

Intramolecular Electrochemical Dehydrogenative N-N Bond Formation for the Synthesis of 1,2,4-Triazolo[1,5-*a*]pyridines

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Supporting Information

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1. General information

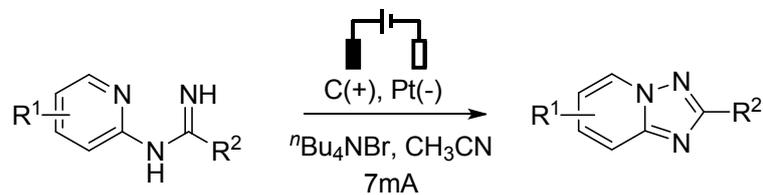
All reagents were obtained from commercial suppliers and used without further purification. Yields for all compounds were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether 40-60 (PE)/EtOAc as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass plate coated with silica gel with fluorescent indicator (GF254) using UV light. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE III 500 MHz using CDCl_3 as solvent with TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to CDCl_3 with 7.28 for ^1H and 77.03 for ^{13}C . Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz. Melting points were measured on a SGW[®] X-4B apparatus and uncorrected. HRMS were recorded on Agilent 6210TOF LC/MS mass spectrometer.

Electrolysis experiments were performed using a DC power supply. Two-electrode undivided cell was used for the synthetic part, only the three-electrode system was used for the cyclic voltammetry (CV) experiments. Normal operational voltage range for this reaction is around 3V–4.5V.

N-(pyridin-2-yl)benzimidamide and related compounds were prepared follow the procedure of literature.¹⁻³

2. Experimental procedure

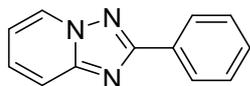
General procedure of synthesizing the products



General procedure: The crude *N*-(pyridin-2-yl)benzimidamide (0.3 mmol), ${}^n\text{Bu}_4\text{NBr}$ or ${}^n\text{Bu}_4\text{NI}$ (0.9 mmol), MeCN (7 mL) or MeCN / THF (5 mL / 2 mL) were added in a 10 mL undivided three-necked round-bottomed flask. Meantime the flask was equipped with graphite rod (ϕ 6 mm, about 10 mm immersion depth in solution) as the anode and platinum plate (10 mm \times 10 mm \times 0.2 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 7 mA under room temperature for 3h (2.6 F/mol). When the reaction was finished, the reaction mixture was transferred to a single-necked flask and dried by rotary evaporator. The mixture was purified by column chromatography through silica gel to provide the desired product.

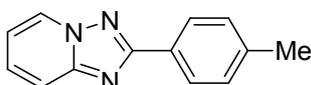
Procedure for gram scale synthesis: The crude *N*-(pyridin-2-yl)benzimidamide (**1a**; 8 mmol), ${}^n\text{Bu}_4\text{NBr}$ (20 mmol) and MeCN (150 mL) were added in a 200 mL undivided beaker-type cell, the mixture was stirred at room temperature. Meantime the flask was equipped with reticulated vitreous carbon (30 mm \times 30 mm \times 10 mm) as the anode and platinum plate (30 mm \times 30 mm \times 0.2 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 42 mA for 15.3 h (3 F/mol). When the reaction was finished, the reaction mixture was transferred to a single-necked flask and the MeCN was recovered by rotary evaporation for repeated use. The given residue was washed with water and extracted with EA (50 mL \times 3). The organic layers were combined, dried over Na_2SO_4 , and concentrated. The given residue was purified by column chromatography through silica gel to provide the desired product **2a**.

3. Synthesis and characterization of the products



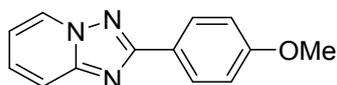
2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (2a):

Following the general procedure, **2a** was purified by PE/EtOAc (6:1) and obtained as a white solid (54 mg, 92% yield); Mp = 128 - 131 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.61 (dt, J = 6.8, 1.1 Hz, 1H), 8.36 - 8.25 (m, 2H), 7.77 (dt, J = 8.9, 1.1 Hz, 1H), 7.59 - 7.42 (m, 4H), 7.01 (td, J = 6.8, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.1, 151.6, 130.7, 130.1, 129.5, 128.7, 128.3, 127.3, 116.4, 113.6. The spectra data matched with values reported in the literature.¹



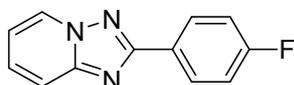
2-(*p*-tolyl)-[1,2,4]triazolo[1,5-a]pyridine (2b):

Following the general procedure, **2b** was purified by PE/EtOAc (6:1) and obtained as a white solid (47 mg, 74% yield); Mp = 162 - 165 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.61 (dt, J = 6.8, 1.2 Hz, 1H), 8.24 - 8.15 (m, 2H), 7.77 (dt, J = 8.9, 1.1 Hz, 1H), 7.52 (ddd, J = 8.9, 6.9, 1.3 Hz, 1H), 7.36 - 7.30 (m, 2H), 7.02 (td, J = 6.9, 1.3 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.2, 151.6, 140.3, 129.5, 129.5, 128.3, 127.3, 116.3, 113.6, 21.5. The spectra data matched with values reported in the literature.¹



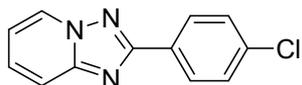
2-(4-methoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (2c):

Following the general procedure, **2c** was purified by PE/EtOAc (6:1) and obtained as a white solid (45 mg, 66% yield); Mp = 135 - 138 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.59 (dt, J = 6.8, 1.1 Hz, 1H), 8.30 - 8.18 (m, 2H), 7.75 (dt, J = 9.0, 1.1 Hz, 1H), 7.51 (ddd, J = 8.9, 6.9, 1.3 Hz, 1H), 7.06-7.02 (m, 2H), 7.00 (td, J = 6.9, 1.2 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.2, 151.6, 140.3, 129.5, 129.5, 128.3, 127.3, 116.3, 113.6, 21.5. The spectra data matched with values reported in the literature.¹



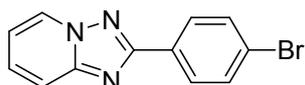
2-(4-fluorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (2d):

Following the general procedure, **2d** was purified by PE/EtOAc (6:1) and obtained as a white solid (42 mg, 65% yield); Mp = 169 - 171 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.60 (dt, J = 6.7, 1.1 Hz, 1H), 8.37 - 8.24 (m, 2H), 7.76 (dt, J = 8.9, 1.2 Hz, 1H), 7.52 (ddd, J = 8.9, 6.9, 1.3 Hz, 1H), 7.24 - 7.14 (m, 2H), 7.02 (td, J = 6.8, 1.3 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.1(d, $J_{\text{C-F}}$ = 250.2 Hz), 163.4, 151.7, 129.6, 129.3(d, $J_{\text{C-F}}$ = 8.4 Hz), 128.3, 127.0(d, $J_{\text{C-F}}$ = 3.5 Hz), 116.4, 115.8(d, $J_{\text{C-F}}$ = 20.2 Hz), 113.7. The spectra data matched with values reported in the literature.¹



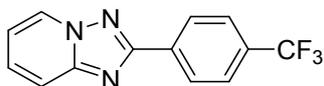
2-(4-chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (2e):

Following the general procedure, **2e** was purified by PE/EtOAc (6:1) and obtained as a white solid (50 mg, 72% yield); Mp = 186 - 189 °C; R_f = 0.30 (PE/EtOAc = 6:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.61 (dt, J = 6.9, 1.1 Hz, 1H), 8.28 - 8.22 (m, 2H), 7.78 (dt, J = 9.0, 1.2 Hz, 1H), 7.55 (ddd, J = 9.0, 6.9, 1.3 Hz, 1H), 7.50 - 7.47 (m, 2H), 7.05 (td, J = 6.9, 1.3 Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 163.2, 151.7, 136.3, 129.9, 129.3, 129.1, 128.7, 128.4, 116.5, 113.9. The spectra data matched with values reported in the literature.¹



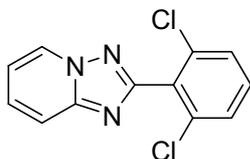
2-(4-bromophenyl)-[1,2,4]triazolo[1,5-a]pyridine (2f):

Following the general procedure, **2f** was purified by PE/EtOAc (6:1) and obtained as a white solid (57 mg, 70% yield); Mp = 214 - 217 °C; R_f = 0.30 (PE/EtOAc = 6:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.60 (dt, J = 6.9, 1.2 Hz, 1H), 8.22 - 8.12 (m, 2H), 7.76 (dt, J = 9.0, 1.2 Hz, 1H), 7.67 - 7.59 (m, 2H), 7.56 - 7.50 (m, 1H), 7.03 (td, J = 6.9, 1.3 Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 164.2, 151.6, 140.3, 129.5, 129.5, 128.3, 127.3, 116.3, 113.6, 21.5. The spectra data matched with values reported in the literature.¹



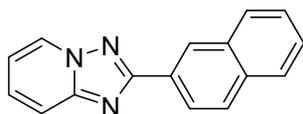
2-(4-(trifluoromethyl)phenyl)-[1,2,4]triazolo[1,5-a]pyridine (2g):

Following the general procedure, **2g** was purified by PE/EtOAc (6:1) and obtained as a white solid (74 mg, 93% yield); Mp = 224 - 227 °C; R_f = 0.30 (PE/EtOAc = 6:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.59 (dt, J = 6.8, 1.1 Hz, 1H), 8.30 - 8.18 (m, 2H), 7.75 (dt, J = 9.0, 1.1 Hz, 1H), 7.51 (ddd, J = 8.9, 6.9, 1.3 Hz, 1H), 7.06 - 7.02 (m, 2H), 7.00 (td, J = 6.9, 1.2 Hz, 1H), 3.89 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.8, 151.7, 134.2, 131.9 (dd, J_{C-F} = 32.4 Hz), 129.9, 128.5, 127.6, 125.7, 124.1 (d, J_{C-F} = 272.8 Hz), 116.7, 114.1, 21.5. The spectra data matched with values reported in the literature.⁵



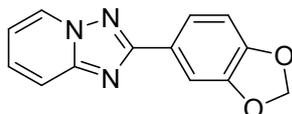
2-(2,6-dichlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (2h):

Following the general procedure, **2h** was purified by PE/EtOAc (6:1) and obtained as a white solid (48 mg, 60% yield); Mp = 128 - 131 °C; R_f = 0.30 (PE/EtOAc = 6:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.69 (dt, J = 6.8, 1.2 Hz, 1H), 7.86 (dt, J = 8.9, 1.2 Hz, 1H), 7.60 (ddd, J = 9.0, 7.0, 1.3 Hz, 1H), 7.48 - 7.42 (m, 2H), 7.37 (dd, J = 8.9, 7.3 Hz, 1H), 7.12 (td, J = 6.9, 1.3 Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.7, 151.2, 136.0, 131.1, 130.8, 129.8, 128.7, 128.0, 117.1, 114.1. The spectra data matched with values reported in the literature.³



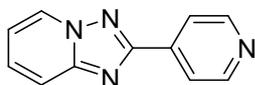
2-(naphthalen-2-yl)-[1,2,4]triazolo[1,5-a]pyridine (2i):

Following the general procedure, **2i** was purified by PE/EtOAc (6:1) and obtained as a white solid (56 mg, 76% yield); Mp = 165 - 167 °C; R_f = 0.30 (PE/EtOAc = 6:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.85 (d, J = 1.5 Hz, 1H), 8.65 (dt, J = 6.8, 1.2 Hz, 1H), 8.40 (dd, J = 8.5, 1.7 Hz, 1H), 8.04-7.95 (m, 2H), 7.94 - 7.87 (m, 1H), 7.81 (dt, J = 8.9, 1.2 Hz, 1H), 7.59 - 7.49 (m, 3H), 7.03 (td, J = 6.9, 1.3 Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 164.2, 151.7, 134.3, 133.4, 129.7, 128.8, 128.4, 128.4, 128.0, 127.8, 127.2, 126.9, 126.4, 124.5, 116.4, 113.7. Calculated for $\text{C}_{16}\text{H}_{11}\text{N}_3$ $[\text{M}+\text{H}]^+$: 246.1026; Found: 246.1035.



