Gold-Catalyzed C5-Alkylation of Indolines and Sequential Oxidative Aromatization: Access to C5-Functionalized Indoles

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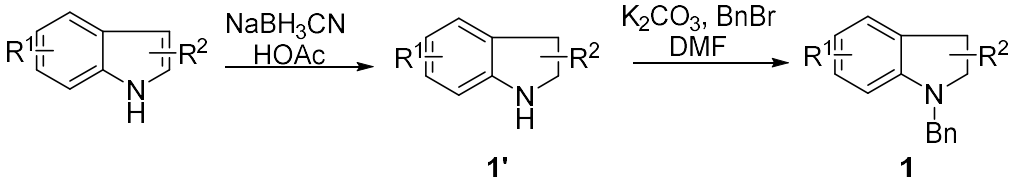
General information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. ^{1}H NMR were recorded on Bruker 300 MHz or 400 MHz spectrometer and ^{13}C NMR were recorded on Bruker 75 MHz, 100 MHz or 125MHz spectrometer in $CDCl_3$. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus. The diazo compounds[1] and ^{t}BuXPhosAuCl[2] were known compounds and prepared according to the literature procedures.

Preparation of substrates

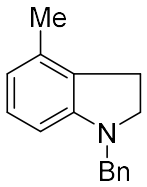
N-substituted indolines were prepared according to the literature procedures.[3] The unreported N-substituted indolines were prepared as below:



1' **1**

To a solution of indole (2.5 mmol) in AcOH (10 mL) was added $NaBH_3CN$ (0.63 g, 10 mmol) in five portions at 0 °C, then the reaction was stirred at RT for 5 h. The solvent was removed under vacuum. The residue was basified with sat. Na_2CO_3 and extracted with EtOAc. The organic layer was dried over Na_2SO_4, filtered and concentrated to give crude **1'**,[3d] which was used directly without purification.

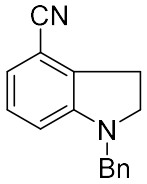
To a mixture of crude **1'** (2.5 mmol) and K_2CO_3 (0.41 g, 3mmol) in DMF (10 mL) was added BnBr (0.47g, 2.75 mmol) at RT, the mixture was stirred at RT for 12 h. The reaction was diluted with Et_2O and washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated; the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether = 1:50-1:20) to give compound **1**.



1-benzyl-4-methylindoline (1b):

Colorless oil (0.45 g, two steps yield: 78%).

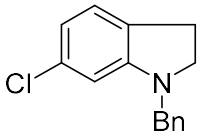
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.23 (m, 5H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.51 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 1H), 4.24 (s, 2H), 3.32 (t, *J* = 8.3 Hz, 2H), 2.89 (t, *J* = 8.3 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.36, 138.64, 134.03, 128.53, 128.49, 127.93, 127.45, 127.09, 119.12, 104.58, 53.78, 53.36, 27.26, 18.63. HRMS (ESI) calcd. for $C_{16}H_{18}N$ $[M+H]^+$: 224.1434, found: 224.1438.



1-benzylindoline-4-carbonitrile (1c):

Yellow oil (0.26 g, two steps yield: 45%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.26 (m, 5H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.85 (dd, *J* = 7.7, 0.8 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 4.29 (s, 2H), 3.46 (t, *J* = 8.5 Hz, 2H), 3.17 (t, *J* = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.77, 137.30, 134.59, 128.71, 128.44, 127.72, 127.50, 119.77, 117.99, 110.07, 108.58, 52.81, 52.77, 28.06. HRMS (ESI) calcd. for $C_{16}H_{15}N_2$ $[M+H]^+$: 235.1230, found: 235.1234.



1-benzyl-6-chloroindoline (1d):

Colorless oil (0.61 g, two steps yield: 81%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.21 (m, 5H), 6.94 (dt, *J* = 7.7, 1.0 Hz, 1H), 6.59 (dd, *J* = 7.7, 1.8 Hz, 1H), 6.43 (d, *J* = 1.8 Hz, 1H), 4.21 (s, 2H), 3.34 (t, *J* = 8.4 Hz,

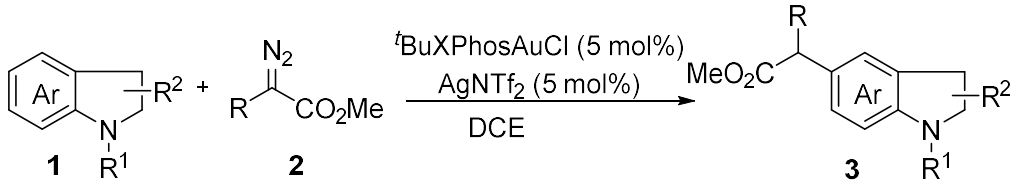
2H), 2.91 (t, J = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.73, 137.81, 133.12, 128.64, 128.46, 127.86, 127.35, 125.05, 117.12, 107.03, 53.66, 53.03, 28.00. HRMS (ESI) calcd. for $C_{15}H_{15}ClN$ $[M+H]^+$: 244.0888, found: 244.0885.

1-benzyl-7-methoxyindoline (1e):

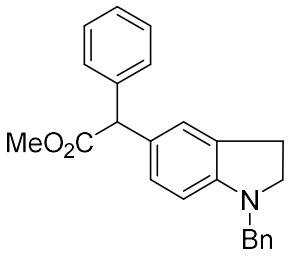
Colorless oil (0.45 g, two steps yield: 76%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.19 (m, 5H), 6.78-6.66 (m, 3H), 4.64 (s, 2H), 3.81 (s, 3H), 3.23 (t, J = 8.7 Hz, 2H), 2.91 (t, J = 8.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.37, 140.45, 139.72, 132.11, 128.39, 128.30, 126.81, 119.38, 117.85, 111.42, 55.79, 55.58, 53.67, 29.20. HRMS (ESI) calcd. for $C_{16}H_{18}NO$ $[M+H]^+$: 240.1383, found: 240.1387.

General procedure for Table 2



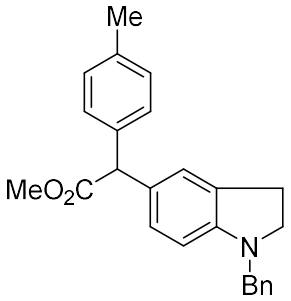
To a tube was added **1** (0.2 mmol), ^{t}BuXPhosAuCl (6.6 mg, 0.01 mmol), $AgNTf_2$ (3.9 mg, 0.01mmol) and DCE (4 mL) under argon atmosphere, then a solution of **2** (0.24 mmol) in DCE (1 mL) was added via a syringe pump over 1 h. The resulting solution was stirred at rt for 8 h. The reaction solution was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc/Petroleum ether = 1:30-1:15 or CH_2Cl_2/ Petroleum ether = 1:5-1:1) to give compound **3**.



methyl 2-(1-benzylindolin-5-yl)-2-phenylacetate (3a):

Yellow oil (61 mg, 85%).

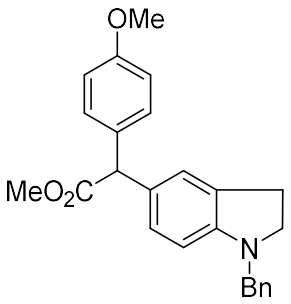
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 10H), 7.04 (s, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 4.92 (s, 1H), 4.21 (s, 2H), 3.72 (s, 3H), 3.30 (t, *J* = 8.3 Hz, 2H), 2.93 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.71, 151.92, 139.51, 138.45, 130.62, 128.53, 128.36, 127.91, 127.78, 127.69, 127.18, 127.06, 124.80, 106.70, 56.51, 53.77, 53.69, 52.27, 28.53. HRMS (ESI) calcd. for $C_{24}H_{24}NO_2$ $[M+H]^+$: 358.1802, found: 358.1805.



methyl 2-(1-benzylindolin-5-yl)-2-(p-tolyl)acetate (3b):

Yellow oil (61 mg, 82%).

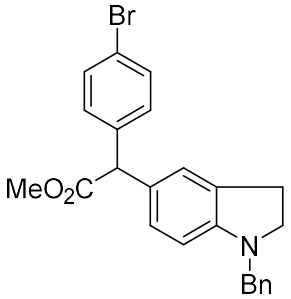
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.41 (d, *J* = 8.1 Hz, 1H), 4.89 (s, 1H), 4.21 (s, 2H), 3.72 (s, 3H), 3.30 (t, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 8.3 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.82, 151.84, 138.46, 136.65, 136.51, 130.55, 129.22, 128.50, 128.36, 127.98, 127.88, 127.58, 127.13, 124.73, 106.67, 56.12, 53.76, 53.68, 52.19, 28.51, 21.07. HRMS (ESI) calcd. for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958, found: 372.1954.



methyl 2-(1-benzylindolin-5-yl)-2-(4-methoxyphenyl)acetate (3c):

Yellow oil (62 mg, 80%).

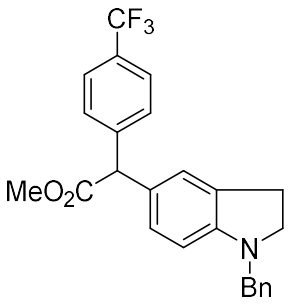
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.18 (m, 7H), 7.02 (s, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.41 (d, *J* = 8.1 Hz, 1H) 4.87 (s, 1H), 4.21 (s, 2H), 3.77 (s, 3H), 3.72 (s, 3H), 3.30 (t, *J* = 8.3 Hz, 2H), 2.93 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.96, 158.60, 151.85, 138.45, 131.64, 130.60, 129.57, 128.52, 128.12, 127.90, 127.51, 127.16, 124.68, 113.91, 106.70, 55.66, 55.29, 53.77, 53.69, 52.22, 28.53. HRMS (ESI) calcd. for $C_{25}H_{26}NO_3$ $[M+H]^+$: 388.1907, found: 388.1911.



methyl 2-(1-benzylindolin-5-yl)-2-(4-bromophenyl)acetate (3d):

Yellow oil (57 mg, 65%).

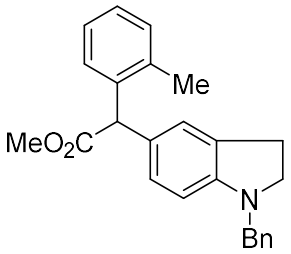
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.37-7.23 (m, 5H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.99 (s, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.41 (d, *J* = 8.1 Hz, 1H), 4.86 (s, 1H), 4.22 (s, 2H), 3.72 (s, 3H), 3.31 (t, *J* = 8.3 Hz, 2H), 2.93 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.24, 152.03, 138.56, 138.33, 131.57, 130.73, 130.29, 128.53, 127.86, 127.58, 127.18, 127.11, 124.61, 121.08, 106.68, 55.85, 53.68, 53.56, 52.34, 28.47. HRMS (ESI) calcd. for $C_{24}H_{23}BrNO_2$ $[M+H]^+$: 436.0907, found: 436.0904.



methyl 2-(1-benzylindolin-5-yl)-2-(4-(trifluoromethyl)phenyl)acetate (3e):

Colorless oil (41 mg, 48%).

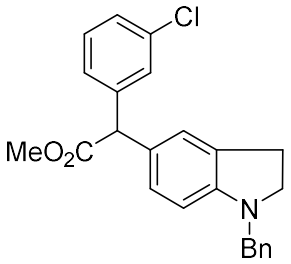
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.37-7.22 (m, 5H), 7.01 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 4.96 (s, 1H), 4.23 (s, 2H), 3.74 (s, 3H), 3.33 (t, *J* = 8.4 Hz, 2H), 2.95 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.02, 152.15, 138.29, 130.84, 128.91, 128.55, 127.86, 127.66, 127.21, 126.71, 125.46, 125.42, 124.63, 124.62, 106.71, 56.21, 53.67, 53.51, 52.44, 28.46. HRMS (ESI) calcd. for $C_{25}H_{23}F_3NO_2$ $[M+H]^+$: 426.1675, found: 426.1679.



methyl 2-(1-benzylindolin-5-yl)-2-(o-tolyl)acetate (3f):

Yellow oil (43 mg, 58%).

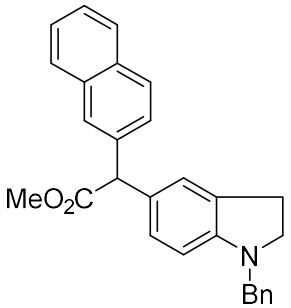
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.29 (m, 4H), 7.29-7.23 (m, 2H), 7.21-7.13 (m, 3H), 6.96 (s, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 5.09 (s, 1H), 4.22 (s, 2H), 3.72 (s, 3H), 3.30 (t, *J* = 8.3 Hz, 2H), 2.93 (t, *J* = 8.3 Hz, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.93, 151.84, 138.47, 137.67, 136.33, 130.60, 130.53, 128.51, 128.00, 127.96, 127.92, 127.15, 127.12, 126.81, 126.16, 125.10, 106.71, 53.77, 53.74, 53.21, 52.26, 28.52, 19.84. HRMS (ESI) calcd. for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958, found: 372.1955.



methyl 2-(1-benzylindolin-5-yl)-2-(3-chlorophenyl)acetate (3g):

Colorless oil (47 mg, 60%).

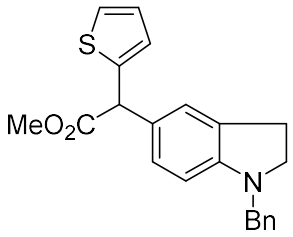
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.29 (m, 5H), 7.29-7.17 (m, 4H), 7.02 (s, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 4.87 (s, 1H), 4.23 (s, 2H), 3.73 (s, 3H), 3.32 (t, *J* = 8.3 Hz, 2H), 2.94 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.11, 152.10, 141.49, 138.35, 134.32, 130.77, 129.71, 128.69, 128.54, 127.87, 127.66, 127.27, 127.19, 126.88, 126.74, 124.67, 106.72, 56.07, 53.71, 53.57, 52.40, 28.48. HRMS (ESI) calcd. for $C_{24}H_{23}ClNO_2$ $[M+H]^+$: 392.1412, found: 392.1416.



methyl 2-(1-benzylindolin-5-yl)-2-(naphthalen-2-yl)acetate (3h):

Colorless oil (53 mg, 65%).

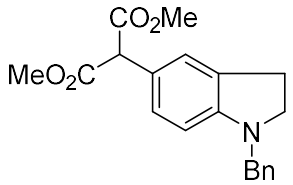
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.73 (m, 4H), 7.49-7.40 (m, 3H), 7.37-7.22 (m, 5H), 7.06 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 5.09 (s, 1H), 4.22 (s, 2H), 3.76 (s, 3H), 3.30 (t, *J* = 8.3 Hz, 2H), 2.93 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.67, 151.95, 138.42, 136.92, 133.38, 132.49, 130.64, 128.52, 128.21, 128.00, 127.89, 127.77, 127.66, 127.60, 127.16, 126.94, 126.92, 126.10, 125.87, 124.90, 106.69, 56.57, 53.73, 53.65, 52.30, 28.50. HRMS (ESI) calcd. for $C_{28}H_{26}NO_2$ $[M+H]^+$: 408.1958, found: 408.1954.



methyl 2-(1-benzylindolin-5-yl)-2-(thiophen-2-yl)acetate (3i):

Colorless oil (65 mg, 90%).

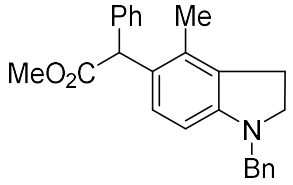
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.22 (m, 5H), 7.20 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.11 (s, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.99-6.89 (m, 2H), 6.42 (d, *J* = 8.1 Hz, 1H), 5.10 (s, 1H), 4.22 (s, 2H), 3.73 (s, 3H), 3.31 (t, *J* = 8.3 Hz, 2H), 2.94 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.82, 152.23, 142.30, 138.38, 130.66, 128.55, 127.89, 127.60, 127.39, 127.20, 126.56, 125.91, 124.98, 124.36, 106.64, 53.71, 53.57, 52.51, 51.80, 28.49. HRMS (ESI) calcd. for $C_{22}H_{22}NO_2S$ $[M+H]^+$: 364.1366, found: 364.1370.



dimethyl 2-(1-benzylindolin-5-yl)malonate (3j):

Colorless oil (29 mg, 42%).

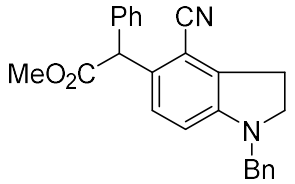
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.24 (m, 5H), 7.13 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.43 (d, *J* = 8.1 Hz, 1H), 4.53 (s, 1H), 4.24 (s, 2H), 3.74 (s, 6H), 3.35 (t, *J* = 8.3 Hz, 2H), 2.98 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.35, 152.67, 138.29, 130.59, 128.57, 128.53, 127.83, 127.18, 125.19, 121.26, 106.48, 57.02, 53.58, 53.32, 52.76, 28.39. HRMS (ESI) calcd. for $C_{20}H_{22}NO_4$ $[M+H]^+$: 340.1543, found: 340.1547.



methyl 2-(1-benzyl-4-methylindolin-5-yl)-2-phenylacetate (3k):

Colorless oil (41 mg, 55%).

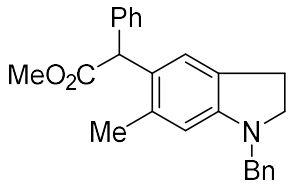
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.21 (m, 10H), 6.91 (d, *J* = 8.1 Hz, 1H), 6.32 (d, *J* = 8.1 Hz, 1H), 5.14 (s, 1H), 4.27-4.17 (m, 2H), 3.72 (s, 3H), 3.32 (t, *J* = 8.0 Hz, 2H), 2.91 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.95, 151.55, 138.84, 138.53, 132.45, 129.53, 128.91, 128.49, 128.45, 127.91, 127.52, 127.12, 126.98, 126.43, 104.41, 53.65, 53.36, 53.25, 52.26, 27.88, 15.68. HRMS (ESI) calcd. for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958, found: 372.194.



methyl 2-(1-benzyl-4-cyanoindolin-5-yl)-2-phenylacetate (3l):

Yellow oil (56 mg, 73%).

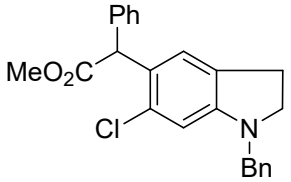
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 10H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 5.30 (s, 1H), 4.24 (s, 2H), 3.75 (s, 3H), 3.46 (t, *J* = 8.5 Hz, 2H), 3.15 (td, *J* = 8.3, 4.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.53, 151.83, 137.85, 137.28, 135.60, 129.34, 128.76, 128.72, 128.62, 128.51, 127.71, 127.53, 116.62, 109.89, 109.24, 54.04, 53.01, 52.81, 52.56, 28.40. HRMS (ESI) calcd. for $C_{25}H_{23}N_2O_2$ $[M+H]^+$: 383.1754, found: 383.1758.



methyl 2-(1-benzyl-6-methylindolin-5-yl)-2-phenylacetate (3m):

Colorless oil (48 mg, 64%).

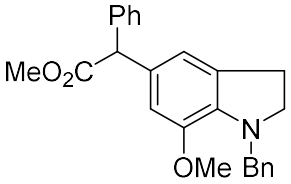
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.18 (m, 10H), 6.96 (s, 1H), 6.33 (s, 1H), 5.14 (s, 1H), 4.29-4.14 (m, 2H), 3.73 (s, 3H), 3.328 (t, *J* = 8.2 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.97, 151.81, 138.92, 138.58, 135.32, 128.82, 128.50, 128.46, 127.96, 127.87, 127.11, 126.95, 125.83, 124.27, 109.09, 53.81, 53.67, 53.04, 52.24, 28.32, 20.34. HRMS (ESI) calcd. for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958, found: 372.1954.



methyl 2-(1-benzyl-6-chloroindolin-5-yl)-2-phenylacetate (3n):

Yellow oil (67 mg, 85%).

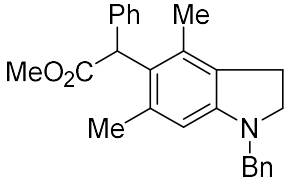
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.22 (m, 10H), 6.91 (s, 1H), 6.46 (s, 1H), 5.41 (s, 1H), 4.20 (s, 2H), 3.74 (s, 3H), 3.33 (t, *J* = 8.5 Hz, 2H), 2.85 (td, *J* = 16.0, 8.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.29, 152.63, 138.24, 137.76, 132.87, 129.19, 128.76, 128.66, 128.62, 127.78, 127.34, 127.23, 125.38, 124.57, 107.26, 53.58, 53.03, 53.01, 52.40, 28.10. HRMS (ESI) calcd. for $C_{24}H_{23}ClNO_2$ $[M+H]^+$: 392.1412, found: 392.1416.



methyl 2-(1-benzyl-7-methoxyindolin-5-yl)-2-phenylacetate (3o):

Yellow oil (36 mg, 47%).

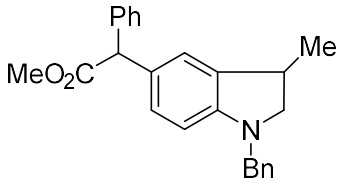
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.20 (m, 10H), 6.70 (s, 1H), 6.67 (s, 1H), 4.93 (s, 1H), 4.61 (s, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 3.21 (t, *J* = 8.7 Hz, 2H), 2.89 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.54, 145.94, 139.76, 139.66, 139.31, 132.16, 129.32, 128.51, 128.47, 128.31, 128.28, 127.10, 126.80, 118.06, 112.05, 56.58, 55.83, 55.41, 53.83, 52.28, 29.16. HRMS (ESI) calcd. for $C_{25}H_{26}NO_3$ $[M+H]^+$: 388.1907, found: 388.1911.



methyl 2-(1-benzyl-4,6-dimethylindolin-5-yl)-2-phenylacetate (3p):

Colorless oil (41 mg, 53%).

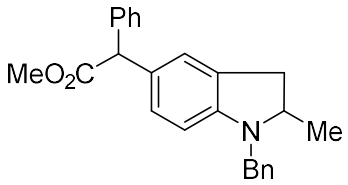
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.19 (m, 8H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.29 (s, 1H), 5.33 (s, 1H), 4.25 (s, 2H), 3.73 (s, 3H), 3.32 (t, *J* = 8.4 Hz, 2H), 2.94-2.84 (m, 2H), 2.15 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.41, 151.27, 138.67, 137.73, 136.84, 133.59, 128.76, 128.49, 128.07, 127.96, 127.56, 127.11, 126.55, 124.51, 107.43, 53.69, 53.26, 52.25, 50.62, 27.95, 21.60, 16.90. HRMS (ESI) calcd. for $C_{26}H_{28}NO_2$ $[M+H]^+$: 386.2115, found: 386.2119.



methyl 2-(1-benzyl-3-methylindolin-5-yl)-2-phenylacetate (3q):

Yellow oil (53 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.20 (m, 10H), 7.04-6.93 (m, 2H), 6.42 (dd, *J* = 8.4, 4.8 Hz, 1H), 4.94 (s, 1H), 4.33 (d, *J* = 14.8 Hz, 1H), 4.08 (d, *J* = 14.8 Hz, 1H), 3.73 (s, 3H), 3.50 (t, *J* = 8.6 Hz, 1H), 3.32-3.21 (m, 1H), 2.83 (td, *J* = 8.5, 1.2 Hz, 1H), 1.26 (dd, *J* = 6.8, 2.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.67, 151.49, 139.56, 139.46, 138.46, 135.55, 128.51, 127.88, 127.85, 127.68, 127.14, 127.03, 123.58, 123.52, 106.70, 61.80, 56.56, 53.48, 52.23, 35.19, 18.59. HRMS (ESI) calcd. for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958, found: 372.1955.

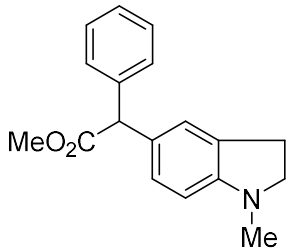


methyl 2-(1-benzyl-2-methylindolin-5-yl)-2-phenylacetate (3r):

Colorless oil (67 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.19 (m, 10H), 7.00 (s, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 6.22 (d, *J* = 8.1 Hz, 1H), 4.89 (s, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 4.15 (d, *J* = 16.0 Hz, 1H), 3.76-3.64 (m, 4H), 3.20-3.05 (m, 1H), 2.70-2.57 (m, 1H), 1.27 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.73, 152.07, 139.55, 139.26, 129.42, 128.53, 128.51, 127.72, 127.69, 127.48, 127.34, 127.04, 126.95, 124.42, 124.38, 106.50,

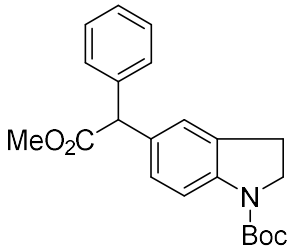
60.89, 56.53, 52.24, 51.27, 37.35, 19.78. HRMS (ESI) calcd. for $C_{25}H_{26}NO_2$ $[M+H]^+$: 372.1958, found: 372.1954.



methyl 2-(1-methylindolin-5-yl)-2-phenylacetate (3s):

Yellow oil (43 mg, 76%).

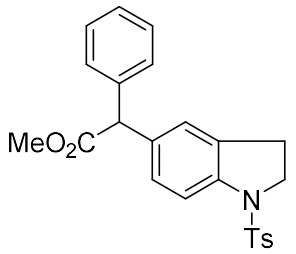
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 4H), 7.26-7.21 (m, 1H), 7.05-6.97 (m, 2H), 6.40 (d, *J* = 8.0 Hz, 1H), 4.92 (s, 1H), 3.73 (s, 3H), 3.28 (t, *J* = 8.2 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H), 2.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.67, 152.71, 139.49, 130.85, 128.49, 127.77, 127.67, 127.01, 124.56, 106.86, 56.49, 56.20, 52.21, 36.20, 28.68. HRMS (ESI) calcd. for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1489, found: 282.1485.



tert-butyl 5-(2-methoxy-2-oxo-1-phenylethyl)indoline-1-carboxylate (3t):

Colorless oil (57 mg, 77%).

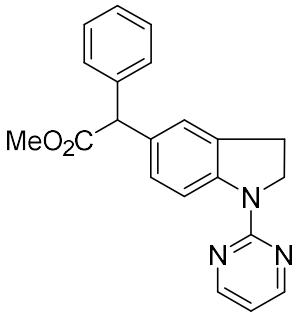
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.15 (m, 6H), 7.09 (d, *J* = 6.2 Hz, 2H), 4.97 (s, 1H), 3.95 (s, 2H), 3.74 (s, 3H), 3.05 (t, *J* = 8.7 Hz, 2H), 1.54 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.25, 152.62, 142.30, 138.96, 132.40, 130.95, 128.61, 128.47, 127.83, 127.21, 124.96, 114.58, 77.25, 56.44, 52.34, 47.73, 29.73, 28.46. HRMS (ESI) calcd. for $C_{22}H_{26}NO_4$ $[M+H]^+$: 368.1856, found: 368.1859.



methyl 2-phenyl-2-(1-tosylindolin-5-yl)acetate (3u):

Colorless oil (38 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.36-7.19 (m, 7H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.04 (s, 1H), 4.94 (s, 1H), 3.89 (t, *J* = 8.5 Hz, 2H), 3.73 (s, 3H), 2.87 (t, *J* = 8.5 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.07, 144.12, 141.28, 138.62, 133.97, 132.17, 129.71, 128.68, 128.44, 128.21, 127.35, 125.29, 114.51, 56.36, 52.40, 50.06, 27.82, 21.56. HRMS (ESI) calcd. for $C_{24}H_{24}NO_4S$ $[M+H]^+$: 422.1421, found: 422.1425.

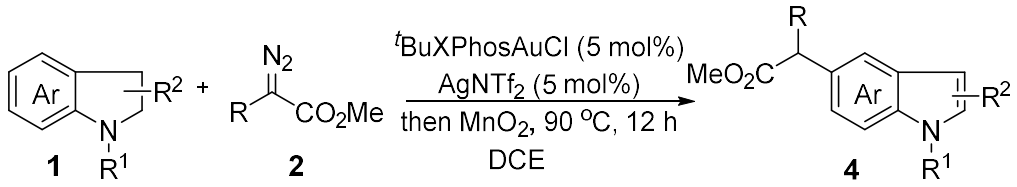


methyl 2-phenyl-2-(1-(pyrimidin-2-yl)indolin-5-yl)acetate (3v):

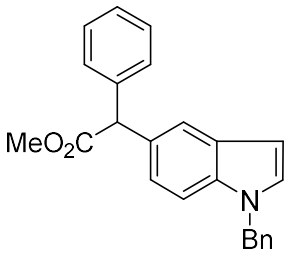
Colorless oil (54 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.9 Hz, 1H), 7.36-7.22 (m, 5H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.67 (t, *J* = 4.8 Hz, 1H), 5.01 (s, 1H), 4.22 (t, *J* = 8.7 Hz, 2H)., 3.75 (s, 3H), 3.16 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.36, 159.20, 157.49, 142.95, 139.13, 132.83, 131.68, 128.57, 128.52, 127.72, 127.16, 124.82, 115.21, 111.51, 56.53, 52.33, 48.91, 27.25. HRMS (ESI) calcd. for $C_{21}H_{20}N_3O_2$ $[M+H]^+$: 346.1550, found: 346.1553.

General procedure for Table 3



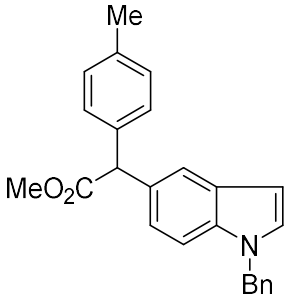
To a tube was added **1** (0.2 mmol), ^{t}BuXPhosAuCl (6.6 mg, 0.01 mmol), $AgNTf_2$ (3.9 mg, 0.01mmol) and DCE (4 mL) under argon atmosphere, then a solution of **2** (0.24 mmol) in DCE (1 mL) was added via a syringe pump over 1 h. After stirring for 8 h at rt, MnO_2 (130 mg, 1.5 mmol) under argon atmosphere, then the mixture was stirred at 90 ^{o}C for 12 h. The mixture was filtered; the filtrate was concentrated under vacuum and the residue was purified by column chromatography (silica gel, eluted with EtOAc/Petroleum ether = 1:30-1:15 or CH_2Cl_2/ Petroleum ether = 1:5-1:1) to give compound **4**.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-phenylacetate (4a):

Yellow oil (50 mg, 71%).

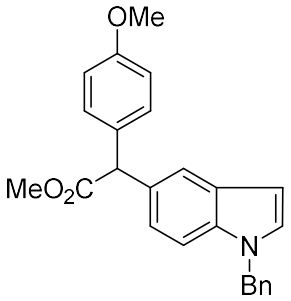
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.5 Hz, 1H), 7.37-7.19 (m, 9H), 7.14-7.06 (m, 4H), 6.49 (dd, *J* = 3.1, 0.4 Hz, 1H), 5.27 (s, 2H), 5.13 (s, 1H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.71, 139.54, 137.43, 135.59, 129.85, 128.81, 128.67, 128.52, 127.70, 127.07, 126.89, 122.64, 120.87, 109.91, 101.89, 57.08, 52.29, 50.23. HRMS (ESI) calcd. for $C_{24}H_{22}NO_2$ $[M+H]^{+}$: 356.1645, found: 356.1641.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-(p-tolyl)acetate (4b):

Colorless oil (55 mg, 75%).

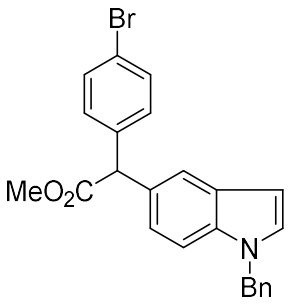
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.4 Hz, 1H), 7.34-7.19 (m, 6H), 7.14-7.05 (m, 6H), 6.49 (d, *J* = 3.1 Hz, 1H), 5.28 (s, 2H), 5.10 (s, 1H), 3.73 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.86, 137.44, 136.69, 136.56, 135.55, 130.04, 129.22, 128.82, 128.79, 128.75, 128.52, 127.67, 126.87, 122.60, 120.77, 109.87, 101.87, 56.70, 52.25, 50.21, 21.09. HRMS (ESI) calcd. for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802, found: 370.1806.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-(4-methoxyphenyl)acetate (4c):

Colorless oil (59 mg, 77%).

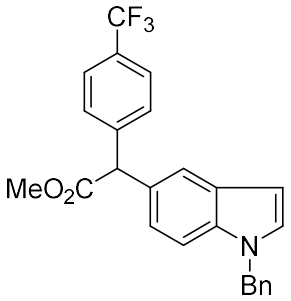
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.31-7.18 (m, 6H), 7.14-7.05 (m, 4H), 6.87-6.79 (m, 2H), 6.49 (d, *J* = 3.1 Hz, 1H), 5.26 (s, 2H), 5.08 (s, 1H), 3.76 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.00, 158.62, 137.45, 135.54, 131.71, 130.19, 129.74, 128.80, 127.69, 127.02, 126.88, 122.54, 120.69, 113.90, 109.91, 101.88, 56.25, 55.29, 52.26, 50.22. HRMS (ESI) calcd. for $C_{25}H_{24}NO_3$ $[M+H]^+$: 386.1751, found: 386.1754.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-(4-bromophenyl)acetate (4d):

Yellow oil (51 mg, 59%).

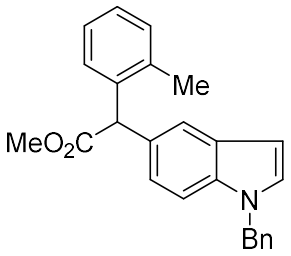
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.35-7.19 (m, 6H), 7.17-7.03 (m, 4H), 6.50 (d, *J* = 3.1 Hz, 1H), 5.29 (s, 2H), 5.07 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.27, 138.58, 137.32, 135.61, 131.56, 130.44, 129.29, 128.98, 128.88, 128.81, 127.73, 126.87, 122.39, 121.12, 120.74, 110.05, 101.88, 56.42, 52.39, 50.24. HRMS (ESI) calcd. for $C_{24}H_{21}BrNO_2$ $[M+H]^+$: 434.0750, found: 434.0753.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-(4-(trifluoromethyl)phenyl)acetate (4e):

Colorless oil (31 mg, 37%).

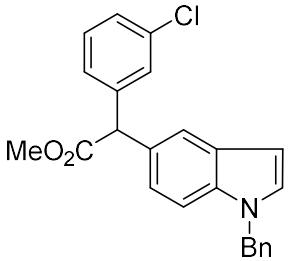
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 9.9 Hz, 3H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.33-7.22 (m, 4H), 7.16-7.06 (m, 4H), 6.51 (d, *J* = 3.1 Hz, 1H), 5.29 (s, 2H), 5.17 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.05, 143.51, 137.28, 135.66, 129.08, 129.06, 128.96, 128.93, 128.82, 127.75, 126.87, 125.52, 125.43, 125.39, 122.37, 120.82, 110.14, 101.89, 56.78, 52.47, 50.26. HRMS (ESI) calcd. for $C_{25}H_{21}F_3NO_2$ $[M+H]^+$: 424.1519, found: 424.1523.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-(o-tolyl)acetate (4f):

Yellow oil (38 mg, 51%).

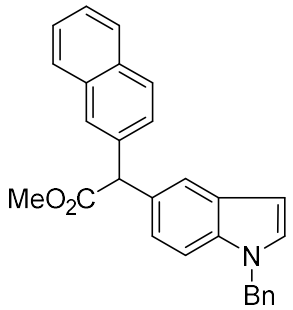
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 1.4 Hz, 1H), 7.32-7.20 (m, 5H), 7.19-7.02 (m, 7H), 6.54-6.44 (m, 1H), 5.31 (s, 1H), 5.28 (s, 2H), 3.73 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.93, 137.73, 137.43, 136.40, 135.58, 130.59, 128.92, 128.82, 128.80, 128.71, 128.20, 127.69, 127.16, 126.92, 126.16, 122.98, 121.21, 109.82, 101.84, 53.80, 52.29, 50.22, 19.89. HRMS (ESI) calcd. for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802, found: 370.1806.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-(3-chlorophenyl)acetate (4g):

Colorless oil (39 mg, 50%).

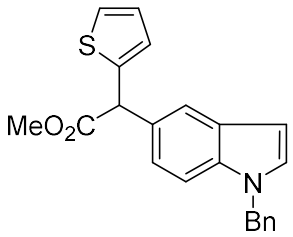
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.5 Hz, 1H), 7.36-7.19 (m, 8H), 7.15-7.07 (m, 4H), 6.58-6.38 (m, 1H), 5.29 (s, 2H), 5.09 (s, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.13, 141.50, 137.32, 135.66, 134.30, 129.68, 129.09, 128.99, 128.89, 128.82, 127.73, 127.28, 126.88, 122.43, 120.83, 110.07, 105.67, 101.90, 56.65, 52.42, 50.25. HRMS (ESI) calcd. for $C_{24}H_{21}ClNO_2$ $[M+H]^+$: 390.1255, found: 390.1259.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-(naphthalen-2-yl)acetate (4h):

Colorless oil (54 mg, 60%).

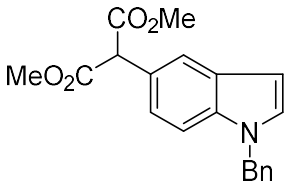
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.74 (m, 4H), 7.61 (s, 1H), 7.50-7.40 (m, 3H), 7.31-7.20 (m, 4H), 7.18-7.06 (m, 4H), 6.50 (d, *J* = 3.1 Hz, 1H), 5.30 (s, 1H), 5.27 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.70, 137.40, 136.97, 135.62, 133.38, 132.51, 129.77, 128.87, 128.84, 128.80, 128.19, 128.03, 127.69, 127.61, 127.14, 127.05, 126.89, 126.09, 125.88, 122.72, 120.98, 109.95, 101.91, 57.16, 52.34, 50.23. HRMS (ESI) calcd. for $C_{28}H_{24}NO_2$ $[M+H]^+$: 406.1802, found: 406.1805.



methyl 2-(1-benzyl-1H-indol-5-yl)-2-(thiophen-2-yl)acetate (4i):

Yellow oil (60 mg, 83%).

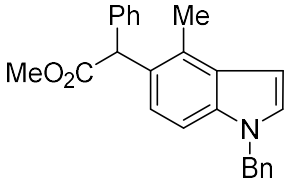
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.31-7.17 (m, 6H), 7.13-7.06 (m, 3H), 6.98 (d, *J* = 3.4 Hz, 1H), 6.92 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.50 (d, *J* = 3.1 Hz, 1H), 5.31 (s, 1H), 5.26 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.87, 142.29, 137.38, 135.81, 129.82, 128.99, 128.88, 128.83, 127.73, 126.91, 126.55, 126.12, 125.07, 122.08, 120.60, 109.99, 101.98, 52.54, 52.41, 50.24. HRMS (ESI) calcd. for $C_{22}H_{20}NO_2S$ $[M+H]^+$: 362.1209, found: 362.1213.



dimethyl 2-(1-benzyl-1H-indol-5-yl)malonate (4j):

Colorless oil (24 mg, 36%).

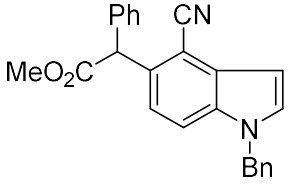
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 1.4 Hz, 1H), 7.34-7.23 (m, 4H), 7.20 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.15-7.09 (m, 3H), 6.54 (dd, *J* = 3.1, 0.56 Hz, 1H), 5.31 (s, 2H), 4.74 (s, 1H), 3.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.34, 151.20, 137.30, 128.99, 128.84, 128.81, 127.72, 126.87, 123.72, 122.74, 121.89, 109.94, 102.00, 57.65, 52.79, 50.23. HRMS (ESI) calcd. for $C_{20}H_{20}NO_4$ $[M+H]^+$: 338.1387, found: 338.1383.



methyl 2-(1-benzyl-4-methyl-1H-indol-5-yl)-2-phenylacetate (4k):

Colorless oil (39 mg, 53%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.18 (m, 8H), 7.16-7.06 (m, 5H), 6.55 (d, *J* = 3.2 Hz, 1H), 5.40 (s, 1H), 5.27 (s, 2H), 3.72 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.05, 139.18, 137.49, 135.26, 129.41, 128.89, 128.79, 128.49, 128.41, 128.09, 127.67, 127.33, 126.94, 126.89, 122.49, 107.57, 100.65, 53.18, 52.25, 50.23, 15.49. HRMS (ESI) calcd. for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802, found: 370.1805.

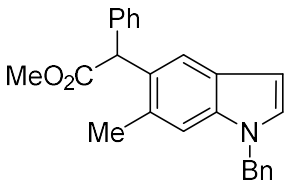


methyl 2-(1-benzyl-4-cyano-1H-indol-5-yl)-2-phenylacetate (4l):

Yellow oil (53 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.21 (m, 11H), 7.11-7.03 (m, 2H), 6.72 (d, *J* = 3.1

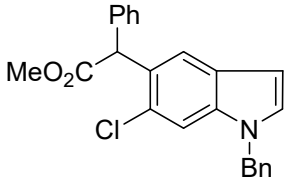
Hz, 1H), 5.62 (s, 1H), 5.29 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.41, 138.08, 136.44, 135.02, 131.47, 130.59, 129.01, 128.79, 128.58, 128.11, 127.55, 126.82, 122.00, 117.45, 114.55, 103.49, 101.11, 54.60, 52.60, 50.53. HRMS (ESI) calcd. for $C_{25}H_{21}N_2O_2$ $[M+H]^+$: 381.1598, found: 381.1595.



methyl 2-(1-benzyl-6-methyl-1H-indol-5-yl)-2-phenylacetate (4m):

Colorless oil (44 mg, 60%).

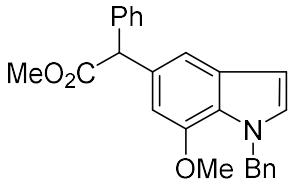
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.34-7.21 (m, 8H), 7.11 (dd, *J* = 10.9, 4.3 Hz, 3H), 7.04 (d, *J* = 3.1 Hz, 1H), 6.46 (d, *J* = 3.1 Hz, 1H), 5.28 (s, 1H), 5.26 (s, 2H), 3.75 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.97, 138.66, 137.60, 135.81, 130.24, 129.10, 128.84, 128.79, 128.47, 128.04, 127.62, 127.05, 127.03, 126.82, 120.47, 111.11, 101.82, 53.90, 52.32, 50.01, 20.78. HRMS (ESI) calcd. for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802, found: 370.1806.



methyl 2-(1-benzyl-6-chloro-1H-indol-5-yl)-2-phenylacetate (4n):

Yellow oil (63 mg, 81%).

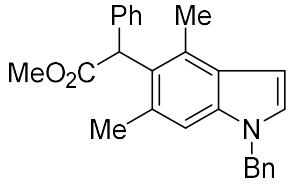
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.38-7.24 (m, 9H), 7.11-7.04 (m, 3H), 6.43 (d, *J* = 3.1 Hz, 1H), 5.54 (s, 1H), 5.22 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.31, 137.92, 136.92, 135.84, 129.41, 129.14, 128.91, 128.70, 128.08, 127.87, 127.82, 127.62, 127.37, 126.80, 122.12, 110.58, 102.25, 54.01, 52.47, 50.26. HRMS (ESI) calcd. for $C_{24}H_{21}ClNO_2$ $[M+H]^+$: 390.1255, found: 390.1258.



methyl 2-(1-benzyl-7-methoxy-1H-indol-5-yl)-2-phenylacetate (4o):

Colorless oil (35 mg, 46%).

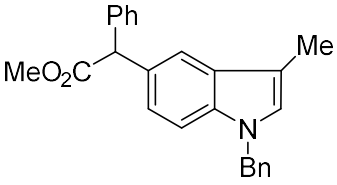
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.19 (m, 8H), 7.15 (d, *J* = 1.0 Hz, 1H), 7.13-7.07 (m, 2H), 7.00 (d, *J* = 3.1 Hz, 1H), 6.56 (d, *J* = 1.2 Hz, 1H), 6.43 (d, *J* = 3.1 Hz, 1H), 5.58 (s, 2H), 5.09 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.66, 147.55, 139.54, 139.40, 130.68, 130.26, 129.46, 128.63, 128.51, 128.47, 127.17, 127.07, 126.82, 125.31, 113.68, 103.71, 102.31, 57.22, 55.35, 52.39, 52.28. HRMS (ESI) calcd. for $C_{25}H_{24}NO_3$ $[M+H]^+$: 386.1751, found: 386.1754.



methyl 2-(1-benzyl-4,6-dimethyl-1H-indol-5-yl)-2-phenylacetate (4p):

Colorless oil (39 mg, 51%).

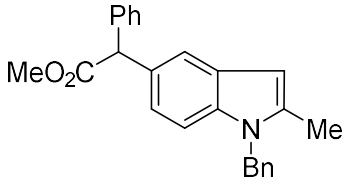
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.12 (m, 10H), 7.06 (d, *J* = 3.2 Hz, 1H), 7.04 (s, 1H), 6.53 (d, *J* = 3.2 Hz, 1H), 5.52 (s, 1H), 5.28 (s, 2H), 3.72 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.47, 137.62, 137.51, 135.34, 131.66, 129.77, 128.92, 128.80, 128.12, 128.06, 127.65, 127.27, 127.00, 126.58, 126.49, 109.43, 100.68, 52.28, 50.95, 50.04, 22.06, 16.75. HRMS (ESI) calcd. for $C_{26}H_{26}NO_2$ $[M+H]^+$: 384.1958, found: 384.1954.



methyl 2-(1-benzyl-3-methyl-1H-indol-5-yl)-2-phenylacetate (4q):

Colorless oil (52 mg, 70%).

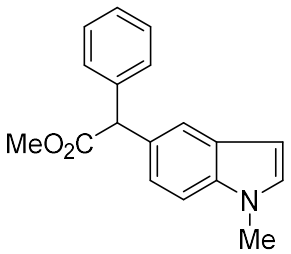
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 1.6 Hz, 1H), 7.38-7.18 (m, 9H), 7.15-7.06 (m, 3H), 6.87 (d, *J* = 0.7 Hz, 1H), 5.20 (s, 2H), 5.15 (s, 1H), 3.74 (s, 3H), 2.29 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.79, 139.68, 137.77, 135.92, 129.03, 129.02, 128.75, 128.63, 128.50, 127.59, 127.03, 126.90, 126.44, 122.52, 118.99, 111.06, 109.70, 57.18, 52.28, 49.91, 9.69. HRMS (ESI) calcd. for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802, found: 370.1806.



methyl 2-(1-benzyl-2-methyl-1H-indol-5-yl)-2-phenylacetate (4r):

Yellow oil (61 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.4 Hz, 1H), 7.38-7.18 (m, 8H), 7.13 (d, *J* = 8.5 Hz, 1H), 7.04 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.96 (d, *J* = 6.8 Hz, 2H), 6.27 (s, 1H), 5.24 (s, 2H), 5.12 (s, 1H), 3.73 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.81, 139.69, 137.80, 137.38, 136.46, 129.75, 128.81, 128.70, 128.48, 128.29, 127.35, 127.01, 126.09, 121.64, 119.66, 109.37, 100.61, 57.13, 52.27, 46.58, 12.85. HRMS (ESI) calcd. for $C_{25}H_{24}NO_2$ $[M+H]^+$: 370.1802, found: 370.1798.

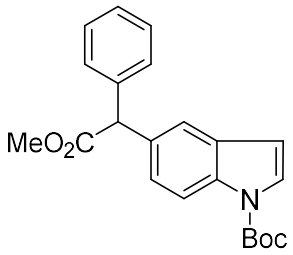


methyl 2-(1-methyl-1H-indol-5-yl)-2-phenylacetate (4s):

Colorless oil (40 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.6 Hz, 1H), 7.37-7.14 (m, 7H), 7.02 (d, *J* = 3.1 Hz, 1H), 6.43 (dd, *J* = 3.1, 0.6 Hz, 1H), 5.15 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.75, 139.65, 135.96, 129.58, 129.40, 128.66, 128.59, 128.50, 127.03, 122.43, 120.81, 109.44, 101.12, 57.08, 52.28, 32.92. HRMS

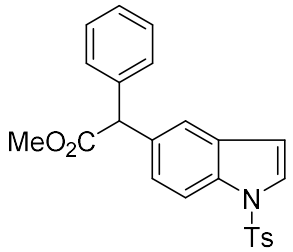
(ESI) calcd. for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1332, found: 280.1336.



tert-butyl 5-(2-methoxy-2-oxo-1-phenylethyl)-1H-indole-1-carboxylate (4t):

Colorless oil (38 mg, 52%).

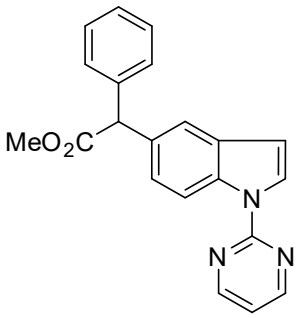
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.58 (d, *J* = 3.4 Hz, 1H), 7.50 (s, 1H), 7.35-7.28 (m, 4H), 7.28-7.23 (m, 2H), 6.52 (d, *J* = 3.4 Hz, 1H), 5.14 (s, 1H), 3.75 (s, 3H), 1.65 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.32, 149.71, 139.09, 133.02, 130.84, 128.86, 128.58, 127.98, 127.20, 126.43, 124.96, 120.87, 115.29, 107.35, 83.78, 56.84, 52.34, 28.19. HRMS (ESI) calcd. for $C_{22}H_{24}NO_4$ $[M+H]^+$: 366.1700, found: 366.1704.



methyl 2-phenyl-2-(1-tosyl-1H-indol-5-yl)acetate (4u):

Colorless oil (28 mg, 33%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.47 (s, 1H), 7.34-7.17 (m, 8H), 6.59 (d, *J* = 3.6 Hz, 1H), 5.09 (s, 1H), 3.73 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.18, 145.04, 138.74, 135.31, 133.94, 133.75, 130.98, 129.96, 128.67, 128.56, 127.35, 126.89, 126.76, 125.39, 121.27, 113.58, 108.98, 56.77, 52.41, 21.60. HRMS (ESI) calcd. for $C_{24}H_{22}NO_4S$ $[M+H]^+$: 420.1264, found: 420.1268.



