[3+2] Cycloaddition of Azide with Aldehyde Hydrazone through an Aminyl Radical-Polar Strategy

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1. General Information

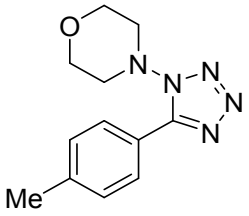
All reactions were carried out under an atmosphere of Ar atmosphere with dry solvents in flame-dried glassware unless otherwise noted. Anhydrous solvent were purchased from J&K® and used as received. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker AVANCE Ⅲ–400 spectrometer at room temperature. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet. High resolution mass spectras were obtained on a high–resolution mass spectrometer in the ESI mode. All other reagents were purchased from commercial sources and used as received.

2. General procedure for azidation of aldehyde hydrazones

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, aldehyde hydrazone 1 (0.10 mmol), $TMSN_3$ (3 equiv, 0.3 mmol, 34.5 mg), $PhI(OAc)_2$ (2 equi- -v, 0.2 mmol, 64.4 mg) and $Cu(OAc)_2$ (0.20 equiv, 0.020 mmol, 3.6 mg), K_2CO_3 (2 e--quiv, 0.2 mmol, 27.6 mg). The flask was evacuated and backfilled with Ar for 3 times. 2 ml CH_3CN was added with syringe under Ar and the reaction mixture was stirred at room temperature and monitored by TLC. After the reaction was finished, the mixture was concentrated under vacuum to remove CH_3CN, and the residue was purified by chromatography on silica gel to afford the 2.

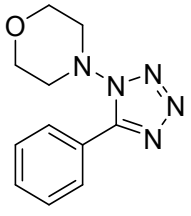
3. Physical Data of the Compounds

4-(5-(p-tolyl)-1H-tetrazol-1-yl)morpholine 2a



The reaction was carried out according to the general procedure (8 h). The residue was purified by flash column chromatography to afford **2a** (75 % yield) as white solid. m.p. 139.1-141.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.0 Hz, 1.78H), 7.35 (d, *J* = 8.0 Hz, 1.89H), 3.95 (t, *J* = 4.0 Hz, 4.38H), 3.42 (t, *J* =4.0 Hz, 4.22H), 2.45(s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.01, 142.18, 129.71, 128.22, 120.32, 66.61, 56.79, 21.61 HRMS (ESI) Calcd for $[M+H]^+$: 246.1349, found: 246.1362

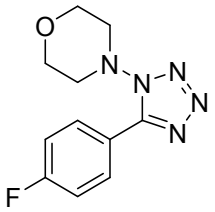
4-(5-phenyl-1H-tetrazol-1-yl)morpholine 2b



The reaction was carried out according to the general procedure (9 h). The residue was

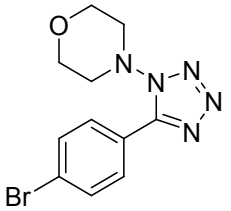
purified by flash column chromatography to afford **2b** (72 % yield) as white solid. m.p. 92.3 – 94.3 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25-8.23 (m, 2.06H), 7.58-7.53 (m, 3.35H), 3.96 (t, *J* = 4.0 Hz, 4.00H), 3.43 (t, *J* =4.0 Hz, 3.83H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.97, 131.66, 129.01, 128.32, 126.20, 123.22, 66.59, 56.85. HRMS (ESI) Calcd for $[M+Na]^{+}$: 254.1012, found: 254.1011.

4-(5-(4-fluorophenyl)-1H-tetrazol-1-yl)morpholine 2c



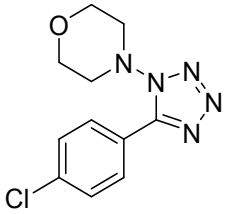
The reaction was carried out according to the general procedure (8 h). The residue was purified by flash column chromatography to afford **2c** (67 % yield) as light yellow solid. m.p. 147.2 – 149.5 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30-8.27 (m, 2.05H), 7.26-7.22 (m, 1.60H), 3.96 (t, *J* = 4.0 Hz, 4.00H), 3.43 (t, *J* =4.0 Hz, 3.91H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.58 (d, *J* =252.0 Hz), 149.15, 130.62 (d, *J* =9 Hz), 119.46 (d, *J* =4 Hz), 116.28(d, *J* =11 Hz), 66.58, 56.85. HRMS (ESI) Calcd for $[M+H]^{+}$: 272.0918, found: 272.0918.

4-(5-(4-bromophenyl)-1H-tetrazol-1-yl)morpholine 2d



The reaction was carried out according to the general procedure (8 h). The residue was purified by flash column chromatography to afford **2d** (62 % yield) as yellow solid. m.p. 163.5 – 166.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.0 Hz, 2.14H), 7.70 (d, *J* = 12.0 Hz, 2.15H), 3.96 (t, *J* = 4.0 Hz, 4.00H), 3.43 (t, *J* =4.0 Hz, 3.91H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.24, 132.39, 129.73, 126.46, 122.23, 66.57, 55.88. HRMS (ESI) Calcd for $[M+H]^{+}$: 310.0298, found: 310.0300.

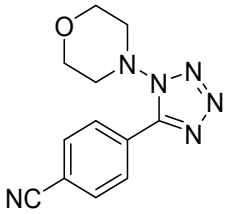
4-(5-(4-chlorophenyl)-1H-tetrazol-1-yl)morpholine 2e



The reaction was carried out according to the general procedure (8 h). The residue was purified by flash column chromatography to afford **2e** (64 % yield) as white solid. m.p.

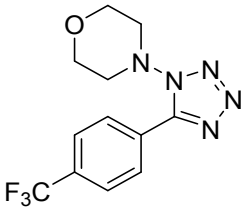
164.3 – 165.4 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 12.0 Hz, 1.96H), 7.53 (d, *J* = 8.0 Hz, 2.08H), 3.96 (t, *J* = 4.0 Hz, 4.00H), 3.43 (t, *J* =4.0 Hz, 3.97H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.14, 138.02, 129.58, 129.41, 121.68, 66.57, 55.88. HRMS (ESI) Calcd for $[M+Na]^+$: 288.0623, found: 288.0623.

4-(1-morpholino-1H-tetrazol-5-yl)benzonitrile 2f



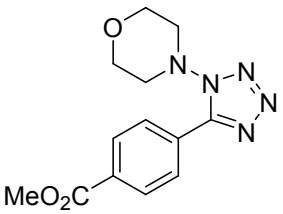
The reaction was carried out according to the general procedure (10 h). The residue was purified by flash column chromatography to afford **2f** (49 % yield) as white solid. m.p. 149.2 – 151.0 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 8.0 Hz, 2.31H), 7.86 (d, *J* = 8.0 Hz, 2.27H), 3.97 (t, *J* = 4.0 Hz, 4.00H), 3.45 (t, *J* =4.0 Hz, 3.97H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.52, 132.77, 128.83, 127.37, 117.79, 115.30, 66.52, 56.06. HRMS (ESI) Calcd for $[M+Na]^+$: 279.0965, found: 279.0951.

4-(5-(4-(trifluoromethyl)phenyl)-1H-tetrazol-1-yl)morpholine 2g



The reaction was carried out according to the general procedure (11 h). The residue was purified by flash column chromatography to afford **2g** (51 % yield) as white solid. m.p. 139.0 – 142.3 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.0 Hz, 2.37H), 7.83 (d, *J* = 8.0 Hz, 2.35H), 3.97 (t, *J* = 4.0 Hz, 4.00H), 3.45 (t, *J* =4.0 Hz, 4.04H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.91, 134.34 (d, *J*= 32.0 Hz), 128.72, 126.63, 126.03 (*J* = 4.0 Hz), 124.87, 122.16, 66.55, 56.00. HRMS (ESI) Calcd for $[M+Na]^+$: 322.0886, found: 322.0885.

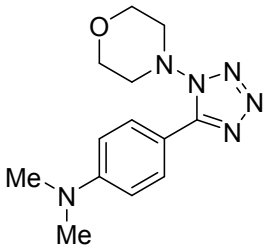
methyl 4-(1-morpholino-1H-tetrazol-5-yl)benzoate 2h



The reaction was carried out according to the general procedure (9 h). The residue was purified by flash column chromatography to afford **2h** (63 % yield) as white solid. m.p. 159.5 – 162.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 – 8.35 (m, 1.90H), 8.19 –

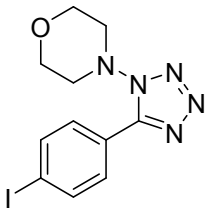
8.22 (m, 1.83H), 3.95 – 3.98 (m, 7.08H), 3.44 (t, *J* =4.0 Hz, 4.00H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.06, 149.25, 132.80, 130.11, 128.30, 127.27, 66.56, 55.95, 52.52. HRMS (ESI) Calcd for $[M+Na]^+$: 312.1067, found: 312.1067.

N,N-dimethyl-4-(1-morpholino-1H-tetrazol-5-yl)aniline 2i



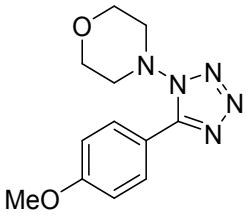
The reaction was carried out according to the general procedure (9 h). The residue was purified by flash column chromatography to afford **2i** (65 % yield) as light yellow solid. m.p. 80.5 – 81.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.0 Hz, 1.83H), 6.77 (d, *J* = 8.0 Hz, 2.03H), 3.95 (t, *J* = 4.0 Hz, 4.00H), 3.40 (t, *J* =4.0 Hz, 3.94H), 3.07 (s, 6.11H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.91, 141.97, 129.60, 128.28, 120.51, 47.37, 21.60. HRMS (ESI) Calcd for $[M+Na]^+$: 297.1434, found: 297.1418.

4-(5-(4-iodophenyl)-1H-tetrazol-1-yl)morpholine 2j



The reaction was carried out according to the general procedure (8 h). The residue was purified by flash column chromatography to afford **2j** (59 % yield) as white solid. Z : E > 20:1. m.p. 178.3 – 180.2 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.0 Hz, 2.03H), 7.91 (d, *J* = 12.0 Hz, 2.17H), 3.95 (t, *J* = 4.0 Hz, 4.00H), 3.42 (t, *J* =4.0 Hz, 3.96H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.37, 138.34, 129.66, 122.68, 98.69, 66.56, 56.88. HRMS (ESI) Calcd for $[M+Na]^+$: 379.9979, found: 379.9979.

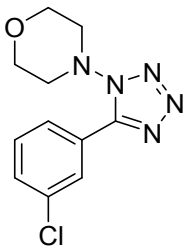
4-(5-(4-methoxyphenyl)-1H-tetrazol-1-yl)morpholine 2k



The reaction was carried out according to the general procedure (8 h). The residue was purified by flash column chromatography to afford **2k** (73 % yield) as white solid. m.p. 104.3 – 106.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.0 Hz, 2.21H), 7.04 (d, *J* = 12.0 Hz, 2.30H), 3.96 (t, *J* = 4.0 Hz, 3.97H), 3.90 (s, 3.27H), 3.42 (t, *J* =4.0 Hz, 4.00H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.10, 149.68, 130.23, 129.95,

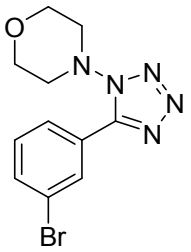
114.40, 69.43, 66.62, 65.72. HRMS (ESI) Calcd for $[M+Na]^+$: 284.1118, found: 284.1118.

4-(5-(3-chlorophenyl)-1H-tetrazol-1-yl)morpholine 2l



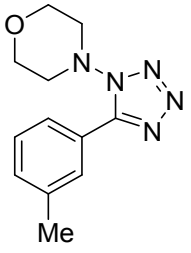
The reaction was carried out according to the general procedure (10 h). The residue was purified by flash column chromatography to afford **2l** (59 % yield) as light yellow solid. m.p. 136.9 – 139.2 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 (t, *J* = 4.0 Hz, 0.94H), 8.14 – 8.17 (m, 1.22H), 7.48 – 7.56 (m, 2.26H), 3.97 (t, *J* =4.0 Hz, 4.00H), 3.43 (t, *J* =4.0 Hz, 4.14H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.83, 136.68, 131.73, 130.39, 126.26, 126.41, 124.85, 66.58, 55.90. HRMS (ESI) Calcd for $[M+Na]^+$: 288.0623, found: 288.0620.

4-(5-(3-bromophenyl)-1H-tetrazol-1-yl)morpholine 2m



The reaction was carried out according to the general procedure (10 h). The residue was purified by flash column chromatography to afford **2m** (54 % yield) as white solid. m.p. 139.0 – 142.3 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (t, *J* = 4.0 Hz, 0.87H), 8.19 – 8.21 (m, 0.98H), 7.69 – 7.72 (m, 1.04H), 3.97 (t, *J* =4.0 Hz, 4.00H), 3.43 (t, *J* =4.0 Hz, 3.82H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.69, 134.63, 131.63, 130.59, 126.83, 125.09, 122.99, 66.59, 55.90. HRMS (ESI) Calcd for $[M+Na]^+$: 332.0117, found: 332.0117.

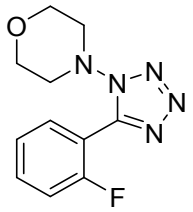
4-(5-(m-tolyl)-1H-tetrazol-1-yl)morpholine 2n



The reaction was carried out according to the general procedure (10 h). The residue was purified by flash column chromatography to afford **2n** (56 % yield) as yellow solid. m.p.

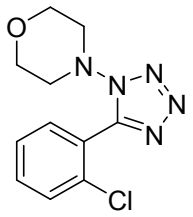
94.1 – 95.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 8.05 (m, 1.74H), 7.37 – 7.45(m, 1.84H), 3.95 (t, *J* =4.0 Hz, 4.00H), 3.42 (t, *J* =4.0 Hz, 3.82H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.07, 138.86, 132.41, 129.10, 128.86, 125.18, 123.06, 66.62, 55.80, 21.47. HRMS (ESI) Calcd for $[M+Na]^{+}$: 268.1169, found: 268.1170.

4-(5-(2-fluorophenyl)-1H-tetrazol-1-yl)morpholine 2o



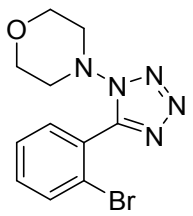
The reaction was carried out according to the general procedure (11 h). The residue was purified by flash column chromatography to afford **2o** (59 % yield) as white solid. m.p. 92.6 – 94.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.68 (m, 2.16H), 7.25 – 7.36 (m, 2.01H), 3.84 (t, *J* = 4.0 Hz, 4.00H), 3.36 (t, *J* = 4.0 Hz, 3.82H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.34, 158.82, 148.71, 133.56 (d, *J* = 9 Hz), 131.51, 124.66 (d, *J* = 4.0 Hz), 116.41 (d, *J* = 21.0 Hz), 66.54, 56.02. HRMS (ESI) Calcd for $[M+Na]^{+}$: 272.0918, found: 272.0920.

4-(5-(2-chlorophenyl)-1H-tetrazol-1-yl)morpholine 2p



The reaction was carried out according to the general procedure (11 h). The residue was purified by flash column chromatography to afford **2p** (69 % yield) as light yellew solid. m.p. 151.2 – 154.3 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.59 (m, 1.93H), 7.42 – 7.44 (m, 1.88H), 3.79 (t, *J* = 6.0 Hz, 4.00H), 3.35 (t, *J* = 4.0 Hz, 3.84H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.05, 134.05, 132.43, 131.66, 130.18, 127.05, 120.35, 66.42, 56.86. HRMS (ESI) Calcd for $[M+H]^{+}$: 266.0803, found: 266.0811.

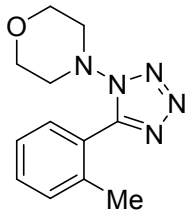
4-(5-(2-bromophenyl)-1H-tetrazol-1-yl)morpholine 2q



The reaction was carried out according to the general procedure (11 h). The residue was purified by flash column chromatography to afford **2q** (54 % yield) as light brown solid.

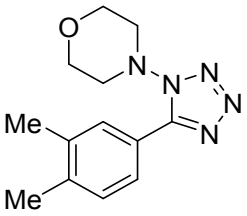
m.p. 136.4 – 139.1 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ.7.75 – 7.77 (m, 0.98H), 7.46 – 7.49 (m, 2.07H), 7.35 – 7.38 (m, 0.94H), 3.78 (t, *J* = 4.0 Hz, 4.00H), 3.36 (t, *J* = 4.0 Hz, 3.82H).. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.60, 133.33, 132.47, 131.66, 127.54, 125.79, 123.27, 66.39, 56.87. HRMS (ESI) Calcd for $[M+Na]^+$: 332.0117, found: 332.0119.

4-(5-(o-tolyl)-1H-tetrazol-1-yl)morpholine 2r



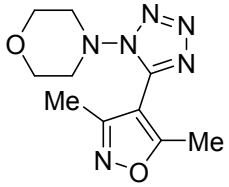
The reaction was carried out according to the general procedure (11 h). The residue was purified by flash column chromatography to afford **2r** (74 % yield) as light yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.48 (m, 1.17H), 7.33 – 7.40 (m, 3.21H), 3.81 (t, *J* = 6.0 Hz, 4.07H), 3.33 (t, *J* = 4.0 Hz, 4.17H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.10, 138.18, 131.01, 130.94, 129.98, 125.86, 122.87, 66.40, 56.93, 20.27. HRMS (ESI) Calcd for $[M+Na]^+$: 268.1169, found: 268.1168.

4-(5-(3,4-dimethylphenyl)-1H-tetrazol-1-yl)morpholine 2s



The reaction was carried out according to the general procedure (11 h). The residue was purified by flash column chromatography to afford **2s** (68 % yield) as white solid. m.p. 129.0 – 131.2 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 8.02 (m, 1.69H), 7.30 (d, *J* = 4.0 Hz, 0.86H), 3.95 (t, *J* = 4.0 Hz, 4.00H), 3.42 (t, *J* = 6.0 Hz, 4.02H), 2.36 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.07, 140.91, 137.48, 130.18, 129.61, 126.52, 120.61, 66.66, 55.75, 19.94, 19.90. HRMS (ESI) Calcd for $[M+Na]^+$: 282.1328, found: 282.1328.

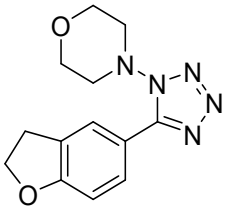
4-(5-(3,5-dimethylisoxazol-4-yl)-1H-tetrazol-1-yl)morpholine 2t



The reaction was carried out according to the general procedure (12 h). The residue was purified by flash column chromatography to afford **2t** (68 % yield) as light yellow liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.89 (t, *J* = 4.05 Hz, 4.00H), 3.36 (t, *J* = 4.0 Hz,

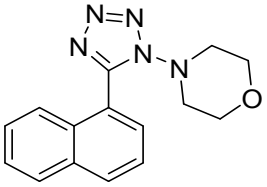
3.72H), 2.57 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.99, 158.76, 144.67, 100.98, 66.39, 56.18, 12.77, 11.23. HRMS (ESI) Calcd for $[M+Na]^+$: 273.1070, found: 273.1070.

4-(5-(2,3-dihydrobenzofuran-5-yl)-1H-tetrazol-1-yl)morpholine 2u



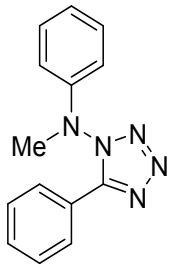
The reaction was carried out according to the general procedure (10 h). The residue was purified by flash column chromatography to afford **2u** (60 % yield) as brown solid. m.p. 126.0 – 128.3 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.10 (m, 1.73H), 6.91 (d, J = 8.0 Hz, 0.93), 3.89 (t, J = 4.0 Hz, 4.00H), 4.69 (t, J = 8.0 Hz, 2.21H), 3.95 (t, J = 6.0 Hz, 4H), 3.41 (t, J = 4.0 Hz, 3.85H), 3.31 (t, J = 8.0 Hz, 2.30H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.94, 149.95, 128.91, 128.23, 125.49, 115.33, 109.72, 71.97, 66.63, 56.70, 29.31. HRMS (ESI) Calcd for $[M+Na]^+$: 296.1118, found: 296.1124.

4-(5-(naphthalen-1-yl)-1H-tetrazol-1-yl)morpholine 2v



The reaction was carried out according to the general procedure (13 h). The residue was purified by flash column chromatography to afford **2v** (53 % yield) as brown liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, J_1 = 4.0 Hz, J_2= 8.00 Hz 1.04H), 7.92 – 7.96 (m, 2.12H), 7.52 – 7.57 (m, 4.29H), 3.72 (t, J = 4.0 Hz, 4H), 3.36 (t, J = 4.0 Hz, 3.79H), 3.31 (t, J = 8.0 Hz, 2.30H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.91, 133.59, 131.78, 128.91, 128.61, 127.57, 126.75, 124.80 (d, J = 14.0 Hz), 120.47, 66.36, 55.99. HRMS (ESI) Calcd for $[M+Na]^+$: 304.1169, found: 304.1174.