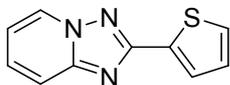
2-(benzo[d][1,3]dioxol-5-yl)-[1,2,4]triazolo[1,5-a]pyridine (2j):

Following the general procedure, **2j** was purified by PE/EtOAc (6:1) and obtained as a white solid (43 mg, 60% yield); Mp = 196 - 198 °C; R_f = 0.30 (PE/EtOAc = 6:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.57 (dt, J = 6.9, 1.1 Hz, 1H), 7.86 (dd, J = 8.1, 1.7 Hz, 1H), 7.79 - 7.68 (m, 2H), 7.50 (ddd, J = 9.0, 6.9, 1.3 Hz, 1H), 6.99 (td, J = 6.9, 1.3 Hz, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 164.0, 151.6, 149.3, 148.1, 129.5, 128.2, 124.9, 121.8, 116.2, 113.4, 108.6, 107.6, 101.4. The spectra data matched with values reported in the literature.⁵



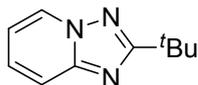
2-(pyridin-4-yl)-[1,2,4]triazolo[1,5-a]pyridine (2k):

Following the general procedure, **2k** was purified by PE/EtOAc (6:1) and obtained as a white solid (37 mg, 62% yield); Mp = 189 - 192 °C; R_f = 0.30 (PE/EtOAc = 6:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.87 - 8.72 (m, 2H), 8.63 (dt, J = 6.8, 1.2 Hz, 1H), 8.21-8.10 (m, 2H), 7.81 (dt, J = 9.0, 1.2 Hz, 1H), 7.58 (ddd, J = 8.9, 6.9, 1.3 Hz, 1H), 7.09 (td, J = 6.9, 1.3 Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 164.2, 151.6, 140.3, 129.5, 129.5, 128.3, 127.3, 116.3, 113.6, 21.5. The spectra data matched with values reported in the literature.¹



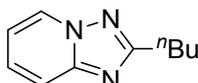
2-(pyridin-4-yl)-[1,2,4]triazolo[1,5-a]pyridine (2l):

Following the general procedure, **2l** was purified by PE/EtOAc (6:1) and obtained as a white solid (42 mg, 70% yield); Mp = 162 - 164 °C; R_f = 0.30 (PE/EtOAc = 6:1); $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.58 (dt, J = 6.8, 1.1 Hz, 1H), 7.90 (dd, J = 3.7, 1.2 Hz, 1H), 7.74 (dt, J = 9.0, 1.2 Hz, 1H), 7.52 (ddd, J = 8.9, 7.0, 1.3 Hz, 1H), 7.46 (dd, J = 5.0, 1.2 Hz, 1H), 7.18 (dd, J = 5.0, 3.6 Hz, 1H), 7.02 (td, J = 6.9, 1.3 Hz, 1H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 164.0, 161.3, 151.6, 129.5, 128.8, 128.3, 123.3, 116.1, 114.2, 113.4, 55.4. The spectra data matched with values reported in the literature.¹



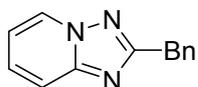
2-(tert-butyl)-[1,2,4]triazolo[1,5-a]pyridine (2m):

Following the general procedure, **2m** was purified by PE/EtOAc (6:1) and obtained as a white solid (33 mg, 62% yield); Mp = 126 - 128 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.53 (dt, J = 6.9, 1.1 Hz, 1H), 7.69 (dt, J = 8.9, 1.1 Hz, 1H), 7.46 (ddd, J = 8.9, 6.9, 1.3 Hz, 1H), 6.95 (td, J = 6.8, 1.3 Hz, 1H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 174.8, 151.1, 129.1, 128.2, 116.1, 112.9, 33.2, 29.7. Calculated for $\text{C}_{10}\text{H}_{13}\text{N}_3$ $[\text{M}+\text{H}]^+$: 176.1182; Found: 176.1191.



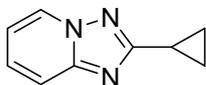
2-butyl-[1,2,4]triazolo[1,5-a]pyridine (2n):

Following the general procedure, **2n** was purified by PE/EtOAc (6:1) and obtained as a colorless liquid (39 mg, 77% yield); R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.50 (dt, J = 6.8, 1.2 Hz, 1H), 7.66 (dt, J = 8.9, 1.2 Hz, 1H), 7.46 (ddd, J = 8.9, 6.9, 1.3 Hz, 1H), 6.95 (td, J = 6.9, 1.3 Hz, 1H), 2.96 - 2.89 (m, 2H), 1.90 - 1.80 (m, 2H), 1.45 (h, J = 7.4 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.7, 151.1, 129.2, 128.0, 115.9, 113.0, 30.5, 28.5, 22.5, 13.8. The spectra data matched with values reported in the literature.³



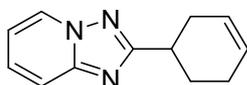
2-benzyl-[1,2,4]triazolo[1,5-a]pyridine (2o):

Following the general procedure, **2o** was purified by PE/EtOAc (6:1) and obtained as a white solid (55 mg, 81% yield); Mp = 80 - 83 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.52 (dt, J = 6.8, 1.2 Hz, 1H), 7.68 (dt, J = 8.9, 1.2 Hz, 1H), 7.47 (ddd, J = 8.7, 6.9, 1.3 Hz, 1H), 7.45 - 7.40 (m, 2H), 7.33 (dd, J = 8.4, 6.9 Hz, 2H), 7.27 - 7.20 (m, 1H), 6.96 (td, J = 6.9, 1.2 Hz, 1H), 4.29 (s, 2H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.2, 151.4, 137.7, 129.4, 129.0, 128.6, 128.2, 126.7, 116.2, 113.3, 35.4. The spectra data matched with values reported in the literature.³



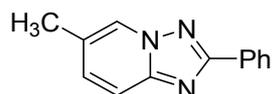
2-cyclopropyl-[1,2,4]triazolo[1,5-a]pyridine (2p):

Following the general procedure, **2p** was purified by PE/EtOAc (6:1) and obtained as a colorless liquid (43 mg, 89% yield); R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.46 (dt, J = 6.8, 1.2 Hz, 1H), 7.60 (dt, J = 8.9, 1.2 Hz, 1H), 7.43 (ddd, J = 8.9, 6.9, 1.3 Hz, 1H), 6.91 (td, J = 6.9, 1.3 Hz, 1H), 2.21 (tt, J = 8.3, 5.0 Hz, 1H), 1.17 - 1.01 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.1, 151.1, 129.2, 127.8, 115.6, 112.9, 9.3, 8.9. Calculated for $\text{C}_9\text{H}_9\text{N}_3$ $[\text{M}+\text{H}]^+$: 160.0869; Found: 160.0876.

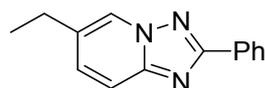


2-(cyclohex-3-en-1-yl)-[1,2,4]triazolo[1,5-a]pyridine (2q):

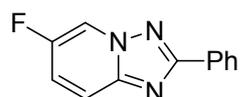
Following the general procedure, **2q** was purified by PE/EtOAc (6:1) and obtained as a white solid (51 mg, 85% yield); Mp = 56 - 59 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.53 (dd, J = 6.8, 1.2 Hz, 1H), 7.69 (dt, J = 9.0, 1.2 Hz, 1H), 7.48 (ddd, J = 8.6, 6.9, 1.3 Hz, 1H), 6.97 (td, J = 6.9, 1.3 Hz, 1H), 5.90-5.68 (m, 2H), 3.24 (dddd, J = 11.8, 9.2, 6.3, 2.7 Hz, 1H), 2.61 - 2.41 (m, 2H), 2.29 - 2.13 (m, 3H), 1.96 (dtd, J = 14.0, 11.4, 6.6 Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 170.8, 151.1, 129.2, 128.2, 126.9, 125.9, 116.1, 113.1, 34.2, 30.2, 27.9, 25.1. Calculated for $\text{C}_{12}\text{H}_{13}\text{N}_3$ $[\text{M}+\text{H}]^+$: 200.1182; Found: 200.119.

**6-methyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4a):**

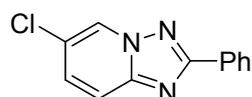
Following the general procedure, **4a** was purified by PE/EtOAc (6:1) and obtained as a white solid (57 mg, 90% yield); Mp = 113 - 116 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.49 - 8.43 (m, 1H), 8.35 - 8.28 (m, 2H), 7.56 - 7.43 (m, 3H), 7.31 - 7.24 (m, 1H), 6.91 (t, J = 6.9 Hz, 1H), 2.71 (d, J = 1.0 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.6, 152.2, 131.0, 129.9, 128.6, 128.2, 127.4, 127.1, 125.9, 113.5, 17.0. The spectra data matched with values reported in the literature.⁴

**6-ethyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4b):**

Following the general procedure, **4b** was purified by PE/EtOAc (6:1) and obtained as a white solid (56 mg, 83% yield); Mp = 65 - 68 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.45 - 8.39 (m, 1H), 8.33-8.25 (m, 2H), 7.70 (d, J = 9.0 Hz, 1H), 7.55-7.44 (m, 3H), 7.41 (dd, J = 9.1, 1.7 Hz, 1H), 2.76 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.8, 150.4, 131.5, 130.9, 130.1, 130.0, 128.7, 127.2, 125.6, 115.7, 25.7, 14.8. Calculated for $\text{C}_{14}\text{H}_{13}\text{N}_3$ $[\text{M}+\text{H}]^+$: 224.1182; Found: 224.1188.

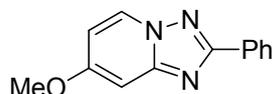
**6-fluoro-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4c):**

Following the general procedure, **4c** was purified by PE/EtOAc (6:1) and obtained as a white solid (59 mg, 92% yield); Mp = 208 - 210 °C; R_f = 0.30 (PE/EtOAc = 6:1); ^1H NMR (500 MHz, CDCl_3) δ 8.57 (ddd, J = 3.2, 2.4, 0.7 Hz, 1H), 8.34-8.21 (m, 2H), 7.75 (ddd, J = 9.7, 5.0, 0.8 Hz, 1H), 7.57 - 7.40 (m, 4H); ^{13}C NMR (126 MHz, CDCl_3) δ 165.2 (d, $J_{\text{C-F}}$ = 2.8 Hz), 153.4 (d, $J_{\text{C-F}}$ = 242.2 Hz), 149.4, 130.5, 130.2, 128.8, 127.3, 121.2 (d, $J_{\text{C-F}}$ = 25.2 Hz), 116.3 (d, $J_{\text{C-F}}$ = 2.5 Hz), 116.0 (d, $J_{\text{C-F}}$ = 39.8 Hz). Calculated for $\text{C}_{12}\text{H}_8\text{FN}_3$ $[\text{M}+\text{H}]^+$: 214.0775; Found: 214.0784

**6-chloro-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4d):**

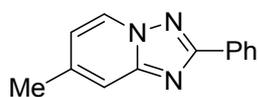
Following the general procedure, **4d** was purified by PE/EtOAc (6:1) and obtained as a white

solid (35 mg, 51% yield); Mp = 165 - 168 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.66 (dd, *J* = 2.0, 0.8 Hz, 1H), 8.35 - 8.24 (m, 2H), 7.72 (dd, *J* = 9.5, 0.8 Hz, 1H), 7.56 - 7.46 (m, 4H); ¹³C NMR (126 MHz, CDCl₃) δ 164.9, 150.3, 131.1, 130.4, 130.3, 128.8, 127.4, 126.7, 121.7, 116.5. The spectra data matched with values reported in the literature.³



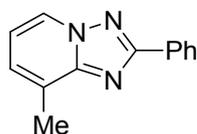
7-methoxy-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4e):

Following the general procedure, **4e** was purified by PE/EtOAc (6:1) and obtained as a white solid (45 mg, 66% yield); Mp = 117 - 120 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.39 (dd, *J* = 7.4, 0.6 Hz, 1H), 8.29 - 8.22 (m, 2H), 7.55 - 7.42 (m, 3H), 7.02 (d, *J* = 2.6 Hz, 1H), 6.68 (dd, *J* = 7.5, 2.6 Hz, 1H), 3.92 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 164.4, 161.2, 153.1, 130.8, 130.0, 128.7, 128.4, 127.2, 107.9, 94.1, 55.9. Calculated for C₁₃H₁₁N₃O [M+H]⁺: 226.0975; Found: 226.0981.