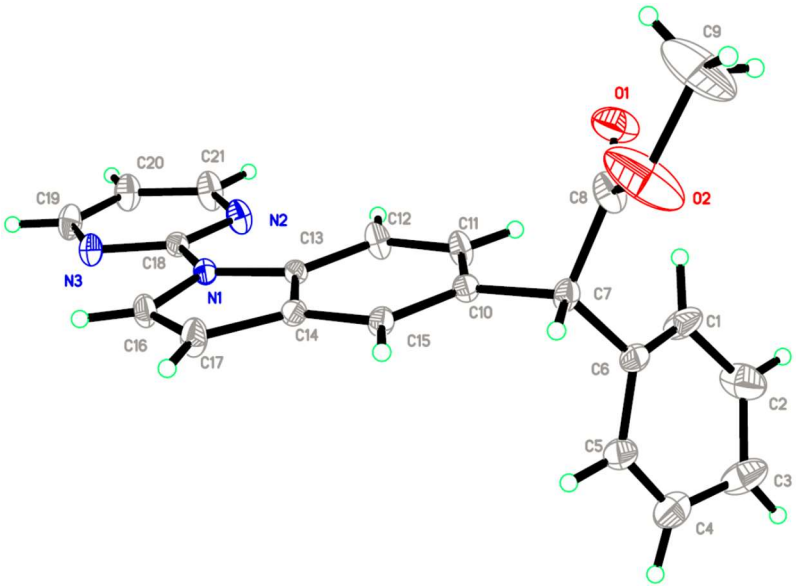
methyl 2-phenyl-2-(1-(pyrimidin-2-yl)-1H-indol-5-yl)acetate (4v):

A white solid (48 mg, 70%), mp: 114-116 ºC.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.7 Hz, 1H), 8.68 (d, *J* = 4.8 Hz, 2H), 8.25 (d, *J* = 3.7 Hz, 1H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.40-7.21 (m, 6H), 7.04 (t, *J* = 4.8 Hz, 1H), 6.65 (dd, *J* = 3.7, 0.5 Hz, 1H), 5.18 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.48, 158.16, 157.68, 139.27, 134.57, 132.35, 131.56, 128.66, 128.54, 127.14, 126.33, 124.44, 120.73, 116.39, 116.22, 107.01, 56.95, 52.33. HRMS (ESI) calcd. for $C_{21}H_{18}N_3O_2$ $[M+H]^+$: 344.1394, found: 344.1397.

X-ray structure of 4v

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1575768, **4v**). The data can be obtained free of charge via the internet at www.ccdc.cam.ac.uk/data_request/cif.



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[1] (a) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063. (b) Sambasivan, R.; Ball, Z. T. *J. Am. Chem. Soc.* **2010**, *132*, 9289. (c) Qu, Z.; Shi, W.; Wang, J. *J. Org. Chem.* **2001**, *66*, 8139. (d) Gratia, S.; Mosesohn, K.; Diver, S. T. *Org. Lett.* **2016**, *18*, 5320. (e) Ma, M.; Li, C.; Peng, L.; Xie, F.; Zhang, X.; Wang, J. *Tetrahedron Lett.* **2005**, *46*, 3927.

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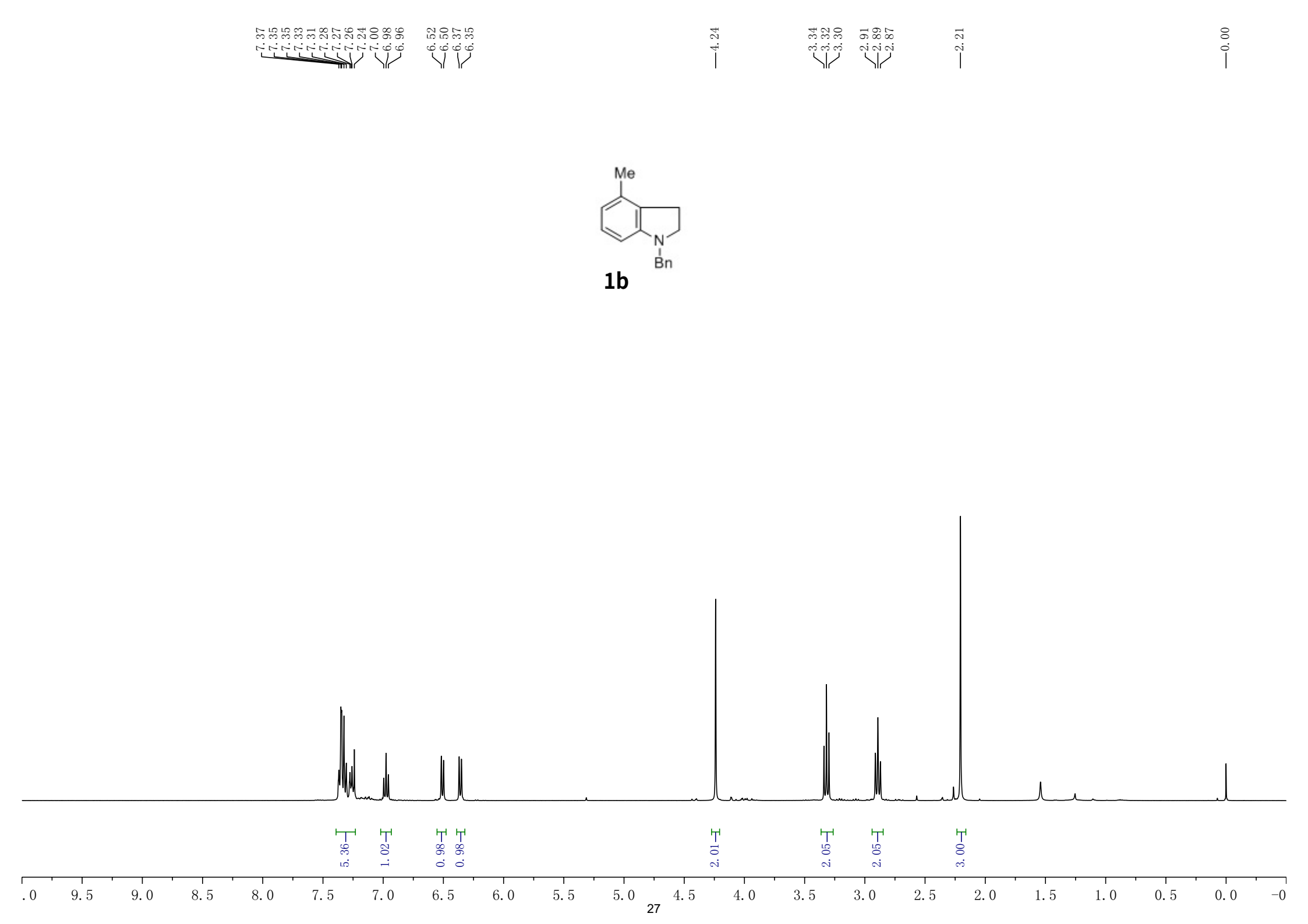
[3] (a) Jiao, L.-Y.; Oestreich, M. *Org. Lett.* **2013**, *15*, 5374. (b) Kojima, M.; Kanai, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 12224. (c) Zhao, J.; Xu, J.; Chen, J.; Wang, X.; He, M. *RSC Adv*. **2015**, *5*, 23727. (d) Xie, W.; Li, B.; Wang, B. *J. Org. Chem.* **2016**, *81*, 396.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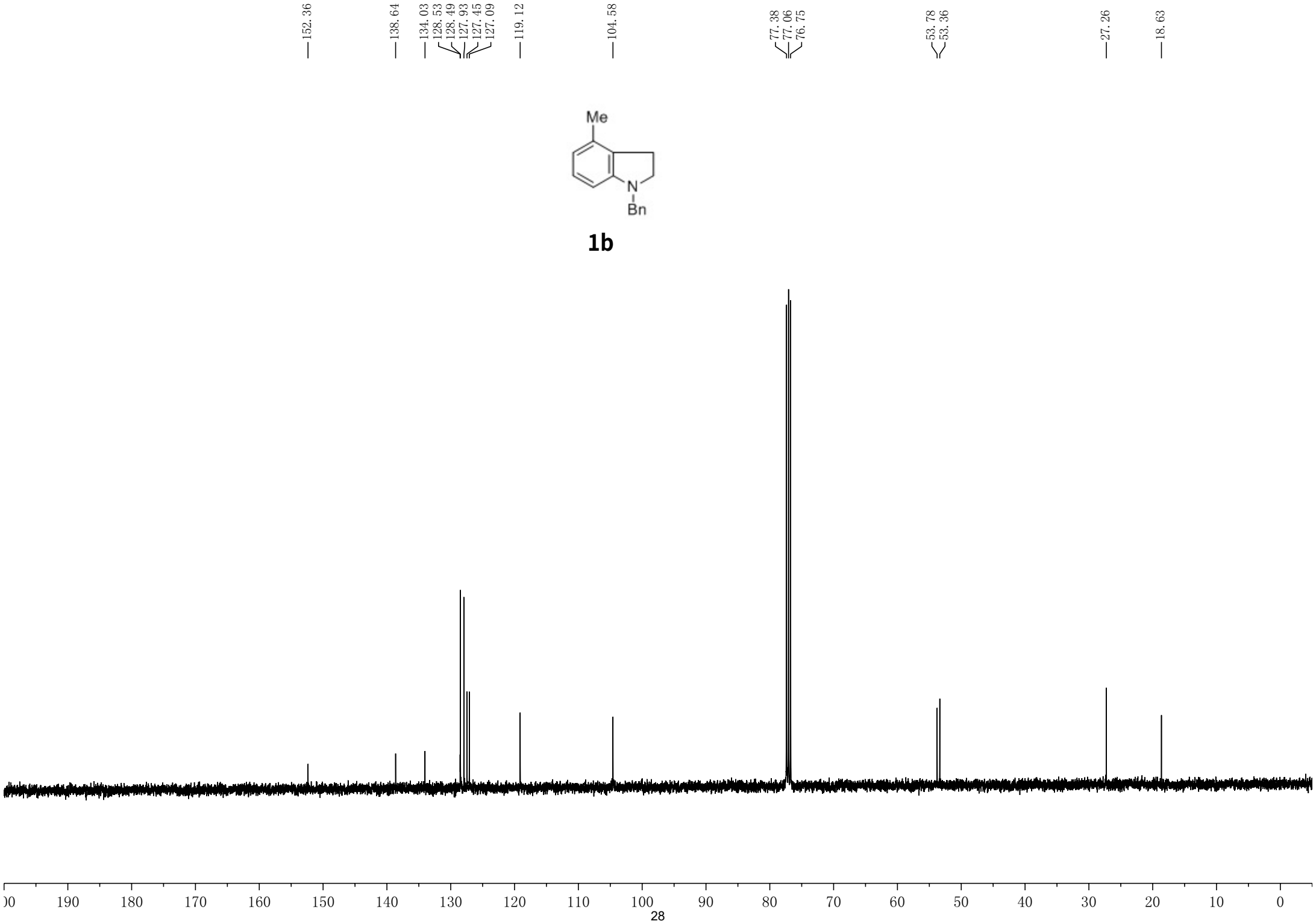
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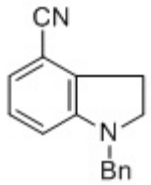
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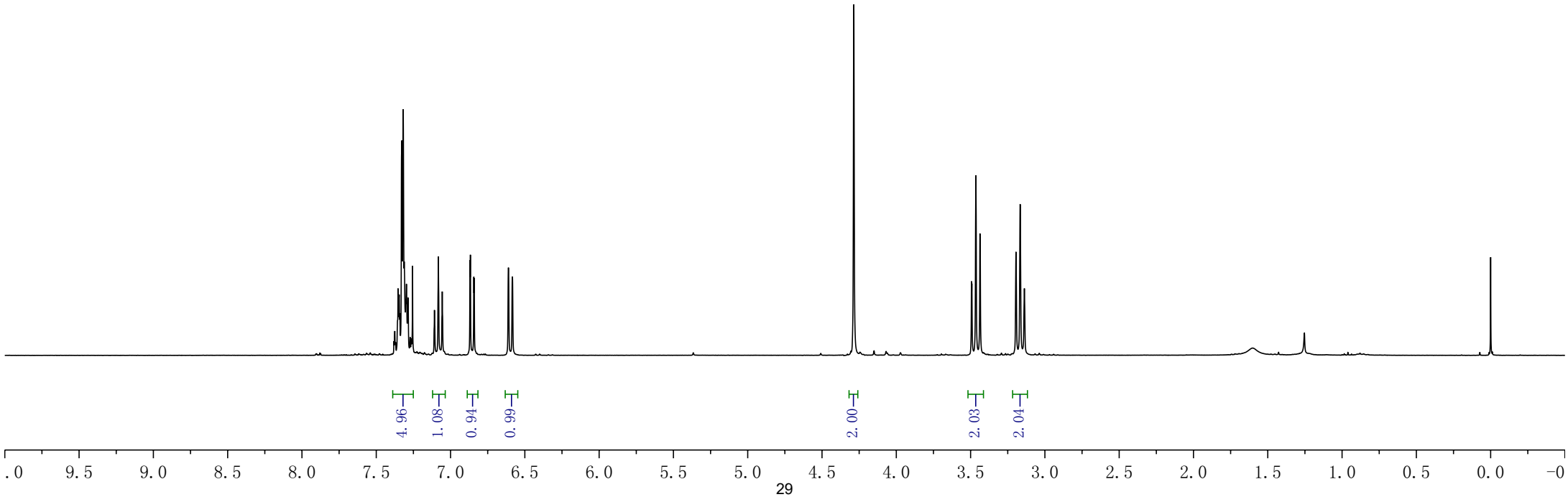
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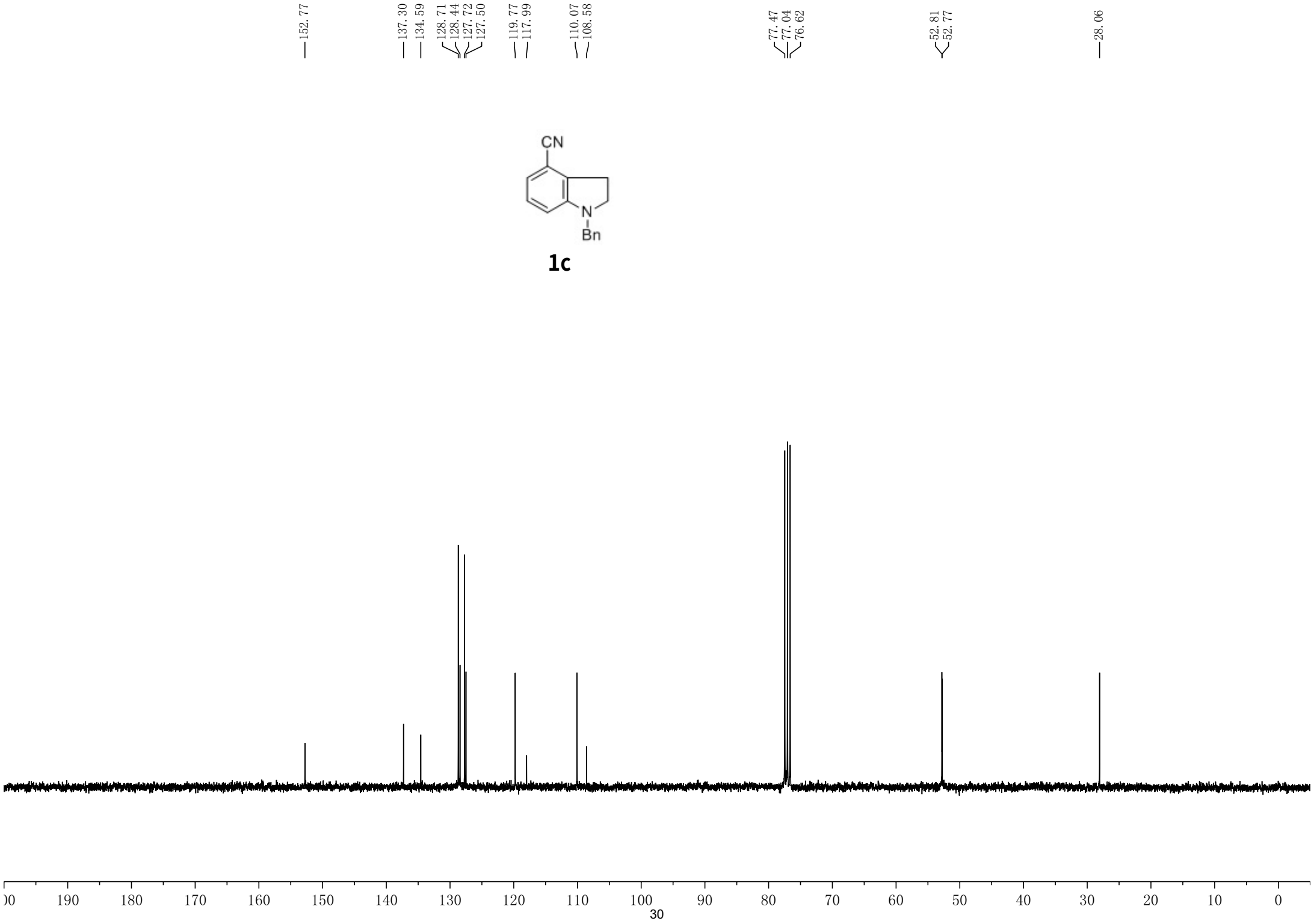
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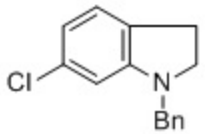
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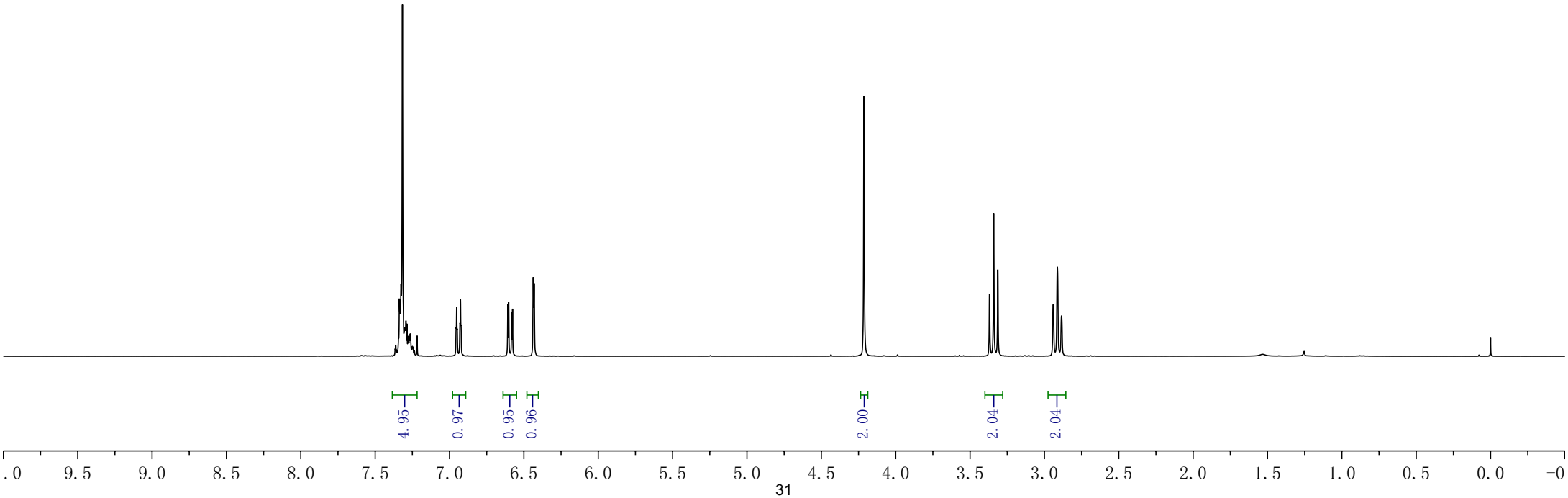
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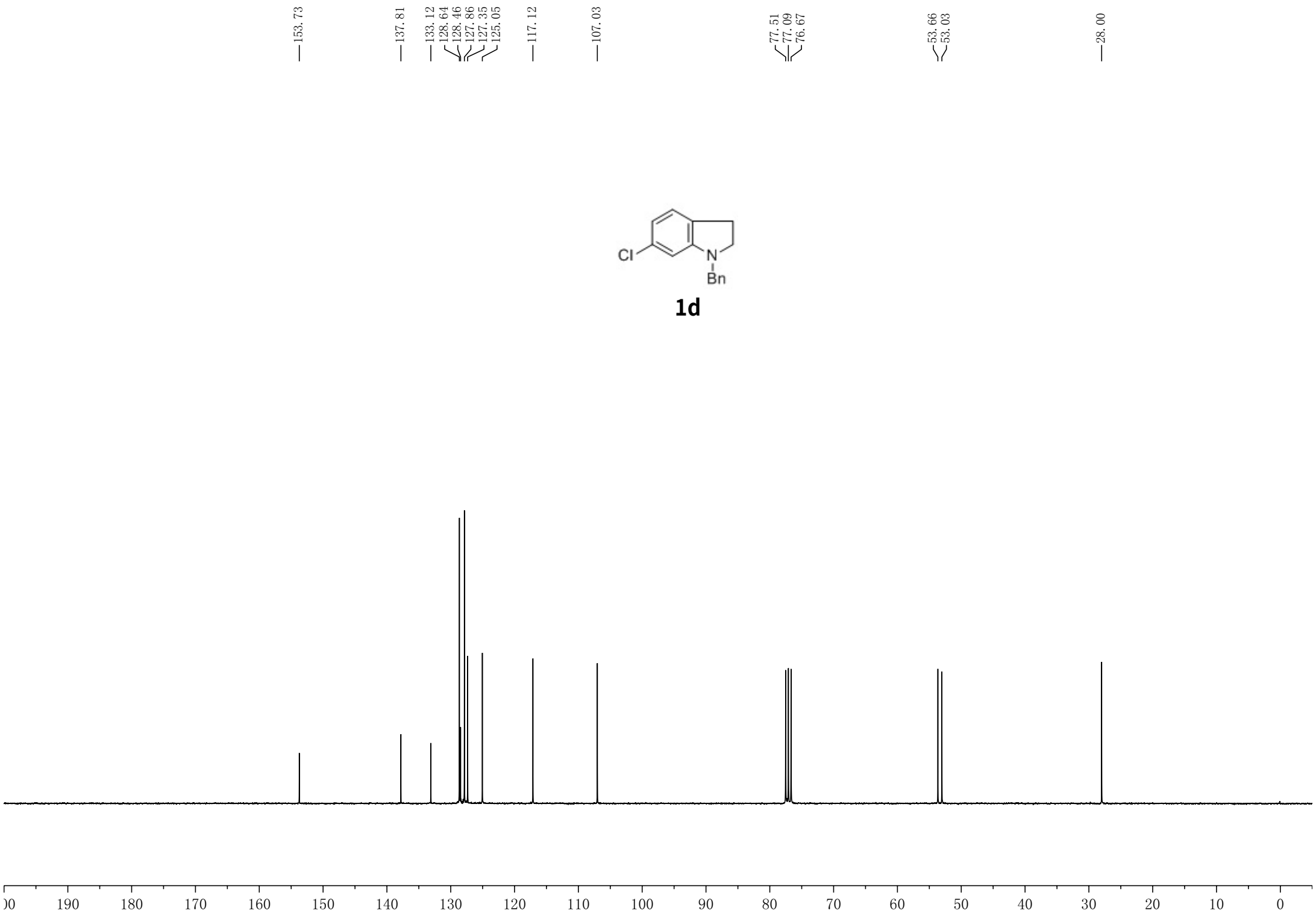
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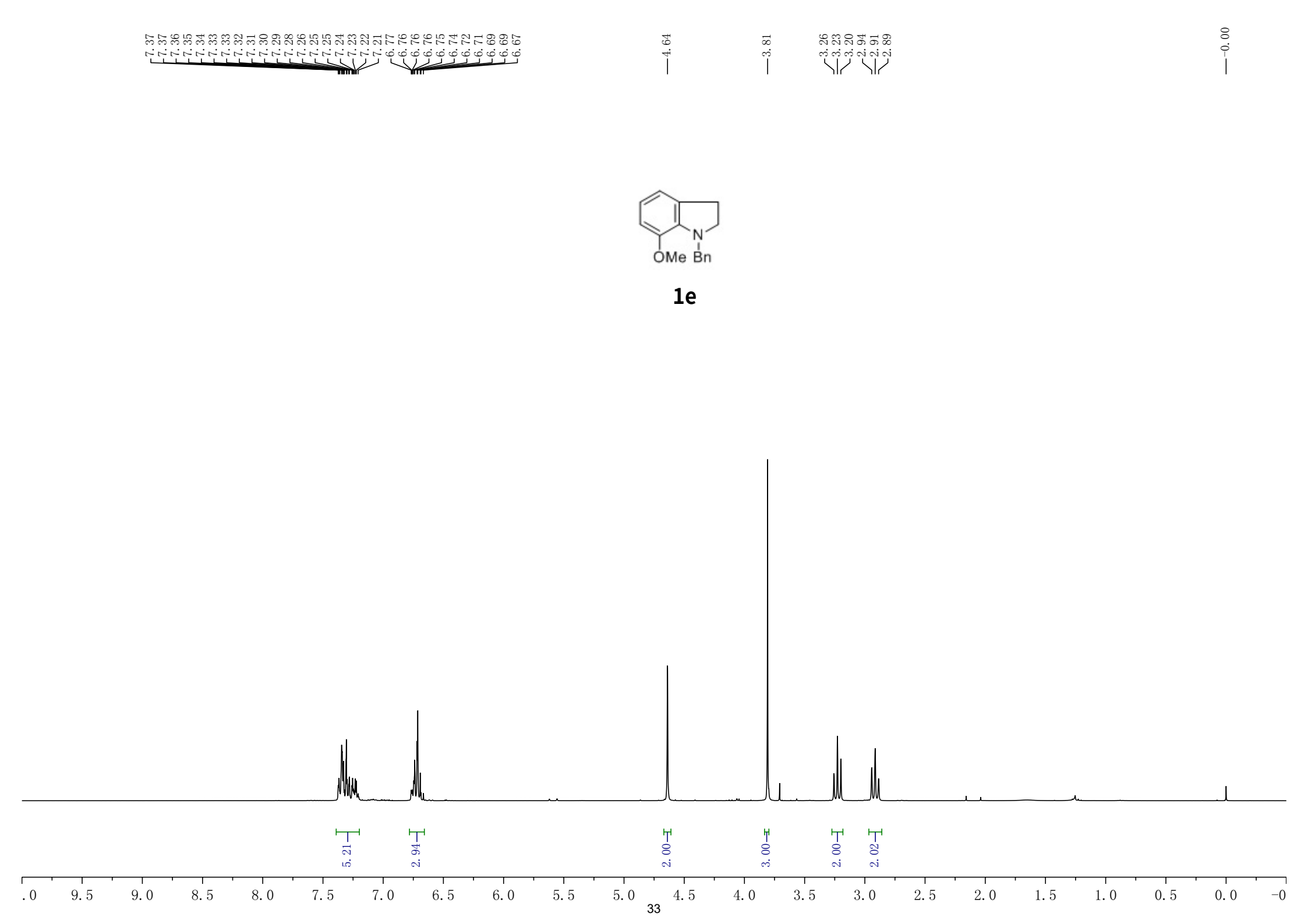
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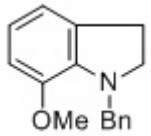

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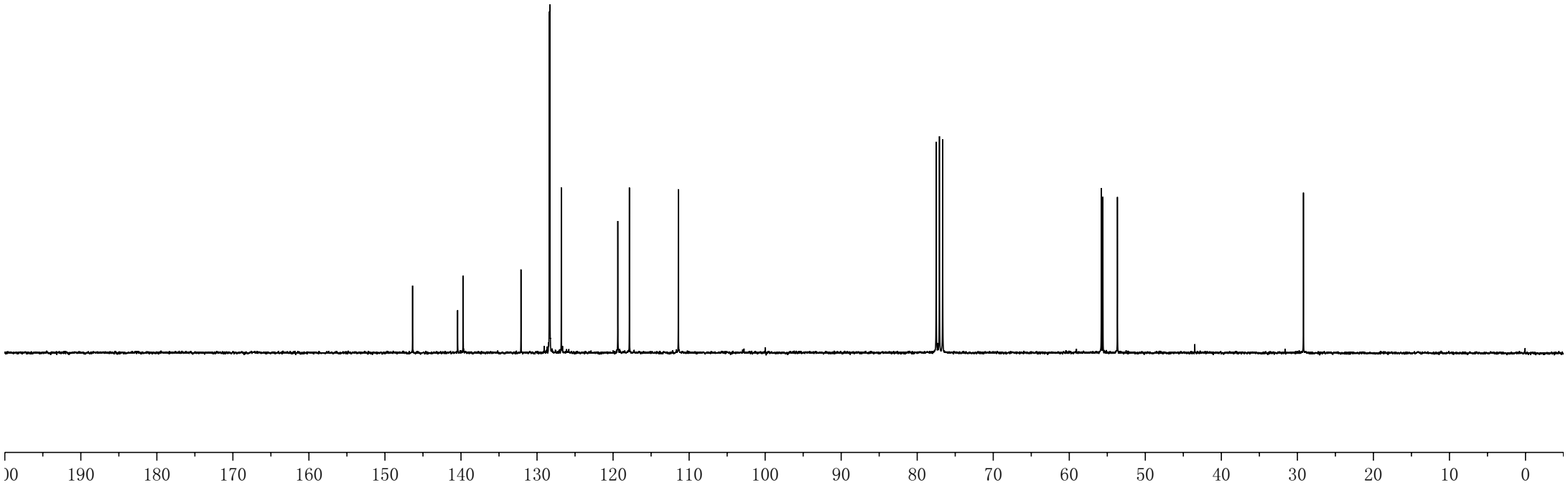

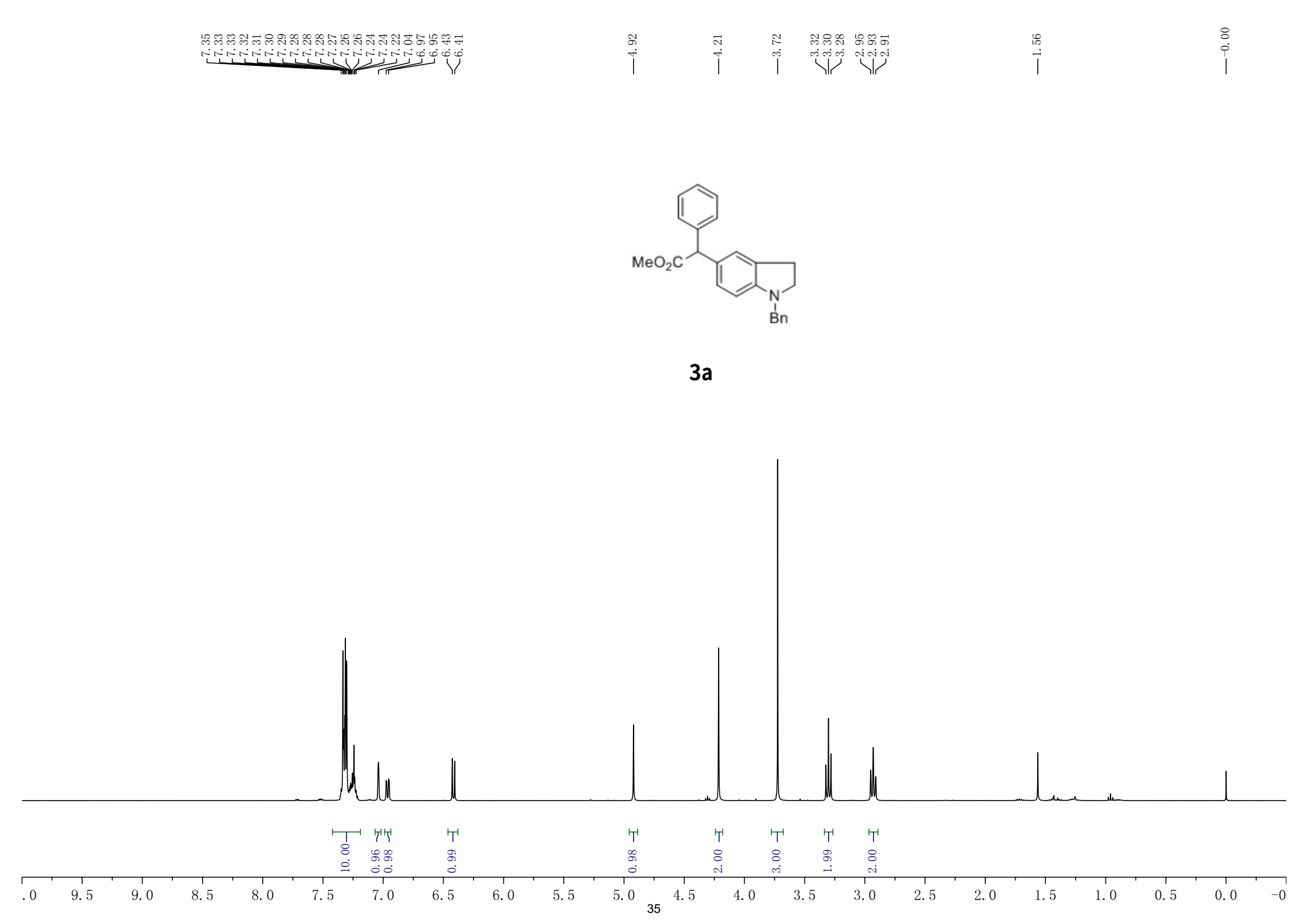
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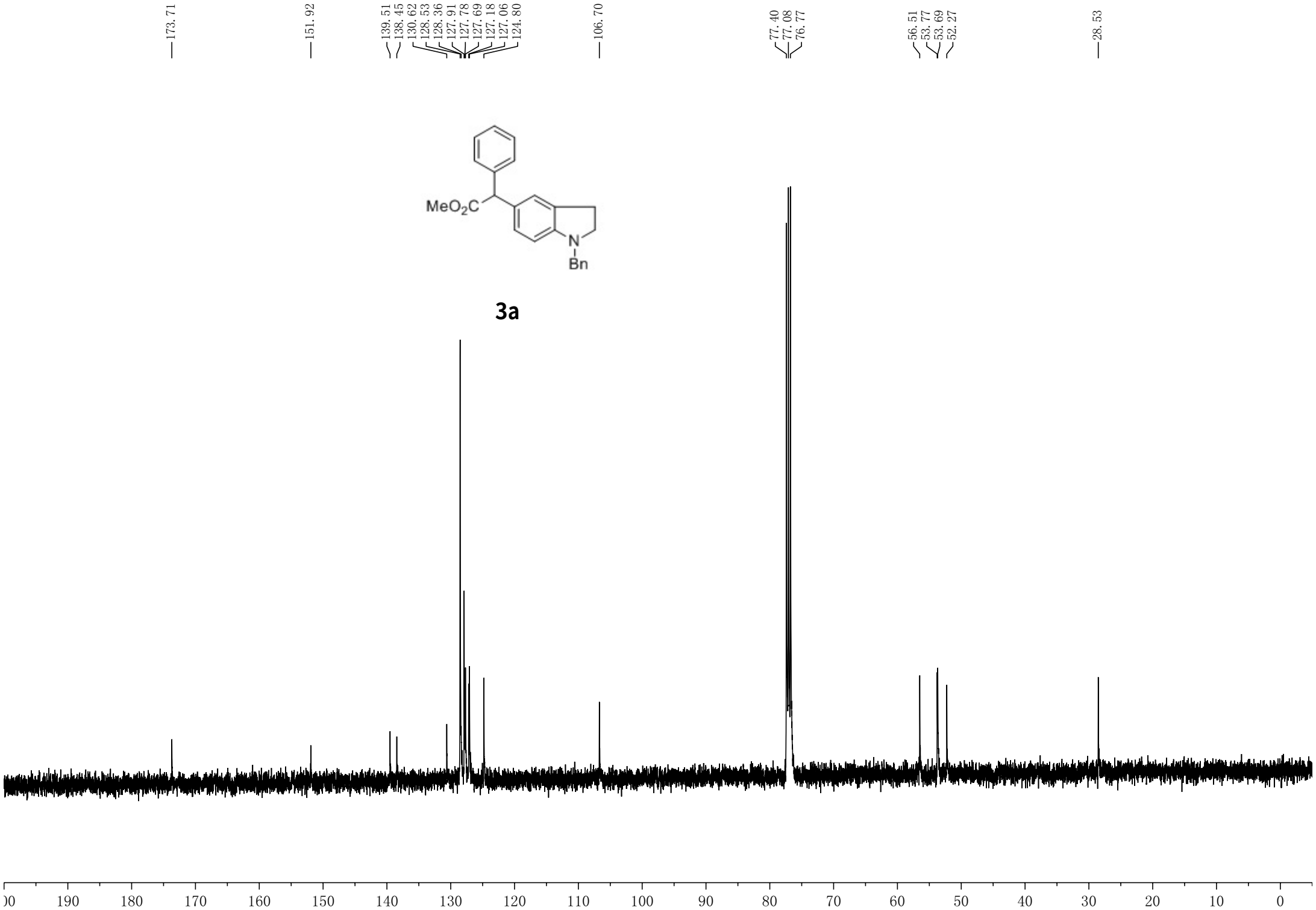
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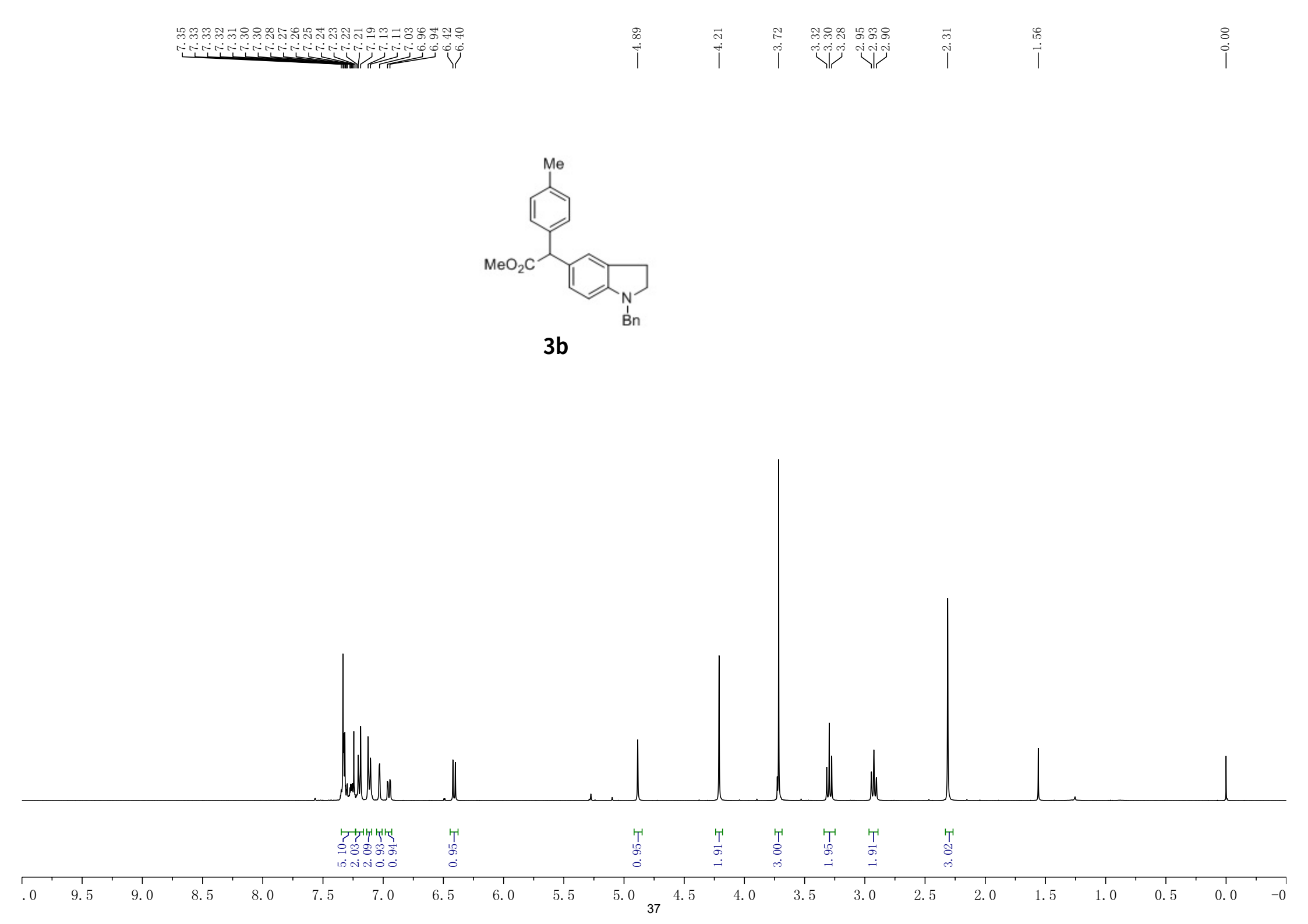
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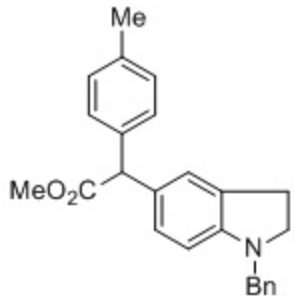

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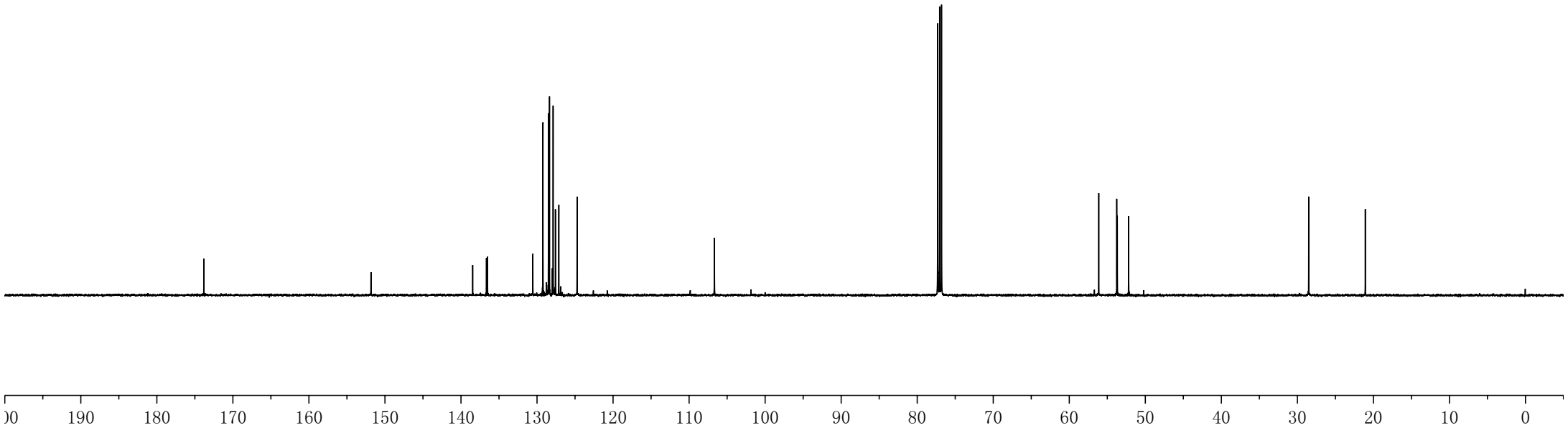

