Supporting materials

An efficient and recyclable heterogeneous catalytic system for the synthesis of 1,2,4-triazoles using air as the oxidant

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General information: All reagents were purchased from commercial suppliers and used without further purification. Metal salts and catalyst supports were commercially available and were used directly. All experiments were carried out under air. Flash chromatography was carried out with Merck silica gel 60 (230-400 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. ^{1}H NMR and ^{13}C NMR (400 and 100 MHz respectively) spectra were recorded in $CDCl_3$ or *d*-DMSO. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (*J*) are given in Hz.

Preparation of CuO_x-ZnO/Al_2O_3-TiO_2

Support Al_2O_3-TiO_2 powder (8g) was added to a 250 mL round-bottom flask. A solution of $Cu(NO_3)_2$-$3H_2O$ (1.205g) and $Zn(NO_3)_2$-$6H_2O$ (1.462g) in deionized water (100 mL) was added to Al_2O_3-TiO_2 powder, and additional deionized water (50 mL) was added to wash down the sides of the flask. Then the flask was submerged into an ultrasound bath for 3h at room temperature. After that, the water was distilled under reduced pressure on a rotary evaporator at 90 ^{o}C for more than 2h. Subsequently, the white powder was dried into an oven under the condition of increasing the temperature from 25 ^{o}C to 110 ^{o}C within 1h and keeping the temperature for another 5h. Finally, the dried white

powder was calcined under the condition of increasing the temperature from 25 ^{o}C to 350 ^{o}C within 1h and keeping the temperature for 2 more hours.

Characterization of Cu-Zn/Al-Ti

The Inductive Coupled Plasma Optical Emission Spectrum (ICP-OES) showed that the contents of catalyst and support are as below:

Catalyst: Cu% = 3.25%, Zn%=3.40%, BET surface area: 97 m^2/g, pore volume (BJH Adsorption): 0.312 cm^3/g, pore size (BJH Adsorption): 112.373 Å.

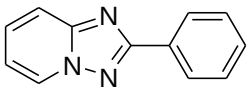
Support: Ti%=24%, Al%=76%

General procedure for Cu-Zn/Al-Ti-catalyzed cyclization

Cu-Zn/Al-Ti (24 mg, 1.6 mol%), 2-aminopyridine (0.72 mmol), benzonitrile (0.6 mmol) and DCB (0.6 mL) were added to a flask with a bar. The flask was stirred at 140 ^{o}C for indicated time under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 3/2 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by ^{1}H and ^{13}C NMR spectroscopic analysis.

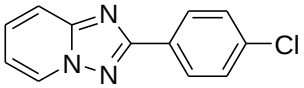
Spectrum data of the products

2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3a)[1]



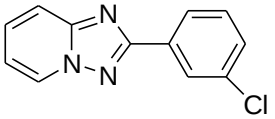
White solid, isolated yield 83%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.56 (d, 1H, J = 6.8 Hz), 8.29-8.26 (m, 2H), 7.73 (d, 1H, J = 8.8 Hz), 7.51-7.44(m, 4H), 6.98-6.94(m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 164.1, 151.6, 130.7, 130.2, 129.4, 128.6, 128.2, 127.2, 116.3, 113.5.

2-(4-chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3b) [1]



White solid, isolated yield 93%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.58-8.56 (m, 1H), 8.22-8.19 (m, 2H), 7.74-7.72 (m, 1H), 7.51(t, 1H, J = 1.6 Hz), 7.47-7.44 (m, 2H), 7.01(t, 1H, J = 1.2 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.2, 151.7, 136.1, 129.7, 129.3, 128.9, 128.6, 128.3, 116.4, 113.8.

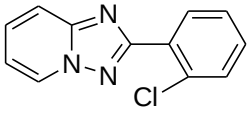
2-(3-chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3c) [1]



White solid, isolated yield 86%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.57 (d, 1H, J = 6.8 Hz), 8.28 (s, 1H), 8.16-8.14 (m, 1H), 7.73 (d, 1H, J = 8.8 Hz), 7.52-7.43 (m, 1H), 7.40(t, 2H, J = 4.8 Hz), 7.01(t, 1H, J = 6.8 Hz); ^{13}C

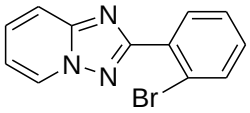
NMR (100MHz, $CDCl_3$): δ = 162.9, 161.7, 134.8, 132.6, 130.1, 130.0, 129.8, 128.4, 127.4, 125.4, 116.5, 113.9.

2-(2-chlorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3d) [1]



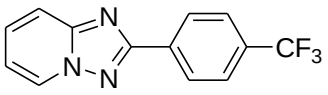
White solid, isolated yield 44%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.62 (d, 1H, J = 6.8 Hz), 7.99-7.96 (m, 1H), 7.77 (d, 1H, J = 9.2 Hz), 7.52-7.49 (m, 2H), 7.37-7.34 (m, 2H), 7.02-6.99 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 162.7, 150.8, 133.1, 132.1, 130.6, 130.5, 129.9, 129.5, 128.4, 126.7, 116.6, 113.8.

2-(2-bromophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3e) [1]



White solid, isolated yield 35%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.65-8.62 (m, 1H), 7.89-7.87 (m, 1H), 7.79 (d, 1H, J = 8.8 Hz), 7.73-7.71 (m, 1H), 7.54-7.50 (m, 1H), 7.43-7.39(m, 1H), 7.31-7.25 (m, 1H), 7.05-7.01 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.7, 150.8, 140.5, 133.9, 132.2, 130.7, 129.6, 128.4, 127.3, 122.1, 116.7, 113.8.

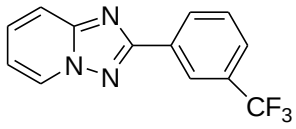
2-(4-(trifluoromethyl)phenyl)-[1,2,4]triazolo[1,5-a]pyridine (3f) [1]



White solid, isolated yield 92%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.60 (d, 1H, J = 6.8 Hz), 8.39 (d, 2H, J = 8.4 Hz), 7.78-7.73 (m, 3H), 7.56-7.51 (m, 1H), 7.07-7.03 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 162.8, 151.8,

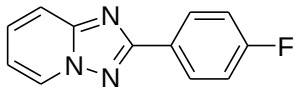
134.2, 131.9, 131.6, 129.9, 128.5, 127.6, 125.7, 125.6, 122.7, 116.7, 114.1.

2-(3-(trifluoromethyl)phenyl)-[1,2,4]triazolo[1,5-a]pyridine (3g) [1]



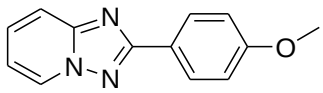
White solid, isolated yield 82%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.59 (d, 1H, J = 6.0 Hz), 8.56 (s, 1H), 8.45 (d, 1H, J = 8.0 Hz), 7.76 (d, 1H, J = 8.8 Hz), 7.71 (d, 1H, J = 6.8 Hz), 7.60 (t, 1H, J = 6.0 Hz), 7.53 (t, 1H, J = 4.8 Hz), 7.02 (t, 1H, J = 6.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$): δ = 162.8, 151.7, 131.6, 130.4, 129.9, 129.2, 128.4, 126.6, 126.5, 124.2, 124.1, 116.5, 114.0.

2-(4-fluorophenyl)-[1,2,4]triazolo[1,5-a]pyridine (3h) [1]



White solid, isolated yield 84%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.56 (d, 1H, J = 7.2 Hz), 8.27-8.23 (m, 2H), 7.51-7.47 (m, 1H), 7.18-7.14 (m, 1H), 7.73-7.71 (m, 2H), 7.01-6.97 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 165.3, 163.3, 162.8, 151.7, 129.6, 129.3, 129.2, 128.3, 127.0, 126.9, 116.3, 115.8, 115.6, 113.6.

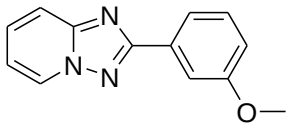
2-(4-methoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (3i) [1]



White solid, isolated yield 66%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.53 (q,

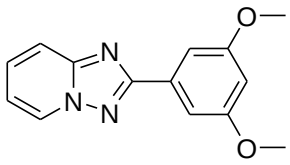
1H, J = 7.6 Hz), 8.20 (q, 2H, J = 8.8 Hz), 7.68 (q, 1H, J = 8.8 Hz), 7.46-7.42 (m, 1H), 6.99 (q, 2H, J = 9.2 Hz), 6.95-6.91 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 164.1, 161.2, 151.7, 129.4, 128.8, 128.2, 123.4, 116.1, 114.1, 113.3, 55.3.

2-(3-methoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (3j) [1]



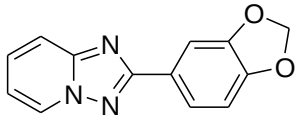
White solid, isolated yield 52%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.83-8.51 (m, 1H), 7.86-7.84 (m, 1H) 7.79-7.78 (m, 1H), 7.68 (q, 1H, J = 8.8), 7.43-7.33 (m, 2H), 6.98-6.95 (m, 1H), 6.92-6.88 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 161.8, 159.8, 151.4, 131.9, 129.6, 129.4, 128.1, 119.6, 116.6, 116.2, 113.5, 111.6, 113.5, 111.6, 55.2.

2-(3,5-dimethoxyphenyl)-[1,2,4]triazolo[1,5-a]pyridine (3k)[2]



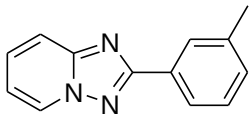
White solid, isolated yield 49%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.57 (d, 1H, J = 6.8 Hz), 7.74 (d, 1H, J = 8.8 Hz), 7.50-7.47 (m, 3H), 7.00-7.96 (m, 1H), 7.43-7.33 (m, 2H), 6.56(t, 1H, J = 2.4 Hz), 3.88 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 164.1, 161.1, 151.6, 132.6, 129.6, 128.3, 116.4, 113.7, 104.9, 103.4, 55.6.

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



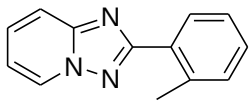
White solid, isolated yield 68%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.53 (d, 1H, J = 6.8 Hz), 7.82 (q, 1H, J = 9.6 Hz), 7.72-7.67 (m, 2H), 7.47-7.43 (m, 1H), 6.95 (t, 1H, J = 6.4 Hz), 6.90 (d, 1H, J = 8.0 Hz), 6.01 (s, 2H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.9, 151.6, 149.2, 147.9, 129.4, 128.2, 124.8, 121.7, 116.1, 113.4, 108.5, 107.5, 101.3.

2-m-tolyl-[1,2,4]triazolo[1,5-a]pyridine (3m) [1]



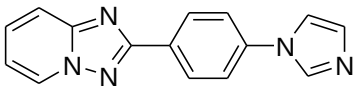
White solid, isolated yield 70%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.57 (d, 1H, J = 6.8 Hz), 8.12-8.08 (m, 2H), 7.73 (d, 1H, J = 8.8 Hz), 7.48-7.44 (m, 1H), 7.40-7.36 (m, 1H), 7.37 (d, 1H, J= 9.2 Hz), 6.97-6.93 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 164.2, 151.5, 138.3, 130.8, 130.5, 129.8, 128.5, 128.2, 127.8, 124.3, 116.2, 113.5, 21.3.

2-o-tolyl-[1,2,4]triazolo[1,5-a]pyridine (3n) [1]



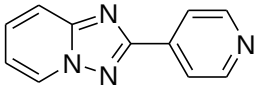
White solid, isolated yield 57%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.62 (d, 1H, J = 6.8 Hz), 8.05 (d, 1H, J = 9.6 Hz), 7.79-7.76 (m, 1H), 7.53-7.49 (m, 1H), 7.35-7.31 (m, 3H), 7.26-7.99 (m, 1H), 2.72 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 165.2, 150.9, 137.7, 131.3, 130.3, 130.1, 129.4, 129.3, 128.3, 125.8, 116.4, 113.4, 21.7.

2-(4-(1H-imidazol-1-yl)phenyl)-[1,2,4]triazolo[1,5-a]pyridine (3o)



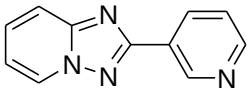
Yellow solid, isolated yield 65%. ^{1}H NMR (400MHz, $CDCl_3$): δ = 8.61 (d, J = 6.8 Hz, 1H), 8.40 (d, J = 8.4 Hz, 2H), 8.02 (s, 1H), 7.79 (m, 2H), 7.52 (m, 4H), 7.05 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.0, 151.8, 134.1, 130.0, 129.8, 128.9, 128.4, 121.4, 116.5, 113.9.

2-(pyridin-4-yl)-[1,2,4]triazolo[1,5-a]pyridine (3p) [1]



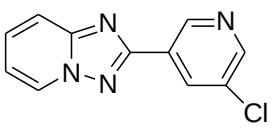
White solid, isolated yield 80%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.73 (s, 2H), 8.61-8.58 (m, 1H), 8.12-8.10 (m, 2H), 7.78-7.75 (m, 1H), 7.56-7.51 (m, 1H), 7.07-7.03 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 161.9, 151.7, 150.4, 138.2, 129.9, 128.5, 121.3, 116.8, 114.3.

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



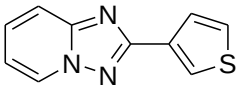
White solid, isolated yield 85%.^{1}H NMR (400MHz, $CDCl_3$): δ = 9.49 (s, 1H), 8.69-8.67 (m, 1H), 8.59 (d, 1H, J= 6.8 Hz), 8.52-8.49 (m, 1H), 7.75 (d, 1H, J = 8.8 Hz), 7.54-7.50 (m, 1H), 7.42-7.38 (m, 1H), 7.02 (t, 1H, J = 6.0 Hz) ; ^{13}C NMR (100MHz, $CDCl_3$): δ = 161.9, 151.7, 150.9, 148.8, 134.5, 129.9, 128.4, 126.9, 123.6, 116.6, 114.0.

2-(5-chloropyridin-3-yl)-[1,2,4]triazolo[1,5-a]pyridine (3r)[3]



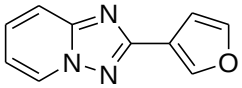
White solid, isolated yield 80%.^{1}H NMR (400MHz, $CDCl_3$): δ = 9.22 (s, 1H), 8.56 (d, 1H, J = 6.8 Hz), 8.45-8.43 (m, 1H), 7.72 (d, 1H, J = 8.8 Hz), 7.54-7.50 (m, 1H), 7.40 (d, 1H, J = 8.4 Hz), 7.05-7.01 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 160.8, 152.6, 151.6, 148.5, 137.1, 130.0, 128.4, 125.8, 124.2, 116.5, 114.2.

2-(thiophen-3-yl)-[1,2,4]triazolo[1,5-a]pyridine (3s) [1]



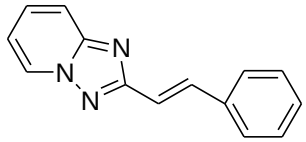
White solid, isolated yield 71%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.55 (d, 1H, J = 6.8 Hz), 8.13-8.12 (m, 1H), 7.79-7.78 (m, 1H), 7.70 (d, 1H, J = 5.2 Hz), 7.49-7.45 (m, 1H), 7.41-7.39 (m, 1H), 6.98-6.95 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 160.8, 151.4, 132.8, 129.6, 128.2, 126.6, 126.3, 125.6, 116.2, 113.5.

2-(furan-3-yl)-[1,2,4]triazolo[1,5-a]pyridine (3t)[3]



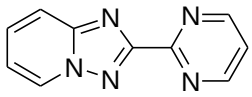
White solid, isolated yield 80%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.55 (d, 1H, J = 6.8 Hz), 8.13-8.12 (m, 1H), 7.79-7.78 (m, 1H), 7.70 (d, 1H, J = 5.2 Hz), 7.49-7.45 (m, 1H), 7.41-7.39 (m, 1H), 6.98-6.95 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 159.1, 151.4, 143.8, 142.8, 129.6, 128.1, 118.1, 116.0, 113.5, 109.1.

(E)-2-styryl-[1,2,4]triazolo[1,5-a]pyridine (3w)



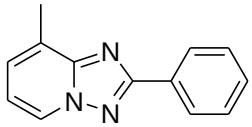
White solid, isolated yield 85%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.53-8.51 (m, 1H), 7.84 (d, 1H, J = 8.4 Hz), 7.69 (d, 1H, J = 8.8 Hz), 7.60 (d, 2H, J = 8.0 Hz), 7.49-7.46 (m, 1H), 7.39 (t, 2H, J = 7.2 Hz), 7.33 (d, 1H, J = 7.2 Hz), 7.247-7.206 (m, 1H), 6.99-6.05 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.6, 151.3, 136.4, 136.1, 129.7, 128.8, 128.7, 128.1, 127.2, 117.5, 116.1, 113.4.

2-(pyrimidin-2-yl)-[1,2,4]triazolo[1,5-a]pyridine (3y)



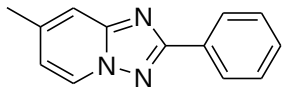
White solid, isolated yield 85%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.95 (d, J = 4.8 Hz, 2H), 8.49 (d, J = 8.4 Hz, 1H), 8.37-8.36 (m, 1H), 7.80 (t, J = 1.6 Hz, 1H), 7.50 (t, J = 4.8 Hz, 1H), 7.12-7.08 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 160.1, 157.7, 157.3, 150.8, 148.2, 138.5, 122.8, 120.3, 114.3.

8-methyl-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3aa) [1]



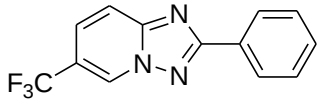
White solid, isolated yield 88%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.44 (d, 1H, J = 6.8 Hz), 8.31-8.28 (t, 2H), 7.51-7.45 (m, 3H), 7.26-7.23 (m, 1H), 6.87 (t, 1H, J = 6.8 Hz), 2.68 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.6, 152.1, 130.9, 129.8, 128.6, 128.1, 127.3, 126.9, 125.8, 113.4, 16.9.

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



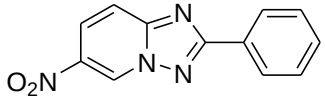
White solid, isolate yield 86%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.42 (d, 1H, J = 6.8 Hz), 8.26-8.23 (m, 2H), 7.49-7.43 (m, 4H), 6.78 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 164.1, 151.8, 140.9, 130.9, 129.9, 128.6, 127.2, 127.1, 116.0, 114.9, 21.5.

2-phenyl-6-(trifluoromethyl)-[1,2,4]triazolo[1,5-a]pyridine (3ac)[1]



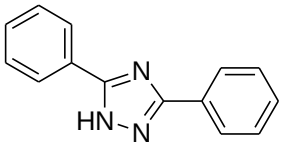
White solid, isolated yield 90%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.93 (d, 1H, J = 0.8 Hz), 8.28-8.26 (m, 2H), 7.83 (d, 1H, J = 9.6 Hz), 7.66-7.63 (m, 1H), 7.51-7.48 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 166.1, 152.2, 130.7, 129.9, 128.8, 127.5, 127.2, 127.1, 125.8, 125.7, 117.0.

6-nitro-2-phenyl-[1,2,4]triazolo[1,5-a]pyridine (3ad)



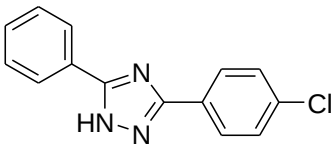
Yellow solid, isolated yield 85%.^{1}H NMR (400MHz, $CDCl_3$): δ = 9.63-9.62 (m, 1H), 8.31-8.28 (m, 3H), 7.82 (t, J = 5.6 Hz, 1H), 7.52 (d, J = 3.2 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 167.9, 152.9, 137.6, 131.2, 129.5, 128.9, 127.8, 127.7, 124.1, 115.6.

3,5-diphenyl-1H-1,2,4-triazole (4a)[1]



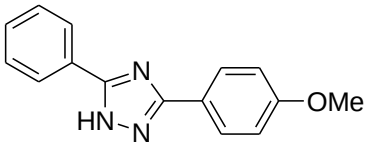
White solid, isolated yield 81%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.06-8.03 (m, 4H), 7.44-7.43 (m, 6H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 159.6, 130.0, 128.9, 126.5.

3-(4-chlorophenyl)-5-phenyl-1H-1,2,4-triazole (4b) [1]



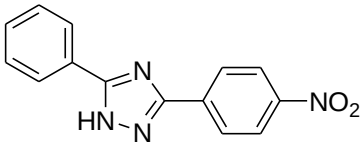
White solid, isolated yield 85%.^{1}H NMR (400MHz, $CDCl_3$): δ = 8.01-7.98 (m, 3H), 7.94-7.92 (m, 1H), 7.39-7.37 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 159.6, 130.0, 129.0, 128.9, 128.8, 128.7, 127.8, 126.5, 126.4.

3-(4-methoxyphenyl)-5-phenyl-1H-1,2,4-triazole (4c) [1]



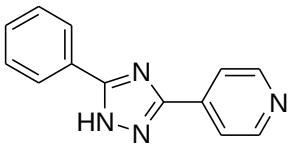
White solid, isolated yield 71%.^{1}H NMR (400MHz, $CDCl_3$): δ = 13.93 (s, 1H), 7.91-7.81 (m, 4H), 7.29-7.23 (m, 3H), 6.75-6.72 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 160.9, 134.0, 129.6, 128.6, 127.9, 126.4, 120.7, 116.5, 114.1, 55.2.

3-(4-nitrophenyl)-5-phenyl-1H-1,2,4-triazole (4d)[4]



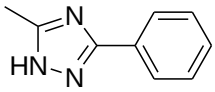
Yellow solid, isolated yield 65%.^{1}H NMR (400MHz, DMSO-d_6): δ = 14.86 (s, 1H), 8.33 (d, J = 8.8 Hz, 4H), 8.11 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ = 159.8, 156.7, 152.9, 147.6, 133.4, 130.4, 129.0, 126.8, 126.2, 124.1, 113.4.

