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Silver-Catalyzed [3 + 2] Cycloaddition Reactioin of Arene-diazonium Salts with 2,2,2-Trifluorodiazoethane (CF_3CHN_2): A Facile Access to 2-Aryl-5-Tifluoromethyltetrazoles

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General Information

^{1}H, ^{19}F and ^{13}C NMR were recorded at 400 MHz (^{1}H NMR), 376 MHz (^{19}F NMR) and 100 MHz (^{13}C NMR), respectively. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ_H = 7.26 ppm, δ_C = 77.20 ppm; DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and dd (doublet of doublets). Coupling constants were reported in Hertz (Hz). High resolution mass spectrometry (HRMS) spectra were obtained on a microTOF-QII or Waters Micromass GCT Premier Instrument. IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. Melting points were measured on a WRS-1A digital melting point apparatus and are uncorrected.

Materials: Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone; CH_2Cl_2 (DCM) and *N*,*N*-dimethylformamide (DMF) was distilled from CaH_2; CH_3CN was distilled from P_2O_5. All commercially available reagents were used without further purification. The diazonium salts were prepared from the corresponding anilines following the procedure below and were used directly. The stock solutions of 2,2,2-trifluorodiazoethane (CF_3CHN_2) in various solvents were prepared from 2,2,2-trifluoroethylamine hydrochloride and stored at –20 ^{o}C. Analytical thin layer chromatography was performed on 0.20 mm silica gel plates. Silica gel (200–300 mesh) was used for flash chromatography.

CAUTION **:** *2,2,2-Trifluorodiazoethane (CF_3CHN_2) is potentially explosive! Although no accident occurred during the course of this study, stringent safety precautions are necessary for all reactions of CF_3CHN_2.*

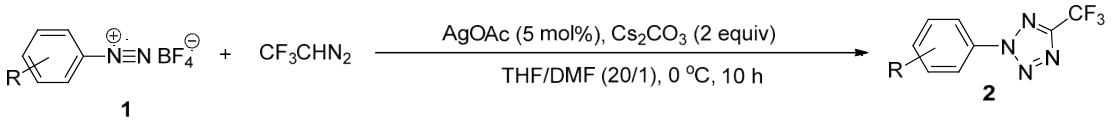
General Procedure

1. Preparation of Arenediazonium Tetrafluoroborates

In a 50 mL round-bottom flask, the aniline (10 mmol) was dissolved in a mixture of absolute ethanol (3 mL) and an aqueous solution of HBF_4 (50%, 2.5 mL, 20 mmol) and *tert*-butyl nitrite (2.7 mL, 20 mmol) was added dropwise to the solution at 0 °C. The reaction was stirred at room temperature for 1 h and diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate that was filtered off and washed with diethyl ether (3 × 10 mL). The arenediazonium tetrafluoroborate was dried in vacuo (10^{-3} mbar) for 10 minutes and was then directly used without further purification.

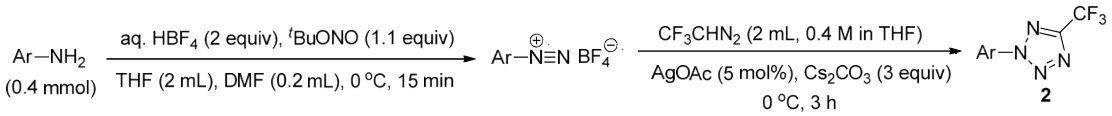
2. Synthesis of 2-Aryl-5-trifluoromethyltrazoles

Standard procedure for the synthesis of 2-aryl-5-trifluoromethyltrtrazoles from the corresponding arenediazonium salts (Method A)



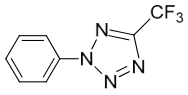
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with AgOAc (3.4 mg, 0.02 mmol, 5 mol%) and Cs_2CO_3 (130.4 mg, 0.8 mmol, 2 equiv). Then DMF (0.2 mL) and a stock solution of CF_3CHN_2 in THF (0.2 M, 4 mL, 2 equiv) were added. The resulting suspension was stirred at 0 °C for 5 minutes before the aryl diazonium salts **1** (0.4 mmol) was added in one portion. The resulting mixture was allowed to stir at 0 °C for 10 hours. Then the mixture was filtered through a Celite plug, rinsed with ethyl acetate. The resulting clear organic solution was concentrated under reduced pressure, and the residue was further purified by a silica gel column chromatography to yield the corresponding 2-aryl-5-trifluoromethyltetrazoles **2**.

Standard procedure for the synthesis of 2-aryl-5-trifluoromethyltrtrazoles from the corresponding aniline derivatives (Method B)

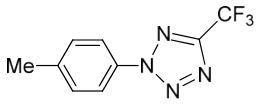


An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with anilines (0.4 mmol). Then dry THF (2 mL) and DMF (0.2 mL) were added. To the resulting solution which was precooled to 0 °C, aqueous HBF_4 (100 μL, 50% in water, 0.8 mmol, 2.0 equiv) was added. After 5 minutes, ^{t}BuONO (66 μL, 90% tech., 0.44 mmol, 1.1 equiv) was added subsequently. The mixture was allowed to stir at 0 °C for 15 minutes before a stock solution of CF_3CHN_2 in THF (0.4 M, 2 mL, 2.0 equiv) was added. After that, AgOAc (3.4 mg, 0.02 mmol, 5 mol%) and Cs_2CO_3 (391.2 mg, 1.2 mmol, 3.0 equiv) were added together. After addition was complete, the mixture was

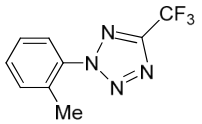
added to stir at 0 °C for additional 3 hours. Then the mixture was filtered through a Celite plug, rinsed with ethyl acetate. The resulting clear organic solution was concentrated under reduced pressure, and the residue was further purified by a silica gel column chromatography to yield the corresponding 2-aryl-5-trifluoromethyltetrazoles **2**.



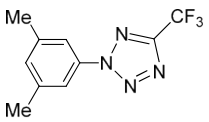
2-phenyl-5-(trifluoromethyl)-2*H*-tetrazole (**2a):** 70.2 mg, 82% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 – 8.12 (m, 2H), 7.65 – 7.53 (m, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.64 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.46 (q, $J_{C\text{-}F}$ = 40.69 Hz), 136.35, 131.10, 130.13, 120.38, 118.64 (q, $J_{C\text{-}F}$ = 268.73 Hz); **IR (KBr)** ν 2961, 1530, 1492, 1159, 759, 686 cm^{-1}; **HRMS** (ESI) found: *m*/*z* 215.0541, $[M+H]^+$ calcd. for $C_8H_6F_3N_4^+$ 215.0539.



2-(p-tolyl)-5-(trifluoromethyl)-2*H*-tetrazole (2b): 85.0 mg, 93% yield; pale yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 2.45 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.65 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.25 (q, $J_{C\text{-}F}$ = 40.63 Hz), 141.63, 134.09, 130.57, 120.18, 118.68 (q, $J_{C\text{-}F}$ = 268.66 Hz), 21.37; **IR (KBr)** ν 3051, 2962, 1530, 1508, 1165, 820 cm^{-1}; **HRMS** (APCI) found: *m*/*z* 229.0699, $[M+H]^+$ calcd. for $C_9H_8F_3N_4^+$ 229.0696.

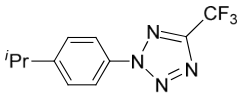


2-(o-tolyl)-5-(trifluoromethyl)-2*H*-tetrazole (2c): 73.9 mg, 81% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.42 (m, 2H), 2.38 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.51 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.23 (q, $J_{C\text{-}F}$ = 40.58 Hz), 135.82, 133.23, 132.33, 131.40, 127.32, 125.42, 118.71 (q, $J_{C\text{-}F}$ = 268.79 Hz), 18.77; **IR (KBr)** ν 3069, 2967, 1528, 1495, 1159, 761 cm^{-1}; **HRMS** (EI) found: *m*/*z* 229.0702, $[M+H]^+$ calcd. for $C_9H_8F_3N_4^+$ 229.0696.

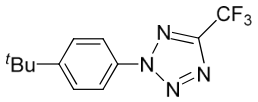


2-(3,5-dimethylphenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2d): 86.2 mg, 89% yield; yellow solid, m.p.: 50.5–51.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 2H), 7.16 (s, 1H), 2.42 (s, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.67 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.22 (q, $J_{C\text{-}F}$ = 40.57

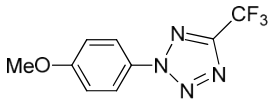
Hz), 140.24, 136.20, 132.64, 118.69 (q, $J_{C\text{-}F}$ = 268.64 Hz), 117.97, 21.37; **IR (KBr)** ν 2930, 1526, 1401, 1148, 853 cm^{-1}; **HRMS** (EI) found: *m*/*z* 242.0786, $[M]^+$ calcd. for $C_{10}H_9F_3N_4^+$ 242.0774.



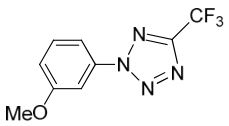
2-(4-isopropylphenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2e): 91.2 mg, 89% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 3.10 – 2.93 (m, 1H), 1.30 (d, *J* = 6.9 Hz, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.67 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.27 (q, $J_{C\text{-}F}$ = 40.60 Hz), 152.46, 134.26, 128.05, 120.35, 118.71 (q, $J_{C\text{-}F}$ = 268.63 Hz), 34.16, 23.83; **IR (KBr)** ν 2967, 2933, 1530, 1508, 1160, 838 cm^{-1}; **HRMS** (EI) found: *m*/*z* 256.0935, $[M]^+$ calcd. for $C_{11}H_{11}F_3N_4^+$ 256.0931.



2-(4-(*tert*-butyl)phenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2f): 96.2 mg, 89% yield; yellow solid, m.p.: 44–45 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 1.38 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.62 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.30 (q, $J_{C\text{-}F}$ = 40.58 Hz), 154.78, 133.96, 127.01, 120.05, 118.71 (q, $J_{C\text{-}F}$ = 268.65 Hz), 35.18, 31.27; **IR (KBr)** ν 2966, 1530, 1158, 837 cm^{-1}; **HRMS** (EI) found: *m*/*z* 270.1093, $[M]^+$ calcd. for $C_{12}H_{13}F_3N_4^+$ 270.1087.

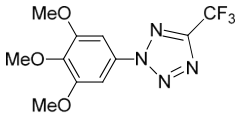


2-(4-methoxyphenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2g): 93.5 mg, 96% yield; yellow solid, m.p.: 49–50 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.88 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.66 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.57, 157.12 (q, $J_{C\text{-}F}$ = 40.54 Hz), 129.66, 121.89, 118.69 (q, $J_{C\text{-}F}$ = 268.60 Hz), 115.03, 55.82; **IR (KBr)** ν 3014, 2972, 2846, 1600, 1509, 1154, 836 cm^{-1}; **HRMS** (APCI) found: *m*/*z* 245.0643, $[M+H]^+$ calcd. for $C_9H_8F_3N_4O^+$ 245.0645.

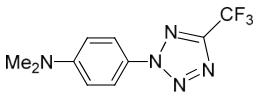


2-(3-methoxyphenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2h): 73.5 mg, 75% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.67 – 7.64 (m, 1H), 7.46 (t, *J* = 8.2 Hz, 1H), 7.07 (dd, *J* = 8.4, 1.7 Hz, 1H), 3.90 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.67 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.79, 157.32 (q, $J_{C\text{-}F}$ = 40.67 Hz), 137.18, 130.93, 118.62 (q,

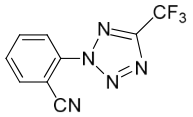
$J_{C\text{-}F}$ = 268.76 Hz), 117.14, 112.37, 105.72, 55.88; **IR (KBr)** ν 3100, 2968, 1614, 1496, 1160, 1031, 861, 778 cm^{-1}; **HRMS** (EI) found: *m*/*z* 244.0570, $[M]^+$ calcd. for $C_9H_7F_3N_4O^+$ 244.0567.



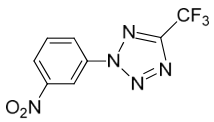
5-(trifluoromethyl)-2-(3,4,5-trimethoxyphenyl)-2*H*-tetrazole (2i): 104.2 mg, 86% yield; white solid, m.p.: 60.5 – 61.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 3.93 (s, 6H), 3.87 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.58 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.12 (q, $J_{C\text{-}F}$ = 40.70 Hz), 154.06, 140.06, 131.76, 118.52 (q, $J_{C\text{-}F}$ = 268.72 Hz), 97.82, 61.10, 56.55; **IR (KBr)** ν 3009, 2980, 2948, 1611, 1505, 1472, 1142, 835 cm^{-1}; **HRMS** (ESI) found: *m*/*z* 305.0854, $[M+H]^+$ calcd. for $C_{11}H_{12}F_3N_4O_3^+$ 305.0856.



***N*,*N*-dimethyl-4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)aniline (2j):** 88.5 mg, 86% yield; white solid, m.p.: 111 – 113 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.2 Hz, 2H), 6.74 (d, *J* = 9.2 Hz, 2H), 3.05 (s, 6H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.51 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.73 (q, $J_{C\text{-}F}$ = 40.29 Hz), 151.82, 125.70, 121.54, 118.86 (q, $J_{C\text{-}F}$ = 268.51 Hz), 111.89, 40.39; **IR (KBr)** ν 2923, 1607, 1517, 1154, 814 cm^{-1}; **HRMS** (EI) found: *m*/*z* 257.0887, $[M]^+$ calcd. for $C_{10}H_{10}F_3N_5^+$ 257.0883.

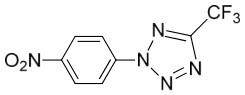


2-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)benzonitrile (2k): 86.0 mg, 90% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.92 (t, *J* = 7.9 Hz, 1H), 7.78 (t, *J* = 7.7 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.57 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.83 (q, $J_{C\text{-}F}$ = 41.28 Hz), 136.60, 135.49, 134.54, 131.70, 124.70, 118.28 (q, $J_{C\text{-}F}$ = 269.18 Hz), 114.83, 107.10; **IR (KBr)** ν 3086, 2262, 1634, 1534, 1496, 1234, 770 cm^{-1}; **HRMS** (EI) found: *m*/*z* 211.0354, $[M\text{-}N_2]^+$ calcd. for $C_9H_4F_3N_3^+$ 211.0352.

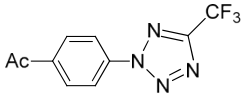


2-(3-nitrophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2l): 92.2 mg, 89% yield; white solid, m.p.: 44 –45 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.57 (dd, *J* = 8.1, 0.8 Hz, 1H), 8.48 – 8.42

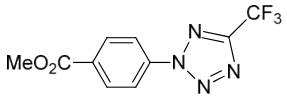
(m, 1H), 7.90 (t, J = 8.2 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.75 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.89 (q, $J_{C\text{-}F}$ = 41.18 Hz), 149.14, 136.78, 131.59, 125.79, 125.55, 118.29 (q, $J_{C\text{-}F}$ = 269.08 Hz), 115.73; **IR (KBr)** ν 3104, 1540, 1353, 1163, 740 cm^{-1}; **HRMS** (EI) found: *m*/*z* 231.0254, $[M\text{-}N_2]^+$ calcd. for $C_8H_4F_3N_3O_2^+$ 231.0251.



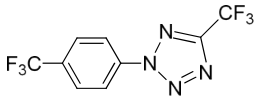
2-(4-nitrophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2m): 78.4 mg, 76% yield; white solid, m.p.: 53 – 55 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (dd, J = 29.6, 9.0 Hz, 4H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.75 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.07 (q, $J_{C\text{-}F}$ = 41.34 Hz), 148.96, 139.95, 125.83, 121.21, 118.03 (q, $J_{C\text{-}F}$ = 269.13 Hz); **IR (KBr)** ν 3080, 1540, 1349, 1232, 860 cm^{-1}; **HRMS** (EI) found: *m*/*z* 231.0250, $[M\text{-}N_2]^+$ calcd. for $C_8H_4F_3N_3O_2^+$ 231.0251.



1-(4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)phenyl)ethanone (2n): 66.5 mg, 65% yield; white solid, m.p.: 146 – 148 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.6 Hz, 2H), 8.17 (d, J = 8.6 Hz, 2H), 2.67 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.71 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.41, 157.69 (q, $J_{C\text{-}F}$ = 40.88 Hz), 138.93, 138.80, 130.25, 120.40, 118.42 (q, $J_{C\text{-}F}$ = 268.94 Hz), 26.85; **IR (KBr)** ν 3054, 2954, 1679, 1532, 1150, 845 cm^{-1}; **HRMS** (EI) found: *m*/*z* 256.0568, $[M]^+$ calcd. for $C_{10}H_7F_3N_4O^+$ 256.0567.

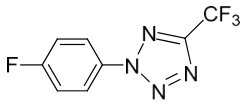


methyl 4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)benzoate (2o): 102.2 mg, 94% yield; white solid, m.p.: 52 – 54 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 – 8.14 (m, 4H), 3.94 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.79 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.51, 157.65 (q, $J_{C\text{-}F}$ = 40.93 Hz), 138.97, 132.49, 131.52, 120.12, 118.43 (q, $J_{C\text{-}F}$ = 268.87 Hz), 52.72; **IR (KBr)** ν 3084, 2959, 1721, 1504, 1157, 865 cm^{-1}; **HRMS** (EI) found: *m*/*z* 272.0518, $[M]^+$ calcd. for $C_{10}H_7F_3N_4O_2^+$ 272.0516.

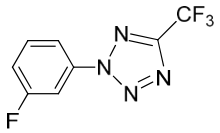


5-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-2*H*-tetrazole (2p): 80.0 mg, 71% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.5 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.03 (s), -63.76 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.90 (q, $J_{C\text{-}F}$ = 41.04 Hz), 138.54, 133.14 (q, $J_{C\text{-}F}$ = 33.22 Hz), 127.56 (q, $J_{C\text{-}F}$ = 3.71 Hz), 123.43 (q, $J_{C\text{-}F}$ = 270.91 Hz), 118.46 (q, $J_{C\text{-}F}$ = 269.05 Hz), 120.75; **IR (KBr)** ν 2963, 1617, 1513, 1326, 1172, 1063,

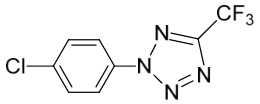
848 cm^{-1}; **HRMS** (EI) found: *m*/*z* 282.0337, $[M]^+$ calcd. for $C_9H_4F_6N_4^+$ 282.0335.



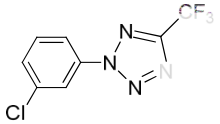
2-(4-fluorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2q): 77.3 mg, 84% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 – 8.07 (m, 2H), 7.35 – 7.26 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.69 (s), –108.30 ~ – 108.60 (m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.91 (d, $J_{C\text{-}F}$ = 251.03 Hz), 157.55 (q, $J_{C\text{-}F}$ = 40.86 Hz), 132.58, 122.54 (d, $J_{C\text{-}F}$ = 8.88 Hz), 118.56 (q, $J_{C\text{-}F}$ = 268.70 Hz), 117.28 (d, $J_{C\text{-}F}$ = 23.49 Hz); **IR (KBr)** ν 3089, 1506, 1157, 840 cm^{-1}; **HRMS** (EI) found: *m*/*z* 232.0375, $[M]^+$ calcd. for $C_8H_4F_4N_4^+$ 232.0367.



2-(3-fluorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2r): 80.0 mg, 86% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.91 (dt, *J* = 8.8, 2.1 Hz, 1H), 7.61 (td, *J* = 8.3, 5.9 Hz, 1H), 7.36 – 7.26 (m, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.77 (s), –108.52 ~ – 108.89 (m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.15 (d, $J_{C\text{-}F}$ = 248.58 Hz), 157.61 (q, $J_{C\text{-}F}$ = 40.94 Hz), 137.21 (d, $J_{C\text{-}F}$ = 10.21 Hz), 131.77 (d, $J_{C\text{-}F}$ = 8.69 Hz), 118.50 (q, $J_{C\text{-}F}$ = 268.85 Hz), 118.19 (d, $J_{C\text{-}F}$ = 21.06 Hz),115.99 (d, $J_{C\text{-}F}$ = 3.49 Hz), 108.33 (d, $J_{C\text{-}F}$ = 27.22 Hz); **IR (KBr)** ν 3090, 1609, 1493, 1162, 880, 786 cm^{-1}; **HRMS** (EI) found: *m*/*z* 232.0770, $[M]^+$ calcd. for $C_8H_4F_4N_4^+$ 232.0767.

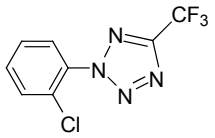


2-(4-chlorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2s): 86.5 mg, 87% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.72 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.56 (q, $J_{C\text{-}F}$ = 40.93 Hz), 137.21, 134.72, 130.36, 121.58, 118.50 (q, $J_{C\text{-}F}$ = 268.86 Hz); **IR (KBr)** ν 2922, 1530, 1492, 1162, 833 cm^{-1}; **HRMS** (EI) found: *m*/*z* 248.0070, $[M]^+$ calcd. for $C_8H_4ClF_3N_4^+$ 248.0072.

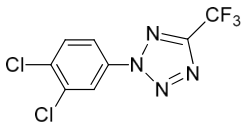


2-(3-chlorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2t): 86.5 mg, 87% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.11 – 8.05 (m, 1H), 7.55 (d, *J* = 4.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.68 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.63 (q, $J_{C\text{-}F}$ = 40.89 Hz), 136.96, 136.15, 131.27, 131.24, 120.67, 118.47 (q, $J_{C\text{-}F}$ = 268.86 Hz), 118.44; **IR (KBr)** ν

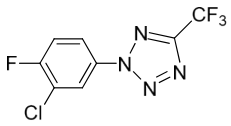
3100, 1596, 1480, 1168, 877, 791 cm^{-1}; **HRMS** (EI) found: *m*/*z* 248.0079, $[M]^+$ calcd. for $C_8H_4ClF_3N_4^+$ 248.0072.



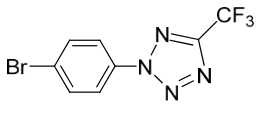
2-(2-chlorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2u): 81.0 mg, 81% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.56 (m, 3H), 7.53 – 7.48 (m, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.51 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.49 (q, $J_{C\text{-}F}$ = 40.84 Hz), 134.26, 132.87, 131.50, 130.02, 128.08, 127.80,118.56 (q, $J_{C\text{-}F}$ = 268.88 Hz); **IR (KBr)** ν 3076, 1531, 1485, 1161, 760 cm^{-1}; **HRMS** (EI) found: *m*/*z* 220.0016, $[M\text{-}N_2]^+$ calcd. for $C_8H_4ClF_3N_2^+$ 220.0011.



2-(3,4-dichlorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2v): 105.5 mg, 93% yield; colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 2.3 Hz, 1H), 8.05 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.70 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.74 (q, $J_{C\text{-}F}$ = 41.05 Hz), 135.70, 135.03, 134.67, 131.95, 122.21, 119.35,118.38 (q, $J_{C\text{-}F}$ = 269.02 Hz); **IR (KBr)** ν 3101, 1530, 1475, 1173, 880, 819 cm^{-1}; **HRMS** (EI) found: *m*/*z* 281.9686, $[M]^+$ calcd. for $C_8H_3Cl_2F_3N_4^+$ 281.9682.

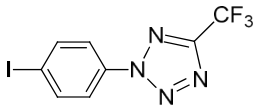


2-(3-chloro-4-fluorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2w): 99.0 mg, 93% yield; colorless liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 6.2, 2.6 Hz, 1H), 8.15 – 8.05 (m, 1H), 7.40 (t, *J* = 8.6 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.71 (s), –110.28 ~ –110.39 (m); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.53 (d, $J_{C\text{-}F}$ = 253.45 Hz), 157.72 (q, $J_{C\text{-}F}$ = 41.01 Hz), 132.66 (d, $J_{C\text{-}F}$ = 3.72 Hz), 123.35 (d, $J_{C\text{-}F}$ = 19.43 Hz), 123.04, 120.34 (d, $J_{C\text{-}F}$ = 7.93 Hz), 118.42 (q, $J_{C\text{-}F}$ = 268.89 Hz), 118.20 (q, $J_{C\text{-}F}$ = 23.08 Hz); **IR (KBr)** ν 3088, 1499, 1162, 881, 824 cm^{-1}; **HRMS** (EI) found: *m*/*z* 265.9977, $[M]^+$ calcd. for $C_8H_3ClF_4N_4^+$ 265.9977.

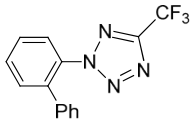


2-(4-bromophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2x): 110.0 mg, 95% yield; yellow solid,

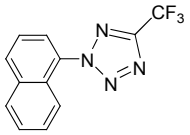
m.p.: 36 – 37 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.69 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.58 (q, $J_{C\text{-}F}$ = 40.87 Hz), 135.20, 133.35, 125.25, 121.76, 118.49 (q, $J_{C\text{-}F}$ = 268.90 Hz); **IR (KBr)** ν 3005, 1530, 1489, 1161, 830 cm^{-1}; **HRMS** (EI) found: *m*/*z* 291.9569, $[M]^+$ calcd. for $C_8H_4BrF_3N_4^+$ 291.9566.



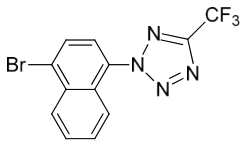
2-(4-iodophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2y): 107.5 mg, 79% yield; red solid, m.p.: 34 – 35 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.86 (m, 4H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.62 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.56 (q, $J_{C\text{-}F}$ = 40.85 Hz), 139.30, 135.88, 121.77, 118.47 (q, $J_{C\text{-}F}$ = 268.89 Hz); **IR (KBr)** ν 3096, 1529, 1485, 1160, 825 cm^{-1}; **HRMS** (EI) found: *m*/*z* 339.9435, $[M]^+$ calcd. for $C_8H_4IF_3N_4^+$ 339.9428.



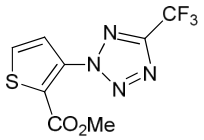
2-([1,1'-biphenyl]-2-yl)-5-(trifluoromethyl)-2*H*-tetrazole (2z): 94.4 mg, 81% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.56 (m, 4H), 7.33 – 7.26 (m, 3H), 7.11 – 6.98 (m, 2H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.60 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.10 (q, $J_{C\text{-}F}$ = 40.62 Hz), 138.76, 136.78, 134.52, 131.88, 131.70, 128.72, 128.64, 128.34, 128.28, 126.42, 118.51 (q, $J_{C\text{-}F}$ = 268.77 Hz); **IR (KBr)** ν 3034, 2965, 1529, 1482, 1160, 763, 701 cm^{-1}; **HRMS** (ESI) found: *m*/*z* 291.0855, $[M+H]^+$ calcd. for $C_{14}H_{10}F_3N_4^+$ 291.0852.



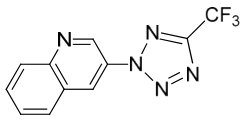
2-(naphthalen-1-yl)-5-(trifluoromethyl)-2*H*-tetrazole (2a′): 91.7 mg, 87% yield; white solid, m.p.: 44 – 45 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 8.01 – 7.97 (m, 1H), 7.96 – 7.91 (m, 1H), 7.87 (d, *J* = 7.4 Hz, 1H), 7.72 – 7.57 (m, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.34 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.52 (q, $J_{C\text{-}F}$ = 40.68 Hz), 134.39, 132.76, 132.34, 128.83, 128.71, 127.62, 126.79, 124.92, 123.91, 122.22, 118.75 (q, $J_{C\text{-}F}$ = 268.86 Hz); **IR (KBr)** ν 2923, 1532, 1399, 1152, 764 cm^{-1}; **HRMS** (EI) found: *m*/*z* 264.0618, $[M]^+$ calcd. for $C_{12}H_7F_3N_4^+$ 264.0618.



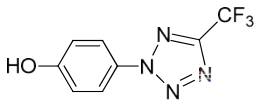
2-(4-bromonaphthalen-1-yl)-5-(trifluoromethyl)-2*H*-tetrazole (2b′): 121.6 mg, 89% yield; white solid, m.p.: 34 – 35 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.4 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.80 – 7.58 (m, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.33 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.63 (q, $J_{C\text{-}F}$ = 40.84 Hz), 132.71, 132.37, 129.54, 129.05, 129.00, 128.17, 127.67, 127.42, 124.01, 122.73, 118.62 (q, $J_{C\text{-}F}$ = 269.00 Hz); **IR (KBr)** ν 2923, 1520, 1390, 1157, 756 cm^{-1}; **HRMS** (EI) found: *m*/*z* 313.9668, $[M\text{-}N_2]^+$ calcd. for $C_{12}H_6BrF_3N_2^+$ 313.9662.



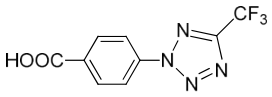
methyl 3-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)thiophene-2-carboxylate (2c′): 90.0 mg, 81% yield; yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 5.3 Hz, 1H), 7.37 (d, *J* = 5.3 Hz, 1H), 3.78 (s, 3H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.53 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.62, 157.15 (q, $J_{C\text{-}F}$ = 40.89 Hz), 135.30, 131.39, 128.98, 126.15, 118.51 (q, $J_{C\text{-}F}$ = 268.79 Hz); **IR (KBr)** ν 3117, 2059, 1727, 1524, 1444, 1267, 1164, 896, 774 cm^{-1}; **HRMS** (ESI) found: *m*/*z* 279.0163, $[M+H]^+$ calcd. for $C_8H_6F_3N_4O_2S^+$ 279.0158.



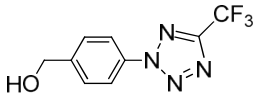
3-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)quinolone (2d′): 84.5 mg, 80% yield; white solid, m.p.: 98–99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.87 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.56 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.86 (q, $J_{C\text{-}F}$ = 41.03 Hz), 148.77, 141.84, 131.82, 129.97, 129.66, 128.91, 128.75, 126.88, 118.47 (q, $J_{C\text{-}F}$ = 269.03 Hz); **IR (KBr)** ν 3067, 1534, 1156, 757 cm^{-1}; **HRMS** (EI) found: *m*/*z* 265.0570, $[M]^+$ calcd. for $C_{11}H_6F_3N_5^+$ 265.0570.



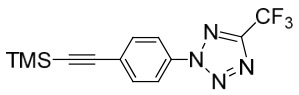
4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)phenol (2e′): 70.0 mg, 76% yield (Method B); white solid, m.p.: 150 – 151 °C; **^{1}H NMR** (400 MHz, DMSO) δ 10.39 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H); **^{19}F NMR** (376 MHz, DMSO) δ –63.05 (s); **^{13}C NMR** (100 MHz, DMSO) δ 160.08, 155.69 (q, $J_{C\text{-}F}$ = 39.79 Hz), 127.73, 122.38, 118.59 (q, $J_{C\text{-}F}$ = 268.07 Hz), 116.44; **IR (KBr)** ν 3300, 3084, 1597, 1510, 1460, 1157, 841 cm^{-1}; **HRMS** (EI) found: *m*/*z* 230.0414, $[M]^+$ calcd. for $C_8H_5F_3N_4O^+$ 230.0410.



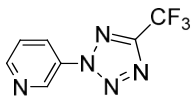
4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)benzoic acid (2f′): 83.6 mg, 81% yield (Method B); white solid, m.p.: 190 – 192 ^{o}C; **^{1}H NMR** (400 MHz, DMSO) δ 8.21 (m, 4H); **^{19}F NMR** (376 MHz, DMSO) δ –62.97 (s); **^{13}C NMR** (100 MHz, DMSO) δ 166.30, 156.12 (q, $J_{C\text{-}F}$ = 40.11 Hz), 138.18, 133.72, 131.29, 120.61, 118.42 (q, $J_{C\text{-}F}$ = 268.32 Hz); **IR (KBr)** ν 3447, 2925, 1674, 1606, 1400, 867 cm^{-1}; **HRMS** (EI) found: *m*/*z* 258.0363, $[M]^+$ calcd. for $C_9H_5F_3N_4O_2^+$ 258.0360.



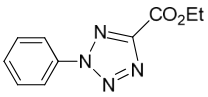
(4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)phenyl)methanol (2g′): 58.6 mg, 60% yield (Method B); yellow liquid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 4.79 (s, 2H), 2.74 (s, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.64 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.31 (q, $J_{C\text{-}F}$ = 40.75 Hz), 144.32, 135.32, 128.11, 120.39, 118.54 (q, $J_{C\text{-}F}$ = 268.77 Hz), 64.12; **IR (KBr)** ν 3292, 2934, 2881, 1531, 1159, 819 cm^{-1}; **HRMS** (EI) found: *m*/*z* 244.0565, $[M]^+$ calcd. for $C_9H_7F_3N_4O^+$ 244.0567.



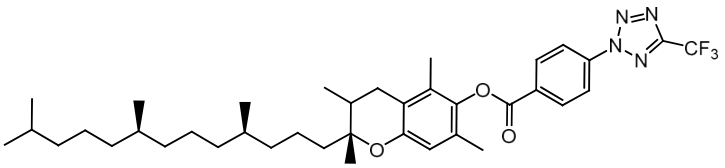
5-(trifluoromethyl)-2-(4-((trimethylsilyl)ethynyl)phenyl)-2*H*-tetrazole (2h′): 81.0 mg, 65% yield (Method B); white solid, m.p.: 73 – 75 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.7 Hz, 2H), 0.28 (s, 9H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.65 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.55 (q, $J_{C\text{-}F}$ = 40.84 Hz), 135.56, 133.63, 126.39, 120.15, 118.57 (q, $J_{C\text{-}F}$ = 268.78 Hz), 103.12, 98.35, -0.06; **IR (KBr)** ν 2922, 2174, 1592, 1502, 1163, 843 cm^{-1}; **HRMS** (EI) found: *m*/*z* 310.0860, $[M]^+$ calcd. for $C_{13}H_{13}F_3N_4Si^+$ 310.0857.



3-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)pyridine (2i′): 58.5 mg, 68% yield (Method B); yellow liquid (Method B); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 8.83 (d, *J* = 4.3 Hz, 1H), 8.46 (d, *J* = 8.2 Hz, 1H), 7.59 (dd, *J* = 8.1, 4.8 Hz, 1H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.66 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.91 (q, $J_{C\text{-}F}$ = 41.05 Hz), 152.11, 141.69, 133.04, 127.79, 124.48, 118.39 (q, $J_{C\text{-}F}$ = 268.99 Hz); **IR (KBr)** ν 3073, 1531, 1483, 1444, 1161, 808, 693 cm^{-1}; **HRMS** (EI) found: *m*/*z* 216.0498, $[M+H]^+$ calcd. for $C_7H_5F_3N_5^+$ 216.0492.



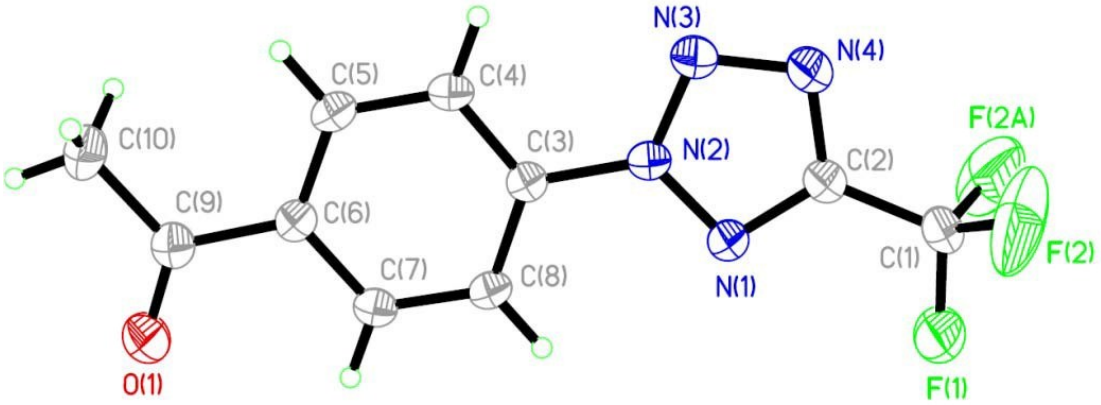
ethyl 2-phenyl-2H-tetrazole-5-carboxylate (2j′): 61.0 mg, 70% yield; yellow solid, m.p.: 69 – 70 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.2 Hz, 2H), 7.57 – 7.46 (m, 3H), 4.53 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.83, 136.39, 130.69, 129.89, 120.32, 62.85, 14.25; **IR (KBr)** ν 2993, 2944, 2911, 1740, 1500, 1218, 764, 677 cm^{-1}; **HRMS** (EI) found: *m*/*z* 218.0802, $[M]^+$ calcd. for $C_{10}H_{10}N_4O_2^+$ 218.0799.



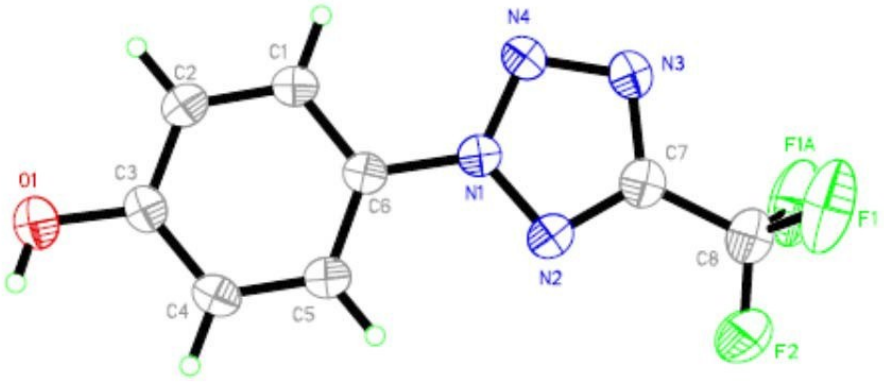
DL-*α*-Tocopherol 4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)benzoate (2k′): 233.4 mg, 87% yield (Method B); colourless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.1 Hz, 2H), 8.36 (d, *J* = 8.2 Hz, 2H), 2.64 (m, 2H), 2.14 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 1.90 – 1.72 (m, 2H), 1.63 – 1.08 (m, 24H), 0.96 – 0.80 (m, 12H); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.54 (s); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.81, 157.86 (q, $J_{C\text{-}F}$ = 40.86 Hz), 149.93, 140.59, 139.41, 132.18, 132.08, 126.83, 125.11, 123.54, 120.46, 118.50 (q, $J_{C\text{-}F}$ = 269.08 Hz), 117.83, 75.39, 39.56, 37.75 – 37.48 (m), 32.97, 32.90, 28.17, 25.00, 24.64, 22.90, 22.81, 21.23, 20.83, 19.94 – 19.79 (m), 13.28, 12.43, 12.07; **IR (KBr)** ν 2925, 2864, 1738, 1229, 1167, 1095, 859, 762 cm^{-1}; **HRMS** (EI) found: *m*/*z* 670.4063, $[M]^+$ calcd. for $C_{38}H_{53}F_3N_4O_3^+$ 670.4065.

X-Ray Crystallographic datas

The X-ray crystallographic structures for **2n**. ORTEP representation with 50% probability thermal ellipsoids. Solvent is omitted for clarity. Crystal data have been deposited to CCDC, number 1412525.

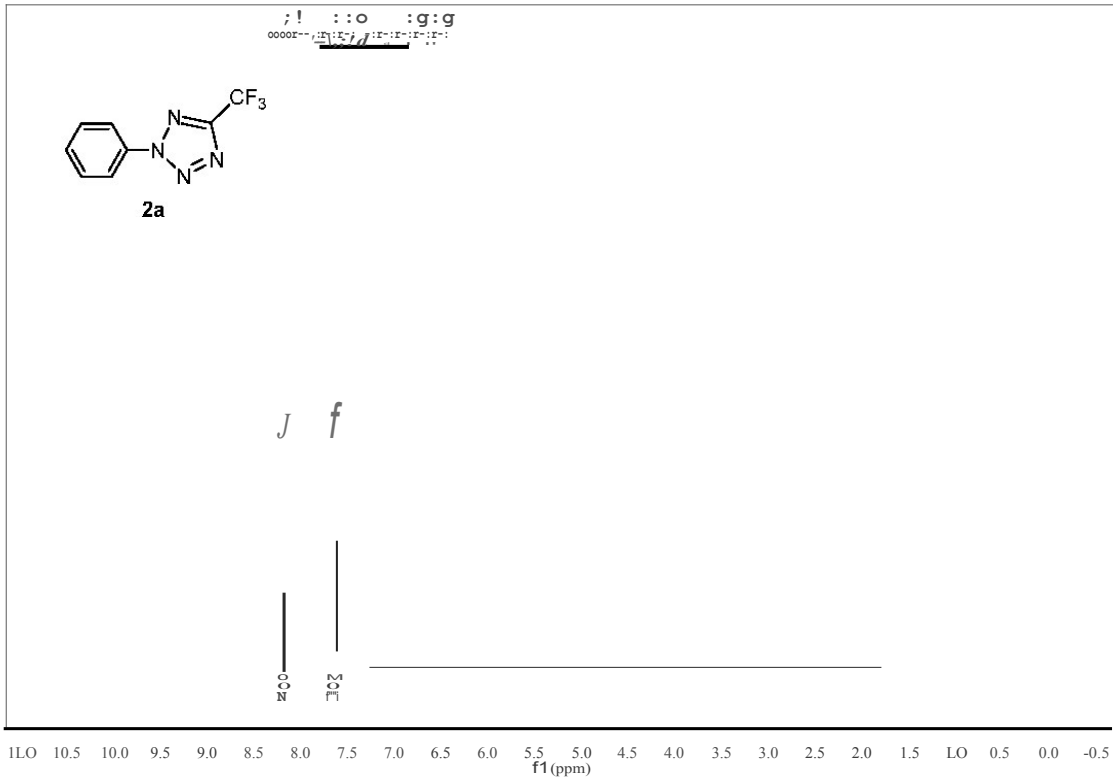


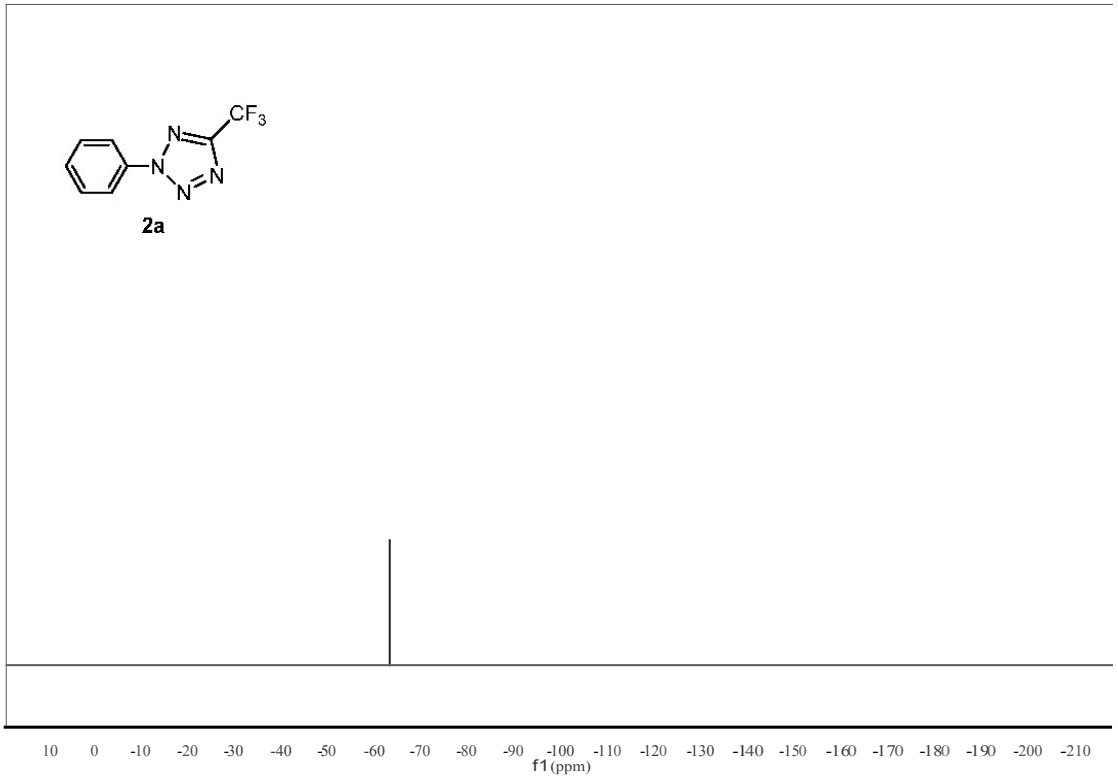
The X-ray crystallographic structures for **2e'**. ORTEP representation with 50% probability thermal ellipsoids. Solvent is omitted for clarity. Crystal data have been deposited to CCDC, number 1412621.