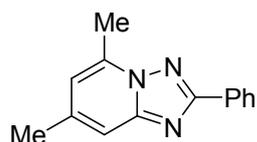
7-methyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4f):

Following the general procedure, **4f** was purified by PE/EtOAc (6:1) and obtained as a white solid (46 mg, 73% yield); Mp = 136 - 138 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.46 (dd, *J* = 6.9, 0.8 Hz, 1H), 8.32 - 8.24 (m, 2H), 7.56 - 7.44 (m, 4H), 6.83 (dd, *J* = 6.9, 1.8 Hz, 1H), 2.50 (d, *J* = 1.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 164.1, 151.8, 141.1, 130.8, 130.0, 128.7, 127.3, 127.2, 116.1, 114.9, 21.6. The spectra data matched with values reported in the literature.⁴



8-methyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4g):

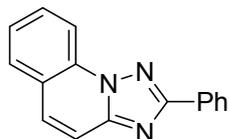
Following the general procedure, **4g** was purified by PE/EtOAc (6:1) and obtained as a white solid (43 mg, 68% yield); Mp = 95 - 98 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.49-8.43 (m, 1H), 8.35 - 8.28 (m, 2H), 7.56 - 7.43 (m, 3H), 7.31 - 7.24 (m, 1H), 6.91 (t, *J* = 6.9 Hz, 1H), 2.71 (d, *J* = 1.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 163.6, 152.2, 131.0, 129.9, 128.6, 128.2, 127.4, 127.1, 125.9, 113.5, 17.0. The spectra data matched with values reported in the literature.⁴



5,7-dimethyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4h):

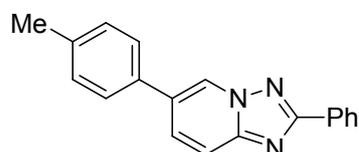
Following the general procedure, **4h** was purified by PE/EtOAc (6:1) and obtained as a white solid (45 mg, 66% yield); Mp = 155 - 157 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.35 - 8.28 (m, 2H), 7.53 - 7.43 (m, 3H), 7.40 (d, *J* = 1.7 Hz, 1H), 6.66 (s, 1H), 2.80 (s, 3H), 2.46 (d, *J* = 1.0 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 163.6, 152.1, 140.6, 137.7,

131.3, 129.8, 128.6, 127.3, 115.3, 112.3, 21.5, 17.5. The spectra data matched with values reported in the literature.⁷



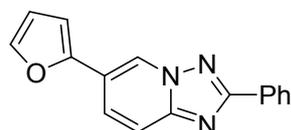
2-phenyl-[1,2,4]triazolo[1,5-a]quinolone (4i):

Following the general procedure, **4i** was purified by PE/EtOAc (6:1) and obtained as a white solid (37 mg, 50% yield); Mp = 136 - 138 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.66 - 8.61 (m, 1H), 8.42 - 8.37 (m, 2H), 7.91 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.86 (d, *J* = 9.3 Hz, 1H), 7.81 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.72 (d, *J* = 9.3 Hz, 1H), 7.60 - 7.52 (m, 3H), 7.52 - 7.47 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 163.3, 149.9, 133.8, 131.0, 130.8, 130.2, 129.9, 128.7, 128.7, 127.2, 125.6, 123.3, 116.1, 114.9. The spectra data matched with values reported in the literature.⁶



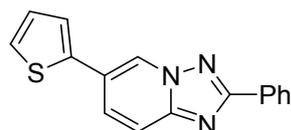
2-phenyl-6-(p-tolyl)-[1,2,4]triazolo[1,5-a]pyridine (4j):

Following the general procedure, **4j** was purified by PE/EtOAc (6:1) and obtained as a white solid (56 mg, 65% yield); Mp = 156 - 159 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.79 (dd, *J* = 1.8, 1.0 Hz, 1H), 8.35 - 8.28 (m, 2H), 7.85 - 7.74 (m, 2H), 7.56 - 7.46 (m, 5H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 164.5, 150.8, 138.4, 133.4, 130.8, 130.1, 130.0, 130.0, 128.7, 128.4, 127.3, 126.8, 125.2, 116.0, 21.2. Calculated for C₁₉H₁₅N₃ [M+H]⁺: 286.1339; Found: 286.1347.



6-(furan-2-yl)-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (4k):

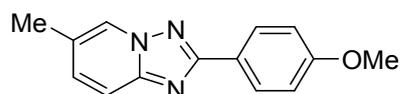
Following the general procedure, **4k** was purified by PE/EtOAc (6:1) and obtained as a powder white solid (18 mg, 25% yield); Mp = 163 - 166 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.93 (t, *J* = 1.3 Hz, 1H), 8.34 - 8.28 (m, 2H), 7.83 - 7.72 (m, 2H), 7.58 - 7.45 (m, 4H), 6.74 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.55 (dd, *J* = 3.4, 1.8 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 164.6, 150.7, 149.6, 143.0, 130.7, 130.1, 128.7, 127.3, 126.8, 123.0, 118.9, 116.2, 112.0, 106.6. HRMS (ESI): Calculated for C₁₆H₁₁N₃O [M+H]⁺: 262.0975; Found: 262.0975.



2-phenyl-6-(thiophen-2-yl)-[1,2,4]triazolo[1,5-a]pyridine (4l):

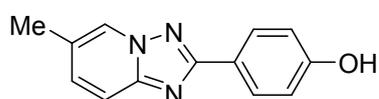
Following the general procedure, **4l** was purified by PE/EtOAc (6:1) and obtained as a white solid (68 mg, 80% yield); Mp = 125 - 128 °C; R_f = 0.30 (PE/EtOAc = 6:1); ¹H NMR (500 MHz, CDCl₃) δ 8.85 (d, *J* = 1.4 Hz, 1H), 8.34 - 8.28 (m, 2H), 7.78 (d, *J* = 1.3 Hz, 2H), 7.55 - 7.46 (m,

3H), 7.41 - 7.34 (m, 2H), 7.16 (dd, $J = 5.1, 3.6$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 164.7, 150.8, 138.9, 130.7, 130.2, 129.2, 128.8, 128.4, 127.3, 126.0, 124.5, 124.3, 122.3, 116.2. Calculated for $\text{C}_{16}\text{H}_{11}\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$: 278.0746; Found: 278.0754.



2-(4-methoxyphenyl)-6-methyl-[1,2,4]triazolo[1,5-a]pyridine (7):

Following the general procedure, **7** was purified by PE/EtOAc (6:1) and obtained as a white solid (68 mg, 80% yield); Mp = 158 - 161 °C; $R_f = 0.30$ (PE/EtOAc = 3:1); ^1H NMR (500 MHz, CDCl_3) δ 8.36 (dt, $J = 2.0, 1.0$ Hz, 1H), 8.26 - 8.17 (m, 2H), 7.62 (dd, $J = 9.0, 0.9$ Hz, 1H), 7.33 (dd, $J = 9.0, 1.7$ Hz, 1H), 7.04 - 6.98 (m, 2H), 3.88 (s, 3H), 2.41 (d, $J = 1.1$ Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 163.7, 161.1, 150.3, 132.2, 128.6, 126.2, 123.6, 123.4, 115.3, 114.1, 55.3, 18.0. The spectra data matched with values reported in the literature.⁴



4-(6-methyl-[1,2,4]triazolo[1,5-a]pyridin-2-yl)phenol (8):

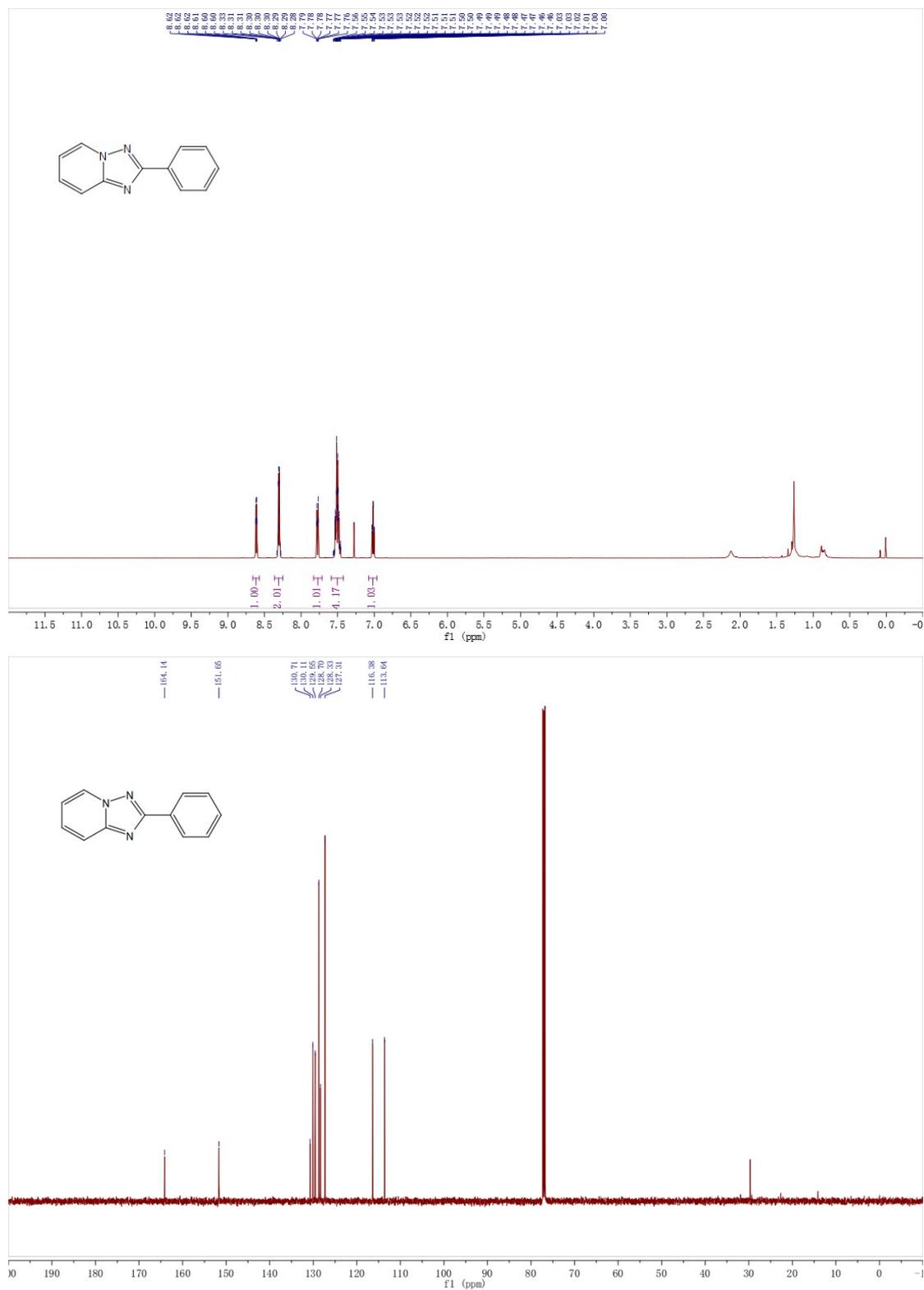
Following the general procedure, **8** was purified by PE/EtOAc (3:1) and obtained as a white solid (68 mg, 83% yield); Mp = 267 - 269 °C; $R_f = 0.20$ (PE/EtOAc = 3:1); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.87 (s, 1H), 8.76 (q, $J = 1.3$ Hz, 1H), 8.06 - 7.96 (m, 2H), 7.76 - 7.64 (m, 1H), 7.50 (dd, $J = 9.0, 1.7$ Hz, 1H), 6.94 - 6.85 (m, 2H), 2.37 (d, $J = 1.0$ Hz, 3H); ^{13}C NMR (126 MHz, DMSO) δ 162.9, 159.1, 149.7, 132.7, 128.3, 126.7, 123.5, 121.7, 115.5, 114.7, 17.3.. Calculated for $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 226.0974; Found: 226.0975.

