Supporting Information *for*

Regioselective synthesis of 3-trifluoromethyl 1,2,4-triazoles via photocycloaddition of sydnone with CF_3CN

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Table of contents

General information

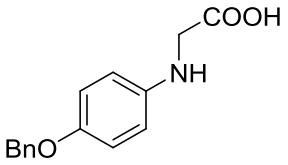
^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded using Bruker AVIII 400 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were reported in parts per million (ppm) downfield from tetramethylsilane and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard and low field is positive. Coupling constants (*J*) are reported in Hertz (Hz). The residual solvent peak was used as an internal reference: ^{1}H NMR ($CDCl_3$ δ 7.26), ^{13}C NMR ($CDCl_3$ δ 77.0), The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. The infrared (IR) spectra were recorded using a Nicolet iS50 at room temperature. HRMS were obtained on State Key Discipline Testing Center for Physical Chemistry of Fuzhou University. NMP, DCM, DMF, DMSO, acetonitrile, methanol, ethanol, toluene, triethylamine, etc. were all ultra-dry reagents, in which were purchased from Energy Chemical Company. Column chromatography purifications were performed by flash chromatography using Merck silica gel 60.

The photocatalytic experimental device was built on a Heidolph magnetic stirrer, and using a 20W 420-430 nm wavelength LED light as the light source. Air cooling was used to assist the heat dissipation of the experimental device. All reaction temperatures were controlled at room temperature.

Caution: It is known that trifluoroacetonitrile is a highly toxic gas (boiling point -64 °C) and must be handled with care. Rapid evolution of CF_3CN gas will occur when this precursor reacts with base. All operations were performed in fume hood in good condition.

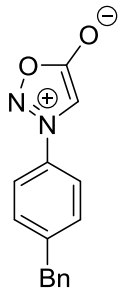
Synthesis of sydnone substrates

Sydnone substrates were prepared according to the published procedures.[1]



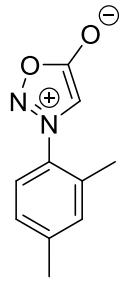
4-(benzyloxy)phenyl)glycine

Following the general procedure[1] and workup, and purification by recrystallization (methanol:H_2O) to give a white solid in 50% yield (1.2 g). Mp: 174.8 – 175.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06 (s, 1H), 7.48 – 7.24 (m, 5H), 6.79 (d, J = 8.2 Hz, 2H), 6.50 (d, J = 8.2 Hz, 2H), 4.96 (s, 2H), 3.73 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.4 (s), 150.5 (s), 143.1 (s), 138.2 (s), 128.8 (s), 128.1 (s), 128.0 (s), 116.2 (s), 113.5 (s), 70.2 (s), 45.9 (s). HRMS (ESI) m/z: calcd. for $C_{15}H_{16}NO_3$ [M + H]$^+$: 258.1152; found: 258.1127.



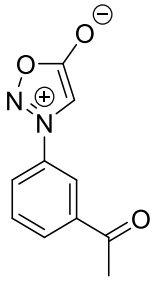
3-(4-benzylphenyl)-1,2,3-oxadiazol-3-ium-5-olate (2e)

Following the general procedure[1] and workup, and purification by recrystallization (a nhydrous ethanol) gave final product **2e** as a brown solid in 53% yield (1.33 g). Mp: 110.8 – 112.2 ℃. R_f (petroleum ether : ethyl acetate 3:1) = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 7.9 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.28 (t, J = 6.9 Hz, 1H), 7.22 (d, J = 7.3 Hz, 2H), 6.76 – 6.67 (m, 1H), 4.12 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2 (s), 146.6 (s), 139.4 (s), 133.0 (s), 130.7 (s), 129.1 (s), 129.0 (s), 126.9 (s), 121.5 (s), 93.7 (s), 41.7 (s). HRMS (ESI) m/z: calcd. for $C_{15}H_{13}N_2O_2$ [M + H]$^+$: 253.0972; found: 253.0970.



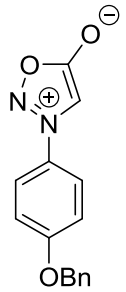
3-(2,4-dimethylphenyl)-1,2,3-oxadiazol-3-ium-5-olate (2i)

Following the general procedure[1] and workup, and purification by recrystallization (anhydrous ethanol) gave final product **2i** as a white solid in 20% yield (380.4 mg). Mp: 110.4 – 111.7 ℃. R_f (petroleum ether : ethyl acetate 3:1) = 0.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.9 Hz, 1H), 7.27 – 7.18 (m, 2H), 6.46 (s, 1H), 2.45 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1 (s), 142.9 (s), 132.9 (s), 132.8 (s), 131.8 (s), 128.1 (s), 125.0 (s), 97.2 (s), 21.4 (s), 17.3 (s). HRMS (ESI) m/z: calcd. for $C_{10}H_{11}N_2O_2$ $[M + H]^+$: 191.0815; found: 191.0815.



3-(3-acetylphenyl)-1,2,3-oxadiazol-3-ium-5-olate (2n)

Following the general procedure[1] and workup, and purification by recrystallization (anhydrous ethanol) gave final product **2n** as a brown solid in 46% yield (939.2 mg). Mp: 166.7 – 167.3 ℃. R_f (petroleum ether : ethyl acetate 3:1) = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.9 Hz, 1H), 6.85 (s, 1H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7 (s), 168.9 (s), 139.0 (s), 135.4 (s), 132.1 (s), 131.0 (s), 125.4 (s), 121.0 (s), 94.0 (s), 26.8 (s). HRMS (ESI) m/z: calcd. for $C_{10}H_9N_2O_3$ $[M + H]^+$: 205.0608; found: 205.0607.

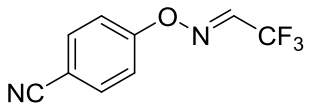


3-(4-(benzyloxy)phenyl)-1,2,3-oxadiazol-3-ium-5-olate (2p)

Following the general procedure[1] and workup, and purification by recrystallization (anhydrous ethanol) gave final product **2p** as a brown solid in 52% yield (1.39 g). Mp: 183.6 – 184.1 ℃. R_f (petroleum ether : ethyl acetate 3:1) = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 2H), 7.52 – 7.33 (m, 5H), 7.17 (d, J = 8.1 Hz, 2H), 6.68 (s, 1H), 5.19 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2 (s), 161.7 (s), 135.7 (s), 128.9 (s), 128.6 (s), 128.0 (s), 127.6 (s), 122.8 (s), 116.3 (s), 93.5 (s), 70.7 (s). HRMS (ESI) m/z: calcd. for $C_{15}H_{13}N_2O_3$ $[M + H]^+$: 269.0921; found: 269.0918.

Synthesis of 2,2,2-trifluoroacetaldehyde *O*-(aryl)oximes

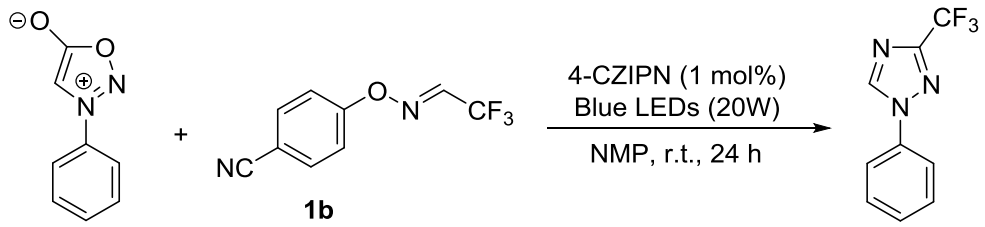
2,2,2-trifluoroacetaldehyde *O*-(aryl)oximes were prepared according to the published procedures.[2]



2,2,2-trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime (1b)

Obtained as a white solid in 82% yield (8.0 g, 37.4 mmol), Mp: 62.1–63.3 °C. R_f (petroleum ether: ethyl acetate 10:1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (q, 3.7 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (s), 142.2 (q, *J* = 38.3 Hz), 134.2 (s), 119.3 (q, *J* = 266.7 Hz), 118.6 (s), 115.3 (s), 107.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.6 (d, *J* = 3.7 Hz). IR (ATR): 3113, 3034, 2977, 2225, 1600, 1492, 1361, 1214, 1137, 941, 904, 827, 674 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_6OF_3N_2$ $[M + H]^+$: 215.0427; found: 215.0424.

Table S1 The influence of the ratio of the reactants and the base effect of the reaction[a,b]

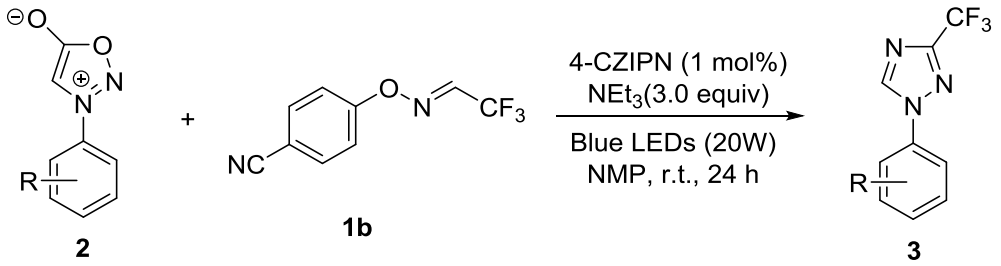


2a **1b** **3a**

Entry	**2a**: **1b**	Base (3.0 equiv)	Time/h	Yield[%]
1	1:1	NEt_3	12	49
2	1:1.5	NEt_3	12	54
3	1:2	NEt_3	12	63
4	1:2	DBU	12	3
5	1:2	Cs_2CO_3	12	0
6	1:2	DABCO	12	0
7	1:2	K_2CO_3	12	0
8	1:2	DIPEA	24	28

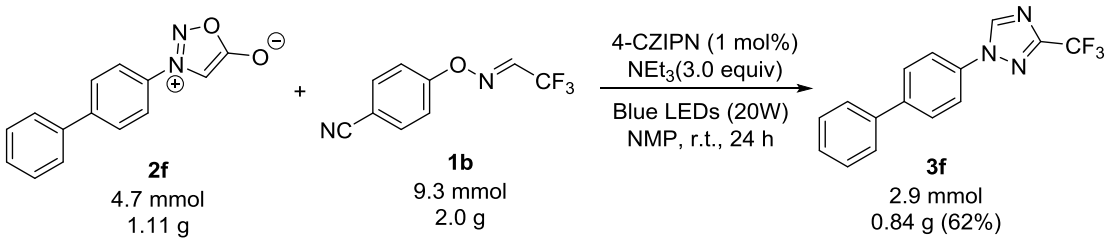
[a] Reaction conditions: solvent (2.0 mL), 20 W bule LEDS used as light source, N_2, DABCO = 1,4-diaza[2.2.2]bicyclooctane; DIPEA = *N*,*N*-diisopropylethylamine. [b] The yield was determined by ^{19}F NMR spectroscopy with $PhOCF_3$ as internal standard.

