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Supporting Information

Synthesis of Quinazolines and Tetrahydroquinazolines: Copper-Catalyzed Tandem Reactions of 2-Bromobenzyl Bromides with Aldehydes and Aqueous Ammonia or Amines

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Supporting Information

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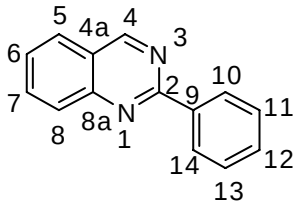
I. General Experimental Information

All the commercial reagents and solvents were used without further purification. Melting points were recorded with a micro melting point apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. High-resolution mass spectra (HRMS) were obtained by using a MicrOTOF mass spectrometer. All reactions were monitored by thin-layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm) and components were visualized by observation under UV light (254 and 365 nm).

II. Synthetic procedures and spectroscopic data

General procedure for the preparation of quinazoline 4.

To a tube containing a solution of 2-bromobenzyl bromide **1** (0.5 mmol) in DMSO (2 mL) were added aldehyde **2** (0.6 mmol), $Cu(OAc)_2$ (0.05 mmol), DMAP (0.15 mmol) and 26% aqueous ammonia **3** (1 mL). Then, the tube was sealed and the mixture was stirred at 80 ^oC under air atmosphere for 24 h. After being cooled to room temperature, the reaction was quenched with aqueous NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with H_2O and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel to afford quinazoline derivatives **4**.



2-Phenylquinazoline (4a): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (71 mg, 68%), mp 101-103 °C (lit[1]. mp 102-103 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.55 (m, 3H; 11-H, 12-H and 13-H), 7.56-7.63 (m, 1H; 6-H), 7.89-7.94 (m, 2H; 5-H and 7-H), 8.09 (d, J = 8.8 Hz, 1H; 8-H), 8.61-8.64 (m, 2H; 10-H and 14-H), 9.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.6 (C-4a), 127.1 (C-5), 127.3 (C-6), 128.6 (C-10 and C-14), 128.7 (C-8, C-11 and C-13), 130.6 (C-12), 134.1 (C-7), 138.1 (C-9), 150.8 (C-8a), 160.5 (C-4), 161.1 (C-2). IR (KBr) ν = 2921, 1601, 1532, 1396, 731 cm^{-1}. MS: m/z 207 $(MH)^+$.

2-*p*-Tolylquinazoline (4b): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (72 mg, 64%), mp 106-108 °C (lit[1]. mp 107-109 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.45 (s, 3H), 7.35 (d, J = 8.0 Hz, 2H), 7.57-7.61 (m, 1H), 7.87-7.92 (m, 2H), 8.06-8.08 (m, 1H), 8.51 (d, J = 8.0 Hz, 2H), 9.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 123.5, 127.0, 127.1, 128.5, 128.6, 129.4, 134.0, 135.3, 140.9, 150.8, 160.5, 161.2. IR (KBr) ν = 2920, 1588, 1551, 1379, 725 cm^{-1}. MS: m/z 221 $(MH)^+$.

2-(4-Bromophenyl)quinazoline (4c): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (103 mg, 72%), mp 124-126 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.61-7.67 (m, 3H), 7.92 (t, J = 8.0 Hz, 2H), 8.07 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 8.0 Hz, 2H), 9.44 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.7, 125.4, 127.2, 127.5, 128.6, 130.2, 131.8, 134.3, 137.0, 150.7, 160.1, 160.6. IR (KBr) ν = 3030,

1522, 1480, 1402, 755 cm^{-1}. MS: m/z 285 $(MH)^+$. HRMS (ESI) calcd for $C_{14}H_{10}BrN_2$: 285.0027 [M+H], found: 285.0015.

2-(4-Nitrophenyl)quinazoline (4d): Eluent: petroleum ether-ethyl acetate (10:1); yellow solid (94 mg, 74%), mp 217-219 °C (lit[2]. mp 218-219 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 7.54 (q, *J* = 13.6 Hz, 2H), 7.61-7.50 (m, 1H), 7.91-7.95 (m, 2H), 8.12 (d, *J* = 8.8 Hz, 1H), 8.62-8.64 (m, 2H), 9.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.6, 127.2, 127.4, 128.6, 128.66, 128.69, 130.8, 134.3, 137.8, 150.7, 160.5, 161.0. IR (KBr) ν = 2926, 1605, 1504, 1322, 742 cm^{-1}. MS: m/z 252 $(MH)^+$.

4-(Quinazolin-2-yl)benzonitrile (4e): Eluent: petroleum ether-ethyl acetate (10:1); yellow solid (77 mg, 66%), mp 193-196 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.69 (t, *J* = 7.6 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.94-7.99 (m, 2H), 8.11 (d, *J* = 7.6 Hz, 1H), 8.75 (d, *J* = 8.4 Hz, 2H), 9.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 113.8, 118.9, 123.9, 127.2, 128.2, 128.8, 129.0, 132.4, 134.5, 142.2, 150.6, 159.1, 160.7. IR (KBr) ν = 2924, 1598, 1515, 1396, 742 cm^{-1}. MS: m/z 232 $(MH)^+$. HRMS (ESI) calcd for $C_{15}H_{10}N_3$: 232.0874 [M+H], found: 232.0871.

2-(4-(Trifluoromethyl)phenyl)quinazoline (4f): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (104 mg, 75%), mp 135-137 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.66 (t, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.92-7.96 (m, 2H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.73 (d, *J* = 8.4 Hz, 2H), 9.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.8, 125.48, 125.52, 125.56, 125.60, 127.2, 127.9, 128.8, 128.9, 134.5, 141.2, 150.6, 159.6, 160.6. IR (KBr) ν = 2924, 1553, 1326, 1070, 804 cm^{-1}. MS: m/z 275 $(MH)^+$. HRMS (ESI) calcd for $C_{15}H_{10}F_3N_2$: 275.0796 [M+H], found: 275.0795.

2-*m*-Tolylquinazoline (4g): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (75 mg, 67%), mp 114-116°C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.49 (s, 3H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.42-7.46 (m, 1H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.88-7.92 (m, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.41-8.43 (m, 2H), 9.46 (d, *J* = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 123.6, 125.8, 127.16, 127.24, 128.6, 129.1, 131.5, 134.1, 138.0, 138.3, 150.8, 160.5, 161.2. IR (KBr) ν = 2916, 1615, 1502, 1396, 721 cm^{-1}. MS: m/z 221 $(MH)^+$. HRMS (ESI) calcd for $C_{15}H_{13}N_2$: 221.1078 [M+H], found: 221.1065.

2-(3-Fluorophenyl)qinazoline (4h): Eluent: petroleum ether-ethyl acetate (20:1); white solid (75 mg, 66%), mp 93-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17-7.22 (m, 1H), 7.46-7.51 (m, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.88-7.92 (m, 2H), 8.07 (d, *J* = 8.8 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 9.43 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 115.3, 115.5, 117.4, 117.6, 123.7, 124.17, 124.21, 127.2, 127.6, 128.7, 130.0, 130.1, 134.3, 140.5, 150.6, 159.78, 159.82, 160.6, 162.1, 164.5. IR (KBr) ν = 2926, 1584, 1516, 1358, 726 cm^{-1}. MS: m/z 225 $(MH)^+$. HRMS (ESI) calcd for $C_{14}H_{10}FN_2$: 225.0828 [M+H], found: 225.0815.

2-(3-Bromophenyl)quinazoline (4i): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (92 mg, 64%), mp 153-155 °C (lit[2]. mp 153-155 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (t, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 2H), 7.91 (t, *J* = 7.6 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.78 (s, 1H), 9.44 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.0, 123.8, 127.1, 127.2, 127.7, 128.7, 130.2, 131.6, 133.5, 134.4, 140.1, 150.6, 159.6, 160.6. IR (KBr) ν = 3021, 1598, 1512, 1402, 761 cm^{-1}. MS: m/z 285 $(MH)^+$.

2-(2-Chlorophenyl)quinazoline (4j): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (81mg, 67%), mp 68-70 °C (lit[2]. mp 69-70 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.56 (m, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.90-7.95 (m, 2H), 8.10 (d, *J* = 8.8 Hz, 1H), 8.62 (d, *J* = 6.8 Hz, 2H), 9.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.6, 127.1, 127.3, 128.6, 128.7, 128.9, 130.6, 134.1, 138.0, 150.8, 160.5, 161.1. IR (KBr) ν = 2924, 1608, 1504, 12884, 745 cm^{-1}. MS: m/z 241 $(MH)^+$.

2-(2-Bromophenyl)quinazoline (4k): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (76 mg, 53%), mp 72-74 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.56 (m, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.89 (t, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 2H), 9.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.6, 127.2, 127.3, 128.60, 128.64, 128.7, 130.6, 134.2, 138.0, 150.8, 160.5, 161.1. IR (KBr) ν = 3062, 1550, 1485, 1402, 772 cm^{-1}. MS: m/z 285 $(MH)^+$. HRMS (ESI) calcd for $C_{14}H_{10}BrN_2$: 285.0027 [M+H], found: 285.0022.

2-(2-Nitrophenyl)quinazoline (4l): Eluent: petroleum ether-ethyl acetate (10:1); yellow solid (91 mg, 72%), mp 93-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51-7.56 (m, 2H), 7.60-7.64 (m, 1H), 7.89-

7.94 (m, 2H), 8.10 (d, J = 8.0 Hz, 1H), 8.61-8.63 (m, 2H), 9.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 123.6, 127.2, 127.3, 127.9, 128.6, 128.7, 130.6, 133.17, 133.22, 134.2, 138.0, 150.8, 160.5, 161.1. IR (KBr) ν = 2914, 1612, 1504, 1318, 736 cm^{-1}. MS: m/z 252 $(MH)^+$. HRMS (ESI) calcd for $C_{14}H_{10}N_3O_2$: 252.0773 [M+H], found: 252.0788.

2-(Pyridin-4-yl)quinazoline (4m): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (38 mg, 37%), mp 124-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (t, J = 7.6 Hz, 1H), 7.96 (t, J = 8.4 Hz, 2H), 8.12 (d, J = 8.4 Hz, 1H), 8.46 (d, J = 6.0 Hz, 2H), 8.80 (d, J = 5.2 Hz, 2H), 9.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 122.4, 124.2, 127.2, 128.4, 128.9, 134.6, 145.4, 150.4, 150.6, 158.9, 160.8. IR (KBr) ν = 2921, 1617, 1544, 1402, 759 cm^{-1}. MS: m/z 208 $(MH)^+$. HRMS (ESI) calcd for $C_{13}H_{10}N_3$: 208.0874 [M+H], found: 208.0879.

Quinazoline (4n): Eluent: petroleum ether-ethyl acetate (5:1); yellow syrup (17 mg, 27%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61-7.65 (m, 1H), 7.87-7.91 (m, 2H), 8.02 (d, J = 8.4 Hz, 1H), 9.30 (s, 1H), 9.37 (s, 1H). IR (KBr) ν = 3053, 1621, 1549, 1402, 756 cm^{-1}. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 125.1, 127.2, 128.0, 128.4, 134.2, 150.0, 155.2, 160.2. MS: m/z 131 $(MH)^+$.

5-Chloro-2-phenylquinazoline (4o): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (79 mg, 65%), mp 81-83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.57 (m, 3H), 7.62 (d, J = 7.6 Hz, 1H), 7.78-7.82 (m, 1H), 8.01 (d, J = 8.0 Hz, 1H), 8.62-8.64 (m, 2H), 9.84 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 121.4, 127.2, 127.8, 128.7, 128.8, 131.0, 131.9, 133.9, 137.5, 151.9, 157.9, 161.7. IR (KBr) ν = 2924, 1566, 1548, 1380, 701 cm^{-1}. MS: m/z 241 $(MH)^+$. HRMS (ESI) calcd for $C_{14}H_{10}ClN_2$: 241.0532 [M+H], found: 241.0523.

Methyl 2-phenylquinazoline-6-carboxylate (4p): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (91 mg, 68%), mp 179-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.02 (s, 3H), 7.55-7.56 (m, 3H), 8.14 (d, J = 8.8 Hz, 1H), 8.49 (d, J = 8.8 Hz, 1H), 8.64-8.65 (m, 2H), 8.69 (s, 1H), 9.57 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 52.6, 122.8, 128.7, 128.8, 128.9, 130.2, 131.3, 133.7, 137.4, 152.7,

161.7, 162.7, 165.9. IR (KBr) ν = 2948, 1719, 1627, 1439, 1254, 703 cm^{-1}. MS: m/z 265 $(MH)^+$. HRMS (ESI) calcd for $C_{16}H_{13}N_2O_2$: 265.0977 [M+H], found: 265.0980.

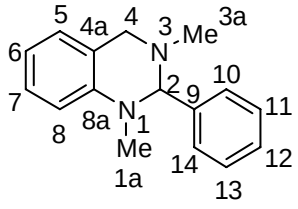
6-Methoxy-2-phenylquinazoline (4q): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (71 mg, 60%), mp 119-122 °C (lit[1]. mp 120-122 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 3.96 (s, 3H), 7.40 (d, J = 3.6 Hz, 1H), 7.48-7.56 (m, 4H), 7.99 (d, J = 8.8 Hz, 1H), 8.57 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2H), 9.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.7, 103.9, 124.5, 127.2, 128.2, 128.6, 130.1, 130.2, 138.2, 147.0, 158.3, 158.8, 159.4. IR (KBr) ν = 2924, 1604, 1532, 1386, 746 cm^{-1}. MS: m/z 237 $(MH)^+$.

2-Phenylbenzo[*h*]quinazoline (4r): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (81 mg, 63%), mp 135-137 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.54-7.61 (m, 3H), 7.74 (d, J = 8.8 Hz, 1H), 7.80-7.87 (m, 3H), 7.93-7.95 (m, 1H), 8.76-8.78 (m, 2H), 9.42 (s, 1H), 9.44-9.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 121.5, 123.0, 125.0, 127.5, 128.1, 128.56, 128.60, 128.7, 130.2, 130.3, 130.7, 135.6, 138.2, 150.9, 158.5, 161.0. IR (KBr) ν = 2924, 1618, 1552, 1402, 739 cm^{-1}. MS: m/z 257 $(MH)^+$. HRMS (ESI) calcd for $C_{18}H_{13}N_2$: 257.1078 [M+H], found: 257.1069.

6-(4-Chlorophenyl)-[1,3]dioxolo[4,5-g]quinazoline (4s): Eluent: petroleum ether-ethyl acetate (20:1); yellow solid (97 mg, 68%), mp 220-221 °C (lit[3]. mp 224-226 °C); ^1H NMR (400 MHz, $CDCl_3$) δ: 6.16 (s, 2H), 7.10 (s, 1H), 7.31 (s, 1H), 7.46 (d, J = 8.0 Hz, 2H), 8.48 (d, J = 7.6 Hz, 2H), 9.13 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 101.9, 102.2, 105.0, 120.8, 128.7, 129.5, 136.4, 136.7, 148.4, 150.3, 154.3, 157.5, 159.1. IR (KBr) ν = 2914, 1478, 1224, 1038, 846, 795 cm^{-1}. MS: m/z 285 $(MH)^+$.

2-(4-Chlorophenyl)-7-fluoroquinazoline (4t): Eluent: petroleum ether-ethyl acetate (20:1); white solid (87 mg, 67%), mp 139-141°C; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.37-7.42 (m, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.67-7.70 (m, 1H), 7.93-7.97 (m, 1H), 8.56 (d, J = 8.0 Hz, 2H), 9.42 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.4, 112.6, 118.0, 118.3, 120.9, 128.9, 129.7, 129.8, 130.0, 136.1, 137.3, 152.3, 159.9, 160.8, 164.8, 167.4. IR (KBr) ν = 2924, 1614, 1539, 1412, 746 cm^{-1}. MS: m/z 259 $(MH)^+$. HRMS (ESI) calcd for $C_{14}H_9ClFN_2$: 259.0438 [M+H], found: 259.0430.

General procedure for the preparation of 1,2,3,4-tetrahydroquinazoline 5. To a tube containing a solution of 2-bromobenzyl bromide **1** (0.5 mmol) in DMSO (2 mL) were added aldehyde **2** (0.6 mmol), $Cu(OAc)_2$ (0.05 mmol), DMAP (0.15 mmol) and 40% aqueous methylamine or 65% aqueous ethylamine **3** (1 mL). Then, the tube was sealed and the mixture was stirred at 80 ^oC under air atmosphere for 14 h. After being cooled to room temperature, the reaction was quenched with NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with H_2O and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel to afford 1,2,3,4-tetrahydroquinazoline derivatives **5**.



1,3-Dimethyl-2-phenyl-1,2,3,4-tetrahydroquinazoline (5a): Eluent: petroleum ether-ethyl acetate (10:1); colorless liquid (81 mg, 67%); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.56 (s, 3H; 3a-H), 2.98 (s, 3H; 1a-H), 3.42 (d, *J* = 15.6 Hz, 1H; 4-H), 3.84 (d, *J* = 16.0 Hz, 1H; 4-H), 4.91 (s, 1H; 2-H), 6.69-6.72 (m, 2H; 6-H and 8-H), 6.92 (d, *J* = 7.2 Hz, 1H; 5-H), 7.21-7.36 (m, 6H; 7-H, 10-H, 11-H, 12-H, 13-H, 14-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.7 (C-3a), 42.4 (C-1a), 49.3 (C-4), 82.1 (C-2), 108.9 (C-8), 115.9 (C-6), 117.9 (C-4a), 127.10 (C-10 and C-14), 127.13 (C-12), 127.8 (C-5), 127.9 (C-7), 128.5 (C-11 and C-13), 140.7 (C-9), 143.6 (C-8a). IR (KBr) ν = 2937, 1610, 1504, 1284, 745 cm^{-1}. MS: m/z 239 $(MH)^+$. HRMS (ESI) calcd for $C_{16}H_{19}N_2$: 239.1548 [M+H], found: 239.1552.

2-(4-Methoxyphenyl)-1,3-dimethyl-1,2,3,4-tetrahydroquinazoline (5b): Eluent: petroleum ether-ethyl acetate (10:1); colorless liquid (93 mg, 69%); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.52 (s, 3H), 2.96 (s, 3H), 3.41 (d, *J* = 16.0 Hz, 1H), 3.79 (s, 3H), 3.83 (d, *J* = 15.6 Hz, 1H), 4.86 (s, 1H), 6.66-6.70 (m, 2H), 6.85-6.87 (m, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 7.16-7.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.6, 42.2, 49.3, 55.3, 81.6, 108.9, 113.8, 115.8, 117.9, 127.1, 127.9, 128.3, 132.8, 143.7, 159.2. IR (KBr) ν = 2978, 1616, 1523, 1284, 742 cm^{-1}. MS: m/z 269 $(MH)^+$. HRMS (ESI) calcd for $C_{17}H_{21}N_2O$: 269.1654 [M+H], found: 269.1650.

2-(4-Bromophenyl)-1,3-dimethyl-1,2,3,4-tetrahydroquinazoline (5c): Eluent: petroleum ether-ethyl acetate (10:1); colourless liquid (111 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.51 (s, 3H), 2.95 (s, 3H), 3.38 (d, *J* = 16.4 Hz, 1H), 3.76 (d, *J* = 16.4 Hz, 1H), 4.83 (s, 1H), 6.66-6.69 (m, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.19-7.22 (m, 1H), 7.43 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.8, 42.3, 49.2, 81.6, 109.0, 116.1, 117.8, 121.7, 127.2, 127.9, 128.9, 131.6, 139.9, 143.3. IR (KBr) ν = 2960, 1604, 1506, 1282, 743 cm^{-1}. MS: m/z 317 $(MH)^+$. HRMS (ESI) calcd for $C_{16}H_{18}BrN_2$: 317.0653 [M+H], found: 317.0655.

1,3-Dimethyl-2-(4-nitrophenyl)-1,2,3,4-tetrahydroquinazoline (5d): Eluent: petroleum ether-ethyl acetate (5:1); yellow liquid (98 mg, 69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.54 (s, 3H), 3.00 (s, 3H), 3.40 (d, *J* = 16.0 Hz, 1H), 3.79 (d, *J* = 16.0 Hz, 1H), 4.94 (s, 1H), 6.68-6.73 (m, 2H), 6.89 (d, *J* = 6.4 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 8.16 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 37.0, 42.4, 49.2, 81.4, 109.3, 116.6, 117.6, 123.8, 127.3, 128.1, 134.4, 142.0, 143.0, 148.3. IR (KBr) ν = 2939, 1610, 1500, 1315, 745 cm^{-1}. MS: m/z 284 $(MH)^+$. HRMS (ESI) calcd for $C_{16}H_{18}N_3O_2$: 284.1399 [M+H], found: 284.1394.

1,3-Dimethyl-2-m-tolyl-1,2,3,4-tetrahydroquinazoline (5e): Eluent: petroleum ether-ethyl acetate (10:1); colorless liquid (82 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.35 (s, 3H), 2.54 (s, 3H), 2.97 (s, 3H), 3.41 (d, *J* = 15.2 Hz, 1H), 3.86 (d, *J* = 15.6 Hz, 1H), 4.87 (s, 1H), 6.67-6.71 (m, 2H), 6.92 (d, *J* = 6.8 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.12 (s, 2H), 7.19-7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.6, 36.7, 42.4, 49.4, 82.2, 108.8, 115.8, 117.9, 124.0, 127.1, 127.87, 127.89, 128.3, 128.6, 138.2, 140.8, 143.7. IR (KBr) ν = 2967, 1604, 1504, 1268, 745 cm^{-1}. MS: m/z 253 $(MH)^+$. HRMS (ESI) calcd for $C_{17}H_{21}N_2$: 253.1704 [M+H], found: 253.1708.

2-(3-Fluorophenyl)-1,3-dimethyl-1,2,3,4-tetrahydroquinazoline (5f): Eluent: petroleum ether-ethyl acetate (10:1); colorless liquid (86 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.51 (s, 3H), 2.97 (s, 3H), 3.39 (d, *J* = 16.4 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 4.86 (s, 1H), 6.67 (t, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 1H), 7.18- 7.25 (m, 1H), 7.27-7.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.7, 36.8, 42.3, 49.2, 81.6, 109.0, 113.9, 114.2, 114.6, 114.8,

116.1, 117.7, 122.6, 122.7, 127.1, 127.9, 129.9, 130.0, 143.2, 143.7, 164.2. IR (KBr) ν = 2960, 1598, 1501, 1273, 743 cm^{-1}. MS: m/z 257 $(MH)^+$. HRMS (ESI) calcd for $C_{16}H_{18}FN_2$: 257.1454 [M+H], found: 257.1459.

1,3-Dimethyl-2-o-tolyl-1,2,3,4-tetrahydroquinazoline (5g): Eluent: petroleum ether-ethyl acetate (10:1); colorless liquid (90 mg, 71%); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.48 (s, 3H), 2.55 (s, 3H), 2.91 (s, 3H), 3.36 (d, *J* = 16.0 Hz, 1H), 3.88 (d, *J* = 16.0 Hz, 1H), 4.96 (s, 1H), 6.68 (t, *J* = 6.8 Hz, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.06-7.10 (m, 1H), 7.20-7.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.8, 36.3, 42.3, 49.1, 79.6, 108.3, 115.6, 117.6, 125.5, 126.1, 127.1, 127.6, 127.9, 131.0, 136.6, 138.6, 144.0. IR (KBr) ν = 2931, 1604, 1504, 1280, 743 cm^{-1}. MS: m/z 253 $(MH)^+$. HRMS (ESI) calcd for $C_{17}H_{21}N_2$: 253.1704 [M+H], found: 253.1696.

1,3-Dimethyl-2-(naphthalen-1-yl)-1,2,3,4-tetrahydroquinazoline (5h): Eluent: petroleum ether-ethyl acetate (10:1); white solid (93 mg, 64%), mp 147-149 °C; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.73 (s, 3H), 3.03 (s, 3H), 3.44 (d, *J* = 15.6 Hz, 1H), 3.93 (d, *J* = 15.6 Hz, 1H), 5.59 (s, 1H), 6.74-6.81 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.55-7.59 (m, 1H), 7.63-7.67 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.6, 42.2, 49.5, 79.9, 108.4, 115.8, 117.4, 124.2, 124.3, 125.0, 125.7, 126.4, 127.4, 128.0, 128.7, 128.8, 131.2, 134.4, 135.3, 144.0. IR (KBr) ν = 2935, 2894, 1605, 1504, 1296, 748 cm^{-1}. MS: m/z 289 $(MH)^+$. HRMS (ESI) calcd for $C_{20}H_{21}N_2$: 289.1704 [M+H], found: 289.1708.

1,3-Dimethyl-2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinazoline (5i): Eluent: petroleum ether- ethyl acetate (10:1); colorless liquid (67 mg, 55%); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.52 (s, 3H), 3.05 (s, 3H), 3.51 (d, *J* = 16.4 Hz, 1H), 4.01 (d, *J* = 16.4 Hz, 1H), 5.13 (s, 1H), 6.68-6.72 (m, 2H), 6.83-6.84 (m, 1H), 6.91-6.93 (m, 2H), 7.19-7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 37.1, 41.6, 49.6, 78.5, 109.6, 116.5, 118.1, 125.4, 125.5, 126.5, 127.0, 127.8, 142.8, 144.4. IR (KBr) ν = 2937, 2877, 1605, 1504, 1283, 747 cm^{-1}. MS: m/z 245 $(MH)^+$. HRMS (ESI) calcd for $C_{14}H_{17}N_2S$: 245.1112 [M+H], found: 245.1116.

1,3-Dimethyl-1,2,3,4-tetrahydroquinazoline (5j): Eluent: petroleum ether-ethyl acetate (5:1); colourless liquid (72 mg, 88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.50 (s, 3H), 2.87 (s, 3H), 3.83 (s, 2H), 3.90 (s, 2H), 6.65-6.71 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.8, 41.6, 55.8, 73.0, 111.4, 117.2, 120.0, 126.9, 127.5, 145.0. IR (KBr) ν = 2926, 1663, 1606, 1504, 749 cm^{-1}. MS: m/z 163 $(MH)^+$. HRMS (ESI) calcd for $C_{10}H_{15}N_2$: 163.1235 [M+H], found: 163.1236.

1,2,3-Trimethyl-1,2,3,4-tetrahydroquinazoline (5k): Eluent: petroleum ether-ethyl acetate (5:1); colourless liquid (75 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.24 (d, *J* = 6.4 Hz, 3H), 2.45 (s, 3H), 2.88 (s, 3H), 3.55 (d, *J* = 16.8 Hz, 1H), 3.92-3.97 (m, 1H), 4.27 (d, *J* = 16.8 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.2, 35.7, 42.2, 48.9, 74.9, 110.3, 116.1, 117.4, 127.0, 127.6, 143.0. IR (KBr) ν = 2934, 1604, 1501, 1290, 746 cm^{-1}. MS: m/z 177 $(MH)^+$. HRMS (ESI) calcd for $C_{11}H_{17}N_2$: 177.1391 [M+H], found: 177.1398.

2-Benzyl-1,3-dimethyl-1,2,3,4-tetrahydroquinazoline (5l): Eluent: petroleum ether-ethyl acetate (5:1); colorless liquid (104 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.47 (s, 3H), 2.76 (s, 3H), 2.99 (d, *J* = 6.4 Hz, 2H), 3.63 (d, *J* = 16.8 Hz, 1H), 4.07 (t, *J* = 6.4 Hz, 1H), 4.51 (d, *J* = 16.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.24-7.40 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 37.8, 39.0, 42.7, 49.2, 81.6, 110.3, 116.1, 117.1, 126.4, 127.3, 127.8, 128.5, 129.6, 138.7, 142.8. IR (KBr) ν = 2932, 1604, 1504, 1286, 747 cm^{-1}. MS: m/z 253 $(MH)^+$. HRMS (ESI) calcd for $C_{17}H_{21}N_2$: 253.1704 [M+H], found: 253.1711.

5,7-Dimethyl-6-phenyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]quinazoline (5m): Eluent: petroleum ether-ethyl acetate (10:1); colourless liquid (105 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.51 (s, 3H), 2.92 (s, 3H), 3.31 (d, *J* = 16.4 Hz, 1H), 3.72 (d, *J* = 15.2 Hz, 1H), 4.81 (s, 1H), 5.85 (s, 2H), 6.36 (s, 1H), 6.44 (s, 1H), 7.21-7.23 (m, 2H), 7.26-7.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 37.4, 42.2, 49.5, 81.9, 92.3, 100.3, 107.6, 109.6, 127.1, 127.8, 128.4, 138.0, 138.9, 140.6, 147.2. IR

(KBr) ν = 2928, 1504, 1235, 1039, 749 cm^{-1}. MS: m/z 283 $(MH)^+$. HRMS (ESI) calcd for $C_{17}H_{18}N_2NaO_2$: 305.1266 [M+Na], found: 305.1252.

5-Chloro-1,3-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinazoline (5n): Eluent: petroleum ether-ethyl acetate (10:1); yellow syrup (104 mg, 76%); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.56 (s, 3H), 3.01 (s, 3H), 3.65 (d, *J* = 16.4 Hz, 1H), 3.76 (d, *J* = 16.4 Hz, 1H), 4.93 (s, 1H), 6.62 (d, *J* = 7.6 Hz, 1H), 6.71-6.74 (m, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.22-7.26 (m, 2H), 7.30-7.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 37.2, 42.6, 47.1, 81.7, 107.4, 115.6, 116.6, 127.0, 128.0, 128.2, 128.6, 133.2, 140.1, 145.0. IR (KBr) ν = 2935, 1593, 1487, 1284, 761 cm^{-1}. MS: m/z 273 $(MH)^+$. HRMS (ESI) calcd for $C_{16}H_{17}ClN_2Na$: 295.0978 [M+Na], found: 295.0983.

Methyl 1,3-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinazoline-6-carboxylate (5o): Eluent: petroleum ether-ethyl acetate (10:1); colorless liquid (101 mg, 68%); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.51 (s, 3H), 3.01 (s, 3H), 3.40 (d, *J* = 16.0 Hz, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.84 (s, 3H), 4.94 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 7.18-7.20 (m, 2H), 7.28-7.34 (m, 3H), 7.59 (s, 1H), 7.90 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.8, 42.2, 48.6, 51.5, 82.2, 108.0, 116.8, 117.0, 126.8, 128.2, 128.6, 128.8, 130.4, 139.8, 147.3, 167.5. IR (KBr) ν = 2944, 1709, 1610, 1517, 1296, 768 cm^{-1}. MS: m/z 297 $(MH)^+$. HRMS (ESI) calcd for $C_{18}H_{21}N_2O_2$: 297.1603 [M+H], found: 297.1611.