4-(5-phenyl-1H-1,2,4-triazol-3-yl)pyridine (4e) [1]



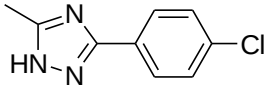
White solid, isolated yield 78%.^{1}H NMR (400MHz, DMSO-d_6): δ = 8.76 (d, J = 5.2 Hz, 2H), 8.13 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 5.6 Hz, 2H), 7.61-7.54 (m, 3H); ^{13}C NMR (100MHz, DMSO-d_6): δ = 162.4, 157.1, 150.2, 137.2, 131.1, 130.1, 128.9, 128.1, 120.0.

5-methyl-3-phenyl-1H-1,2,4-triazole (4f) [1]



White solid, isolated yield 79%.^{1}H NMR (400MHz, $CDCl_3$): δ = 13.23 (s, 1H), 8.00-7.93 (m, 2H), 7.38-7.36 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 160.4, 155.9, 132.2, 129.9, 128.7, 127.3, 126.4, 12.1.

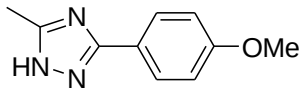
3-(4-chlorophenyl)-5-methyl-1H-1,2,4-triazole (4g) [1]



White solid, isolated yield 80%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.94 (d, 2H, J = 8.4 Hz), 7.39 (d, 2H, J = 8.4 Hz), 2.48 (s, 3H); ^{13}C NMR

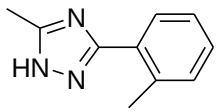
(100MHz, $CDCl_3$): δ = 161.9, 154.3, 135.4, 128.9, 128.7, 127.6, 12.4.

3-(4-methoxyphenyl)-5-methyl-1H-1,2,4-triazole (4h) [1]



White solid, isolated yield 64%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.91 (d, 2H, J = 9.2 Hz), 6.88 (d, 2H, J = 8.8 Hz), 3.78 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 160.1, 152.8, 133.9, 127.6, 116.4, 113.8, 55.2, 40.7.

5-methyl-3-o-tolyl-1H-1,2,4-triazole (4i) [1]



White solid, isolated yield 45%.^{1}H NMR (400MHz, $CDCl_3$): δ = 7.32-7.18 (m, 4H), 2.51 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 160.3, 155.7, 136.8, 131.0, 129.4, 128.8, 20.9, 12.5.

Reference:

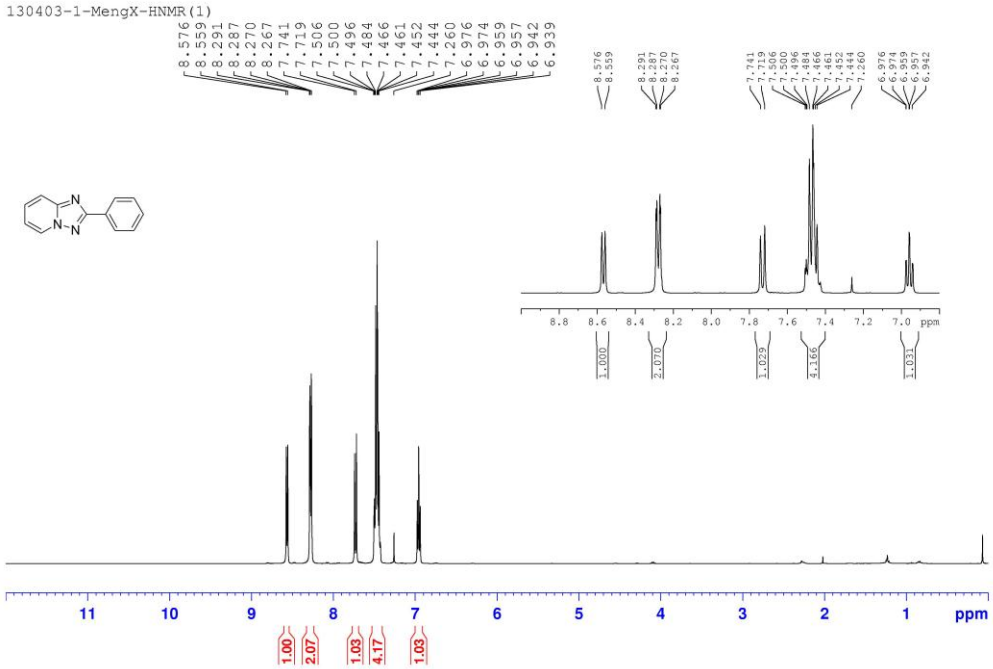
[1] S. Ueda and H. Nagasawa, J. Am. Chem. Soc., 2009, **131**, 15080.

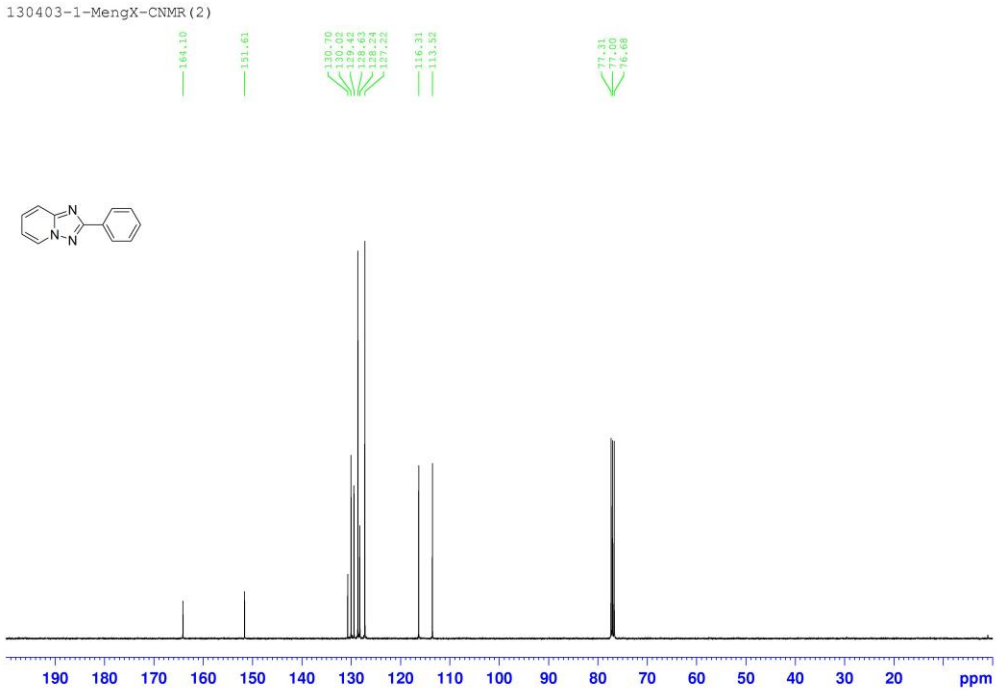
[2] G. Hajos, G. Timari, A. Messmer, A. Zagyva, I. Miskolczi and J. G Schantl, *Monatshefte fuer Chemie* 1995, **126**, 1213.

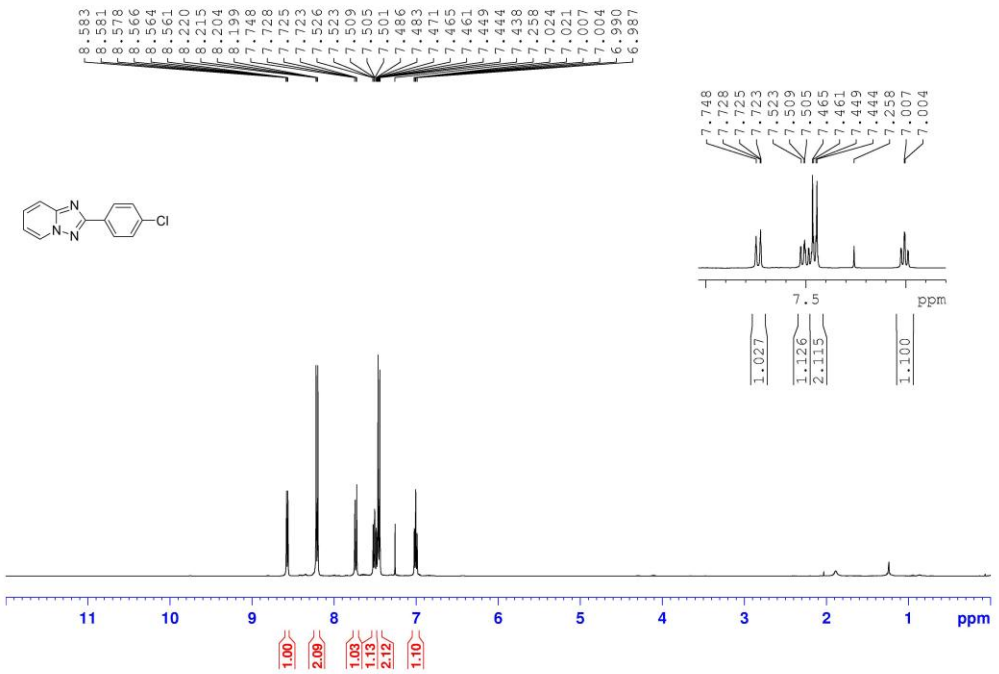
[3] J. P. Pauchard and A. E. Siegrist, *Helv. Chem. Acta* 1978, **61**, 142.

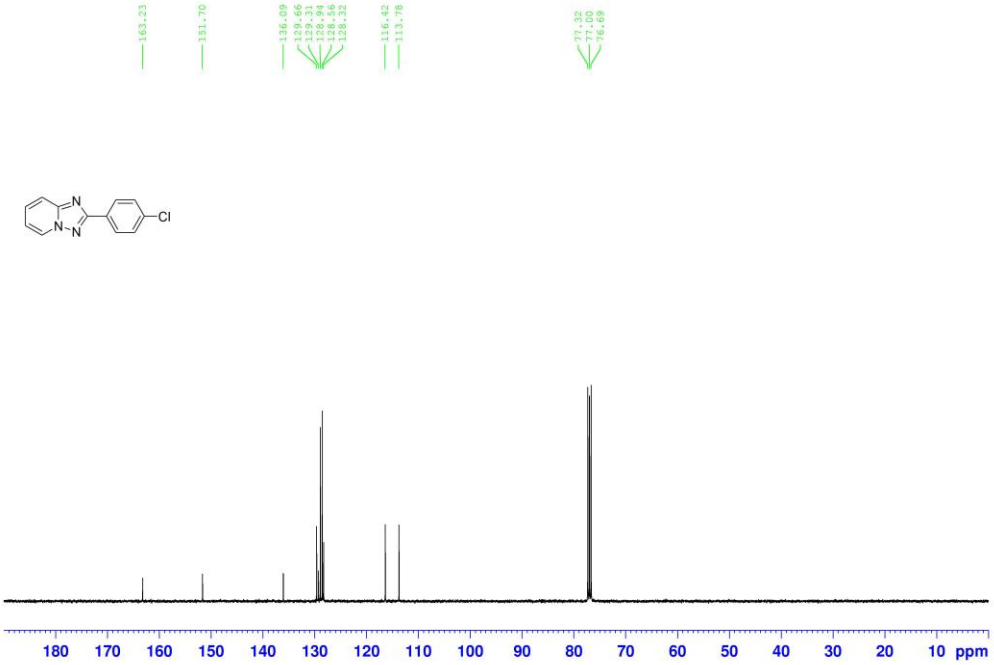
[4] T. Okamoto, M. Hirobe, Y. Tamai and E.Yabe, *Chem. Pharm. Bull.* 1966, **14**, 506.

Copy of the spectrums




130403-1-MengX-CNMR(2)
164.10
151.61
130.70
130.02
129.42
128.63
128.24
127.22
116.31
113.52
77.31
77.00
76.68
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


8.583
8.581
8.578
8.566
8.564
8.561
8.220
8.215
8.204
8.199
7.748
7.728
7.725
7.723
7.526
7.523
7.509
7.505
7.501
7.486
7.483
7.471
7.465
7.461
7.449
7.444
7.438
7.258
7.024
7.021
7.007
7.004
6.990
6.987
Cl
7.5 ppm
1.027
1.126
2.115
1.100
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.09
1.03
1.13
2.12
1.10


163.23
151.70
136.09
129.66
129.31
128.94
128.56
128.32
116.42
113.78
77.32
77.00
76.69
Cl
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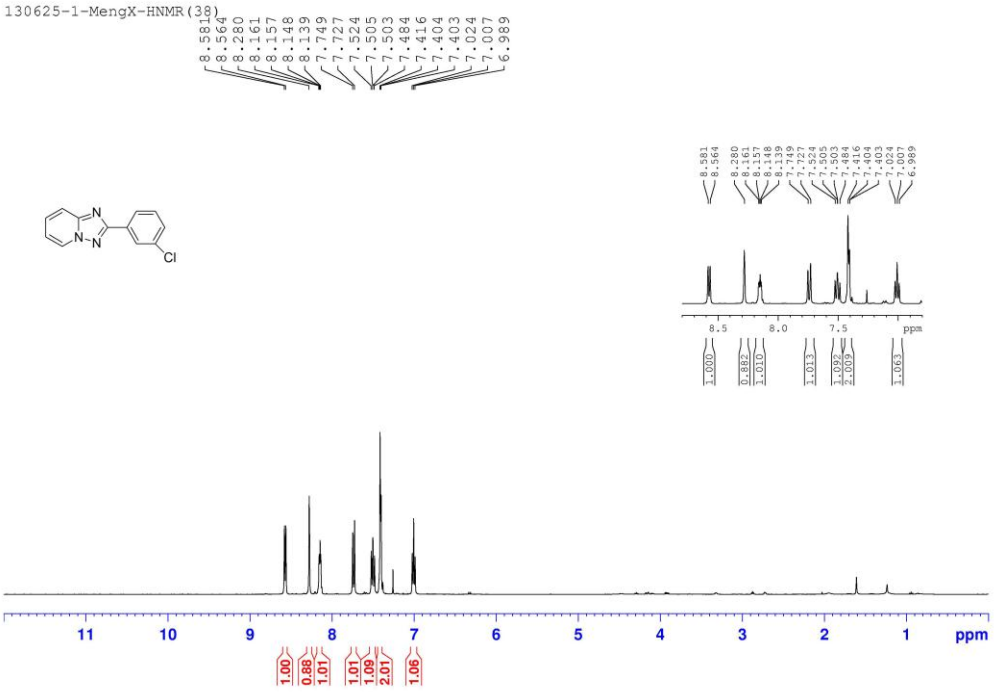
130625-1-MengX-HNMR(38)
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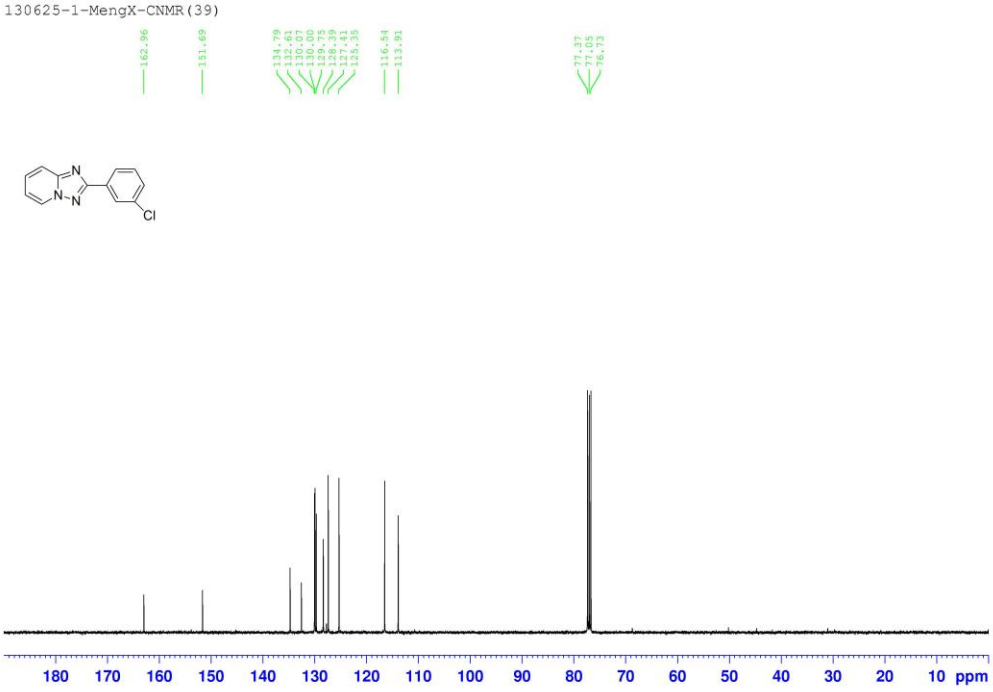
8.564
8.280
8.161
8.157
8.148
8.139
7.749
7.727
7.524
7.505
7.503
7.484
7.416
7.404
7.403
7.024
7.007
6.989
Cl
8.5
8.0
7.5
ppm
1.000
0.882
1.010
1.013
1.092
2.009
1.063
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.88
1.01
1.01
1.09
2.01
1.06


130625-1-MengX-CNMR(39)
162.96
151.69
134.79
132.61
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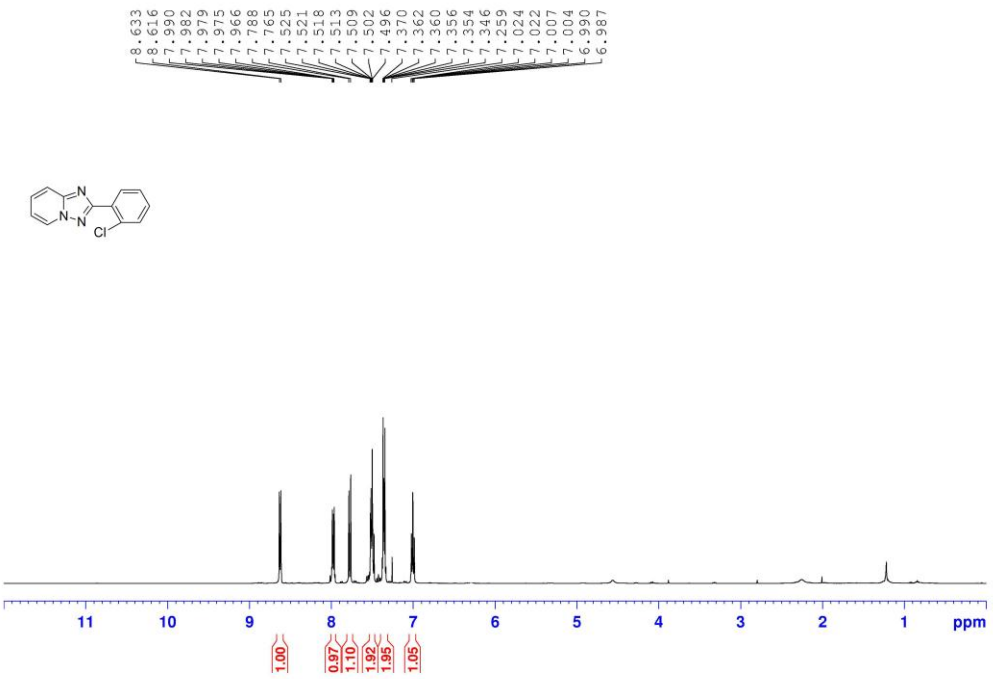
130.00
129.75
128.39
127.41
125.35
116.54
113.91
77.37
77.05
76.73
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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8.616
7.990
7.982
7.979
7.975
7.966
7.788
7.765
7.525
7.521
7.518
7.513
7.509
7.502
7.496
7.370
7.362
7.360
7.356
7.354
7.346
7.259
7.024
7.022
7.007
7.004
6.990
6.987
Cl
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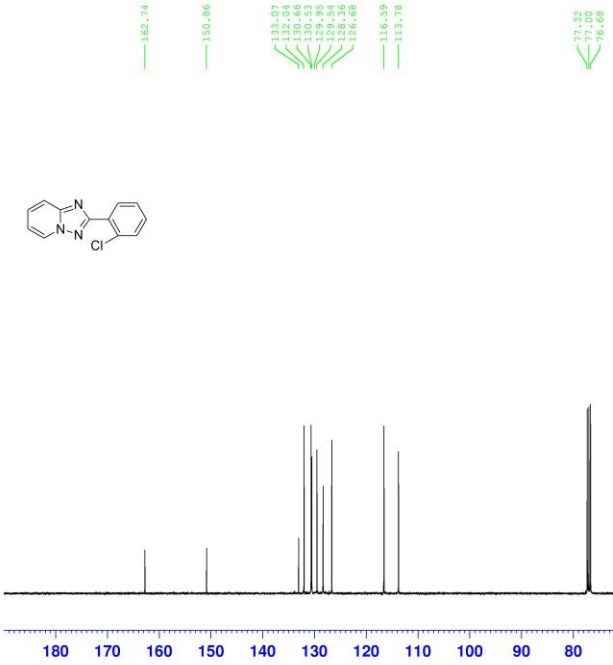
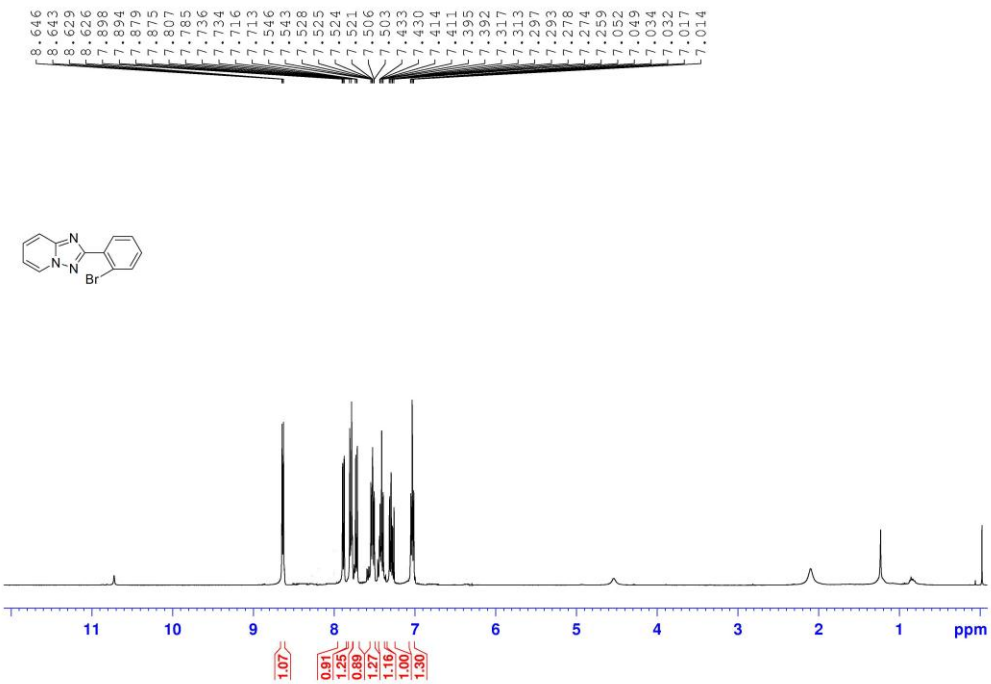
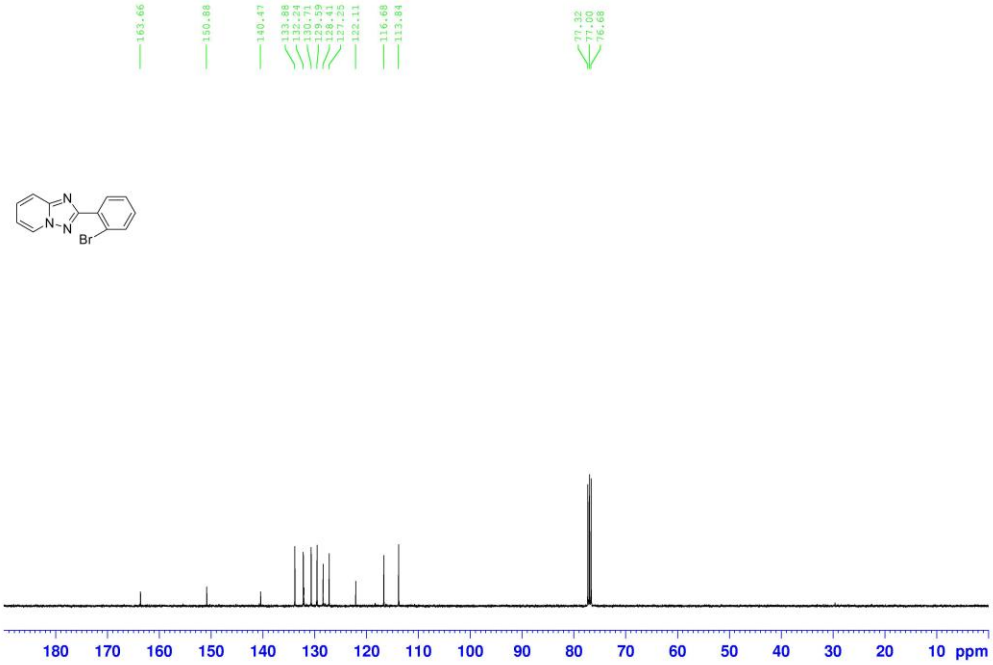
1.00
0.97
1.10
1.92
1.95
1.05