General procedure for the synthesis of 3



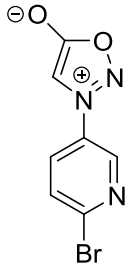
To a 10 ml Schlenk tube was added sydnones **2** (0.50 mmol, 1.0 equiv), 2,2,2-trifluoroacetaldehyde *O*-(4′-cyanophenyl)oxime **1b** (214.1 mg, 1.0 mmol , 2.0 equiv), NEt_3 (151.5 mg, 208.2 μL, 1.5 mmol, 3.0 equiv), 4-CzIPN (3.9 mg, 0.005 mmol, 0.01 equiv), and 2 mL of NMP under N_2 atomsphere. The reaction was stirred for 24 hours under the irradiation of blue LEDs (20 W, at approximately 2 cm away from the LED beads at room temperature) until the sydnones was consumed (followed by TLC). The mixture was poured into the separatory funnel, then water and ethyl acetate was added. The organic layer was washed with water, brine, and dried over anhydrous sodium sulfate. The solution was filtered and the filtrate was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain 1-aryl-3-(trifluoromethyl)-1*H*-1,2,4-triazoles **3**.

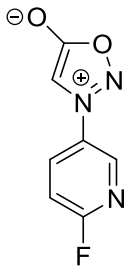
Procedure for the gram-scale synthesis of 3f

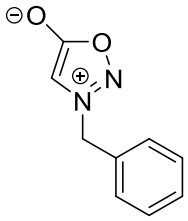


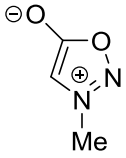
A 100 mL round bottom flask was charged with **2f** (1.11 g, 4.7 mmol), NEt_3 (1.4 g, 1.9 mL, 14.0 mmol, 3.0 equiv), NMP (20.0 mL) under N_2 atmosphere and then a solution of **1b** (2.0 g, 9.3 mmol, 2 equiv) in NMP was added dropwise into the flask via constant pressure funnel. The reaction was stirred for 24 hours at room temperature under the irradiation of blue LEDs (20 W). After the reaction was terminated, the solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate (10:1) as eluent to obtain **3f** in yield of 62% (0.84 g).

Unsuccessful reaction with other sydnone substrates



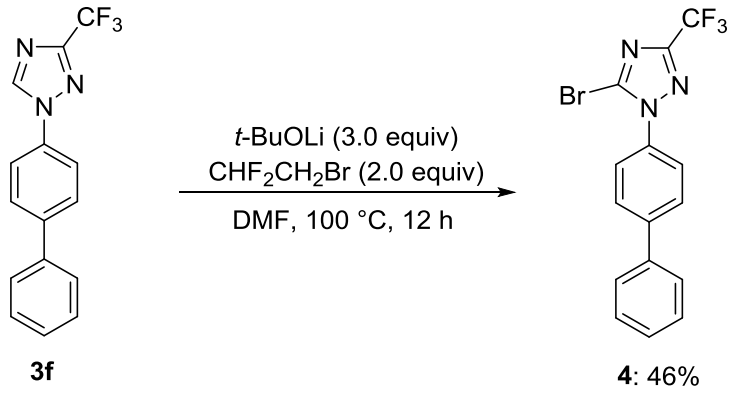






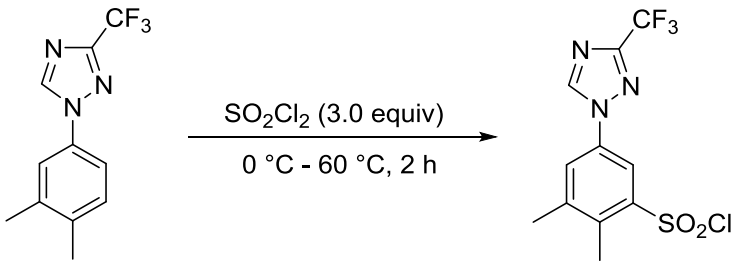
Product derivatization

(a)



In a glove box, a 10 mL Schlenk tube was charged with 1-([1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (**3f**) (144.6 mg, 0.50 mmol, 1.0 equiv), *t*-BuOLi (120.0 mg, 1.5 mmol, 3.0 equiv), CHF_2CH_2Br (144.9 mg, 85.0 μL, 1.0 mmol, 2.0 equiv), and DMF (2 mL). The resulting mixture was stirred at 100 ℃ for 12 hours. After the tube was cooled to room temperature, the mixture was added with deionized water (15 mL). and poured into separatory funnel. The aqueous was extracted with ethyl acetate (10 ml × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate to give product 1-([1,1'-biphenyl]-4-yl)-5-bromo-3-(trifluoromethyl)-1*H*-1,2,4-triazole (**4**) as a yellow oil in 46% yield.

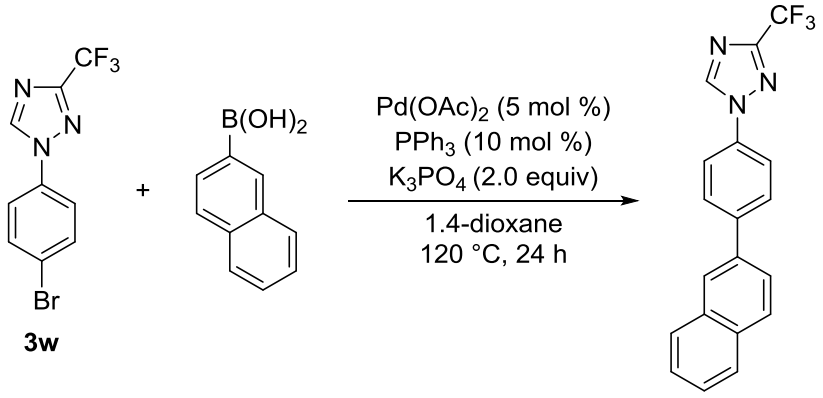
(b)



3h **5**: 32%

To a 10 mL Schlenk tube was added 1-(3,4-dimethylphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole **(3h)** (38.0 mg, 0.20 mmol, 1.0 equiv). The reaction system was cooled in an ice bath and sulfurochloridic acid (69.6 mg, 39.7μL, 0.60 mmol, 3.0 equiv) was added to the tube. The reaction tube was sealed with a Teflon cap and the mixture was left to react at 60 ^{o}C for 2 hours. After the reaction was terminated, the mixture was poured into the separatory funnel, and water and ethyl acetate was added. The organic layer was washed with water, brine, and dried over anhydrous sodium sulfate. The solution was filtered and the filtrate was vacuumed to remove the solvent. The crude product was purified by column chromatography (silica gel) with petroleum ether and ethyl acetate as eluent to obtain 2,3-dimethyl-5-(3-methyl-1*H*-1,2,4-triazol-1-yl)benzenesulfonyl chloride (**5**) in 32% yield.

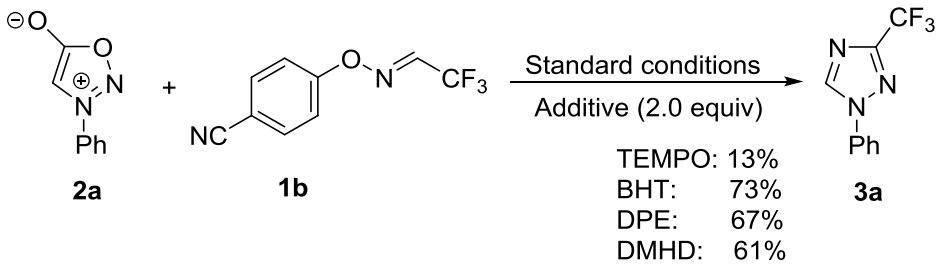
(c)



In a glove box, a 10 mL Schlenk tube was charged with 1-(4-bromophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (**3w**) (146.0 mg, 0.50 mmol, 1.0 equiv), 2-naphthylboronic acid (85.9 mg, 0.50 mmol, 1.0 equiv), and $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 0.050 equiv), PPh_3 (13.1 mg, 0.050 mmol, 0.10 equiv), K_3PO_4 (212.2 mg, 1.0 mmol, 2.0 equiv) and 1,4-dioxane (2 mL). The resulting mixture was stirred at 120 ℃ for 24 hours. After the tube was cooled to room temperature, the mixture was filtered through celite. The filtrate was added with deionized water (15 mL). The mixture was poured into separatory funnel. The aqueous was extracted with ethyl acetate (10 ml × 3). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel with petroleum ether and ethyl acetate to give coupling product 1-(4-(naphthalen-2-yl)phenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (**6**) as a white solid in 85% yield.

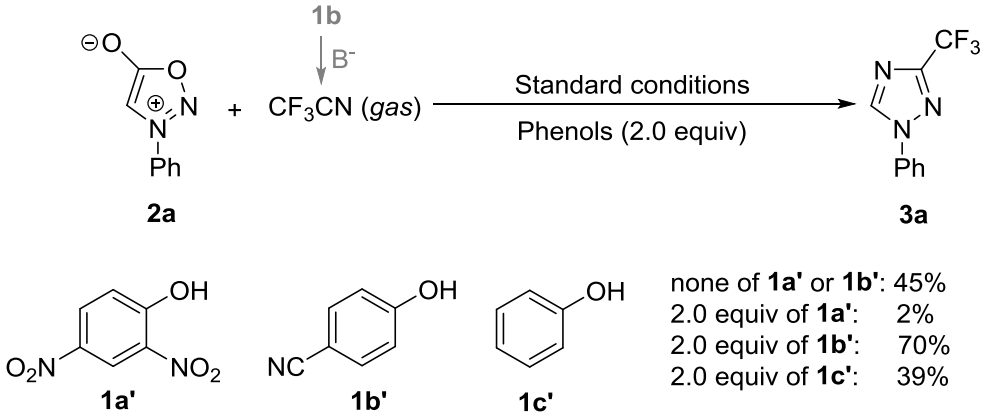
Control experiment

(a) Radical trapping studies



To a 10 mL Schlenk tube was added sydnones **2a** (32.4 mg, 0.20 mmol, 1.0 equiv), **1b** (85.0 mg, 0.40 mmol, 2.0 equiv), NEt_3 (60.6 mg, 83.2 μL, 0.60 mmol, 3.0 equiv), 4-CzIPN (0.80 mg, 0.010 mmol, 0.050 equiv), radical scavenger or triplet quencher (2.0 equiv) and 2 ml of NMP under N_2 atomsphere. The reaction was stirred for 24 hours under the irradiation of blue LEDs (20 W, at approximately 2 cm away from the LED beads at room temperature). After the reaction was terminated, (trifluoromethoxy)benzene (13.2 μL, 0.10 mmol, 0.50 equiv) was added to the reaction mixture. The mixture was shaken and 1 mL of reaction solution was transferred to an NMR tube, and the NMR signal of the mixture was analyzed by ^{19}F NMR to obtain the corresponding results.

(b) Effect of addition phenols



To a 10 ml Schlenk tube was added sydnones **2a** (32.4 mg, 0.20 mmol, 1.0 equiv), CF_3CN (balloon with excess gas), NEt_3 (60.6 mg, 83.2 μl , 0.60 mmol, 3.0 equiv), 4-CzIPN (0.80 mg, 0.010 mmol, 0.050 equiv), phenols (2.0 equiv) and 2 ml of NMP under N_2 atomsphere. The reaction was stirred for 24 hours under the irradiation of blue LEDs (20 W, at approximately 2 cm away from the LED beads at room temperature). After the reaction was terminated, (trifluoromethoxy)benzene (13.2 μL, 0.10 mmol, 0.50 equiv) was added to the reaction mixture. The mixture was shaken and 1 mL of reaction solution was transferred to an NMR tube, and the NMR signal of the mixture was analyzed by ^{19}F NMR to obtain the corresponding results.

