Supporting Information

Synthesis of 2-Aminobenzonitriles through Nitrosation Reaction and Sequential Iron(III)-Catalyzed C−C Bond Cleavage of 2-Arylindoles

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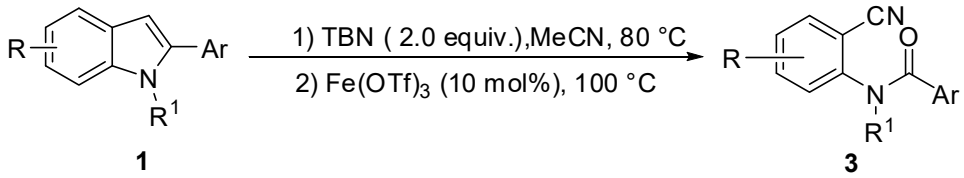
Contents

1. General Experimental Information:

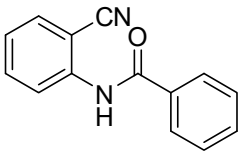
^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 MHz spectrometers. The data are reported as follows: Chemical shifts were given in parts per million (ppm, δ), referenced to the peak of tetramethylsilane, defined at δ = 0.00 (^{1}H NMR), the solvent peak of dimethyl sulfoxide (δ = 40.00 ppm) for ^{13}C NMR. Coupling constants were quoted in Hz (J). ^{1}H NMR Spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). High resolution mass spectra were acquired on an LTQ FT spectrometer, and were obtained by peak matching. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Chromatography was performed using with 300-400 mesh silica gel (SiO_2). Unless otherwise noted, all reactions were performed under nitrogen atmosphere. All reagents and solvents were used as received from commercial suppliers unless otherwise stated.

2. General procedure for synthesis of 2-aminobenzonitriles 3



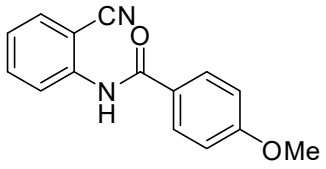
1 **3**

General procedure A: A dry Teflon-sealed reaction tube equipped with a stir bar was charged with 2-arylindoles **1** (0.3 mmol), TBN (0.062 g, 0.6 mmol, 2.0 equiv.), MeCN (3.0 mL). The reaction mixture was stirred at 80 °C for 0.5–5 h until **1a** was consumed completely (monitored by TLC). Then, $Fe(OTf)_3$ (0.015 g, 10 mol%) was added and stirred at 100 °C for 10–18 h. At this time, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to afford the corresponding 2-aminobenzonitriles **3**.



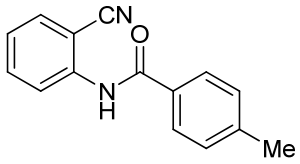
3a

***N*-(2-Cyanophenyl)benzamide (3a)** was prepared by general procedure A. **1a** (0.058 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 0.5 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 12 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3a** as a pale yellow solid (0.061 g, 92%). Mp: 158–159 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.63 (s, 1H), 8.02 (t, J = 7.2 Hz, 2H), 7.90 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.77–7.73 (m, 1H), 7.66–7.56 (m, 4H), 7.46–7.42 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.1, 140.9, 134.3, 134.0, 133.6, 132.7, 129.1, 128.3, 127.3, 126.8, 117.5, 109.8; IR (thin film) 3454, 3287, 2230, 1650, 1602, 1485, 1430, 765 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{11}N_2O$ $[M + H]^+$: 223.0866, found: 223.0864.



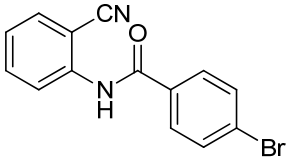
3b

***N*-(2-Cyanophenyl)-4-methoxybenzamide (3b)** was prepared by general procedure A. **1b** (0.067 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 0.5 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 14 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3b** as a pale yellow solid (0.021 g, 28%). Mp: 174–175 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.44 (s, 1H), 8.00 (dd, J = 8.0 Hz, 2.4 Hz, 2H), 7.87 (dd, J = 9.5 Hz, 1.2 Hz, 1H), 7.76–7.71 (m, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.43–7.39 (m, 1H), 7.11 (dd, J = 6.8 Hz, 1.5 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.5, 162.8, 141.1, 134.1, 133.5, 130.3, 127.2, 126.6, 126.1, 117.5, 114.3, 109.7, 56.0; IR (thin film) 3430, 2858, 2245, 1651, 1607, 1528, 1446, 1304, 764 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{13}N_2O_2$ $[M + H]^+$: 253.0972, found: 253.0965.



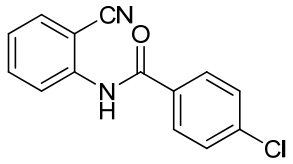
3c

***N*-(2-Cyanophenyl)-4-methylbenzamide (3c)** was prepared by general procedure A. **1c** (0.062 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 2 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 10 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3c** as a pale yellow solid (0.057 g, 81%). Mp: 168–169 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.54 (s, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.88 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.76–7.72 (m, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.0, 142.8, 141.0, 134.2, 133.6, 131.2, 129.6, 128.3, 127.3, 126.7, 117.5, 109.8, 21.5; IR (thin film) 3433, 3267, 2923, 2231, 1647, 1604, 1438, 765 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$: 237.1022, found: 273.1023.



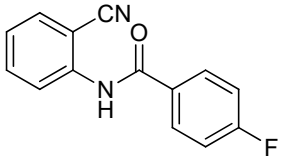
3d

4-Bromo-*N*-(2-cyanophenyl)benzamide (3d) was prepared by general procedure A. **1d** (0.081 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 3 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 11 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3d** as a pale yellow solid (0.077 g, 86%). Mp: 186–187 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.71 (s, 1H), 7.97–7.93 (m, 2H), 7.90 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.81–7.73 (m, 3H), 7.60 (d, J = 7.6 Hz, 1H), 7.46–7.42 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.3, 140.6, 134.3, 133.6, 133.1, 132.1, 130.4, 127.3, 127.0, 126.5, 117.4, 109.8; IR (thin film) 3492, 3296, 2225, 1659, 1529, 838, 765 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{10}BrN_2O$ $[M + H]^+$: 300.9971, found: 300.9969.



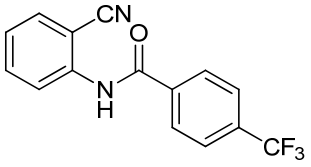
3e

4-Chloro-*N*-(2-cyanophenyl)benzamide (3e). **1e** (0.068 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 2.5 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C ran for 10 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3e** as a yellow solid (0.067 g, 87%). Mp: 190–191 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.71 (s, 1H), 8.04–8.01 (m, 2H), 7.90 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.78–7.73 (m, 2H), 7.67–7.64 (m, 2H), 7.60 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.47–7.42 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.1, 140.6, 137.5, 134.3, 133.6, 132.7, 130.2, 129.2, 127.3, 127.0, 117.4, 109.8; IR (thin film) 3454, 3287, 2224, 1656, 1530, 841, 765 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{10}ClN_2O$ $[M + H]^+$: 257.0476, found: 257.0479.



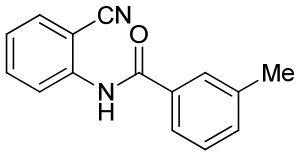
3f

***N*-(2-Cyanophenyl)-4-fluorobenzamide (3f)** was prepared by general procedure A. **1f** (0.063 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 3 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 12 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3f** as a pale yellow solid (0.063 g, 88%). Mp: 189–190 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.66 (s, 1H), 8.11–8.07 (m, 2H), 7.90 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.78–7.74 (m, 1H), 7.61 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.47–7.40 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.2 (d, J = 247.9 Hz), 165.1, 140.8, 134.3, 133.6, 131.1 (d, J = 8.8 Hz), 130.5 (d, J = 2.9 Hz), 127.4, 126.9, 117.4, 116.2 (d, J = 21.2 Hz), 109.9; IR (thin film) 3433, 3287, 2225, 1654, 1604, 1501, 849, 762 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{10}FN_2O$ $[M + H]^+$: 241.0772, found: 241.0770.



3g

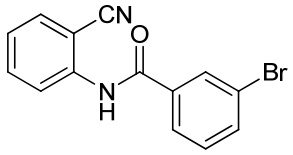
***N*-(2-Cyanophenyl)-4-(trifluoromethyl)benzamide (3g)** was prepared by general procedure A. **1g** (0.078 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 4 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 18 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3g** as a pale yellow solid (0.073 g, 84%). Mp: 174–175 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.87 (s, 1H), 8.21 (d, J = 7.6 Hz, 2H), 7.98 (dd, J = 8.0 Hz, 1.2 Hz, 2H), 7.91 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.1, 140.4, 137.8, 134.4, 133.7, 132.6 (q, J = 32.0 Hz), 129.2, 127.0, 127.2, 126.1 (q, J = 3.6 Hz), 125.7 (q, J = 271.3 Hz), 117.3, 109.9; IR (thin film) 3435, 3261, 2924, 2234, 1660, 1524, 1382, 766 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{10}F_3N_2O$ $[M + H]^+$: 291.0740, found: 291.0770.



3h

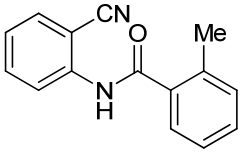
***N*-(2-Cyanophenyl)-3-methylbenzamide (3h)** was prepared by general procedure A. **1h** (0.062 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 1 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 10 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3h** as a yellow solid (0.063 g, 89%). Mp: 153–154 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.59 (s, 1H), 7.88 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.84–7.80 (m, 2H), 7.76–7.72 (m, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.46–7.41 (m, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.2, 140.9, 138.4, 134.2, 134.1, 133.6, 133.2, 128.9, 128.8, 127.2, 126.7, 125.4, 117.5, 109.8, 21.4; IR (thin film) 3435, 2926, 2225, 1662, 1531, 1448,

1384, 759 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$: 237.1022, found: 237.1022.



3i

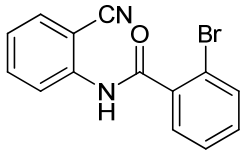
3-Bromo-*N*-(2-cyanophenyl)benzamide (3i) was prepared by general procedure A. **1i** (0.081 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 2 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 17 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3i** as a yellow solid (0.059 g, 66%). Mp: 178–179 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.76 (s, 1H), 8.19 (t, J = 1.6 Hz, 1H), 8.01 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.90–7.84 (m, 2H), 7.76–7.74 (m, 1H), 7.60–7.53 (m, 2H), 7.47–7.45 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.7, 140.5, 136.2, 135.4, 134.3, 133.6, 131.4, 130.9, 127.5, 127.4, 127.0, 122.3, 117.3, 109.8; IR (thin film) 3432, 2228, 1651, 1590, 1462, 972, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}BrN_2O$ $[M + H]^+$: 300.9971, found: 300.9975.



3j

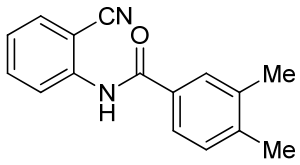
***N*-(2-Cyanophenyl)-2-methylbenzamide (3j)** was prepared by general procedure A. **1j** (0.062 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 1 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 10 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3f** as a white solid (0.048 g, 68%). Mp: 144–145 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.59 (s, 1H), 7.89 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.62 (dd, J = 13.6 Hz, 1.2 Hz, 2H), 7.45 (dd, J = 13.6 Hz, 1.2 Hz, 2H), 7.36 (t, J = 6.0 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.5, 140.6, 136.4, 136.3, 134.3, 133.6, 131.2, 130.6, 127.9, 127.0, 126.8, 126.2, 117.5, 109.5, 19.9; IR (thin film) 3453, 2925, 2228,

1652, 1481, 1380, 759 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$: 237.1022, found: 237.1031.



3k

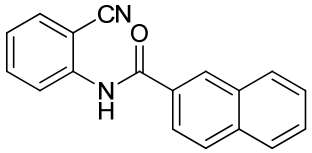
2-Bromo-*N*-(2-cyanophenyl)benzamide (3k) was prepared by general procedure A. **1k** (0.081 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 4 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 11 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3k** as an orange solid (0.058 g, 64%). Mp: 172–173 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.81 (s, 1H), 7.89 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.80 (t, J = 7.6 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.61 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.56 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.48–7.42 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.7, 140.0, 138.5, 134.4, 133.8, 133.4, 132.1, 129.5, 128.2, 127.0, 126.7, 119.5, 117.2, 108.9; IR (thin film) 3431, 3225, 2225, 1658, 1524, 1447, 762 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}BrN_2O$ $[M + H]^+$: 300.9971, found: 300.9969.



3l

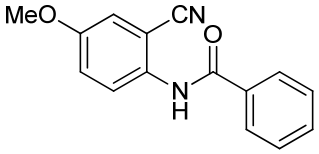
***N*-(2-Cyanophenyl)-3,4-dimethylbenzamide (3l)** was prepared by general procedure A. **1l** (0.066 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 0.5 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 120 °C for 18 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3l** as a yellow solid (0.069 g, 92%). Mp: 149–150 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.50 (s, 1H), 7.87 (d, J = 7.6 Hz, 1H), 7.81 (s, J = 8.0 Hz, 1H), 7.77–7.72 (m, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 7.2 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.1, 141.5, 141.1, 137.0, 134.2, 133.5,

131.5, 130.0, 129.3, 127.2, 126.6, 125.8, 117.5, 109.8, 19.9, 19.9; IR (thin film) 3458, 3372, 3030, 2930, 2227, 1670, 1380, 760 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2O$ $[M + H]^+$: 251.1179, found: 251.1176.



3m

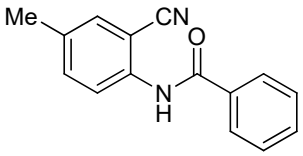
***N*-(2-Cyanophenyl)-2-naphthamide (3m)** was prepared by general procedure A. **1m** (0.073 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 1 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 11 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3m** as a orange solid (0.076 g, 93%). Mp: 189–190 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.86 (s, 1H), 8.70 (s, 1H), 8.12 (t, J = 8.8 Hz, 3H), 8.03 (d, J = 7.6 Hz, 1H), 7.92 (d, J = 7.2 Hz, 1H), 7.79 (t, J = 8.0 Hz, 1H), 7.68 (dd, J = 10.8 Hz, 1.2 Hz, 3H), 7.46 (t, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.3, 141.0, 135.0, 134.3, 133.6, 132.5, 131.4, 129.5, 129.0, 128.7, 128.6, 128.2, 127.5, 127.2, 126.8, 124.8, 117.5, 109.9; IR (thin film) 3453, 3280, 2227, 1653, 1580, 1527, 825, 761 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{13}N_2O$ $[M + H]^+$: 273.1022, found: 273.1017.



3ab

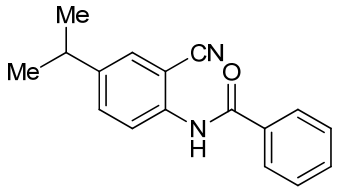
***N*-(2-Cyano-4-methoxyphenyl)benzamide (3ab)** was prepared by general procedure A. **1ab** (0.067 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 0.5 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 12 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3ab** as a pale yellow solid (0.060 g, 79%). Mp: 148–149 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.44 (s, 1H), 8.00 (d, J = 7.6 Hz, 2H), 7.63 (d, J = 7.2 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 7.49 (dd, J = 6.0 Hz, 1.2 Hz, 2H), 7.33 (dd, J = 8.8 Hz, 1.2 Hz, 1H),

3.83 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.2, 157.5, 134.1, 133.8, 132.5, 129.3, 129.0, 128.2, 120.8, 117.4, 117.2, 111.1, 56.4; IR (thin film) 3450, 2920, 2850, 2222, 1750, 1658, 1384,764 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{13}N_2O_2$ [M + H]$^+$: 253.0972, found: 253.0969.



3ac

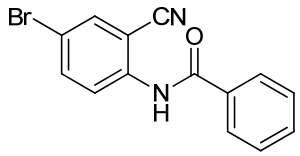
***N*-(2-Cyano-4-methylphenyl)benzamide (3ac)** as prepared by general procedure A. **1ac** (0.062 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C ran for 0.5 h; then add Fe(OTf)$_3$ (0.015 g, 10 mol%), 100 °C ran for 11 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3ac** as a pale yellow solid (0.064 g, 91%). Mp: 192–193 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.53 (s, 1H), 8.01 (d, J = 7.2 Hz, 2H), 7.69 (s, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 3H), 7.47 (d, J = 8.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.1, 138.4, 136.7, 134.9, 134.1, 133.5, 132.5, 129.0, 128.3, 127.4, 117.5, 109.8, 20.6; IR (thin film) 3430, 2940, 2228, 1640, 1520, 1380, 765 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{13}N_2O$ [M + H]$^+$: 237.1022, found: 237.1027.



3ad

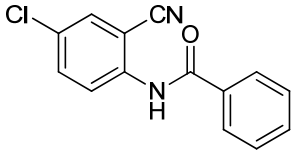
***N*-(2-Cyano-4-isopropylphenyl)benzamide (3ad)** was prepared by general procedure A. **1ad** (0.071 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 1 h; then add Fe(OTf)$_3$ (0.015 g, 10 mol%), 100 °C for 15 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3ad** as a pale yellow solid (0.059 g, 75%). Mp: 118–119 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.54 (s, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.74 (d, J = 2.0 Hz, 1H), 7.65 (t, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 2H), 7.50 (d, J = 8.0 Hz, 1H), 3.01–2.94

(m, 1H), 1.24 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.2, 147.3, 138.6, 134.1, 132.6, 132.4, 131.1, 129.0, 128.3, 127.4, 117.6, 109.8, 33.3, 24.0; IR (thin film) 3445, 3006, 2925, 2224, 1653, 1548, 1387, 1240, 768 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{17}N_2O$ $[M + H]^+$: 265.1335, found: 265.1335.



3ae

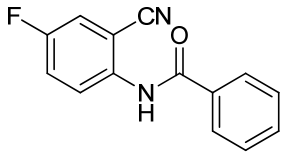
***N*-(4-Bromo-2-cyanophenyl)benzamide (3n)** was prepared by general procedure A. **1ae** (0.081 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 2 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 120 °C for 14 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3ae** as a pale yellow solid (0.053 g, 59%). Mp: 166–167 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.68 (s, 1H), 8.19 (d, J = 2.8 Hz, 1H), 8.01 (t, J = 7.2 Hz, 2H), 7.96 (dd, J = 8.8 Hz, 1.2 Hz, 1H), 7.67 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.59–7.54 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.0, 140.4, 137.2, 135.7, 133.8, 132.8, 129.1, 128.9, 128.4, 118.4, 116.1, 111.5; IR (thin film) 3432, 3063, 2229, 1655, 1598, 862, 715 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{10}BrN_2O$ $[M + H]^+$: 300.9971, found: 300.9967.



3af

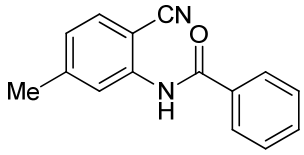
***N*-(4-Chloro-2-cyanophenyl)benzamide (3af)** was prepared by general procedure A. **1af** (0.068 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 2 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 13 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3af** as a pale orange solid (0.038 g, 50%). Mp: 174–175 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.69 (s, 1H), 8.08 (s, 1H), 8.01 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.8 Hz, 1H), 7.65–7.55 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.1, 140.0, 134.4, 133.8,

132.9, 132.8, 130.6, 129.1, 128.8, 128.3, 116.2, 111.2; IR (thin film) 3453, 2231, 1663, 1598, 876, 716 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{10}ClN_2O$ $[M + H]^+$: 257.0476, found: 257.0474.



3ag

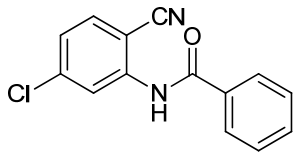
***N*-(2-Cyano-4-fluorophenyl)benzamide (3ag)** as prepared by general procedure A. **1ag** (0.063 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 4 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 120 °C for 10 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3ag** as a white solid (0.032 g, 44%). Mp: 184–185 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.63 (s, 1H), 8.08 (s, 1H), 8.01 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.8 Hz, 1H), 7.65–7.55 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.2, 160.7 (d, J = 244.2 Hz), 137.6, 133.9, 132.7, 129.8 (d, J = 8.8 Hz), 129.1, 128.3, 121.9 (d, J =21.9 Hz), 120.3 (d, J = 26.2 Hz), 116.3, 111.4 (d, J = 10.2 Hz); IR (thin film) 3429, 3054, 2234, 1655, 1490, 826, 713 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{10}FN_2O$ $[M + H]^+$: 241.0772, found: 241.0772.



3ah

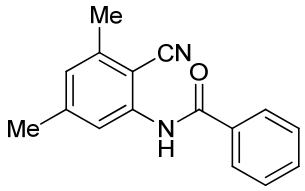
***N*-(2-Cyano-5-methylphenyl)benzamide (3ah)** was prepared by general procedure A. **1ah** (0.062 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 1 h; then add $Fe(OTf)_3$ (0.015 g, 10 mol%), 100 °C for 13 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3ah** as a pale yellow solid (0.041 g, 58%). Mp: 127–128 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.56 (s, 1H), 8.01 (t, J = 7.2 Hz, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.66−7.62 (m, 1H), 7.59−7.55 (m, 2H), 7.43 (s, 1H), 7.27 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 2.41 (s, 3H); ^{13}C

NMR (100 MHz, DMSO-d_6): δ 166.1, 145.0, 140.8, 134.1, 133.3, 132.6, 129.1, 128.3, 127.8, 127.6, 117.7, 106.9, 21.8; IR (thin film) 3268, 2959, 2920, 2222, 1761, 1653, 1522, 1480, 1259, 1182, 820, 710 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_2O$ [M + H]$^+$: 237.1022, found: 237.1029



3ai

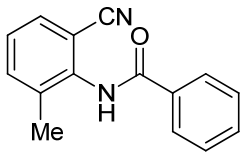
***N*-(5-Chloro-2-cyanophenyl)benzamide (3ai)** was prepared by general procedure A. **1ai** (0.068 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 1 h; then add $Fe(OTf)_3$ (0.015 g,10 mol%), 100 °C for 12 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3ai** as a pale yellow solid (0.046 g, 60%). Mp: 145–146 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.73 (s, 1H), 8.00 (t, J = 7.2 Hz, 2H), 7.95 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.74 (d, J = 2.0 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.60–7.52 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.2, 142.3, 138.7, 135.2, 133.7, 132.9, 129.2, 129.1, 128.4, 126.9, 116.8, 108.3; IR (thin film) 3436, 2853, 2222, 1657, 1570, 1515, 818, 711 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}ClN_2O$ [M + H]$^+$: 257.0476, found: 257.0477.



3aj

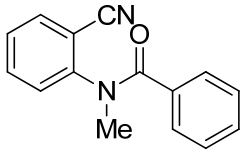
***N*-(2-Cyano-3,5-dimethylphenyl)benzamide (3aj)** was prepared by general procedure A. **1aj** (0.066 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 1.5 h; then add $Fe(OTf)_3$ (0.015 g,10 mol%), 100 °C for 12 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3aj** as a yellow solid (0.045 g, 60%). Mp: 118–119 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.49 (s, 1H), 8.00 (t, J = 7.6 Hz, 2H), 8.63 (d, J = 7.2 Hz, 1H), 7.60 (t, J = 7.6 Hz, 2H), 7.24 (s, 1H), 7.17 (s, 1H), 2.47 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100

MHz, DMSO-d_6): δ 166.2, 144.2, 142.5, 141.1, 134.2, 132.6, 129.1, 128.7, 128.2, 125.3, 116.7, 107.7, 21.7, 20.6; IR (thin film) 3431, 2921, 2216, 1659, 1611, 1450, 851, 709 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{15}N_2O$ $[M + H]^+$: 251.1179, found: 251.1179.



3ak

***N*-(2-Cyano-6-methylphenyl)benzamide (3ak)** was prepared by general procedure A. **1ak** (0.062 g, 0.30 mmol), TBN (0.062 g, 0.6 mmol), MeCN (3.0 mL), 80 °C for 0.5 h; then add $Fe(OTf)_3$ (0.015 g,10 mol%), 100 °C for 13 h. Purification using medium pressure chromatography (1:10; ethyl acetate: petroleum ether) afforded **3ak** as a pale yellow solid (0.052 g, 73%). Mp: 159–160 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.42 (s, 1H), 8.04 (t, J = 7.6 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.69 (dd, J = 7.2 Hz, 14.4 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.2, 139.5, 137.5, 135.9, 134.1, 132.5, 131.2, 129.1, 128.2, 128.1, 117.6, 112.7, 18.1; IR (thin film) 3418, 3064, 2924, 2228, 1649, 1600, 1384, 705 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$: 237.1022, found: 237.1021.

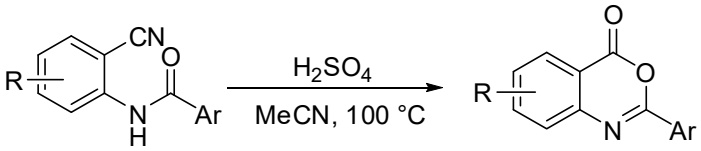


3n

***N*-(2-Cyanophenyl)-N-methylbenzamide (3n).** Compound **4n** (0.071 g, 0.30 mmol) , $Fe(OTf)_3$ (0.015 g,10 mol%), MeCN (3.0 mL), 100 °C for 11 h. Purification using medium pressure chromatography (1:2; ethyl acetate: petroleum ether) afforded **3n** as a yellow oil (0.063 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.6 Hz, 1H), 7.49 (s, 1H), 7.35 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 4.8 Hz, 2H), 7.21 (s, 3H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 147.5, 135.0, 133.8, 133.6, 130.1, 129.4,

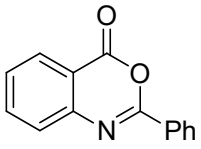
128.2, 127.9, 127.6, 116.2, 111.8, 36.2; IR (thin film) 3059, 2926, 2223, 1643, 1594, 1364, 1175, 767 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$: 237.1022, found: 237.1021.

3. General procedure for Synthesis of 2-arylbenzoxazinones 5



3 **5**

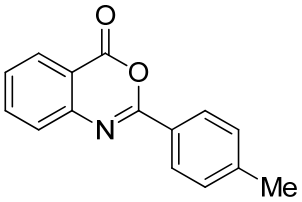
General procedure B: A dry Teflon-sealed reaction tube equipped with a stir bar was charged with 2-aminobenzonitriles **3** (0.2 mmol), MeCN (2.0 mL), H_2SO_4 (0.039 g, 2.0 equiv., 98%), 100 °C ran for 17–24 h until the reaction was completed (detected by TLC). After completion, the reaction mixture was cooled to room temperature, neutralized with sat.$NaHCO_3$ and extracted with DCM (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to give the corresponding 2-arylsubstituted 2-arylbenzoxazinones **5.**



5a

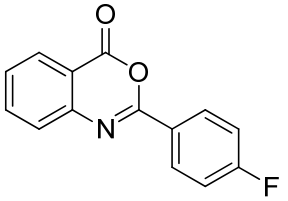
2-Phenyl-4H-benzo[d][1,3]oxazin-4-one (5a) was prepared by general procedure B. **3a** (0.044g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 18 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5a** as a white solid (0.036 g, 81%). Mp: 110–111 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 8.18 (dd, J = 6.8 Hz, 1.2 Hz, 2H), 8.12 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.95−7.91 (m, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.67−7.62 (m, 1H), 7.61−7.56 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.3, 156.9, 146.7, 137.3, 133.2, 130.5, 129.4, 129.0, 128.5, 128.3, 127.4, 117.4; IR (thin film) 1764, 1617, 1473, 1313, 1254, 1009, 764, 684 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_{10}NO_2$ $[M + H]^+$: 224.0706,

found: 224.0707.



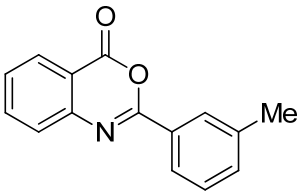
5c

2-*p*-Tolyl-4H-benzo[d][1,3]oxazin-4-one (5c) was prepared by general procedure B. **3c** (0.047 g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 17 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5c** as a white solid (0.042 g, 88%). Mp: 145–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14−8.09 (m, 3H), 7.74−7.70 (m, 1H), 7.59 (d, J = 7.6 Hz, 1H), 8.12 (q, J = 7.6 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 157.2, 147.1, 143.3, 136.4, 129.4, 128.5, 128.2, 127.9, 127.3, 127.0, 116.9, 21.6; IR (thin film) 3001, 2921, 1752, 1664, 1520, 1387, 1241, 767 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{12}NO_2$ $[M + H]^+$: 238.0863, found: 238.0864.



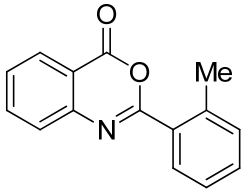
5f

2-(4-Fluorophenyl)-4H-benzo[d][1,3]oxazin-4-one (5f) was prepared by general procedure B. **3f** (0.048g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 19 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5f** as a pale yellow solid (0.037 g, 77%). Mp: 167–168 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.26−8.23 (m, 2H), 8.16 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.97−7.93 (m, 1H), 7.72 (t, J = 7.6 Hz, 1H), 7.64−7.60 (m, 1H), 7.45−7.41 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.5 (d, J = 250 Hz), 159.3, 156.1, 146.7, 137.4, 131.1 (d, J = 8.8 Hz), 129.1, 128.5, 127.3, 127.2 (d, J = 2.9 Hz), 117.3, 116.8 (d, J = 21.9 Hz); IR (thin film) 3071, 1926, 1763, 1619, 1510, 1483 843, 770 cm^{-1}; HRMS (ESI) m/z calcd for $C_{14}H_9FNO_2$ $[M + H]^+$: 242.0612, found: 242.0613.



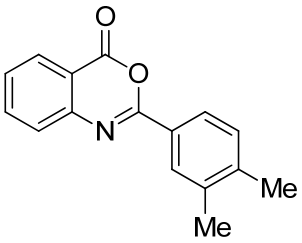
5h

2-*m*-Tolyl-4H-benzo[d][1,3]oxazin-4-one (5h) was prepared by general procedure B. **3h** (0.047g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 19 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5h** as a white solid (0.039 g, 83%). Mp: 110–111 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.14 (dd, J = 8.0 Hz, 1.2 Hz 1H), 7.97−7.94 (m, 2H), 7.93−7.91 (m, 1H), 7.70 (t, J = 7.6 Hz, 1H), 7.62−7.58 (m, 1H), 7.46−7.44 (m, 2H), 2.40(s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.3, 156.9, 146.7, 138.9, 137.3, 133.9, 130.4, 129.4, 129.0, 128.6, 128.5, 127.4, 125.5, 117.4, 21.4; IR (thin film) 2994, 2943, 1755, 1621, 1473, 1319, 1259, 767 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{12}NO_2$ [M + H]$^+$: 238.0863, found: 238.0863.



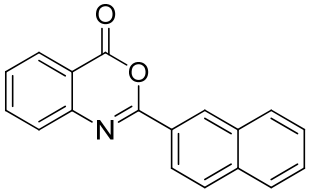
5j

2-*o*-Tolyl-4H-benzo[d][1,3]oxazin-4-one (5j) was prepared by general procedure B. **3j** (0.047g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 23 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5j** as a white solid (0.036 g, 76%). Mp: 107–108 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.76 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 158.2, 146.8, 139.1, 136.4, 131.9, 131.5, 130.1, 129.8, 128.4, 128.4, 127.2, 126.0, 116.7, 22.1; IR (thin film) 2961, 2933, 1757, 1618, 1468, 1317, 1216,765 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{12}NO_2$ [M + H]$^+$: 238.0863, found: 238.0863.



5l

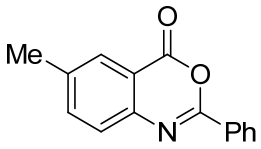
2-(3,4-Dimethylphenyl)-4H-benzo[d][1,3]oxazin-4-one (5l) was prepared by general procedure B. **3l** (0.050g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 24 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5l** as a white solid (0.039 g, 78%). Mp: 151–152 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 8.00 (s, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 7.2 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.43 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.19 (t, J = 5.6 Hz, 1H), 2.27 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 157.4, 147.2, 142.2, 137.2, 136.5, 130.0, 129.2, 128.5, 127.9, 127.6, 127.0, 125.9, 116.9, 20.0, 19.7; IR (thin film) 2940, 2908, 1749, 1663, 1580, 1470, 1384, 724 cm^{-1}; HRMS (ESI) m/z calcd for $C_{16}H_{14}NO_2$ $[M + H]^+$: 252.1019, found: 252.1019.



5m

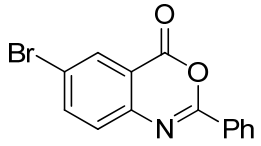
2-(Naphthalen-2-yl)-4H-benzo[d][1,3]oxazin-4-one (5m) was prepared by general procedure B. **3m** (0.054 g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 18 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5m** as a white yellow (0.050 g, 91%). Mp: 201−202 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.37 (q, J = 8.4 Hz, 1H), 8.27 (q, J = 8.0 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.89−7.82 (m, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.61−7.50 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 157.1, 147.0, 136.6, 135.2, 132.7, 129.5, 129.3, 128.6, 128.5, 128.3, 128.2 127.8, 127.3, 127.2, 126.8, 124.1, 117.0; IR (thin film) 3051, 1761, 1600, 1570, 1482, 1261, 1218,

766 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{12}NO_2$ $[M + H]^+$: 274.0863, found: 274.0861.



5ac

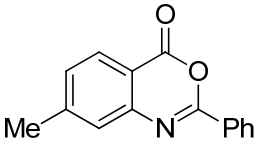
6-Methyl-2-phenyl-4H-benzo[d][1,3]oxazin-4-one (5ac) was prepared by general procedure B. **3ac** (0.047 g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 24 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5ac** as a white yellow (0.035 g,74%). Mp: 130–131 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 8.16 (s, 2H), 7.92 (s, 1H), 7.75 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.60 (t, J = 8.8 Hz, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.3, 156.1, 144.6, 139.1, 138.3, 133.0, 130.5, 129.4, 128.1, 128.0, 127.2, 117.0, 21.2; IR (thin film) 2919, 1752, 1630, 1490, 1384, 1260 1022, 688 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{12}NO_2$ $[M + H]^+$: 238.0863, found: 238.0863.



5ae

6-Bromo-2-phenyl-4H-benzo[d][1,3]oxazin-4-one (5ae) was prepared by general procedure B. **3ae** (0.060 g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), then 100 °C for 20 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5ae** as a white solid (0.048 g, 79%). Mp: 184–185 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 2.4 Hz, 1H), 8.30 (t, J = 7.2 Hz, 2H), 7.92 (dd, J = 8.8 Hz, 1.2 Hz, 1H), 7.60 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 7.54 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 157.4, 145.8, 139.7, 132.9, 131.1, 129.8, 128.9, 128.8, 128.4, 121.4, 118.3; IR (thin film) 3031, 1719, 1629, 1425, 1373, 1241, 1303 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{14}H_9BrNO_2$ $[M + H]^+$: 301.9811,

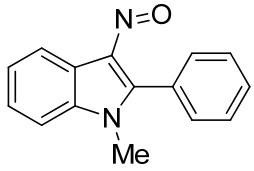
found: 301.9812.



5ah

7-Methyl-2-phenyl-4H-benzo[d][1,3]oxazin-4-one (5ah) was prepared by general procedure B. **3ah** (0.047 g, 0.20 mmol), MeCN (2.0 mL), H_2SO_4 (2.0 equiv), 100 °C for 20 h, Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **5ah** as a white solid (0.029 g, 62%). Mp: 187−189 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (t, J = 7.2 Hz, 2H), 8.13 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.53 (dd, J = 6.8 Hz, 1.2 Hz, 3H), 7.34 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 157.2, 148.1, 147.0, 132.5, 130.4, 129.6, 128.7, 128.4, 128.3, 127.2, 114.4, 22.1; IR (thin film) 3031, 1719, 1629, 1425, 1373, 1241, 1303 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{12}NO_2$ [M + H]$^+$: 238.0863, found: 238.0864.

4. Synthesis of nitrosoindole 4n

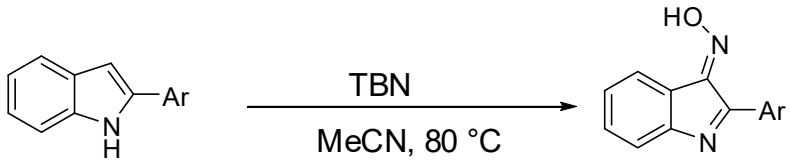


4n

1-Methyl-3-nitroso-2-phenyl-1H-indole (4n). 1n (0.311 g, 1.5 mmol), TBN (0.309 g, 3.0 mmol, 2.0 equiv.), MeCN (5.0 mL), stirred at rt. for 2 h until the reaction was completed (detected by TLC). Purification using medium pressure chromatography (4:1; ethyl acetate: petroleum ether) afforded **4n** as a green solid (0.252 g, 71%). Mp: 140–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21−8.19 (m, 2H), 7.93 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.39−7.32 (m, 4H), 7.15 (t, J = 7.6 Hz, 1H), 4.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 136.2, 131.7, 130.5, 128.5, 127.3, 127.3, 126.0, 121.7, 121.6, 109.6, 109.5, 31.8; IR (thin film) 3053, 2944, 1910, 1807, 1465, 1361, 1241, 744 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}N_2O$ [M + H]$^+$: 237.1022,

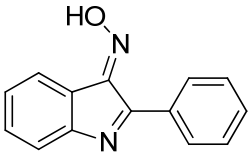
found: 237.1020.

5. General procedure for synthesis of compound 2a, 2c, and 2aa



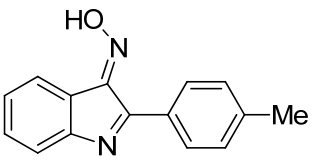
1 **2**

Procedure C: A dry Teflon-sealed reaction tube equipped with a stir bar was charged with 2-arylindoles **1** (1.0 mmol), TBN (0.202 g, 2.0 mmol, 2.0 equiv.), MeCN (3.0 mL). The reaction mixture was stirred at 80 °C for 0.5-1 h until **1** was consumed completely (monitored by TLC). At this time, the reaction mixture was cooled to room temperature, filtered and washed with DCM. The corresponding oximes **2** were obtained as solid.



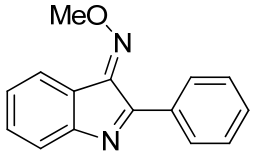
2a

(*E*)-2-Phenyl-3H-indol-3-one oxime (2a) was prepared by general procedure C. **1a** (0.193 g, 1.0 mmol), TBN (2.0 mmol, 2.0 equiv.), MeCN (3.0 mL), 80 °C for 0.5 h; Then the reaction mixture was cooled to room temperature, filtered and washed with DCM to afford **2a** as a yellow solid (0.220 g, 99%). Mp: 274–275 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.92 (s, 1H), 8.26 (d, J = 6.8 Hz, 2H), 8.13 (d, J = 7.2 Hz, 1H), 7.57−7.46 (m, 5H), 7.39−7.31 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.6, 154.6, 132.5, 132.4, 131.8, 131.4, 130.4, 130.1, 129.9, 129.0, 128.7, 127.7; IR (thin film) 3435, 3049, 1841, 1592, 1492, 1273, 1208, 1027, 751 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{14}H_{11}N_2O$ $[M + H]^+$: 223.0866, found: 223.0864.



2c

(*E*)-2-*p*-Tolyl-3H-indol-3-one oxime (2c) was prepared by general procedure C. **1c** (0.207 g, 1.0 mmol), TBN (2.0 mmol, 2.0 equiv.), MeCN (3.0 mL), 80 °C for 1 h; Then the reaction mixture was cooled to room temperature, filtered and washed with DCM to afford **2c** as a yellow solid (0.168 g, 71%). Mp: 247–248 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.90 (s, 1H), 8.19 (d, J = 7.6 Hz, 2H), 8.11 (d, J = 6.8 Hz, 1H), 7.54 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 16.4 Hz, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.8, 141.5, 131.8, 131.7, 131.6, 131.6, 129.9, 129.8, 129.7, 127.6, 126.7, 126.6, 21.6; IR (thin film) 3781, 3449, 3044, 1818, 1639, 1607, 1501, 1354, 1284, 760 cm^{-1}; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{13}N_2O$ [M + H]$^{+}$: 237.1022, found: 237.1023.