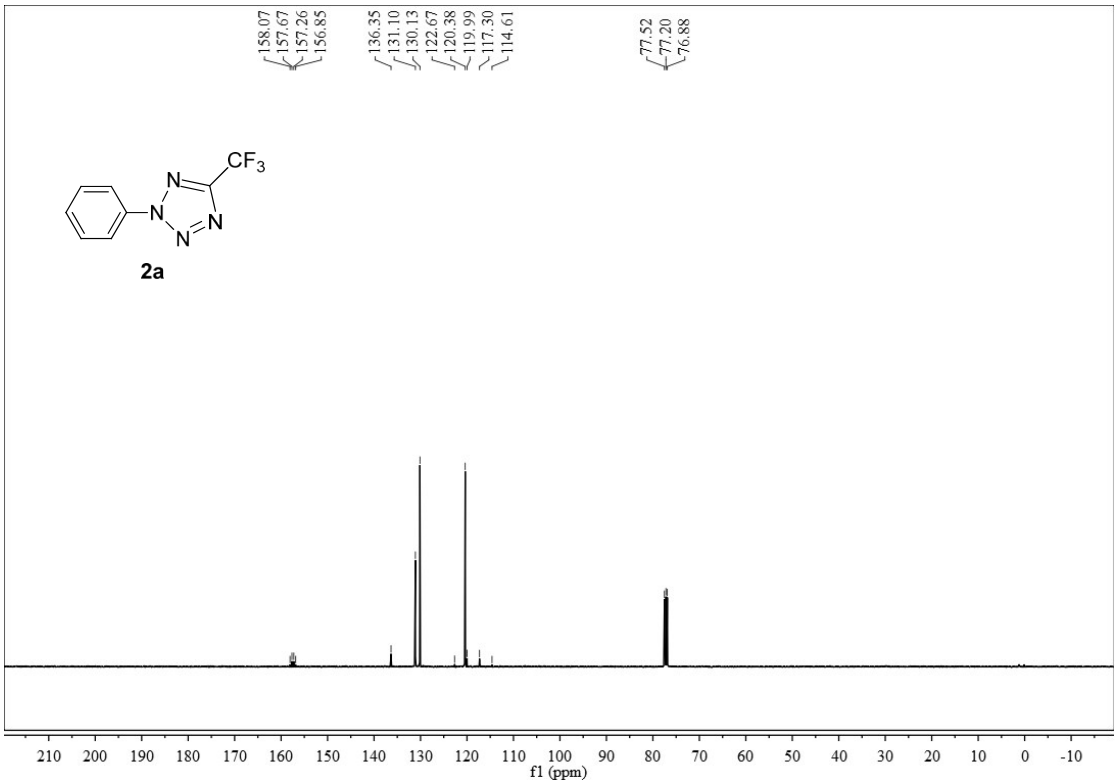


NMR Spectra of 2-Aryl-5-Substituted Tetrazoles

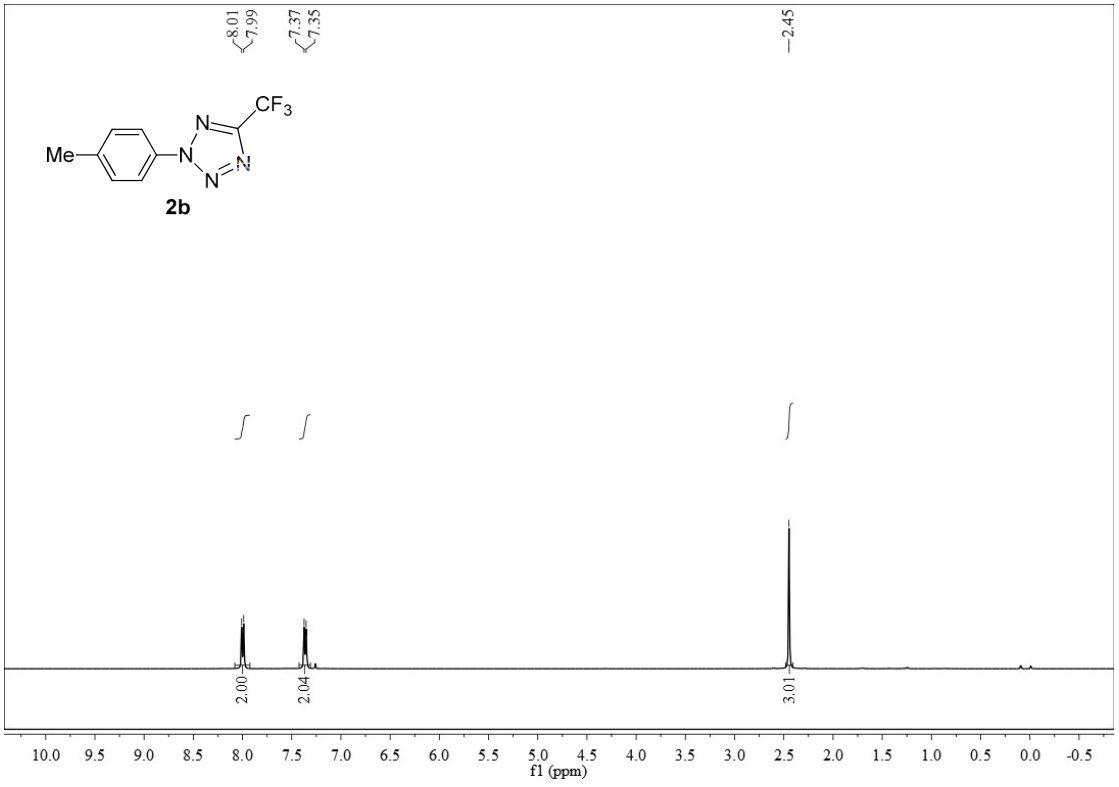
2-phenyl-5-(trifluoromethyl)-2H-tetrazole (2a)

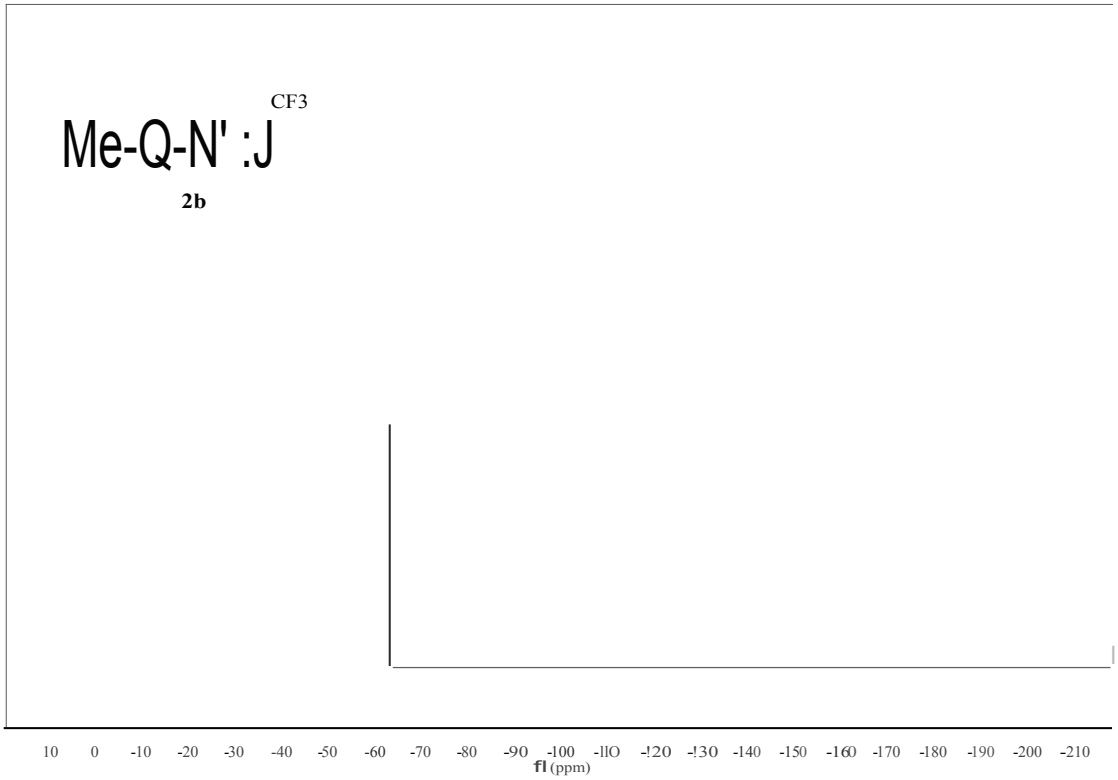


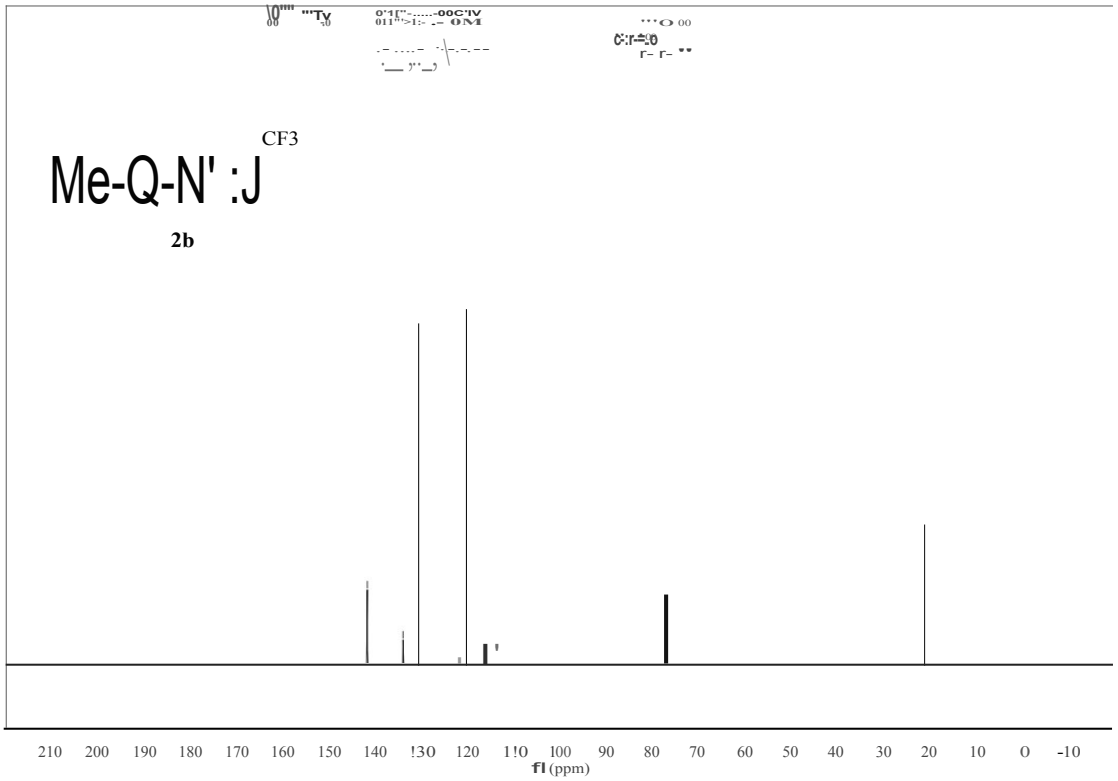




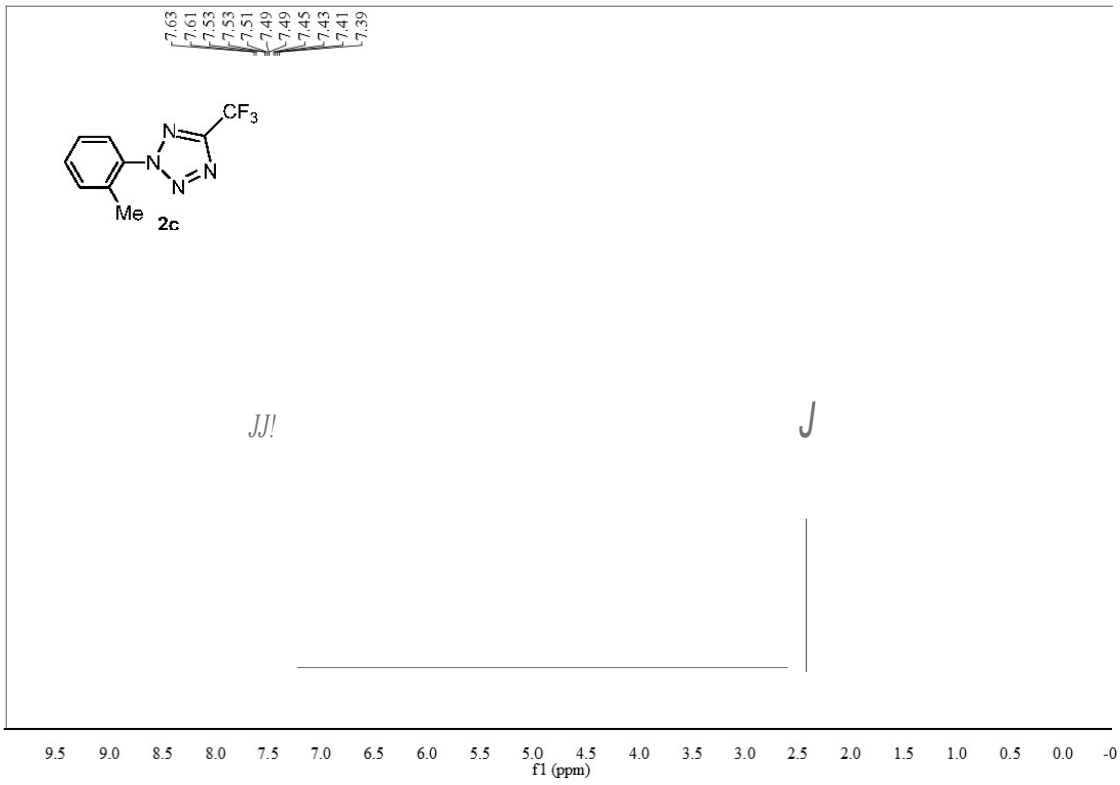
2-(p-tolyl)-5-(trifluoromethyl)-2*H*-tetrazole (2b)

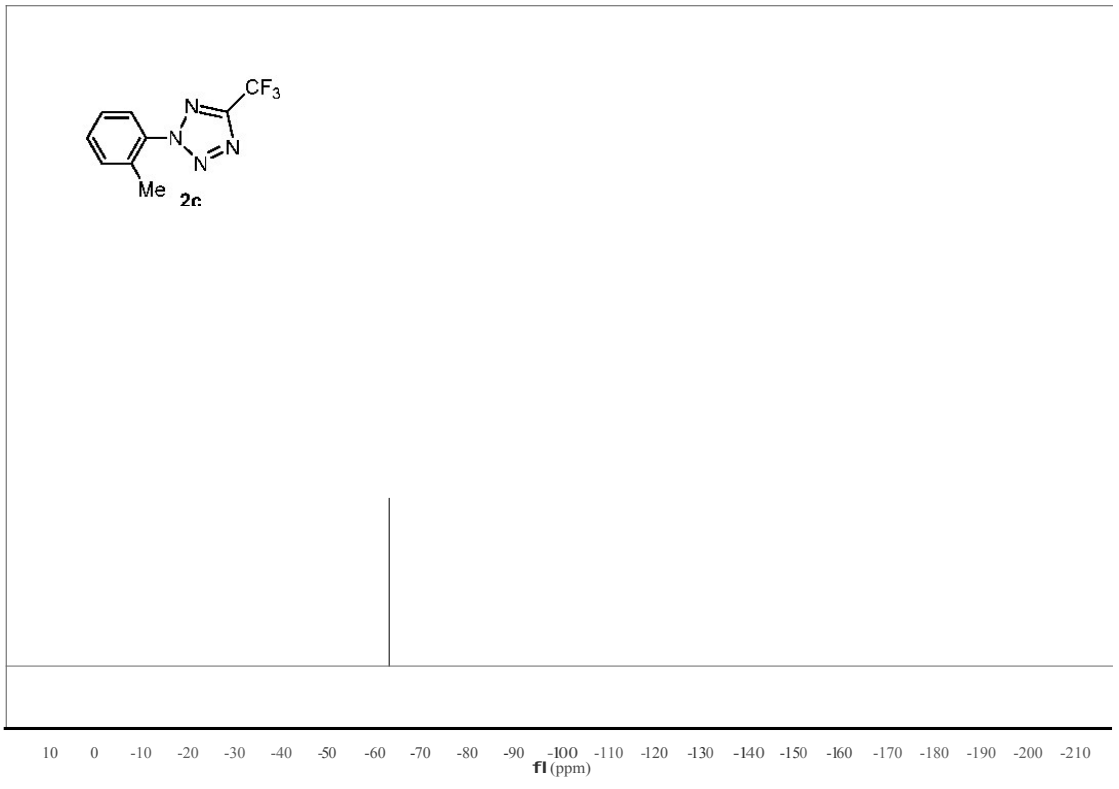


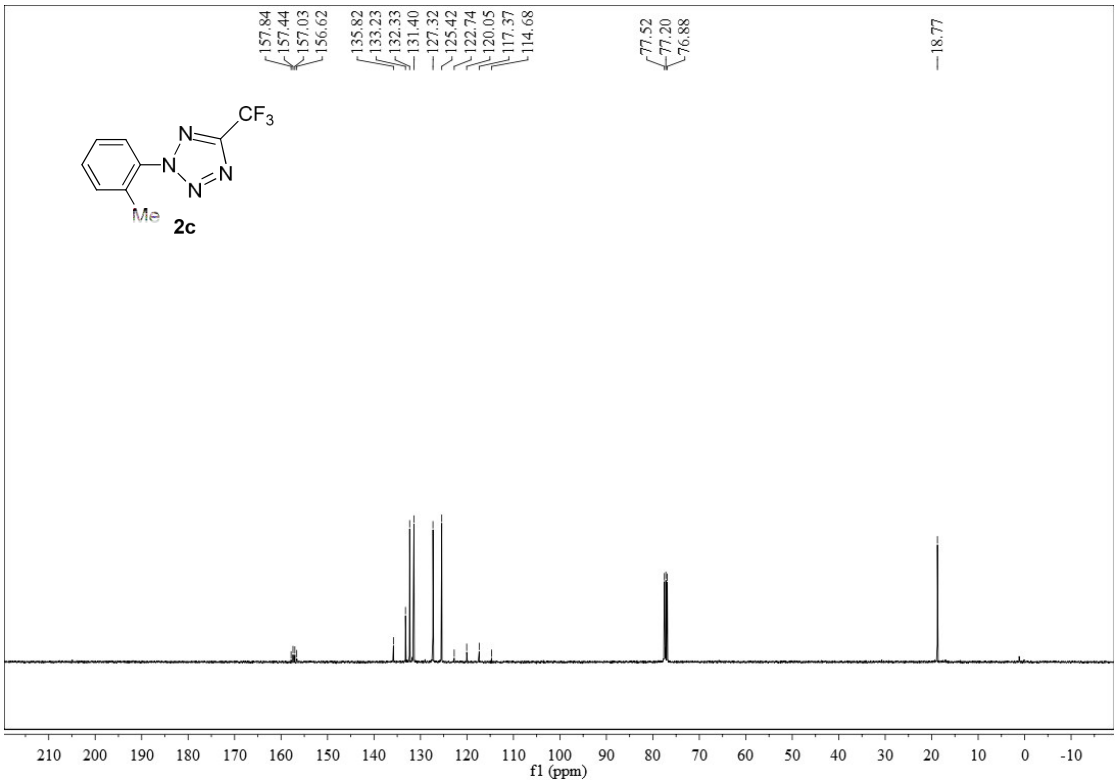

CF3
Me-Q-N' :J
2b
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


CF3
Me-Q-N' :J
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

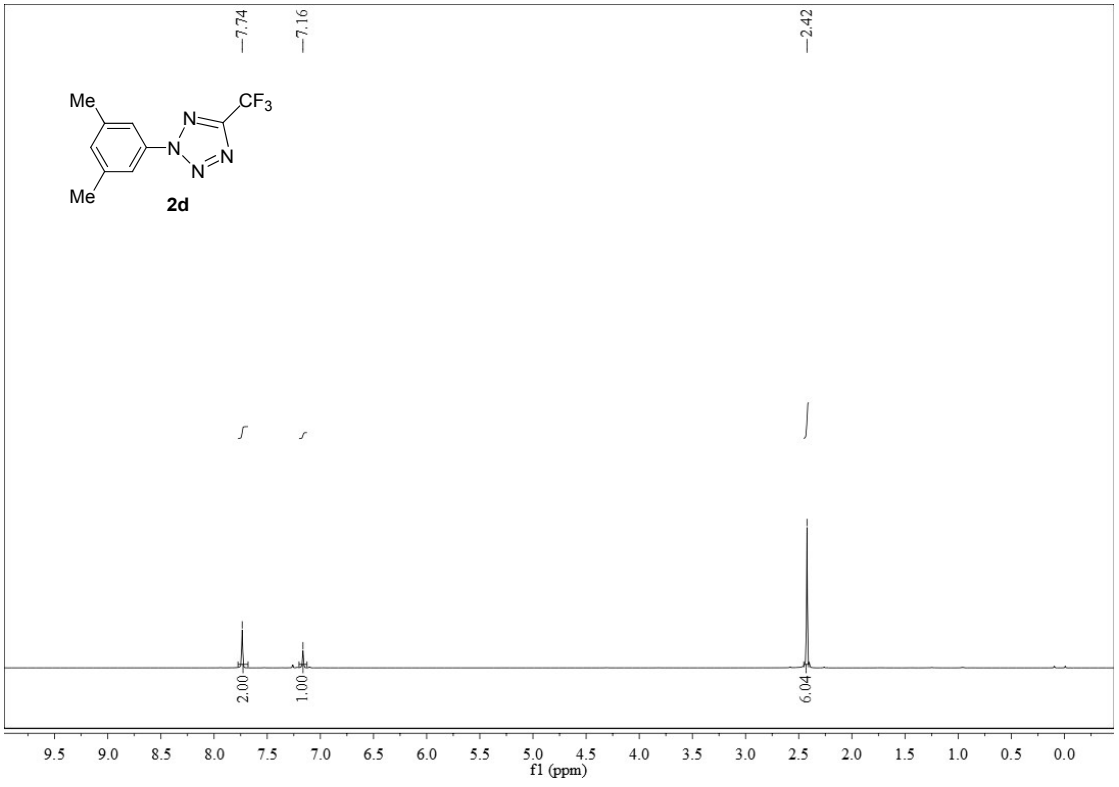
2-(**o-tolyl)-5-(trifluoromethyi)-2H-tetrazole** (2c)

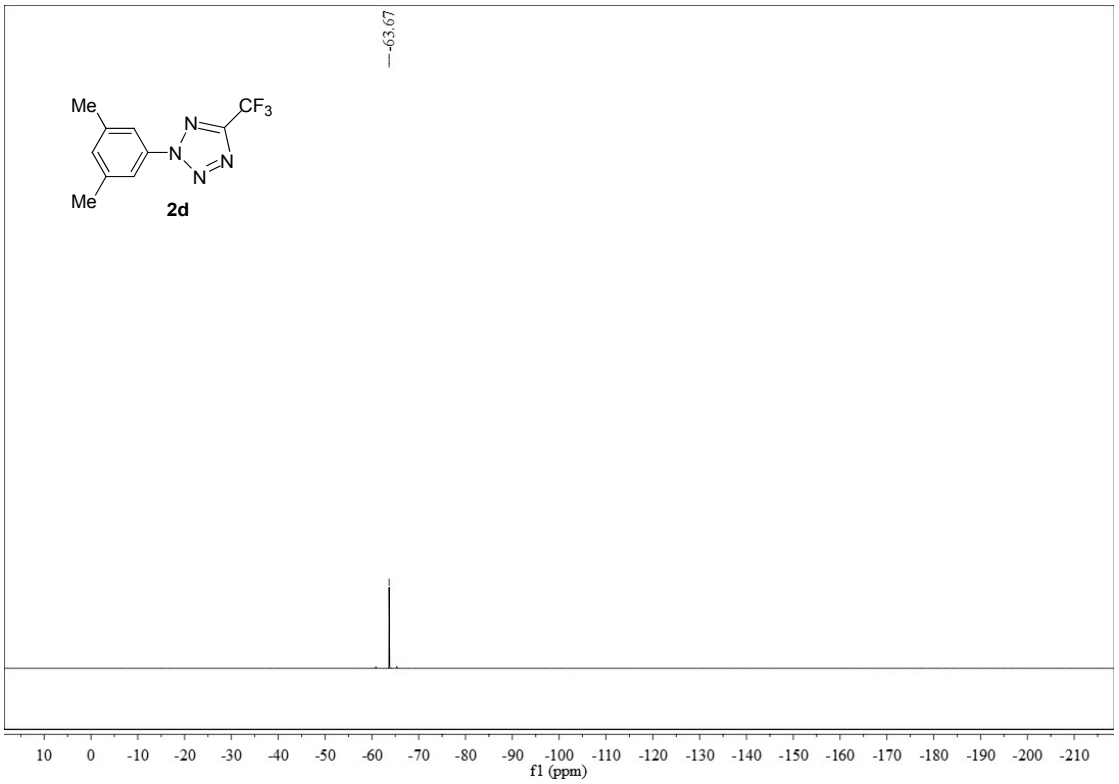


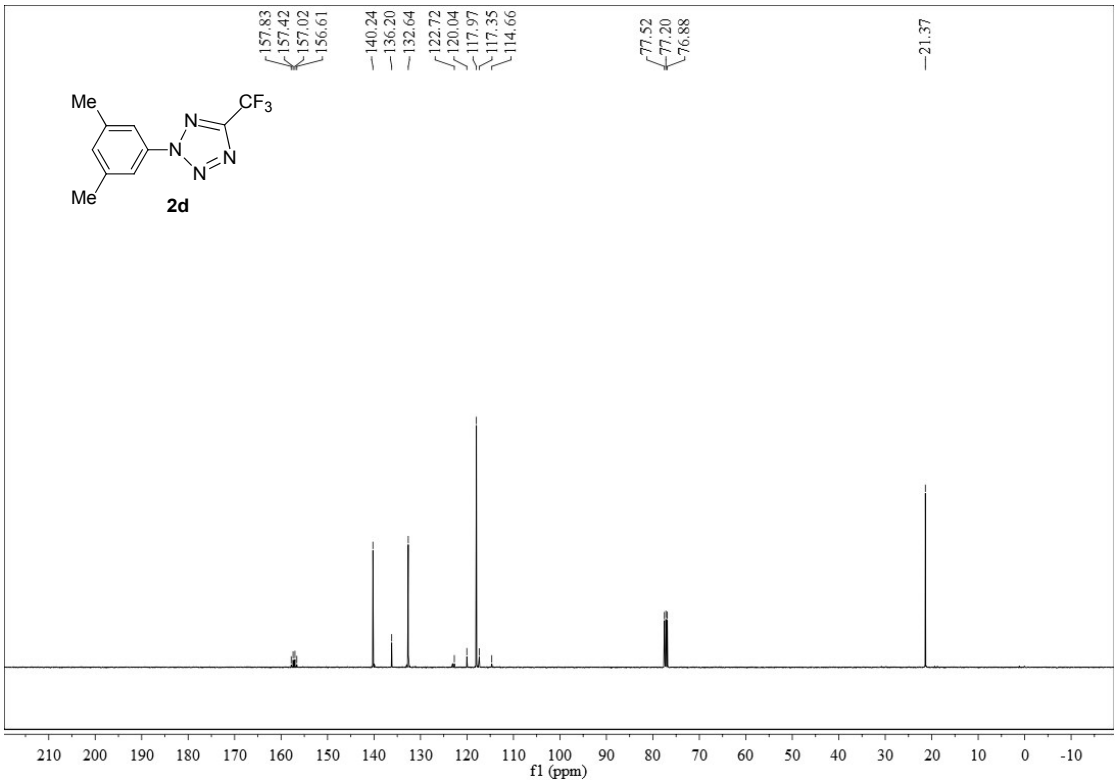




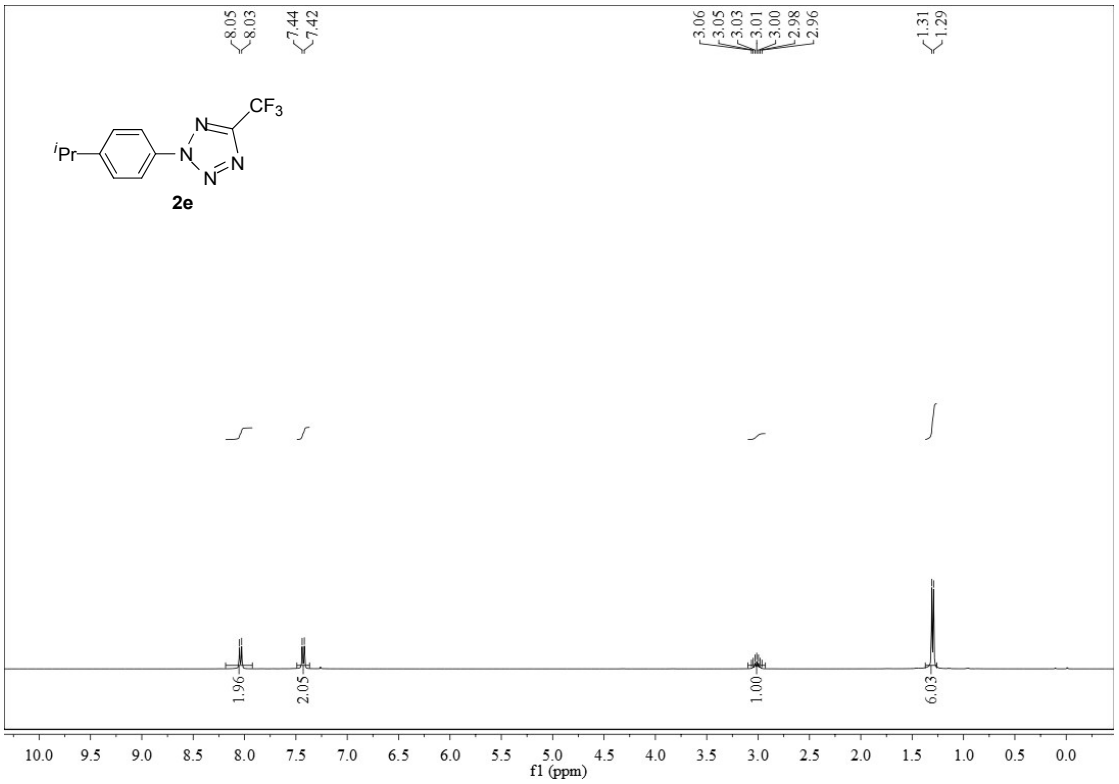
2-(3,5-dimethylphenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2d)

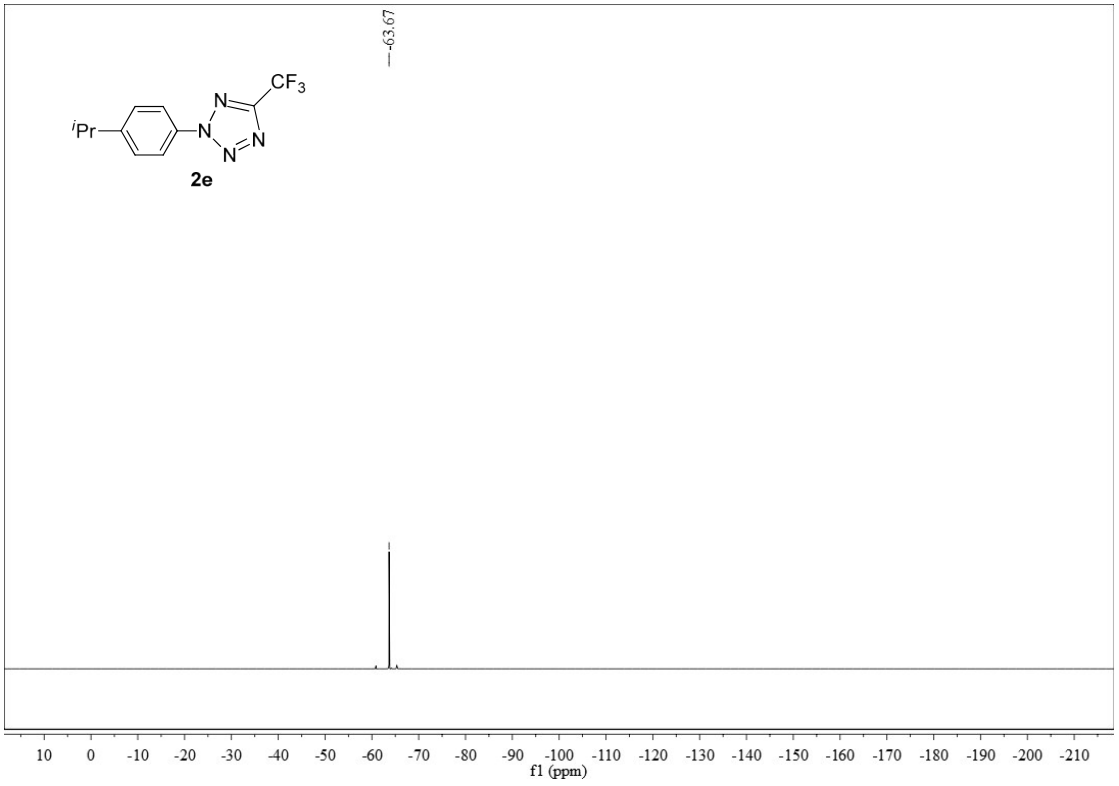


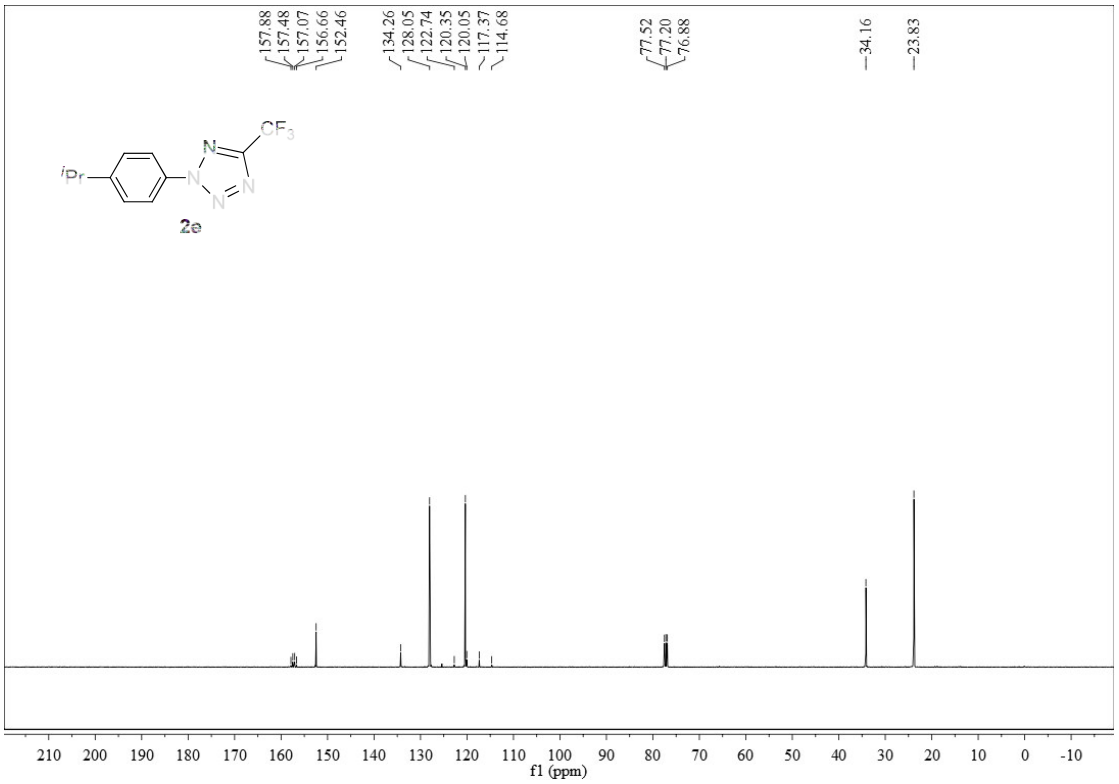

-63.67
Me
Me
CF3
N
N
N
N
2d
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


157.83
157.42
157.02
156.61
140.24
136.20
132.64
122.72
120.04
117.97
117.35
114.66
77.52
77.20
76.88
21.37
Me
Me
CF3
N
N
N
N
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

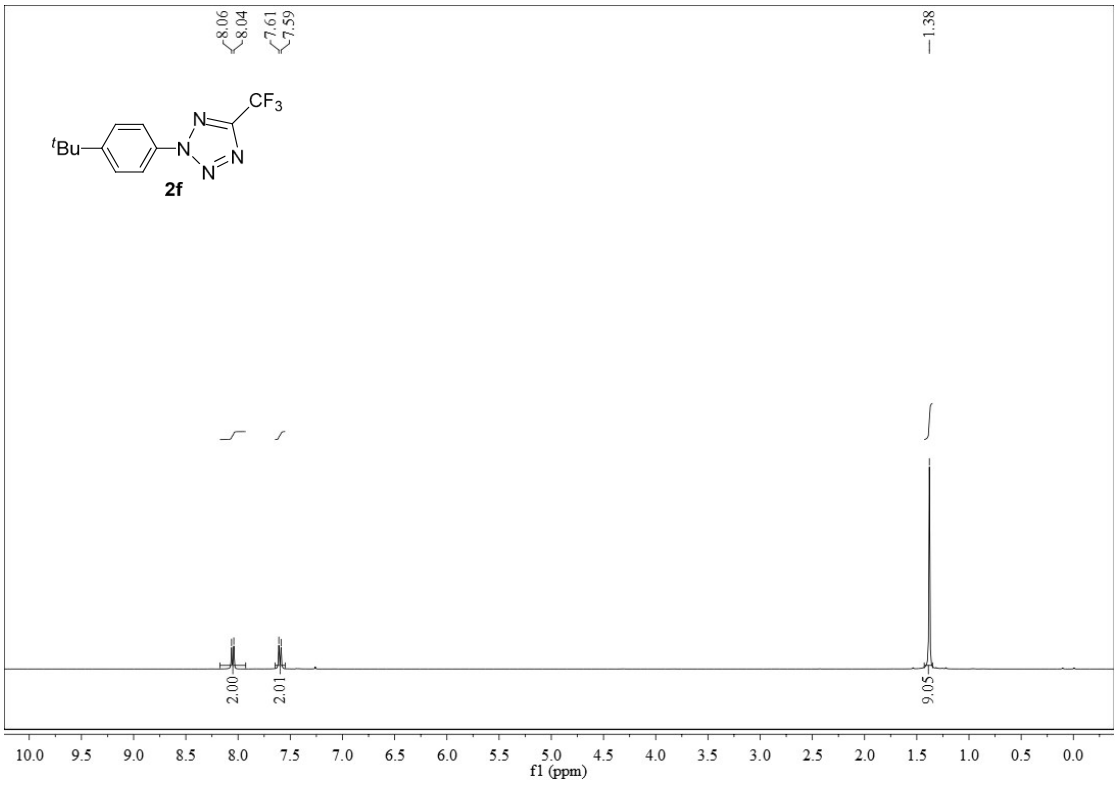
2-(4-isopropylphenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2e)

