Supporting Information

Copper-Catalyzed Regioselective Tri- and Tetrafunctionalization of Alkenylboronic Acids to Synthesize Tetrahydrocarbazol-1-ones and Indolo[2,3-*a*]carbazoles

Hong-Yan Bi[+], Cheng-Jing Li[+], Cui Wei[+], Cui Liang, and Dong-Liang Mo*

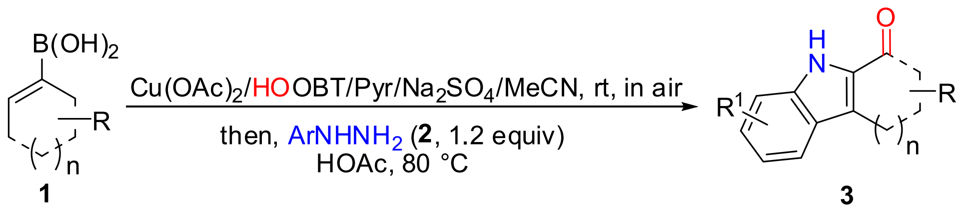
State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, Ministry of Science and Technology of China; School of Chemistry and Pharmaceutical Sciences, Guangxi Normal University, 15 Yu Cai Road, Guilin, 541004, China

Contents

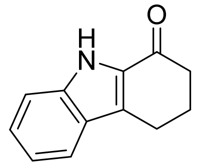
1. General experimental information

^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 or 500 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. 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 reagents and solvents were obtained from commercial sources and, where appropriate, purified prior to use. Alkenylboronic acid **1a**, *N*-hydroxylbenzotriazin-4-one (HOOBT), and arylhydrazines **2a-2j** were purchased from Sigma-Aldrich.

2. Synthesis of tetrahydrocarbazol-1-ones 3aa-3ia

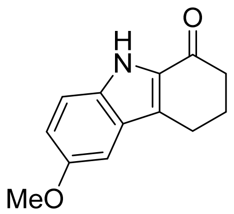


General procedure A: In a 25 mL reaction flask was charged with alkenylboronic acids **1** (0.9 mmol, 3.0 equiv.), HOOBT (0.3 mmol), $Cu(OAc)_2$ (5.4 mg, 20 mol%), and Na_2SO_4 (400 mg) under an air atmosphere, MeCN (3.0 mL) and pyridine (72 uL, 0.9 mmol, 3.0 equiv) were then added. The reaction mixture was stirred vigorously at room temperature for 18−24 h until HOOBT disappeared (monitored by TLC). Then, arylhydrazine **2** (0.36 mmol, 1.2 equiv.) and HOAc (5 mL) were added to the reaction mixture and then stirred at 80 ˚C for 10-24 h. At this time, the reaction was quenched by H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). Then, the combined organic layers were washed by $NaHCO_3$ (10 mL) and brine (10 mL), dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/6, ethyl acetate/petroleum ether) to provide compounds **3aa-3ia**.



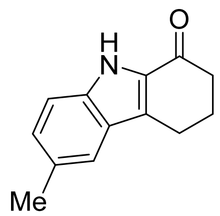
3aa

2,3,4,9-Tetrahydro-1H-carbazol-1-one (3aa). A brown solid, 0.043 g, 79% yield; mp: 155−156°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.38−7.34 (m, 1H), 7.16−7.12 (m, 1H), 3.03 (t, J = 6.0 Hz, 2H), 2.70−2.66 (m, 2H), 2.30−2.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 138.0, 131.2, 129.6, 127.0, 125.8, 121.3, 120.3, 121.6, 38.2, 25.0, 21.4; HRMS (ESI) m/z calcd for $C_{12}H_{12}NO$ $(M+H)^+$ 186.0913, found 186.0910.



3ab

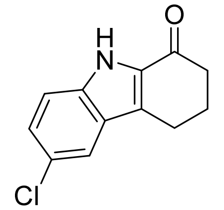
6-Methoxy-2,3,4,9-tetrahydro-1H-carbazol-1-one (3ab). A brown solid, 0.074 g, 85% yield; mp: 198−199 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.34 (d, J = 8.8 Hz, 1H), 7.06−7.01 (m, 2H), 3.87 (s, 3H), 3.00−2.97 (s, 2H), 2.67−2.64 (m, 2H), 2.30−2.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 154.5, 133.2, 131.8, 128.8, 126.1, 118.6, 113.4, 101.3, 55.7, 38.2, 25.0, 21.4; HRMS (ESI) m/z calcd for $C_{13}H_{14}NO_2$ $(M+H)^+$ 216.1019, found 216.1018.



3ac

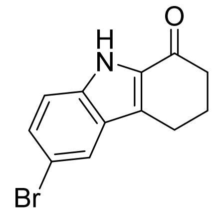
6-Methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one (3ac). A brown solid, 0.048 g, 80% yield; mp: 173−174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.50 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.46 (d, J = 8.8 Hz, 1H), 7.38−7.34 (m, 1H), 7.16−7.12 (m, 1H), 3.03 (t, J = 6.0 Hz, 2H), 2.70−2.66 (m, 2H), 2.30−2.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

191.1, 136.9, 132.6, 129.1, 127.7, 127.4, 124.0, 115.3, 112.5, 38.6, 25.0, 21.2; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NO$ $(M+H)^+$ 200.1070, found 200.1068.



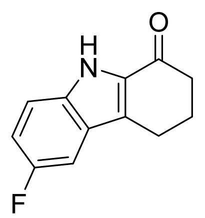
3ad

6-Chloro-2,3,4,9-tetrahydro-1H-carbazol-1-one (3ad). A brown solid, 0.049 g, 75% yield; mp: 171−172 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 11.80 (s, 1H), 7.74 (s, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 2.02 (br, 2H), 2.57−2.54 (m, 2H), 2.14−2.11 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 191.2, 136.7, 132.8, 127.8, 126.7, 126.6, 124.7, 120.9, 114.9, 38.4, 25.0, 21.2; HRMS (ESI) *m/z* calcd for $C_{12}H_{11}ClNO$ $(M+H)^+$ 220.0524, found 220.0516.



3ae

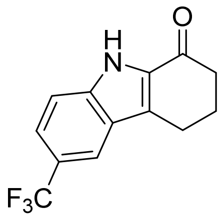
6-Bromo-2,3,4,9-tetrahydro-1H-carbazol-1-one (3ae). A brown solid, 0.058 g, 74% yield; mp: 186−187 °C; ^1H NMR (500 MHz, DMSO-d_6): δ 11.81 (s, 1H), 7.90 (s, 1H), 7.41−7.34 (m, 2H), 2.92−2.90 (m, 2H), 2.56−2.55 (m, 2H), 2.14−2.13 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 191.1, 136.9, 132.6, 129.1, 127.7, 127.4, 124.0, 115.3, 112.5, 38.6, 25.0, 21.2; HRMS (ESI) *m/z* calcd for $C_{12}H_{11}BrNO$ $(M+H)^+$ 264.0019, found 264.0024.



3af

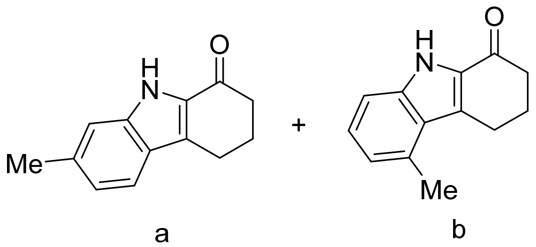
6-Fluoro-2,3,4,9-tetrahydro-1H-carbazol-1-one (3af). A brown solid, 0.036 g, 60%

yield; mp: 197−198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.47 (s, 1H), 7.42−7.39 (m, 1H), 7.29 (d, J = 10.0 Hz, 1H), 7.15−7.11 (m, 1H), 3.00 (t, J = 6.0 Hz, 2H), 2.70 (t, J = 6.0 Hz, 2H), 2.30−2.25 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.7, 158.8 (d, J = 236 Hz), 134.5, 132.6, 129.2 (d, J = 5.8 Hz), 126.0 (d, J = 9.5 Hz), 116.1 (d, J = 27 Hz), 113.7 (d, J = 8.7 Hz), 105.7 (d, J = 23 Hz), 38.2, 24.9, 21.3; ^{19}F NMR (100 MHz, $CDCl_3$): δ -122.8; HRMS (ESI) m/z calcd for $C_{12}H_{11}FNO$ $(M+H)^+$ 204.0819, found 204.0808.



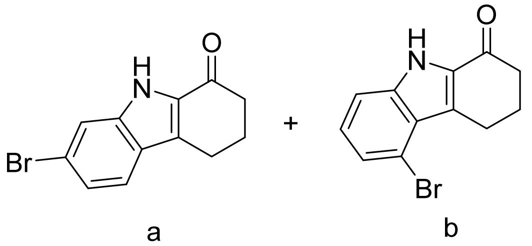
3ag

6-(Trifluoromethyl)-2,3,4,9-tetrahydro-1H-carbazol-1-one (3ag). A brown solid, 0.021 g, 29% yield; mp: 160−161 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.73 (s, 1H), 7.97 (s, 1H), 7.60−7.55 (m, 2H), 3.06−3.04 (m, 2H), 2.74 (t, J = 5.2 Hz, 2H), 2.34−2.30 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.7, 139.0, 132.5 (q, J = 274 Hz), 125.1, 123.3, 123.2, 123.0 (q, J = 33 Hz), 119.4 (q, J = 3.6 Hz), 113.1, 38.2, 24.8, 21.2; HRMS (ESI) m/z calcd for $C_{13}H_{11}F_3NO$ $(M+H)^+$ 254.0787, found 254.0801.



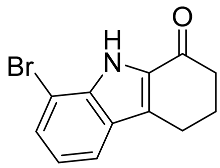
3ah (a/b = 2:1)

Indole 3ah, a brown solid, 0.053 g, 89% yield. mp: 156−157 °C; **3ah (a)**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.27−7.25 (m, 1H), 6.99 (d, J = 8.4 Hz, 1H), 2.67 (s, 3H), 3.00 (t, J = 6.0 Hz, 2H), 2.66−2.63 (m, 2H), 2.46 (s, 3H), 2.28−2.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.3, 138.2, 133.7, 130.9, 129.8, 125.2, 122.5, 120.9, 110.3, 37.7, 25.0, 22.1, 20.1; **3ah (b)**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24 (s, 1H), 7.21−7.219 (m, 2H), 6.86 (d, J = 6.8 Hz, 1H), 3.26 (t, J = 6.0 Hz, 2H), 2.67 (s, 3H), 2.66−2.63 (m, 2H), 2.28−2.24 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 138.5, 137.5, 131.0, 129.8, 126.9, 123.7, 121.3, 112.2, 38.1, 25.1, 23.9, 21.4; HRMS (ESI) m/z calcd for $C_{13}H_{14}NO$ $(M+H)^+$ 200.1070, found 200.1068.



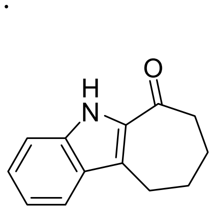
3ai (a/b = 1:0.8)

Indole 3ai, a brown solid, 0.048 g, 75% yield. mp: 185−186 °C; **3ai (a)**: ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 11.80 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.25−7.23 (m, 1H), 3.00-2.94 (m, 2H), 2.61−2.60 (m, 2H), 2.23−2.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 191.0, 139.0, 132.3, 128.5, 127.3, 124.3, 123.6, 119.4, 115.6, 38.2, 24.9, 21.2; **3ai (b)**:^{1}H NMR (400 MHz, $CDCl_3$): *δ* 12.01 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.31−7.29 (m, 1H), 7.21−7.19 (m, 1H), 3.42−3.27 (m, 2H), 2.56−2.55 (m, 2H), 2.18−2.14 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 191.2, 139.5, 132.6, 137.7, 124.7, 124.1, 116.1, 123.2, 113.0, 38.5, 25.0, 23.1; HRMS (ESI) *m/z* calcd for $C_{12}H_{11}BrNO$ $(M+H)^+$ 264.0019, found 264.0003.



3aj

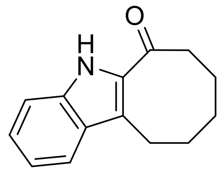
8-Bromo-2,3,4,9-tetrahydro-1H-carbazol-1-one (3aj). A brown solid, 0.039 g, 65% yield. mp: 154−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.88 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 3.01 (t, *J* = 6.0 Hz, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 2.30−2.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 191.1, 136.5, 131.4, 130.0, 129.0, 127.0, 121.4, 120.5, 105.8, 38.2, 24.8, 21.5; HRMS (ESI) *m/z* calcd for $C_{12}H_{11}BrNO$ $(M+H)^+$ 264.0019, found 264.0029.



3ba

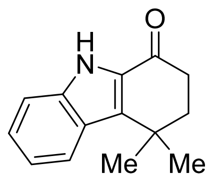
7,8,9,10-Tetrahydrocyclohepta[b]indol-6(5H)-one (3ba). A brown solid, 0.041 g, 68% yield; mp: 140−141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.21 (s, 1H), 7.65 (d, *J* =

8.0 Hz, 1H), 7.38−7.31 (m, 2H), 7.13−7.09 (m, 1H), 3.15−3.12 (m, 2H), 2.85 (t, *J* = 6.0 Hz, 2H), 2.10−1.98 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 194.9, 136.6, 132.7, 127.8, 126.5, 124.5, 121.2, 120.0, 111.9, 42.8, 26.6, 25.6, 22.8; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NO$ $(M+H)^+$ 200.1070, found 200.1066.



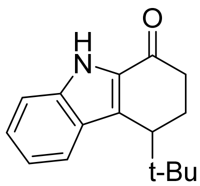
3ca

8,9,10,11-Tetrahydro-5H-cycloocta[b]indol-6(7H)-one (3ca). A brown solid, 0.039 g, 60% yield; mp: 171−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.16 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.41−7.33 (m, 2H), 7.16−7.12 (m, 1H), 3.32 (t, *J* = 6.8 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 1.87−1.76 (m, 4H), 1.48−1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 193.8, 136.4, 135.1, 128.0, 126.4, 121.8, 120.9, 120.1, 112.0, 40.5, 25.3, 23.8, 23.2, 22.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO$ $(M+H)^+$ 214.1226, found 214.1224.



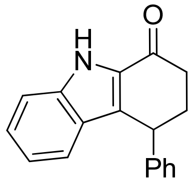
3da

4,4-Dimethyl-2,3,4,9-tetrahydro-1H-carbazol-1-one (3da). A brown solid, 0.042 g, 67% yield; mp: 153−154 °C; ^{1}H NMR (400 MHz, DMSO-d_6): *δ* 11.59 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.31−7.27 (m, 1H), 7.08−7.05 (m, 1H), 2.87−2.82 (m, 2H), 2.47−2.42 (m, 2H), 1.08 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): *δ* 190.3, 138.8, 130.8, 126.5, 126.1, 121.5, 120.1, 113.3, 52.3, 36.8, 35.2, 28.7; HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NO(M+H)^+$ 214.1226, found 214.1223.



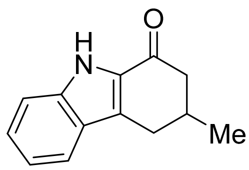
3ea

4-(Tert-butyl)-2,3,4,9-tetrahydro-1H-carbazol-1-one (3ea). A brown solid, 0.044 g, 61% yield; mp: 184−185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.41−7.37 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 3.20−3.15 (m, 1H), 2.76−2.66 (m,1H), 2.50−2.43 (m,1H), 2.20−2.13 (m,1H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.8, 138.1, 131.0, 129.6, 127.0, 126.0, 121.3, 120.4, 112.5, 48.2, 40.1, 32.8, 27.5, 22.8; IR (thin film) 3030, 2922, 1724, 1643, 1433, 1325, 1149, 743 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{19}NO$ (M+H)$^+$ 242.1539, found 242.1537.



3fa

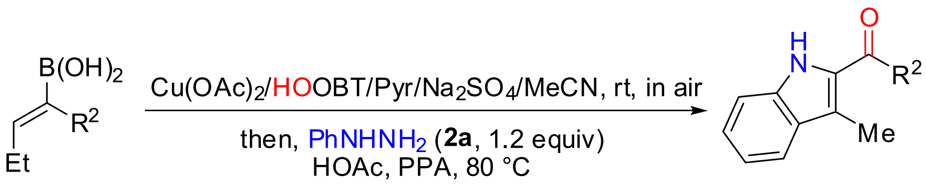
4-Phenyl-2,3,4,9-tetrahydro-1H-carbazol-1-one (3fa). A brown solid, 0.040 g, 51% yield; mp: 188−189 °C; ^{1}H NMR (400 MHz, DMSO): δ 11.70 (s, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.45−7.41 (m, 3H), 7.38−7.24 (m, 4H), 7.10 (d, J = 7.6 Hz, 1H), 3.62−3.59 (m, 1H), 3.31−3.26 (m, 1H), 3.14−3.00 (m, 2H), 2.68−2.63 (m, 1H); ^{13}C NMR (100 MHz, DMSO): δ 189.9, 144.6, 138.8, 131.5, 129.0, 127.7, 127.6, 127.1, 126.8, 125.6, 121.8, 120.3, 113.3, 45.5, 43.4, 29.5. IR (thin film) 3033, 2932, 1647, 1471, 1384, 1282, 1190, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{16}NO$ (M+H)$^+$ 262.1226, found 262.1225.



3ga

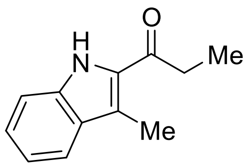
3-**Methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one (3ga)**. A brown solid, 0.048 g, 81% yield; mp: 120−121 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.45−7.35 (m, 2H), 7.17 (t, J = 7.2 Hz, 1H), 3.18−3.13 (m, 2H), 2.71−2.39 (m, 4H), 1.24 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.2, 138.1, 131.0, 129.0, 127.0, 125.8, 121.3, 120.4, 112.6, 46.4, 33.0, 29.7, 21.4; HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NO$ (M+H)$^+$ 200.1070, found 200.1083.

3. Synthesis of indoles 3ha and 3ia



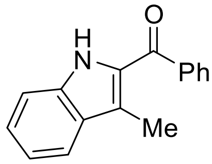
1h, **1i** **3ha**, **3ia**

General procedure B: In a 25 mL reaction flask was charged with alkenylboronic acids **1** (0.9 mmol, 3.0 equiv.), HOOBT (0.3 mmol), $Cu(OAc)_2$ (5.4 mg, 20 mol%), and Na_2SO_4 (400 mg) under an air atmosphere, MeCN (3.0 mL) and pyridine (72 uL, 0.9 mmol, 3.0 equiv) were then added. The reaction mixture was stirred vigorously at room temperature for 18−24 h until HOOBT disappeared (monitored by TLC). Then, phenylhydrazine **2a** (0.36 mmol, 1.2 equiv.), PPA (0.3 mmol, 1.0 equiv) and HOAc (5 mL) were added to the reaction mixture and then stirred at 80 ˚C for 10-24 h. At this time, the reaction was quenched by H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). Then, the combined organic layers were washed by $NaHCO_3$ (10 mL) and brine (10 mL), dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/6, ethyl acetate/petroleum ether) to provide compounds **3ha** and **3ia**.



3ha

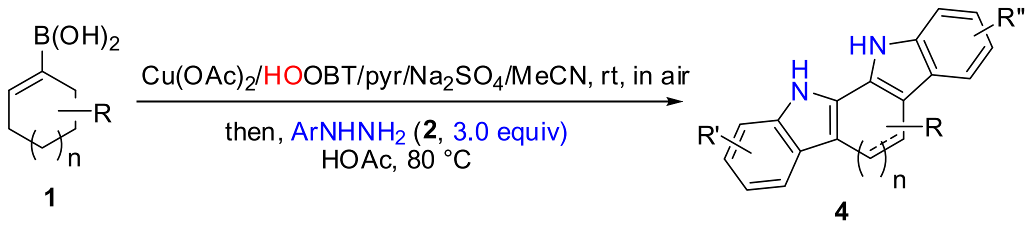
1-(3-Methyl-1H-indol-2-yl)propan-1-one (3ha). A yellow solid, 0.025 g, 45% yield; mp: 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.38−7.31 (m, 2H), 7.16−7.12 (m, 1H), 3.00 (q, J = 7.2 Hz, 2H), 2.65−2.64 (m, 3H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ193.8, 135.9, 132.3, 132.3, 128.9, 126.2, 121.1, 120.0, 117.9, 111.8, 34.3, 11.2, 8.0; IR (thin film) 3077, 2923, 1732, 1640, 1432, 1226, 1026, 740 cm^{-1}; HRMS (ESI) m/z calcd for $C_{12}H_{14}NO$ $(M+H)^+$ 188.1070, found 188.1068.



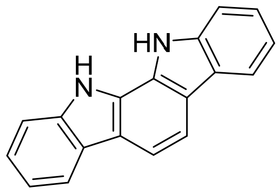
3ia

(3-Methyl-1H-indol-2-yl)(phenyl)methanone (3ia). A yellow solid, 0.038 g, 53% yield; mp: 109−110°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (s, 1H), 7.78 (d, J = 7.2 Hz, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.61−7.58 (m, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.41−7.35 (m, 2H), 7.18 (t, J = 7.2 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 139.4, 136.6, 132.0, 131.6, 129.0, 128.8, 128.5, 126.5, 121.3, 120.5, 120.2, 111.8, 11.2; IR (thin film) 3069, 2973, 1694, 1642, 1450, 1242, 1108, 773 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{16}H_{14}NO$ $(M+H)^+$ 236.1070, found 236.1068.

4. Synthesis of indolo[2,3-*a*]carbazoles 4

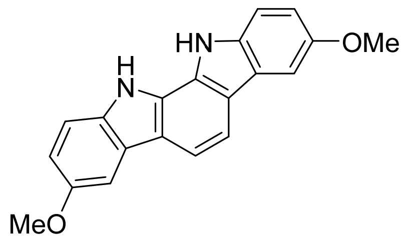


General procedure C: In a 25 mL reaction flask was charged with alkenylboronic acids **1** (0.9 mmol, 3.0 equiv.), HOOBT (0.3 mmol), $Cu(OAc)_2$ (5.4 mg, 20 mol%), and Na_2SO_4 (400 mg) under an air atmosphere, MeCN (3.0 mL) and pyridine (72 uL, 0.9 mmol, 3.0 equiv) were then added. The reaction mixture was stirred vigorously at room temperature for 18−24 h until HOOBT disappeared (monitored by TLC). Then, arylhydrazine **2** (0.9 mmol, 3.0 equiv.) [or Ar^1NHH_2 (1.5 equiv.) for 10 h, then adding Ar^2NHNH_2 (1.5 equiv.)] and HOAc (5 mL) were added to the reaction mixture and then stirred at 80 ˚C for 10-24 h. At this time, the reaction was quenched by H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). Then, the combined organic layers were washed by $NaHCO_3$ (10 mL) and brine (10 mL), dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/6, ethyl acetate/petroleum ether) to provide compounds **4**.



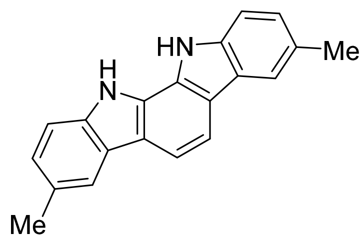
4aa

11,12-Dihydroindolo[2,3-*a*]carbazole (4aa). A yellow solid, 0.051 g, 66% yield. Mp: 280−281 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.07 (s, 2H), 8.16 (d, J = 7.6 Hz, 2H), 7.91−7.88 (m, 2H), 7.72 (d, J = 8.0 Hz, 2H), 7.41−7.38 (m, 2H), 7.23−7.19 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.5, 126.1, 125.0, 124.3, 120.6, 120.2, 119.4, 112.1. IR (thin film) 3067, 2963, 1656, 1451, 1329, 1262, 1098, 803 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{13}N_2$ $(M+H)^+$ 257.1073, found 257.1077.



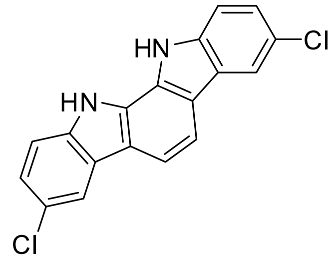
4bb

3,8-Dimethoxy-11,12-dihydroindolo[2,3-*a*]carbazole (4bb). A yellow solid, 0.028 g, 30% yield. mp: 284−285 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.82 (s, 2H), 7.84 (s, 2H), 7.69−7.68 (m, 2H), 7.59 (d, J = 8.8 Hz, 2H), 7.03−7.00 (m, 2H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.8, 134.3, 126.9, 124.7, 120.4, 114.2, 112.7, 111.8, 102.8, 56.1; IR (thin film) 3042, 2923, 1607, 1412,30 1384, 1284, 1021, 744 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{15}N_2O_2$ $(M-H)^-$ 315.1139, found 315.1135.



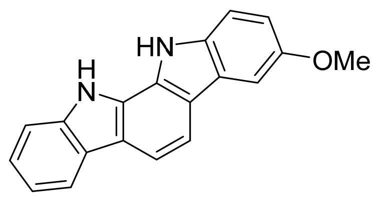
4cc

3,8-Dimethyl-11,12-dihydroindolo[2,3-*a*]carbazole (4cc). A yellow solid, 0.060 g, 70% yield. mp>300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.87 (s, 2H), 7.92 (s, 2H), 7.82 (s, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 2.50 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 137.7, 127.9, 126.4, 126.2, 124.4, 120.2, 119.9, 111.8, 111.7, 21.7; IR (thin film) 3046, 2926, 1607, 1412, 1384, 1282, 1023, 727 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{17}N_2$ $(M+H)^+$ 285.1386, found 285.1394.



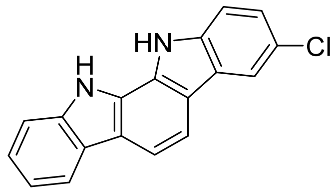
4dd

3,8-Dichloro-11,12-dihydroindolo[2,3-*a*]carbazole (4dd). A yellow solid, 0.062 g, 64% yield. mp: 302−303 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 11.39 (s, 2H), 8.28−8.24 (m, 2H), 7.96 (s, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 137.9, 126.8, 125.4, 124.9, 123.9, 120.2, 119.8, 113.6, 112.8; IR (thin film) 3043, 2924, 1607, 1466, 1384, 1279, 1094, 728 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_9Cl_2N_2$ $(M-H)^-$ 323.0148, found 323.0145.



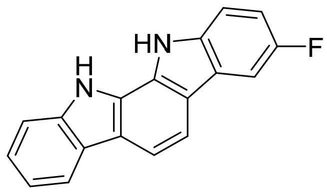
4ab

3-Methoxy-11,12-dihydroindolo[2,3-*a*]carbazole (4ab). Using **2a** (0.45 mmol, 1.5 equiv.) and **2b** (0.45 mmol, 1.5 equiv.). A yellow solid, 0.045 g, 53% yield. mp: 282−283 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.06 (s, 1H), 10.84 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.91−7.85 (m, 2H), 7.72−7.67 (m, 2H), 7.62 (d, J = 8.8 Hz, 1H), 7.40−7.36 (m, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.05−7.02 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.8, 139.4, 134.4, 126.9, 126.2, 124.9, 124.7, 124.3, 120.7, 120.4, 120.1, 119.4, 114.3, 112.8, 112.2, 112.0, 111.7, 102.9, 56.1; IR (thin film) 3066, 2925, 1609, 1464, 1385, 1211, 1025, 744 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{13}N_2O$ $(M-H)^-$ 285.1033, found 285.1029.



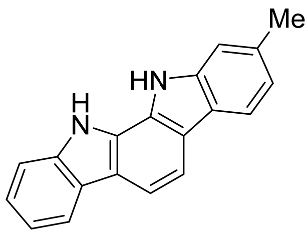
4ad

3-Chloro-11,12-dihydroindolo[2,3-*a*]carbazole (4ad). Using **2a** (0.45 mmol, 1.5 equiv.) and **2d** (0.45 mmol, 1.5 equiv.). A yellow solid, 0.047 g, 54% yield. mp>300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.22 (s, 1H), 11.13 (s, 1H), 8.27−8.23 (m, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.96−7.93 (m, 2H), 7.73−7.69 (m, 2H), 7.42−7.38 (m, 2H), 7.23−7.19 (m,1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.5, 137.9, 127.0, 125.9, 125.6, 125.2, 124.7, 124.1, 123.8, 121.1, 120.3, 119.8, 119.7, 119.5, 113.5, 112.5, 112.3, 112.1; IR (thin film) 3060, 2955, 1644, 1425, 1384, 1223, 1026, 618 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{12}ClN_2$ $(M+H)^+$ 291.0684, found 291.0661.



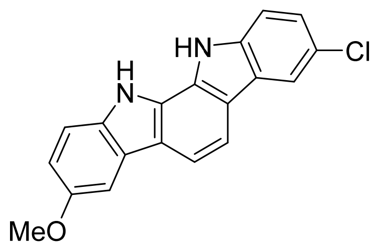
4af

3-Fluoro-11,12-dihydroindolo[2,3-*a*]carbazole (4af). Using **2a** (0.45 mmol, 1.5 equiv.) and **2f** (0.45 mmol, 1.5 equiv.). A yellow solid, 0.053 g, 64% yield. mp: 288−289 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.13 (s, 1H), 11.10 (s, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.92−7.89 (m, 2H), 7.70−7.68 (m, 2H), 7.41−7.38 (m, 1H), 7.26−7.19 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.4 (d, J = 231 Hz), 139.5, 136.0, 127.4, 126.0, 125.1, 124.8 (d, J = 10.2 Hz), 124.2, 120.9, 120.4 (d, J = 4.3 Hz), 120.2, 119.4, 113.0, 112.9, 112.7 (d, J = 25.6 Hz), 112.4, 112.1, 105.7(d, J = 23 Hz); ^{19}F NMR (100 MHz, $CDCl_3$): δ −124.6; IR (thin film) 3055, 2926, 1608, 1464, 1384, 1283, 1023, 744 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{10}FN_2$ $(M-H)^-$ 273.0833, found 273.0827.



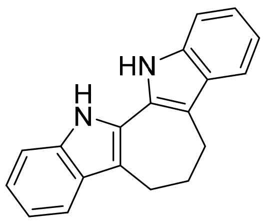
4ah (1:1)

2-Methyl-11,12-dihydroindolo[2,3-*a*]carbazole (4ah). Using **2a** (0.45 mmol, 1.5 equiv.) and **2h** (0.45 mmol, 1.5 equiv.). A yellow solid, 0.043 g, 53% yield. mp: 273−274 °C; *one isomer*: ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.10 (s, 1H), 11.00 (s, 1H), 8.14−8.11 (m, 2H), 8.01 (d, J = 7.6 Hz, 1H), 7.88−7.82 (m, 2H), 7.54−7.48 (m, 2H), 7.21−7.16 (m, 2H), 3.36 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 139.9, 139.5, 134.4, 126.2, 126.0, 125.0, 124.9, 124.2, 122.8, 121.1, 120.8, 120.2, 120.0, 119.9, 119.4, 114.2, 112.0, 111.9, 22.2; *another iosmer:* ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 11.01 (s, 1H), 11.89 (s, 1H), 7.95−7.90 (m, 2H), 7.70−7.66 (m, 2H), 7.40−7.35 (m,2H), 7.29−7.26 (m, 1H), 7.03−6.97 (m, 2H), 2.86 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 139.5, 139.4, 132.1, 126.0, 125.9, 124.9, 124.3, 124.8, 124.2, 122.1, 120.9, 120.7, 120.2, 120.0, 119.3, 112.0, 111.8, 109.7, 21.2; IR (thin film) 3058, 2925, 1607, 1455, 1384, 1284, 1023, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{13}N_2$ (M-H)$^-$ 269.1084, found 269.1061.



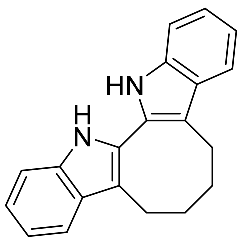
4bd

3-Chloro-8-methoxy-11,12-dihydroindolo[2,3-*a*]carbazole (4bd). Using **2b** (0.45 mmol, 1.5 equiv.) and **2d** (0.45 mmol, 1.5 equiv.). A yellow solid, 0.048 g, 50% yield. mp: 270−271 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.22 (s, 1H), 10.91 (s, 1H), 8.23 (s, 1H), 7.92−7.88 (m, 2H), 7.71−7.69 (m, 2H), 7.61 (d, J = 8.4 Hz, 1H), 7.39−7.36 (m, 1H), 7.05−7.02 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.9, 137.9, 134.4, 127.0, 126.7, 125.7, 124.6, 124.5, 123.8, 121.2, 119.7, 119.6, 114.6, 113.5, 112.9, 112.7, 111.9, 102.9, 56.1; IR (thin film) 3069, 2925, 1608, 1467, 1384, 1284, 1023, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{12}N_2O$ (M-H)$^-$ 319.0643, found 319.0639.



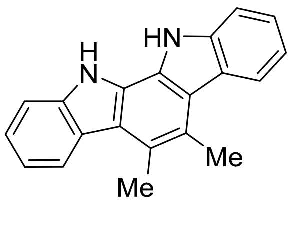
4ba

6,7,12,13-Tetrahydro-5H-cyclohepta[1,2-*b*:7,6-*b*']diindole (4ba). A yellow solid, 0.055 g, 67% yield. mp: 240−241 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.89 (s, 2H), 7.49 (d, J = 9.5 Hz, 2H), 7.42 (d, J = 10.0 Hz, 2H), 7.12−7.08 (m, 2H), 7.03−6.99 (m, 2H), 3.12−3.10 (m, 4H), 2.12−2.10 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 136.1, 129.1, 128.1, 122.0, 119.5, 118.3, 113.5, 111.3, 26.1, 23.9; IR (thin film) 3043, 2923, 1607, 1440, 1384, 1286, 1014, 742 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}N_2$ (M+H)$^+$ 273.1386, found 273.1385.



4ca

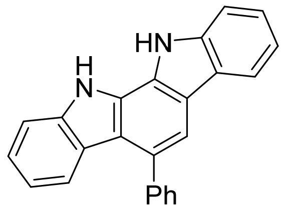
5,6,7,8,13,14-Hexahydrocycloocta[1,2-*b*:8,7-*b*']diindole (4ca). A yellow solid, 0.057 g, 66% yield. mp: 222−223 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 11.00 (m, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.13−7.10 (m, 2H), 7.04−7.00 (m, 2H), 2.98−0.90 (m, 4H), 1.83−1.80 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 139.9, 128.9, 128.2, 122.0, 119.2, 118.5, 113.4, 111.6, 26.8, 22.8; IR (thin film) 3056, 2924, 1606, 1465, 1384, 1282, 1042, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{19}N_2$ (M+H)$^+$ 287.1543, found 287.1548.



4da

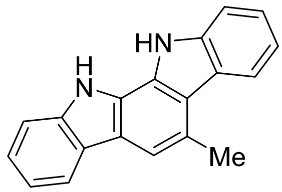
5,6-Dimethyl-11,12-dihydroindolo[2,3-*a*]carbazole (4da). A yellow solid (0.045 g, 53%). Mp: 291−292 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.03 (s, 2H), 8.28 (d, J =

7.6 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.41−7.37 (m, 2H), 7.23−7.19 (m, 2H), 2.90 (m, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 139.7, 124.7, 124.4, 124.3, 122.3, 121.3, 119.6, 119.2, 111.8, 16.4; IR (thin film) 3048, 2923, 1608, 1453, 1384, 1256, 1019, 741 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{20}H_{17}N_2$ $(M+H)^+$ 258.1386, found 285.1357.



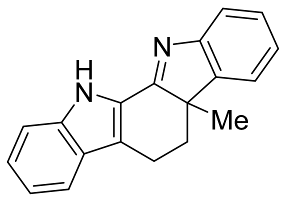
4fa

5-Phenyl-11,12-dihydroindolo[2,3-*a*]carbazole (4fa). A yellow solid, 0.068 g, 68% yield. mp: 288−289 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 11.29 (s, 1H), 11.09 (s, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 7.75−7.65 (m, 5H), 7.60−7.56 (m, 2H), 7.52−7.49 (m, 1H), 7.42 −7.31 (m, 3H), 7.22−7.18 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 142.4, 139.8, 139.7, 130.0, 129.3, 128.9, 127.6, 126.3, 125.5, 125.3, 124.8, 124.2, 123.8, 121.5, 120.5, 120.4, 119.5, 119.0, 118.0, 113.3, 112.2, 112.1; IR (thin film) 3055, 2925, 1608, 1450, 1383, 1210, 1026, 746 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{24}H_{15}N_2$ $(M-H)^-$ 331.1241, found 331.1260.



4ga

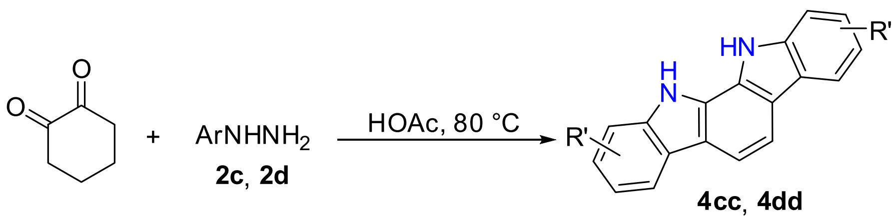
5-Methyl-11,12-dihydroindolo[2,3-*a*]carbazole (4ga). A yellow solid, 0.051 g, 63% yield. mp: 268−269 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 11.19 (s, 1H), 10.96 (s, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.73−7.68 (m, 3H), 7.43−7.36 (m, 2H), 7.25−7.17 (m, 2H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$): δ 139.7, 139.6, 126.1, 125.0, 124.9, 124.8, 124.6, 124.1, 122.1, 120.5, 120.2, 119.6, 119.4, 119.3, 112.6, 112.1, 111.9, 21.5; IR (thin film) 3048, 2923, 1608, 1455, 1384, 1283, 1019, 742 cm$^{-1;}$ HRMS (ESI) *m/z* calcd for $C_{19}H_{13}N_2$ $(M-H)^-$ 269.1084, found 269.1081.



4ja

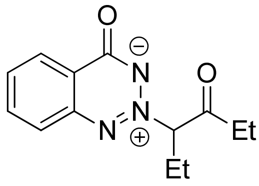
4b-Methyl-4b,5,6,11-tetrahydroindolo[2,3-*a*]carbazole (4ja). A brown solid, 0.042 g, 65% yield. mp:93−94 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.2 (s, 1H), 7.66−7.62 (m, 2H), 7.44−7.21 (m, 5H), 7.14 (t, J = 7.2 Hz, 1H), 3.26−3.18 (m, 2H), 2.64−2.59 (m, 1H), 2.04−1.99 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9, 154.9, 144.5, 138.7, 128.7, 128.1, 127.8, 126.6, 125.1, 125.0, 122.9, 121.8, 120.2, 119.9, 119.8, 112.4, 53.5, 34.4, 22.5, 19.5. IR (thin film) 3056, 2924, 1729, 1615, 1497, 1266, 1012, 744 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{19}H_{17}N_2$ $(M+H)^+$ 273.1386, found 273.1381.

5. Synthesis of compounds 4cc and 4dd from cyclohexenane-1,2-dione



General procedure D: In a 25 mL round-bottom flask was charged with cyclohexane-1,2-dione (56 mg, 0.5 mmol) and $ArNHNH_2$ (**2c** or **2d**, 1.5 mmol, 3.0 equiv.) under air. HOAc (5 mL) was added to the reaction mixture. The reaction mixture was then heated to 80 °C for 24 h. After the completion of the reaction, then the reaction was quenched with H_2O (10 mL). The reaction mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with $NaHCO_3$ (2 × 10 mL), brine (10 mL), dried over Na_2SO_4 and filtered. Evaporation of the solvent under the reduced pressure afforded the crude product. Purification by silica gel chromatography (petroleum ether/ethyl acetate, V:V = 1:6) afforded compound **4cc** (20 mg, 14% yield) or **4dd** (58 mg, 36%).

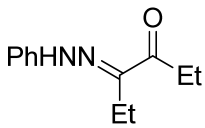
6. Synthesis of α-nitrogenated ketone 5h and hydrazone 6



5h

In a 25 mL reaction flask was charged with alkenylboronic acid **1h** (0.9 mmol, 3.0 equiv.), HOOBT (0.3 mmol), $Cu(OAc)_2$ (5.4 mg, 20 mol%), and Na_2SO_4 (400 mg) under an air atmosphere. MeCN (3.0 mL) and pyridine (72 uL, 0.9 mmol, 3.0 equiv) were then added. The reaction mixture was stirred vigorously at room temperature for 18−24 h until HOOBT disappeared (monitored by TLC). At this time, the reaction was quenched by H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). Then, the combined organic layers were dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, 1/6 to 2/1, ethyl acetate/petroleum ether) to provide α-nitrogenated ketones **5h**.

4-Oxo-2-(4-oxohexan-3-yl)-4H-benzo[d][1,2,3]triazin-2-ium-3-ide (5h). A light yellow solid, 0.065 g, 87%. mp: 95−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, J = 7.6 Hz, 1H), 7.94−7.86 (m, 3H), 5.27 (dd, J = 10.8 Hz, 4.8 Hz, 1H), 2.58−2.48 (m, 3H), 2.43−2.36 (m, 1H), 1.10 (t, J = 7.2 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 167.6, 146.2, 134.6, 133.9, 126.6, 125.6, 118.0, 87.7, 32.6, 23.7, 10.3, 7.3; IR (thin film) 3059, 2936, 1723, 1646, 1458, 1240, 1110, 778 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{13}H_{16}N_3O_2$ $(M+H)^+$ 246.1237, found 246.1233.



6

In a 25 mL flask was charged with compound **5h** (0.073 g, 0.3 mmol), phenylhydrazine **2a** (0.36 mmol, 1.2 equiv.) and HOAc (5.0 mL). The reaction mixture was stirred vigorously at 80 °C for 4 h. At this time, the reaction was quenched by H_2O (10 mL) and extracted with DCM (3 × 10 mL). Then, the organic layers were washed by $NaHCO_3$ (10 mL), dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, 1:10, ethyl acetate/petroleum ether) to provide compound **6**.

4-(2-Phenylhydrazono)hexan-3-one (6). A brown solid, 0.030 g, 49% yield; mp: 52−53 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.35−7.31 (m, 3H), 7.22−7.20 (m, 2H), 7.01−6.97 (m,1H), 2.99 (q, J = 7.2 Hz, 2H), 2.58 (q, J = 7.6 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.0, 145.1, 143.2, 129.4, 122.0, 113.8, 29.5, 14.9, 9.6, 8.9; IR (thin film) 3069, 2973, 1694, 1642, 1450, 1242, 1108, 773 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{17}N_2$ $(M+H)^+$ 205.1335, found 205.1337.

7. Gram scale preparations of compounds 3aa and 4aa

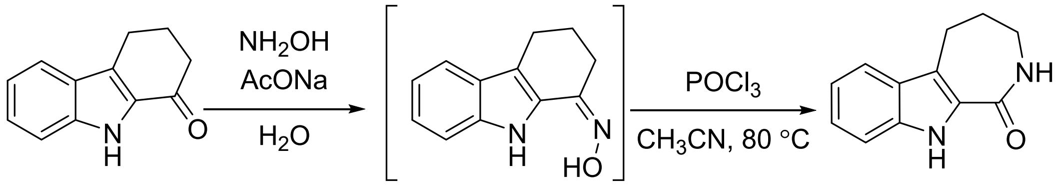
Procedure for preparing 3aa: In a 250 mL round-bottom flask was charged with alkenylboronic acid **1a** (3.0 g, 24 mmol, 3.0 equiv.), HOOBT (1.3 g, 8 mmol), $Cu(OAc)_2$ (288 mg, 20 mol%), and Na_2SO_4 (10 g) under an air atmosphere. MeCN (80 mL) and pyridine (1.92 mL, 24 mmol, 3.0 equiv.) were then added. The reaction mixture was stirred vigorously at room temperature for 24 h until HOOBT disappeared (monitored by TLC). Then, phenylhydrazine **2a** (1.0 g, 9.6 mmol, 1.2 equiv.) and HOAc (80 mL) were added to the reaction mixture and then stirred at 80 ˚C for 24 h. At this time, the reaction was poured into H_2O (100 mL) and extracted with EtOAc (3 × 60 mL). Then, the combined organic layers were washed by $NaHCO_3$ (2 ×50 mL) and brine (50 mL), dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/6, ethyl acetate/petroleum ether) to provide compound **3aa** as a yield solid (1.11 g, 75% yield).