162.74
150.86
133.07
132.04
130.66
130.33
129.95
129.54
128.36
126.68
116.59
113.78
77.32
77.00
76.68
Cl
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.646
8.643
8.629
8.626
7.898
7.894
7.879
7.875
7.807
7.785
7.736
7.734
7.716
7.713
7.546
7.543
7.528
7.525
7.524
7.521
7.506
7.503
7.433
7.430
7.414
7.411
7.395
7.392
7.317
7.313
7.297
7.293
7.278
7.274
7.259
7.052
7.049
7.034
7.032
7.017
7.014
Br
11 10 9 8 7 6 5 4 3 2 1 ppm
1.07
0.91
1.25
0.89
1.27
1.16
1.00
1.30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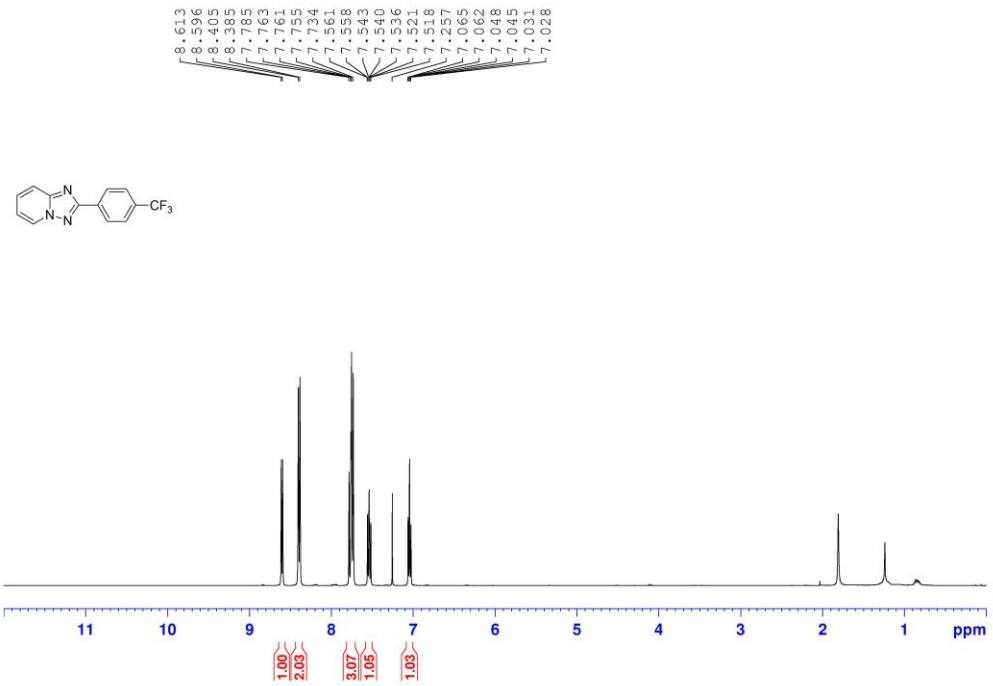
150.88
140.47
133.88
132.24
130.71
129.59
128.41
127.25
122.11
116.68
113.84
77.32
77.00
76.68
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.613
8.596
8.405
8.385
7.785
7.763
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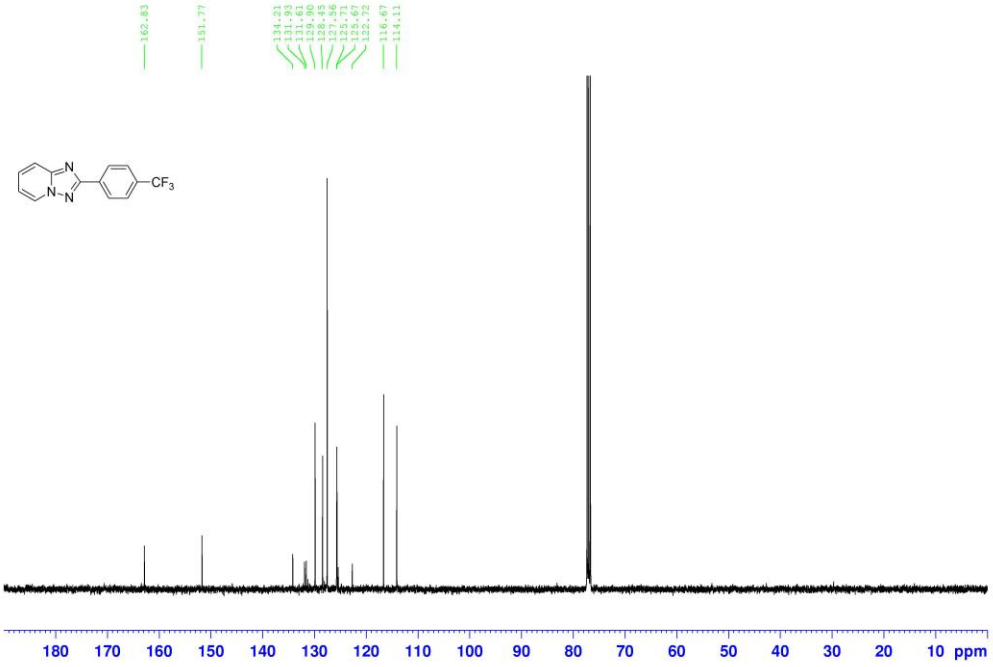
7.755
7.734
7.561
7.558
7.543
7.540
7.536
7.521
7.518
7.257
7.065
7.062
7.048
7.045
7.031
7.028
CF3
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.03
3.07
1.05
1.03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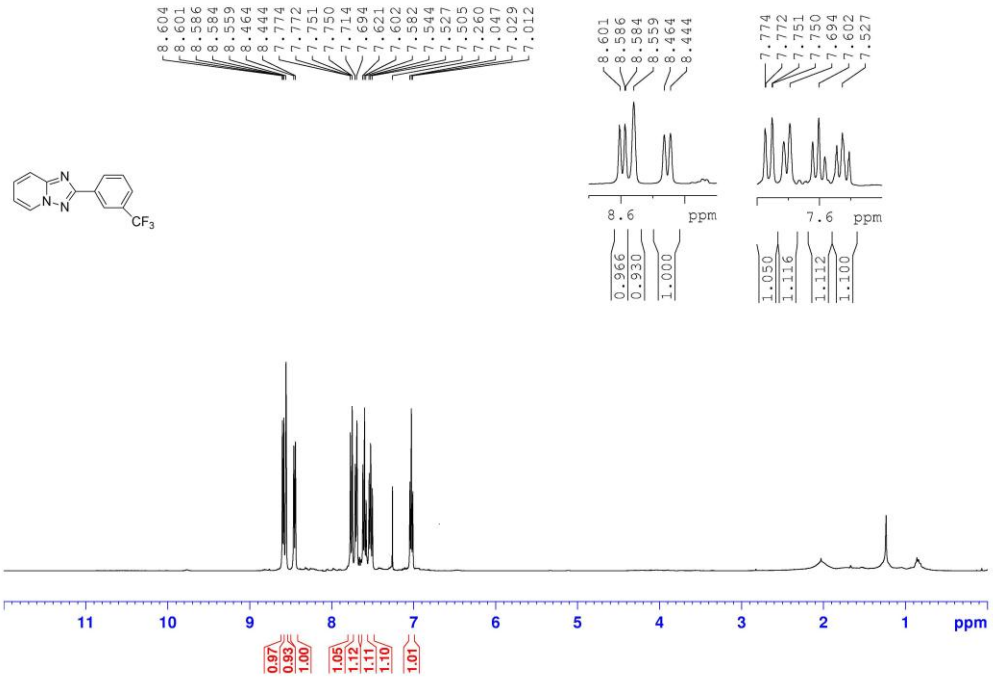
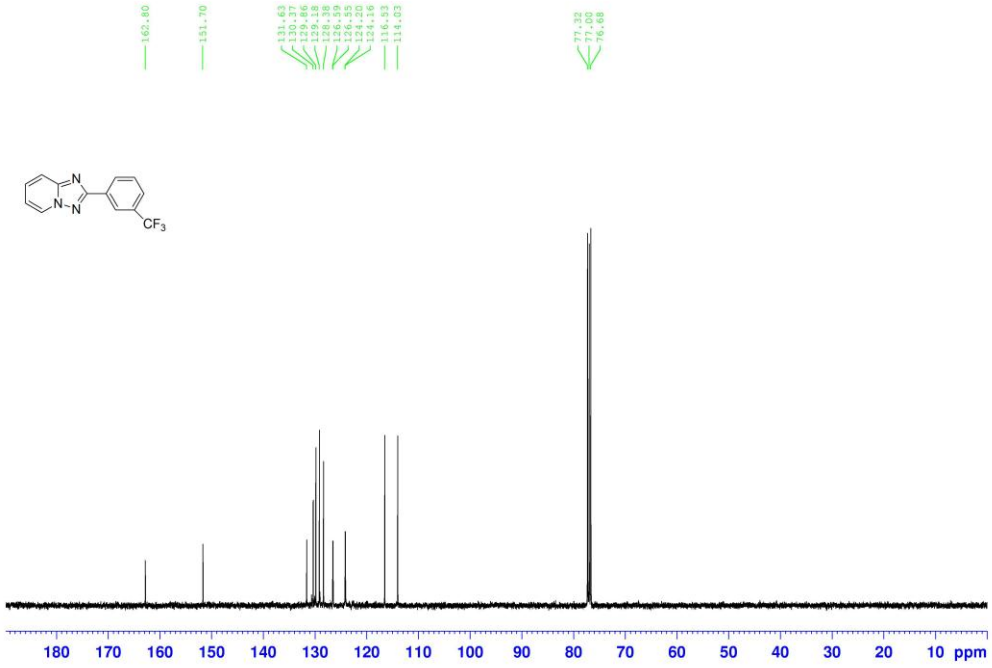
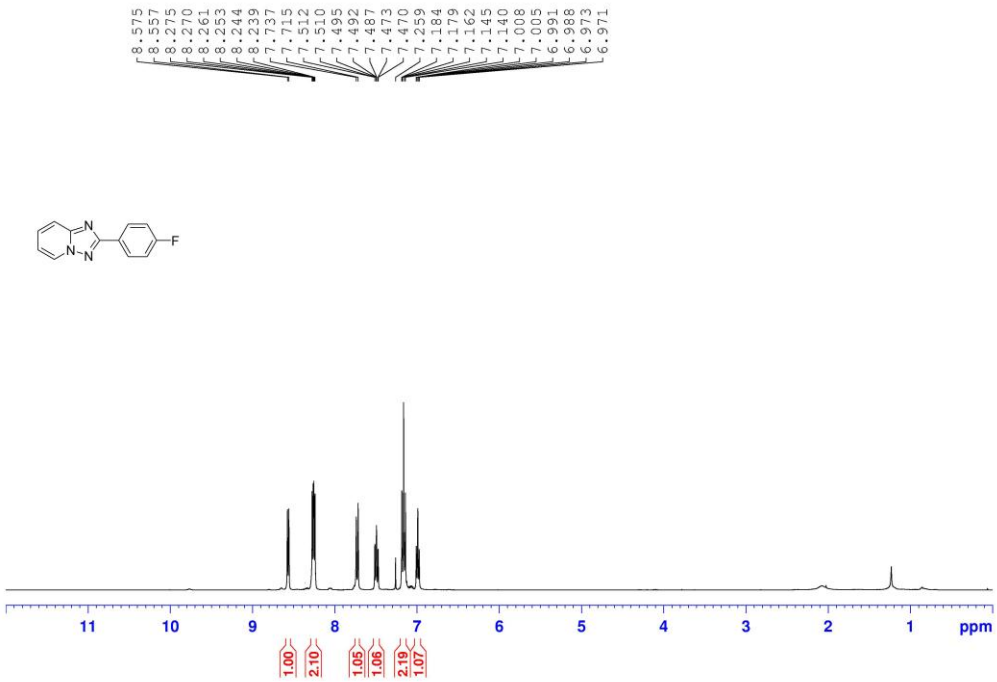
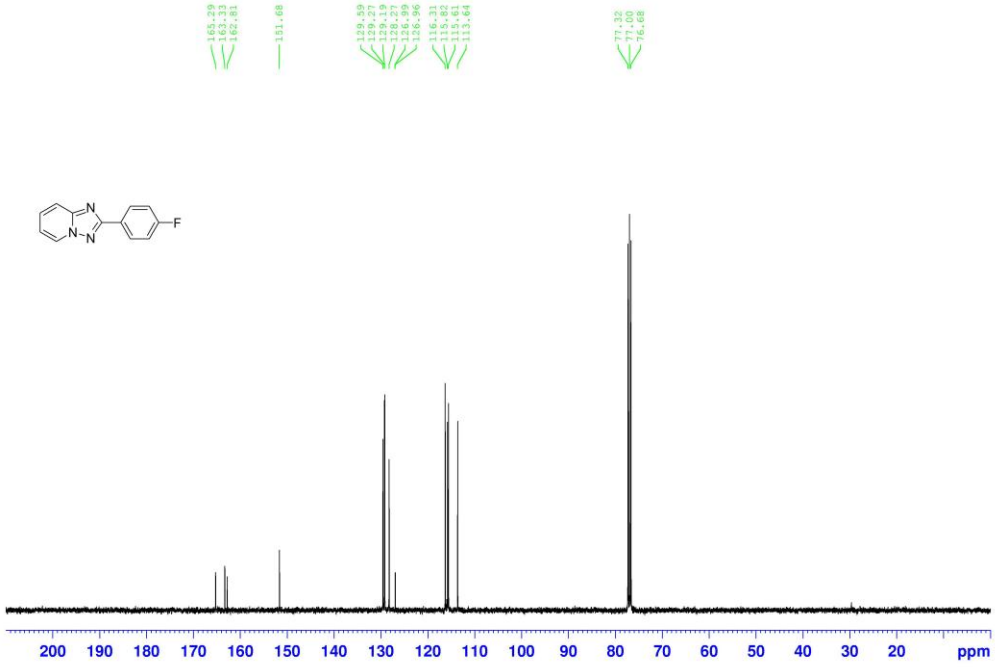
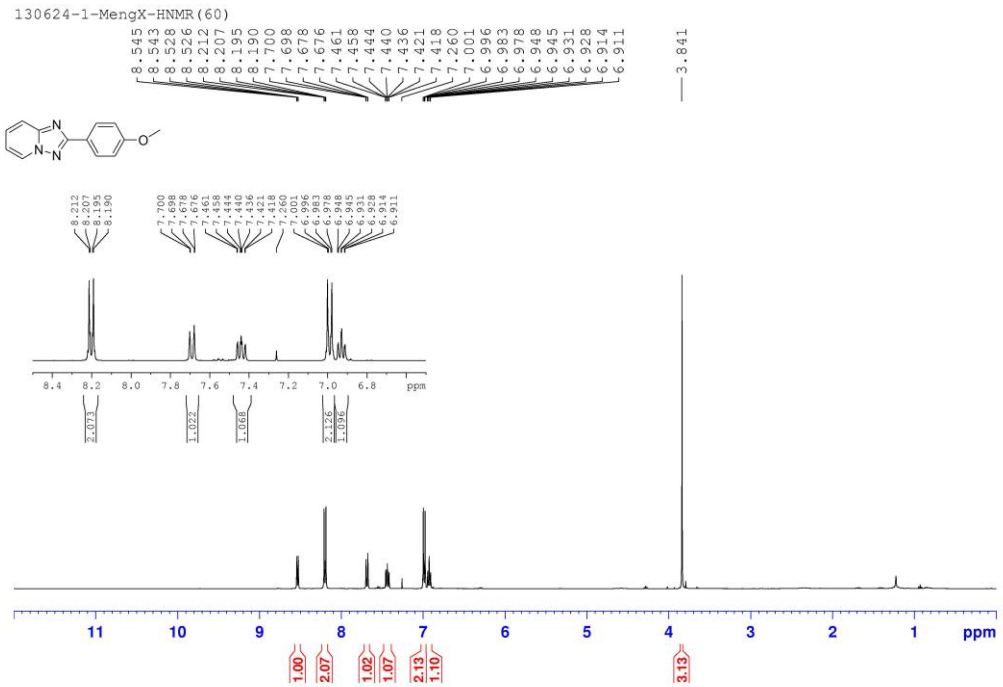
125.67
122.72
116.67
114.11
CF3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

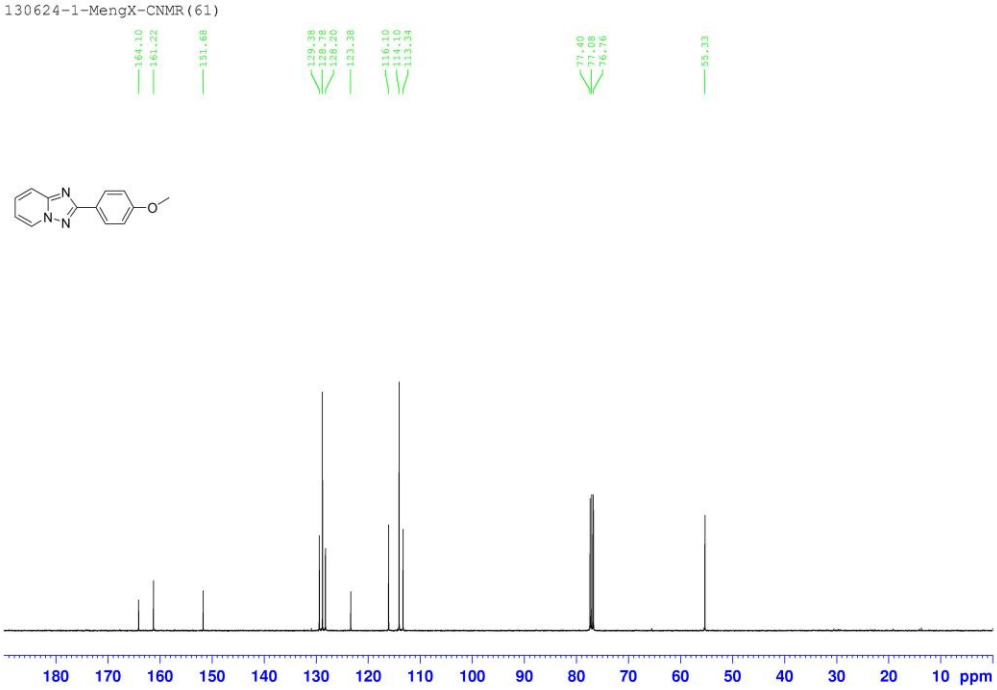

8.604
8.601
8.586
8.584
8.559
8.464
8.444
7.774
7.772
7.751
7.750
7.714
7.694
7.621
7.602
7.582
7.544
7.527
7.505
7.260
7.047
7.029
7.012
CF3
8.6 ppm
7.6 ppm
0.966
0.930
1.000
1.050
1.116
1.112
1.100
11 10 9 8 7 6 5 4 3 2 1 ppm
0.97
0.93
1.00
1.05
1.12
1.11
1.10
1.01

