Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Ruthenium-Catalysed Oxidative Synthesis of Heterocycles from Alcohols

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General Methods: Reactions which required the use of anhydrous, inert atmosphere techniques were carried out under an atmosphere of nitrogen. All reactions were carried out in oven-dried, nitrogen-purged glassware. All solvents were purchased anhydrous from Sigma Aldrich. TLC using polythene backed plates precoated with Macherey-Nagel Sil G/UV_{254nm} neutral silica were used to monitor reactions where appropriate. Visualisation of these plates was by 254 nm UV light and/or $KMnO_4$ dip followed by gentle warming. Flash column chromatography was carried out using Davisil LC 60 Å silica gel (35-70 micron) purchased from Fluorochem. IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrometer with only selected absorbances quoted as ν in cm^{-1}. ^1H NMR spectra were run in DMSO-d_6 on a Bruker Avance 400 (400 MHz) instrument and recorded at the following frequencies: proton (^1H – 400 MHz). ^{13}C NMR spectra were run in DMSO-d_6 on a Bruker Avance 300 (300 MHz) instrument and recorded at the following frequencies: carbon (^{13}C – 75.4 MHz). The following abbreviations are used: s, singlet; d, doublet; t, triplet; app. t, apparent triplet; q, quartet; app. q, apparent quartet; dd, doublet of doublets; m, multiplet and br, broad. Structural assignments of both protons and carbons were achieved with comparisons from analogous literature compounds; references are given in most cases.

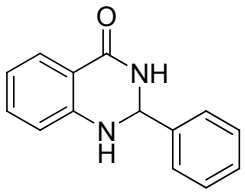
A micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) was used; this was coupled to an Agilent 1200 LC system (Agilent Technologies, Waldbronn, Germany). The LC system was used as an autosampler only. 10 μL of sample was injected into a 30:70 flow of water:acetonitrile at 0.6 mL/min to the mass spectrometer. For each acquisition 10 μL of a calibrant of 5 mM sodium formate was injected after the sample. The observed mass and isotope pattern perfectly matched the corresponding theoretical values as calculated from the expected elemental formula. Unless preparative details are provided, all reagents were commercially available and purchased from either Acros Organics, Sigma Aldrich, Alfa Aesar, Avocado, Fluka, Lancaster, Maybridge or Strem chemical companies.

Experimental Methods:

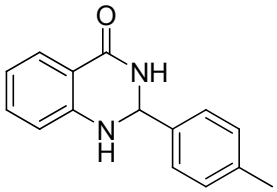
Representative Procedure for Formation of 2,3-Dihydroquinazolines: To an oven-dried, nitrogen Young's tube containing containing $Ru(PPh_3)_3(CO)(H)_2$ (46 mg, 0.05 mmol), Xantphos (29 mg, 0.05 mmol), 2-aminobenzamide (136 mg, 1 mmol) and NH_4Cl (11 mg, 0.2 mmol) were added benzyl alcohol (103 μL, 1 mmol), crotononitrile (0.20 mL, 2.5 mmol) and toluene (1 mL). The reaction was then heated to reflux for 14 h. On completion, the reaction was allowed to cool to room temperature before the solvent was removed in vacuo. The crude product was purified by recrystallization from acetone to afford the product in good yield.

Representative Procedure for Formation of Quinazolines: To an oven-dried, nitrogen Young's tube containing containing $Ru(PPh_3)_3(CO)(H)_2$ (46 mg, 0.05 mmol), Xantphos (29 mg, 0.05 mmol) and 2-aminobenzamide (136 mg, 1 mmol) were added benzyl alcohol (103 μL, 1 mmol), crotononitrile (0.20 mL, 2.5 mmol) and toluene (1 mL). The reaction was then heated to reflux for 24 h. On completion, the reaction was allowed to cool to room temperature before the solvent was removed in vacuo. The crude product was purified by recrystallization from toluene to afford the product in good yield.

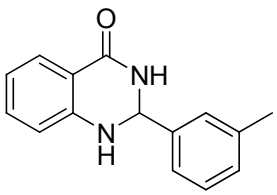
Representative Procedure for Formation of 2*H*-1,2,4-Benzothiadiazine-1,1-dioxides: To an oven-dried, nitrogen Young's tube containing containing $Ru(PPh_3)_3(CO)(H)_2$ (46 mg, 0.05 mmol), Xantphos (29 mg, 0.05 mmol) and 2-aminobenzenesulfonamide (136 mg, 1 mmol) were added benzyl alcohol (103 μL, 1 mmol), crotononitrile (0.20 mL, 2.5 mmol) and toluene (1 mL). The reaction was then heated to reflux for 24 h. On completion, the reaction was allowed to cool to room temperature before the solvent was removed in vacuo. The crude product was purified by recrystallization from ethanol to afford the product in good yield.



2-Phenyl-2,3-dihydroquinazolin-4(1*H*)-one[1] (Entry 1, Table 2): According to the representative procedure the title compound was isolated as a colourless crystalline solid (175 mg, 78%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 8.28 (1H, br s), 7.61 (1H, dd, J = 7.6 1.6 Hz), 7.47-7.50 (2H, m), 7.32-7.41 (3H, m), 7.24 (1H, ddd, J = 8.4 7.2 1.6 Hz), 7.10 (1H, br s), 6.74 (1H, dd, J = 8.4 0.8 Hz), 6.67 (1H, ddd, J = 7.6 7.2 0.8 Hz), 5.75 (1H, br s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 163.5, 147.8, 141.5, 133.2, 128.4, 128.2, 127.3, 126.8, 117.0, 114.9, 114.3, 66.5; HRMS(ESI-TOF): calcd. for $C_{14}H_{12}N_2OH^+$: 225.1022. Found: 225.1045 (MH^+), 247.0882 (MNa^+).

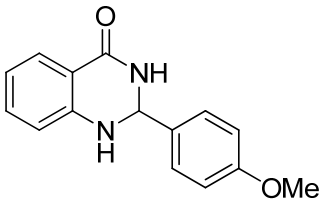


2-*p*-Tolyl-2,3-dihydroquinazolin-4(1*H*)-one[1] (Entry 2, Table 2): According to the representative procedure the title compound was isolated as a colourless crystalline solid (164 mg, 69%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 8.22 (1H, br s), 7.60 (1H, dd, J = 8.0 1.6 Hz), 7.37 (2H, d, J = 8.0 Hz), 7.23 (1H, ddd, J = 8.0 7.2 1.6 Hz), 7.19 (2H, d, J = 8.0 Hz), 7.04 (1H, br s), 6.73 (1H, d, J = 8.0 Hz), 6.66 (1H, ddd, J = 8.0 7.2 0.8 Hz), 5.70 (1H, br s), 2.29 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 163.6, 147.9, 138.6, 133.2, 128.8, 127.3, 126.8, 117.0, 114.9, 114.3, 66.3, 20.7; HRMS(ESI-TOF): calcd. for $C_{15}H_{14}N_2OH^+$: 239.1184. Found: 239.1217 (MH^+), 261.1021 (MNa^+).

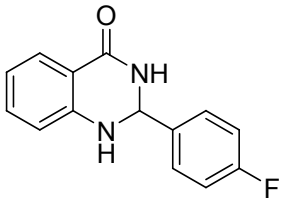


2-*m*-Tolyl-2,3-dihydroquinazolin-4(1*H*)-one[2] (Entry 3, Table 2): According to the representative procedure the title compound was isolated as a colourless crystalline solid (172 mg, 72%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 8.22 (1H, br s), 7.60

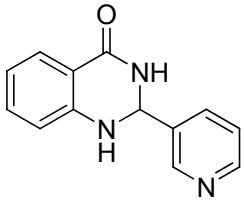
(1H, dd, *J* = 7.6 1.6 Hz), 7.32 (1H, br s), 7.27-7.28 (2H, m), 7.23 (1H, ddd, *J* = 8.4 7.2 1.6 Hz), 7.15-7.17 (1H, m), 7.06 (1H, br s), 6.73 (1H, dd, *J* = 8.4 0.8 Hz), 6.67 (1H, ddd, *J* = 7.6 7.2 1.2 Hz), 5.71 (1H, br s), 2.31 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 163.5, 147.8, 141.4, 137.3, 133.2, 129.0, 128.1, 127.4, 127.2, 123.9, 117.0, 114.8, 114.3, 66.5, 21.0; HRMS(ESI-TOF): calcd. for $C_{15}H_{14}N_2OH^+$: 239.1184. Found: 239.1224 (MH^+), 261.1035 (MNa^+).



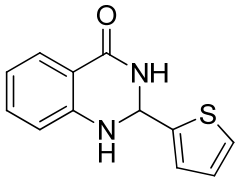
2-(4-Methoxyphenyl)-3,2-dihydroquinazolin-4-(1*H*)-one[1] (Entry 4, Table 2): According to the representative procedure the title compound isolated as a colourless crystalline solid (181 mg, 71%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 8.17 (1H, br s), 7.61 (1H, dd, *J* = 7.6 1.6 Hz), 7.41 (2H, d, *J* = 8.4 Hz), 7.23 (1H, ddd, *J* = 8.0 7.2 1.6 Hz), 7.00 (1H, br s), 6.94 (2H, d, *J* = 8.4 Hz), 6.73 (1H, d, *J* = 7.6 Hz), 6.67 (1H, ddd, *J* = 8.0 7.2 1.2 Hz), 5.70 (1H, br s), 3.75 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 163.6, 159.3, 147.9, 133.4, 133.1, 128.1, 127.2, 117.0, 114.9, 114.3, 113.5, 66.2, 55.1; HRMS(ESI-TOF): calcd. for $C_{15}H_{14}N_2O_2H^+$: 255.1133. Found: 225.1128 (MH^+), 277.0958 (MNa^+).



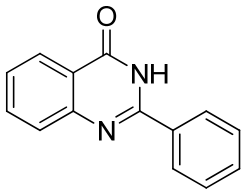
2-(4-Fluorophenyl)-3,2-dihydroquinazolin-4-(1*H*)-one[1] (Entry 5, Table 2): According to the representative procedure the title compound isolated as a colourless crystalline solid (181 mg, 71%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 8.28 (1H, br s), 7.61 (1H, dd, *J* = 8.0 1.6 Hz), 7.54 (2H, dd, *J* = 8.4 5.6 Hz), 7.20-7.27 (3H, m), 7.09 (1H, br s), 6.75 (1H, d, *J* = 7.6 Hz), 6.68 (1H, ddd, *J* = 7.6 7.2 1.6 Hz), 5.77 (1H, br s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 163.4, 162.0 (d, *J* = 244 Hz), 147.7, 137.7 (d, *J* = 3 Hz), 133.2, 128.9 (d, *J* = 8 Hz), 127.3, 117.1, 115.0 (d, *J* = 21 Hz), 114.8, 114.3, 65.8; HRMS(ESI-TOF): calcd. for $C_{14}H_{11}N_2OFH^+$: 243.0933. Found: 243.0932 (MH^+).



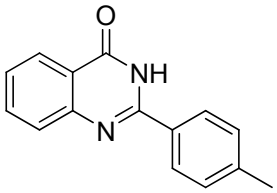
2-(Pyridin-3-yl)-2,3-dihydroquinazoline-4(1*H*)-one (Entry 6, Table 2): According to the representative procedure the title compound was isolated as a yellow crystalline solid (142 mg, 63%). m. p. 218-220 °C; IR : ν_{max}/cm^{-1} (neat) 3258, 1652, 1614, 1520, 1487, 1431, 1386, 1300, 782, 752, 713, 625; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 8.67 (1H, d, J = 2.8 Hz), 8.56 (1H, dd, J = 4.4 1.6 Hz), 7.90 (1H, dt, J = 8.0 2.0 Hz), 7.63 (1H, dd, J = 7.6 1.6 Hz), 7.44 (1H, ddd, J = 8.0 4.8 0.8 Hz), 7.27 (1H, ddd, J = 8.0 7.2 1.6 Hz), 7.18 (1H, br s), 6.76 (1H, dd, J = 8.0 0.4 Hz), 6.71 (1H, ddd, J = 7.6 7.2 1.2 Hz), 5.86 (1H, br s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 163.5, 149.6, 148.3, 147.7, 136.7, 134.6, 133.4, 127.3, 123.5, 117.4, 115.0, 114.5, 64.6; HRMS(ESI-TOF): calcd. for $C_{13}H_{11}N_3OH^+$: 248.0800. Found: 248.0795 (MNa^+); CHN: *Anal. Calc.* for $C_{13}H_{11}N_3O$: C, 69.32%, H, 4.92%, N, 18.66%; Found: C, 69.21%, H, 4.75%, N, 18.52.



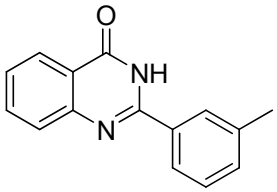
2-(Thiophen-2-yl)-2,3-dihydroquinazoline-4(1*H*)-one (Entry 7, Table 2): According to the representative procedure the title compound was isolated as a colourless crystalline solid (143 mg, 62%). m. p. 211-213 °C; IR : ν_{max}/cm^{-1} (neat) 3290, 1652, 1609, 1517, 1439, 764, 711, 684; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 8.44 (1H, br s), 7.61 (1H, dd, J = 7.6 1.6 Hz), 7.45 (1H, dd, J = 4.8 1.2 Hz), 7.24-7.28 (2H, m), 7.12 (1H, d, J = 3.2 Hz), 6.98 (1H, dd, J = 4.8 3.6 Hz), 6.76 (1H, d, J = 8 Hz), 6.70 (1H, ddd, J = 7.6 7.2 0.8 Hz), 6.01 (1H, t, J = 2.4 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 163.0, 147.1, 146.3, 133.3, 127.2, 126.4, 125.8, 125.6, 117.4, 115.0, 114.6, 62.5; HRMS(ESI-TOF): calcd. for $C_{12}H_{10}N_2OSH^+$: 231.0592. Found: 231.0608 (MH^+), 253.0445 (MNa^+); CHN: *Anal. Calc.* for $C_{12}H_{10}N_2OS$: C, 62.59%, H, 4.38%, N, 12.16%; Found: C, 62.42%, H, 4.35%, N, 12.00%.



2-Phenylquinazolin-4-(3*H*)-one[1] (Entry 1, Table 3): According to the representative procedure the title compound isolated as a colourless crystalline solid (160 mg, 72%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.54 (1H, br s), 8.15-8.20 (3H, m), 7.84 (1H, ddd, J = 8.0 7.2 1.6 Hz), 7.74-7.76 (1H, m), 7.51-7.62 (4H, m); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 162.2, 152.3, 148.6, 134.5, 132.7, 131.3, 128.5, 127.7, 127.4, 127.4, 126.5, 125.8, 120.9; HRMS(ESI-TOF): calcd. for $C_{14}H_{10}N_2OH^+$: 223.0866. Found: 223.0967 (MH^+), 245.0707 (MNa^+).

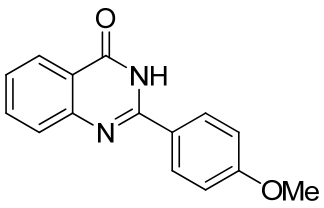


2-*p*-Tolylquinazolin-4-(3*H*)-one[3] (Entry 2, Table 3): According to the representative procedure the title compound isolated as a colourless crystalline solid (111 mg, 47%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.46 (1H, br s), 8.14 (1H, dd, J = 8.0 1.2 Hz), 8.10 (2H, d, J = 8.0 Hz), 7.83 (1H, ddd, J = 8.0 7.2 1.6 Hz), 7.71-7.74 (1H, m), 7.51 (1H, ddd, J = 8.0 7.2 1.2 Hz), 7.36 (2H, d, J = 8.0 Hz), 2.40 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 162.3, 152.2, 148.7, 141.4, 134.5, 129.8, 129.1, 127.6, 127.3, 126.3, 125.8, 120.8, 20.9; HRMS(ESI-TOF): calcd. for $C_{15}H_{13}N_2OH^+$: 237.1022. Found: 237.1112 (MH^+), 259.0858 (MNa^+).

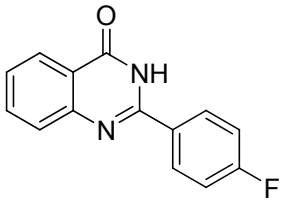


2-*m*-Tolylquinazolin-4-(3*H*)-one[4] (Entry 3, Table 3): According to the representative procedure the title compound isolated as a colourless crystalline solid (170 mg, 72%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.47 (1H, br s), 8.15 (1H, dd, J = 8.0 1.2 Hz), 8.03 (1H, br s), 7.97 (1H, d, J = 7.2 Hz), 7.84 (1H, ddd, J = 8.4 7.2 1.6 Hz), 7.73-7.76 (1H, m), 7.52 (1H, ddd, J = 7.6 7.2 1.2 Hz), 7.39-7.45 (2H, m),

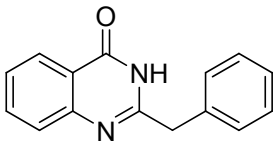
2.41 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 162.1, 152.3, 148.6, 137.8, 134.4, 132.5, 131.9, 128.4, 128.2, 127.3, 126.4, 125.7, 124.8, 120.9, 20.9; HRMS(ESI-TOF): calcd. for $C_{15}H_{13}N_2OH^+$: 237.1022. Found: 237.1113 (MH^+), 259.0848 (MNa^+).



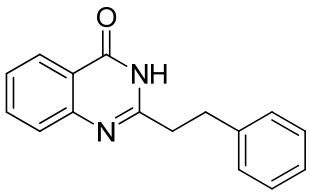
2-(4-Methoxyphenyl)quinazolin-4-(3*H*)-one[1] (Entry 4, Table 3): According to the representative procedure the title compound isolated as a colourless crystalline solid (177 mg, 70%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.41 (1H, br s), 8.19 (2H, d, J = 8.8 Hz), 8.13 (1H, dd, J = 8.0 1.2 Hz), 7.81 (1H, ddd, J = 8.0 7.2 1.6 Hz), 7.69-7.71 (1H, m), 7.48 (1H, ddd, J = 7.8 7.2 1.2 Hz), 7.09 (2H, d, J = 8.8 Hz), 3.85 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 162.3, 161.8, 151.8, 148.8, 134.4, 129.4, 127.2, 127.2, 127.1, 126.0, 125.7, 124.7, 120.6, 113.9, 55.3; HRMS(ESI-TOF): calcd. for $C_{15}H_{13}N_2O_2H^+$: 253.0972. Found: 253.1064 (MH^+), 275.0803 (MNa^+).



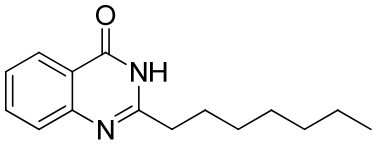
2-(4-Fluorophenyl)quinazolin-4-(3*H*)-one[5] (Entry 5, Table 3): According to the representative procedure the title compound isolated as a colourless crystalline solid (161 mg, 67%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.57 (1H, br s), 8.25 (2H, dd, J = 8.4 4.8 Hz), 8.15 (1H, d, J = 7.6 Hz), 7.84 (1H, t, J = 7.6 Hz), 7.74 (1H, d, J = 8.0 Hz), 7.52 (1H, t, J = 7.6 Hz), 7.39 (2H, app. t, J = 8.8 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 163.9 (d, J = 249 Hz), 162.2, 151.3, 148.5, 134.5, 130.3 (d, J = 9 Hz), 129.1 (d, J = 3 Hz), 127.3, 126.5, 125.8, 120.8, 115.5 (d, J = 22 Hz); HRMS(ESI-TOF): calcd. for $C_{14}H_9N_2OFH^+$: 241.0772. Found: 241.0807 (MH^+).



2-Benzylquinazolin-4-(3*H*)-one[4] (Entry 6, Table 3): According to the representative procedure the title compound isolated as a colourless crystalline solid (208 mg, 85%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.41 (1H, br s), 8.07 (1H, ddd, J = 7.6 1.2 0.4 Hz), 7.77 (1H, ddd, J = 8.4 7.2 1.6 Hz), 7.60 (1H, d, J = 7.6 Hz), 7.46 (1H, ddd, J = 8.0 7.2 1.2 Hz), 7.37-7.40 (2H, m), 7.30-7.34 (2H, m), 7.22-7.26 (1H, m), 3.93 (2H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 161.8, 155.9, 148.8, 136.5, 134.3, 128.8, 128.4, 126.8, 126.7, 126.1, 125.6, 120.7, 40.7; HRMS(ESI-TOF): calcd. for $C_{15}H_{13}N_2OH^+$: 237.1022. Found: 237.1122 (MH^+), 259.0890 (MNa^+).

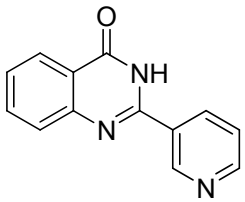


2-Phenethylquinazolin-4-(3*H*)-one[6] (Entry 7, Table 3): According to the representative procedure the title compound isolated as a colourless crystalline solid (208 mg, 83%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.25 (1H, br s), 8.08 (1H, ddd, J = 8.0 1.6 0.4 Hz), 7.78 (1H, ddd, J = 8.0 7.2 1.6 Hz), 7.62 (1H, dd, J = 8.0 0.4 Hz), 7.46 (1H, ddd, J = 8.0 7.2 1.2 Hz), 7.28-7.29 (4H, m), 7.17-7.21 (1H, m), 3.03-3.07 (2H, m), 2.88-2.92 (2H, m); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 161.7, 156.5, 148.8, 140.7, 134.2, 128.3, 128.3, 126.7, 126.0, 125.9, 125.6, 120.8, 36.2, 32.4; HRMS(ESI-TOF): calcd. for $C_{16}H_{14}N_2OH^+$: 251.1179. Found: 251.1276 (MH^+), 273.1008 (MNa^+).

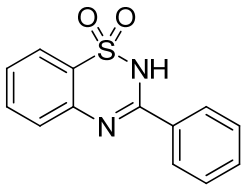


2-Heptyl-2,3-dihydroquinazoline-4(1*H*)-one (Entry 8, Table 3): According to the representative procedure the title compound was isolated as a colourless crystalline solid (200 mg, 82%). m. p. 143-145 °C; IR : ν_{max}/cm^{-1} (neat) 2917, 2854, 1670, 1611, 1468, 886, 766, 688, 647; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 12.16 (1H, br s), 8.08 (1H, dd, J = 8.0 1.2 Hz), 7.77 (1H, ddd, J = 8.4 7.2 1.6 Hz), 7.59 (1H, d, J = 7.6

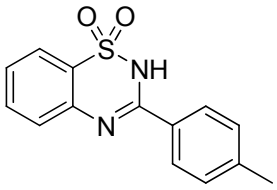
Hz), 7.45 (1H, ddd, J = 8.0 7.2 1.2 Hz), 2.59 (2H, t, J = 7.6 Hz), 1.68-1.76 (2H, m), 1.24-1.31 (8H, m), 0.86 (3H, t, J = 7.2 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 161.7, 157.4, 148.8, 134.1, 126.6, 125.6, 125.6, 120.7, 34.4, 31.0, 28.4, 28.3, 26.7, 21.9, 13.8; HRMS(ESI-TOF): calcd. for $C_{15}H_{20}N_2OH^+$: 245.1648. Found: 245.1757 (MH^+), 267.1549 (MNa^+); CHN: *Anal. Calc.* for $C_{15}H_{20}N_2O$: C, 73.74%, H, 8.25%, N, 11.47%; Found: C, 73.63%, H, 8.23%, N, 11.40%.