Cyclic voltammetry experiment

Cyclic voltammetry was carried out on a Admiral Instruments workstation using a Pt wire working electrode, Saturated calomel solution reference electrode and Platinum counter electrode. The measurements were taken at room temperature under air, MeCN containing 0.1 M Bu_4NPF_6 as the electrolyte. Reported spectra were recorded at 200 mV/s.

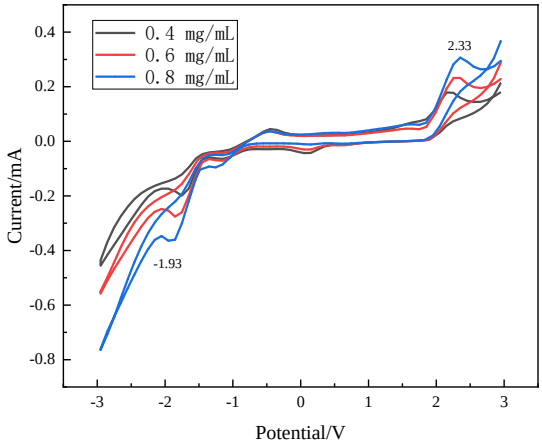


Figure S1. Cyclic voltammetry of *N*-phenylsydnone (**2a**)

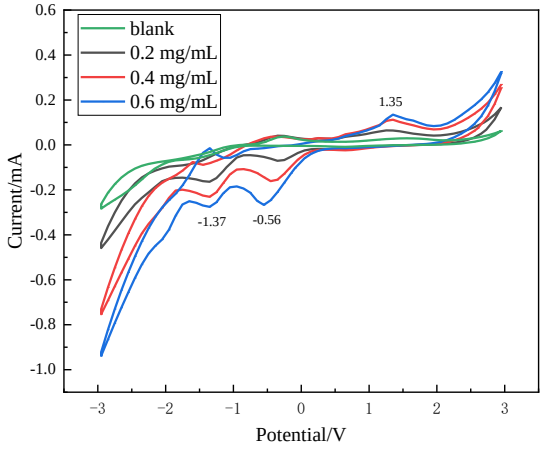


Figure S2. Cyclic voltammetry of **1a′**

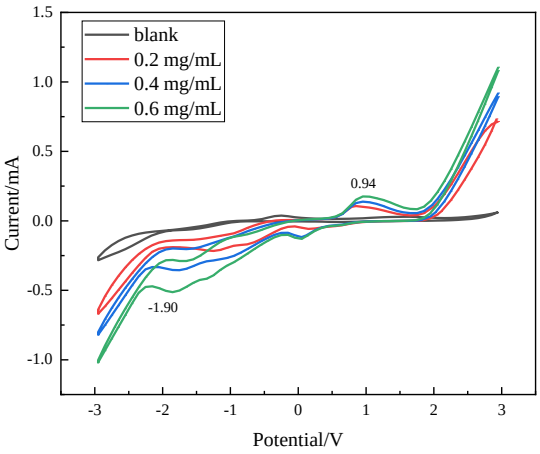


Figure S3. Cyclic voltammetry of **1b′**

Fluorescence quenching experiment

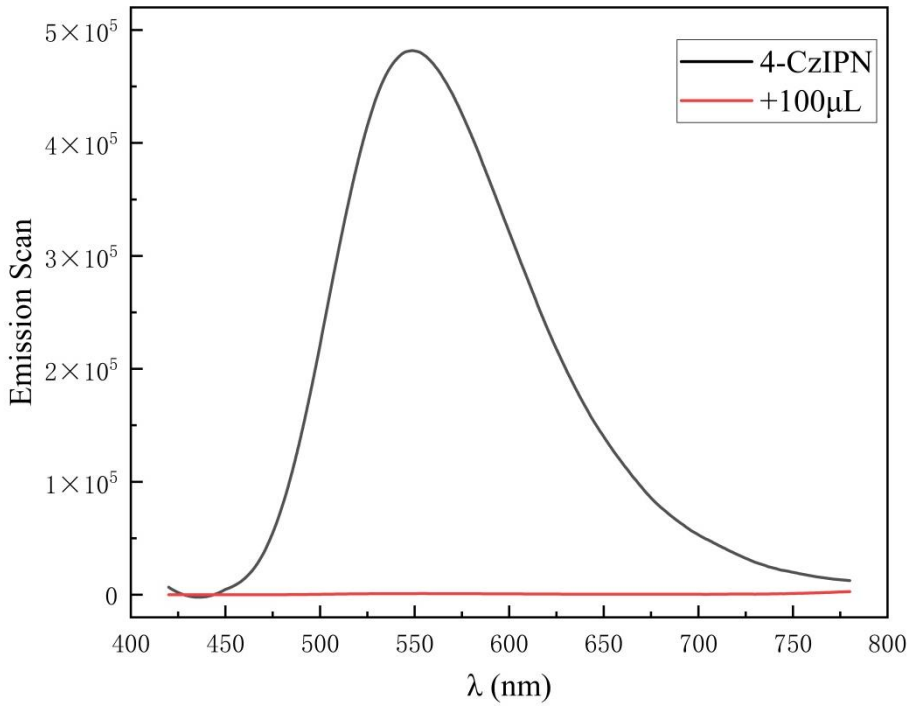


Figure S4. Fluorescence quenching of 4-CzIPN (10 μM in NMP) upon titration with 2,4-dinitrophenol (**1a′**) (100 mM in NMP)

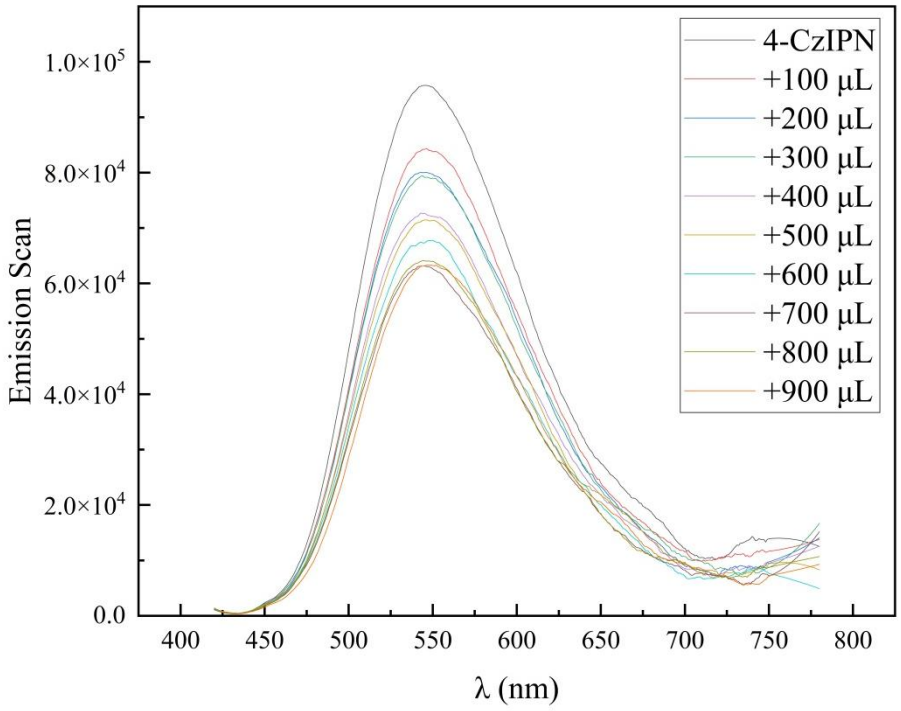


Figure S5. Fluorescence quenching of 4-CzIPN (10 μM in NMP) upon titration with 4-cyanophenol (**1b′**) (100 mM in NMP)

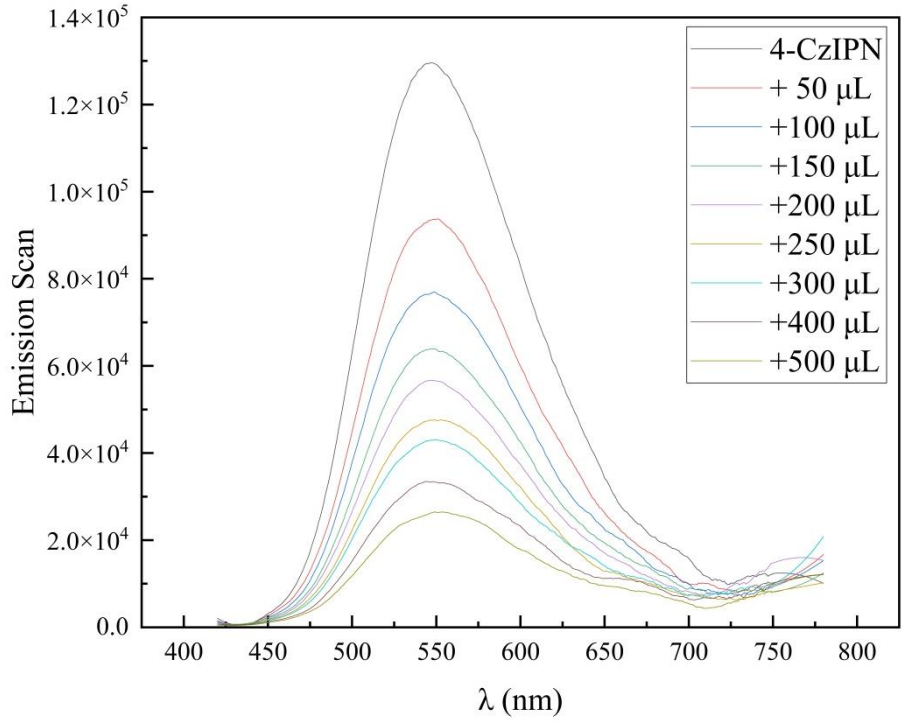


Figure S6. Fluorescence quenching of 4-CzIPN (10 µM in NMP) upon titration with sydnone (**2a**) (100 mM in NMP)

Infrared experiment for the analysis of the evidence of hydrogen bonding between of 4-CzIPN with 1b′

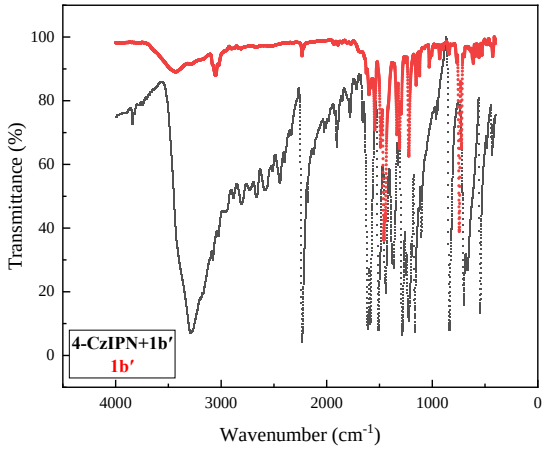


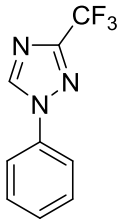
Figure S7. Infrared spectrum： interaction between of 4-CzIPN with **1b′**

Experimental procedure: Taking a sample of 10 mg and a small amount of chromatographically purified potassium bromide were placed them in a mortar. Then the mixture was evenly grinded under the baking of infrared light. Using a clean medicine spoon is taken above powder into the tableting cavity, and the mixture was pressed into a thin sheet under the pressure within 0.5-0.7 MPa. Excess powder was clean with an ear-washing ball, and Sample was placed under infrared baking to remove the residue moisture. Data was afforded from the infrared spectrum with transmittance at the wavenumber of 400-4000 cm^{-1}.