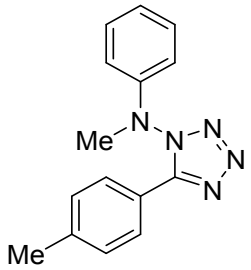
N-methyl-N,5-diphenyl-1H-tetrazol-1-amine 2w



The reaction was carried out according to the general procedure (12 h). The residue was purified by flash column chromatography to afford **2w** (52 % yield) as brown solid. Z : E > 20:1. m.p. 94.7 – 96.7 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.15 (m,

1.96H), 7.47 – 7.57 (m, 3.18H), 7.28 – 7.33 (m, 2.02H), 7.04 – 7.09 (m, 1.03H), 7.67 – 7.69 (m, 2.06H), 2.54 (s, 3.00H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.83, 147.50, 131.96, 129.69, 129.18, 128.22, 123.27, 122.65, 115.19, 42.87. HRMS (ESI) Calcd for $[M+Na]^+$: 274.1063, found: 274.1065.

N-methyl-N-phenyl-5-(p-tolyl)-1H-tetrazol-1-amine 2x



The reaction was carried out according to the general procedure (10 h). The residue was purified by flash column chromatography to afford **2x** (60 % yield) as brown solid. m.p. 104.7 – 108.6 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, J = 8.0 Hz 1.79H), 7.28 – 7.32 (m, 3.79H), 7.04 – 7.08 (m, 0.93H), 6.67 (dd, J_1 = 4.0 Hz, J_2= 6.0 Hz 1.74H), 3.52 (s, 2.98H), 2.41 (s, 3.00H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.86, 147.50, 142.56, 129.88, 129.65, 128.11, 123.15, 119.76, 115.11, 42.71, 21.61. HRMS (ESI) Calcd for $[M+Na]^+$: 288.1220, found: 288.1223.

4. X-Crystallographic Data

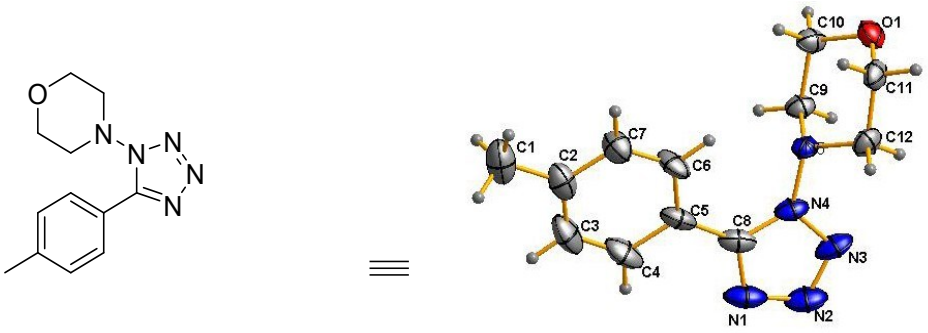


Table S1. Crystal data and structure refinement for **3aa**

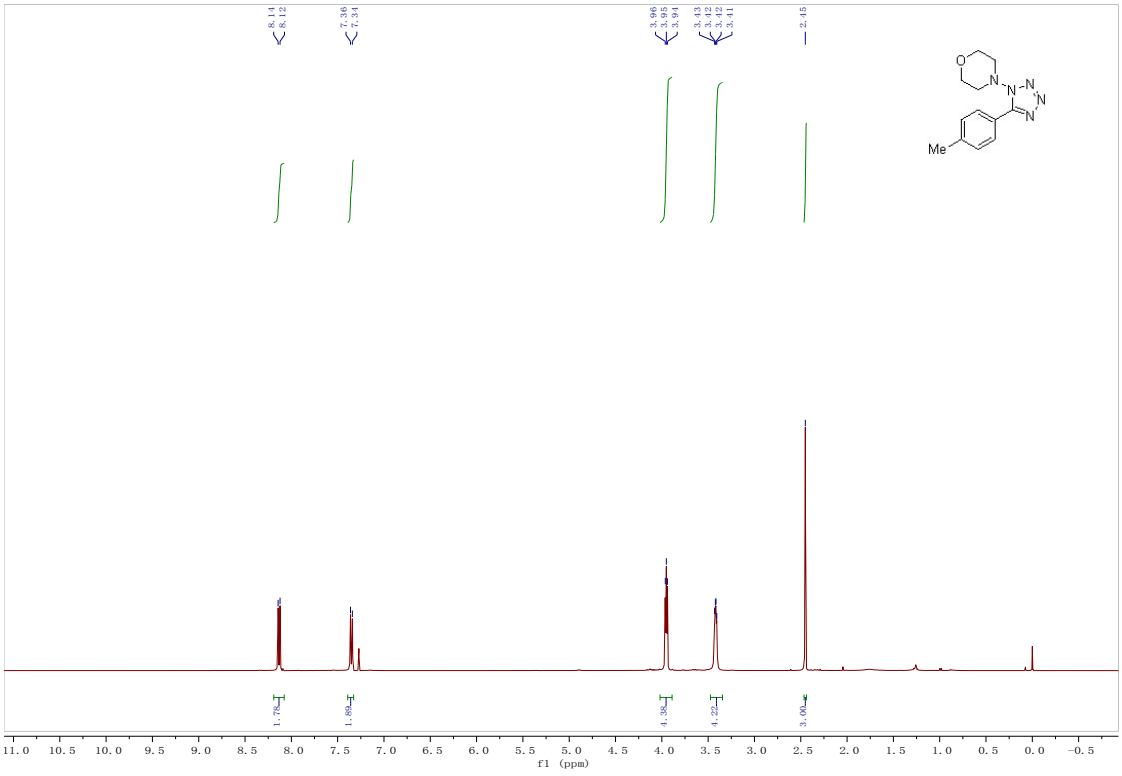
Identification code	
Empirical formula	$C_{12}H_{15}N5O$
Formula weight	245.29
Temperature	293(2)K
Wavelength	0.71073Å
Crystal system, space group	Monoclinic, *Pca*21
Unit cell dimensions	a = 12.406(9) Å alpha = 90 deg.
	b = 5.786(4) Å beta = 90 deg
	c = 34.77(3) Å gamma = 90 deg.
Volume	2496(3) $Å^3$
Z, Calculated density	8, 1.306Mg/m^3
Absorption coefficient	$0.089mm^{-1}$
F(000)	1040.0
Crystal size	0.28 x 0.26 x 0.22 mm
Theta range for data collection	2.93 to 26.75 deg
Limiting indices	-15<=h=<15, -5<=k=<7, -45<=l=<44
Reflections collected / unique	5503 / 3646 [R(int) = 0.0861]
Completeness to theta = 27.49	99.5%
Absorption correction	multi-scan
Max. and min. transmission	0.9788, 0.9731
Data / restraints / parameters	5503 / 1 / 328
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R_1 = 0.0676, wR_2 = 0.1766
R indices (all data)	R_1 = 0.1124, wR_2 = 0.1544
Largest diff. peak and hole	0.216 and -0.240 e.A^-3
Final R indices [I>2sigma(I)]	R_1 = 0.0676, wR_2 = 0.1766

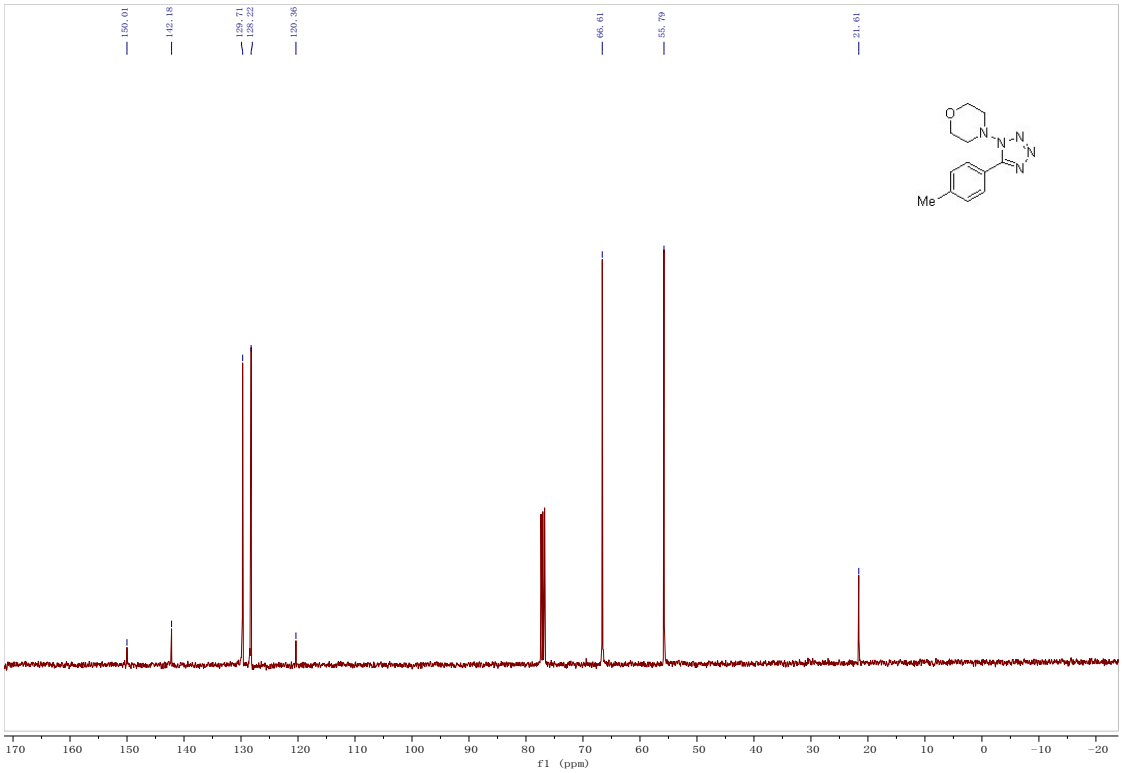
C(1)-C(2)	1.500(9)	C(18)-C(19)	1.381(9)
C(1)-H(1A)	0.9600	C(18)-H(18)	0.9300
C(1)-H(1B)	0.9600	C(19)-H(19)	0.9300
C(1)-H(1C)	0.9600	C(20)-N(6)	1.330(6)
C(2)-C(3)	1.378(10)	C(20)-N(9)	1.350(7)
C(2)-C(7)	1.400(9)	C(21)-N(10)	1.485(7)
C(3)-C(4)	1.386(10)	C(21)-C(22)	1.522(7)
C(3)-H(3)	0.9300	C(21)-H(21A)	0.9700
C(4)-C(5)	1.397(8)	C(21)-H(21B)	0.9700
C(4)-H(4)	0.9300	C(22)-O(2)	1.418(6)
C(5)-C(6)	1.416(7)	C(22)-H(22A)	0.9700
C(5)-C(8)	1.464(9)	C(22)-H(22B)	0.9700
C(6)-C(7)	1.376(8)	C(23)-O(2)	1.422(7)
C(6)-H(6)	0.9300	C(23)-C(24)	1.509(8)
C(7)-H(7)	0.9300	C(23)-H(23A)	0.9700
C(8)-N(1)	1.324(7)	C(23)-H(23B)	0.9700
C(8)-N(4)	1.353(8)	C(24)-N(10)	1.481(6)
C(9)-N(5)	1.475(7)	C(24)-H(24A)	0.9700
C(9)-C(10)	1.525(7)	C(24)-H(24B)	0.9700
C(9)-H(9A)	0.9700	N(1)-N(2)	1.384(8)
C(9)-H(9B)	0.9700	N(2)-N(3)	1.301(7)
C(10)-O(1)	1.429(6)	N(3)-N(4)	1.364(6)
C(10)-H(10A)	0.9700	N(4)-N(5)	1.414(6)
C(10)-H(10B)	0.9700	N(6)-N(7)	1.363(8)
C(11)-O(1)	1.421(7)	N(7)-N(8)	1.301(7)
C(11)-C(12)	1.526(7)	N(8)-N(9)	1.362(6)
C(11)-H(11A)	0.9700	N(9)-N(10)	1.414(6)
C(11)-H(11B)	0.9700	C(2)-C(1)-H(1A)	109.5
C(12)-N(5)	1.469(7)	C(2)-C(1)-H(1B)	109.5
C(12)-H(12A)	0.9700	H(1A)-C(1)-H(1B)	109.5
C(12)-H(12B)	0.9700	C(2)-C(1)-H(1C)	109.5
C(13)-C(14)	1.512(9)	H(1A)-C(1)-H(1C)	109.5
C(13)-H(13A)	0.9600	H(1B)-C(1)-H(1C)	109.5
C(13)-H(13B)	0.9600	C(3)-C(2)-C(7)	116.6(6)
C(13)-H(13C)	0.9600	C(3)-C(2)-C(1)	121.9(6)
C(14)-C(15)	1.376(8)	C(7)-C(2)-C(1)	121.4(6)
C(14)-C(19)	1.407(9)	C(2)-C(3)-C(4)	122.3(6)
C(15)-C(16)	1.393(8)	C(2)-C(3)-H(3)	118.8
C(15)-H(15)	0.9300	C(4)-C(3)-H(3)	118.8
C(16)-C(17)	1.385(7)	C(3)-C(4)-C(5)	120.8(6)
C(16)-H(16)	0.9300	C(3)-C(4)-H(4)	119.6
C(17)-C(18)	1.394(7)	C(5)-C(4)-H(4)	119.6
C(17)-C(20)	1.475(8)	C(4)-C(5)-C(6)	117.6(6)

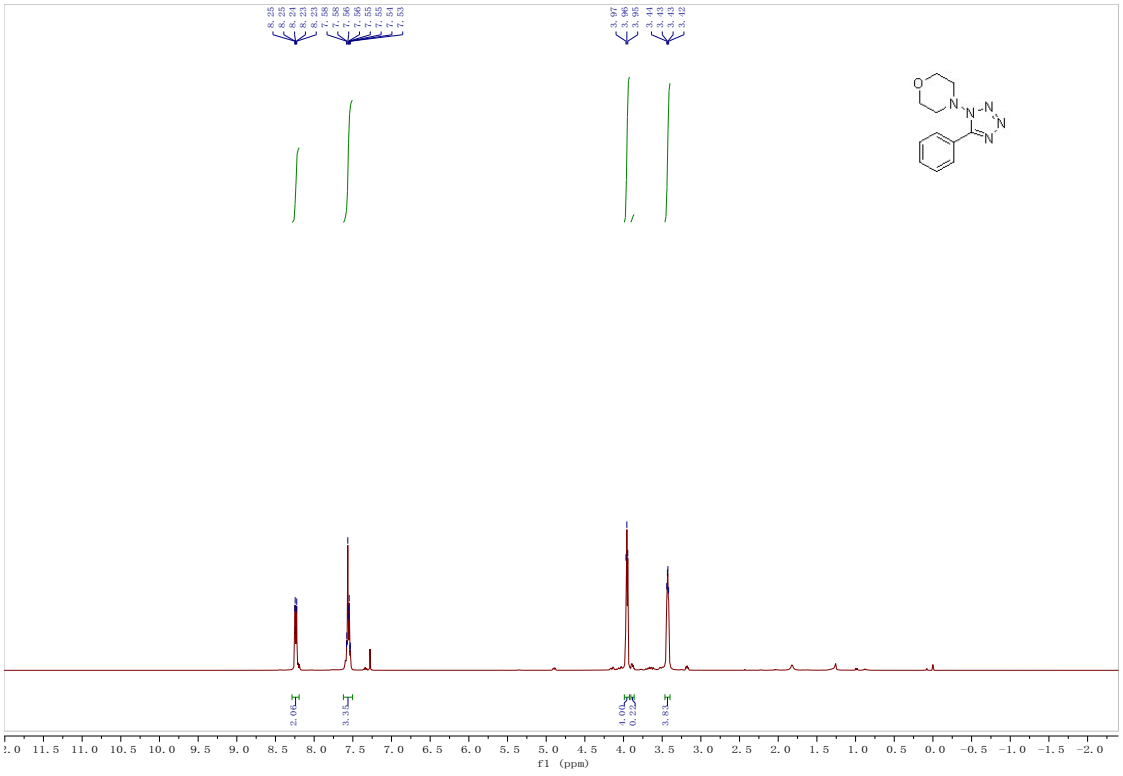
C(4)-C(5)-C(8)	119.1(5)	C(14)-C(15)-C(16)	121.9(6)
C(6)-C(5)-C(8)	123.3(5)	C(14)-C(15)-H(15)	119.1
C(7)-C(6)-C(5)	119.8(5)	C(16)-C(15)-H(15)	119.1
C(7)-C(6)-H(6)	120.1	C(17)-C(16)-C(15)	120.3(5)
C(5)-C(6)-H(6)	120.1	C(17)-C(16)-H(16)	119.8
C(6)-C(7)-C(2)	122.8(6)	C(15)-C(16)-H(16)	119.8
C(6)-C(7)-H(7)	118.6	C(16)-C(17)-C(18)	118.7(5)
C(2)-C(7)-H(7)	118.6	C(16)-C(17)-C(20)	123.4(5)
N(1)-C(8)-N(4)	107.1(5)	C(18)-C(17)-C(20)	117.8(5)
N(1)-C(8)-C(5)	124.2(5)	C(19)-C(18)-C(17)	120.3(5)
N(4)-C(8)-C(5)	128.7(4)	C(19)-C(18)-H(18)	119.8
N(5)-C(9)-C(10)	106.9(4)	C(17)-C(18)-H(18)	119.8
N(5)-C(9)-H(9A)	110.3	C(18)-C(19)-C(14)	121.4(5)
C(10)-C(9)-H(9A)	110.3	C(18)-C(19)-H(19)	119.3
N(5)-C(9)-H(9B)	110.3	C(14)-C(19)-H(19)	119.3
C(10)-C(9)-H(9B)	110.3	N(6)-C(20)-N(9)	106.9(5)
H(9A)-C(9)-H(9B)	108.6	N(6)-C(20)-C(17)	123.9(5)
O(1)-C(10)-C(9)	111.4(4)	N(9)-C(20)-C(17)	129.2(4)
O(1)-C(10)-H(10A)	109.3	N(10)-C(21)-C(22)	107.8(4)
C(9)-C(10)-H(10A)	109.3	N(10)-C(21)-H(21A)	110.1
O(1)-C(10)-H(10B)	109.3	C(22)-C(21)-H(21A)	110.1
C(9)-C(10)-H(10B)	109.3	N(10)-C(21)-H(21B)	110.1
H(10A)-C(10)-H(10B)	108.0	C(22)-C(21)-H(21B)	110.1
O(1)-C(11)-C(12)	111.3(4)	H(21A)-C(21)-H(21B)	108.5
O(1)-C(11)-H(11A)	109.4	O(2)-C(22)-C(21)	111.4(4)
C(12)-C(11)-H(11A)	109.4	O(2)-C(22)-H(22A)	109.3
O(1)-C(11)-H(11B)	109.4	C(21)-C(22)-H(22A)	109.3
C(12)-C(11)-H(11B)	109.4	O(2)-C(22)-H(22B)	109.3
H(11A)-C(11)-H(11B)	108.0	C(21)-C(22)-H(22B)	109.3
N(5)-C(12)-C(11)	106.9(4)	H(22A)-C(22)-H(22B)	108.0
N(5)-C(12)-H(12A)	110.3	O(2)-C(23)-C(24)	111.4(4)
C(11)-C(12)-H(12A)	110.3	O(2)-C(23)-H(23A)	109.3
N(5)-C(12)-H(12B)	110.3	C(24)-C(23)-H(23A)	109.3
C(11)-C(12)-H(12B)	110.3	O(2)-C(23)-H(23B)	109.3
H(12A)-C(12)-H(12B)	108.6	C(24)-C(23)-H(23B)	109.3
C(14)-C(13)-H(13A)	109.5	H(23A)-C(23)-H(23B)	108.0
C(14)-C(13)-H(13B)	109.5	N(10)-C(24)-C(23)	107.4(4)
H(13A)-C(13)-H(13B)	109.5	N(10)-C(24)-H(24A)	110.2
C(14)-C(13)-H(13C)	109.5	C(23)-C(24)-H(24A)	110.2
H(13A)-C(13)-H(13C)	109.5	N(10)-C(24)-H(24B)	110.2
H(13B)-C(13)-H(13C)	109.5	C(23)-C(24)-H(24B)	110.2
C(15)-C(14)-C(19)	117.2(6)	H(24A)-C(24)-H(24B)	108.5
C(15)-C(14)-C(13)	121.8(6)	C(8)-N(1)-N(2)	106.8(5)
C(19)-C(14)-C(13)	120.9(6)	N(3)-N(2)-N(1)	110.6(4)

N(2)-N(3)-N(4)	105.5(5)	N(7)-N(8)-N(9)	104.4(5)
C(8)-N(4)-N(3)	110.0(4)	C(20)-N(9)-N(8)	110.3(4)
C(8)-N(4)-N(5)	128.0(4)	C(20)-N(9)-N(10)	127.9(4)
N(3)-N(4)-N(5)	121.9(4)	N(8)-N(9)-N(10)	121.7(4)
N(4)-N(5)-C(12)	110.8(4)	N(9)-N(10)-C(24)	110.7(4)
N(4)-N(5)-C(9)	111.1(4)	N(9)-N(10)-C(21)	110.6(4)
C(12)-N(5)-C(9)	110.7(4)	C(24)-N(10)-C(21)	109.3(4)
C(20)-N(6)-N(7)	106.2(5)	C(11)-O(1)-C(10)	109.5(4)
N(8)-N(7)-N(6)	112.2(4)	C(22)-O(2)-C(23)	110.1(4)