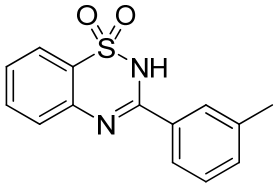
2-(Pyridin-3-yl)quinazolin-4-(3*H*)-one[3] (Entry 9, Table 3): According to the representative procedure the title compound isolated as a colourless crystalline solid (141 mg, 63%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.73 (1H, br s), 9.30 (1H, d, J = 2.0 Hz), 8.76 (1H, dd, J = 4.8 1.6 Hz), 8.50 (1H, ddd, J = 8.0 2.4 1.6 Hz), 8.17 (1H, dd, J = 8.0 1.2 Hz), 7.86 (1H, ddd, J = 8.0 7.8 1.6 Hz), 7.77 (1H, dd, J = 8.0 0.8 Hz), 7.58 (1H, ddd, J = 8.0 4.8 0.8 Hz), 7.56 (1H, ddd, J = 8.0 7.2 1.2 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 162.1, 151.7, 150.7, 148.7, 148.4, 135.3, 134.6, 128.6, 127.4, 126.8, 125.8, 123.4, 121.0; HRMS(ESI-TOF): calcd. for $C_{13}H_9N_3OH^+$: 224.0818. Found: 224.0886 (MH^+), 246.0625 (MNa^+).



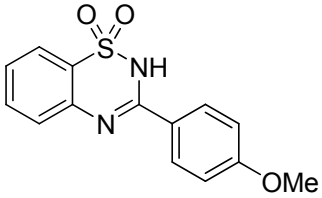
(Entry 1, Table 4)[7]: According to the representative procedure the title compound isolated as a colourless crystalline solid (209 mg, 81%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.19 (1H, br s), 8.04-8.06 (2H, m), 7.87 (1H, dd, J = 8.0 1.6 Hz), 7.69-7.76 (2H, m), 7.62-7.65 (3H, m), 7.51 (1H, ddd, J = 8.0 7.2 1.2 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 154.7, 135.4, 133.0, 132.7, 131.7, 128.8, 128.2, 126.6, 123.2, 121.4, 118.4; HRMS(ESI-TOF): calcd. for $C_{13}H_{10}N_2O_2SH^+$: 259.0541. Found: 259.0559 (MH^+), 281.038 (MNa^+).



(Entry 2, Table 4)[7]: According to the representative procedure the title compound isolated as a yellow crystalline solid (212 mg, 78%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.09 (1H, br s), 7.98 (1H, d, J = 8.4 Hz), 7.86 (1H, dd, J = 8.0 1.6 Hz), 7.74 (1H, ddd, J = 8.4 7.2 1.2 Hz), 7.65 (1H, d, J = 7.6 Hz), 7.50 (1H, ddd, J = 8.4 7.2 1.2 Hz), 7.45 (2H, d, J = 8.0 Hz), 2.43 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 154.5, 143.2, 135.4, 133.0, 129.3, 128.8, 128.1, 126.5, 123.2, 121.4, 118.3, 21.0; HRMS(ESI-TOF): calcd. for $C_{14}H_{12}N_2O_2SH^+$: 273.0698. Found: 273.0692 (MH^+), 295.0534 (MNa^+).

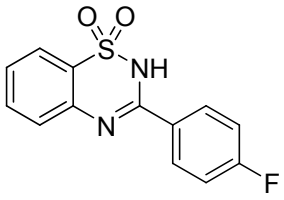


(Entry 3, Table 4)[7]: According to the representative procedure the title compound isolated as a yellow crystalline solid (223 mg, 82%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.15 (1H, br s), 7.83-7.87 (3H, m), 7.74 (1H, ddd, J = 8.4 7.2 1.2 Hz), 7.63 (1H, dd, J = 8.4 0.8 Hz), 7.48-7.53 (3H, m), 2.44 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 154.8, 138.3, 135.4, 133.4, 133.1, 131.7, 128.7, 128.6, 126.6, 125.4, 123.3, 121.4, 118.4, 20.9; HRMS(ESI-TOF): calcd. for $C_{14}H_{12}N_2O_2SH^+$: 273.0697. Found: 273.0674 (MH^+).

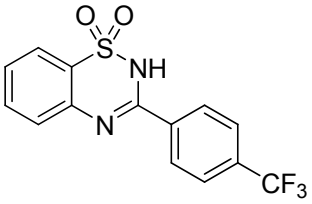


(Entry 4, Table 4)[7]: According to the representative procedure the title compound isolated as a colourless crystalline solid (251 mg, 87%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 11.99 (1H, br s), 8.06 (2H, d, J = 8.8 Hz), 7.84 (1H, dd, J = 8.0 1.2 Hz), 7.72 (1H, ddd, J = 8.4 7.2 1.6 Hz), 7.64 (1H, dd, J = 8.0 0.8 Hz), 7.48 (1H, ddd, J = 8.0 7.2 1.2 Hz), 7.17 (2H, d, J = 9.2 Hz), 3.88 (3H, s); ^{13}C NMR (75.4 MHz, DMSO-

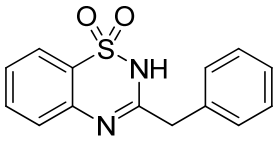
d_6, 25 °C) δ 162.9, 154.2, 135.5, 132.9, 130.2, 126.3, 123.5, 123.2, 121.5, 118.3, 114.1, 55.6; HRMS(ESI-TOF): calcd. for $C_{14}H_{12}N_2O_3SH^+$: 289.0647. Found: 289.0642 (MH^+), 311.0483 (MNa^+).



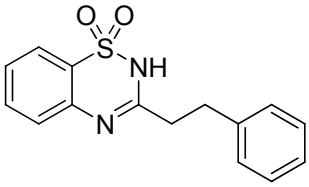
(Entry 5, Table 4): According to the representative procedure the title compound was isolated as a colourless crystalline solid (180 mg, 65%). m. p. >300 °C; IR : ν_{max}/cm^{-1} (neat) 3262, 1605, 1557, 1506, 1465, 1278, 1158, 1142, 1124, 815, 761, 733; ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ 12.20 (1H, br s), 8.14 (2H, dd, J = 8.8 5.6 Hz), 7.87 (1H, dd, J = 8.0 1.6 Hz), 7.75 (1H, ddd, J = 8.4 7.2 1.2 Hz), 7.63 (1H, d, J = 7.6 Hz), 7.47-7.54 (3H, m); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 164.7 (d, J = 251 Hz), 153.7, 135.4, 133.1, 131.0 (d, J = 9 Hz), 128.2 (d, J = 3 Hz), 126.7, 123.3, 121.4, 118.4, 115.9 (d, J = 22 Hz); HRMS(ESI-TOF): calcd. for $C_{13}H_9N_2O_2FSH^+$: 277.0447. Found: 277.0431 (MH^+), 299.0259 (MNa^+); CHN: *Anal. Calc.* for $C_{13}H_9N_2O_2FS$: C, 56.51%, H, 3.28%, N, 10.14%; Found: C, 56.42%, H, 3.34%, N, 10.10%.



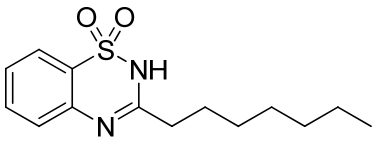
(Entry 6, Table 4)[7]: According to the representative procedure the title compound isolated as a yellow crystalline solid (225 mg, 69%). ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.40 (1H, br s), 8.26 (2H, d, J = 8.0 Hz), 8.02 (2H, d, J = 8.4 Hz), 7.89 (1H, dd, J = 8.0 1.2 Hz), 7.76 (1H, ddd, J = 8.4 7.2 1.6 Hz), 7.64 (1H, dd, J = 8.4 0.8 Hz), 7.53 (1H, ddd, J = 8.4 7.6 1.2 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 153.5, 135.7 (d, J = 1 Hz), 135.3, 133.2, 132.2 (d, J = 32 Hz), 129.2, 127.5 (q, J = 254 Hz), 127.0, 125.7 (d, J = 4 Hz), 125.6 (d, J = 12 Hz), 123.4, 121.4, 118.5; HRMS(ESI-TOF): calcd. for $C_{14}H_9N_2O_2F_3SH^+$: 327.0415. Found: 327.0400 (MH^+), 349.0236 (MNa^+).



(Entry 7, Table 4)[7]: According to the representative procedure the title compound isolated as a grey crystalline solid (196 mg, 72%). ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 12.24 (1H, br s), 7.78 (1H, dd, J = 8.0 1.2 Hz), 7.68 (1H, ddd, J = 8.0 7.6 1.6 Hz), 7.44 (1H, ddd, J = 8.0 7.6 1.2 Hz), 7.34-7.39 (5H, m), 7.27-7.32 (1H, m), 3.87 (2H, s); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C) δ 158.5, 135.1, 135.0, 133.1, 129.0, 128.6, 127.1, 126.4, 123.4, 121.0, 117.4, 41.5; HRMS(ESI-TOF): calcd. for $C_{14}H_{12}N_2O_2SH^+$: 273.0697. Found: 273.0696 (MH^+), 295.0570 (MNa^+).

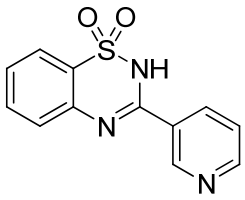


(Entry 8, Table 4): According to the representative procedure the title compound was isolated as a pale yellow crystalline solid (226 mg, 79%). m. p. 237-239 °C; IR : ν_{max}/cm^{-1} (neat) 3258, 3180, 1607, 1577, 1527, 1474, 1280, 1266, 1149, 1127, 757, 742, 694; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 11.97 (1H, br s), 7.79 (1H, dd, J = 8.0 1.6 Hz), 7.66 (1H, ddd, J = 8.4 7.2 1.2 Hz), 7.43 (1H, ddd, J = 8.4 7.2 0.8 Hz), 7.27-7.32 (5H, m), 7.18-7.24 (1H, m), 2.98-3.02 (2H, m), 2.83-2.87 (2H, m); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 159.4, 140.1, 135.0, 133.0, 128.4, 128.3, 126.2, 123.4, 121.2, 117.2, 36.9, 31.6; HRMS(ESI-TOF): calcd. for $C_{15}H_{14}N_2O_2SH^+$: 287.0849. Found: 287.0880 (MH^+), 309.0736 (MNa^+); CHN: *Anal. Calc.* for $C_{15}H_{14}N_2O_2S$: C, 62.92%, H, 4.93%, N, 9.78%; Found: C, 62.94%, H, 4.99%, N, 9.66%.

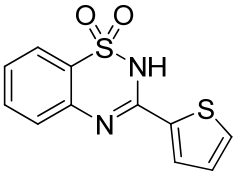


(Entry 9, Table 4): According to the representative procedure the title compound was isolated as a colourless crystalline solid (236 mg, 84%). m. p. >300 °C; IR : ν_{max}/cm^{-1} (neat) 2926, 2852, 1612, 1532, 1481, 1270, 1155, 1133, 754; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 11.94 (1H, br s), 7.78 (1H, dd, J = 8.0 1.2 Hz), 7.66 (1H, ddd, J

= 8.6 7.2 1.2 Hz), 7.43 (1H, ddd, *J* = 8.0 7.2 0.8 Hz), 7.31 (1H, dd, *J* = 8.6 0.8 Hz), 2.53 (2H, t, *J* = 7.2 Hz), 1.63-1.71 (2H, m), 1.25-1.35 (8H, m), 0.86 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 160.3, 135.1, 133.0, 126.1, 123.4, 121.1, 117.2, 35.2, 31.0, 28.3, 28.1, 26.0, 22.0, 13.9; HRMS(ESI-TOF): calcd. for $C_{14}H_{20}N_2O_2SH^+$: 281.1318. Found: 281.1369 (MH^+), 303.1203 (MNa^+); CHN: *Anal. Calc*. for $C_{14}H_{20}N_2O_2S$: C, 59.97%, H, 7.19%, N, 9.99%; Found: C, 59.96%, H, 7.21%, N, 9.94%.

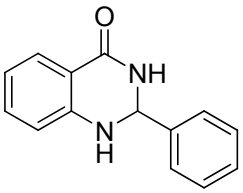


(Entry 10, Table 4): According to the representative procedure the title compound was isolated as an orange crystalline solid (135 mg, 52%). m. p. >300 °C; IR : ν_{max}/cm^{-1} (neat) 3296, 1607, 1596, 1529, 1475, 1437, 1288, 1155, 1127, 1075, 829, 761, 699; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 12.39 (1H, br s), 9.19 (1H, dd, *J* = 2.4 0.8 Hz), 8.86 (1H, dd, *J* = 4.8 1.6 Hz), 8.39 (1H, ddd, *J* = 8.0 2.4 1.6 Hz), 7.89 (1H, dd, *J* = 8.0 1.6 Hz), 7.76 (1H, ddd, *J* = 8.4 7.2 1.6 Hz), 7.67 (1H, ddd, *J* = 8.0 4.8 0.8 Hz), 7.61 (1H, dd, *J* = 8.0 0.8 Hz), 7.53 (1H, ddd, *J* = 8.0 7.2 0.8 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 153.2, 153.1, 148.9, 136.1, 135.4, 133.2, 128.0, 126.9, 123.7, 123.4, 121.4, 118.4; HRMS(ESI-TOF): calcd. for $C_{12}H_9N_3O_2SH^+$: 260.0494. Found: 260.0484 (MH^+), 282.0309 (MNa^+); CHN: *Anal. Calc*. for $C_{12}H_9N_3O_2S$: C, 55.59%, H, 3.50%, N, 16.21%; Found: C, 55.70%, H, 3.65%, N, 16.10%.

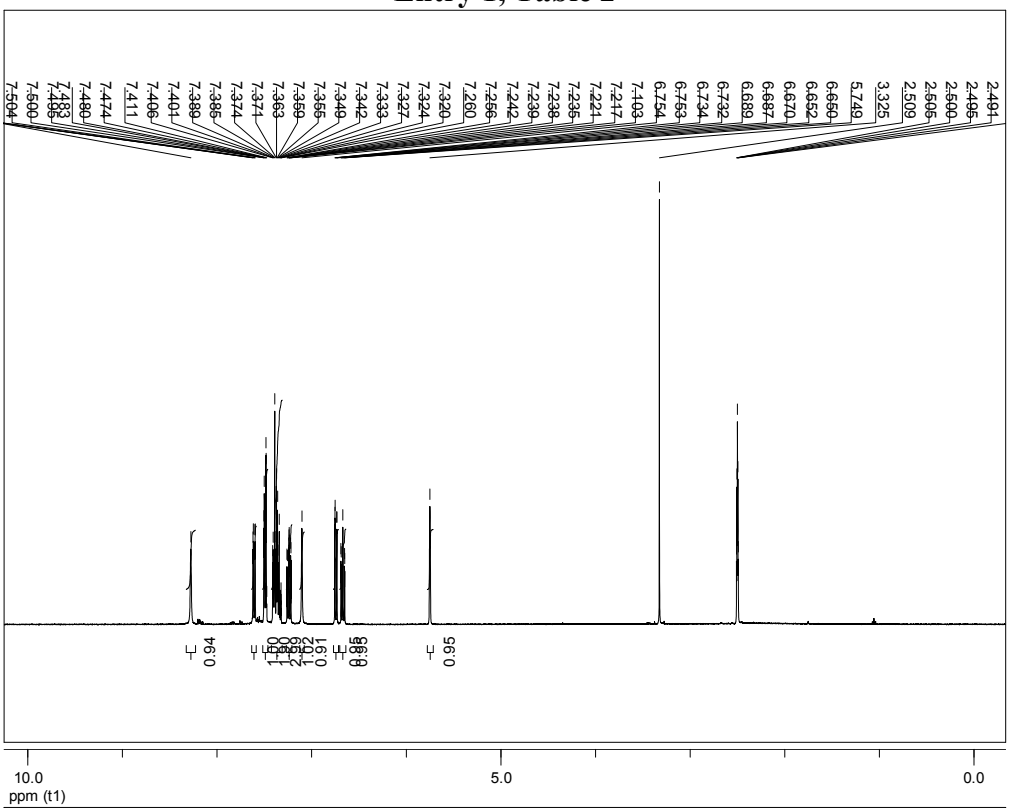


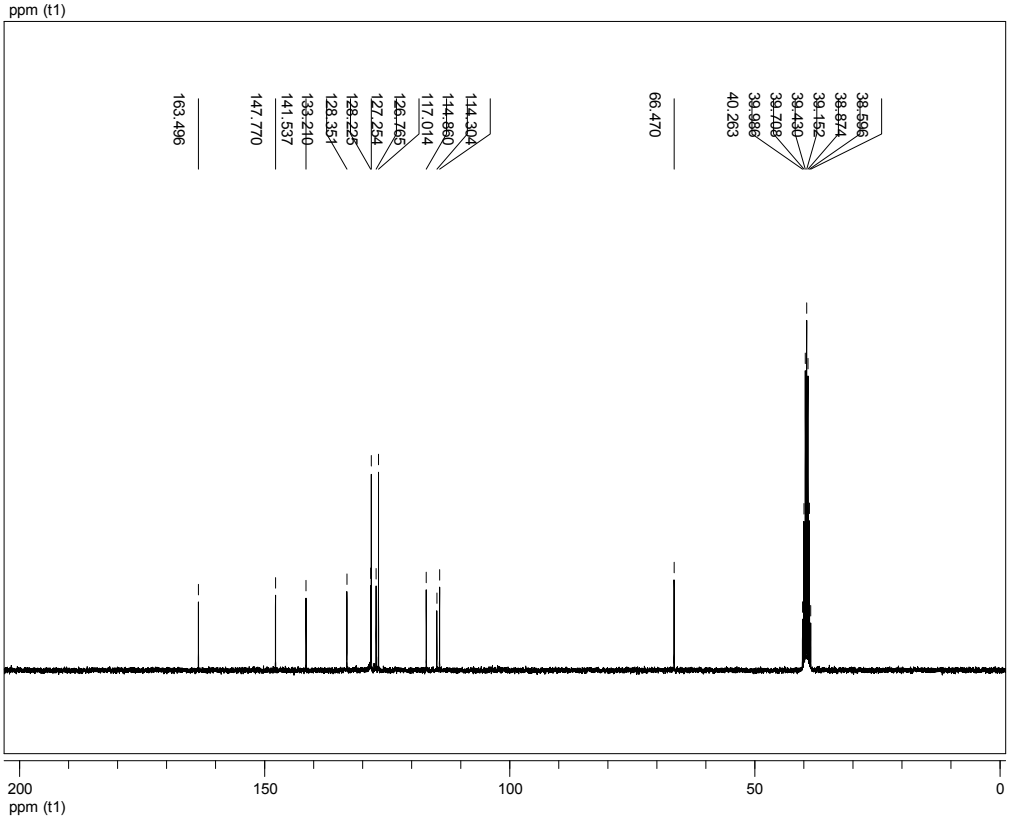
(Entry 11, Table 4): According to the representative procedure the title compound was isolated as an yellow crystalline solid (93 mg, 35%). m. p. >300 °C; IR : ν_{max}/cm^{-1} (neat) 3207, 1610, 1567, 1515, 1282, 1262, 1153, 1131, 1076, 757, 734; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ 12.15 (1H, br s), 8.23 (1H, dd, *J* = 3.6 1.2 Hz), 8.04 (1H, dd. *J* = 4.8 1.2 Hz), 7.84 (1H, dd, *J* = 8.0 1.2 Hz), 7.74 (1H, ddd, *J* = 8.4 7.2 1.6

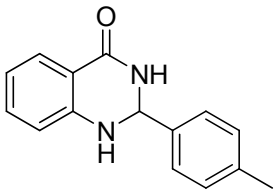
Hz), 7.61 (1H, dd, J = 8.0 0.8 Hz), 7.49 (1H, ddd, J = 8.0 7.2 1.2 Hz), 7.34 (1H, dd, J = 5.2 3.6 Hz); ^{13}C NMR (75.4 MHz, DMSO-d_6, 25 °C): δ 149.5, 135.4, 135.3, 134.3, 133.2, 131.7, 128.8, 126.5, 123.2, 121.6, 118.1; HRMS(ESI-TOF): calcd. for $C_{11}H_8N_2O_2S_2H^+$: 265.0105. Found: 265.0078 (MH^+), 286.9915 (MNa^+); CHN: *Anal. Calc*. for $C_{11}H_8N_2O_2S_2$: C, 49.98%, H, 3.05%, N, 10.60%; Found: C, 49.90%, H, 3.07%, N, 10.70%.



