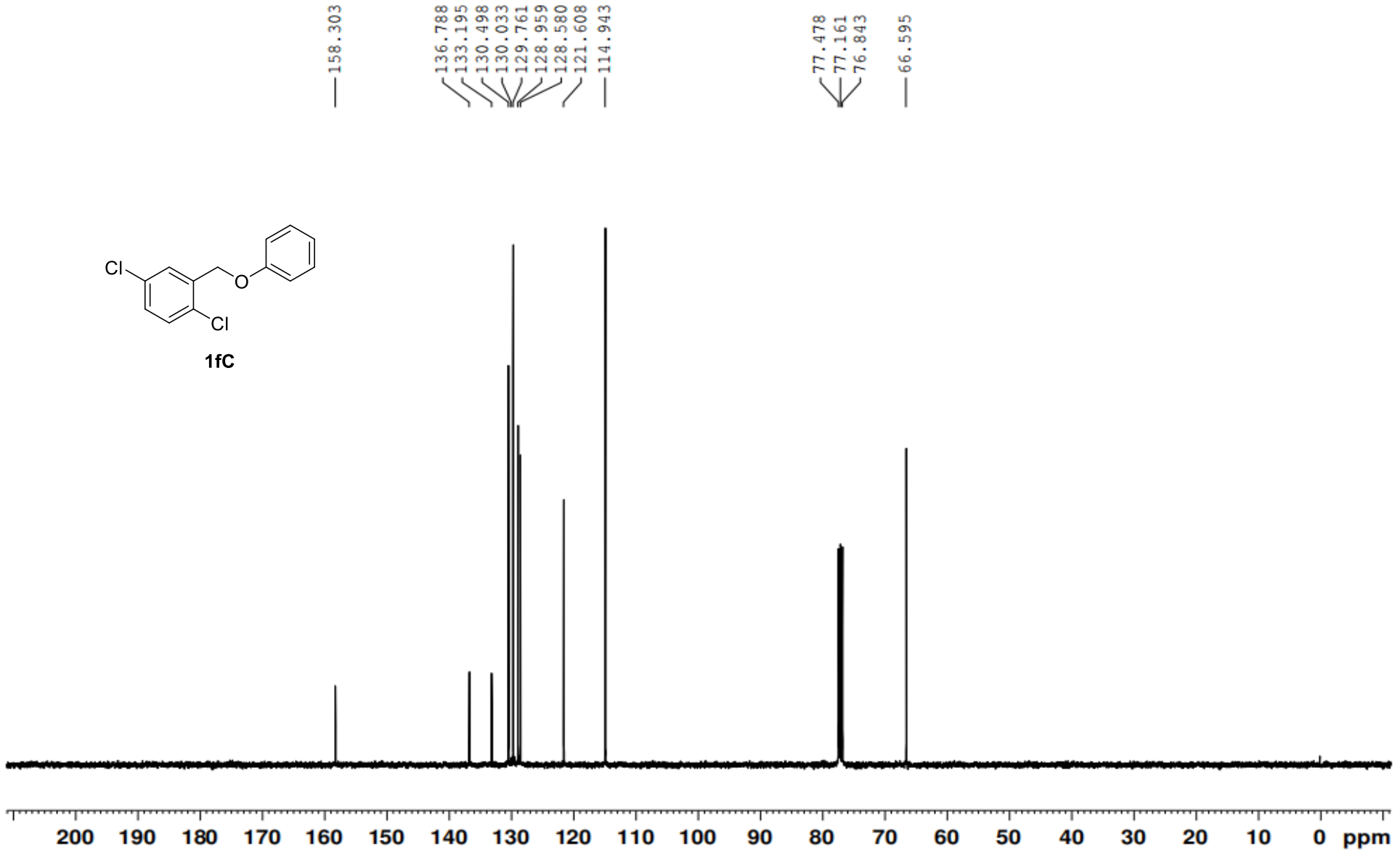


Figure S20. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1fC.**

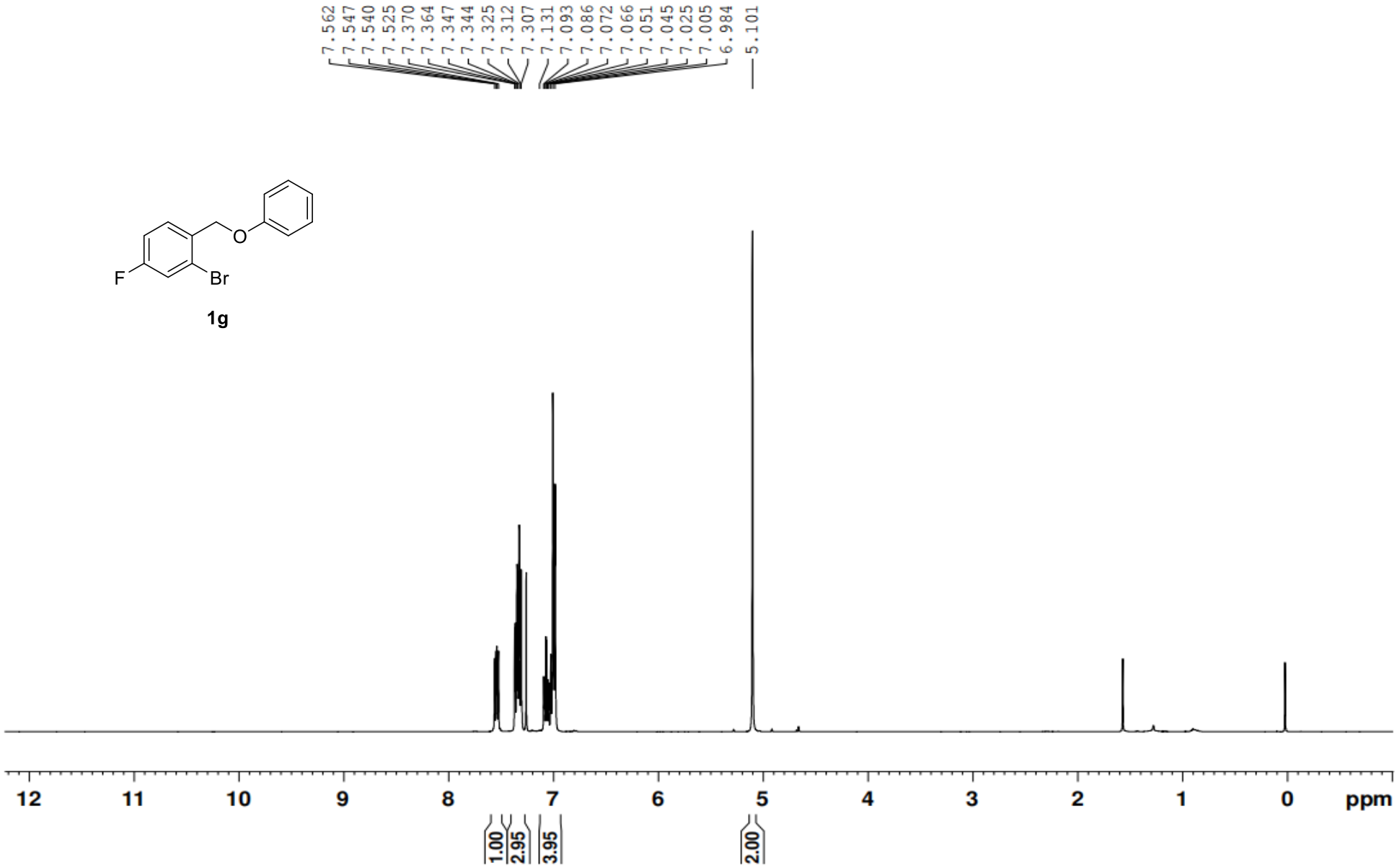


Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1g.**

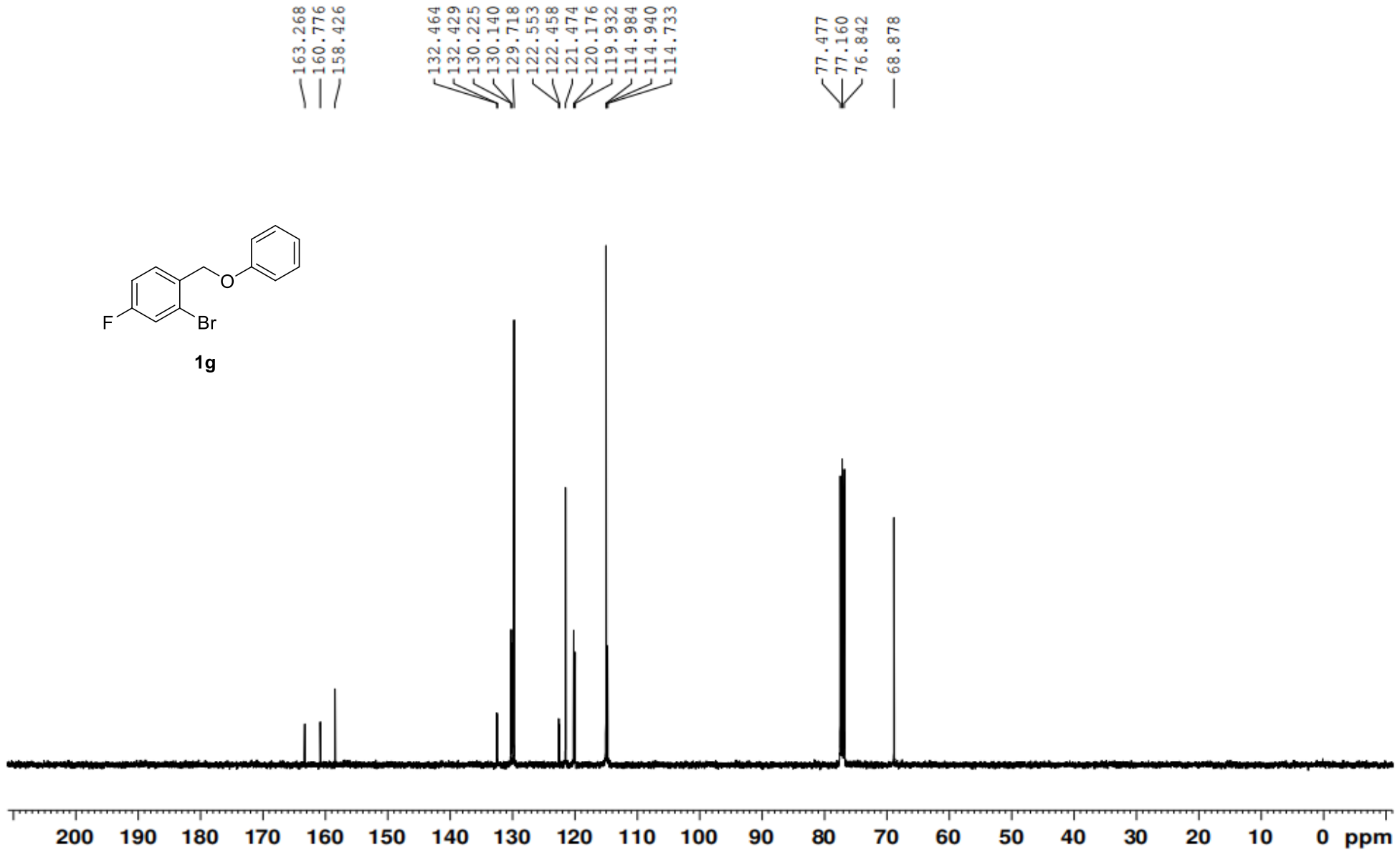


Figure S22. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1g.**

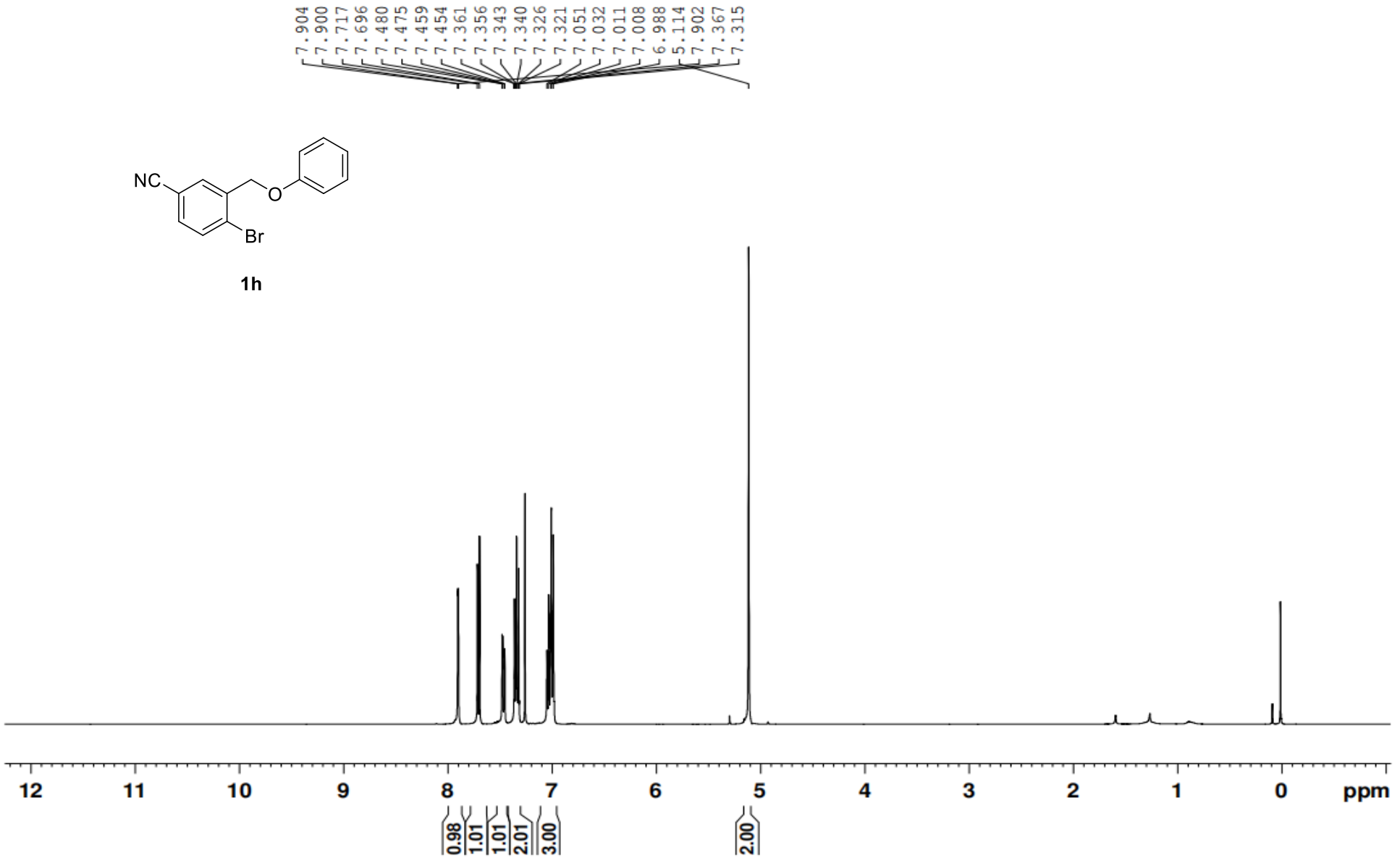


Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1h.**

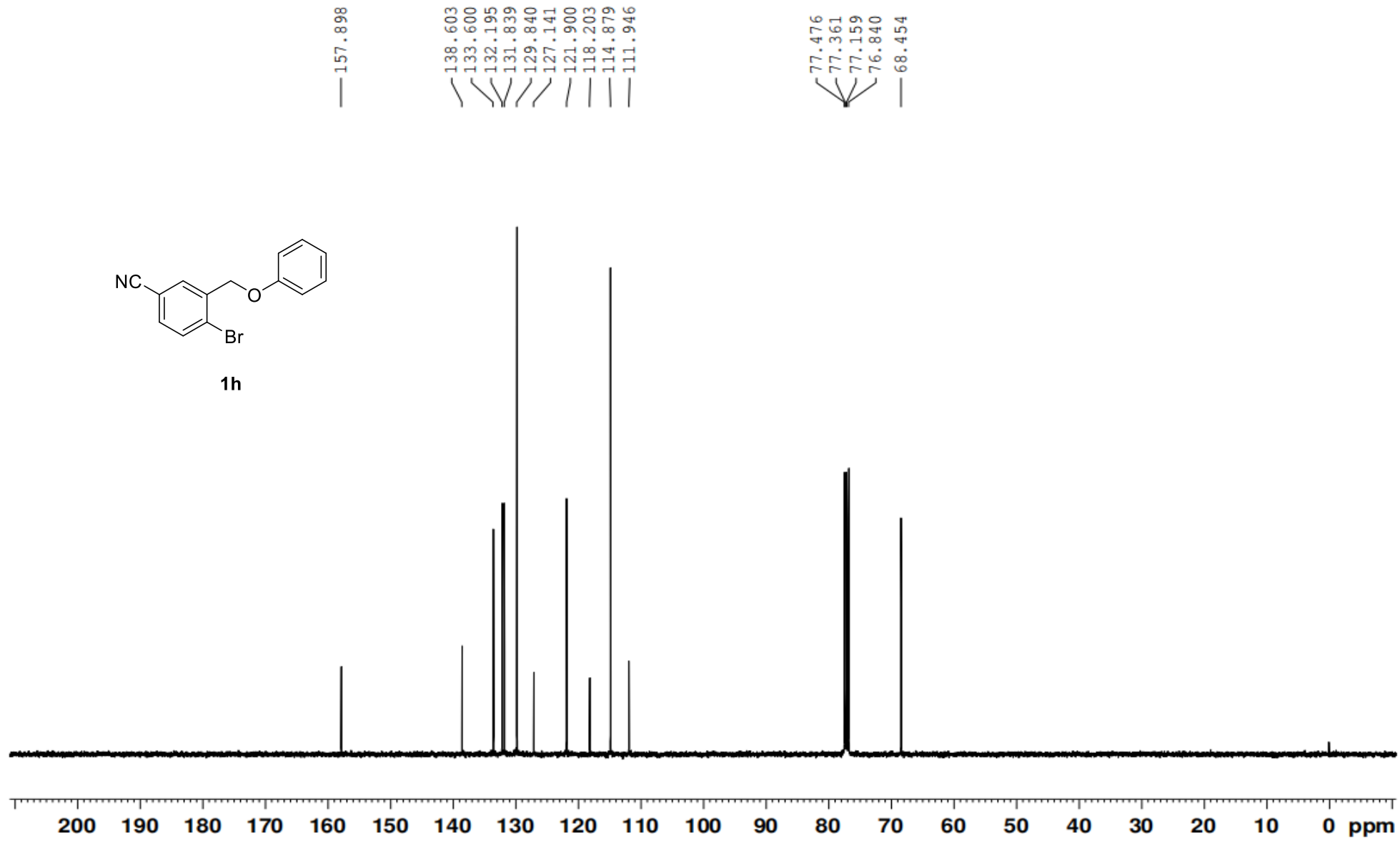


Figure S24. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1h.**

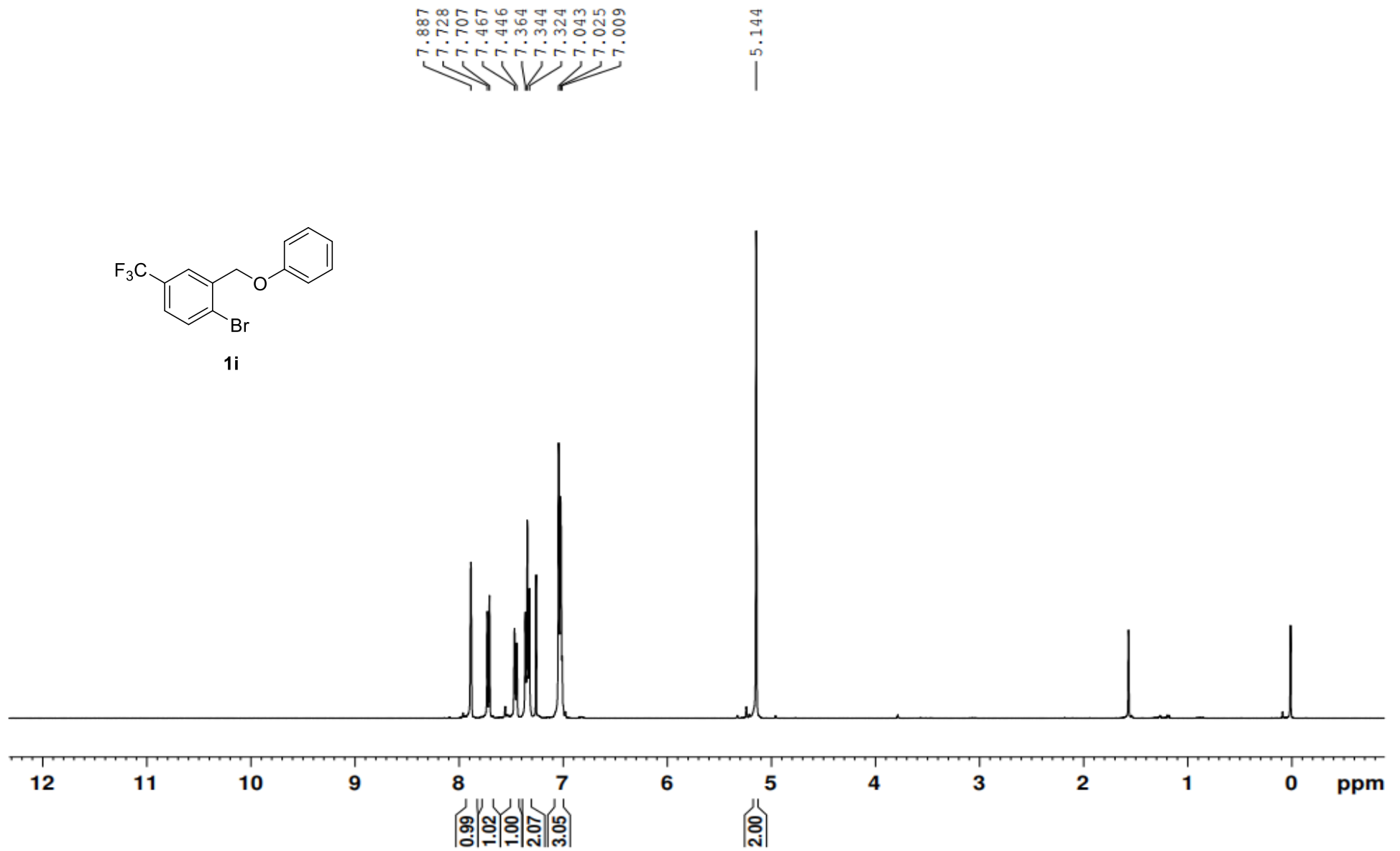


Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1i.**

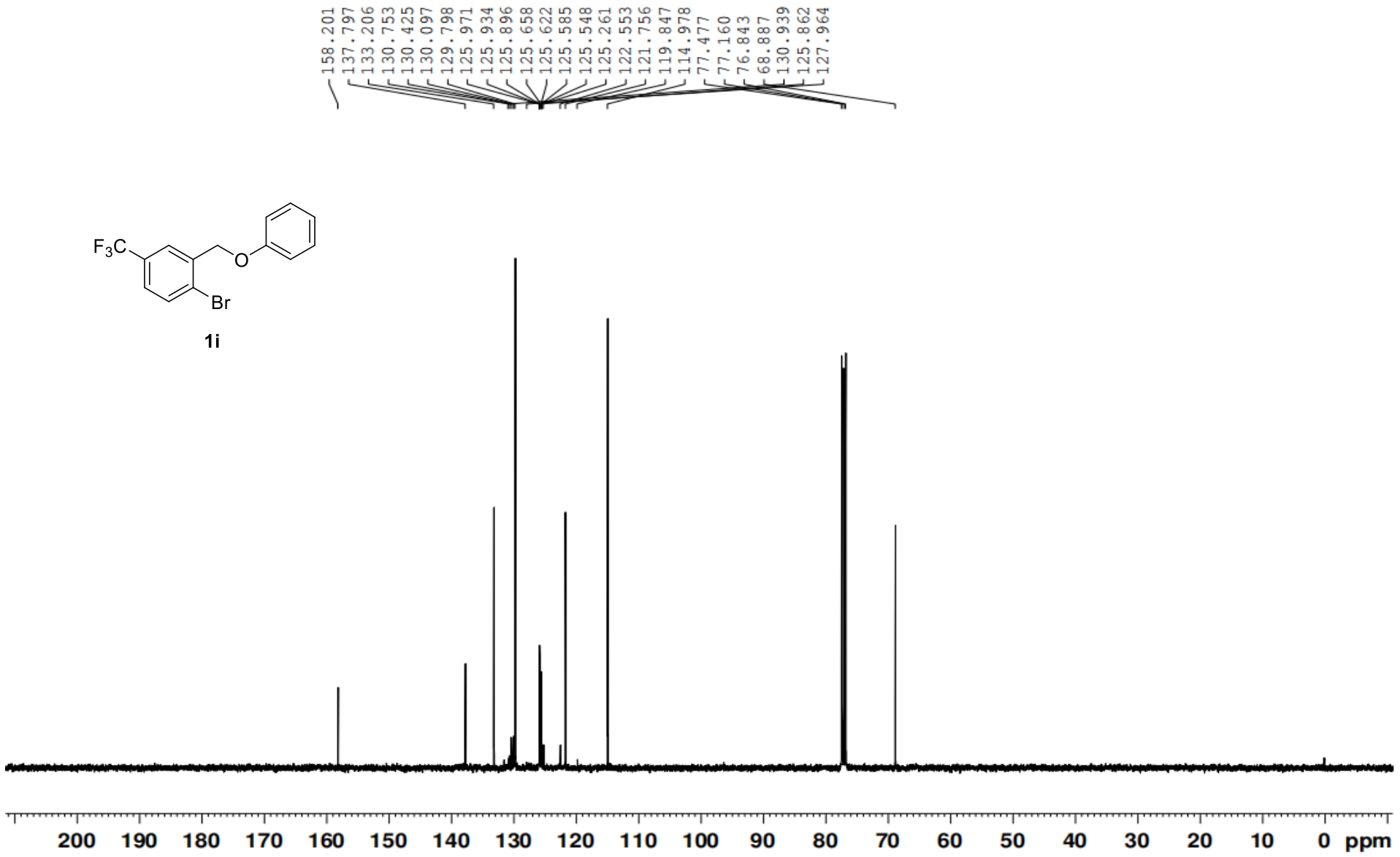


Figure S26. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1i.**

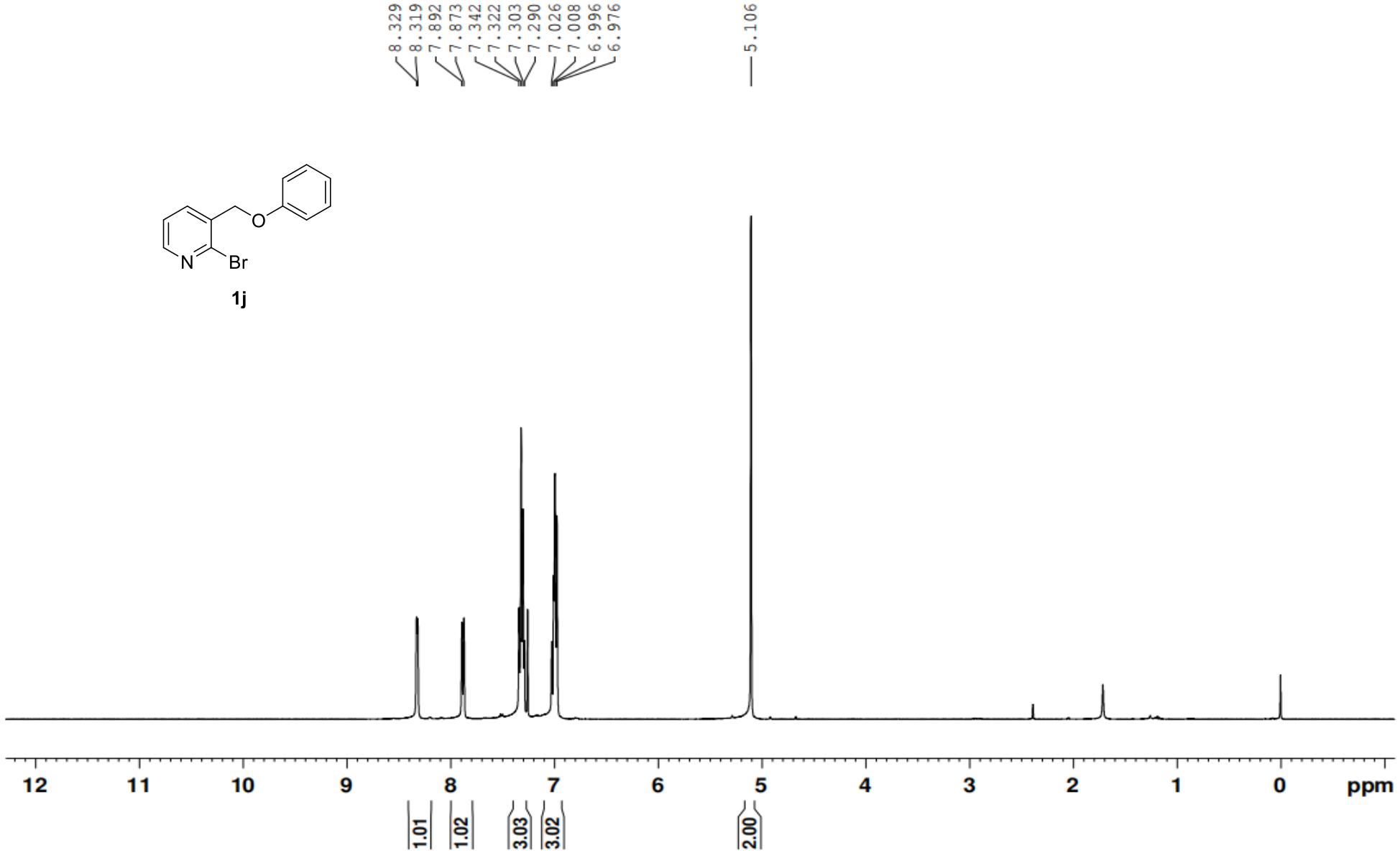


Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1j.**

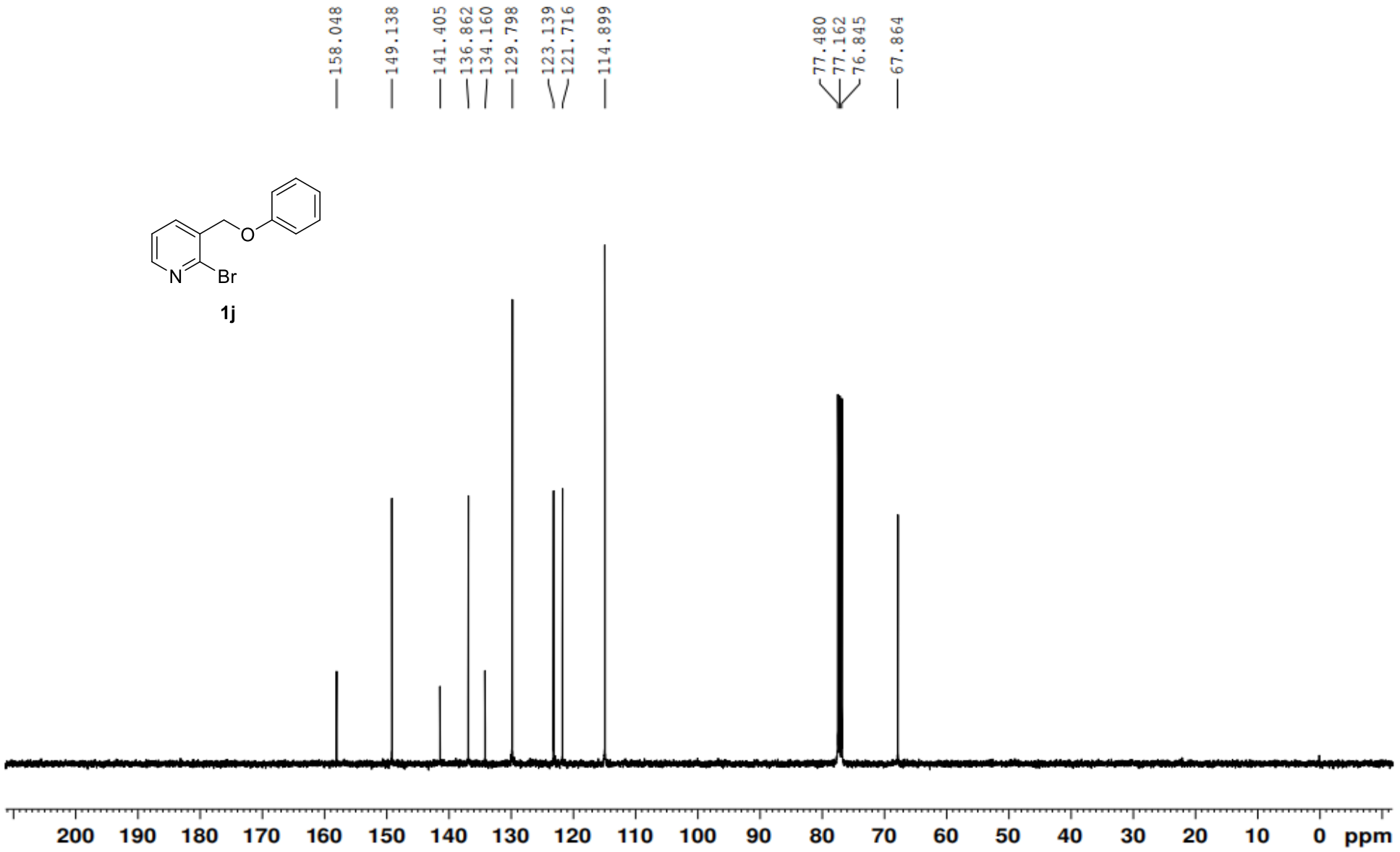


Figure S28. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1j.**

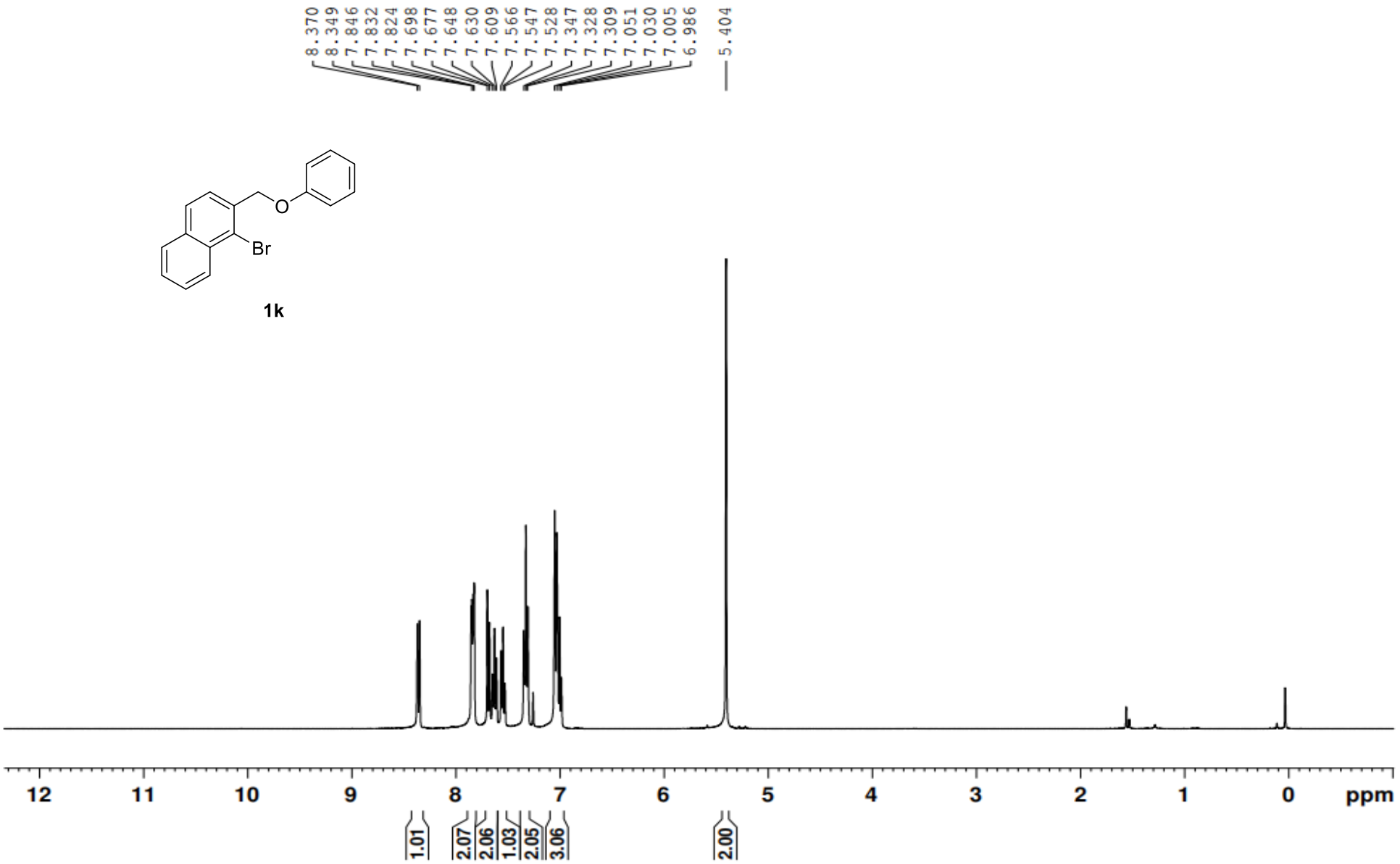


Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1k.**

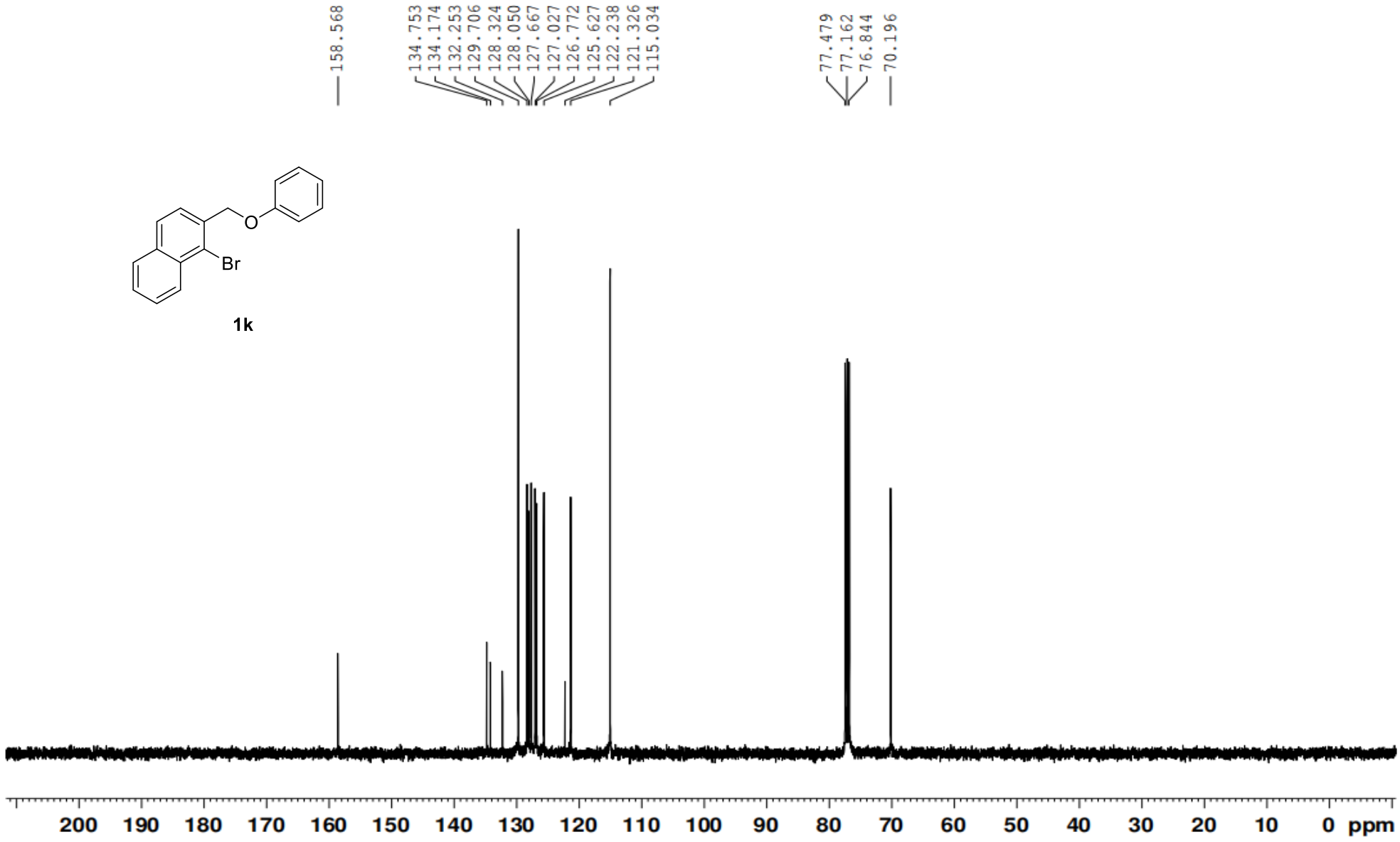


Figure S30. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1k.**