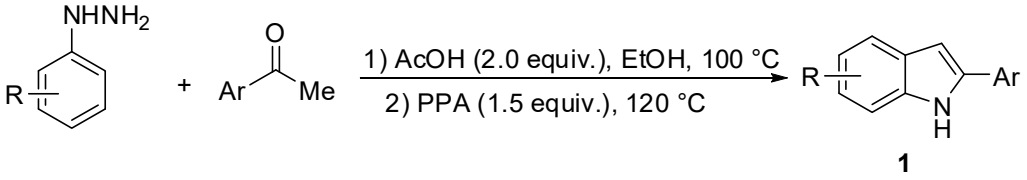


2aa

(*E*)-2-Phenyl-3H-indol-3-one *O*-methyl oxime (2aa). To a suspended solution of NaH (0.120 g, 60% dispersion in mineral oil, 3.0 mmol, 1.5 equiv) in DMF (3.0 mL), **2a** (0.444 g, 2.0 mmol) in DMF (3 mL) was added dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 15 min and additional 1 h at room temperature. The mixture was then cooled to 0 °C, treated with iodomethane (0.56 mL, 3.0 mmol, 1.5 equiv), and allowed to warm to room temperature. After 30 min, the reaction mixture was cooled to 0 °C, quenched with saturated NH_4Cl (5.0 mL), and extracted with ether (3 × 20 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification using medium pressure chromatography (10:1; ethyl acetate: petroleum ether) afforded **2aa** as a yellow oil (0.431 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 7.2 Hz, 1H), 7.62 (t, J = 5.6 Hz, 2H), 7.41 (dd, J = 8.4 Hz, 1.2 Hz, 3H), 7.23−7.13 (m, 3H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 154.8, 153.9, 132.4, 132.0, 130.8, 129.7, 128.3, 127.3, 127.0, 122.1, 120.8, 64.7; IR (thin film) 3017, 2940, 2816, 1603, 1439, 1350,

1266, 751 cm^{-1}; HRMS (ESI) m/z calcd for $C_{15}H_{13}N_2O$ $[M + H]^+$: 237.1022, found: 237.1021.

6. General procedure for synthesis of 2-arylindoles 1



1

Procedure D: A mixture of acetophenone (10 mmol), phenylhydrazine (1.2 equiv), HOAc (20 mmol) and EtOH (6.0 mL) were taken in a 100 mL round bottom flask. Then, the reaction mixture was refluxed at 100 °C. When the reaction was completed (detected by TLC), it was cooled to room temperature. The EtOH was evaporated in vacuo, and then recrystallized with EtOAc and hexane. Next, freshly prepared phenylhydrazone (10 mmol) were taken in a 100 mL round bottom flask and 1.5 equiv. of polyphosphoric acid (PPA) was added at one time and the solution was refluxed. After completion, the reaction mixture was cooled to room temperature, quenched with cold H_2O (10 mL) and extracted with EtOAc (3 × 10mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane as the eluent to afford the corresponding 2-arylindoles **1**.

Indoles (**1a-m, 1af)**[1], **1n**[2], (**1ab-ae, 1ag-ak)**[3] were prepared according to literature methods and their spectra data matched literature values.

7. References

[1] Hong, X. H.; Tan, Q. T.; Liu, B. X.; Xu, B. *Angew. Chem. Int. Ed.* **2017**, *56*, 3961.

[2] Bhunia, S. K.; Polley, A.; Natarajan, R.; Jana, R. *Chem. Eur. J*. **2015**, *21*, 16786.

[3] Wu, L. J.; Deng, G. B.; Liang, Y. *Org. Biomol. Chem.* **2017**, *15*, 6808.

8. X-ray structures for compounds 3a, 3af, 2c, and 5a

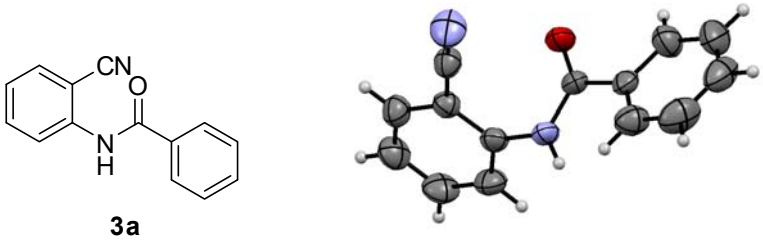


Figure S1: ORTEP diagram of **3a** at 50% ellipsoid probability.

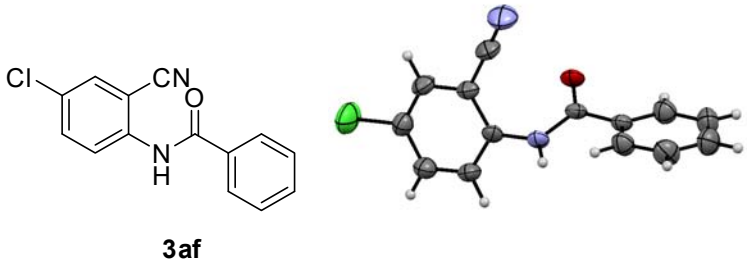


Figure S2: ORTEP diagram of **3af** at 50% ellipsoid probability.

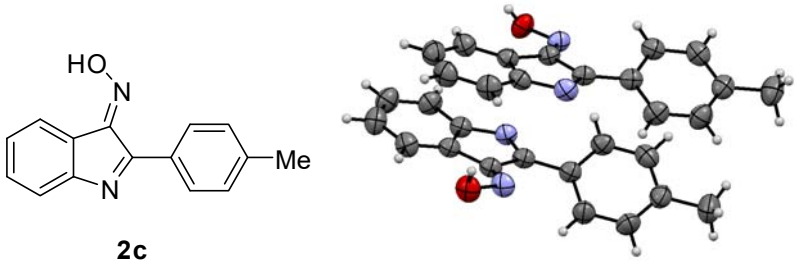


Figure S3: ORTEP diagram of **2c** at 50% ellipsoid probability.

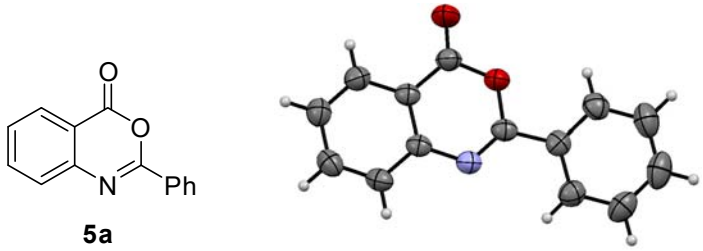
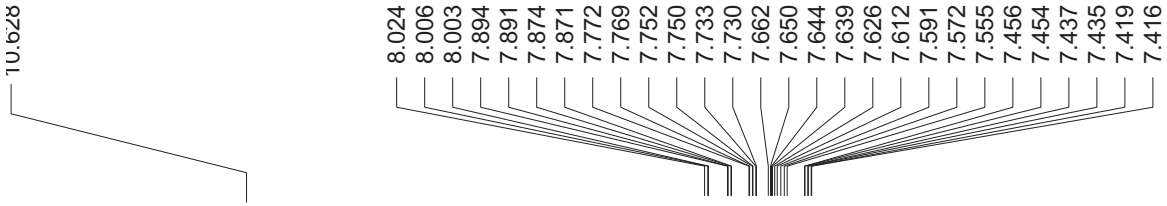


Figure S4: ORTEP diagram of **5a** at 50% ellipsoid probability. (The X-ray structure of compound **5a** has been previously reported, see: Thilagavathy, R.; Kavitha, H. P.; Arulmozhi, R.; Vennila, J. P.; Manivannan, V. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2009**, *65*, o127.)

9. NMR spectra for compounds 3, 5, 4n, and 2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8.006
8.003
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7.871
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7.730
7.662
7.650
7.644
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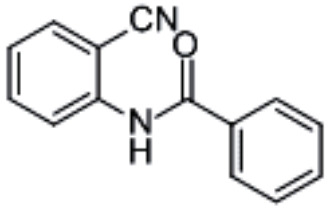
7.419
7.416