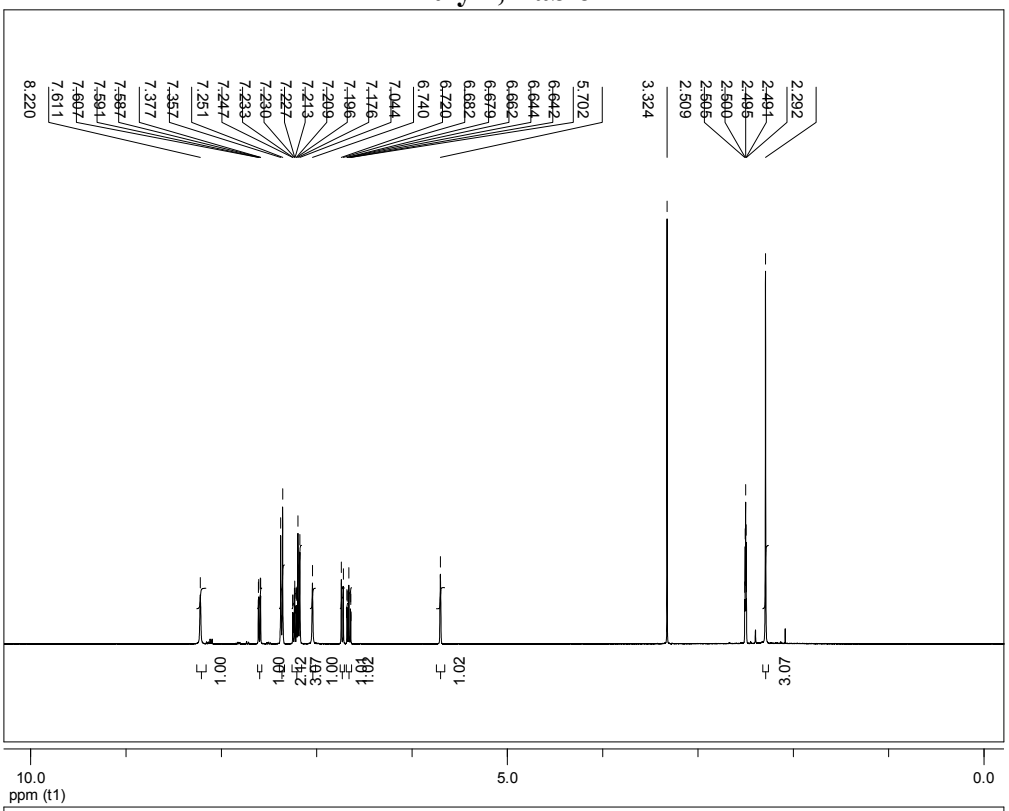
Entry 1, Table 2

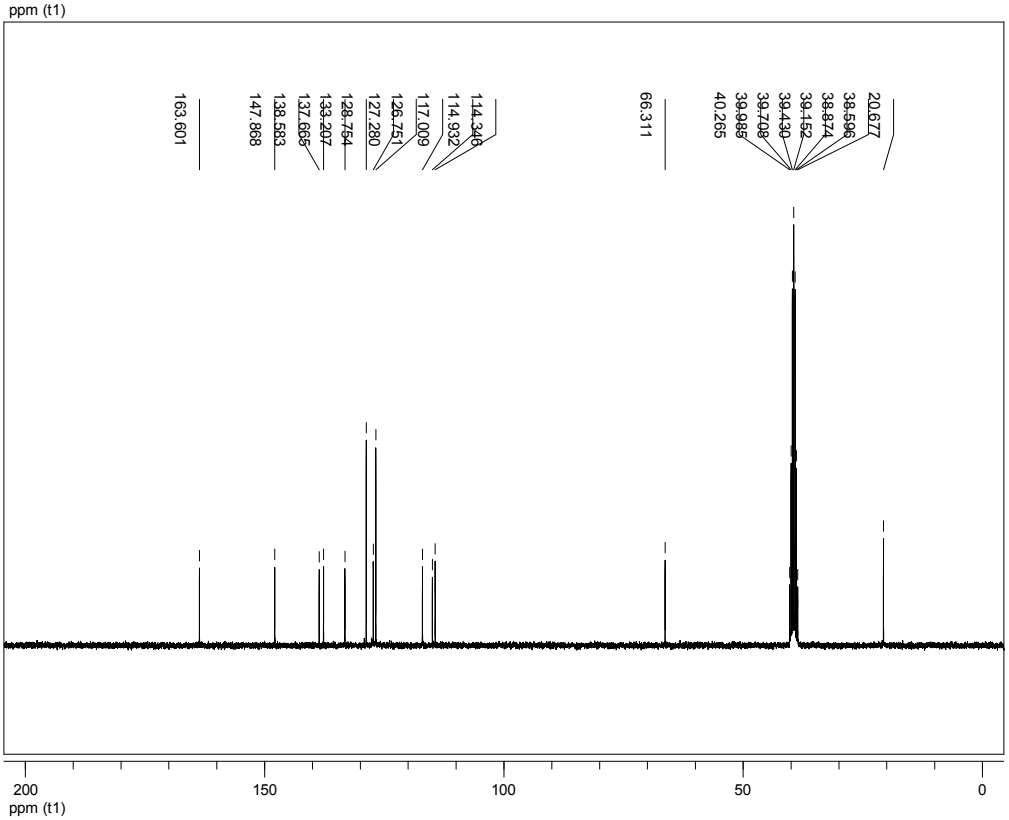


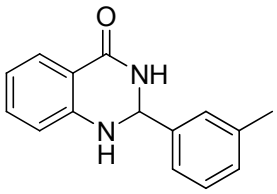




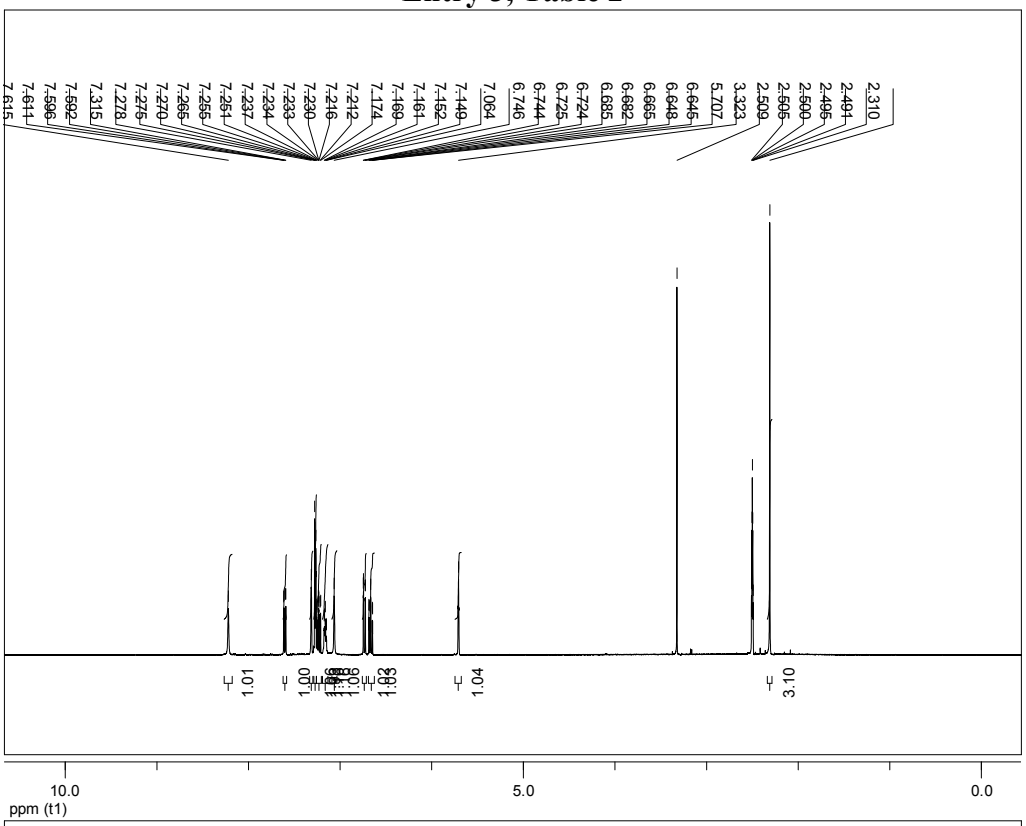
Entry 2, Table 2

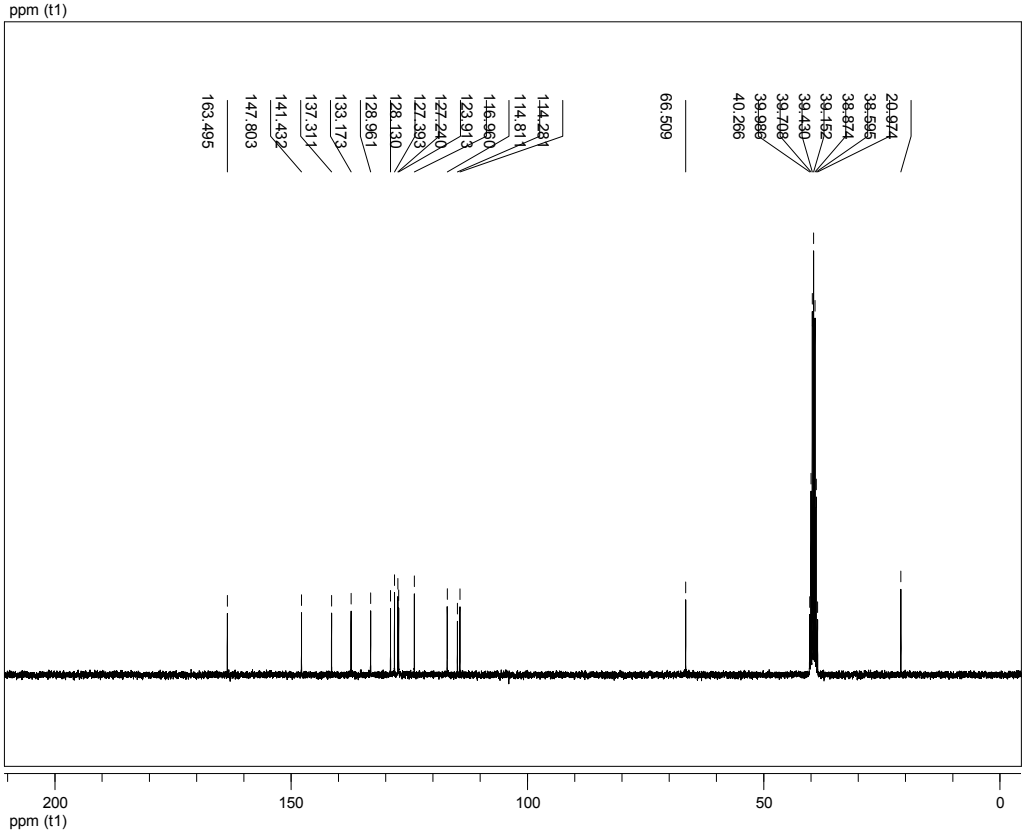


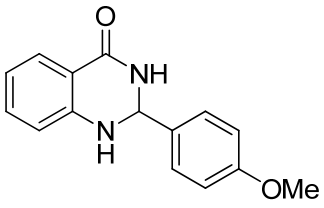




Entry 3, Table 2







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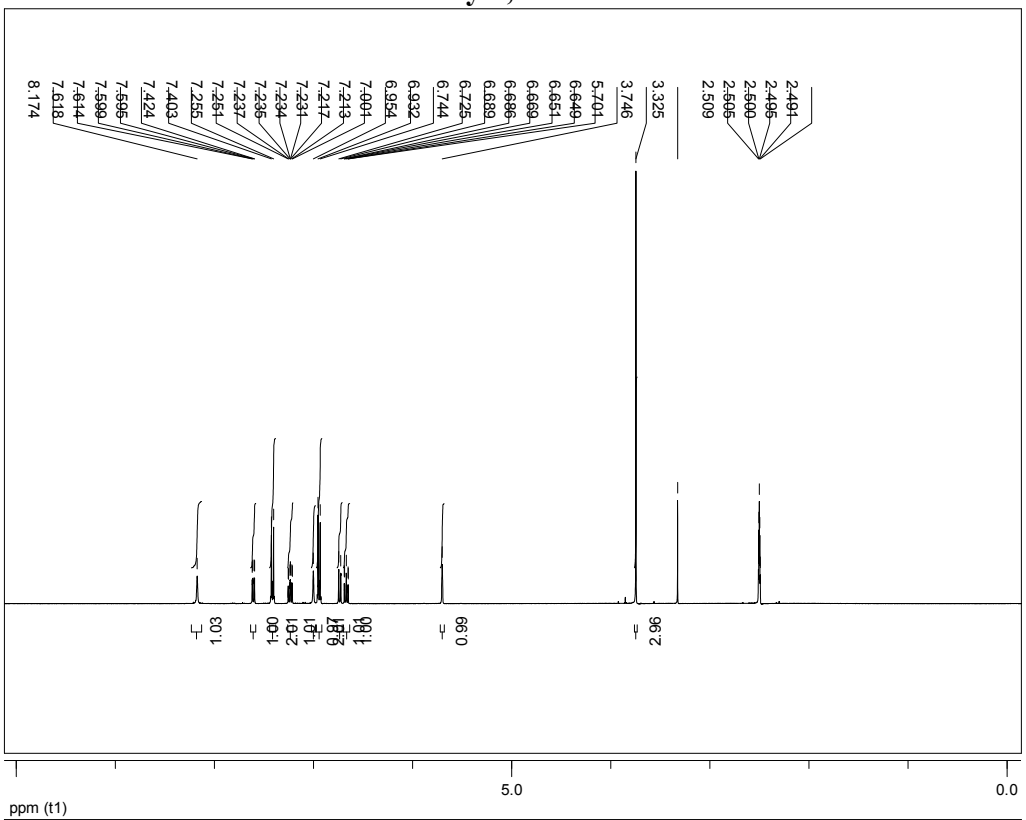

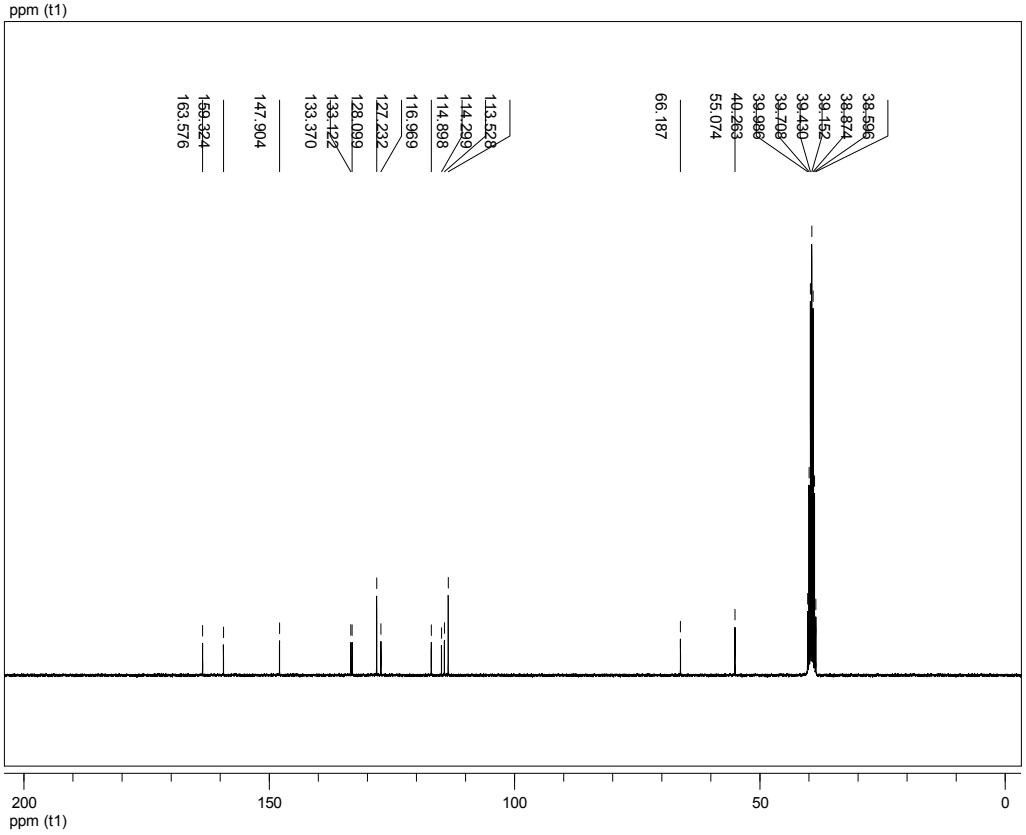

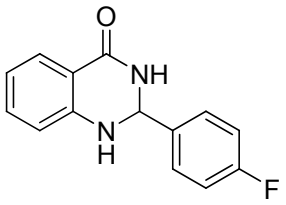

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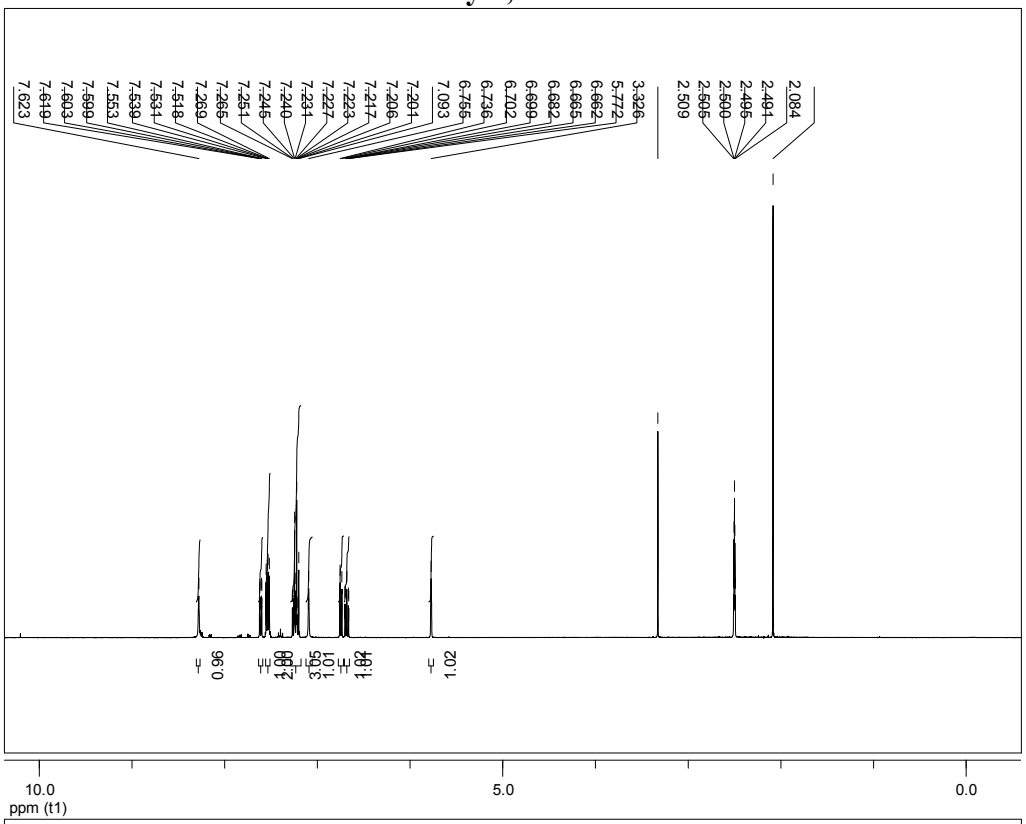

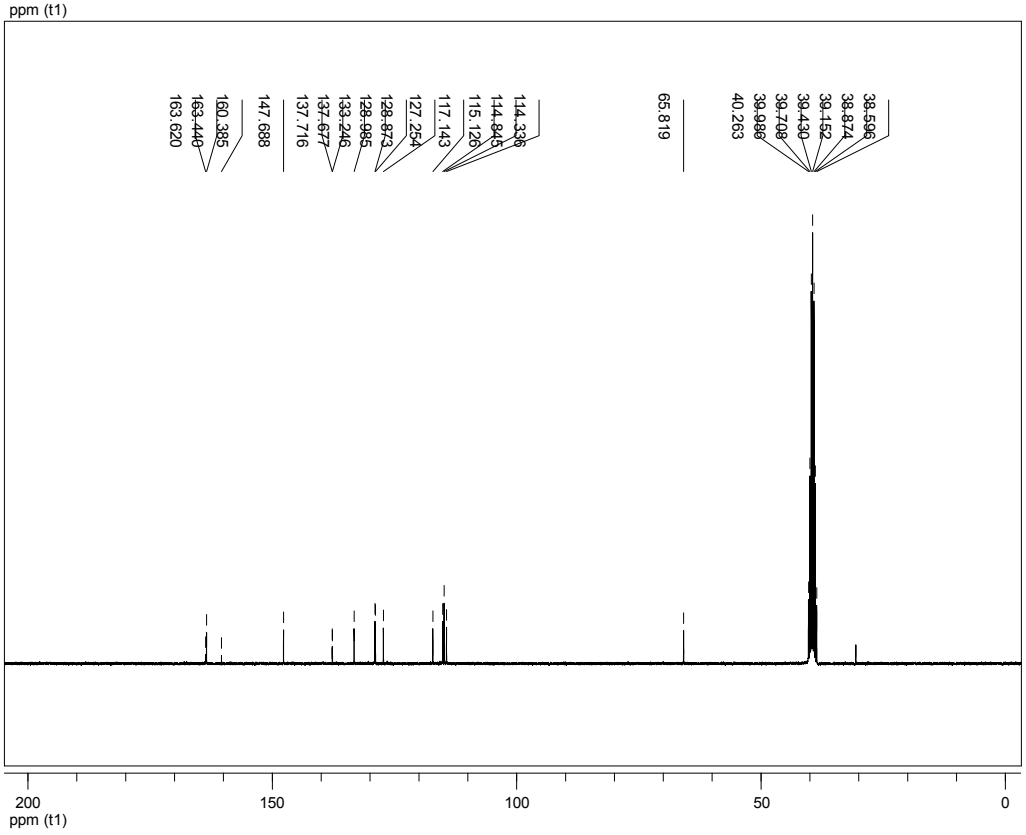

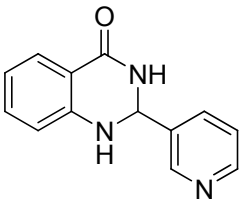

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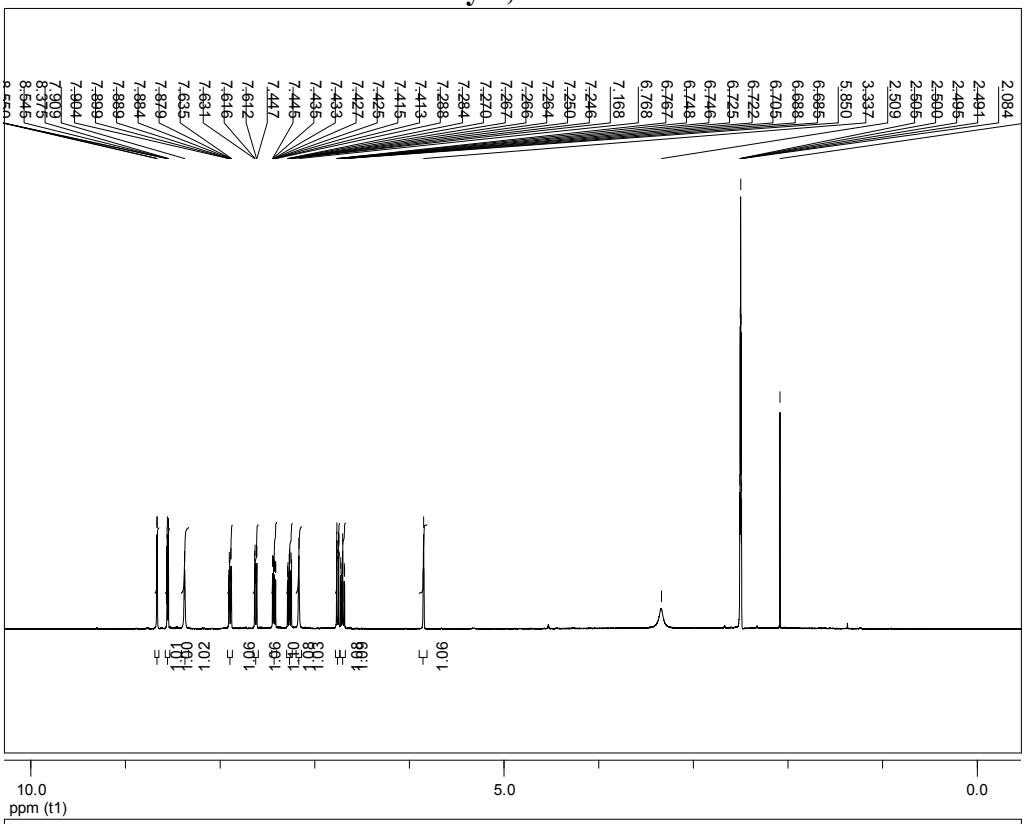