Conclusion: The free OH stretching vibration absorption peak is located in the region of 3640~3610 cm^{-1}, and the peak shape is sharp. There is a strong and broad absorption peak at 3289 cm^{-1}, which is because the hydroxyl group is a strong polar group. Its H often acts as the s orbital of the proton donor and the p orbital of the common proton acceptor to be effectively overlapped to form hydrogen bond. When the hydroxyl groups form a hydrogen bond, the stretching vibration absorption peak of O-H shifts to the low frequency direction, and a broad and strong absorption peak appears in the region of 3200~3400 cm^{-1}. With the increase of the sample concentration or direct testing of solid samples, the movement phenomenon is more

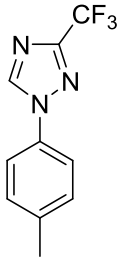
pronounced. The infrared spectrum of 4-cyanophenol can be seen that the 3289 cm^{-1} is considered to be the O-H stretching vibration infrared absorption peak under hydrogen bond pattern. The hydrogen bond may be formed from cyano group of 4-CzIPN.

Data for compounds



1-phenyl-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3a)

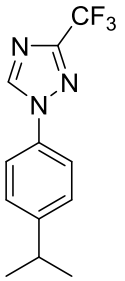
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3a** as a yellow liquid in 72% yield (153.8 mg). R_f (petroleum ether : ethyl acetate 4:1) = 0.70. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.69 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.7 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1 (q, J = 40.0 Hz), 142.4 (s), 136.3 (s), 130.1 (s), 129.4 (s), 120.6 (s), 119.2 (q, J = 270.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 1600, 1493, 1471, 1236, 1134, 1069, 977, 755, 681 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_7F_3N_3$ [M + H]$^+$: 214.0587; found: 214.0586.



1-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3b)

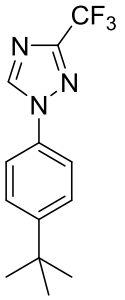
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3b** as a yellow liquid in 52% yield (118.1 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (q, J = 39.8 Hz), 142.3 (s), 139.7 (s), 134.1 (s), 130.6 (s), 120.5 (s), 119.2 (q, J = 270.0 Hz), 21.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 1504, 1473, 1231, 1141, 1070, 976, 814, 749 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{10}H_9F_3N_3$ [M + H]$^+$: 228.0743;

found: 228.0740.



1-(4-isopropylphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3c)

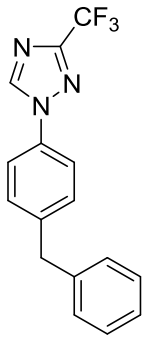
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3c** as a yellow liquid in 48% yield (122.5 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 3.08 – 2.90 (m, 1H), 1.29 (d, J = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (q, J = 39.9 Hz), 150.6 (s), 142.3 (s), 134.2 (s), 128.0 (s), 120.7 (s), 119.2 (q, J = 270.2 Hz), 34.0 (s), 24.0 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 2971, 1508, 1473, 1236, 1187, 1144, 977, 834 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{12}H_{13}F_3N_3$ $[M + H]^+$: 256.1056; found: 256.1054.



1-(4-(*tert*-butyl)phenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3d)

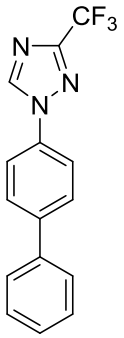
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3d** as a yellow liquid in 51% yield (137.3 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.61. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.63 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (q, J = 39.8 Hz), 152.9 (s), 142.3 (s), 133.9 (s), 127.0 (s), 120.4 (s), 119.3 (q, J = 270.0 Hz), 35.0 (s), 31.3 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 2967, 1510, 1469, 1232, 1181, 1144, 1065, 973, 834, 555 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{13}H_{15}F_3N_3$ [M + H]$^+$: 270.1213; found: 270.1212.



1-(4-benzylphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3e)

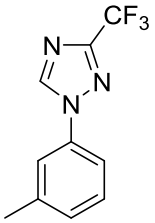
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3e** as a brown liquid in 52% yield (157.7 mg). R_f (petroleum ether : ethyl acetate 4:1) = 0.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.42 – 7.27 (m, 4H), 7.24 (d, *J* = 6.7 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 2H), 4.05 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (q, *J* = 39.8 Hz), 142.9 (s), 142.3 (s), 140.1 (s), 134.5 (s), 130.5 (s), 129.0 (s), 128.8 (s), 126.6 (s), 120.8 (s), 119.0 (q, *J* = 258.1 Hz), 41.5 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 1504, 1464, 1234, 1135, 1072, 973, 746 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{12}F_3N_3$ [M]$^+$: 303.0978; found: 303.0983.



1-([1,1'-biphenyl]-4-yl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3f)

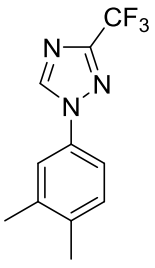
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3f** as a yellow

solid in 74% yield (214.0 mg). Mp: 158.3 – 159.6 ℃. R_f (petroleum ether : ethyl acetate 5:1) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.79 – 7.70 (m, 4H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1 (q, *J* = 39.9 Hz), 142.5 (s), 142.3 (s), 139.4 (s), 135.4 (s), 129.2 (s), 128.7 (s), 128.3 (s), 127.2 (s), 120.8 (s), 119.2 (q, *J* = 270.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 1471, 1261, 1232, 1148, 975, 838, 734, 700 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{11}F_3N_3$ $[M + H]^+$: 290.0900; found: 290.0899.



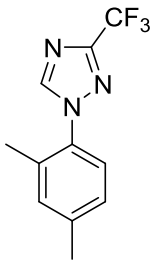
1-(*m*-tolyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3g)

Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3g** as a yellow liquid in 50% yield (113.5 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 7.52 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0 (q, *J* = 39.9 Hz), 142.4 (s), 140.5 (s), 136.3 (s), 130.2 (s), 129.9 (s), 121.3 (s), 119.2 (q, *J* = 270.0 Hz), 117.6 (s), 21.5 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 1614, 1469, 1232, 1185, 1142, 1073, 985, 844, 783, 681 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{10}H_9F_3N_3$ $[M + H]^+$: 228.0743; found: 228.0743.



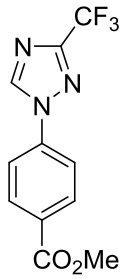
1-(3,4-dimethylphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3h)

Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3h** as a yellow liquid in 49% yield (118.2 mg). R_f (petroleum ether : ethyl acetate 4:1) = 0.79. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.49 (s, 1H), 7.41 (d, J = 8.1 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (q, J = 39.8 Hz), 142.3 (s), 138.9 (s), 138.3 (s), 134.2 (s), 130.9 (s), 121.7 (s), 119.2 (q, J = 270.2 Hz), 117.8 (s), 20.0 (s), 19.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 2922, 1504, 1467, 1236, 1183, 1146, 1073, 1014, 808 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{11}H_{11}F_3N_3$ $[M + H]^+$: 242.0900; found: 242.0897.



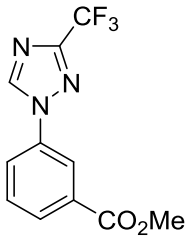
1-(2,4-dimethylphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3i)

Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3i** as a yellow liquid in 29% yield (69.9 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.26 – 7.19 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (q, J = 50.6 Hz), 145.5 (s), 140.8 (s), 133.7 (s), 133.1 (s), 132.4 (s), 127.8 (s), 126.0 (s), 119.3 (q, J = 268.8 Hz), 21.3 (s), 17.8 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 2952, 1745, 1498, 1267, 1152, 976, 817 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{11}H_{11}F_3N_3$ $[M + H]^+$: 242.0900; found: 242.0899.



methyl 4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-1-yl)benzoate (3j)

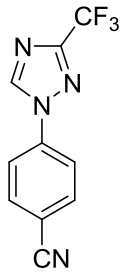
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3j** as a yellow solid in 37% yield (100.3 mg). Mp: 132.3 – 133.4 ℃. R_f (petroleum ether : ethyl acetate 4:1) = 0.64. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.23 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (s), 155.5 (q, *J* = 40.1 Hz, 1C), 142.6 (s), 139.4 (s), 131.7 (s), 130.9 (s), 119.9 (s), 119.0 (q, *J* = 270.2 Hz), 52.7 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (s, 3F). IR (ATR): ν 3132, 2948, 1712, 1602, 1469, 1428, 1287, 1257, 1142, 1069, 975 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{11}H_8F_3N_3O_2$ $[M]^+$: 271.0569; found: 271.0599.



methyl 3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-1-yl)benzoate (3k)

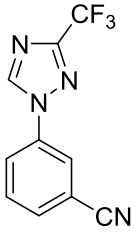
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3k** as a yellow solid in 77% yield (208.8 mg). Mp: 164.2 – 165.8 ℃. R_f (petroleum ether : ethyl acetate 4:1) = 0.61. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.36 (s, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (s), 155.2 (q, *J* = 40.0 Hz), 142.4 (s), 136.4 (s), 132.2 (s), 130.3 (s), 130.1 (s), 124.6 (s), 121.0 (s), 119.0 (q, *J* = 270.2 Hz), 52.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (s, 3F). IR (ATR): ν 3131, 1694, 1478, 1319, 1294, 1231, 1152, 754 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{11}H_9F_3N_3O_2$ $[M + H]^+$:

272.0641; found: 272.0641.



4-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-1-yl)benzonitrile (3l)

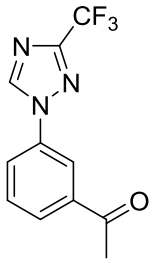
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3l** as a yellow solid in 33% yield (78.5 mg). Mp: 174.8 – 175.6 ℃. R_f (petroleum ether : ethyl acetate 4:1) = 0.54. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.99 – 7.83 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8 (q, *J* = 40.4 Hz), 142.6 (s), 139.2 (s), 134.3 (s), 120.6 (s), 118.9 (q, *J* = 270.5 Hz), 117.5 (s), 113.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.4 (s, 3F). IR (ATR): ν 3136, 2231, 1603, 1504, 1464, 1254, 1149, 967, 837, 553 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{10}H_5F_3N_4$ $[M]^+$: 238.0461; found: 238.0468.