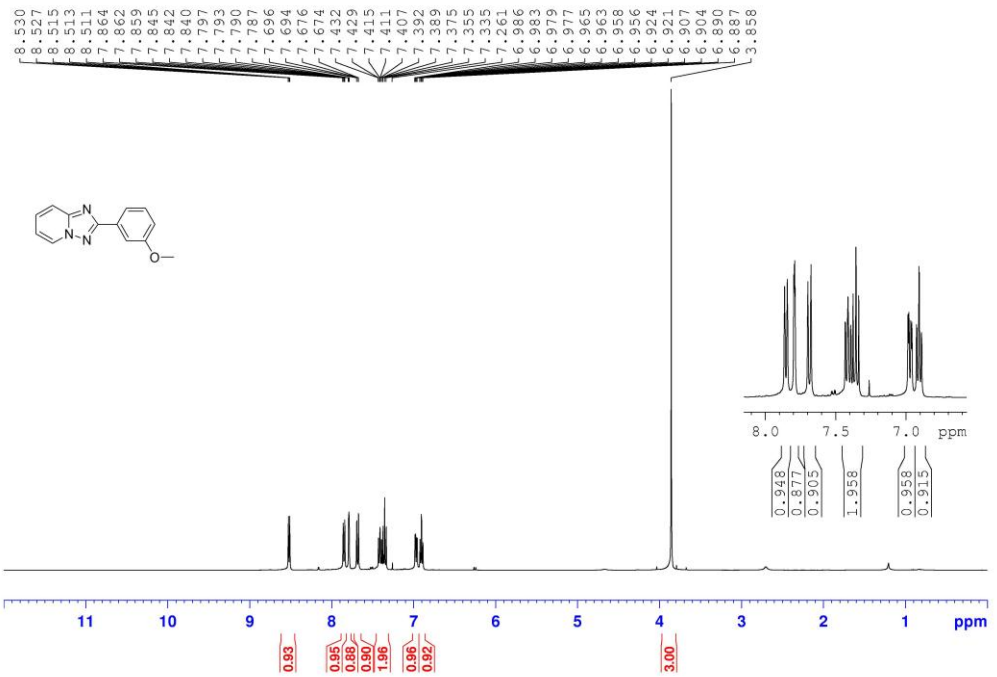

162.80
151.70
131.63
130.37
129.86
129.18
128.38
126.59
126.55
124.20
124.16
116.53
114.03
77.32
77.00
76.68
CF3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

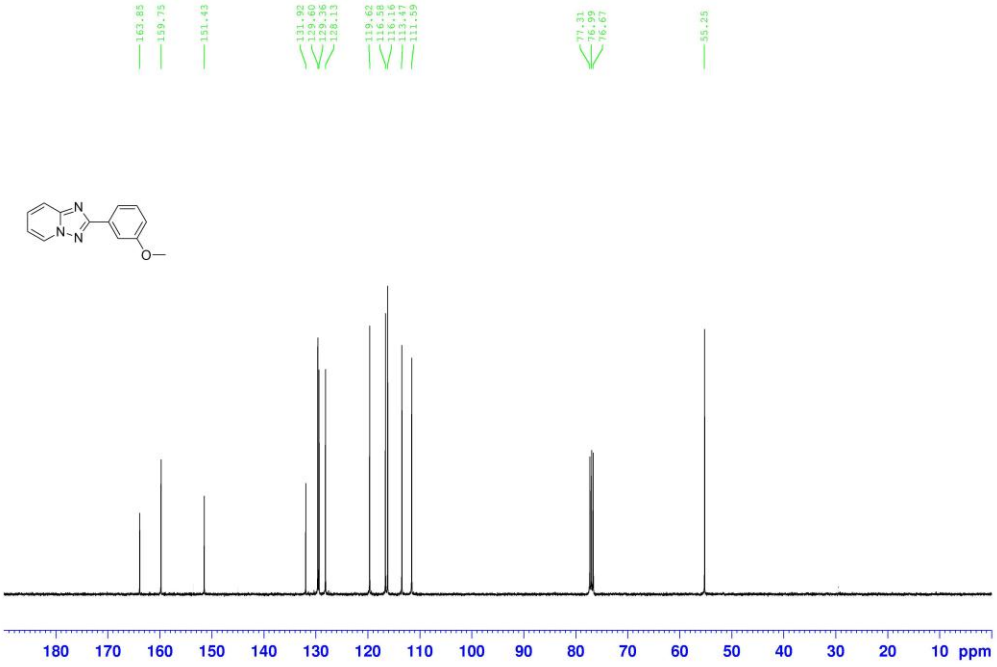

8.575
8.557
8.275
8.270
8.261
8.253
8.244
8.239
7.737
7.715
7.512
7.510
7.495
7.492
7.487
7.473
7.470
7.259
7.184
7.179
7.162
7.145
7.140
7.008
7.005
6.991
6.988
6.973
6.971
F
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.10
1.05
1.06
2.19
1.07

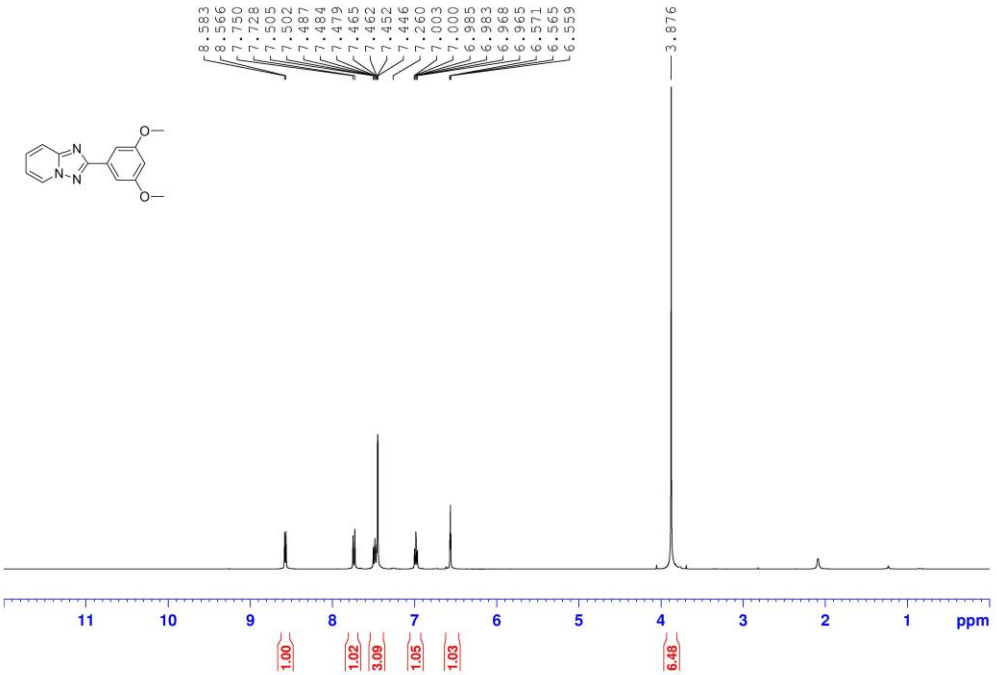

165.29
163.33
162.81
151.68
139.59
129.27
128.19
128.27
126.99
126.96
116.31
115.82
115.61
113.64
77.32
77.00
76.68
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

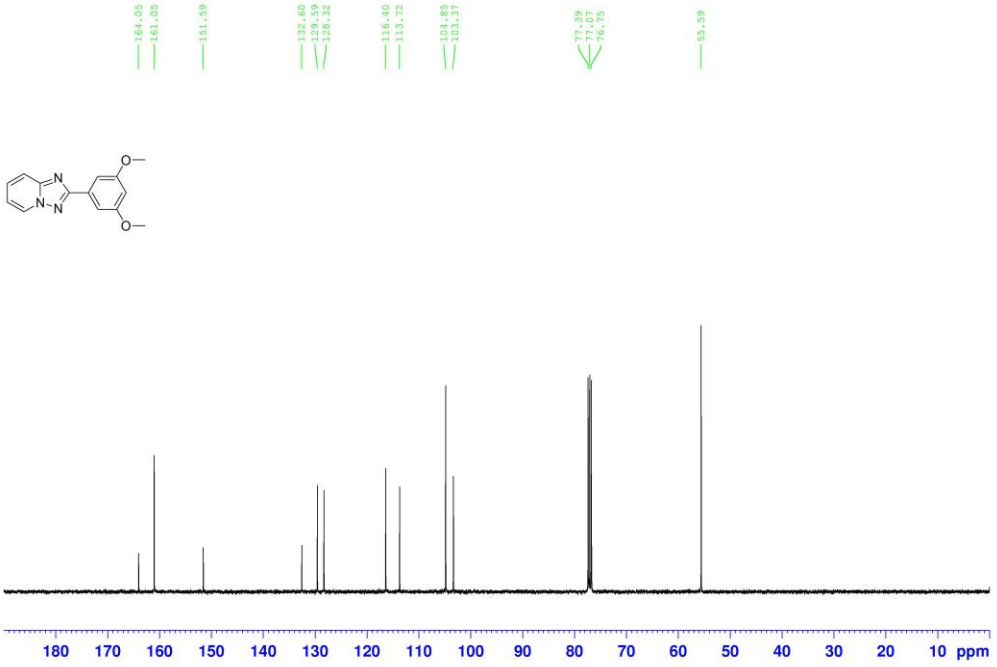

130624-1-MengX-HNMR(60)
8.545
8.543
8.528
8.526
8.212
8.207
8.195
8.190
7.700
7.698
7.678
7.676
7.461
7.458
7.444
7.440
7.436
7.421
7.418
7.260
7.001
6.996
6.983
6.978
6.948
6.945
6.931
6.928
6.914
6.911
3.841
O
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 ppm
2.073
1.022
1.068
2.126
1.096
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.07
1.02
1.07
2.13
1.10
3.13

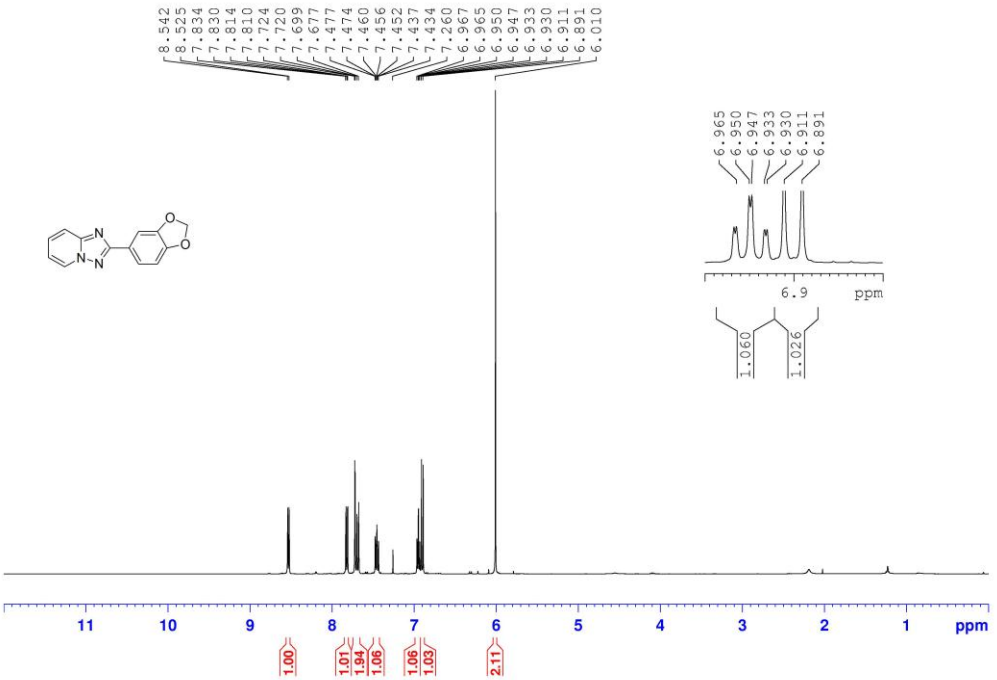

130624-1-MengX-CNMR(61)
164.10
161.22
151.68
129.38
128.78
128.20
123.38
116.10
114.10
113.34
77.40
77.08
76.76
55.33
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

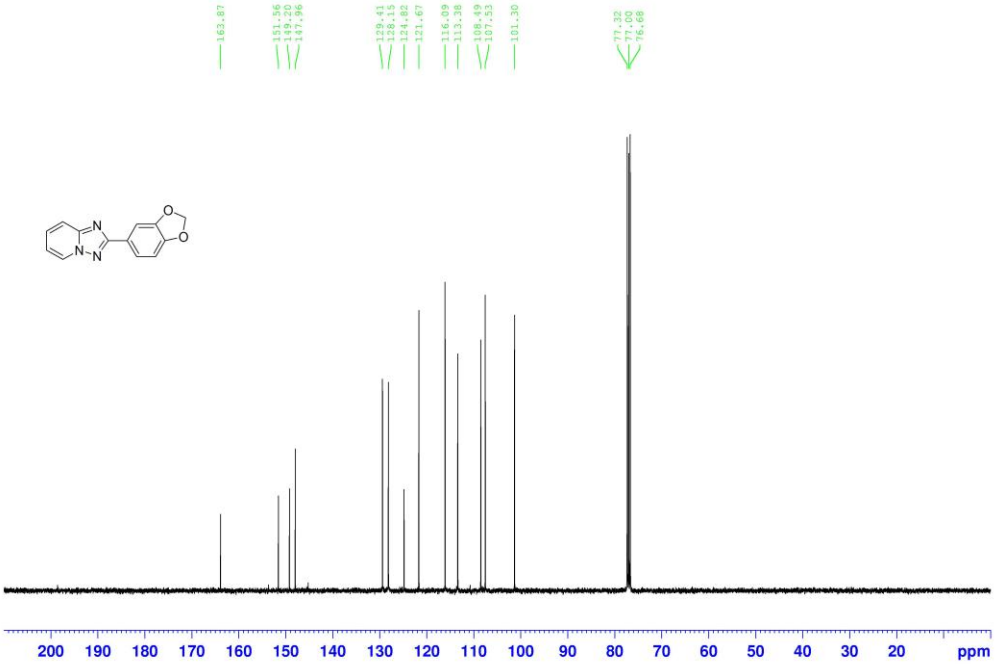

8.530
8.527
8.515
8.513
8.511
7.864
7.862
7.859
7.845
7.842
7.840
7.797
7.793
7.790
7.787
7.696
7.694
7.676
7.674
7.432
7.429
7.415
7.411
7.407
7.392
7.389
7.375
7.355
7.335
7.261
6.986
6.983
6.979
6.977
6.965
6.963
6.958
6.956
6.924
6.921
6.907
6.904
6.890
6.887
3.858
O
8.0 7.5 7.0 ppm
0.948
0.877
0.905
1.958
0.958
0.915
11 10 9 8 7 6 5 4 3 2 1 ppm
0.93
0.95
0.88
0.90
1.96
0.96
0.92
3.00

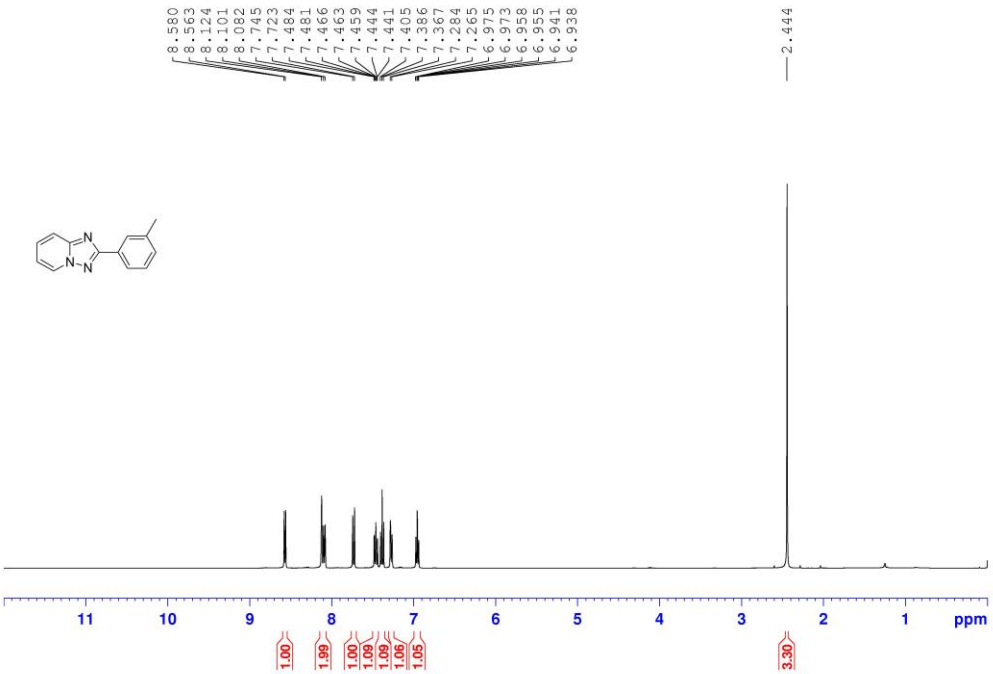

163.85
159.75
151.43
131.92
129.60
129.36
128.13
119.62
116.88
116.16
113.47
111.59
77.31
76.99
76.67
55.25
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

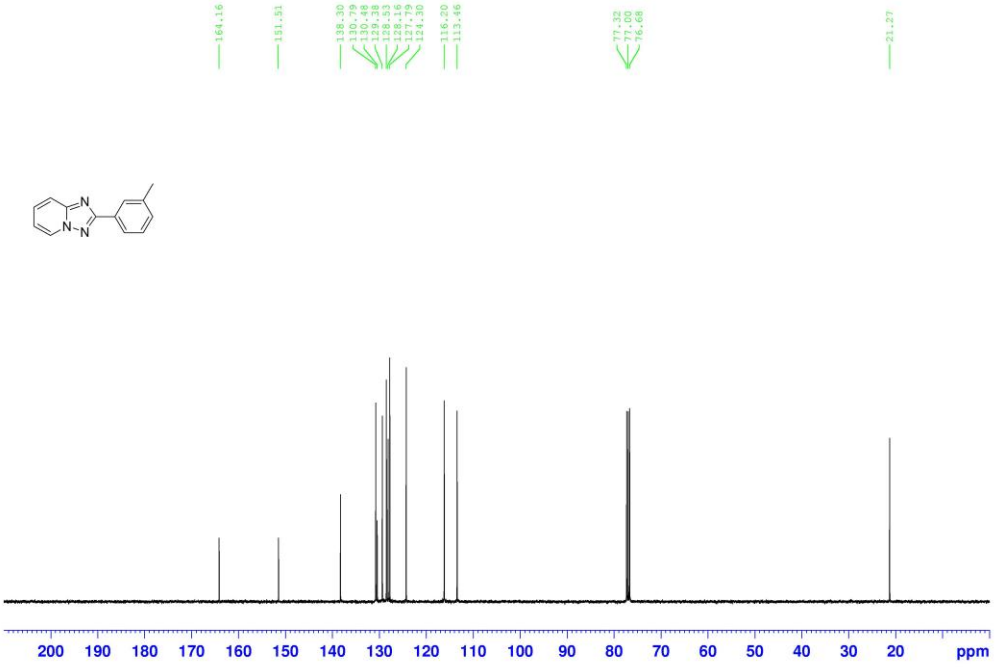

8.583
8.566
7.750
7.728
7.505
7.502
7.487
7.484
7.479
7.465
7.462
7.452
7.446
7.260
7.003
7.000
6.985
6.983
6.968
6.965
6.571
6.565
6.559
3.876
O
O
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.02
3.09
1.05
1.03
6.48

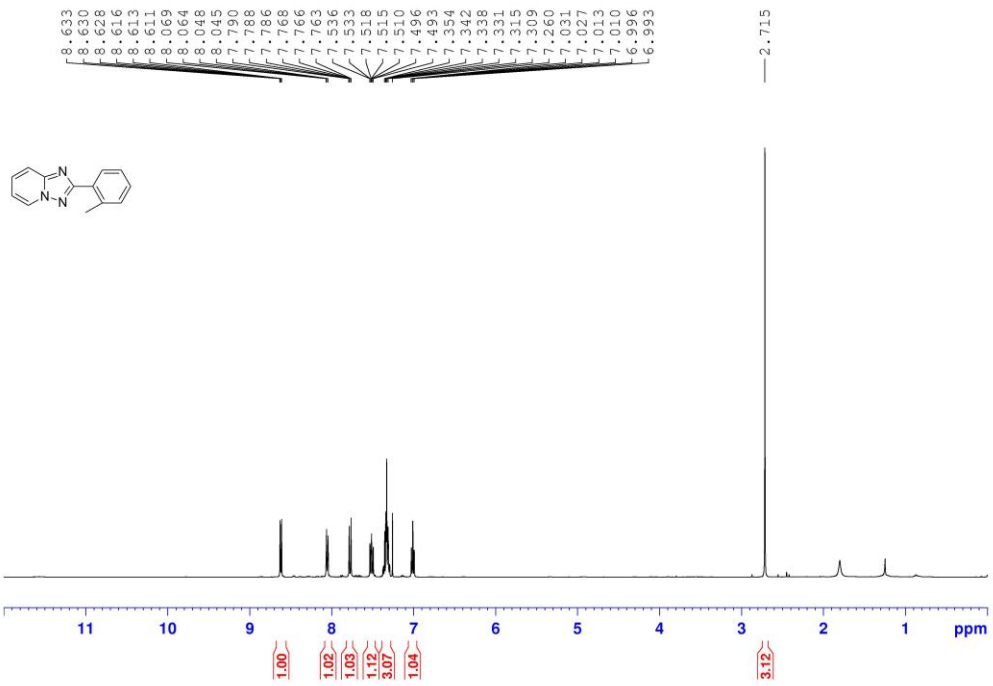

164.05
161.05
151.59
132.60
129.59
128.32
116.40
113.72
104.85
103.37
77.39
77.07
76.75
55.59
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