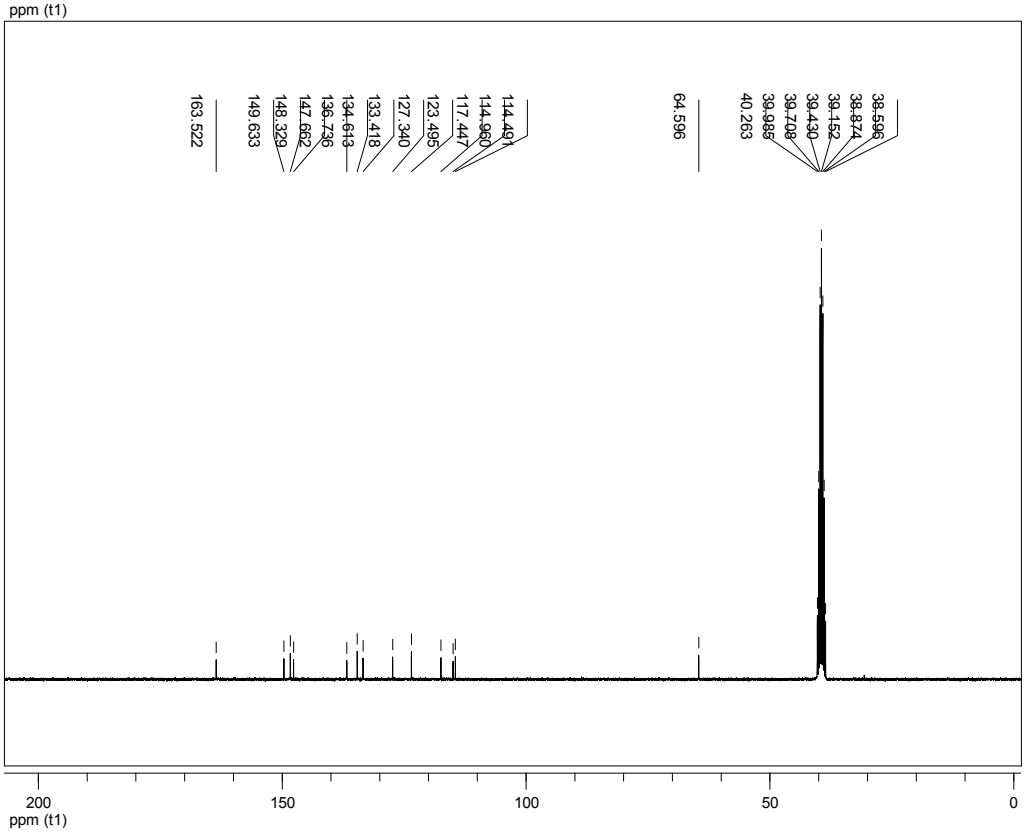

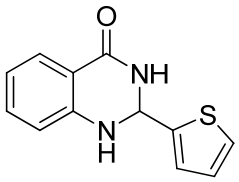

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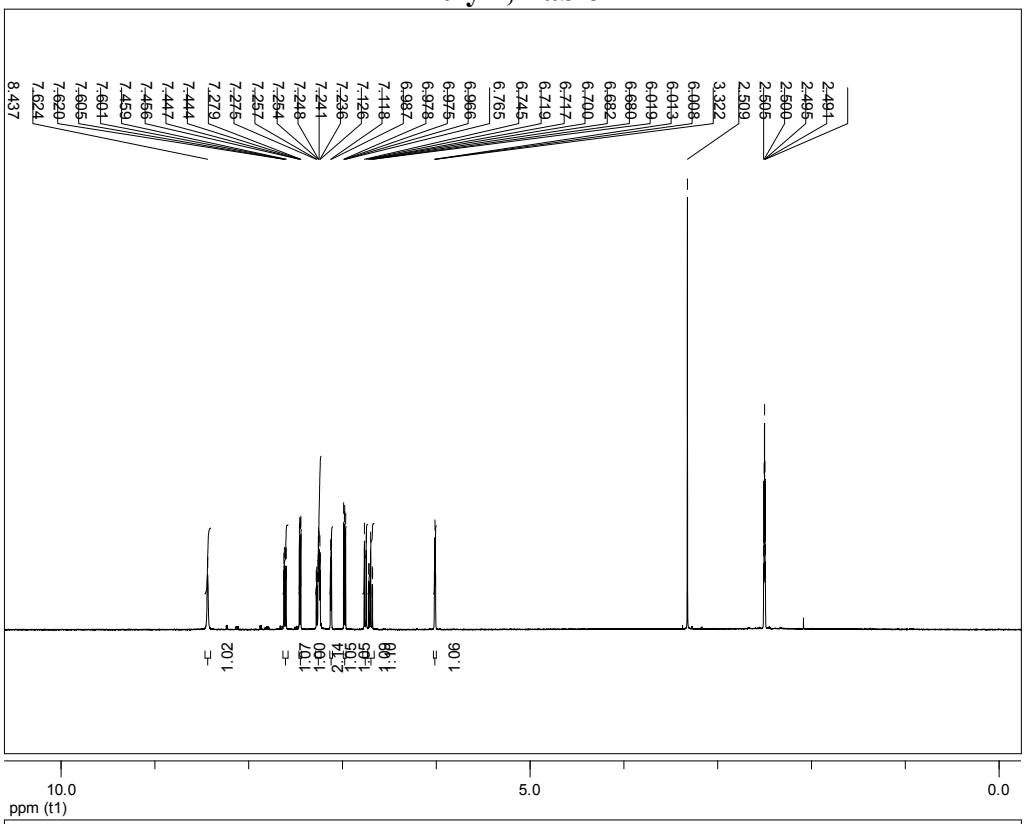

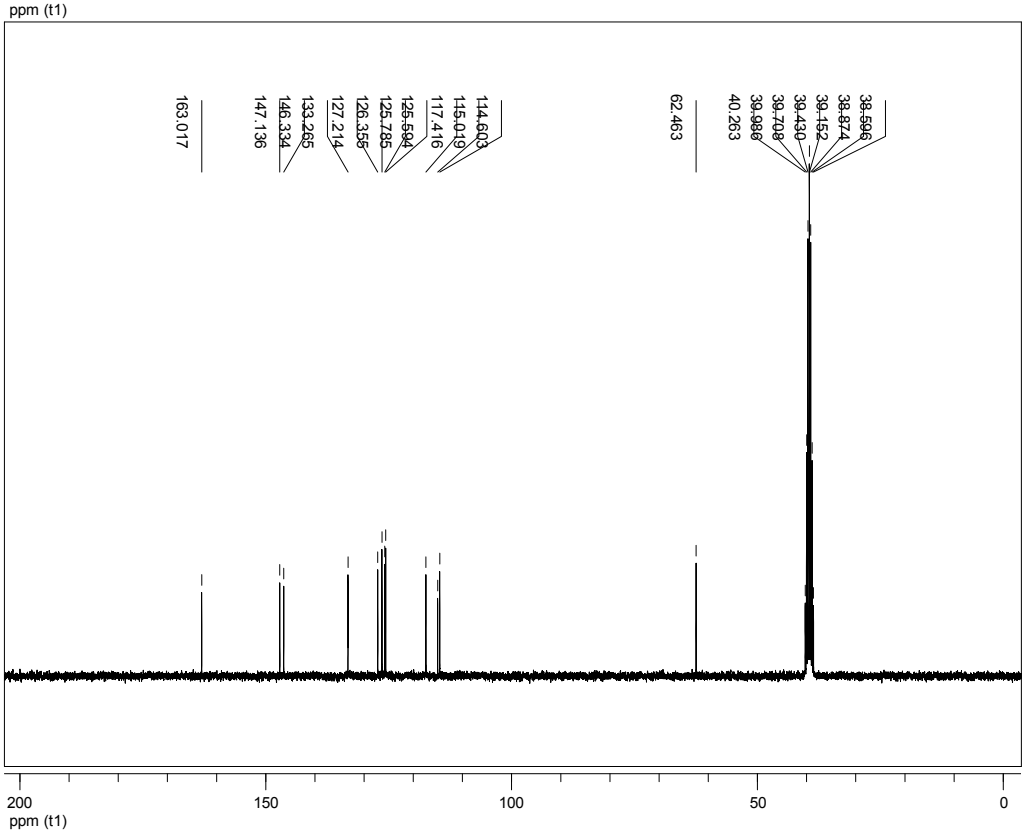

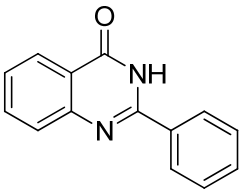

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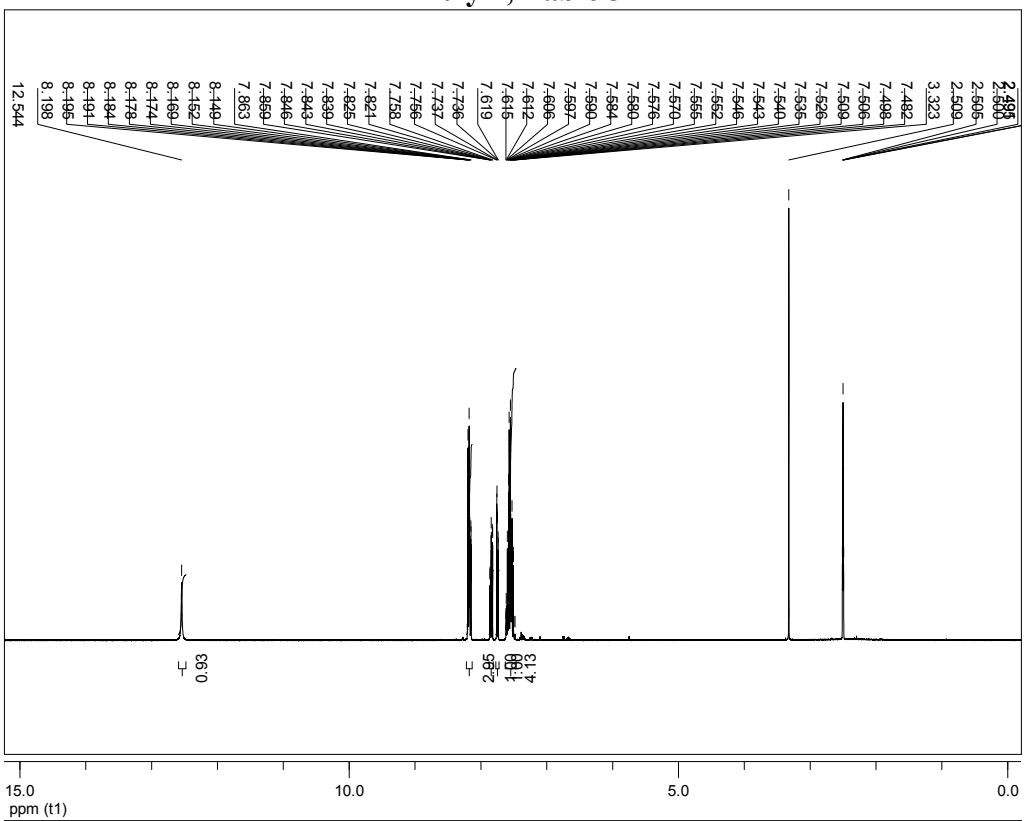

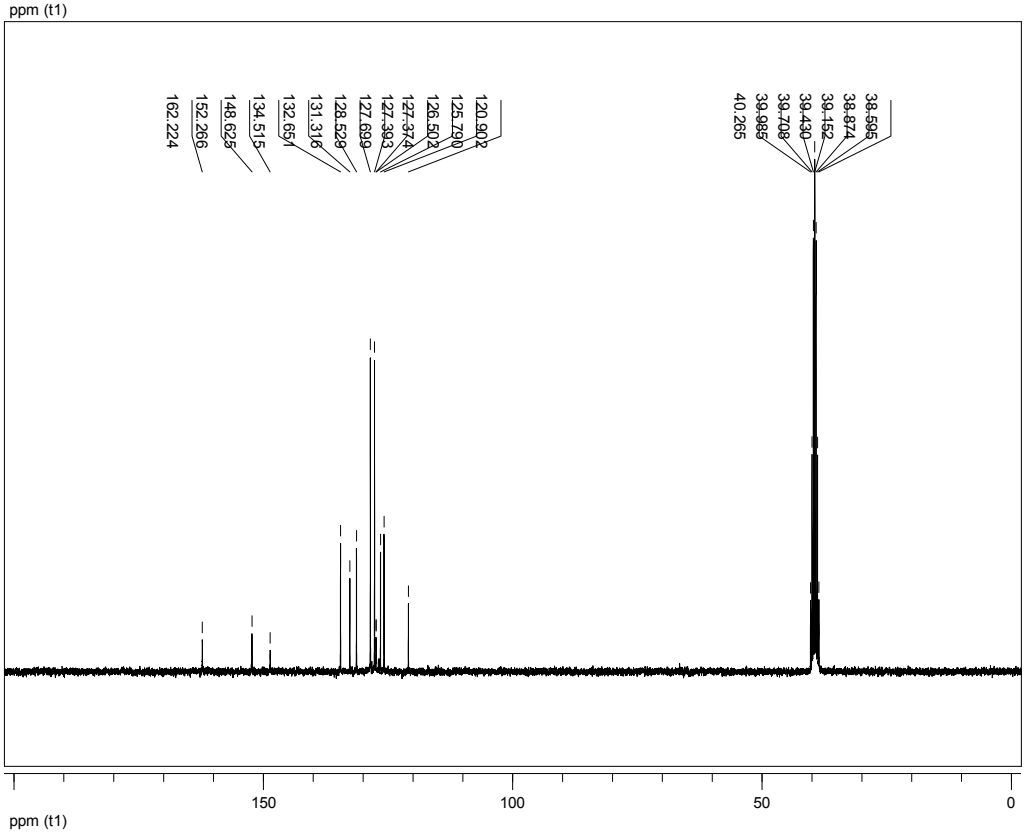

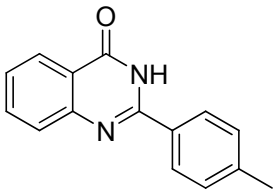

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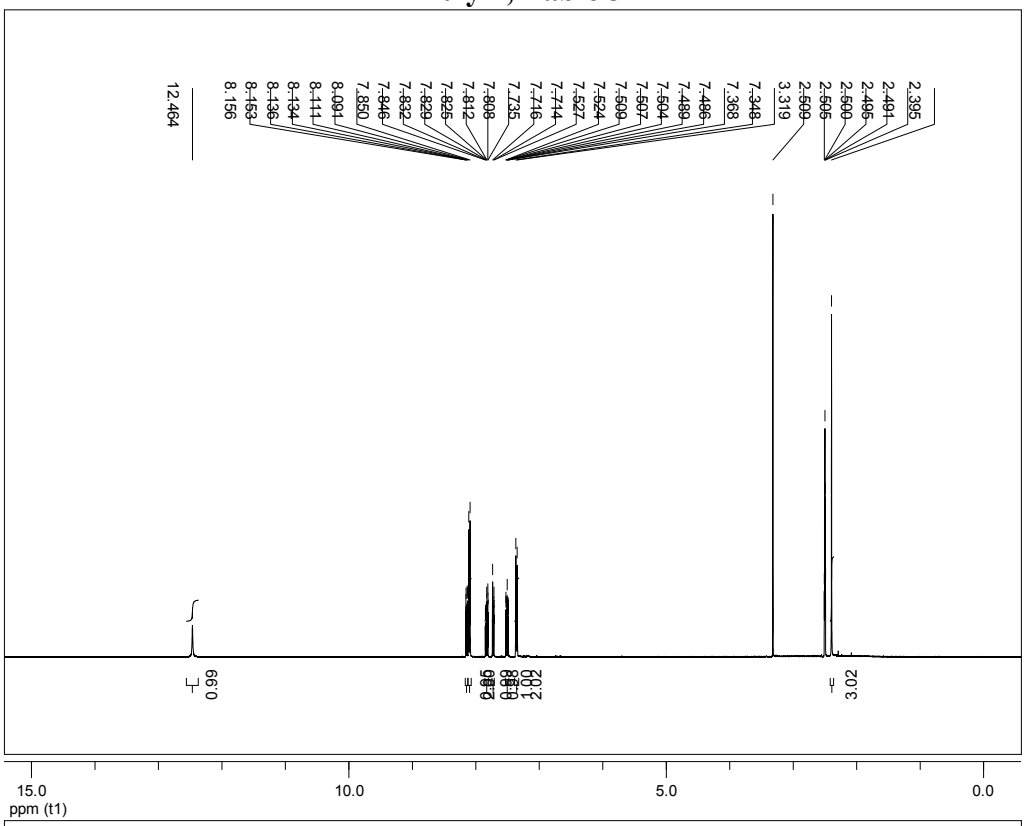

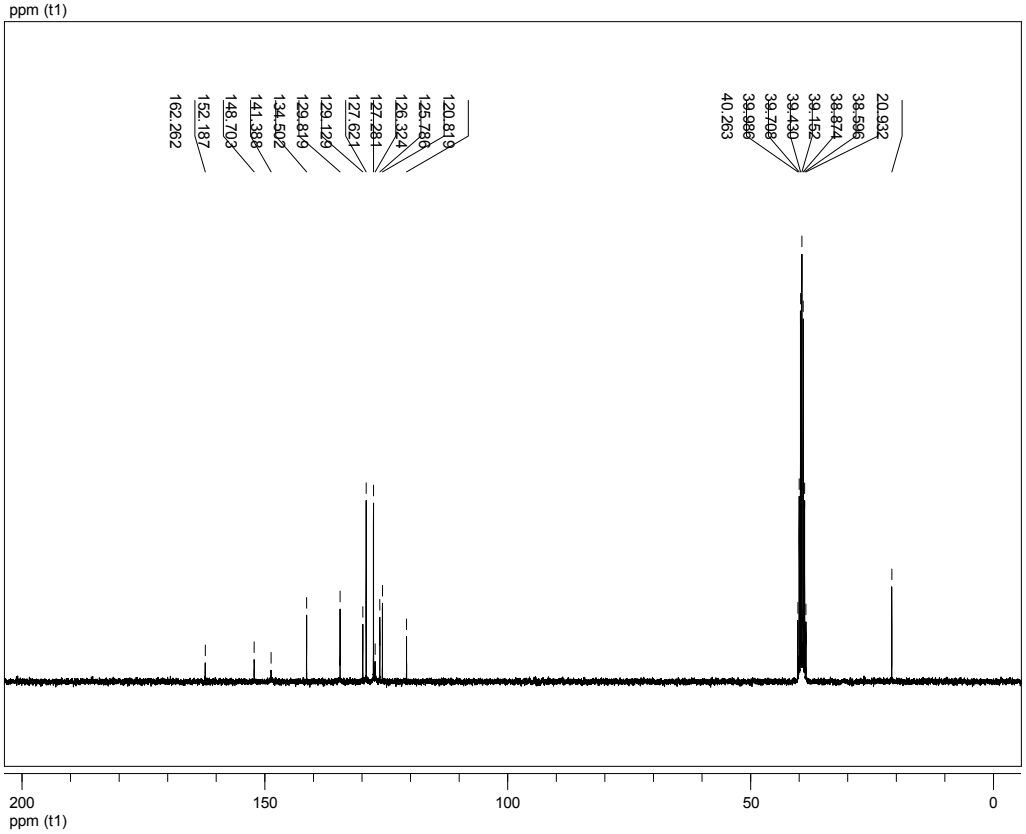

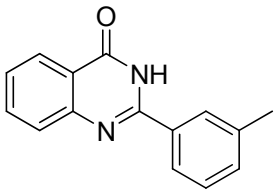

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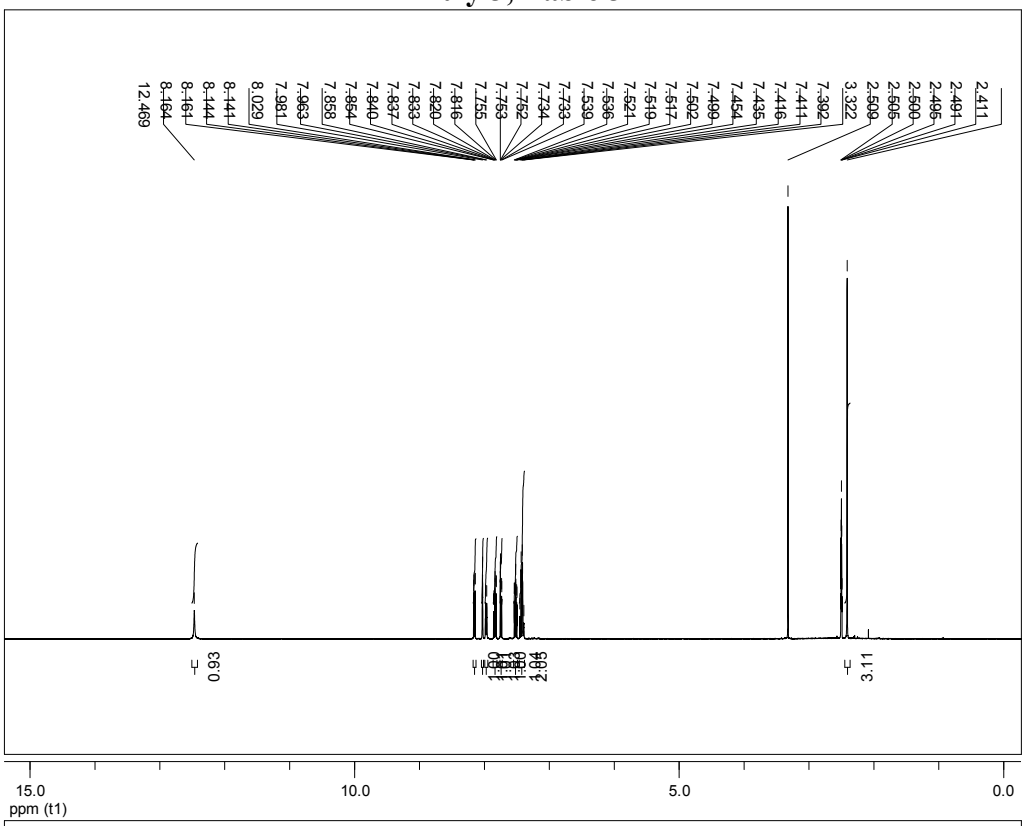

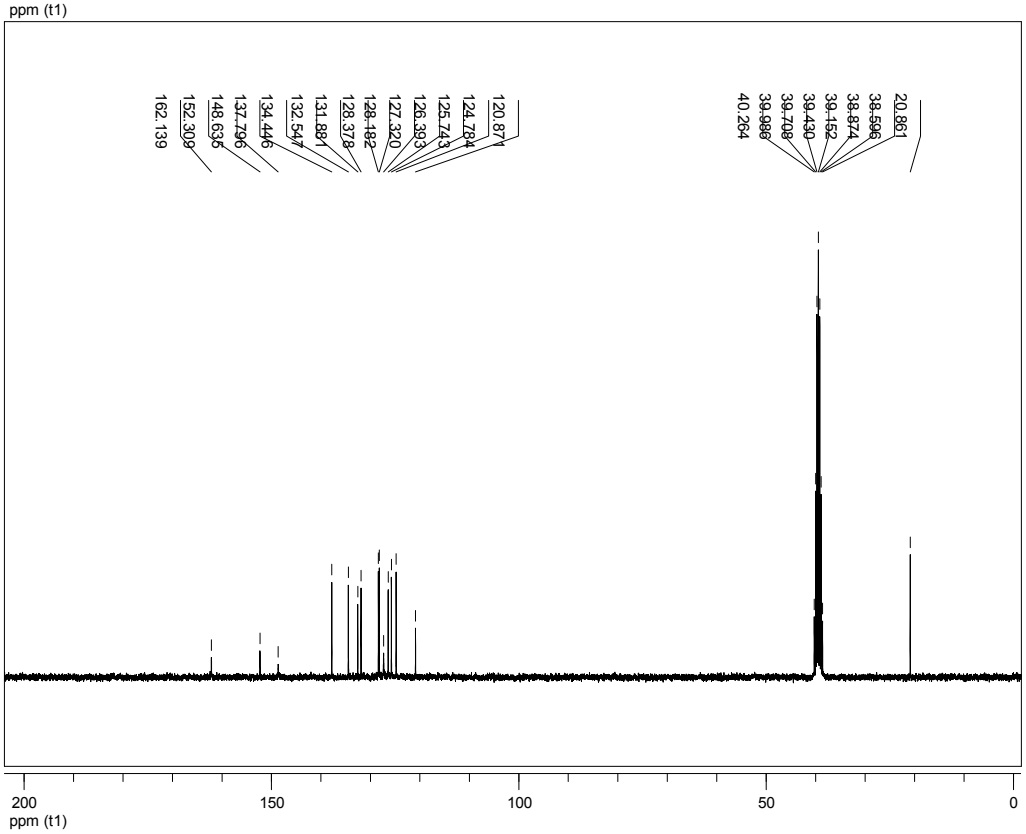

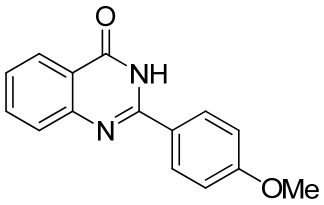

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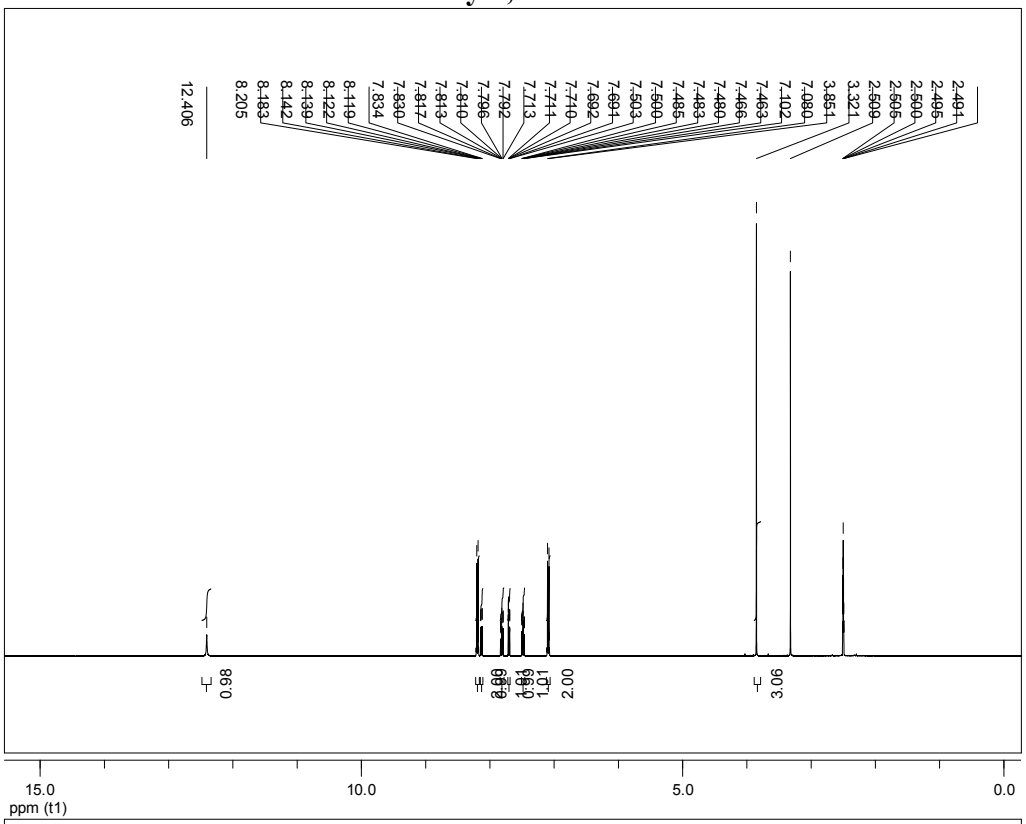