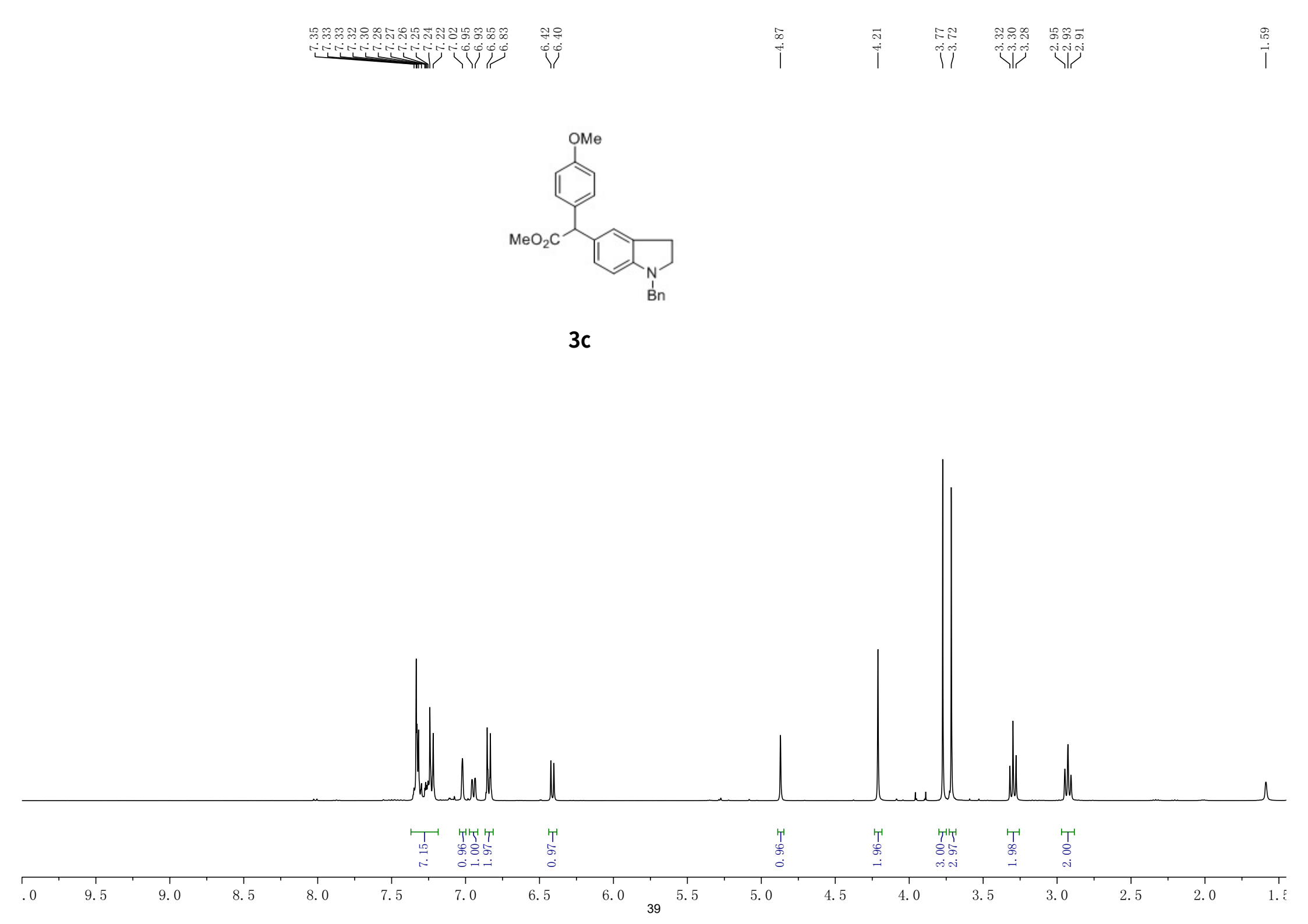
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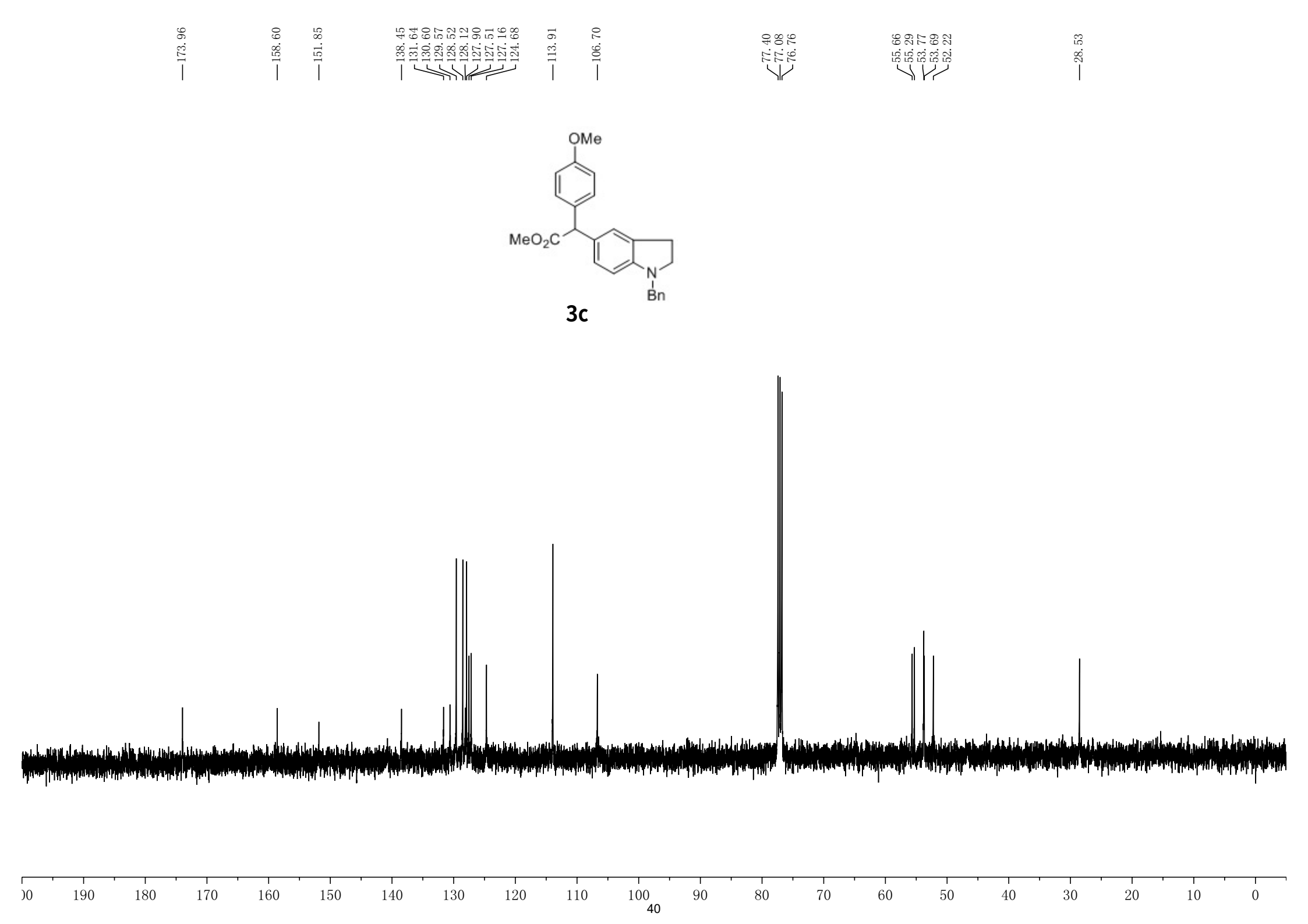
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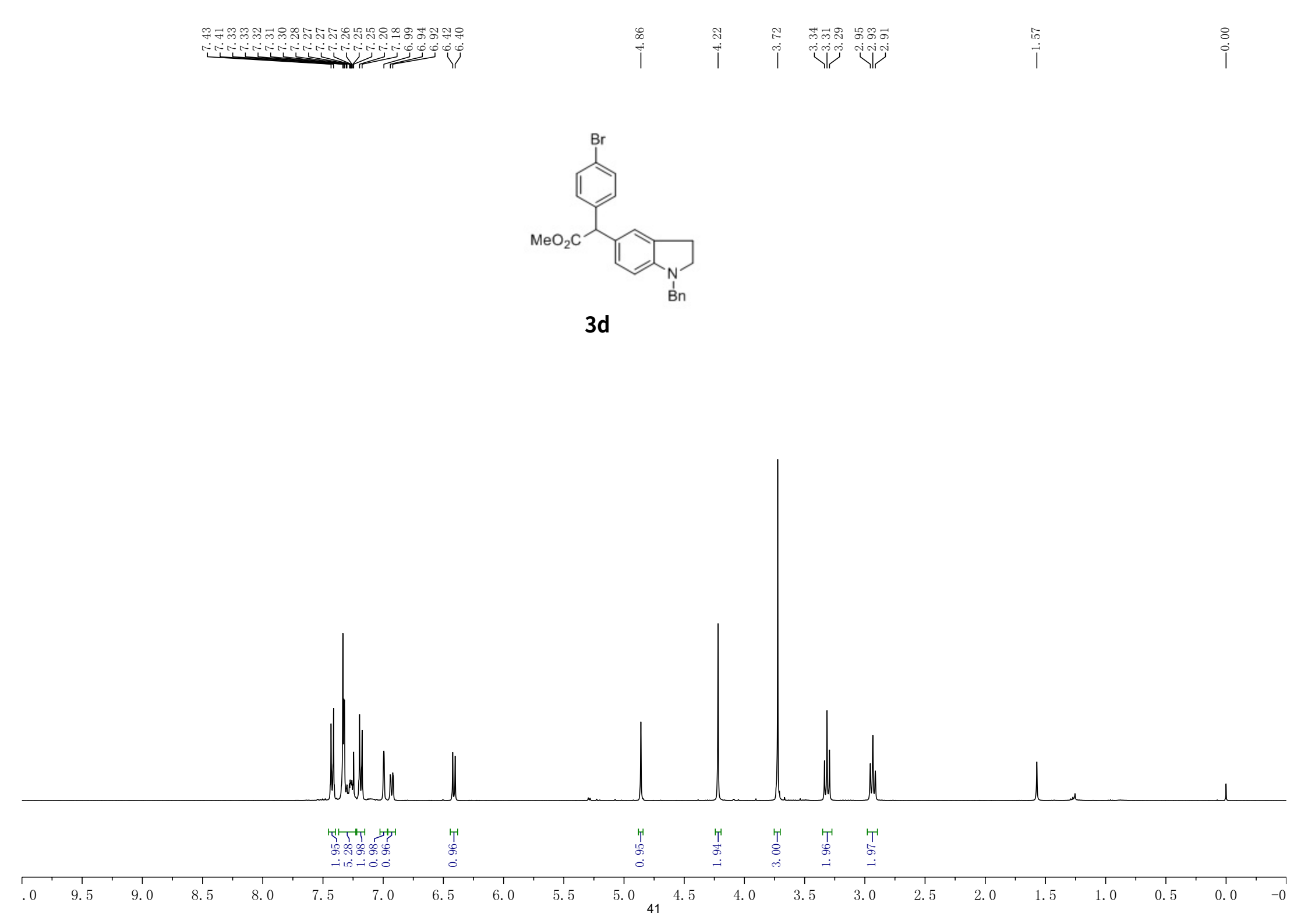
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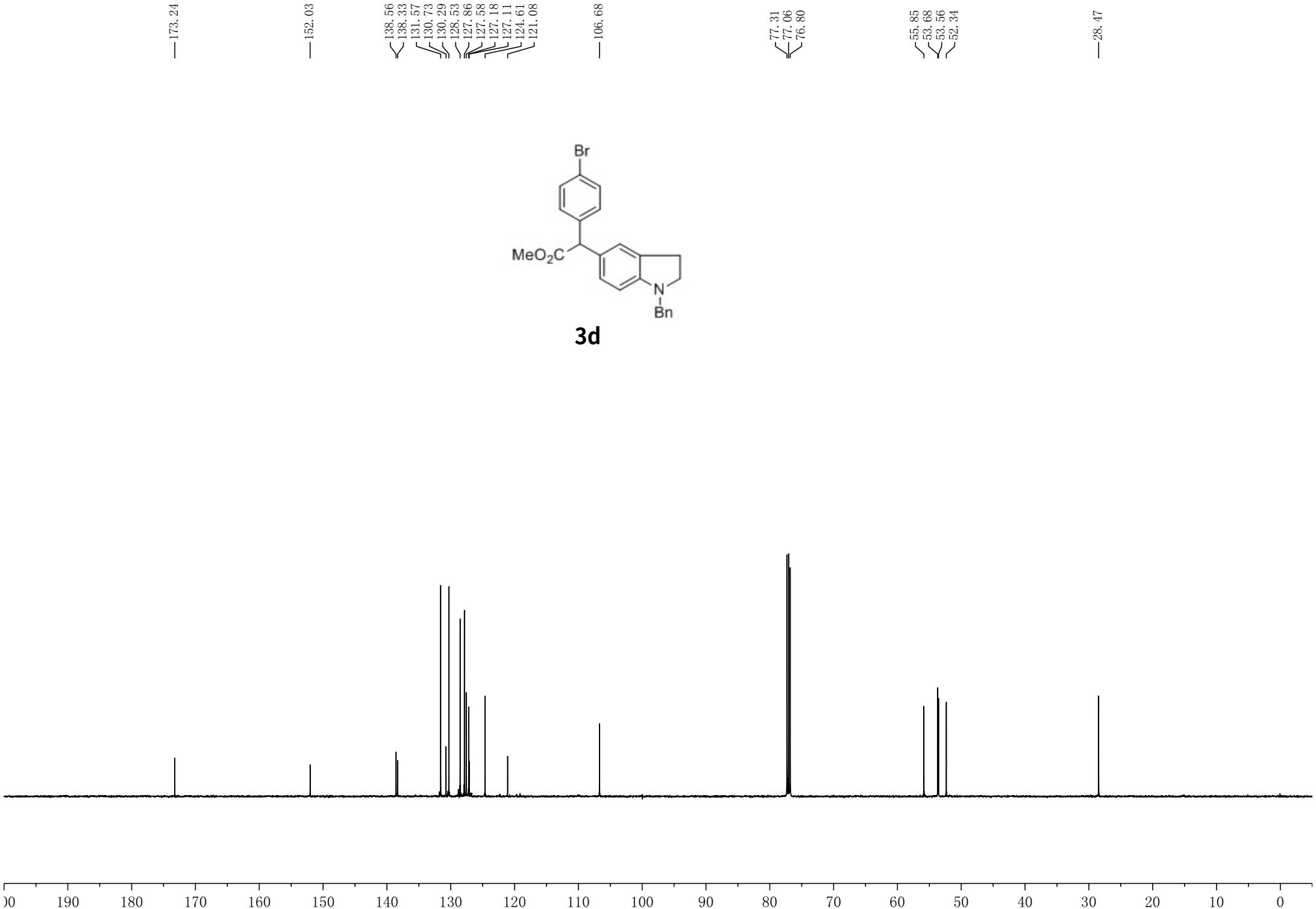
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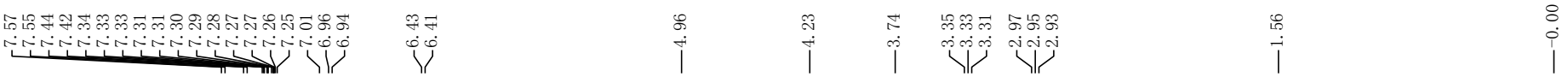
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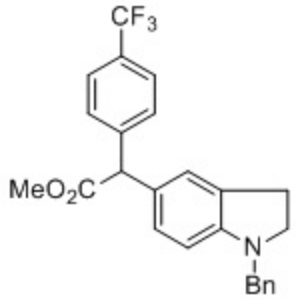
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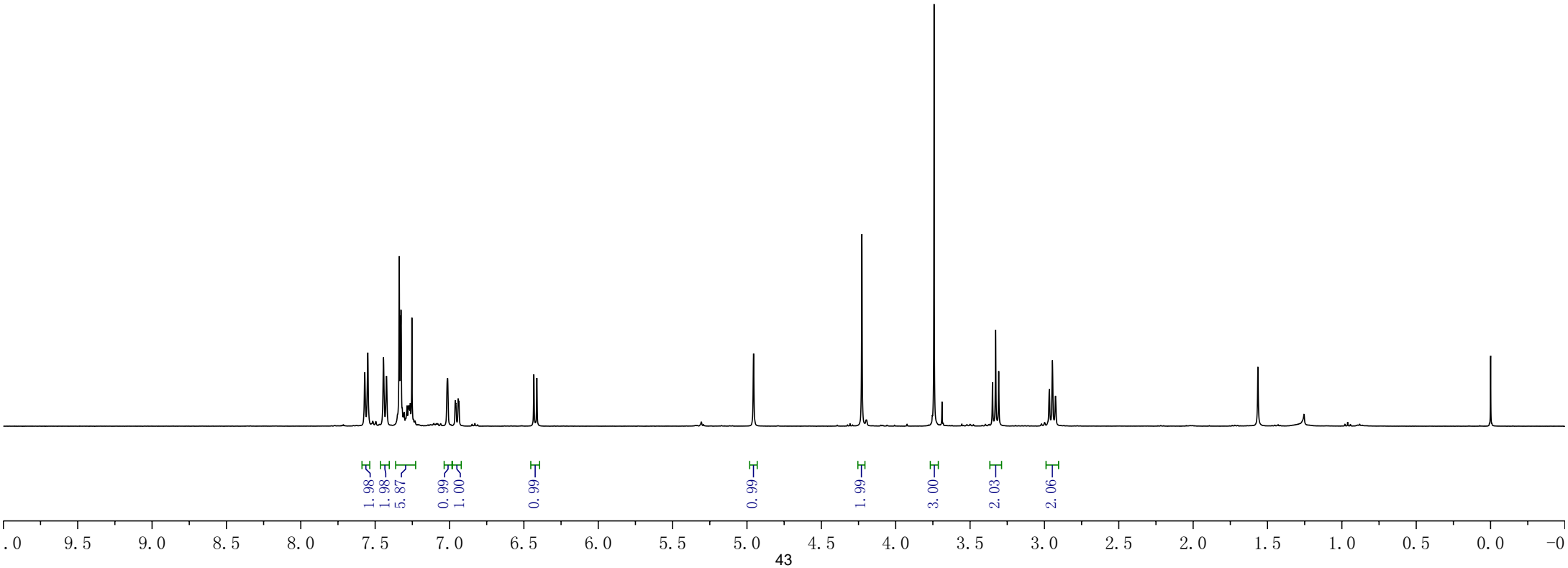
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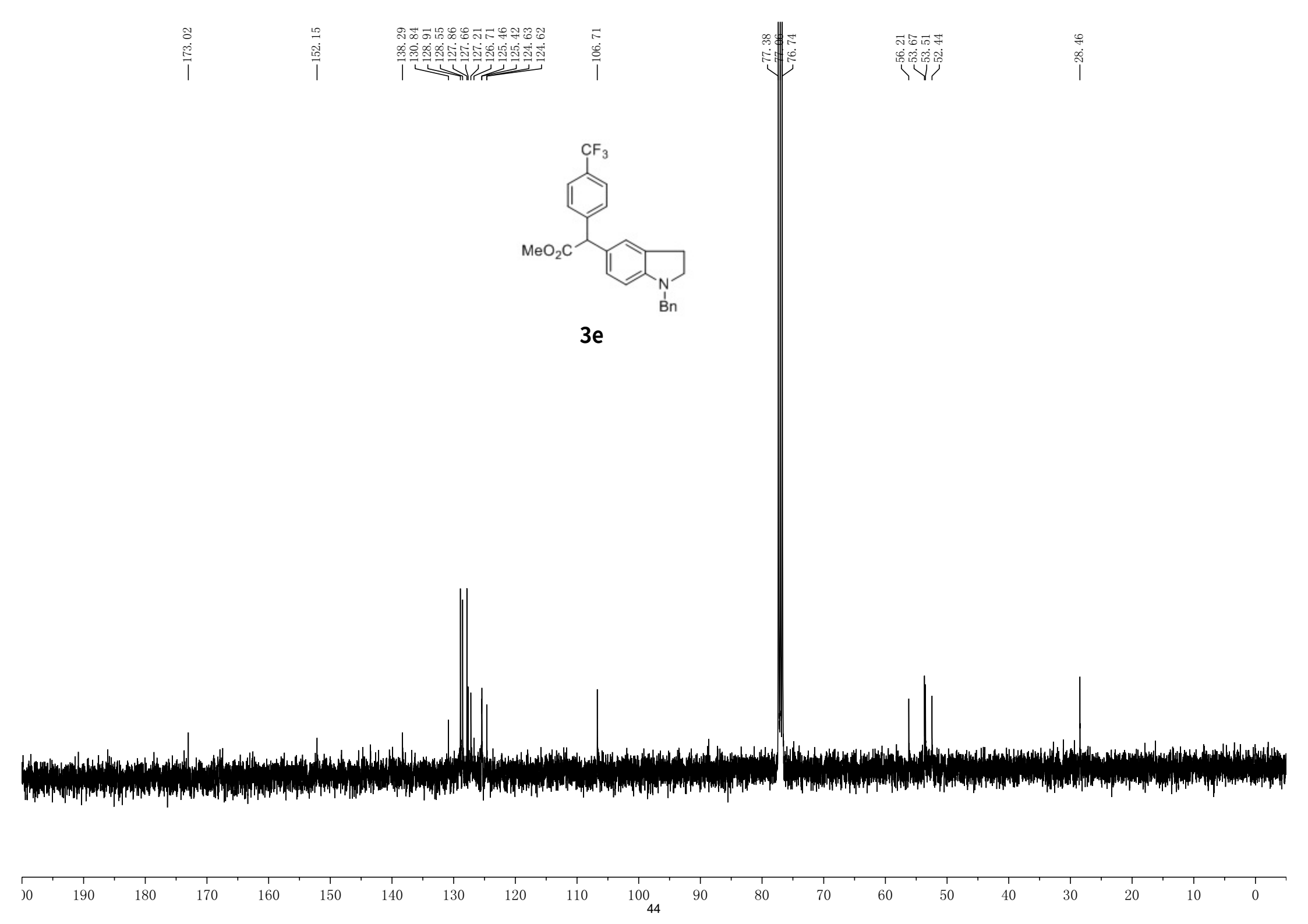
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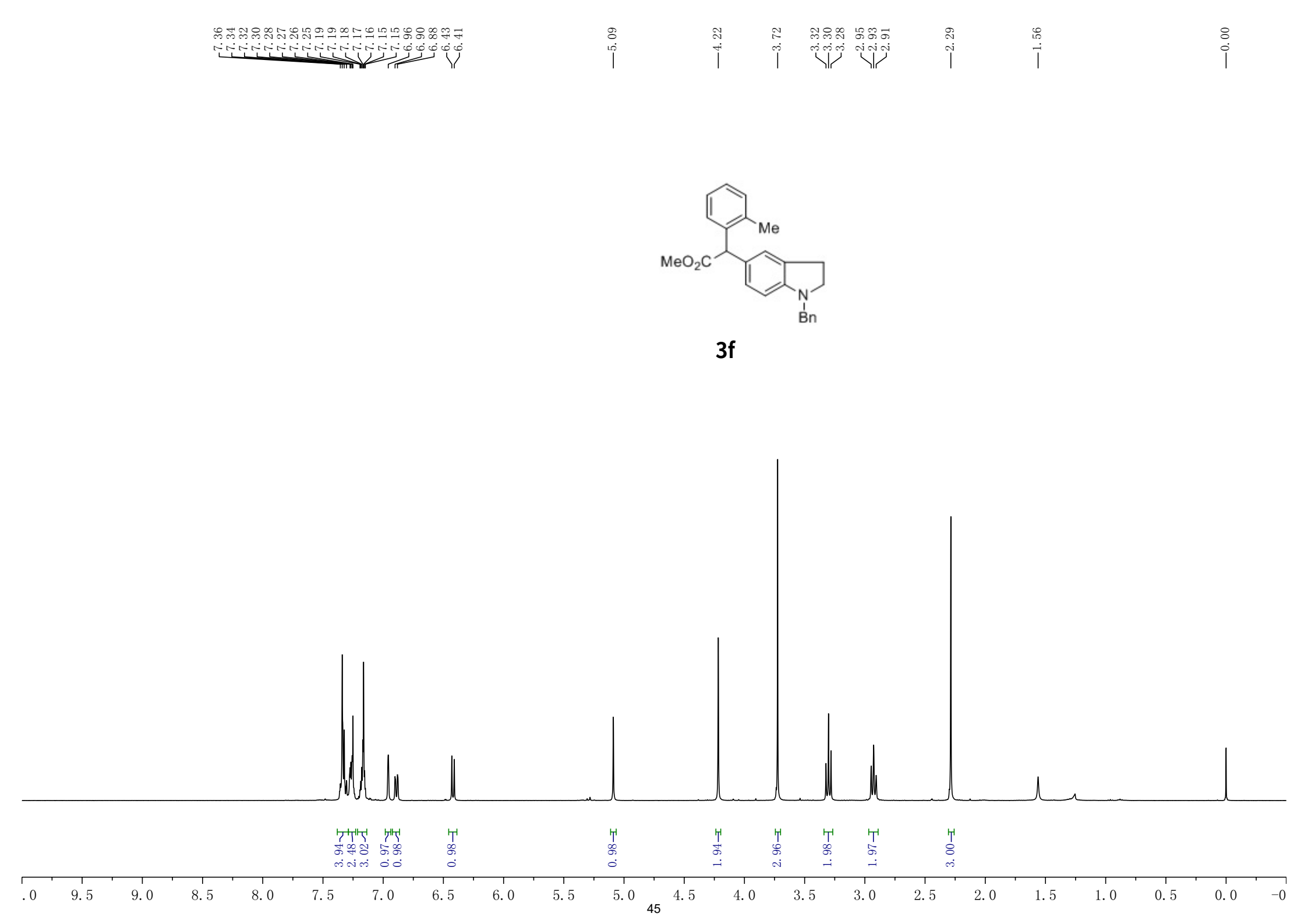
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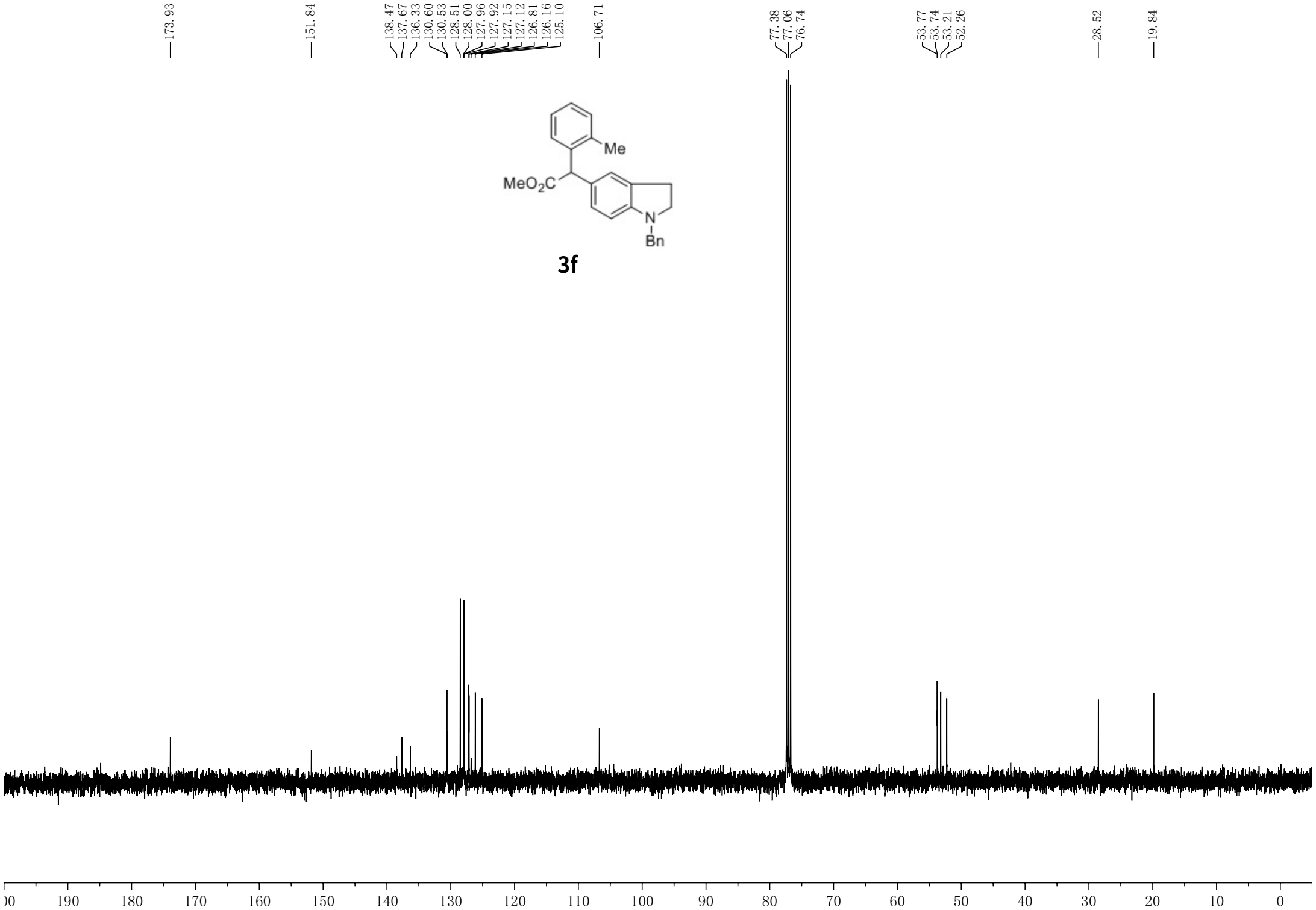
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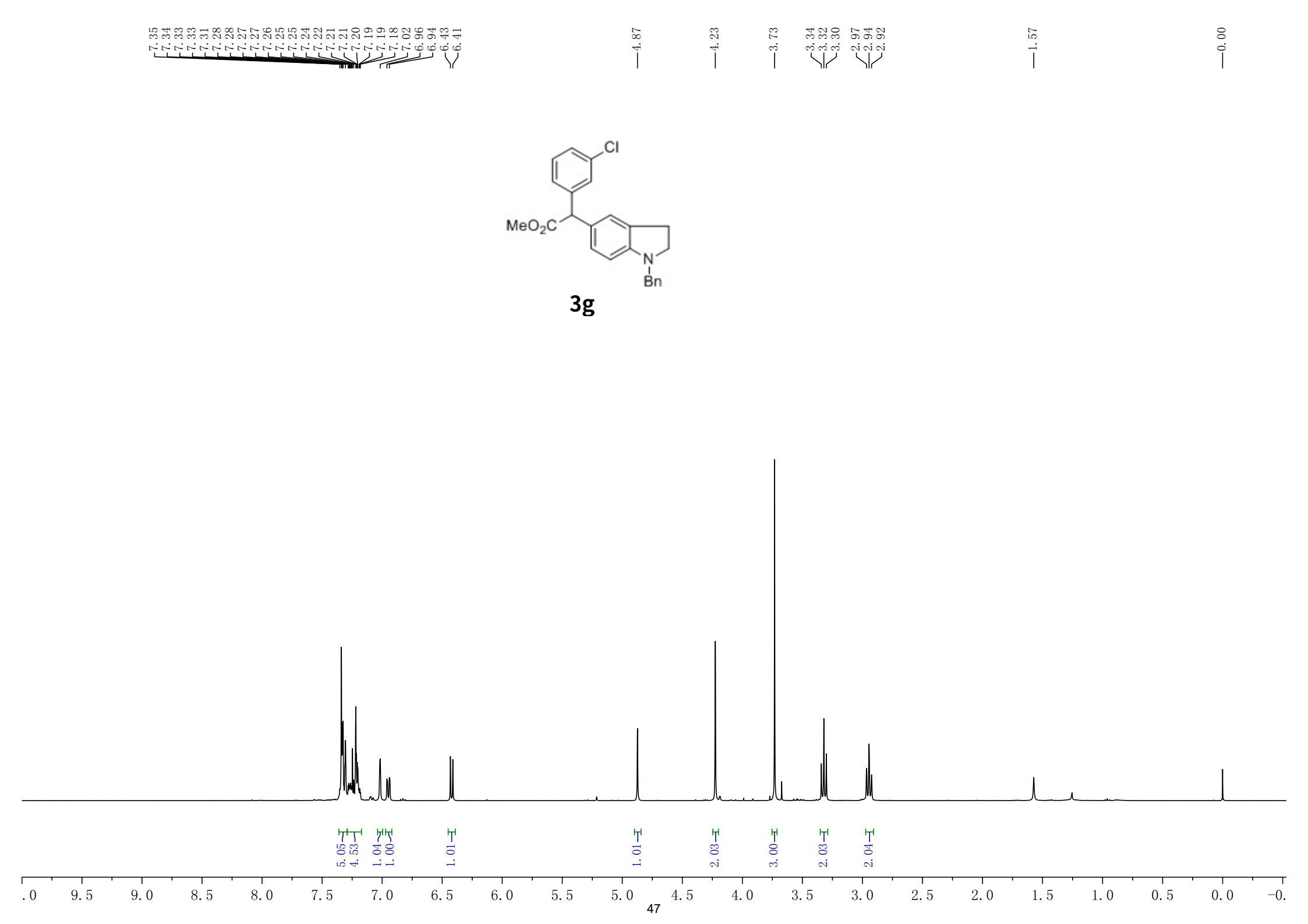
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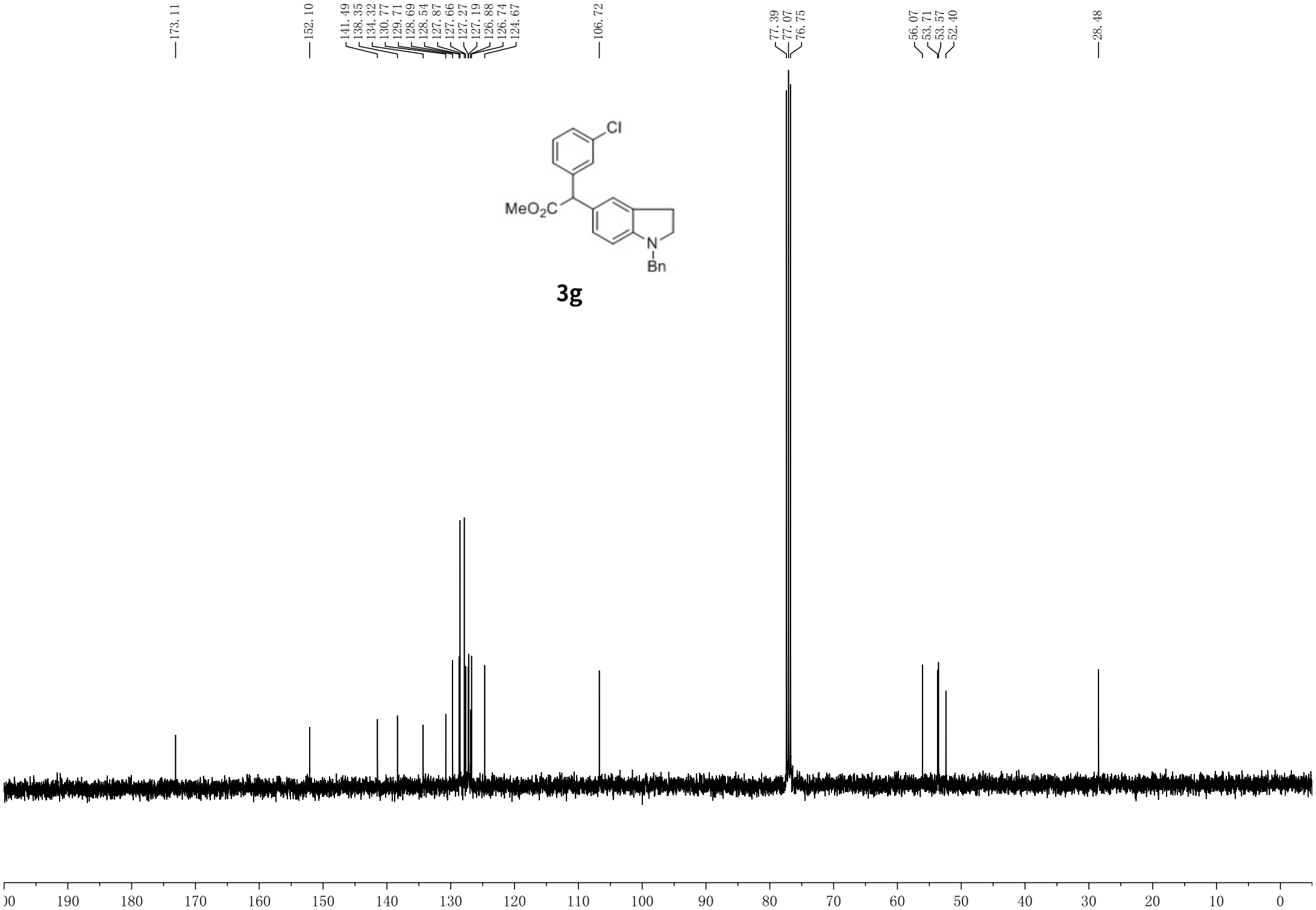
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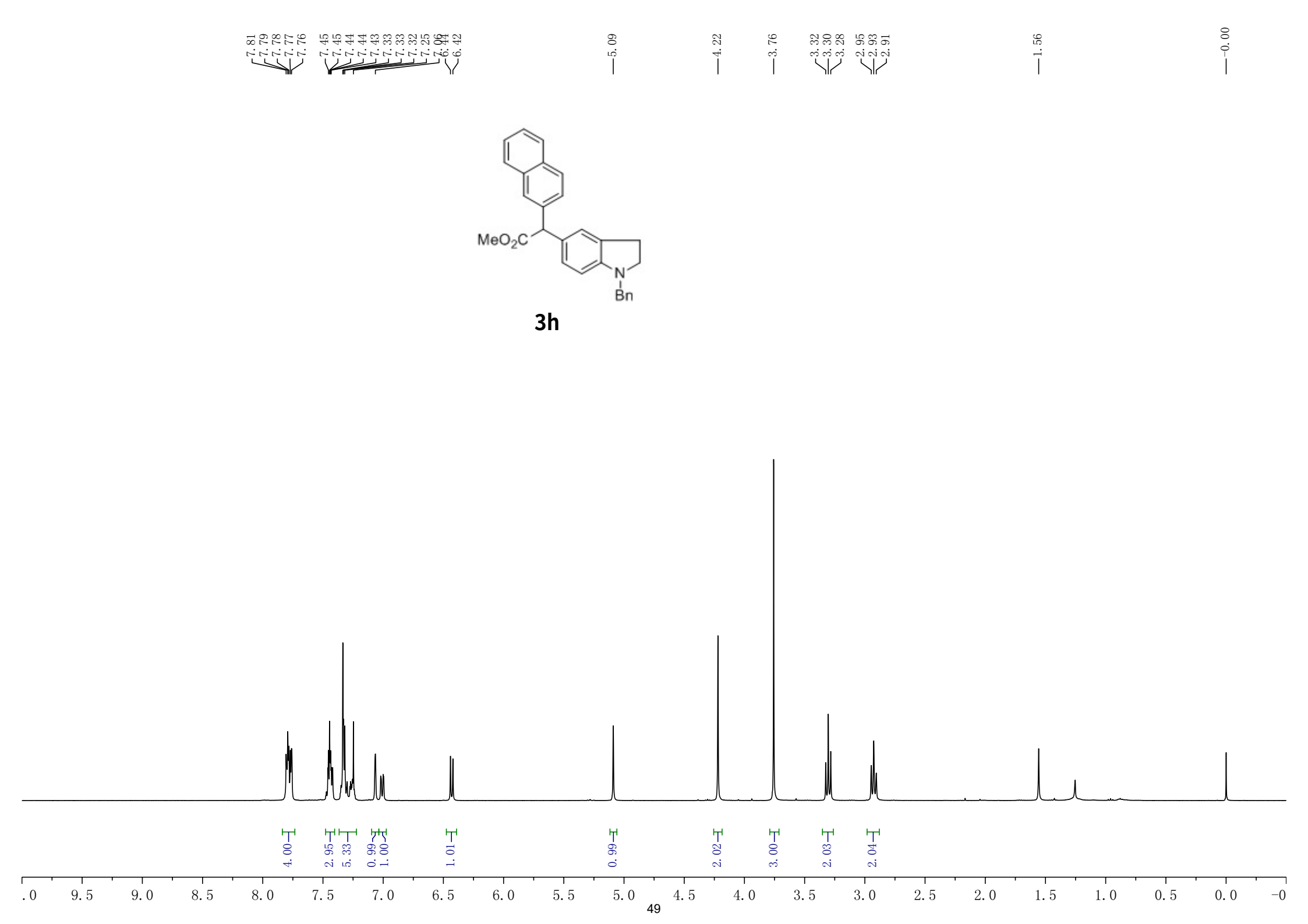
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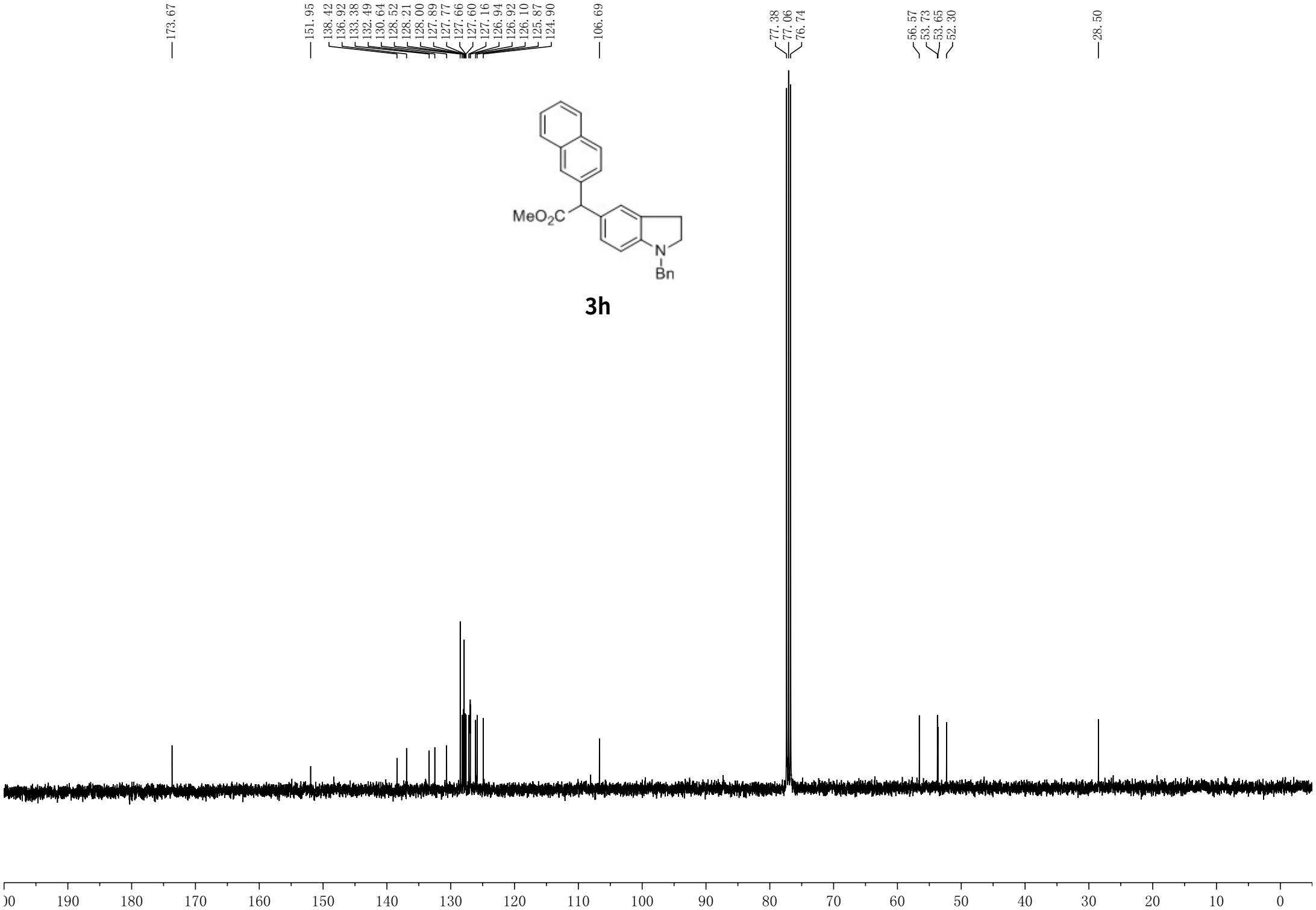
3h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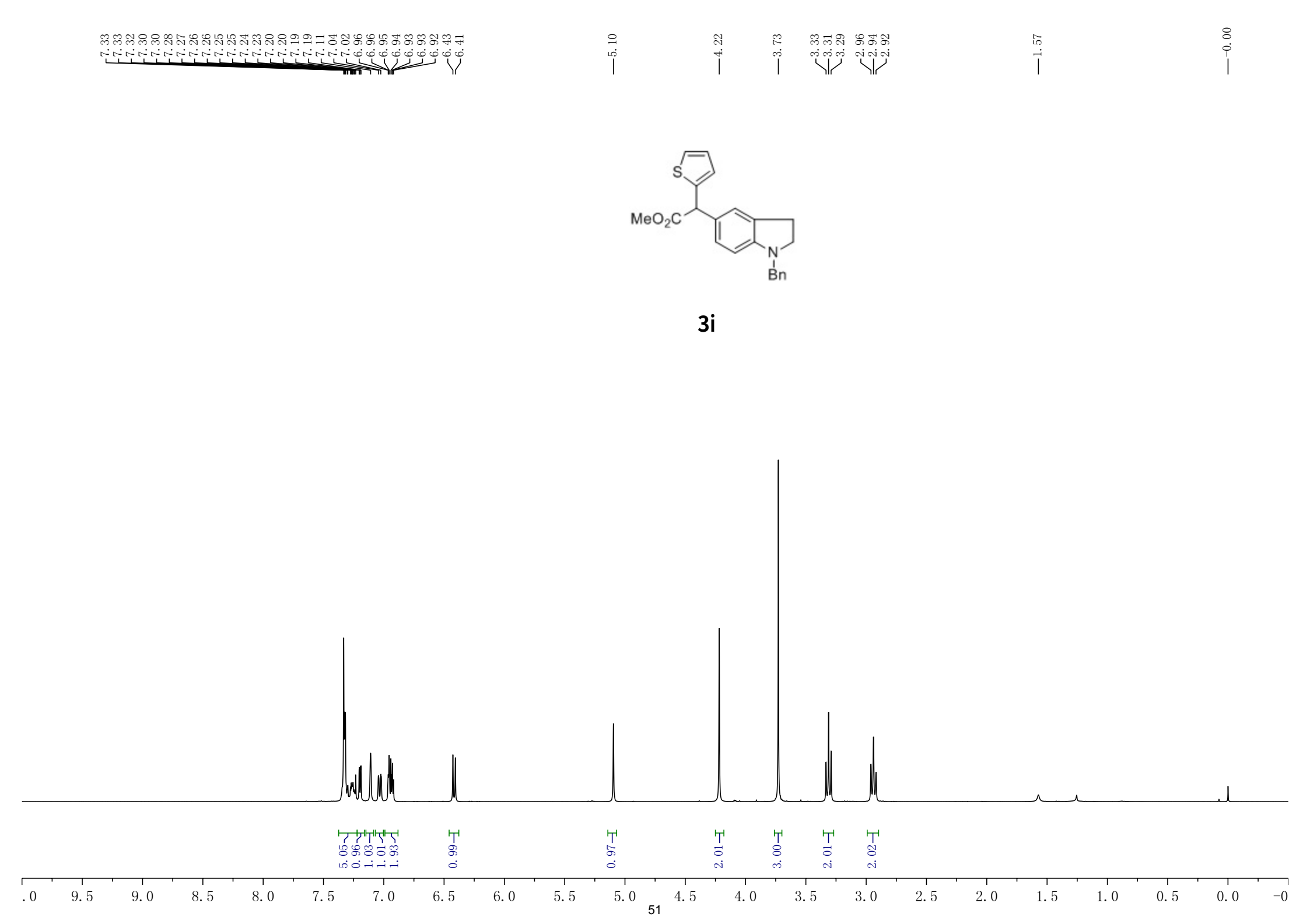
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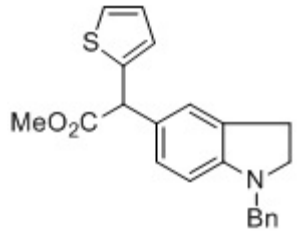

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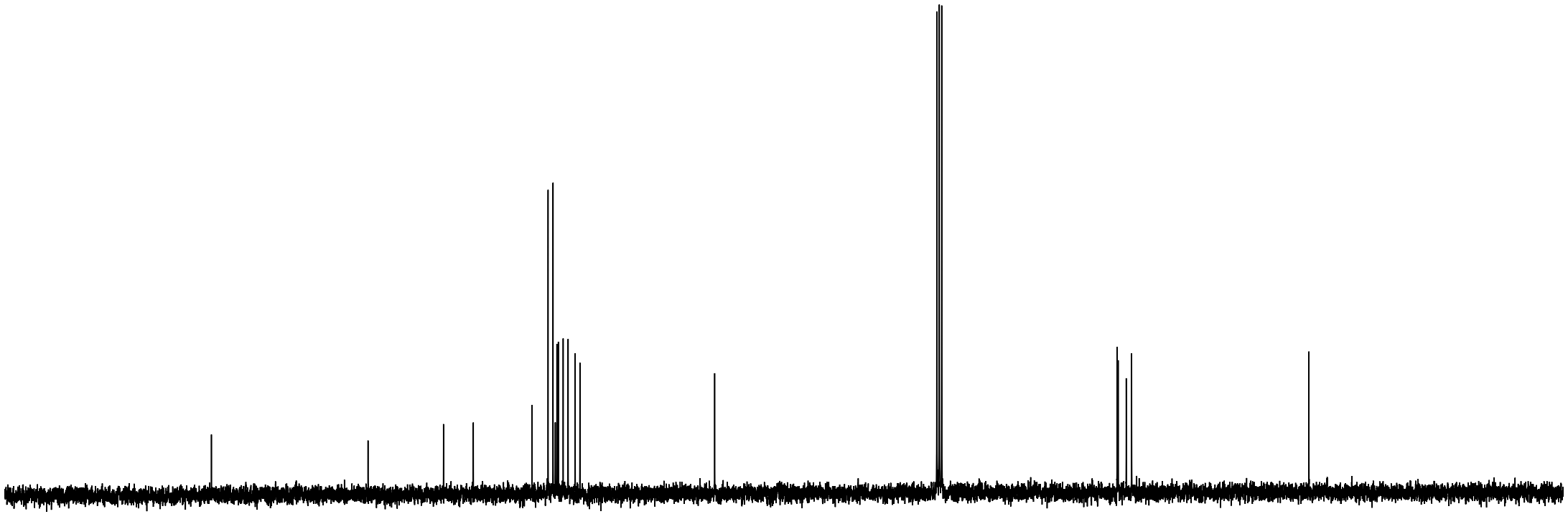