1,3-Diethyl-2-phenyl-1,2,3,4-tetrahydroquinazoline (5p): Eluent: petroleum ether-ethyl acetate (10:1); colourless liquid (85 mg, 64%); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.17-1.26 (m, 6H), 2.58-2.71 (m, 2H), 3.04-3.13 (m, 1H), 3.44 (d, *J* = 16.4 Hz, 1H), 3.56-3.65 (m, 1H), 3.77 (d, *J* = 16.4 Hz, 1H), 5.05 (s, 1H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 6.4 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.24-7.29 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.2, 13.4, 29.7, 42.8, 47.1, 77.6, 108.4, 115.1, 117.4, 127.3, 127.4, 127.6, 127.7, 128.3, 138.8, 142.6. IR (KBr) ν = 2968, 1610, 1504, 1274, 745 cm^{-1}. MS: m/z 267 $(MH)^+$. HRMS (ESI) calcd for $C_{18}H_{23}N_2$: 267.1861 [M+H], found: 267.1866.

2-(3-Chlorophenyl)-1,3-diethyl-1,2,3,4-tetrahydroquinazoline (5q): Eluent: petroleum ether-ethyl acetate (10:1); colourless liquid (101 mg, 70%); ^1H NMR (400 MHz, $CDCl_3$) δ: 1.19-1.26 (m, 6H), 2.57-2.72 (m, 2H), 3.02-3.11 (m, 1H), 3.46 (d, *J* = 16.0 Hz, 1H), 3.61-3.70 (m, 1H), 3.76 (d, *J* = 16.4

Hz, 1H), 5.01 (s, 1H), 6.63 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 6.8 Hz, 1H), 7.17-7.26 (m, 4H), 7.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.1, 13.4, 42.8, 47.1, 77.3, 108.6, 115.4, 117.5, 125.5, 127.5, 127.6, 127.7, 127.8, 129.6, 134.3, 142.2, 144.3. IR (KBr) ν = 2968, 1604, 1503, 1273, 743 cm^{-1}. MS: m/z 301 $(MH)^+$. HRMS (ESI) calcd for $C_{18}H_{22}ClN_2$: 301.1471 [M+H], found: 301.1477.

1,3-Diethyl-1,2,3,4-tetrahydroquinazoline (5r): Eluent: petroleum ether-ethyl acetate (5:1); colorless liquid (82 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15-1.21 (m, 6H), 2.63 (q, *J* = 7.2 Hz, 2H), 3.32 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 2H), 4.06 (s, 2H), 6.61-6.65 (m, 2H), 6.91 (d, *J* = 6.8 Hz, 1H), 7.07-7.12 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.9, 13.0, 43.5, 47.0, 53.8, 68.5, 110.7, 116.3, 119.5, 127.3, 127.5, 143.8. IR (KBr) ν = 2968, 1605, 1504, 1271, 745 cm^{-1}. MS: m/z 191 $(MH)^+$. HRMS (ESI) calcd for $C_{12}H_{18}N_2Na$: 213.1368 [M+Na], found: 213.1374.

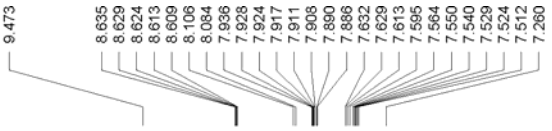
Procedure for the preparation of 1-methyl-2-phenyl-1,2,3,4-tetrahydroquinazoline (7). To a tube containing a solution of 2-bromobenzyl amine **6** (0.5 mmol) in DMSO (2 mL) were added benzaldehyde **2a** (0.6 mmol), $Cu(OAc)_2$ (0.05 mmol), DMAP (0.15 mmol) and 40% aqueous methylamine **3b** (1 mL). Then, the tube was sealed and the mixture was stirred at 80 ^{o}C under air atmosphere for 12 h. After being cooled to room temperature, the reaction was quenched with NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with H_2O and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel to afford **7**.

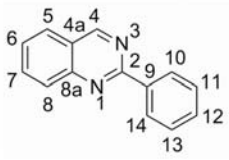
1-Methyl-2-phenyl-1,2,3,4-tetrahydroquinazoline (7): Eluent: petroleum ether-ethyl acetate (5:1); colorless liquid (87 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.86 (s, 3H), 3.75 (d, *J* = 16.8 Hz, 1H), 3.86 (d, *J* = 16.0 Hz, 1H), 5.22 (s, 1H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.30-7.39 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 35.9, 43.4, 75.8, 110.5, 116.0, 122.3, 125.4, 127.2, 127.9, 128.6, 141.1, 145.0. IR (KBr) ν = 2937, 1603, 1501, 1284, 743 cm^{-1}. MS: m/z 225 $(MH)^+$. HRMS (ESI) calcd for $C_{15}H_{17}N_2$: 225.1391 [M+H], found: 225.1382.

Procedure for the preparation of *N*-methyl-2-((methylamino)methyl)aniline (8). To a tube containing a solution of 2-bromobenzyl bromide **1a** (0.5 mmol) in DMSO (2 mL) were added $Cu(OAc)_2$ (0.05 mmol), DMAP (0.15 mmol) and 40% aqueous methylamine **3b** (1 mL). Then, the tube was sealed and the mixture was stirred at 80 ^oC under air for 12 h. After being cooled to room temperature, the reaction was quenched with NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were washed with H_2O and brine, and then dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by chromatography on silica-gel to afford **8**.

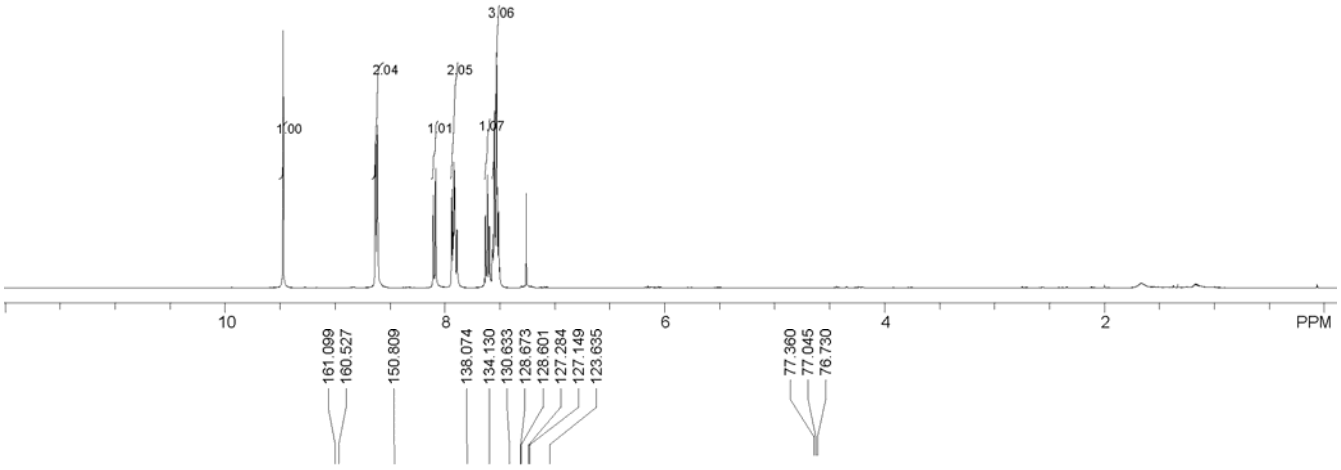
***N*-Methyl-2-((methylamino)methyl)aniline (8):** Eluent: petroleum ether-ethyl acetate (1:1); colorless liquid (64 mg, 85%); ^1H NMR (400 MHz, $CDCl_3$) δ: 2.44 (s, 3H), 2.87 (s, 3H), 3.76 (s, 2H), 6.67 (t, J = 8.0 Hz, 2H), 7.06 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.2, 6.0, 55.4, 109.6, 116.0, 123.6, 128.7, 129.6, 149.4. IR (KBr) ν = 2924, 1652, 1591, 1264, 758 cm^{-1}. MS: m/z 151 $(MH)^+$. HRMS (ESI) calcd for $C_9H_{15}N_2$: 151.1235 [M+H], found: 151.1238.

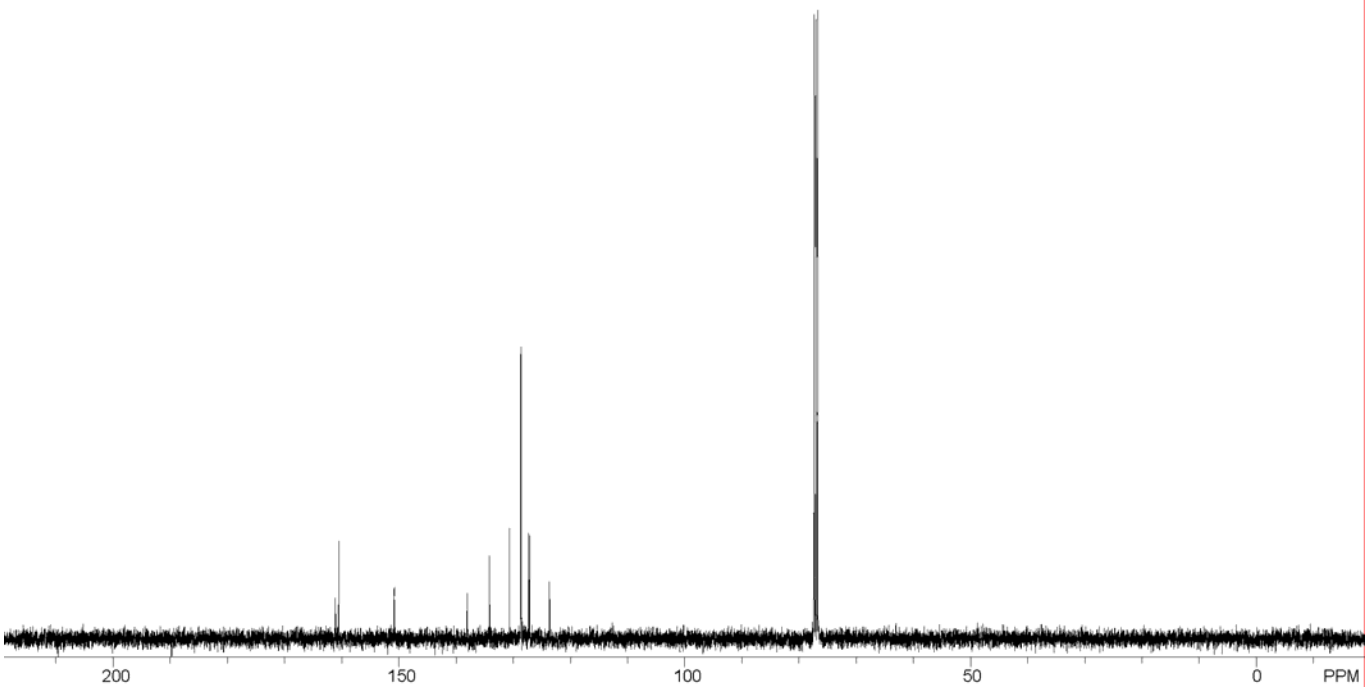
III. Copies of ^{1}H and ^{13}C NMR spectra of 4a-4t