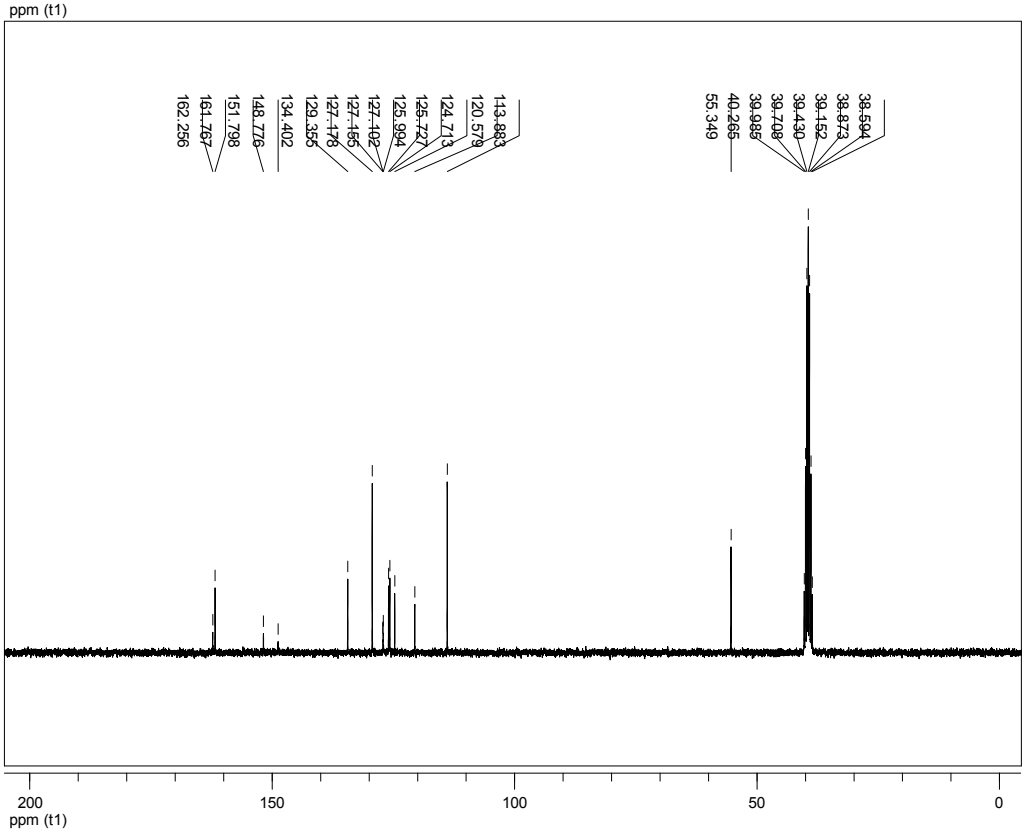

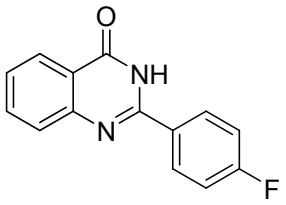

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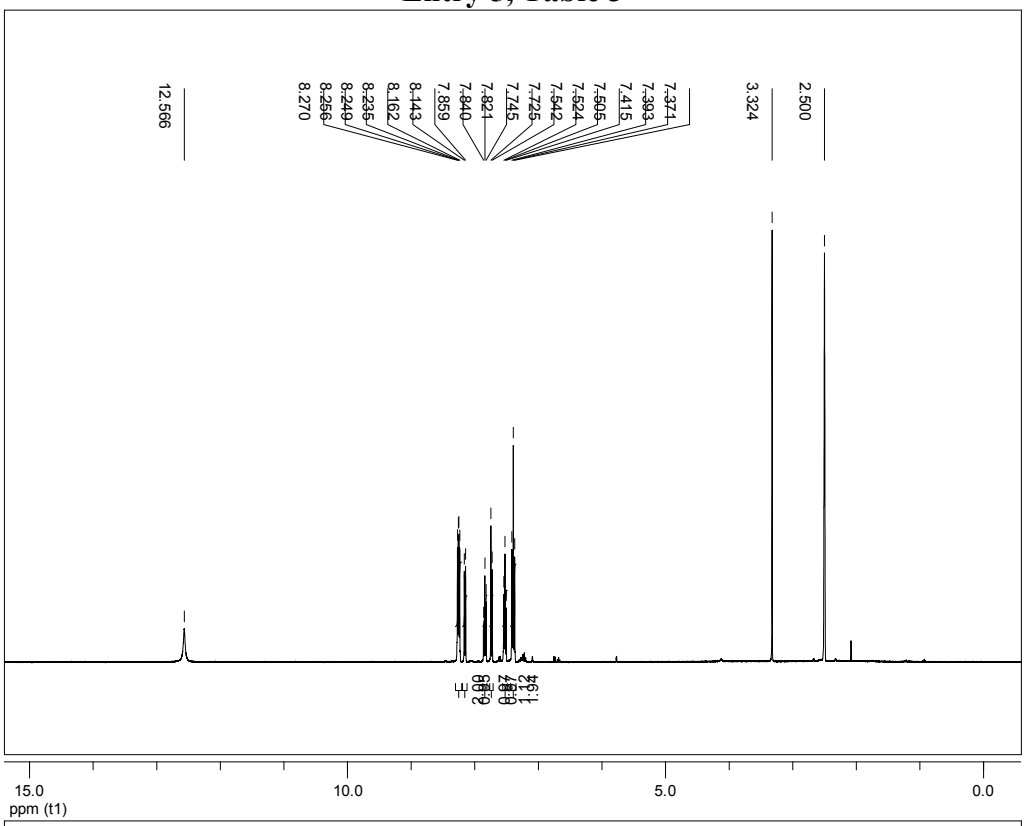

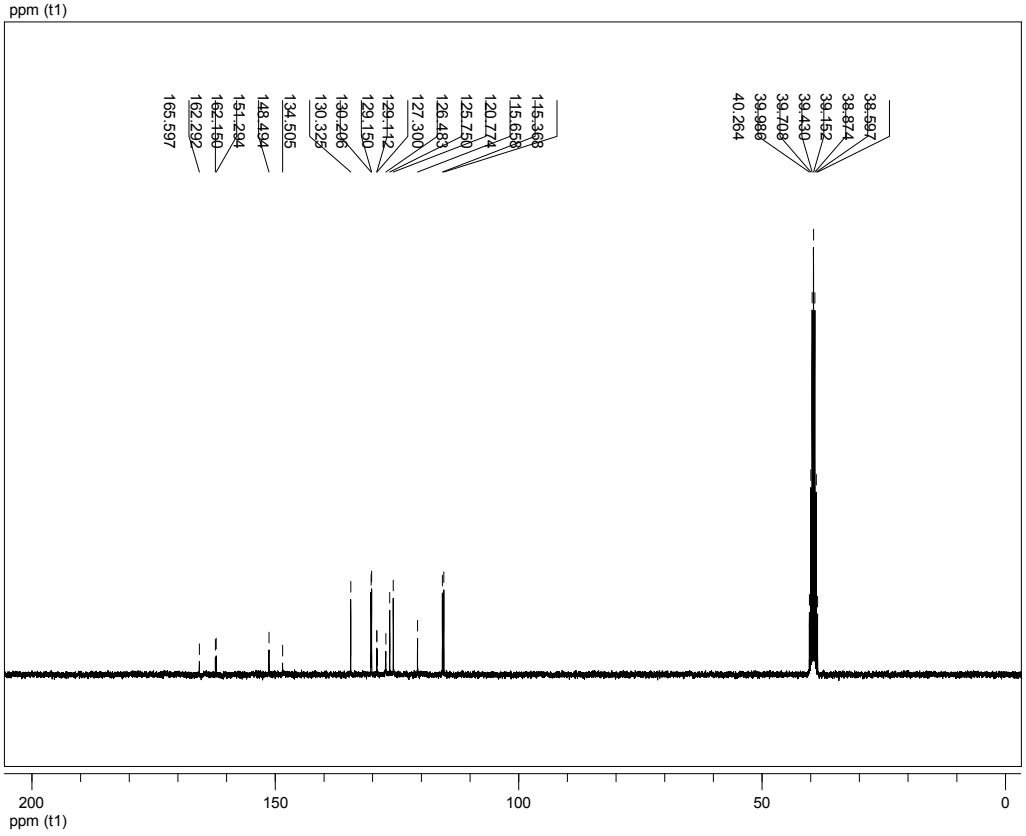

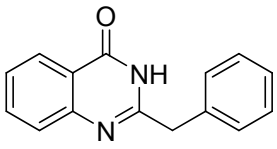

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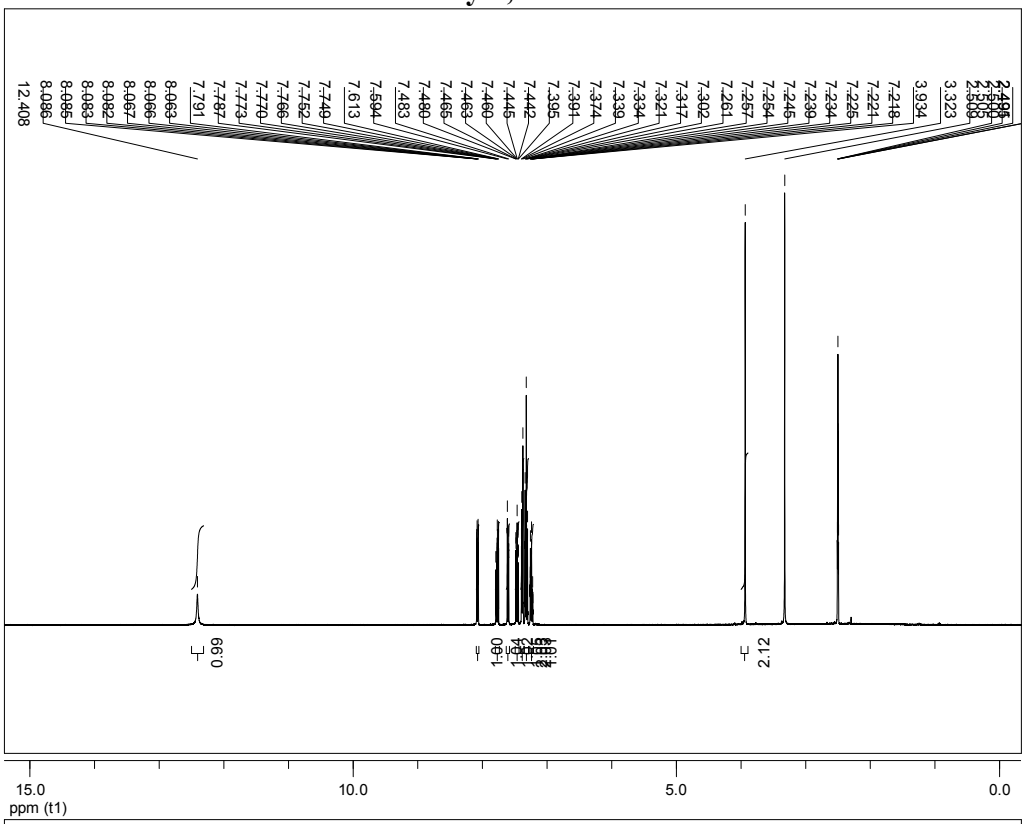

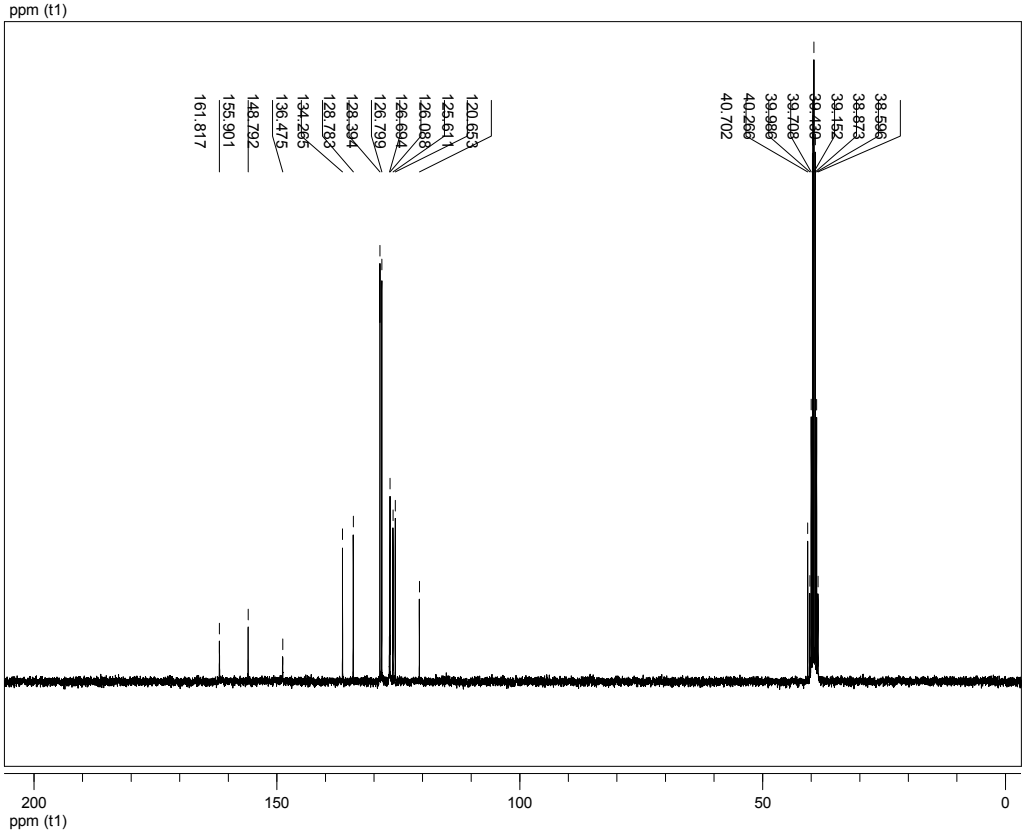

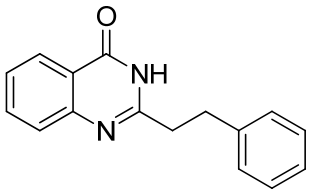

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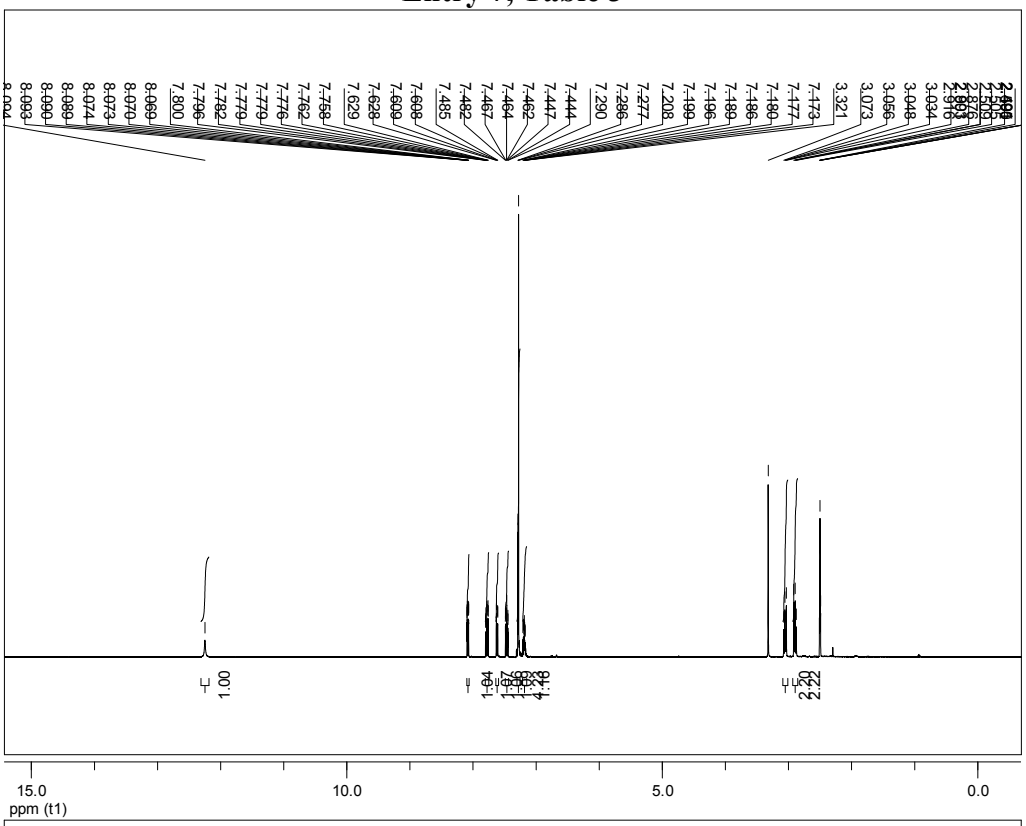

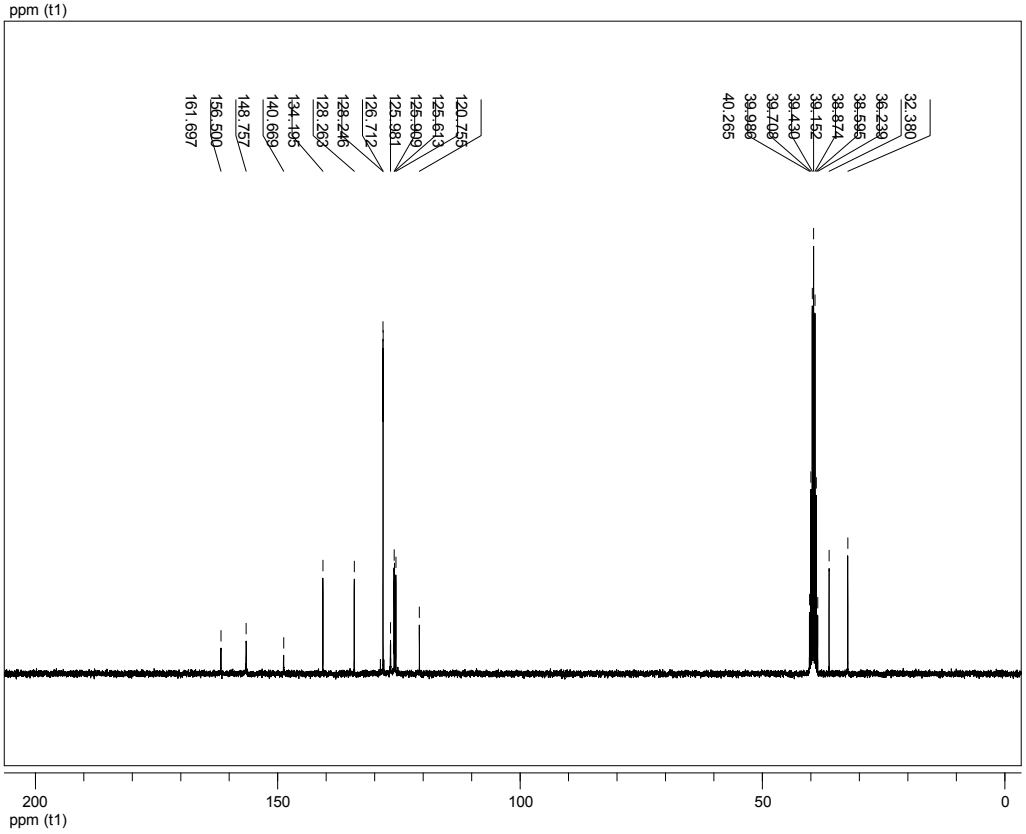

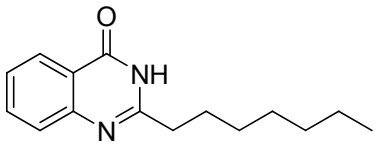

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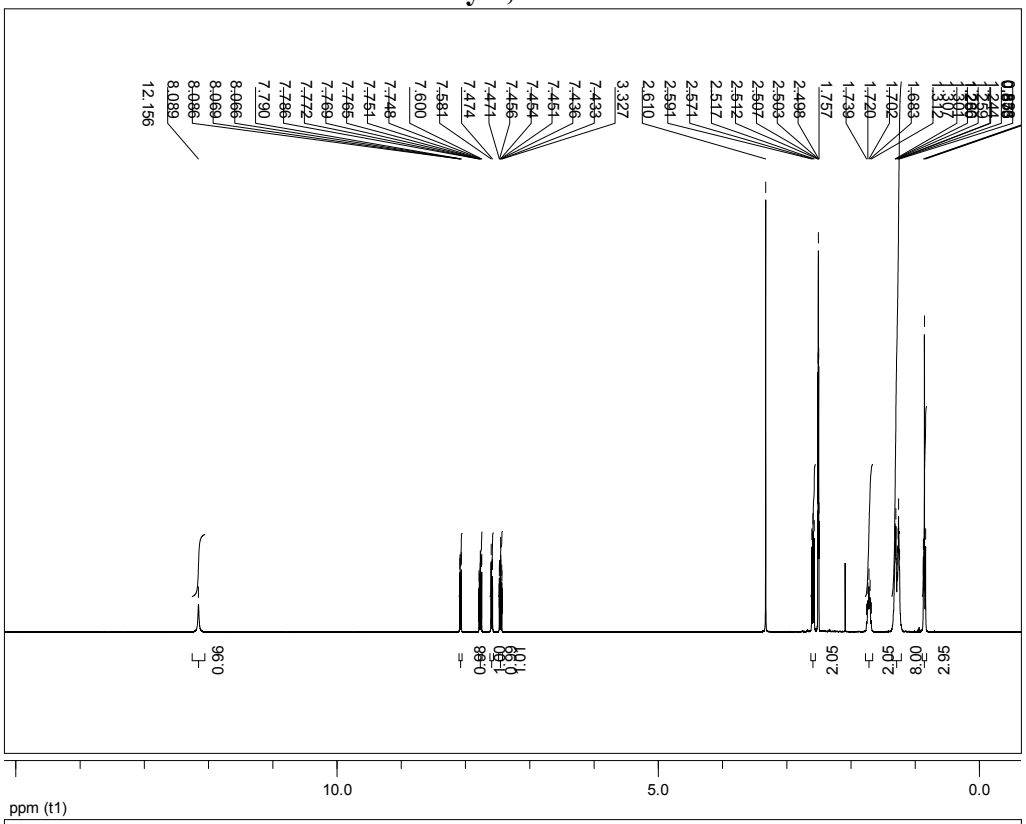