3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-1-yl)benzonitrile (3m)

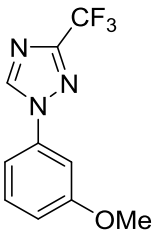
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3m** as a yellow solid in 58% yield (138.1 mg). Mp: 158.2 – 159.1 ℃. R_f (petroleum ether : ethyl acetate 4:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.10 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.74 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6 (q, *J* = 40.3 Hz), 142.6 (s), 136.9 (s), 132.7 (s), 131.3 (s), 124.3 (s), 123.7 (s), 118.9 (q, *J* = 270.4 Hz), 117.2 (s), 114.6 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (s, 3F). IR (ATR): ν 3119, 2248, 1592, 1467, 1263, 1146, 1070, 982,

808, 675 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{10}H_6F_3N_4$ $[M + H]^+$: 239.0539; found: 239.0545.



1-(3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-1-yl)phenyl)ethan-1-one (3n)

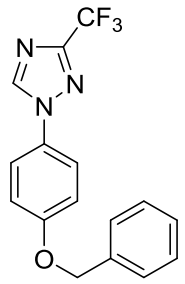
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3n** as a white solid in 41% yield (104.6 mg). Mp: 138.0 – 139.9 ℃. R_f (petroleum ether : ethyl acetate 4:1) = 0.48. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.31 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5 (s), 155.4 (q, *J* = 40.1 Hz), 142.5 (s), 138.8 (s), 136.8 (s), 130.7 (s), 129.1 (s), 124.8 (s), 119.6 (s), 119.1 (q, *J* = 270.3 Hz), 26.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 3112, 1677, 1471, 1351, 1204, 1155, 1138, 983, 787, 685 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{11}H_9F_3N_3O$ $[M]^+$: 256.0614; found: 255.0613.



1-(3-methoxyphenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3o)

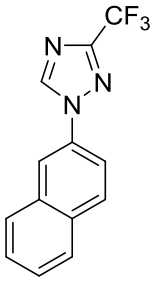
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3o** as a yellow liquid in 27% yield (65.6 mg). R_f (petroleum ether : ethyl acetate 4:1) = 0.71. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.33 – 7.23 (m, 2H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (s), 155.0

(q, J = 40.1 Hz), 142.4 (s), 137.3 (s), 130.9 (s), 119.5 (q, J = 247.4 Hz), 115.1 (s), 112.3 (s), 106.5 (s), 55.8 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 1609, 1473, 1146, 984, 848, 683 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{10}H_9F_3N_3O$ [M + H]$^+$: 244.0692; found: 244.0692.



1-(4-(benzyloxy)phenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3p)

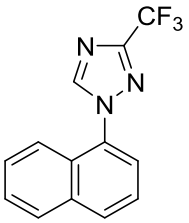
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3p** as a yellow solid in 46% yield (146.8 mg). Mp: 124.7 – 125.2 ℃. R_f (petroleum ether : ethyl acetate 5:1) = 0.50. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.61 (d, J = 7.6 Hz, 2H), 7.54 – 7.40 (m, 5H), 7.13 (d, J = 7.6 Hz, 2H), 5.16 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 (s), 154.8 (q, J = 39.7 Hz), 142.3 (s), 136.2 (s), 129.8 (s), 128.9 (s), 128.4 (s), 127.6 (s), 122.4 (s), 119.2 (q, J = 270.0 Hz), 116.1 (s), 70.5 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 3126, 1612, 1506, 1469, 1244, 1142, 1126, 1008, 975, 830 cm^{-1}. HRMS (EI) m/z: calcd. for $C_{16}H_{12}F_3N_3O$ [M]$^+$: 319.0927; found: 319.0936.



1-(naphthalen-2-yl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3q)

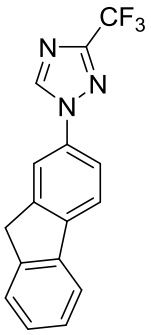
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3q** as a brown

liquid in 70% yield (184.5 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.08 (s, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.63 – 7.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0 (q, *J* = 39.9 Hz), 142.5 (s), 133.6 (s), 133.2 (s), 133.0 (s), 130.4 (s), 128.3 (s), 128.1 (s), 127.8 (s), 127.5 (s), 119.2 (q, *J* = 270.2 Hz), 118.7 (s), 118.3 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.0 (s, 3F). IR (ATR): ν 1600, 1465, 1236, 1222, 1185, 1148, 1061, 989, 857, 742, 469 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{13}H_9F_3N_3$ $[M + H]^+$: 264.0743; found: 264.0741.



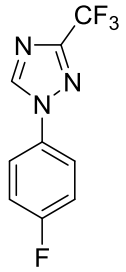
1-(naphthalen-1-yl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3r)

Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3r** as a brown liquid in 27% yield (71.1 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.06 (d, *J* = 7.1 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.69 – 7.52 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2 (q, *J* = 40.0 Hz), 146.4 (s), 134.4 (s), 132.6 (s), 131.2 (s), 128.6 (s), 128.5 (s), 128.4 (s), 127.5 (s), 125.0 (s), 124.1 (s), 121.9 (s), 119.3 (q, *J* = 270.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.0 (s, 3F). IR (ATR): ν 1473, 1234, 1187, 1144, 1032, 989, 946, 797, 767 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{13}H_9F_3N_3$ $[M + H]^+$: 264.0743; found: 264.0743.



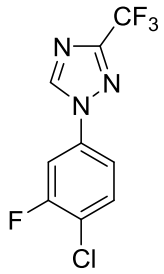
1-(9*H*-fluoren-2-yl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3s)

Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3s** as a yellow solid in 39% yield (117.5 mg). Mp: 192.9 – 193.3 ℃. R_f (petroleum ether : ethyl acetate 4:1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.44 (m, *J* = 7.2 Hz, 2H), 4.02 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0 (q, *J* = 40.0 Hz), 145.2 (s), 143.6 (s), 143.0 (s), 142.4 (s), 140.2 (s), 134.8 (s), 127.9 (s), 127.3 (s), 125.4 (s), 120.9 (s), 120.5 (s), 119.5 (s), 119.3 (q, *J* = 270.0 Hz), 117.7 (s), 37.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 1487, 1464, 1396, 1240, 1194, 1155, 982, 729 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{16}H_{11}F_3N_3$ $[M + H]^+$: 302.0900; found: 302.0899.



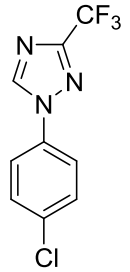
1-(4-fluorophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3t)

Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3t** as a yellow liquid in 61% yield (141.0 mg). R_f (petroleum ether : ethyl acetate 4:1) = 0.74. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.77 – 7.63 (m, 2H), 7.25 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8 (d, *J* = 250.4 Hz), 155.2 (q, *J* = 40.0 Hz), 142.5 (s), 132.6 (d, *J* = 3.1 Hz), 122.7 (d, *J* = 8.8 Hz), 119.1 (q, *J* = 270.2 Hz), 117.2 (d, *J* = 23.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F), -110.9 - -111.0 (m, 1F). IR (ATR): ν 1528, 1469, 1234, 1138, 1067, 977, 836, 746, 622, 524 cm^{-1}. HRMS (EI) m/z: calcd. for $C_9H_5F_4N_3$ $[M]^+$: 231.0414; found: 231.0421.



1-(4-chloro-3-fluorophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3u)

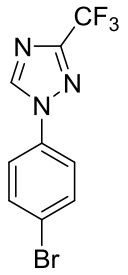
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3u** as a yellow liquid in 58% yield (154.0 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.61. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.68 – 7.57 (m, 2H), 7.51 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5 (d, *J* = 252.5 Hz), 155.3 (q, *J* = 40.3 Hz), 142.3 (s), 135.6 (d, *J* = 8.8 Hz), 132.0 (s), 122.2 (d, *J* = 17.7 Hz), 118.8 (q, *J* = 270.5 Hz), 116.2 (d, *J* = 4.0 Hz), 109.4 (d, *J* = 26.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (s, 3F), -110.1 (t, *J* = 8.0 Hz, 1F). IR (ATR): ν 1598, 1495, 1473, 1234, 1146, 1050, 990, 876, 746 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_5ClF_4N_3$ $[M + H]^+$: 266.0103; found: 266.0102.



1-(4-chlorophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3v)

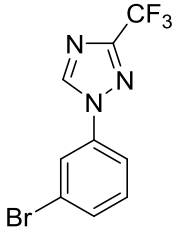
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3v** as a yellow liquid in 62% yield (153.5 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2 (q, *J* = 40.0 Hz), 142.4 (s), 135.3 (s), 134.8 (s), 130.3 (s), 121.7 (s), 119.1 (q, *J* = 270.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 1495, 1469, 1234, 1142, 1095, 1065, 977, 828, 736, 514 cm^{-1}.

HRMS (ESI) m/z: calcd. for $C_9H_6ClF_3N_3$ $[M + H]^+$: 248.0197; found: 248.0196.



1-(4-bromophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3w)

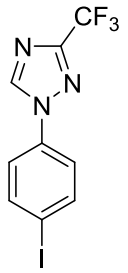
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3w** as a yellow liquid in 68% yield (198.6 mg). R_f (petroleum ether : ethyl acetate 5:1) = 0.67. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.68 (d, J = 8.6 Hz, 2H), 7.59 (d, J = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (q, J = 40.0 Hz), 142.3 (s), 135.3 (s), 133.3 (s), 123.1 (s), 121.9 (s), 119.1 (q, J = 271.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 1487, 1471, 1248, 1238, 1183, 1148, 1065, 975, 824, 748 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_9H_6BrF_3N_3$ $[M + H]^+$: 291.9692; found: 291.9693.



1-(3-bromophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3x)

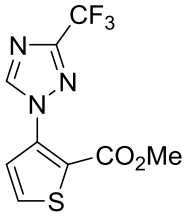
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3x** as a yellow liquid in 53% yield (154.8 mg). R_f (petroleum ether : ethyl acetate 4:1) = 0.75. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.93 (s, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (q, J = 40.1 Hz), 142.4 (s), 137.2 (s), 132.5 (s), 131.4 (s), 130.1 (s), 123.7 (s), 119.0 (q, J = 270.2 Hz), 118.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (s, 3F). IR (ATR): ν 1592, 1478, 1237, 1132, 1072, 982, 757, 669 cm^{-1}. HRMS (ESI) m/z: calcd. for

$C_9H_6BrF_3N_3$ [M + H]$^+$: 291.9692; found: 291.9693.



