Copper-catalysed regioselective azidation of arenes by C-H activation directed by pyridine

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General

^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature using 400 MHz spectrometer. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were obtained by peak matching. Melting points are reported uncorrected and measured on BUCHI M-565 melting point apparatus. Infrared spectra were obtained using a diamond attenuated total reflectance (ATR) accessory on Shimadzu IR-affinity 1S. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV-254 fluorescent indicator. Liquid chromatography was performed using indicated solvent system on 60-120 mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried as per standard procedure. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Solvents were dried prior to use.

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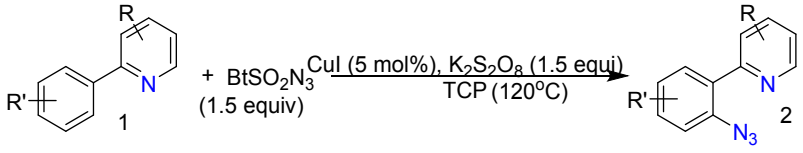
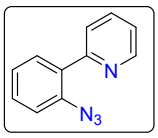
Note: Organic azides are potentially explosive, and extra care must be taken during the experiments. Using blast shields is recommended although we have experienced no explosion during this work. The Imidazole sulphonyl azide ($ImSO_2N_3$) and Benzotriazole sulphonyl azide ($BtSO_2N_3$) were prepared by the reported methods.[1]

General procedures (I) for the synthesis of azide compounds

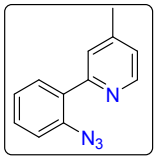


To a solution of 2-phenylpyridine (1.0 mmol, 155 mg) and $BtSO_2N_3$ (336 mg, 1.5 mmol) in 1,2,3-TCP (5.0 mL) under nitrogen atmosphere, CuI (9.1 mg, 0.05 mmol) and $K_2S_2O_8$ (405 mg, 1.5 mmol) was added. The reaction mixture was heated to 120 °C and stirred until the starting material had completely reacted (monitored by TLC). Upon cooling to room temperature, the reaction mixture was quenched with water (25 ml) and the reaction mixture was extracted with Ethyl acetate (EtOAc) (25 X 3 ml). The collected organic phase was vacuum dried and the resulting residue was purified by silica gel chromatography using Ethyl acetate/Hexane as eluent to afford the desired product.

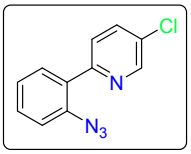
a) **2-(2-azidophenyl)pyridine (2a) :** a was obtained according to the general procedure (I) in 92% yield as yellow solid (low melting, waxy), R_f = 0.3 (30% EtOAc/Hexane). IR (ν_{max}, cm^{-1});3379, 2123, 2107, 1633; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.72 (dd, *J* = 4.6, 1.5 Hz, 1H), 7.76 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.53 – 7.39 (m, 2H), 7.39 – 7.26 (m, 1H), 7.29 – 7.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.73, 149.44, 137.13, 135.73, 132.13, 131.43, 129.62, 125.03, 124.53, 122.12, 118.63. HRMS *m/z* (ESI) calcd. for $C_{11}H_9N_4$ $(M+H)^+$ 197.0783, found 197.0783.The NMR data agree with those reported in literature.[2]



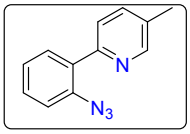
b) **2-(2-azidophenyl)-4-methylpyridine (2b):** was obtained according to the general procedure (I) in 84% yield; yellow oily; R_f = 0.3 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.54 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.64 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.29 – 7.15 (m, 2H), 7.12-7.02 (m, 1H) 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.53, 149.23, 146.73, 137.13, 132.32, 131.23, 129.52, 125.53, 125.13, 123.23, 118.63, 21.13. HRMS *m/z* (ESI) calcd. for $C_{12}H_{11}N_4$ $(M+H)^+$ 211.0978, found 211.0978. The NMR data agree with those reported in literature.[2]



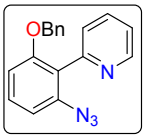
c) **2-(2-azidophenyl)-5-chloropyridine (2c):** was obtained according to the general procedure (I) in 83% yield; yellow oily; R_f = 0.32 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.56 (d, *J* = 2.4 Hz, 1H), 7.67 – 7.57 (m, 3H), 7.38 (td, *J* = 7.5, 2.0 Hz, 1H), 7.28 – 7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.82, 148.32, 137.22, 135.52, 131.31, 131.01, 130.62, 129.92, 125.41, 125.02, 118.81. HRMS *m/z* (ESI) calcd. for $C_{11}H_8ClN_4$ $(M+H)^+$ 231.0432, found 231.0432. The NMR data agree with those reported in literature.[2]



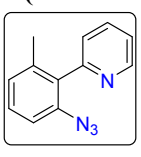
d) **2-(2-azidophenyl)-5-methylpyridine (2d):** was obtained according to the general procedure (I) in 79% yield; yellow oily; R_f = 0.3 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 1.3 Hz, 1H), 7.68 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.49 (td, *J* = 7.4, 1.5 Hz, 1H), 7.44 – 7.32 (m, 2H), 7.29-7.20 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.32, 148.61, 147.7, 135.72, 135.24, 131.5, 129.29, 123.5, 121.9, 116.1, 115.1, 18.34. HRMS *m/z* (ESI) calcd. for $C_{12}H_{11}N_4$ $(M+H)^+$ 211.0978, found 211.0978. The NMR data agree with those reported in literature.[2]



e) **2-(2-azido-6-(benzyloxy)phenyl)pyridine (2e):** was obtained according to the general procedure (I) in 81% yield**;** yellow oily; R_f = 0.36 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.48 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.47 – 7.27 (m, 8H), 7.26 (s, 1H), 7.12 (dd, *J* = 7.4, 2.1 Hz, 1H), 6.81 (ddd, *J* = 7.7, 5.0, 1.2 Hz, 1H), 5.11(s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.96, 152.37, 149.17, 137.69, 137.4, 136.67, 129.09, 128.72, 128.1, 127.27, 123.32, 123.12, 121.48, 111.01, 106.09, 70.86. HRMS *m/z* (ESI) calcd. for $C_{18}H_{14}N_4O$ $(M+H)^+$ 303.1241, found 303.1242.

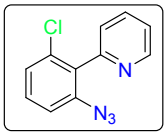


f) **2-(2-azido-6-methylphenyl)pyridine (2f):** was obtained according to the general procedure (I) in 90% yield; yellow oily; R_f = 0.32 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.36 – 7.25 (m, 3H), 7.29 – 7.19 (m, 1H), 7.17 – 7.06 (m, 2H), 2.10 (d, *J* = 1.0 Hz, 3H); .^{13}C NMR (100 MHz, $CDCl_3$) δ



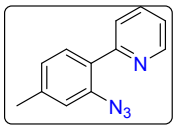
156.43, 149.33, 138.33, 138.13, 136.12, 132.42, 129.16, 126.52, 125.13, 122.23, 115.82, 20. HRMS *m/z* (ESI) calcd. for $C_{12}H_{11}N_4$ $(M+H)^+$ 211.0978, found 211.0978. The NMR data agree with those reported in literature.[2]

g) **2-(2-azido-6-chlorophenyl)pyridine (2g):** was obtained according to the general procedure (I)



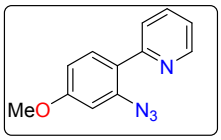
in 86% yield; yellow oily; R_f = 0.32 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.75 (td, *J* = 8.0, 1.3 Hz, 1H), 7.38 – 7.24 (m, 4H), 7.15 (dd, *J* = 7.9, 1.0 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.12, 149.58, 140.12, 136.12, 134.72, 131.52, 129.82, 125.62, 125.32, 122.72, 116.82. HRMS *m/z* (ESI) calcd. for $C_{11}H_8ClN_4$ $(M+H)^+$ 231.0432, found 231.0432.

h) **2-(2-azido-4-methylphenyl)pyridine (2h):** was obtained according to the general procedure (I)



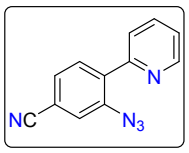
in 82% yield; yellow oily; R_f = 0.3 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.74 – 8.68 (m, 1H), 7.72 (ddd, *J* = 8.1, 4.0, 2.0 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.59 (dd, *J* = 2.0, 1.1 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.10 (dd, *J* = 4.0, 2.5 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.72,149.53, 140.13, 136.72, 135.72, 131.32, 129.42, 126.02, 124.72, 122.02, 119.52, 21.13. HRMS *m/z* (ESI) calcd. for $C_{12}H_{11}N_4$ $(M+H)^+$ 211.0978, found 211.0978. The NMR data agree with those reported in literature.[3]

i) **2-(2-azido-4-methoxyphenyl)pyridine (2i):** was obtained according to the general procedure (I)



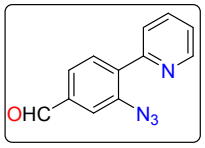
in 76% yield; yellow oily; R_f = 0.38 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.64 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.78 – 7.66 (m, 2H), 7.39 (td, *J* = 8.0, 1.3 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 6.85 – 6.71 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.72, 155.41, 149.21, 138.12, 135.86, 132.51, 125.11, 124.51, 121.41, 109.7, 104.3, 55.98. HRMS *m/z* (ESI) calcd. For $C_{12}H_{11}N_4O$ $(M+H)^+$ 227.0927, found 227.0927 The NMR data agree with those reported in literature.[2]

j) **3-azido-4-(pyridin-2-yl)benzonitrile (2j):** was obtained according to the general procedure (I)



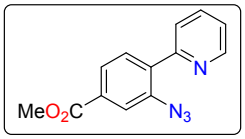
in 56% yield; yellow oily; R_f = 0.4 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.91 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 2.0 Hz, 1H), 7.43 (td, *J* = 7.9, 1.3 Hz, 1H), 7.39 – 7.28 (m, 3H), 7.26 (s, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 155.06, 149.8, 140.16, 136.29, 135.71, 130.55, 127.67, 123.15, 122.13, 121.67, 117.88, 110.9. HRMS m/z (ESI) calcd. For $C_{12}H_8N_5$ $(M+H)^+$ 222.0774, found 222.0774.

k) **3-azido-4-(pyridin-2-yl)benzonitrile (2k):** was obtained according to the general procedure (I)

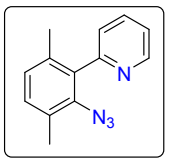


in 52% yield; bright yellow oily; R_f = 0.5 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.07 (d, *J* = 1.2 Hz, 1H), 8.78 – 8.72 (m, 1H), 7.90 (d, *J* = 7.1 Hz, 1H), 7.82 – 7.70 (m, 4H), 7.34 (td, *J* = 5.4, 2.5 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 190.74, 154.43, 149.52, 138.73, 137.23, 136.12, 132.32, 126.69, 125.62, 123.13, 121.3, 118.12. HRMS *m/z* (ESI) calcd. For $C_{12}H_9N_4O$ $(M+H)^+$ 225.0772, found 225.0771. The NMR data agree with those reported in literature.[2]

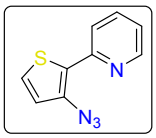
l) **methyl 3-azido-4-(pyridin-2-yl)benzoate (2l):** was obtained according to the general procedure (I) in 52% yield; light yellow oily; R_f = 0.5 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 – 8.60 (m, 1H), 8.21 (d, *J* = 1.9 Hz, 1H), 7.73 – 7.57 (m, 4H), 7.19 – 7.08 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.74, 154.53, 149.54, 137.53, 136.03, 135.83, 131.53, 131.33, 125.73, 124.73, 122.63, 120.03, 52.04. HRMS *m/z* (ESI) calcd. for $C_{13}H_{11}N_4O_2$ $(M+H)^+$ 255.0875, found 255.0877. The NMR data agree with those reported in literature.[2]



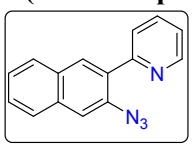
m) **2-(2-azido-3,6-dimethylphenyl)pyridine (2m):** was obtained according to the general procedure (I) in 32% yield; yellow amorphous low meting solid; solidify into sticky mass at 15-17°C; R_f = 0.32 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.68 – 8.62 (m, 1H), 7.77 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.34 – 7.19 (m, 3H), 7.17 – 7.08 (m, 1H), 2.36 (s, 3H), 2.17 (s, 3H); 13C NMR (100 MHz, $CDCl_3$) δ 156.14, 149.03, 137.53, 136.49, 134.97, 129.71, 128.89, 127.17, 123.25, 122.92, 122.23, 21.58, 16.3. HRMS *m/z* (ESI) calcd. for $C_{13}H_{13}N_4$ $(M+H)^+$ 225.1135, found 225.1135.



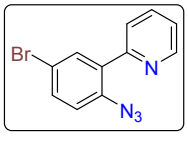
n) **2-(3-azidothiophen-2-yl)pyridine (2n):** was obtained according to the general procedure (I) in 75% yield; yellow oily; R_f = 0.42 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.85 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.73 (td, *J* = 8.0, 1.3 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.4 Hz, 1H), 7.27 (ddd, *J* = 7.8, 4.9, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.73, 149.28, 138.11, 137.01, 123.92, 122.45, 120.71, 119.86, 118.54. HRMS *m/z* (ESI) calcd. for $C_9H_7N_4S$ $(M+H)^+$ 203.0386, found 203.0387.



