Electrochemical cycloaddition of hydrazones with cyanamide for the synthesis of substituted 5-amine- 1,2,4-triazoles

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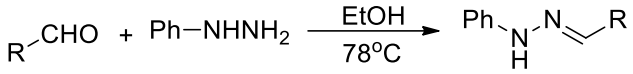
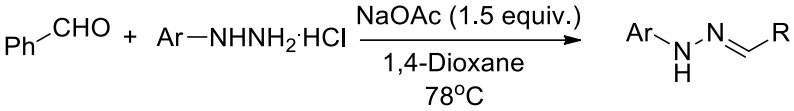
1. General procedure for the synthesis of starting Materials



Scheme S1

The synthesis of hydrazones was according to a modified procedure. A mixture of arylaldehyde (10 mmol), phenylhydrazine (10 mmol) and absolute ethanol (25ml) in a 100 mL flask was stirred and refluxed for 6 h. After the completion of the reaction, most of the solvent was removed under reduced pressure, and the solid was filtered and washed with petroleum ether and water to obtain final products, which was used for next step without furtther purification.



Scheme S2

A mixture of benzaldehyde (10 mmoll) and sodium acetate (1.5 equiv), ethanol (25 mL) and water (2ml) were added into 100ml flask, the corresponding arylhydrazine hydrochloride was added by small portions. The mixture was stirred at 78°C for 6h. After the completion of the reaction, most of the solvent was removed under reduced pressure, and the solid was filtered and washed with petroleum ether and water to obtain final products, which was used for next step without furtther purification.

2. General information.

All reagents and solvents were purchased from commercial suppliers and used without further purifification, The NMR spectra were recorded at bruker 400 MHz (^{1}H) and 100 MHz (^{13}C) in DMSO-d_6 using TMS as as internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, m = multiplet. Melting points were measured with micro melting point apparatus. The power supply is Maisheng DC regulated power supply, and the electrode of platinum plate (1cm*1cm*0.1mm), graphite rod (diameter 0.6mm), and the reaction vessel (10ml)with 3 electrode holes.

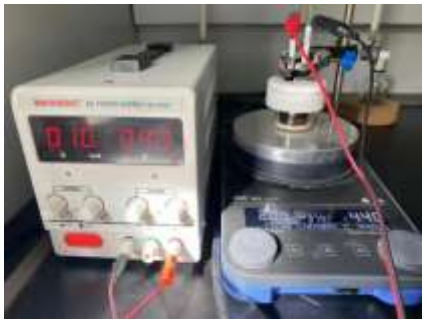
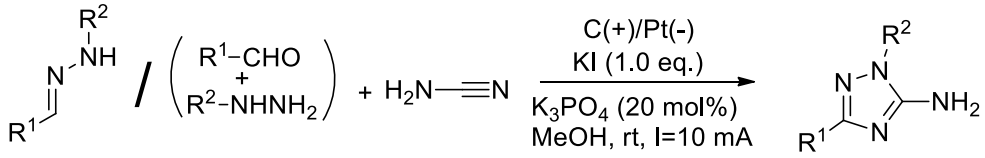


Fig. S1 The reaction equipment of the reaction.

3. General procedure for the synthesis of 1,2,4-triazole derivatives.



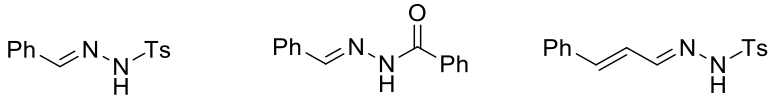
Scheme S3

An undivided cell (10ml) was equipped with graphite rod anode (Φ6 mm), Pt plate cathode (1 cm × 1 cm). Hydrazones **1** (0.3 mmol), cyanamide **2** (0.6 mmol), KI (1.0 equiv.), K_3PO_4 (20 mol%) and MeOH (8 mL) were added into the cell at room temperature (or aldehydes **4** (0.3 mmol), hydrazines (0.3 mmol), cyanamide **2** (0.6 mmol), KI (1.0 equiv.), K_3PO_4 (20 mol%) and MeOH (8 mL) were added into the cell at room temperature). The mixture was stirred and electrolyze under constant current conditions (10mA) for 5h. When the reaction was finished, the mixture was then dried over $MgSO_4$ and removed under vacuum to obtain crude products. The residue was purified by column chromatography on silica gel using the eluent with petroleum ether/EtOAc (1/1).

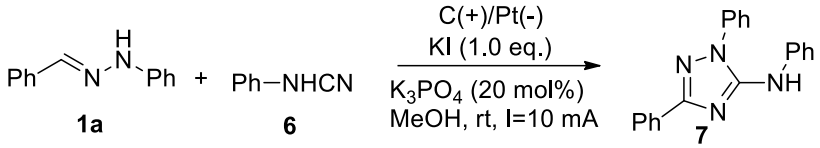
4. The electrochemical method by employing different hydrazones and cyanamides

To further broaden the scope of this protocol, several different type hydrazones including N'-benzylidene-4-methylbenzenesulfonohydrazide, N'-benzylidenebenzohydrazide and 4-methyl-N'-(3-phenylallylidene)benzenesulfonohydrazide were reacted with 2a under the standard conditions (Scheme s4-a), and no desired products was observed by LC-MS. When the functional cyanamides, such as N-phenylcyanamide and N-cyanobenzamide, was employed, only a small amount of products are produced according to LCMS (See Fig. S2 and Fig. S3).

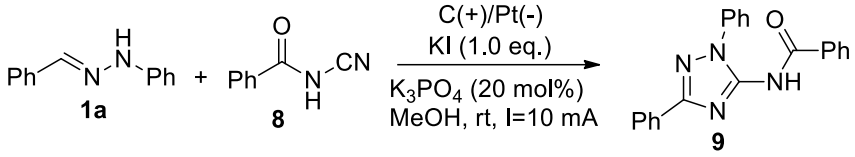
(a) Different hydrazones failed to apply with this reaction



(b) The reaction of **1a** and N-phenylcyanamide



(c)(The reaction of **1a** and N-cyanobenzamide



Scheme S4.

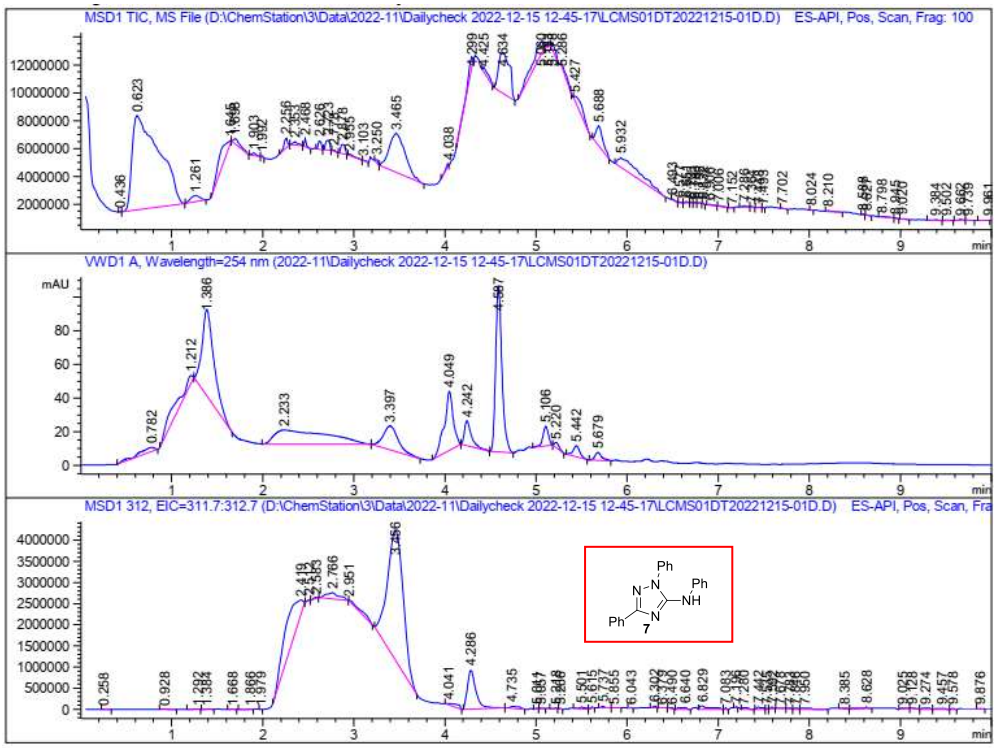


Fig. S2

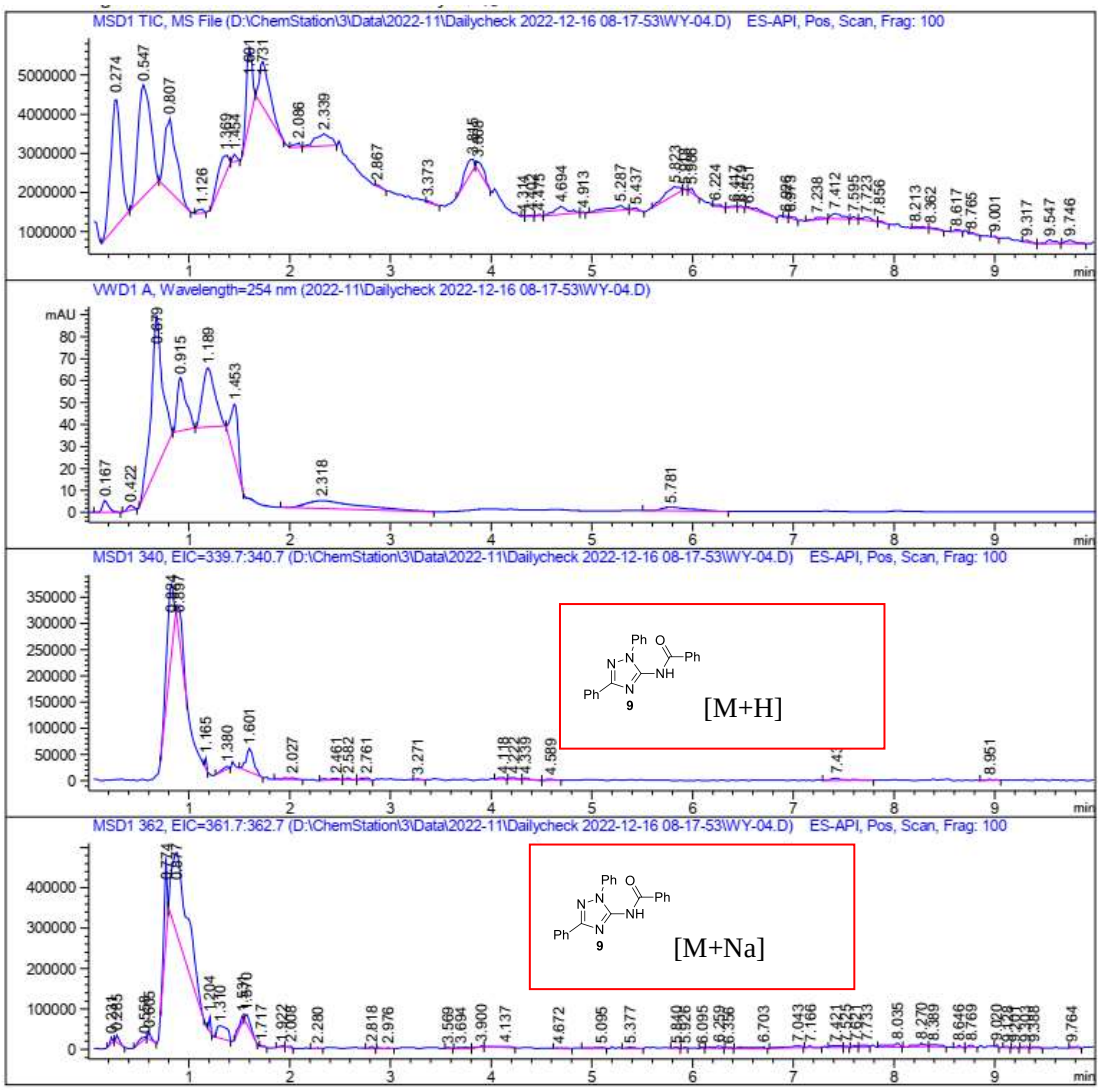
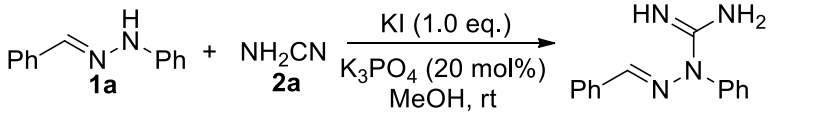


Fig. S3

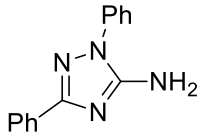
5. The investigation of the mechanism



No observed by LCMS

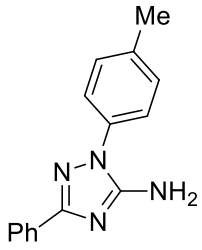
Control experiment was conducted by the employment of **1a** and **2a** under the standard conditions without current, and only starting material **1a** was observed by LCMS.

6. Spectra data of the products

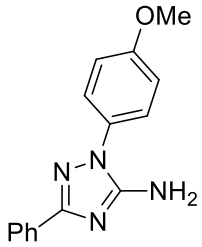


1,3-diphenyl-1H-1,2,4-triazol-5-amine, **3aa**, mp 146-147 °C, yellow solid, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.93 (m, 2H), 7.57 – 7.50 (m, 2H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.40 – 7.29 (m, 4H), 5.09 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.39, 154.23, 136.89,

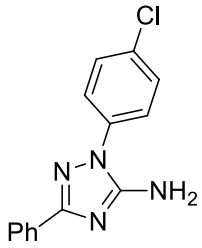
130.94, 129.91, 129.22, 128.55, 128.24, 126.18, 123.53. LCMS (ESI) calcd for $C_{14}H_{12}N_4$ (positive mode) 236.2, found 236.7.



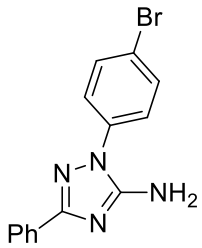
3-phenyl-1-(p-tolyl)-1H-1,2,4-triazol-5-amine, **3ab**, yellow oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 – 7.89 (m, 2H), 7.54 – 7.48 (m, 2H), 7.49 – 7.38 (m, 4H), 7.38 – 7.31 (m, 2H), 6.51 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.78, 137.07, 130.31, 129.24, 128.99, 126.00, 123.39, 40.18, 39.97, 39.76, 21.09. LCMS (ESI) calcd for $C_{15}H_{14}N_4$ (positive mode) 250.2, found 250.7.



1-(4-methoxyphenyl)-3-phenyl-1H-1,2,4-triazol-5-amine, **3ac**, mp 171-173 ^{o}C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 – 7.87 (m, 2H), 7.54 – 7.46 (m, 2H), 7.47 – 7.33 (m, 3H), 7.08 (d, J = 9.0 Hz, 2H), 6.41 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.79, 158.29, 155.86, 132.00, 130.60, 129.17, 128.98, 125.94, 125.56, 115.01, 55.94.LCMS (ESI) calcd for $C_{15}H_{14}N_4O$ (positive mode) 266.2, found 266.6.

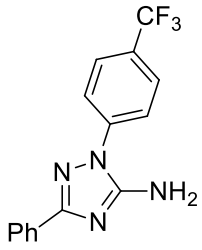


1-(4-chlorophenyl)-3-phenyl-1H-1,2,4-triazol-5-amine, **3ad**, mp 174-176 ^{o}C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (dq, J = 6.4, 1.2 Hz, 2H), 7.70 – 7.63 (m, 2H), 7.63 – 7.56 (m, 2H), 7.48 – 7.35 (m, 3H), 6.68 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.91, 155.98, 136.56, 131.76, 131.68, 129.86, 129.44, 129.03, 126.09, 125.10, 40.17, 39.96, 39.75. LCMS (ESI) calcd for $C_{14}H_{11}N_4Cl$ (positive mode) 270.7, found 270.6.

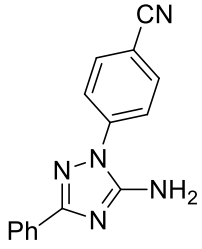


3-phenyl-[1,2,4]triazolo[4,3-a]pyridine, **3ae**, mp 165-167 ^{o}C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 – 7.90 (m, 2H), 7.77 – 7.67 (m, 2H), 7.64 – 7.56 (m, 2H), 7.53 – 7.33 (m, 3H), 6.68 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.94, 155.95, 136.98, 132.78, 131.66,

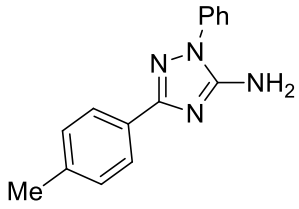
129.45, 129.04, 126.10, 125.33, 120.07, 40.17, 39.96, 39.75. LCMS (ESI) calcd for $C_{14}H_{11}N_4Br$ (positive mode) 315.1, found 314.7 and 316.7.



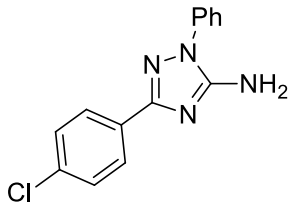
3-phenyl-1-(4-(trifluoromethyl)phenyl)-1H-1,2,4-triazol-5-amine, **3af**, mp 144-146 °C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (ddd, J = 8.3, 2.7, 1.5 Hz, 2H), 7.90 (s, 4H), 7.52 – 7.36 (m, 3H), 6.85 (d, J = 4.7 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.33, 156.21, 131.48, 129.61, 129.06, 127.11, 127.07, 126.19, 123.21, 40.15, 39.94, 39.73. ^{19}F NMR (376 MHz, DMSO-d_6) δ -60.85. LCMS (ESI) calcd for $C_{15}H_{11}F_3N_4$ (positive mode) 304.2, found 304.6.



4-(5-amino-3-phenyl-1H-1,2,4-triazol-1-yl)benzonitrile, **3ag**, yellow oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 – 8.00 (m, 2H), 7.99 – 7.94 (m, 2H), 7.90 – 7.84 (m, 2H), 7.51 – 7.38 (m, 3H), 6.90 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.49, 156.27, 141.36, 134.20, 131.33, 129.75, 129.10, 126.24, 123.01, 118.96, 109.27. LCMS (ESI) calcd for $C_{15}H_{11}N_5$ (positive mode) 261.2, found 261.7.

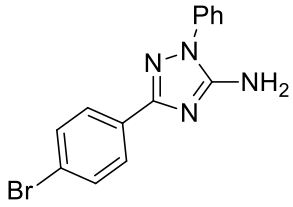


1-phenyl-3-(p-tolyl)-1H-1,2,4-triazol-5-amine, **3ah**, mp 140-142 °C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 (d, J = 8.0 Hz, 2H), 7.62 (dd, J = 8.4, 1.5 Hz, 2H), 7.54 (t, J = 7.9 Hz, 2H), 7.40 (d, J = 7.2 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 6.55 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.75, 155.72, 138.72, 137.79, 129.89, 129.57, 129.15, 127.47, 126.04, 123.24, 21.41. LCMS (ESI) calcd for $C_{15}H_{14}N_4$ (positive mode) 250.2, found 250.7.

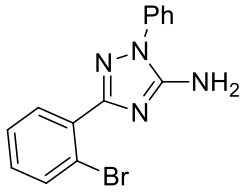


3-(4-chlorophenyl)-1-phenyl-1H-1,2,4-triazol-5-amine, **3ai**, mp 155-156 °C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 – 7.93 (m, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.59 – 7.47 (m, 4H), 7.45 – 7.34 (m, 1H), 6.62 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.79, 155.97, 137.63, 133.90, 130.73, 129.93, 129.13, 127.76, 127.70, 123.40. LCMS (ESI) calcd for $C_{14}H_{11}N_4Cl$

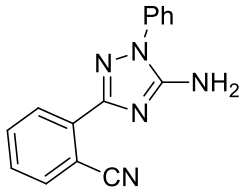
(positive mode) 270.7, found 270.6.



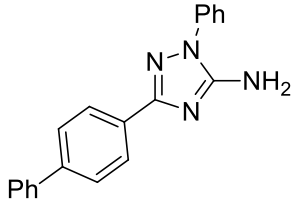
3-(4-bromophenyl)-1-phenyl-1H-1,2,4-triazol-5-amine, **3aj**, mp 177-179 °C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 – 7.86 (m, 2H), 7.69 – 7.57 (m, 4H), 7.54 (dd, *J* = 8.6, 7.1 Hz, 2H), 7.46 – 7.35 (m, 1H), 6.62 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.84, 155.96, 137.62, 132.05, 131.08, 129.93, 128.05, 127.71, 123.40, 122.56. LCMS (ESI) calcd for $C_{14}H_{11}N_4Br$ (positive mode) 315.1, found 314.5 and 316.5.



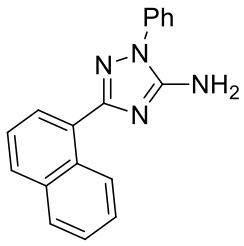
3-(2-bromophenyl)-1-phenyl-1H-1,2,4-triazol-5-amine, **3ak**, mp 160-162 °C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.74 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.55 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.43 – 7.37 (m, 1H), 7.34 (td, *J* = 7.7, 1.8 Hz, 1H), 6.62 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.48, 155.26, 137.65, 134.21, 132.89, 131.80, 130.81, 129.94, 127.99, 127.58, 123.17, 121.26. LCMS (ESI) calcd for $C_{14}H_{11}N_4Br$ (positive mode) 315.1, found 314.5 and 316.5.



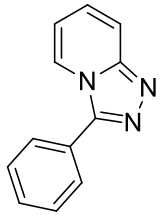
2-(5-amino-1-phenyl-1H-1,2,4-triazol-3-yl)benzonitrile, **3al**, mp 213-215 °C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.92 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.79 (td, *J* = 7.8, 1.4 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.64 – 7.52 (m, 3H), 7.48 – 7.40 (m, 1H), 6.75 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.53, 155.86, 137.47, 135.26, 133.77, 133.69, 130.00, 129.87, 128.92, 127.84, 123.21, 118.91, 116.95. LCMS (ESI) calcd for $C_{15}H_{11}N_5$ (positive mode) 261.2, found 261.7.



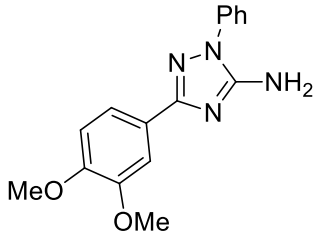
3-([1,1'-biphenyl]-4-yl)-1-phenyl-1H-1,2,4-triazol-5-amine, **3am**, yellow oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.75 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.52 – 7.39 (m, 5H), 7.38 – 7.25 (m, 9H), 6.40 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 130.90, 130.43, 129.72, 129.36, 129.27, 128.19, 127.62, 127.17, 127.02, 122.70, 116.95. LCMS (ESI) calcd for $C_{20}H_{16}N_4$ (positive mode) 312.3, found 312.7.



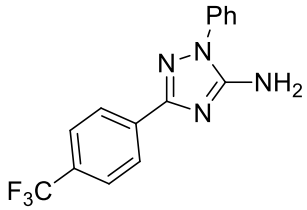
3-(naphthalen-1-yl)-1-phenyl-1H-1,2,4-triazol-5-amine, **3an**, yellow oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.35 – 9.20 (m, 1H), 8.22 (dt, J = 7.3, 1.4 Hz, 1H), 7.99 (dt, J = 8.0, 1.7 Hz, 2H), 7.84 – 7.68 (m, 2H), 7.68 – 7.52 (m, 5H), 7.52 – 7.35 (m, 1H), 6.71 (d, J = 2.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.47, 155.25, 137.77, 134.11, 130.70, 130.00, 129.85, 128.85, 128.57, 127.67, 127.63, 127.17, 127.04, 126.34, 125.81, 123.38. LCMS (ESI) calcd for $C_{18}H_{14}N_4$ (positive mode) 286.3, found 286.7.