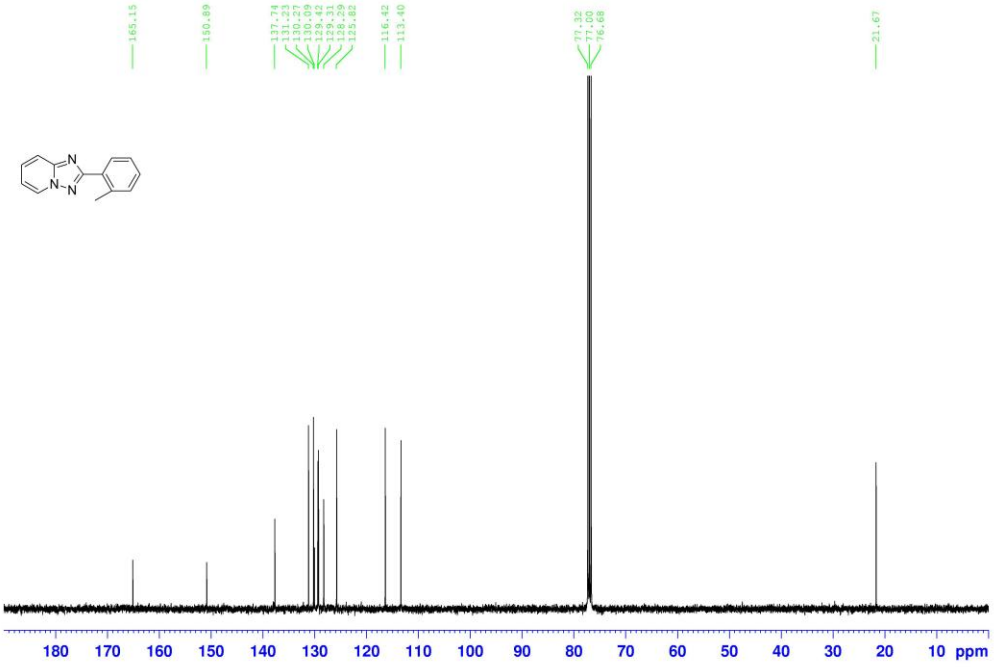

8.542
8.525
7.834
7.830
7.814
7.810
7.724
7.720
7.699
7.677
7.477
7.474
7.460
7.456
7.452
7.437
7.434
7.260
6.967
6.965
6.950
6.947
6.933
6.930
6.911
6.891
6.010
6.965
6.950
6.947
6.933
6.930
6.911
6.891
6.9 ppm
1.060
1.026
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.01
1.94
1.06
1.06
1.03
2.11

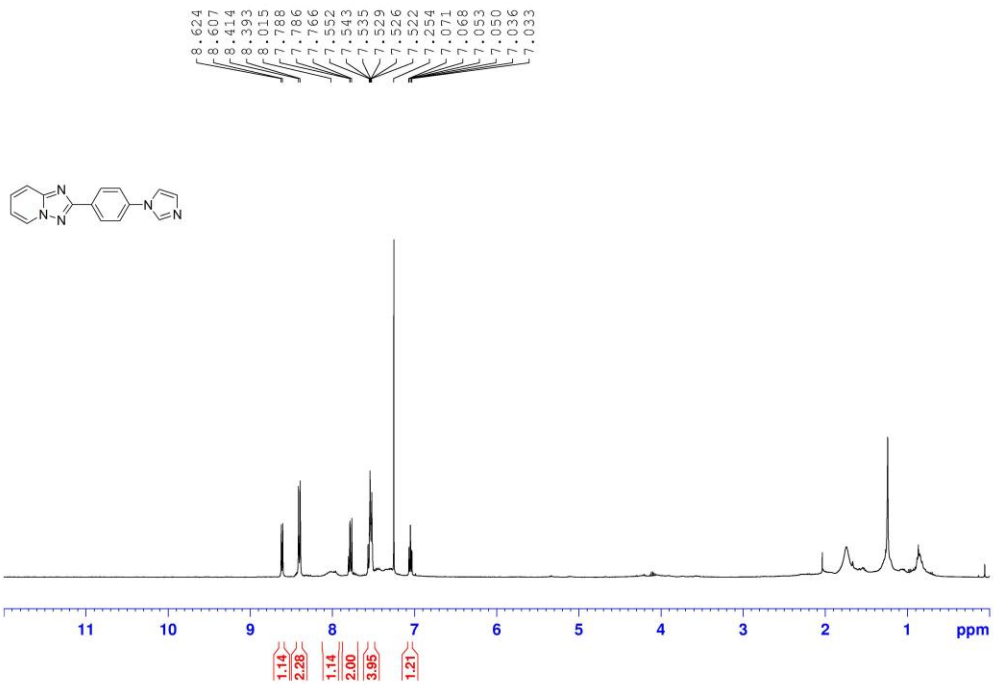

163.87
151.56
149.20
147.96
129.41
128.15
124.82
121.67
116.09
113.38
108.49
107.53
101.30
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

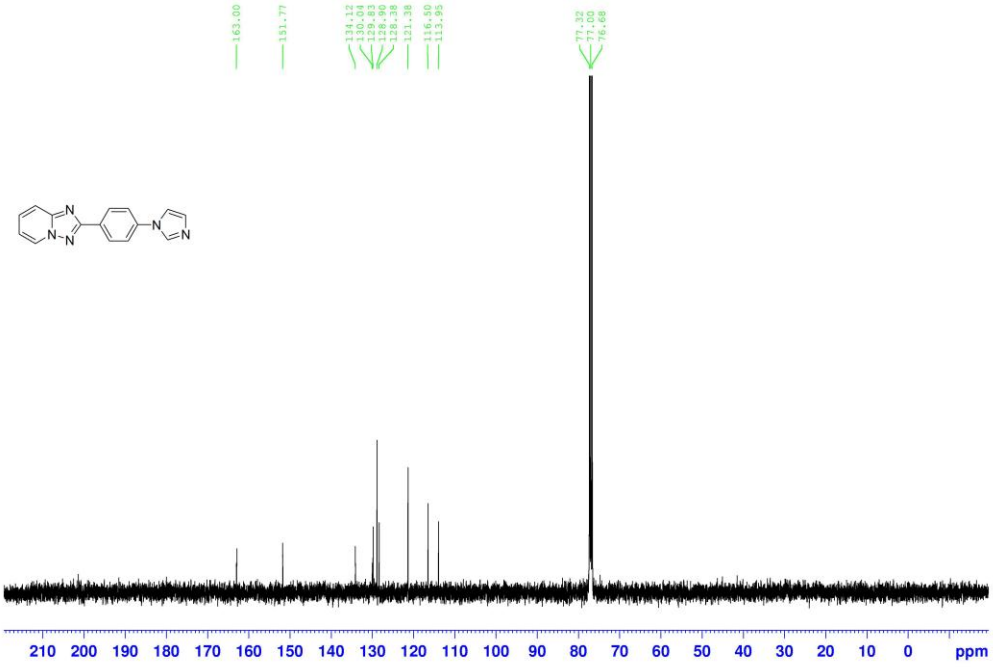

8.580
8.563
8.124
8.101
8.082
7.745
7.723
7.484
7.481
7.466
7.463
7.459
7.444
7.441
7.405
7.386
7.367
7.284
7.265
6.975
6.973
6.958
6.955
6.941
6.938
2.444
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.99
1.00
1.09
1.09
1.06
1.05
3.30

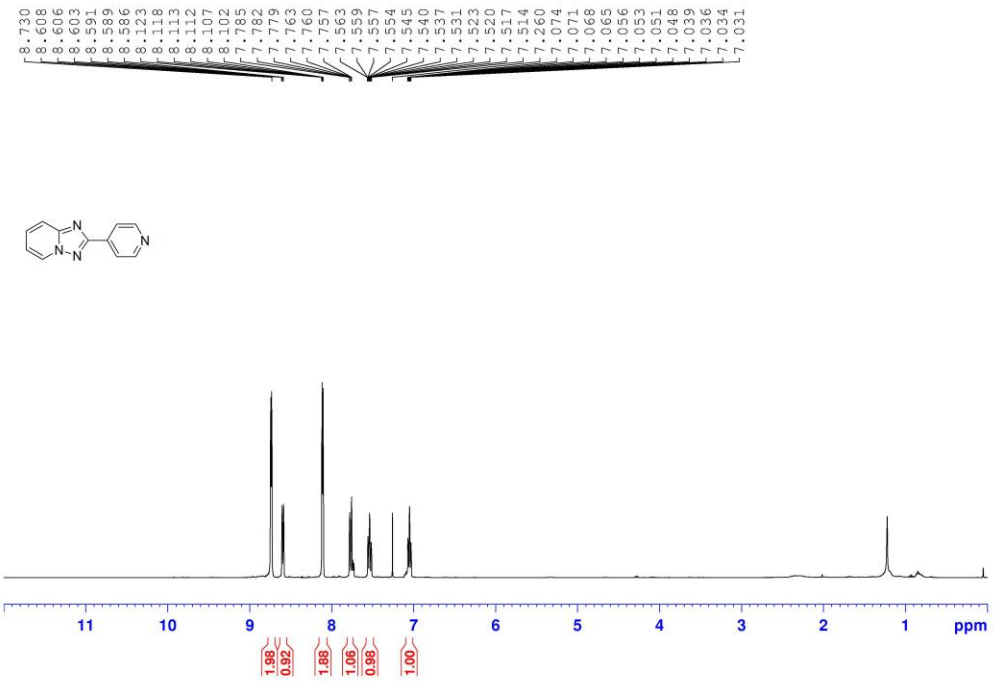

164.16
151.51
138.30
130.79
130.48
129.38
128.53
128.16
127.79
124.30
116.20
113.46
77.32
77.00
76.68
21.27
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

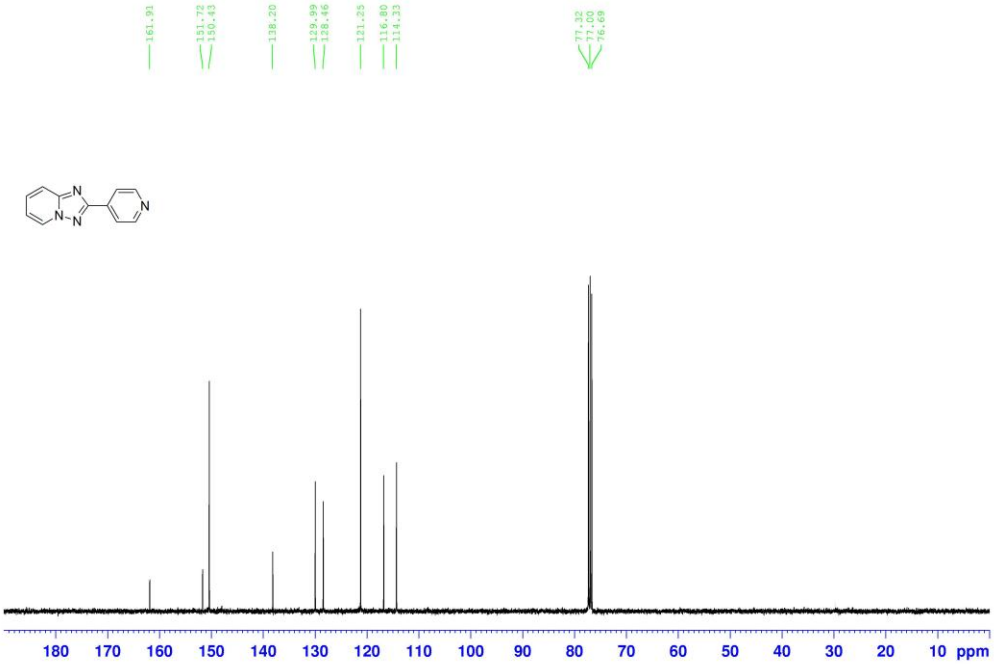

8.633
8.630
8.628
8.616
8.613
8.611
8.069
8.064
8.048
8.045
7.790
7.788
7.786
7.768
7.766
7.763
7.536
7.533
7.518
7.515
7.510
7.496
7.493
7.354
7.342
7.338
7.331
7.315
7.309
7.260
7.031
7.027
7.013
7.010
6.996
6.993
2.715
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.02
1.03
1.12
3.07
1.04
3.12

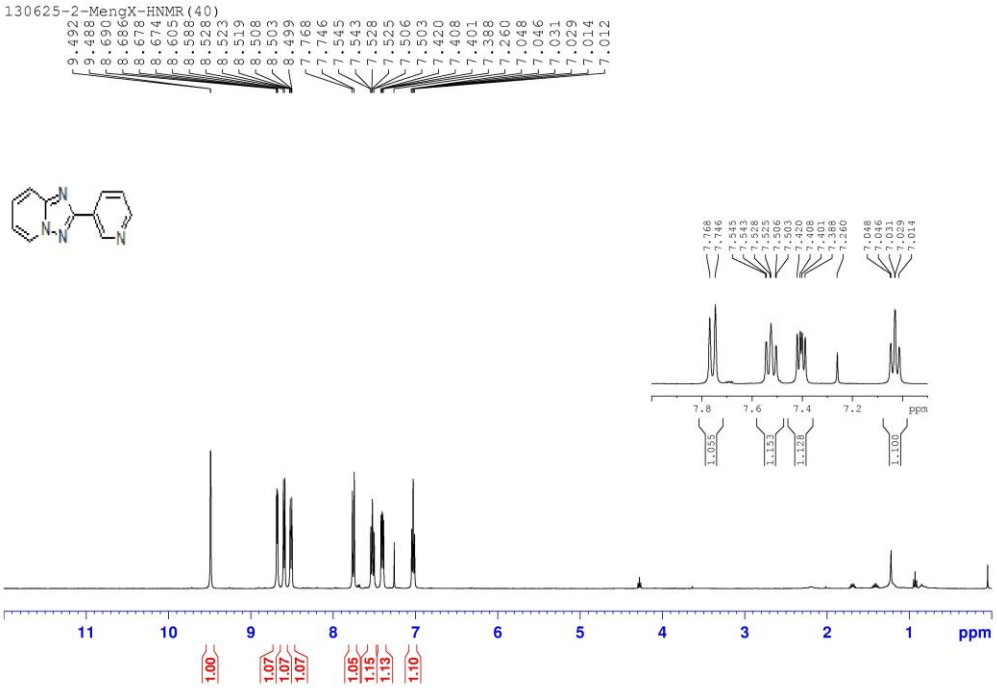

165.15
150.89
137.74
131.23
130.73
130.09
129.42
129.31
128.29
125.82
116.42
113.40
77.32
77.00
76.68
21.67
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

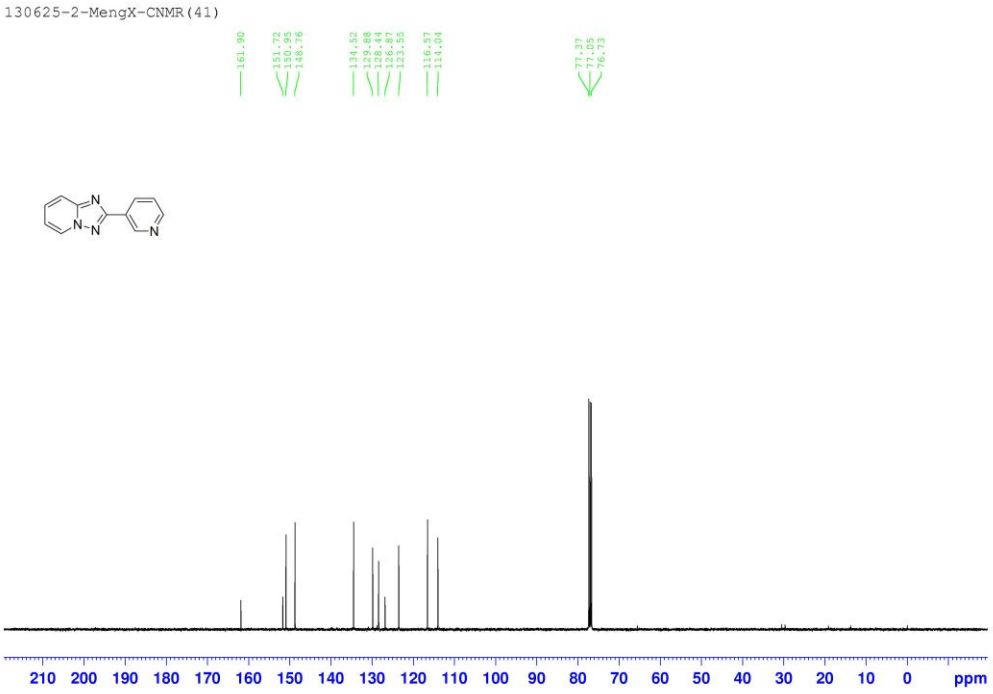

8.624
8.607
8.414
8.393
8.015
7.788
7.786
7.766
7.552
7.543
7.535
7.529
7.526
7.522
7.254
7.071
7.068
7.053
7.050
7.036
7.033
11 10 9 8 7 6 5 4 3 2 1 ppm
1.14
2.28
1.14
2.00
3.95
1.21

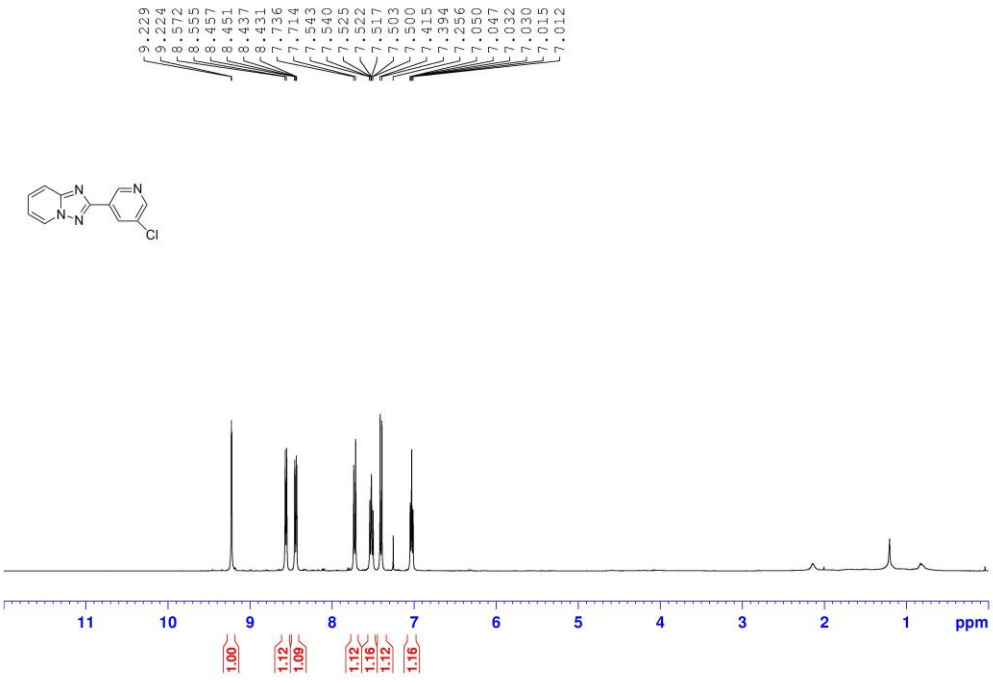

163.00
151.77
134.12
130.04
129.83
128.90
128.78
128.38
121.38
116.50
113.95
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

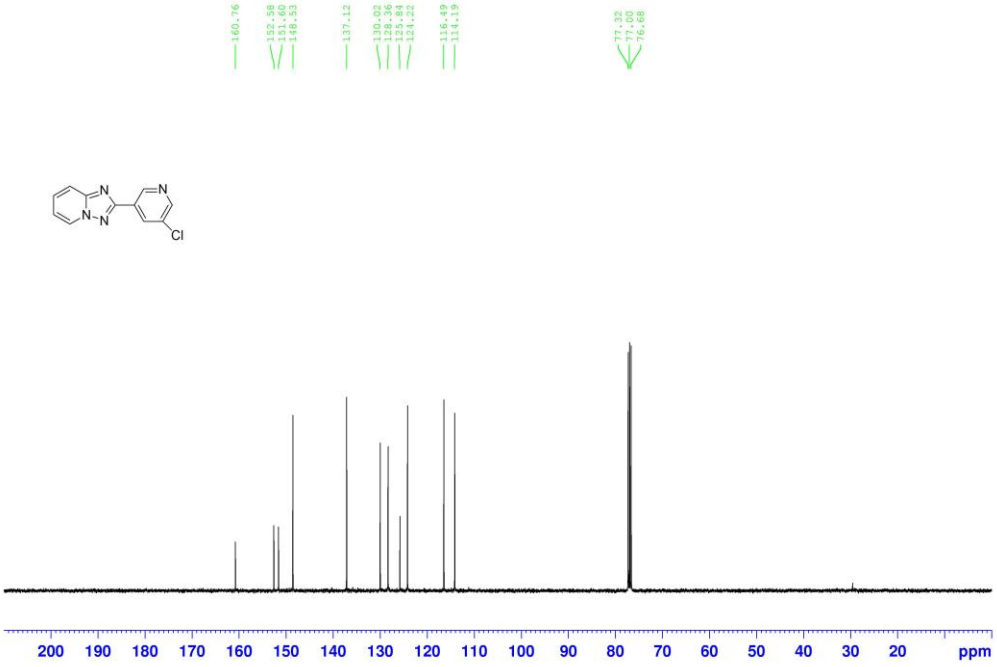

8.730
8.608
8.606
8.603
8.591
8.589
8.586
8.123
8.118
8.113
8.112
8.107
8.102
7.785
7.782
7.779
7.763
7.760
7.757
7.563
7.559
7.557
7.554
7.545
7.540
7.537
7.531
7.523
7.520
7.517
7.514
7.260
7.074
7.071
7.068
7.065
7.056
7.053
7.051
7.048
7.039
7.036
7.034
7.031
11 10 9 8 7 6 5 4 3 2 1 ppm
1.98
0.92
1.88
1.06
0.98
1.00