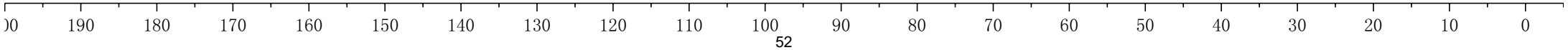

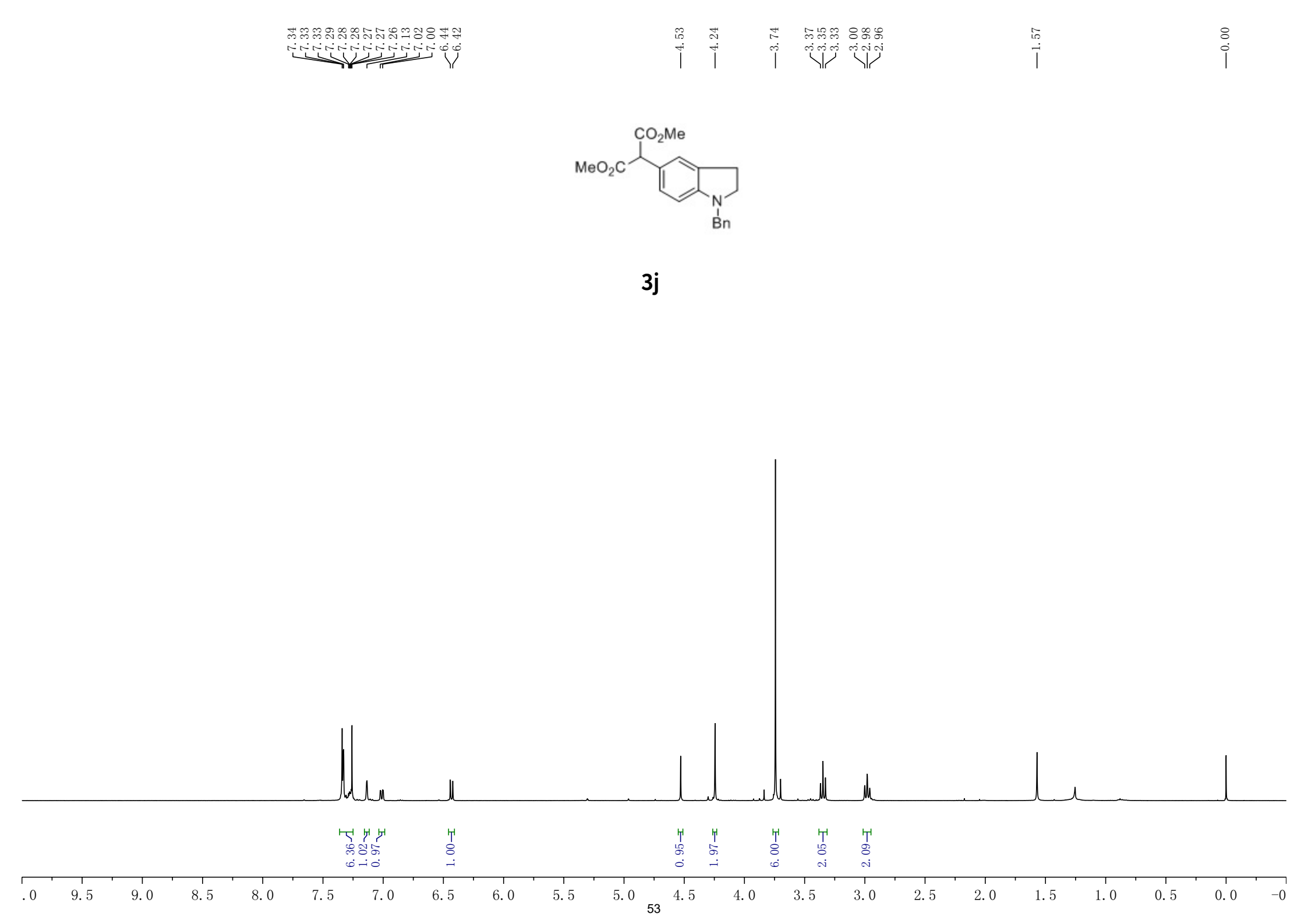
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Bn
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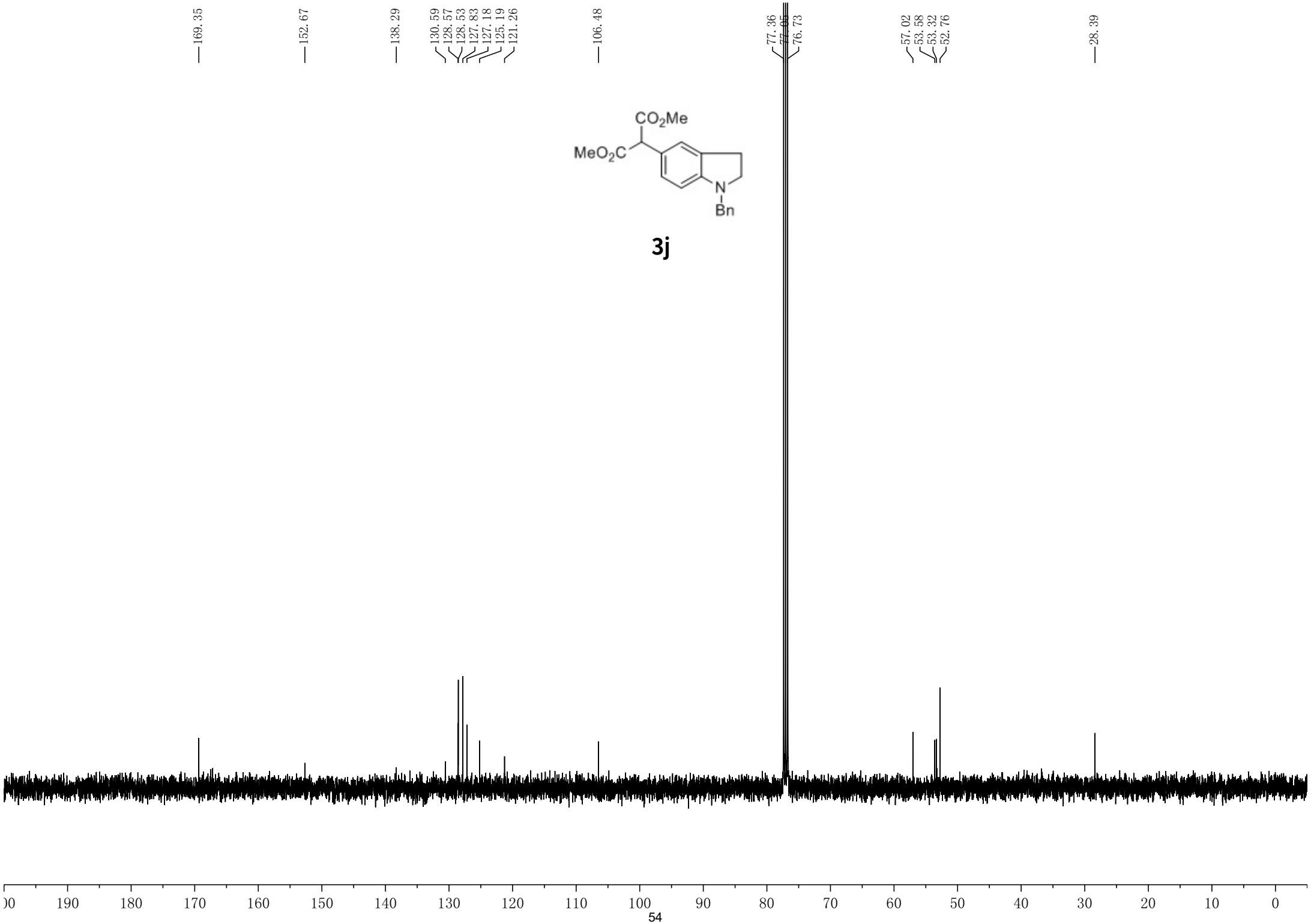
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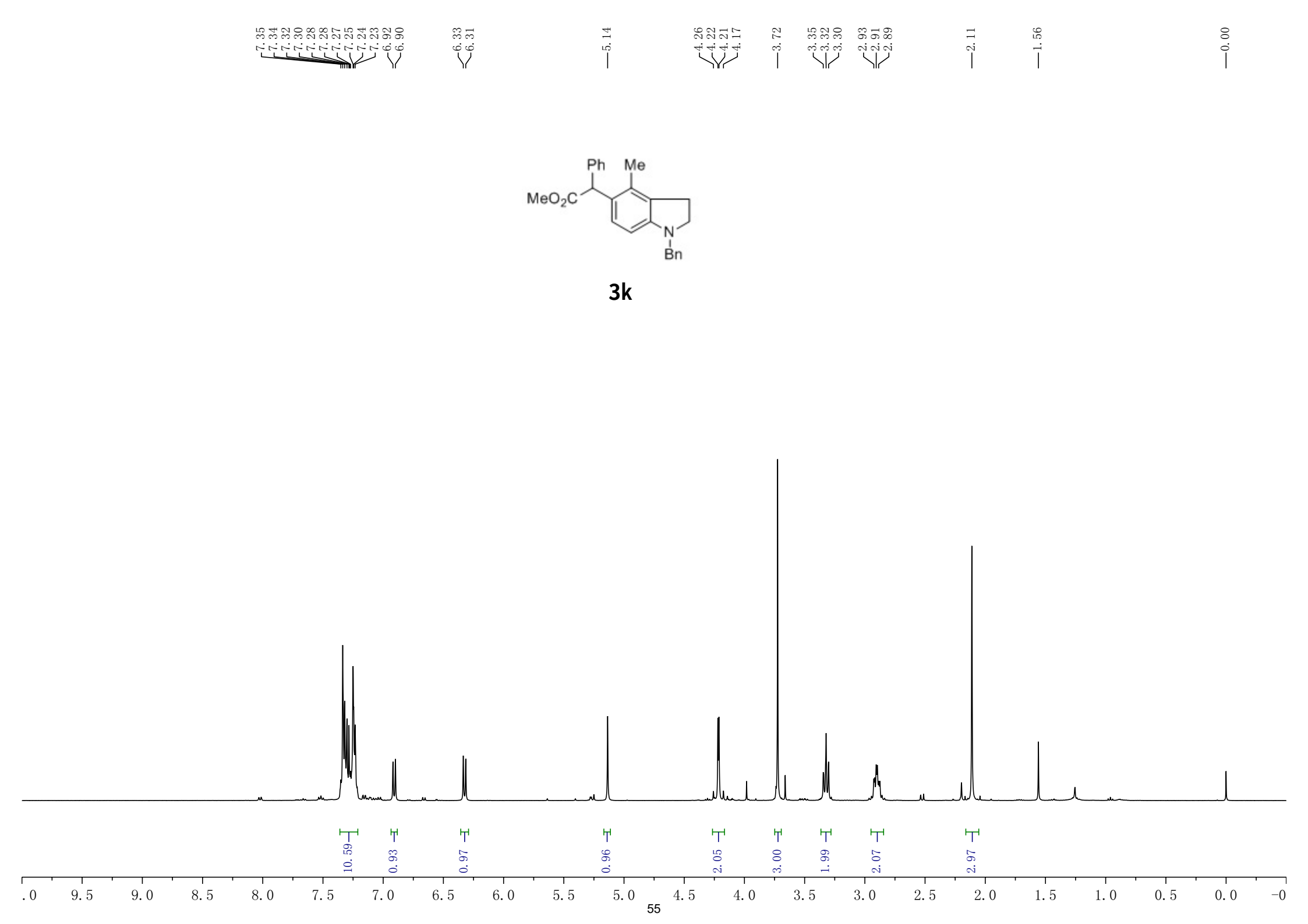
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3k

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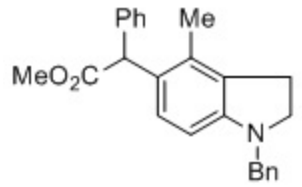

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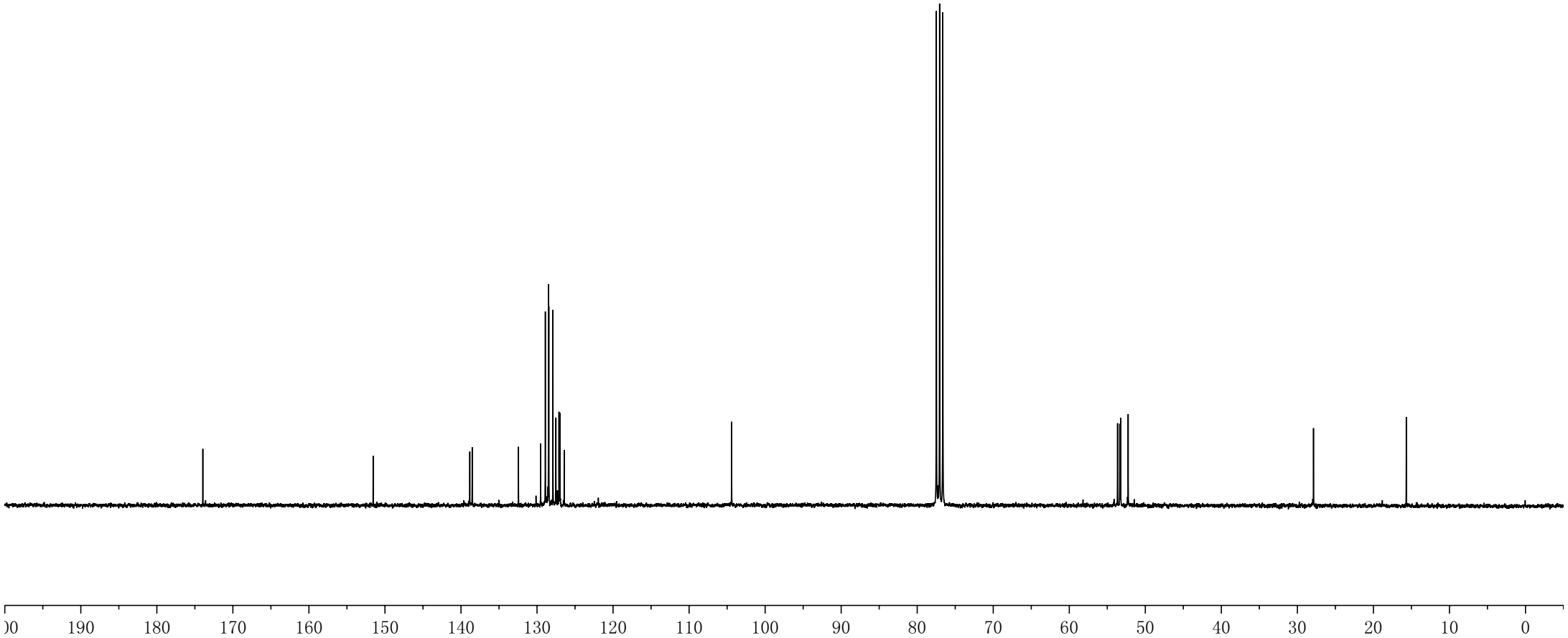

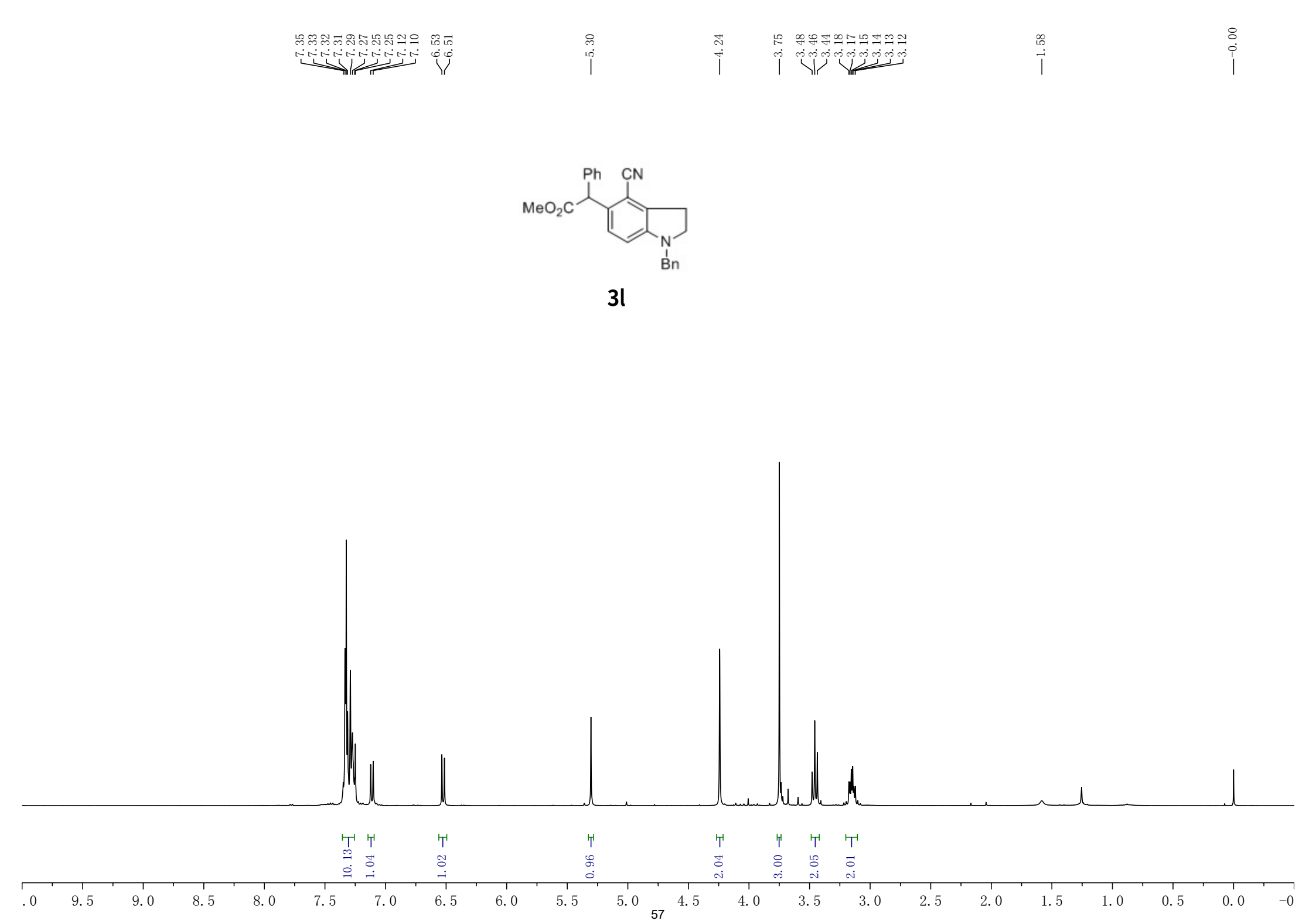
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3l

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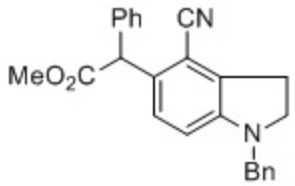

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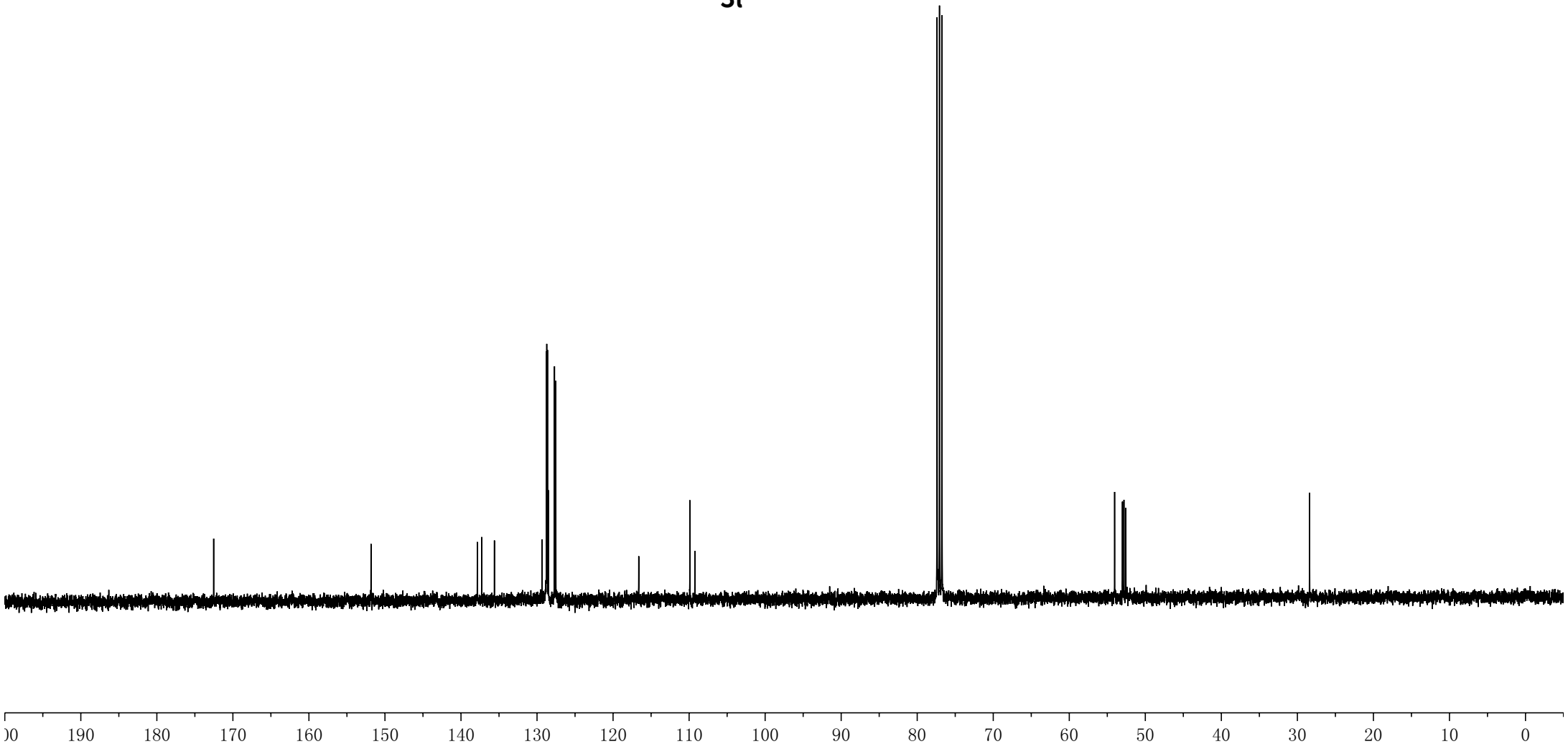

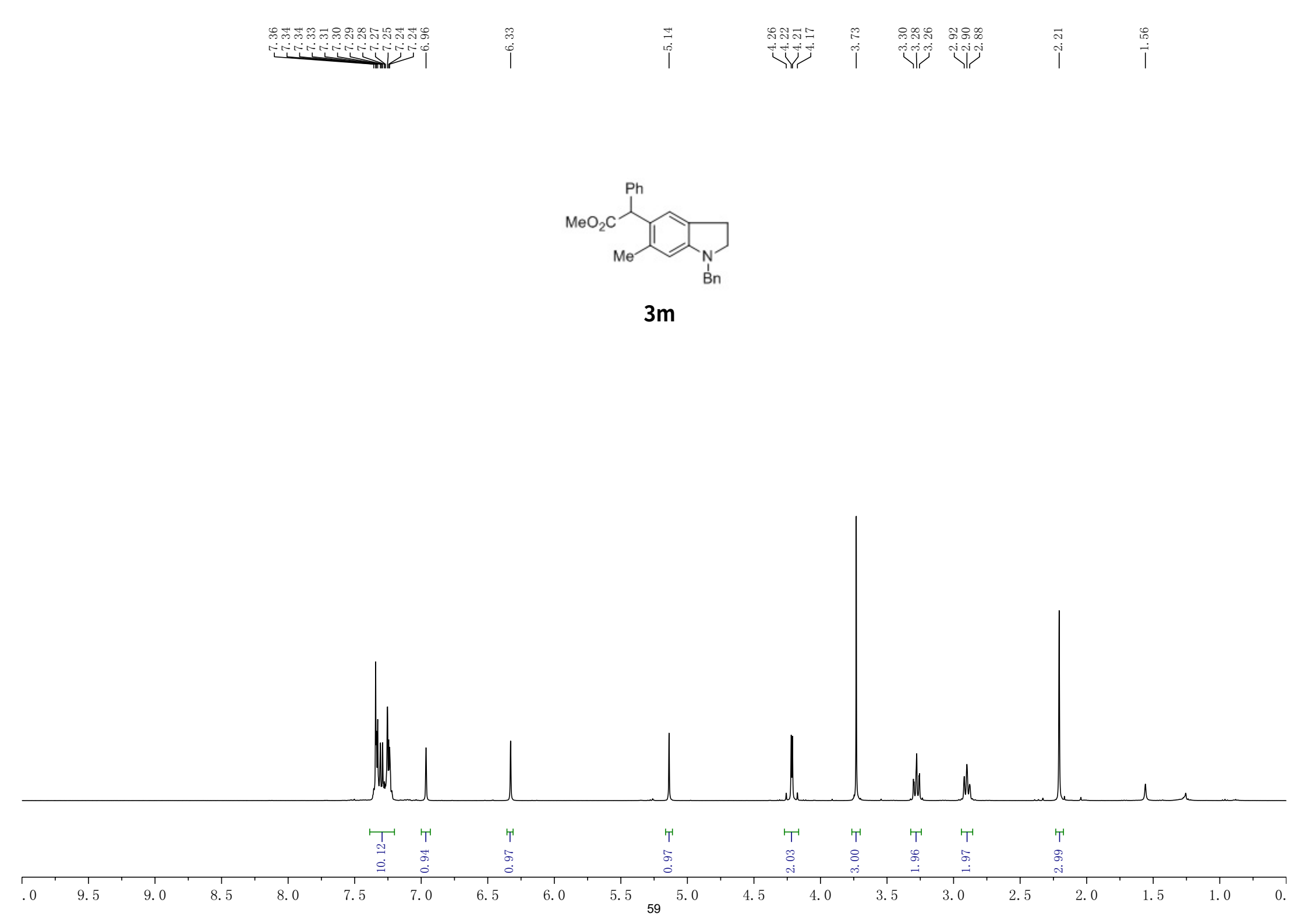
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3m

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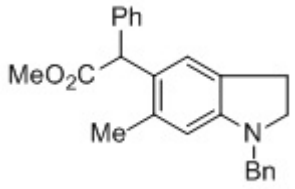

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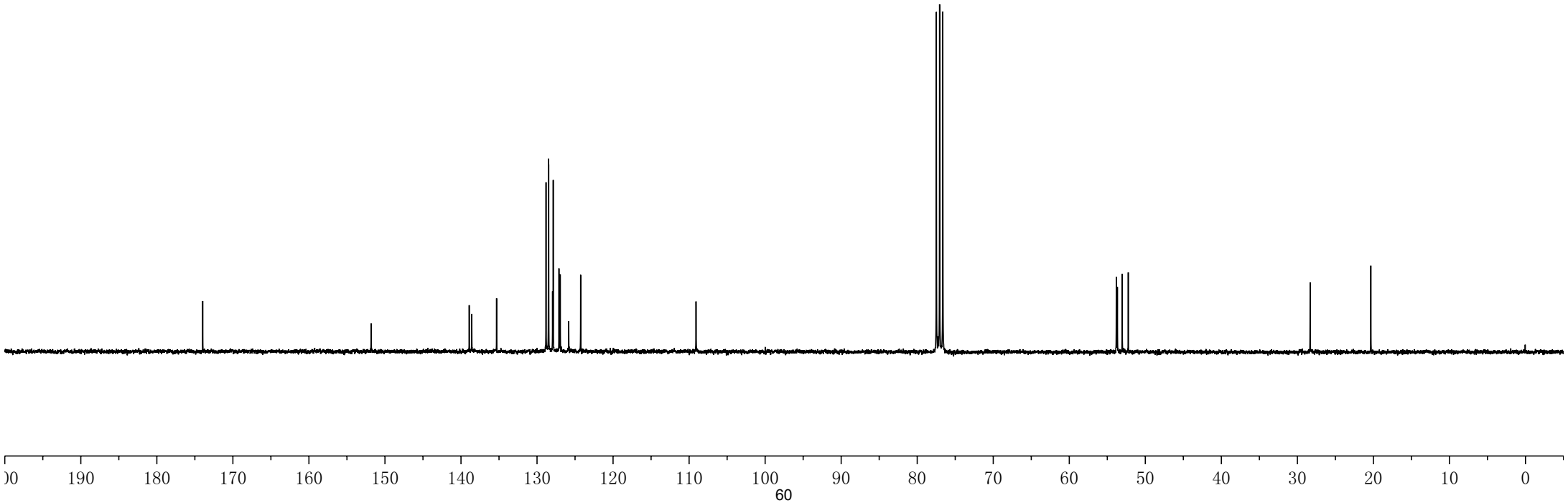

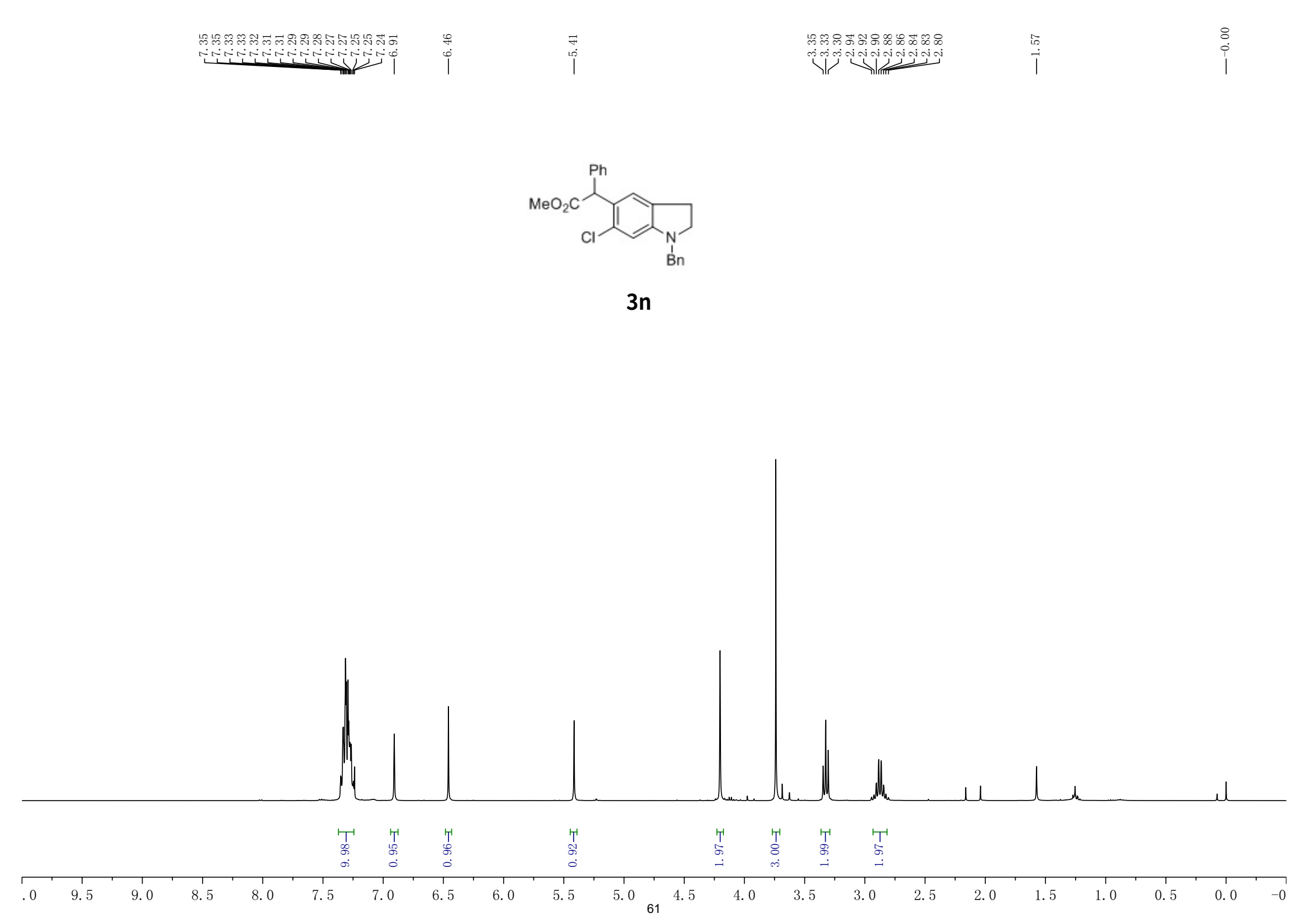
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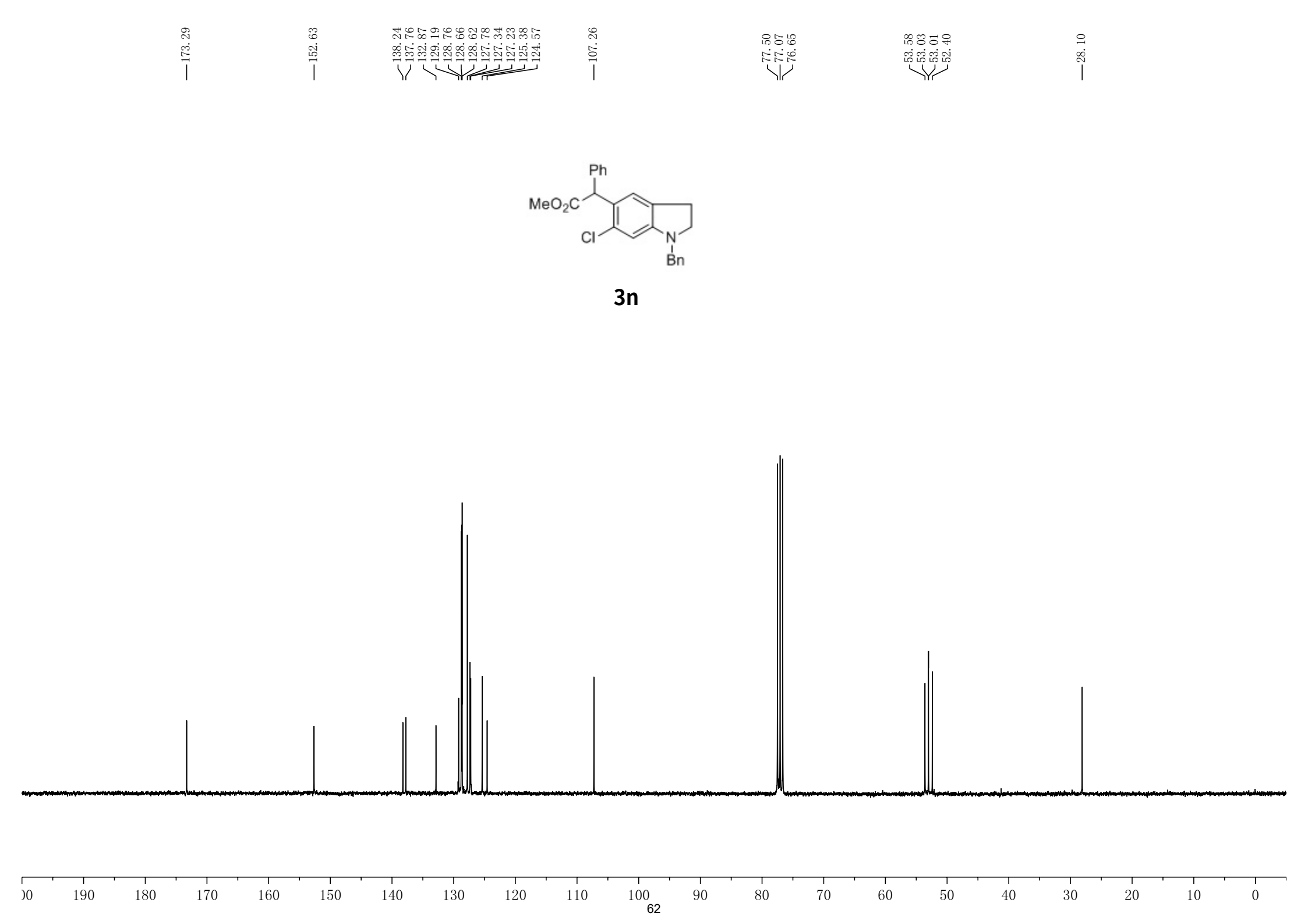
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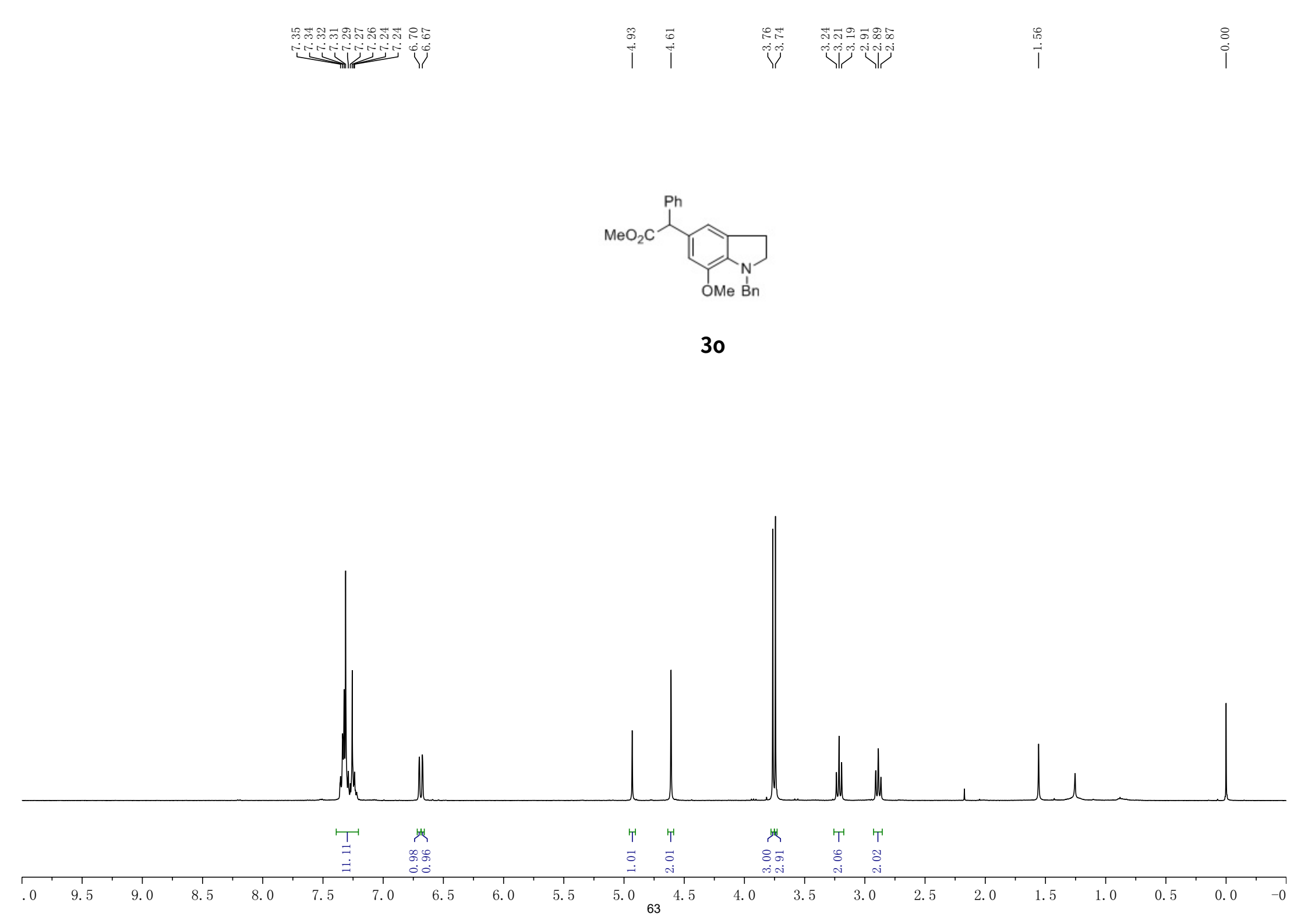
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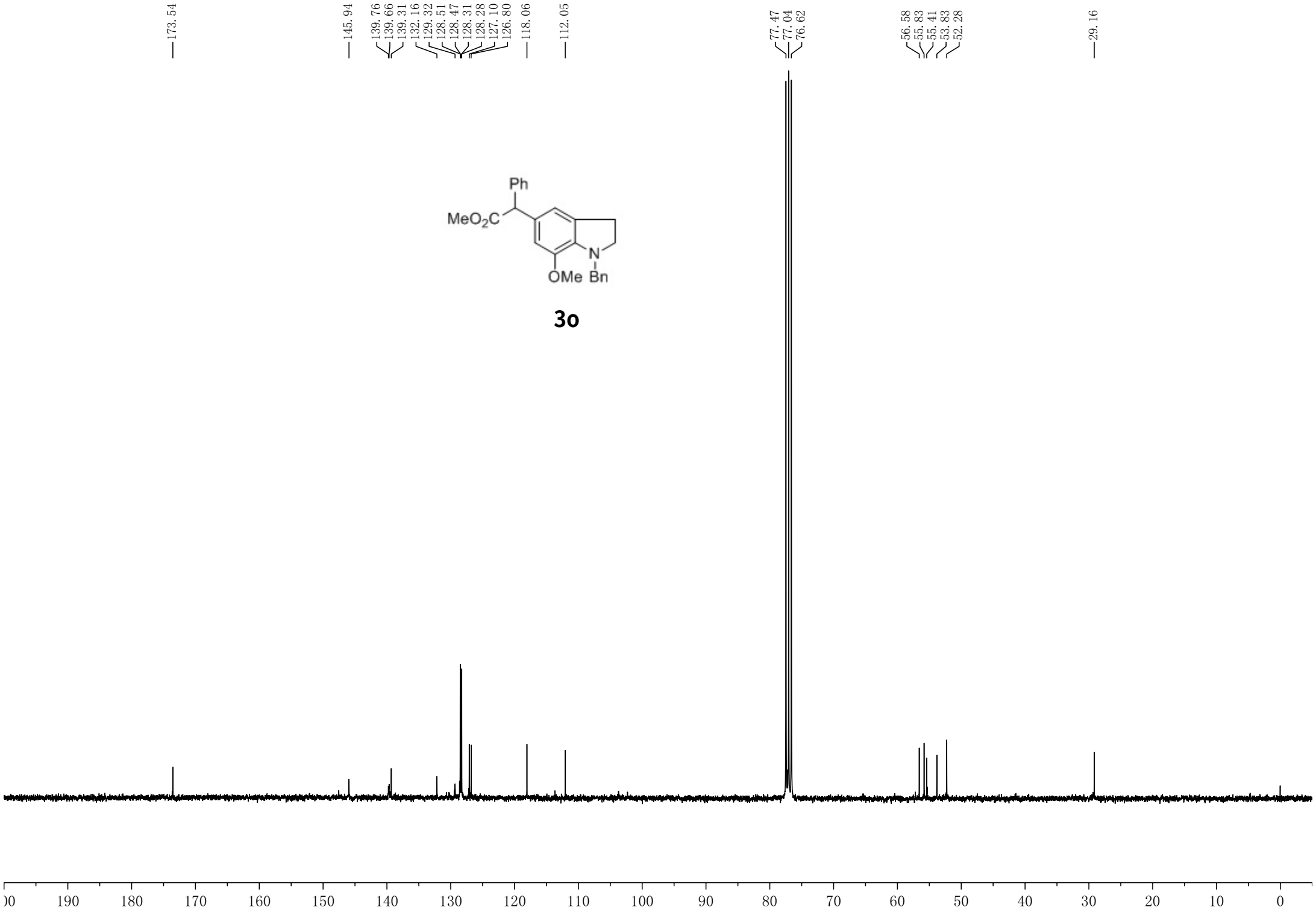
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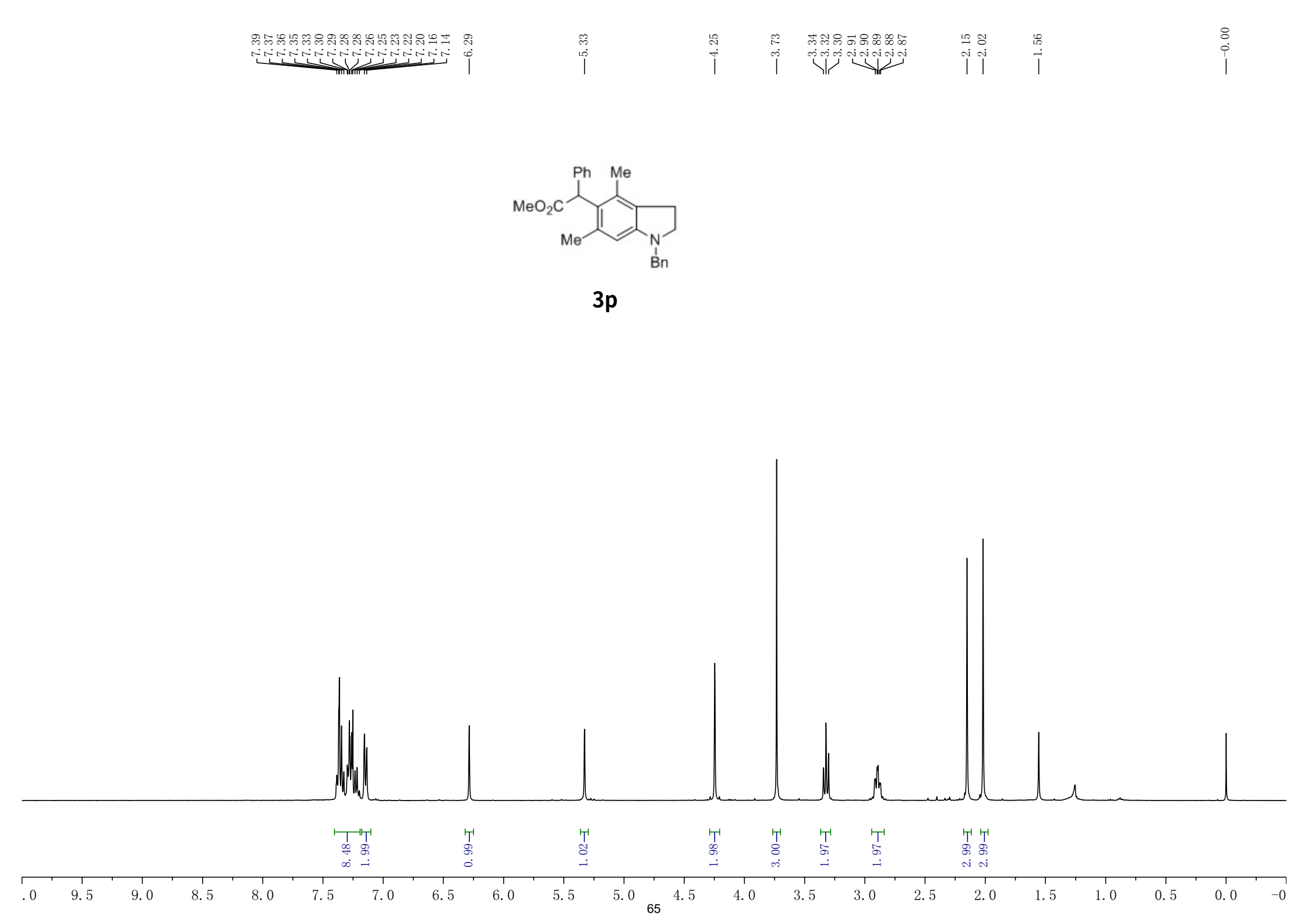
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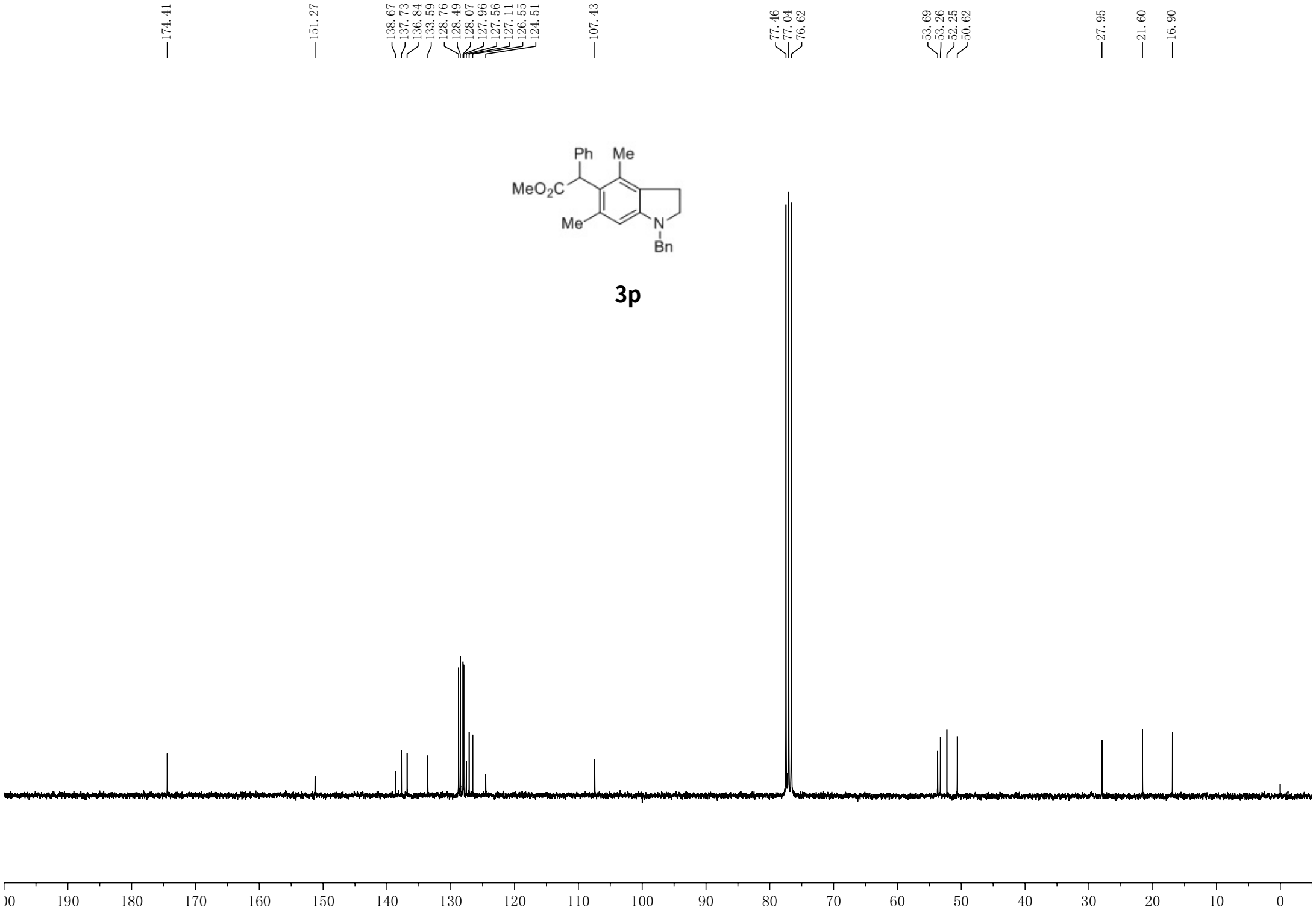
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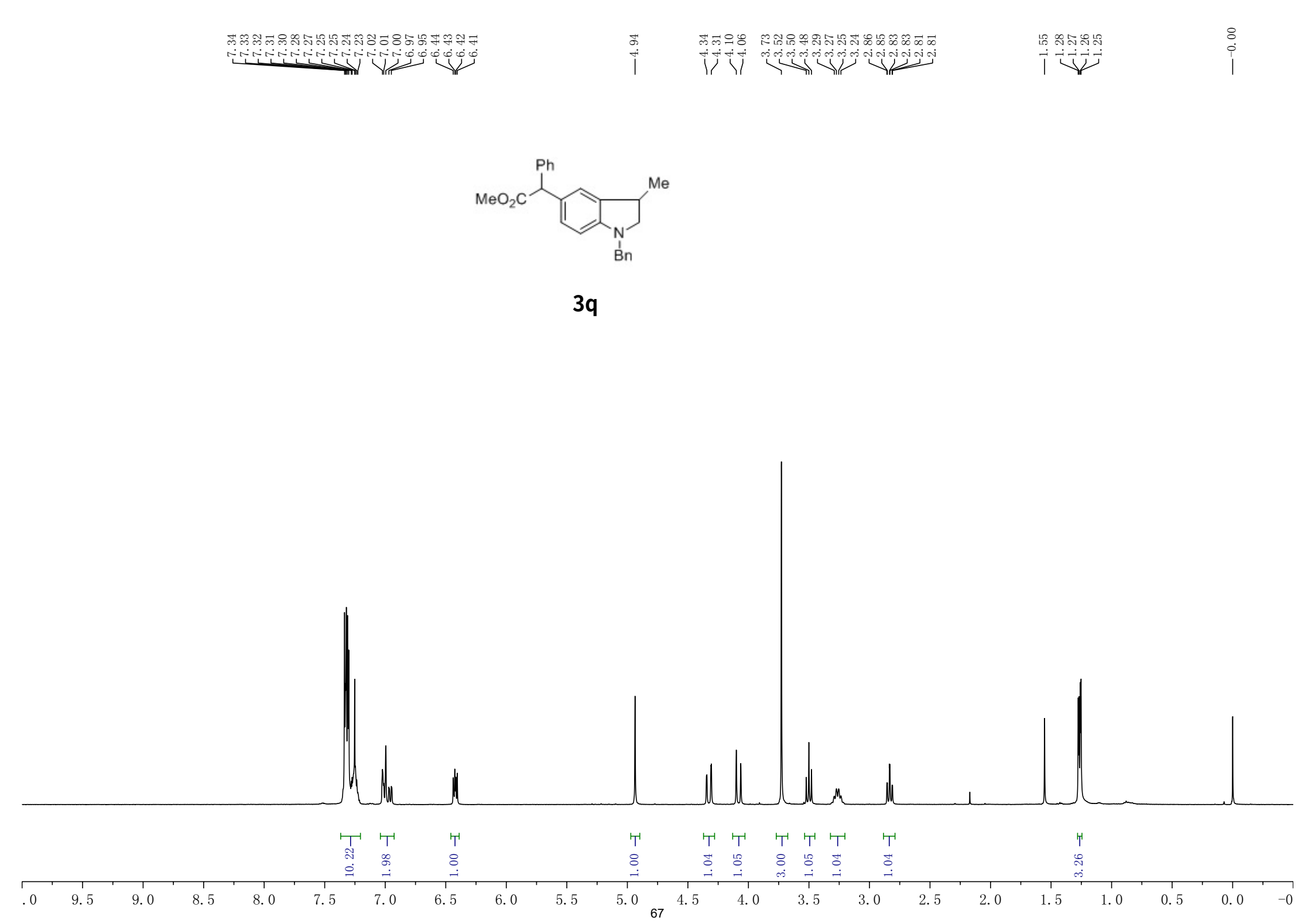
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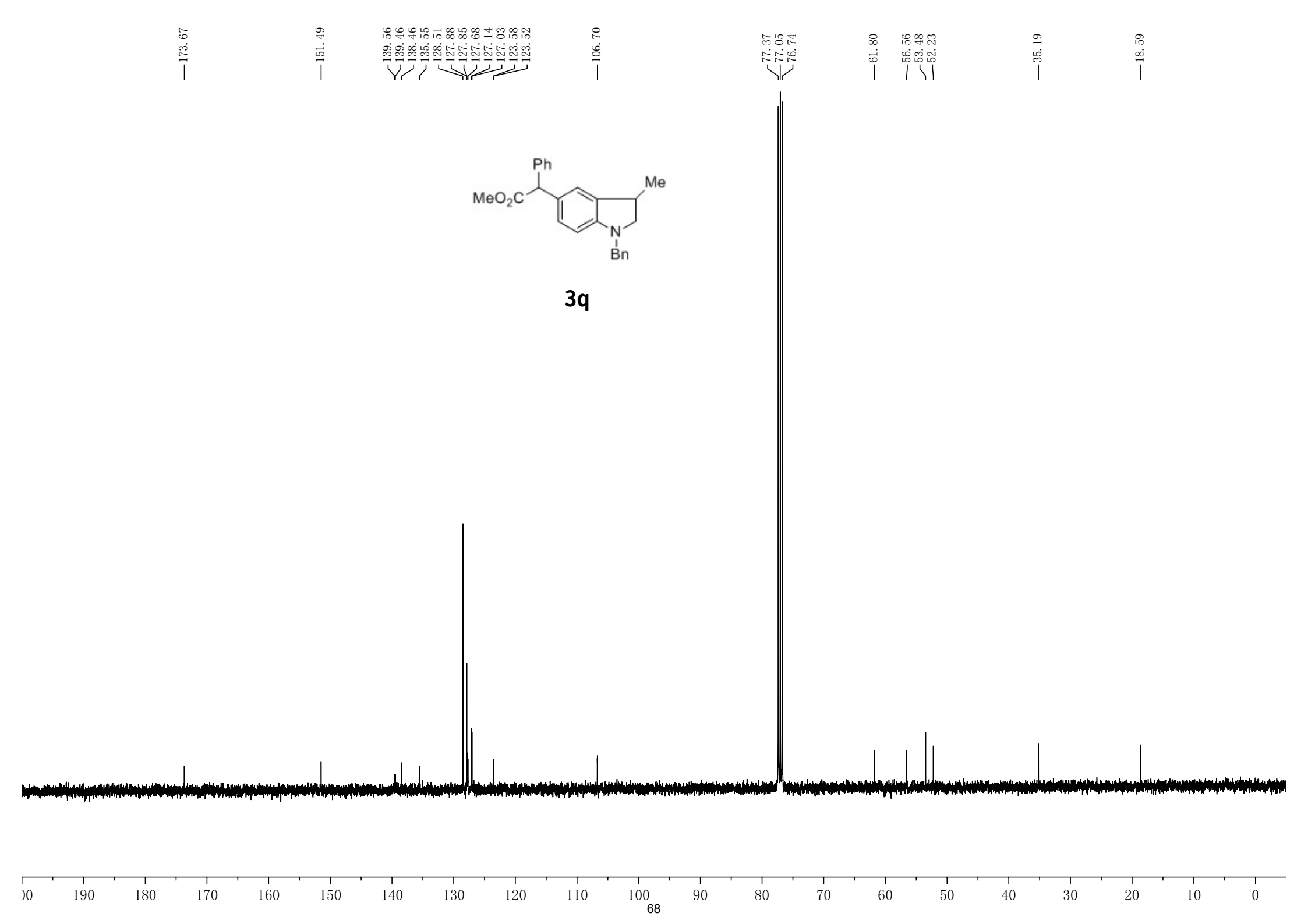
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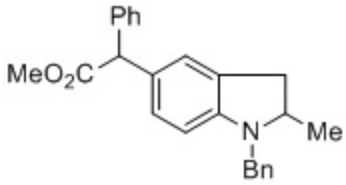
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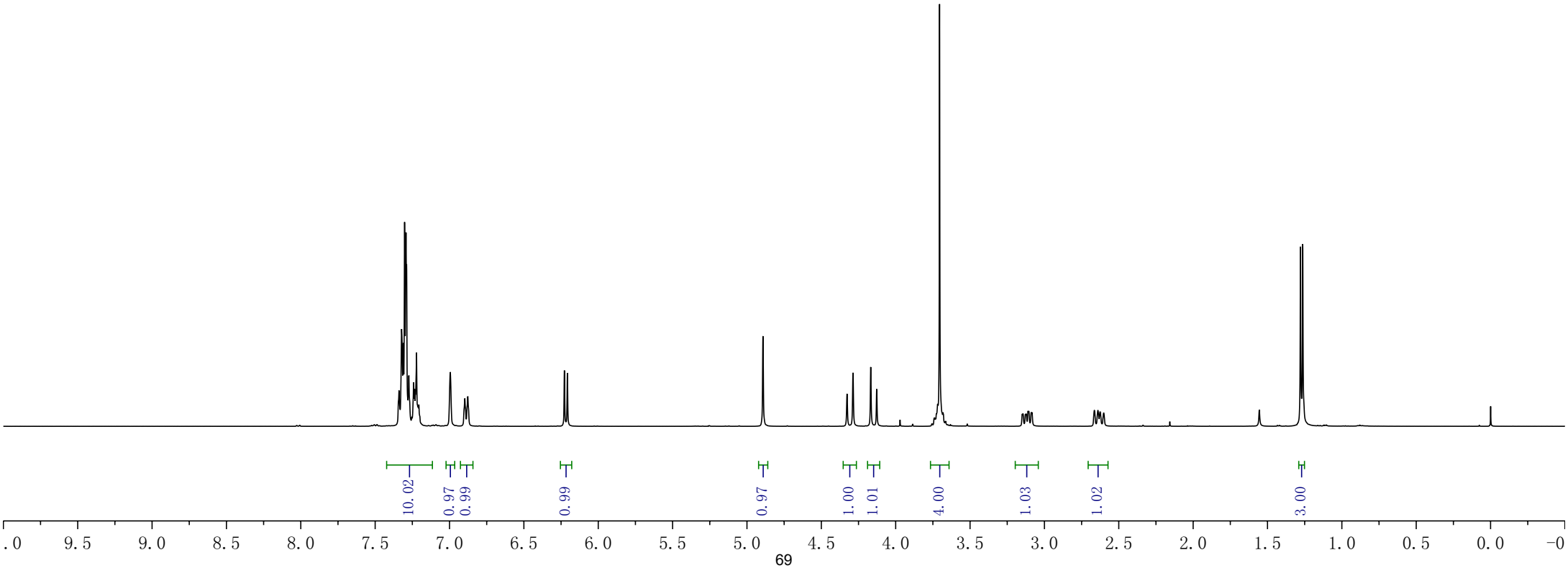
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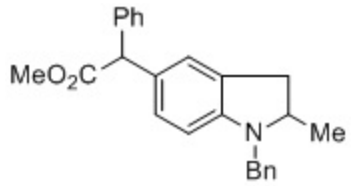