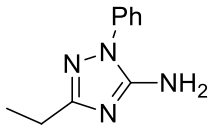
3-phenyl-[1,2,4]triazolo[4,3-a]pyridine, **3at**, mp 140-142 ^{o}C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.57 (dt, J = 7.0, 1.1 Hz, 1H), 7.94 – 7.79 (m, 3H), 7.67 – 7.51 (m, 3H), 7.51 – 7.36 (m, 1H), 7.06 – 6.97 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.46, 146.45, 130.44, 129.74, 128.55, 128.40, 127.05, 124.35, 116.11, 114.92.



3-(3,4-dimethoxyphenyl)-1-phenyl-1H-1,2,4-triazol-5-amine, **3au**, mp 158-160 ^{o}C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 – 7.59 (m, 2H), 7.56 – 7.49 (m, 3H), 7.47 (d, J = 1.9 Hz, 1H), 7.40 (d, J = 7.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 6.52 (s, 2H), 3.80 (d, J = 2.6 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.64, 155.67, 149.92, 149.05, 137.79, 129.89, 127.45, 124.59, 123.30, 118.77, 112.08, 109.26, 55.96, 55.81. LCMS (ESI) calcd for $C_{16}H_{16}N_4O_2$ (positive mode) 296.3, found 296.6.

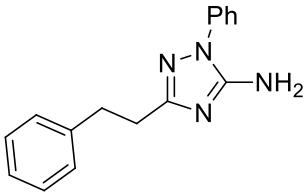


1-phenyl-3-(4-(trifluoromethyl)phenyl)-1H-1,2,4-triazol-5-amine, **3av**, mp 202-204 ^{o}C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 – 8.06 (m, 2H), 7.90 – 7.76 (m, 2H), 7.71 – 7.60 (m, 2H), 7.60 – 7.53 (m, 2H), 7.51 – 7.35 (m, 1H), 6.68 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 156.12, 129.97, 127.90, 126.60, 126.09, 126.05, 123.53, 40.17, 39.97, 39.76. ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.06. LCMS (ESI) calcd for $C_{15}H_{11}F_3N_4$ (positive mode) 304.2, found 304.6.

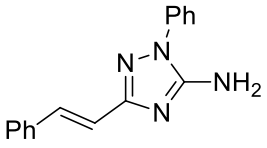


3-ethyl-1-phenyl-1H-1,2,4-triazol-5-amine, **3aw**, mp 114-116 ^{o}C, yellow solid,

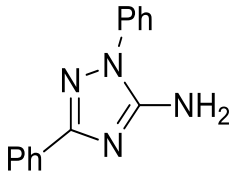
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 – 7.45 (m, 4H), 7.36 – 7.29 (m, 1H), 6.32 (s, 2H), 2.47 (q, J = 7.6 Hz, 2H), 1.18 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.60, 155.14, 137.93, 129.78, 126.97, 122.79, 21.81, 12.76. LCMS (ESI) calcd for $C_{10}H_{12}N_4$ (positive mode) 188.2, found 188.7.



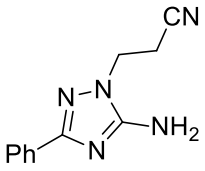
3-phenethyl-1-phenyl-1H-1,2,4-triazol-5-amine, **3ax**, yellow oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 – 7.43 (m, 4H), 7.38 – 7.23 (m, 5H), 7.23 – 7.14 (m, 1H), 6.37 (s, 2H), 2.97 (dd, J = 9.5, 6.5 Hz, 2H), 2.82 – 2.70 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.95, 155.18, 141.98, 137.89, 129.80, 128.75, 127.03, 126.35, 122.80, 33.90, 30.35. LCMS (ESI) calcd for $C_{16}H_{16}N_4$ (positive mode) 264.3, found 264.7.



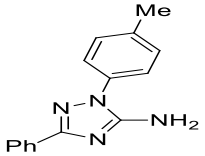
1-phenyl-3-styryl-1H-1,2,4-triazol-5-amine, **3ay**, mp 203-205 ^{o}C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.65 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.53 (dd, J = 8.7, 7.1 Hz, 2H), 7.39 (td, J = 6.6, 5.9, 2.3 Hz, 3H), 7.34 – 7.28 (m, 2H), 7.01 (d, J = 16.2 Hz, 1H), 6.53 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.75, 155.40, 137.70, 136.70, 132.80, 129.91, 129.25, 128.66, 127.42, 127.28, 123.04, 119.03. LCMS (ESI) calcd for $C_{16}H_{14}N_4$ (positive mode) 262.3, found 262.6.



3-(furan-2-yl)-1-phenyl-1H-1,2,4-triazol-5-amine, **3az**, mp 149-151 ^{o}C, yellow solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 (dd, J = 1.8, 0.8 Hz, 1H), 7.59 (dd, J = 8.6, 1.4 Hz, 2H), 7.53 (dd, J = 8.8, 7.0 Hz, 2H), 7.41 (d, J = 7.2 Hz, 1H), 6.82 (dd, J = 3.4, 0.9 Hz, 1H), 6.62 – 6.58 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.54, 152.42, 147.15, 143.91, 137.54, 129.93, 127.63, 123.27, 112.00, 109.27. LCMS (ESI) calcd for $C_{12}H_{10}N_4O$ (positive mode) 226.2, found 226.6.

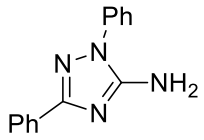


3-(5-amino-3-phenyl-1H-1,2,4-triazol-1-yl)propanenitrile, **3ba**, mp 239-242 ^{o}C, white solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, J = 7.4 Hz, 1H), 7.49 – 7.33 (m, 2H), 6.49 (s, 1H), 4.26 – 4.15 (m, 1H), 3.04 – 2.95 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.17, 156.55, 132.19, 128.98, 128.90, 125.82, 118.91, 41.94, 17.83. LCMS (ESI) calcd for $C_{11}H_{11}N_5$ (positive mode) 213.2, found 213.6.

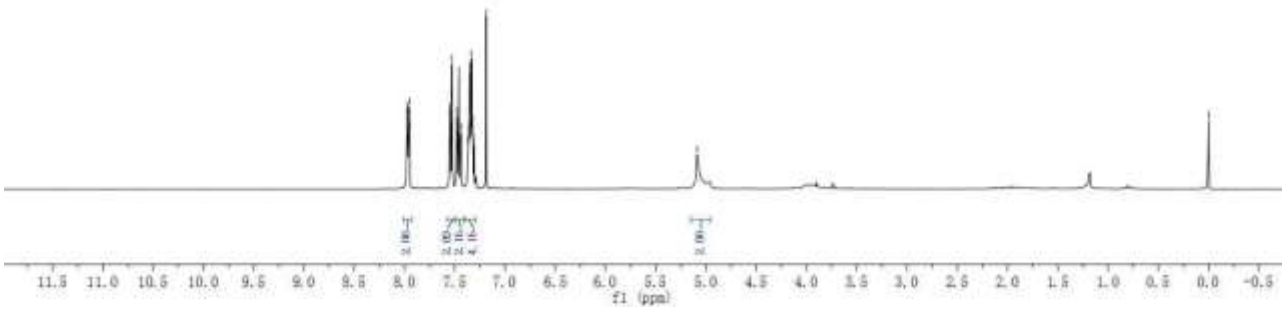


1-(tert-butyl)-3-phenyl-1H-1,2,4-triazol-5-amine, 3bb, mp 101-104 ^{o}C, white

solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 – 7.77 (m, 2H), 7.43 – 7.24 (m, 3H), 5.99 (s, 2H), 1.56 (d, J = 1.2 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.26, 132.64, 128.80, 128.53, 125.62, 116.92, 57.55, 28.87. LCMS (ESI) calcd for $C_{12}H_{16}N_4$ (positive mode) 216.2, found 216.7


Ph
N
N
NH2
N
Ph

,**3aa**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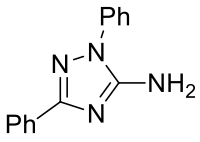
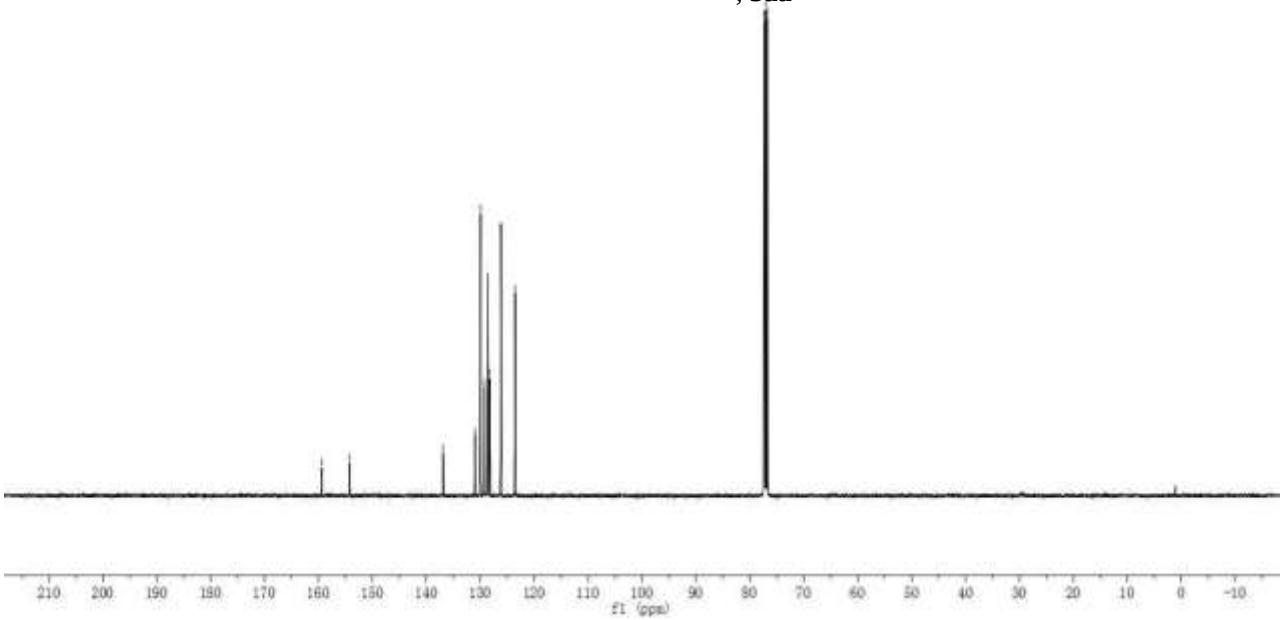
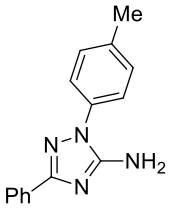
f1 (ppm)

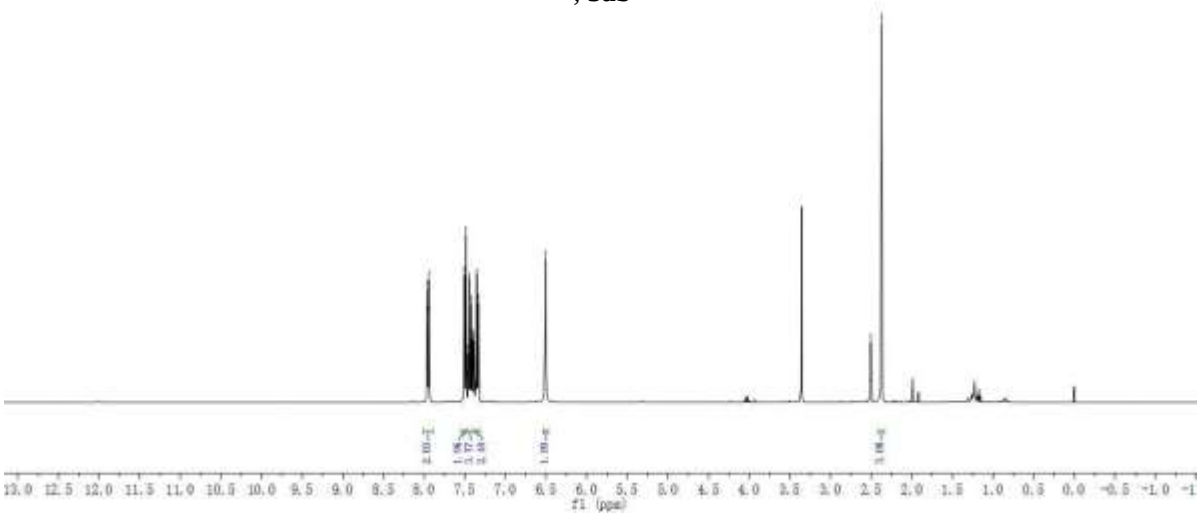

Ph
N
N
NH2
N
Ph

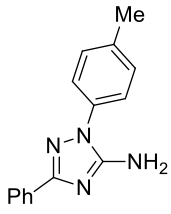
, **3aa**


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

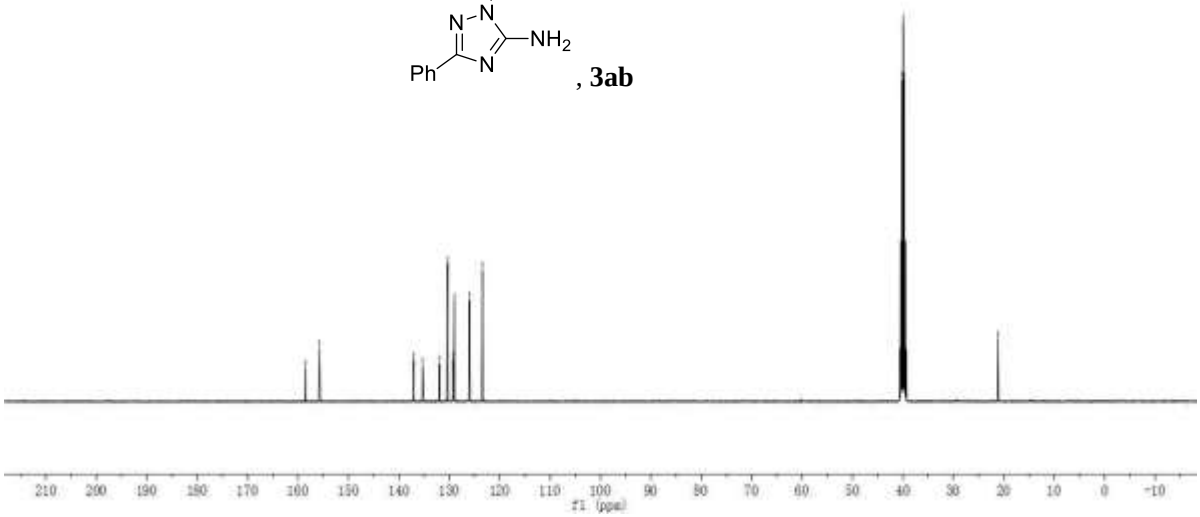


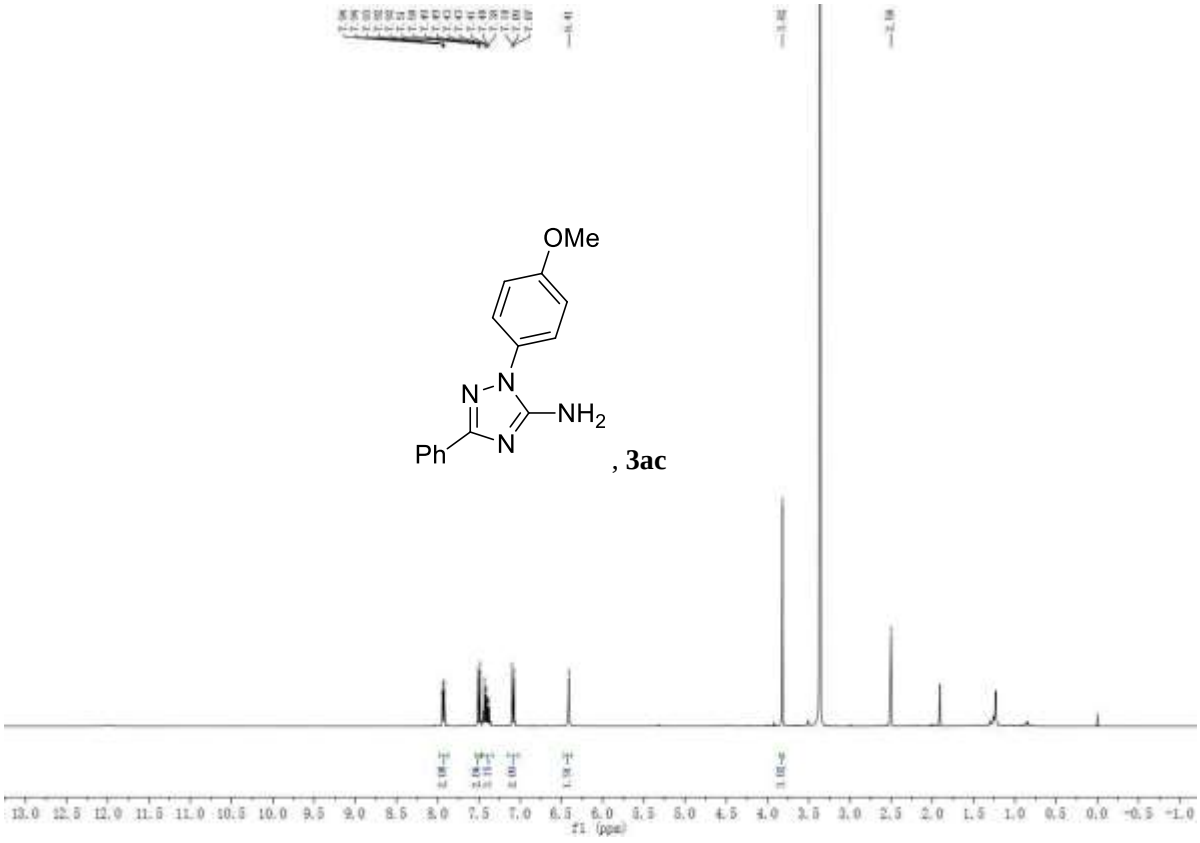
, 3ab





, 3ab





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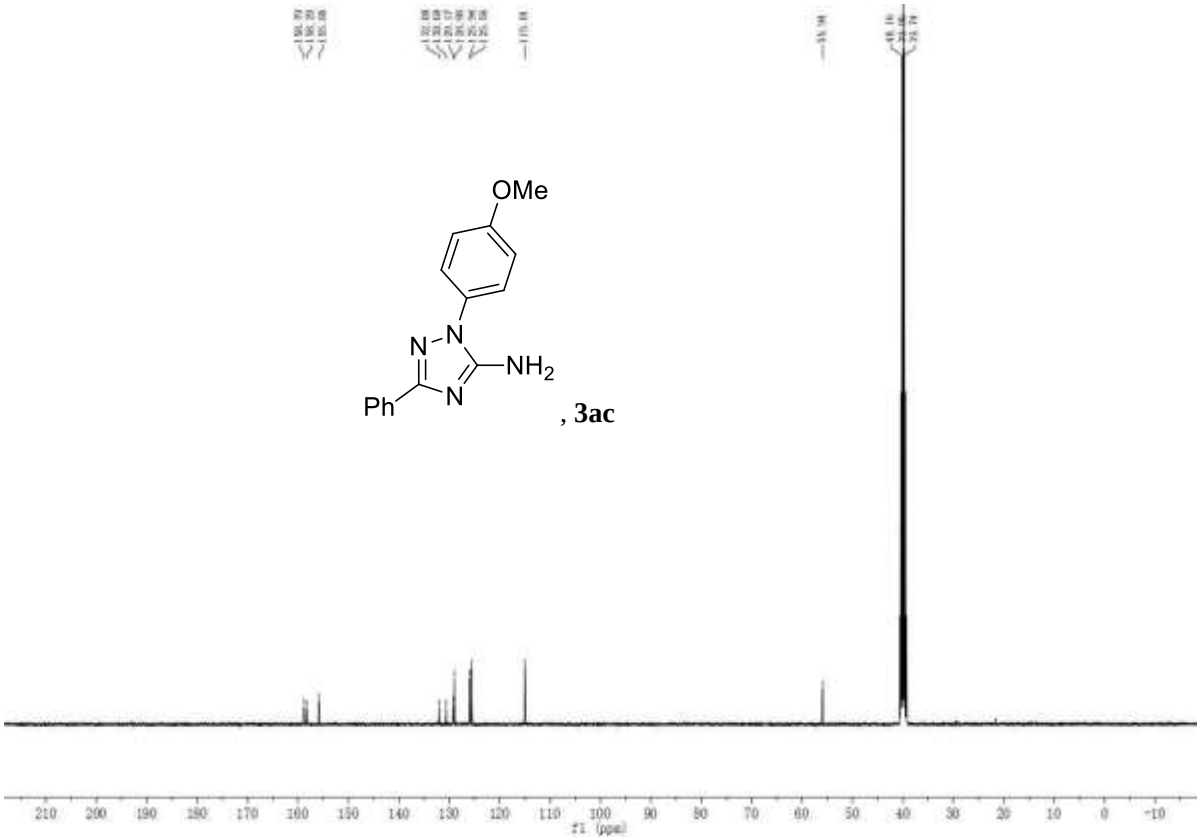
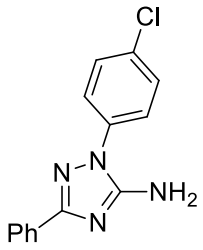