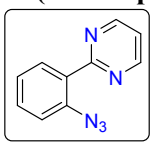
o) **2-(3-azidonaphthalen-2-yl)pyridine (2o):** was obtained according to the general procedure (I) in 81% yield; light yellow waxy solid; R_f = 0.38 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (dd, *J* = 4.9, 1.2 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.99 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.86 (ddd, *J* = 7.8, 4.4, 1.4 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.43 (td, *J* = 7.9, 1.2 Hz, 1H), 7.33 – 7.22 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.92, 149.87, 135.57, 134.81, 133.67, 129.34, 126.93, 126.67, 125.25, 124.8, 124.77, 124.58, 123.61, 122.52, 115.82. HRMS *m/z* (ESI) calcd. for $C_{15}H_{11}N_4$ $(M+H)^+$ 247.0979, found 247.0978. The NMR data agree with those reported in literature.[2]



p) **2-(2-azido-5-bromophenyl)pyridine (2p):** was obtained according to the general procedure (I) in 82% yield; yellow oily; R_f = 0.35 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.73 (dd, *J* = 4.5, 1.2 Hz, 1H), 7.83 (t, *J* = 2.4 Hz, 1H), 7.80 – 7.65 (m, 3H), 7.32 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.13 (ddd, *J* = 7.4, 4.5, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.13, 149.53, 136.32, 135.92, 134.35, 134.32, 133.62, 132.52, 124.76, 124.72, 122.52, 120.32, 118.12. HRMS m/z (ESI) calcd. for $C^{11}H^8BrN^4$ (M+H)+ 274.9927, found 274.9926. The NMR data agree with those reported in literature.[2]

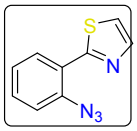


q) **2-(2-azidophenyl)pyrimidine (3c):** was obtained according to the general procedure (I) in 72% yield; yellow oily; R_f = 0.38 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-d) δ 8.79 (d, *J* = 5.0 Hz, 2H), 7.74 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.42 (td, *J*

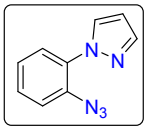


= 7.4, 2.0 Hz, 1H), 7.20 – 7.12 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.02, 157.22, 138.12, 132.02, 131.02, 130.72, 124.81, 119.64, 119.01. The NMR data agree with those reported in litructure.[2]

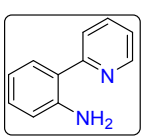
r) **2-(2-azidophenyl)thiazole (3e):** was obtained according to the general procedure (I) in 78% yield; yellow oily; R_f = 0.42 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.79 (m, 2H), 7.75 (dd, *J* = 7.4, 2.2 Hz, 1H), 7.70 – 7.54 (m, 2H), 7.46 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.38, 145.26, 137.99, 130.77, 129.61, 124.63, 122.02, 120.34, 117.19, 117.16. HRMS *m/z* (ESI) calcd. for $C_9H_6N_4S$ $(M+H)^+$ 203.0386, found 203.0386.



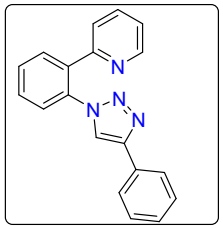
s) **1-(2-azidophenyl)-1H-pyrazole (3d):** was obtained according to the general procedure (I) in 42% yield; yellow oily; R_f = 0.3 (30% EtOAc/Hexane); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 2.1 Hz, 1H), 7.77 (d, *J* = 1.6 Hz, 1H), 7.62 (t, *J* = 1.8 Hz, 1H), 7.40 (dd, *J* = 6.7, 2.7 Hz, 1H), 7.31 – 7.19 (m, 2H), 6.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.03, 132.53, 131.73, 131.13, 128.53, 126.53, 125.33, 125.3, 119.12, 107.2. HRMS *m/z* (ESI) calcd. for $C_{10}H_8N_5$ $(M+H)^+$ 198.0774, found 198.0774. The NMR data agree with those reported in litructure.[2]



t) **2-(pyridin-2-yl)aniline (4a):** To the suspension of 2-(2-azidophenyl)pyridine (0.05 mmol, 10 mg) and NH_4Cl (40 mg, 0.075 mmol) in EtOH (5 mL) and water(2 mL), zinc (54 mg, 1 mmol)was added, the mixture was stirred at room temperature for 20h and reaction progress was monitored by TLC. The reaction mixture was filtered through a Celite pad and washed with EtOAc. The combined filtrate was concentrated, the residue dissolved in EtOAc (50 mL) and washed with brine solution (40 mL). The organic layer was dried over sodium sulphate and concentrated. The residue was purified by silica gel chromatography EtOAc/Hexane to give ~8 mg (92%) product. canary yellow, mp 77-78°C. R_f = 0.4 (45% MeOH/Chloroform); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 5.1 Hz, 1H), 7.78 (dd, *J* = 7.4, 2.0 Hz, 1H), 7.65 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.51 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.18 (td, *J* = 7.5, 1.9 Hz, 1H), 7.07 (ddd, *J* = 5.1, 1.9, 0.9 Hz, 1H), 6.83 – 6.72 (m, 2H), 5.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.34, 147.74, 146.33, 136.73, 129.74, 129.33, 122.13, 122.03, 120.83, 117.53, 117.13. HRMS *m/z* (ESI) calcd. for $C_{11}H_{10}N_2$ $(M+H)^+$ 171.0916, found 171.0917.The NMR data agree with those reported in literature.[2]

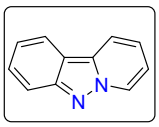


u) **2-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)phenyl)pyridine (4d):** 2-(2-Azidophenyl)pyridine (0.2 mmol, 40 mg), phenylacetylene (0.22 mmol, 22 mg), $CuSO_4$•$5H_2O$ (0.01 mmol, 2.6 mg), and sodium ascorbate (0.02 mmol, 4 mg) were added to a 2:1 mixture of DMF-water (10 mL). The reaction mixture was stirred for 24 h at room temperature. Reaction mixture was vacuum evaporated over rotary evaporator. Water (15 mL) was added and the mixture was extracted with EtOAc (30 X 3ml). The organic layer was combined, washed with brine (50 mL) and dried over anhydrous sodium sulphate. The solvent was evaporated and the residue was purified by silica gel chromatography using EtOAc/Hexane (50%) to afford



triazole (24 mg, 81%) as a white solid. mp 123-125 °C; R_f = 0.6 (10% MeOH/$CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 – 8.61 (m, 1H), 8.27 (s, 1H), 7.85 – 7.77 (m, 1H), 7.69 – 7.62 (m, 1H), 7.60 – 7.51 (m, 2H), 7.50 – 7.33 (m, 4H), 7.20 – 6.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.56, 155.53, 149.53, 147.43, 147.4, 147.35, 147.32, 136.43, 136.12, 135.02, 131.12, 130.12, 130.09, 130.06, 130.02, 129.99, 129.72, 128.73, 128.69, 128.12, 126.28, 126.24, 125.97, 124.62, 124.59, 124.05, 123.65, 123.62, 121.92. HRMS m/z (ESI) calcd. for $C_{19}H_{15}N_4$ $(M+H)^+$ 299.1291, found 299.1292. The NMR data agree with those reported in literature.[2]

v) **pyrido[1,2-b]indazole (4c):** 2-(2-Azidophenyl)pyridine (0.05 mmol, 10 mg) and dry dioxane (10 mL) were taken into round bottom flask tube under nitrogen and heated with stirring at 125°C for 24h. The reaction progress was monitored with TLC. The solvent was removed on a rotary evaporator and the residue was purified by silica gel chromatography using EtOAc/Hexane to afford the products indazole in 82% yield. Off white compound, mp 86°C, R_f = 0.5 (10% MeOH/$CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.84-8.74 (m, 1H), 8.20-8.08 (m, 2H), 7.85 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.35 (dd, *J* = 5.4, 3.4 Hz, 2H), 7.30 (td, *J* = 7.6, 1.6 Hz, 1H), 7.16 (ddd, *J* = 8.9, 7.5, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.23, 132.73, 128.32, 128.03, 122.12, 121.72, 119.72, 119.66, 119.63, 119.6, 118.02, 115.95, 115.52. HRMS *m/z* (ESI) calcd. for $C_{11}H_8N_2$ (M+H)+ 169.0761, found 169.0762. The NMR data agree with those reported in literature.[2,3]



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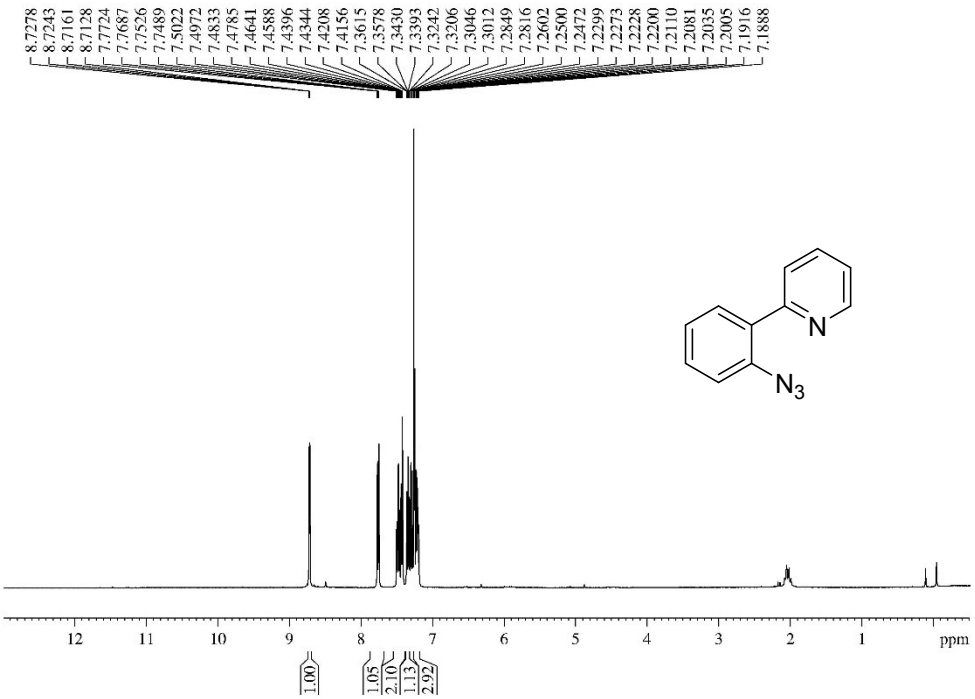
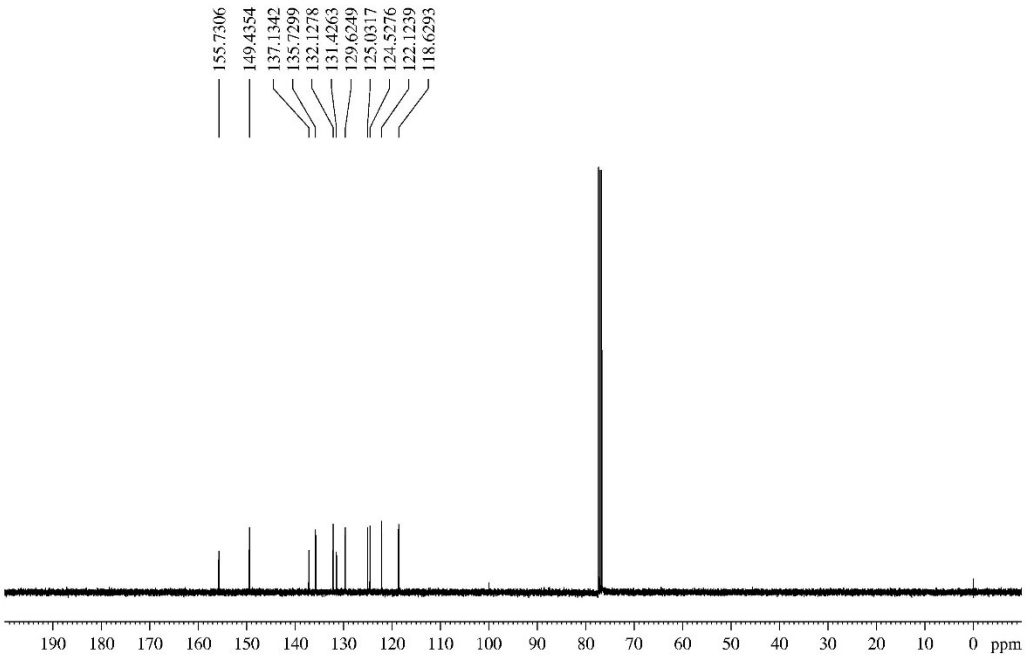
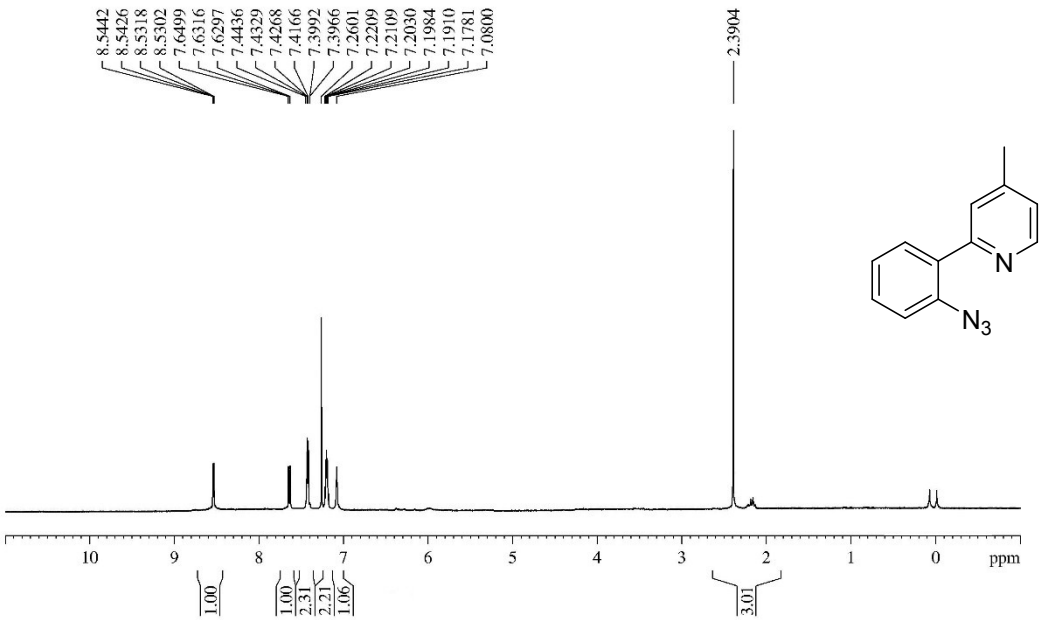
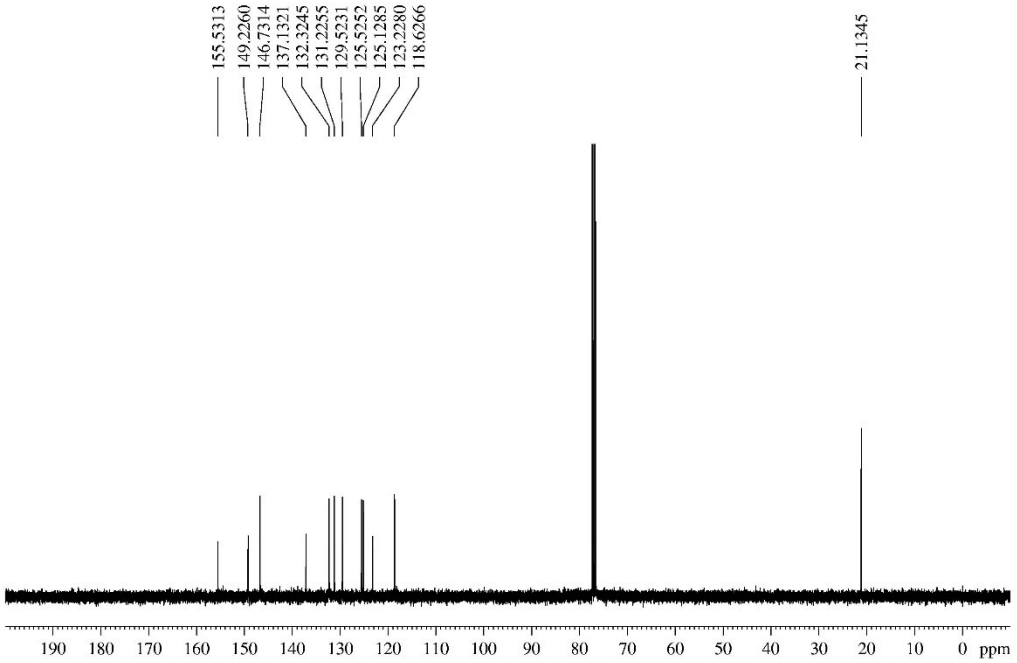
1. (a) E. D. Goddard-Borger and R. V. Stick, Organic letters, 2007, 9, 3797-3800.; (b) 1. A. R. Katritzky, M. El Khatib, O. Bol'shakov, L. Khelashvili and P. J. Steel, The Journal of organic chemistry, 2010, 75, 6532-6539..
2. F. Xie, Z. Qi and X. Li, Angewandte Chemie, 2013, 125, 12078-12082.
3. A. L. Pumphrey, H. Dong and T. G. Driver, Angewandte Chemie International Edition, 2012, 51, 5920-5923.



