Supporting Information

A Mild and Efficient Synthesis of Aminofurazans

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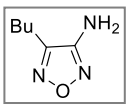
Contents

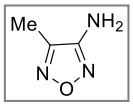
Experimental

IR spectra were recorded on a Perkin-Elmer Model 577 instrument in KBr pellets. ^{1}H, ^{13}C, and ^{15}N spectra were acquired on a Bruker AM-300 instrument (300.13, 75.47 and 21.69 MHz, respectively) in $CDCl_3$ or DMSO-d_6 at 299 K. The chemical shifts of ^{1}H and ^{13}C nuclei were reported relative to TMS, for ^{15}N – relative to $MeNO_2$ high-filed chemical shifts are given with a minus sign. Mass-spectra were recorded on a Varian MAT-311A instrument. Elemental analysis was performed on a PerkinElmer 2400 Series II instrument. The reaction progress and purity of the obtained compounds were controlled by TLC on Kieselgel 60 F_{254} plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm). Melting points were determined on Gallenkamp melting point apparatus and they are uncorrected.

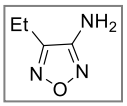
General Procedure for the preparation of 3-amino-4-R-furazans from bromomethyl ketones. 1-Bromohexan-2-one (3 g, 16.75 mmol) was dissolved in DMSO (3.6 mL, 3.9 g. 50.3 mmol). Water (5 mL) was added dropwise over 10 min to the solution at room temperature (water bath). Hydroxylamine hydrochloride (6.99 g, 100.56 mmol) was then added and the reaction mixture diluted with ethylene glycol (15 mL). To the stirred slurry sodium hydroxide (5.36 g, 134.1 mmol) was added in small portions over a 15-min period at 20-30°C. During the addition of NaOH, a white precipitate first precipitated out, then the reaction mixture turns pink, and subsequently is divided into 2 layers: red and white (red oil floats on top). After the addition was complete, the mixture was stirred at 20 °C for an additional 10 min. This mixture was then heated at 70°C for 1 h; almost immediately, the color changes from pink to yellow. After the reaction mixture cooled to room temperature, hydroxylamine hydrochloride (3.49 g, 50.28 mmol) was added in one portion, and then NaOH (5.36 g, 134.1 mmol) was added in small portions at 20-30°C (ice-water bath). The cooling bath was removed and the mixture stirred for 10 additional minutes at room temperature. Then the mixture was heated so that it boiled after 1 hour. When the temperature reached 60 ° C, urea (2.01 g, 33.52 mmol) was added in one portion. When the reaction mixture boils (~116 °C), it was refluxed for 2 h and then cooled to room temperature. The mixture was stirred at ambient temperature overnight before being diluted with water (200 mL), and extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with water (4 × 50 mL), dried with $MgSO_4$, and concentrated in vacuo, and the residue crystallised.



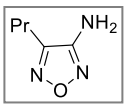
3-Amino-4-butylfurazan (**6a**). Yield 65%, mp 54-55 °C (from hexane). ^{1}H NMR ($CDCl_3$): δ 4.42 (s, 2H), 2.57 (t, 2H, 1.66 (m, 2H), 1.37 (m, 2H), 0.89 (t, 3H); ^{13}C NMR ($CDCl_3$) δ:155.0, 147.7, 28.5, 22.1, 22.0, 13.4; ^{15}N NMR (DMSO-*d*6): δ 24.7, -18.3, -344.0. IR (KBr, ν/cm^{-1}):3424, 3333, 3211, 2959, 2935, 2872, 1629, 1532, 1455, 1382, 1349, 1266, 1206, 996, 872, 790, 704, 671. Anal. calcd. (%) for $C_6H_{11}N_3O$ (141.17): C 51.05, H 7.85, N 29.77; found: C 51.12, H 7.88, N 29.69.



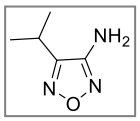
3-Amino-4-methylfurazan (**6b**). Yield 67%, mp 72-73°C (from CCl_4), lit[S1] mp 72.8-73.8°C. All spectroscopic data were in accord with those previously reported.[S1]



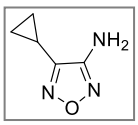
3-Amino-4-ethylfurazan (**6c**). Yield 73%, mp 71.3-71.6 °C (from hexane), lit[S1] mp 71.3-71.6°C. ^{1}H NMR ($CDCl_3$): δ 4.37 (s, 2H), 2.59 (dd, 2H), 1.29 (t, 3H); ^{13}C NMR ($CDCl_3$): δ 154.7, 148.6, 16.1, 10.8. IR (KBr, ν/cm^{-1}): 3408, 3342, 3264, 3227, 2997, 2952, 2890, 2780, 1647, 1601, 1533, 1461, 1449, 1378, 1355, 1216, 1046, 1003, 966, 894, 872. Anal. calcd. (%) for $C_4H_7N_3O$ (113.12): C 42.47, H 6.24, N 37.15; found: C 42.52, H 6.23, N 37.10.



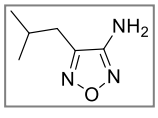
3-Amino-4-propylfurazan (**6d**). Yield (81%), mp 32.2-32-5°C (from hexane), lit[S1] mp 31.4-31.9°C. ^{1}H NMR ($CDCl_3$): δ 4.57 (s, 2H), 2.52 (t, 2H), 1.69 (m, 2H), 0.90 (m, 3H); ^{13}C NMR ($CDCl_3$) δ: 150.0, 142.5, 19.1, 14.8, 8.3. IR (KBr, ν/cm^{-1}): 3453, 3347, 3250, 3219, 2967, 2937, 2877, 1634, 1523, 1463, 1445, 1383, 1260, 1209,1091, 986, 876, 812. Anal. calcd. (%) for $C_5H_9N_3O$ (127.15): C 47.23, H 7.14, N 33.05; found: C 47.26, H 7.17, N 32.99.



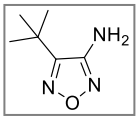
3-Amino-4-isopropylfurazan (**6e**). Yield 48%, mp 42-43 °C (from hexane). ^{1}H NMR (DMSO-d_6): δ 6.02 (s, 2H), 2.99 (m, 1H), 1.22 (d, 6H); ^{13}C NMR (DMSO-d_6) δ: 155.3, 152.6, 23.1, 20.3; ^{15}N NMR (DMSO-d_6): δ 21.8, -20.7, -338.6. IR (KBr, ν/cm^{-1}): 3415, 3315, 3261, 3228, 2975, 2936, 2977, 2776, 1647, 1600, 1528, 1468, 1439, 1387, 1354, 1295, 1226, 1149, 1094, 986, 895, 873, 753, 620, 575, 528. Anal. calcd. (%) for $C_5H_9N_3O$ (127.15): C 47.23, H 7.14, N 33.05; found: C 47.28, H 7.15, N 33.00.



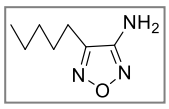
3-Amino-4-cyclopropylfurazan (**6f**). Yield 70%, mp 55-56 °C (from hexane). ^{1}H NMR (DMSO-d_6): δ 6.14 (s, 2H), 1.89 (m, 1H), 1.02 (m, 2H), 0.85 (m, 2H); ^{13}C NMR (DMSO-d_6) δ: 156.2, 150.3, 8.1, 8.0, 3.2; ^{15}N NMR (DMSO-d6): δ 17.9, -20.8, -338.7. IR (KBr, ν/cm^{-1}): 3424, 3334, 3257, 3220, 1639, 1599, 1539, 1440, 1389, 1227, 1178, 1064, 1044, 1029, 985, 891, 865, 832. Anal. calcd. (%) for $C_5H_7N_3O$ (125.13): C 47.99, H 5.64, N 35.58; found: C 48.07, H 5.68, N 35.53.



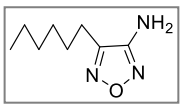
3-Amino-4-*iso*butylfurazan (**6g**). Yield 61%, mp 84-85 °C (from hexane). ^{1}H NMR (DMSO-d_6): δ 6.01 (s, 2H), 2.48 (s, 2H), 1.96 (m, 1H), 0.90 (d, 6H); ^{13}C NMR (DMSO-d_6) δ: 156.7, 147.5, 30.7, 26.8, 22.4, 22.3; ^{15}N NMR (DMSO-d_6): δ 23.5, -21.5, -338.7. IR (KBr, ν/cm^{-1}): 3412, 3329, 3248, 3212, 2958, 2929, 2872, 1631, 1527, 1468, 1443, 1387, 1369, 1298, 1267, 1218, 1170, 1102, 989, 881. Anal. calcd. (%) for $C_6H_{11}N_3O$ (141.17): C 51.05, H 7.85, N 29.77; found: C 51.11, H 7.87, N 29.73.



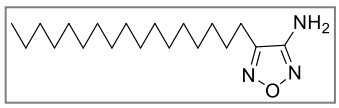
3-Amino-4-*tert*-butylfurazan (**6h**). Yield 32%, mp 103-104 °C (from petroleum ether), lit[S1] mp 101-104 °C. All spectroscopic data were in accord with those previously reported.[S1]



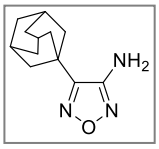
3-Amino-4-pentylfurazan (**6i**). Yield 47%, mp 58.5-59.0 °C (from hexane). ^{1}H NMR (DMSO-d_6): δ 6.04 (s, 2H), 2.58 (m, 2H), 1.61 (t, 2H), 1.30 (t, 4H), 0.86 (t, 3H); ^{13}C NMR (DMSO-d_6) δ: 155.9, 147.9, 30.6, 26.0, 21.7, 21.6, 13.7. IR (KBr, ν/cm^{-1}): 3419, 3332, 3248, 3212, 2958, 2933, 2862, 1629, 1531, 1459, 1380, 1319, 1256, 1202, 1103, 997, 873, 792. Anal. calcd. (%) for $C_7H_{13}N_3O$ (155.20): C 54.17, H 8.44, N 27.08; found: C 54.21, H 8.46, N 27.00.



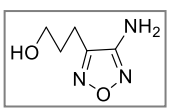
3-Amino-4-hexylfurazan (**6j**). Yield 52%, mp 49.5-50 °C (from hexane). ^{1}H NMR (DMSO-d_6): δ 6.00 (s, 2H), 2.58 (m, 2H), 1.59 (m, 2H), 1.26 (m, 6H), 0.83 (s, 3H); ^{13}C NMR (DMSO-d_6) δ: 155.8, 147.8, 30.8, 28.1, 26.3, 21.9, 21.7, 13.7; ^{15}N NMR (DMSO-d_6): δ 22.6, -21.3, -338.8. IR (KBr, ν/cm^{-1}): 3419, 3332, 3212, 2957, 2931, 2859, 1628, 1531, 1457, 1380, 1298, 1243, 1199, 1105, 981, 916, 873, 791. Anal. calcd. (%) for $C_8H_{15}N_3O$ (169.23): C 56.78, H 8.93, N 24.83; found: C 56.81, H 8.97, N 24.77.



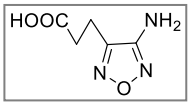
3-Amino-4-heptadecylfurazan (**6k**). Yield 37%, mp 95-97 °C (from hexane). ^{1}H NMR (DMSO-d_6): δ 6.05 (s, 2H), 1.23 (s, 30H), 0.85 (t, 5H); ^{13}C NMR (DMSO-d_6) δ: 154.7, 147.5,31.9, 31.5, 30.2, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 29.2, 27.1, 26.8, 22.7, 22.7, 14.1; IR (KBr, ν/cm^{-1}): 3445, 3340, 3239, 2919, 2850, 1728, 1631, 1534, 1463, 1378, 1292, 1183, 1081, 985, 888, 866, 793. MS (EI), *m/z*: 323 [M]$^+$, 306 [M-NH$_2$]$^+$, 293 [M – NO]$^+$, 278, 265, 252, 238, 222, 210, 204, 194, 180, 168, 154, 138, 124, 112, 99, 83, 69, 55, 43. Anal. calcd. (%) for $C_{19}H_{37}N_3O$ (323.53): C 70.54, H 11.53, N 12.99; found: C 70.61, H 11.58, N 12.93.



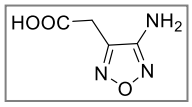
3-Amino-4-(adamantan-1-yl)furazan (**6l**). Yield 21%, mp 158-159 °C (from CCl_4), lit[S1] mp 158-159°C. All spectroscopic data were in accord with those previously reported.[S1]



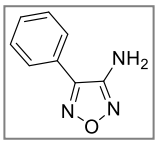
3-(3-Aminofurazan-4-yl)propan-1-ol (**6m**) Yield 8%, mp 128-130 °C (from CCl_4). ^{1}H NMR (DMSO-*d*6): δ 6.04 (s, 2H), 4.58 (d, 1H), 3.46 (m, 2H), 2.64 (m, 2H), 1.78 (m, 2H); ^{13}C NMR (DMSO-d_6) δ:155.9, 148.0, 59.7, 29.5, 18.5; Anal. calcd. (%) for $C_5H_9N_3O_2$ (143.15): C 41.95, H 6.34, N 29.36; found: C 42.01, H 6.35, N 29.31.



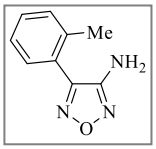
3-(3-Aminofurazan-4-yl)propanoic acid (**6n**) Yield 11%, mp 135-136 °C (from H_2O). ^{1}H NMR (DMSO-d_6): δ 11.0 (br.s), 6.11 (br.s, 2H), 2.44 (m, 2H), 2.56 (m, 2H); ^{13}C NMR (DMSO-d_6) δ: 171.9, 156.4, 146.9, 29.7, 19.2. IR (KBr, ν/cm^{-1}): 3452, 3363, 3177, 3131, 3057, 3001, 2928, 2853, 2781, 1695, 1632, 1544, 1468, 1448, 1353, 1324, 1248, 1196, 1019, 997, 924, 843. Anal. calcd. (%) for $C_5H_7N_3O_3$ (157.13): C 38.22, H 4.49, N 26.74; found: C 38.30, H 4.52, N 26.71.



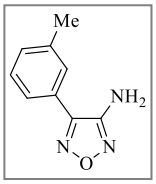
3-(3-Aminofurazan-4-yl)acetic acid (**6o**). Yield 63%, mp 91-92 °C (from hexane/ethyl acetate), lit[S8] mp 89-90°C. All spectroscopic data were in accord with those previously reported.[S8]



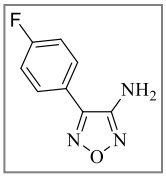
3-Amino-4-phenylfurazan (**8a**). Yield 67%, mp 100-101 °C (from hexane), lit[S2] mp 100-101 °C. ^{1}H NMR (DMSO-d_6): δ 7.80 (t, 2H), 7.54 (t, 3H), 6.22 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 155.4, 147.0, 130.3, 129.2, 127.8, 125.7; ^{15}N NMR (DMSO-d_6): δ 25.8, -14.6, -337.7; Anal. calcd. (%) for $C_8H_7N_3O$ (161.16): C 59.62, H 4.38, N 26.07; found: C 59.66, H 4.35, N 26.01.



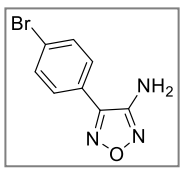
3-Amino-4-(*o*-tolyl)furazan (**8b**). Yield 70%, mp 88-90 °C (from hexane), lit[S2] mp 88-90 °C. ^{1}H NMR ($CDCl_3$): δ = 7.48-7.31 (m, 4H), 4.47 (s, 2H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 154.8, 146.9, 137.9, 131.1, 130.3, 129.0, 126.2, 124.0, 19.6. Anal. calcd. (%) for $C_9H_9N_3O$ (175.19): C 61.70, H 5.18, N 23.99; found: C 61.77, H 5.21, N 23.92.



3-Amino-4-(*m*-tolyl)furazan (**8c**). Yield 74%, mp 78-79 °C (from hexane), lit[S2] mp 78-79 °C. ^{1}H NMR ($CDCl_3$): δ 7.52-7.27 (m, 4H), 4.47 (s, 2H), 2.42 (s, 3H).; ^{13}C NMR ($CDCl_3$) δ:154.3, 147.0, 139.3, 131.3, 129.2, 128.2, 125.3, 124.5, 21.3. Anal. calcd. (%) for $C_9H_9N_3O$ (175.19): C 61.70, H 5.18, N 23.99; found: C 61.73, H 5.20, N 23.95.

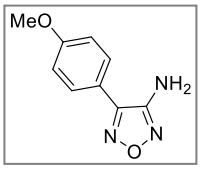


3-Amino-4-(4-fluorophenyl)furazan (**8d**). Yield 78%, mp 134-135 °C (from petroleum ether/$CHCl_3$ 1/1), lit[S2] mp 134-135 °C. All spectroscopic data were in accord with those previously reported.[S2]

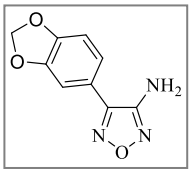


3-Amino-4-(4-bromophenyl)furazan (**8e**). Yield 73%, mp 146-147°C (from hexane), lit[S2] mp 146-147 °C. ^{1}H NMR (DMSO-d_6): δ 7.72 (m, 4H), 6.23 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 160.2, 151.2, 137.1, 134.8, 129.8, 128.9; ^{15}N NMR (DMSO-d_6): δ 31.53, 9.02, -332.43. IR (KBr, ν/cm^{-1}): 3480, 3459, 3327, 3245, 3205, 1631, 1596, 1561, 1528, 1473, 1427, 1389,

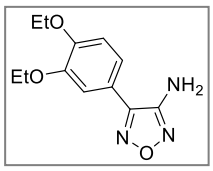
1307, 1076, 1049, 1011, 983, 882, 832. Anal. calcd. (%) for $C_8H_6BrN_3O$ (240.06): C 40.03, H 2.52, N 17.50; found: C 40.10, H 2.54, N 17.46.



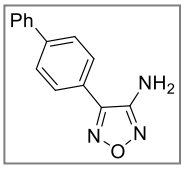
3-Amino-4-(4-methoxyphenyl)furazan (**8f**). Yield 81%, mp 104-105°C (from hexane), Lit[S2] mp 104-105°C. All spectroscopic data were in accord with those previously reported.[S2]



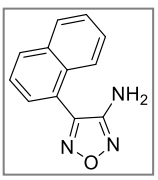
3-Amino-4--(benzo[d][1,3]dioxol-5-yl)furazan (**8g**). Yield 75%, mp 175-177 °C (from CH_3CN). ^{1}H NMR (DMSO-d_6): δ 7.27 (d, 2H), 7.08 (d, 1H), 6.14 (s, 2H), 6.12 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 160.1, 154.0, 152.9, 151.6, 127.2, 124.0, 113.9, 112.8, 106.7. IR (KBr, ν/cm^{-1}): 3454, 3373, 3253, 3212, 3009, 2918, 2790, 1644, 1629, 1587, 1536, 1501, 1484, 1413, 1353, 1303, 1256, 1156, 1106, 1036, 985, 933, 883, 865, 814. Anal. calcd. (%) for $C_9H_7N_3O_3$ (205.17): C 52.69, H 3.44, N 20.48; found: C 52.72, H 3.40, N 20.41.



3-Amino-4-(3,4-diethoxyphenyl)furazan (**8h**). Yield 84%, mp 186-187 °C (from CH_3CN). ^{1}H NMR (DMSO-d_6): δ 7.33 (d, 1H), 7.28 (d, 1H), 7.10 (d, 1H), 6.15 (s, 2H), 4.15 (d, 2H), 4.08 (d, 2H), 1.36 (t, 6H); ^{13}C NMR (DMSO-d_6) δ: 155.2, 149.9, 148.4, 146.7, 120.6, 117.7, 113.2, 14.6, 112.2, 63.8,14.7. Anal. calcd. (%) for $C_{12}H_{15}N_3O_3$ (249.27): C 57.82, H 6.07, N 16.86; found: C 57.87, H 6.10, N 16.79.

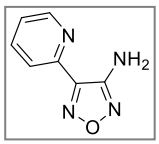


3-Amino-4-([1,1'-biphenyl]-4-yl)furazan (**8i**). Yield 48%, mp 168-170 °C (from $CHCl_3$). ^{1}H NMR (DMSO-d_6): δ 7.85 (d, 2H), 7.75 (d, 1H); 7.53-7.42 (m, 3H), 6.25 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 155.4, 146.6, 141.9, 139.1, 129.0 (2C), 128.3 (2C), 128.05, 127.3 (2C), 126.7 (2C), 124.6; ^{15}N NMR (DMSO-d_6): δ 30.9, -9.3, -332.4. IR (KBr, ν/cm^{-1}): 3459, 3327, 3244, 3206, 3036, 1633, 1554, 1542, 1501, 1479, 1449, 1424, 1389, 1327, 1305, 1062, 987, 917, 889, 845. Anal. calcd. (%) for $C_{14}H_{11}N_3O$ (237.26): C 70.87, H 4.67, N 17.71; found: C 70.80, H 4.69, N 17.65.

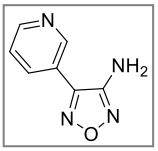


3-Amino-4-(naphthalen-1-yl)furazan (**8i**). Yield 70%, mp 118-119 °C (from CH_3CN). ^{1}H NMR (DMSO-d_6): δ 8.15 (d, 2H), 8.08 (t, 2H), 7.83-7.61 (m, 5H), 6.10 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 156.2, 146.4, 133.3, 130.8, 130.5, 128.5, 127.3, 126.6, 125.5, 124.6, 122.3; ^{15}N NMR (DMSO-d_6): δ 33.6, -13.0, -332.0. IR (KBr, ν/cm^{-1}): 3418, 3312, 3238, 3058, 1634, 1588, 1528, 1506, 1459, 1418, 1342, 1301, 1253, 1215, 1189, 1128, 1060, 1007, 957, 879, 860, 822. MS (EI), *m/z*: 211 [M]$^+$, 196 [M-NH$_2$]$^+$, 181 [M – NO]$^+$, 169, 153, 140, 127, 114, 101, 87, 77, 63, 58, 51,

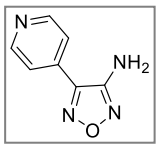
43, 39, 30. Anal. calcd. (%) for $C_{12}H_9N_3O$ (211.22): C 68.24, H 4.29, N 19.89; found: C 68.29, H 4.33, N 19.85.



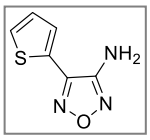
3-Amino-4-(pyridin-2-yl)furazan (**8k**). Yield 65%, mp 128-129 °C (from ^{i}PrOH), lit[S3] mp 128-128.5 °C. ^{1}H NMR (DMSO-d_6): δ 8.63 (d, 1H), 8.02 (d, 1H), 7.90 (t, 1H), 7.45 (t, 1H), 6.73 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 155.6, 149.1, 146.9, 143.8, 137.8, 124.9, 122.3. IR (KBr, ν/cm^{-1}): 3420, 3308, 3180, 3072, 2368, 1632, 1592, 1572, 1564, 1520, 1468, 1448, 1424, 1332, 1288, 1248, 1152, 1096, 1076,1048, 1000, 988, 904, 868. Anal. calcd. (%) for $C_7H_6N_4O$ (162.15): C 51.85, H 3.73, N 34.55; found: C 51.87, H 3.75, N 34.50.



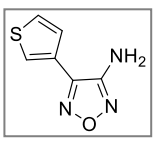
3-Amino-4-(pyridin-3-yl)furazan (**8l**). Yield 61%, mp 161-163 °C (from ^{i}PrOH), lit[S3] mp 161-163 °C. ^{1}H NMR (DMSO-d_6): δ 8.63 (d, 1H), 8.02 (d, 1H), 7.90 (t, 1H), 7.45 (t, 1H), 6.73 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 155.6, 149.1, 146.9, 143.8, 137.8, 124.9, 122.3. IR (KBr, ν/cm^{-1}): 3344, 3192, 3064, 2344, 1664, 1604, 1588, 1572, 1528, 1476, 1432, 1404, 1344, 1312, 1196, 1128, 1072, 1032, 984, 936, 908. Anal. calcd. (%) for $C_7H_6N_4O$ (162.15): C 51.85, H 3.73, N 34.55; found: C 51.89, H 3.74, N 34.59.



3-Amino-4-(pyridin-4-yl)furazan (**8m**). Yield 32%, mp 207-208 °C (from ^{i}PrOH), lit[S3] mp 207-208 °C. ^{1}H NMR (DMSO-d_6): δ 8.94 (d, 1H), 8.73 (dd, 1H), 8.16 (m, 1H), 7.58 (m, 1H), 6.34 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 160.4, 156.0, 153.1, 150.0, 140.5, 129.0, 127.0. IR (KBr, ν/cm^{-1}): 3348, 3184, 3044, 2792, 1660, 1612, 1588, 1552, 1528, 1484, 1428, 1400, 1332, 1308, 1228, 1132, 1060, 996, 960, 920, 888. Anal. calcd. (%) for $C_7H_6N_4O$ (162.15): C 51.85, H 3.73, N 34.55; found: C 51.87, H 3.75, N 34.58.

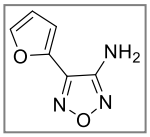


3-Amino-4-(thiophen-2-yl)furazan (**8n**). Yield 47%, mp 114-115 °C (from ^{i}PrOH), lit[S2] mp 114-115 °C. ^{1}H NMR (DMSO-d_6): δ 7.80 (d, 1H), 7.77 (d, 1H), 7.25 (t, 1H), 6.32 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 154.4, 142.5, 129.3, 128.7, 128.3, 125.7; IR (KBr, ν/cm^{-1}): 3450, 3324, 3242, 3211, 3107, 1635, 1595, 1548, 1489, 1424, 1345, 1289, 1234, 1060, 1000, 953, 903, 872, 849, 833. Anal. calcd. (%) for $C_6H_5N_3OS$ (167.19): C 43.11, H 3.01, N 25.13; found: C 43.18, H 3.04, N 25.08.

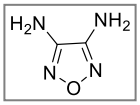


3-Amino-4-(thiophen-3-yl)furazan (**8o**). Yield 52%, mp 101-103 °C (from ^{i}PrOH). ^{1}H NMR (DMSO-d_6): δ 6.23 (s, 2H), 7.55 (d, 1H), 7.79 (m, 1H), 8.21 (d, 1H); ^{13}C NMR (DMSO-d_6) δ: 125.5, 126.4, 126.5, 127.8, 143.1, 154.9; ^{15}N NMR (DMSO-d_6): δ31.53, 9.02,

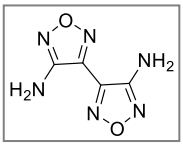
-332.43. IR (KBr, ν/cm^{-1}): 3407, 3316, 3240, 3113, 1635, 1584, 1551, 1491, 1430, 1417, 1375, 1283, 1195, 1137, 1085, 1052, 994, 865, 788. Anal. calcd. (%) for $C_6H_5N_3OS$ (167.19): C 43.11, H 3.01, N 25.13; found: C 43.15, H 3.03, N 25.09.



3-Amino-4-(furan-2-yl)furazan (**8p**). Yield 47%, mp 107-108 °C (from hexane). ^{1}H NMR (DMSO-d_6): δ 7.93 (d, 1H), 7.29 (d, 1H), 6.72 (dd, 1H), 6.27 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 145.1, 145.4, 140.2, 139.9, 112.5, 112.0; IR (KBr, ν/cm^{-1}): 3460, 3340, 3236, 3136, 1644,1572, 1520, 1464, 1428, 1384, 1308, 1228, 1168, 1064, 1024, 992, 908, 888, 872, 816, 752; Anal. calcd. (%) for $C_6H_5N_3O_2$ (151.13): C 47.69, H 3.33, N 27.81; found: C 47.75, H 3.36, N 27.76.



3,4-Diaminofurazan (**9**) Yield 57%, mp 185-186 °C (from H_2O), lit[S4] mp 179-180 °C. All spectroscopic data were in accord with those previously reported.[S4]



4,4'-Diaminobifurazan (**10**) Yield 32%, mp 299-300°C (dec), lit[S5] mp 300 °C (dec). ^{1}H NMR (DMSO-d_6): δ 6.45 (s, 2H); ^{13}C NMR (DMSO-d_6) δ: 155.5, 137.09; ^{15}N NMR (DMSO-d_6): δ 27.4, -16.5, -333.6. Anal. calcd. (%) for $C_4H_4N_6O_2$ (168.12): C 28.58, H 2.40, N 49.99; found: C 28.64, H 2.45, N 49.94.

X-ray study

All X-ray experiments were carried out using SMART APEX2 CCD diffractometer (λ(Mo-Kα)=0.71073 Å, graphite monochromator, ω-scans) at 100K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package.[S6] The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXTL program.[S7] The details of data collection and crystal structures refinement are summarized in Table S1 along with CCDC numbers which contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for compounds **6c**, **8h**, **8n**, and **8k**.

	6c	**8h**	**8n**	**8k**
Formula	$C_4H_7N_3O$	$C_{12}H_{15}N_3O_3$	$C_6H_5N_3OS$	$C_7H_6N_4O$
Mw	113.13	249.27	167.19	162.16
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic
Space group	*P*-1	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
a, Å	6.8785(19)	12.3025(7)	5.4688(7)	3.8205(2)
b, Å	8.749(2)	11.3020(7)	6.1708(8)	15.6562(10)
c, Å	9.943(4)	10.0707(6)	20.871(3)	12.1910(8)
α, deg.	106.629(7)	90	90	90
β, deg.	97.777(7)	113.4710(10)	90	94.4960(10)
γ, deg.	106.062(5)	90	90	90
V, Å^3	535.8(3)	1284.40(13)	704.32(16)	726.95(8)
Z	4	4	4	4
d_{cryst}, g·cm^{-3}	1.402	1.298	1.577	1.482
F(000)	240	528	344	336
μ, mm^{-1}	0.106	0.095	0.395	0.107
θ range, deg.	2.20 – 28.00	1.81 – 28.00	1.95 – 29.28	2.12 – 28.00
rflns collected	5549	18743	8247	7967
independent rflns	2564	3090	1930	1741
R_{int}	0.0383	0.0299	0.0760	0.0253
Completeness to θ	99.3	100.0	99.9	100.0
refined parameters	163	173	108	117
GOF (F^2)	0.983	1.078	1.091	1.087
rflns with $I>2\sigma(I)$	1734	2522	1613	1486
$R_1(F)$ ($I>2\sigma(I)$)[a]	0.0447	0.0440	0.0612	0.0367
$wR_2(F^2)$ (all data)[b]	0.1031	0.1271	0.1271	0.0941
Largest diff. peak/hole, *e*·Å^{-3}	0.252 / -0.214	0.322 / -0.232	0.373 / -0.506	0.267 / -0.213
CCDC number	2278313	2278314	2278315	2278316

[a] $R_1 = \sum||F_o| - |F_c||/\sum(F_o)$; [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{½}$

The structure of compounds **6c**, **8h**, **8n**, and **8k** were established by single crystal X-ray diffraction. An asymmetric unit cell of **8h**, **8n**, **8k** contains one molecule while two symmetrically independent molecules are observed in the crystal of aminofurazan **6c** bearing alkyl substituent. General view is presented in Figures S1-S4.

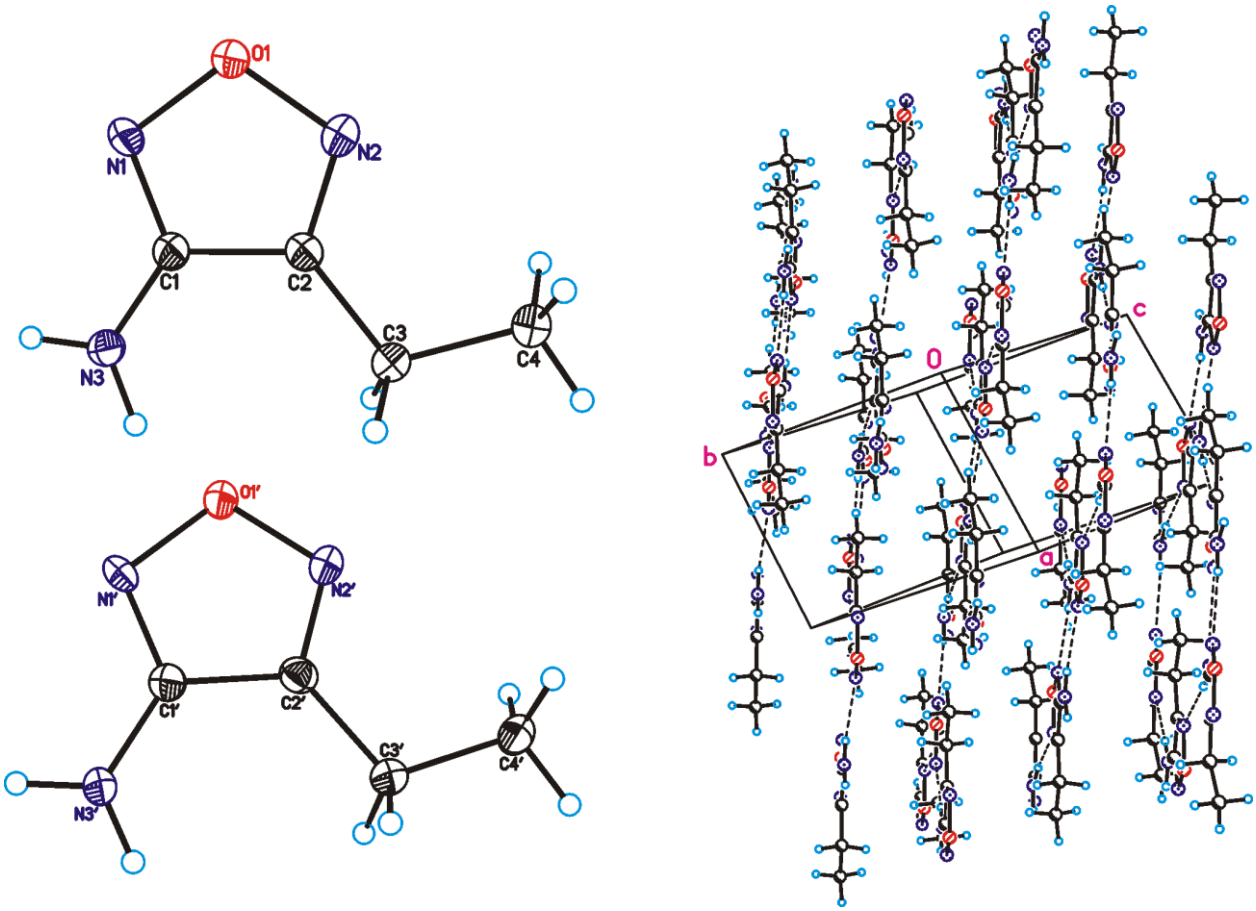


Figure S1. Molecular view (both independent molecules A and A' are shown) and crystal packing fragment of compound **6c**.

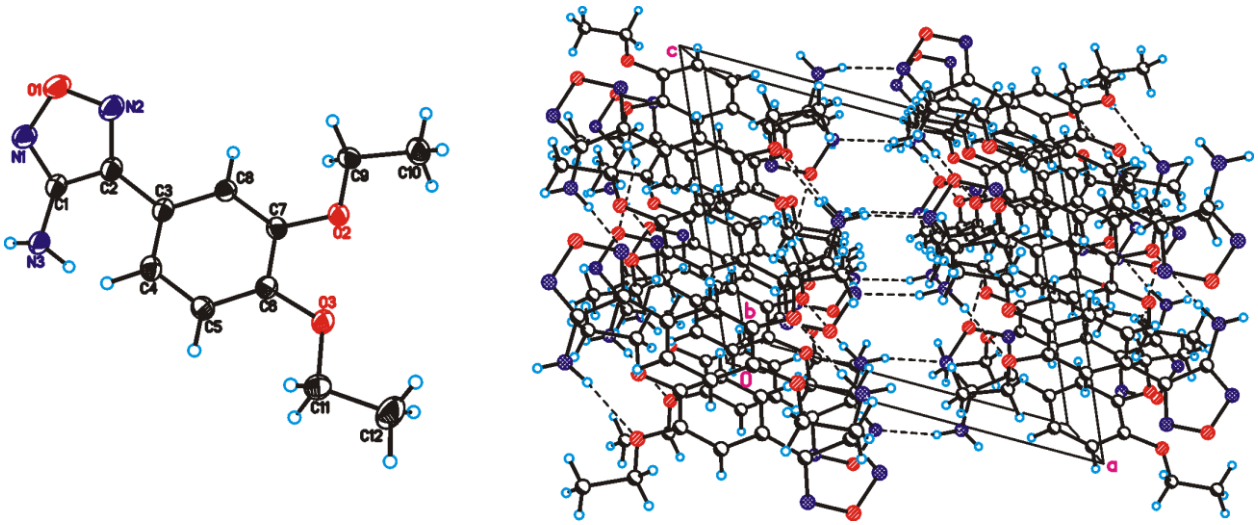


Figure S2. Molecular view and crystal packing fragment of compound **8h**.

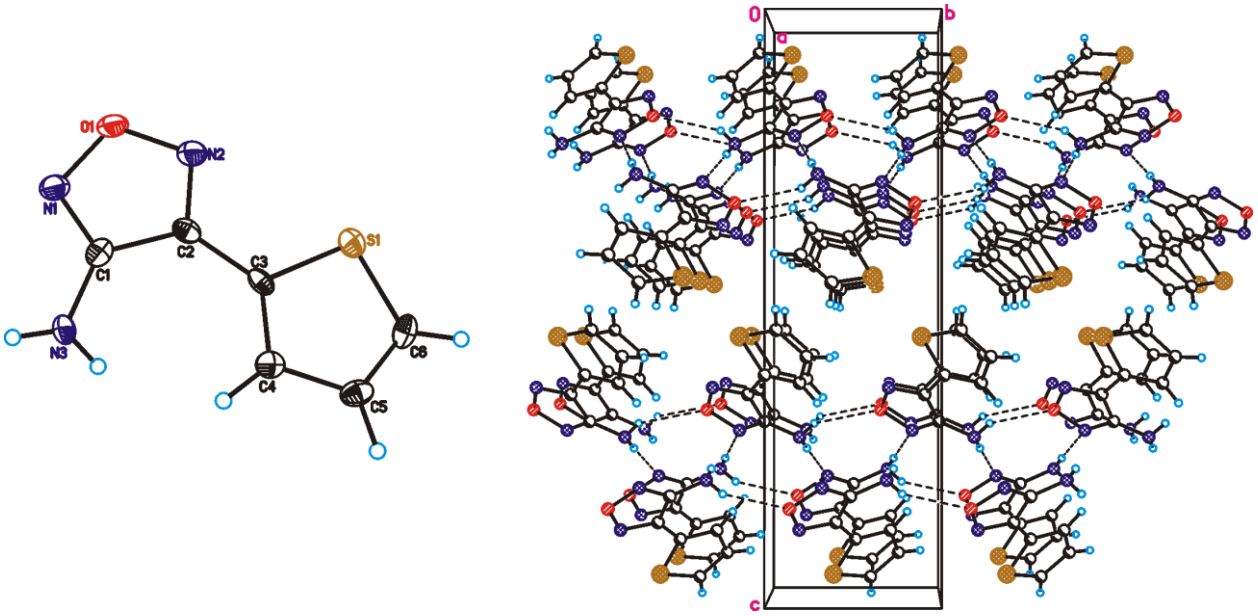


Figure 3S. Molecular view and crystal packing fragment of compound **8n**.