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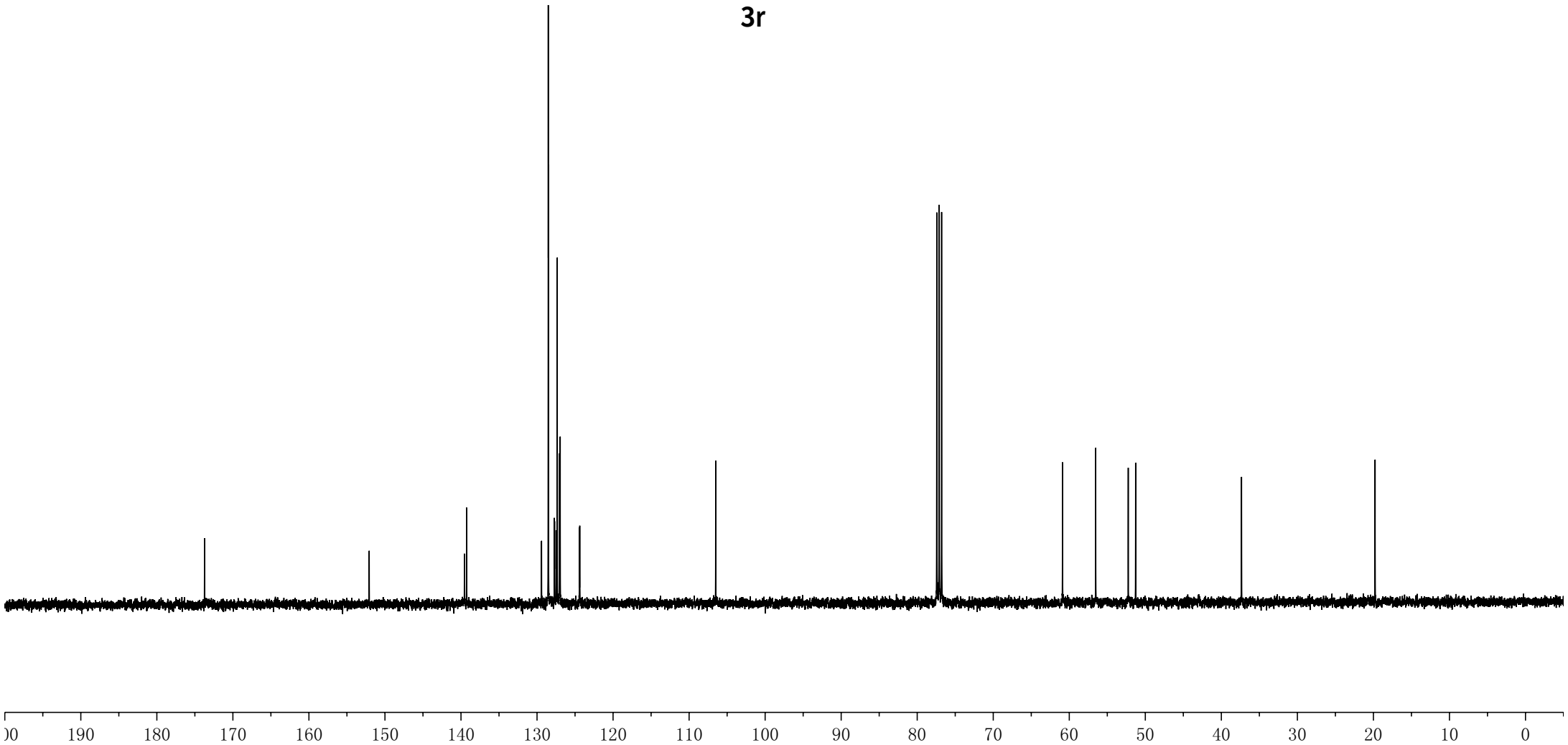