1-(4-iodophenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (3y)

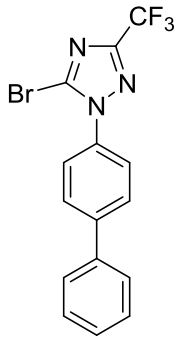
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3y** as a brown solid in 60% yield (202.4 mg). Mp: 70.5 – 71.3 ℃. R_f (petroleum ether : ethyl acetate 5:1) = 0.61. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.87 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (q, J = 40.1 Hz), 142.3 (s), 139.2 (s), 136.0 (s), 122.0 (s), 119.2 (q, J = 281.5 Hz), 94.4 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 1483, 1469, 1236, 1151, 1055, 973, 822, 751 cm^{-1}. HRMS (EI) m/z: calcd. for $C_9H_5IF_3N_3$ [M]$^+$: 338.9475; found: 338.9471.



methyl 3-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-1-yl)thiophene-2-carboxylate (3z)

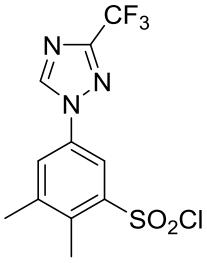
Following the general procedure and workup, and purification by column chromatogr aphy (silica gel, petroleum ether : ethyl acetate 10:1) gave final product **3z** as a yellow solid in 36% yield (99.8 mg). Mp: 107.6 – 108.8 ℃. R_f (petroleum ether : ethyl acetate 4:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 7.67 (d, J = 5.4 Hz, 1H), 7.46 (d, J = 5.4 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8 (s), 154.3 (q, J = 40.0 Hz), 147.3 (s), 137.4 (s), 131.6 (s), 126.5 (s), 122.9 (s), 119.1 (q, J = 270.1 Hz), 52.9 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.2 (s, 3F). IR (ATR): ν 1702, 1467, 1433, 1271, 1240, 1132, 979, 774 cm^{-1}. HRMS (ESI) m/z: calcd. for

$C_9H_7F_3N_3O_2S$ $[M + H]^+$: 278.0206; found: 278.0205.



1-([1,1'-biphenyl]-4-yl)-5-bromo-3-(trifluoromethyl)-1*H*-1,2,4-triazole (4)

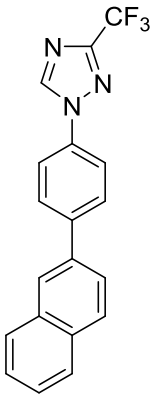
Purification by column chromatography (silica gel, petroleum ether : ethyl acetate 4:1) gave product **4** as a yellow oil in 46% yield (228.4 mg). R_f (petroleum ether : ethyl acetate 4:1) = 0.88. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8 (q, *J* = 40.8 Hz), 143.5 (s), 143.1 (s), 139.4 (s), 134.3 (s), 129.2 (s), 128.5 (s), 128.3 (s), 127.4 (s), 125.2 (s), 118.6 (q, *J* = 270.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.9 (s, 3F). IR (ATR): ν 2923, 1461, 1376, 1177, 1118, 1106, 984, 837, 811, 754 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{15}H_{10}BrF_3N_3$ $[M + H]^+$: 368.0005; found: 368.0001.



2,3-dimethyl-5-(3-(trifluoromethyl)-1*H*-1,2,4-triazol-1-yl)benzenesulfonyl chloride (5)

Purification by column chromatography (silica gel, petroleum ether : ethyl acetate 4:1) gave product **5** as a yellow oil in 32% yield (10.9 mg). R_f (petroleum ether : ethyl acetate 4:1) = 0.65. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.29 (s, 1H), 7.96 (s, 1H), 2.80 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3 (q, *J* = 43.8 Hz),

144.5 (s), 143.4 (s), 142.4 (s), 137.8 (s), 133.7 (s), 127.7 (s), 118.8 (q, J = 271.6 Hz), 117.9 (s), 21.0 (s), 16.2 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.3 (s, 3F). IR (ATR): ν 2923, 1609, 1480, 1369, 1293, 1182, 1146, 1092, 987, 698, 566 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{11}H_{10}ClF_3N_3O_2S$ $[M + H]^+$: 340.0129; found: 340.0129.



1-(4-(naphthalen-2-yl)phenyl)-3-(trifluoromethyl)-1*H*-1,2,4-triazole (6)

Purification by column chromatography (silica gel, petroleum ether : ethyl acetate 4:1) gave product **6** as a white solid in 85% yield (144.2 mg). Mp: 183.6 – 184.1 ℃. R_f (petroleum ether : ethyl acetate 4:1) = 0.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.10 (s, 1H), 8.05 – 7.87 (m, 5H), 7.83 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.5 Hz, 1H), 7.57 (t, J = 3.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2 (q, J = 39.6 Hz), 142.4 (s), 142.3 (s), 136.7 (s), 135.4 (s), 133.7 (s), 133.1 (s), 129.0 (s), 128.9 (s), 128.4 (s), 127.8 (s), 126.8 (s), 126.6 (s), 126.2 (s), 125.2 (s), 120.9 (s), 119.2 (q, J = 270.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -65.1 (s, 3F). IR (ATR): ν 3048, 1478, 1260, 1237, 1163, 1123, 979, 834, 811, 749 cm^{-1}. HRMS (ESI) m/z: calcd. for $C_{19}H_{13}F_3N_3$ $[M + H]^+$: 340.1056; found: 340.1056.

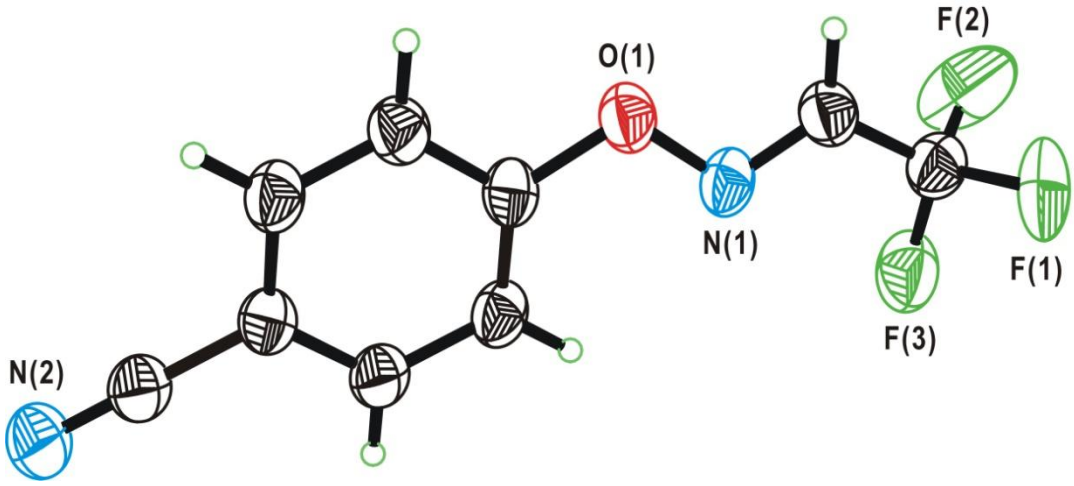
Crystal structure analyses

The crystal samples of **1b** and **3f** were prepared by slow volatilization in a DCM/ petroleum ether (1:1) solvent mixture. The suitable crystals of **1b** (CCDC 2088601) and **3f** (CCDC CCDC 2156038) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 ºC, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the SMART suite of programs and for absorption effects with SADABS.[3] Structure solution and refinement were carried out with the SHELXTL suite of programs. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms

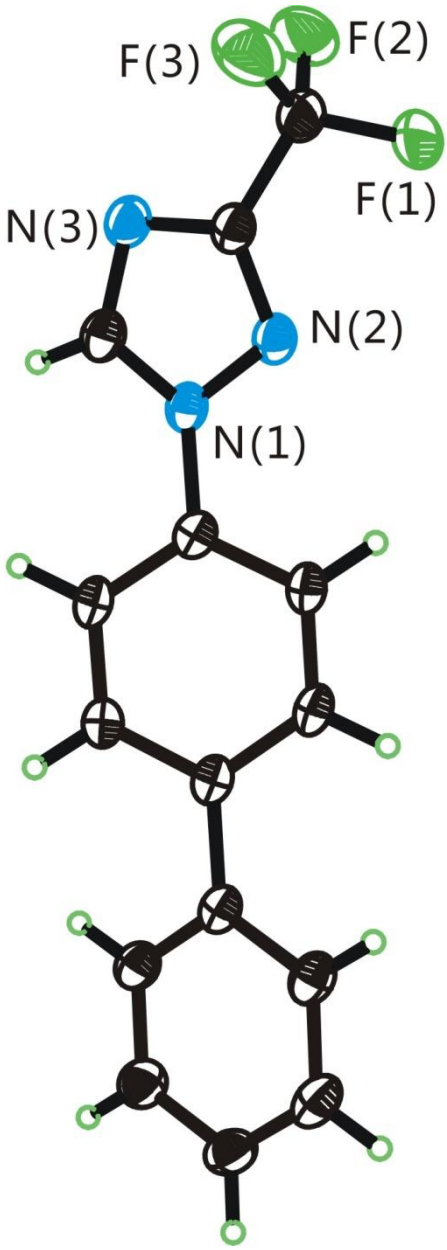
Table S1. Crystal data and structure refinement for compounds

Compounds	**1b** (CCDC 2088601)	**3f** (CCDC 2156038)
Empirical formula	$C_9H_5F_3N_2O$	$C_{15}H_{10}F_3N_3$
Formula weight	214.15	289.26
Temperature/K	296 K	296 K
Wavelength/Å	1.54178	0.71073
Crystal system	monoclinic	orthorhombic
a/Å	17.5653(19)	7.3715(7)
b/Å	4.4815(5)	15.6061(16)
c/Å	24.060(2)	11.7583(14)
α/°	90.00	90.00
β/°	93.245(11)	106.836(4
γ/°	90.00	90.00
Volume/$Å^3$	1890.9(3)	1294.7(2)
Z	8	4
Density (calc.)/cm^3	1.504	1.484
Absorption coefficient /mm^{-1}	1.251	0.121
F(000)	864.0	592.0
Crystal size/mm	0.1×0.05×0.05	0.2×0.1×0.1
Theta range for data collection / °	3.68~66.81	2.231~29.587
Reflections collected	1610	3637
Independent reflections	1206	2198
Data/restraints/parameters	1610/0/136	3637/0/190
Goodness-of-fit on F^2	1.096	1.014
Final R indexes [I>=2σ (I)]	0.0778	0.0541
Final R indexes [all data]	0.0998	0.1073
Largest diff. peak and hole / e $Å^{-3}$	0.30/-0.27	0.33/-0.31