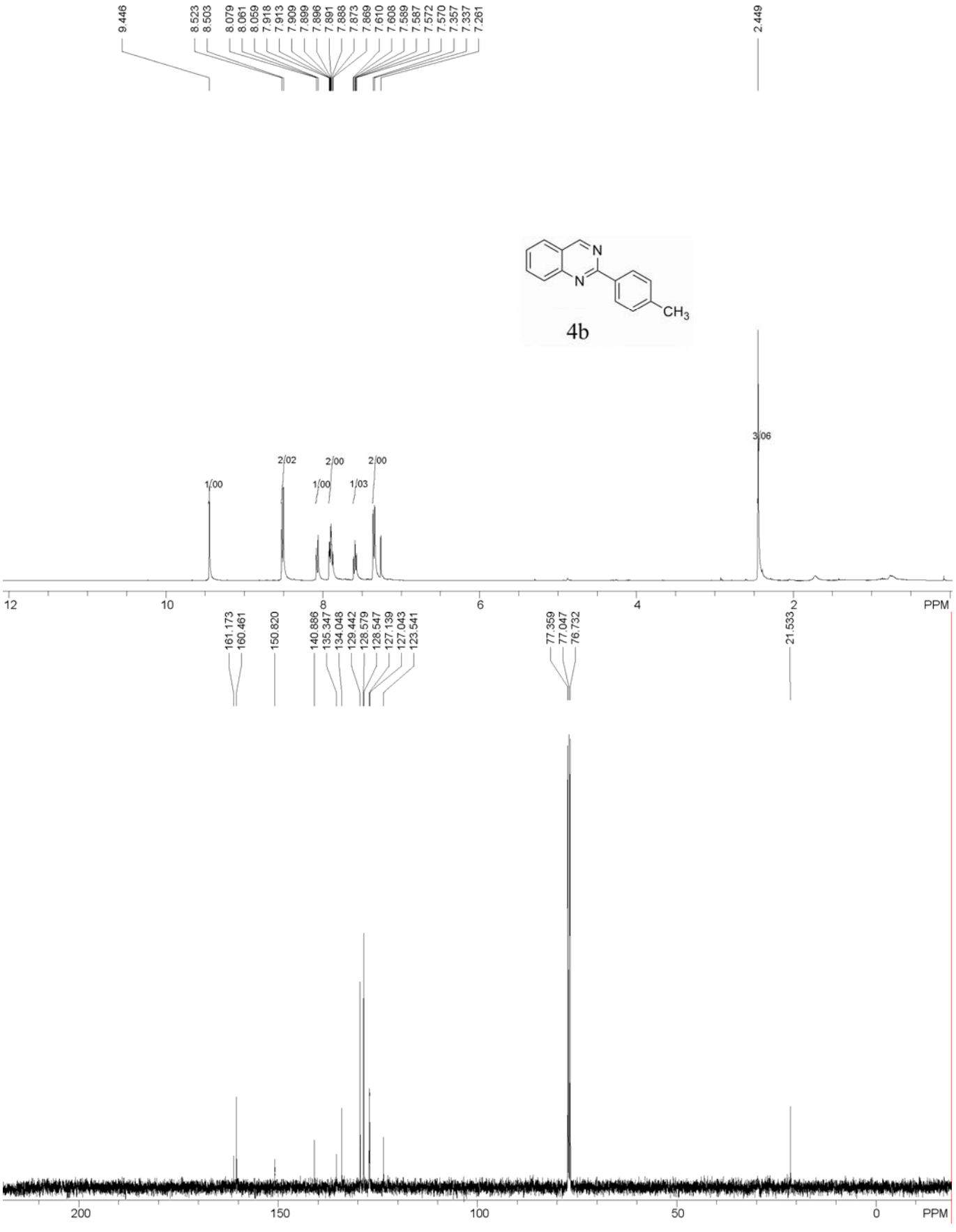




4a



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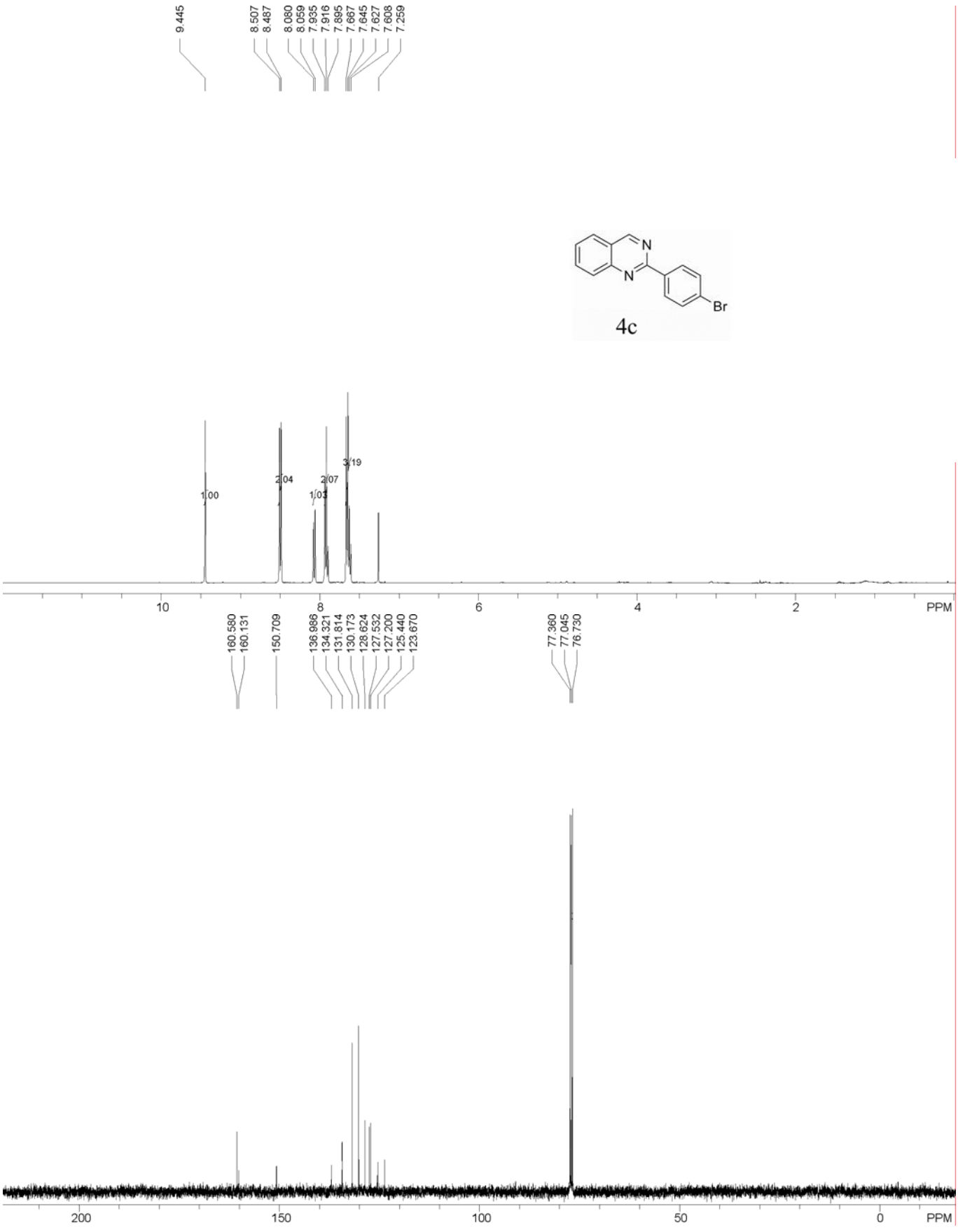
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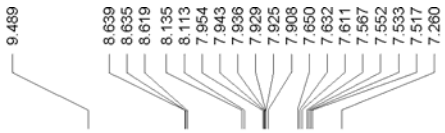
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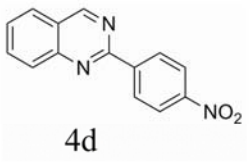
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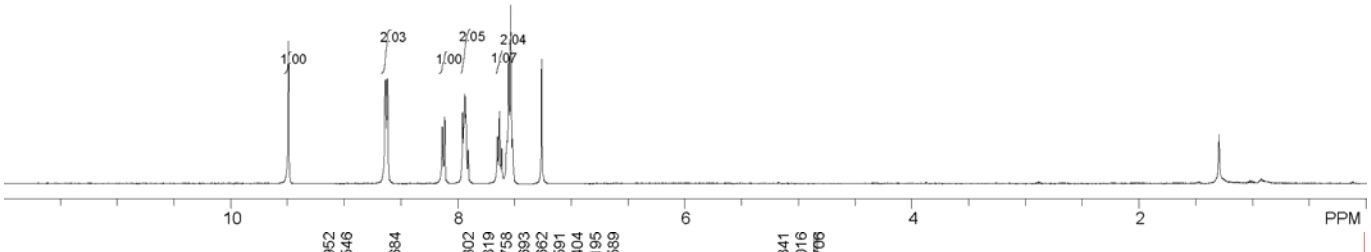
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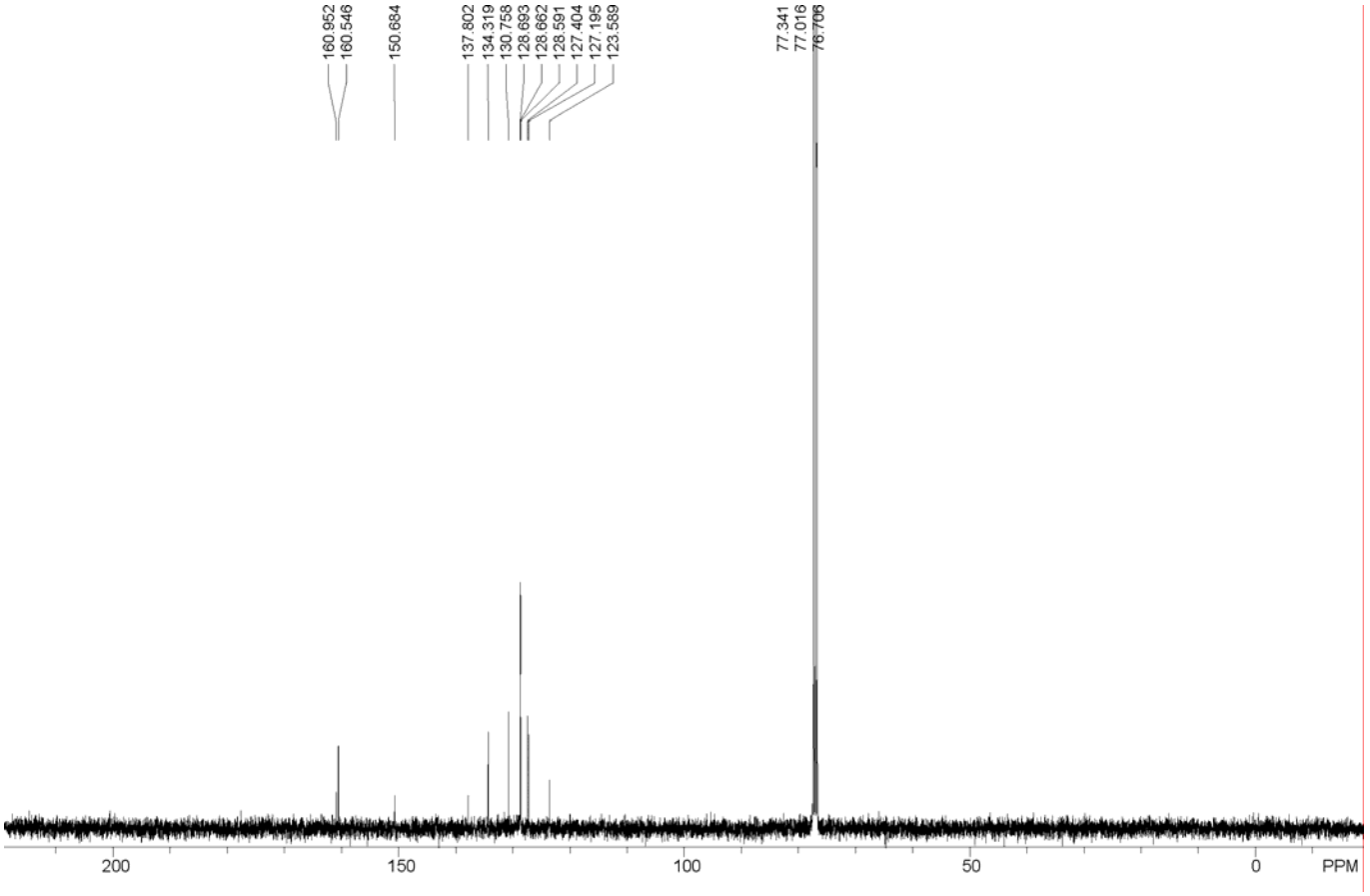
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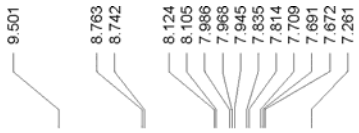
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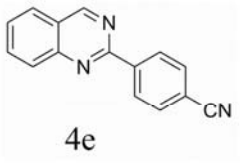
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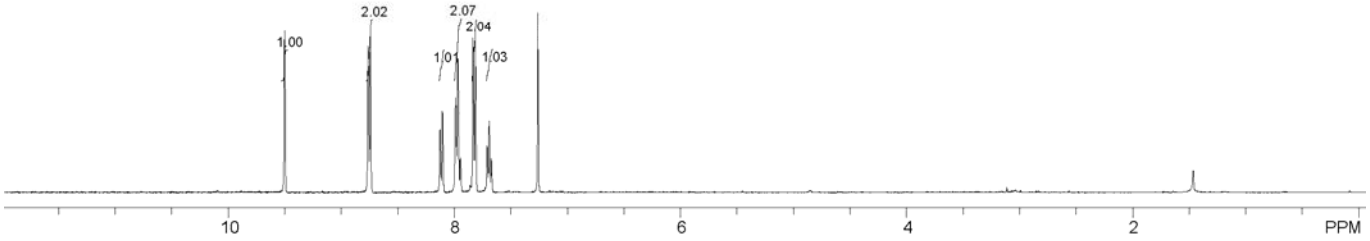
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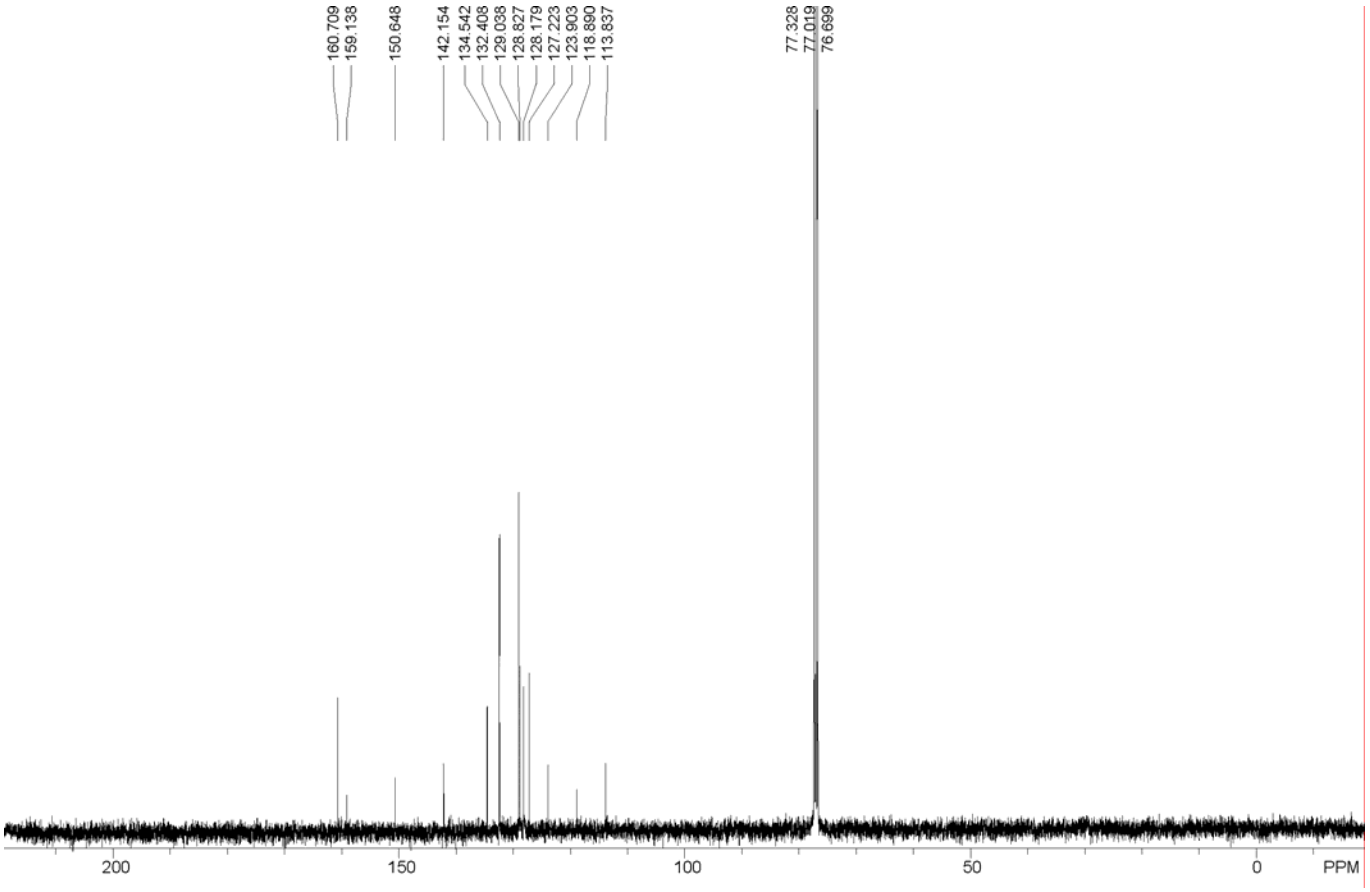
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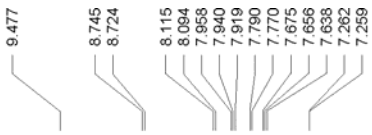
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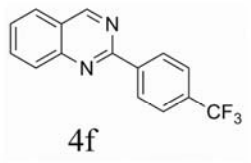
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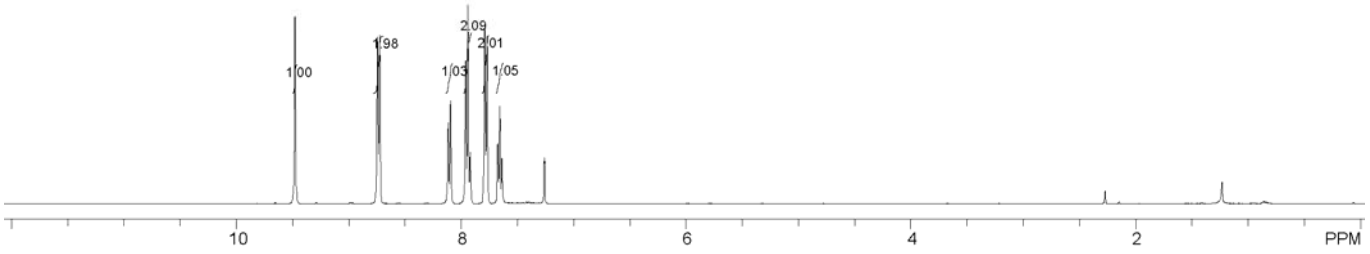
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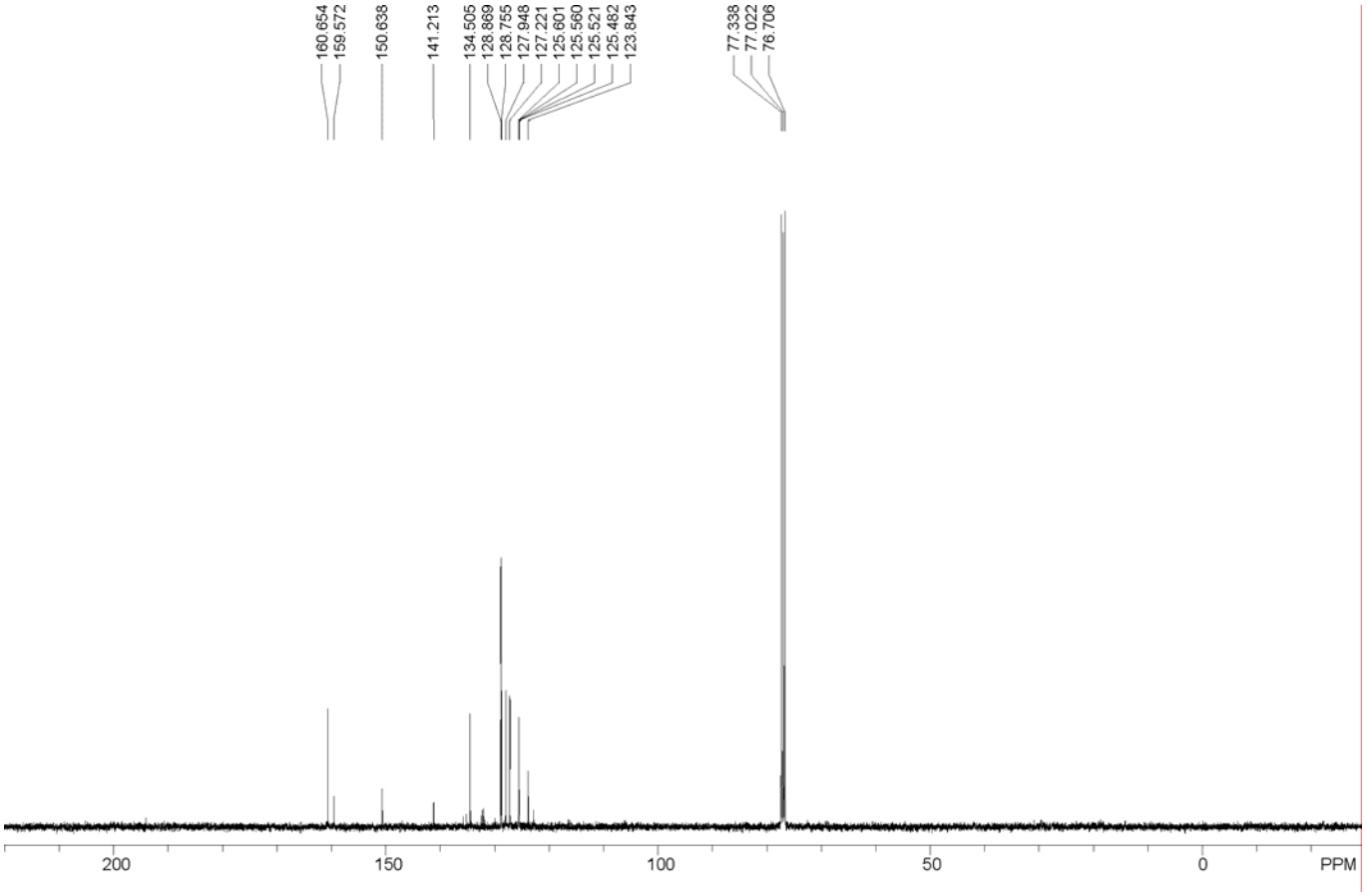
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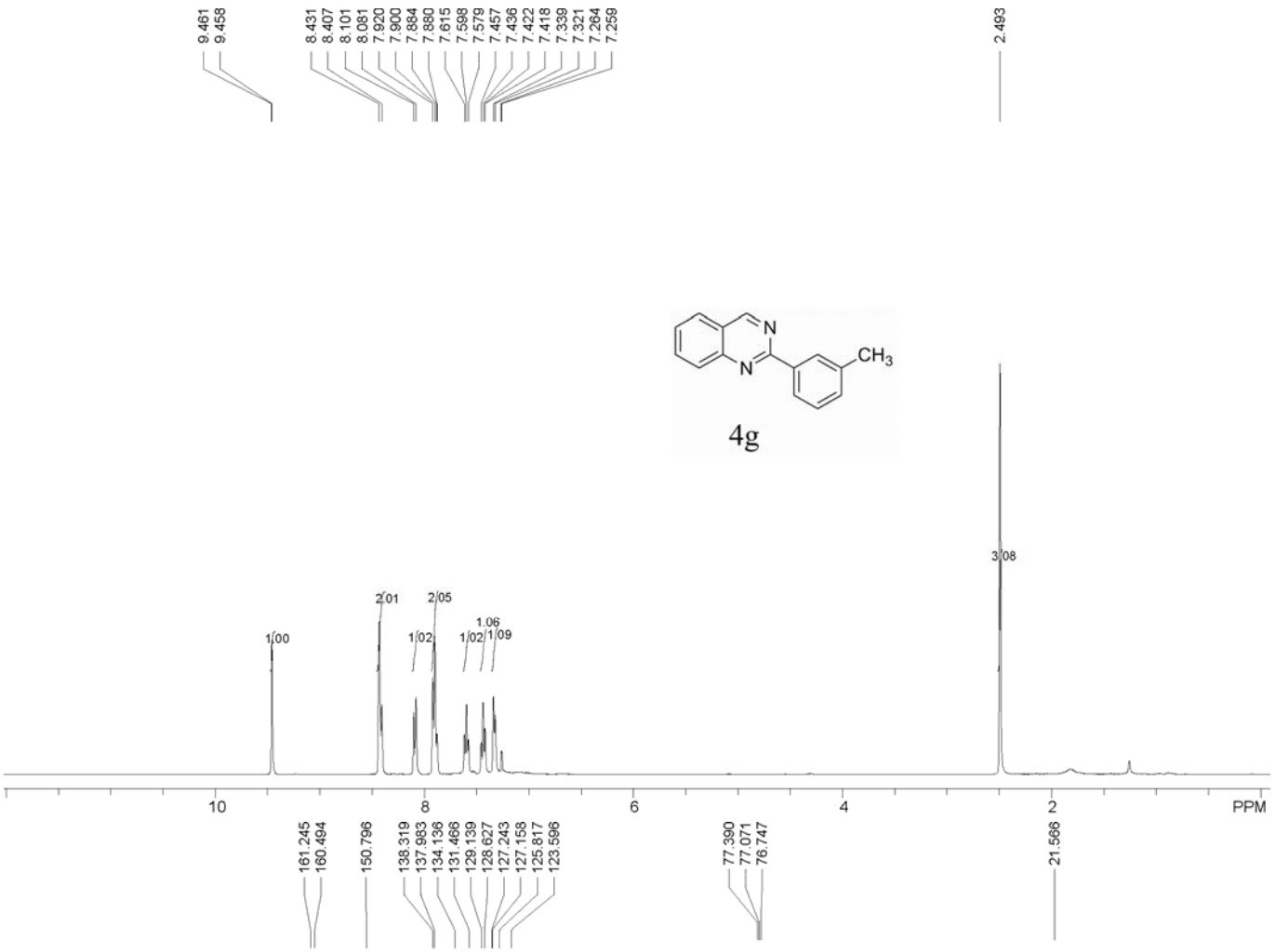
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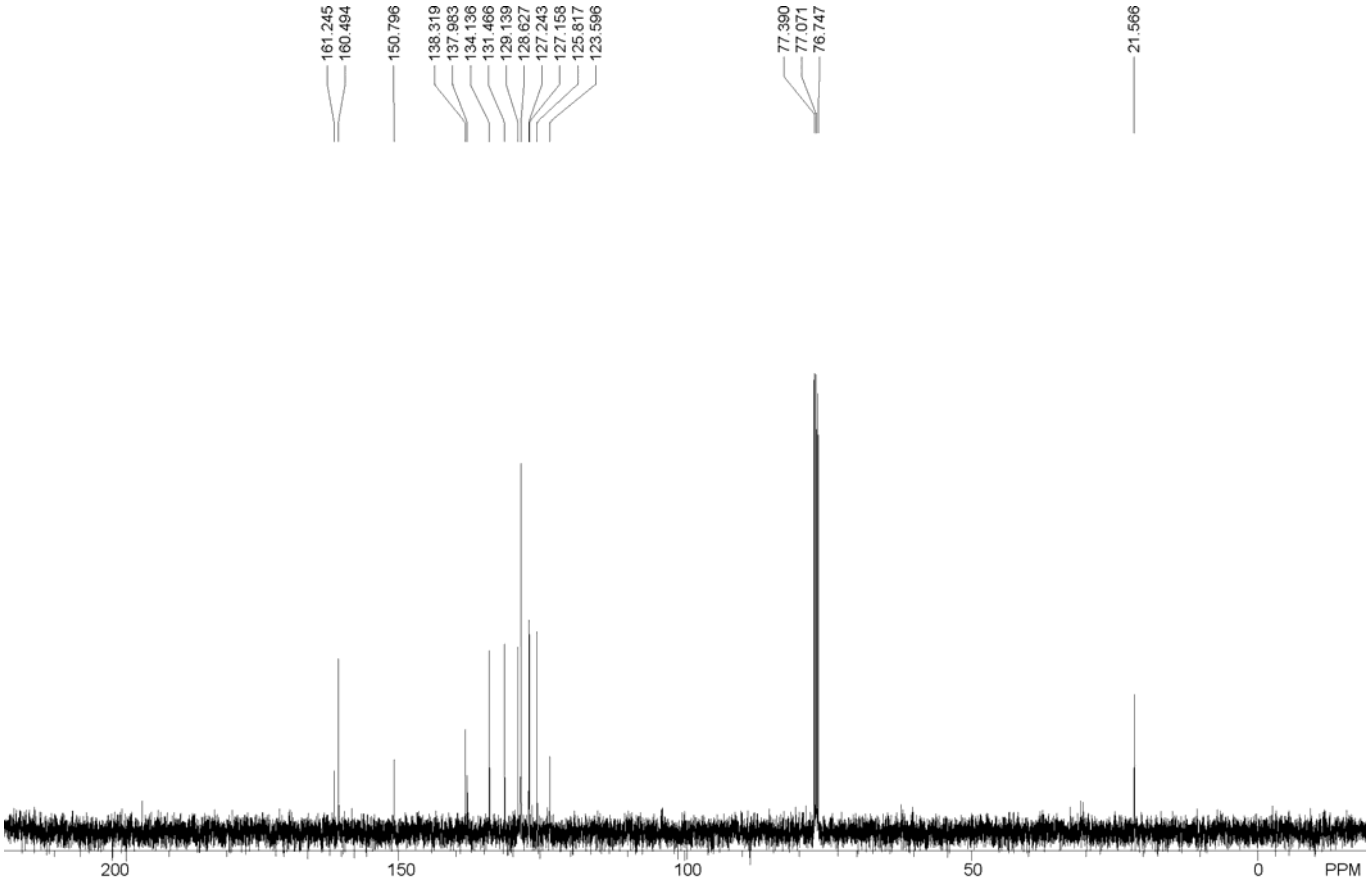
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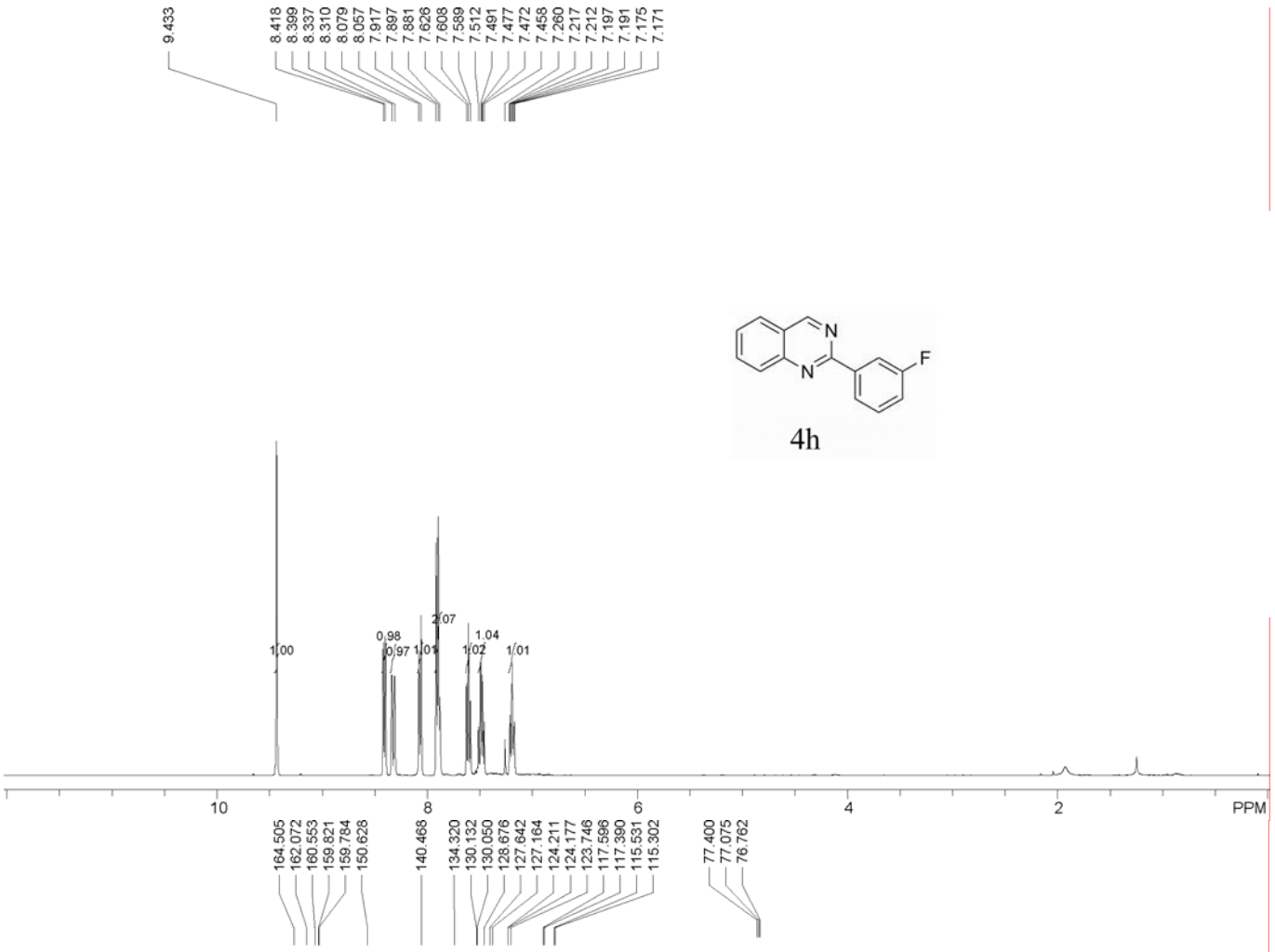
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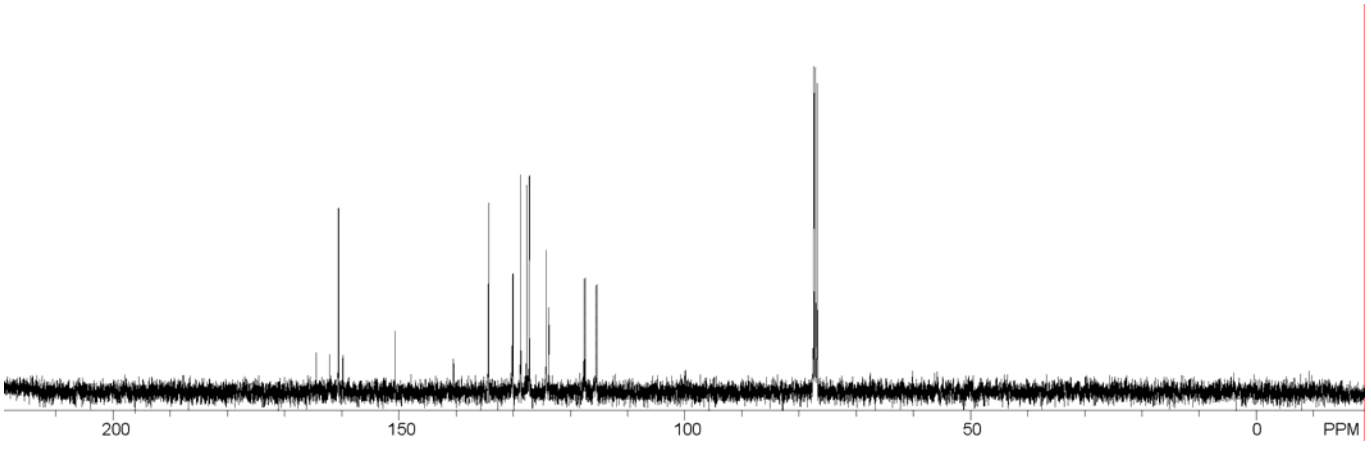
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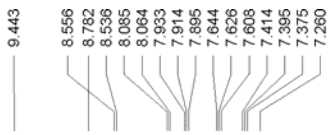
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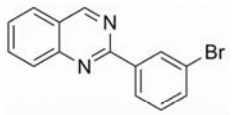
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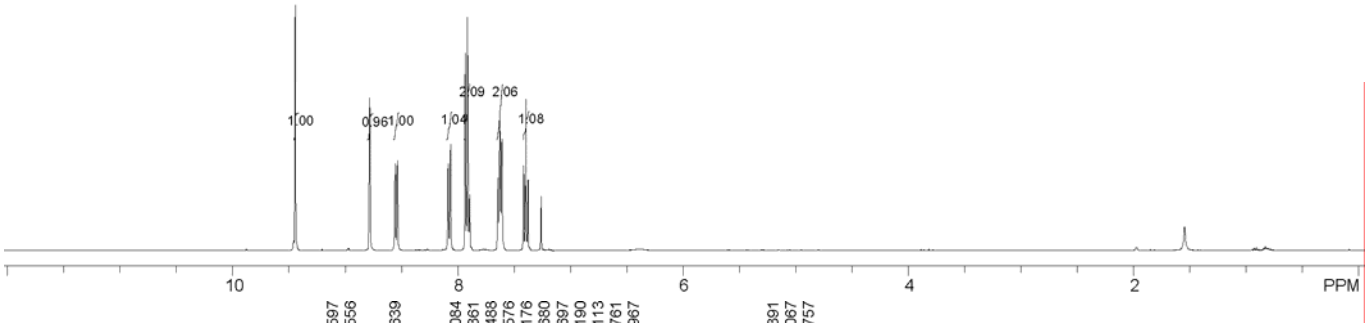
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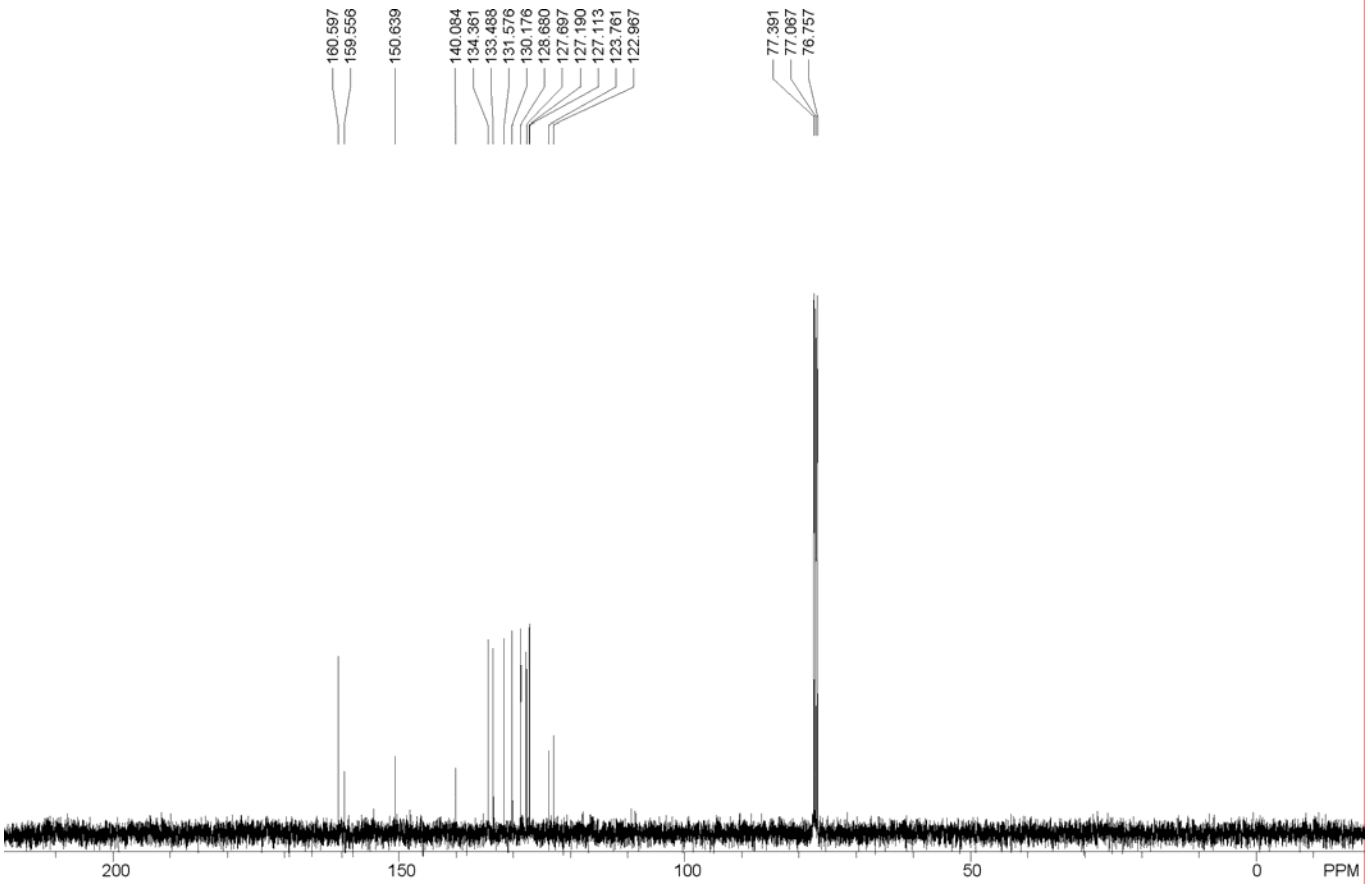
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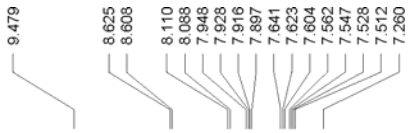
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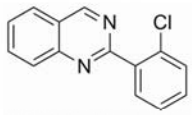
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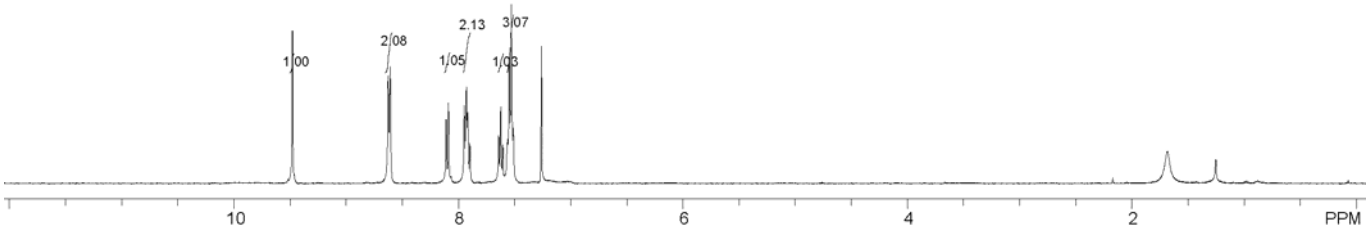
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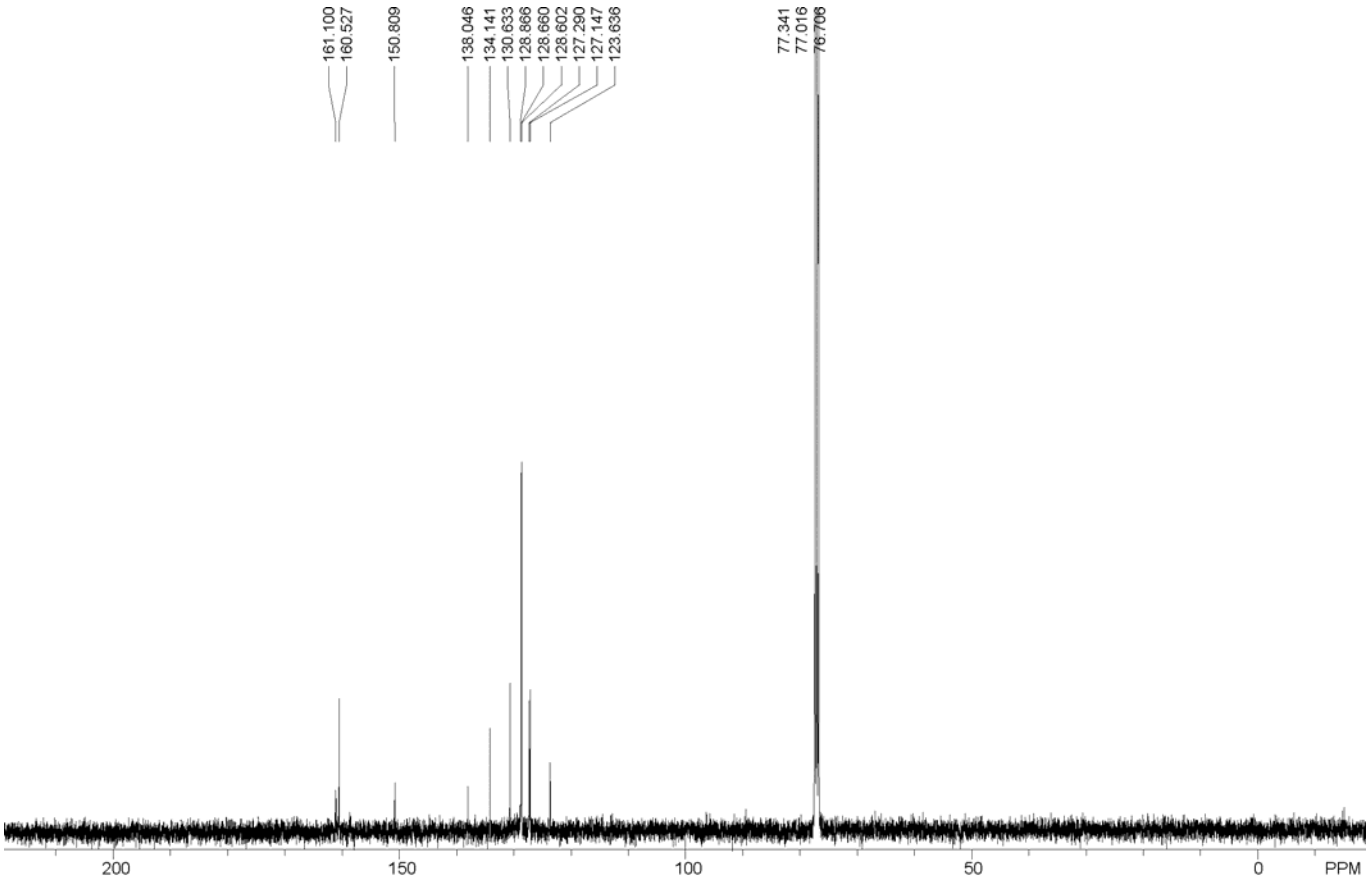
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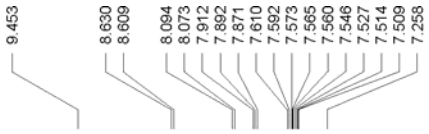
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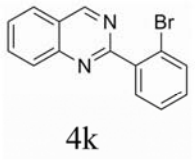
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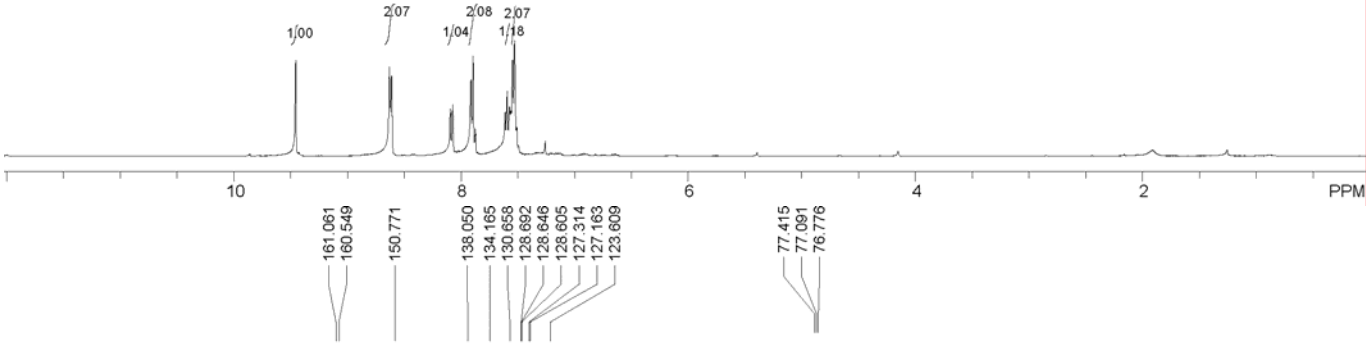
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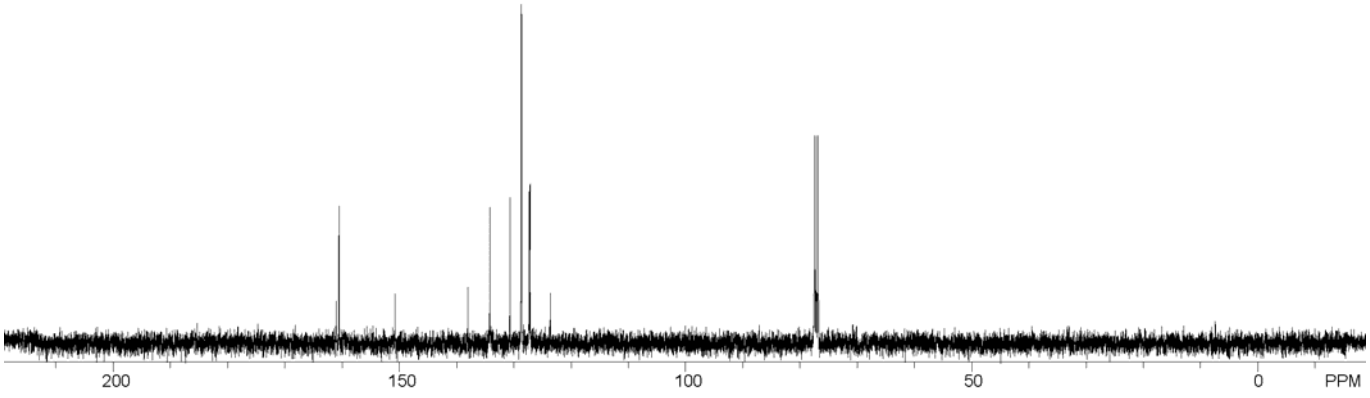
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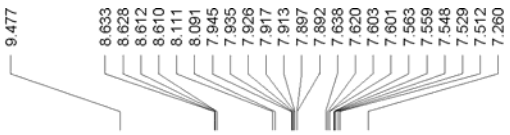
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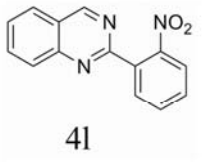
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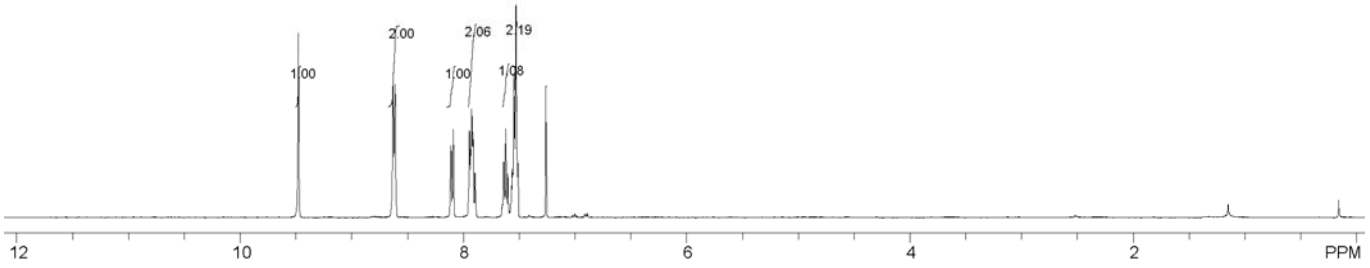
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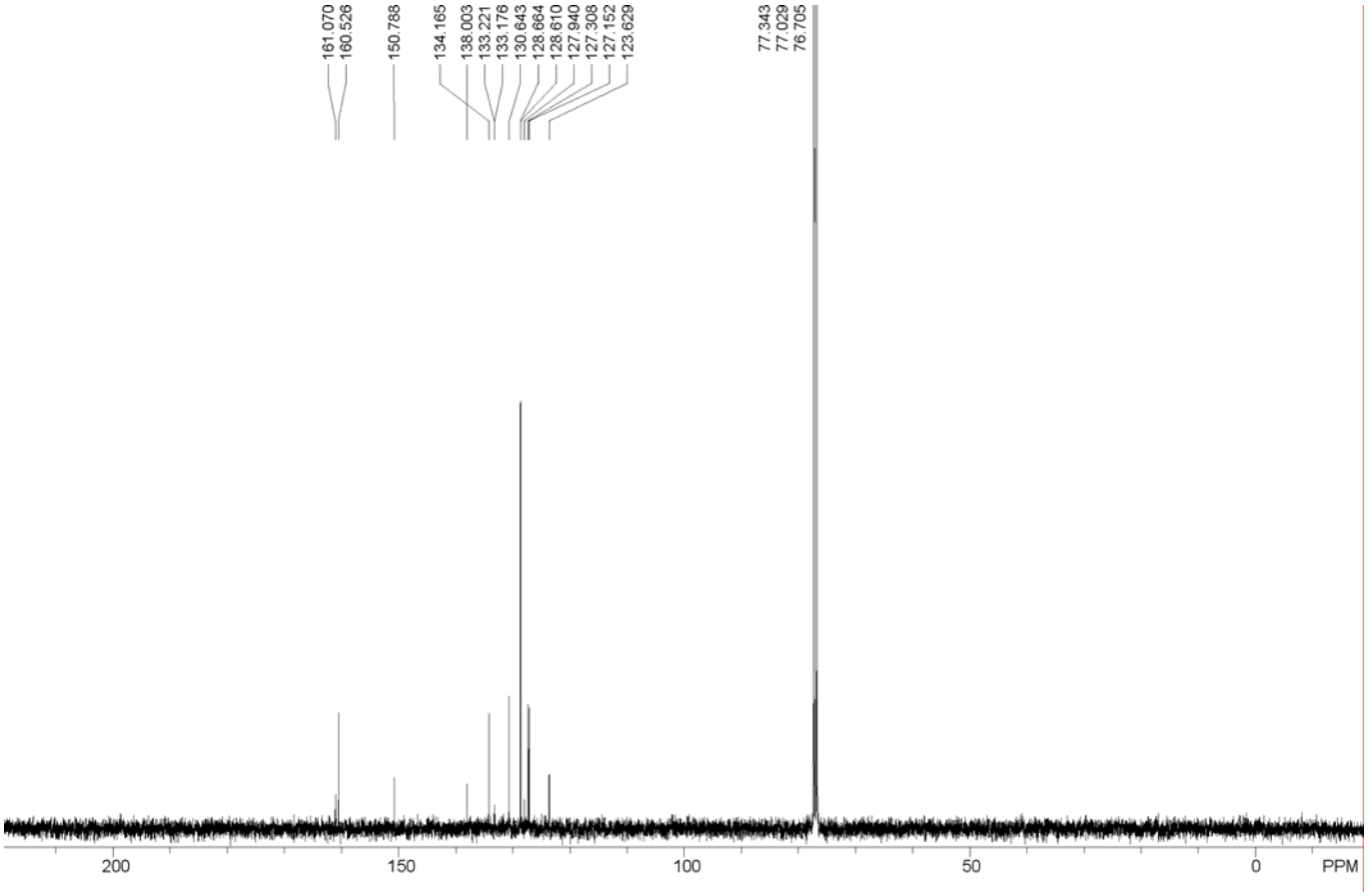
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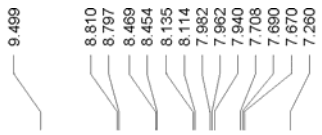
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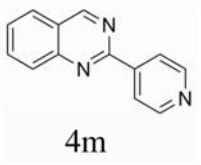