, **3ac**



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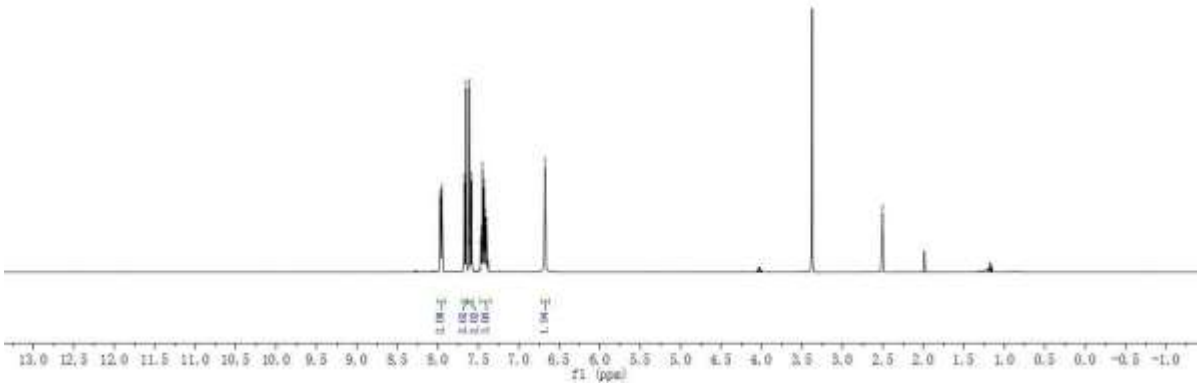
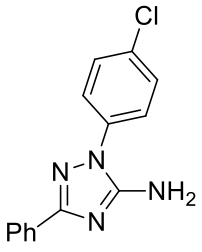
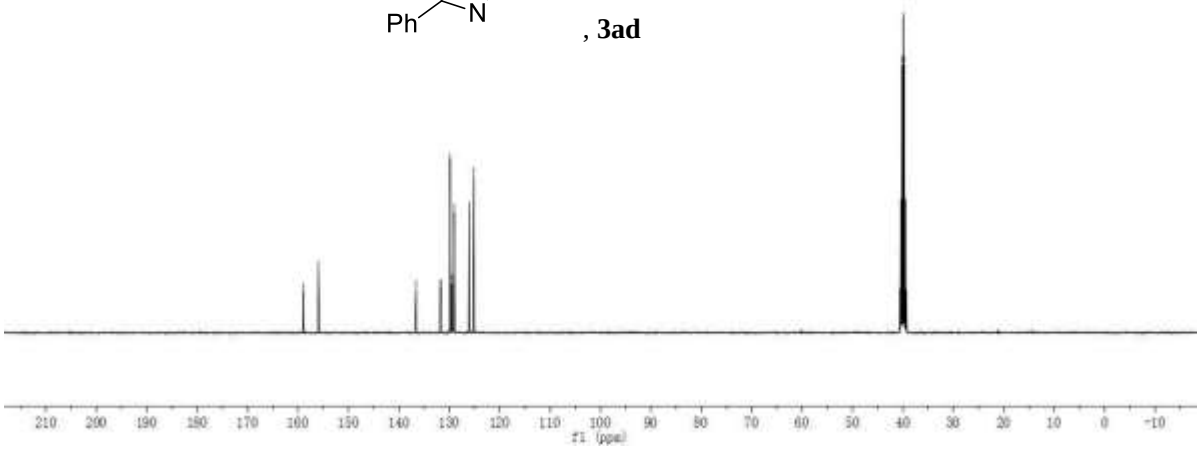
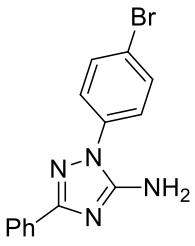


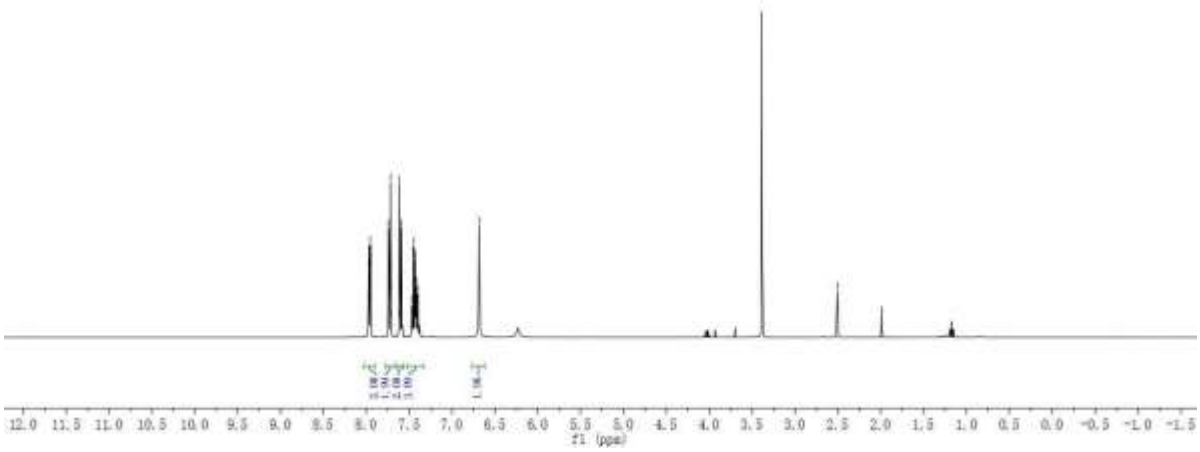


, **3ad**




Br
N
N
NH2
Ph
N

, **3ae**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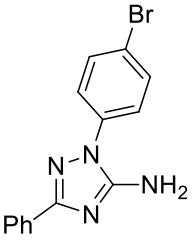
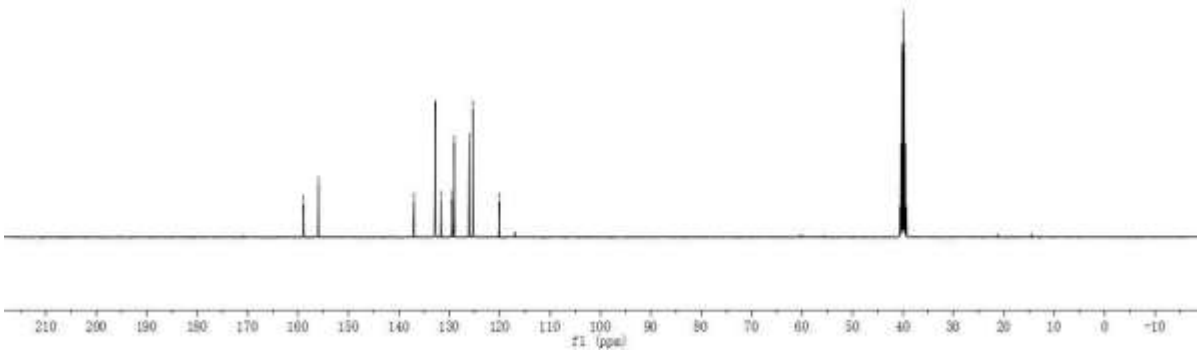
f1 (ppm)


Br
N
N
NH2
Ph
N

, **3ae**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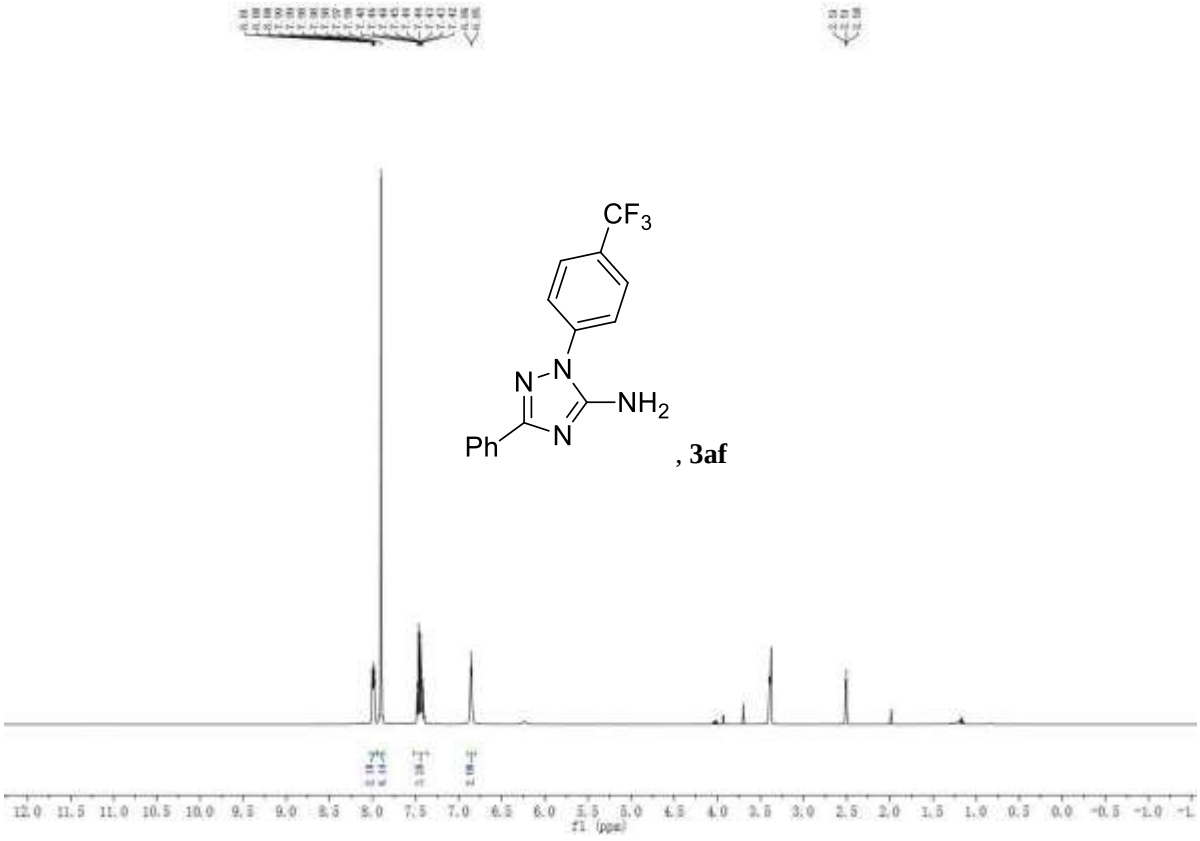
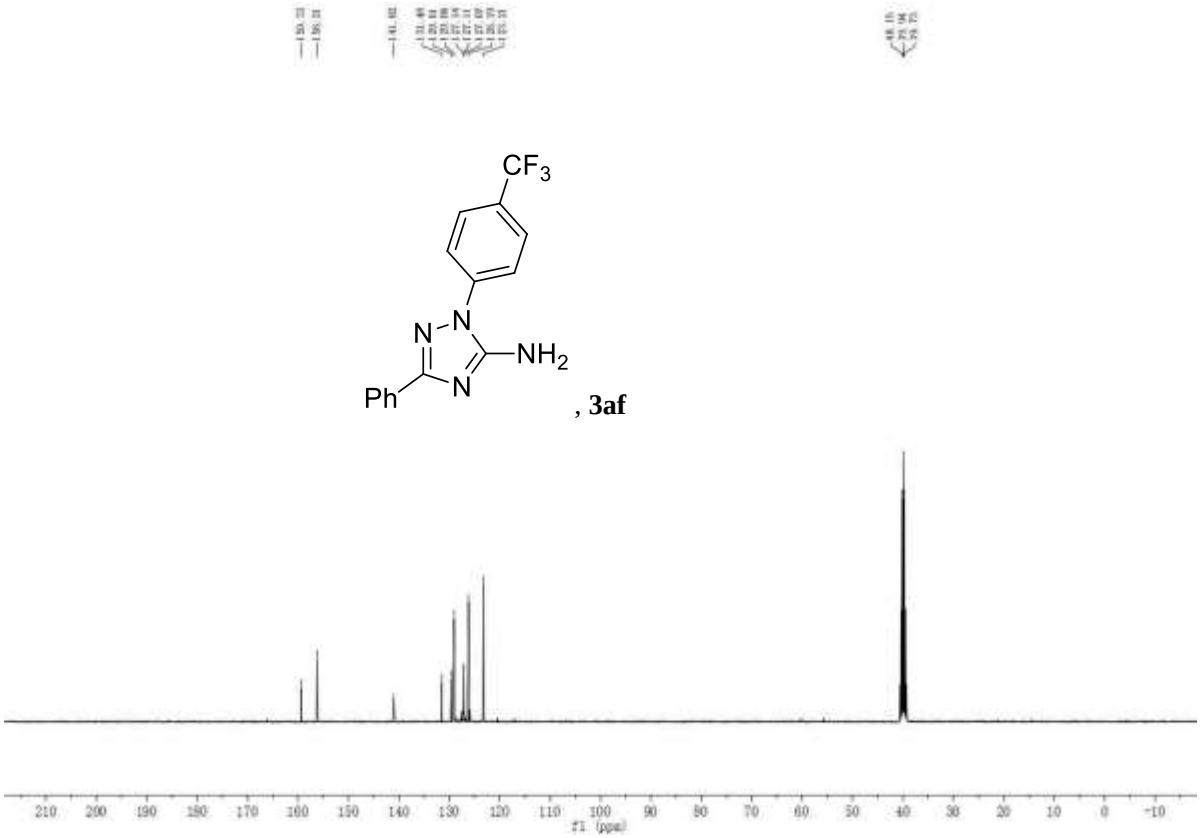
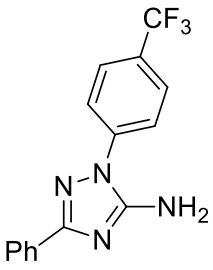
f1 (ppm)


CF3
N
N
NH2
N
Ph
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

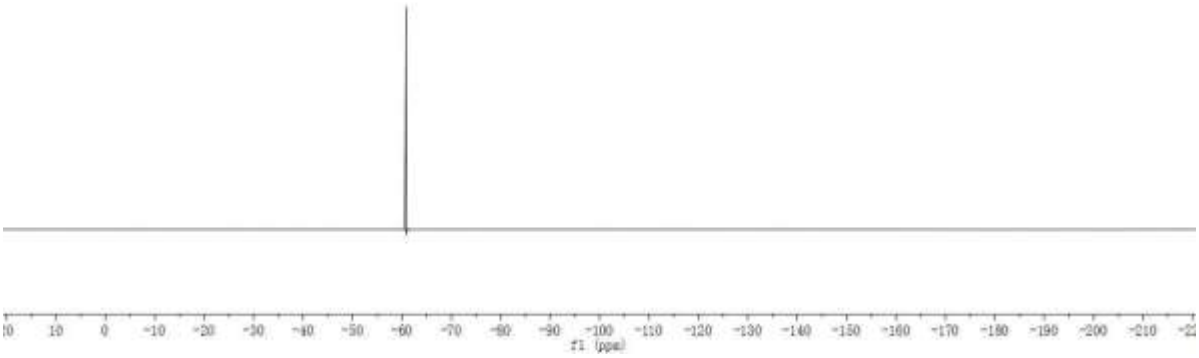
, **3af**

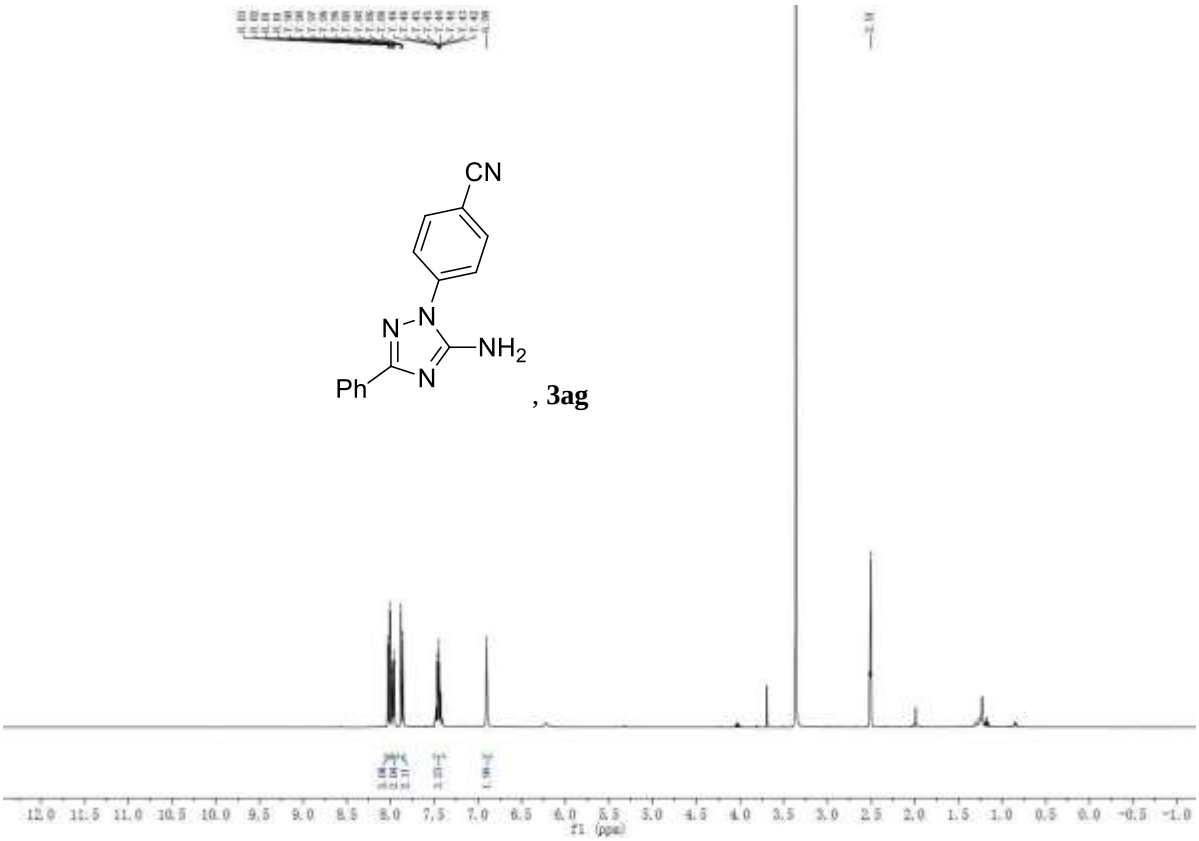

CF3
N
N
NH2
N
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

, **3af**

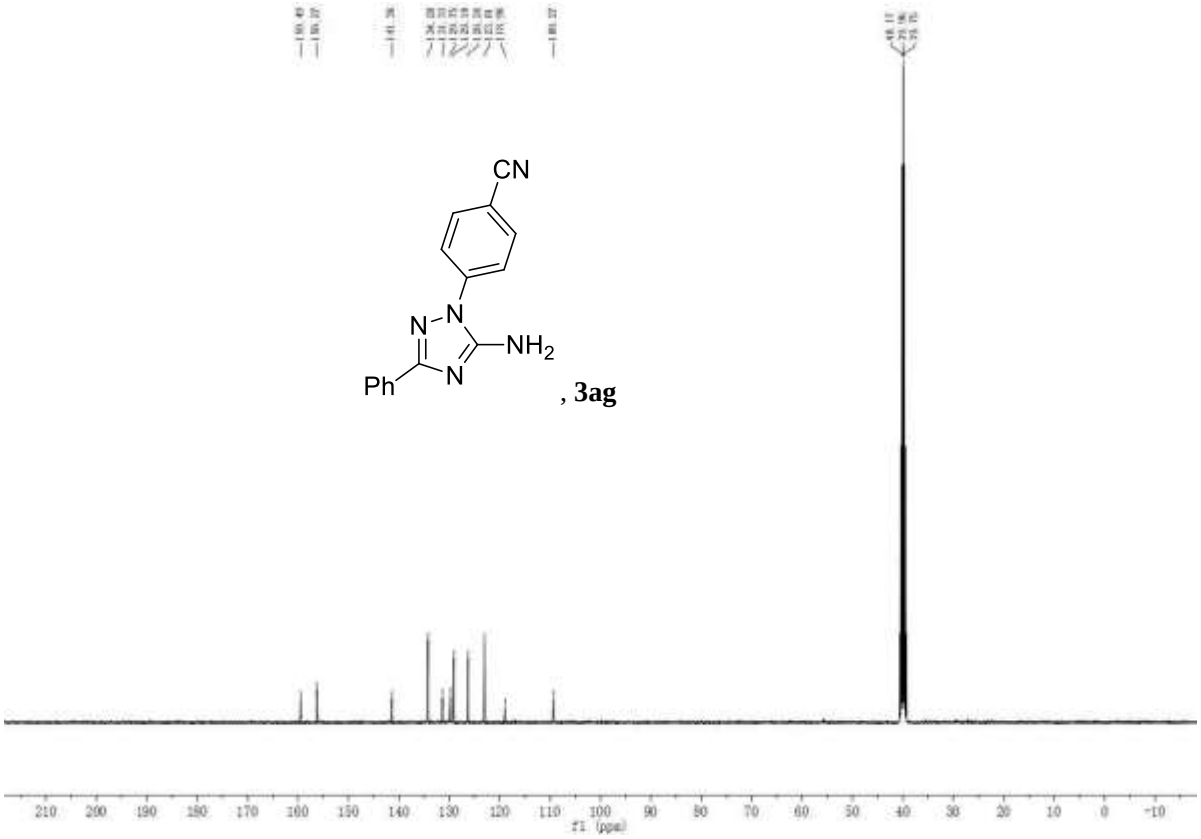


, **3af**





, **3ag**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N
NH2
Ph
N
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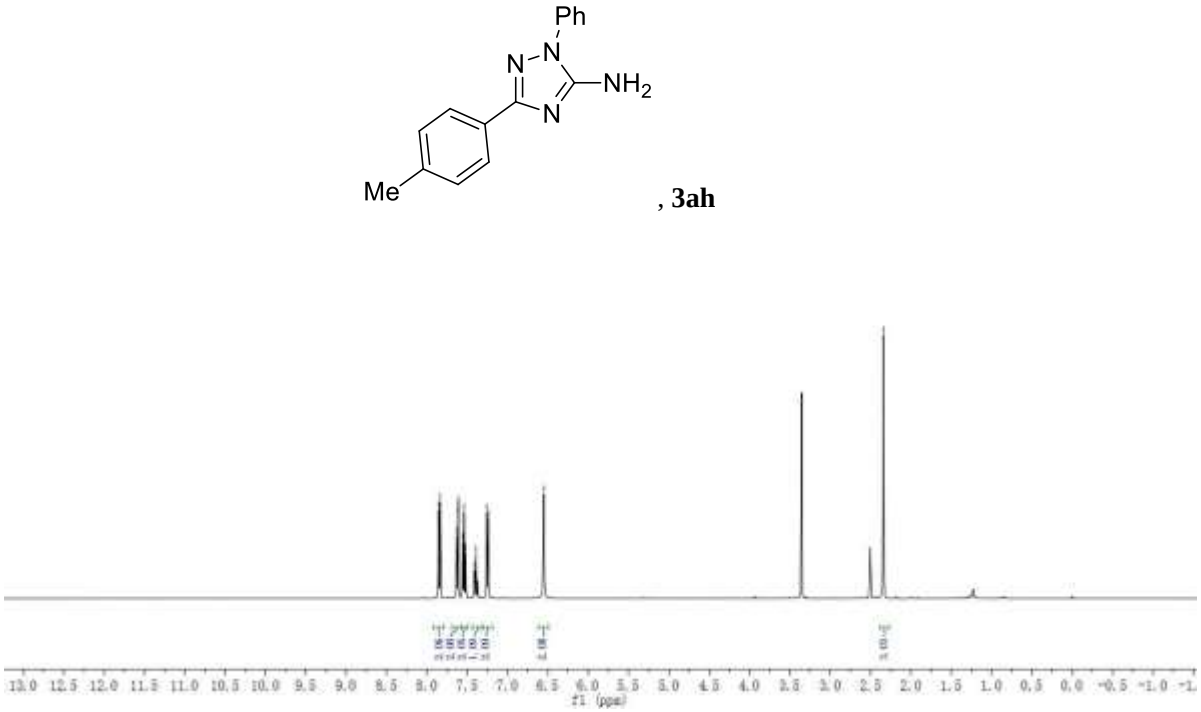
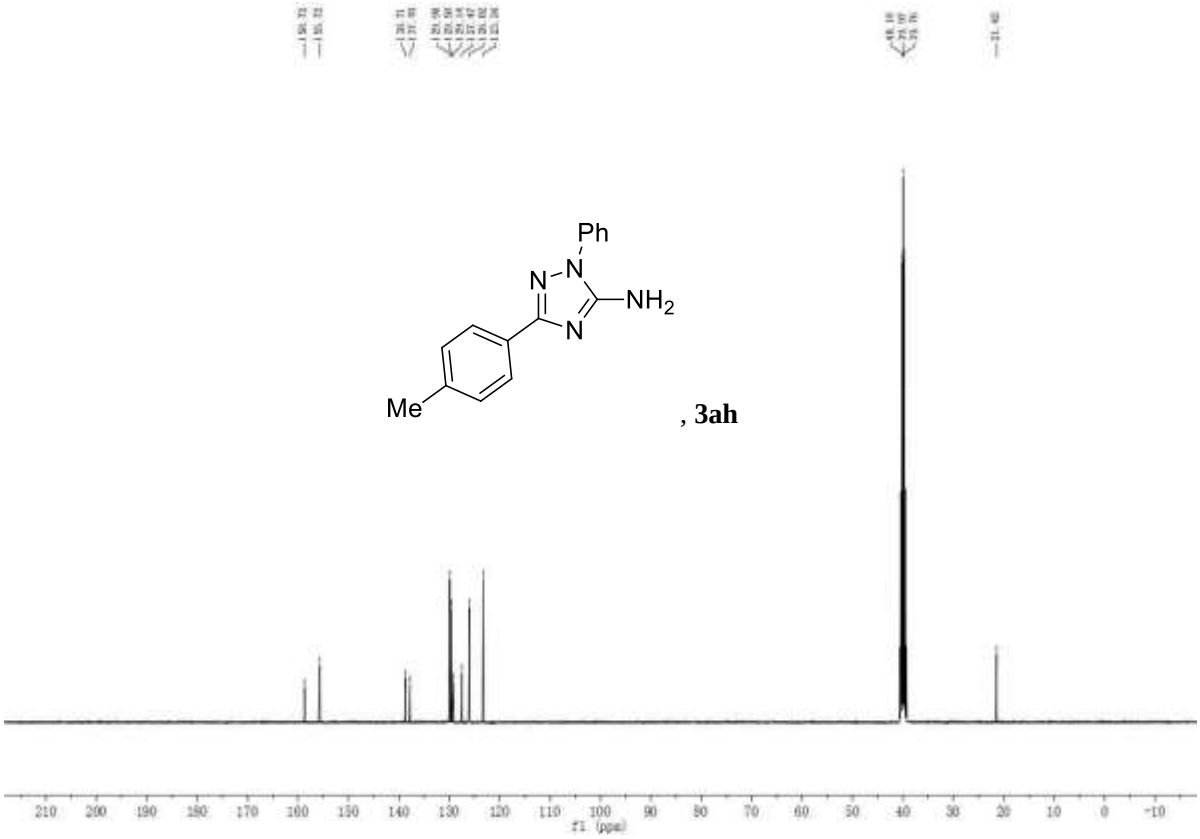
f1 (ppm)