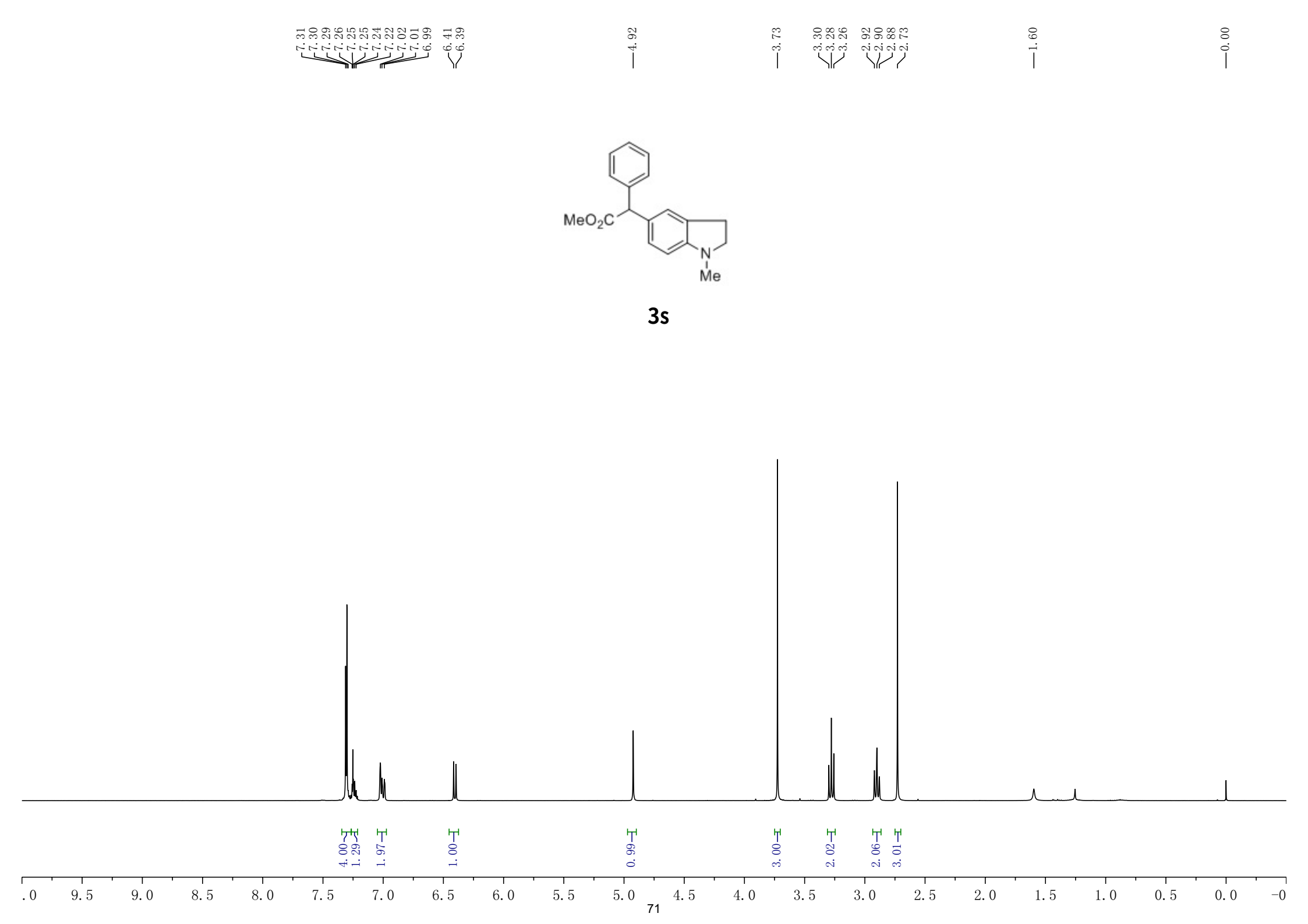
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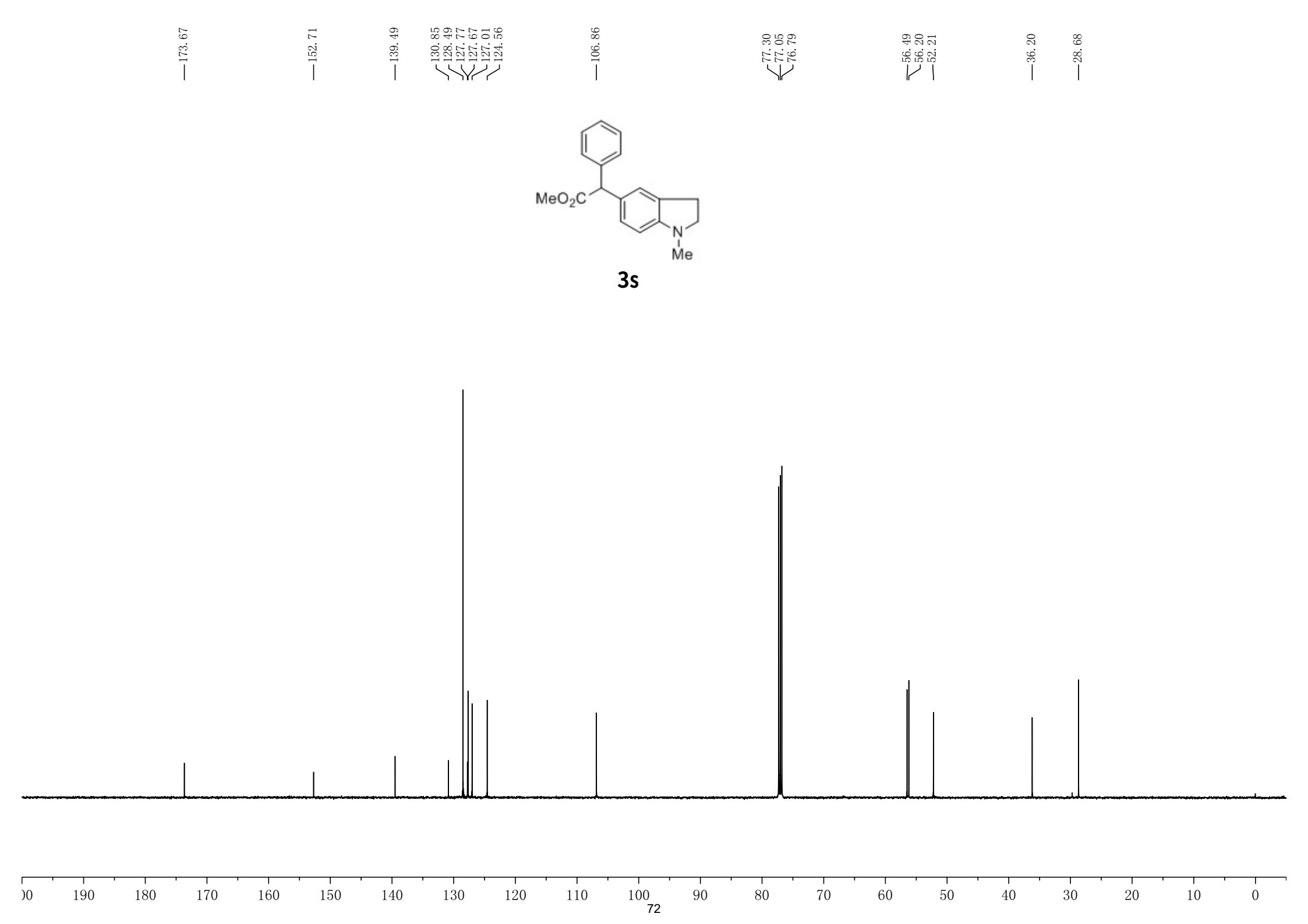
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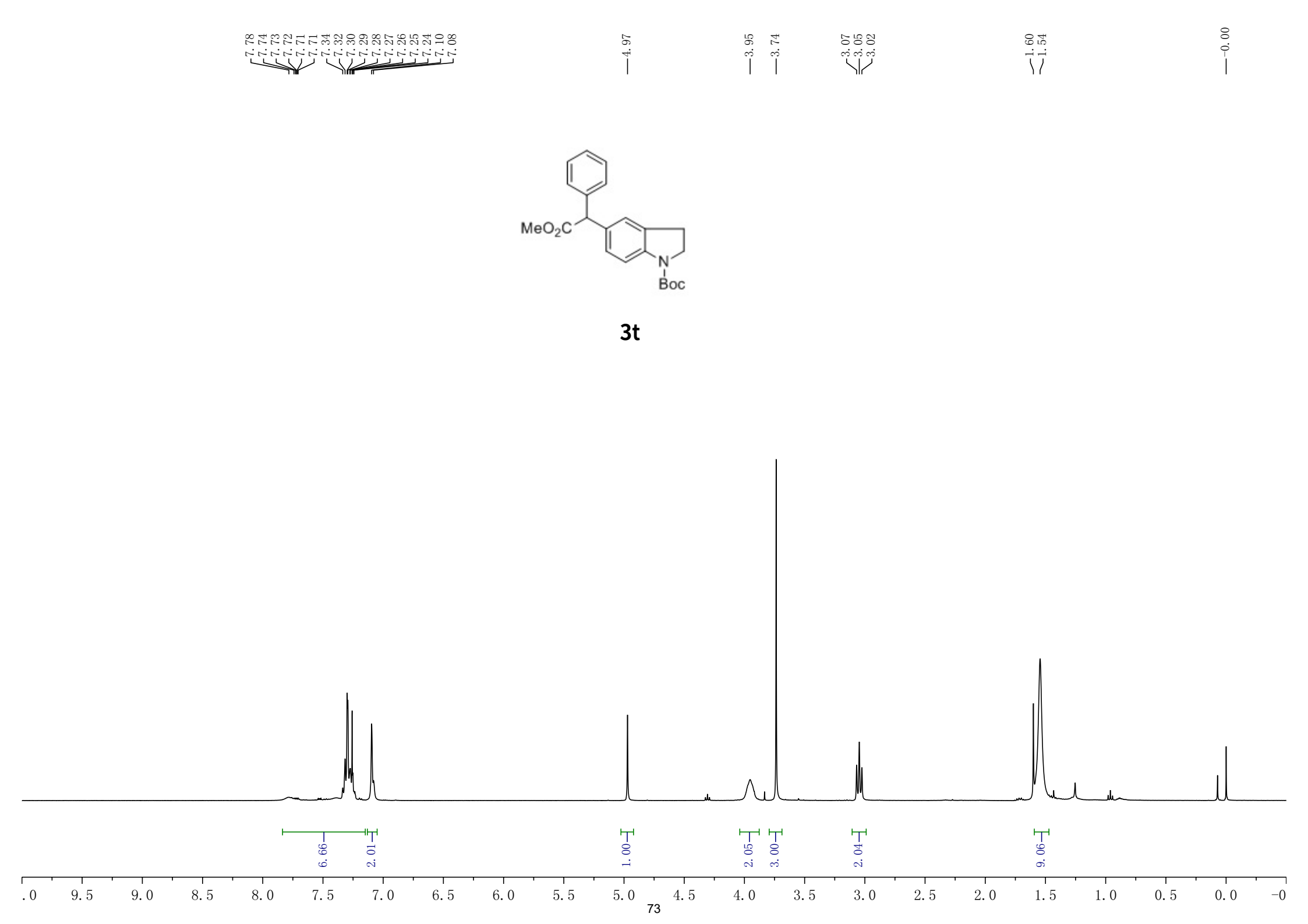
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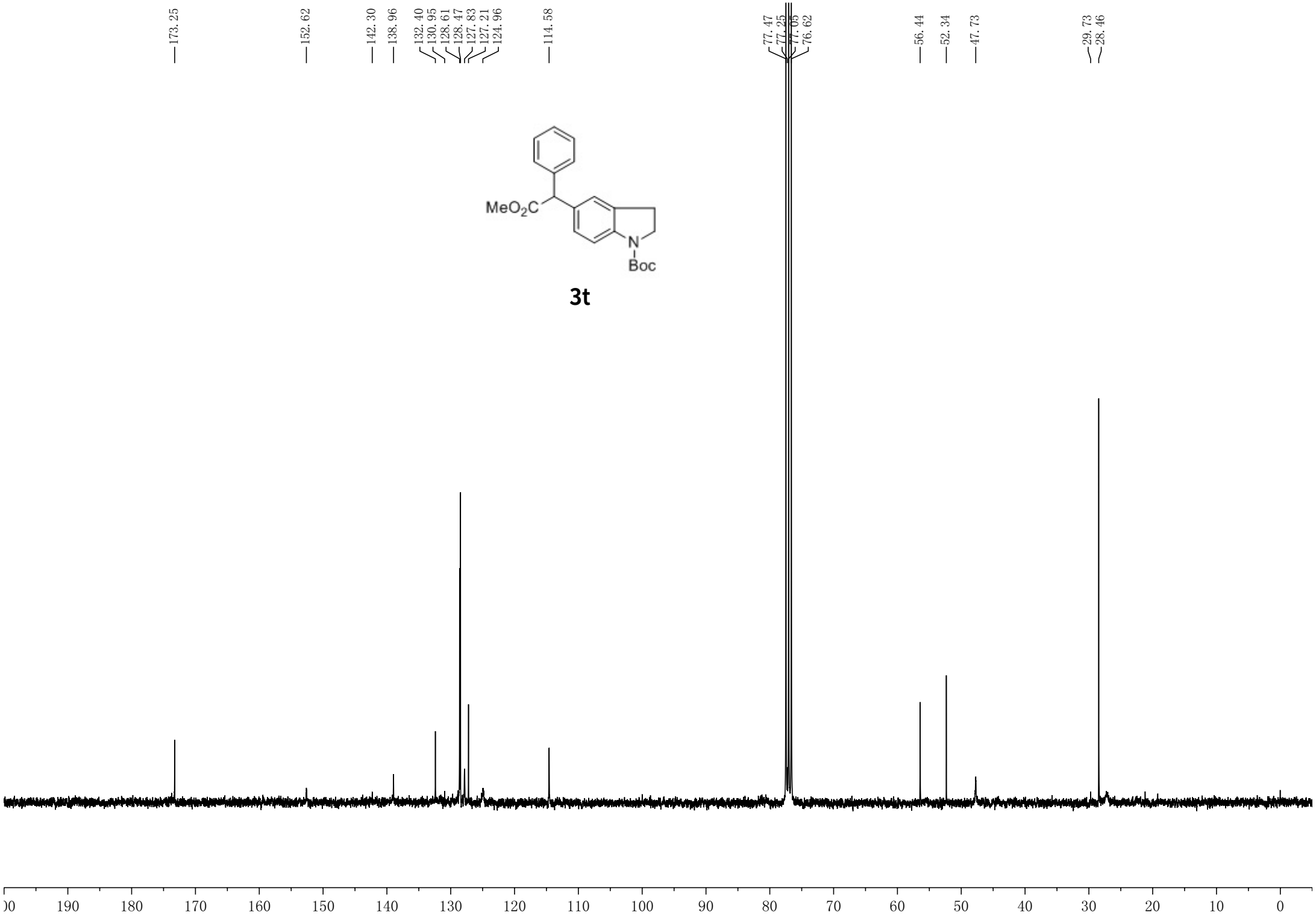
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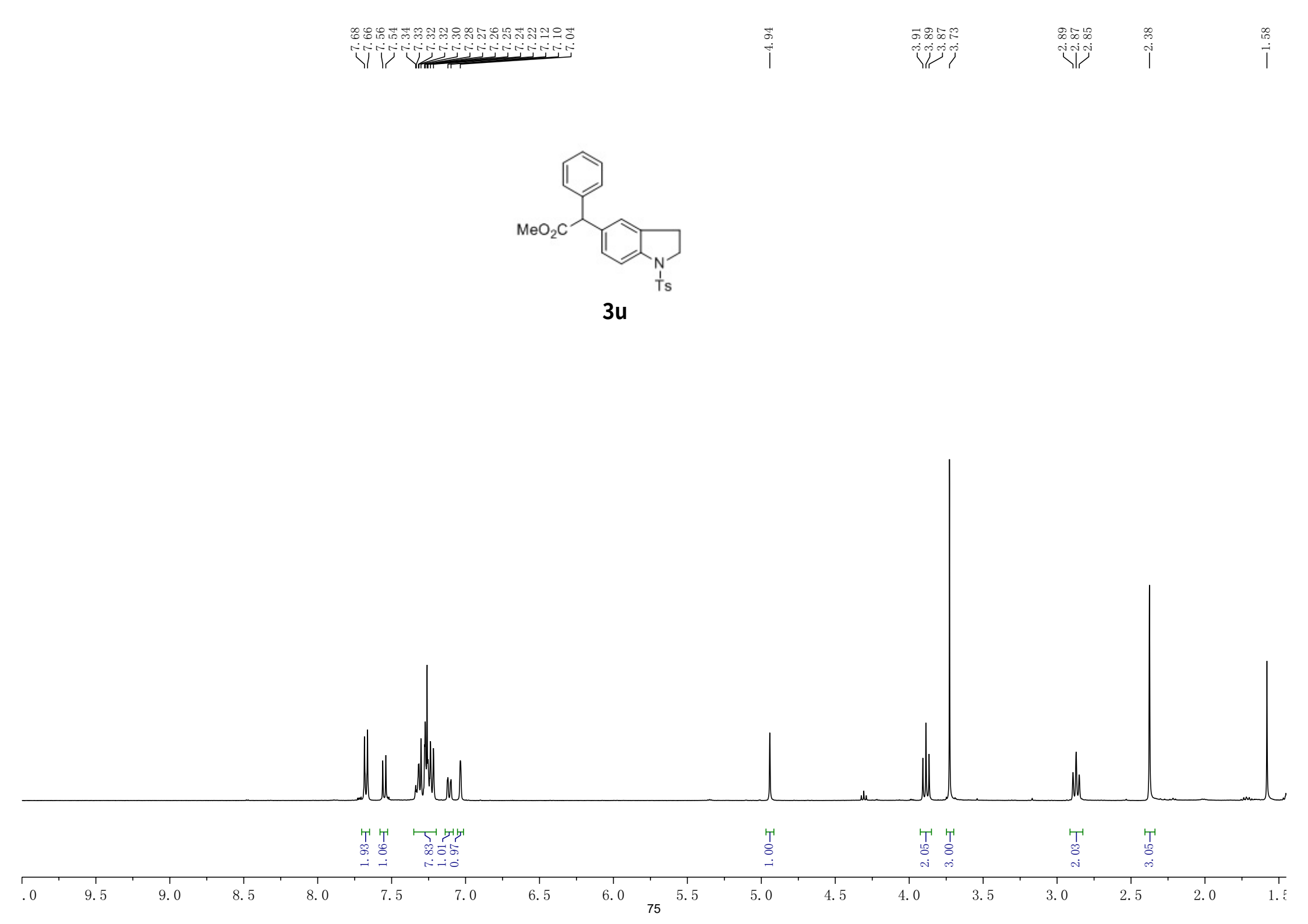
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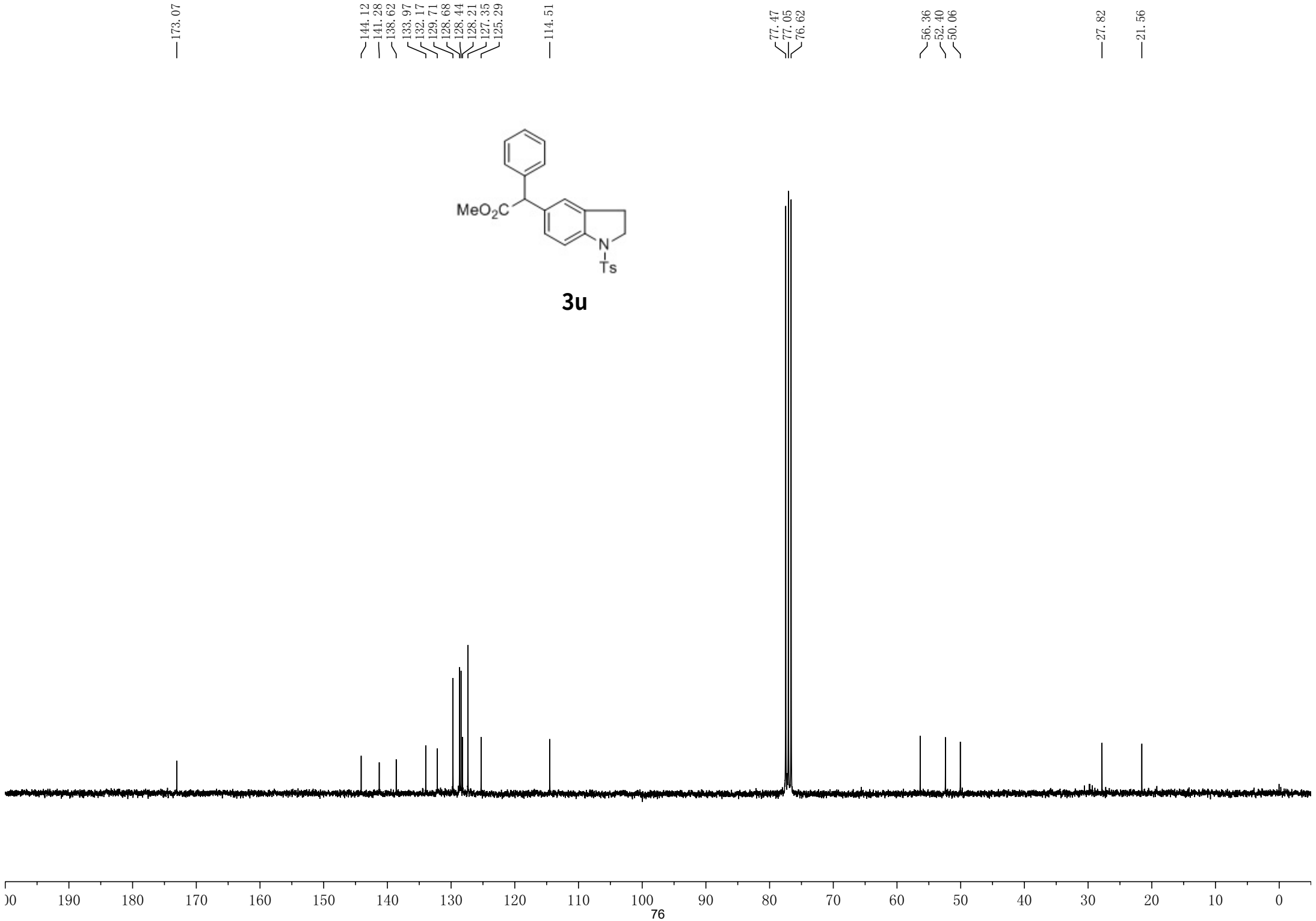
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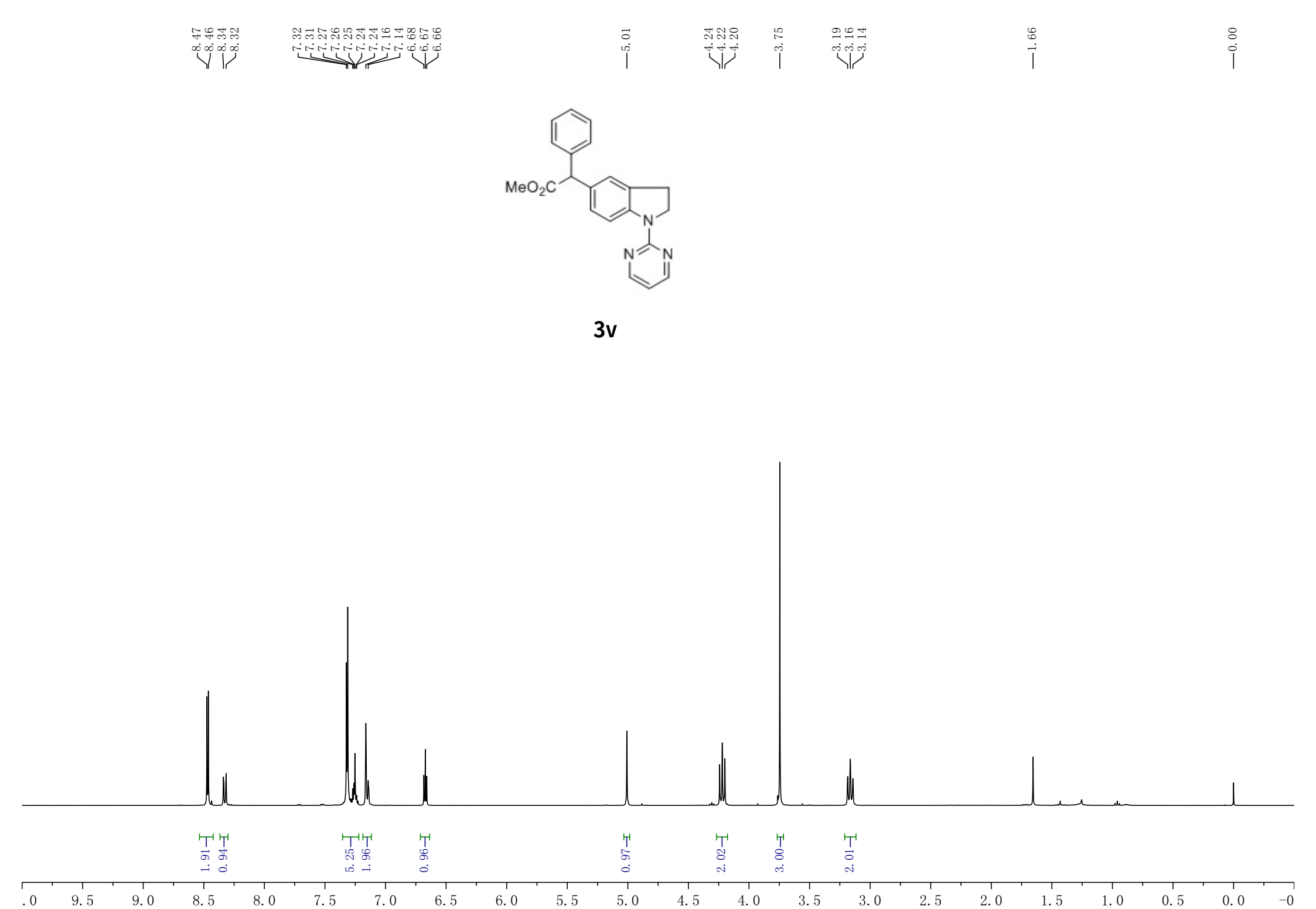
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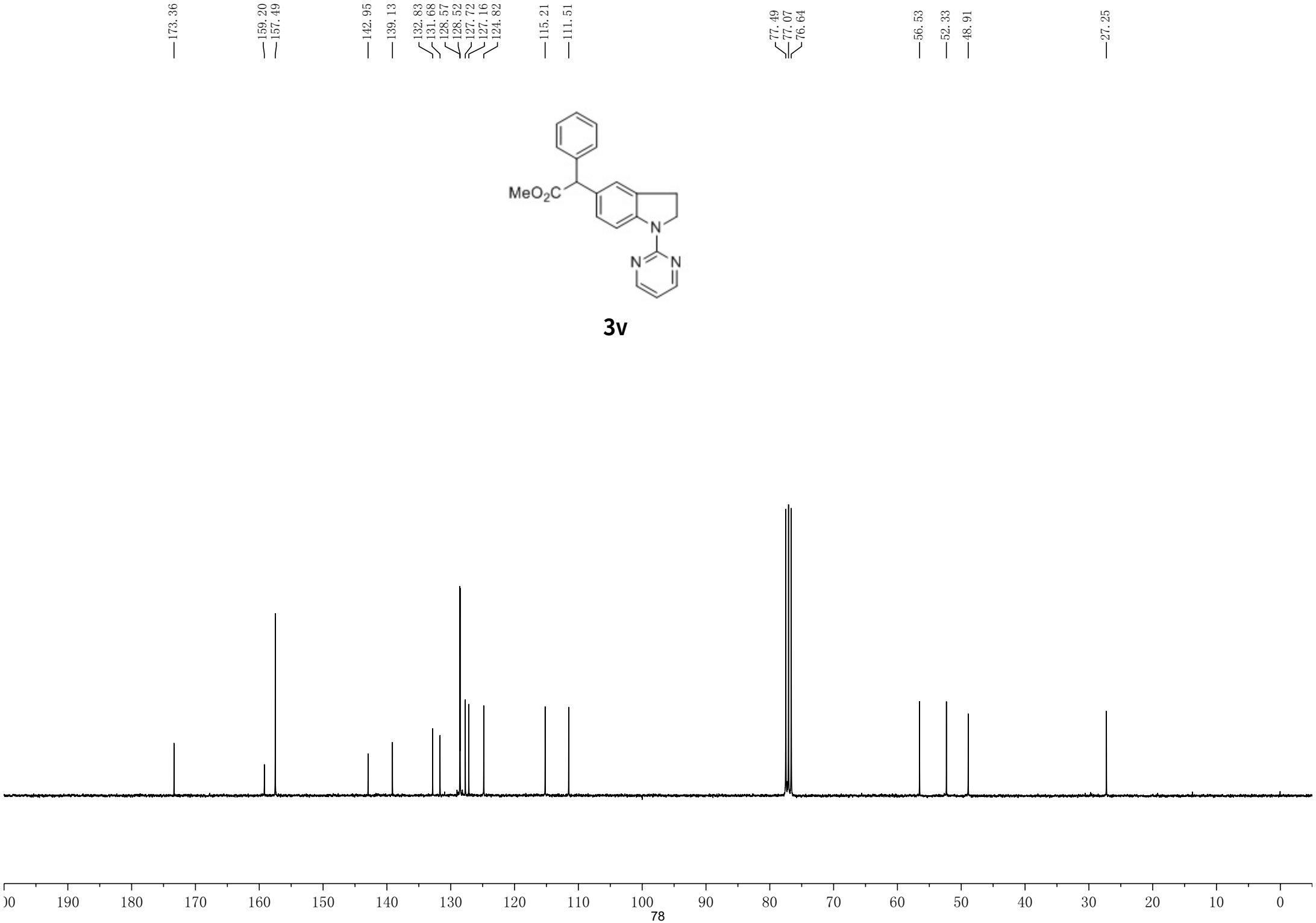
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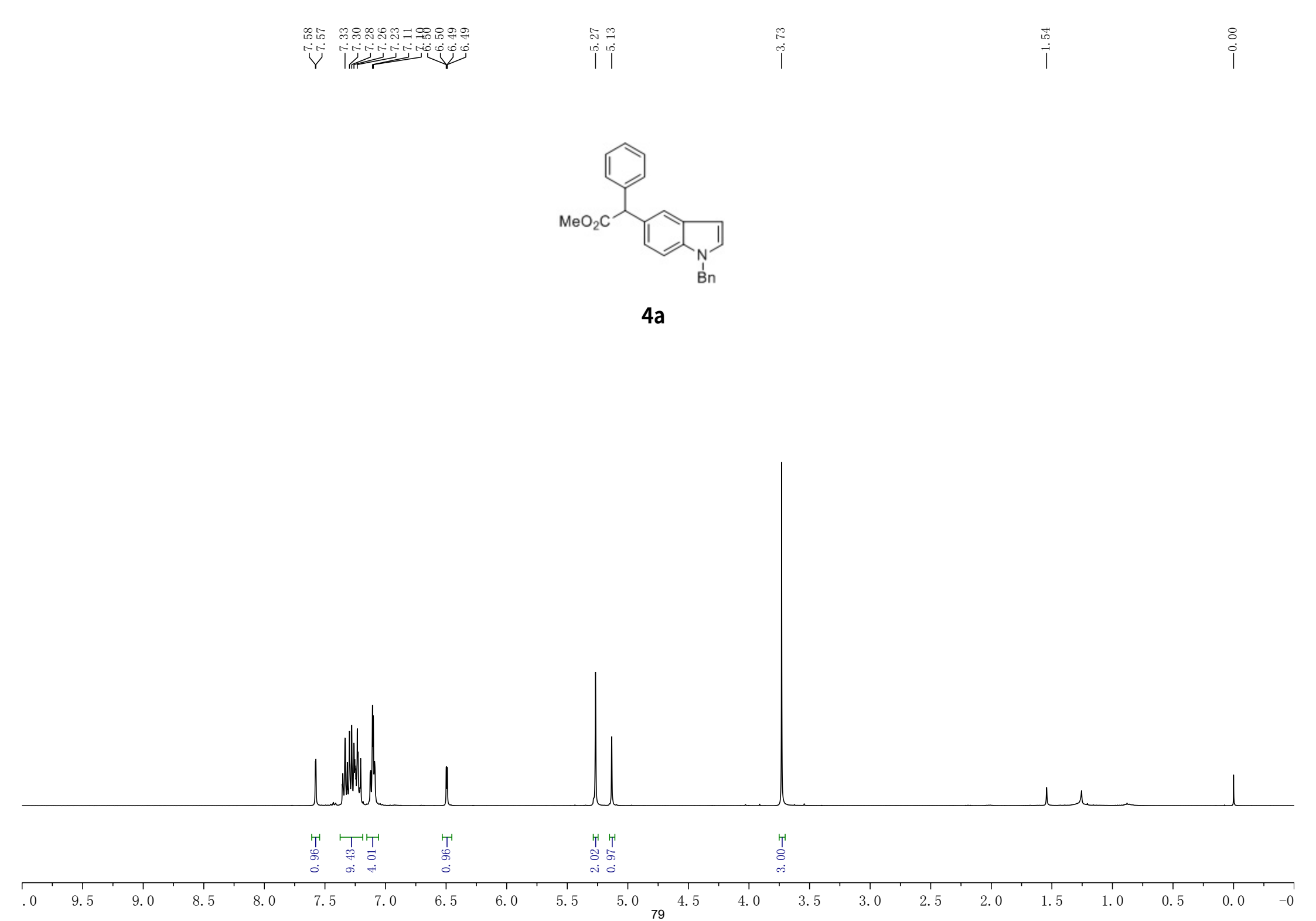
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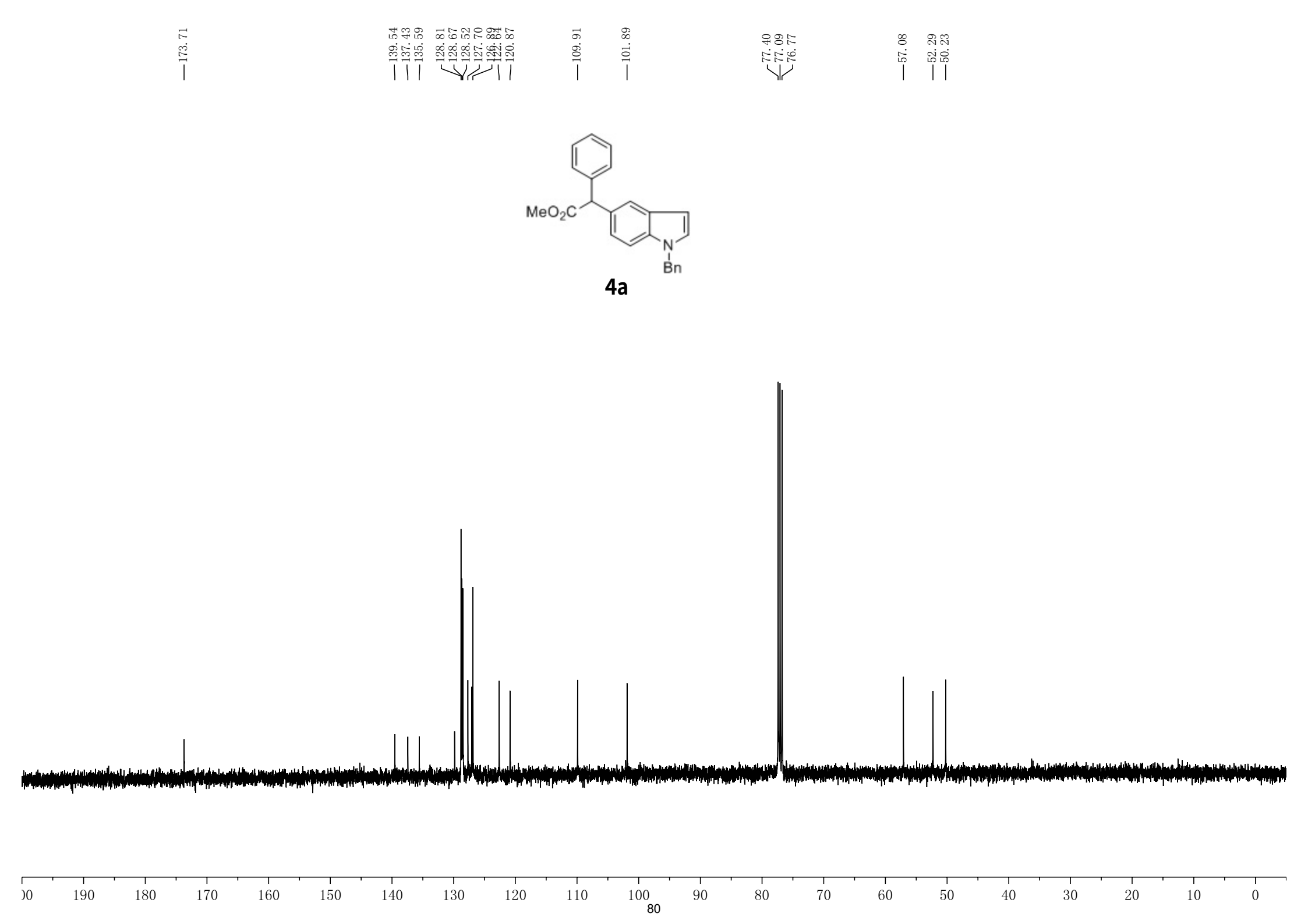
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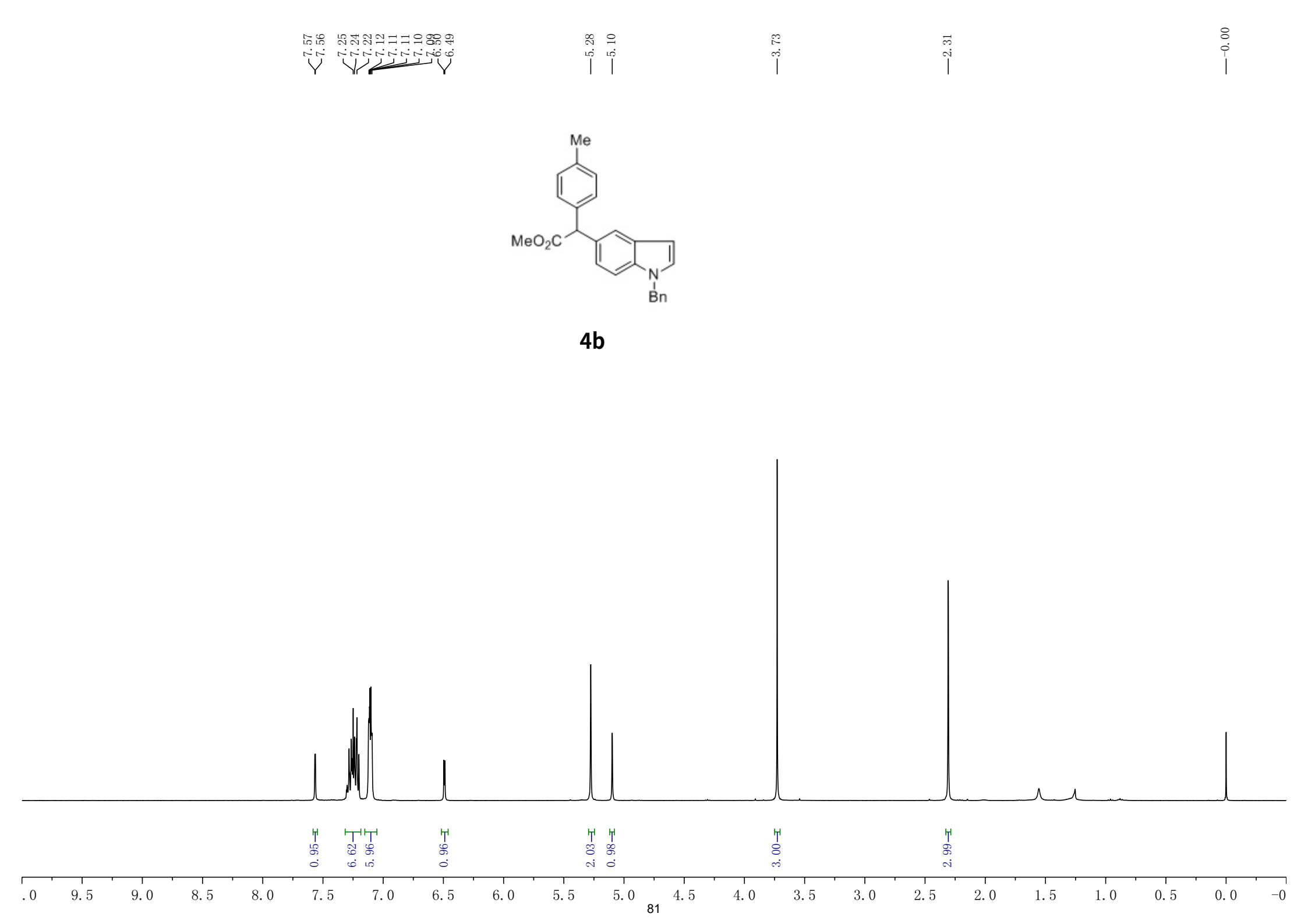
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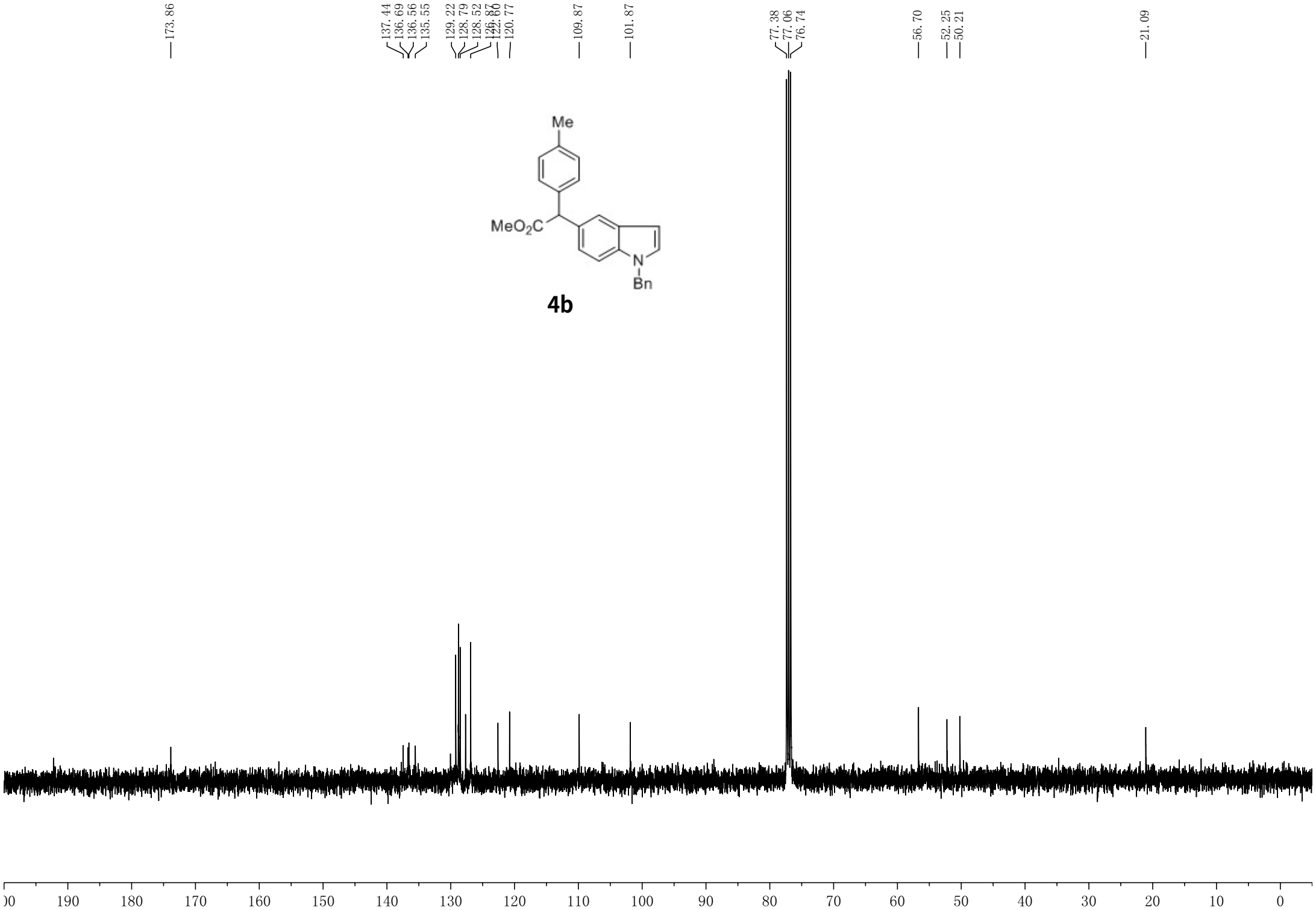
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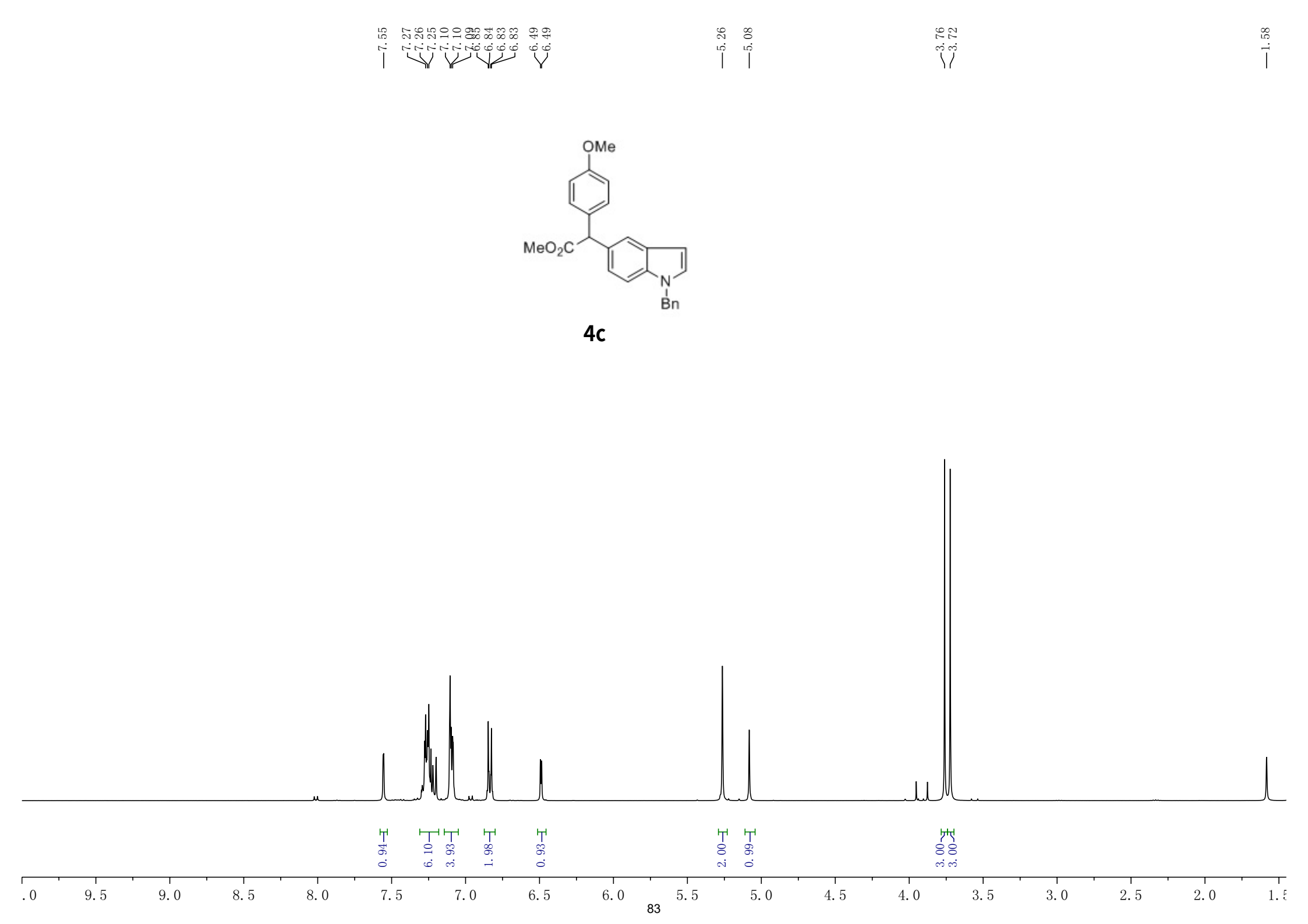
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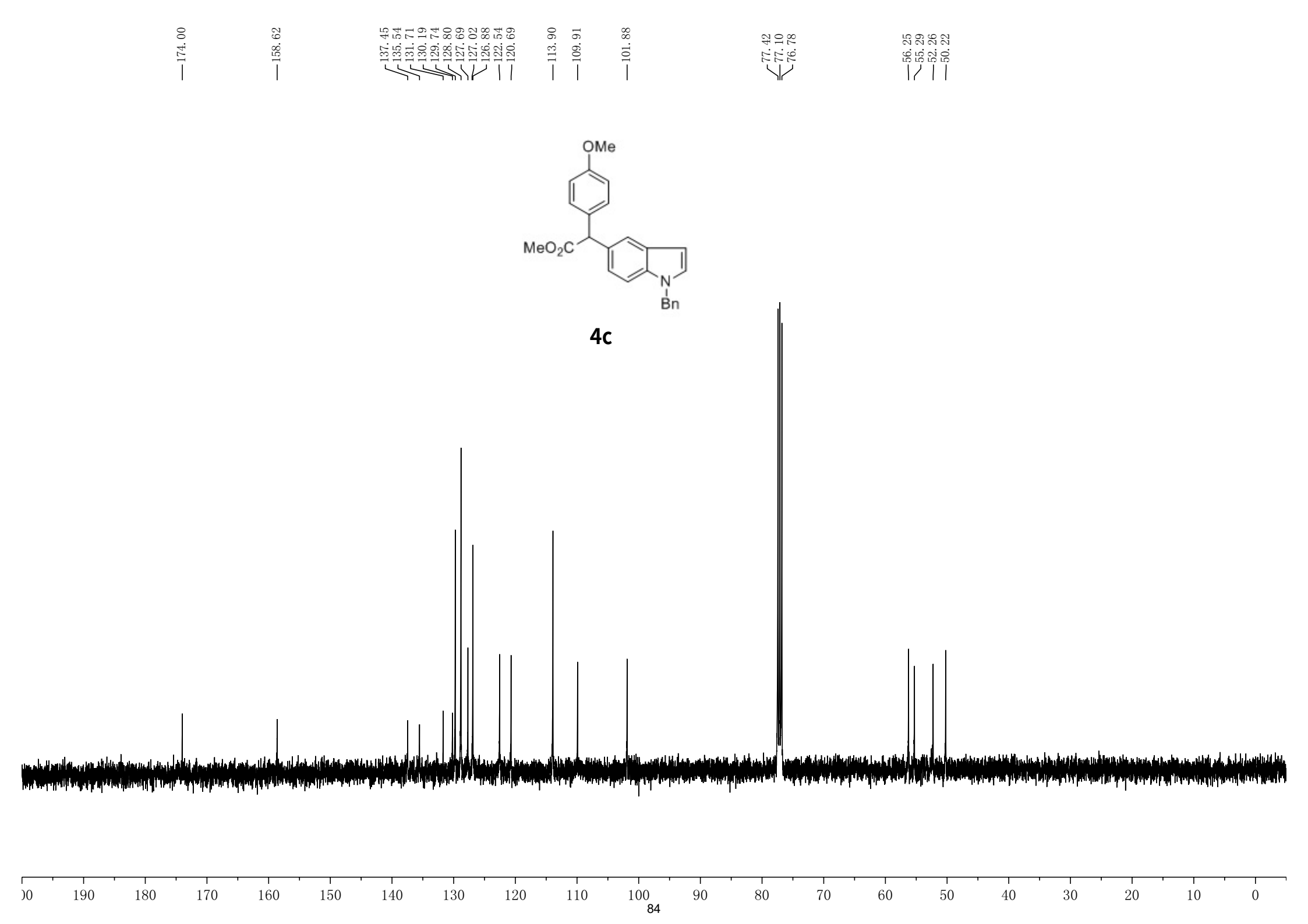
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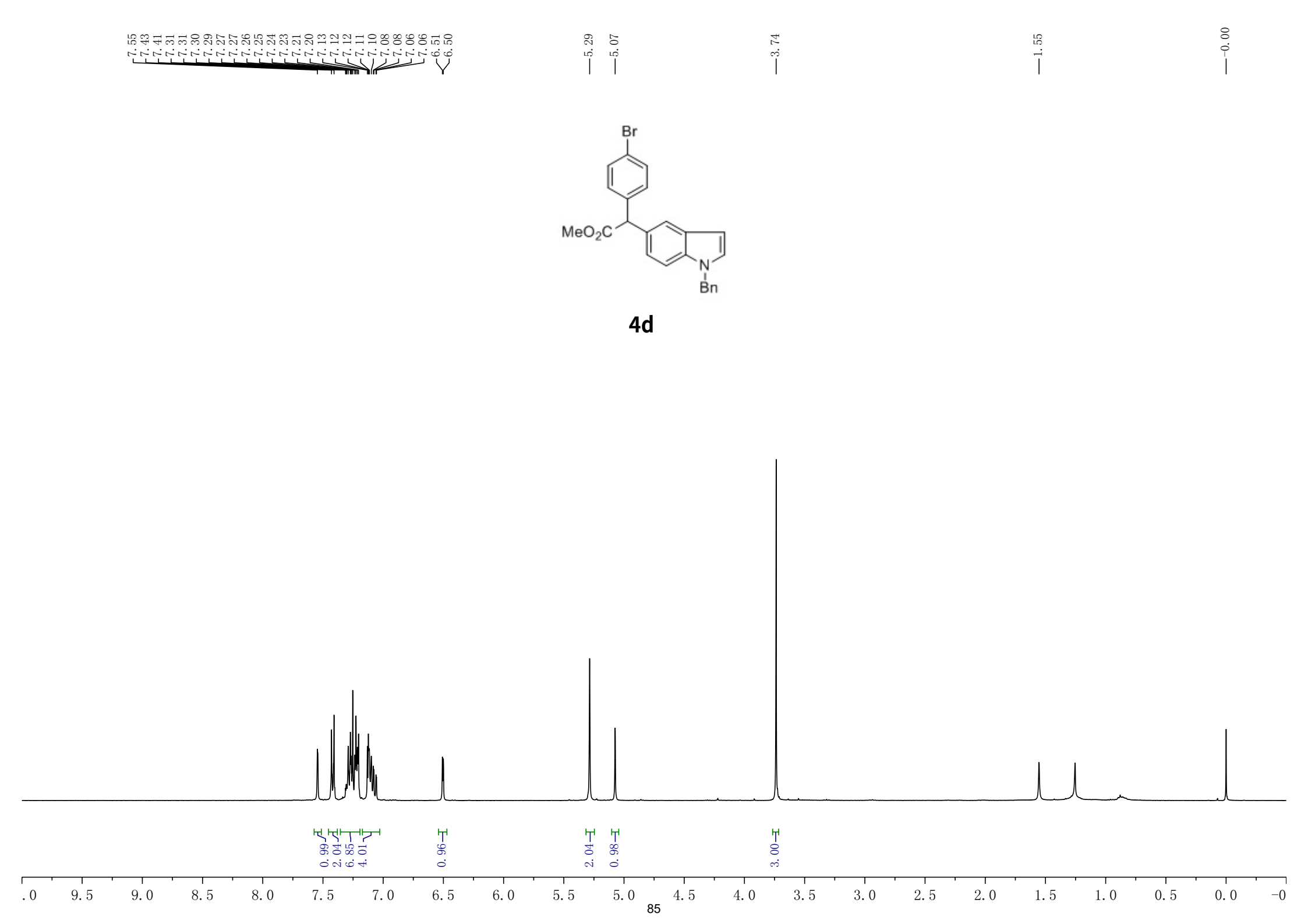
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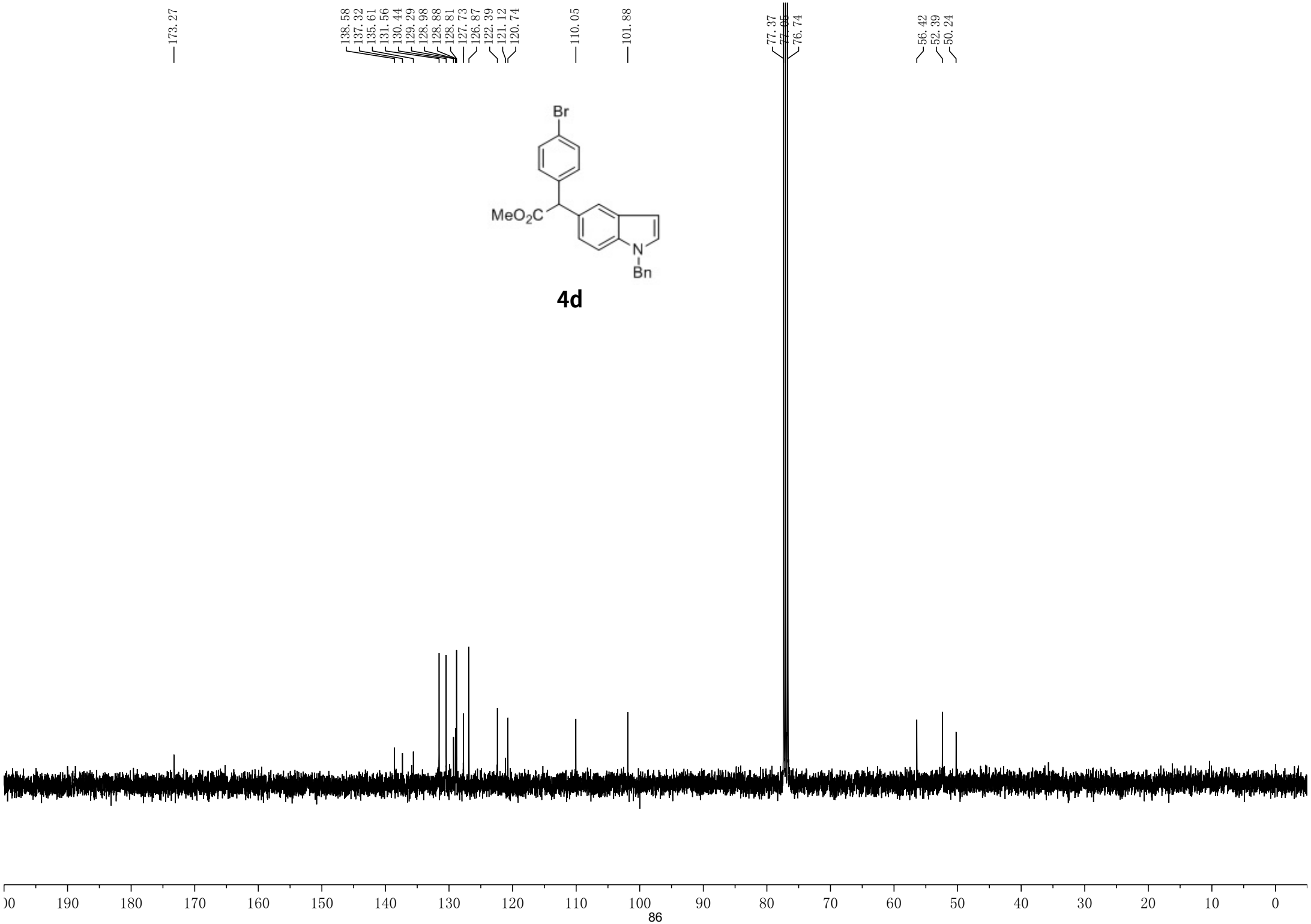
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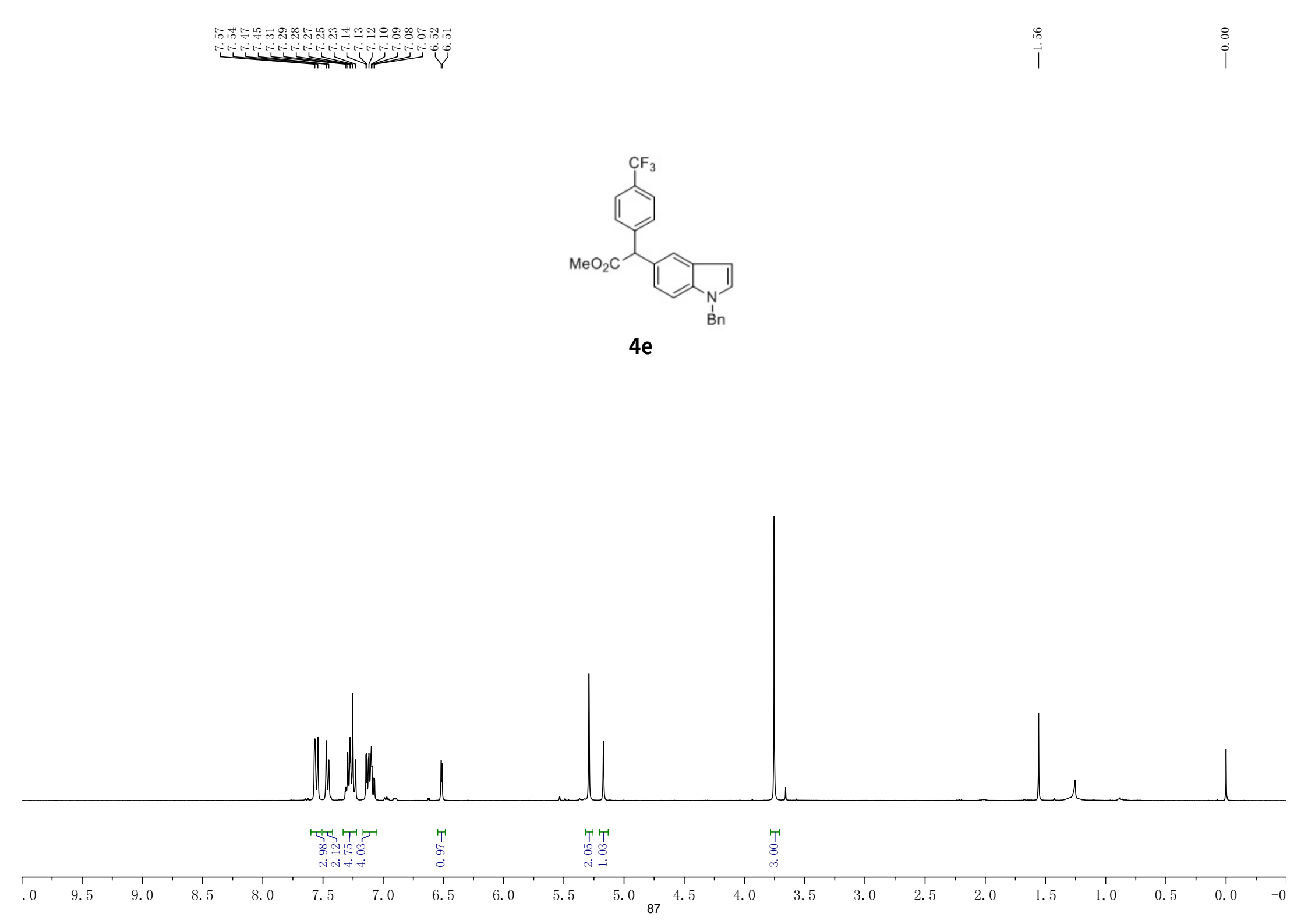
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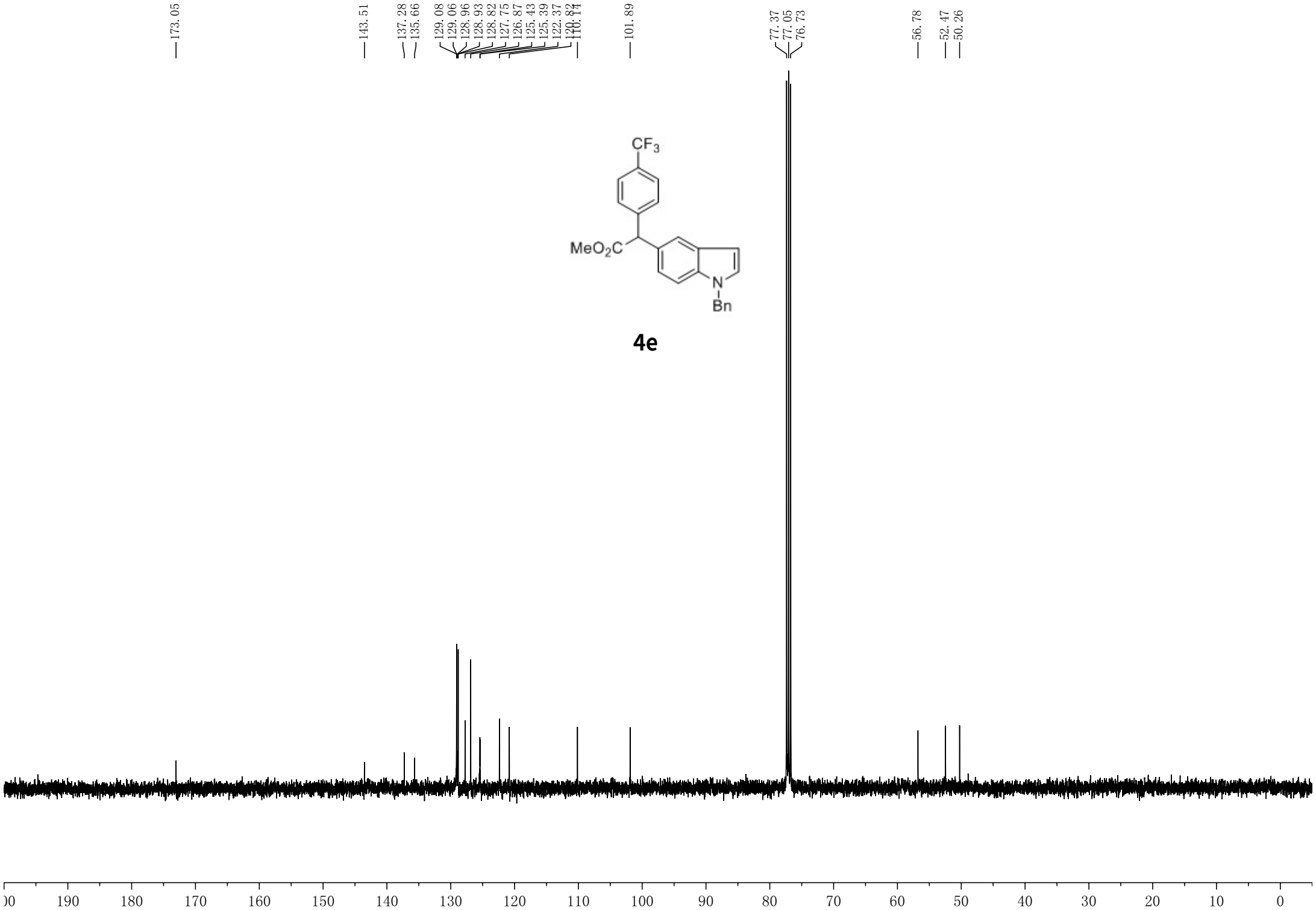
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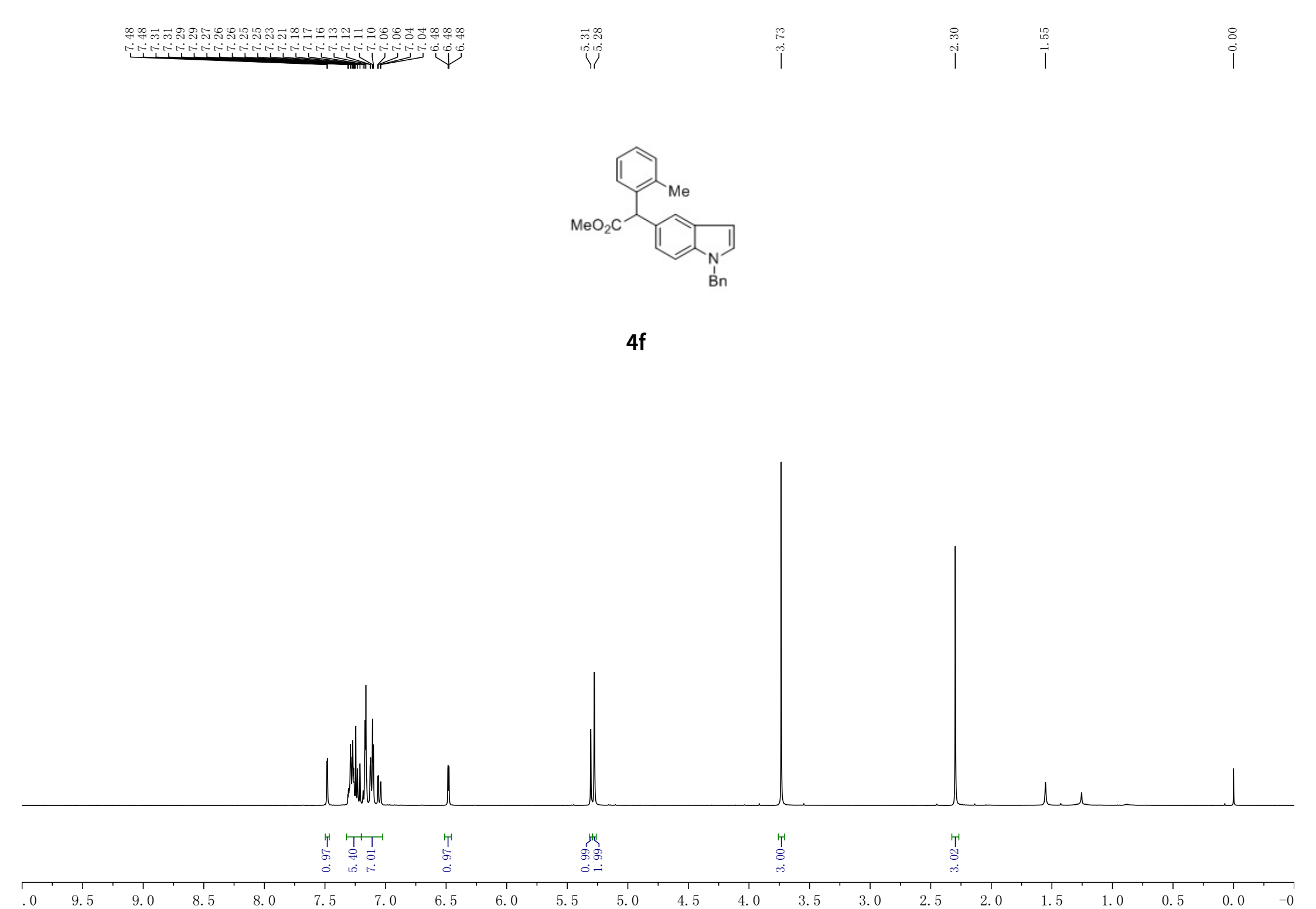
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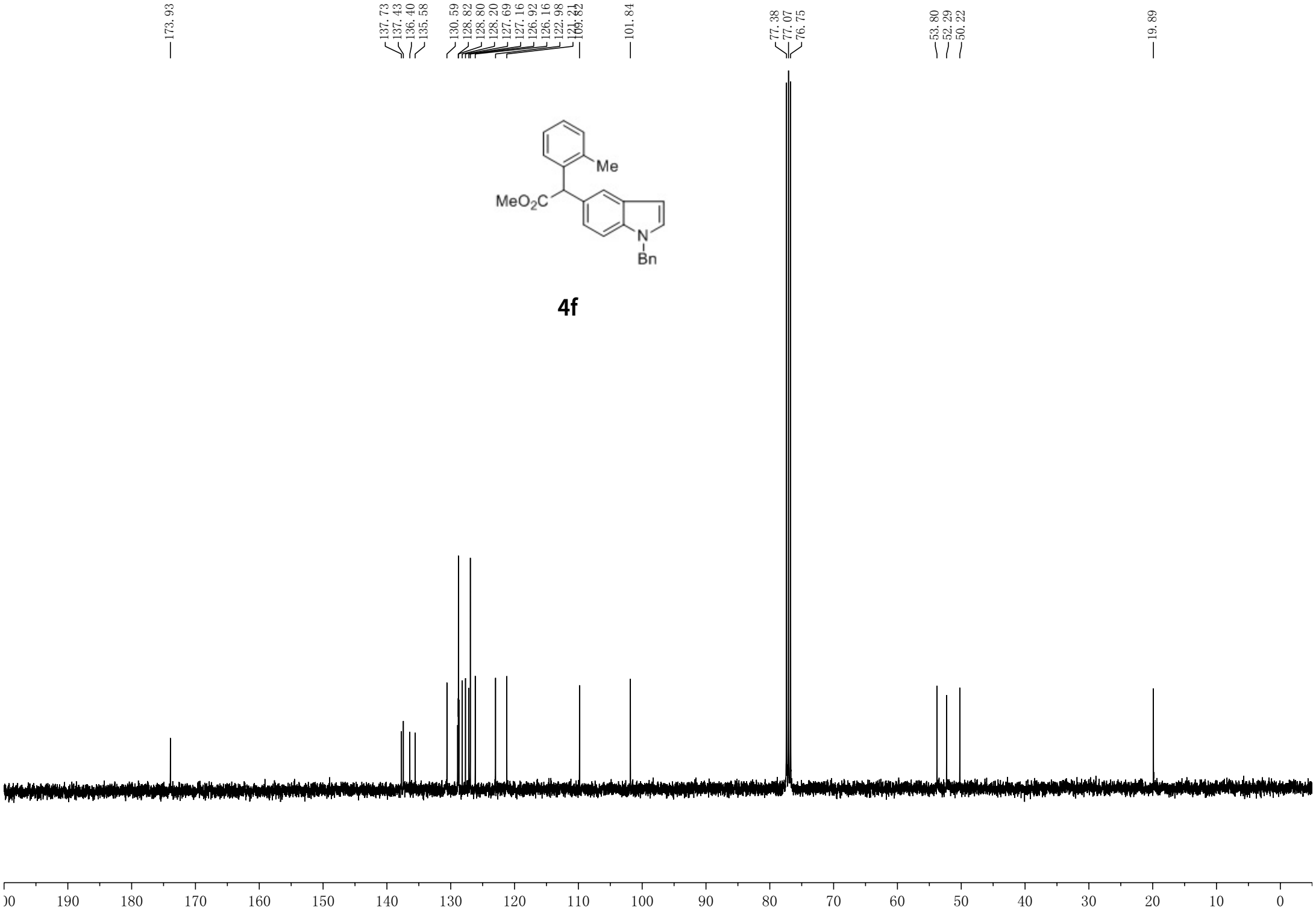
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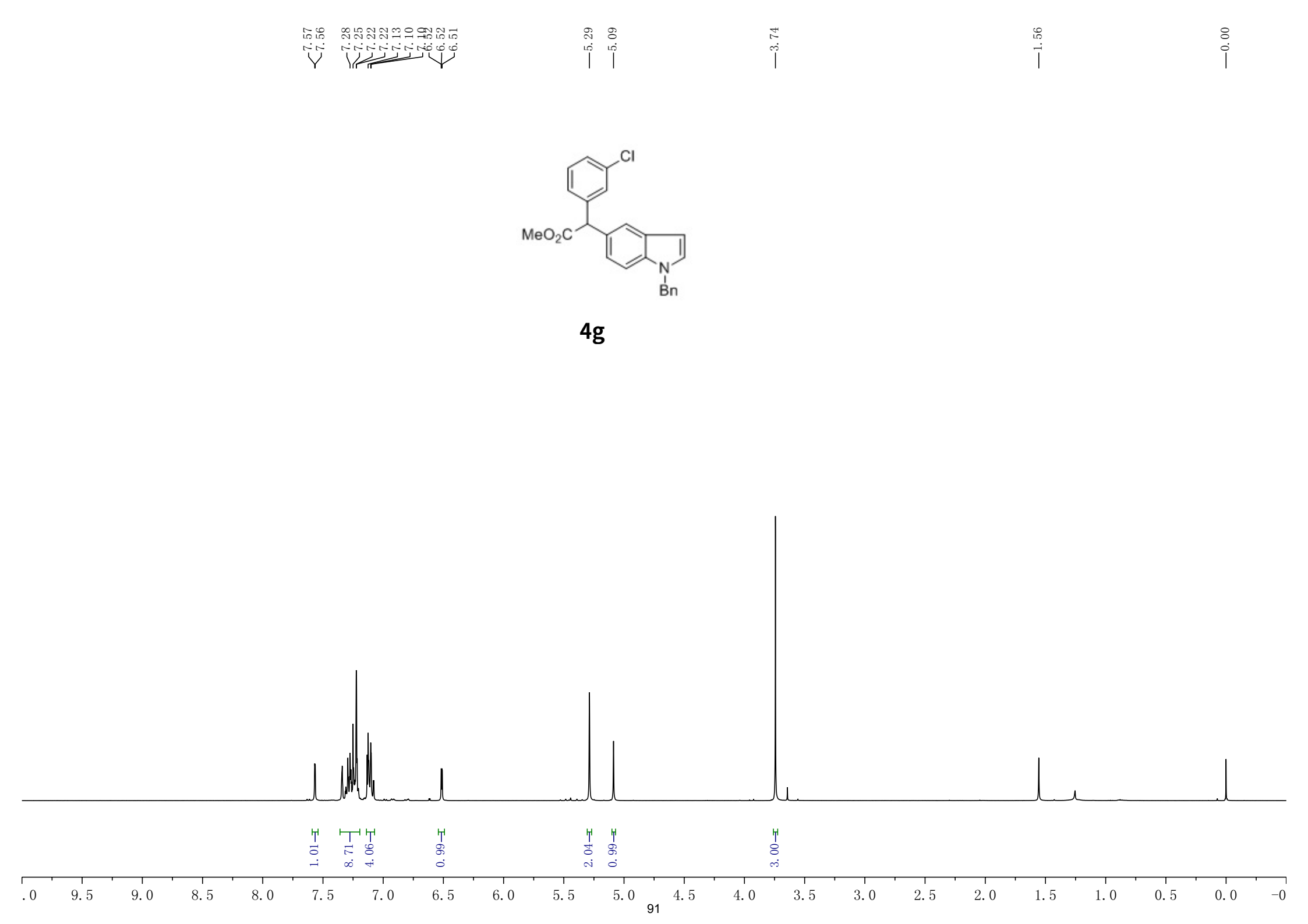
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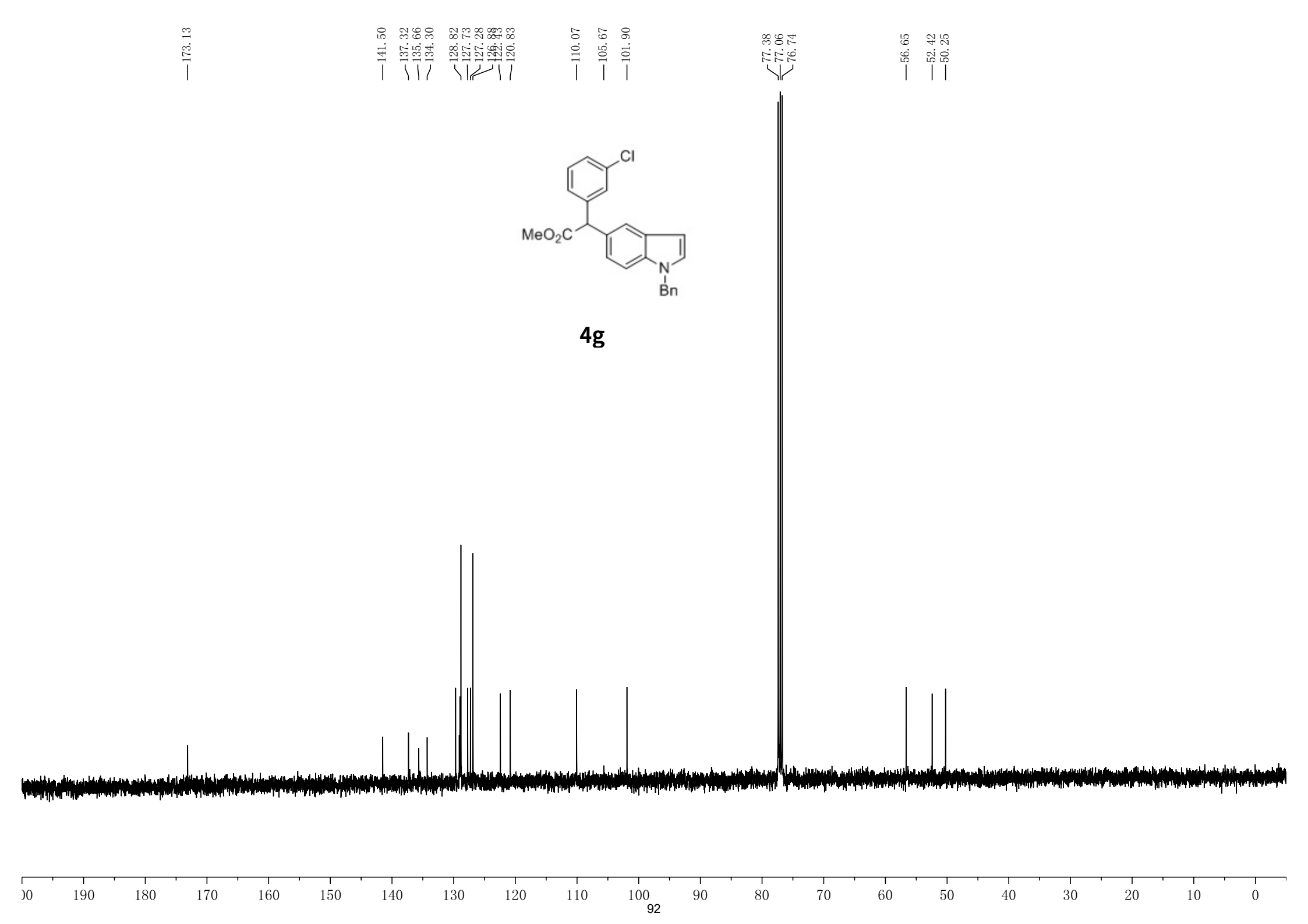
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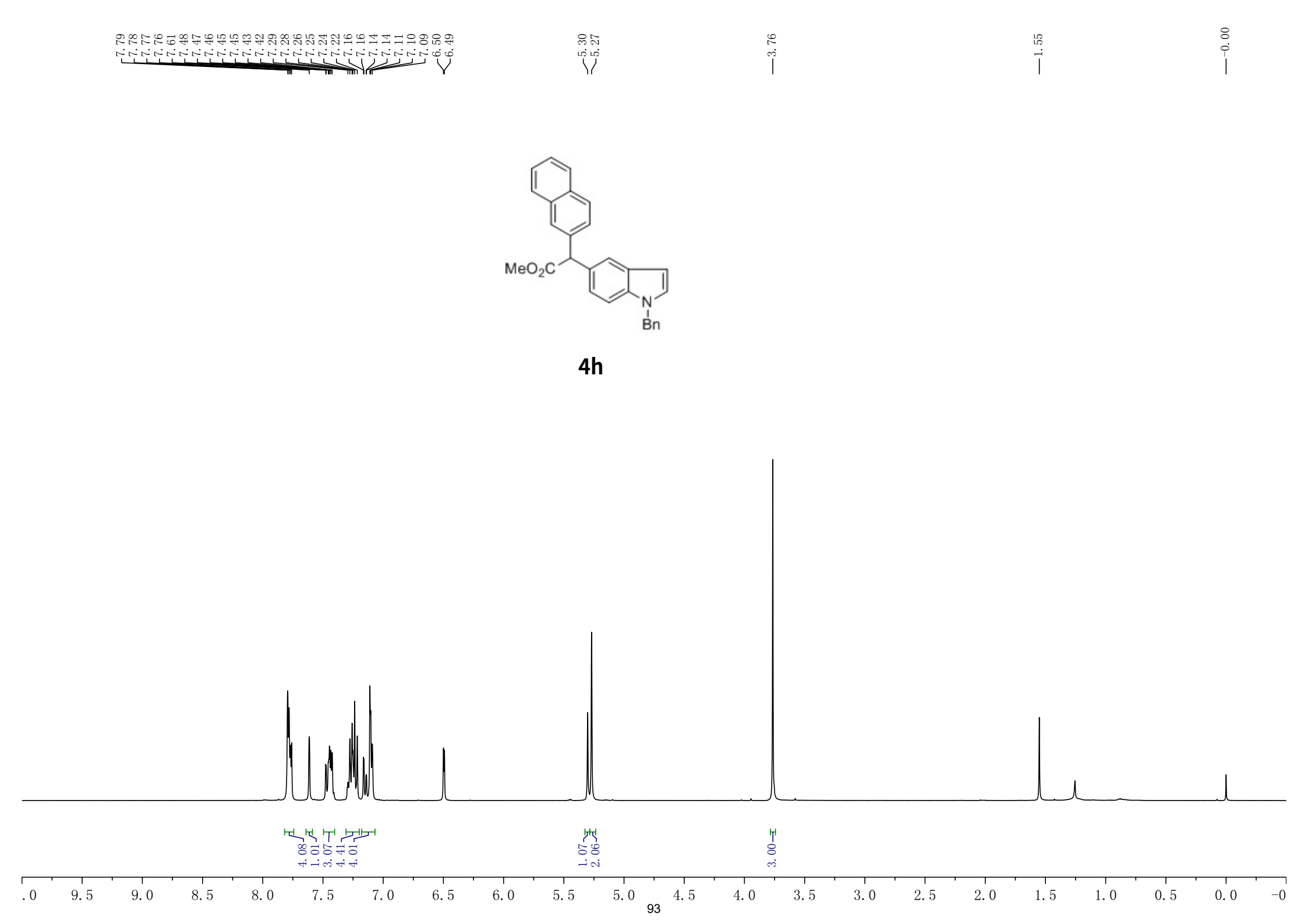
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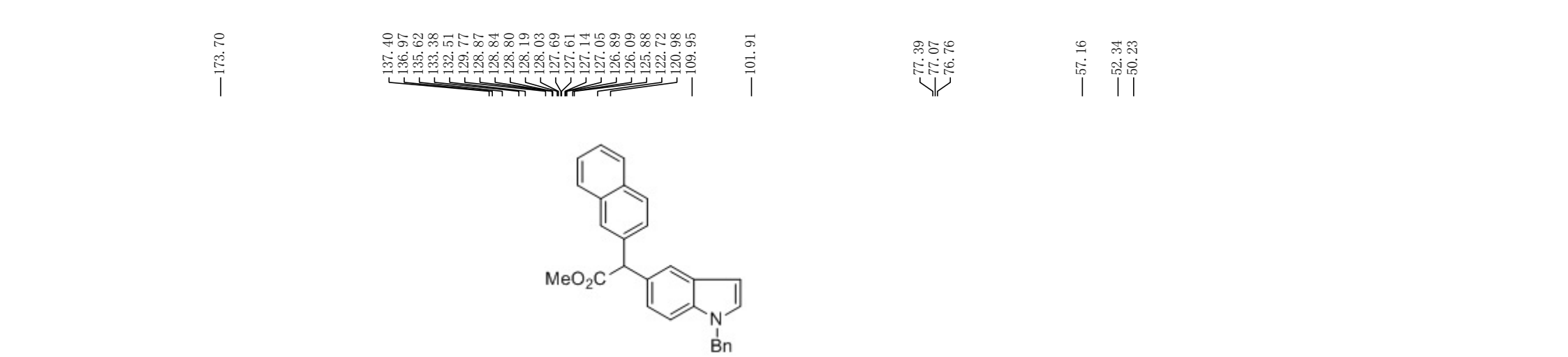
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Bn