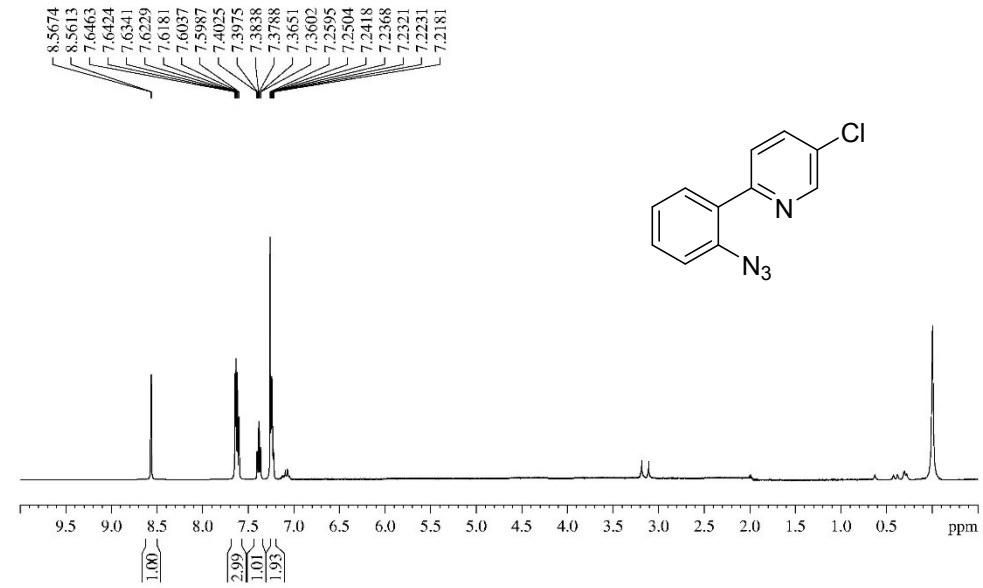


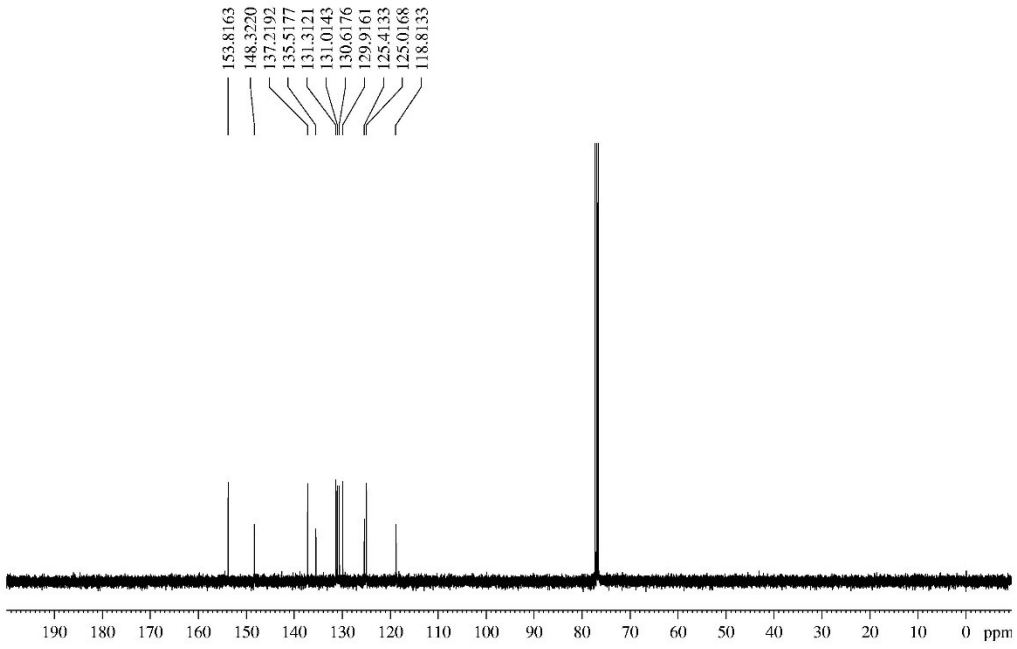
^{1}H and ^{13}C Spectra of 2a



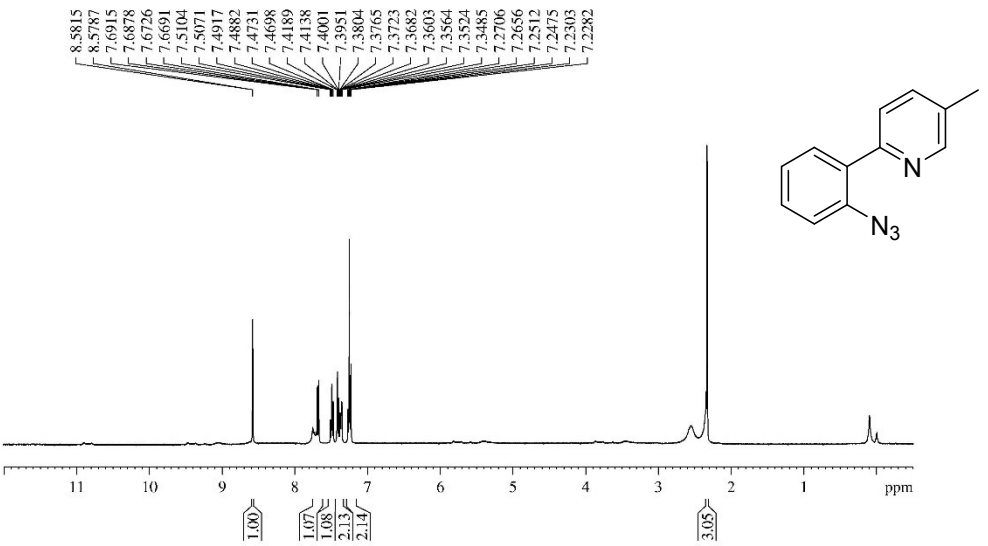


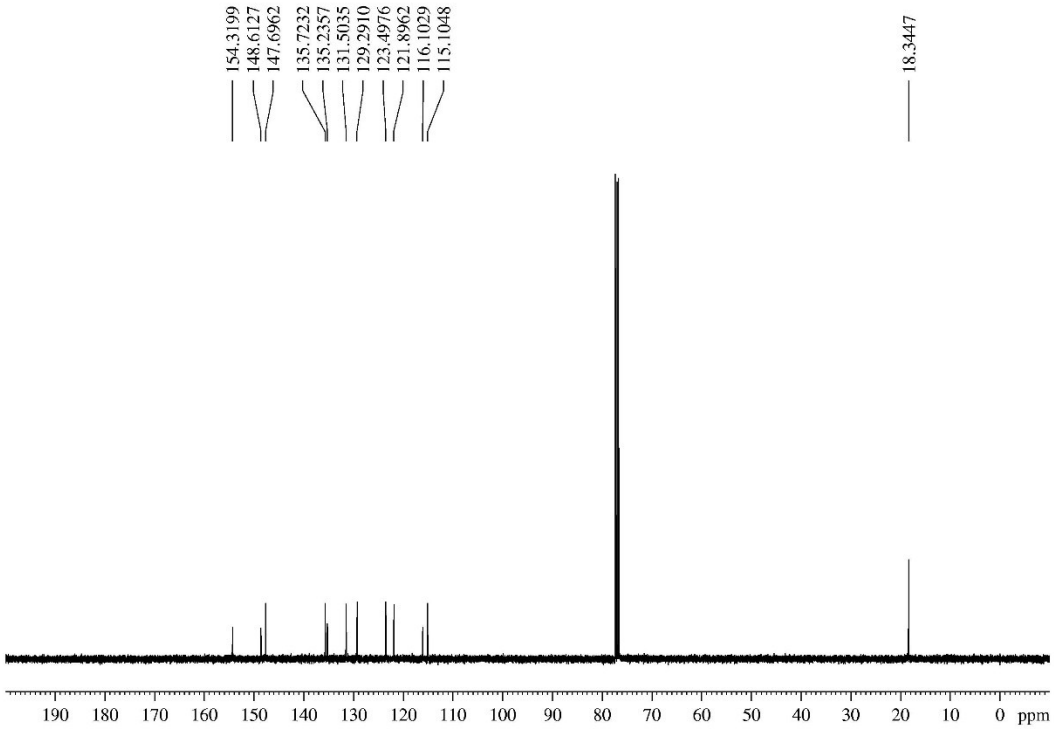
^{1}H and ^{13}C Spectra of 2b



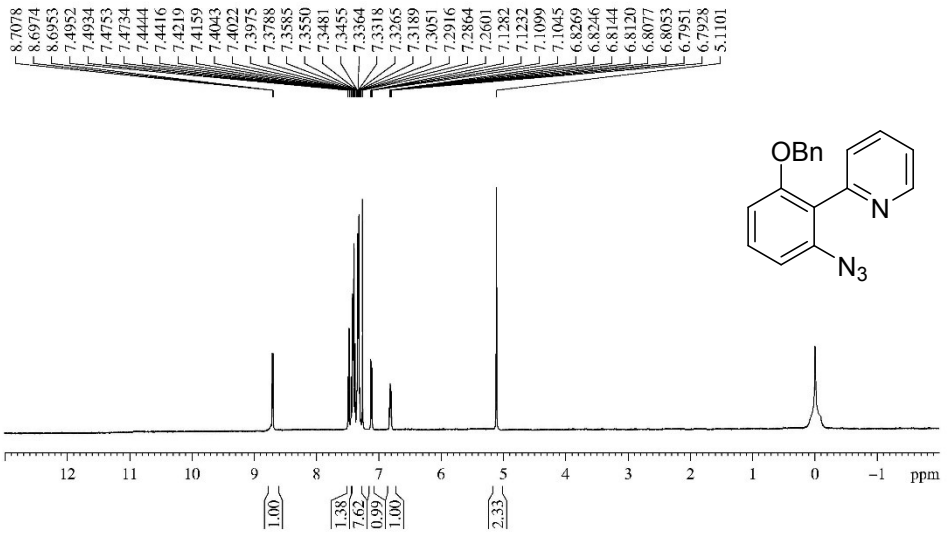


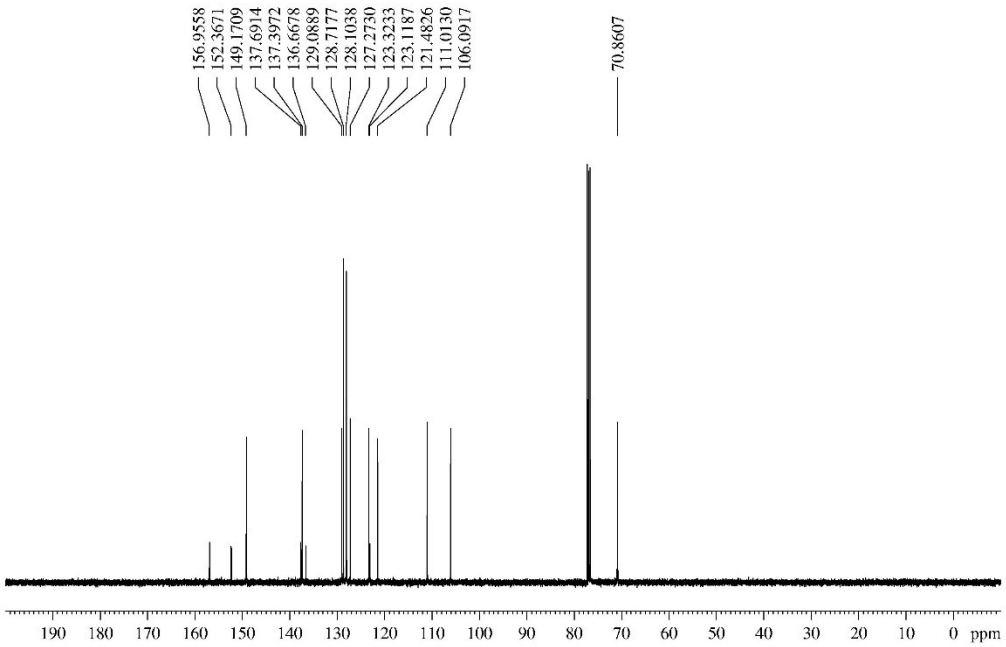
^{1}H and ^{13}C Spectra of 2c



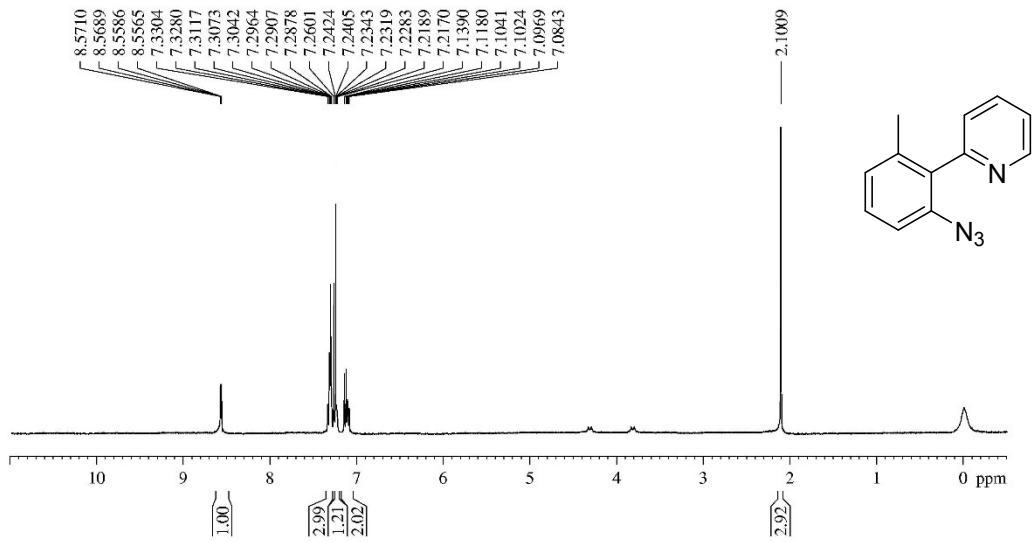