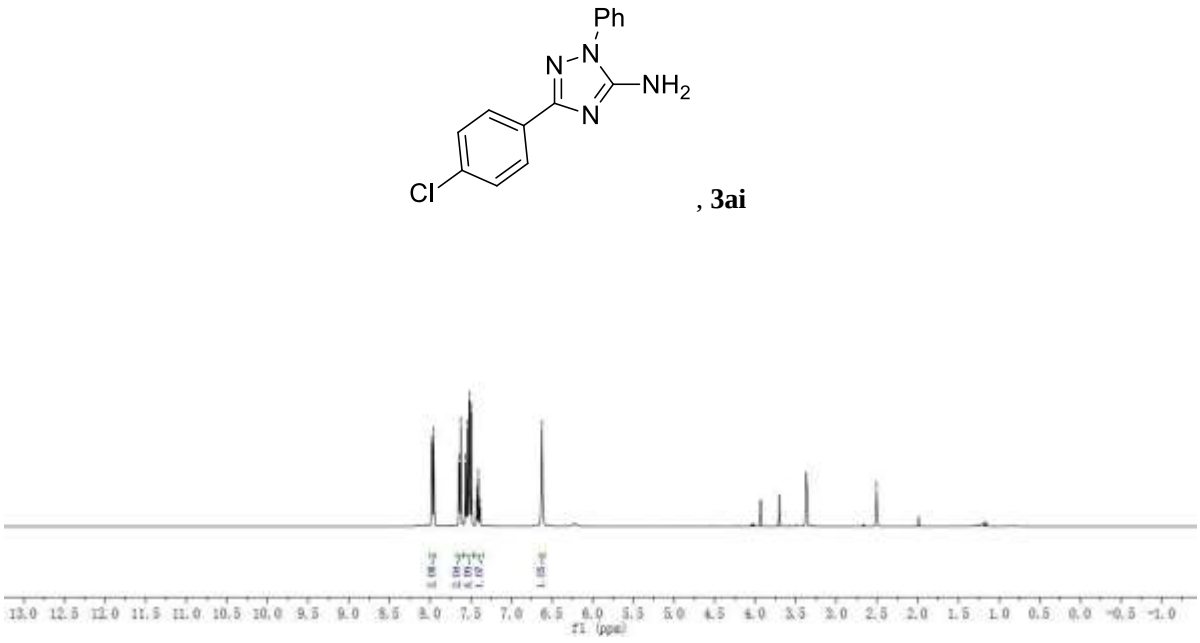
, **3ag**


Ph
N
N
NH2
N
Me
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

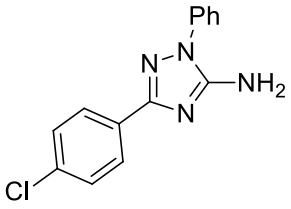
, **3ah**


Ph
N
N
NH2
N
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

, **3ah**


Ph
N
N
NH2
N
Cl
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

, **3ai**



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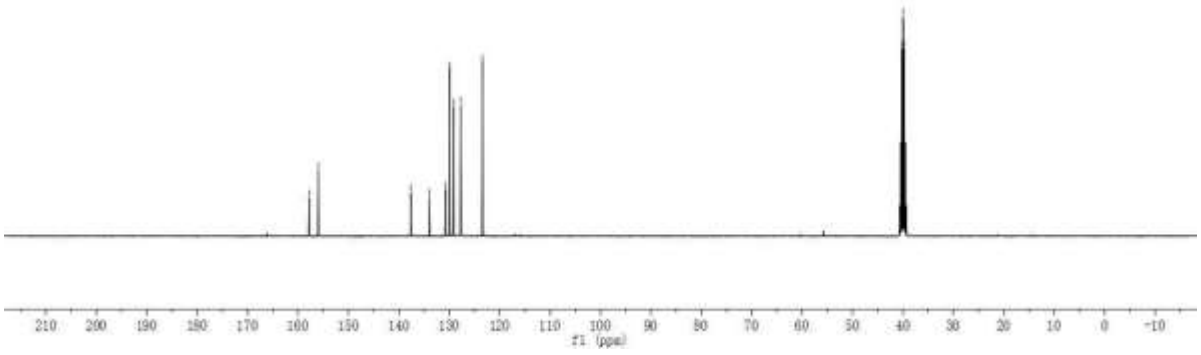

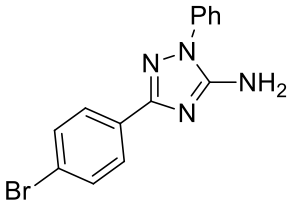

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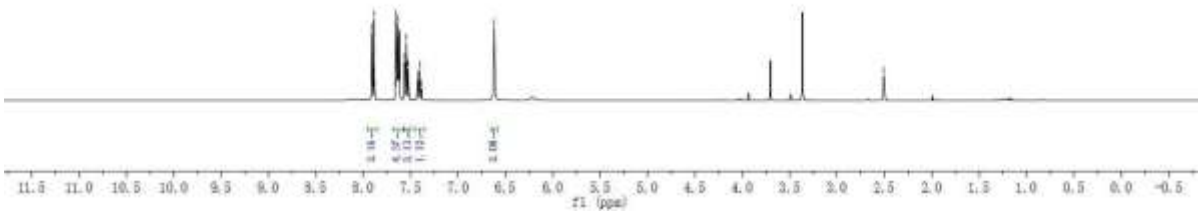

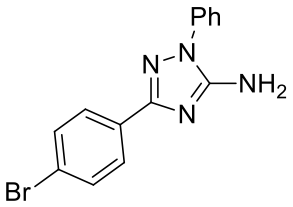

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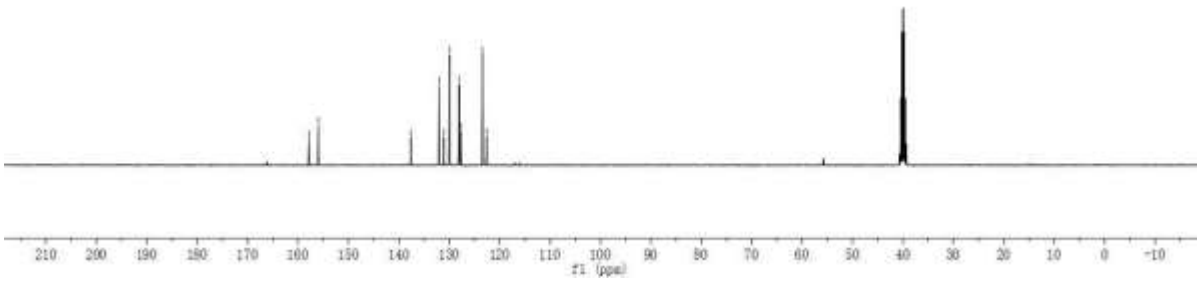

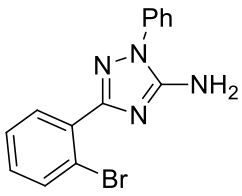

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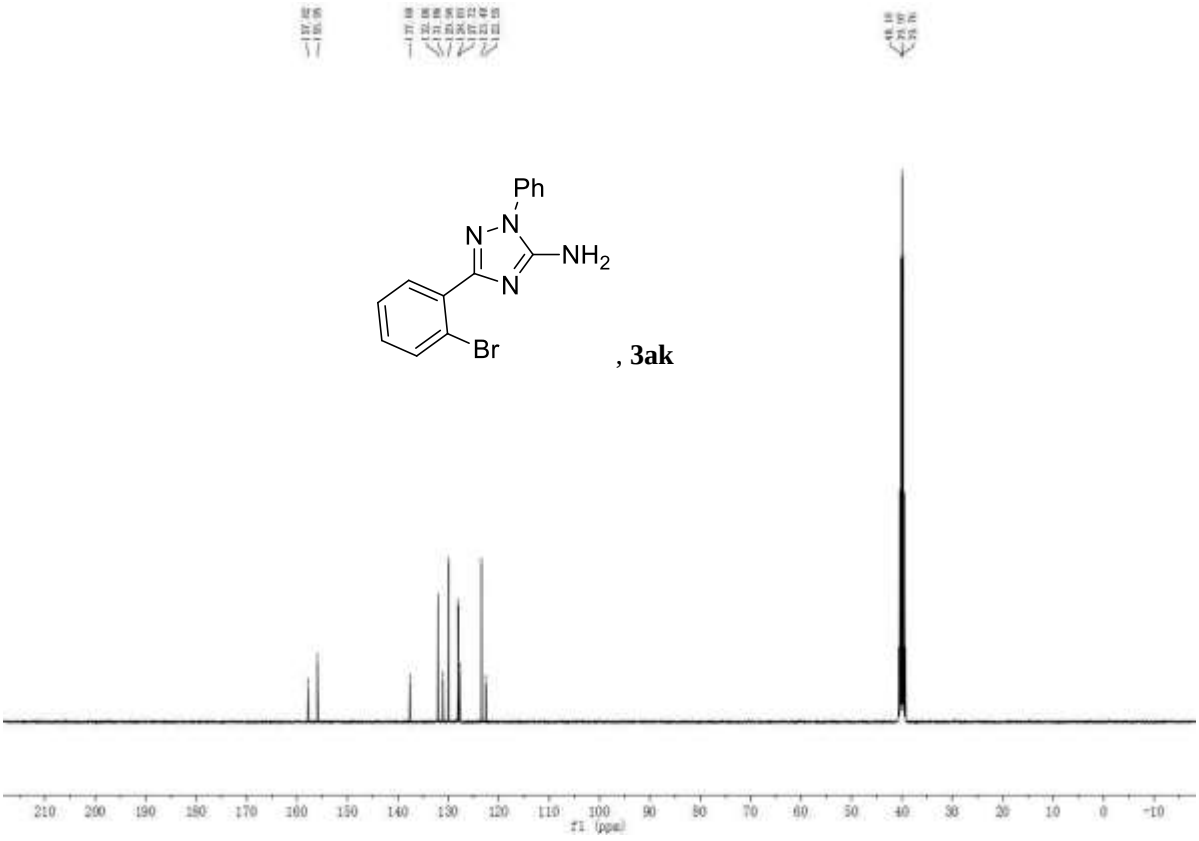
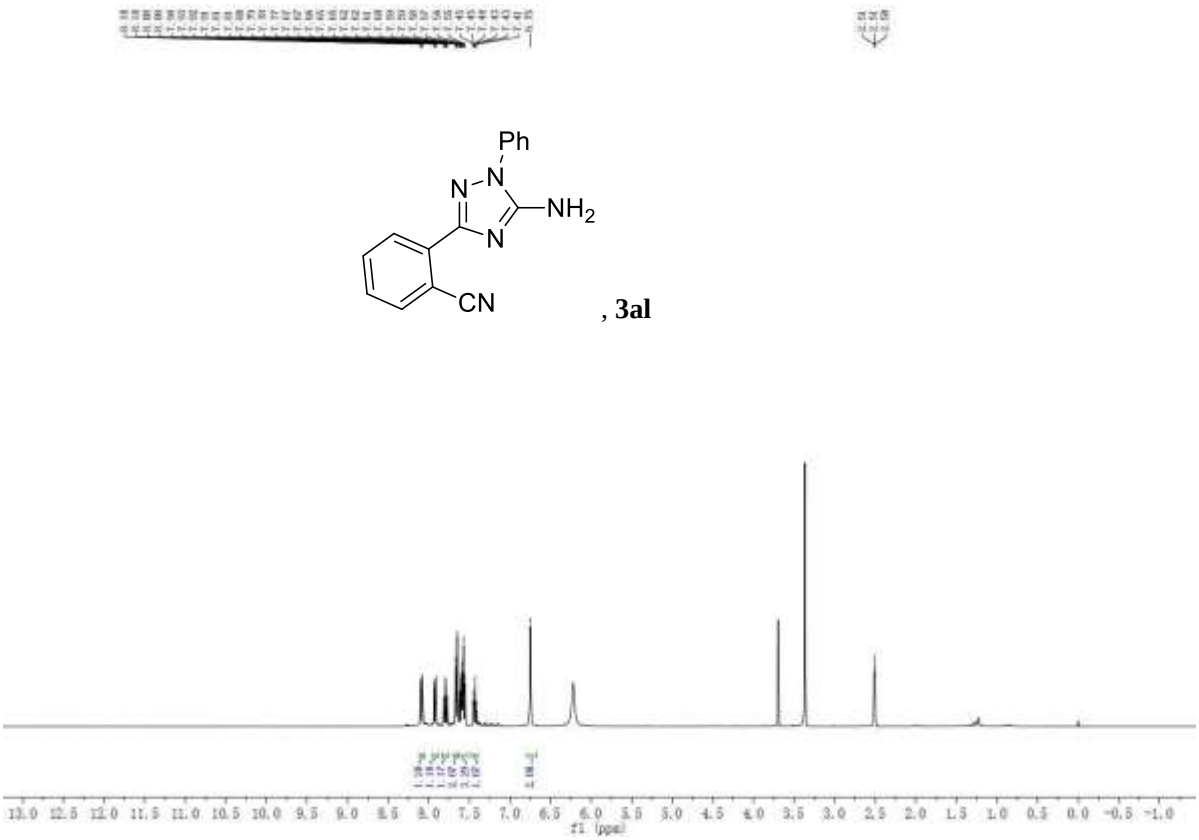
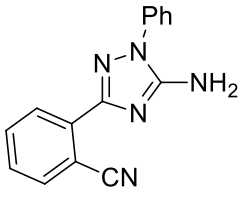

Ph
N
N
NH2
N
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

, **3ak**


Ph
N
N
NH2
N
CN
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

, **3al**



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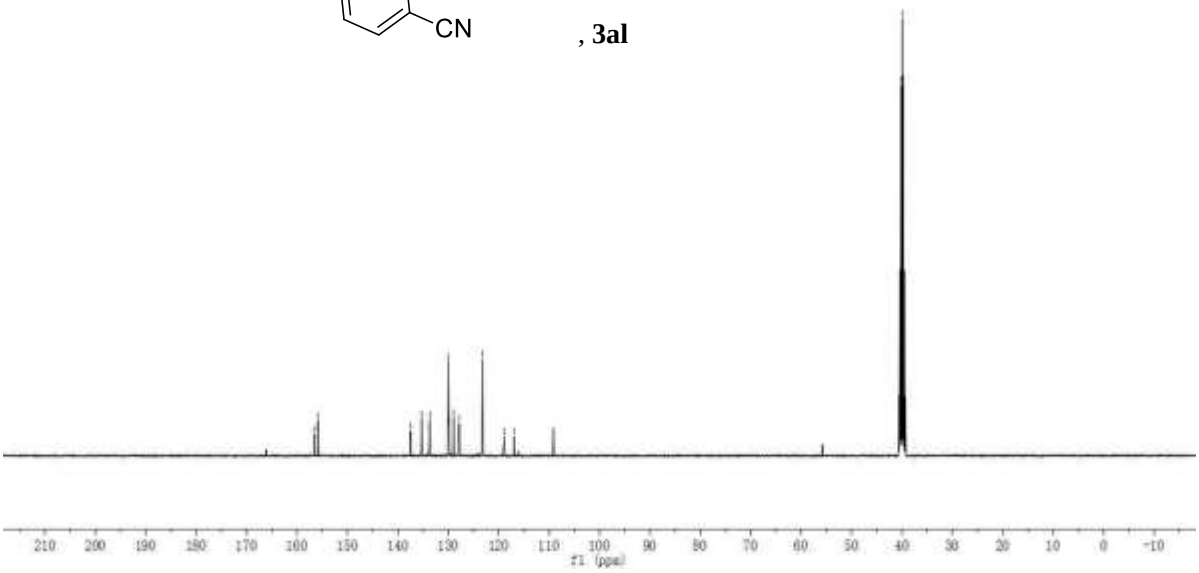

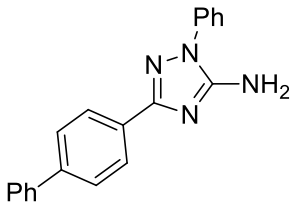

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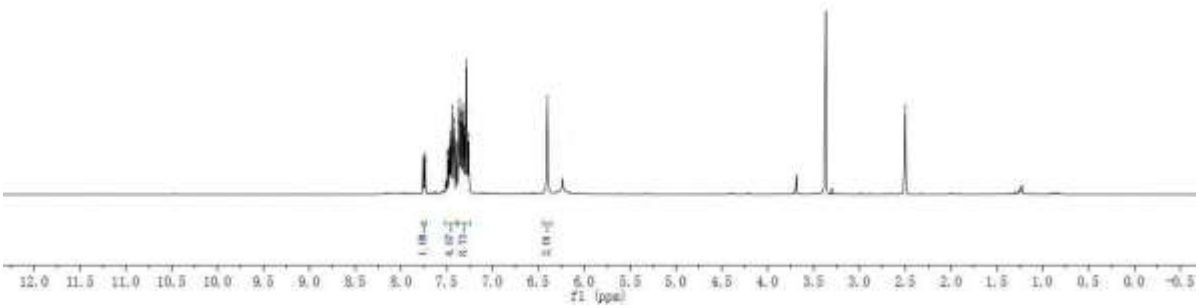

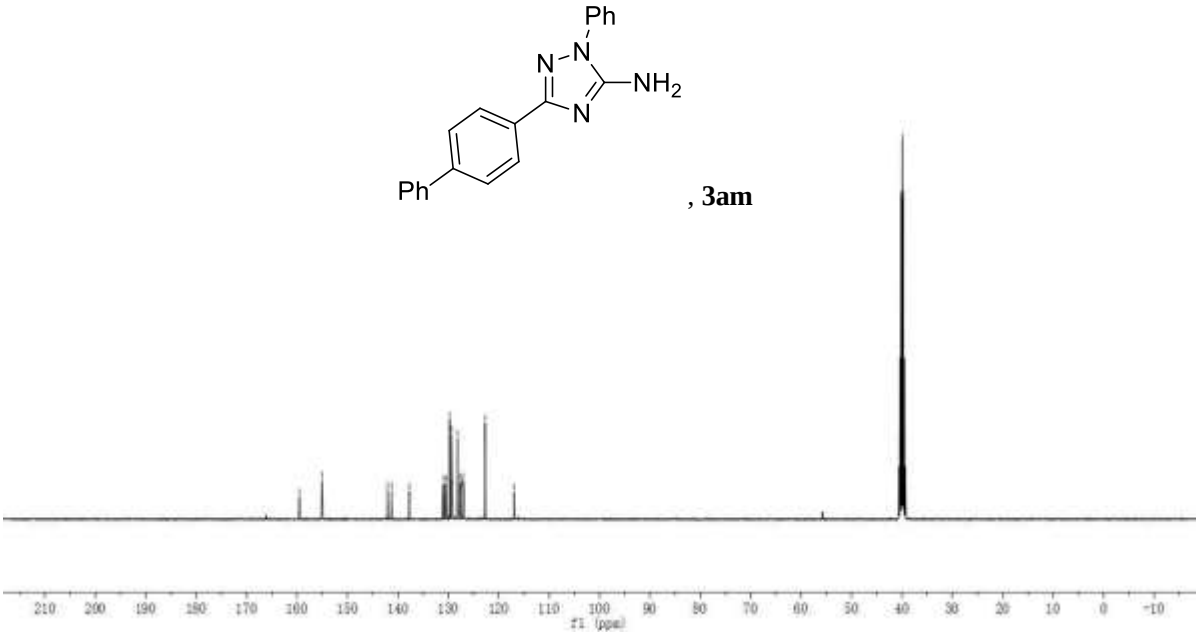

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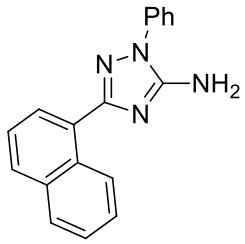

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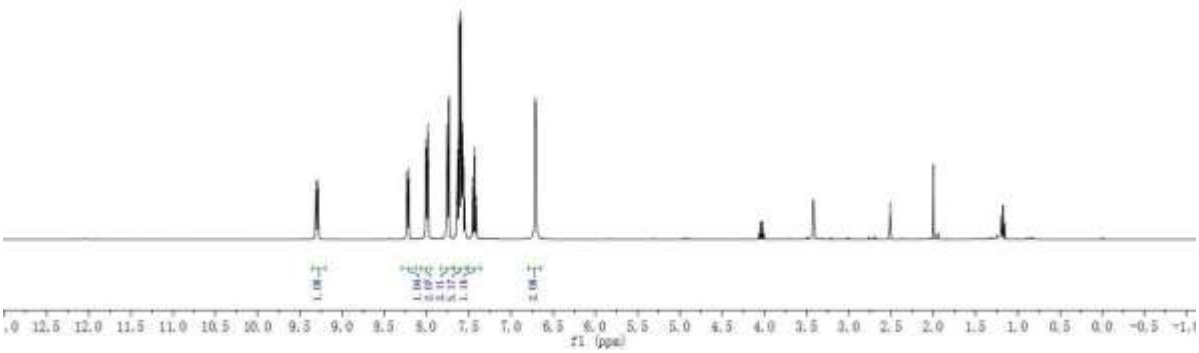
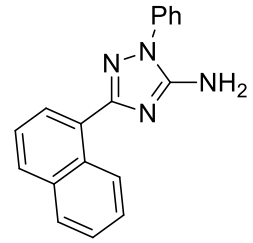
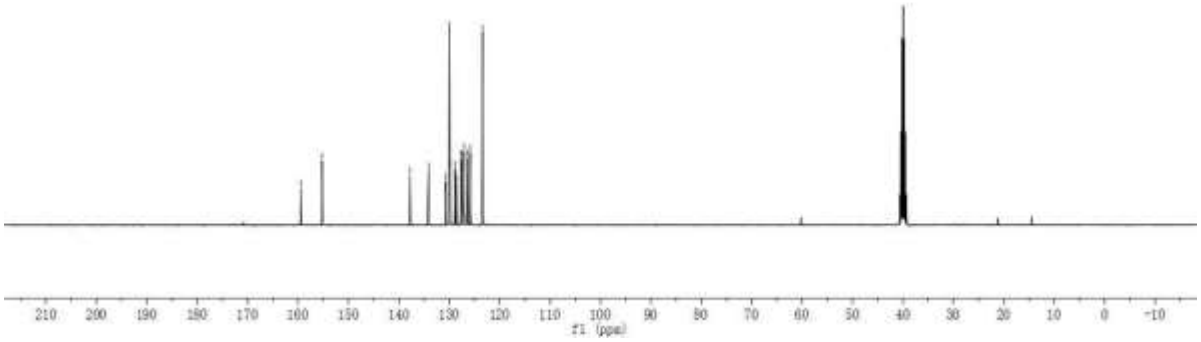
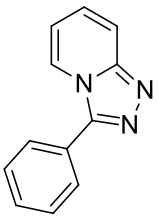