4. References

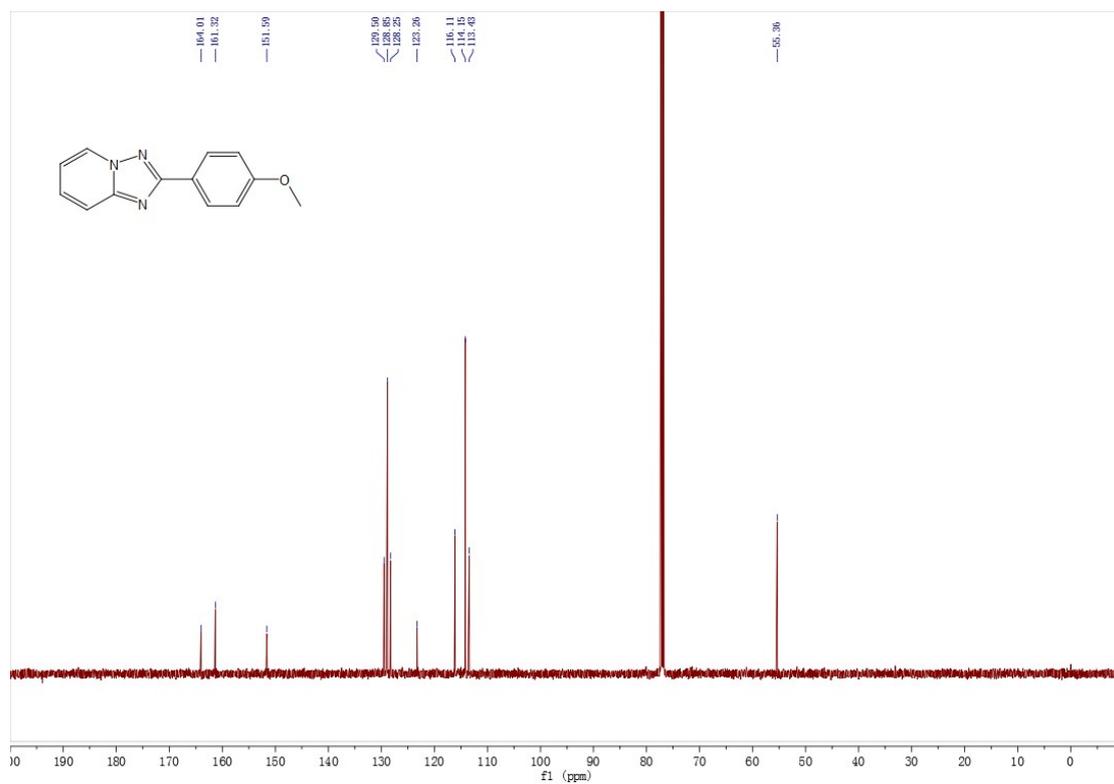
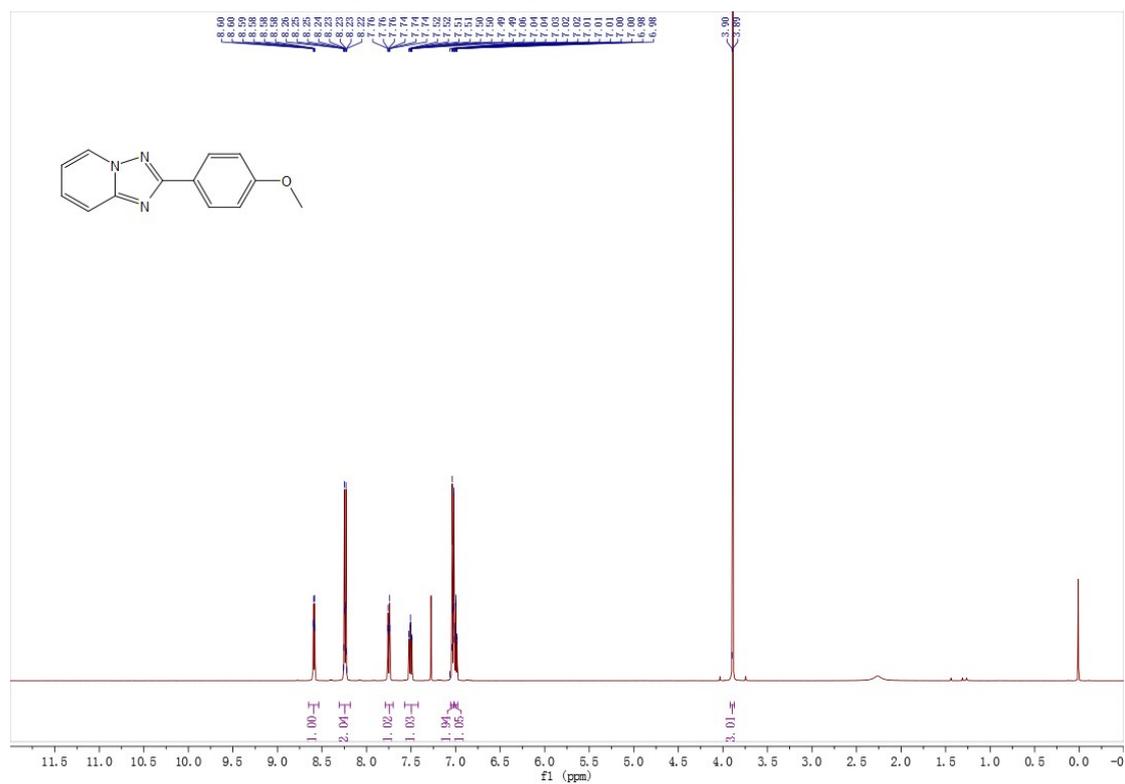
1. S. Ueda, H. Nagasawa, *J. Am. Chem. Soc.*, 2009, **131**, 15080-15081.
2. H. B. Zhao, Z. W. Hou, Z. J. Liu, Z. F. Zhou, J. Song, H. C. Xu, *Angew. Chem. Int. Ed.* 2017, **56**, 587 - 590.
3. Z. Zheng, S. Ma, L. Tang, D. Zhang-Negrerie, Y. Du, K. Zhao, *J. Org. Chem.* 2014, **79**, 4687-4693.
4. L. Song, X. Tian, Z. Lv, E. Li, J. Wu, Y. Liu, W. Yu, J. Chang, *J. Org. Chem.* 2015, **80**, 7219-7225.
5. X. Meng, C. Yu, P. Zhao, *RSC Adv.*, 2014, **4**, 8612-8616.
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7. K. T. Potts, H. R. Burton, J. Bhattacharyya, *J. Org. Chem.* 1966, **31**, 260-265.

5. NMR spectra.

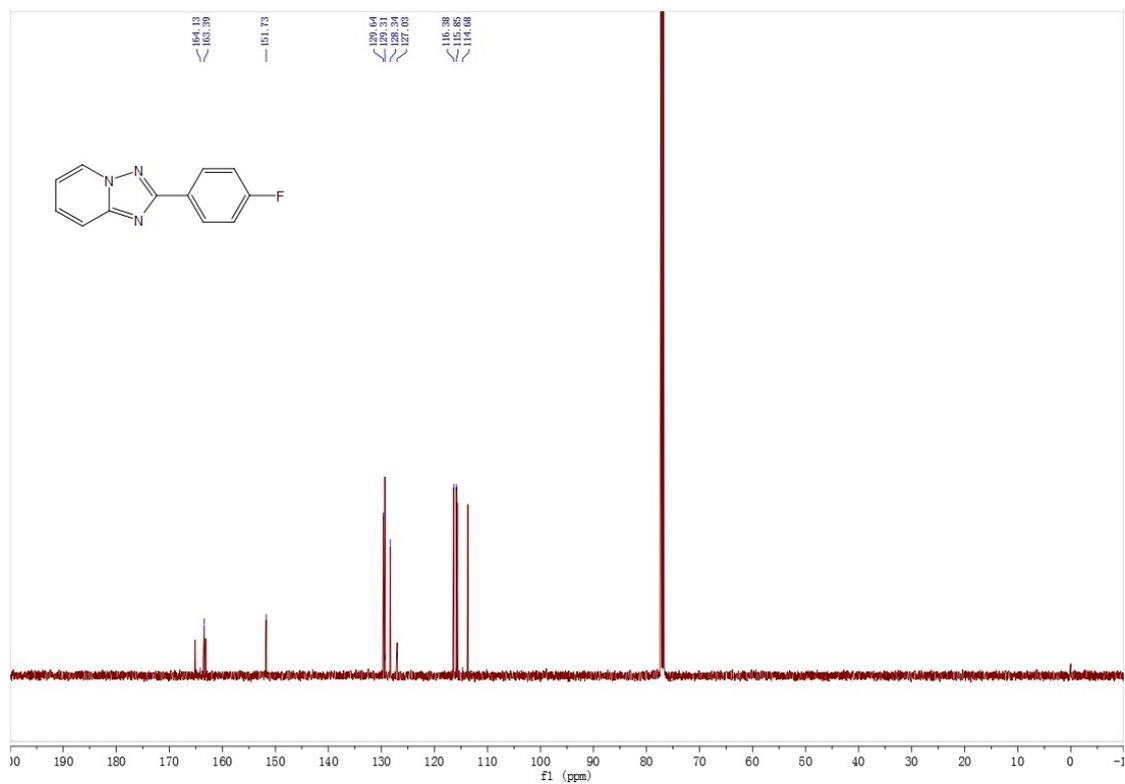
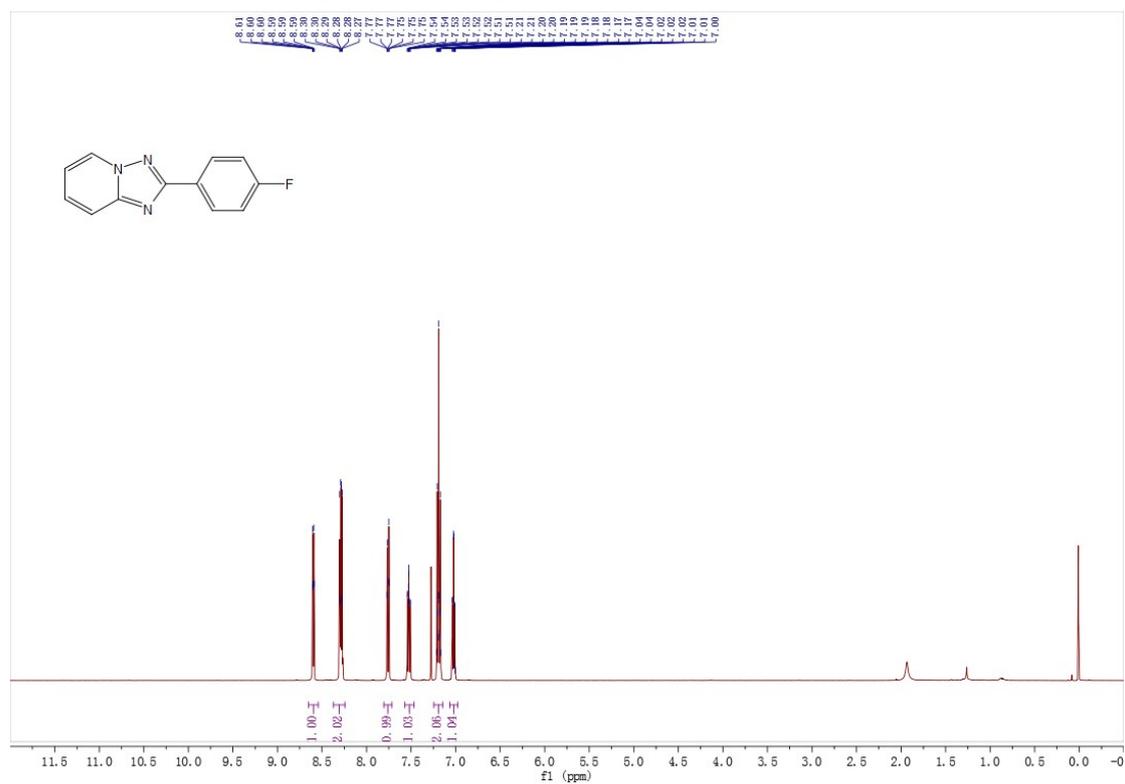
2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (2a):



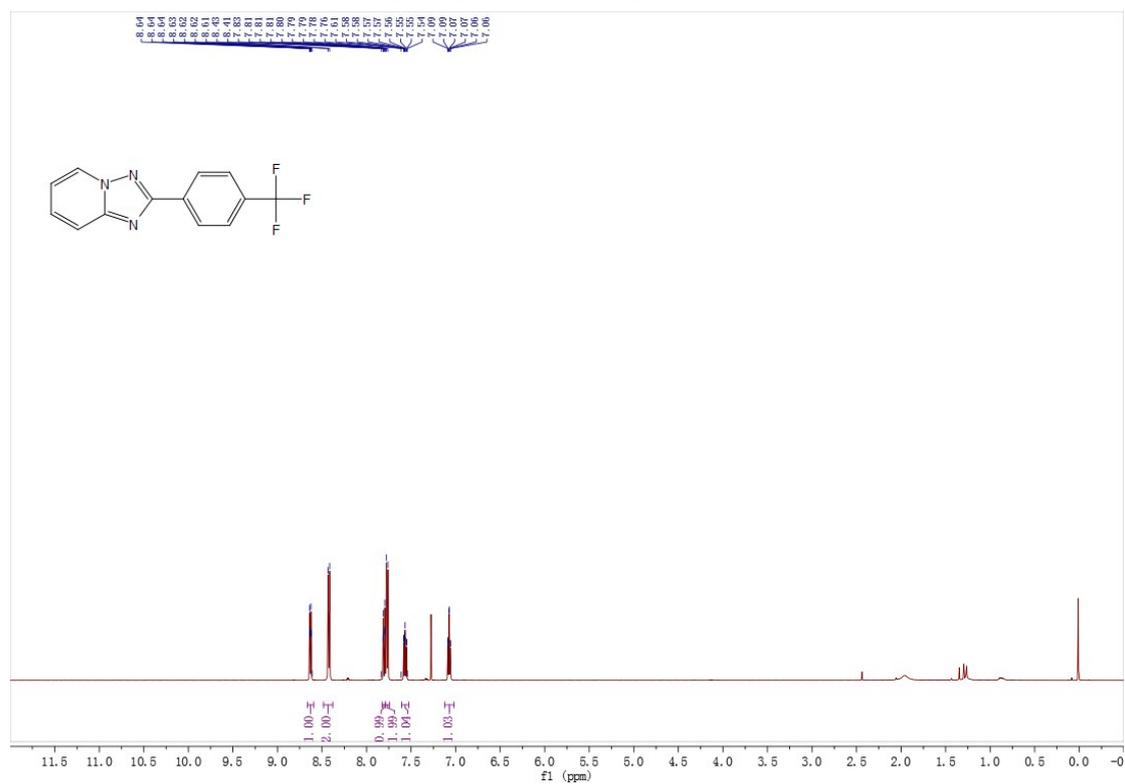
2-(4-methoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (2c):