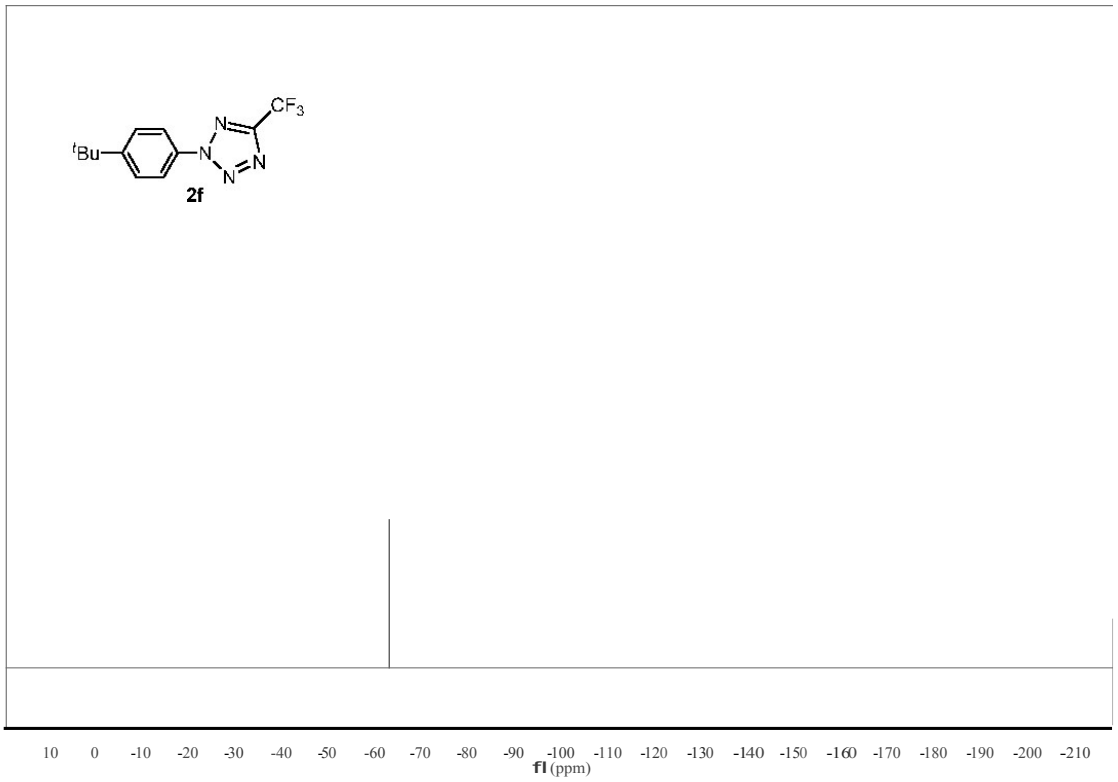


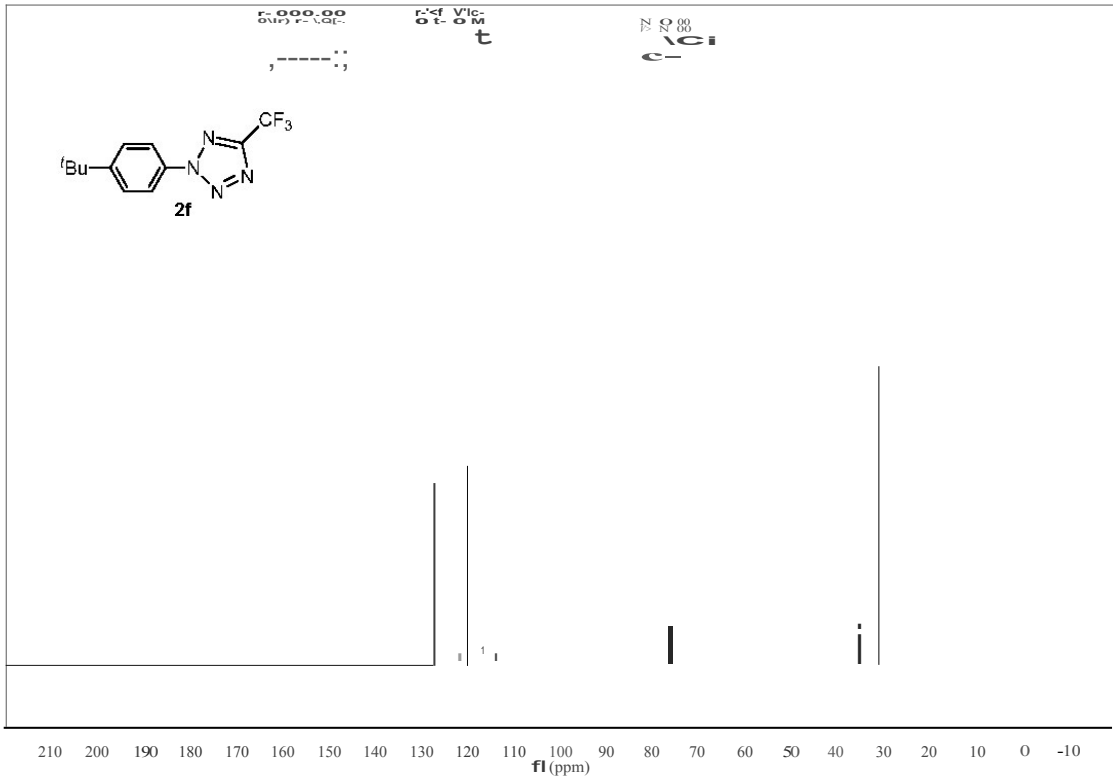




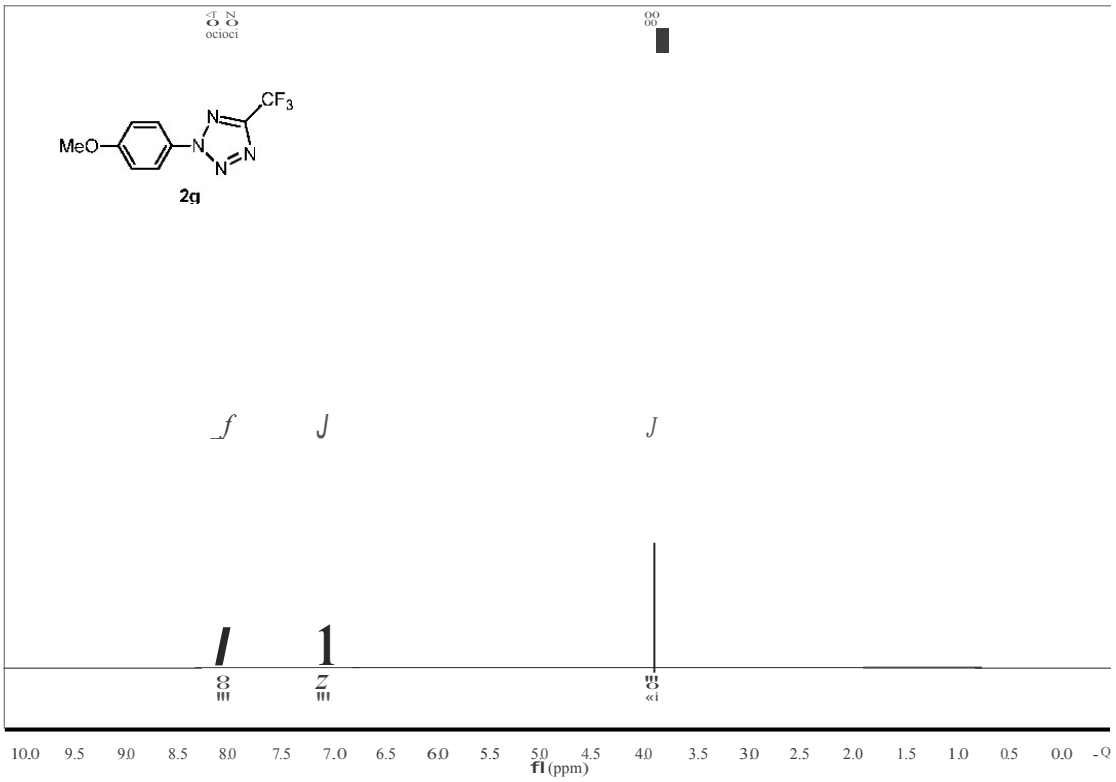
2-(4-(*tert*-butyl)phenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2f)

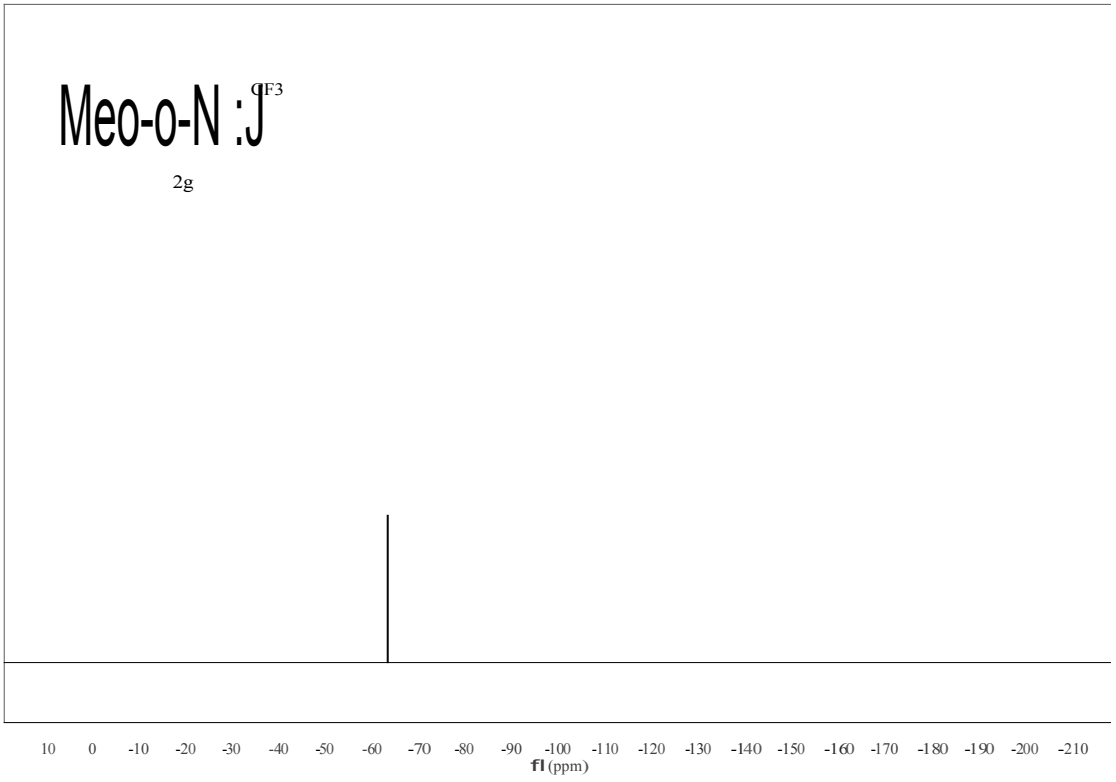


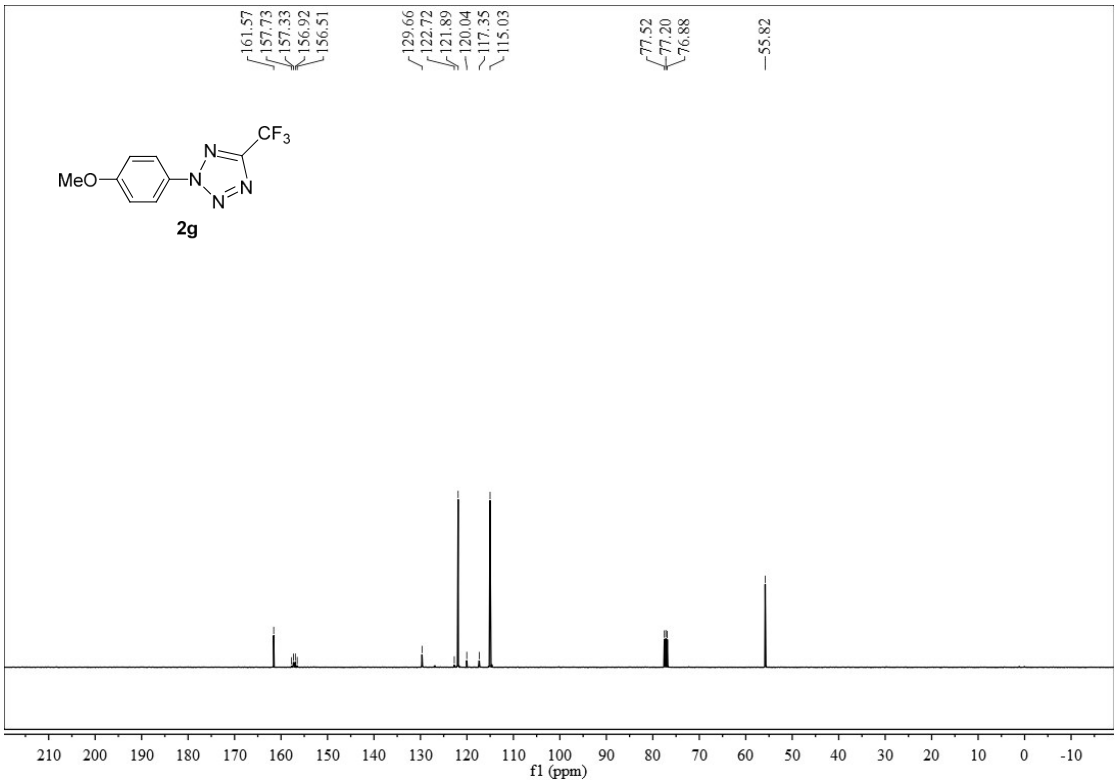

tBu
CF3
N
N
N
2f
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


tBu
CF3
N
N
N
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

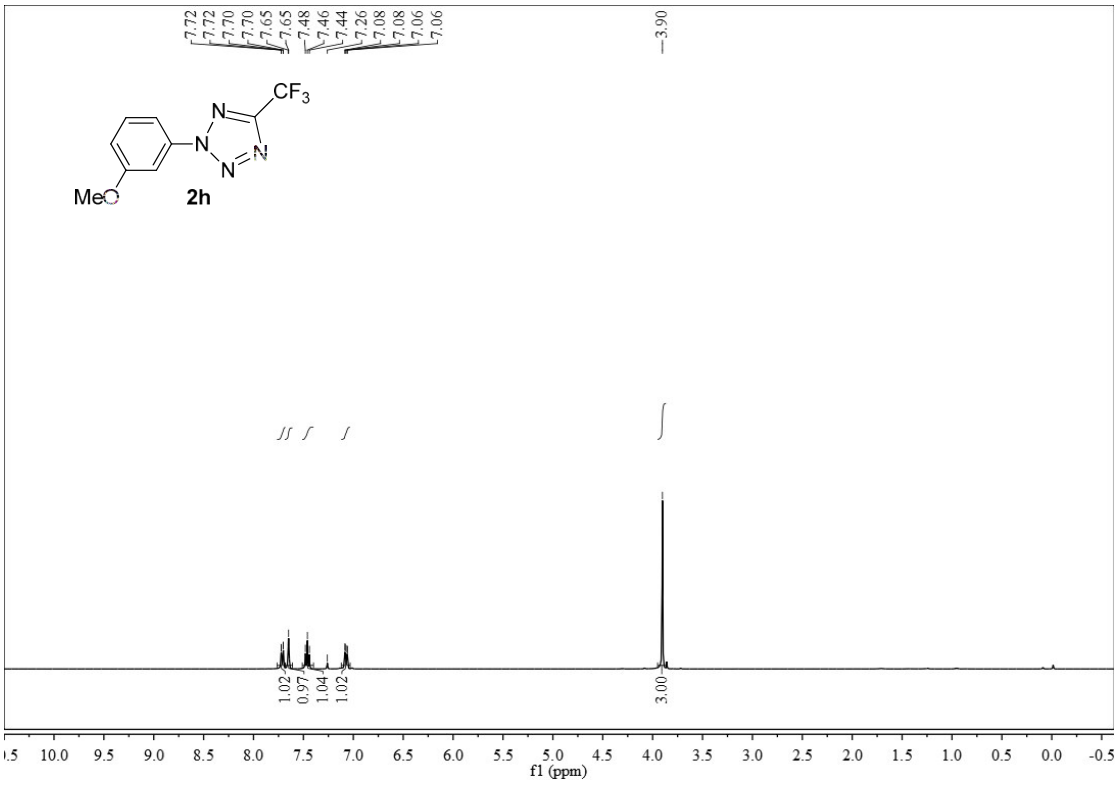
2-(**4-methoxyphenyl)-5-(trifluoromethyi)-2H-tetrazole** (2g)

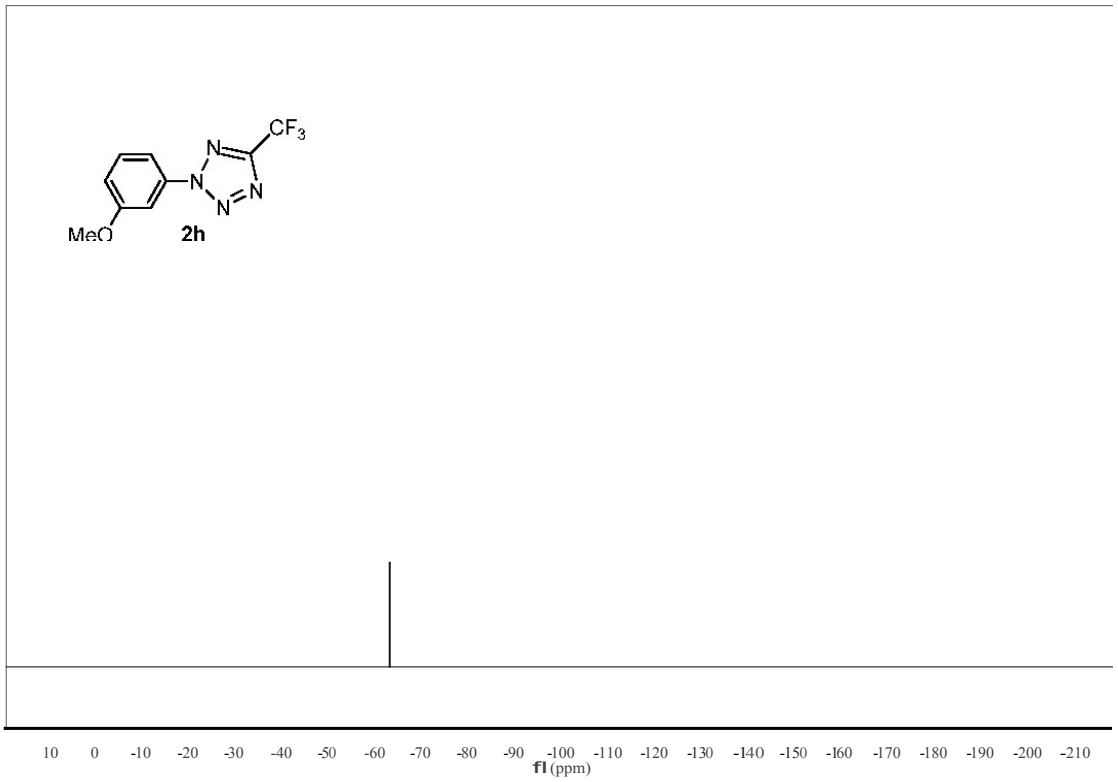


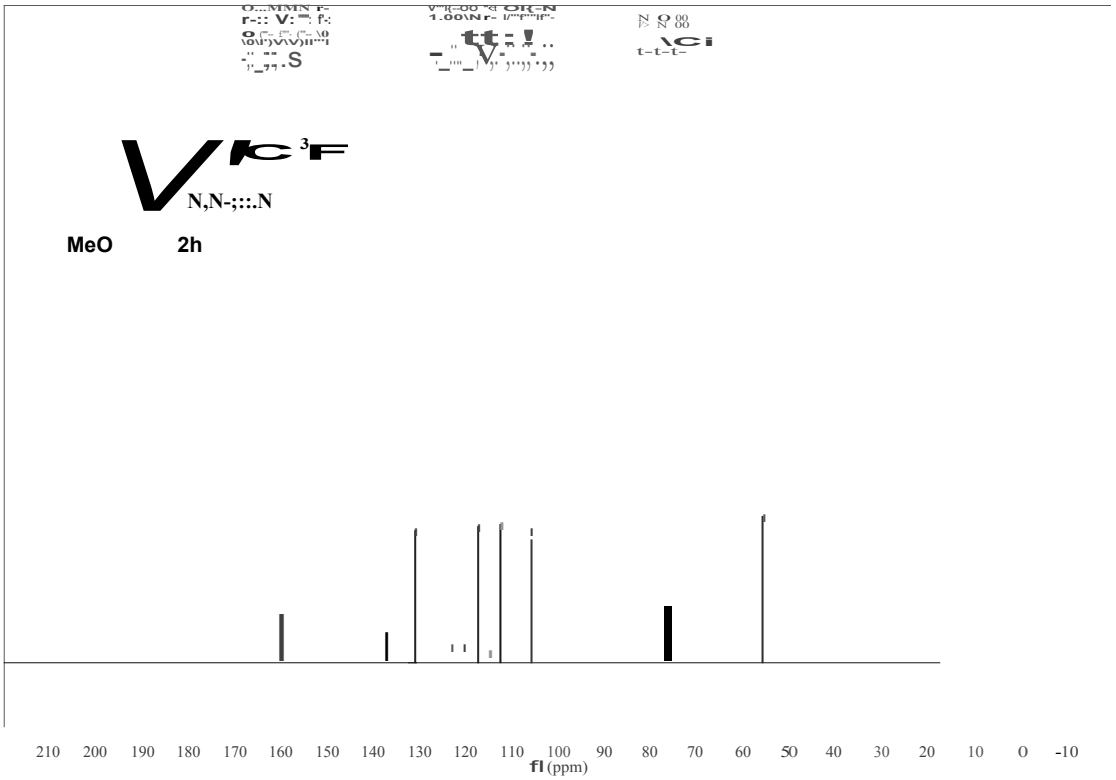




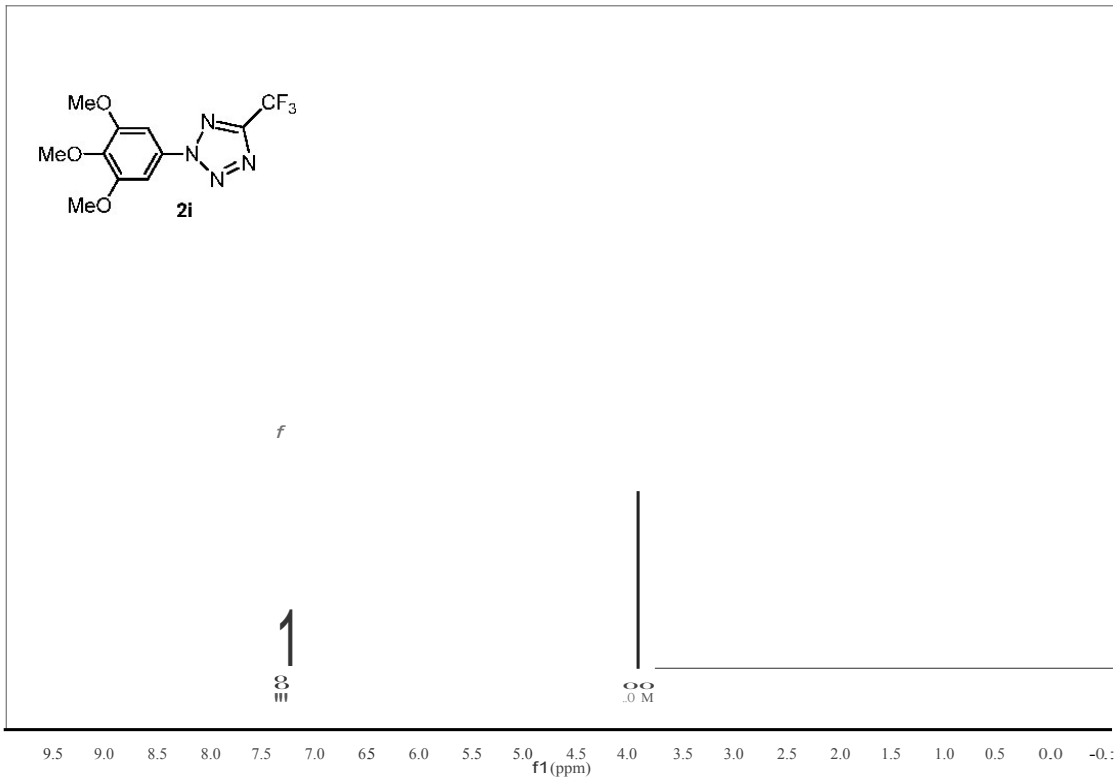
2-(3-methoxyphenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2h)

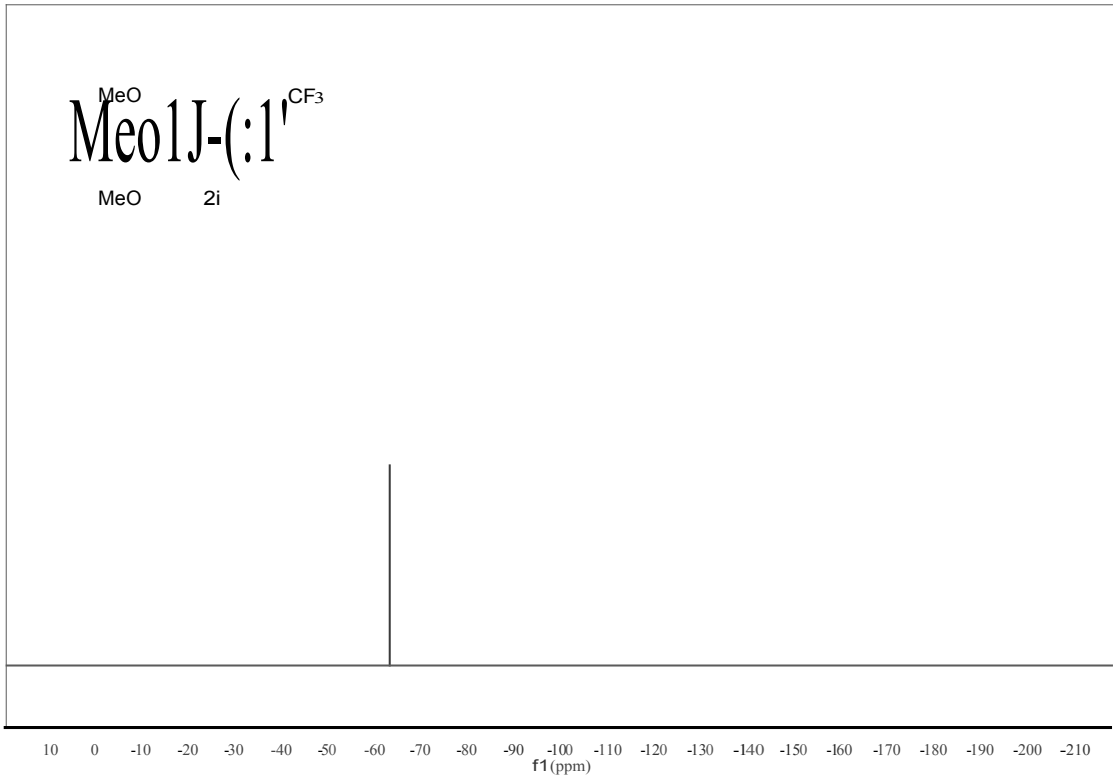


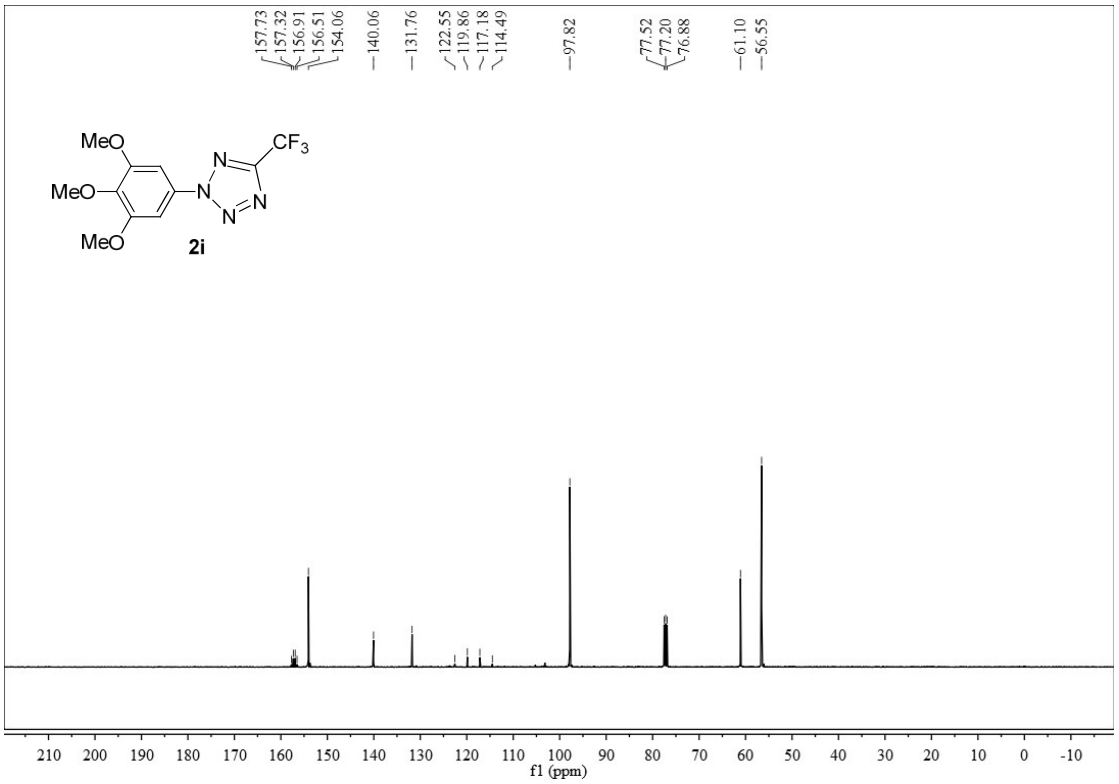

CF3
N
N
N
MeO
2h
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
fl (ppm)


N,N-;::.N
MeO
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
fl (ppm)

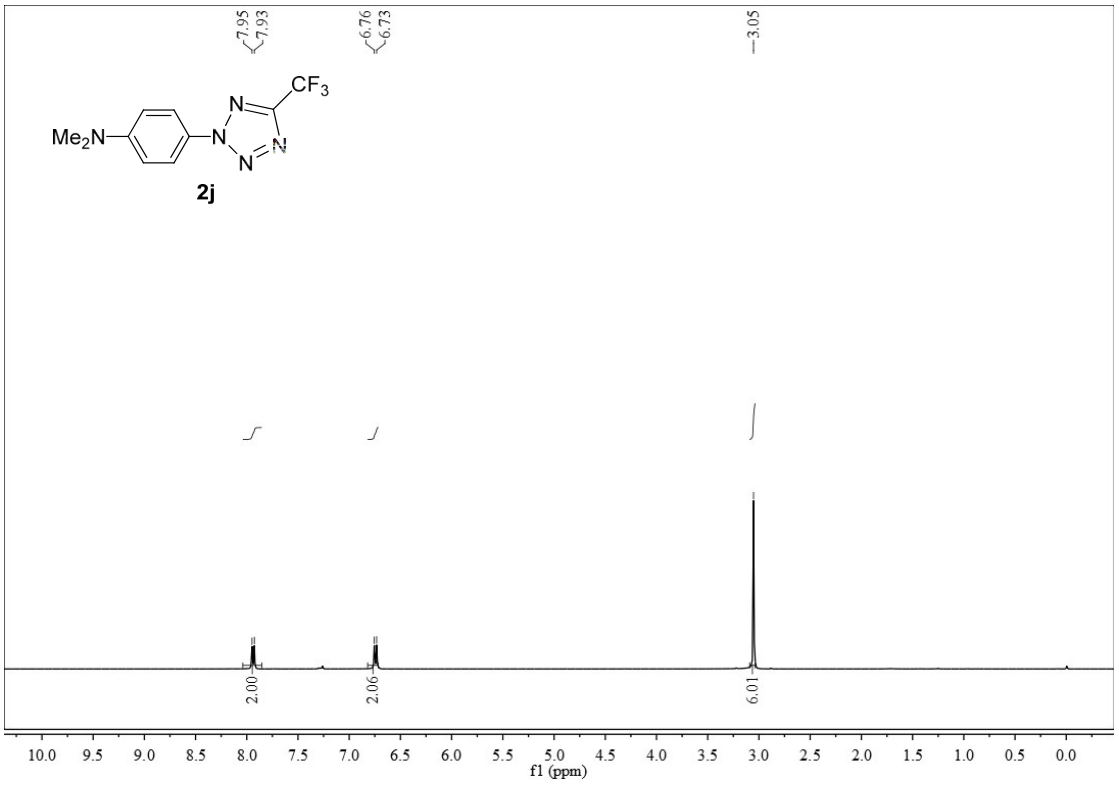
5-(trifluoromethyl)-2-(3,4,5-trimethoxyphenyl)-2H-tetrazole (2i)

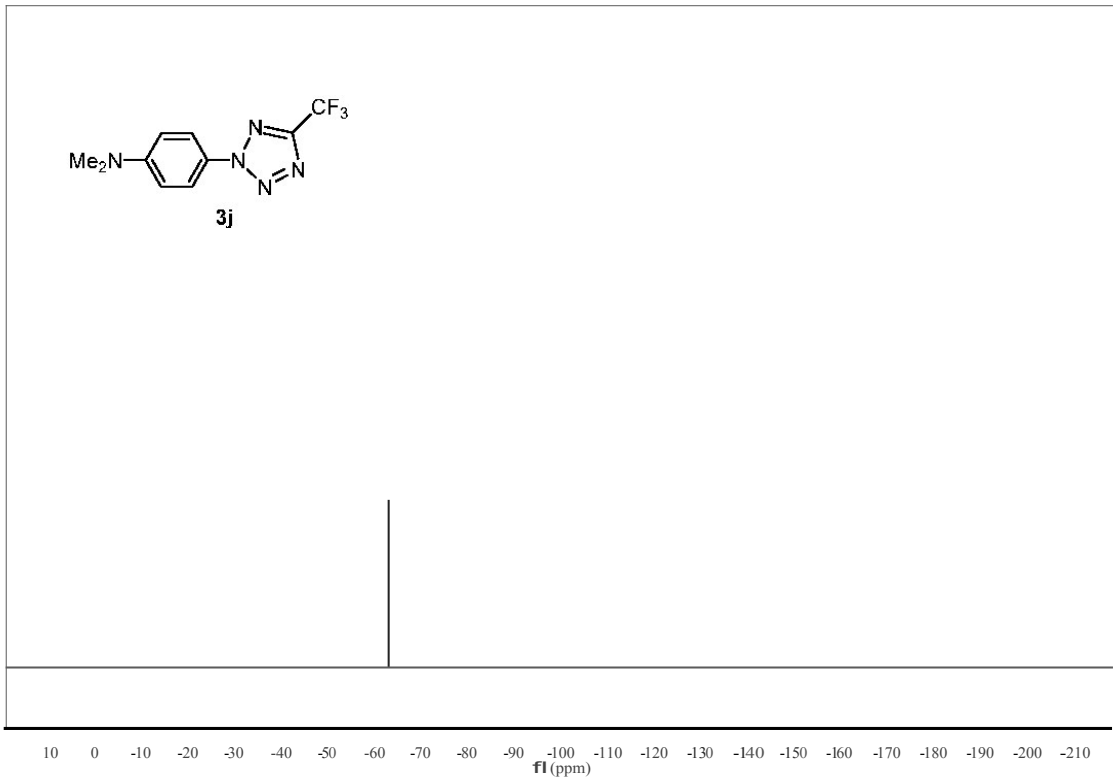


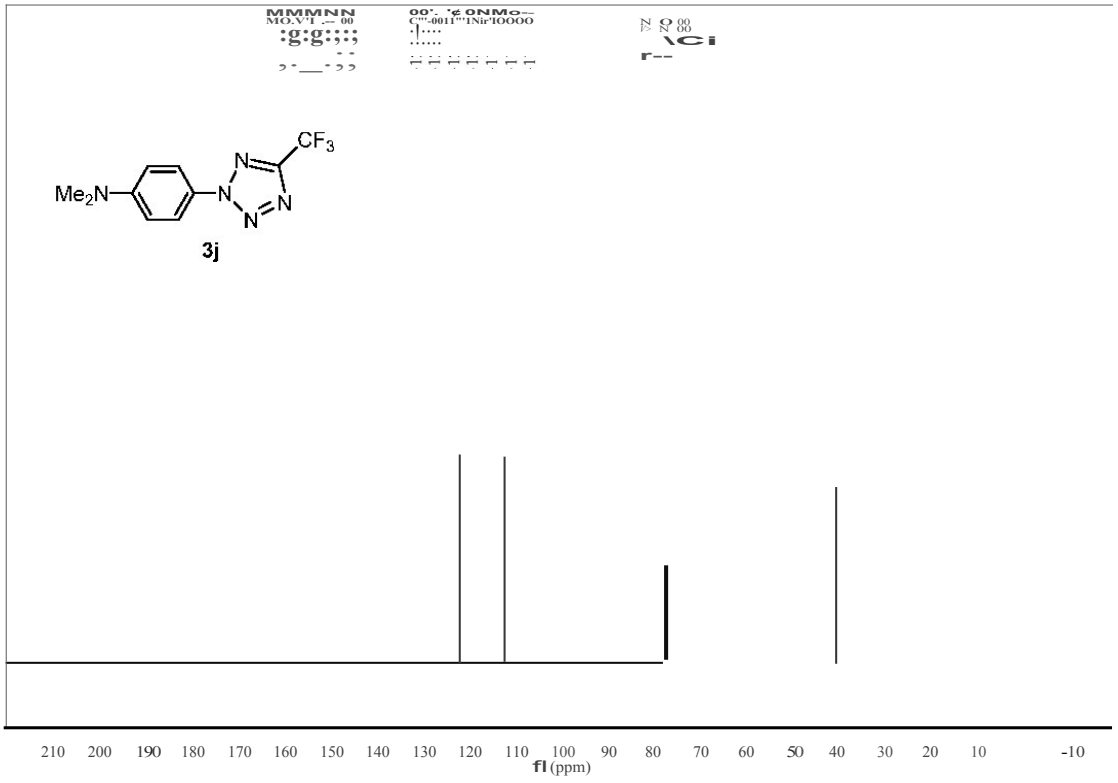




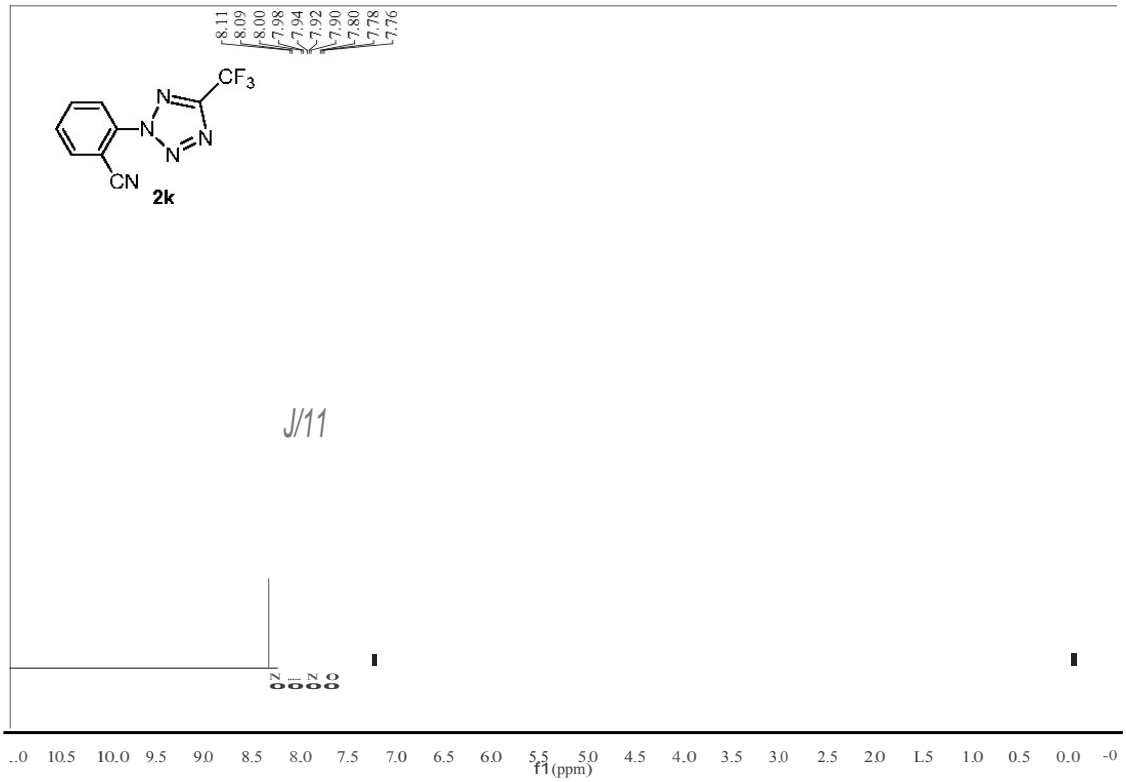
***N*,*N*-dimethyl-4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)aniline (2j)**