5. Copies of 1H NMR, 13C NMR.



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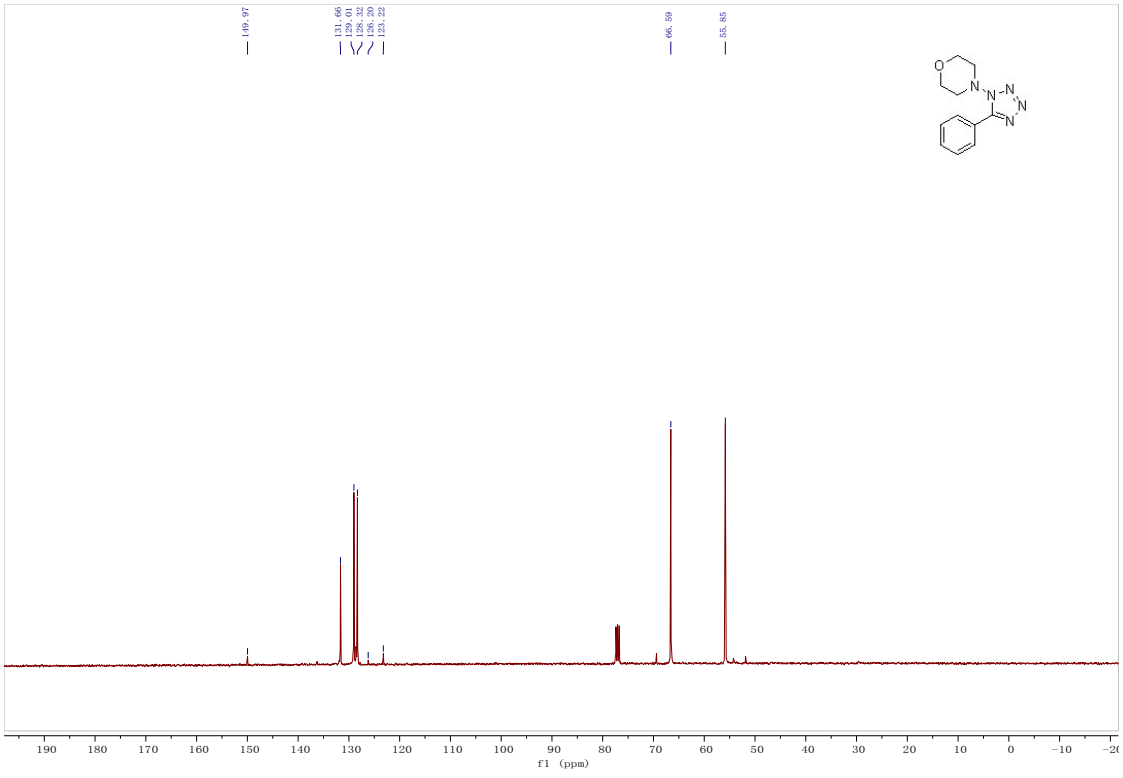
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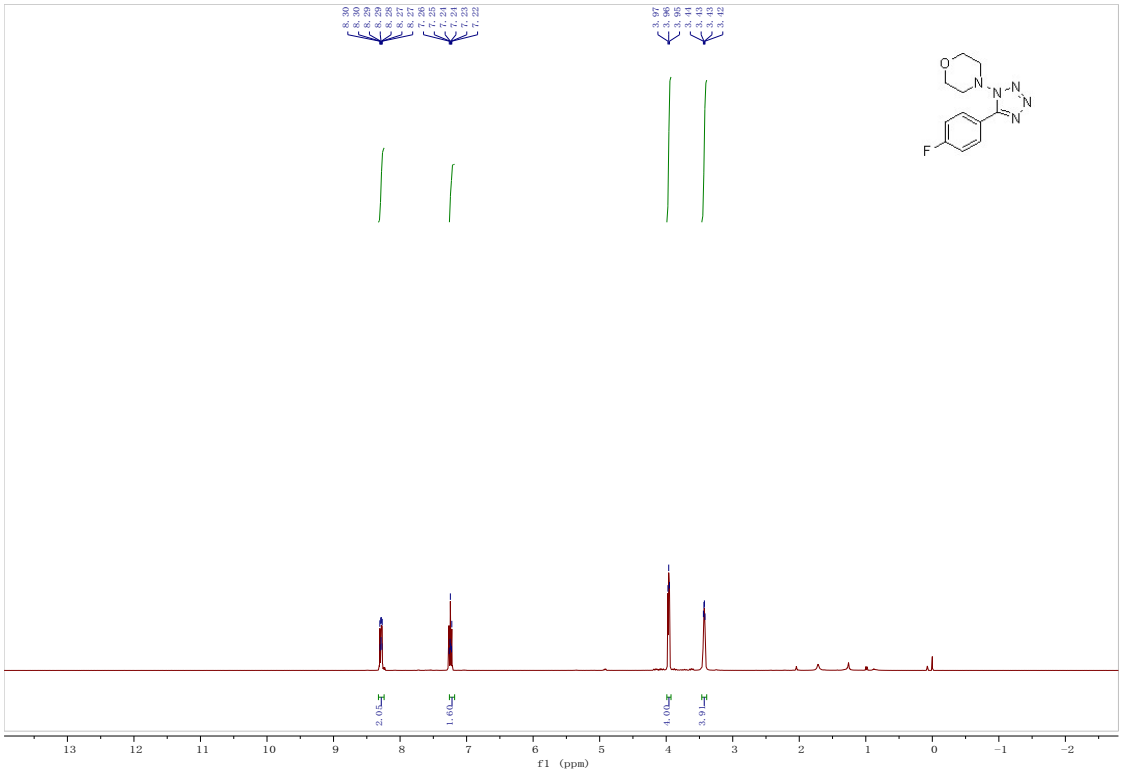
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3.91
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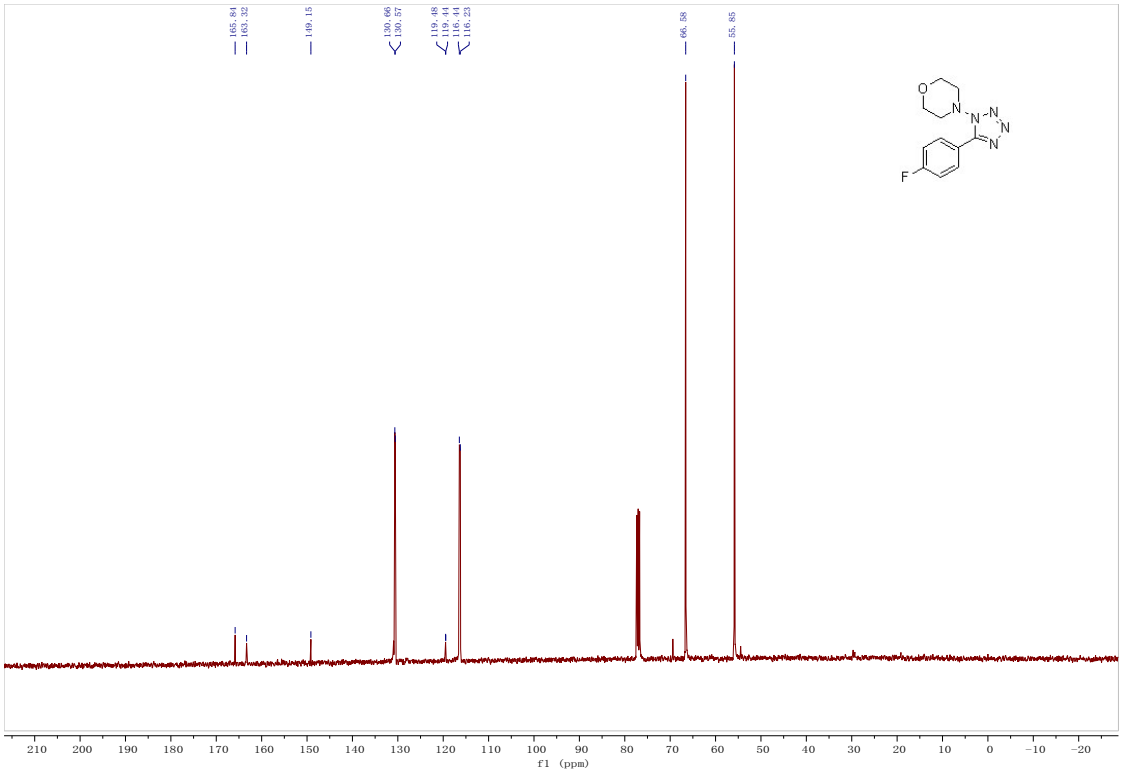
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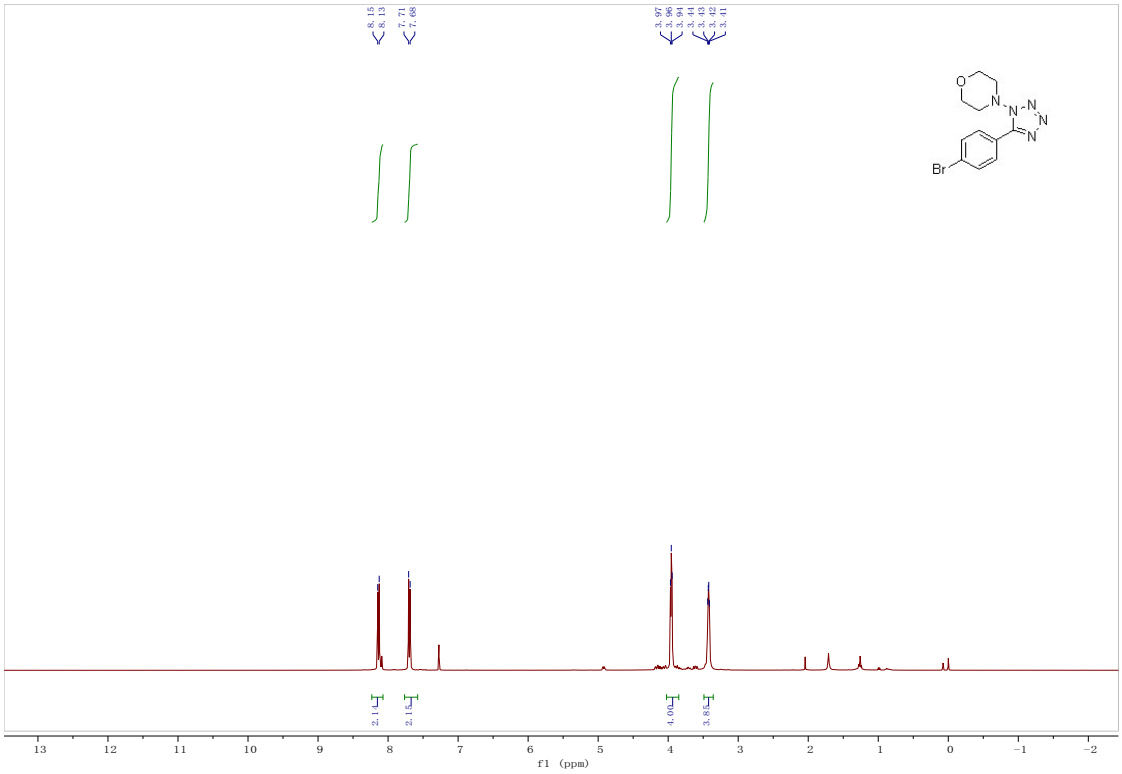
f1 (ppm)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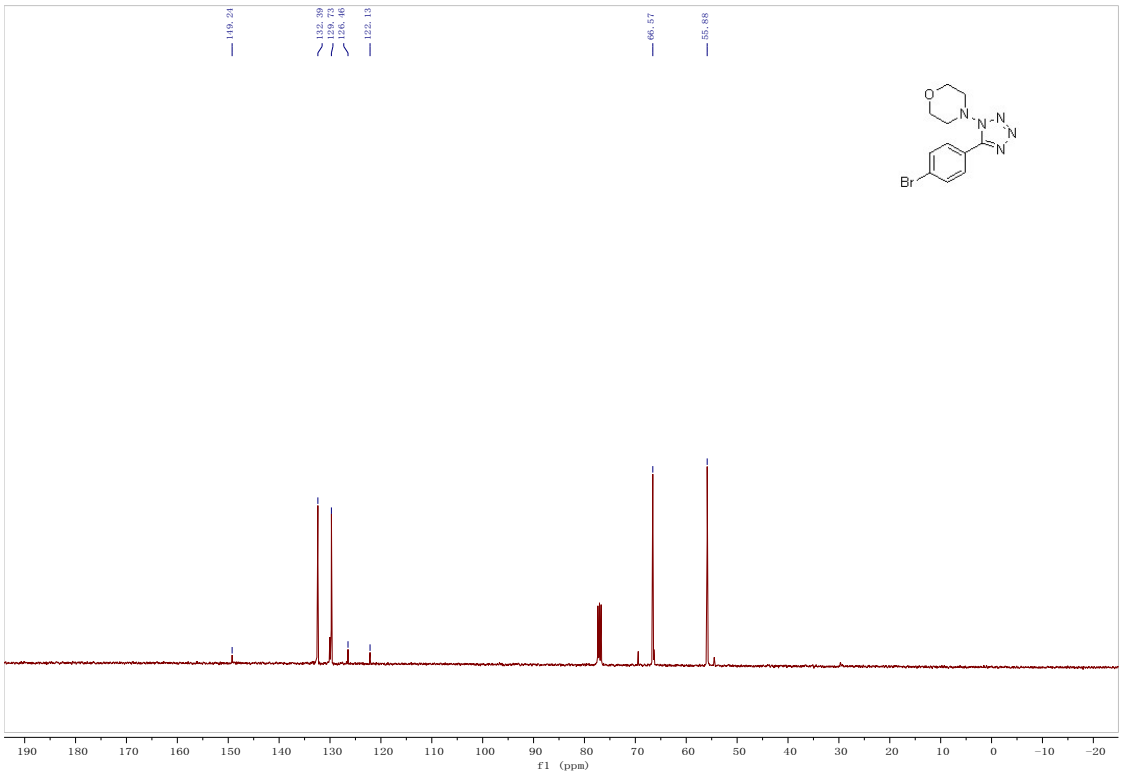
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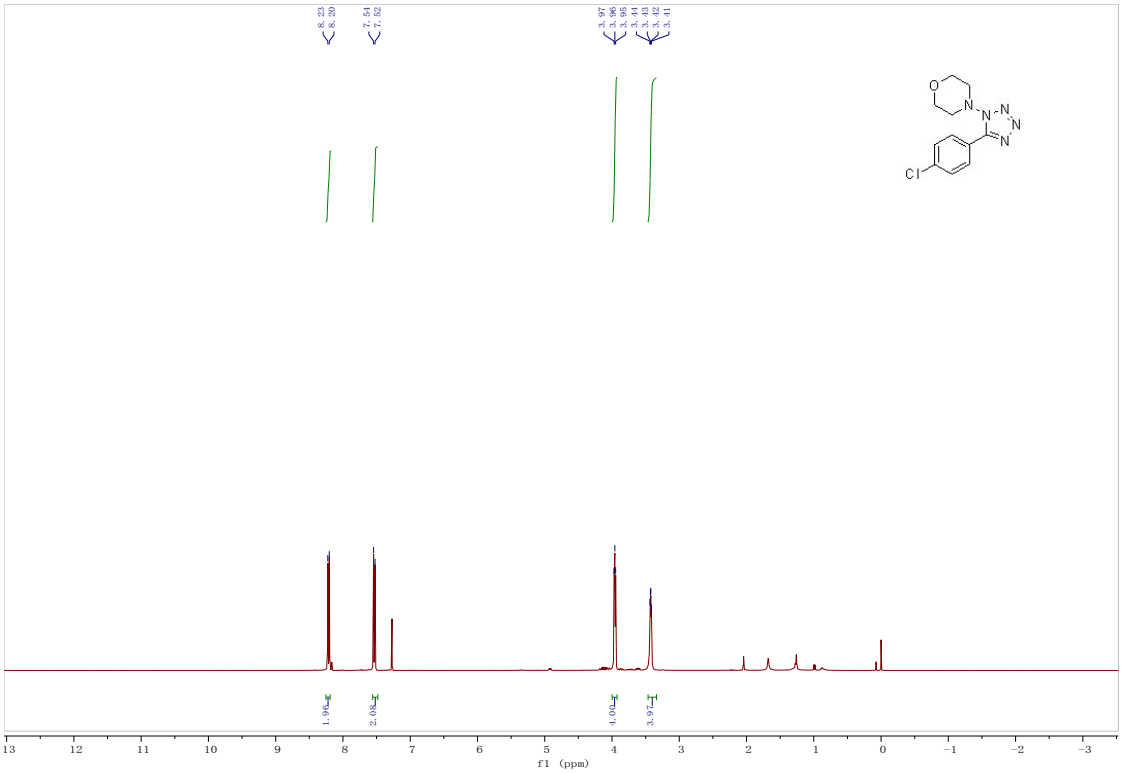
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Cl
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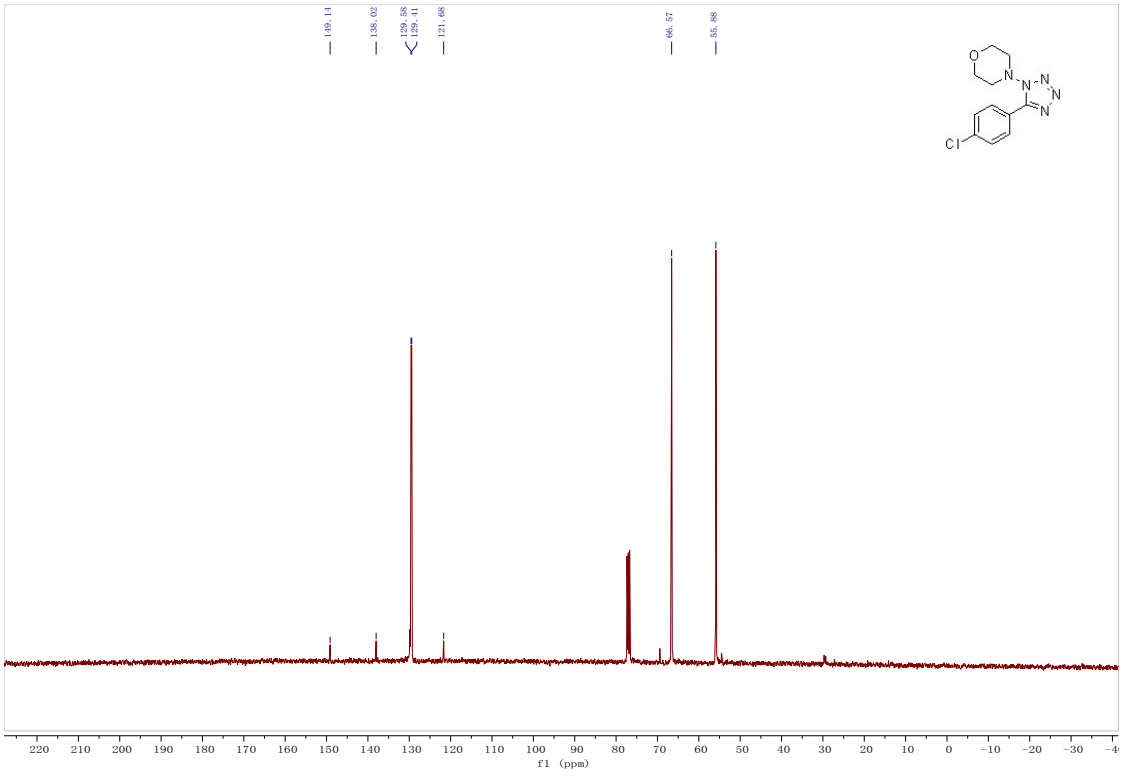
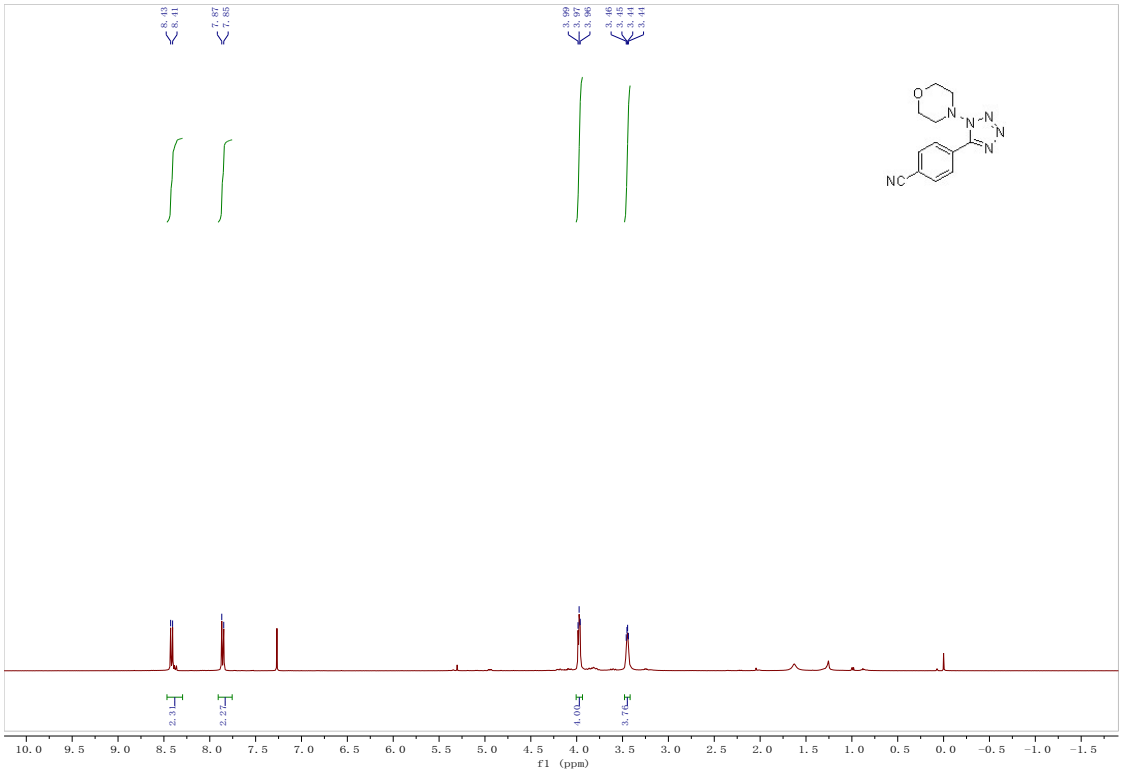
4.00
3.97
13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)