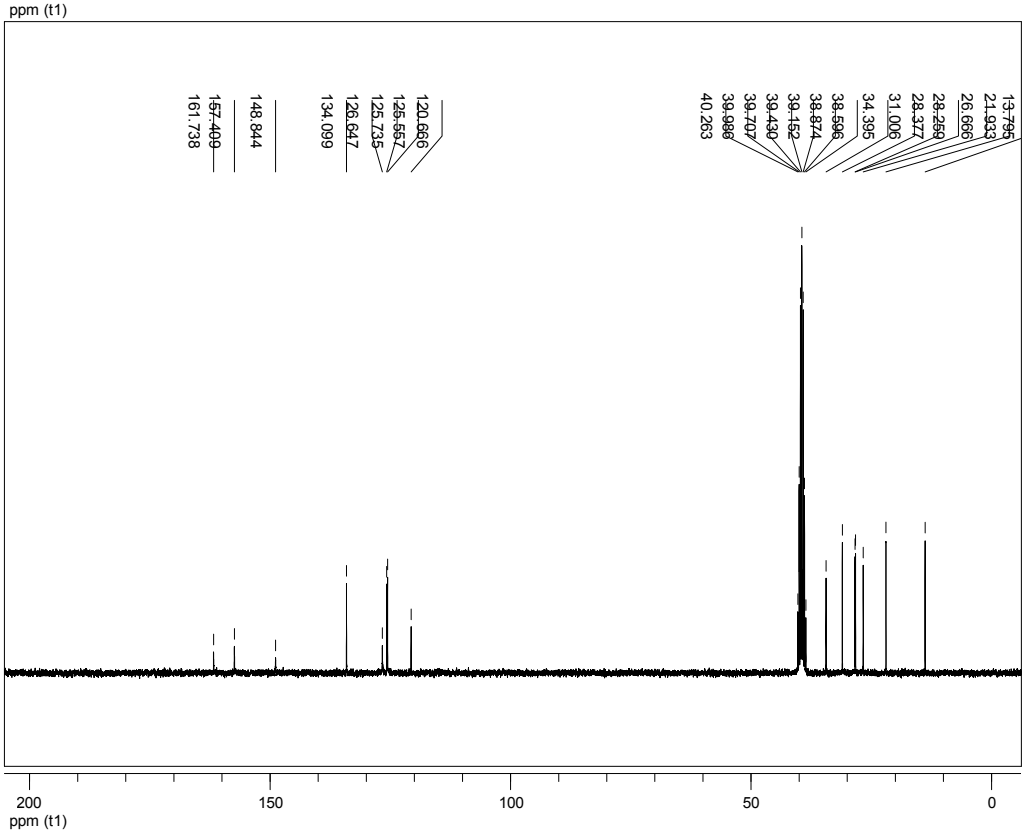

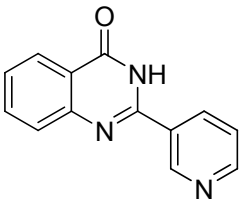

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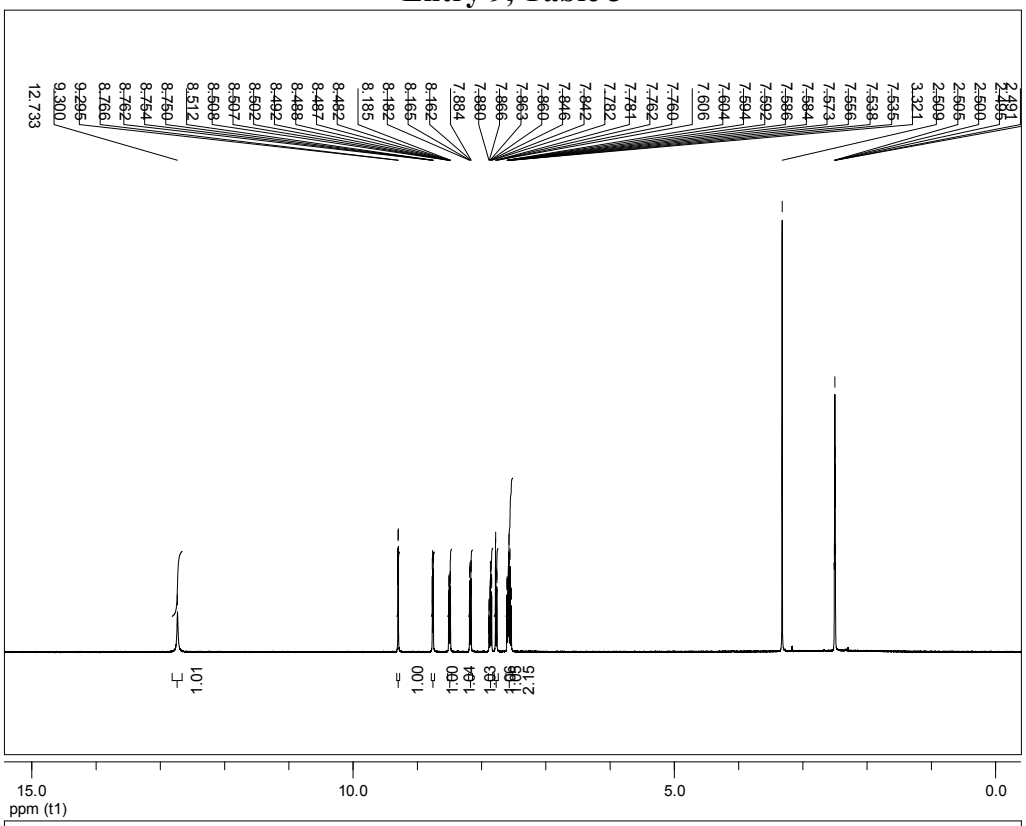

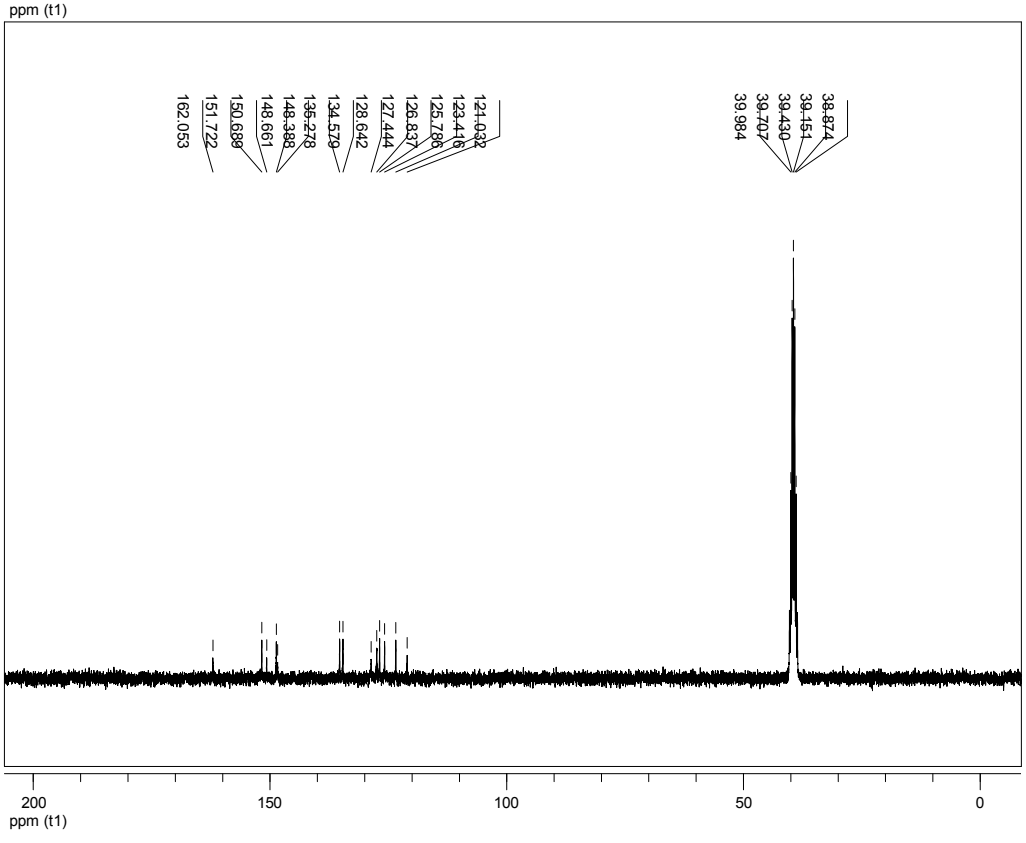

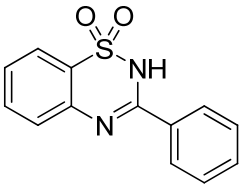

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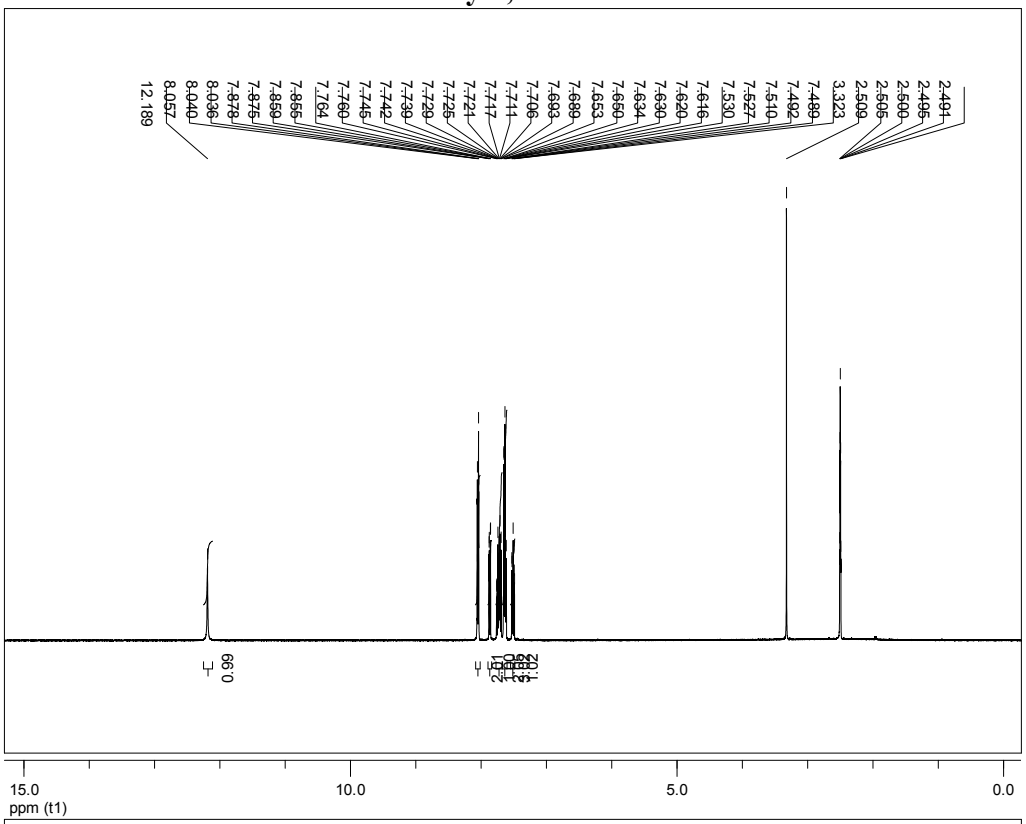

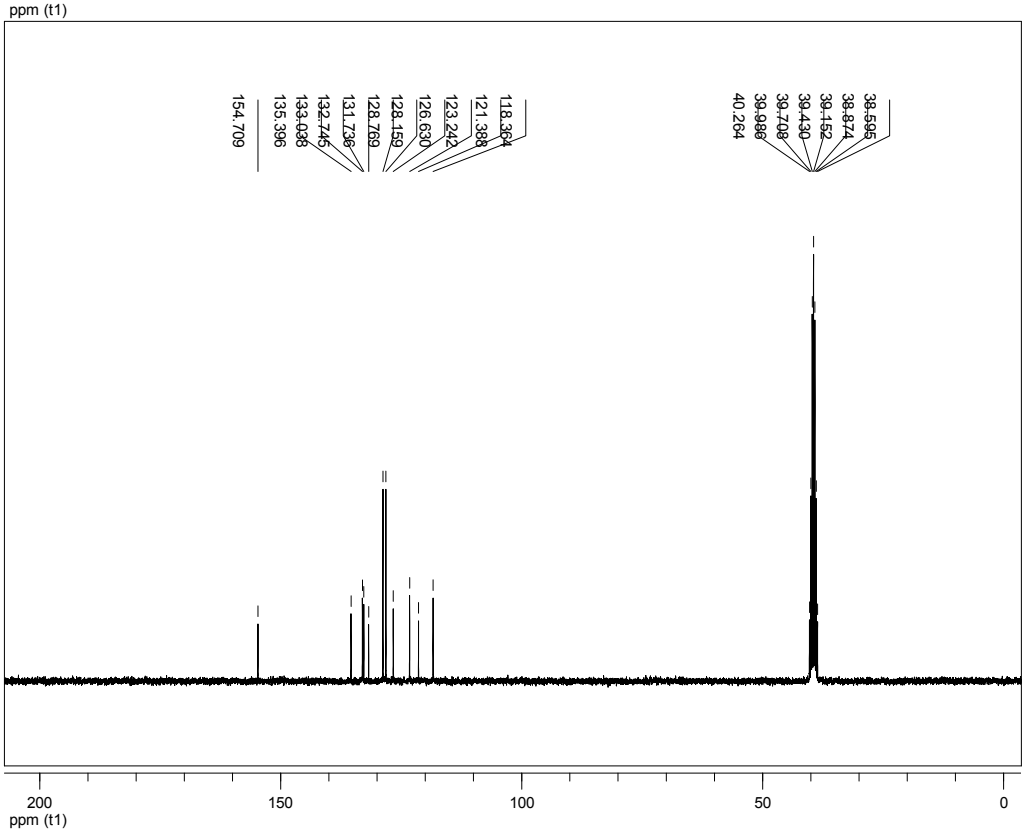

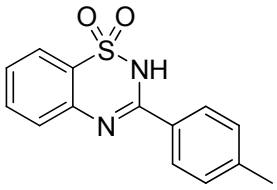

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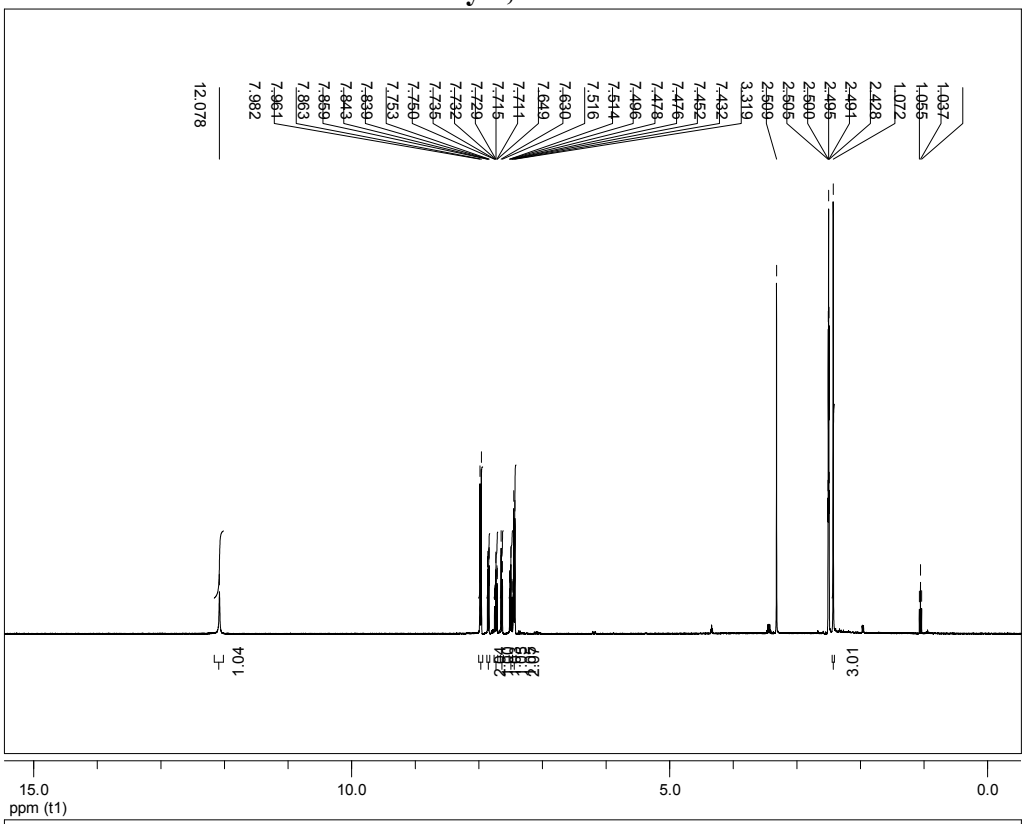

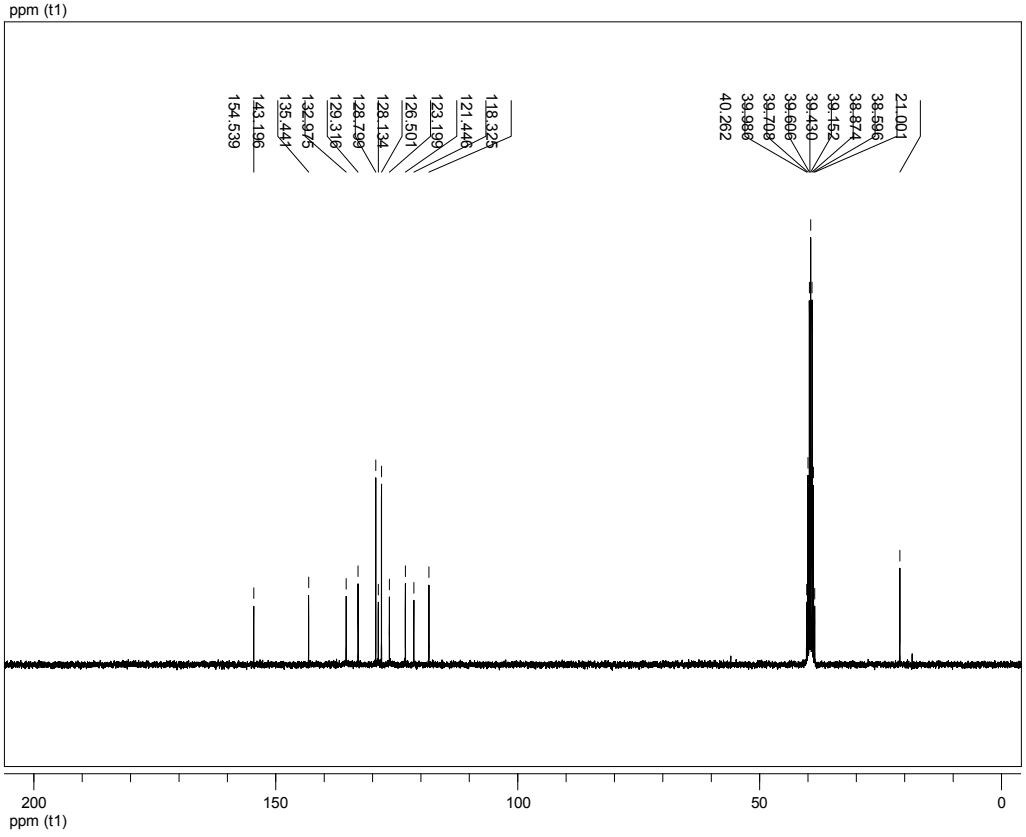

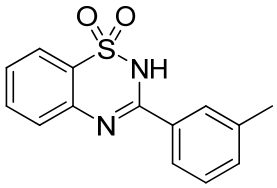

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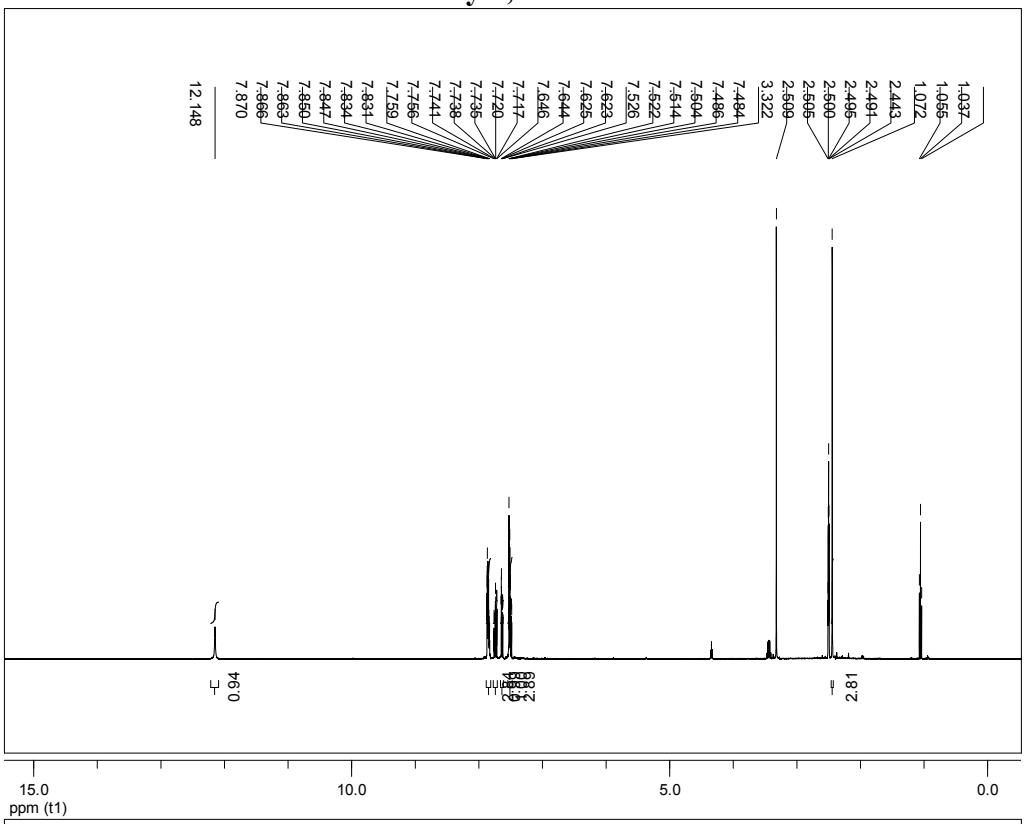