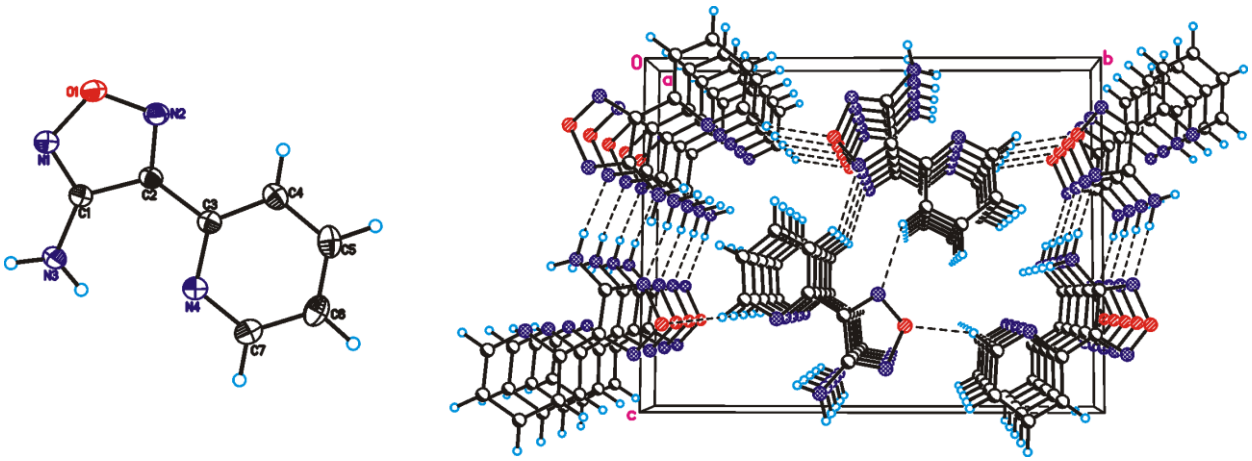


Figure 4S. Molecular view and crystal packing fragment of compound **8k**.

References

[S1] A. B. Sheremetev, Yu. L. Shamshina and D. E. Dmitriev, *Russ. Chem. Bull.,* **2005**, *54*, 1032-1037. **DOI**: 10.1007/s11172-005-0352-y

[S2] A. B. Sheremetev, *Russ. Chem. Bull.,* **2005**, *54*, 1057-1059. **DOI**: 10.1007/s11172-005-0359-4

S3 Y. N. Matyushin, T. S. Kon'kova, E. A. Miroshnichenko, A. V. Inozemtsev, A. B. Sheremetev, D. E. Dmitriev, A. V. Popov, V. P. Ivshin, Energies of isomerization of furazanylpyridines, *Proc. 41th International Annual Conference of ICT, Energetic Materials for High Performance, Insensitive and Zero Pollution*, June 29 - July 2, **2010**, Karlsruhe, FRG, 60/1-11.

[S4] A. Gunasekaran, T. Jayachandran, J.H. Boyer and M.L. Trudell, *J. Heterocycl. Chem*., **1995**, *32*, 1405-1407.

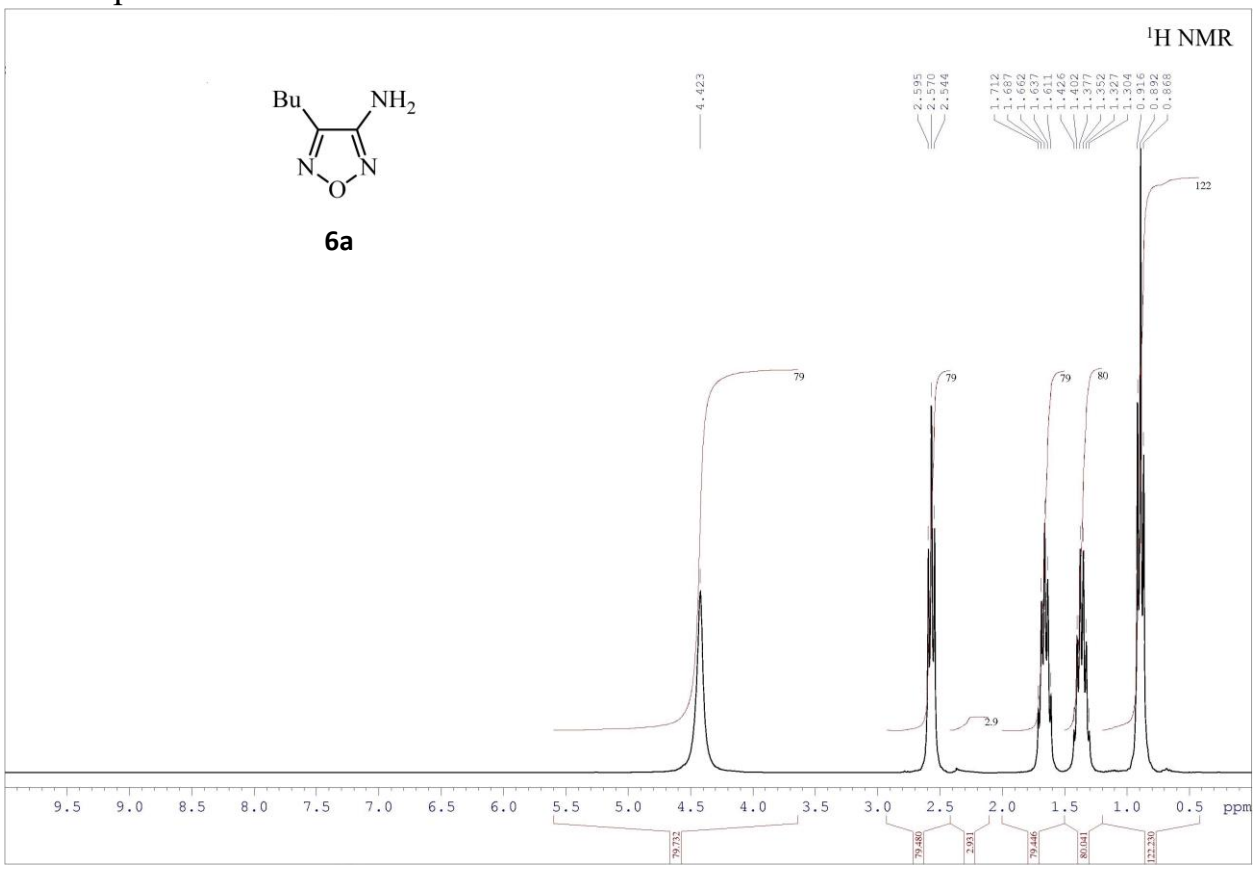
[S5] A. B. Sheremetev, V. O. Kulagina, I. A. Kryazhevskikh, T. M. Melnikova and N. S. Aleksandrova, *Russ. Chem. Bull.,* **2002**, *51*, (8), 1533-1539. **DOI**: 10.1023/A:1020931511013

[S6]. *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA, **2009**.

[S7]. G. M. Sheldrick, *Acta Crystallogr*., **2015**, *C71*, 3-8.

[S8]. I. V. Tselinskii, S. F. Mel'nikova, M. P. Zelenov. Acid-base properties of 1, 2, 5-oxadiazoles. III. Furazanylacetic acids. *Zhurnal Organicheskoi Khimii*, **1996**, *32*, 766-769 [*Russ. J. Org. Chem*., **1996**, *32*, 734-737 (Engl.Transl.)]

NMR spectra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O
N
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1.662
1.637
1.611
1.426
1.402
1.377
1.352
1.327
1.304
0.916
0.892
0.868
122
79
79
79
80
2.9
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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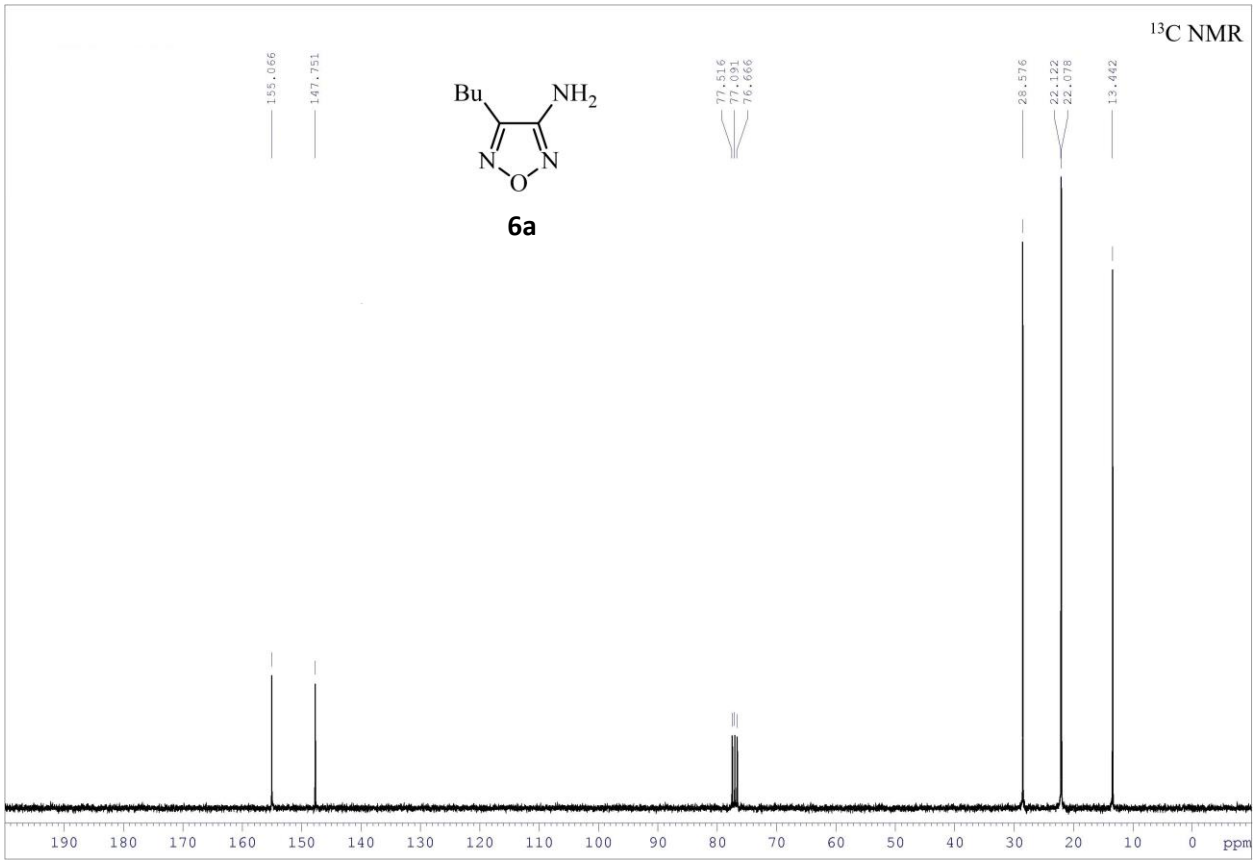
79.480
2.951
79.446
80.041
122.230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O
N
6a
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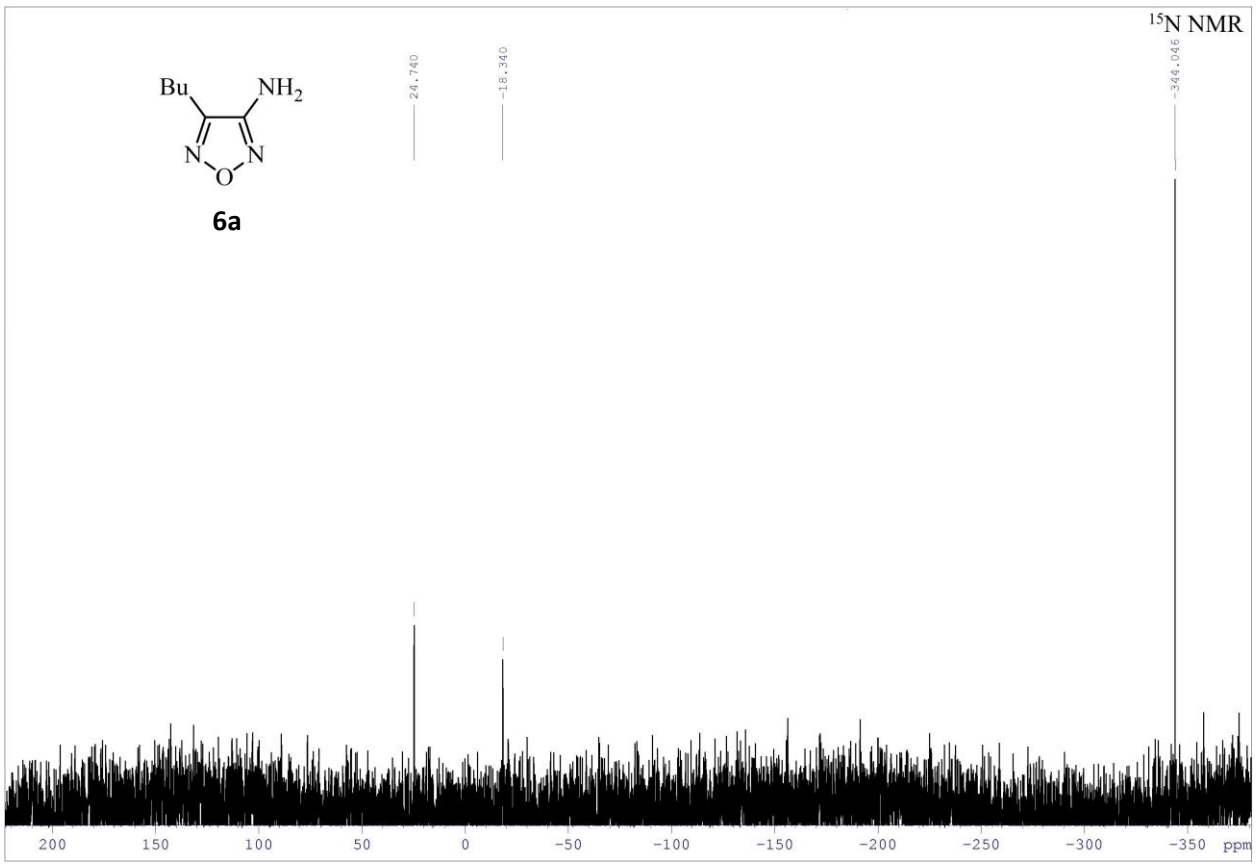
13.442
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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-200
-250
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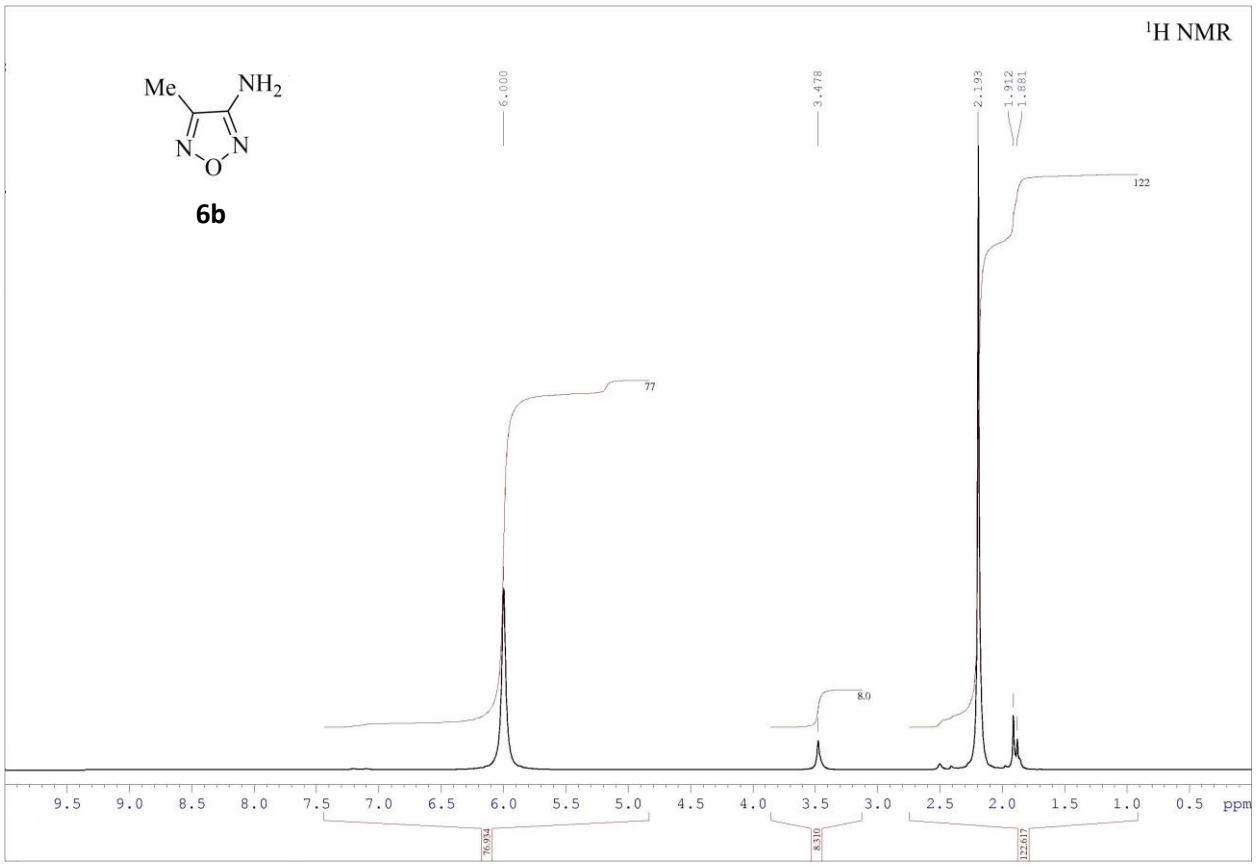
-350
ppm

6a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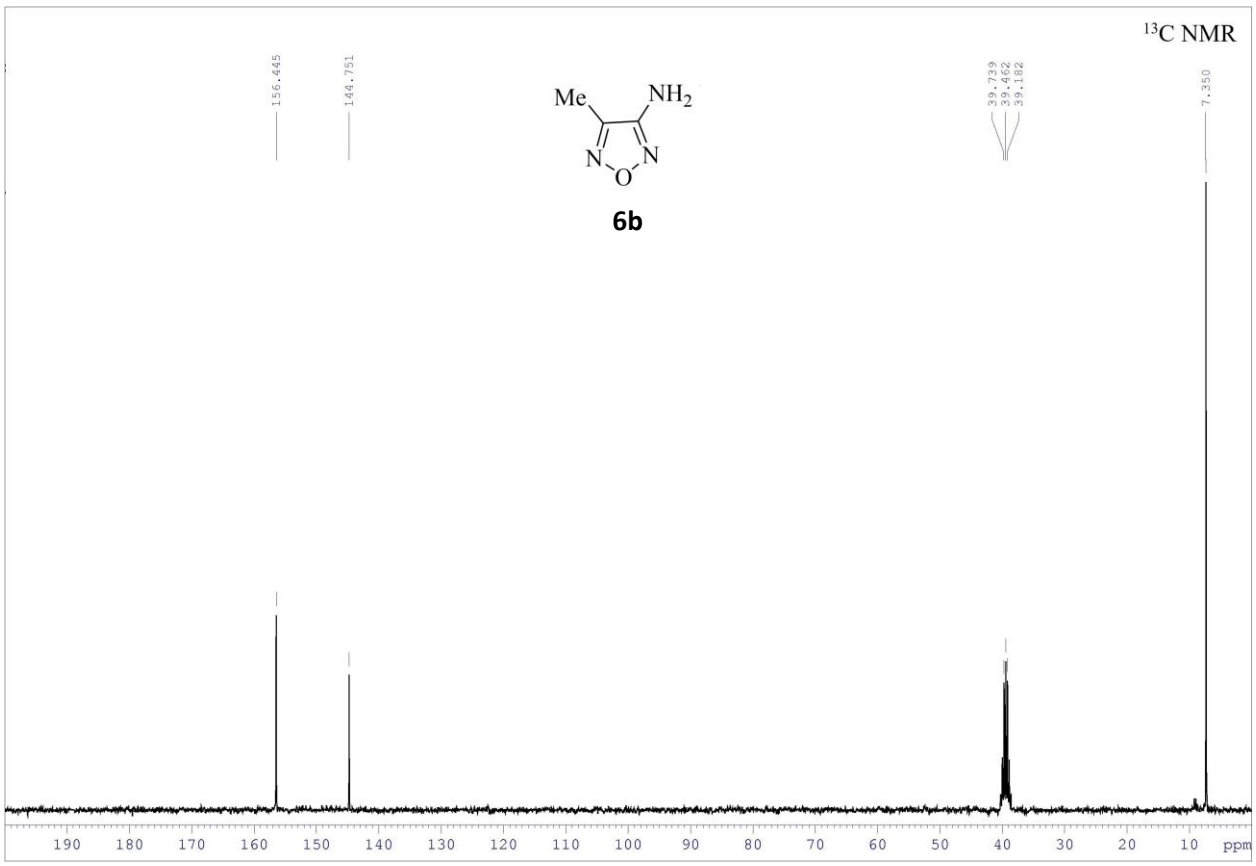
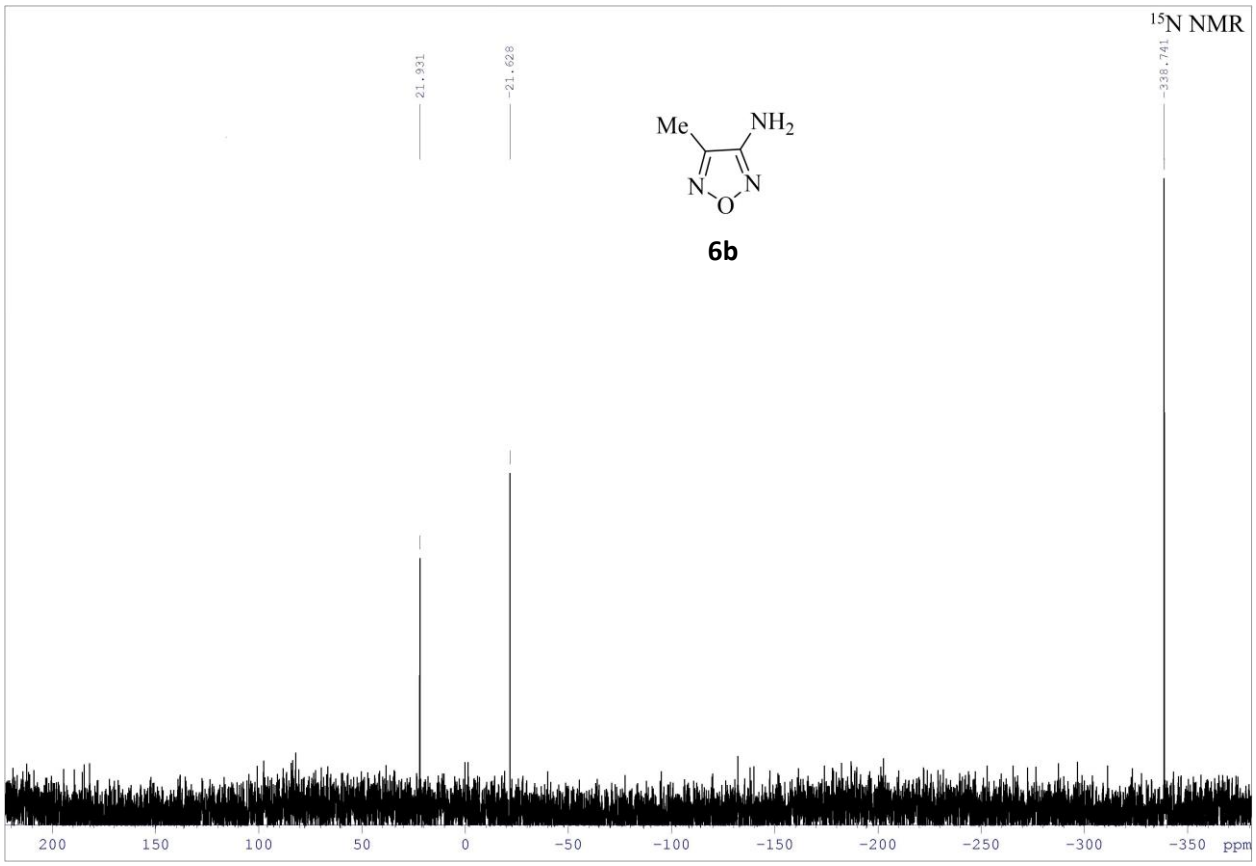
77
8.0
122
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
76.934
8.310
122.617

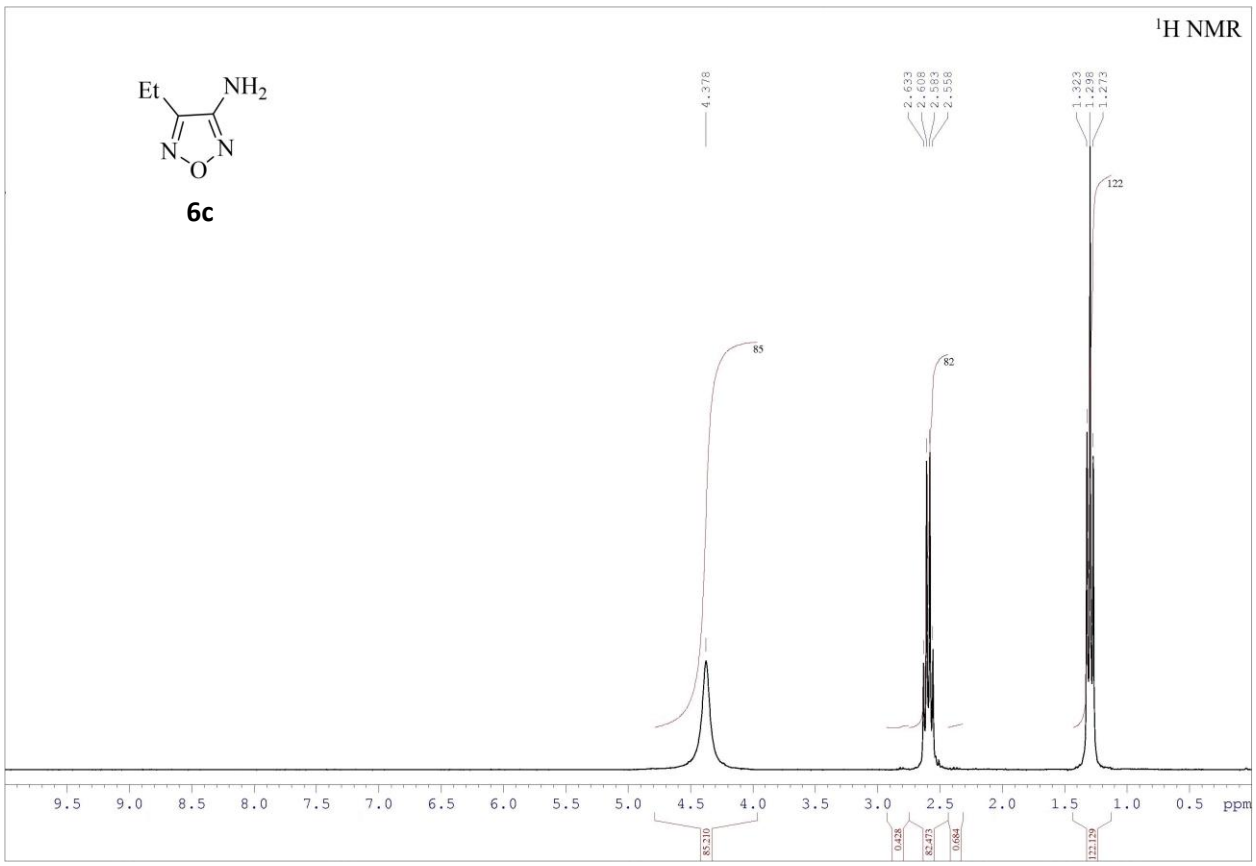
6b

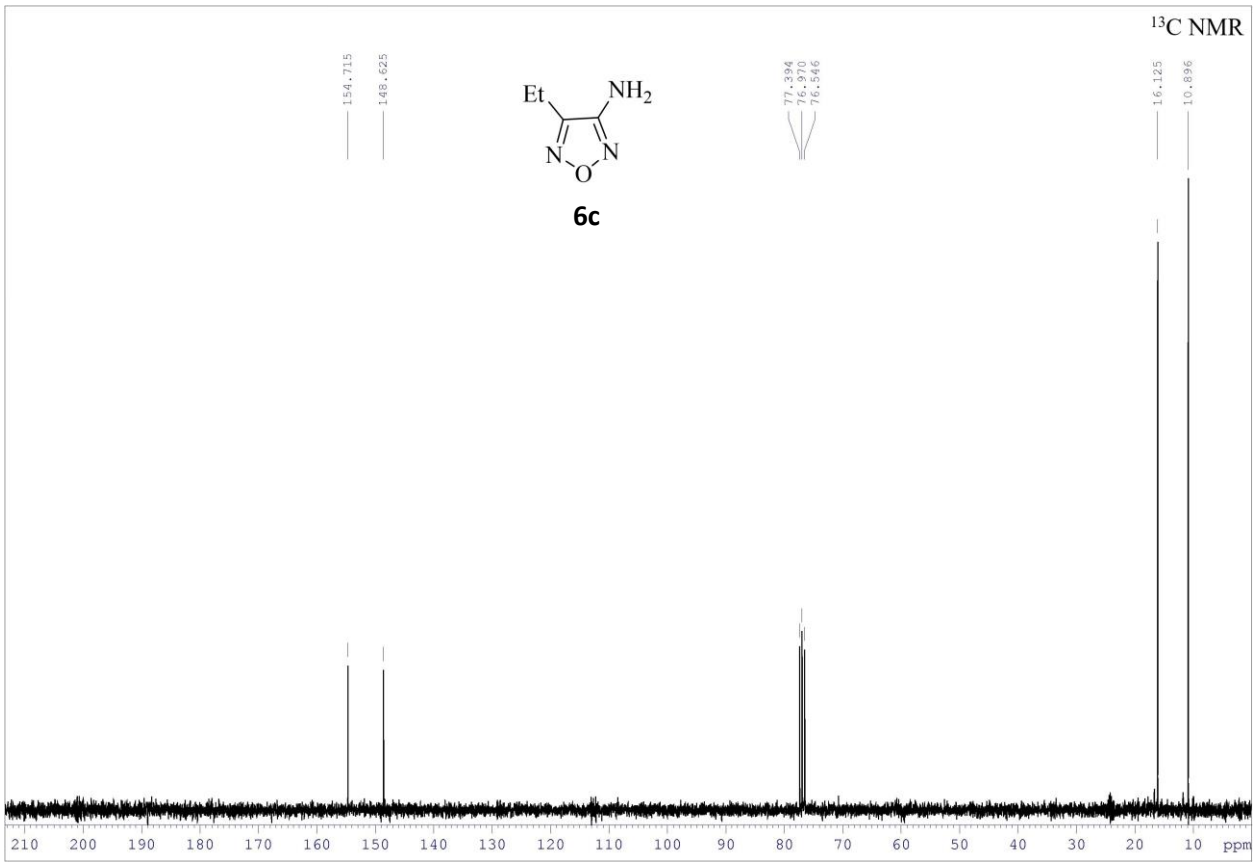

^{13}C NMR
156.445
144.751
39.739
39.462
39.182
7.350
Me
NH$_2$
N
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

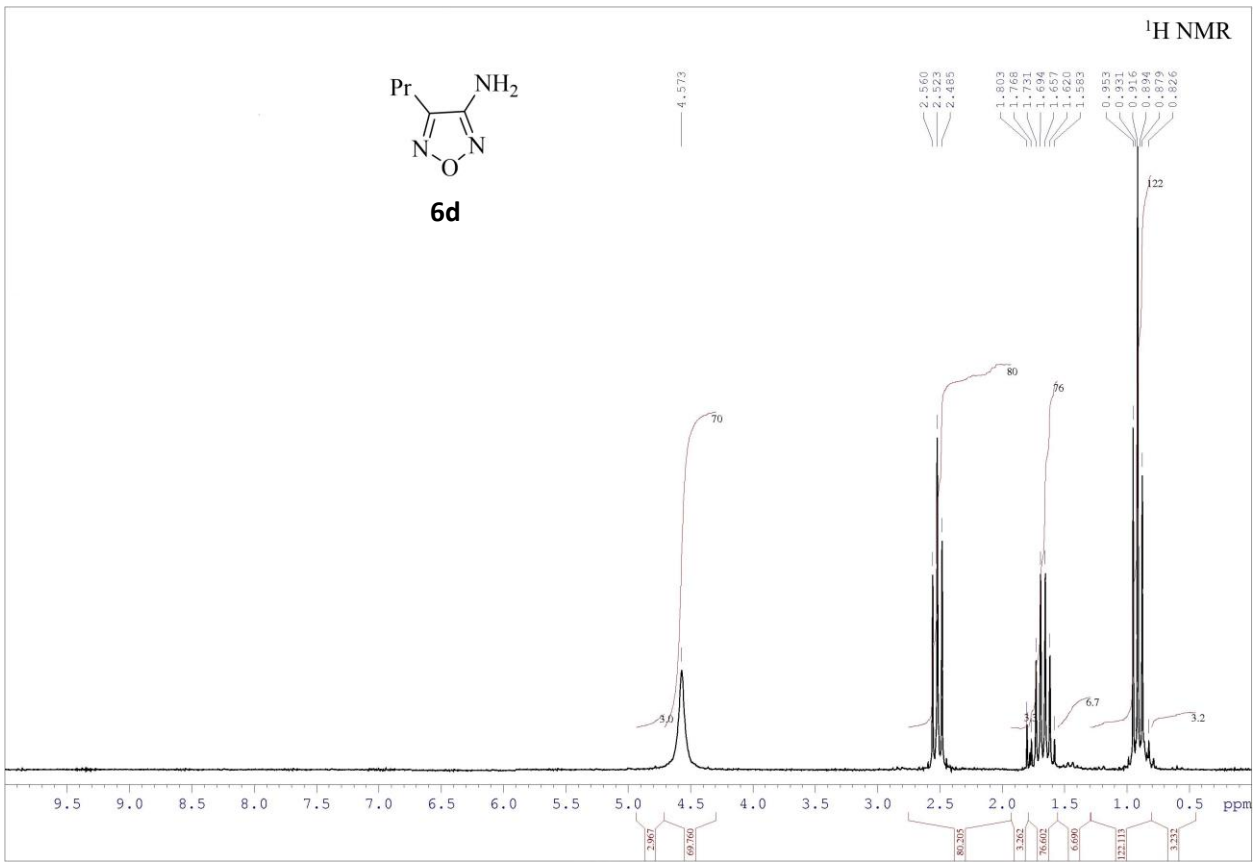
6b

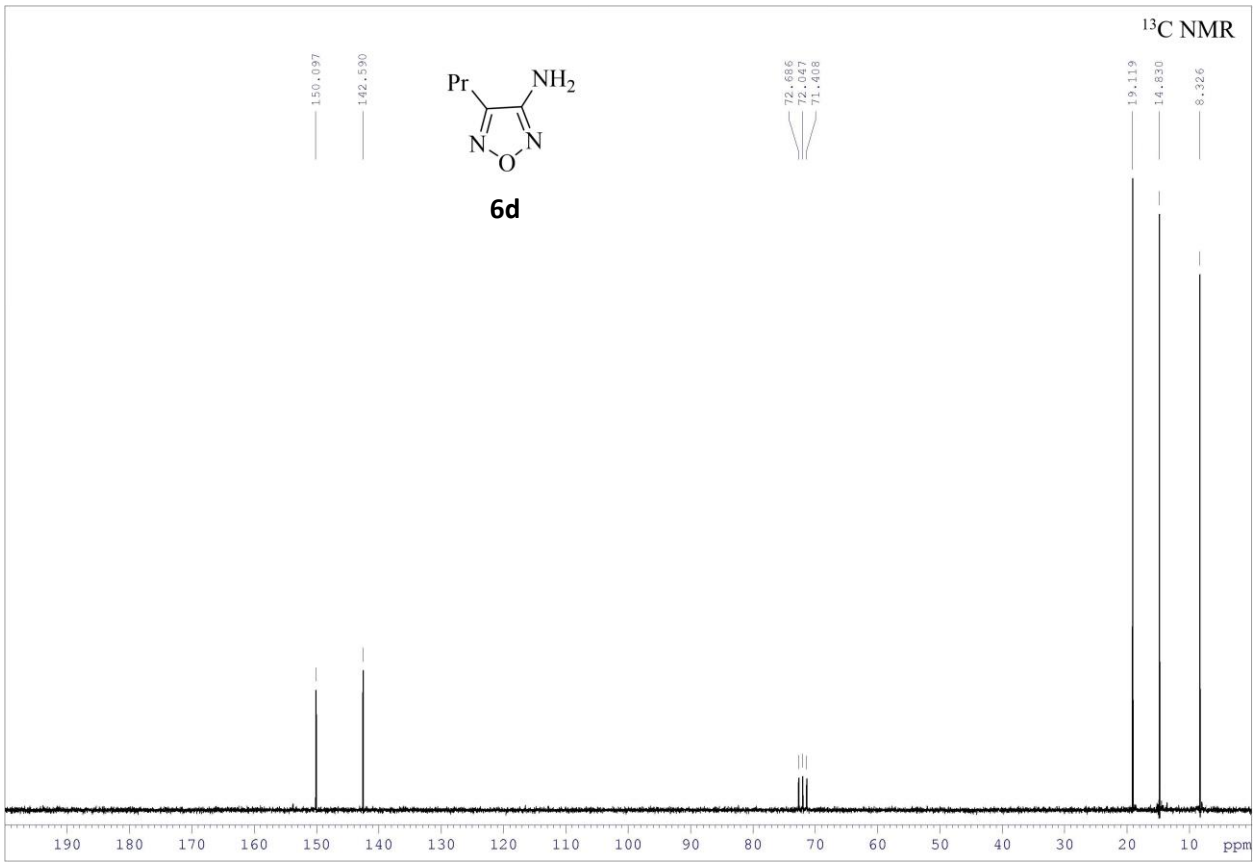

^{15}N NMR
21.931
-21.628
-338.741
Me
NH$_2$
N
O
N
200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm

