Electronic Supplementary Material (ESI) for Green Chemistry.

Electrochemical Synthesis of 1,2,4-Triazole-Fused Heterocycles

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Supporting Information

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1. General information

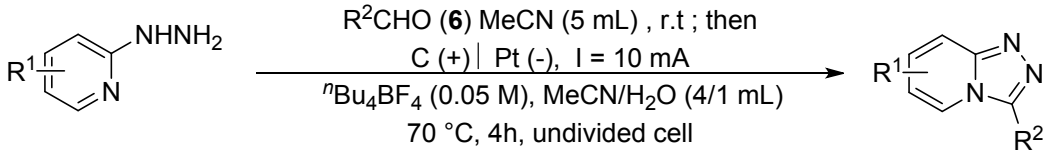
All reagents were obtained from commercial suppliers and used without further purification. Yields for all compounds were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether 40-60 (PE)/EtOAc as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass pate coated with silica gel with fluorescent indicator (GF254) using UV light. The ^{1}H 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 ^{1}H and 77.16 for ^{13}C, and to DMSO-d_6 with 2.50 for ^{1}H and 39.52 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.

2-hydrazinopyridine and related compounds were prepared follow the procedure of literature.[1]

Caution! Acetonitrile (MeCN) can be metabolised to produce hydrogen cyanide. Appropriate protective measures should be taken to avoid direct contaction during operation.

2. General procedure of synthesizing the products

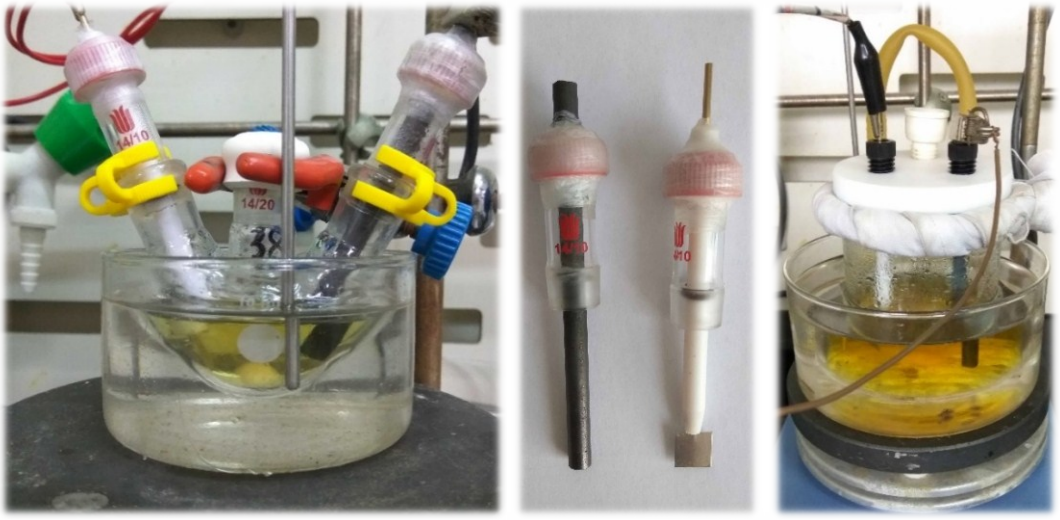


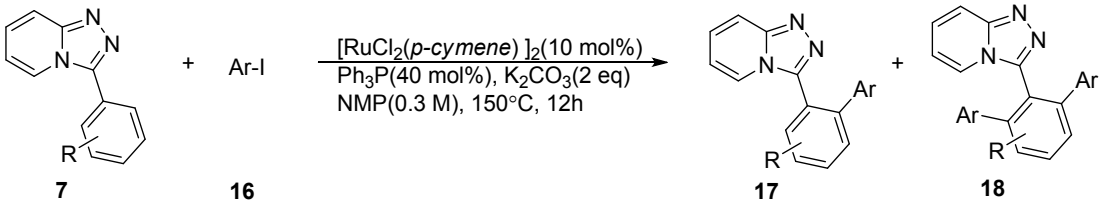
5 **1**

General procedure A: The crude 2-hydrazinopyridines (**5**; 0.6 mmol), aldehyde (**6**; 0.5 mmol) and MeCN (5 mL) were added in a 10 mL undivided three-necked round-bottomed flask, the mixture was stirred at room temperature or heated until TLC indicated that condensation was complete. Then, $^{n}Bu_4NBF_4$ (0.5 mmol) was added followed by MeCN (4 mL) and H_2O (1 mL). 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×10 mm×0.2 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 70 °C for 4 h (2.98 F). 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 CH_2Cl_2 (10 mL x 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 **1**.

Procedure for gram scale synthesis: The crude 2-hydrazinopyridines (**5**; 12 mmol), aldehyde (**6**; 10 mmol) and MeCN (50 mL) were added in a 200 mL undivided beaker-type cell, the mixture was stirred at room temperature or heated until TLC indicated that condensation was complete. Then, $^{n}Bu_4NBF_4$ (10 mmol) was added followed by MeCN (40 mL) and H_2O (10 mL). Meantime the flask was equipped with graphite rod (ϕ 6 mm, about 20 mm immersion

depth in solution) as the anode and platinum plate (10 mm×10 mm×0.2 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 100 mA under 70 °C for 8 h (2.98 F). 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 CH_2Cl_2 (100 mL x 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 **1**.





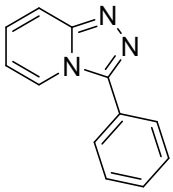
7 **16** **17** **18**

General procedure B: In a 10 mL microwave tube was charged with 1,2,4-triazolo[4,3-a]pyridines (**7**; 0.3 mmol), aryl iodide (**16**; 0.6 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.03 mmol), Ph_3P (0.12 mmol), K_2CO_3 (0.6mmol) and N-Methyl pyrrolidone (NMP) 1mL. The reaction mixture was stirred at 150 °C for 12 h. When the reaction was finished, the reaction mixture was washed with water and extracted with EtOAc (15 mL x 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 **17** and **18**.

Notes:

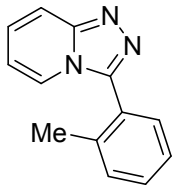
1. MeCN can be recovered by rotary evaporation for repeated use.
2. $^{n}Bu_4NBF_4$ could be purified by recrystallization from water for repeated use.

3. Synthesis and characterization of the products:



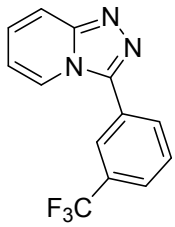
3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (7a):

Following the general procedure A, **7a** was purified by EtOAc and obtained as an off-white solid (83.9 mg, 86% yield); M_p = 171–173 °C; R_f = 0.30 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.88 – 7.82 (m, 3H), 7.63 – 7.55 (m, 3H), 7.31 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.89 (td, *J* = 6.8, 1.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 146.8, 130.3, 129.4, 128.3, 127.5, 126.5, 122.7, 116.6, 114.5.HRMS m/z (ESI): calcd for $C_{12}H_{10}N_3$ $[M + H]^+$ 196.0869, found 196.0879. The spectra data matched with values reported in the literature.[2]



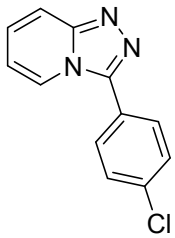
3-(o-tolyl)-[1,2,4]triazolo[4,3-a]pyridine (7b):

Following the general procedure A, **7b** was purified by EtOAc and obtained as an off-white solid. (87.8mg, 84% yield); M_p = 148–150 °C; R_f = 0.22 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.3 Hz, 1H), 7.80 (d, *J* = 7.0 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.45 – 7.40 (m, 1H), 7.37 (td, *J* = 7.3, 1.4 Hz, 1H), 7.30 (ddd, *J* = 9.3, 6.5, 1.2 Hz, 1H), 6.84 (td, *J* = 6.7, 1.1 Hz, 1H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 146.3, 138.6, 131.1, 130.5, 130.3, 127.1, 126.3, 125.6, 122.7, 116.6, 113.9, 19.8.The spectra data matched with values reported in the literature.[3]



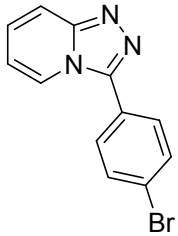
3-(3-(trifluoromethyl)phenyl)-[1,2,4]triazolo[4,3-a]pyridine (7c):

Following the general procedure A, **7c** was purified by EtOAc and obtained as a light yellow solid (114.5 mg, 87% yield); M_p = 154–155 °C; R_f = 0.45 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.0 Hz, 1H), 8.14 (d, *J* = 1.7 Hz, 1H), 8.11 – 8.05 (m, 1H), 7.89 (d, *J* = 9.3 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.76 (t, *J* = 7.8 Hz, 1H), 7.36 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.97 (td, *J* = 6.8, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 145.4, 131.9 (q, *J*(C, F) = 33.1 Hz), 131.3, 130.0, 127.6, 127.5, 126.9 (q, *J*(C, F) = 3.9 Hz), 125.1 (q, *J*(C, F) = 3.9 Hz), 122.3, 117.0, 114.9.The spectra data matched with values reported in the literature.[2]



3-(4-chlorophenyl)-[1,2,4]triazolo[4,3-a]pyridine (7da):

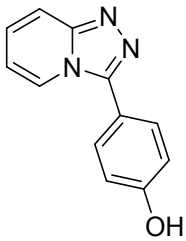
Following the general procedure A, **7da** was purified by EtOAc and obtained as an off-white solid (74.7 mg, 65% yield); M_p = 198-200 °C; R_f = 0.40 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.84 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.60 – 7.53 (m, 2H), 7.31 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.91 (ddd, *J* = 7.5, 6.6, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 145.8, 136.4, 129.7, 129.5, 127.3, 125.1, 122.4, 116.9, 114.6.The spectra data matched with values reported in the literature.[2]



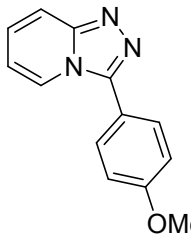
3-(4-bromophenyl)-[1,2,4]triazolo[4,3-a]pyridine (7db):

Following the general procedure A, **7db** was purified by EtOAc and obtained as a white solid (87.6 mg, 64% yield); M_p = 200-202 °C; R_f = 0.40 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.1 Hz, 1H), 7.86 (d, *J* = 9.3 Hz, 1H), 7.74 (s, 4H), 7.32 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.92 (ddd, *J* = 7.4, 6.6,

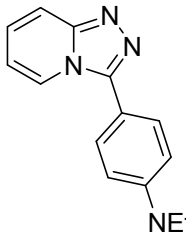
1.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 145.8, 132.6, 129.6, 127.2, 125.6, 124.7, 122.4, 117.0, 114.6. The spectra data matched with values reported in the literature.[4]



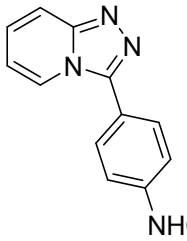
4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)phenol (7dc):
Following the general procedure A, **7dc** was purified by EtOAc and obtained as a white solid (65.5 mg, 62% yield); M_p = 248-249 °C; R_f = 0.22 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.03 (s, 1H), 8.48 (dd, *J* = 7.1, 1.2 Hz, 1H), 7.81 (dd, *J* = 9.3, 1.2 Hz, 1H), 7.76 – 7.64 (m, 3H), 7.39 (ddd, *J* = 9.2, 6.5, 1.1 Hz, 1H), 7.03 – 6.95 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 159.0, 149.6, 146.2, 129.7, 127.5, 123.8, 117.1, 116.0, 115.6, 114.1.The spectra data matched with values reported in the literature.[2]



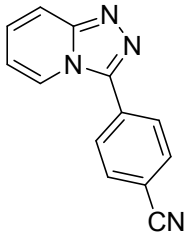
3-(4-methoxyphenyl)-[1,2,4]triazolo[4,3-a]pyridine (7dd):
Following the general procedure A, **7dd** was purified by EtOAc and obtained as an off-white solid (94.6 mg, 84% yield); M_p = 121-123 °C; R_f = 0.30 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.80 (d, *J* = 9.3 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.26 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.84 (td, *J* = 6.8, 1.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 150.4, 146.7, 129.8, 126.9, 122.6, 118.9, 116.8, 114.8, 114.0, 55.5. The spectra data matched with values reported in the literature.[2]



4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)-N,N-diethylaniline (7de):
Following the general procedure A, **7de** was purified by EtOAc and obtained as a yellow oil (113.2 mg, 85% yield); R_f= 0.40 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.78 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.22 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.85 – 6.78 (m, 3H), 3.44 (q, *J* = 7.1 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H). The spectra data matched with values reported in the literature.[1]

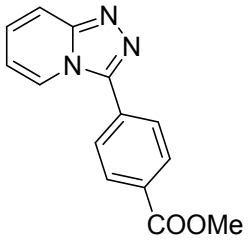


N-(4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)phenyl)acetamide (7df):
Following the general procedure A, **7df** was purified by EtOAc and obtained as a white solid (94.6 mg, 75% yield); M_p = 247-248 °C; R_f = 0.2 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.25 (s, 1H), 8.56 (dt, *J* = 7.1, 1.2 Hz, 1H), 7.90 – 7.78 (m, 5H), 7.42 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 7.02 (td, *J* = 6.8, 1.1 Hz, 1H), 2.11 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.7, 140.7, 128.6, 127.7, 123.9, 120.8, 119.2, 115.6, 114.3, 24.1; HRMS m/z (ESI): calcd for $C_{14}H_{13}N_4O$ $[M + H]^+$ 253.1084, found 253.1082.

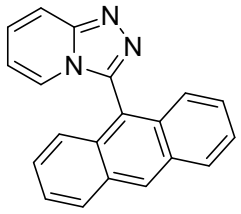


3-(4-cyanophenyl)-[1,2,4]triazolo[4,3-a]pyridine (7dg):
Following the general procedure A, **7dg** was purified by CH_2Cl_2/MeOH (50:1) and obtained as a white solid (59.5 mg, 54% yield); M_p = 260-261 °C; R_f = 0.30 (CH_2Cl_2/MeOH = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.31 (m, 1H), 8.06 – 8.01 (m, 2H), 7.90 (dd, *J* = 8.8, 1.8 Hz, 3H), 7.38 (ddd, *J* = 9.3, 6.6, 1.1 Hz, 1H), 6.99 (td, *J* = 6.8, 1.1 Hz, 1H); ^{13}C NMR (126 MHz,

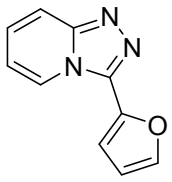
$CDCl_3$) 151.0, 145.0, 133.1, 131.1, 128.5, 127.7, 122.3, 118.0, 117.2, 115.1, 113.8. The spectra data matched with values reported in the literature.[2]



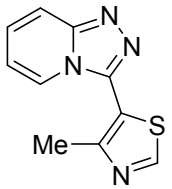
Methyl 4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)benzoate (7dh):
Following the general procedure A, **7dh** was purified by EtOAc and obtained as an off-white solid (88.6 mg, 70% yield); M_p = 178-180 °C; R_f = 0.2 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.68 (dt, *J* = 7.0, 1.1 Hz, 1H), 8.21 – 8.15 (m, 2H), 8.13 – 8.08 (m, 2H), 7.91 (dt, *J* = 9.3, 1.1 Hz, 1H), 7.48 (ddd, *J* = 9.3, 6.6, 1.1 Hz, 1H), 7.09 (td, *J* = 6.8, 1.1 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 165.7, 150.3, 145.1, 131.0, 130.4, 129.9, 128.3, 128.1, 124.1, 115.7, 114.8, 52.4. The spectra data matched with values reported in the literature.[5]



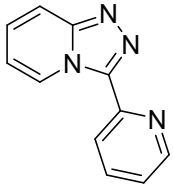
3-(anthracen-9-yl)-[1,2,4]triazolo[4,3-a]pyridine (7e):
Following the general procedure A, **7e** was purified by EtOAc and obtained as a light green solid (138.7 mg, 94% yield); M_p = 255-256 °C; R_f = 0.4 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 2H), 8.00 (d, *J* = 9.4 Hz, 1H), 7.54 (ddd, *J* = 8.2, 4.9, 2.7 Hz, 2H), 7.47 – 7.43 (m, 4H), 7.36 (ddd, *J* = 9.4, 6.5, 1.2 Hz, 1H), 7.33 (dd, *J* = 7.0, 1.3 Hz, 1H), 6.72 (td, *J* = 6.8, 1.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 144.3, 131.7, 131.4, 130.7, 128.9, 127.5, 127.5, 125.8, 125.0, 123.1, 116.7, 114.0; HRMS *m/z* (ESI): calcd for $C_{20}H_{14}N_3$ $[M + H]^+$ 296.1182, found 296.1196.



3-(furan-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (7f):
Following the general procedure A, **7f** was purified by EtOAc and obtained as a light brown solid (70.4 mg, 76% yield); M_p = 92-93 °C; R_f = 0.4 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 7.1 Hz, 1H), 7.83 (d, *J* = 9.3 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.34 – 7.26 (m, 2H), 6.94 (td, *J* = 6.8, 1.1 Hz, 1H), 6.66 (dd, *J* = 3.5, 1.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 143.6, 143.0, 139.6, 127.5, 124.3, 116.6, 114.6, 112.1, 111.2. The spectra data matched with values reported in the literature.[2]

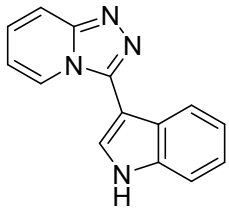


5-([1,2,4]triazolo[4,3-a]pyridin-3-yl)-4-methylthiazole (7g):
Following the general procedure A, **7g** was purified by EtOAc and obtained as a brown solid (54.0 mg, 50% yield); M_p = 127-129 °C; R_f = 0.1 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.01 (dt, *J* = 6.9, 1.1 Hz, 1H), 7.89 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.38 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.97 (td, *J* = 6.7, 1.0 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 154.1, 150.5, 139.2, 127.7, 122.6, 116.9, 115.0, 114.8, 16.6; HRMS *m/z* (ESI): calcd for $C_{10}H_9N_4S$ $[M + H]^+$ 217.0542, found 217.0546.



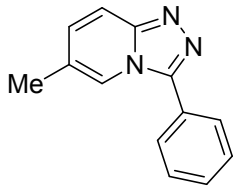
3-(pyridin-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (7h):
Following the general procedure A, **7h** was purified by EtOAc and obtained as a black solid (40.2 mg, 41% yield); M_p =117-119 °C; R_f = 0.5 (EtOAc); ^{1}H

NMR (500 MHz, $CDCl_3$) δ 9.84 (dt, *J* = 7.1, 1.2 Hz, 1H), 8.71 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 8.55 (dt, *J* = 8.1, 1.1 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.40 – 7.34 (m, 2H), 6.97 (td, *J* = 6.8, 1.1 Hz, 1H). The spectra data matched with values reported in the literature.[2]



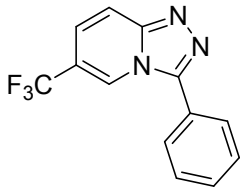
3-(1H-indol-3-yl)-[1,2,4]triazolo[4,3-a]pyridine (7i):

Following the general procedure A, **7i** was purified by EtOAc and obtained as a pinkish-white solid (87.8 mg, 75% yield); M_p = 244-246 °C R_f = 0.1 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.89 (s, 1H), 8.65 (dt, *J* = 7.1, 1.1 Hz, 1H), 8.26 (d, *J* = 2.8 Hz, 1H), 8.16 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.84 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.55 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.40 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 7.26 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.19 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.03 (td, *J* = 6.7, 1.1 Hz, 1H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 148.8, 142.8, 136.1, 127.1, 125.6, 125.0, 124.3, 122.5, 120.8, 120.3, 115.6, 113.8, 111.9, 101.3; HRMS *m/z* (ESI): calcd for $C_{14}H_{11}N_4$ $[M + H]^+$ 235.0978, found 235.0981.



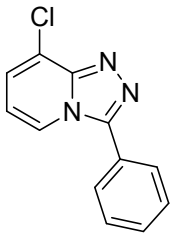
6-methyl-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (7j):

Following the general procedure A, **7j** was purified by EtOAc and obtained as a light yellow solid (94.2 mg, 90% yield); M_p = 185-187 °C; R_f = 0.3 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.3 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.74 (dd, *J* = 9.5, 1.1 Hz, 1H), 7.63 – 7.54 (m, 3H), 7.15 (dd, *J* = 9.4, 1.5 Hz, 1H), 2.35 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 146.3, 130.6, 130.1, 129.3, 128.3, 126.9, 124.2, 119.6, 116.0, 18.3. The spectra data matched with values reported in the literature.[2]



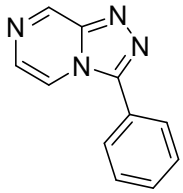
3-phenyl-6-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine (7k):

Following the general procedure A, **7k** was purified by EtOAc and obtained as a white solid (69.8 mg, 53% yield); M_p = 93-95 °C; R_f = 0.5 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 1.4 Hz, 1H), 7.97 (d, *J* = 9.6 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.67 – 7.61 (m, 3H), 7.43 (dd, *J* = 9.6, 1.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 148.0, 131.0, 129.7, 128.4, 125.5, 123.3 (q, *J*(C, F) = 2.2 Hz), 122.8 (d, *J*(C, F) = 272 Hz), 122.2 (q, *J*(C, F) = 5.9 Hz), 119.0(d, *J*(C, F) = 34.7 Hz), 118.0. The spectra data matched with values reported in the literature.[2]



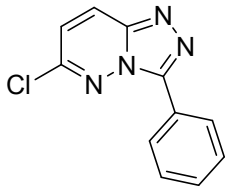
8-chloro-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (7l):

Following the general procedure A, **7l** was purified by CH_2Cl_2/MeOH (50:1) and obtained as a white solid (101.1 mg, 88% yield); M_p = 157-159 °C; R_f = 0.5 (CH_2Cl_2/MeOH = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.0, 0.9 Hz, 1H), 7.86 – 7.79 (m, 2H), 7.62 – 7.57 (m, 3H), 7.35 (dd, *J* = 7.1, 0.9 Hz, 1H), 6.84 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 148.3, 130.6, 129.4, 128.5, 126.2, 125.9, 123.0, 121.4, 114.0.The spectra data matched with values reported in the literature.[2]



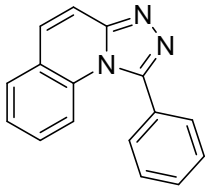
3-phenyl-[1,2,4]triazolo[4,3-a]pyrazine (7m):

Following the general procedure A, **7m** was purified by EtOAc and obtained as an off-white solid (74.6 mg, 76% yield); M_p = 161-163 °C; R_f = 0.3 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (d, *J* = 1.6 Hz, 1H), 8.23 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.95 (d, *J* = 4.8 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.66 – 7.61 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 146.0, 145.1, 130.9, 130.4, 129.6, 128.1, 125.6, 115.2. The spectra data matched with values reported in the literature.[3]



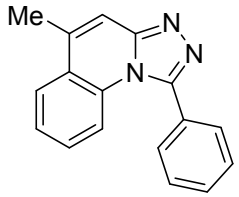
6-chloro-3-phenyl-[1,2,4]triazolo[4,3-b]pyridazine (7n):

Following the general procedure A, **7n** was purified by EtOAc and obtained as a white solid (98.0 mg, 85% yield); M_p = 197-199 °C; R_f = 0.4 (CH_2Cl_2/MeOH = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.45 (m, 2H), 8.17 (d, *J* = 9.6 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.17 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4, 148.1, 143.6, 130.7, 128.8, 127.7, 126.6, 125.5, 121.8. The spectra data matched with values reported in the literature.[2]



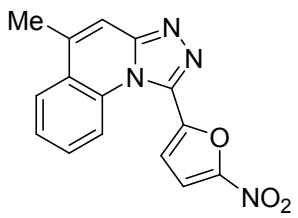
1-phenyl-[1,2,4]triazolo[4,3-a]quinoline (7o):

Following the general procedure A, **7o** was purified by EtOAc and obtained as an off-white solid (92.0 mg, 75% yield); M_p = 135-137 °C; R_f = 0.5 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.74 – 7.69 (m, 3H), 7.66 – 7.55 (m, 5H), 7.47 (td, *J* = 7.6, 1.1 Hz, 1H), 7.36 (ddd, *J* = 8.7, 7.2, 1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 149.1, 131.9, 130.5, 130.0, 129.7, 129.5, 129.3, 129.1, 128.9, 126.1, 124.6, 116.7, 115.1.The spectra data matched with values reported in the literature.[2]



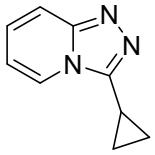
5-methyl-1-phenyl-[1,2,4]triazolo[4,3-a]quinoline (7p):

Following the general procedure A, **7p** was purified by PE/EtOAc (1:1) and obtained as a brown solid (92.1 mg, 71% yield); M_p = 153-154 °C; R_f = 0.5 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.68 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.64 – 7.57 (m, 4H), 7.54 (d, *J* = 1.3 Hz, 1H), 7.49 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.7, 7.2, 1.5 Hz, 1H), 2.65 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 148.7, 136.6, 131.7, 130.4, 129.9, 129.8, 129.1, 128.6, 125.9, 125.9, 125.1, 116. 9, 114.0, 19.6; HRMS m/z (ESI): calcd for $C_{17}H_{14}N_3$ $[M + H]^+$ 260.1182, found 260.1186. The spectra data matched with values reported in the literature.[6]



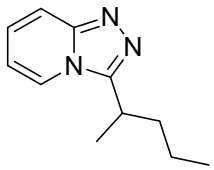
5-methyl-1-(5-nitrofuran-2-yl)-[1,2,4]triazolo[4,3-a]quinoline (7q):

Following the general procedure A, **7q** was purified by PE/EtOAc (1:1) and obtained as a yellow solid (80.9 mg, 55% yield); M_p = 182-183 °C; R_f = 0.2 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 1H), 7.71 – 7.68 (m, 1H), 7.65 – 7.58 (m, 4H), 7.32 (d, *J* = 3.7 Hz, 1H), 2.71 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6 , 144.2 , 138.4 , 137.9 , 130.9 , 129.8 , 127.0 , 126.3 , 125.2 , 117.0 , 116.7 , 113.7 , 112.6 , 19.7; HRMS *m/z* (ESI): calcd for $C_{15}H_{11}N_4O_3$ $[M + H]^+$ 295.0826, found 295.0826. The spectra data matched with values reported in the literature.[6b]



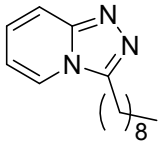
3-cyclopropyl-[1,2,4]triazolo[4,3-a]pyridine (8a):

Following the general procedure A, **8a** was purified by EtOAc and obtained as a colorless oil (70.0 mg, 88% yield); R_f = 0.1 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.72 (dq, *J* = 9.5, 1.3 Hz, 1H), 7.24 (ddd, *J* = 9.3, 6.5, 1.2 Hz, 1H), 6.86 (td, *J* = 6.7, 1.1 Hz, 1H), 2.09 – 2.05 (m, 1H), 1.23 – 1.16 (m, 4H). The spectra data matched with values reported in the literature.[7]



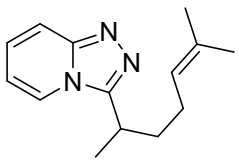
3-(pentan-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (8b):

Following the general procedure A, **8b** was purified by EtOAc and obtained as a light yellow oil (81.4 mg, 86% yield); R_f = 0.2 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.73 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.21 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.82 (td, *J* = 6.8, 1.0 Hz, 1H), 3.27 (h, *J* = 7.0 Hz, 1H), 1.99 (dddd, *J* = 13.2, 10.1, 7.2, 5.7 Hz, 1H), 1.77 (dddd, *J* = 13.5, 10.2, 7.0, 5.5 Hz, 1H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.36 (dddt, *J* = 20.5, 13.1, 10.2, 5.0 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.7, 149.8, 126.4, 121.9, 116.7, 113.3, 36.9, 30.2, 20.4, 18.3, 13.9; HRMS *m/z* (ESI): calcd for $C_{11}H_{16}N_3$ $[M + H]^+$ 190.1339, found 190.1330.



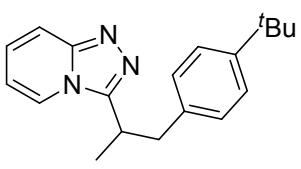
3-nonyl-[1,2,4]triazolo[4,3-a]pyridine (8c):

Following the general procedure A, **8c** was purified by EtOAc and obtained as a white solid (106.7 mg, 87% yield); M_p = 81-82 °C; R_f = 0.3 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.75 (dd, *J* = 9.3, 1.2 Hz, 1H), 7.23 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.84 (td, *J* = 6.8, 1.0 Hz, 1H), 3.10 – 3.05 (m, 2H), 1.91 (p, *J* = 7.7 Hz, 2H), 1.50 – 1.42 (m, 2H), 1.33 – 1.22 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H).



3-(6-methylhept-5-en-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (8d):

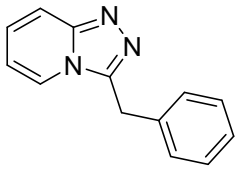
Following the general procedure A, **8d** was purified by EtOAc and obtained as a light yellow oil (88.3 mg, 77% yield); R_f = 0.3 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.74 (dt, *J* = 9.3, 1.1 Hz, 1H), 7.22 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.82 (td, *J* = 6.8, 1.1 Hz, 1H), 5.06 (ddq, *J* = 7.1, 5.6, 1.4 Hz, 1H), 3.27 (h, *J* = 6.9 Hz, 1H), 2.14 – 2.07 (m, 1H), 2.07 – 2.01 (m, 2H), 1.88 – 1.80 (m, 1H), 1.64 (q, *J* = 1.2 Hz, 3H), 1.50 (d, *J* = 7.0 Hz, 3H), 1.44 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.5, 149.7, 132.6, 126.4, 123.4, 121.9, 116.7, 113.3, 34.8, 29.6, 25.6, 25.5, 18.5, 17.6; HRMS m/z (ESI): calcd for $C_{14}H_{20}N_3$ $[M + H]^+$ 230.1652, found 230.1655.



3-(1-(4-(tert-butyl)phenyl)propan-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (8e):

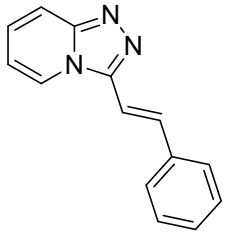
Following the general procedure A, **8e** was purified by EtOAc and obtained as an off-white solid (127.6 mg, 87% yield); M_p = 146-148 °C; R_f = 0.4 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dt, *J* = 9.3, 1.2 Hz, 1H), 7.44 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.12 (ddd, *J* = 9.3,

6.5, 1.1 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.57 (td, *J* = 6.8, 1.1 Hz, 1H), 3.44 (dt, *J* = 7.8, 6.8 Hz, 1H), 3.19 (dd, *J* = 13.4, 7.9 Hz, 1H), 3.10 (dd, *J* = 13.4, 7.0 Hz, 1H), 1.61 (d, *J* = 6.9 Hz, 3H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2 , 149.7 , 136.2 , 128.6 ,128.6 , 126.2 , 125.4 ,125.4 , 121.6 , 116.5 , 112.8 , 41.9 , 34.4 , 33.2 , 31.3 , 31.3 , 31.3 , 18.9; HRMS *m/z* (ESI): calcd for $C_{19}H_{24}N_3$ $[M + H]^+$ 294.1965, found 294.1969.



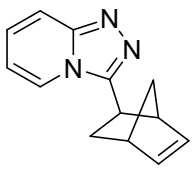
3-benzyl-[1,2,4]triazolo[4,3-a]pyridine (8f):

Following the general procedure A, **8f** was purified by EtOAc and obtained as an off-white solid (96.3 mg, 92% yield); M_p = 165-166 °C; R_f = 0.2 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.3 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.32 (t, *J* = 7.1 Hz, 2H), 7.27 – 7.19 (m, 4H), 6.72 (td, *J* = 6.8, 1.0 Hz, 1H), 4.56 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 145.3, 134.5, 129.1, 128.4, 127.4, 126.8, 122.2, 116.6, 113.7, 31.4.



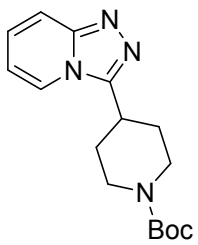
(E)-3-styryl-[1,2,4]triazolo[4,3-a]pyridine (8g):

Following the general procedure A, **8g** was purified by EtOAc and obtained as a yellow solid (80.8 mg, 73% yield); M_p = 185-187 °C; R_f = 0.5 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.16 (m, 1H), 7.91 (d, *J* = 16.2 Hz, 1H), 7.80 (d, *J* = 9.3 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.34 (m, 1H), 7.31 – 7.25 (m, 1H), 7.18 (d, *J* = 16.2 Hz, 1H), 6.93 (td, *J* = 6.8, 1.1 Hz, 1H). The spectra data matched with values reported in the literature.[2]



3-((1S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (8h):

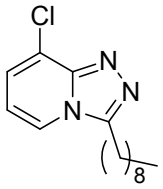
Following the general procedure A, **8h** was purified by EtOAc and obtained as a semi-liquid colorless solid (82.4 mg, 78% yield); R_f = 0.2 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 9.3 Hz, 1H), 7.21 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.83 (td, *J* = 6.8, 1.1 Hz, 1H), 6.29 (dd, *J* = 5.8, 3.1 Hz, 1H), 5.83 (dd, *J* = 5.7, 2.9 Hz, 1H), 3.60 (ddd, *J* = 9.3, 4.5, 3.4 Hz, 1H), 3.48 (dq, *J* = 3.3, 1.6 Hz, 1H), 3.10 – 3.06 (m, 1H), 2.32 (ddd, *J* = 11.5, 9.3, 3.8 Hz, 1H), 1.91 (ddd, *J* = 11.5, 4.6, 2.6 Hz, 1H), 1.66 – 1.63 (m, 1H), 1.53 (dt, *J* = 8.5, 1.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0 , 149.1 , 137.6 , 132.5 , 126.4 , 122.0 , 116.7 , 113.2 , 49.6 , 45.4 , 42.4 , 34.6 , 30.3; HRMS *m/z* (ESI): calcd for $C_{13}H_{14}N_3$ $[M + H]^+$ 212.1182, found 212.1184.



tert-butyl 4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)piperidine-1-carboxylate (8i):

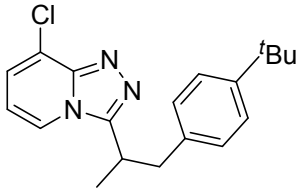
Following the general procedure A, **8i** was purified by EtOAc and obtained as a white solid (111.8 mg, 74% yield); M_p = 164-165 °C; R_f = 0.2 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.58 – 8.52 (m, 1H), 7.73 (dt, *J* = 9.3, 1.1 Hz, 1H), 7.34 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 6.97 (td, *J* = 6.7, 1.1 Hz, 1H), 4.08 – 3.99 (m, 2H), 3.50 (tt, *J* = 11.2, 3.7 Hz, 1H), 3.00 (s, 2H), 2.00 (dd, *J* = 13.5, 3.5 Hz, 2H), 1.78 – 1.66 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 153.9,

149.0, 149.0, 127.2, 123.7, 115.4, 113.1, 78.7, 39.5, 31.0, 29.2, 28.1; HRMS *m/z* (ESI): calcd for $C_{16}H_{23}N_4O_2$ $[M + H]^+$ 303.1816, found 303.1821.



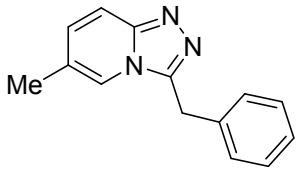
8-chloro-3-nonyl-[1,2,4]triazolo[4,3-a]pyridine (8J):

Following the general procedure A, **8J** was purified by PE/EtOAc (1:2) and obtained as an off-white solid (92.3 mg, 66% yield); M_p = 81-82 °C; R_f = 0.3 (PE/EtOAc = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.0, 0.9 Hz, 1H), 7.29 (dd, *J* = 7.1, 0.8 Hz, 1H), 6.81 (t, *J* = 7.0 Hz, 1H), 3.12 – 3.07 (m, 2H), 1.88 (p, *J* = 7.7 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.38 – 1.32 (m, 2H), 1.30 – 1.23 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 147.9, 125.3, 122.9, 120.7, 113.3, 31.8, 29.4, 29.3, 29.2, 26.7, 24.9, 22.6, 14.1; HRMS *m/z* (ESI): calcd for $C_{15}H_{23}ClN_3$ $[M + H]^+$ 280.1575, found 280.1570.



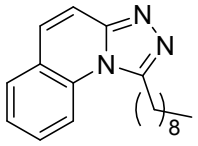
3-(1-(4-(tert-butyl)phenyl)propan-2-yl)-8-chloro-[1,2,4]triazolo[4,3-a]pyridine (8k):

Following the general procedure A, **8k** was purified by PE/EtOAc (1:1) and obtained as a pinkish-white solid (106.5 mg, 65% yield); M_p = 145-146 °C; R_f = 0.3 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.0, 0.8 Hz, 1H), 7.21 – 7.16 (m, 3H), 6.97 – 6.93 (m, 2H), 6.50 (t, *J* = 7.0 Hz, 1H), 3.42 (dp, *J* = 8.3, 6.9 Hz, 1H), 3.18 (dd, *J* = 13.4, 8.3 Hz, 1H), 3.11 (dd, *J* = 13.4, 6.7 Hz, 1H), 1.62 (d, *J* = 6.9 Hz, 3H), 1.26 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 149.7, 147.7, 136.1, 128.6, 125.5, 125.1, 122.6, 120.4, 112.6, 41.9, 34.4, 33.7, 31.3, 18.8; HRMS *m/z* (ESI): calcd for $C_{19}H_{23}N_3$ $[M + H]^+$ 328.1575, found 328.1591.