CN
O
N
H

3a

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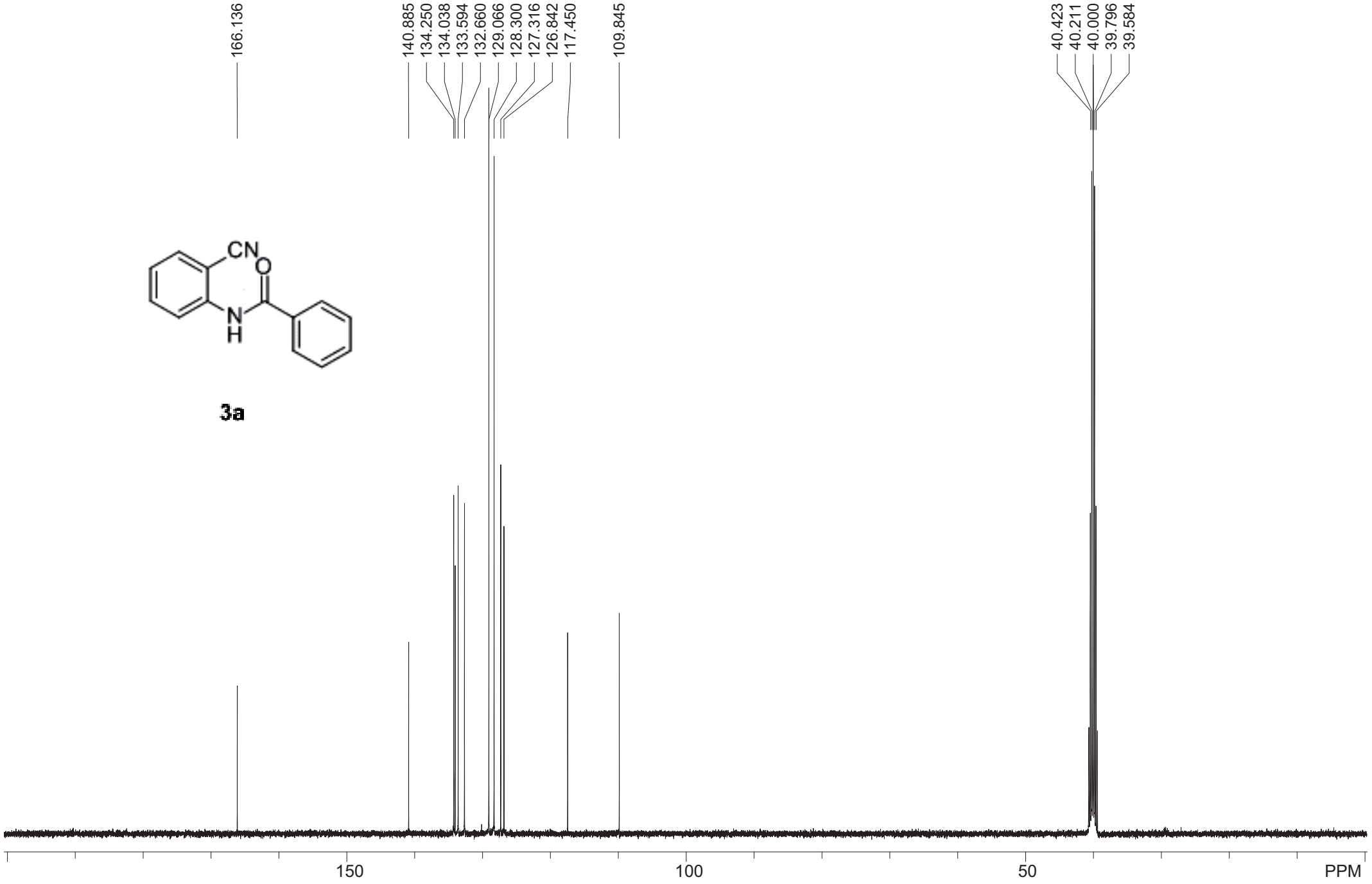
1.00
1.00
10
8
6
4
2
PPM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133.594
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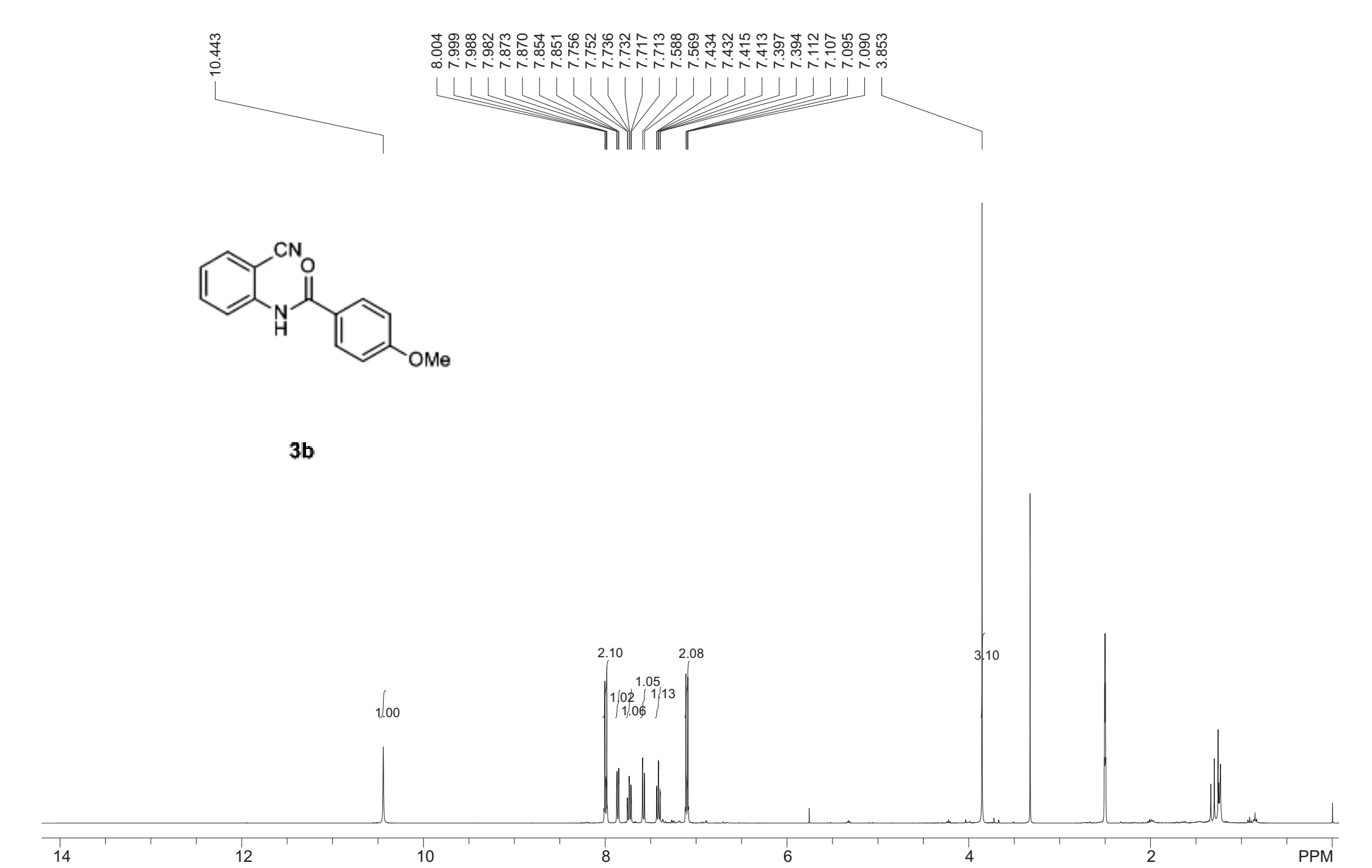
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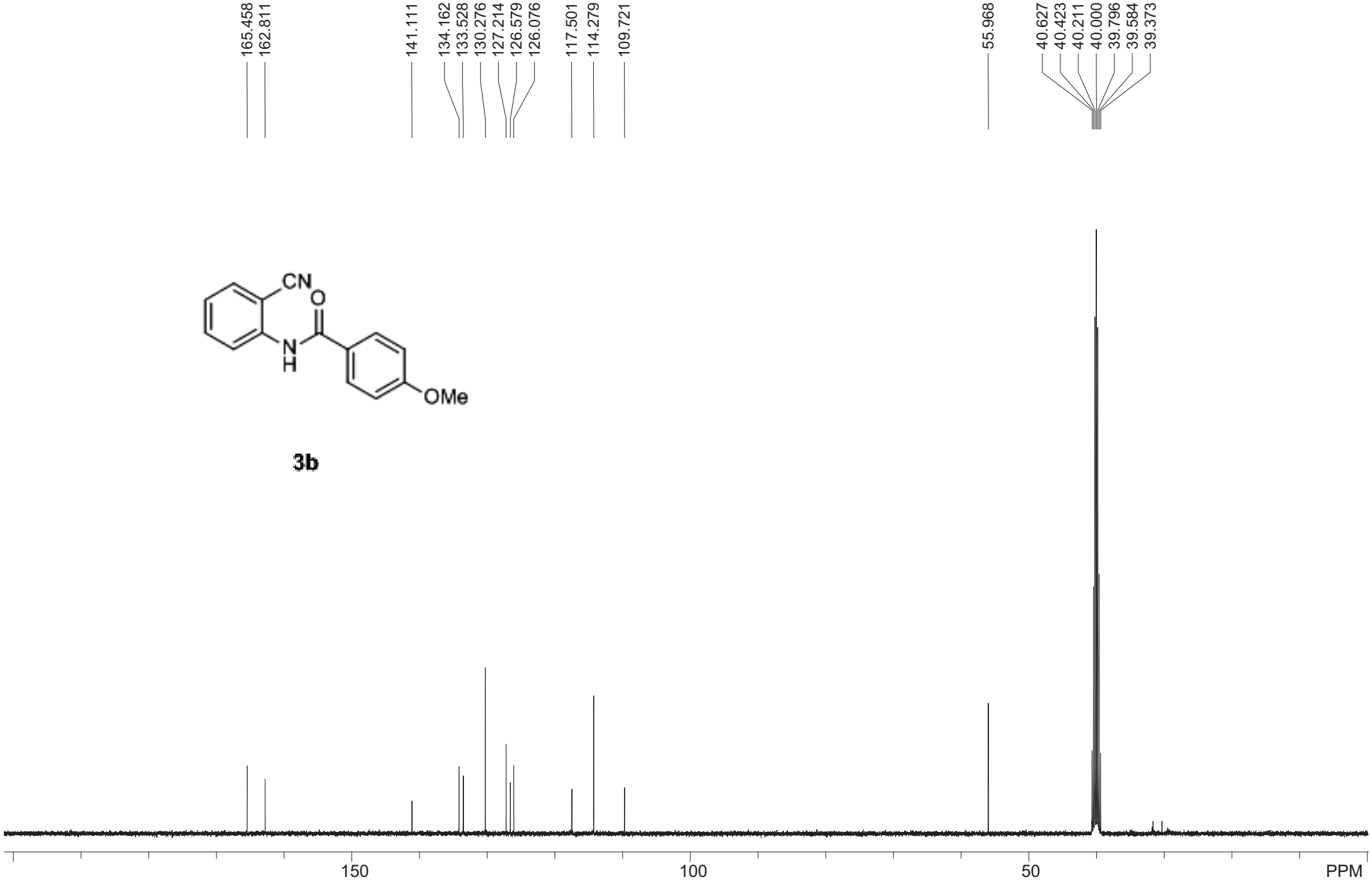
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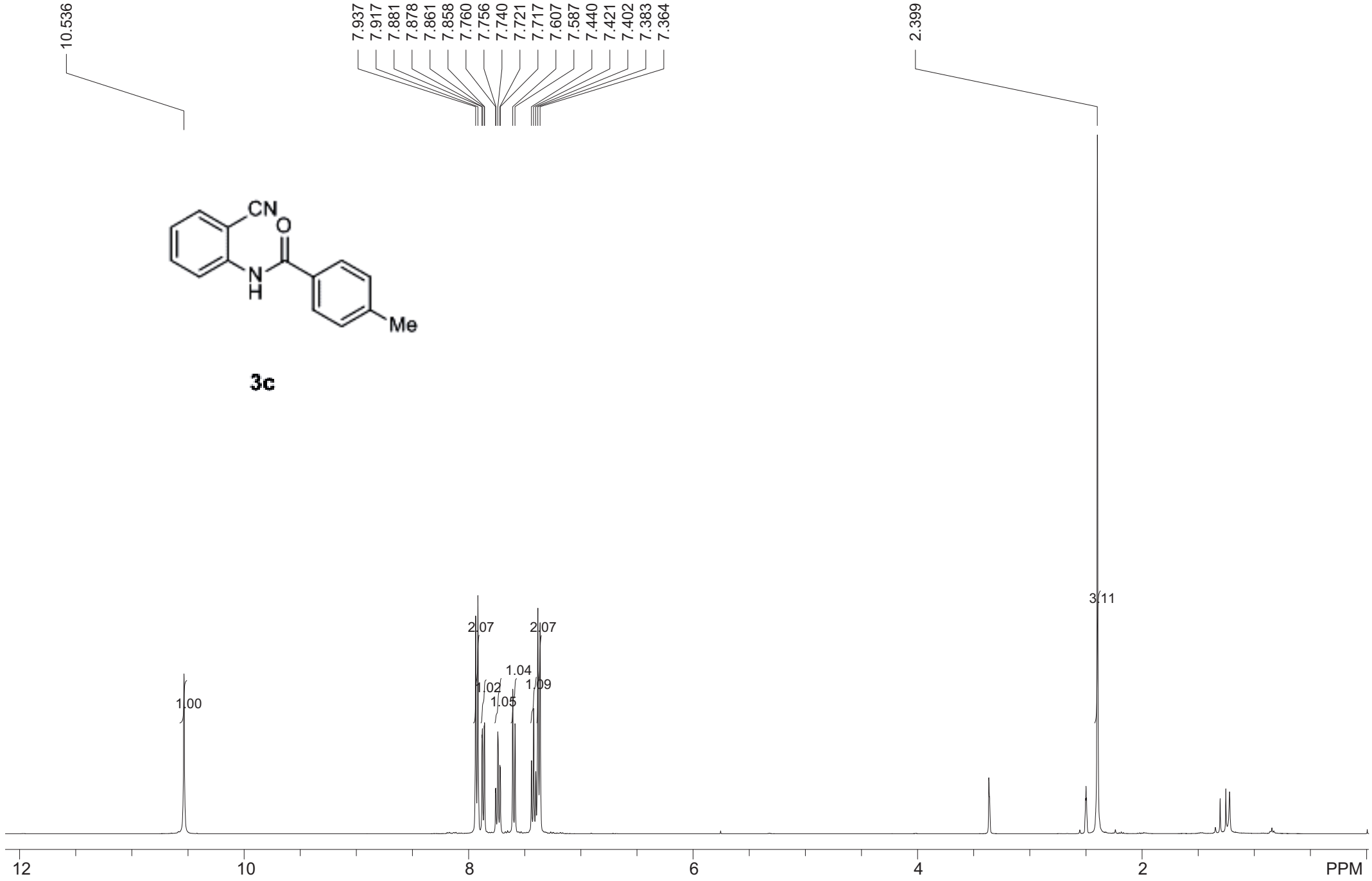
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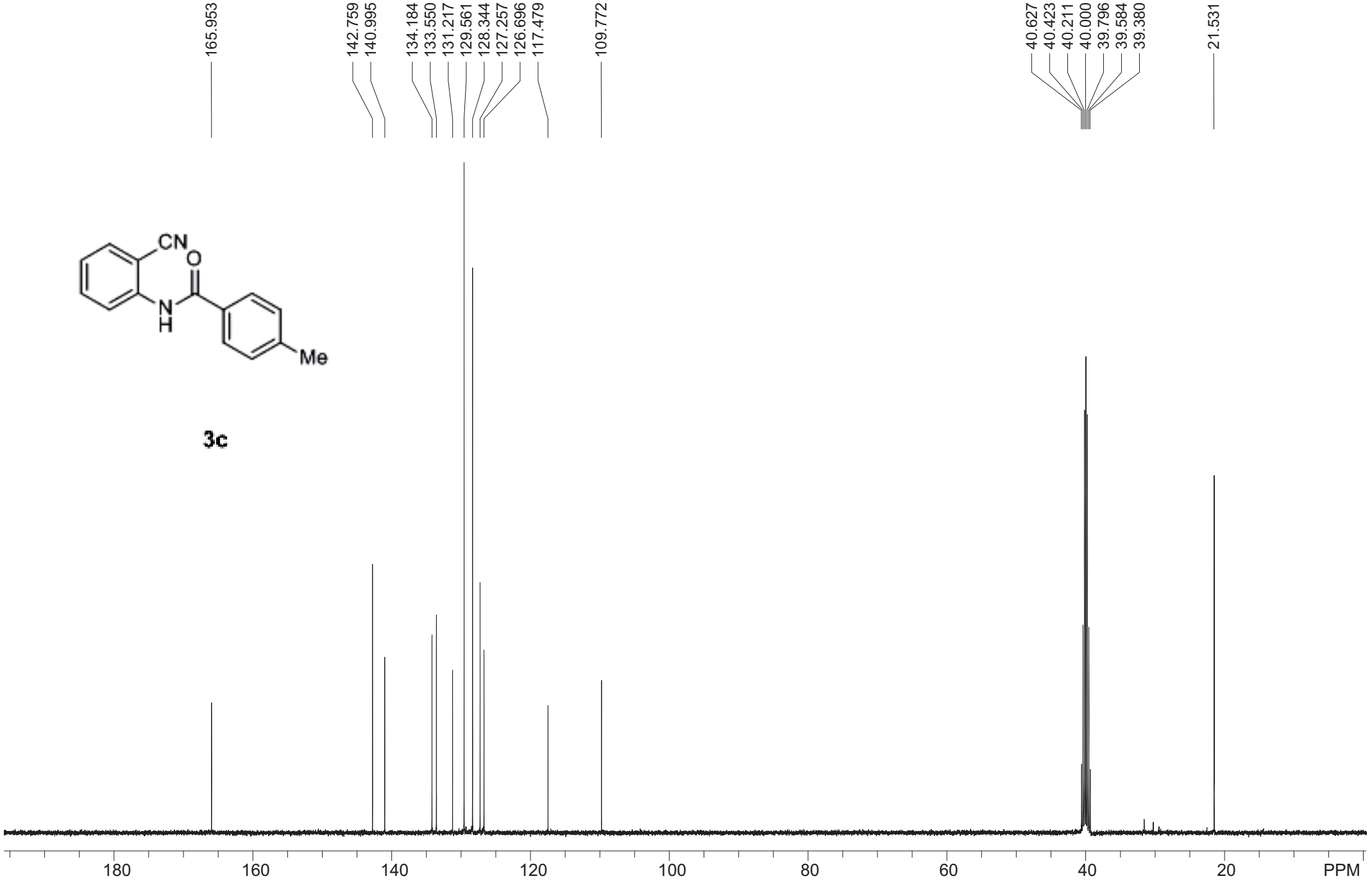
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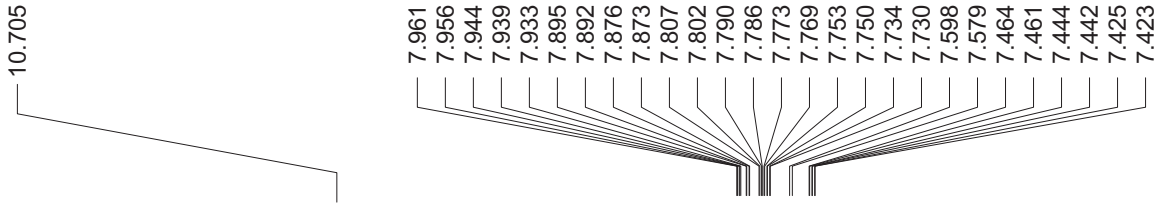
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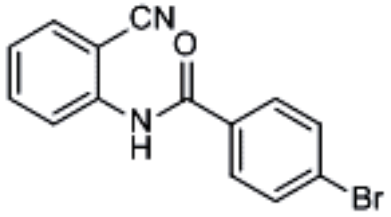
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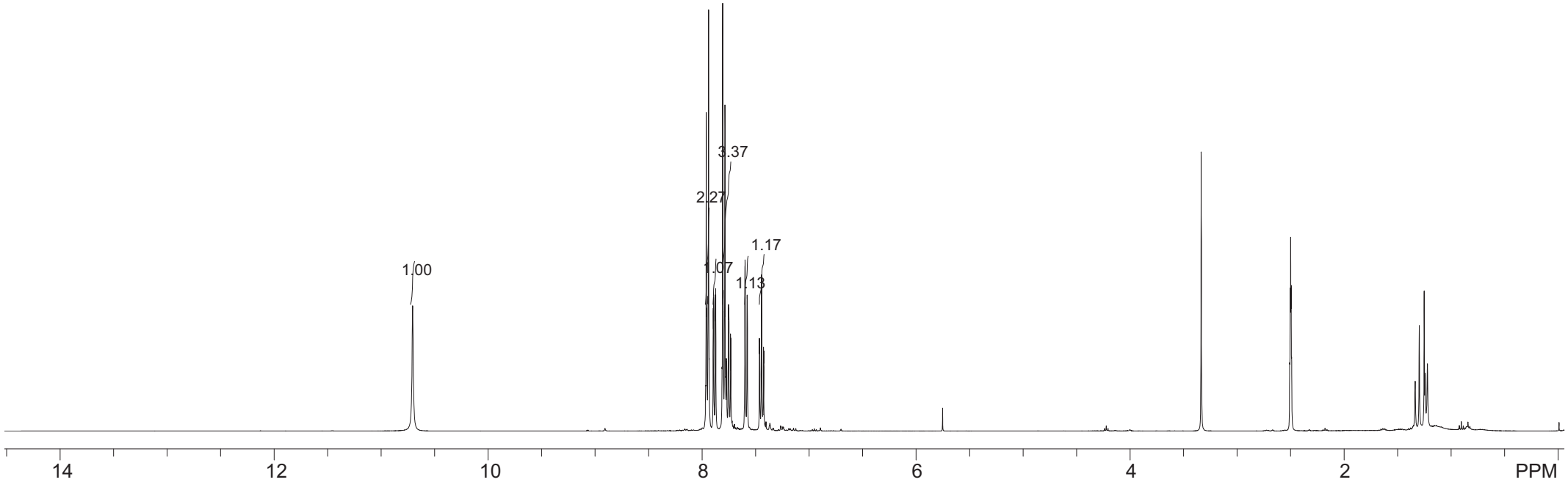
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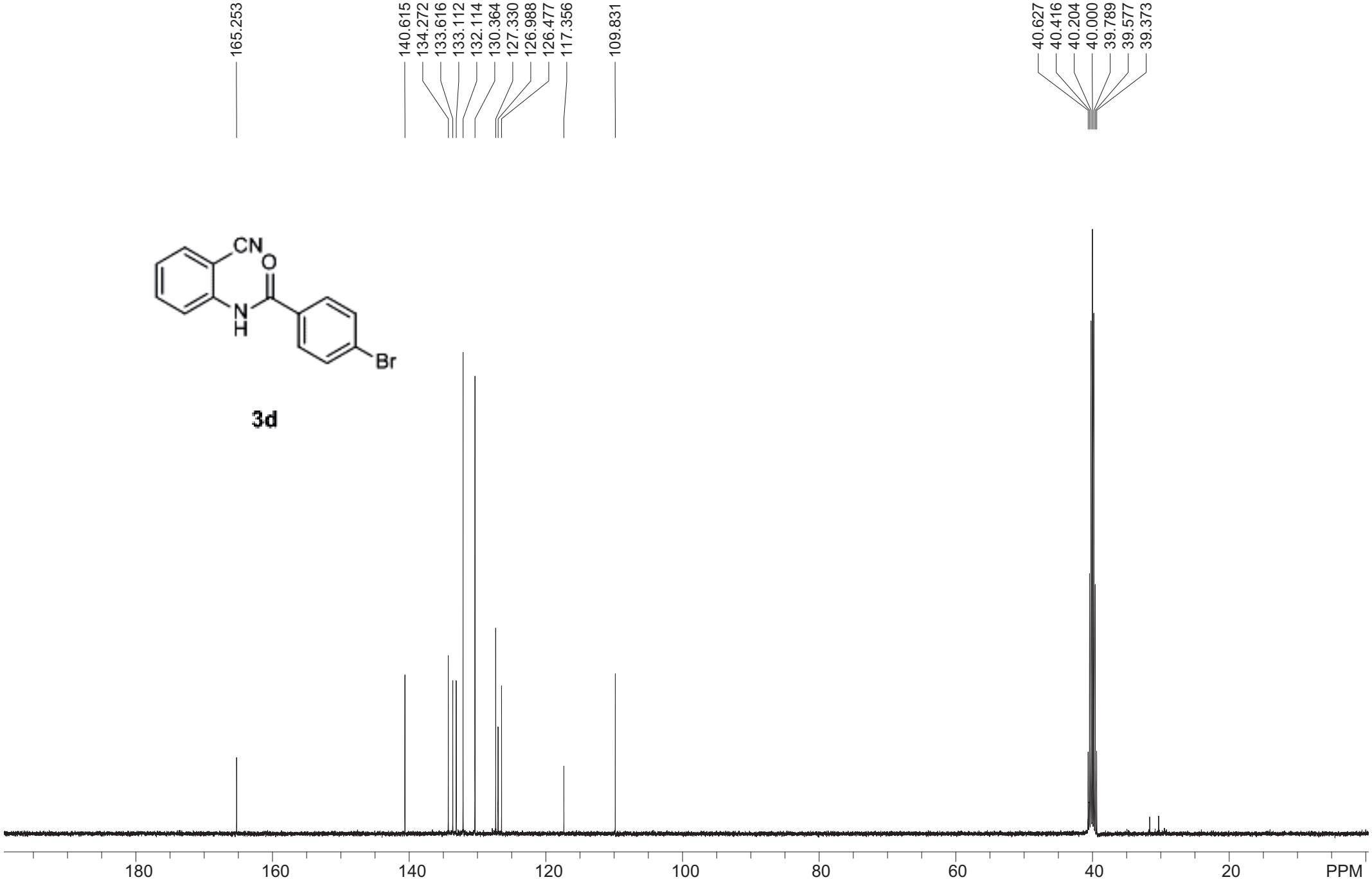
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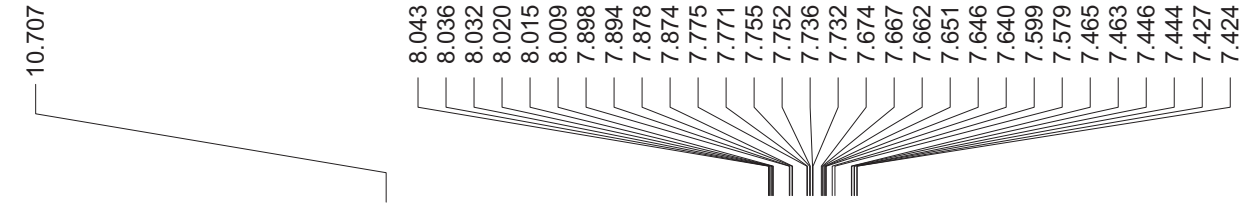
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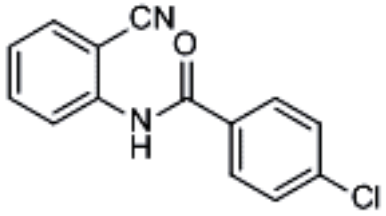
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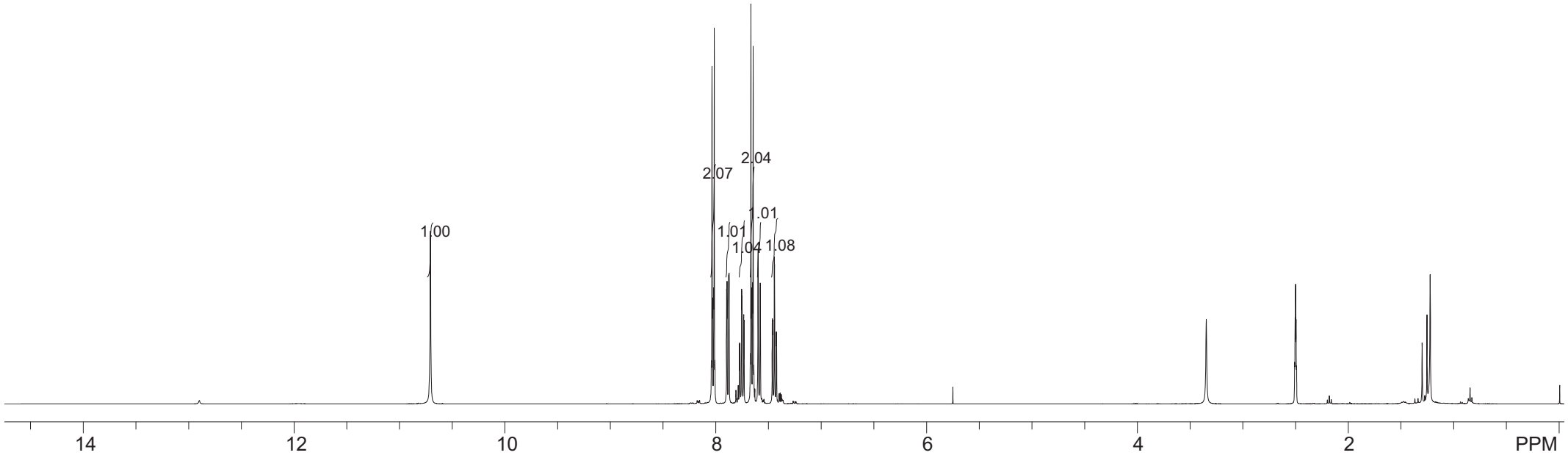
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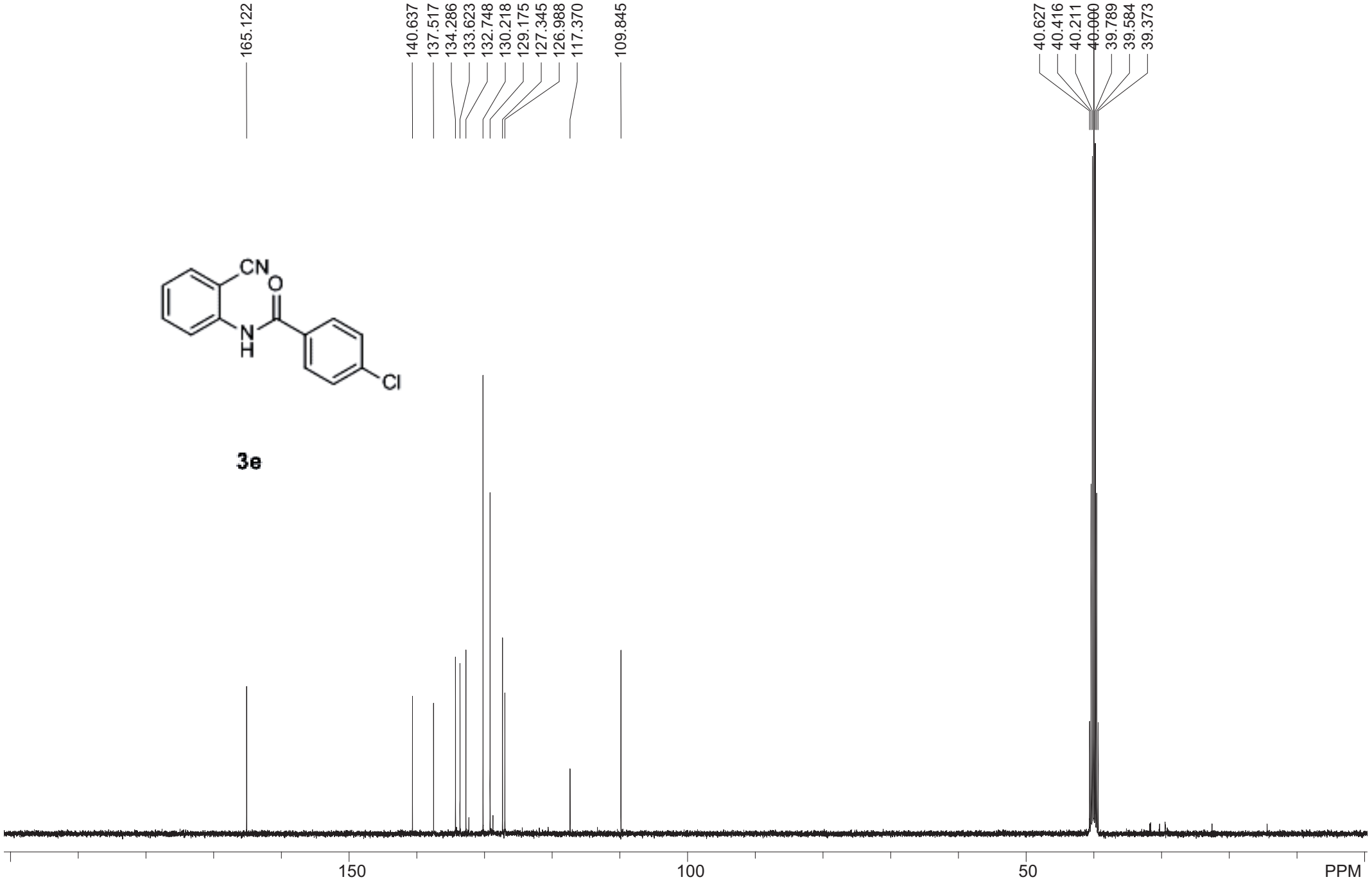
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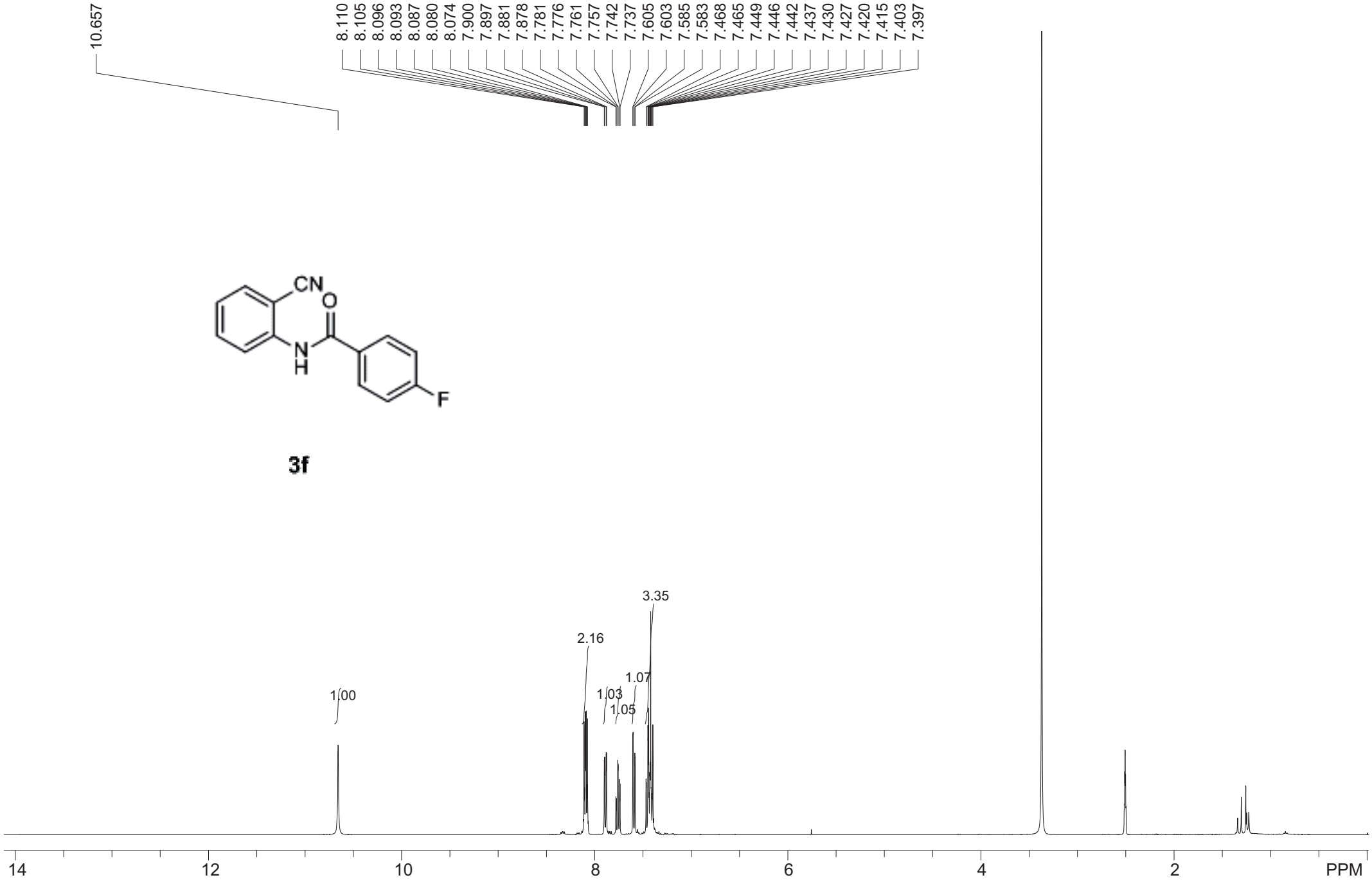
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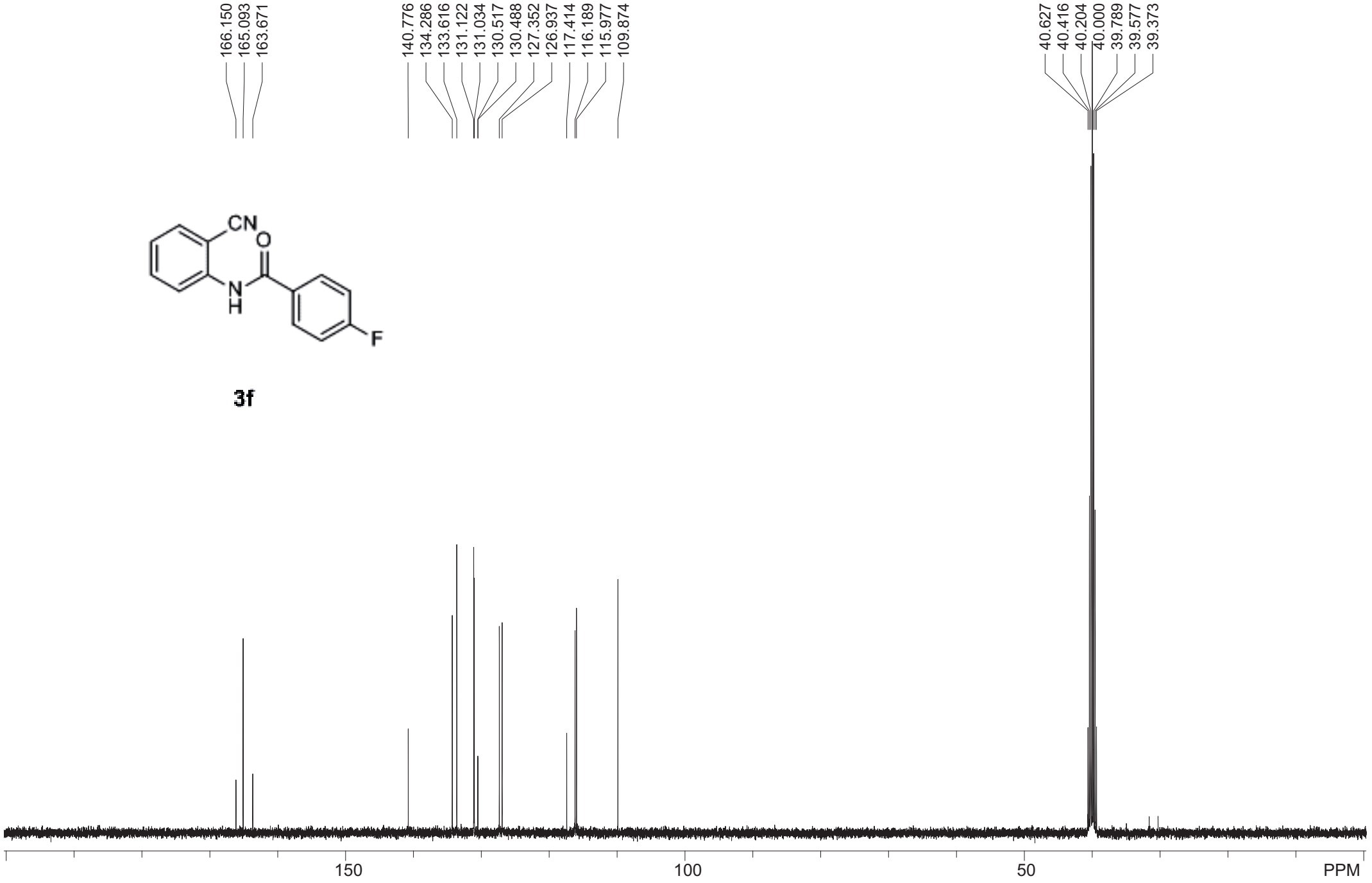
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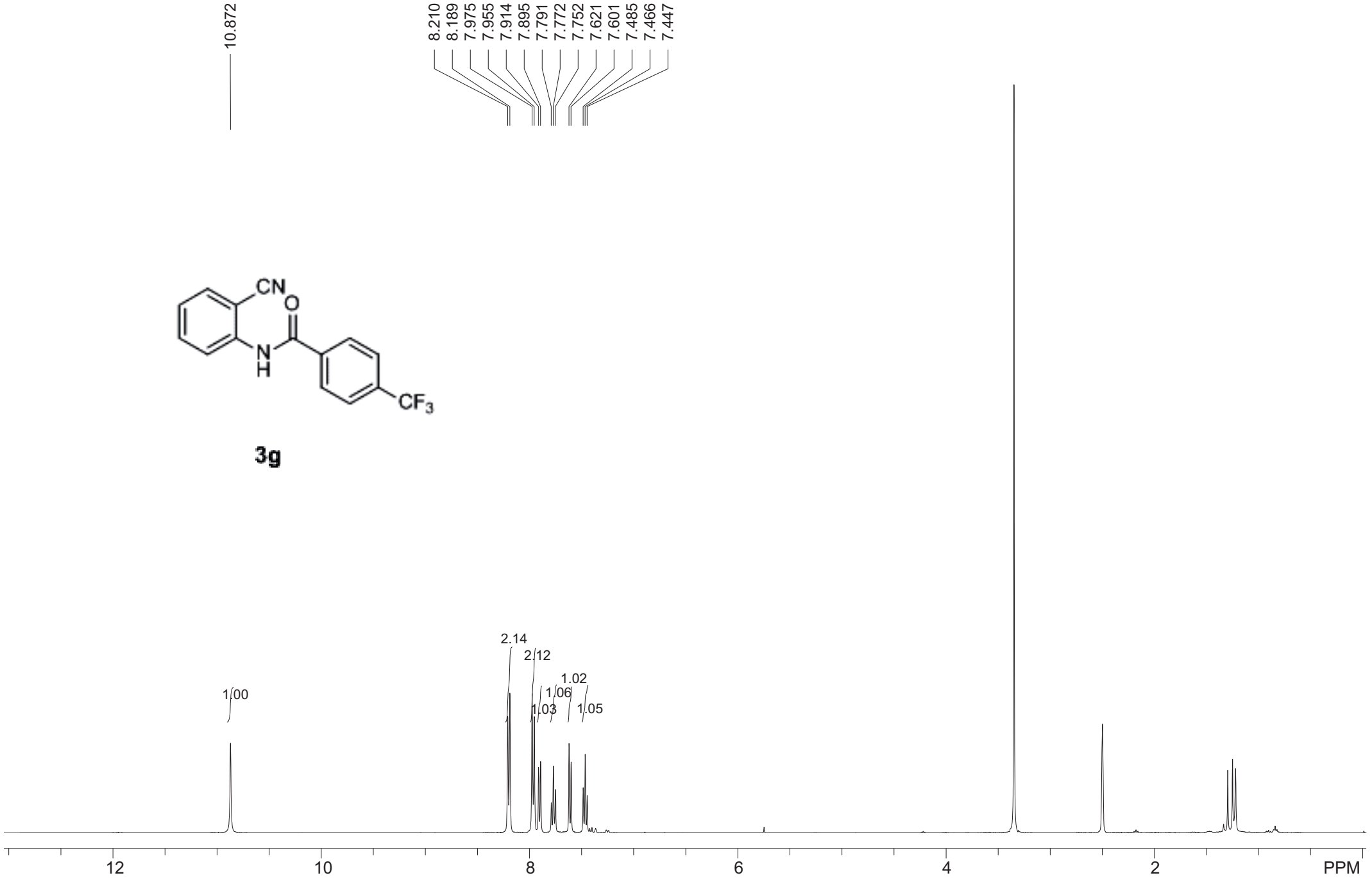
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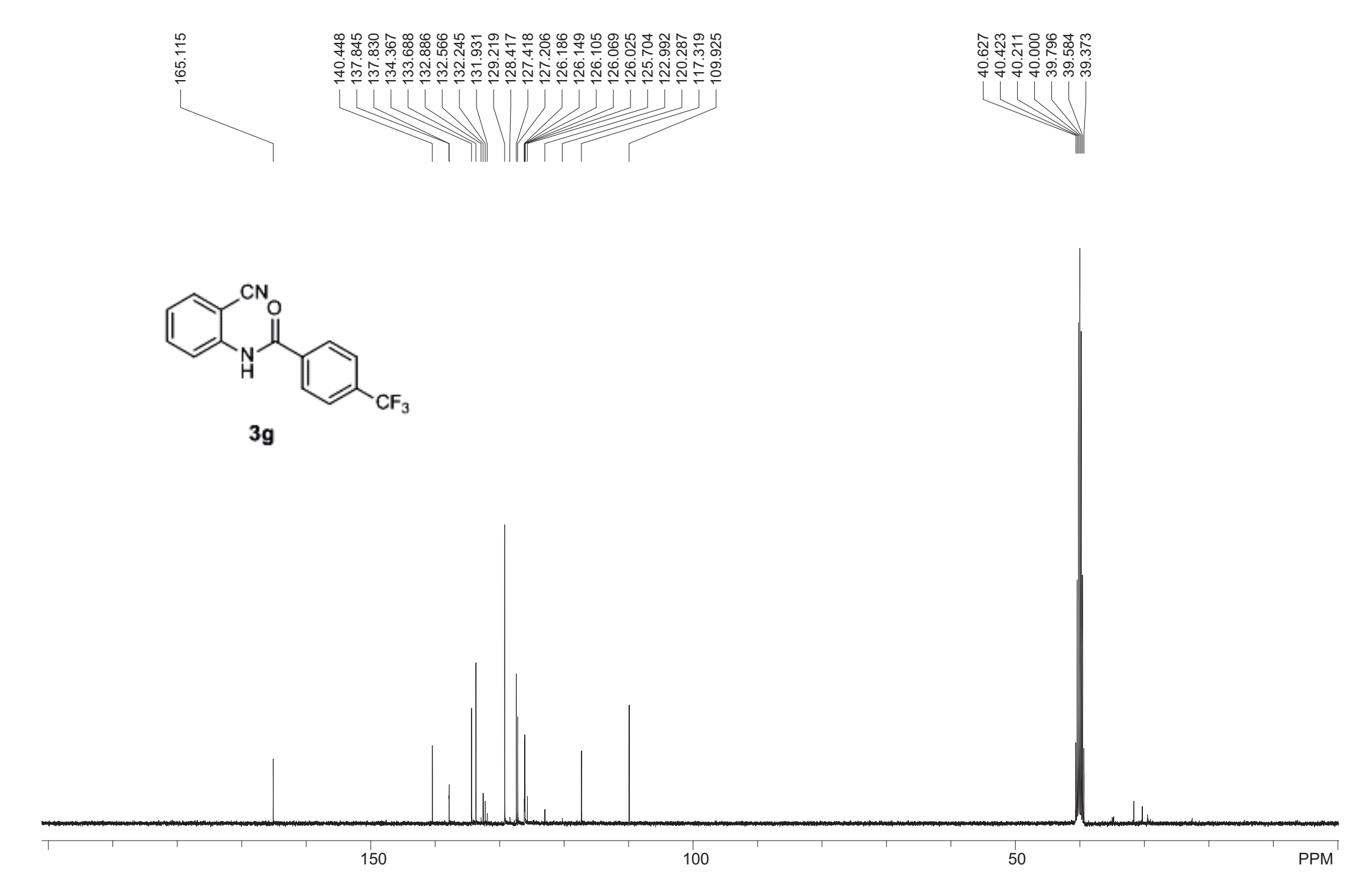
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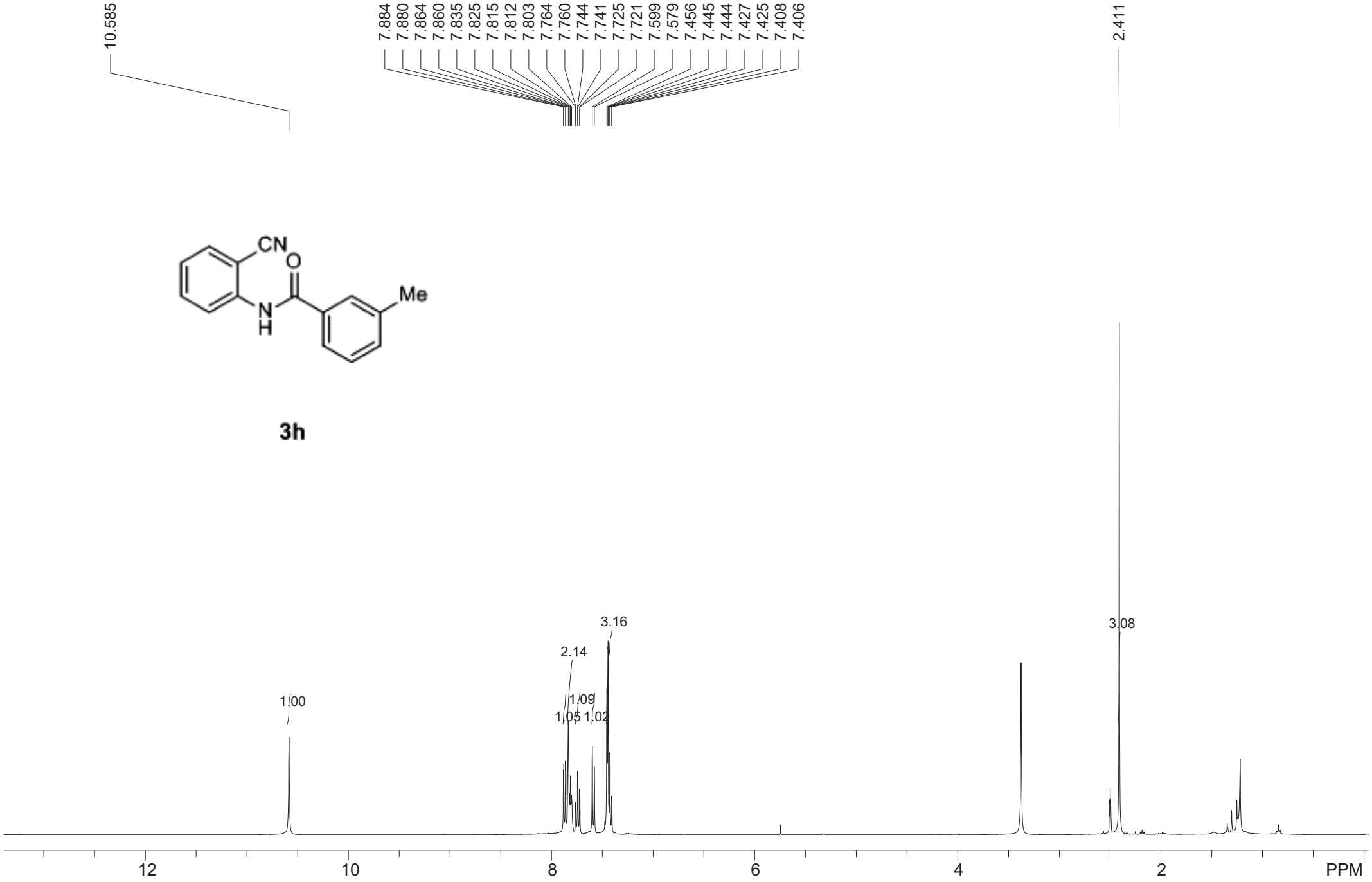
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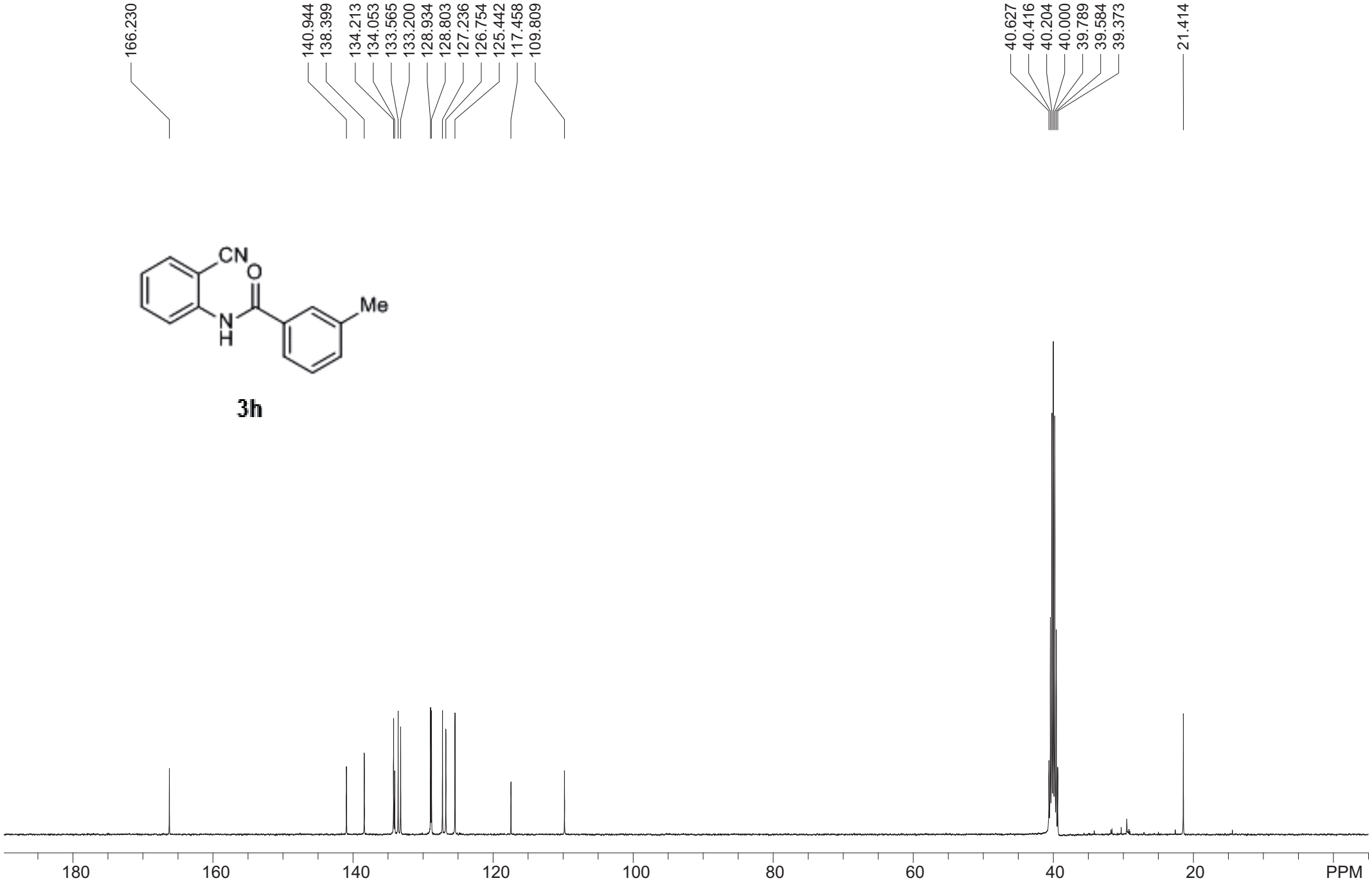
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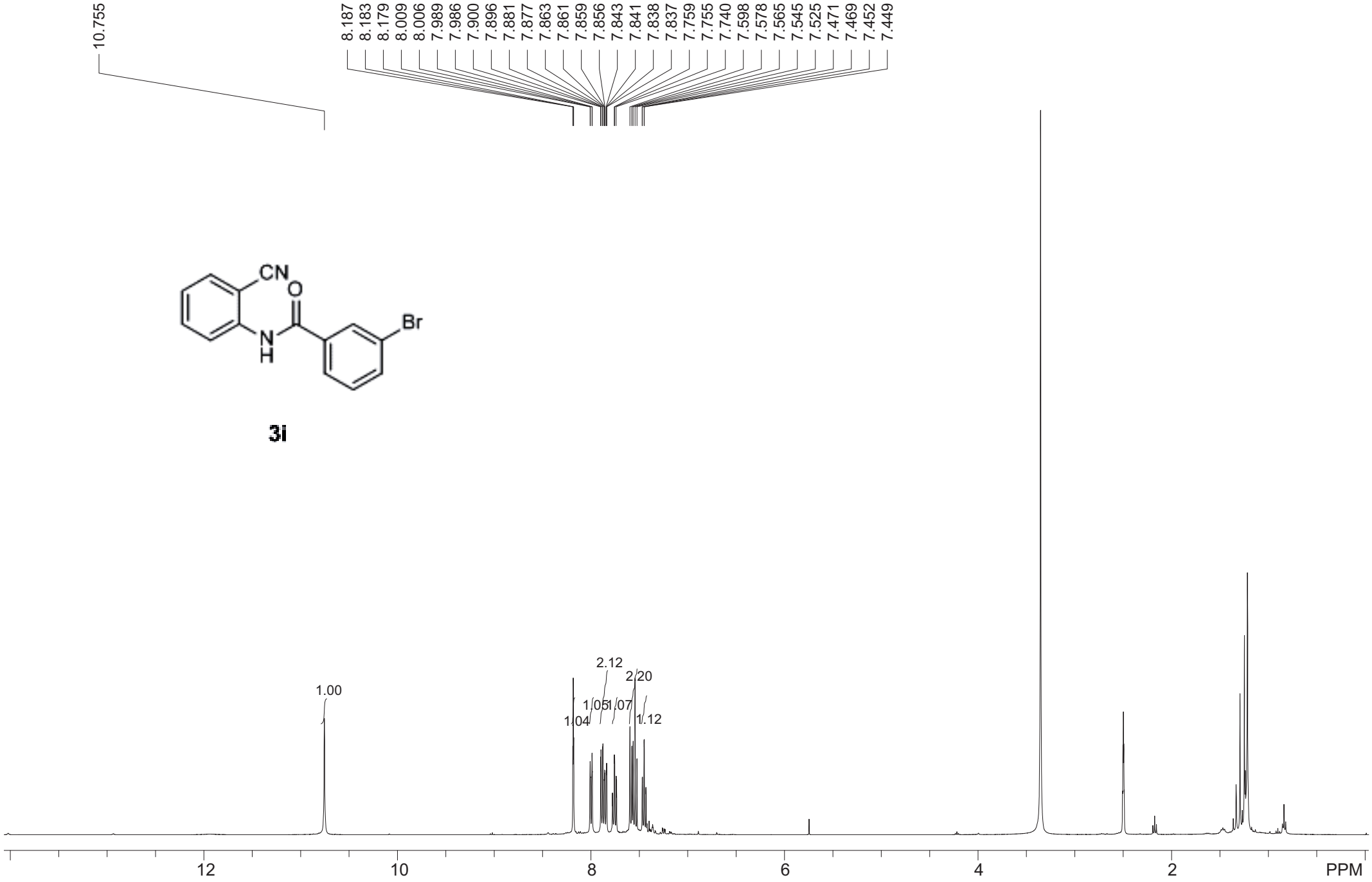
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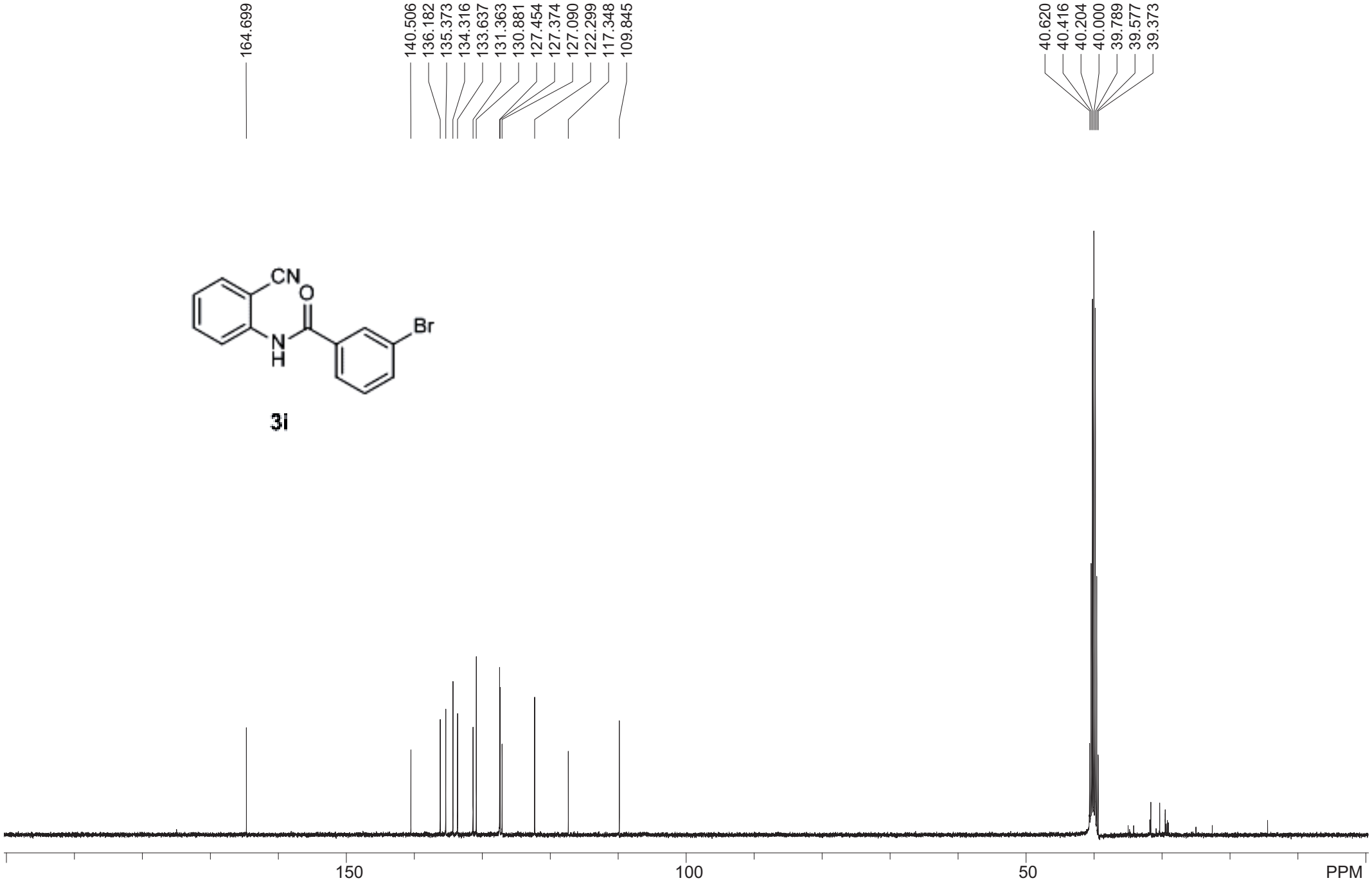
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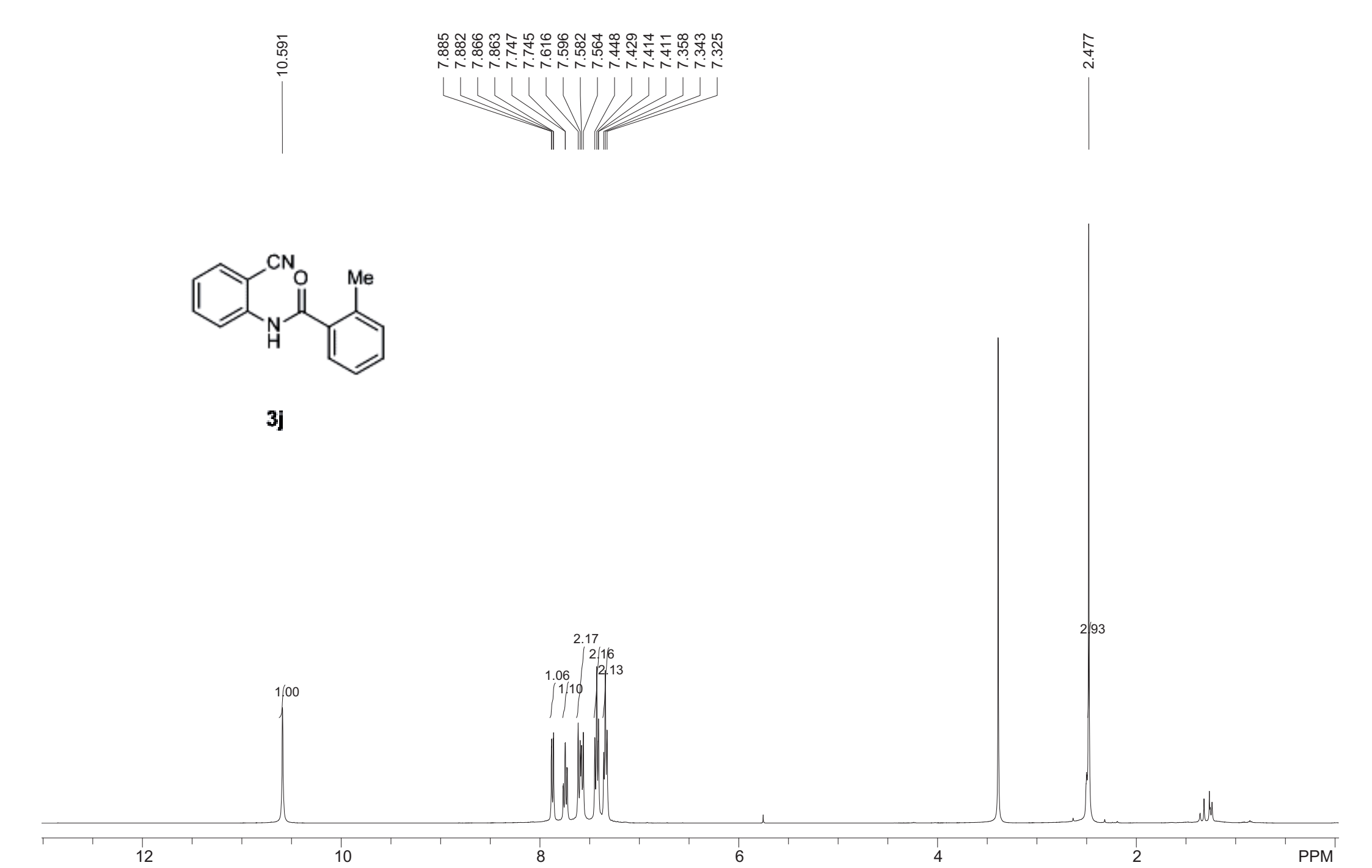
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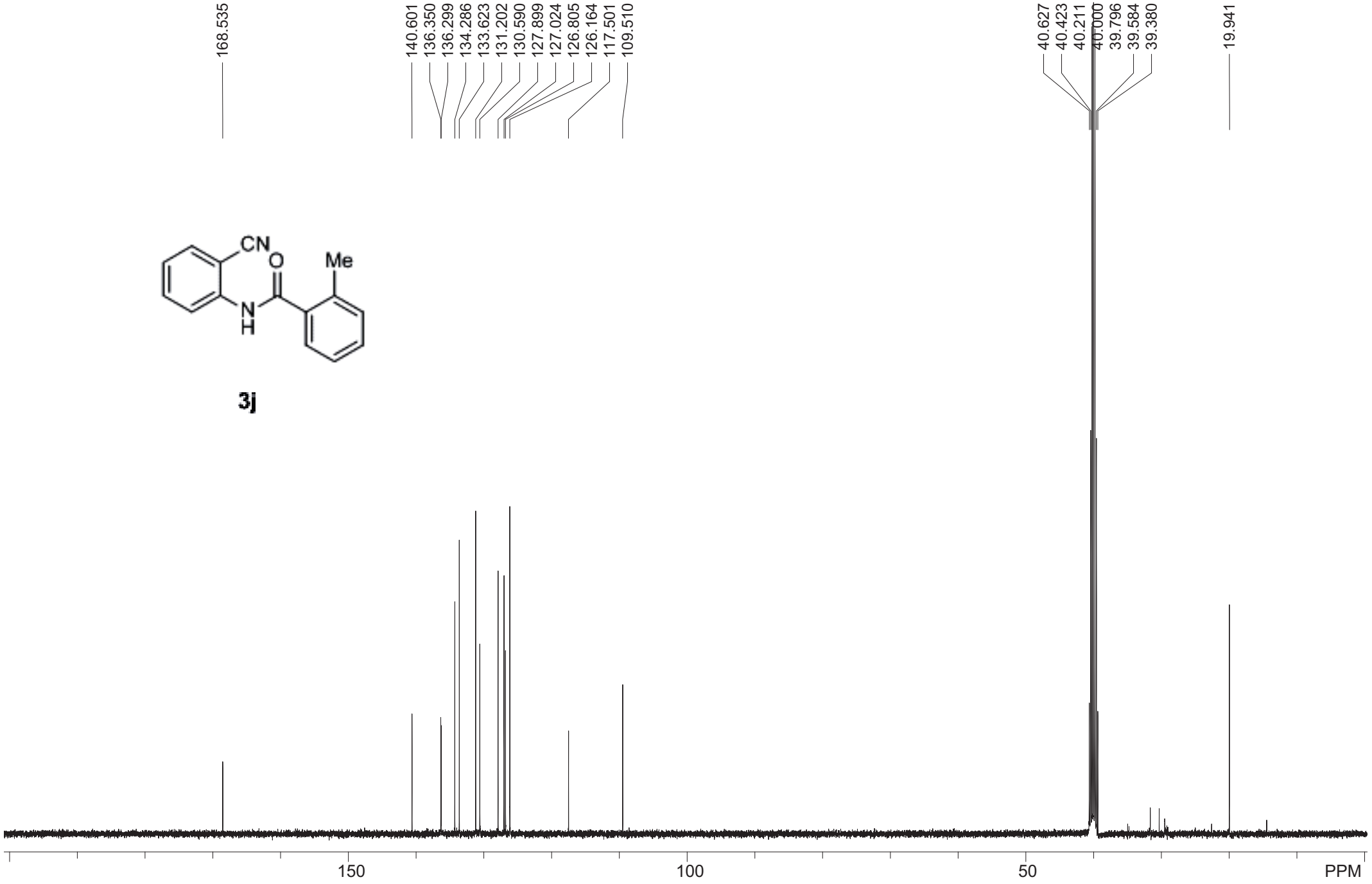
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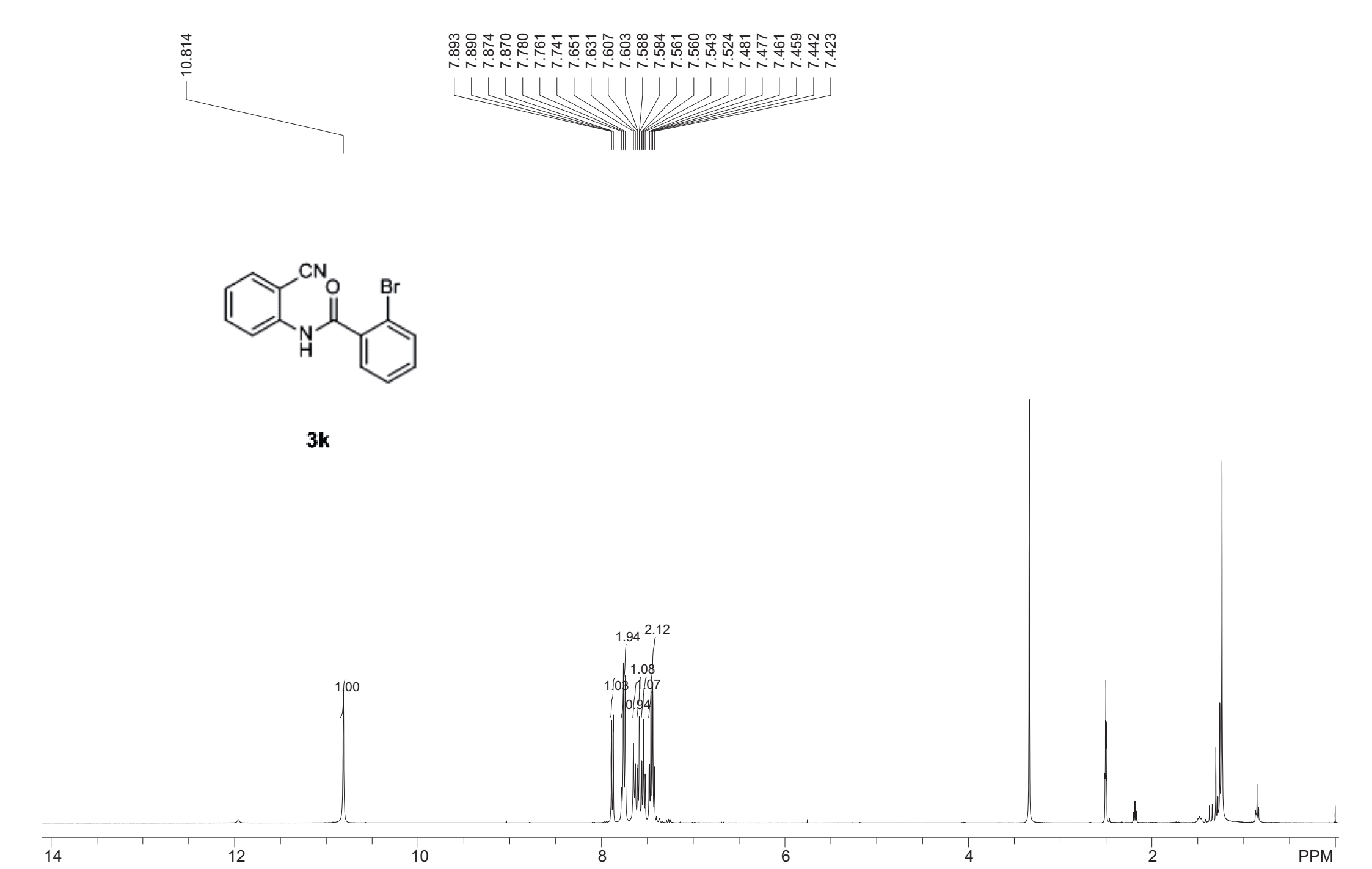