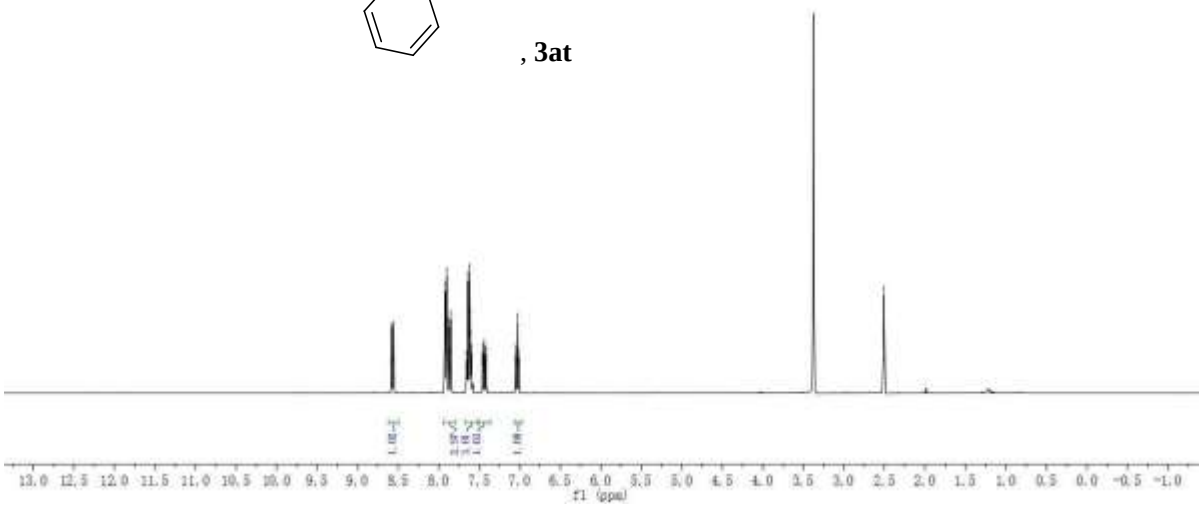

Ph
N
N
NH2
N

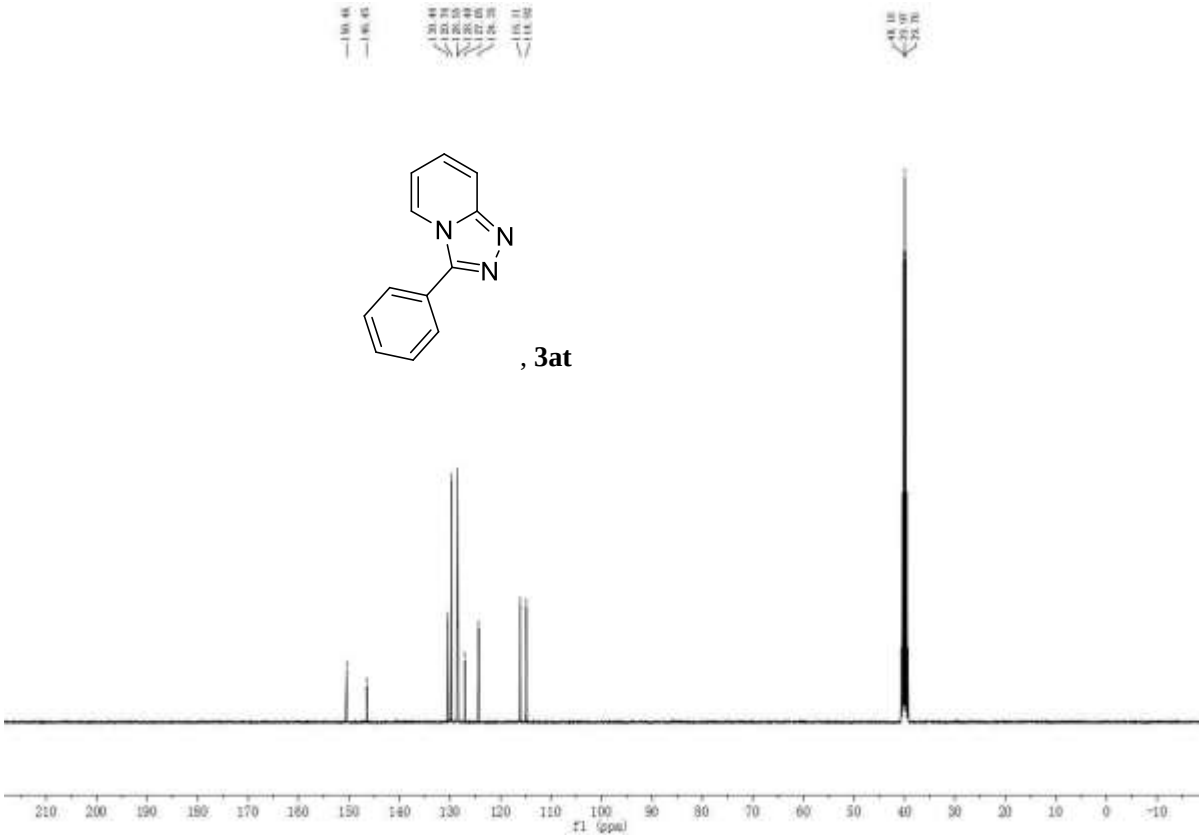
,3an


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N
N

, 3at


13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



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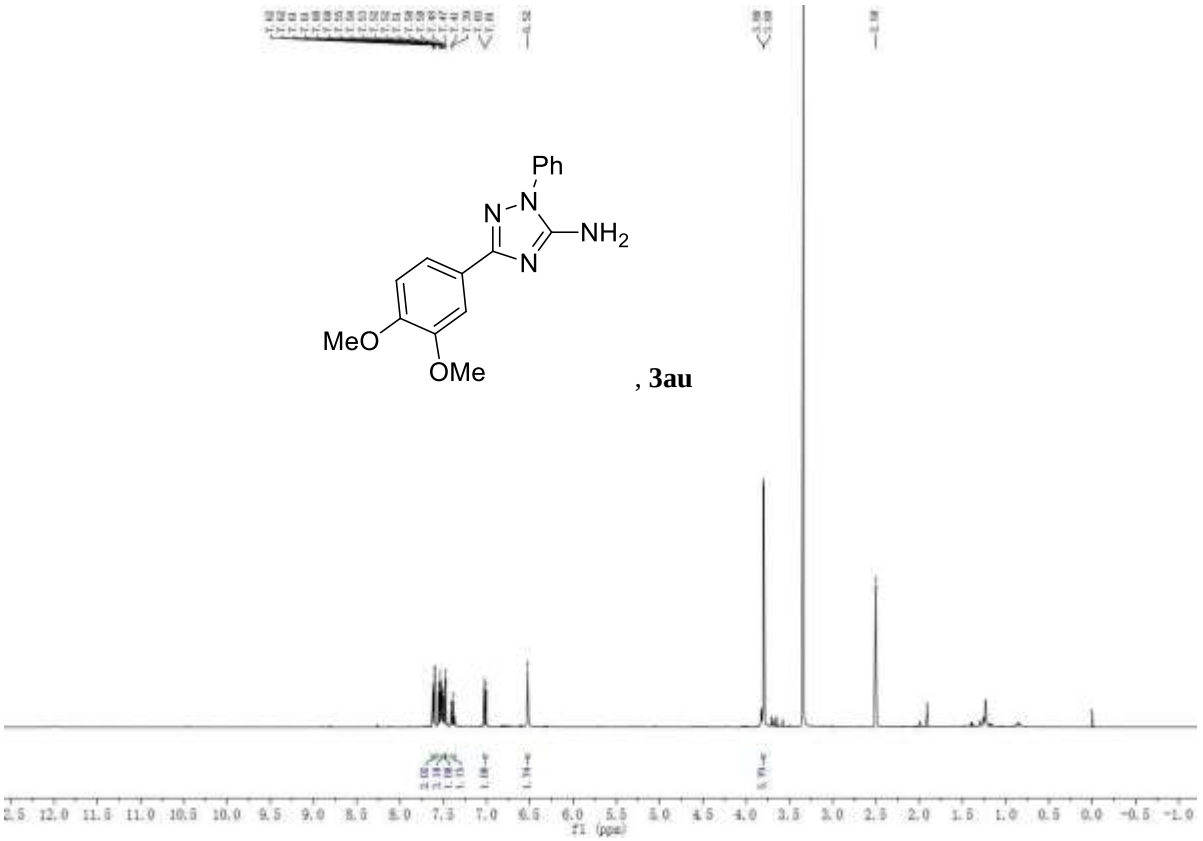

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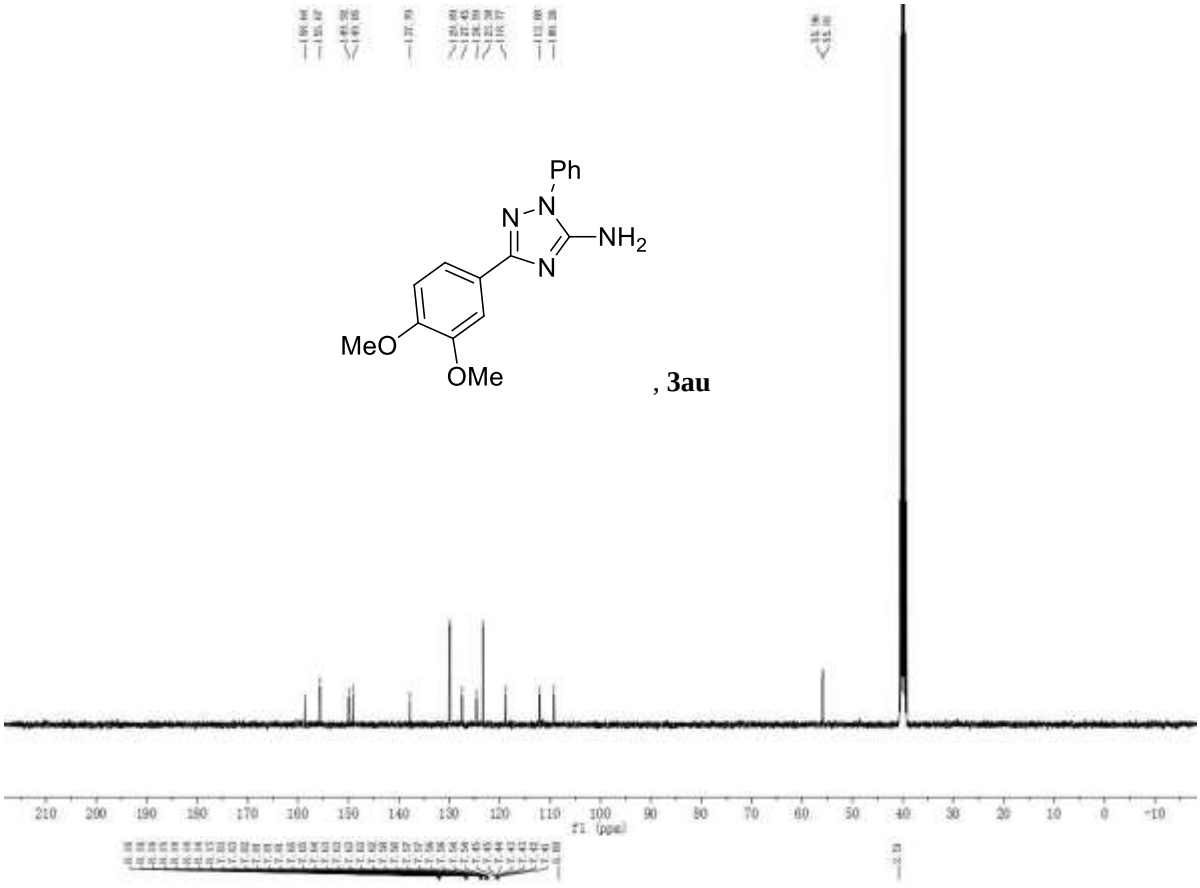

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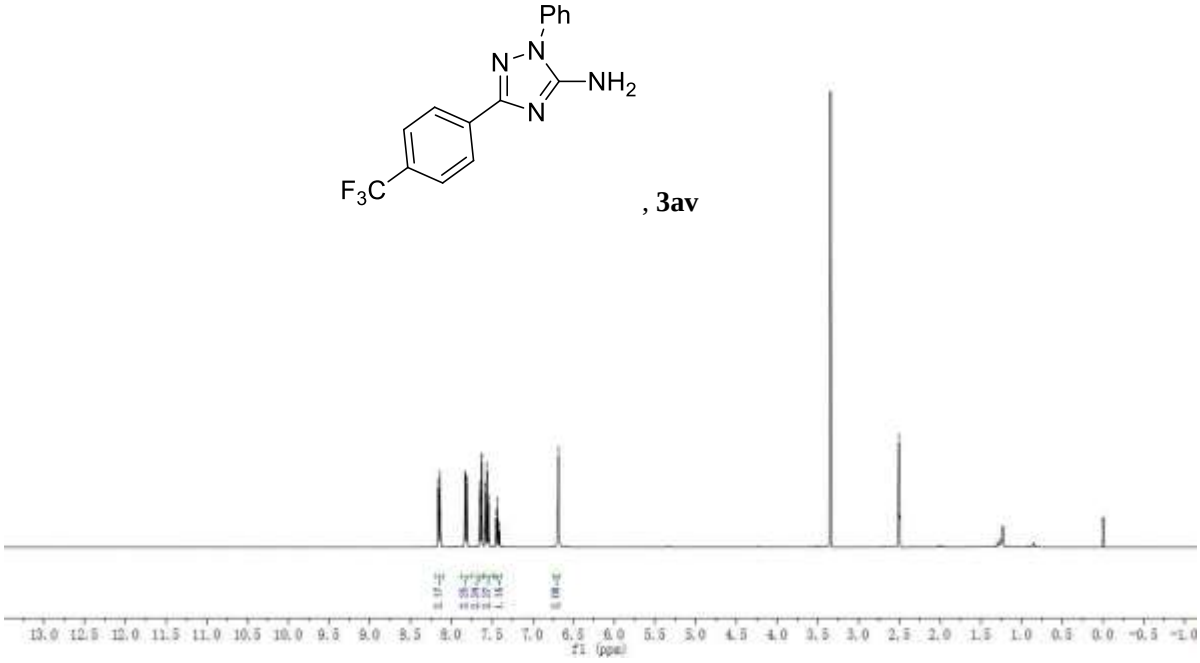

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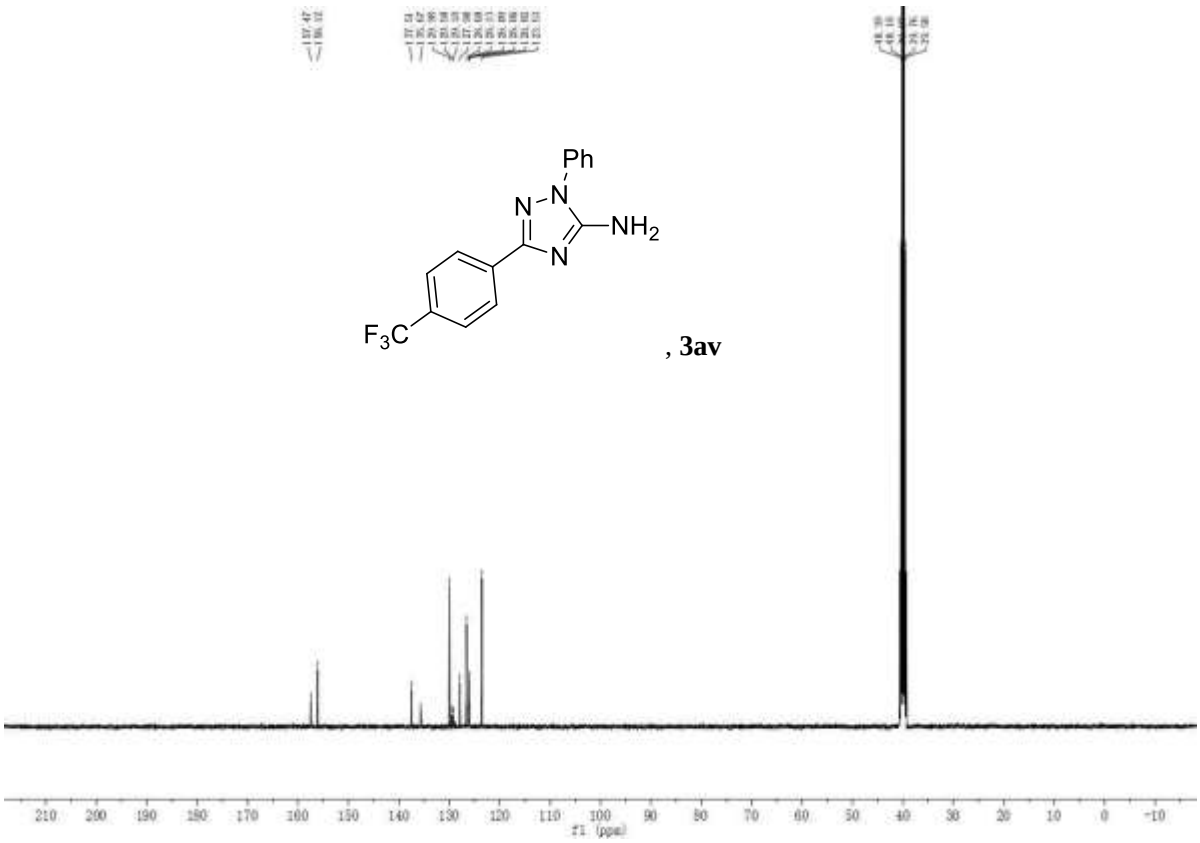

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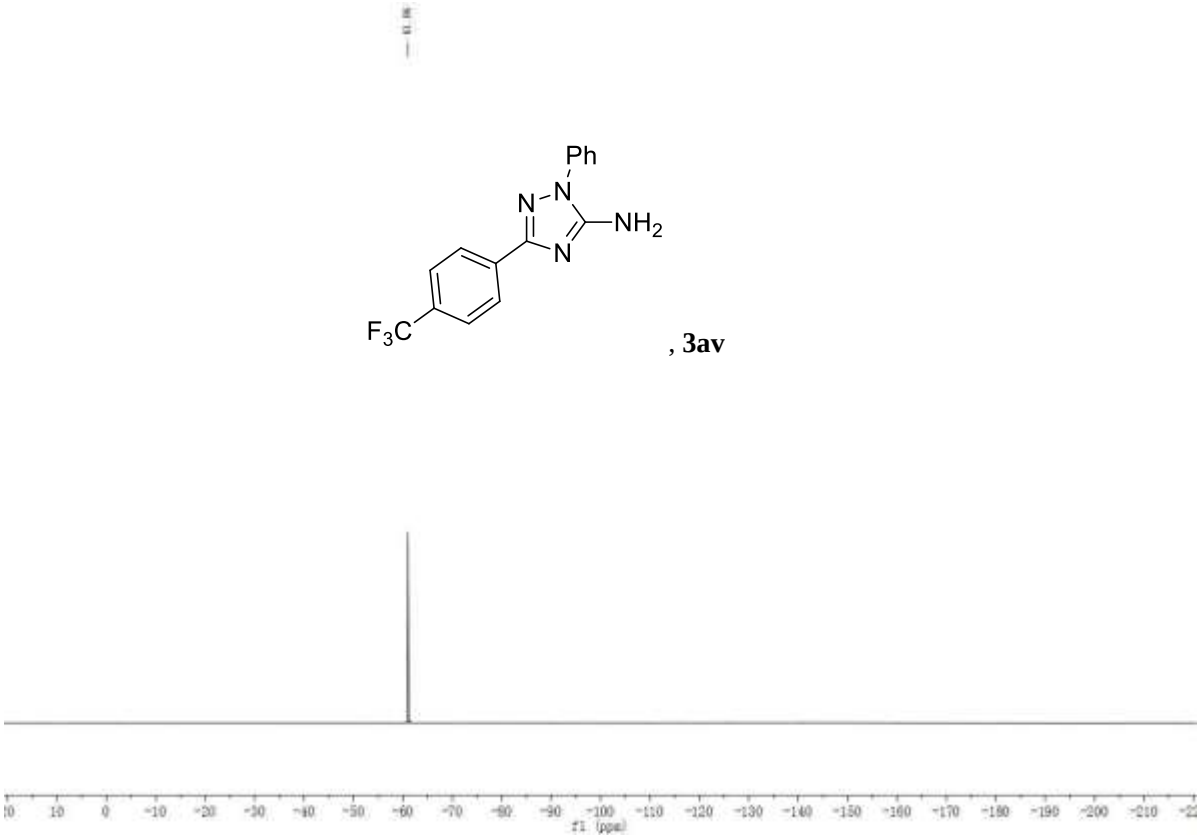

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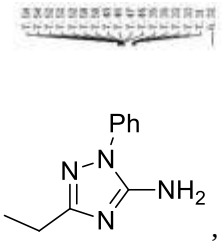

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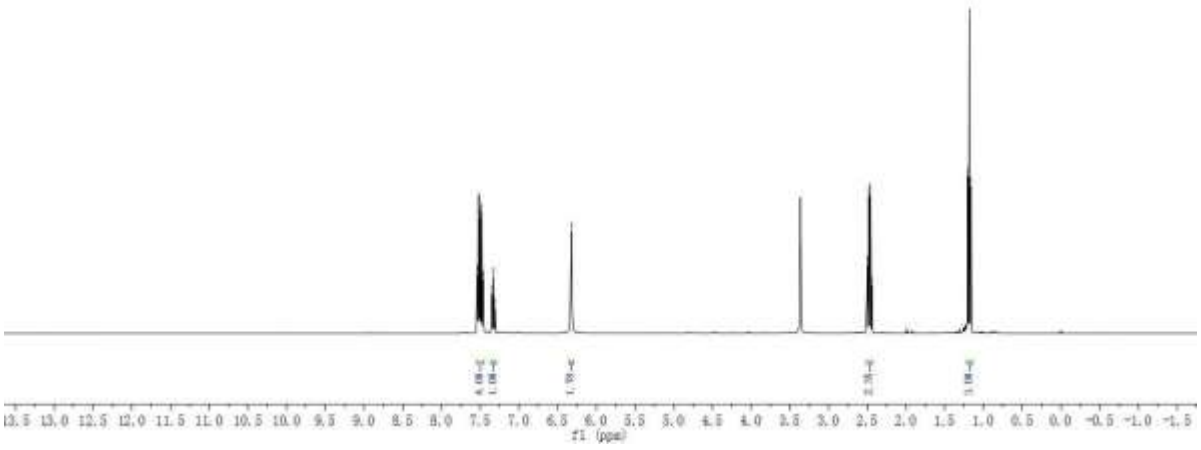