149.14
138.02
129.58
129.41
121.68
66.57
55.88
O
N
N
N
N
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)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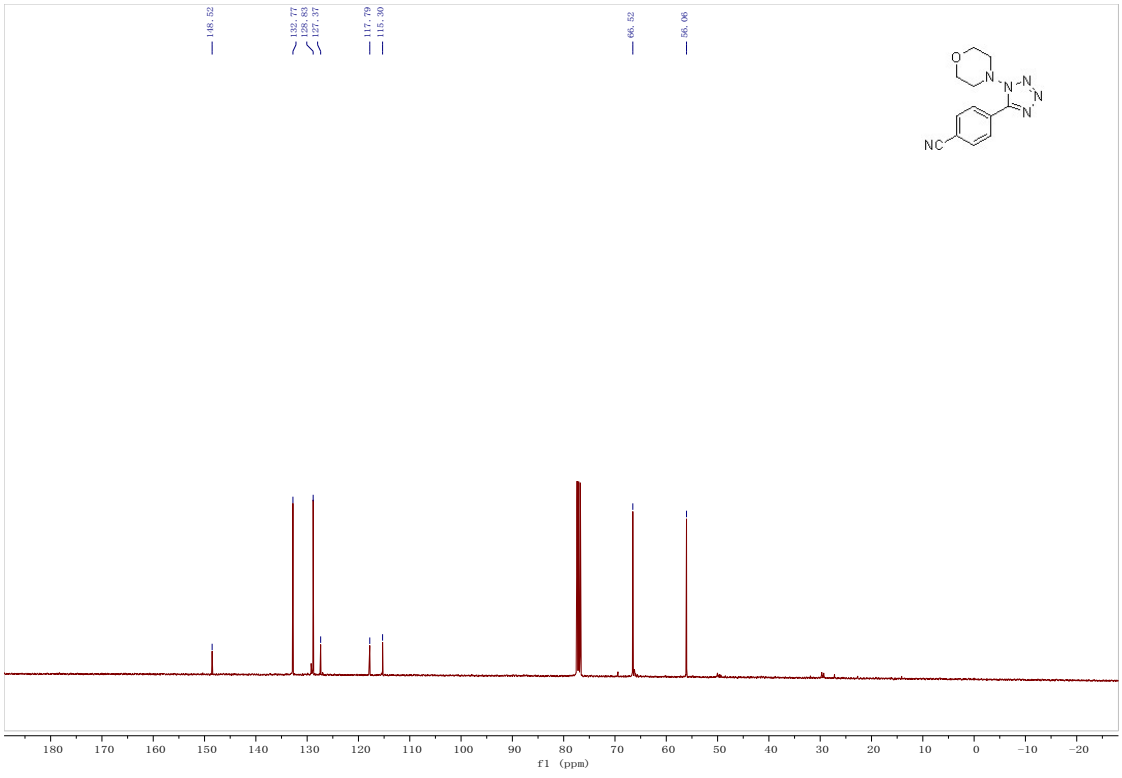
8.41
7.87
7.85
3.99
3.97
3.96
3.46
3.45
3.44
3.44
2.31
2.27
4.00
3.76
f1 (ppm)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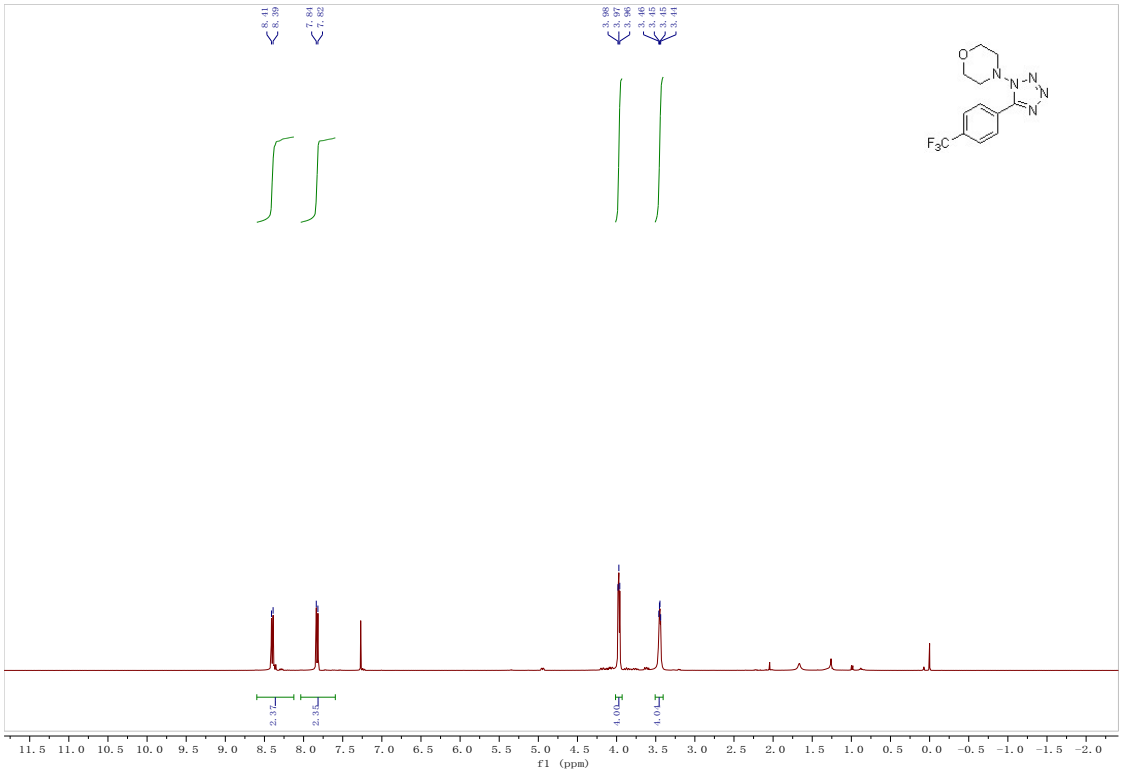
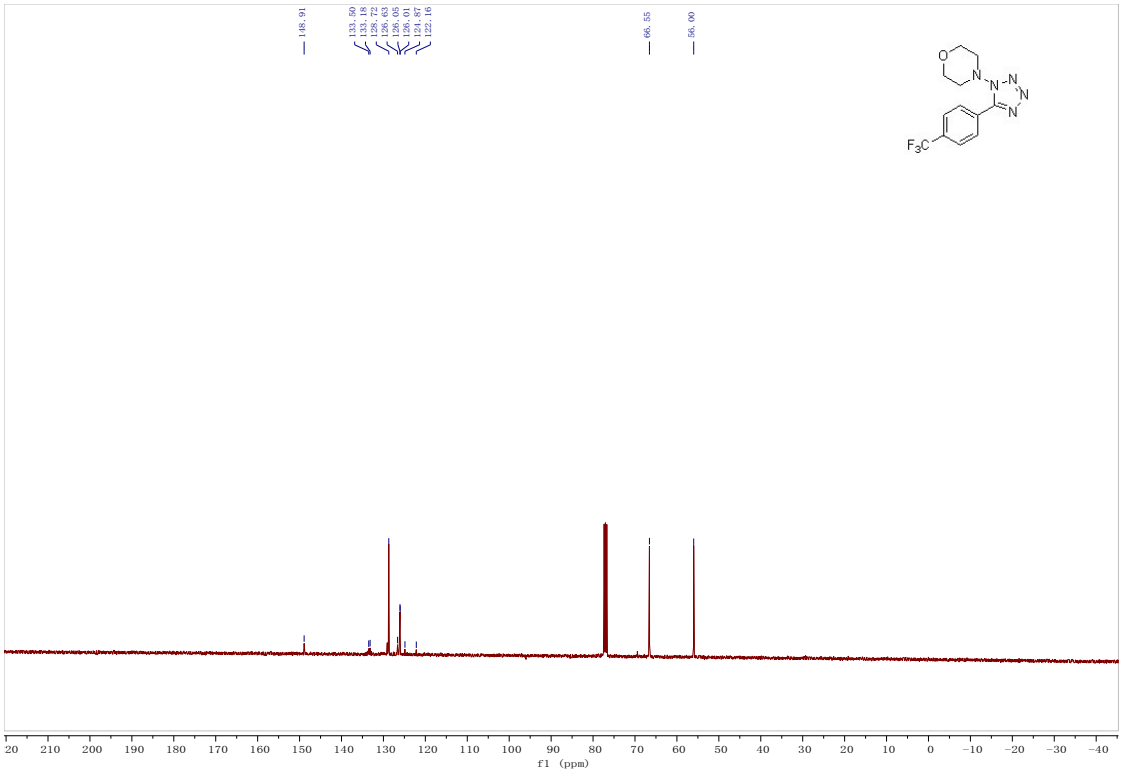
127.37
117.79
115.30
66.52
56.06
f1 (ppm)


8.41
8.39
7.84
7.82
3.98
3.97
3.96
3.46
3.45
3.45
3.44
F3C
2.37
2.35
4.00
4.04
f1 (ppm)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133.50
133.18
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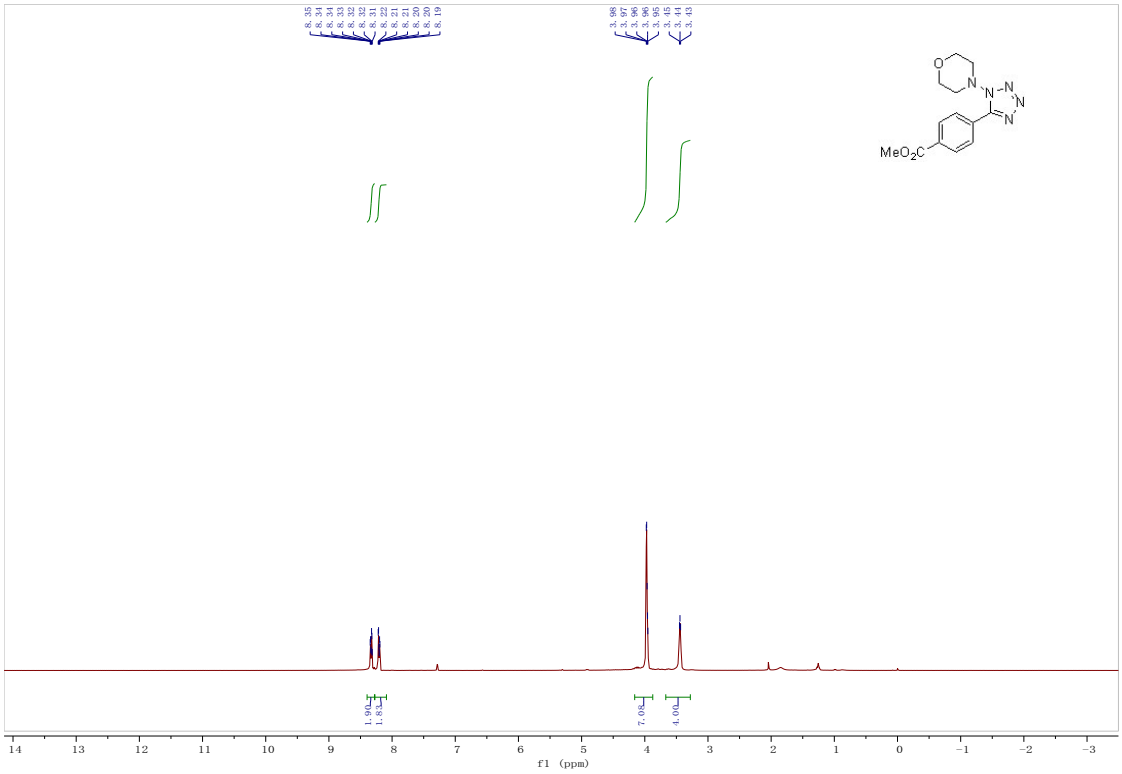
126.63
126.05
126.01
124.87
122.16
66.55
66.00
F3C
f1 (ppm)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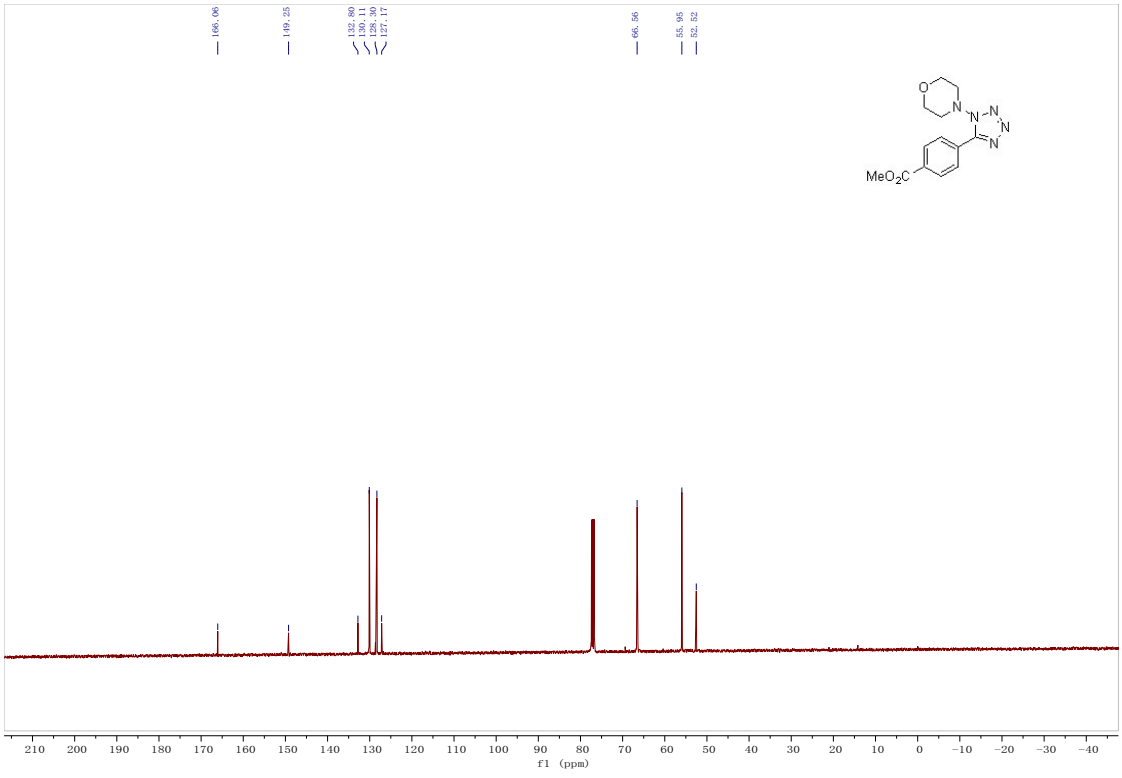
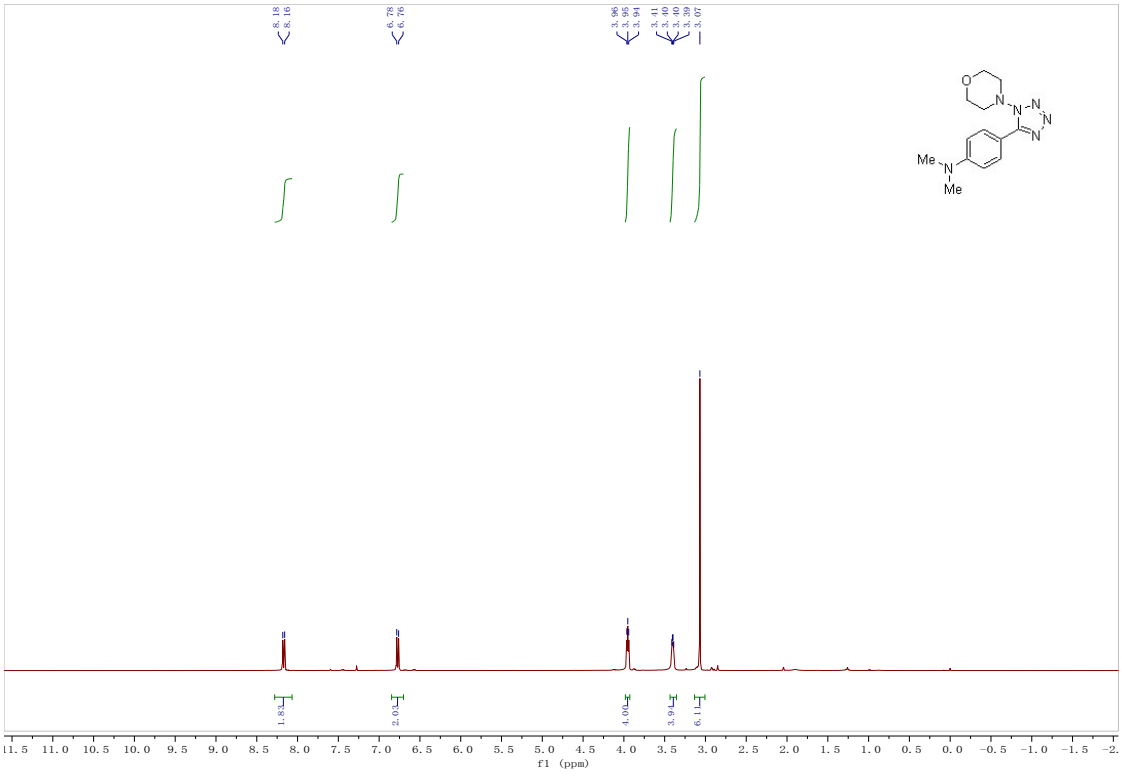
8.34
8.34
8.33
8.32
8.32
8.31
8.22
8.21
8.21
8.20
8.20
8.19
3.98
3.97
3.96
3.96
3.95
3.45
3.44
3.43
O
N
N
N
N
N
MeO2C
1.94
1.93
7.08
4.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)