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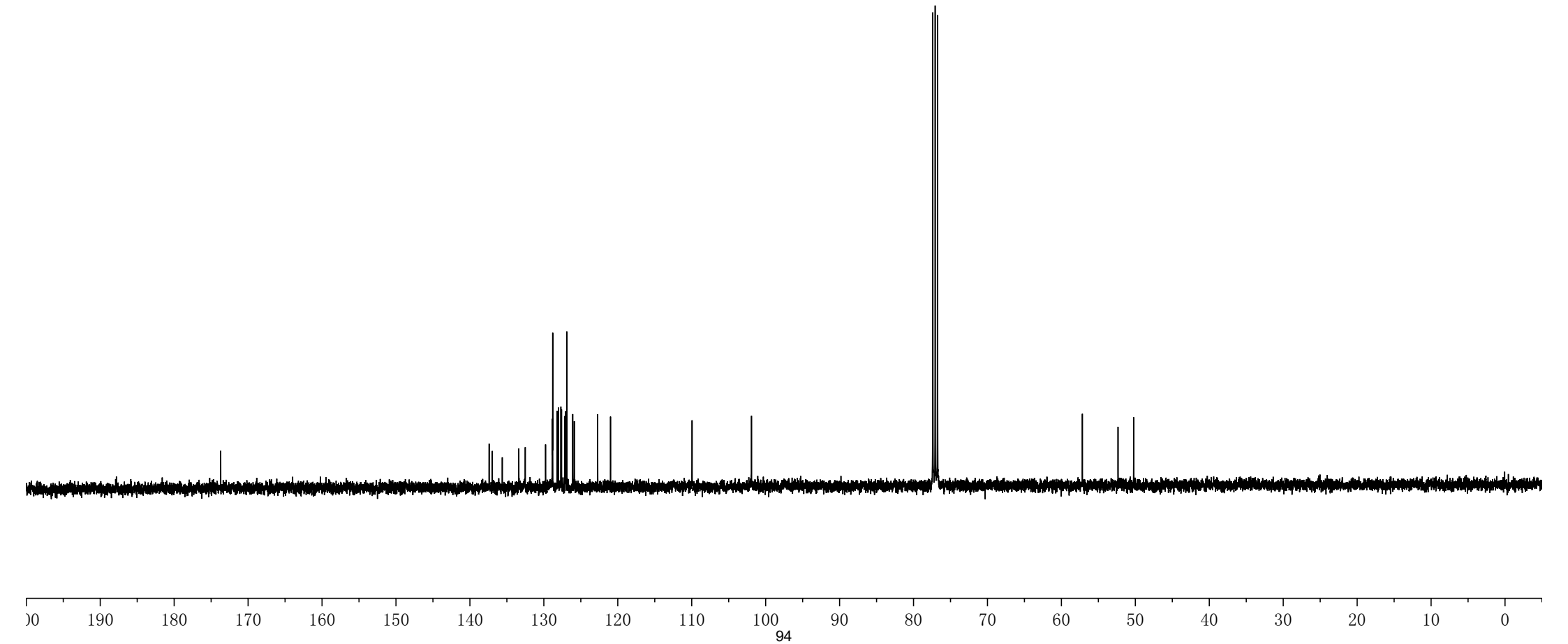
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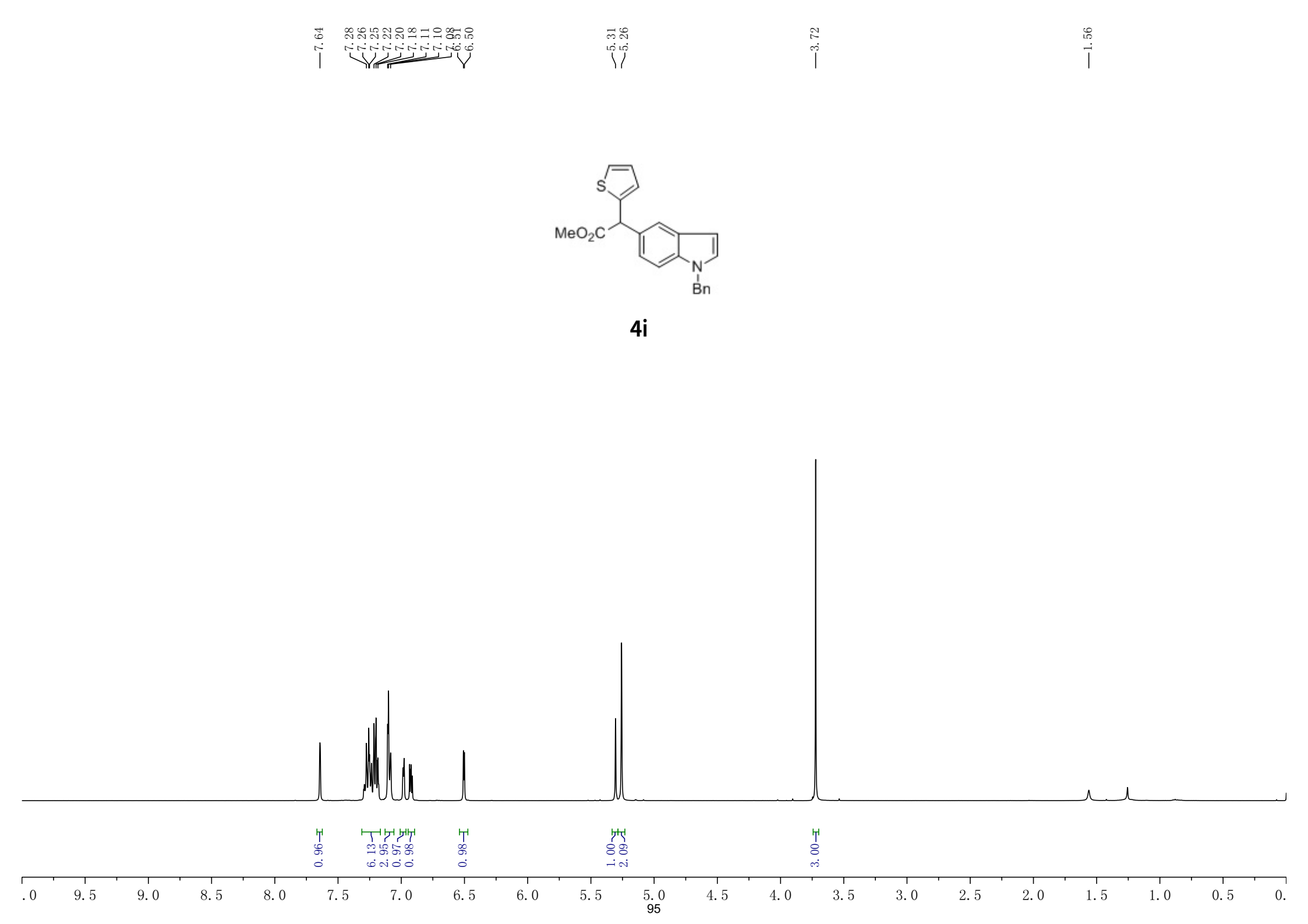
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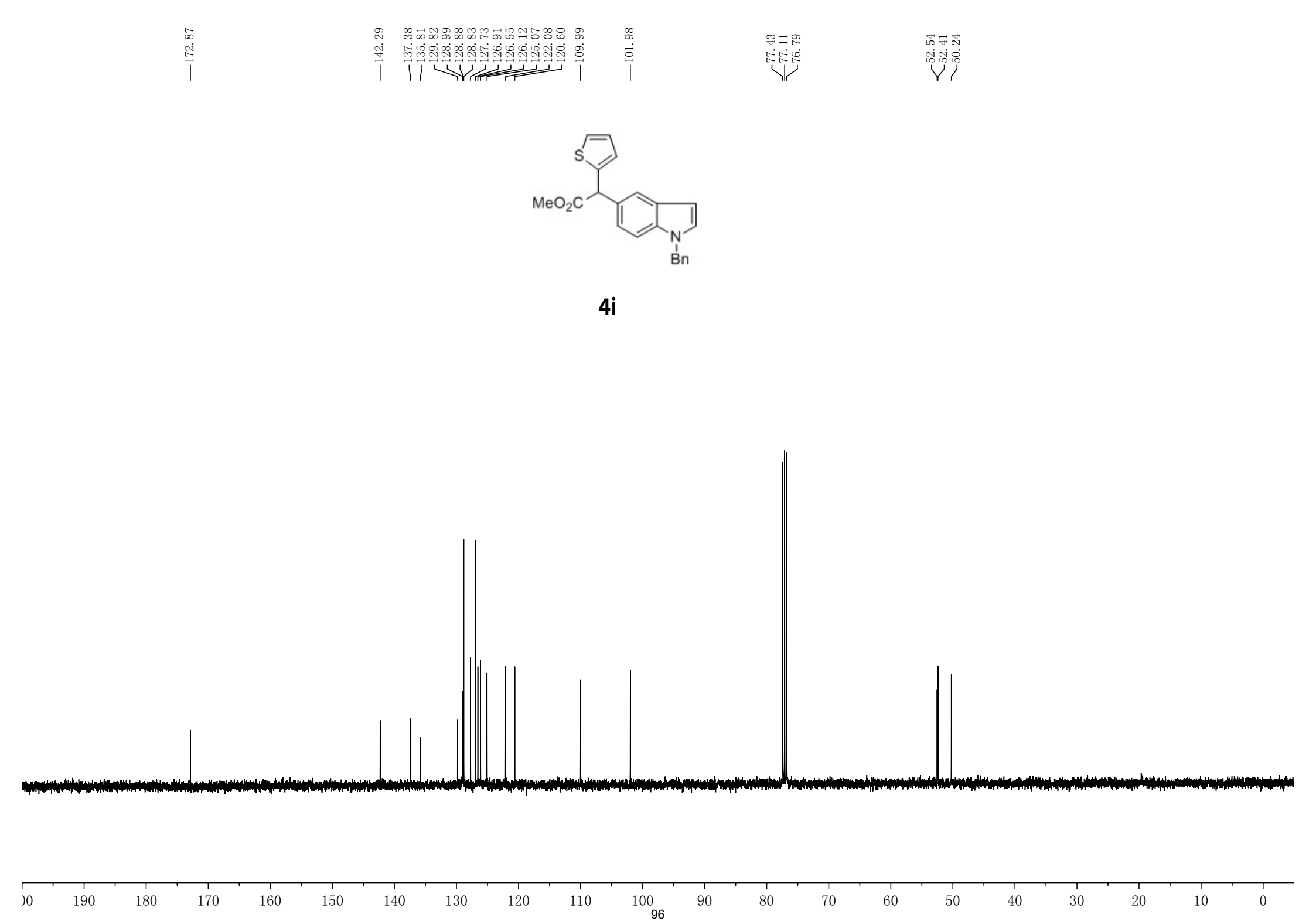
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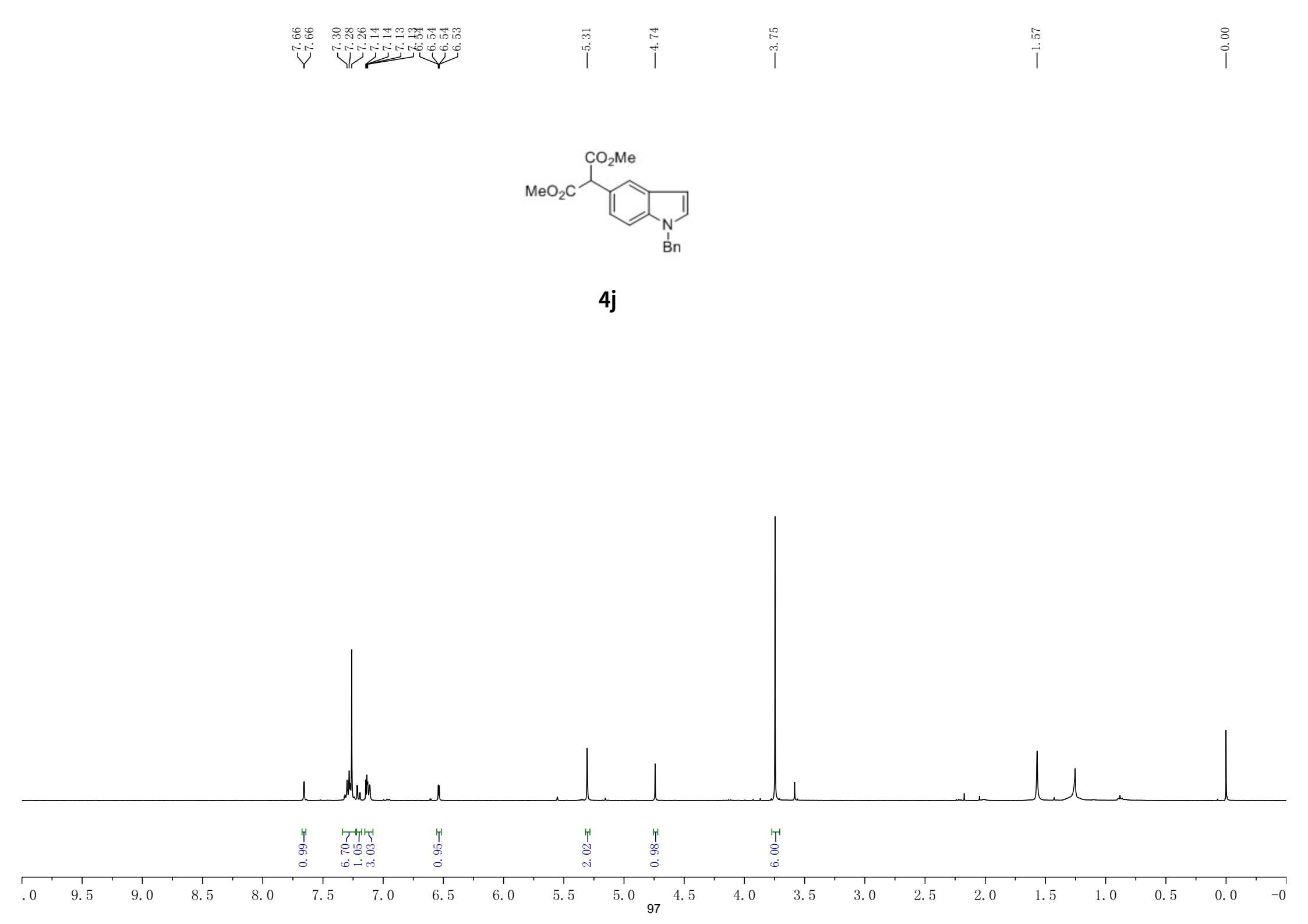
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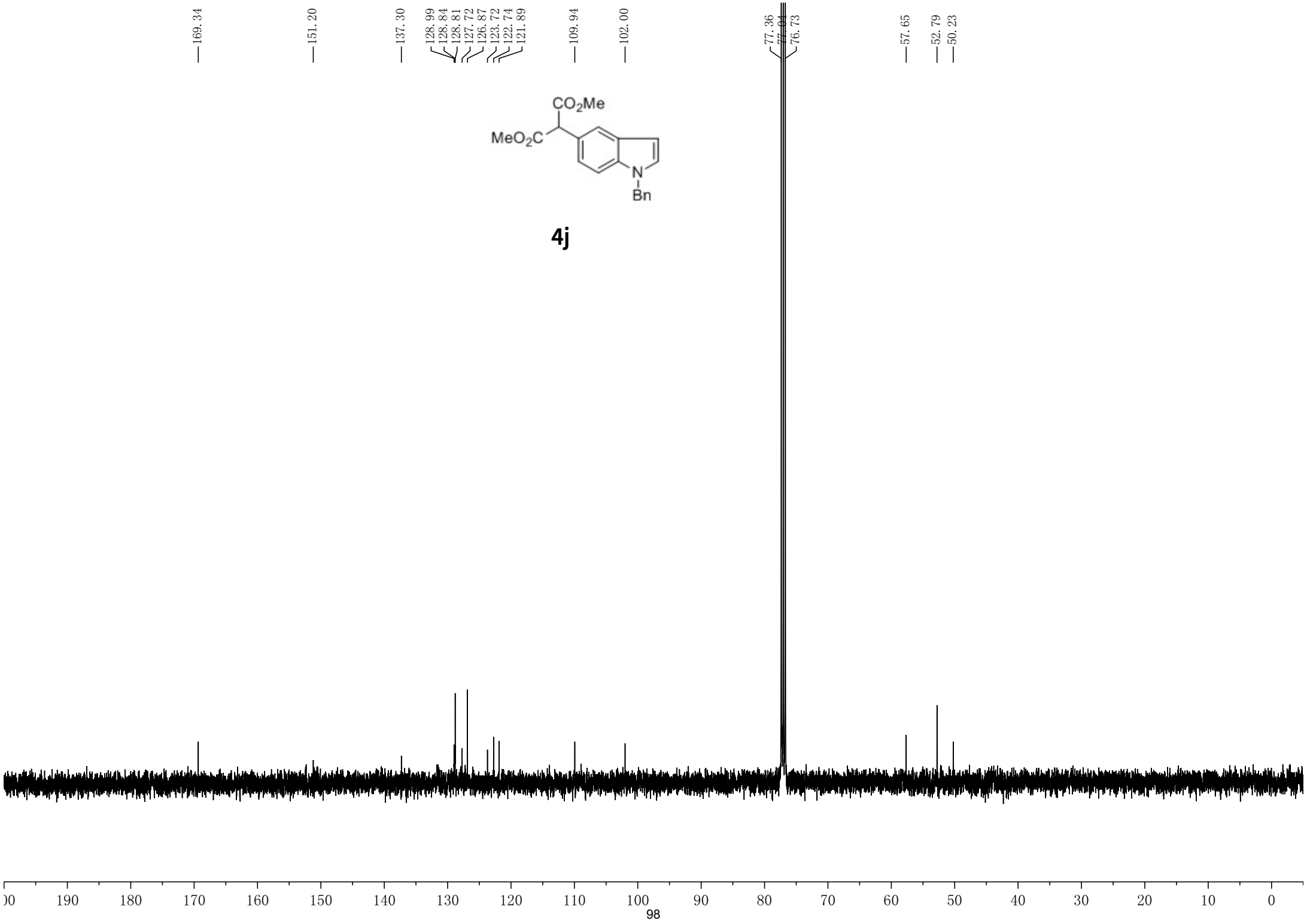
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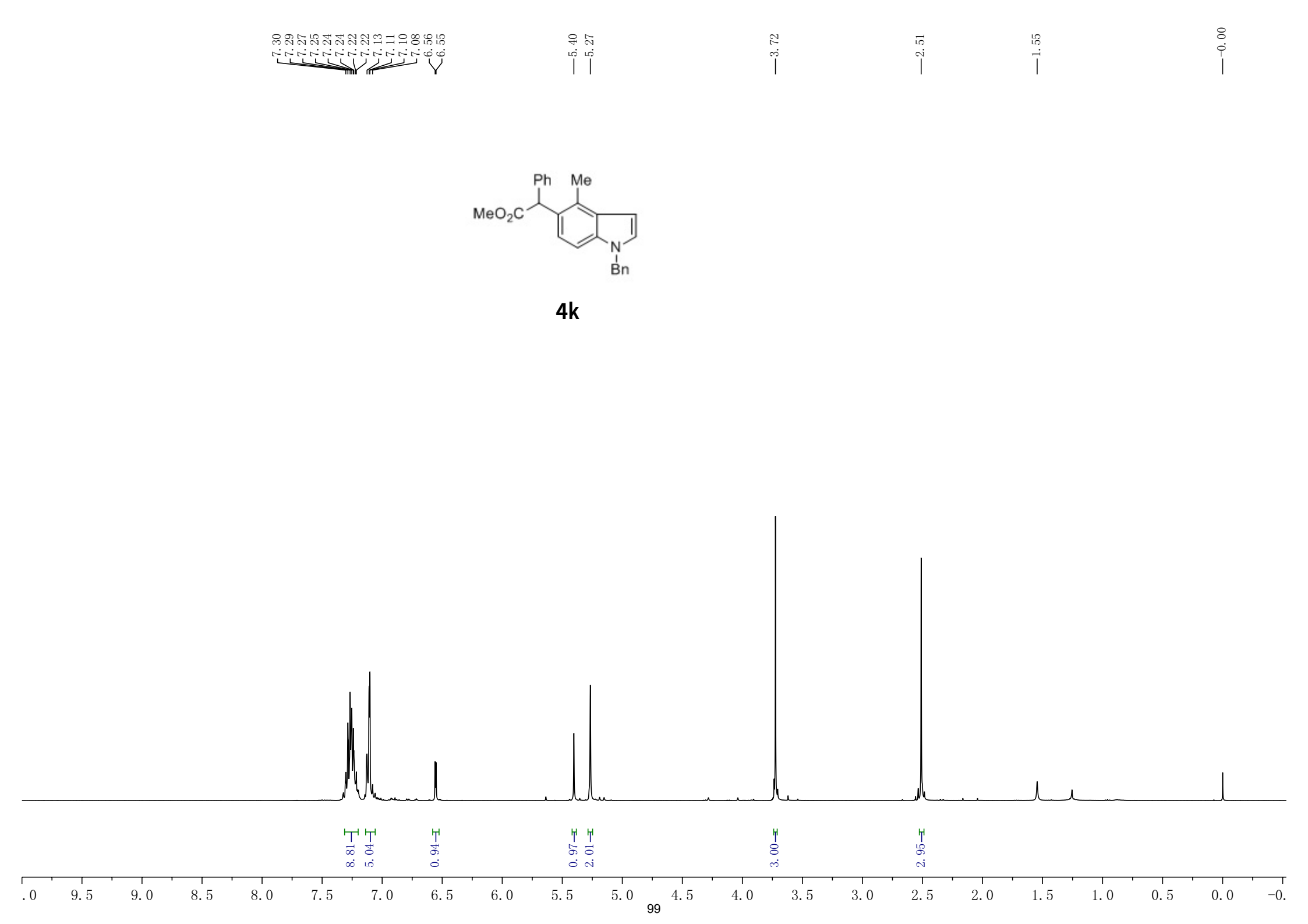
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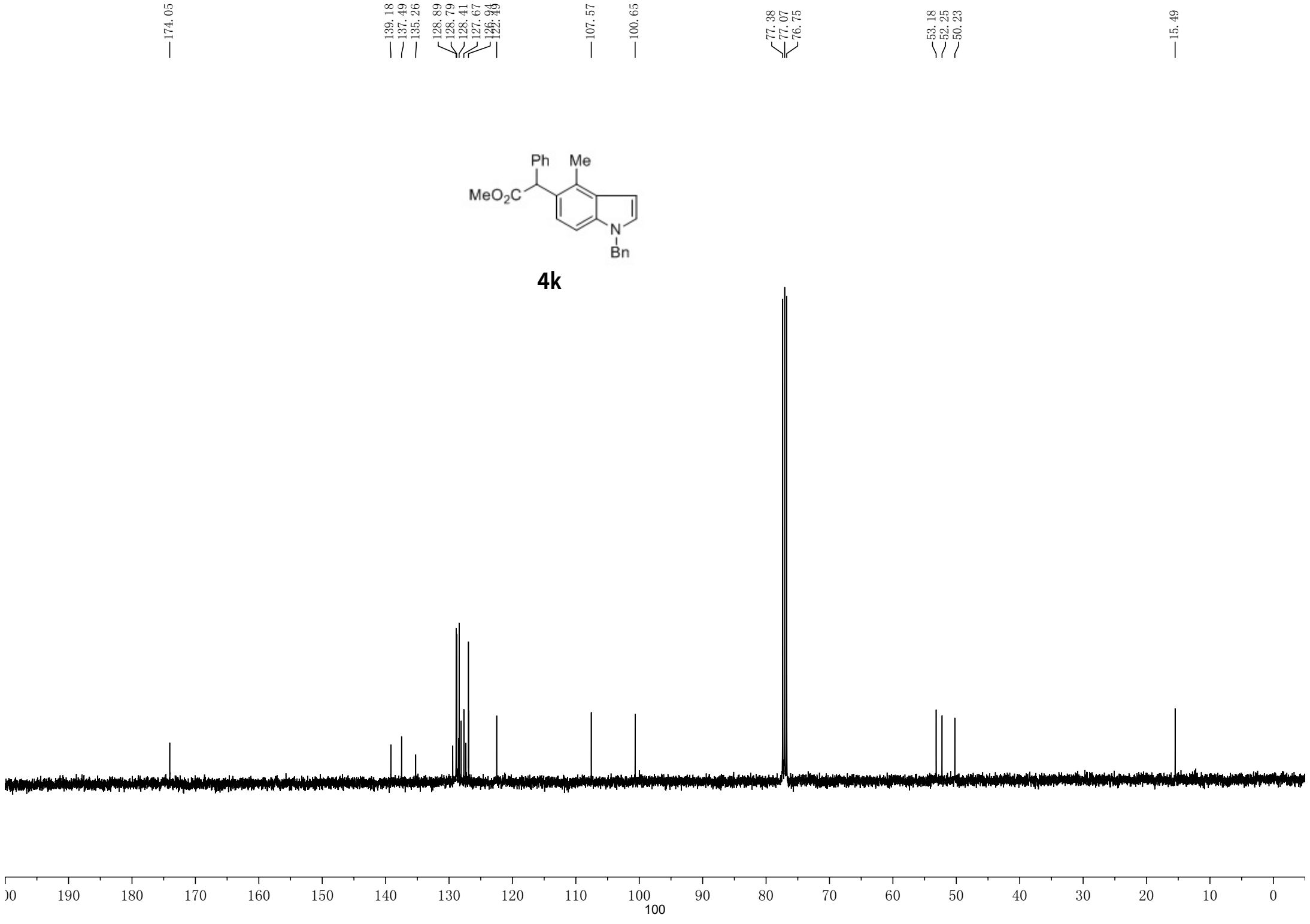
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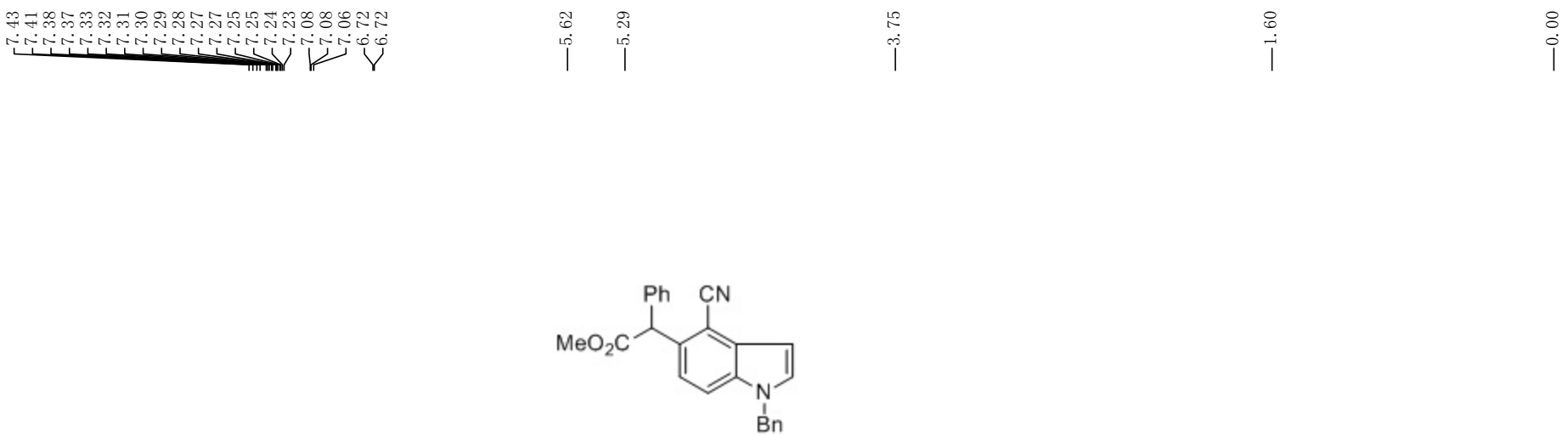
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4l

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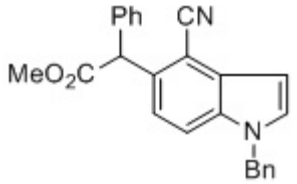

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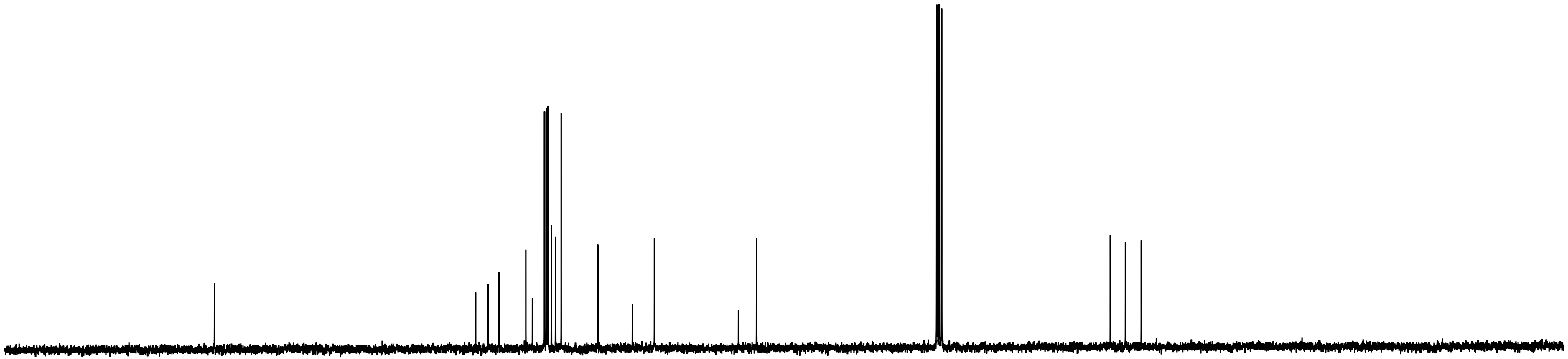