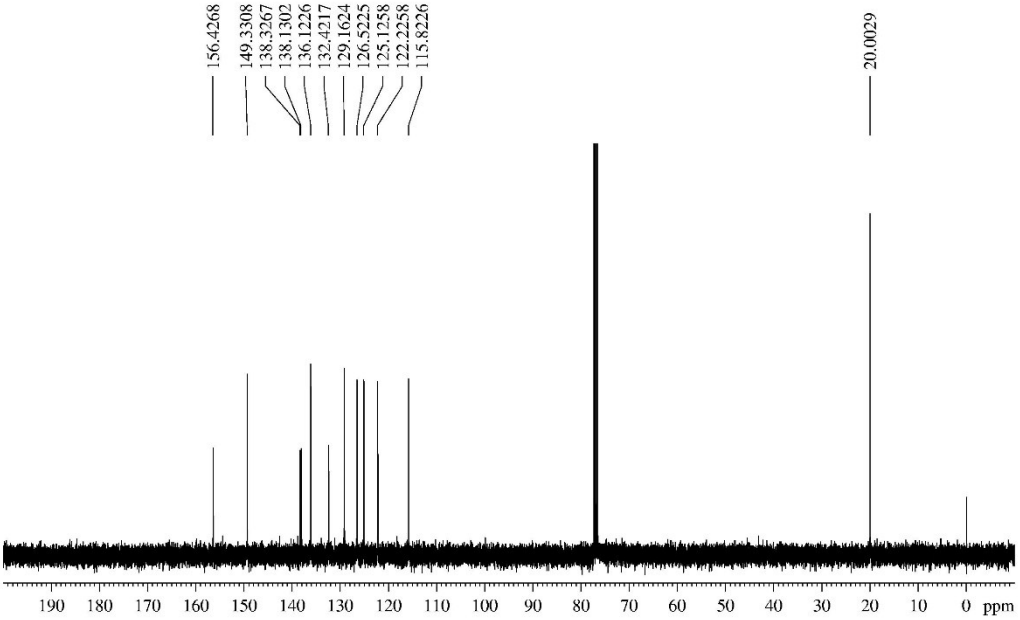
^{1}H and ^{13}C Spectra of 2d



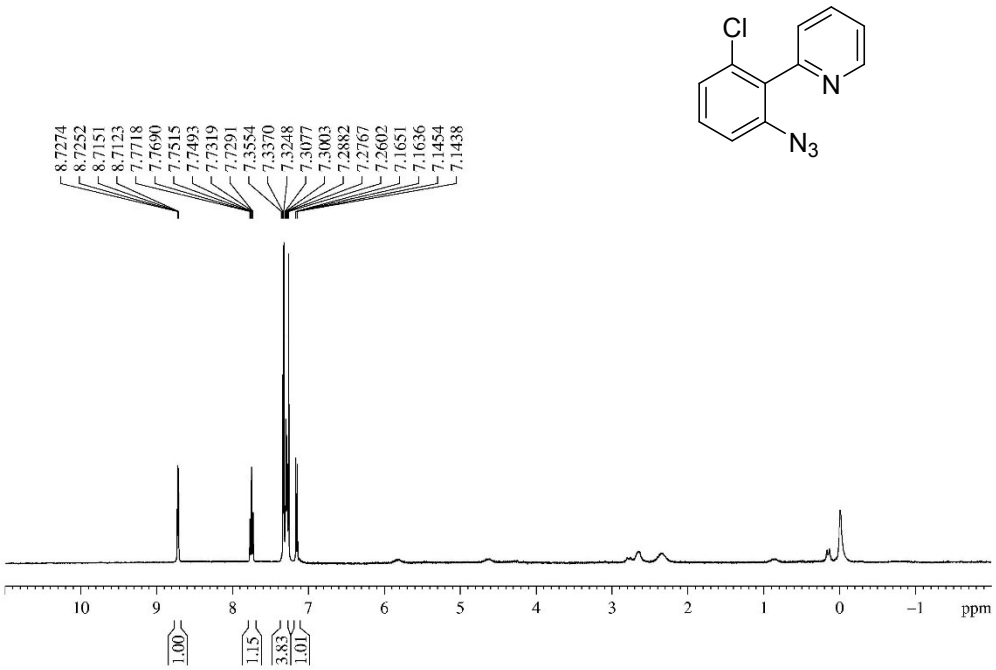


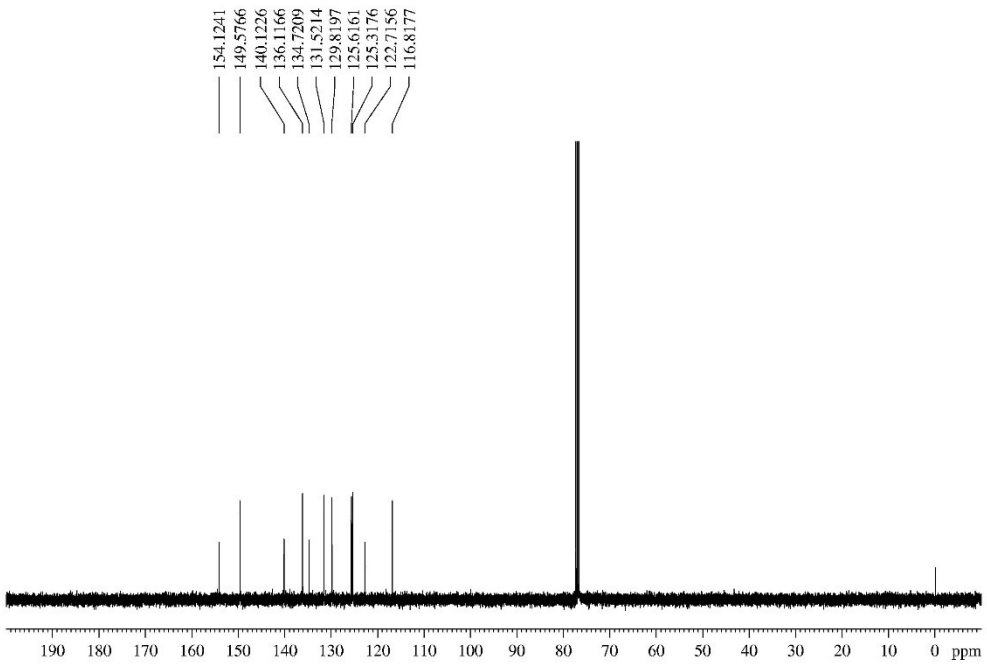
^{1}H and ^{13}C Spectra of 2e



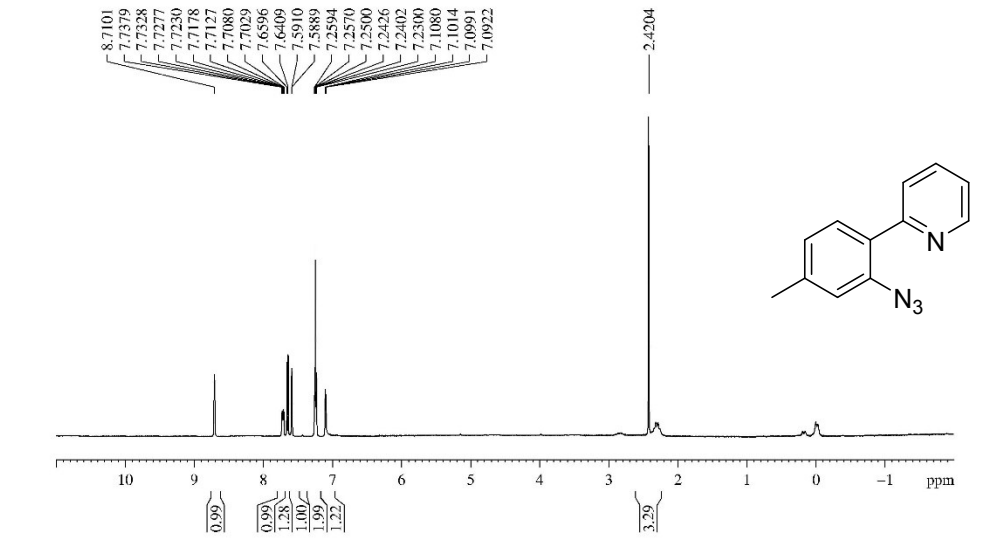


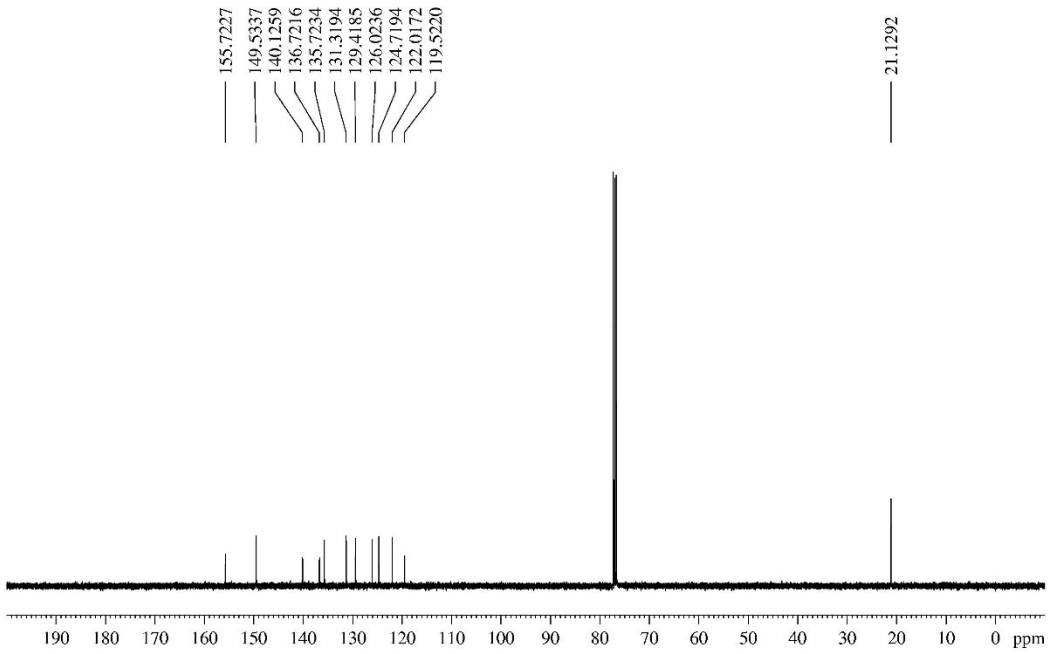
^{1}H and ^{13}C Spectra of 2f



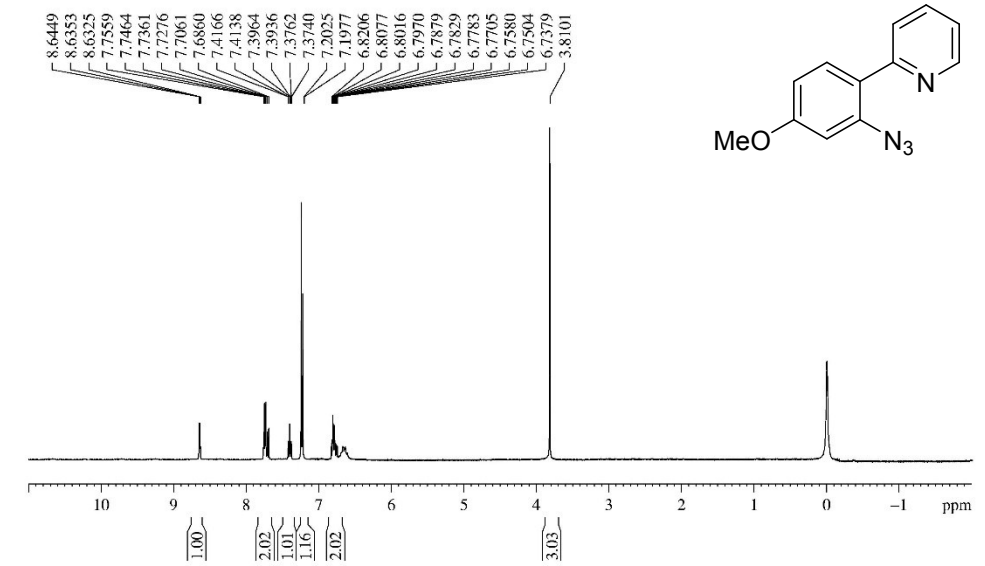


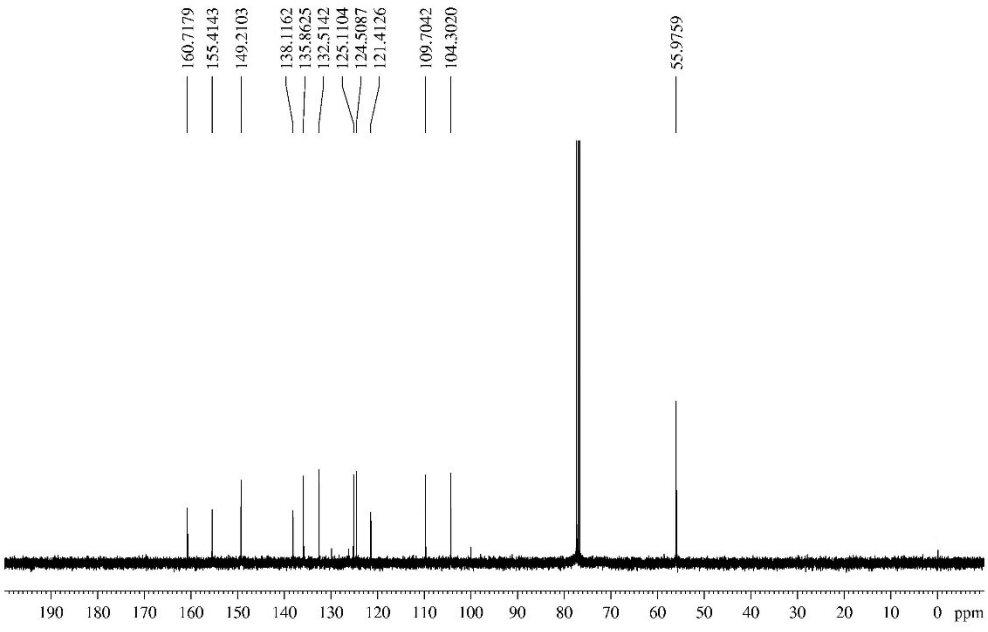