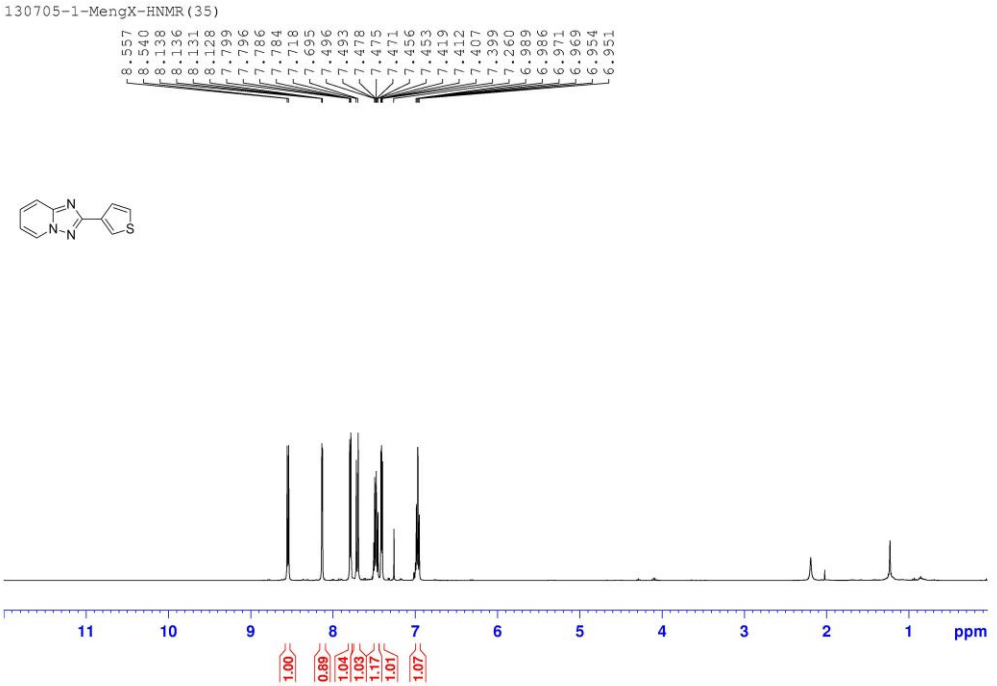

161.91
151.72
150.43
138.20
129.99
128.46
121.25
116.80
114.33
77.32
77.00
76.68
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

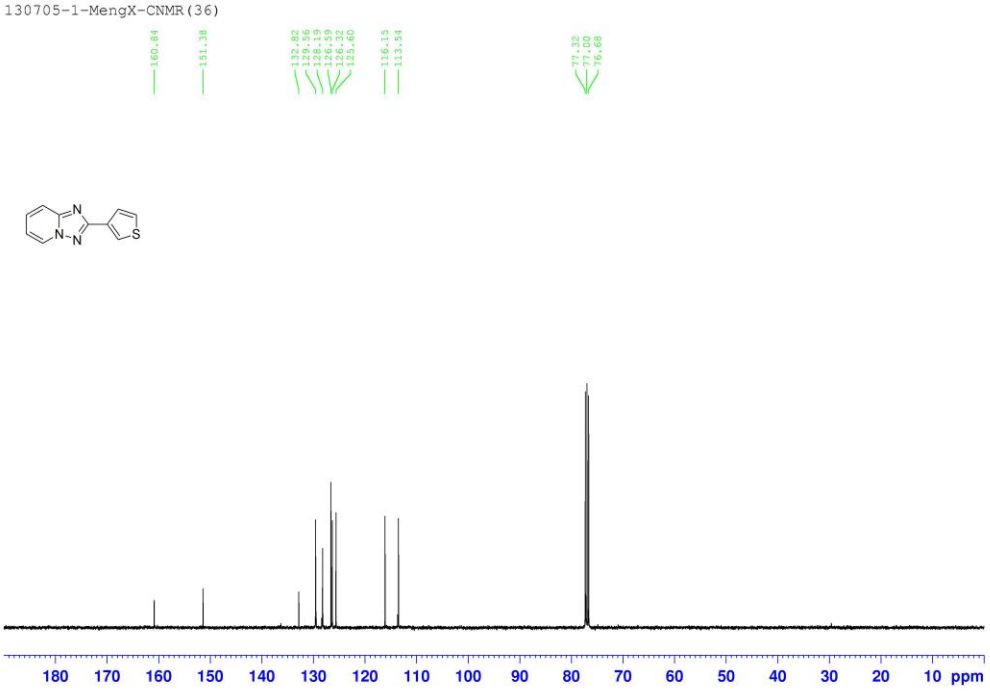

130625-2-MengX-HNMR(40)
9.492
9.488
8.690
8.686
8.678
8.674
8.605
8.588
8.528
8.523
8.519
8.508
8.503
8.499
7.768
7.746
7.545
7.543
7.528
7.525
7.506
7.503
7.420
7.408
7.401
7.388
7.260
7.048
7.046
7.031
7.029
7.014
7.012
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.07
1.07
1.07
1.05
1.15
1.13
1.10
7.8 7.6 7.4 7.2 ppm
1.055
1.153
1.128
1.100

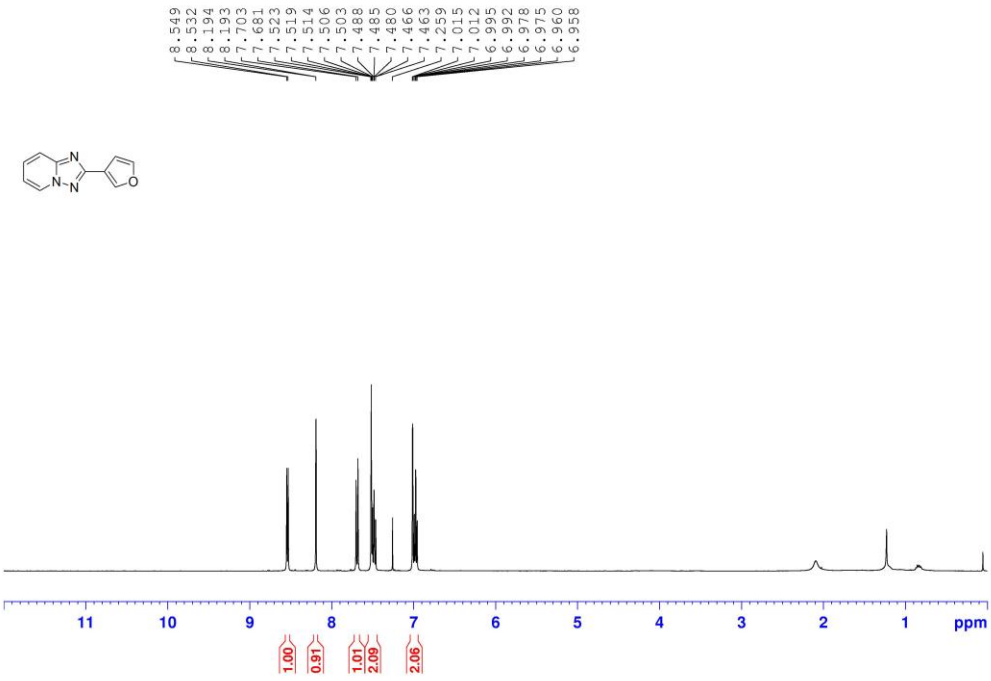

130625-2-MengX-CNMR(41)
161.90
151.72
150.95
148.76
134.52
129.88
128.44
126.87
123.55
116.57
114.04
77.37
77.05
76.73
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

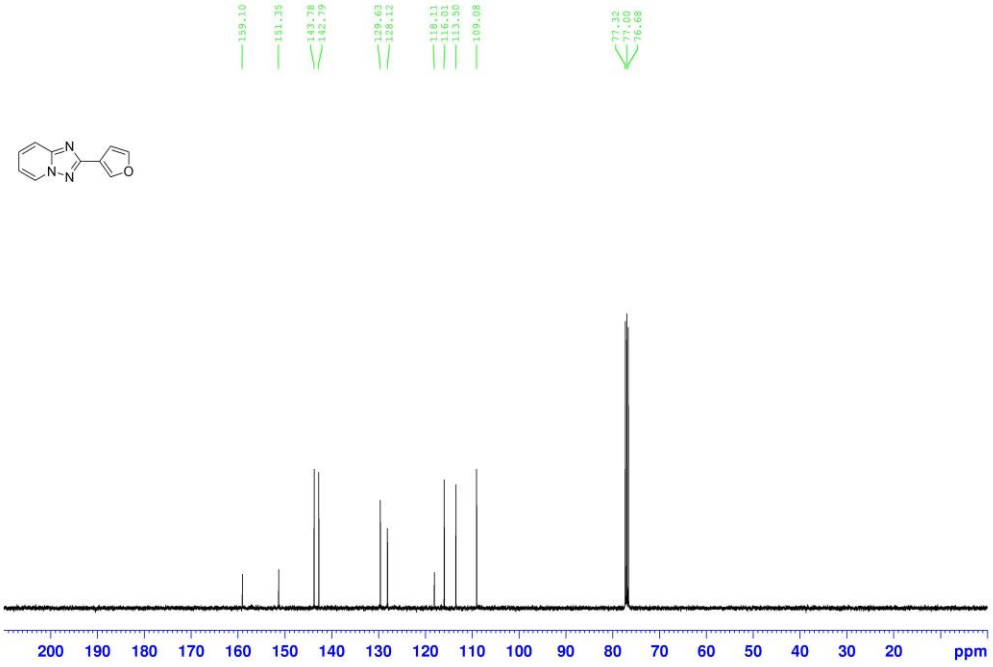

9.229
9.224
8.572
8.555
8.457
8.451
8.437
8.431
7.736
7.714
7.543
7.540
7.525
7.522
7.517
7.503
7.500
7.415
7.394
7.256
7.050
7.047
7.032
7.030
7.015
7.012
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.12
1.09
1.12
1.16
1.12
1.16

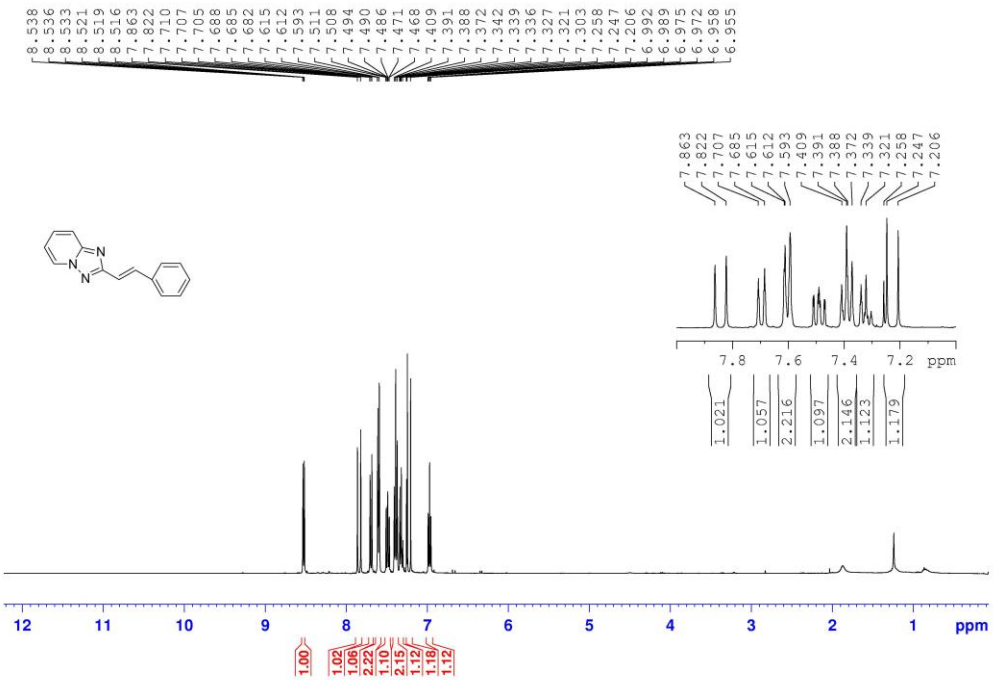

160.76
152.38
151.60
148.53
137.12
130.02
128.36
125.84
124.22
116.49
114.19
77.32
77.00
76.68
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

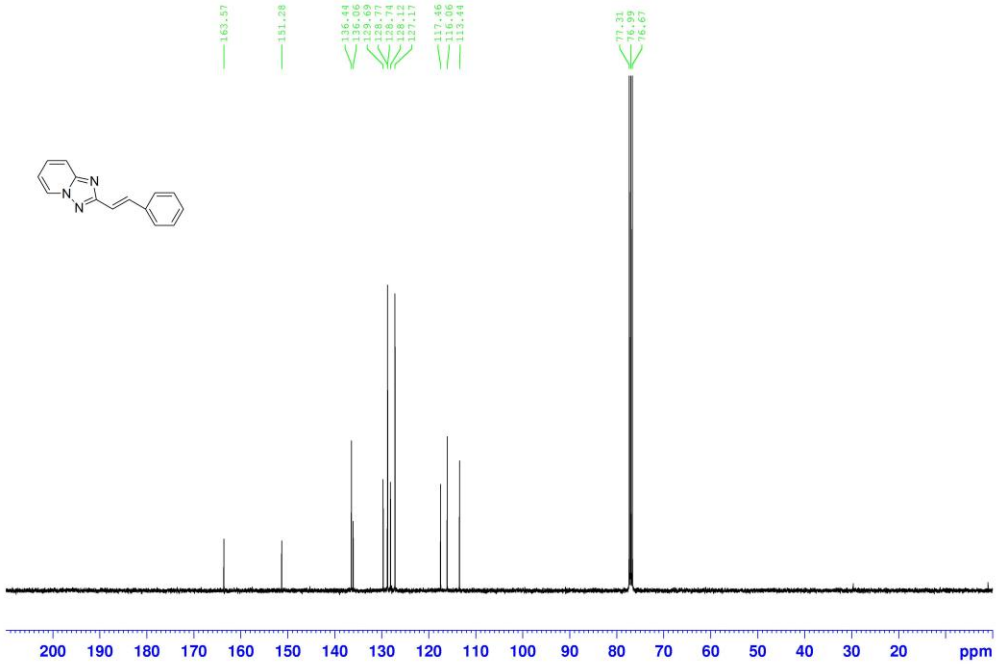

130705-1-MengX-HNMR(35)
8.557
8.540
8.138
8.136
8.131
8.128
7.799
7.796
7.786
7.784
7.718
7.695
7.496
7.493
7.478
7.475
7.471
7.456
7.453
7.419
7.412
7.407
7.399
7.260
6.989
6.986
6.971
6.969
6.954
6.951
S
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.89
1.04
1.03
1.17
1.01
1.07

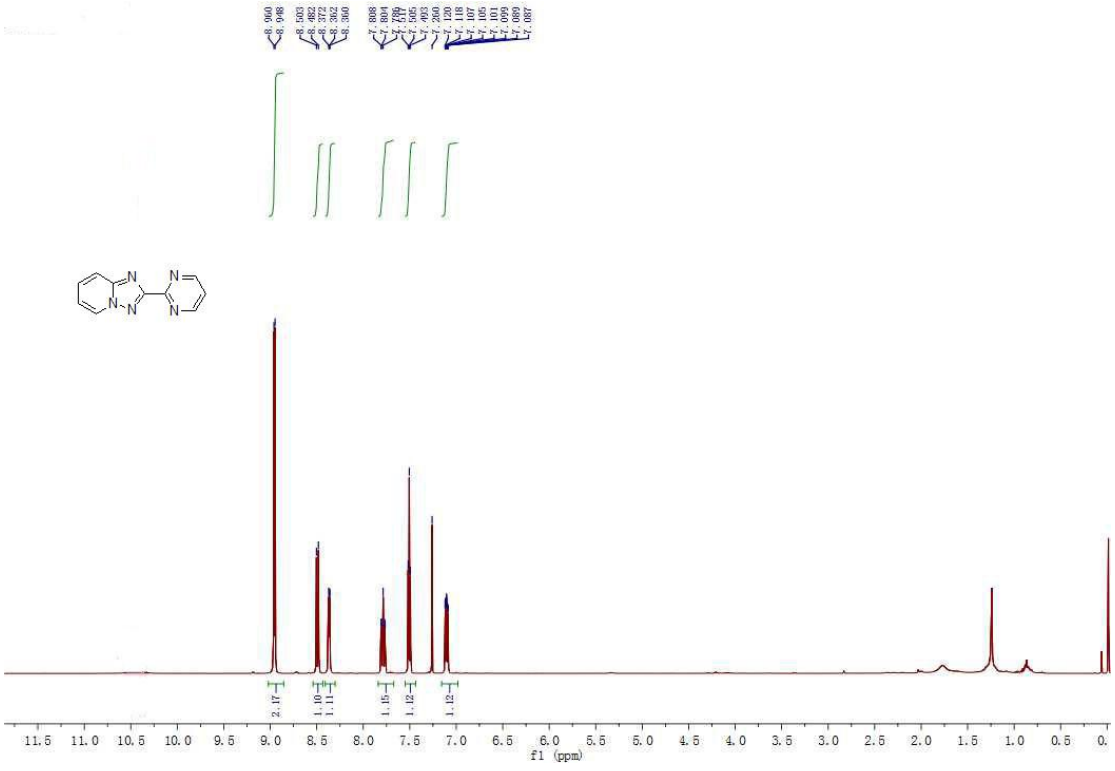

130705-1-MengX-CNMR(36)
160.84
151.38
132.82
129.56
128.19
126.59
126.32
125.60
116.15
113.54
77.32
77.00
76.68
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

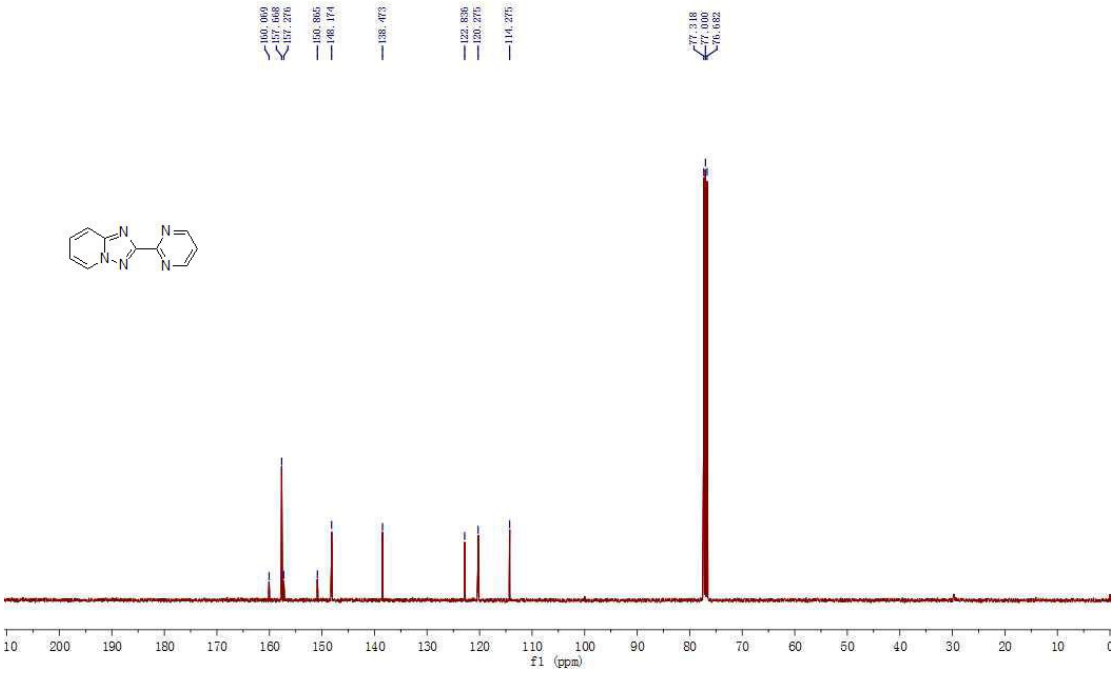

8.549
8.532
8.194
8.193
7.703
7.681
7.523
7.519
7.514
7.506
7.503
7.488
7.485
7.480
7.466
7.463
7.259
7.015
7.012
6.995
6.992
6.978
6.975
6.960
6.958
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
0.91
1.01
2.09
2.06

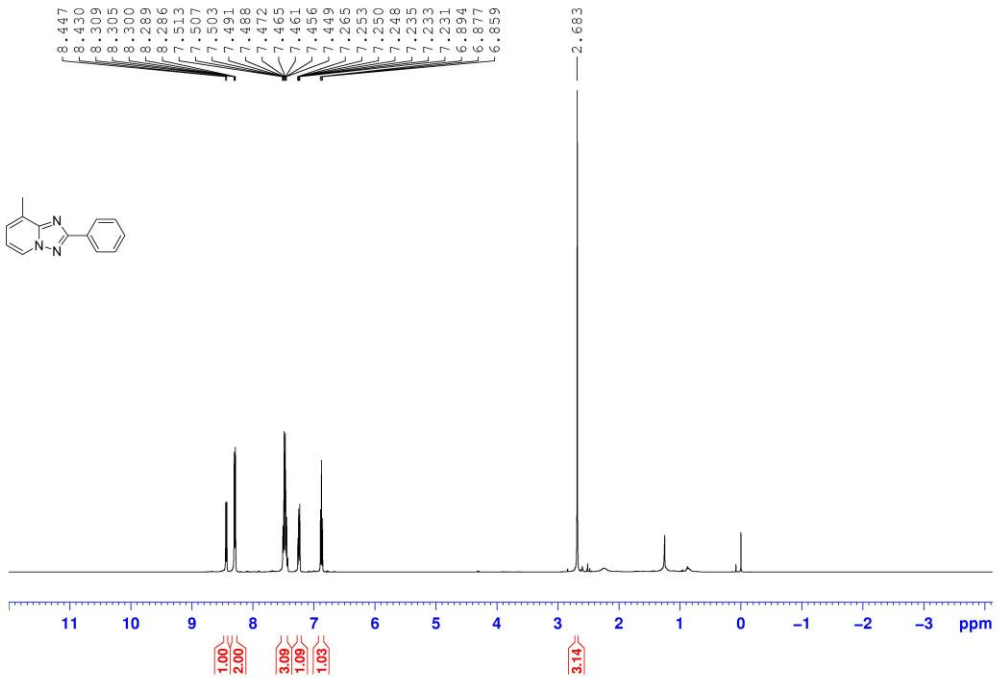

159.10
151.35
143.78
142.79
129.63
128.12
118.11
116.01
113.50
109.08
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