Altermatively, after revmoval of the solvent the crude product was purified by recrystallized by EtOH twice to provide **3aa** as a yellow solid (1.05 g, 71% yield).

Procedure for preparing 4aa: In a 250 mL round-bottom flask was charged with alkenylboronic acid **1a** (3.0 g, 24 mmol, 3.0 equiv.), HOOBT (1.3 g, 8 mmol), $Cu(OAc)_2$ (288 mg, 20 mol%), and Na_2SO_4 (10 g) under an air atmosphere. MeCN (80 mL) and pyridine (1.92 mL, 24 mmol, 3.0 equiv.) were then added. The reaction mixture was stirred vigorously at room temperature for 24 h until HOOBT disappeared (monitored by TLC). Then, phenylhydrazine **2a** (2.5 g, 24 mmol, 3.0 equiv.) and HOAc (80 mL) were added to the reaction mixture and then stirred at 80 ˚C for 36 h. At this time, the reaction was poured into H_2O (100 mL) and extracted with EtOAc (3 × 60 mL). Then, the combined organic layers were washed by $NaHCO_3$ (2 ×50 mL) and brine (50 mL), dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/6, ethyl acetate/petroleum ether) to provide compound **4aa** as a brown solid (1.25 g, 61% yield).

Altermatively, after revmoval of the solvent the crude product was purified by recrystallized by EtOH twice to provide **4aa** as a yellow solid (1.33 g, 65% yield).

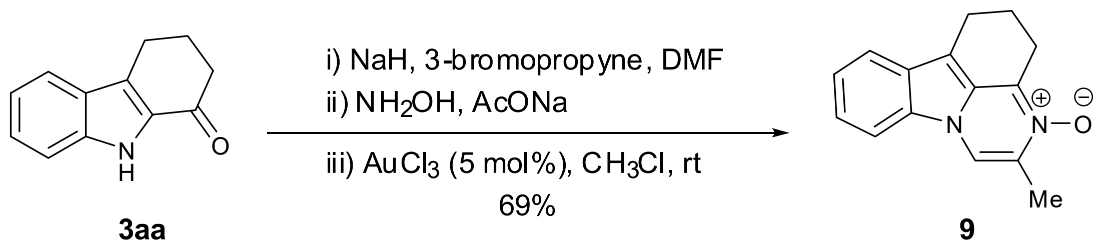
8. Synthesis of indole scaffolds 8 and 11



In a 25 mL flask, indole **3aa** (93 mg, 0.5 mmol) in ethanol (5 mL) was added to the mixture of NH_2OH (2.0 equiv) and anhydrous AcONa (2.0 equiv) in H_2O (5 mL). The reaction mixture was heated to 70 °C for 24 h. After the completion of the reaction, ethanol was removed under the reduced pressure, then H_2O (10 mL) was added to the residue. The reaction mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtered. Evaporation of the solvent under the reduced pressure afforded the corresponding oxime as a brown solid, which was used directly in the next step.

A round-bottom flask was charged with the above crude oxime. Then, a solution of $POCl_3$ in MeCN (0.4 mol/L) was added to the reaction mixture at 0 °C and heated to reflux until the oxime intermediate was completely disappeared (monitored by TLC). At this time, the reaction mixture was poured into cool saturated aqueous $NaHCO_3$ (10 mL). The organic layer was separated and the water phase was extracted with EtOAc (10 mL × 2). The combined organic layers were washed with brine (10 mL × 1), dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by silica gel chromatography (petroleum ether/ethyl acetate, V:V = 1:2) afforded product **8**.

2,3,4,5-Tetrahydroazepino[3,4-*b*]indol-1(10H)-one (8). A white solid, 0.063 g, 63% yield; mp: 225−226 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.41−7.26 (m, 2H), 7.16−7.12 (m, 1H), 6.10 (s,1H), 3.52−3.49 (m, 2H), 3.17−3.14 (m, 2H), 2.25−2.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4, 135.8, 128.1, 126.3, 125.2, 120.3, 119.8, 118.9, 111.7, 45.0, 26.7, 25.8; IR (thin film) 3050, 2923, 1631, 1546, 1479, 1333, 1154, 741 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{12}H_{13}N_2$ $(M+H)^+$ 201.1022, found 201.1017.

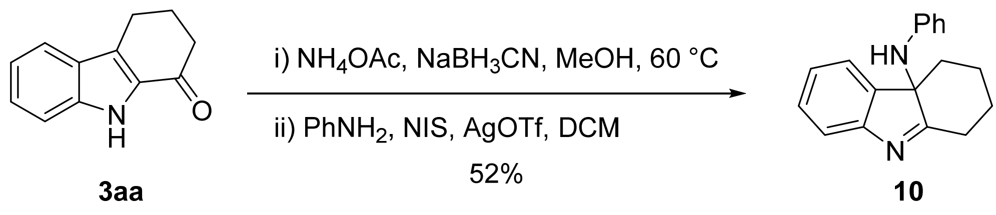


To a solution of indole **3aa** (93 mg, 0.5 mmol) in DMF (5 mL), NaH (0.75 mol) was added slowly at 0 °C. After the completion of addition, the reaction mixture was stirred for 30 min and then 3-brompropyne (0.75 mmol) was carefully added dropwise to the solution. The reaction mixture was stirred for 4 h at room temperature. The reaction was quenched by H_2O (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtered. Evaporation of the solvent under the reduced pressure afforded the crude alkynylindole as a yellow solid, which was used directly in the next step.

In a 25 mL sealed-flask, a solution of the above alkynylindole in ethanol (5 mL) was added to NH_2OH (2.0 equiv.) and AcONa (2.0 equiv.) in H_2O (5 mL). The reaction mixture was heated to 70 °C for 24 h. After the completion of the reaction, ethanol was removed under the reduced pressure, then H_2O (10 mL) was added to the residue. The mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and filtered. Evaporation of the solvent under the reduced pressure afforded the corresponding oxime as a brown solid, which was used directly in the next step.

In a 25 mL flask, the above crude oxime was dissolved in $CHCl_3$ (5 mL) and $AuCl_3$ (5 mol %) was added to the mixture. The reaction mixture was stirred at room temperature for 60 h. Then, the solvent was evaporated under the reduced pressure. Purification using medium pressure chromatography (ethyl acetate: ethanol, V:V = 8:1) afforded compound **9** as a yellow solid.

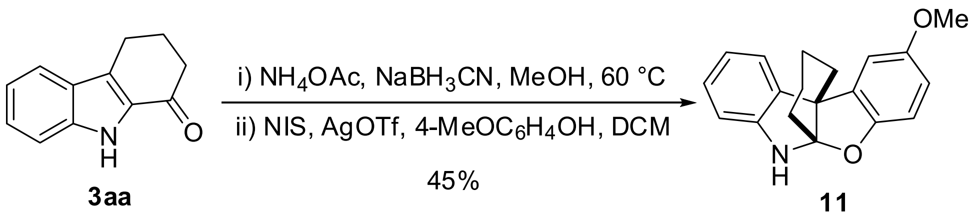
Methyl-5,6-dihydro-4H-pyrazino[3,2,1-*jk*]carbazole 3-oxide (9), a yellow solid, 0.081 g, 69% yield; mp: 197−198 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.74−7.73 (m, 2H), 7.37−7.36 (m, 2H), 3.22 (t, J = 5.2 Hz, 2H), 3.02 (t, J = 5.2 Hz, 2H), 2.47 (s, 3H), 2.24 (t, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 129.7, 129.2, 127.6, 127.3, 122.8, 122.1, 119.7, 115.2, 110.6, 107.2, 23.4, 22.2, 20.1, 14.9; IR (thin film) 3099, 2925, 1729, 154, 1449, 1291, 1983, 745 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2O$ $(M+H)^+$ 239.1179, found 239.1173.



In a 25 mL flask was charged with indole **3aa** (0.093 g, 0.5 mmol), NH_4OAc (0.385 g, 5 mmol) and MeOH (5 mL). $NaBH_3CN$ (0.158 g, 2.5 mmol) was added portions. The reaction mixture was heated at 60 °C for 10 h. Then the reaction was quenched by H_2O (10 mL), extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over with Na_2SO_4 and filtered. The solvent was removed under the reduced pressure and the crude tetrahydrocarbazole was used directely to next step.

To a solution of the above crude tetrahydrocarbazole in dichloromethane (3 mL), N-iodosuccinimide (NIS, 0.123 g, 0.55 mmol, 1.1 equiv.) was added at room temperature. The reaction mixture was stirred for 30 min. Then, the reaction was cooled down to 0 °C. Aniline (0.117 g, 1.25 mmol, 2.5 equiv.), AgOTf (0.256 g, 1.0 mmol, 2.0 equiv.), NaOH (0.040 g, 1.0 mmol, 2.0 equiv) were added. The resulting mixture was stirred for 3 h (monitored by TLC). At this time, the reaction was quenched by $NaHCO_3$ (10 mL) and extracted with DCM (3 × 10 mL). Then, dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, 1/20 to 1/6, ethyl acetate/petroleum ether) to provide product **10** as a white solid.

***N*-phenyl-1,2,3,4-tetrahydro-4aH-carbazol-4a-amine (10)**. A white solid, 0.068 g, 52% yield; mp: 196−197 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 7.2 Hz, 1H), 7.38−7.34 (m, 1H), 7.18−7.14 (m, 1H), 6.95−6.91 (m, 2H), 6.61 (d, J = 7.2 Hz, 1H), 6.06 (d, J = 8.0 Hz, 1H), 4.31 (s, 1H), 2.84−2.81 (m, 1H), 2.63−2.50 (m,2H), 2.22−2.20 (m, 1H), 2.02−1.94 (m, 1H), 1.72−1.68 (m, 1H), 1.57−1.49 (m,1H), 1.26−1.18 (m,1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.6, 153.5, 145.5, 141.6, 129.1, 128.6, 125.6, 121.7, 121.0, 118.3, 113.1, 69.9, 43.0, 29.7, 29.5, 20.9. IR (thin film) 3060, 2929, 1744, 1661, 1443, 1211, 1081, 756 cm^{-1}; HRMS (ESI) *m/z* calcd for $C_{18}H_{19}N_2$ $(M+H)^+$ 263.1543, found 263.1548.

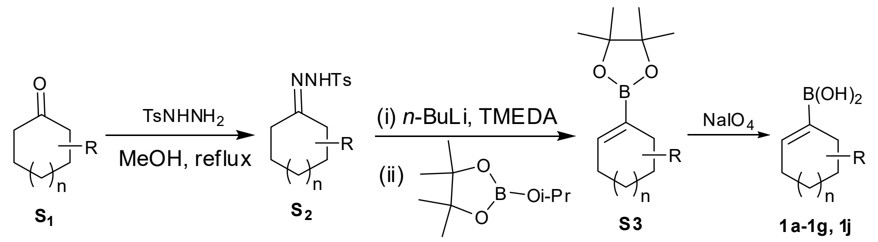


In a 25 mL flask was charged with indole **3aa** (0.093 g, 0.5 mmol), NH_4OAc (0.385 g, 5 mmol) and MeOH (5 mL). $NaBH_3CN$ (0.158 g, 2.5 mmol) was added portions. The reaction mixture was heated at 60 °C for 10 h. Then the reaction was quenched by H_2O (10 mL), extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude tetrahydrocarbazole was used directely to next step.

To a solution of crude tetrahydrocarbazole in dichloromethane (3 mL), *N*-iodosuccinimide (NIS, 0.123 g, 0.55 mmol, 1.1 equiv) was added at room temperature. The reaction mixture was stirred for 30 min. Then, the reaction was cooled down to 0 °C. 4-$MeOC_6H_4OH$ (0.155 g, 1.25 mmol, 2.5 equiv), AgOTf (0.256 g, 1.0 mmol, 2.0 equiv), NaOH (0.040 g, 1.0 mmol, 2.0 equiv) were added. The resulting mixture was stirred for 3 h monitored by TLC). At this time, the reaction was quenched by $NaHCO_3$ (10 mL) and extracted with DCM (3 × 10 mL). Then, dried over with Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (the crude residue was dry loaded with silica gel, 1/10, ethyl acetate/petroleum ether) to provide product **11.**

2-Methoxy-6*H*-5a,10b-butanobenzofuro[2,3-*b*]indole (11). A white solid, 0.066 g, 45% yield; mp: 157−158 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.07−7.03 (m, 2H), 6.93 (s, 1H), 6.78−6.69 (m, 2H), 6.64−6.59 (m, 2H), 4.74 (s, 1H), 3.78 (s, 3H), 2.42−2.39 (m,1H), 2.22−2.19 (m,1H), 1.93−1.87 (m,1H), 1.71−1.33 (m,7H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.4, 153.0, 146.6, 134.2, 133.2, 127.8, 122.8, 120.0, 112.3, 109.6, 109.5, 109.4, 56.4, 56.0, 32.4, 31.9, 20.7, 19.9. IR (thin film) 3061, 2935, 1609, 1482, 1266, 1166, 1028, 786 $cm^{-1;}$ HRMS (ESI) *m/z* calcd for $C_{19}H_{20}NO$ $(M+H)^+$ 294.1489, found 294.1479.

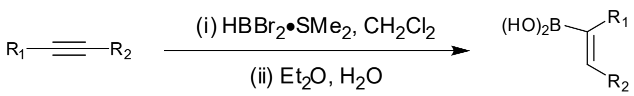
9. Synthesis of alkenylboronic acids 1a-1j



General procedure for cyclic alkenylboronic acids 1a-1g and 1j: A mixture of ketone **S1** (10 mmol) and 4-methylbenzenesulfonohydrazide (10 mmol) in hot MeOH (10 mL) were heated at 70 °C for 2 h to obtain the corresponding crude **S2** as white precipitate, which was filtered and washed with petroleum ether (5 mL × 3) and dried under vacuum to afford *N*-tosylhydrazone **S2**.

A 100 mL round bottom flask was charged with *N*-tosylhydrazone **S2** (1.0 equiv), hexanes (3 mL/mmol hydrazone), and TMEDA (3mL/mmol hydrazone). The resulting slurry was cooled to -78 ºC with a dry ice-acetone bath and a 2.5 M *n*-BuLi solution in hexane (4.0 equiv) was added *via* syringe. The reaction mixture was allowed to stir at -78 ºC for 1 h and then allowed to warm to 25 ºC. After stirring for an additional 2 h, the reaction mixture was cooled to -78 ºC again with a dry ice-acetone bath and $B(Oi\text{-}Pr)_3$ or $B(OMe)_3$ was added *via* syringe. The reaction was quenched with water (30 mL) and extracted with diethyl ether (3 × 40 mL). The combined organic layers were then washed with brine (40 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude sample product of **S3**.

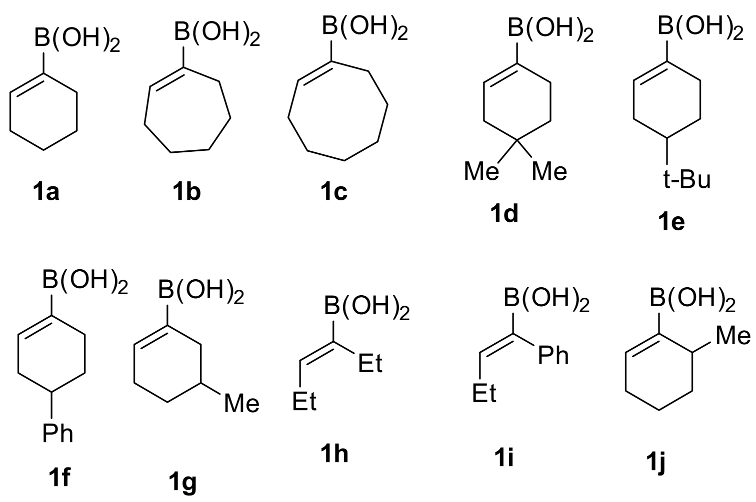
A scintillation vial was charged with alkenyl boronic acid pinacol ester **S3** (1 equiv), $NaIO_4$ (3 equiv), and NH_4OAc (3 equiv). These reagents were then diluted with a mixture of acetone and water in a 1:1 ratio to form a 0.04 M solution of the alkenyl boronic acid pinacol ester. The resulting slurry was allowed to stir vigorously for 24-48 h. The slurry was then filtered and diluted with ethyl acetate or diethyl ether. The organic layer was then washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to give pure alkenyl boronic acids **1a-1g** and **1j**.



1h-1i

General procedure for linear alkenylboronic acids 1h and 1i: A round bottom flask was charged with an alkyne (10 mmol, 1.0 equiv) under N_2 and cooled to 0 ºC with an ice-water bath. A 1M solution of $HBBr_2{\cdot}SMe_2$ in CH_2Cl_2 (12 mL, 1.2 equiv) was added slowly for 5 min and allowed to stir for 2 h. The reaction mixture was then added to 60 mL of a 10 : 1 mixture of diethyl ether and water, and then allowed to stir for 15 min. The reaction mixture was diluted with additional diethyl ether (40 mL) and H_2O (20 mL). The organic layer was separated, washed with brine (2 × 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give a crude sample of the alkenyl boronic acids **1h-1i**, which was used to next step directly without purification.

All alkenylboronic acids **1a-1j** were prepared as described in the literatures, and spectral data matched literature values.[1-2]

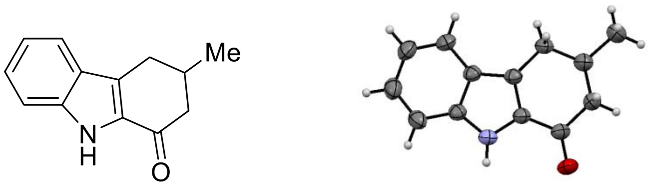


10. References

[1] C.-H. Chen, Q.-Q. Liu, X.-P. Ma, Y. Feng, C. Liang, C.-X. Pan, G.-F. Su, D.-L. Mo, *J. Org. Chem.* 2017, **82**, 6417.

[2] A. S. Patil, D.-L. Mo, H.-Y. Wang, D. S. Mueller and L. L. Anderson, *Angew. Chem. Int. Ed.* 2012, **51**, 7799.

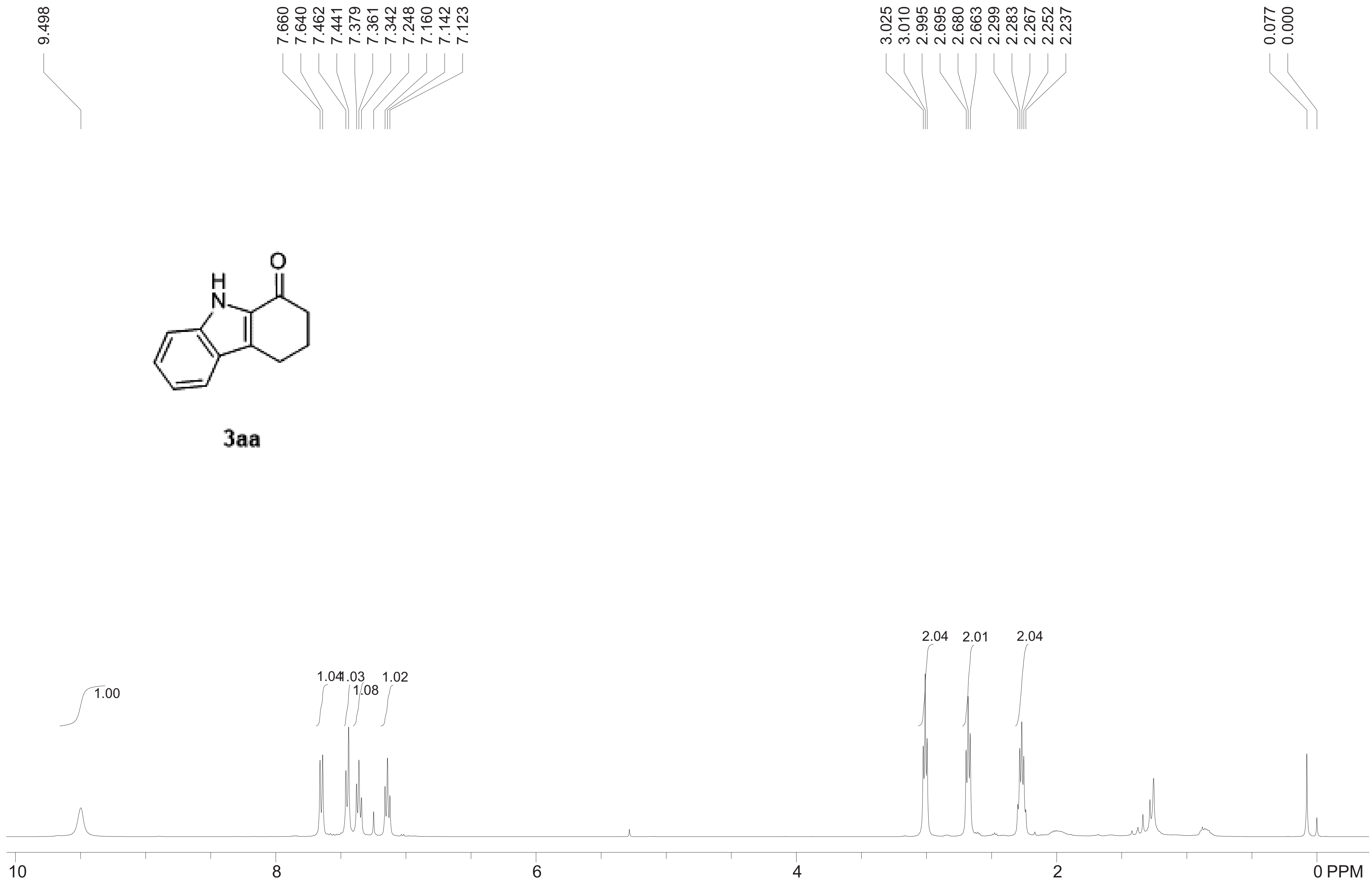
11. X-ray structures for compound 3ga



3ga

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

12. NMR spectra for compounds 3, 4, 5h, 6 and 8-11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H
N
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8
6
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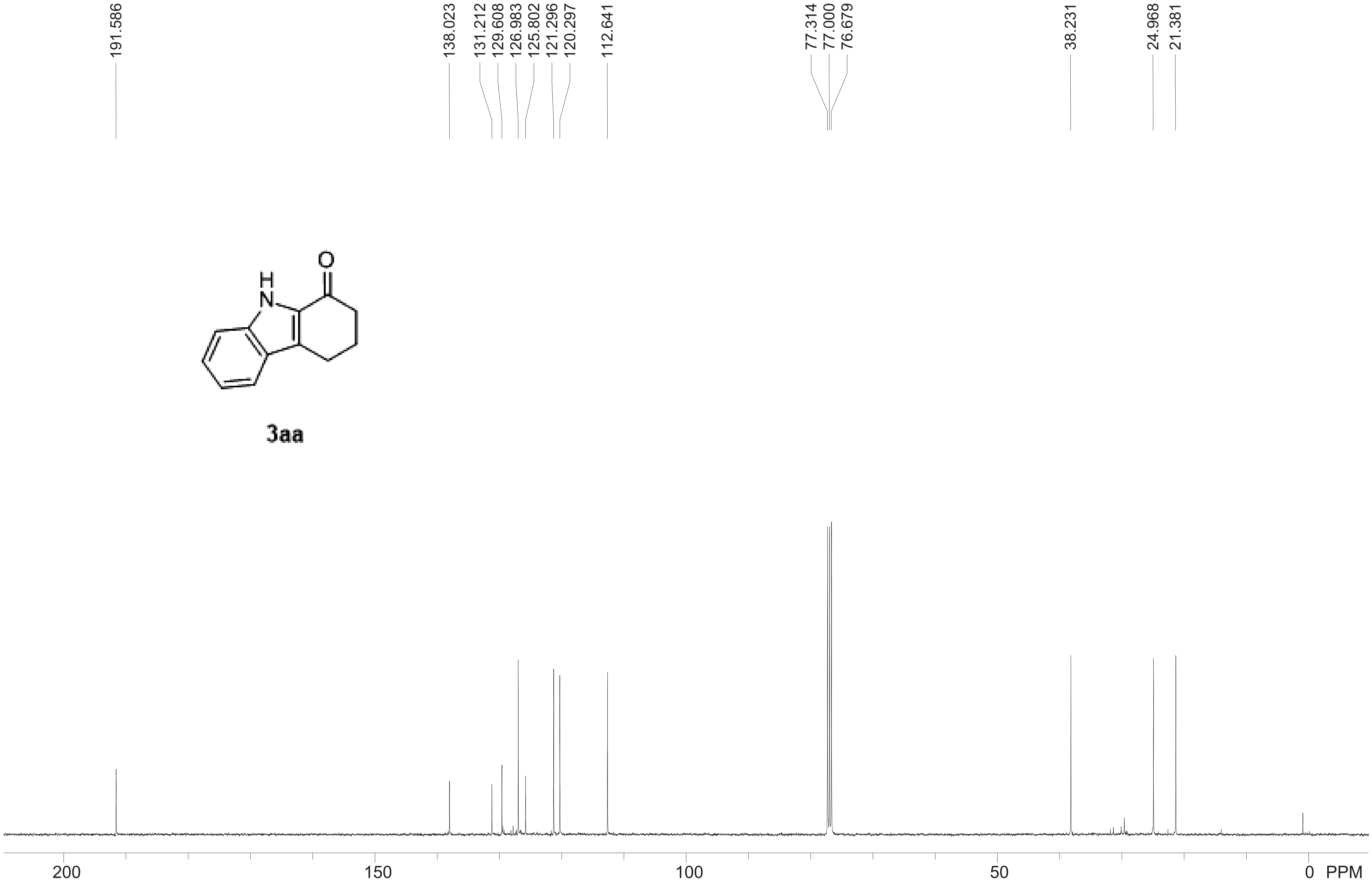

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O
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N

3aa


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7.336
7.314
7.260
7.062
7.057
7.040
7.035
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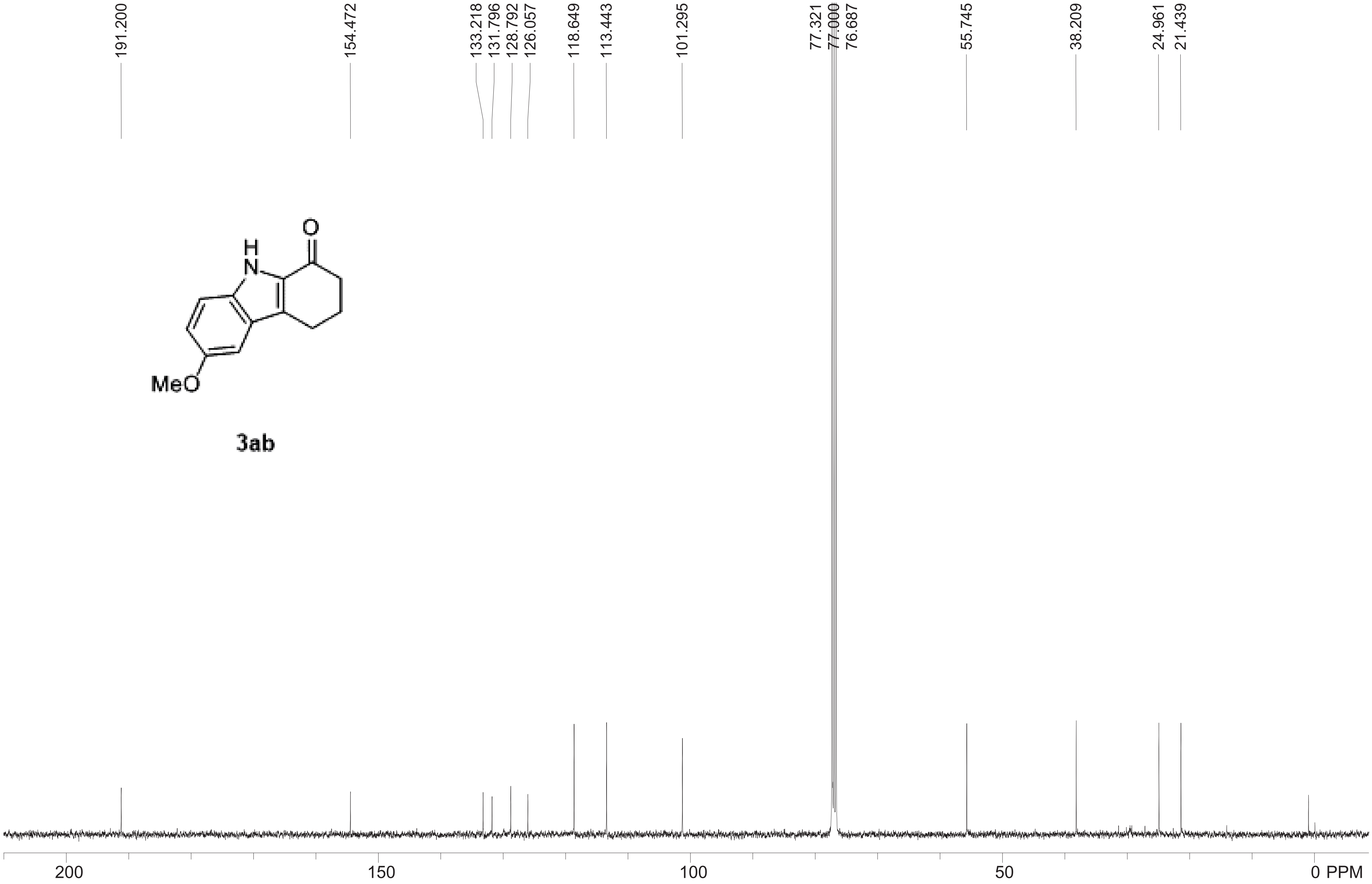
3ab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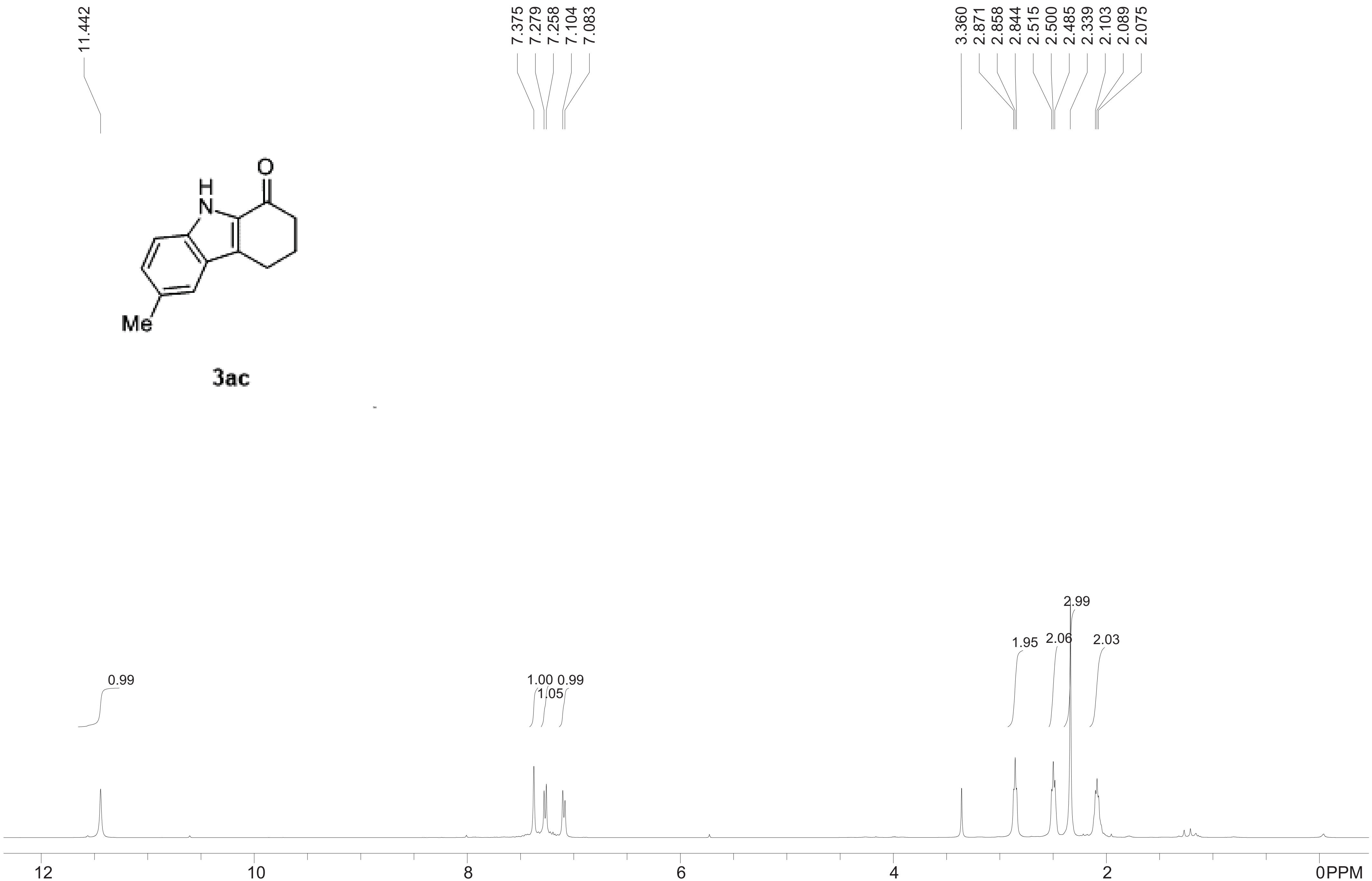

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7.375
7.279
7.258
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7.083
3.360
2.871
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2.844
2.515
2.500
2.485
2.339
2.103
2.089
2.075
H
N
O
Me
0.99
1.00
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2.06
2.99
2.03
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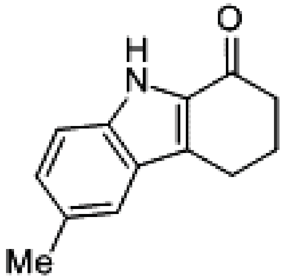
3ac



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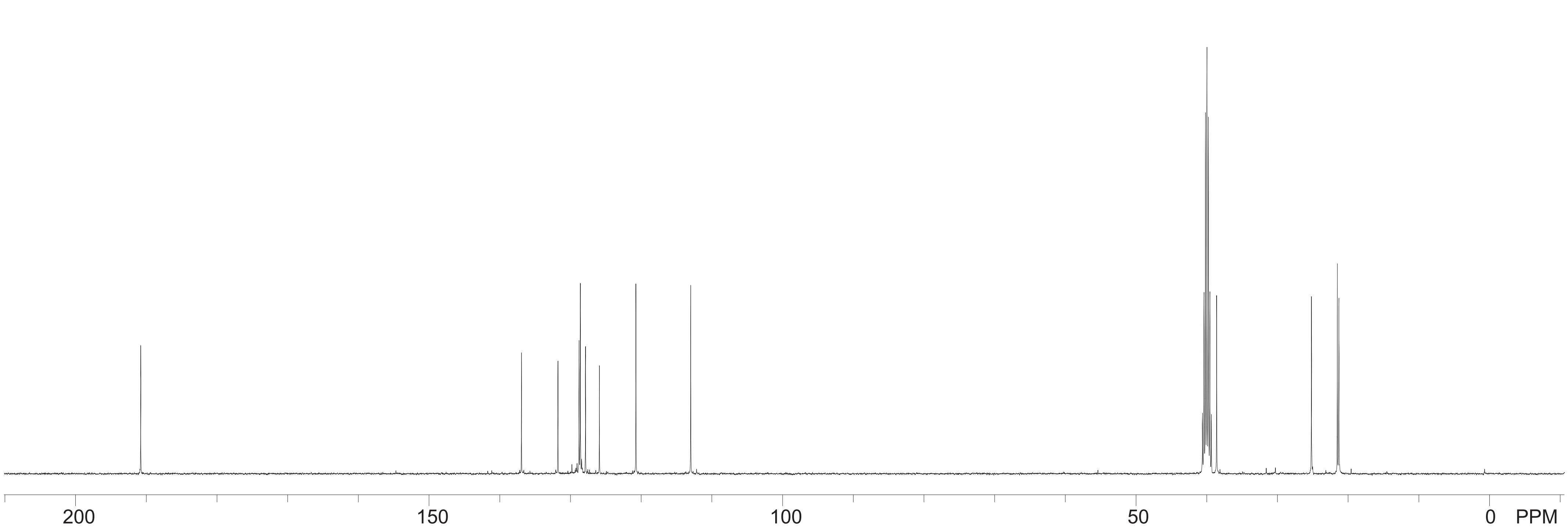

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125.916
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113.002
40.627
40.416
40.211
40.000
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39.373
38.622
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21.560
21.341
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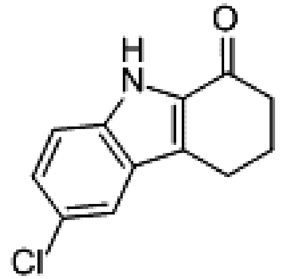
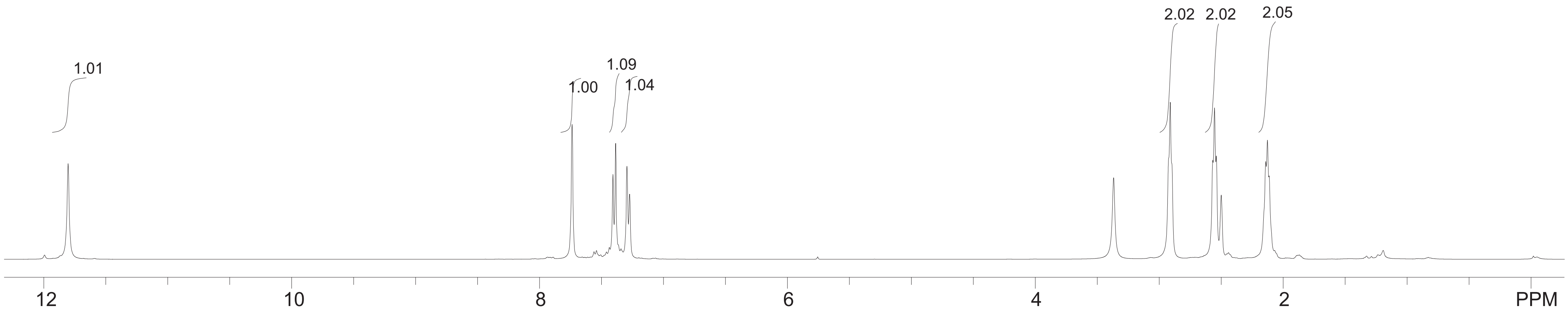
50
0
PPM



3ad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2.568
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2.128
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1.00
1.09
1.04
2.02
2.02
2.05
12
10
8
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2
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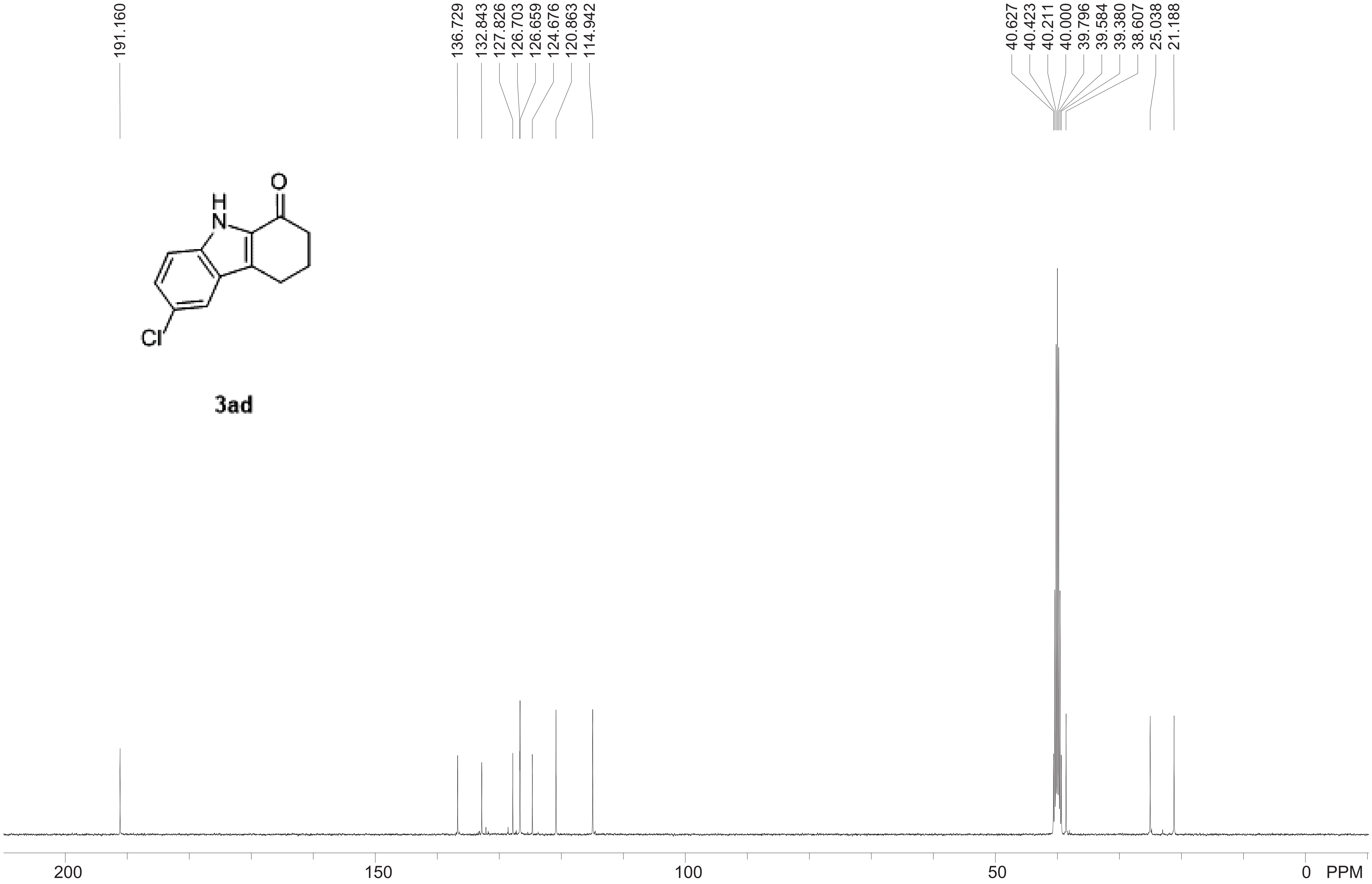
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120.863
114.942
40.627
40.423
40.211
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39.584
39.380
38.607
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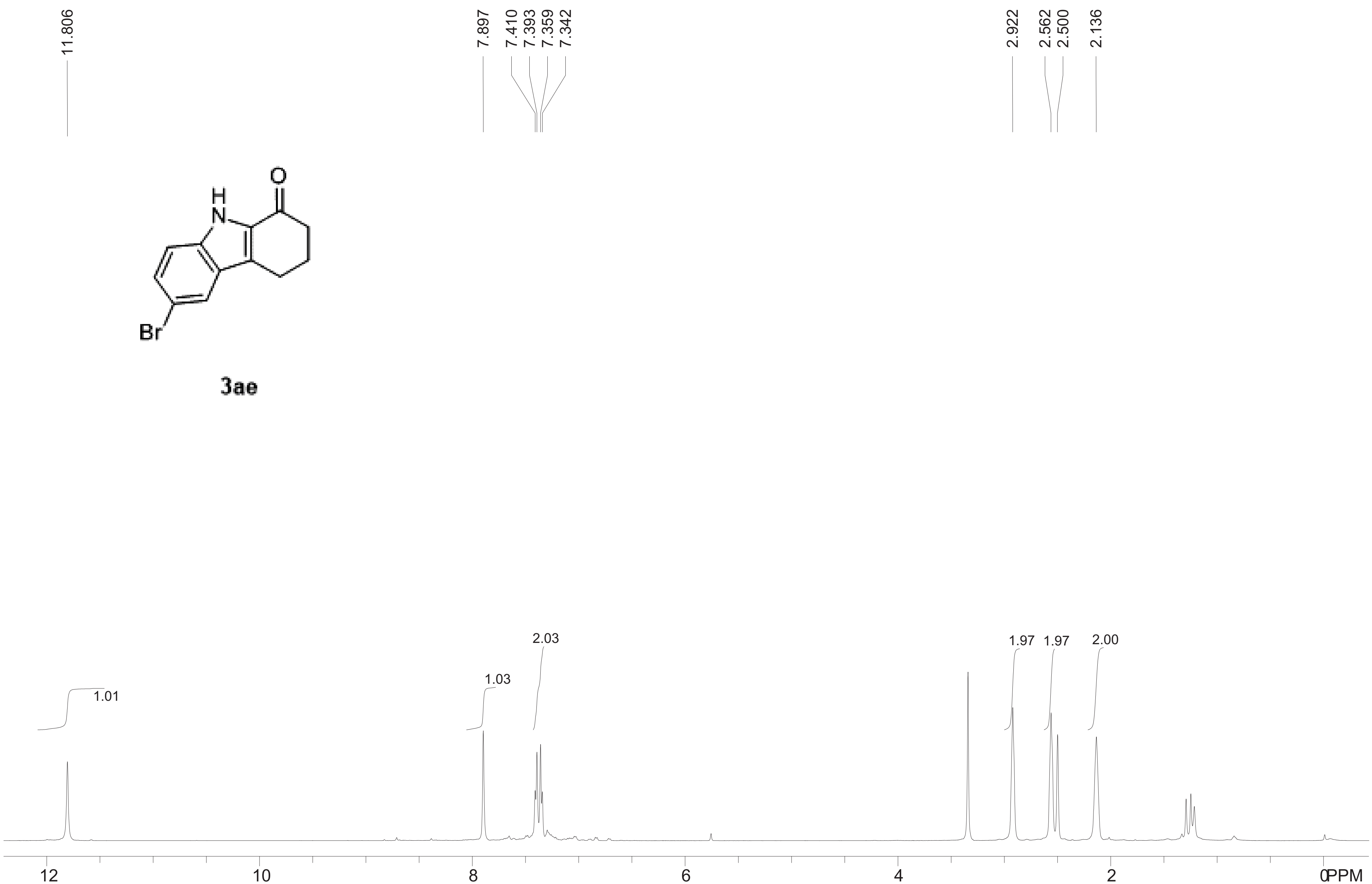
3ad
200
150
100
50
0 PPM