^{1}H and ^{13}C Spectra of 2g



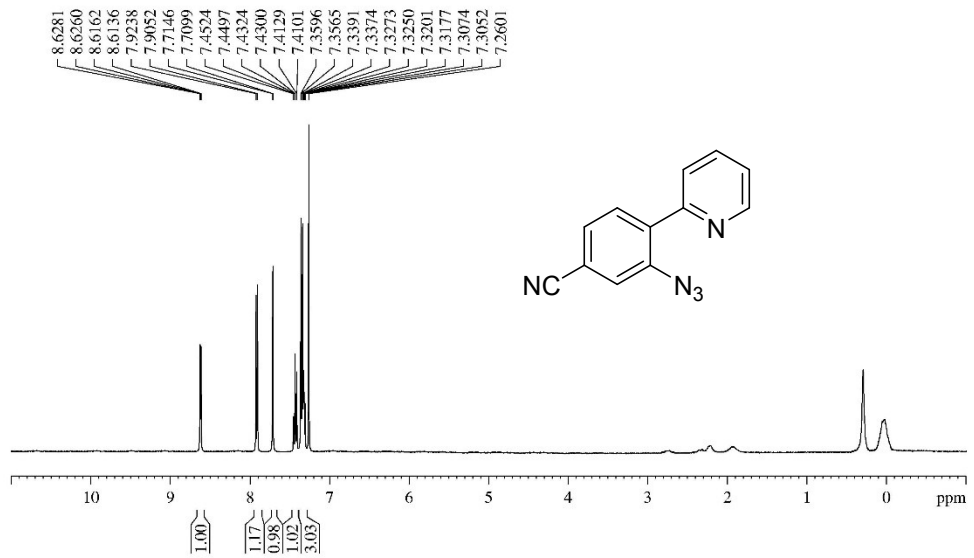


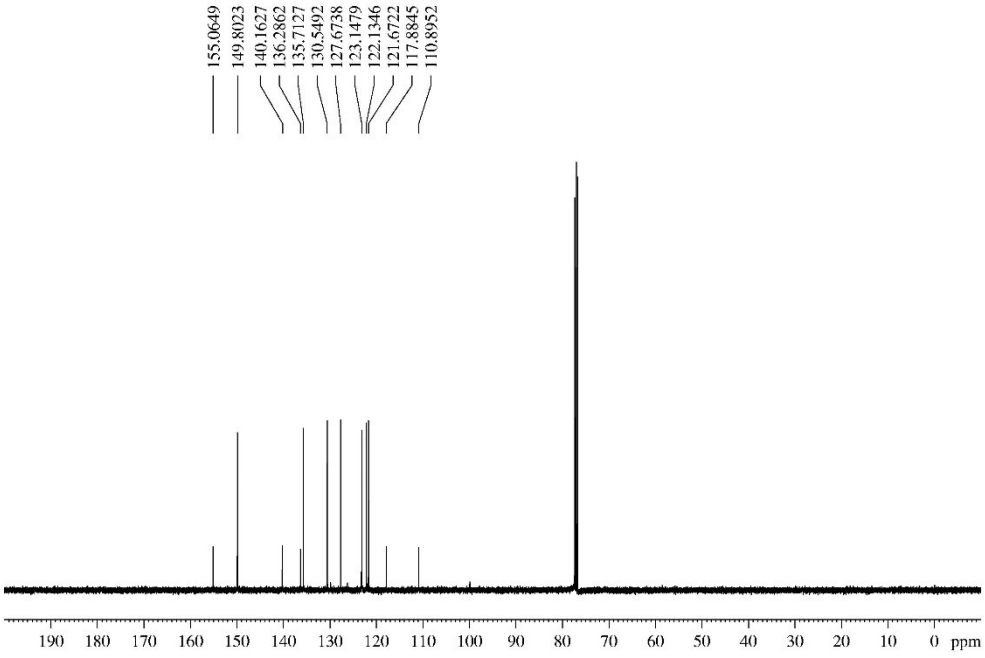
^{1}H and ^{13}C Spectra of 2h



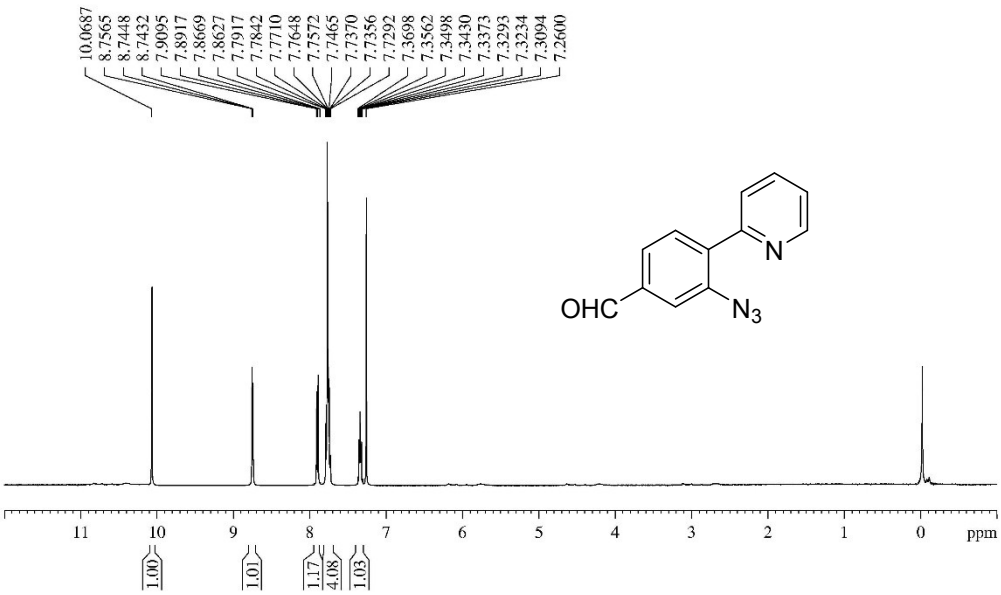


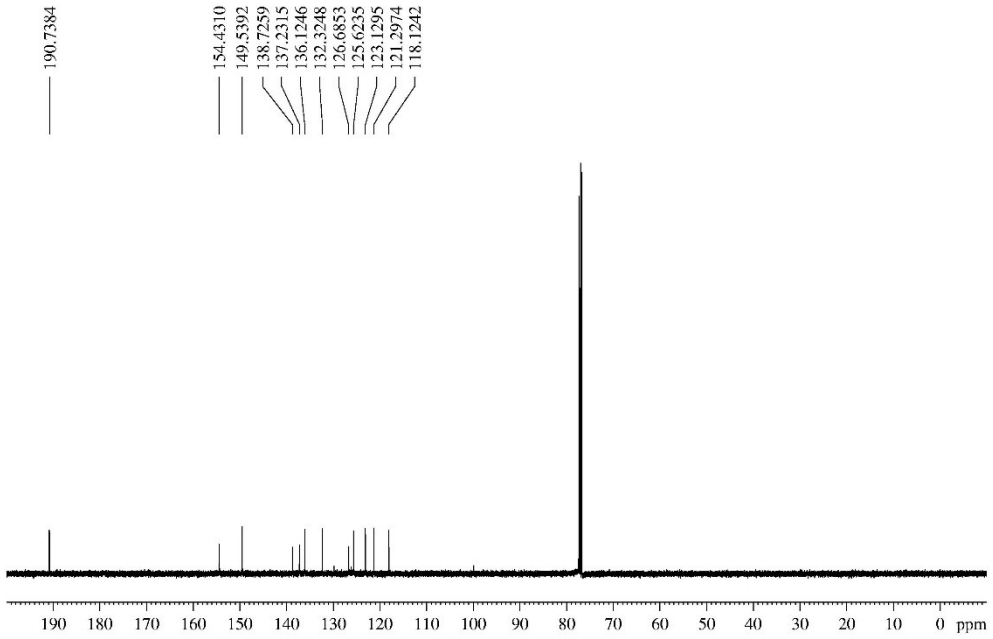
^{1}H and ^{13}C Spectra of 2i



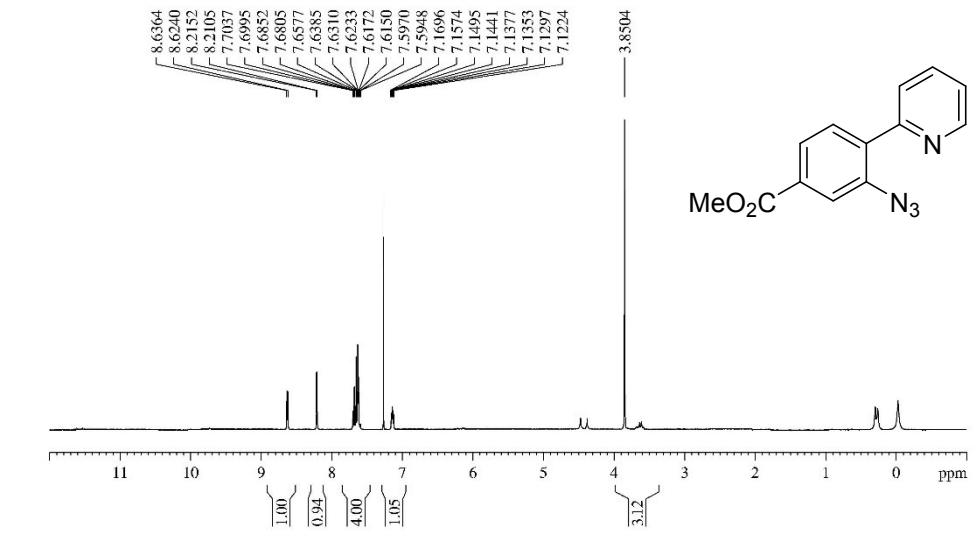


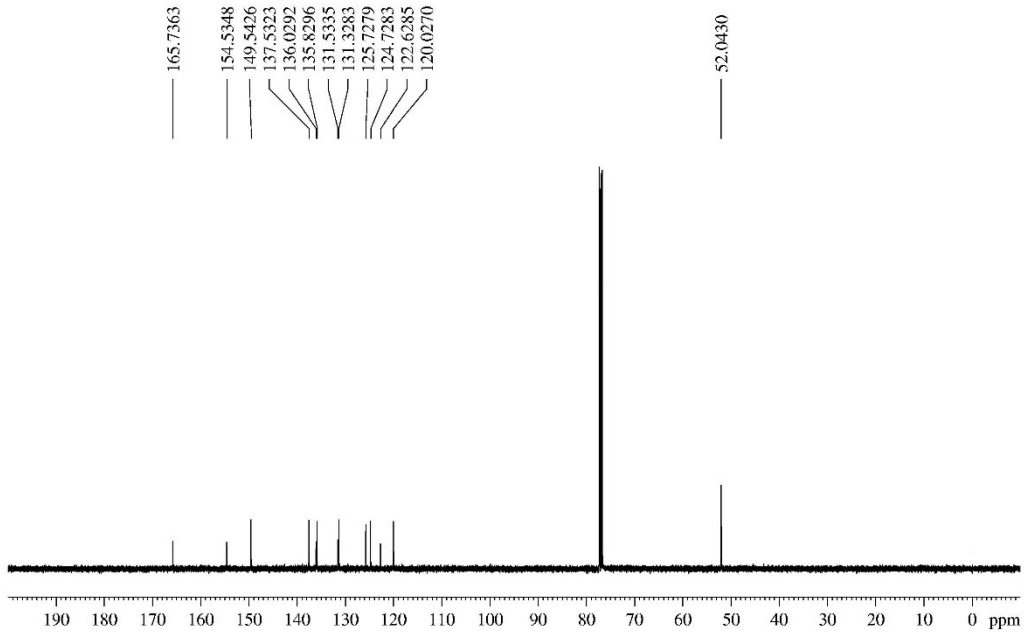
^{1}H and ^{13}C Spectra of 2j