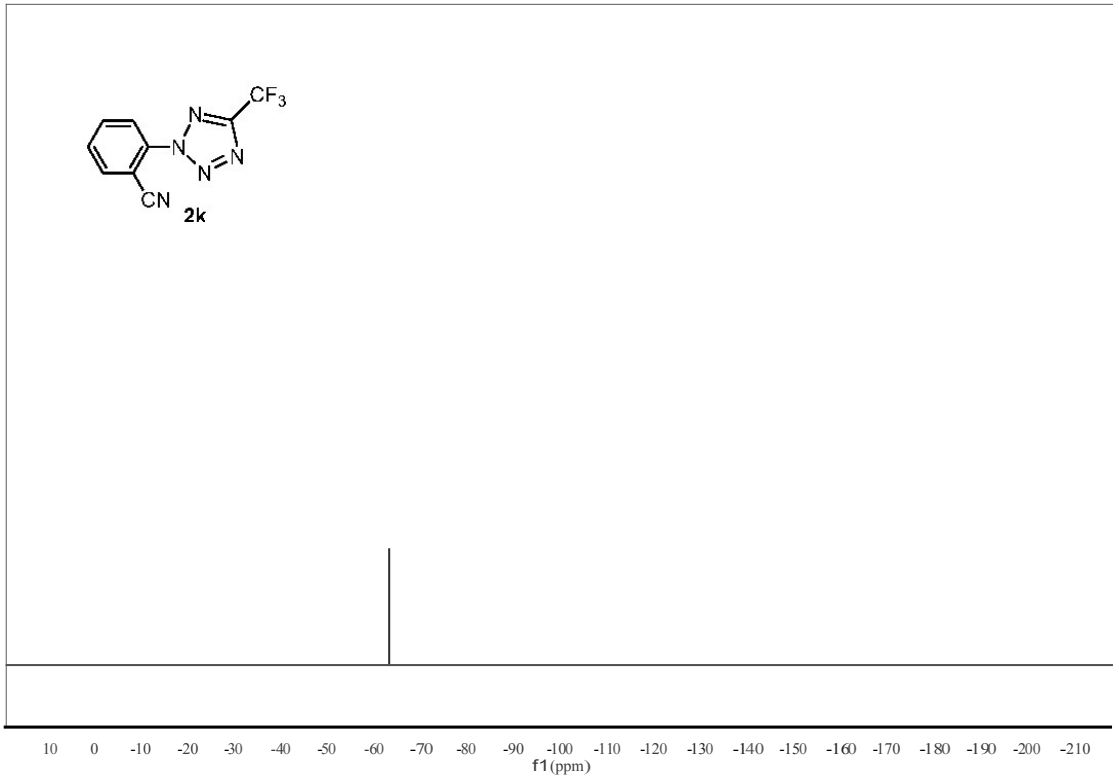


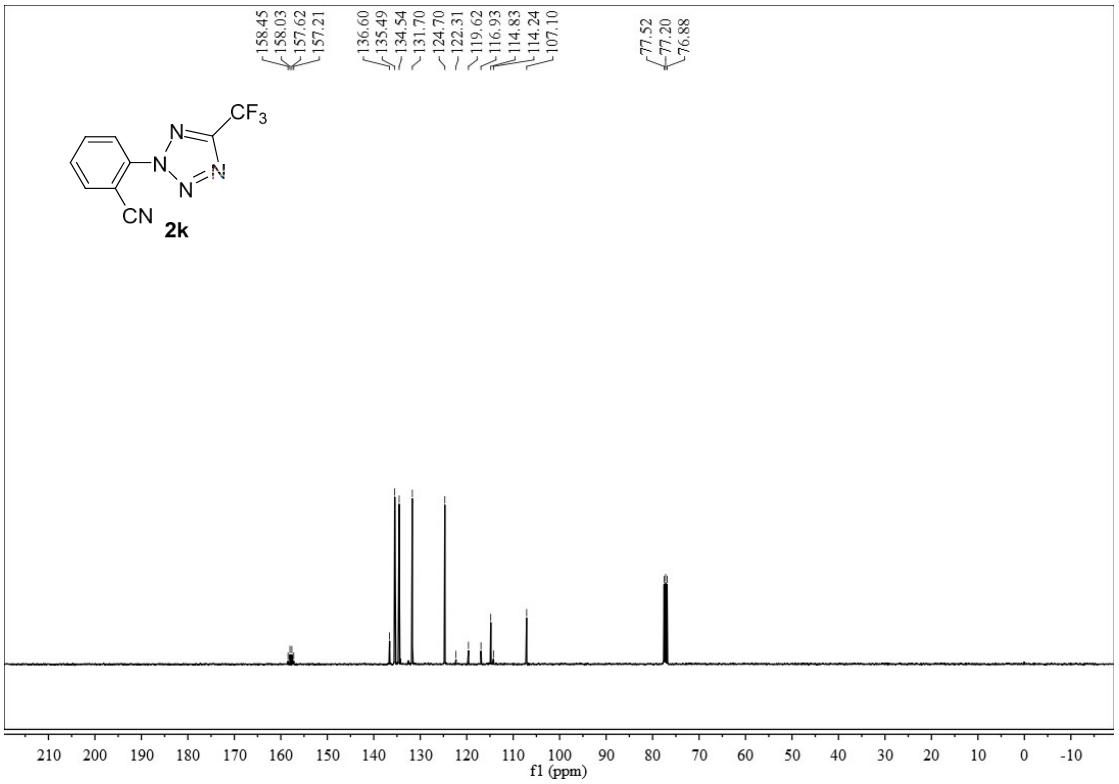

CF3
Me2N
N
N
N
3j
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


CF3
Me2N
N
N
N
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 -10
f1 (ppm)

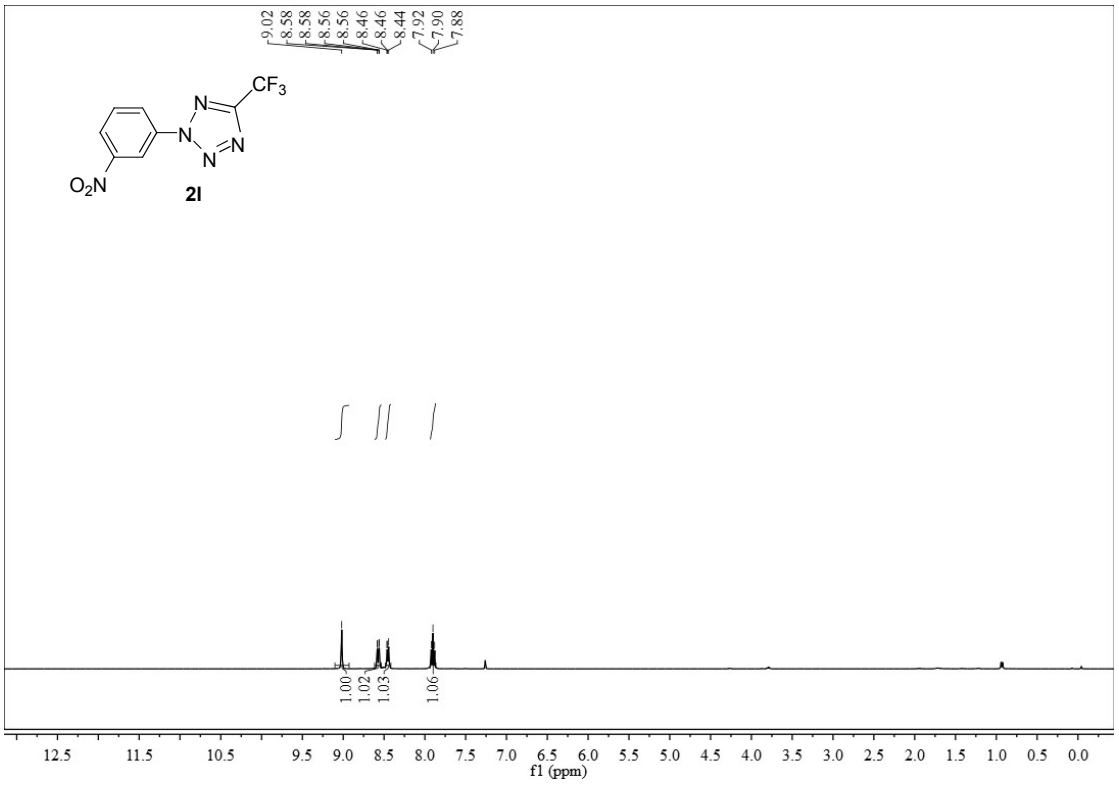
2-(5-(trifluoromethyl)-2H-tetrazol-2-yl)benzonitrile (2k)

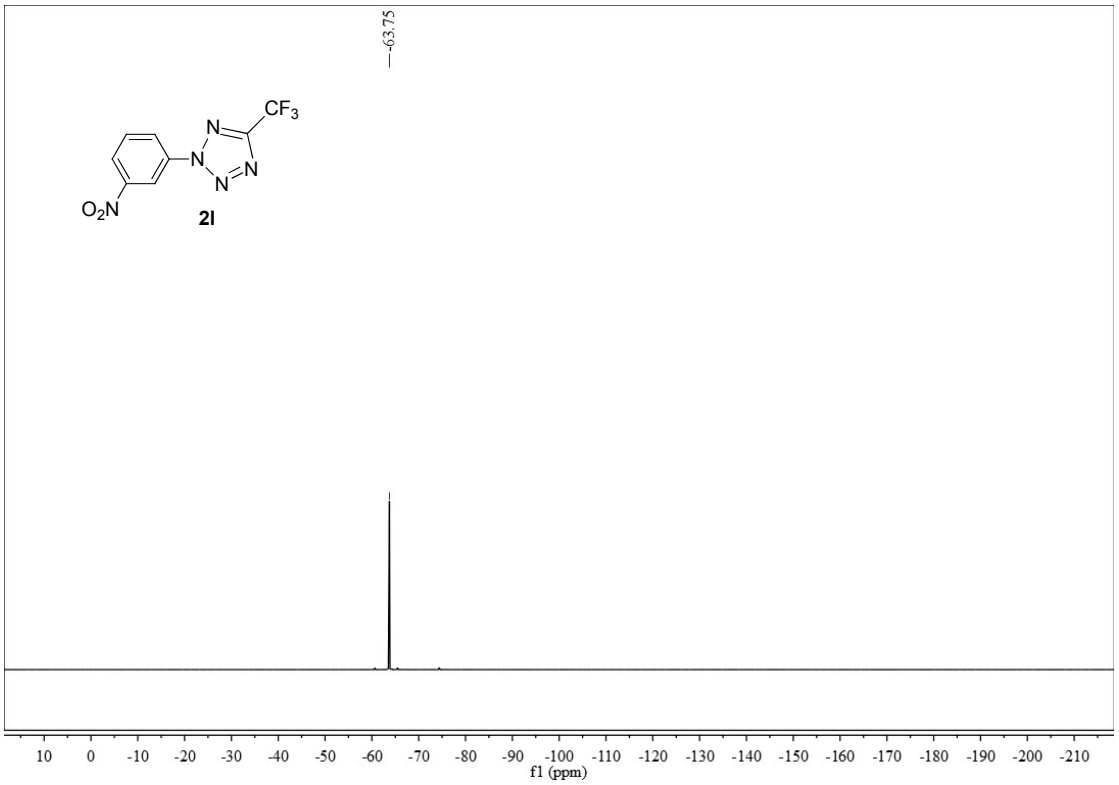


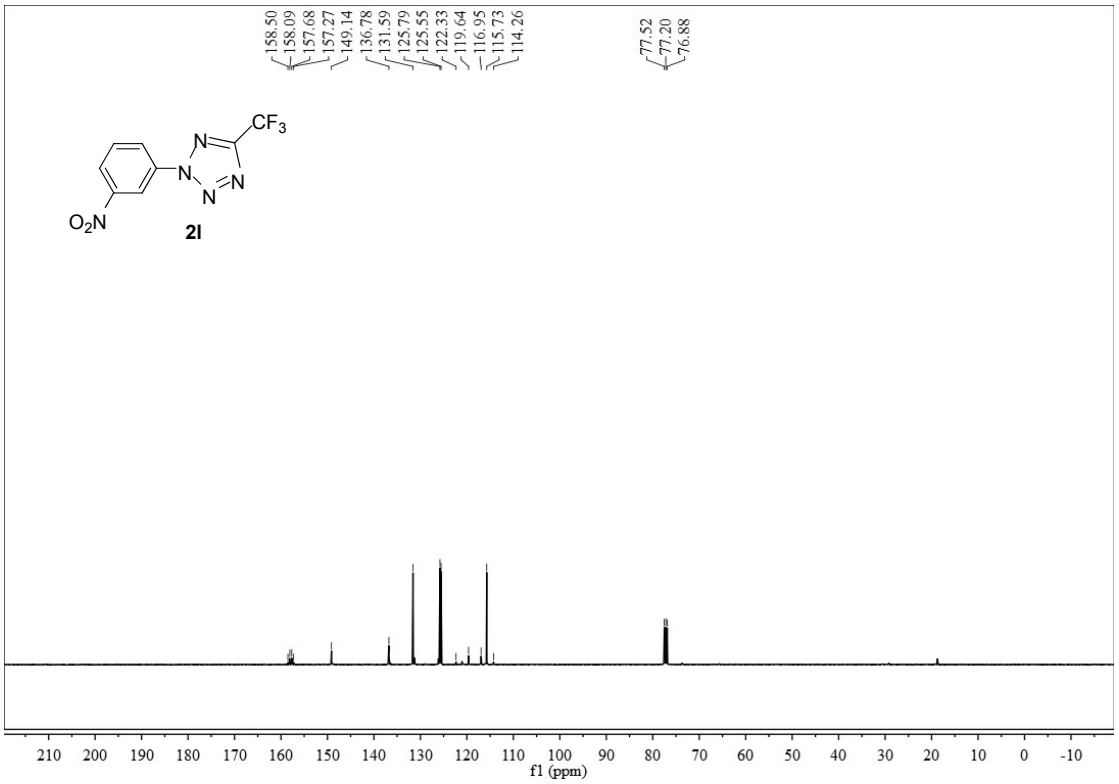




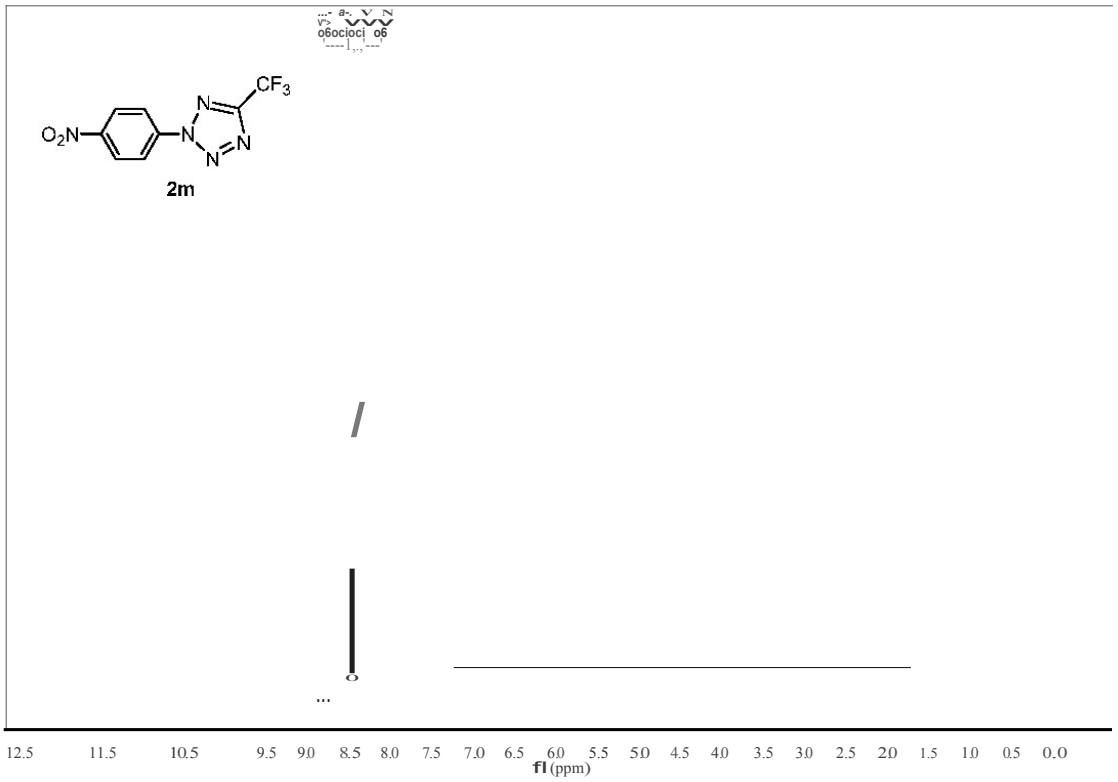
2-(3-nitrophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2l)

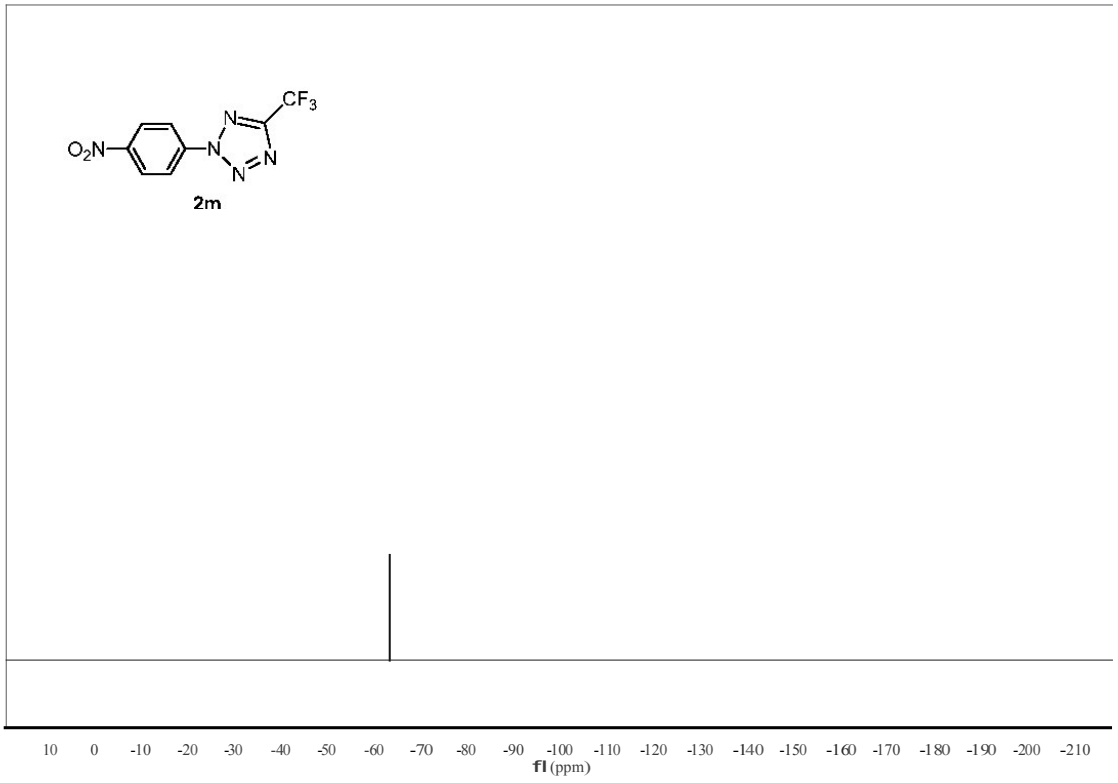


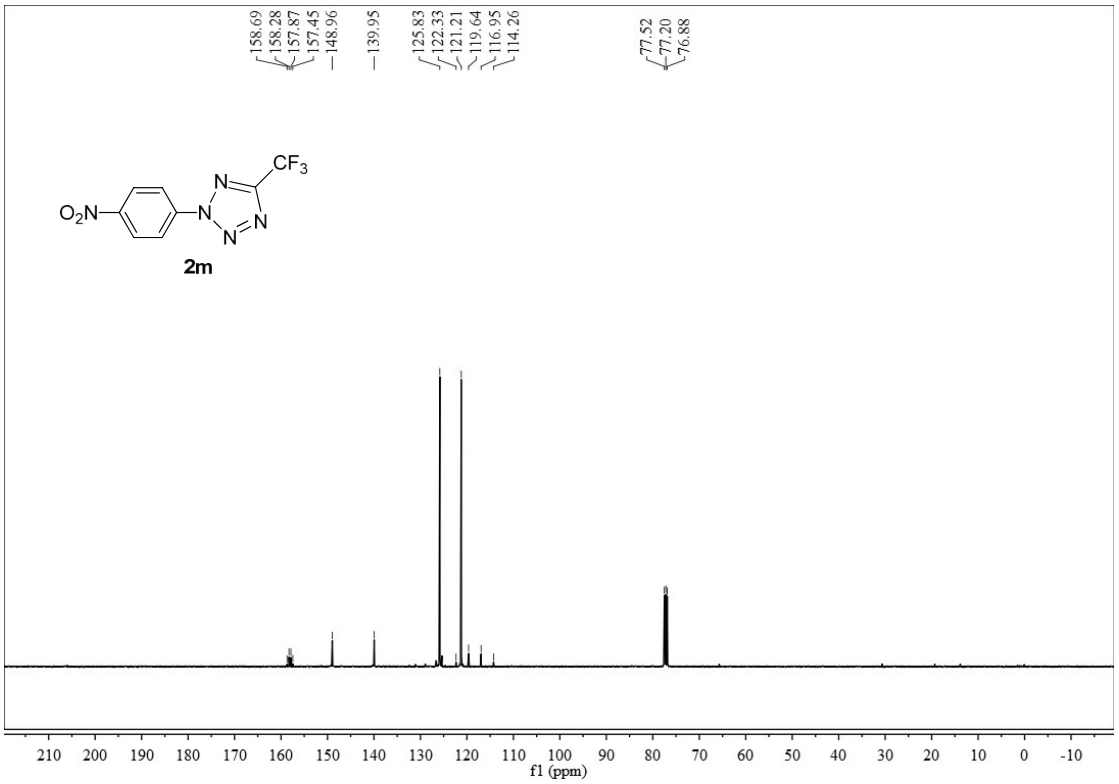

-63.75
CF3
N
N
N
N
O2N
2l
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


158.50
158.09
157.68
157.27
149.14
136.78
131.59
125.79
125.55
122.33
119.64
116.95
115.73
114.26
77.52
77.20
76.88
CF3
N
N
N
N
O2N
2l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

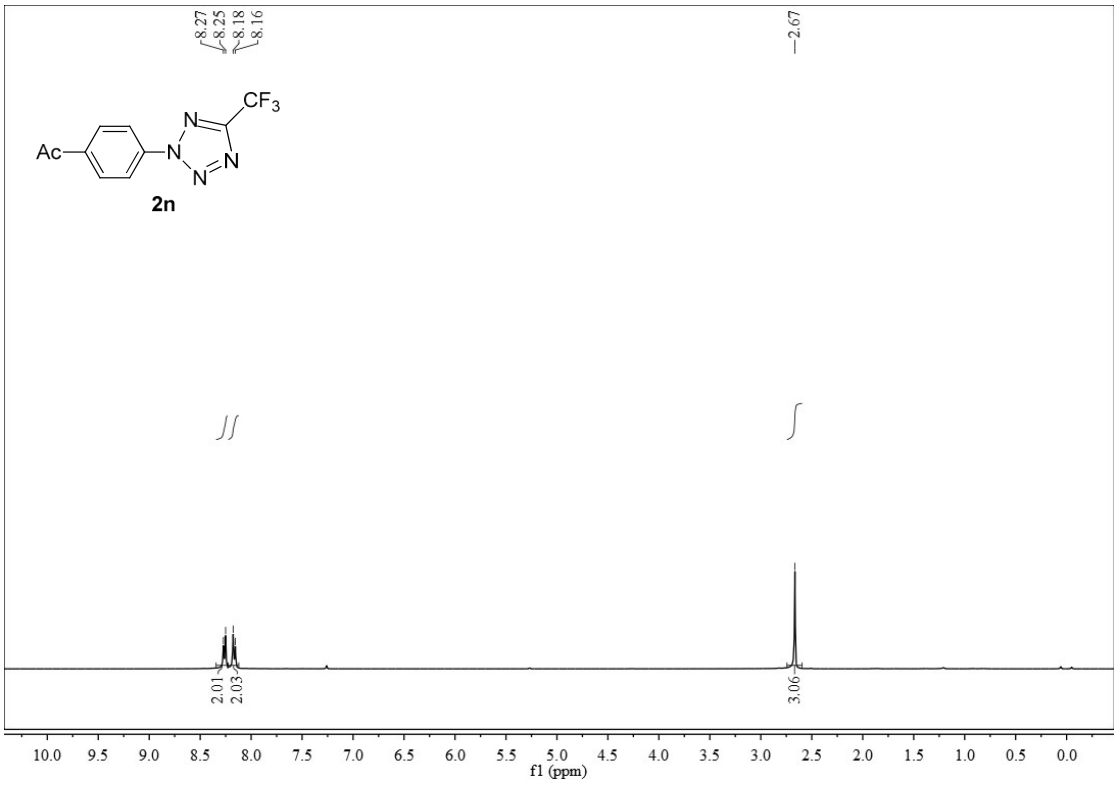
2-(4-nitrophenyl)-5-(trifluoromethyi)-2H-tetrazole (2m)

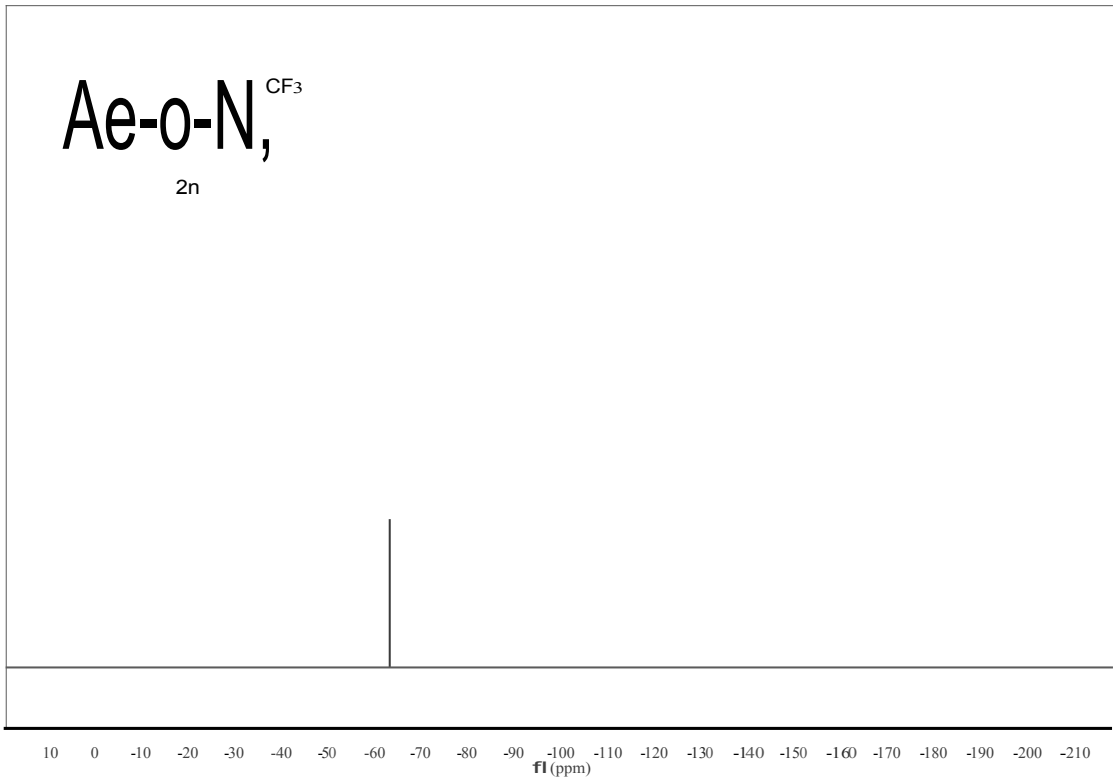


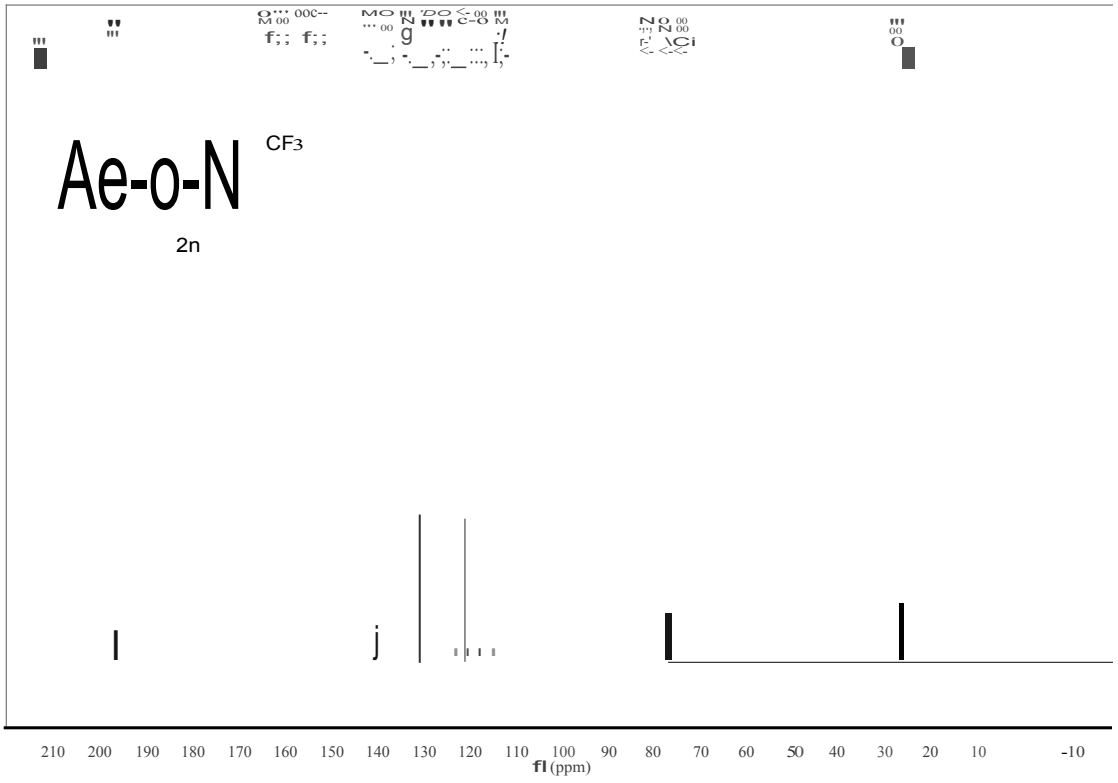




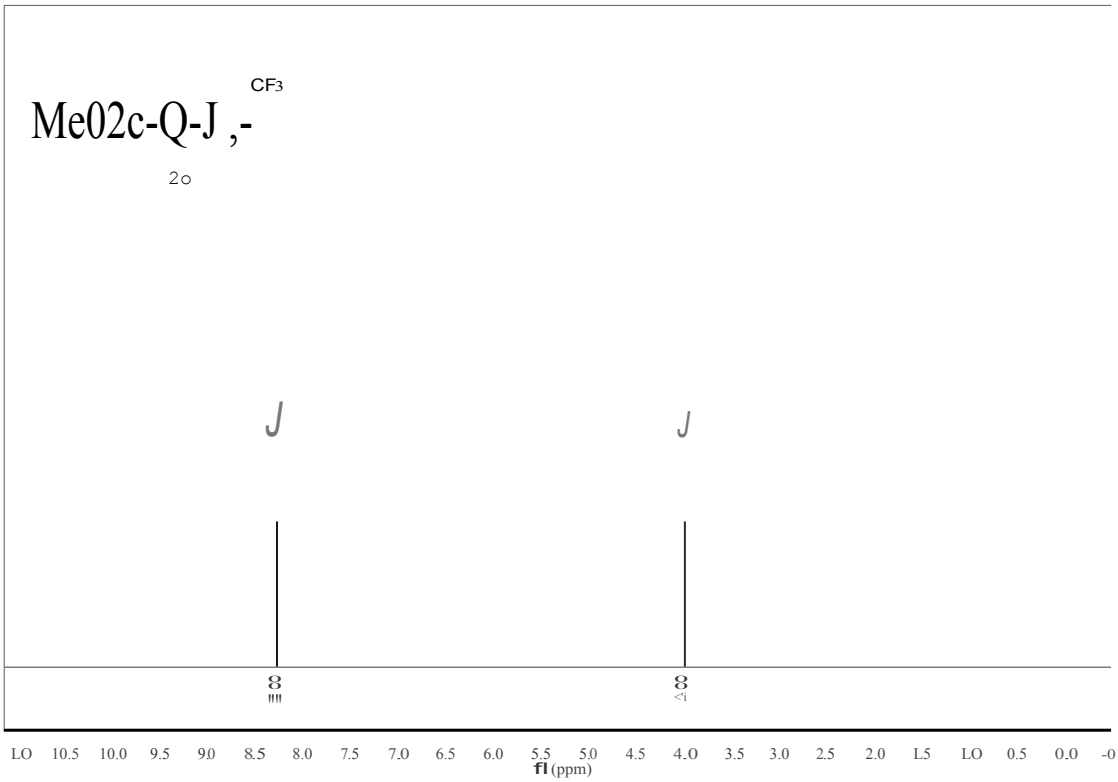
1-(4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)phenyl)ethanone (2n)

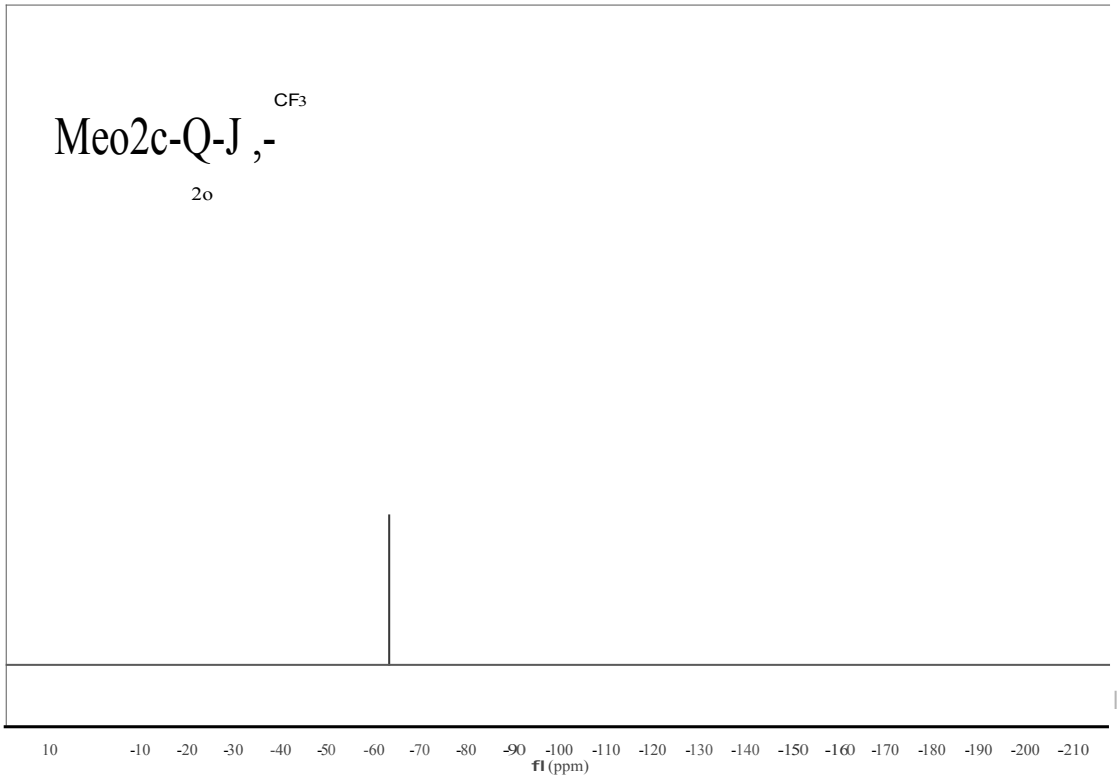


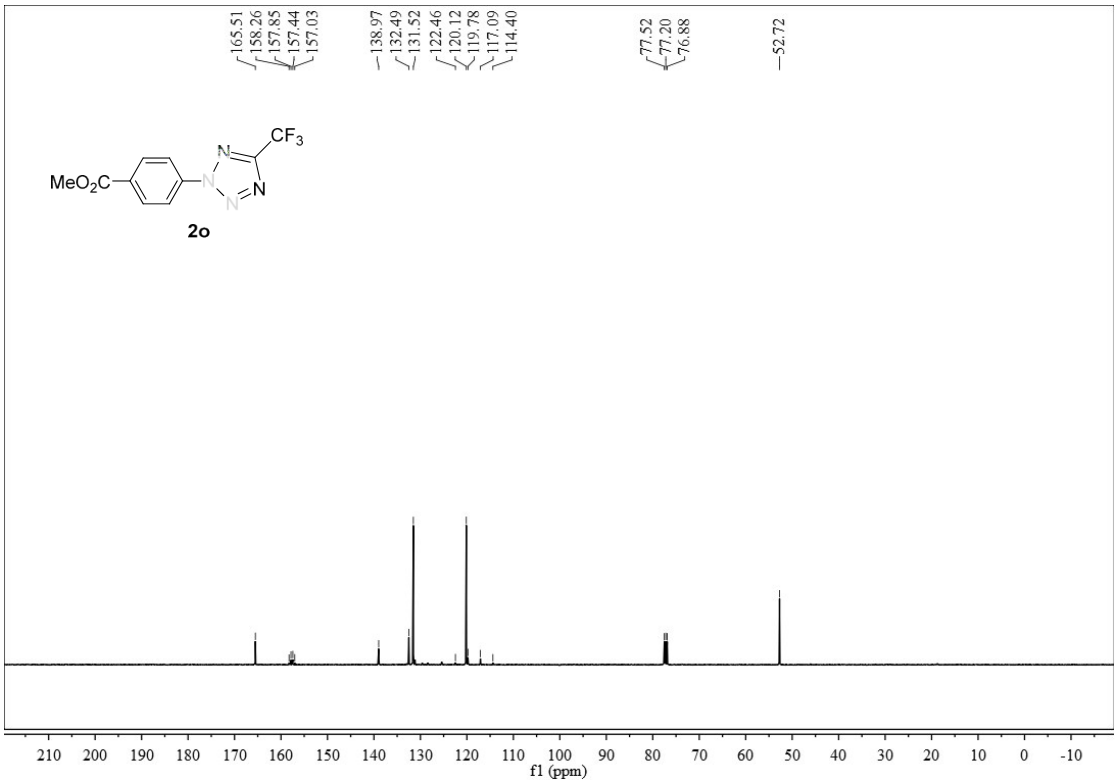

Ae-o-N,
CF3
2n
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
fl (ppm)


Ae-o-N
CF3
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 -10
fl (ppm)

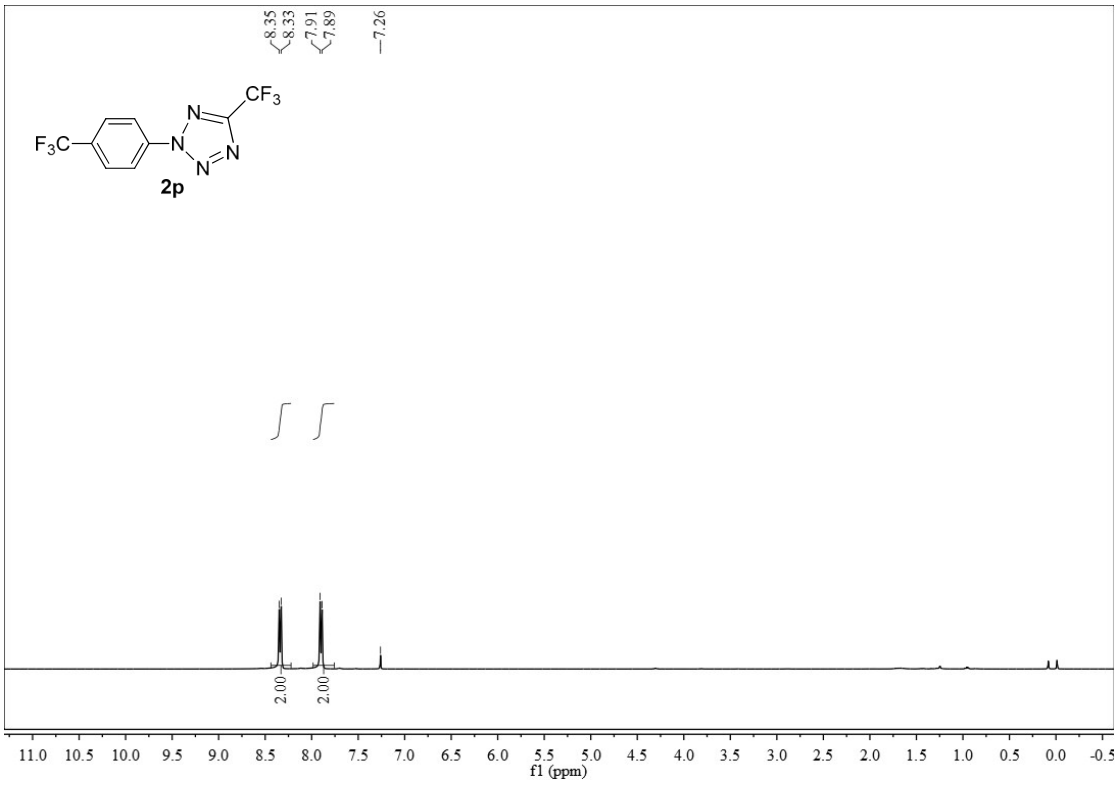
methyl 4-(5-(trifluoromethyi)-2H-tetrazol-2-yl)benzoate (2o)