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7.410
7.393
7.359
7.342
2.922
2.562
2.500
2.136
H
N
O
Br
1.01
1.03
2.03
1.97
1.97
2.00
12
10
8
6
4
2
0PPM

3ae


191.116
136.903
132.618
129.091
127.706
127.415
123.968
115.317
112.504
40.496
40.423
40.335
40.255
40.168
40.000
39.832
39.665
39.497
38.579
25.009
21.154
O
H
N
Br
3ae
200
150
100
50
0 PPM


9.470
7.421
7.411
7.399
7.388
7.287
7.262
7.156
7.151
7.134
7.129
7.111
7.106
2.986
2.971
2.957
2.699
2.683
2.667
2.307
2.292
2.277
2.261
2.247
0.074
-0.000
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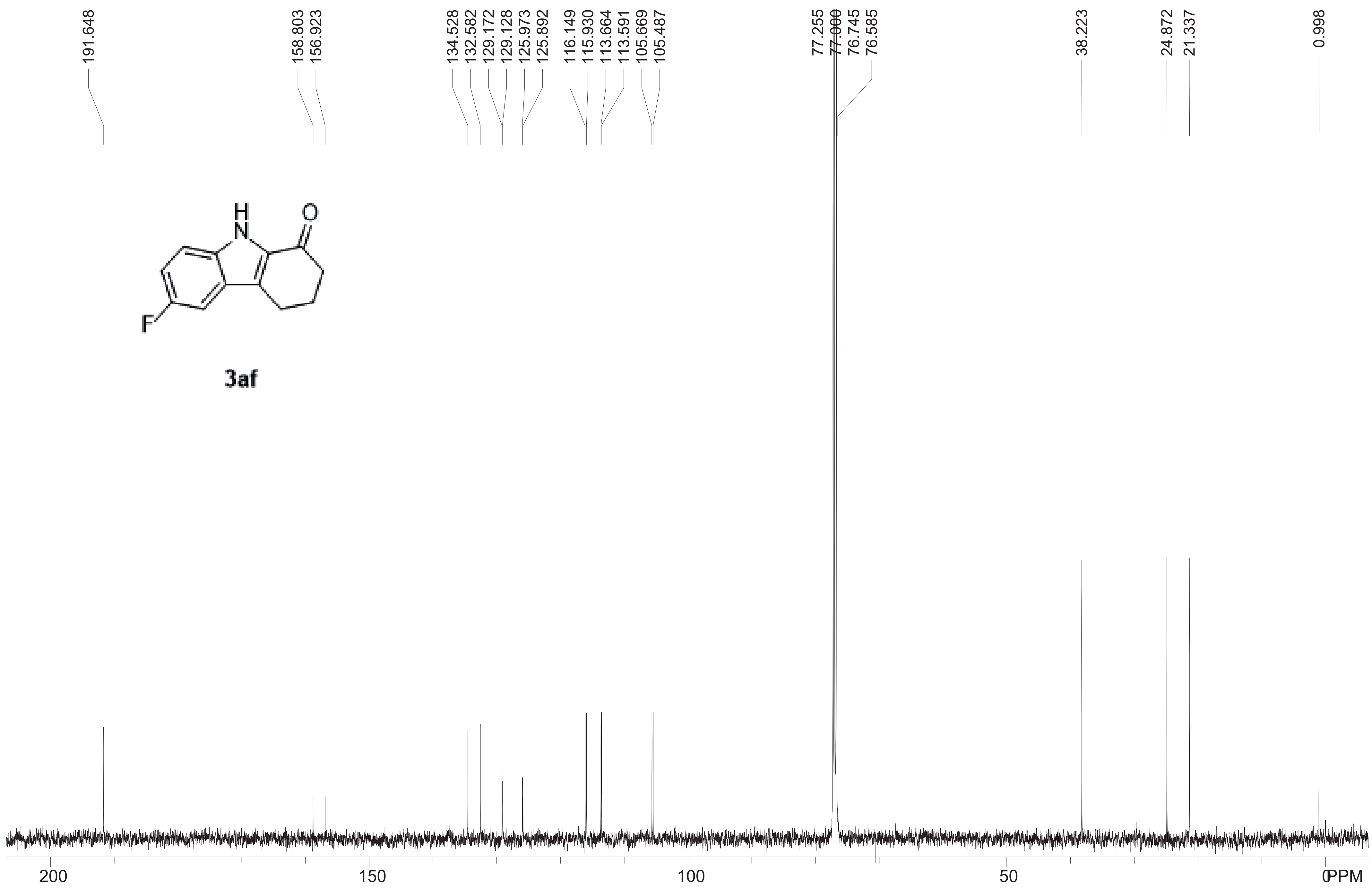
1.07
0.99
2.06
1.99
2.01
10
8
6
4
2
0 PPM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125.892
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105.669
105.487
77.255
77.000
76.745
76.585
38.223
24.872
21.337
0.998
H
N
O
F
3af
200
150
100
50
0
PPM


O
H
N
F
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-122.769
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-40
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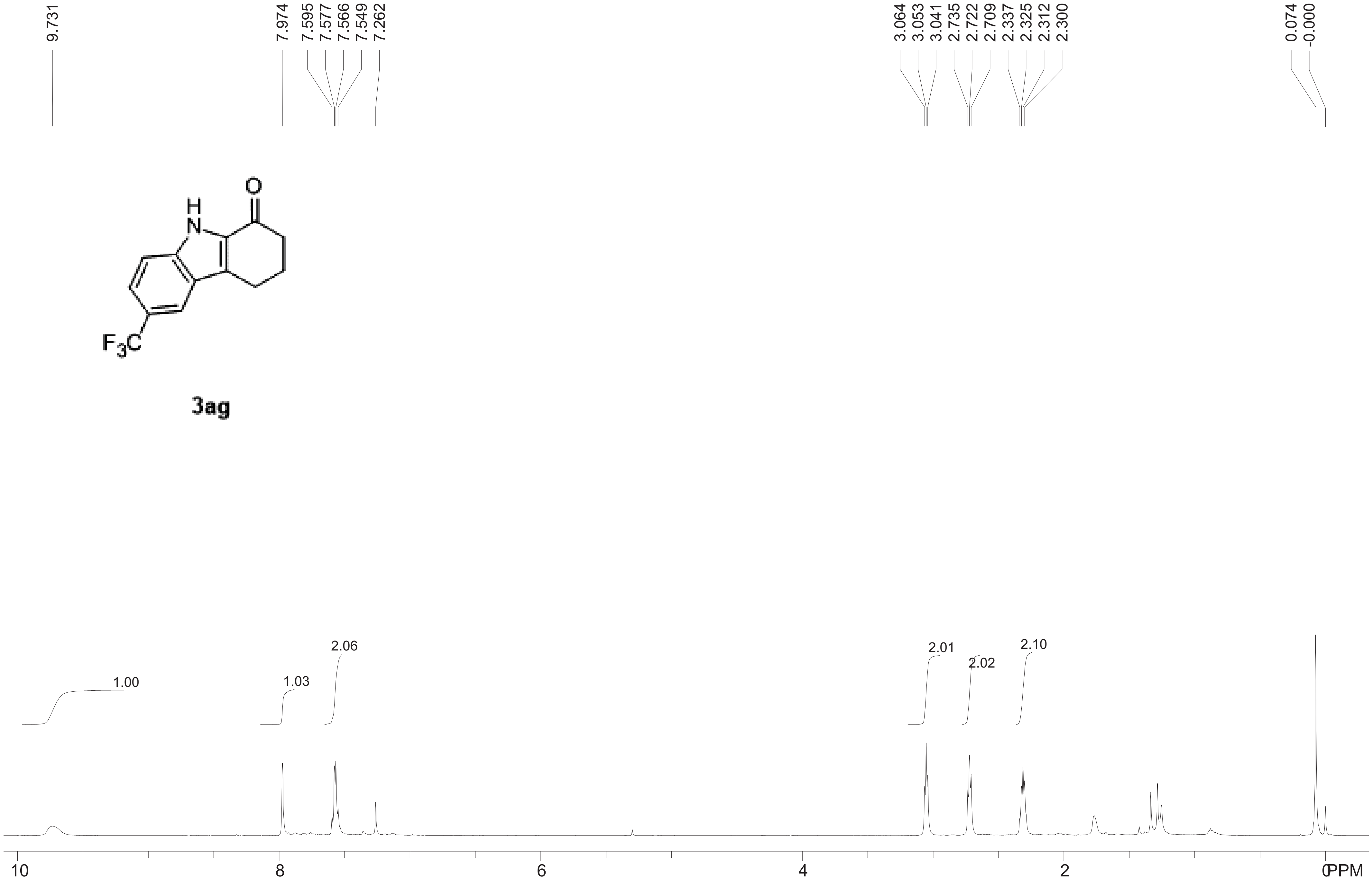
PPM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3.053
3.041
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2.722
2.709
2.337
2.325
2.312
2.300
0.074
-0.000
H
N
O
F3C
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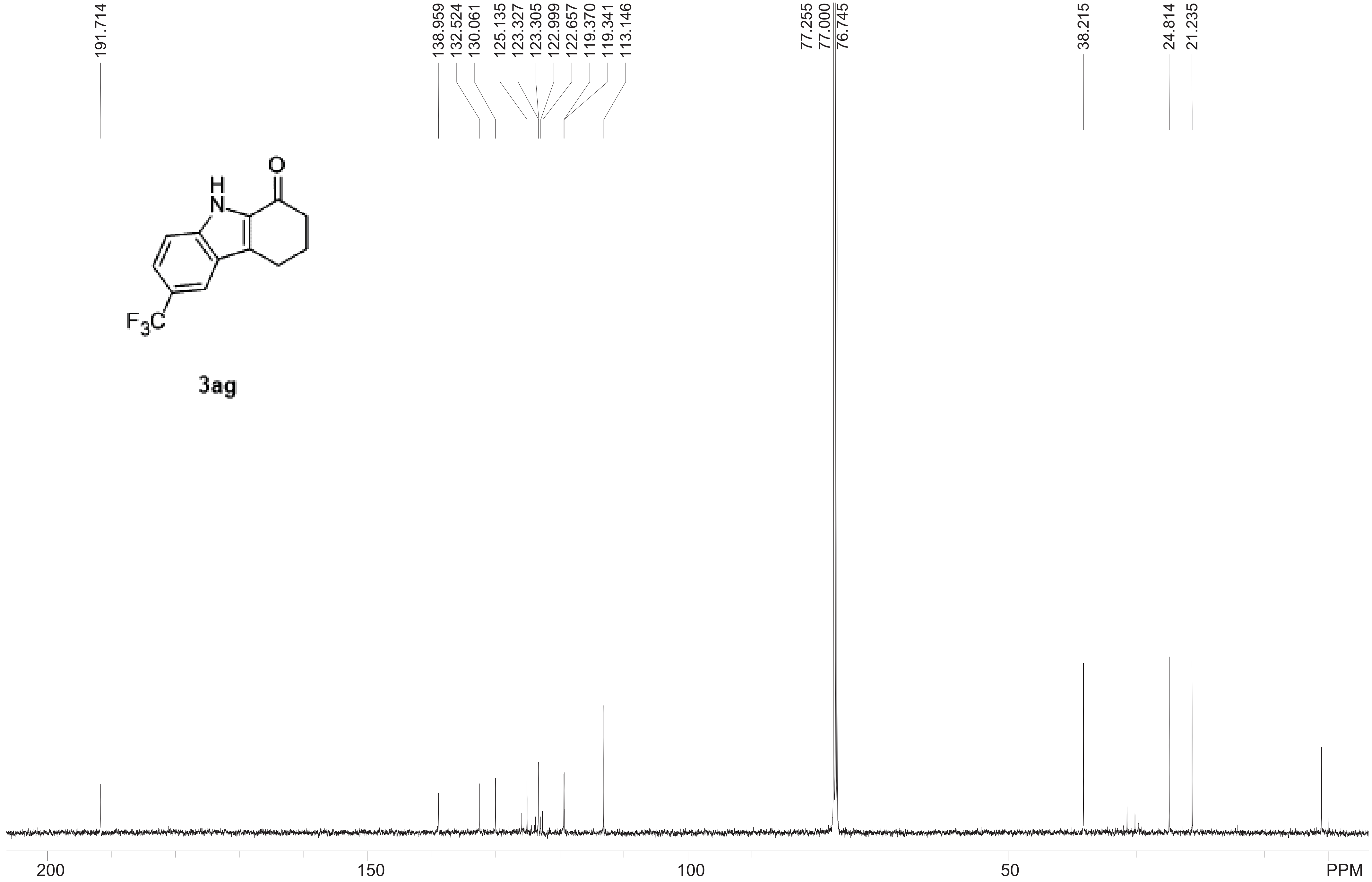
1.03
2.06
2.01
2.02
2.10
10
8
6
4
2
0
PPM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122.999
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119.370
119.341
113.146
77.255
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38.215
24.814
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H
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O
F3C
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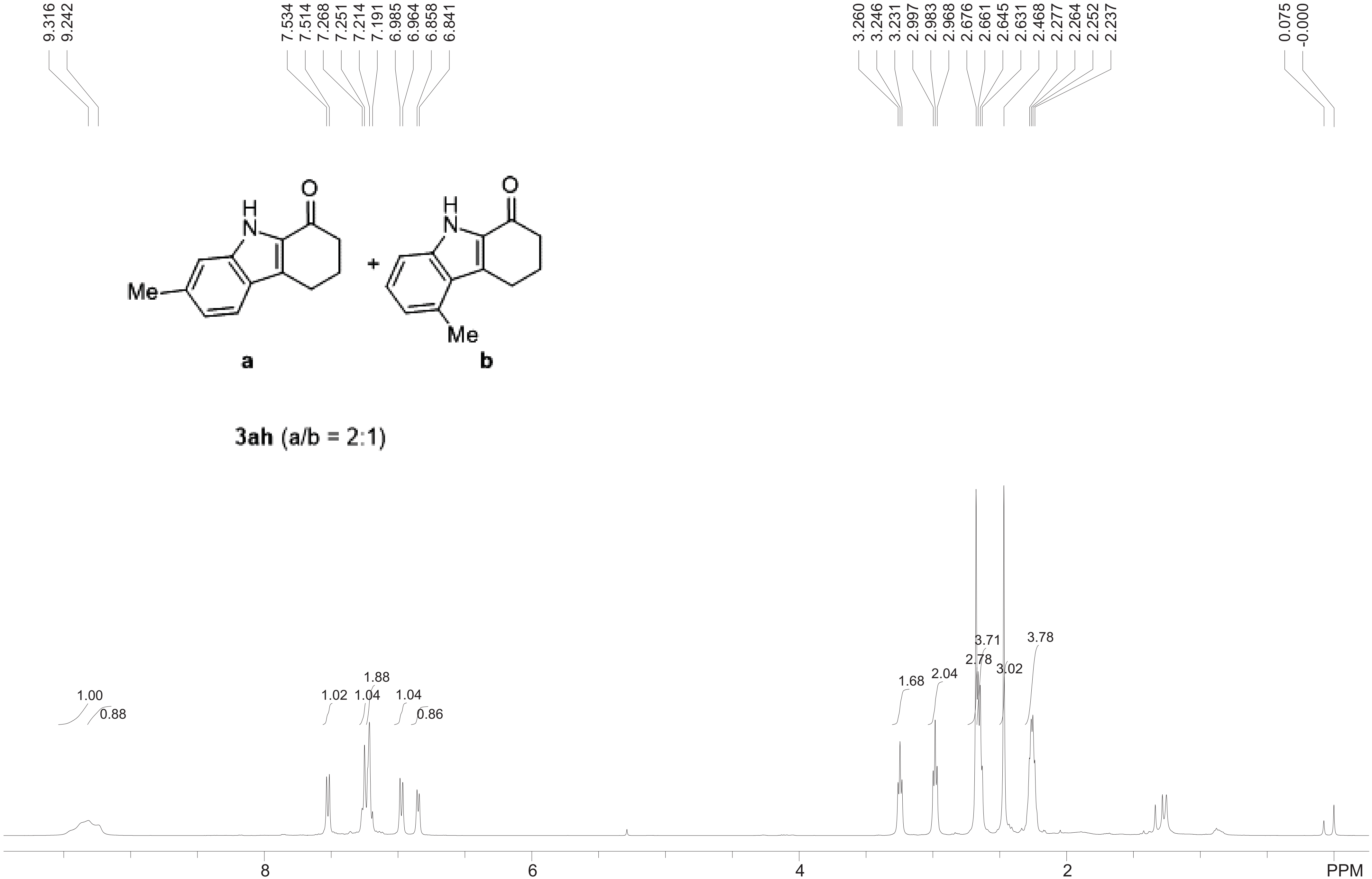
200
150
100
50
PPM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7.514
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7.251
7.214
7.191
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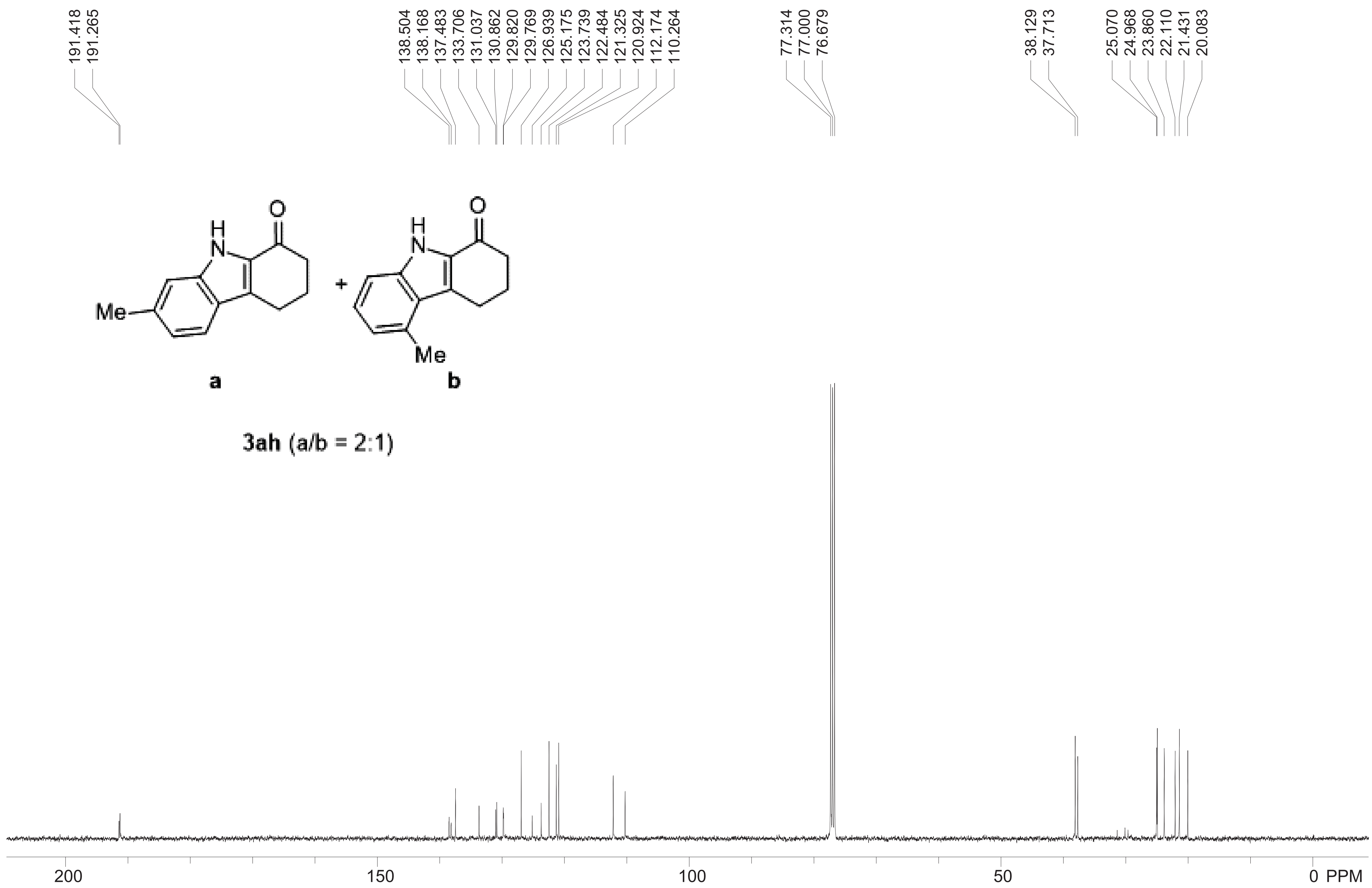
6.964
6.858
6.841
3.260
3.246
3.231
2.997
2.983
2.968
2.676
2.661
2.645
2.631
2.468
2.277
2.264
2.252
2.237
0.075
-0.000
H
N
O
Me
+
H
N
O
Me
a
b
3ah (a/b = 2:1)
1.00
0.88
1.02
1.04
1.88
1.04
0.86
1.68
2.04
2.78
3.71
3.02
3.78
8
6
4
2
PPM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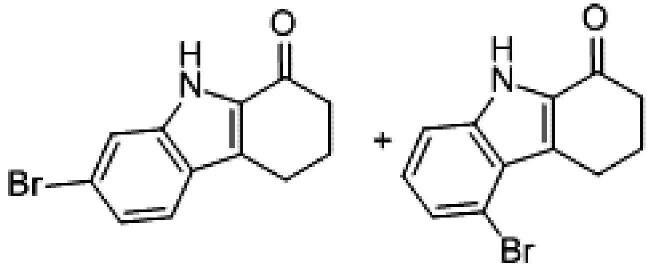
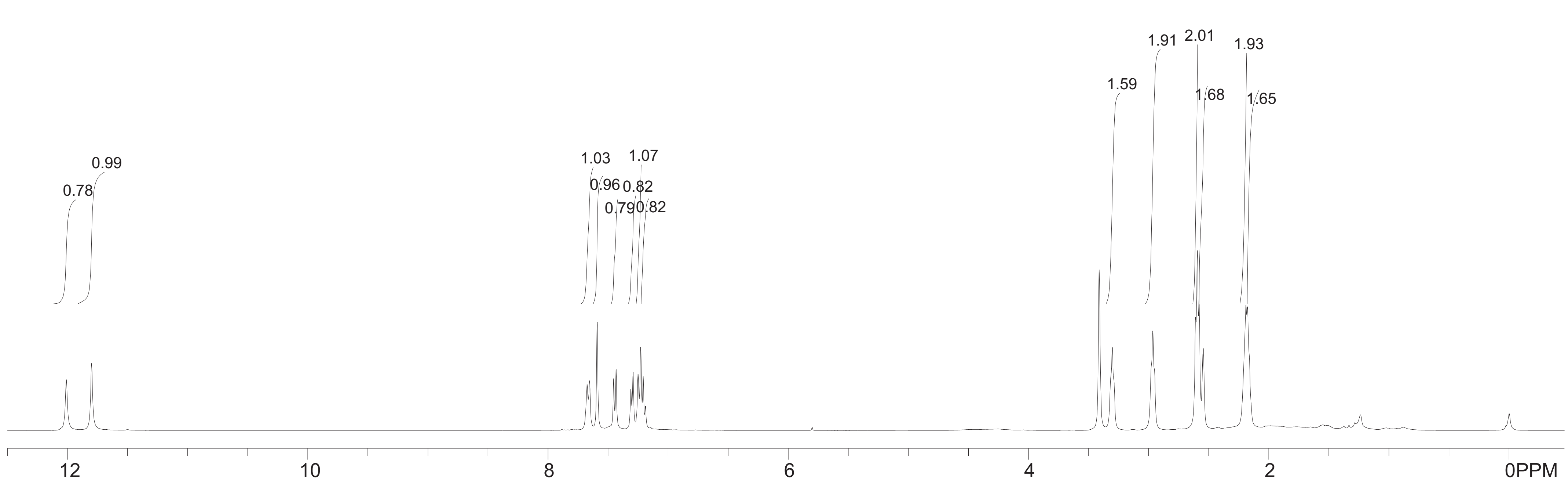
138.504
138.168
137.483
133.706
131.037
130.862
129.820
129.769
126.939
125.175
123.739
122.484
121.325
120.924
112.174
110.264
77.314
77.000
76.679
38.129
37.713
25.070
24.968
23.860
22.110
21.431
20.083
H
N
O
Me
+
a
b
3ah (a/b = 2:1)
200
150
100
50
0 PPM



a b

3ai (a/b = 1:0.8)



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7.310
7.292
7.250
7.228
7.208
7.188
3.302
2.965
2.609
2.595
2.579
2.546
2.190
2.178
-0.000
0.78
0.99
1.03
0.96
0.79
1.07
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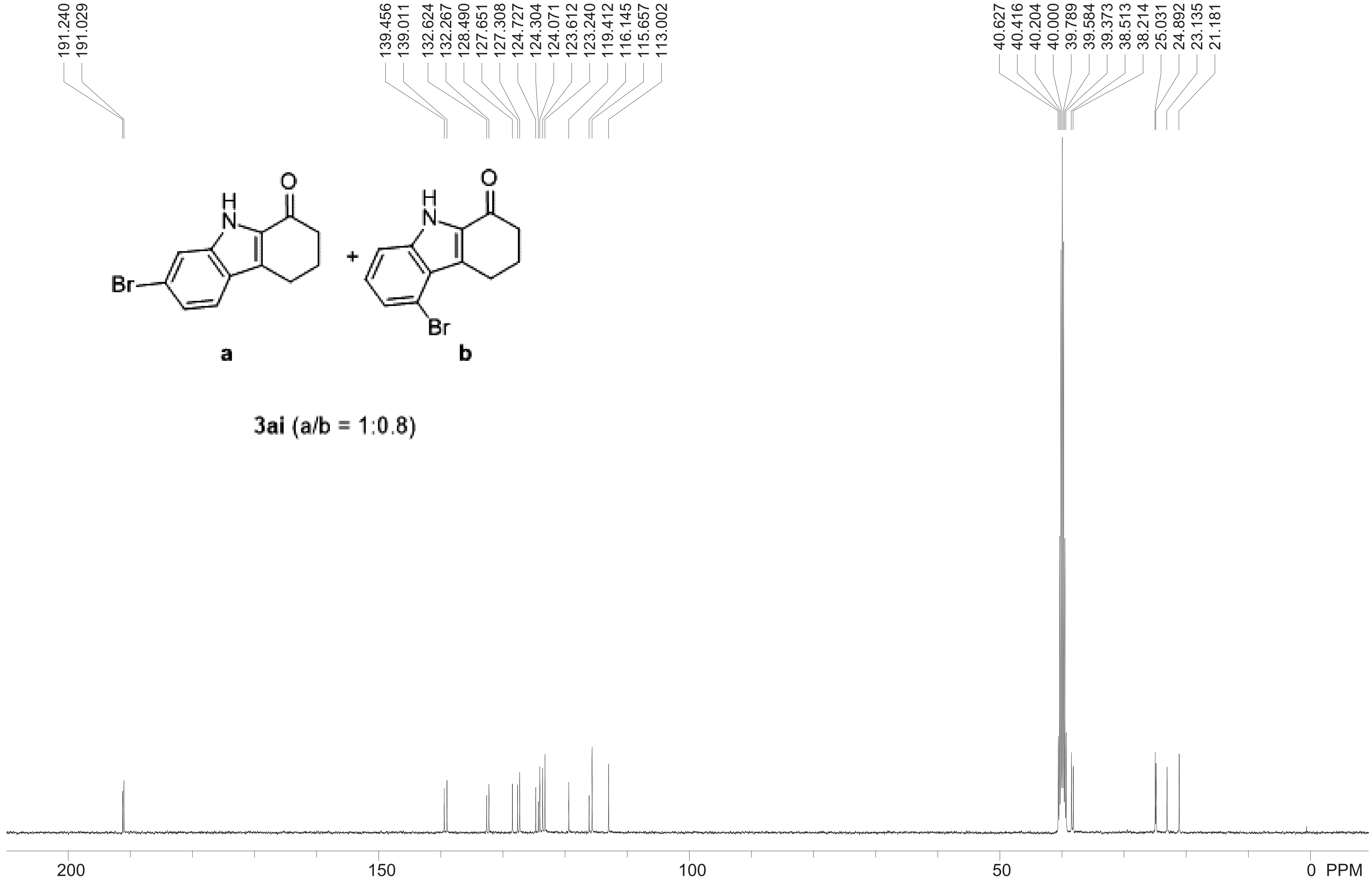
1.91
2.01
1.68
1.93
1.65
12
10
8
6
4
2
0PPM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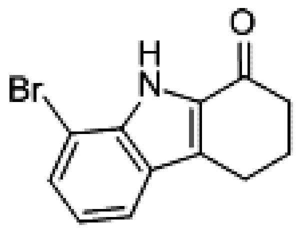
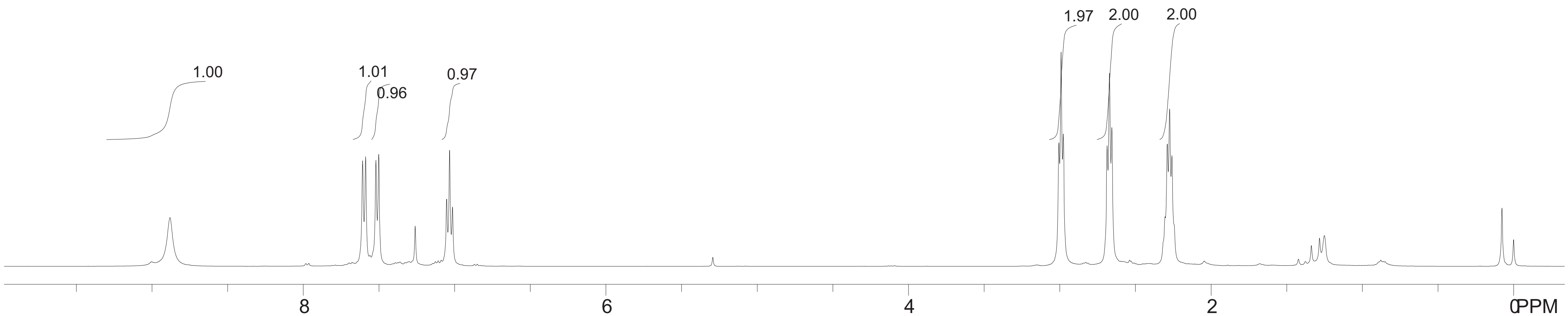
124.071
123.612
123.240
119.412
116.145
115.657
113.002
40.627
40.416
40.204
40.000
39.789
39.584
39.373
38.513
38.214
25.031
24.892
23.135
21.181
H
N
O
Br
+
a
b
3ai (a/b = 1:0.8)
200
150
100
50
0 PPM



3aj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7.501
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7.053
7.033
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2.687
2.671
2.655
2.304
2.289
2.274
2.259
0.077
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1.01
0.96
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1.97
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2.00
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4
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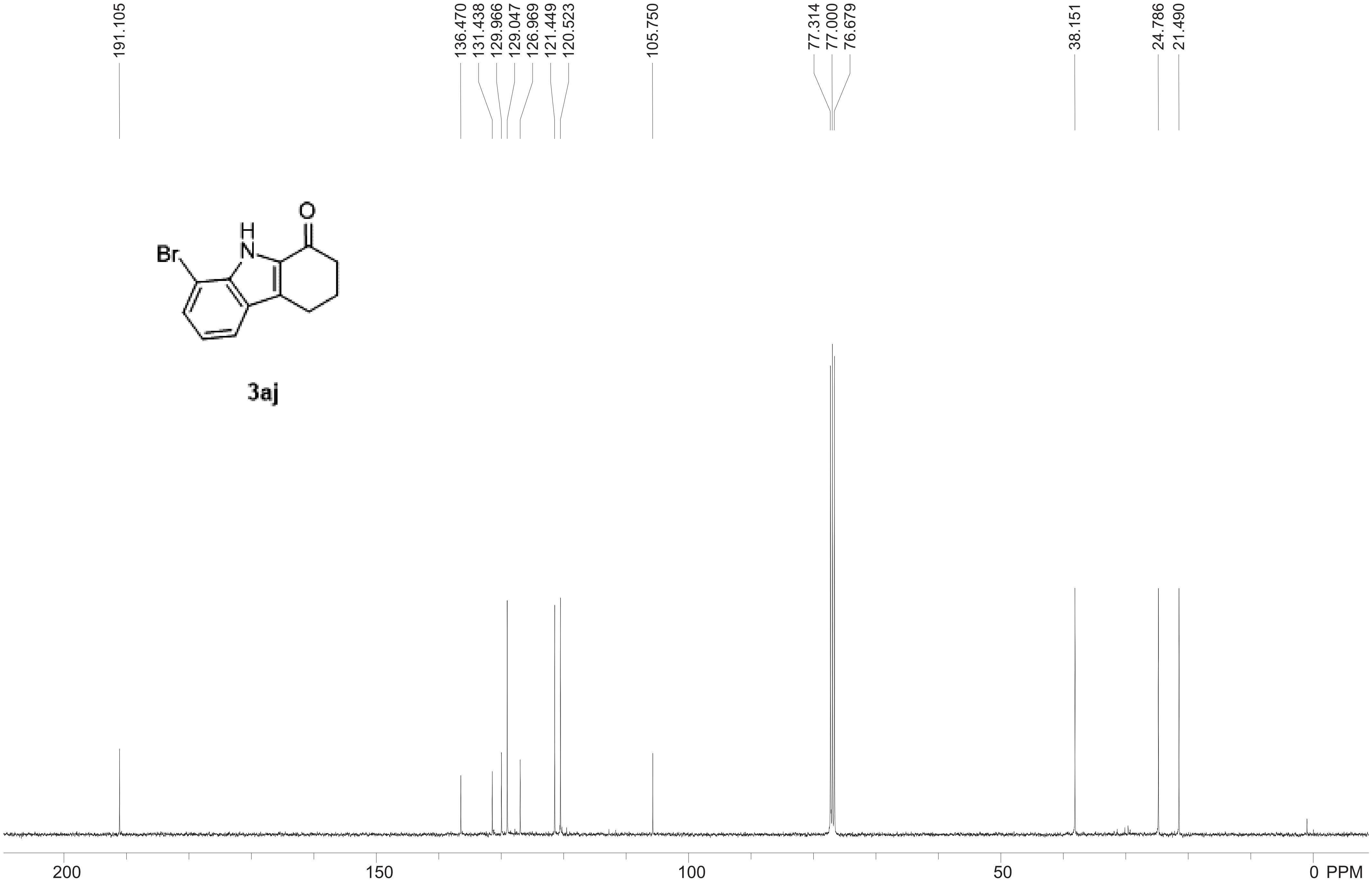
0
PPM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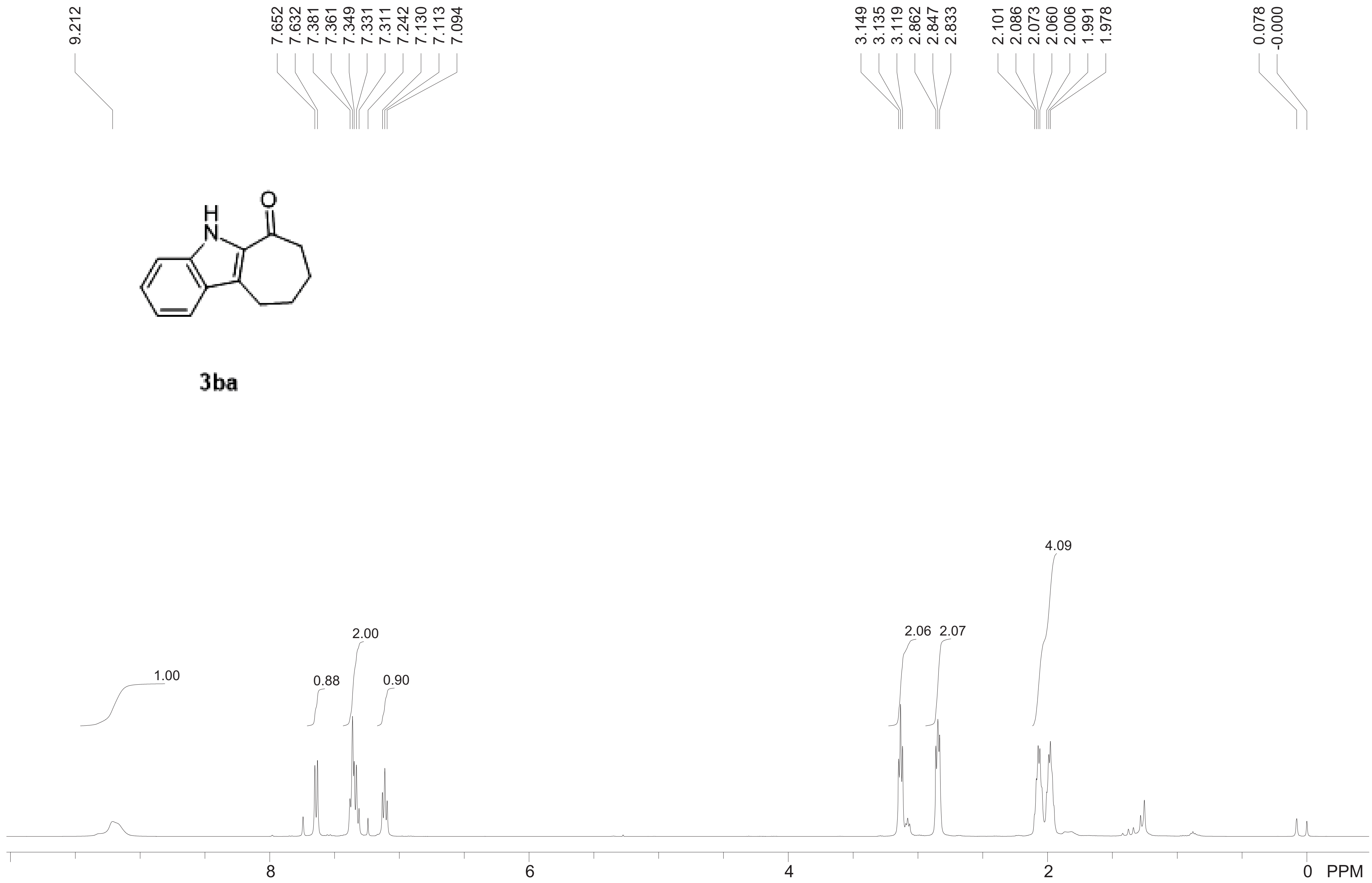
38.151
24.786
21.490
Br
H
N
O
200
150
100
50
0 PPM

3aj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7.311
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3.149
3.135
3.119
2.862
2.847
2.833
2.101
2.086
2.073
2.060
2.006
1.991
1.978
0.078
-0.000
H
N
O
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4.09
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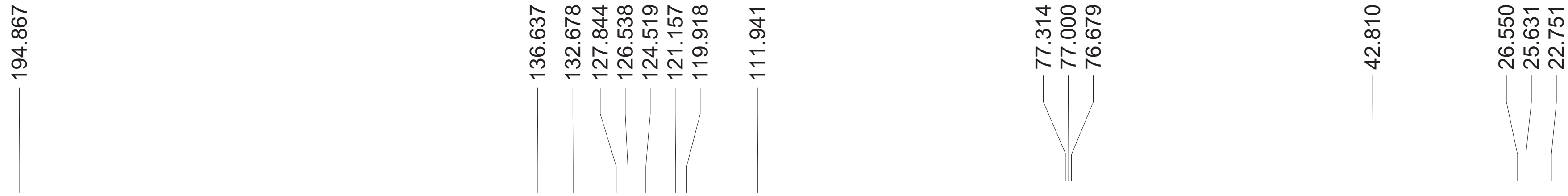
0
PPM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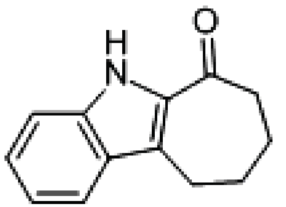
22.751