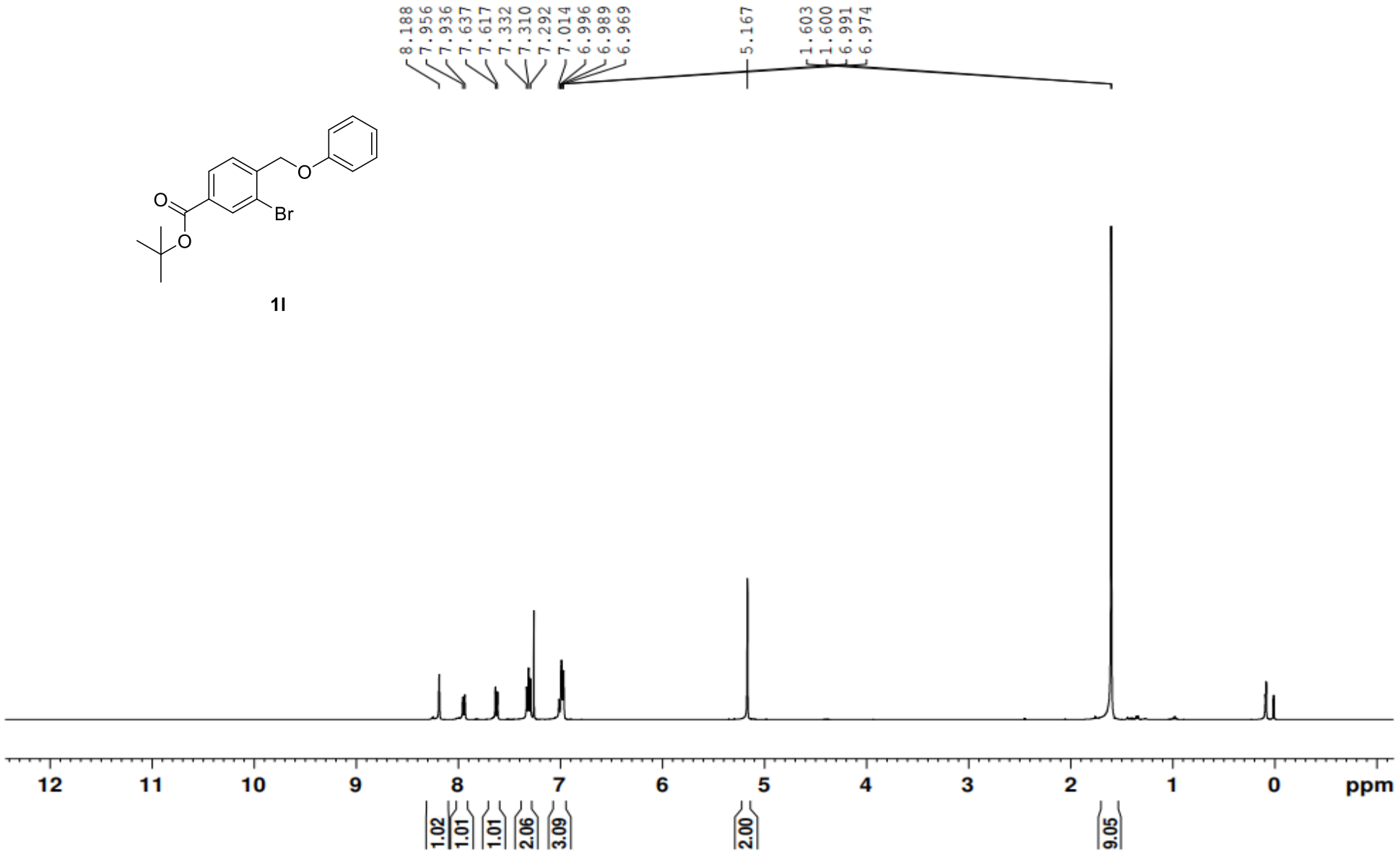


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1l.**

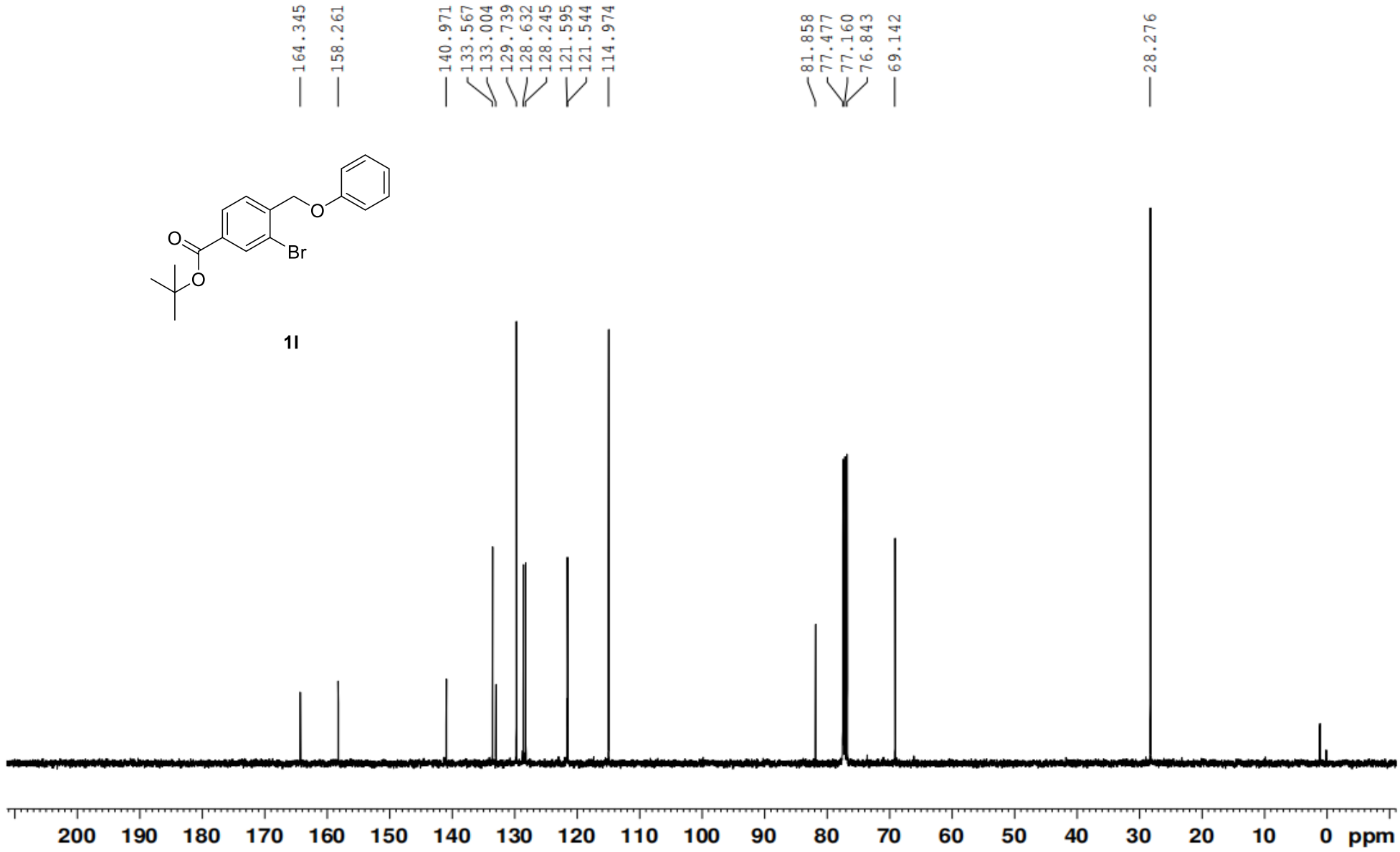


Figure S32. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1l.**

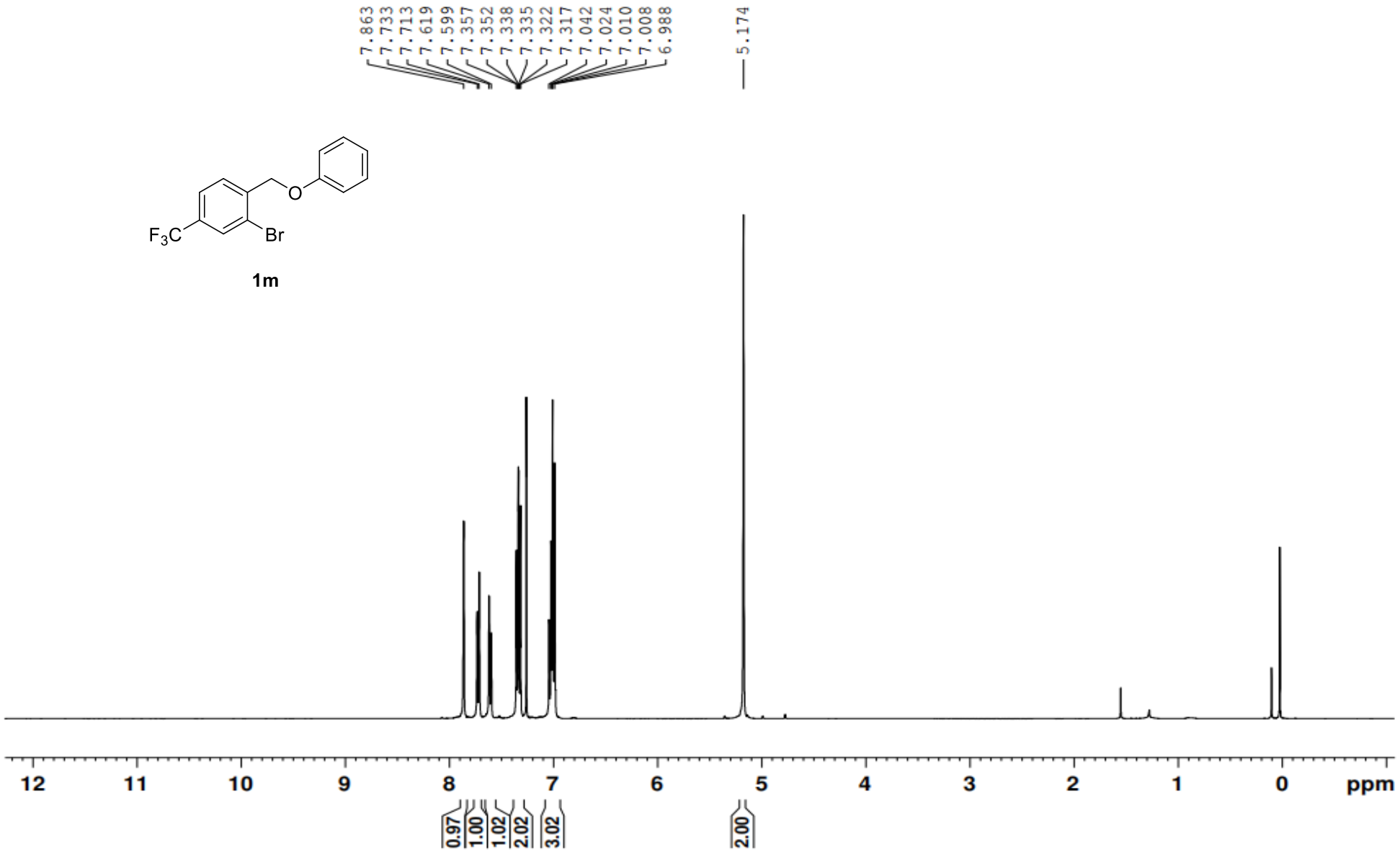


Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1m.**

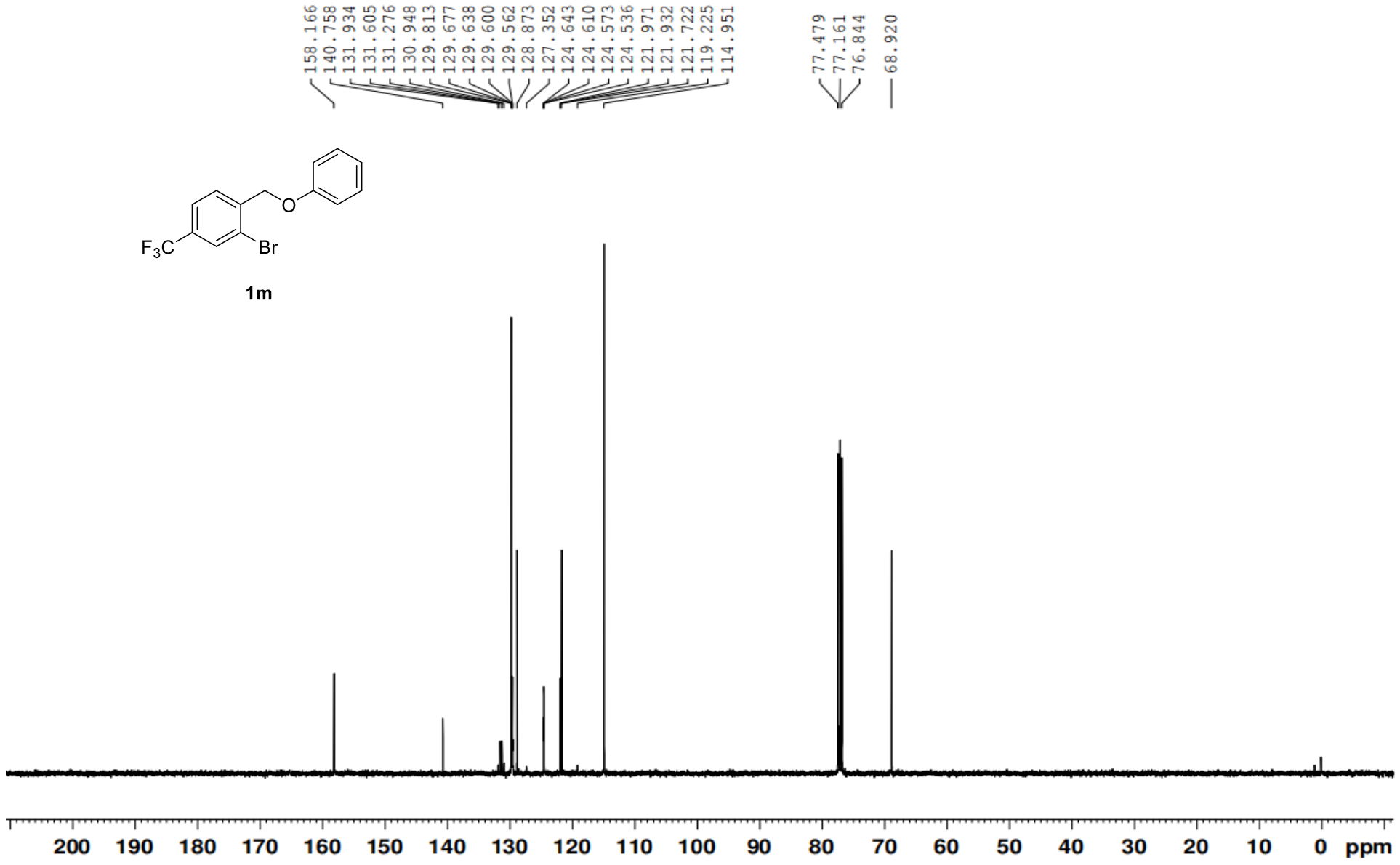


Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1m.**

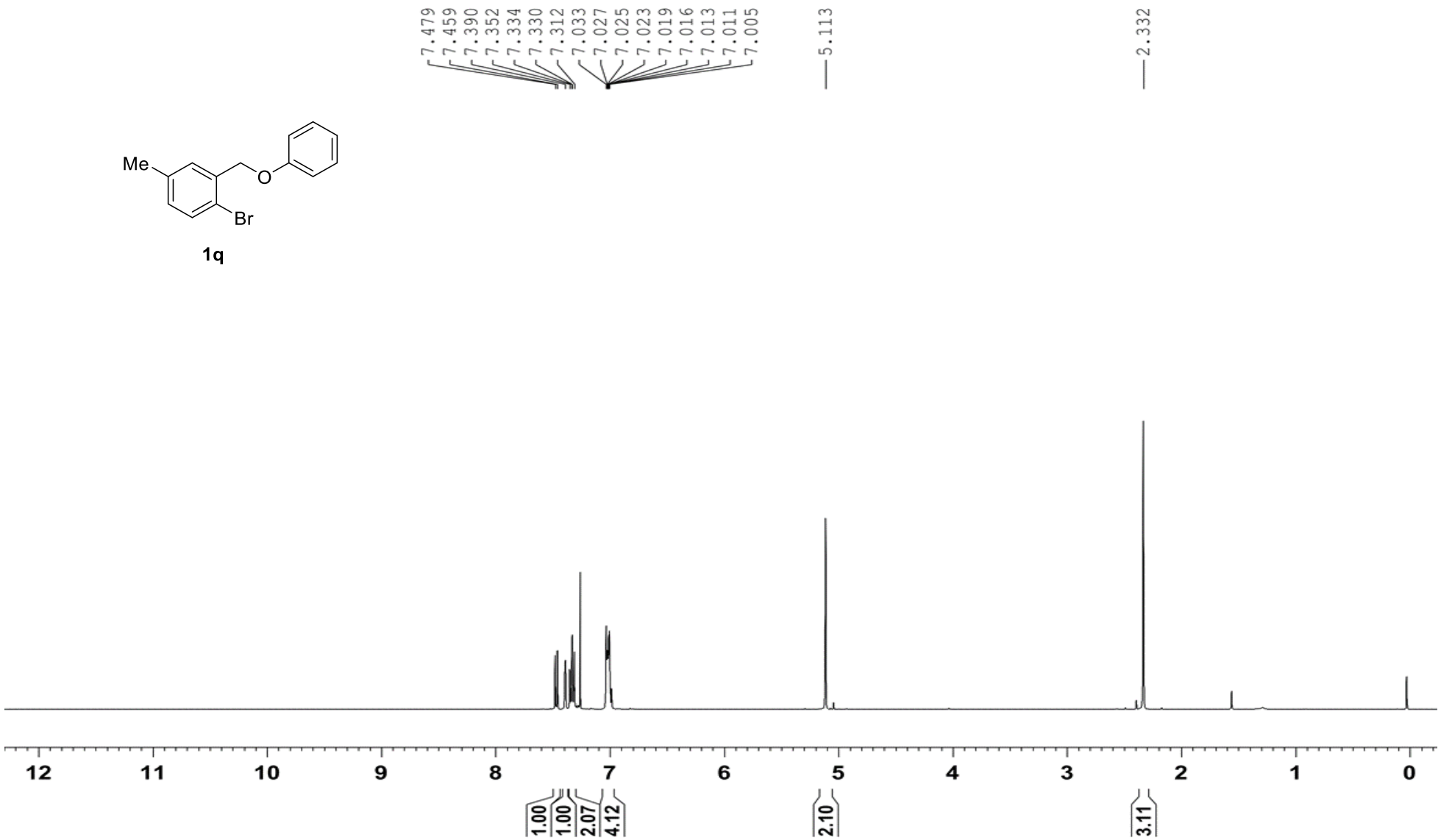


Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1q.**

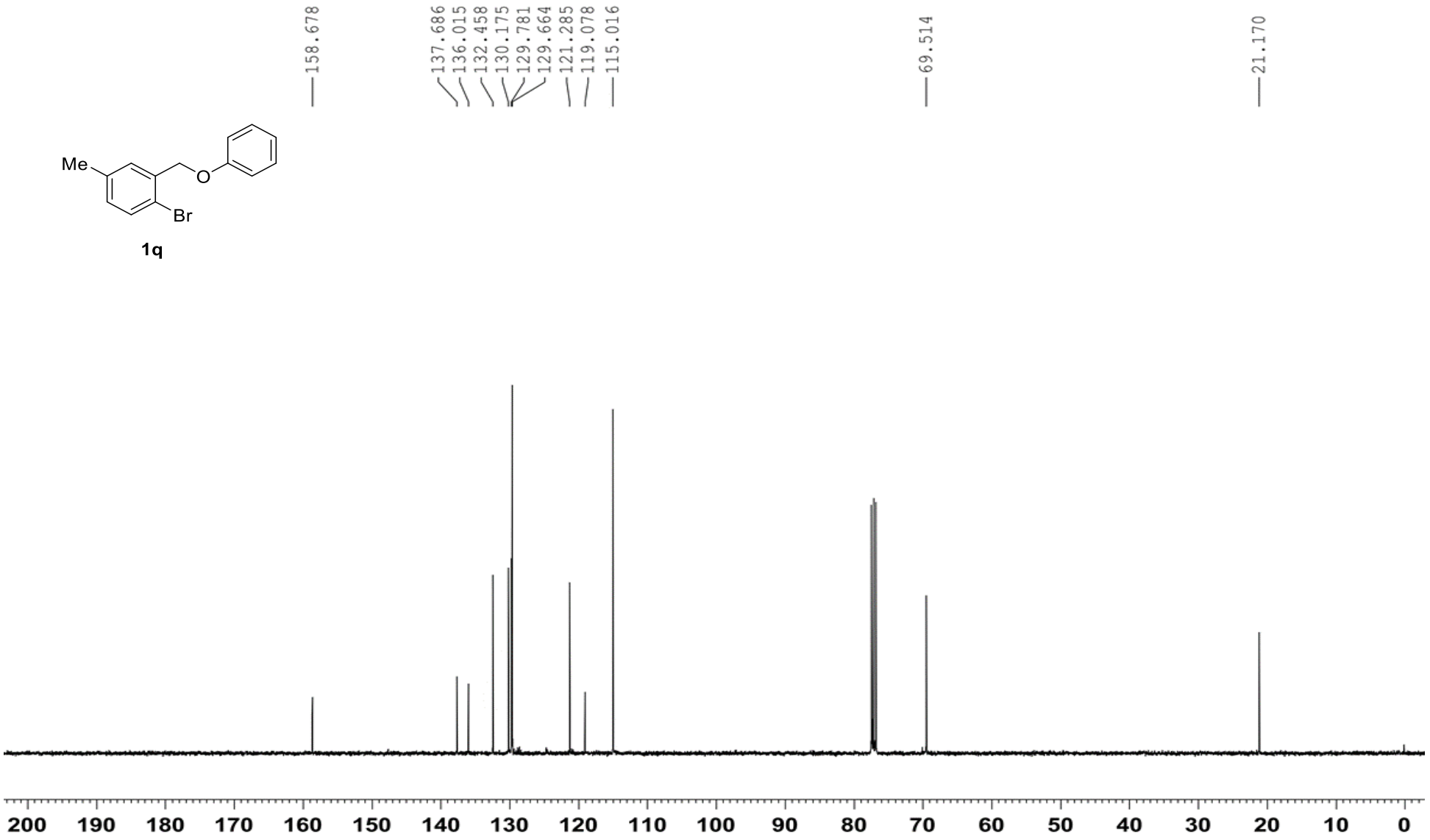


Figure S36. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1q.**

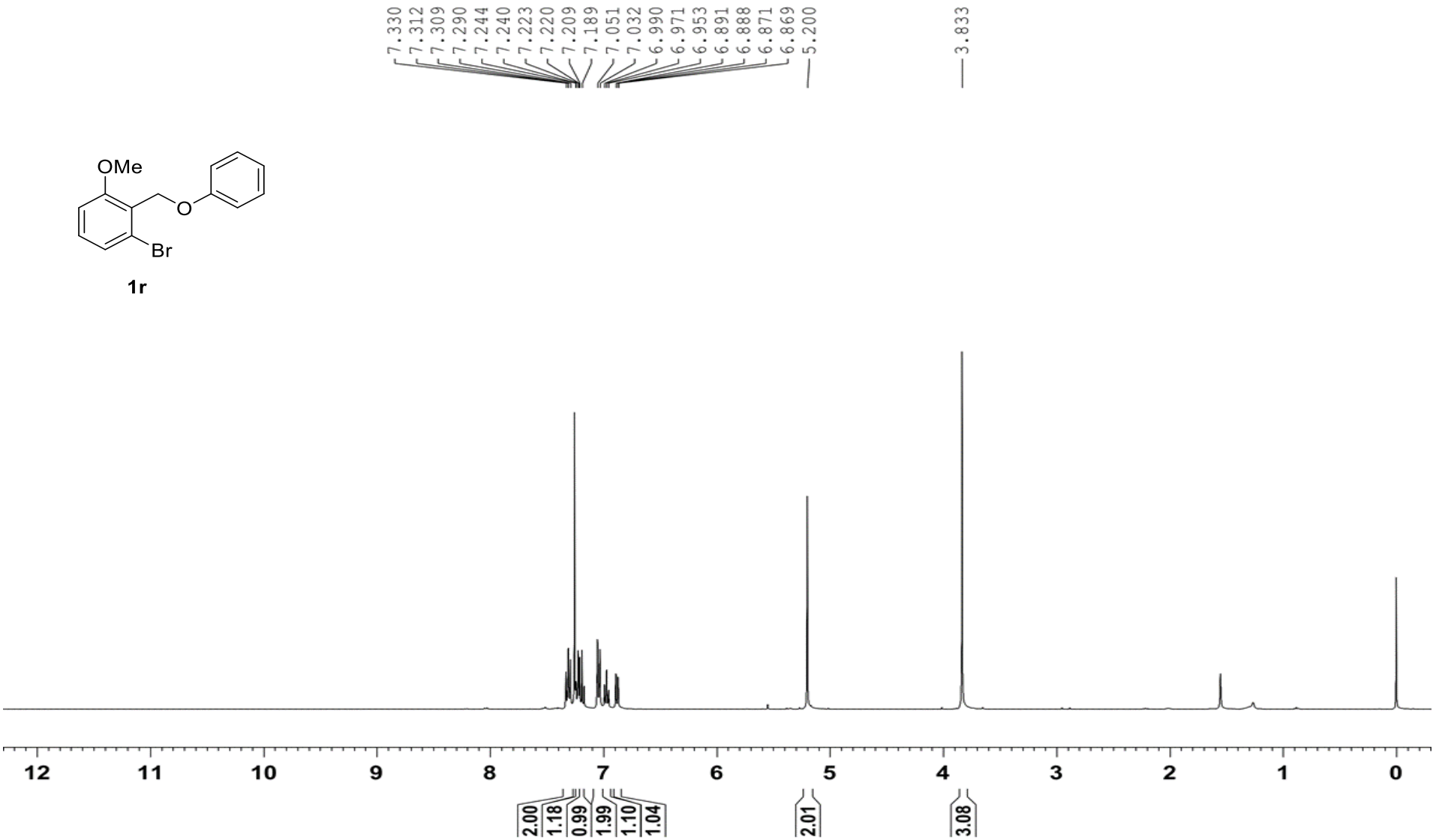


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1r.**

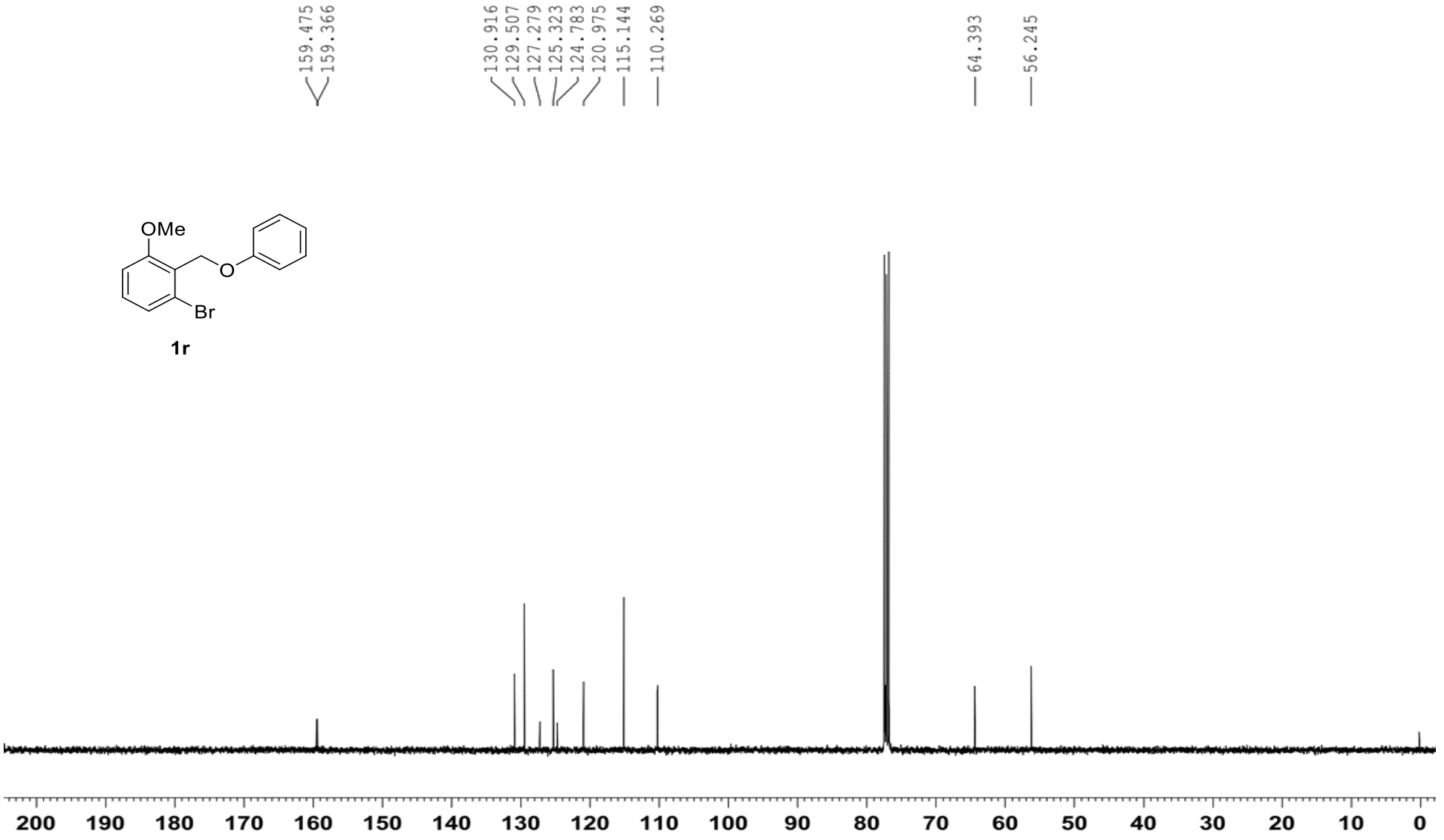


Figure S38. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1r.**

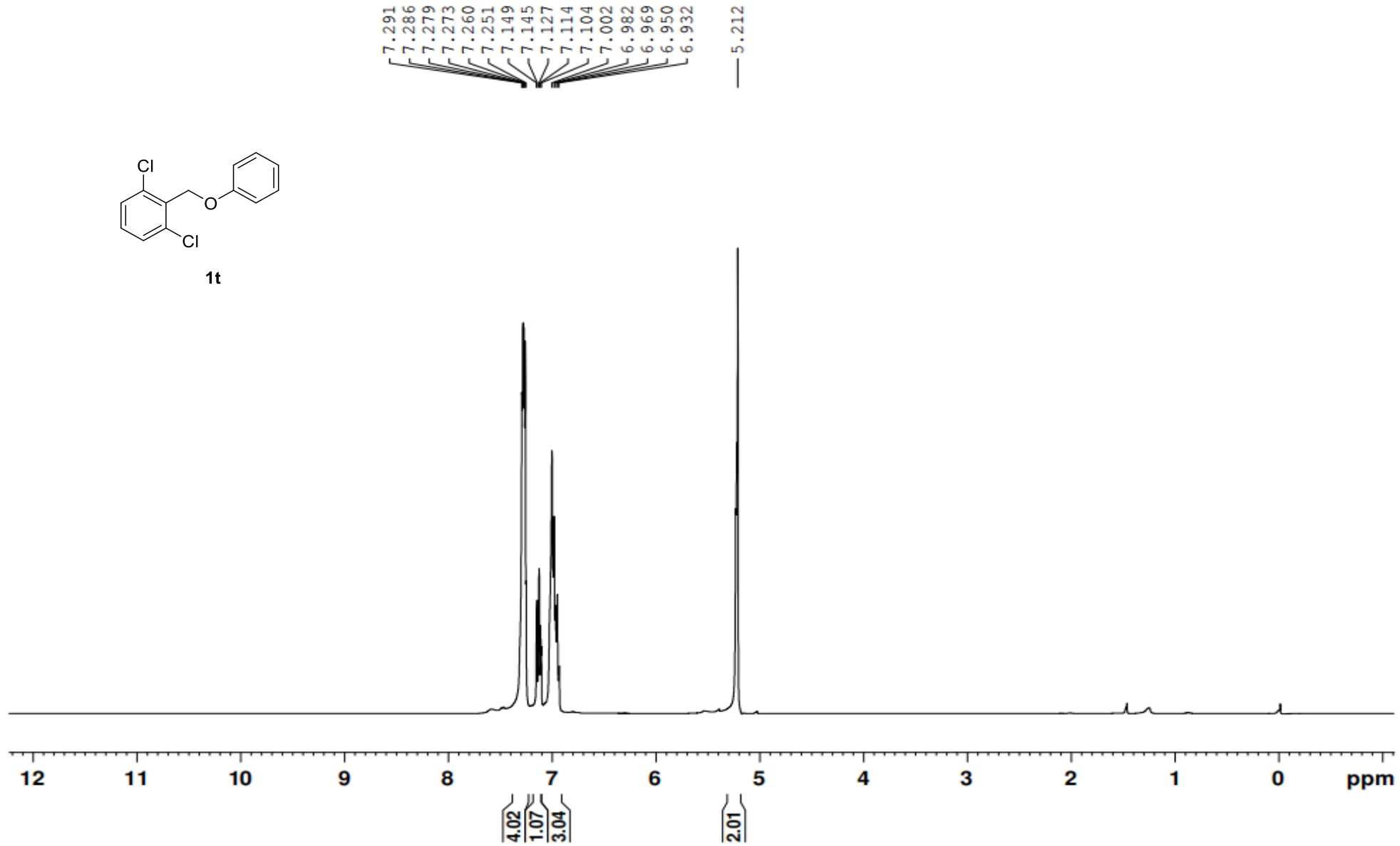


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1t.**

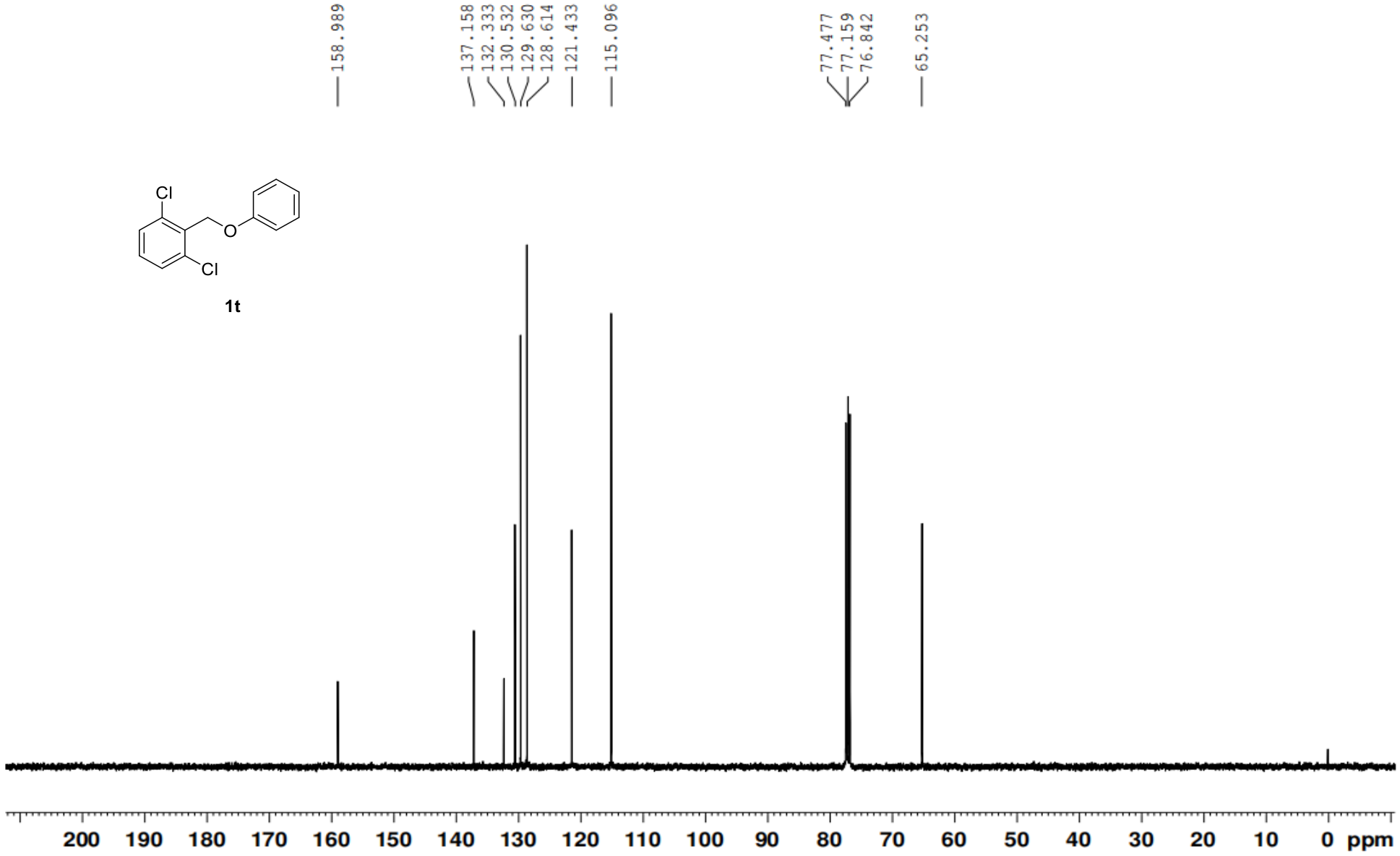


Figure S40. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1t.**

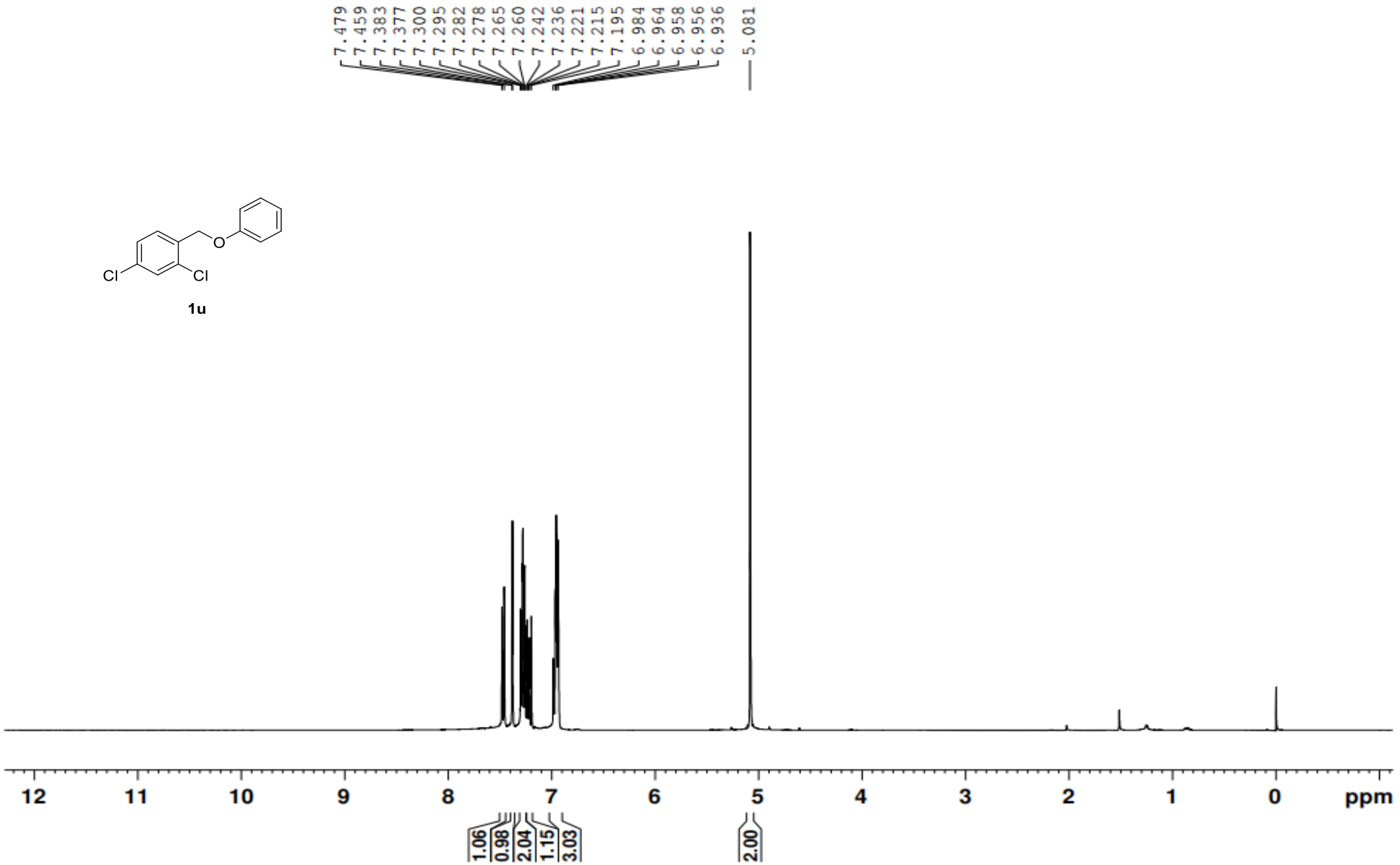


Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1u.**