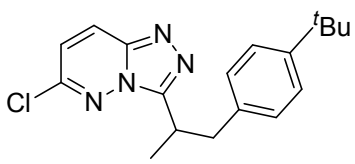
3-benzyl-6-methyl-[1,2,4]triazolo[4,3-a]pyridine (8l):

Following the general procedure A, **8l** was purified by EtOAc and obtained as a white solid (79.3 mg, 71% yield); M_p = 158-160 °C; R_f = 0.2 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.22 – 8.17 (m, 1H), 7.66 (dd, *J* = 9.4, 1.0 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.24 (dd, *J* = 6.0, 2.7 Hz, 1H), 7.20 (dd, *J* = 9.4, 1.5 Hz, 1H), 4.51 (s, 2H), 2.25 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 148.5, 145.1, 136.0, 130.4, 128.6, 128.5, 126.7, 122.9, 120.5, 114.7, 29.6, 17.4; HRMS *m/z* (ESI): calcd for $C_{14}H_{14}N_3$ $[M + H]^+$ 224.1182, found 224.1190. The spectra data matched with values reported in the literature.[6a]



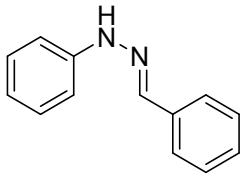
1-nonyl-[1,2,4]triazolo[4,3-a]quinoline (8m):

Following the general procedure A, **8m** was purified by PE/EtOAc (1:1) and obtained as a white solid (112.3 mg, 76% yield); M_p = 89-91 °C; R_f = 0.3 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ8.17 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.69 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.63 (d, *J* = 9.5 Hz, 1H), 7.54 (td, *J* = 7.6, 1.0 Hz, 1H), 7.50 (d, *J* = 9.5 Hz, 1H), 3.48 – 3.43 (m, 2H), 2.09 – 2.02 (m, 2H), 1.58 (ddd, *J* = 12.6, 8.5, 6.3 Hz, 2H), 1.45 – 1.39 (m, 2H), 1.33 – 1.25 (m, 8H), 0.90 – 0.87 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 150.2, 150.0, 132.4, 129.5, 129.3, 129.2, 126.0, 124.8, 116.1, 115.5, 31.9, 29.5, 29.5, 29.4, 29.3, 26.8, 22.7, 14.2; HRMS *m/z* (ESI): calcd for $C_{19}H_{26}N_3$ $[M + H]^+$ 296.2121, found 294.2127.



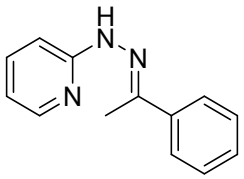
3-(1-(4-(tert-butyl)phenyl)propan-2-yl)-6-chloro-[1,2,4]triazolo[4,3-b]pyridazine (8n):

Following the general procedure A, **8n** was purified by PE/EtOAc (1:1) and obtained as a white solid (74.0 mg, 45% yield); M_p = 147-149 °C; R_f = 0.4 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.6 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.10 – 7.05 (m, 2H), 7.02 (d, *J* = 9.6 Hz, 1H), 3.82 (dp, *J* = 8.0, 7.0 Hz, 1H), 3.28 (dd, *J* = 13.5, 7.2 Hz, 1H), 3.05 (dd, *J* = 13.5, 8.0 Hz, 1H), 1.54 (d, *J* = 7.0 Hz, 3H), 1.28 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 148.5, 136.0, 128.8, 126.3, 125.1, 121.6, 40.5, 34.4, 32.1, 31.4, 29.7, 17.7; HRMS *m/z* (ESI): calcd for $C_{18}H_{21}ClN_4Na$ $[M + Na]^+$ 351.1347, found 351.1340.



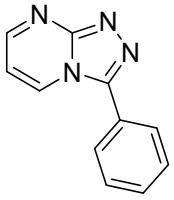
1-benzylidene-2-phenylhydrazine (10):

Following the general procedure A, **10** was purified by PE/EtOAc (10:1) and obtained as a white solid (88.3 mg, 90% yield); M_p = 90-91 °C; R_f = 0.25 (PE/EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 3H), 7.42 – 7.38 (m, 2H), 7.35 – 7.29 (m, 3H), 7.17 – 7.13 (m, 2H), 6.91 (tt, *J* = 7.3, 1.2 Hz, 1H). The spectra data matched with values reported in the literature.[8]



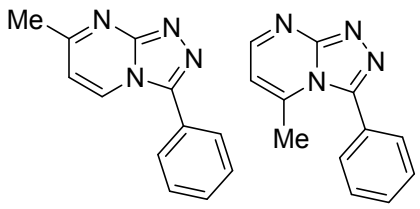
2-(2-(1-phenylethylidene)hydrazinyl)pyridine (13):

Following the general procedure A, **13** was purified by PE/EtOAc (10:1) and obtained as a white solid (93 mg, 88% yield); M_p = 90-92 °C; R_f = 0.2 (PE/EtOAc = 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.16 (ddd, *J* = 5.0, 1.9, 0.9 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.64 (ddd, *J* = 8.8, 7.1, 1.9 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.37 – 7.33 (m, 1H), 6.80 (ddd, *J* = 7.2, 5.0, 1.0 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 147.4, 143.1, 138.7, 138.2, 128.3, 128.3, 125.7, 115.8, 107.8, 12.3. The spectra data matched with values reported in the literature.[9]



3-phenyl-[1,2,4]triazolo[4,3-a]pyrimidine (15a):

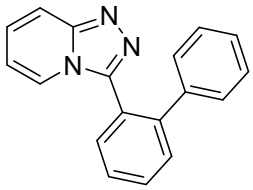
Following the general procedure A (*under room temperature*), **15a** was purified by EtOAc and obtained as a white solid (76 mg, 77% yield); M_p = 173-175 °C; R_f = 0.3 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 3.8, 1.9 Hz, 1H), 8.64 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.87 – 7.81 (m, 2H), 7.64 – 7.55 (m, 3H), 6.98 (dd, *J* = 7.0, 3.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.1, 153.9, 145.7, 130.8, 130.7, 129.5, 128.0, 125.9, 110.2.The spectra data matched with values reported in the literature.[10]



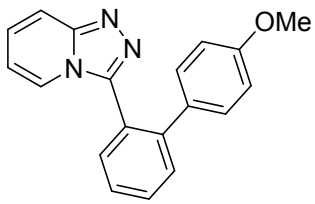
The mixture of 7-methyl-3-phenyl-[1,2,4]triazolo[4,3-a]pyrimidine and 5-methyl-3-phenyl-[1,2,4]triazolo[4,3-a]pyrimidine (15b):

Following the general procedure A (*under room temperature*), **15b** was purified by EtOAc and obtained as a white solid (70.4 mg, 67% yield); M_p = 174-175 °C;

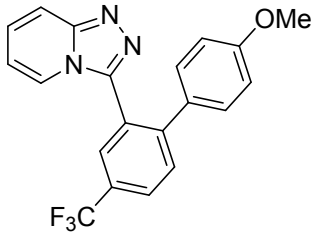
R_f = 0.3 (EtOAc); ^{1}H NMR and ^{13}C NMR see the spectra. HRMS *m/z* (ESI): calcd for $C_{12}H_{11}N_4$ $[M+H]^+$ 211.0939, found 211.0984.



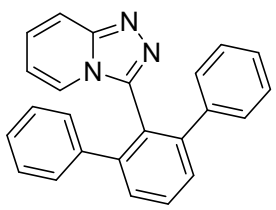
3-([1,1'-biphenyl]-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (17aa):
Following the general procedure B, **17aa** was purified by PE/EtOAc (1:1) and obtained as a white solid (35.0 mg, 43% yield); M_p = 149-151 °C; R_f = 0.2 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.63 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.56 (td, *J* = 7.5, 1.5 Hz, 1H), 7.24 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.17 – 7.10 (m, 5H), 7.07 (ddd, *J* = 9.3, 6.5, 1.2 Hz, 1H), 6.40 (td, *J* = 6.8, 1.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.7, 147.0, 141.5, 139.5, 132.5, 131.0, 130.3, 128.6, 128.1, 128.0, 127.6, 126.7, 124.8, 122.4, 115.9, 112.9; HRMS *m/z* (ESI): calcd for $C_{18}H_{14}N_3$ $[M+H]^+$ 272.1182, found 272.118.



3-(4'-methoxy-[1,1'-biphenyl]-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (17ab):
Following the general procedure B, **17ab** was purified by PE/EtOAc (1:1) and obtained as a white solid (40.6 mg, 45% yield); R_f = 0.2 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.59 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.12 – 7.04 (m, 3H), 6.69 – 6.63 (m, 2H), 6.43 (td, *J* = 6.8, 1.0 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 149.7, 147.2, 141.2, 132.5, 131.9, 130.9, 130.1, 129.2, 127.6, 126.8, 124.6, 122.5, 115.9, 114.1, 113.0, 55.2; HRMS *m/z* (ESI): calcd for $C_{19}H_{16}N_3O$ $[M+H]^+$ 302.1288, found 302.1286.

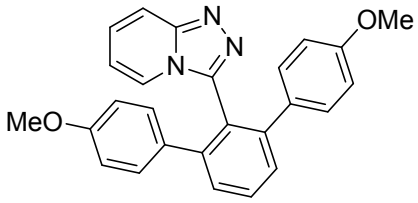


3-(4'-methoxy-4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (17cb):
Following the general procedure B, **17cb** was purified by PE/EtOAc (1:1) and obtained as a white solid (98.6 mg, 89% yield); M_p = 169-170 °C; R_f = 0.4 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 1.9 Hz, 1H), 7.89 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.72 (dt, *J* = 9.4, 1.1 Hz, 2H), 7.22 (dt, *J* = 7.0, 1.2 Hz, 1H), 7.13 (ddd, *J* = 9.3, 6.5, 1.1 Hz, 1H), 7.11 – 7.06 (m, 2H), 6.72 – 6.66 (m, 2H), 6.48 (td, *J* = 6.8, 1.0 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 150.0, 146.0, 144.5, 130.7, 130.4, 130.1, 129.8, 129.2, 127.6, 127.1, 125.4, 123.7, 122.2, 116.2, 114.4, 113.5, 55.2; HRMS *m/z* (ESI): calcd for $C_{20}H_{15}F_3N_3O$ $[M+H]^+$ 370.1162, found 370.1157.



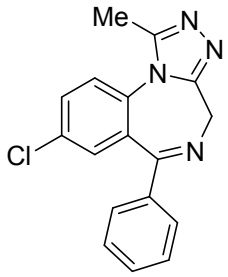
3-([1,1':3',1''-terphenyl]-2'-yl)-[1,2,4]triazolo[4,3-a]pyridine (18aa):
Following the general procedure B, **18aa** was purified by PE/EtOAc (1:1) and obtained as a white solid (8.3 mg, 8% yield); Mp = 211-213 °C; R_f = 0.5 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 9.3 Hz, 1H), 7.36 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.15 – 7.08 (m, 10H), 7.04 (ddd, *J* = 9.3, 6.5, 1.2 Hz,

1H), 6.49 (td, *J* = 6.8, 1.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 145.0, 144.5, 139.8, 130.9, 129.6, 128.4, 128.1, 127.4, 126.6, 123.2, 121.9, 116.0, 113.3; HRMS *m/z* (ESI): calcd for $C_{24}H_{18}N_3$ $[M+H]^+$ 348.1495, found 348.1494.



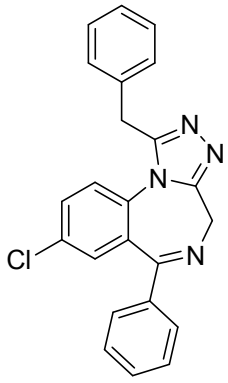
3-(4,4''-dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)-[1,2,4]triazolo[4,3-a]pyridine (18ab):

Following the general procedure B, **18ab** was purified by PE/EtOAc (1:1) and obtained as a white solid (11.0 mg, 9% yield); R_f = 0.5 (PE/EtOAc = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (t, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 6.9 Hz, 1H), 7.09 – 7.06 (m, 1H), 7.05 – 7.02 (m, 4H), 6.65 (d, *J* = 8.7 Hz, 4H), 6.51 (t, *J* = 6.7 Hz, 1H), 3.69 (s, 6H).



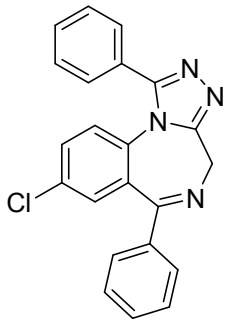
8-chloro-1-methyl-6-phenyl-4H-benzo[f][1,2,4]triazolo[4,3-a][1,4]diazepine (21a):

Following the general procedure A, **21a** was purified by CH_2Cl_2/MeOH (50:1) and obtained as a white solid (92.6 mg, 60% yield); M_p = 228-229 °C; R_f = 0.3 (CH_2Cl_2/MeOH = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.49 – 7.42 (m, 3H), 7.41 – 7.35 (m, 2H), 5.48 (d, *J* = 12.8 Hz, 1H), 4.09 (d, *J* = 12.8 Hz, 1H), 2.63 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 155.0, 150.2, 138.5, 133.2, 132.2, 131.7, 131.7, 130.9, 130.6, 129.3, 128.4, 124.7, 46.3, 12.3.The spectra data matched with values reported in the literature.[11]



1-benzyl-8-chloro-6-phenyl-4H-benzo[f][1,2,4]triazolo[4,3-a][1,4]diazepine (21b):

Following the general procedure A, **21b** was purified by PE/EtOAc (1:2) and obtained as a white solid (106mg, 55% yield); M_p = 184-186 °C; R_f = 0.2 (PE/EtOAc = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.34 (dd, *J* = 8.5, 7.1 Hz, 2H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.24 – 7.15 (m, 5H), 7.02 (dd, *J* = 7.6, 1.9 Hz, 2H), 5.49 (d, *J* = 12.8 Hz, 1H), 4.52 – 4.34 (m, 2H), 4.06 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 155.8, 152.6, 138.4, 134.8, 133.3, 132.0, 131.3, 131.1, 130.8, 130.6, 129.1, 128.9, 128.3, 128.3, 127.1, 124.8, 46.2, 32.1. The spectra data matched with values reported in the literature.[11]



8-chloro-1,6-diphenyl-4H-benzo[f][1,2,4]triazolo[4,3-a][1,4]diazepine (21c):

Following the general procedure A, **21c** was purified by PE/EtOAc (1:2) and obtained as a white solid (96.4 mg, 52% yield); M_p = 194-196 °C; R_f = 0.2 (PE/EtOAc = 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.57 – 7.44 (m, 9H), 7.38 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 5.57 (d, *J* = 13.0 Hz, 1H), 4.18 (d, *J* = 13.0 Hz, 1H). ^{13}C NMR

(126 MHz, $CDCl_3$) δ 168.3, 156.9, 153.2, 138.5, 133.1, 133.0, 131.3, 131.2, 131.1, 130.5, 130.5, 129.3, 129.0, 128.6, 128.5, 126.4, 126.3, 46.5. The spectra data matched with values reported in the literature.[11]

4. References:

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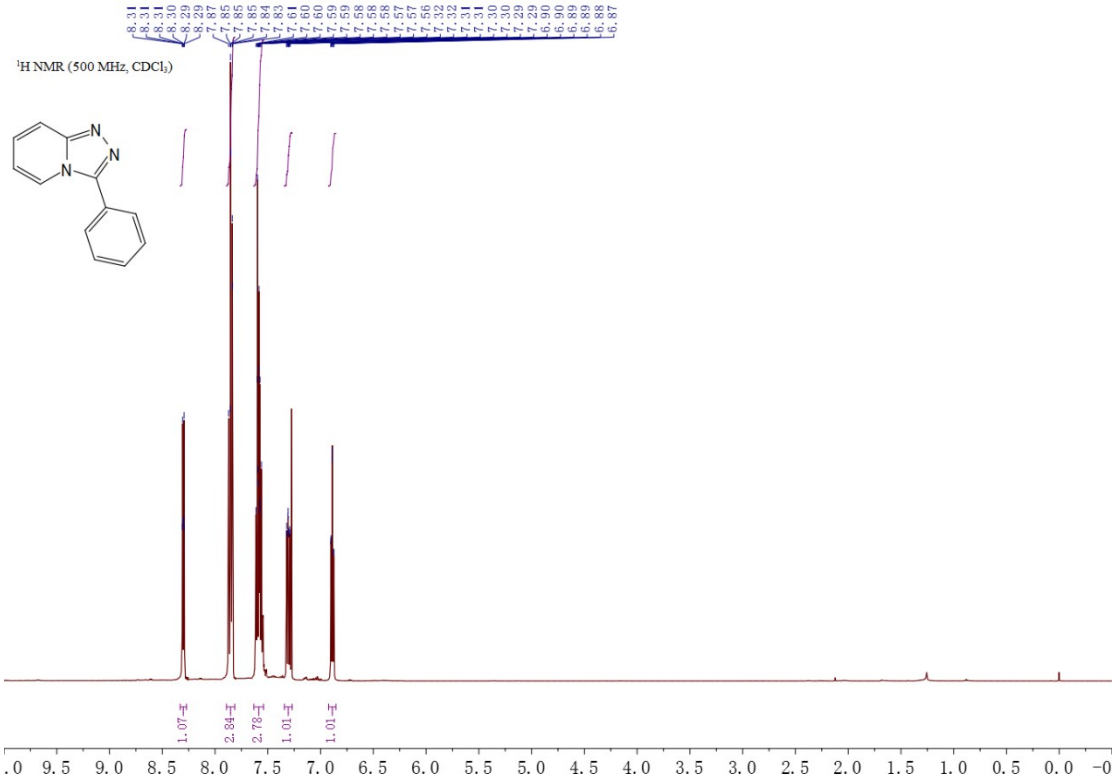
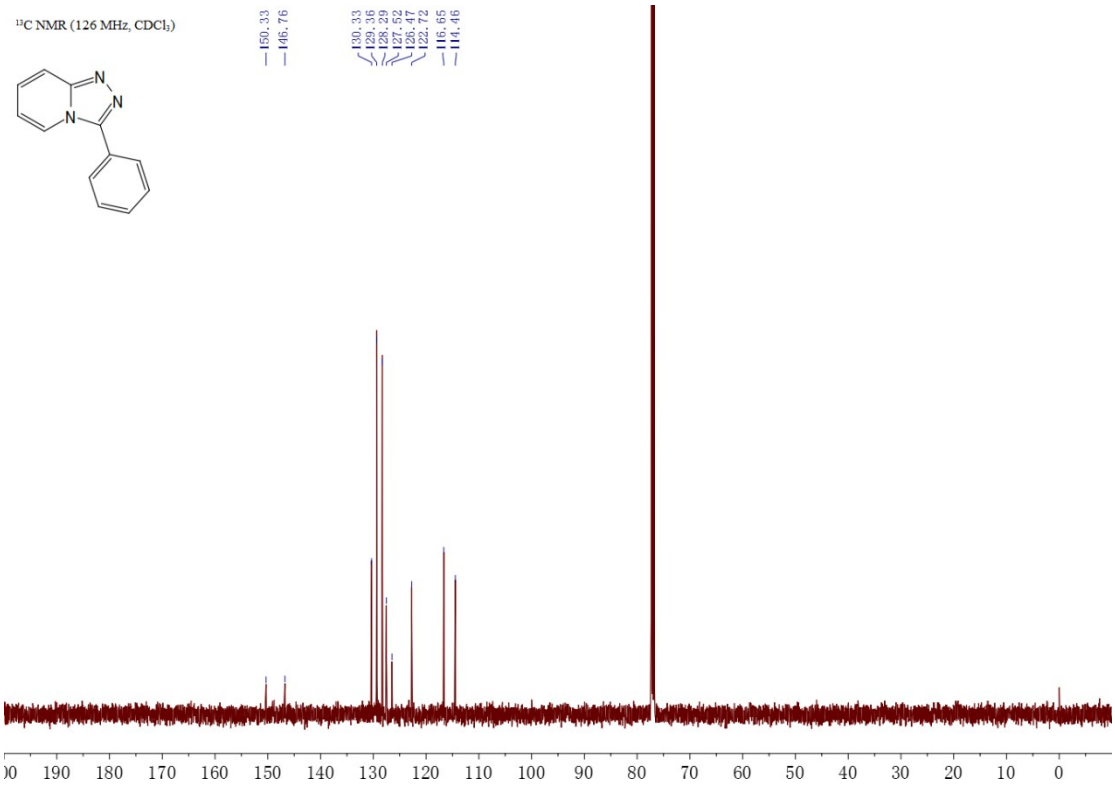
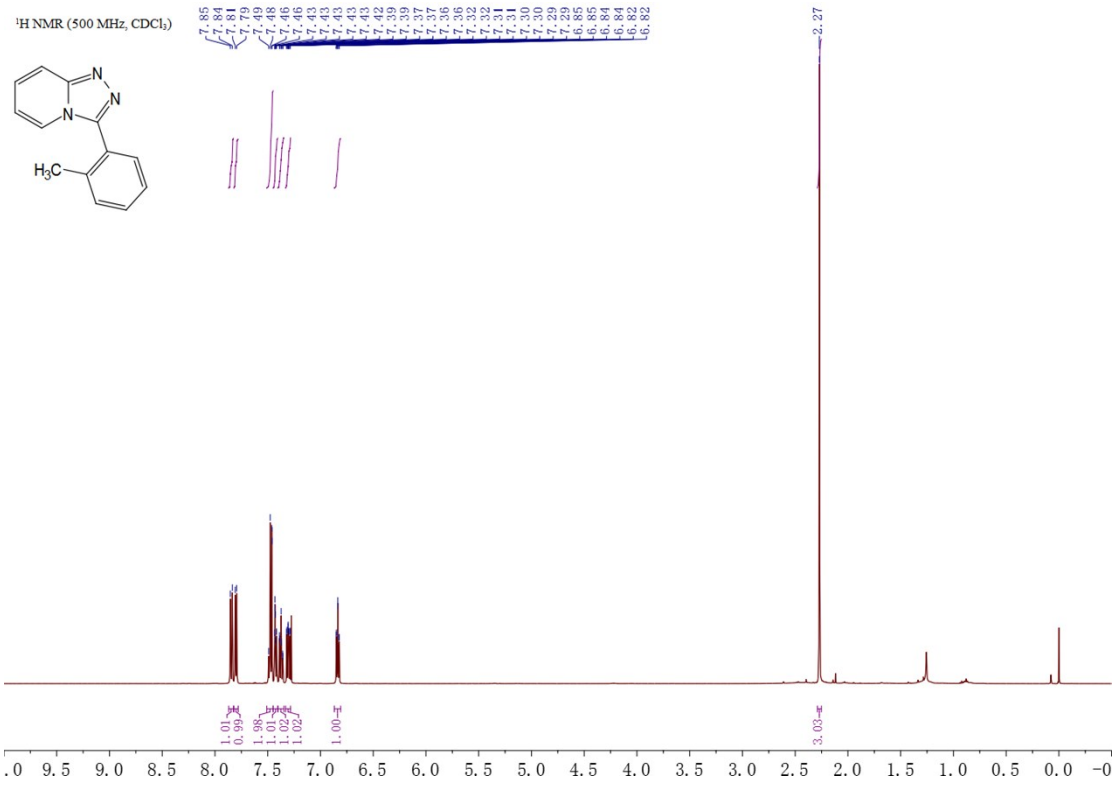
5. NMR spectra.

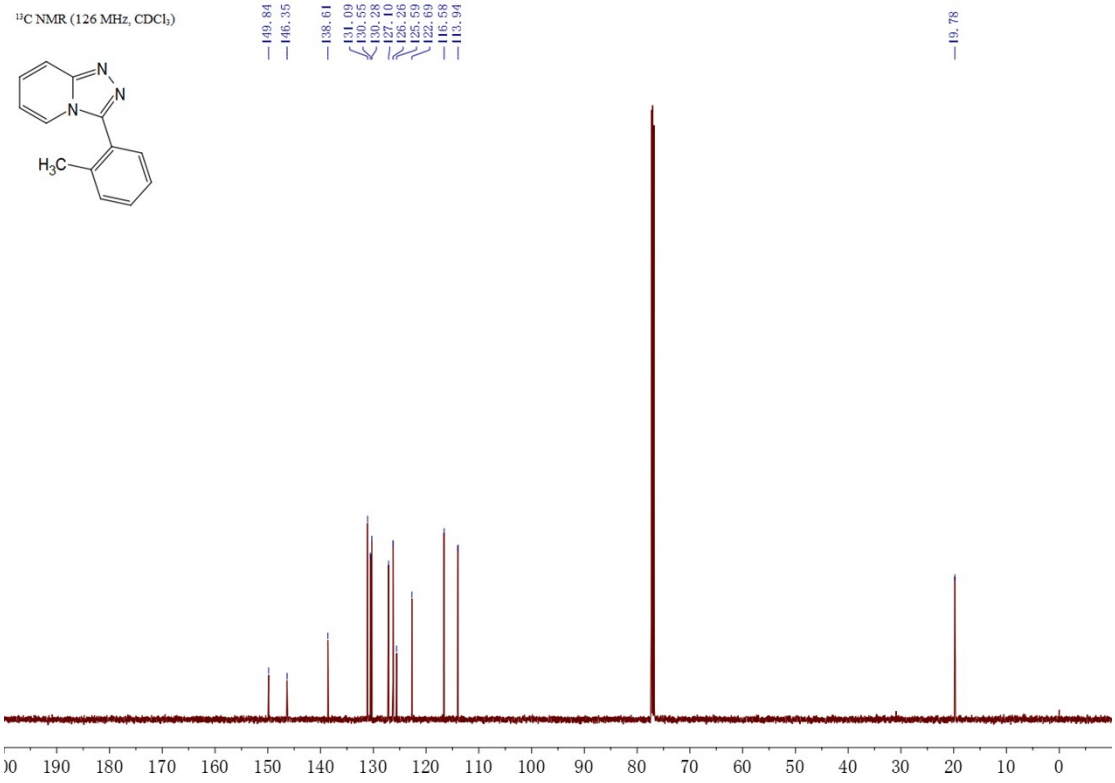
3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (7a)



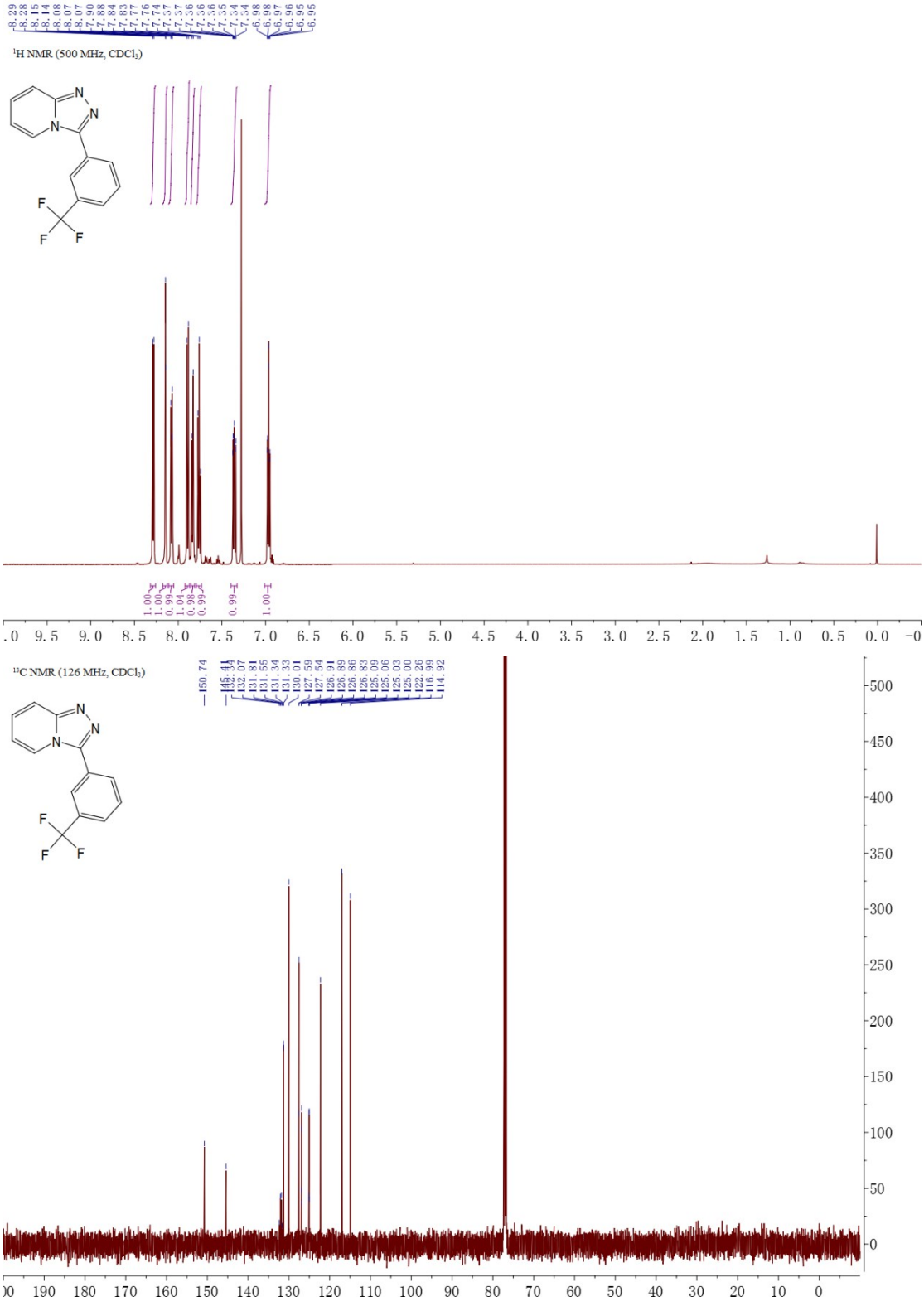


3-(o-tolyl)-[1,2,4]triazolo[4,3-a]pyridine (7b)

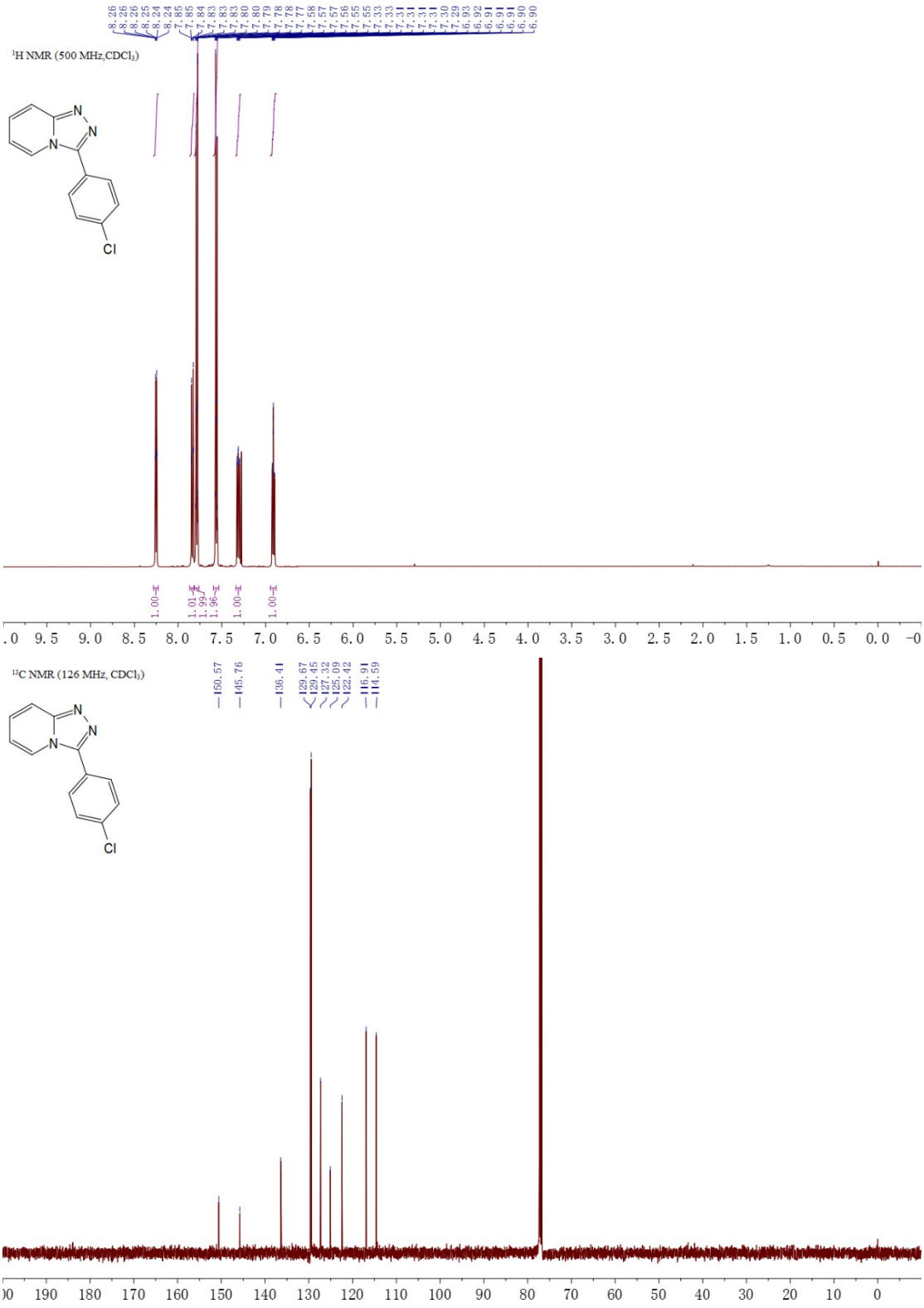




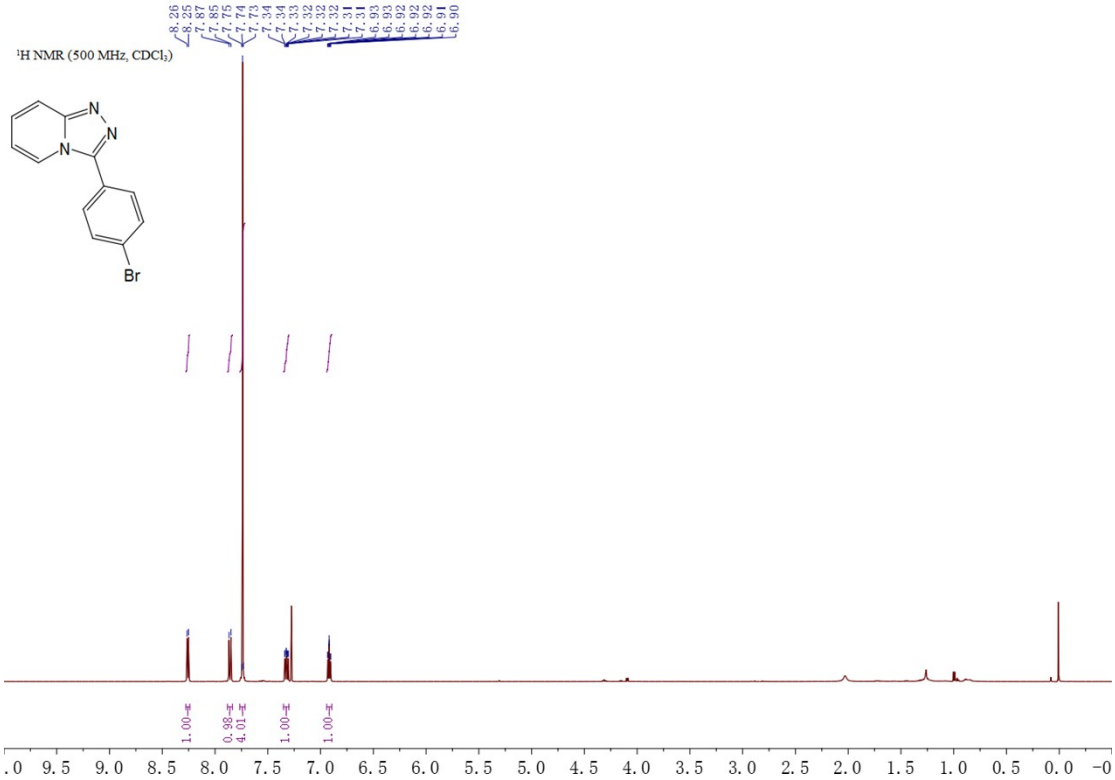
3-(3-(trifluoromethyl)phenyl)-[1,2,4]triazolo[4,3-a]pyridine (7c)