ORTEP diagrams



ORTEP diagram of compound 1b. Thermal ellipsoids are drawn at 40% probability



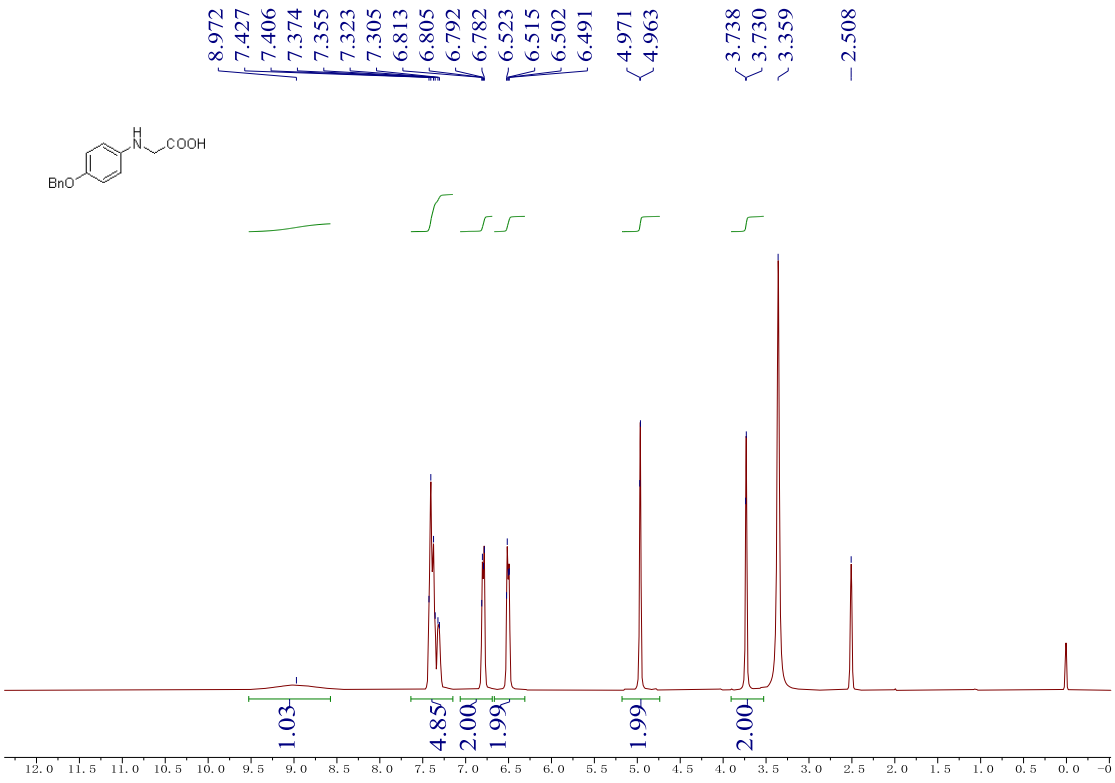
ORTEP diagram of compound 3f. Thermal ellipsoids are drawn at 40% probability

References:

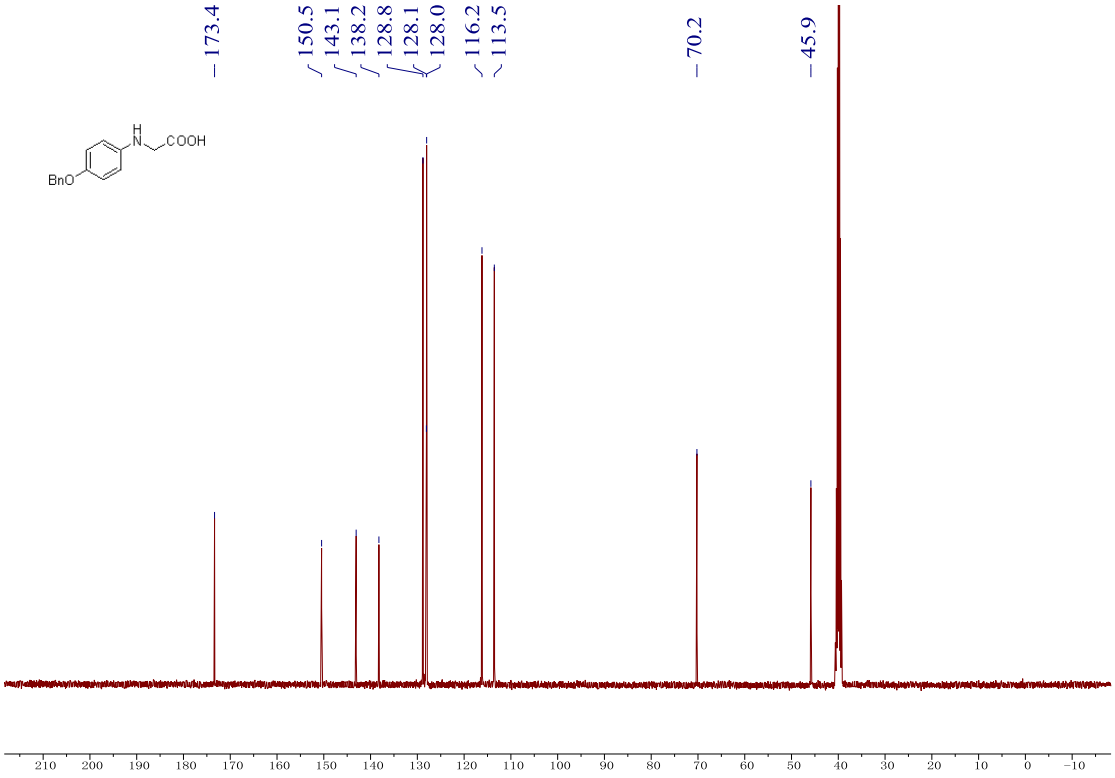
1. H. Liu, D. Audisio, L. Plougastel, E. Decuypere, D.-A. Buisson, O. Koniev, S. Kolodych, A. Wagner, M. Elhabiri, A. Krzyczmonik, S. Forsback, O. Solin, V. Gouverneur and F. Taran, *Angew. Chem. Int. Ed.*, 2016, **55**, 12073-12077.
2. B. Lin, Y. Yao, Y. Huang and Z. Weng, *Org. Lett.*, 2022, **24**, 2055-2058.
3. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.

Copies of ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra

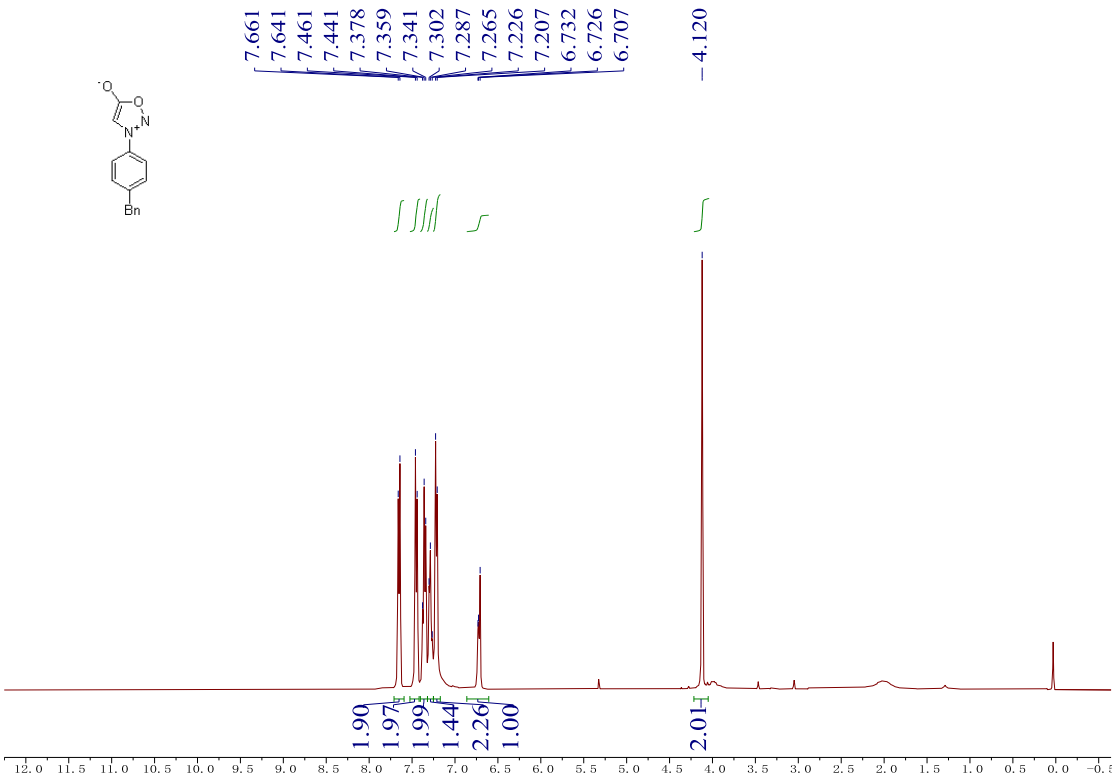
^{1}H NMR spectra of 4-(benzyloxy)phenyl)glycine (400 MHz, DMSO-d_6)



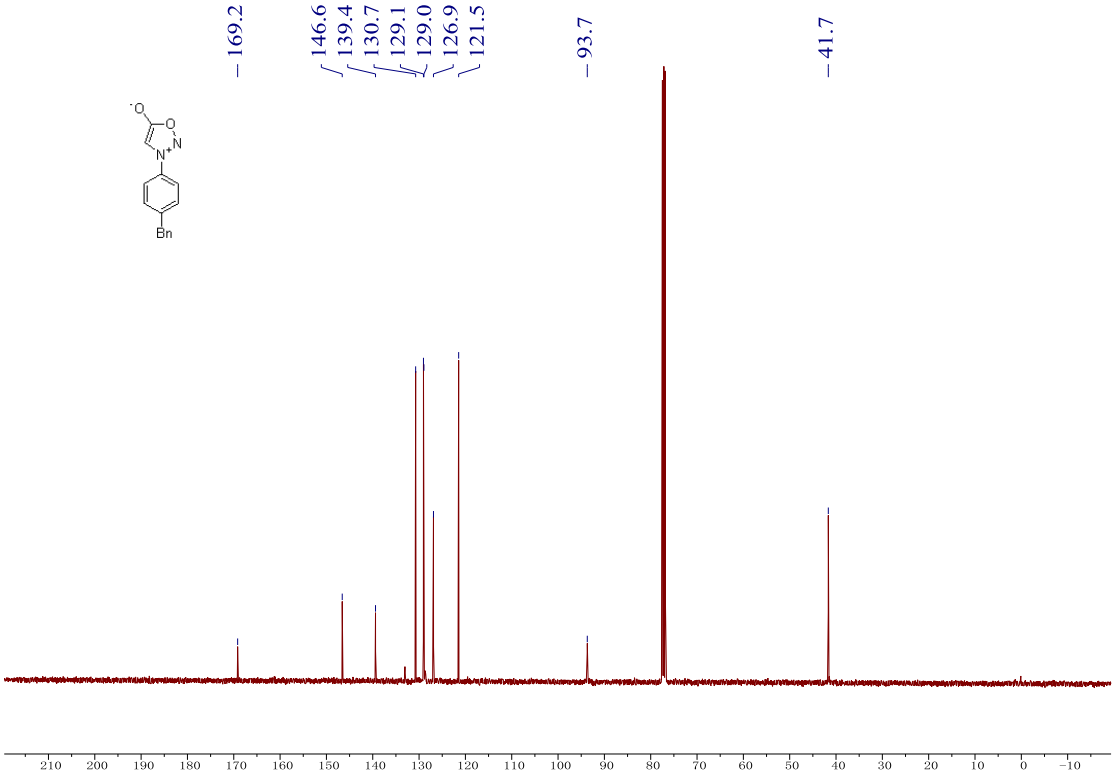
^{13}C{^{1}H} NMR spectra of 4-(benzyloxy)phenyl)glycine (101 MHz, DMSO-d_6)