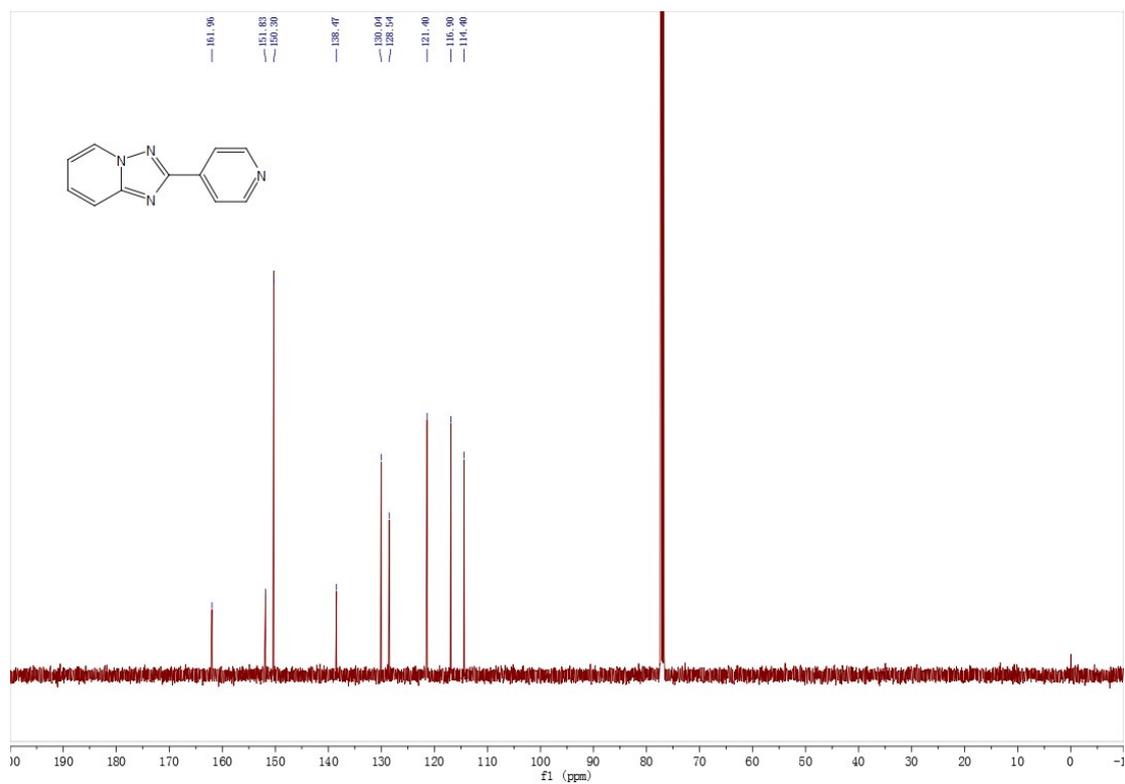
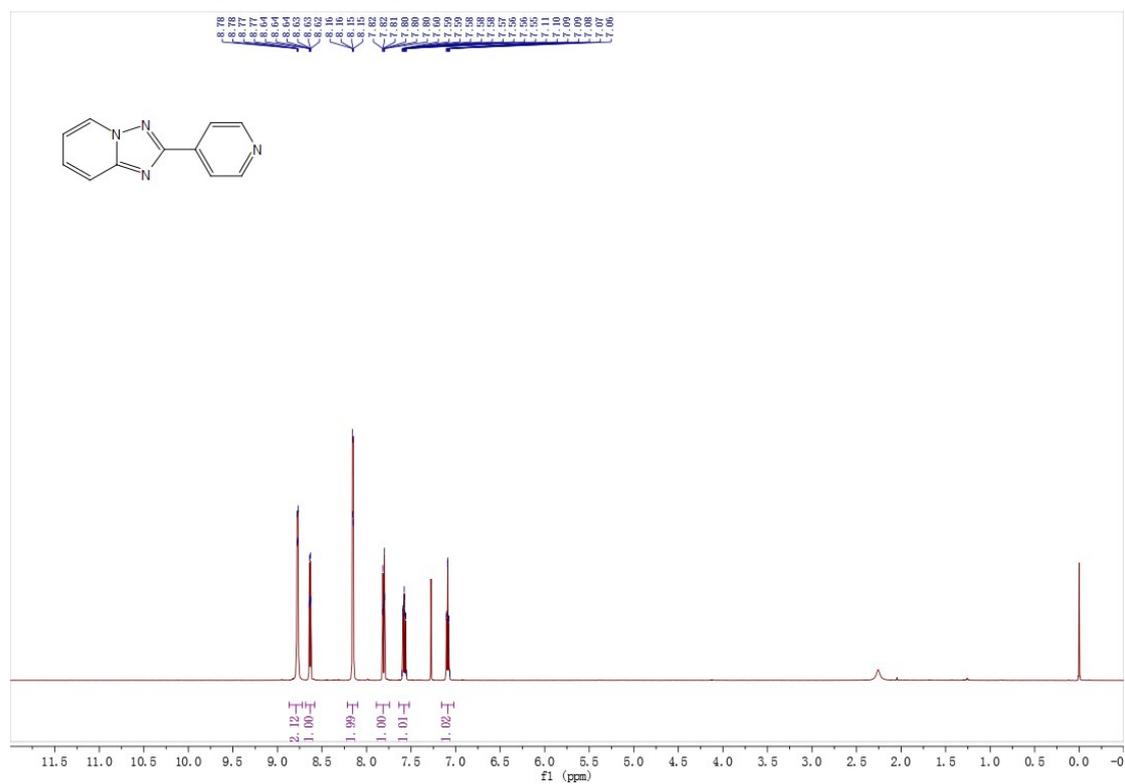
2-(4-fluorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (2d):



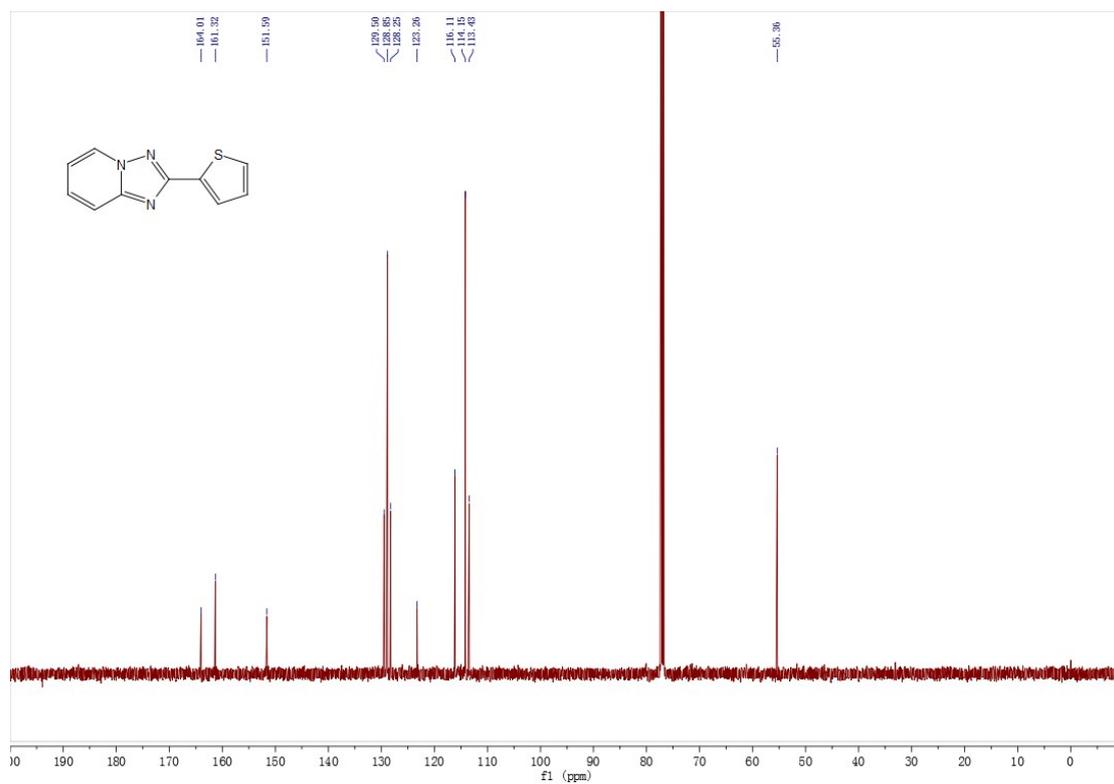
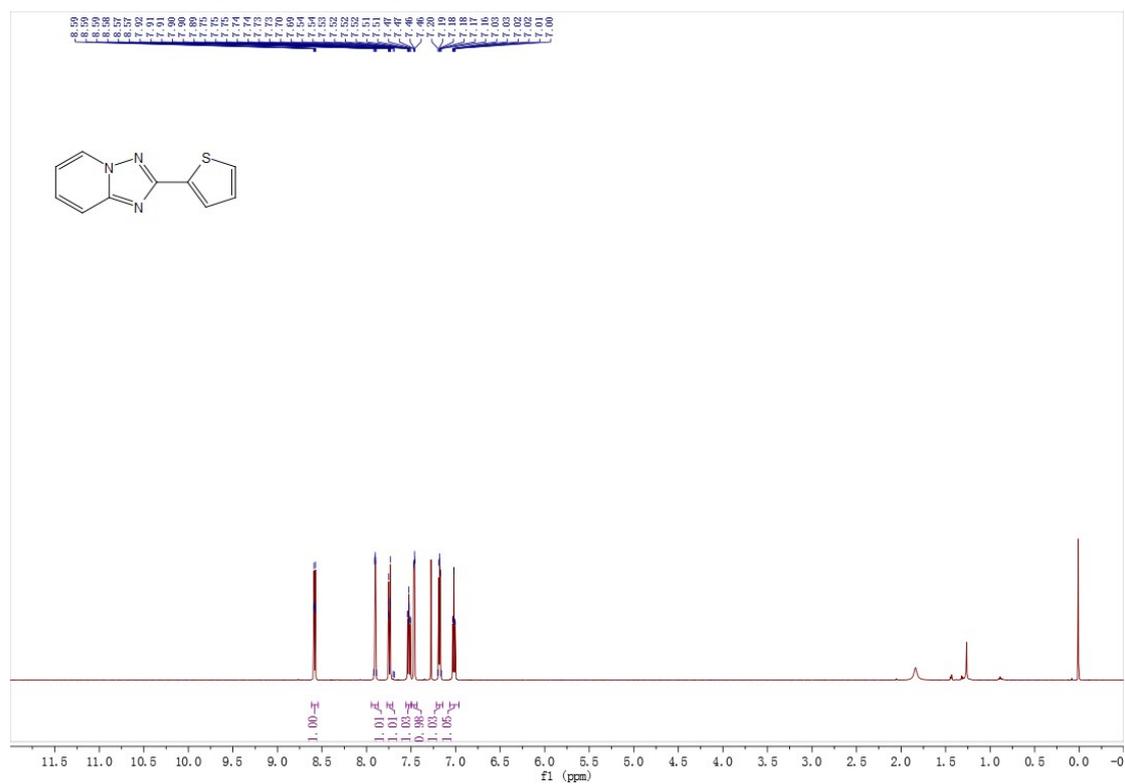
2-(4-(trifluoromethyl)phenyl)-[1,2,4]triazolo[1,5,a]pyridine (2g):