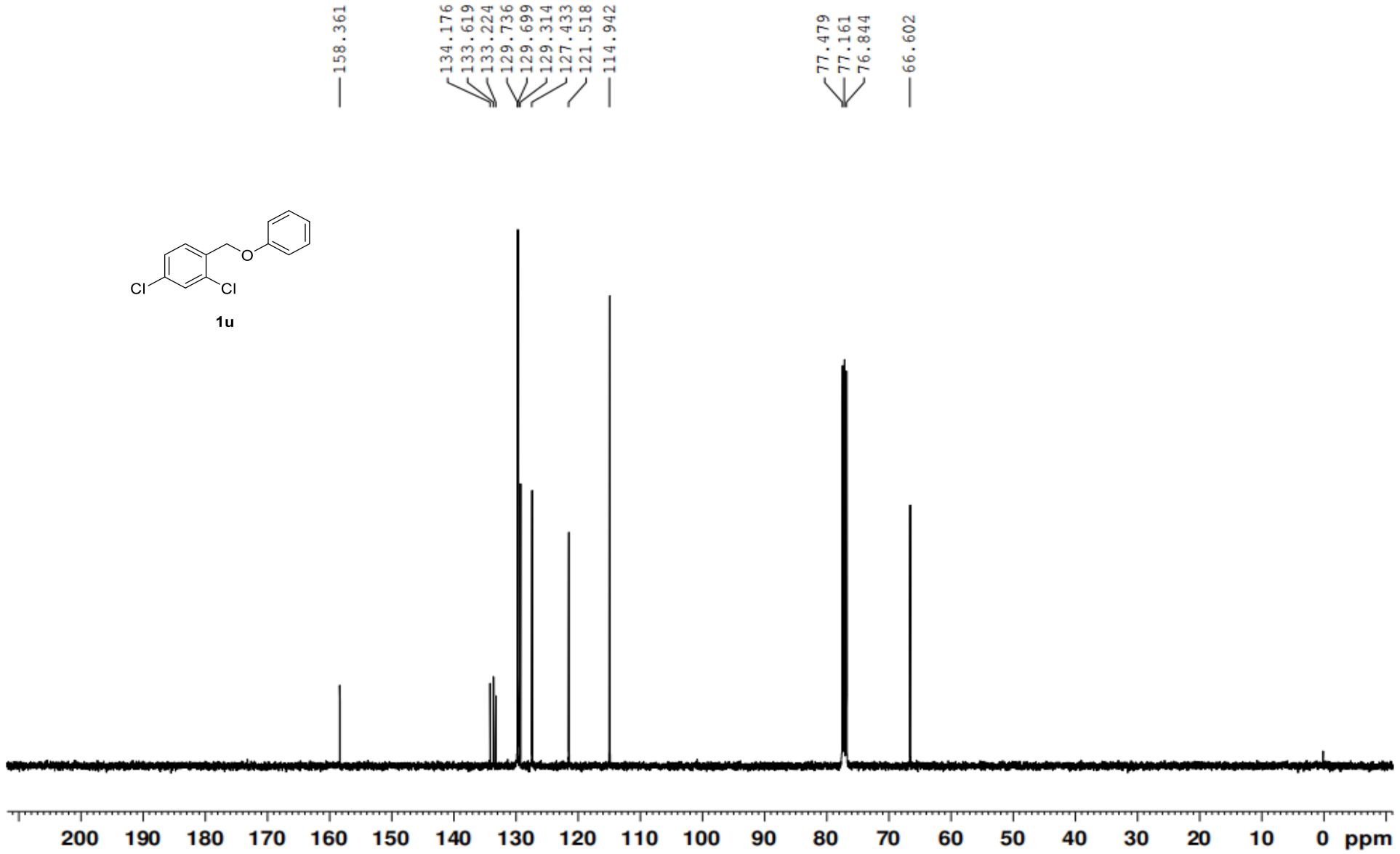


Figure S42. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1u.**

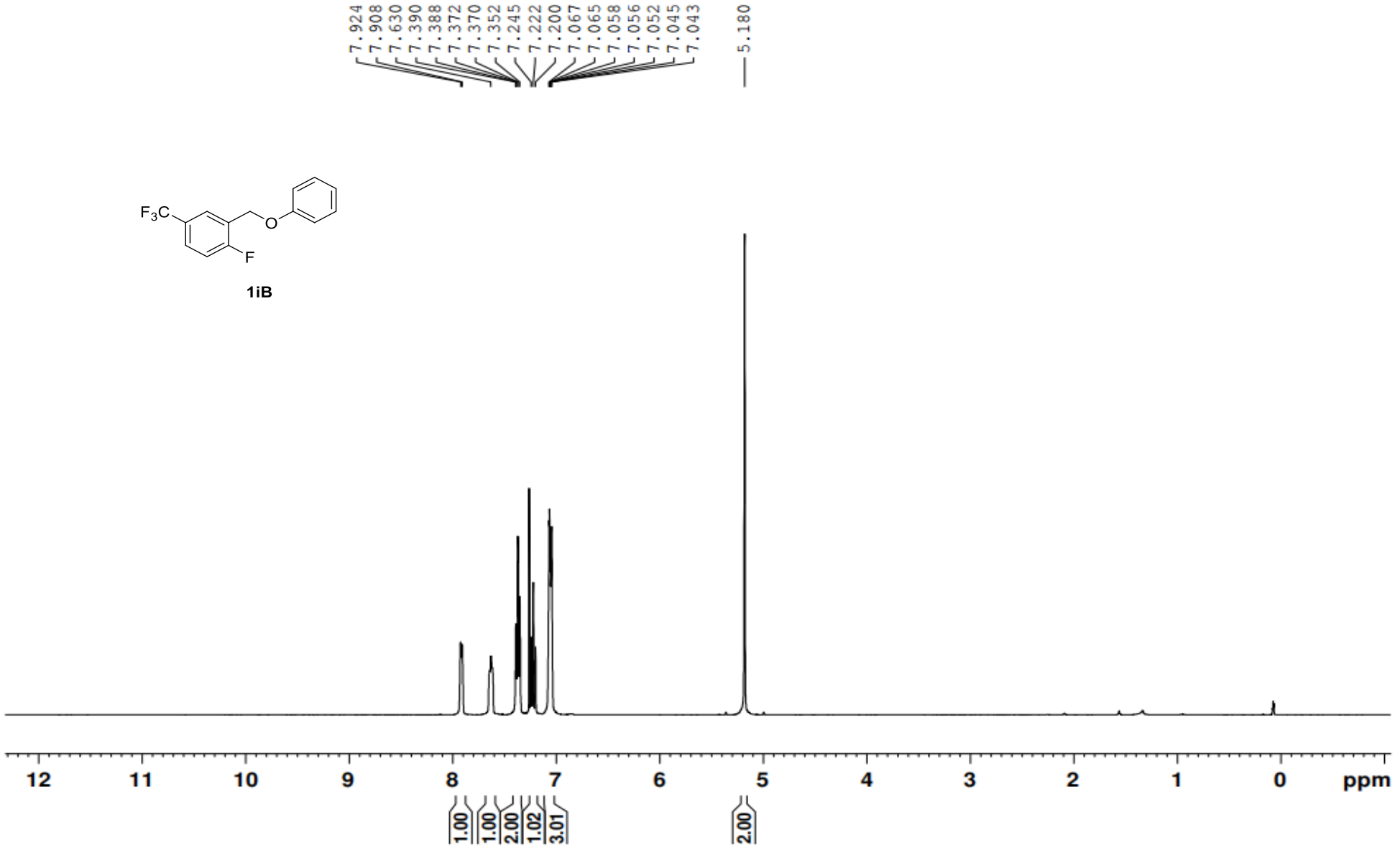


Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1iB.**

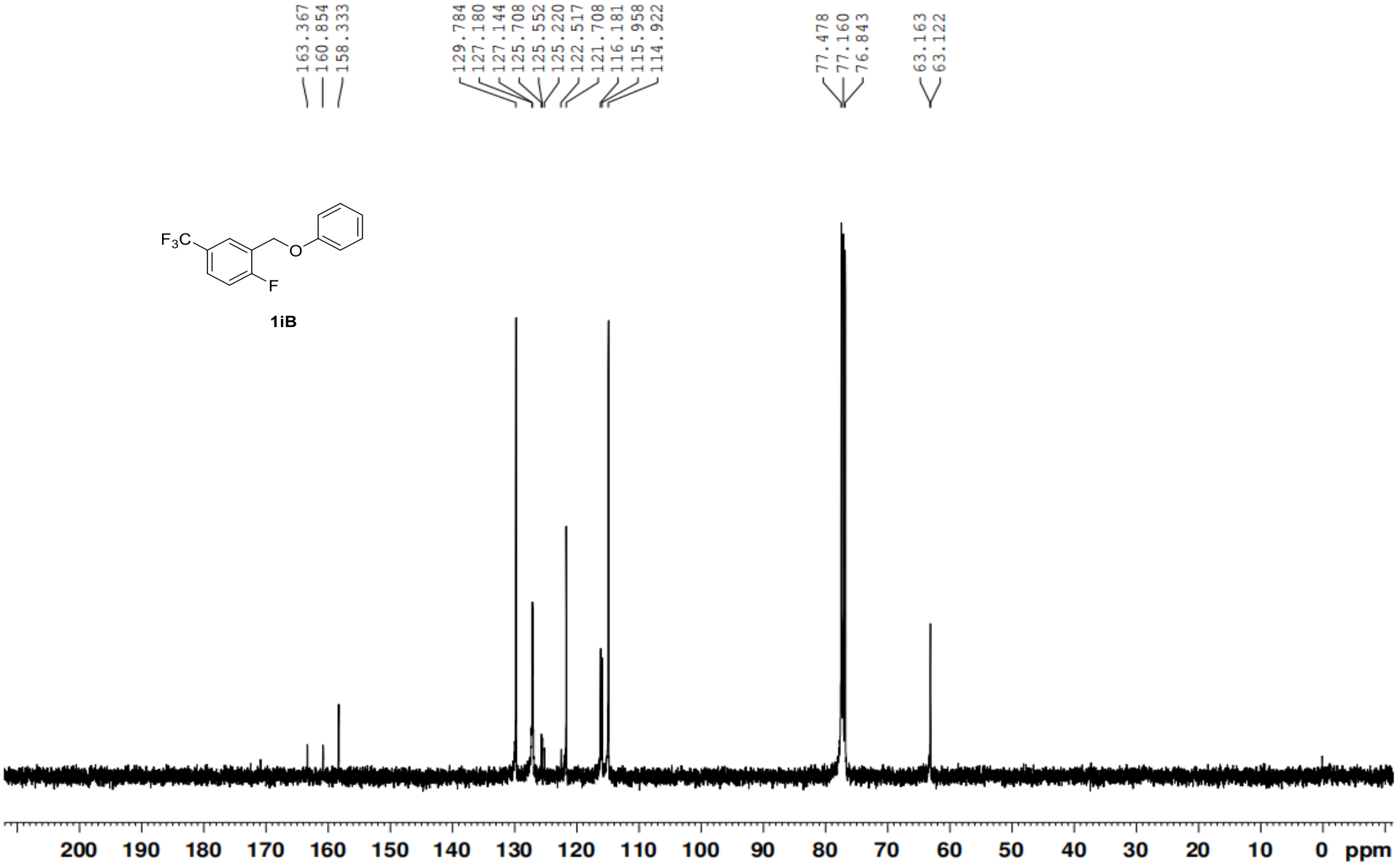


Figure S44. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1iB.**

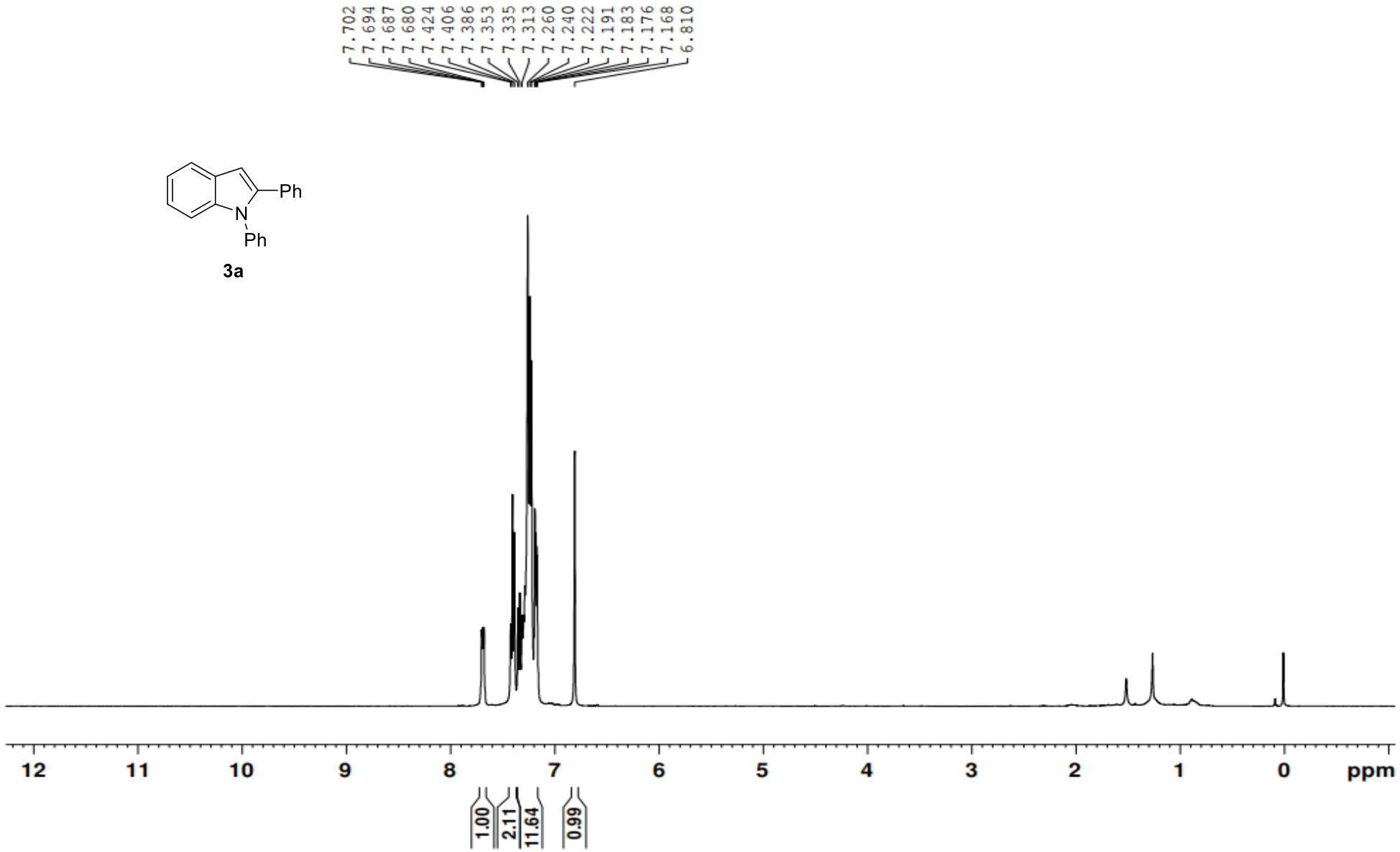


Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a.**

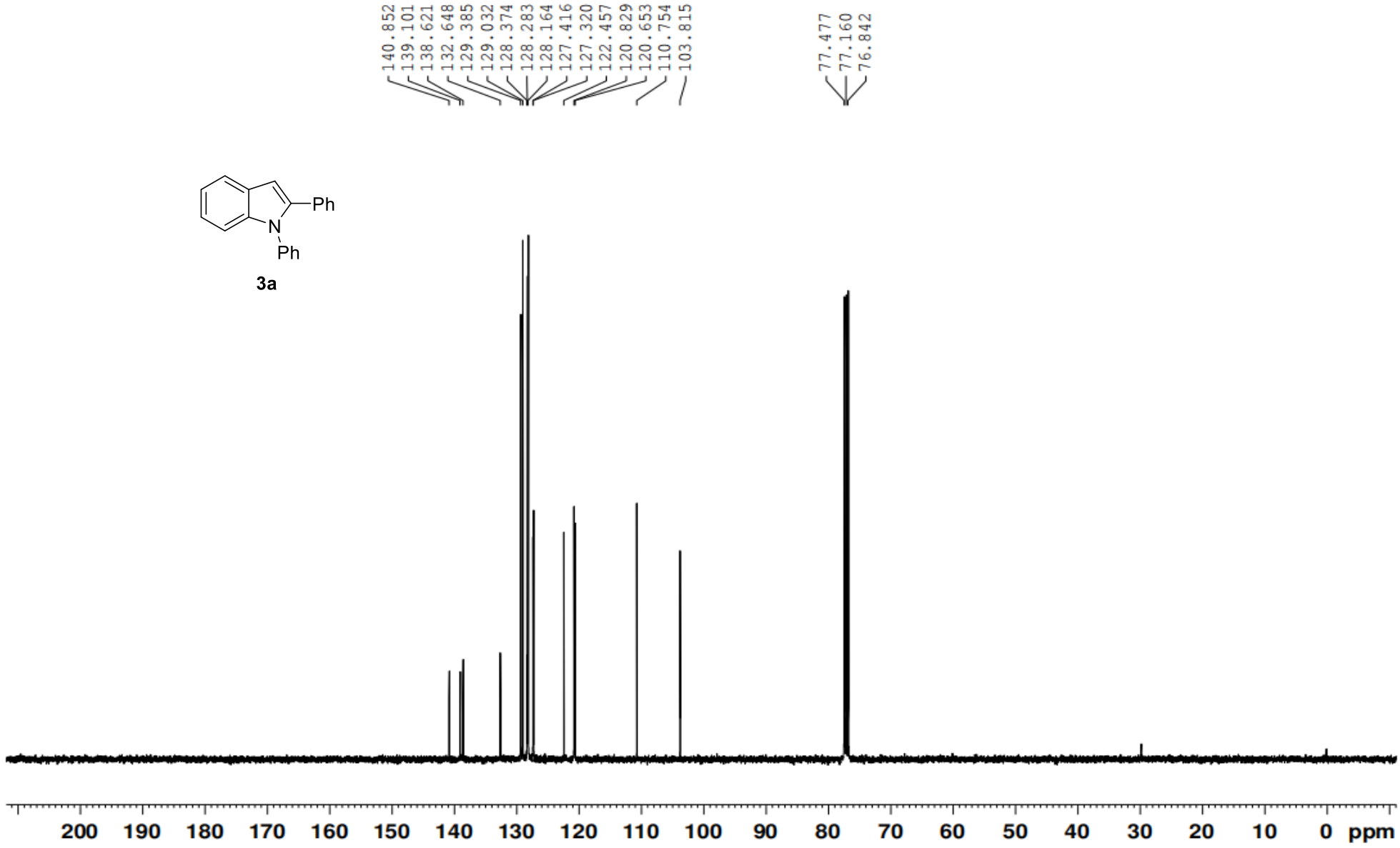


Figure S46. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3a.**

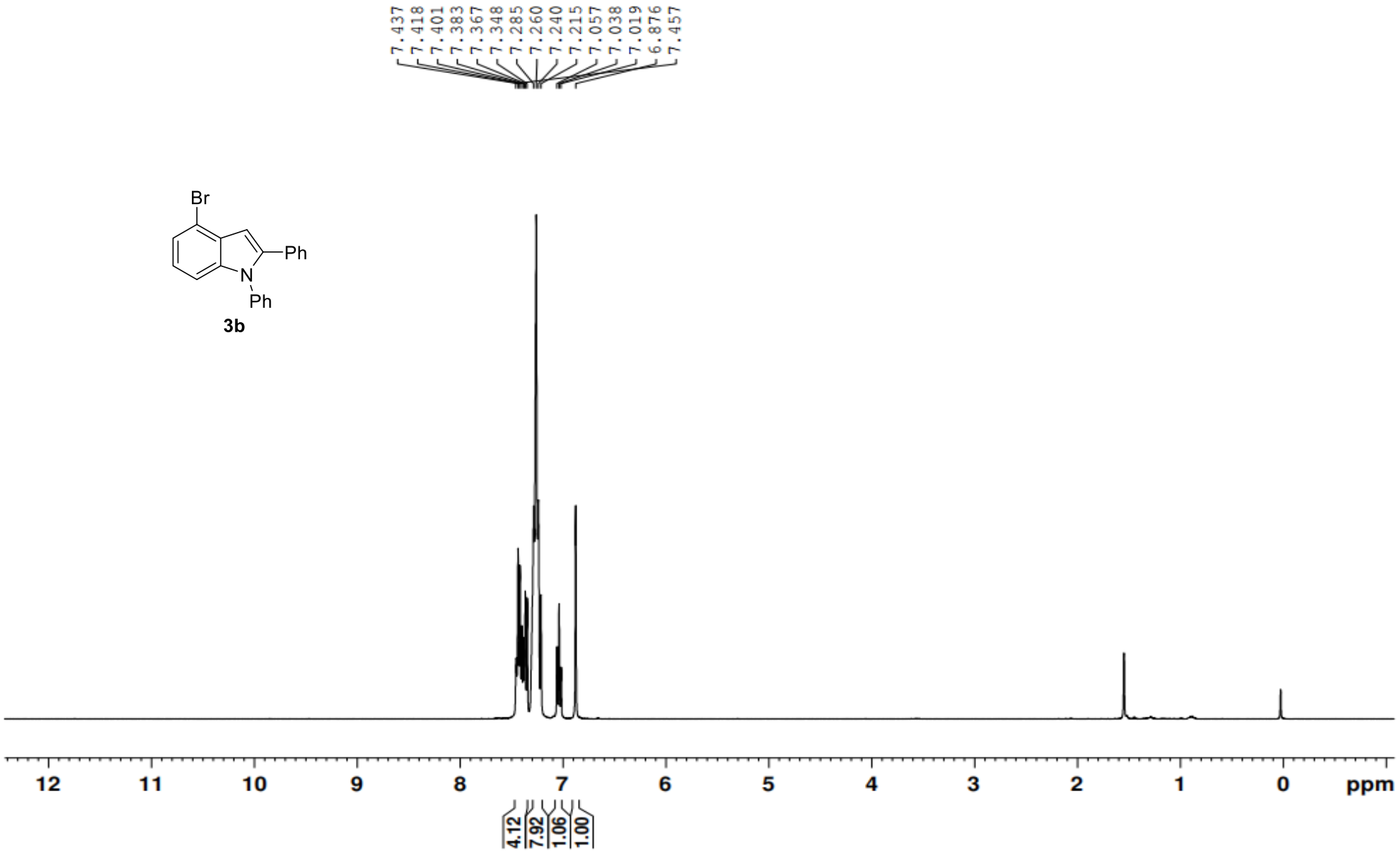


Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b.**

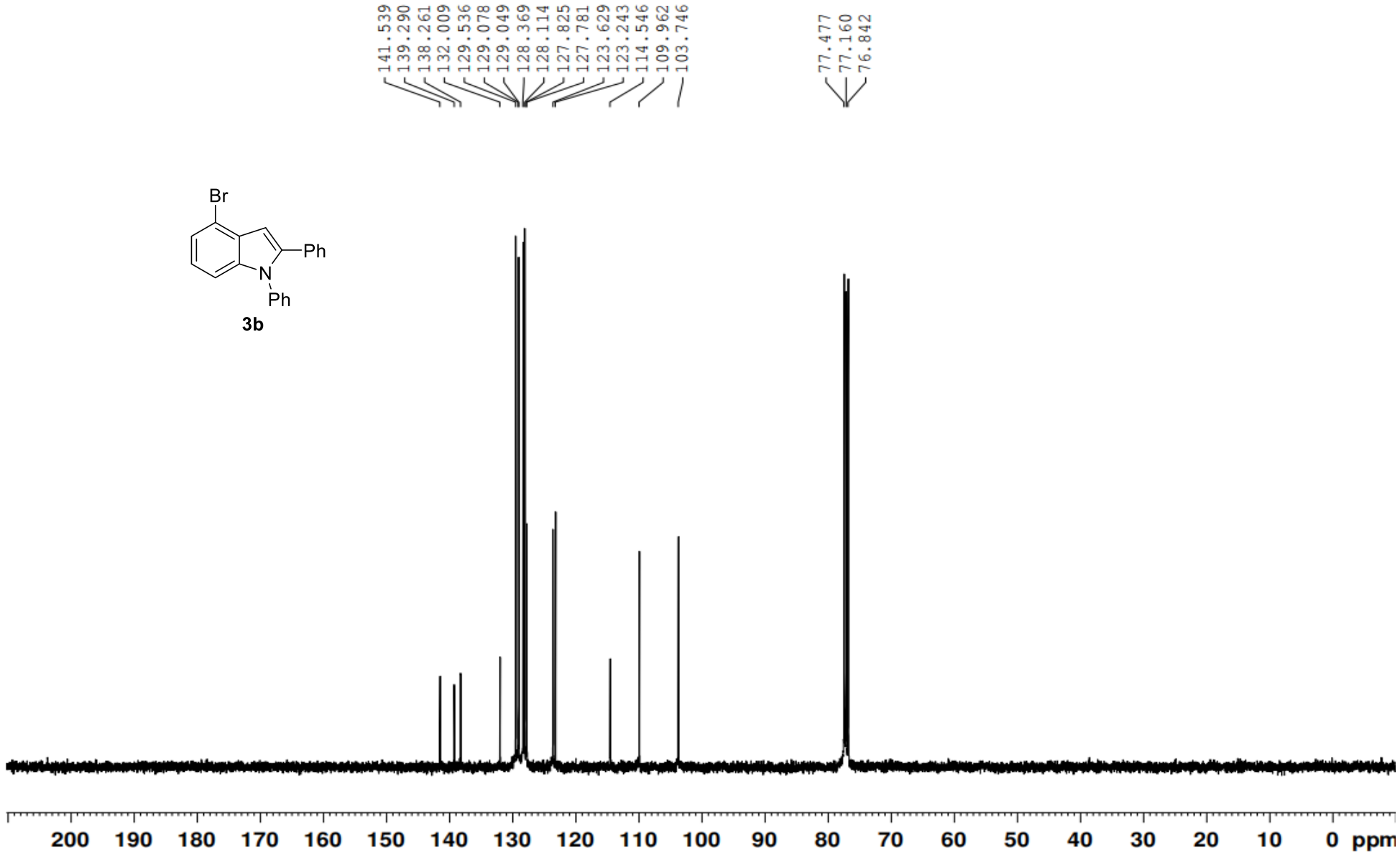


Figure S48. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3b.**

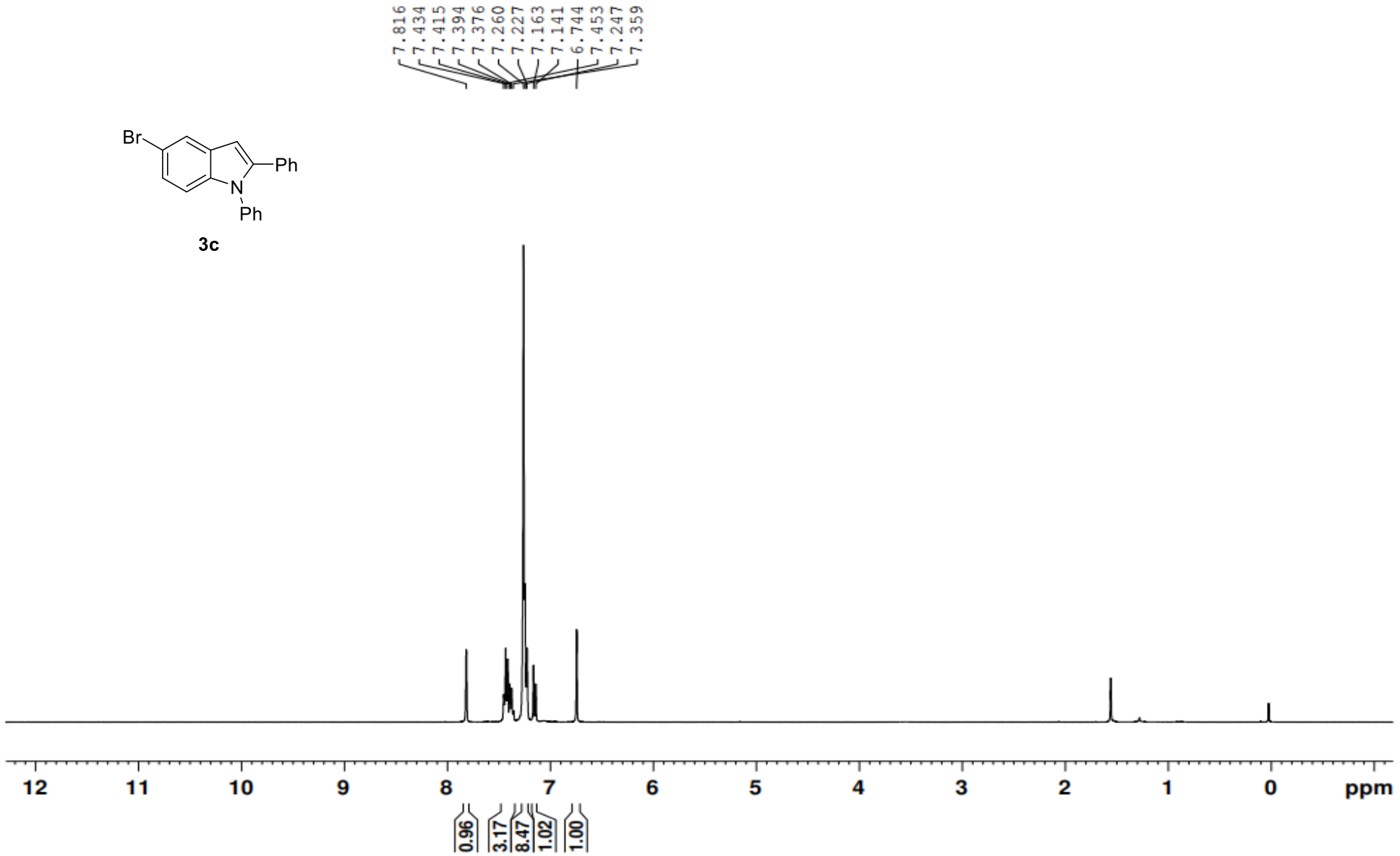


Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c.**

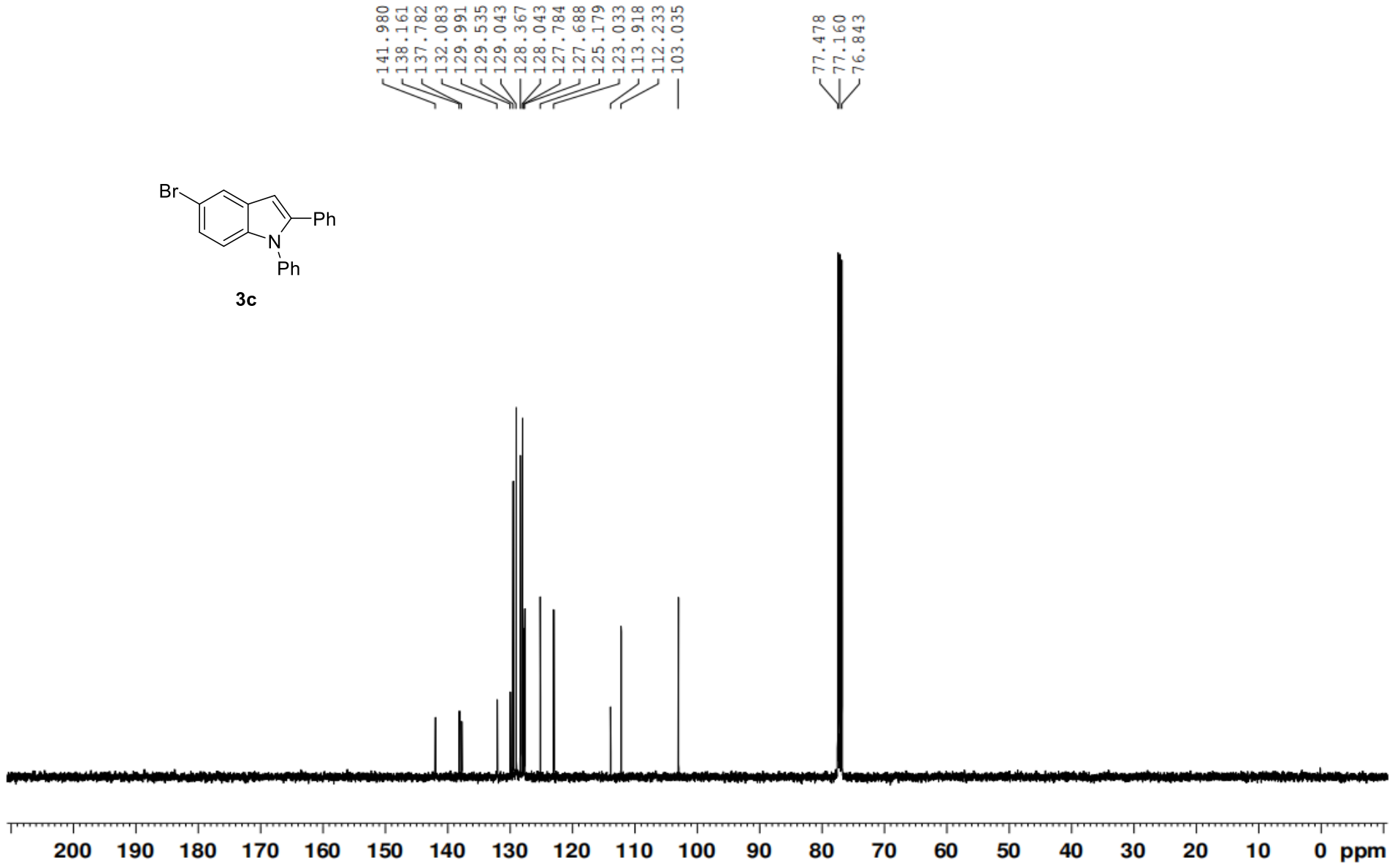


Figure S50. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3c.**

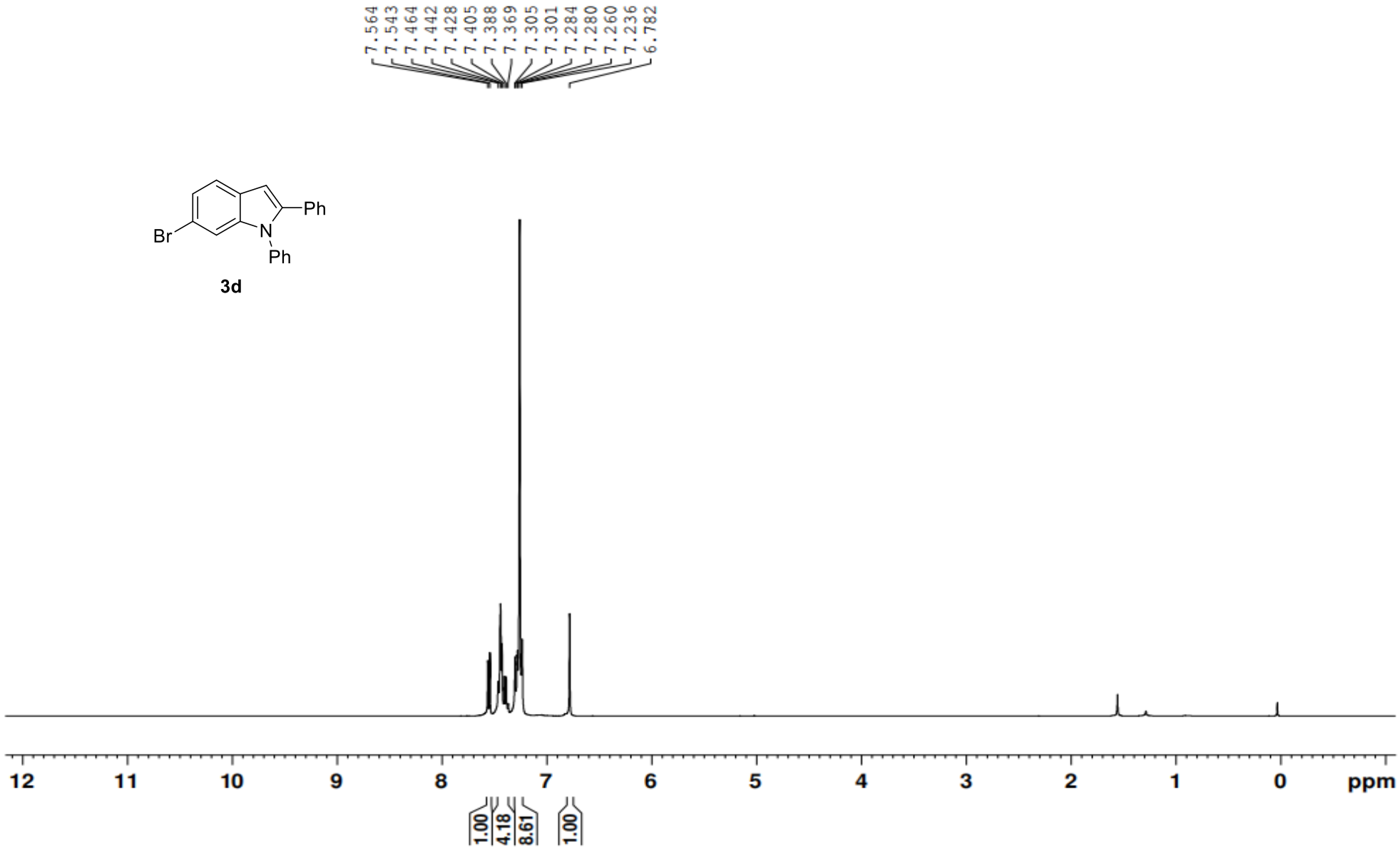


Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d.**

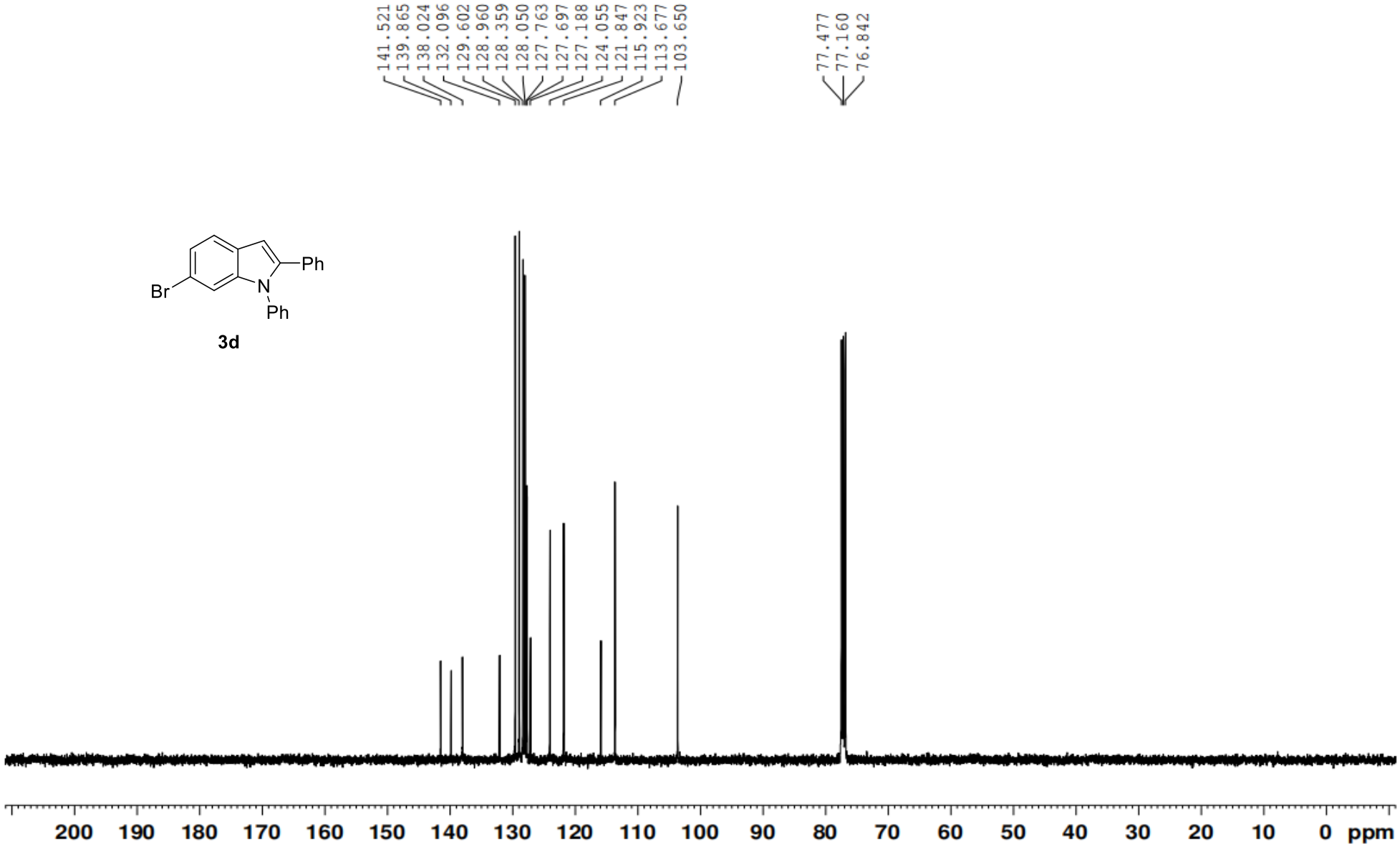


Figure S52. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3d.**