H
N
O

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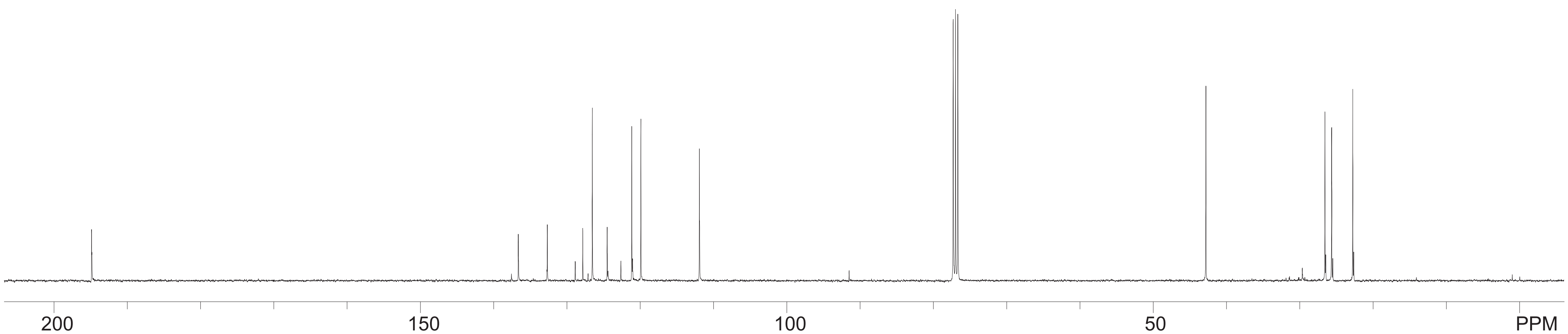
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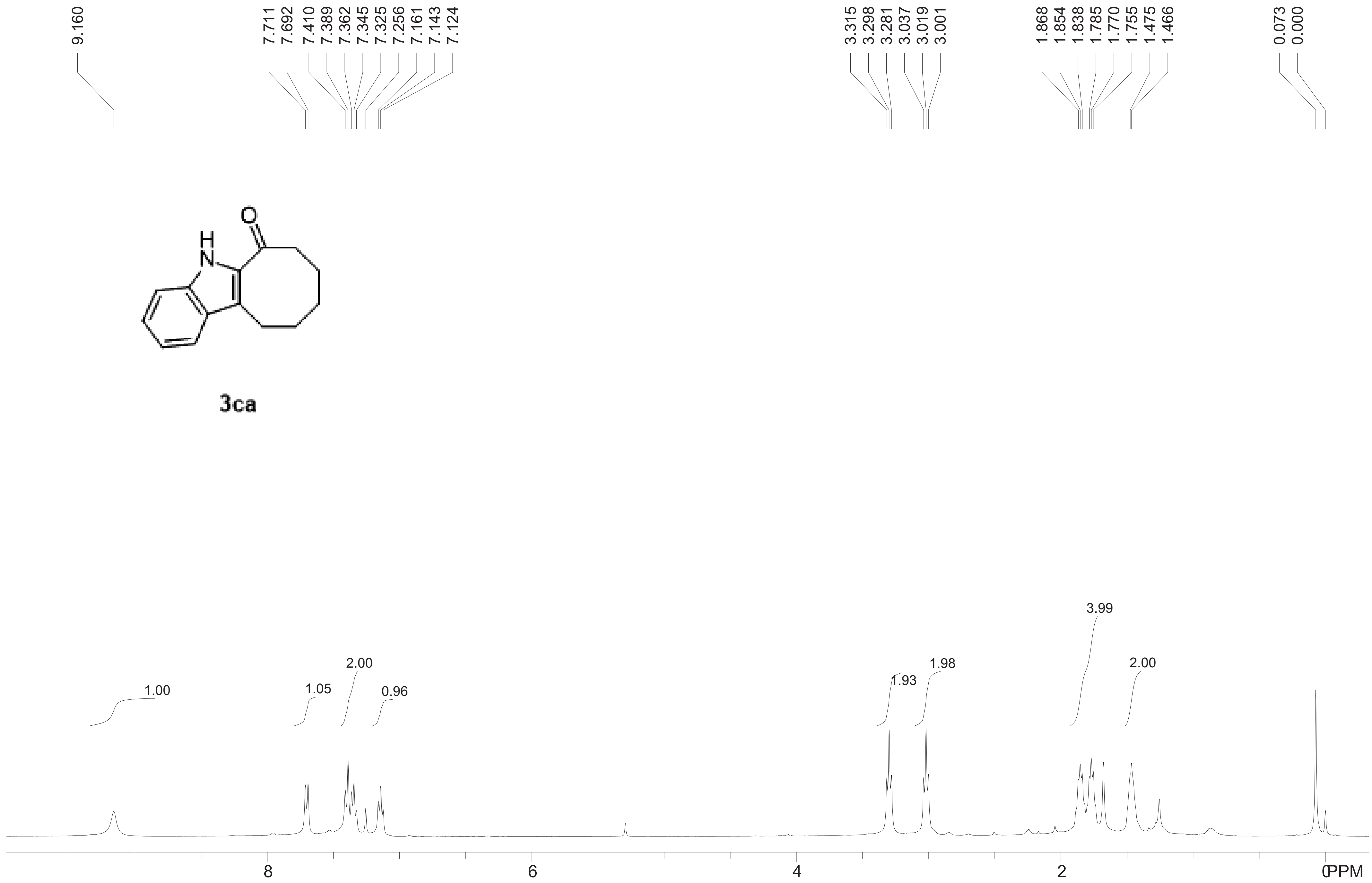
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7.161
7.143
7.124
3.315
3.298
3.281
3.037
3.019
3.001
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1.854
1.838
1.785
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1.475
1.466
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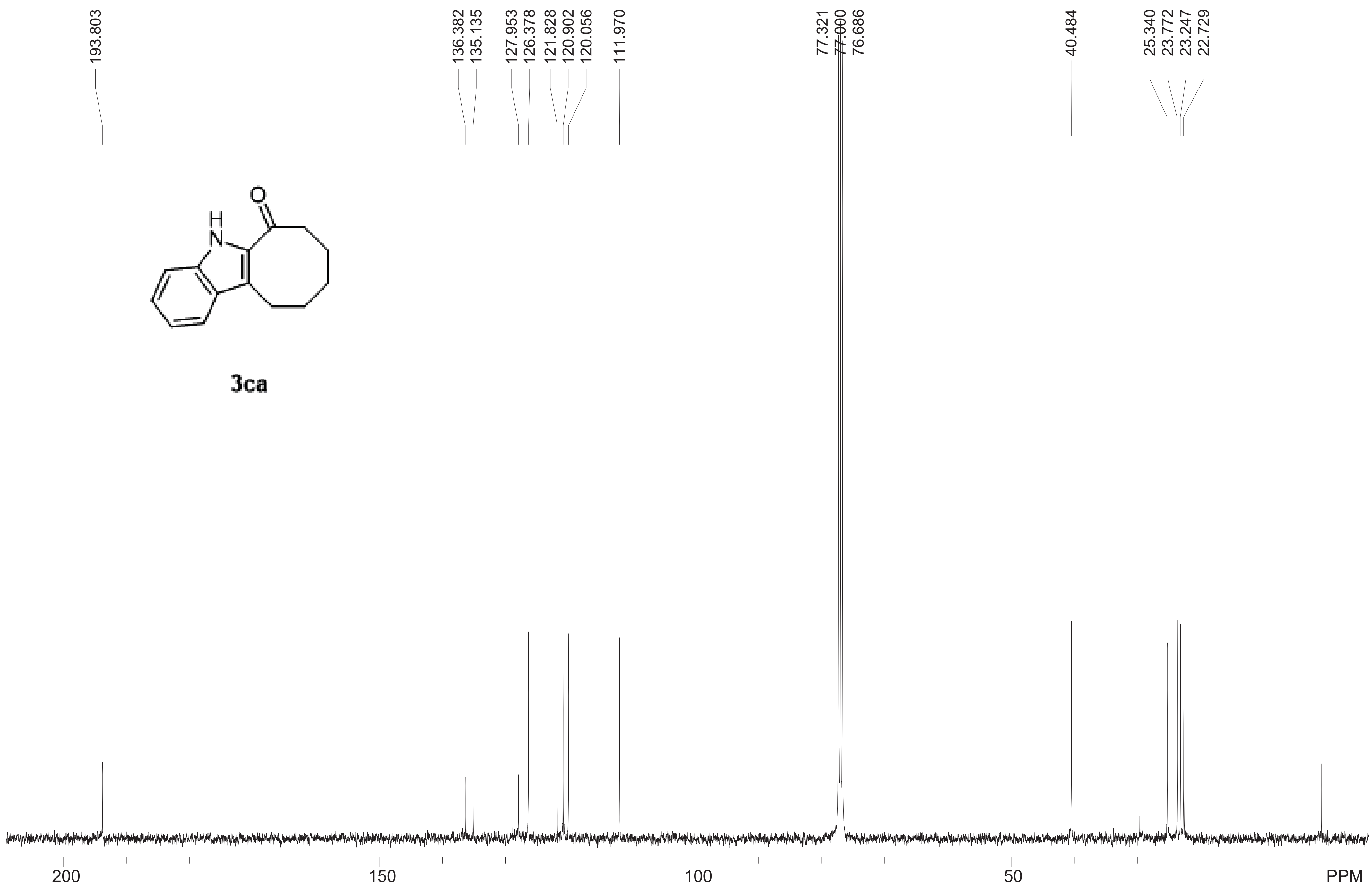
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77.000
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22.729
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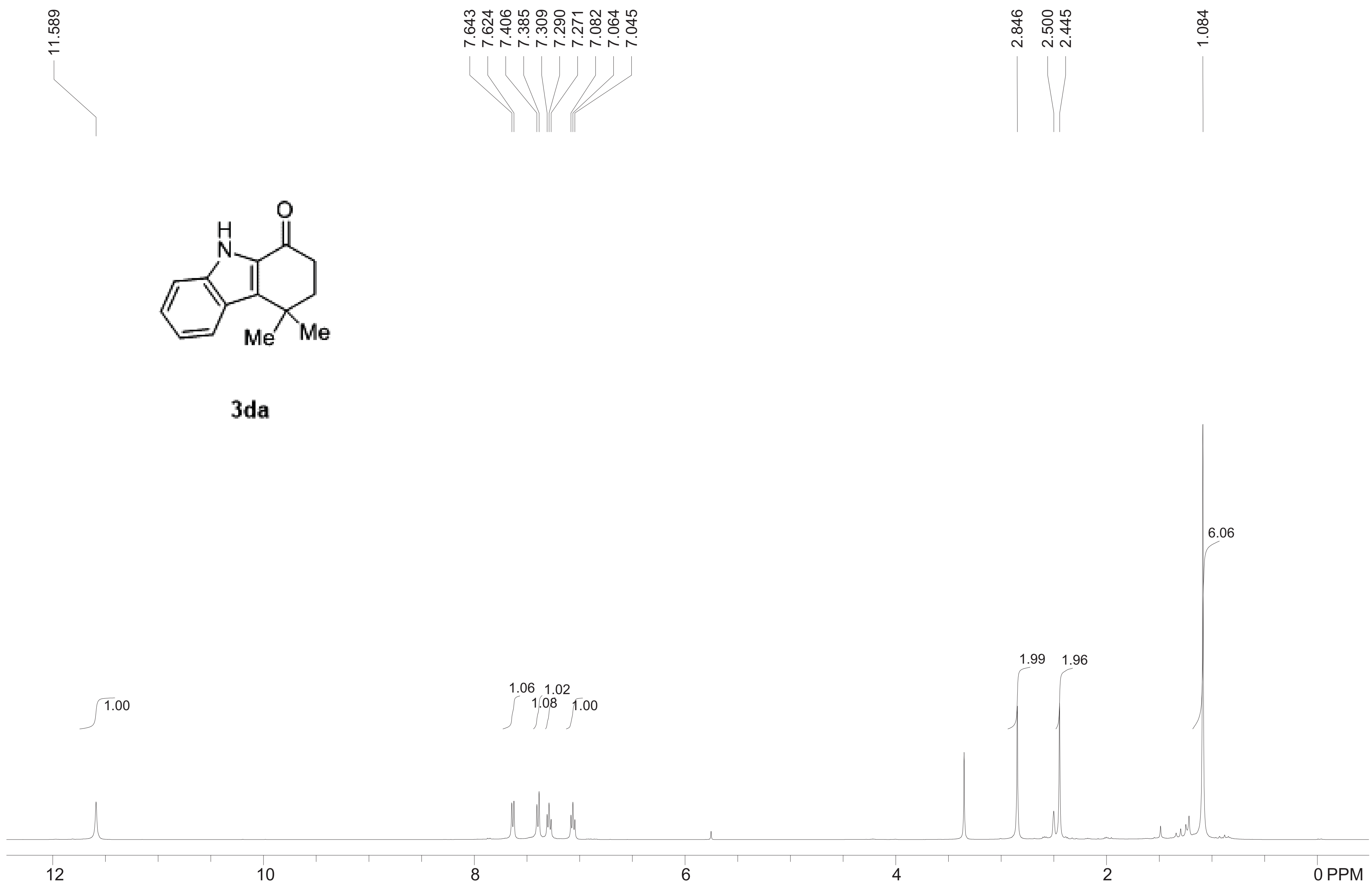
200
150
100
50
PPM



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2.500
2.445
1.084
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1.02
1.00
1.99
1.96
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4
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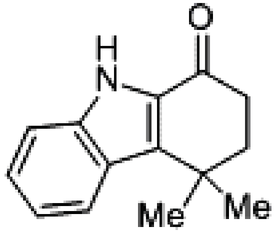
0 PPM


O
H
N
Me
Me

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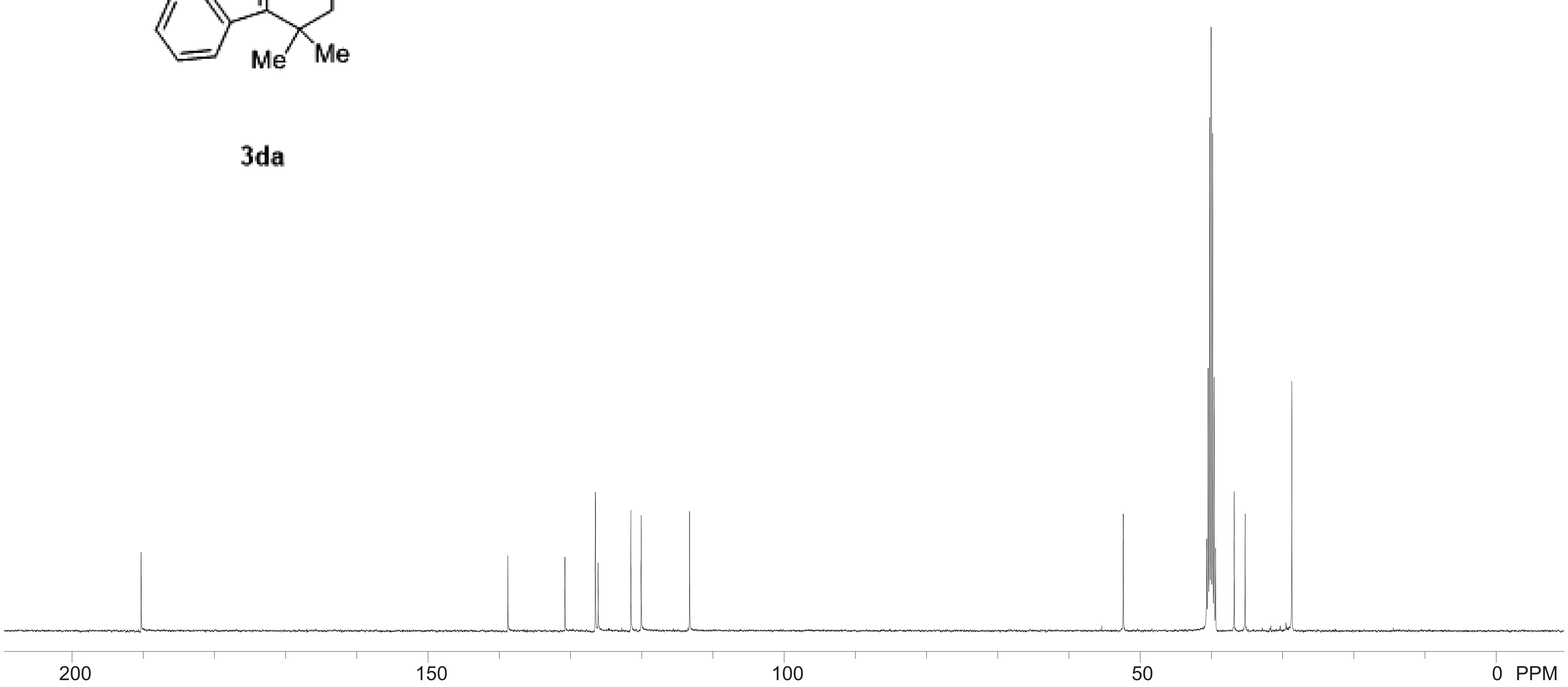
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40.627
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39.796
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36.763
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28.669
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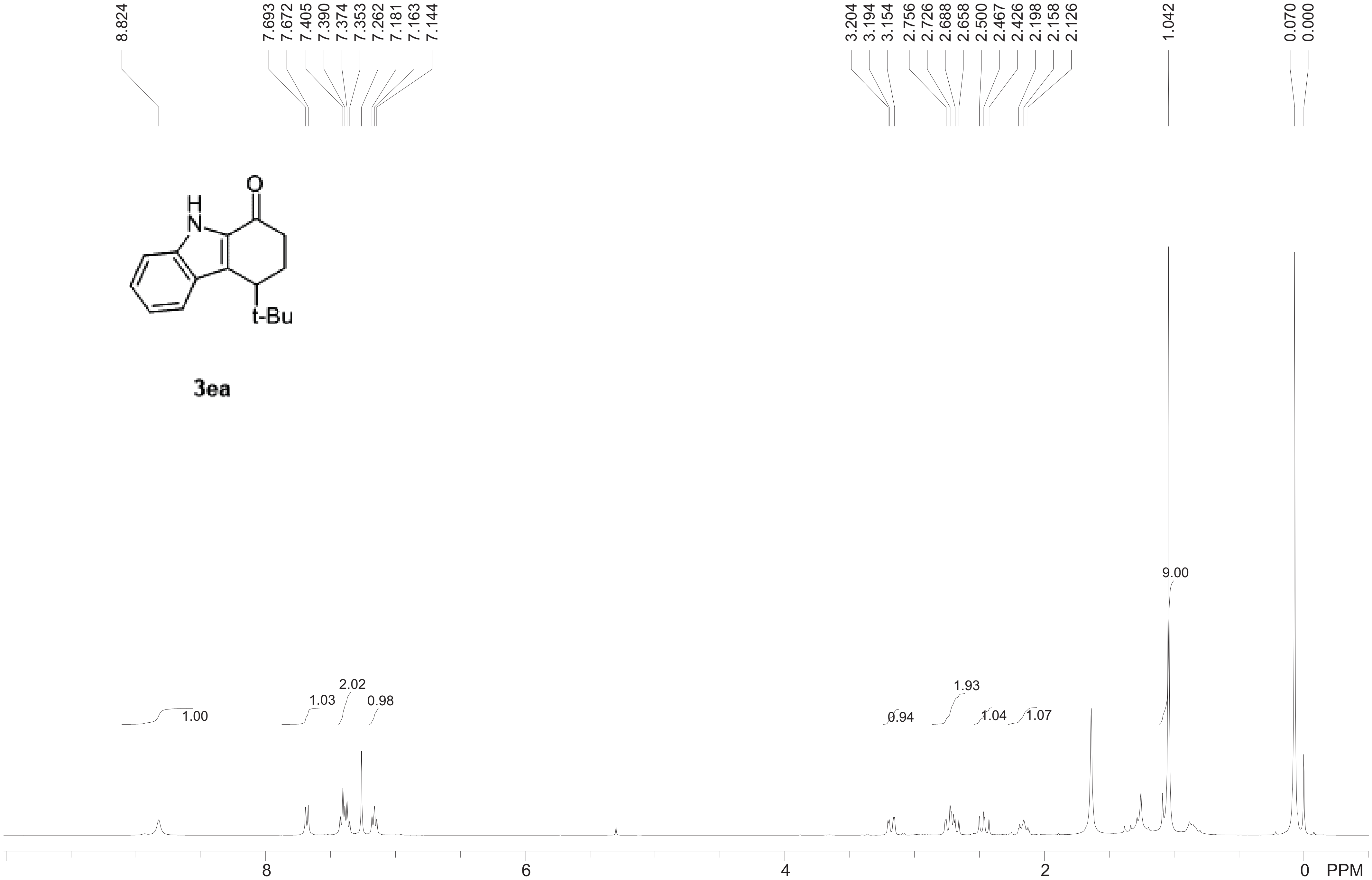
150
100
50
0 PPM



3ea

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3.204 3.194 3.154 2.756 2.726 2.688 2.658 2.500 2.467 2.426 2.198 2.158 2.126
1.042
0.070 0.000
1.00
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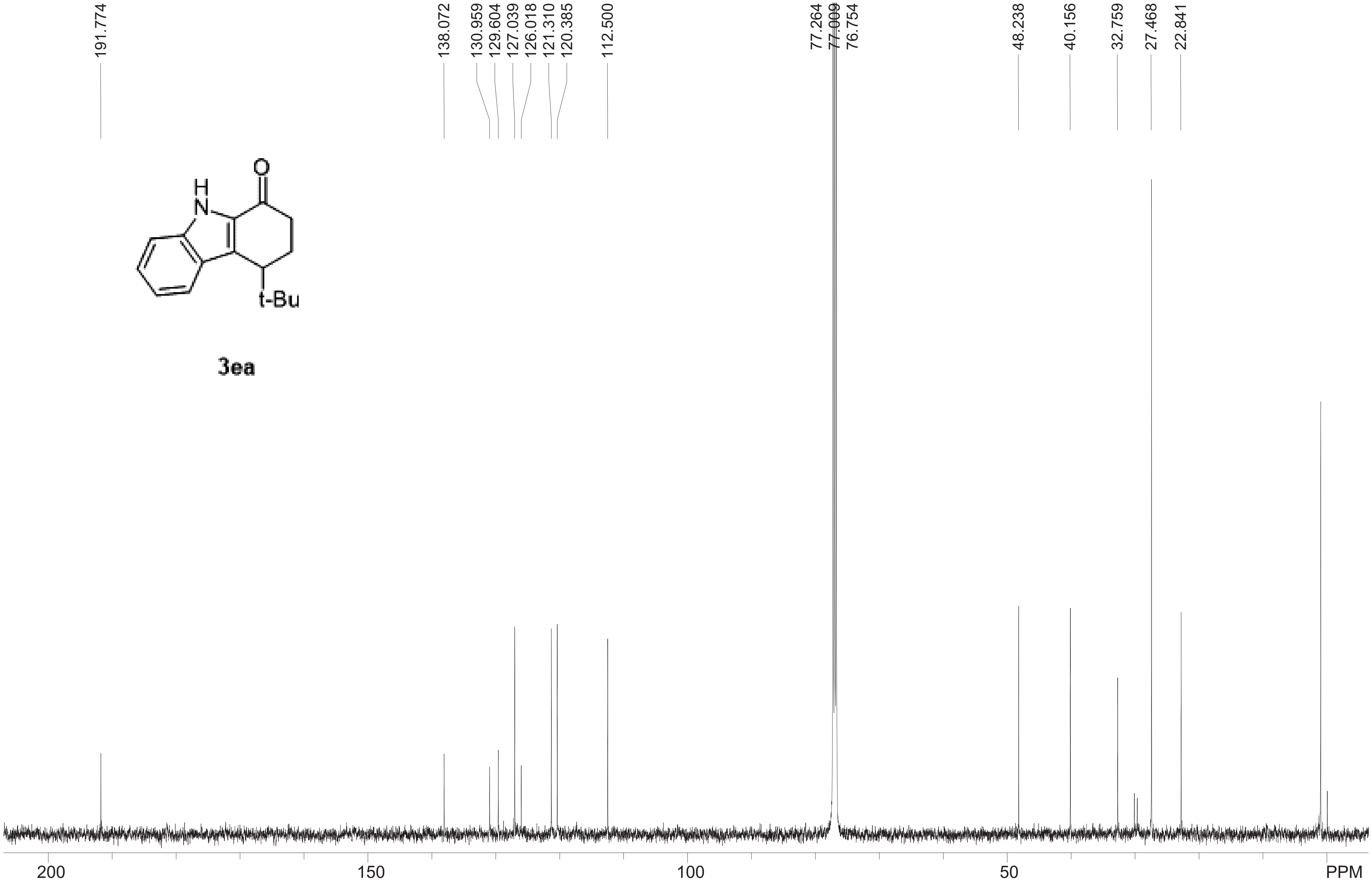
PPM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77.009
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O
t-Bu
3ea
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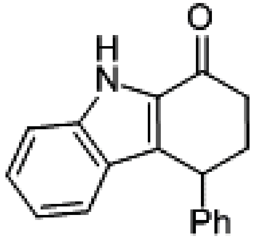
100
50
PPM



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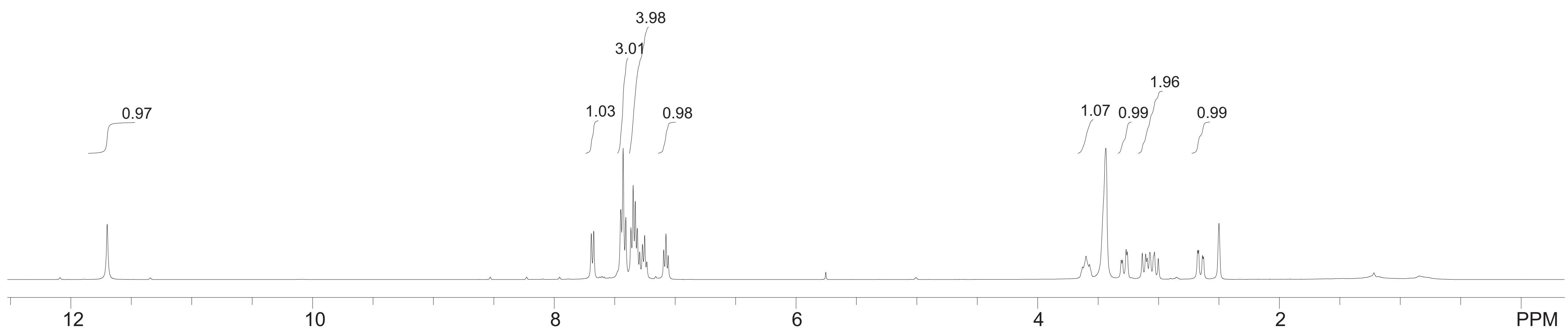
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3.601 3.436 3.309 3.299 3.269 3.258 3.135 3.107 3.073 3.041 3.002 2.677 2.669 2.636 2.628 2.500
0.97
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1.96
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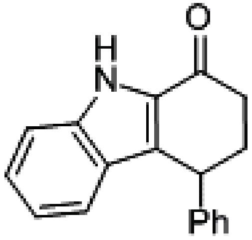
PPM



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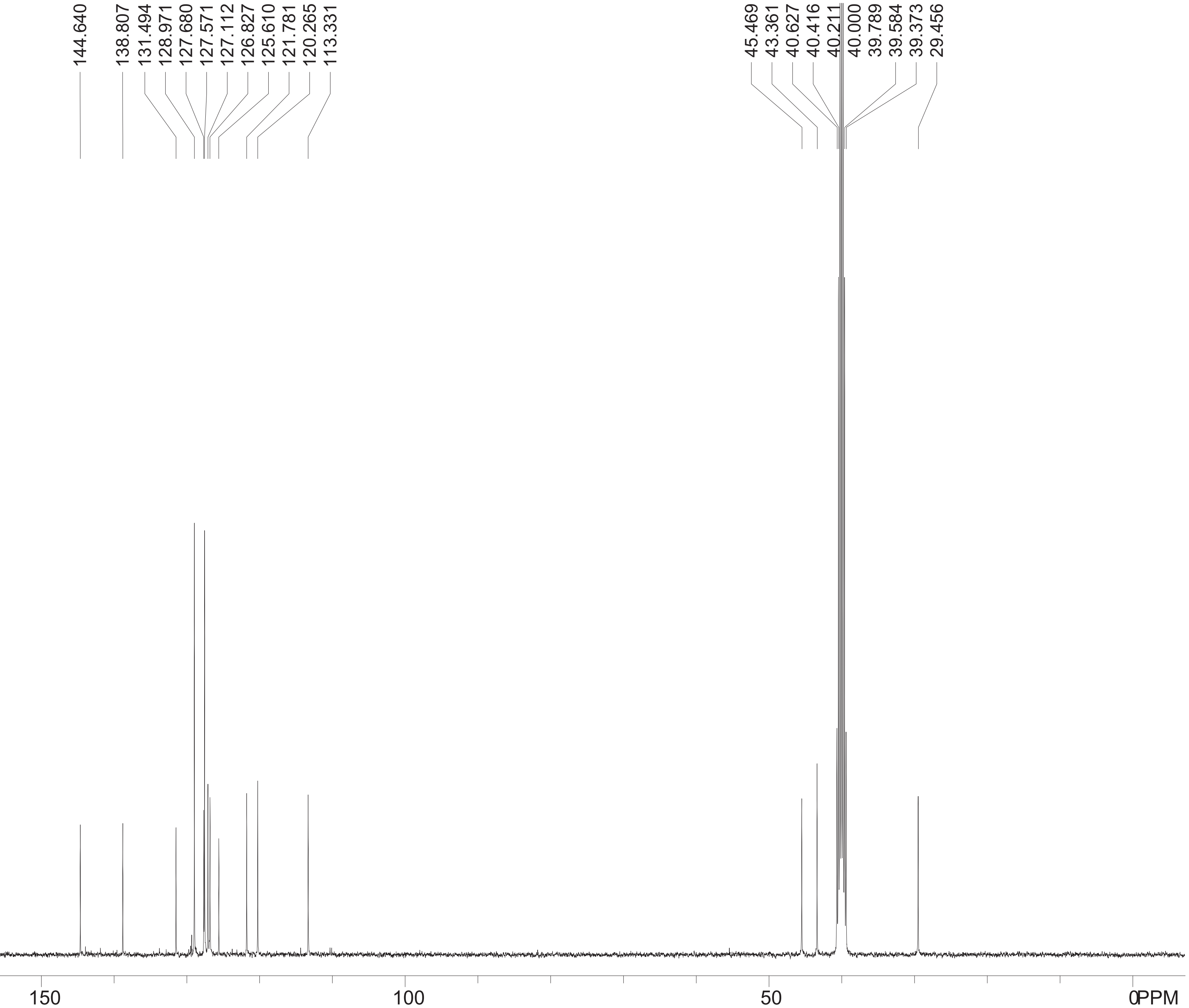