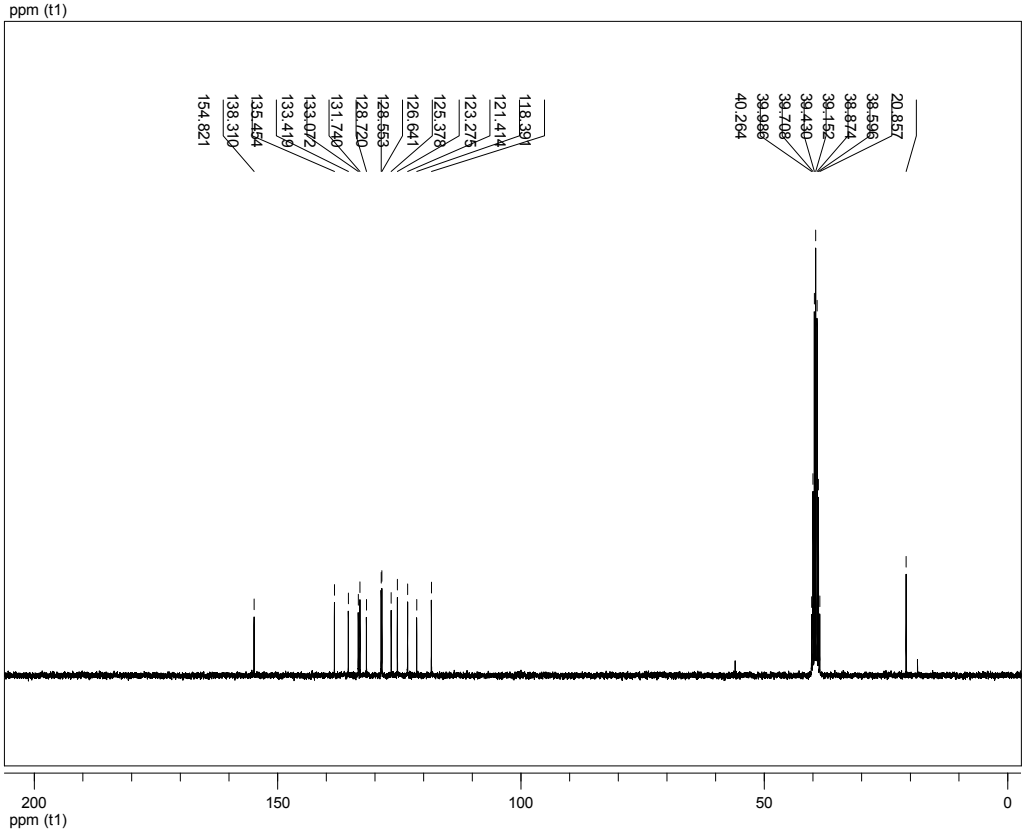

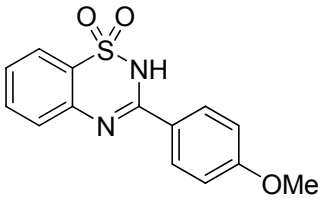

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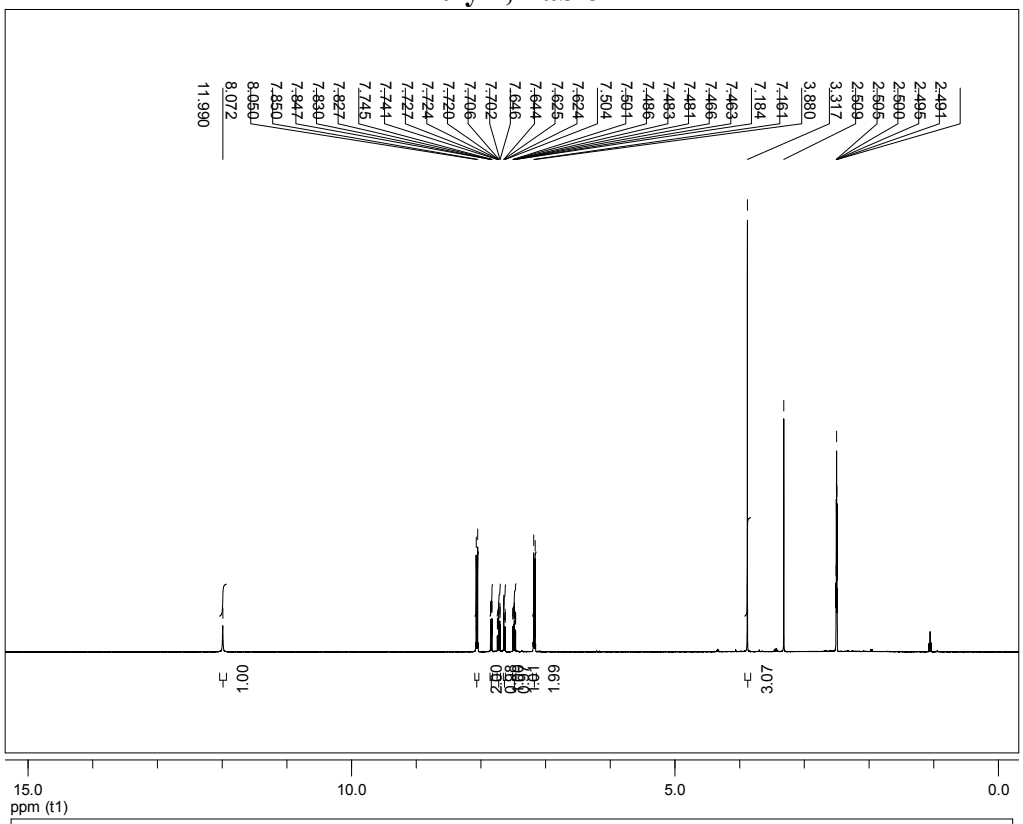

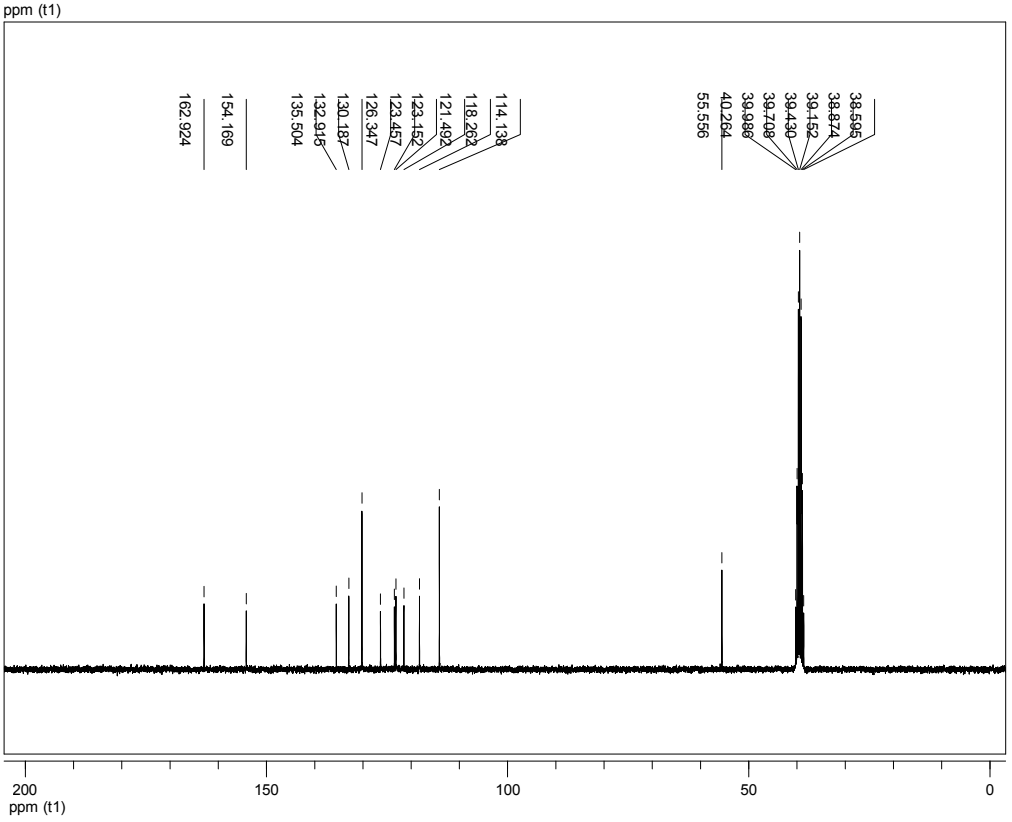

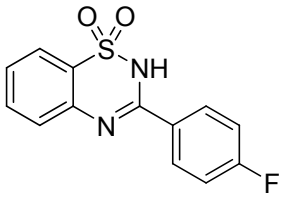

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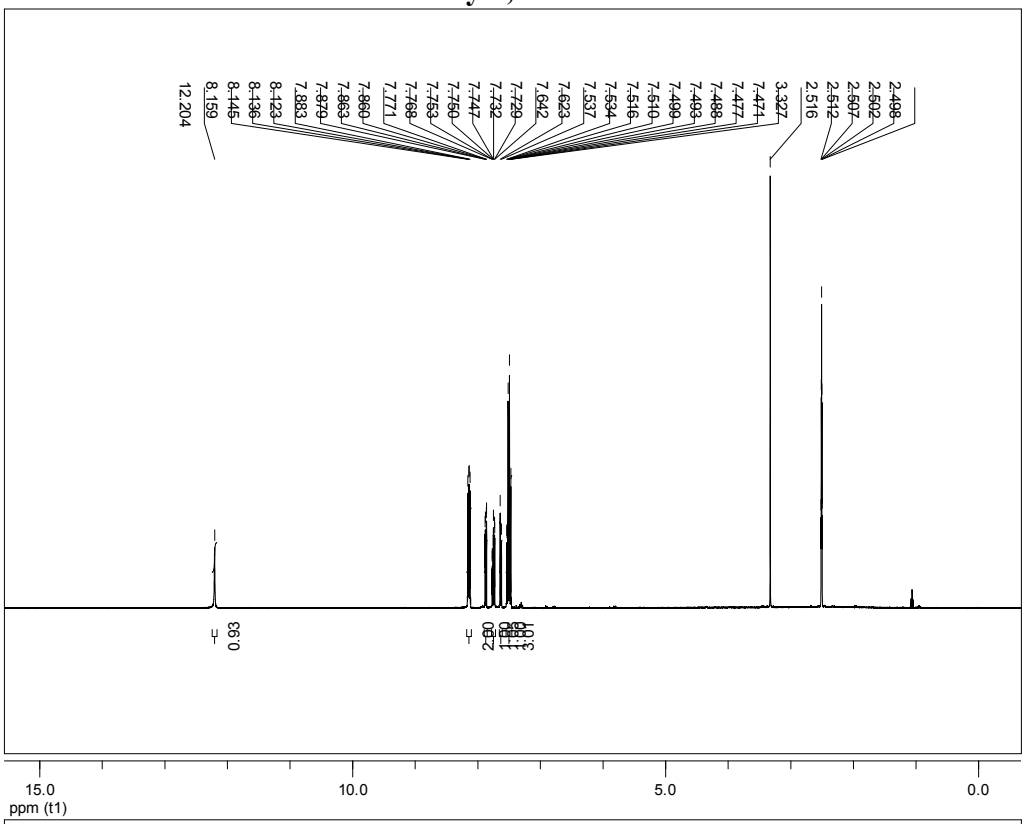

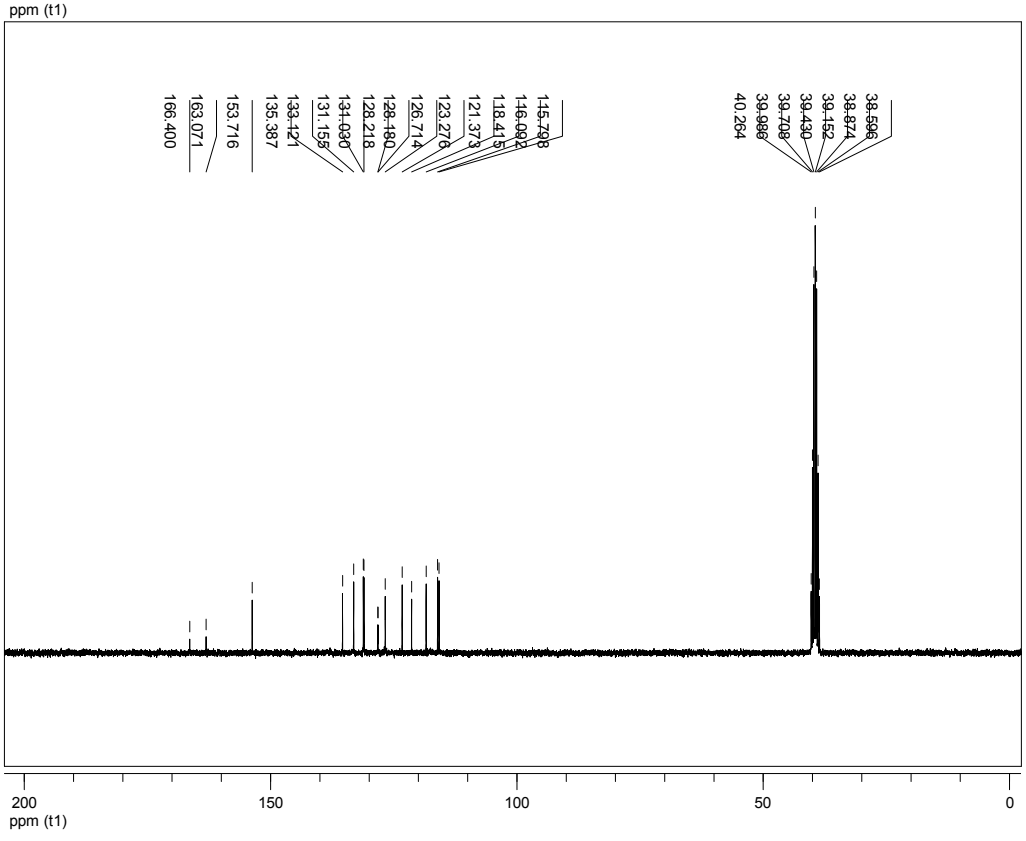

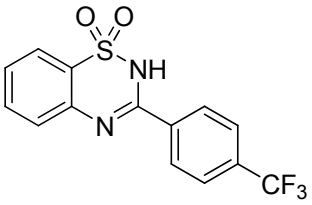

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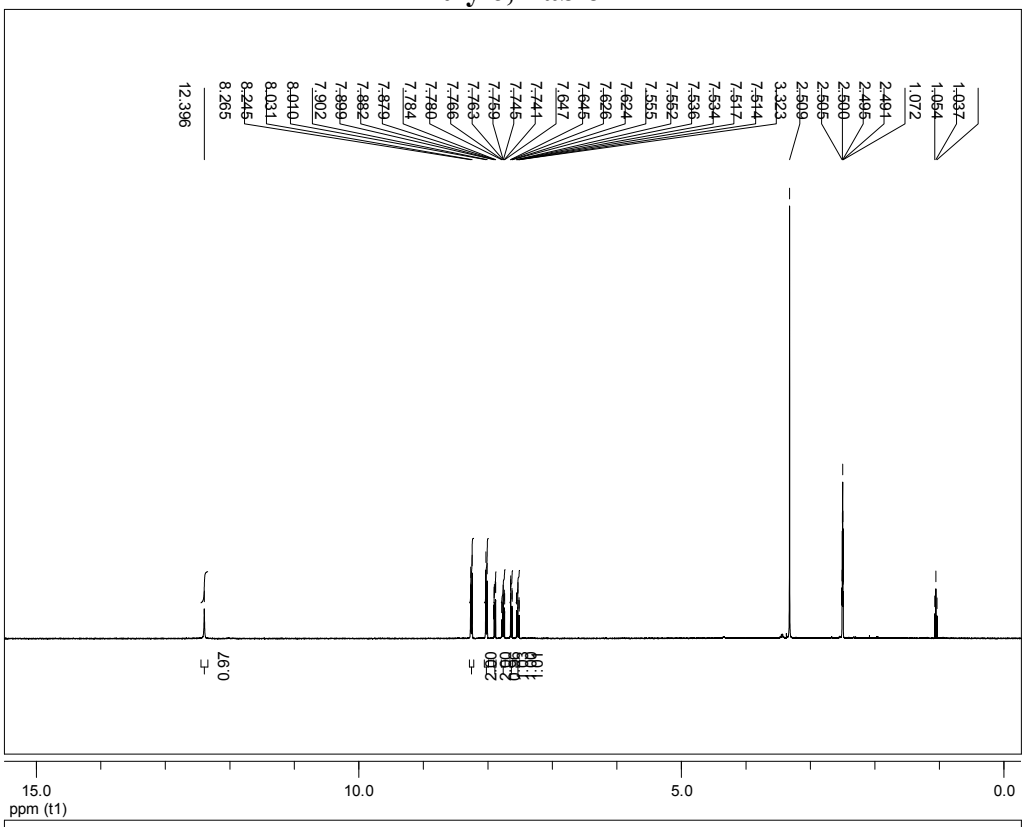
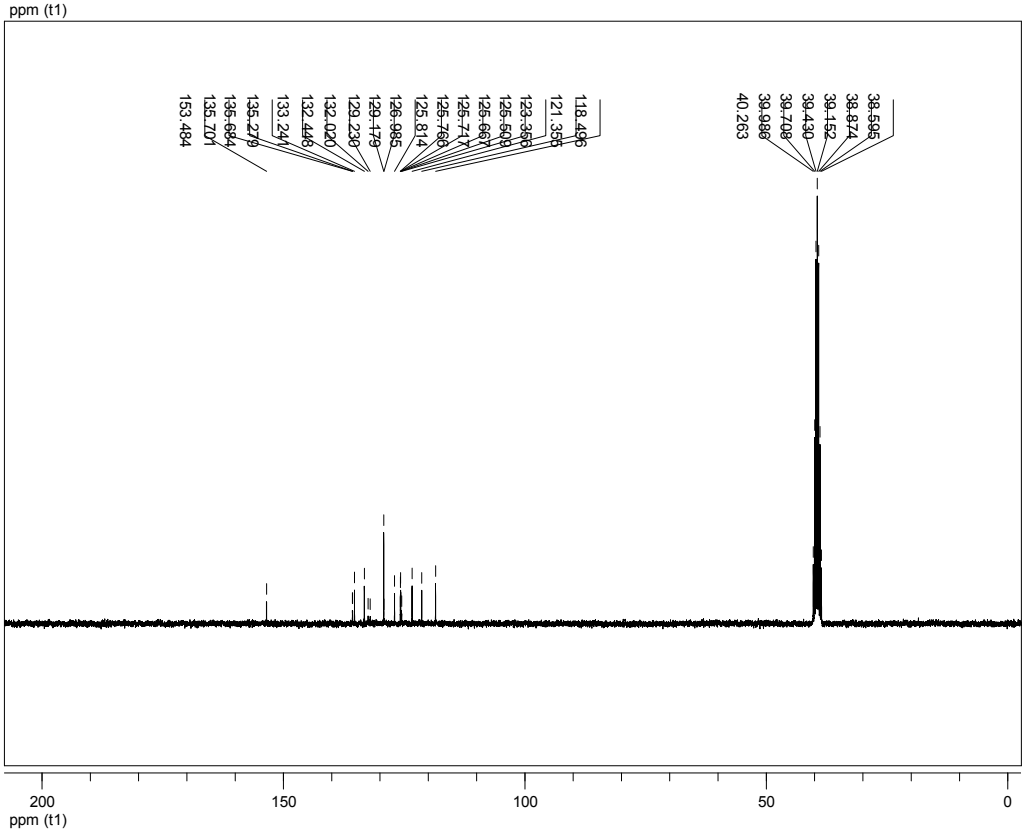
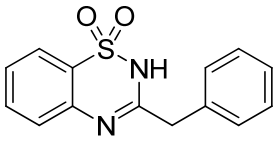
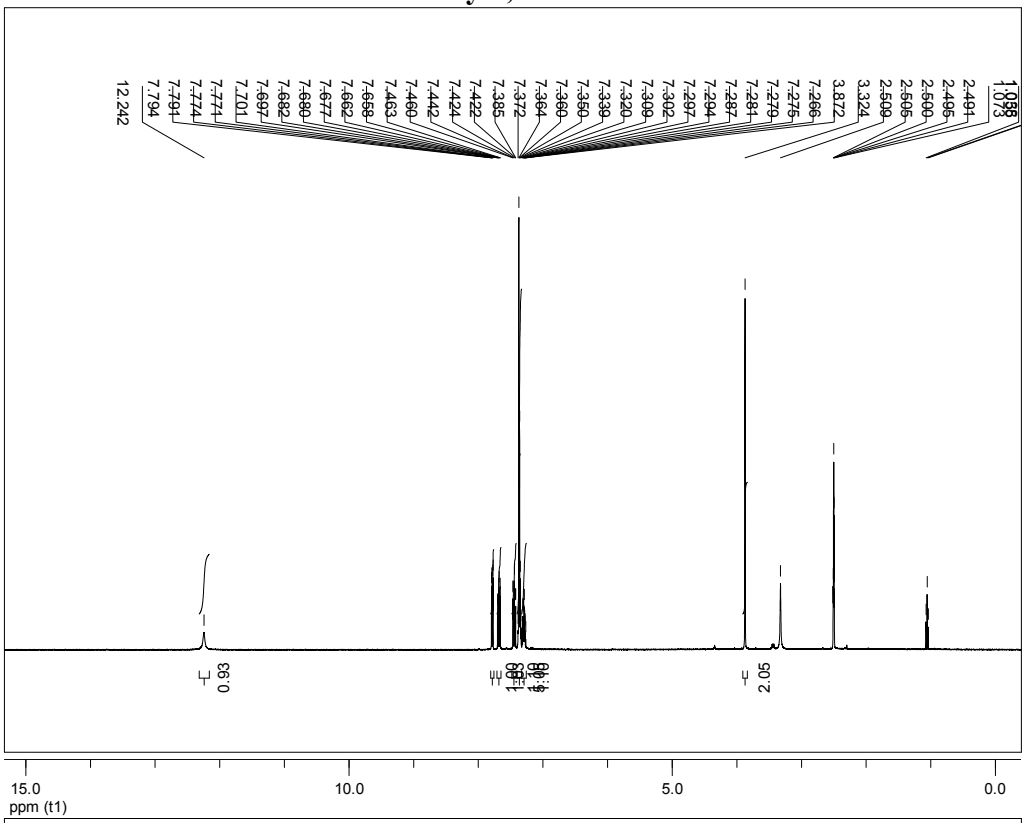
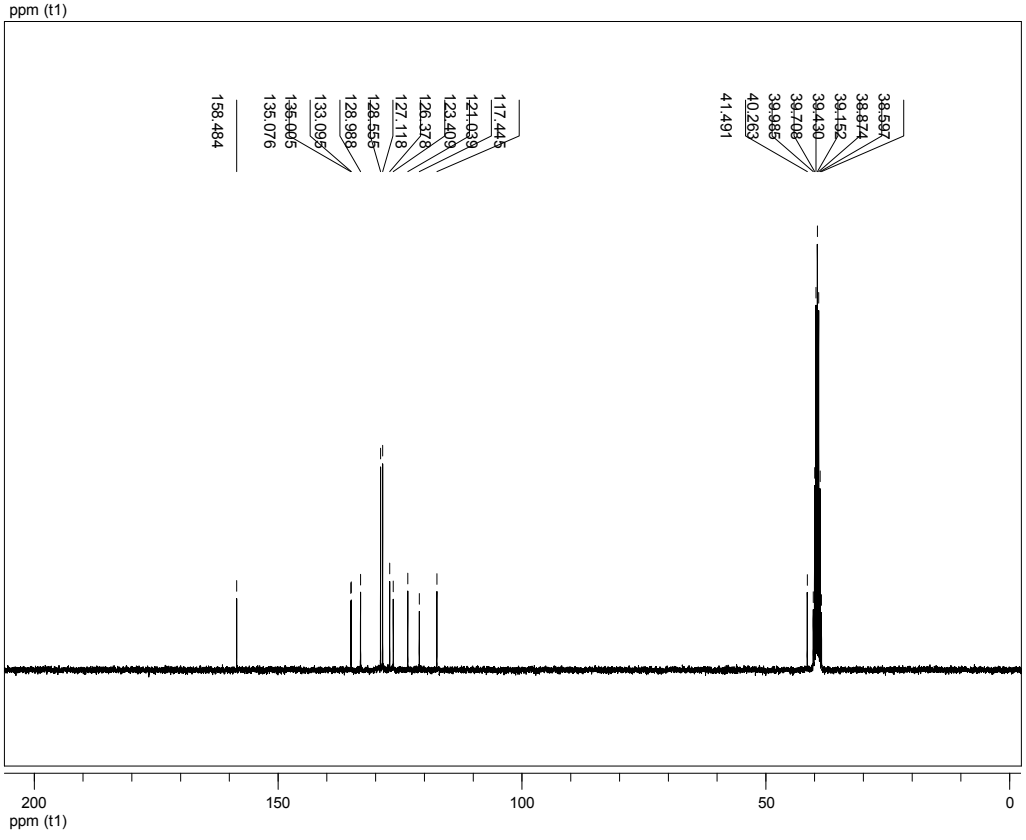