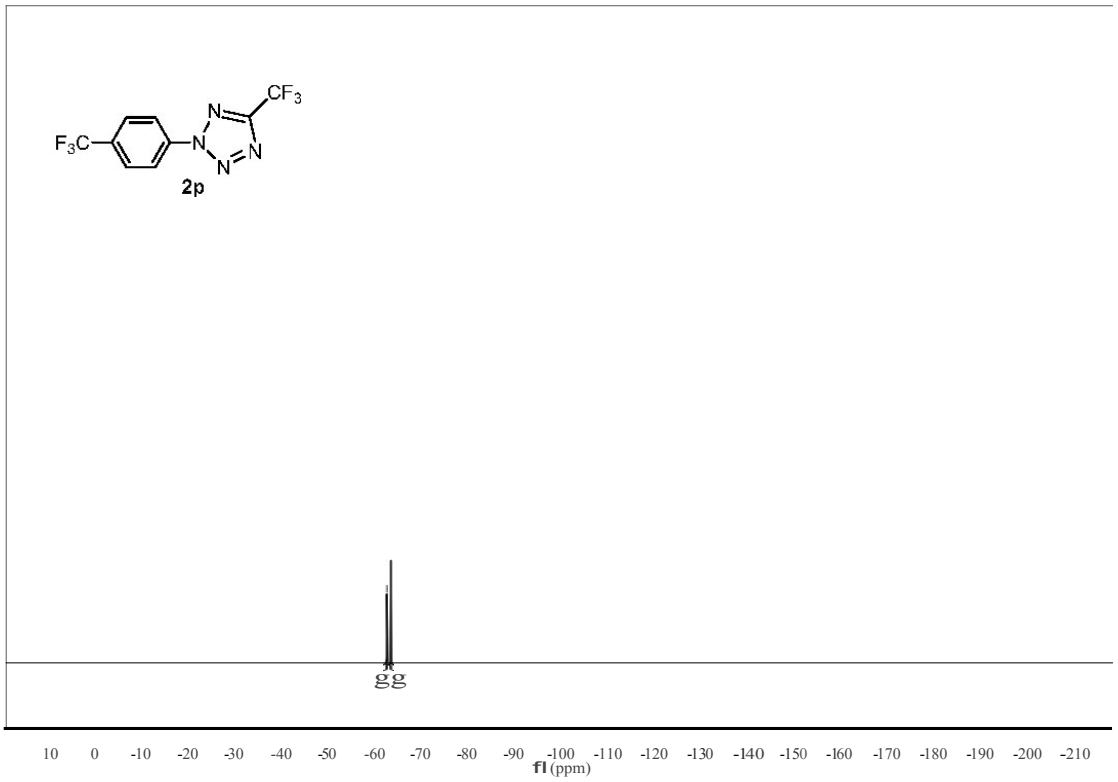


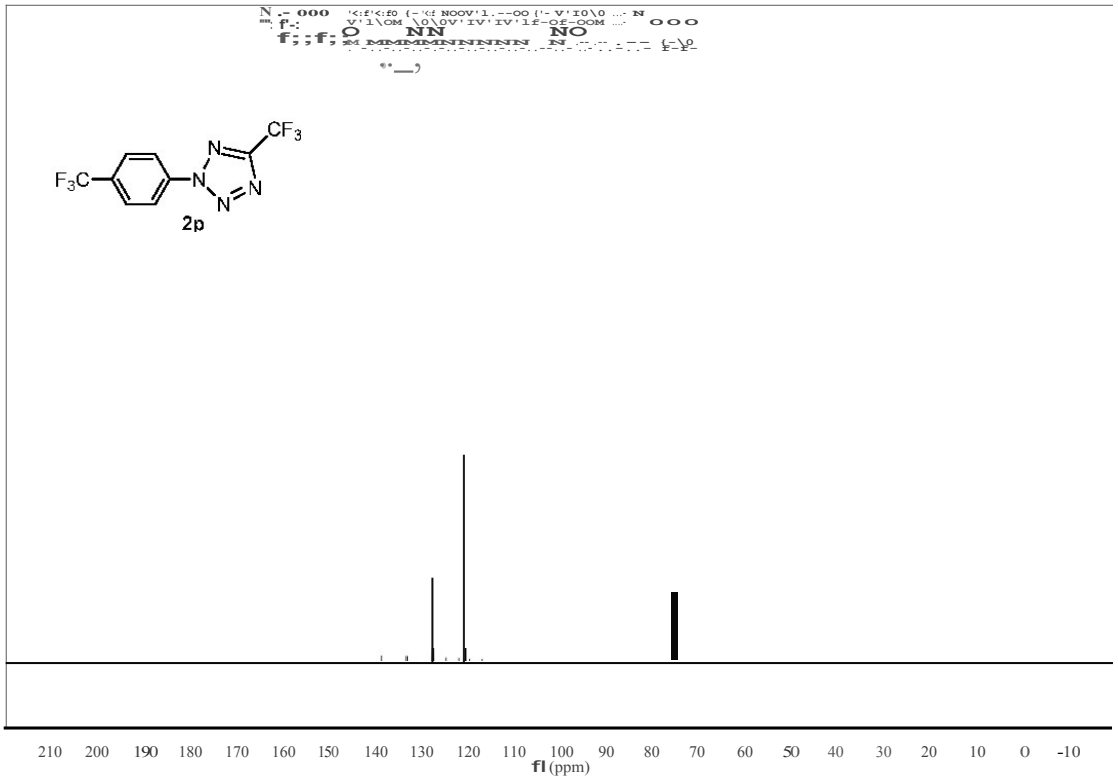




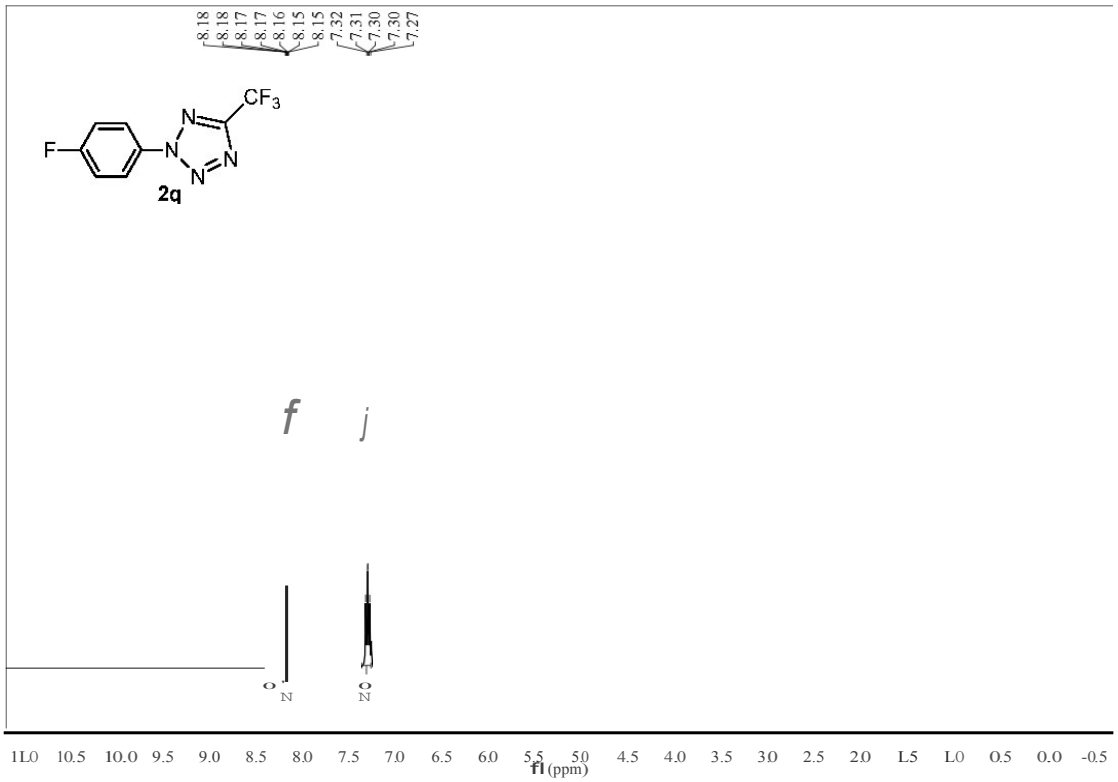
5-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)-2*H*-tetrazole (2p)

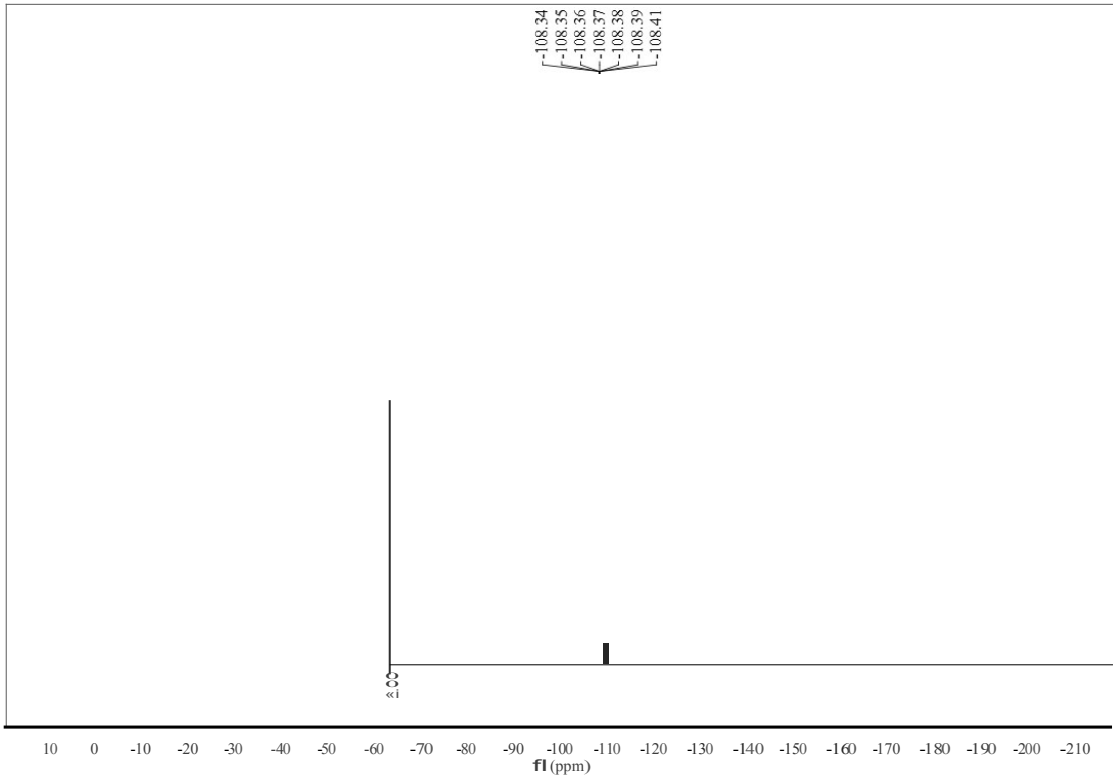


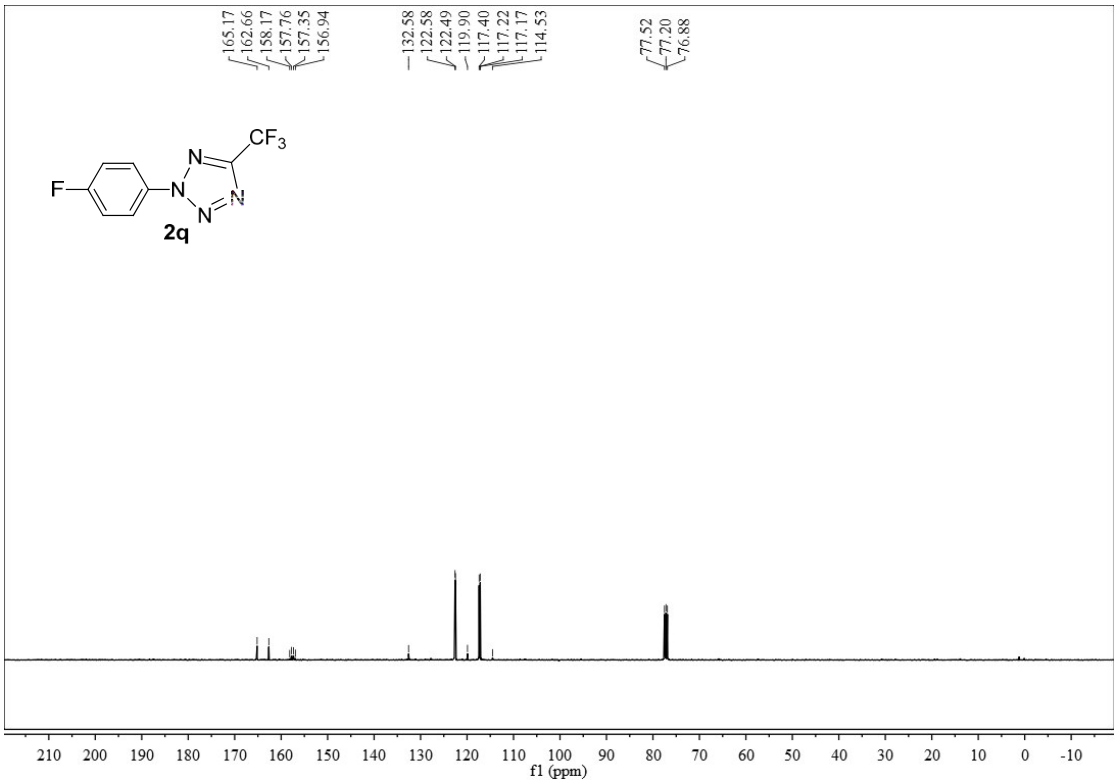

F3C
CF3
N
N
N
2p
gg
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
fl (ppm)


F3C
CF3
N
N
N
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
fl (ppm)

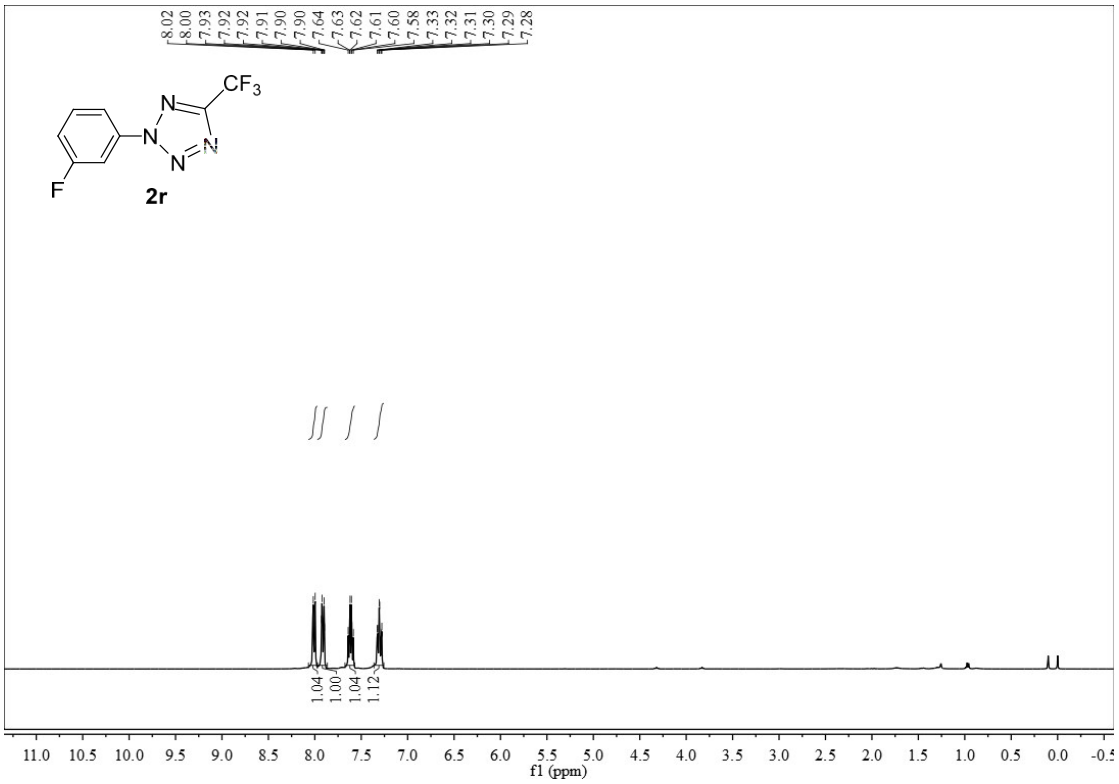
2-(4-fluorophenyl)-5-(trifluoromethyl)-2H-tetrazole (2q)

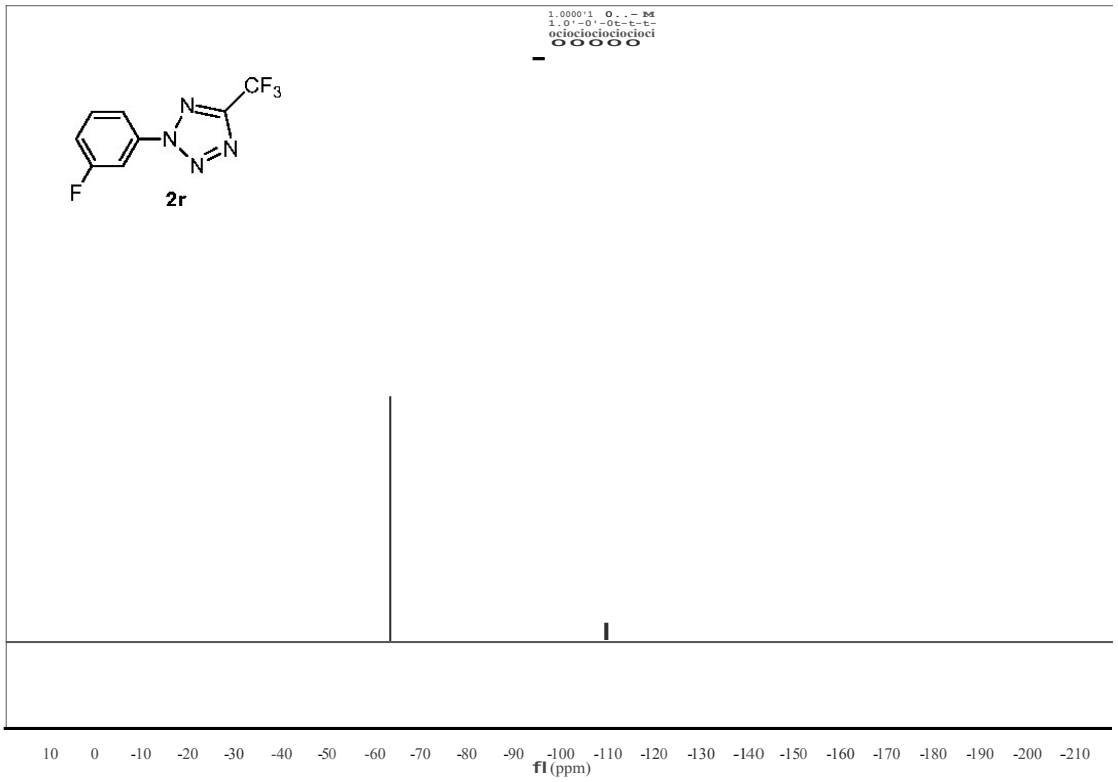


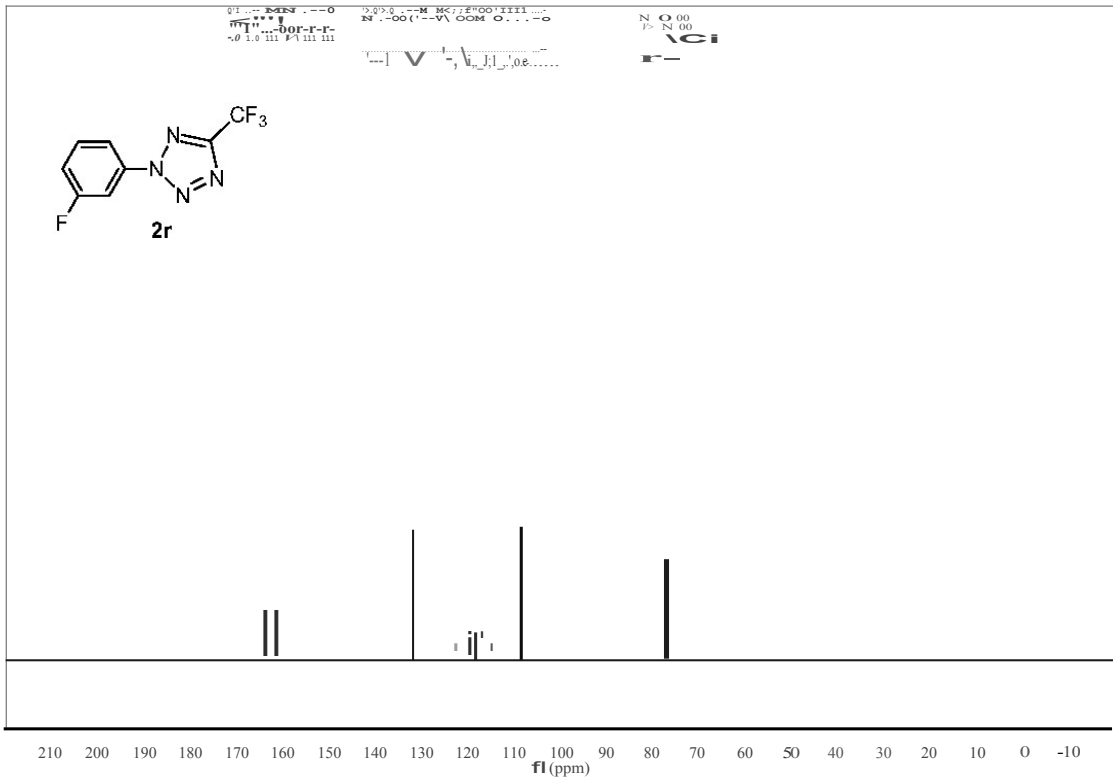




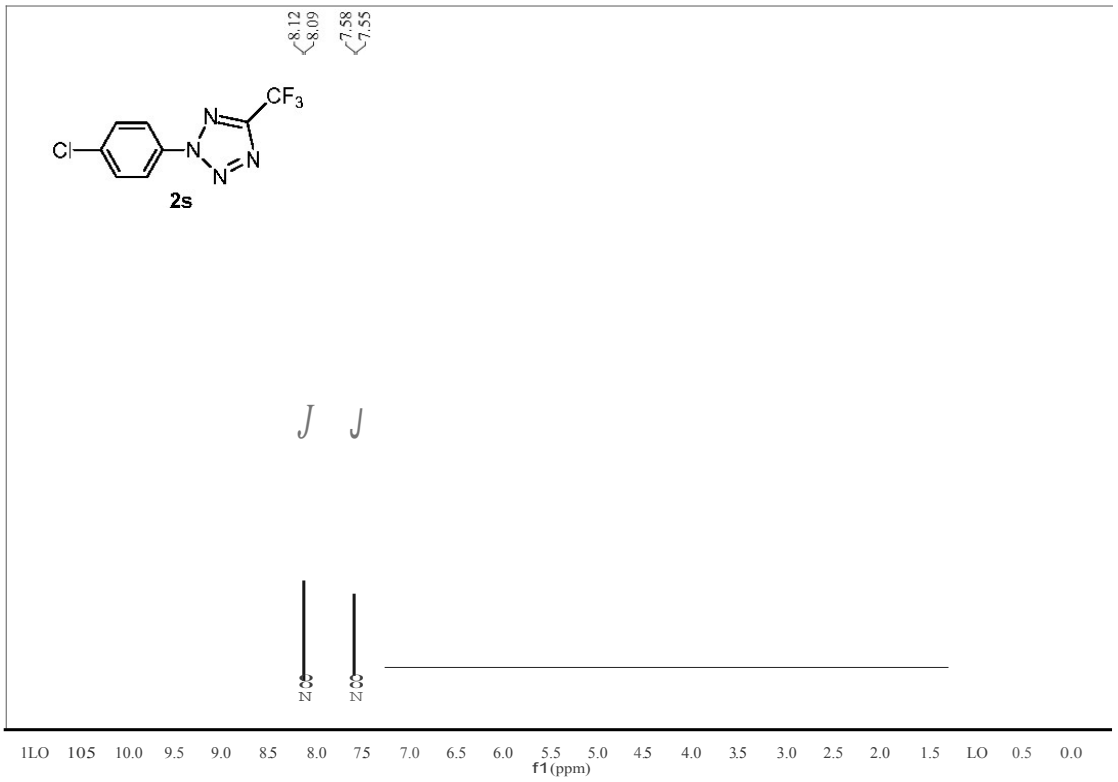
2-(3-fluorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2r)

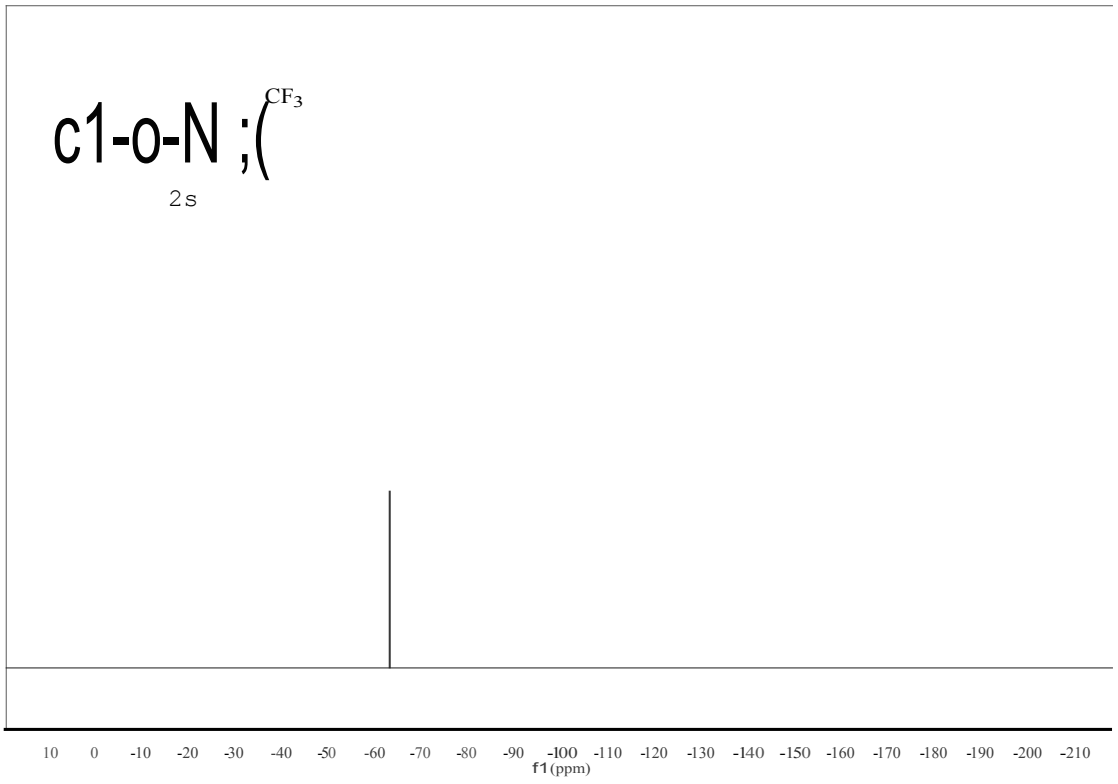


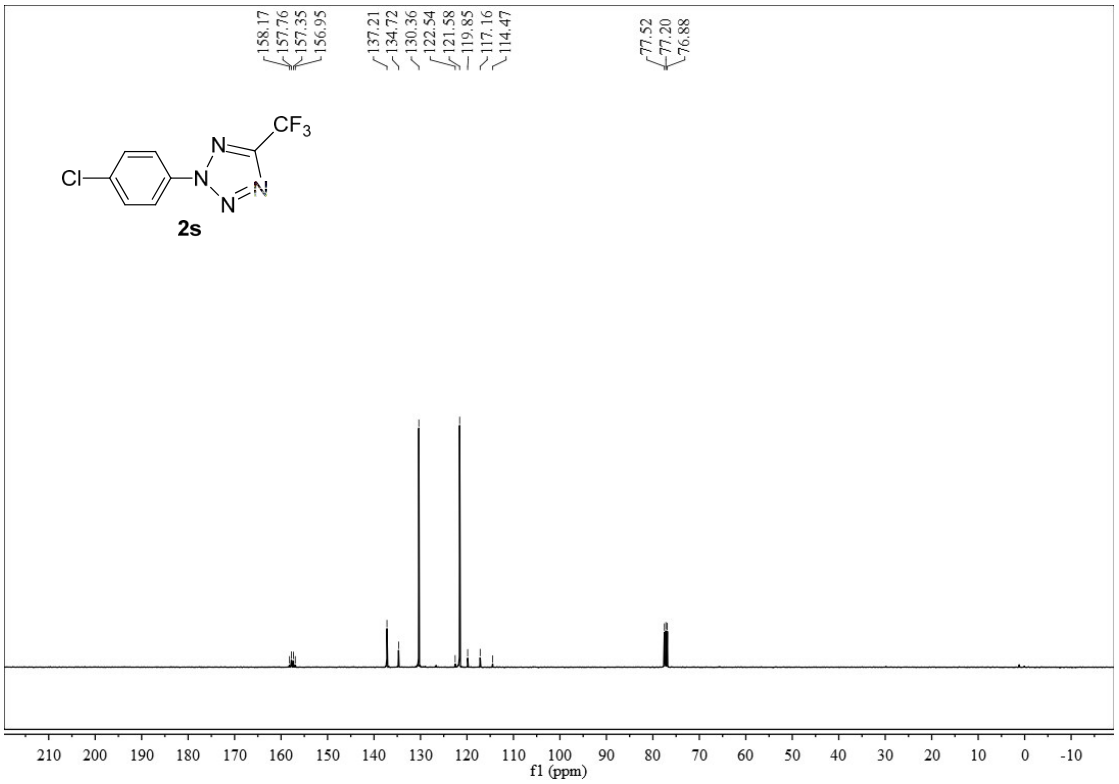

CF3
N
N
N
F
2r
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


CF3
N
N
N
F
2r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

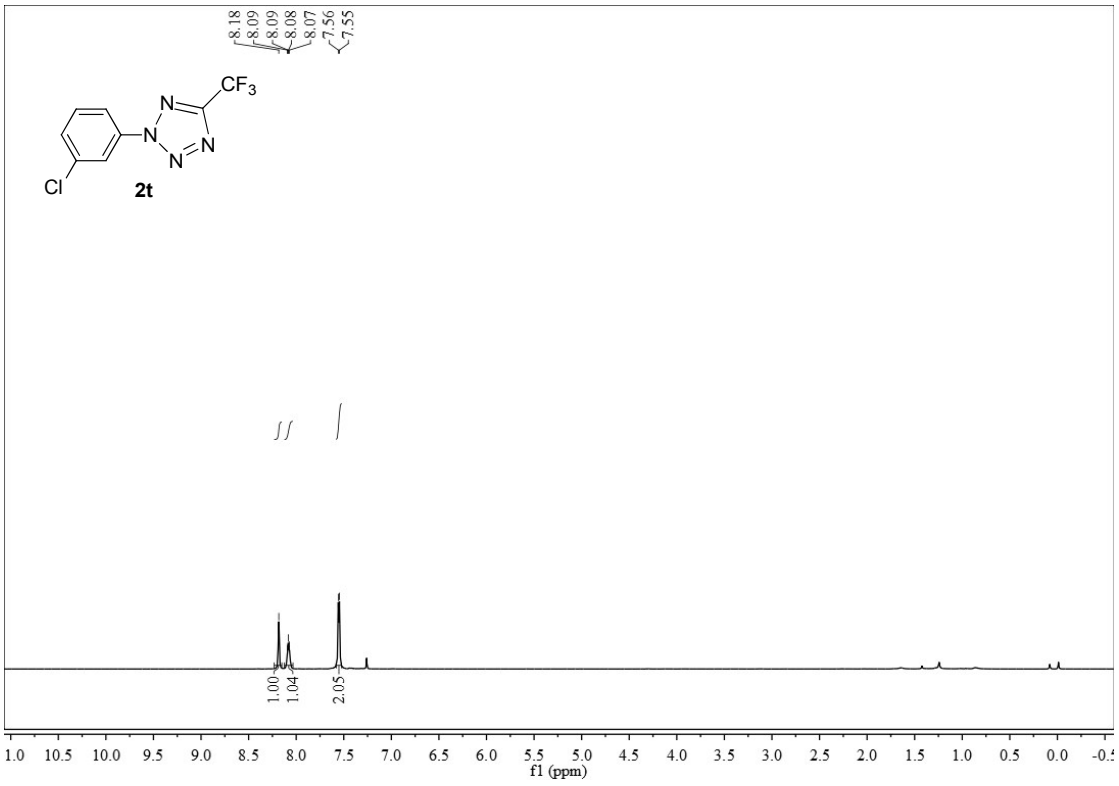
2-(**4-chlorophenyl)-5-(trifluoromethyl)-2H-tetrazole** (2s)

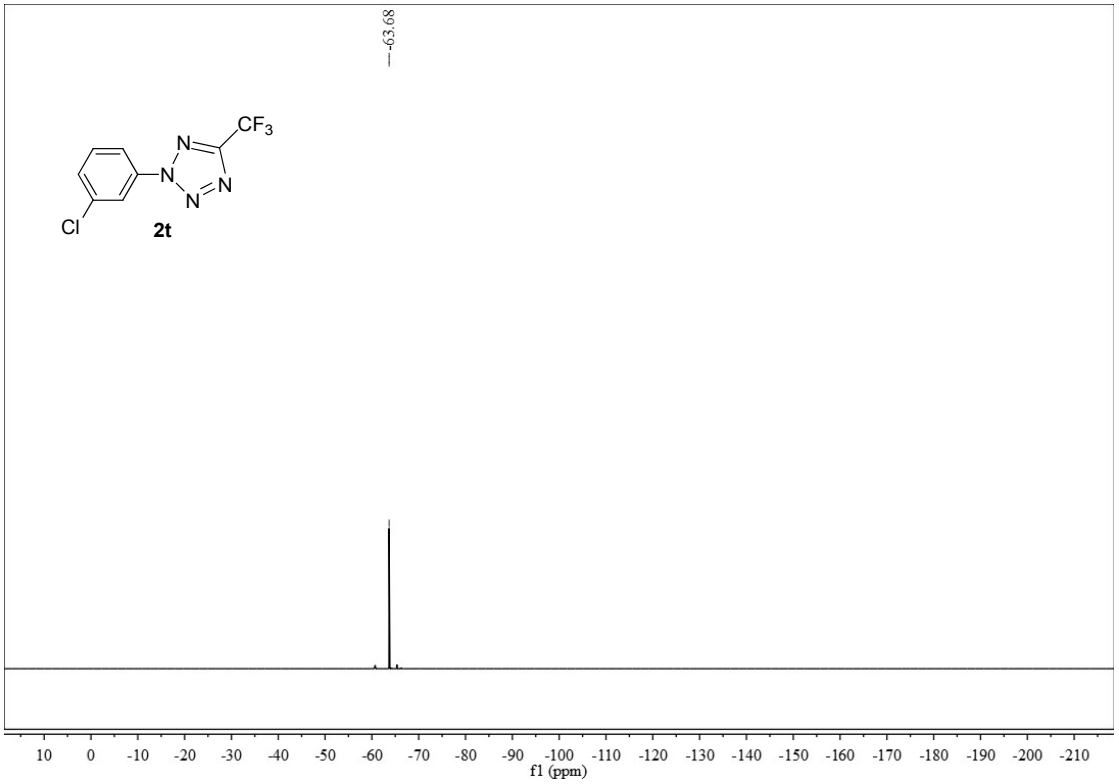


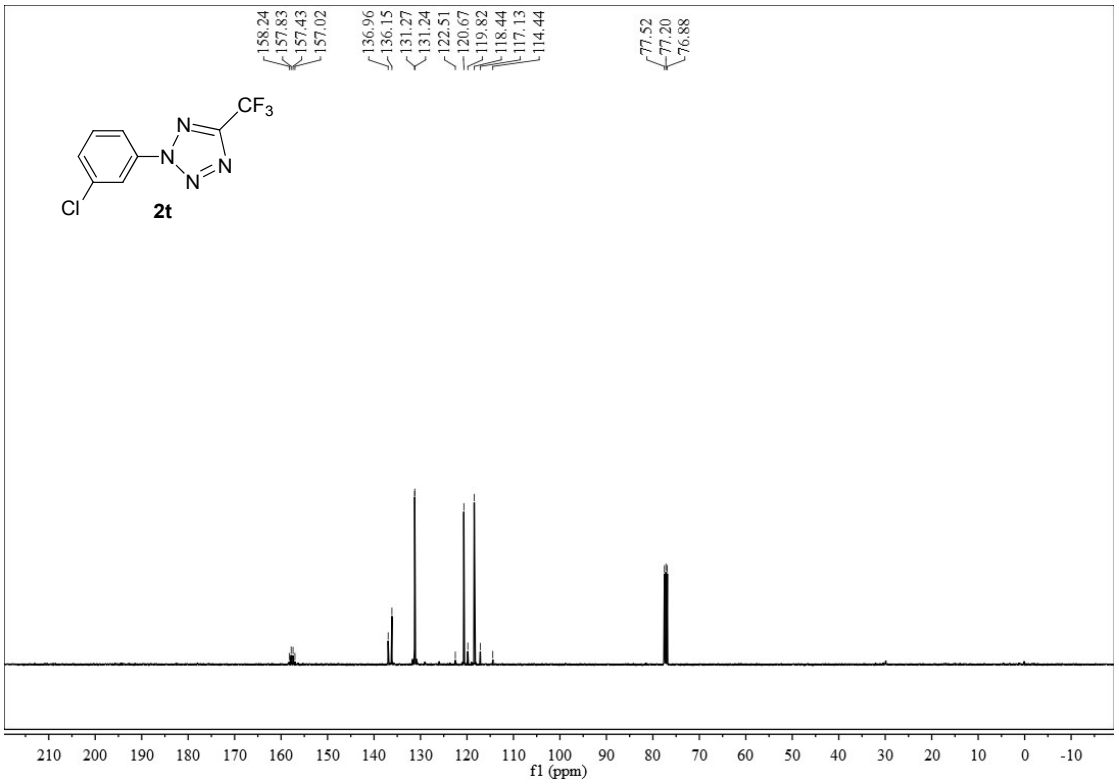




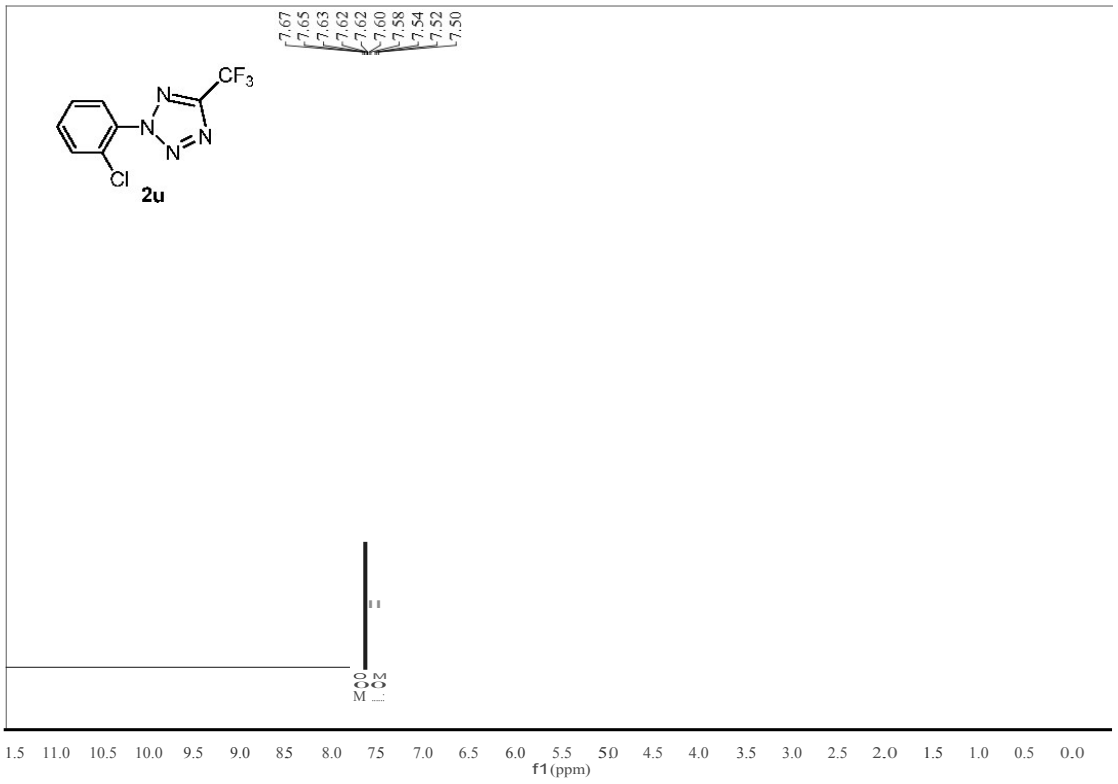
2-(3-chlorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2t)