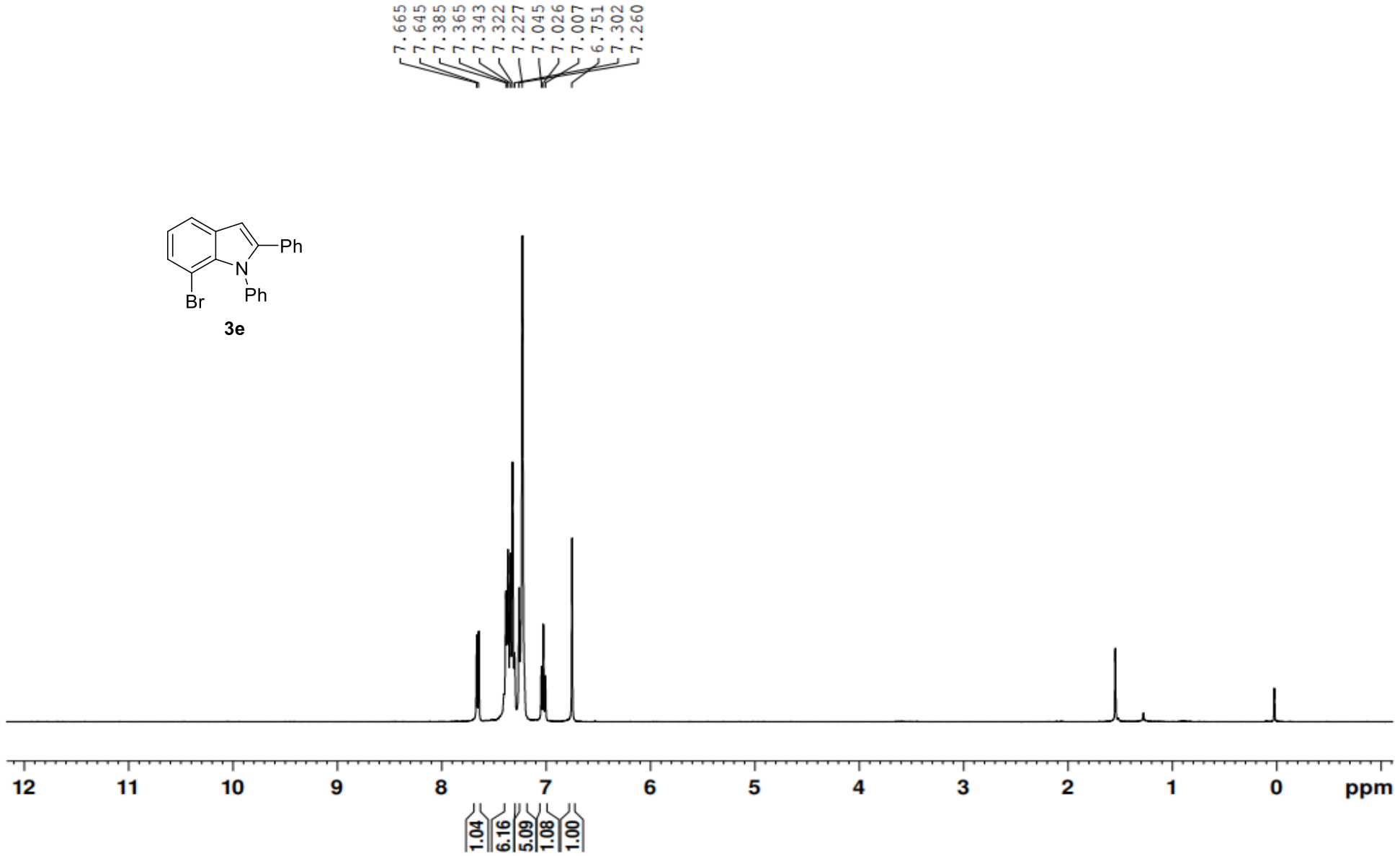


Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e.**

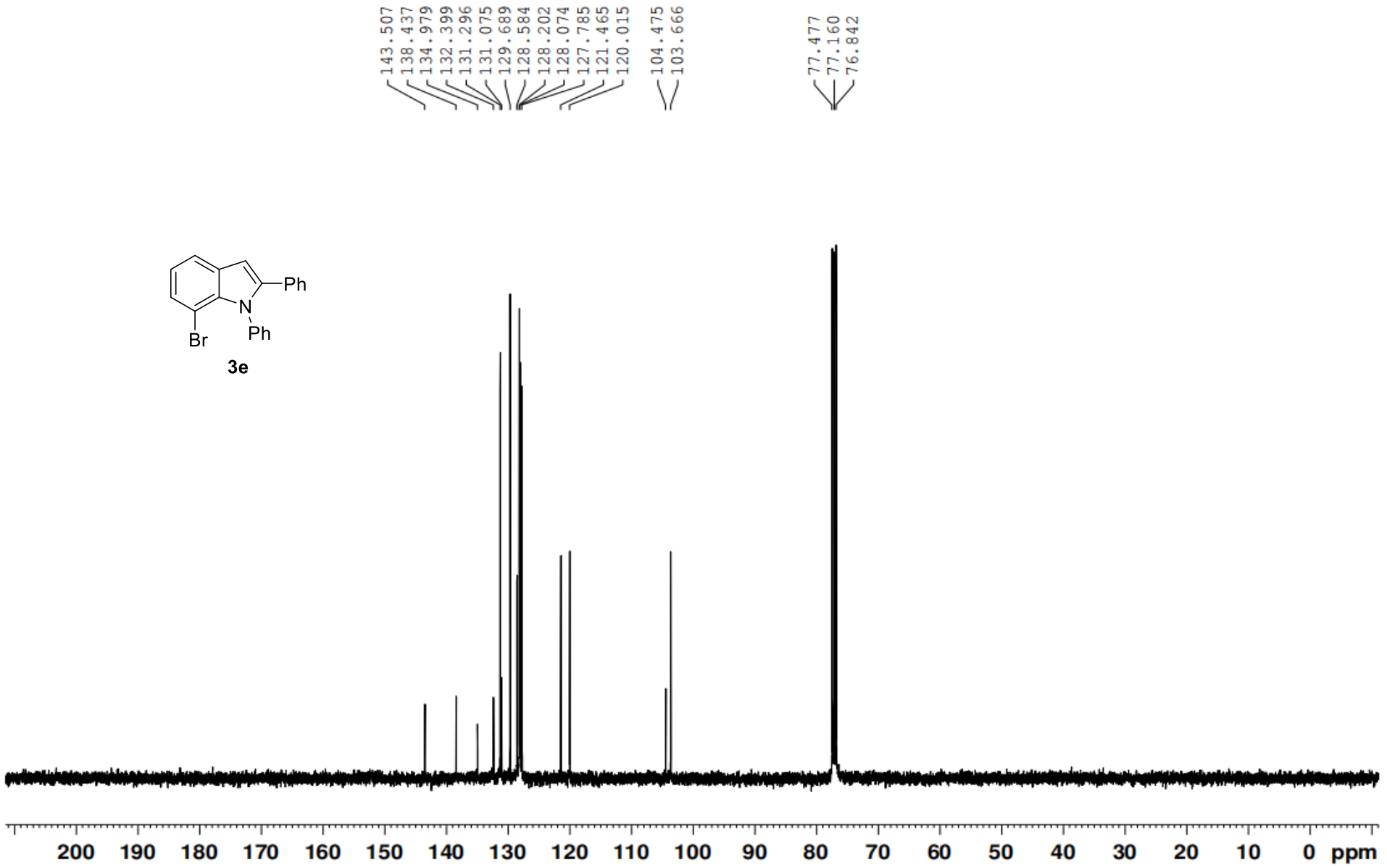


Figure S54. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3e.**

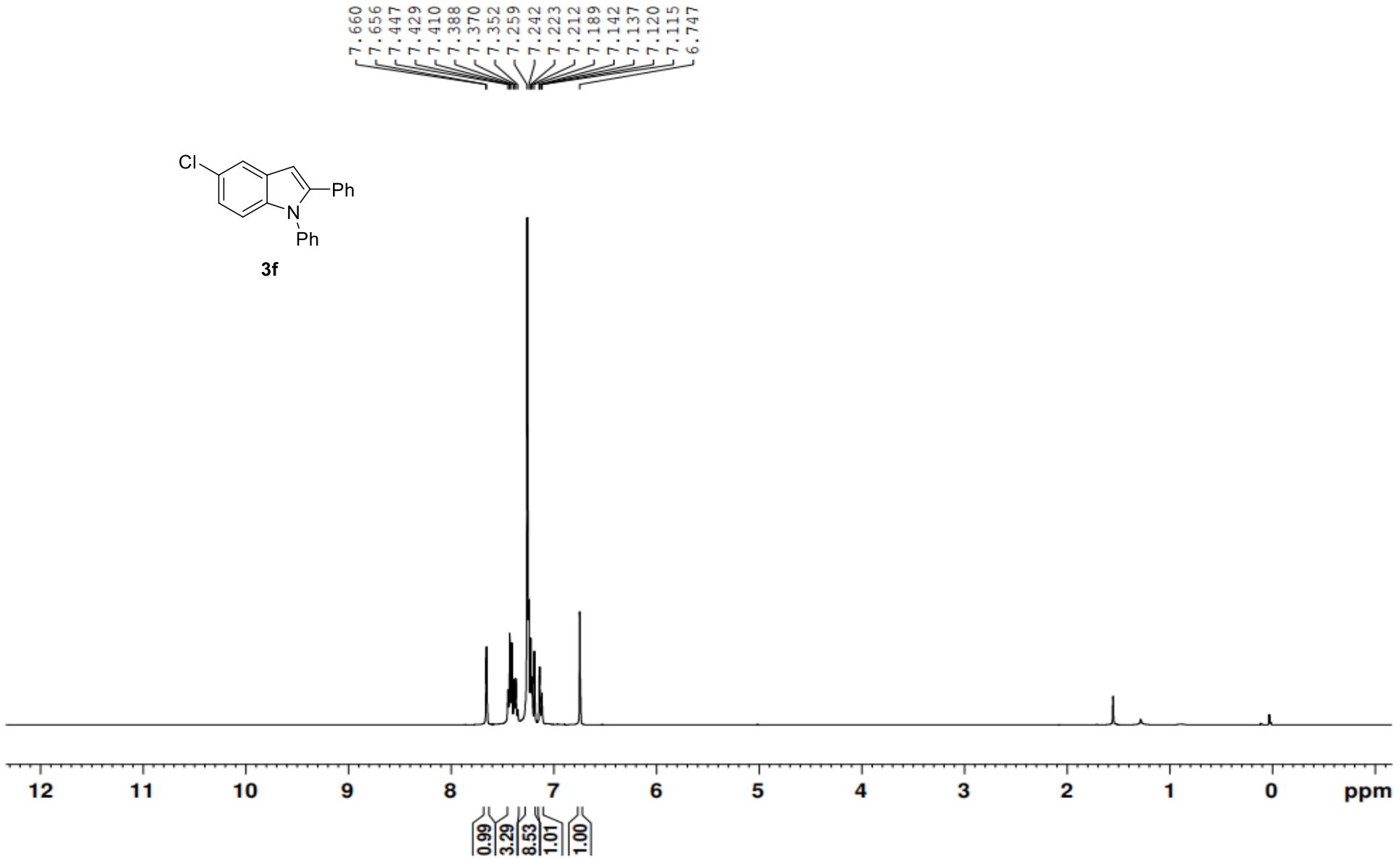


Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f.**

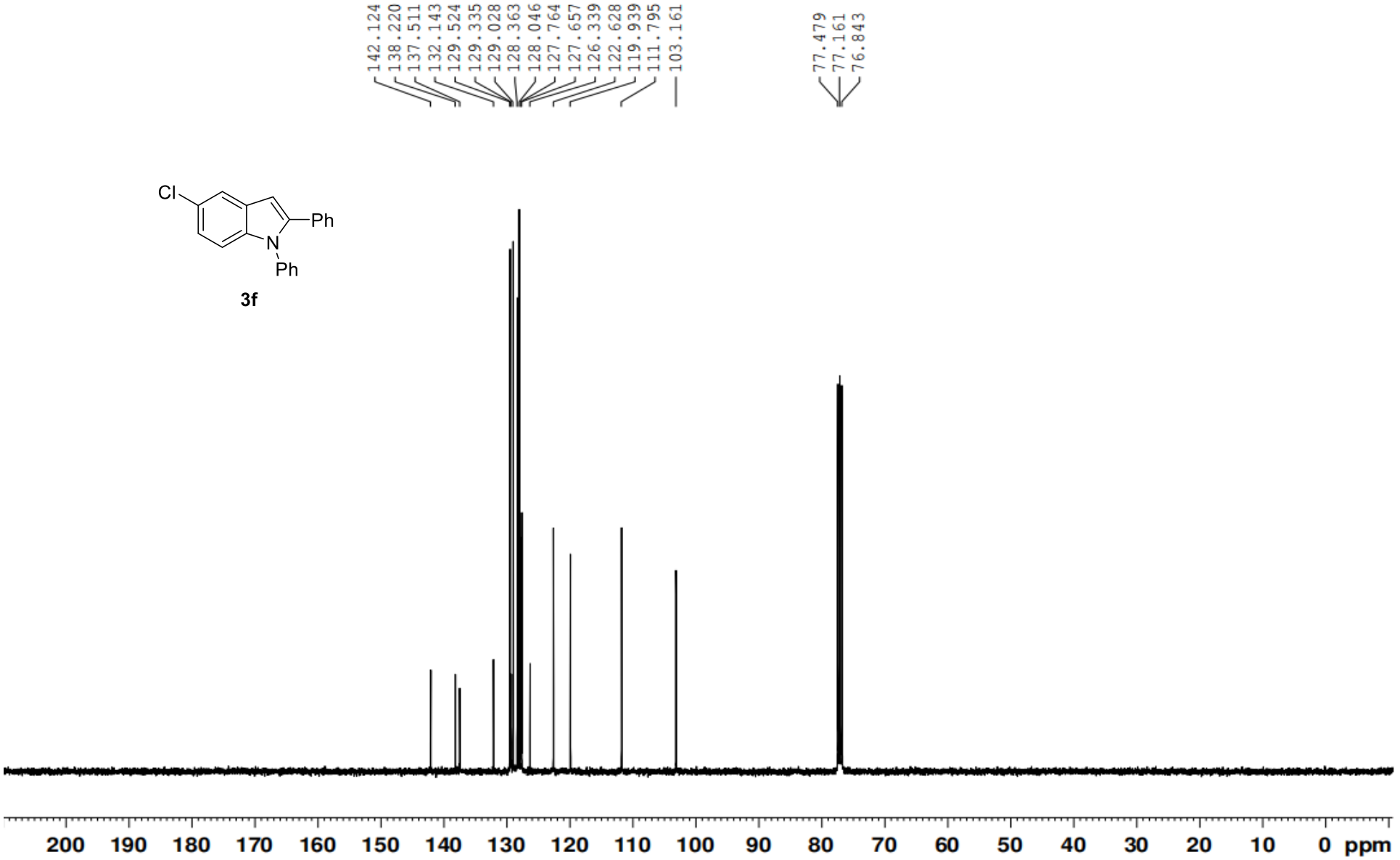


Figure S56. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3f.**

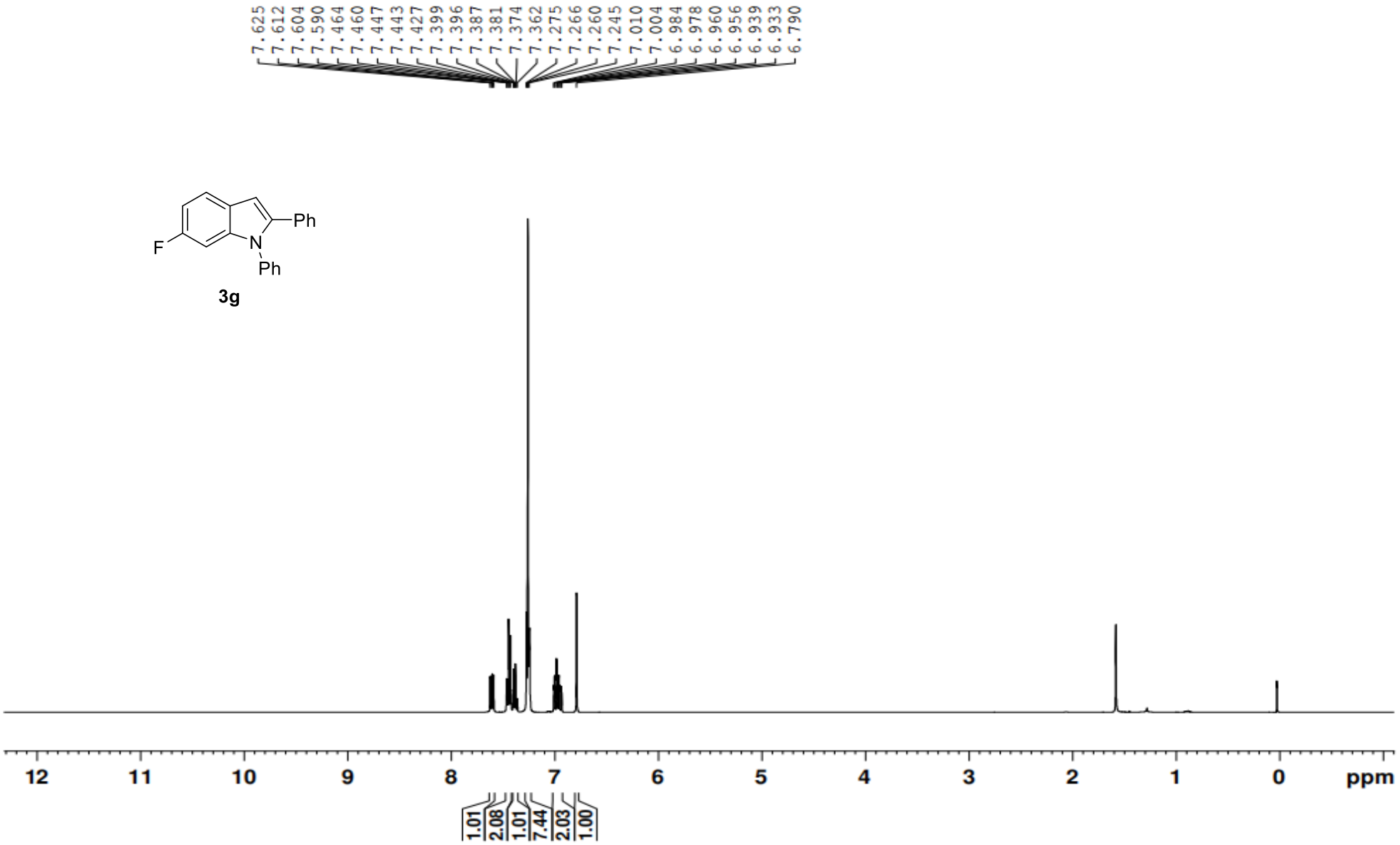


Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g.**

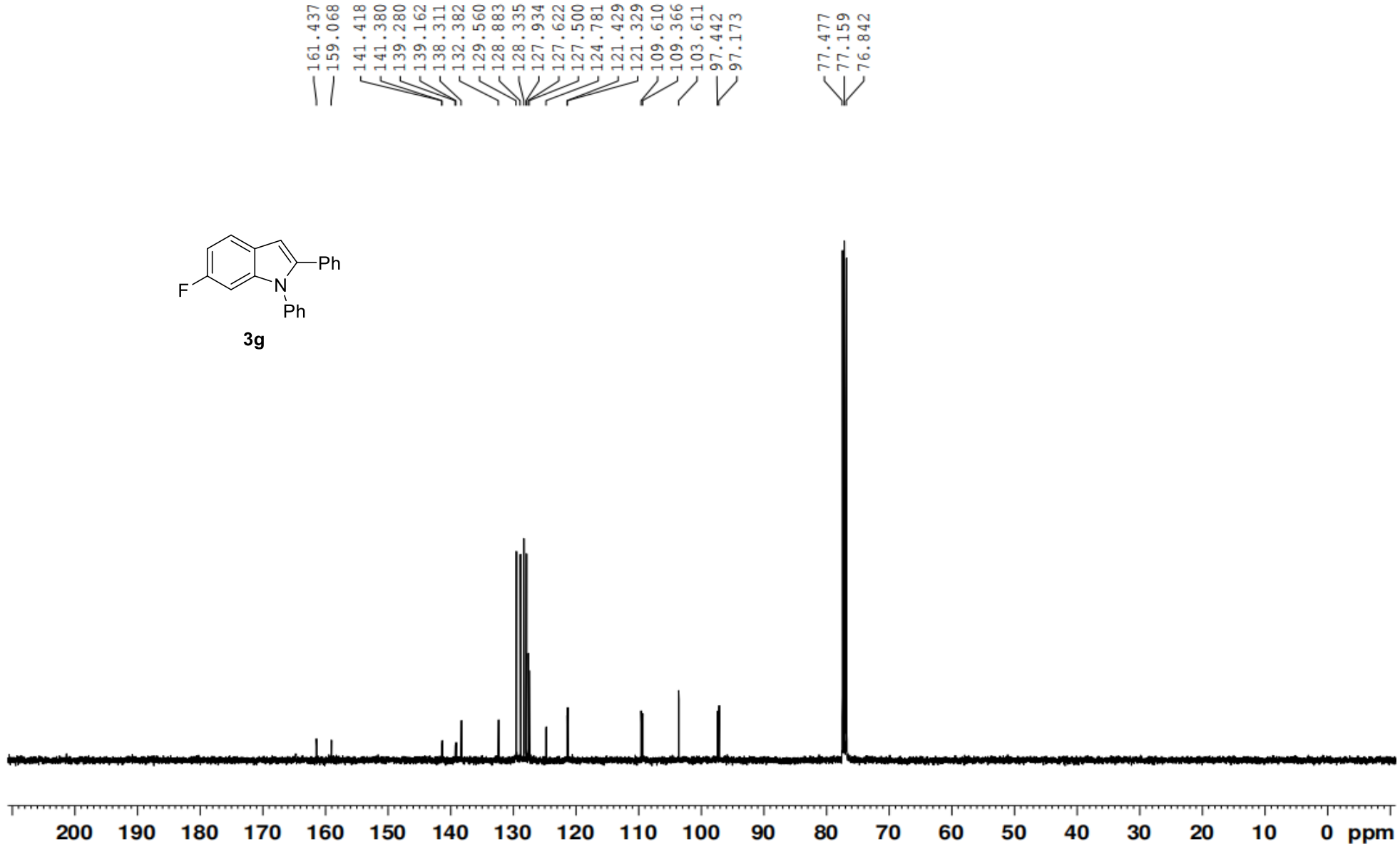


Figure S58. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3g.**

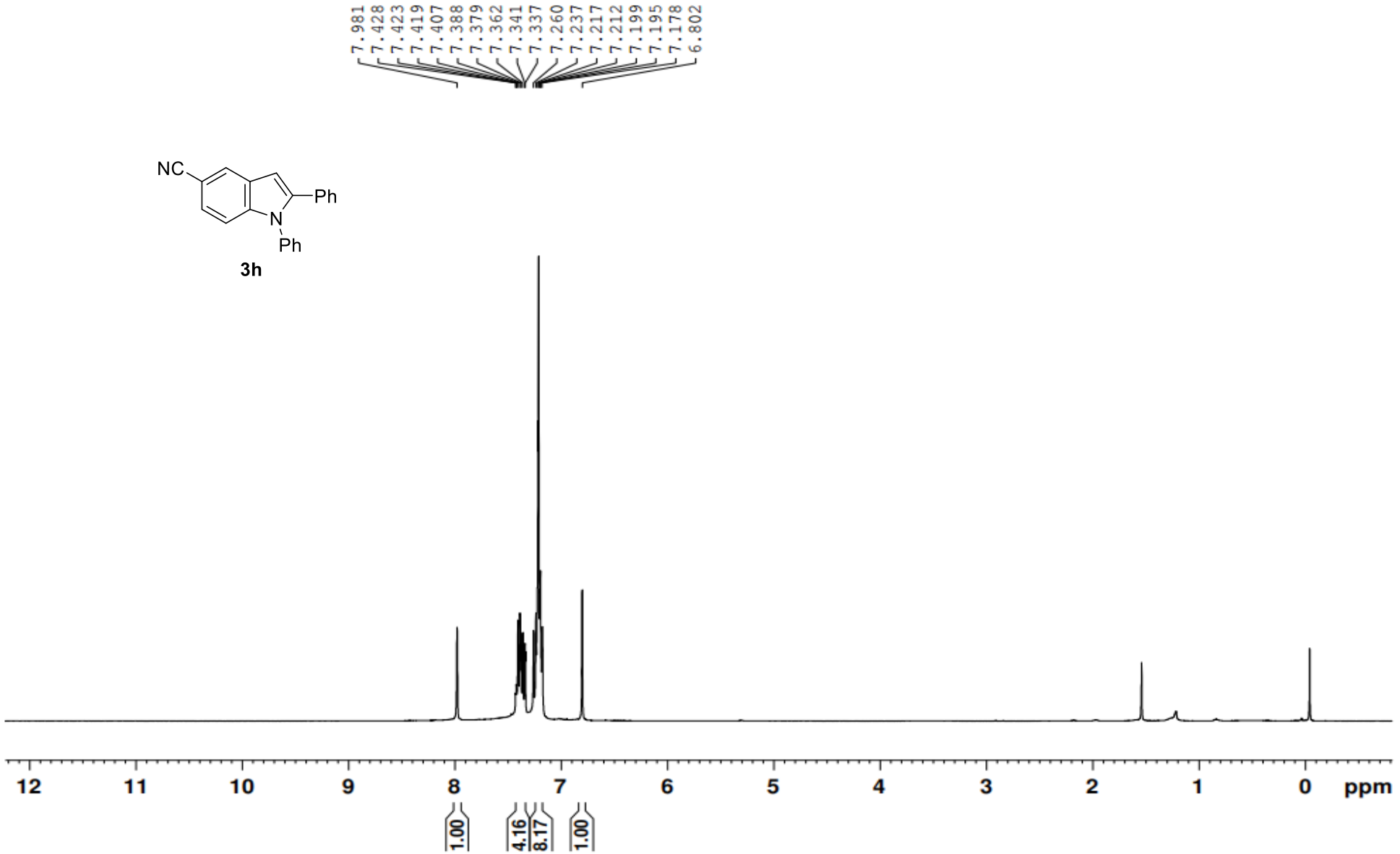


Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h.**

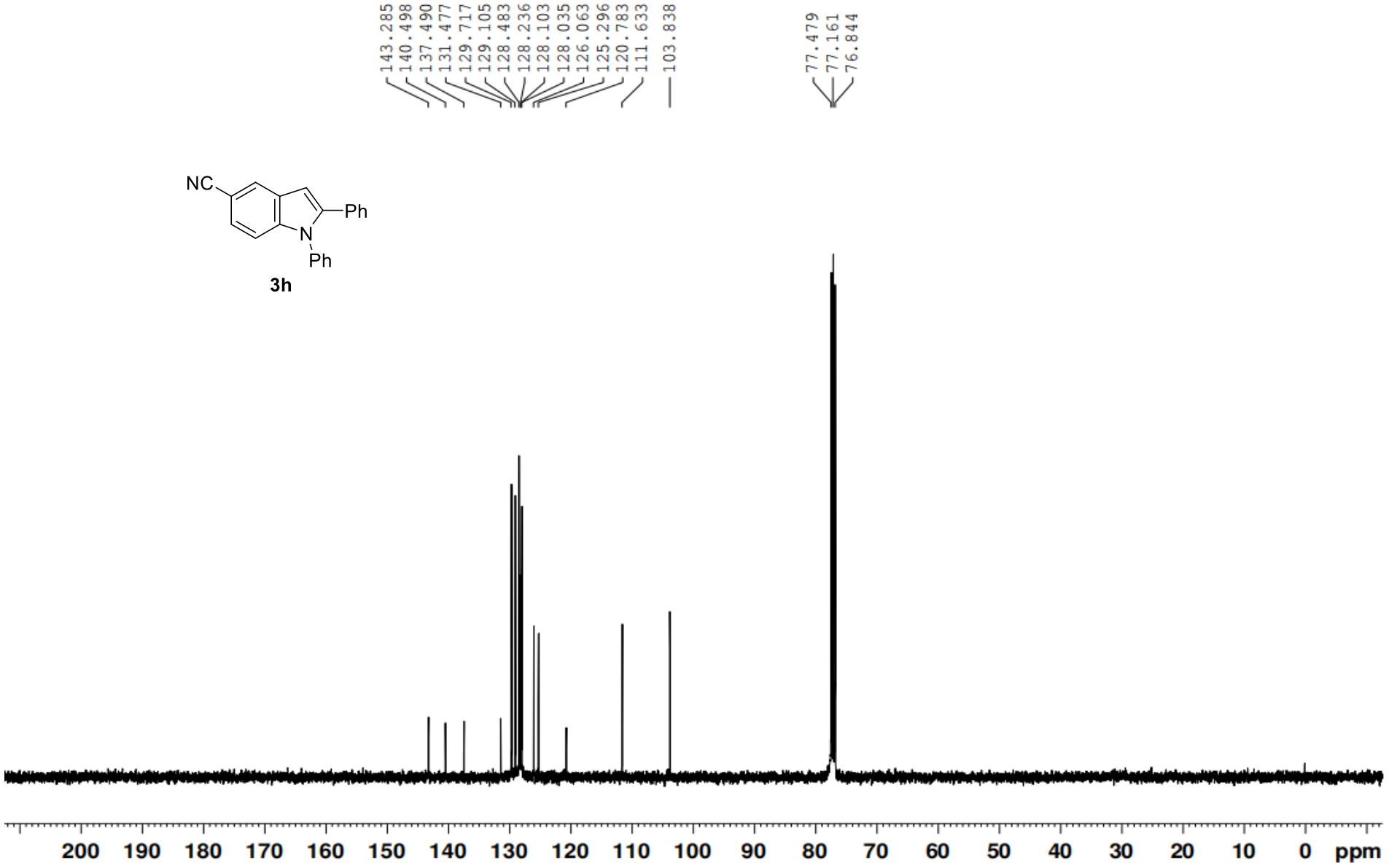


Figure S60. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3h.**

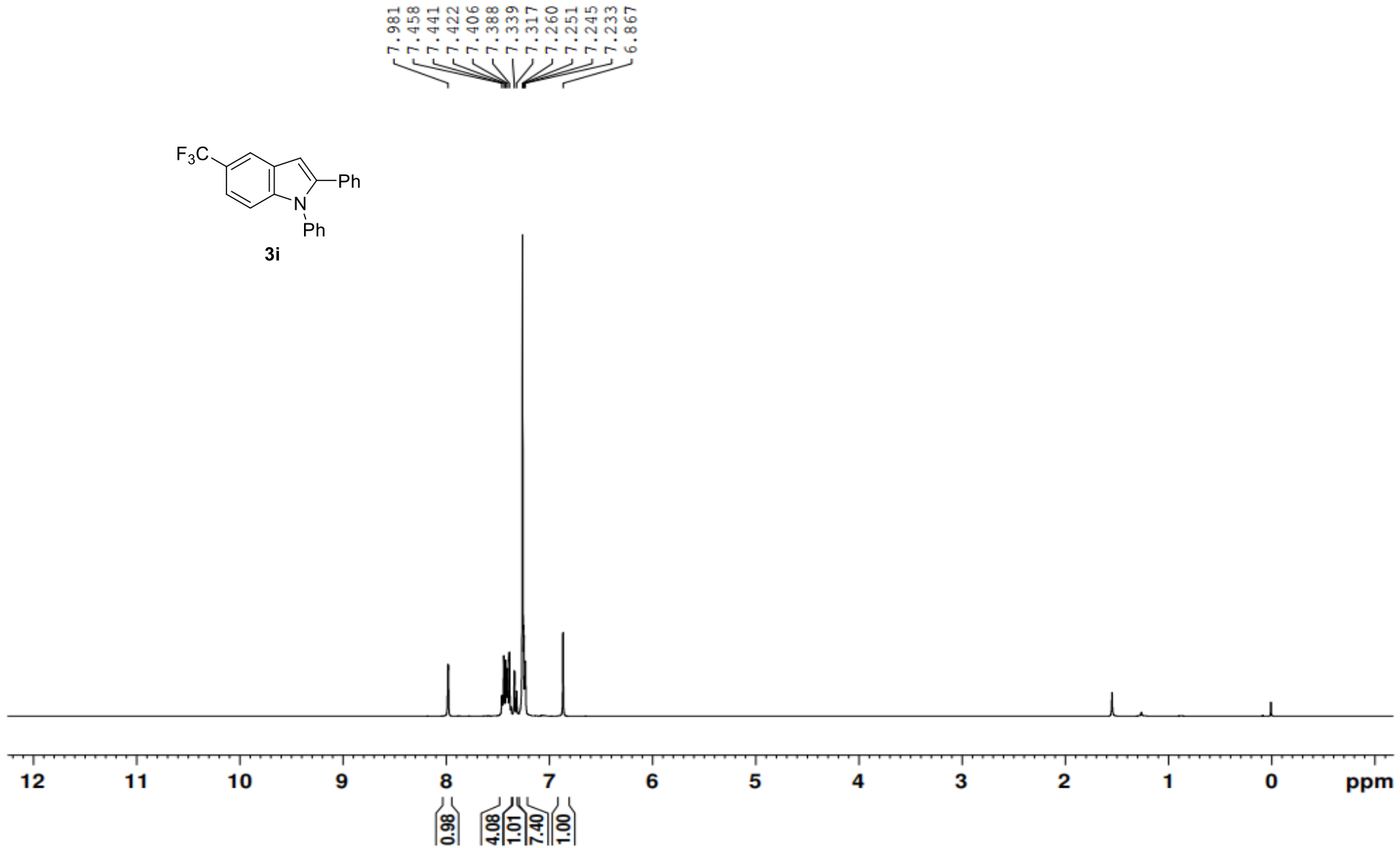


Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i.**

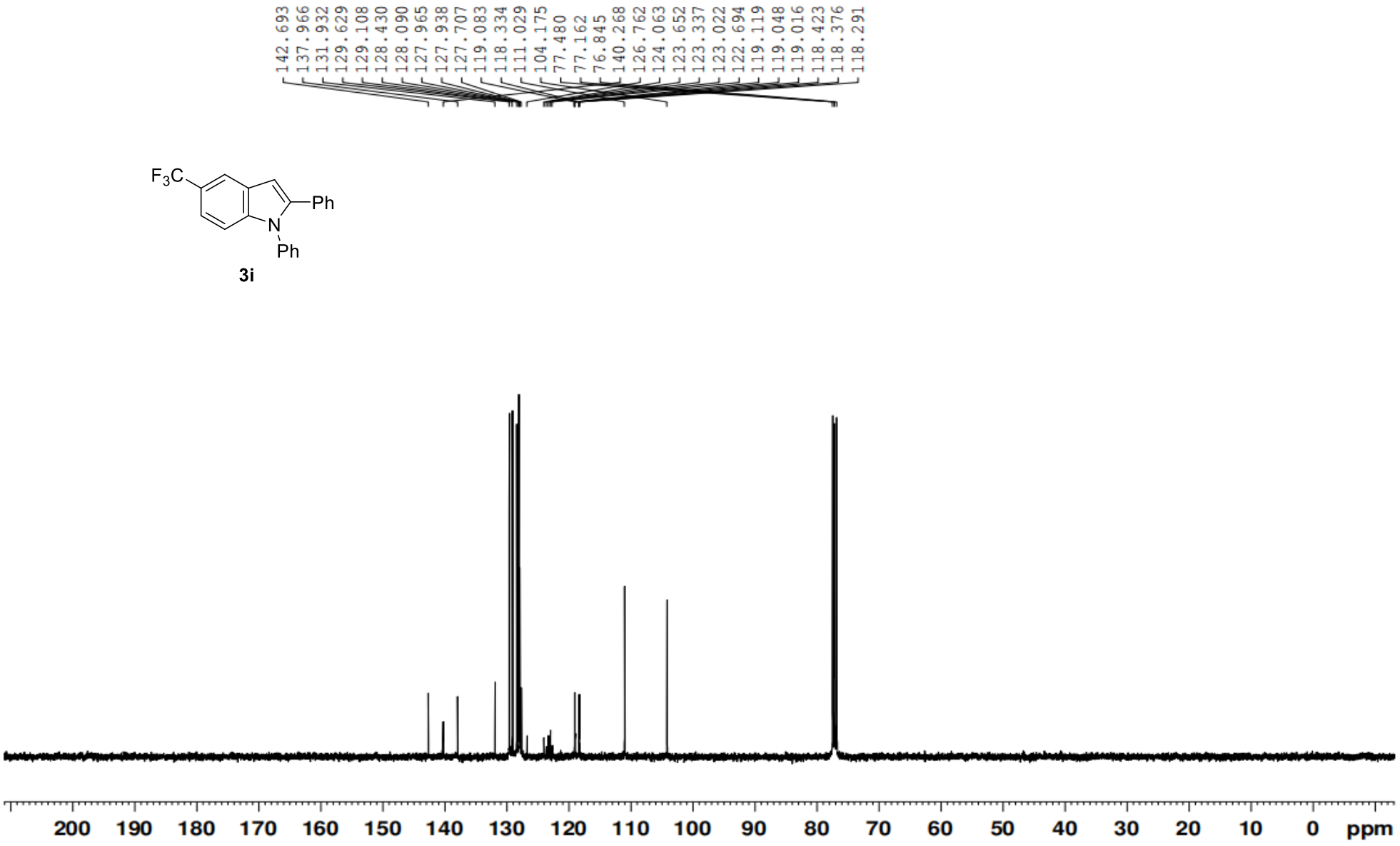


Figure S62. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3i.**

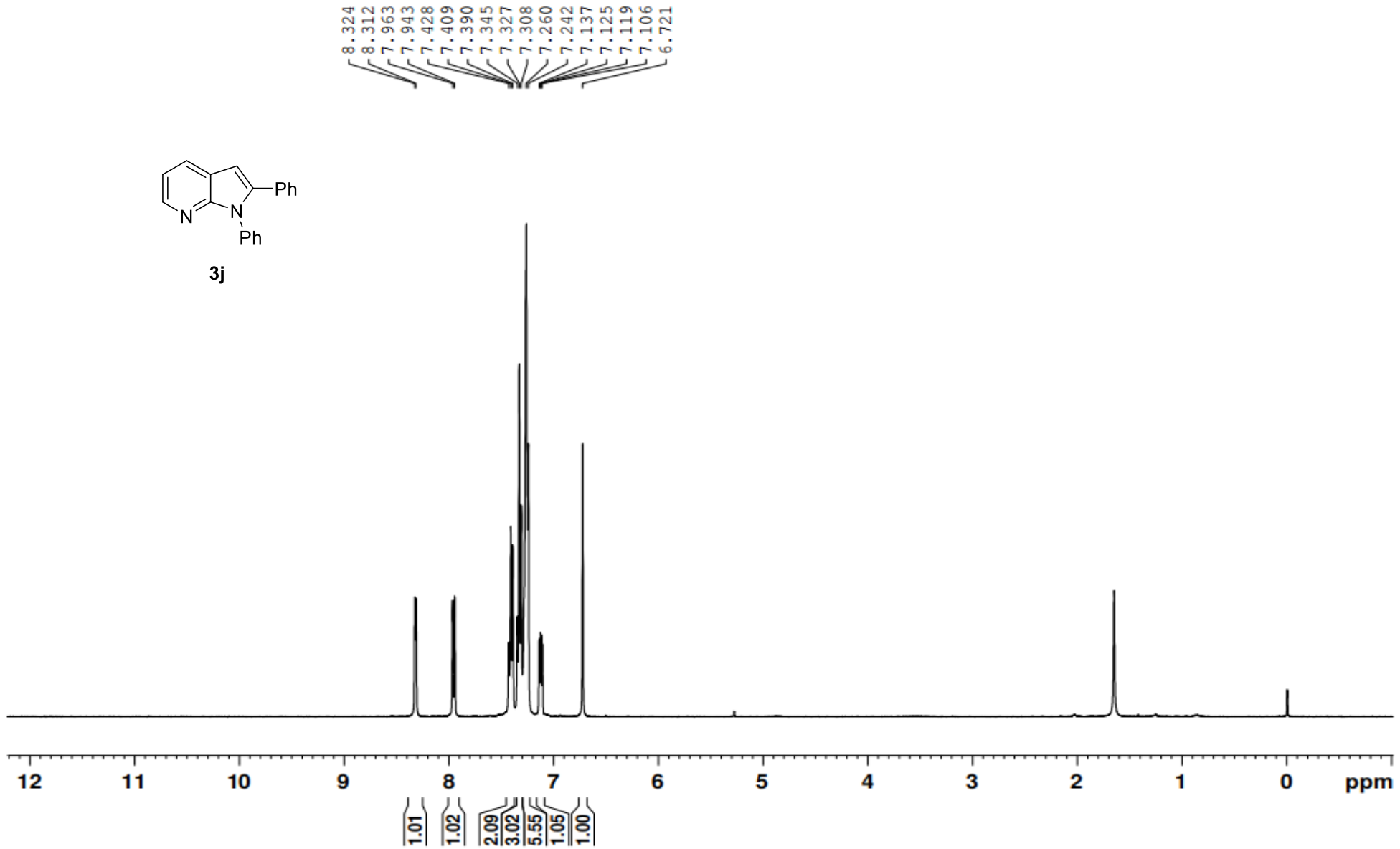


Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j.**