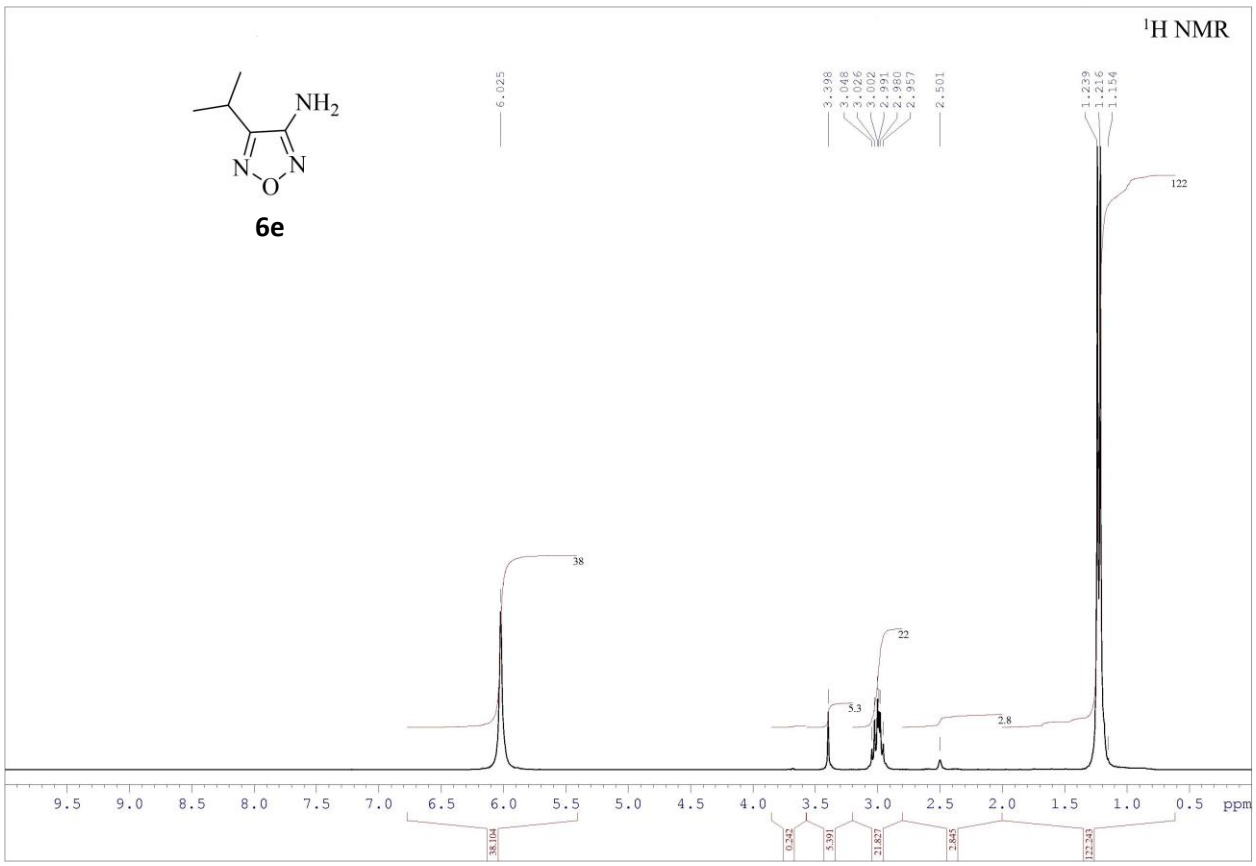
6b

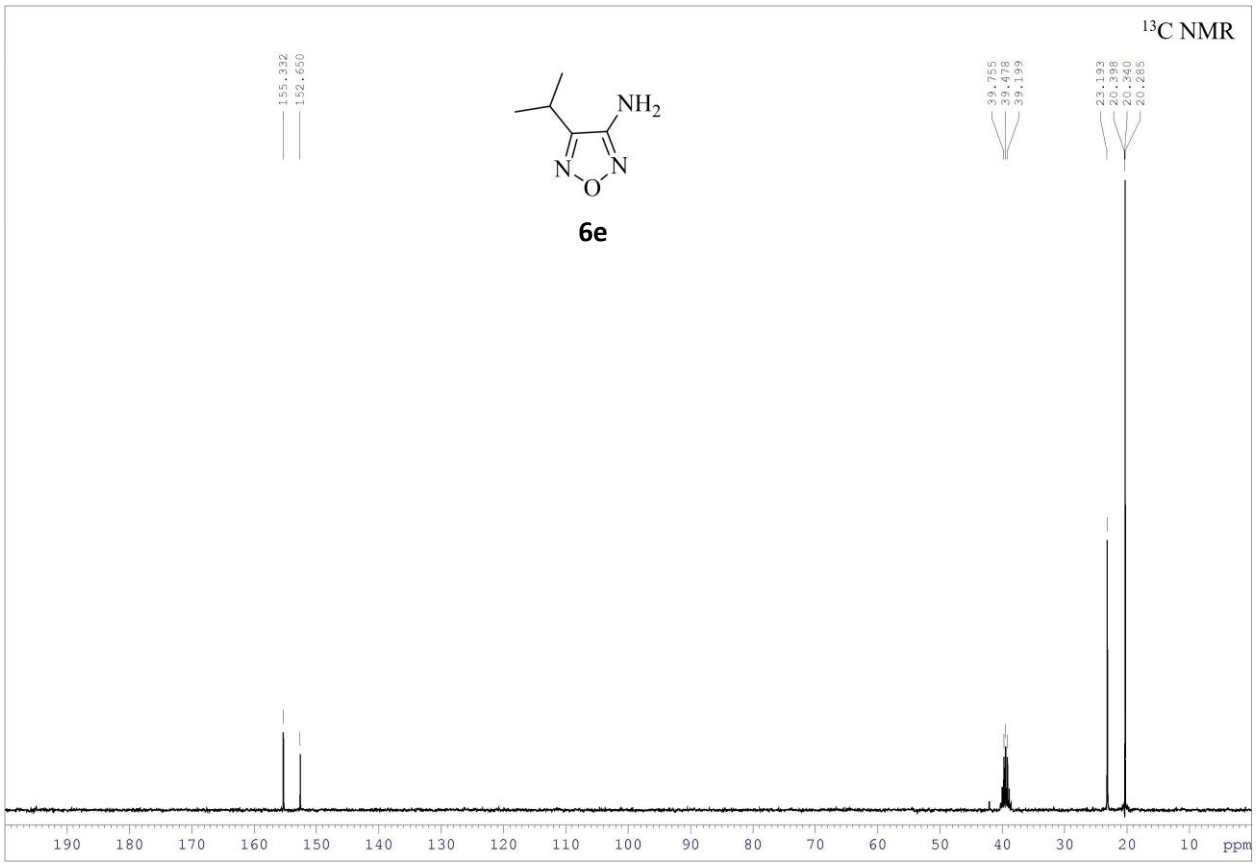

^{1}H NMR
Et
NH$_2$
N
O
N
6c
4.378
2.633
2.608
2.583
2.558
1.323
1.298
1.273
122
85
82
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
85.210
0.428
82.475
0.684
123.129

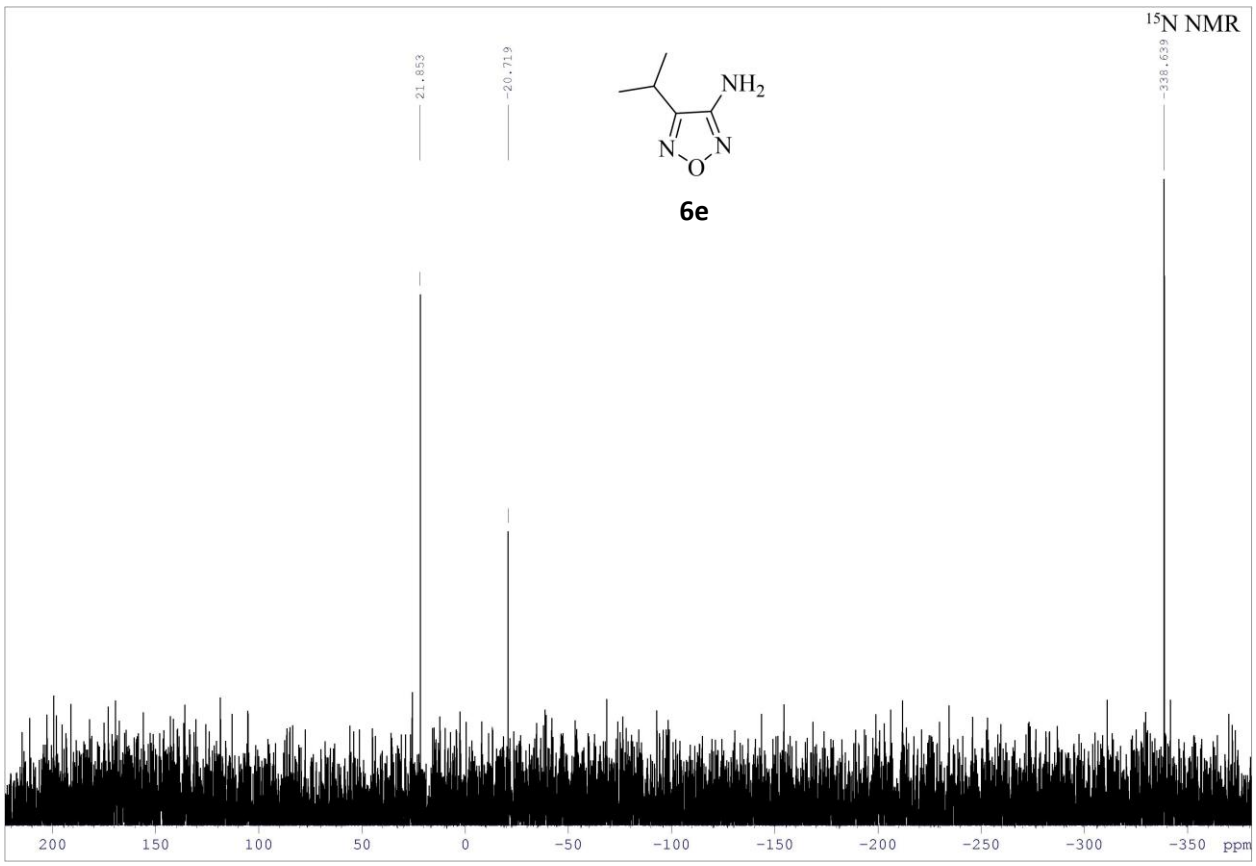

^{13}C NMR
154.715
148.625
77.394
76.970
76.546
16.125
10.896
Et
NH$_2$
N
O
N
6c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{1}H NMR
Pr
NH$_2$
N
O
N
6d
4.573
2.560
2.523
2.485
1.803
1.768
1.731
1.694
1.657
1.620
1.583
0.953
0.931
0.916
0.894
0.879
0.826
122
80
76
70
6.7
3.2
3.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.967
69.760
80.205
3.262
76.602
6.690
122.113
3.232

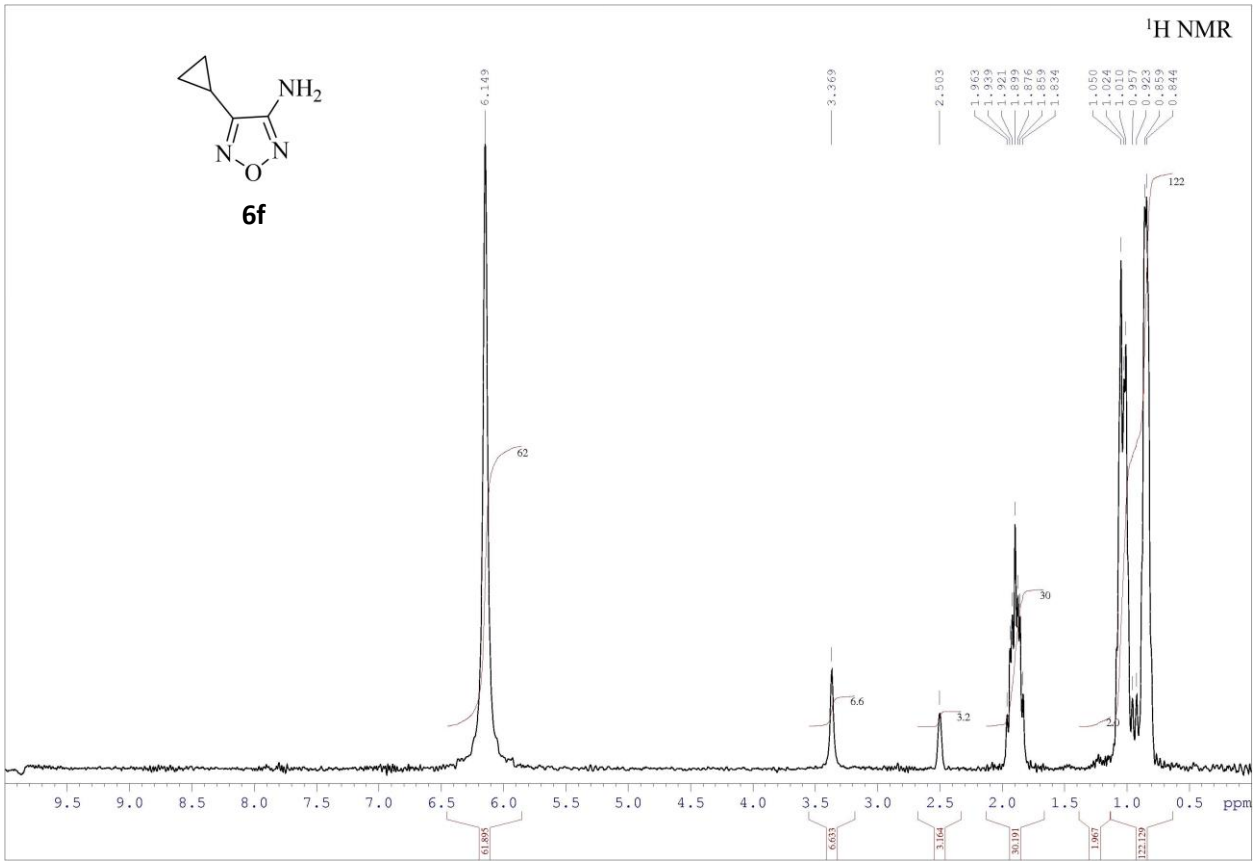

^{13}C NMR
150.097
142.590
72.686
72.047
71.408
19.119
14.830
8.326
Pr
NH$_2$
N
O
N
6d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{1}H NMR
NH$_2$
N
O
N
6e
6.025
3.398
3.048
3.026
3.002
2.981
2.960
2.957
2.501
1.239
1.216
1.154
122
38
22
5.3
2.8
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
38.104
0.242
5.991
21.827
2.845
122.243

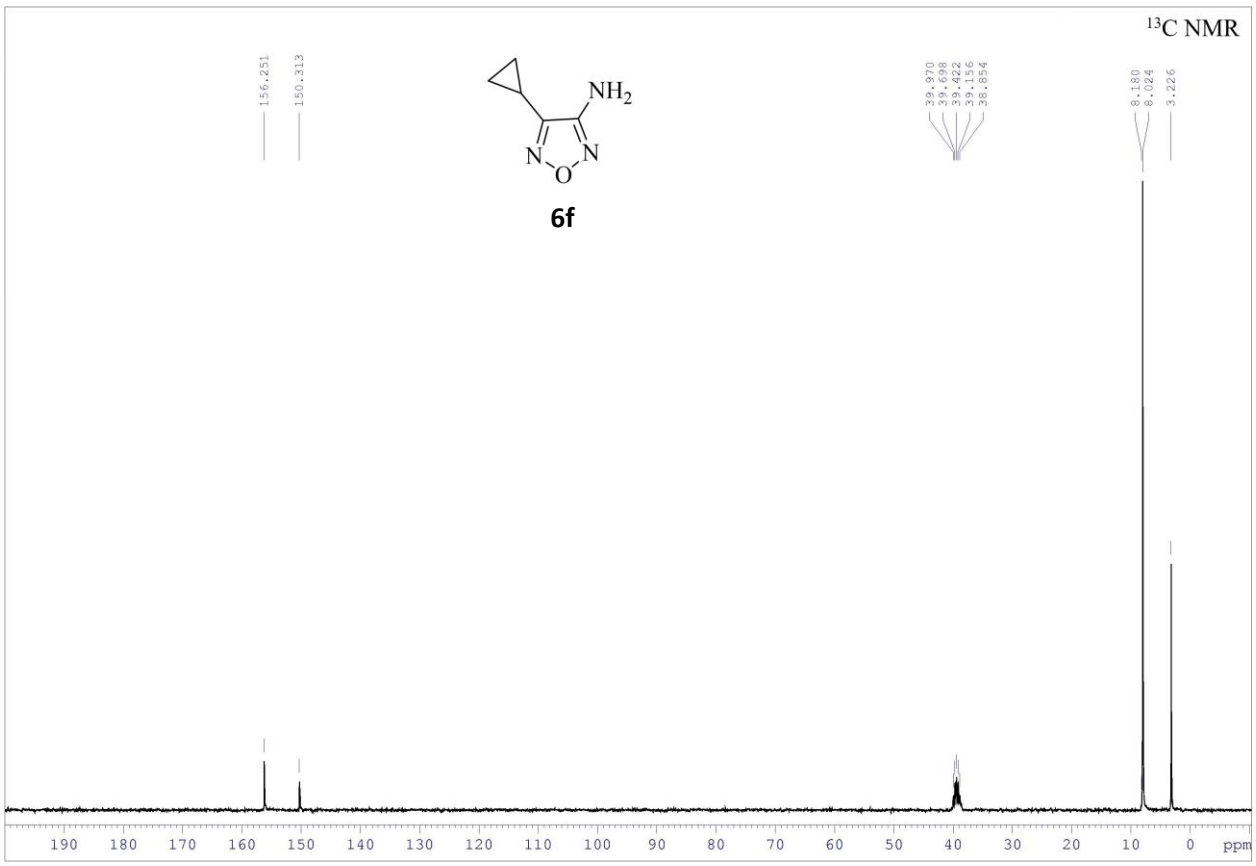

^{13}C NMR
155.332
152.650
NH$_2$
N
O
N
6e
39.755
39.478
39.199
23.193
20.398
20.340
20.285
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{15}N NMR
21.853
-20.719
-338.639
NH2
N
O
N
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

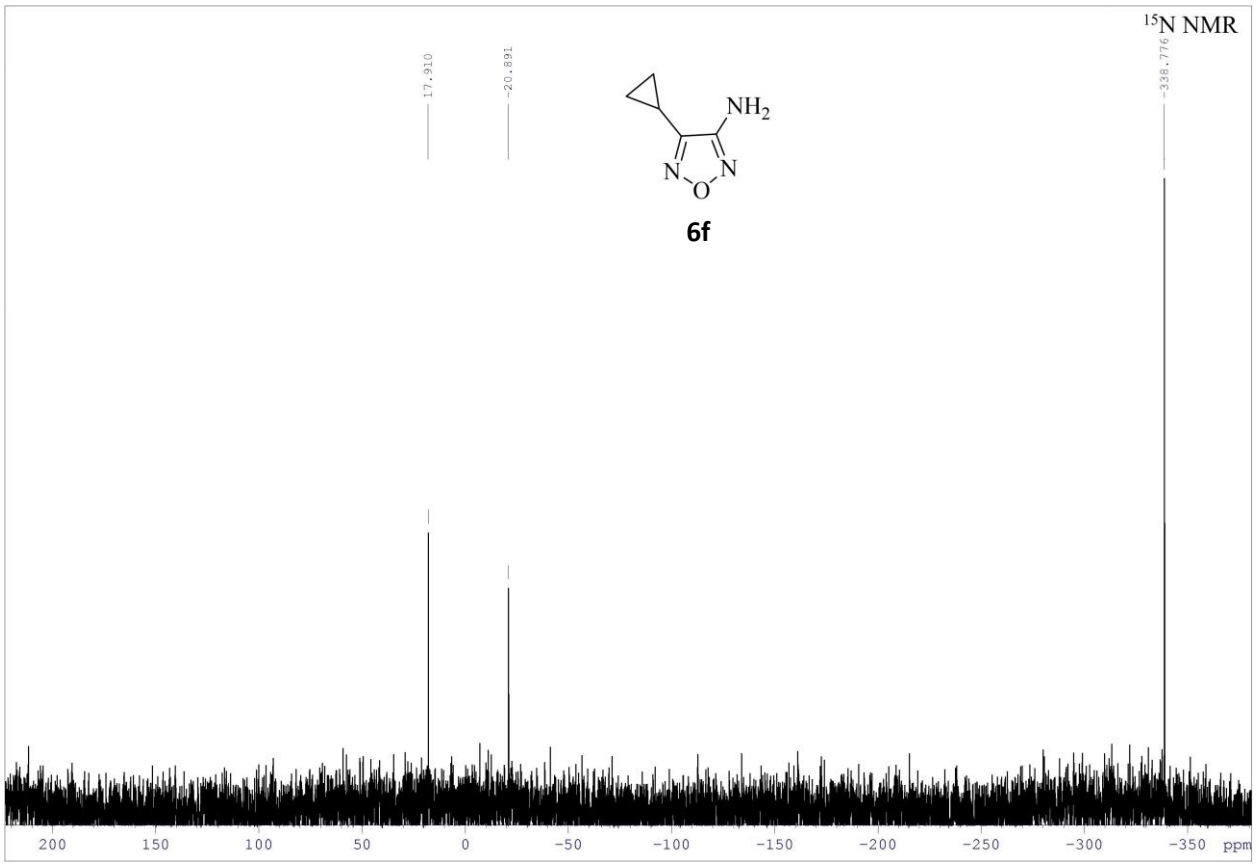
6e


^{1}H NMR
NH2
N
O
N
6.149
3.369
2.503
1.963
1.939
1.921
1.899
1.876
1.859
1.834
1.050
1.024
1.010
0.957
0.923
0.859
0.844
122
62
30
6.6
3.2
2.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
61.895
6.633
3.164
30.191
1.967
122.129

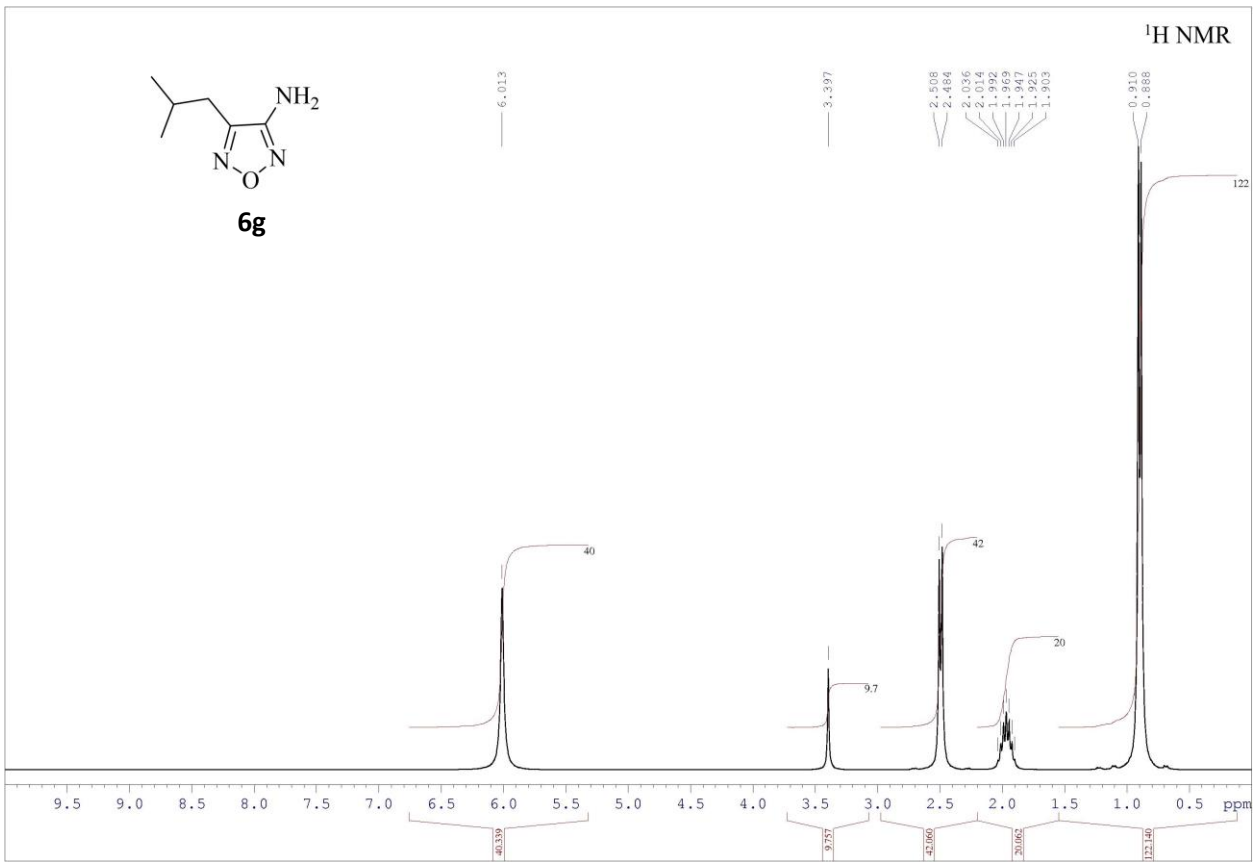
6f

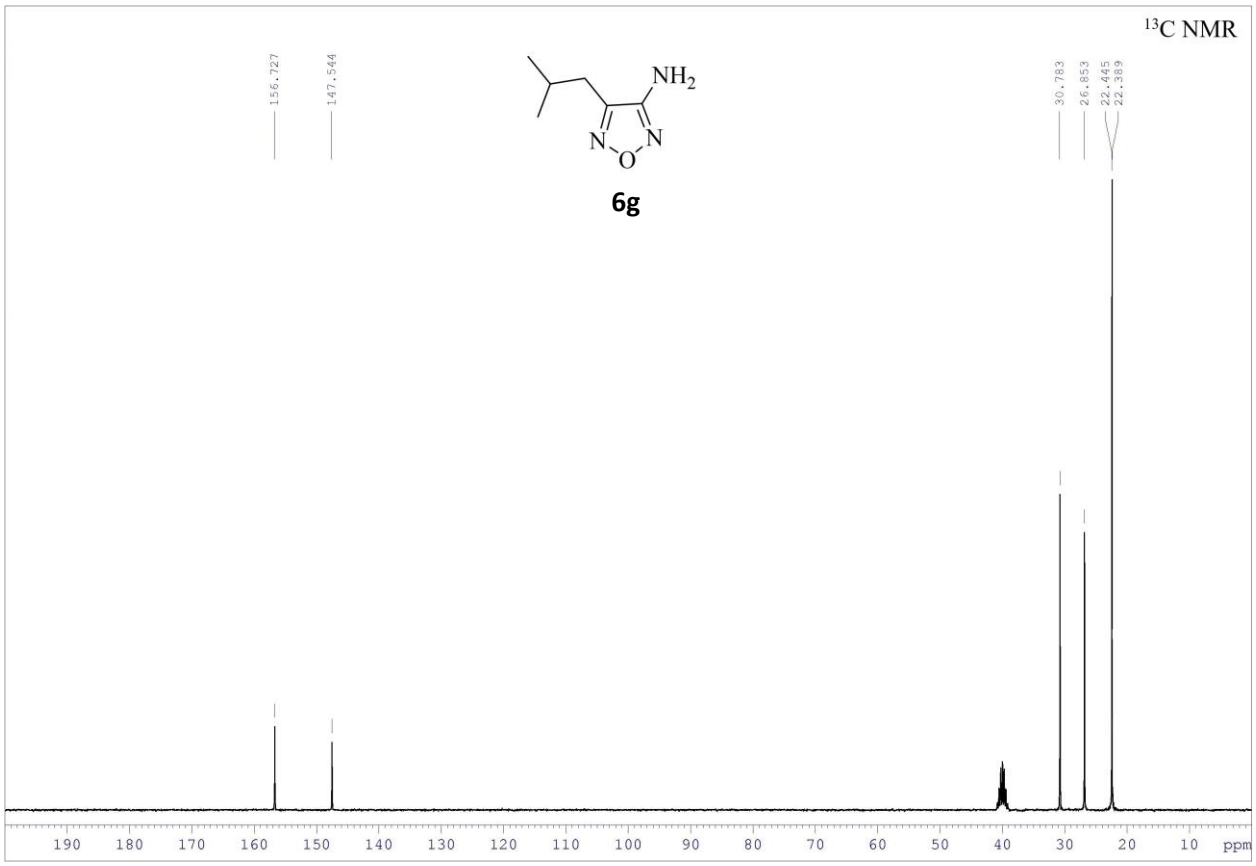

^{13}C NMR
156.251
150.313
39.970
39.698
39.422
39.156
38.854
8.180
8.024
3.226
NH2
N
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

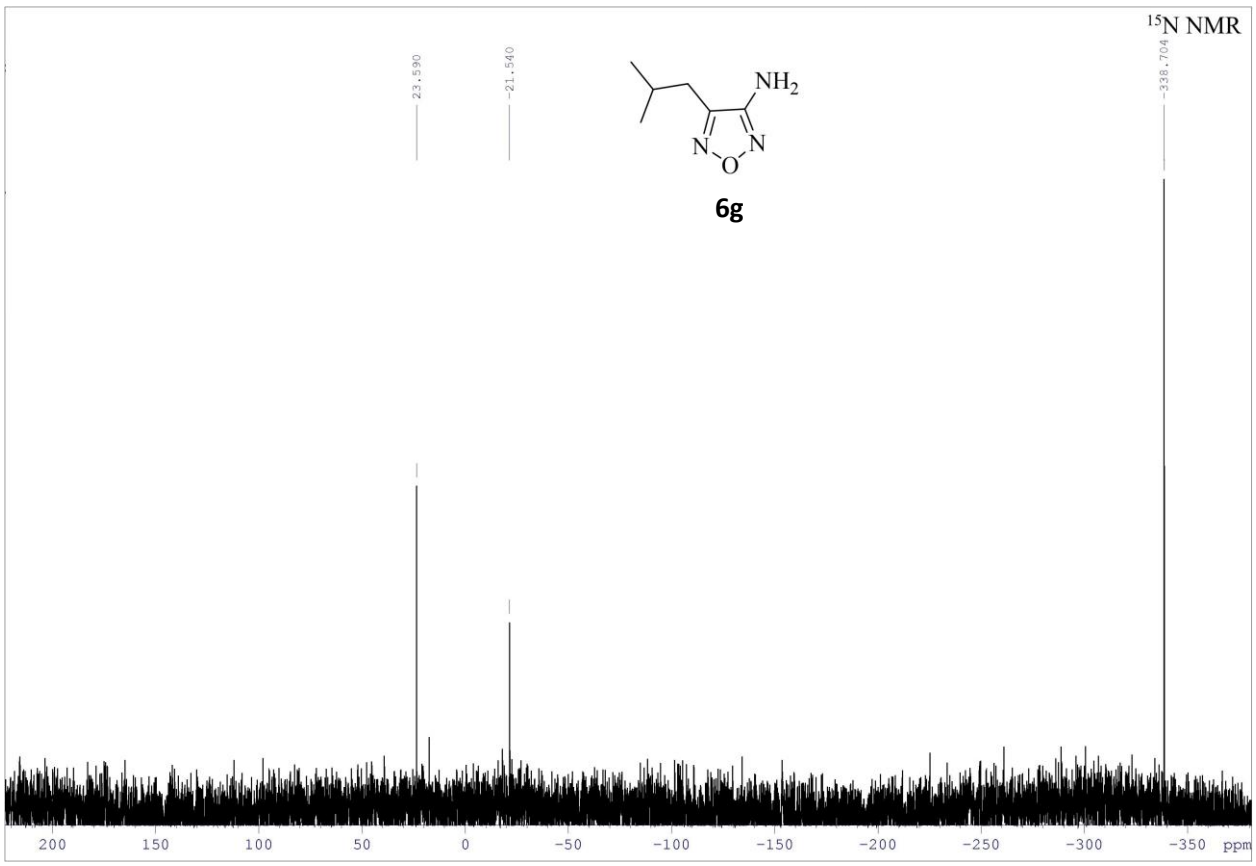
6f


^{15}N NMR
17.910
-20.891
-338.776
NH2
N
O
N
200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm

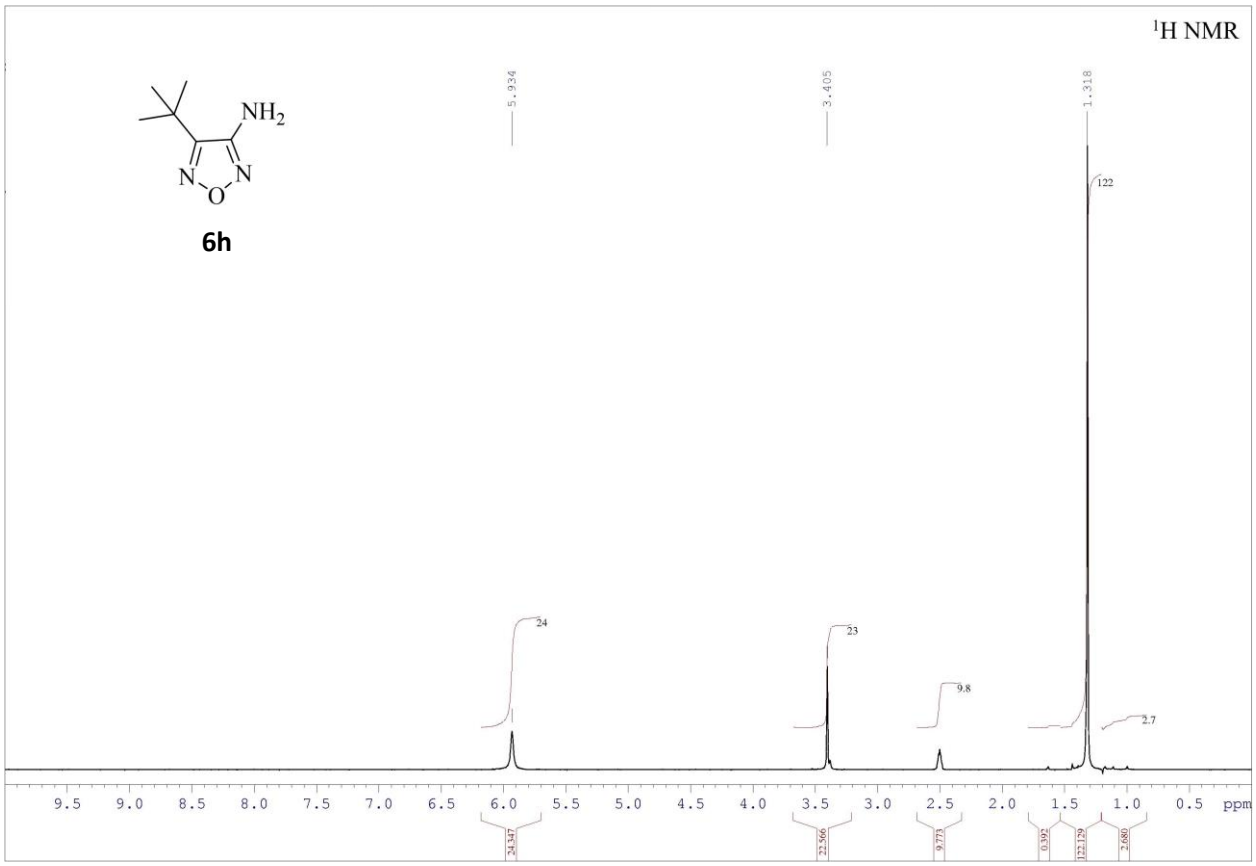
6f


^{1}H NMR
NH2
N
O
N
6g
6.013
3.397
2.508
2.484
2.036
2.014
1.992
1.969
1.947
1.925
1.903
0.910
0.888
122
40
42
20
9.7
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
40.339
9.757
42.060
20.062
122.140

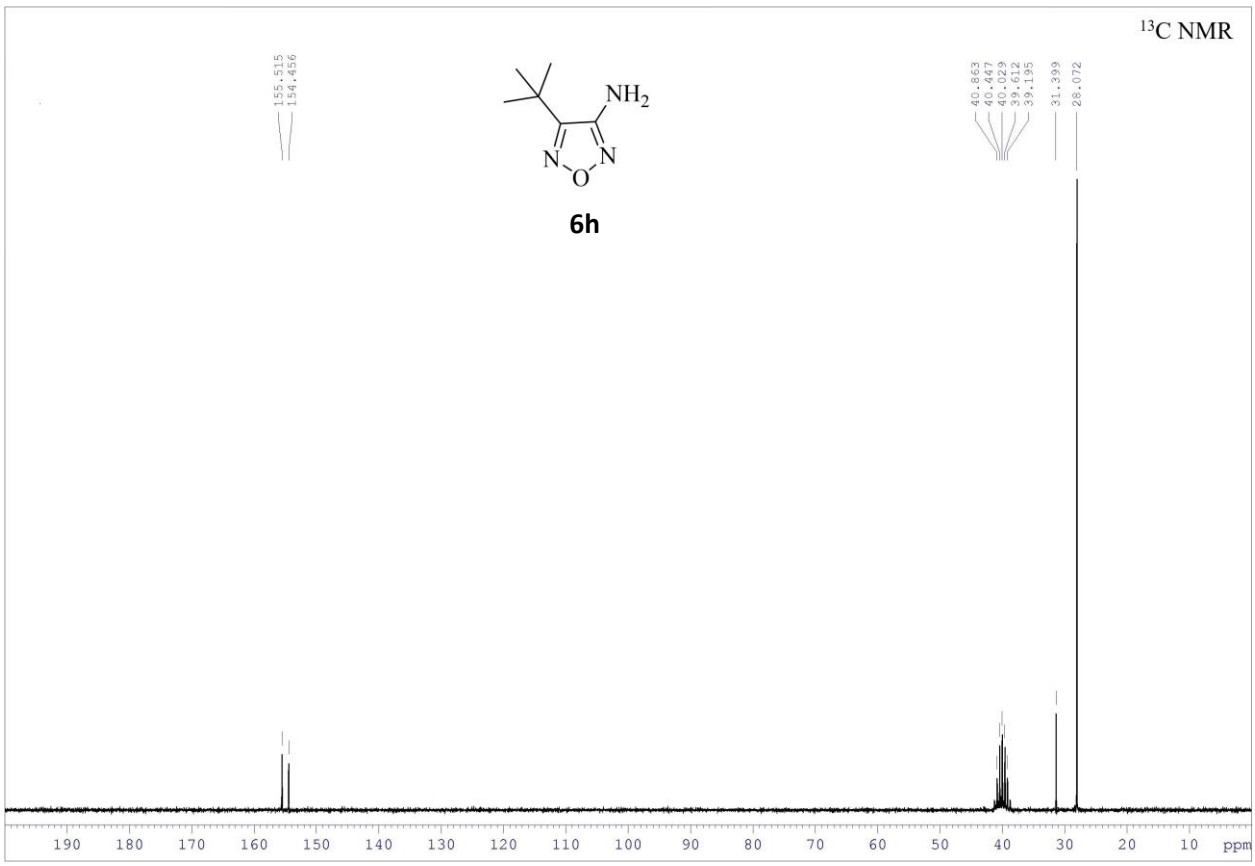

^{13}C NMR
156.727
147.544
NH2
N
O
N
6g
30.783
26.853
22.445
22.389
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{15}N NMR
23.590
-21.540
-338.704
NH2
N
O
N
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