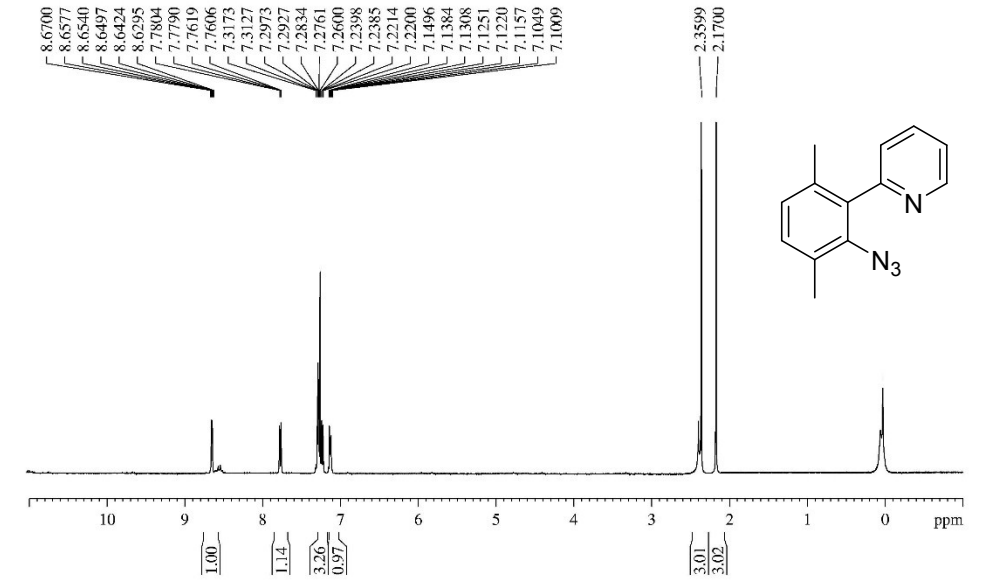


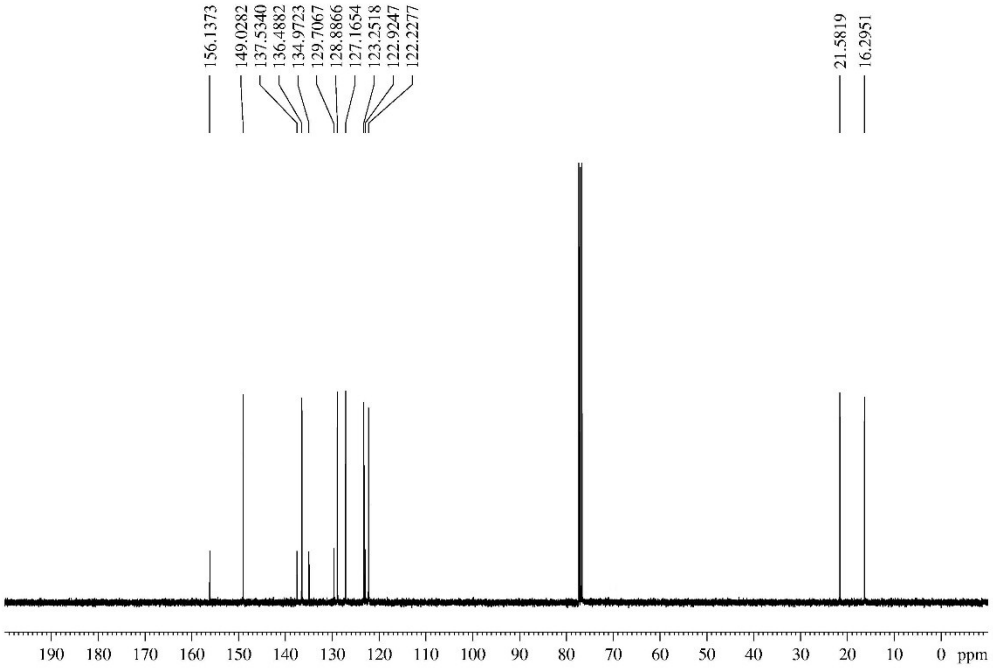
^{1}H and ^{13}C Spectra of 2k



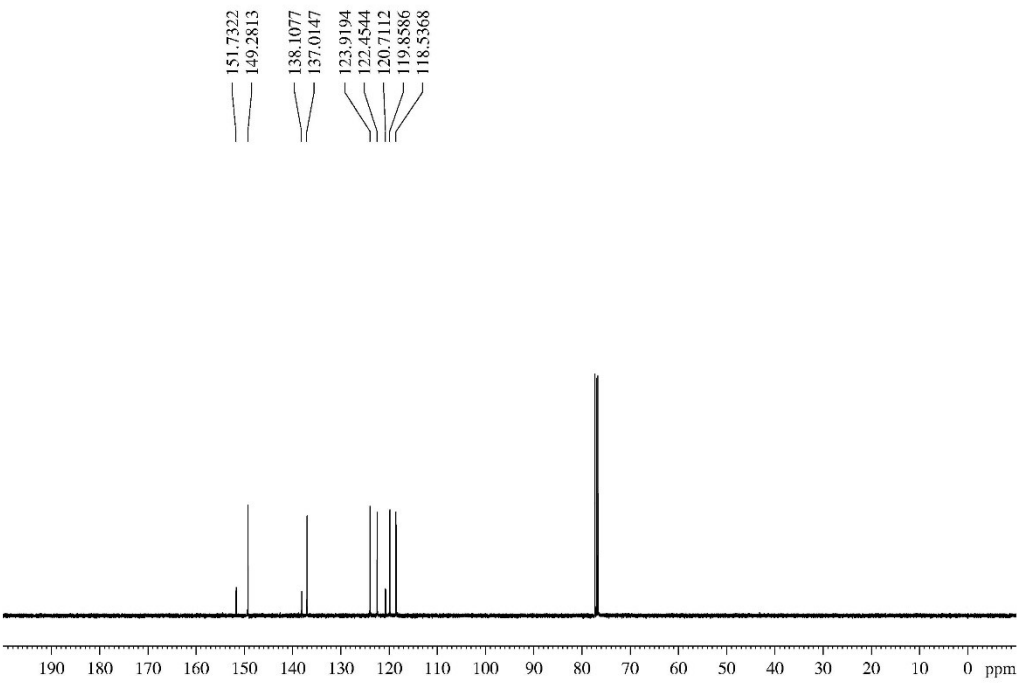


^{1}H and ^{13}C Spectra of 2l

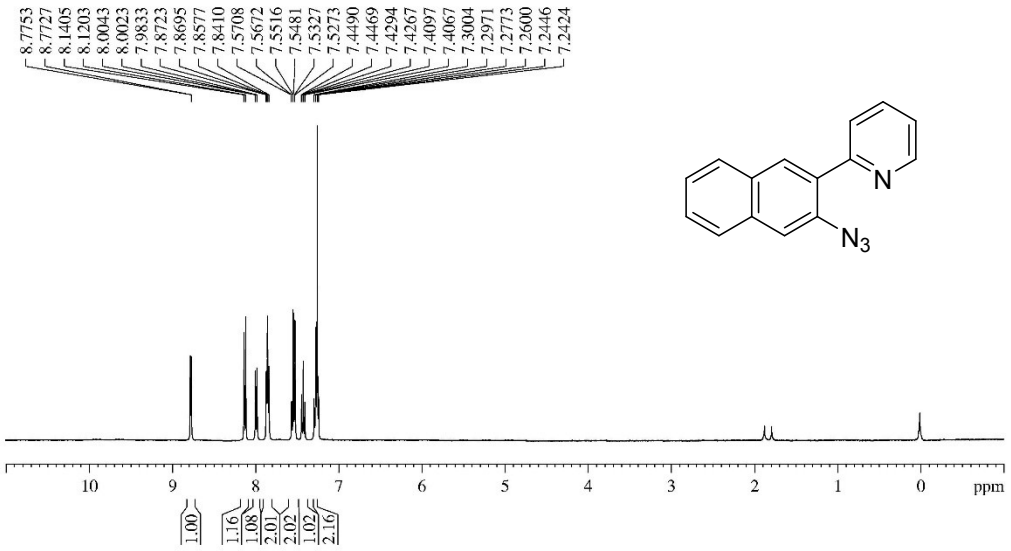


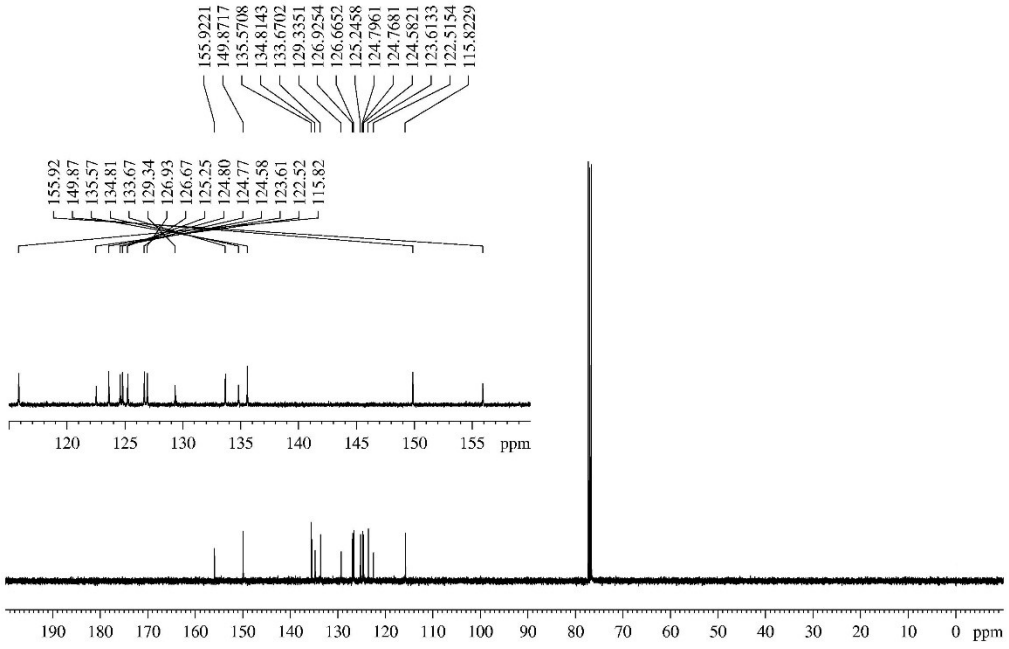


^{1}H and ^{13}C Spectra of 2m

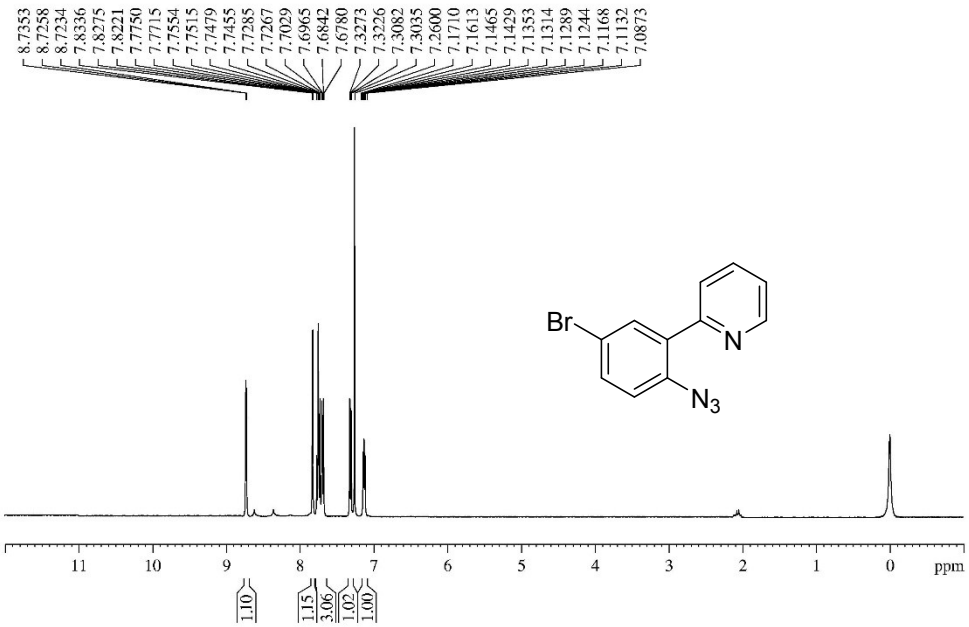


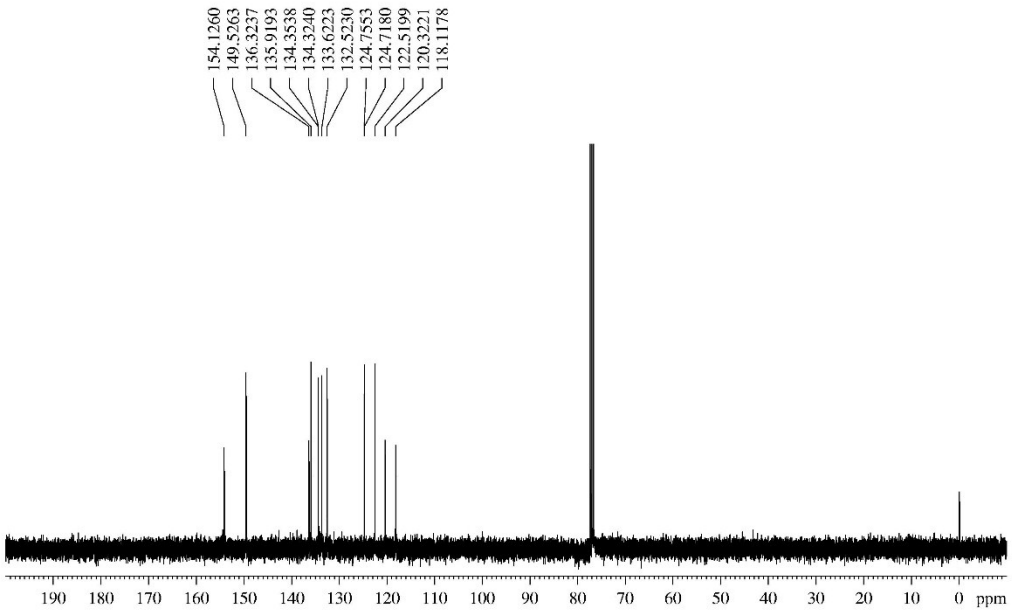