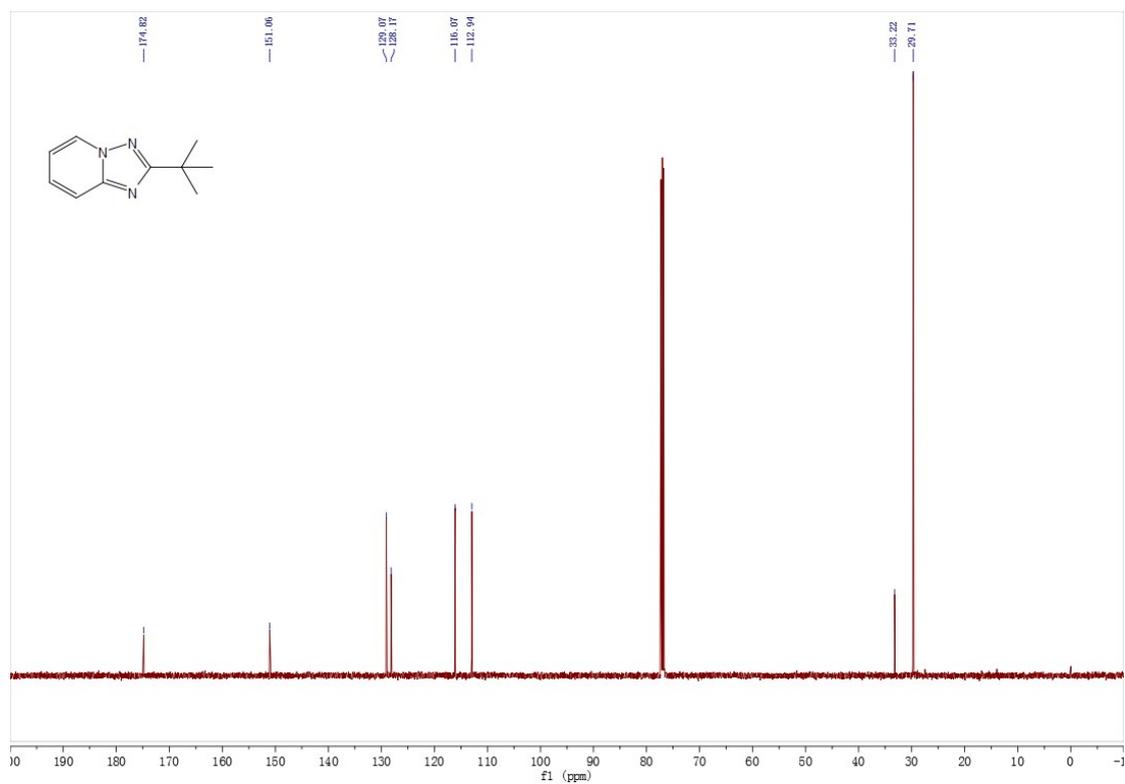
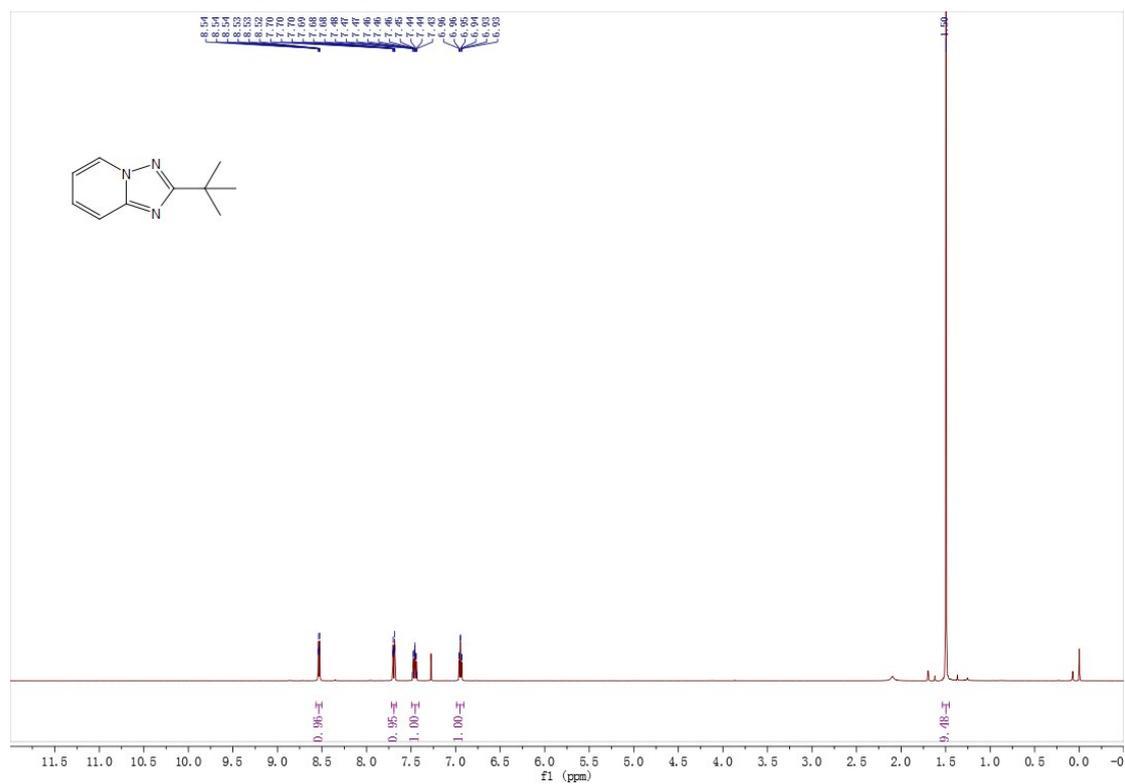
2-(pyridin-4-yl)-[1,2,4]triazolo[5,4-b]pyridine (2k):



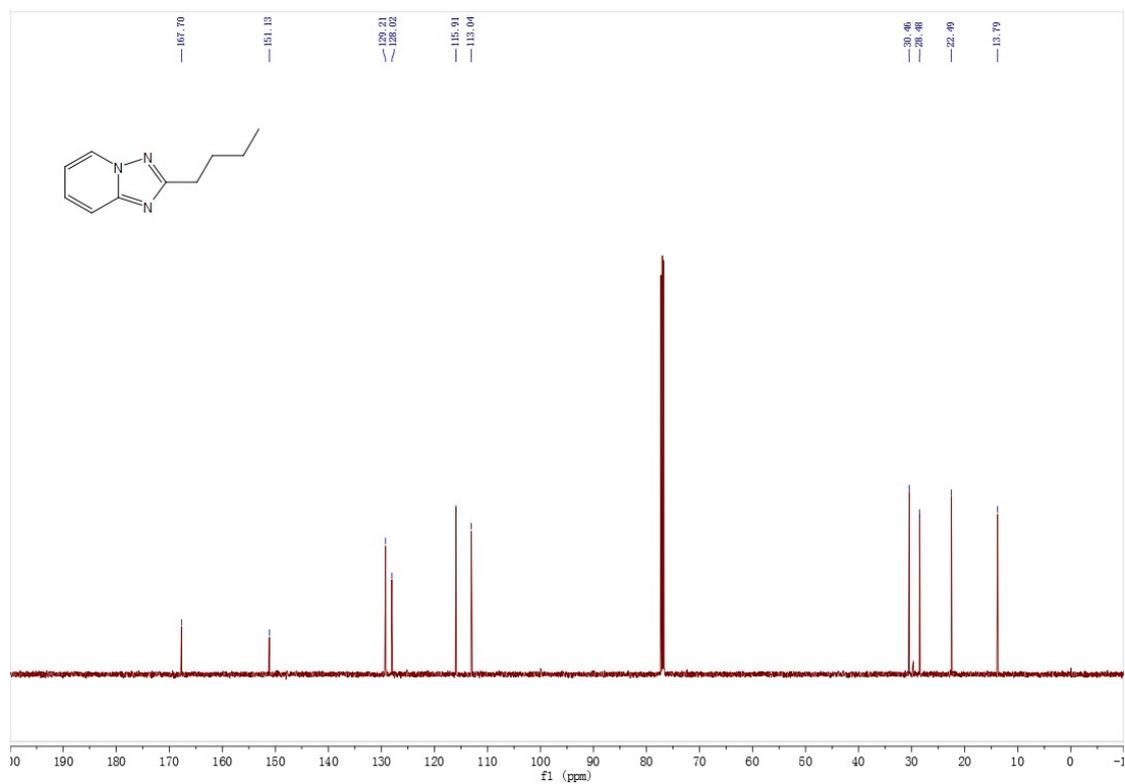
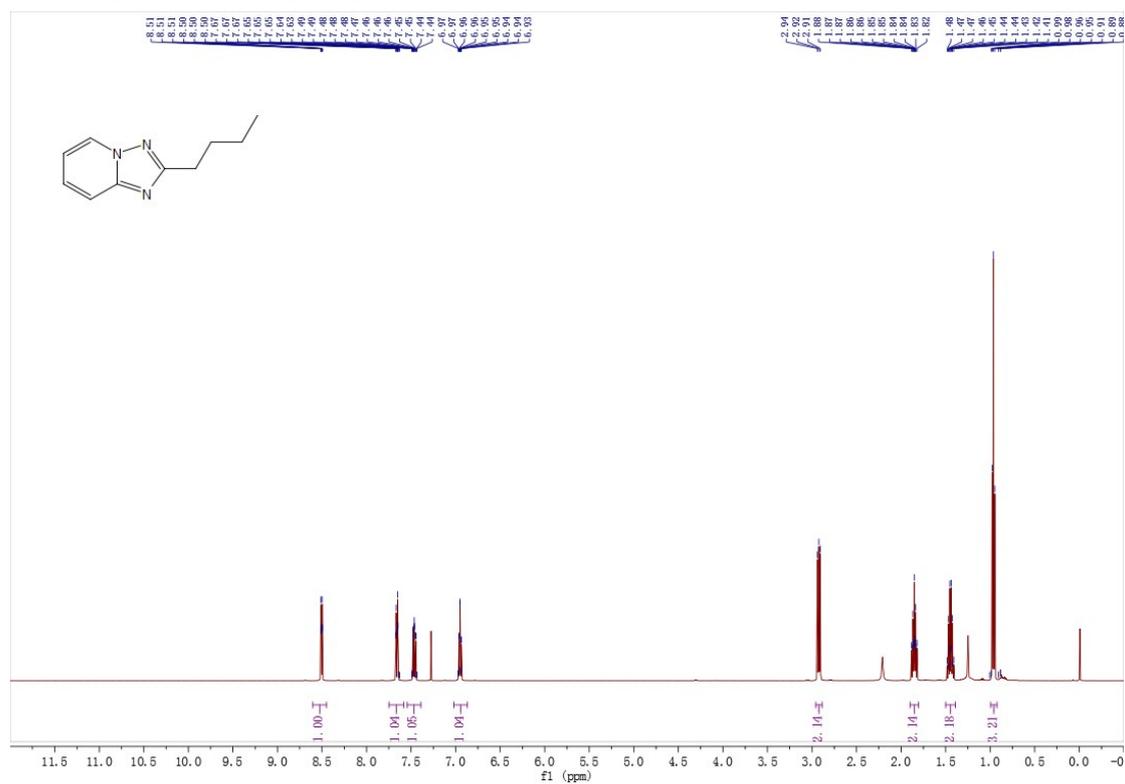
2-(pyridin-4-yl)-[1,2,4]triazolo[5,4-b]pyridine (2l):



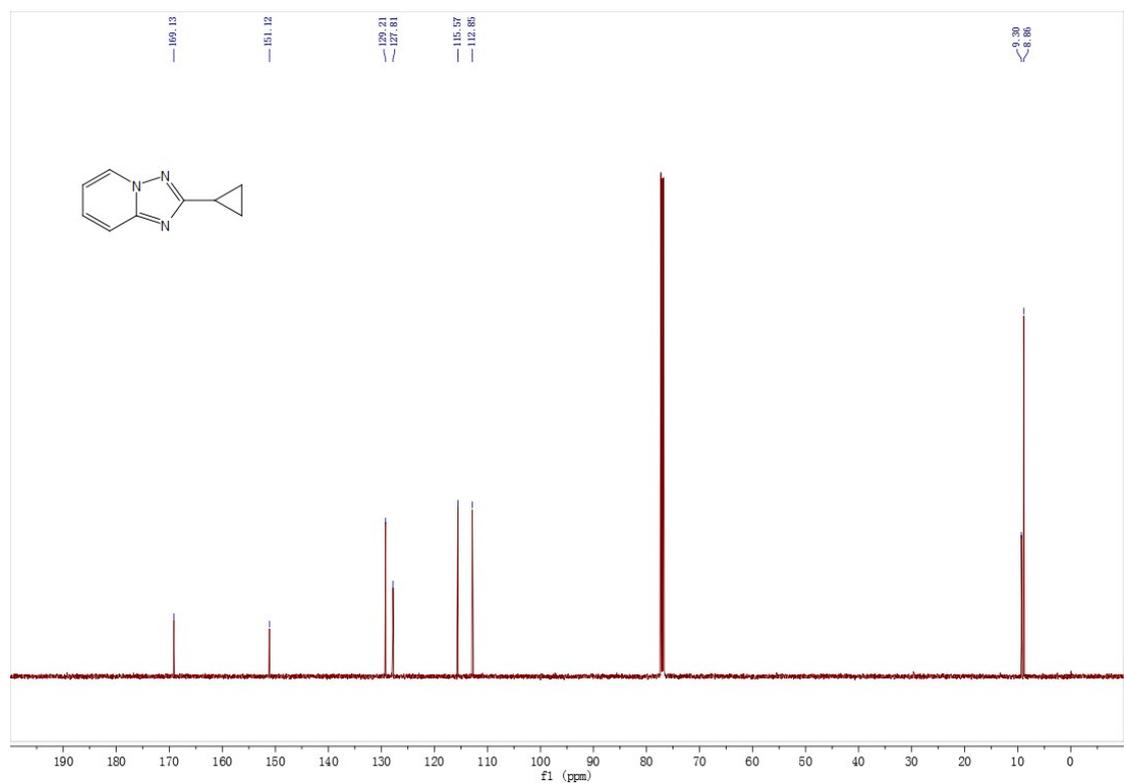
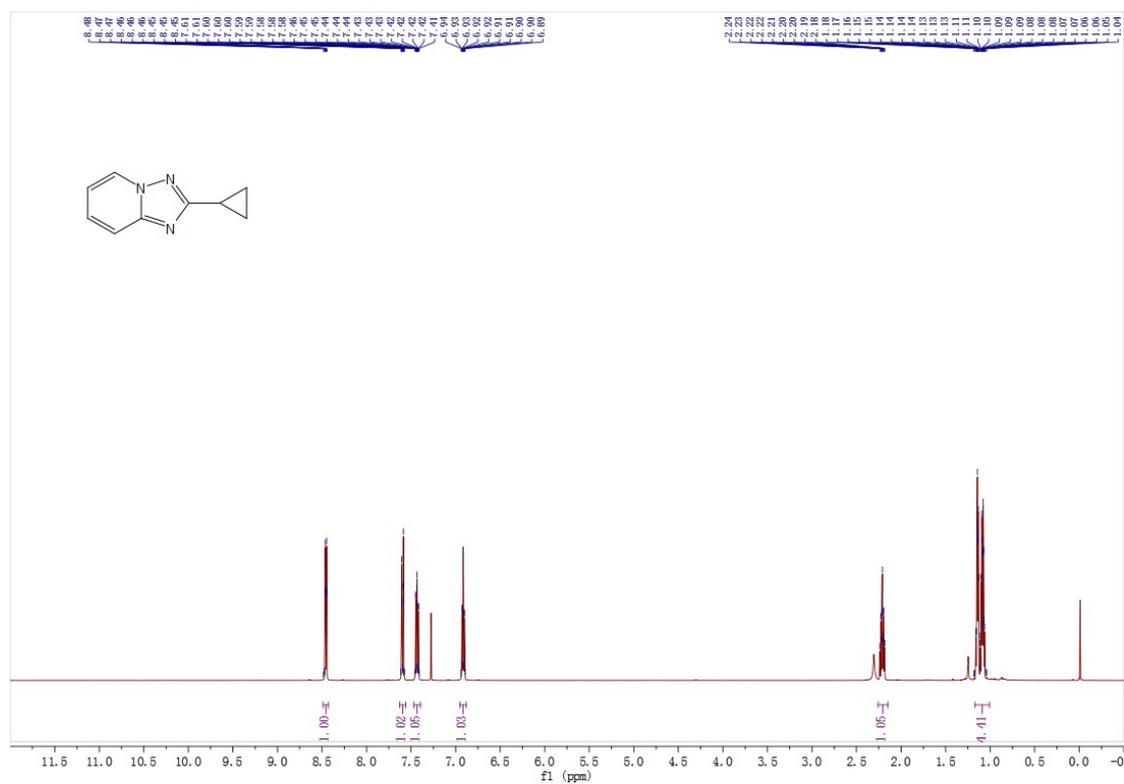
2-(tert-butyl)-[1,2,4]triazolo[1,5,a]pyridine (2m):