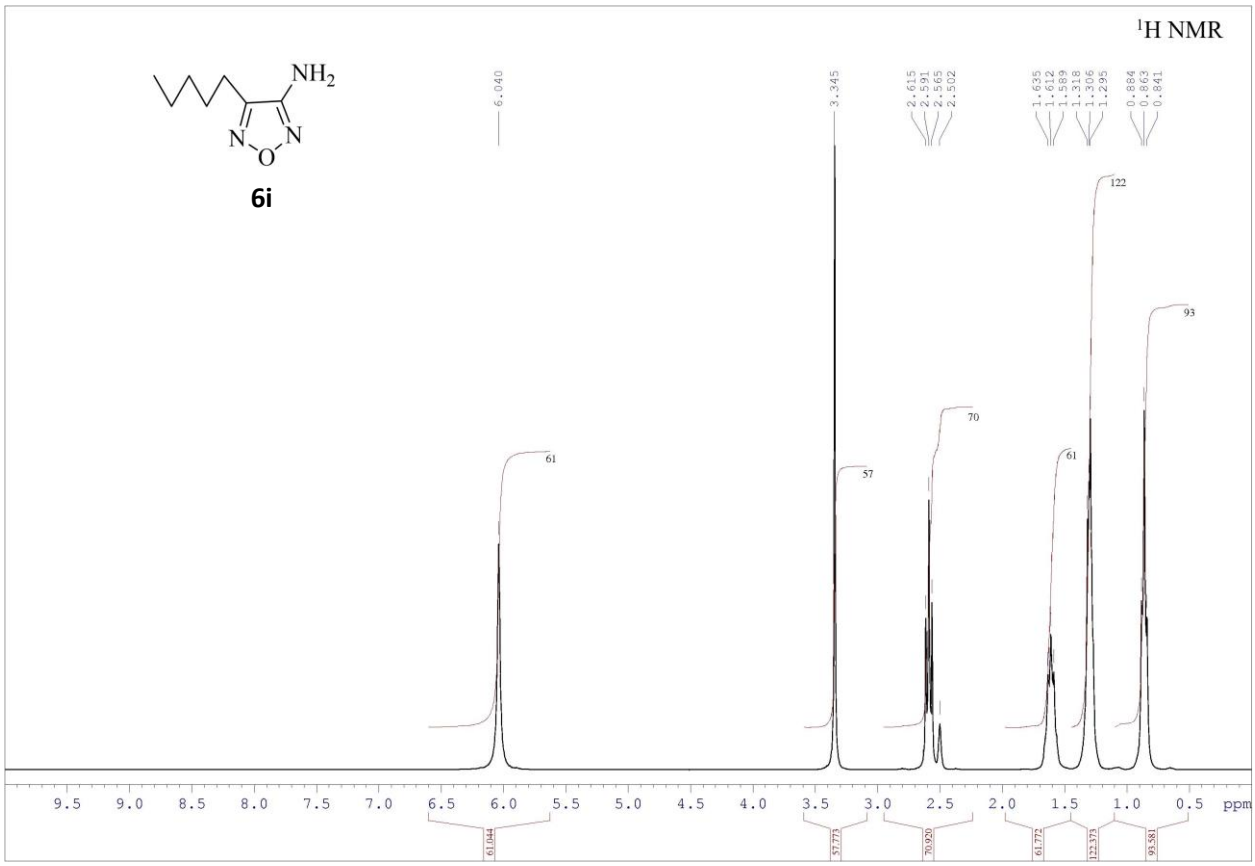
6g


^{1}H NMR
5.934
3.405
1.318
122
24
23
9.8
2.7
NH2
N
O
N
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
24.347
25.566
9.773
0.392
122.129
2.680

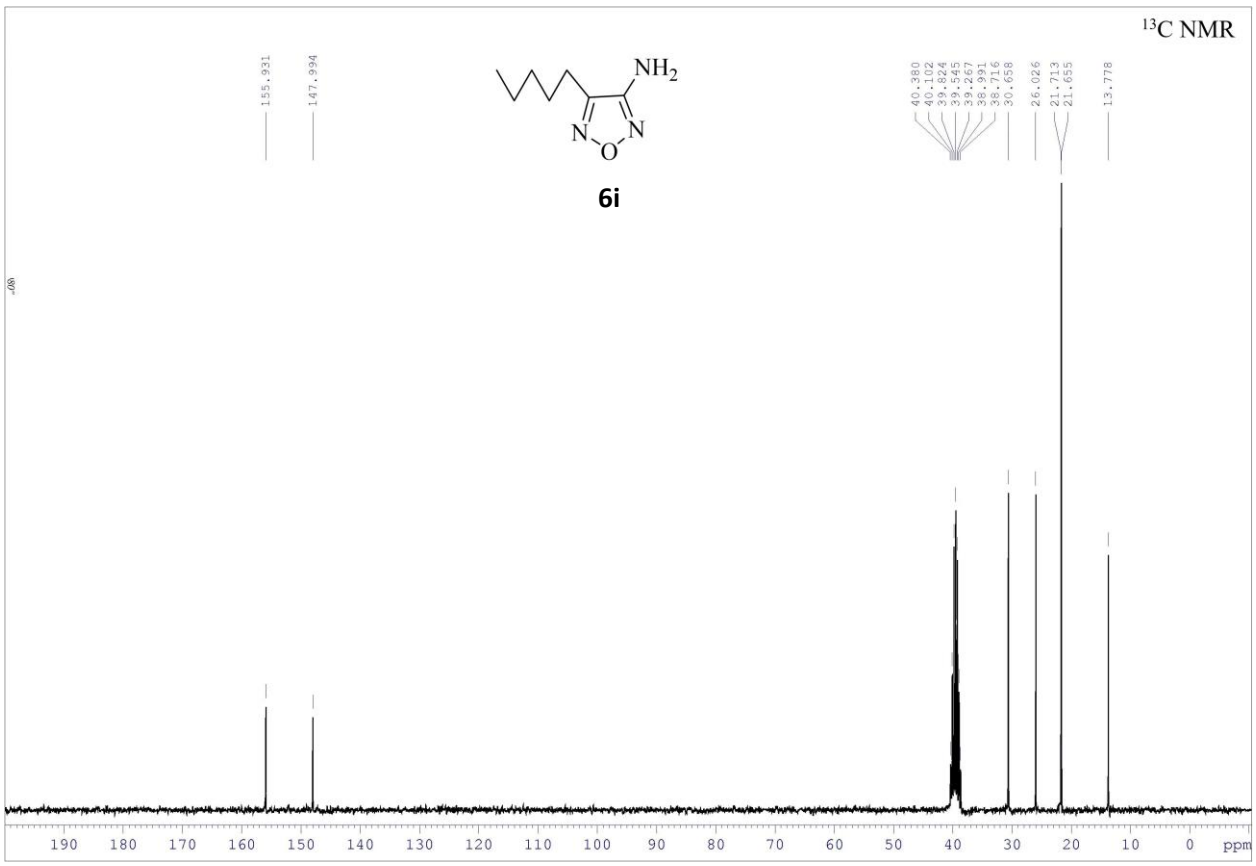
6h


^{13}C NMR
155.515
154.456
NH2
N
O
N
40.863
40.447
40.029
39.612
39.195
31.399
28.072
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

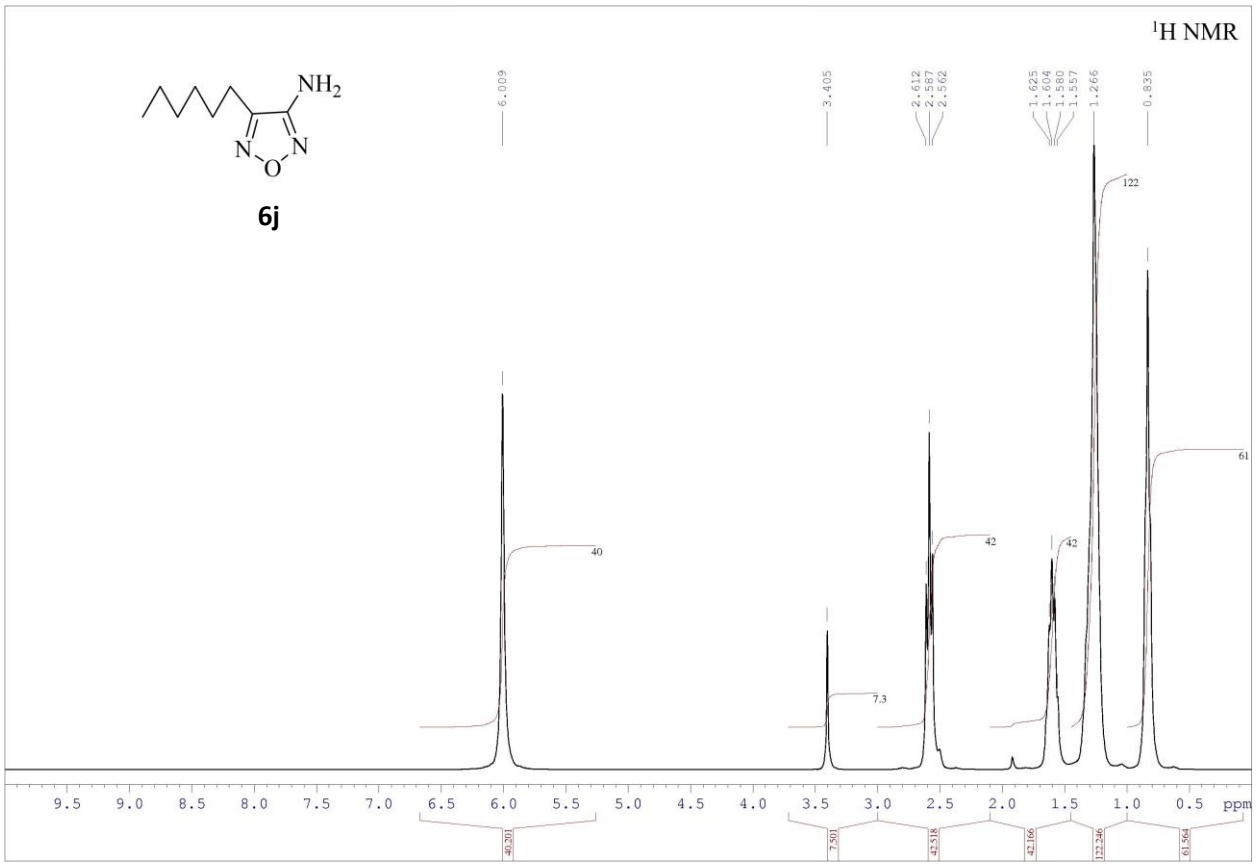
6h


^{1}H NMR
NH2
N
O
N
6.040
3.345
2.615
2.591
2.565
2.502
1.635
1.612
1.589
1.318
1.306
1.295
0.884
0.863
0.841
122
93
70
61
57
61
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
61.044
57.773
70.920
61.772
123.373
95.581

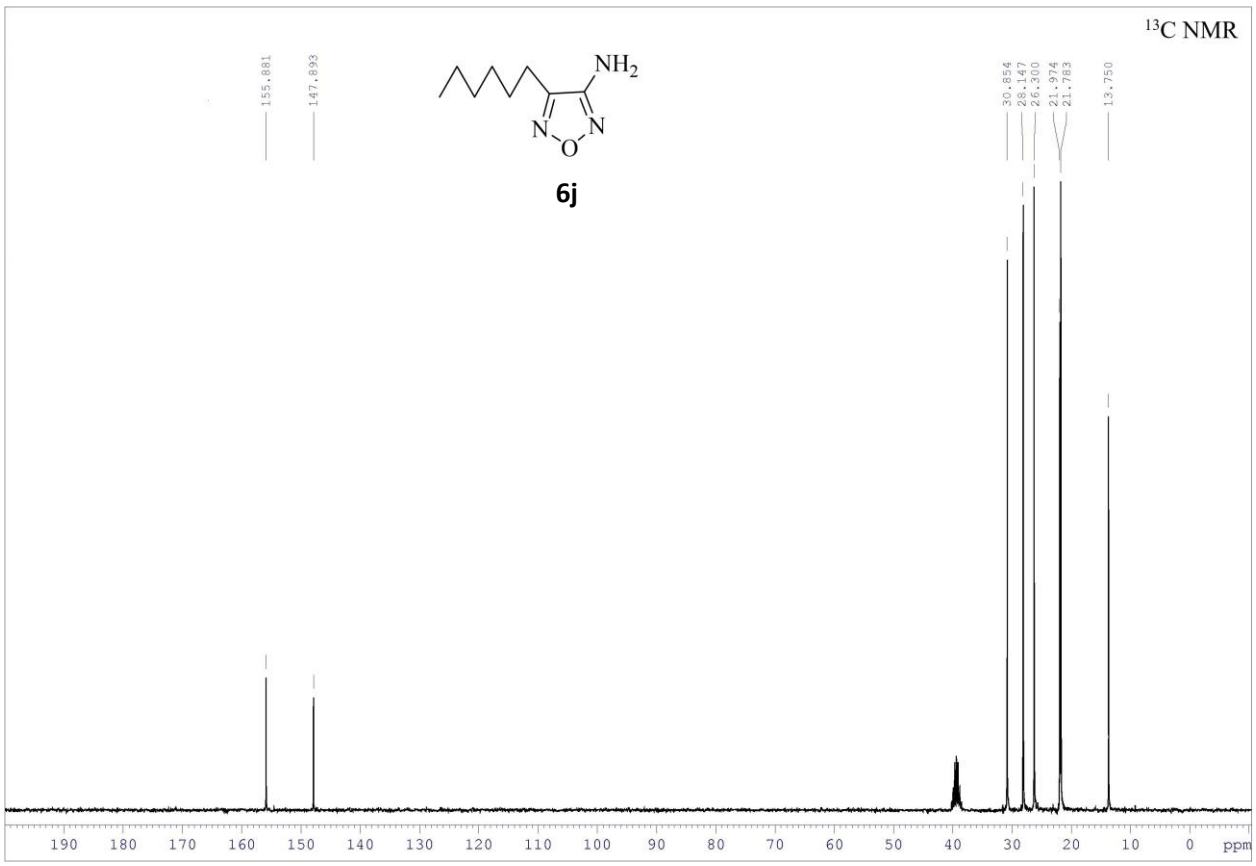
6i


^{13}C NMR
155.931
147.994
NH2
N
O
N
40.380
40.102
39.824
39.545
39.267
38.989
38.711
30.658
26.026
21.713
21.655
13.778
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

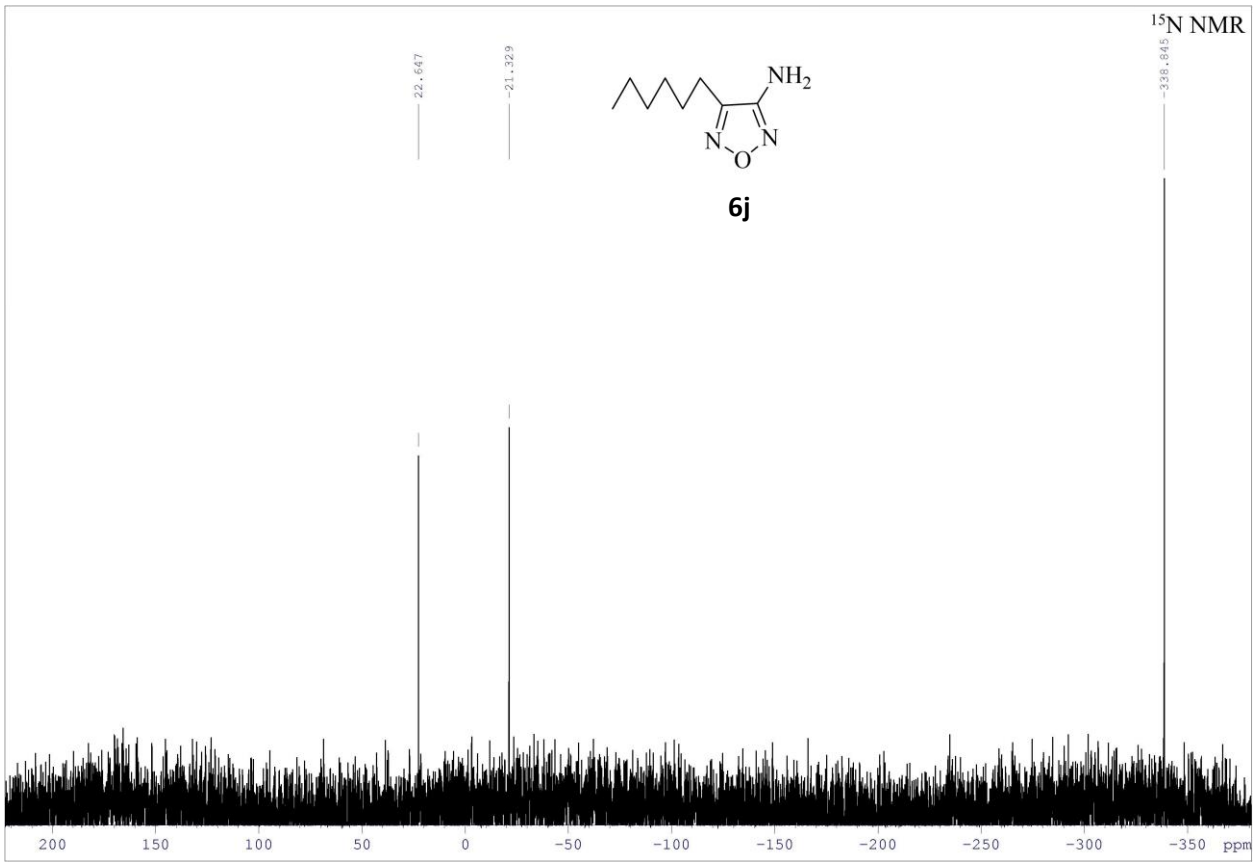
6i


^{1}H NMR
NH2
N
O
N
6.009
3.405
2.612
2.587
2.562
1.625
1.604
1.580
1.557
1.266
0.835
40
7.3
42
42
122
61
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
40.203
7.501
42.518
42.166
122.246
61.564

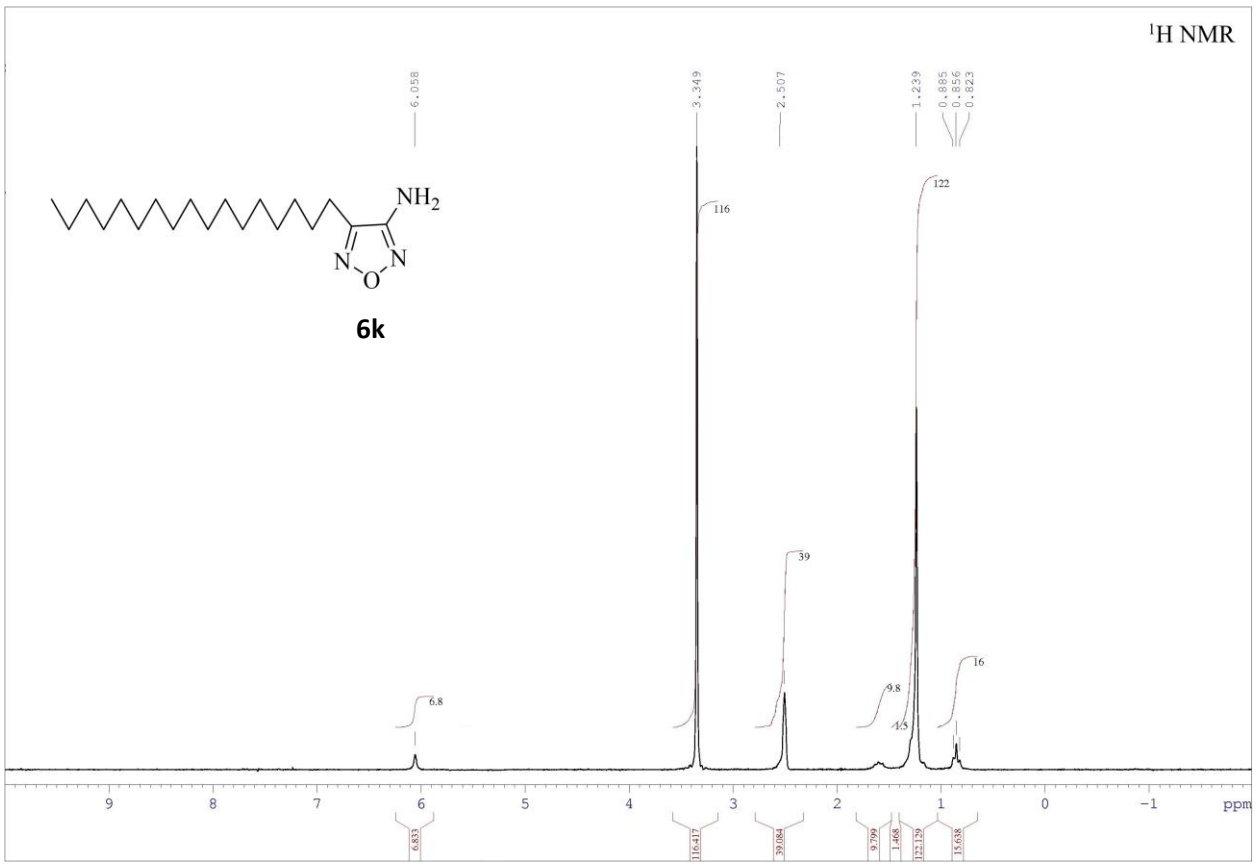
6j

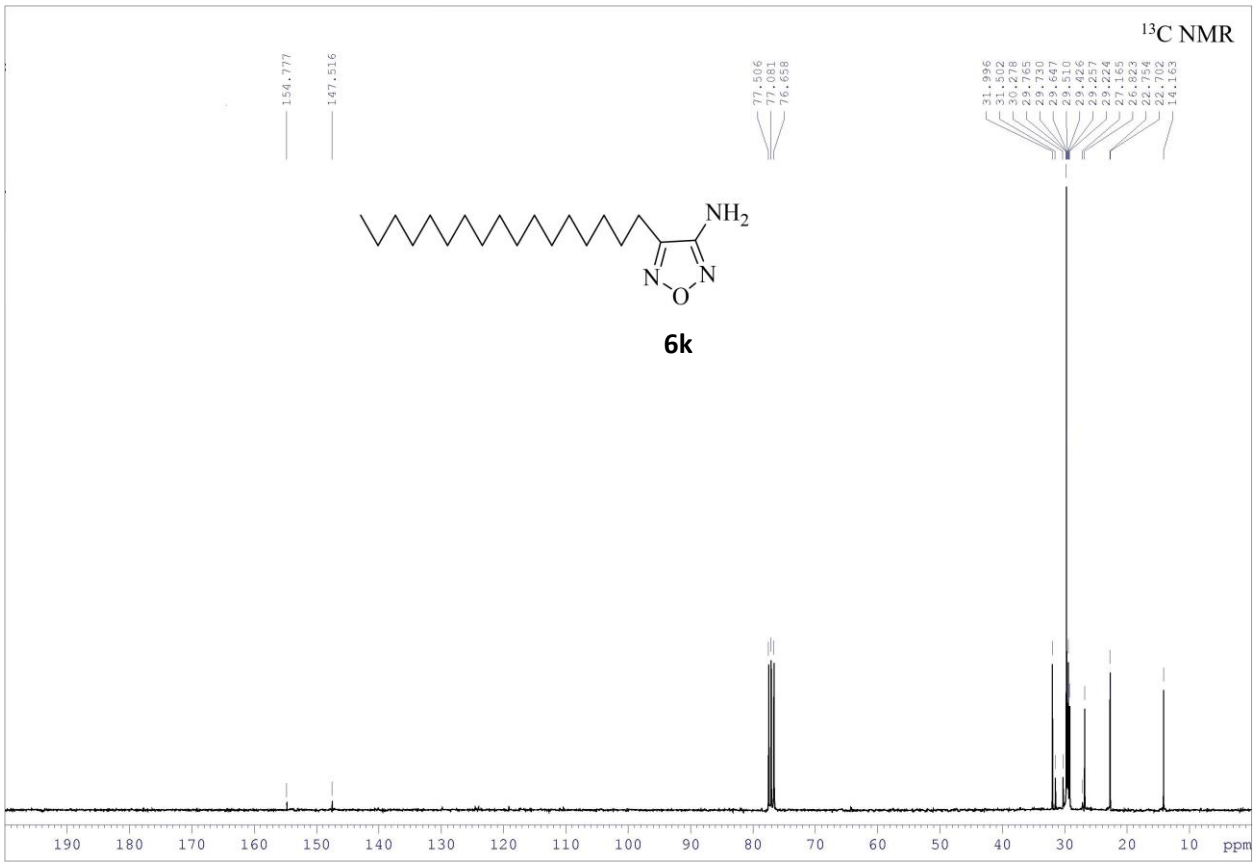

^{13}C NMR
155.881
147.893
NH2
N
O
N
30.854
28.147
26.300
21.974
21.783
13.750
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

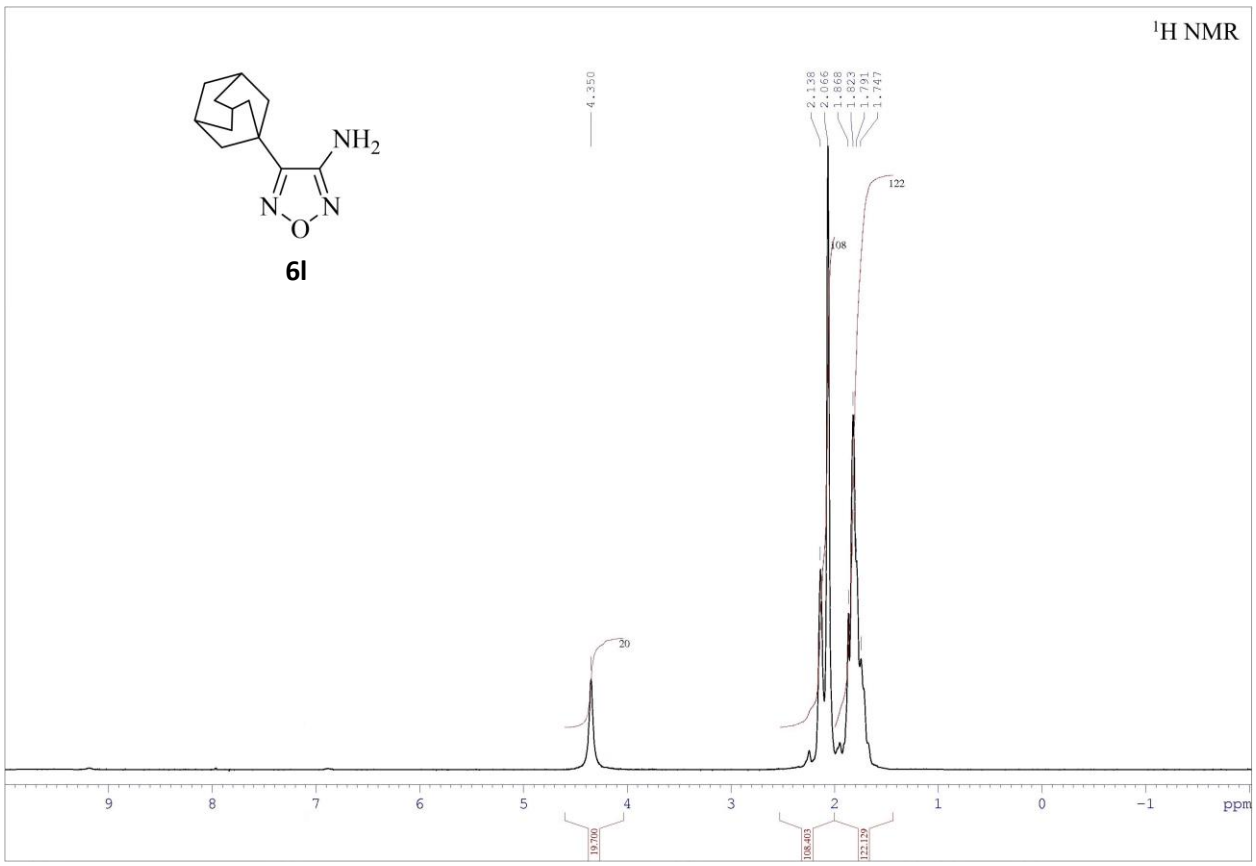
6j

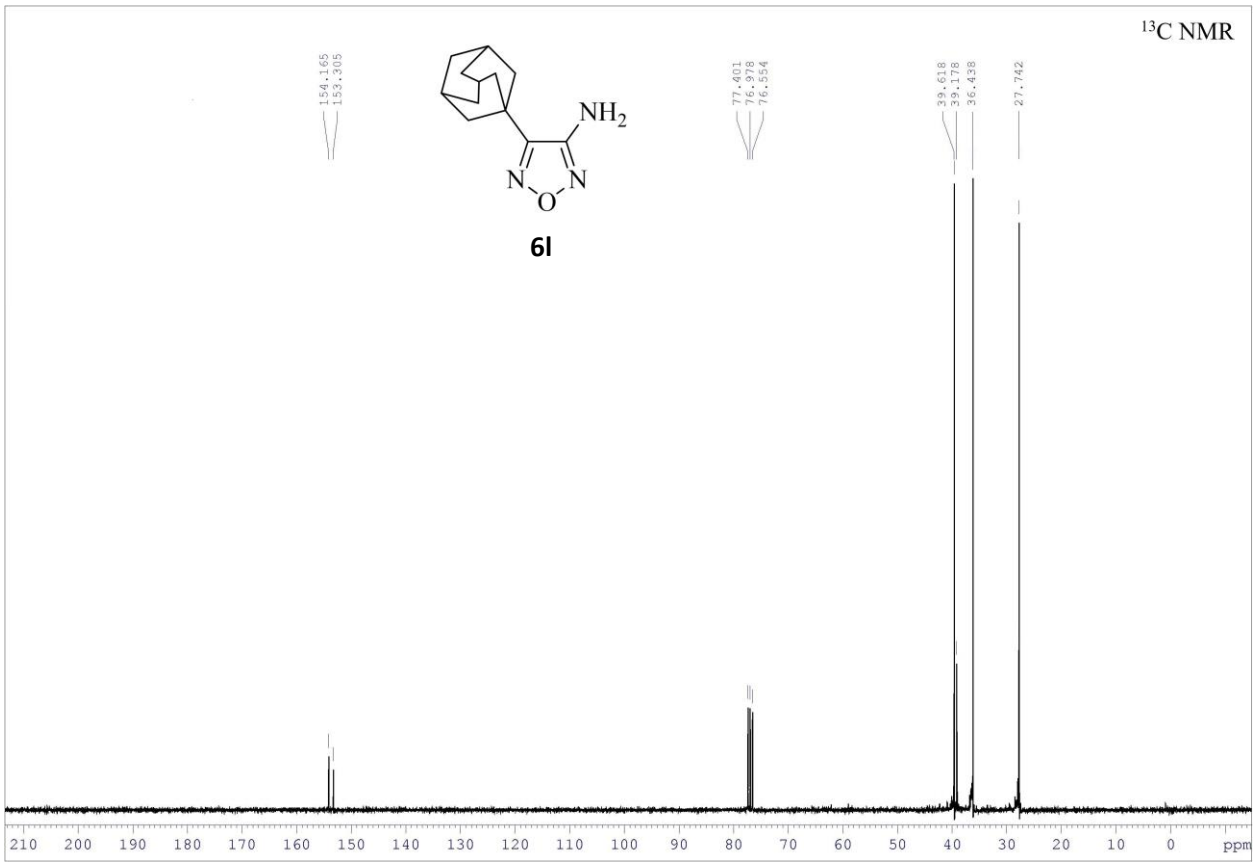

^{15}N NMR
22.647
-21.329
NH2
N
O
N
-338.845
200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm

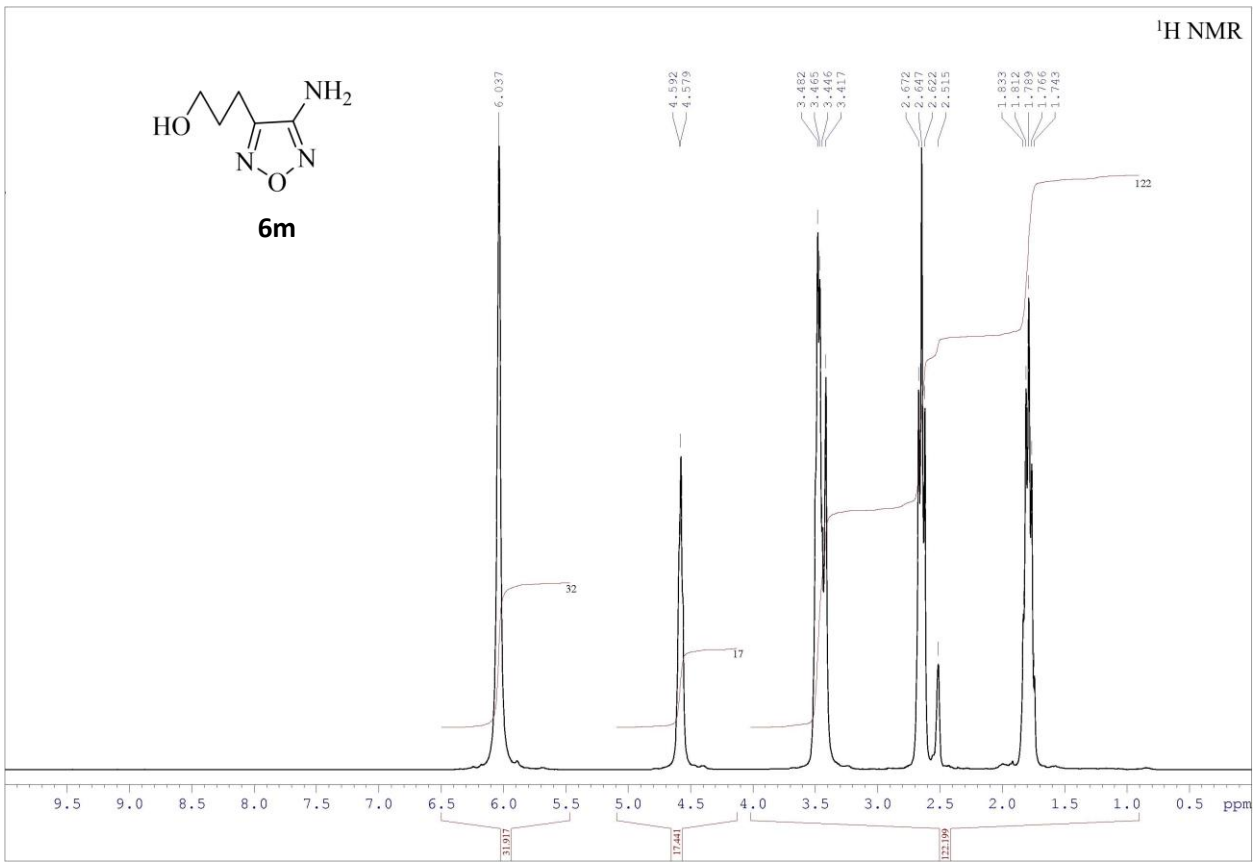
6j

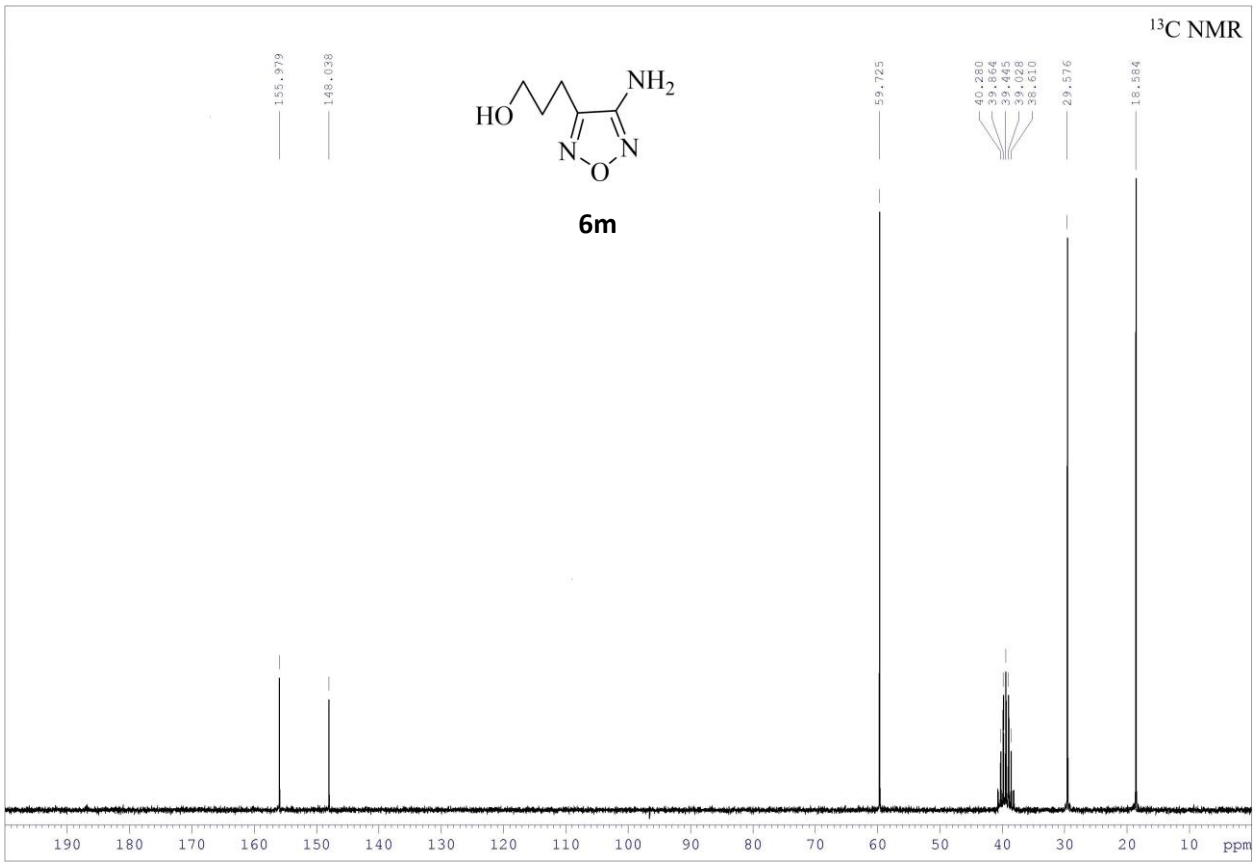

^{1}H NMR
6.058
3.349
2.507
1.239
0.885
0.856
0.823
NH2
N
O
N
6k
116
122
39
16
9.8
6.8
1.5
9
8
7
6
5
4
3
2
1
0
−1
ppm
6.833
116.417
39.084
9.799
1.468
122.129
15.638


^{13}C NMR
154.777
147.516
77.506
77.081
76.658
31.996
31.502
30.278
29.765
29.730
29.647
29.510
29.426
29.257
29.224
27.165
26.823
22.754
22.702
14.163
NH2
N
O
N
6k
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

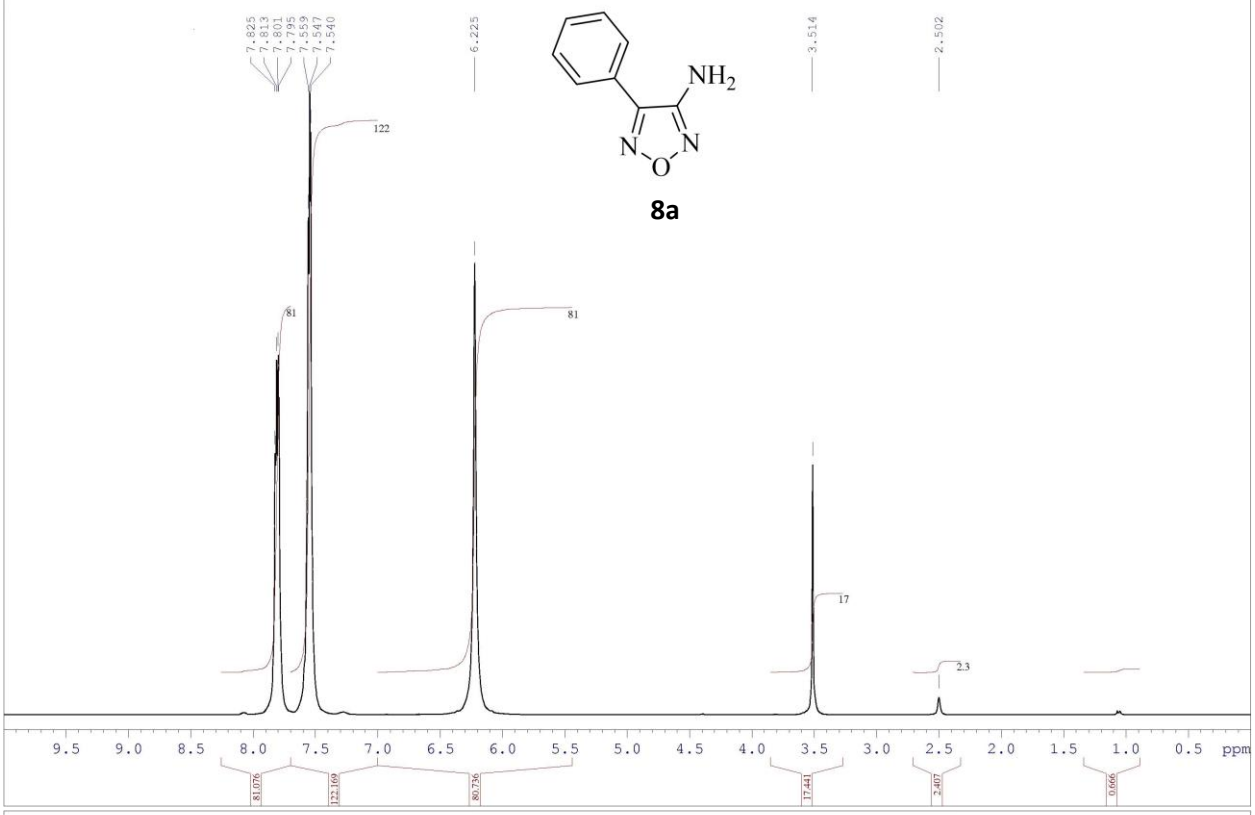

^{1}H NMR
NH2
N
O
N
6l
4.350
2.138
2.066
1.868
1.823
1.791
1.747
122
108
20
19.700
108.403
122.129
9
8
7
6
5
4
3
2
1
0
−1
ppm