166.06
149.25
132.80
130.11
128.30
127.17
66.56
55.95
52.52
O
N
N
N
N
N
MeO2C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
f1 (ppm)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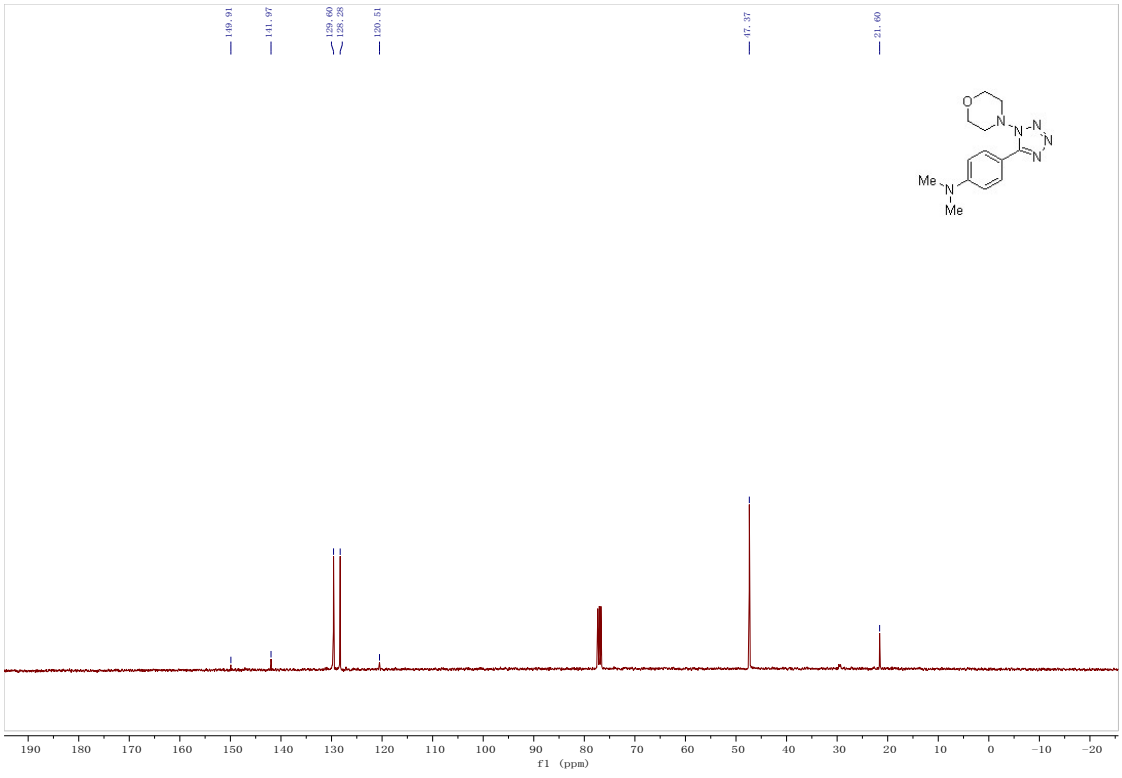
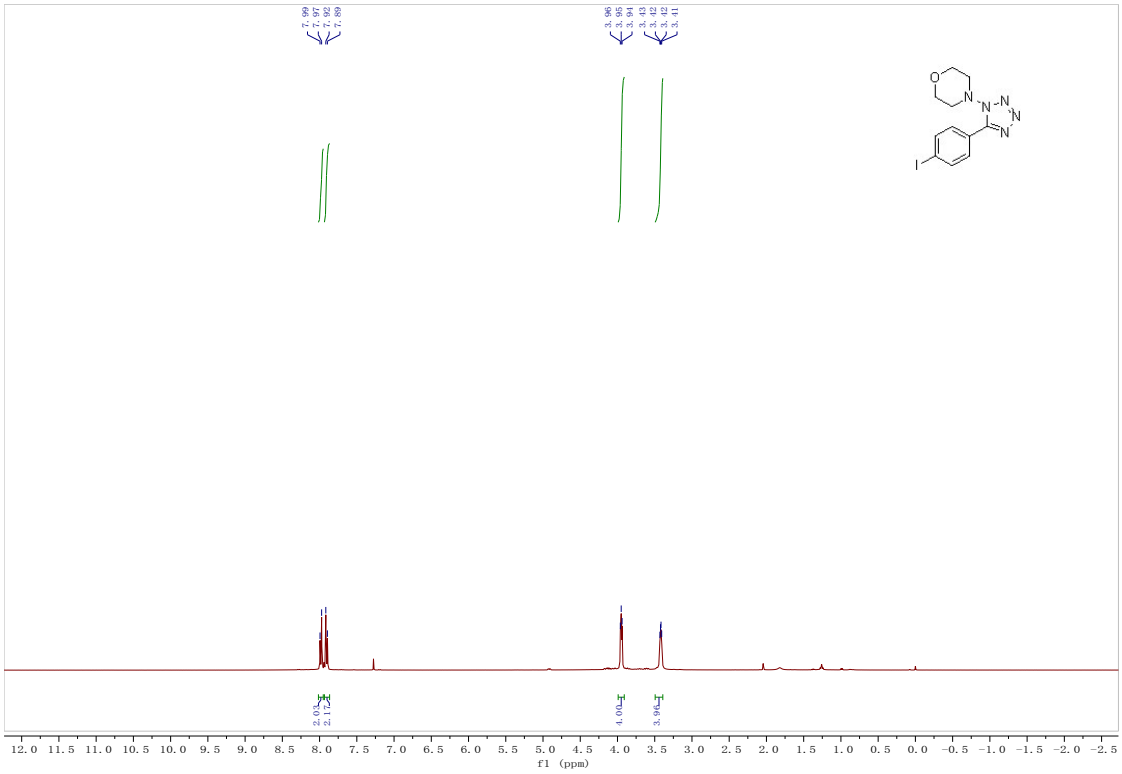
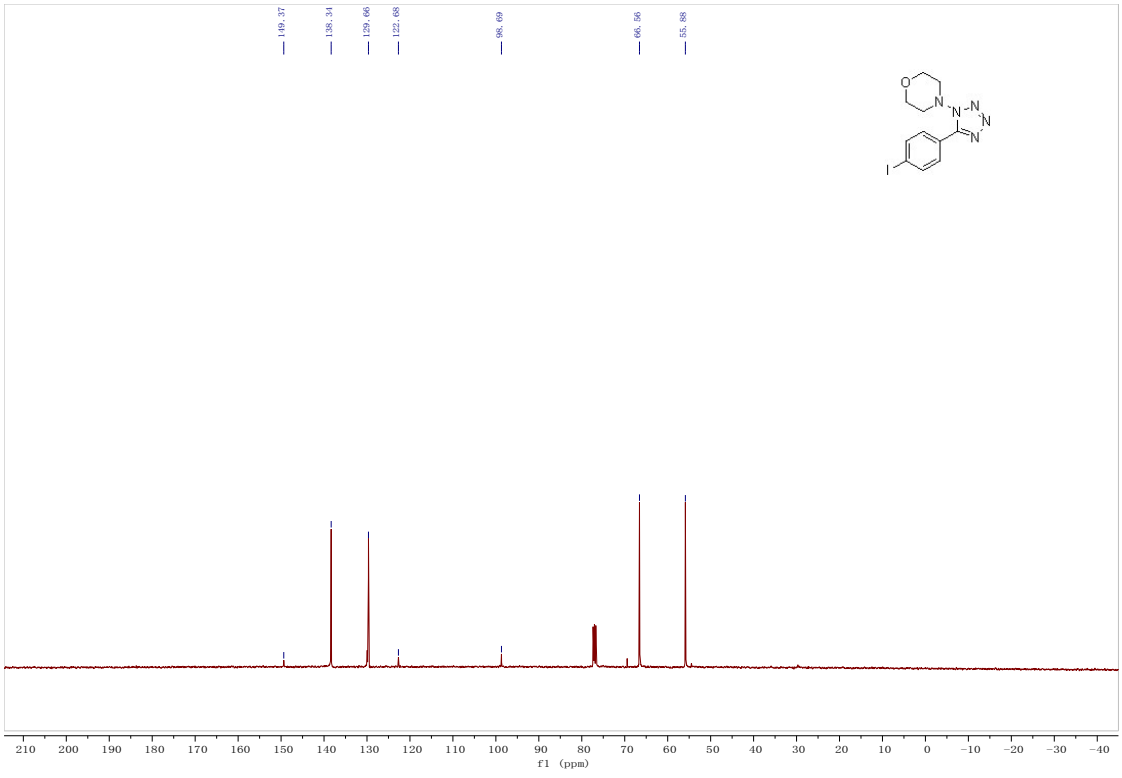
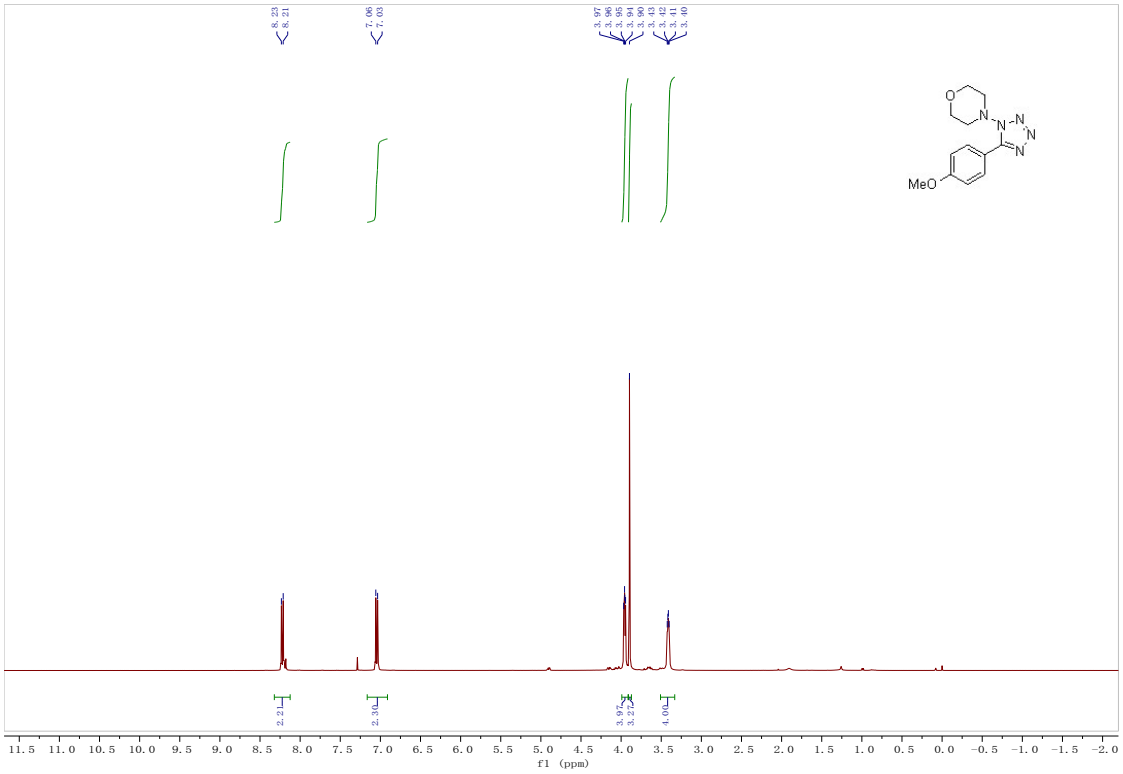
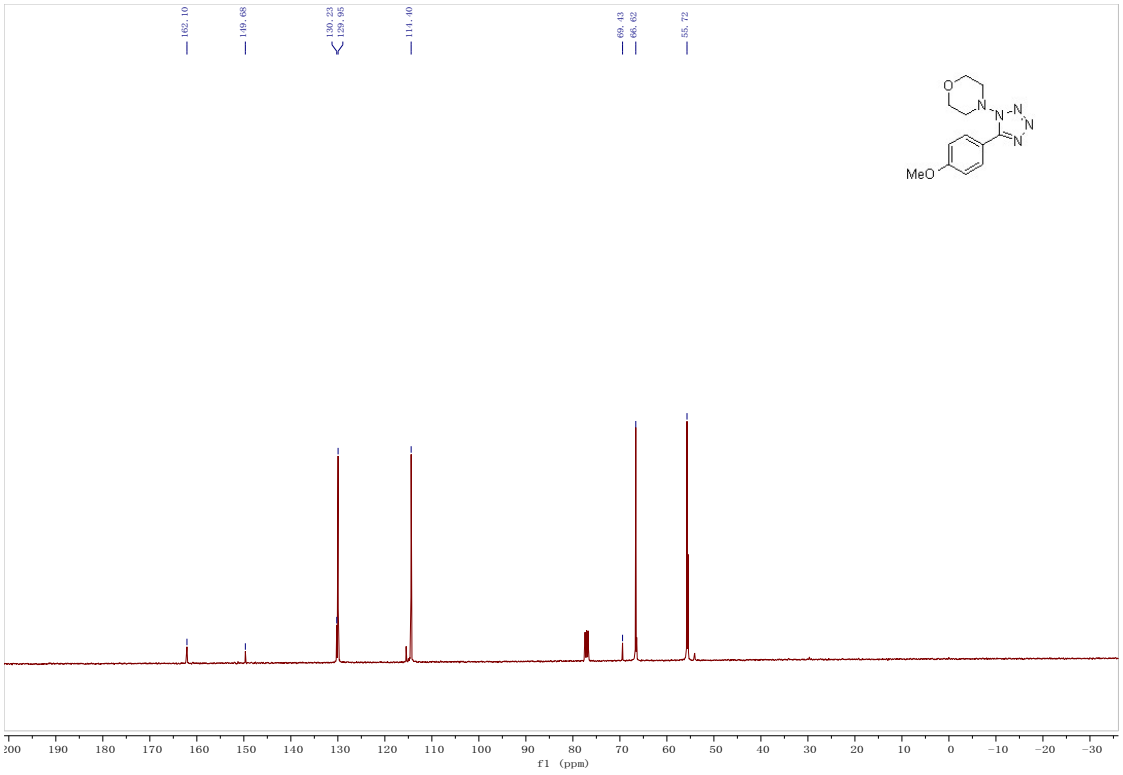
8.16
6.78
6.76
3.96
3.95
3.94
3.41
3.40
3.40
3.39
3.38
3.07
Me
N
Me
1.83
2.03
4.00
3.91
6.11
f1 (ppm)


149.91
141.97
129.69
128.28
120.51
47.37
21.60
Me
N
Me
f1 (ppm)


7.99
7.97
7.92
7.89
3.96
3.95
3.94
3.43
3.42
3.41
2.03
2.17
4.00
3.96
f1 (ppm)


149.37
138.34
129.66
122.68
98.69
66.56
55.88
f1 (ppm)


8.23
8.21
7.06
7.03
3.97
3.96
3.95
3.94
3.90
3.43
3.42
3.41
3.40
MeO
2.21
2.30
3.97
3.27
4.00
f1 (ppm)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149.68
130.23
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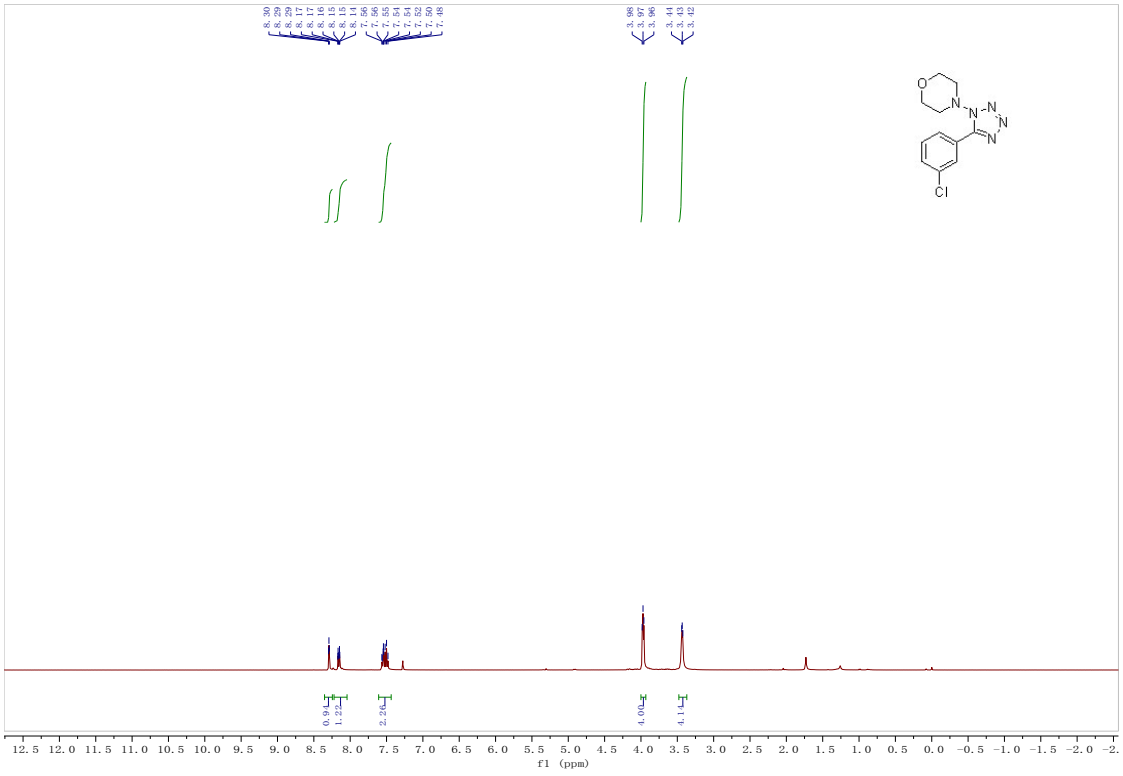
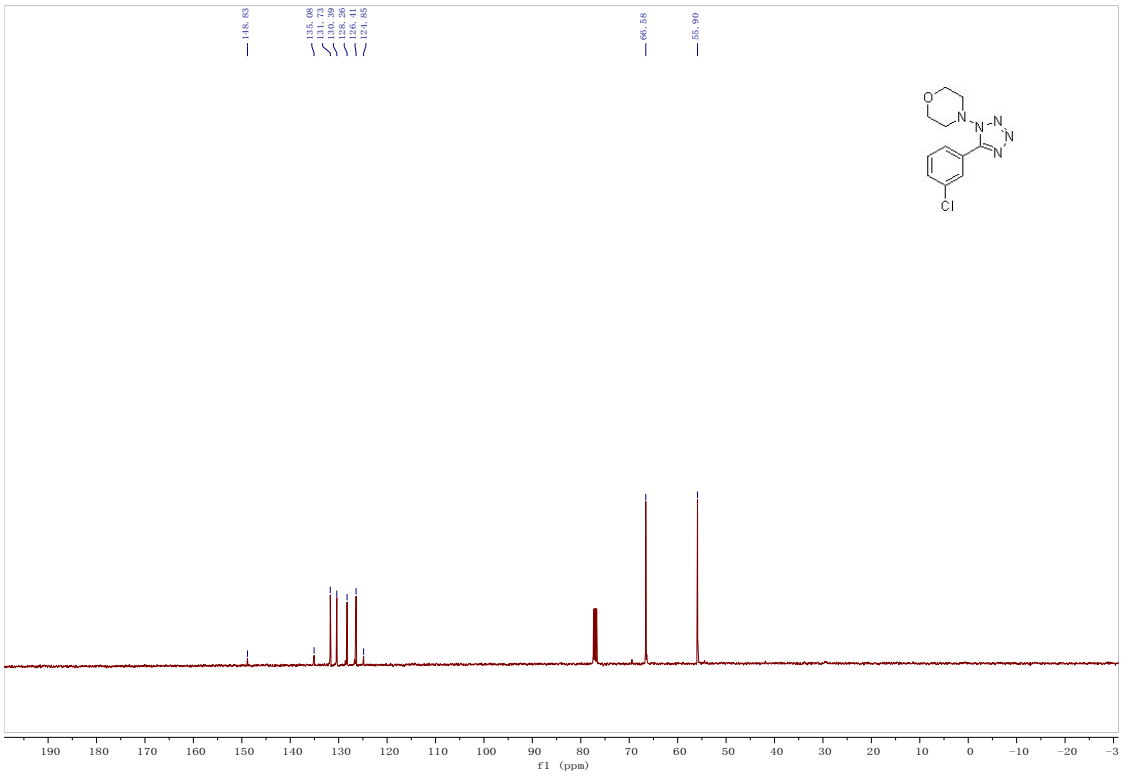
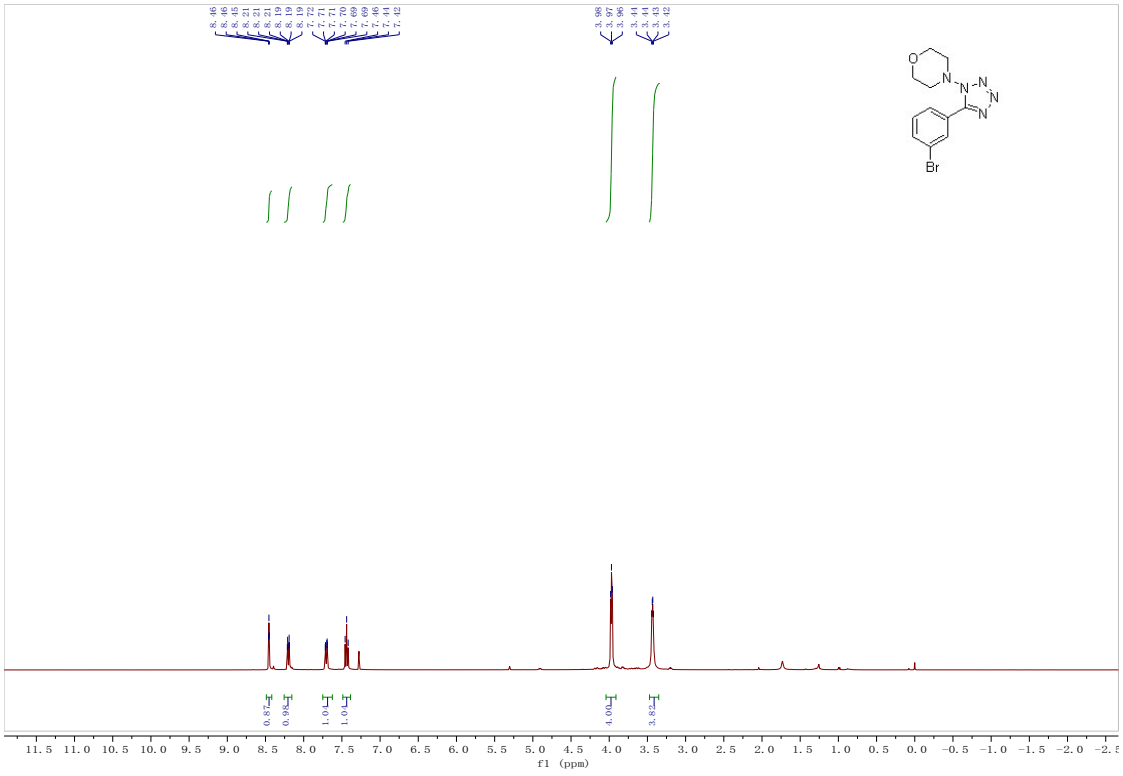
114.40
69.43
66.62
55.72
MeO
f1 (ppm)


8.30
8.29
8.29
8.17
8.17
8.16
8.16
8.15
8.15
8.14
8.14
7.56
7.55
7.55
7.54
7.54
7.53
7.52
7.50
7.48
3.98
3.97
3.96
3.44
3.43
3.42
O
N
N
N
N
N
Cl
0.91
1.22
2.24
4.00
4.14
f1 (ppm)


148.83
135.08
131.73
130.39
128.26
126.41
124.85
66.58
55.90
O
N
N
N
N
N
Cl
f1 (ppm)