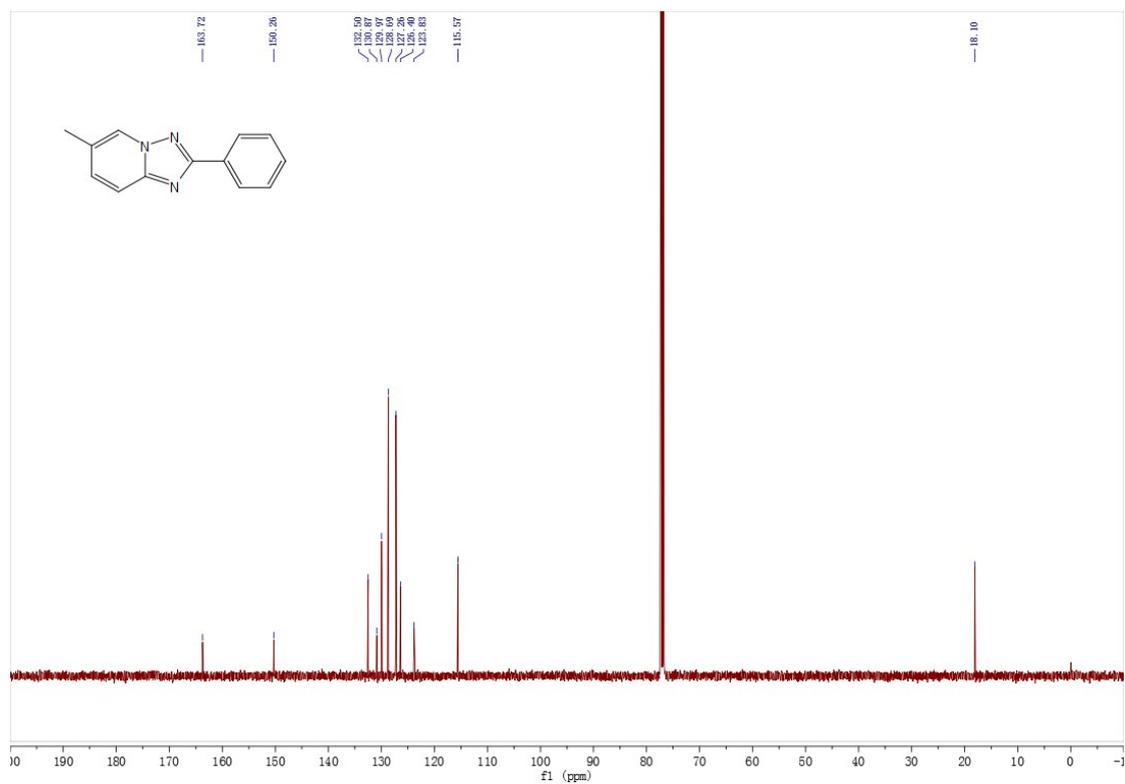
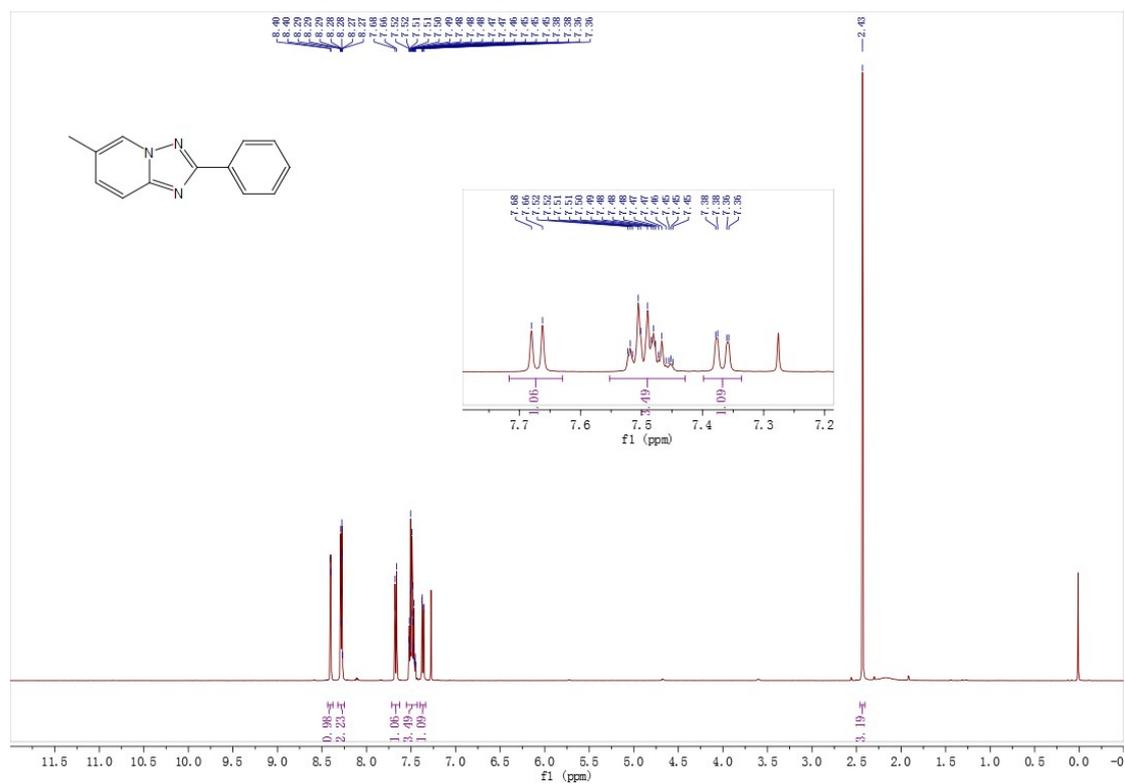
2-butyl-[1,2,4]triazolo[1,5,a]pyridine (2n):



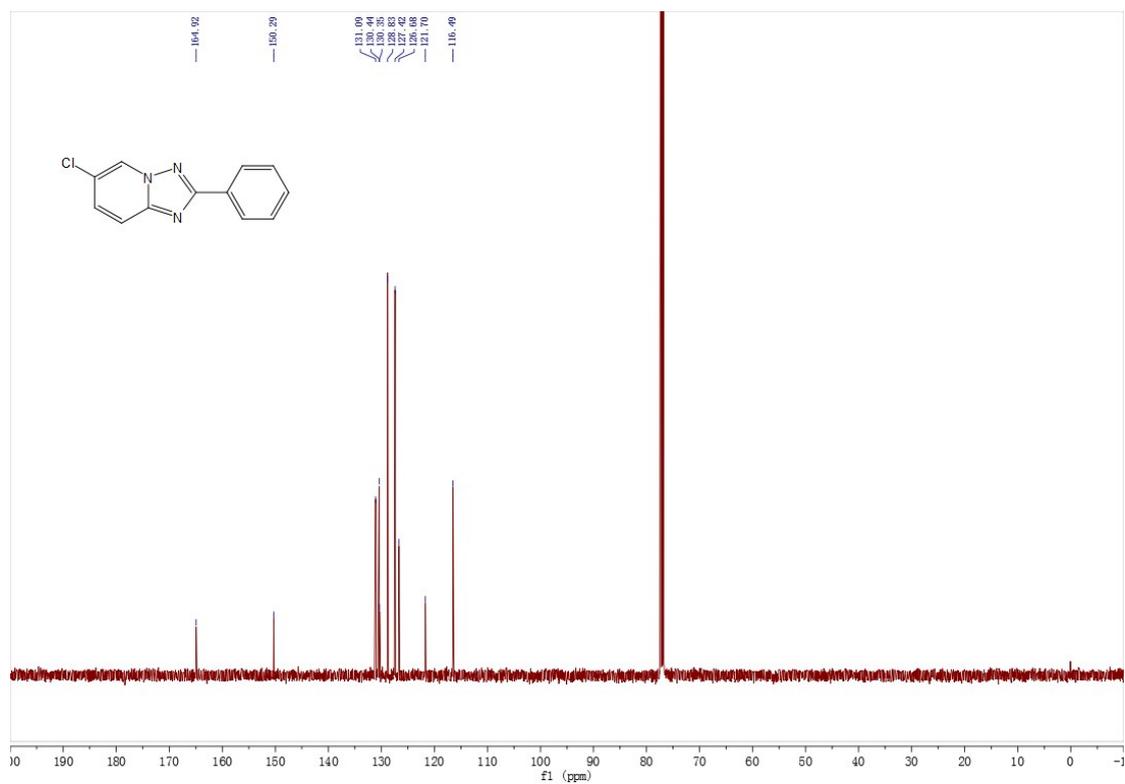
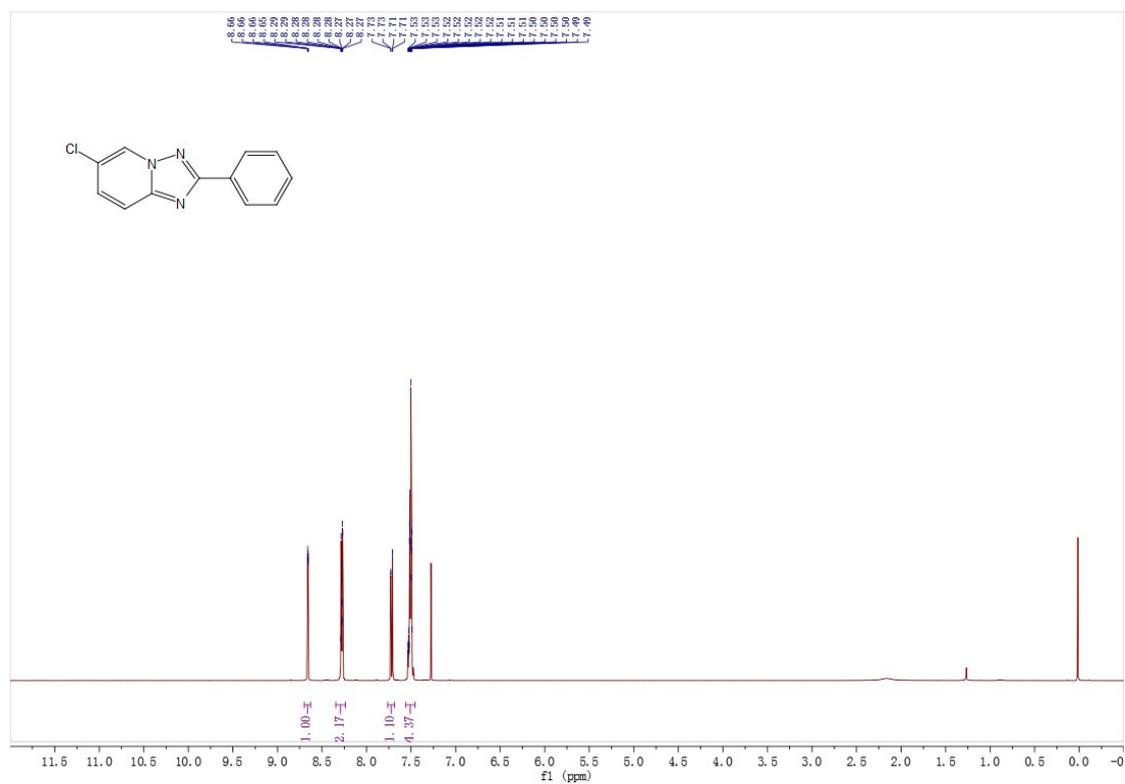
2-cyclopropyl-[1,2,4]triazolo[1,5,a]pyridine (2p):