^{13}C NMR
154.165
153.305
NH2
N
O
N
6l
77.401
76.978
76.554
39.618
39.178
36.438
27.742
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


^{1}H NMR
HO
NH$_2$
N
O
N
6m
6.037
4.592
4.579
3.482
3.465
3.446
3.417
2.672
2.647
2.622
2.515
1.833
1.812
1.789
1.766
1.743
32
17
122
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
31.917
17.441
122.199

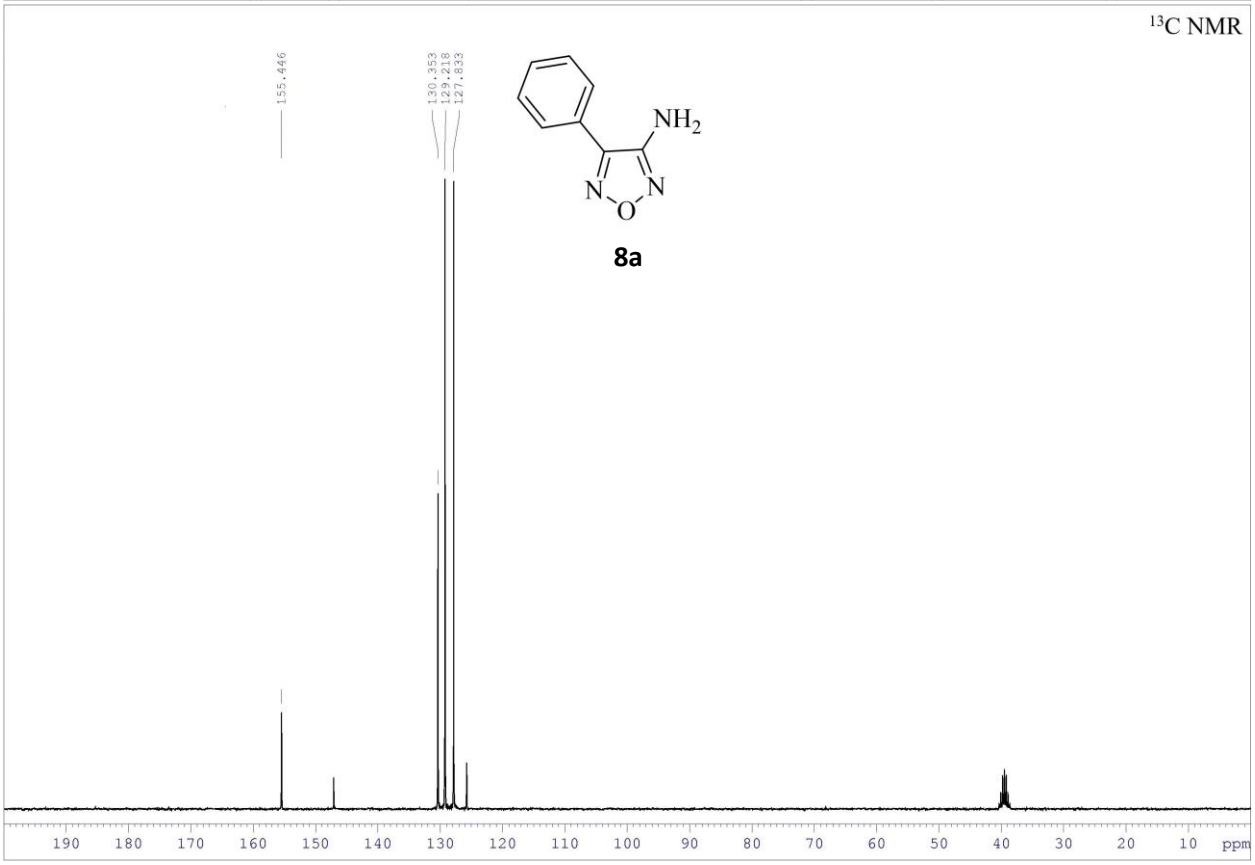

^{13}C NMR
HO
NH$_2$
N
O
N
6m
155.979
148.038
59.725
40.280
39.864
39.445
39.028
38.610
29.576
18.584
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

^{1}H NMR

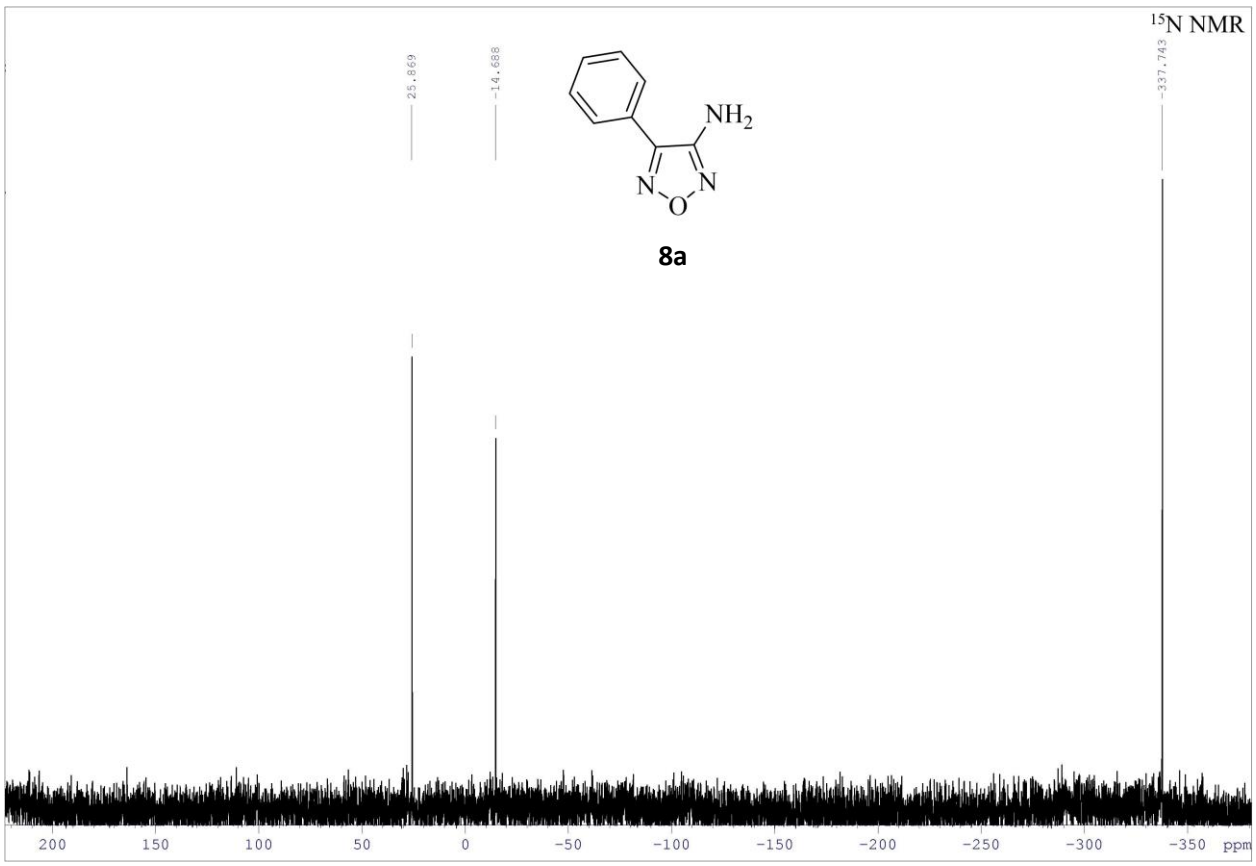


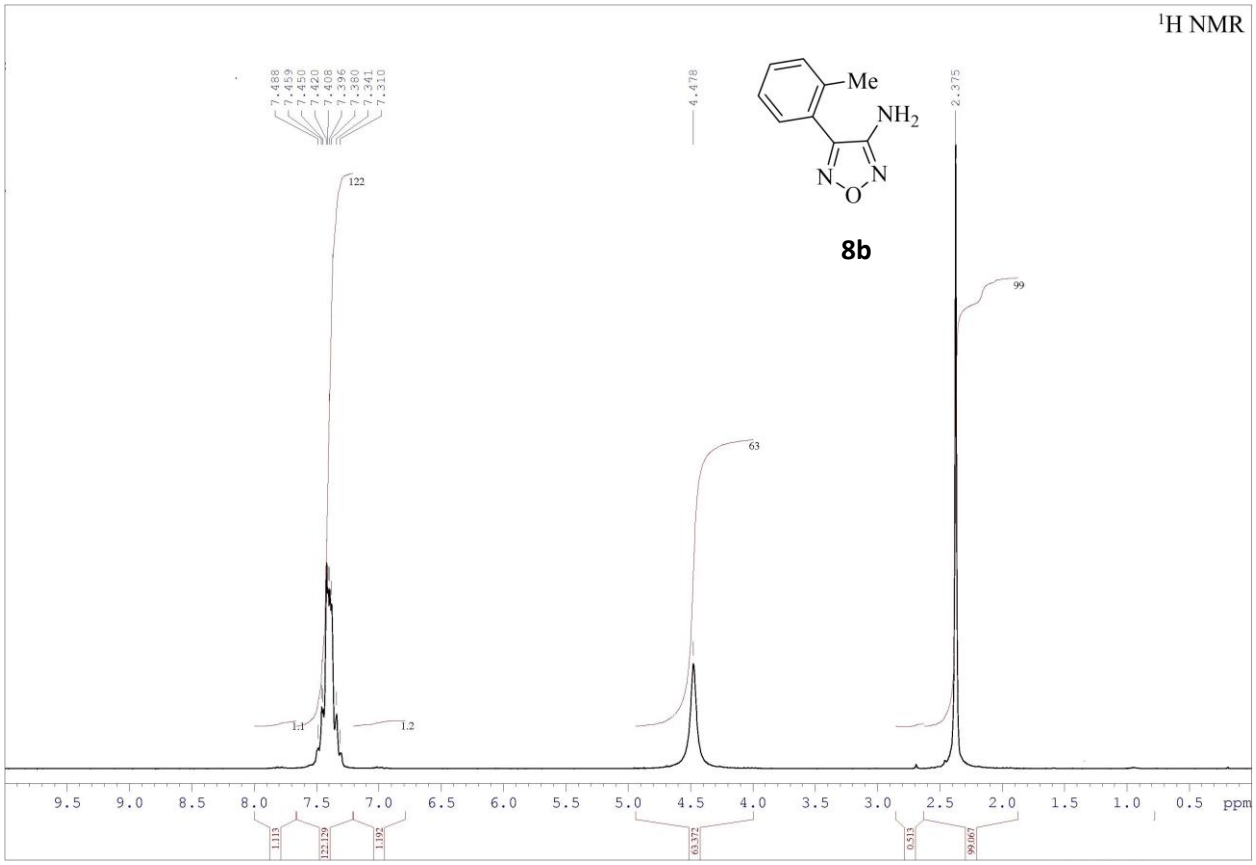
8a

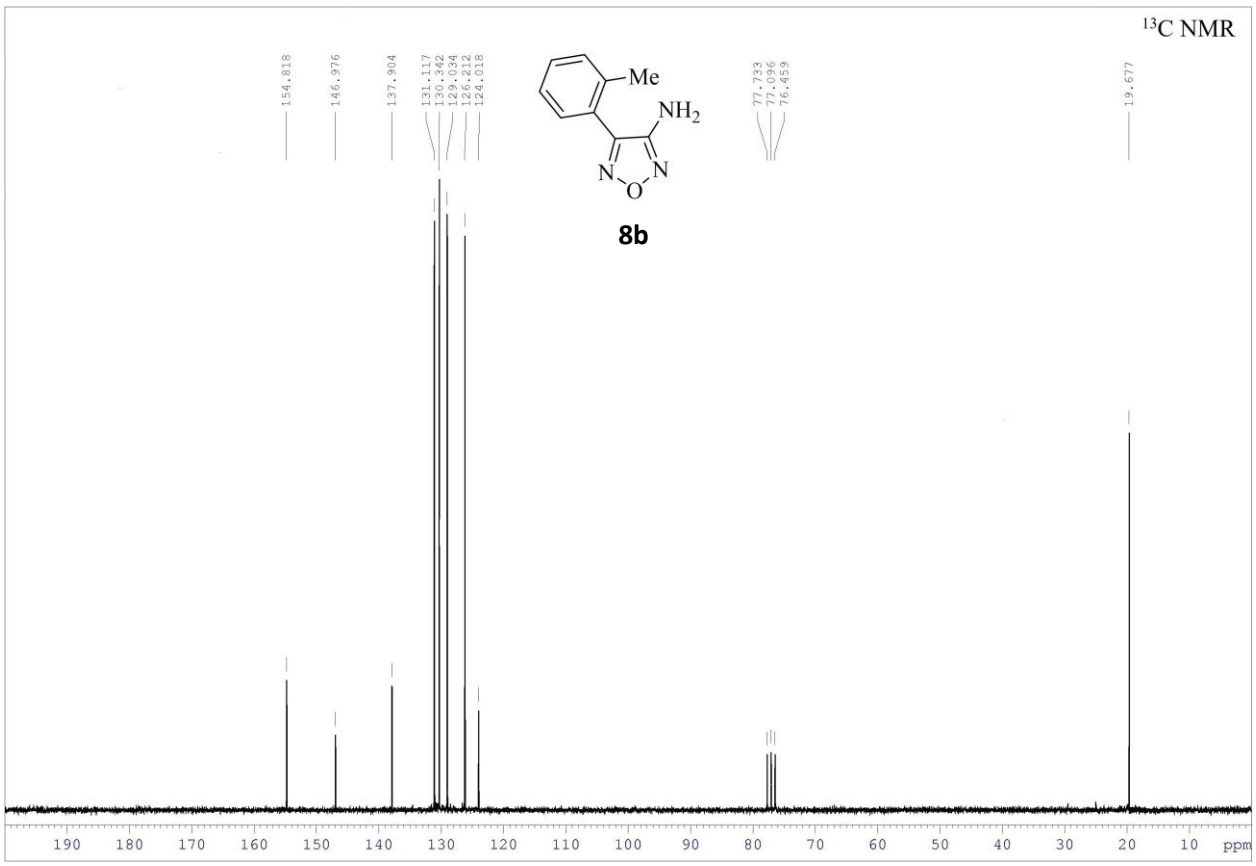
^{13}C NMR

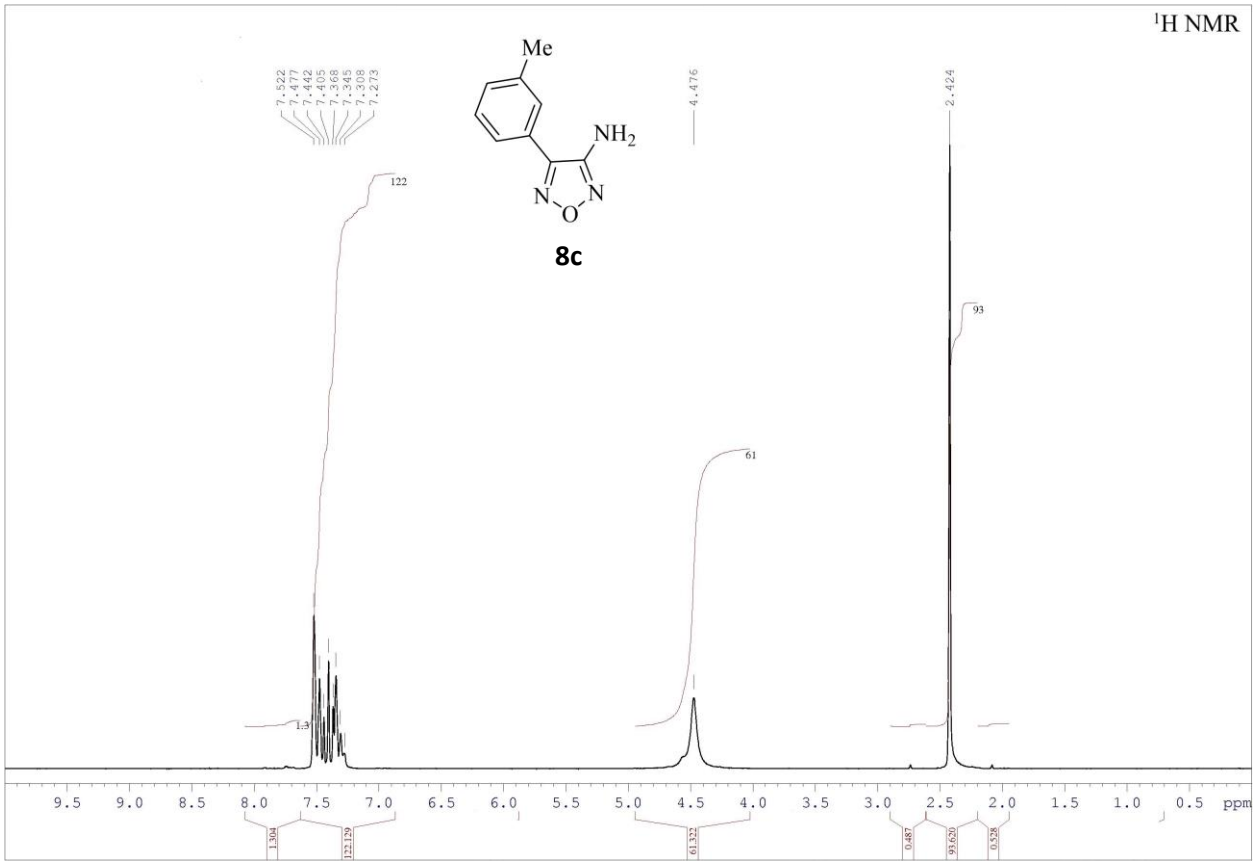


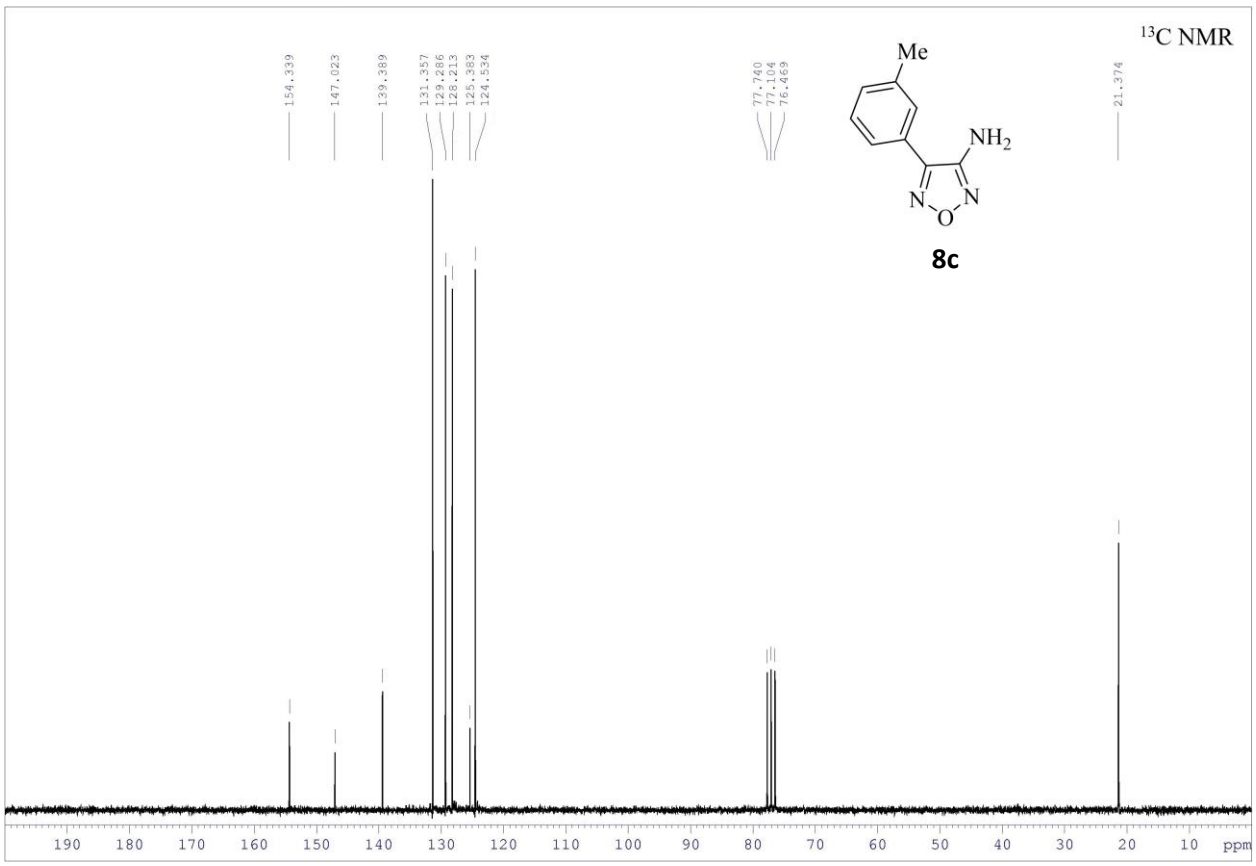
8a


^{15}N NMR
25.869
-14.688
-337.743
NH2
N
O
N
8a
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

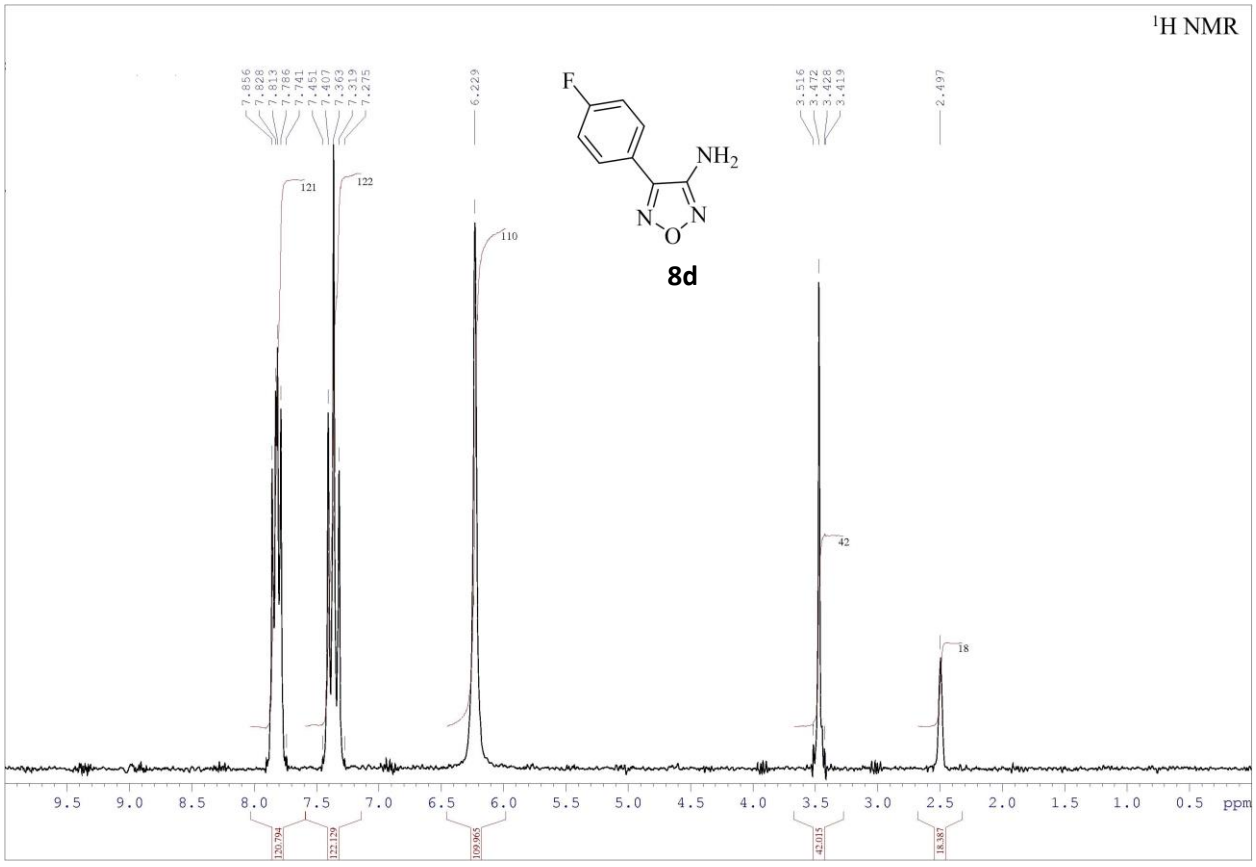

^{1}H NMR
7.488
7.459
7.450
7.420
7.408
7.396
7.380
7.341
7.310
4.478
2.375
Me
NH2
N
O
N
8b
122
63
99
1.1
1.2
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.113
122.129
1.192
63.372
0.513
99.067


^{13}C NMR
154.818
146.976
137.904
131.117
130.342
129.034
126.212
124.018
77.733
77.096
76.459
19.677
Me
NH2
N
O
N
8b
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

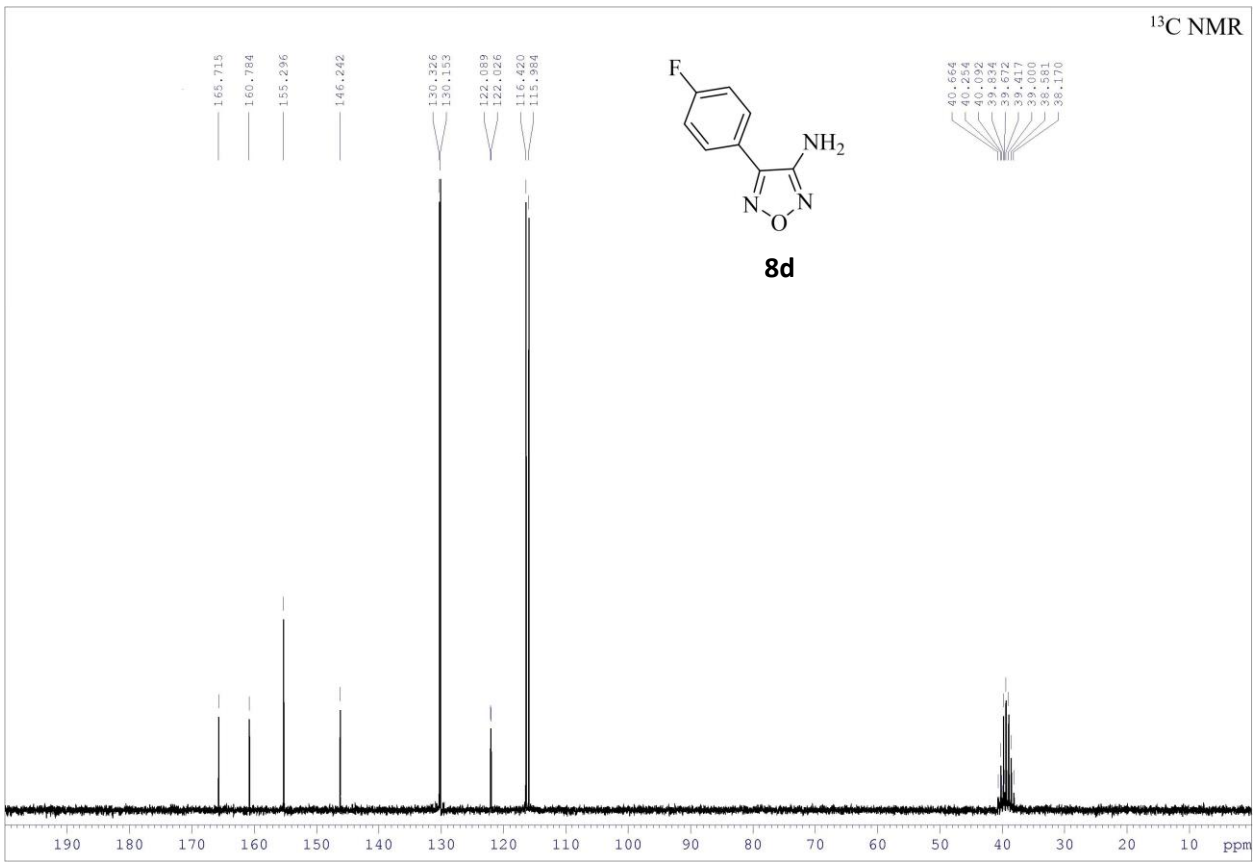

^{1}H NMR
7.522
7.477
7.442
7.405
7.368
7.345
7.308
7.273
4.476
2.424
Me
NH2
N
O
N
8c
122
61
93
1.3
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.304
122.129
61.322
0.487
93.620
0.528

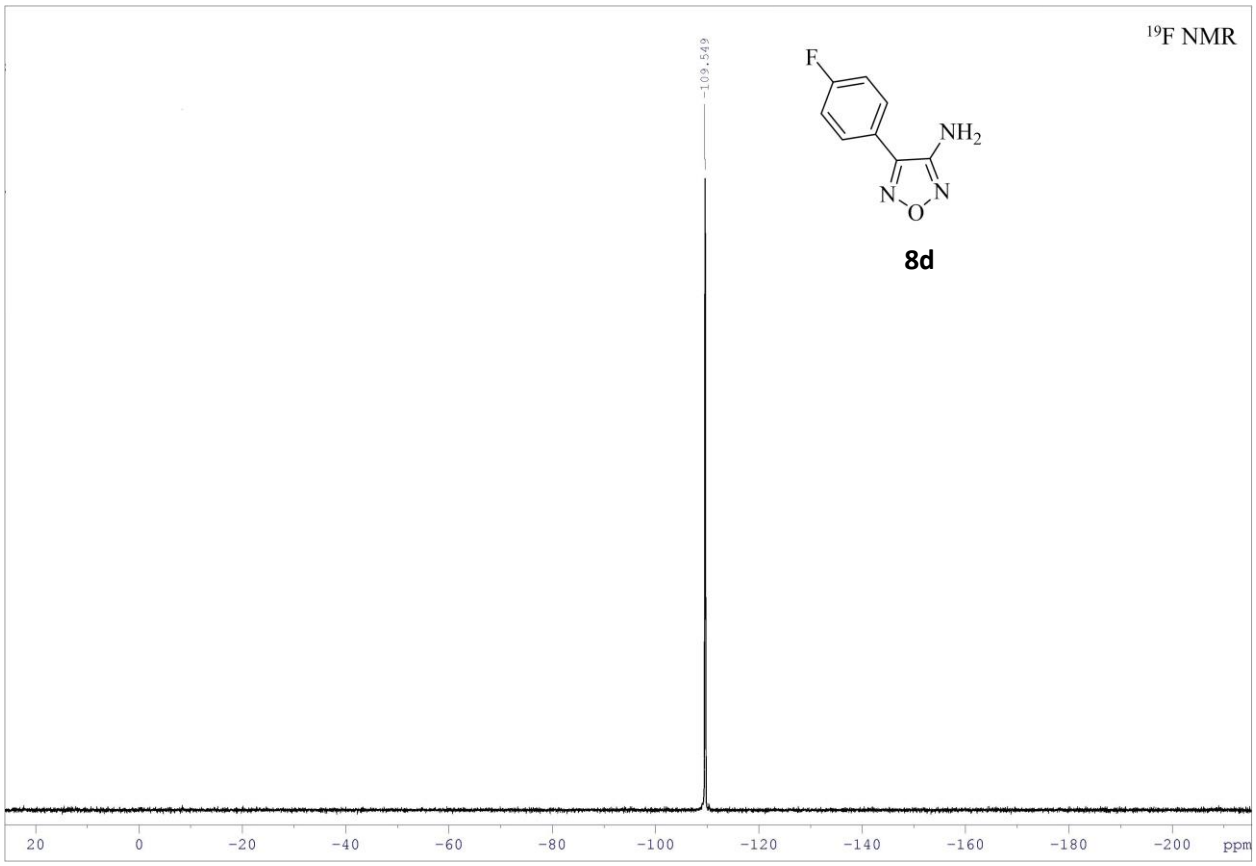

^{13}C NMR
154.339
147.023
139.389
131.357
129.286
128.213
125.383
124.534
77.740
77.104
76.469
21.374
Me
NH$_2$
N
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

8c

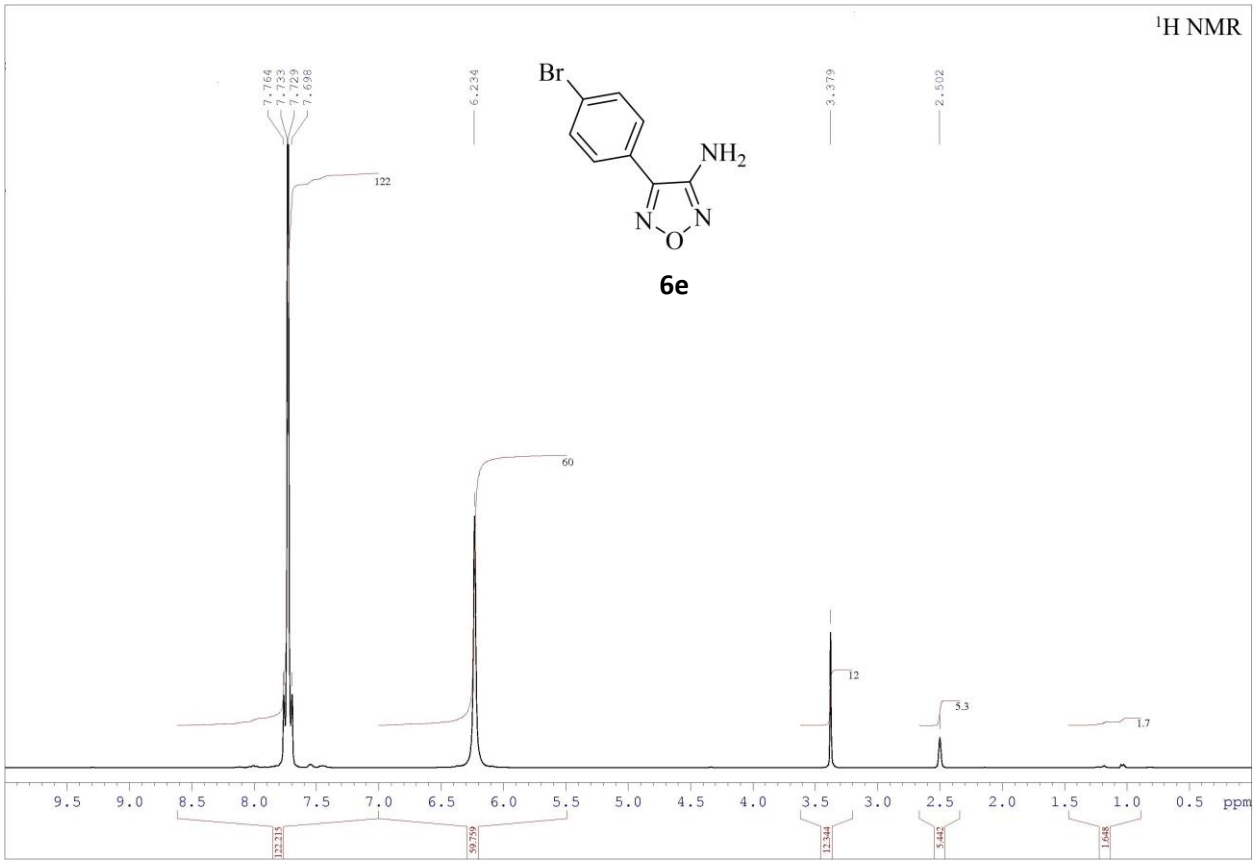

^{1}H NMR
7.856
7.828
7.813
7.786
7.741
7.451
7.407
7.363
7.319
7.275
6.229
3.516
3.472
3.428
3.419
2.497
F
NH$_2$
N
O
N
121
122
110
42
18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
120.794
122.129
109.965
42.015
18.387

8d


^{13}C NMR
165.715
160.784
155.296
146.242
130.326
130.153
122.089
122.026
116.420
115.984
40.664
40.254
40.092
39.834
39.672
39.417
39.000
38.581
38.170
F
NH2
N
O
N
8d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

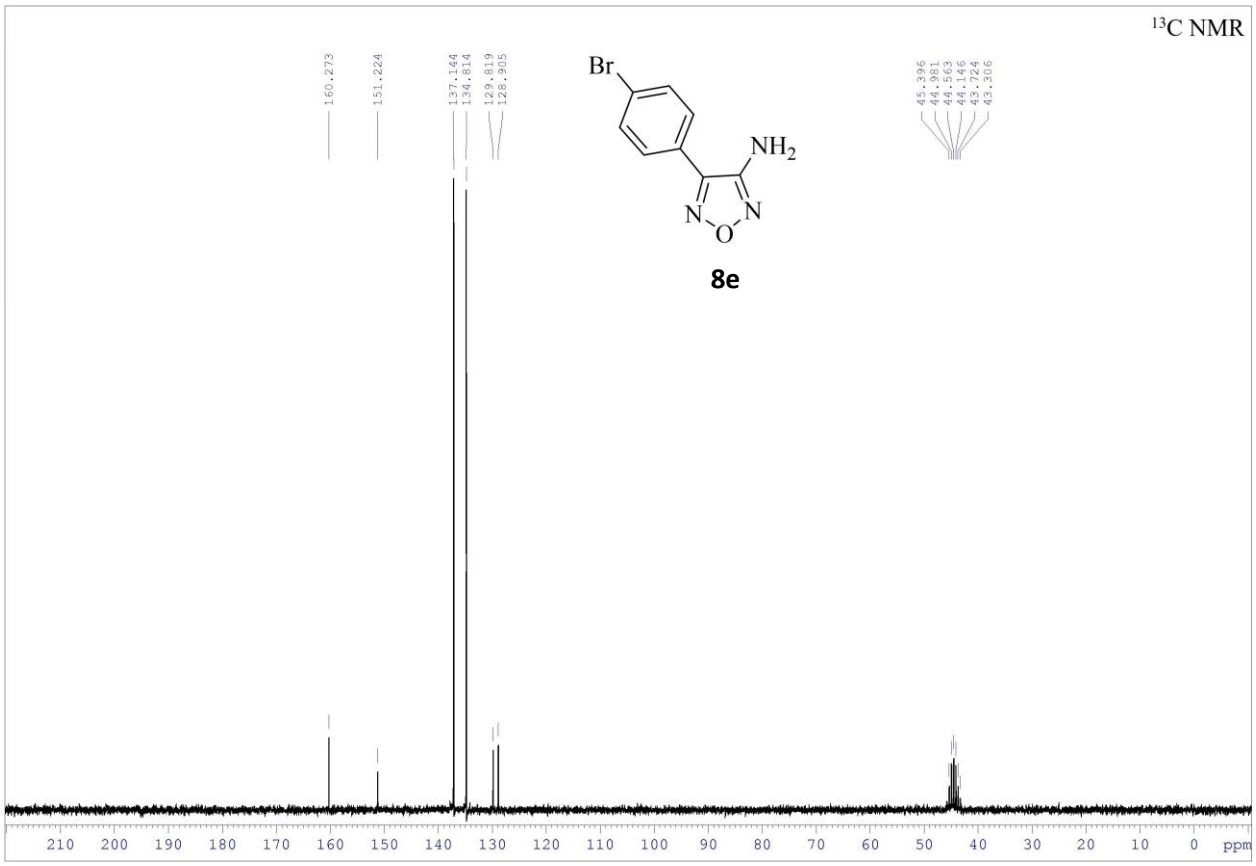

^{19}F NMR
-109.549
F
NH2
N
O
N
8d
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