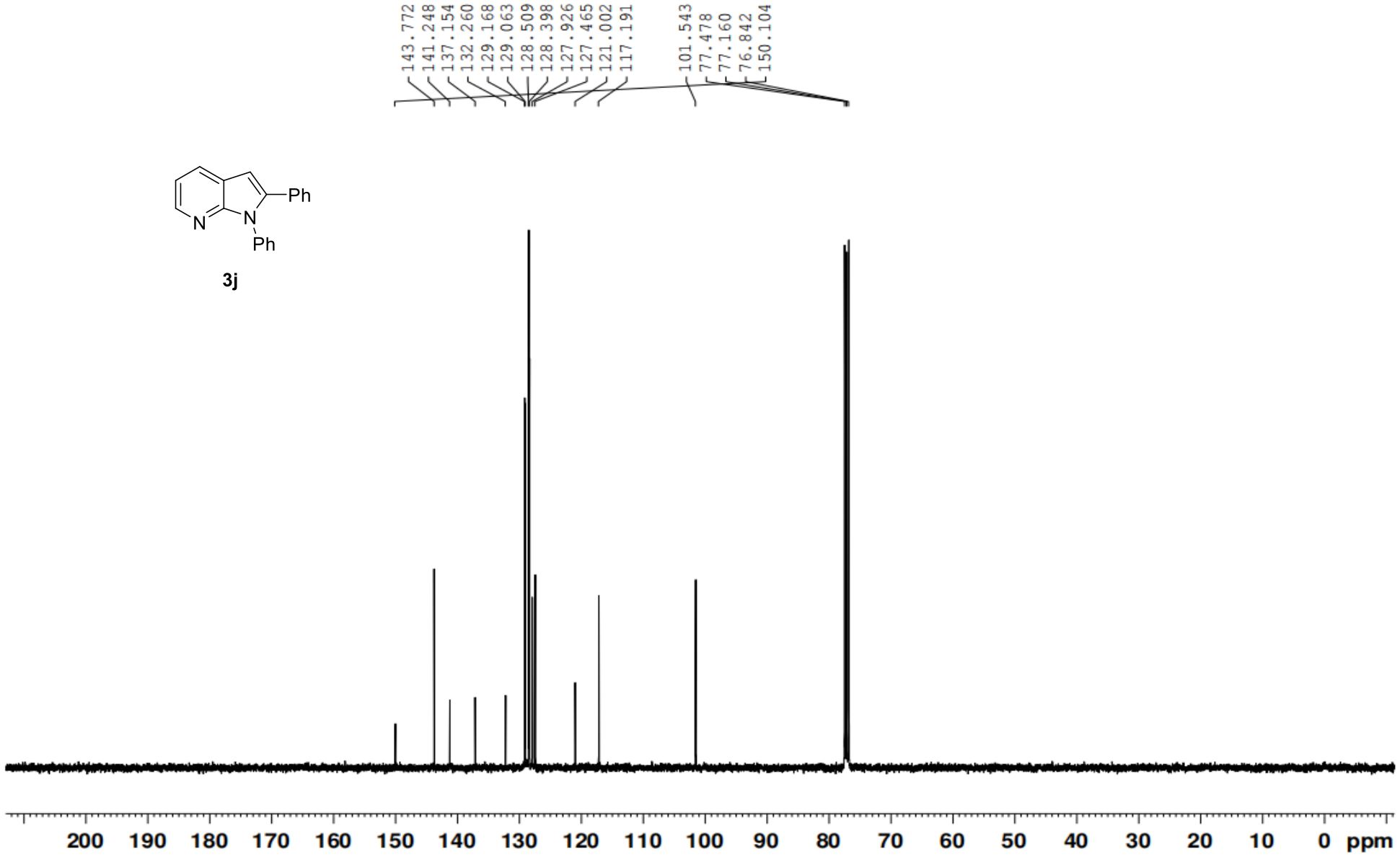


Figure S64. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3j.**

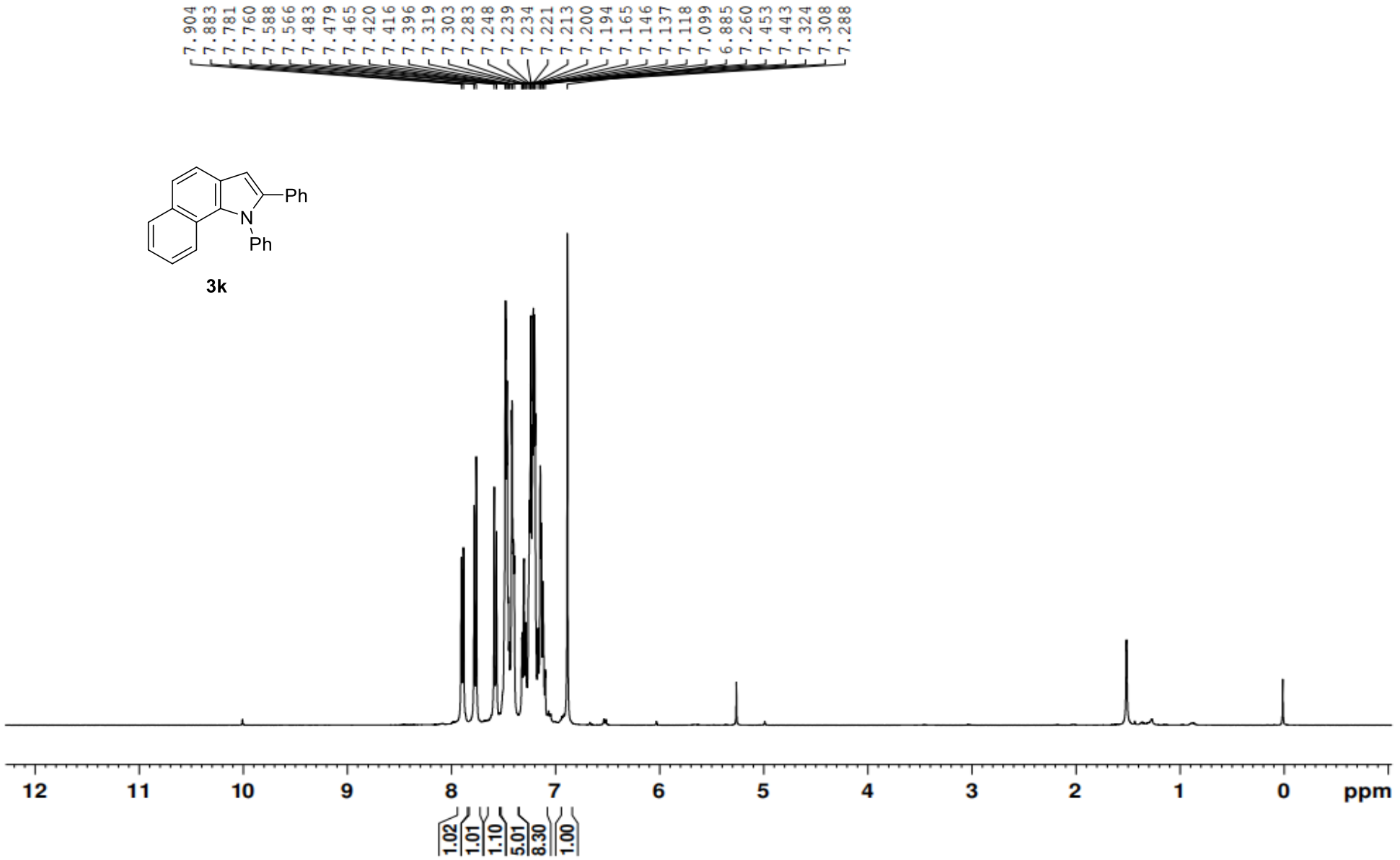


Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k.**

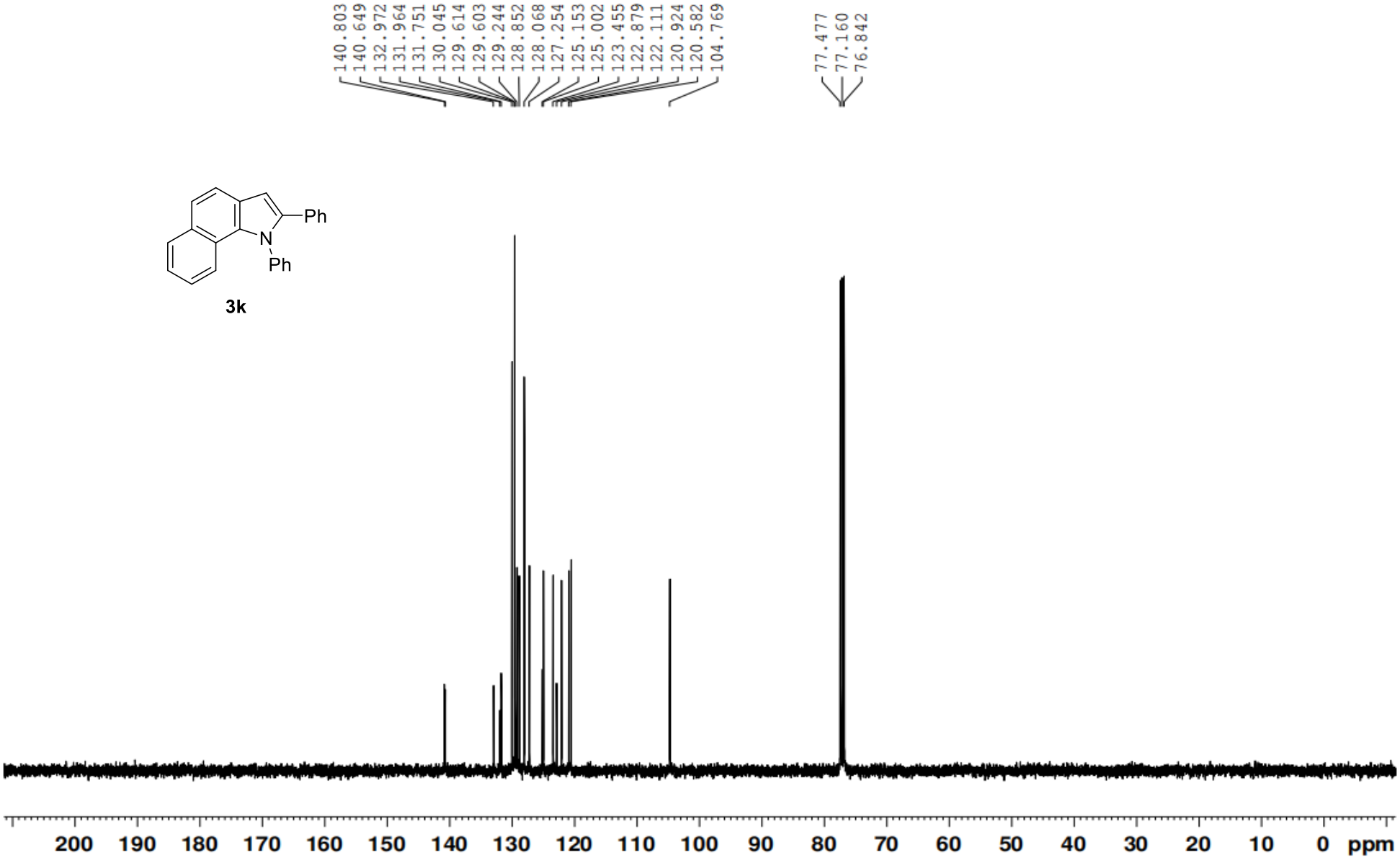


Figure S66. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3k.**

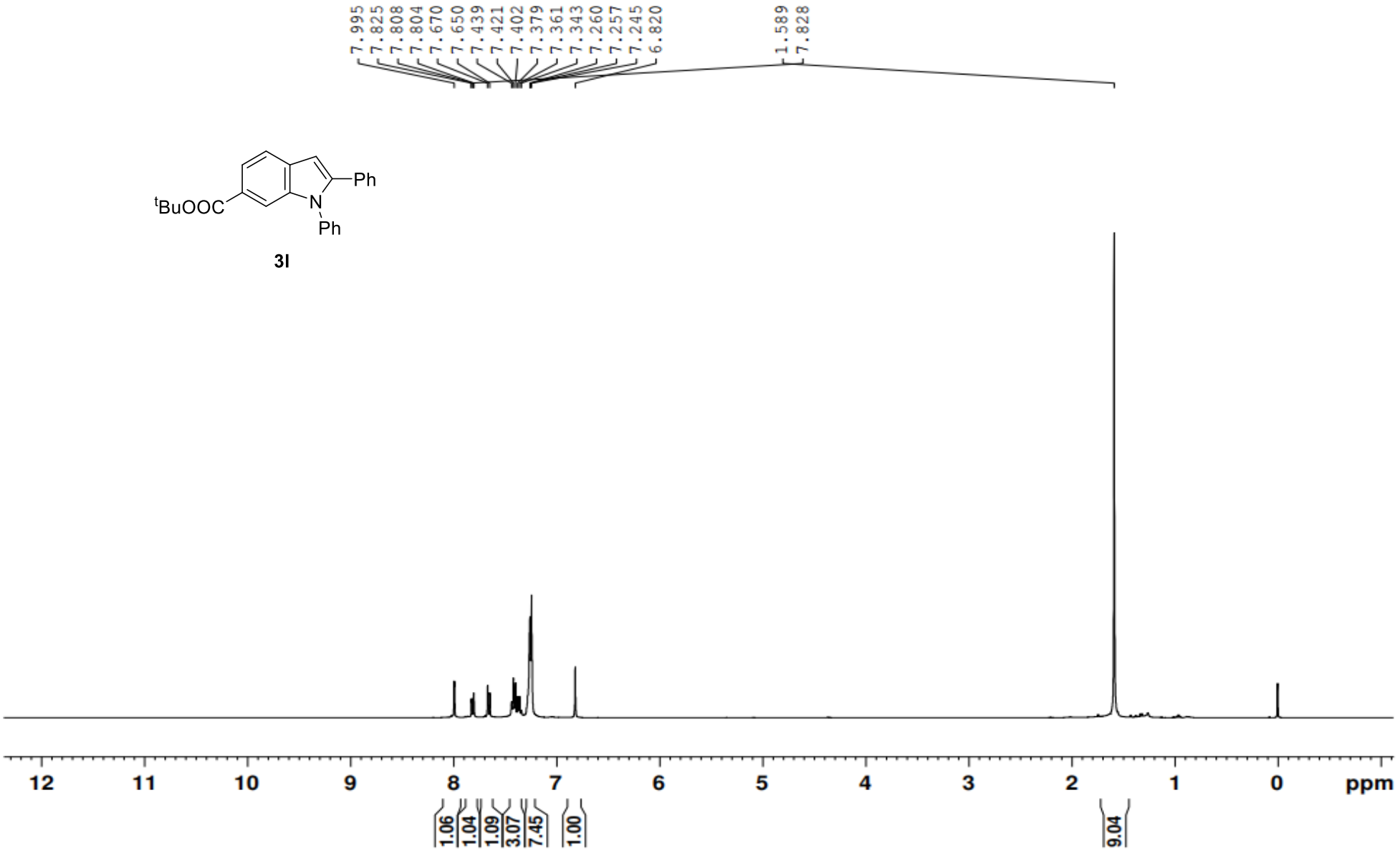


Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l.**

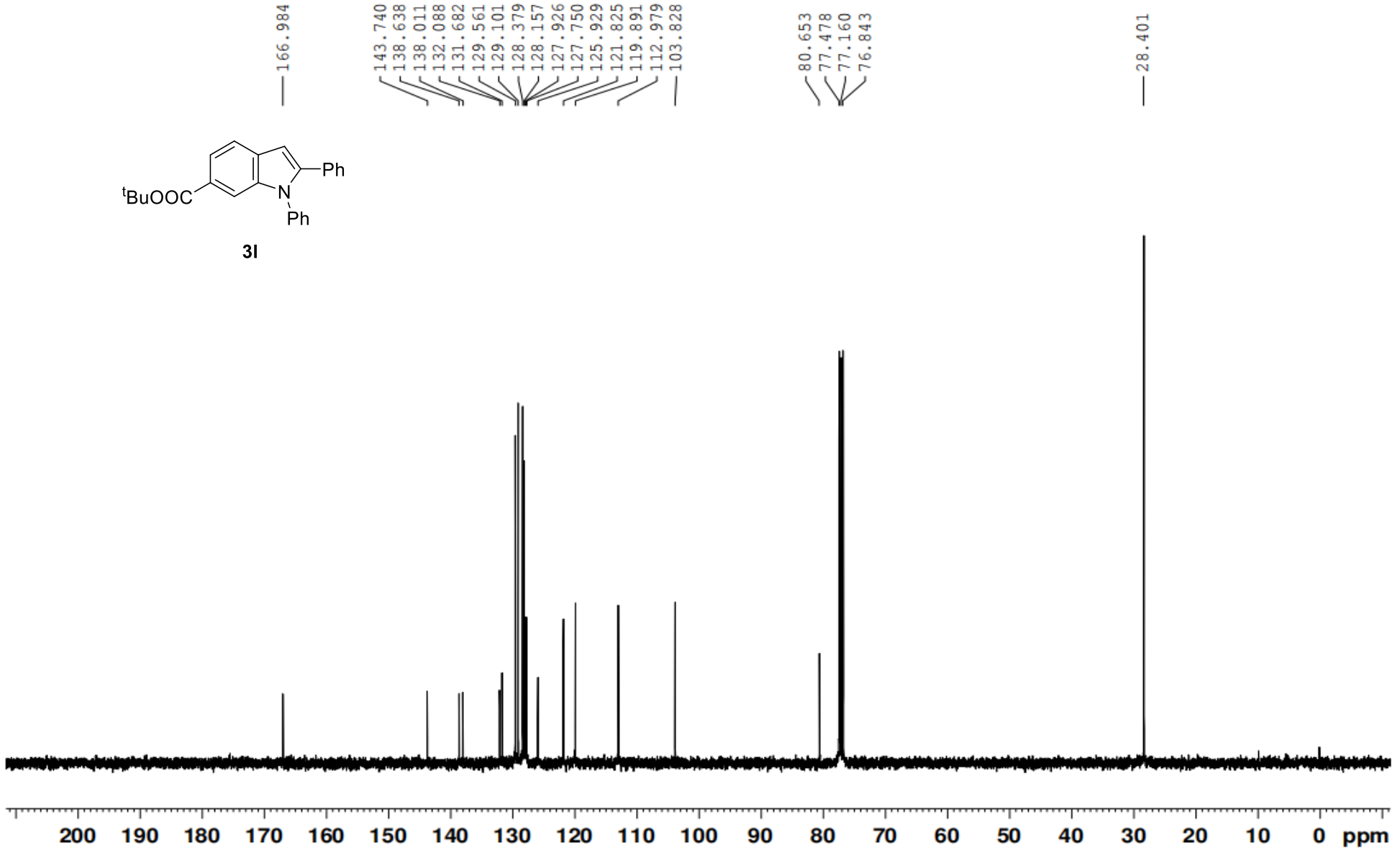


Figure S68. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3l.**

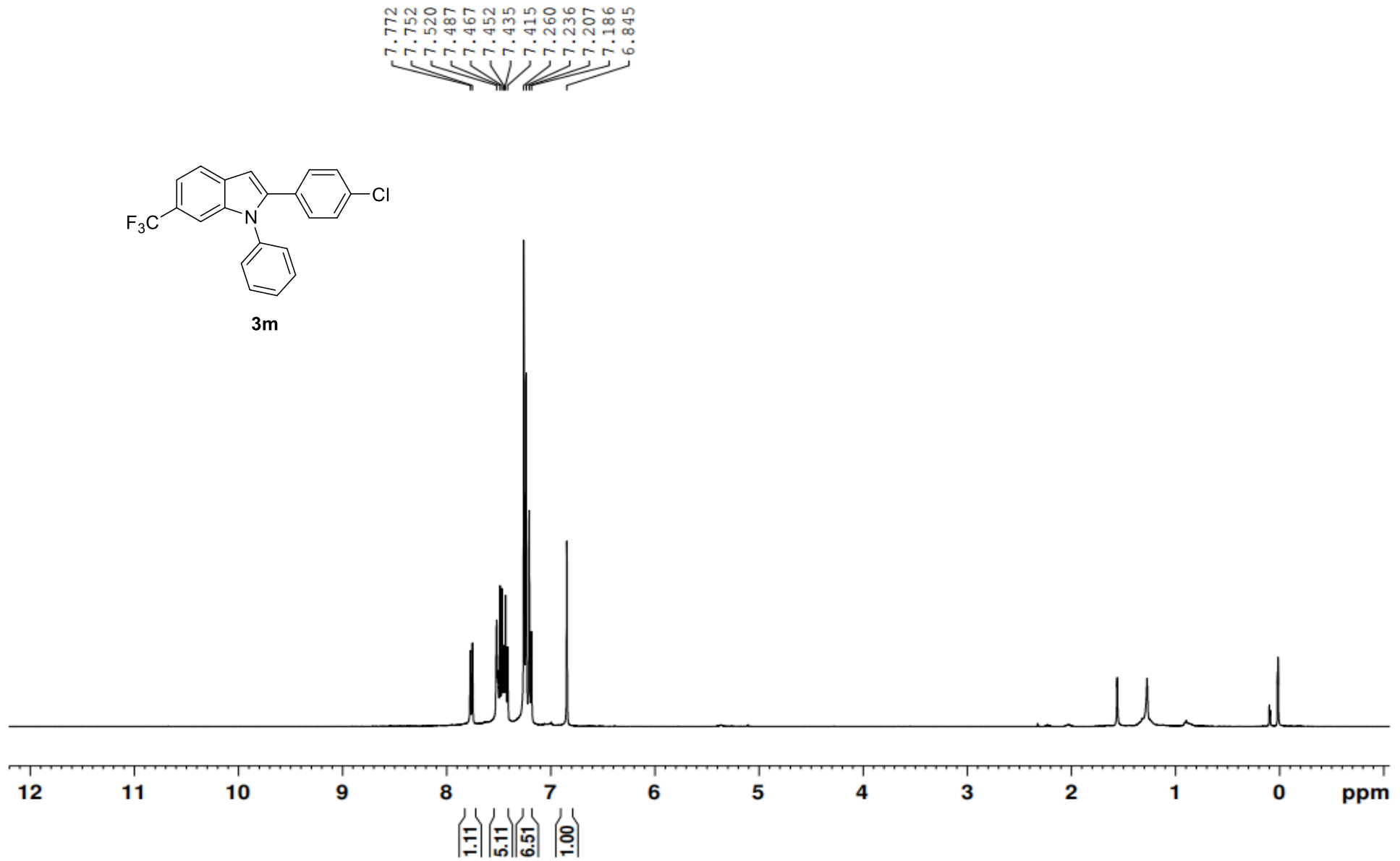


Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m.**

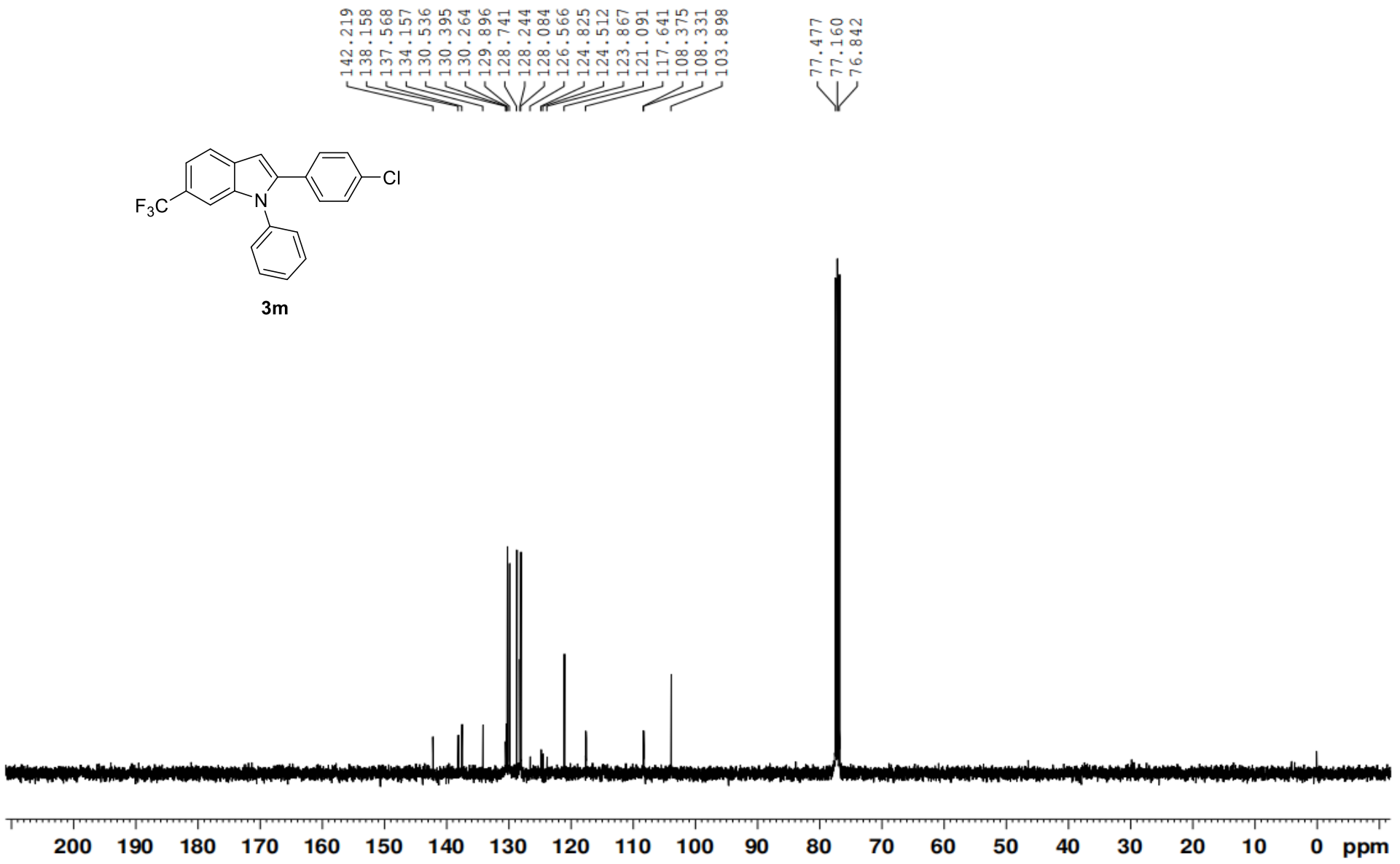


Figure S70. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3m.**

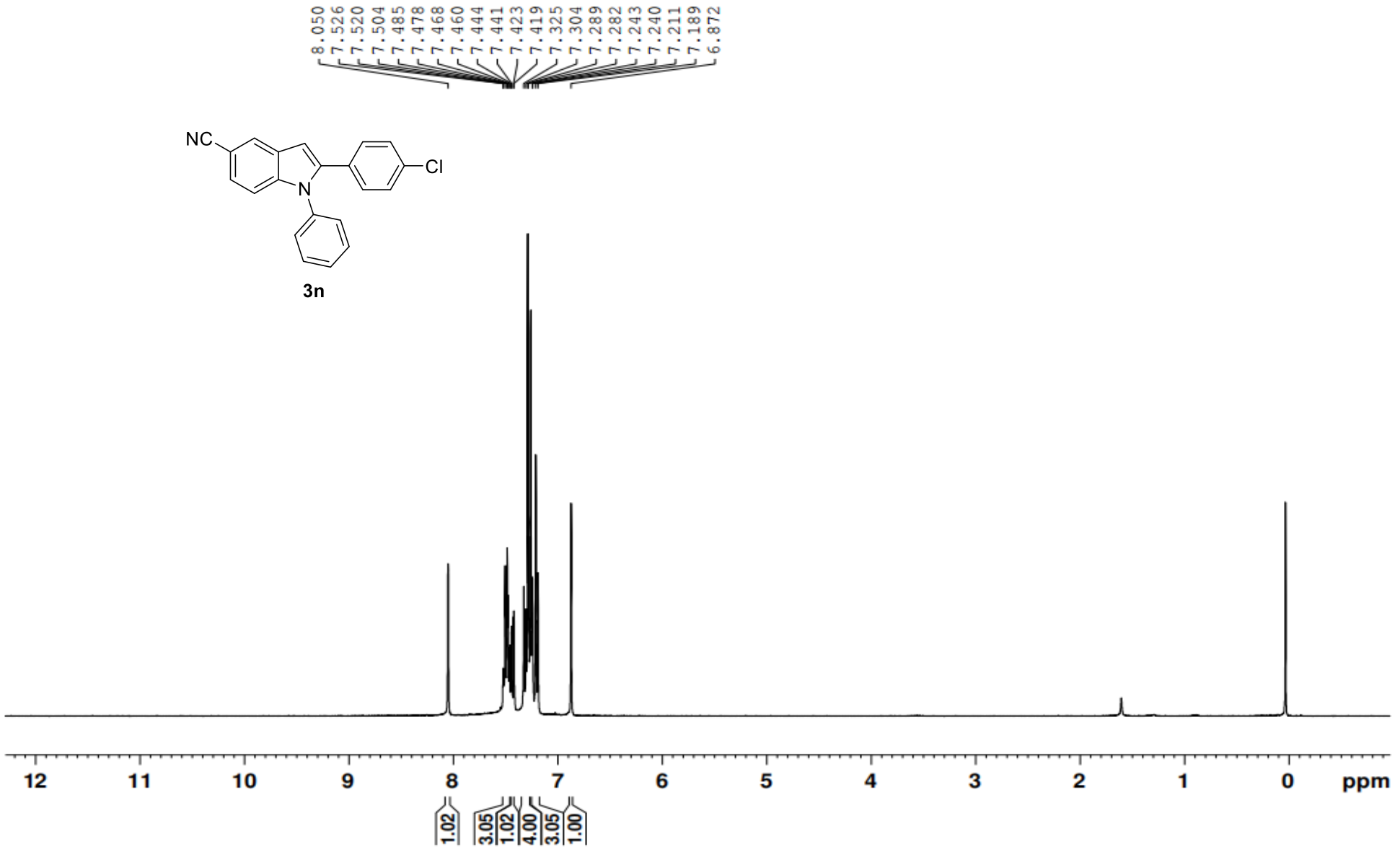


Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n.**

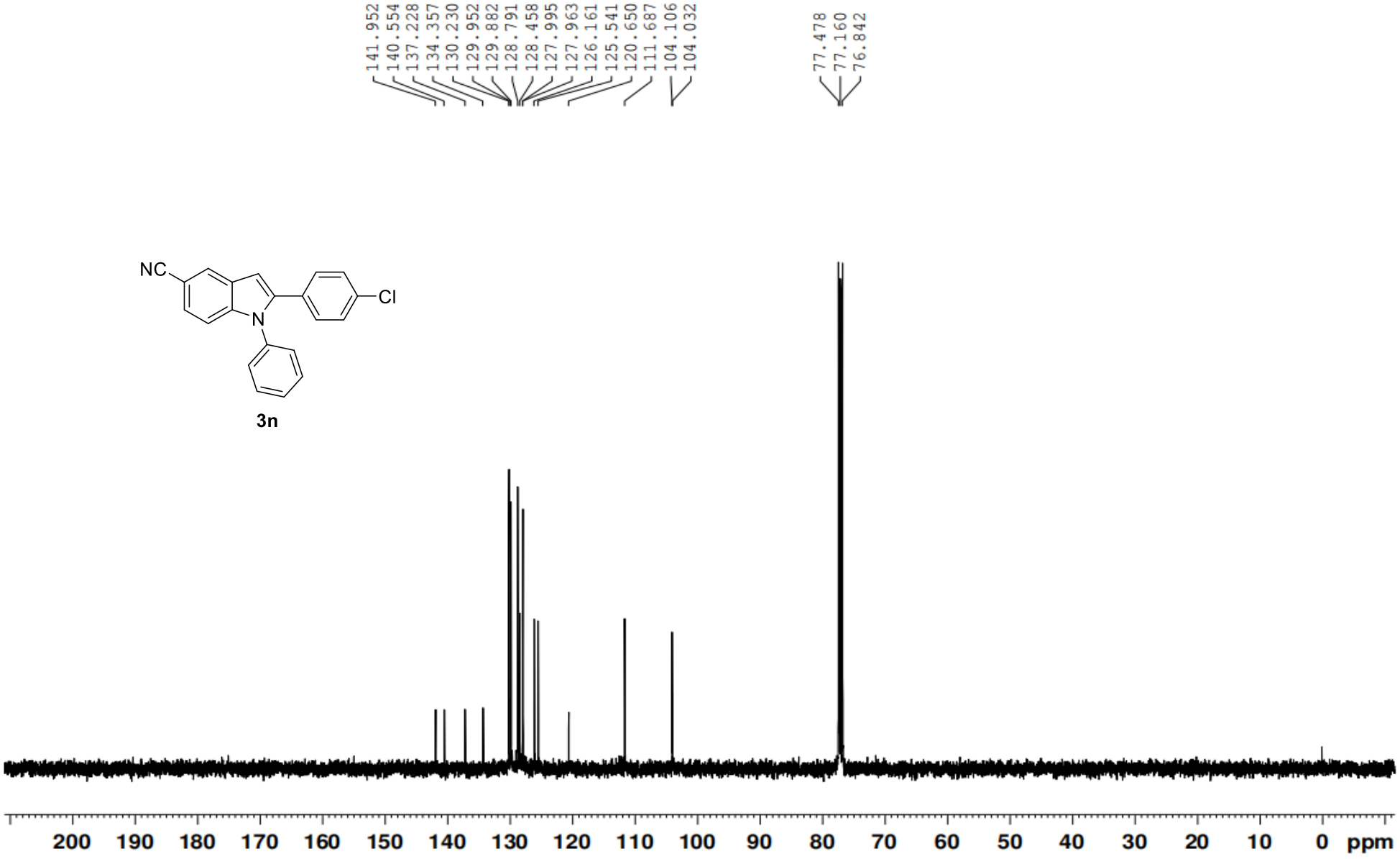


Figure S72. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3n.**

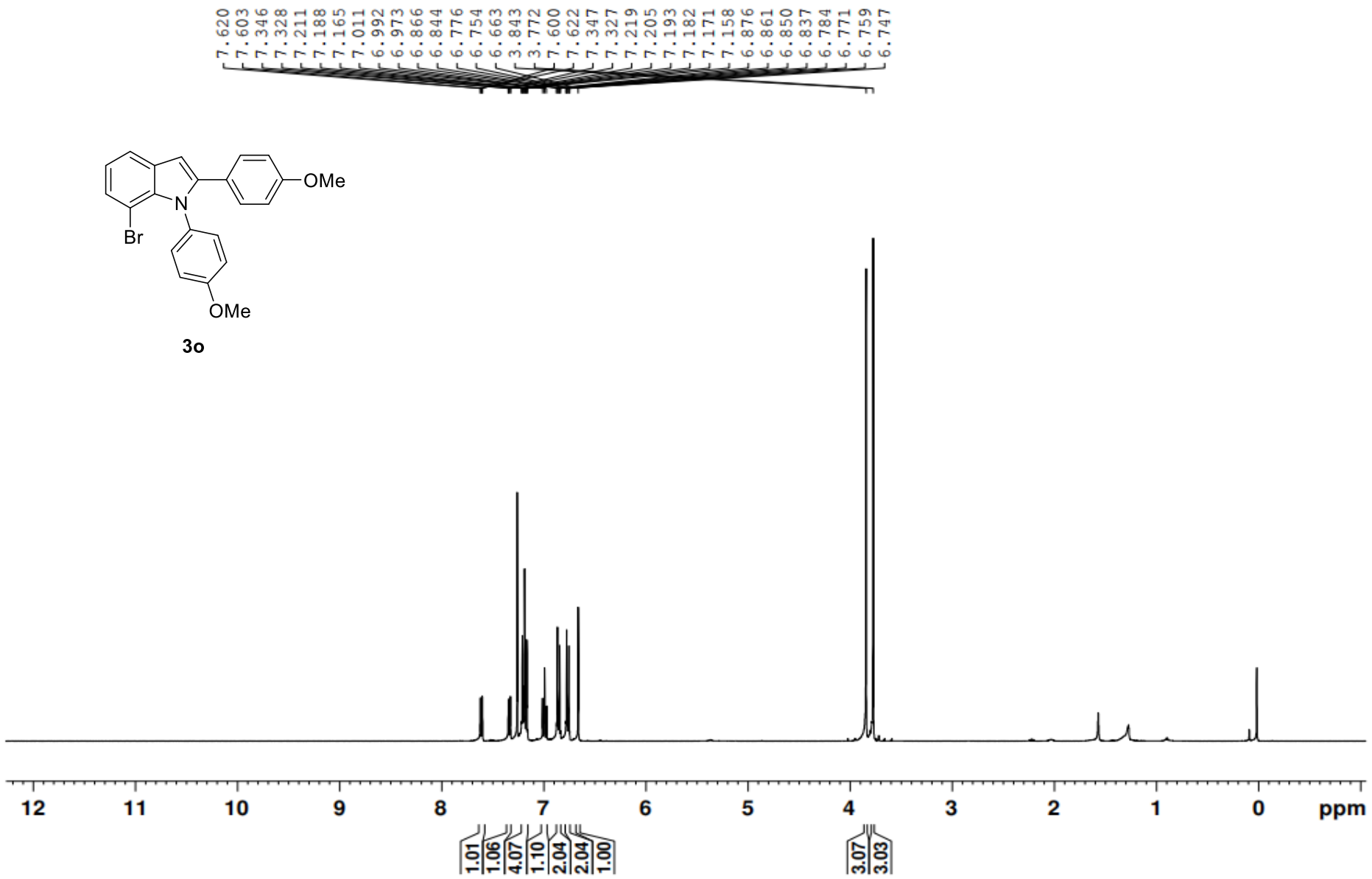


Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o.**

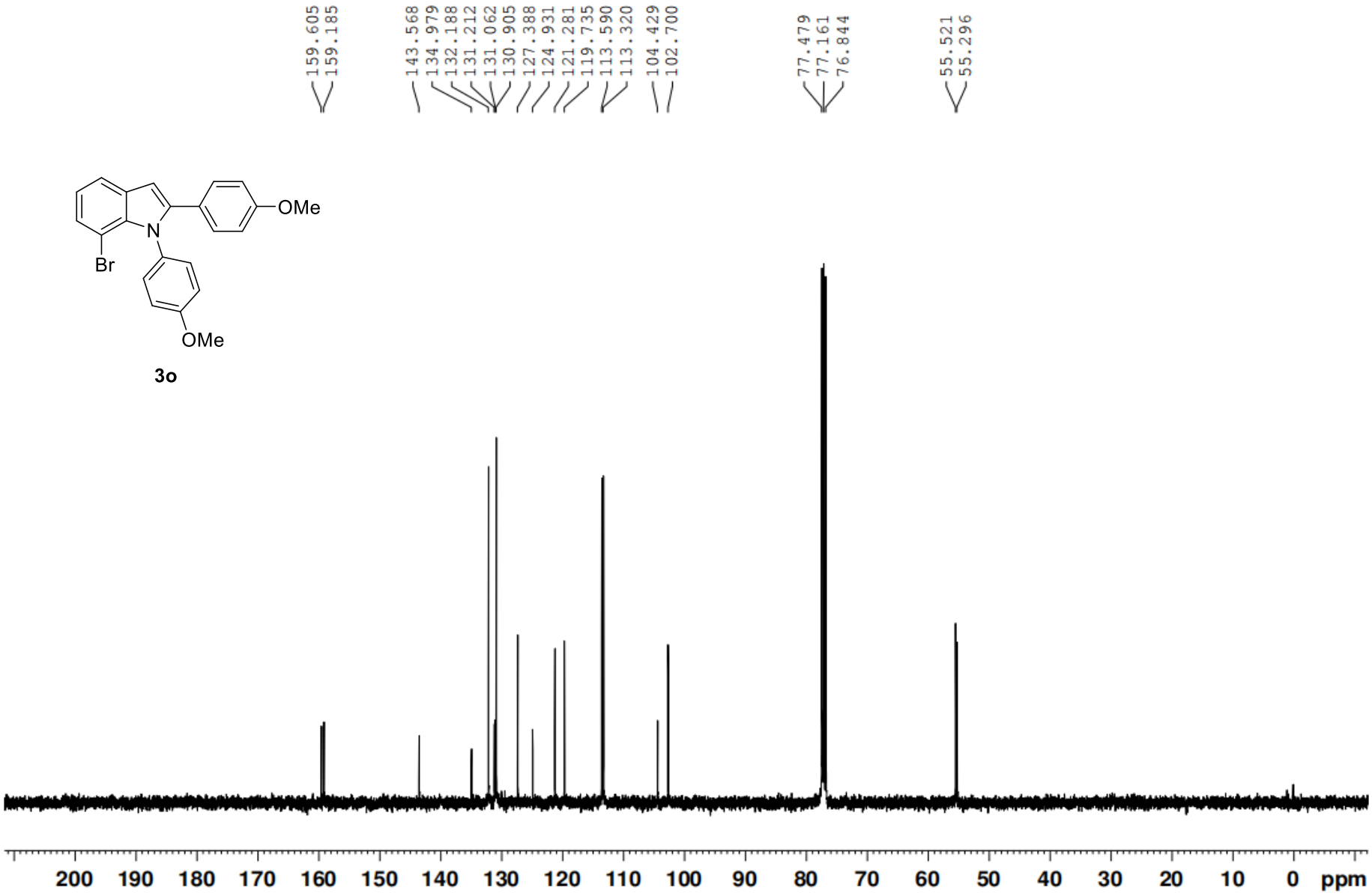


Figure S74. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3o.**