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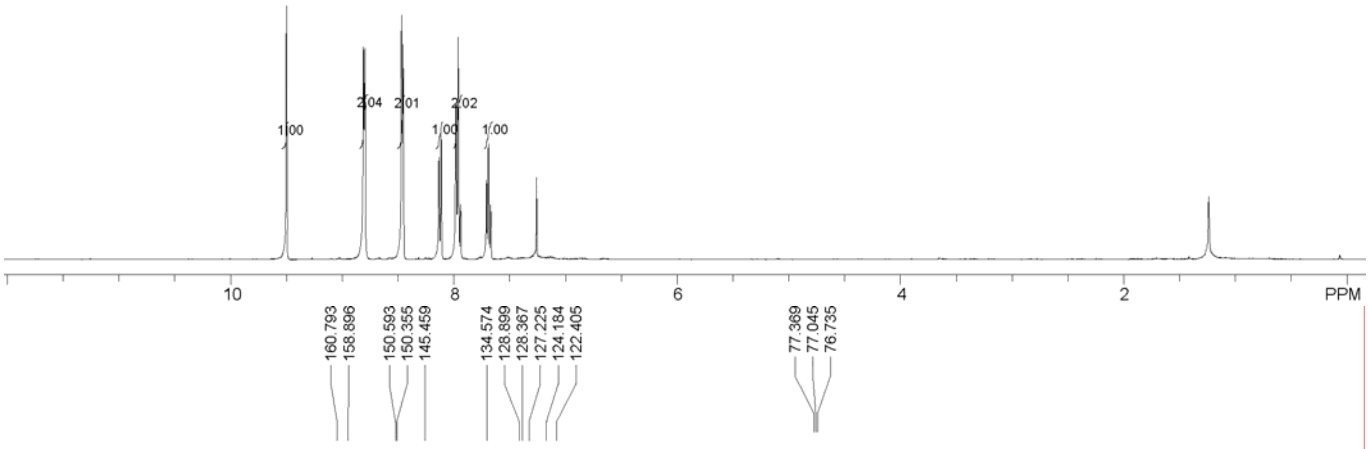
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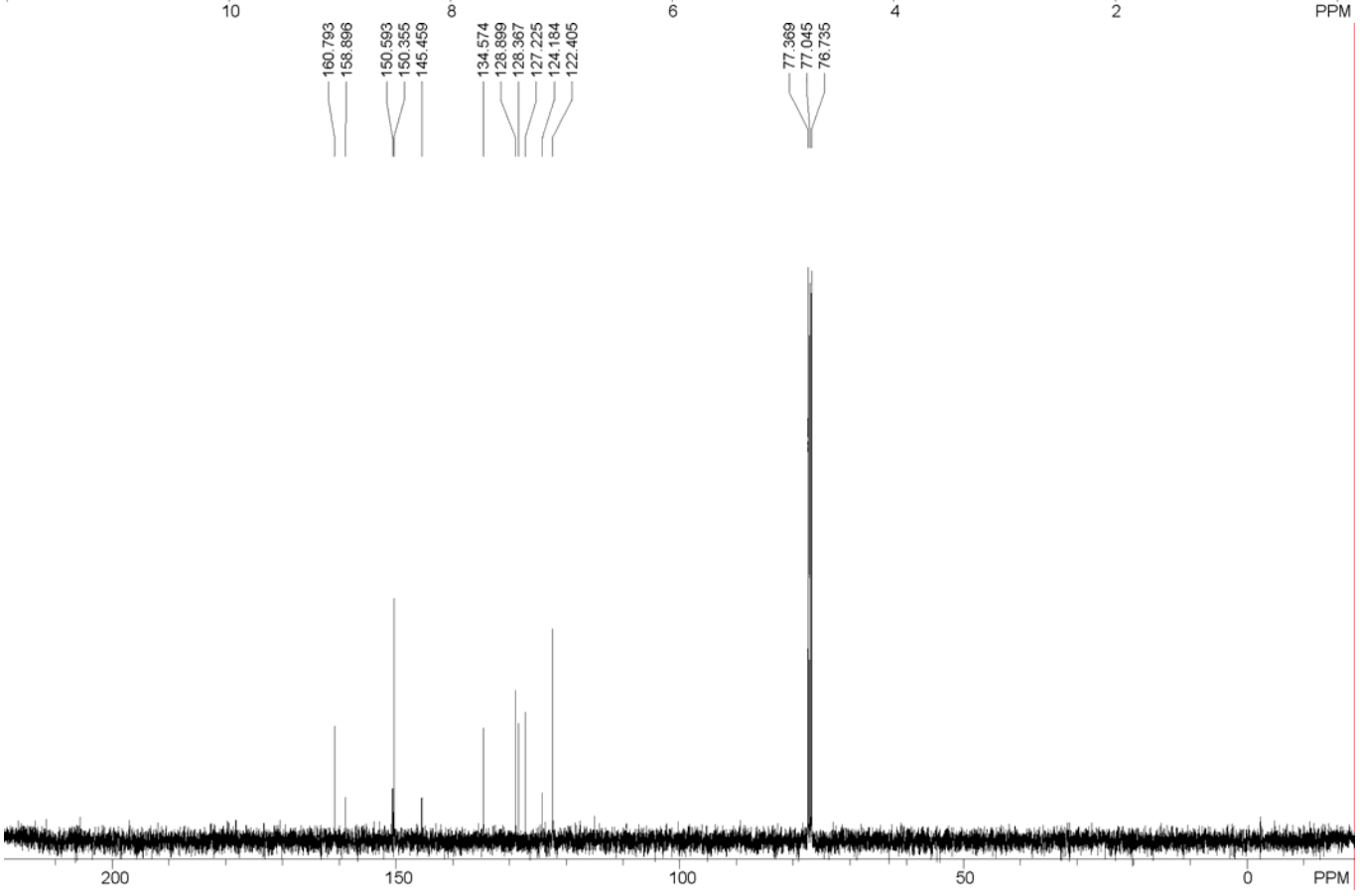
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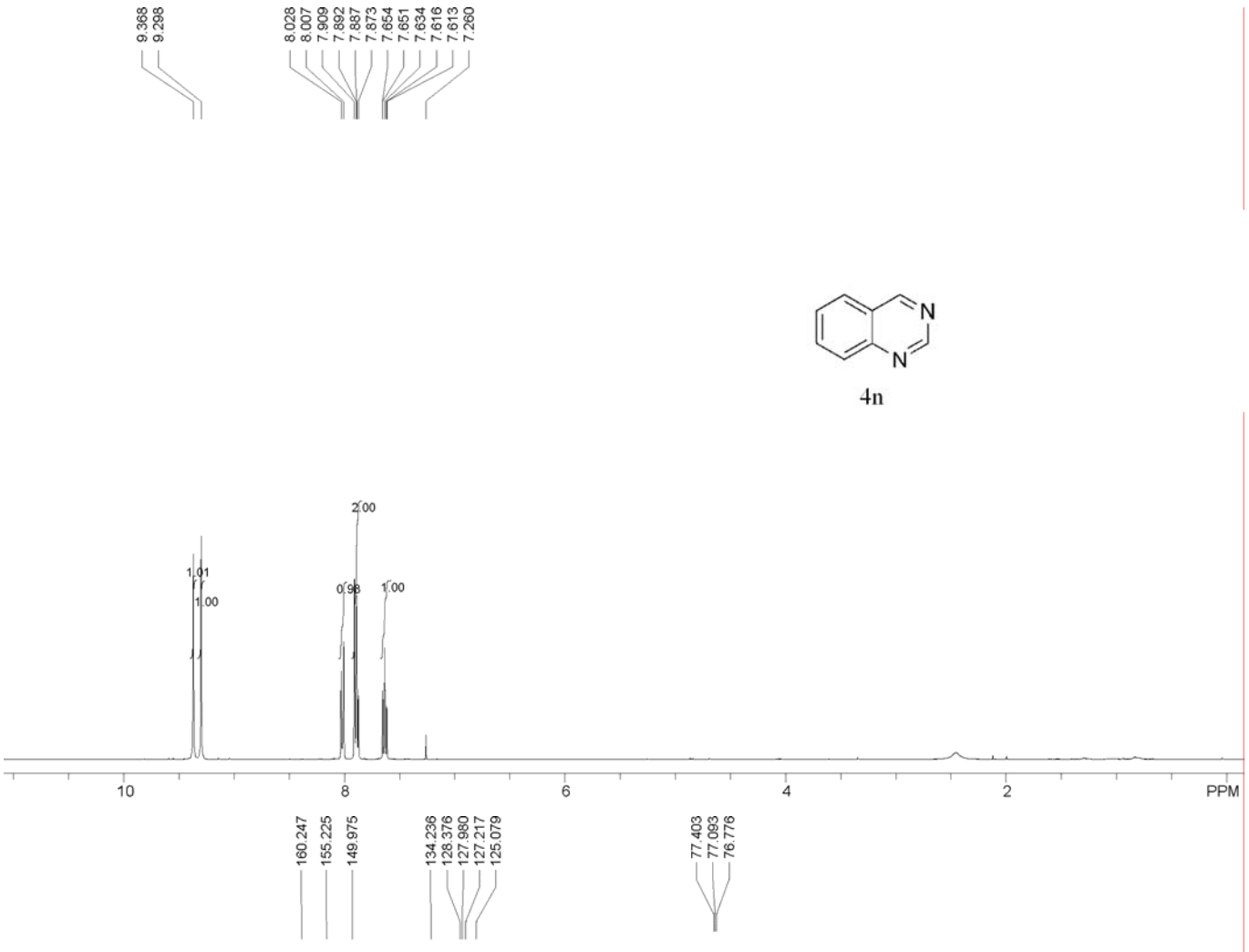
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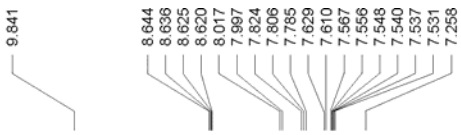
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7.567
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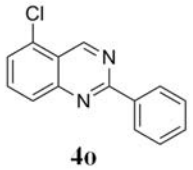
7.537
7.531
7.258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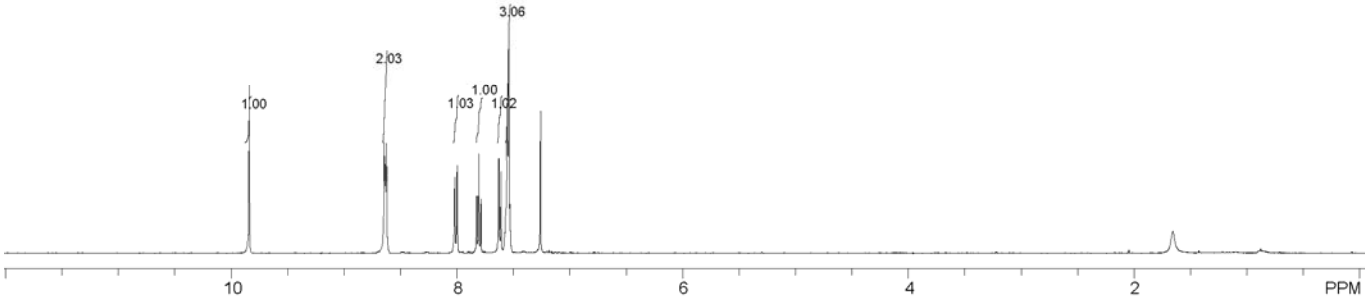
N

4o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1.02
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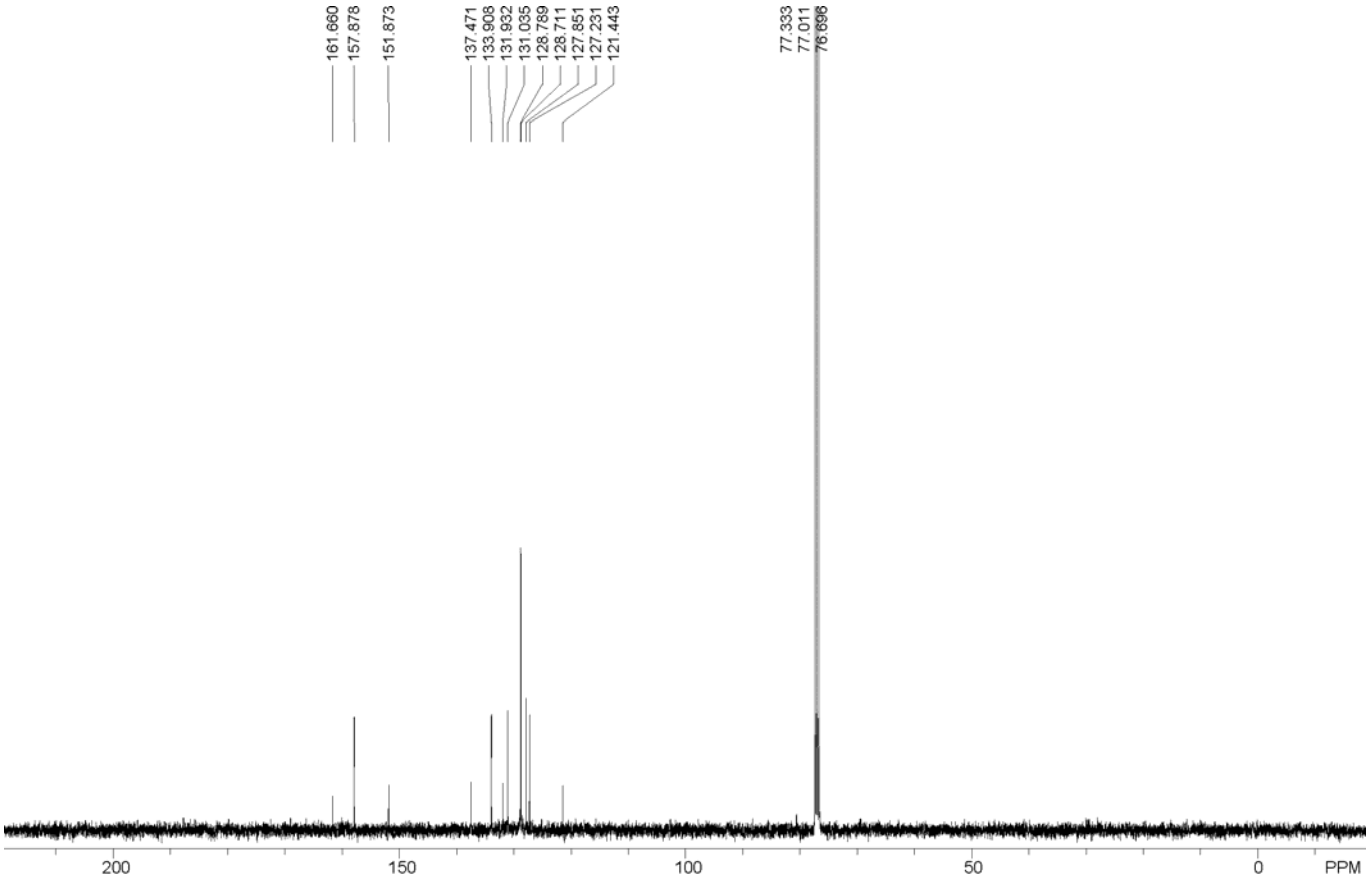
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151.873
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131.932
131.035
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127.851
127.231
121.443
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77.011
76.696
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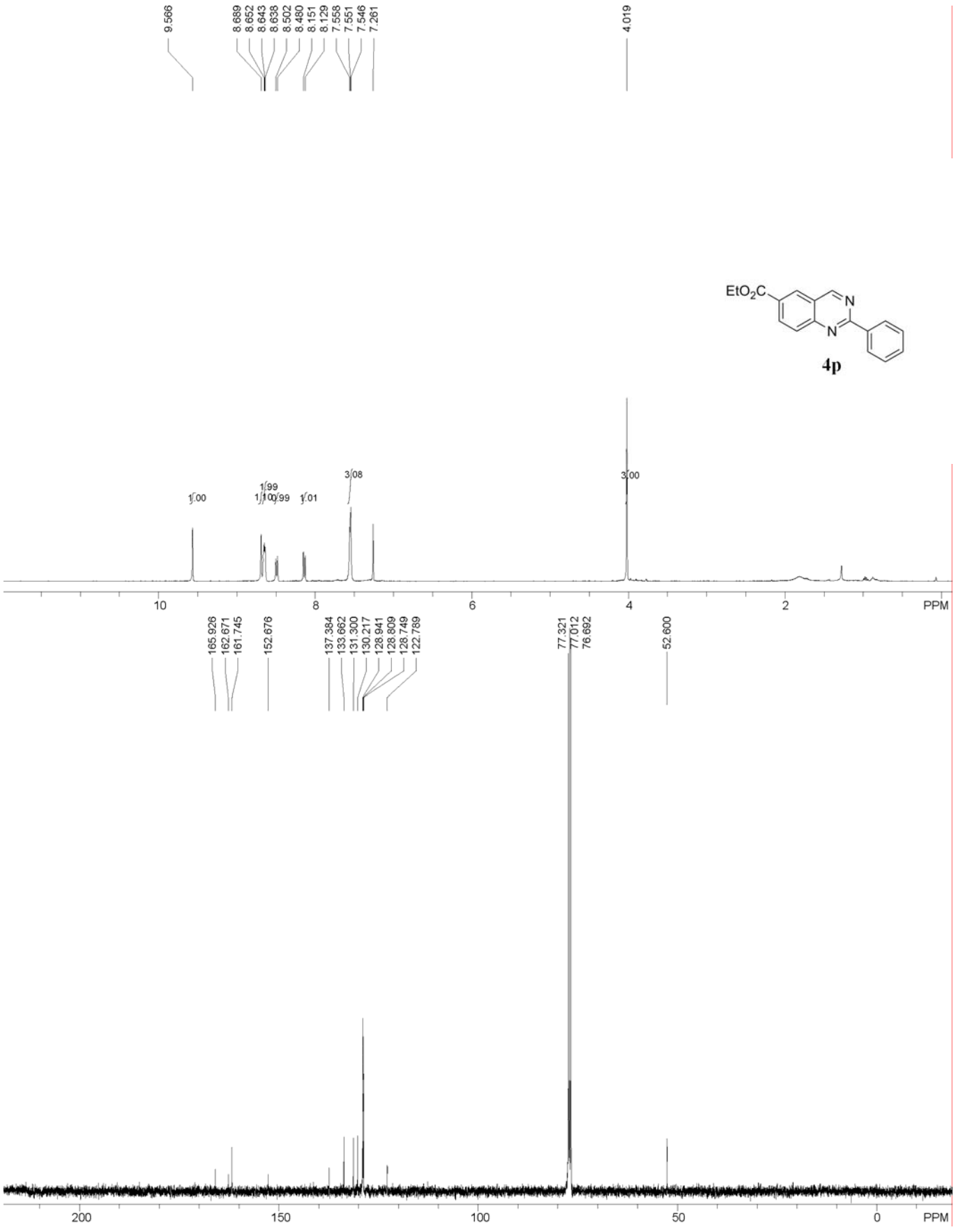
100
50
0
PPM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7.551
7.546
7.261
4.019
EtO2C
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N
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1.99
1.10
0.99
1.01
3.08
3.00
10
8
6
4
2
PPM
165.926
162.671
161.745
152.676
137.384
133.662
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130.217
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122.789
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77.012
76.692
52.600
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150
100
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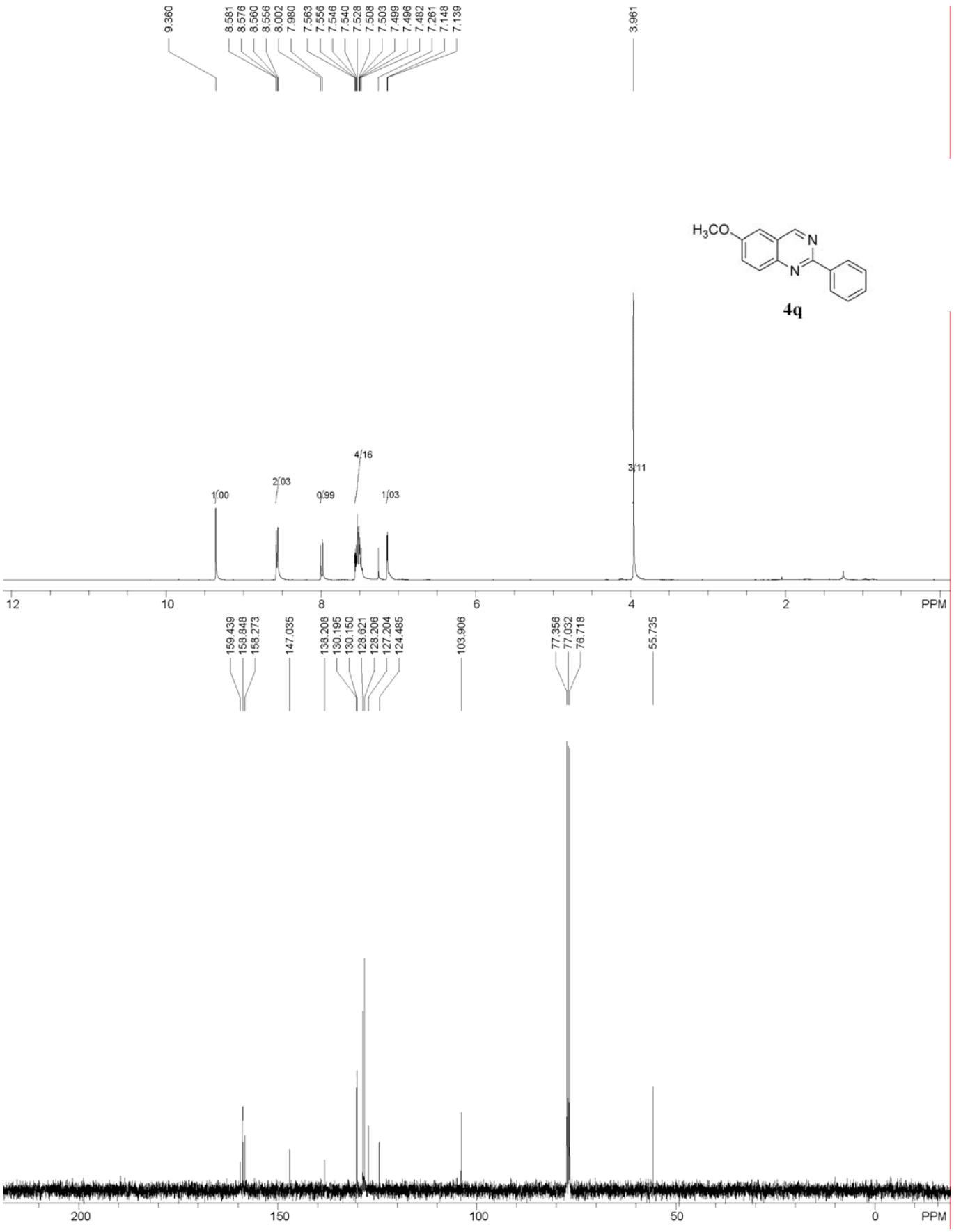
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7.508
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7.499
7.496
7.482
7.261
7.148
7.139
3.961
H3CO
N
N
4q
1.00
2.03
0.99
4.16
1.03
3.11
12
10
8
6
4
2
PPM
159.439
158.848
158.273
147.035
138.208
130.195
130.150
128.621
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124.485
103.906
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77.032
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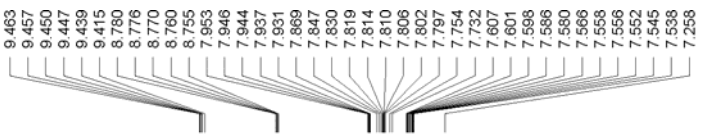
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9.450
9.447
9.439
9.415
8.780
8.776
8.770
8.760
8.755
7.953
7.946
7.944
7.937
7.931
7.869
7.847
7.830
7.819
7.814
7.810
7.806
7.802
7.797
7.754
7.732
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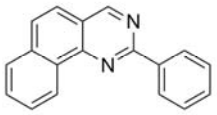
7.556
7.552
7.545
7.538
7.258