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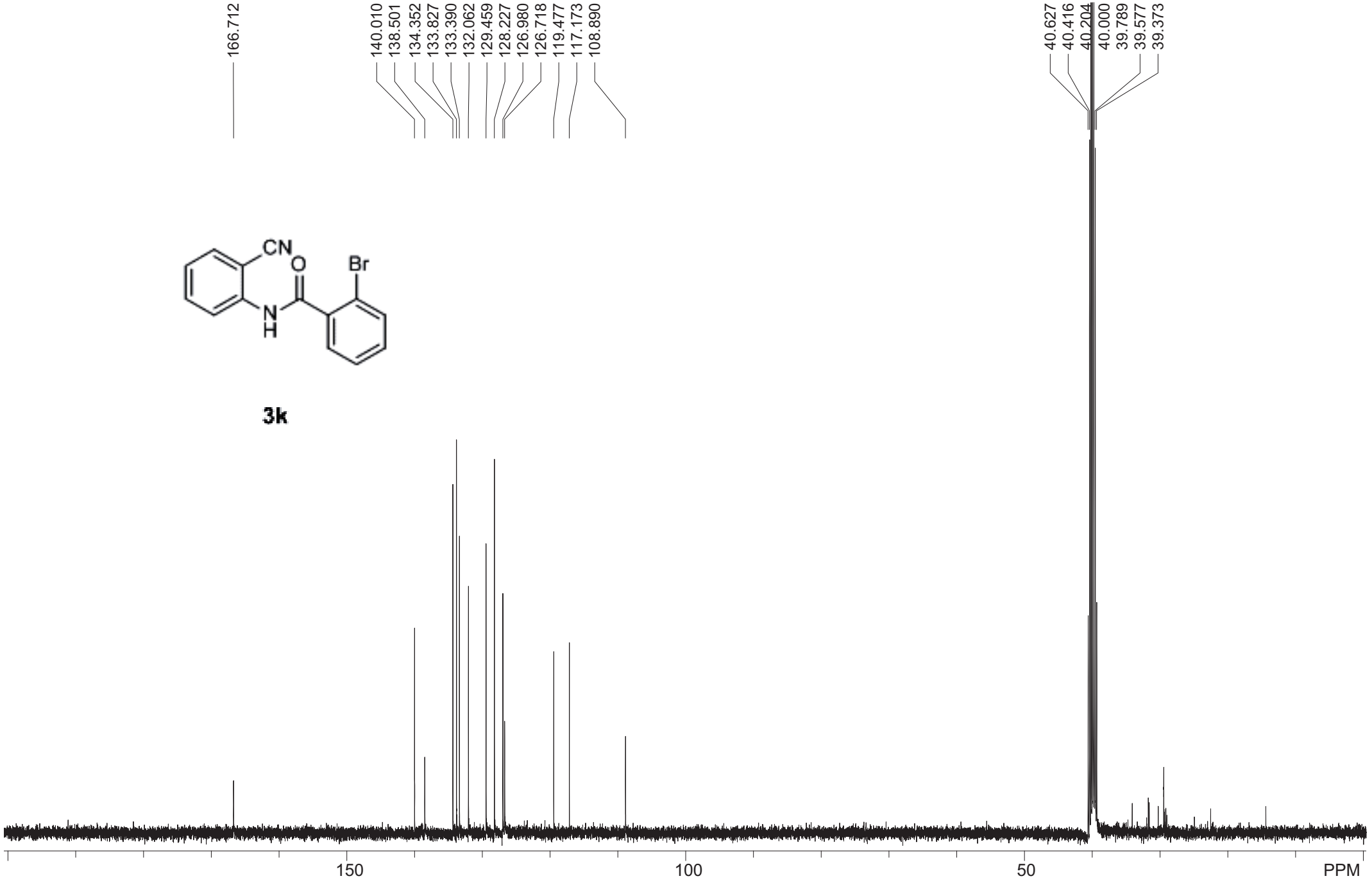
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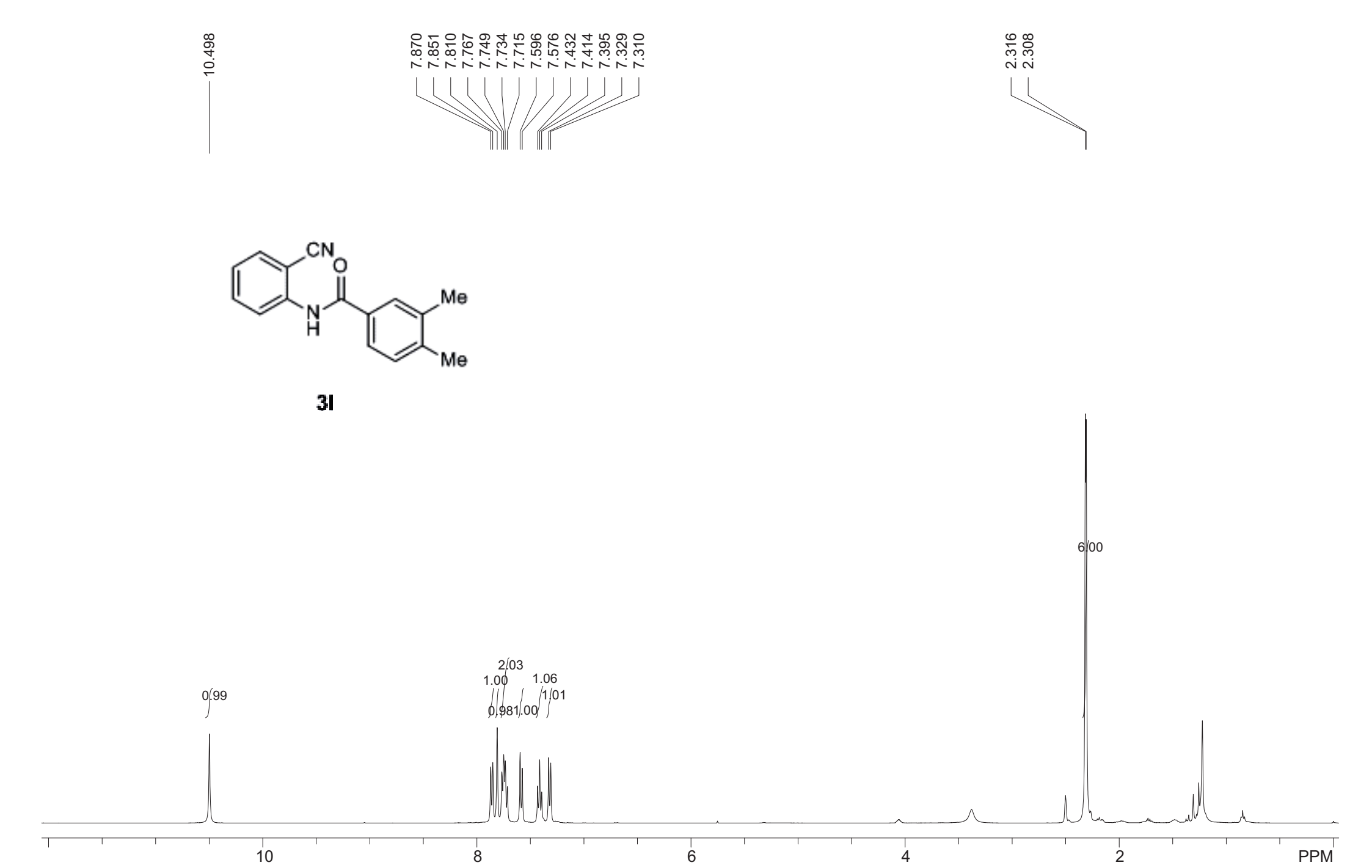
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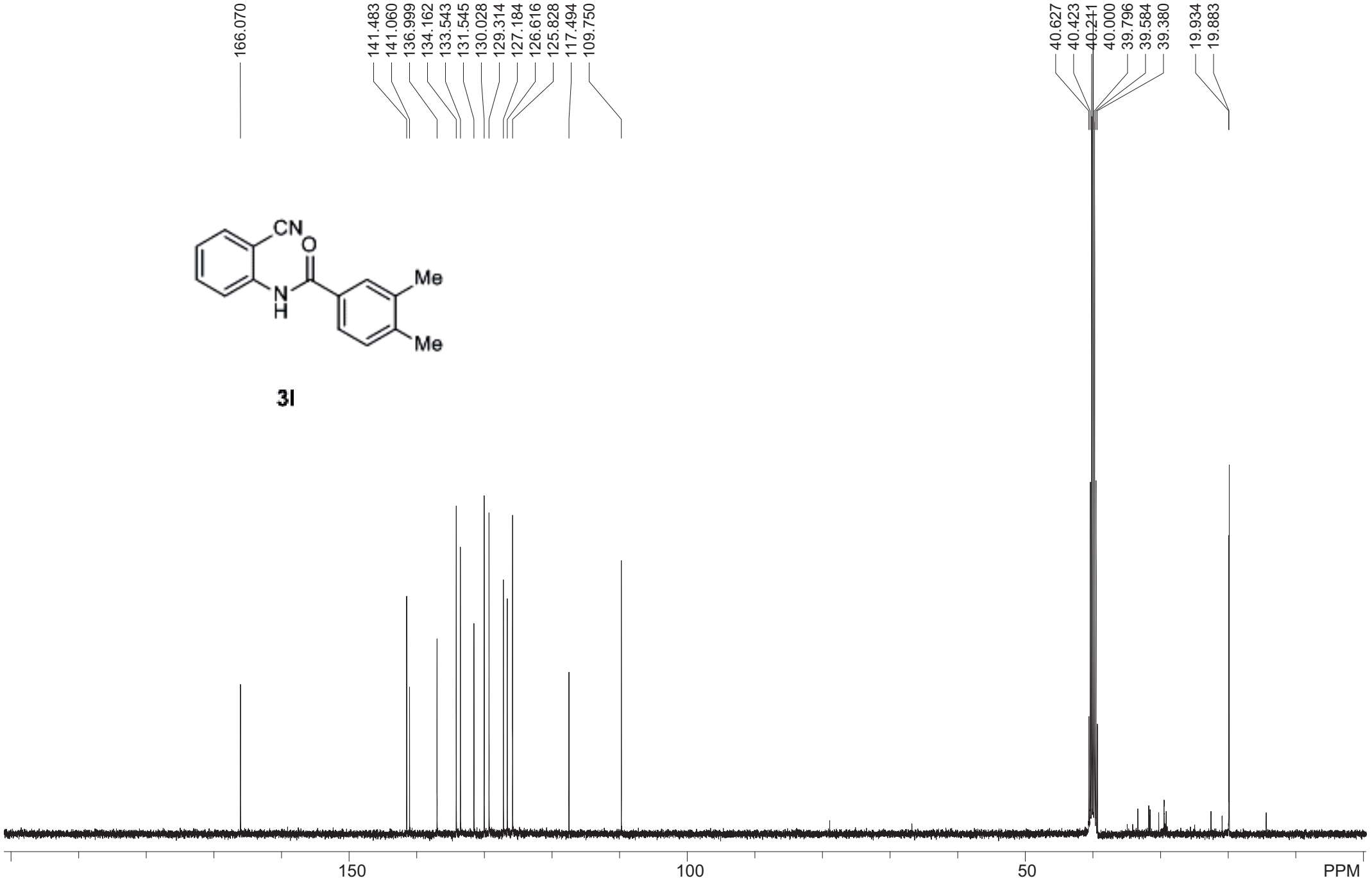
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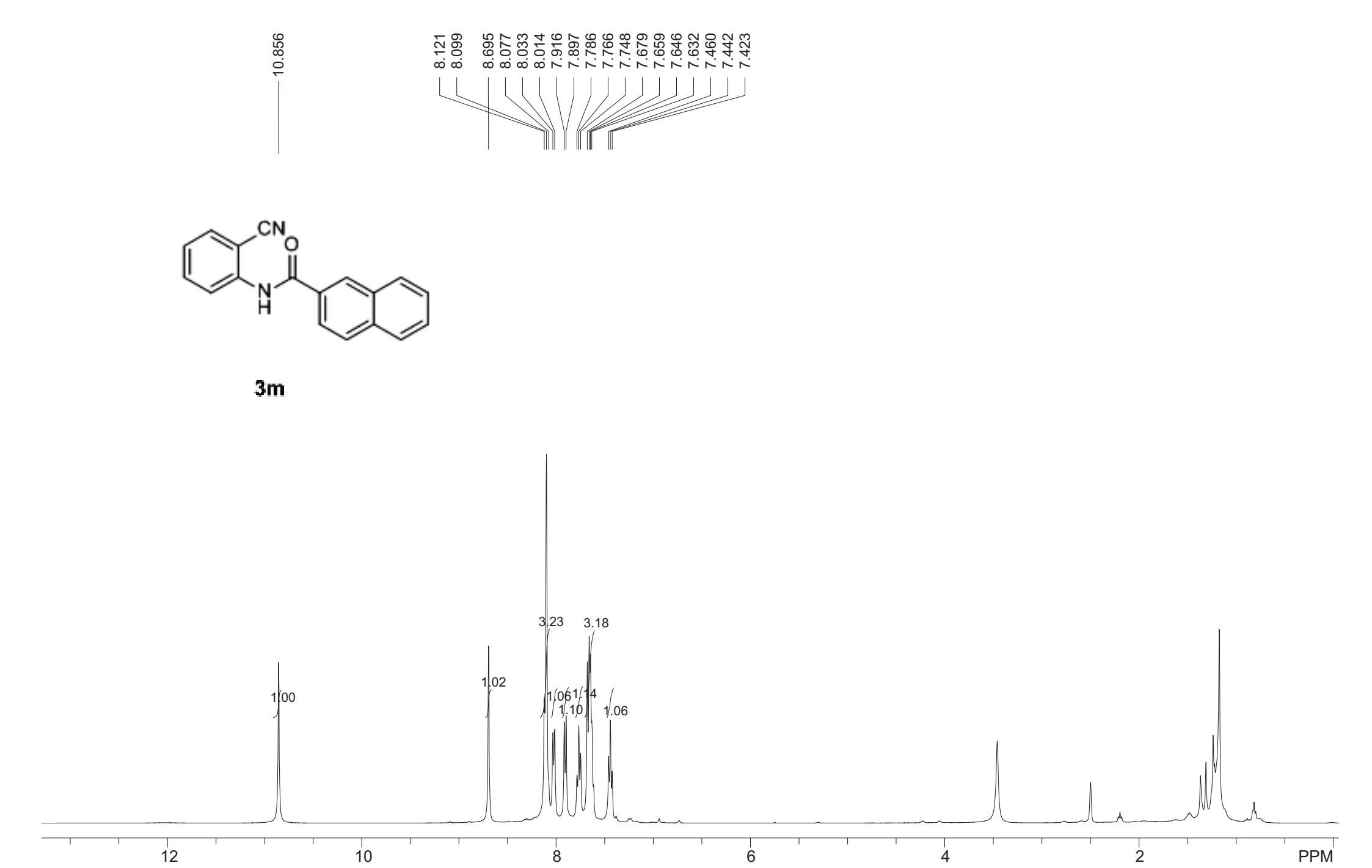
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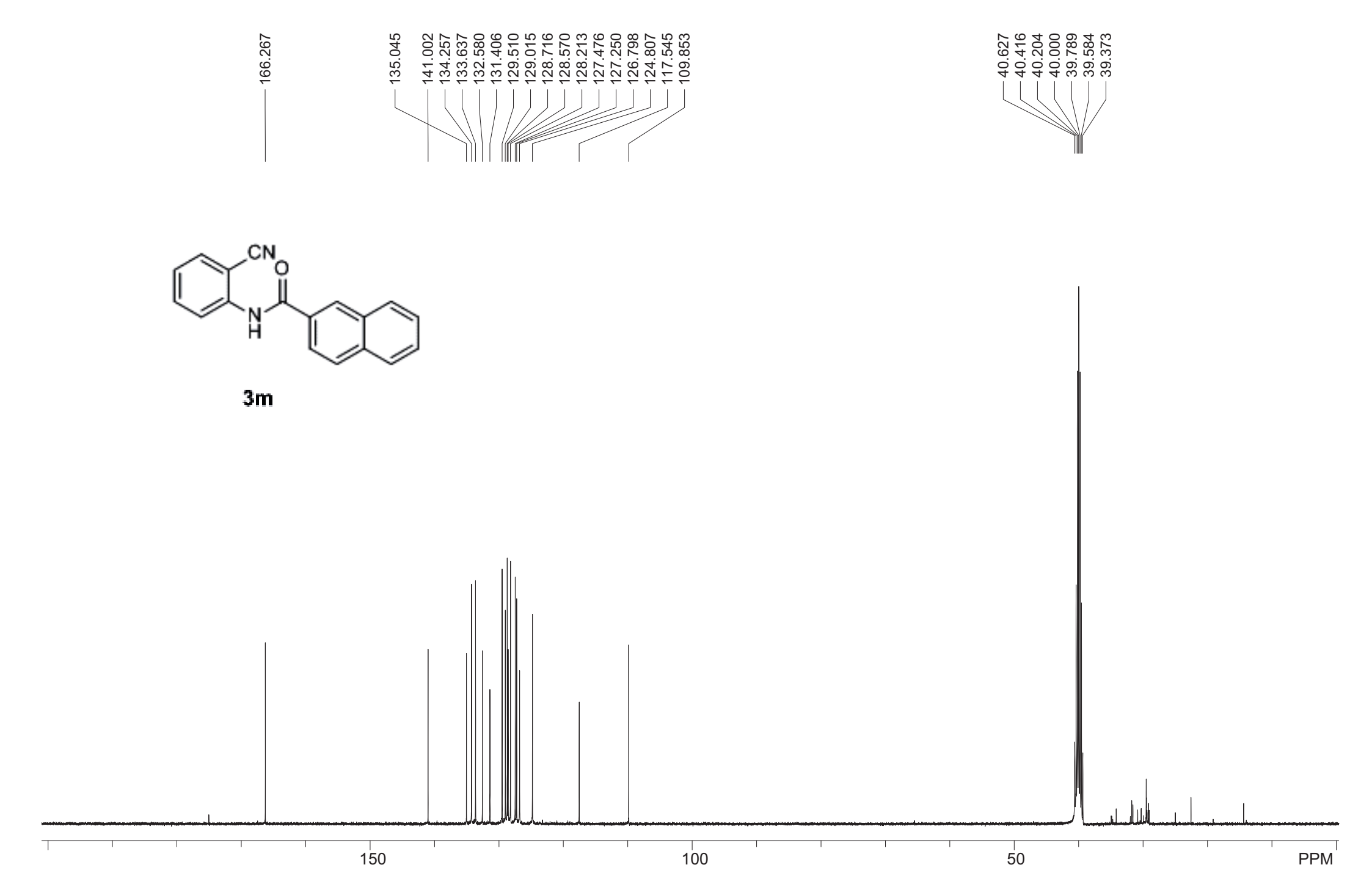
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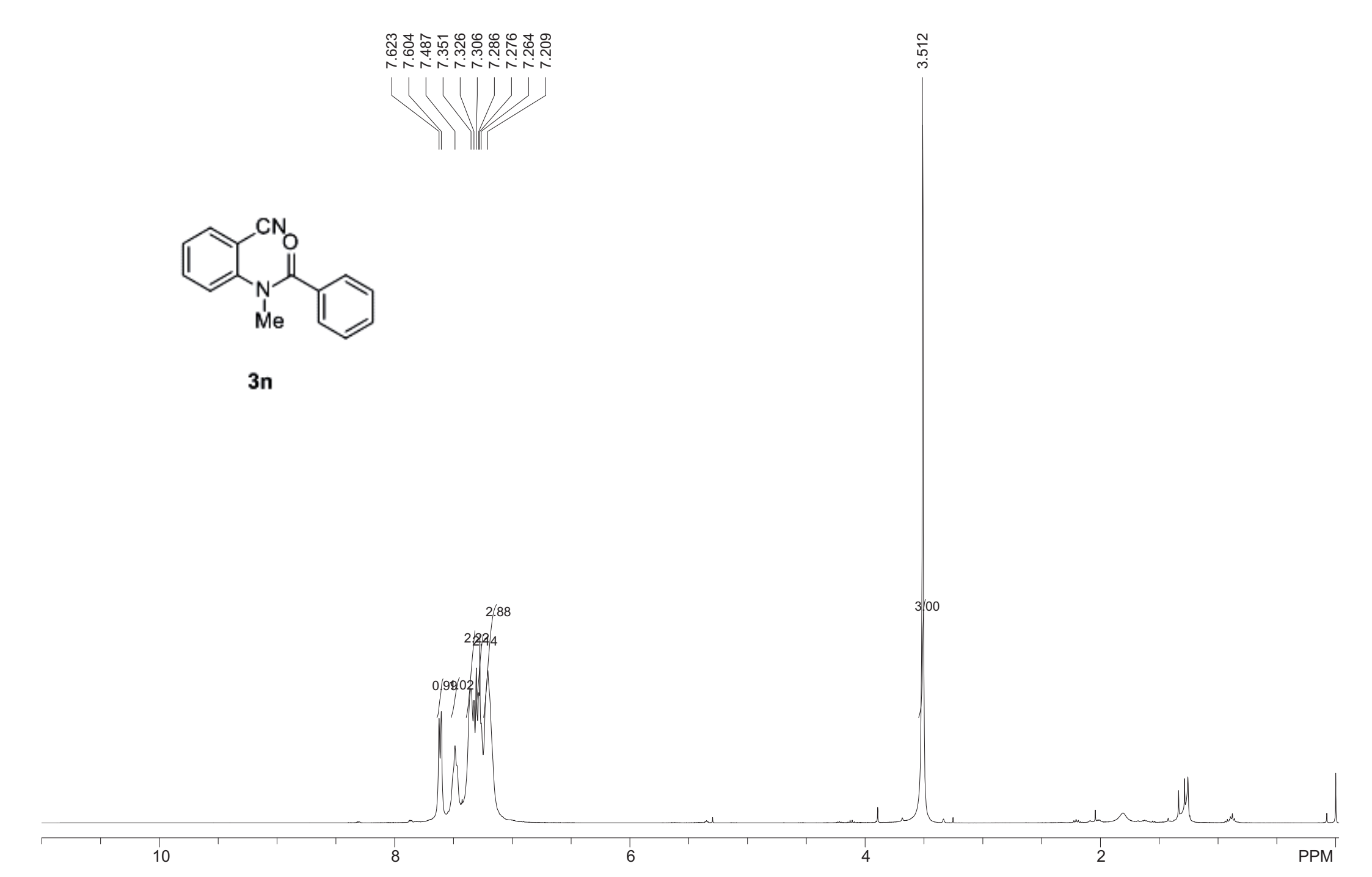
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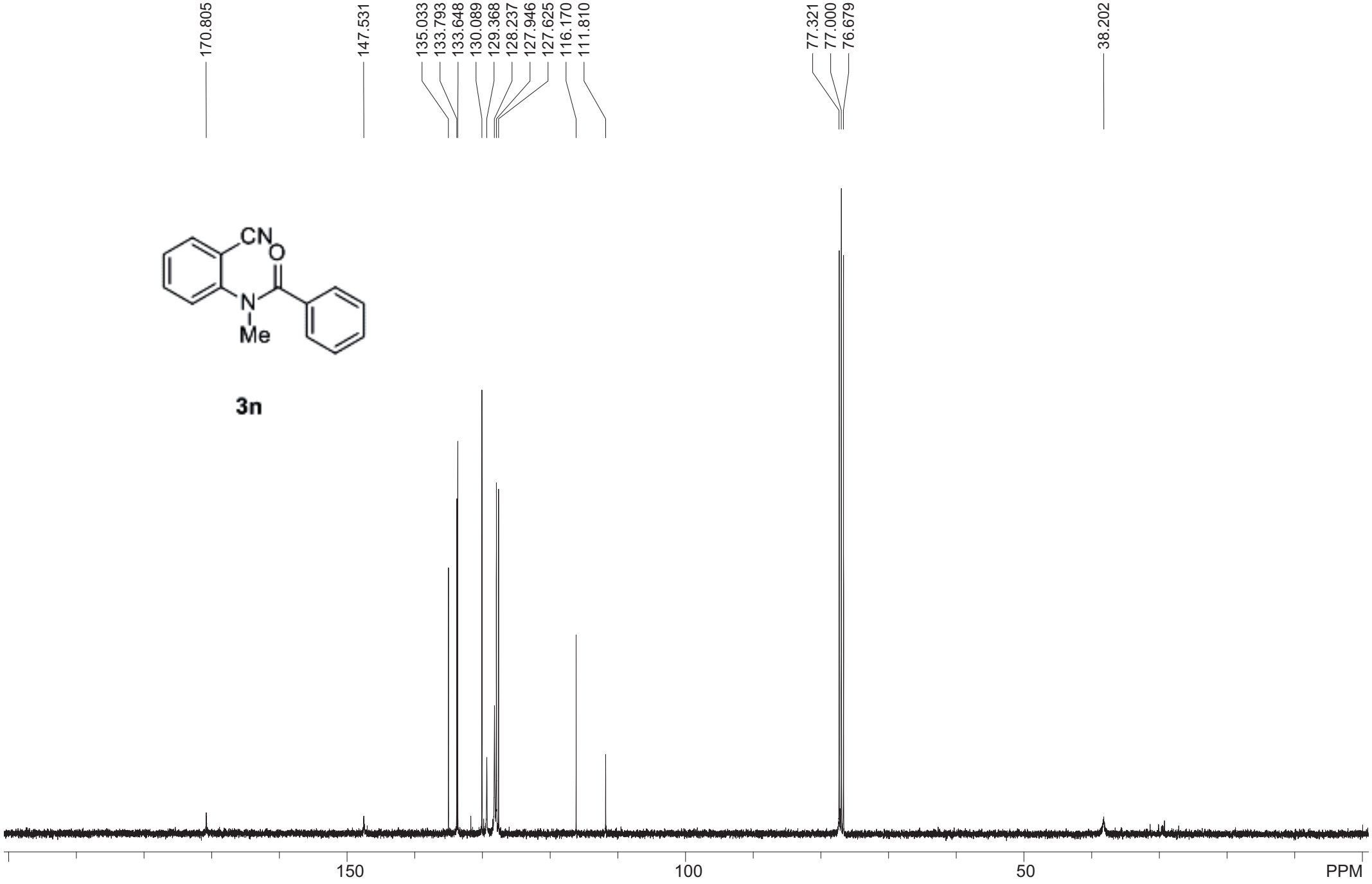
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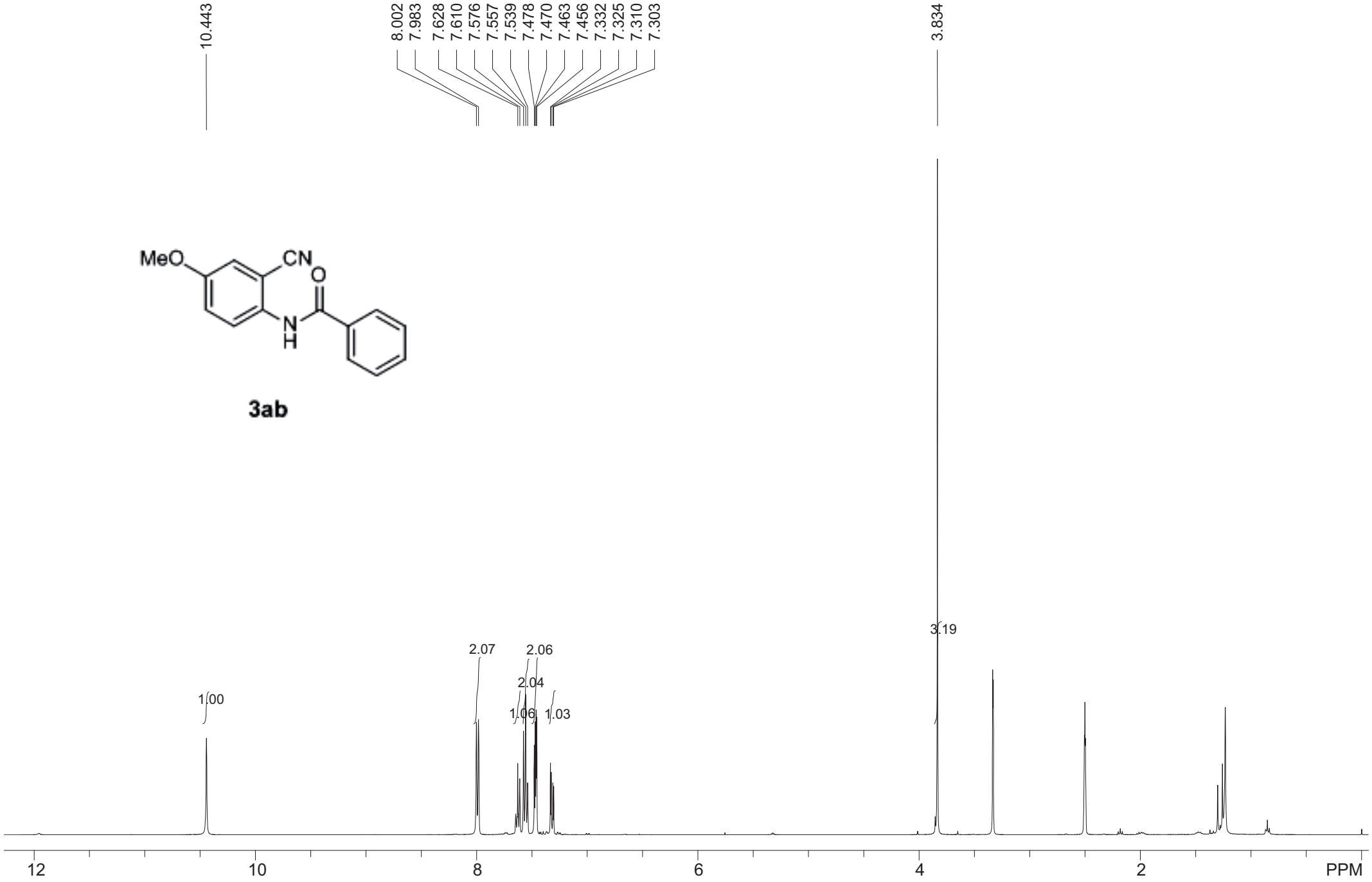
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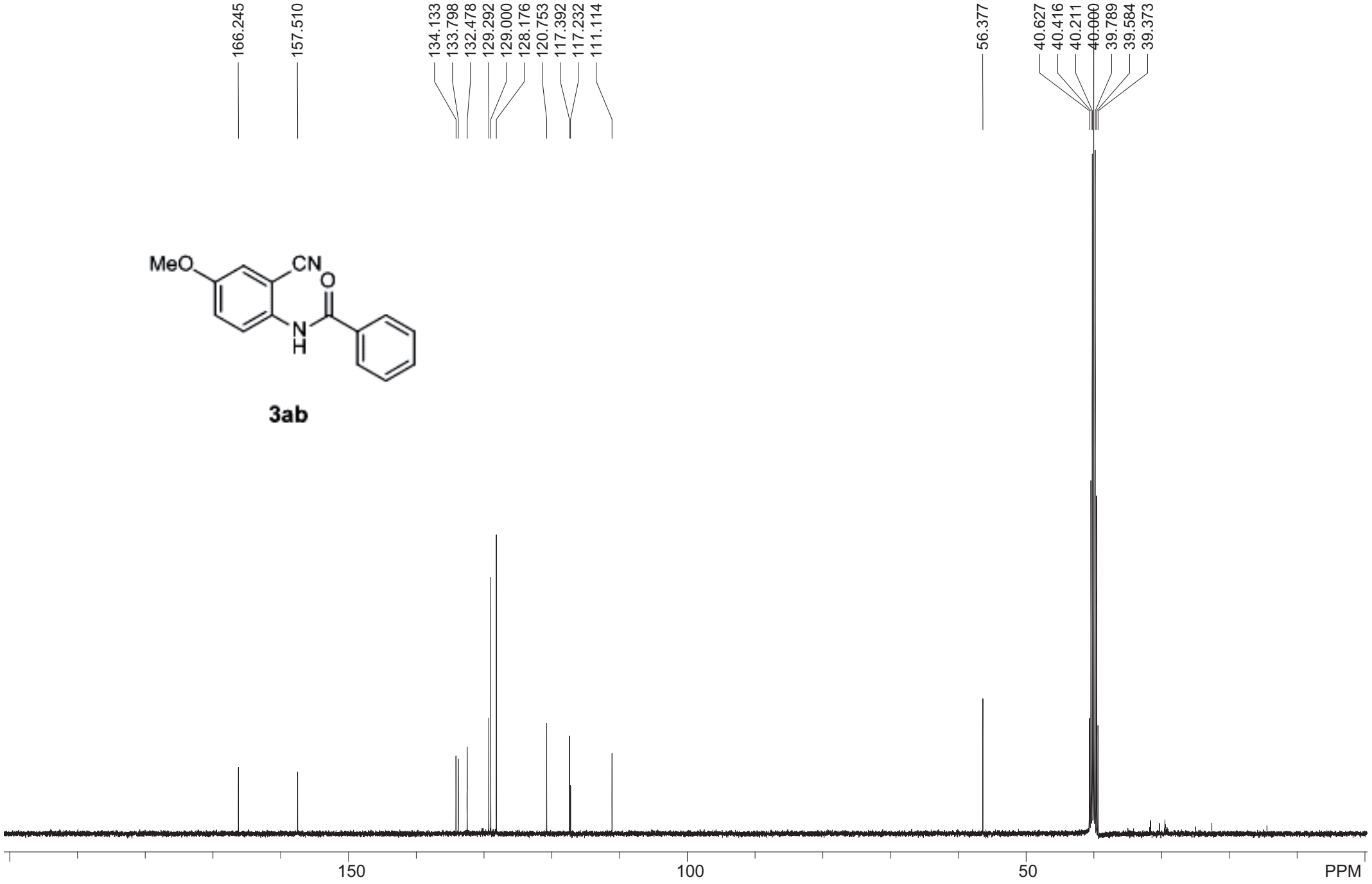
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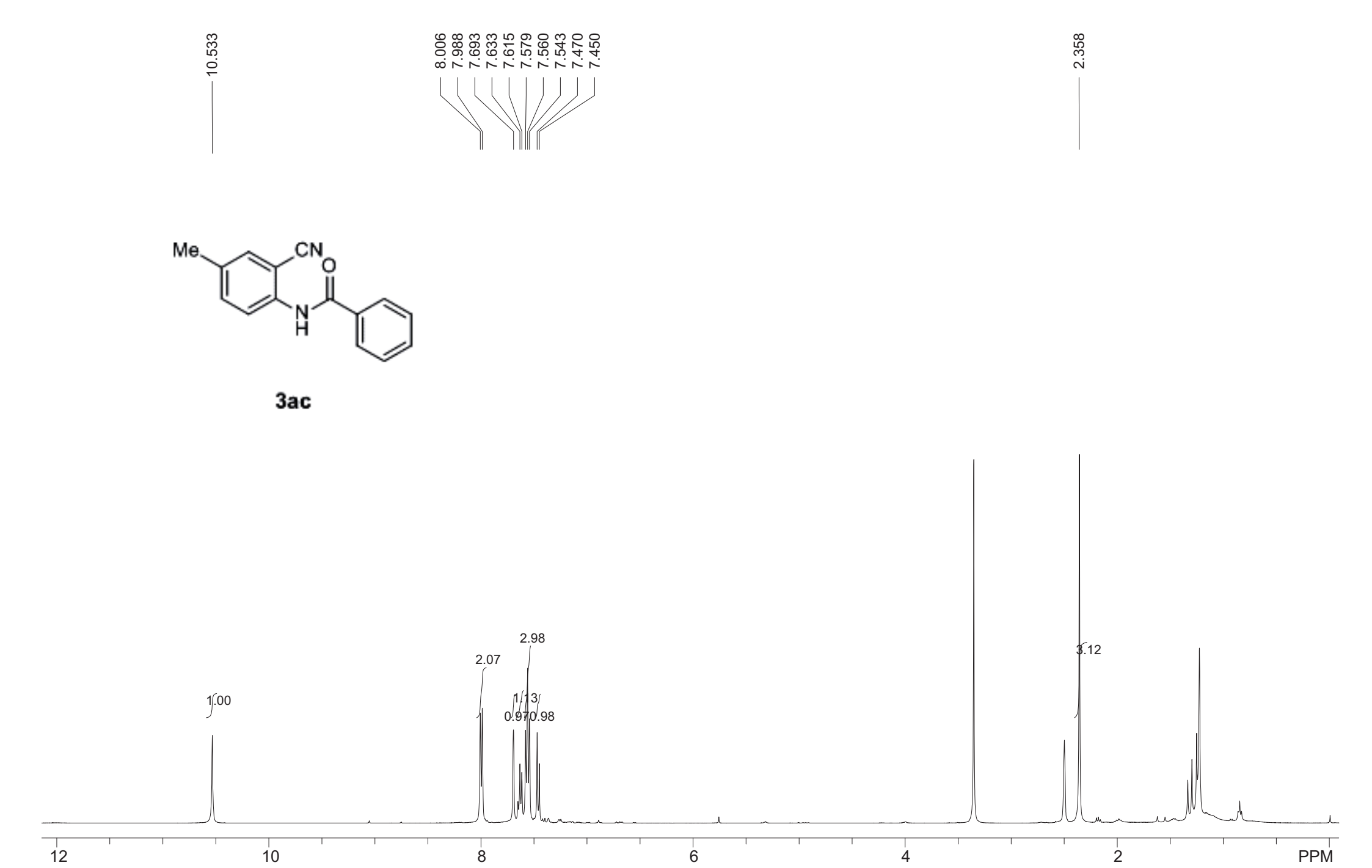
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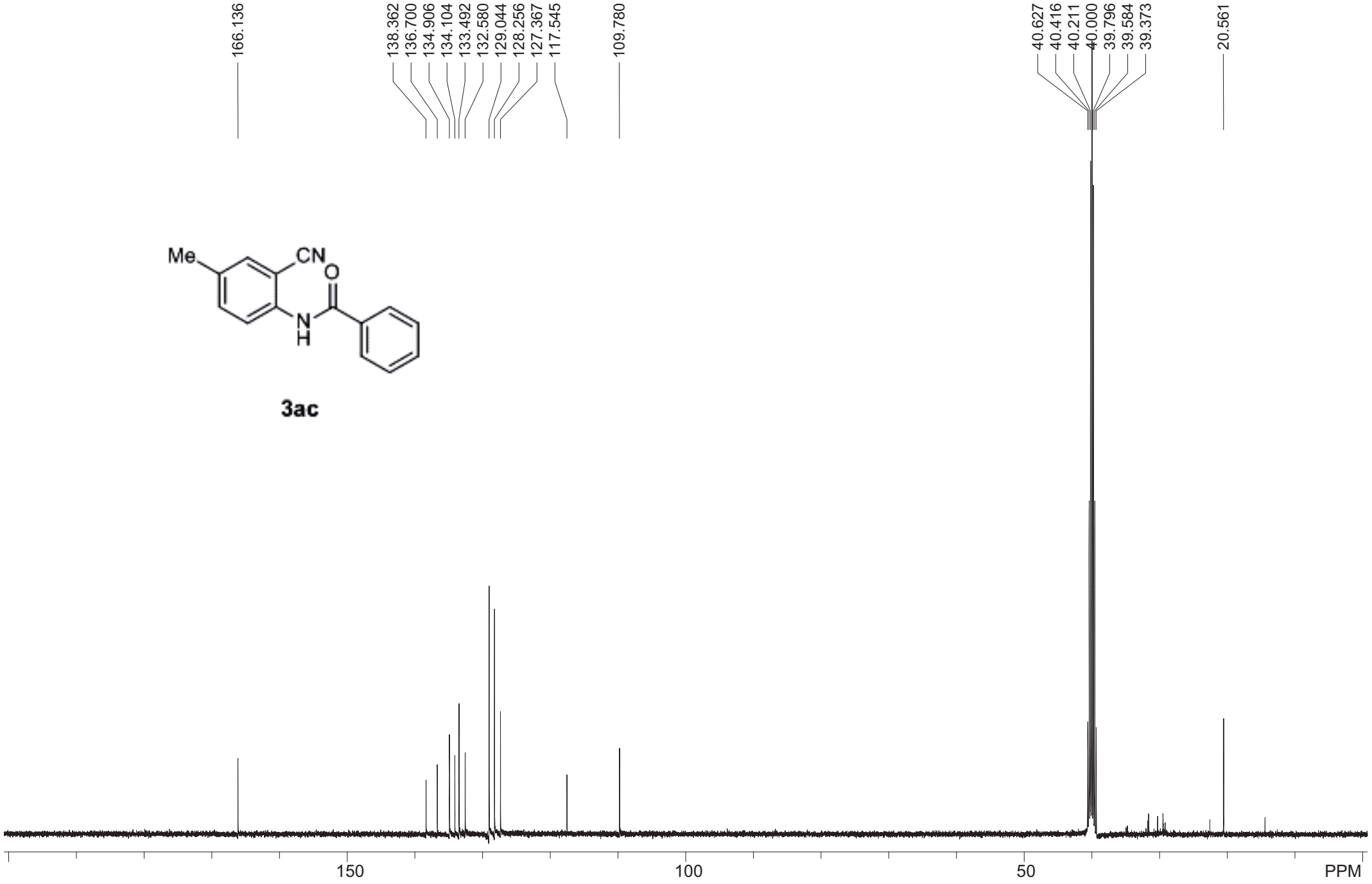
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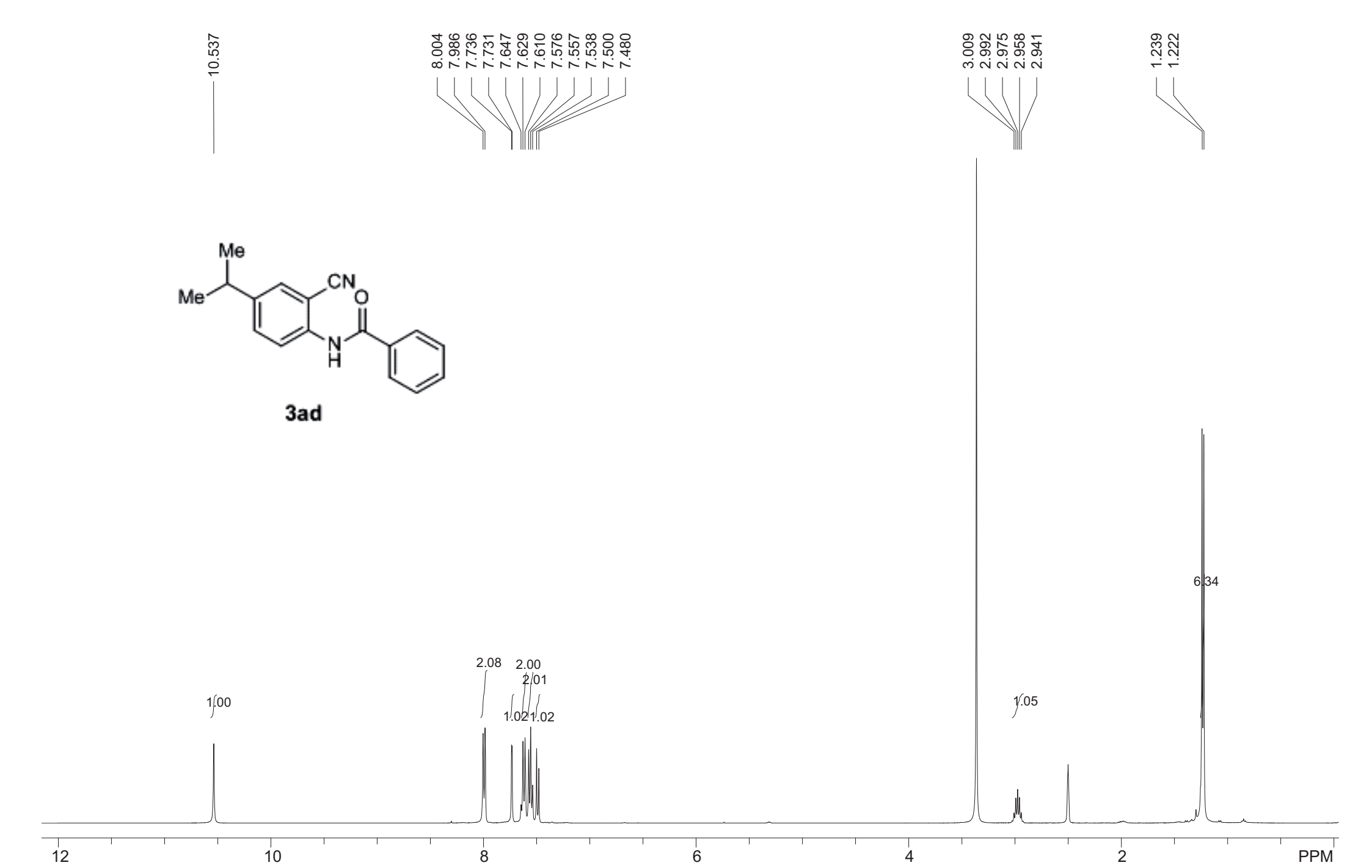
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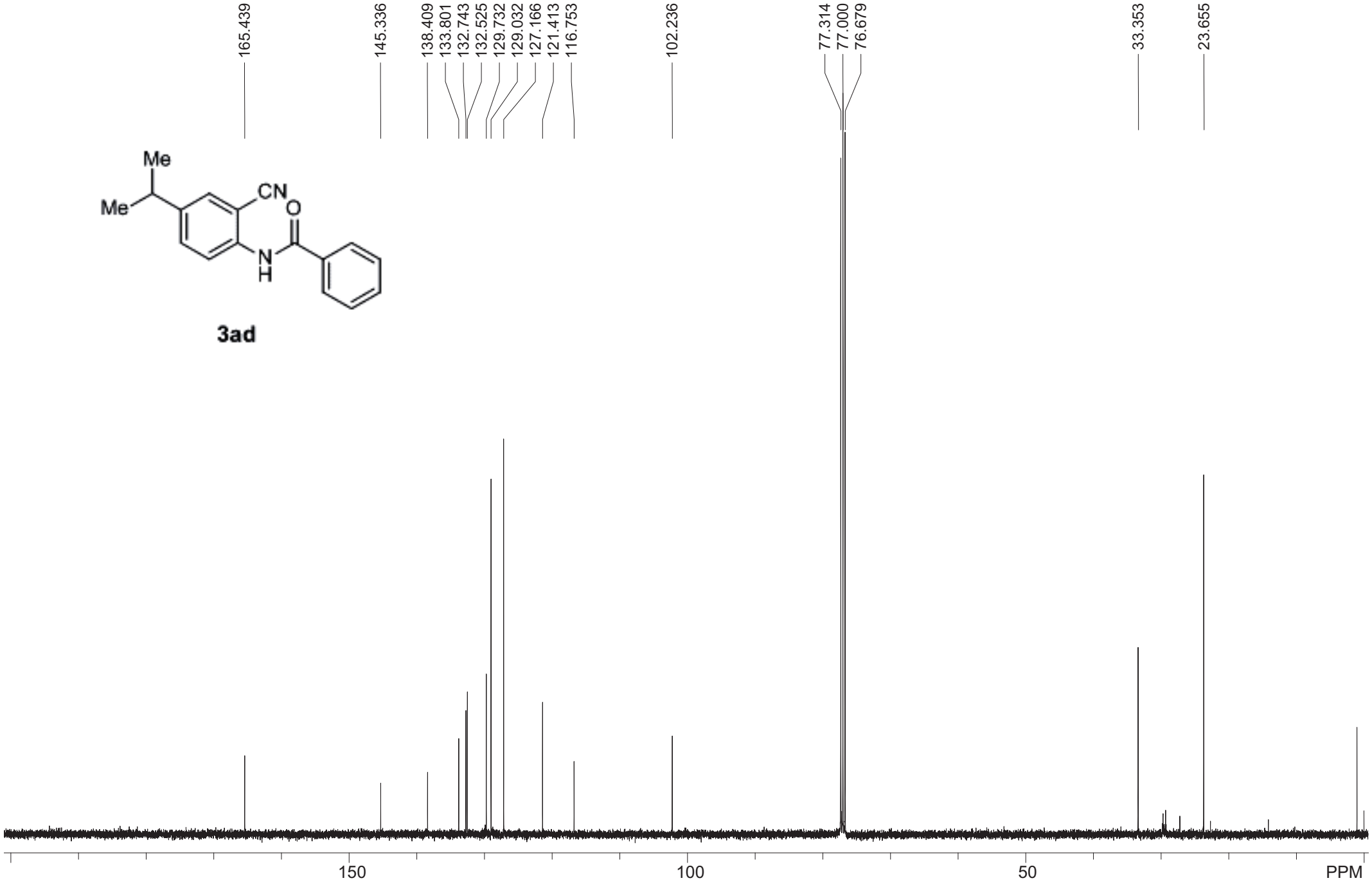
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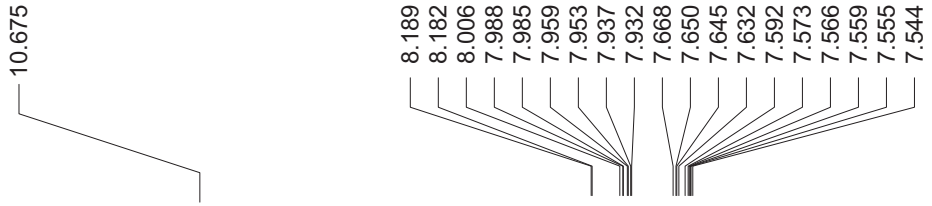
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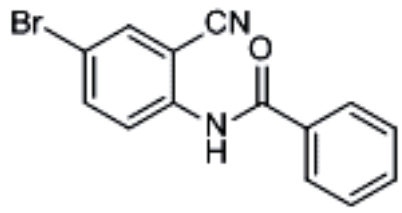
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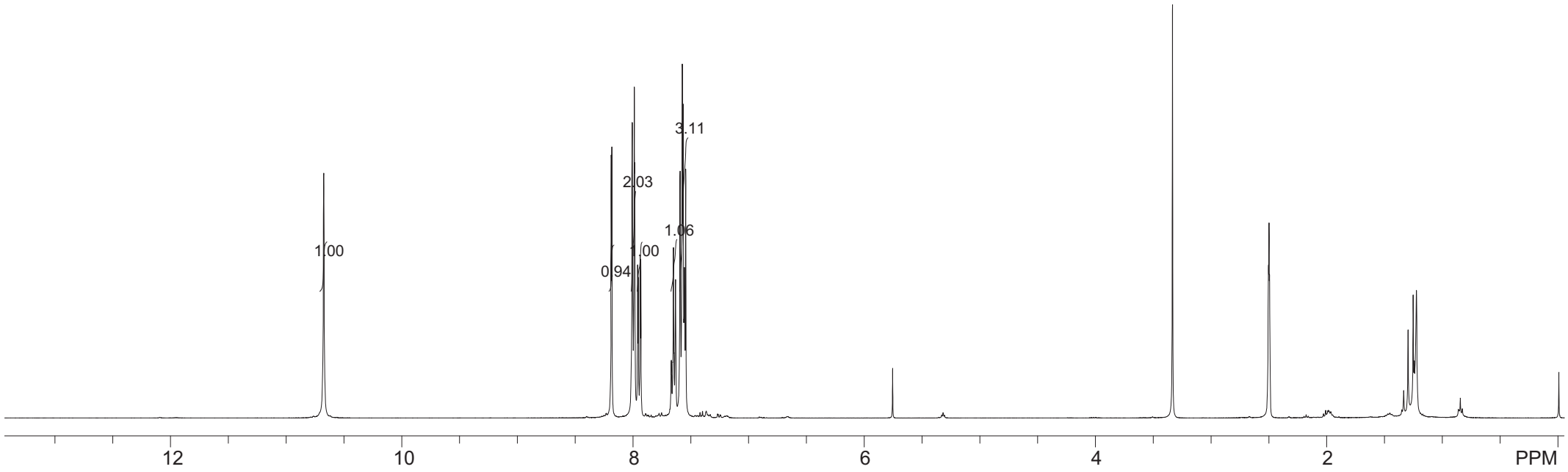
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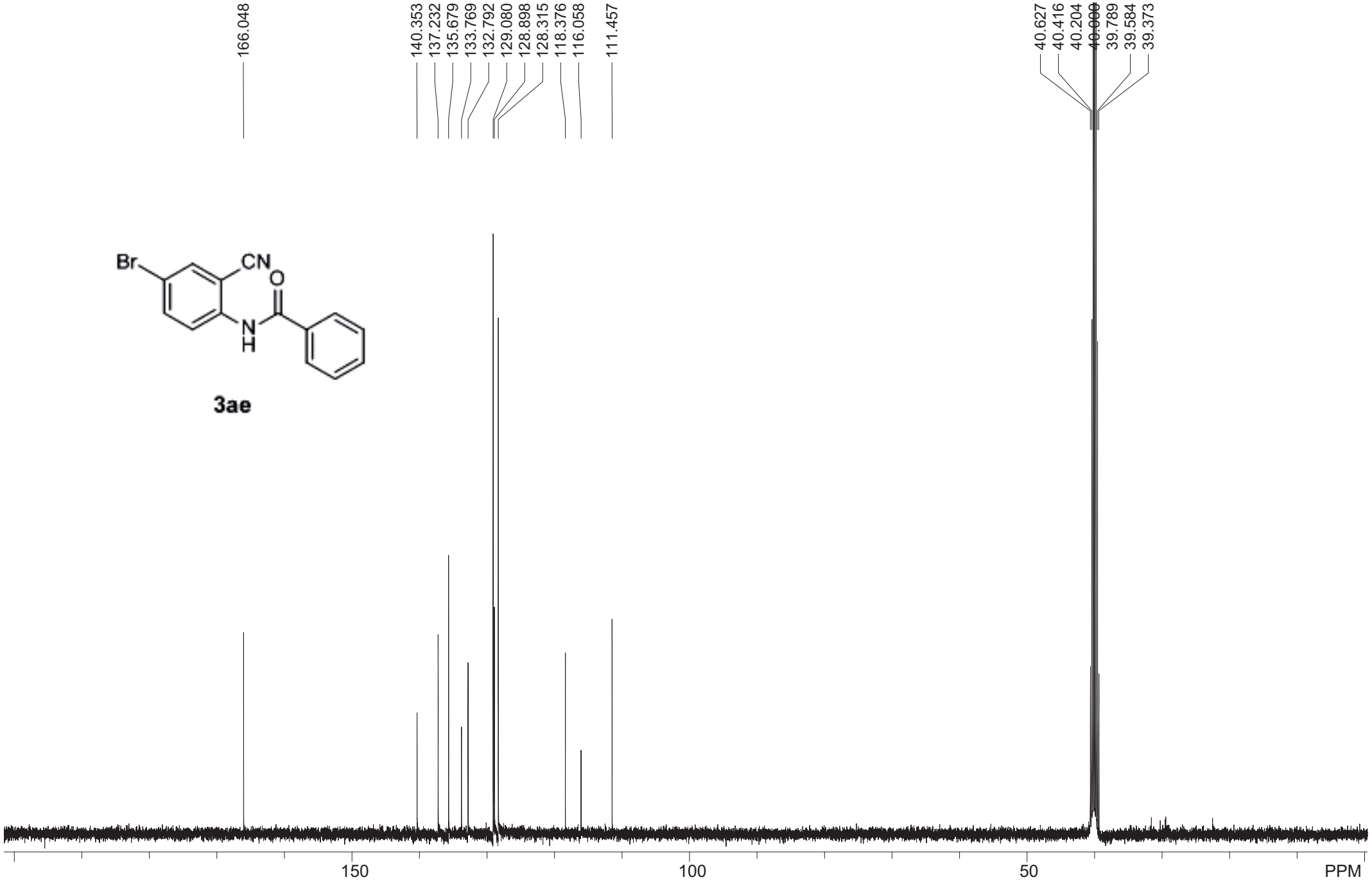
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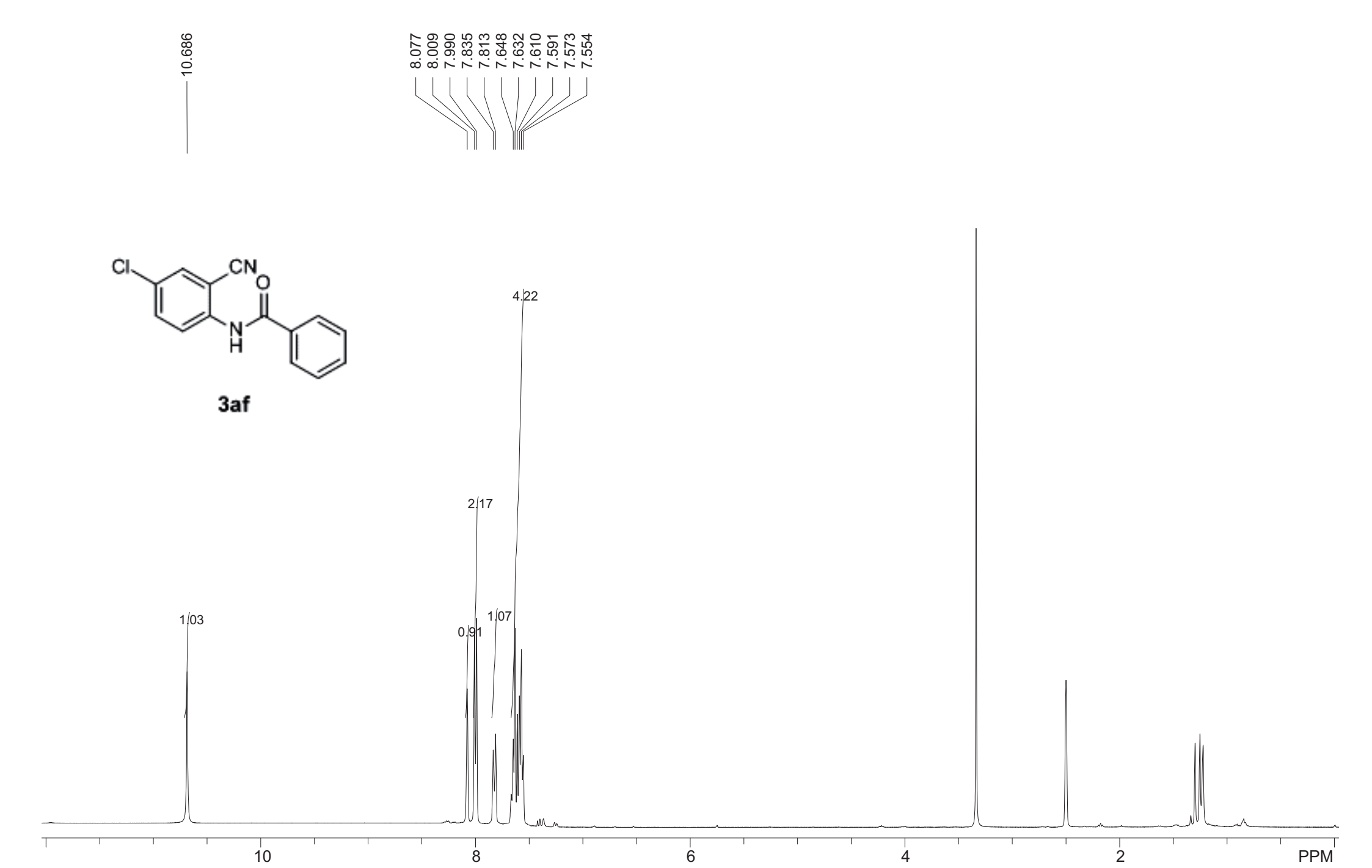
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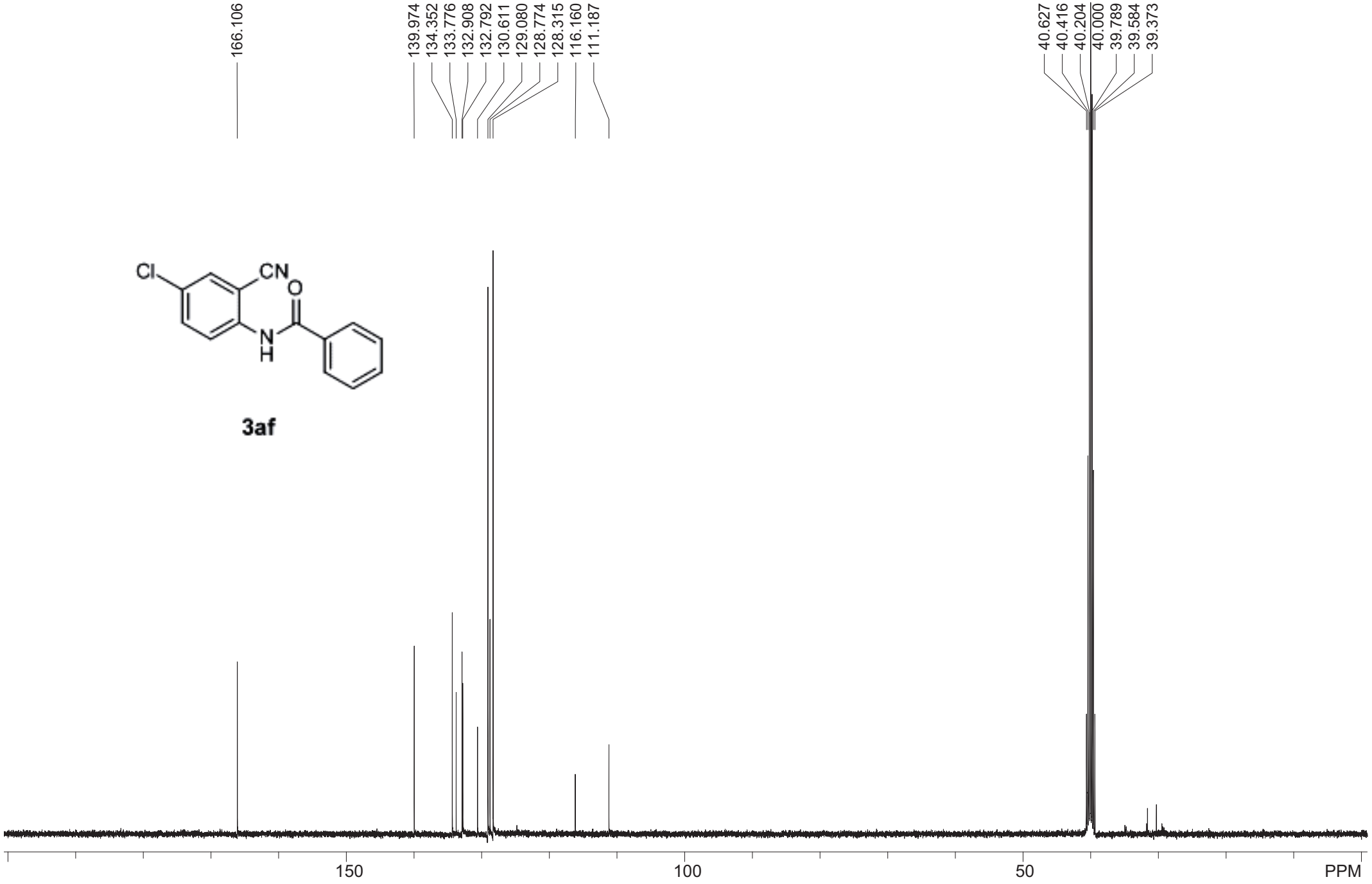
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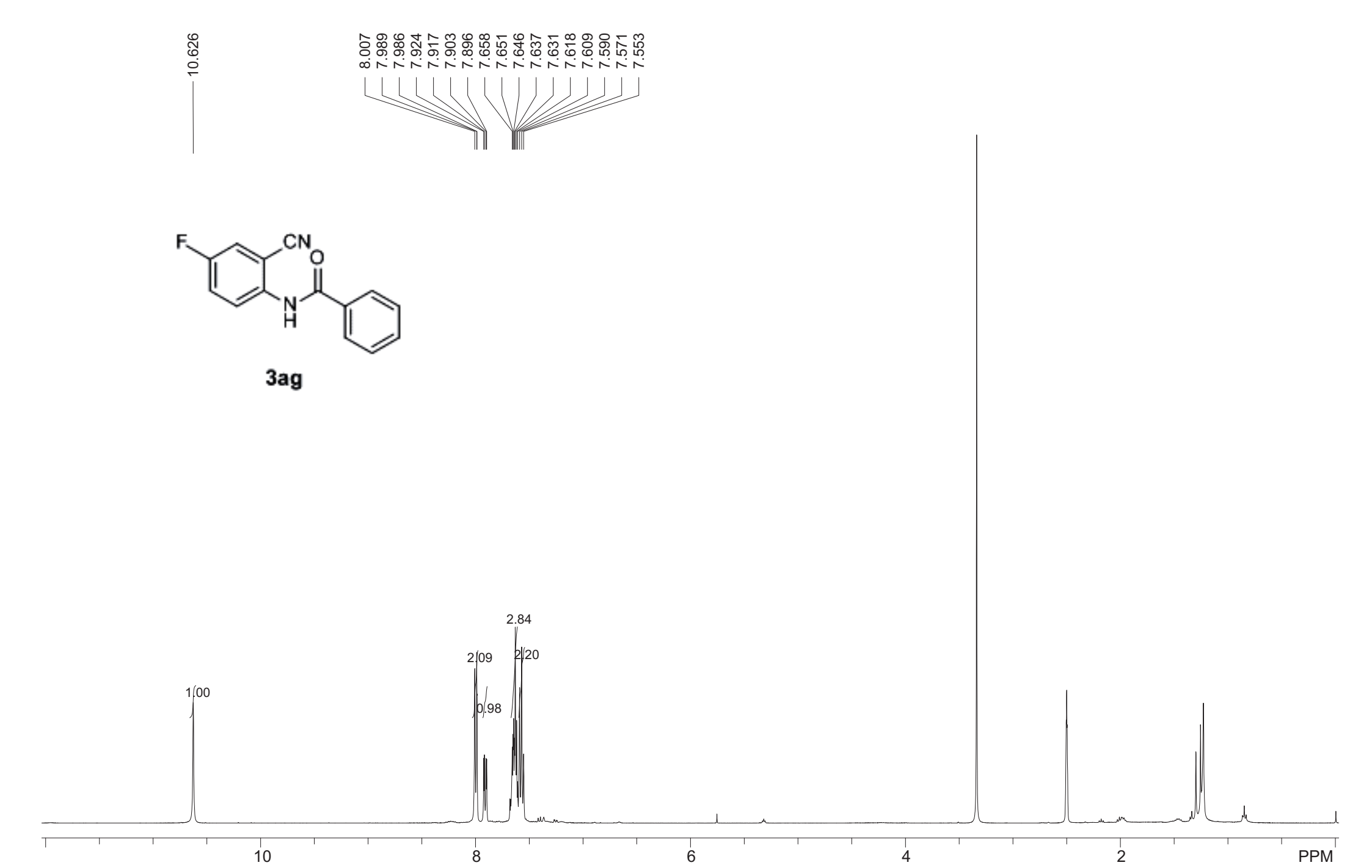
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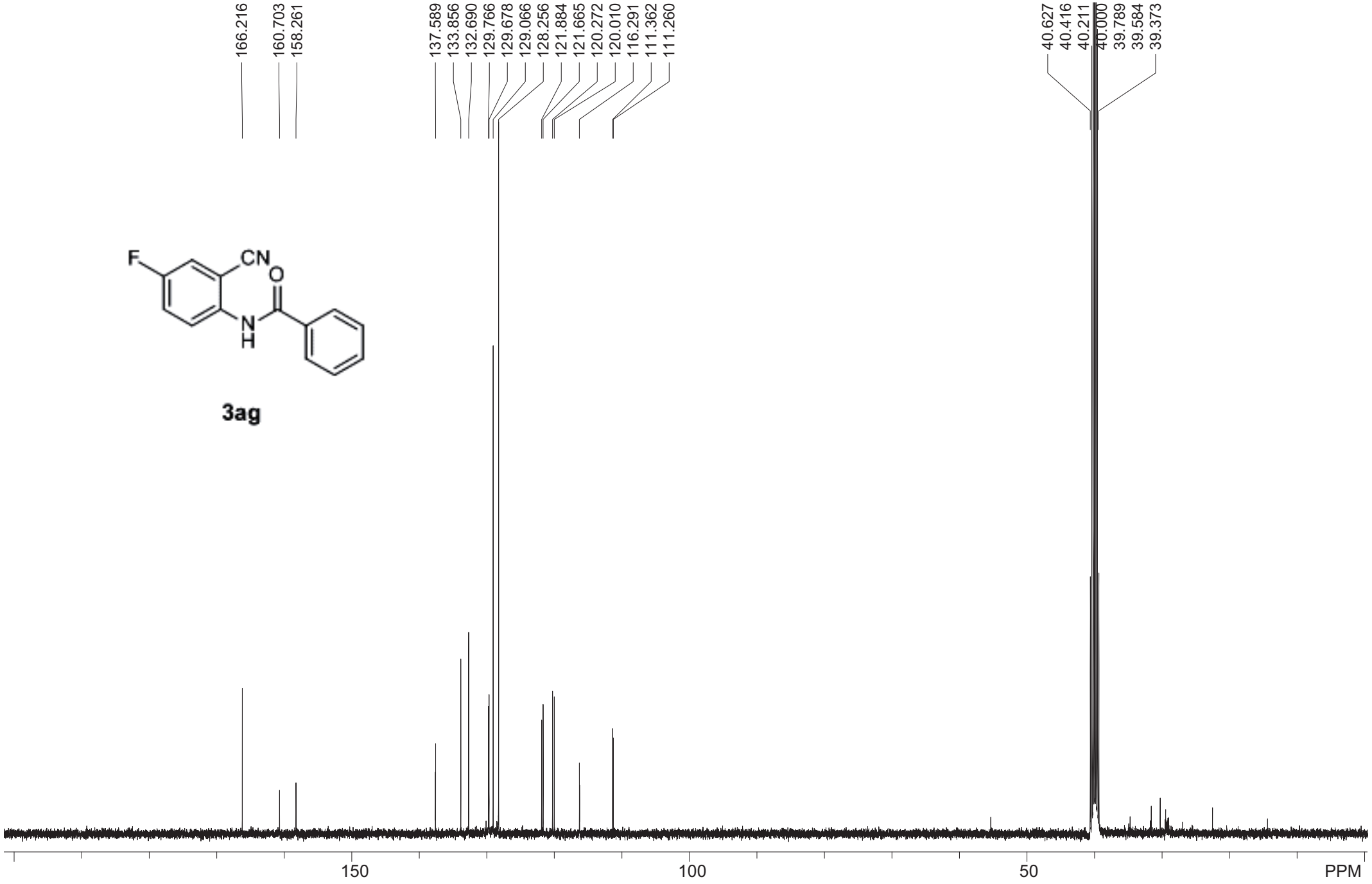
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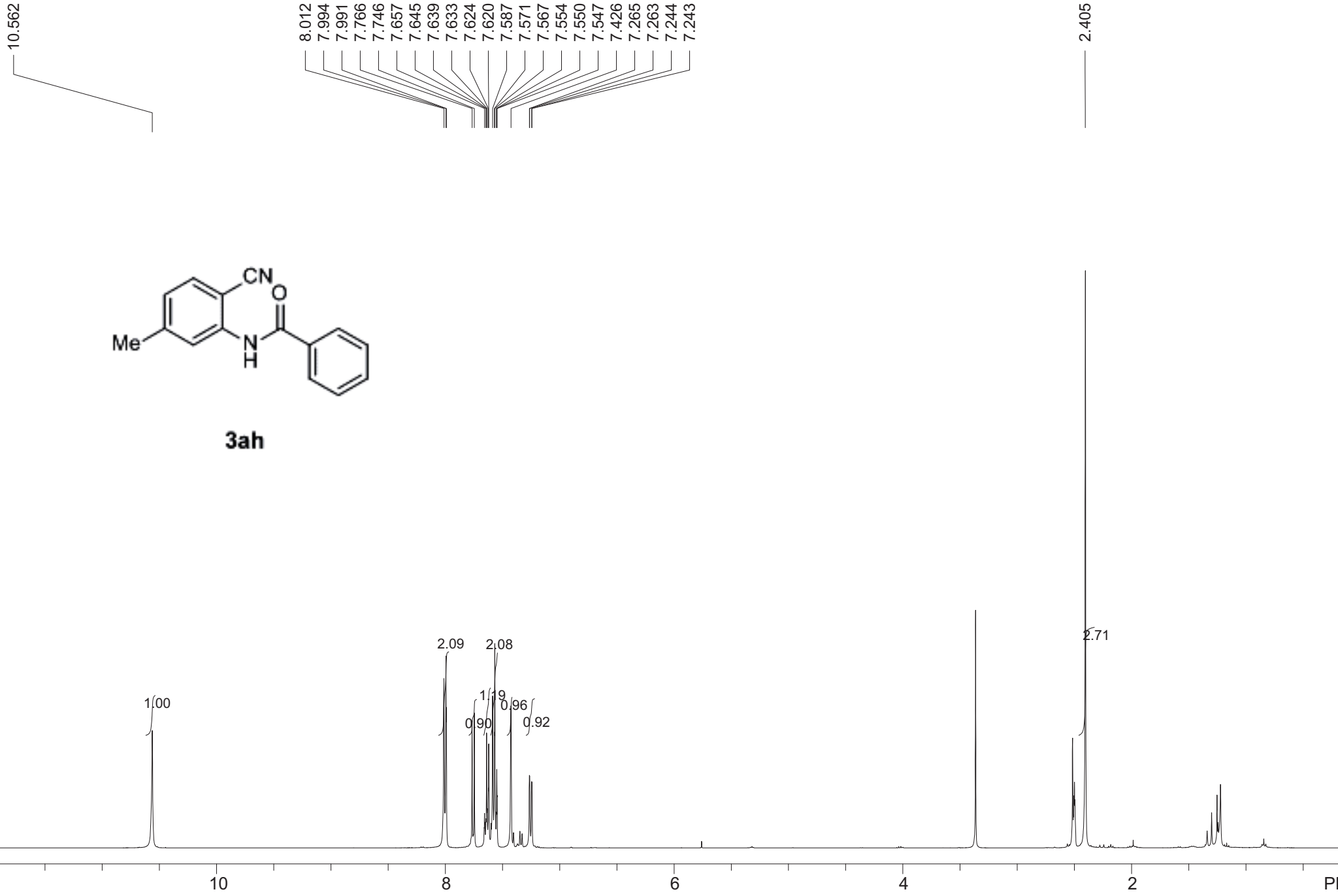
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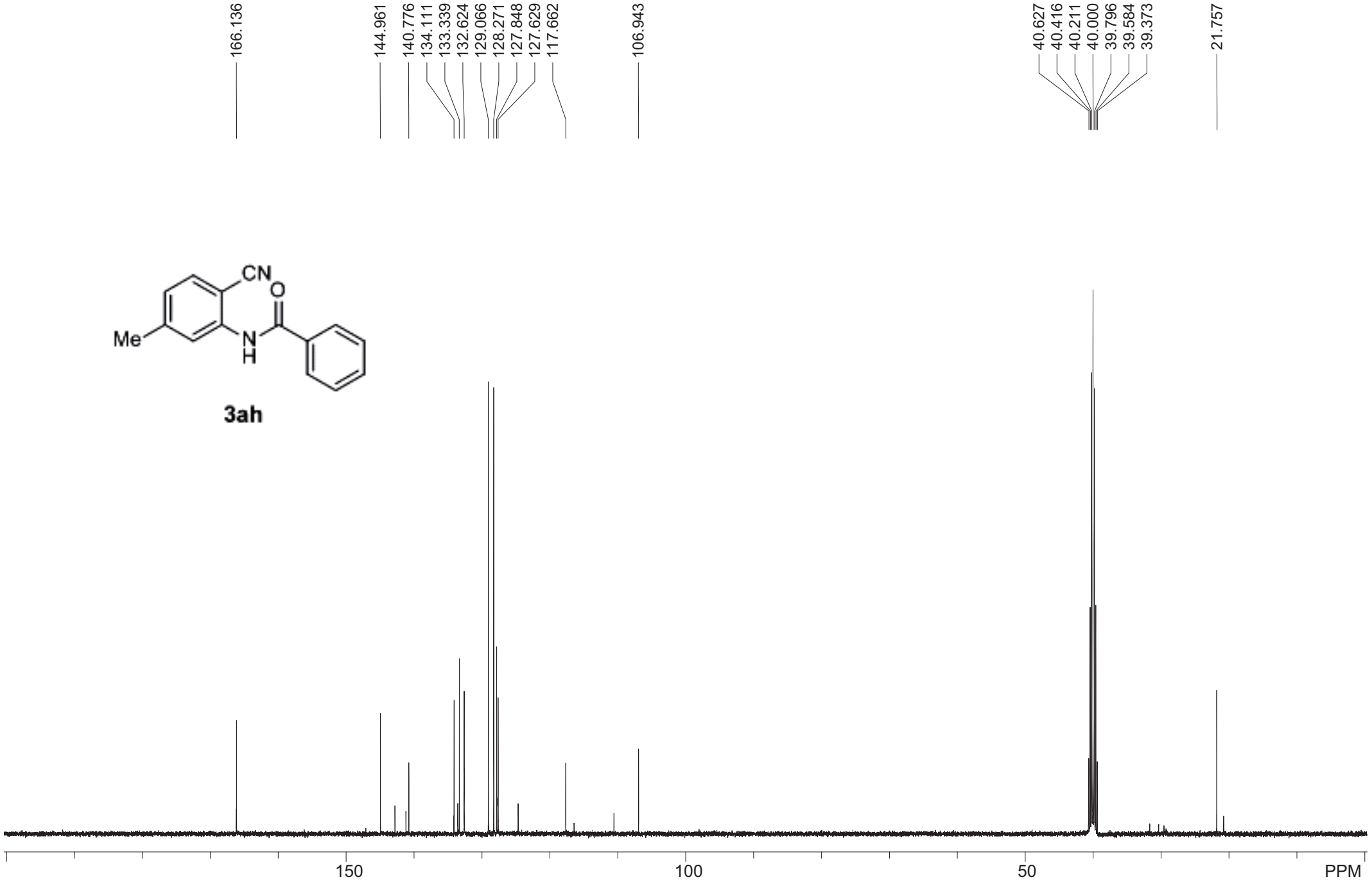
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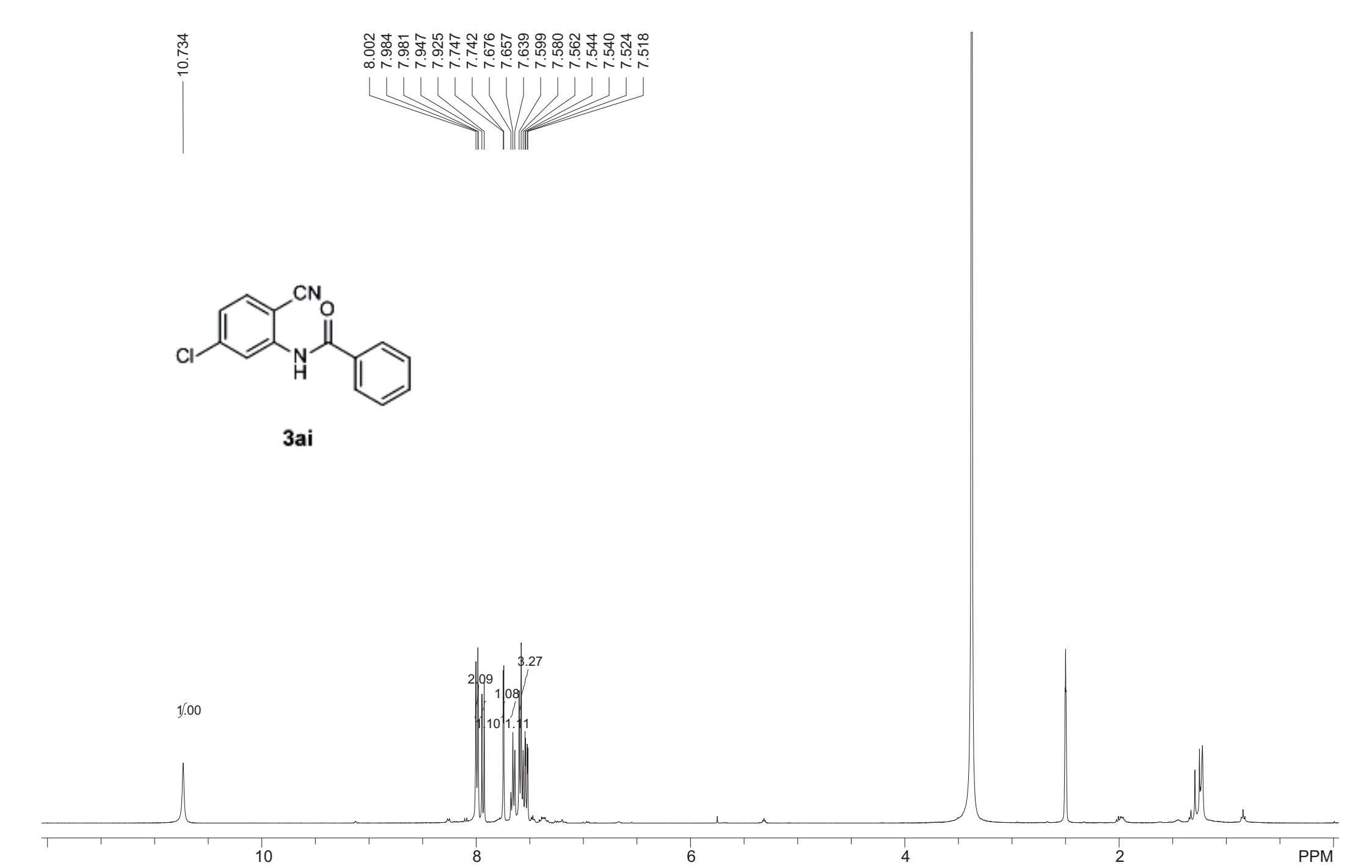
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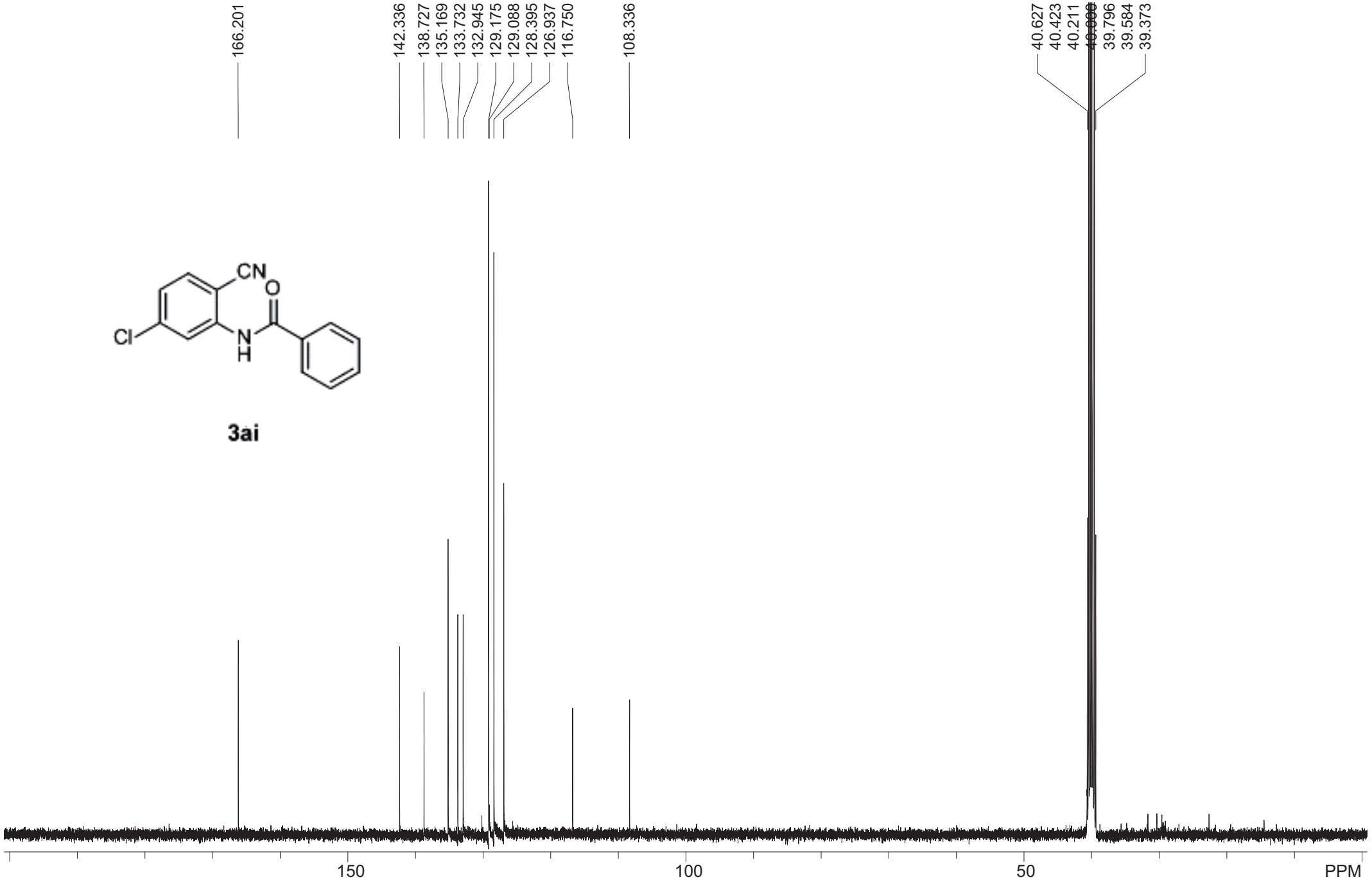