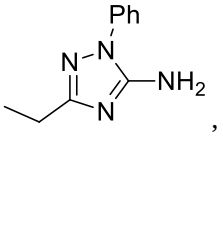

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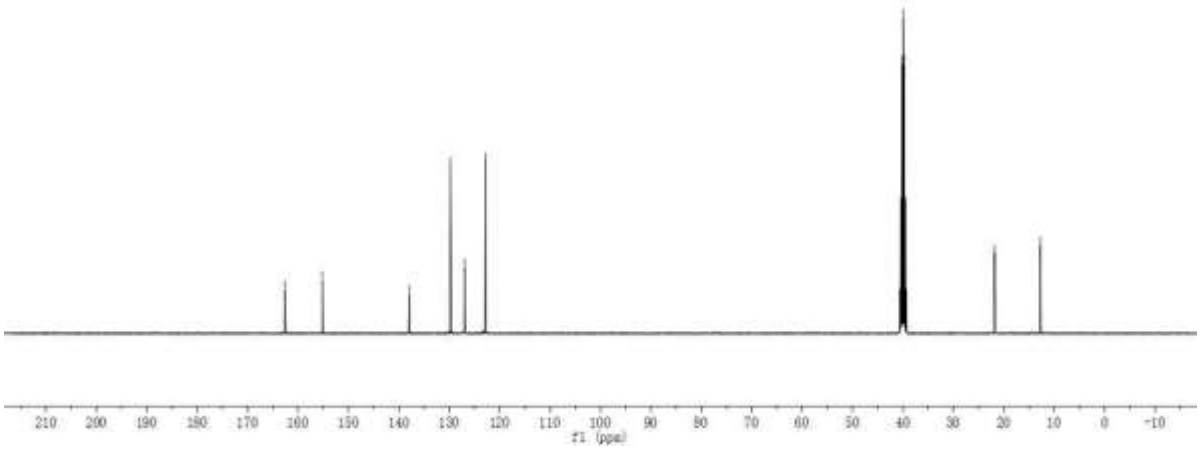
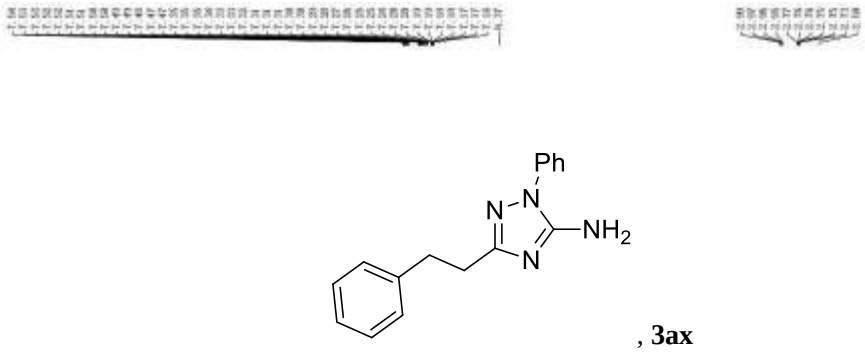
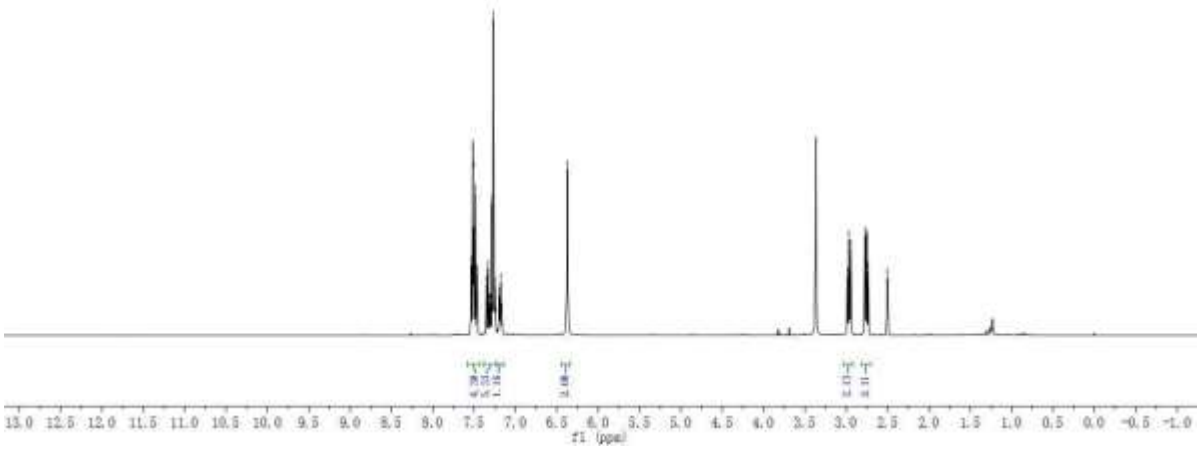



Ph
N
N
NH2
N

, 3ax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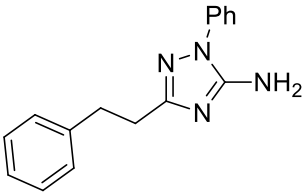
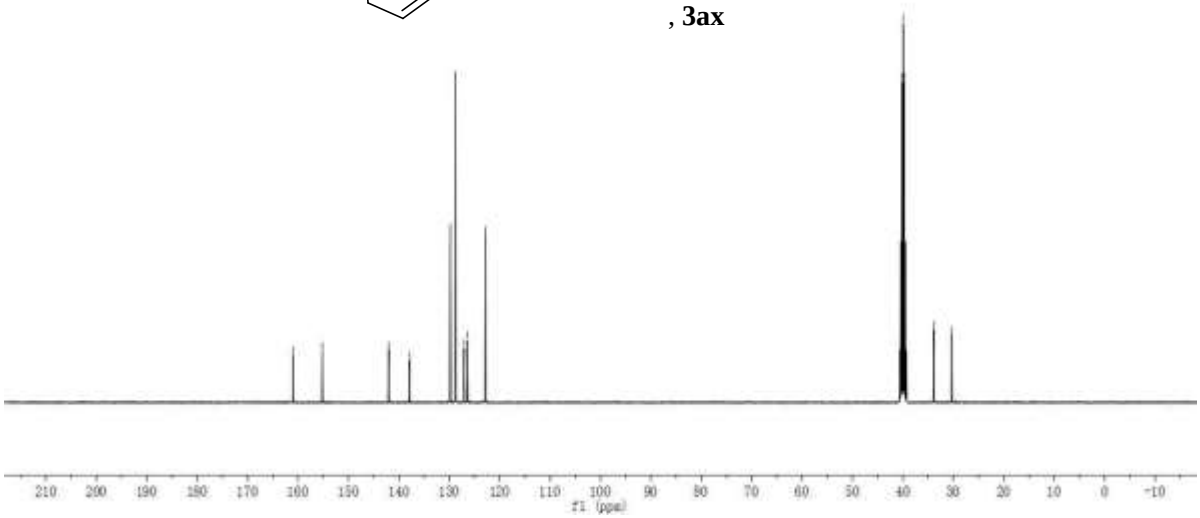
f1 (ppm)


Ph
N
N
NH2
N

, 3ax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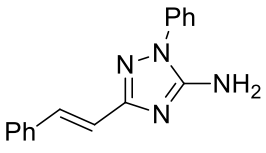
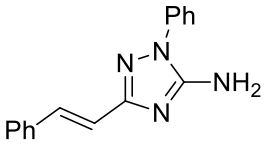
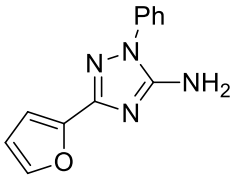
f1 (ppm)



, 3ay



, 3ay



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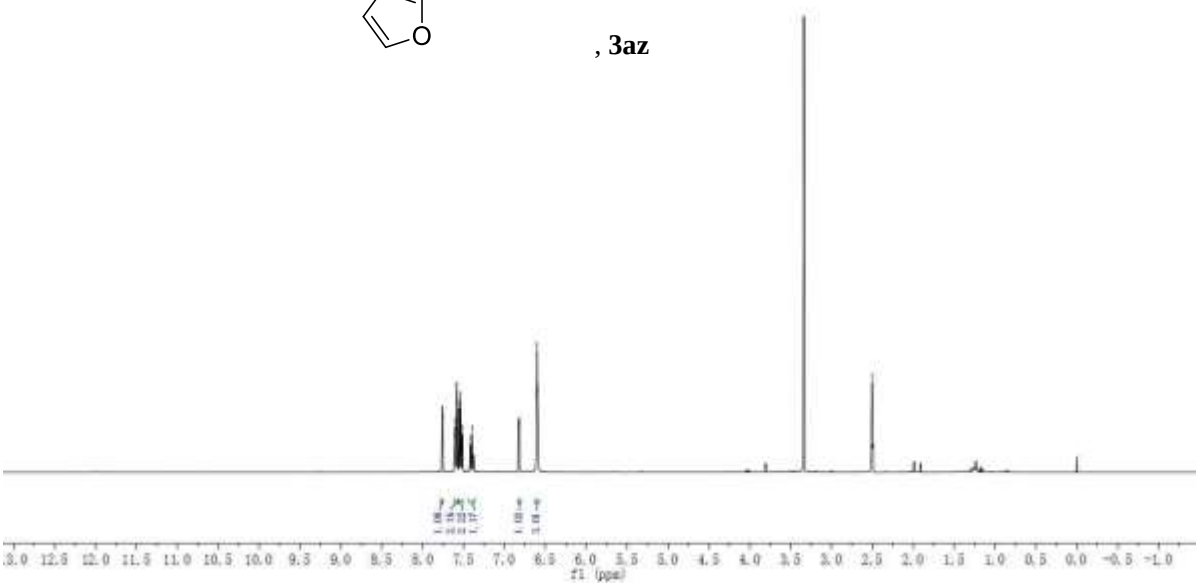
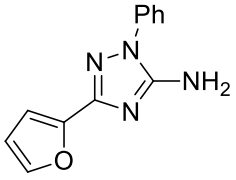
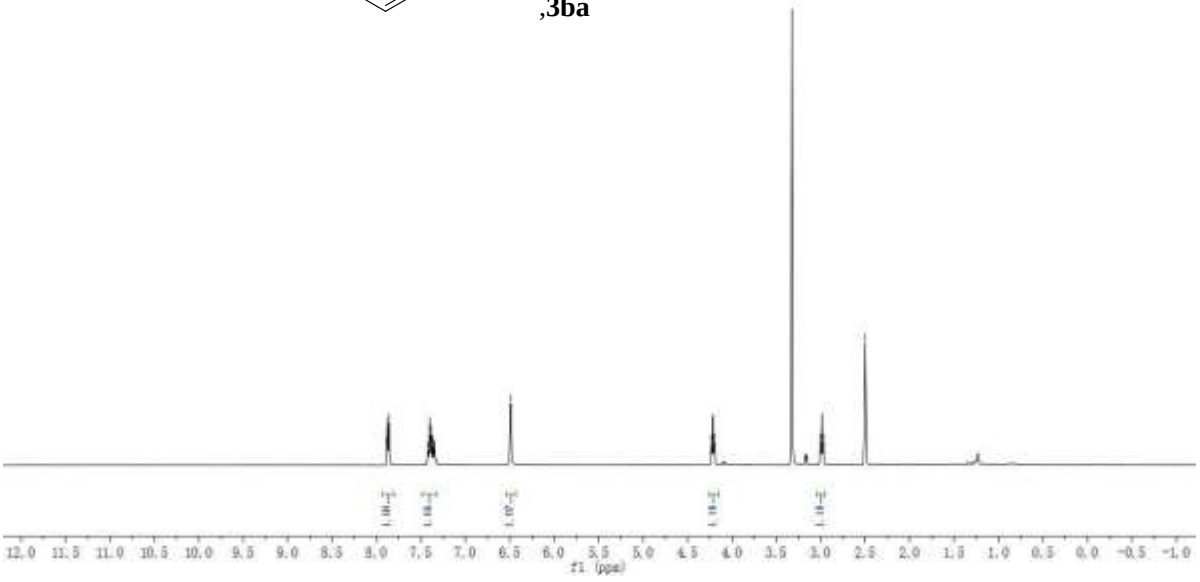




, **3az**

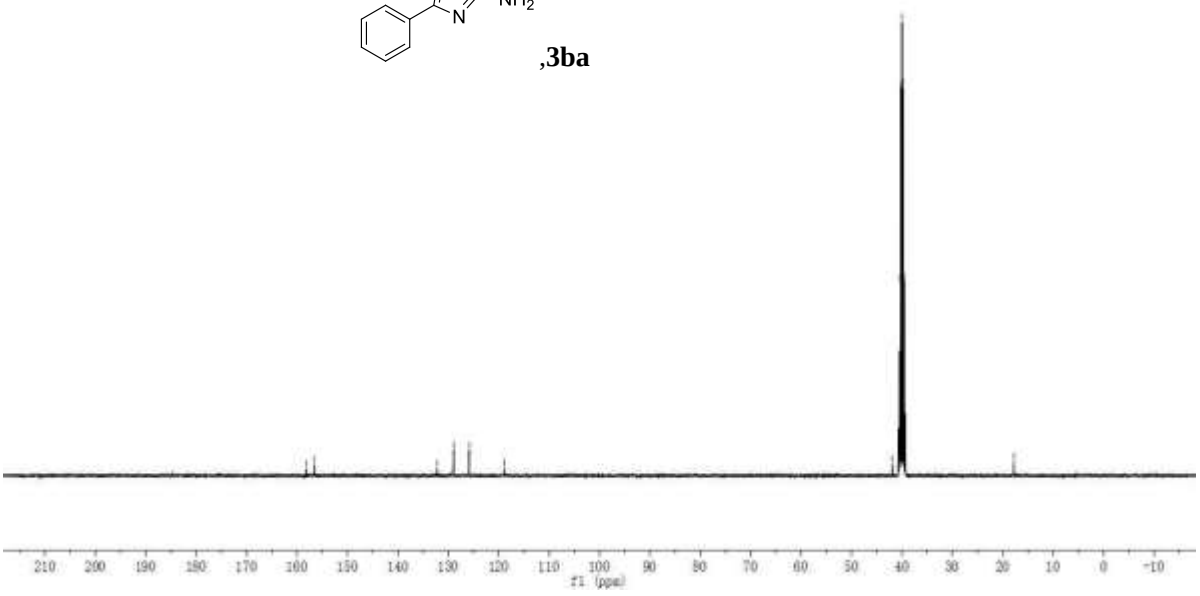

CN
N
N
NH2
N

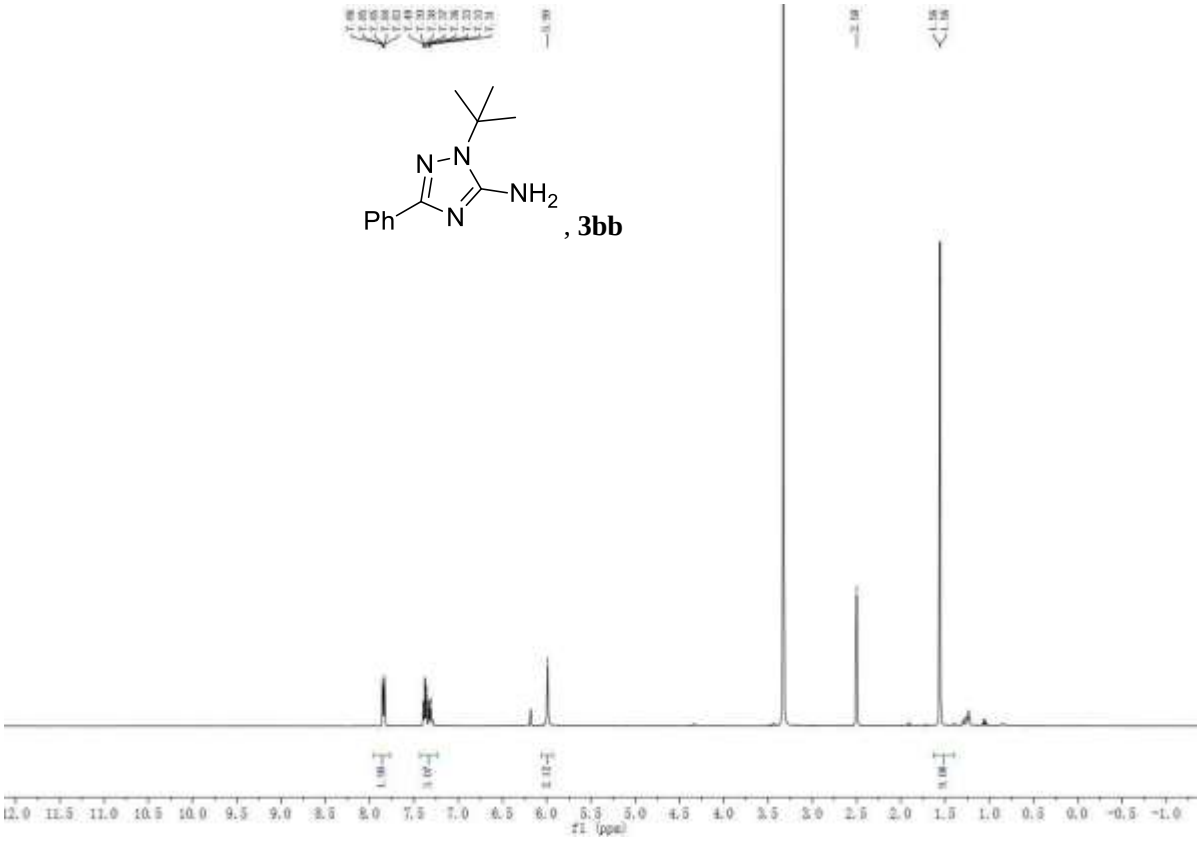
,3ba


12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

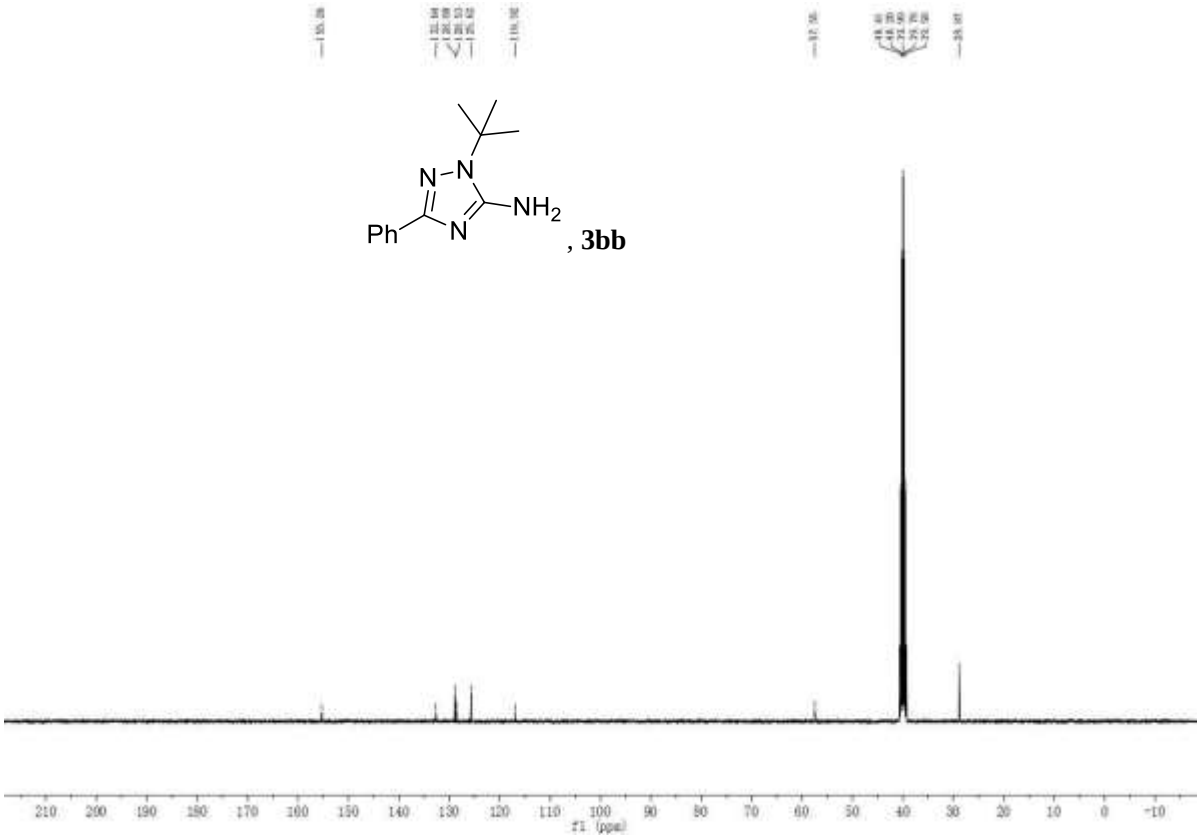

CN
N
N
NH2
N

,3ba

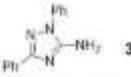

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
N
NH2
Ph
N
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