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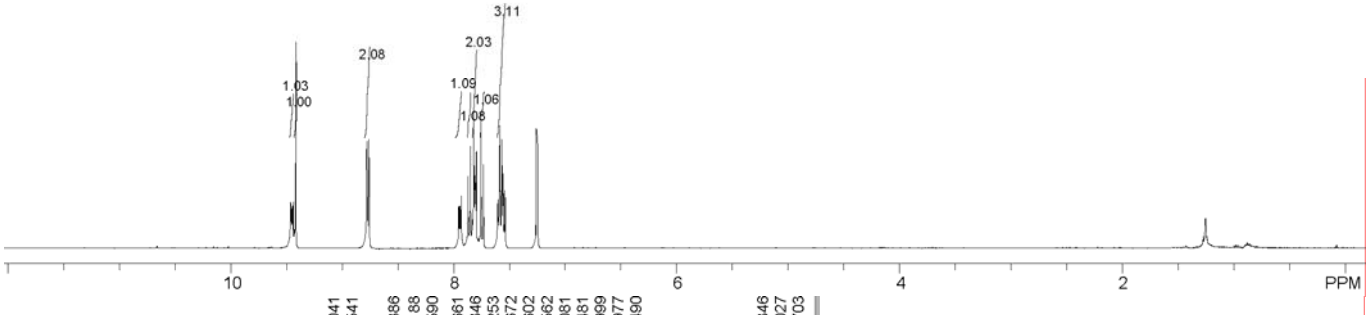
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2.08
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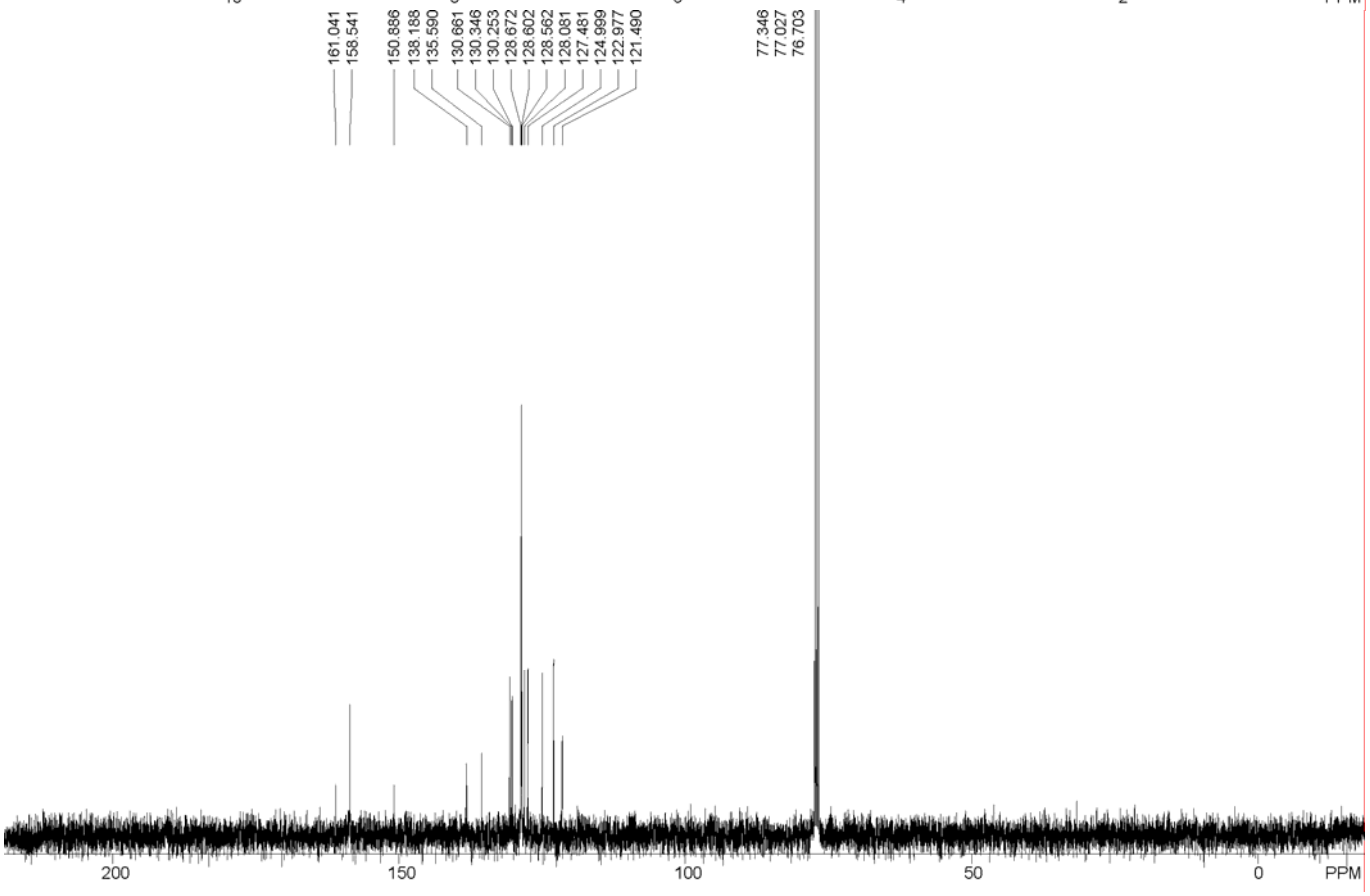
1.00
1.09
1.06
1.08
10
8
6
4
2
PPM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138.188
135.590
130.661
130.346
130.253
128.672
128.602
128.562
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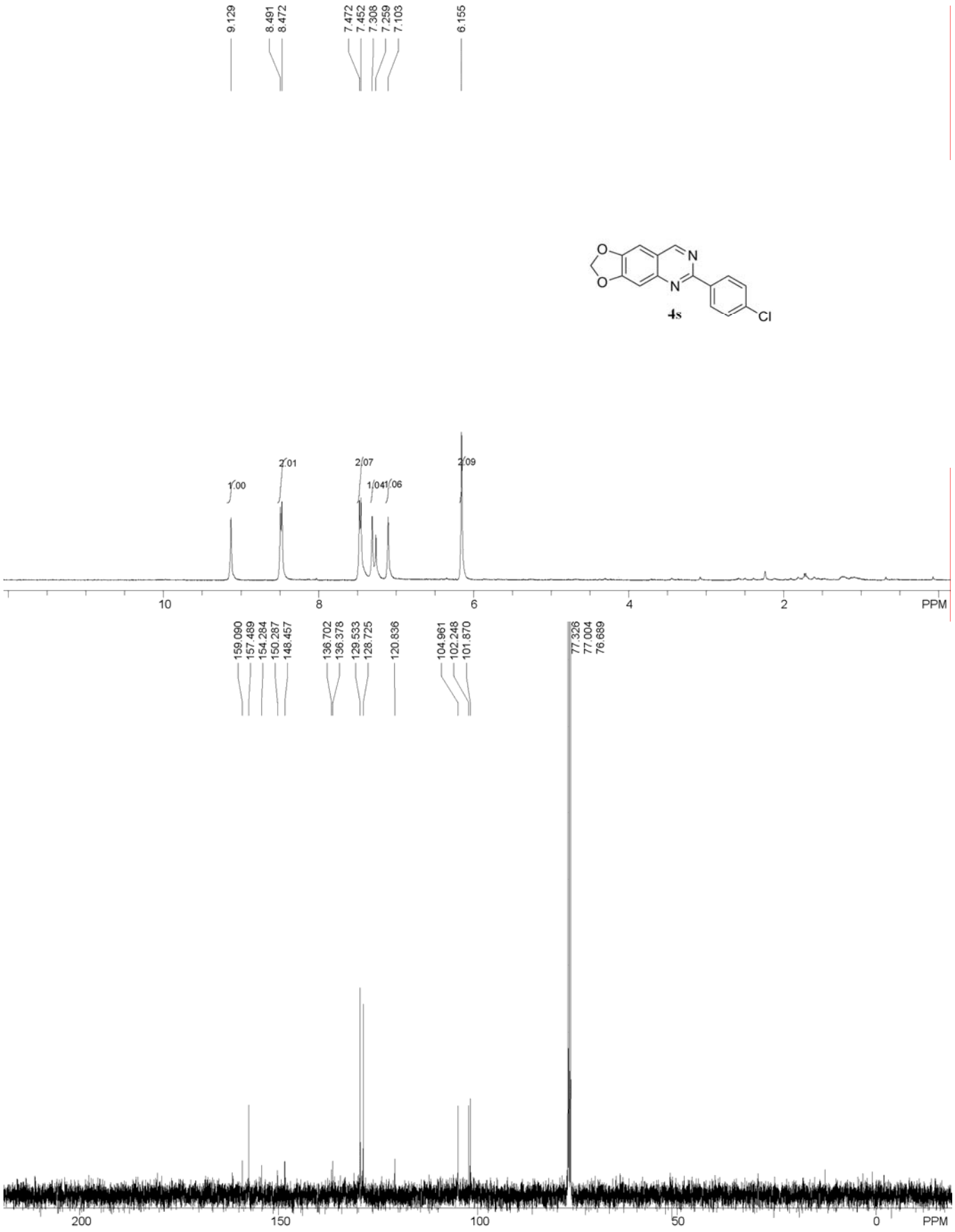
127.481
124.999
122.977
121.490
77.346
77.027
76.703
200
150
100
50
0
PPM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8.472
7.472
7.452
7.308
7.259
7.103
6.155
O
O
N
N
Cl
4s
1.00
2.01
2.07
1.04
1.06
2.09
10
8
6
4
2
PPM
159.090
157.489
154.284
150.287
148.457
136.702
136.378
129.533
128.725
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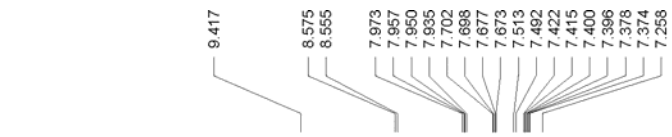
104.961
102.248
101.870
77.326
77.004
76.689
200
150
100
50
0
PPM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7.950
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7.702
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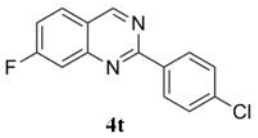
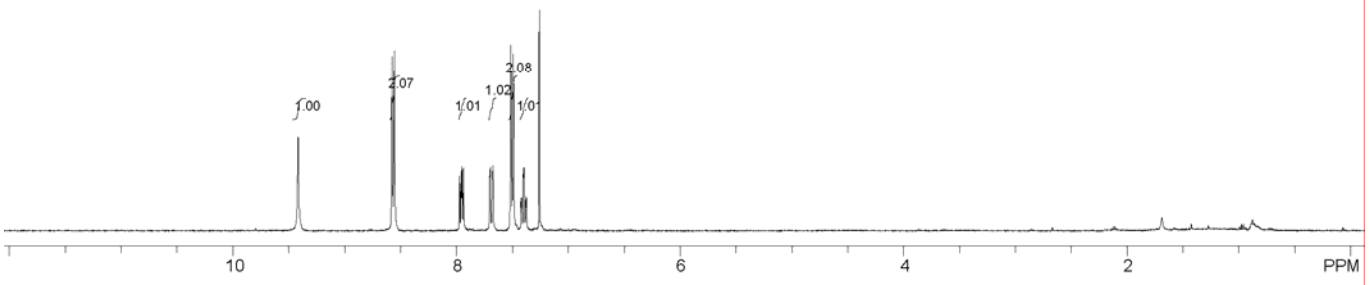
7.677
7.673
7.513
7.492
7.422
7.415
7.400
7.396
7.378
7.374
7.258


F
N
N
Cl

4t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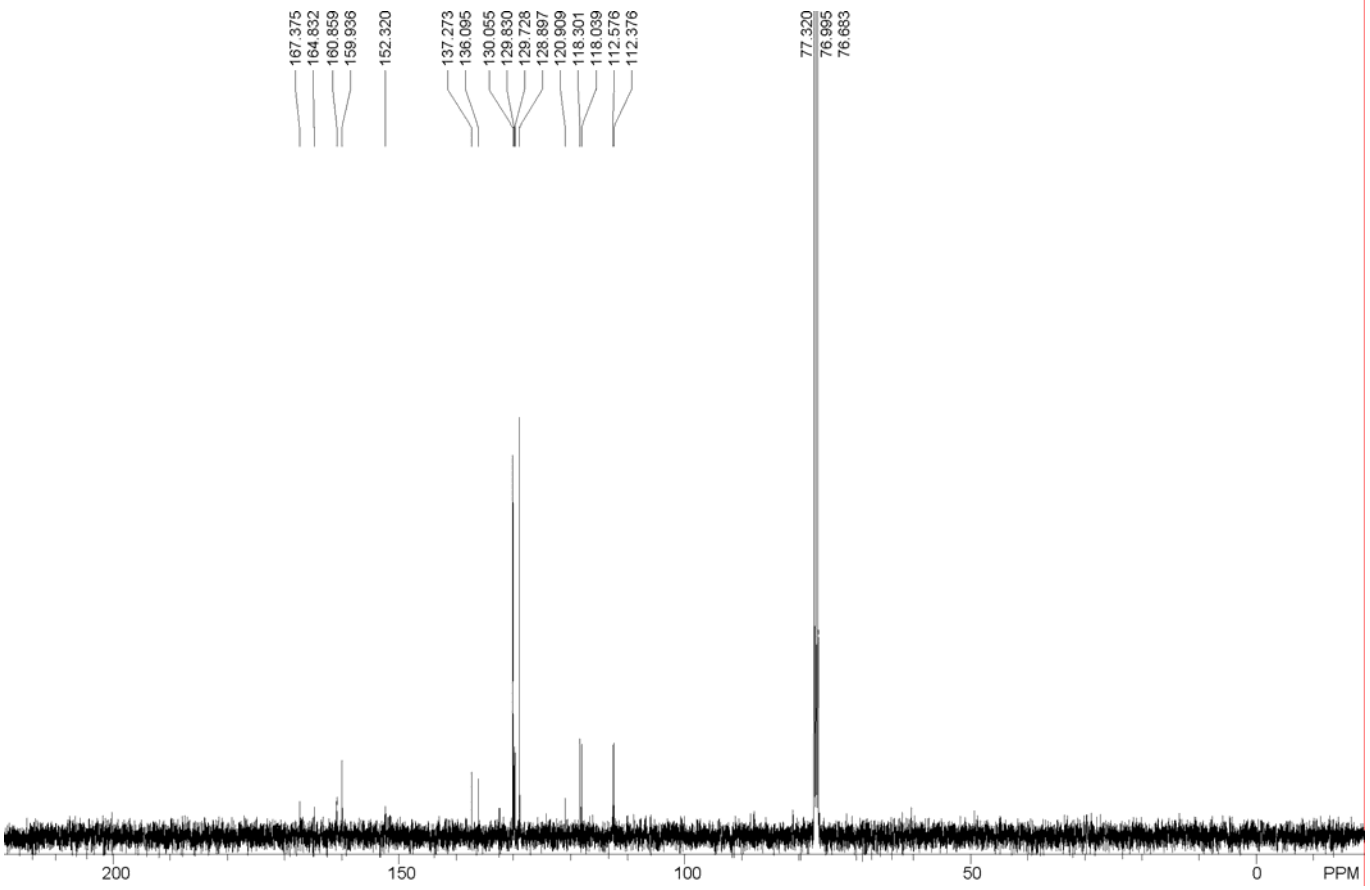
1.01
1.02
2.08
1.01
10
8
6
4
2
PPM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137.273
136.095
130.055
129.830
129.728
128.897
120.909
118.301
118.039
112.576
112.376
77.320
76.995
76.683
200
150
100
50
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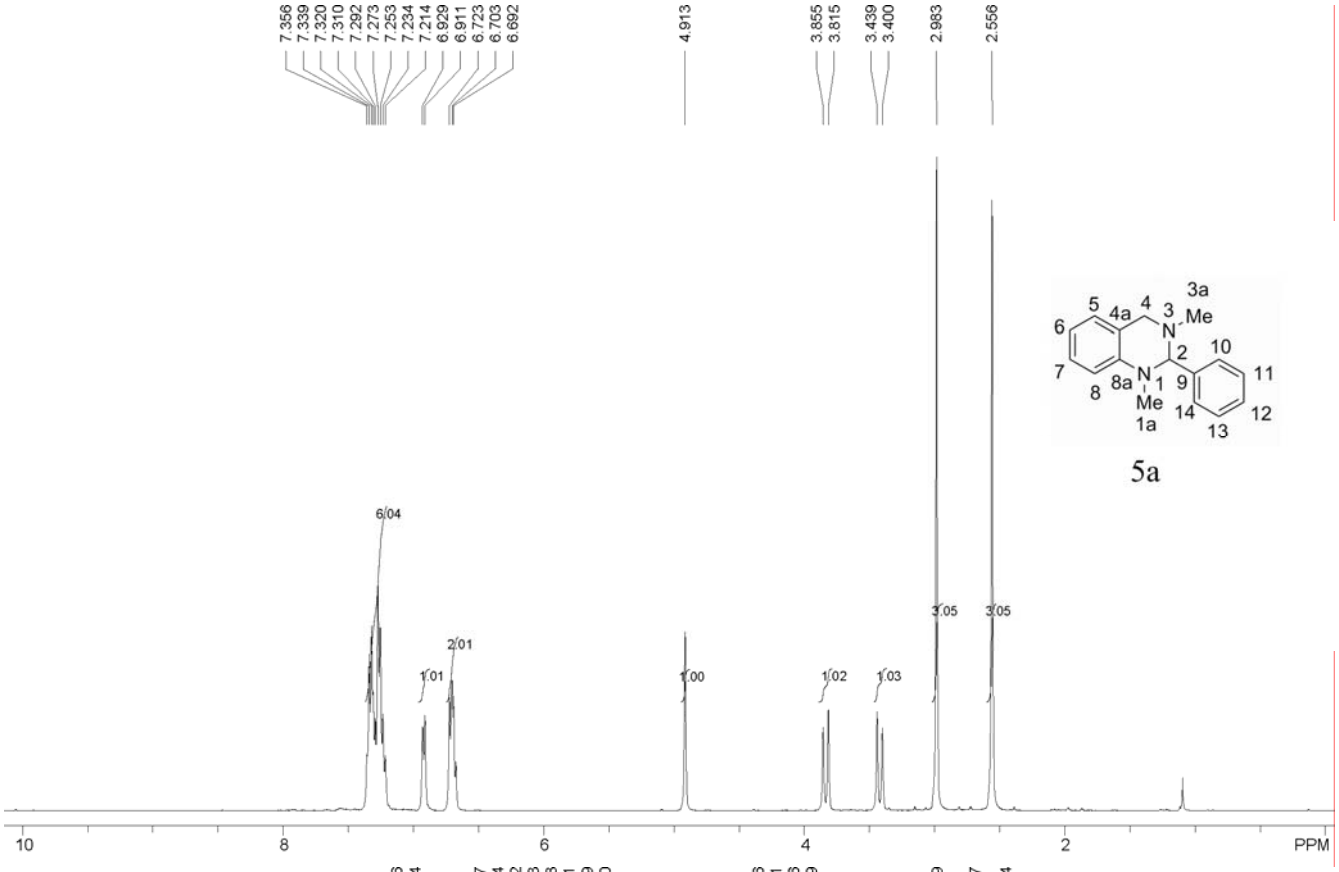
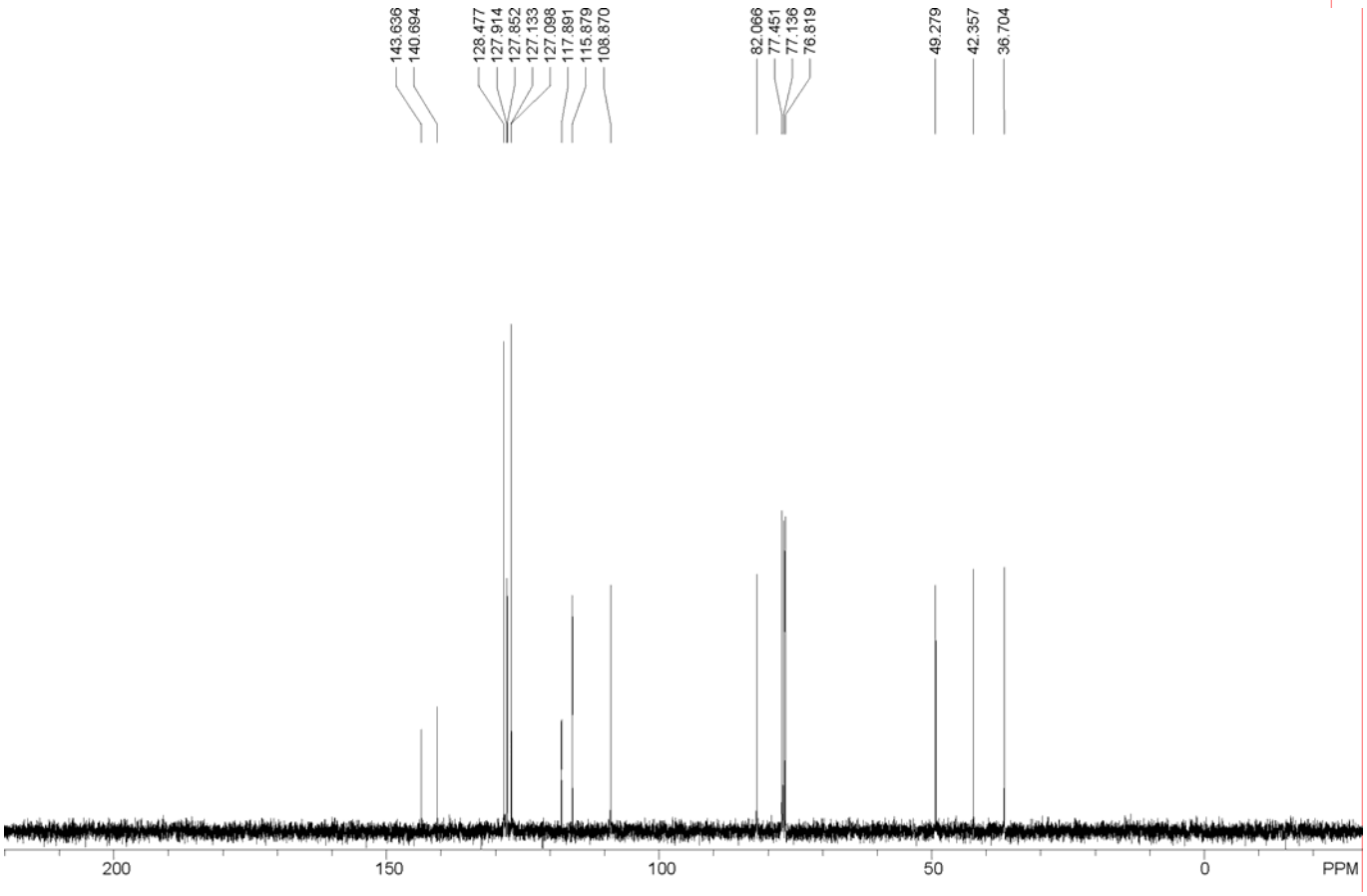
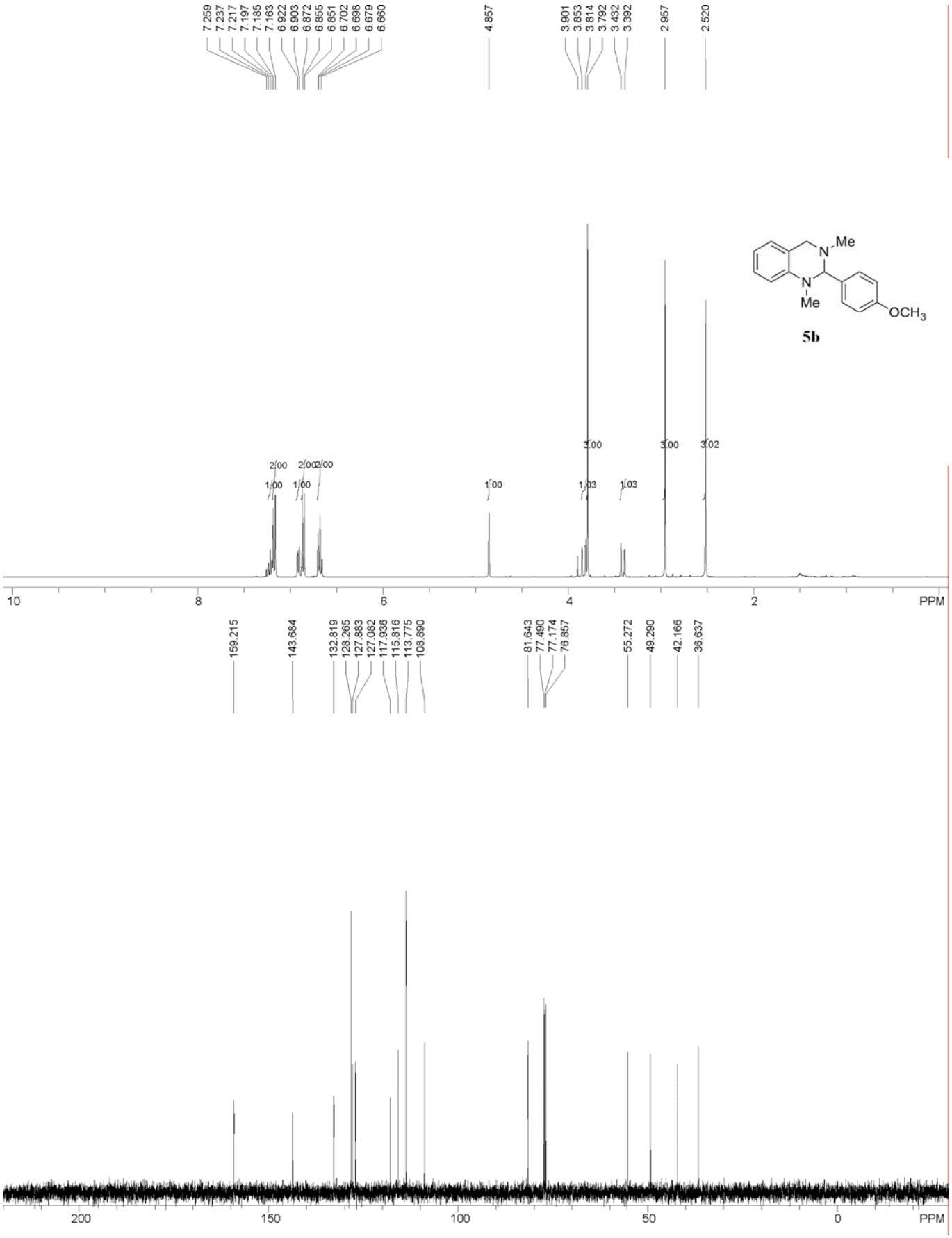
PPM