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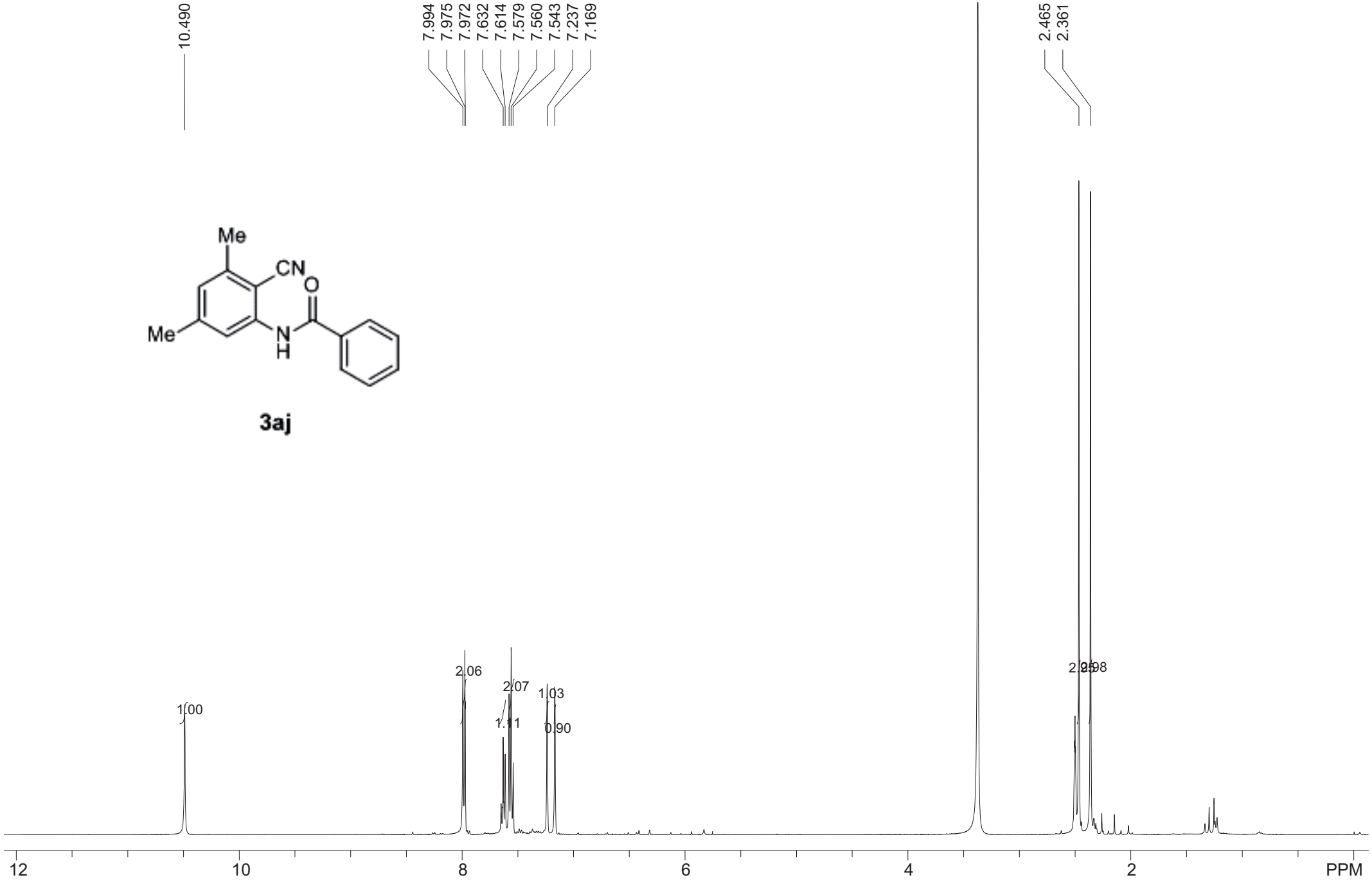
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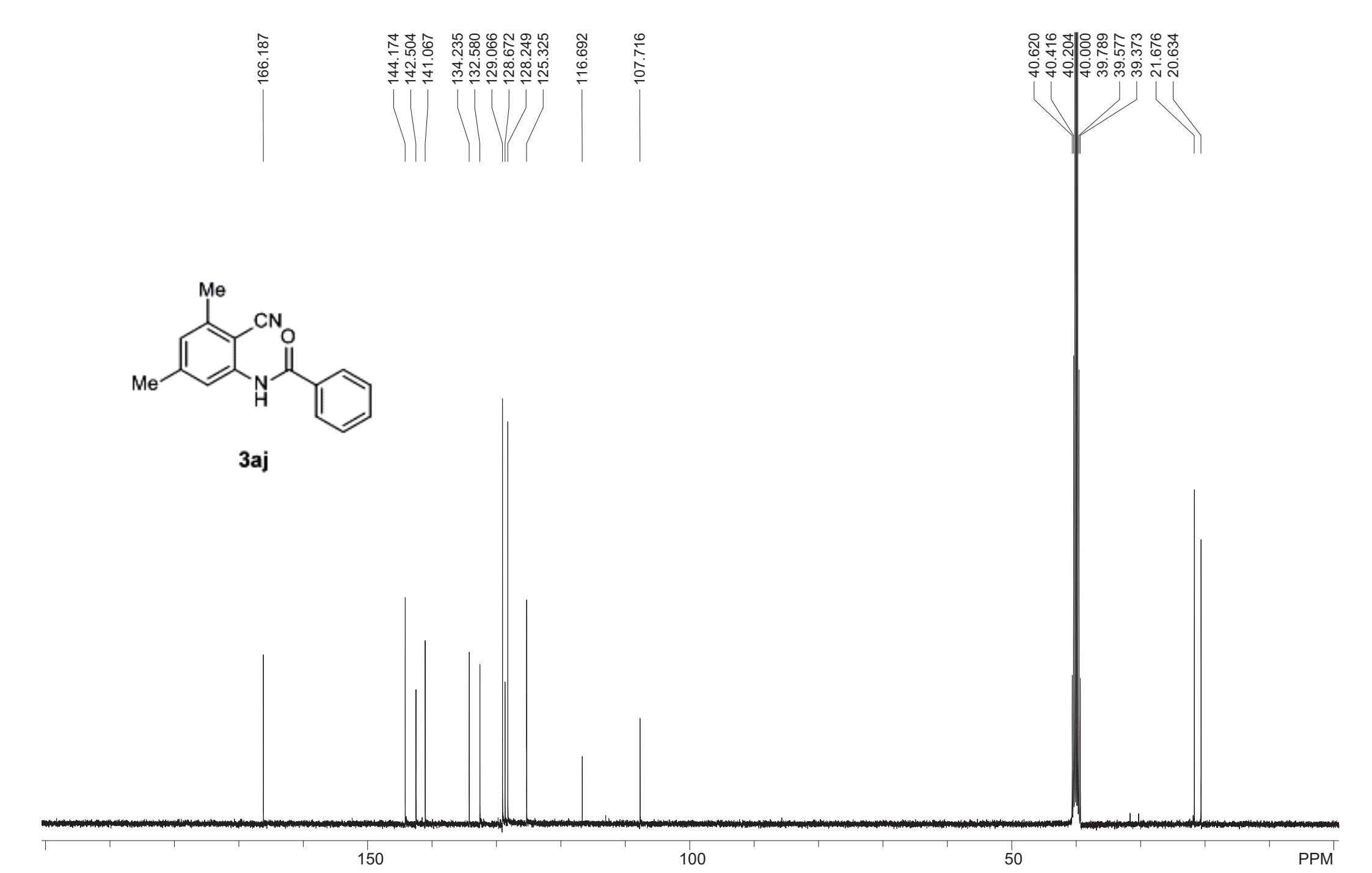
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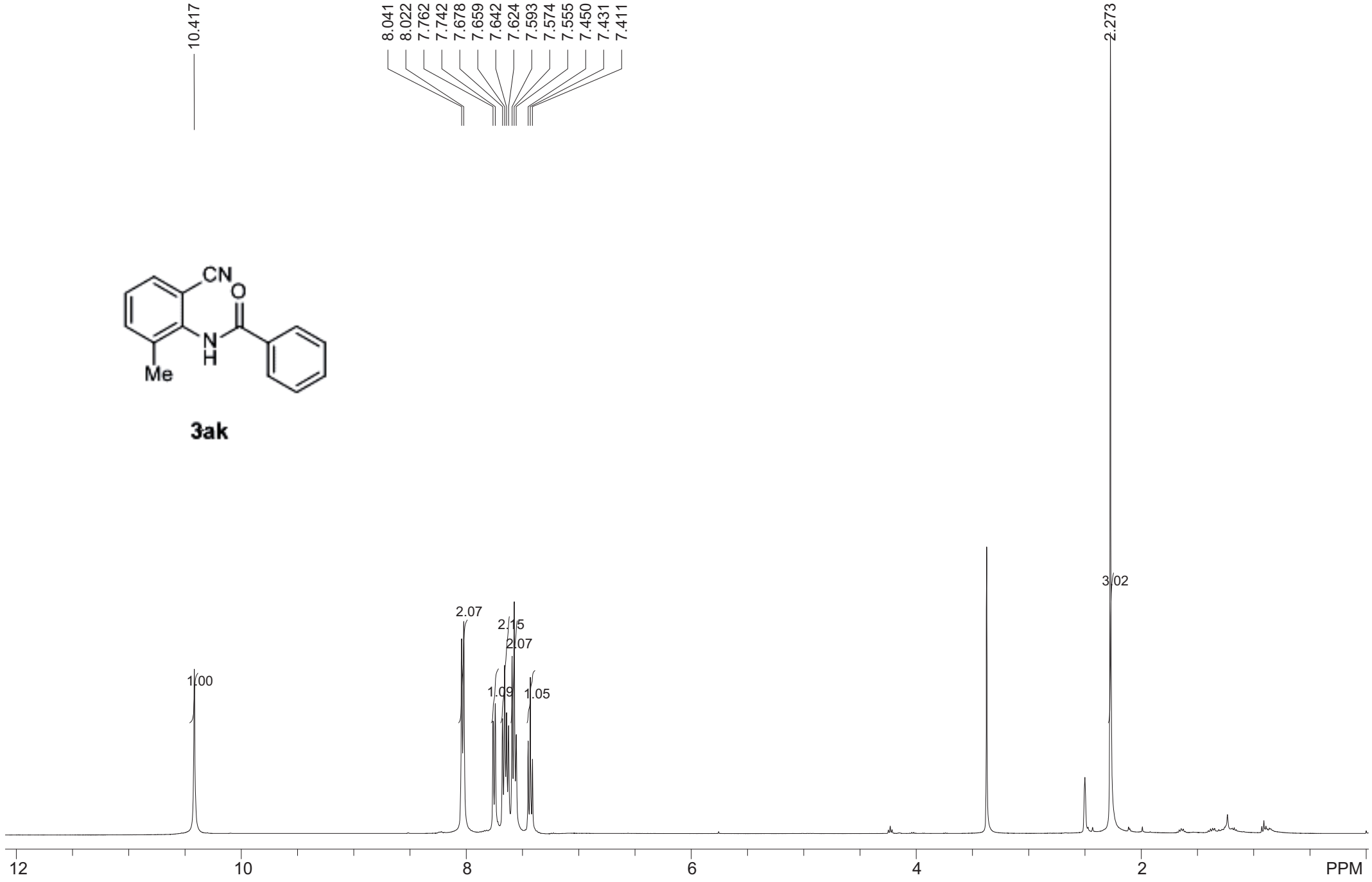
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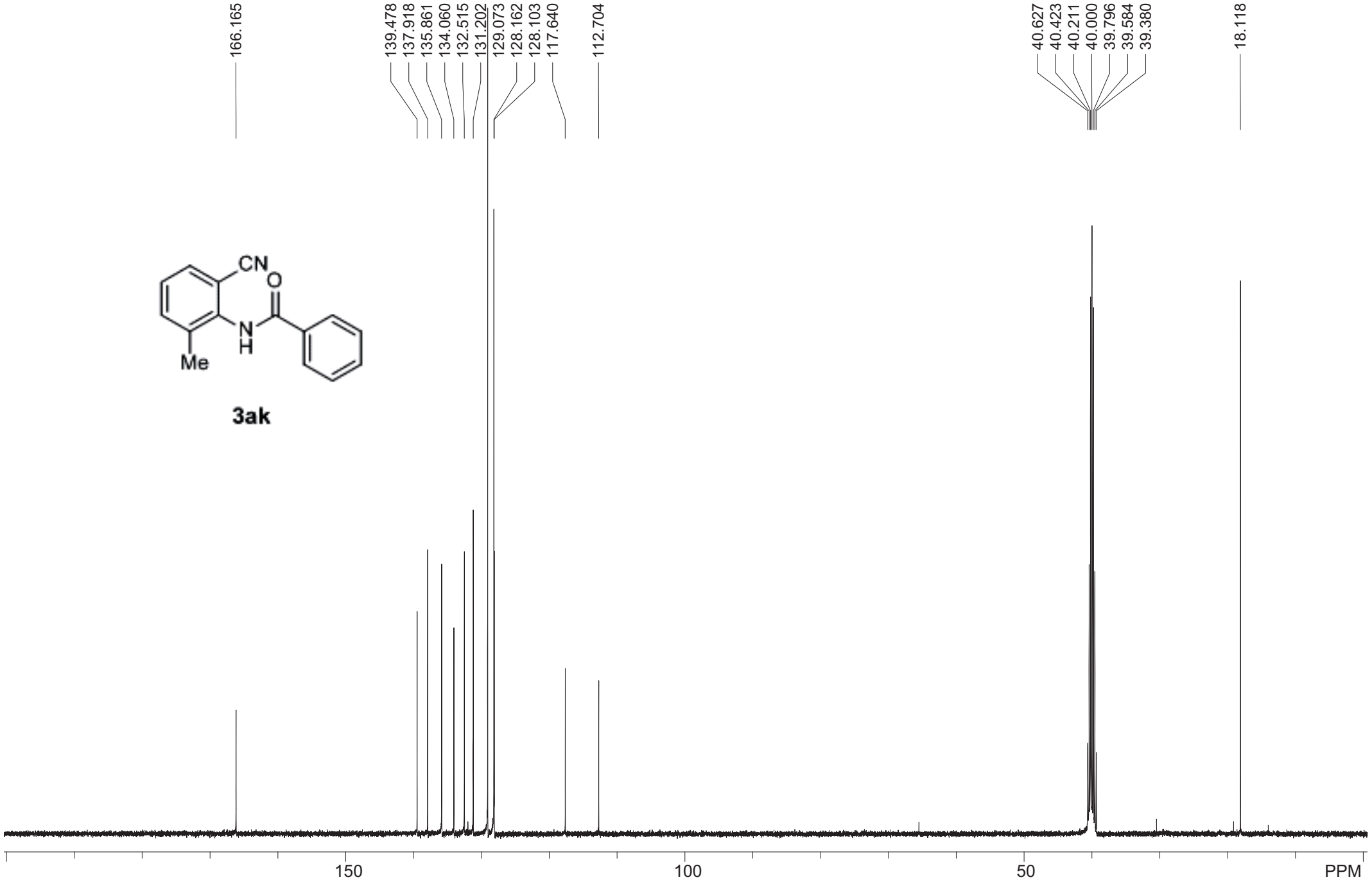
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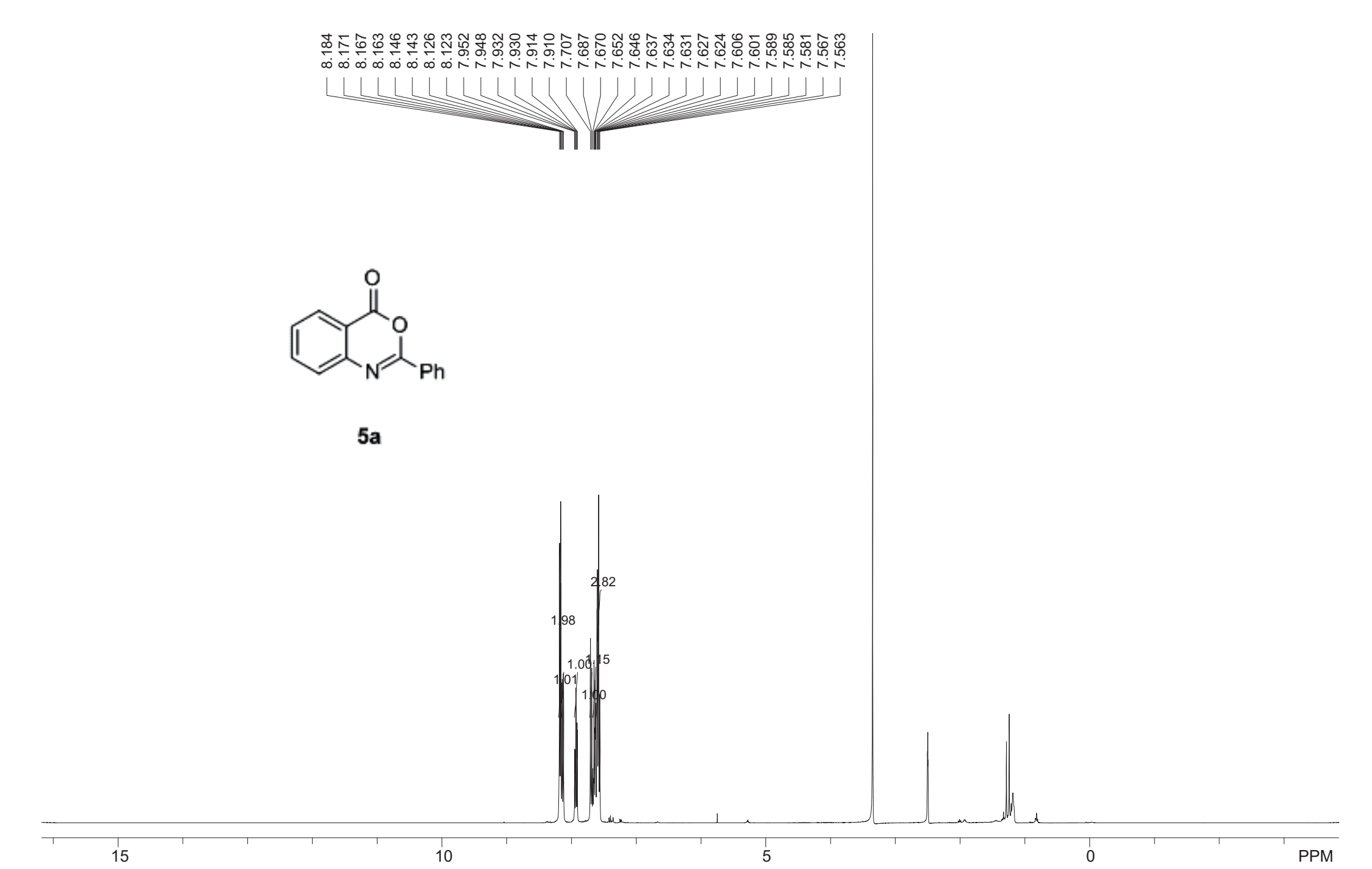
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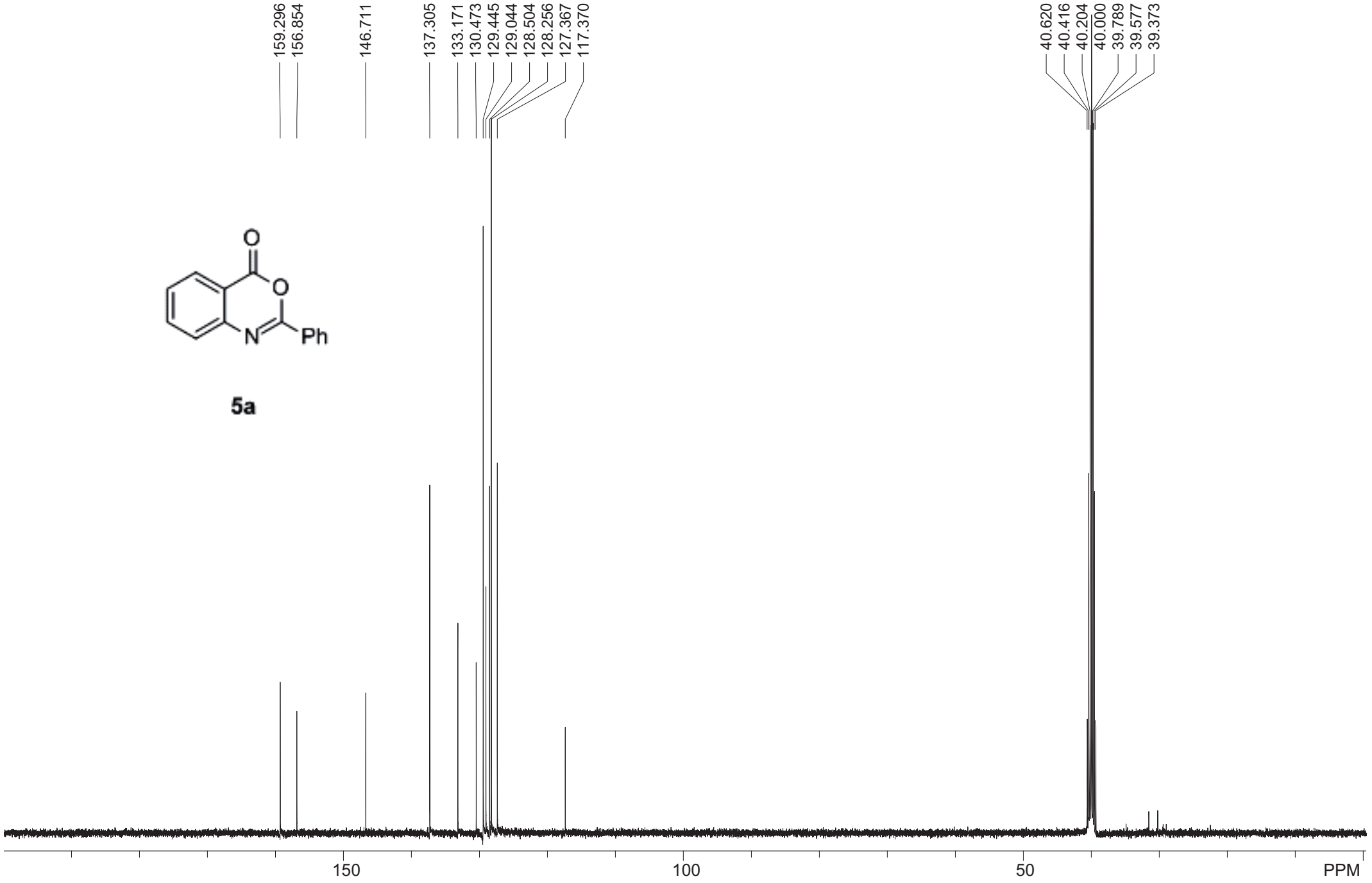
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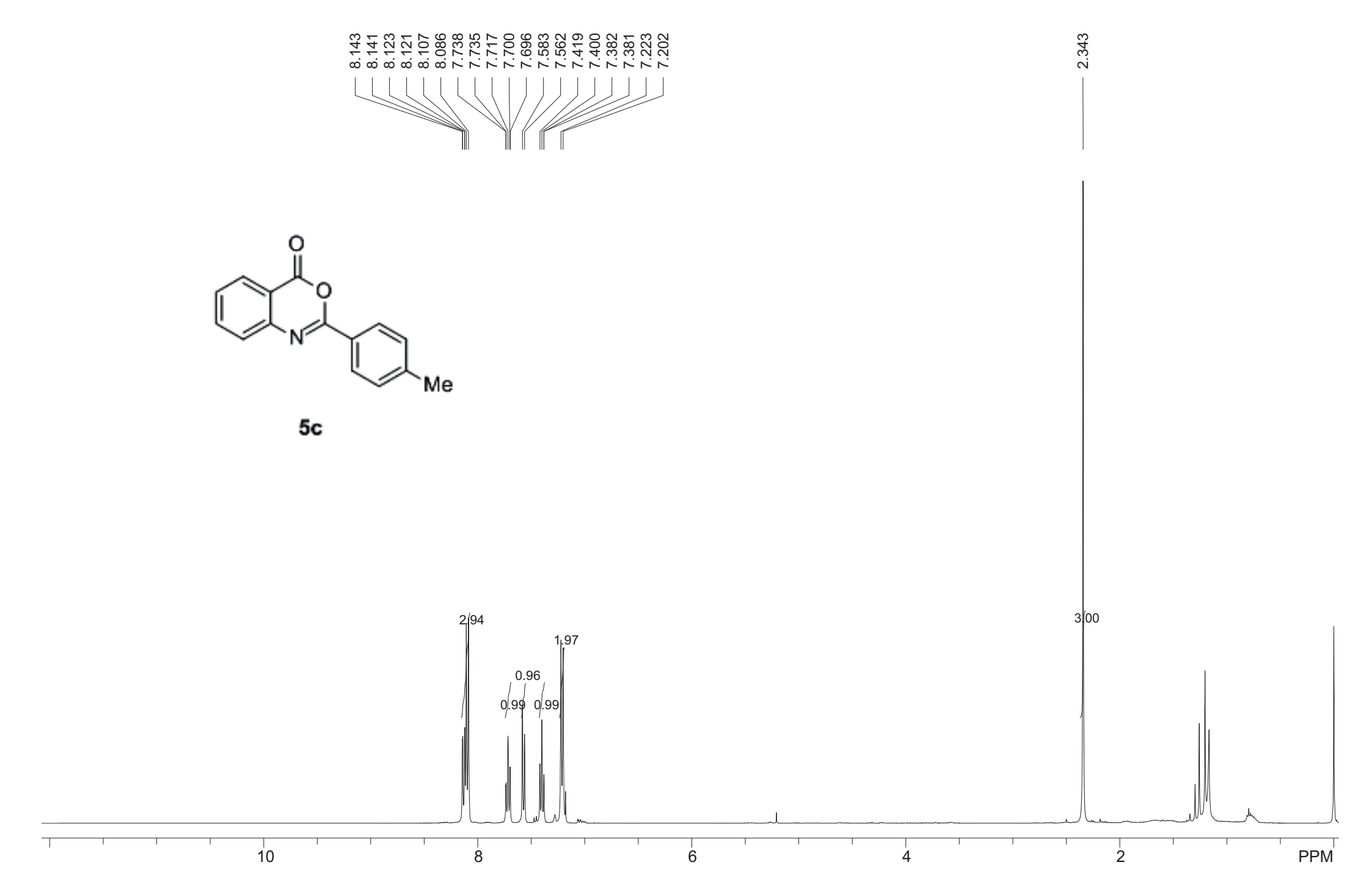
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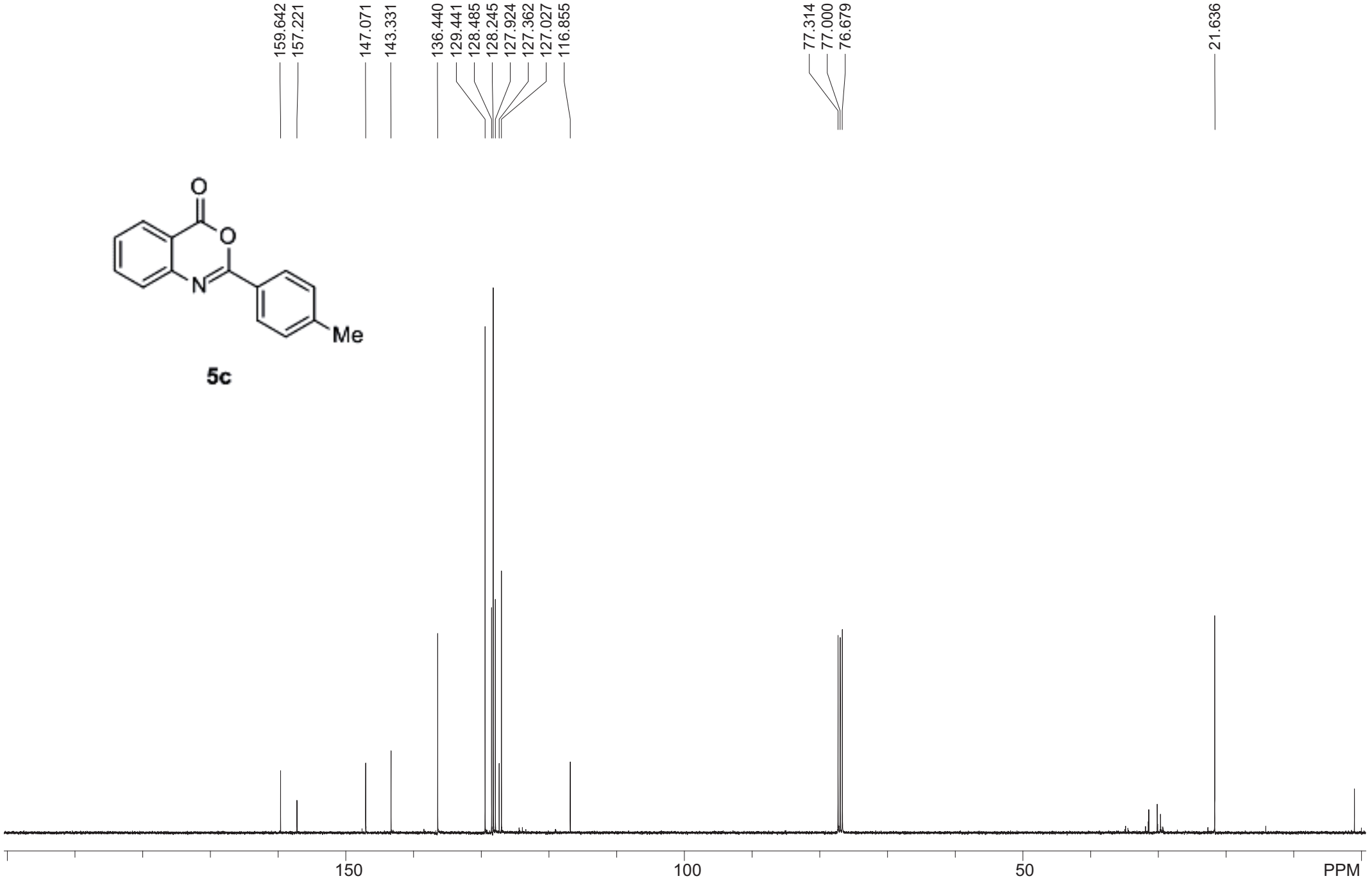
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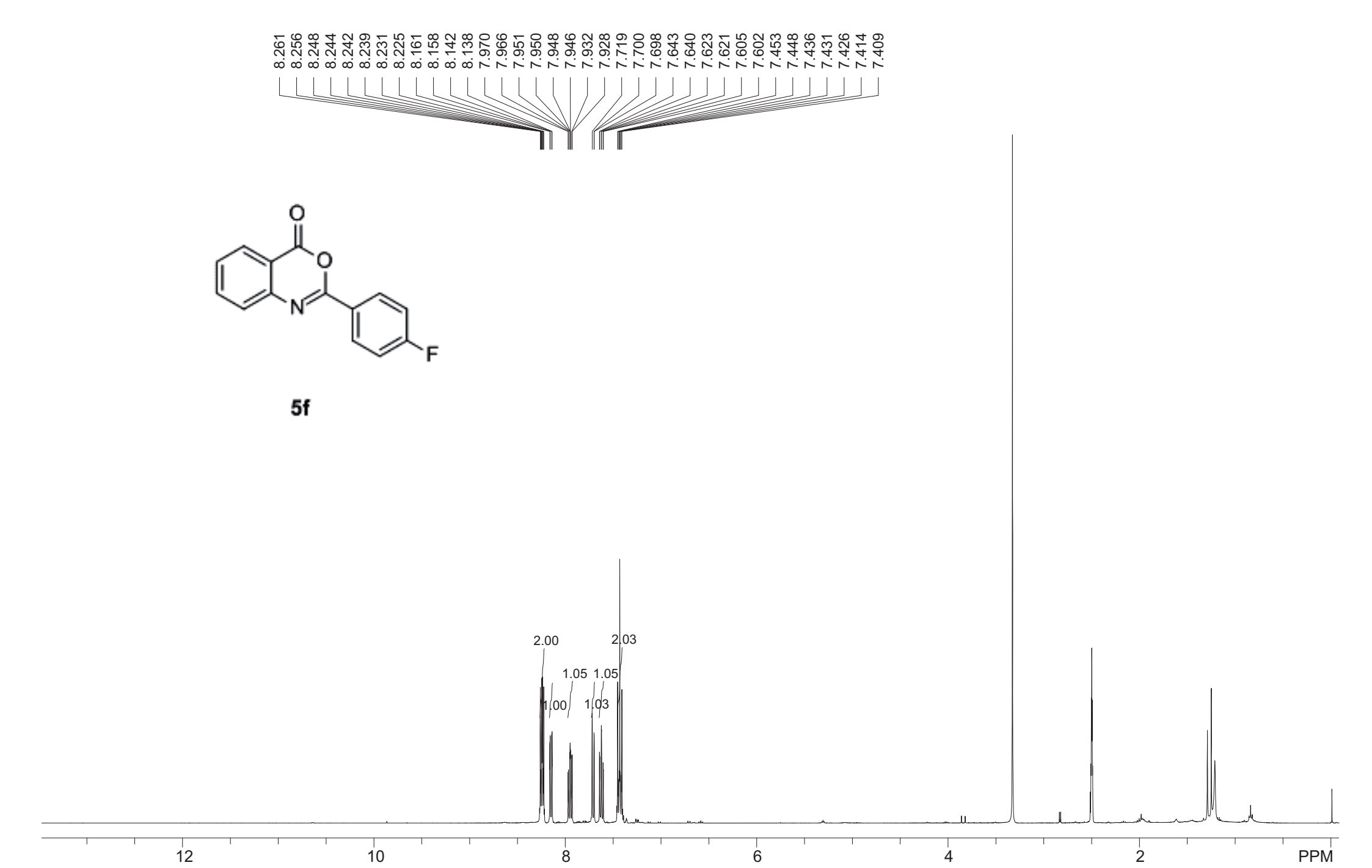
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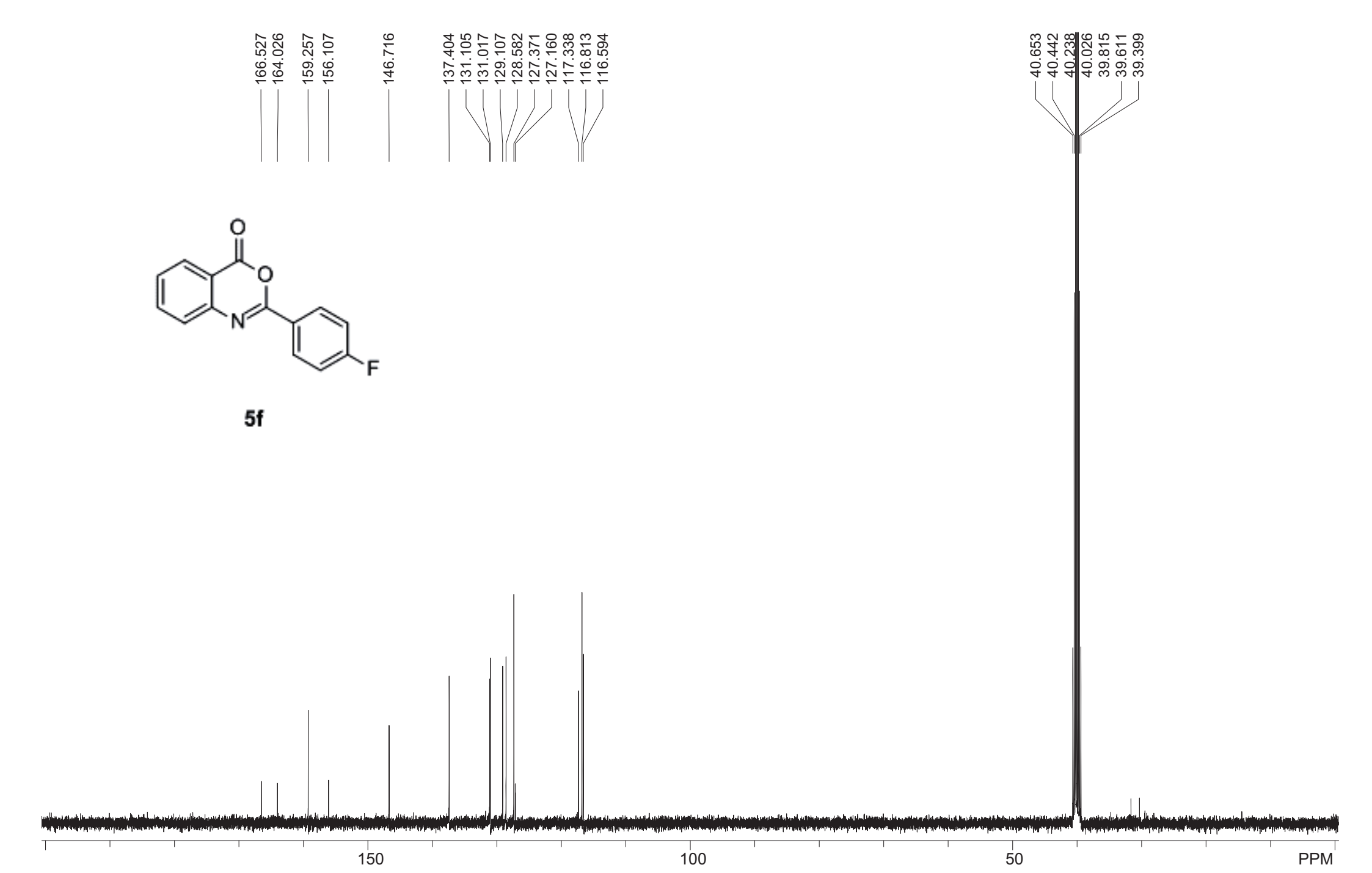
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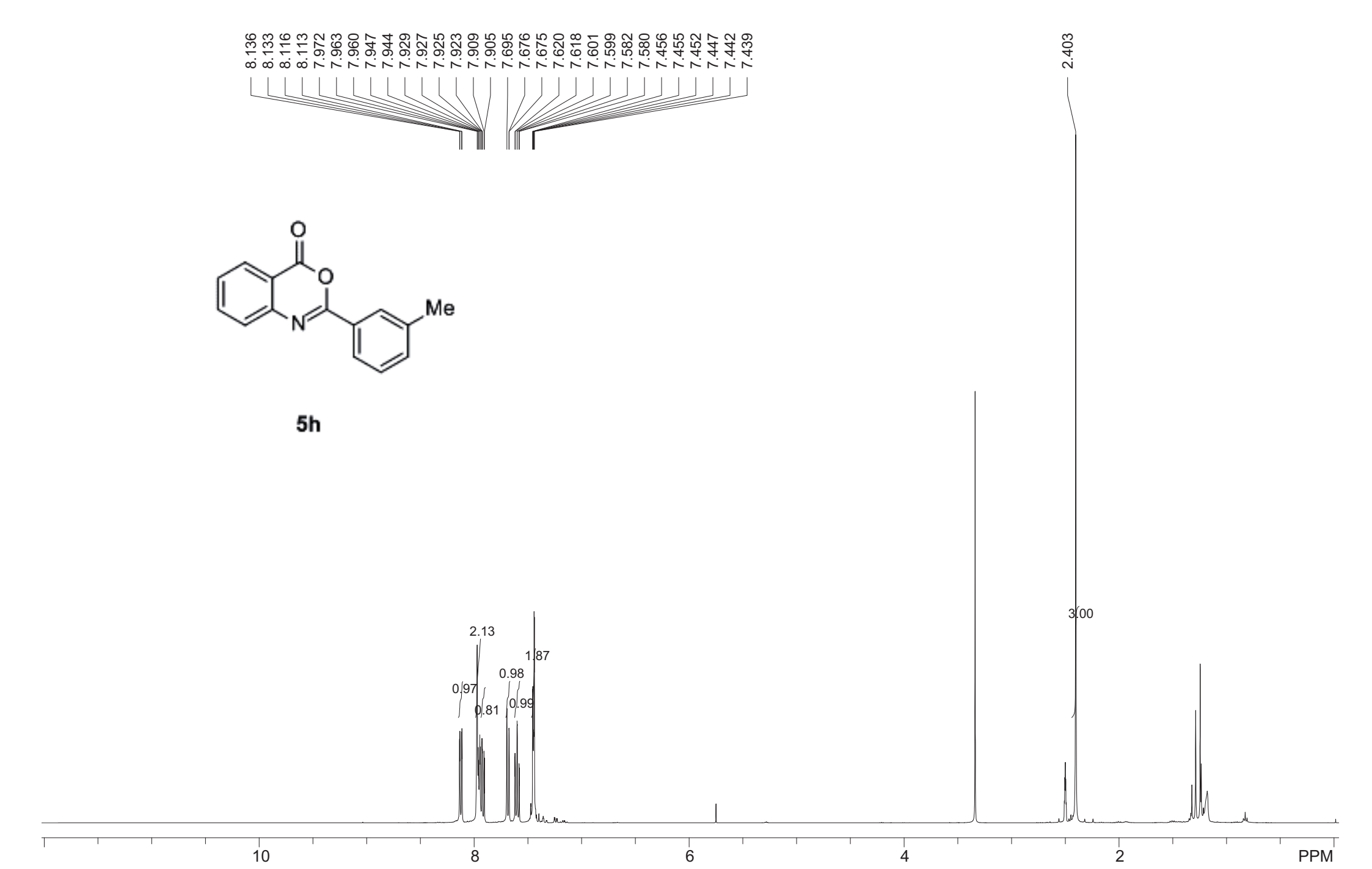
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8.133
8.116
8.113
7.972
7.963
7.960
7.947
7.944
7.929
7.927
7.925
7.923
7.909
7.905
7.695
7.676
7.675
7.620
7.618
7.601
7.599
7.582
7.580
7.456
7.455
7.452
7.447
7.442
7.439
2.403
O
O
N
Me
5h
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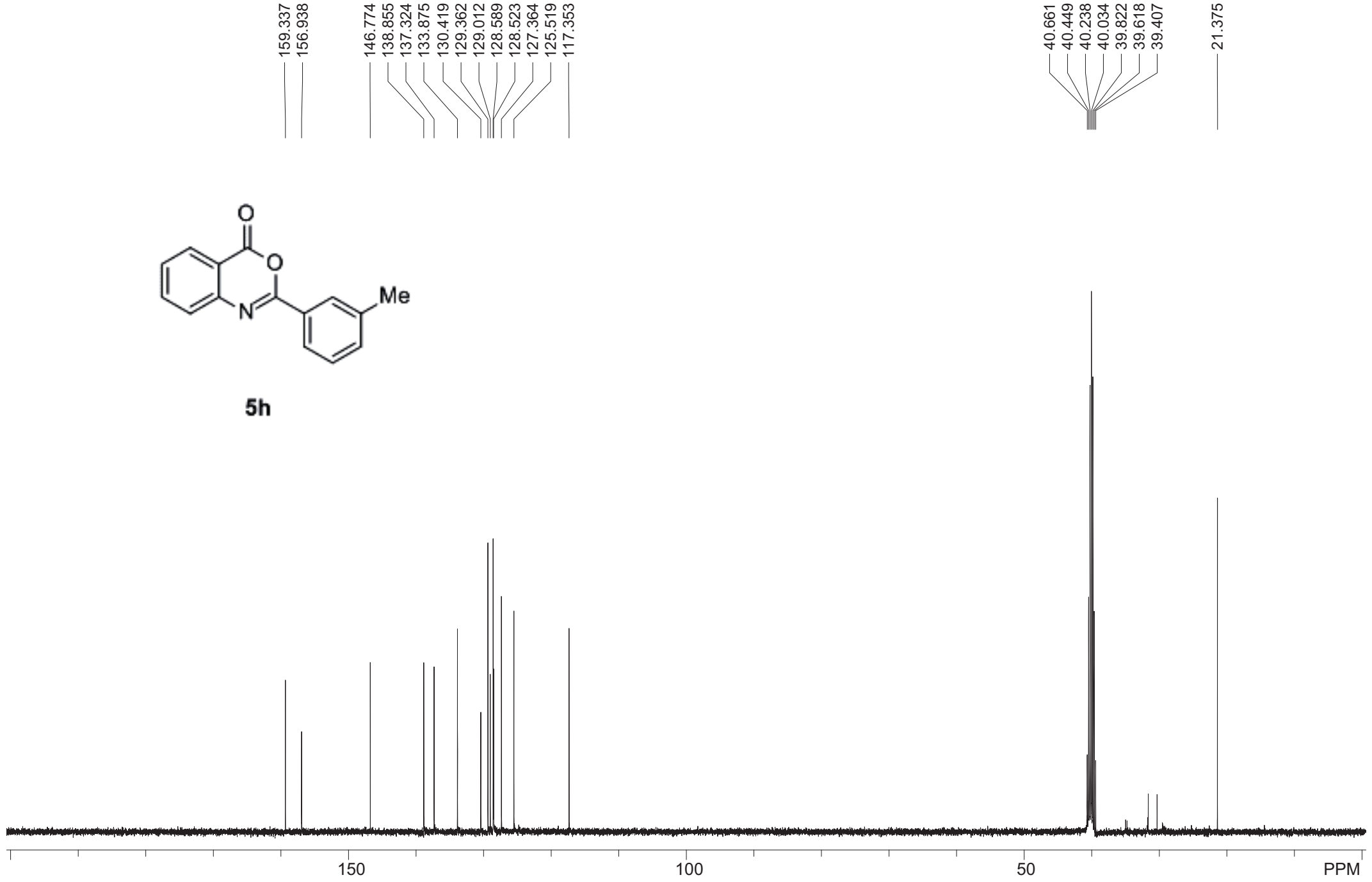
1.87
0.98
0.97
0.81
0.99
3.00
10
8
6
4
2
PPM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156.938
146.774
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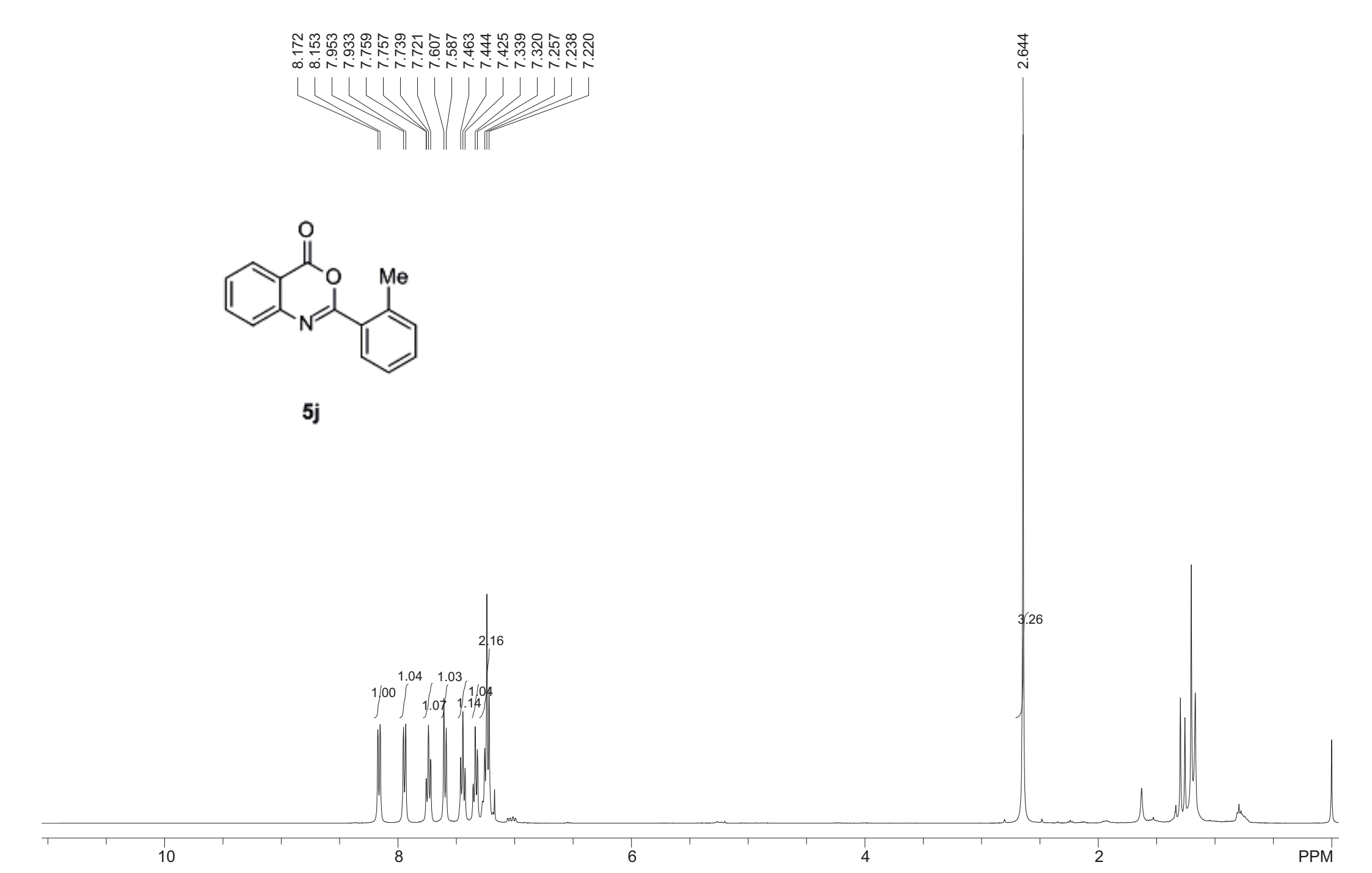
133.875
130.419
129.362
129.012
128.589
128.523
127.364
125.519
117.353
40.661
40.449
40.238
40.034
39.822
39.618
39.407
21.375
O
O
N
Me
5h
150
100
50
PPM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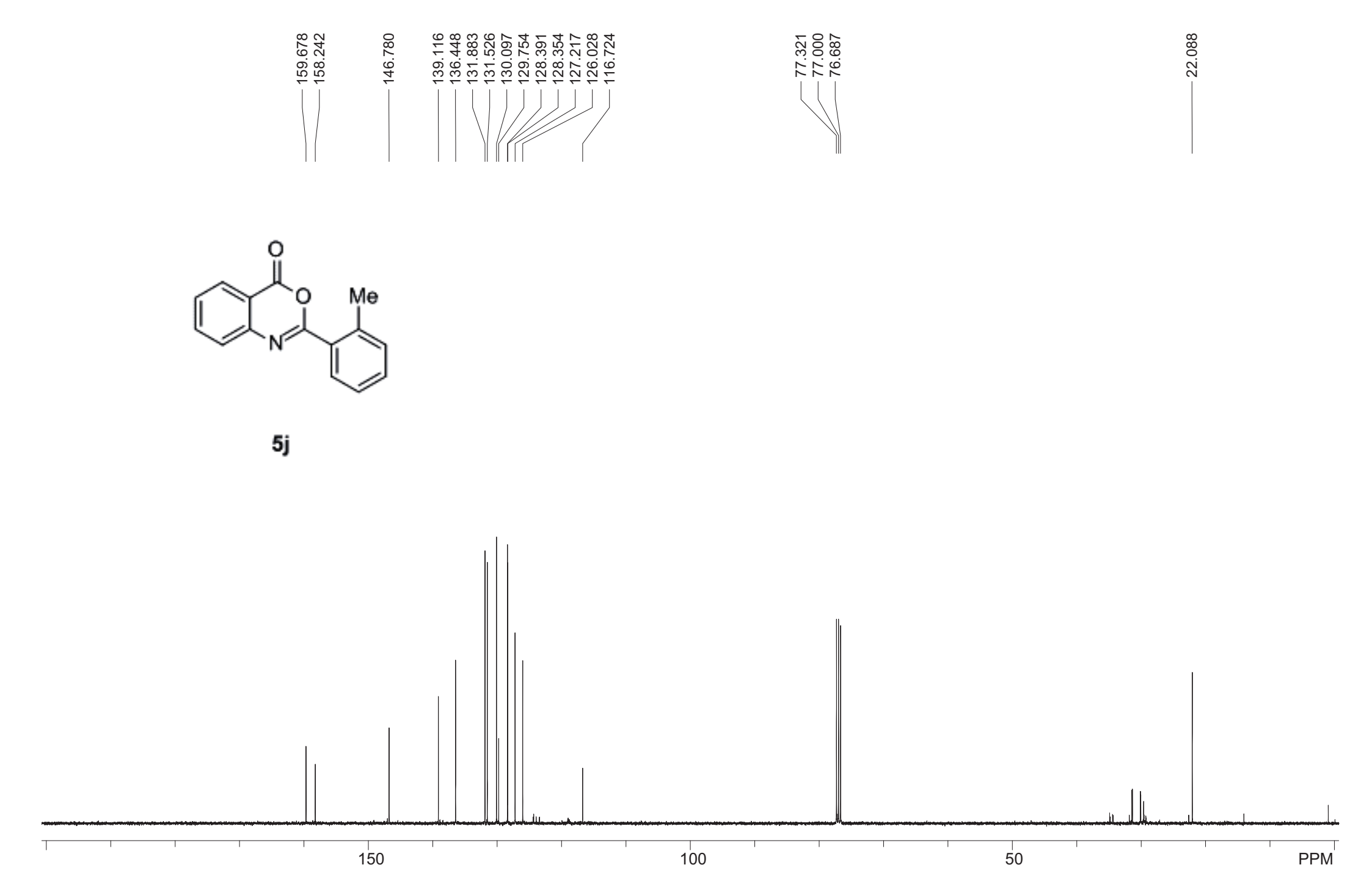
8.153
7.953
7.933
7.759
7.757
7.739
7.721
7.607
7.587
7.463
7.444
7.425
7.339
7.320
7.257
7.238
7.220
2.644
O
O
Me
N
5j
1.00
1.04
1.03
1.07
1.14
1.04
2.16
3.26
10
8
6
4
2
PPM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146.780
139.116
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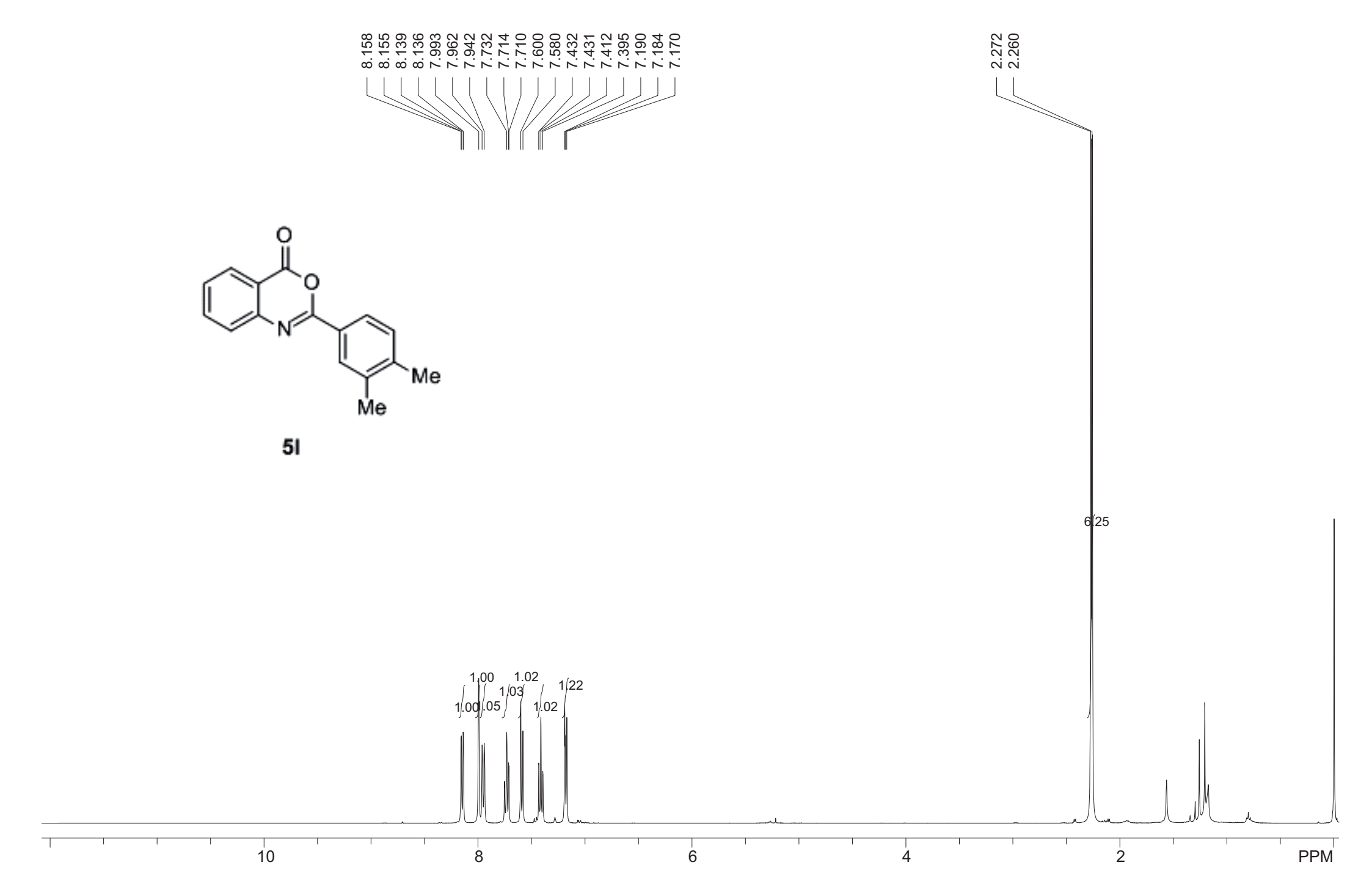
131.883
131.526
130.097
129.754
128.391
128.354
127.217
126.028
116.724
77.321
77.000
76.687
22.088
O
O
N
Me
150
100
50
PPM