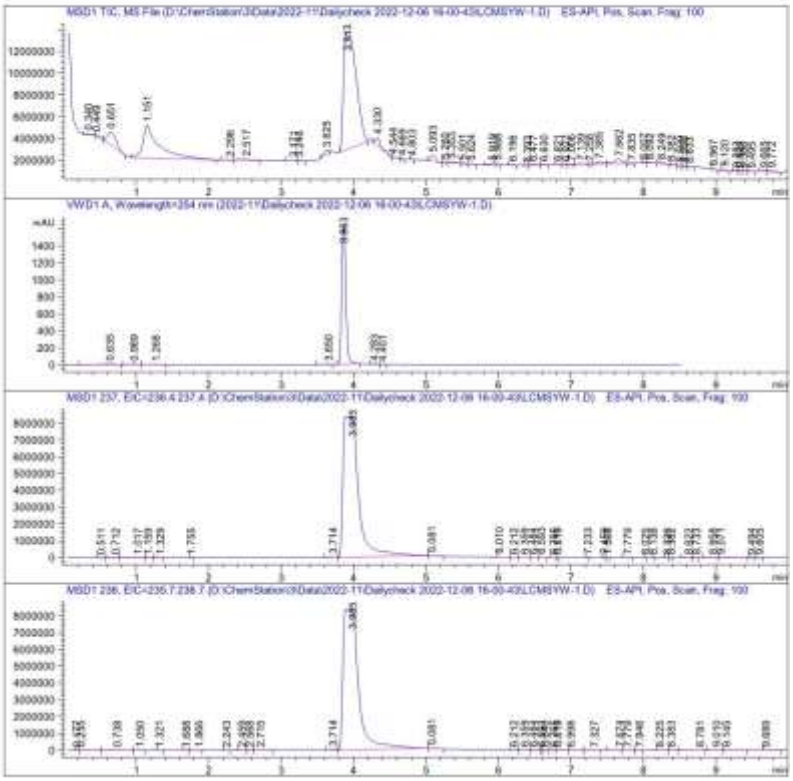
, **3bb**


N
N
NH2
Ph
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

, **3bb**



3aa


MSD1 TIC, MS File (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-1.D) ES-API, Pos, Scan, Frag: 100
VWD1 A, Wavelength=254 nm (2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-1.D)
MSD1 237, EIC=236.4:237.4 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-1.D) ES-API, Pos, Scan, Frag: 100
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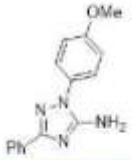
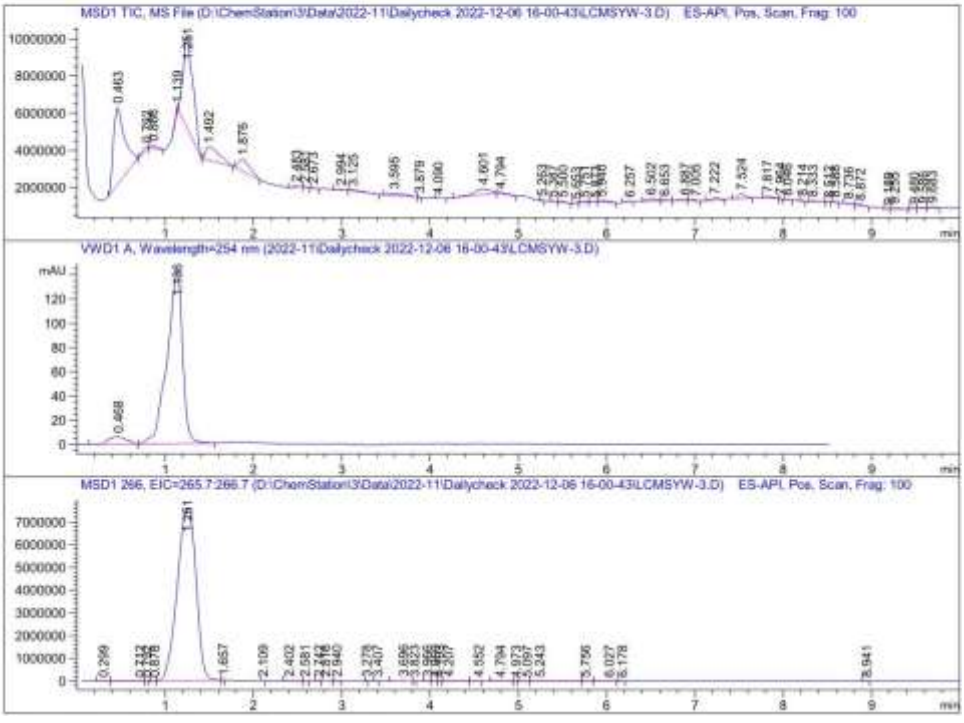
mAU
min



3ac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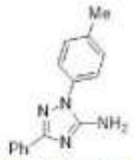
MSD1 266, EIC=265.7:266.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-3.D) ES-API, Pos, Scan, Frag: 100
mAU
min


Me
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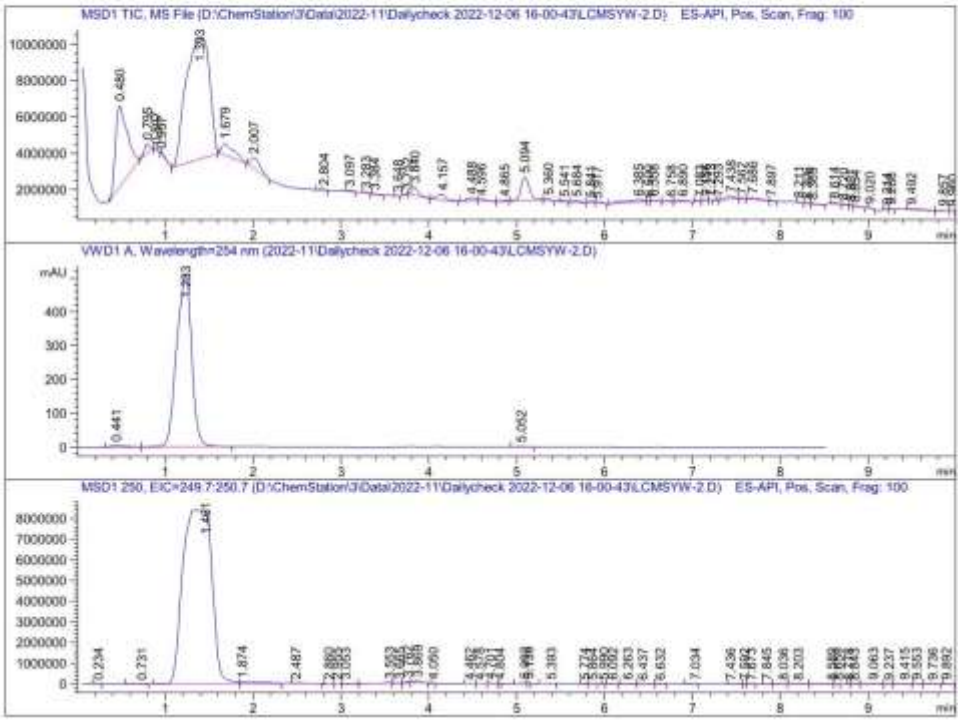
N
NH2
Ph
N

3ab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mAU
MSD1 250, EIC=249.7:250.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-2.D) ES-API, Pos, Scan, Frag: 100
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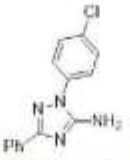
Cl
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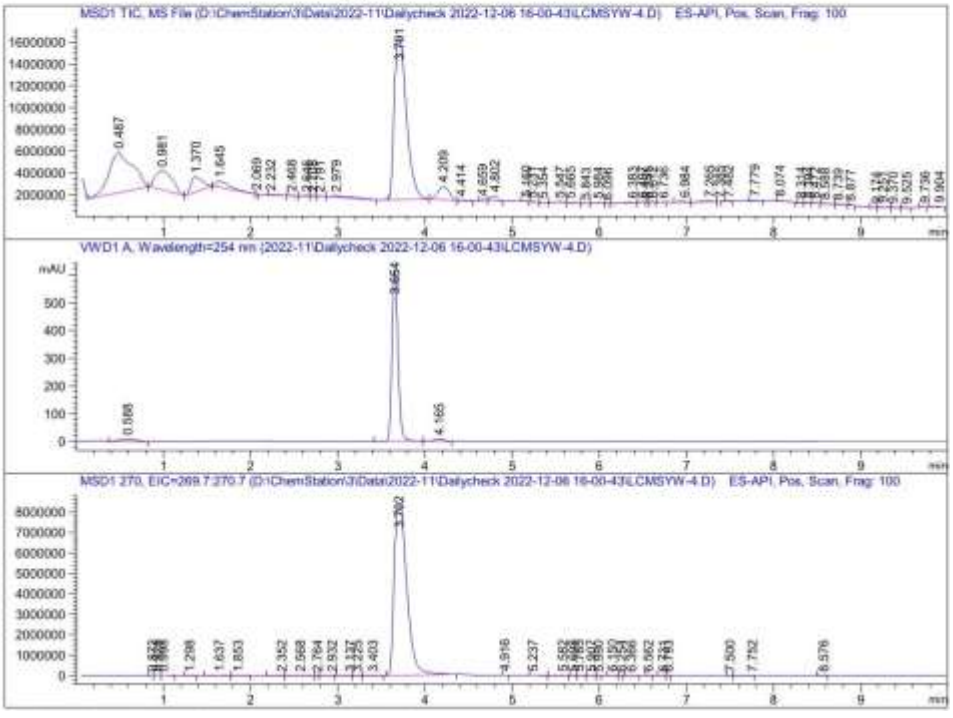
N
NH2
Ph
N

3ad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VWD1 A, Wavelength=254 nm (2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-4.D)
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MSD1 270, EIC=269.7:270.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-4.D) ES-API, Pos, Scan, Frag: 100
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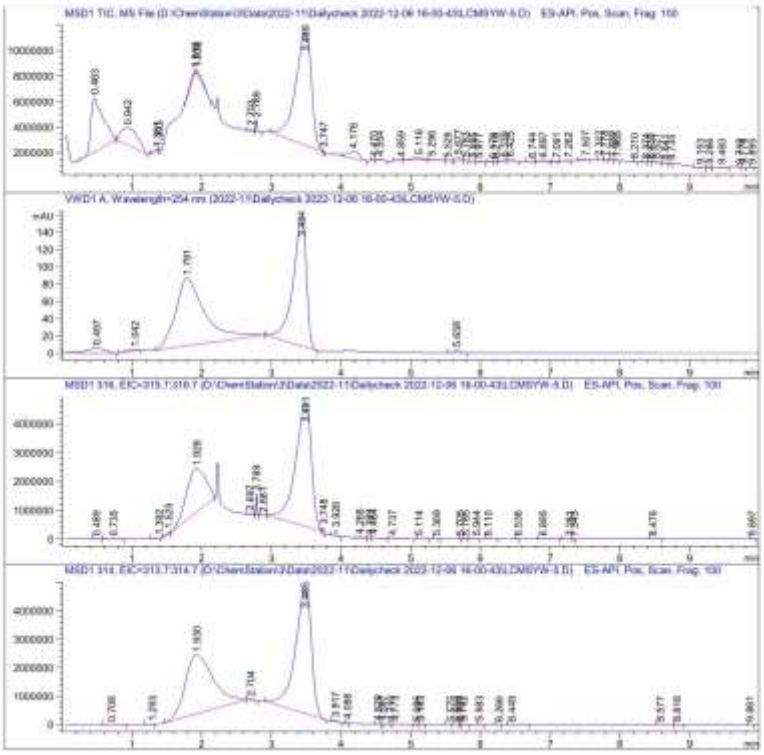
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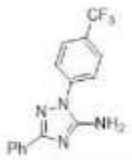

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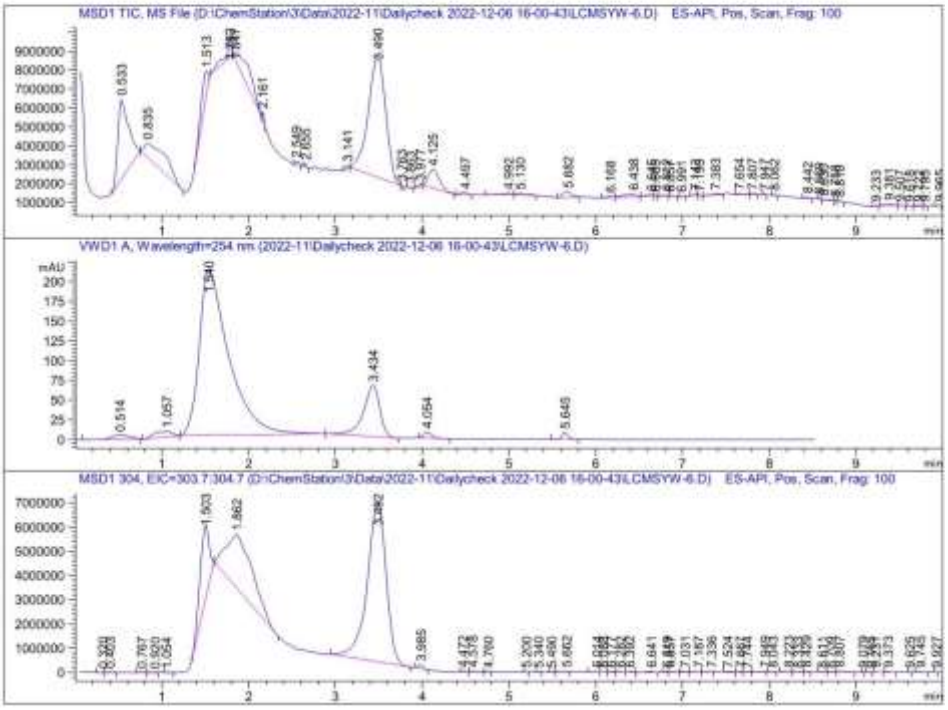
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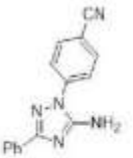
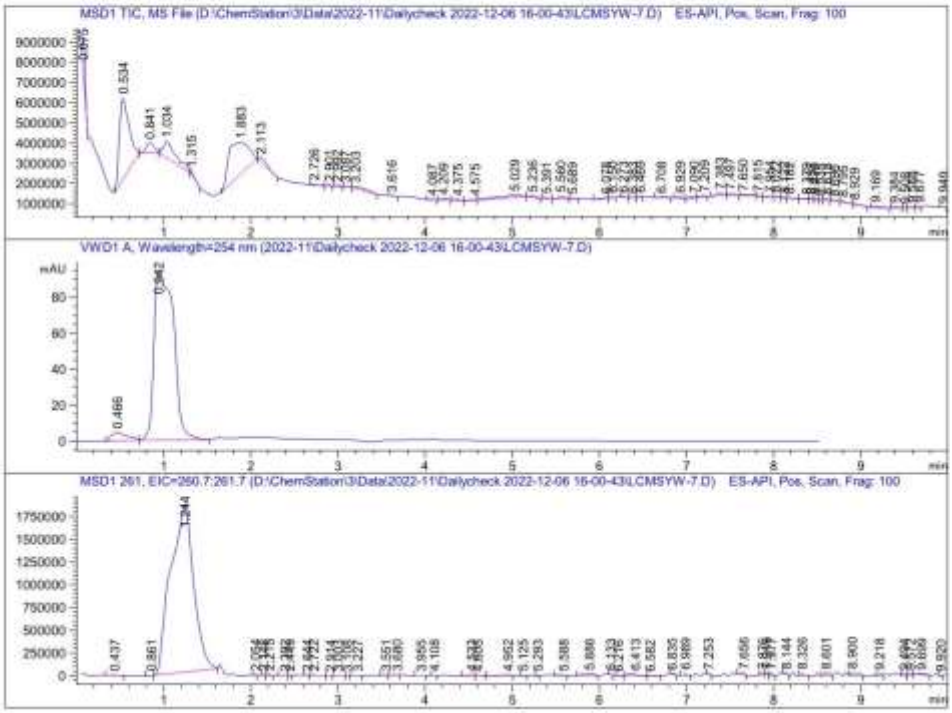
MSD1 304, EIC=303.7:304.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-6.D) ES-API, Pos, Scan, Frag: 100


CN
N
N
NH2
Ph
N

3ag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mAU
MSD1 261, EIC=260.7:261.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-7.D) ES-API, Pos, Scan, Frag: 100
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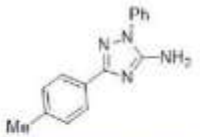
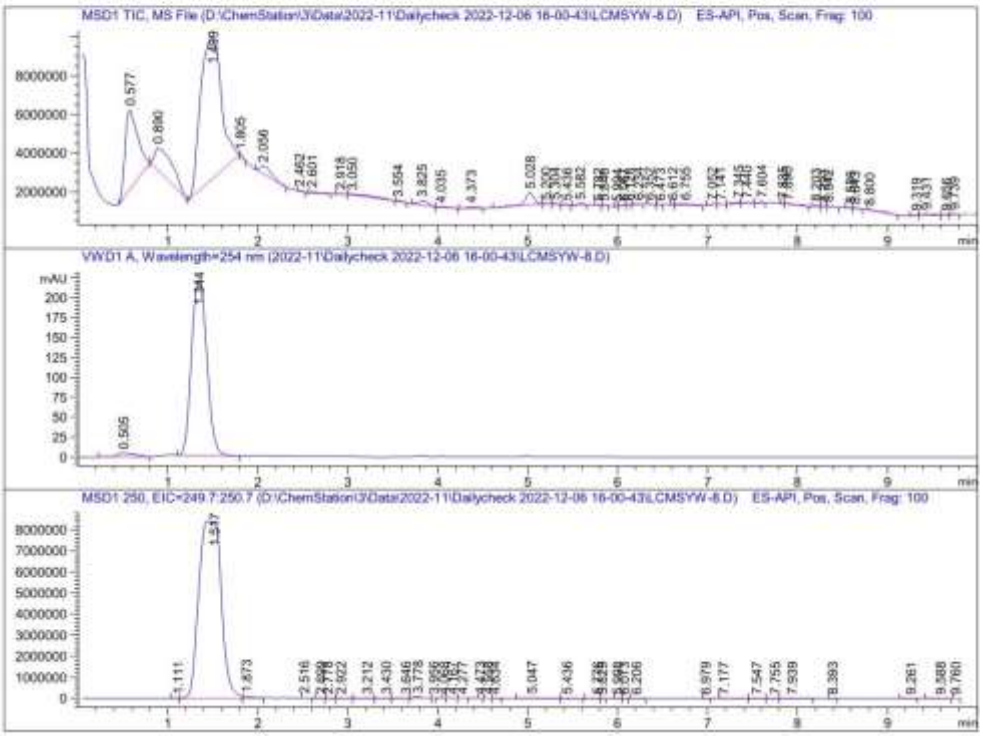

Ph
N
N
NH2
N
Me

3ah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VWD1 A, Wavelength=254 nm (2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-8.D)
mAU
MSD1 250, EIC=249.7:250.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-8.D) ES-API, Pos, Scan, Frag: 100
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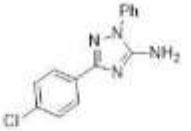

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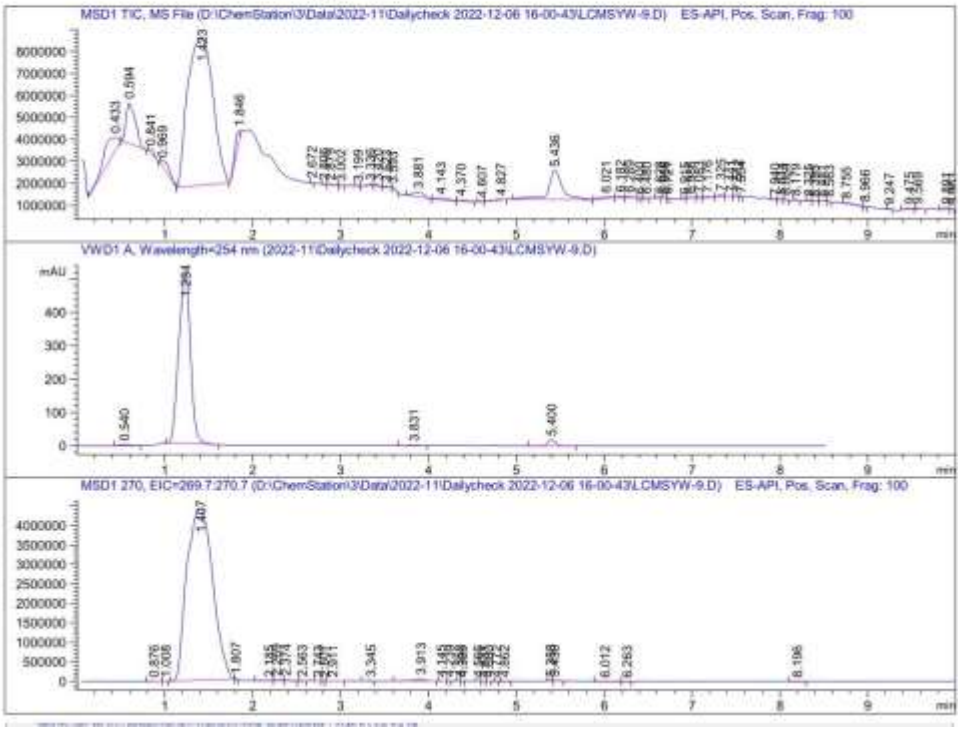
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mAU
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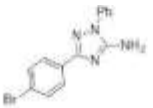

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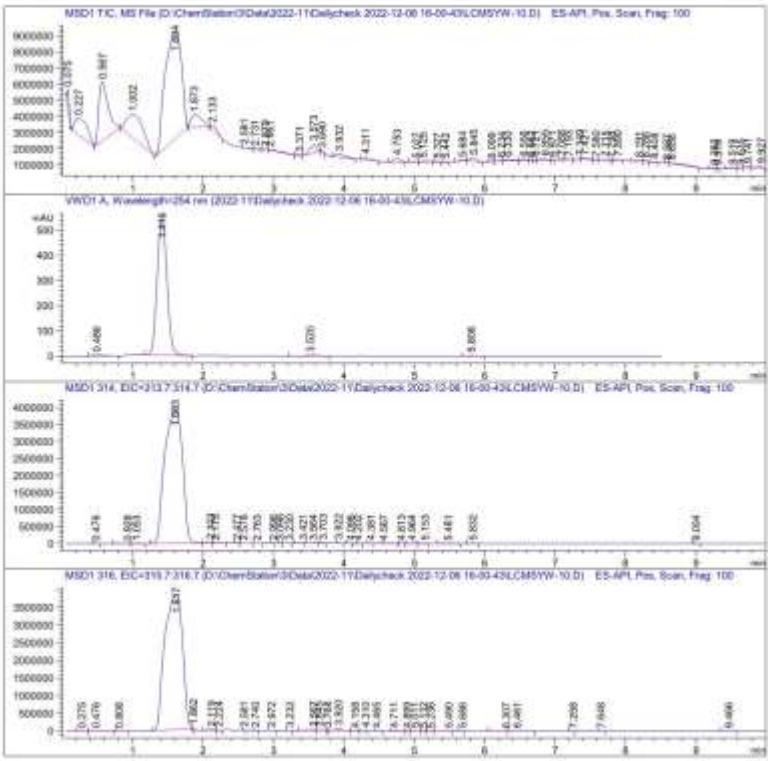
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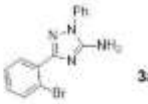

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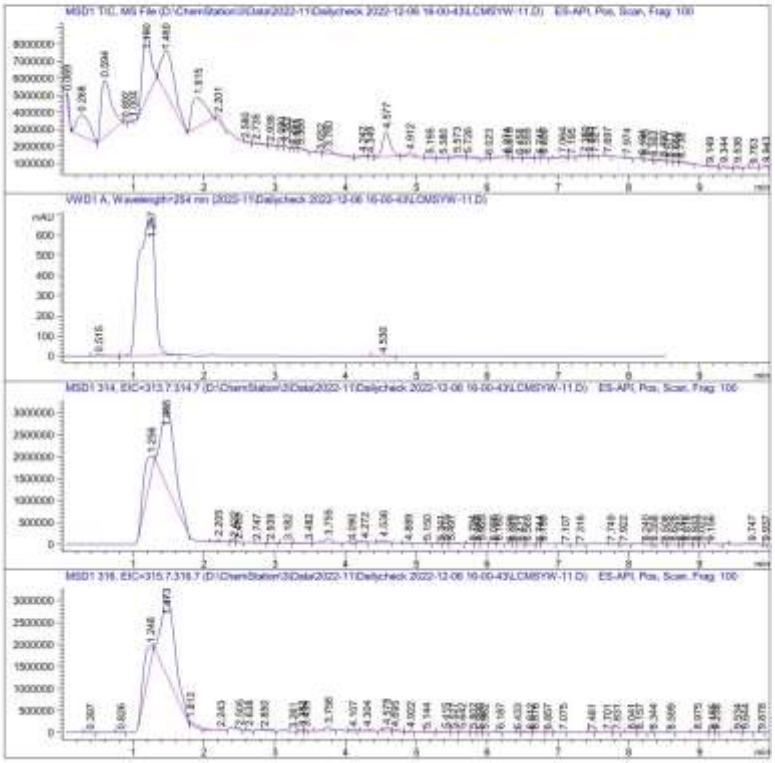
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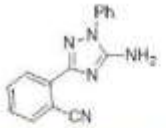