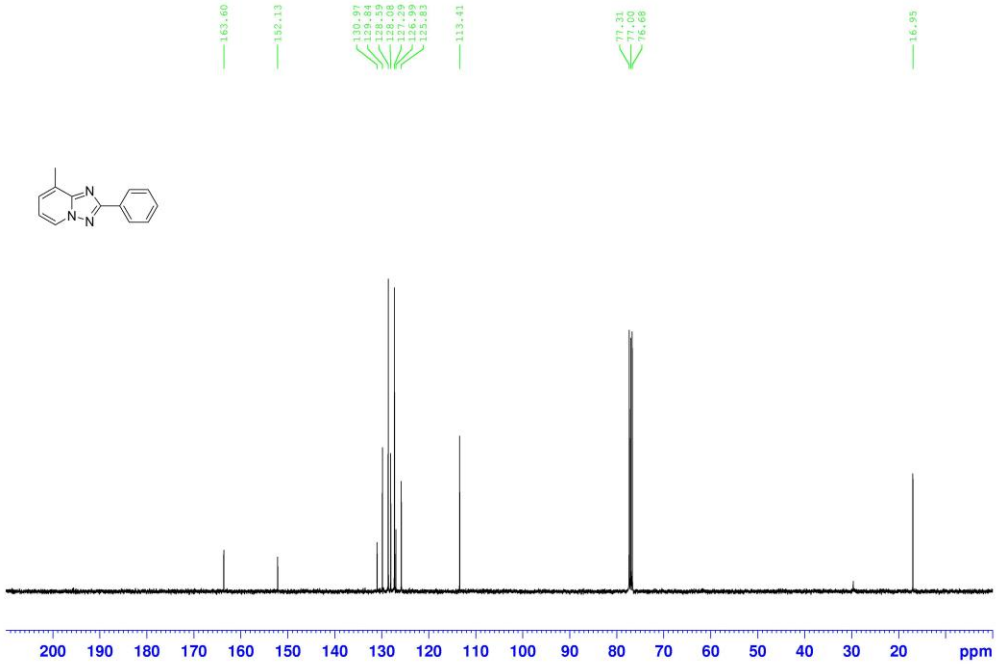

8.538
8.536
8.533
8.521
8.519
8.516
7.863
7.822
7.710
7.707
7.705
7.688
7.685
7.682
7.615
7.612
7.593
7.511
7.508
7.494
7.490
7.486
7.471
7.468
7.409
7.391
7.388
7.372
7.342
7.339
7.336
7.327
7.321
7.303
7.258
7.247
7.206
6.992
6.989
6.975
6.972
6.958
6.955
7.8 7.6 7.4 7.2 ppm
1.021
1.057
2.216
1.097
2.146
1.123
1.179
12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
1.02
1.06
2.22
1.10
2.15
1.12
1.18
1.12

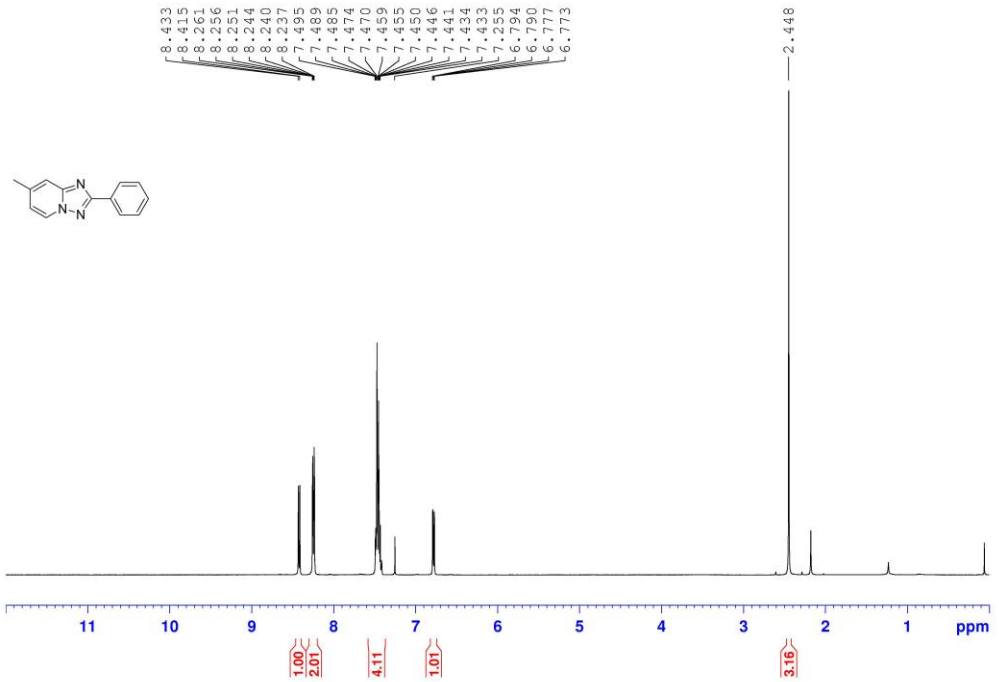

163.57
151.28
136.44
136.06
129.69
128.77
128.74
128.12
127.17
117.46
116.96
113.44
77.31
76.99
76.67
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

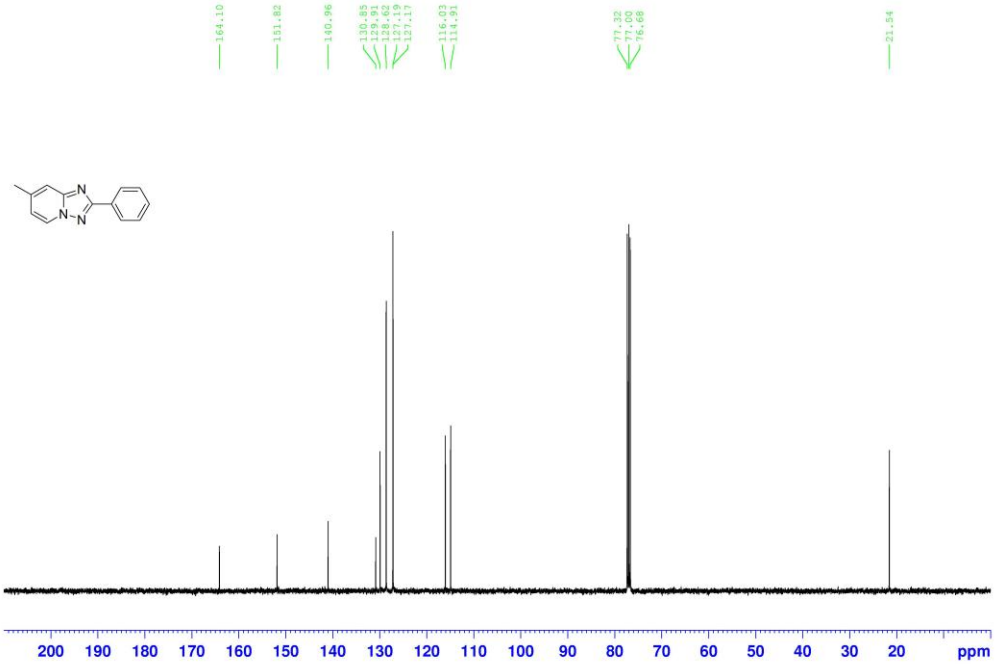

8.960
8.948
8.503
8.492
8.372
8.362
8.360
7.888
7.804
7.799
7.505
7.493
7.250
7.120
7.118
7.107
7.105
7.091
7.089
7.087
2.17
1.10
1.11
1.15
1.12
1.12
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

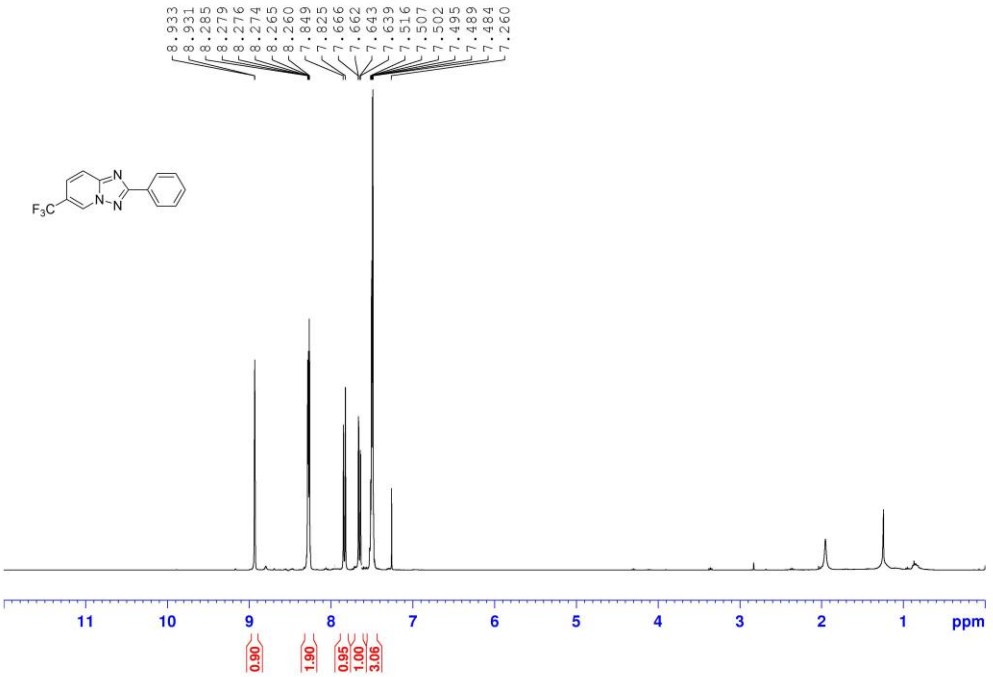

160.069
157.668
157.276
150.865
148.174
138.473
122.836
120.275
114.275
77.318
77.000
76.682
f1 (ppm)

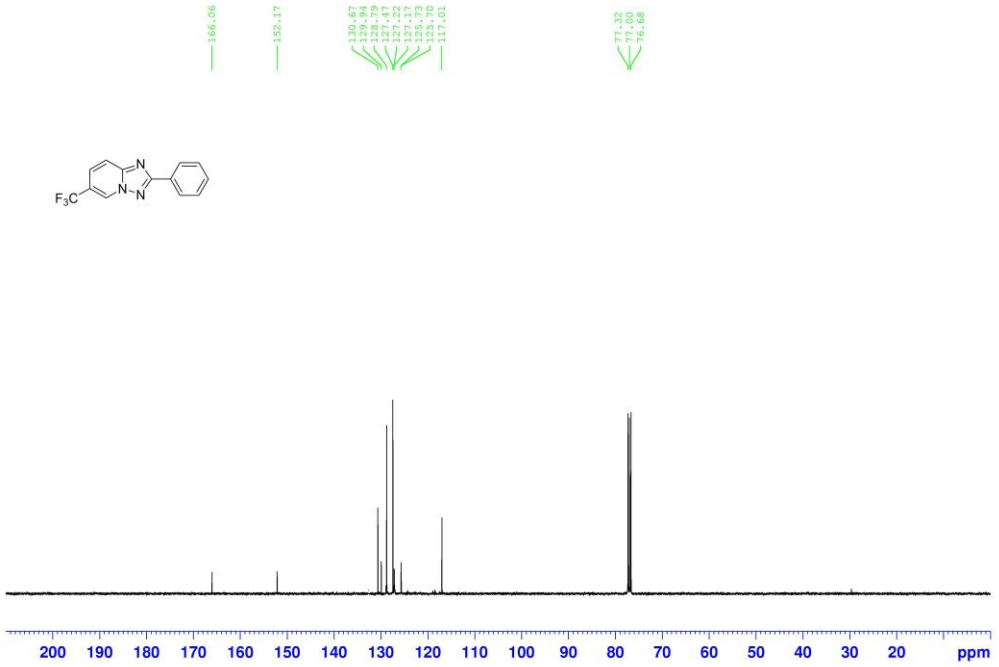

8.447
8.430
8.309
8.305
8.300
8.289
8.286
7.513
7.507
7.503
7.491
7.488
7.472
7.465
7.461
7.456
7.449
7.265
7.253
7.250
7.248
7.235
7.233
7.231
6.894
6.877
6.859
2.683
ppm
1.00
2.00
3.09
1.09
1.03
3.14

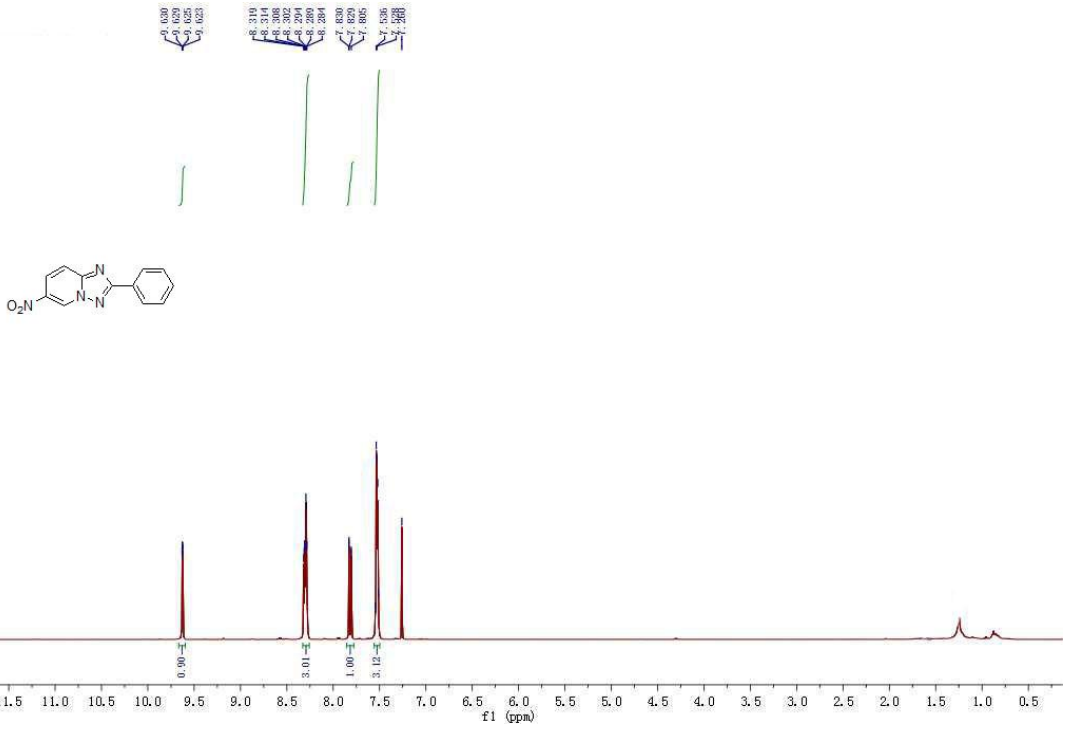

163.60
152.13
130.97
129.84
128.59
128.08
127.29
126.99
125.83
113.41
77.31
77.00
76.68
16.95
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

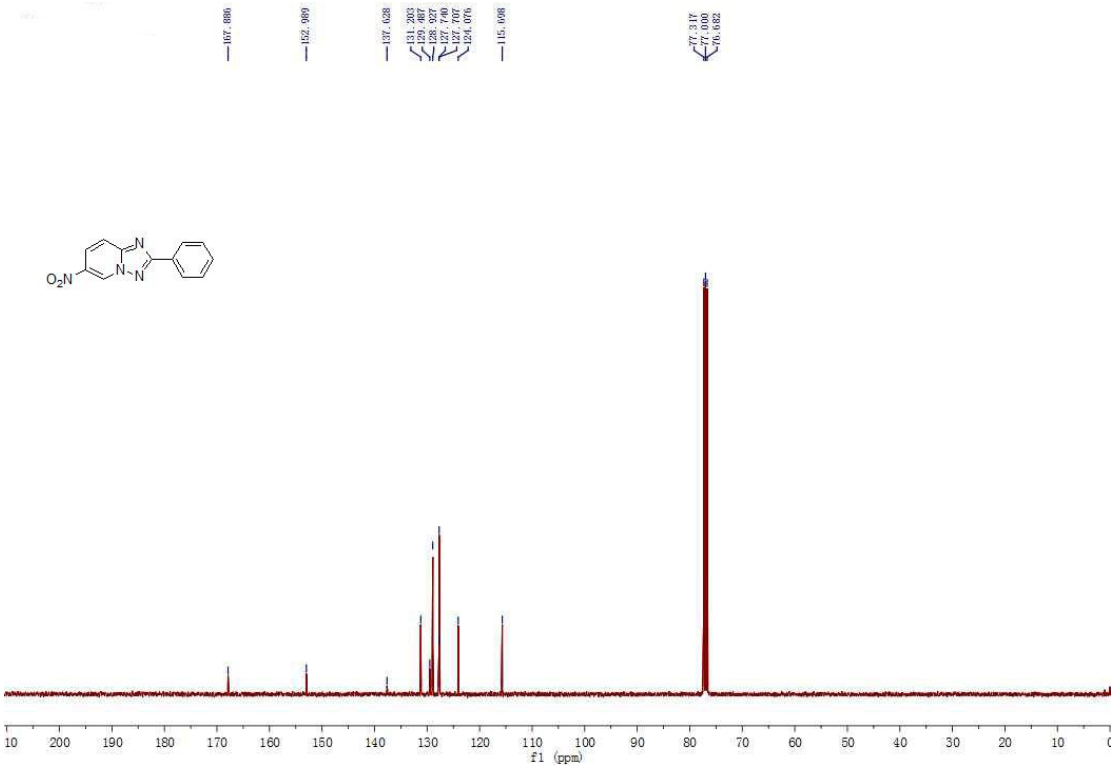

8.433
8.415
8.261
8.256
8.251
8.244
8.240
8.237
7.495
7.489
7.485
7.474
7.470
7.459
7.455
7.450
7.446
7.441
7.434
7.433
7.255
6.794
6.790
6.777
6.773
2.448
11 10 9 8 7 6 5 4 3 2 1 ppm
1.00
2.01
4.11
1.01
3.16

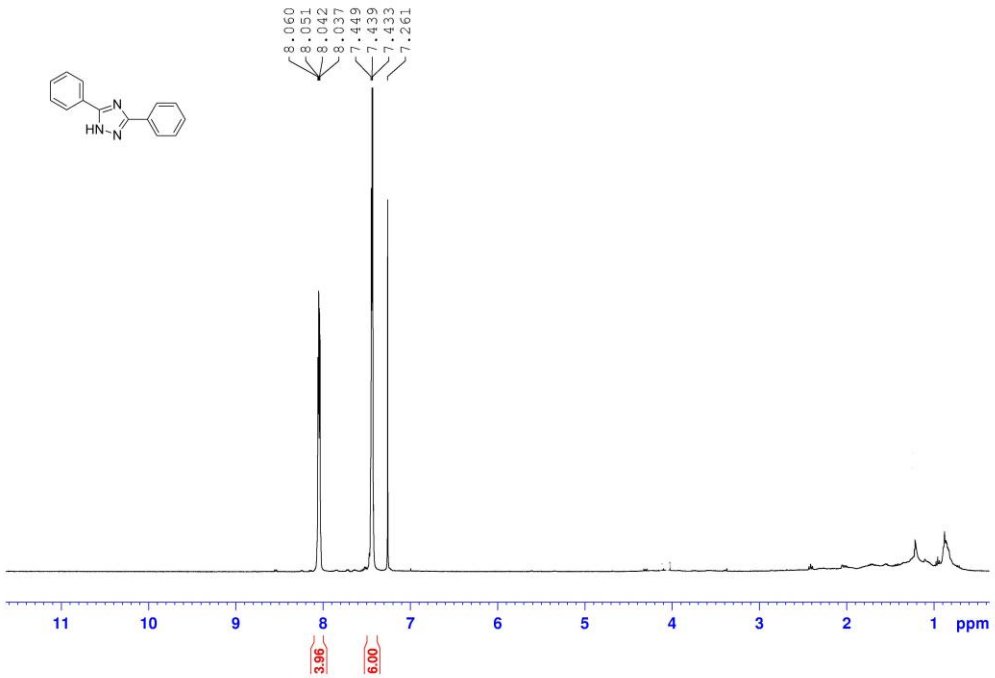

164.10
151.82
140.96
130.85
129.91
128.62
127.19
127.17
116.03
114.91
77.32
77.00
76.68
21.54
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