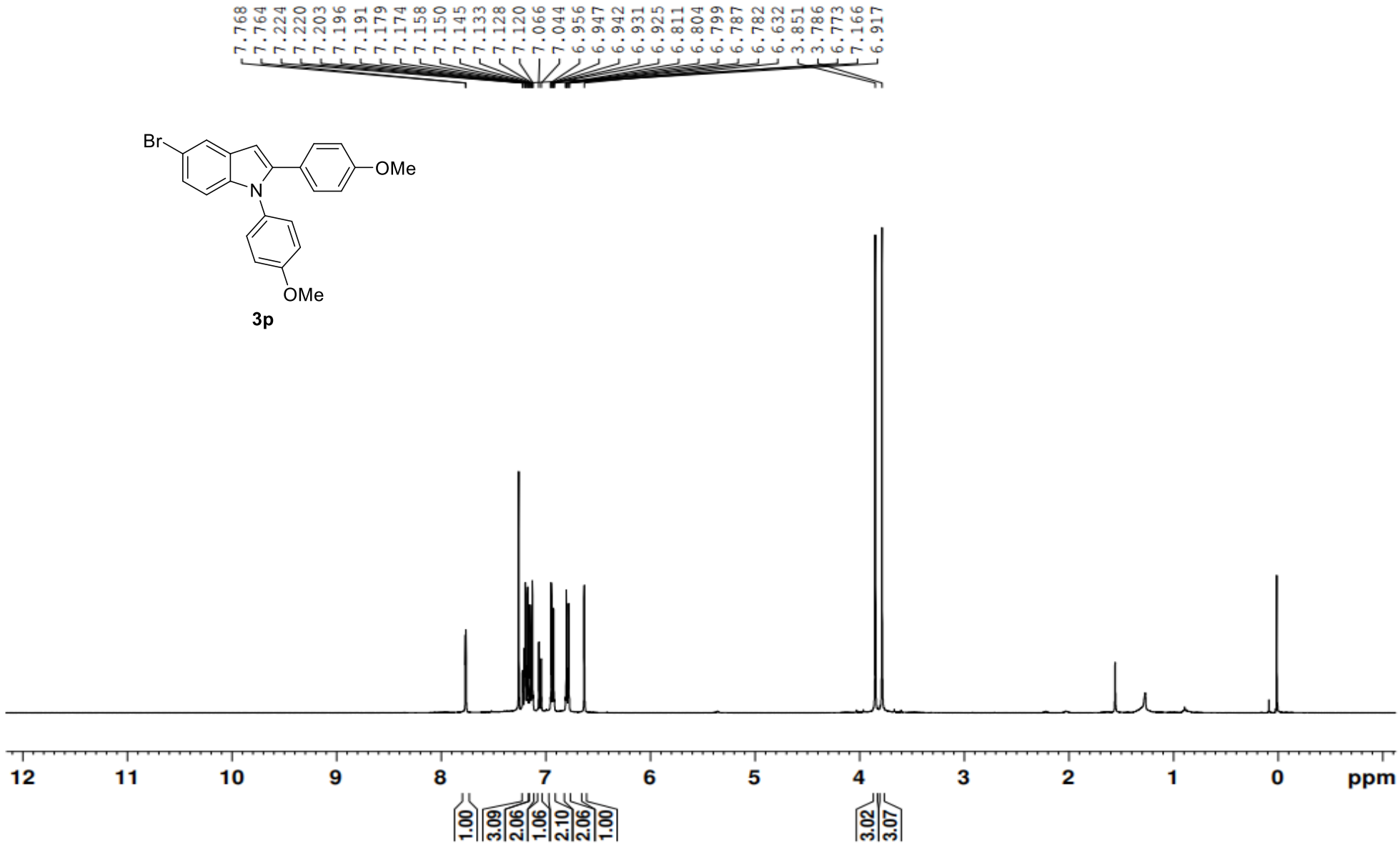


Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3p.**

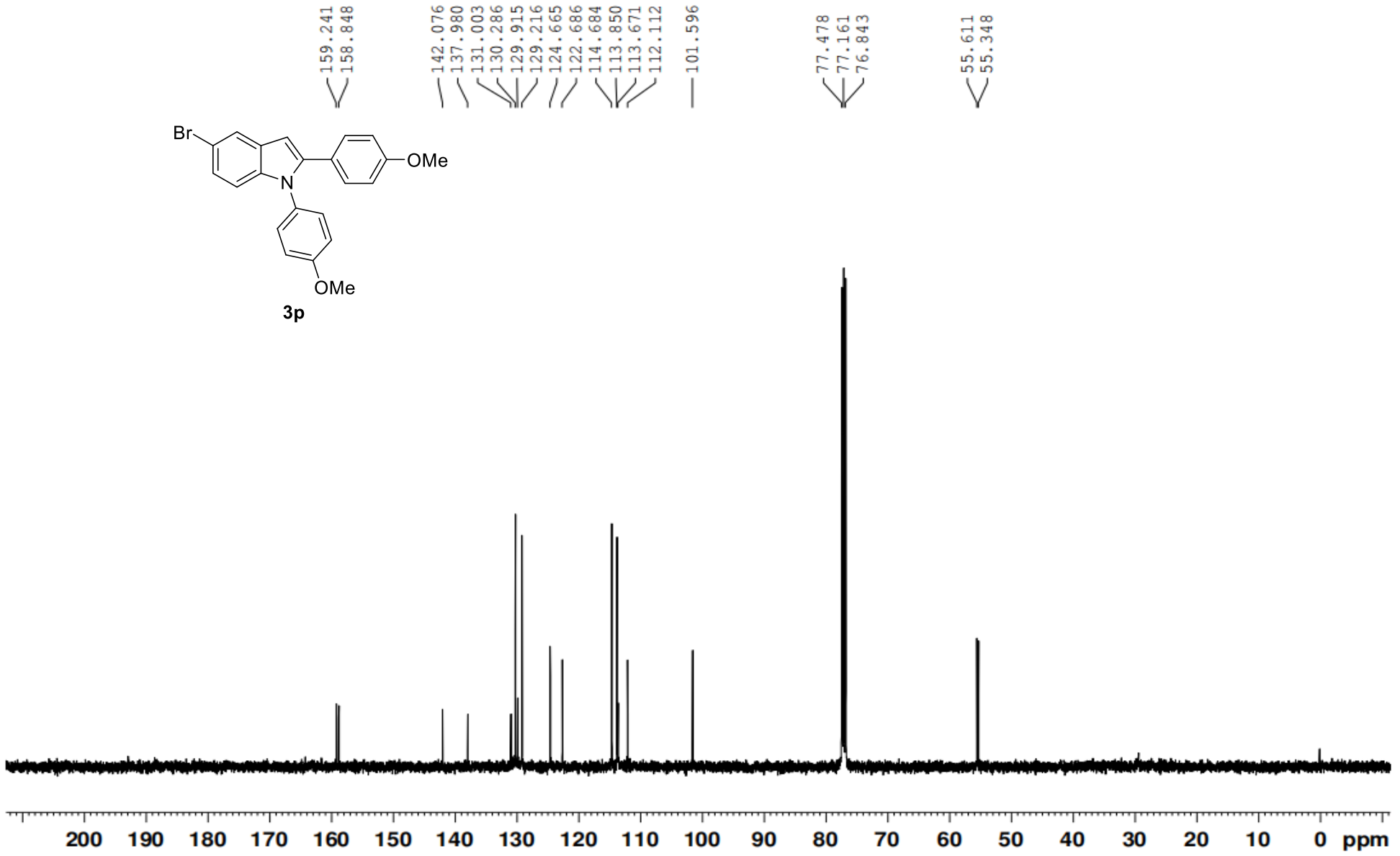


Figure S76. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3p.**

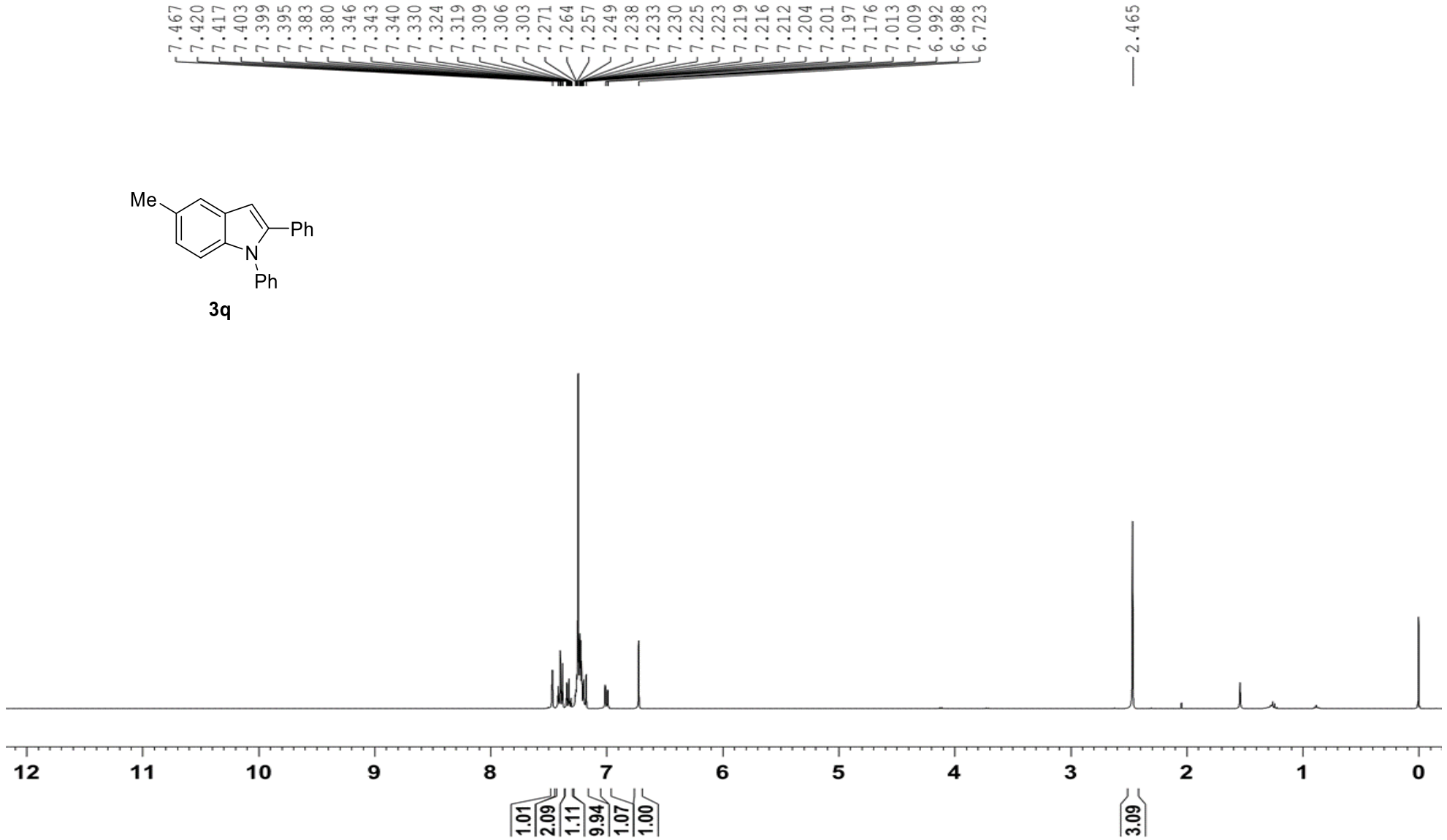


Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q.**

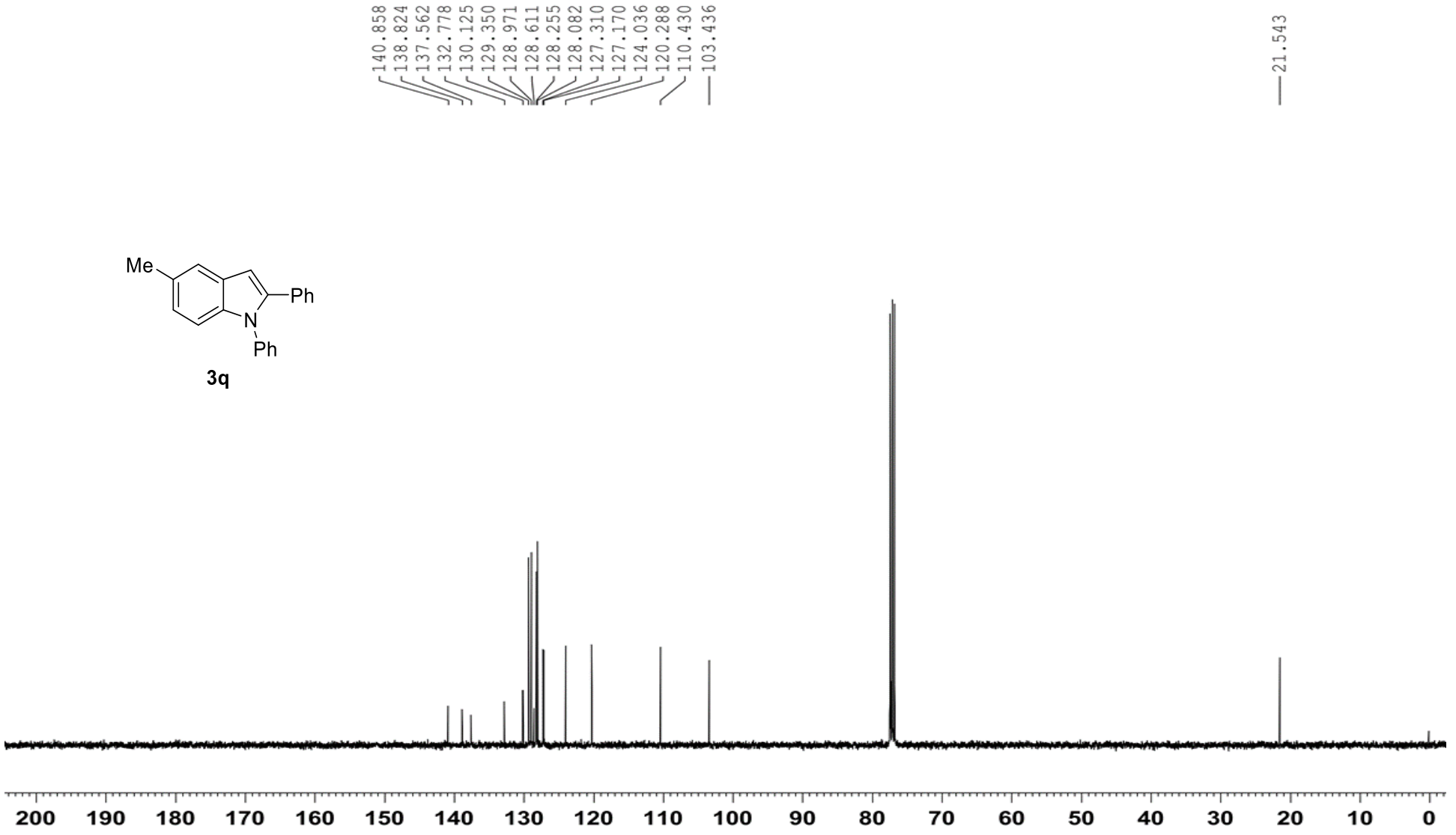


Figure S78. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3q.**

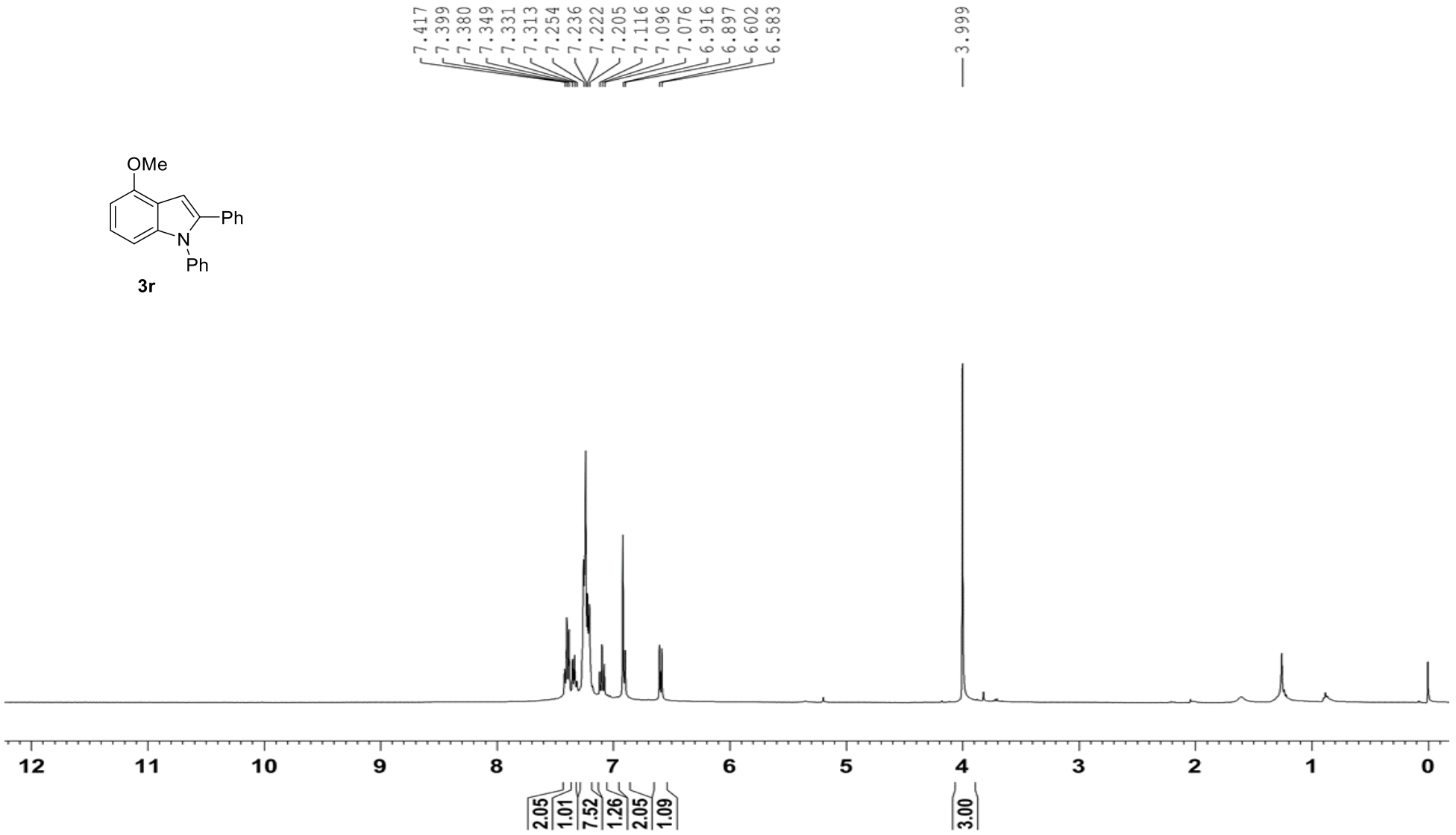


Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3r.**

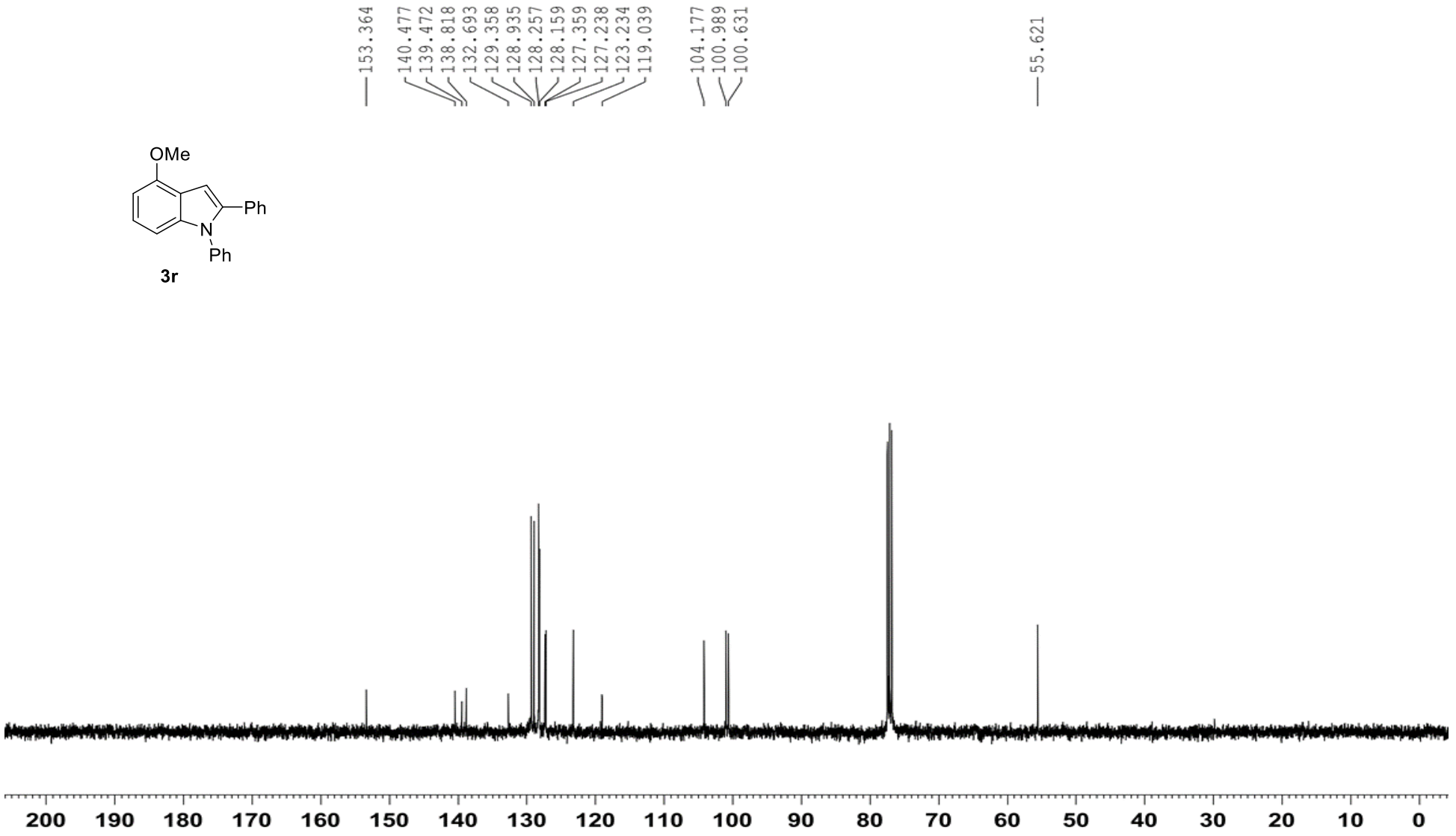


Figure S80. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3r.**

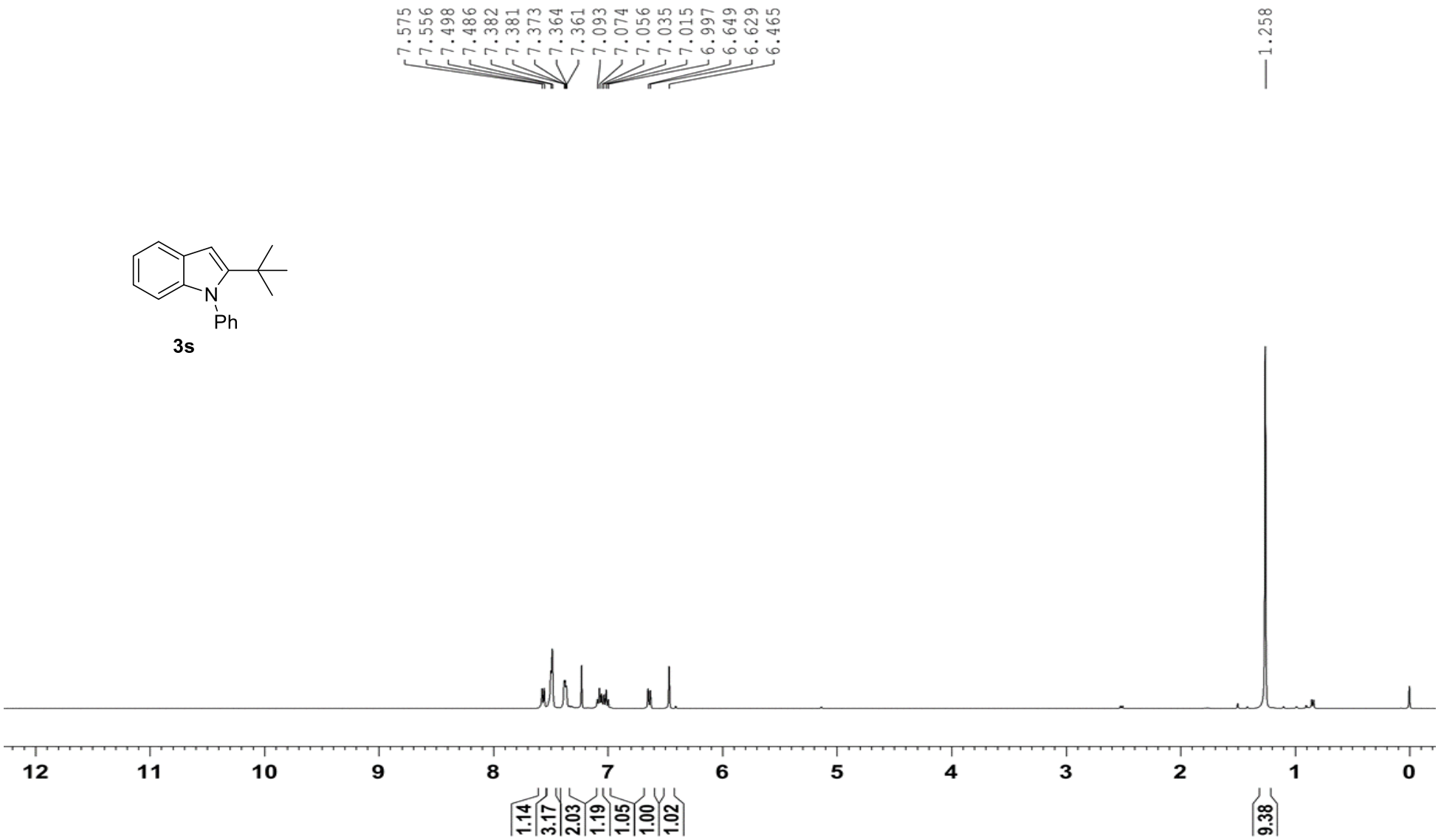


Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3s.**

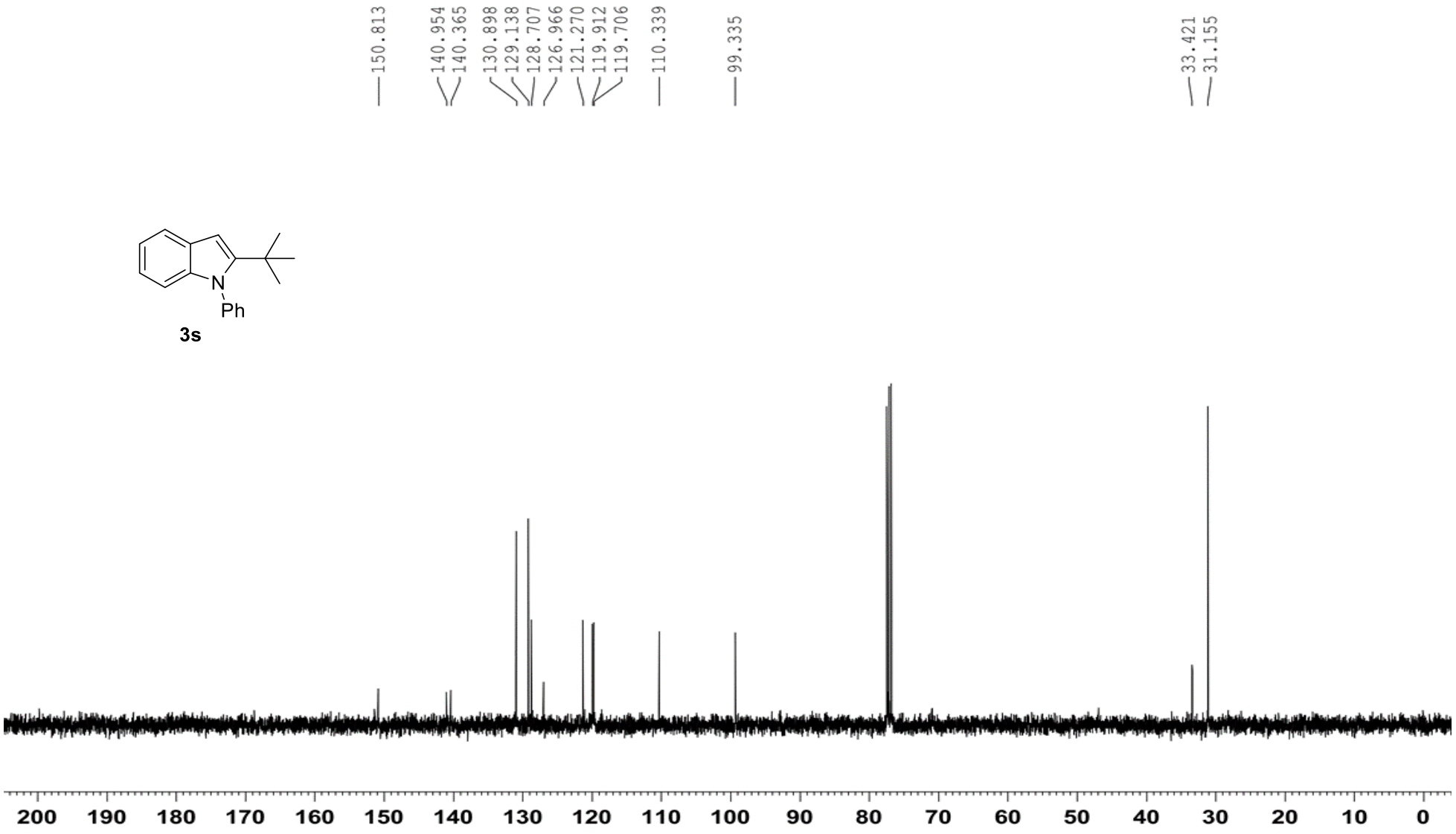


Figure S82. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3s.**

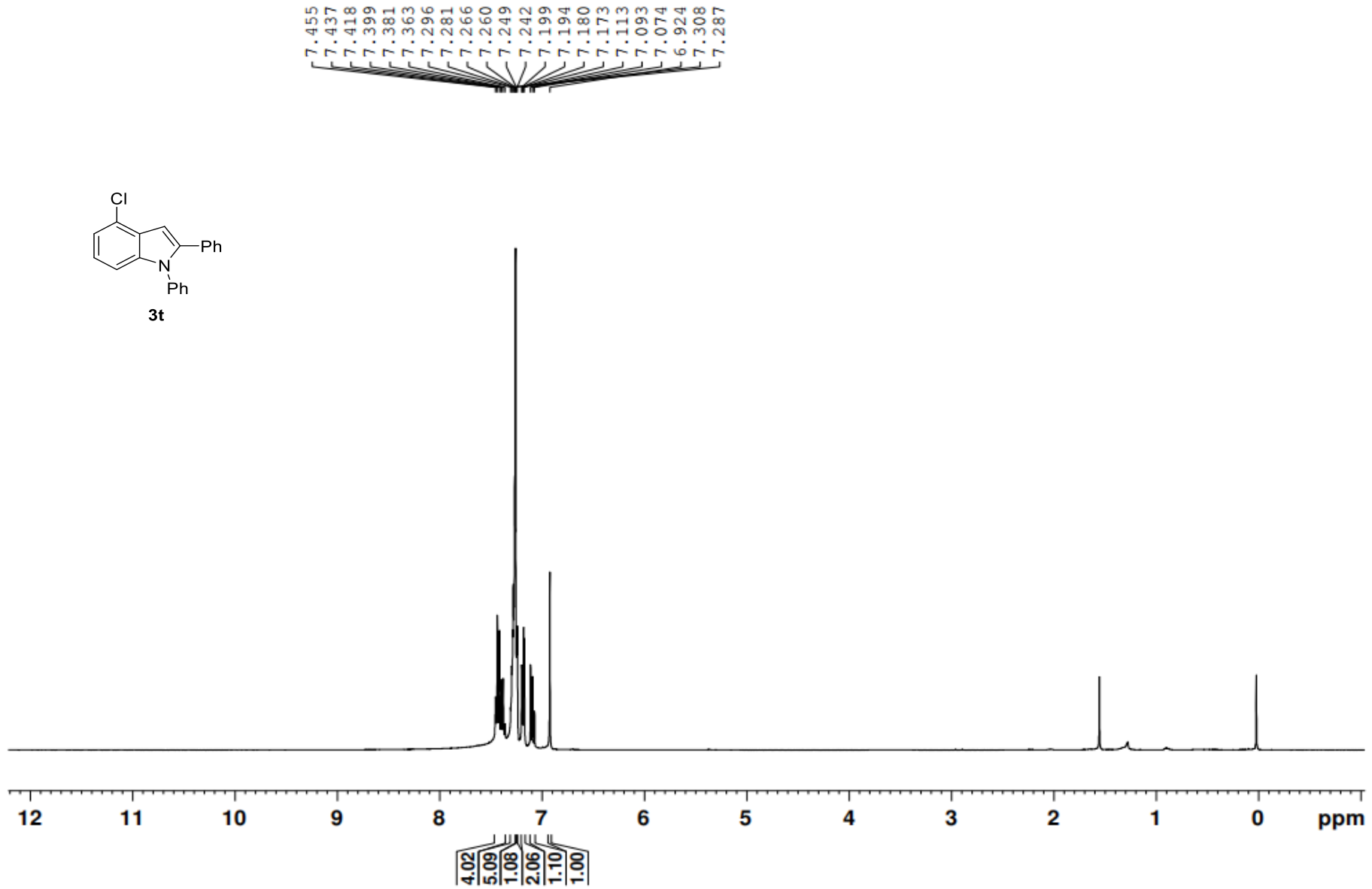


Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3t.**

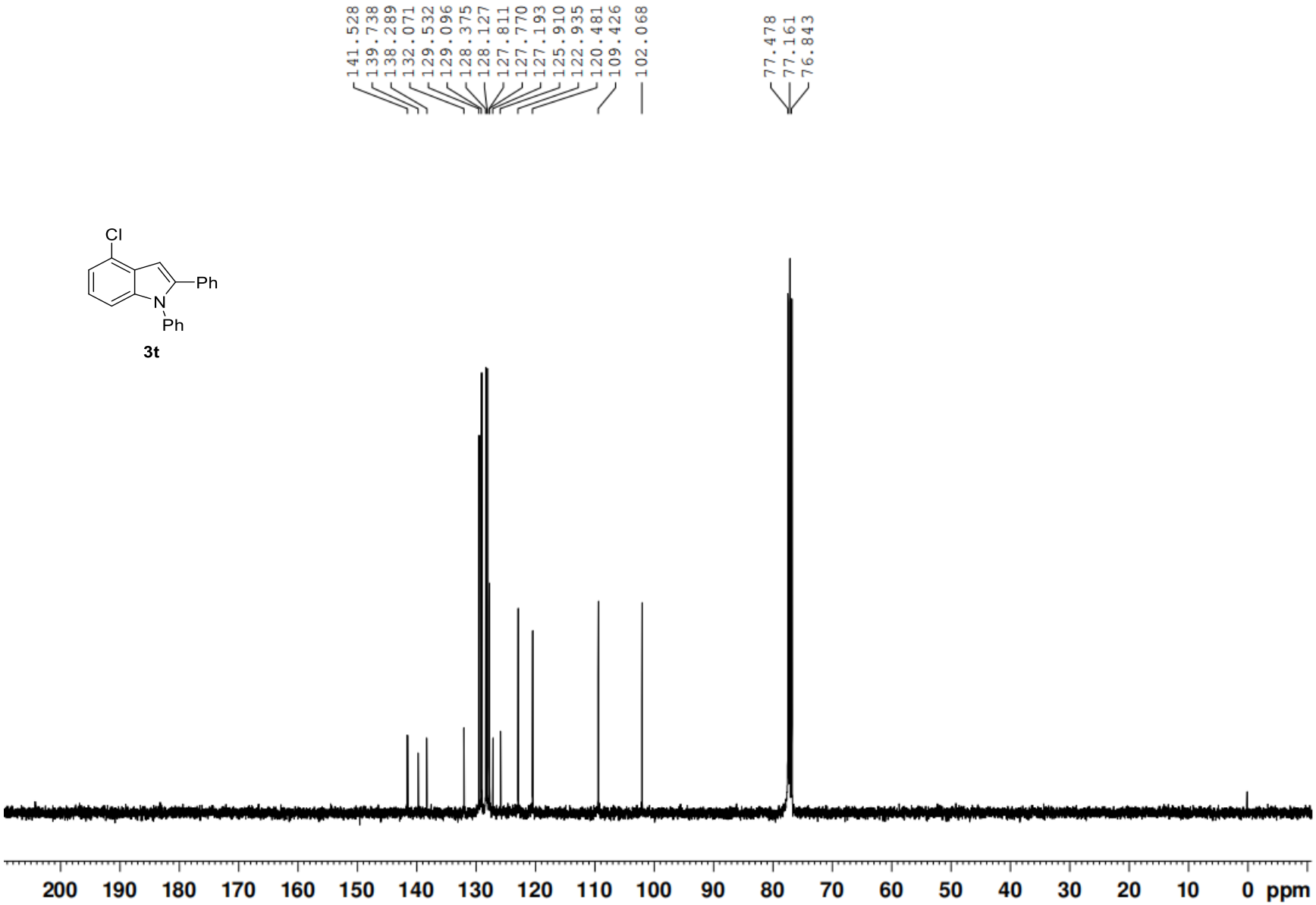


Figure S84. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3t.**

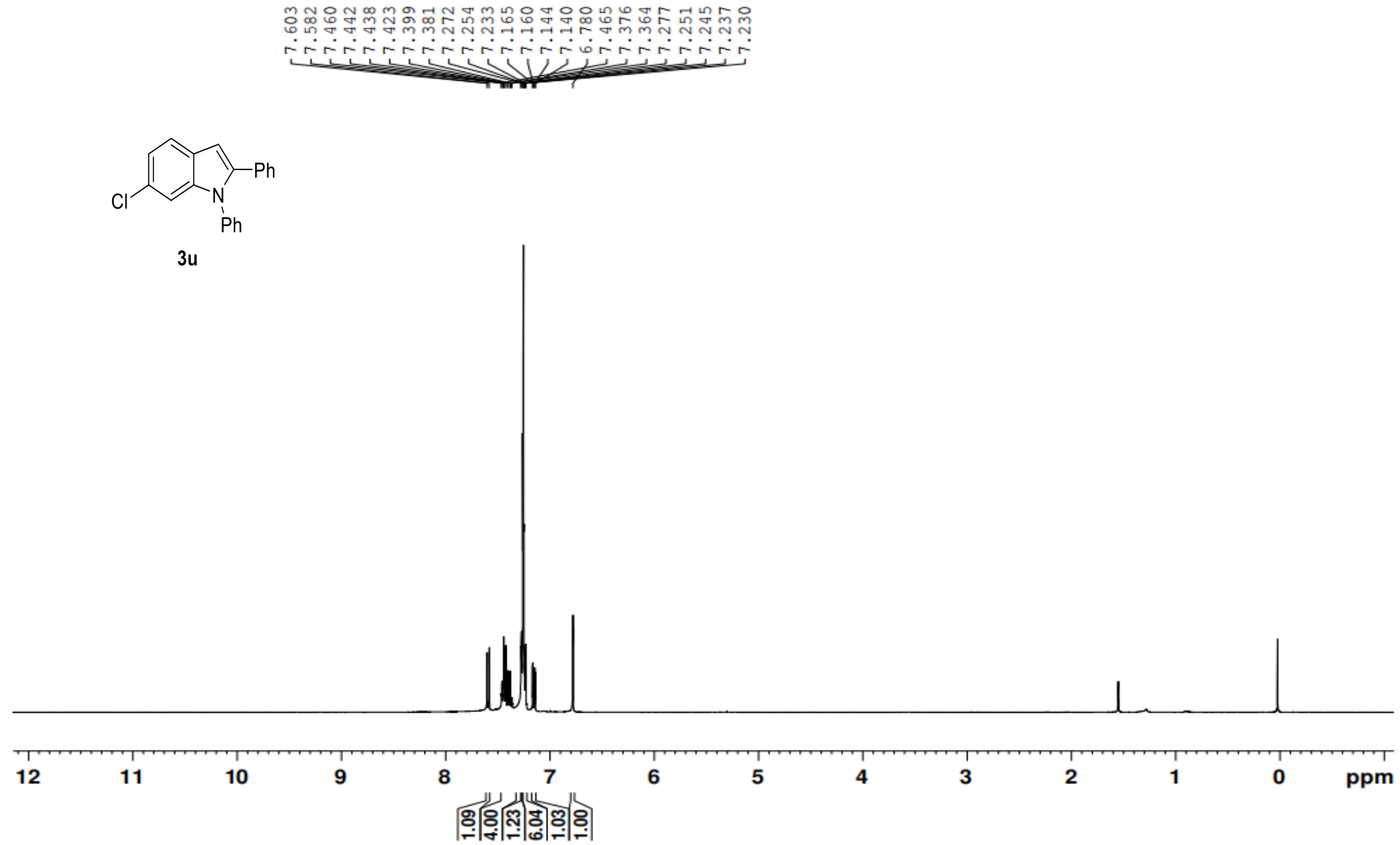


Figure S85. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3u.**