5j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8.155
8.139
8.136
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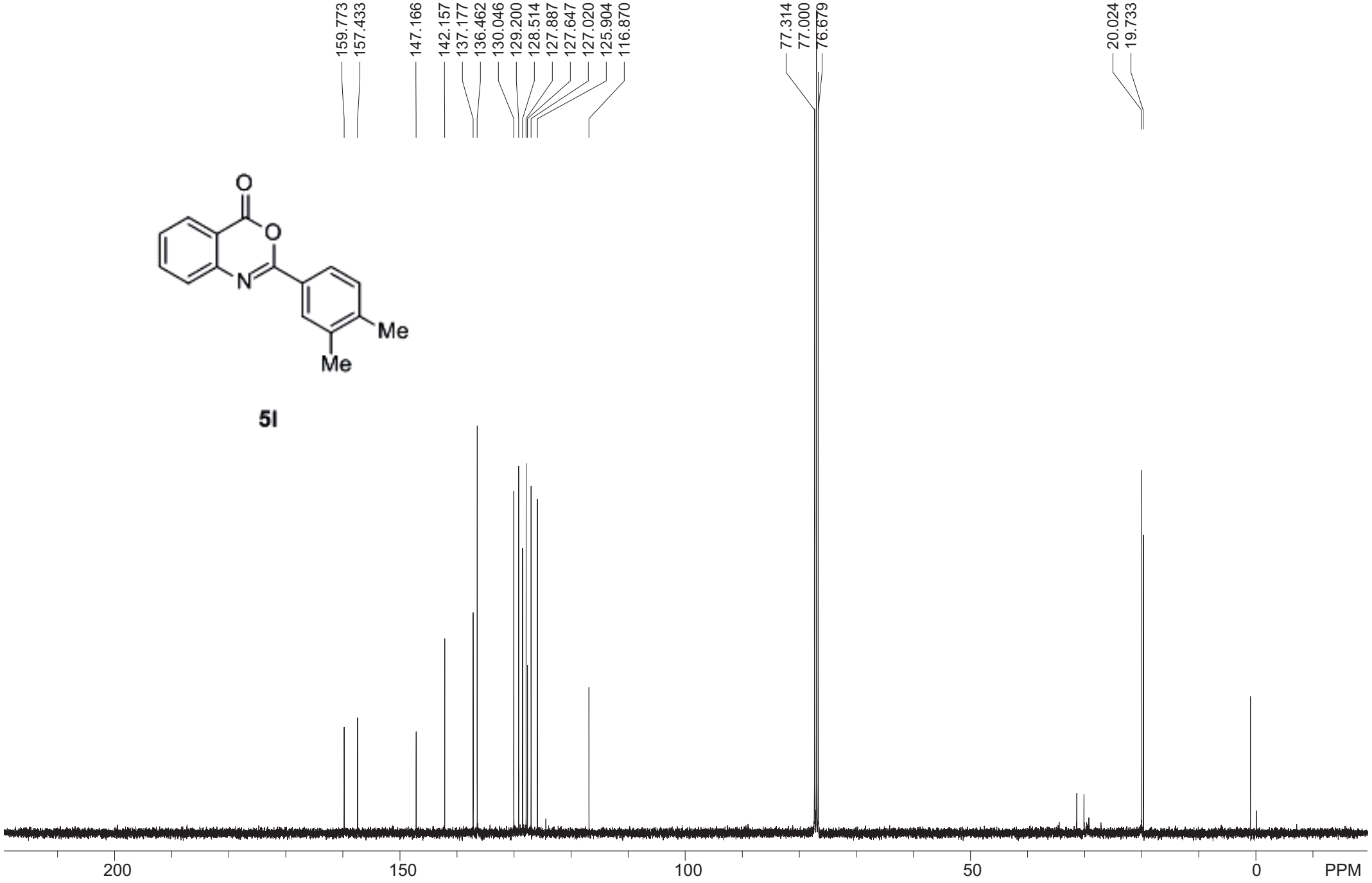
7.962
7.942
7.732
7.714
7.710
7.600
7.580
7.432
7.431
7.412
7.395
7.190
7.184
7.170
2.272
2.260
O
O
N
Me
Me
5l
6.25
1.00
1.00
1.05
1.03
1.02
1.02
1.22
10
8
6
4
2
PPM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142.157
137.177
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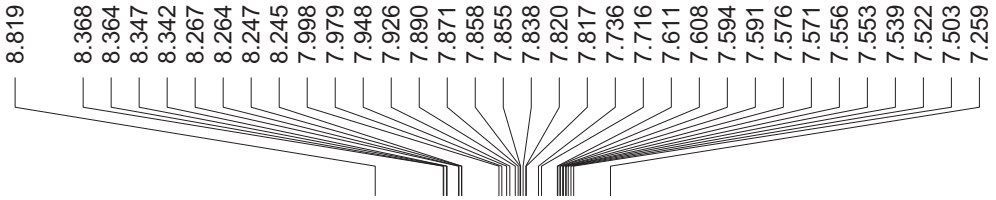
130.046
129.200
128.514
127.887
127.647
127.020
125.904
116.870
77.314
77.000
76.679
20.024
19.733
O
O
N
Me
Me
200
150
100
50
0
PPM