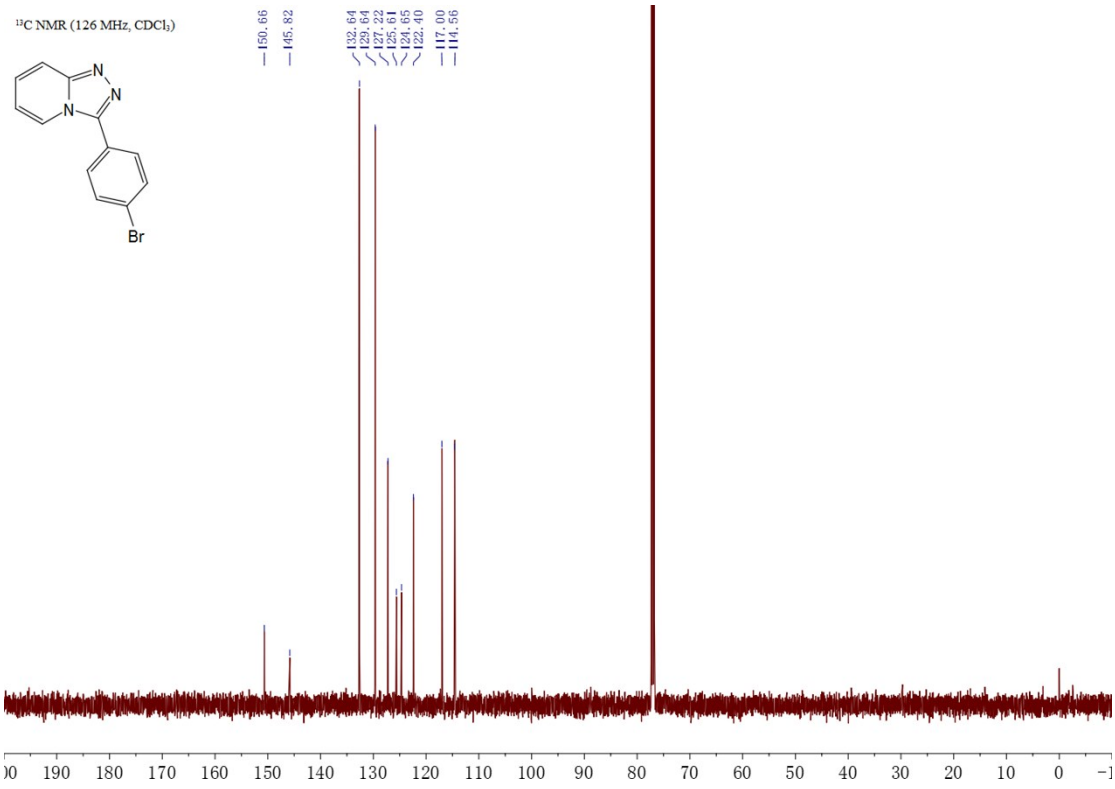


3-(4-chlorophenyl)-[1,2,4]triazolo[4,3-a]pyridine (7da)

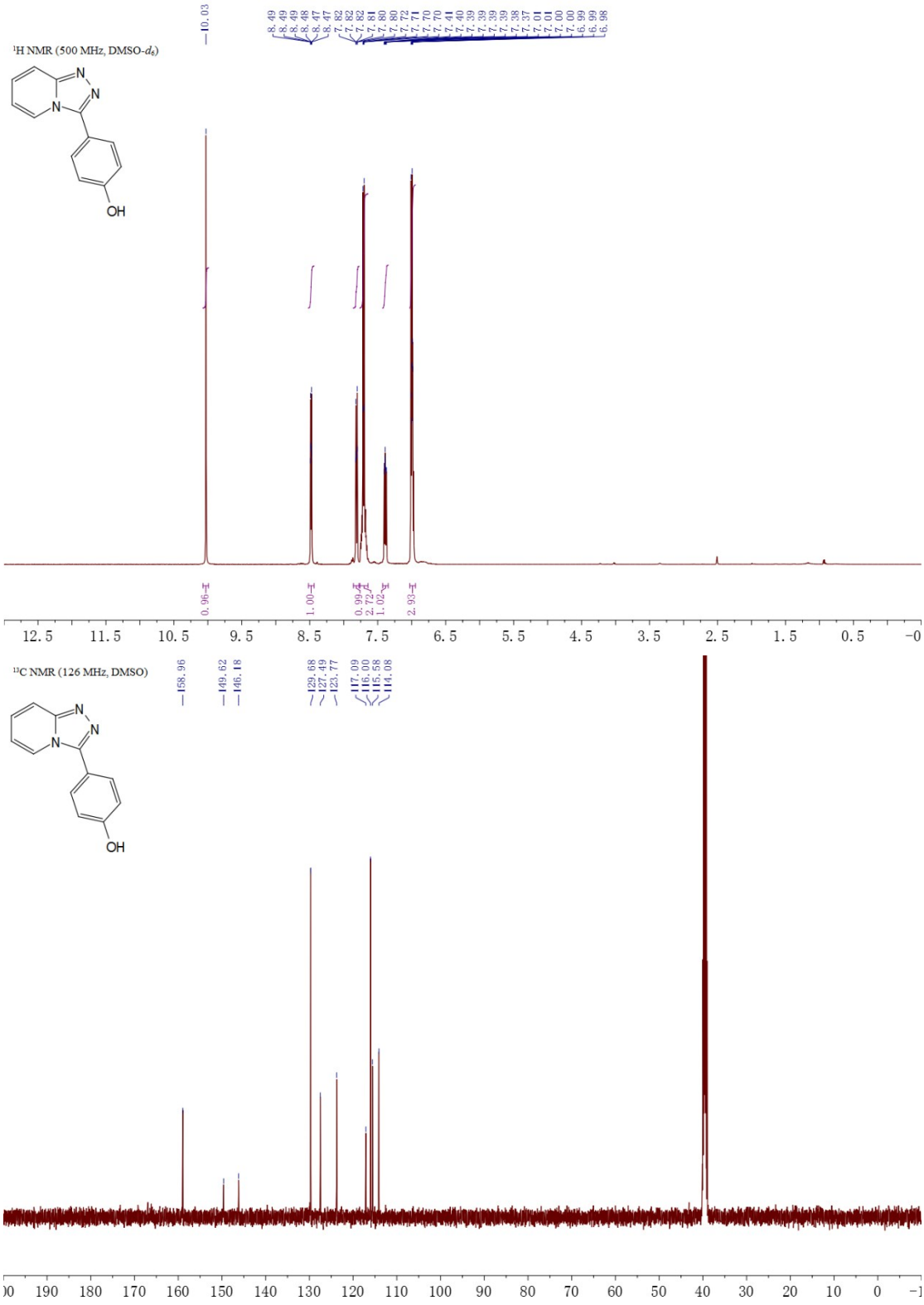


3-(4-bromophenyl)-[1,2,4]triazolo[4,3-a]pyridine (7db)

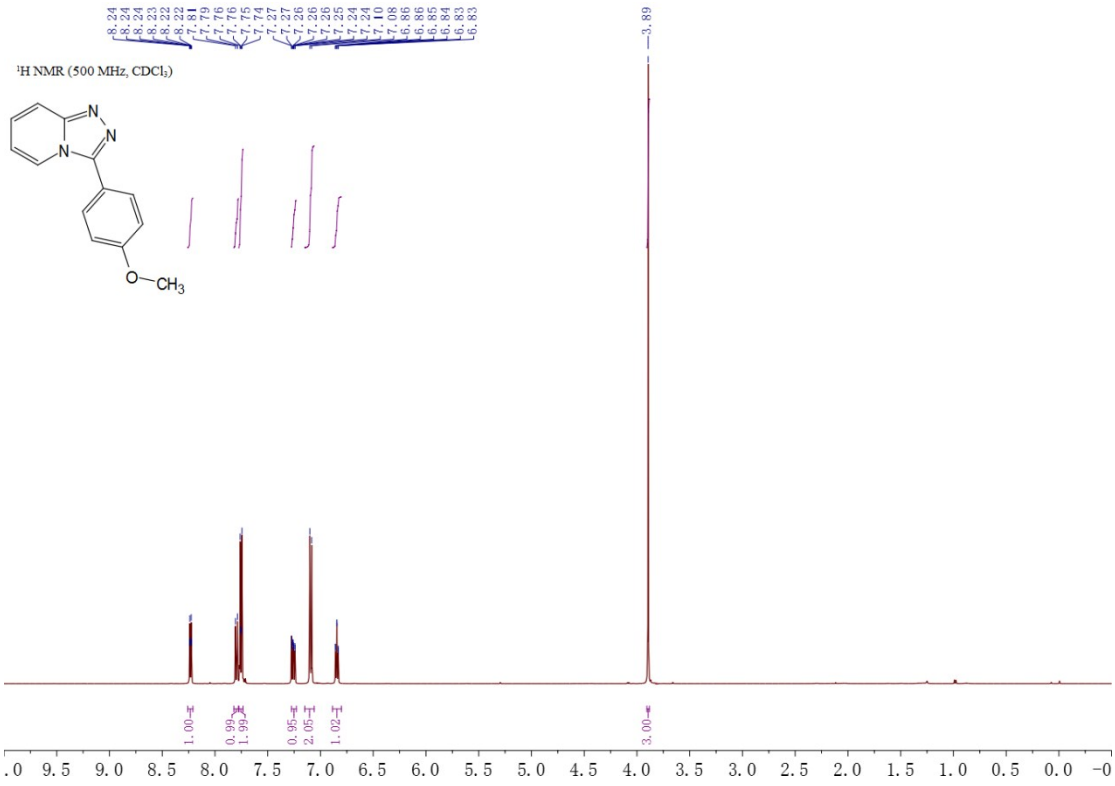


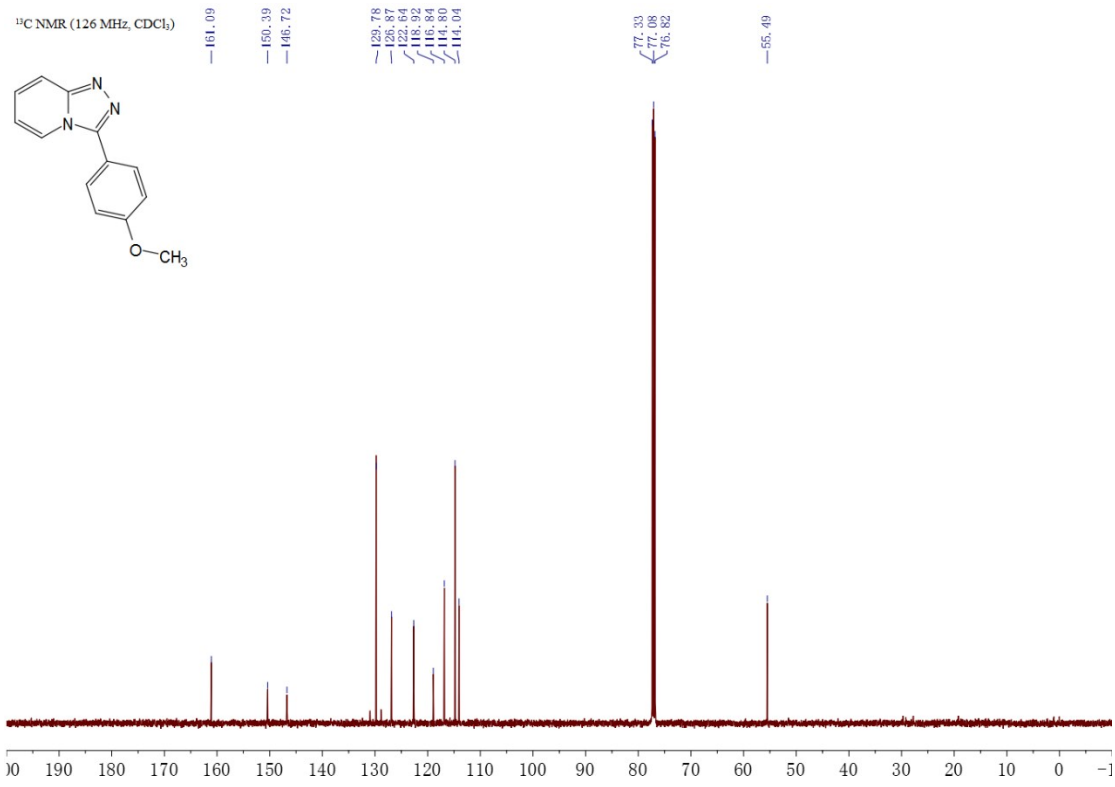


4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)phenol (7dc)

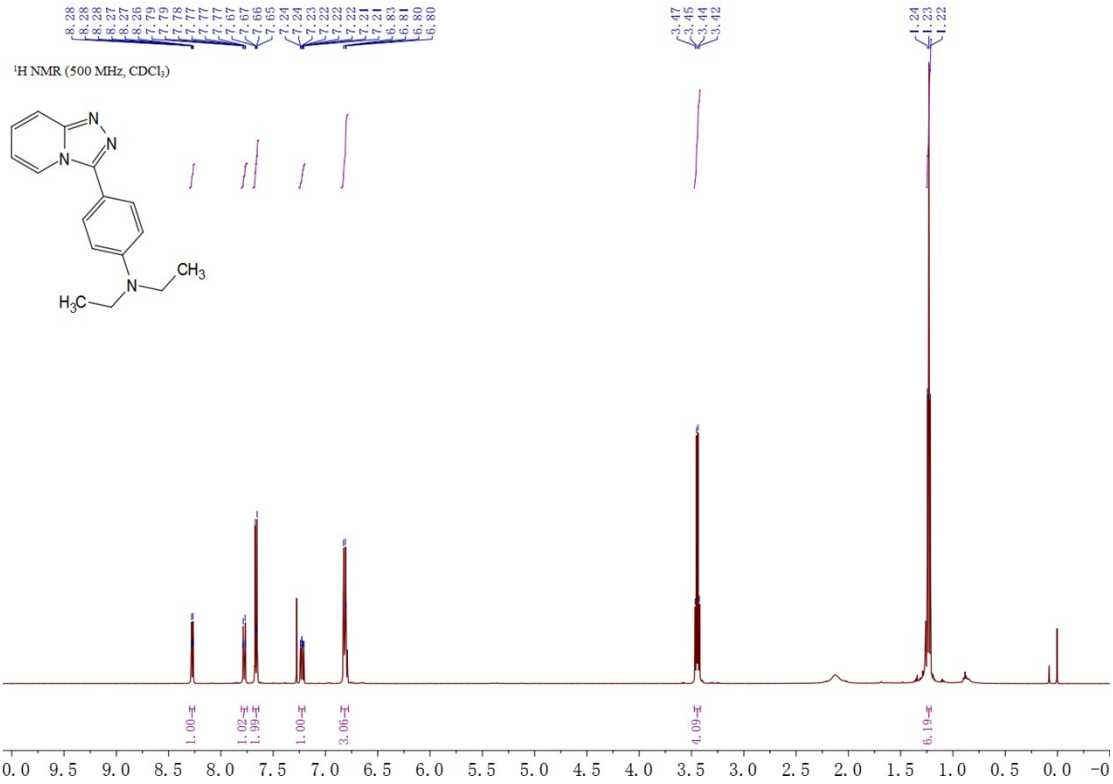


3-(4-methoxyphenyl)-[1,2,4]triazolo[4,3-a]pyridine (7dd)

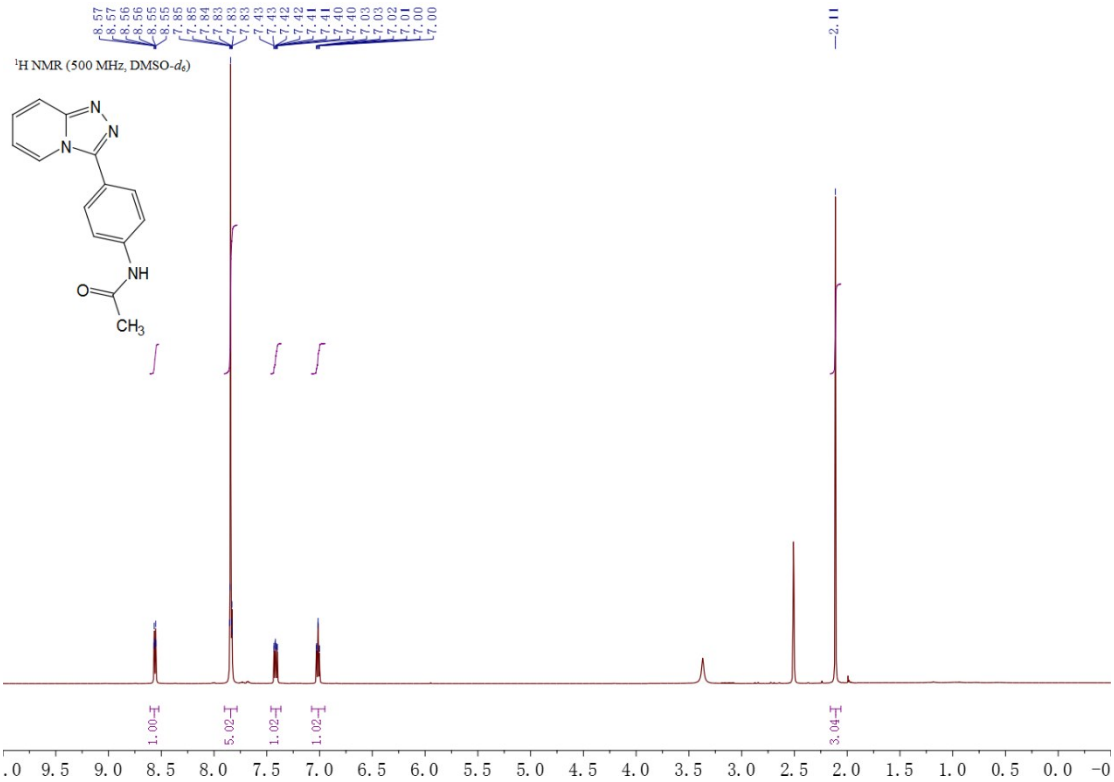


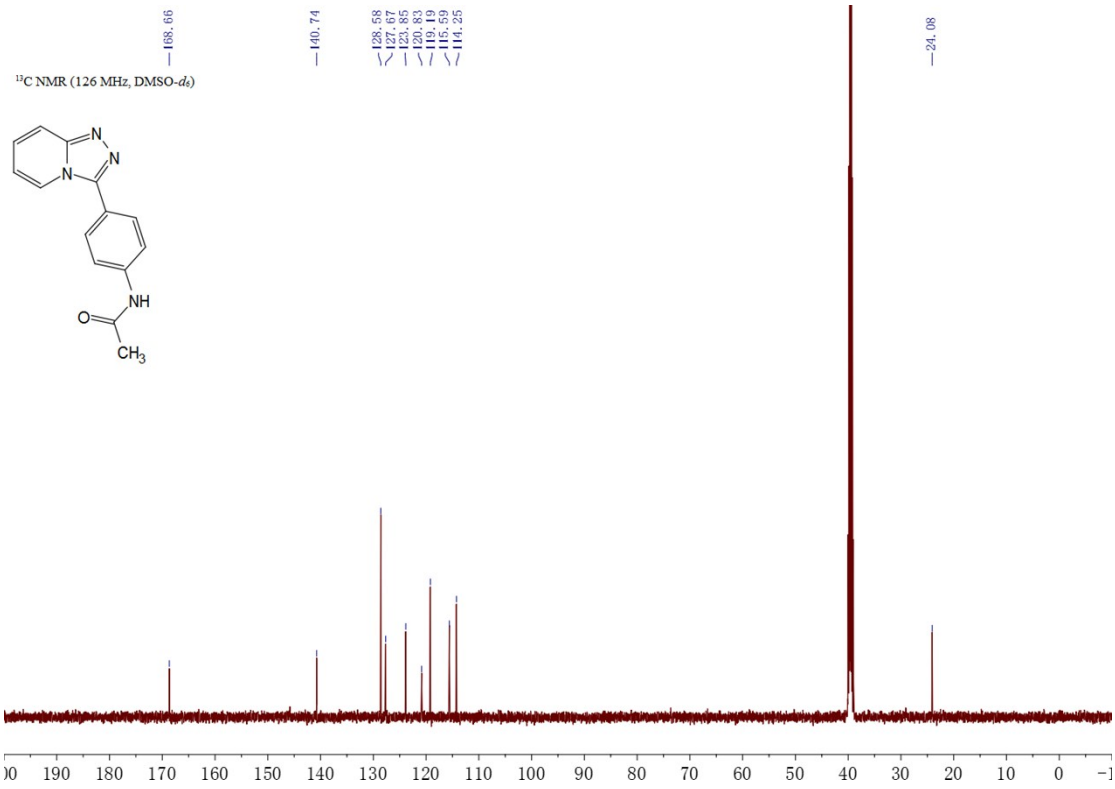


4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)-N,N-diethylaniline (7de)

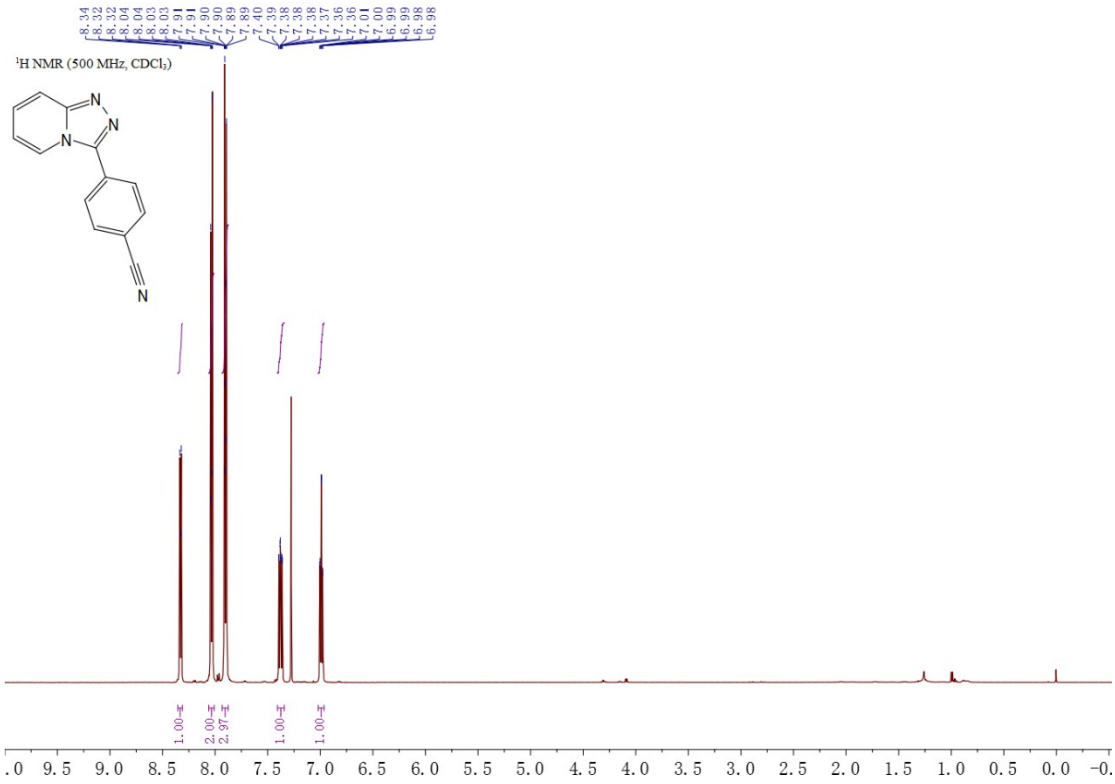


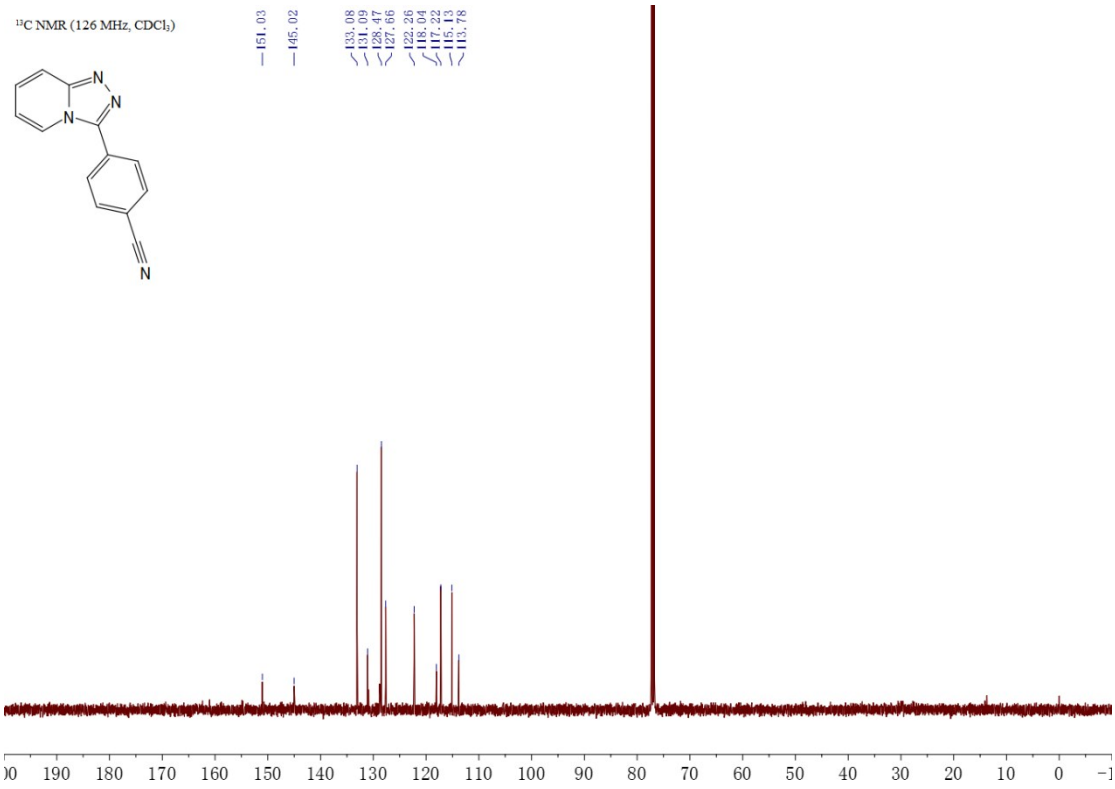
N-(4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)phenyl)acetamide (7df)



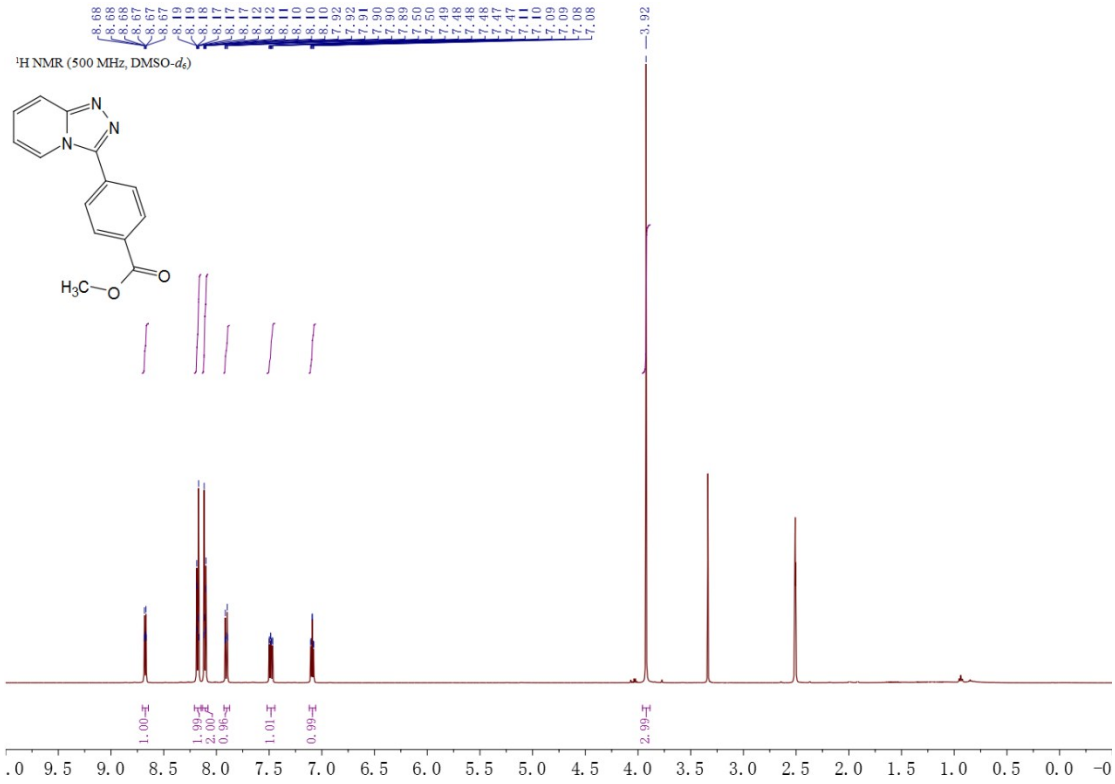


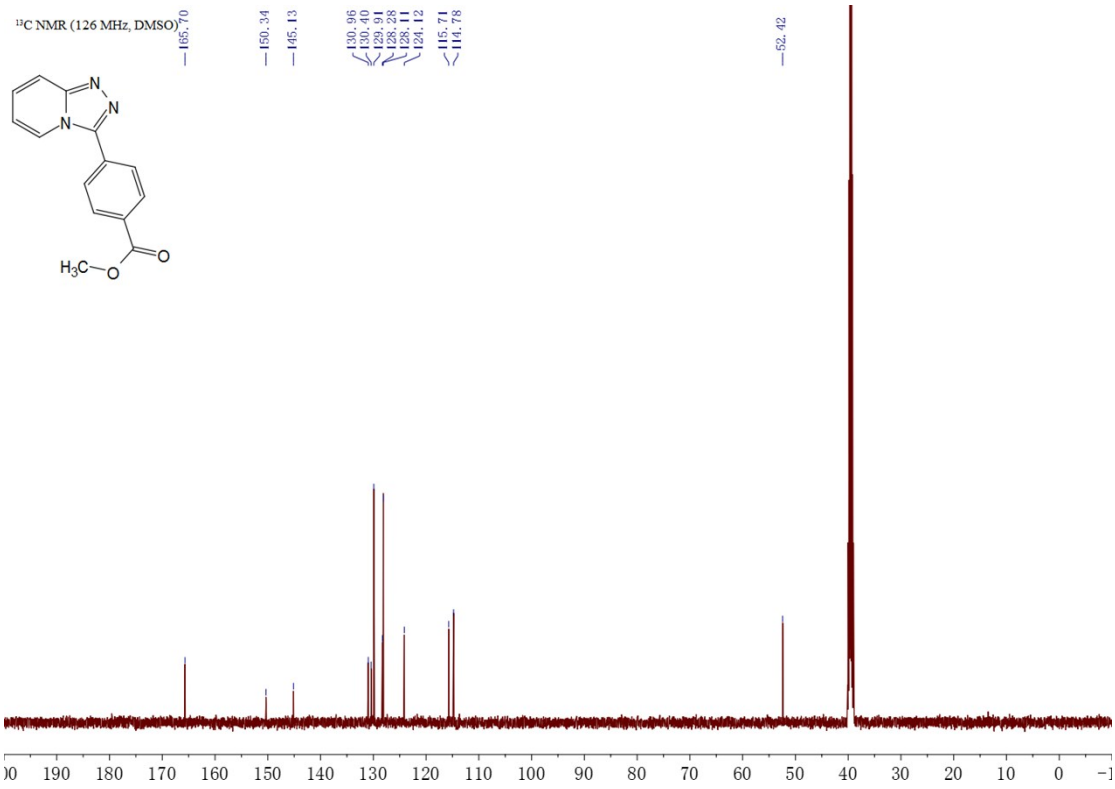
3-(4-cyanophenyl)-[1,2,4]triazolo[4,3-a]pyridine (7dg)



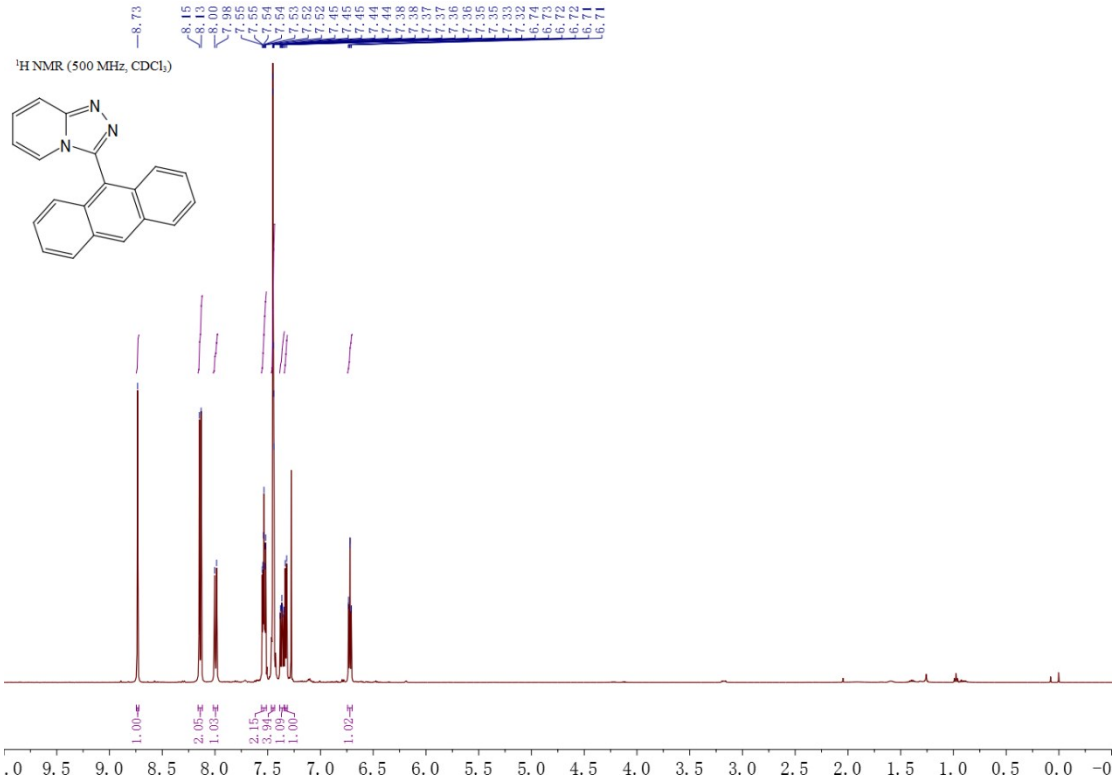


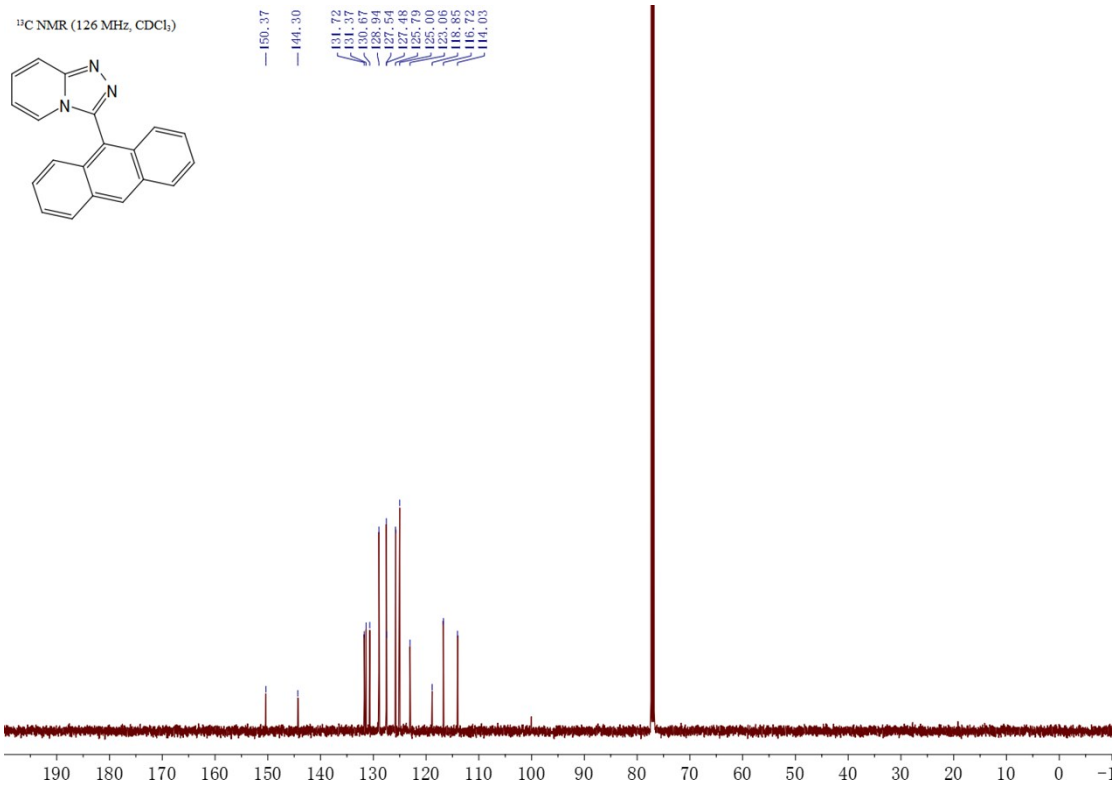
Methyl 4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)benzoate (7dh)