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113.331
45.469
43.361
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40.000
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29.456
200
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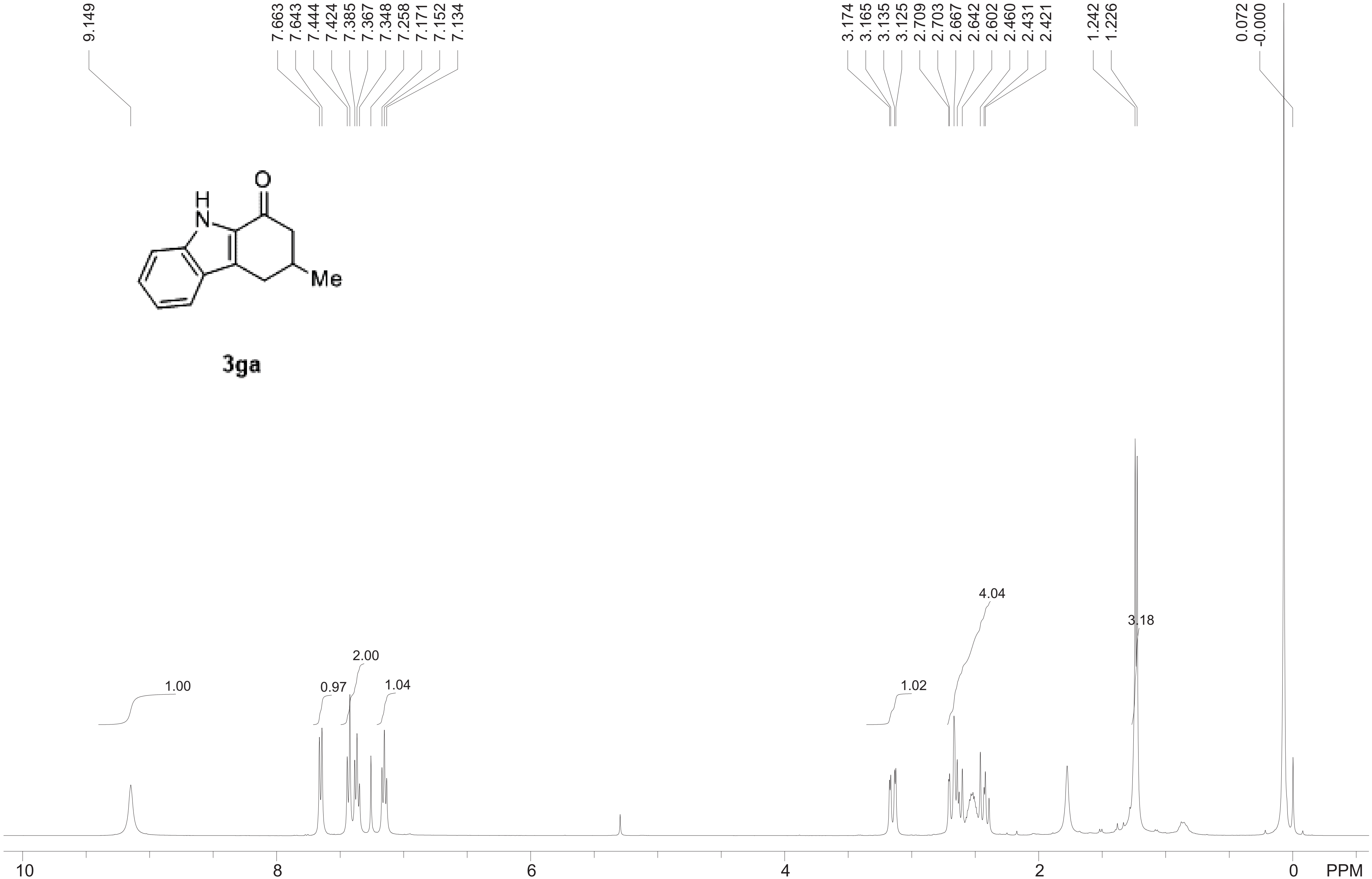
100
50
0PPM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2.421
1.242
1.226
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-0.000
H
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Me
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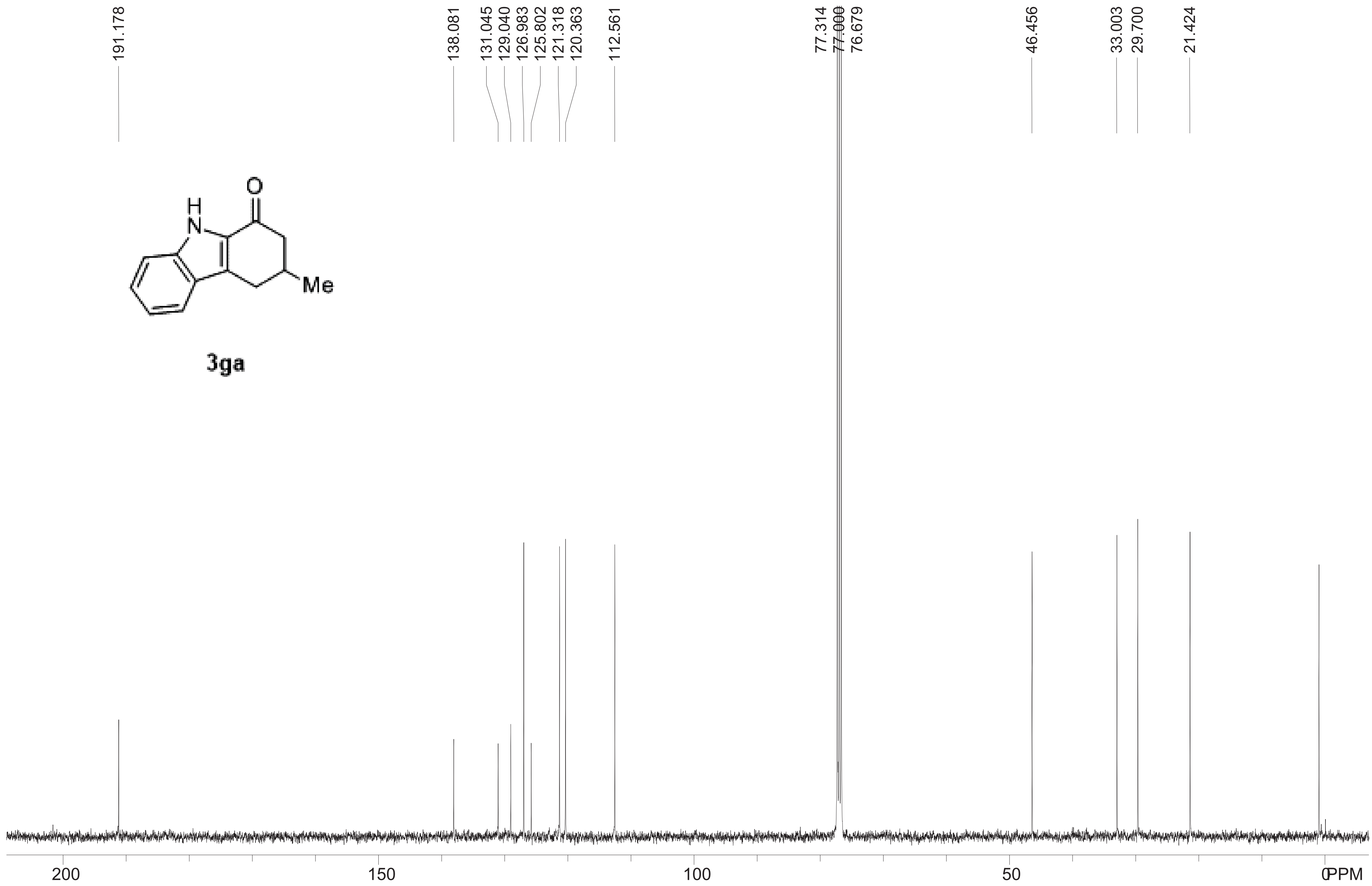
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77.000
76.679
46.456
33.003
29.700
21.424
H
N
O
Me
3ga
200
150
100
50
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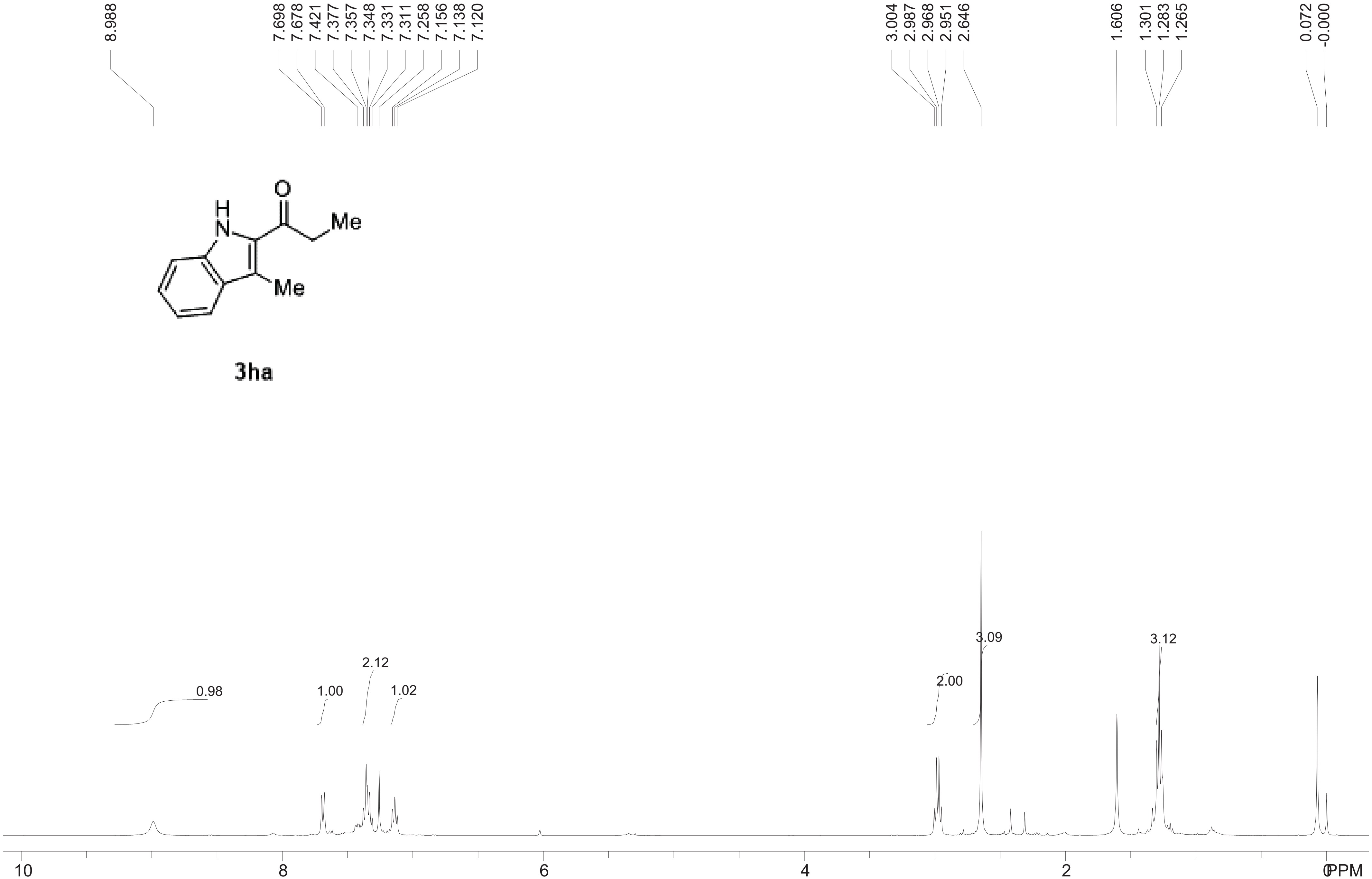
PPM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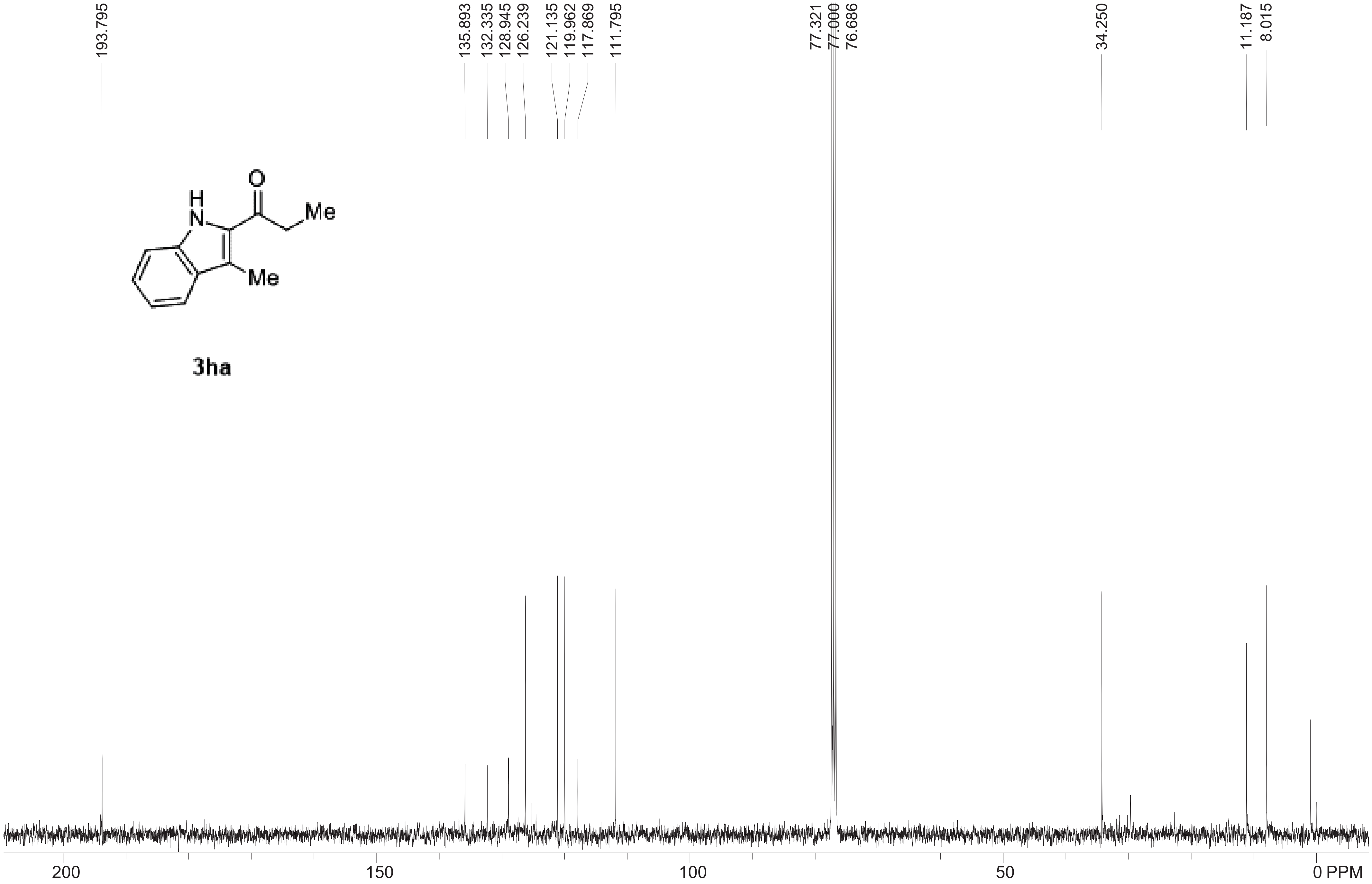
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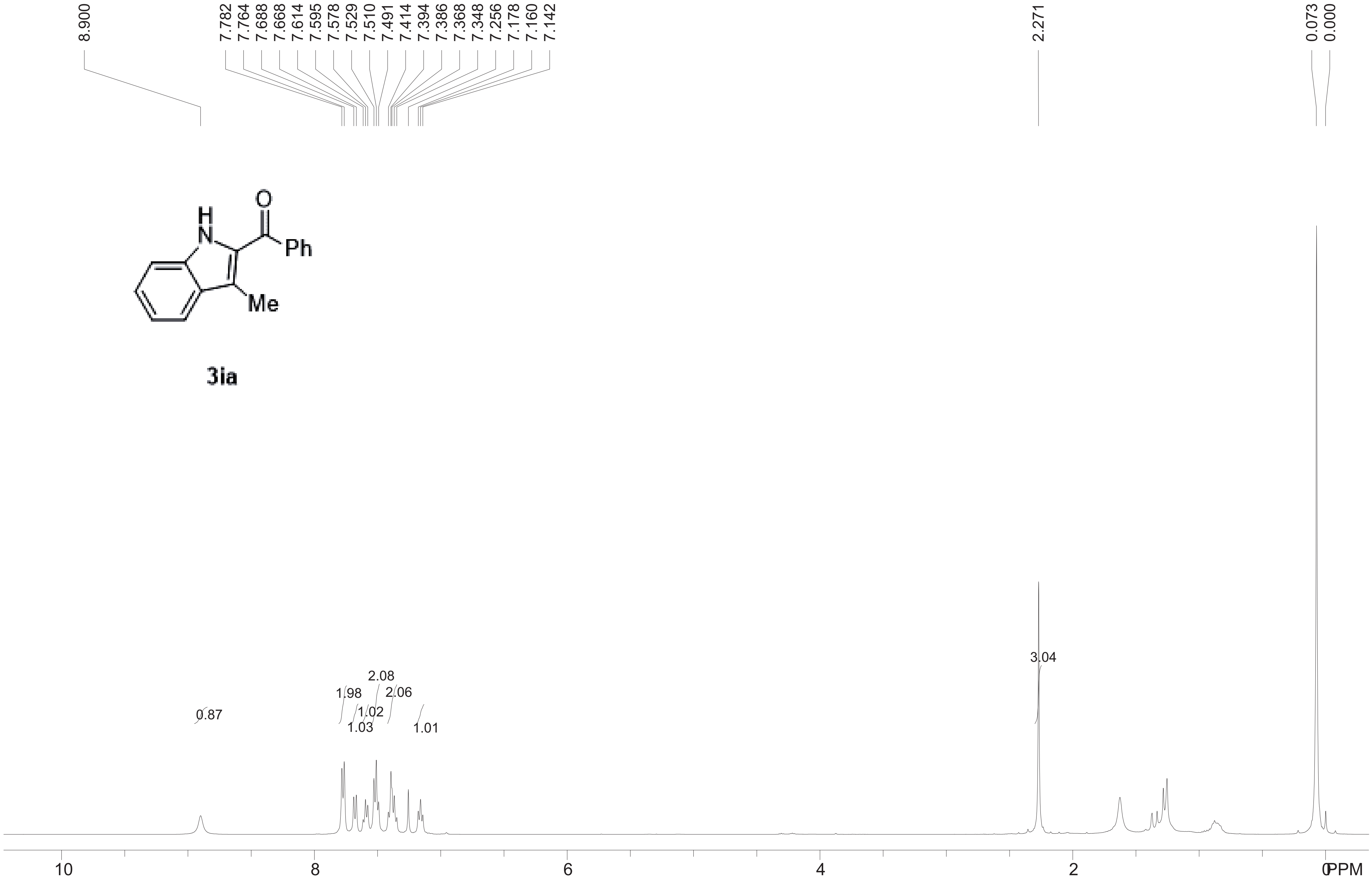
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Ph
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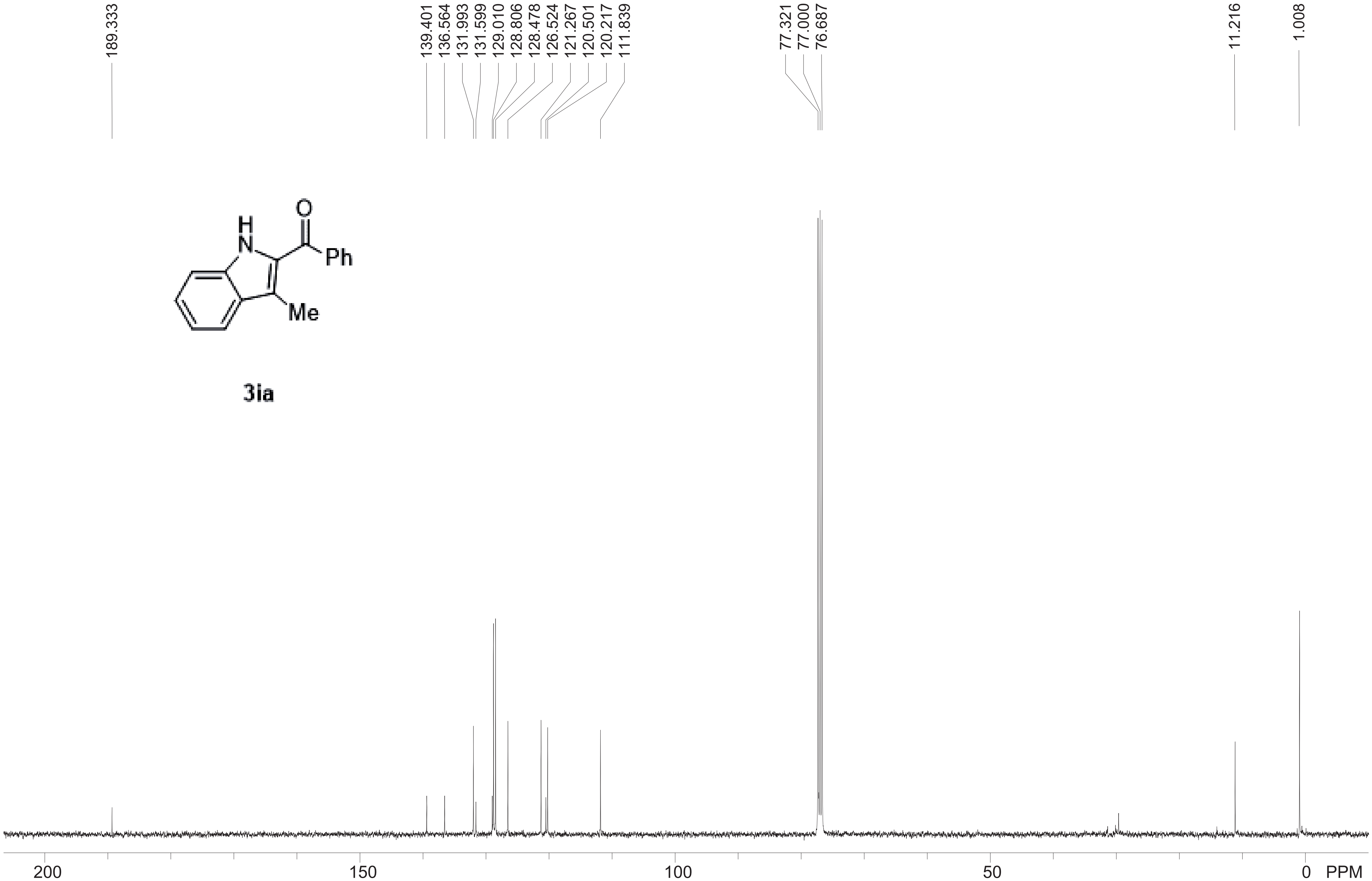
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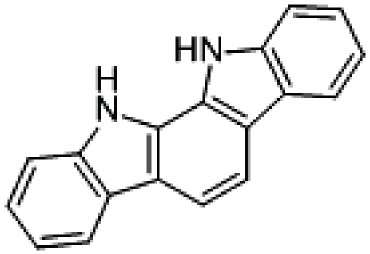
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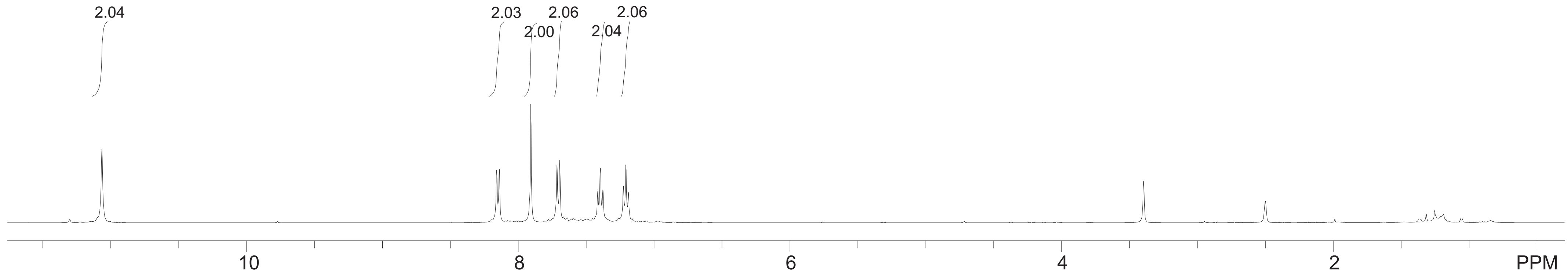
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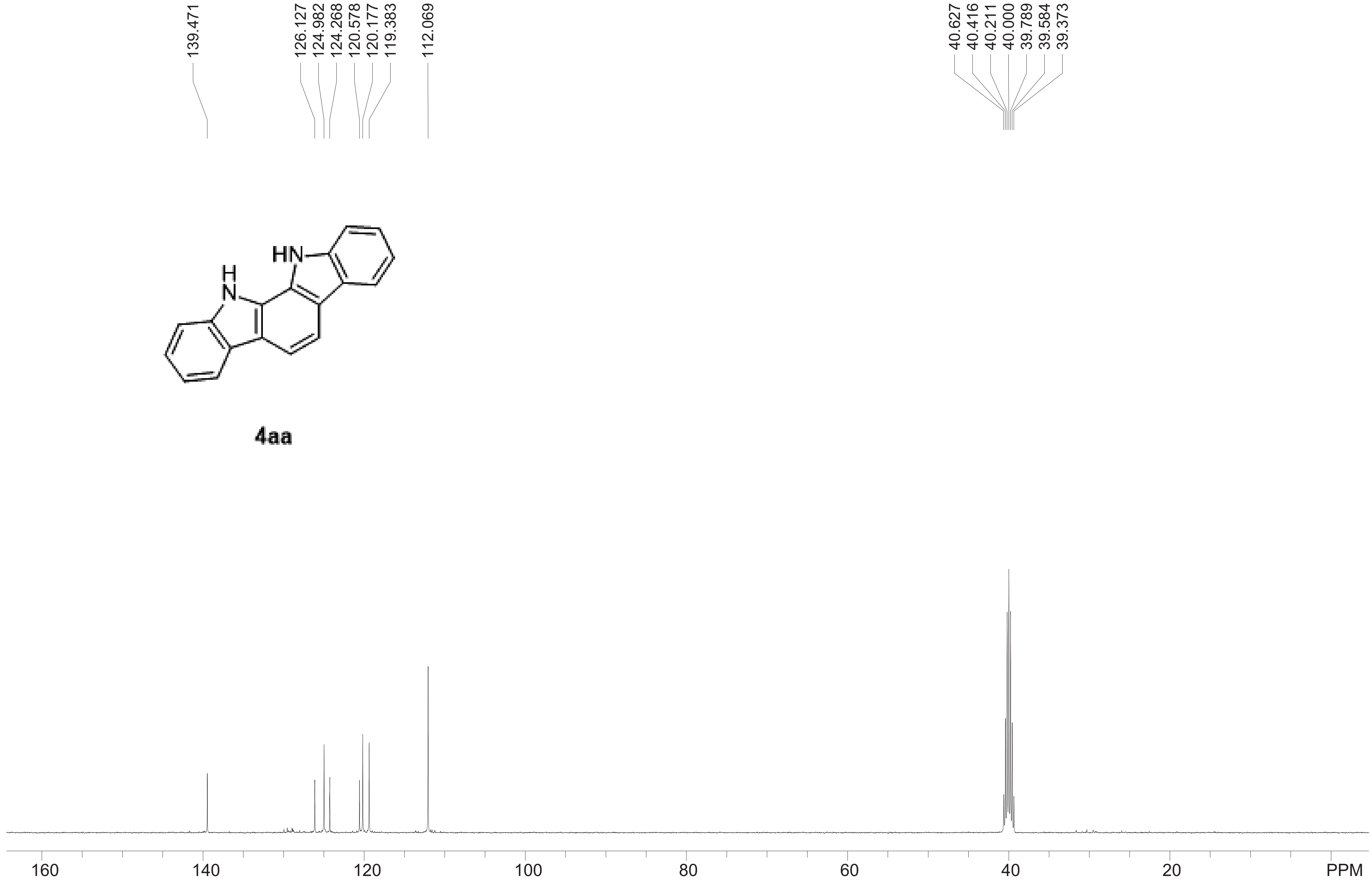
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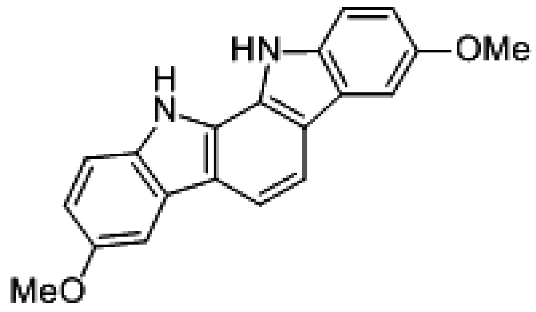
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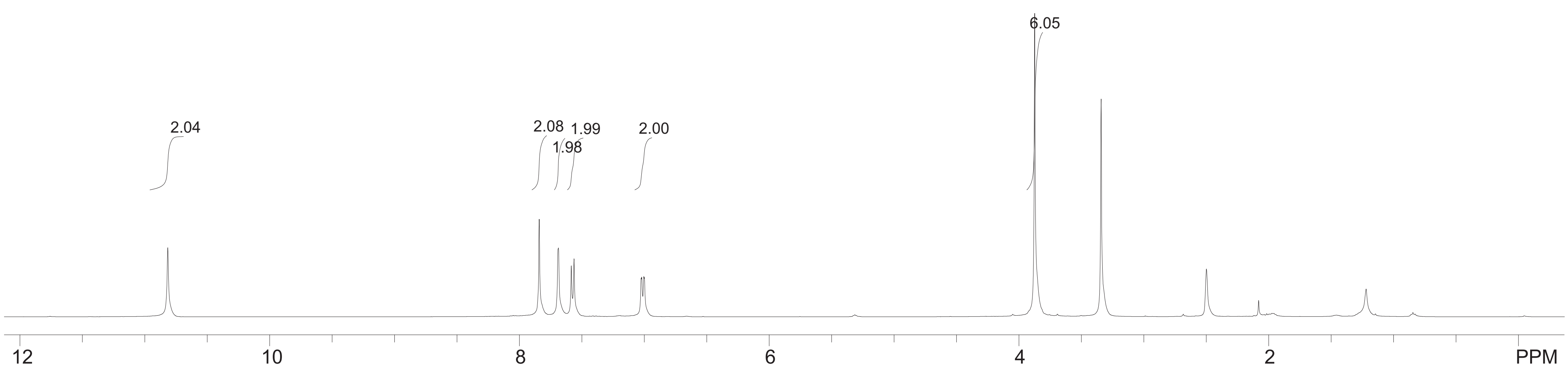
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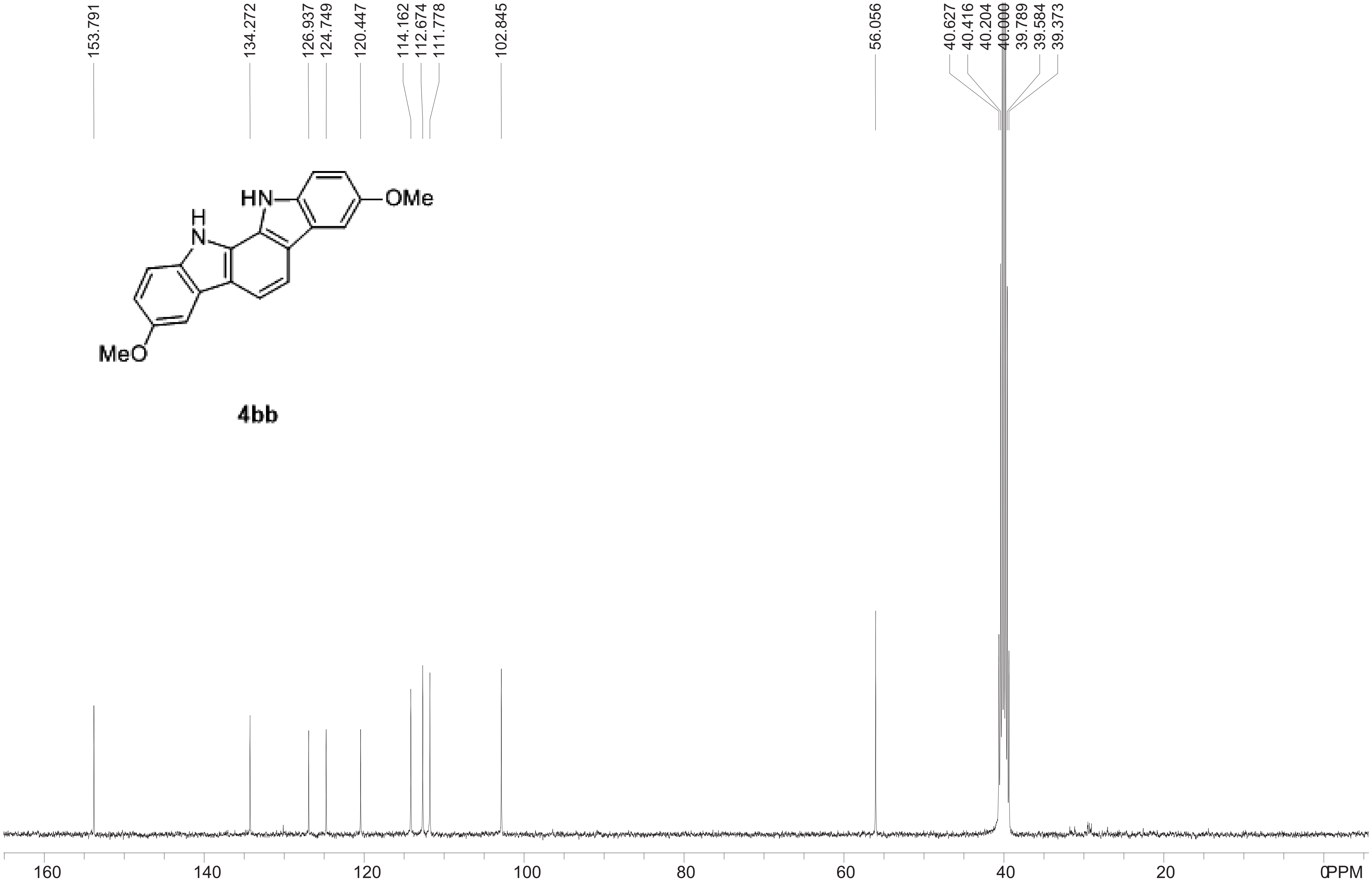
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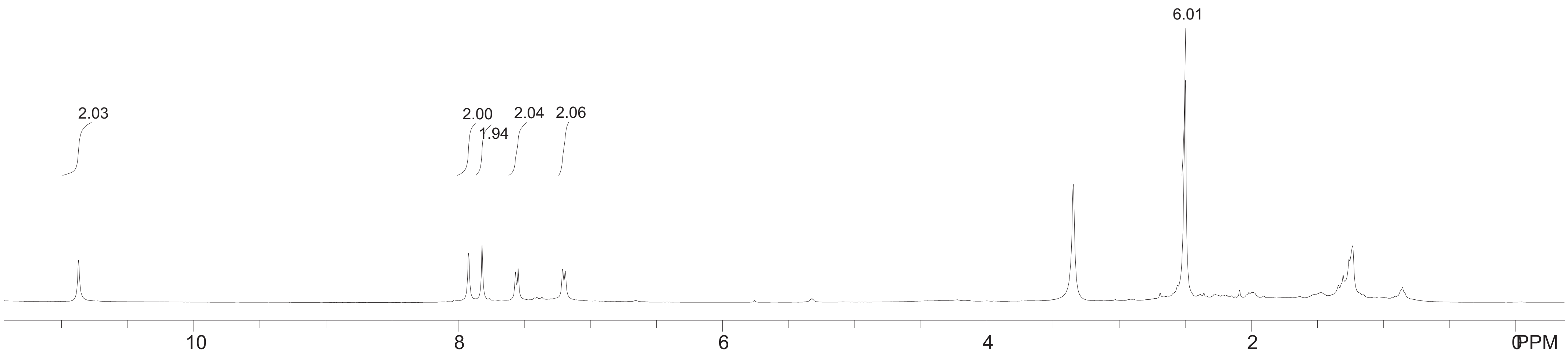

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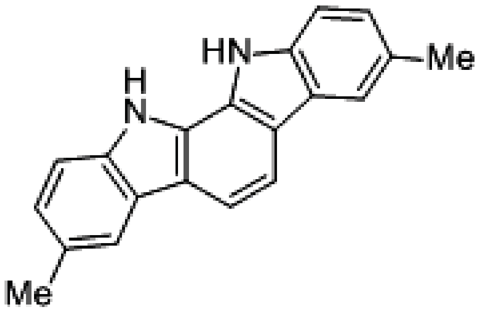

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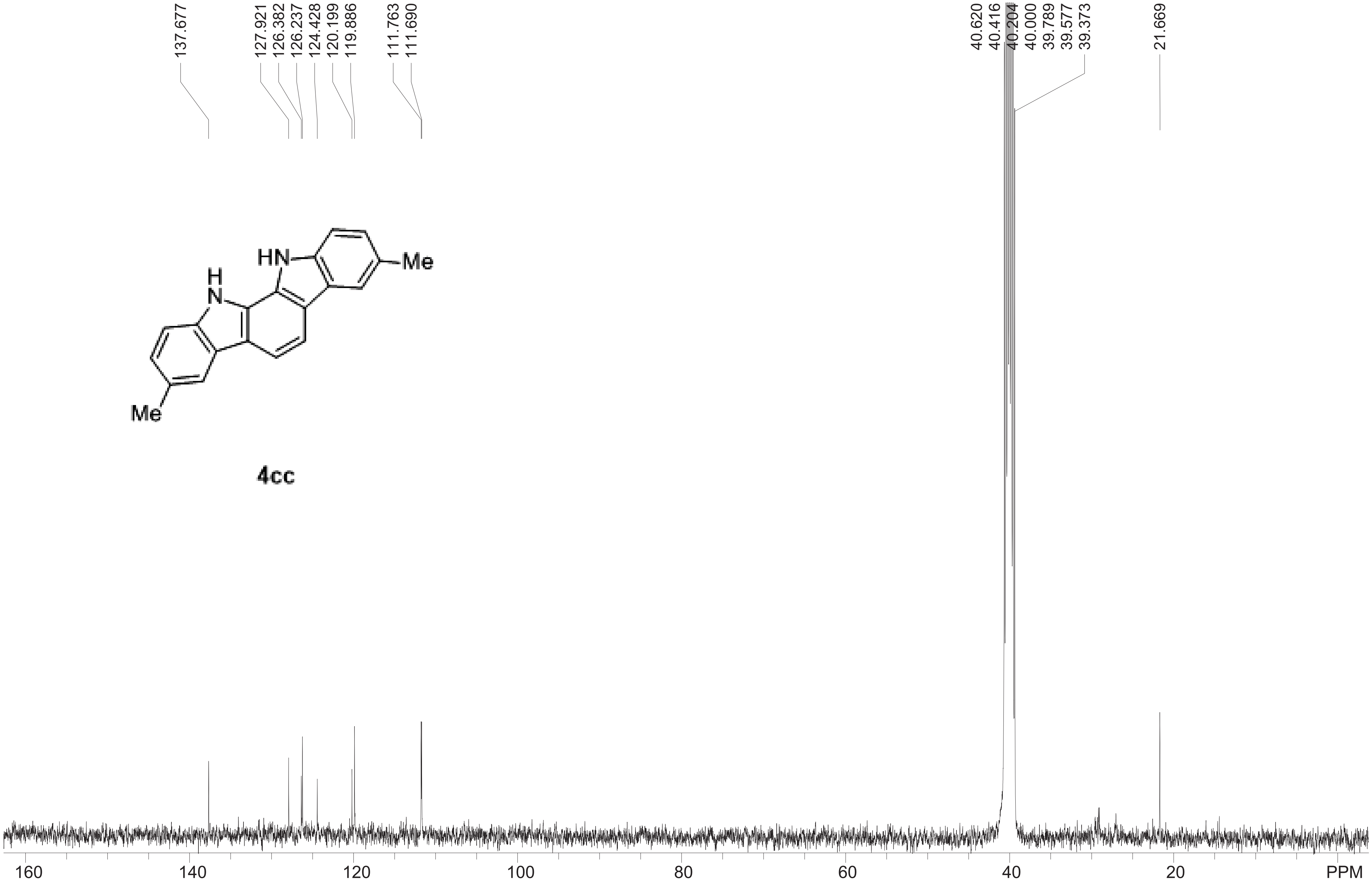
Me
Me

4cc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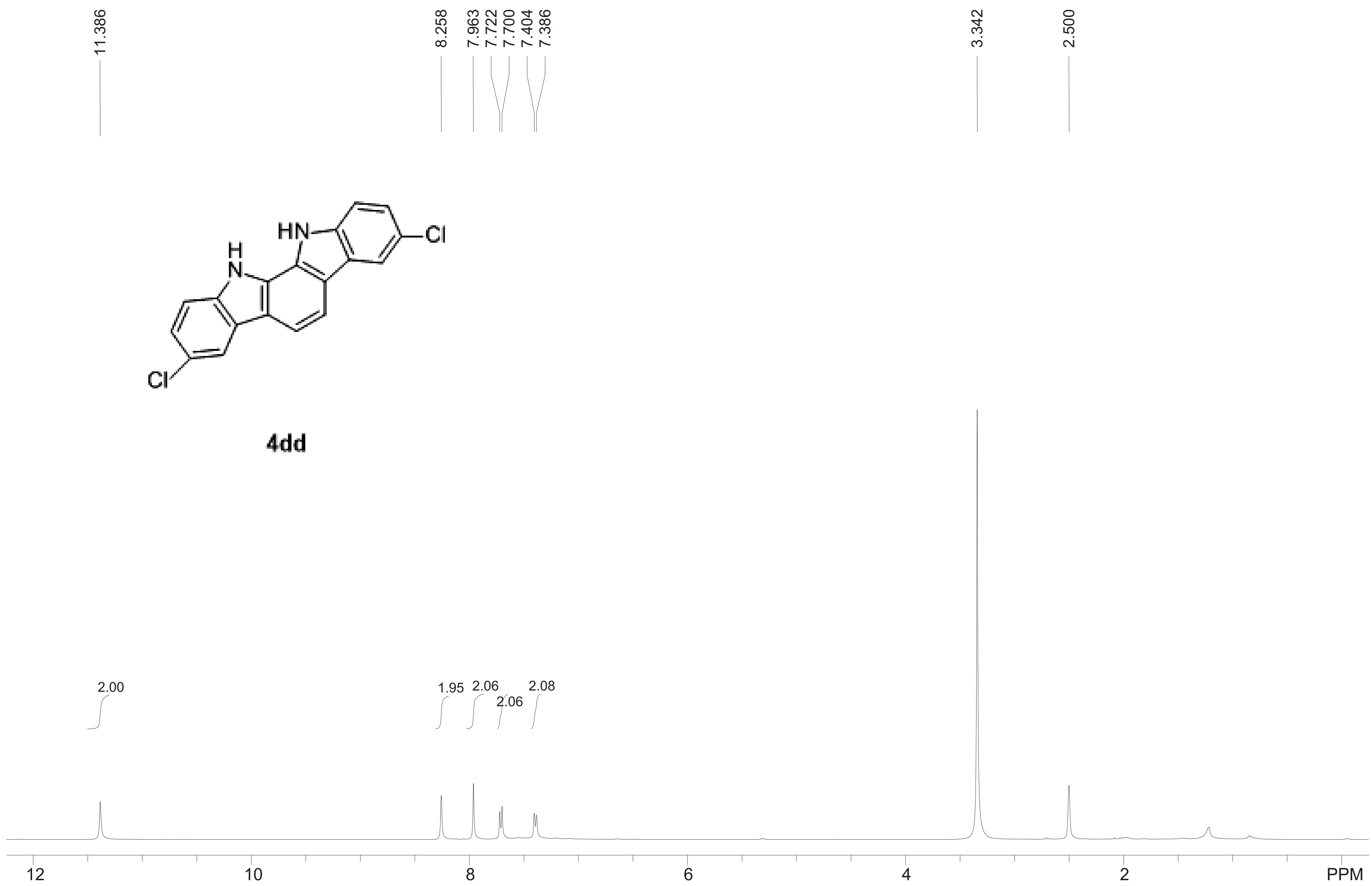
20
PPM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2
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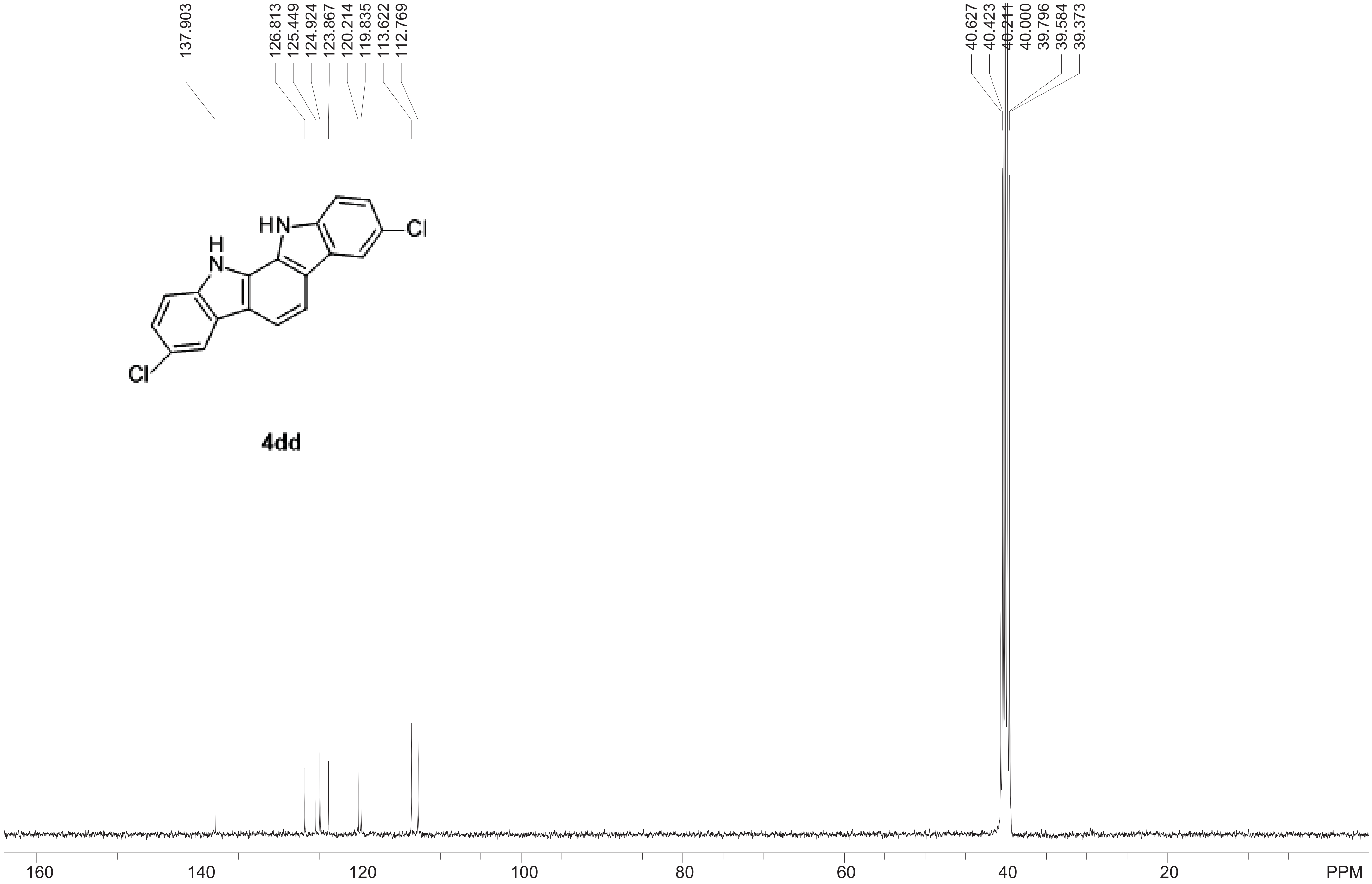
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20
PPM

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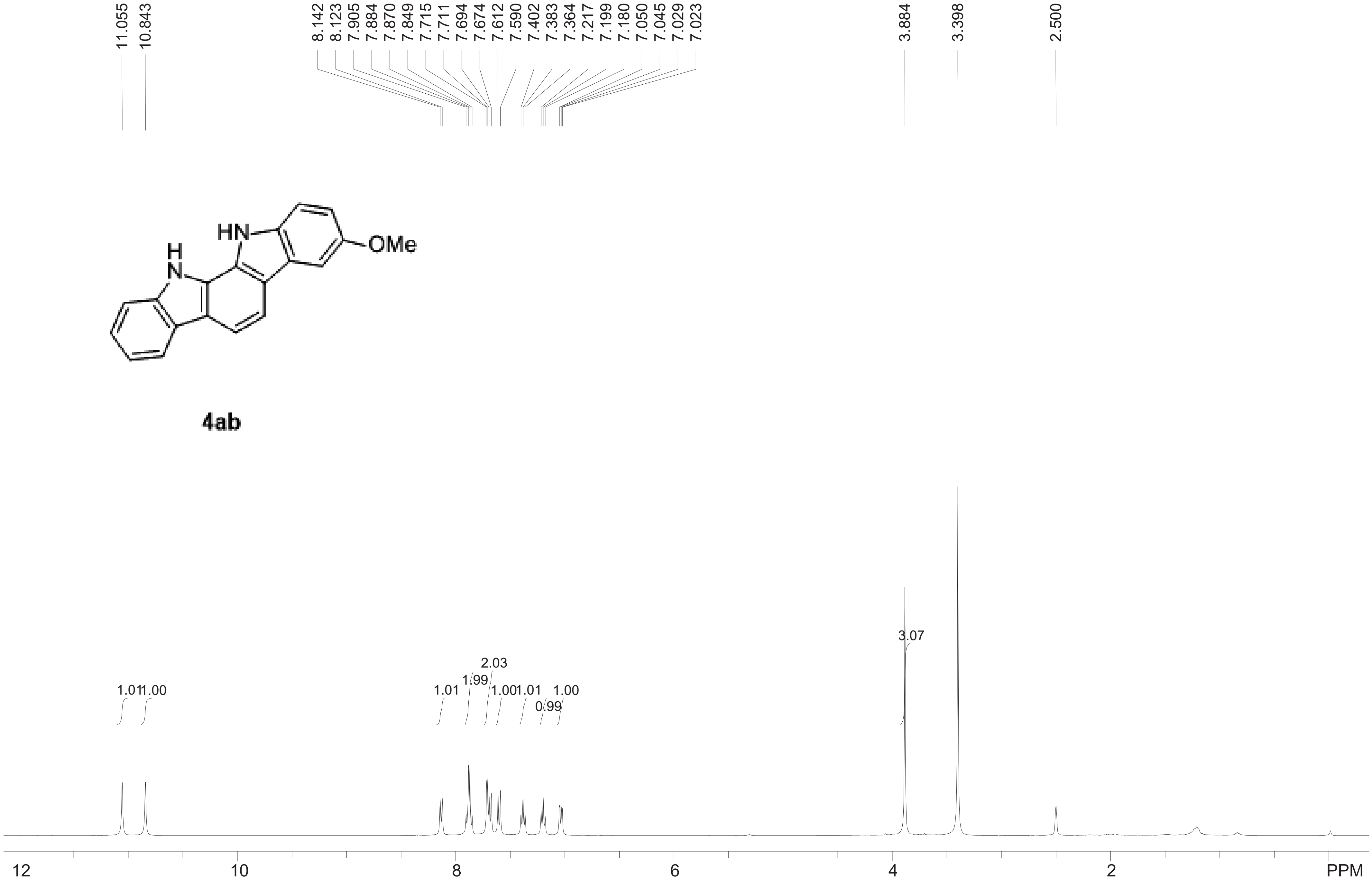