5l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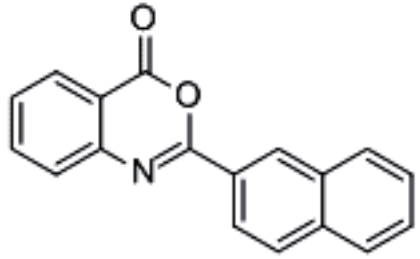
8.364
8.347
8.342
8.267
8.264
8.247
8.245
7.998
7.979
7.948
7.926
7.890
7.871
7.858
7.855
7.838
7.820
7.817
7.736
7.716
7.611
7.608
7.594
7.591
7.576
7.571
7.556
7.553
7.539
7.522
7.503
7.259


O
O
N

5m

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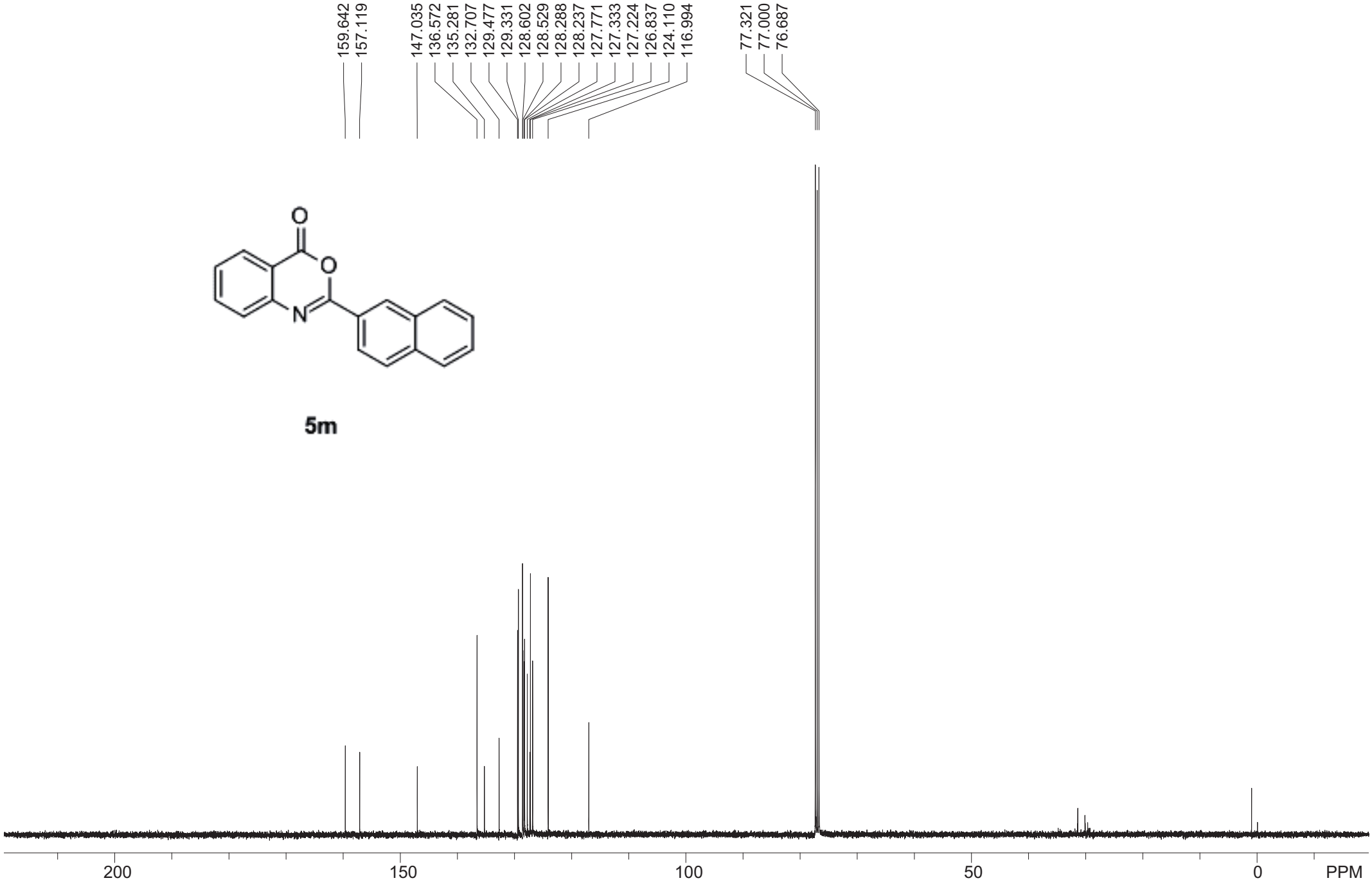
1.01
1.02
1.02
1.03
2.10
3.20
1.04
12
10
8
6
4
2
PPM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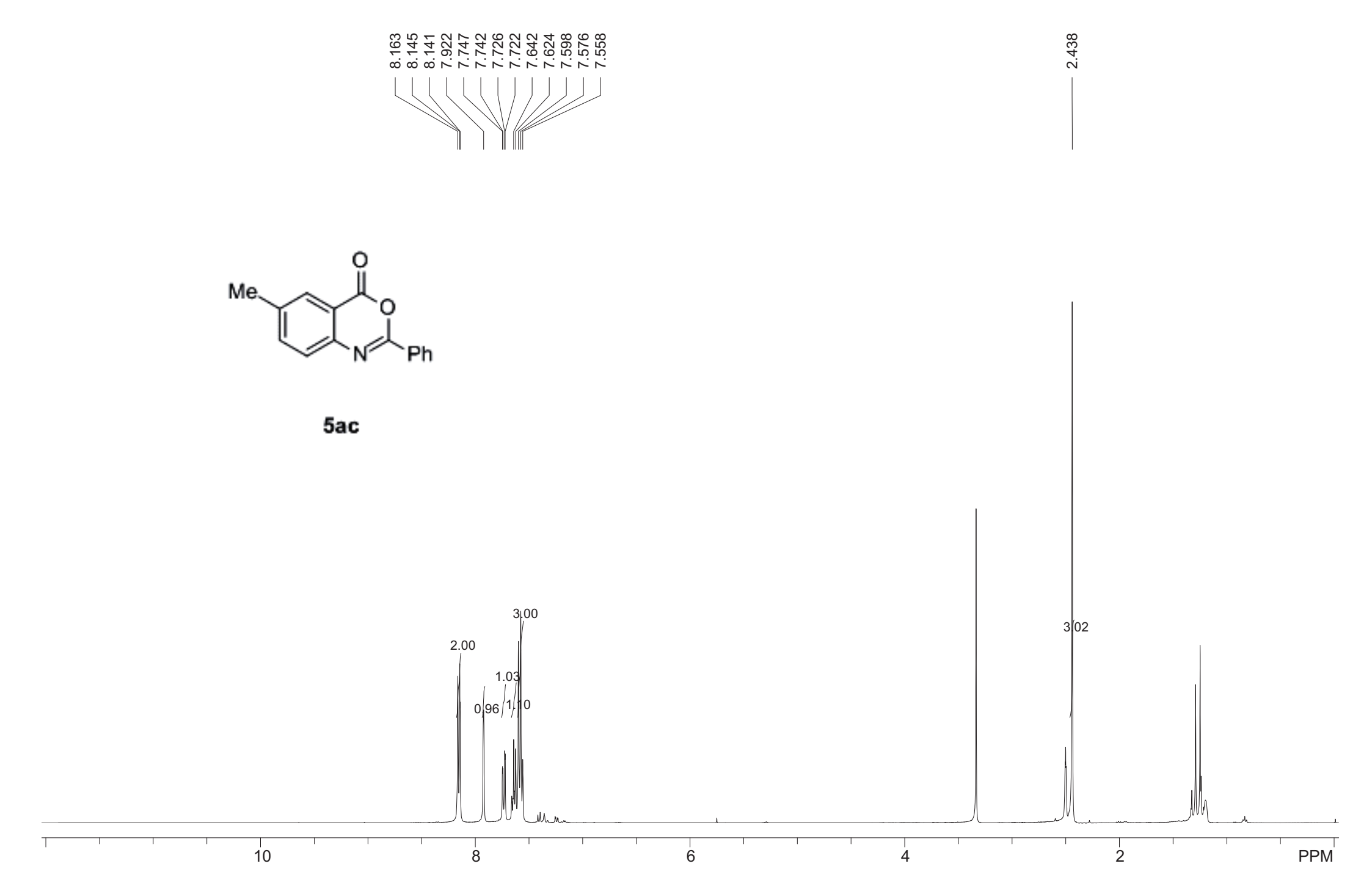
135.281
132.707
129.477
129.331
128.602
128.529
128.288
128.237
127.771
127.333
127.224
126.837
124.110
116.994
77.321
77.000
76.687
O
O
N
5m
200
150
100
50
0
PPM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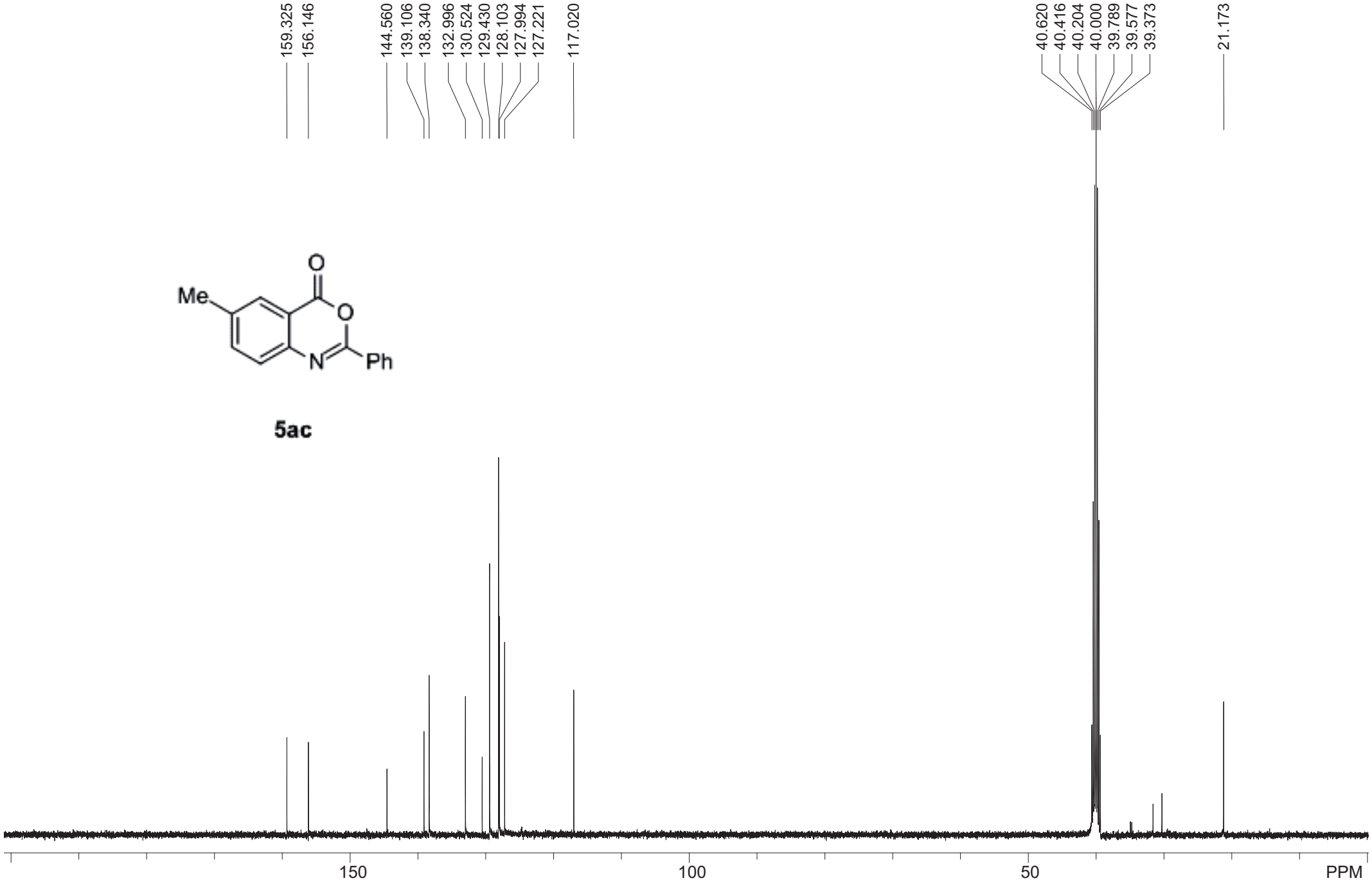
8.145
8.141
7.922
7.747
7.742
7.726
7.722
7.642
7.624
7.598
7.576
7.558
2.438
O
Me
O
N
Ph
5ac
3.00
2.00
1.03
0.96
1.10
3.02
10
8
6
4
2
PPM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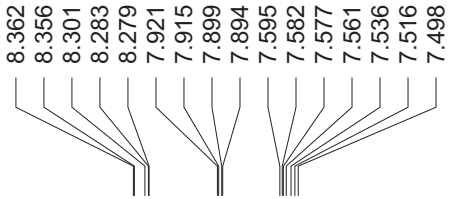
144.560
139.106
138.340
132.996
130.524
129.430
128.103
127.994
127.221
117.020
40.620
40.416
40.204
40.000
39.789
39.577
39.373
21.173
O
Me
O
N
Ph
150
100
50
PPM

5ac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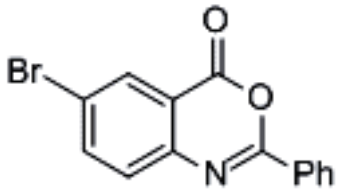
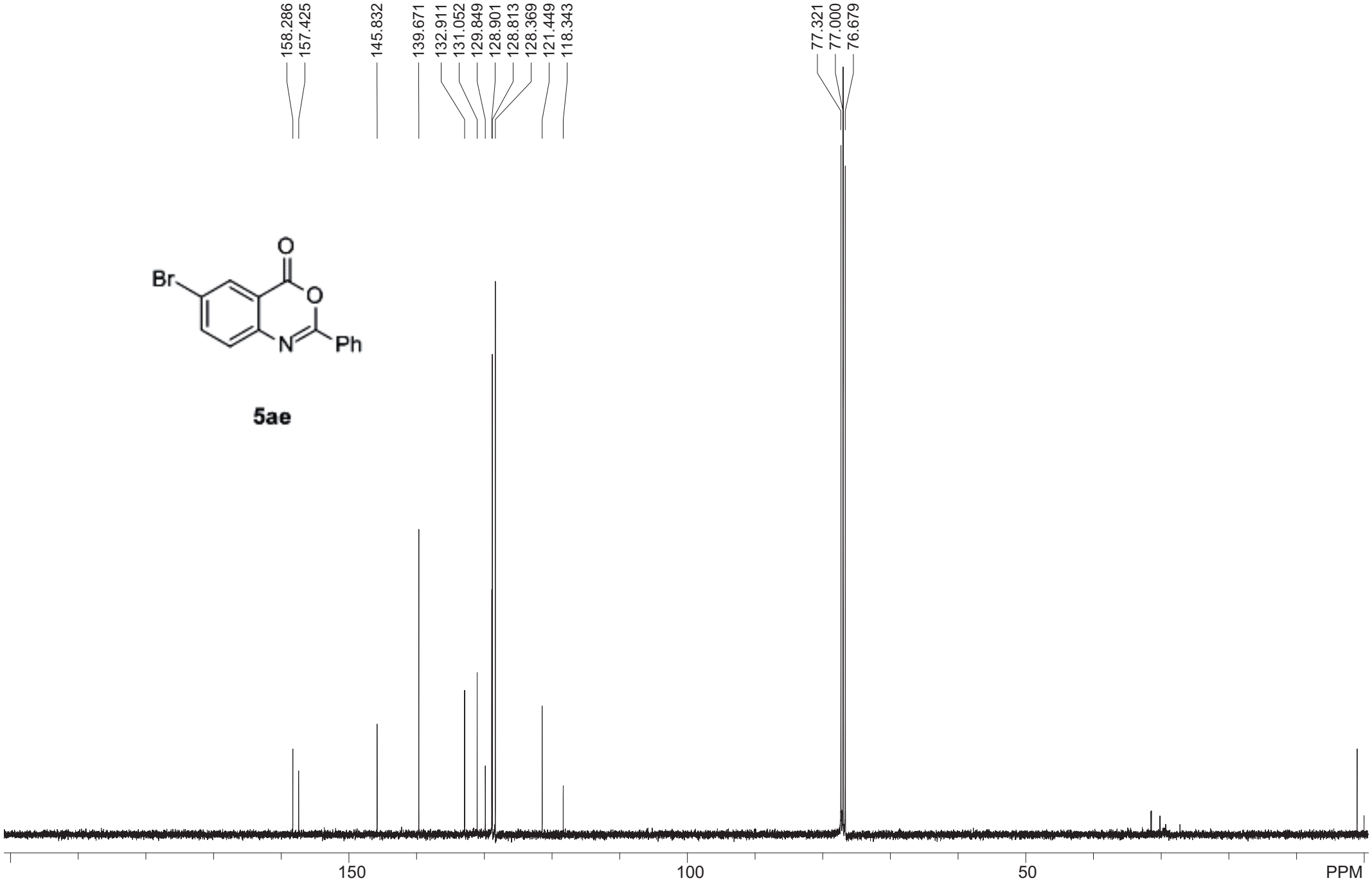
8.356
8.301
8.283
8.279
7.921
7.915
7.899
7.894
7.595
7.582
7.577
7.561
7.536
7.516
7.498