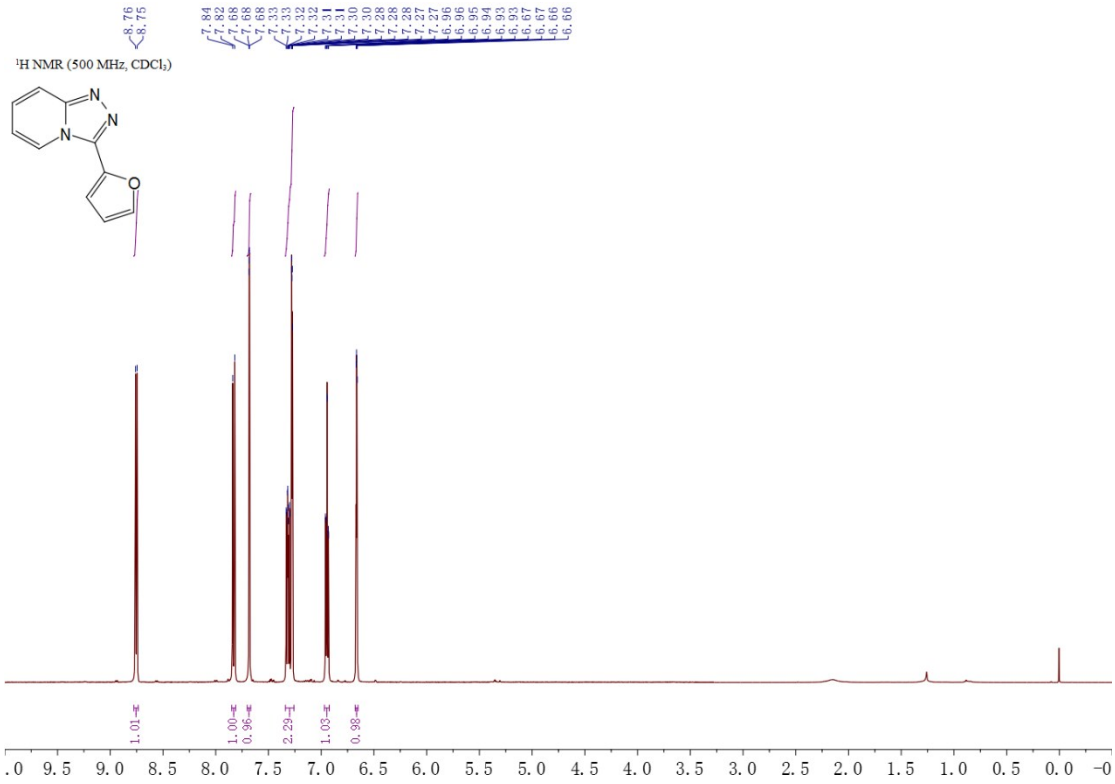


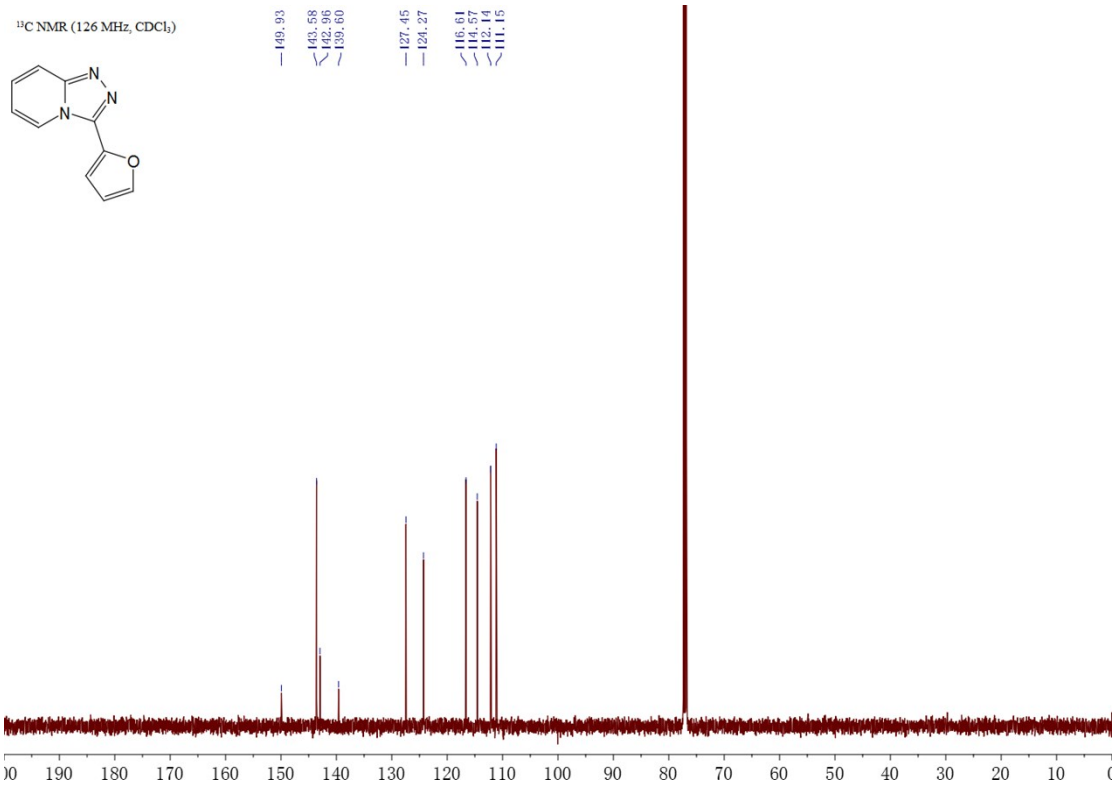
3-(anthracen-9-yl)-[1,2,4]triazolo[4,3-a]pyridine (7e)



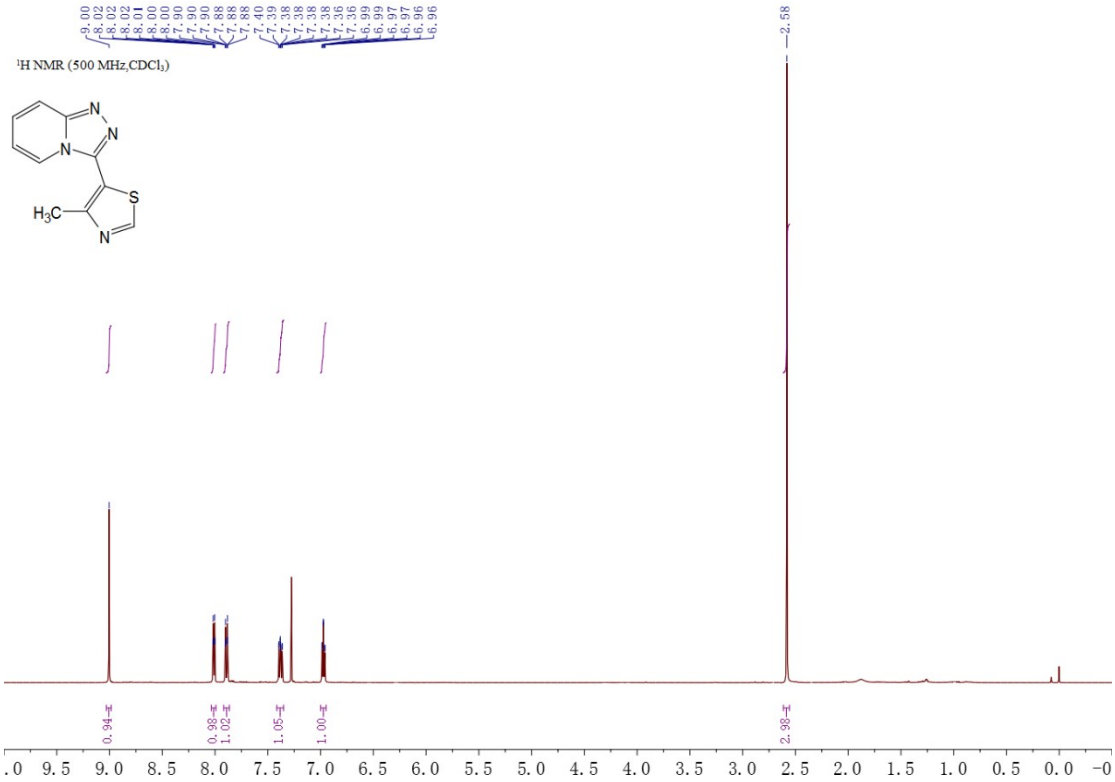


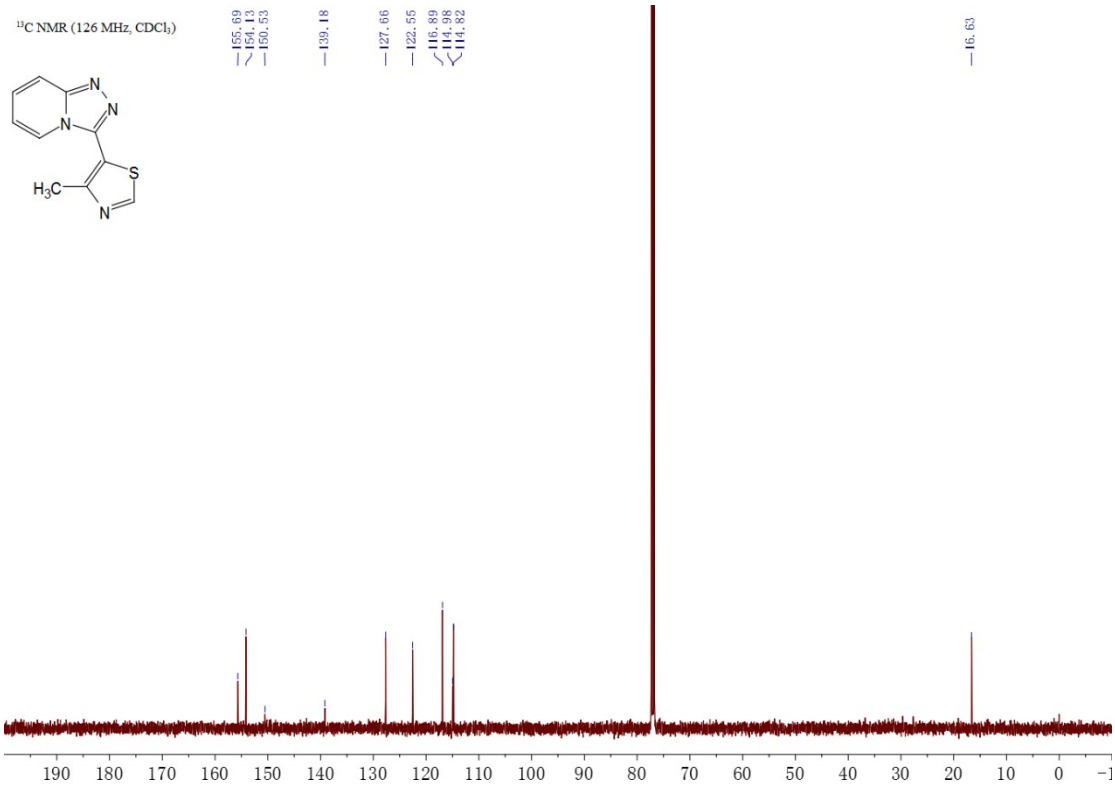
3-(furan-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (7f)



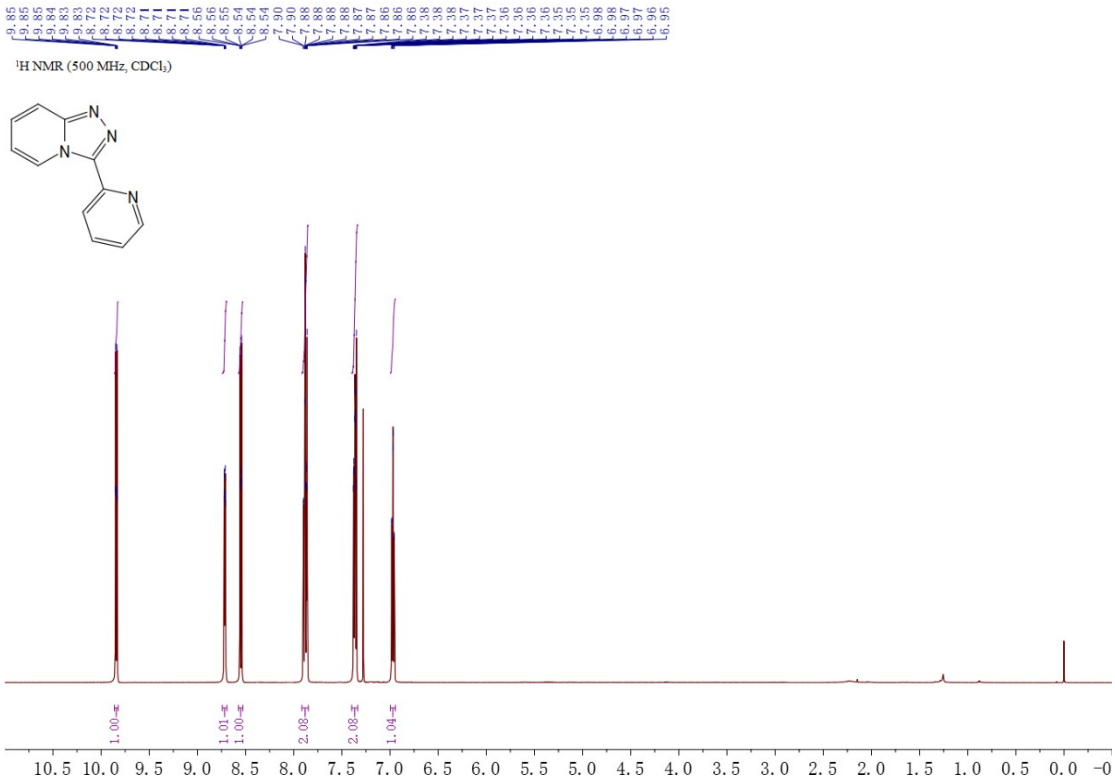


5-([1,2,4]triazolo[4,3-a]pyridin-3-yl)-4-methylthiazole (7g)

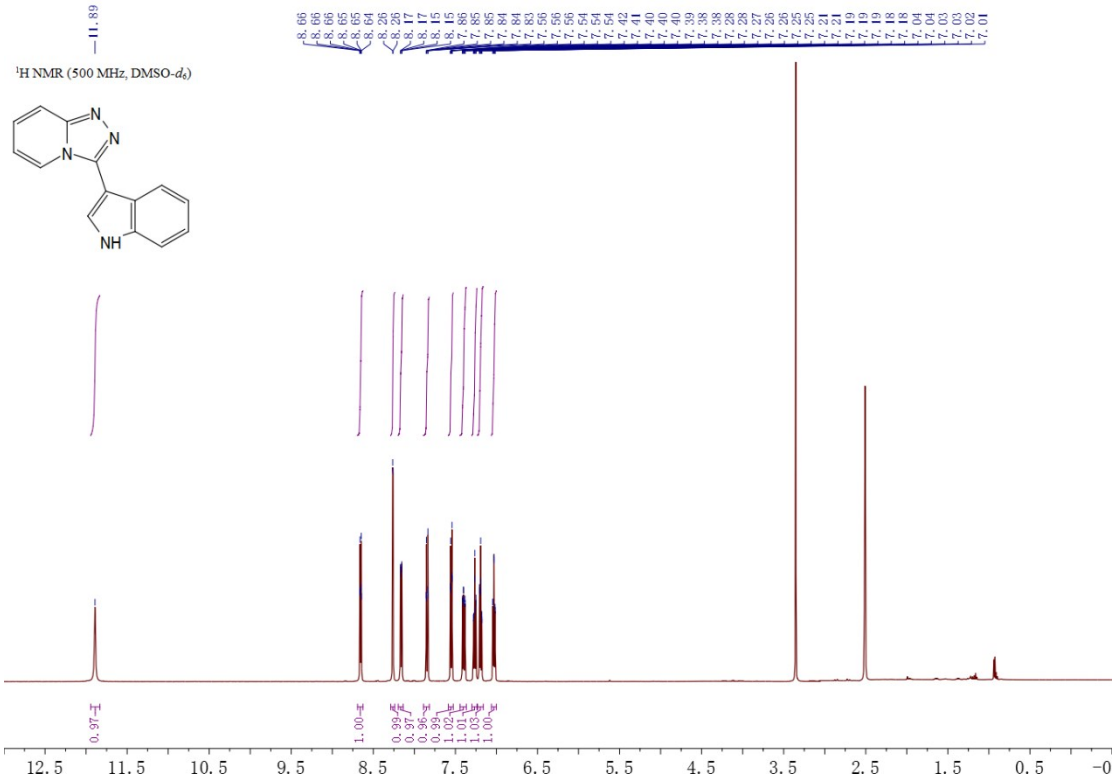


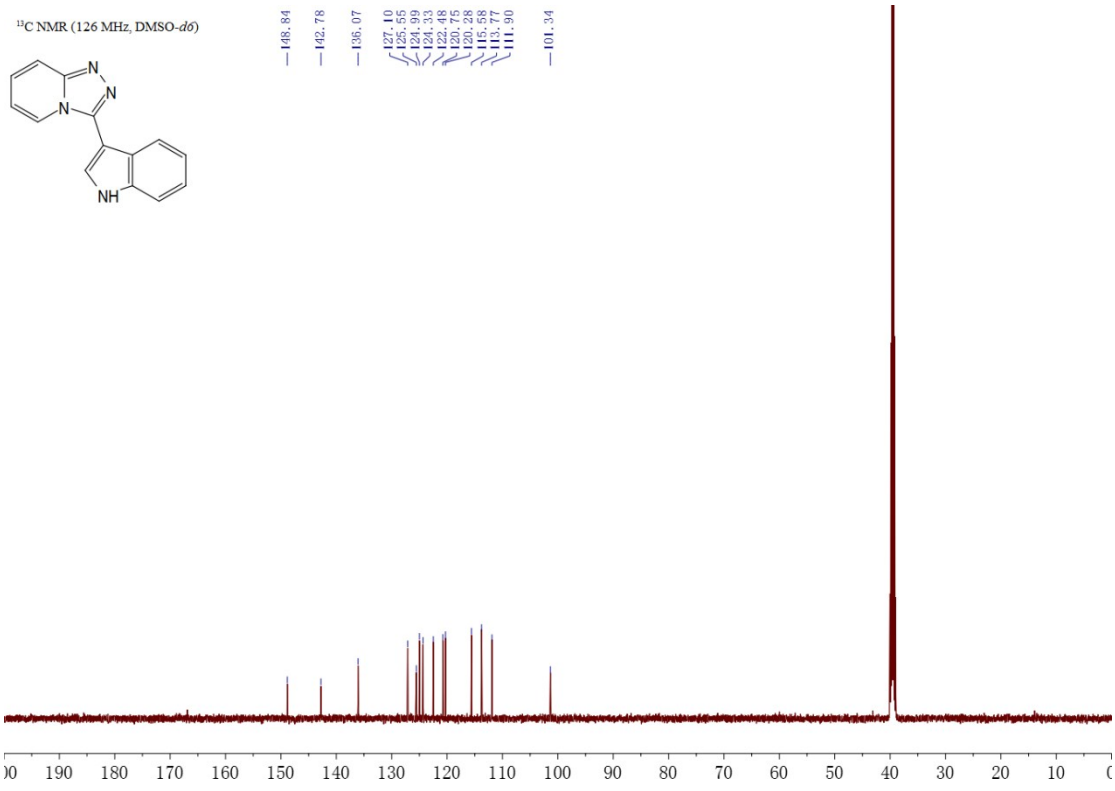


3-(pyridin-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (7h)

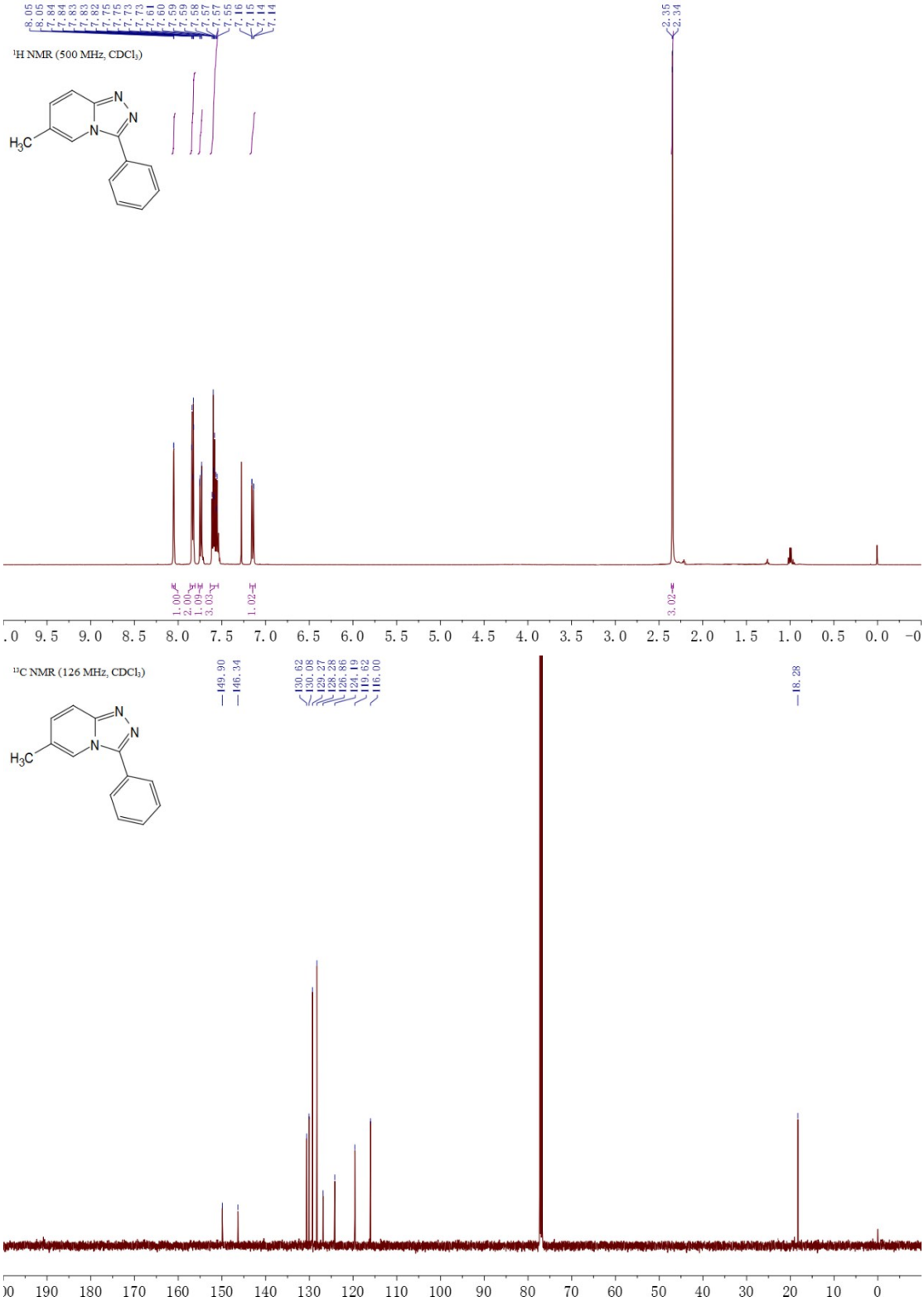


3-(1H-indol-3-yl)-[1,2,4]triazolo[4,3-a]pyridine (7i)

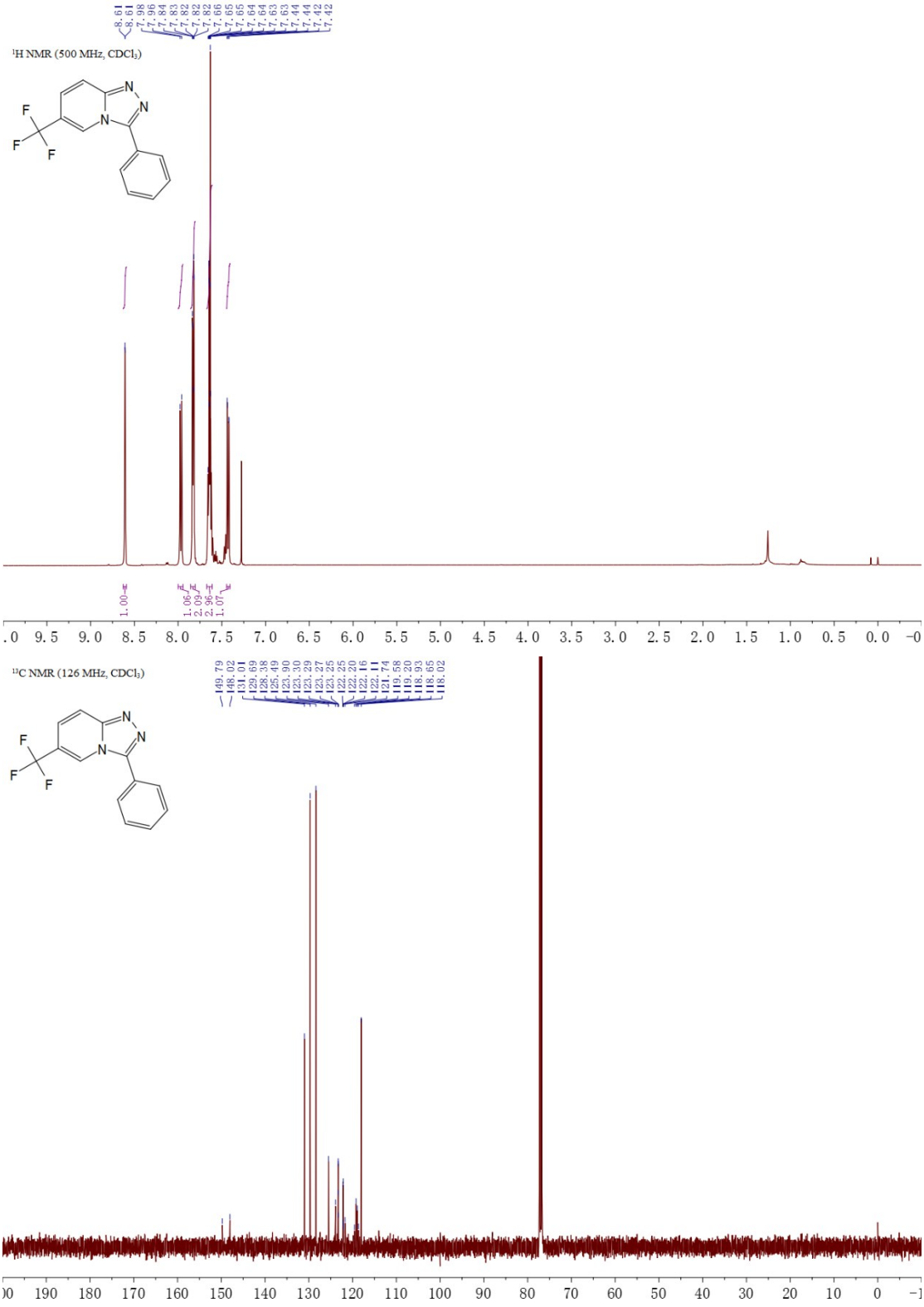




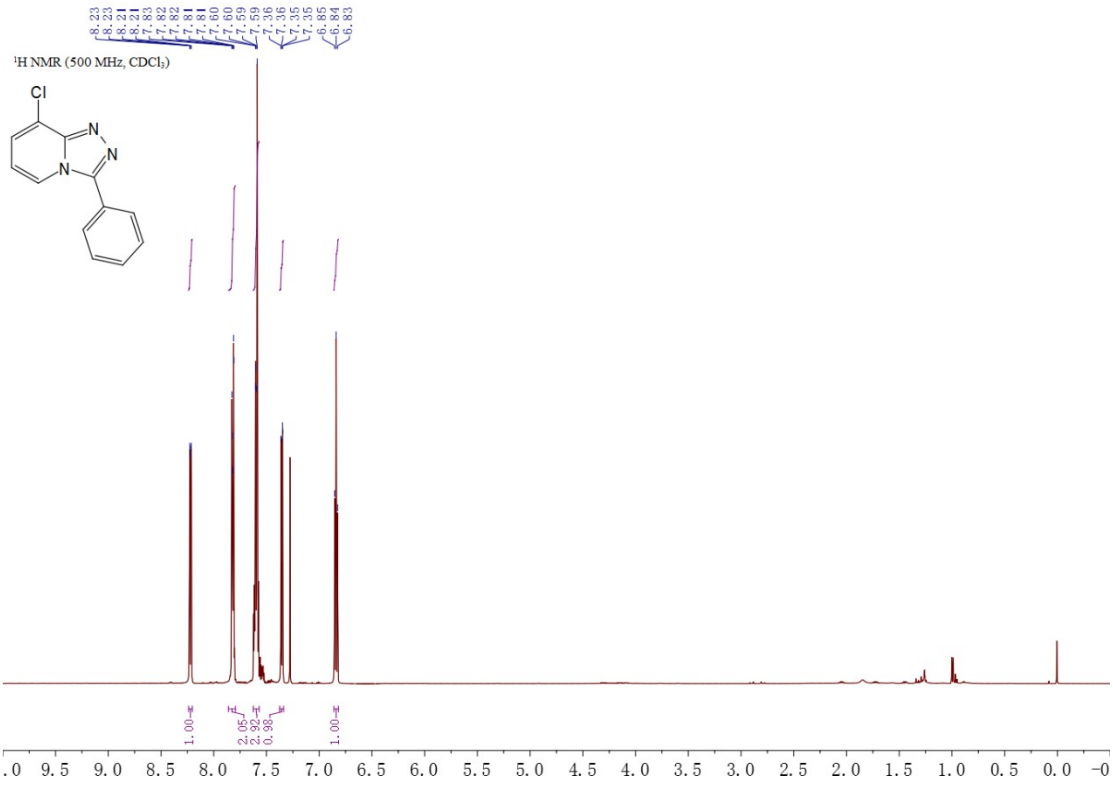
6-methyl-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (7j)

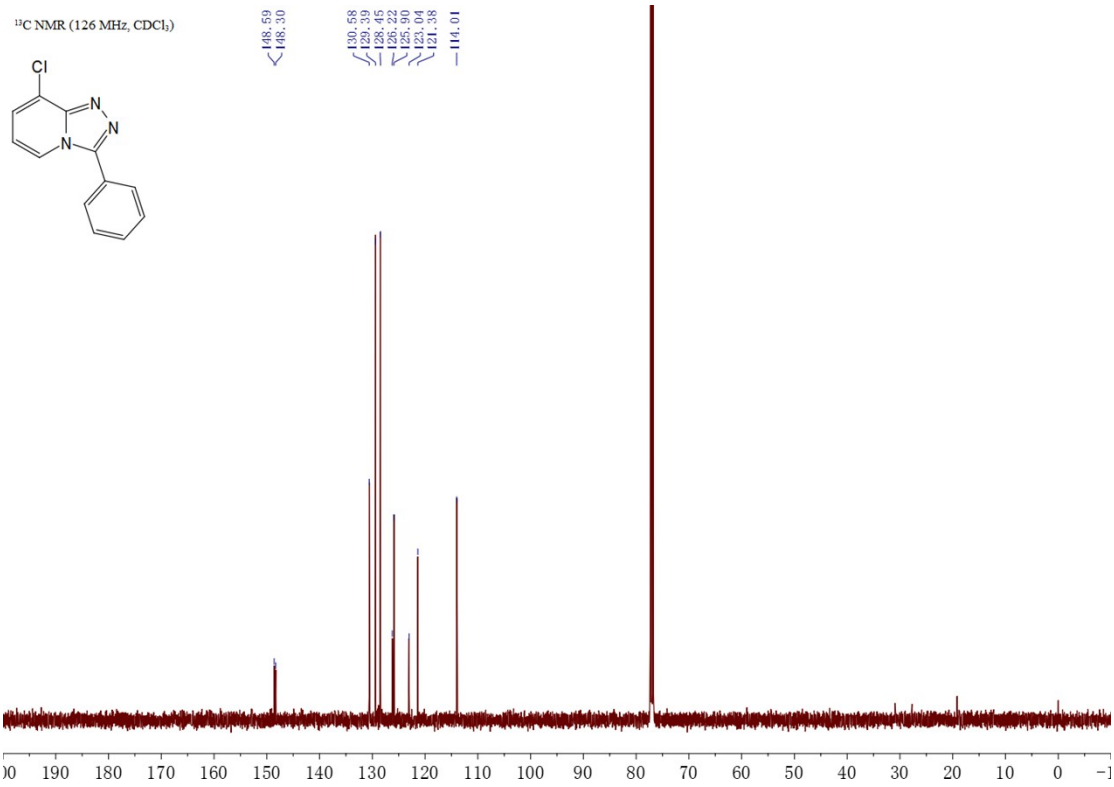


3-phenyl-6-(trifluoromethyl)-[1,2,4]triazolo[4,3-a]pyridine (7k)

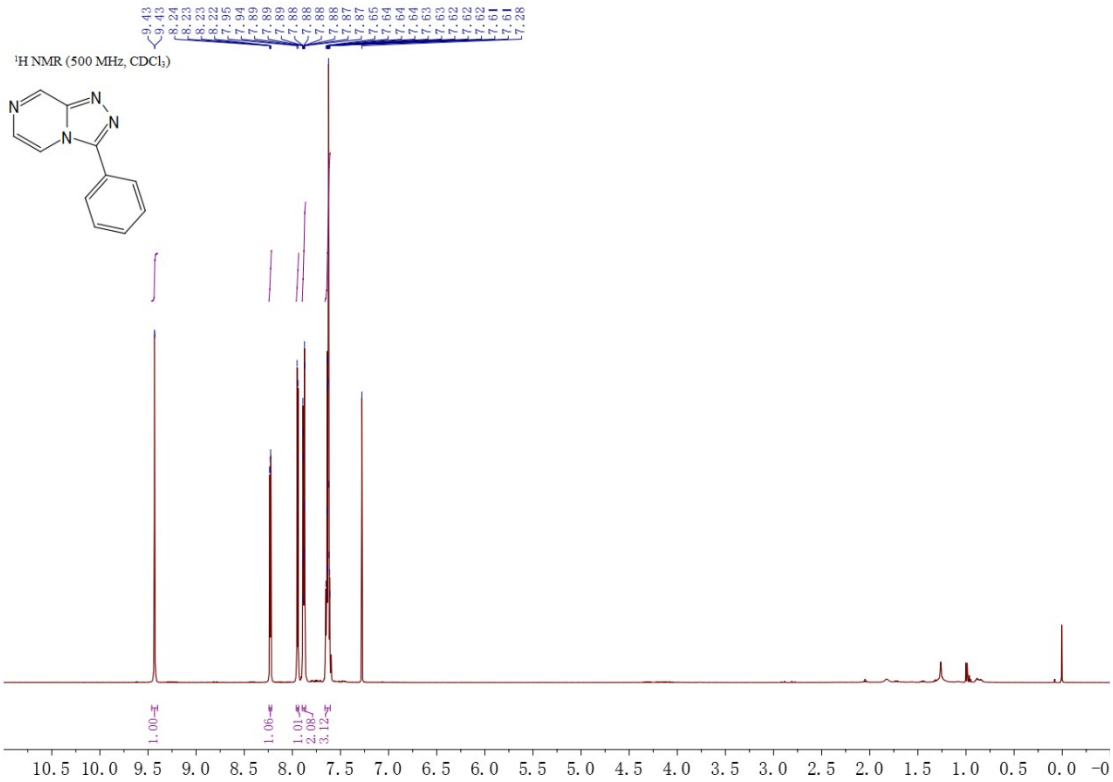


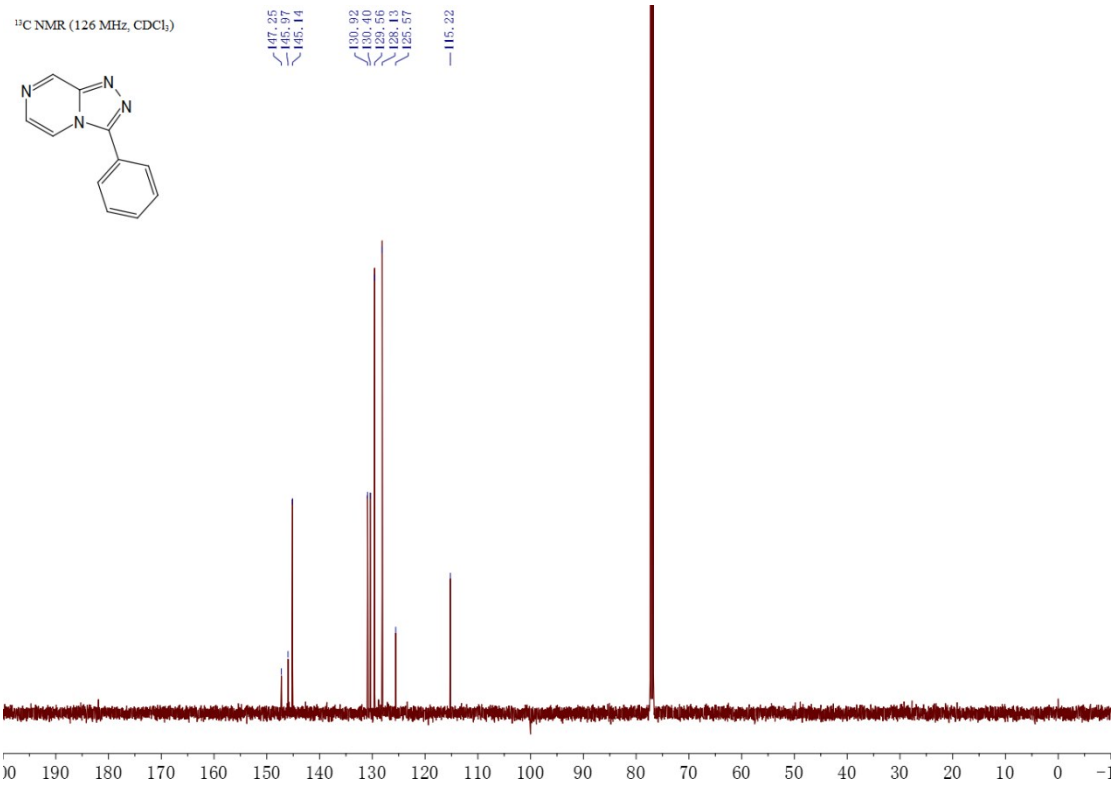
8-chloro-3-phenyl-[1,2,4]triazolo[4,3-a]pyridine (7l)