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OMe
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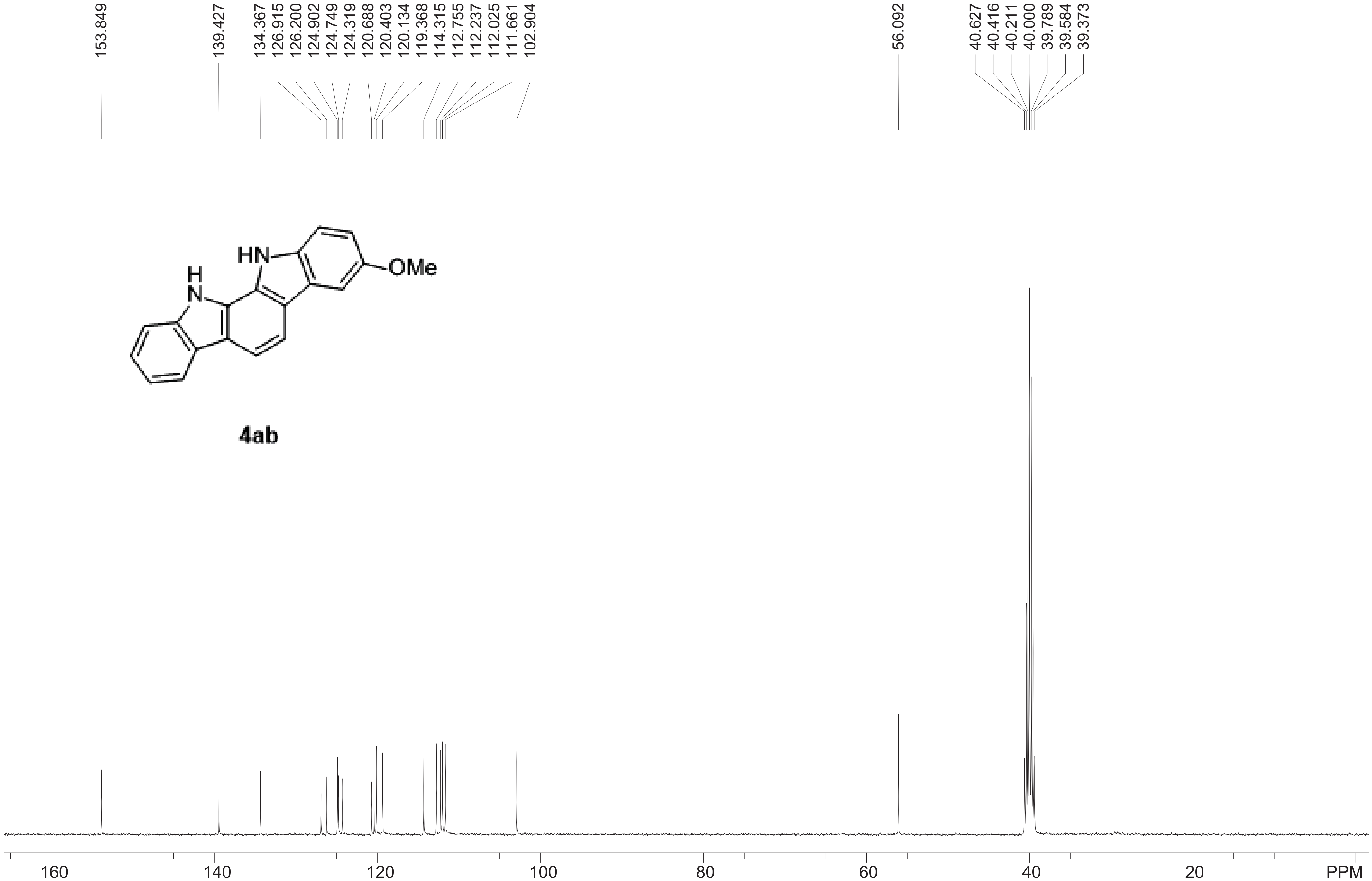
4ab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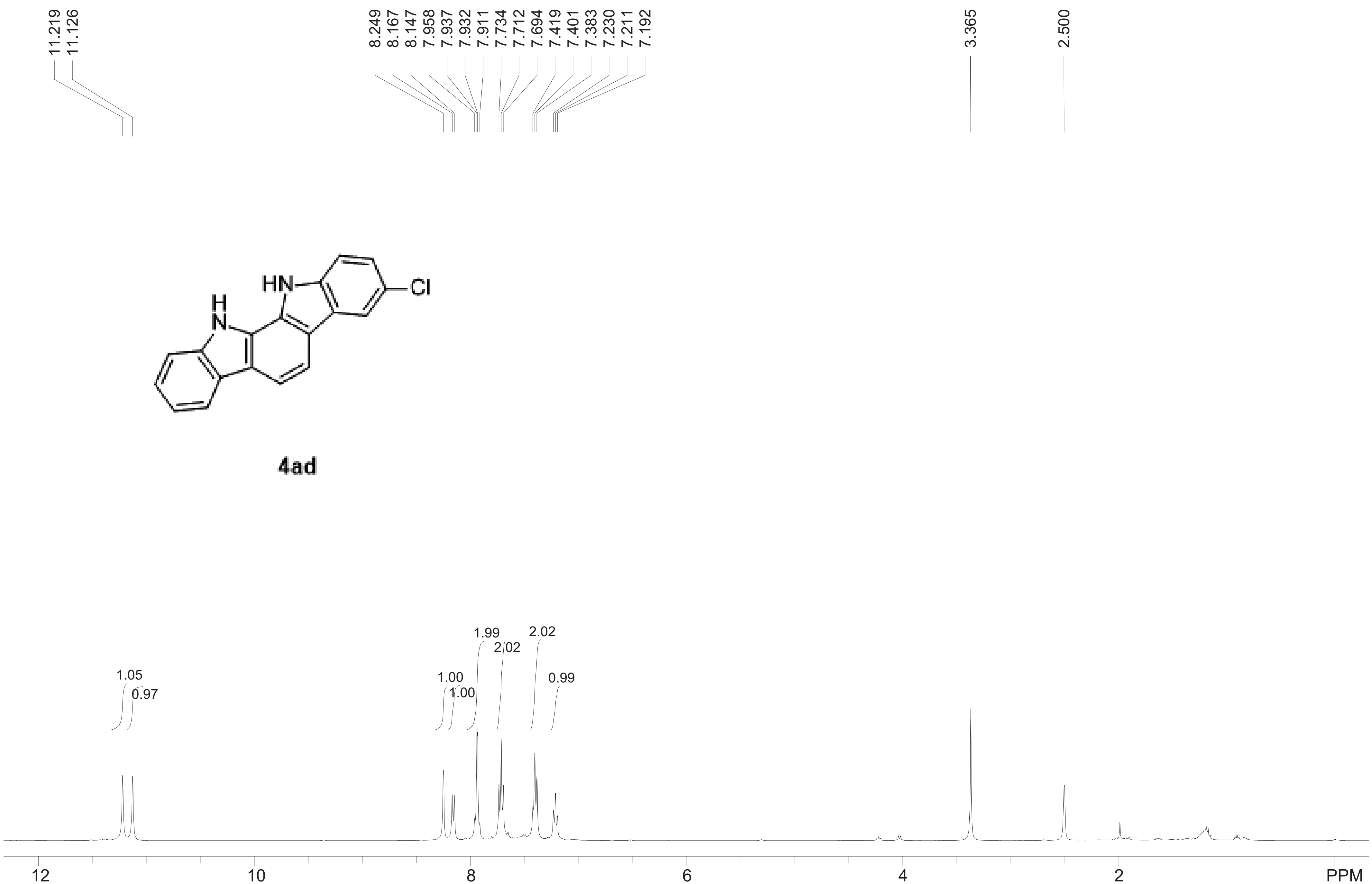
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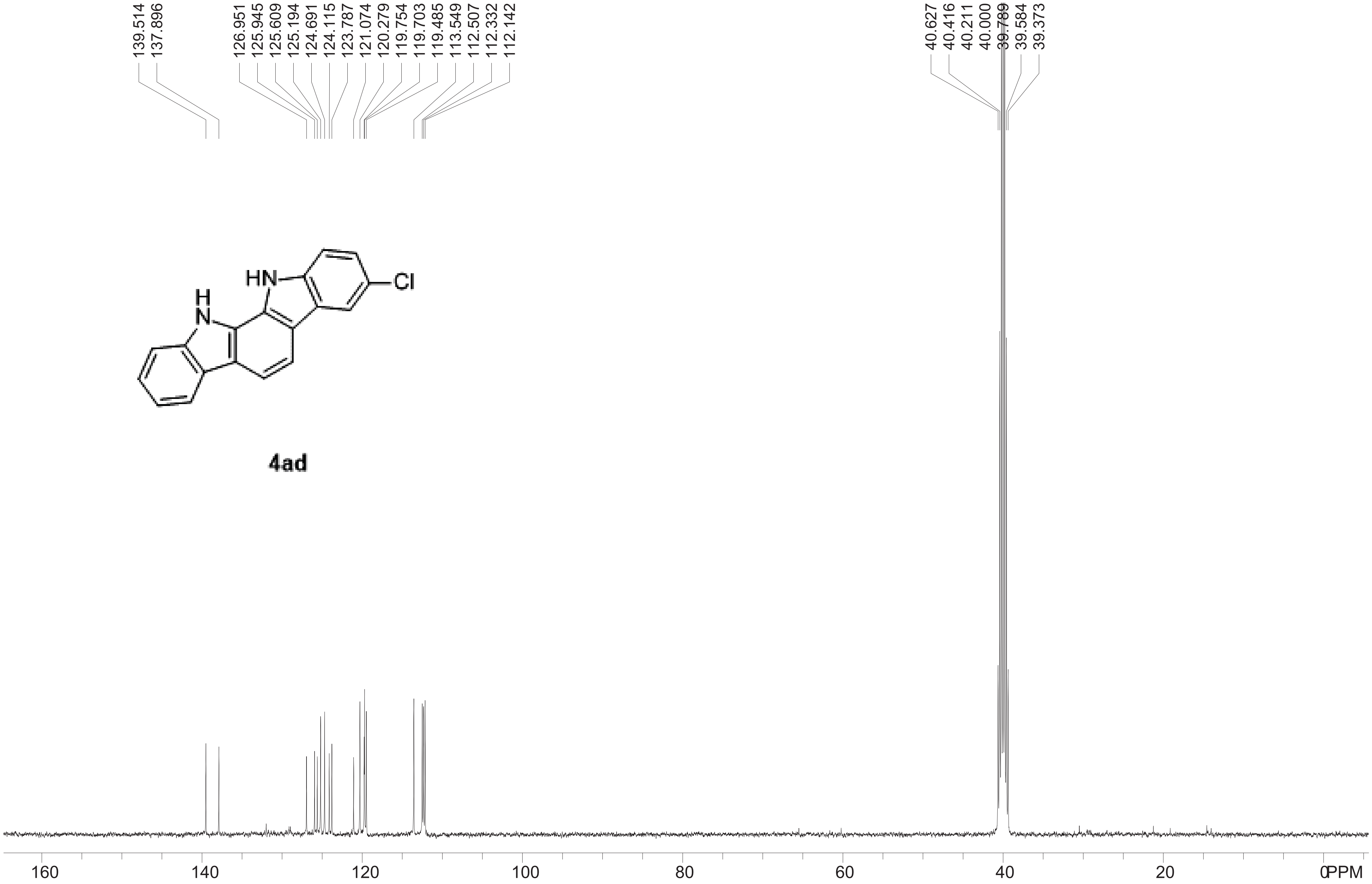
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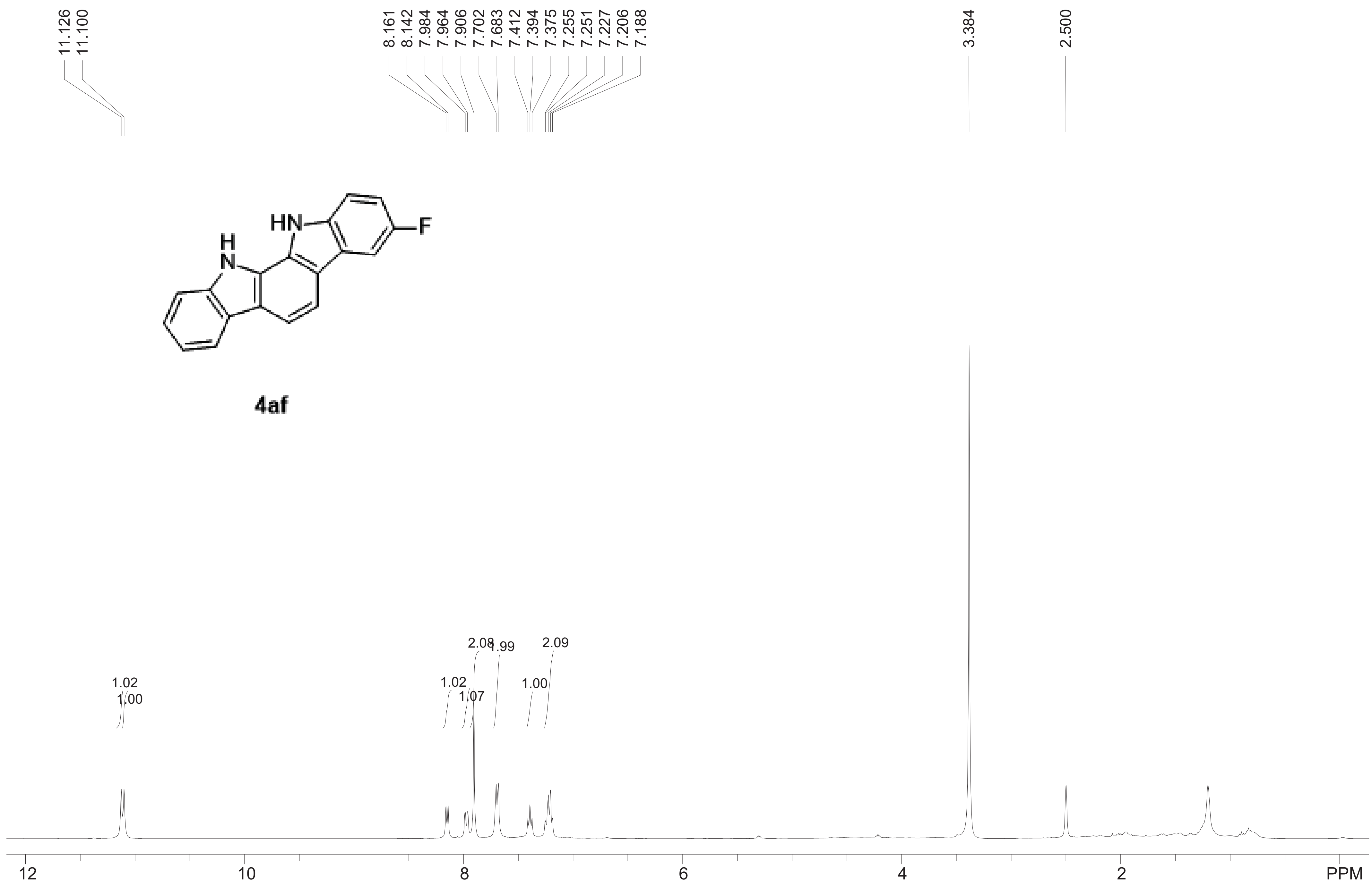
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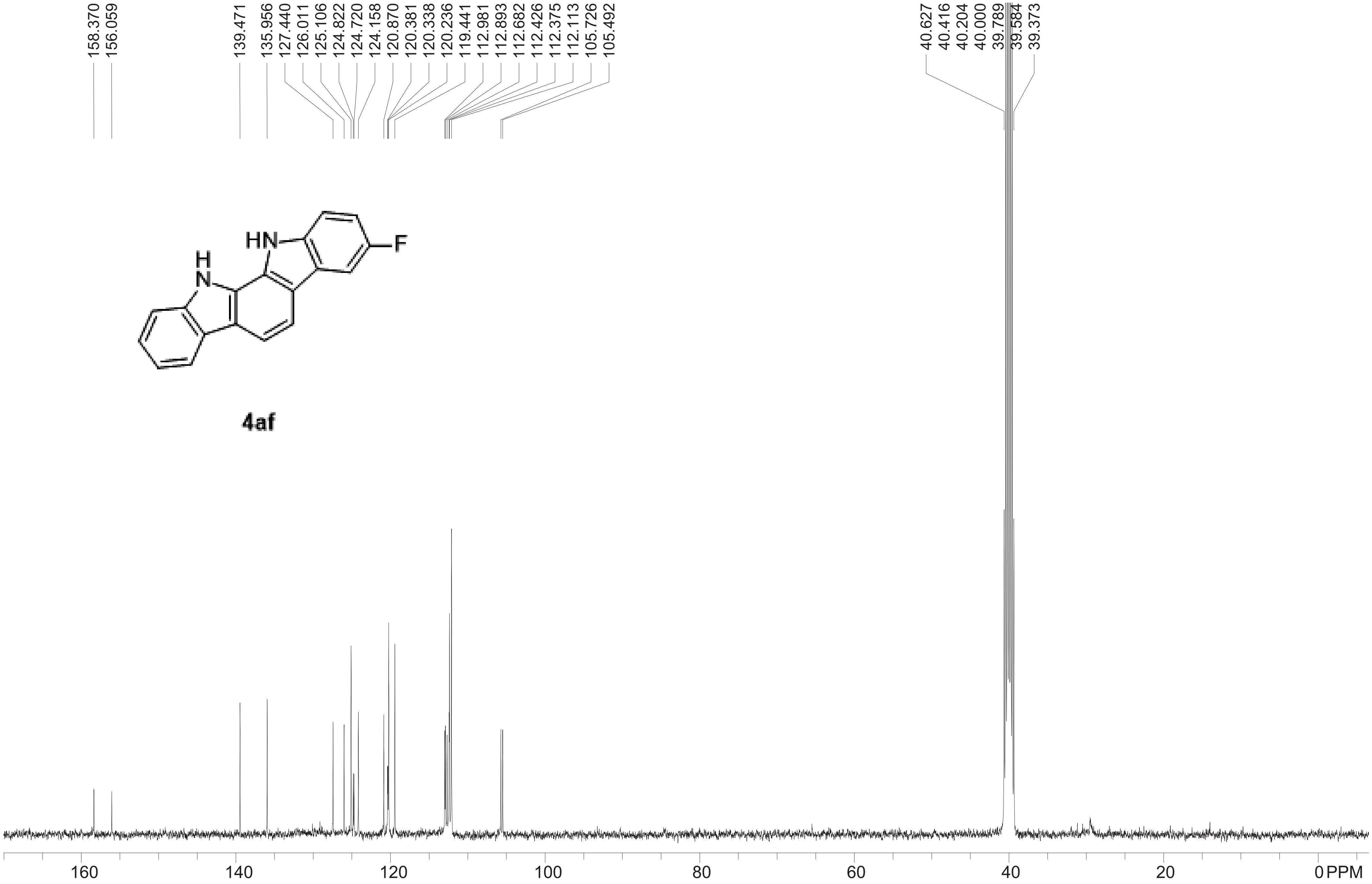
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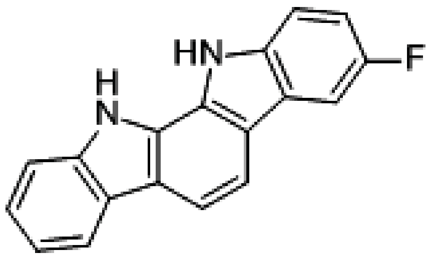

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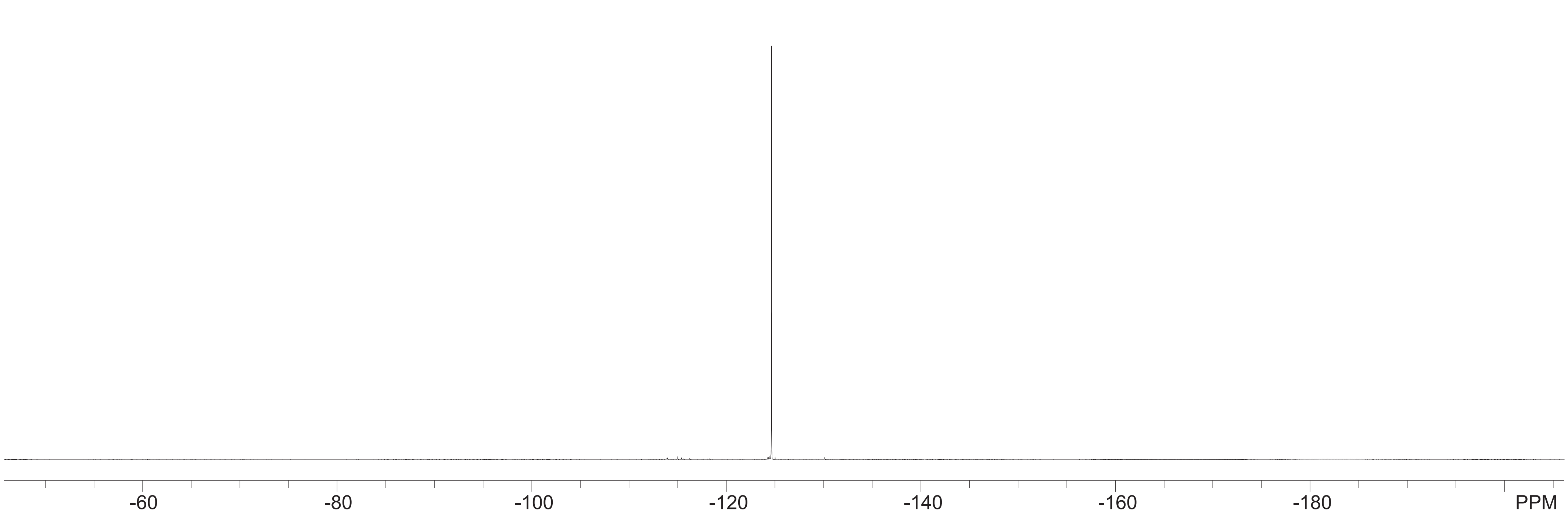

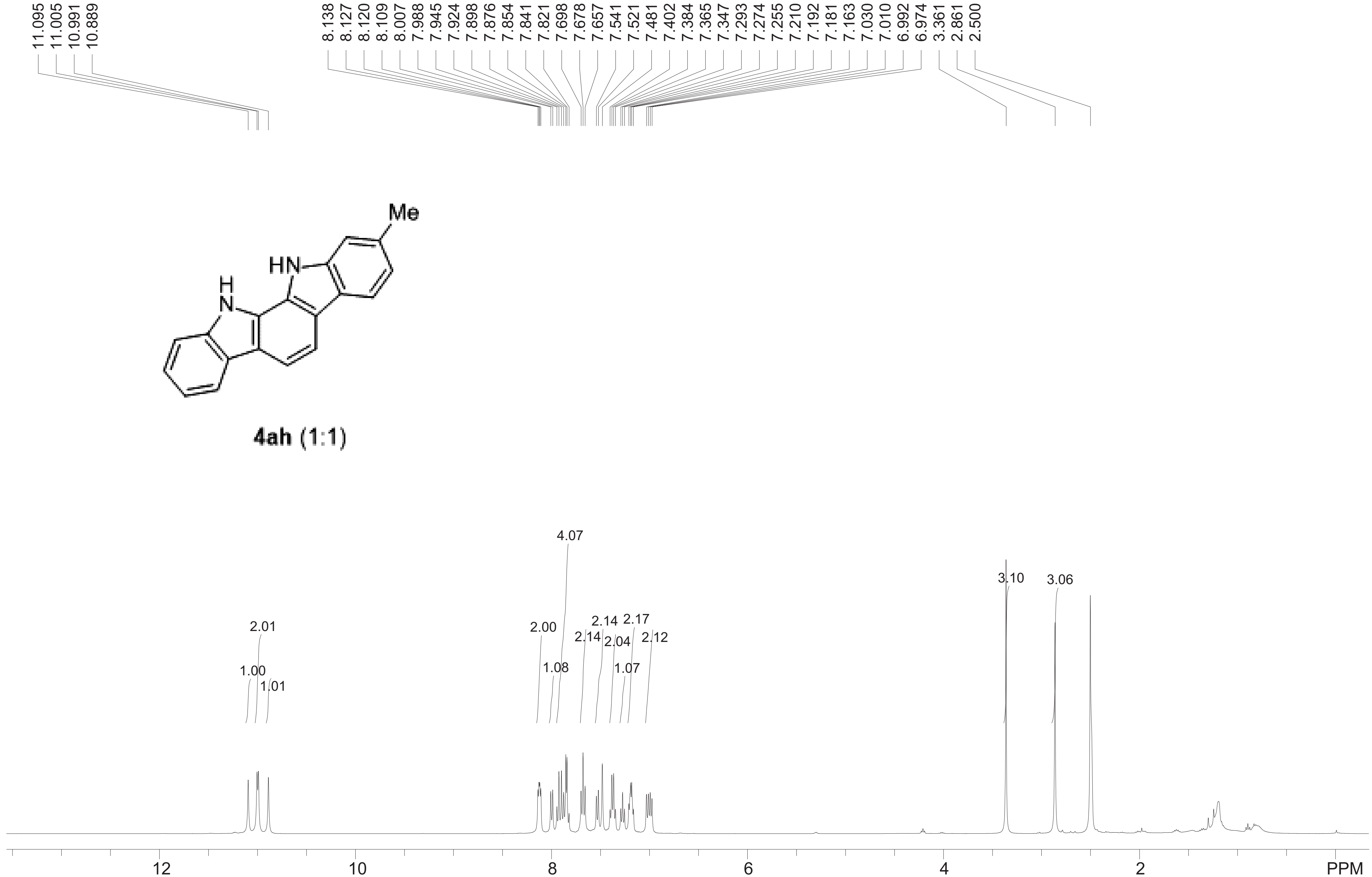
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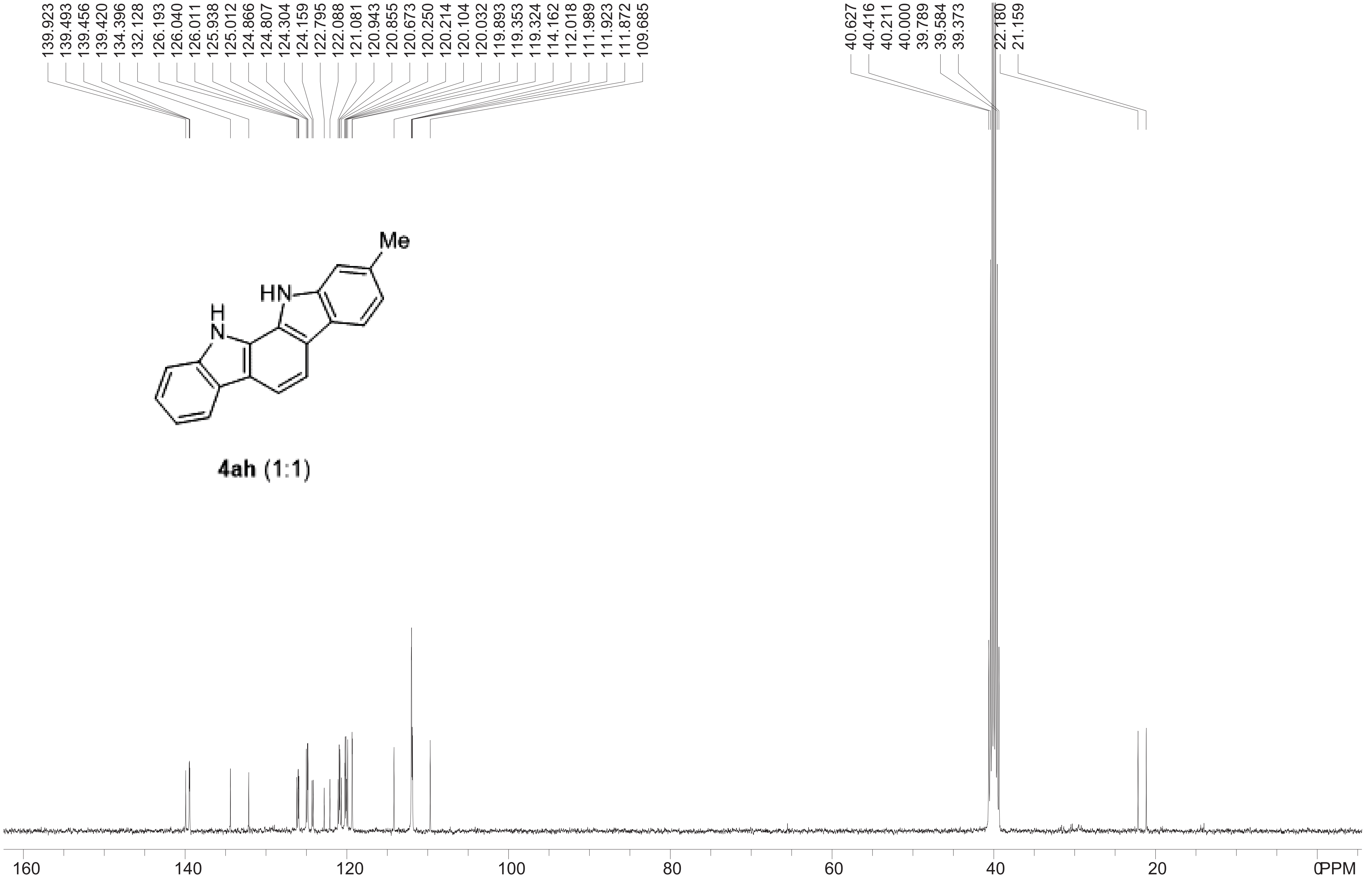
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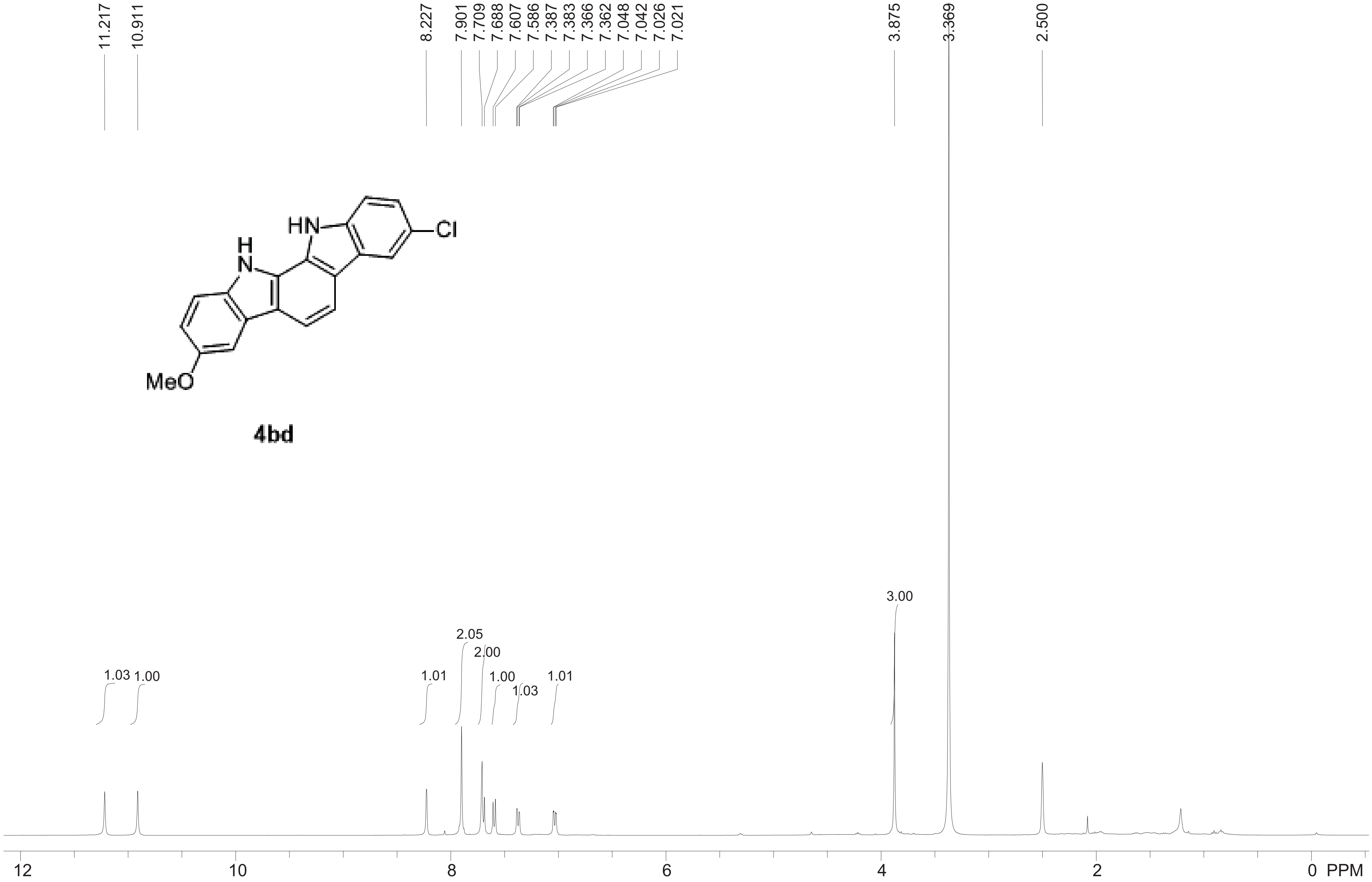
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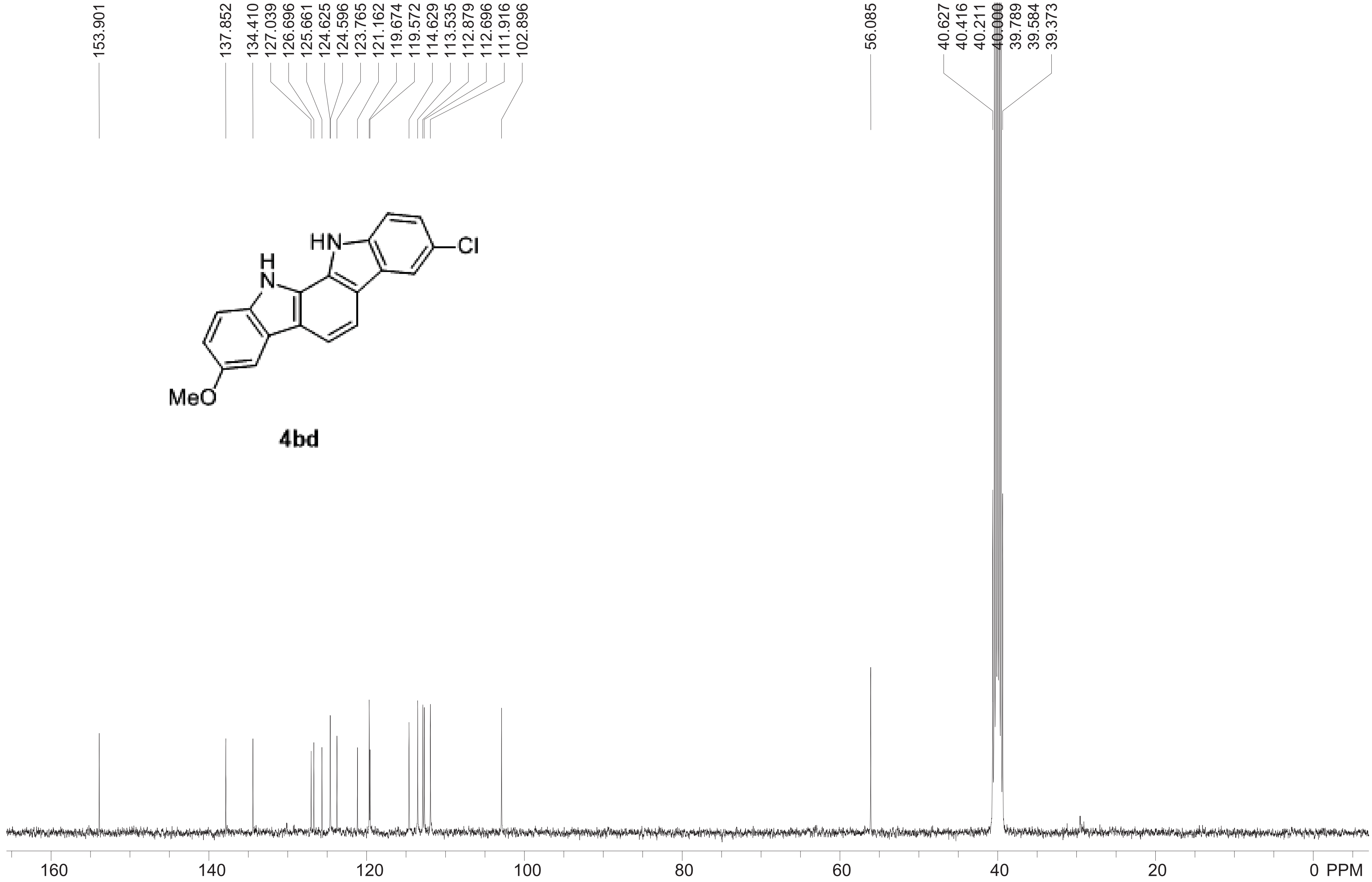
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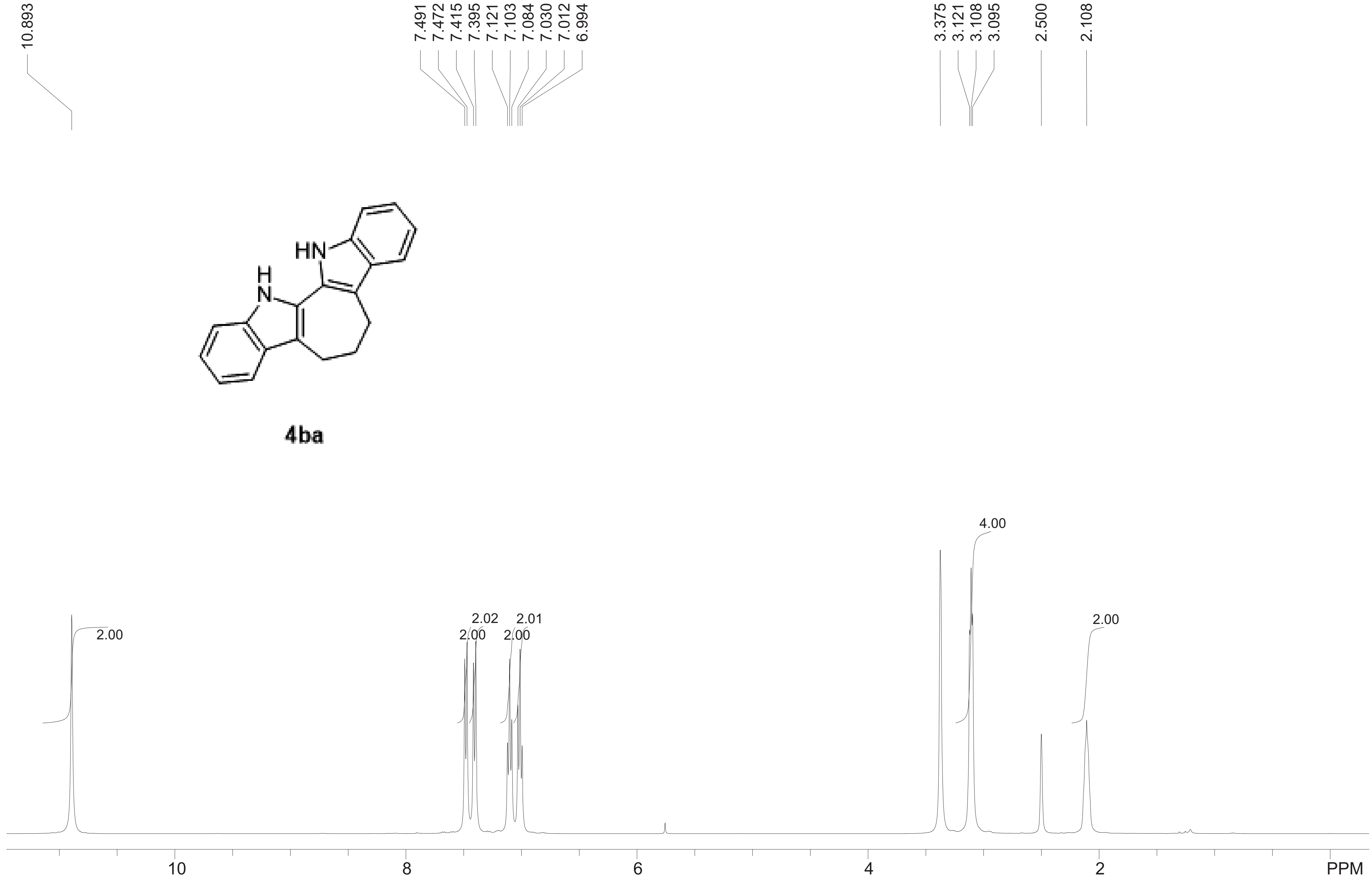
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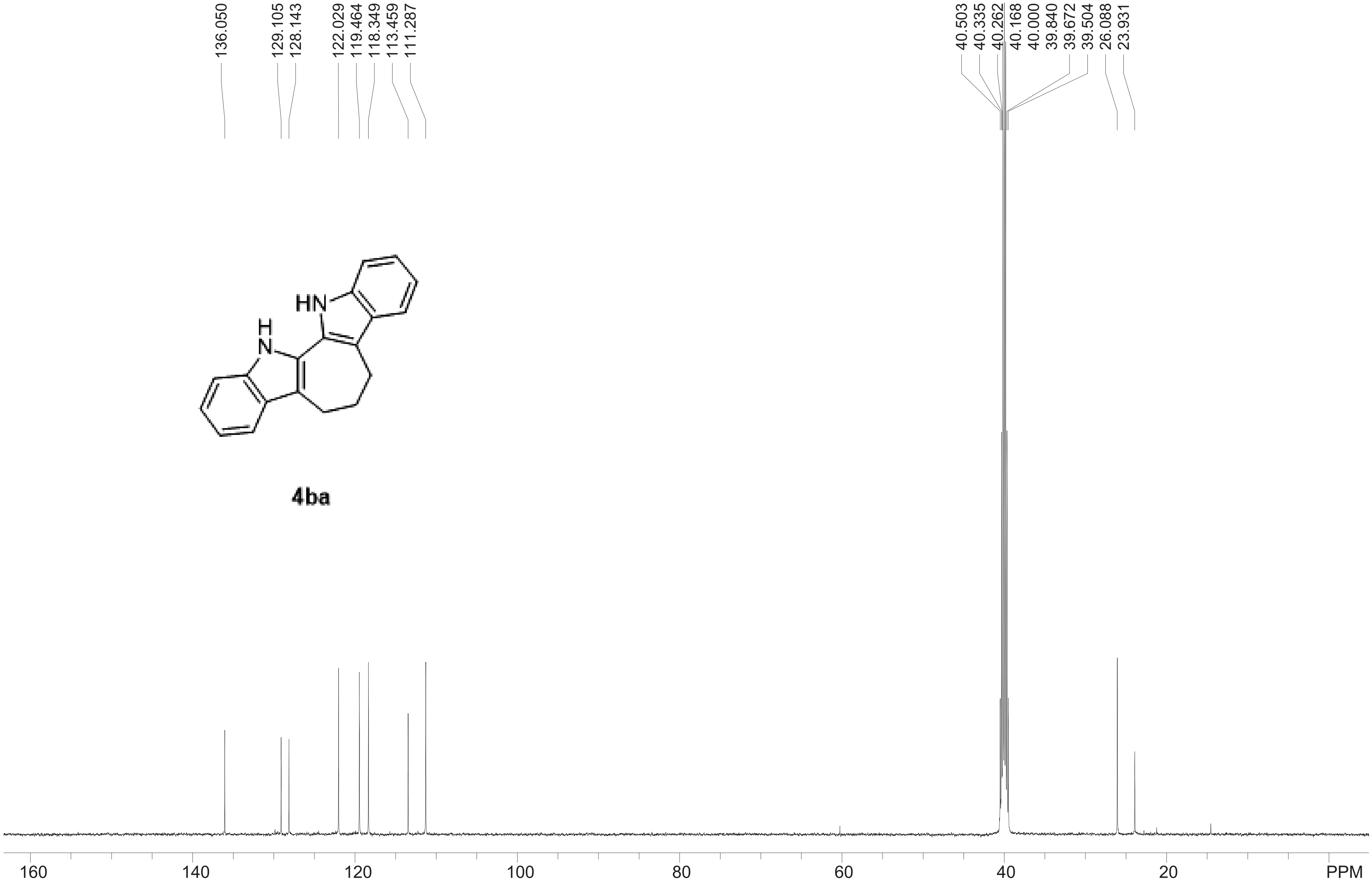
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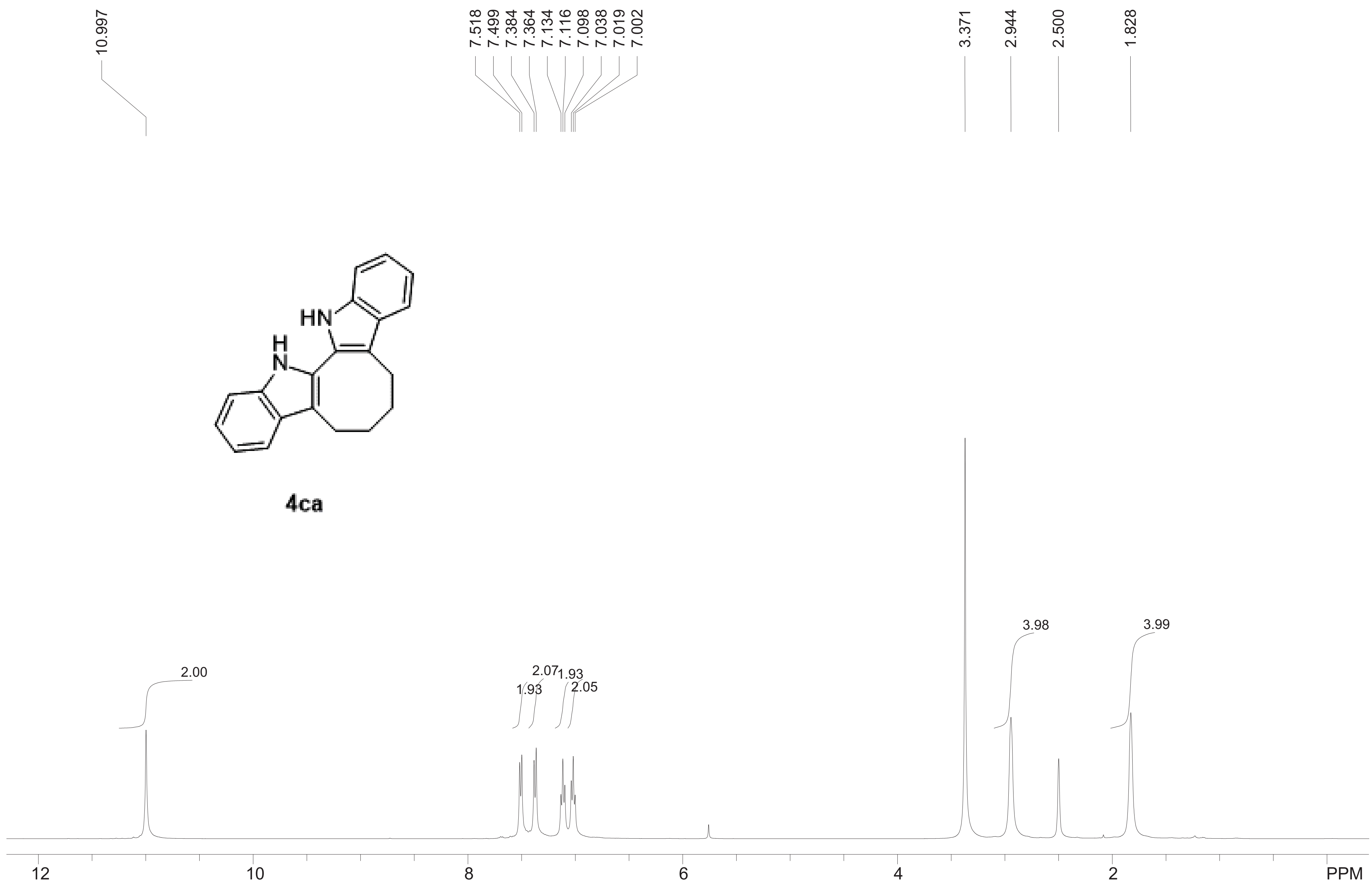
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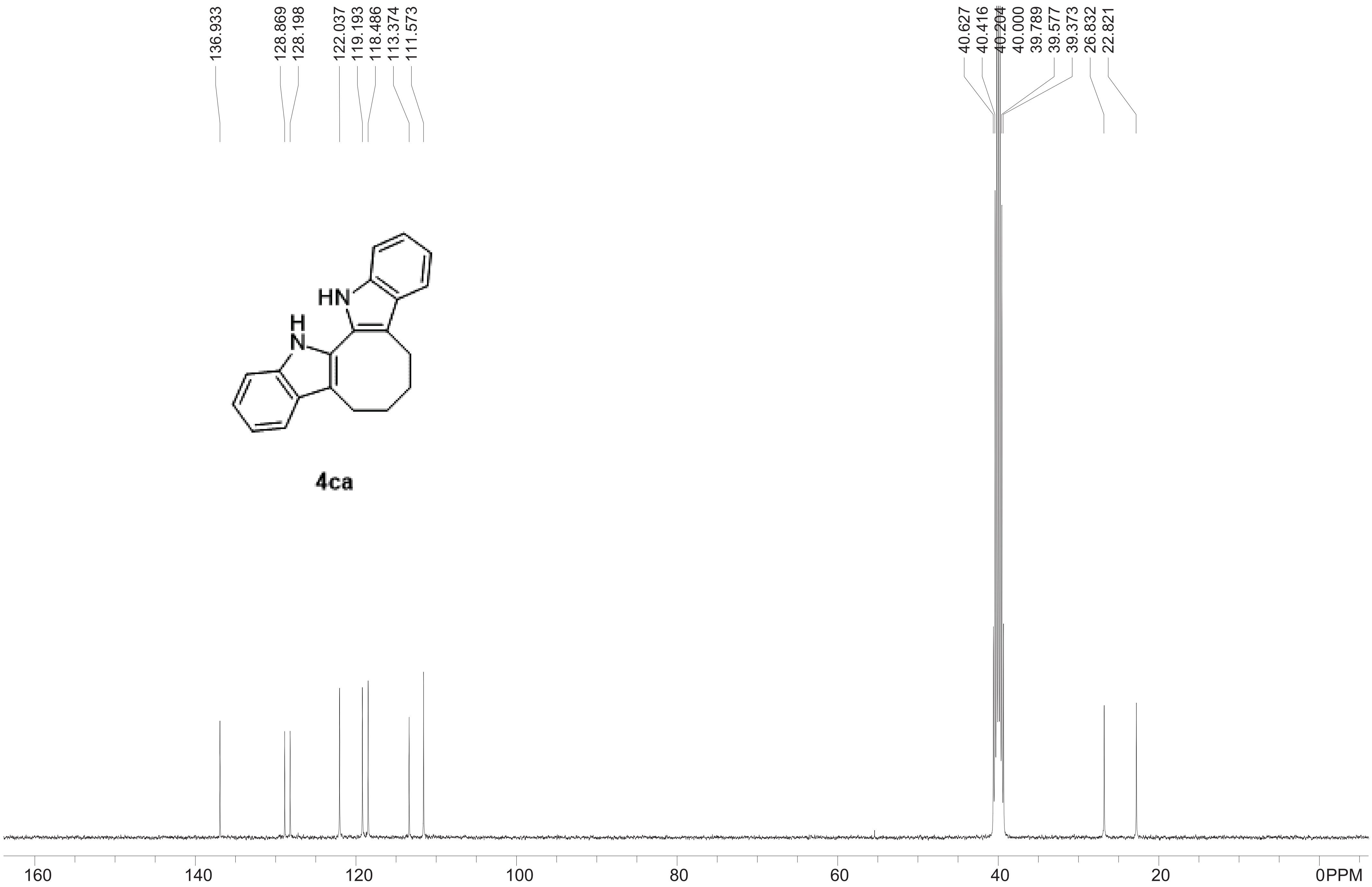
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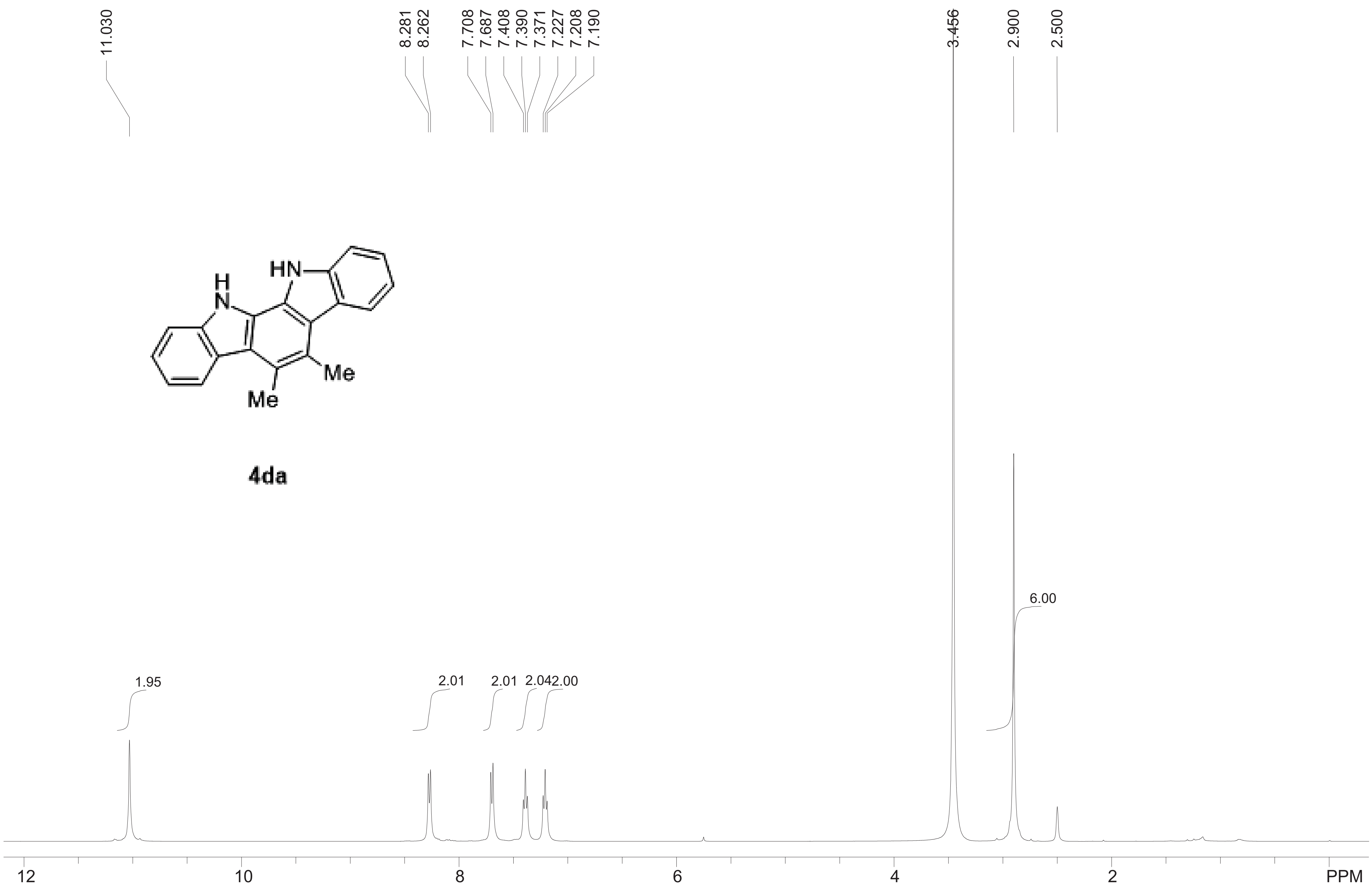
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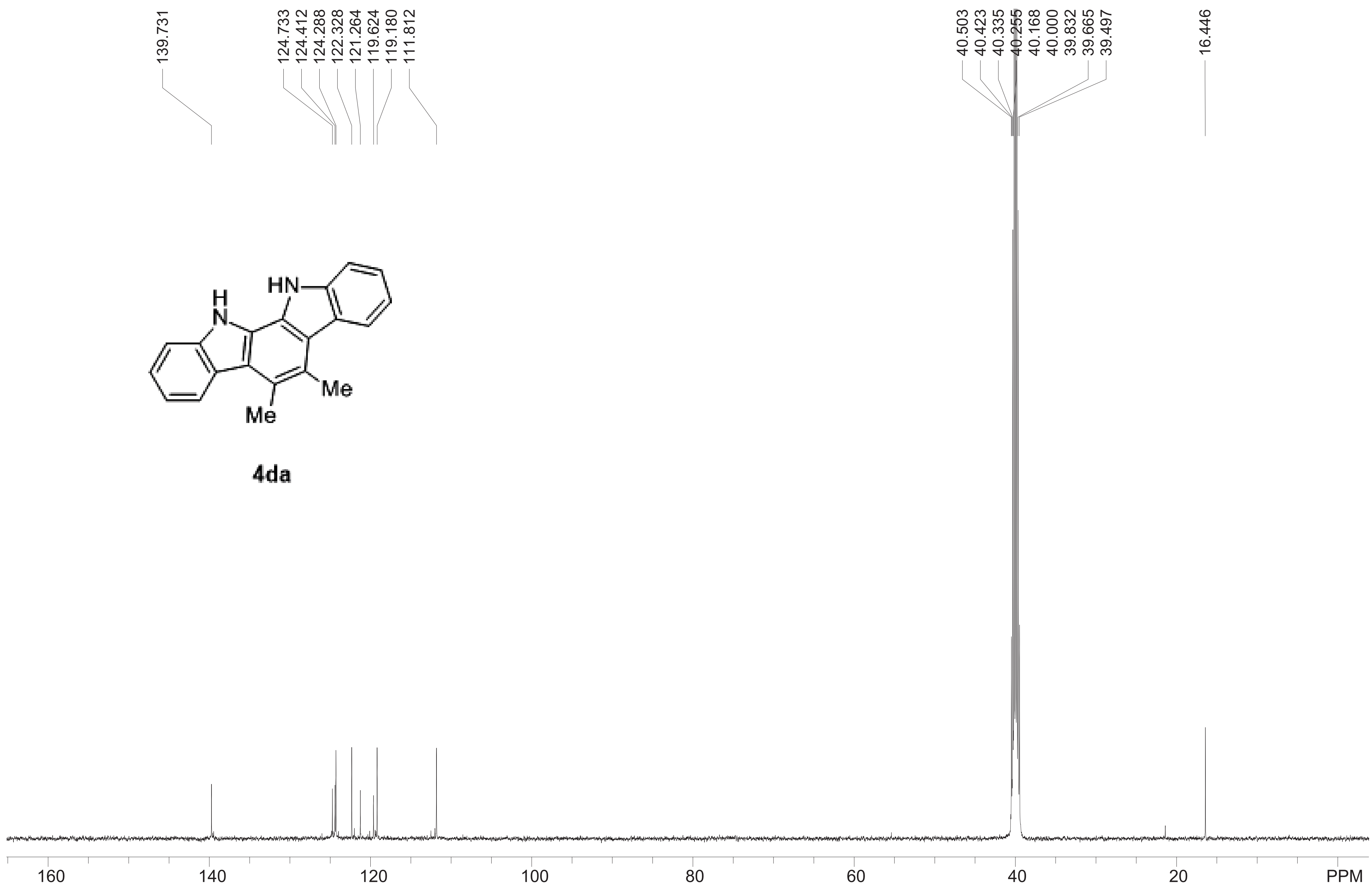
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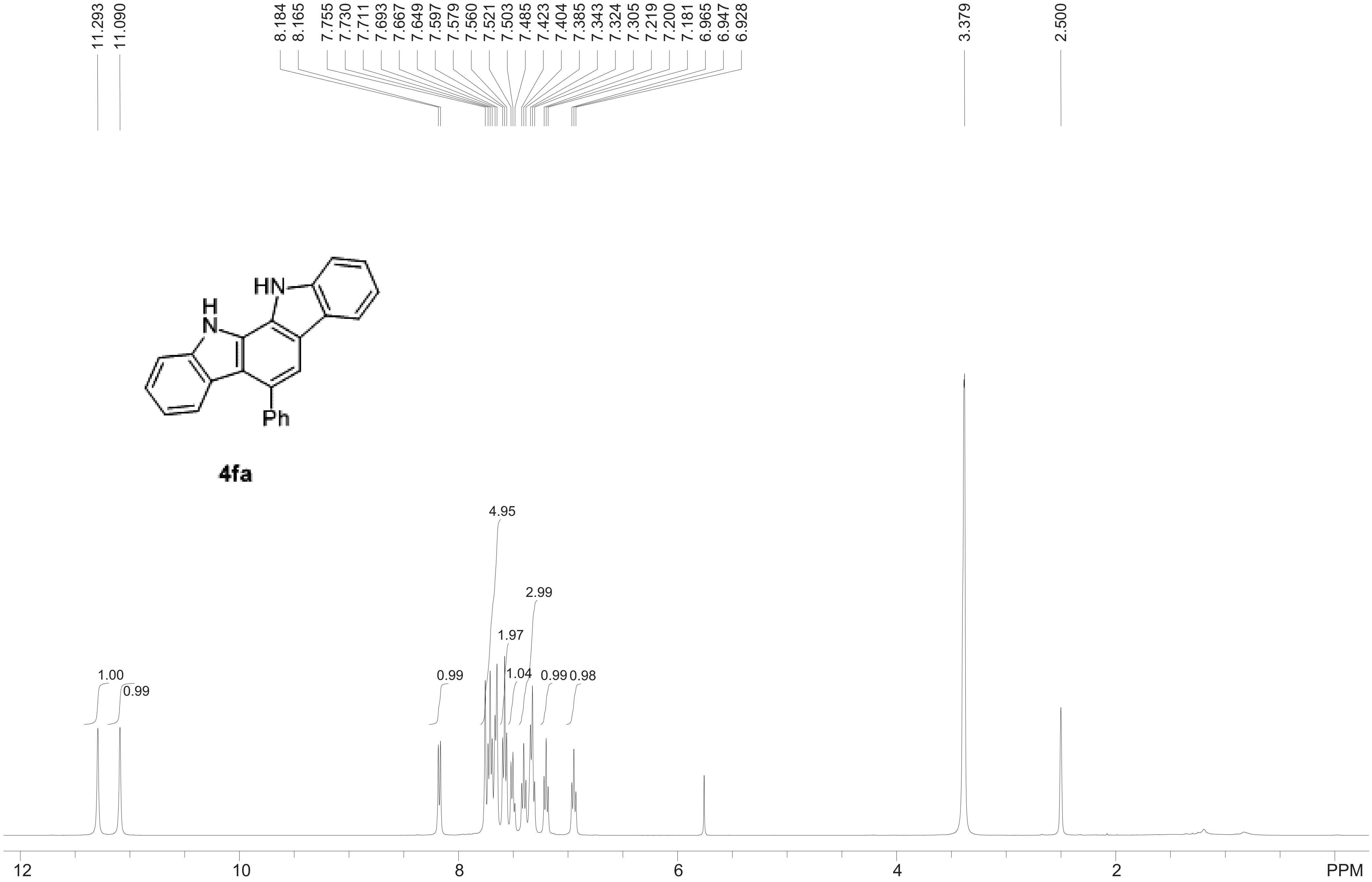
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7.521
7.503
7.485
7.423
7.404
7.385
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7.305
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Ph
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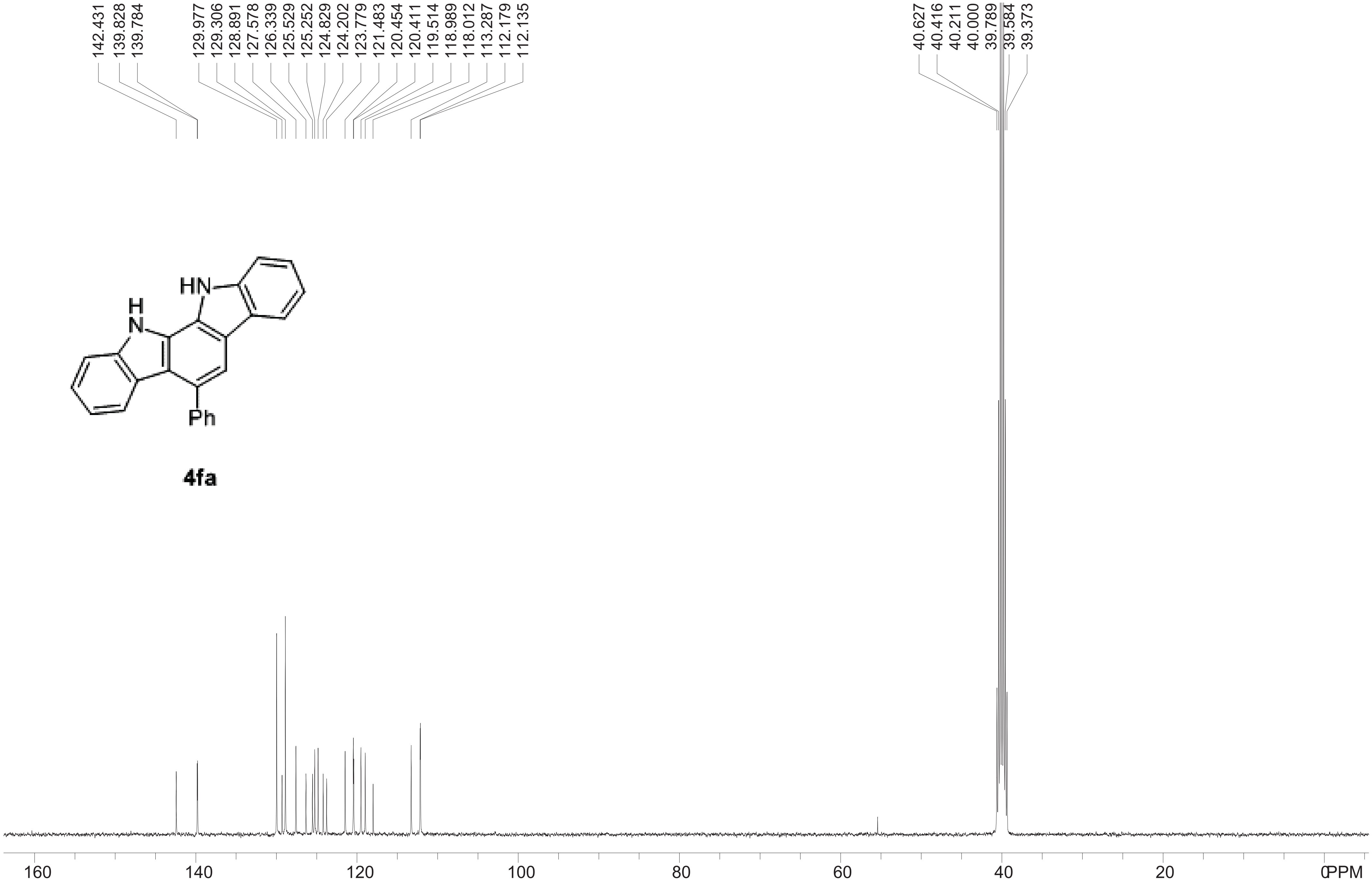
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123.779
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120.454
120.411
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118.989
118.012
113.287
112.179
112.135
40.627
40.416
40.211
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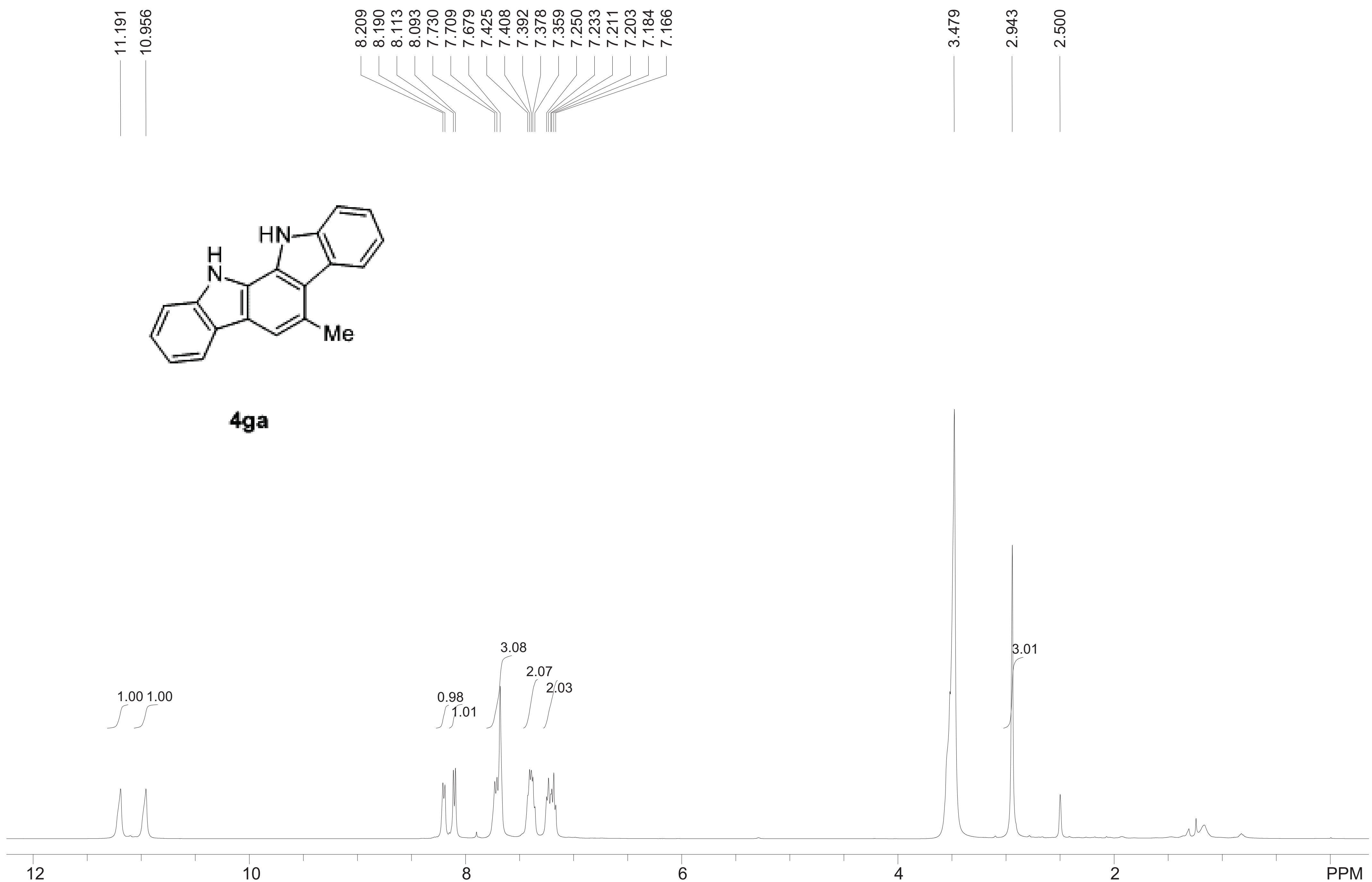