^{1}H and ^{13}C Spectra of 2n



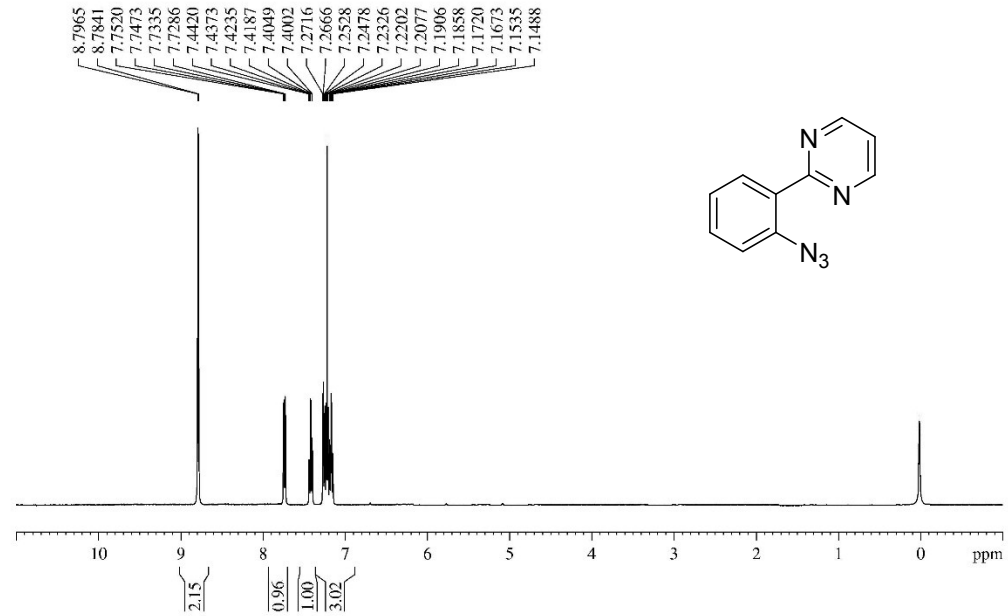


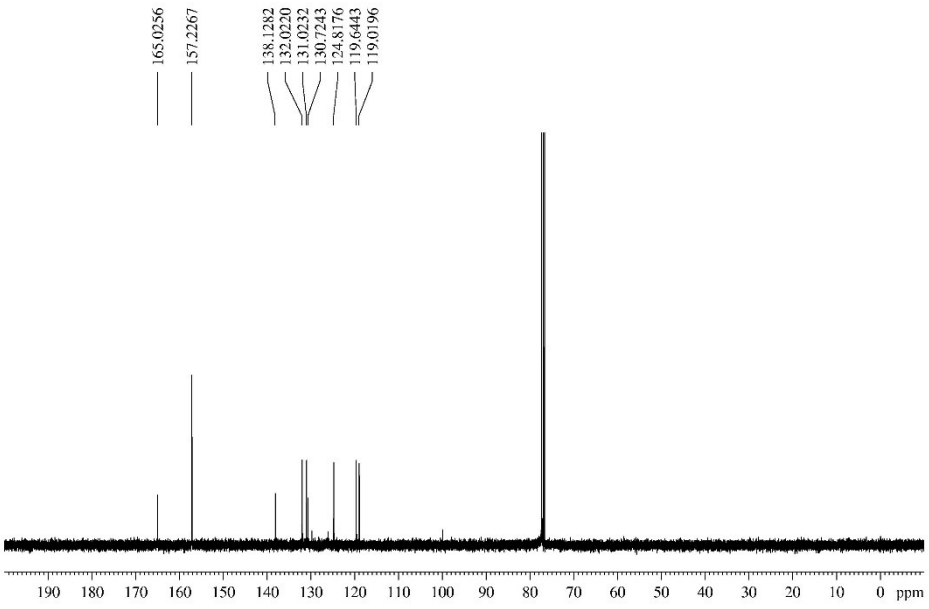
^{1}H and ^{13}C Spectra of 2o



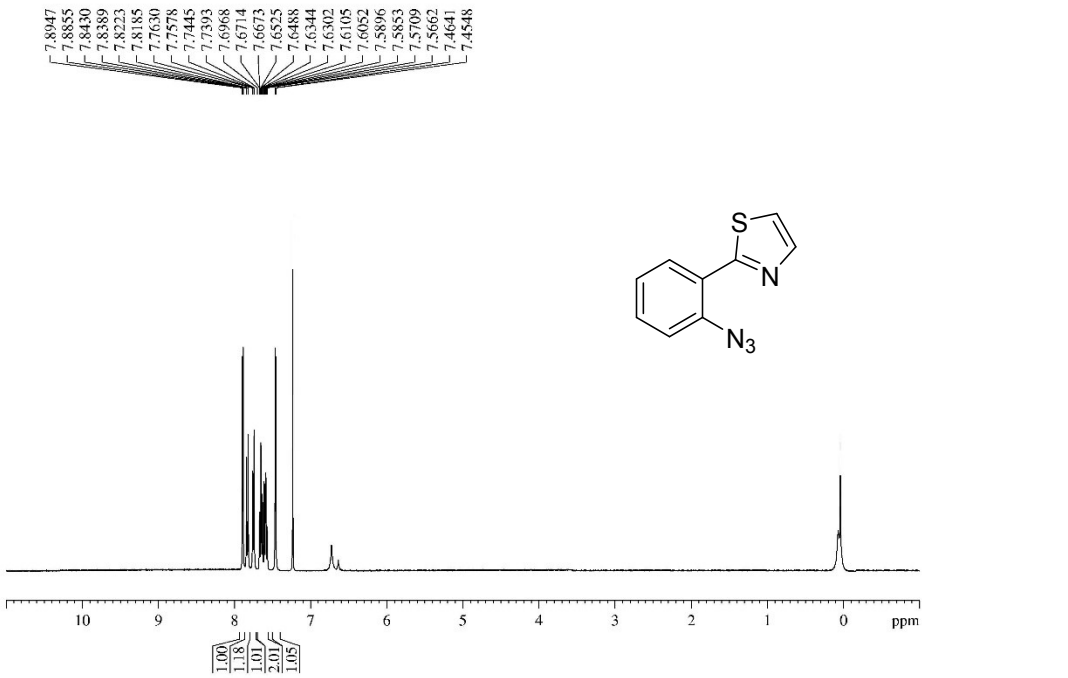


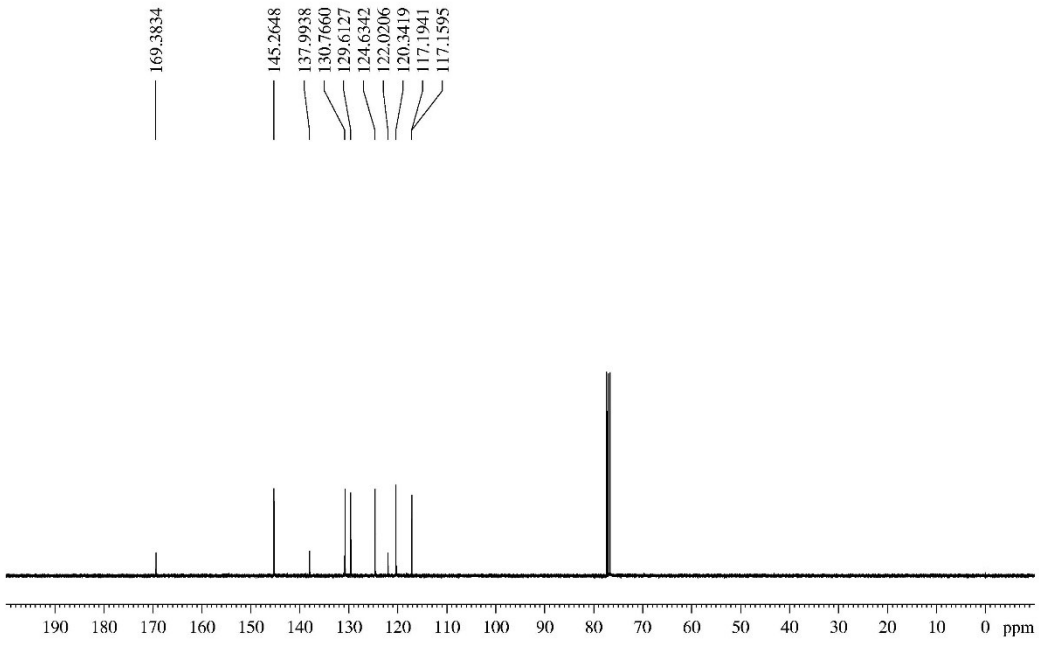
^{1}H and ^{13}C Spectra of 2p



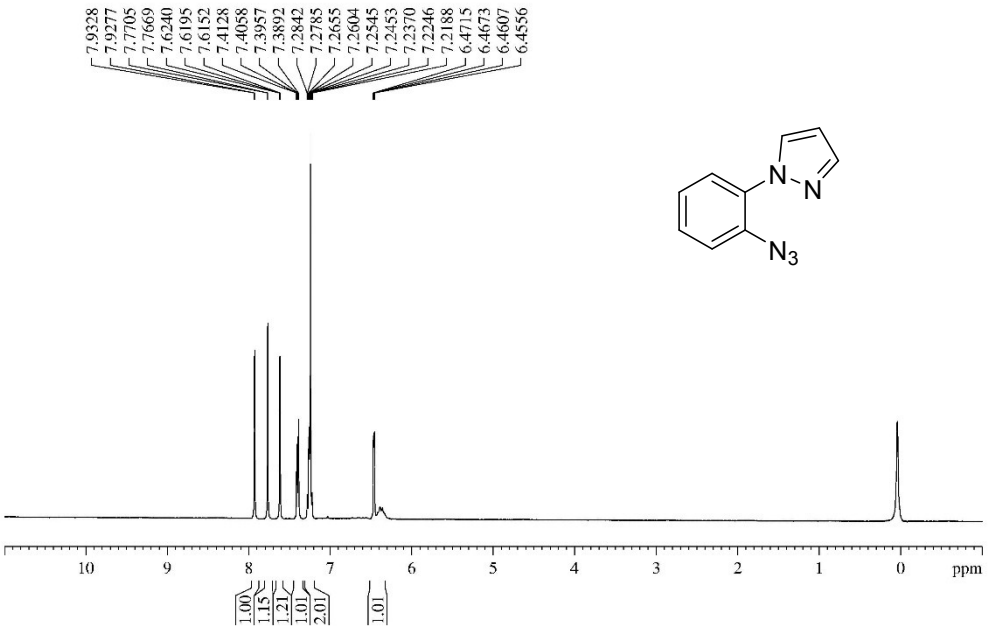


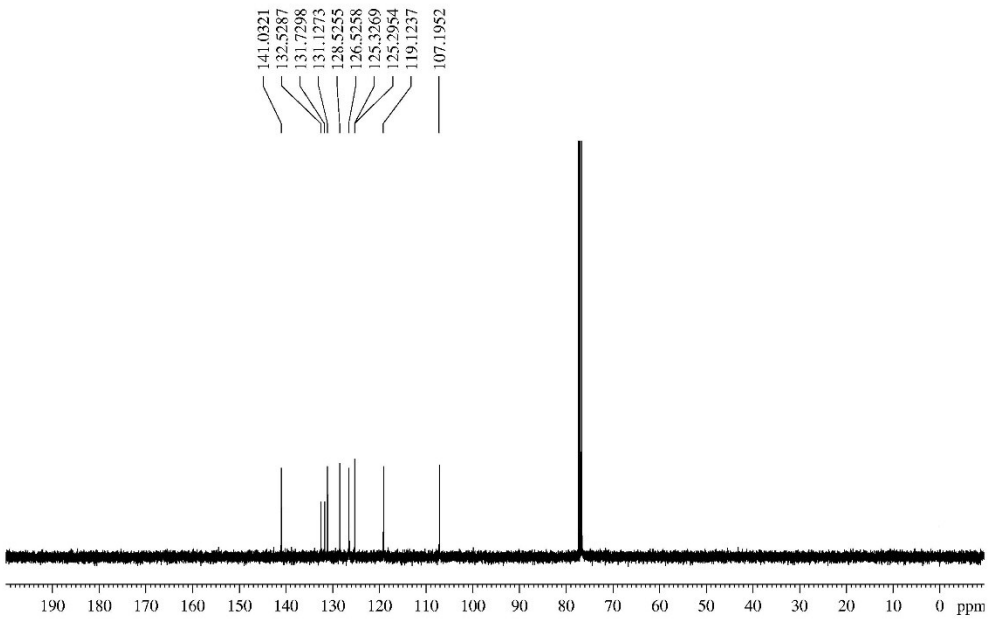
^{1}H and ^{13}C Spectra of 3c



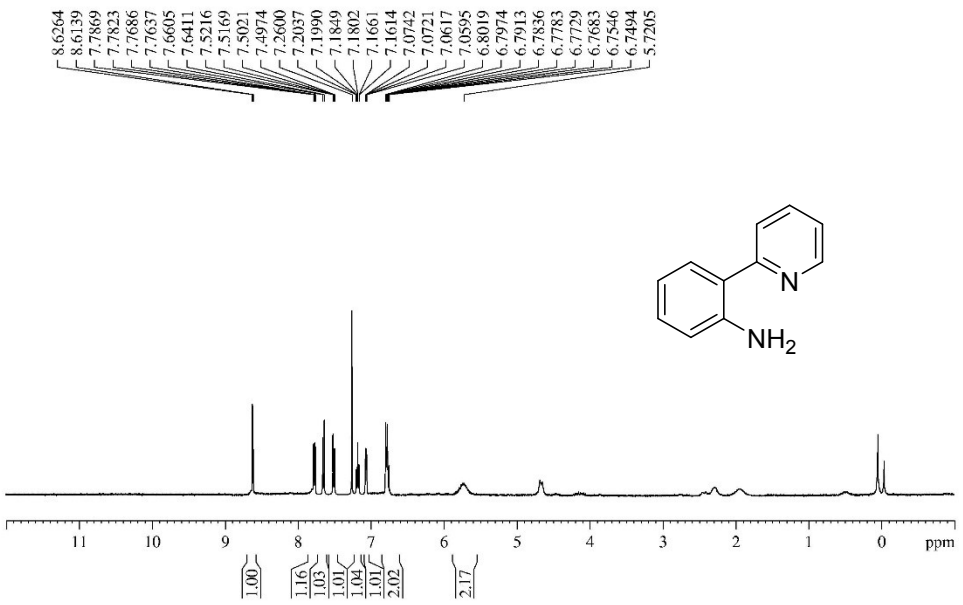