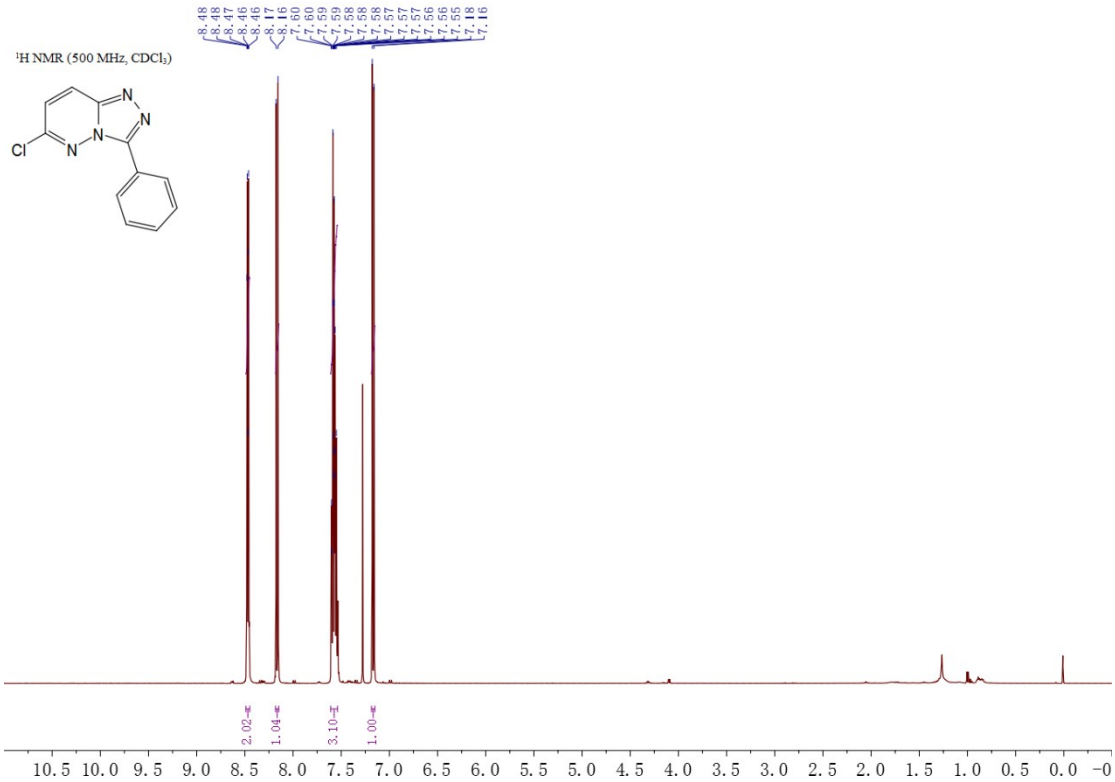


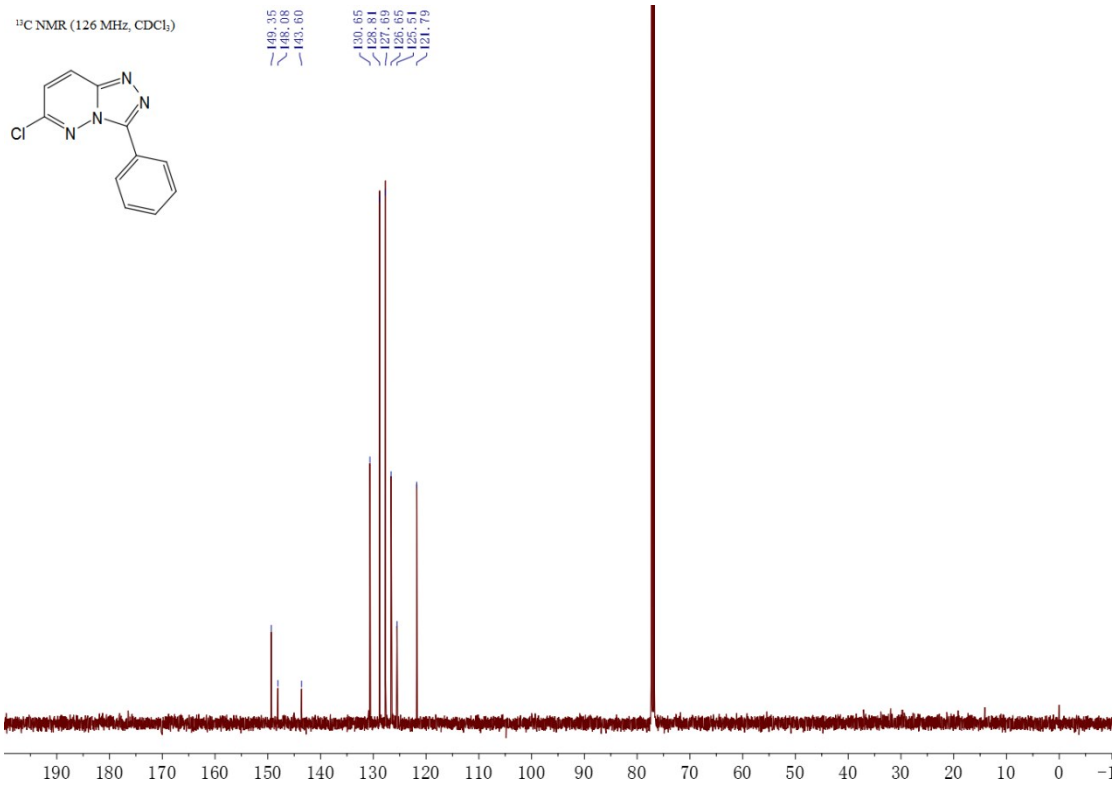
3-phenyl-[1,2,4]triazolo[4,3-a]pyrazine (7m)



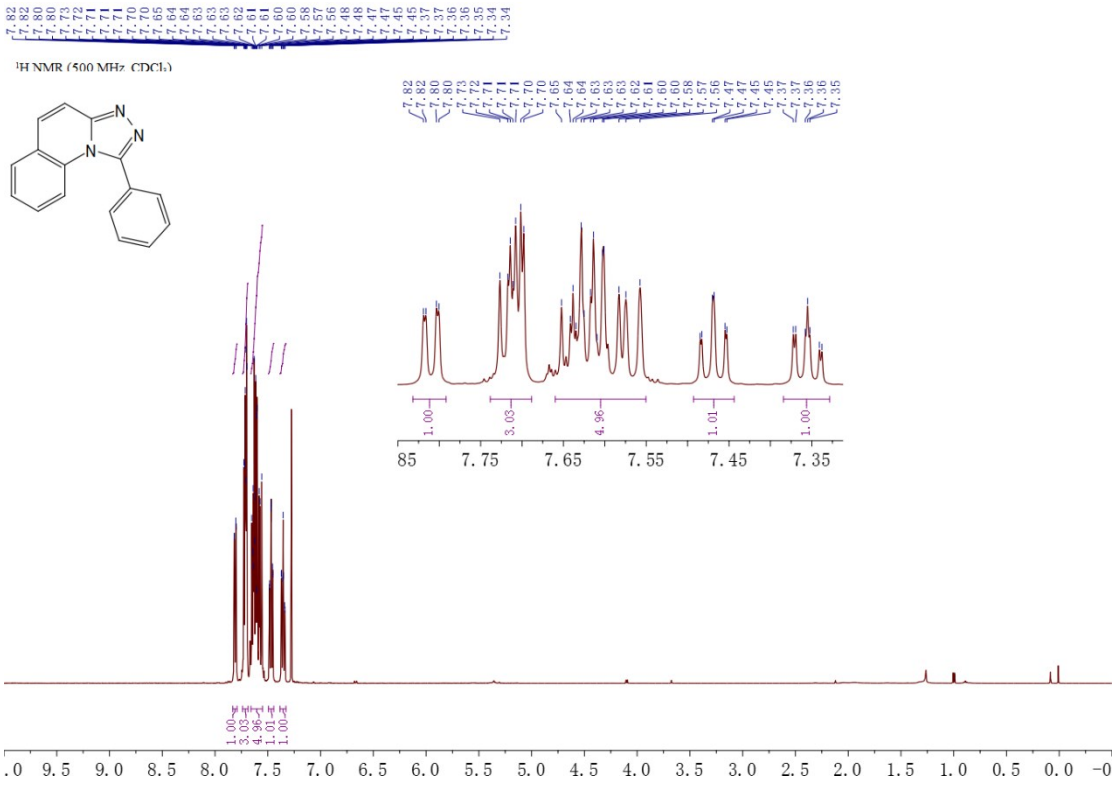


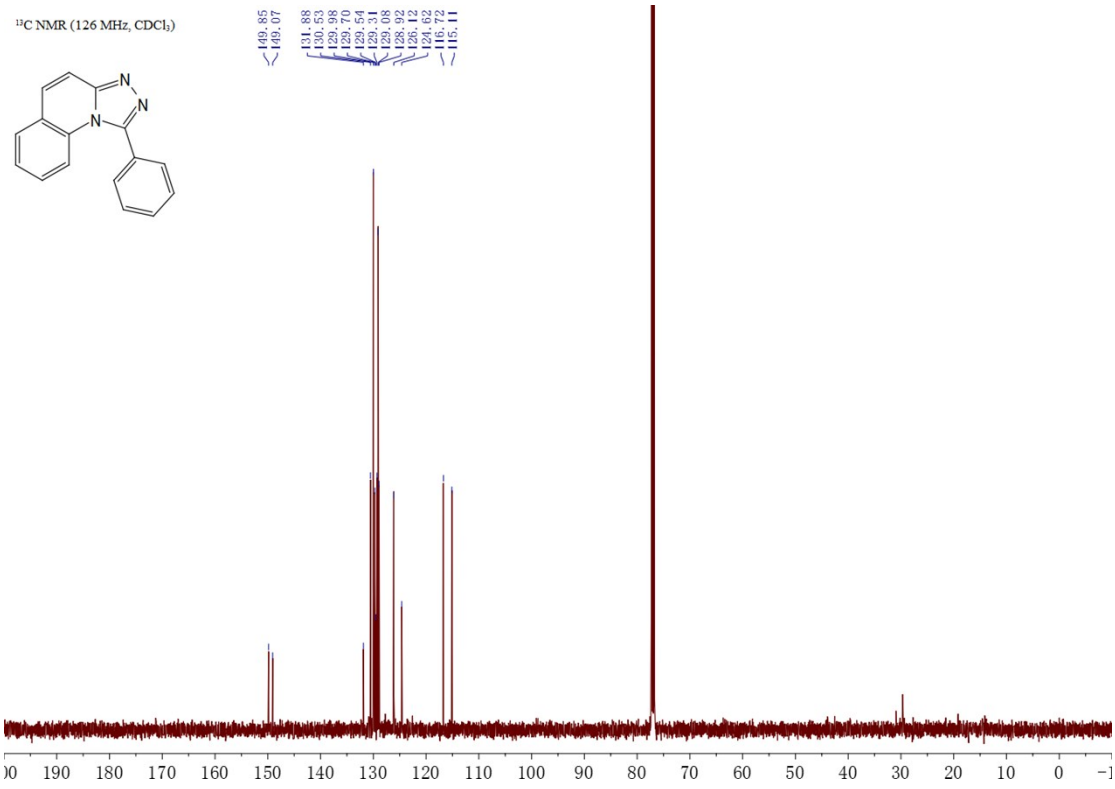
6-chloro-3-phenyl-[1,2,4]triazolo[4,3-b]pyridazine (7n)



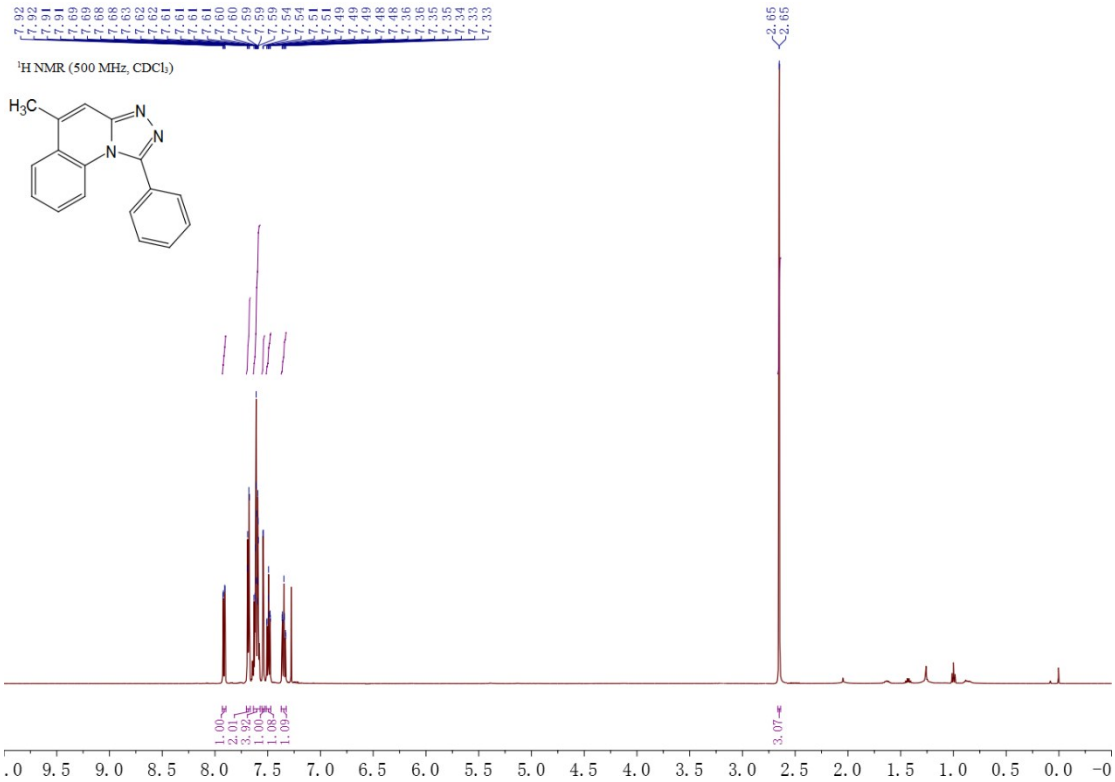


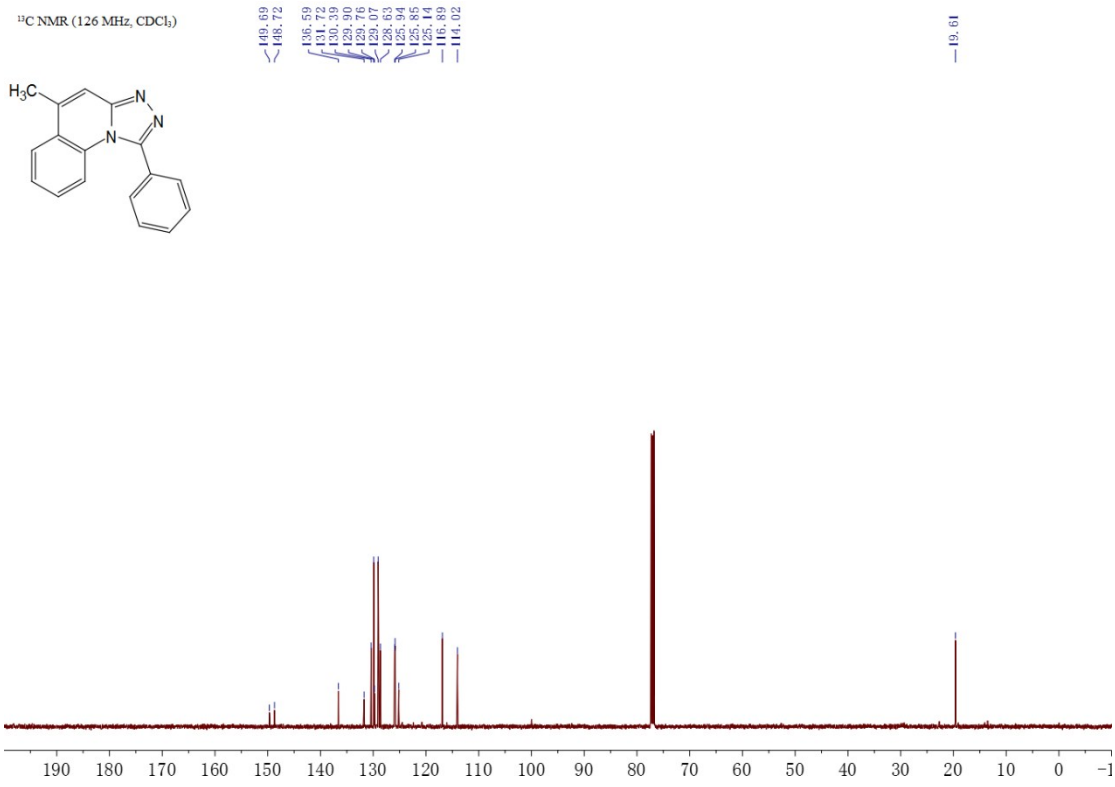
1-phenyl-[1,2,4]triazolo[4,3-a]quinoline (7o)



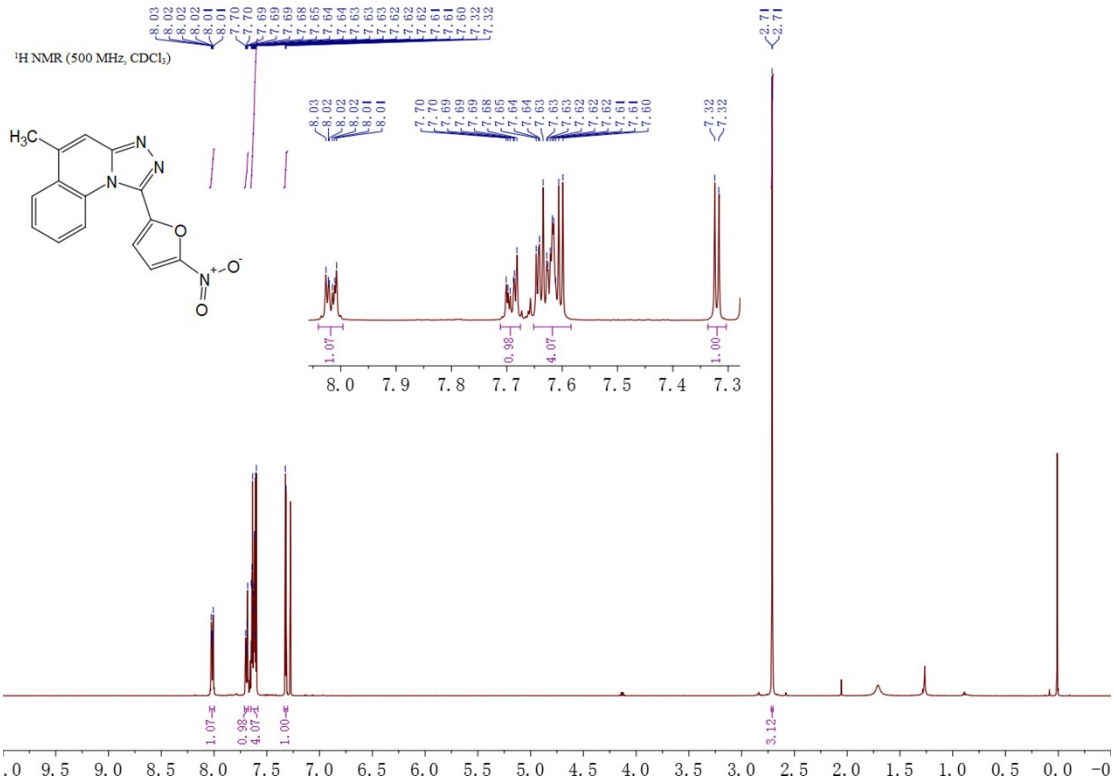


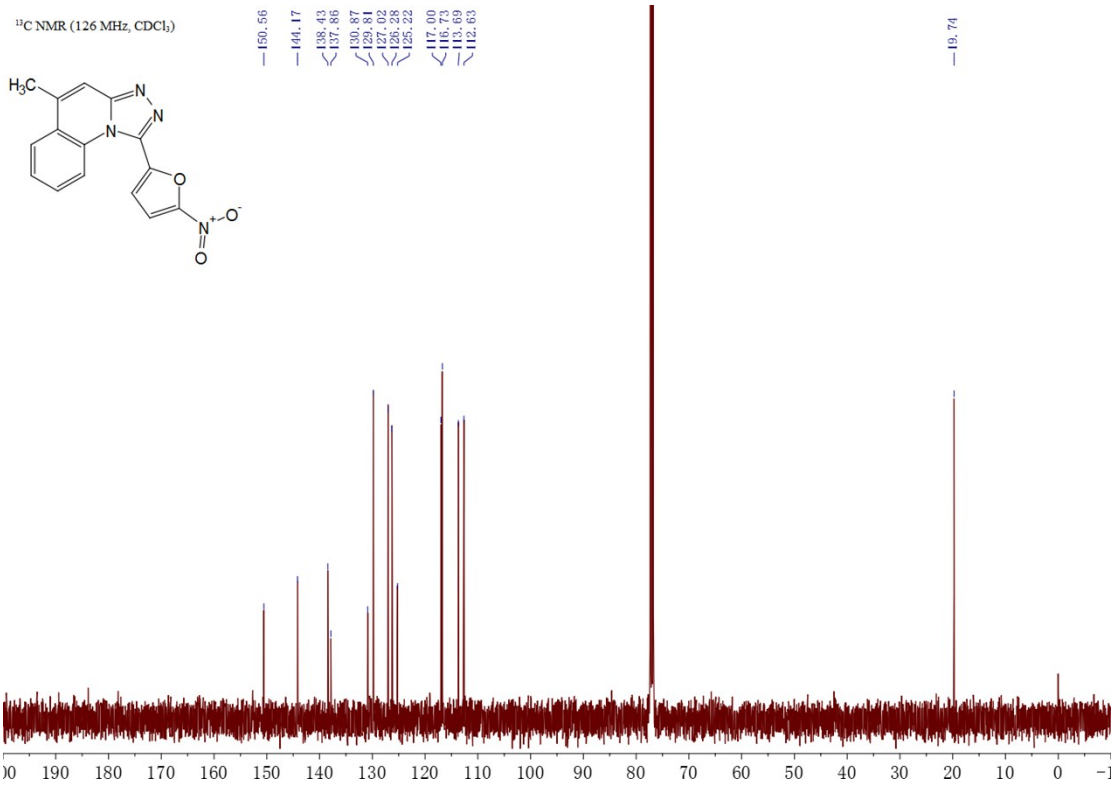
5-methyl-1-phenyl-[1,2,4]triazolo[4,3-a]quinoline (7p)



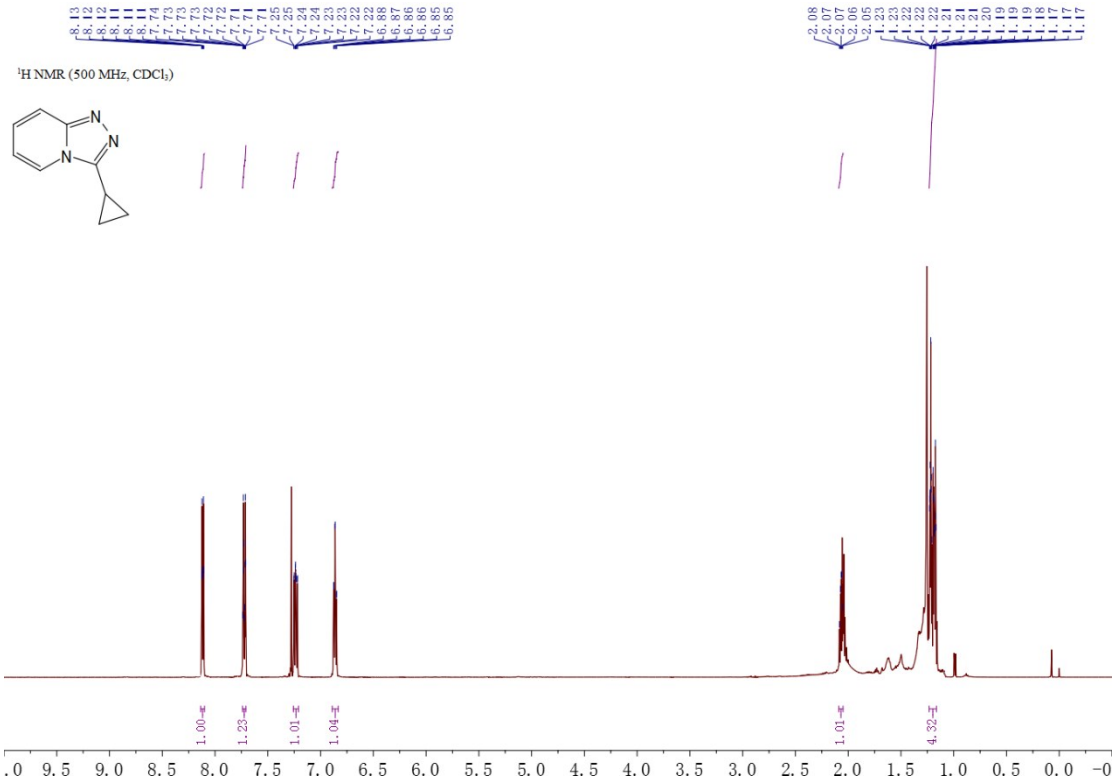


5-methyl-1-(5-nitrofuran-2-yl)-[1,2,4]triazolo[4,3-a]quinoline (7q)

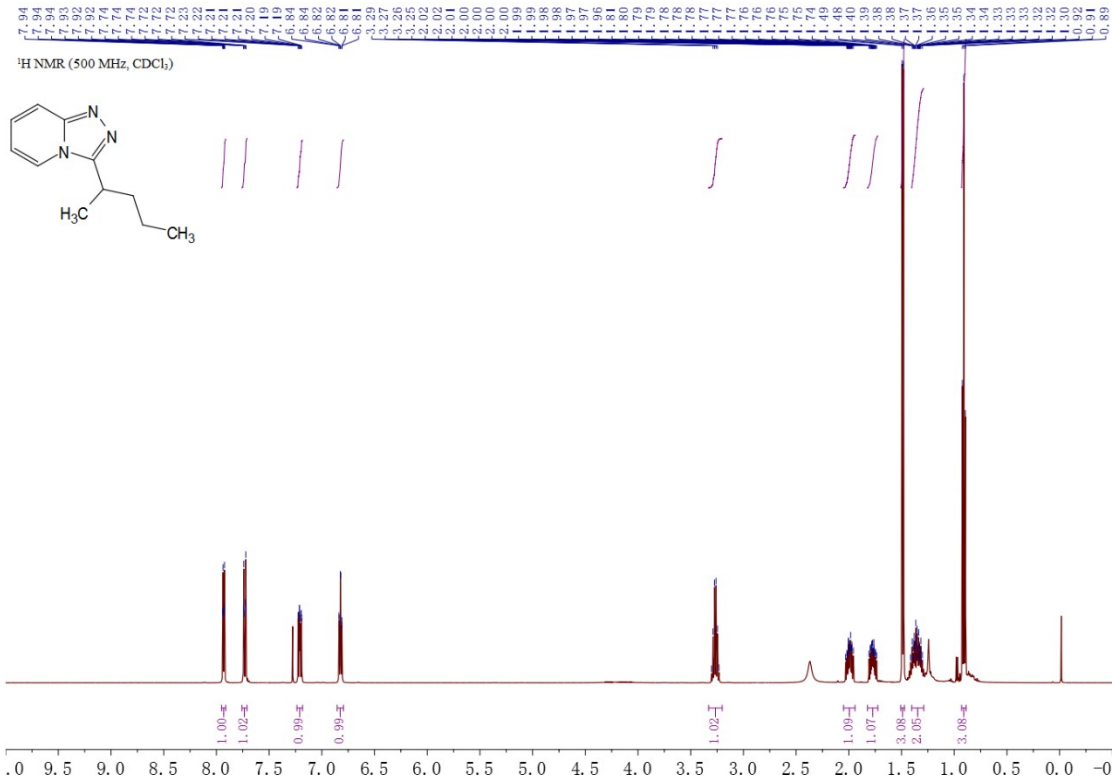


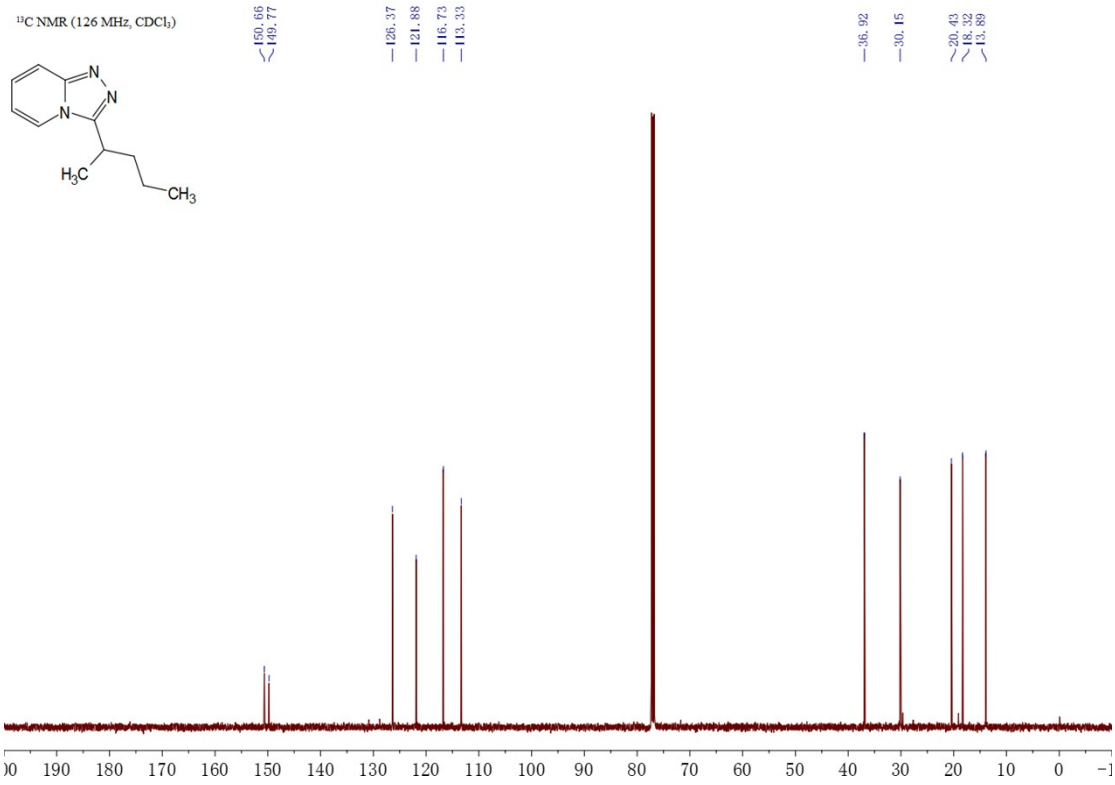


3-cyclopropyl-[1,2,4]triazolo[4,3-a]pyridine (8a)

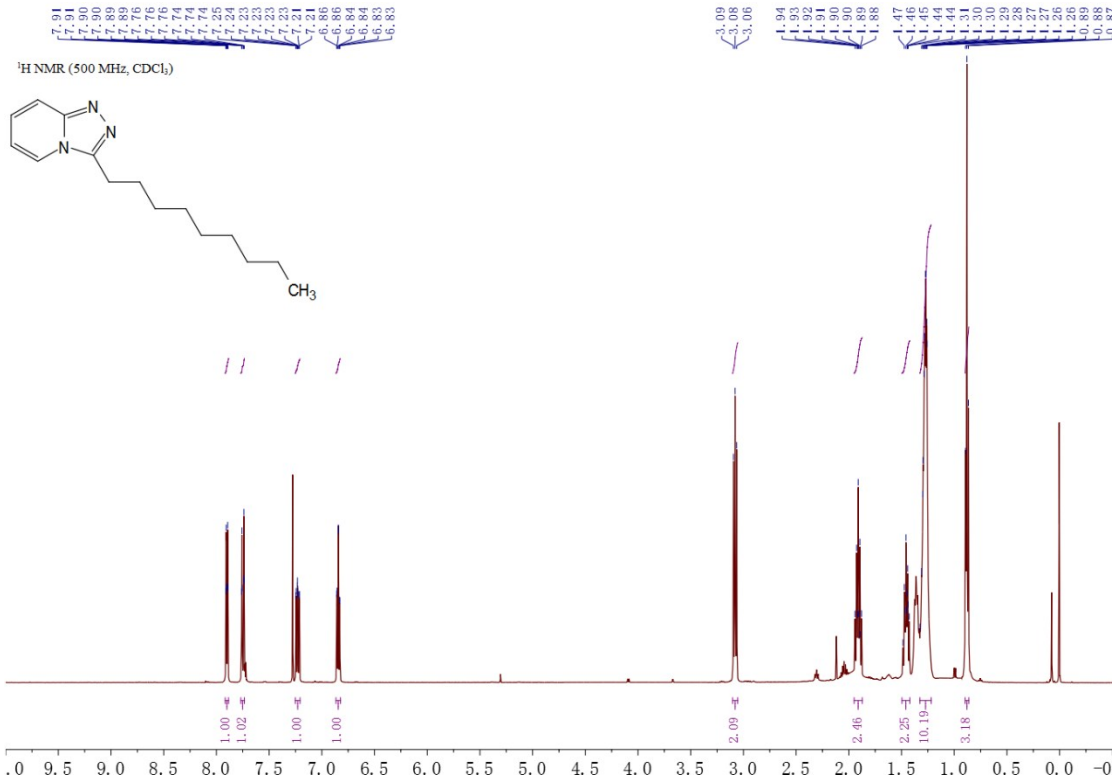


3-(pentan-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (8b)

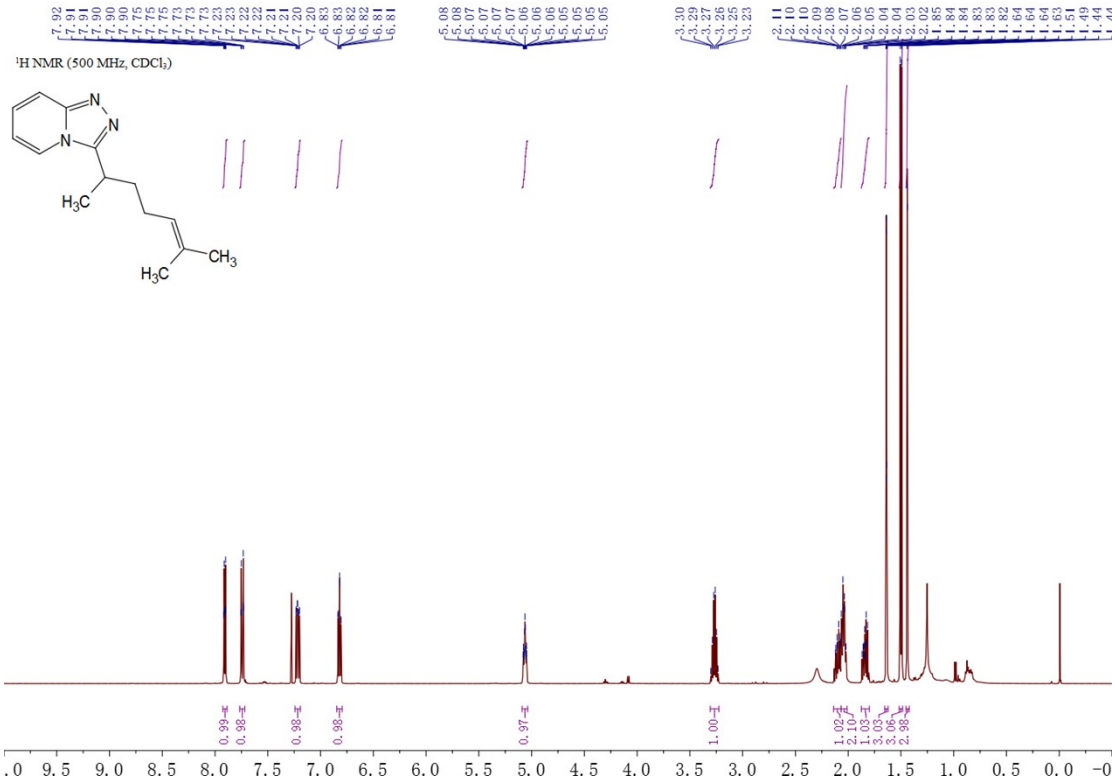


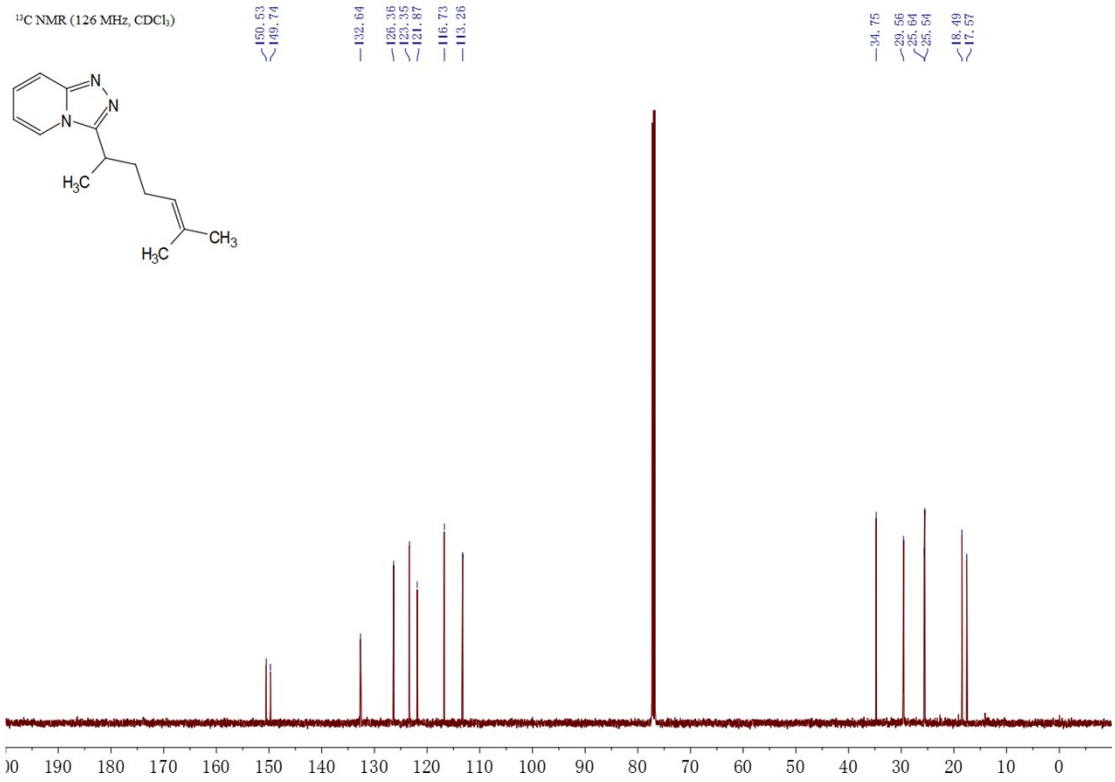


3-nonyl-[1,2,4]triazolo[4,3-a]pyridine (8c)