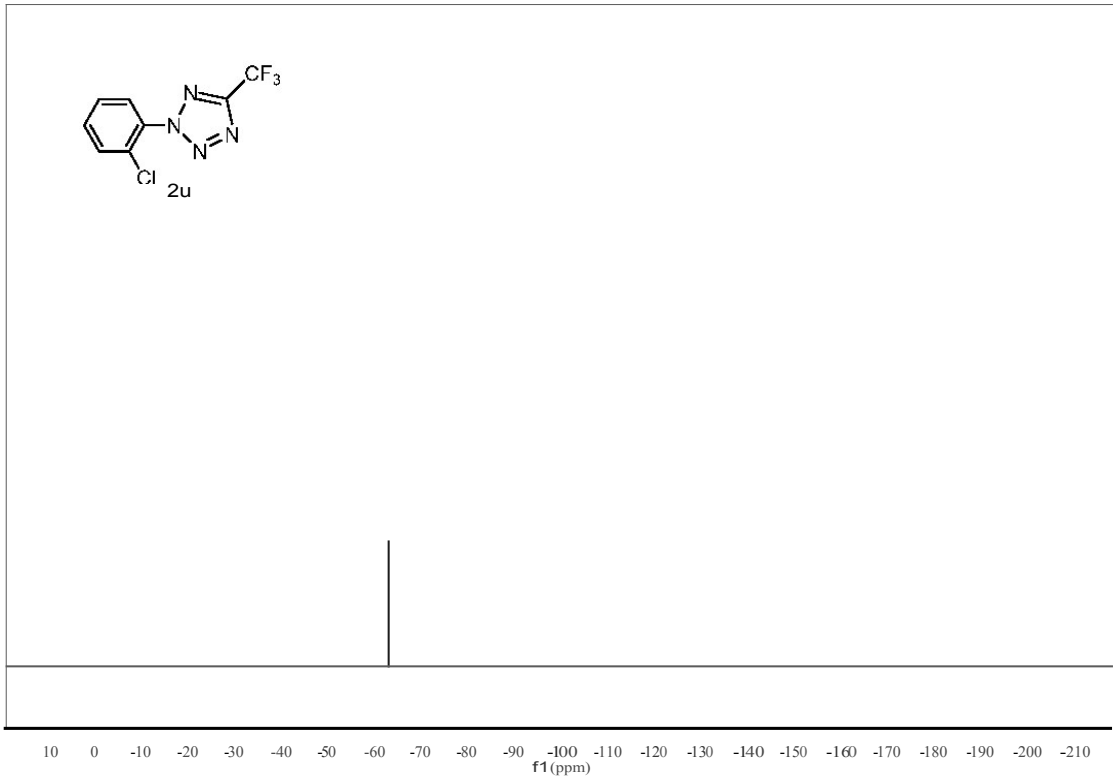


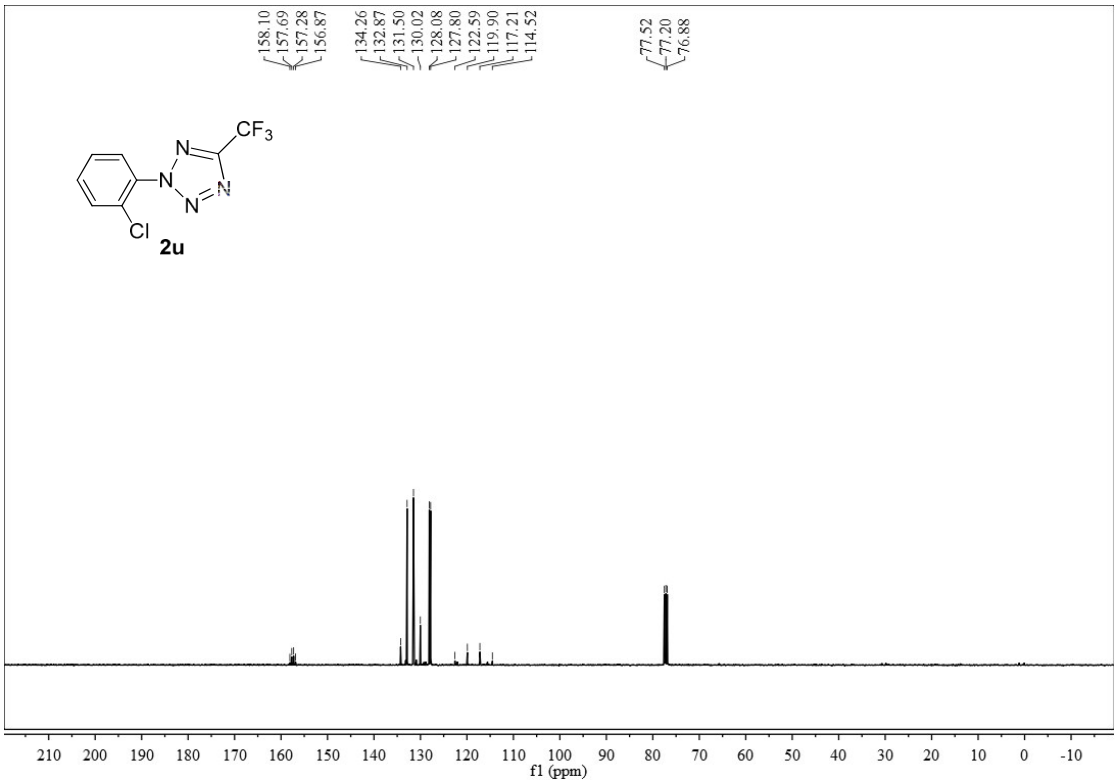

-63.68
CF3
N
N
N
N
Cl
2t
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


158.24
157.83
157.43
157.02
136.96
136.15
131.27
131.24
122.51
120.67
119.82
118.44
117.13
114.44
77.52
77.20
76.88
CF3
N
N
N
N
Cl
2t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

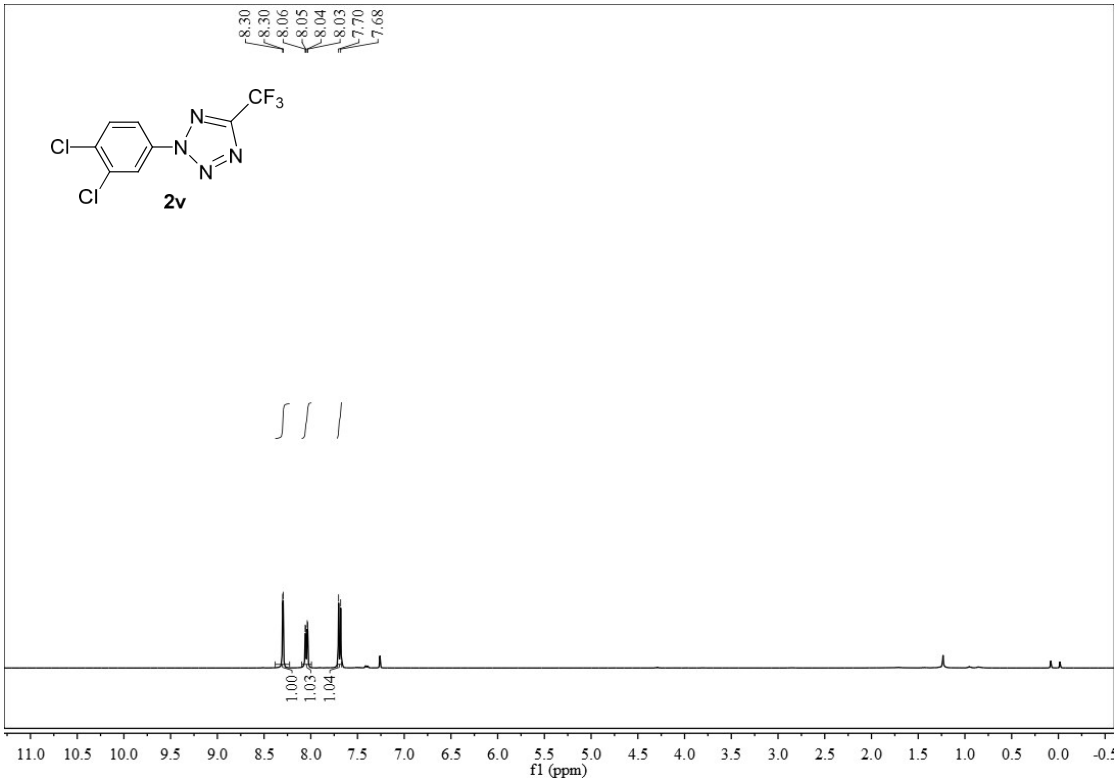
2-(2-chlorophenyl)-5-(trifluoromethyl)-2H-tetrazole (2u)

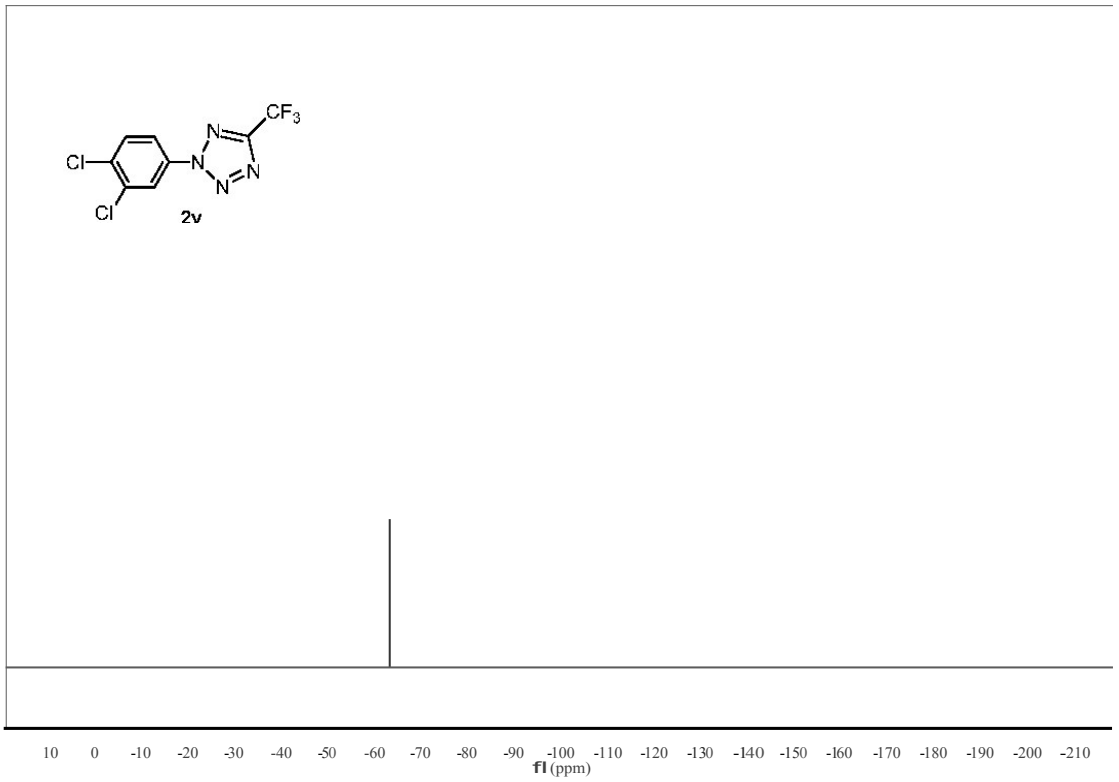


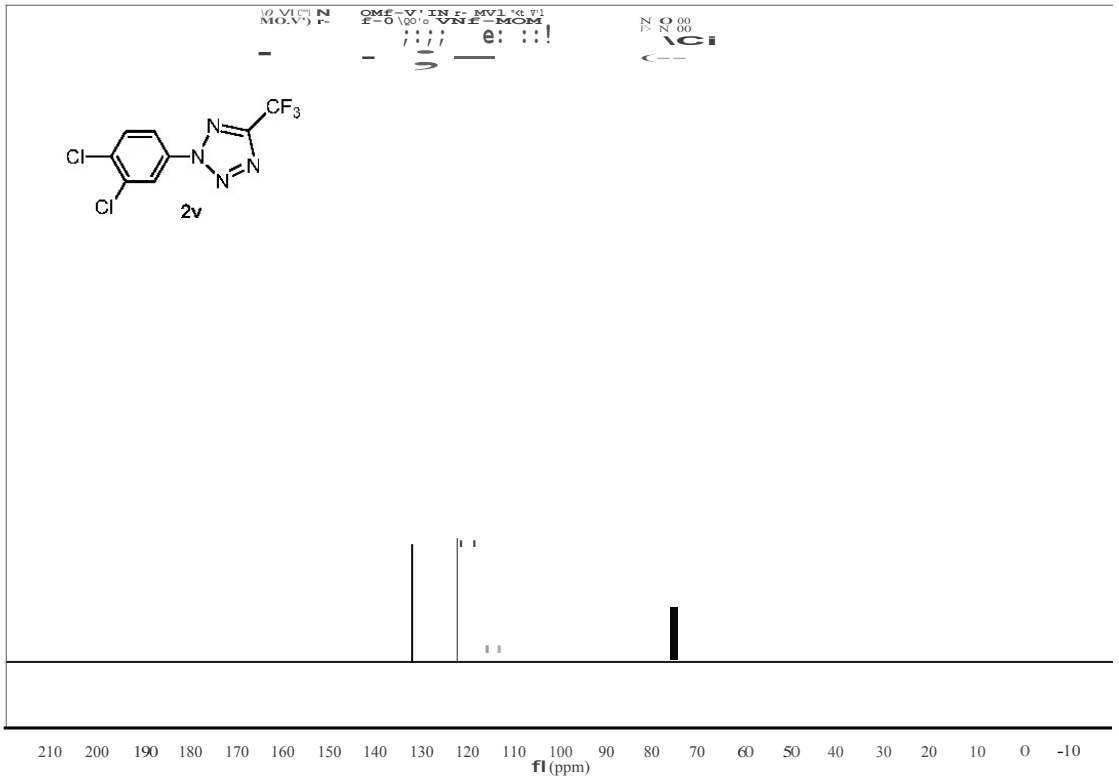




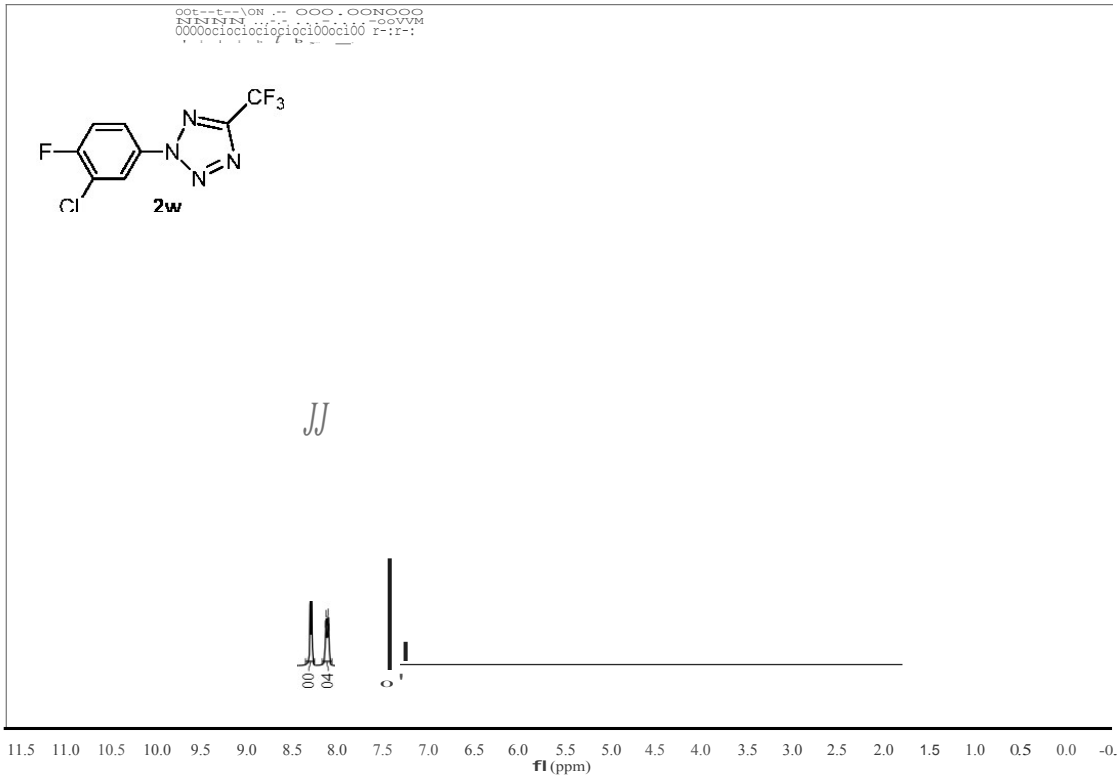
2-(3,4-dichlorophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2v)

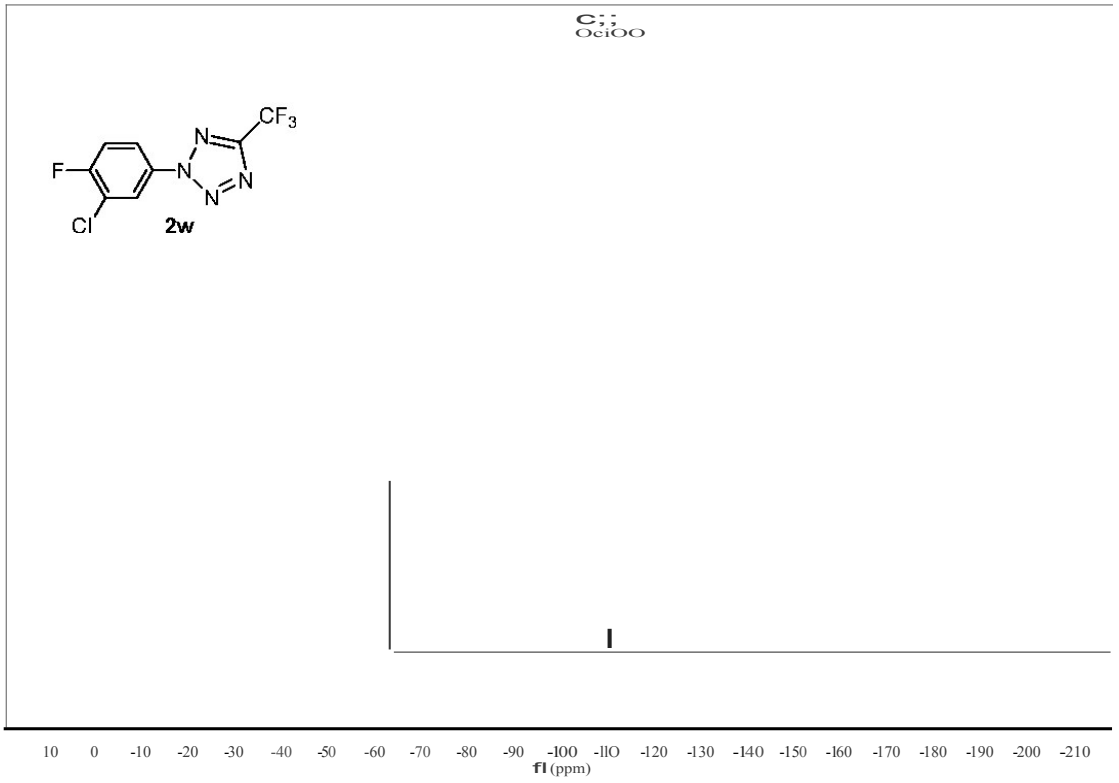


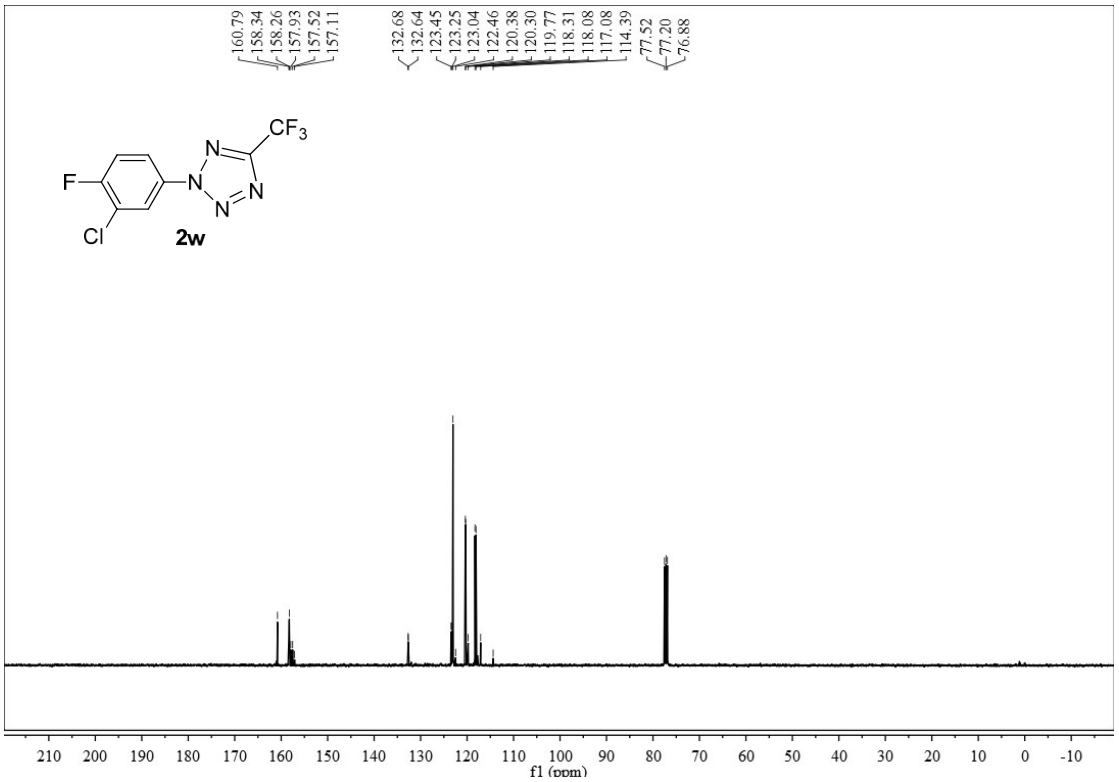

CF3
N
N
N
Cl
Cl
2v
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
fl (ppm)


CF3
N
N
N
Cl
Cl
2v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
fl (ppm)

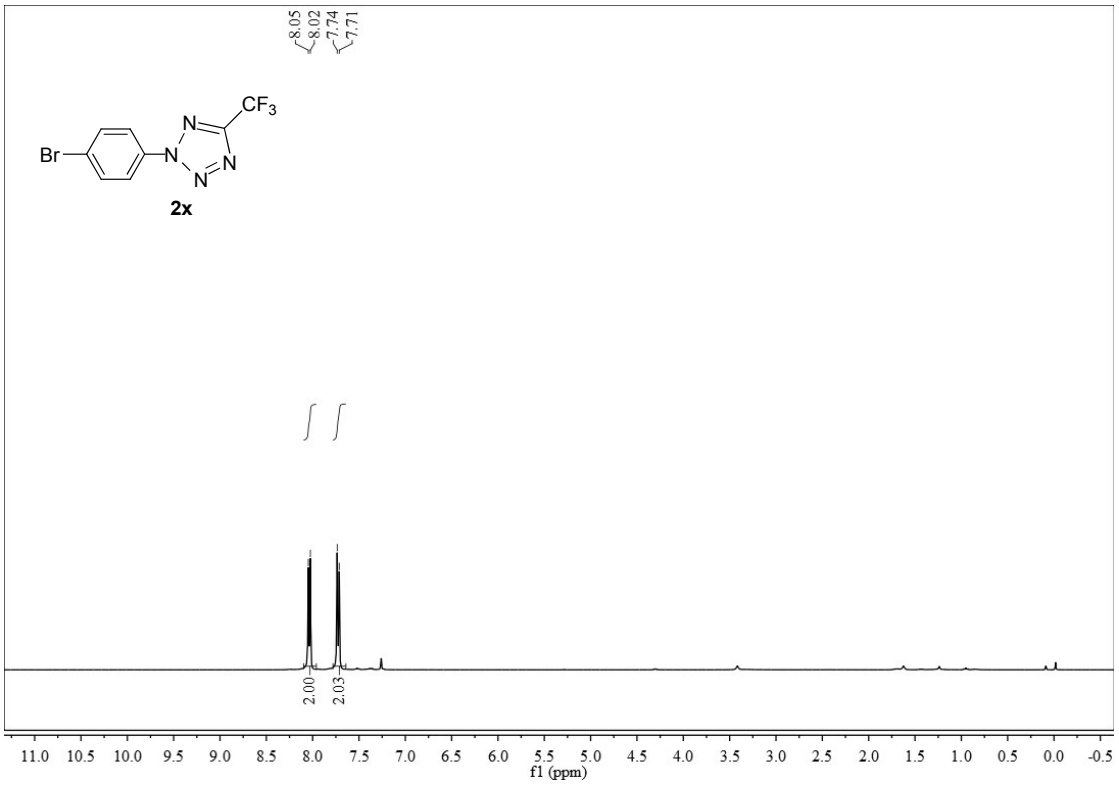
2-(3-chloro-4-fluorophenyl)-5-(trifluoromethyl)-2H-tetrazole (2w)

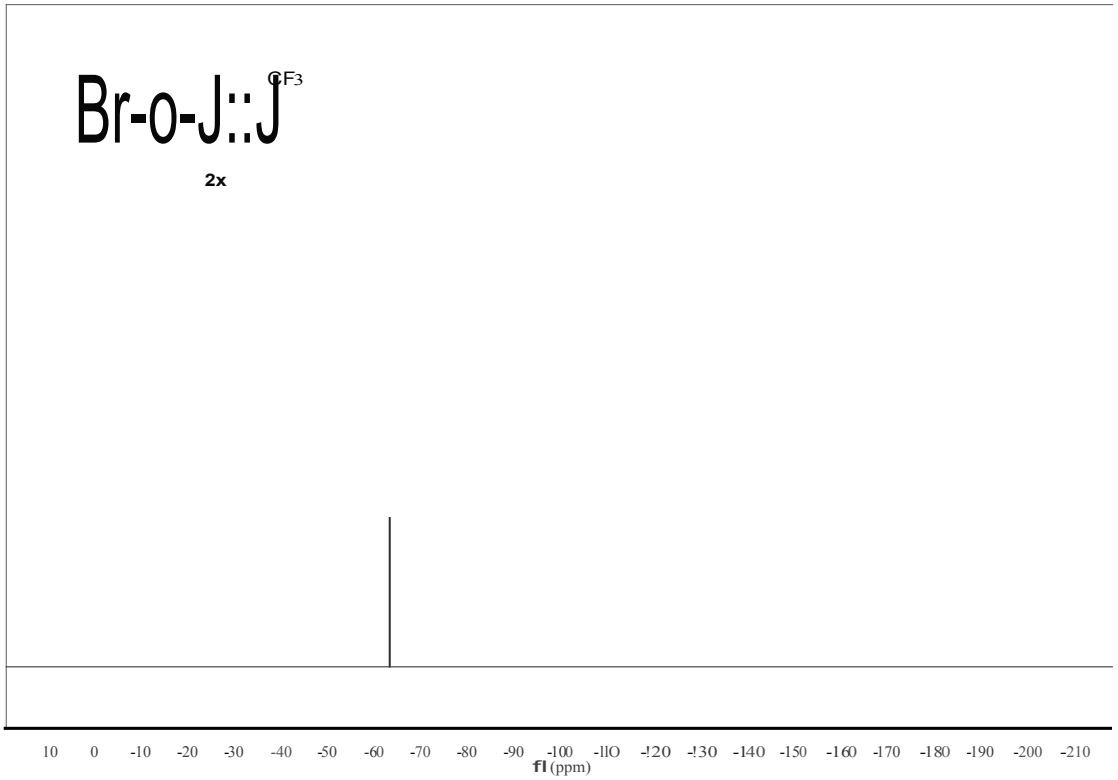


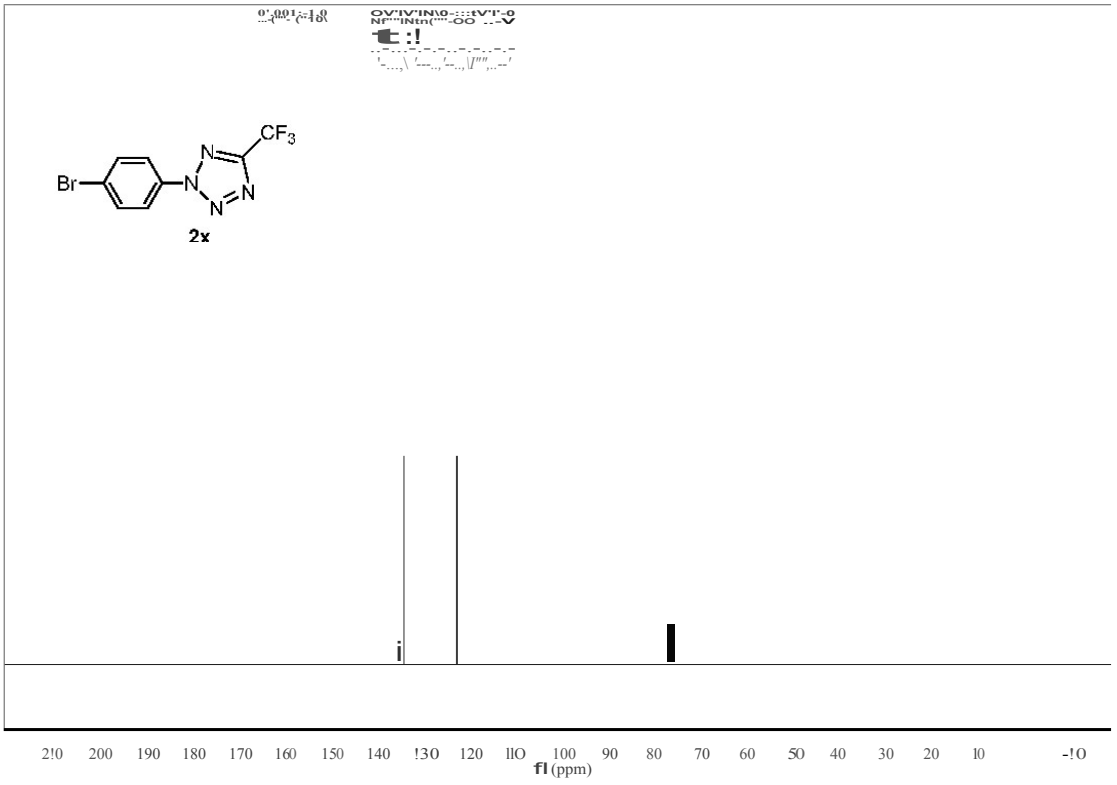




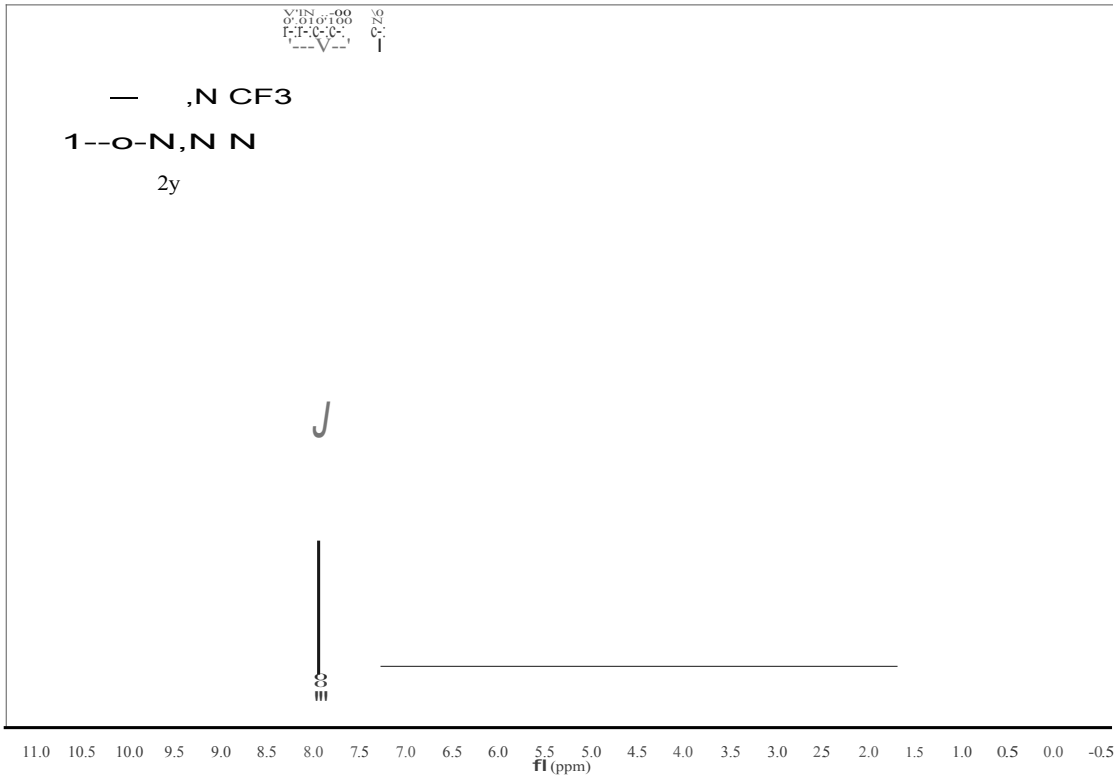
2-(4-bromophenyl)-5-(trifluoromethyl)-2*H*-tetrazole (2x)

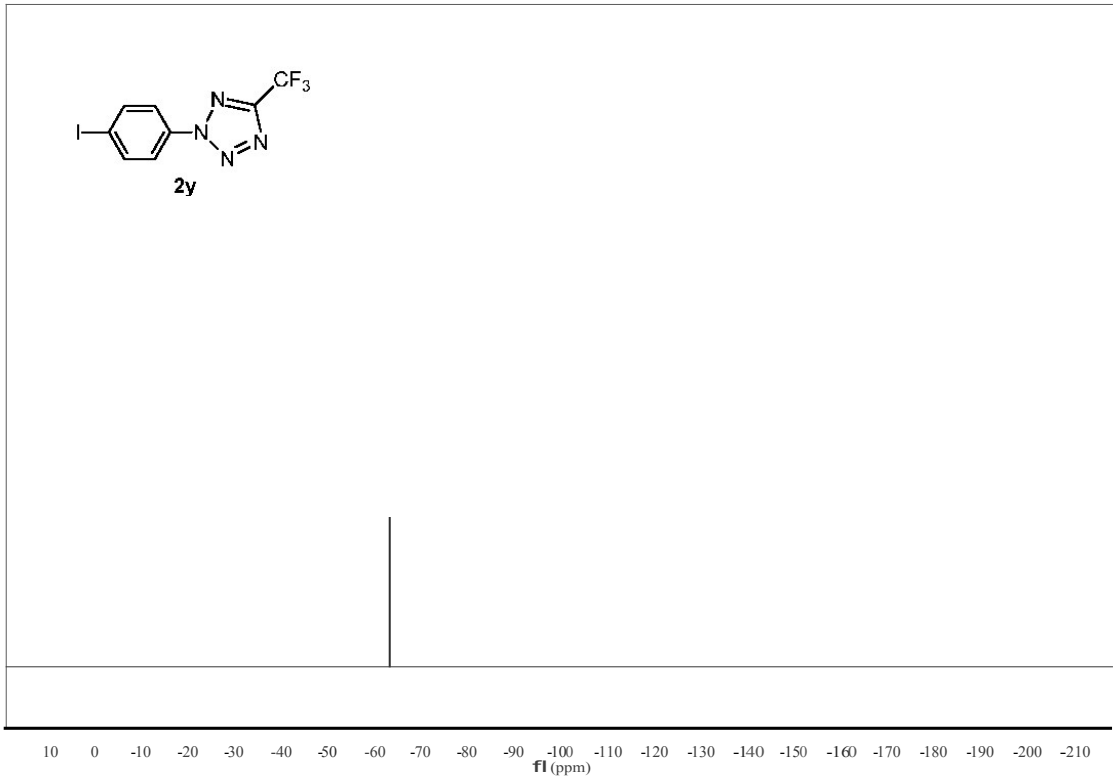


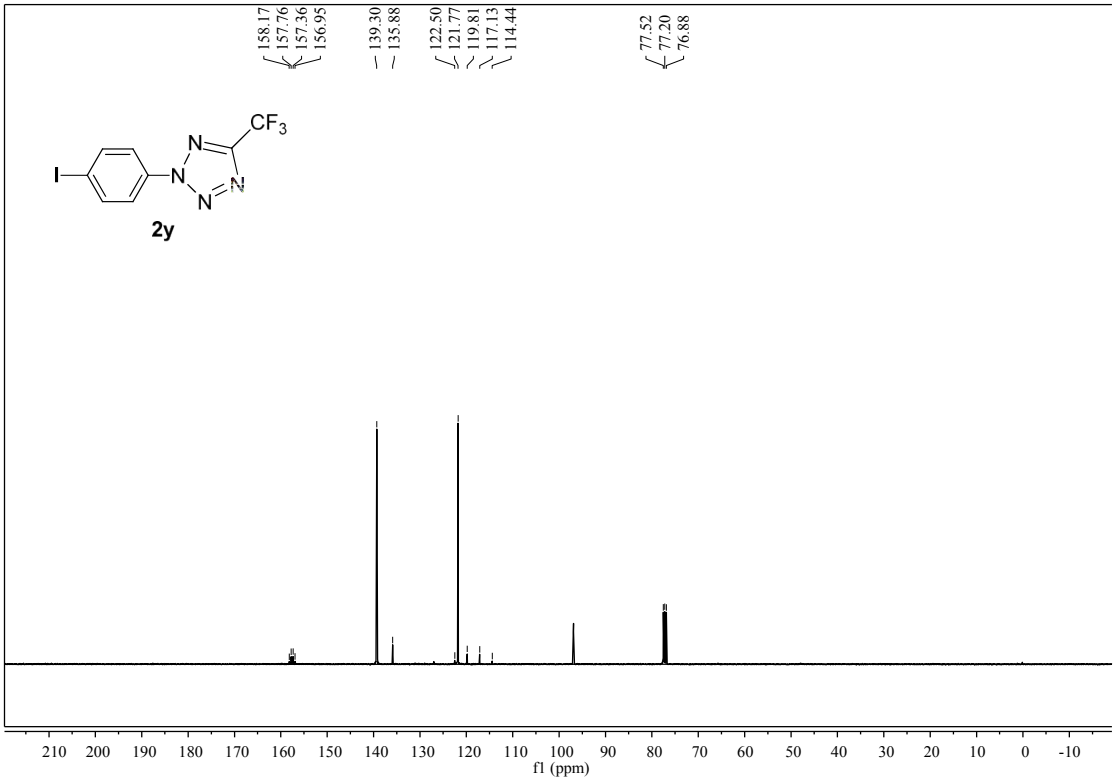

Br-o-J::J
CF3
2x
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -llO -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
fl (ppm)


Br
N
N
N
CF3
2x
i
2!0 200 190 180 170 160 150 140 !30 120 llO 100 90 80 70 60 50 40 30 20 l0 -!0
fl (ppm)

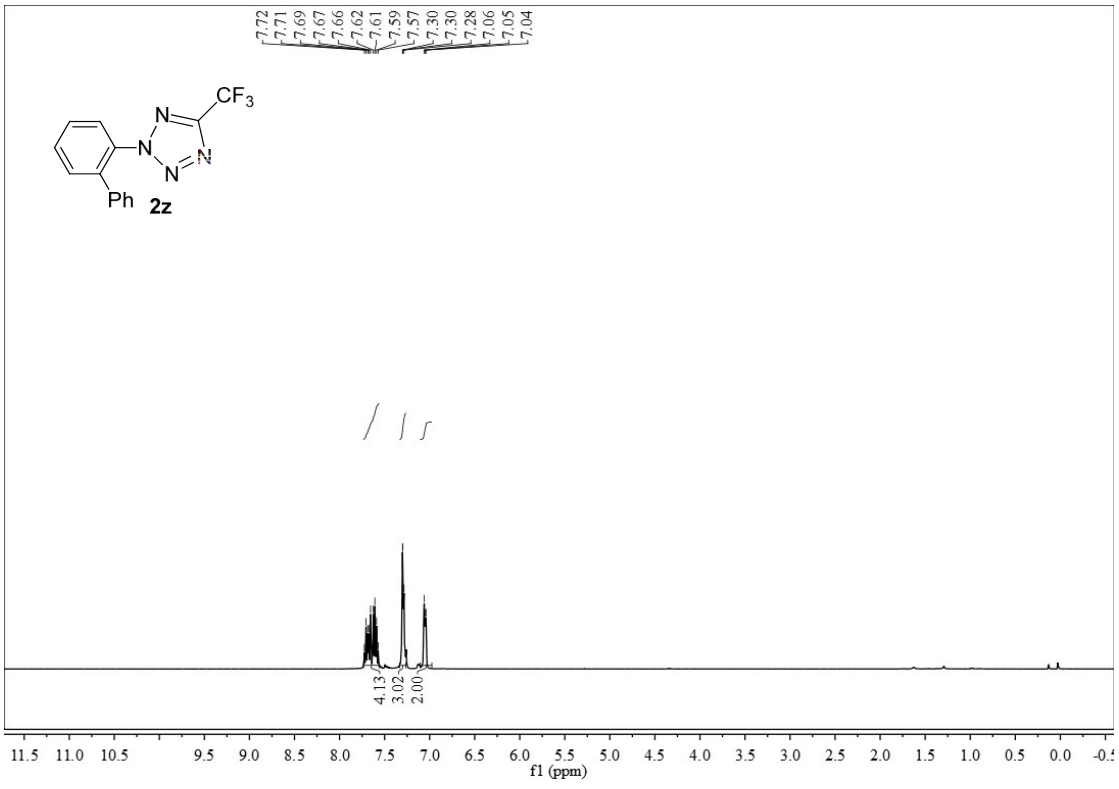
2-(4-iodophenyl)-5-(tritluoromethyi)-2H-tetrazole (2y)