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7.250
7.233
7.211
7.203
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7.166
3.479
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2.500
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H
N
Me
4ga
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8
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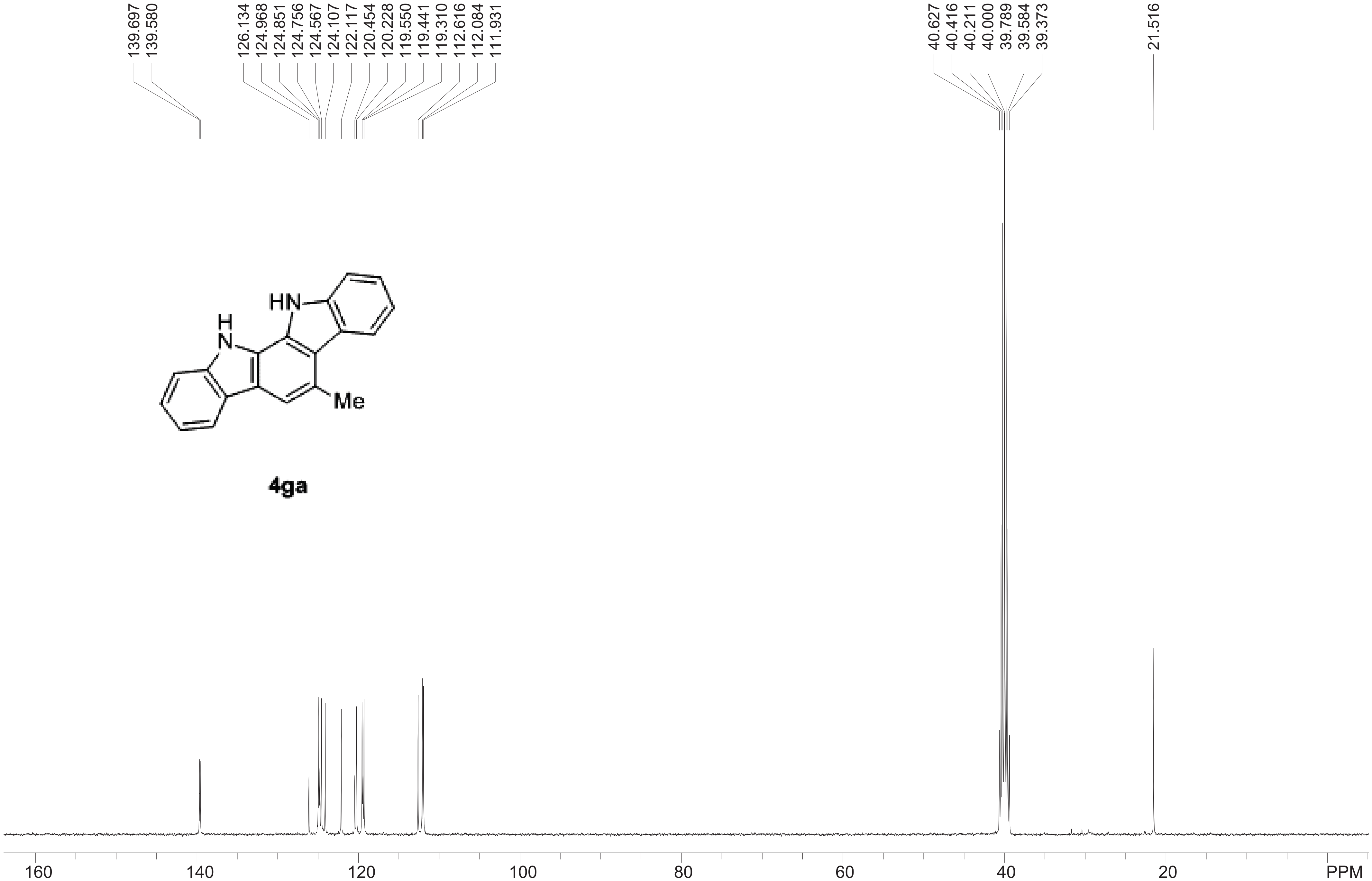
2
PPM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112.616
112.084
111.931
40.627
40.416
40.211
40.000
39.789
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140
120
100
80
60
40
20
PPM
HN
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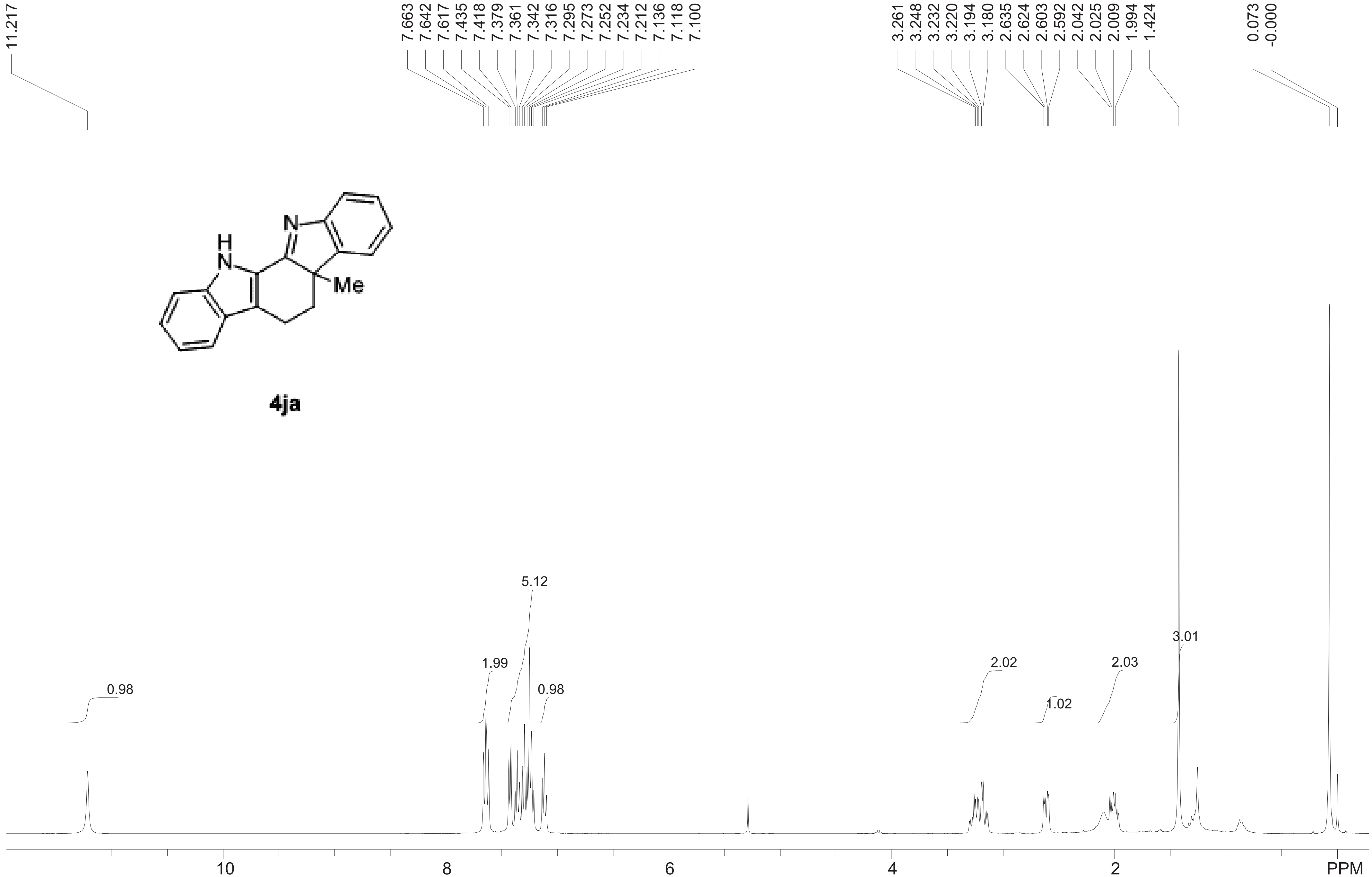
N
Me

4ga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7.212
7.136
7.118
7.100
3.261
3.248
3.232
3.220
3.194
3.180
2.635
2.624
2.603
2.592
2.042
2.025
2.009
1.994
1.424
0.073
-0.000
N
H
N
Me
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3.01
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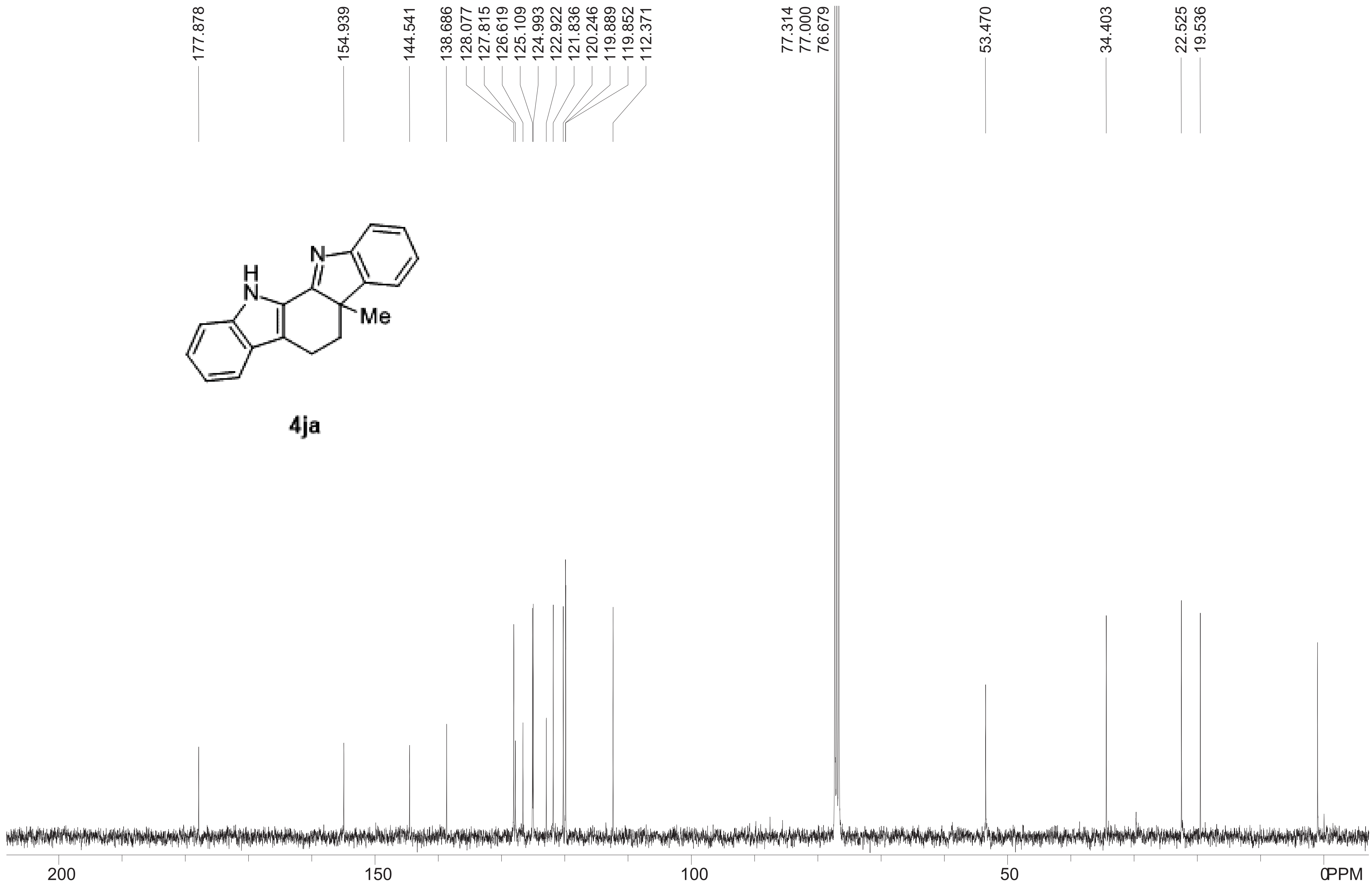
2
PPM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77.314
77.000
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4ja
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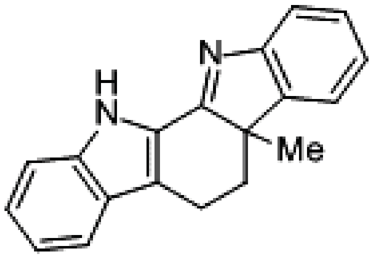
PPM



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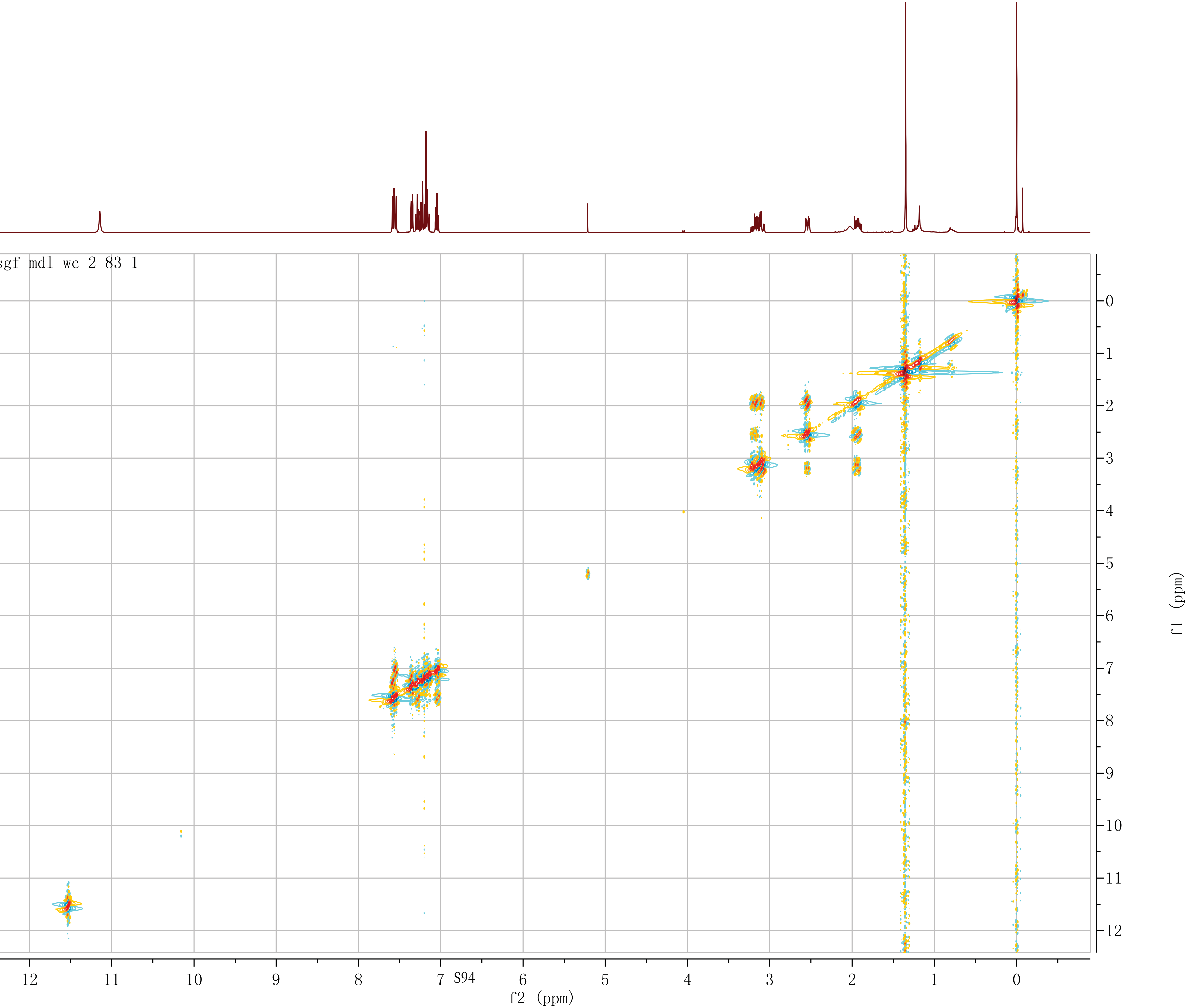

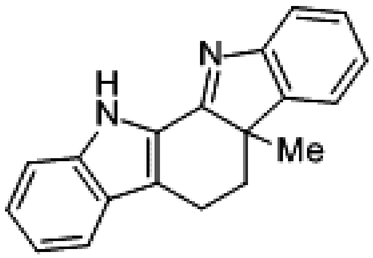

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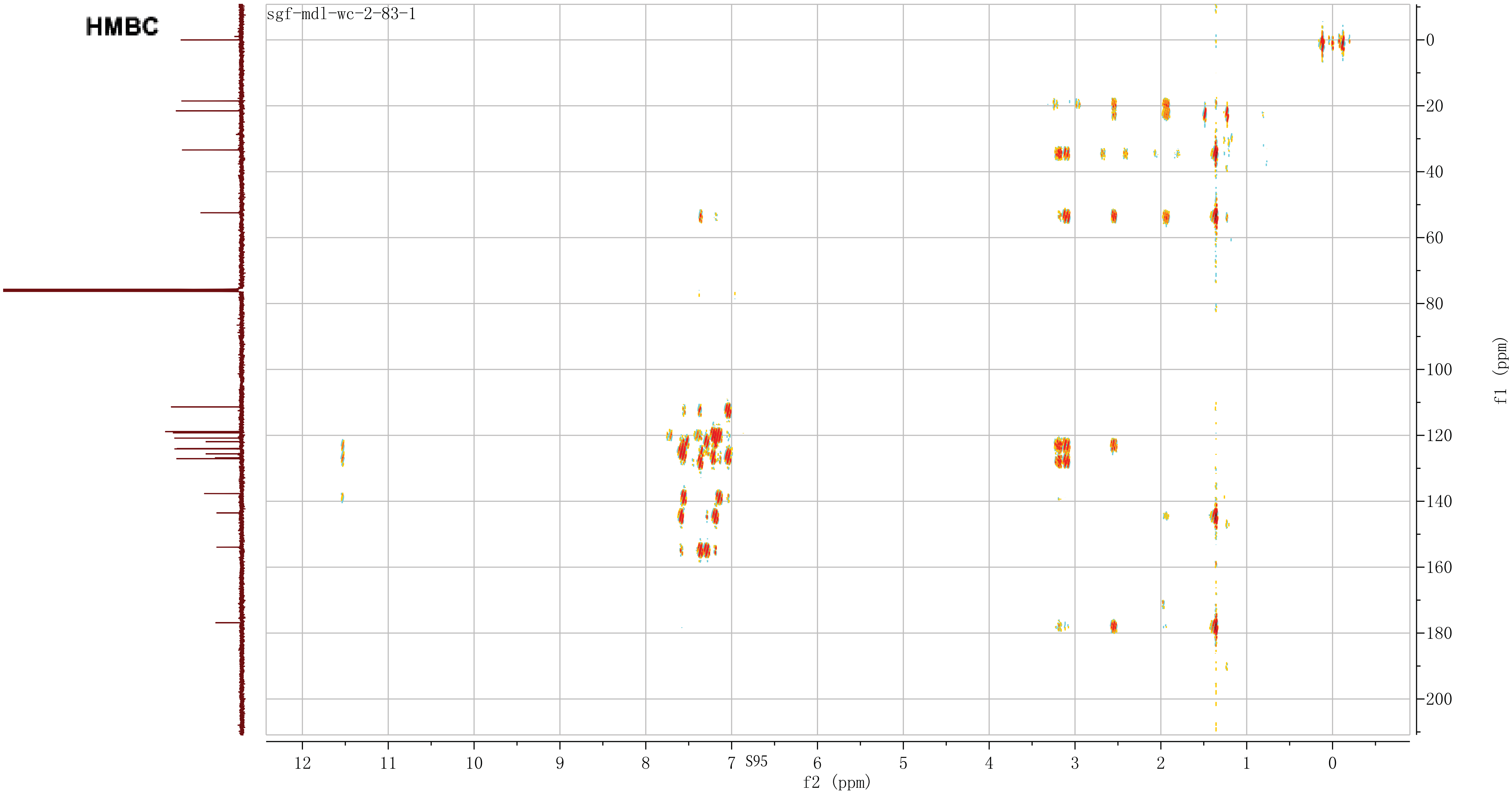
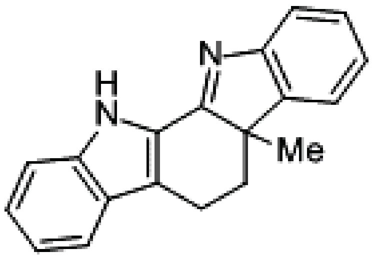
HMBC





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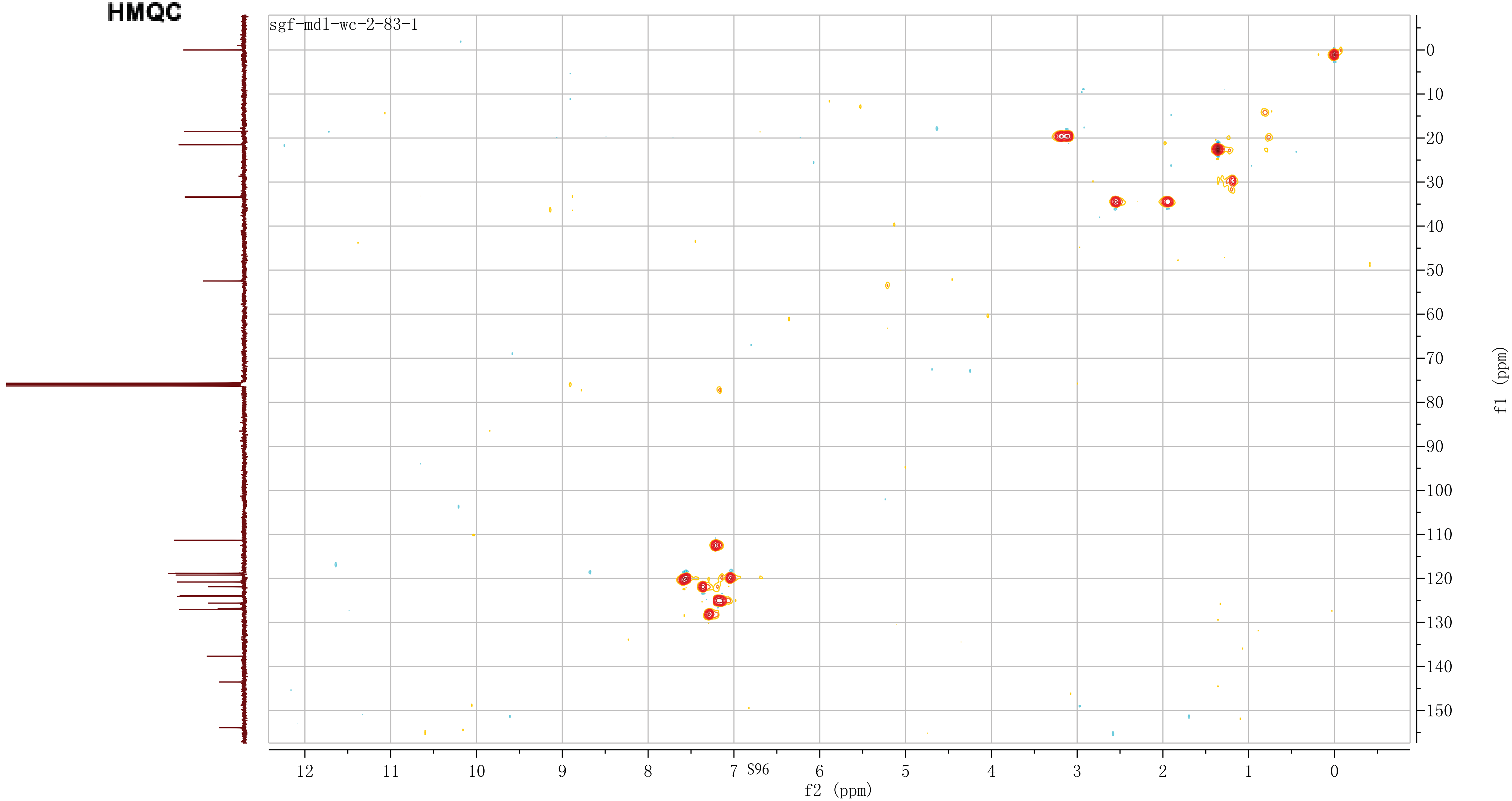
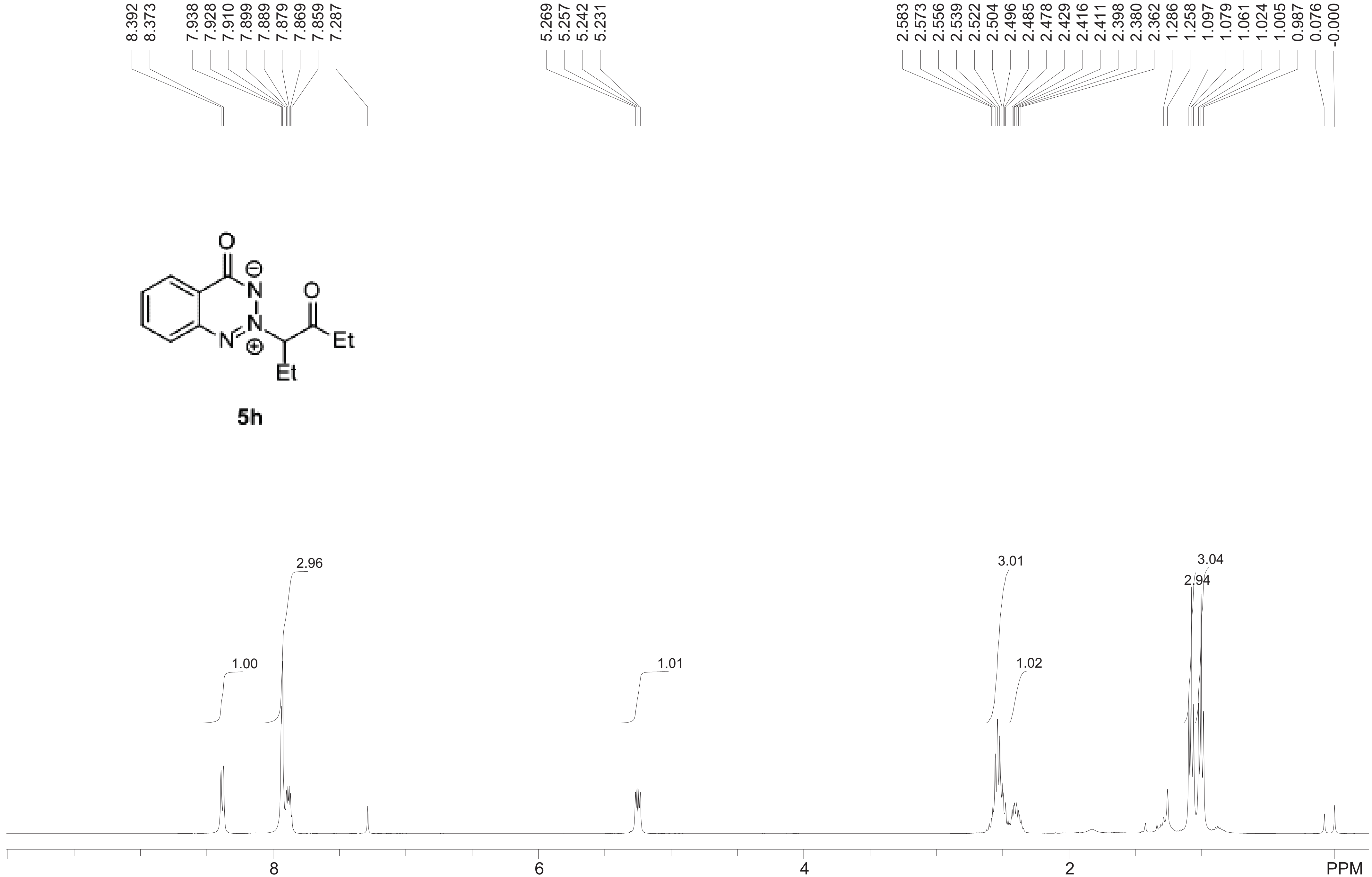
HMQC