^{1}H NMR

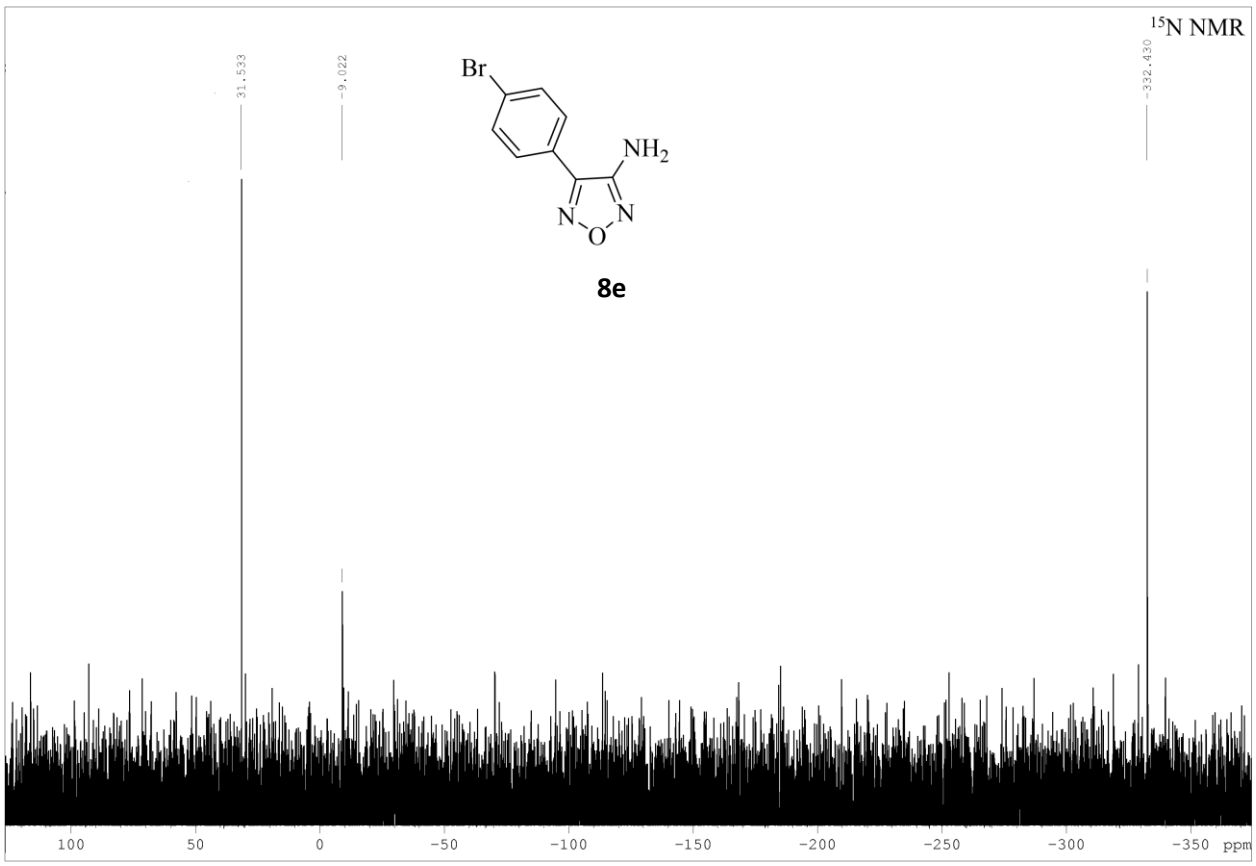


6e

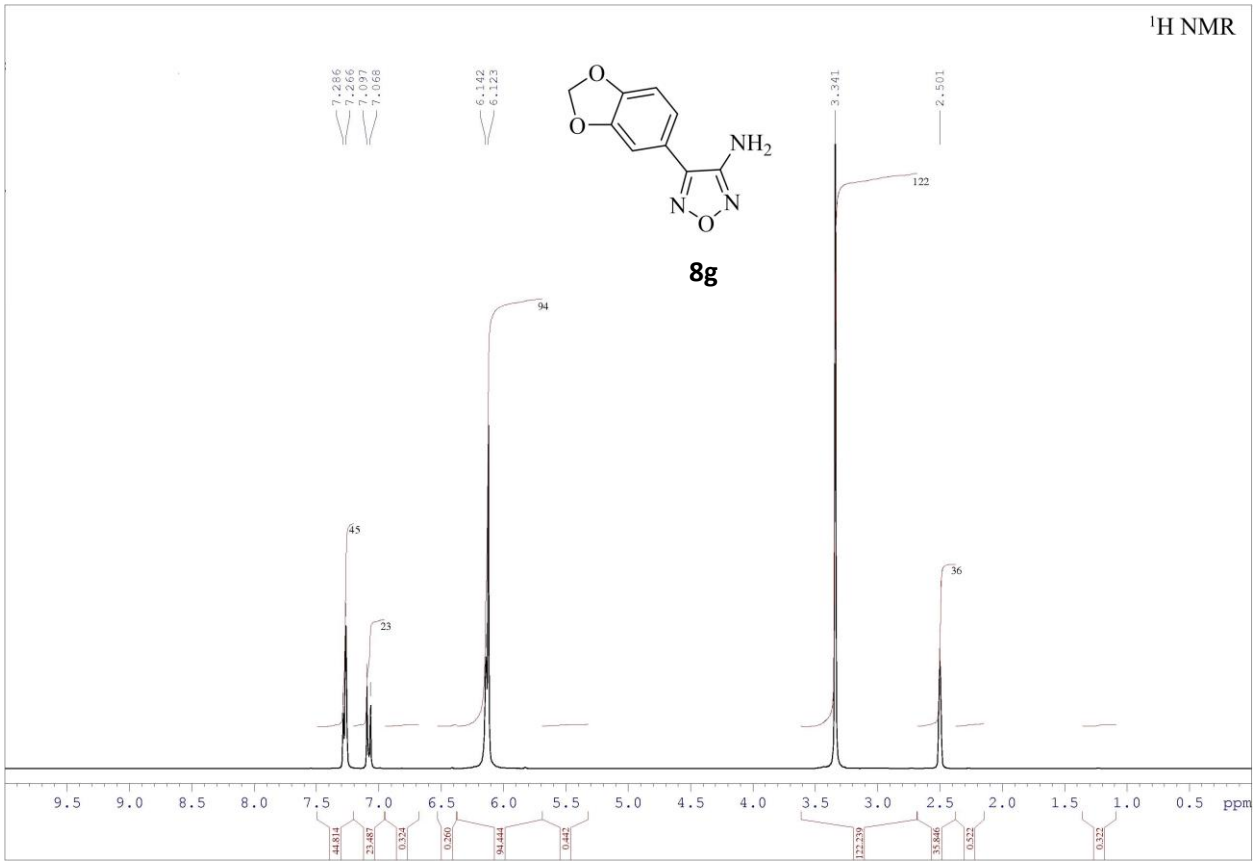
^{13}C NMR



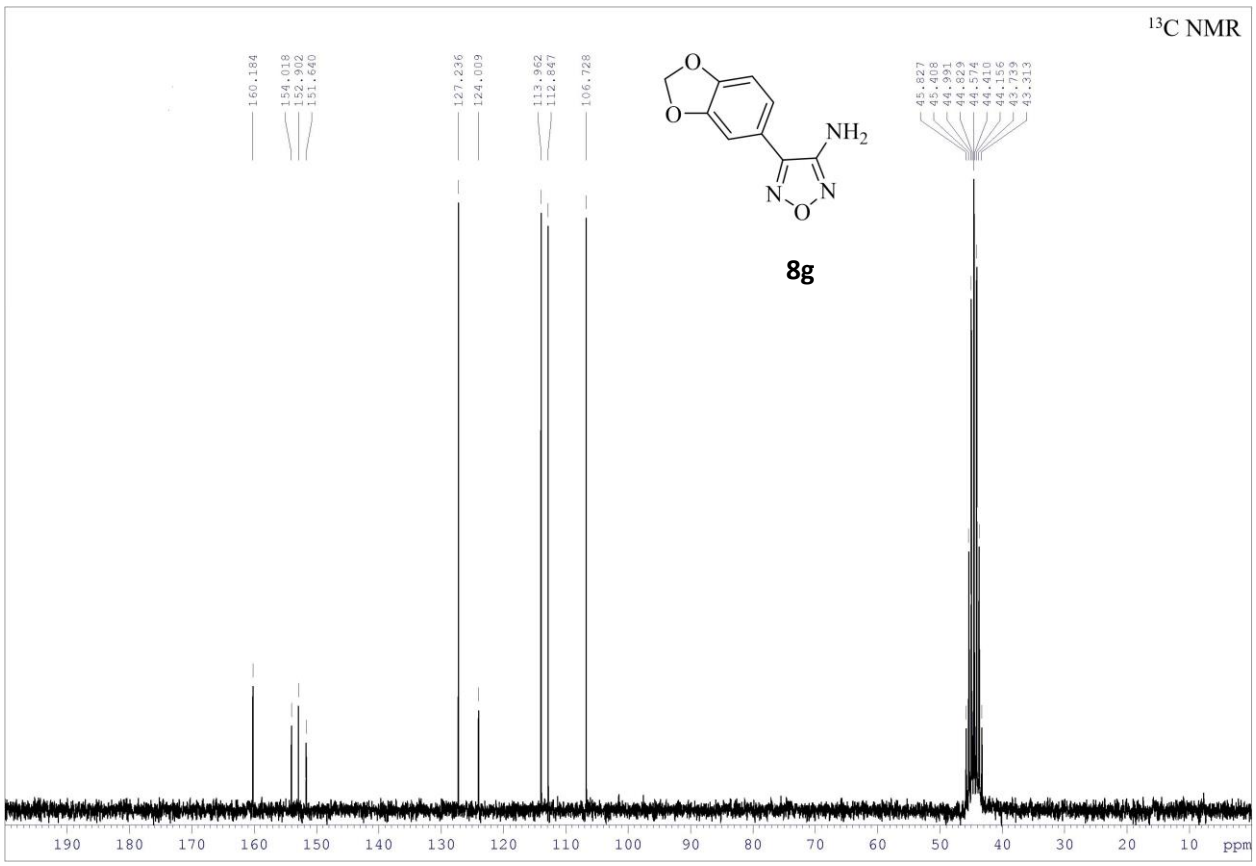
8e

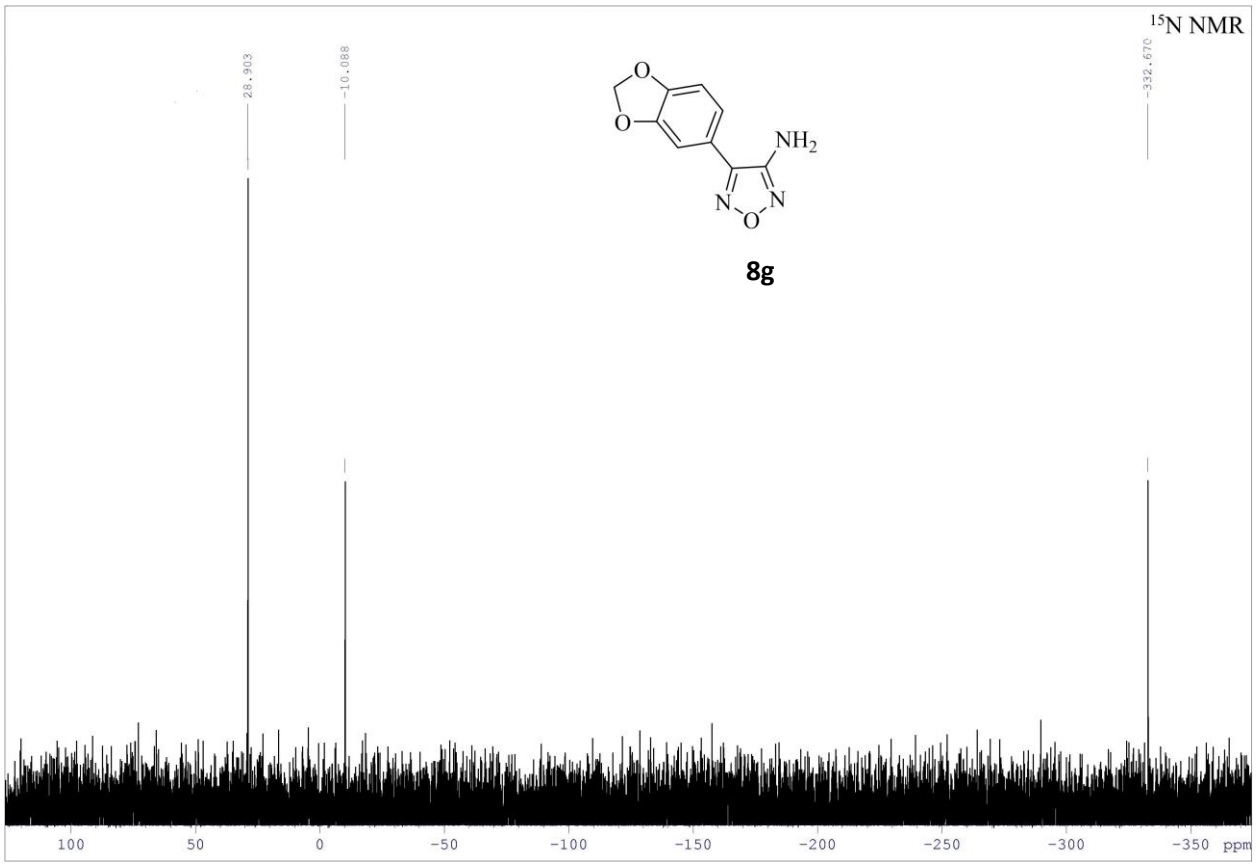

^{15}N NMR
31.533
-9.022
-332.430
Br
NH$_2$
N
O
N
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

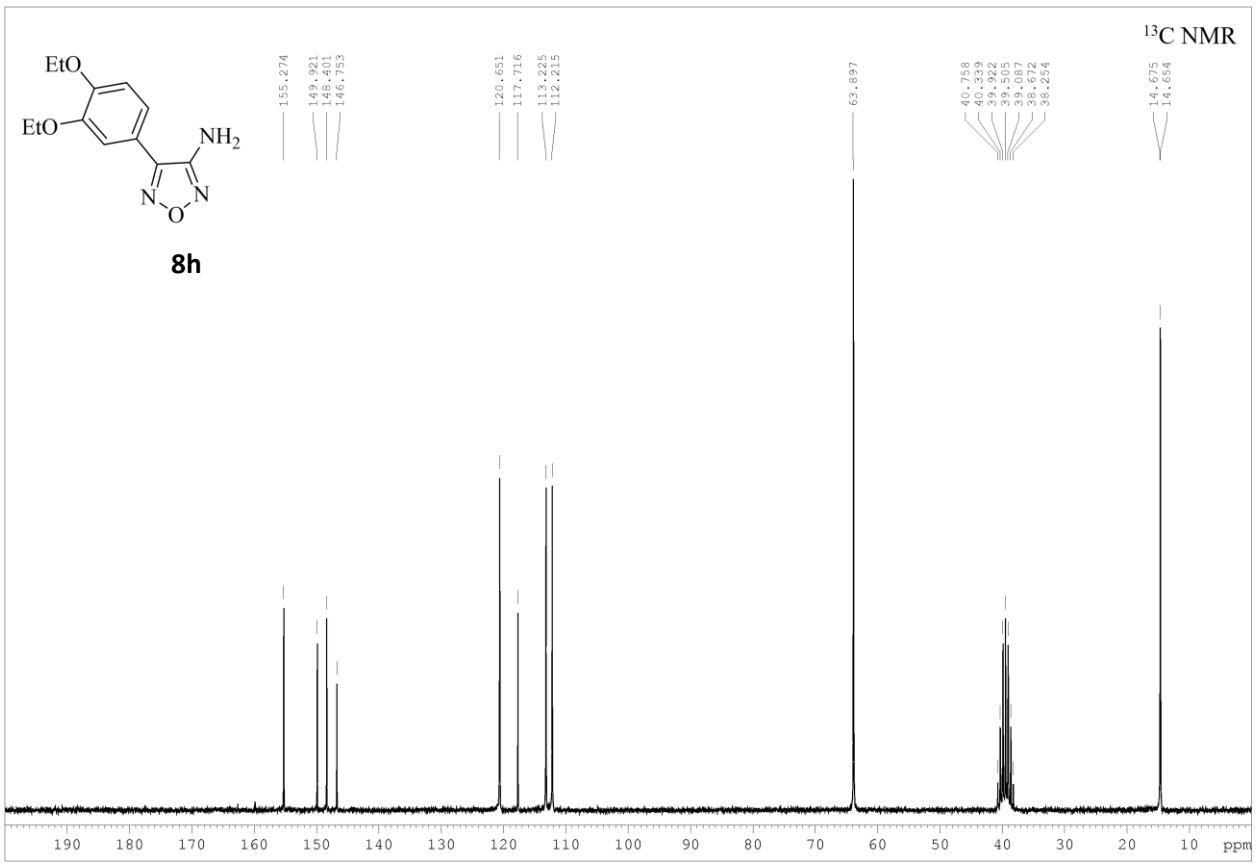
8e

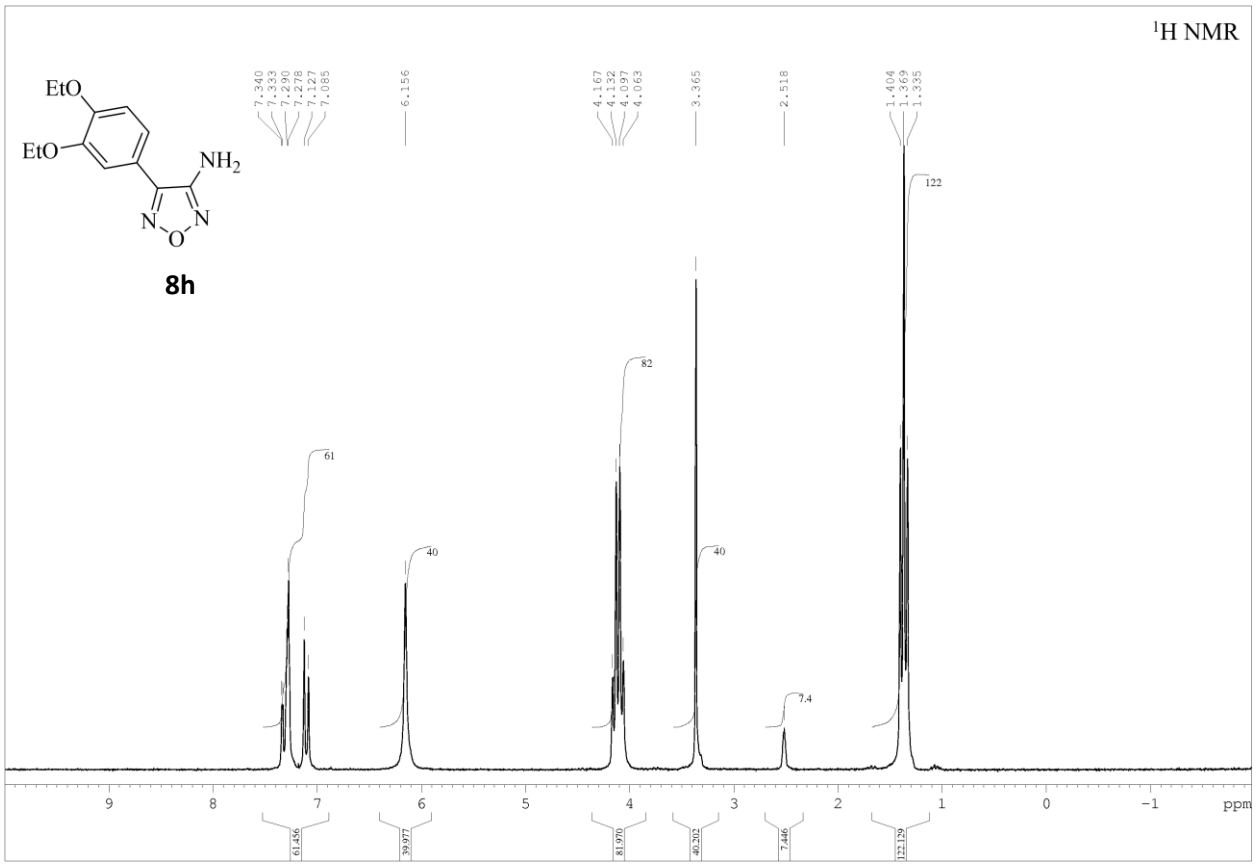

^{1}H NMR
7.286
7.266
7.097
7.068
6.142
6.123
3.341
2.501
O
O
NH$_2$
N
O
N
122
94
45
23
36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.814
3.487
0.324
0.260
9.444
0.442
122.239
35.846
0.322

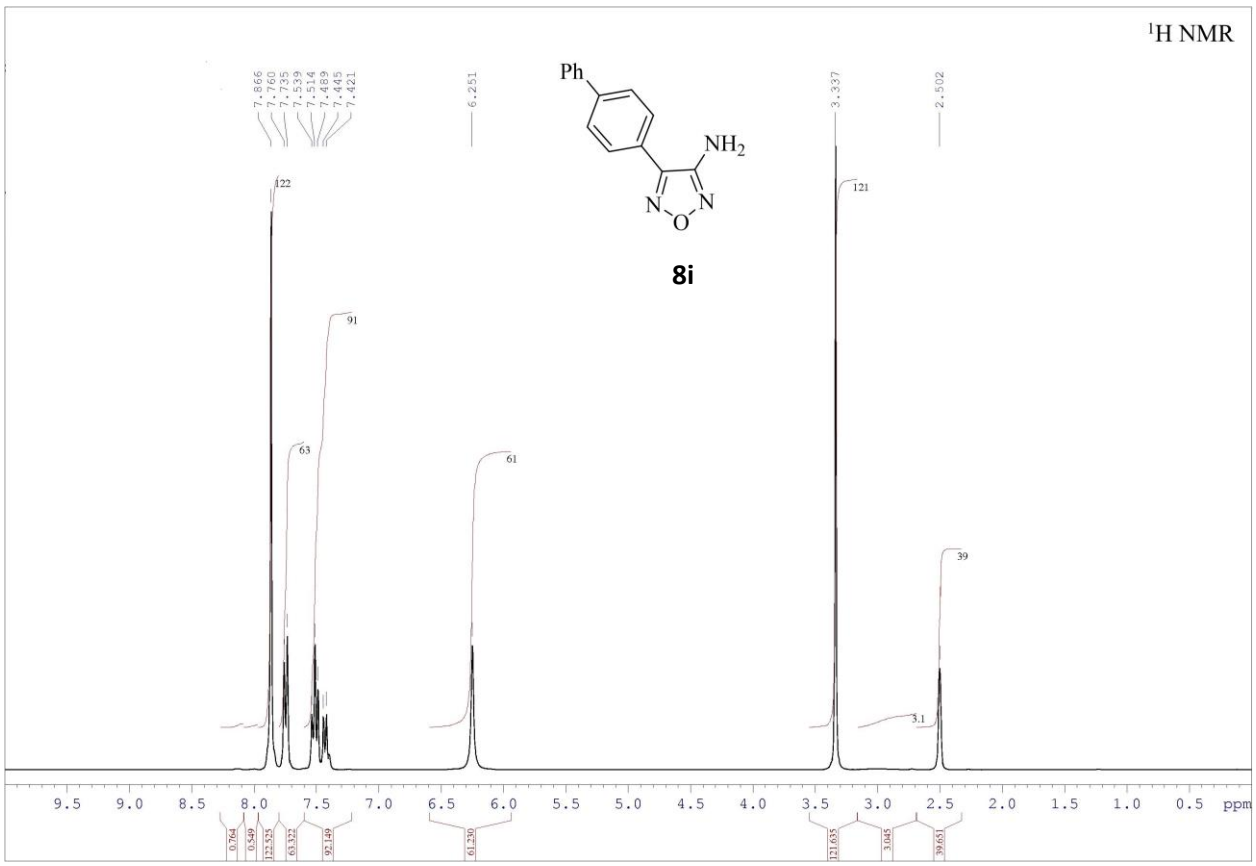
8g

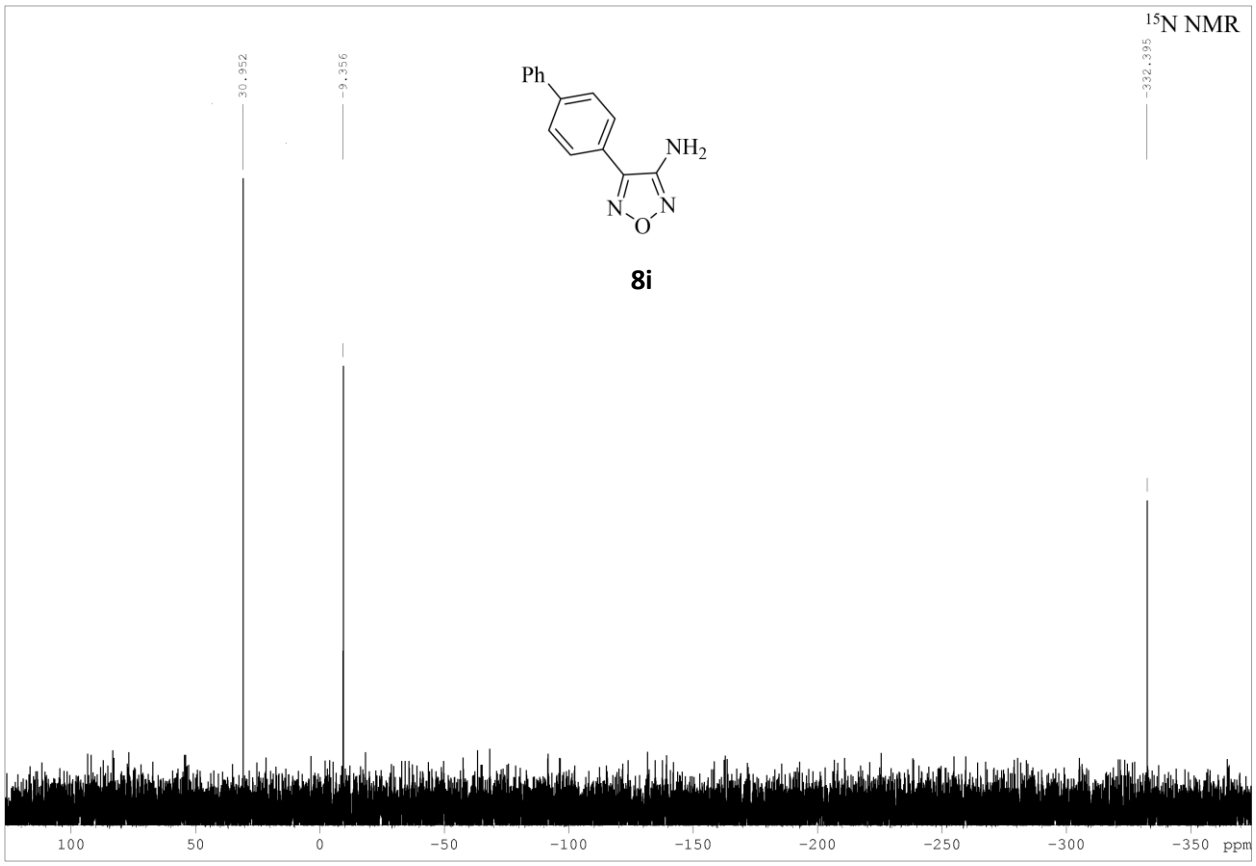

^{13}C NMR
160.184
154.018
152.902
151.640
127.236
124.009
113.962
112.847
106.728
45.827
45.408
44.991
44.829
44.574
44.410
44.156
43.739
43.313
NH2
8g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

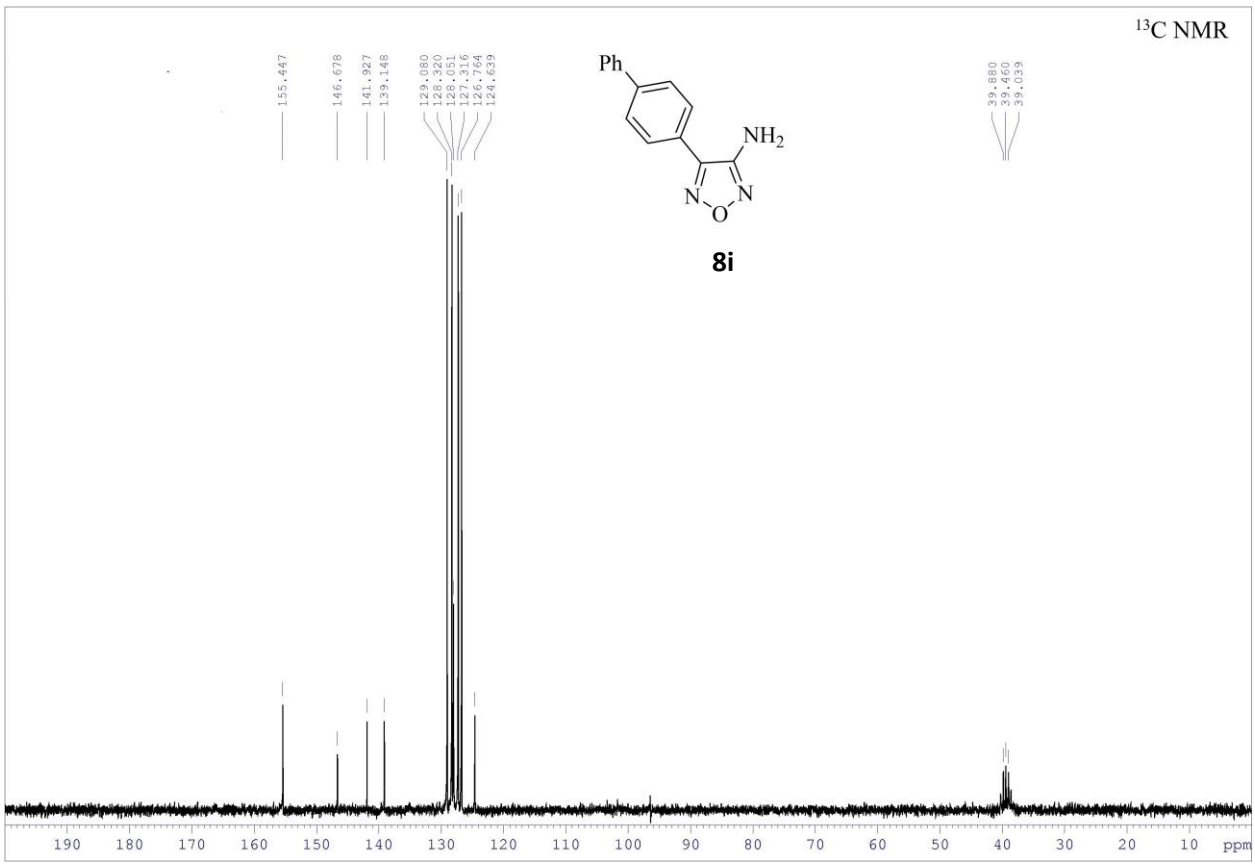

^{15}N NMR
28.903
-10.088
-332.670
NH2
8g
100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm


^{13}C NMR
EtO
EtO
NH$_2$
N
O
N
8h
155.274
149.921
148.401
146.753
120.651
117.716
113.225
112.215
63.897
40.758
40.339
39.922
39.505
39.087
38.672
38.254
14.675
14.654
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

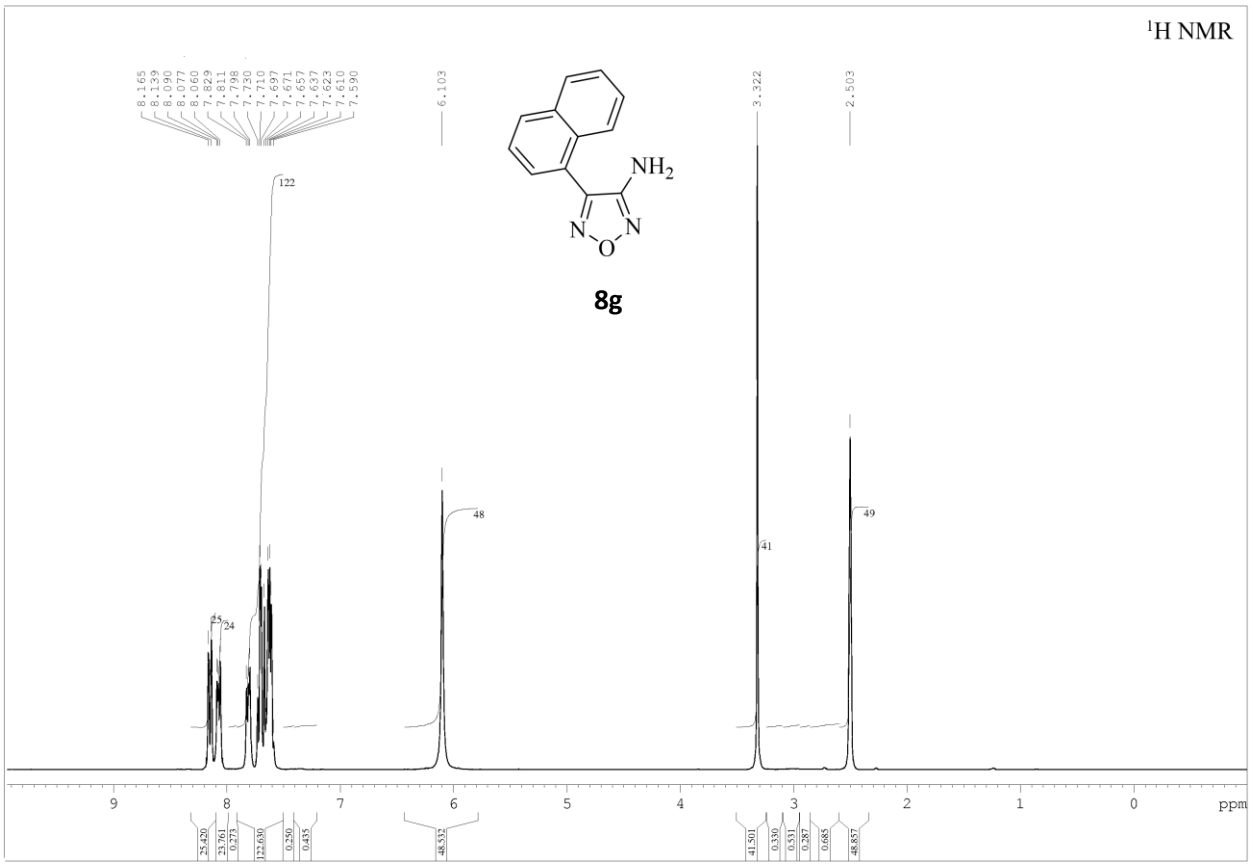

^{1}H NMR
EtO
EtO
NH$_2$
N
O
N
8h
7.340
7.333
7.290
7.278
7.227
7.085
6.156
4.167
4.132
4.097
4.063
3.365
2.518
1.404
1.369
1.335
61
40
82
40
7.4
122
9 8 7 6 5 4 3 2 1 0 −1 ppm
61.456
39.977
81.970
40.202
7.446
122.129


^{1}H NMR
7.866
7.760
7.735
7.539
7.514
7.489
7.445
7.421
6.251
3.337
2.502
Ph
NH$_2$
N
O
N
8i
122
91
63
61
121
39
3.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.764
0.549
125.535
63.322
92.149
61.230
121.635
3.045
39.651

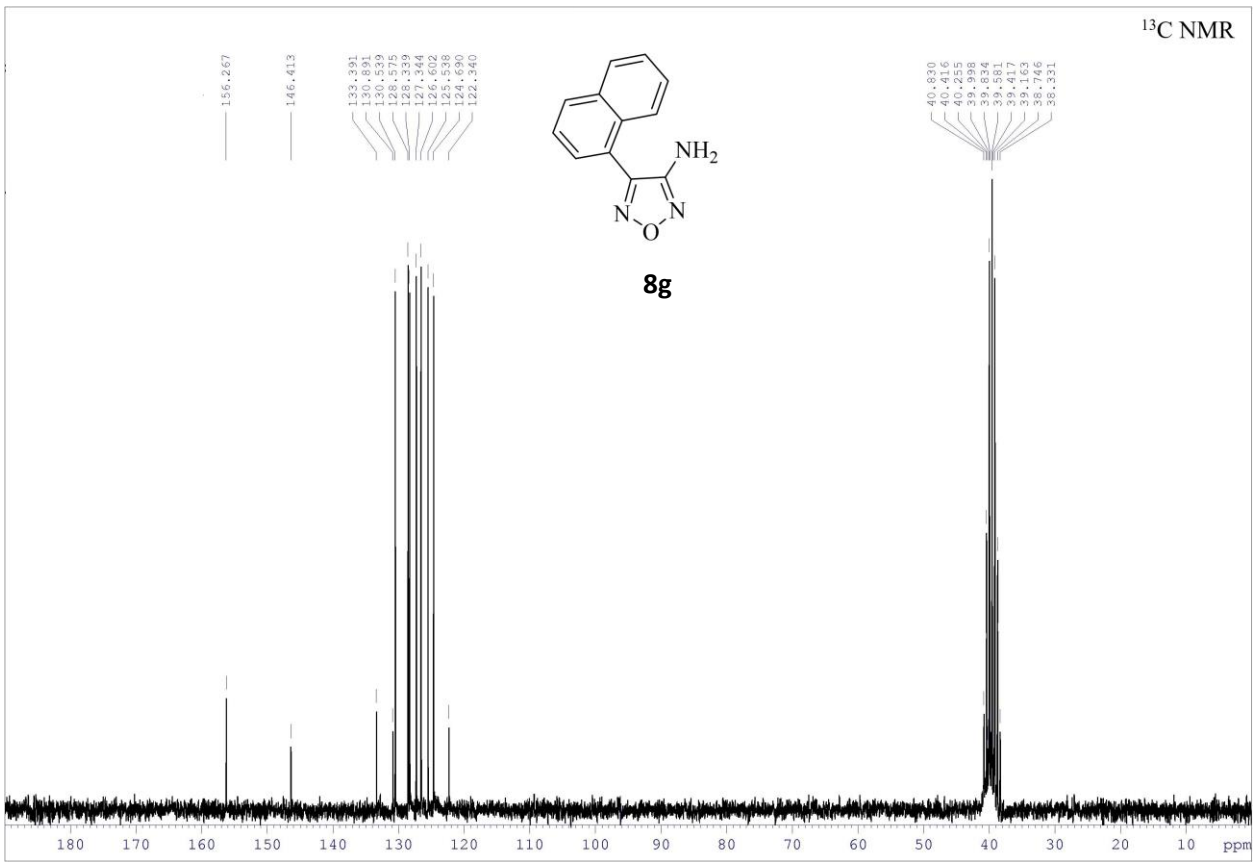

^{15}N NMR
30.952
-9.356
-332.395
Ph
NH$_2$
N
O
N
8i
100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm