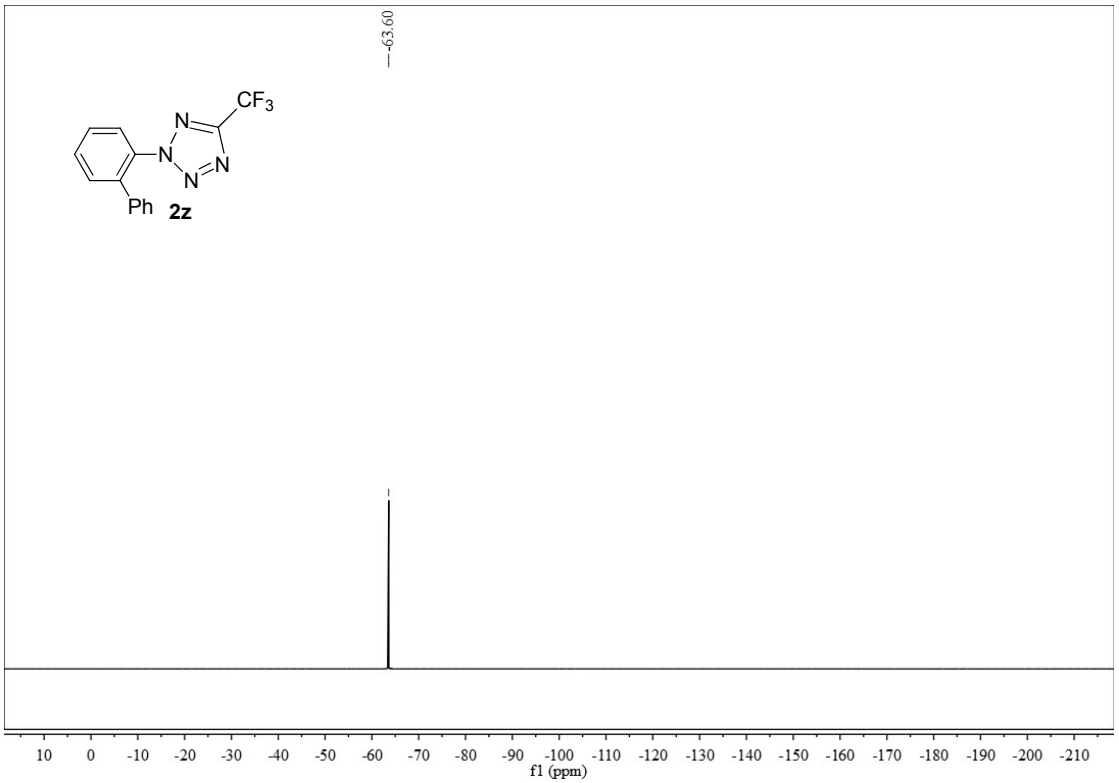


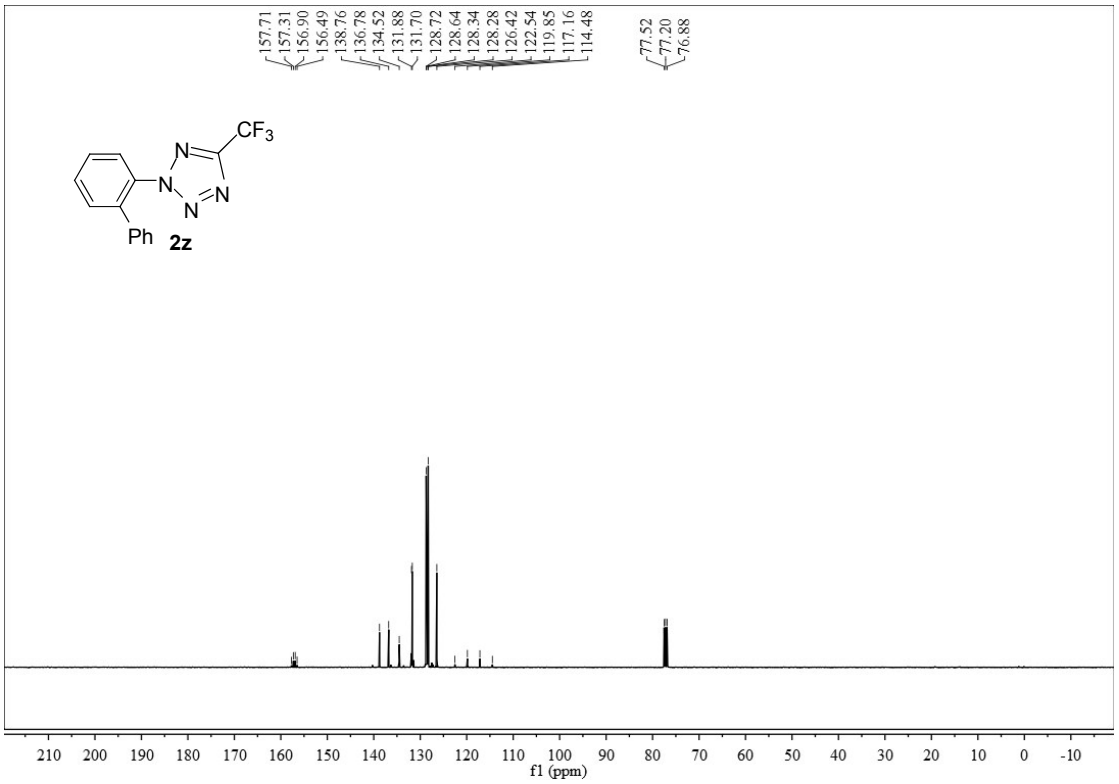




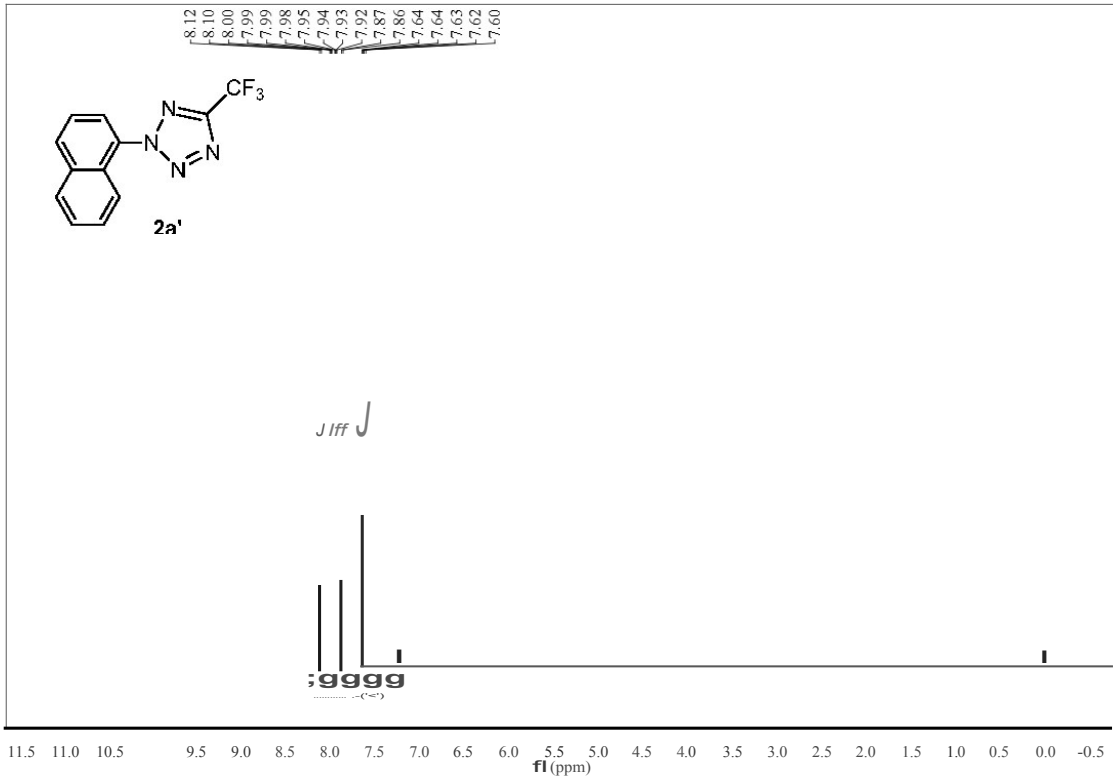
2-([1,1'-biphenyl]-2-yl)-5-(trifluoromethyl)-2*H*-tetrazole (2z)

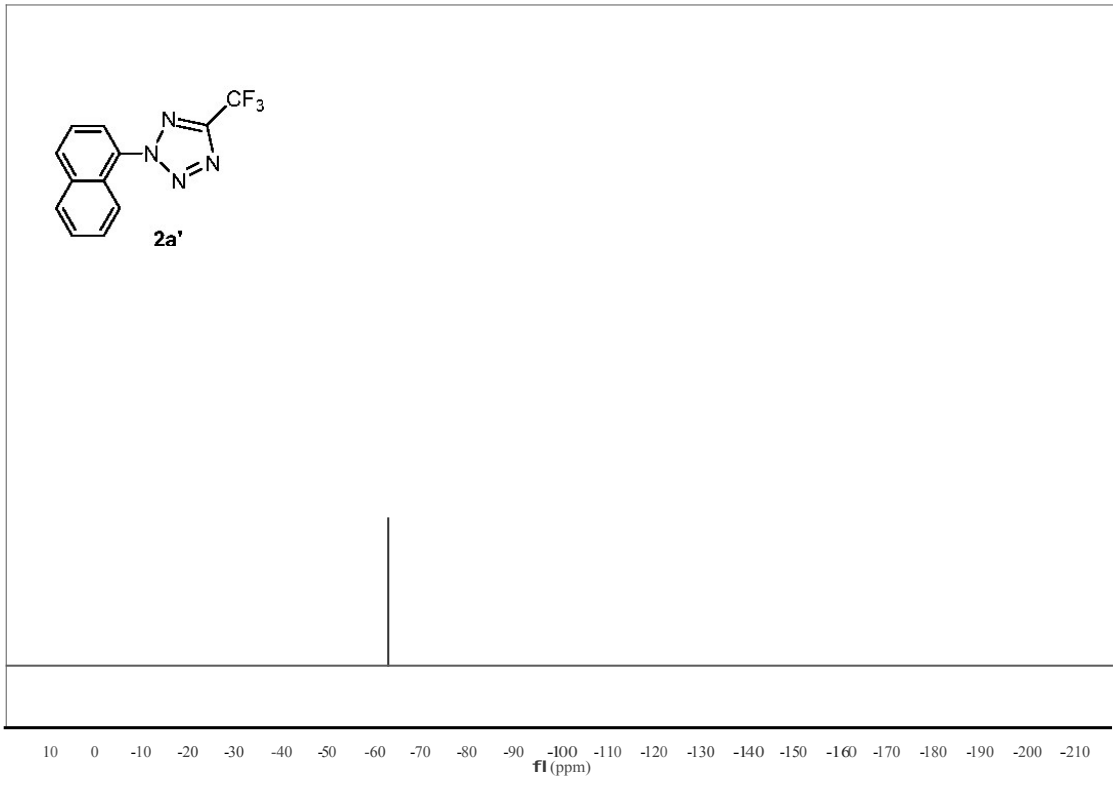


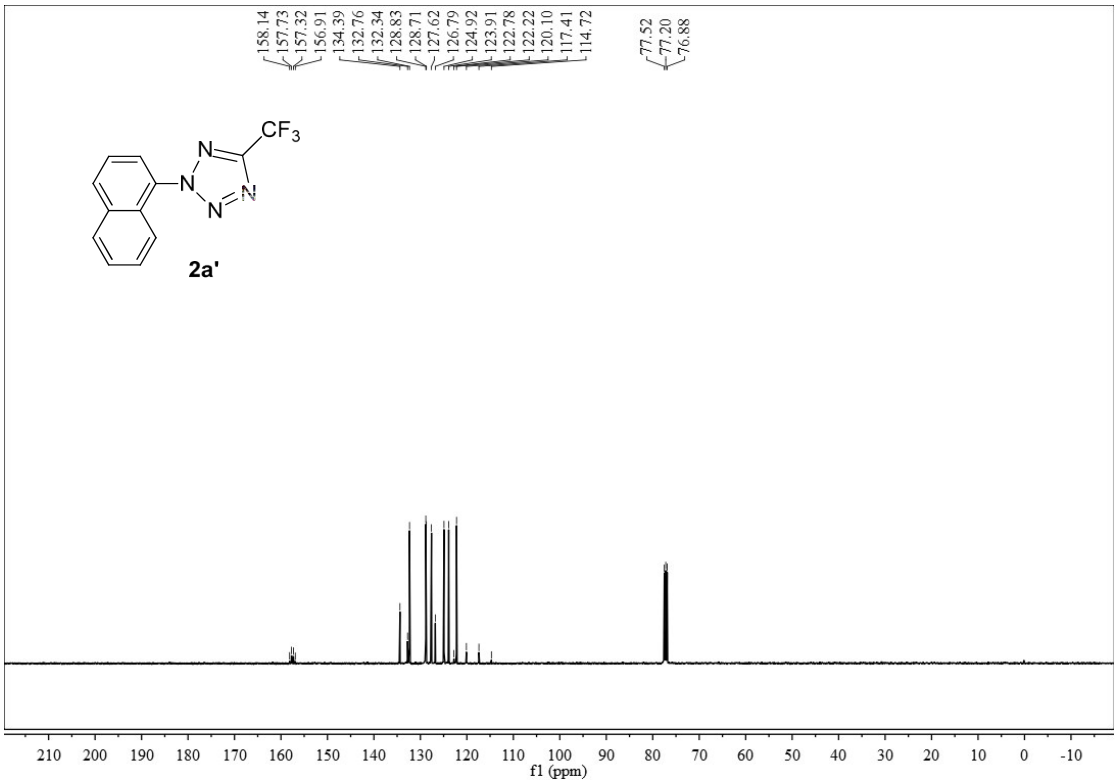

-63.60
CF3
N
N
N
N
Ph
2z
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


157.71
157.31
156.90
156.49
138.76
136.78
134.52
131.88
131.70
128.72
128.64
128.34
128.28
126.42
122.54
119.85
117.16
114.48
77.52
77.20
76.88
CF3
N
N
N
N
Ph
2z
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

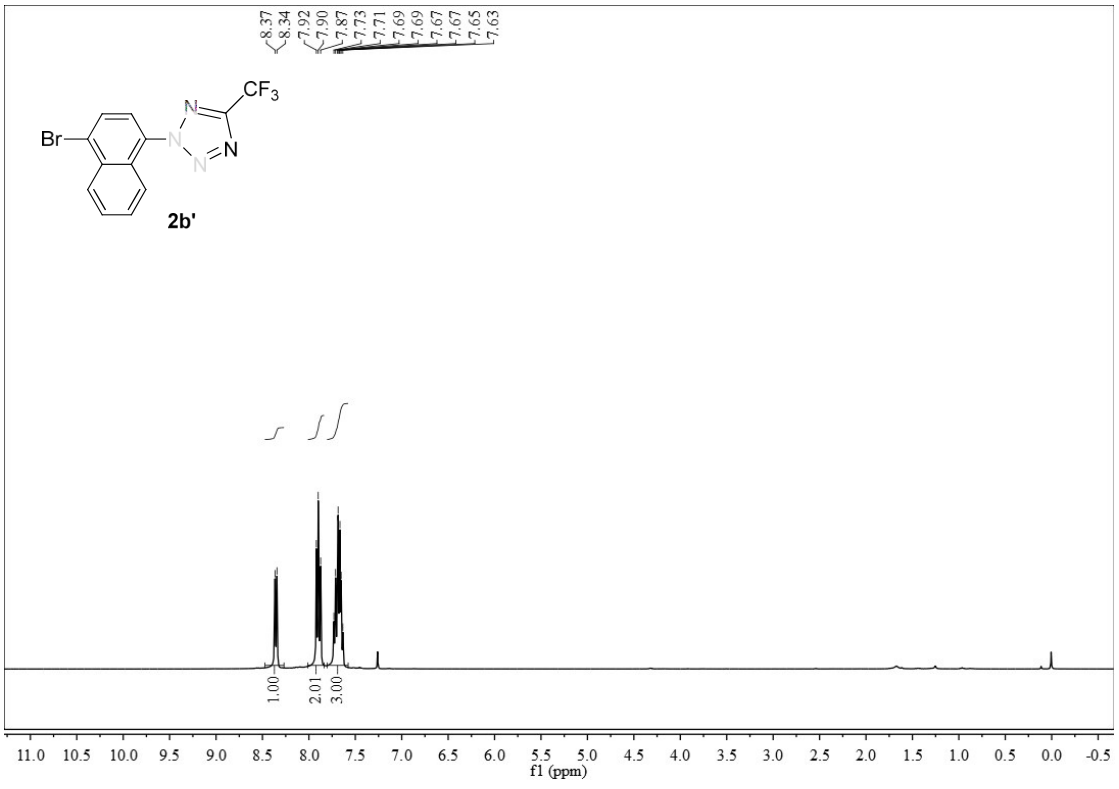
2-(naphthalen-1-yl)-5-(trifluoromethyl)-2H-tetrazole (2a')

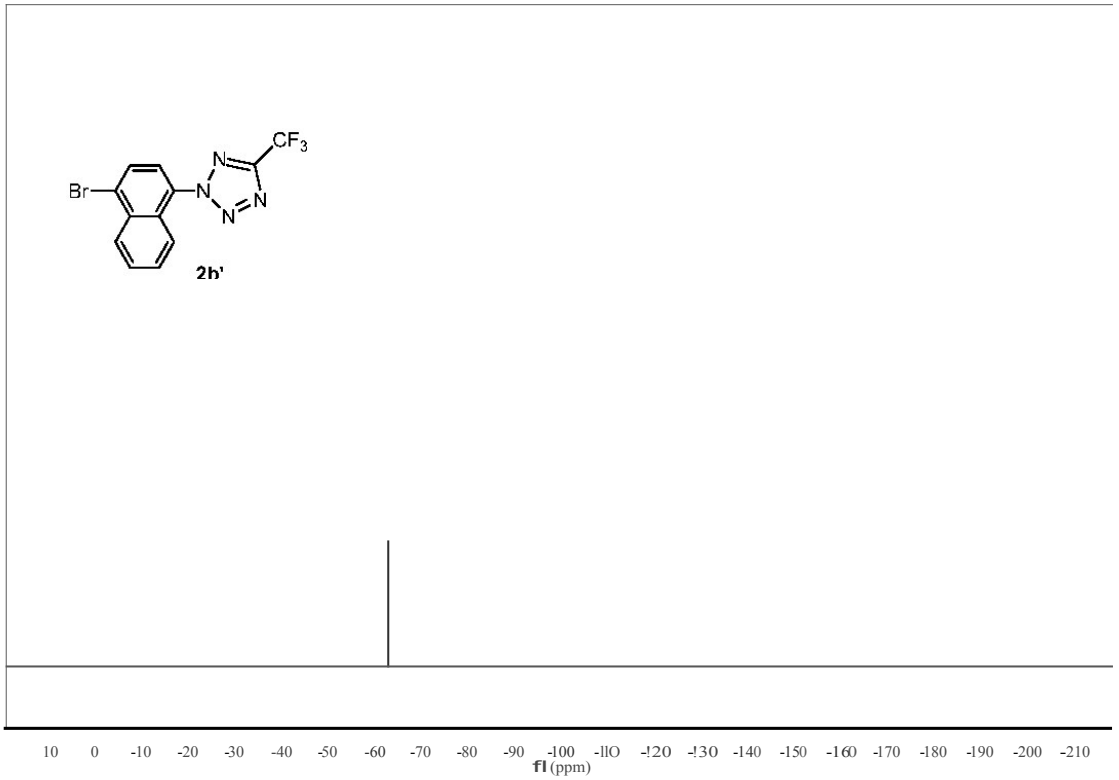


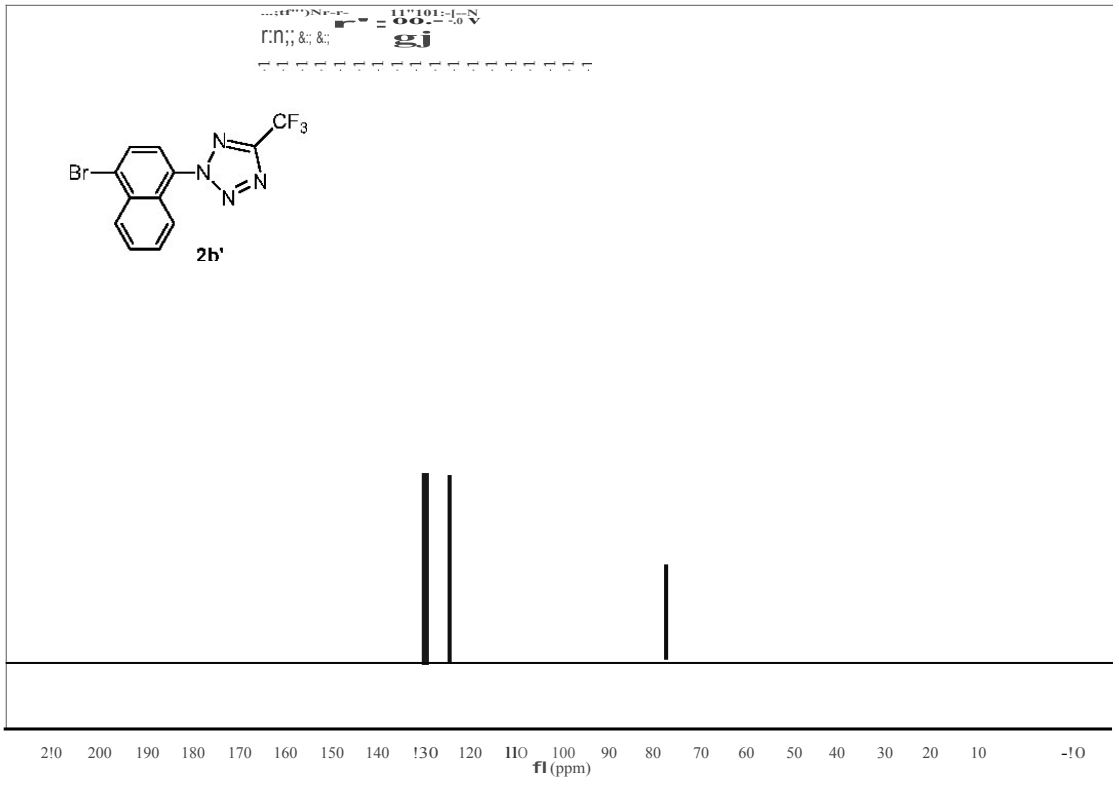




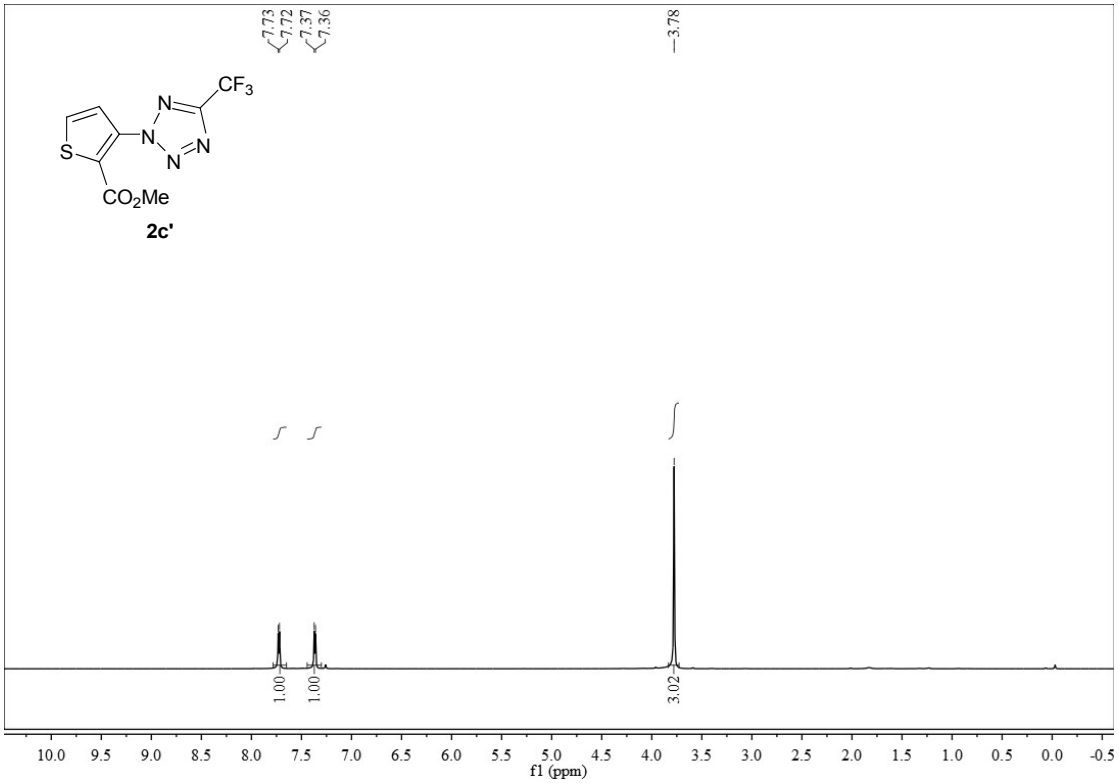
2-(4-bromonaphthalen-1-yl)-5-(trifluoromethyl)-2*H*-tetrazole (2b′)

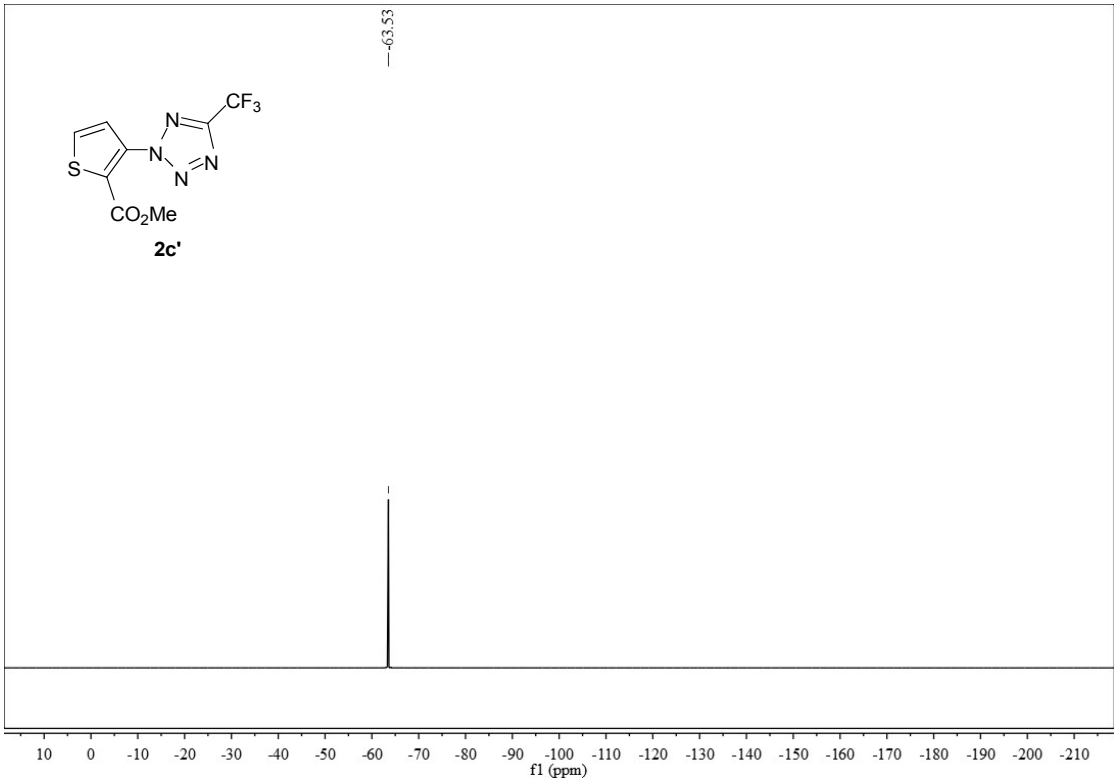


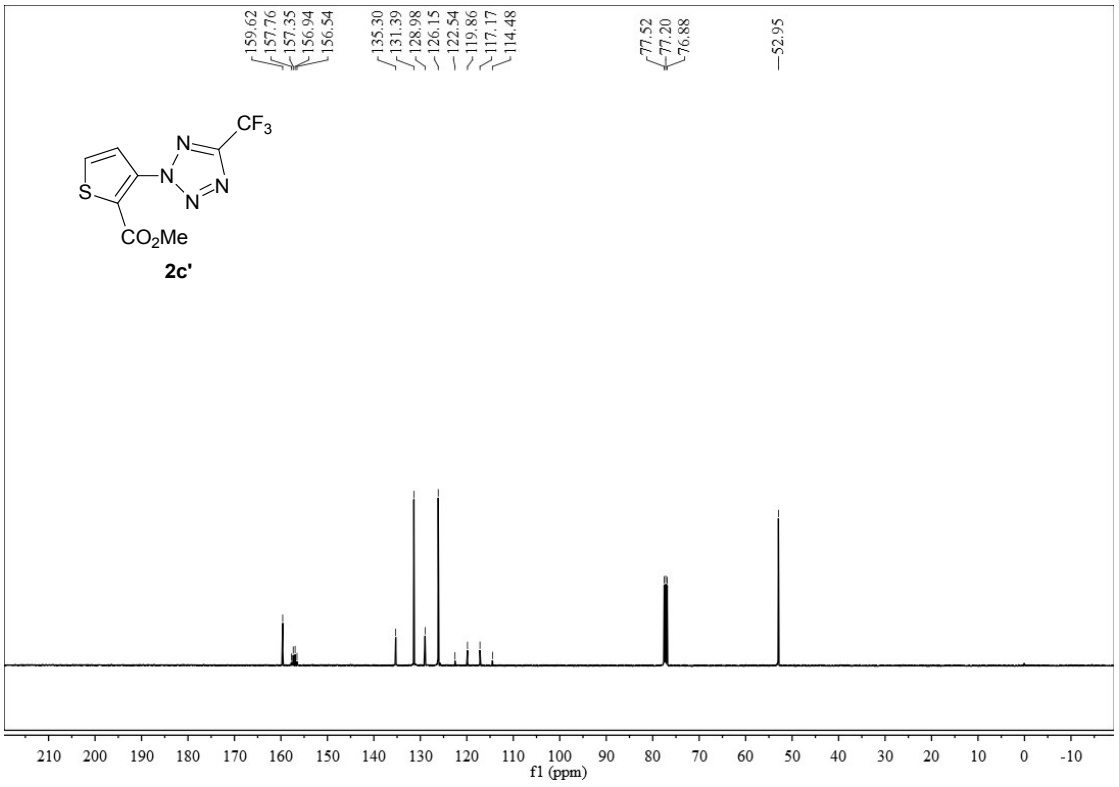

Br
N
N
N
CF3
2h'
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
fl (ppm)


Br
N
N
N
CF3
2h'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 -10
fl (ppm)

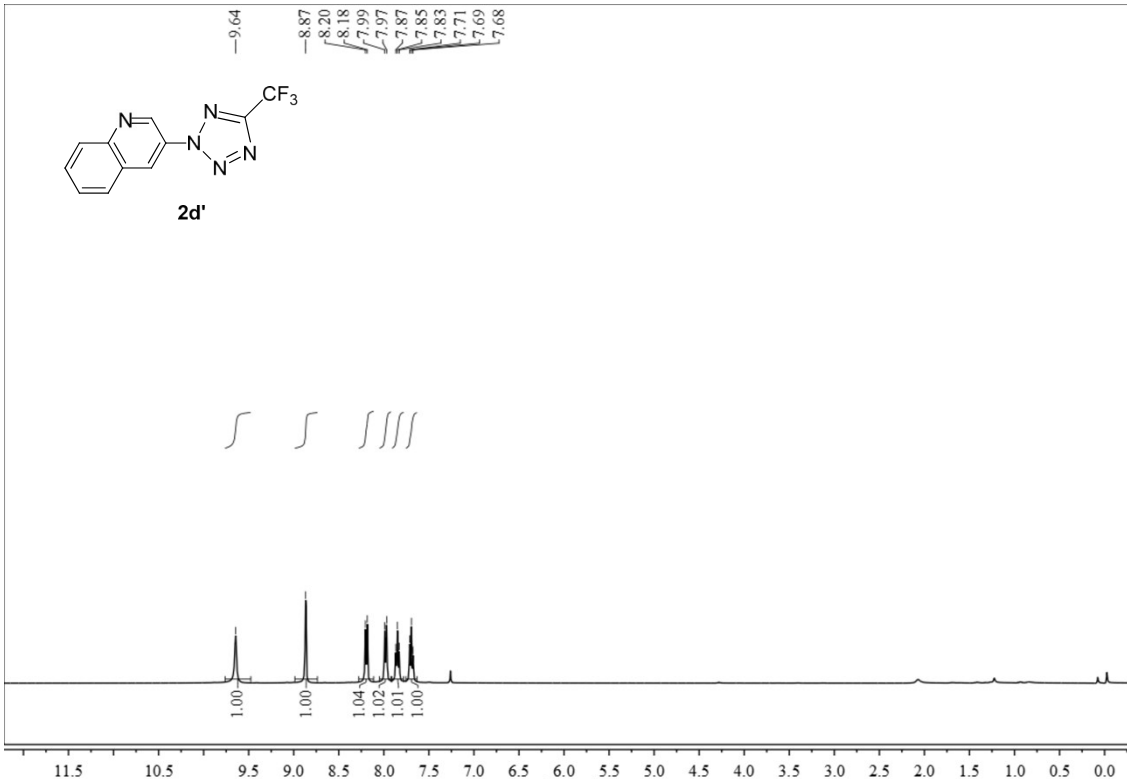
methyl 3-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)thiophene-2-carboxylate (2c′)

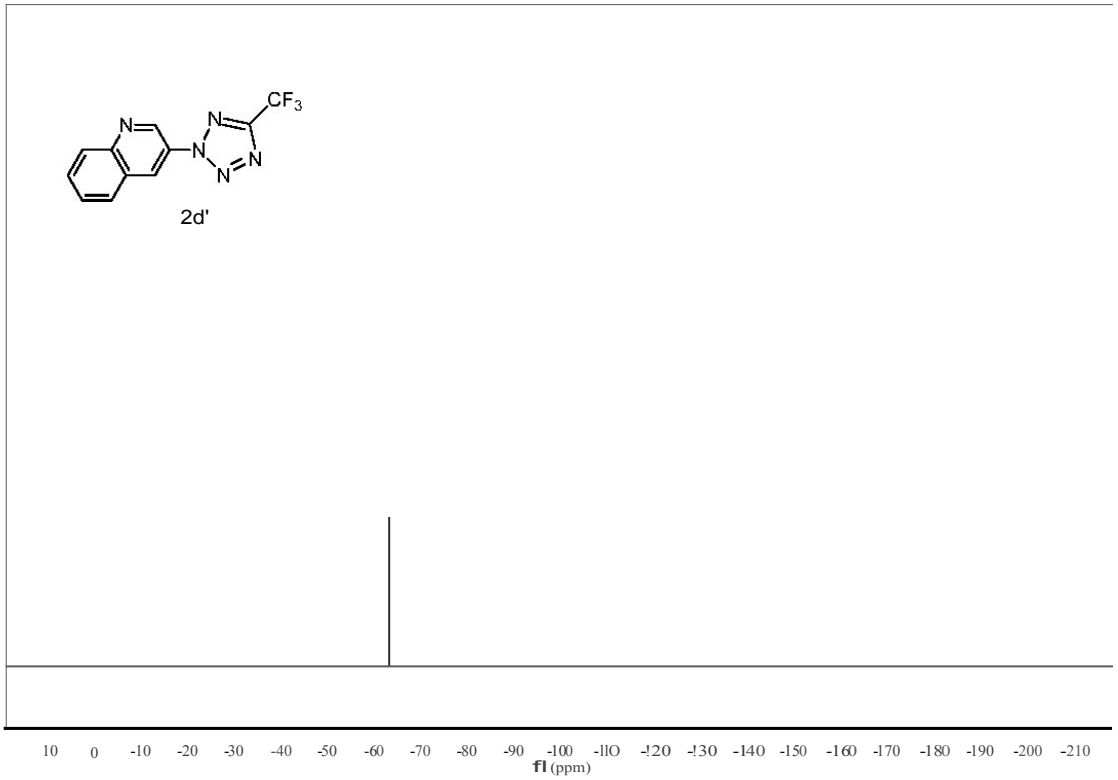


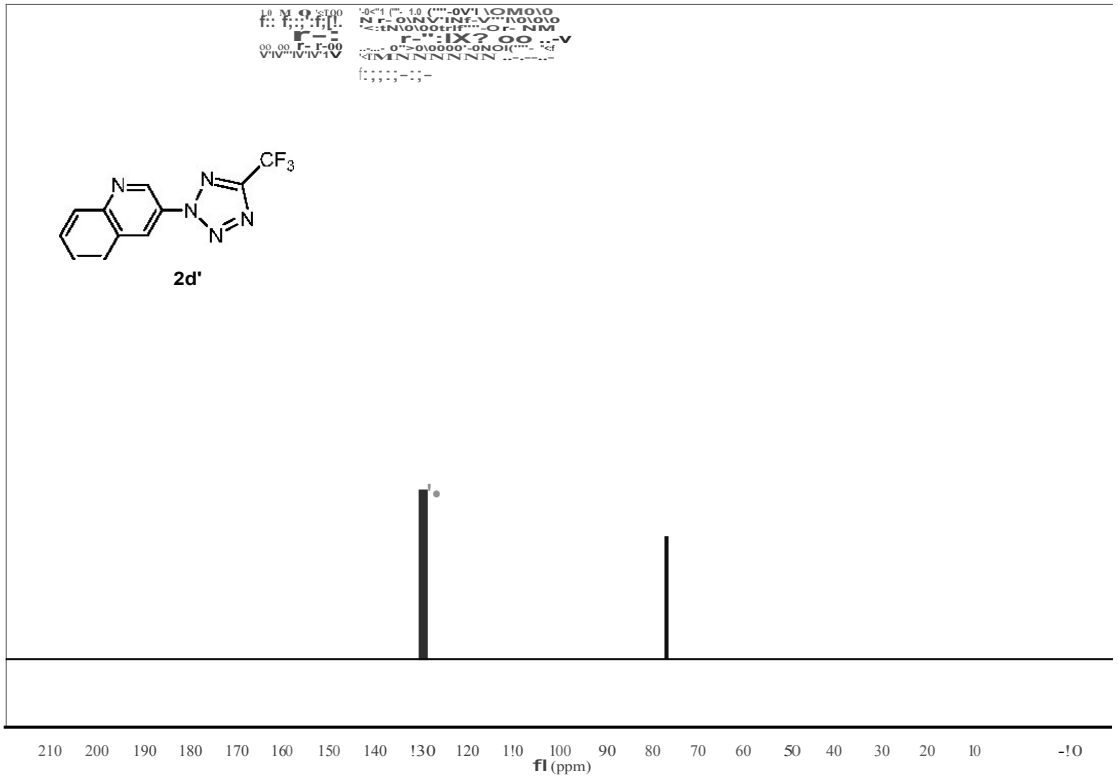




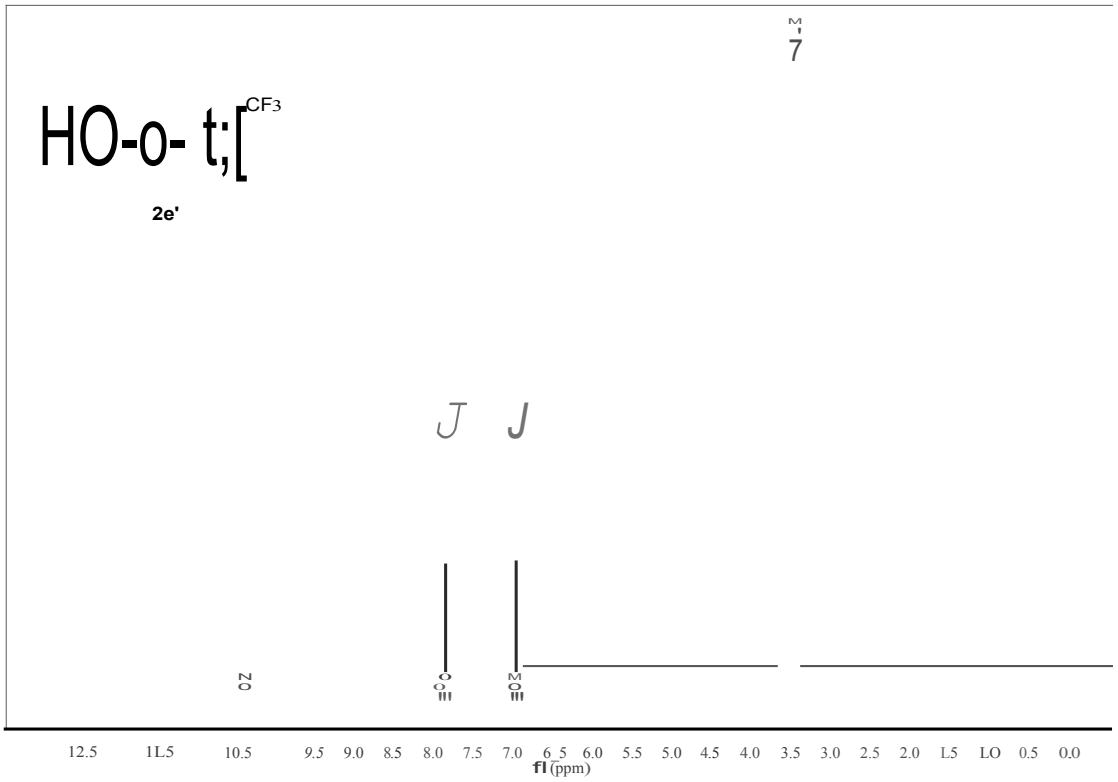
3-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)quinolone (2d′)

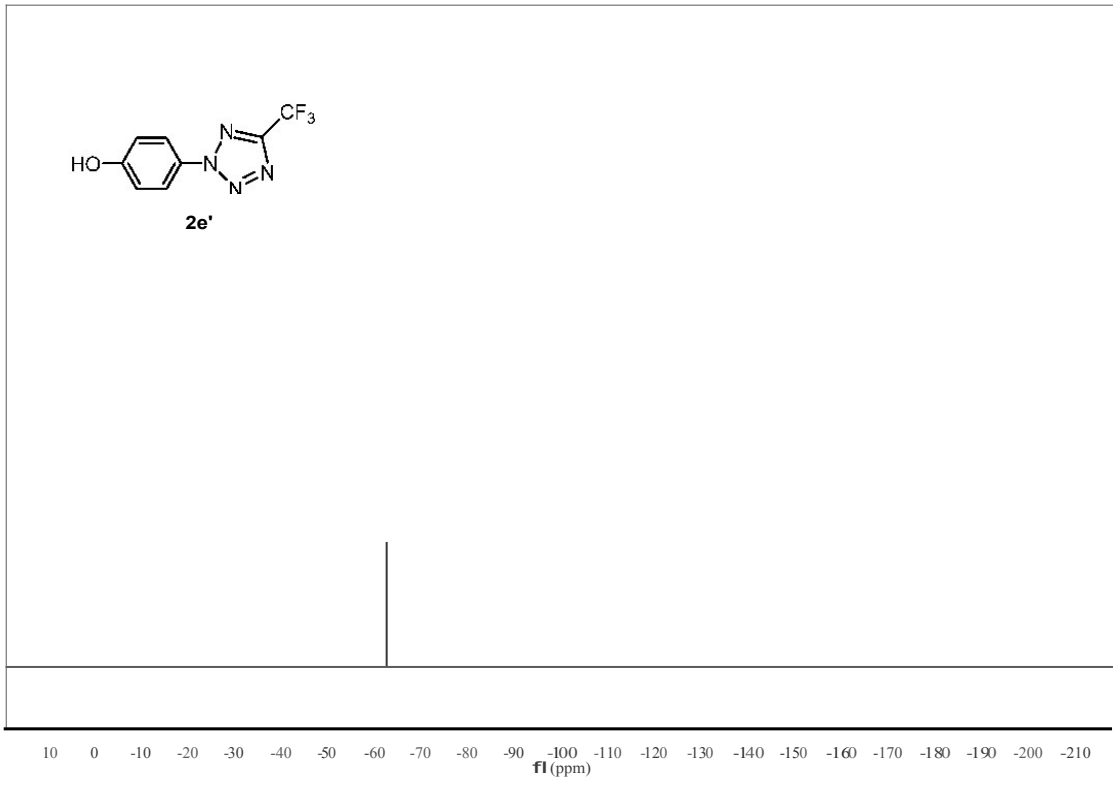


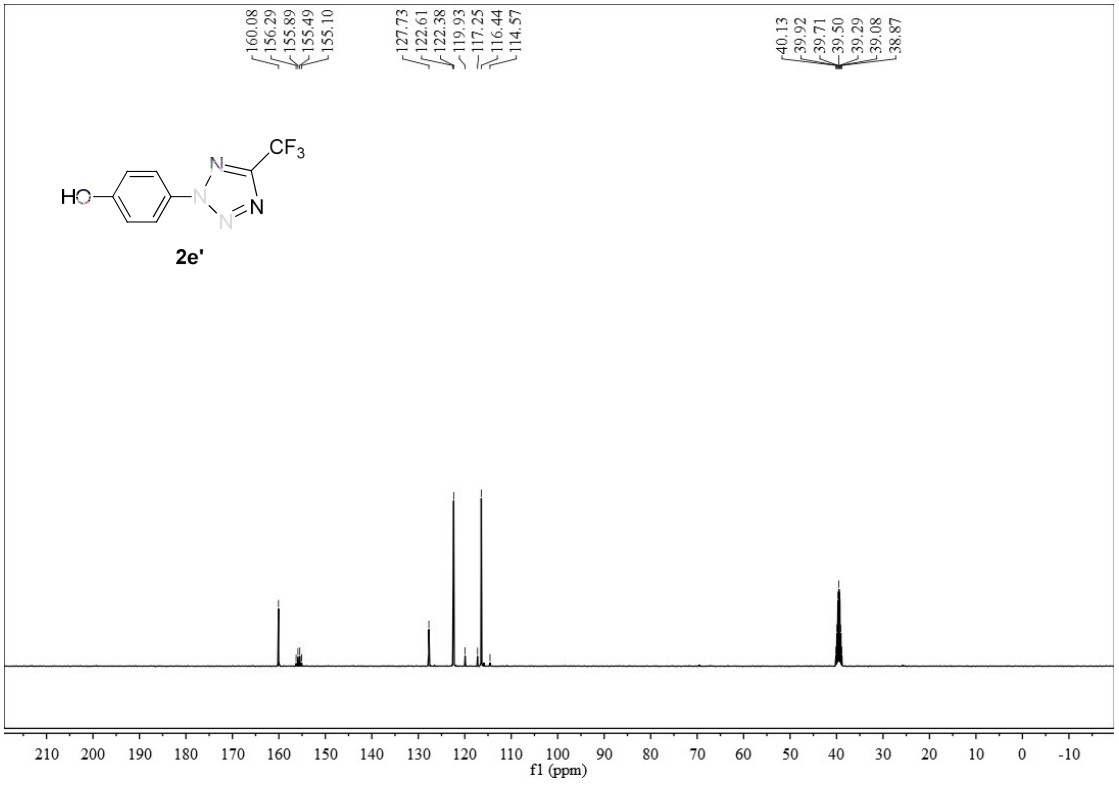

CF3
N
N
N
N
2d'
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


CF3
N
N
N
N
2d'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 -10
f1 (ppm)