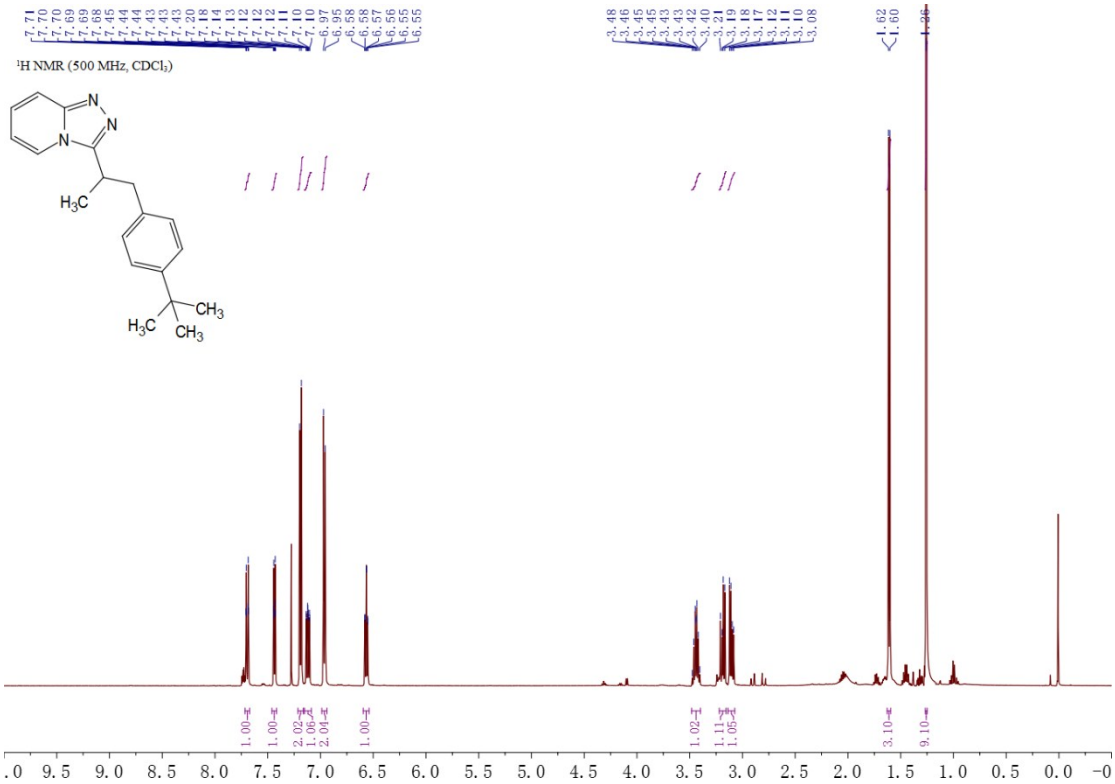


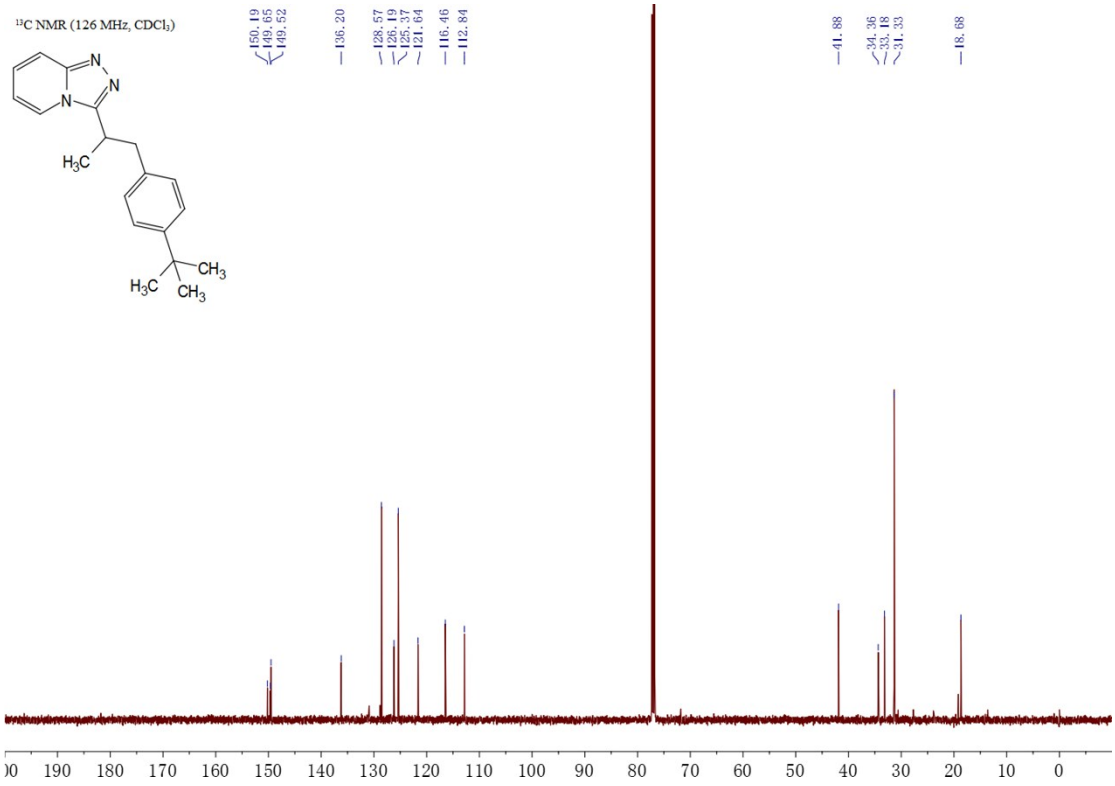
3-(6-methylhept-5-en-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (8d)



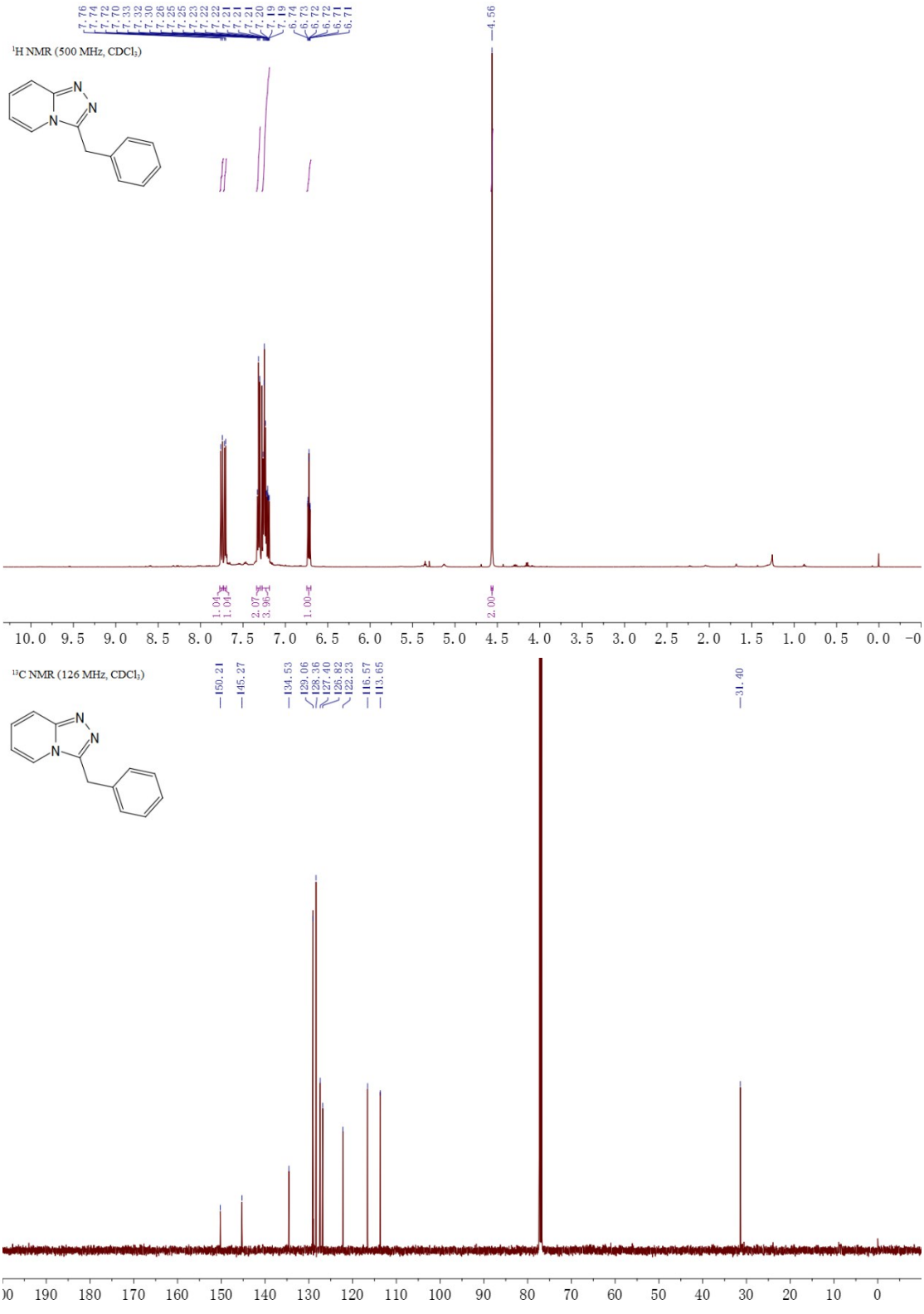


3-(1-(4-(tert-butyl)phenyl)propan-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (8e)

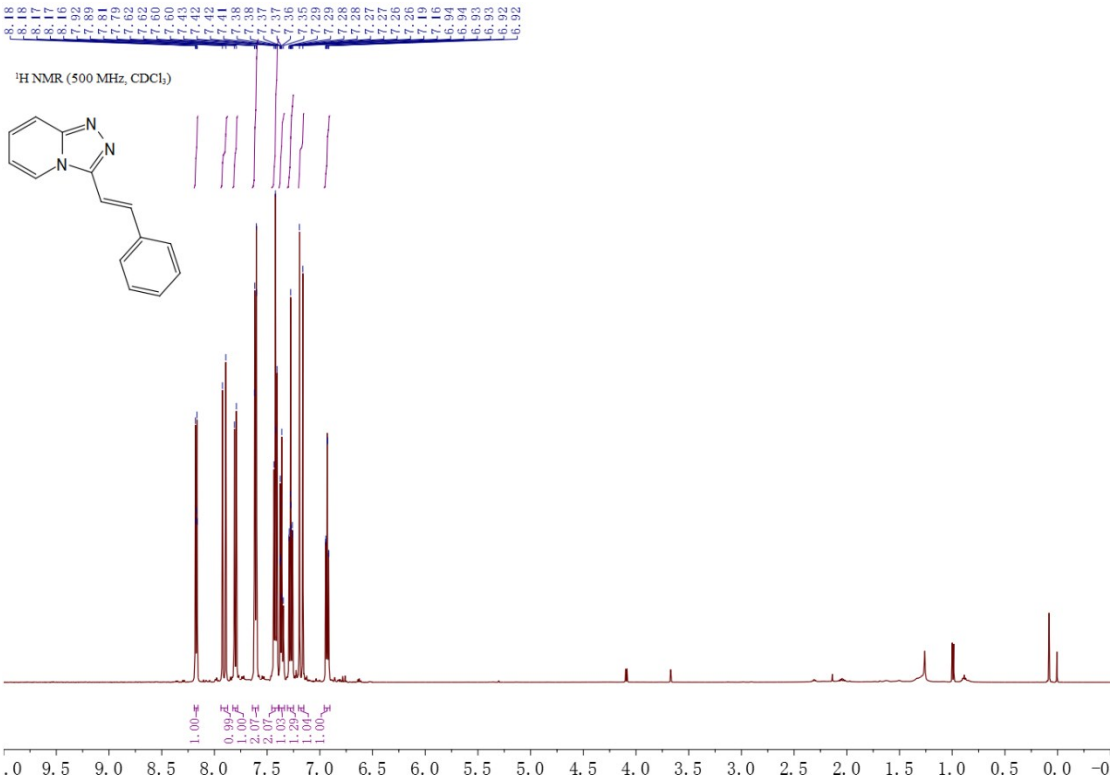




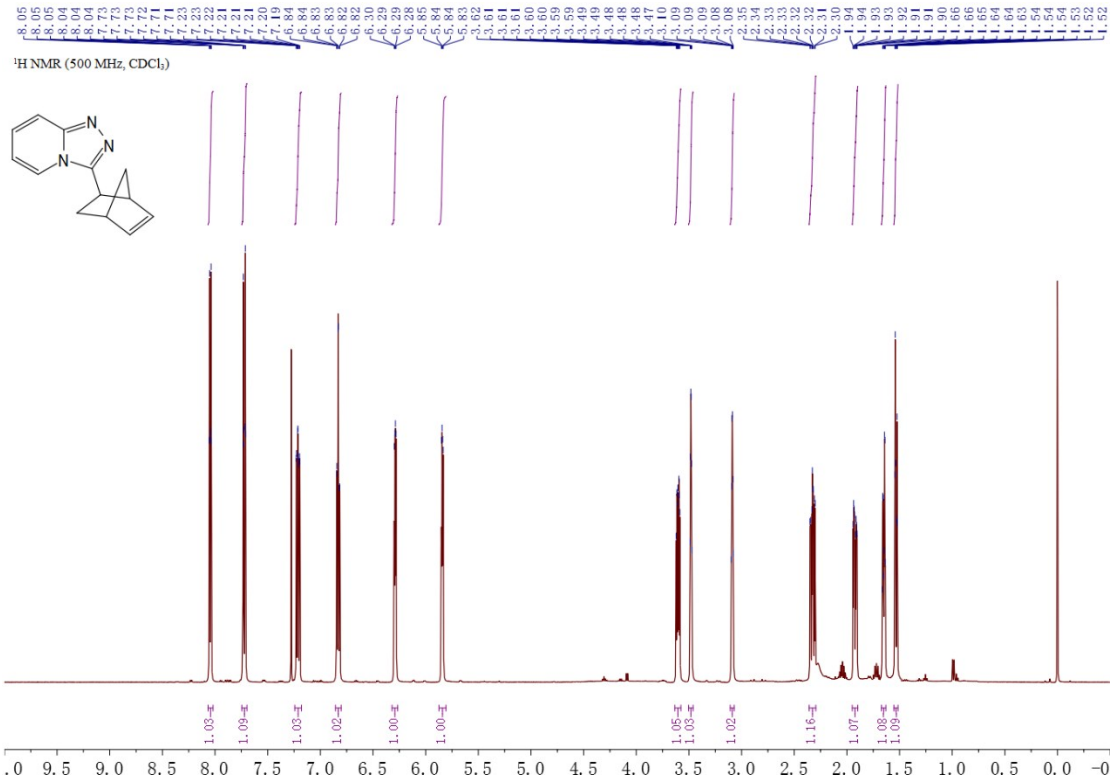
3-benzyl-[1,2,4]triazolo[4,3-a]pyridine (8f)

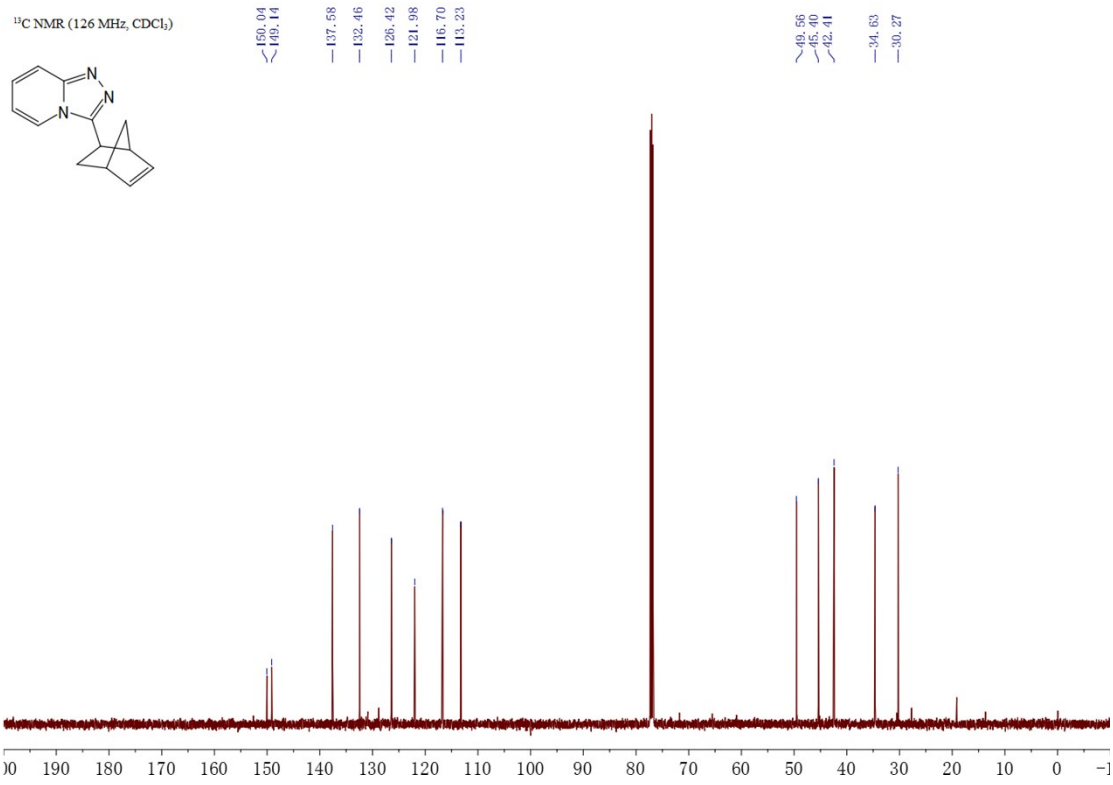


(E)-3-styryl-[1,2,4]triazolo[4,3-a]pyridine (8g)

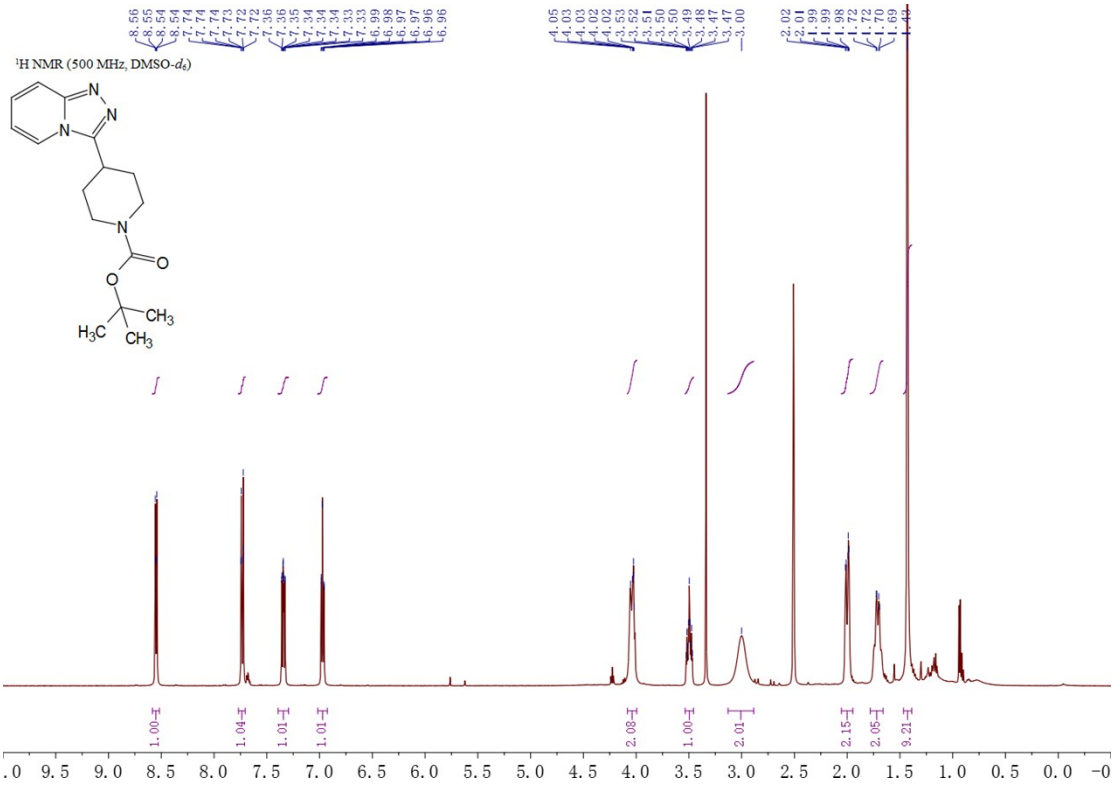


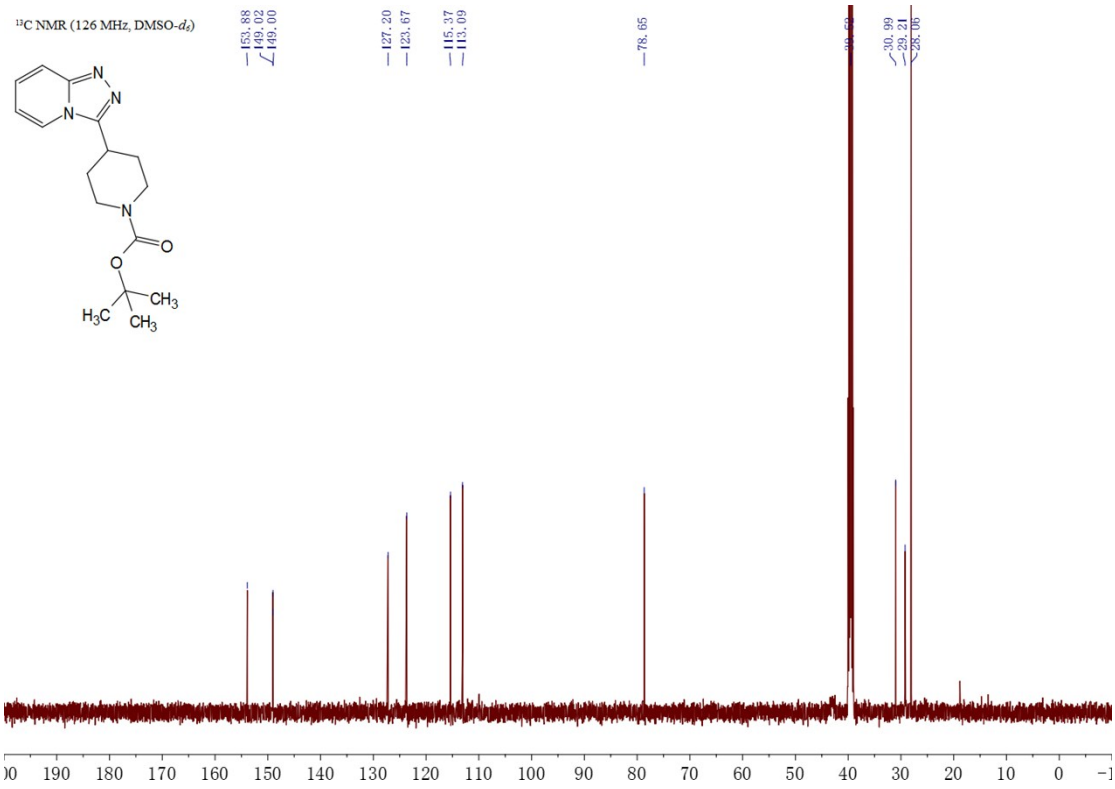
3-((1S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (8h)



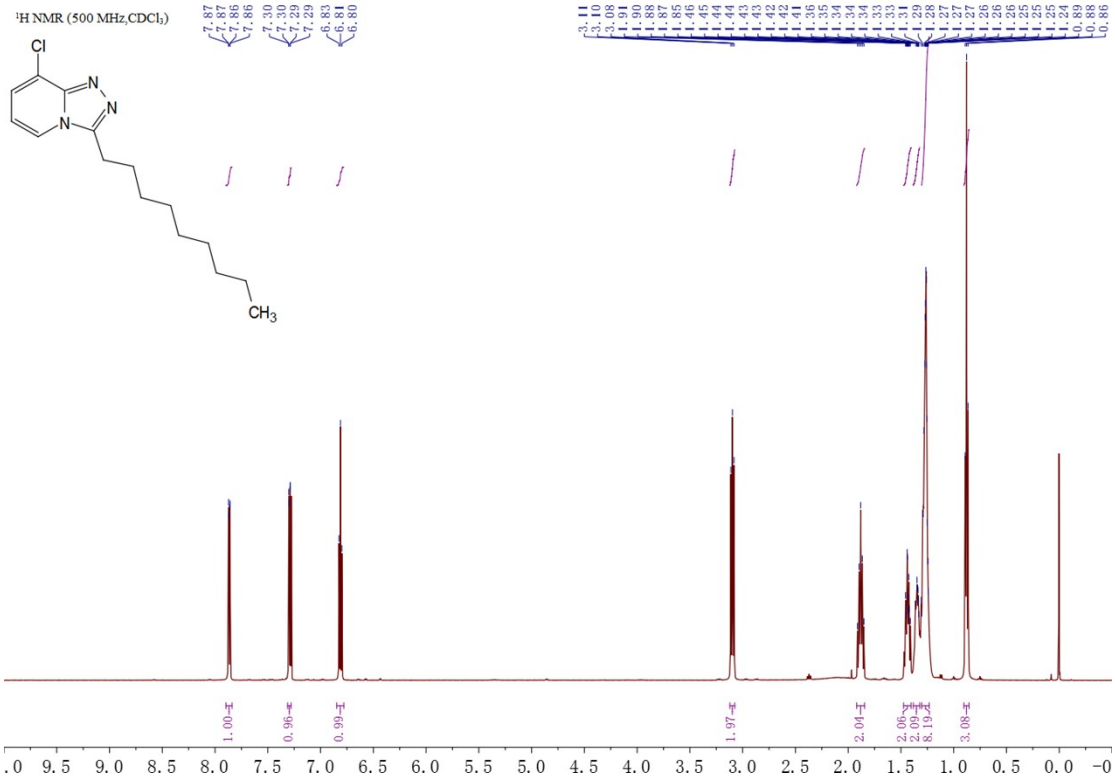


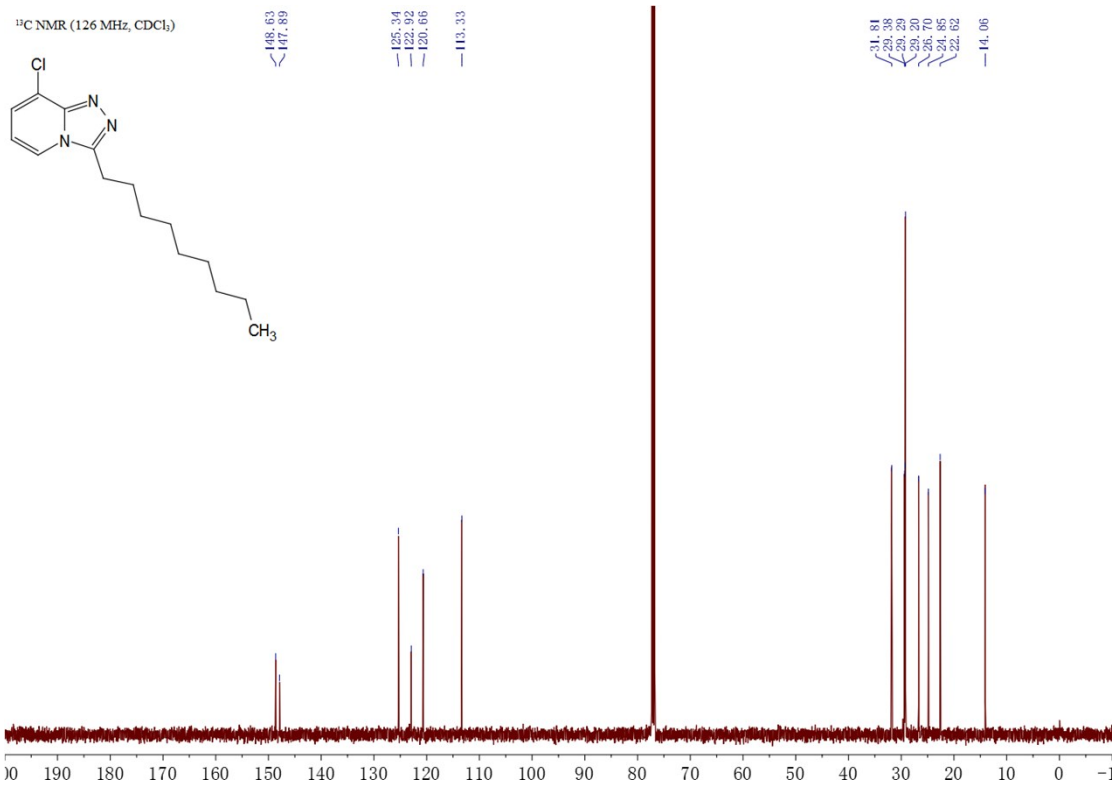
tert-butyl 4-([1,2,4]triazolo[4,3-a]pyridin-3-yl)piperidine-1-carboxylate (8i)



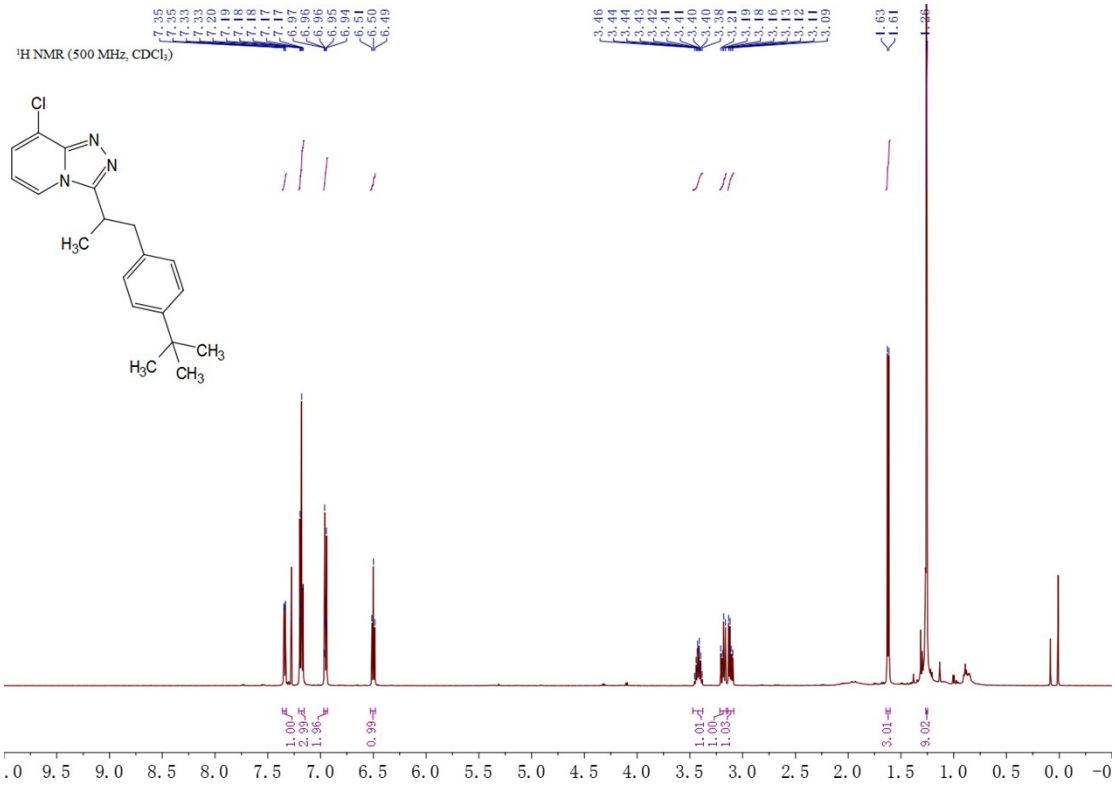


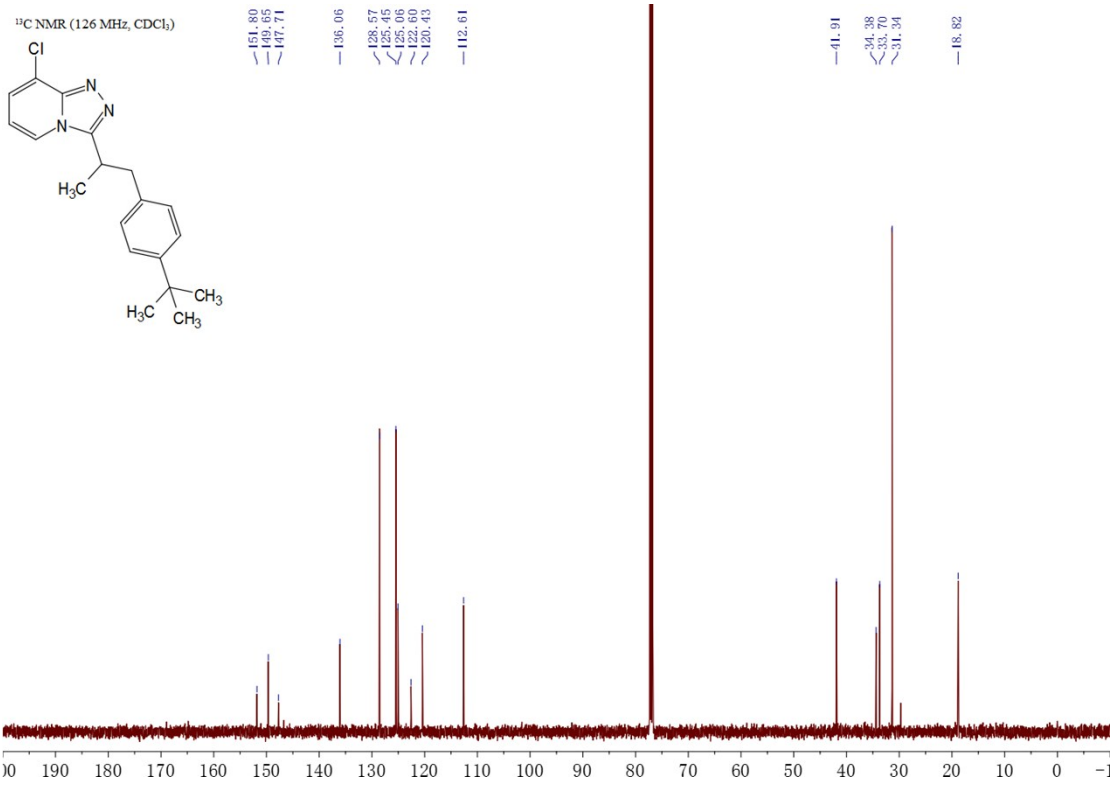
8-chloro-3-nonyl-[1,2,4]triazolo[4,3-a]pyridine (8j)