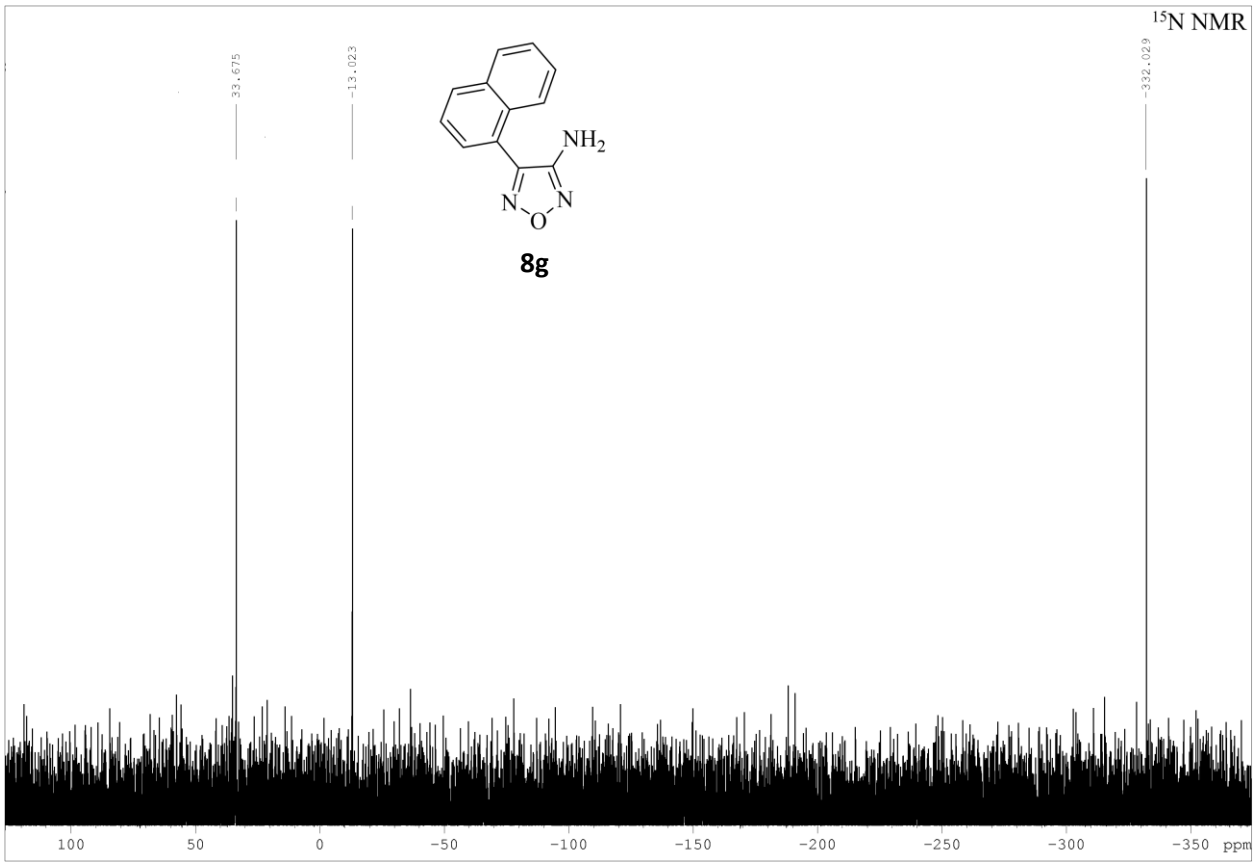

^{13}C NMR
155.447
146.678
141.927
139.148
129.080
128.320
128.051
127.316
126.764
124.639
39.880
39.460
39.039
Ph
NH$_2$
N
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

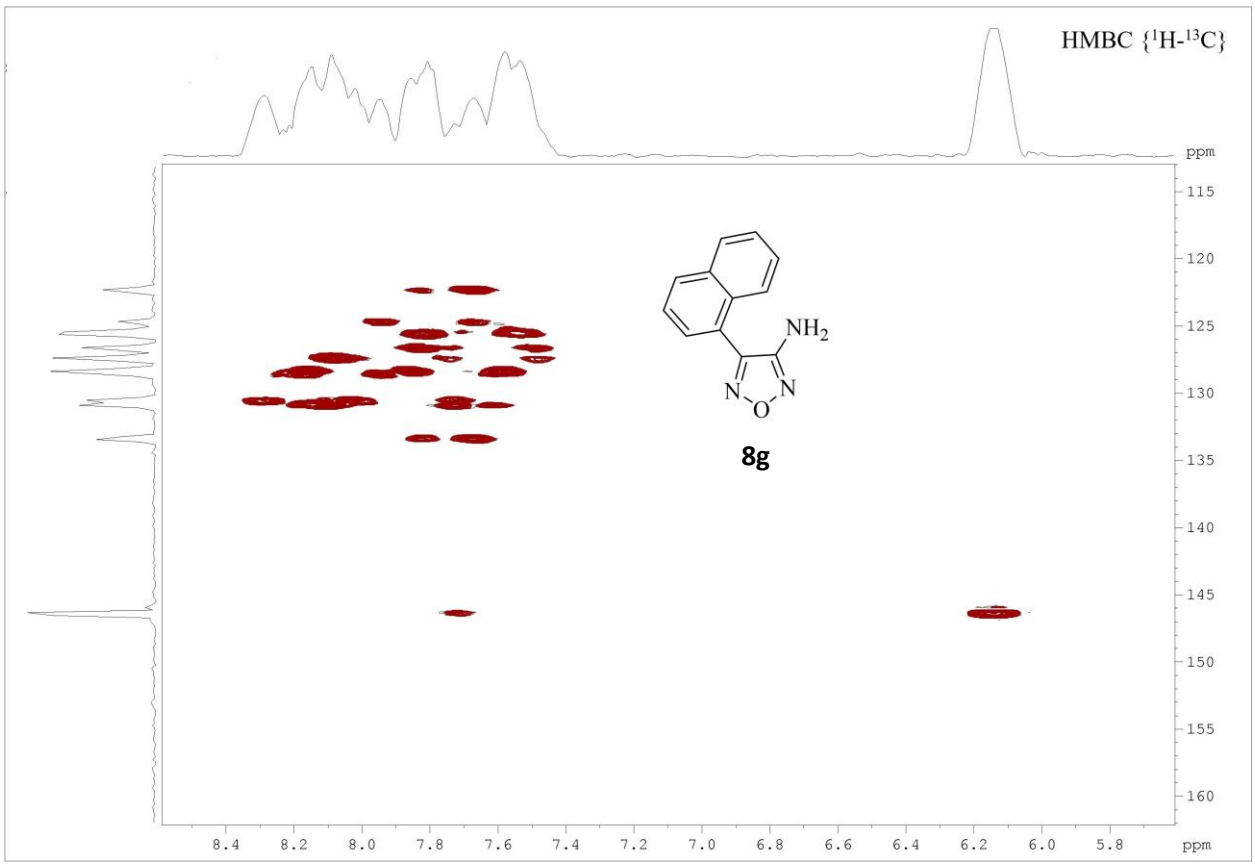
8i


^{1}H NMR
8.165
8.139
8.090
8.077
8.067
7.829
7.811
7.798
7.730
7.710
7.697
7.671
7.657
7.637
7.623
7.610
7.590
6.103
3.322
2.503
122
48
41
49
25
24
NH$_2$
N
O
N
9 8 7 6 5 4 3 2 1 0 ppm
25.420
23.761
0.273
122.630
0.250
0.435
48.532
41.501
0.330
0.531
0.287
0.685
48.857

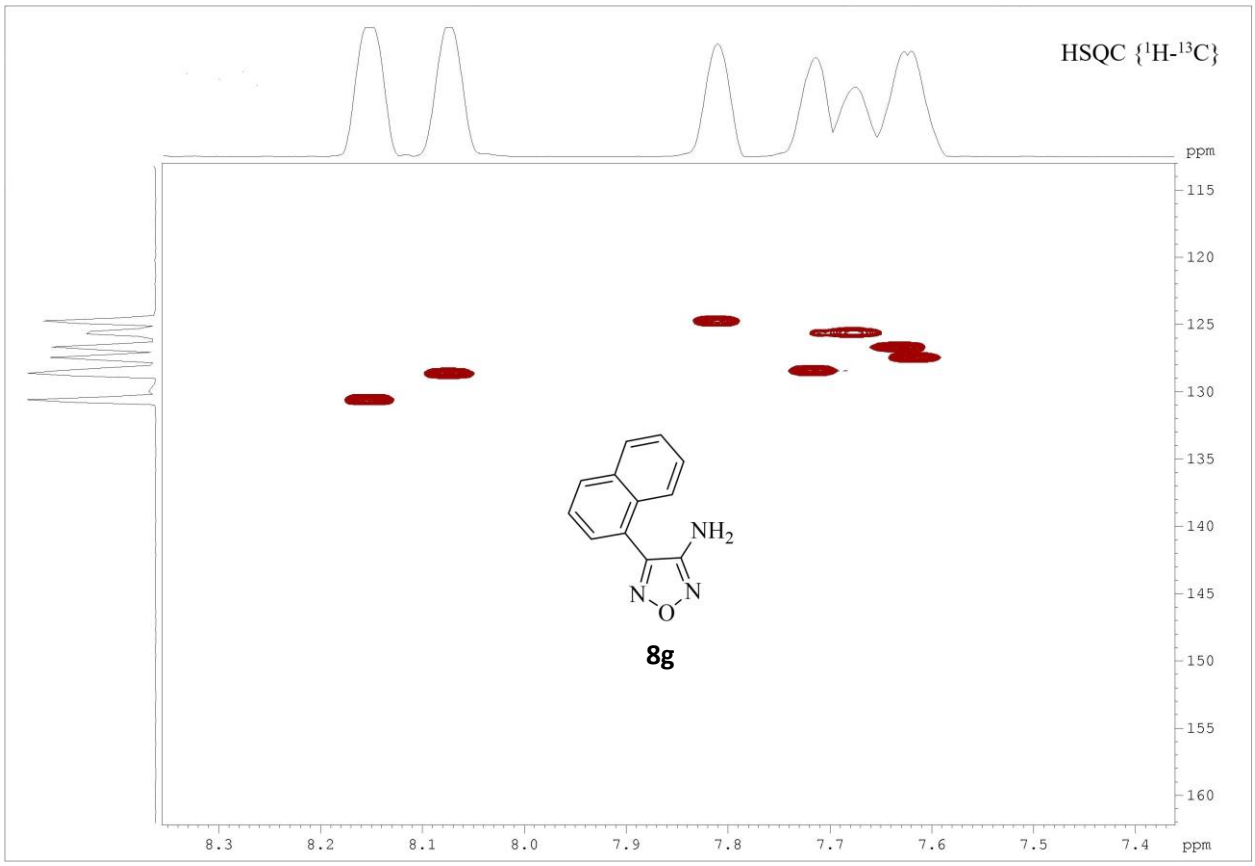
8g


^{13}C NMR
156.267
146.413
133.391
130.681
130.449
129.575
128.339
127.344
126.602
125.538
124.690
122.340
40.830
40.416
40.255
39.998
39.834
39.581
39.417
39.163
38.746
38.331
NH2
N
O
N
8g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{15}N NMR
33.675
-13.023
-332.029
NH2
N
O
N
8g
100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm

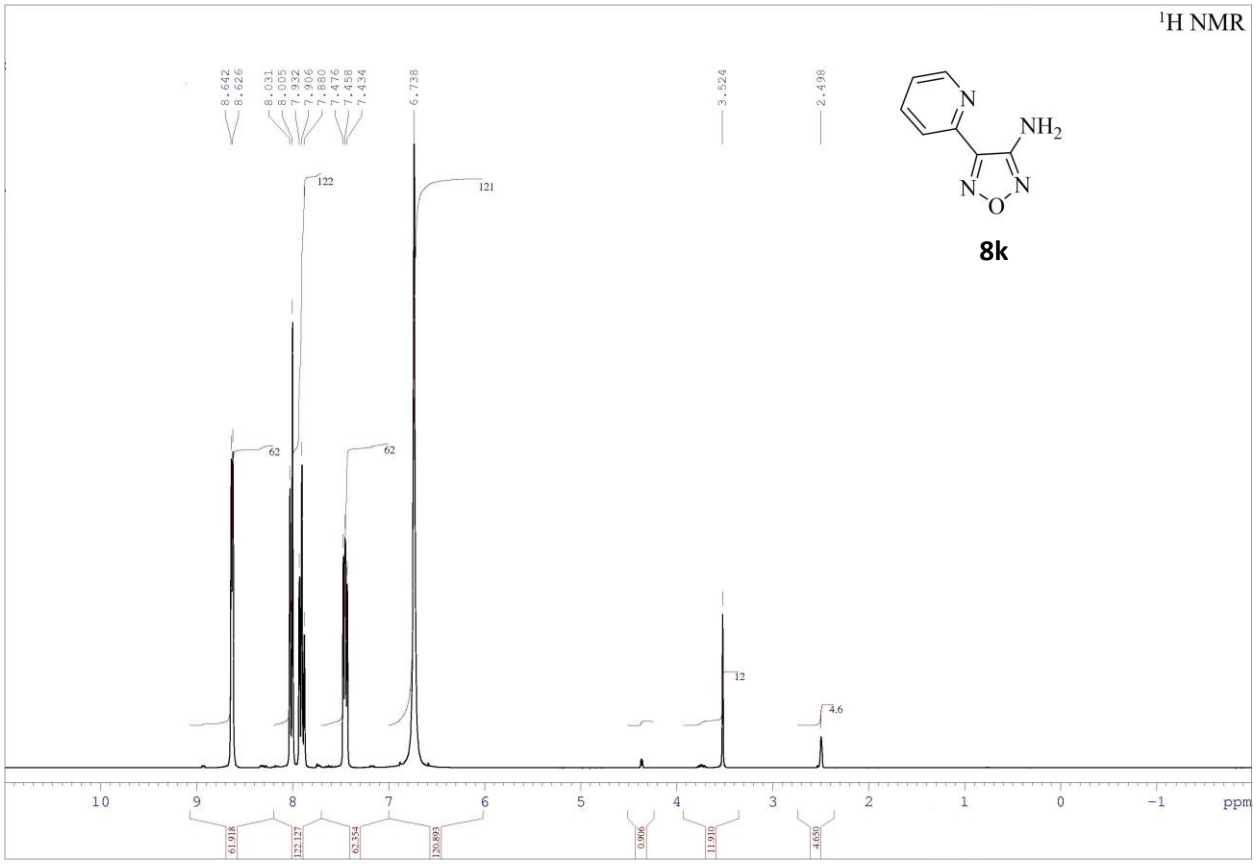

HMBC {1H-13C}
ppm
115
120
125
130
135
140
145
150
155
160
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
ppm
NH2
N
O
N

8g


HSQC {1H-13C}
ppm
115
120
125
130
135
140
145
150
155
160
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
ppm
NH2
N
O
N