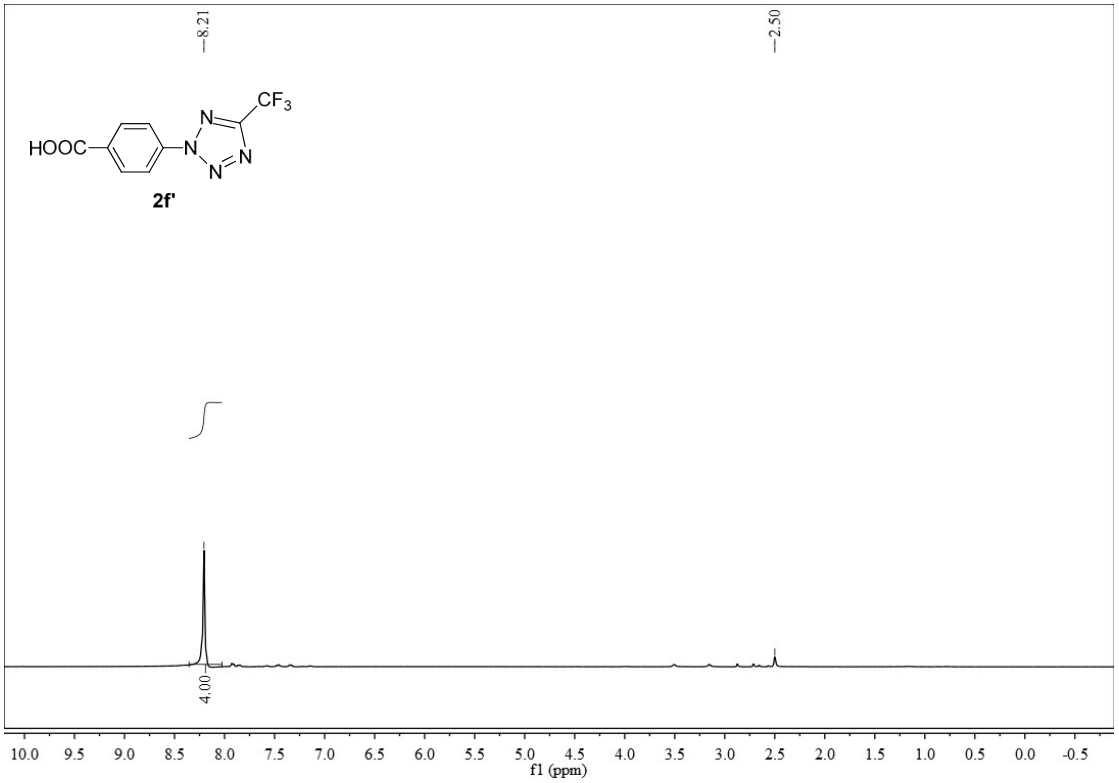
4-(5-(trifluoromethyi)-2H-tetrazol-2-yl)phenol (2e')

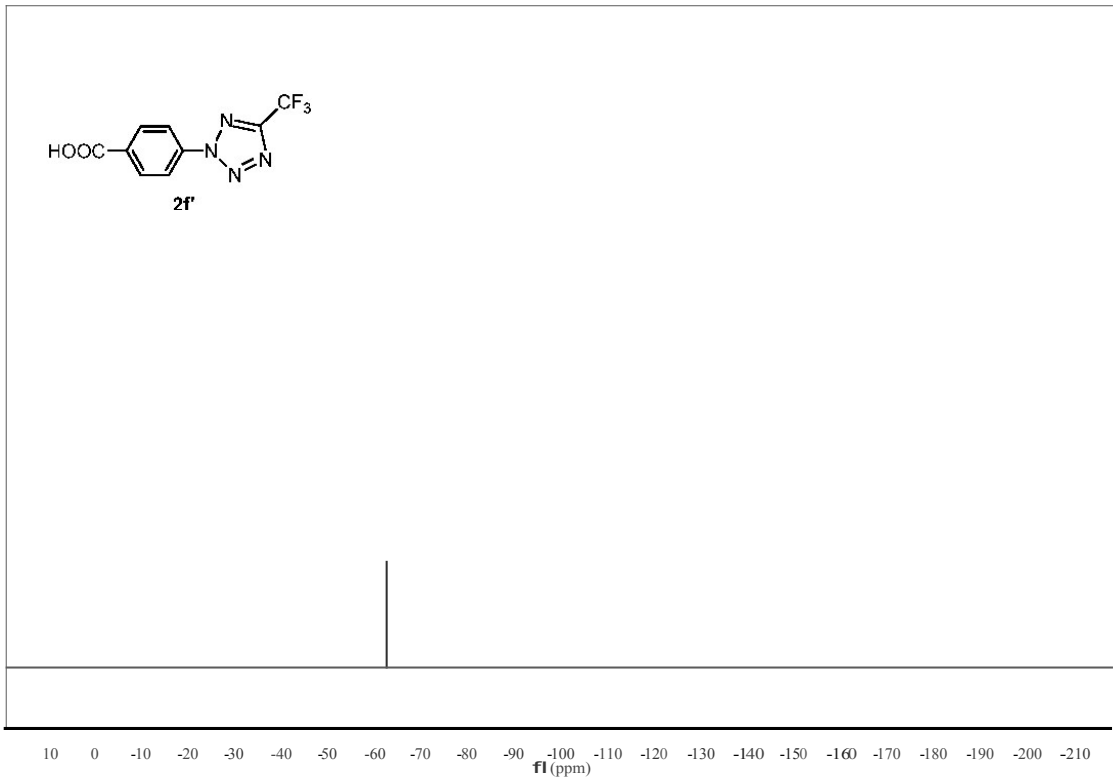


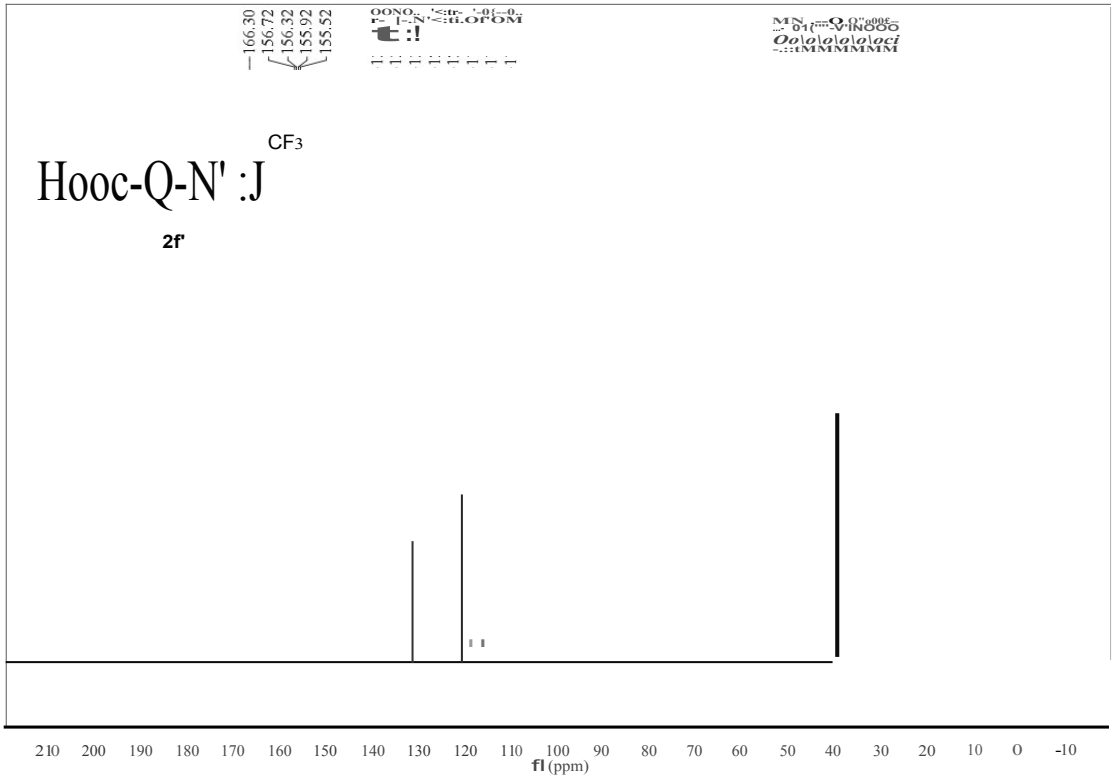




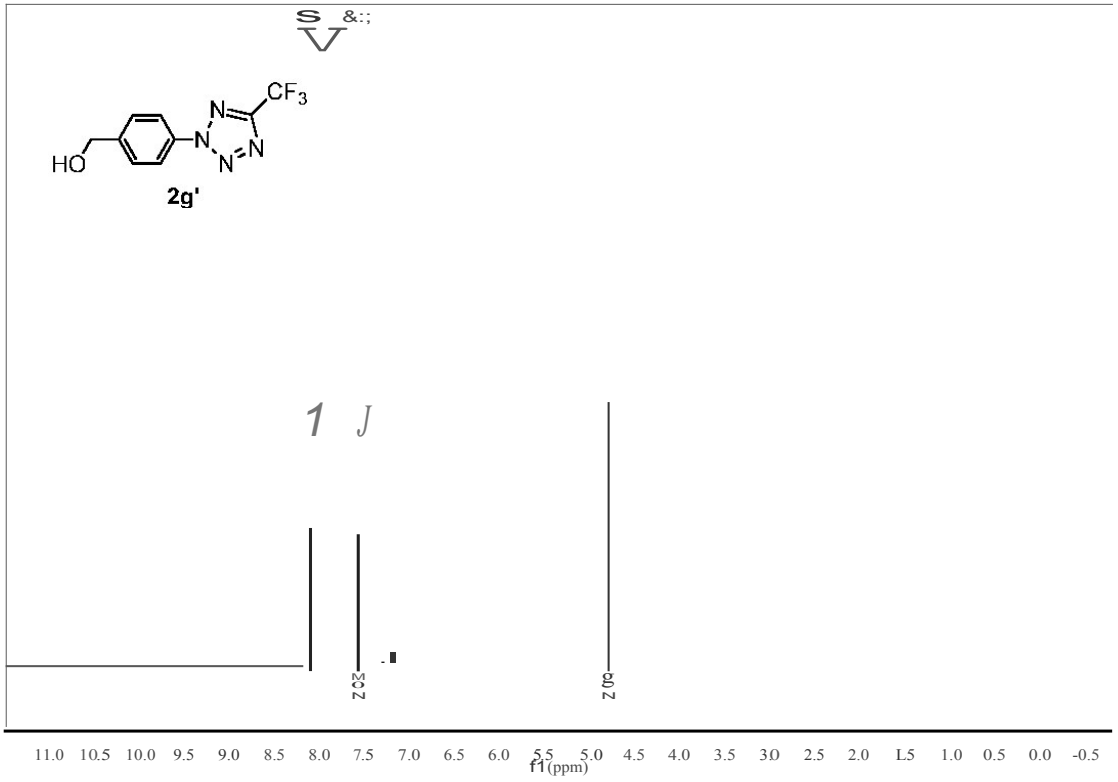
4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)benzoic acid (2f')

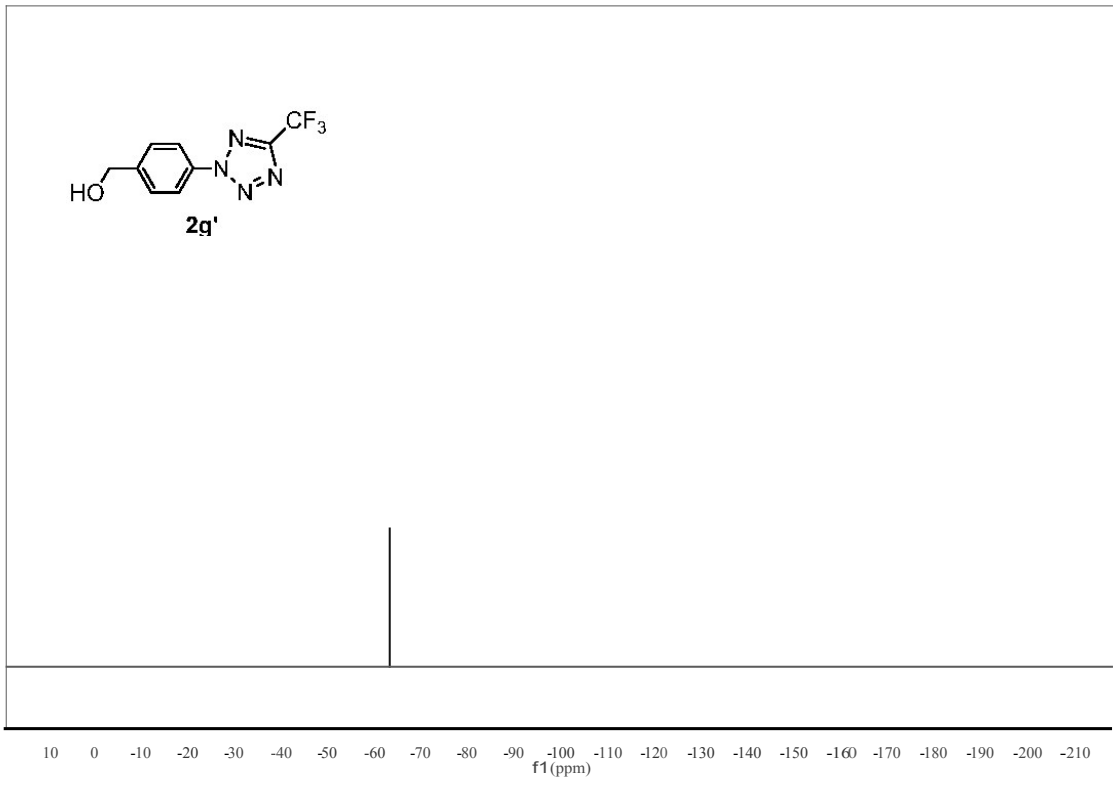


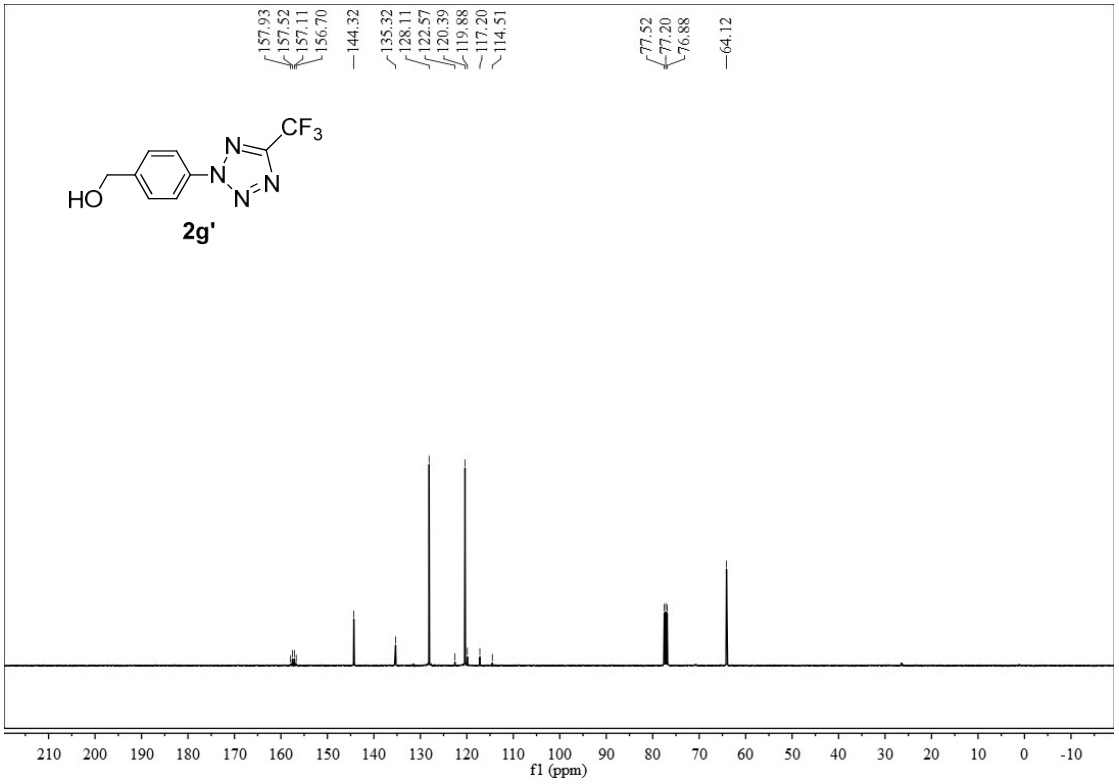

HOOC
N
N
N
N
CF3
2f'
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


166.30
156.72
156.32
155.92
155.52
CF3
Hooc-Q-N' :J
2f'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

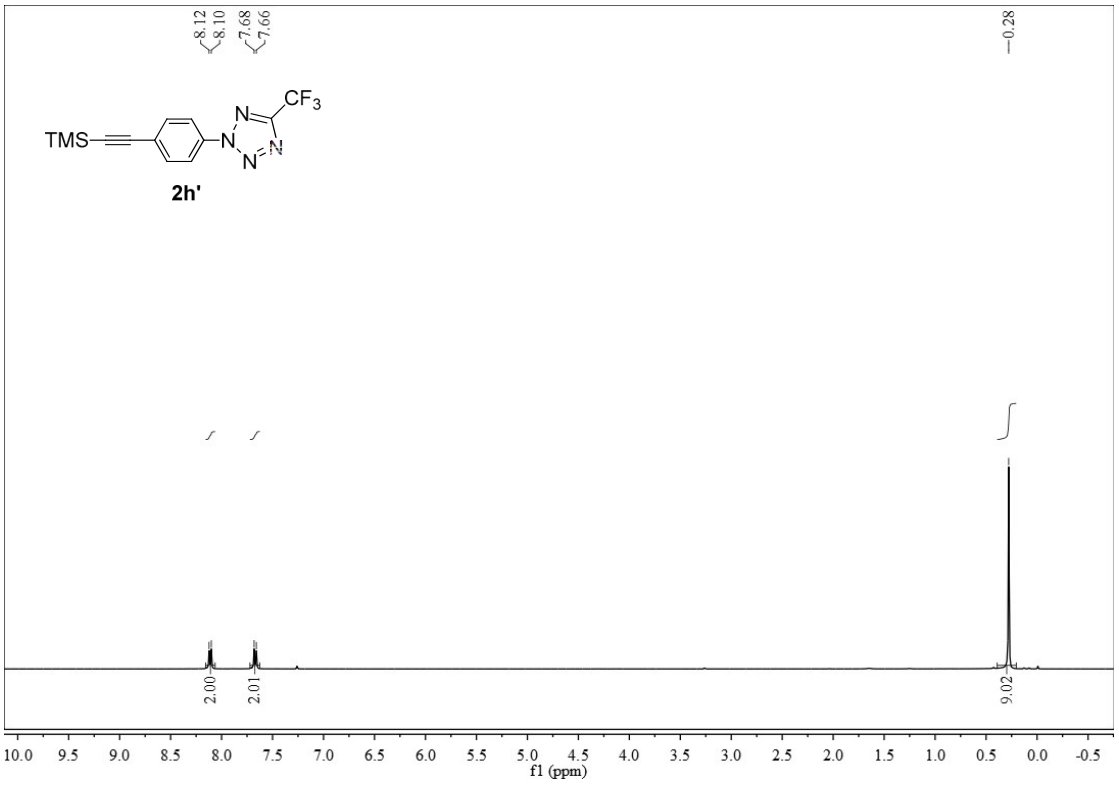
(4-(5-(trifluoromethyl)-2H-tetrazol-2-yl)phenyl)methanol (2g')

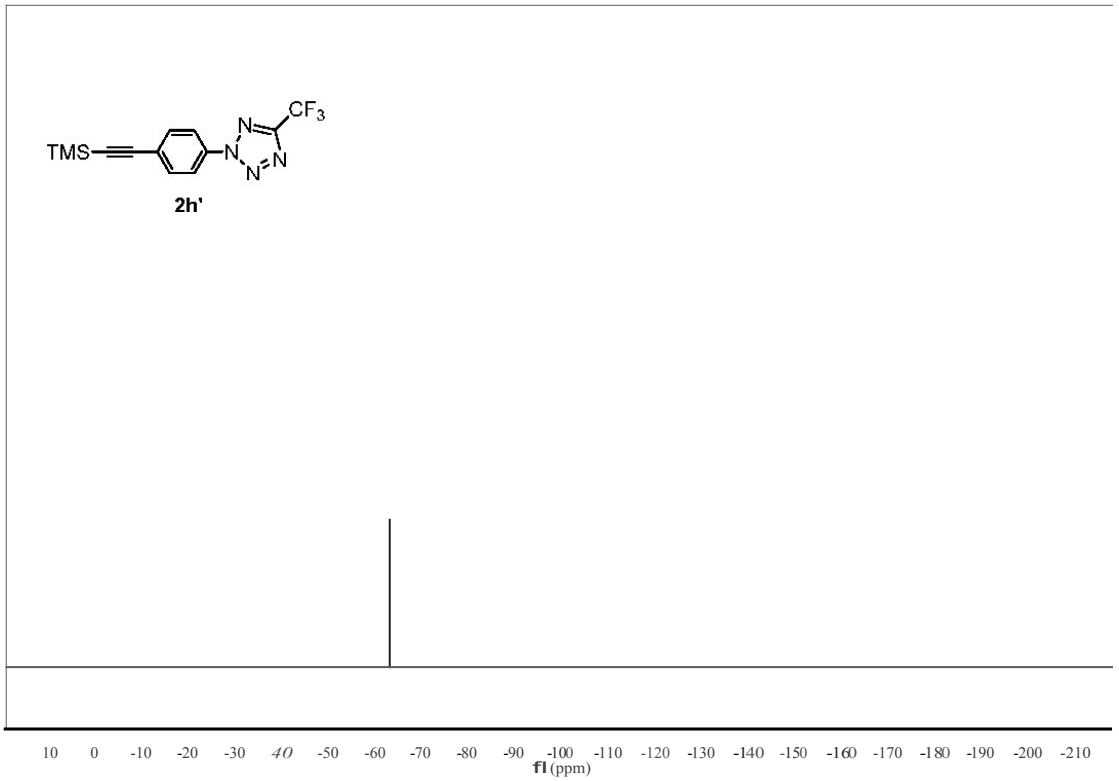


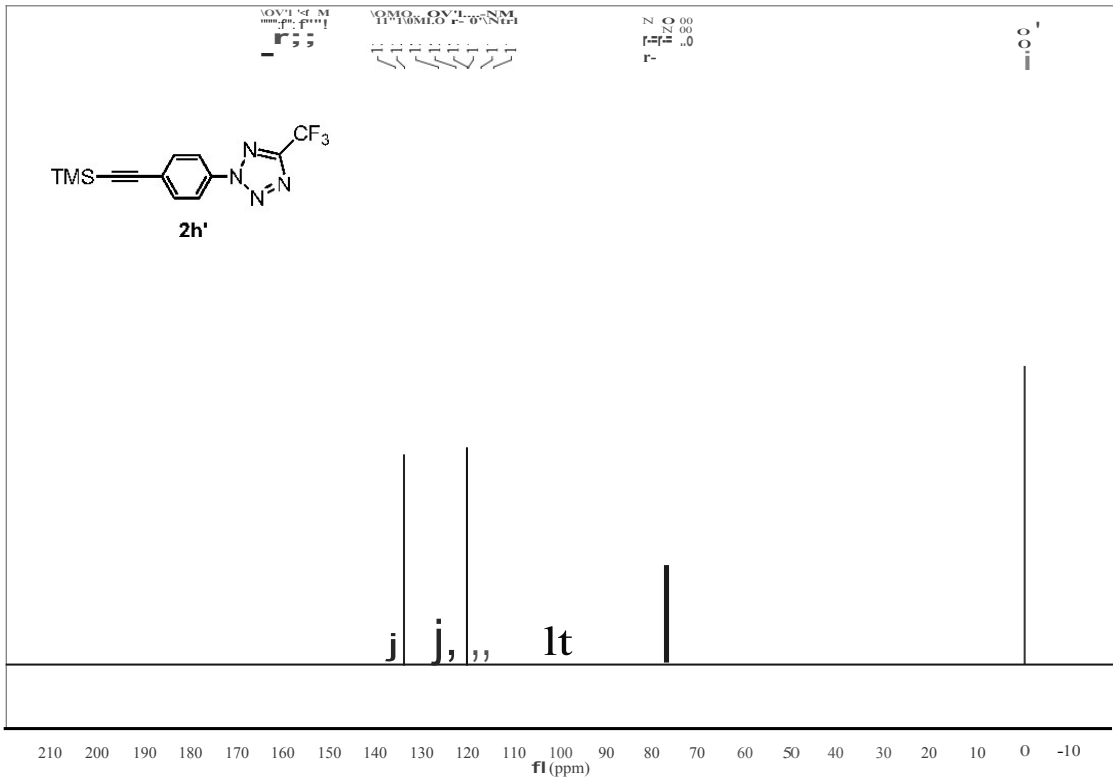




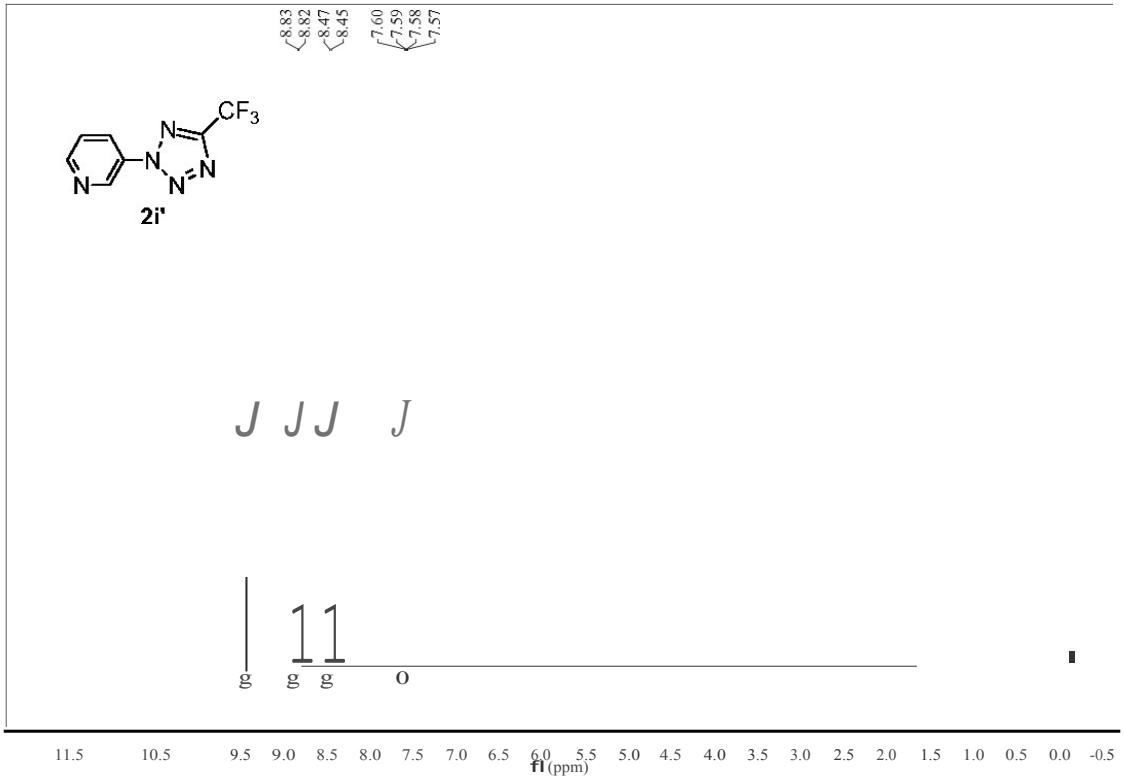
5-(trifluoromethyl)-2-(4-((trimethylsilyl)ethynyl)phenyl)-2*H*-tetrazole (2h′)

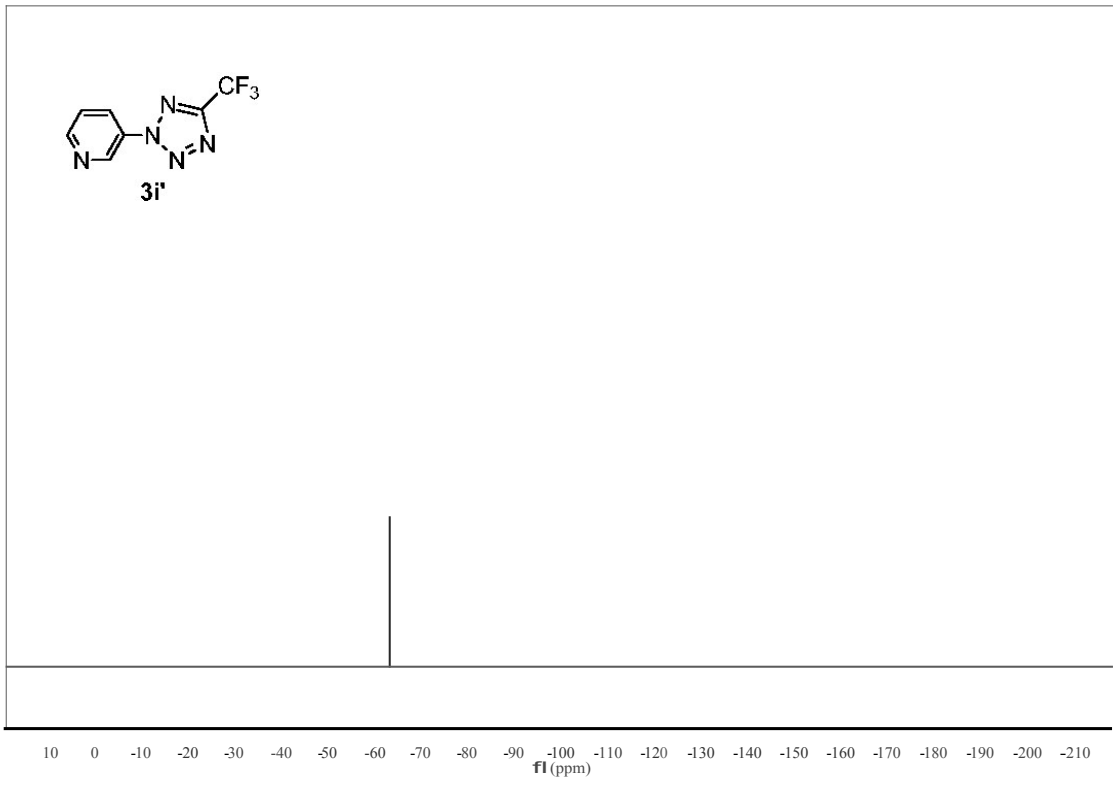


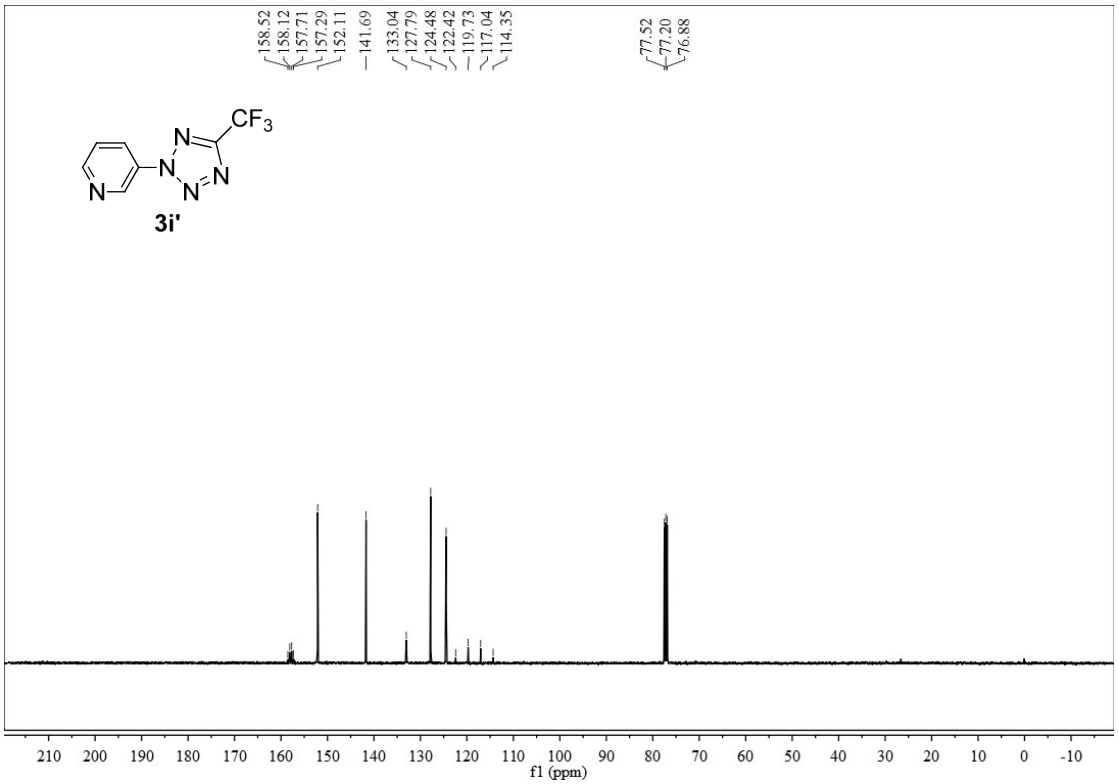

TMS
CF3
N
N
N
2h'
10 0 -10 -20 -30 40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
fl (ppm)


TMS
CF3
N
N
N
2h'
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
fl (ppm)

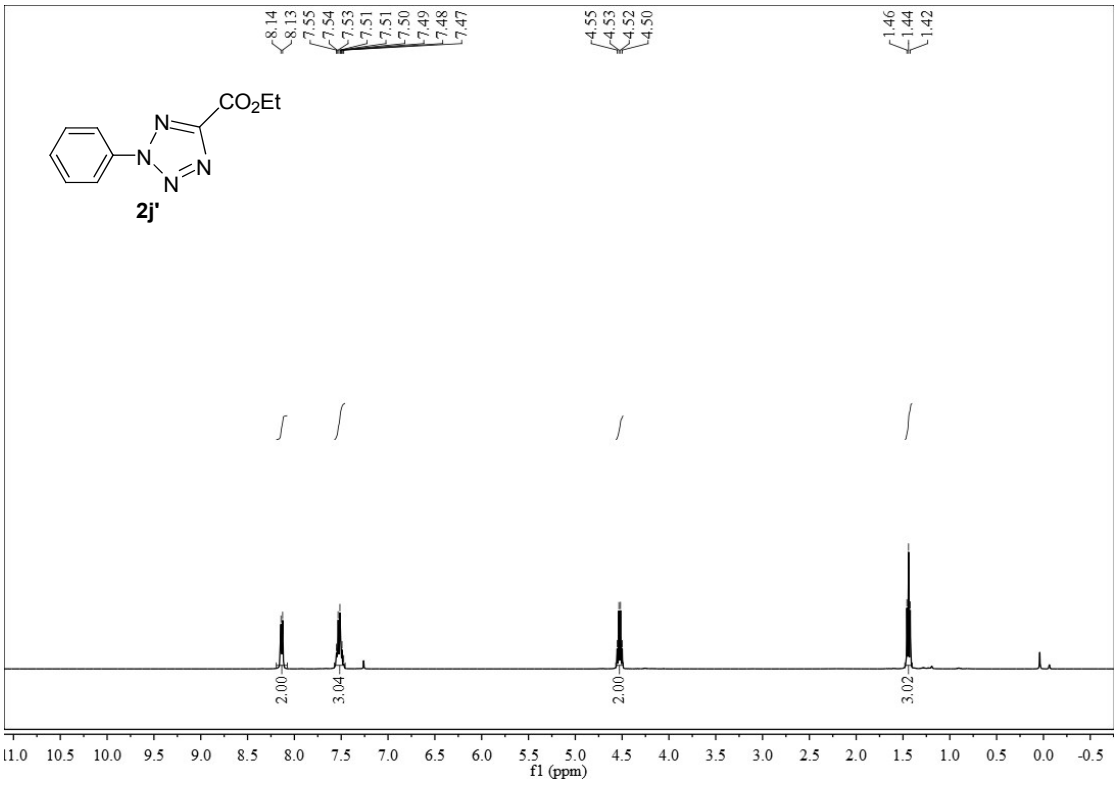
3-(5-(trifluoromethyi)-2H-tetrazol-2-yl)pyridine (2i')

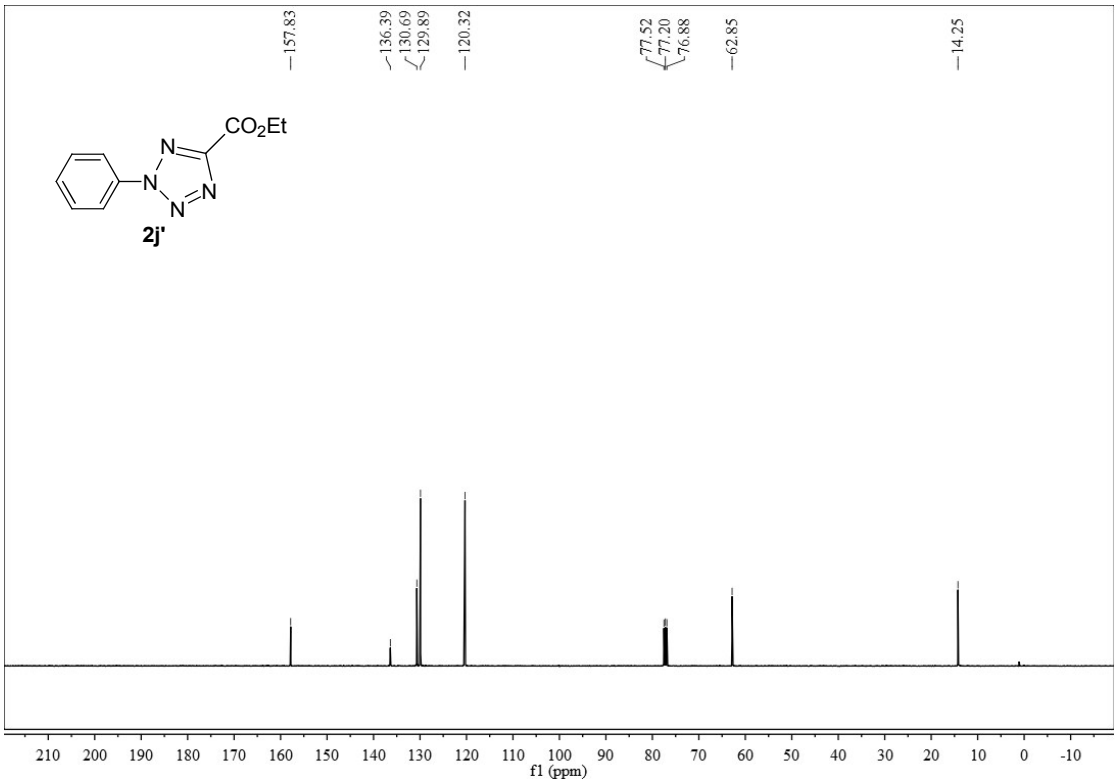






ethyl 2-phenyl-2H-tetrazole-5-carboxylate (2j′)





DL-*α*-Tocopherol 4-(5-(trifluoromethyl)-2*H*-tetrazol-2-yl)benzoate (2k′)