IV. Copies of ^{1}H and ^{13}C NMR spectra of 5a-5r



5a

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6.851
6.702
6.698
6.679
6.660
4.857
3.901
3.853
3.814
3.792
3.432
3.392
2.957
2.520
Me
N
N
Me
OCH3
5b
2.00
2.00
2.00
1.00
1.00
1.00
1.03
1.03
3.00
3.00
3.02
10
8
6
4
2
PPM
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127.883
127.082
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115.816
113.775
108.890
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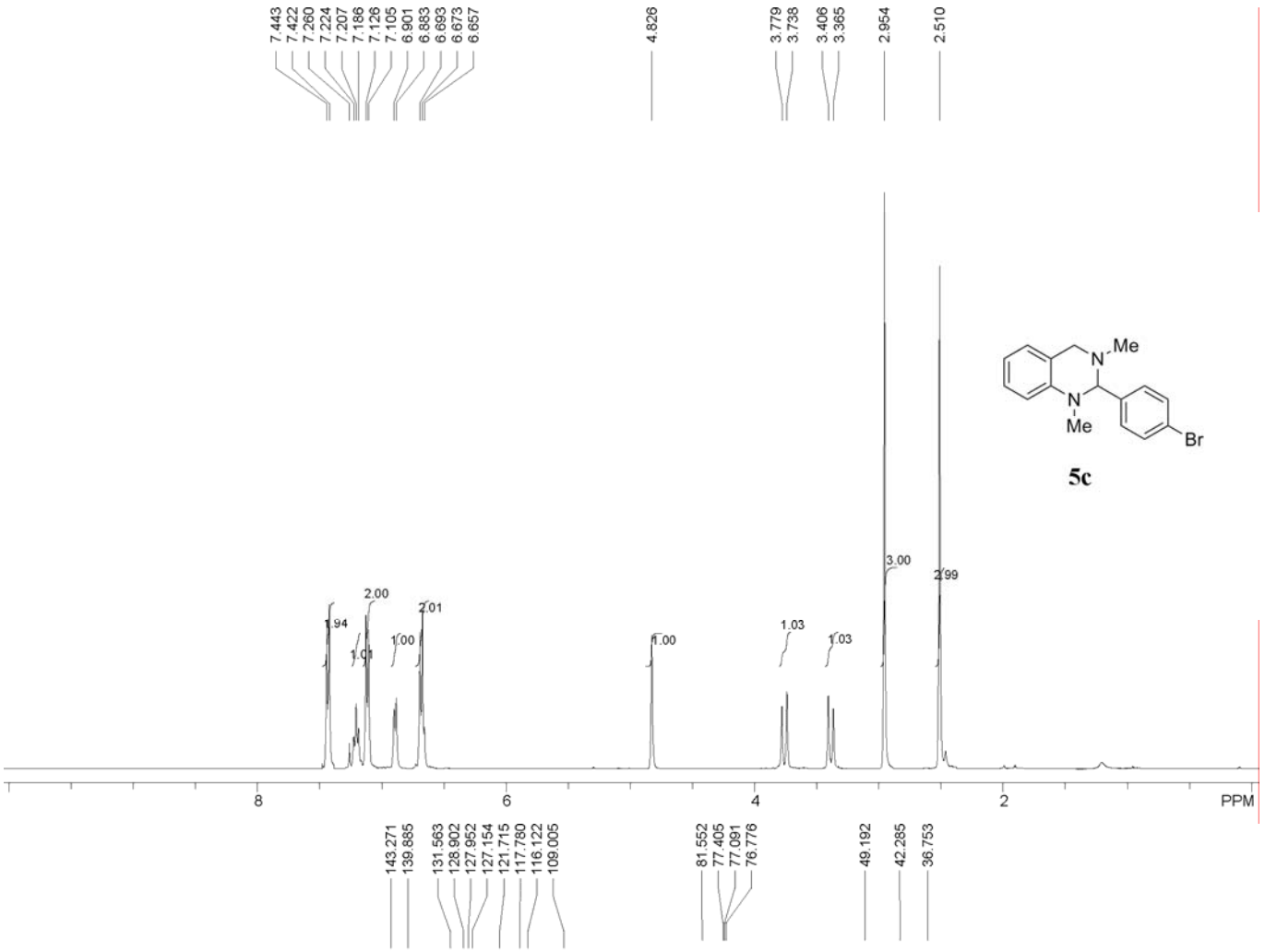
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7.126
7.105
6.901
6.883
6.693
6.673
6.657
4.826
3.779
3.738
3.406
3.365
2.954
2.510
Me
N
N
Me
Br
5c
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1.00
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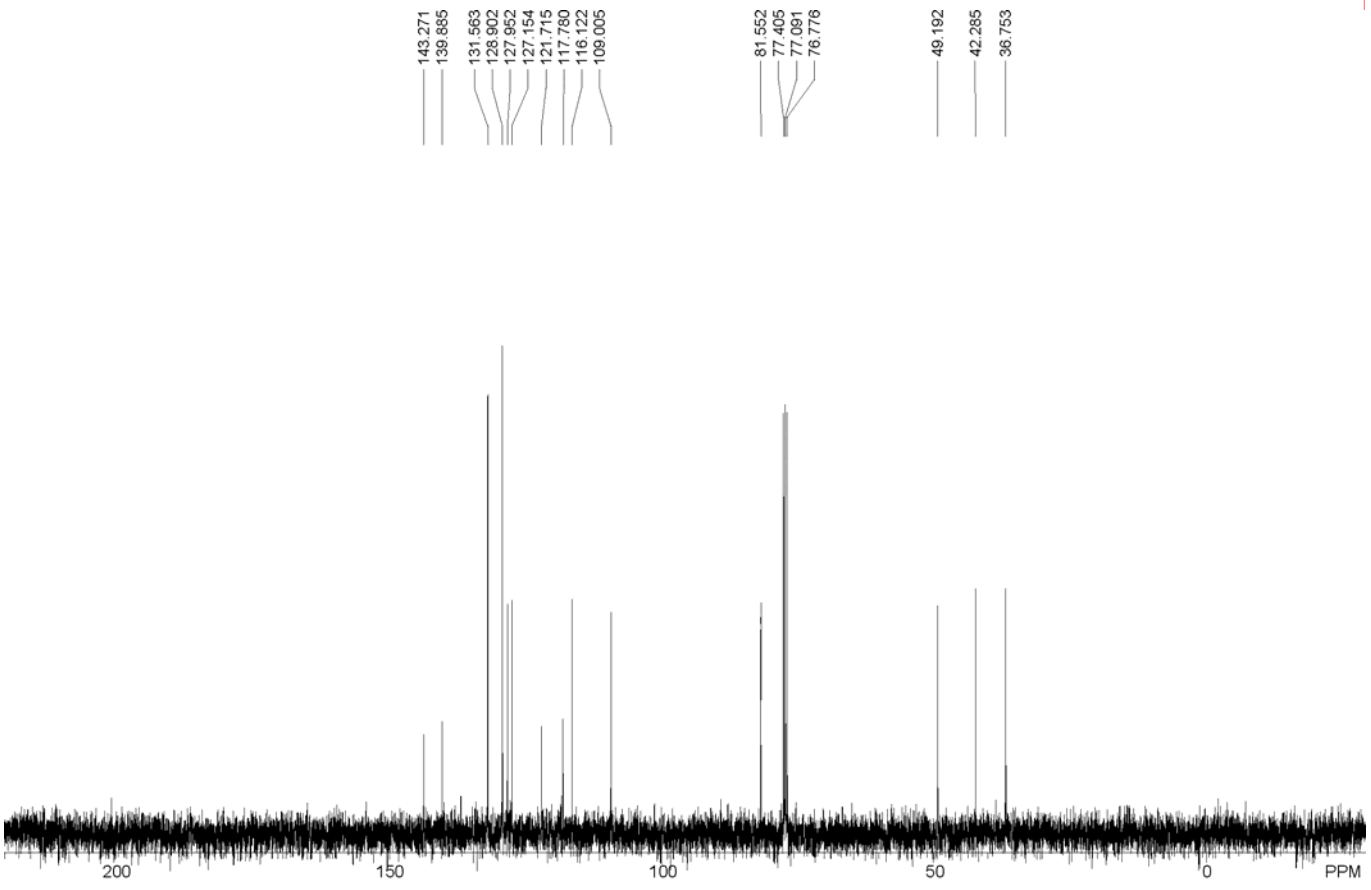
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77.091
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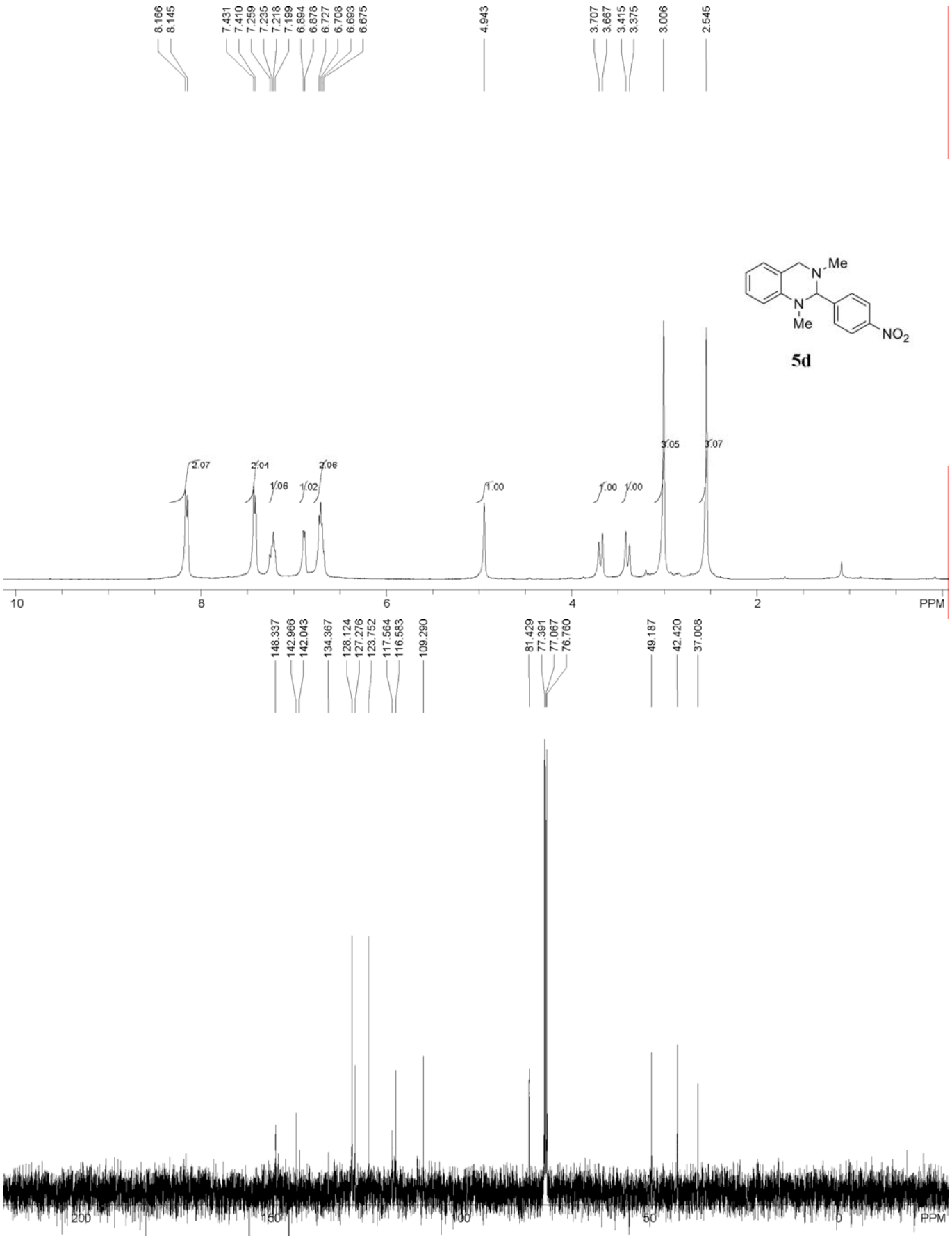
0
PPM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6.693
6.675
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3.667
3.415
3.375
3.006
2.545
Me
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N
Me
NO2
5d
2.07
2.04
1.06
1.02
2.06
1.00
1.00
1.00
3.05
3.07
10
8
6
4
2
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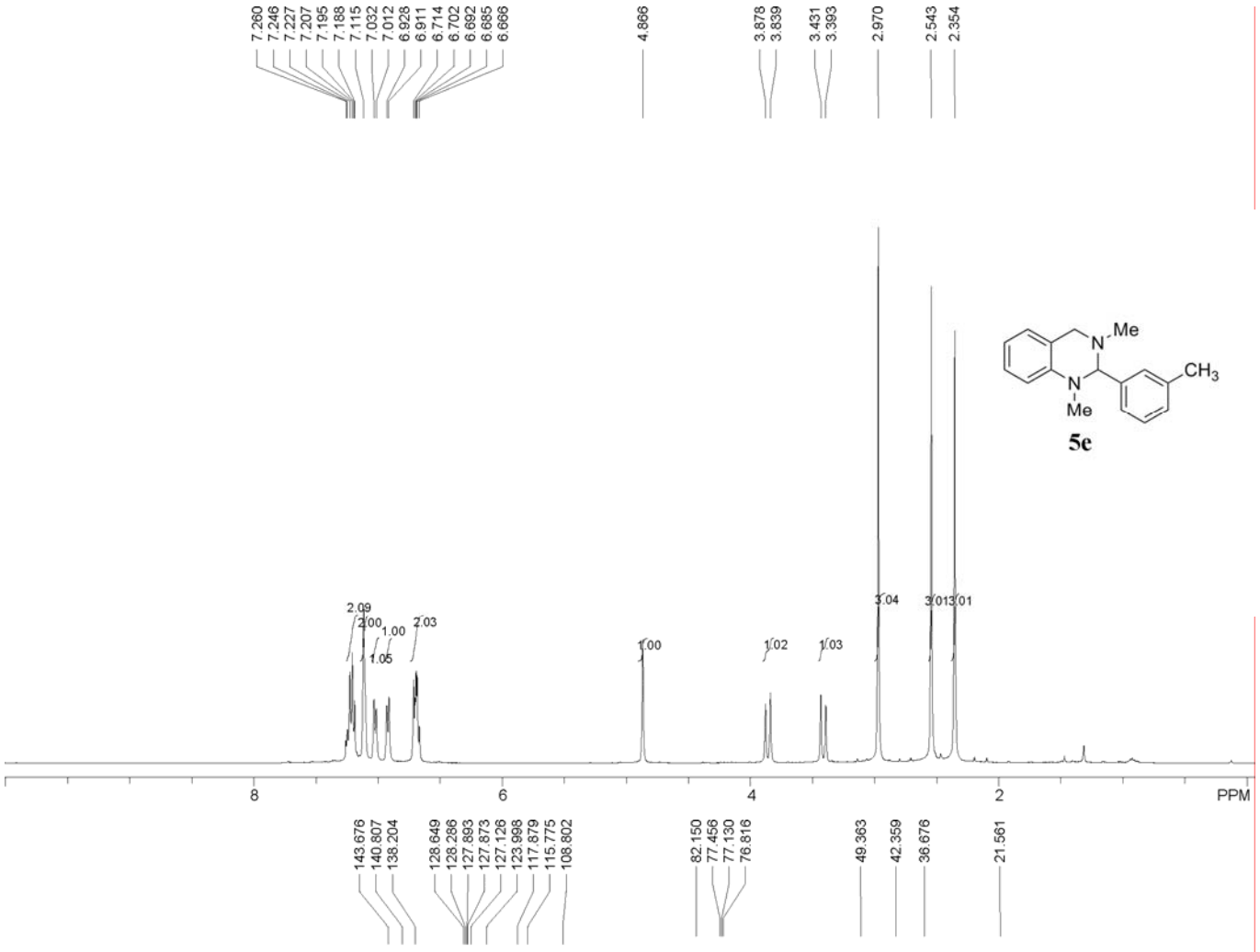
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6.911
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6.702
6.692
6.685
6.666
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3.839
3.431
3.393
2.970
2.543
2.354
Me
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CH3
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Me
5e
2.09
2.00
1.00
1.05
2.03
1.00
1.02
1.03
3.04
3.01
3.01
8
6
4
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127.126
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77.130
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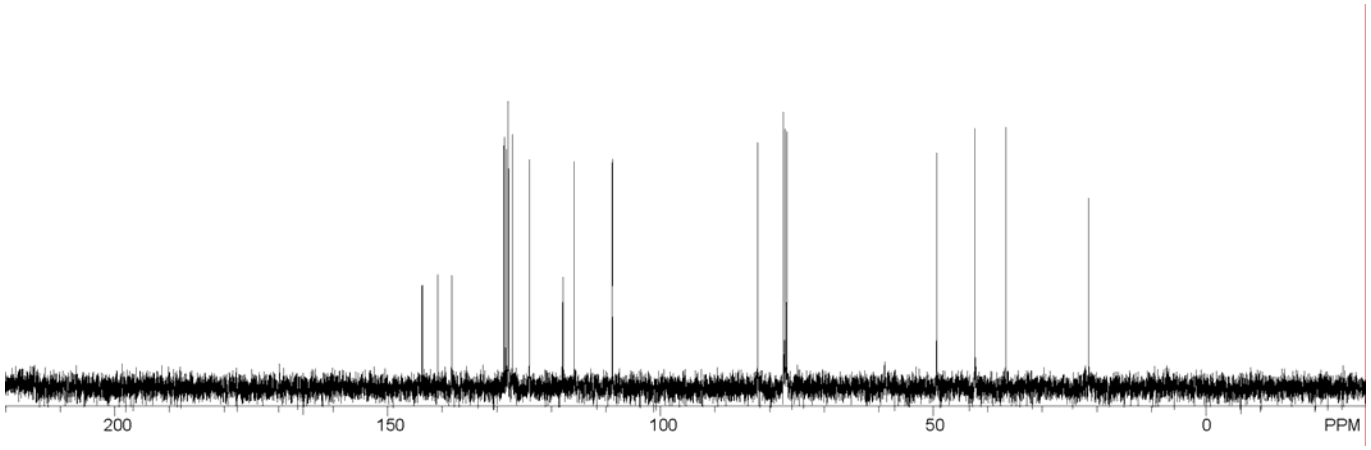
36.676
21.561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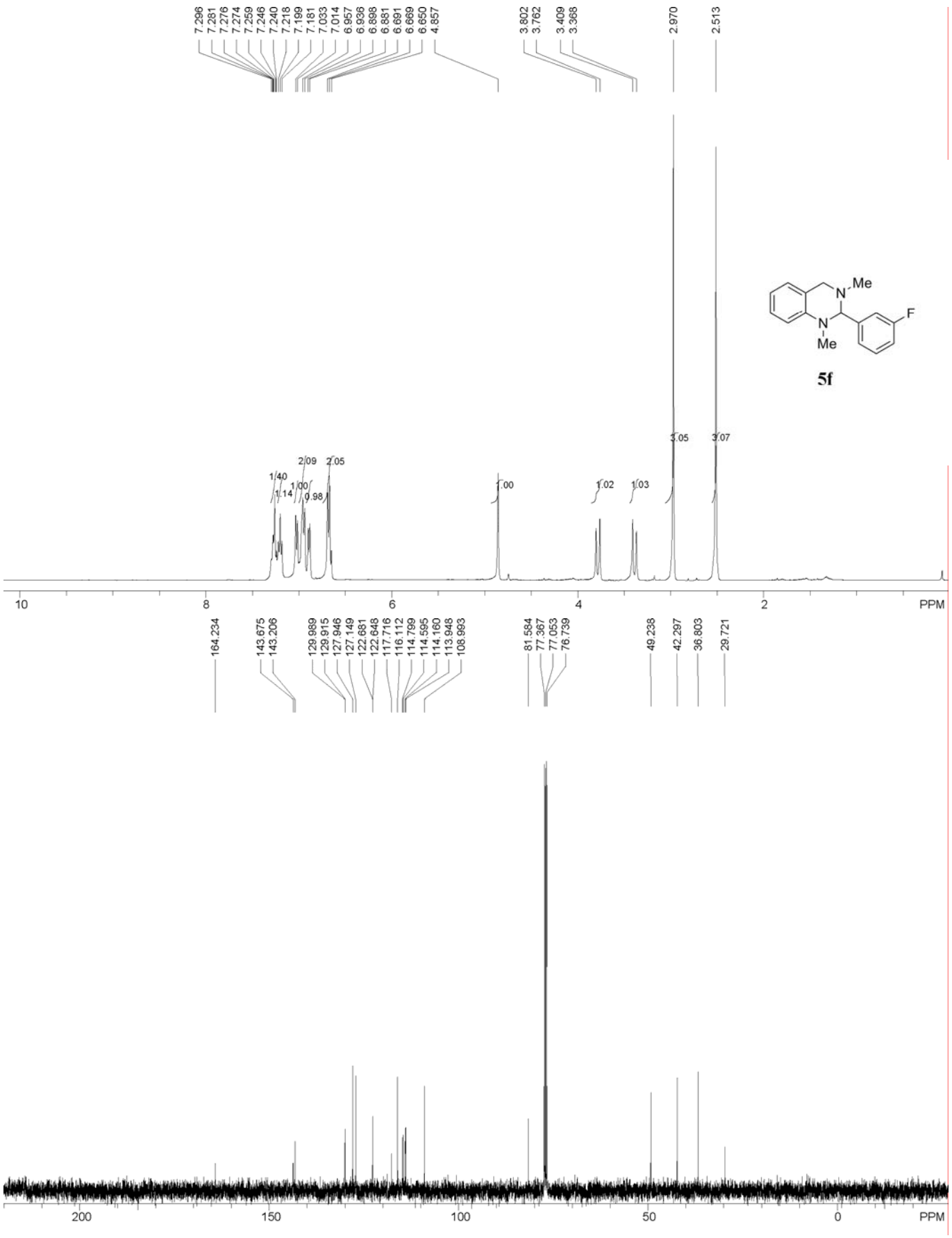
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6.881
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3.762
3.409
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2.513
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3.05
3.07
10
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4
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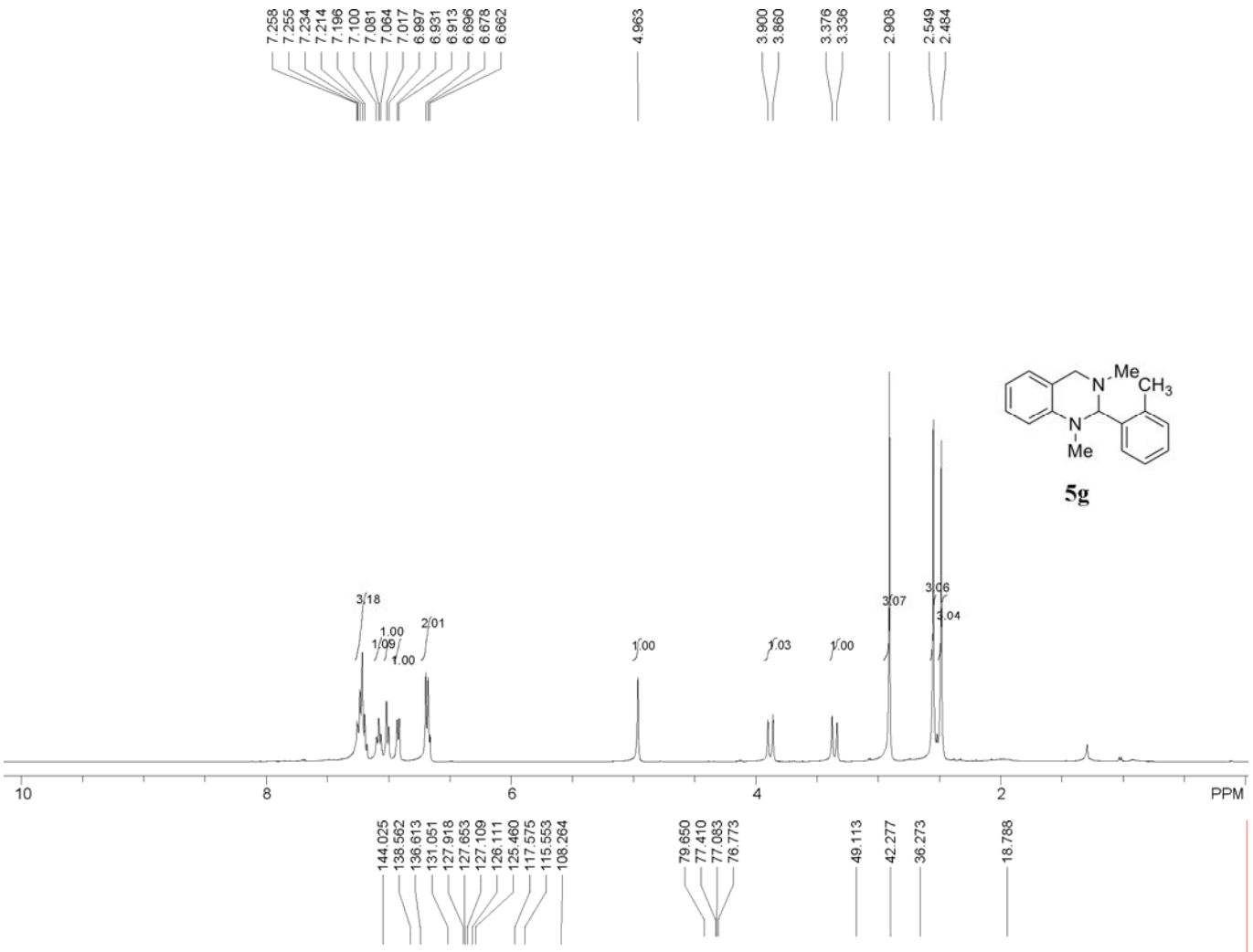
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6.913
6.896
6.678
6.662
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3.900
3.860