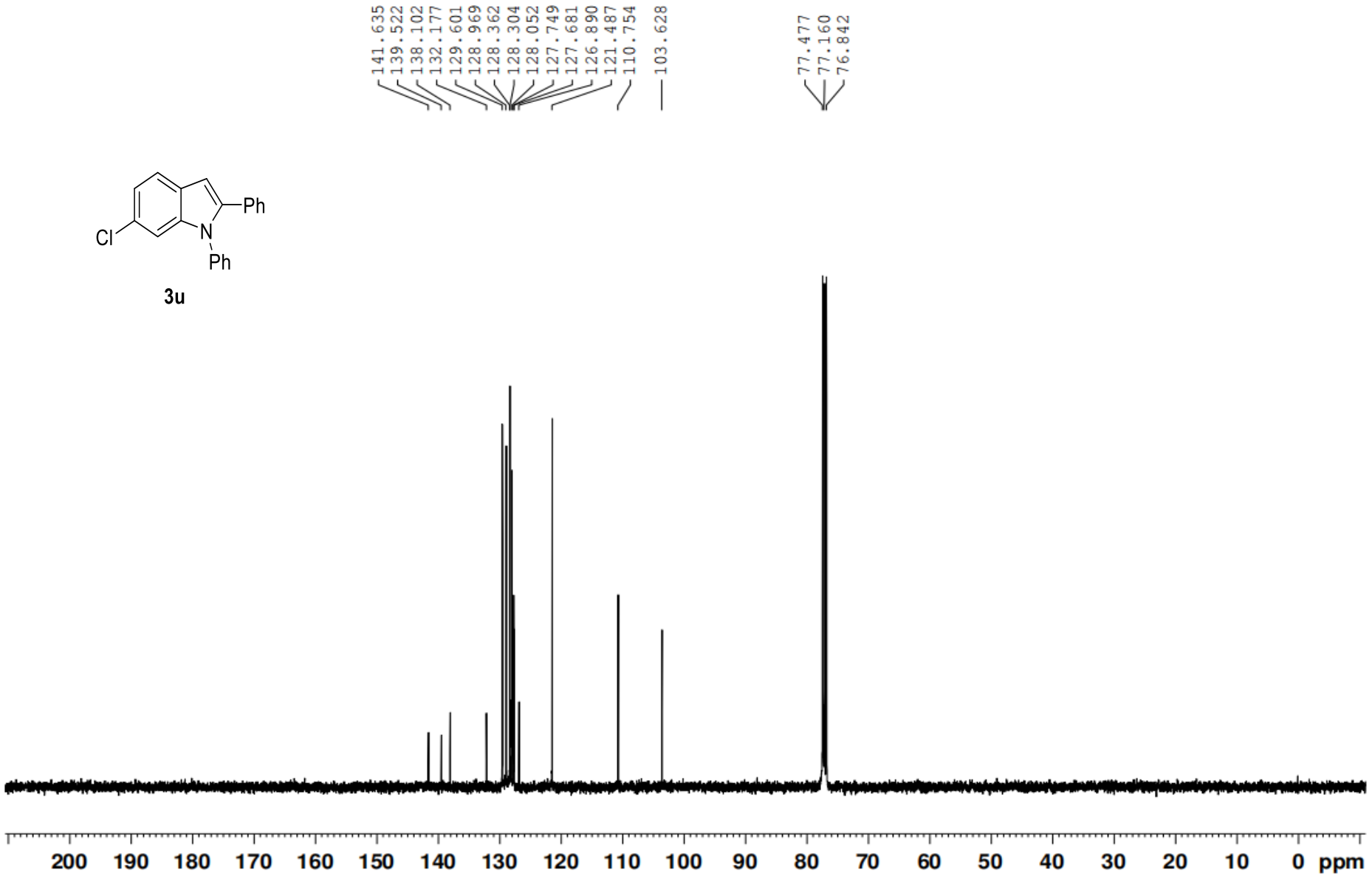


Figure S86. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3u.**

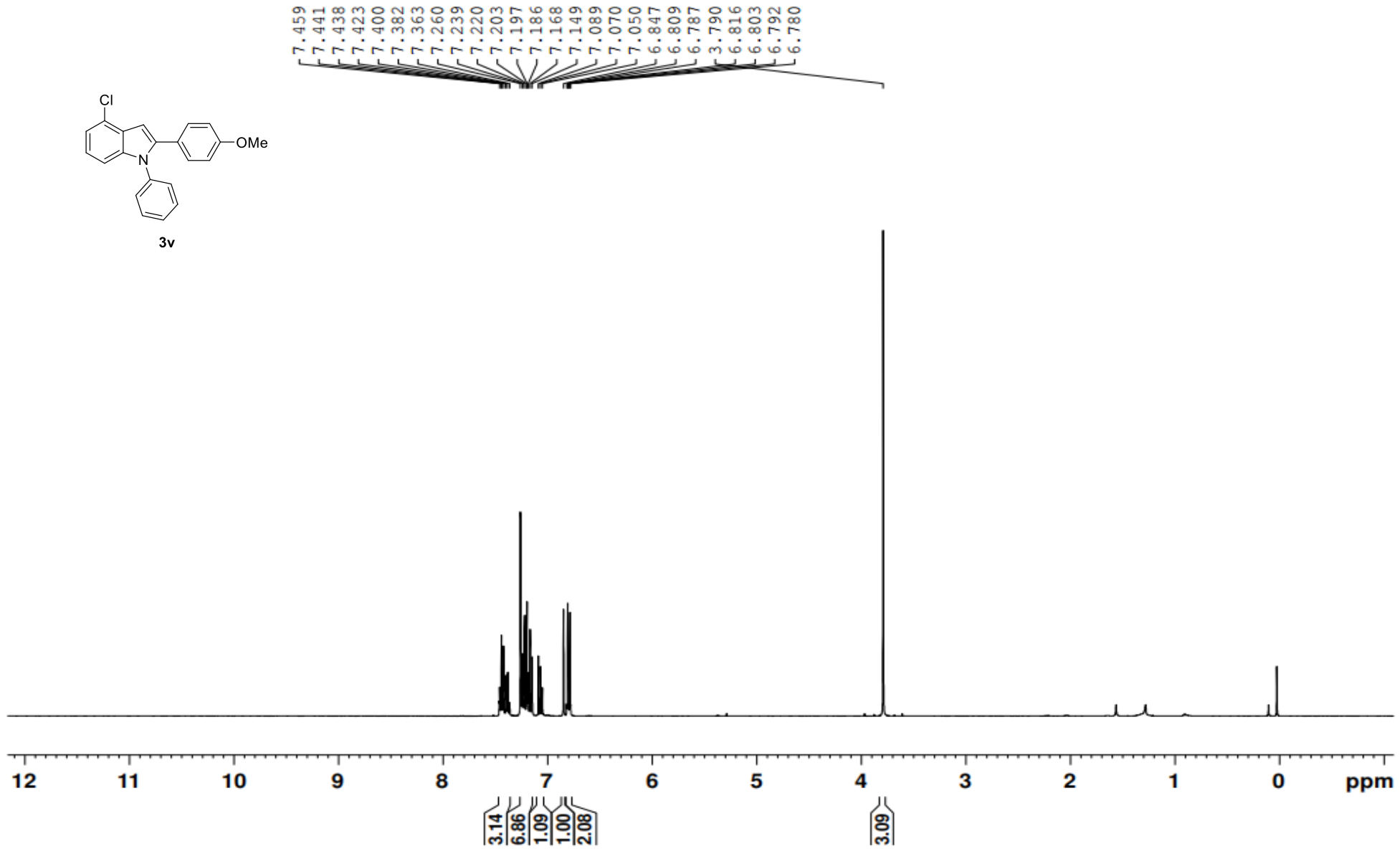


Figure S87. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3v.**

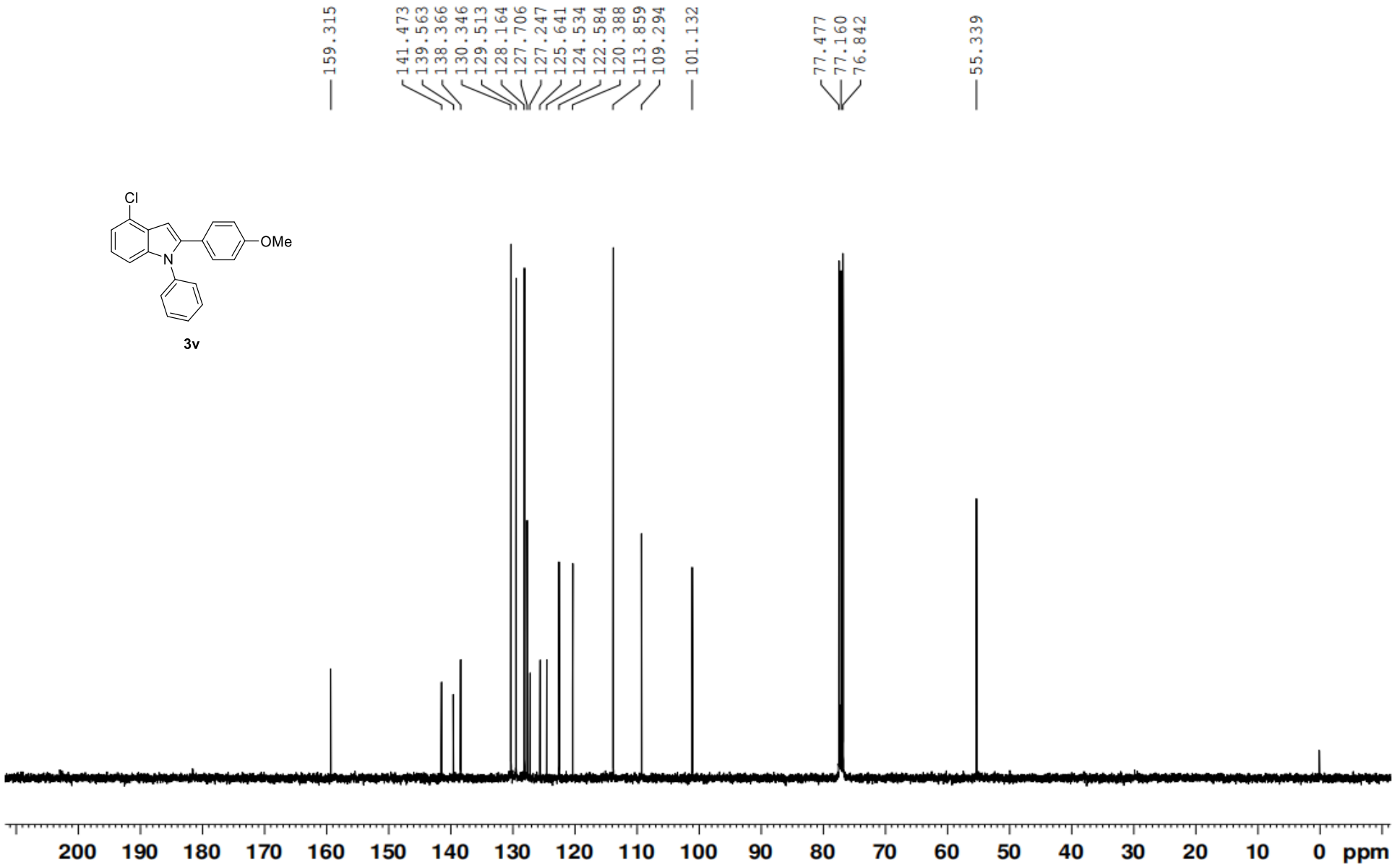


Figure S88. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3v.**

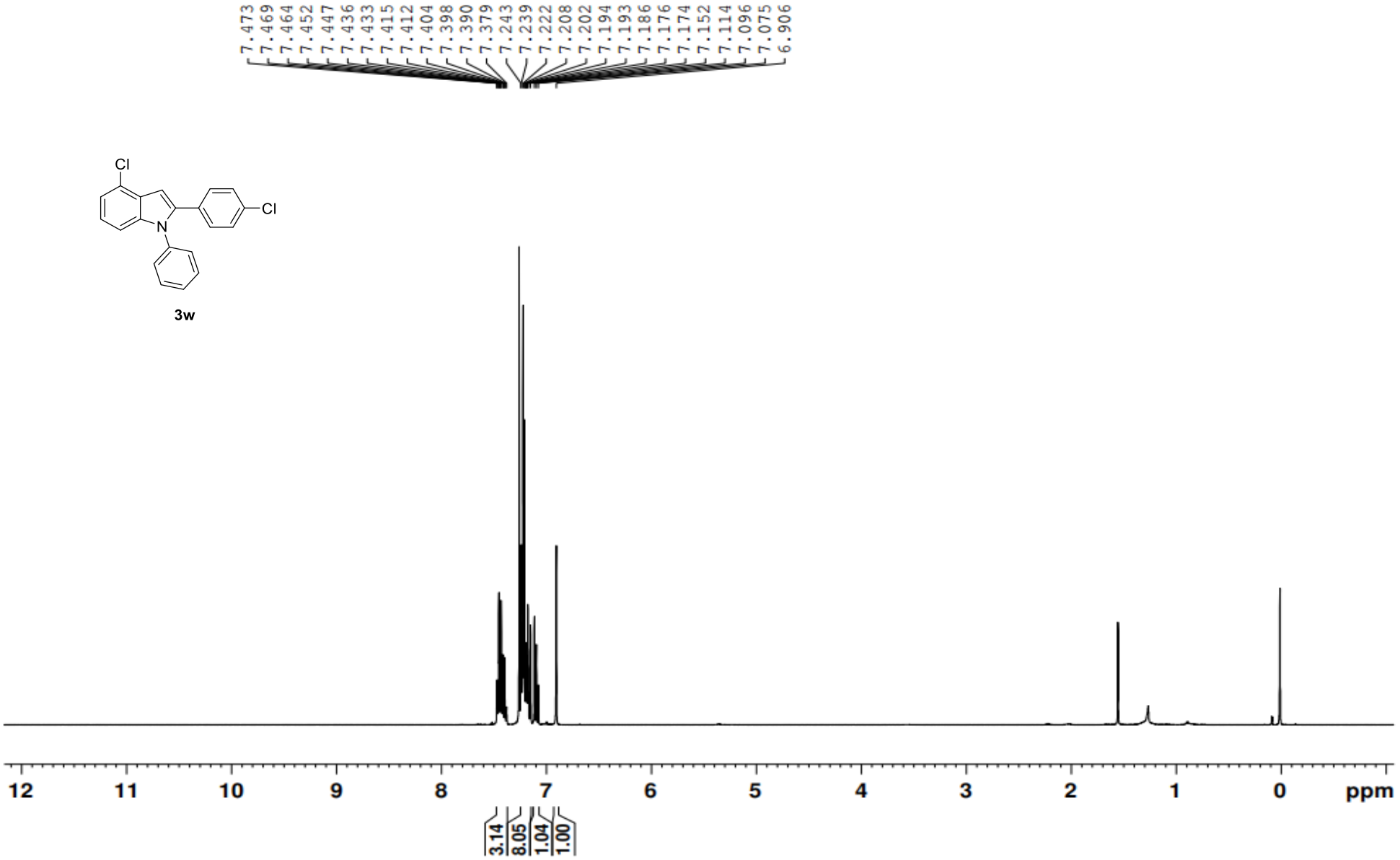


Figure S89. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3w.**

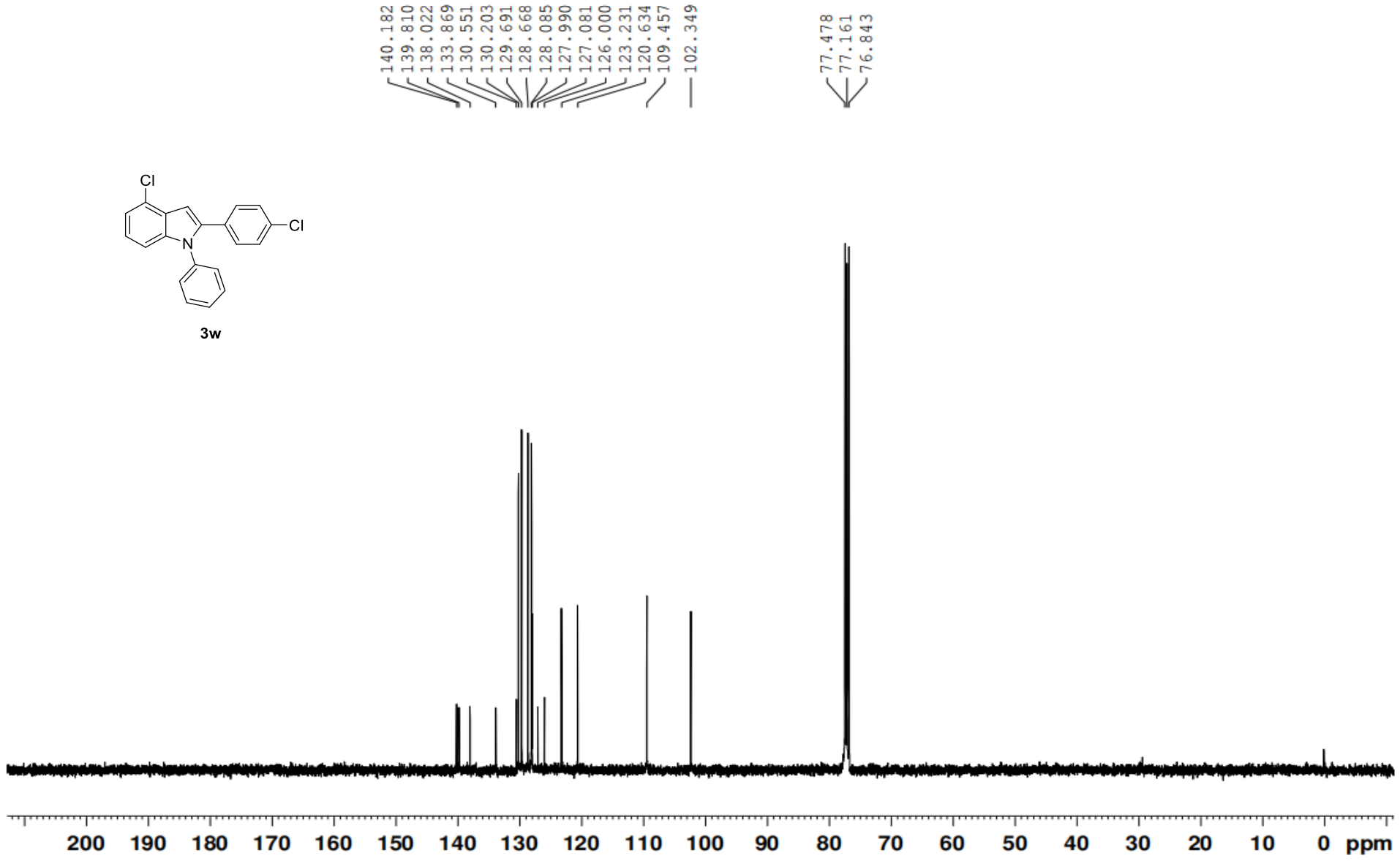


Figure S90. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3w.**

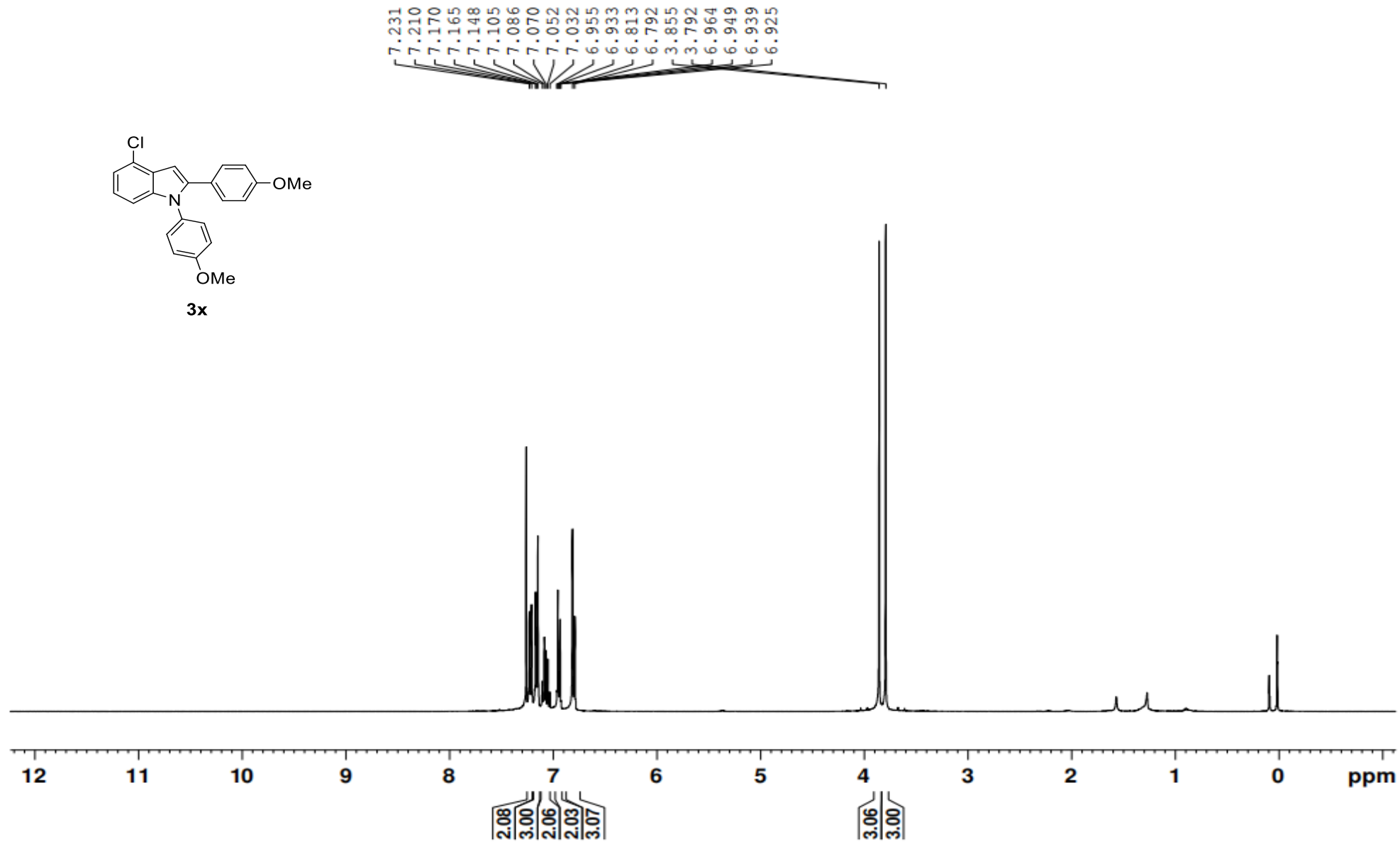


Figure S91. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3x.**

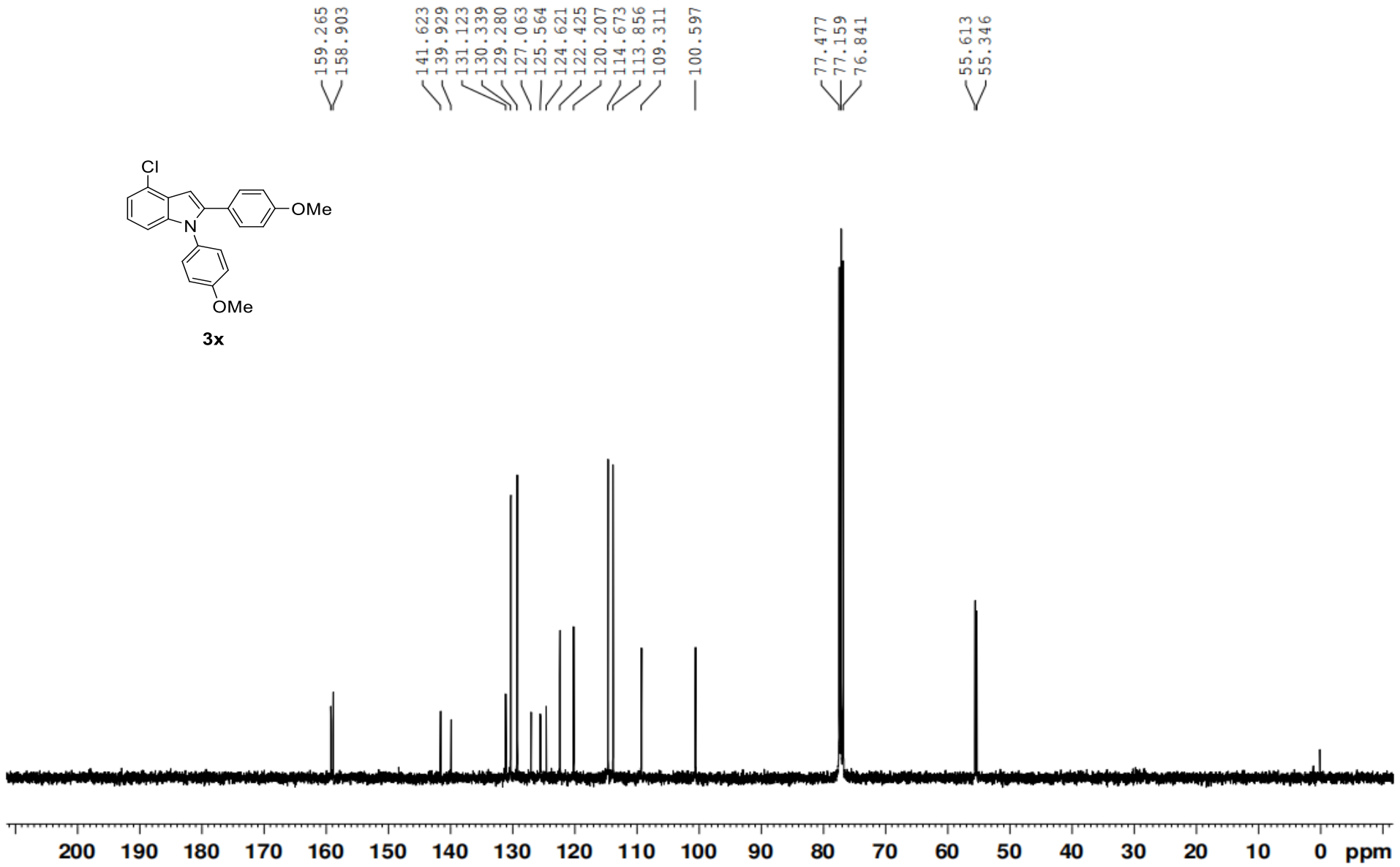


Figure S92. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3x.**

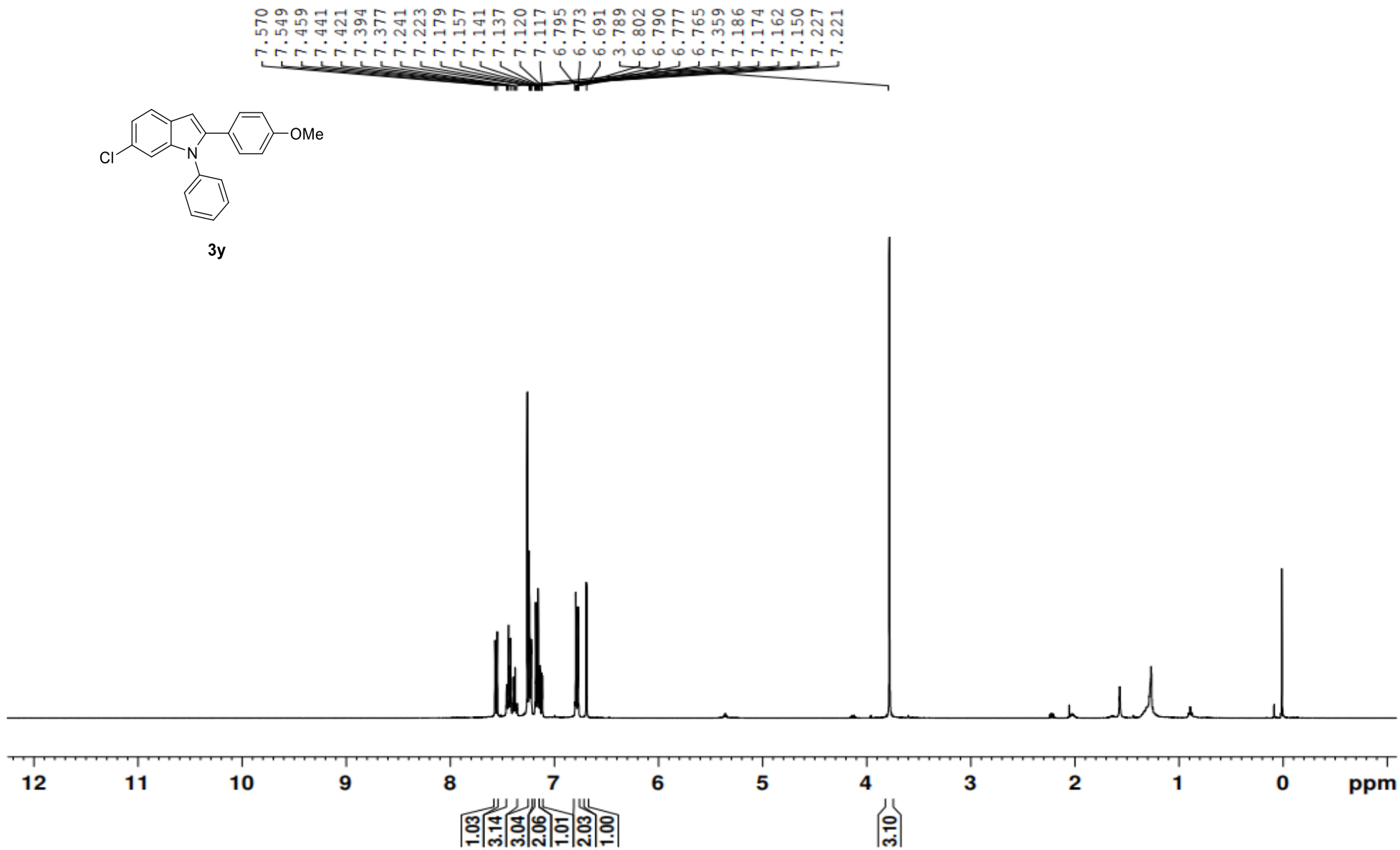


Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3y.**

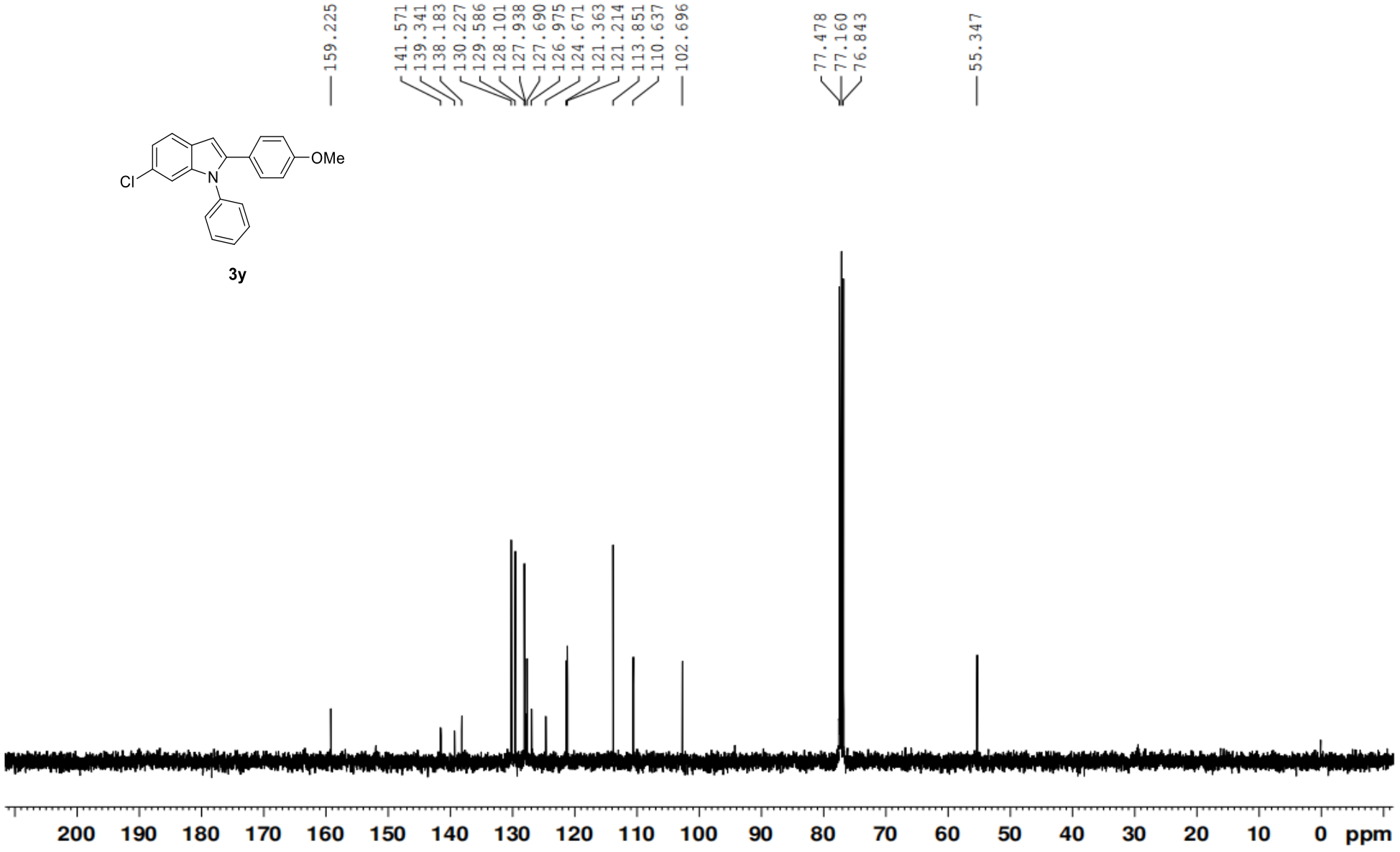


Figure S94. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3y.**

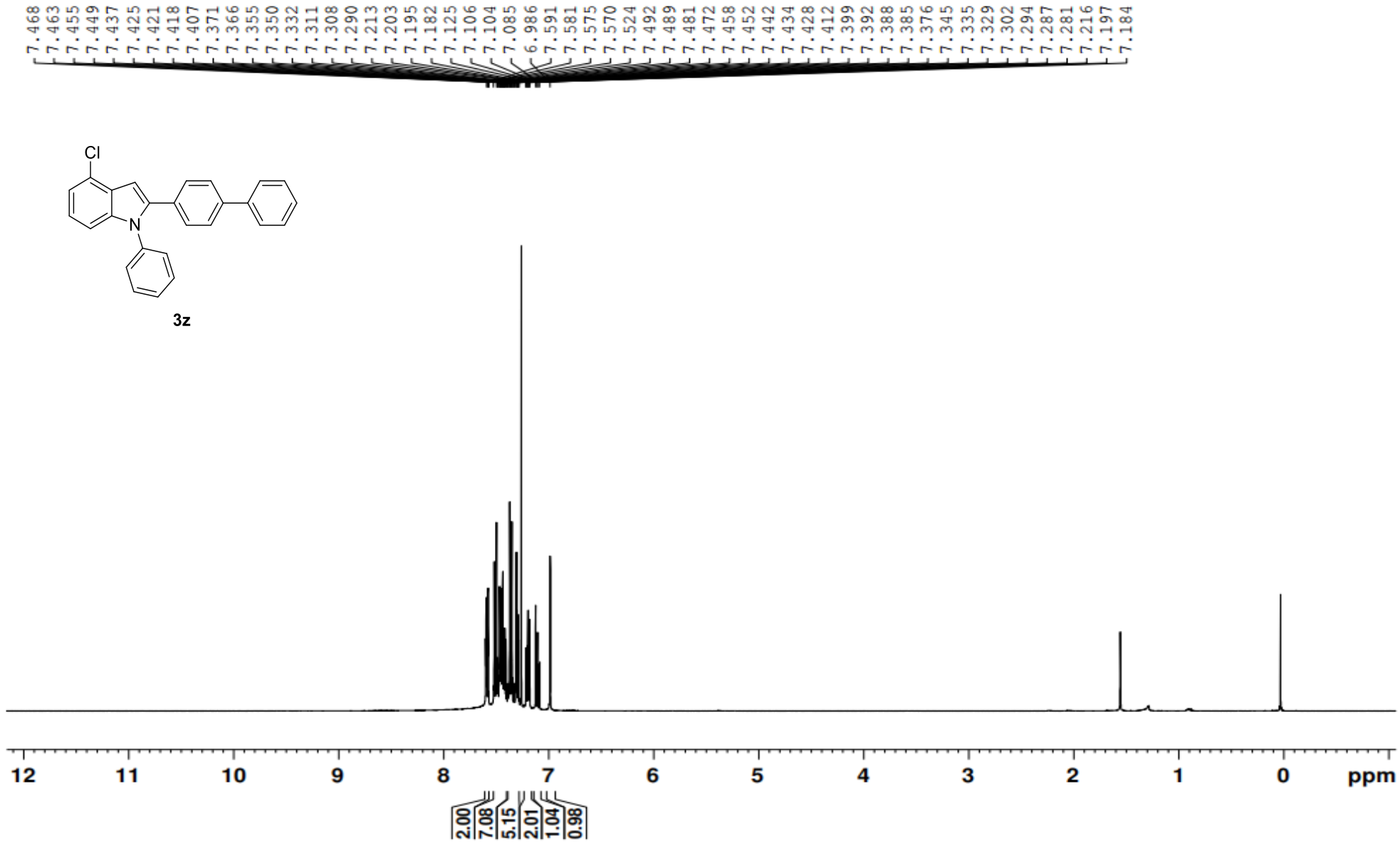


Figure S95. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3z.**

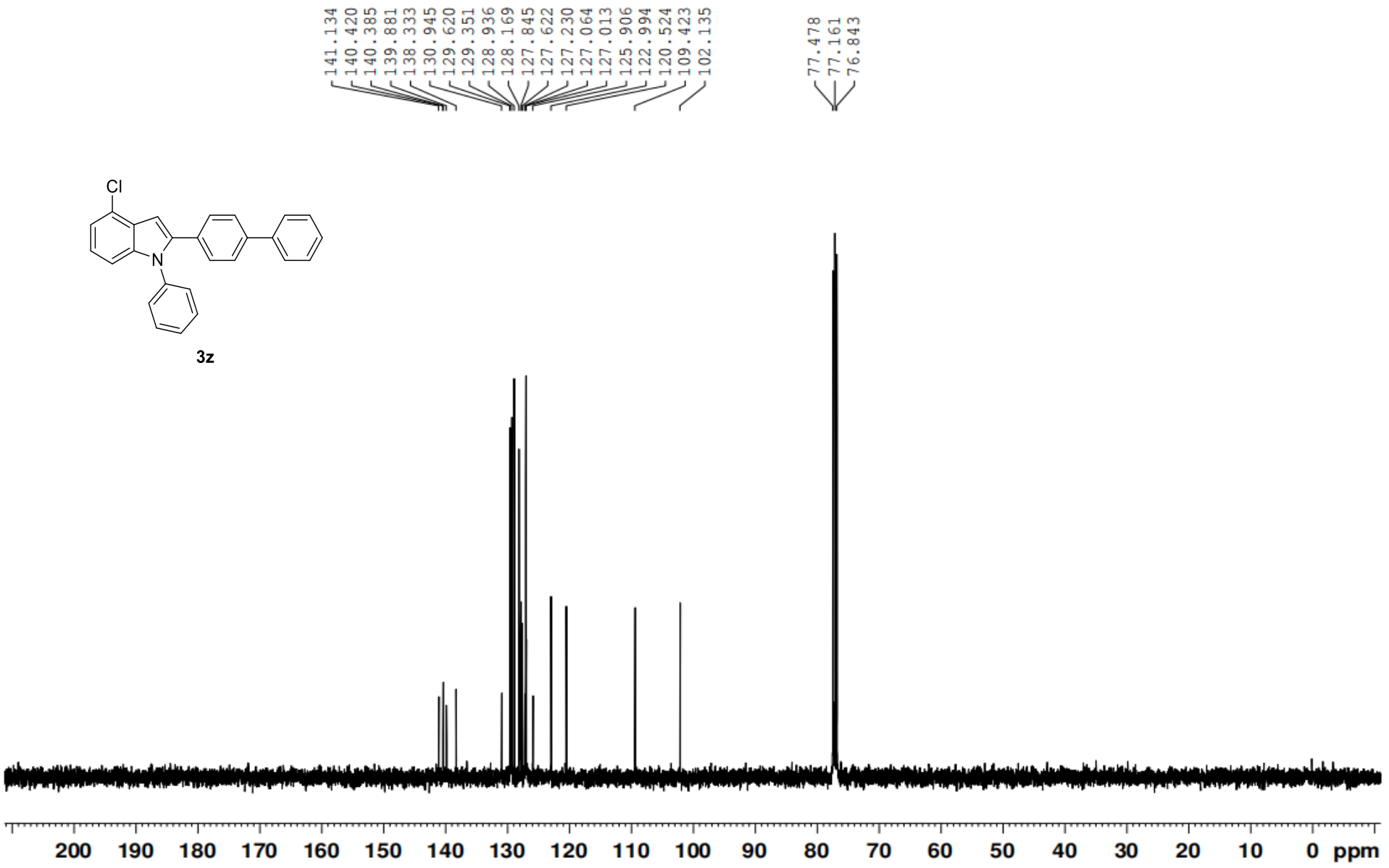