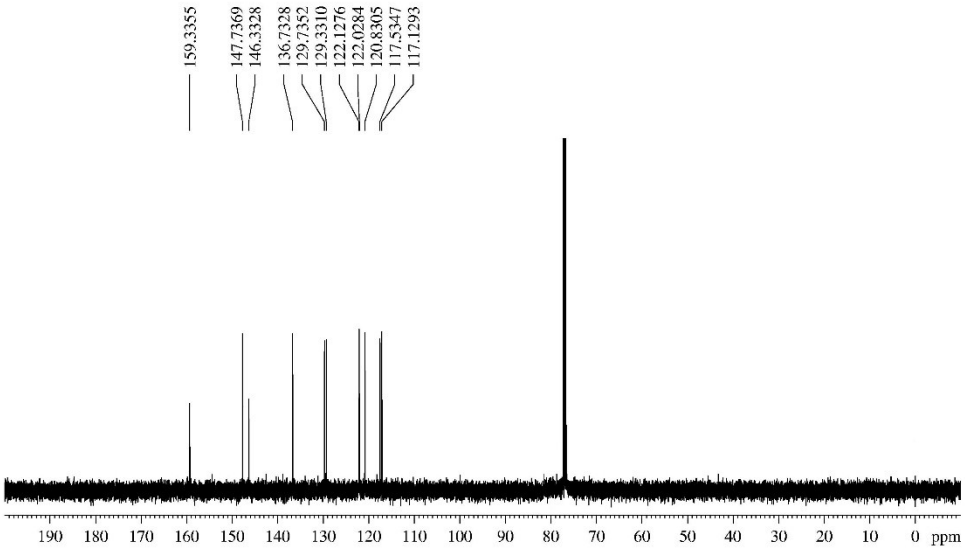
^{1}H and ^{13}C Spectra of 3e



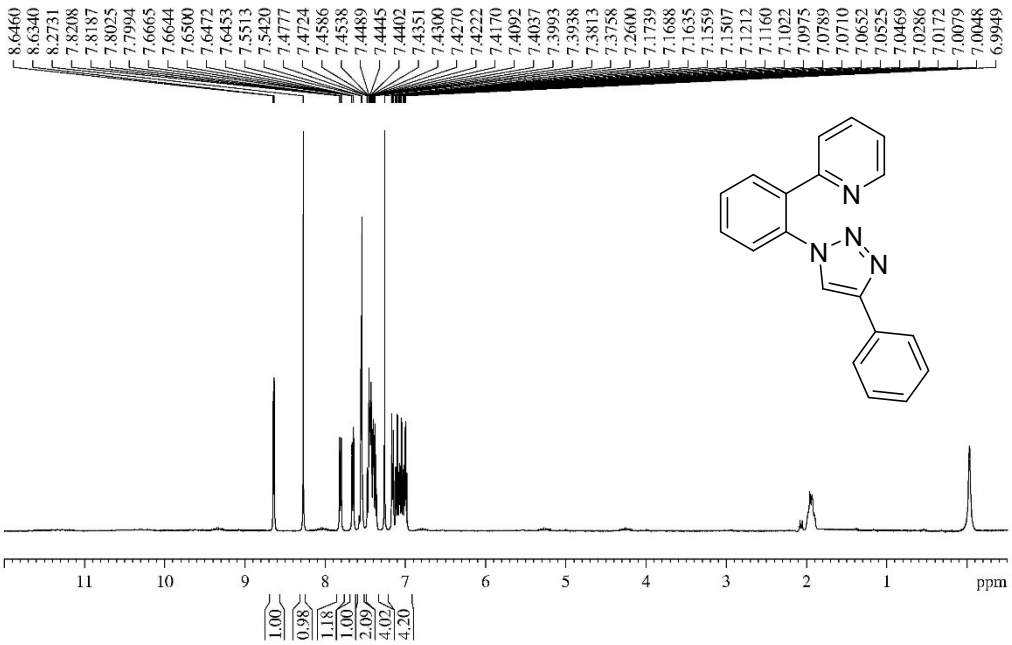


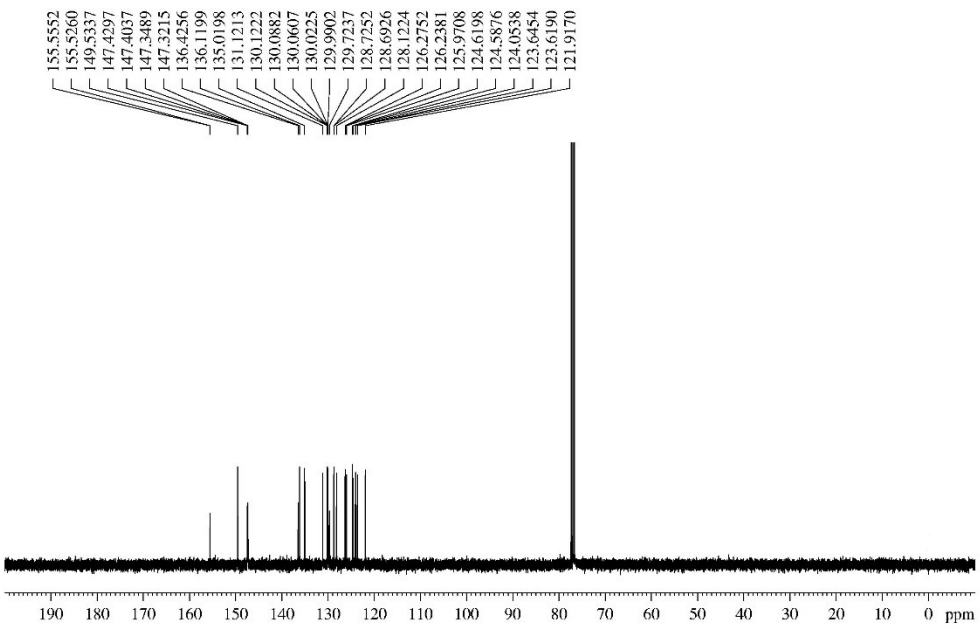
^{1}H and ^{13}C Spectra of 3d



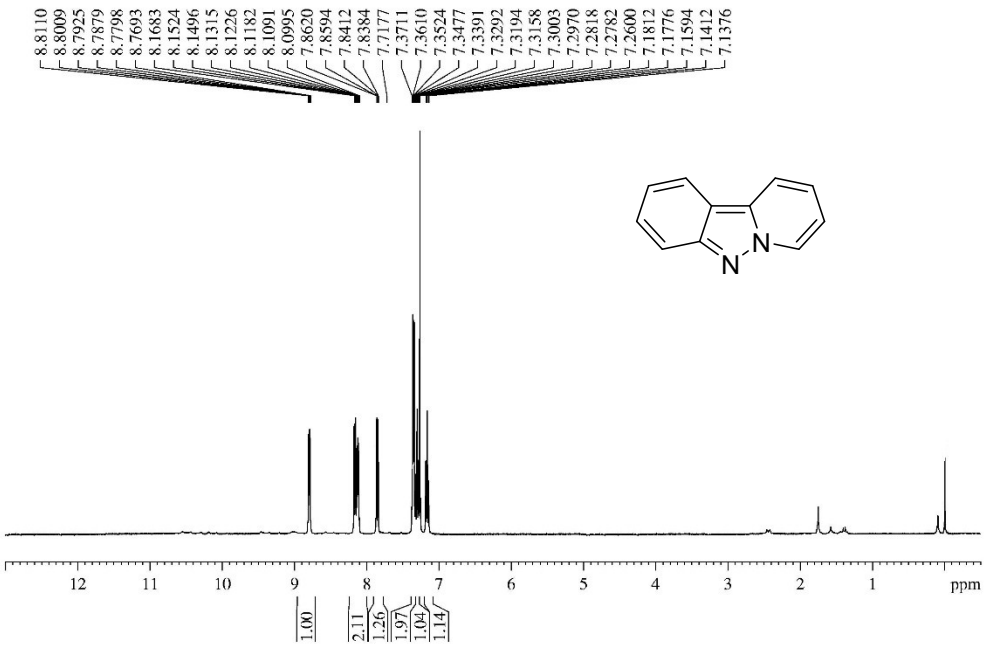


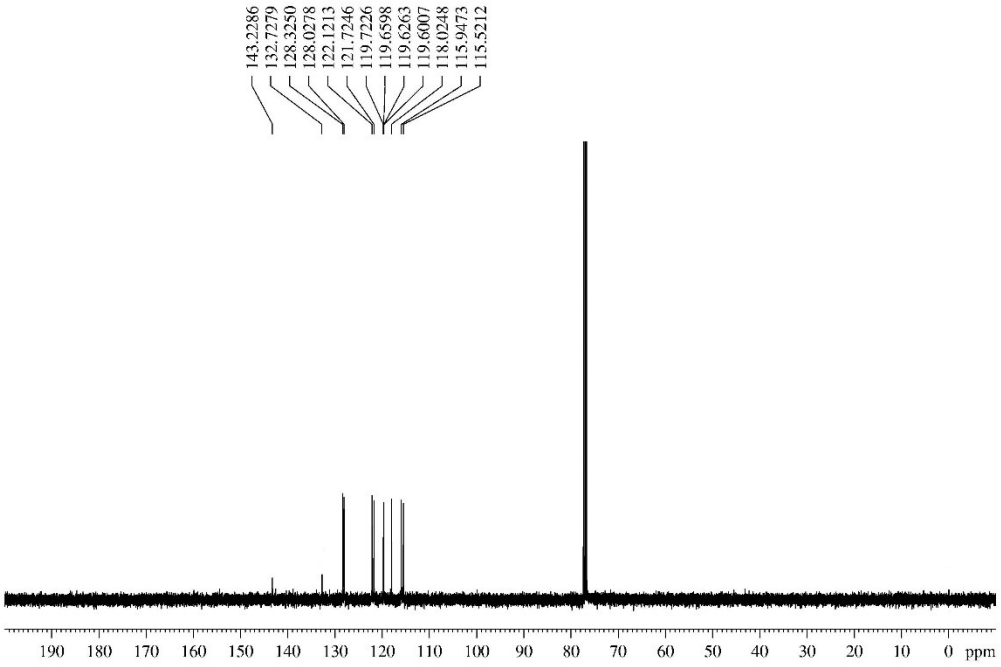
^{1}H and ^{13}C Spectra of 4a





^{1}H and ^{13}C Spectra of 4d





^{1}H and ^{13}C Spectra of 4c