8.46
8.46
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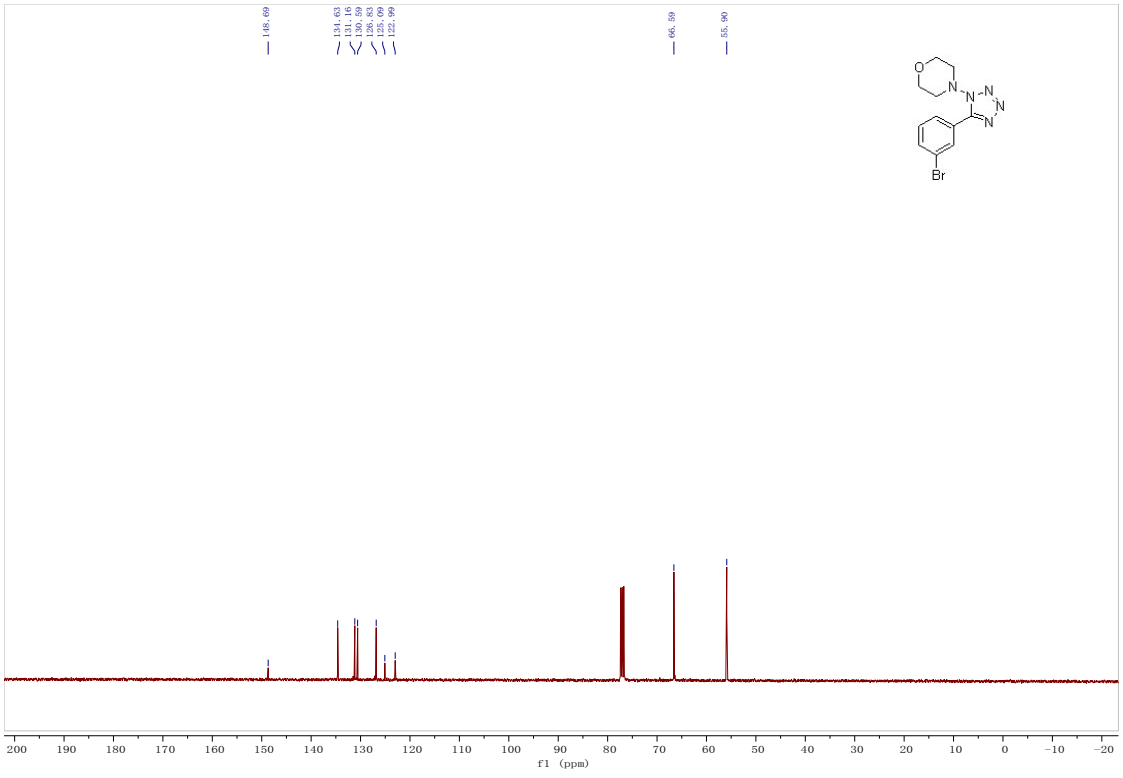
8.19
7.72
7.71
7.71
7.70
7.69
7.69
7.46
7.44
7.42
3.98
3.97
3.96
3.44
3.44
3.43
3.42
O
N
N
N
N
N
Br
0.87
0.98
1.01
1.04
4.00
3.82
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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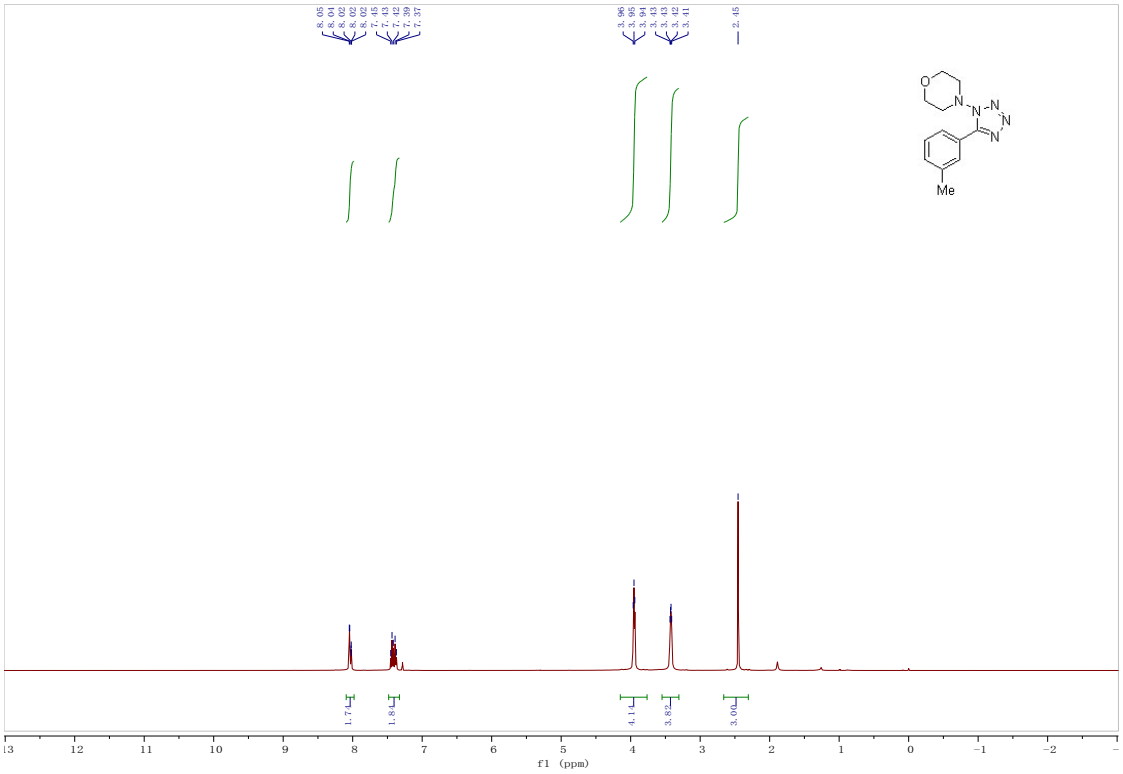
134.63
131.16
130.59
126.83
125.69
122.99
66.59
55.90
O
N
N
N
N
N
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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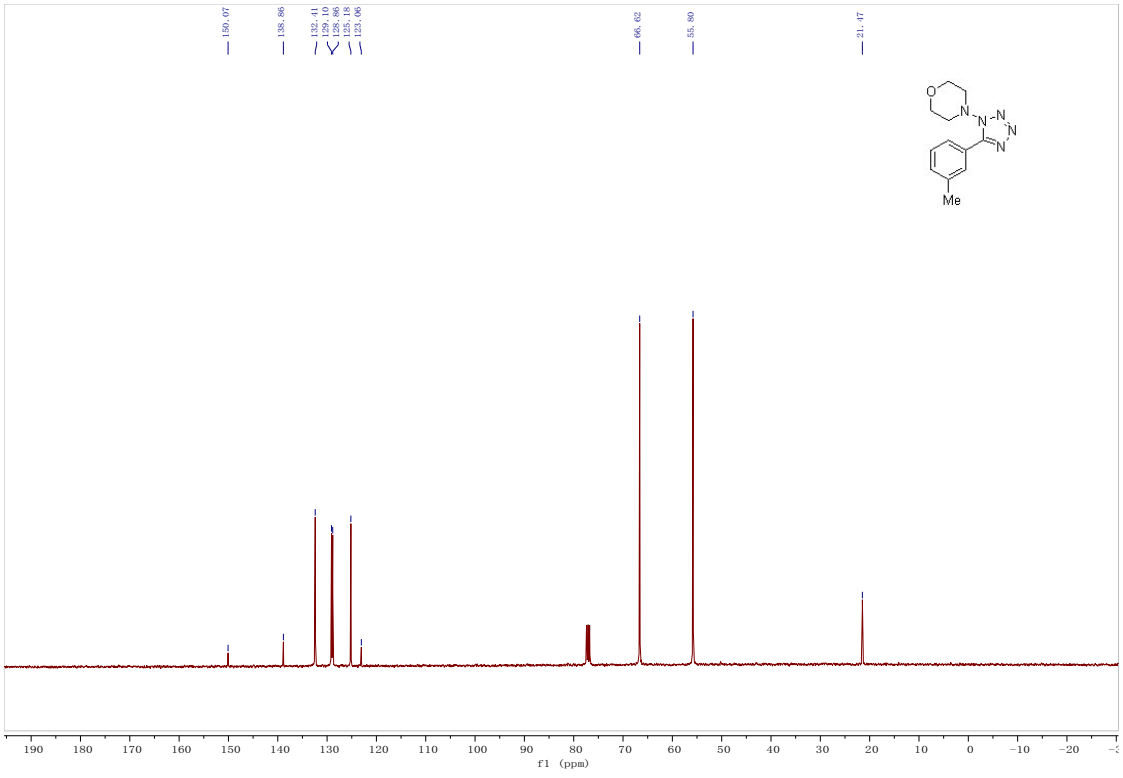
8.04
8.02
8.02
7.45
7.43
7.42
7.39
7.37
3.96
3.95
3.94
3.43
3.42
3.41
2.45
1.74
1.84
4.11
3.82
3.04
Me
f1 (ppm)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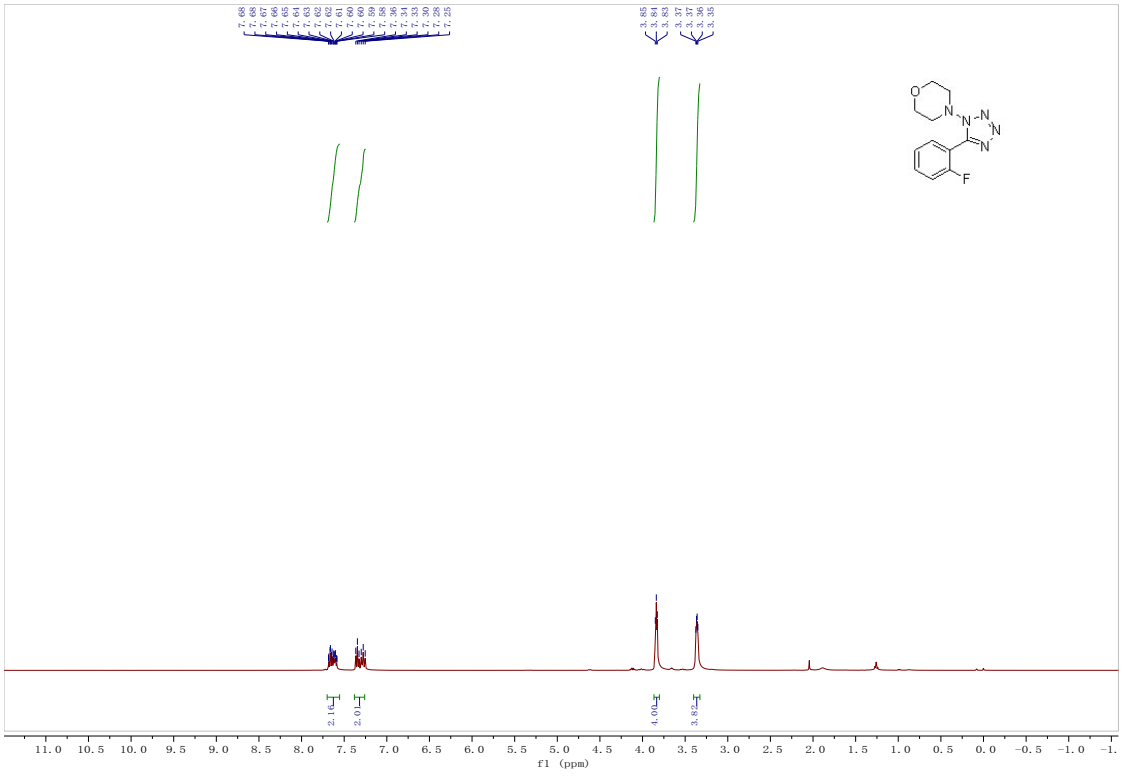
Me
f1 (ppm)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7.68
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7.63
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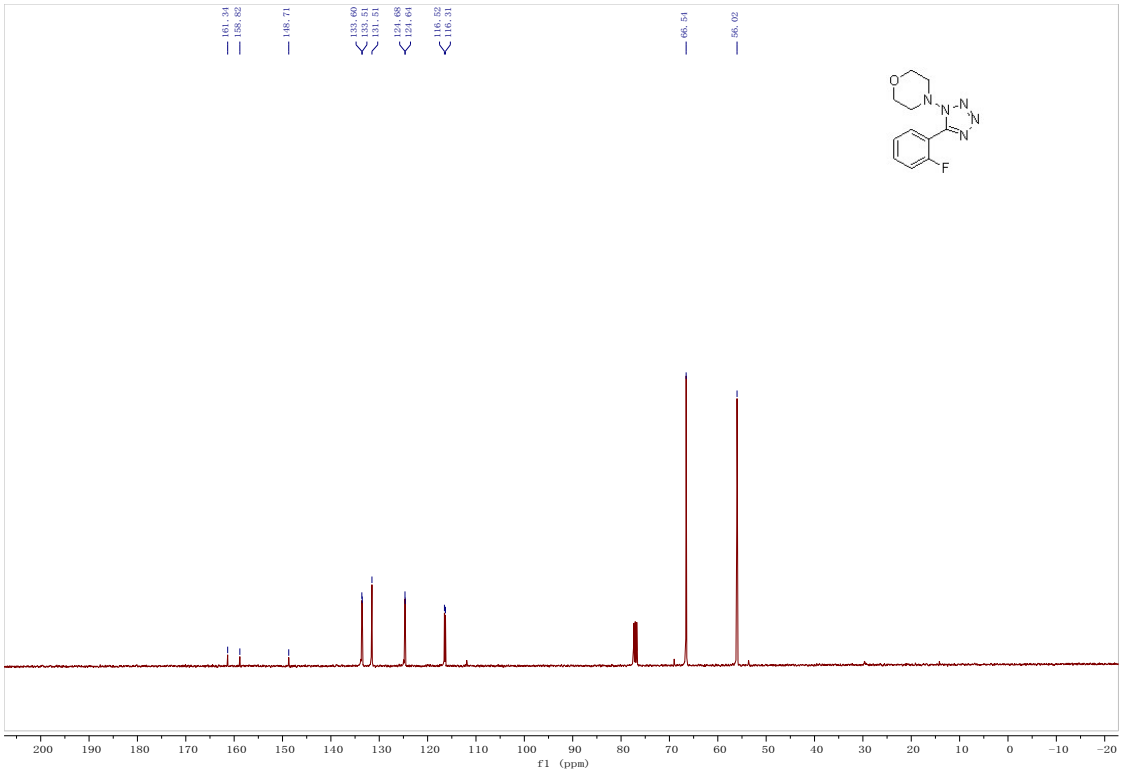
7.62
7.61
7.60
7.60
7.59
7.58
7.36
7.34
7.33
7.30
7.28
7.25
3.85
3.84
3.83
3.37
3.37
3.36
3.35
O
N
N
N
N
F
2.16
2.01
4.00
3.82
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)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131.51
124.68
124.64
116.52
116.31
66.54
56.02
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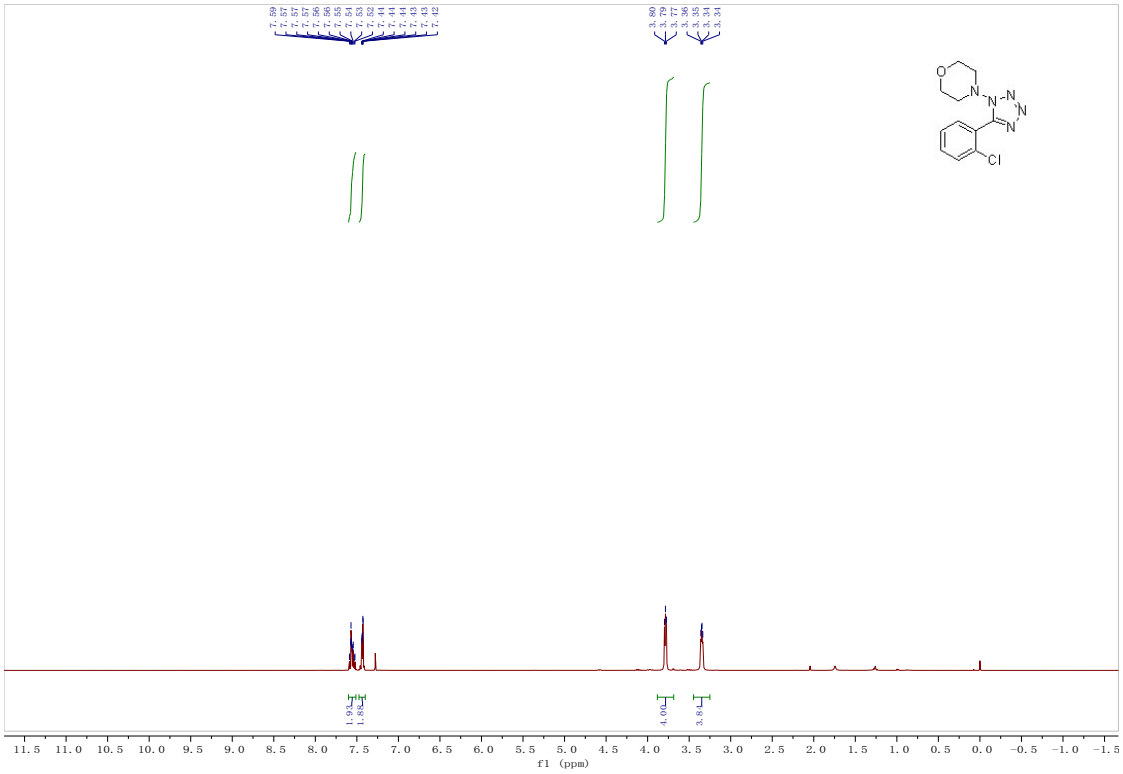
N
N
N
N
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.57
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7.54