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5.269
5.257
5.242
5.231
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2.573
2.556
2.539
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2.504
2.496
2.485
2.478
2.429
2.416
2.411
2.398
2.380
2.362
1.286
1.258
1.097
1.079
1.061
1.024
1.005
0.987
0.076
-0.000
O
N
N
N
O
Et
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3.01
1.02
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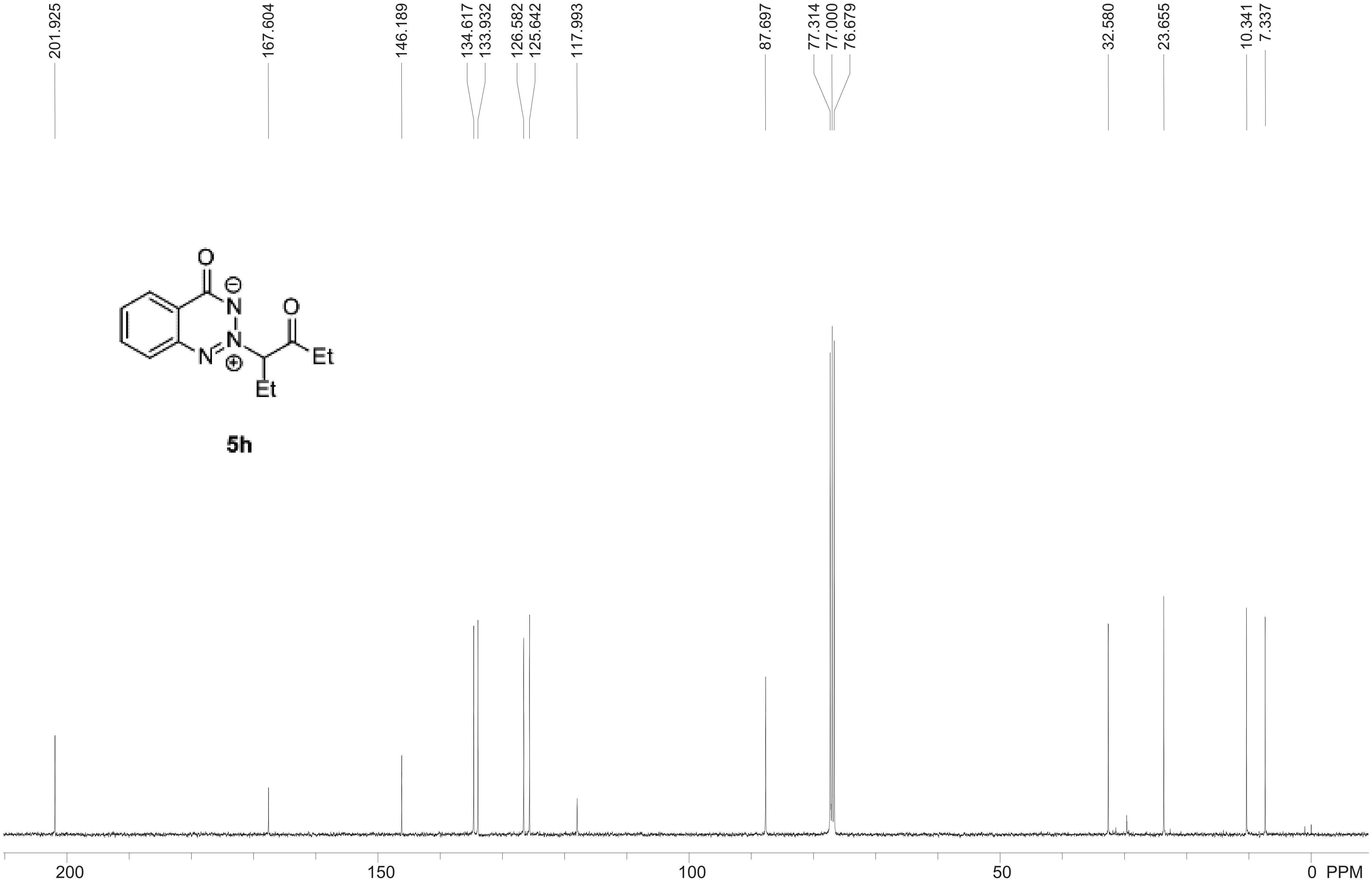
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133.932
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117.993
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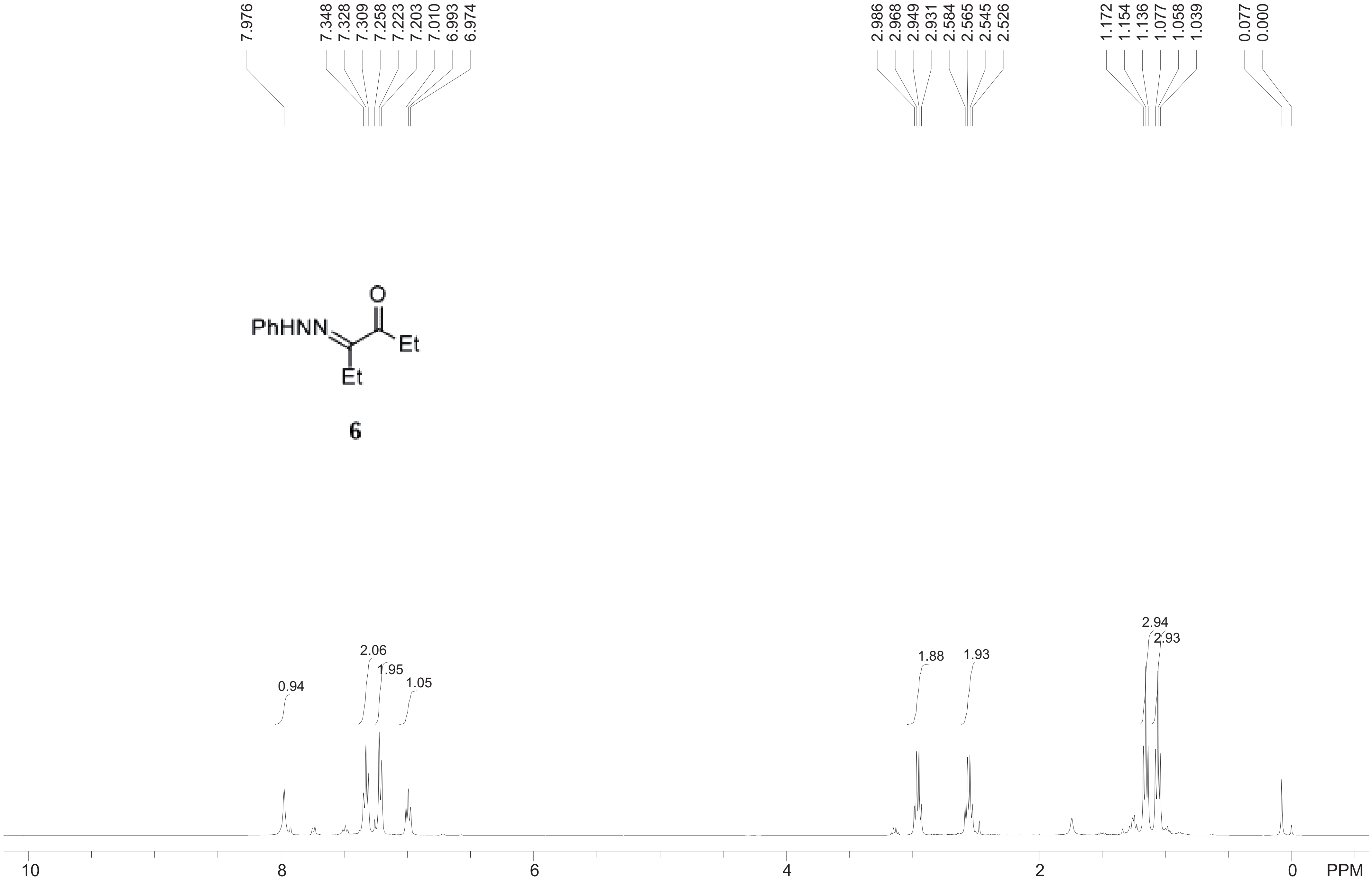
200
150
100
50
0 PPM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7.223
7.203
7.010
6.993
6.974
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2.968
2.949
2.931
2.584
2.565
2.545
2.526
1.172
1.154
1.136
1.077
1.058
1.039
0.077
0.000
PhHNN
O
Et
Et
6
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1.05
1.88
1.93
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10
8
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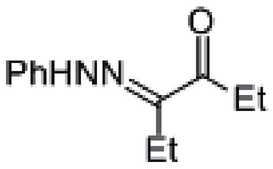
4
2
0
PPM



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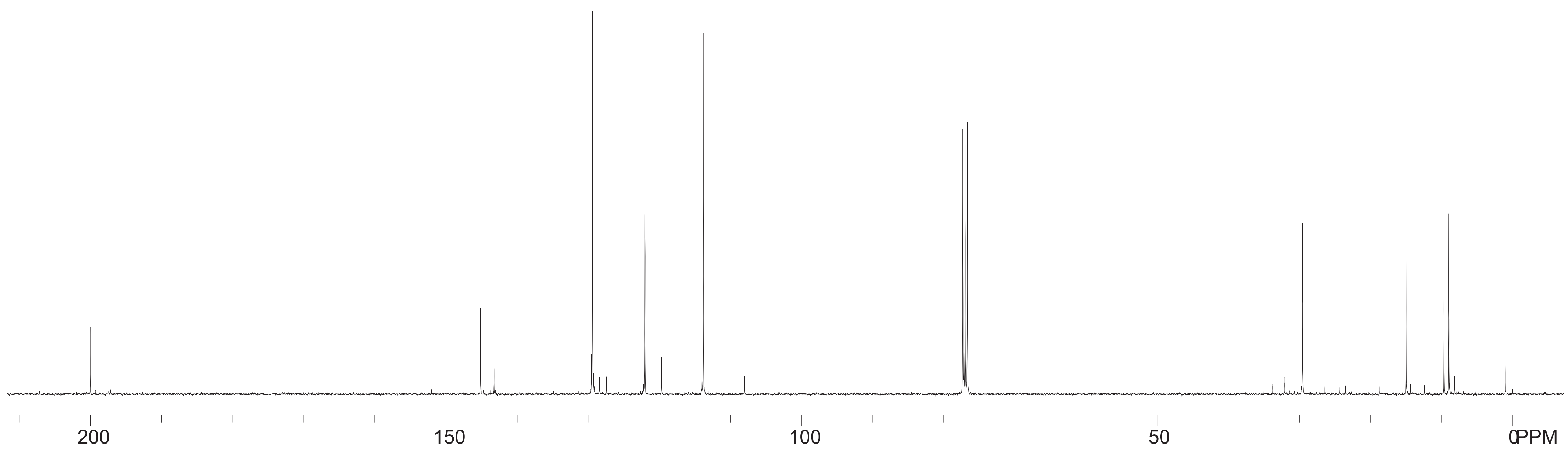
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77.000
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29.503
14.927
9.590
8.905
200
150
100
50
0
PPM


9.027
7.623
7.604
7.384
7.322
7.262
7.156
7.137
7.119
6.097
3.523
3.510
3.499
3.488
3.172
3.157
3.141
2.248
2.224
2.209
2.194
0.070
0.000
NH
N
H
O
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2.09
0.99
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1.98
2.05
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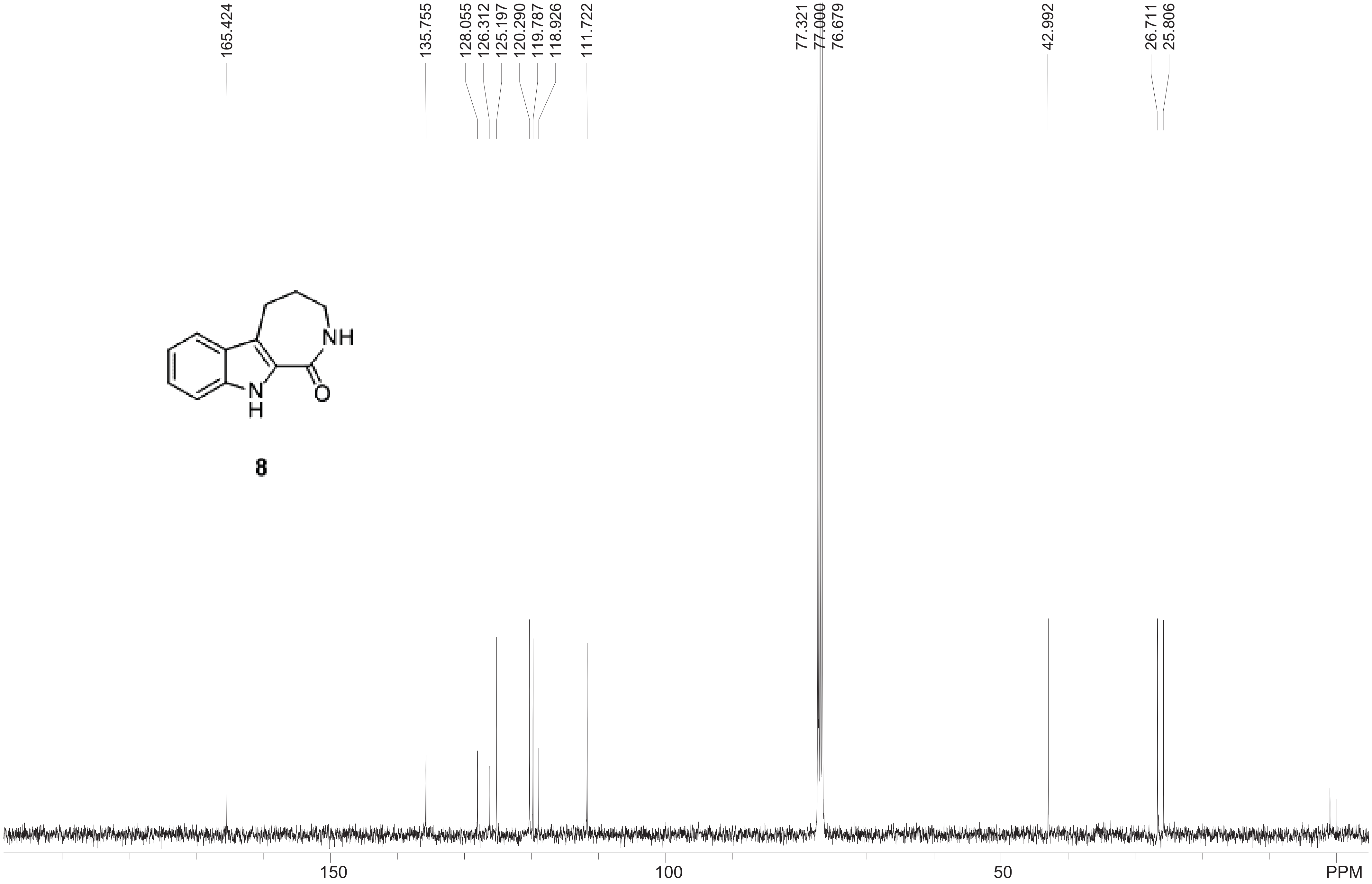
6
4
2
0
PPM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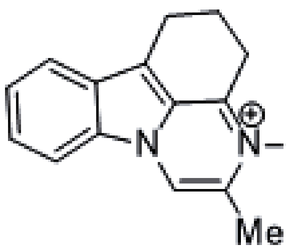
100
50
PPM

8



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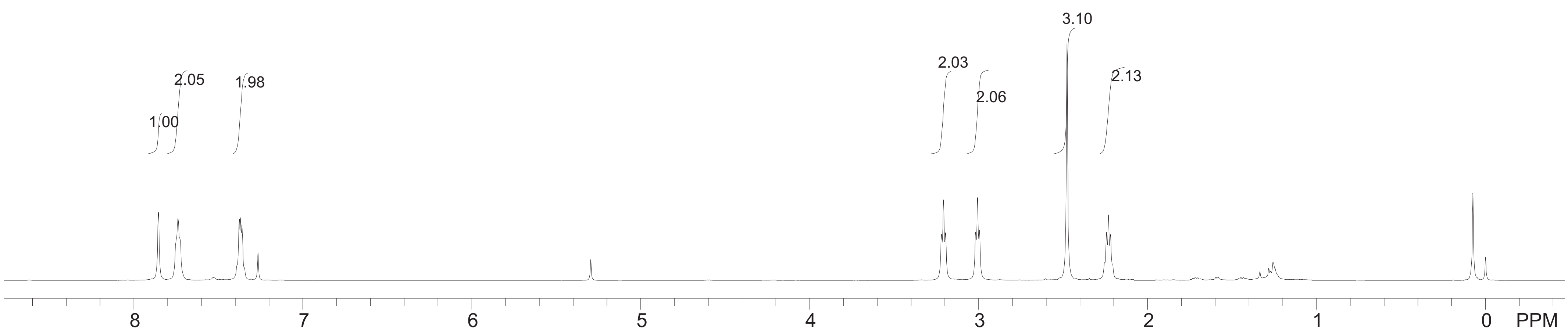
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3.209
3.196
3.019
3.007
2.995
2.477
2.244
2.232
2.220
0.074
-0.001
1.00
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2.06
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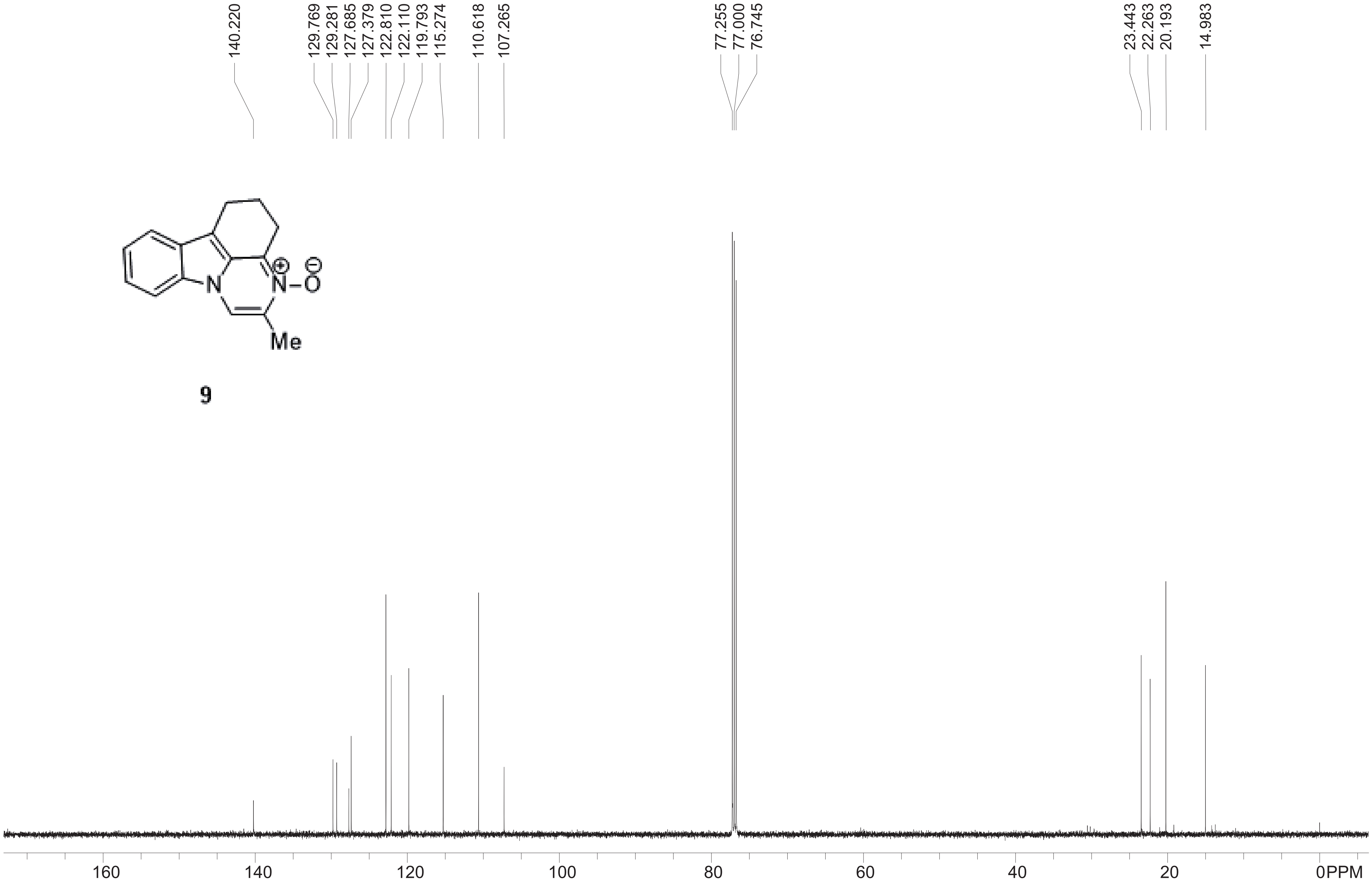
PPM



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110.618
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77.000
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40
20
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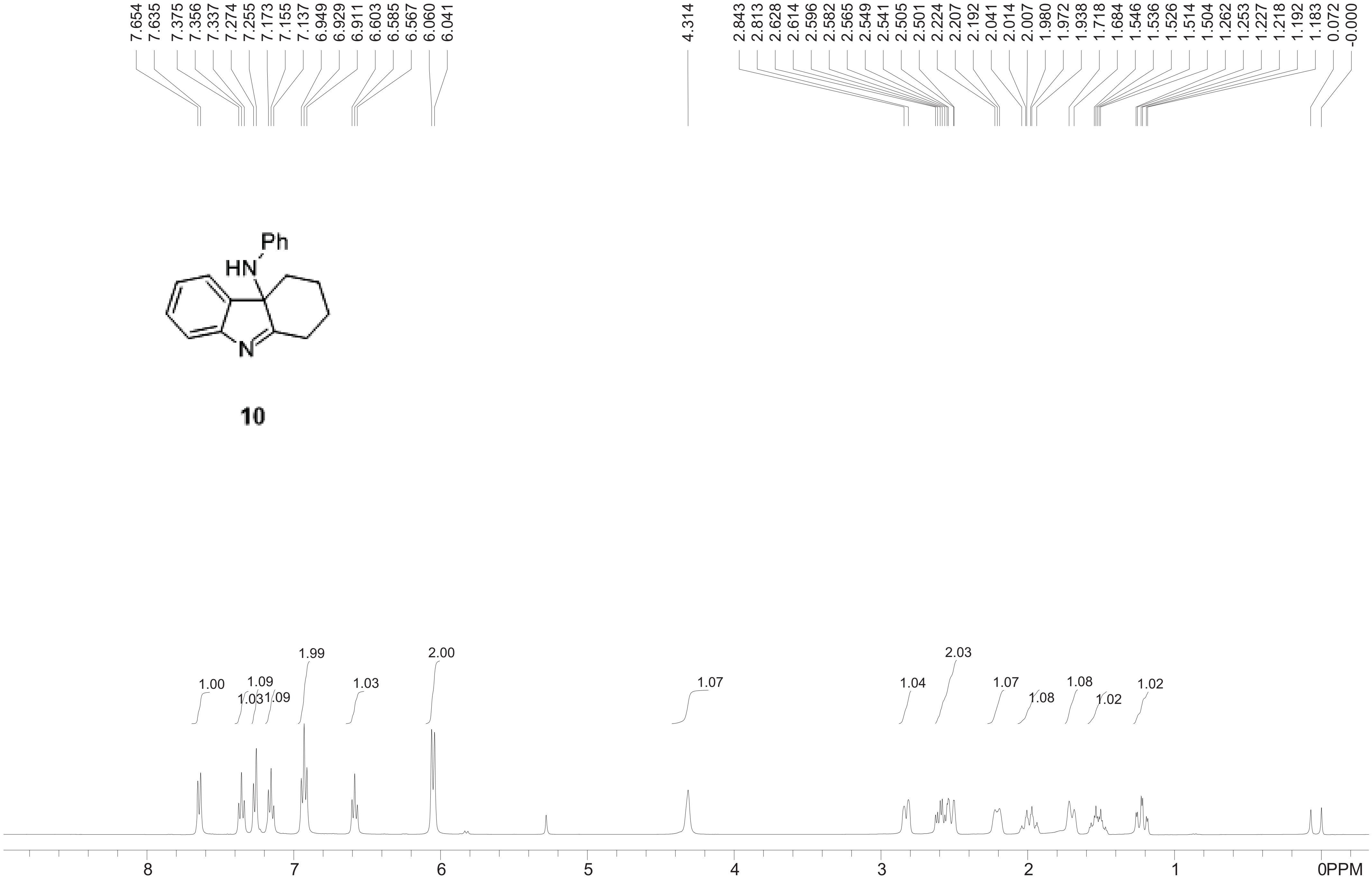
9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6.929
6.911
6.603
6.585
6.567
6.060
6.041
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2.843
2.813
2.628
2.614
2.596
2.582
2.565
2.549
2.541
2.505
2.501
2.224
2.207
2.192
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Ph
HN
N
10
1.00
1.09
1.03
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1.03
2.00
1.07
1.04
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1.08
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6
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2
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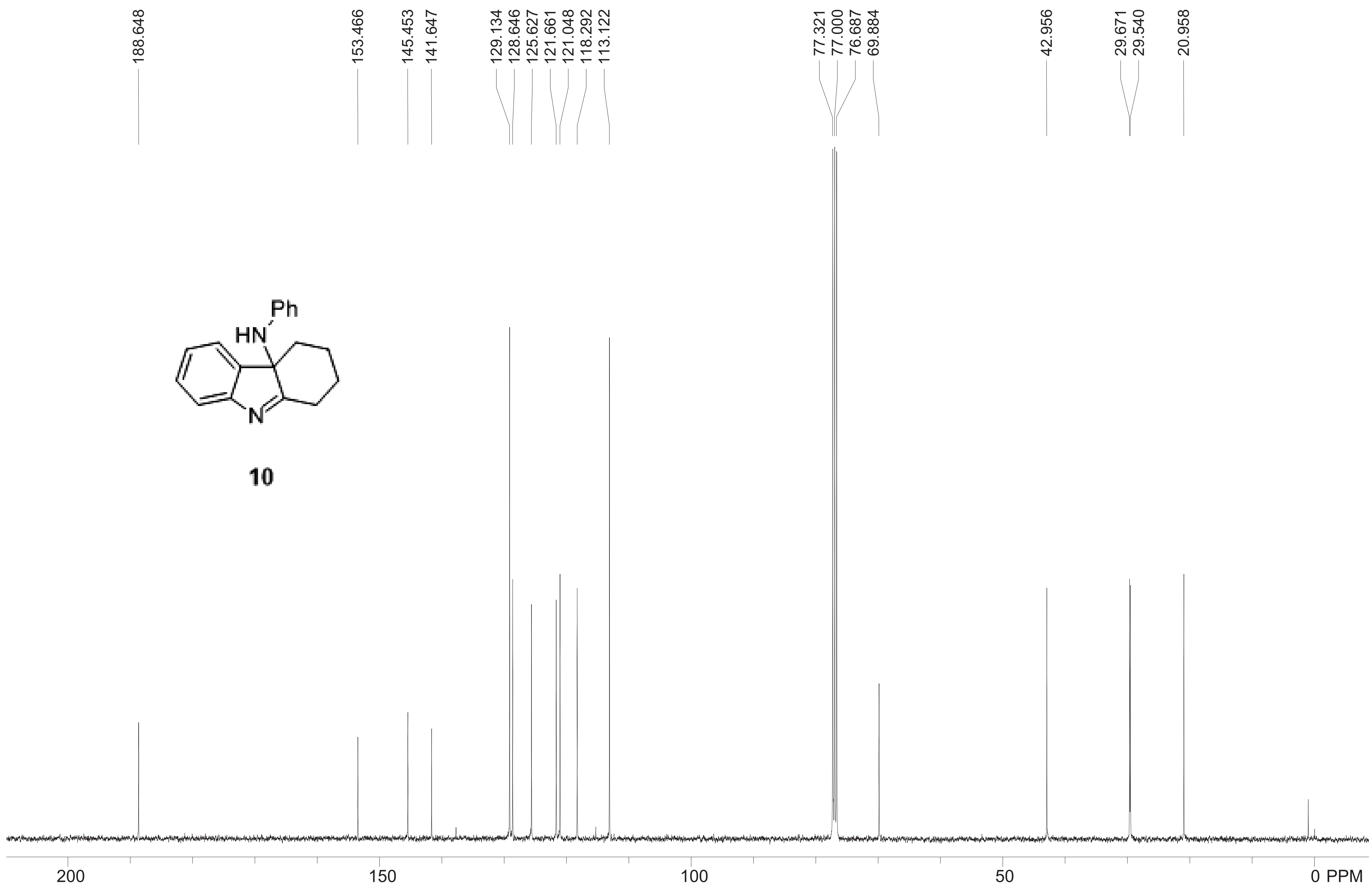
0PPM



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77.000
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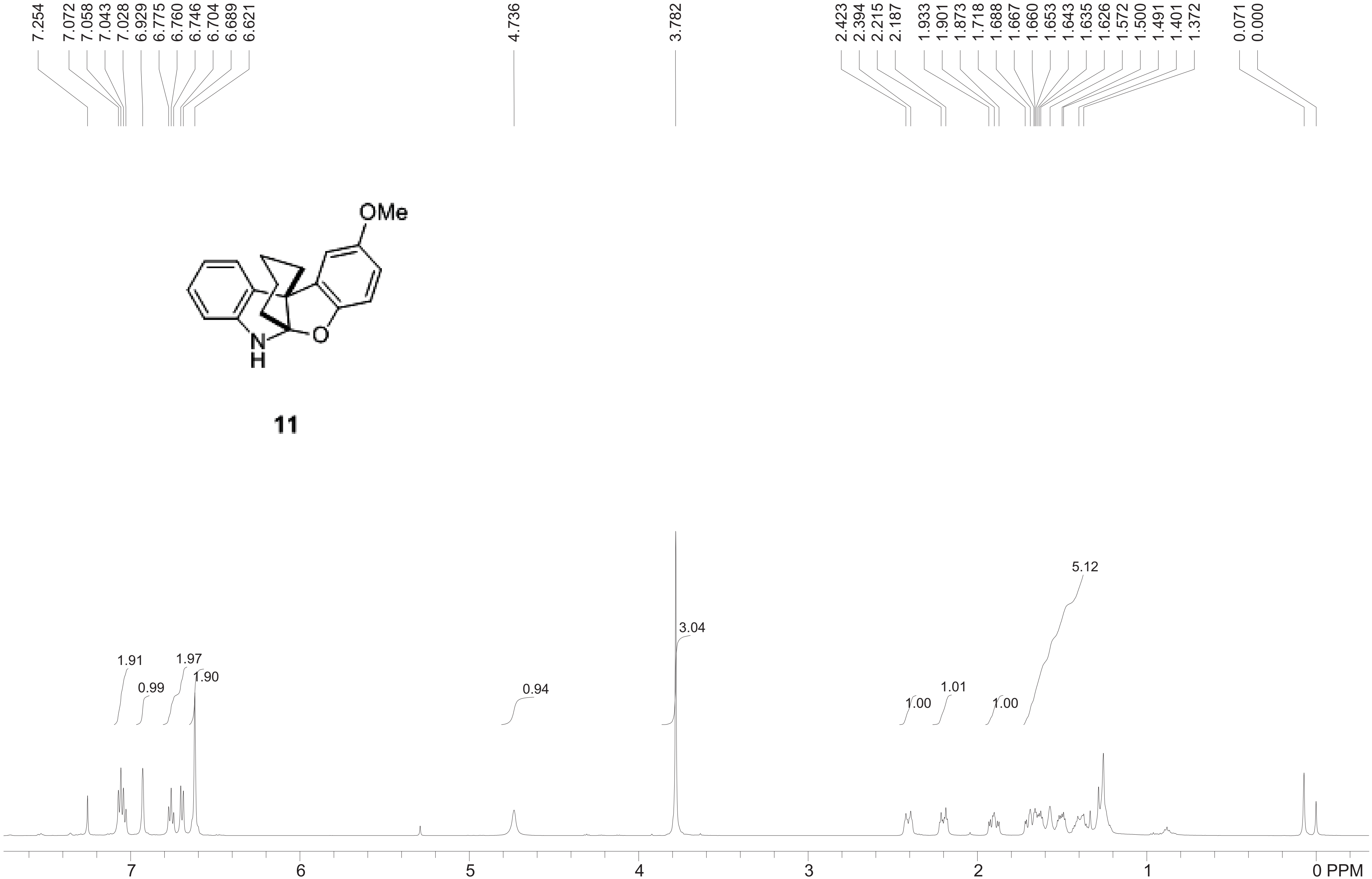
50
0 PPM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4.736
3.782
2.423
2.394
2.215
2.187
1.933
1.901
1.873
1.718
1.688
1.667
1.660
1.653
1.643
1.635
1.626
1.572
1.500
1.491
1.401
1.372
0.071
0.000
OMe
N
H
O
1.91
0.99
1.97
1.90
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1.00
1.01
1.00
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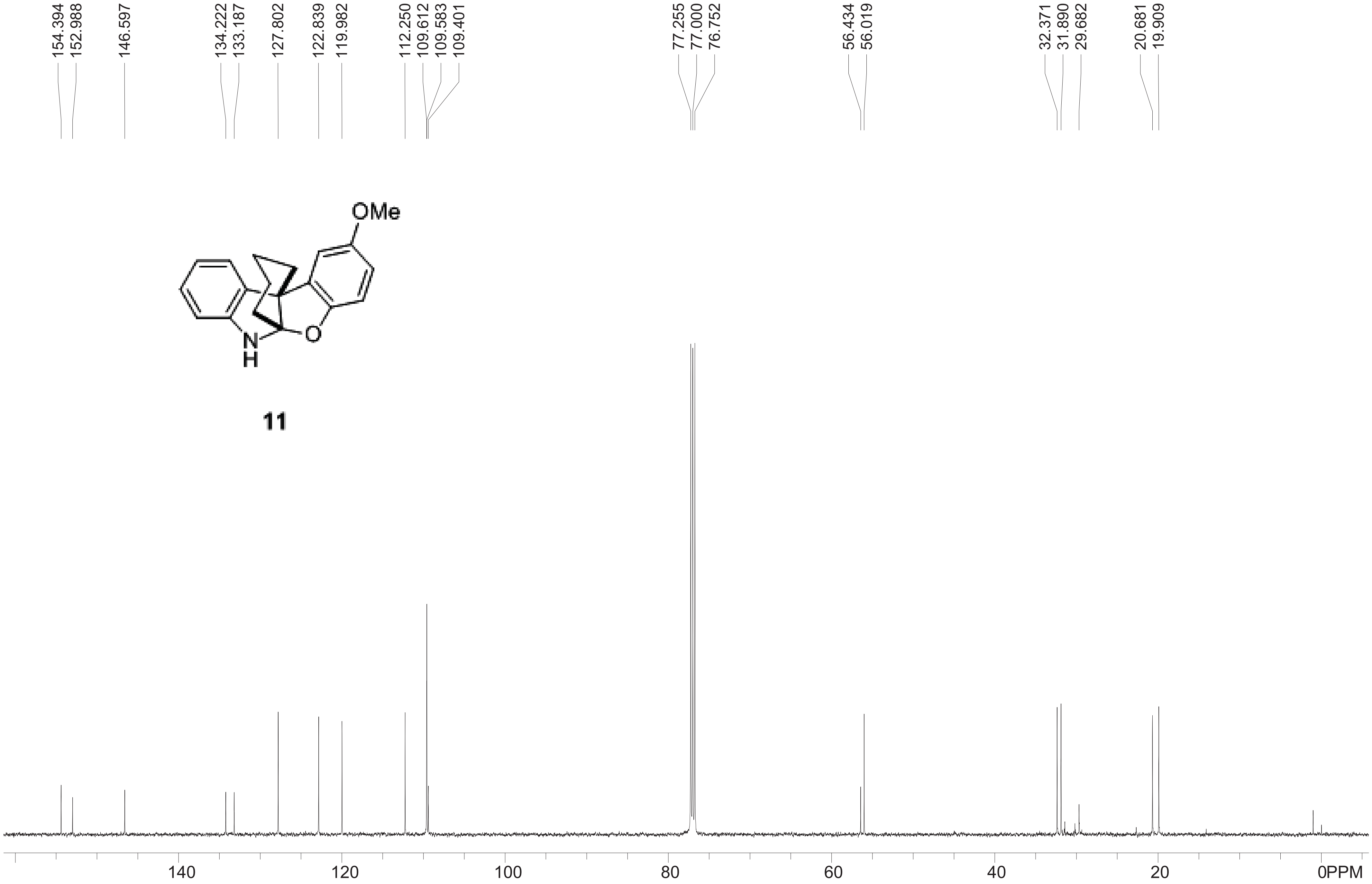
5
4
3
2
1
0 PPM

11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134.222
133.187
127.802
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109.612
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109.401
77.255
77.000
76.752
56.434
56.019
32.371
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19.909
OMe
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H
O
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120
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80
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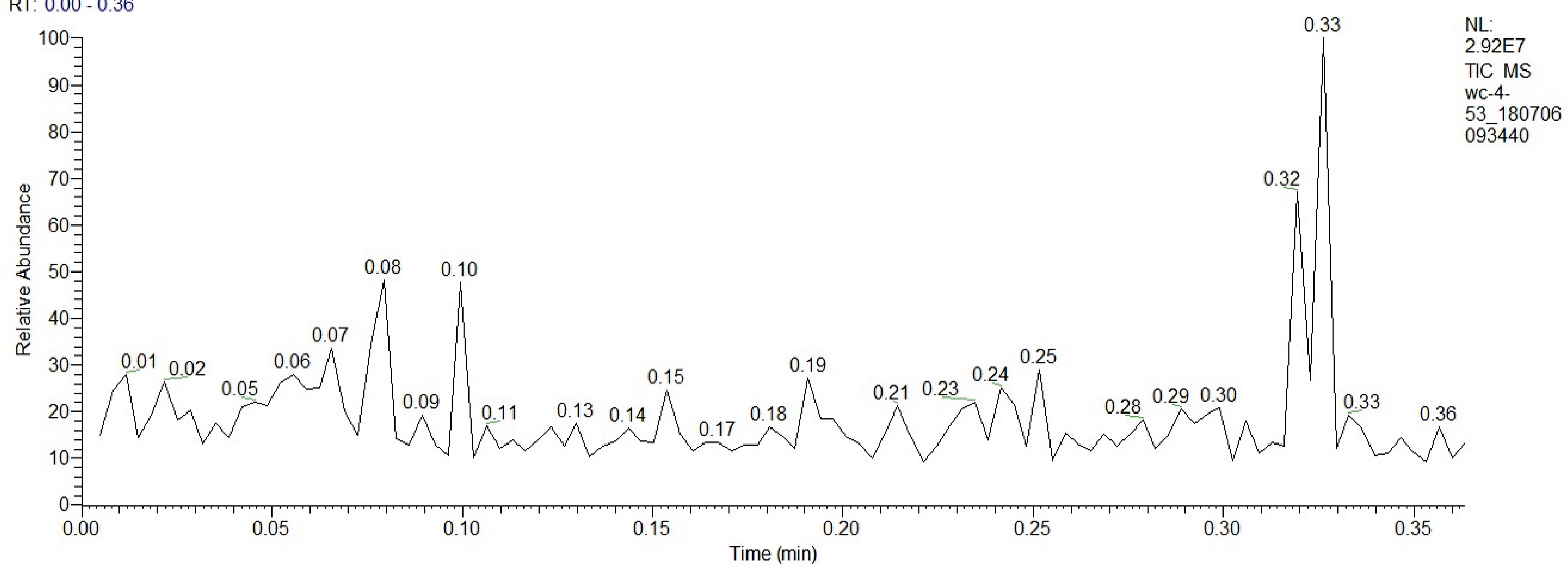
40
20
0PPM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NL:
2.92E7
TIC MS
wc-4-
53_180706
093440
Relative Abundance
Time (min)
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0.02
0.05
0.06
0.07
0.08
0.09
0.10
0.11
0.13
0.14
0.15
0.17
0.18
0.19
0.21
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0.24
0.25
0.28
0.29
0.30
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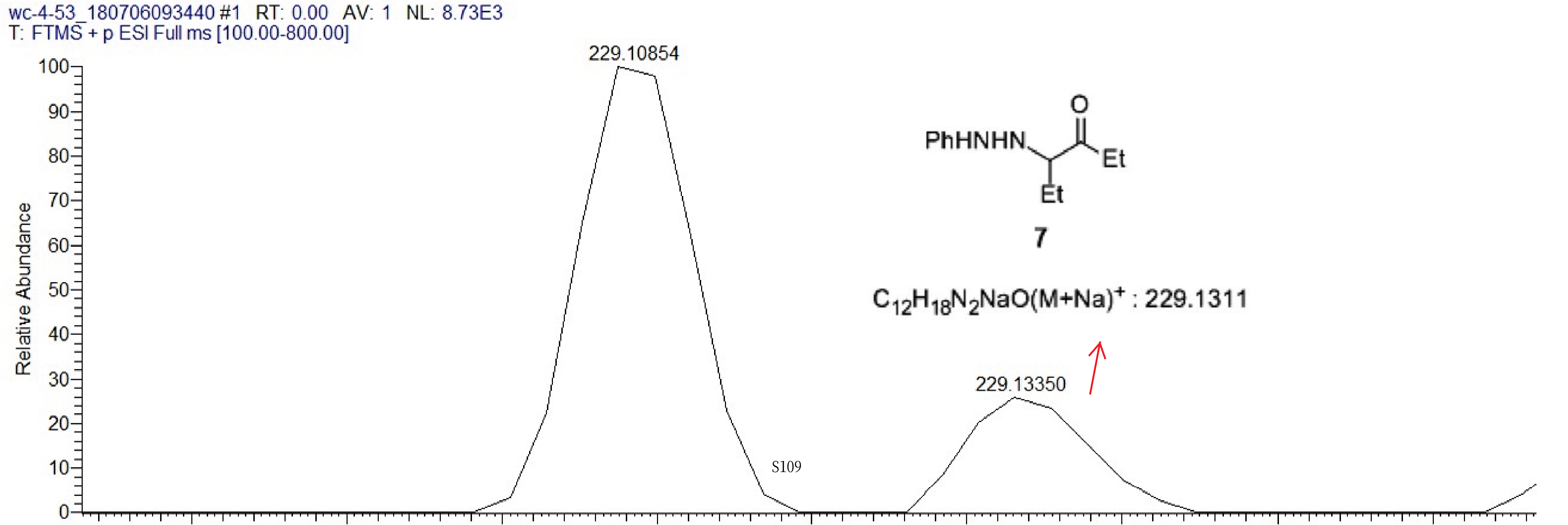
0.33
0.33
0.36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T: FTMS + p ESI Full ms [100.00-800.00]
Relative Abundance
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229.13350
PhHNHN
O
Et
Et
7
$C_{12}H_{18}N_2NaO(M+Na)^+$: 229.1311