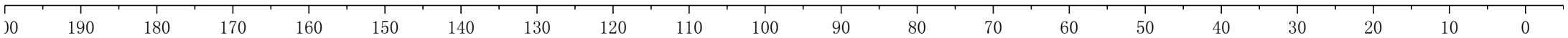


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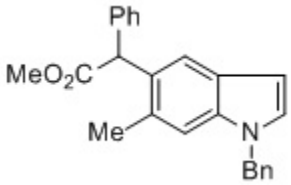
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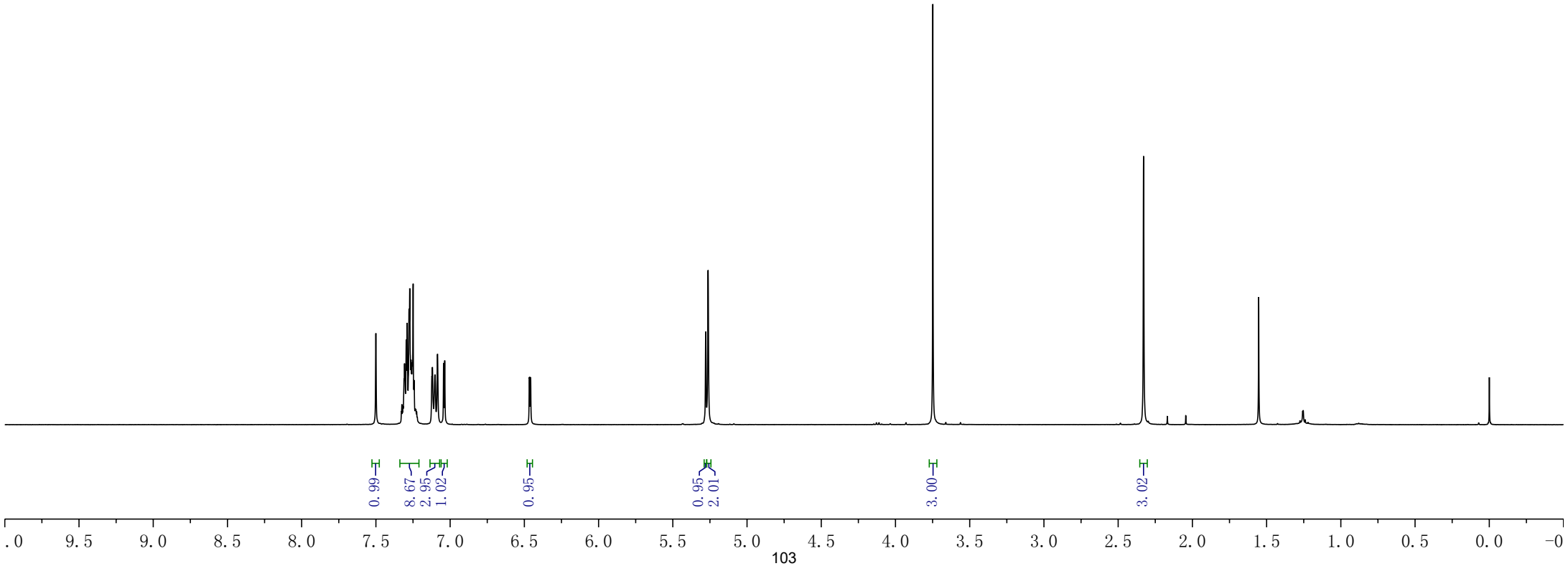
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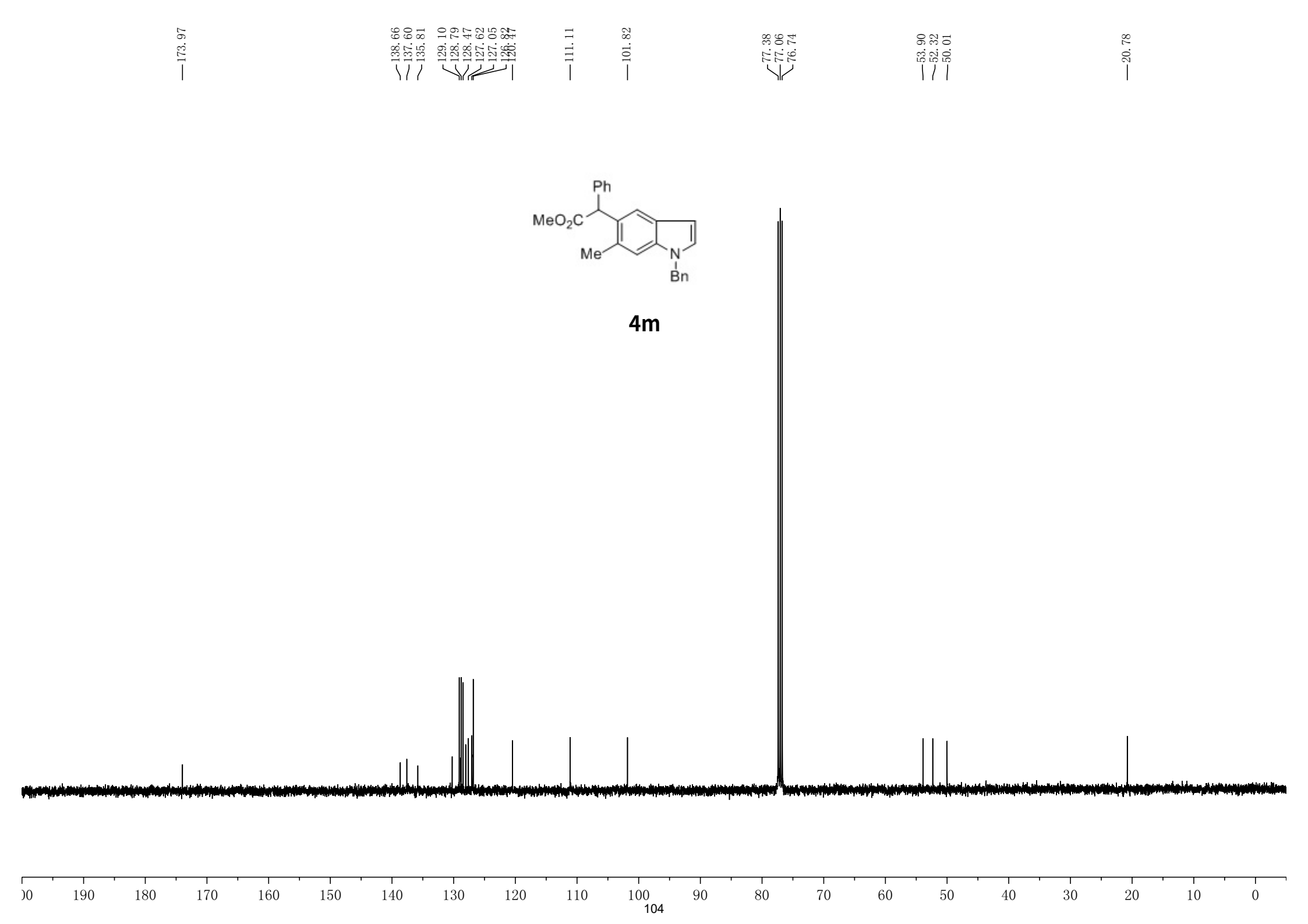
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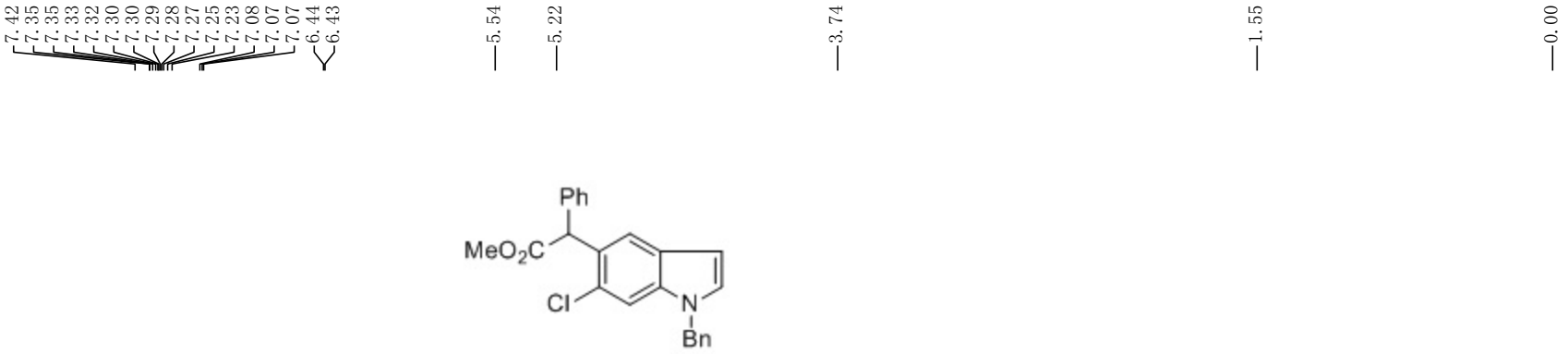
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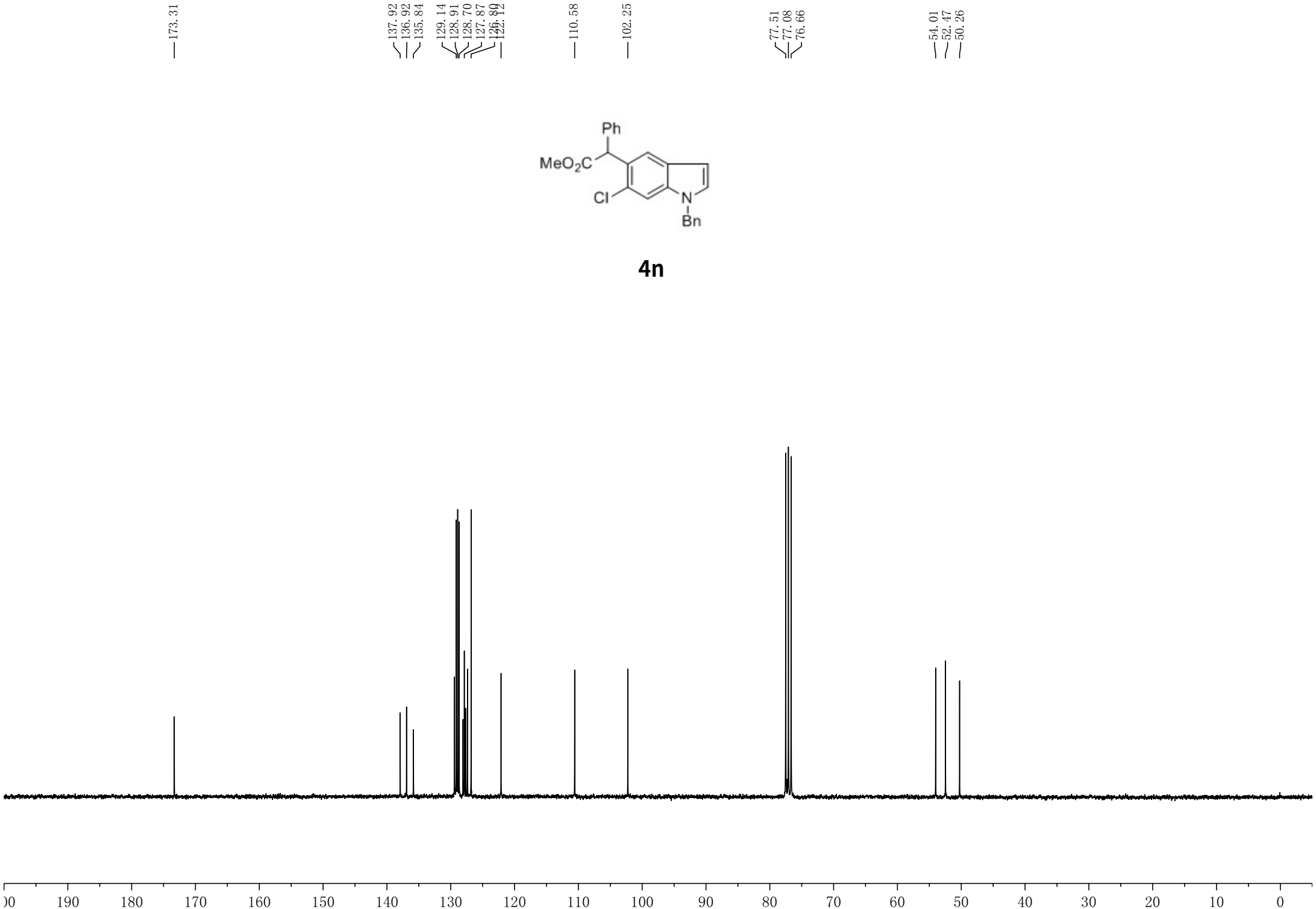
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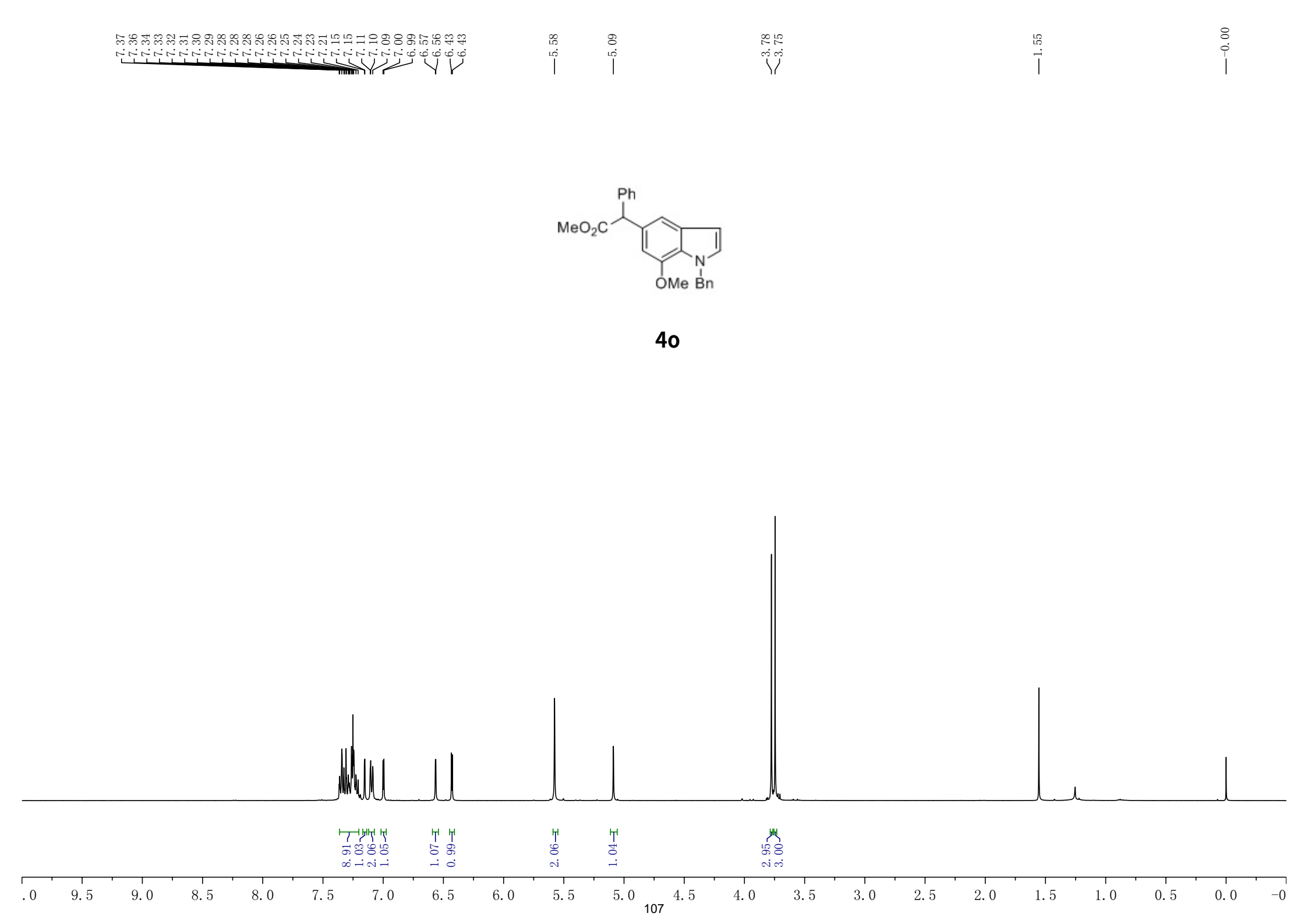
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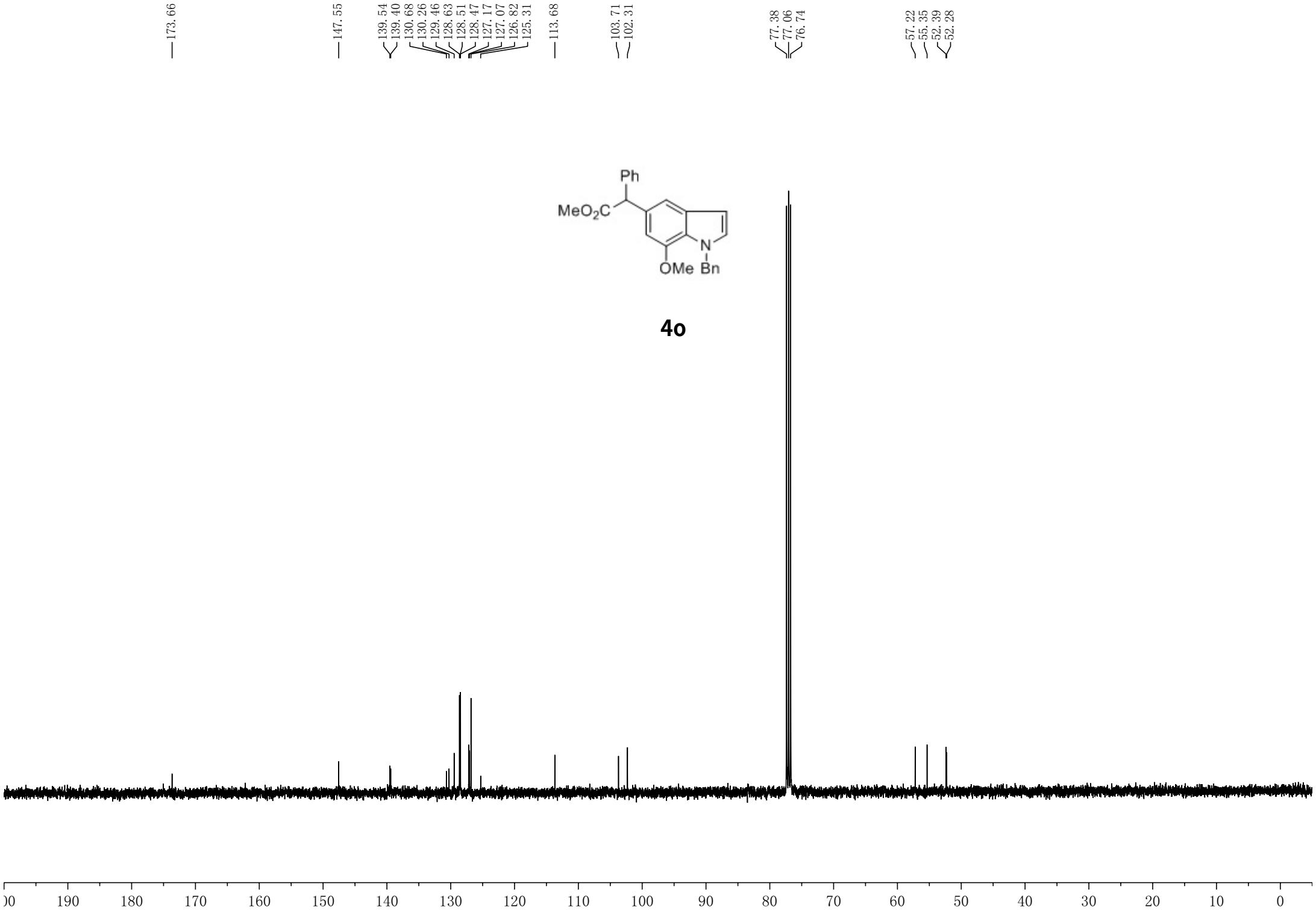
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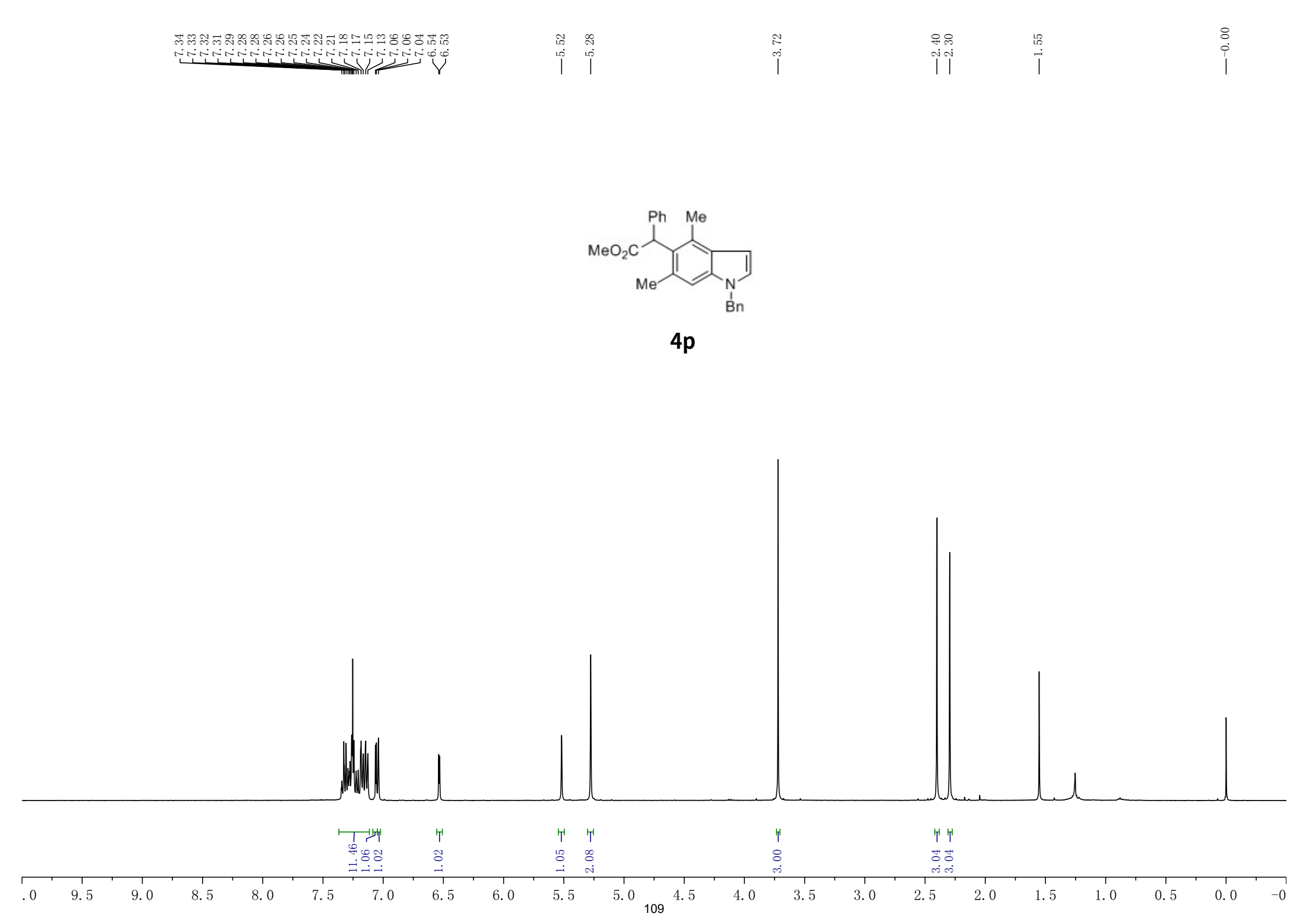
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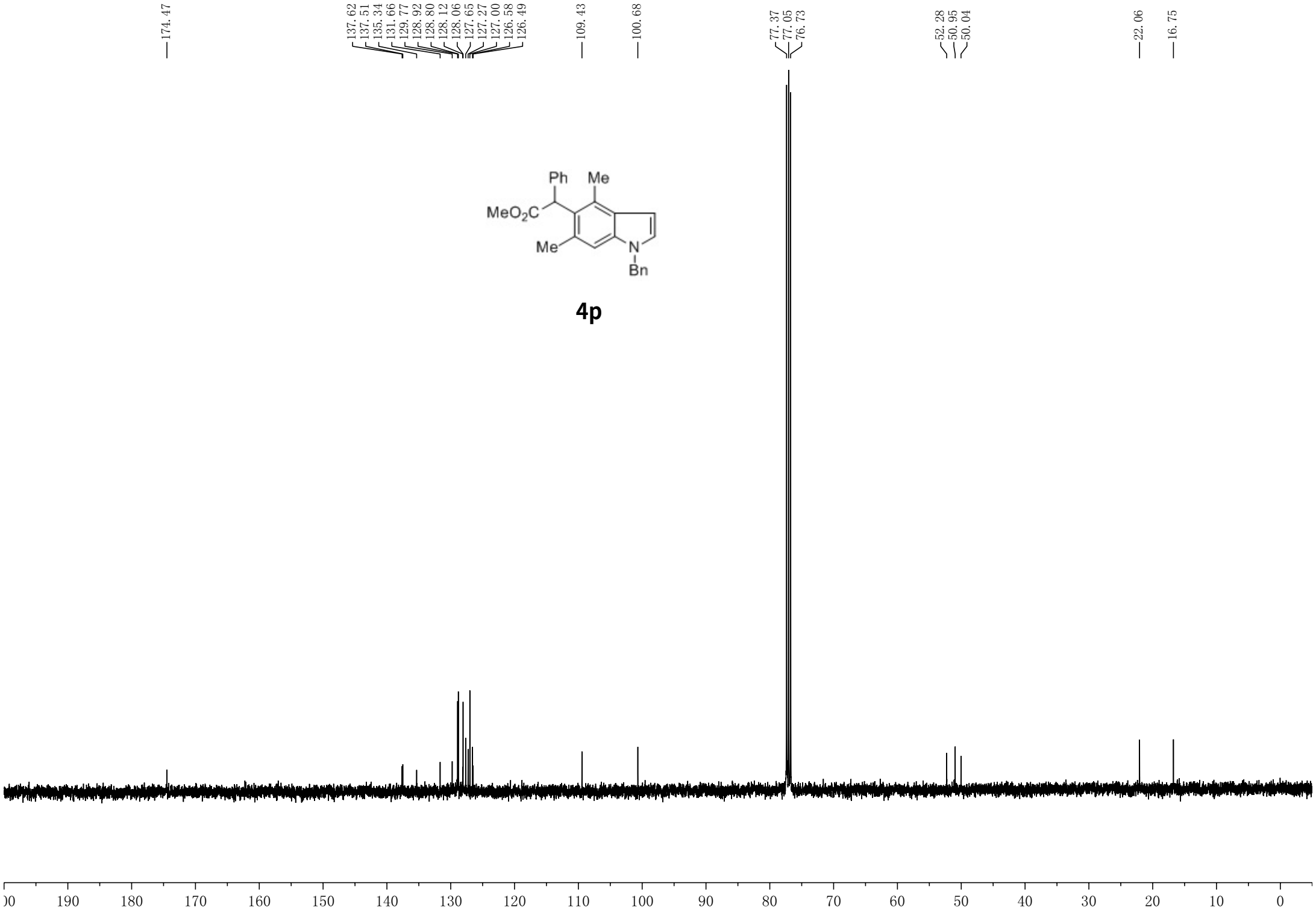
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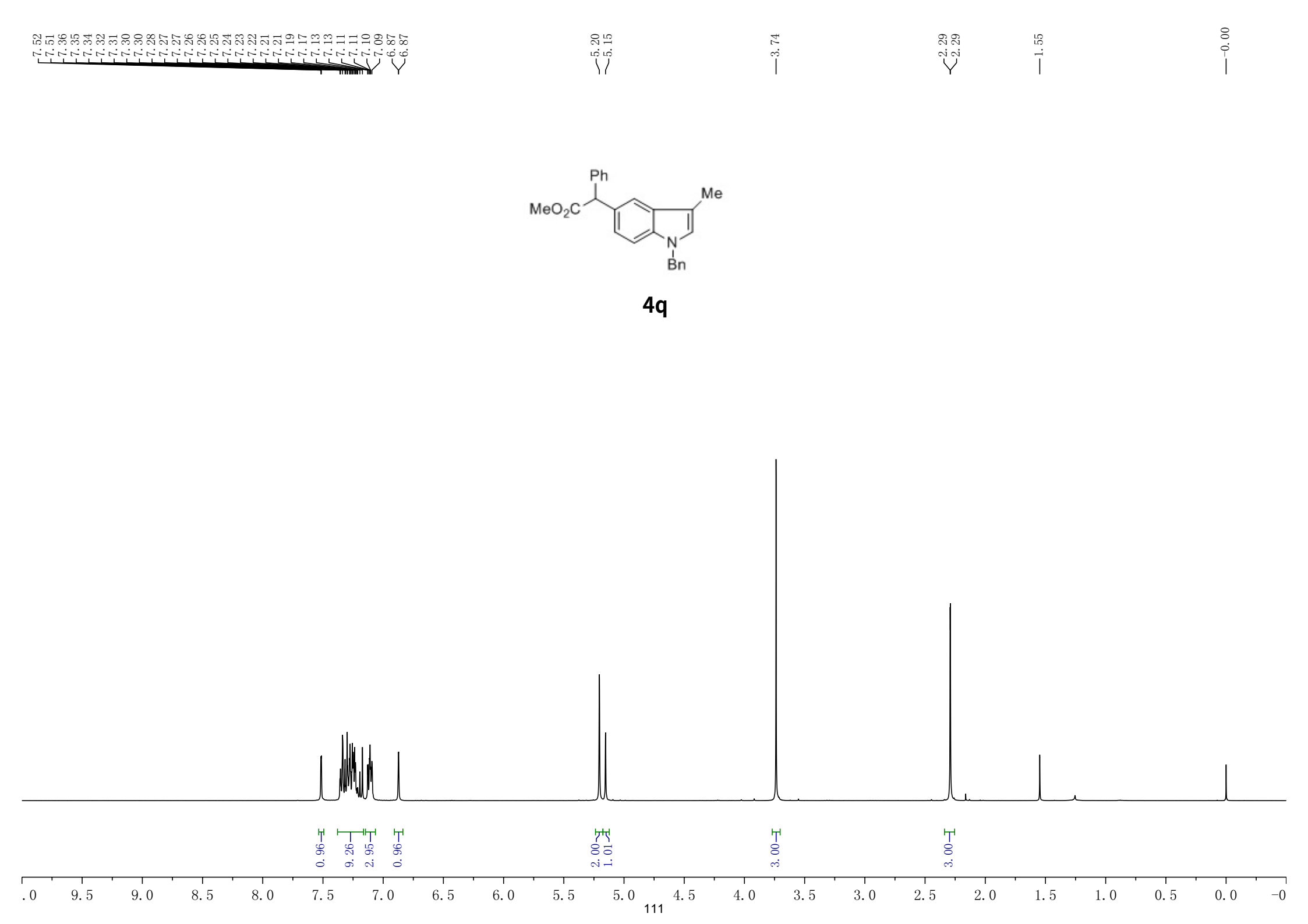
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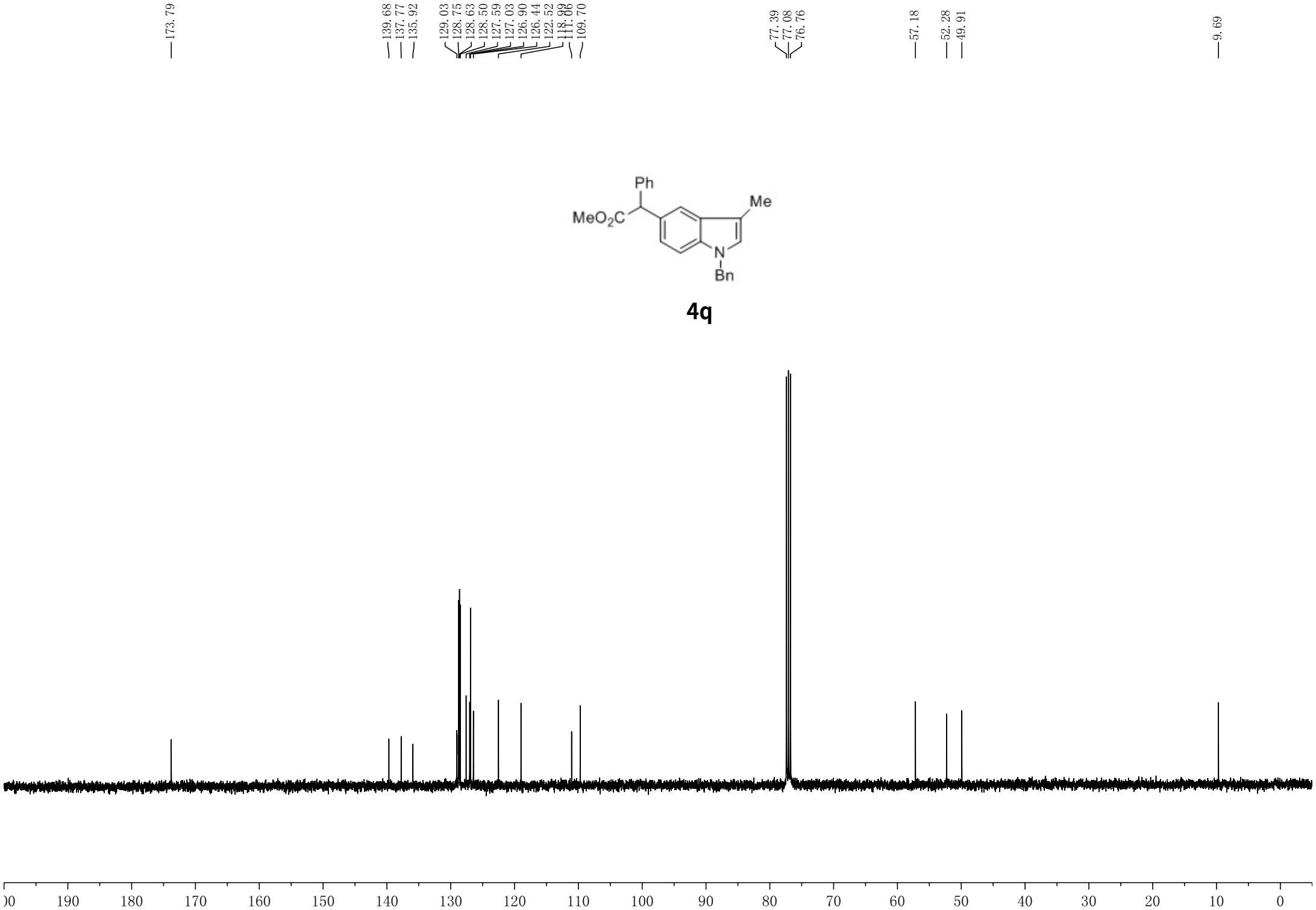
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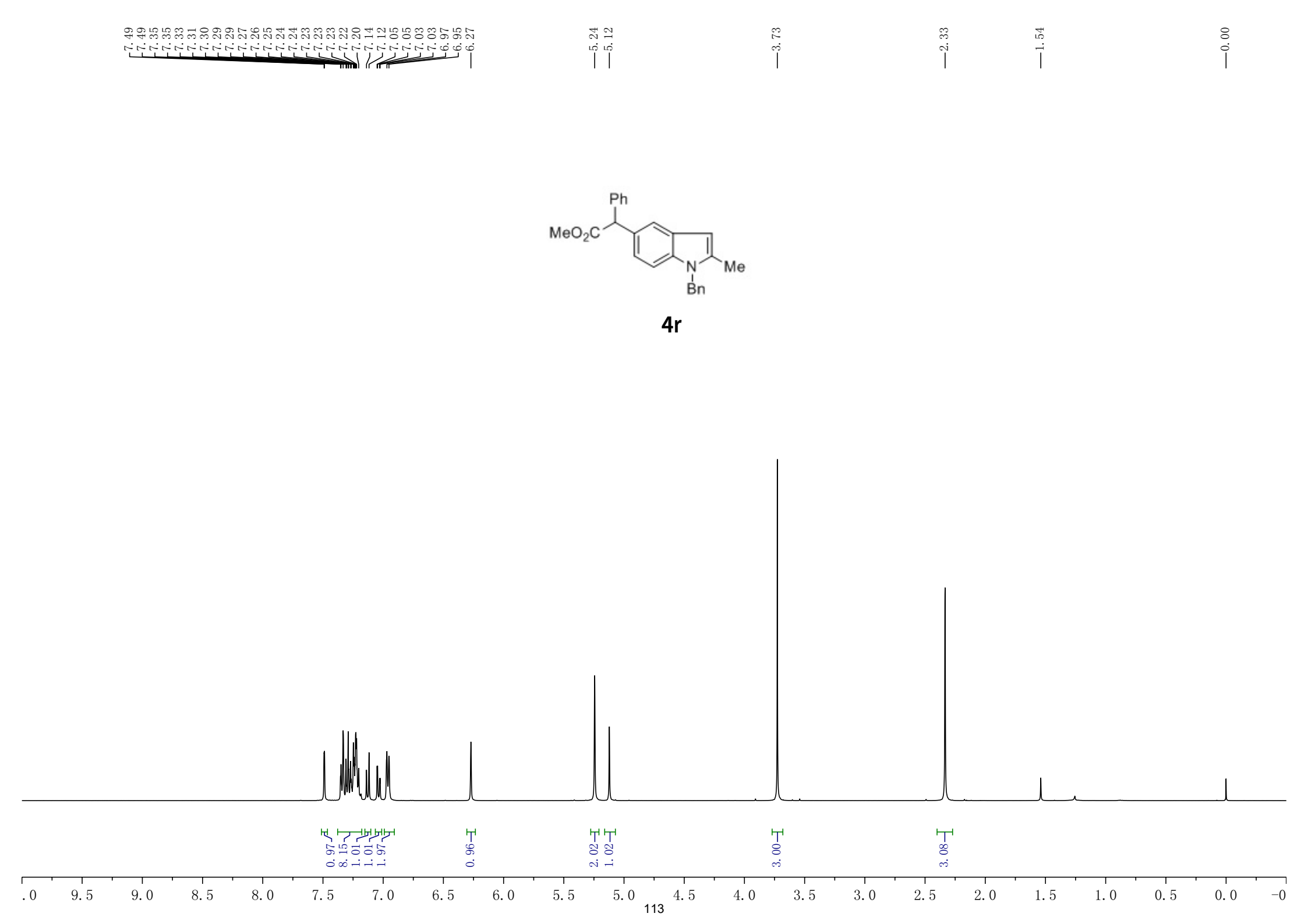
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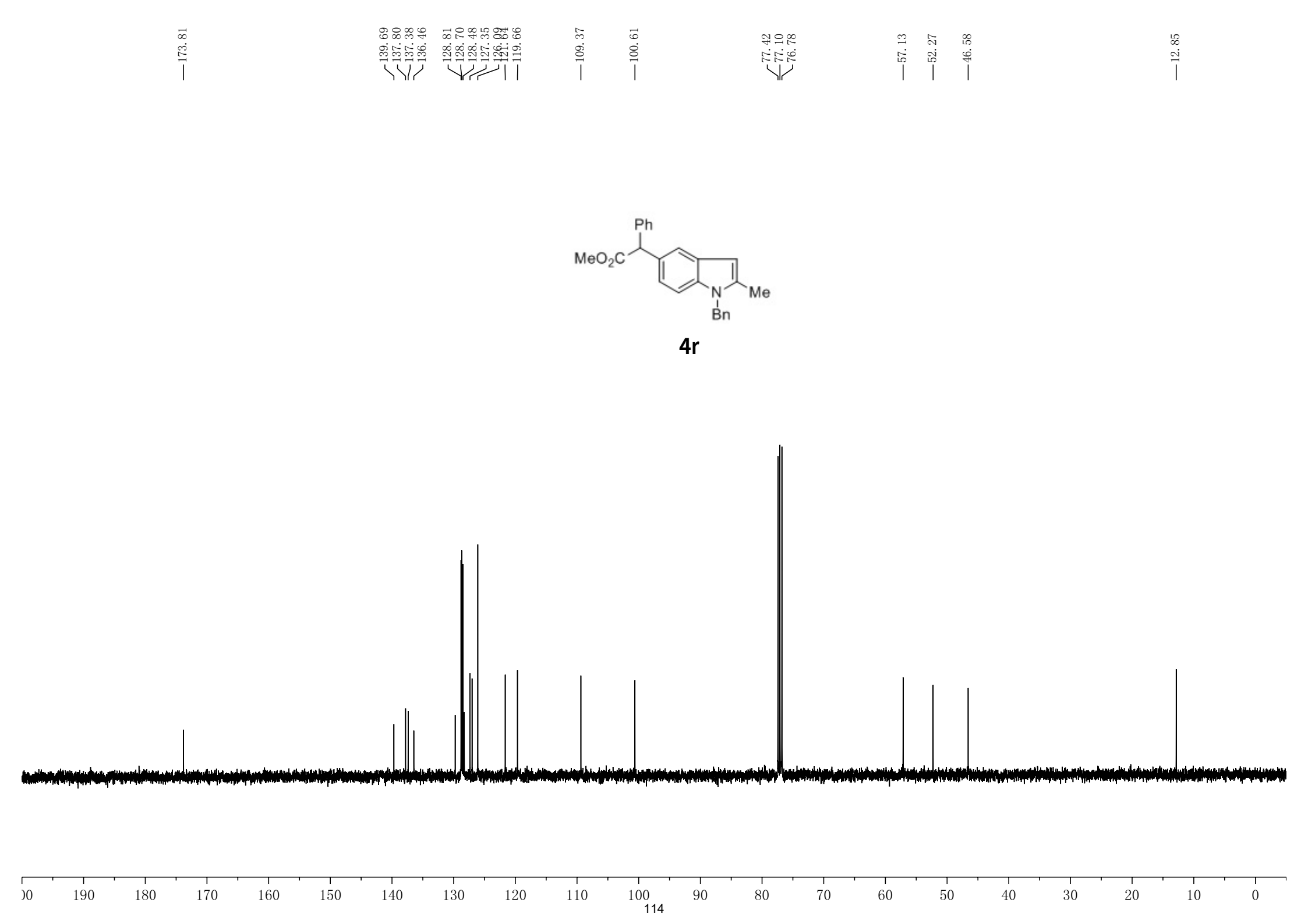
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Me
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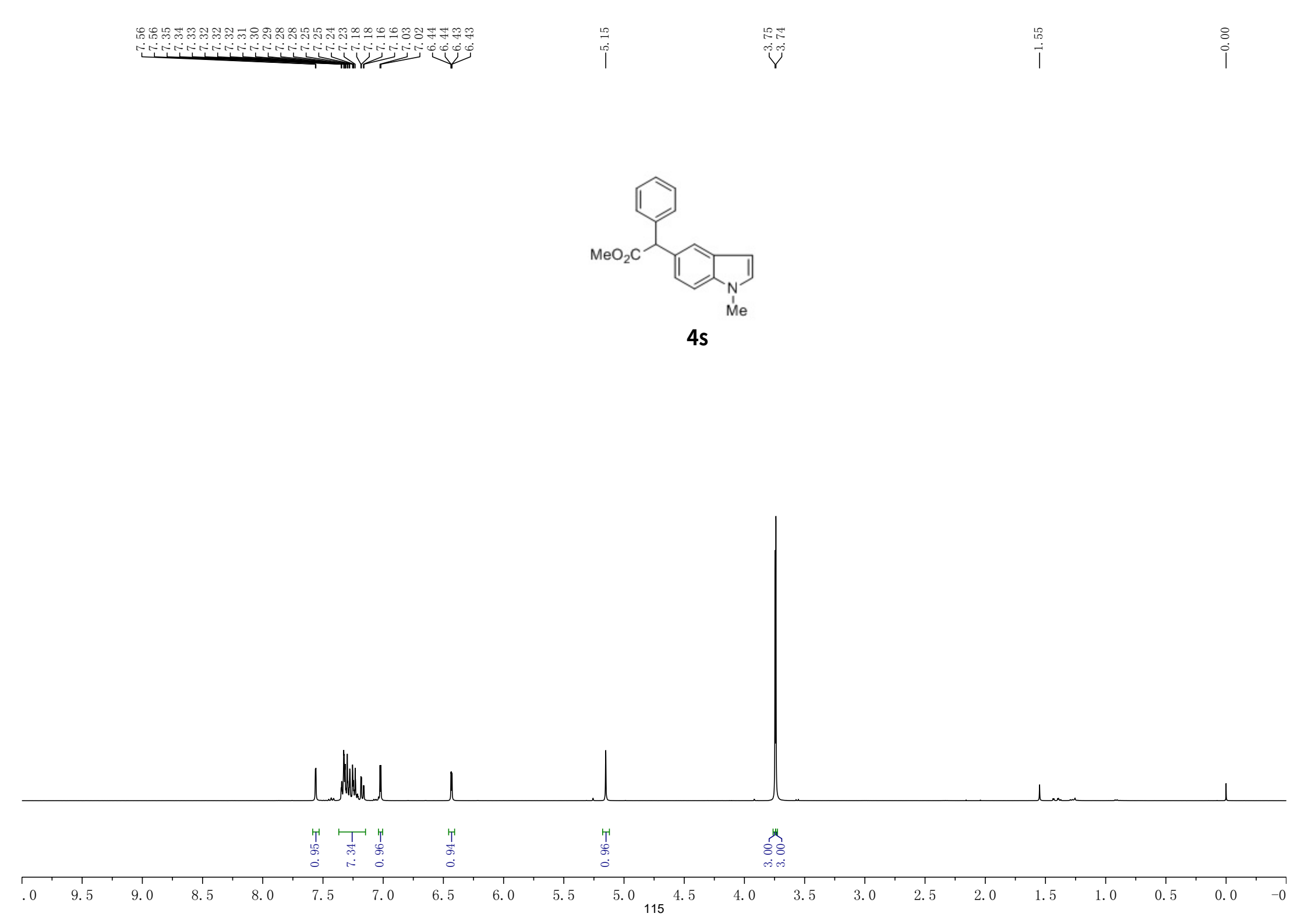
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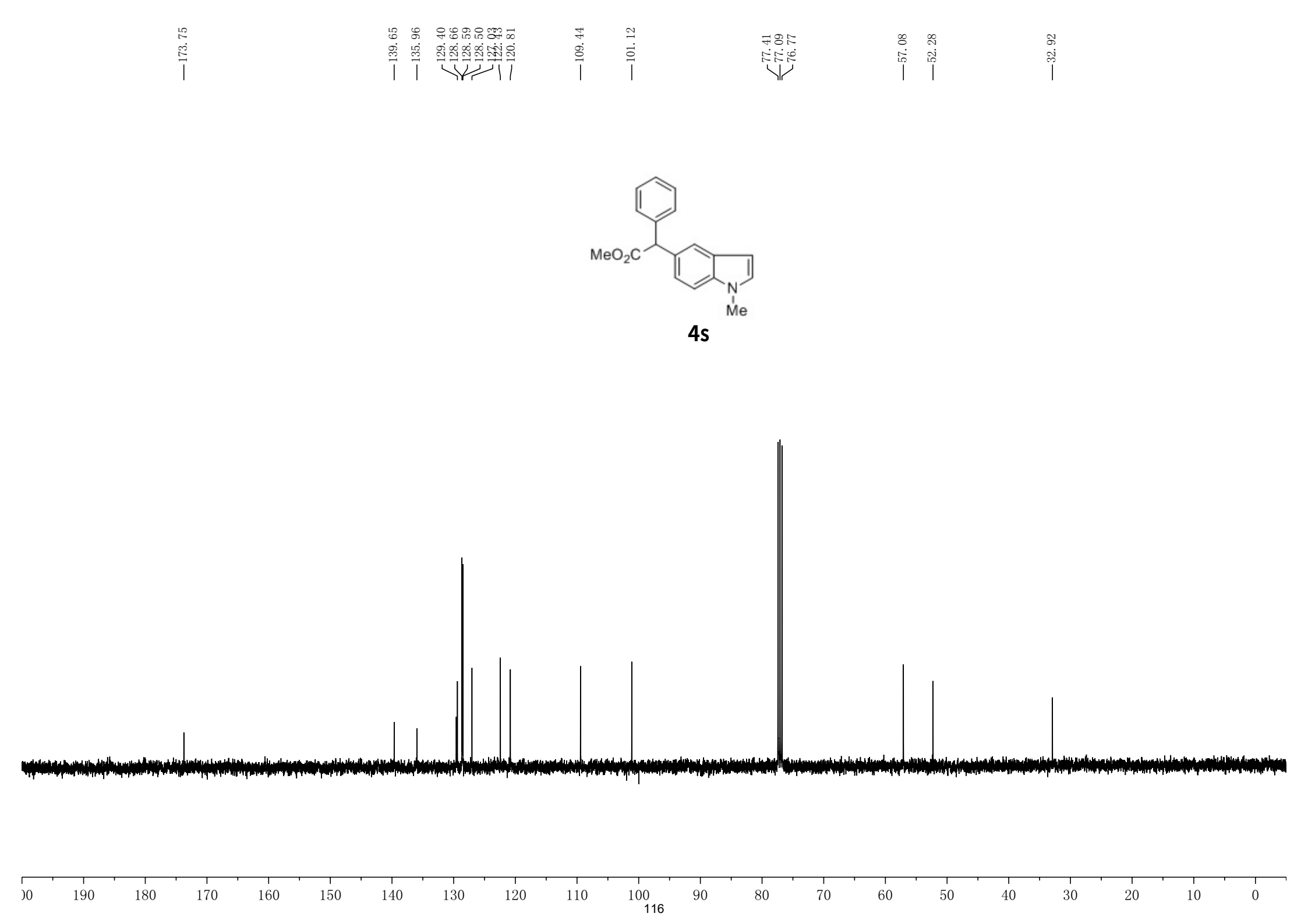
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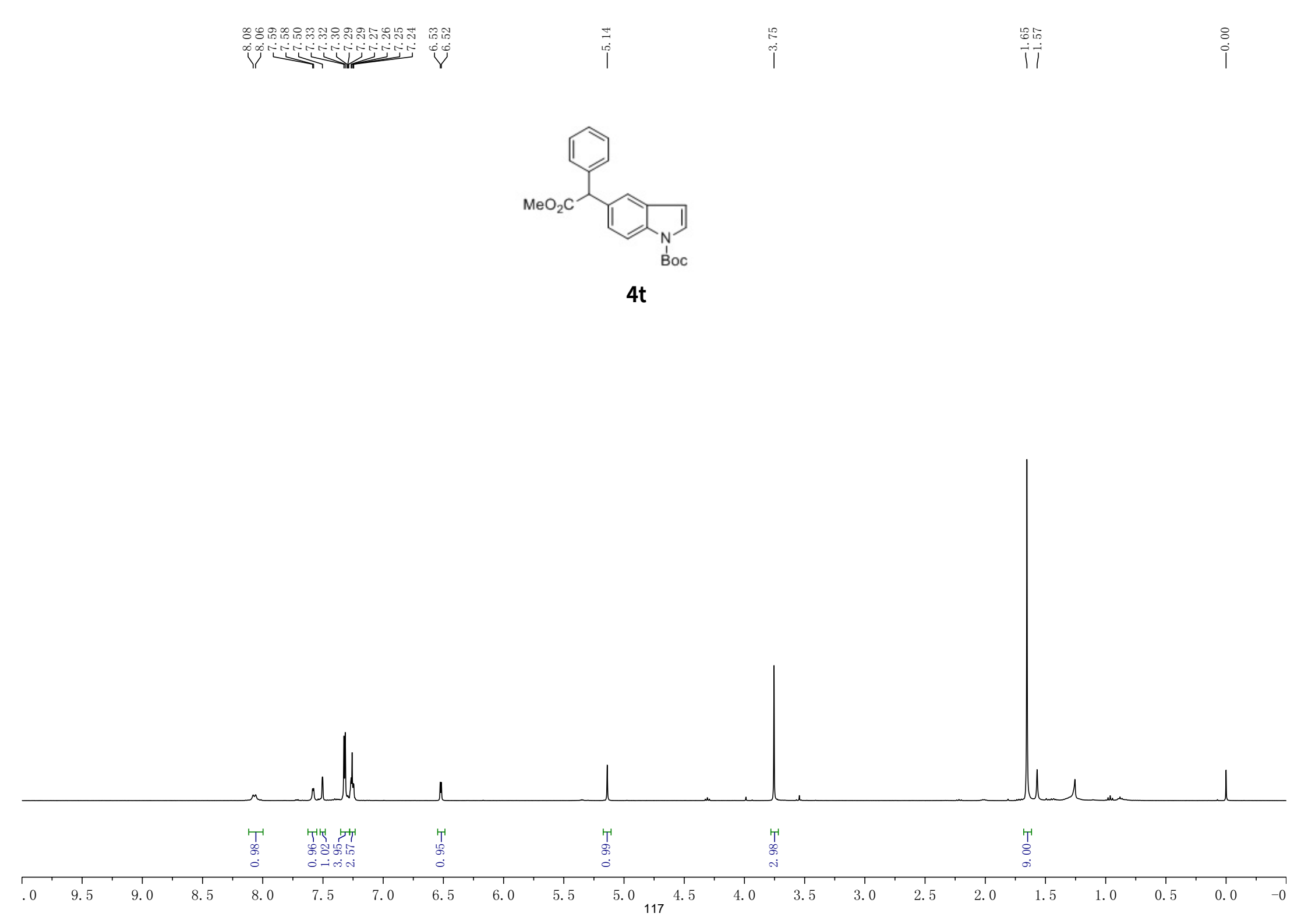
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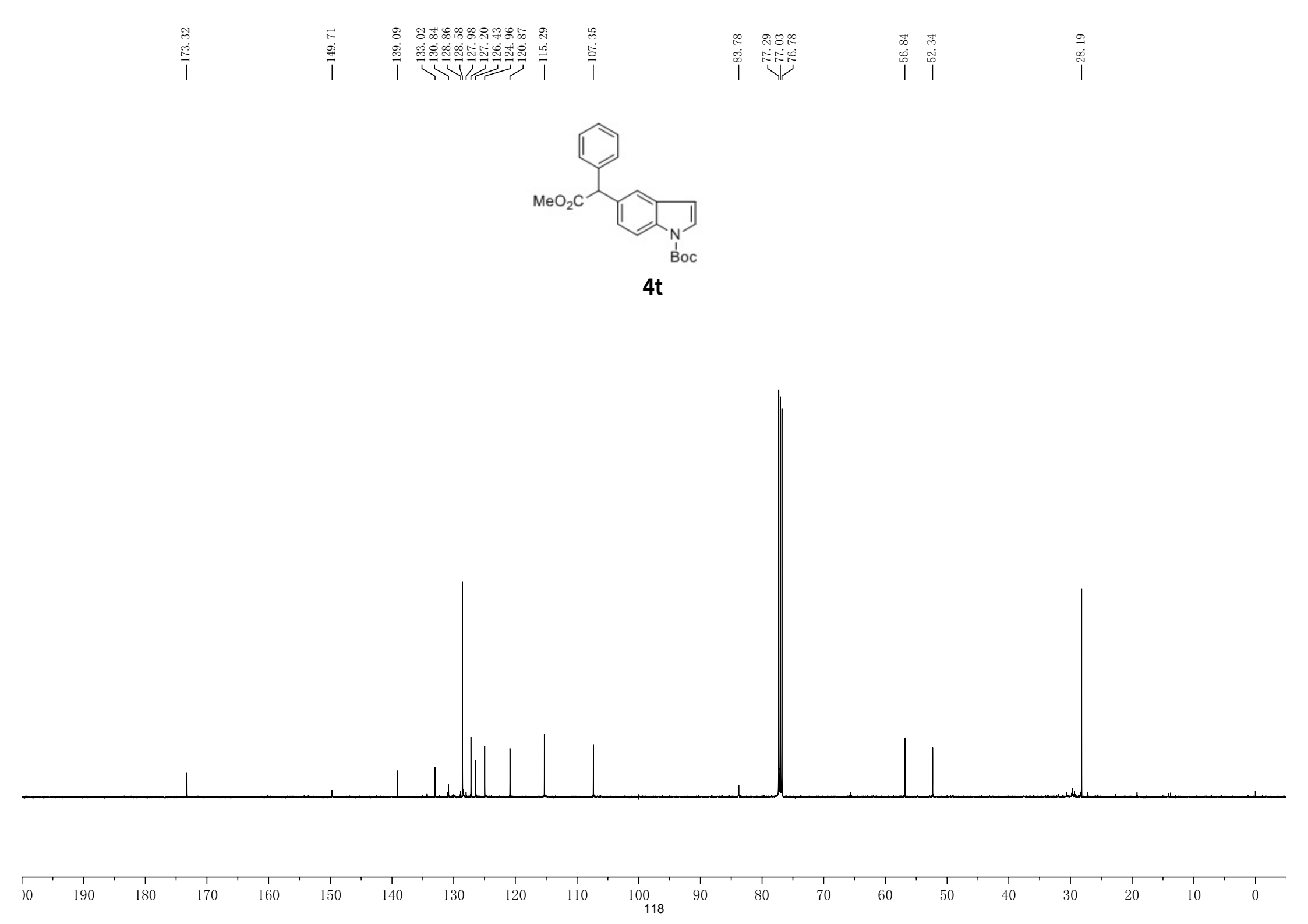
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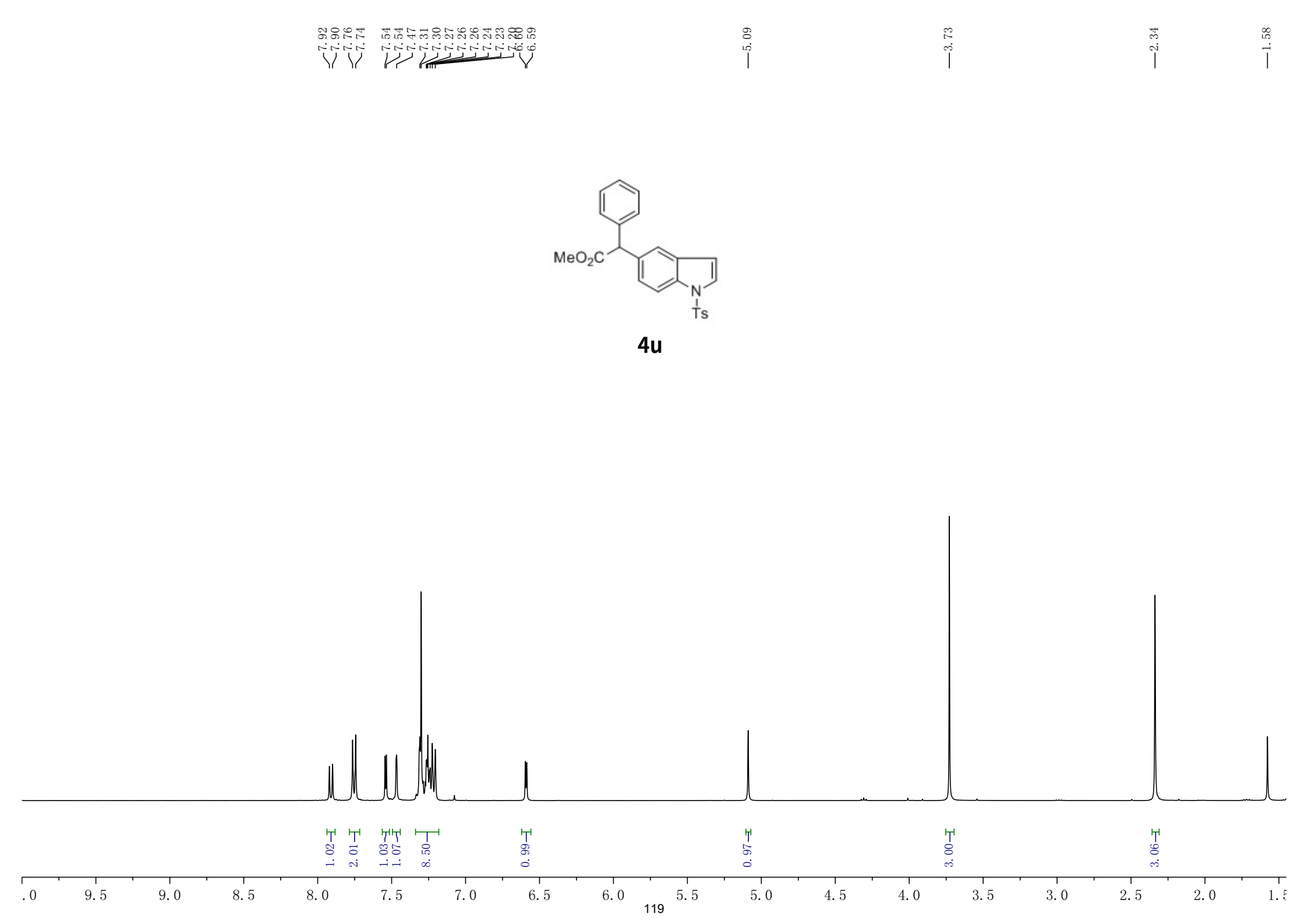
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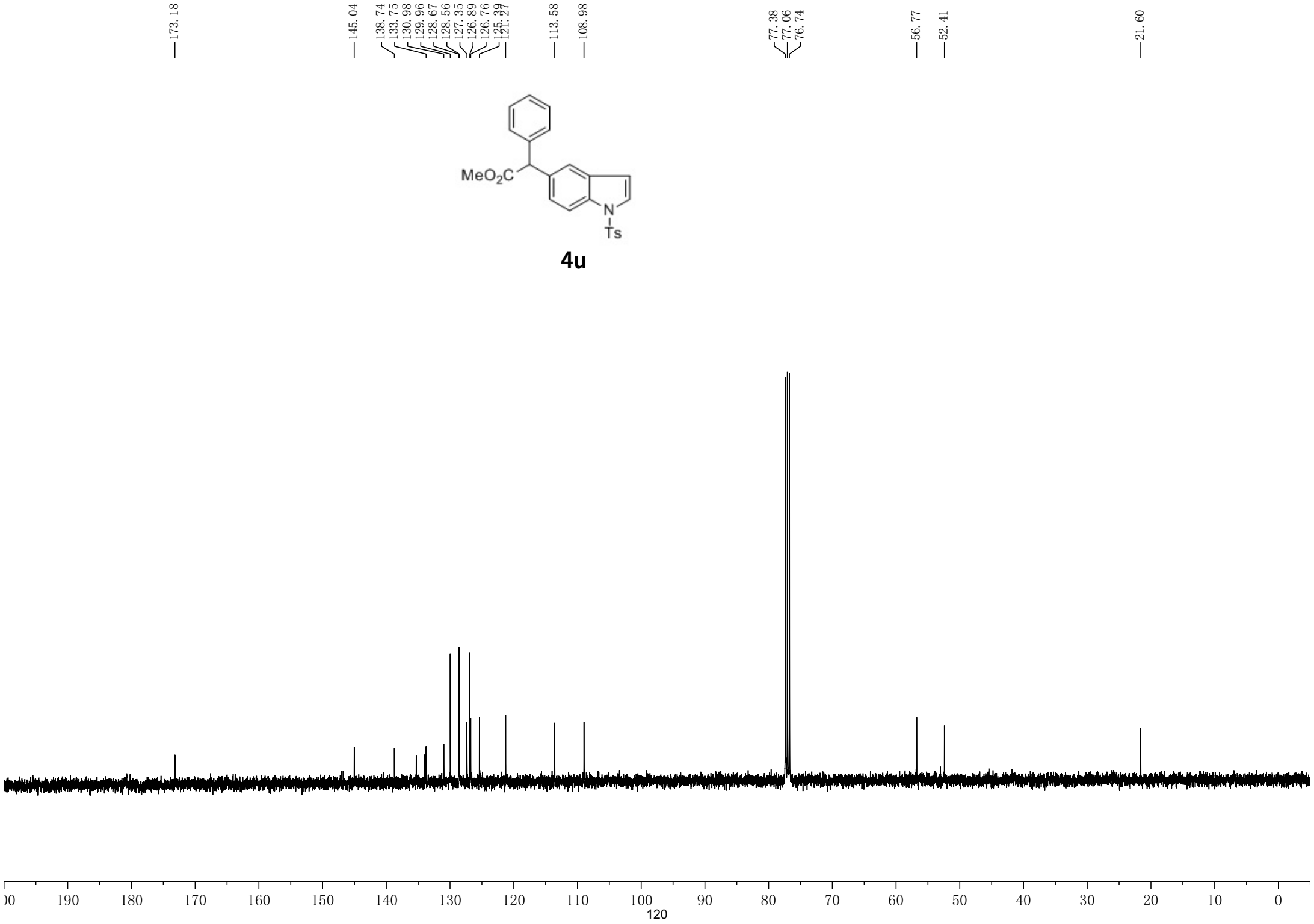
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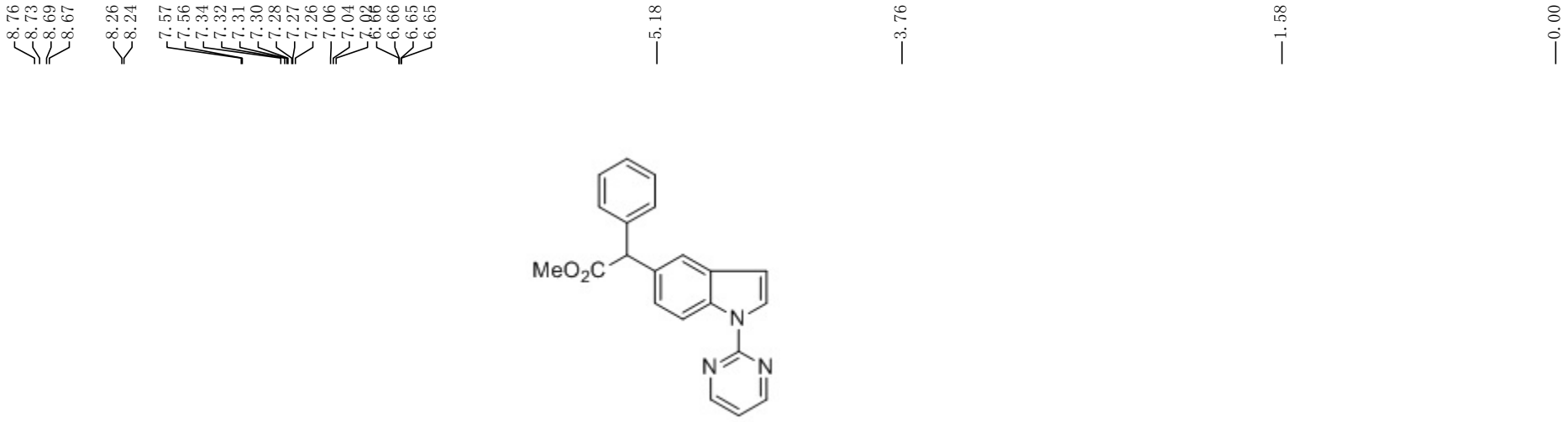
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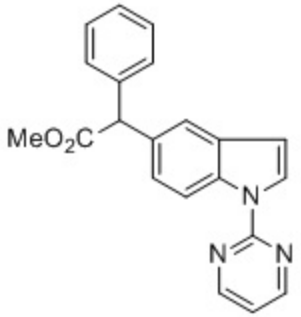

4v