Figure S96. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3z.**

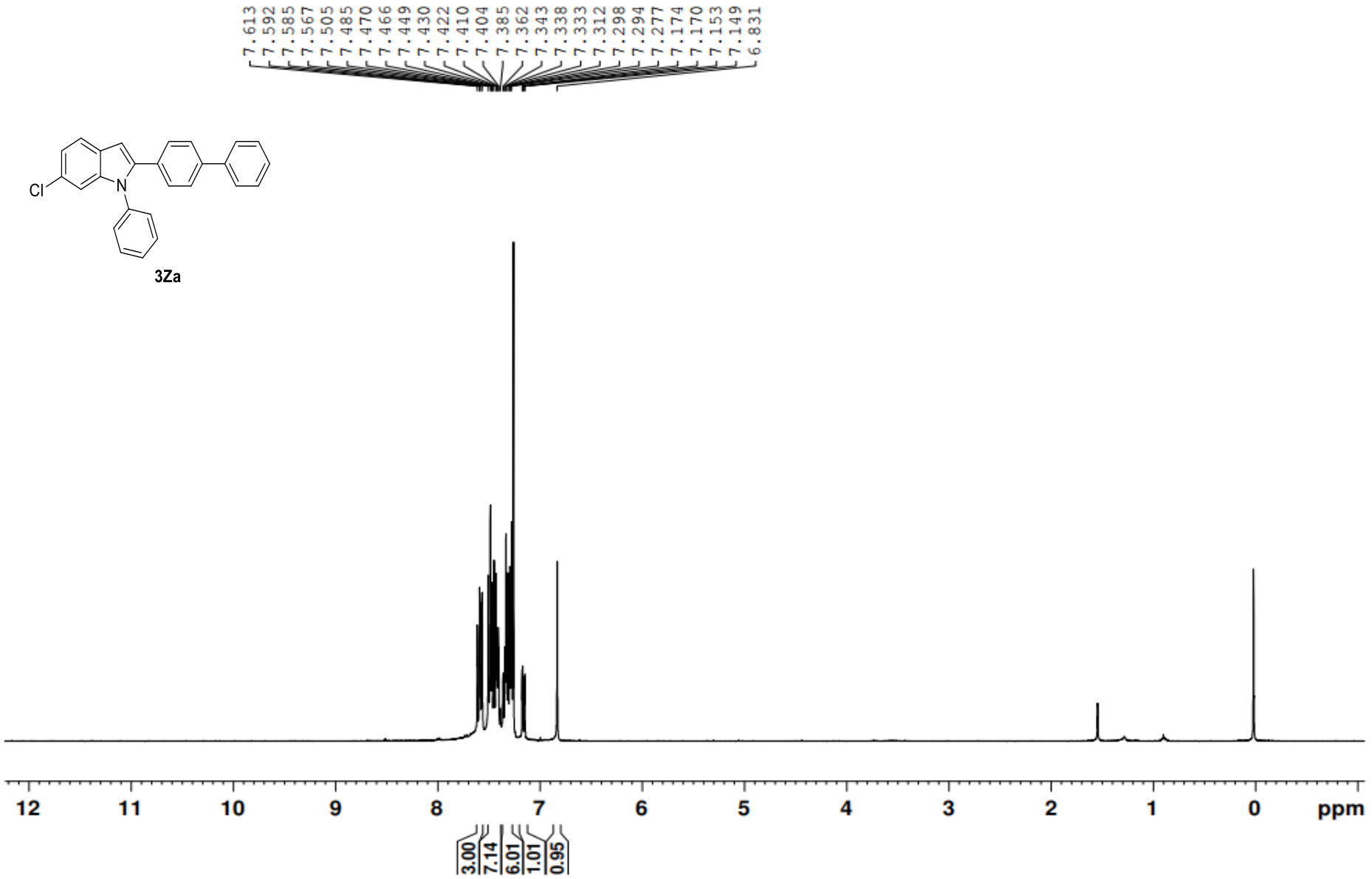


Figure S97. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3Za.**

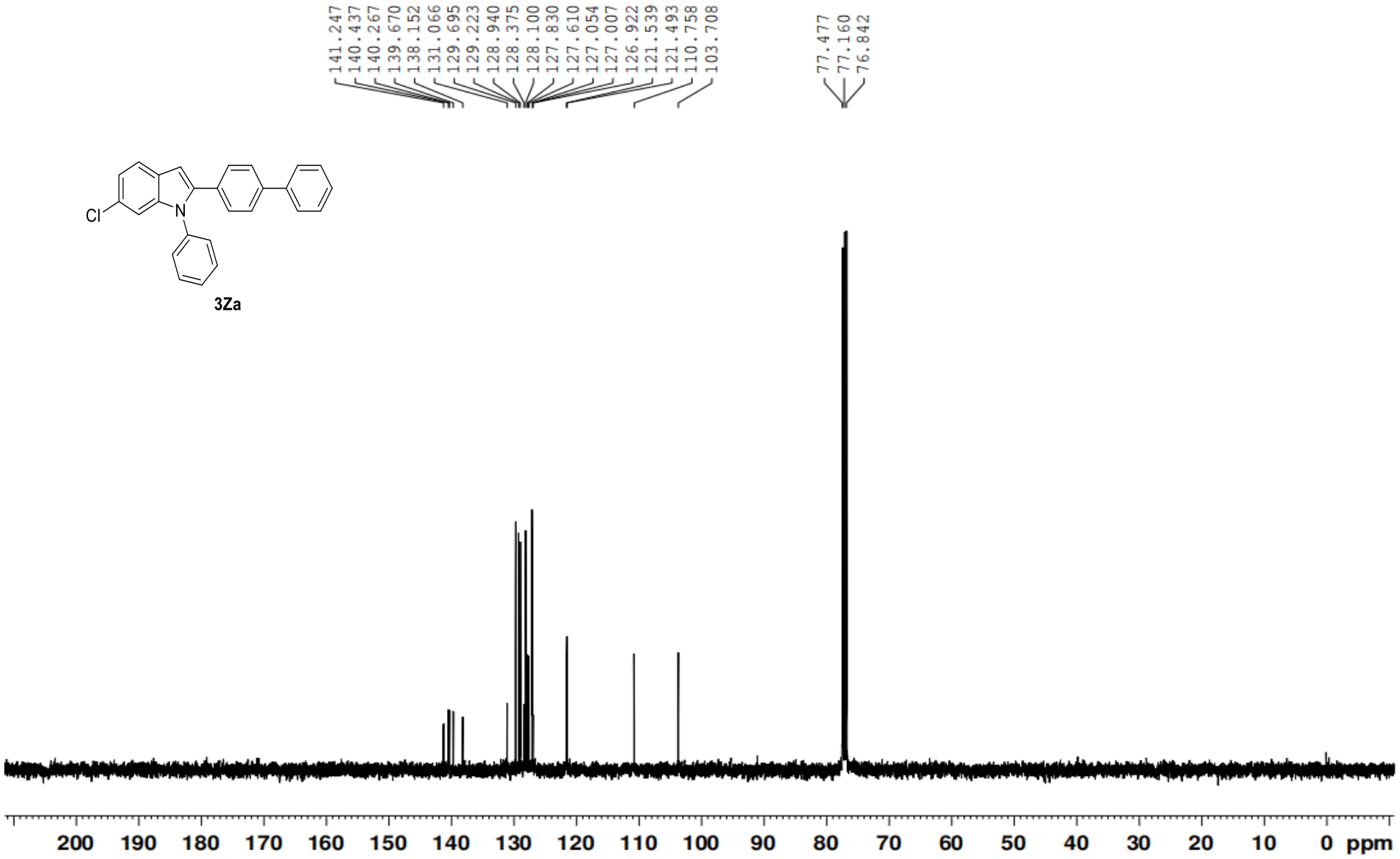


Figure S98. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3Za.**

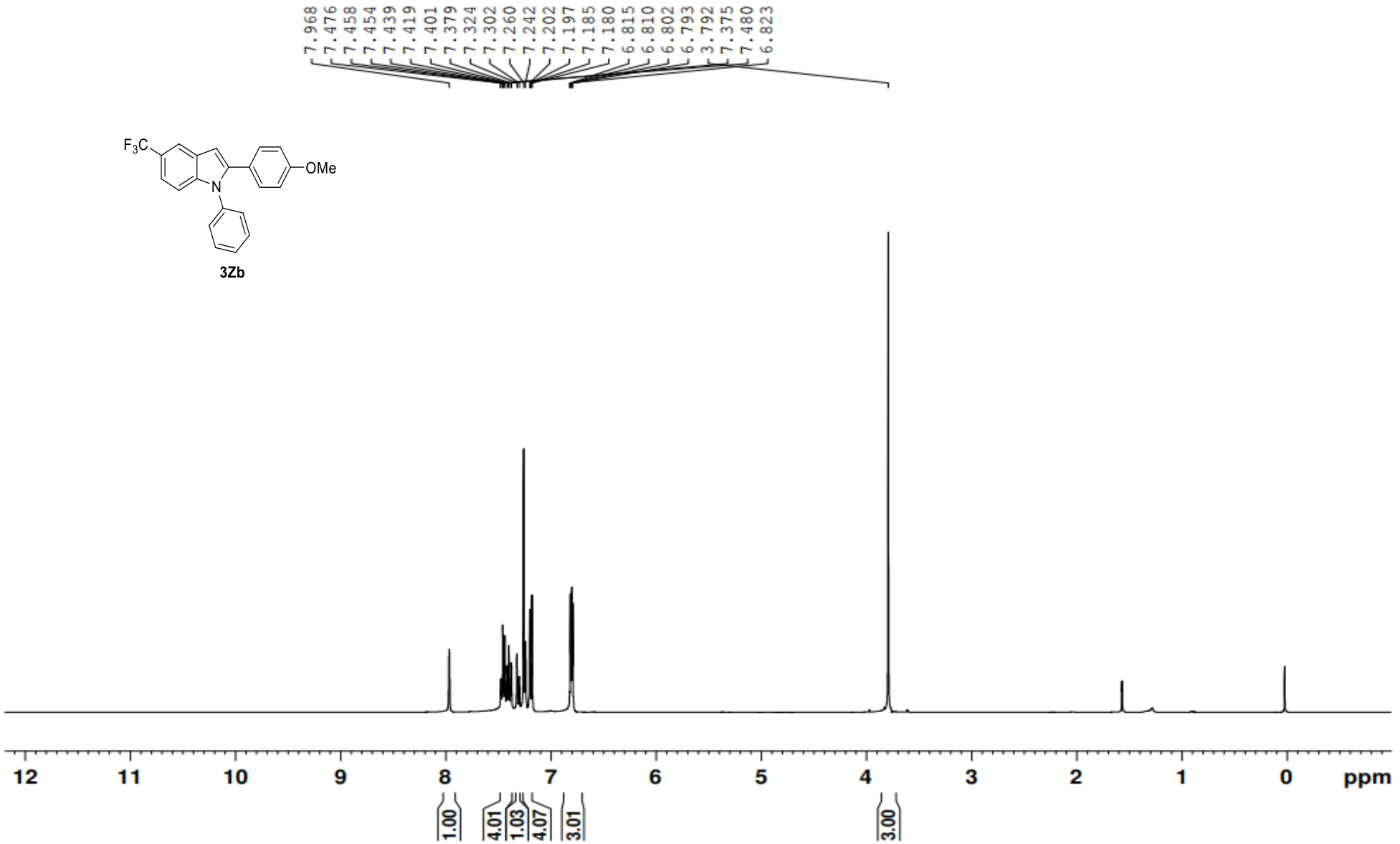


Figure S99. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3Zb.**

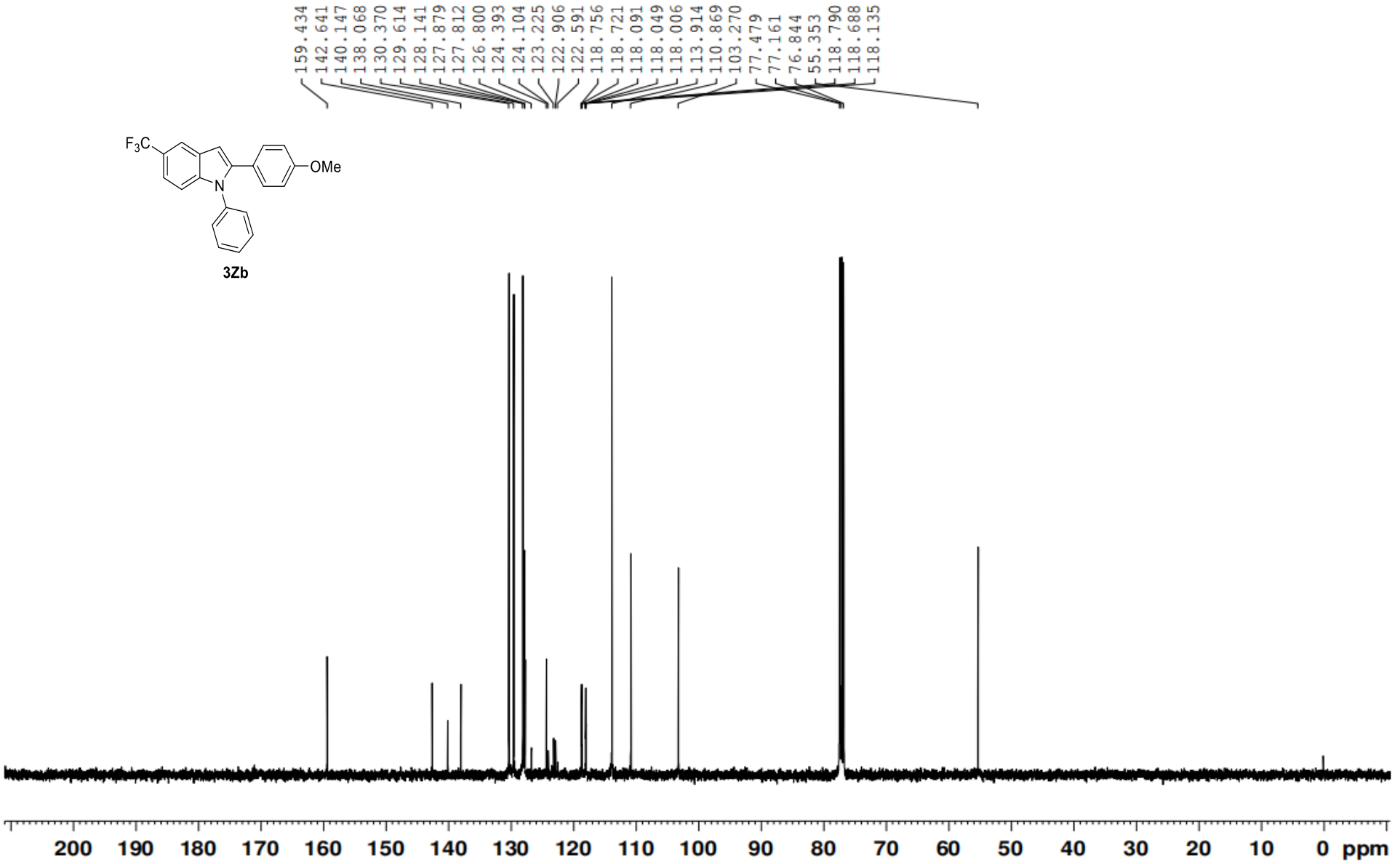


Figure S100. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3Zb.**

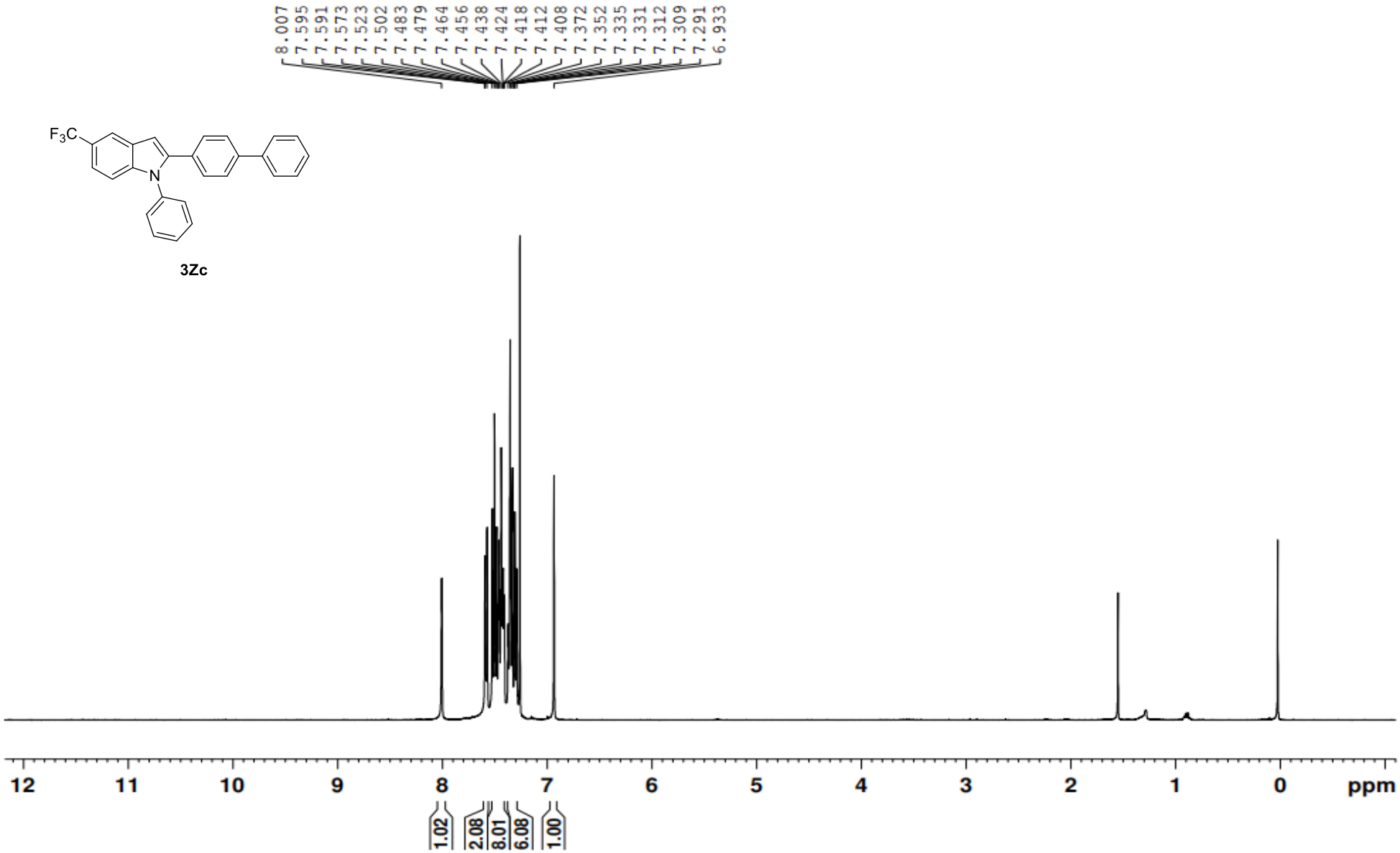


Figure S101. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3Zc.**

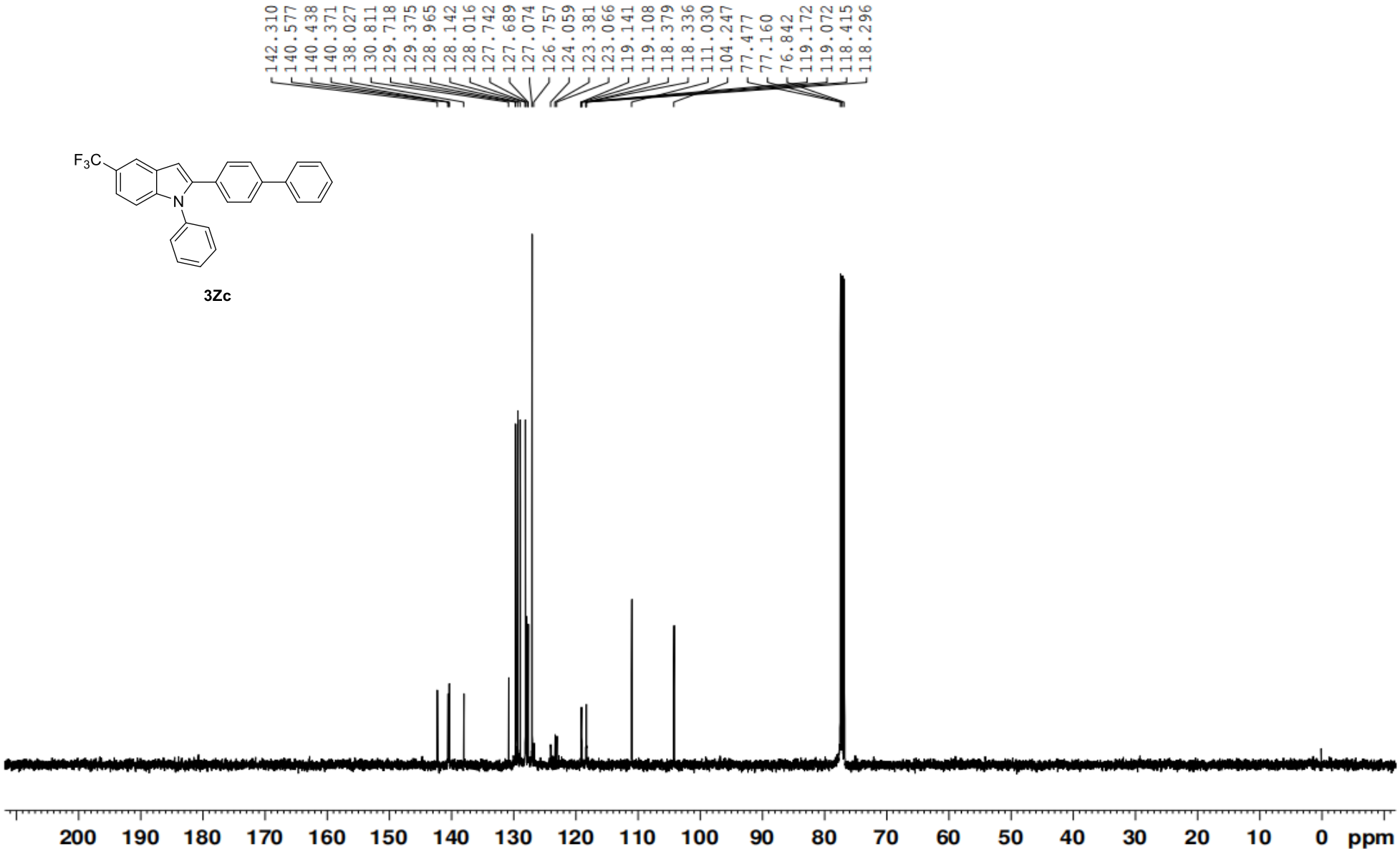


Figure S102. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3Zc.**

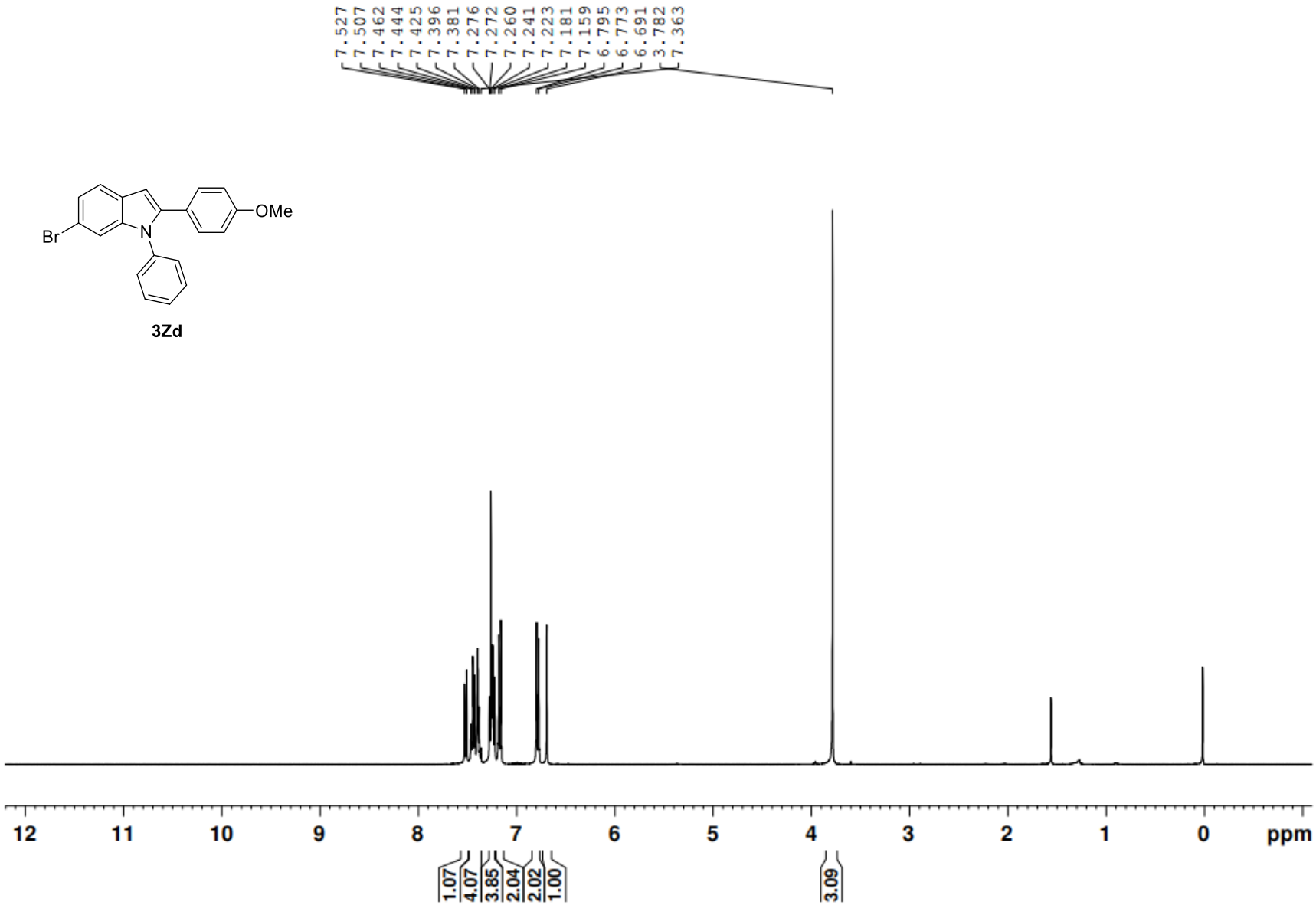


Figure S103. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3Zd.**

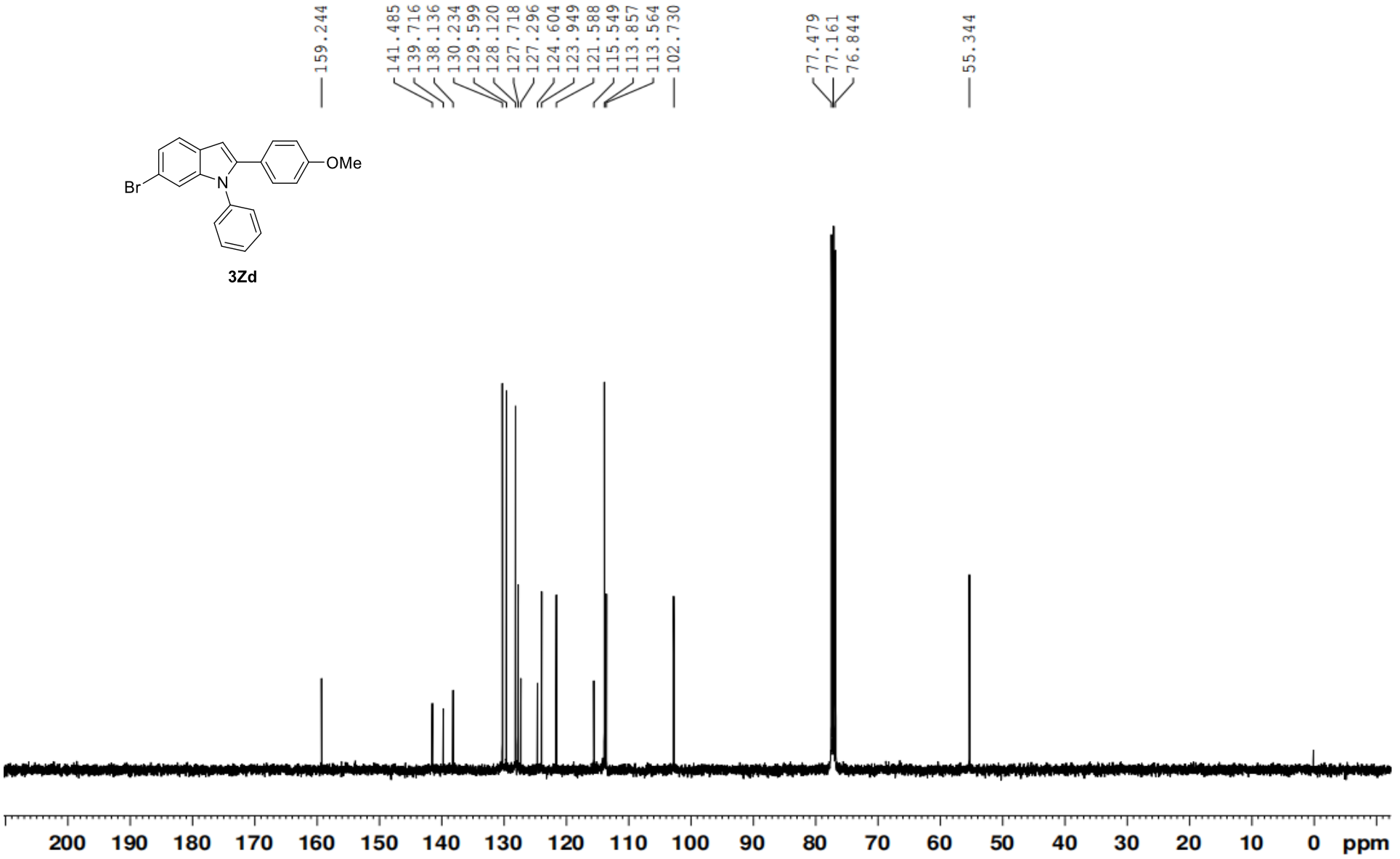


Figure S104. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3Zd.**

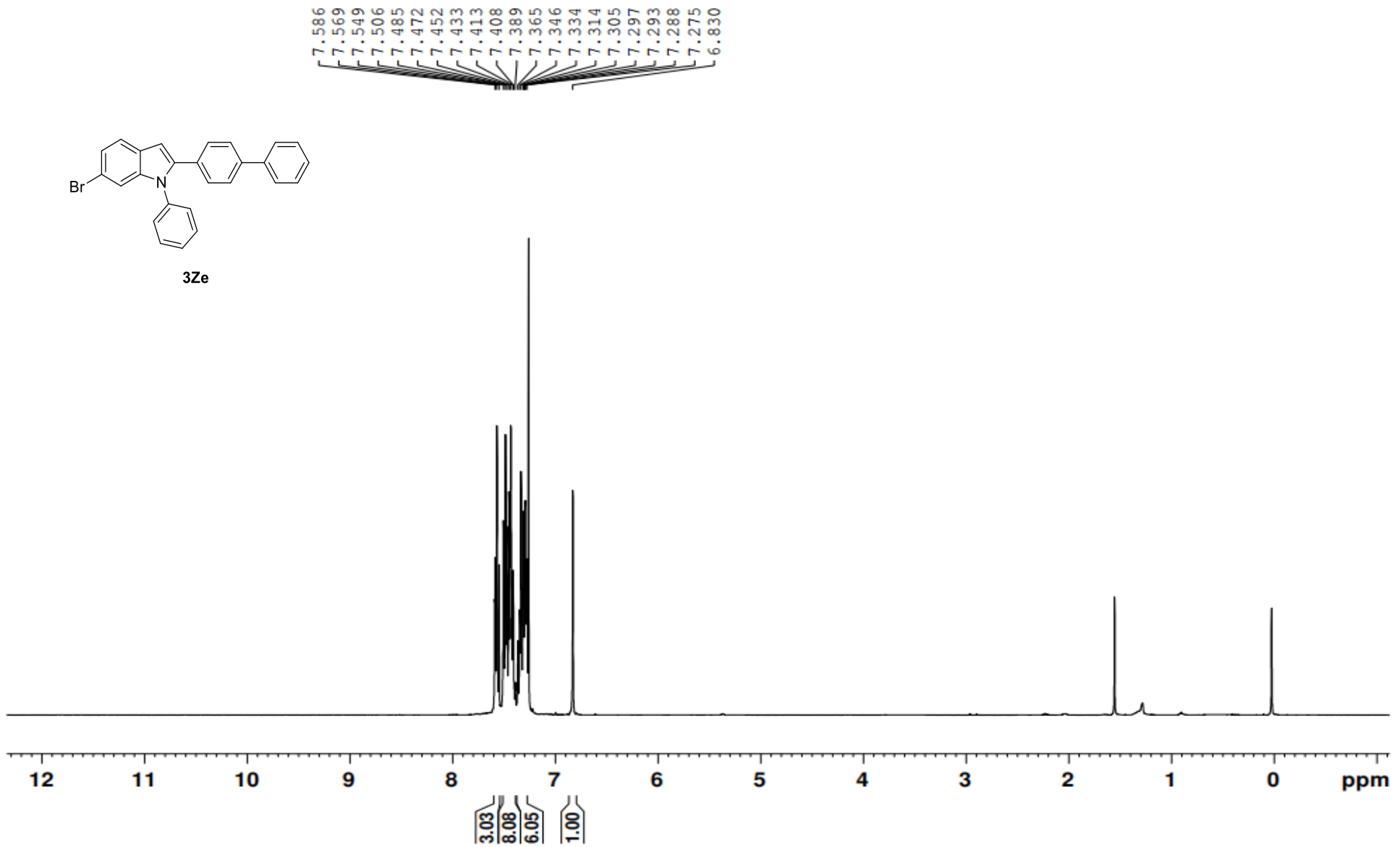


Figure S105. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3Ze.**

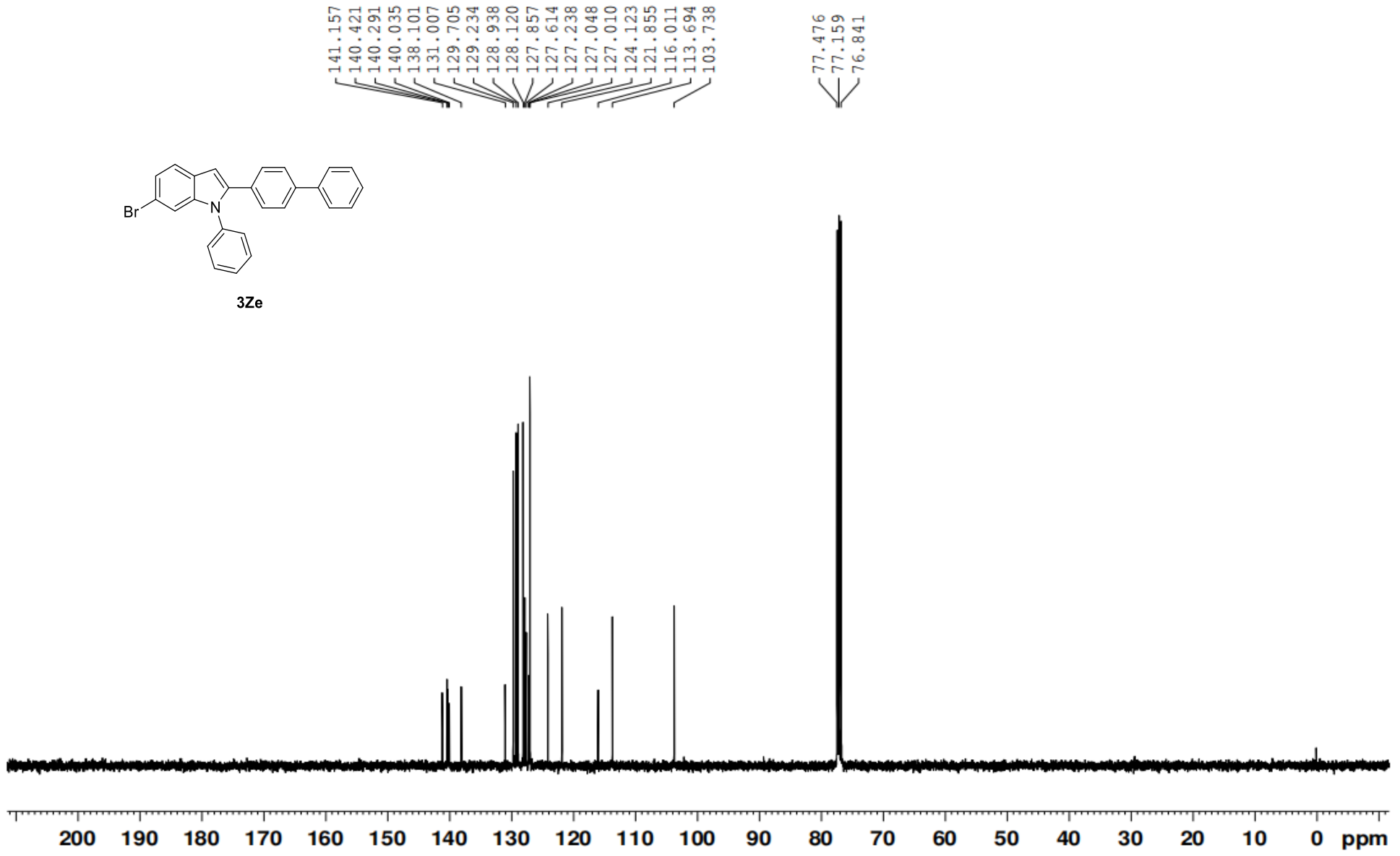


Figure S106. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3Ze.**