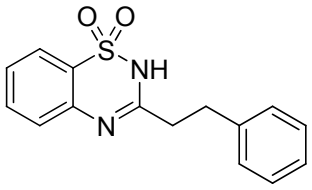




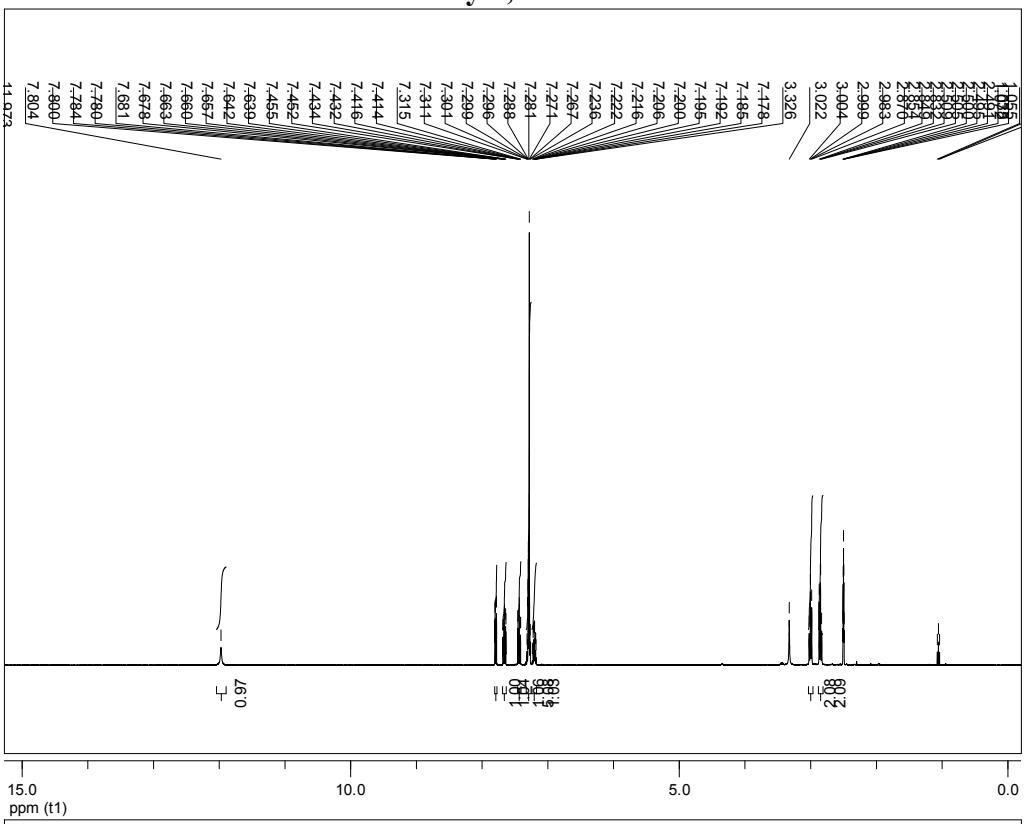
Entry 7, Table 4

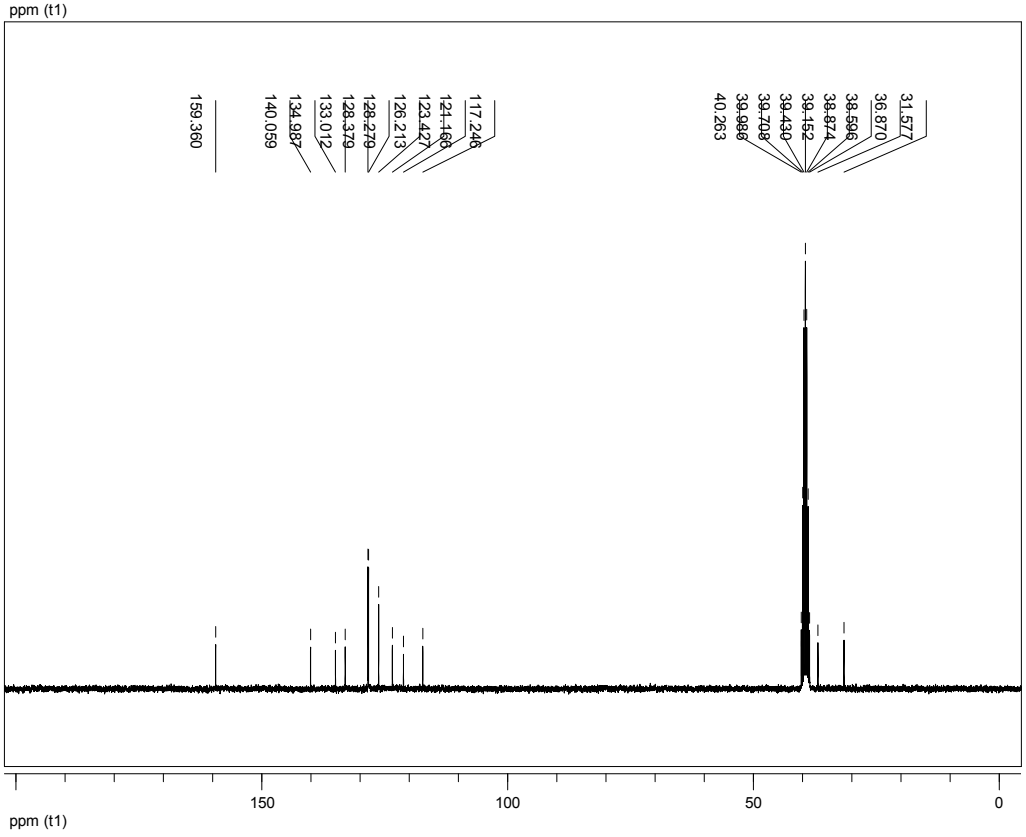


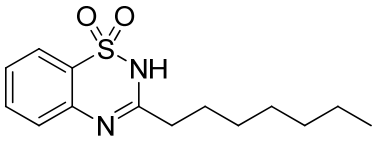




Entry 8, Table 4







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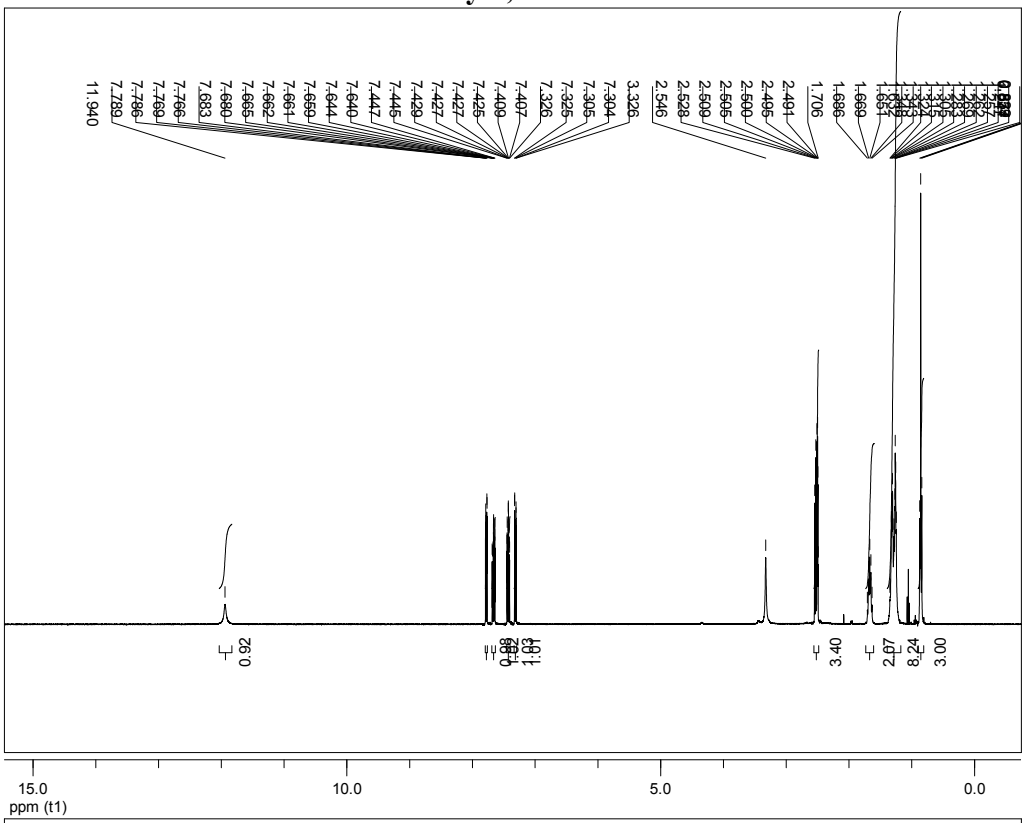
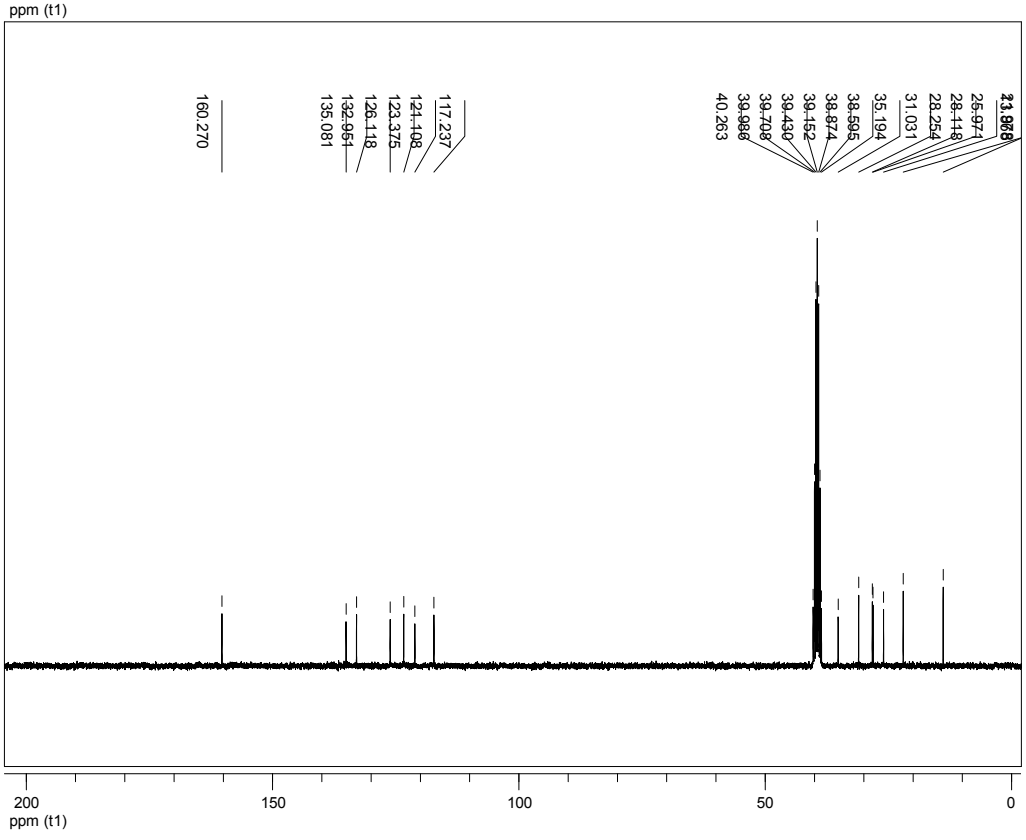
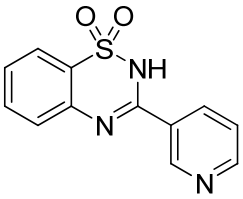
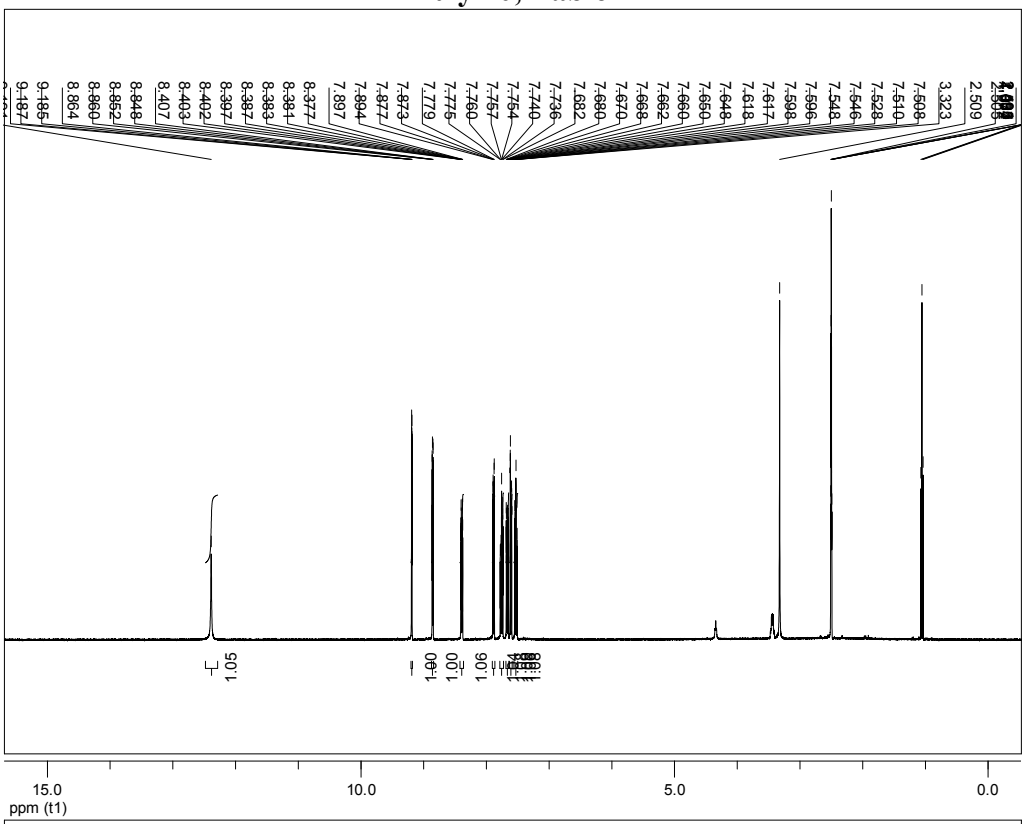
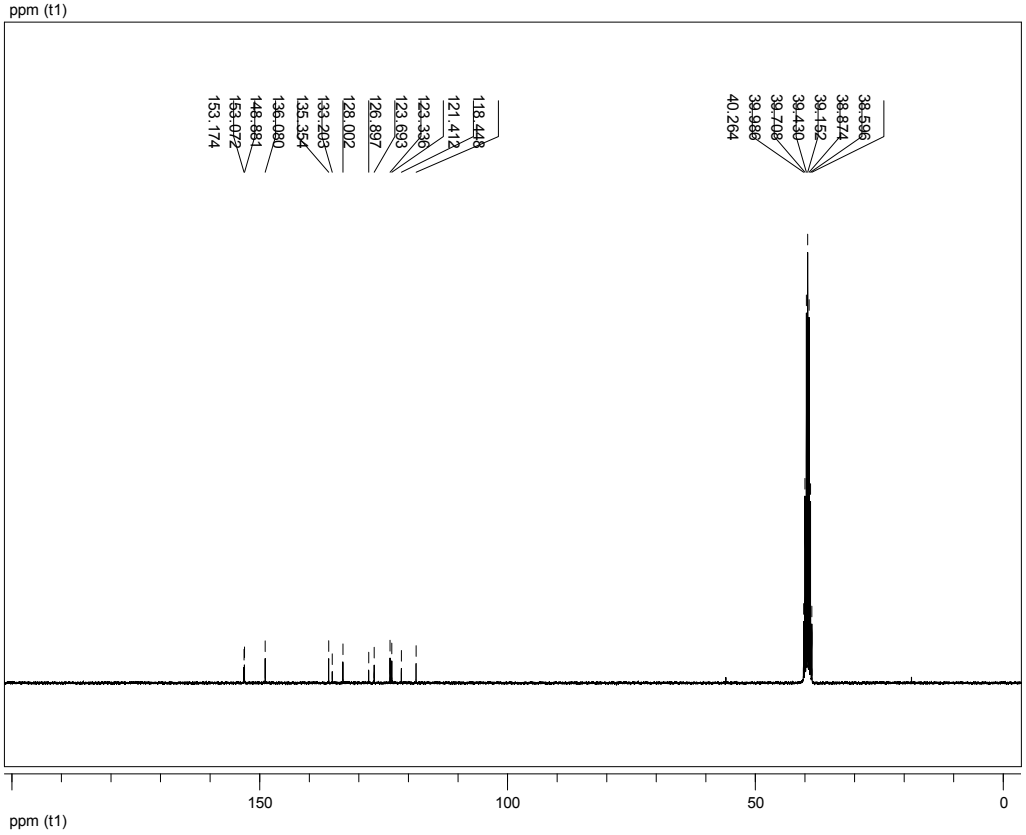


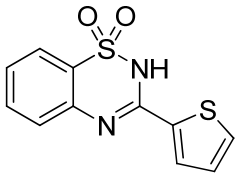




Entry 10, Table 4







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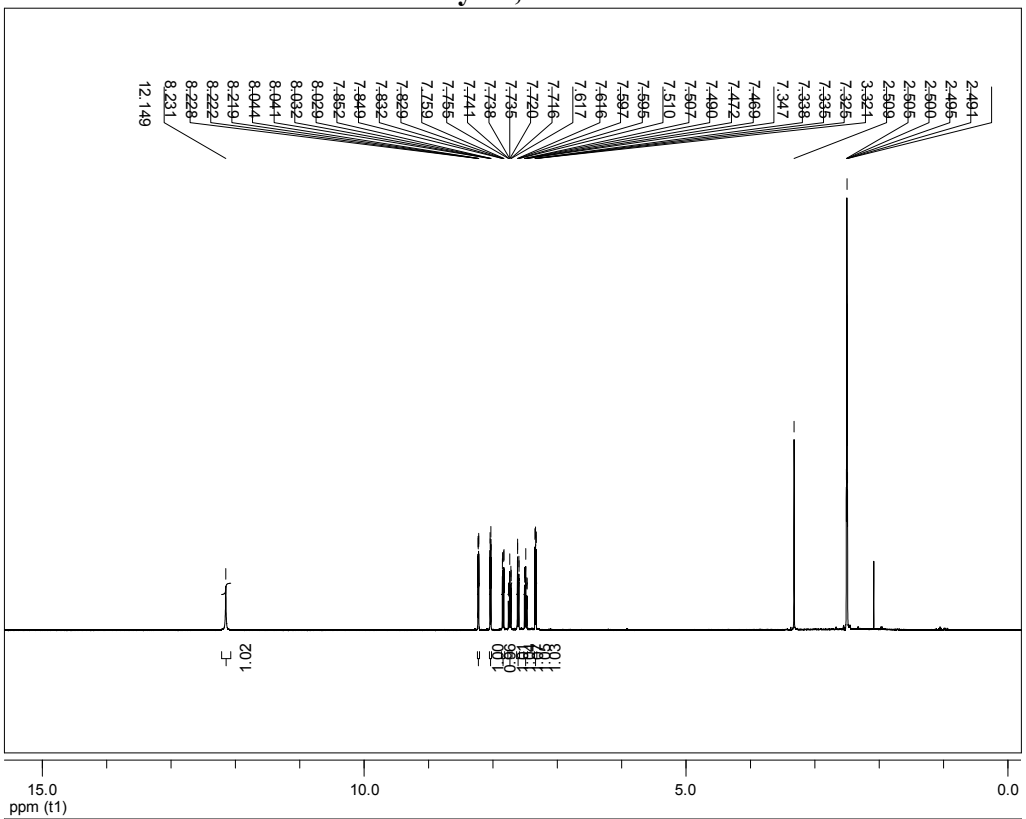

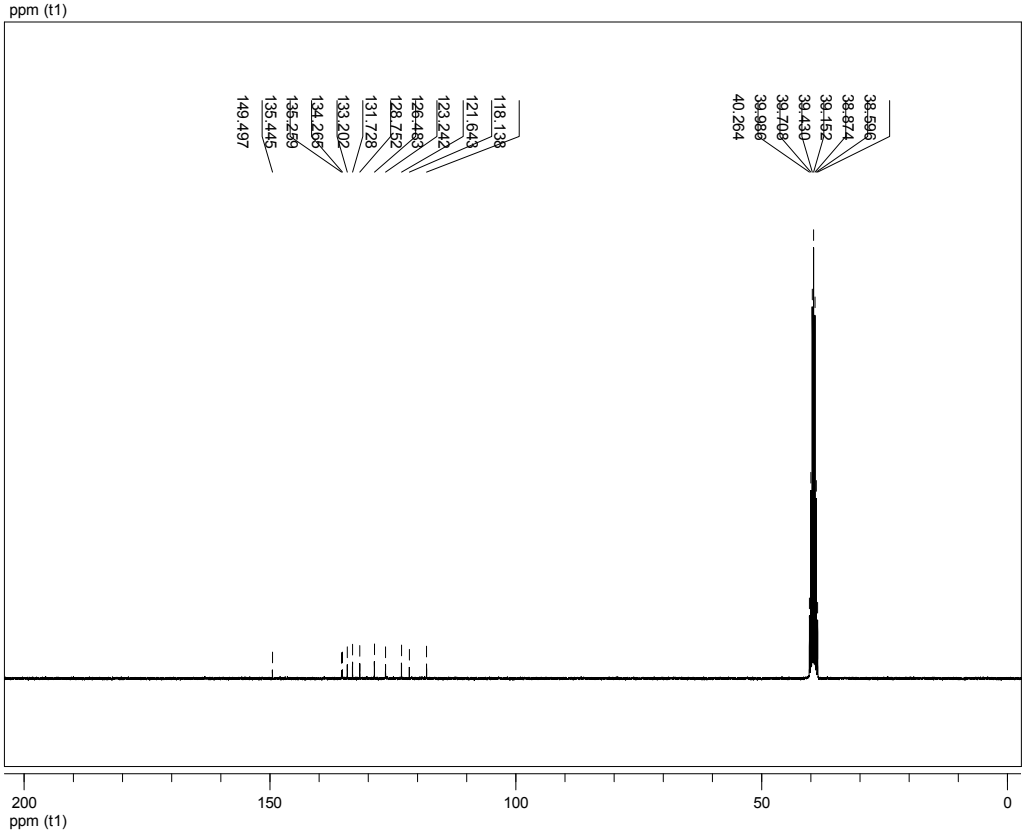

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