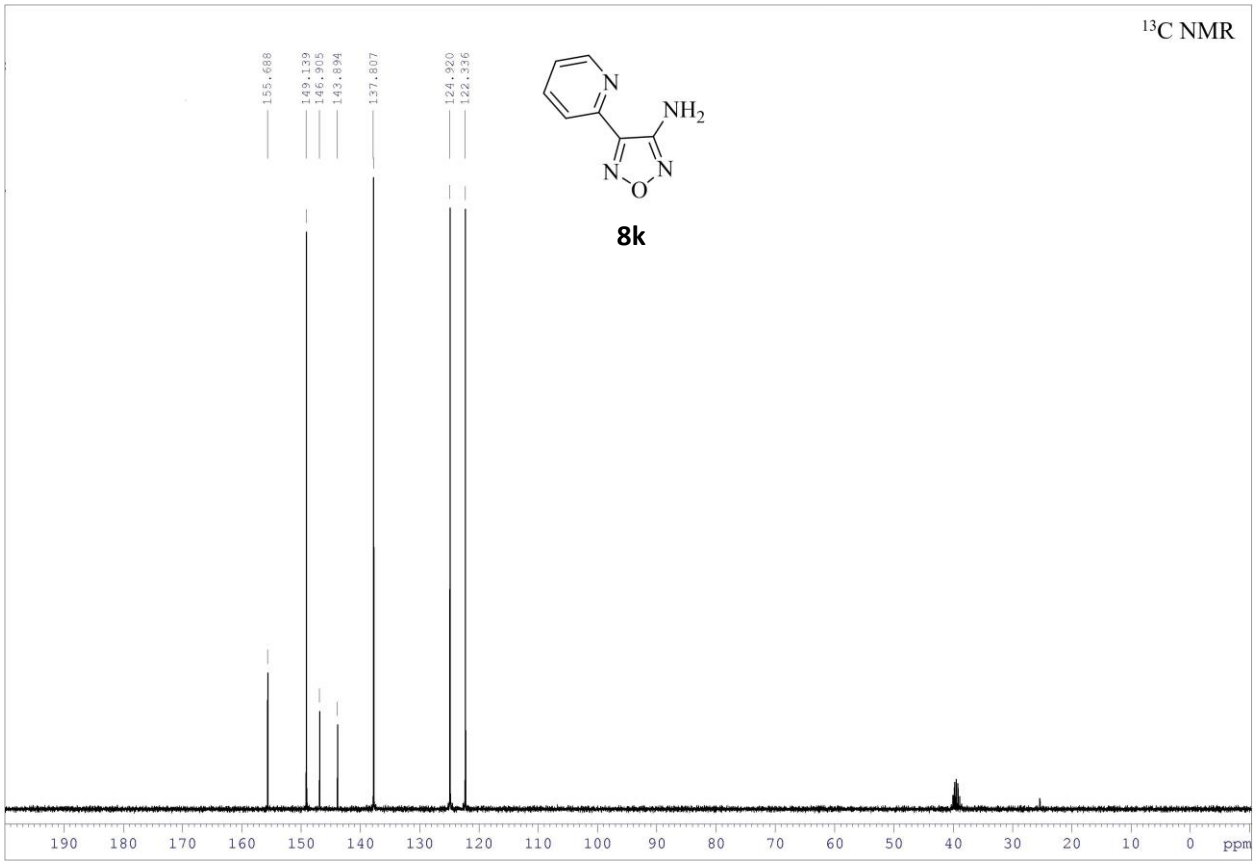
8g

^{1}H NMR



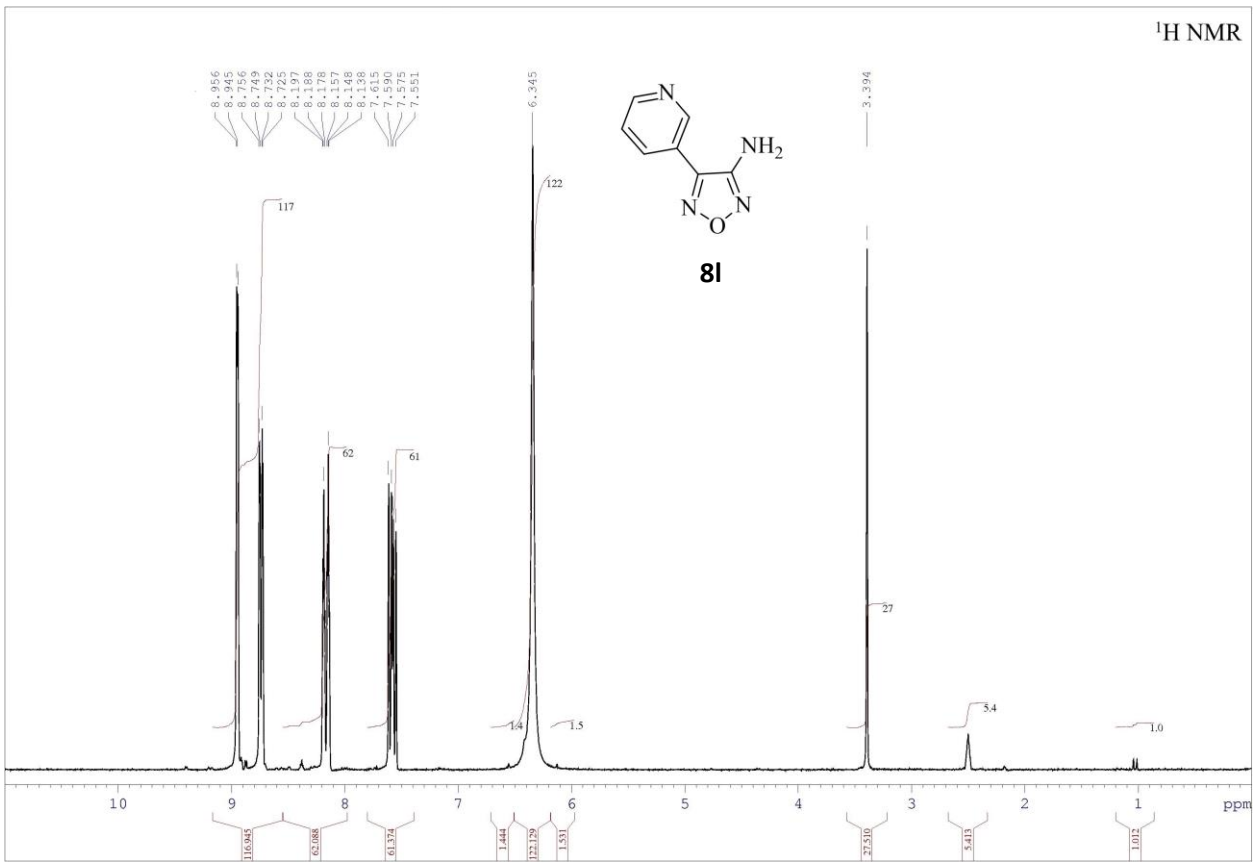
8k

^{13}C NMR



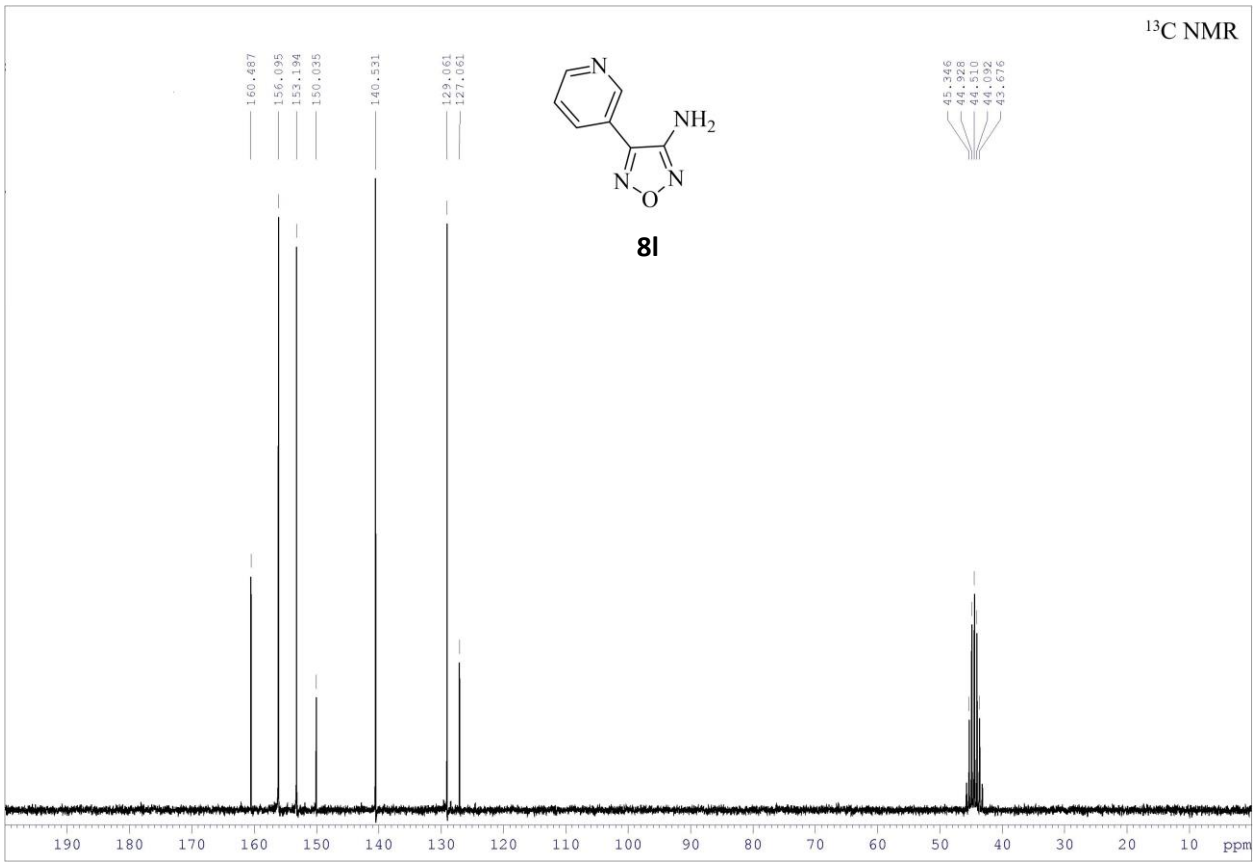
8k

^{1}H NMR



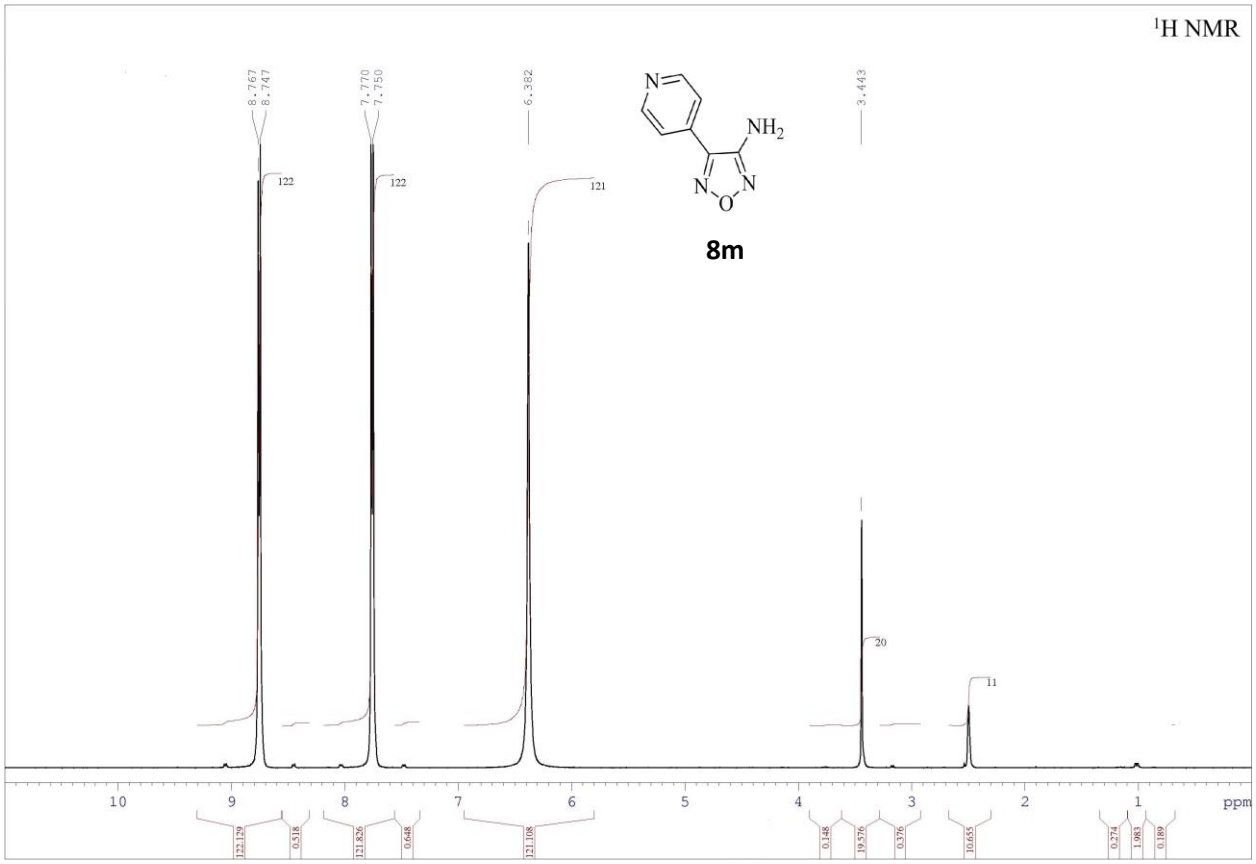
8l

^{13}C NMR



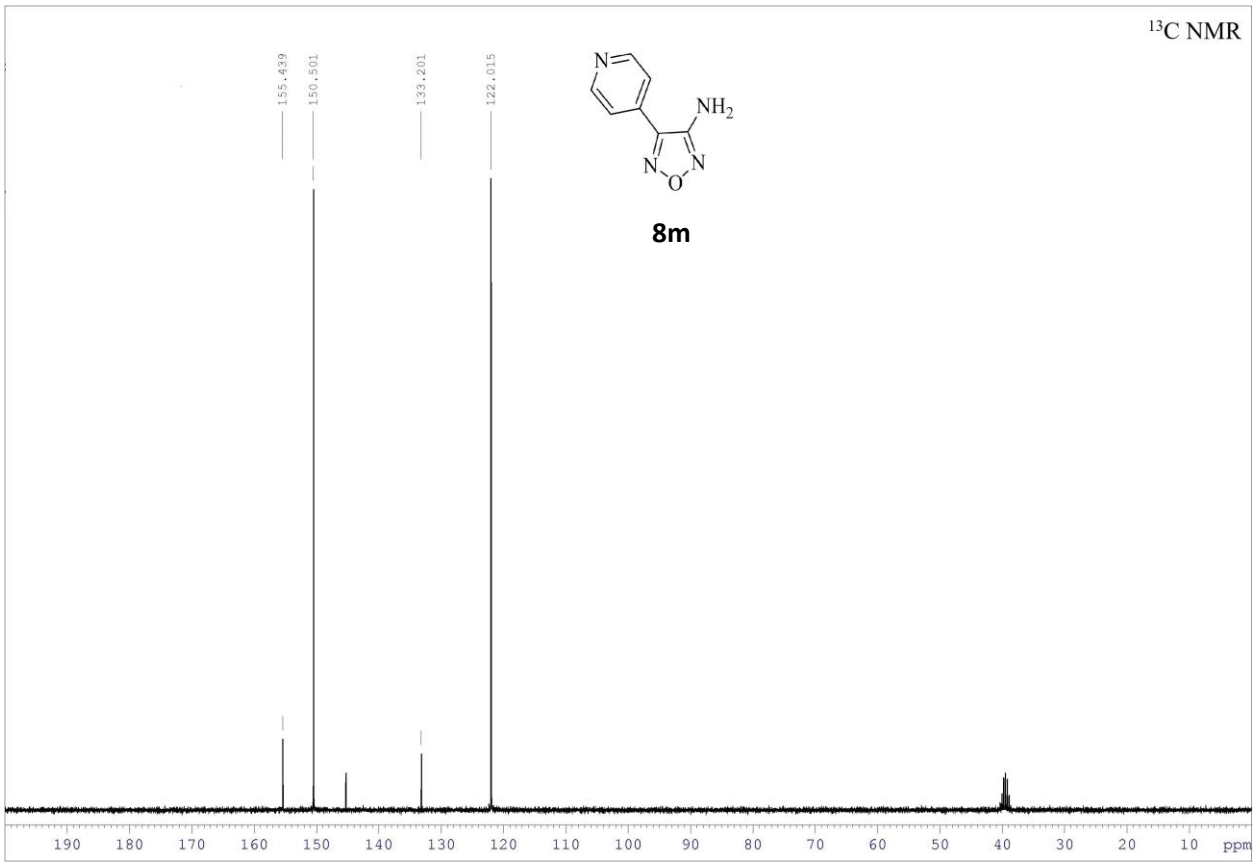
8l

^{1}H NMR

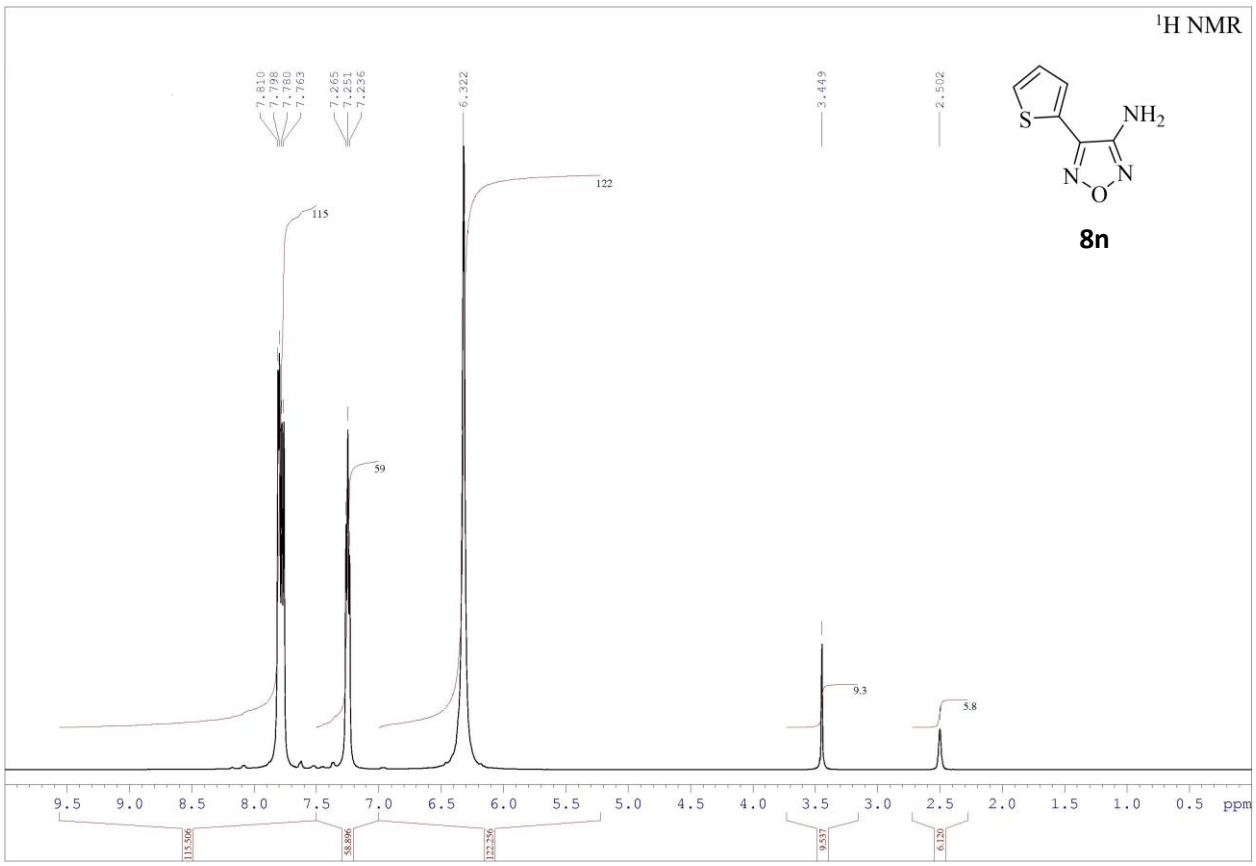


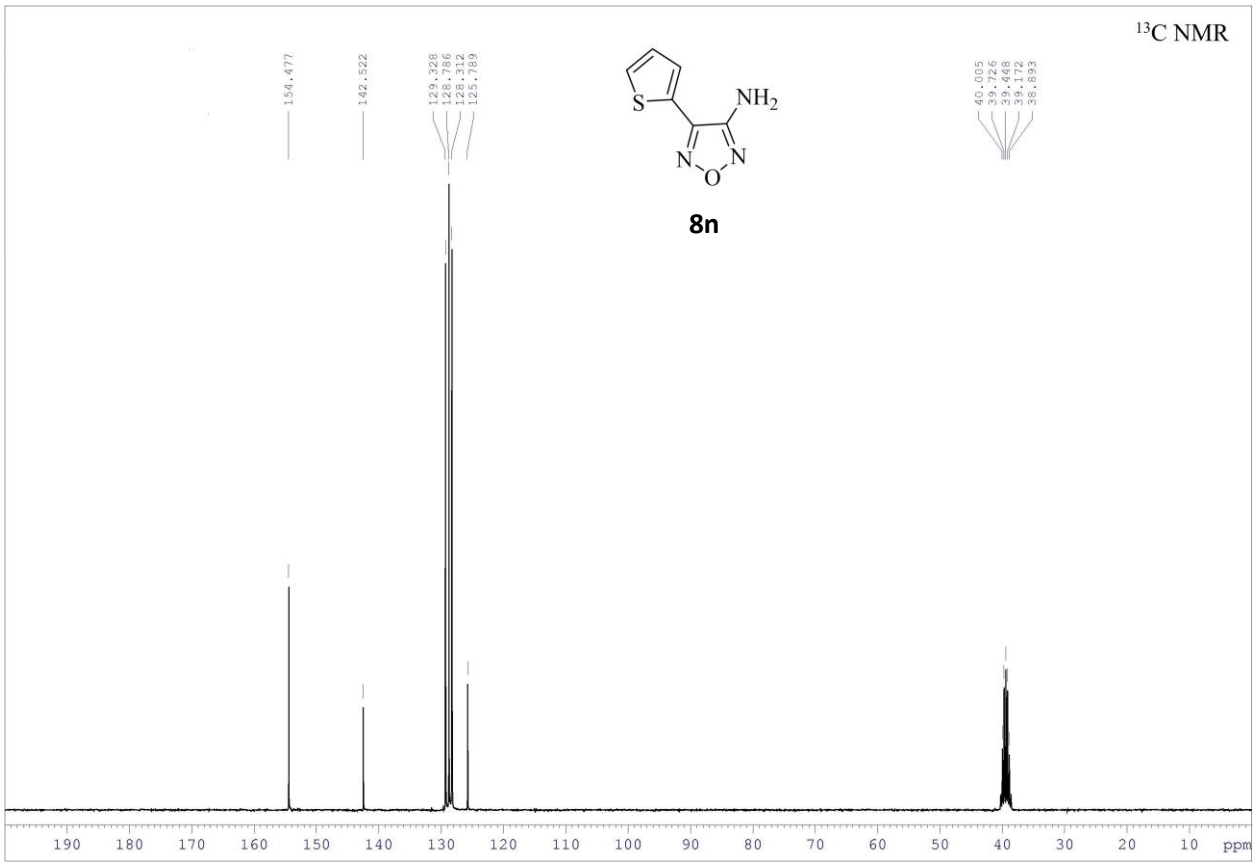
8m

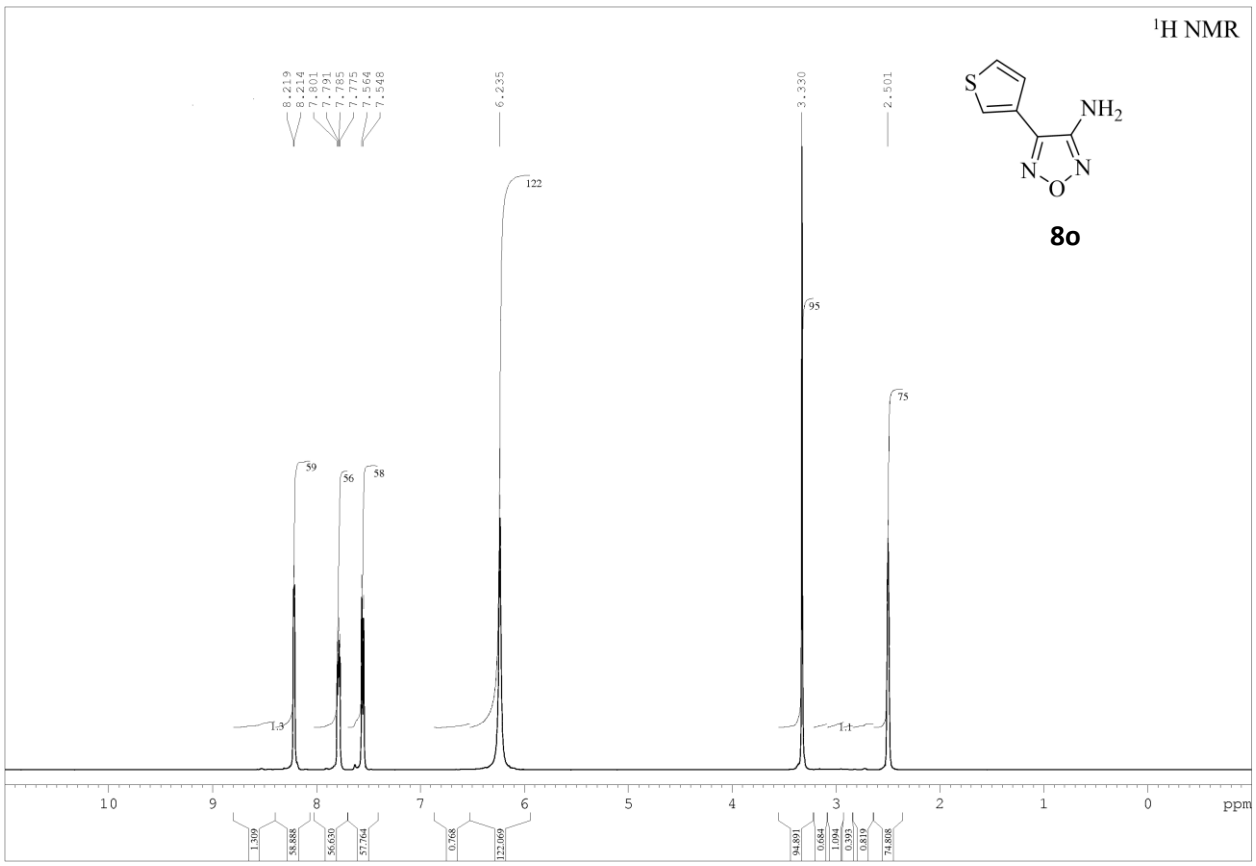
^{13}C NMR

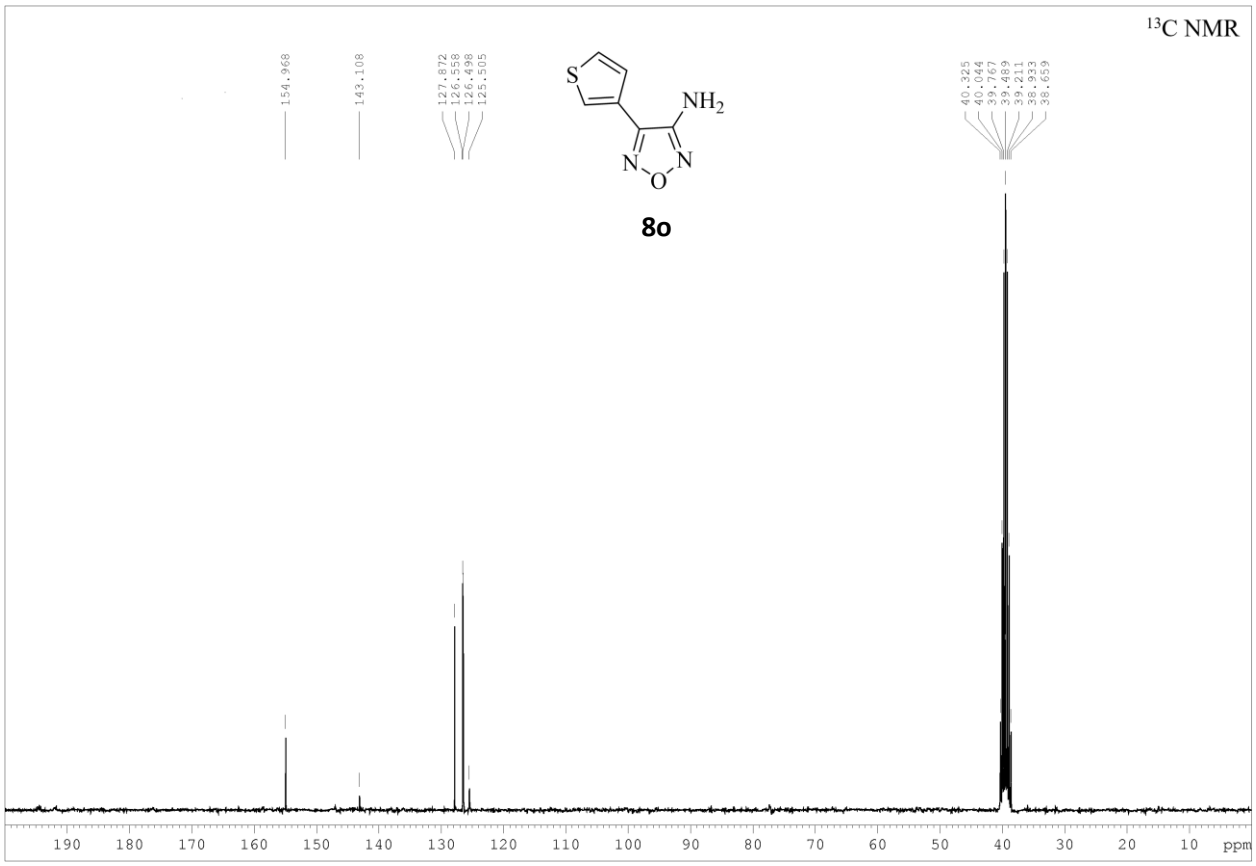


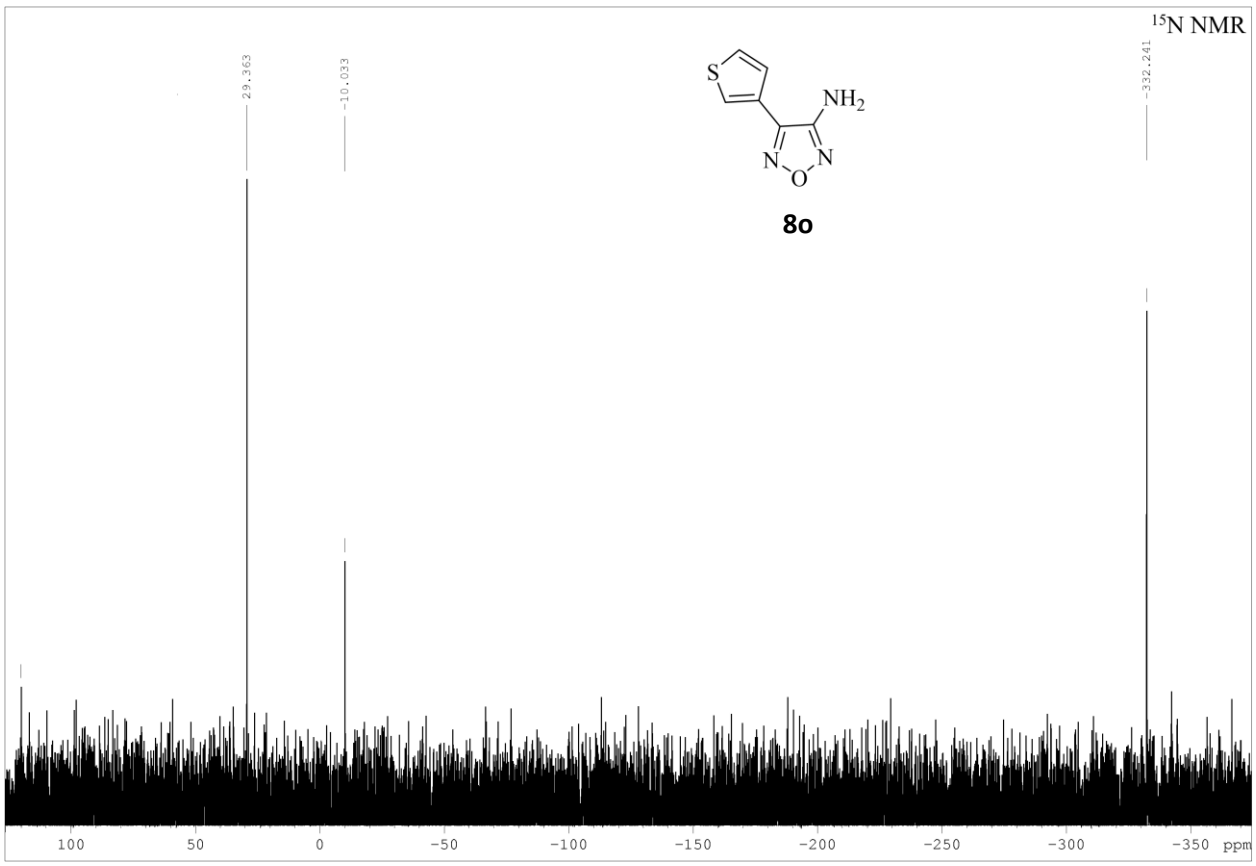
8m


^{1}H NMR
7.810
7.798
7.780
7.763
7.265
7.251
7.236
6.322
3.449
2.502
122
115
59
9.3
5.8
NH$_2$
S
N
O
N
8n
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
115.506
58.896
122.256
9.337
6.120

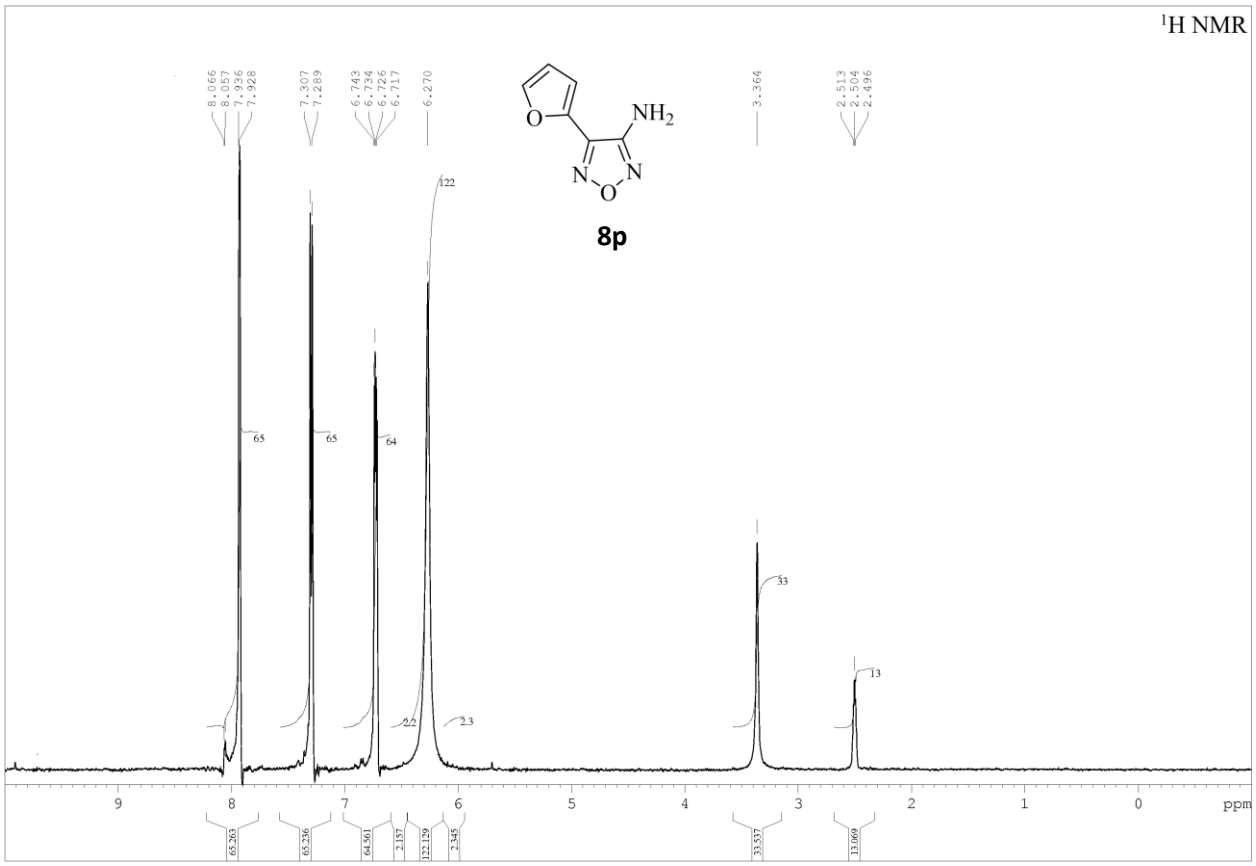

^{13}C NMR
154.477
142.522
129.328
128.786
128.312
125.789
40.005
39.726
39.448
39.172
38.893
NH$_2$
S
N
O
N
8n
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


^{1}H NMR
8.219
8.214
7.801
7.791
7.785
7.775
7.564
7.548
6.235
3.330
2.501
122
95
75
59
56
58
1.3
1.1
10
9
8
7
6
5
4
3
2
1
0
ppm
1.309
58.888
56.630
57.764
0.768
122.069
94.891
0.684
1.094
0.393
0.819
74.808
S
NH$_2$
N
O
N
8o

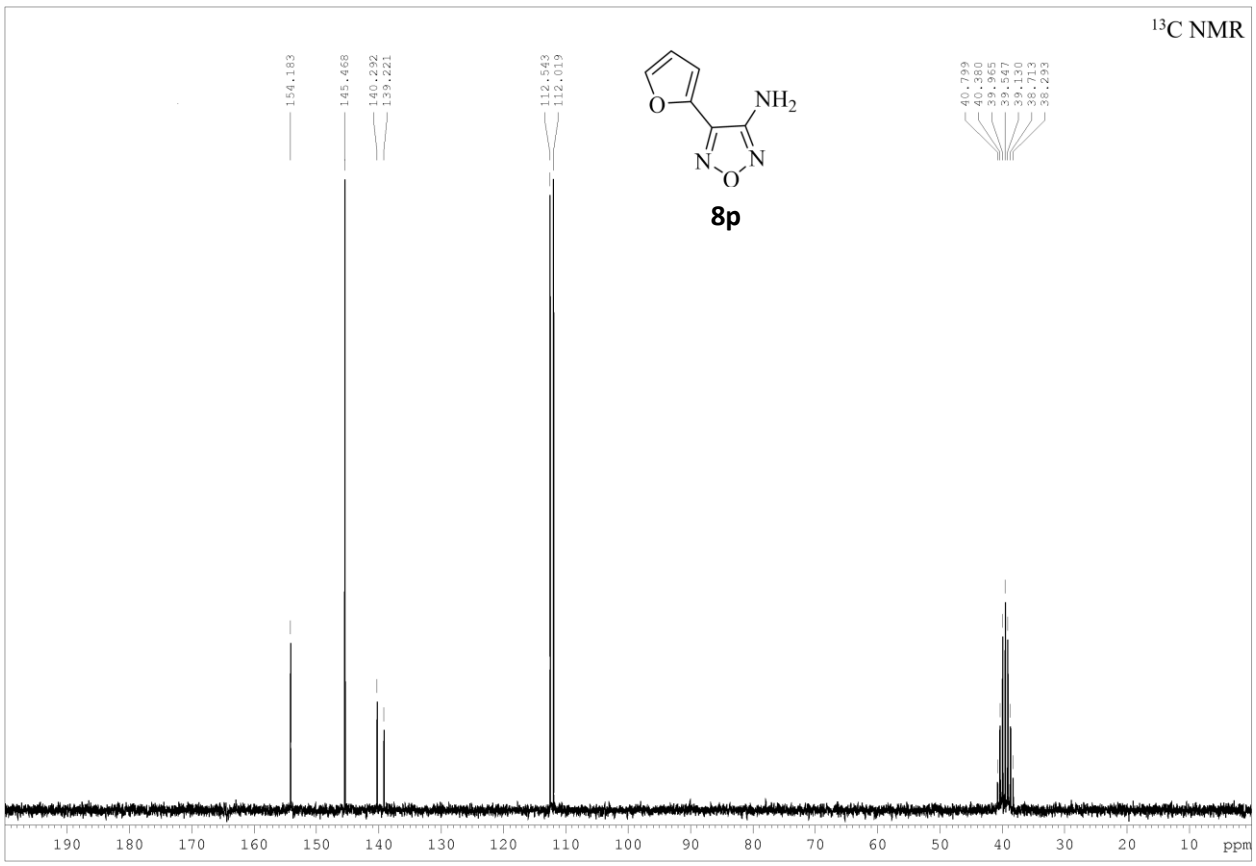

^{13}C NMR
154.968
143.108
127.872
126.558
126.498
125.505
40.325
40.044
39.767
39.489
39.211
38.933
38.659
S
NH$_2$
N
O
N
8o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


15N NMR
29.363
-10.033
-332.241
S
NH2
N
O
N
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

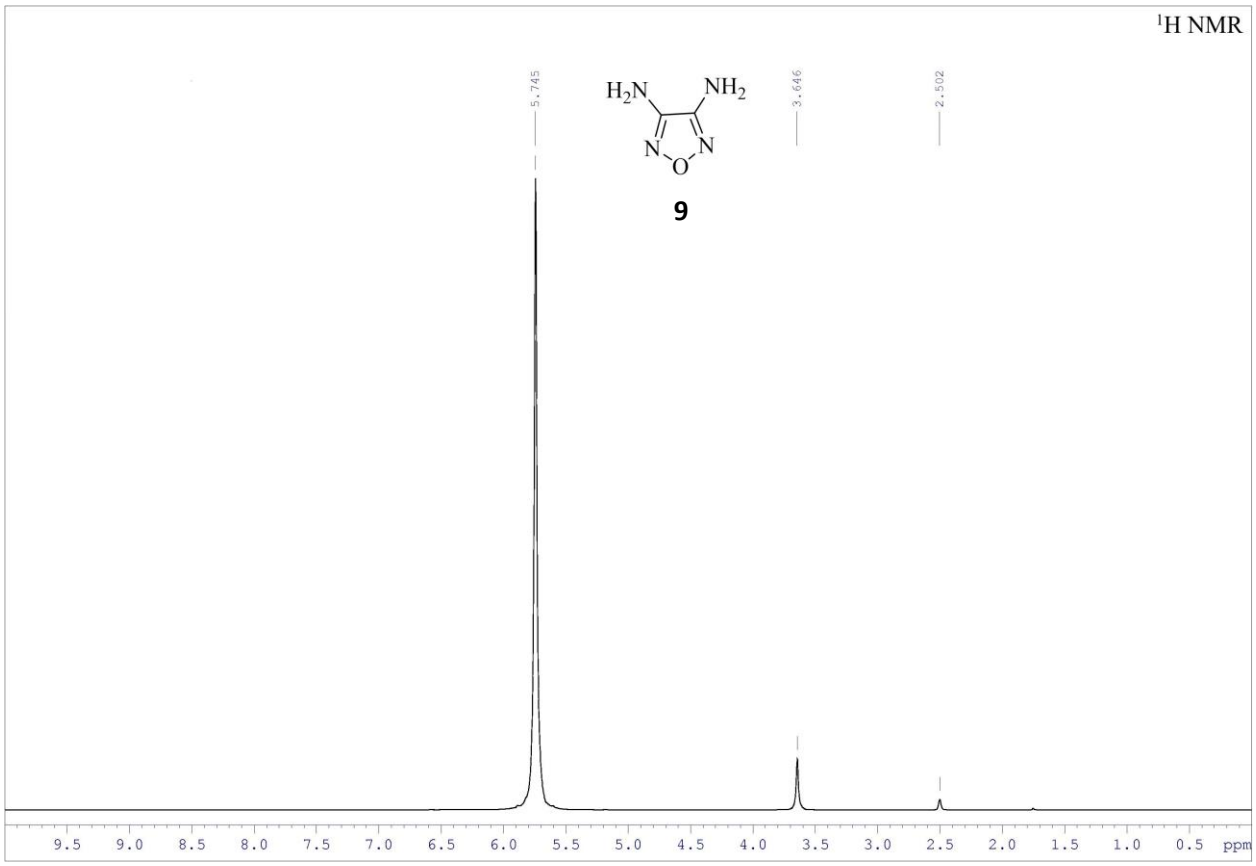
8o


1H NMR
8.066
8.057
7.936
7.928
7.307
7.289
6.743
6.734
6.726
6.717
6.270
3.364
2.513
2.504
2.496
O
NH2
N
O
N
122
65
65
64
33
13
2.2
2.3
9
8
7
6
5
4
3
2
1
0
ppm
65.263
65.226
64.561
3.157
122.129
3.345
33.537
13.069

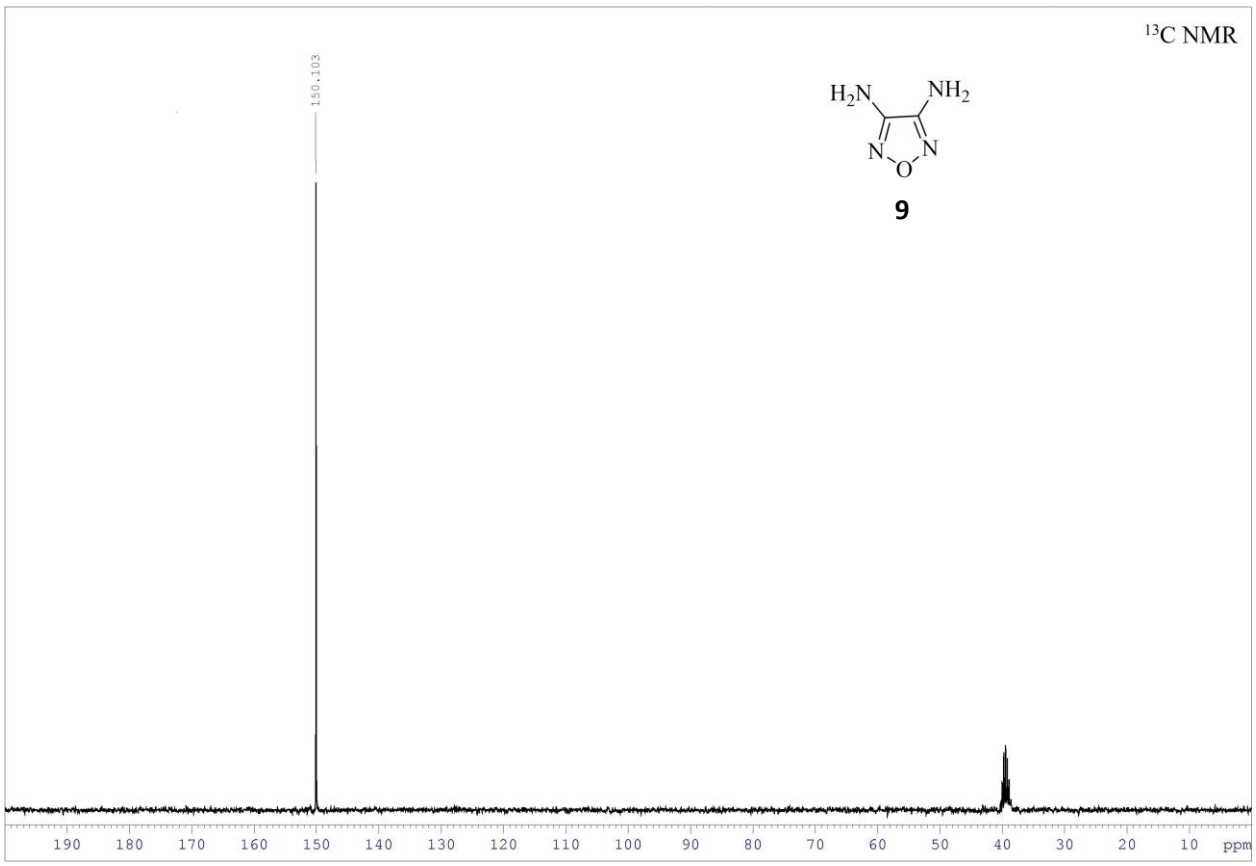
8p


^{13}C NMR
154.183
145.468
140.292
139.221
112.543
112.019
40.799
40.380
39.965
39.547
39.130
38.713
38.293
NH2
O
N
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

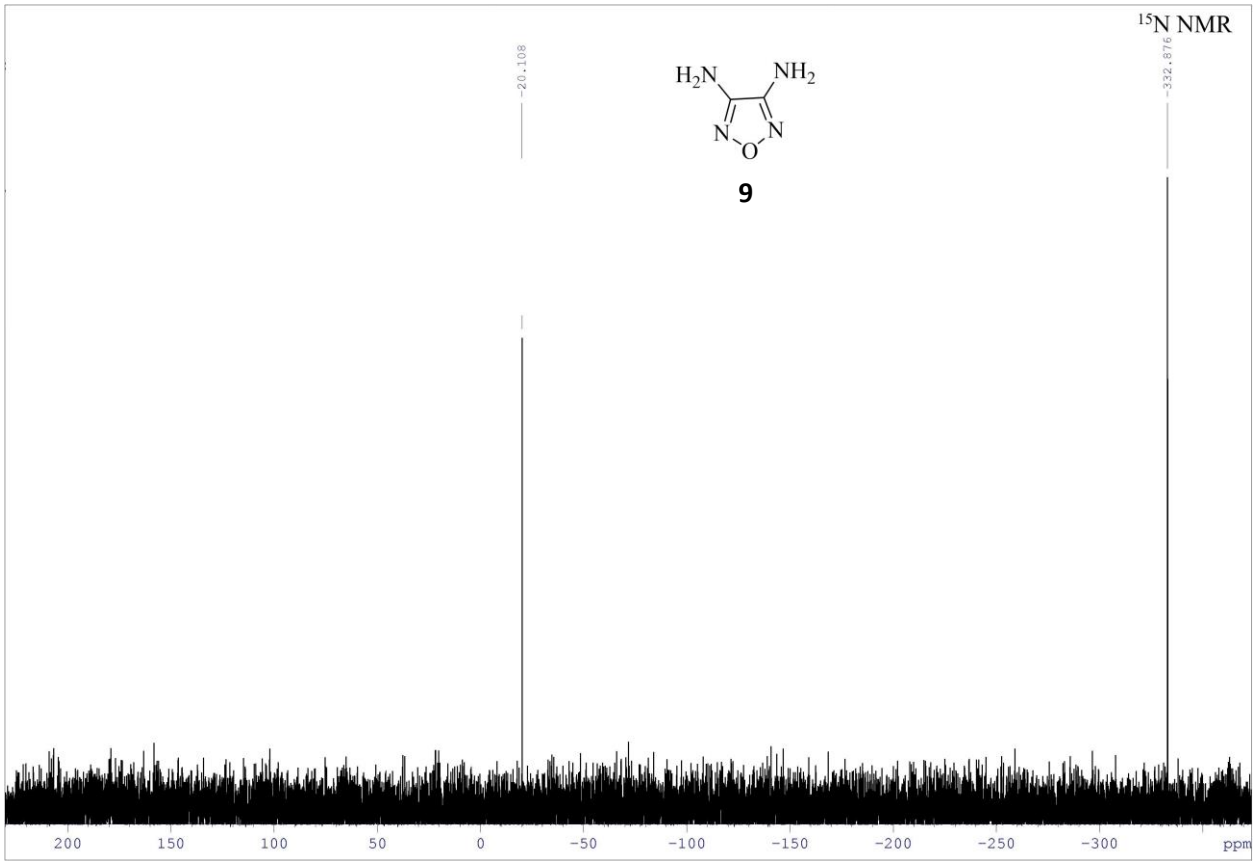
8p


^{1}H NMR
5.745
3.646
2.502
H2N
NH2
N
O
N
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

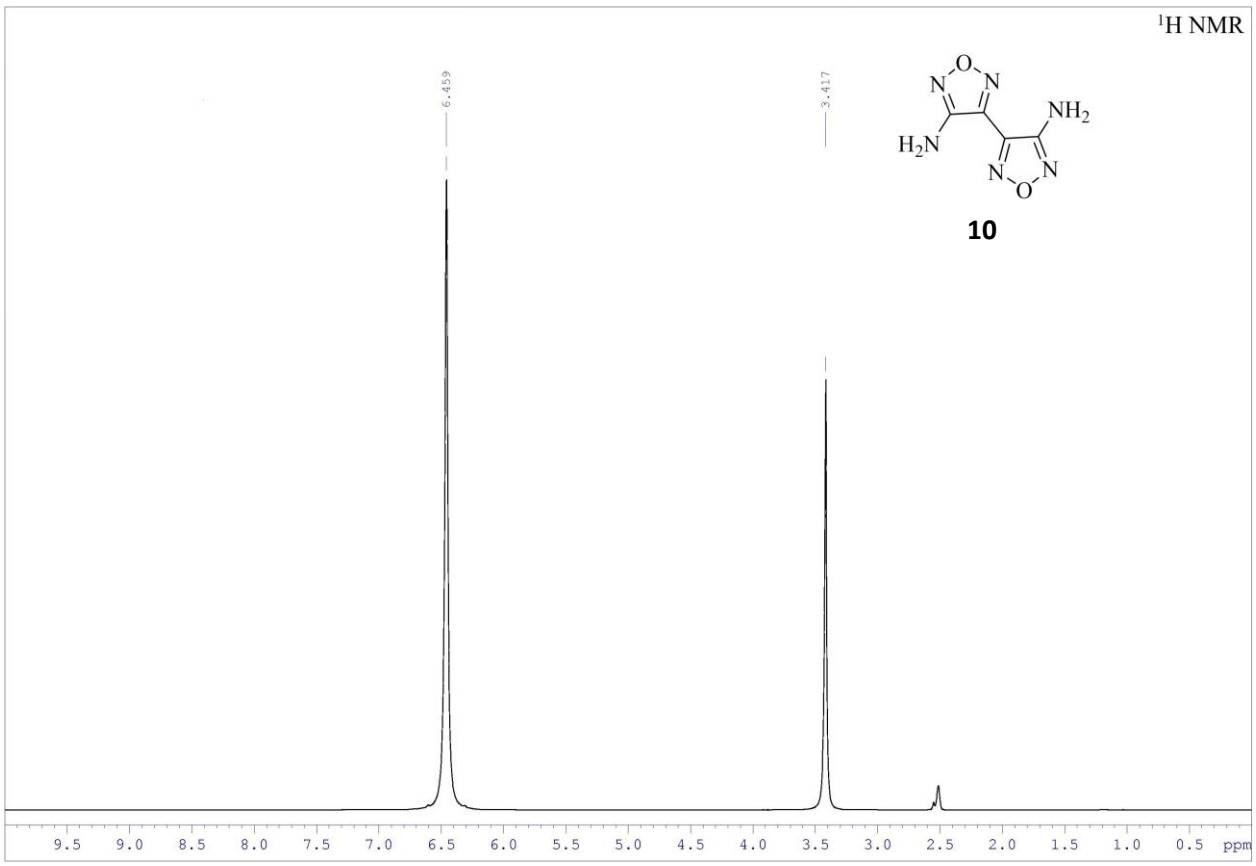
9


^{13}C NMR
150.103
H_2N
NH_2
N
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

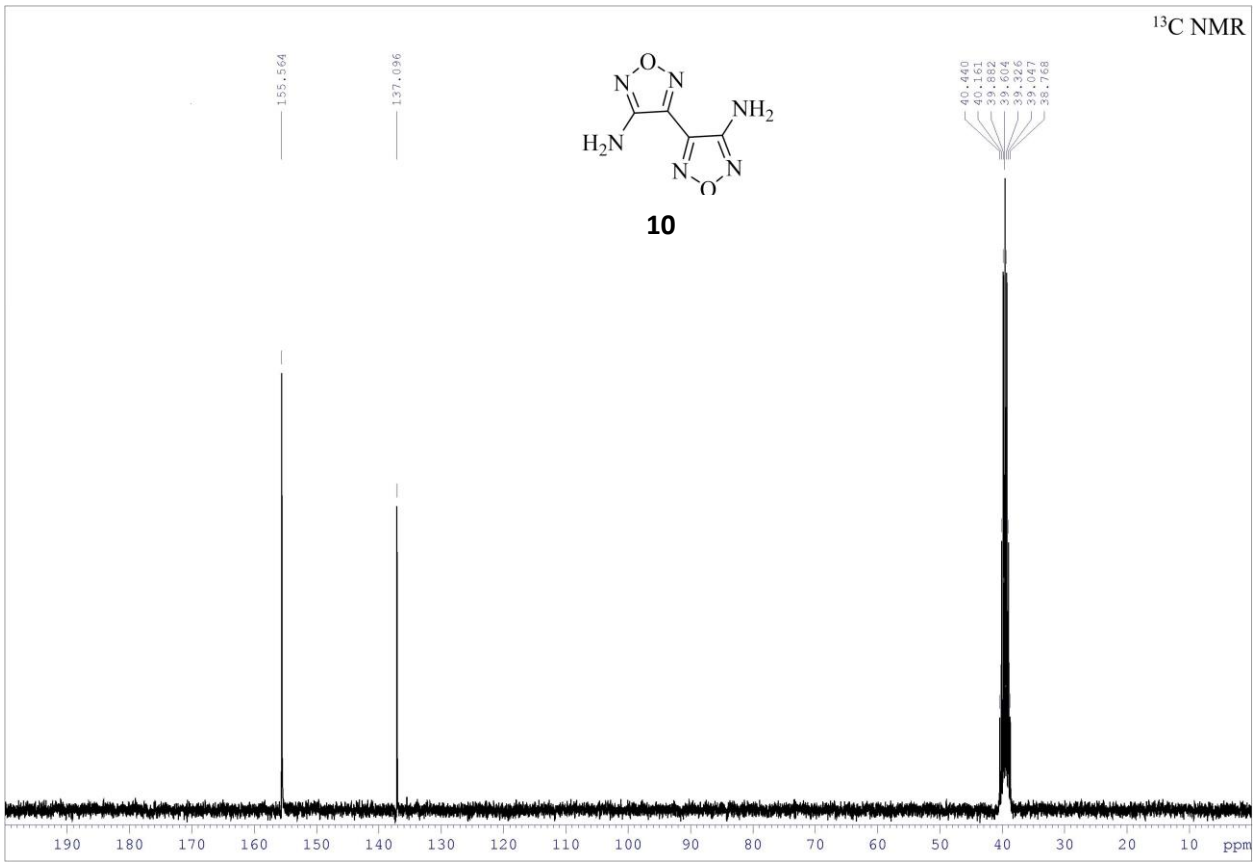
9


^{15}N NMR
-20.108
-332.876
H_2N
NH_2
N
O
N
200 150 100 50 0 -50 -100 -150 -200 -250 -300 ppm

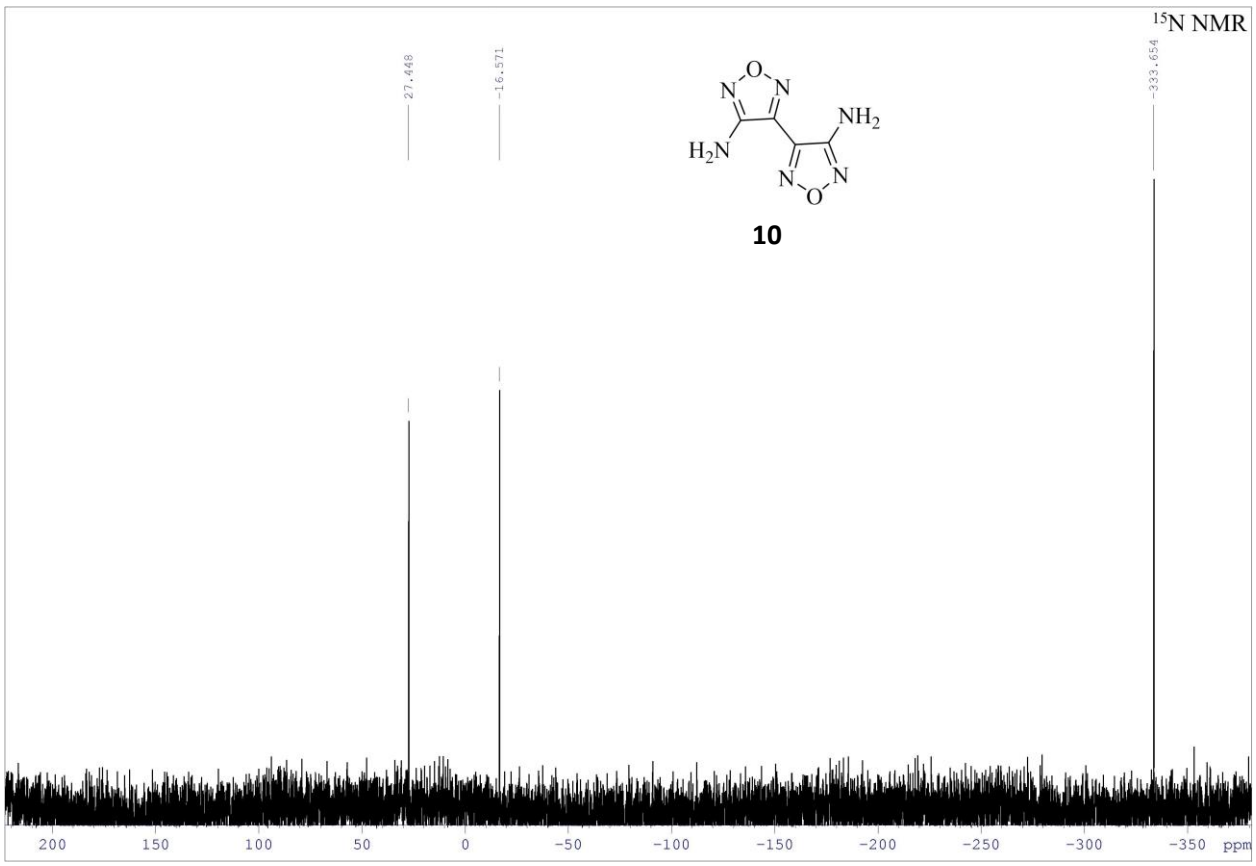
9


^{1}H NMR
6.459
3.417
H_2N
NH_2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

10


^{13}C NMR
155.564
137.096
40.440
40.161
39.882
39.604
39.326
39.047
38.768
H_2N
NH_2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

10


^{15}N NMR
27.448
-16.571
-333.654
H_2N
NH_2
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm

10