3.376
3.336
2.908
2.549
2.484
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CH3
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Me
5g
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1.09
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1.00
1.03
1.00
3.07
3.06
3.04
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PPM
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136.613
131.051
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125.460
117.575
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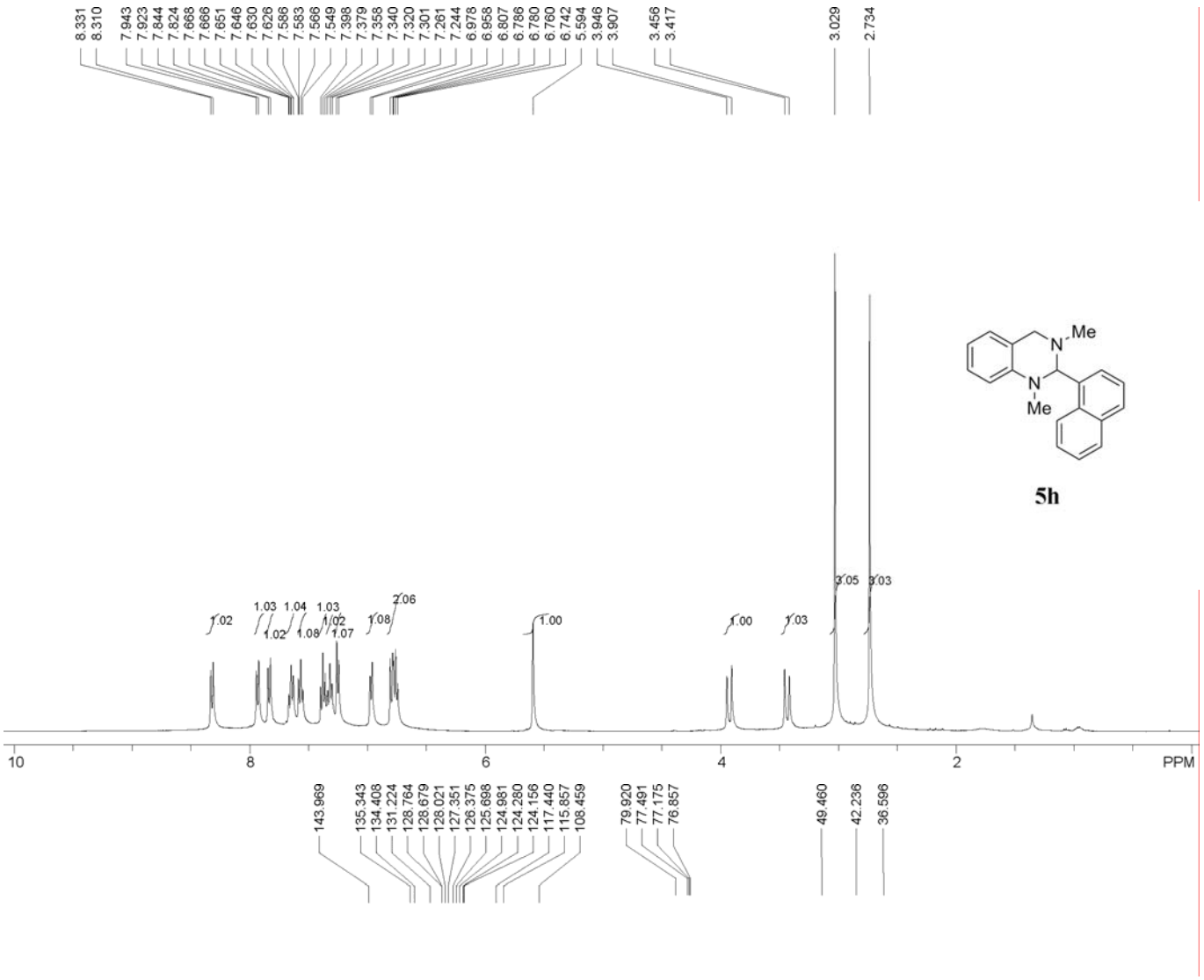
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3.907
3.456
3.417
3.029
2.734
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1.04
1.08
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1.00
1.03
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10
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2
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125.698
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50
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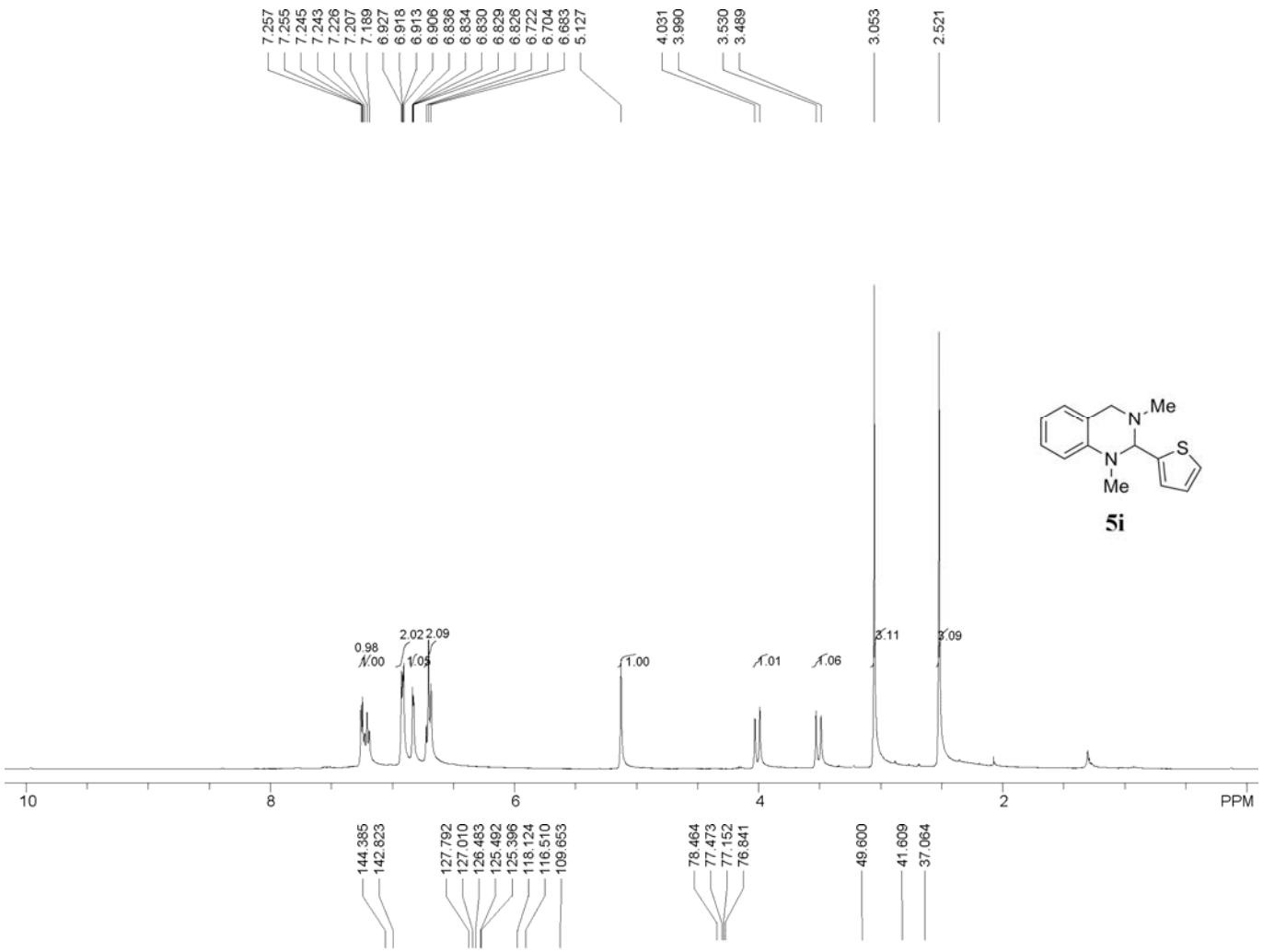
PPM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6.704
6.683
5.127
4.031
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3.530
3.489
3.053
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1.00
1.01
1.06
3.11
3.09
10
8
6
4
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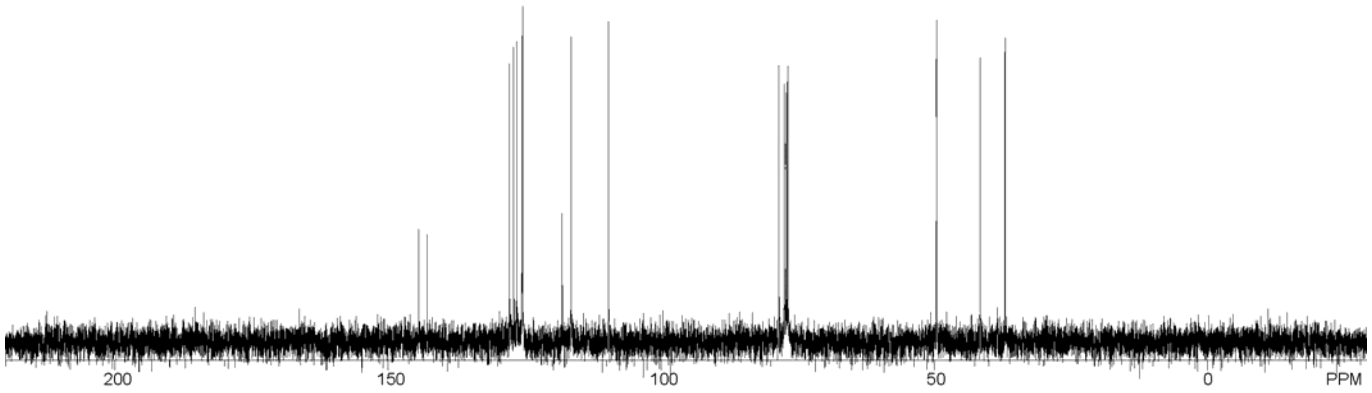
37.064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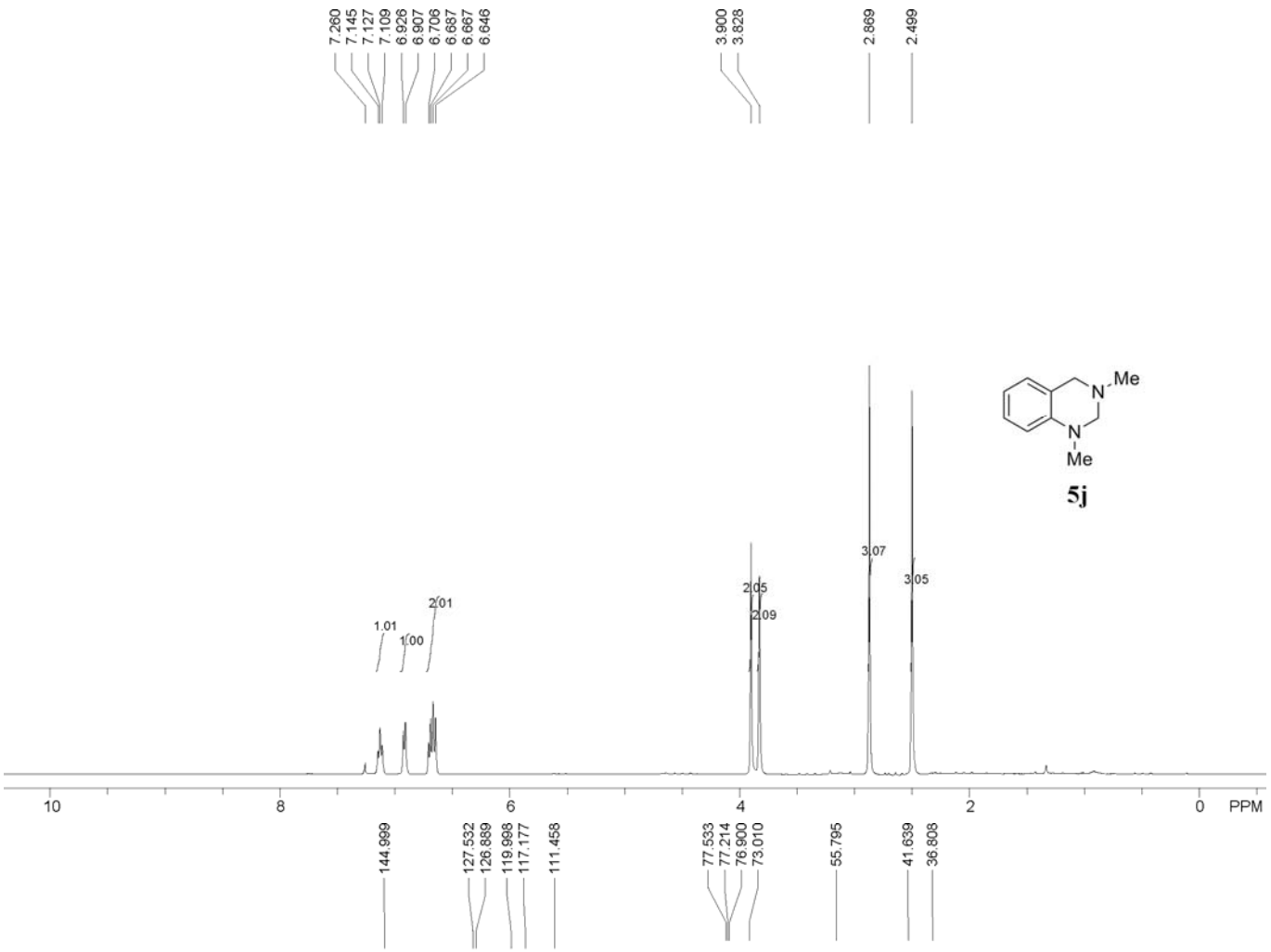
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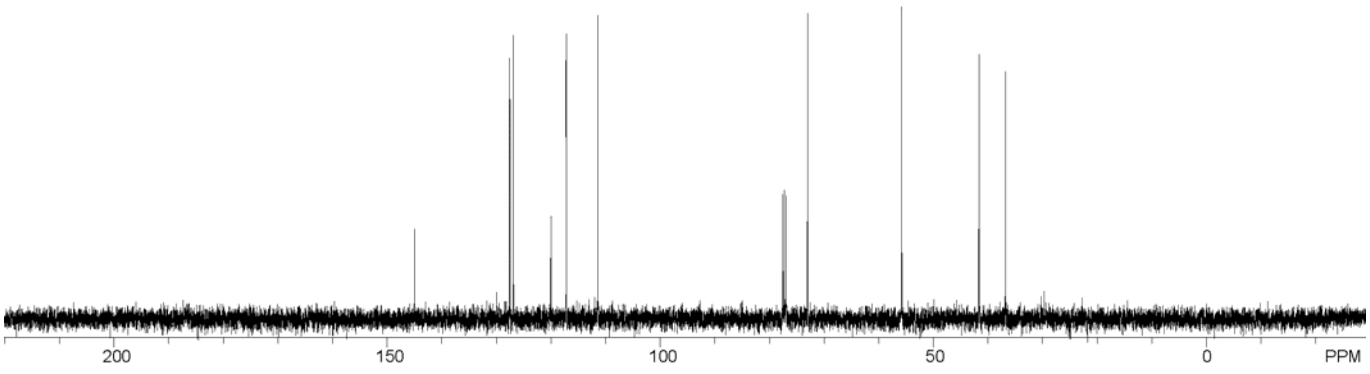
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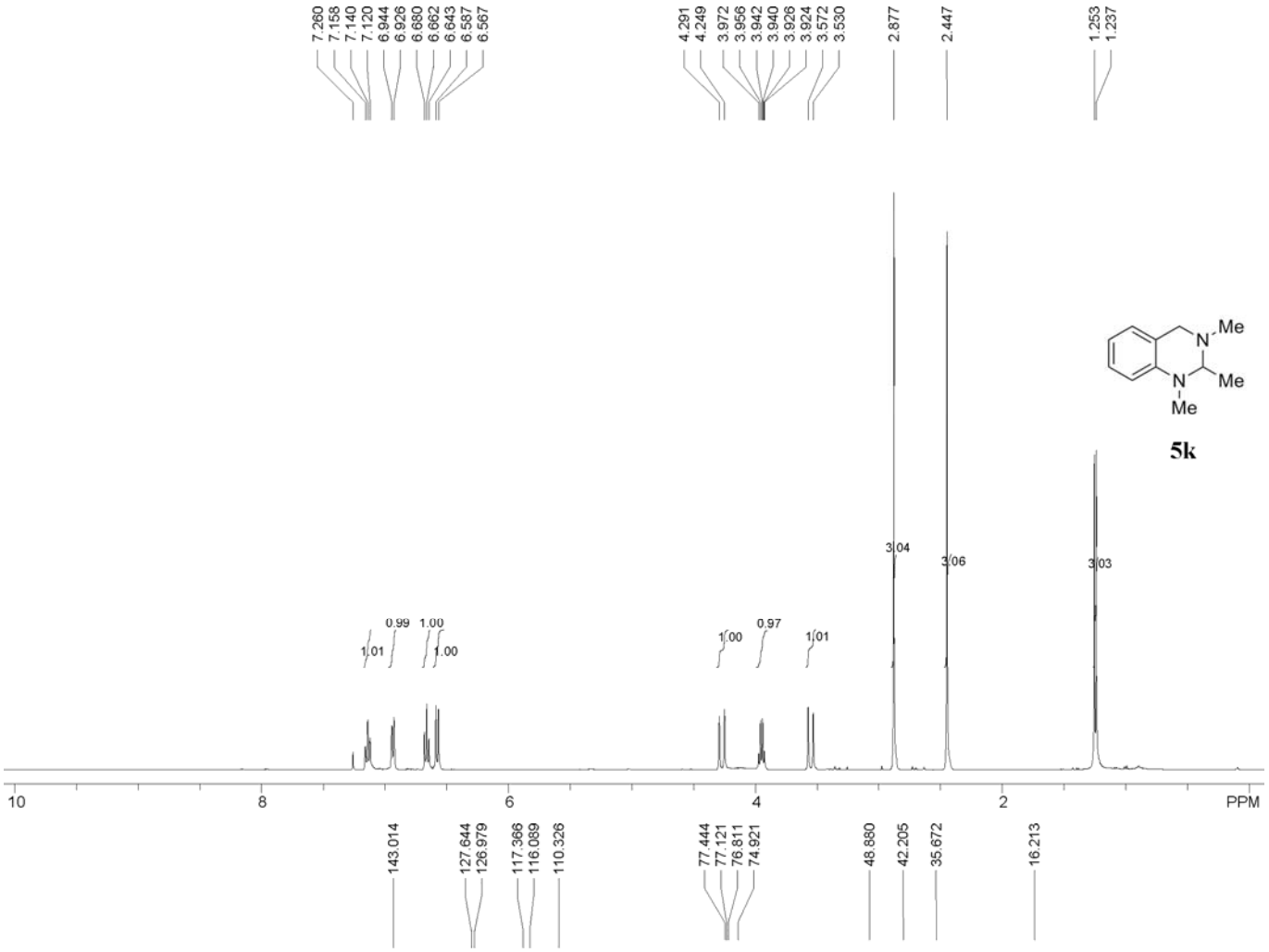
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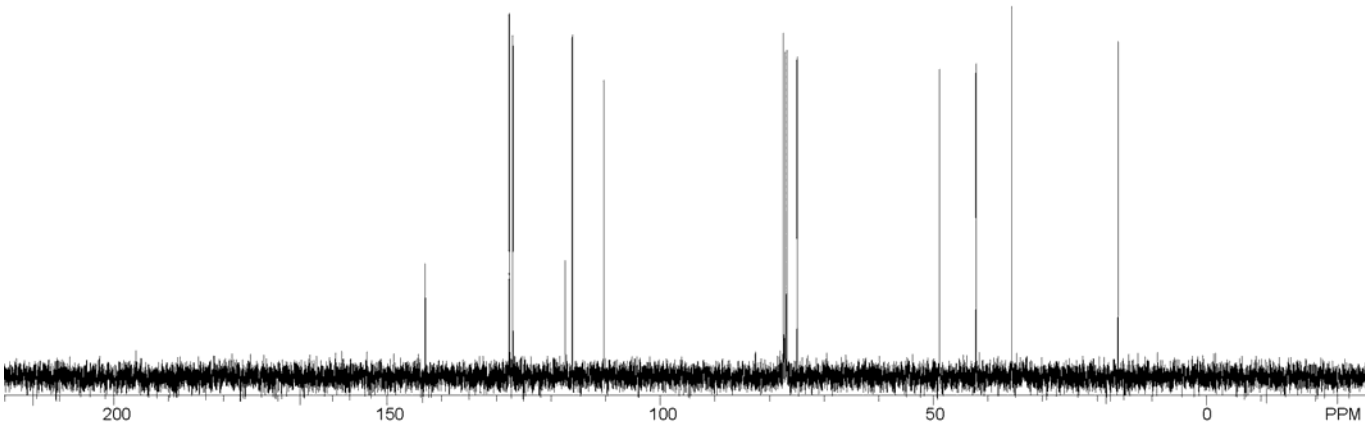
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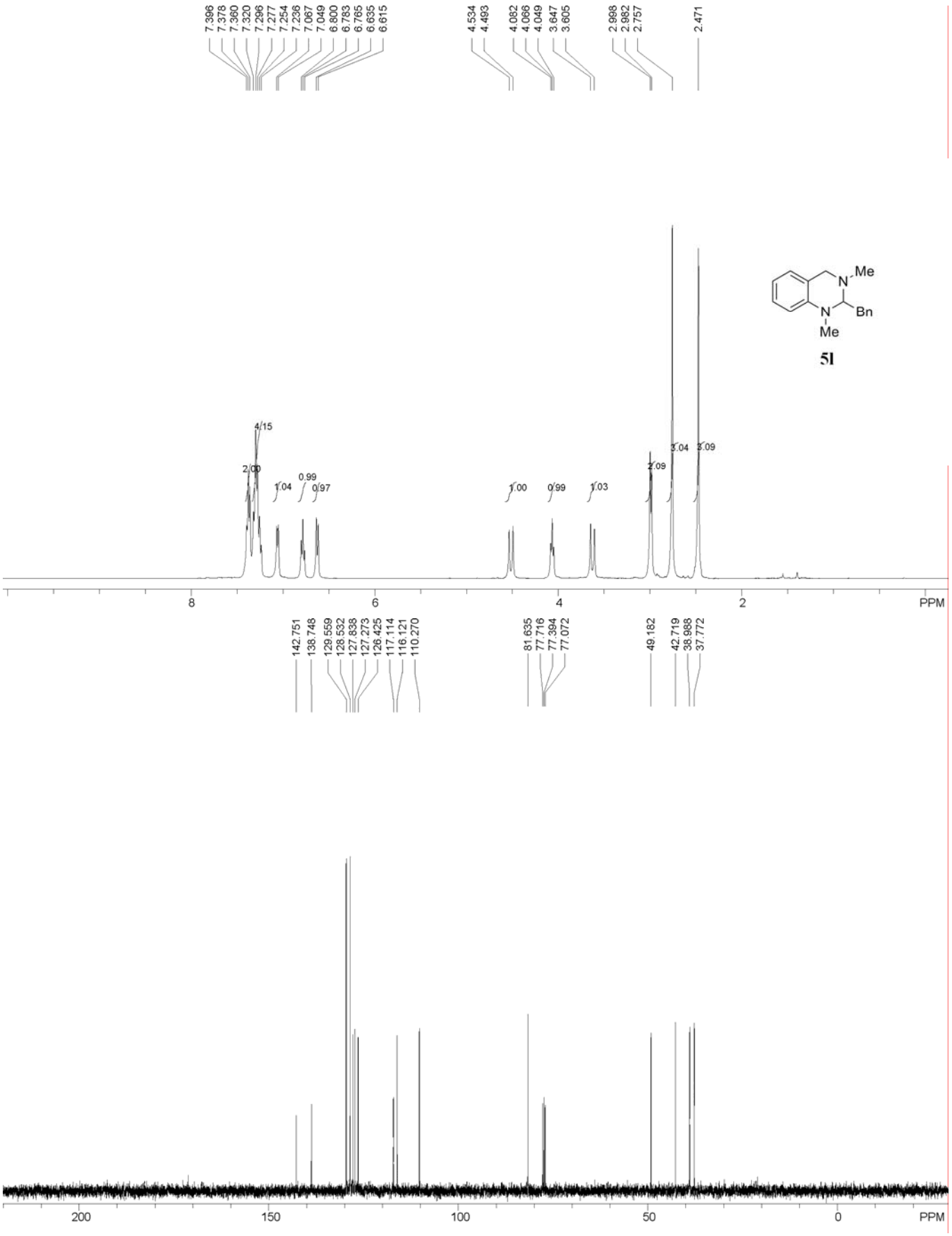
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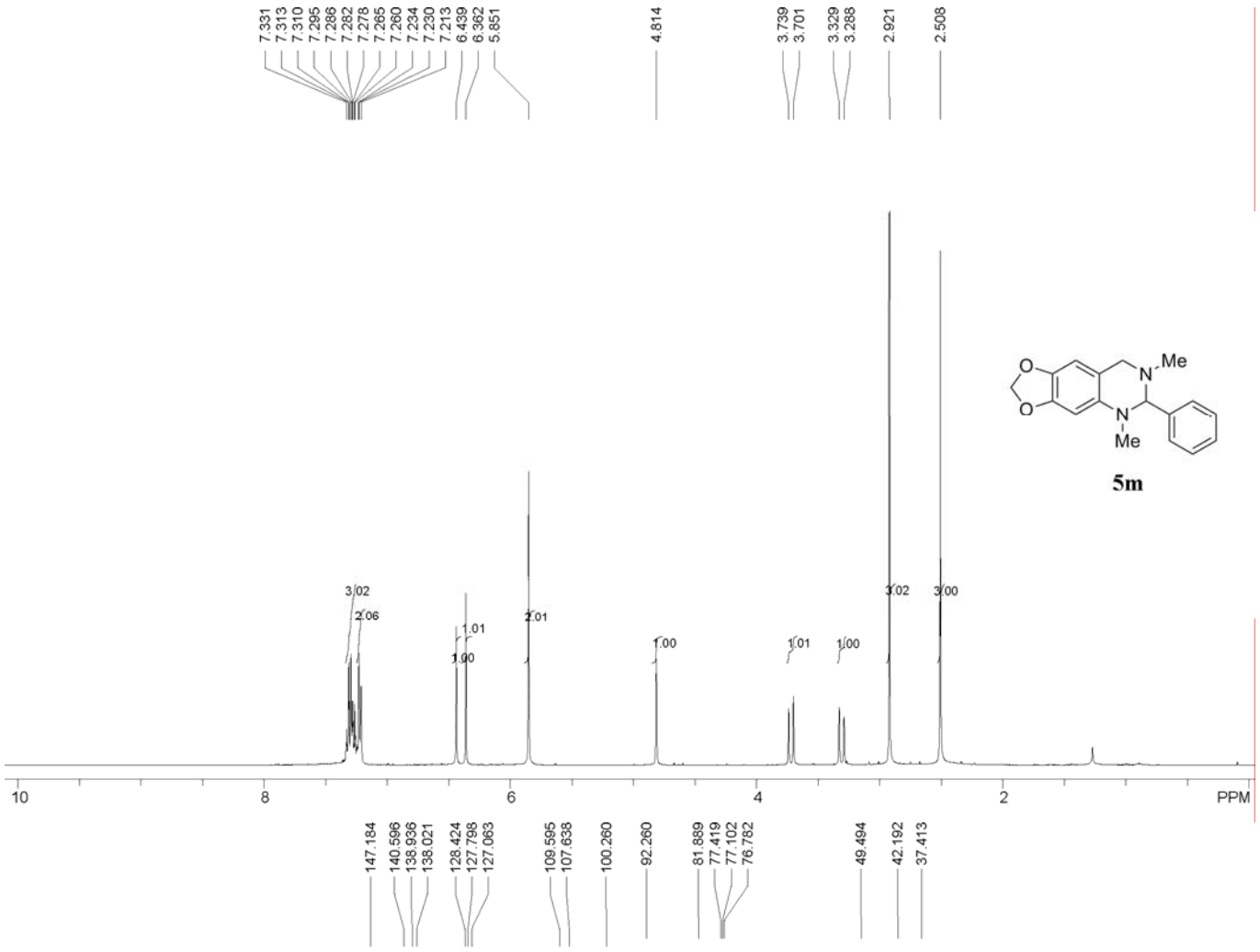
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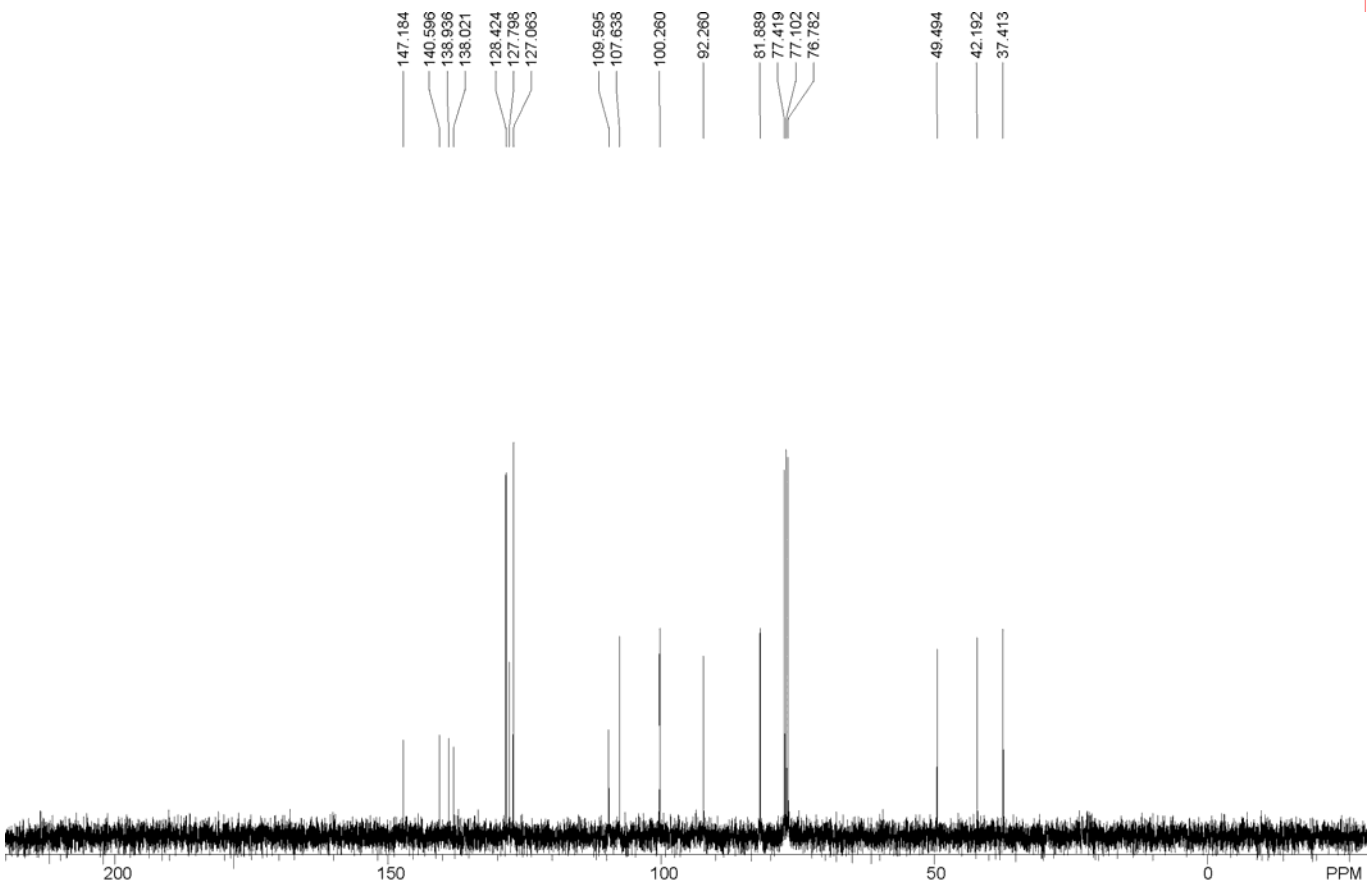
5m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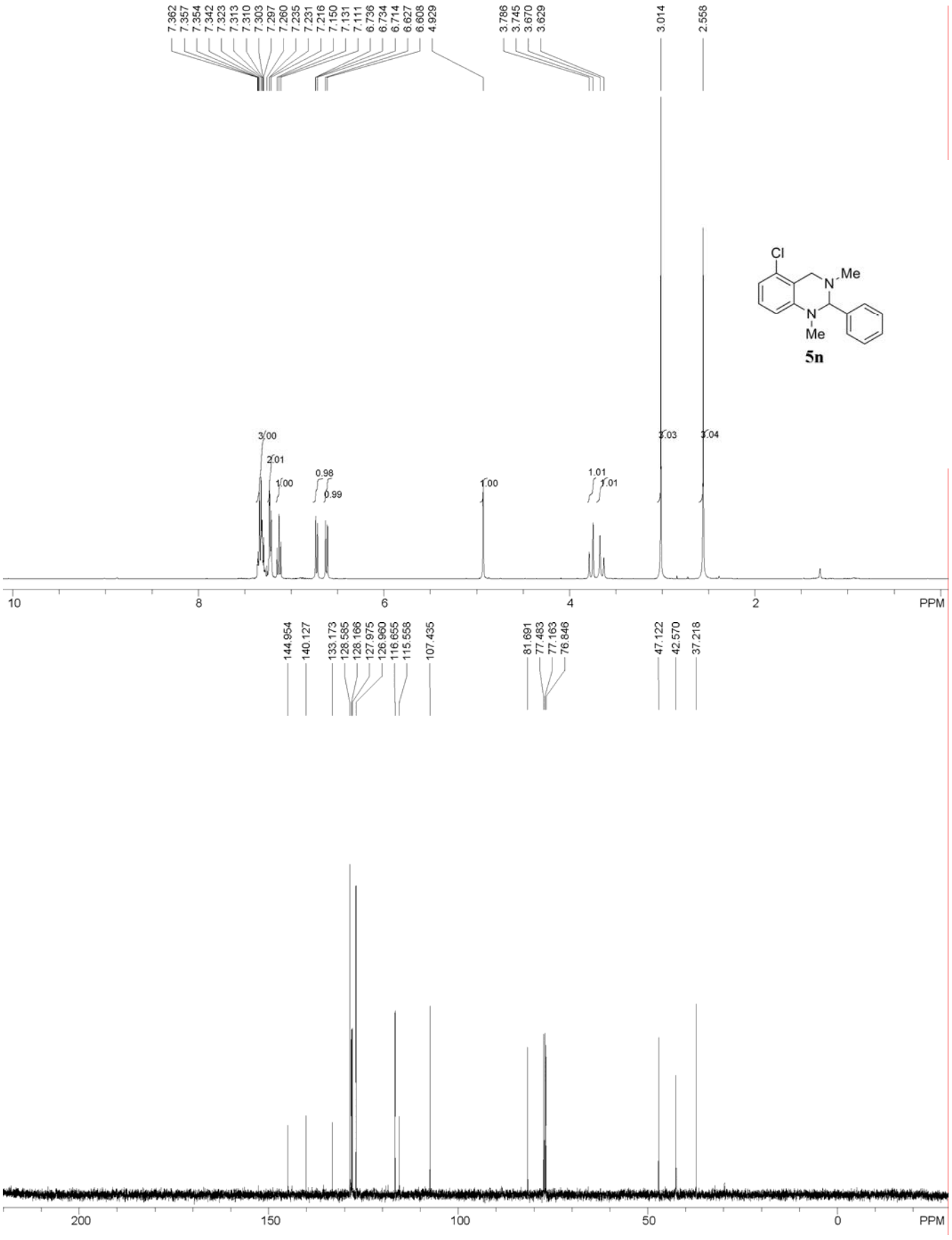
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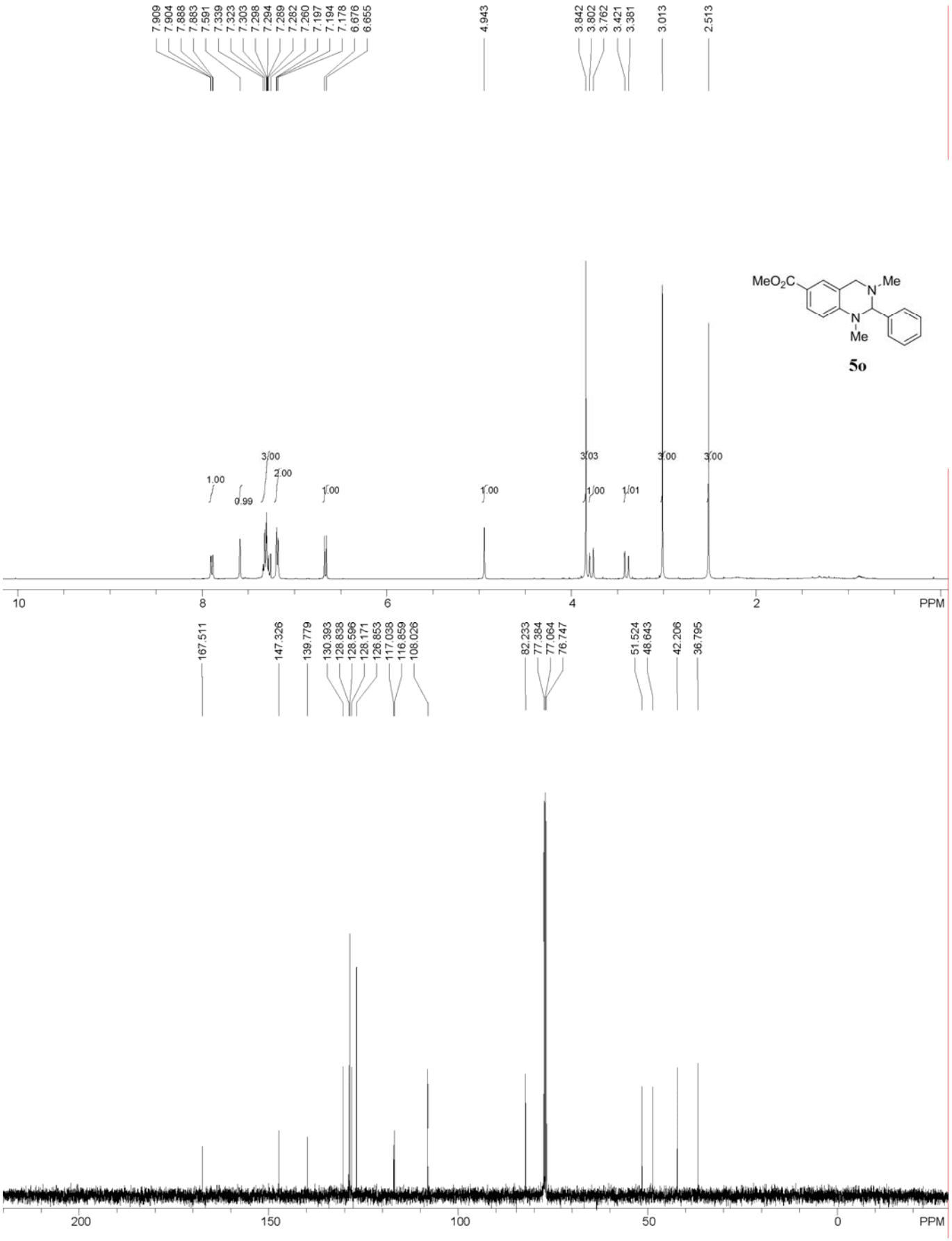
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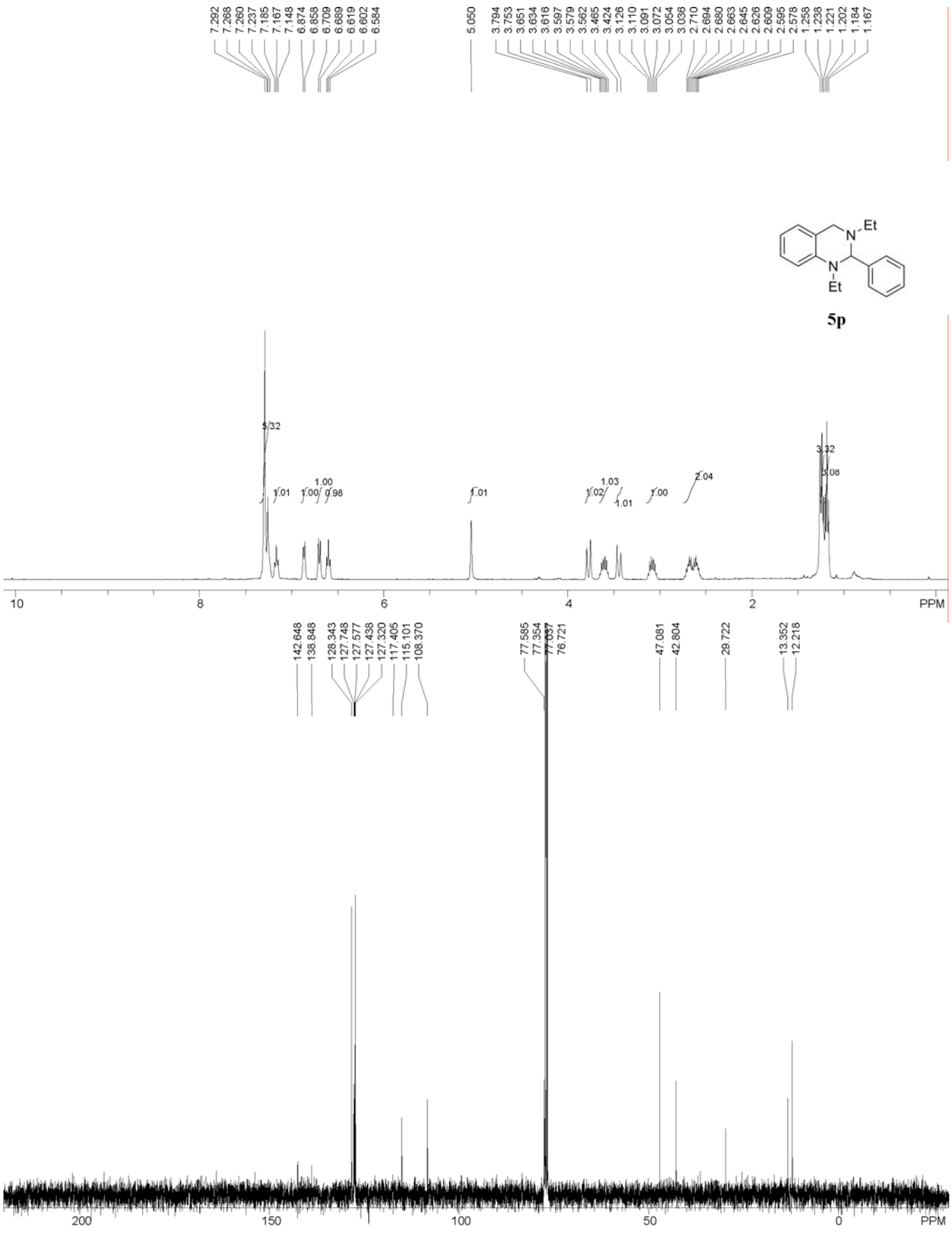
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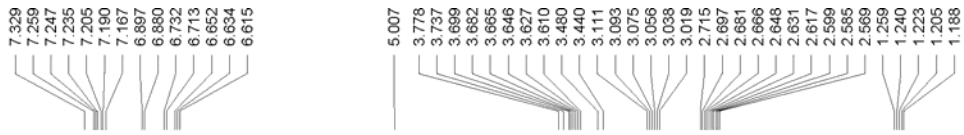
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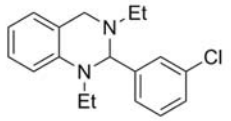
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Et