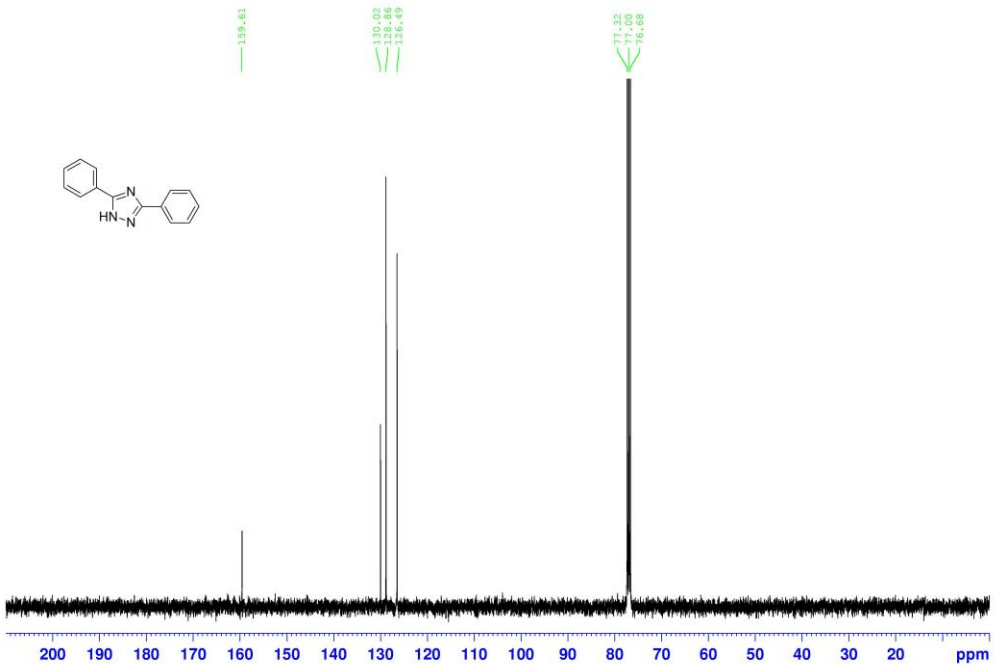

8.933
8.931
8.285
8.279
8.276
8.274
8.265
8.260
7.849
7.825
7.666
7.662
7.643
7.639
7.516
7.507
7.502
7.495
7.489
7.484
7.260
F3C
11 10 9 8 7 6 5 4 3 2 1 ppm
0.90
1.90
0.95
1.00
3.06

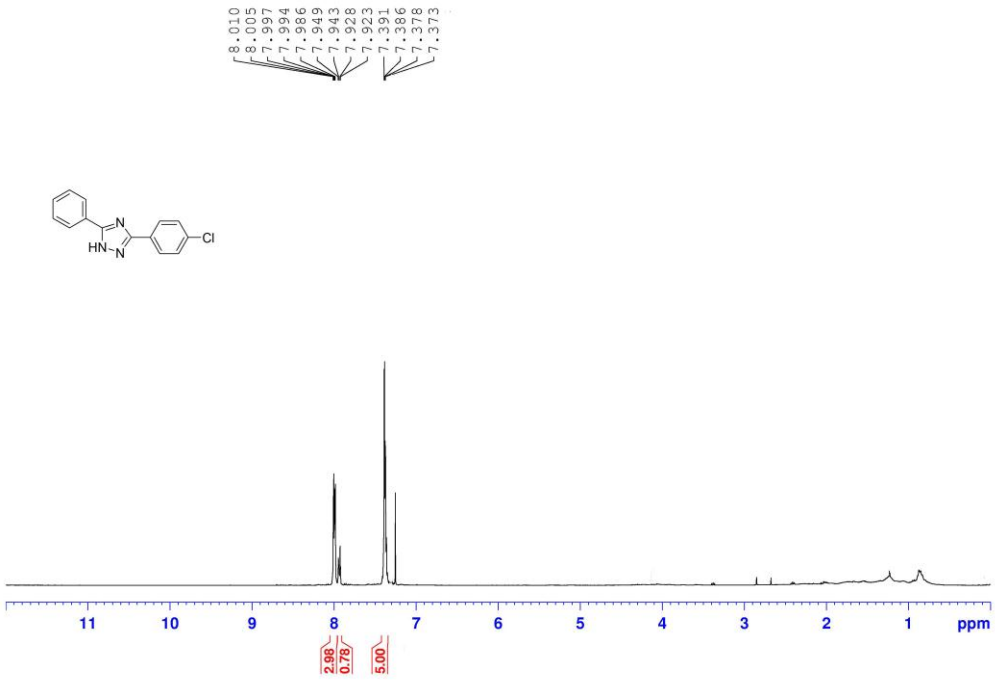

166.06
152.17
130.67
129.94
128.79
127.47
127.32
127.17
125.73
125.70
117.01
77.32
77.00
76.68
F3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

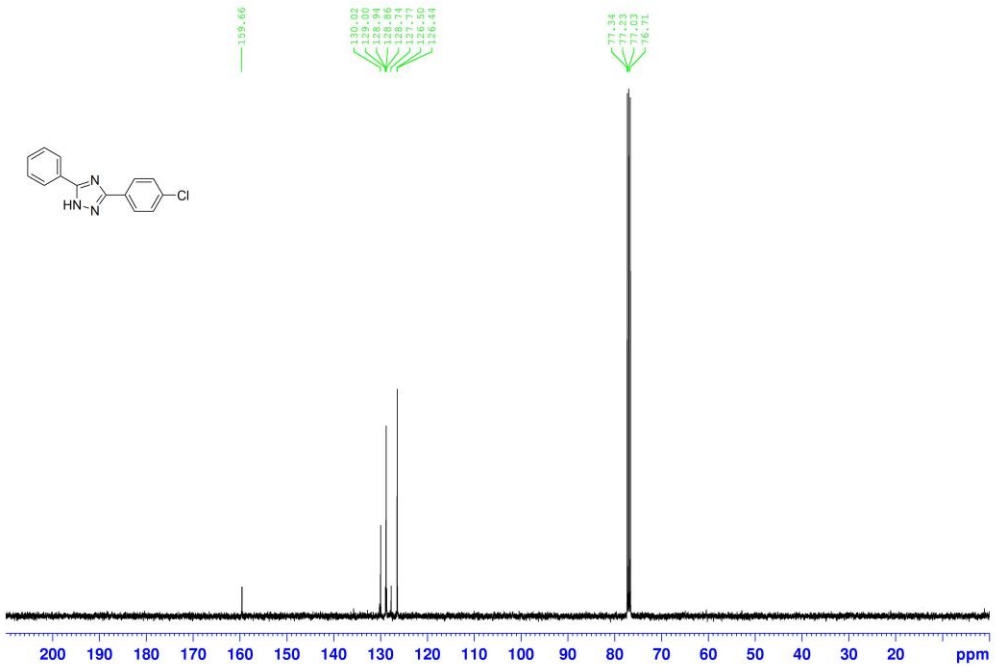

9.639
9.629
9.625
9.623
8.319
8.314
8.308
8.302
8.294
8.289
8.284
7.830
7.829
7.805
7.536
O2N
0.90
3.01
1.00
3.12
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

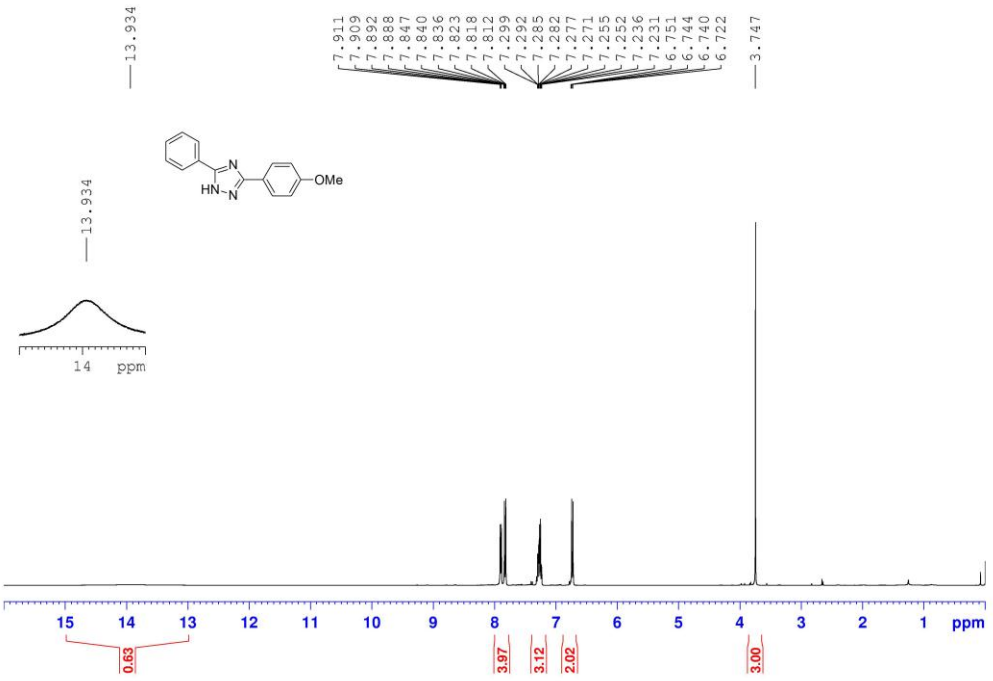

167.886
152.989
137.028
131.203
129.087
128.927
127.740
127.707
124.076
115.098
77.317
77.000
76.682
O2N
N
N
N
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

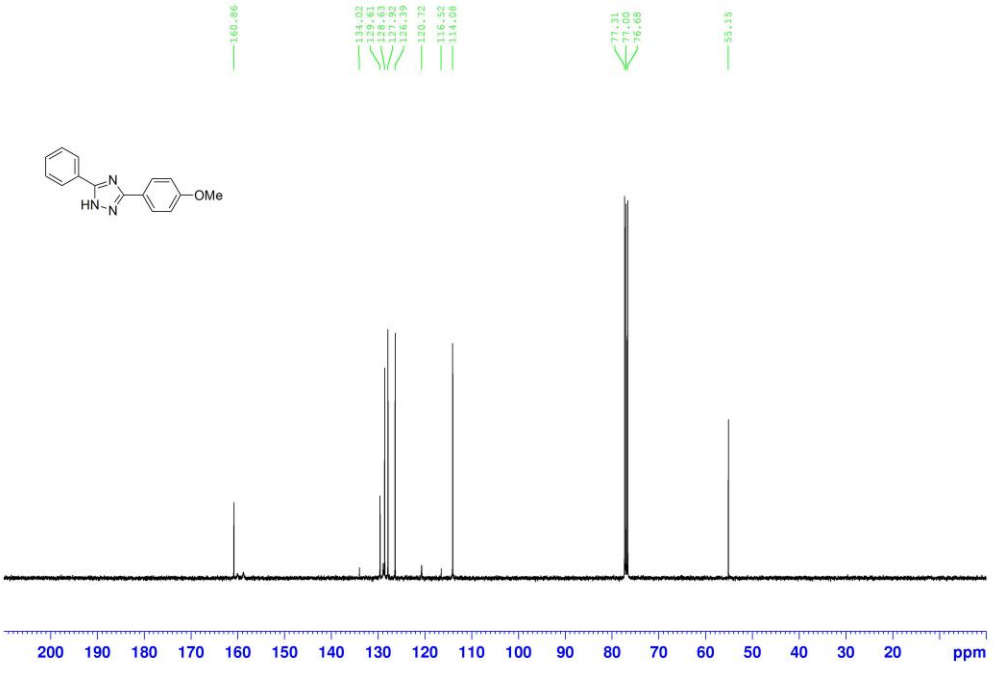


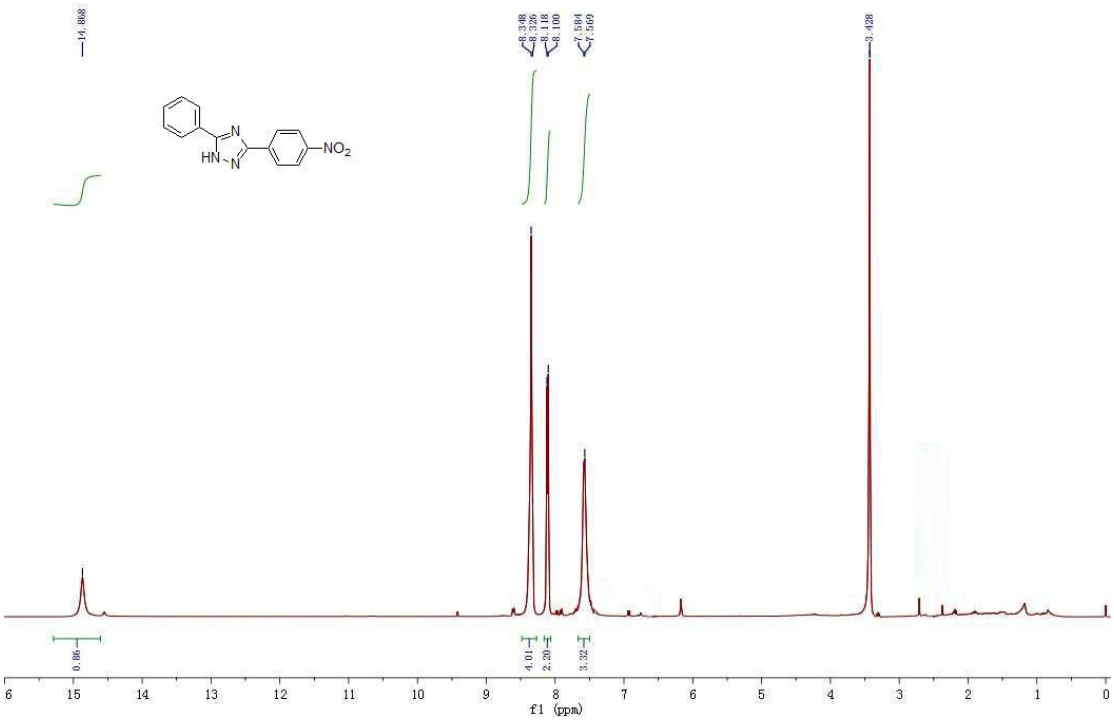


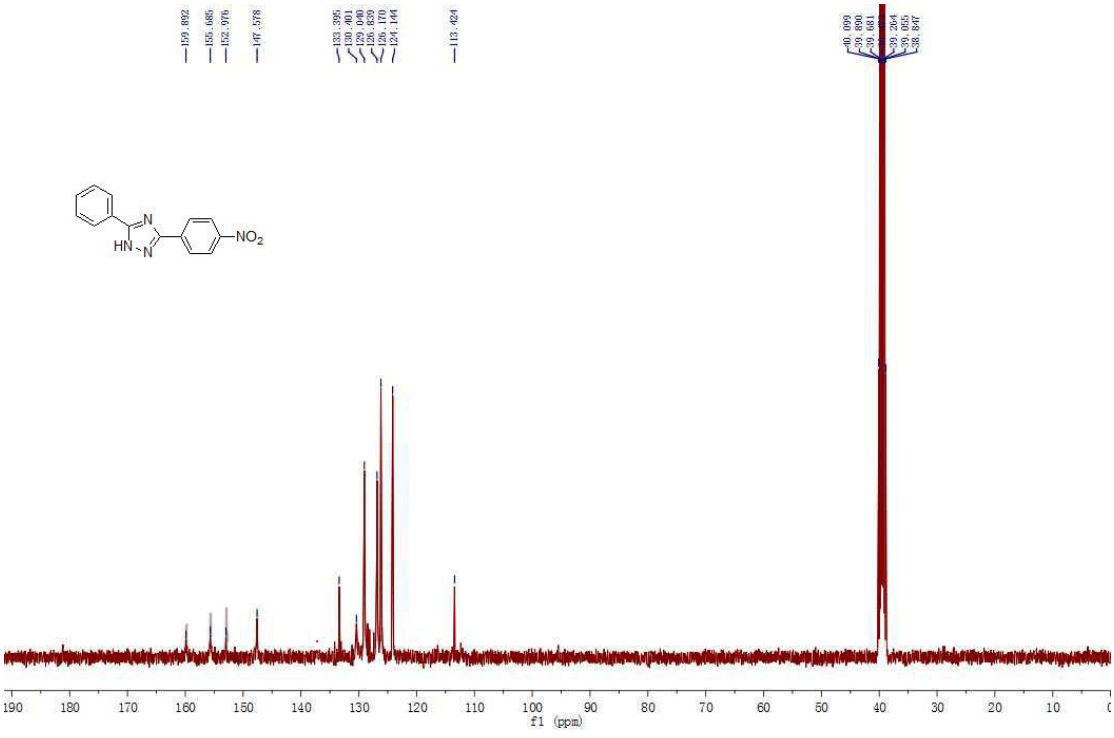


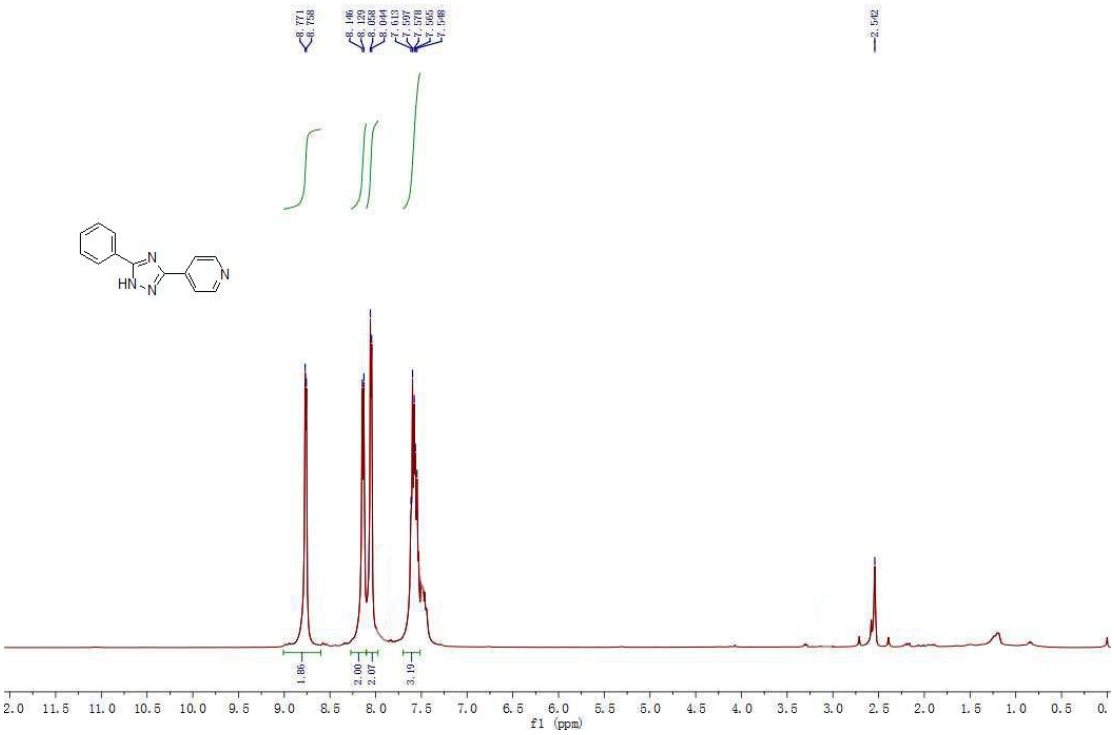


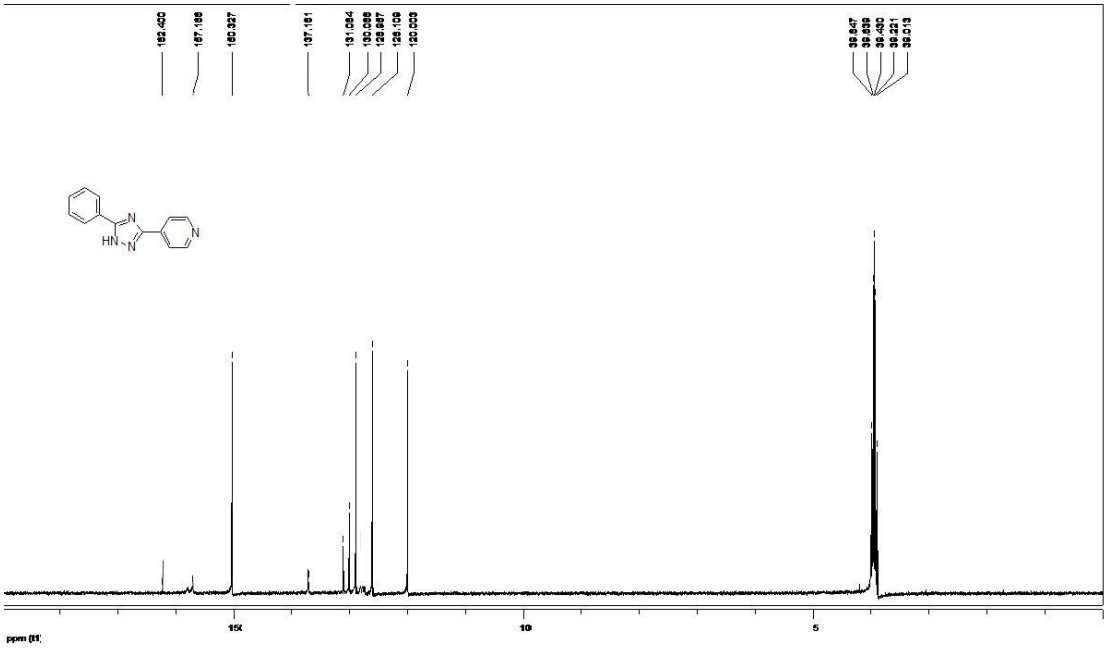

13.934
7.911
7.909
7.892
7.888
7.847
7.840
7.836
7.823
7.818
7.812
7.299
7.292
7.285
7.282
7.277
7.271
7.255
7.252
7.236
7.231
6.751
6.744
6.740
6.722
3.747
OMe
HN
N
N
13.934
14 ppm
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.63
3.97
3.12
2.02
3.00


160.86
134.02
129.61
129.43
128.32
126.39
120.72
116.32
114.08
77.31
77.00
76.68
55.15
OMe
HN
N
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


14.868
8.398
8.396
8.118
8.100
7.584
7.569
3.428
HN
N
N
NO2
0.86
4.01
2.20
3.32
f1 (ppm)


159.892
155.685
152.976
147.578
133.395
130.401
129.040
126.839
126.170
124.164
113.424
40.099
39.890
39.681
39.264
39.055
38.847
HN
N
N
NO2
f1 (ppm)


8.771
8.736
8.146
8.129
8.058
8.044
7.613
7.597
7.578
7.565
7.198
2.542
1.86
2.00
2.07
3.19
f1 (ppm)


162.420
157.166
150.327
137.181
131.084
130.068
128.687
128.156
120.033
39.647
39.538
39.430
39.321
39.213
150
100
50
ppm (f1)