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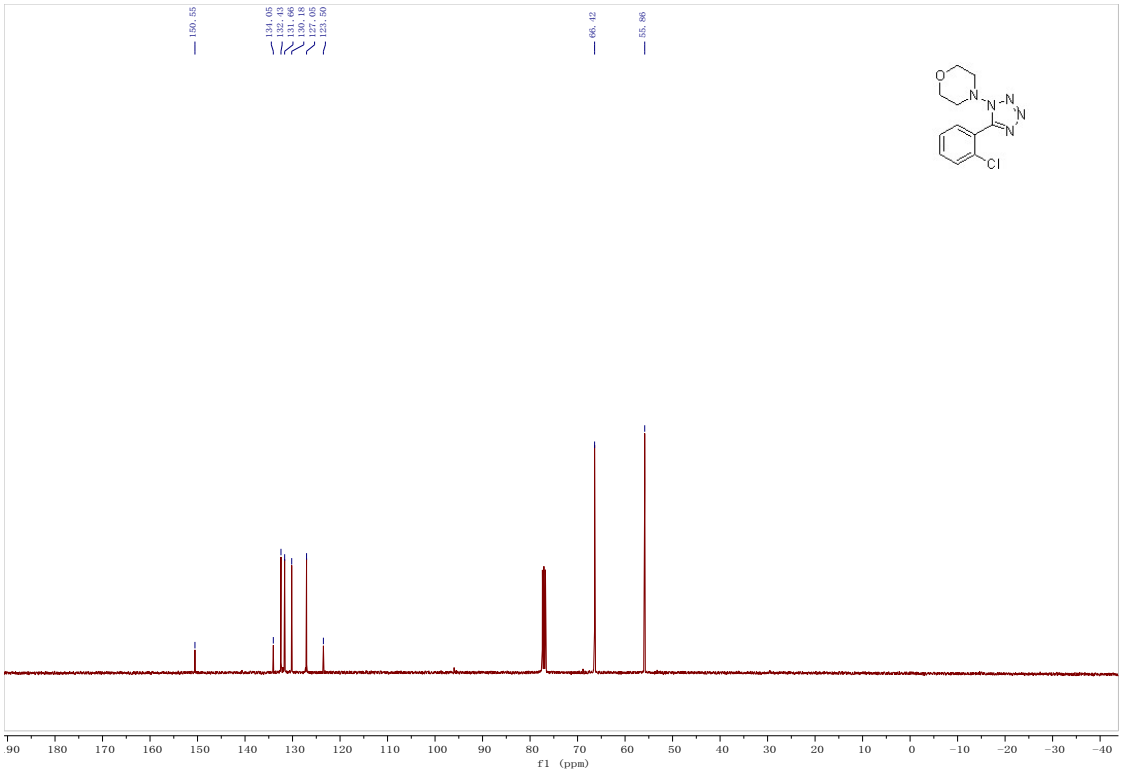
7.52
7.44
7.44
7.44
7.44
7.43
7.43
7.42
3.80
3.79
3.77
3.36
3.35
3.34
3.34
1.93
1.84
4.00
3.84
f1 (ppm)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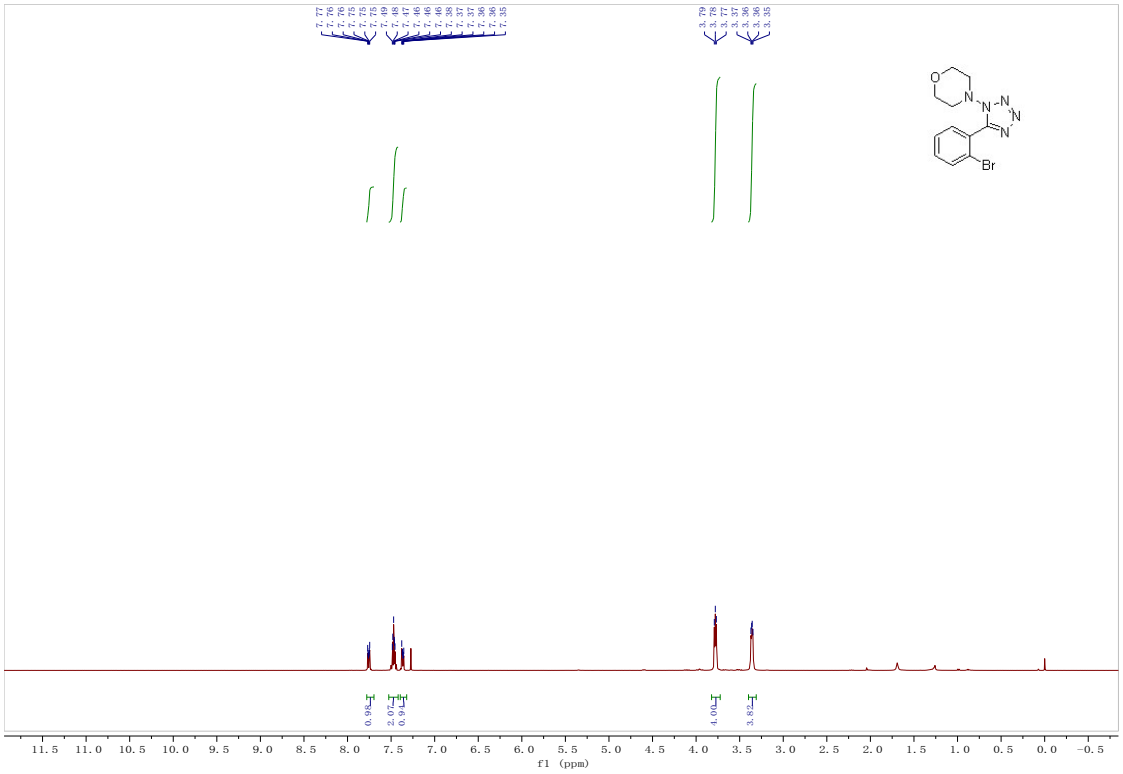
f1 (ppm)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7.76
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7.75
7.75
7.49
7.47
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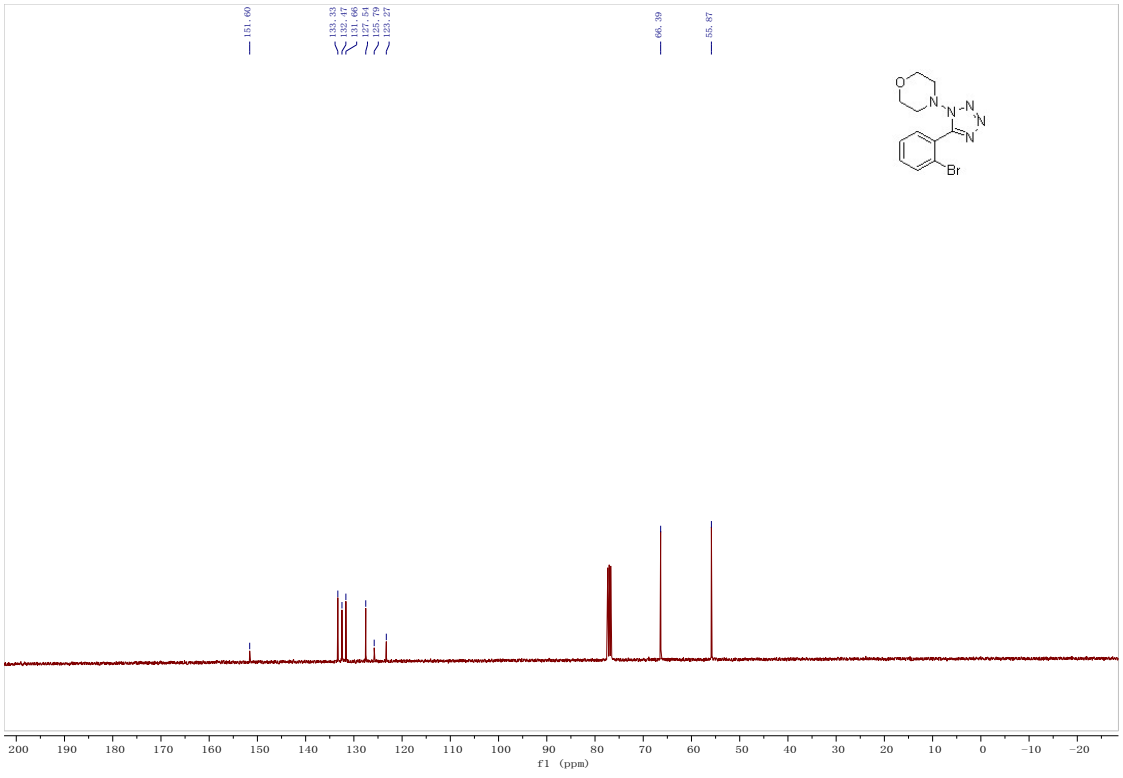
7.46
7.46
7.38
7.37
7.37
7.36
7.36
7.35
3.79
3.78
3.77
3.37
3.36
3.36
3.35
O
N
N
N
N
Br
0.98
2.07
0.94
4.00
3.82
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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131.66
127.84
125.79
123.27
66.39
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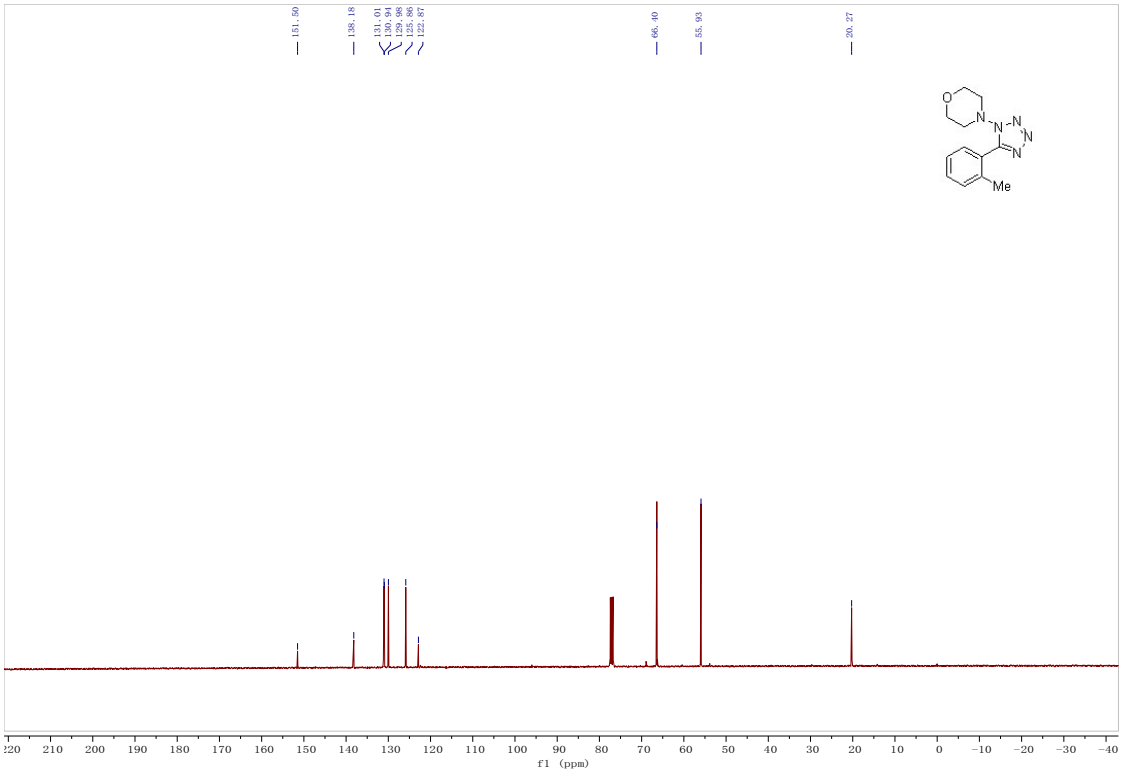
N
N
N
N
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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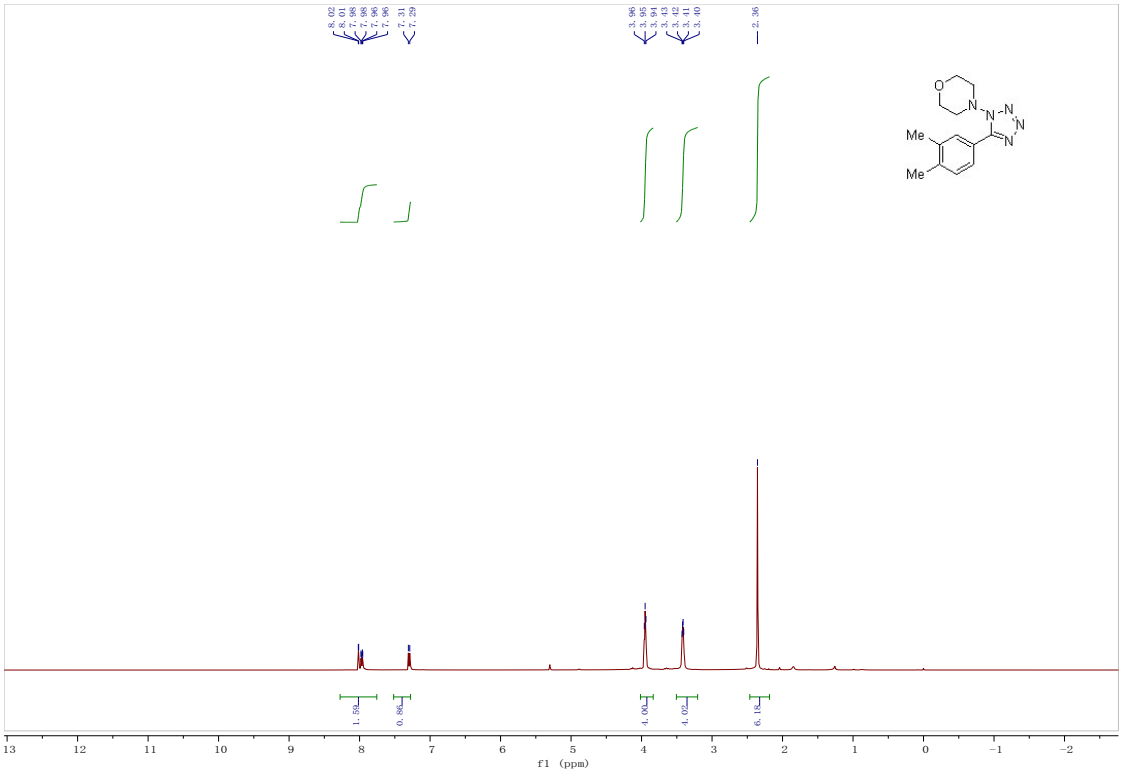
129.98
125.86
122.87
66.40
55.93
20.27
Me
f1 (ppm)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8.01
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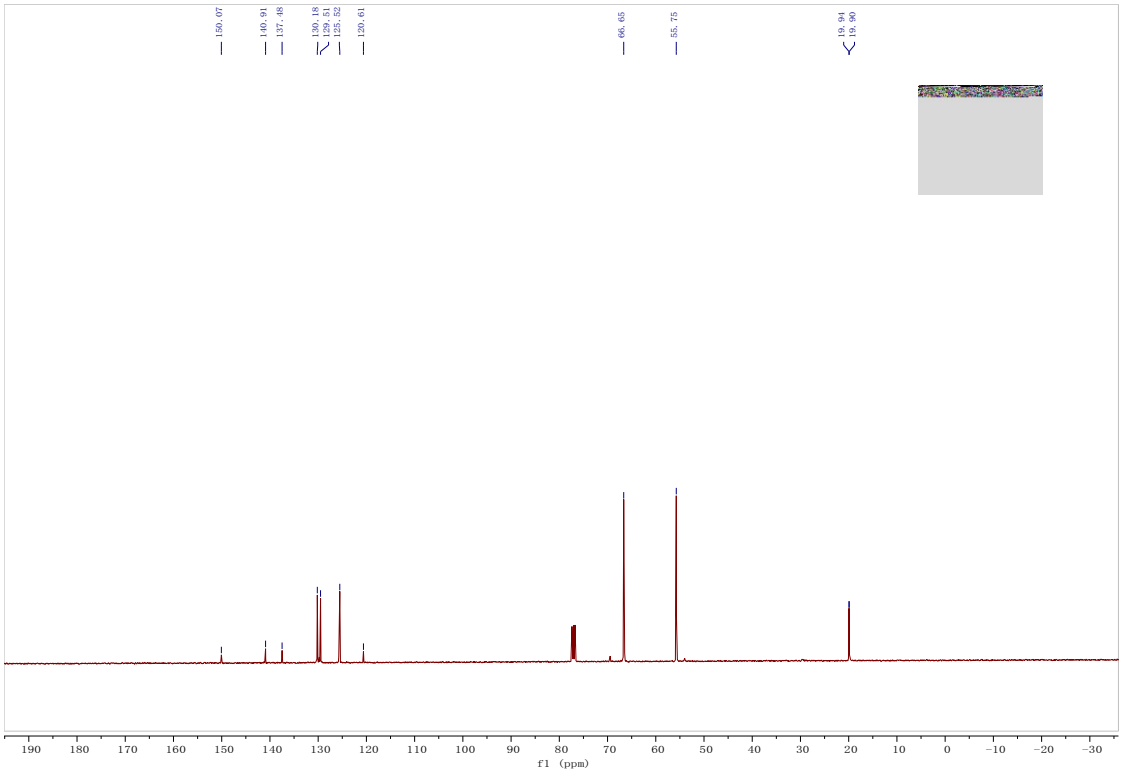
7.98
7.96
7.96
7.31
7.29
3.96
3.95
3.94
3.43
3.42
3.41
3.40
2.36
Me
Me
1.59
0.86
4.00
4.02
6.18
f1 (ppm)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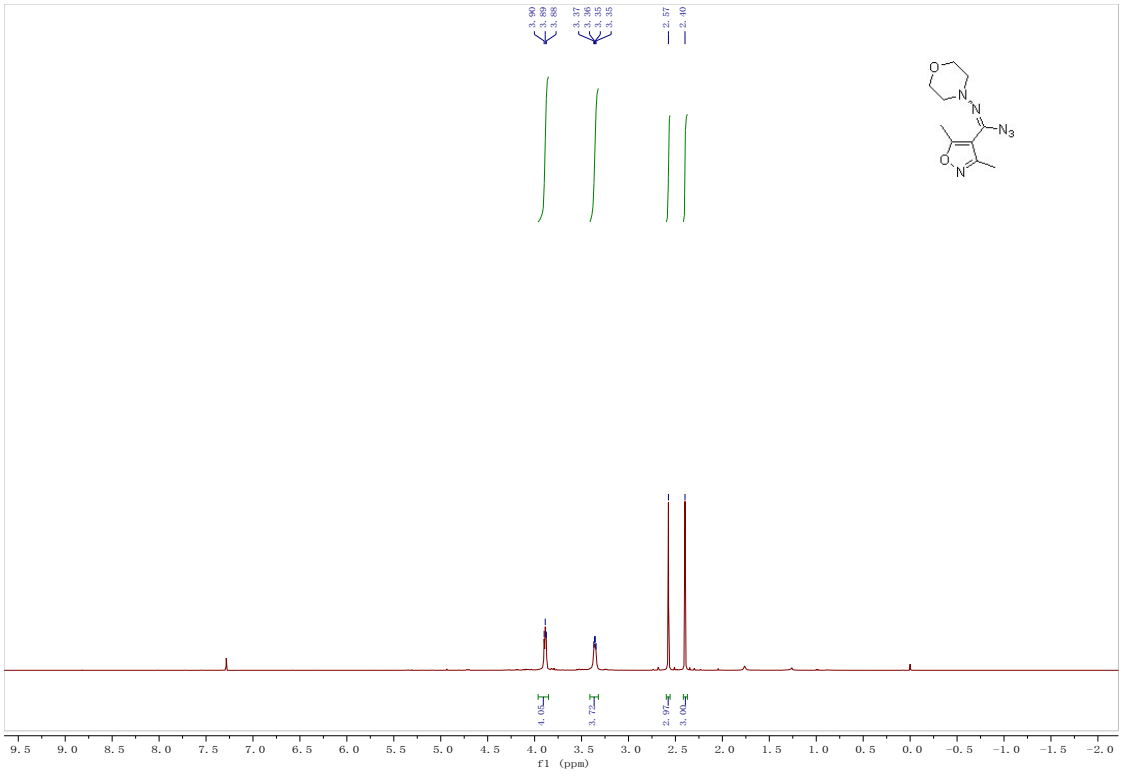
120.61
66.65
55.75
19.94
19.90
f1 (ppm)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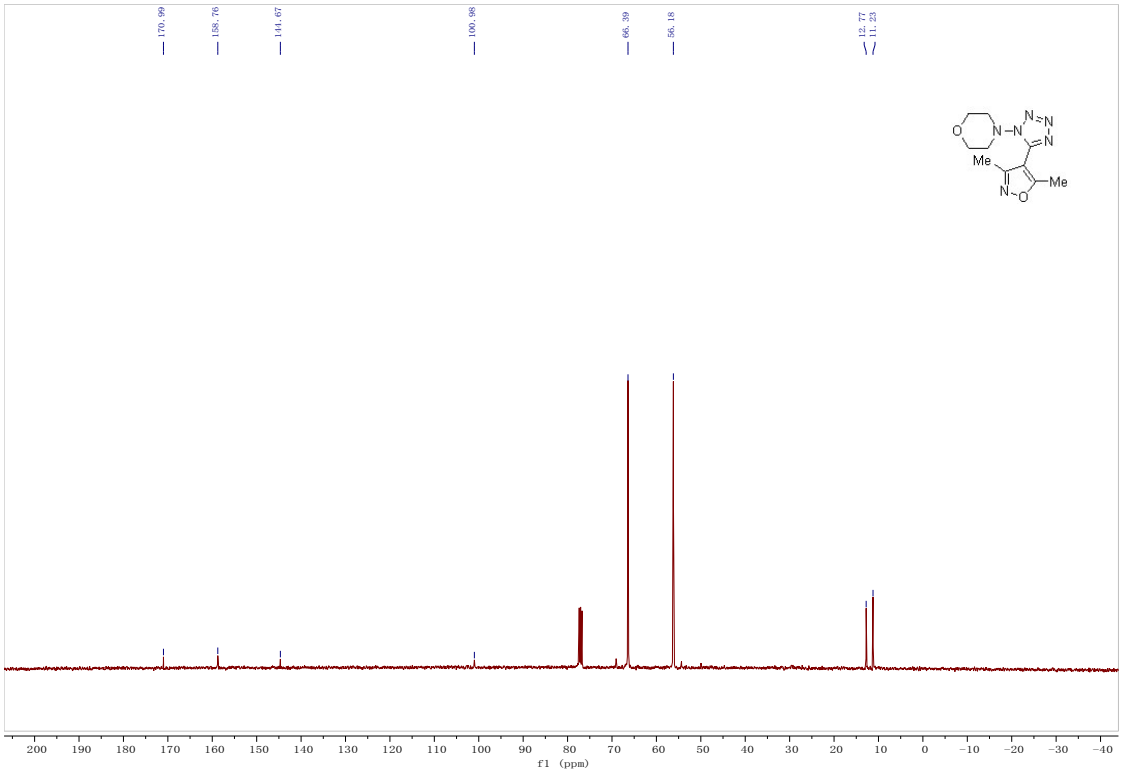
3.35
2.57
2.40
4.05