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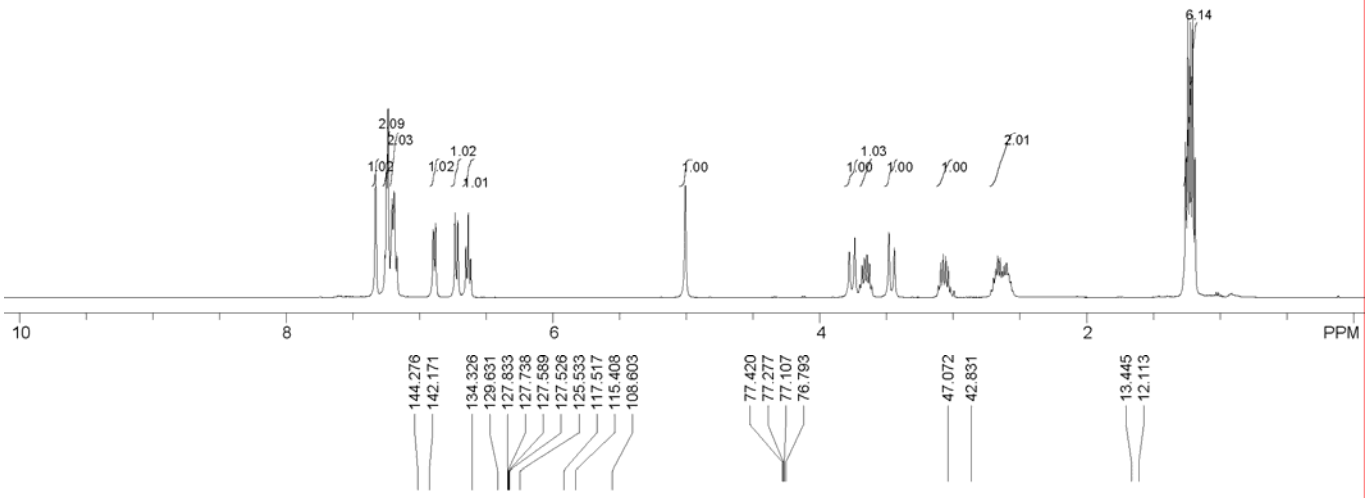
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4
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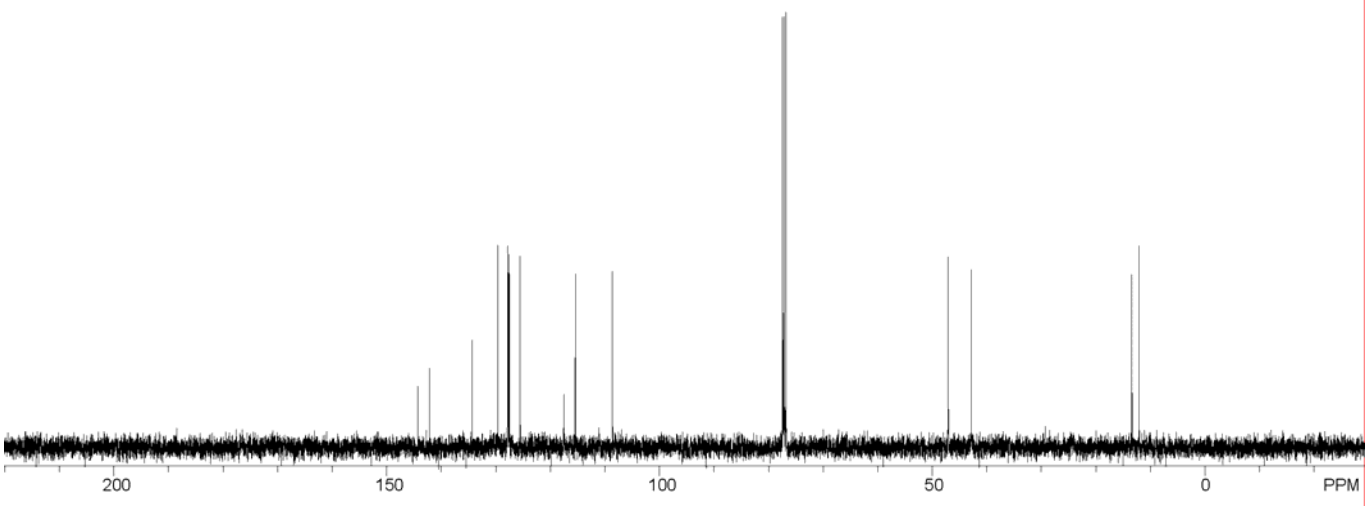
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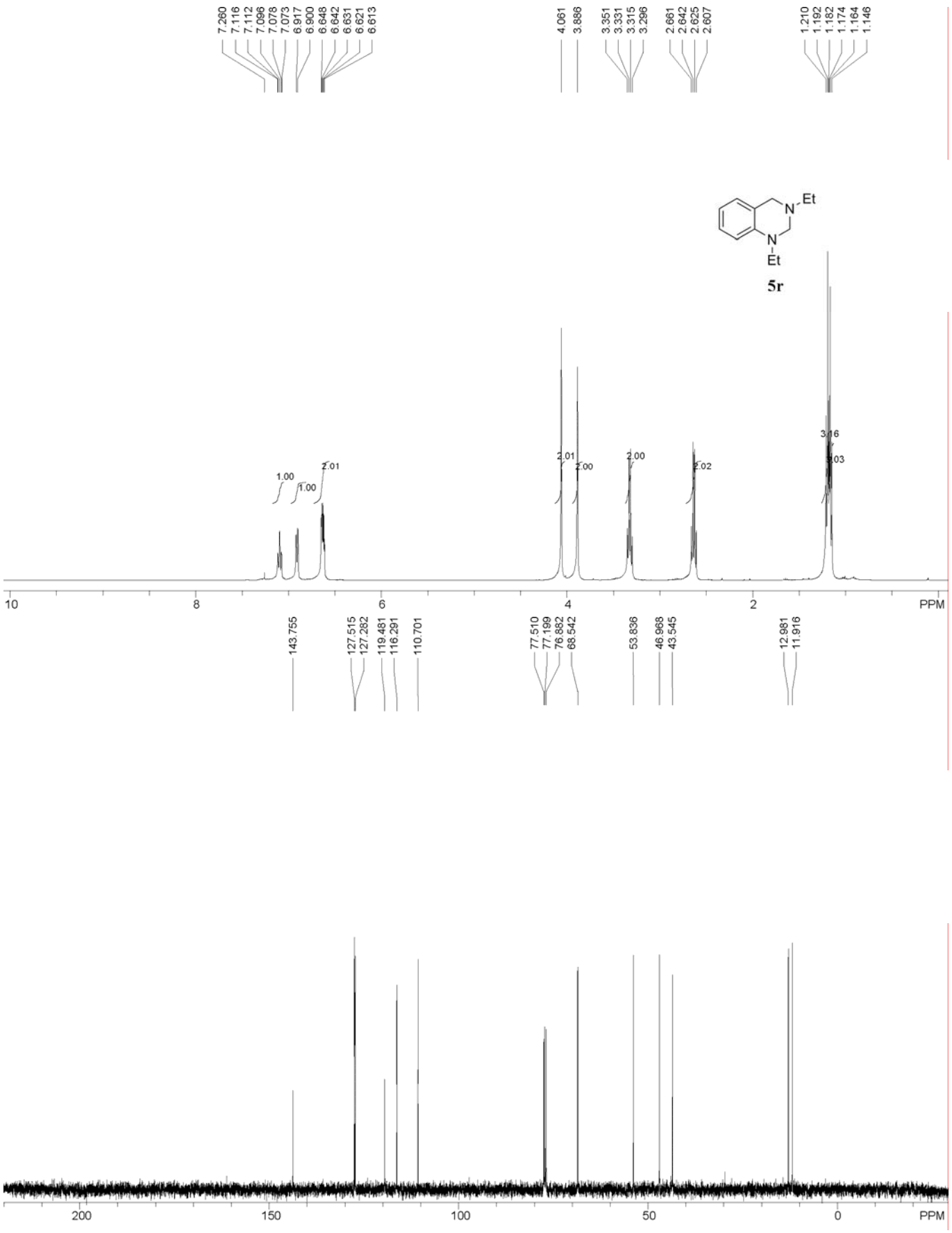
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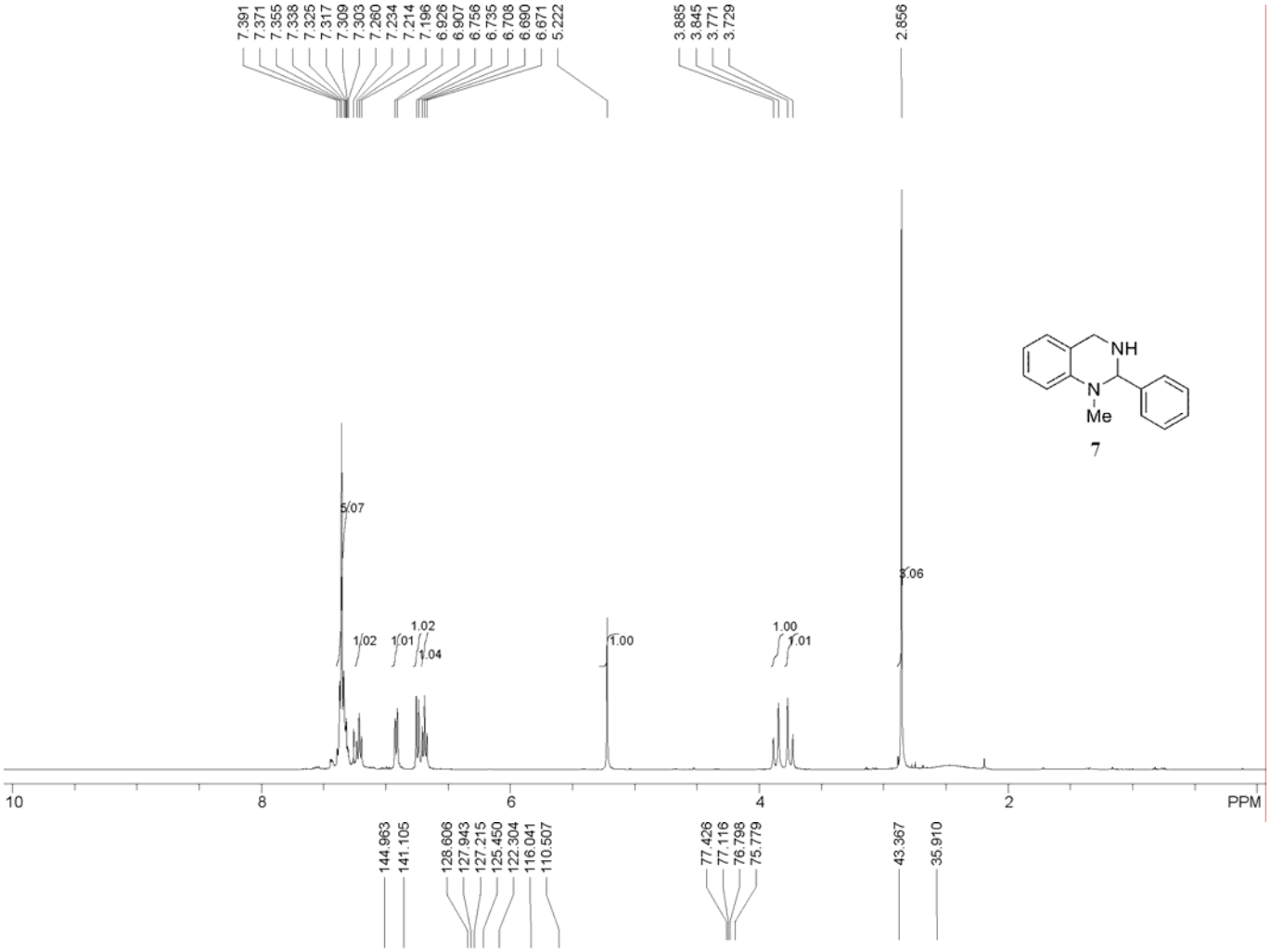
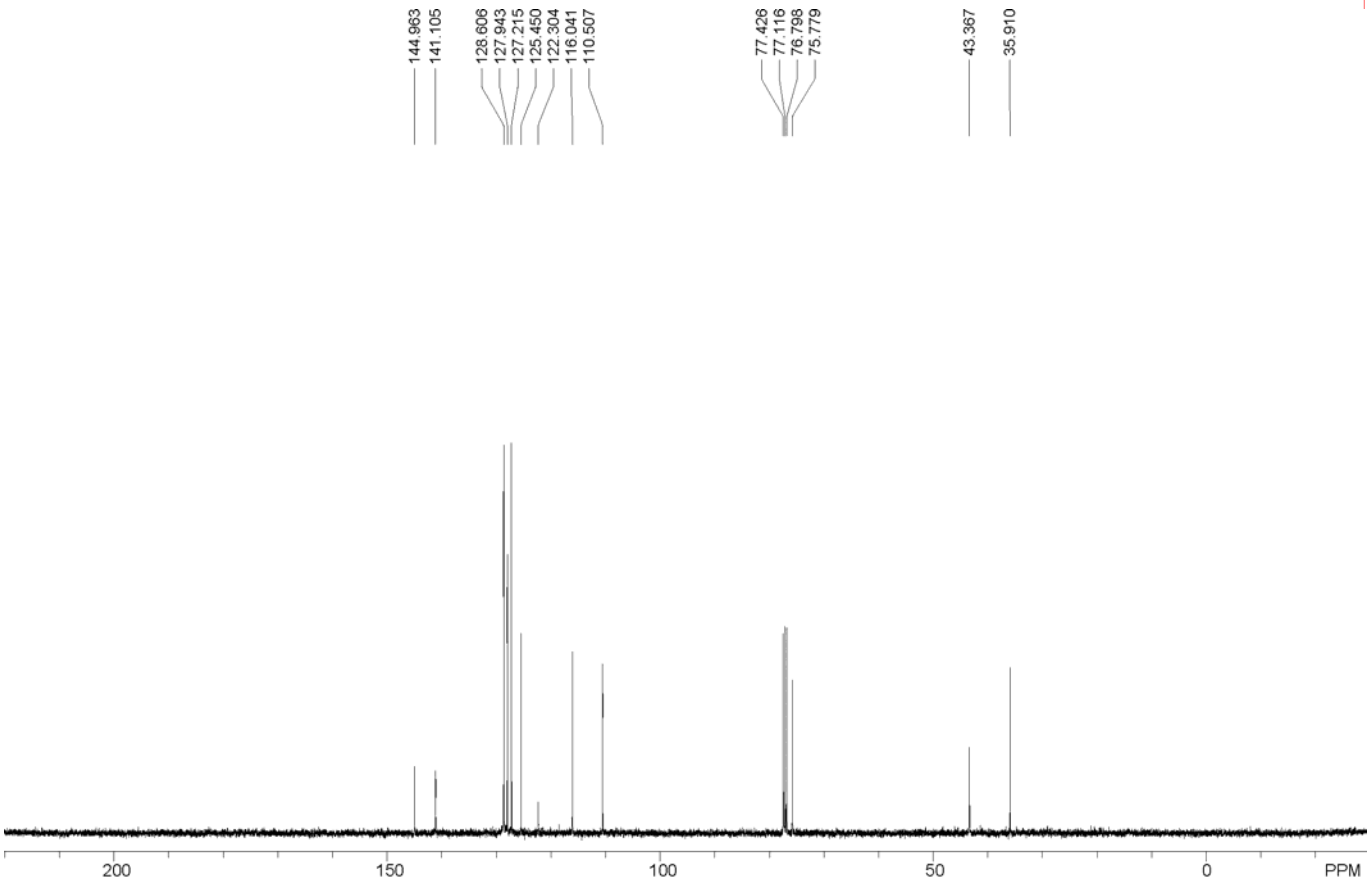
V. Copies of ^{1}H and ^{13}C NMR spectra of 7





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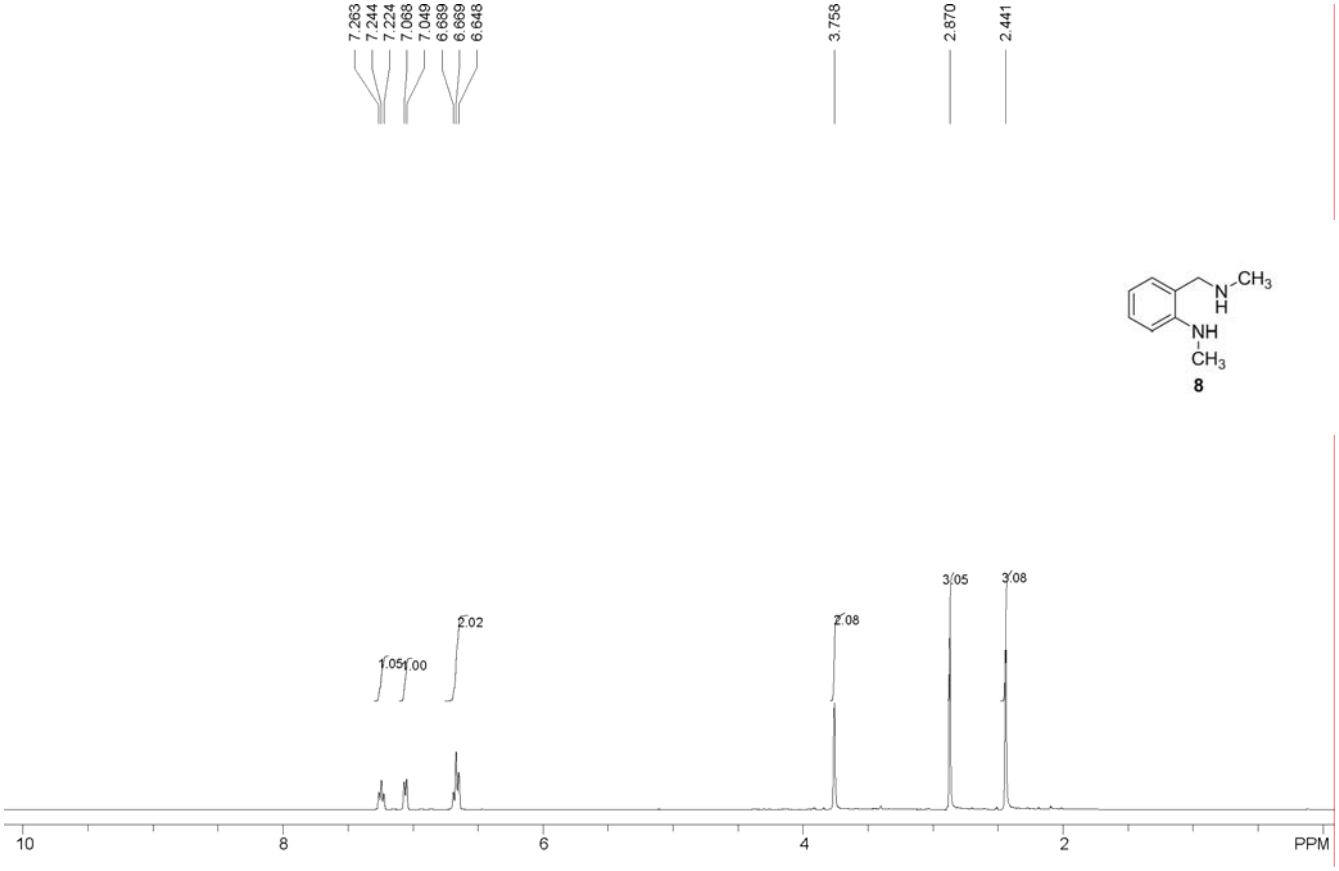

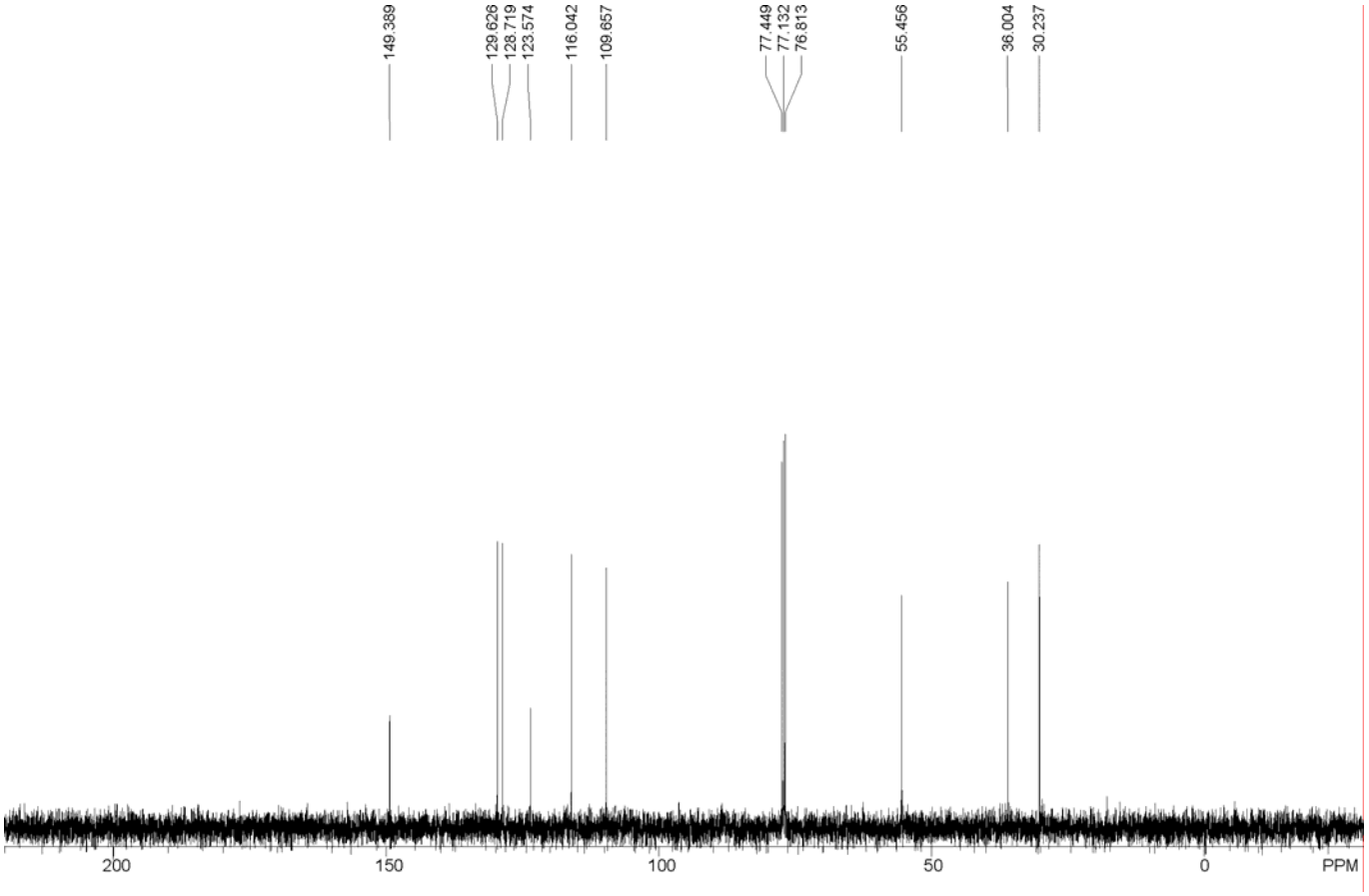

VII. References

[1] C. Wang, S. Li, H. Liu, Y. Jiang, H. Fu, *J. Org. Chem*. **2010,** *75*, 7936-7938.

[2] B. Han, X. L. Yang, C. Wang, Y. M. Bai, T. C. Pan, X. Chen, W. Yu, *J. Org. Chem*. **2012**, *77*, 1136-1142.

[3] C. C. Malakar, A. Baskakova, J. Conrad, U. Beifuss, *Chem. Eur. J.* **2012**, *18*, 8882-8885.