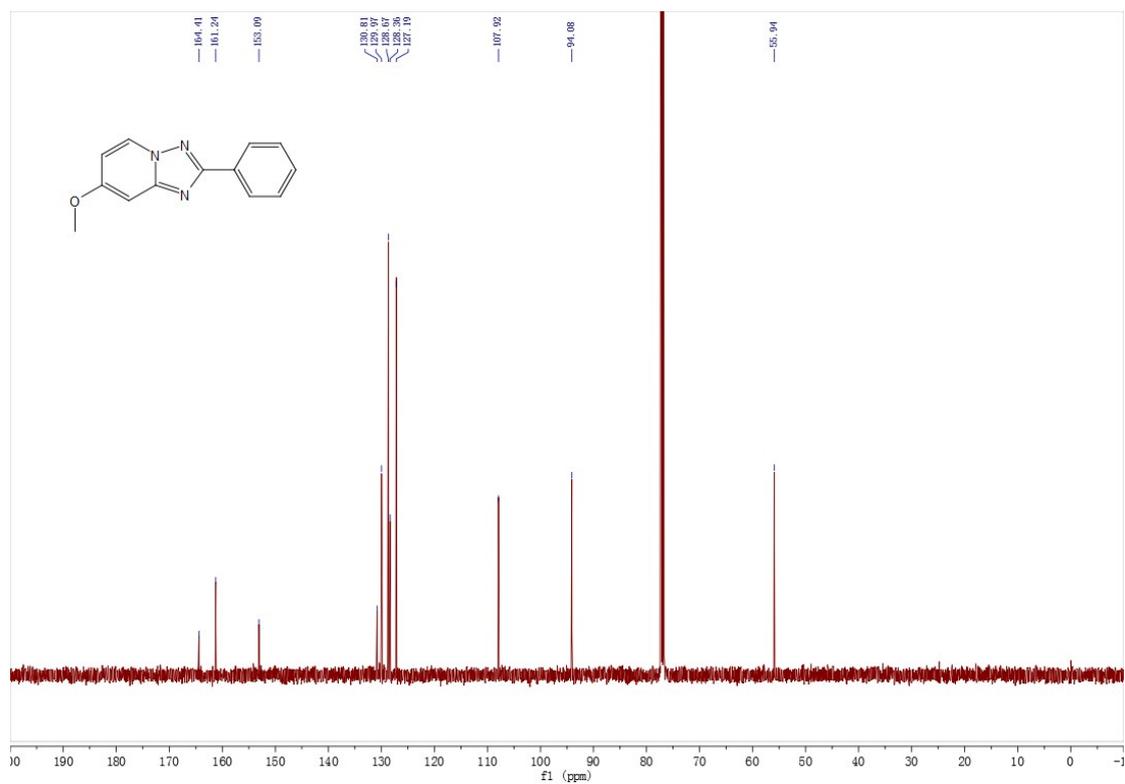
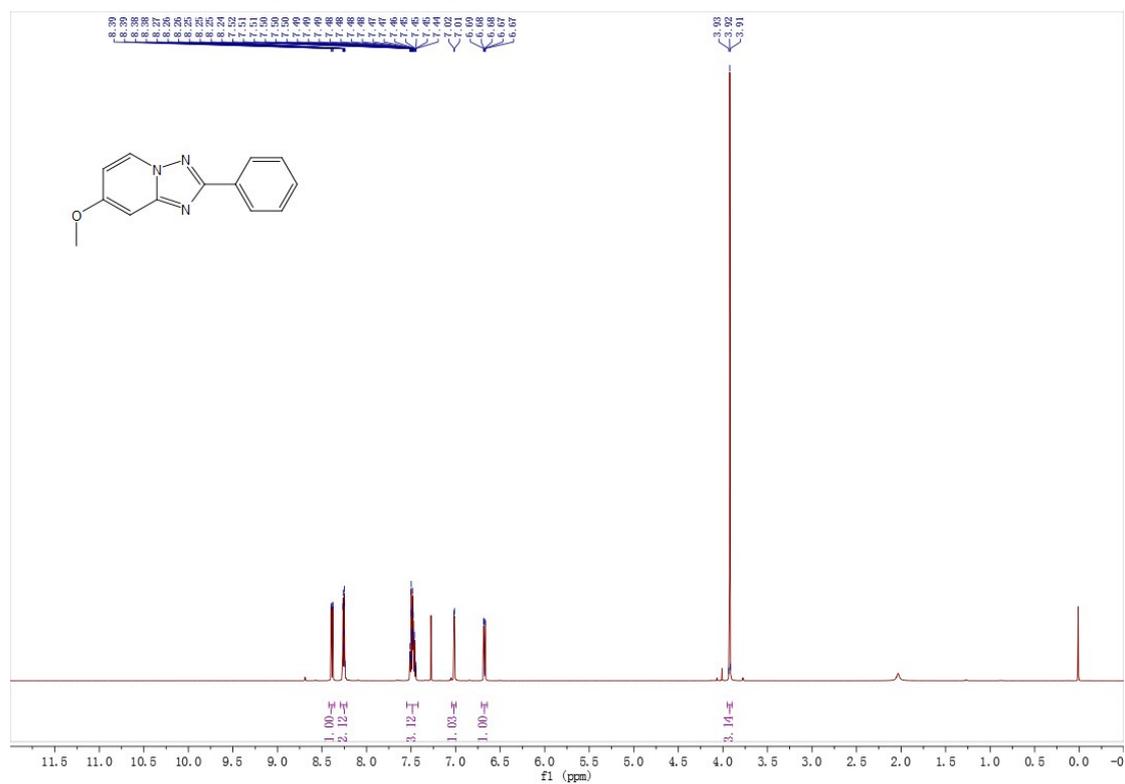
6-methyl-2-phenyl-[1,2,4]triazolo[1,5,a]pyridine (4a):



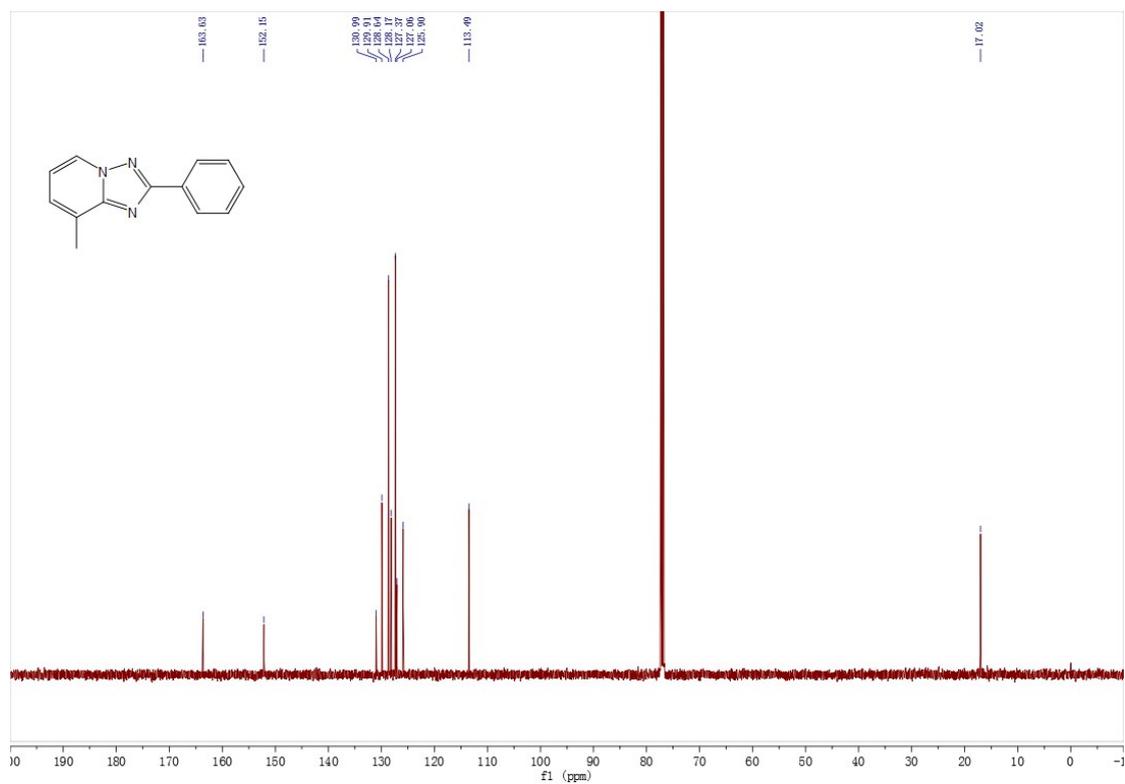
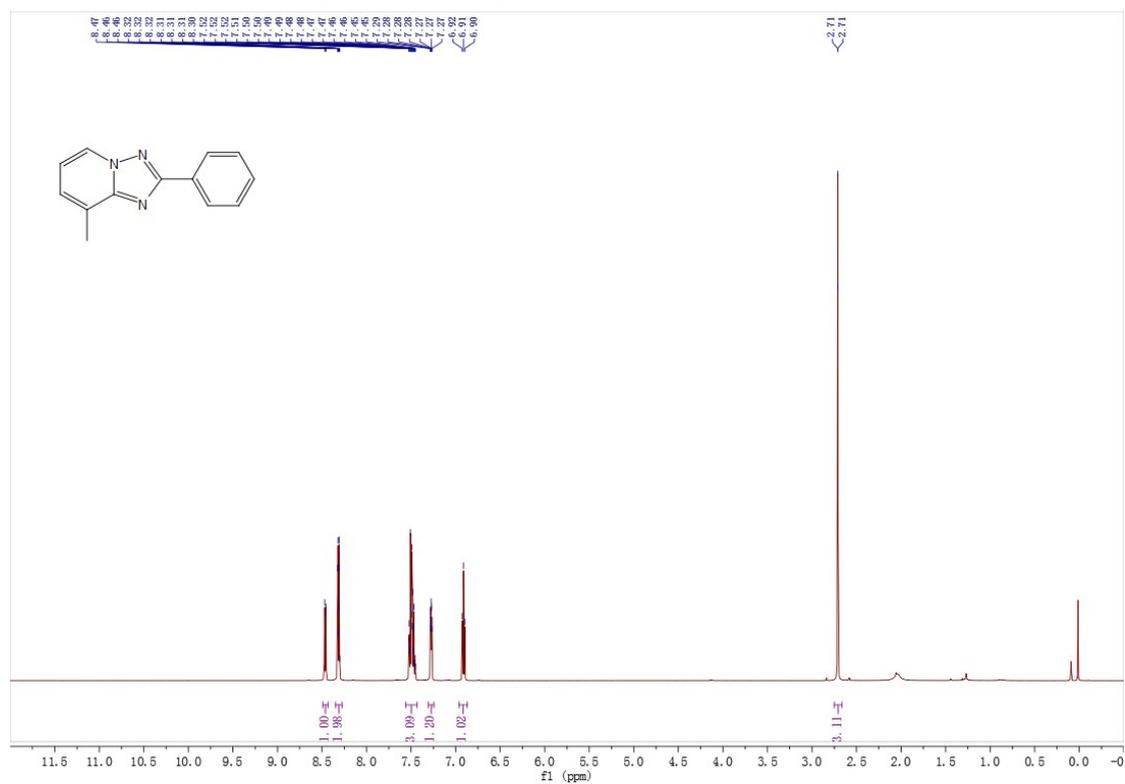
6-chloro-2-phenyl-[1,2,4]triazolo[1,5,a]pyridine (4d):



7-methoxy-2-phenyl-[1,2,4]triazolo[1,5,a]pyridine (4e):



8-methyl-2-phenyl-[1,2,4]triazolo[1,5,a]pyridine (4g):



4-(6-methyl-[1,2,4]triazolo[1,5-a]pyridin-2-yl)phenol (8):