O
Br
O
N
Ph

5ae

2.14
2.22
2.16
1.00
1.07
10
8
6
4
2
PPM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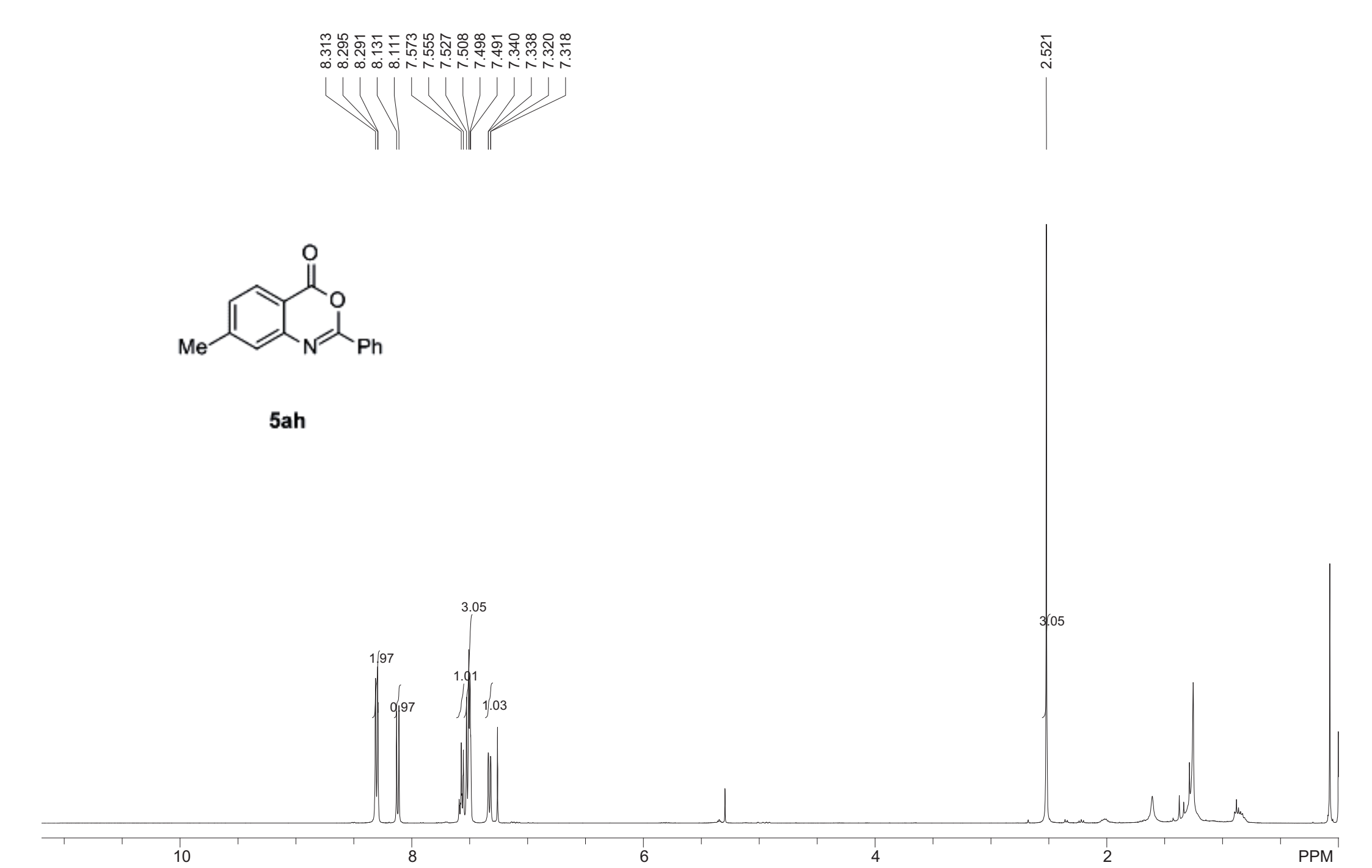
157.425
145.832
139.671
132.911
131.052
129.849
128.901
128.813
128.369
121.449
118.343
77.321
77.000
76.679
O
Br
O
N
Ph
150
100
50
PPM

5ae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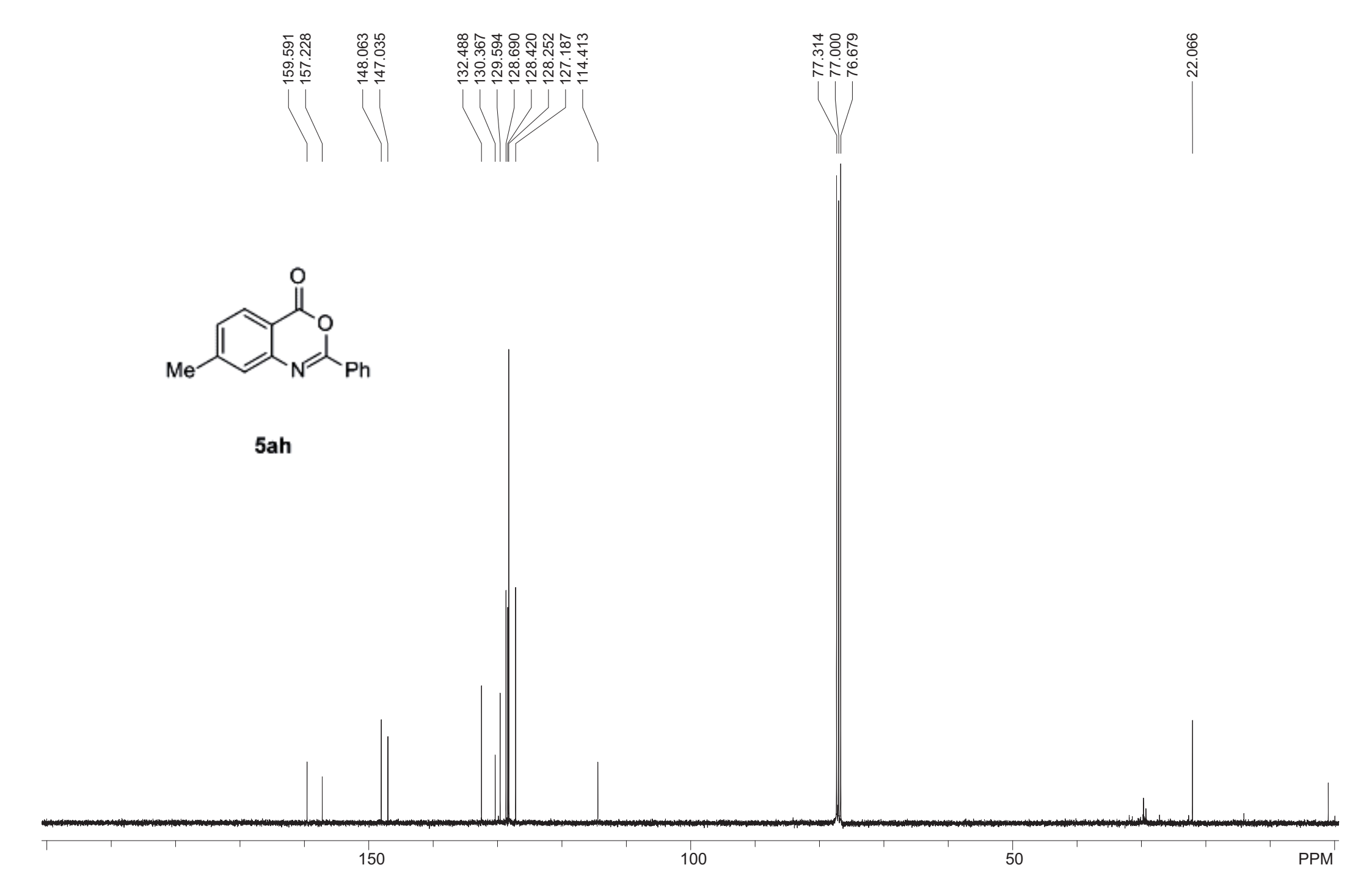
8.291
8.131
8.111
7.573
7.555
7.527
7.508
7.498
7.491
7.340
7.338
7.320
7.318
2.521
O
O
Me
N
Ph
5ah
3.05
1.97
1.01
0.97
1.03
3.05
10
8
6
4
2
PPM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157.228
148.063
147.035
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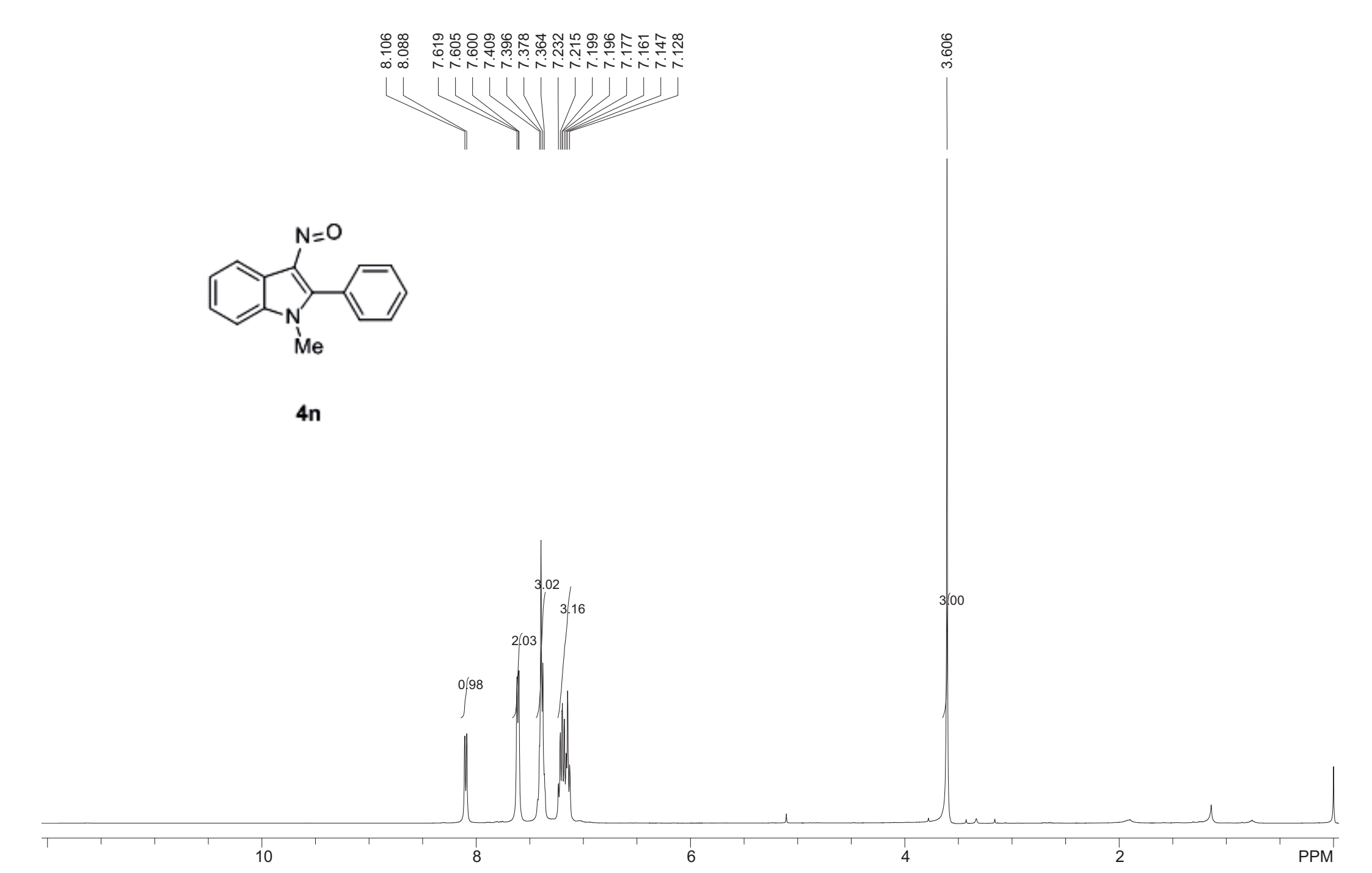
129.594
128.690
128.420
128.252
127.187
114.413
77.314
77.000
76.679
22.066
O
O
Me
N
Ph
150
100
50
PPM

5ah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8.088
7.619
7.605
7.600
7.409
7.396
7.378
7.364
7.232
7.215
7.199
7.196
7.177
7.161
7.147
7.128
3.606
N=O
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Me
4n
0.98
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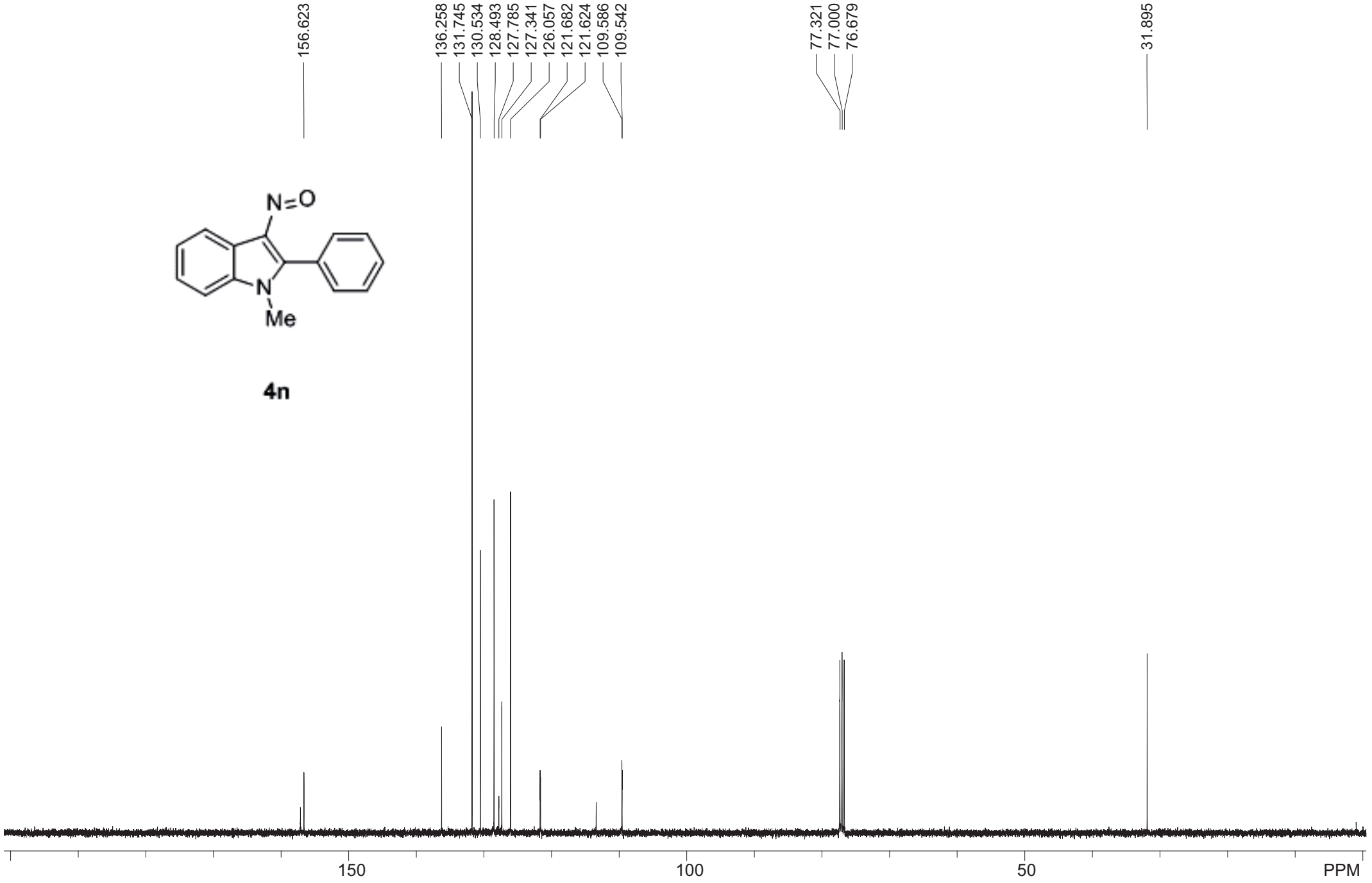
3.02
3.16
3.00
10
8
6
4
2
PPM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136.258
131.745
130.534
128.493
127.785
127.341
126.057
121.682
121.624
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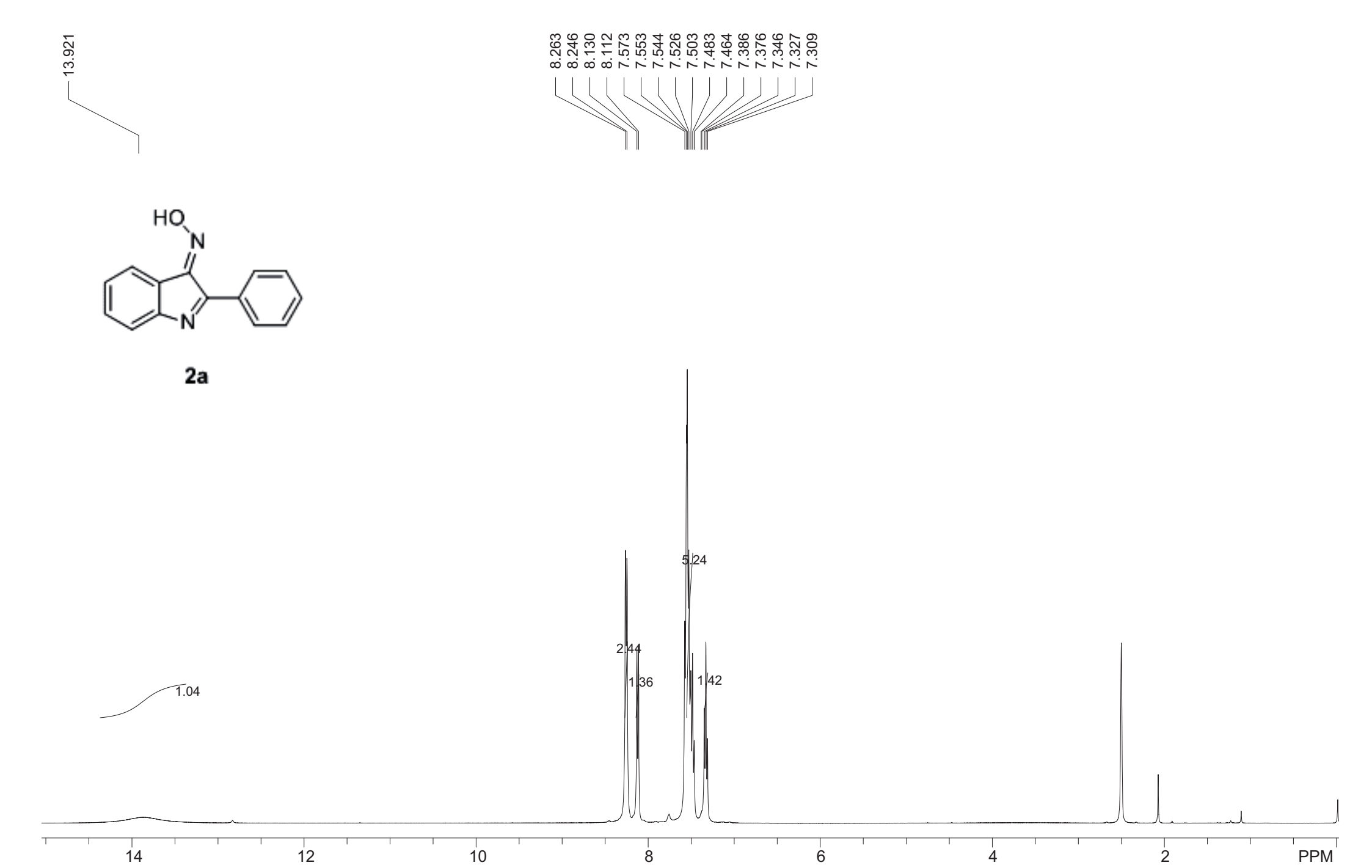
77.321
77.000
76.679
31.895
N=O
N
Me
150
100
50
PPM

4n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8.246
8.130
8.112
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7.553
7.544
7.526
7.503
7.483
7.464
7.386
7.376
7.346
7.327
7.309
HO
N
N
2a
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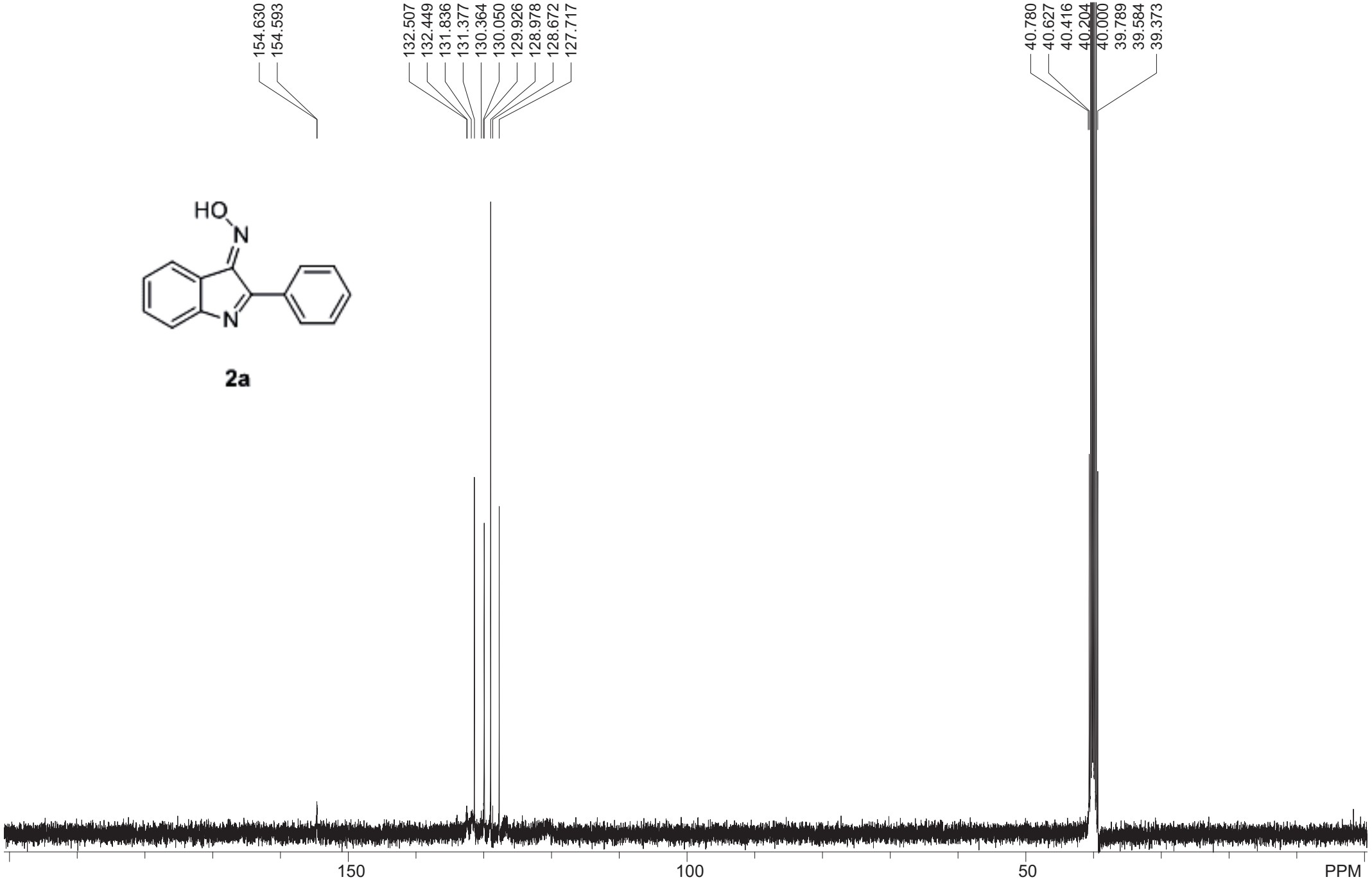
2.44
1.36
1.42
1.04
14
12
10
8
6
4
2
PPM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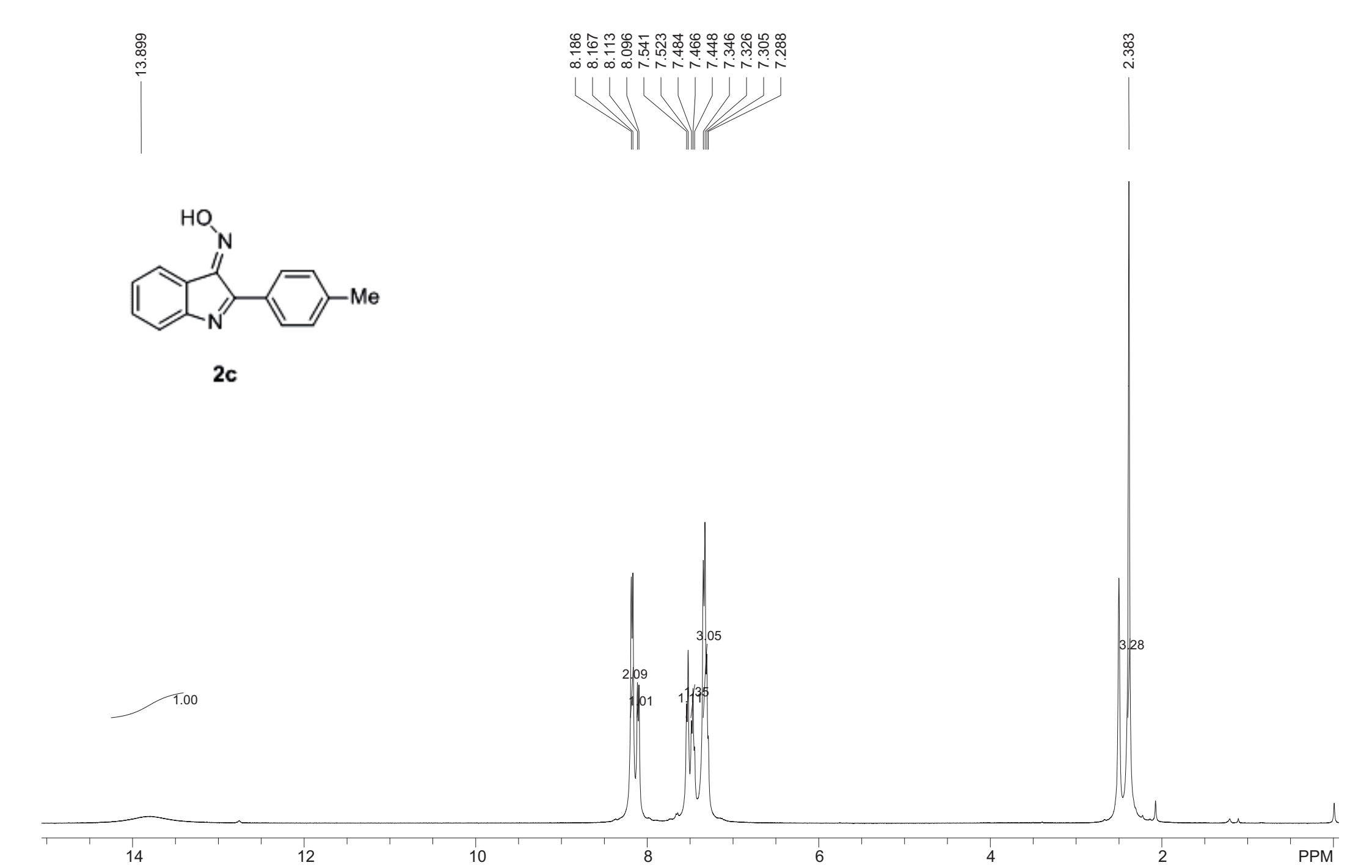
132.449
131.836
131.377
130.364
130.050
129.926
128.978
128.672
127.717
40.780
40.627
40.416
40.204
40.000
39.789
39.584
39.373
HO
N
N
150
100
50
PPM

2a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8.167
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7.523
7.484
7.466
7.448
7.346
7.326
7.305
7.288
2.383
HO
N
Me
N
2c
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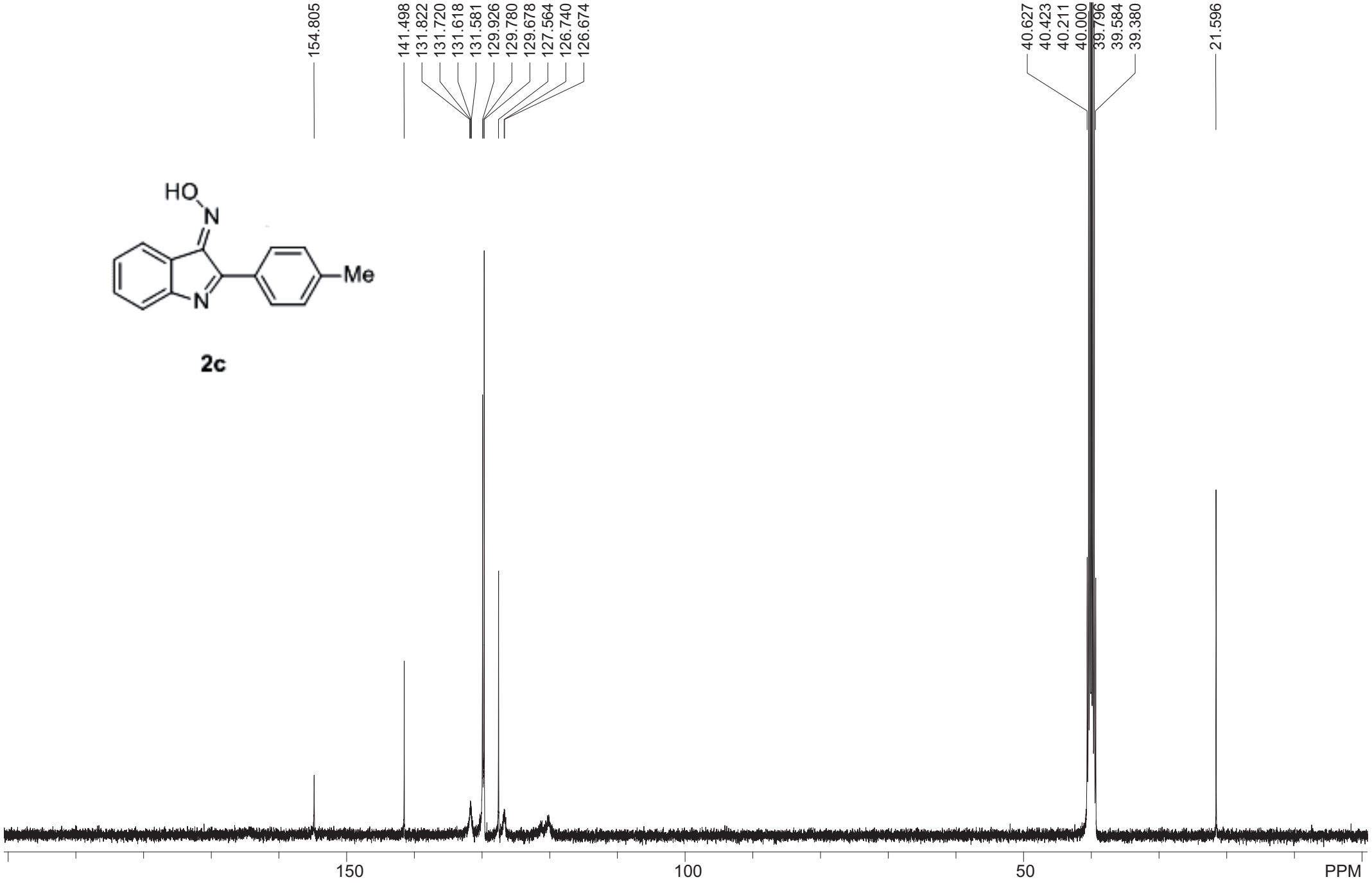
2.09
1.01
3.05
1.35
3.28
14
12
10
8
6
4
2
PPM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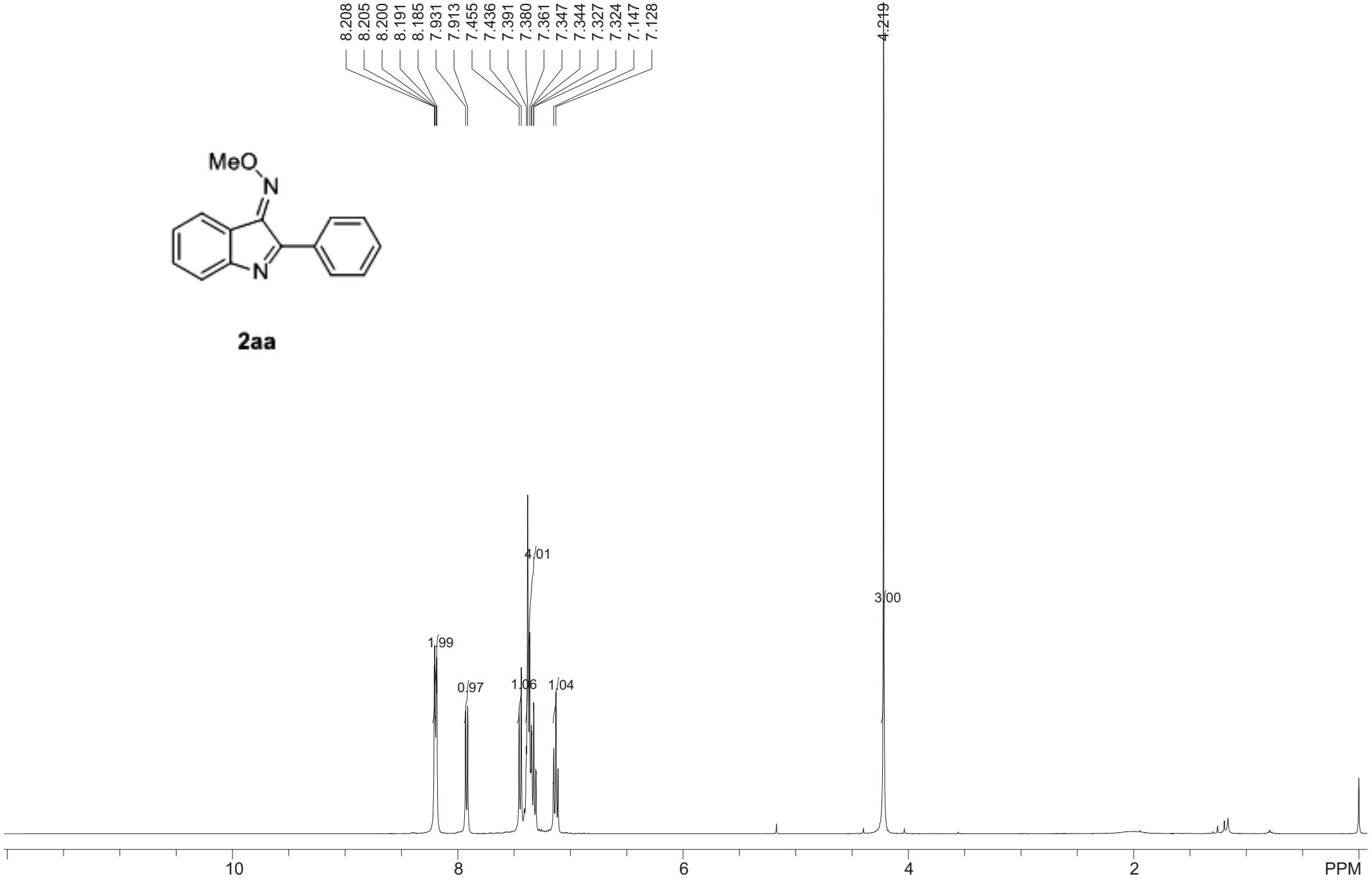
131.822
131.720
131.618
131.581
129.926
129.780
129.678
127.564
126.740
126.674
40.627
40.423
40.211
40.000
39.796
39.584
39.380
21.596
HO
N
N
Me
150
100
50
PPM

2c


8.208
8.205
8.200
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8.185
7.931
7.913
7.455
7.436
7.391
7.380
7.361
7.347
7.344
7.327
7.324
7.147
7.128
4.219
MeO
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N
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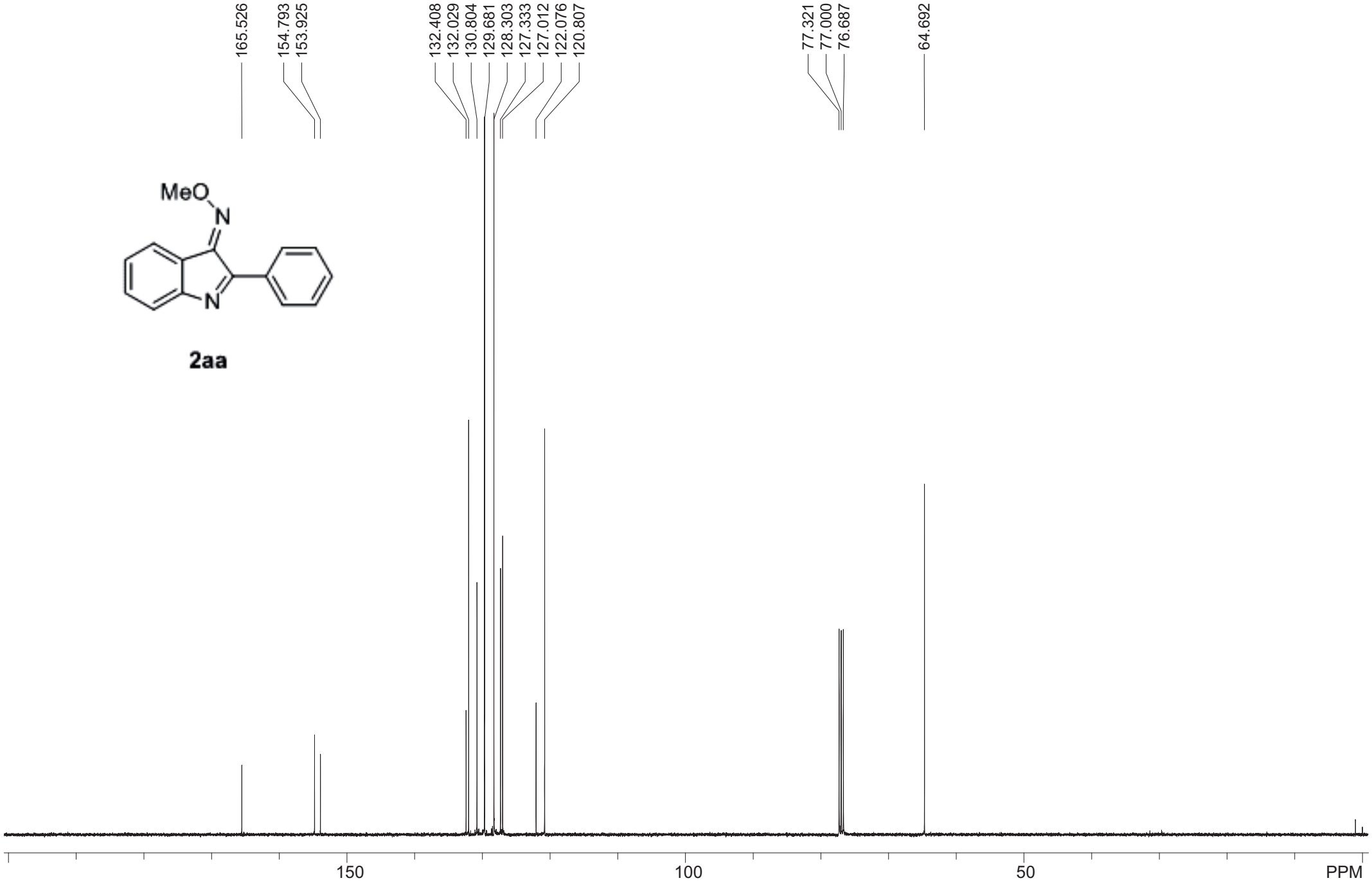
3.00
1.99
0.97
1.06
1.04
10
8
6
4
2
PPM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130.804
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127.012
122.076
120.807
77.321
77.000
76.687
64.692
MeO
N
N
2aa
150
100
50
PPM

^{18}O-labeling experiment