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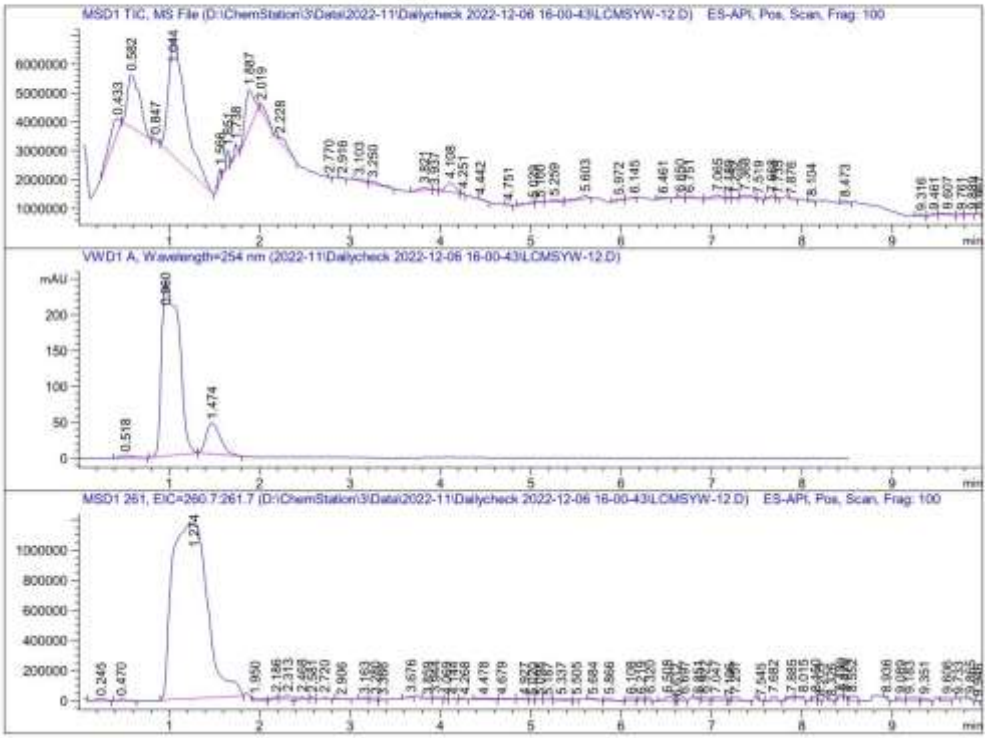
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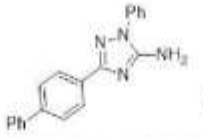

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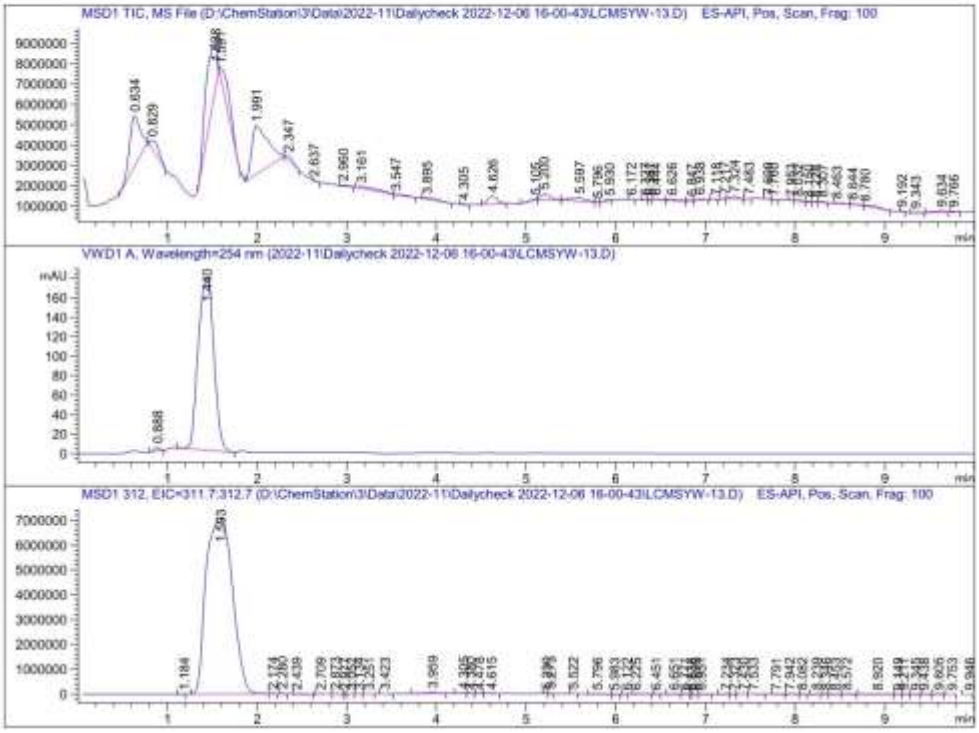
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mAU
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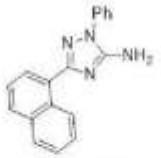

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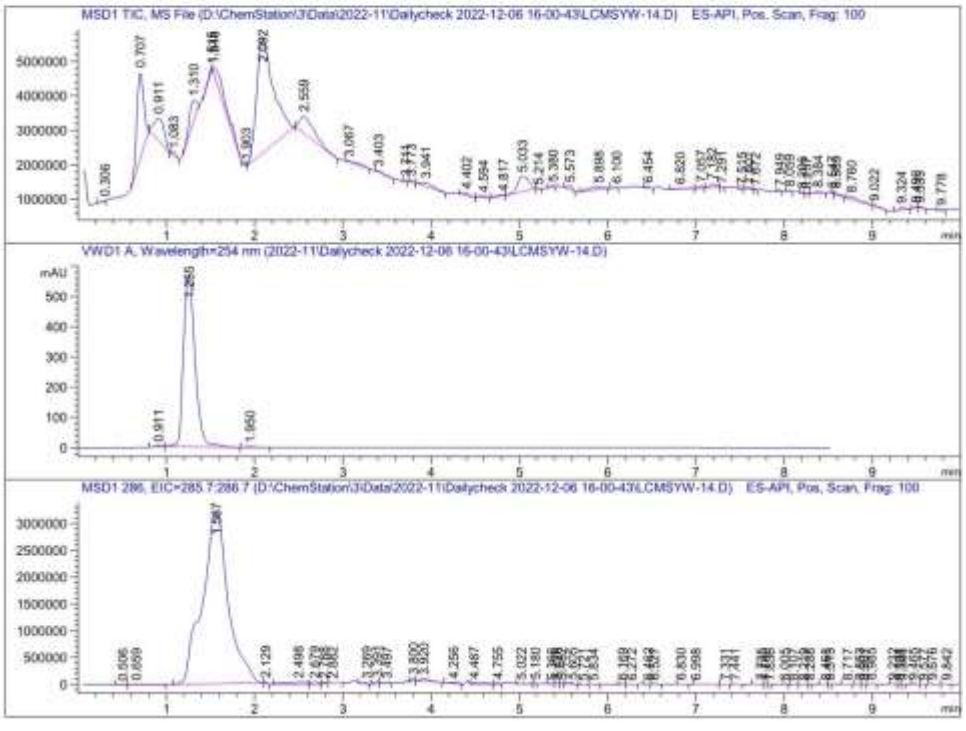
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mAU
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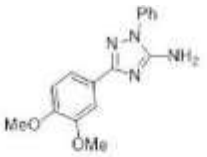
min


Ph
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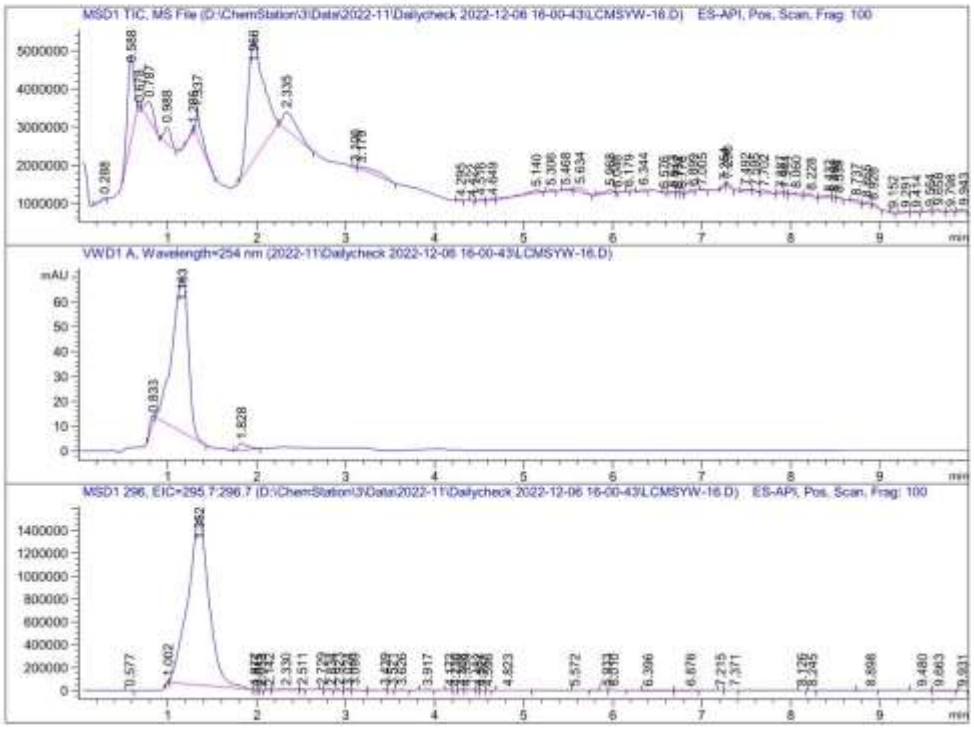
N
NH2
N
MeO
OMe

3au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mAU
MSD1 296, EIC=295.7:296.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-16.D) ES-API, Pos, Scan, Frag: 100
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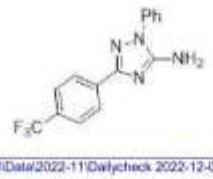
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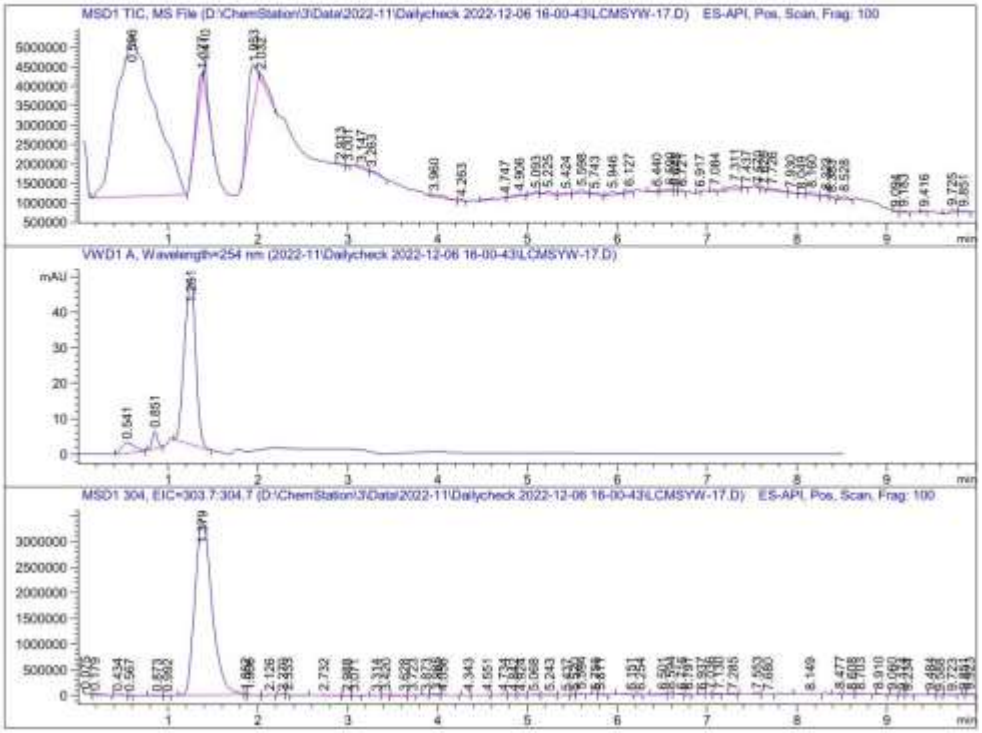
N
N
NH2
N
F3C

3av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VWD1 A, Wavelength=254 nm (2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-17.D)
mAU
MSD1 304, EIC=303.7:304.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-17.D) ES-API, Pos, Scan, Frag: 100
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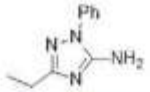
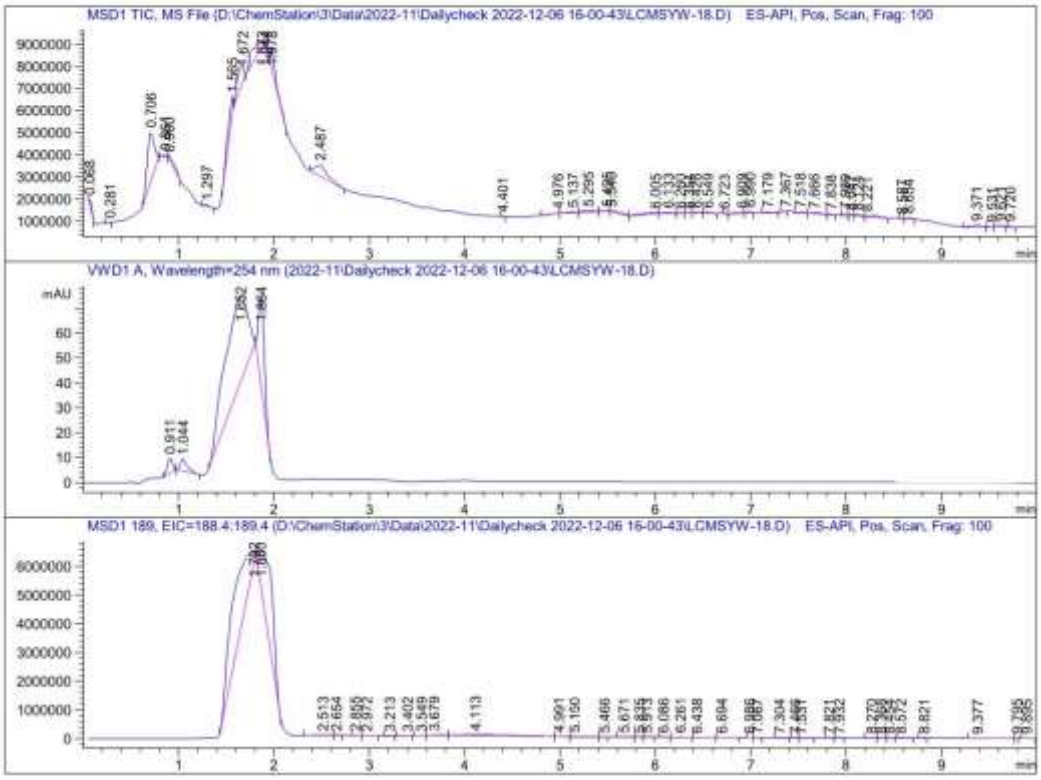

Ph
N
N
NH2

3aw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VWD1 A, Wavelength=254 nm (2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-18.D)
mAU
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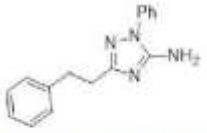
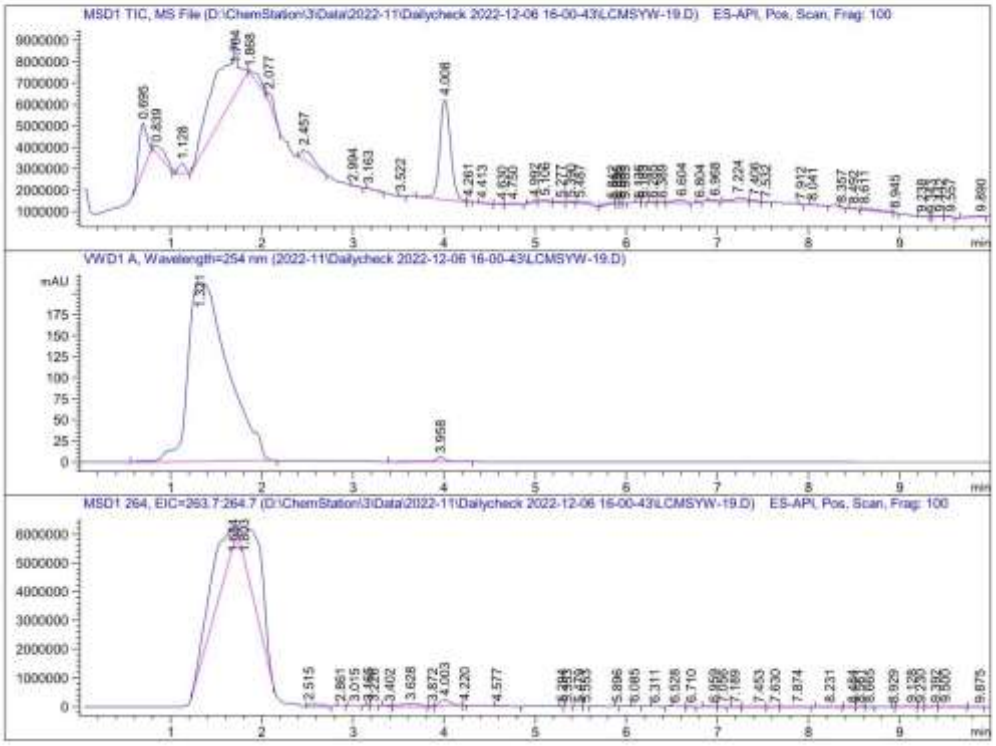

Ph
N
N
NH2

3ax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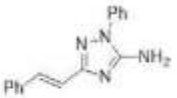
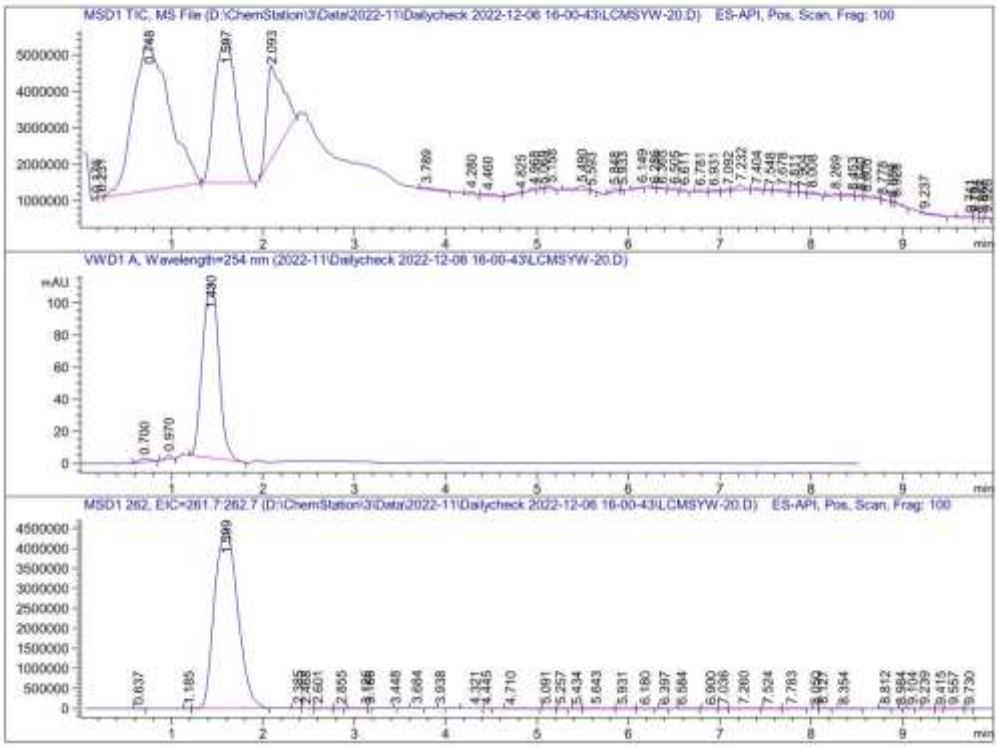
mAU
MSD1 264, EIC=263.7:264.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-19.D) ES-API, Pos, Scan, Frag: 100
min



3ay


MSD1 TIC, MS File (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-20.D) ES-API, Pos, Scan, Frag: 100
VWD1 A, Wavelength=254 nm (2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-20.D)
MSD1 262, EIC=261.7:262.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-20.D) ES-API, Pos, Scan, Frag: 100
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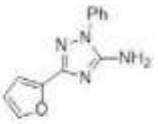
min



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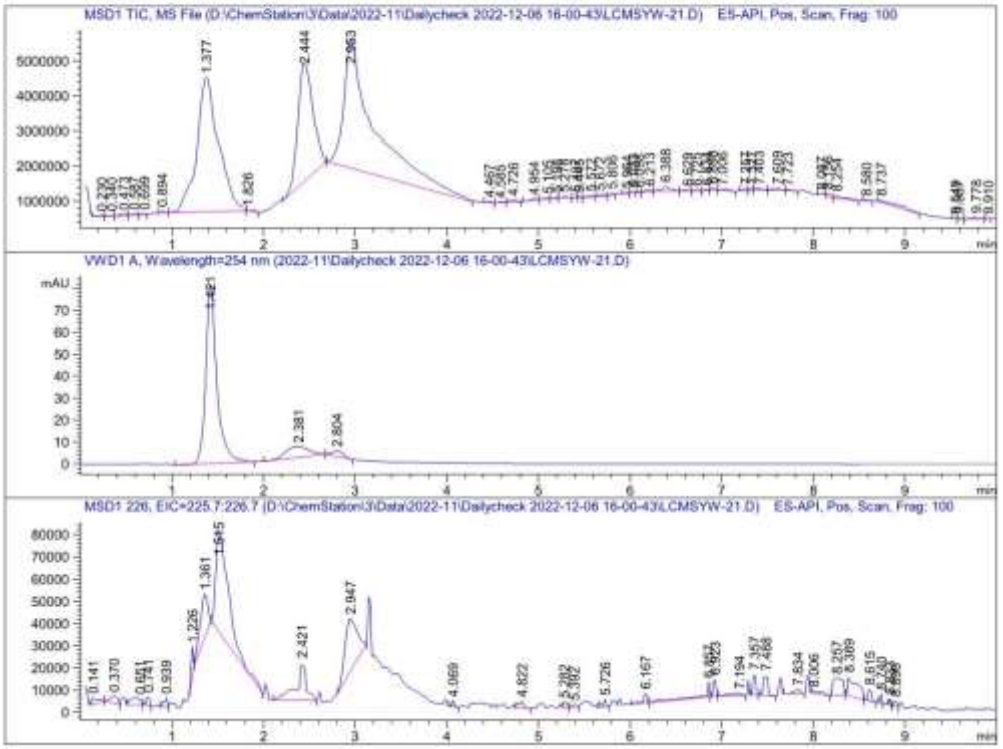
MSD1 TIC, MS File (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-21.D) ES-API, Pos, Scan, Frag: 100
VWD1 A, Wavelength=254 nm (2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-21.D)
MSD1 226, EIC=225.7:226.7 (D:\ChemStation\3\Data\2022-11\Dailycheck 2022-12-06 16-00-43\LCMSYW-21.D) ES-API, Pos, Scan, Frag: 100
mAU
min