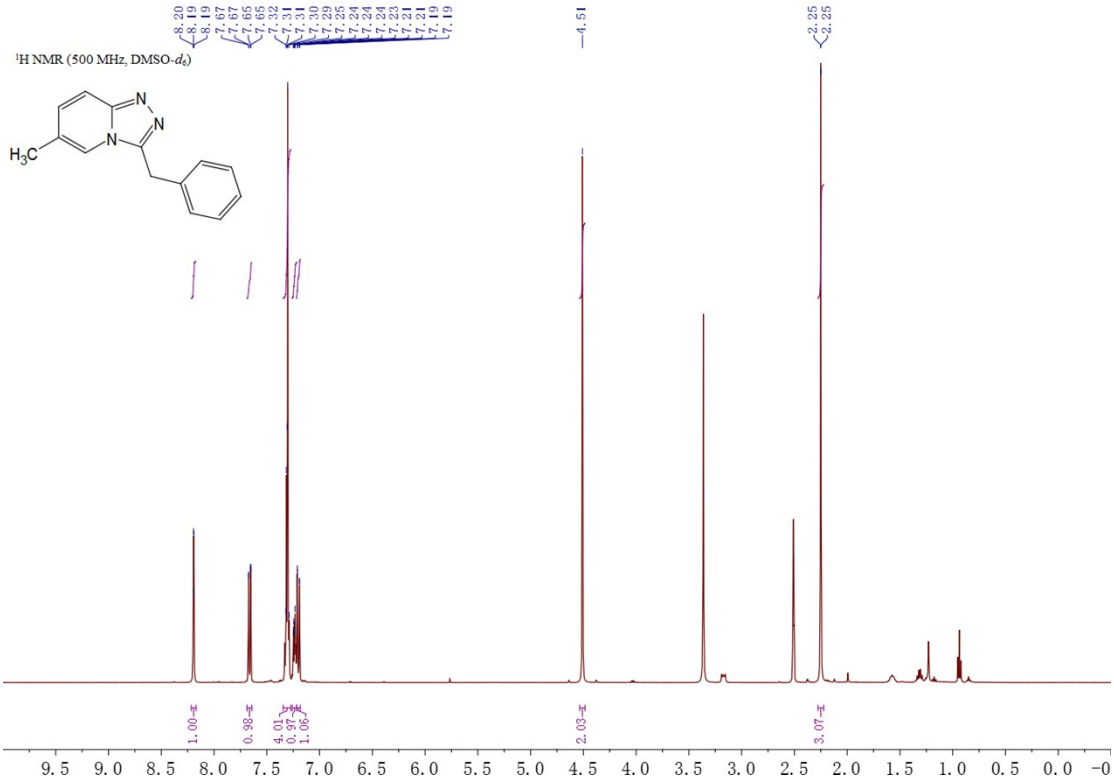


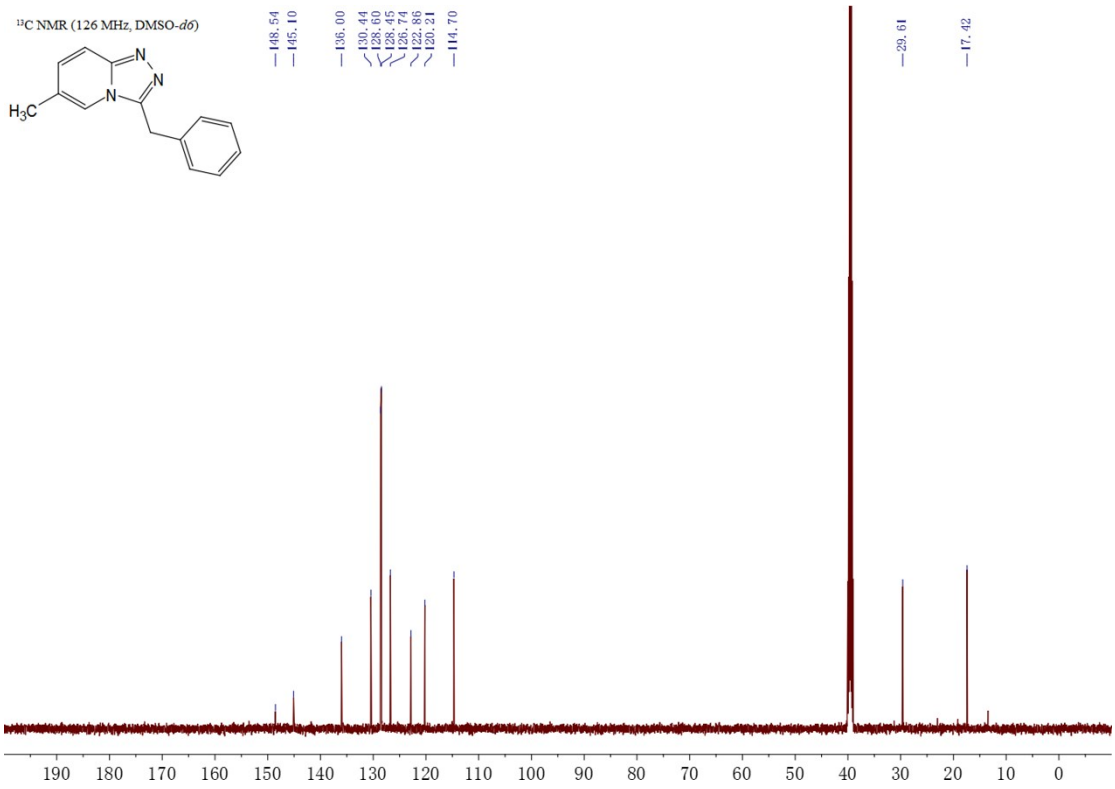
3-(1-(4-(tert-butyl)phenyl)propan-2-yl)-8-chloro-[1,2,4]triazolo[4,3-a]pyridine (8k)



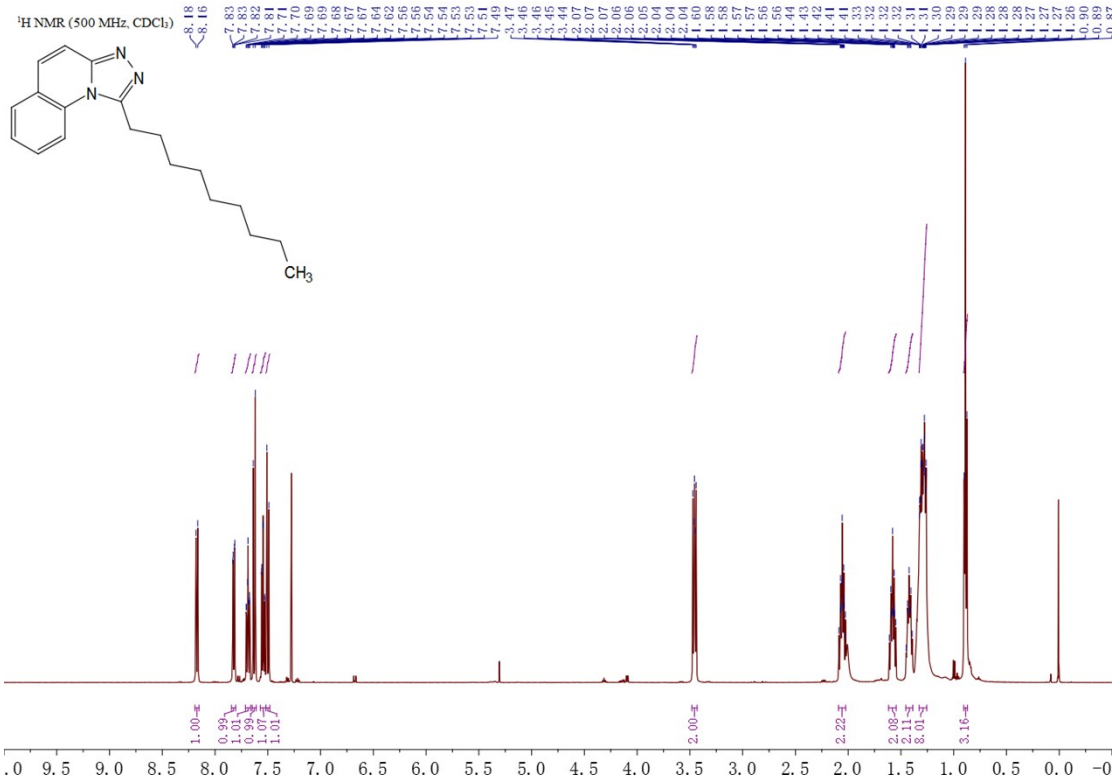


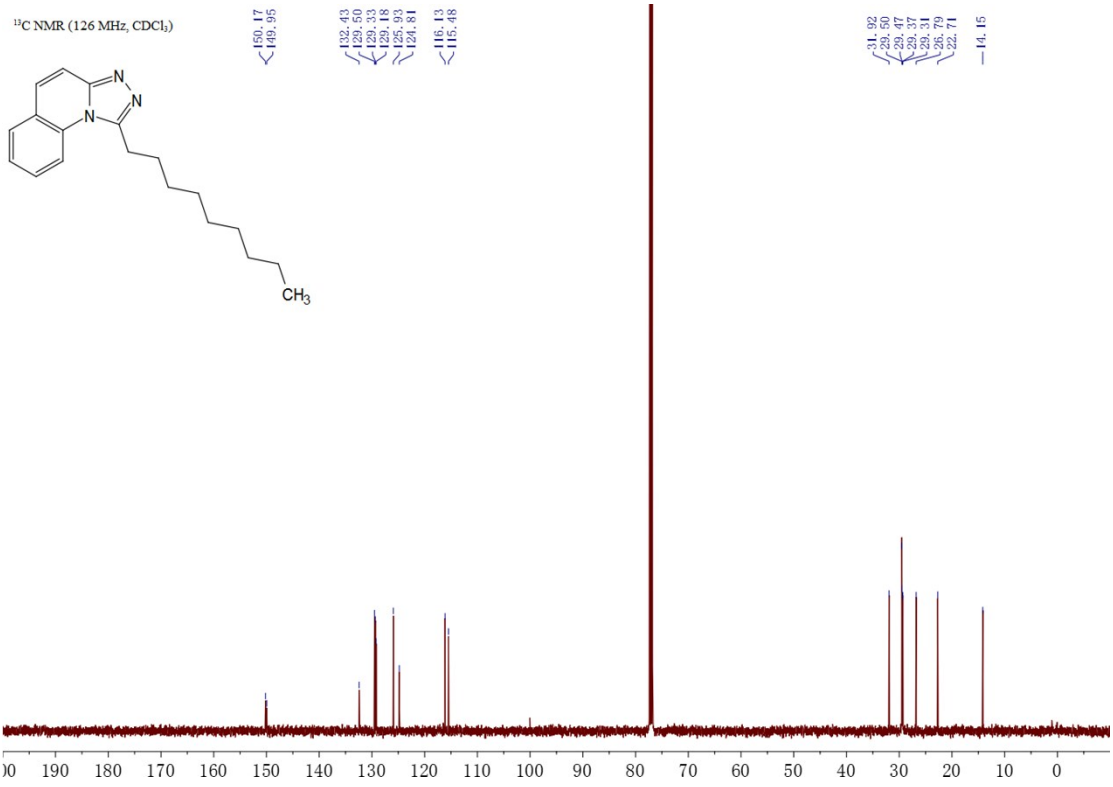
3-benzyl-6-methyl-[1,2,4]triazolo[4,3-a]pyridine (8l)



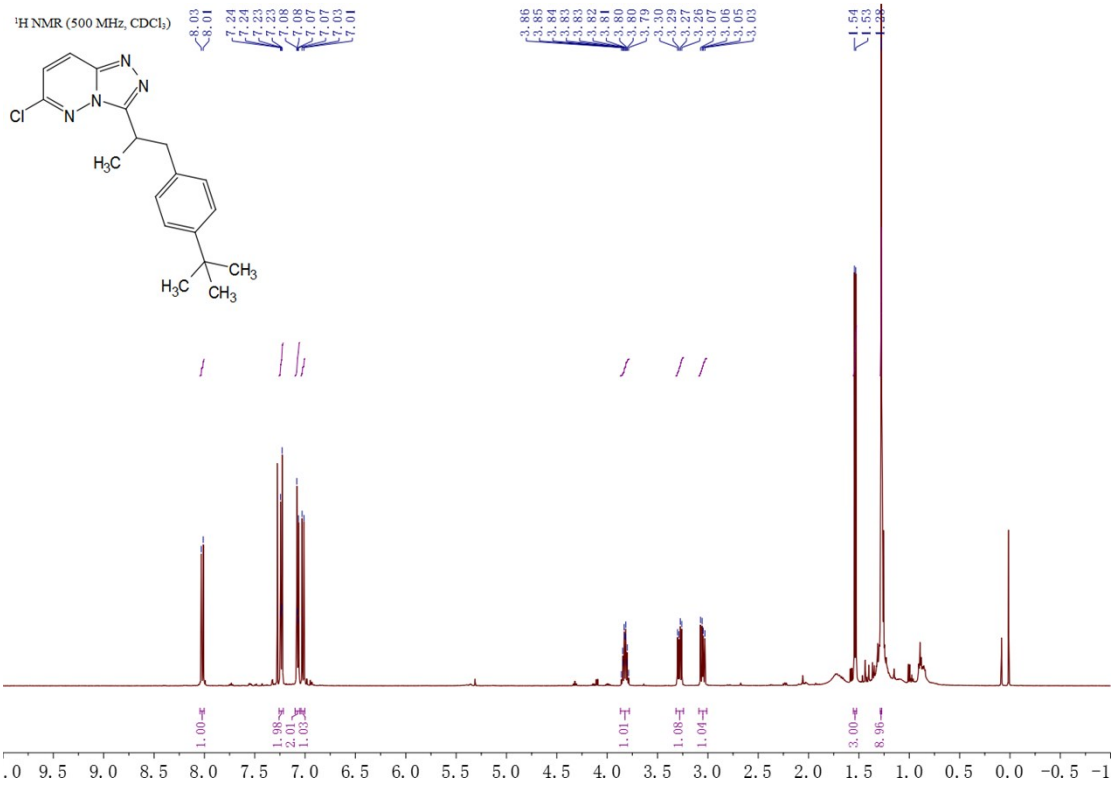


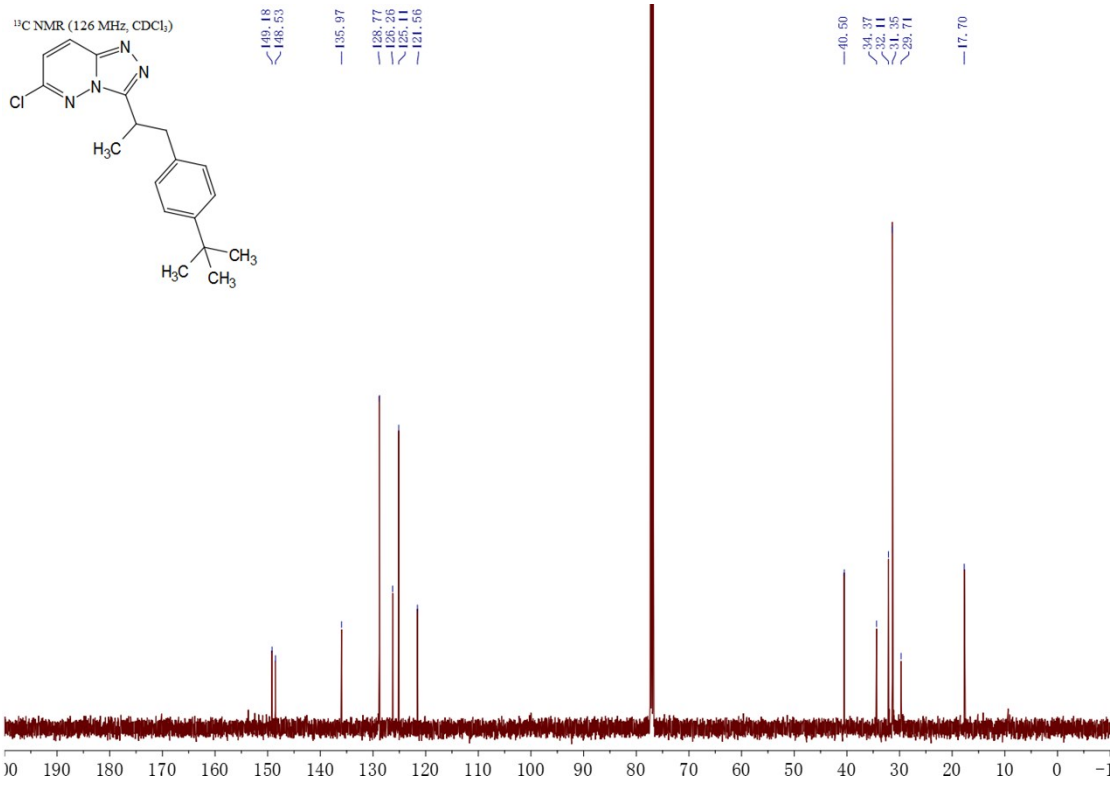
1-nonyl-[1,2,4]triazolo[4,3-a]quinoline (8m)



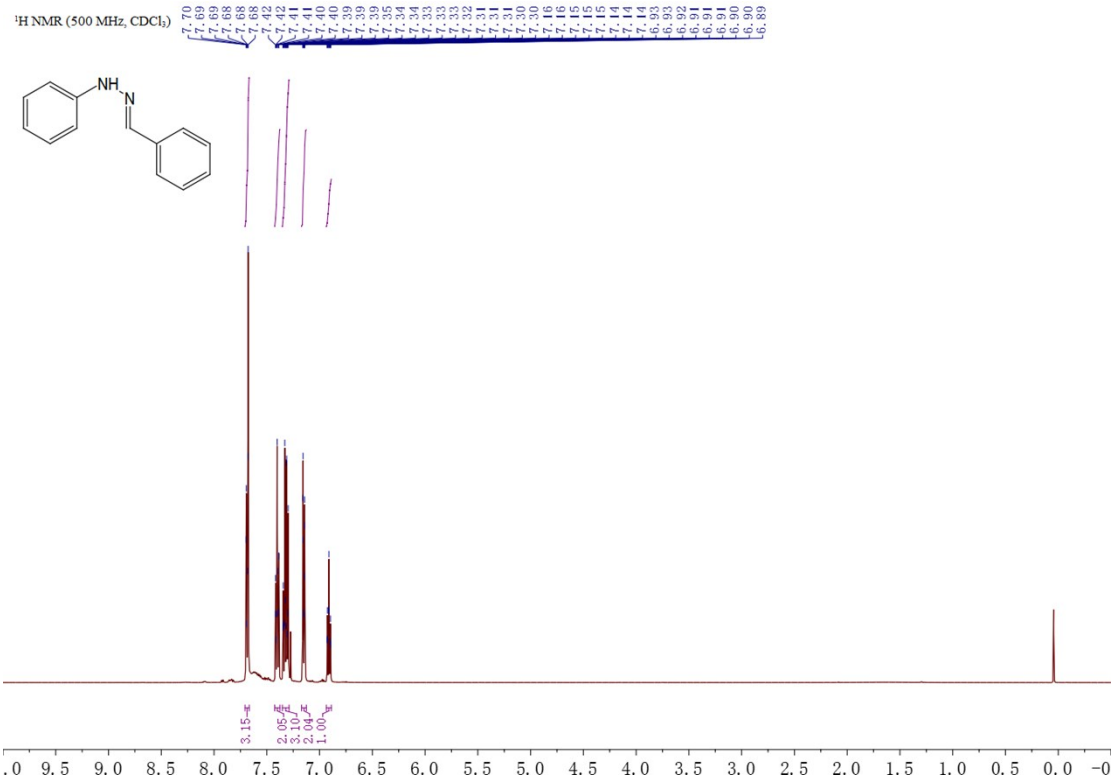


3-(1-(4-(tert-butyl)phenyl)propan-2-yl)-6-chloro-[1,2,4]triazolo[4,3-b]pyridazine (8n)

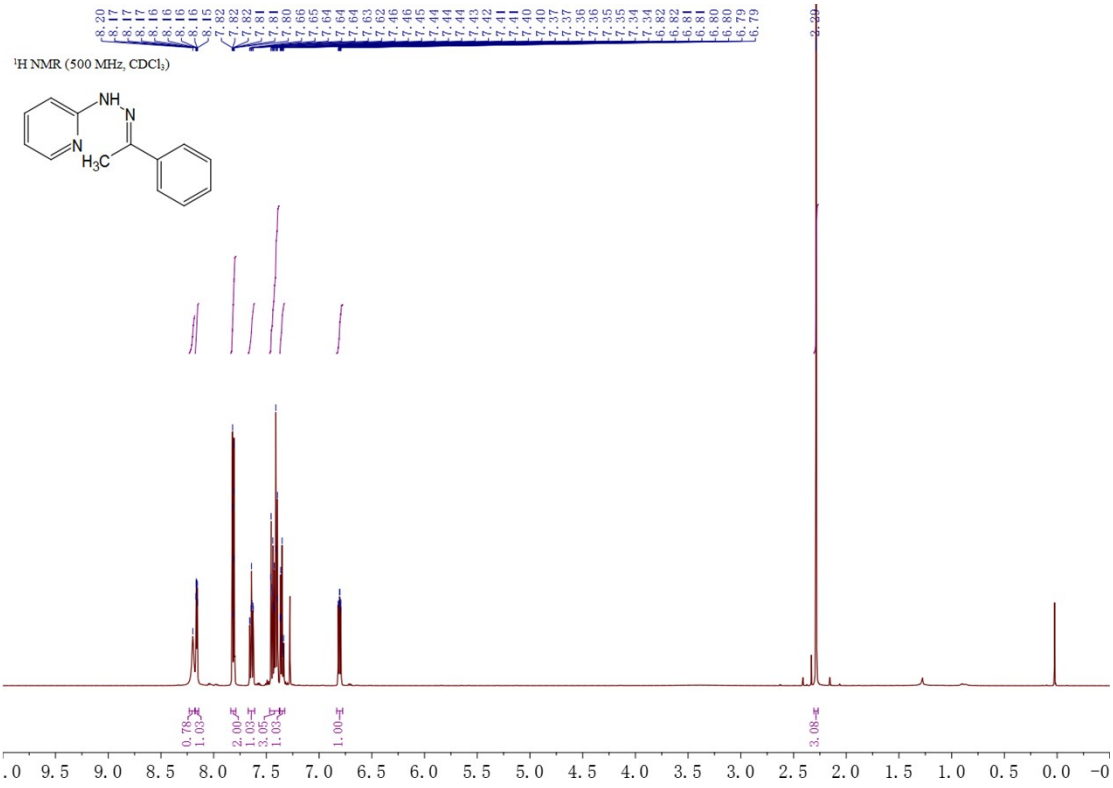


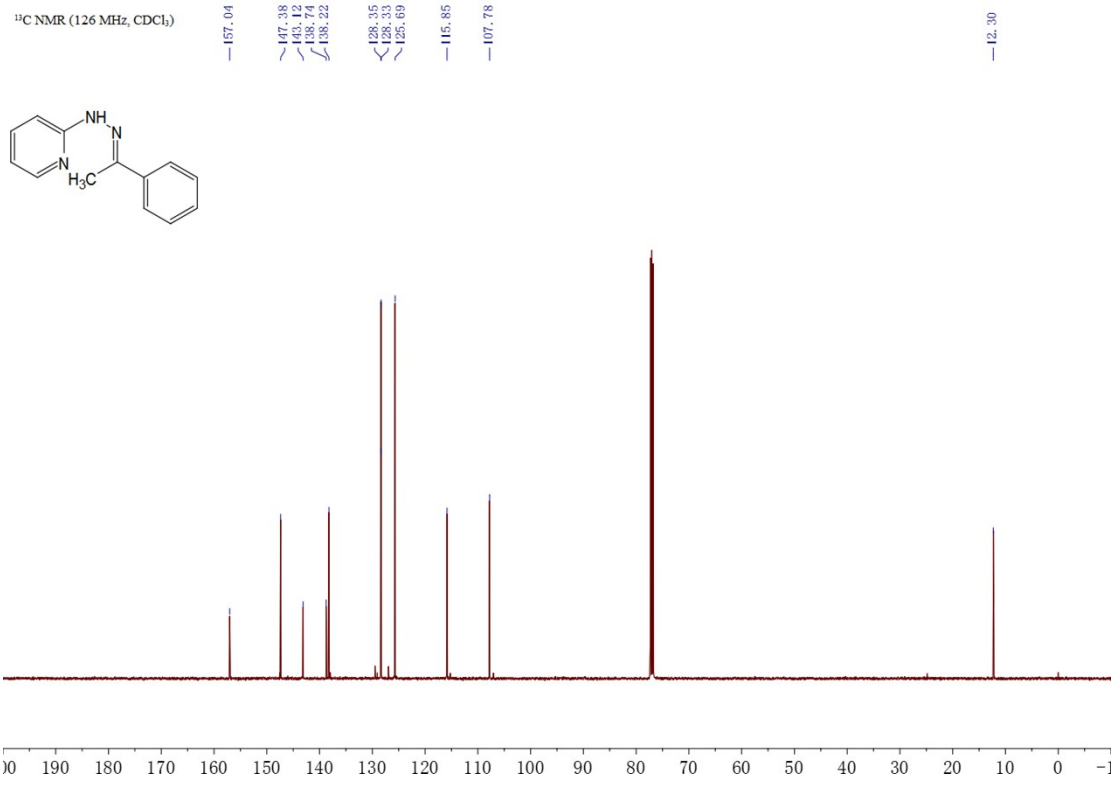


1-benzylidene-2-phenylhydrazine (10):

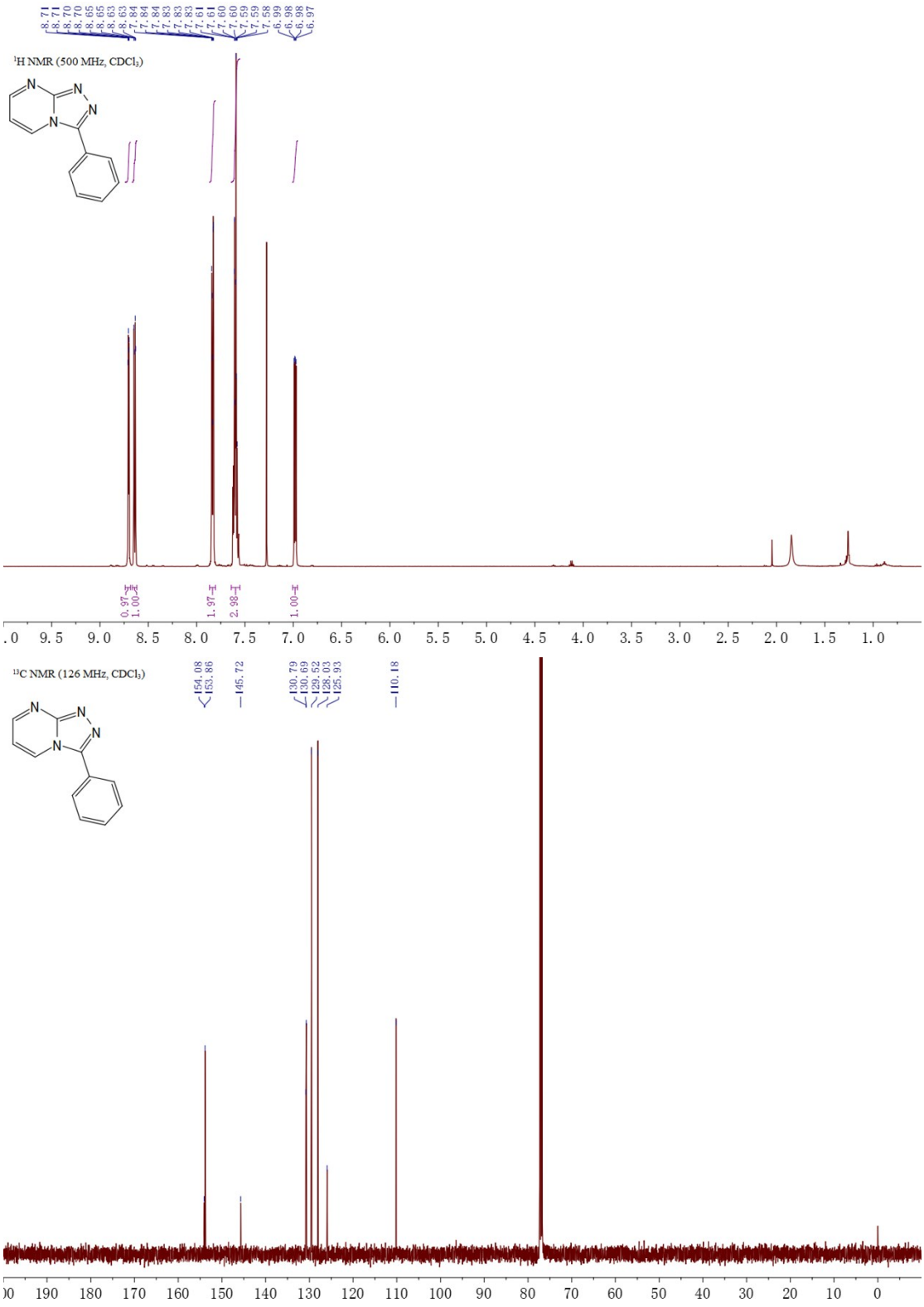


2-(2-(1-phenylethylidene)hydrazinyl)pyridine (13):

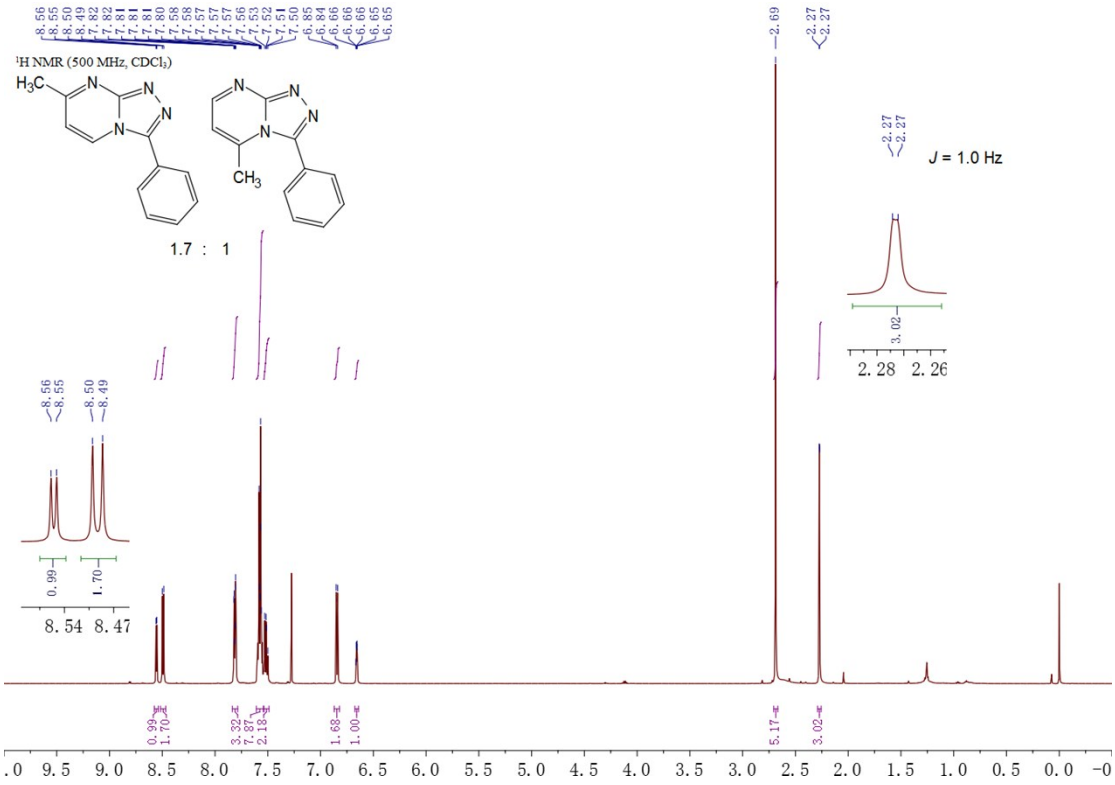


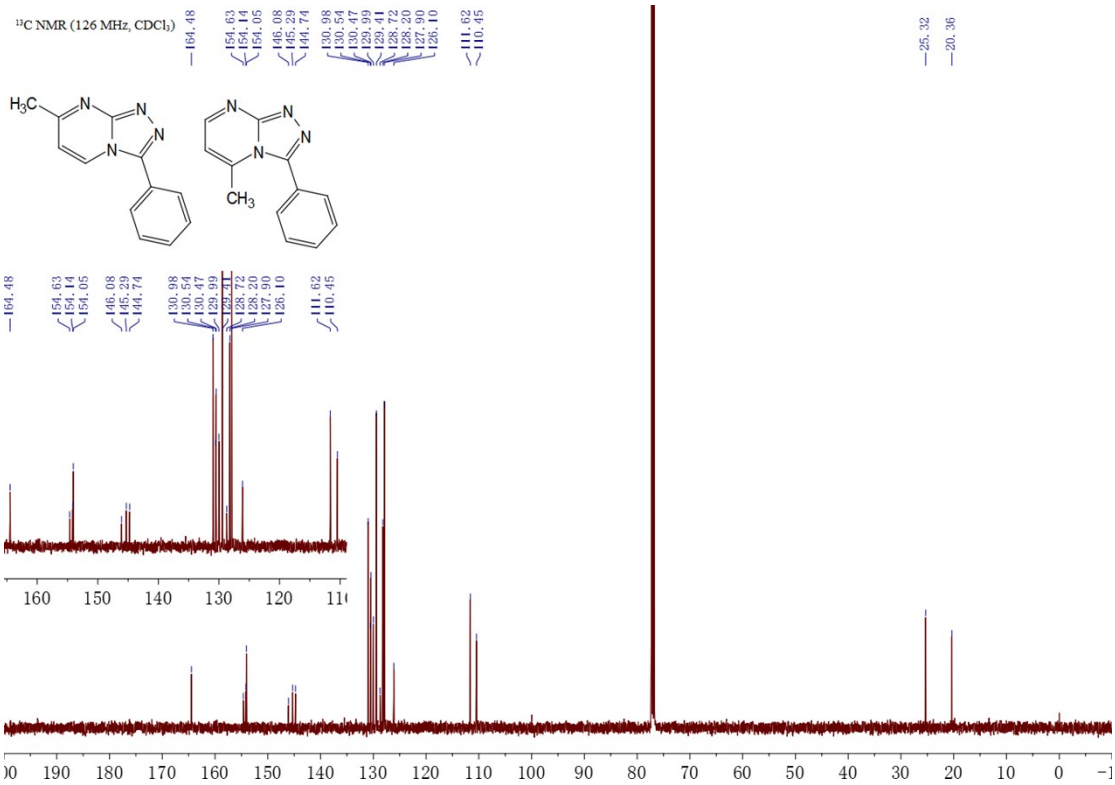


3-phenyl-[1,2,4]triazolo[4,3-a]pyrimidine (15a)

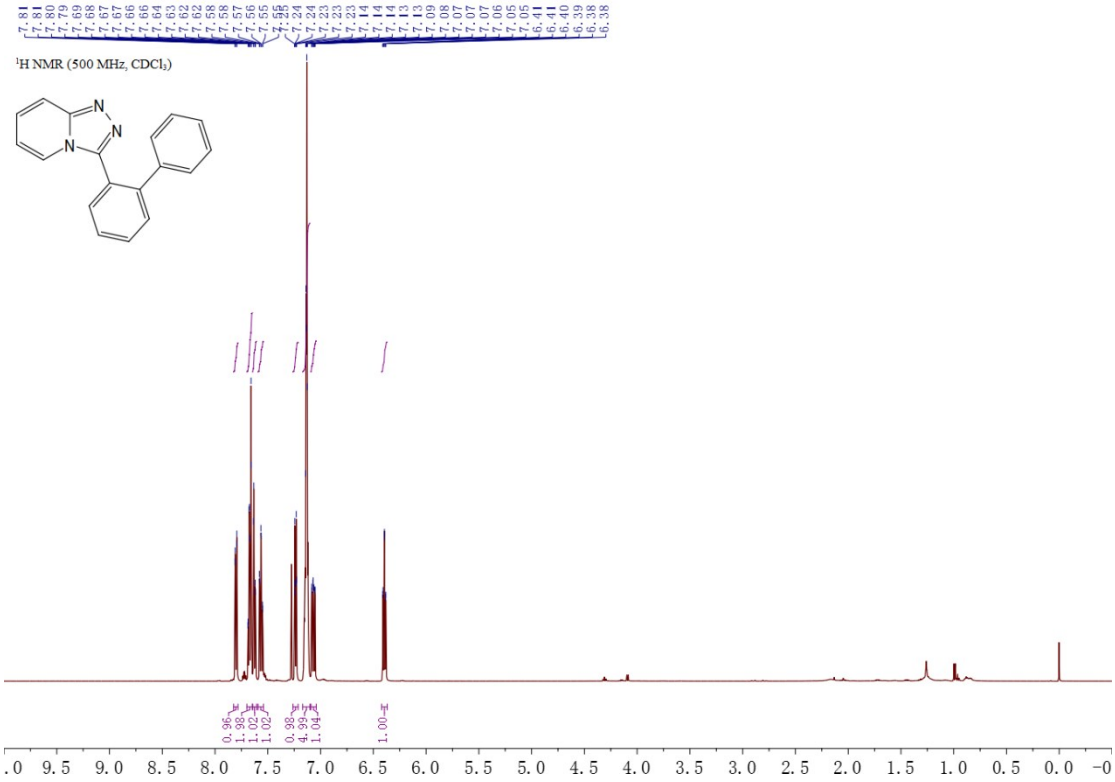


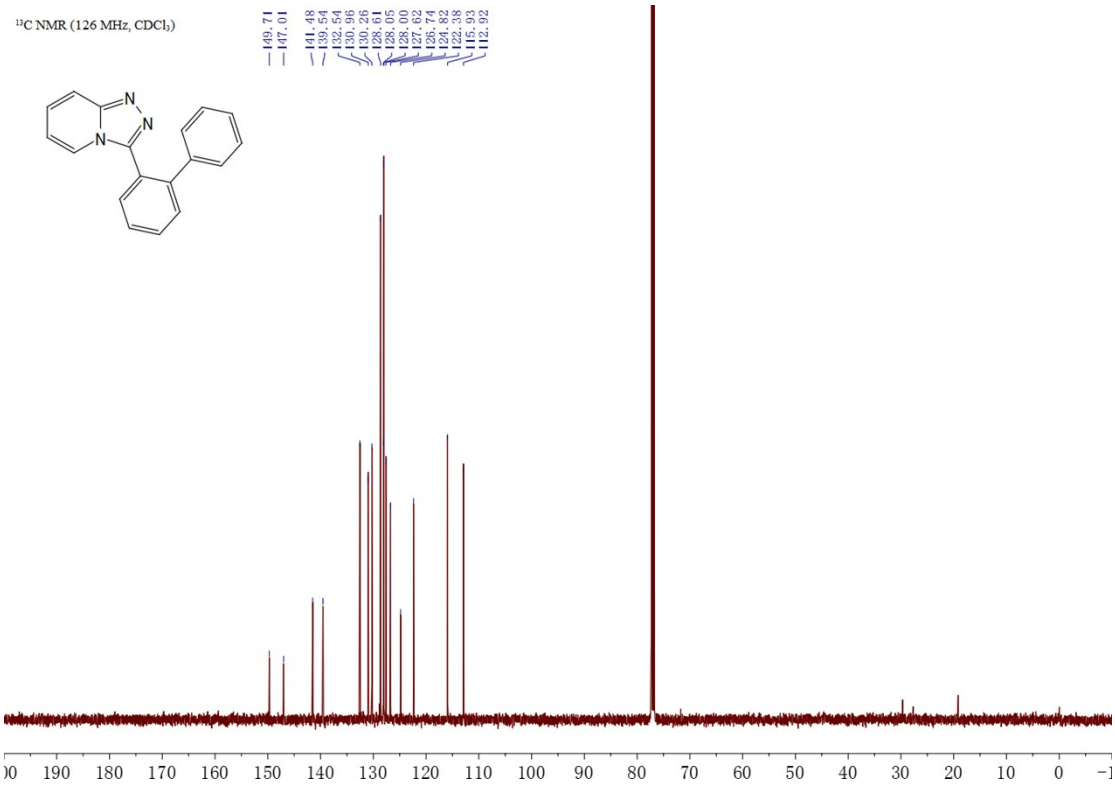
The mixture of 7-methyl-3-phenyl-[1,2,4]triazolo[4,3-a]pyrimidine and 5-methyl-3-phenyl-[1,2,4]triazolo[4,3-a]pyrimidine (15b):