3.72
2.97
3.00
f1 (ppm)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12.77
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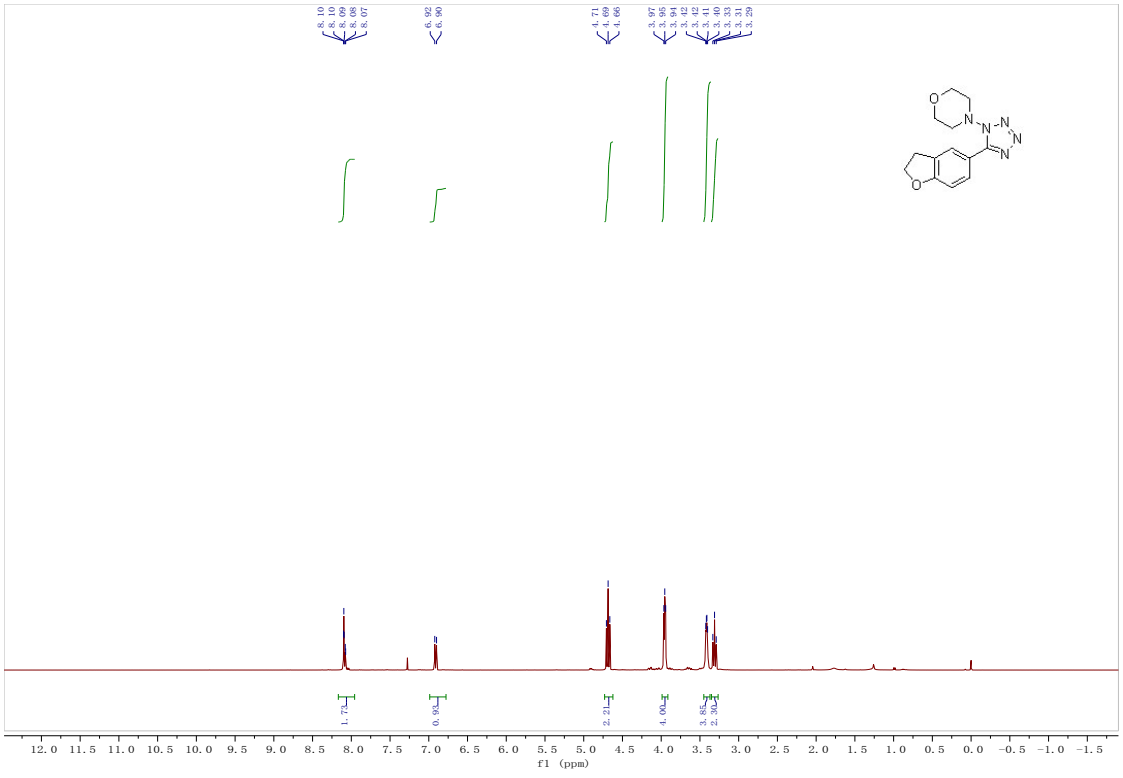
Me
Me
f1 (ppm)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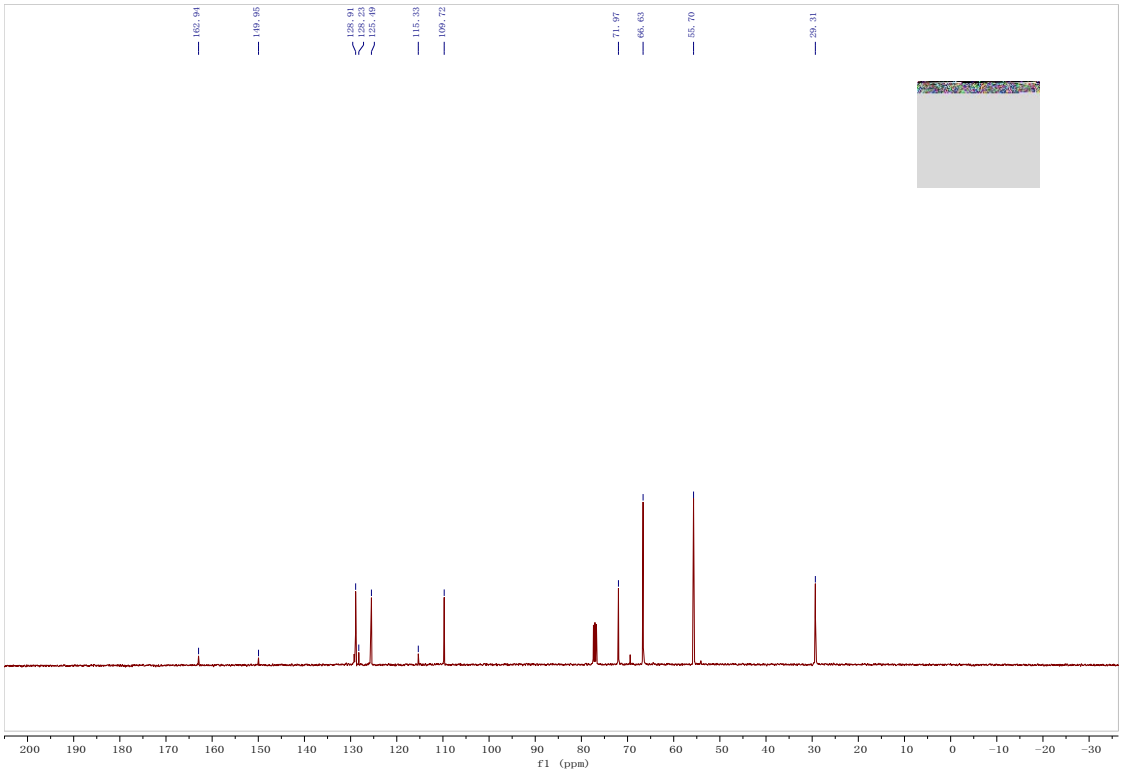
8.09
8.08
8.07
6.92
6.90
4.71
4.69
4.66
3.97
3.95
3.94
3.42
3.41
3.40
3.35
3.31
3.29
1.72
0.93
2.21
4.00
3.85
2.30
f1 (ppm)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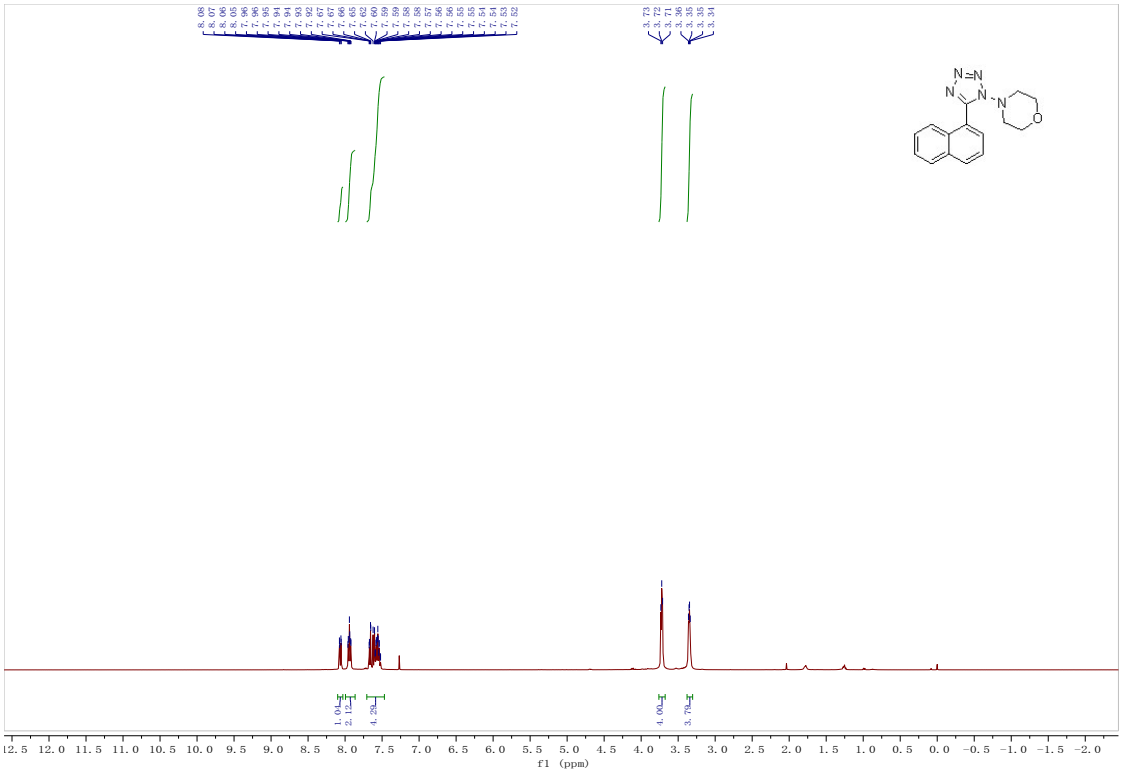
109.72
71.97
66.63
65.70
29.31
f1 (ppm)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8.07
8.06
8.05
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7.95
7.94
7.93
7.92
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4.00
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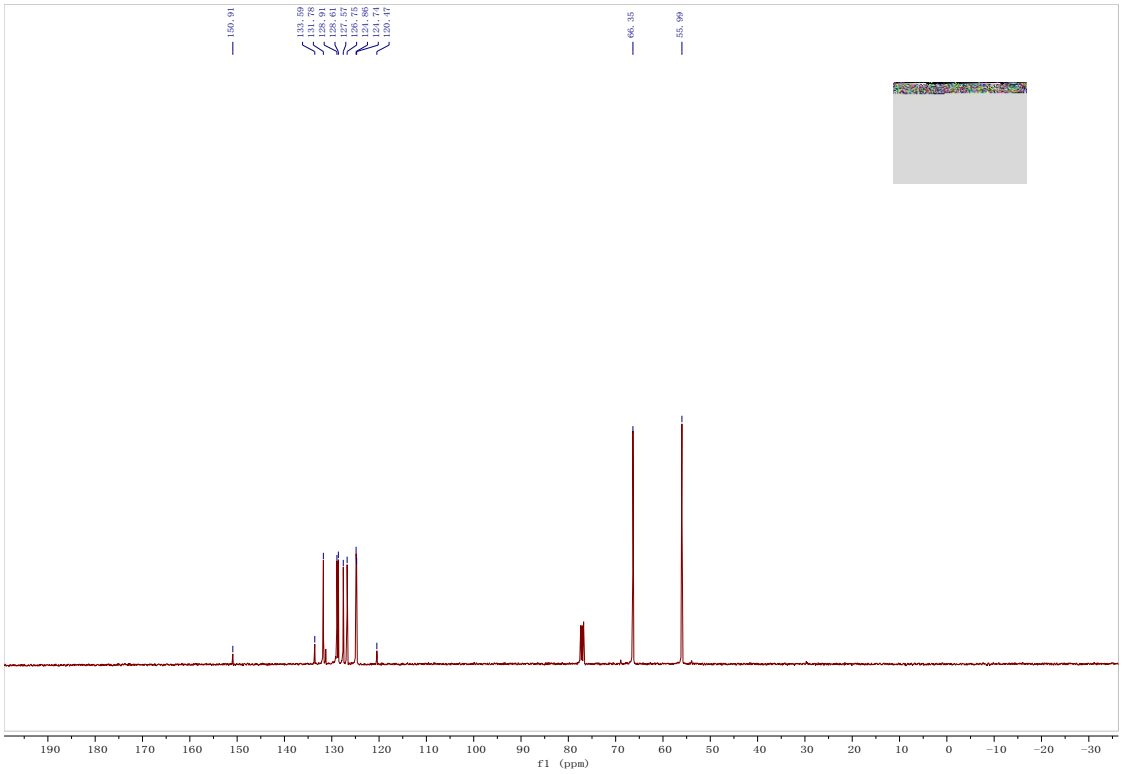
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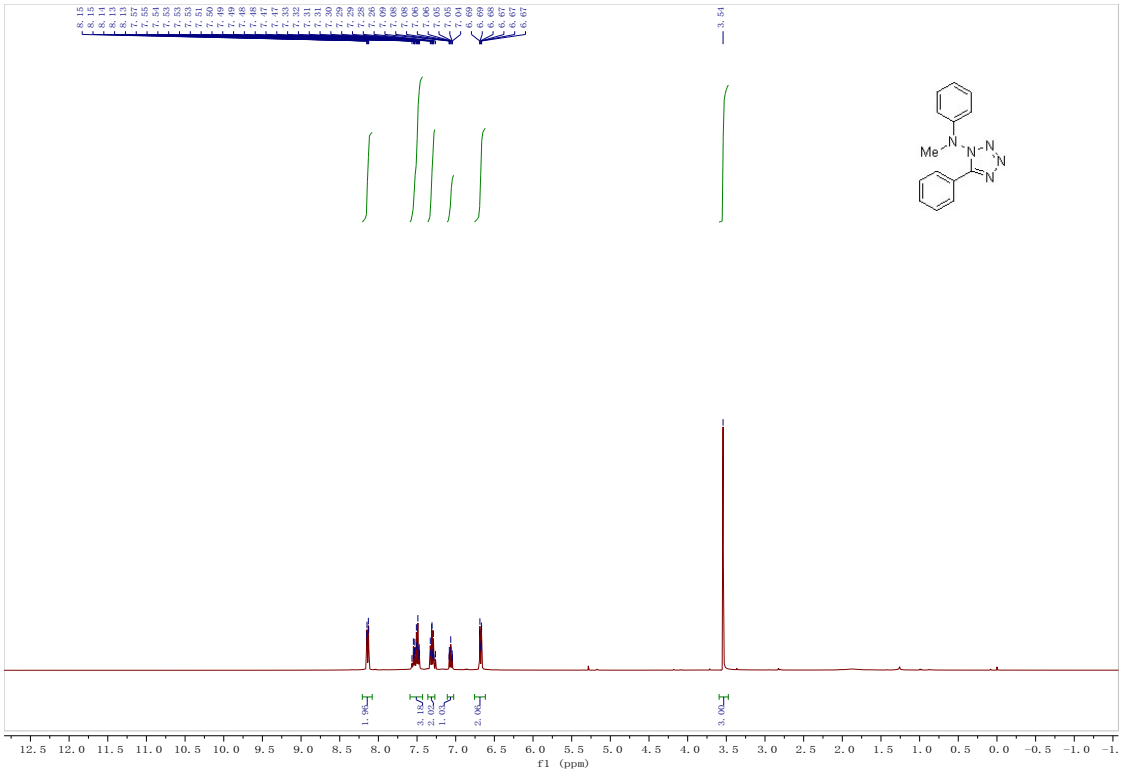
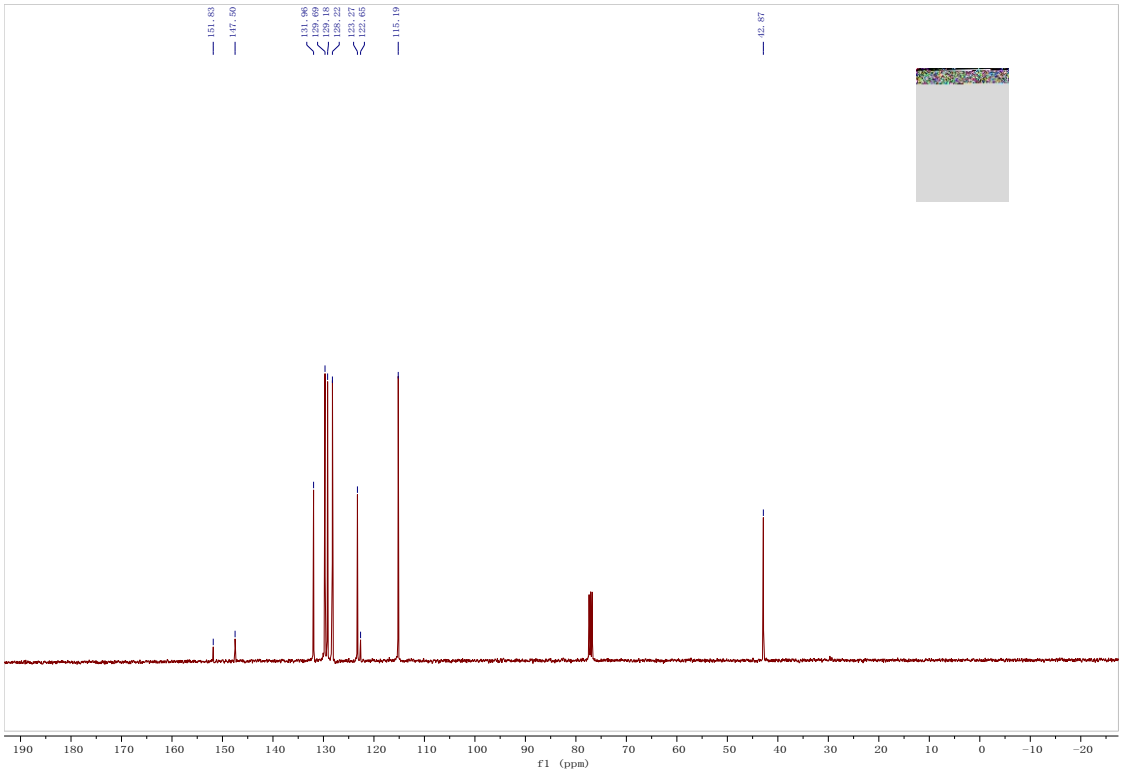
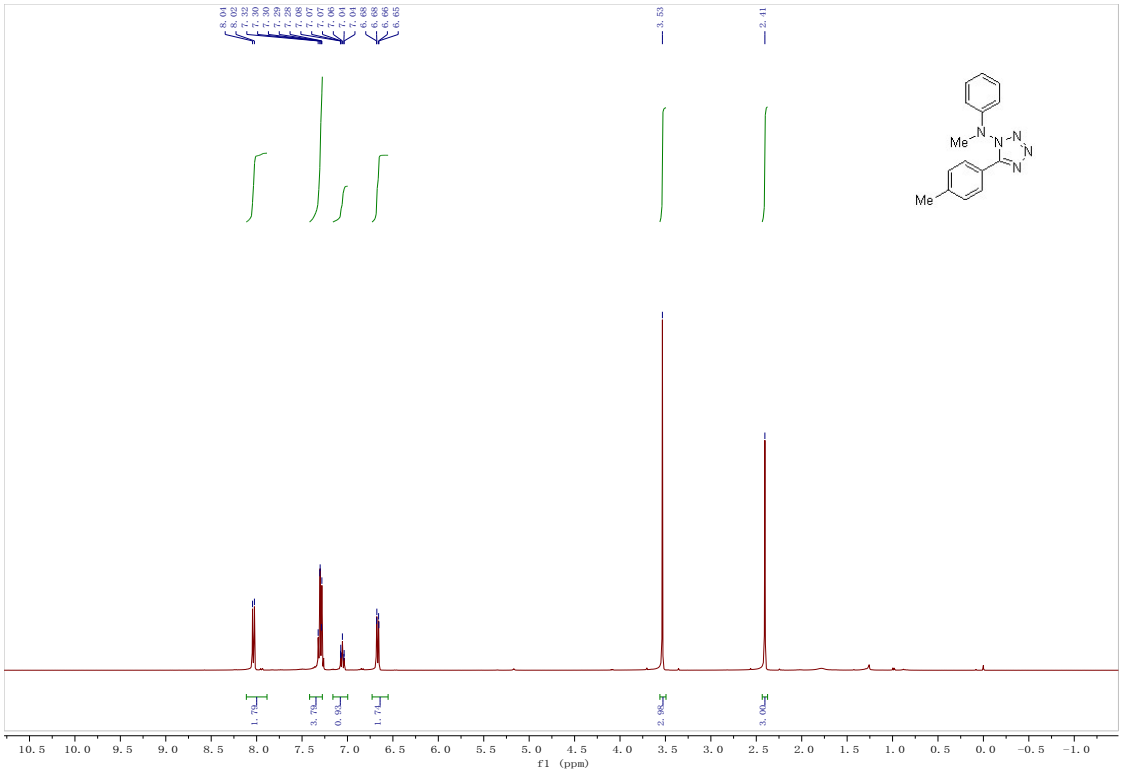
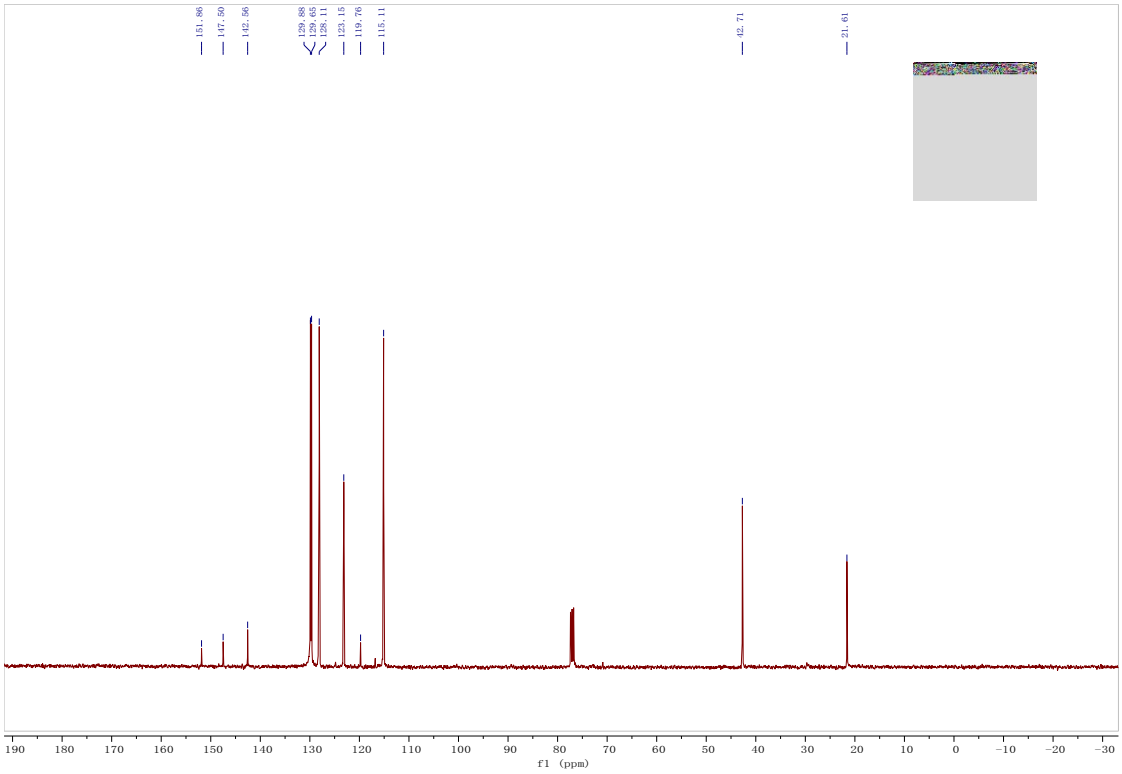
133.59
131.78
129.91
128.61
127.57
126.75
121.96
121.74
120.47
66.35
55.99
f1 (ppm)


3.54
Me
N
N
N
N
1.96
3.18
2.02
1.03
2.06
3.00
f1 (ppm)


151.83
147.50
131.96
129.69
129.18
128.22
123.27
122.65
118.19
42.87
f1 (ppm)


8.04
8.02
7.32
7.30
7.30
7.29
7.28
7.08
7.07
7.07
7.06
7.04
7.04
6.68
6.66
6.65
3.53
2.41
Me
N
N
N
N
Me
1.79
3.79
0.93
1.71
2.98
3.00
f1 (ppm)


151.86
147.50
142.56
129.88
129.65
126.11
123.15
119.76
116.11
42.71
21.61
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)