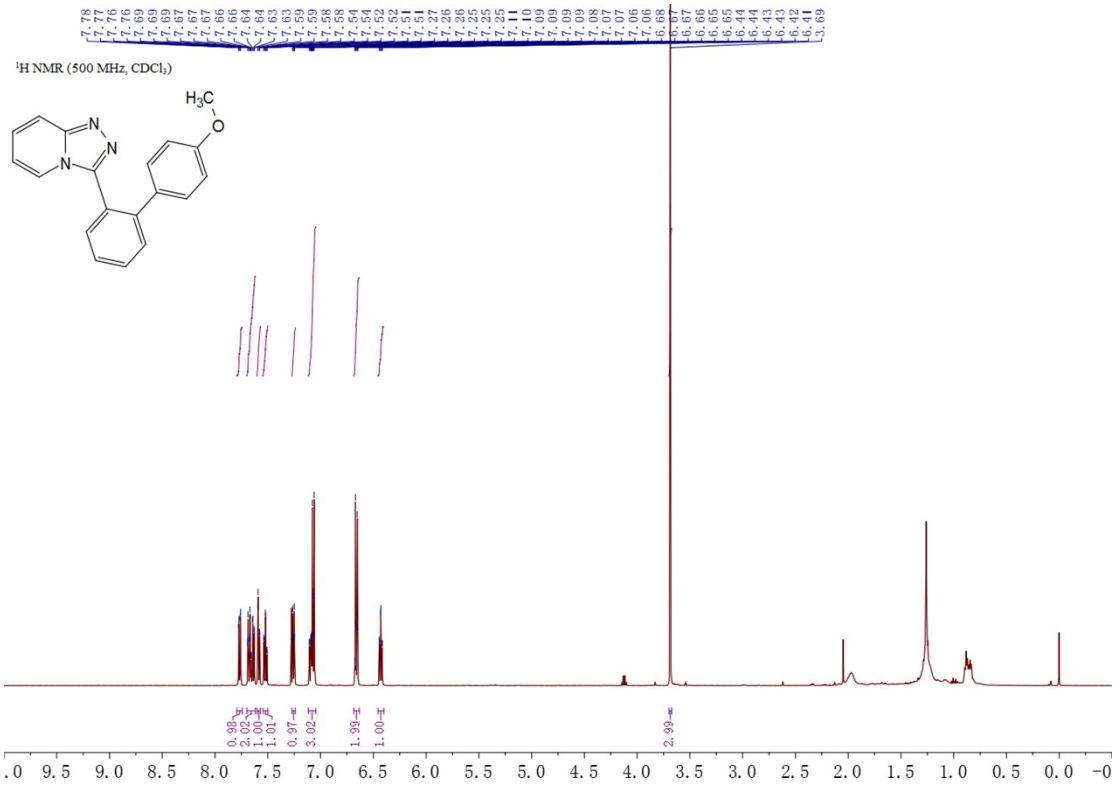


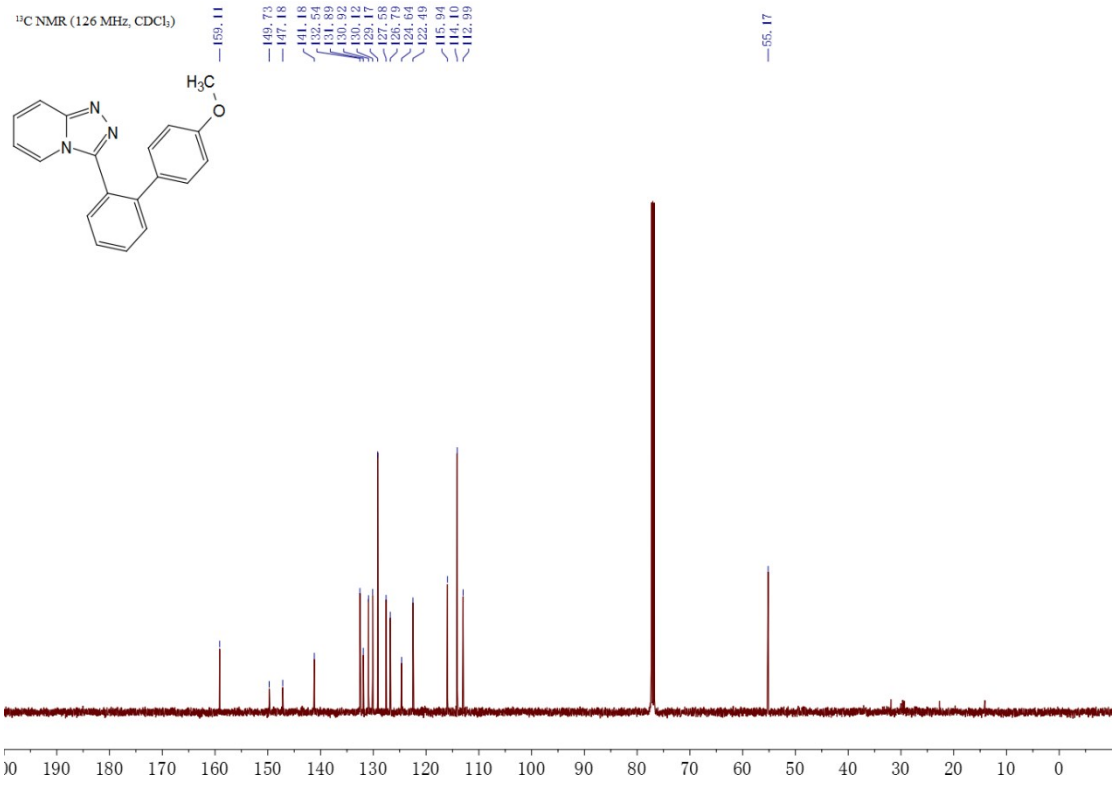
3-([1,1'-biphenyl]-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (17aa):



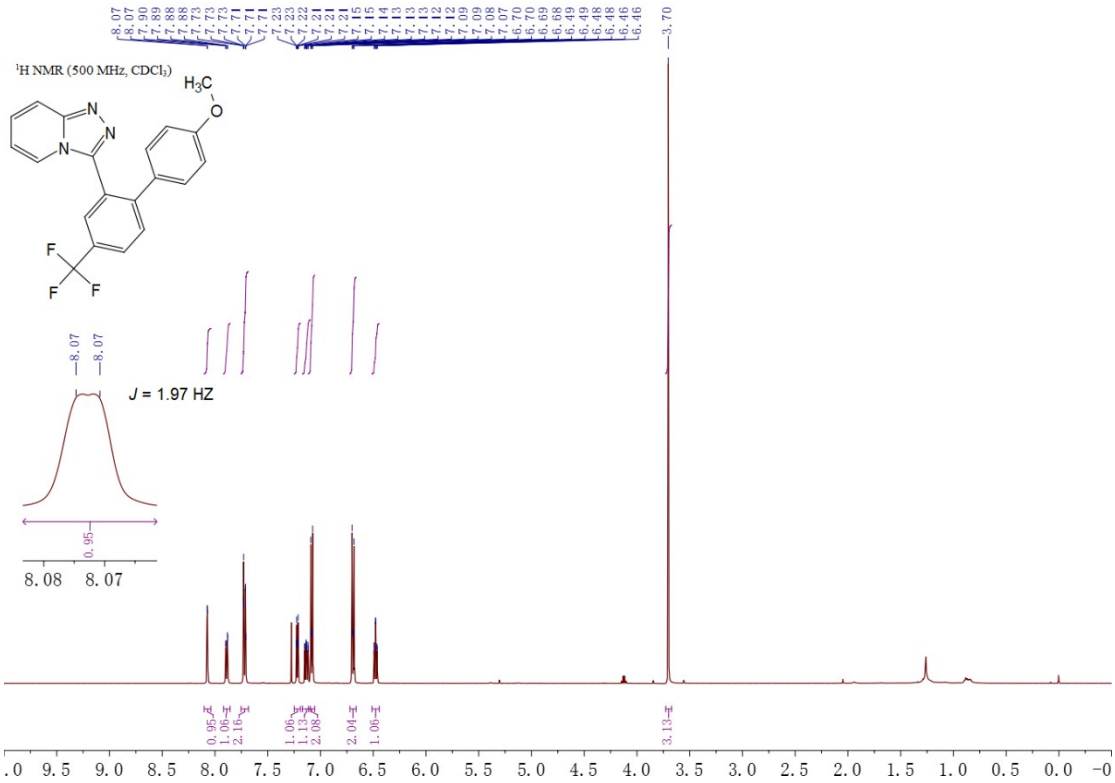


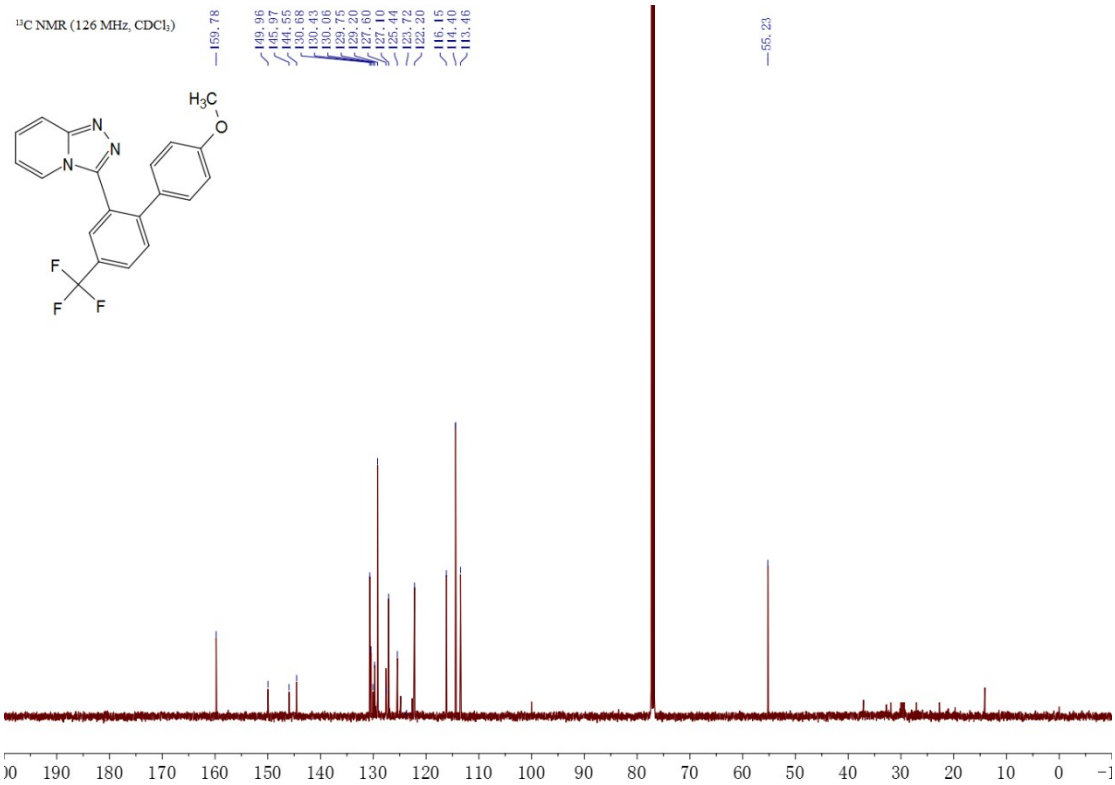
3-(4'-methoxy-[1,1'-biphenyl]-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (17ab)



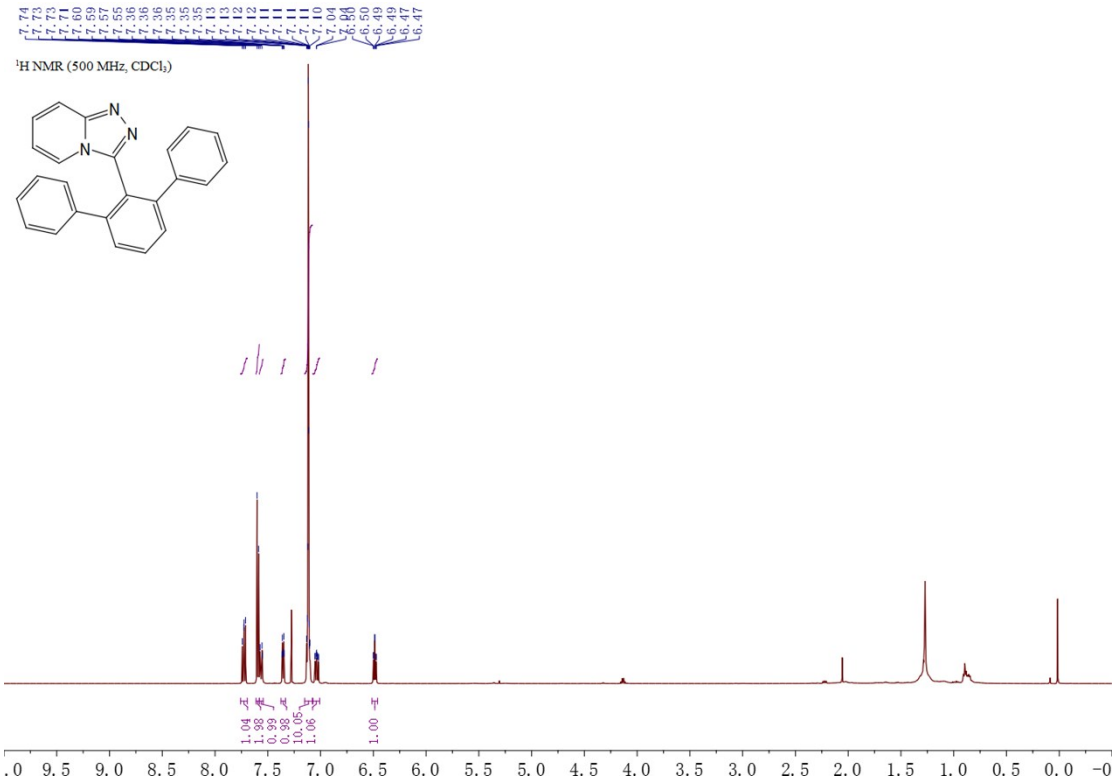


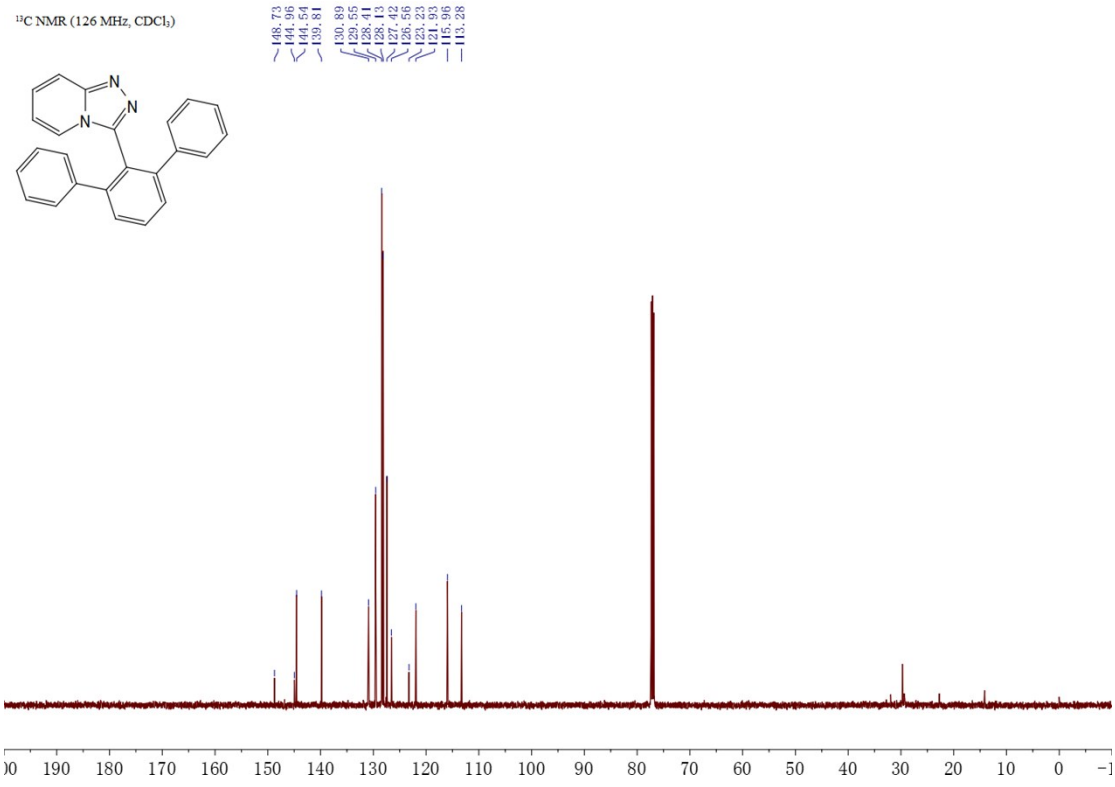
3-(4'-methoxy-4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)-[1,2,4]triazolo[4,3-a]pyridine (17cb):



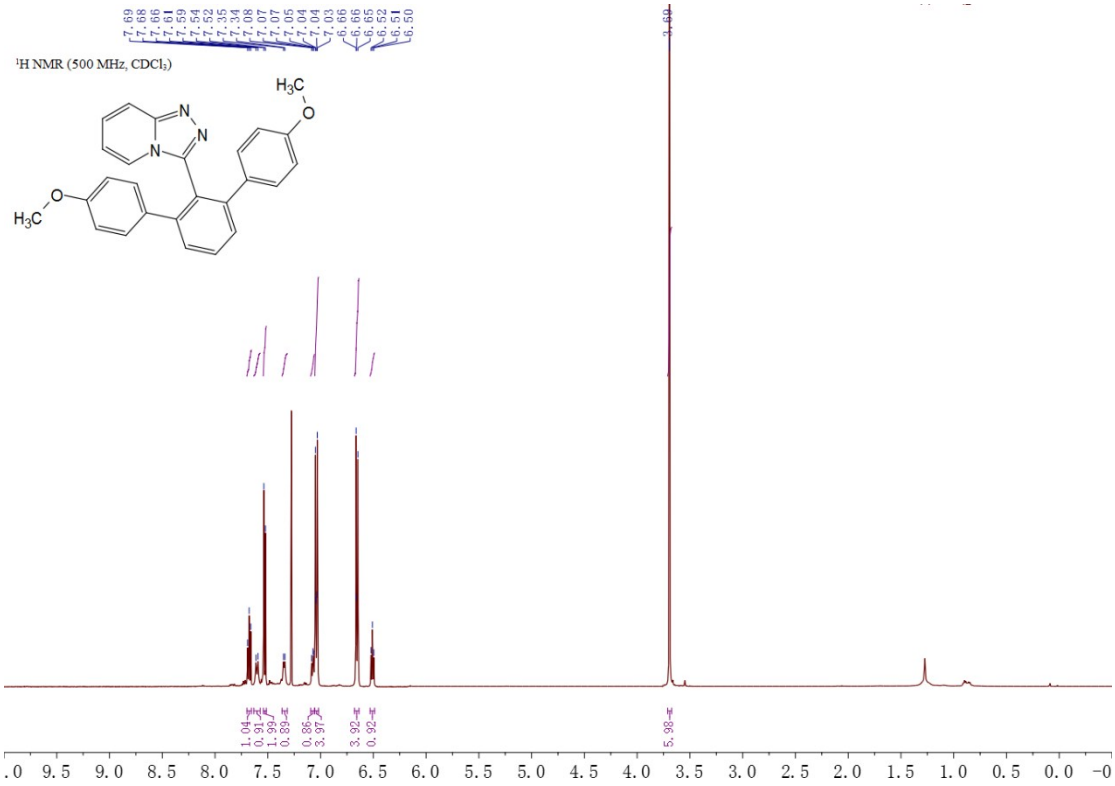


3-([1,1':3',1''-terphenyl]-2'-yl)-[1,2,4]triazolo[4,3-a]pyridine (18aa):

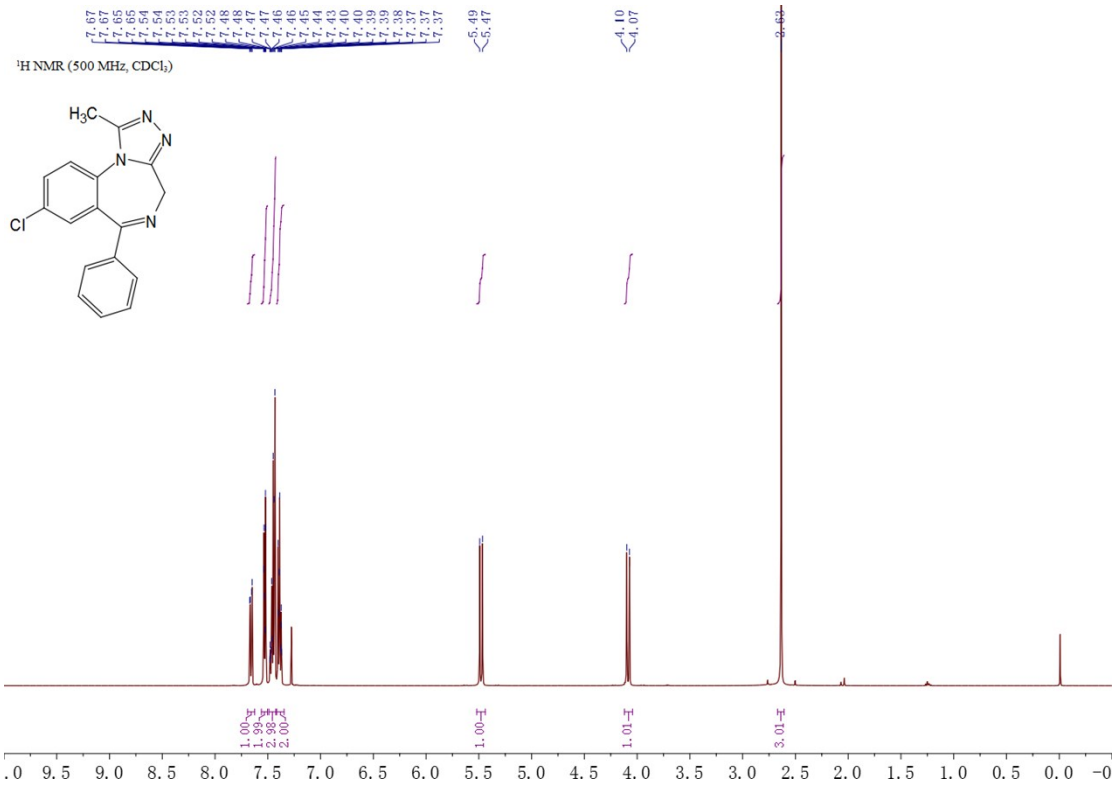


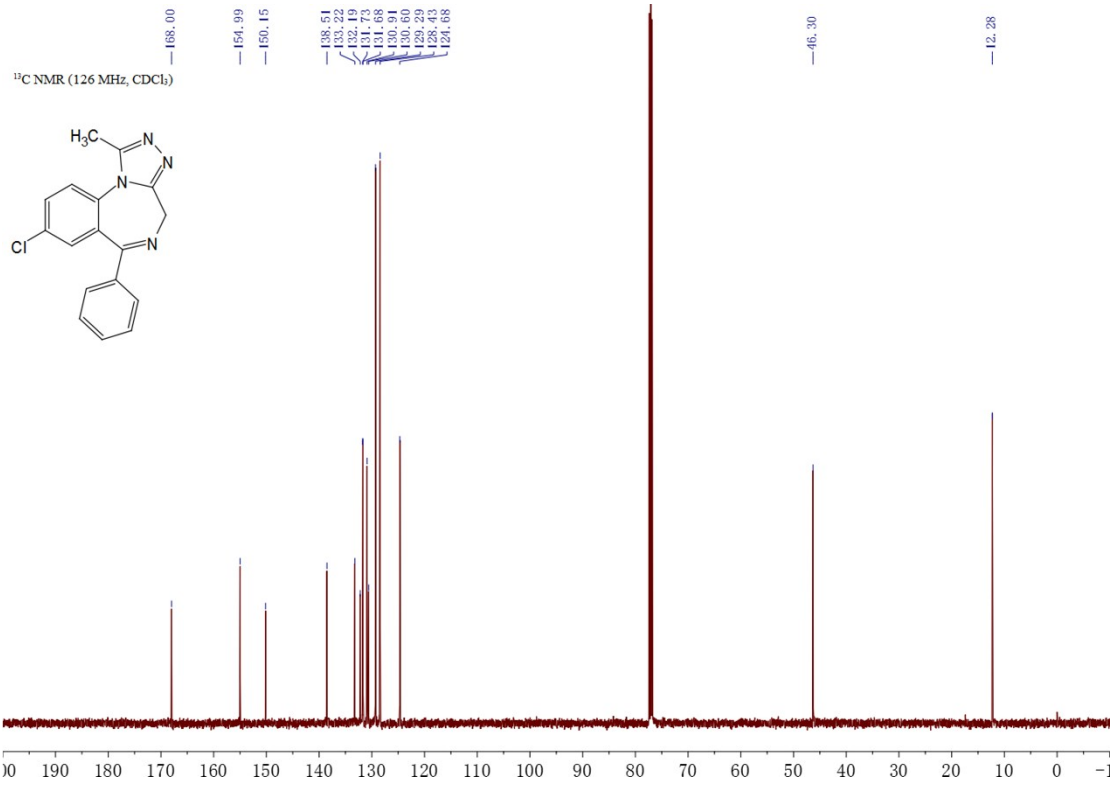


3-(4,4''-dimethoxy-[1,1':3',1''-terphenyl]-2'-yl)-[1,2,4]triazolo[4,3-a]pyridine (18ab):

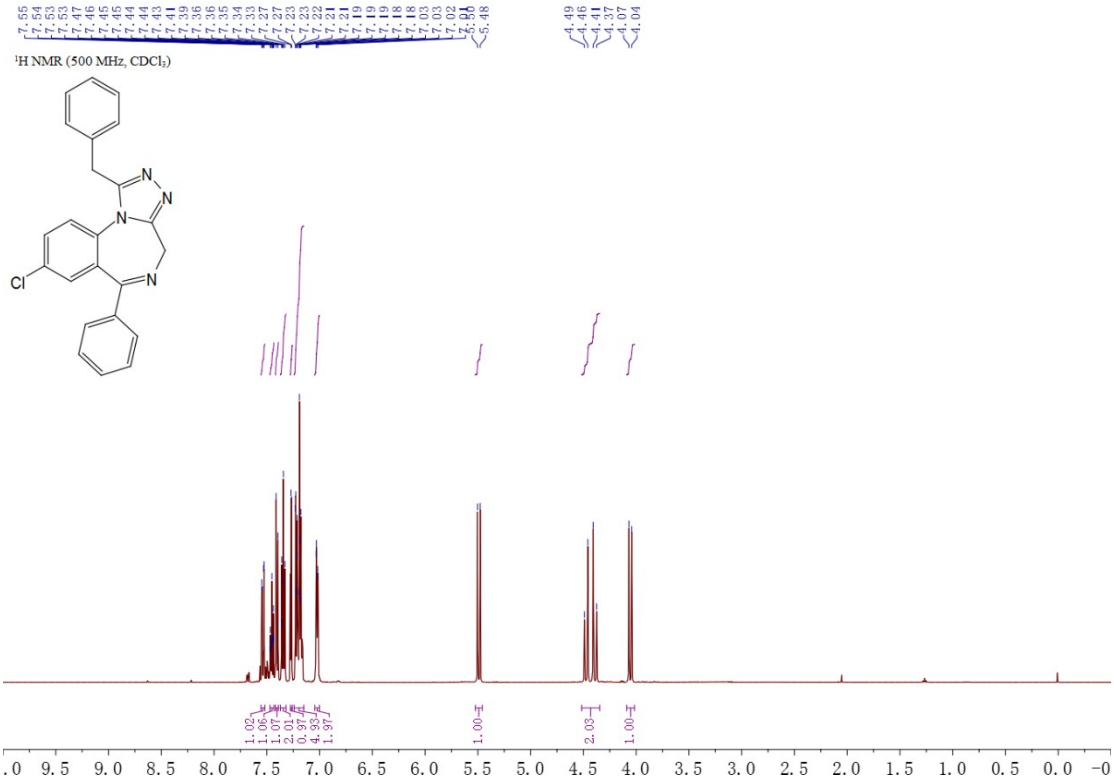


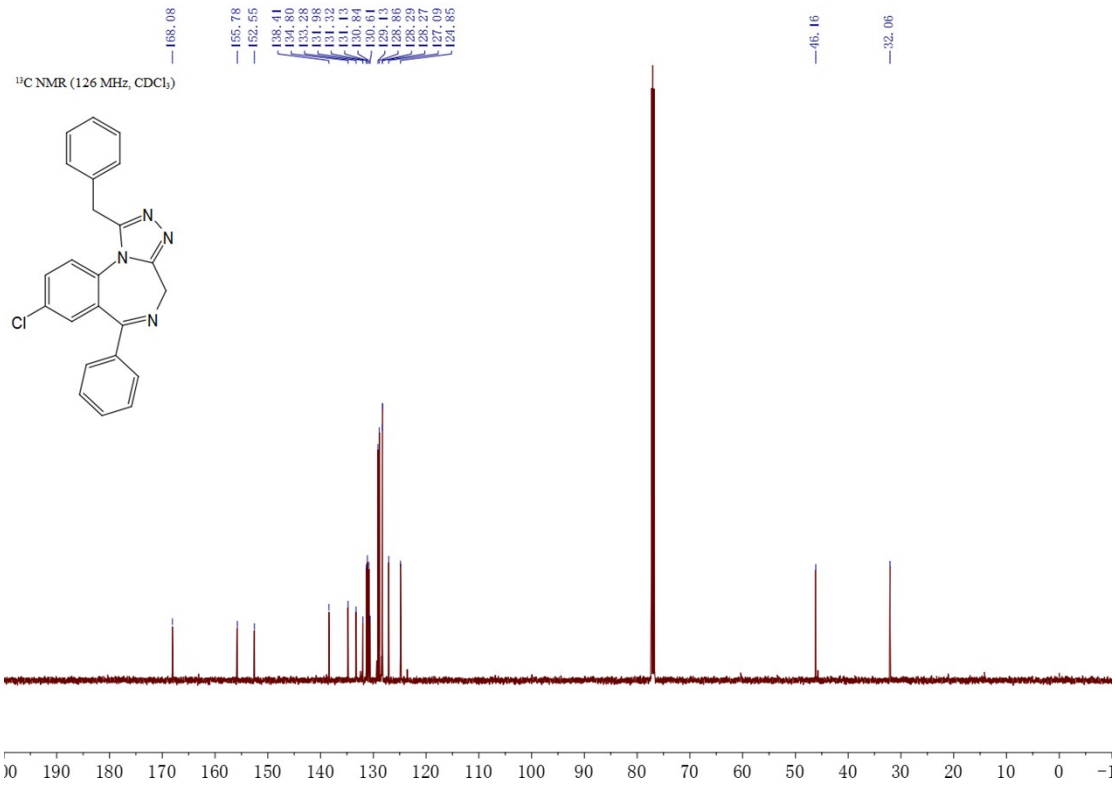
8-chloro-1-methyl-6-phenyl-4H-benzo[f][1,2,4]triazolo[4,3-a][1,4]diazepine (21a):



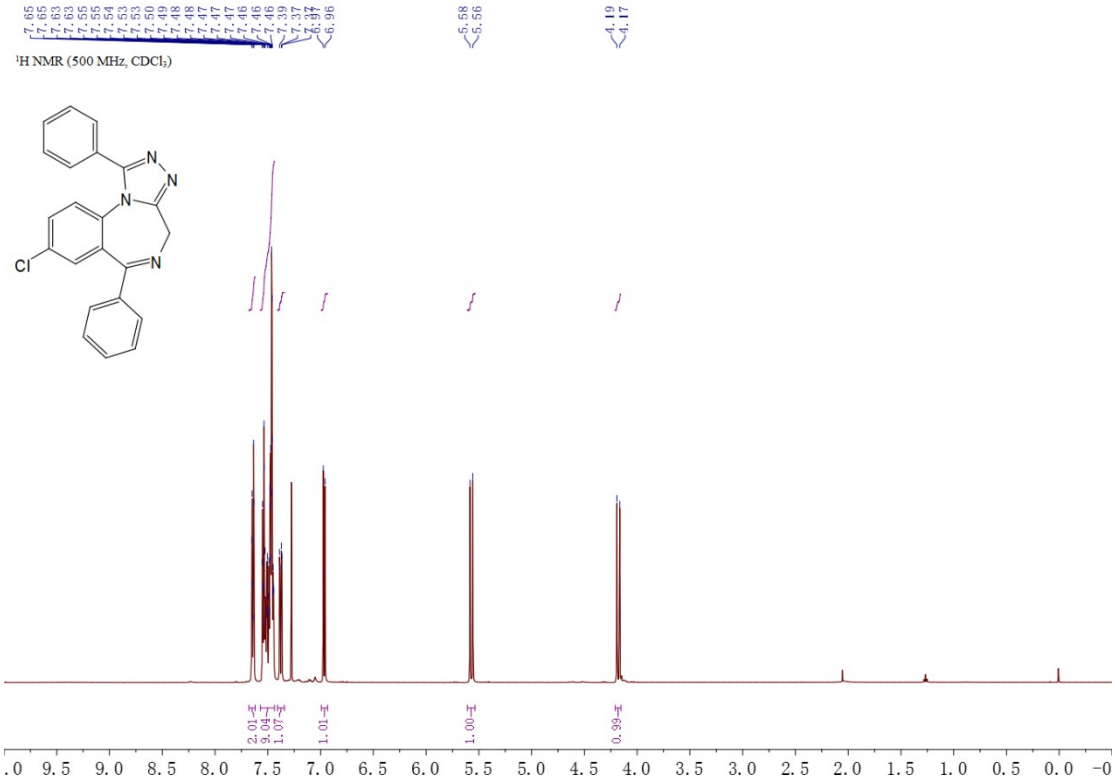


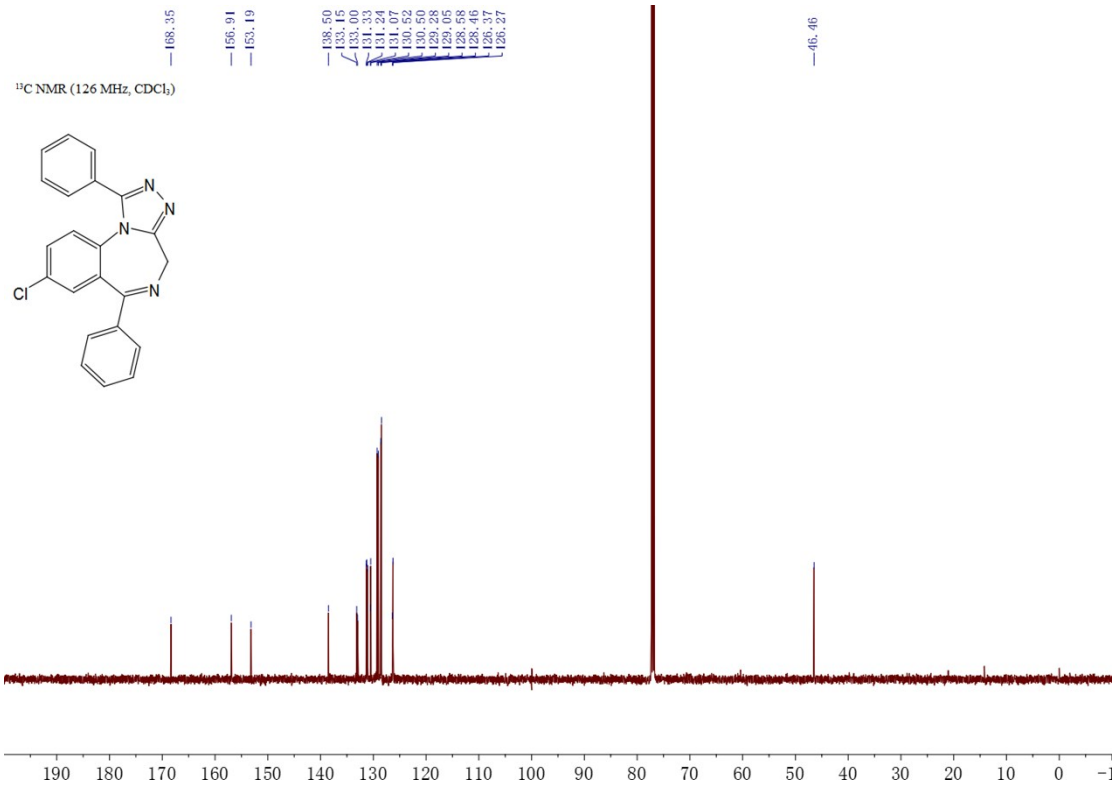
1-benzyl-8-chloro-6-phenyl-4H-benzo[f][1,2,4]triazolo[4,3-a][1,4]diazepine (21b):





8-chloro-1,6-diphenyl-4H-benzo[f][1,2,4]triazolo[4,3-a][1,4]diazepine (21c):

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153.19
138.50
133.15
133.00
131.33
131.24
131.07
130.52
130.50
129.28
129.05
128.58
128.46
126.37
126.27
46.46
13C NMR (126 MHz, CDCl3)
Cl
N
N
N
N
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180
170
160
150
140
130
120
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