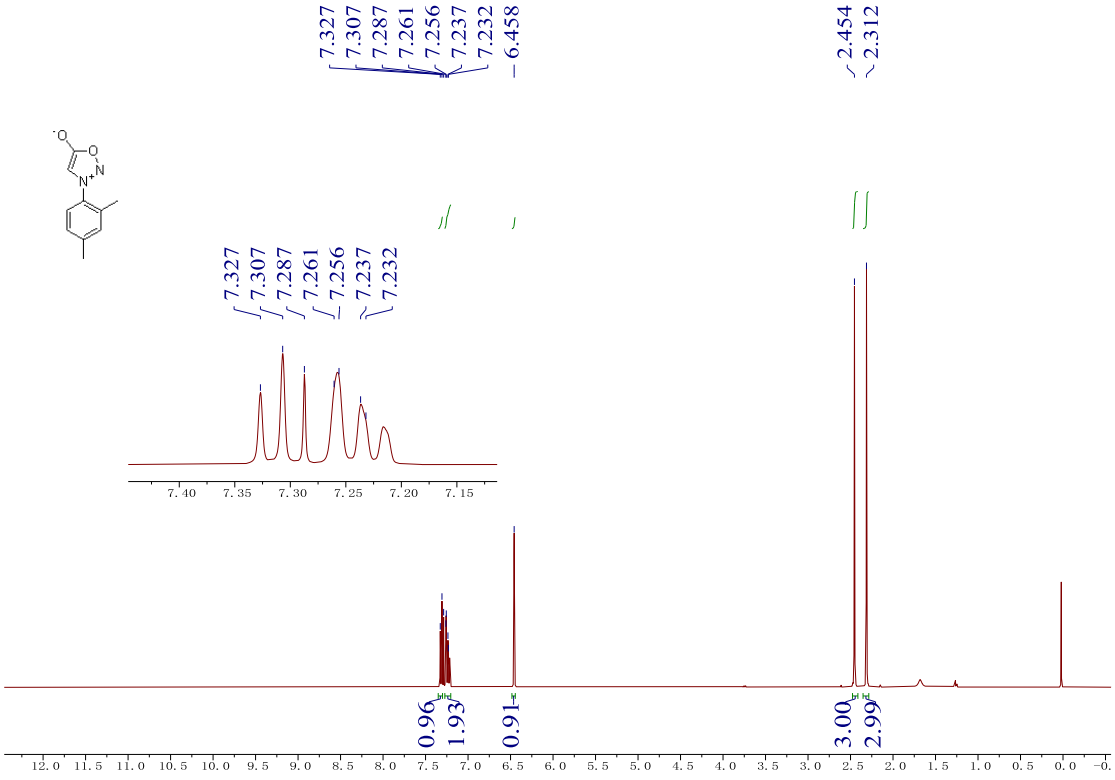
^{1}H NMR spectra of 2e (400 MHz, $CDCl_3$)



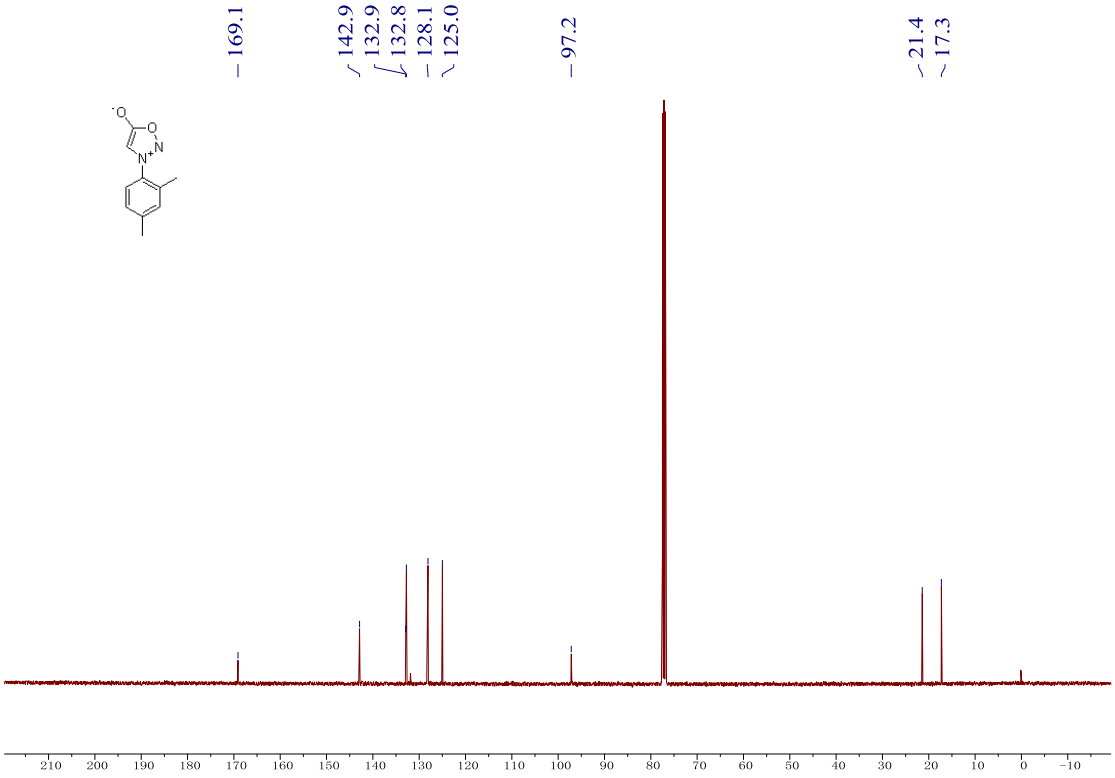
^{13}C{^{1}H} NMR spectra of 2e (101 MHz, $CDCl_3$)



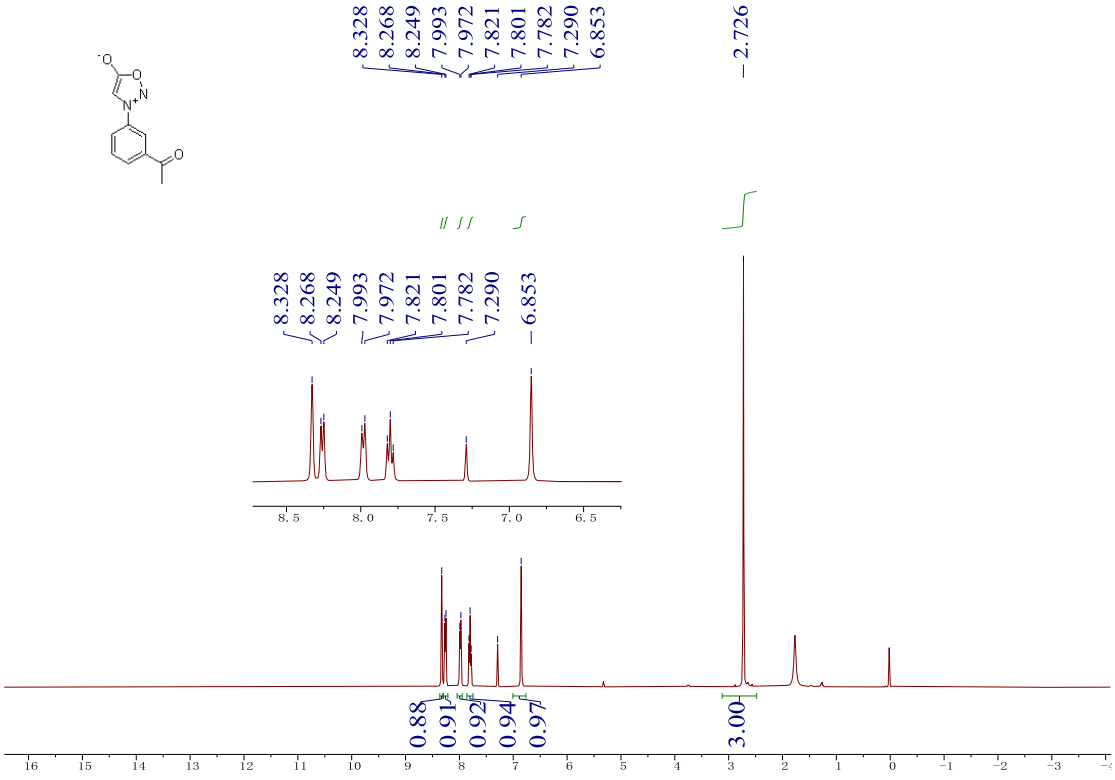
^{1}H NMR spectra of 2i (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR spectra of 2i (101 MHz, $CDCl_3$)



^{1}H NMR spectra of 2n (400 MHz, $CDCl_3$)



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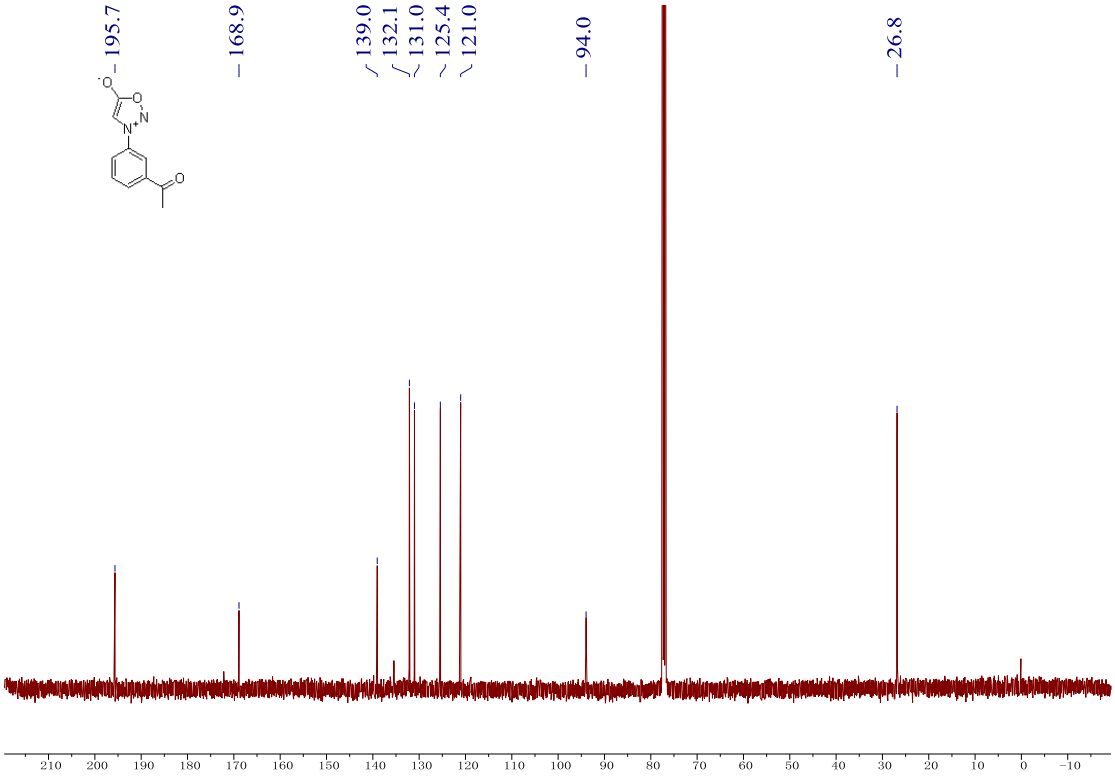
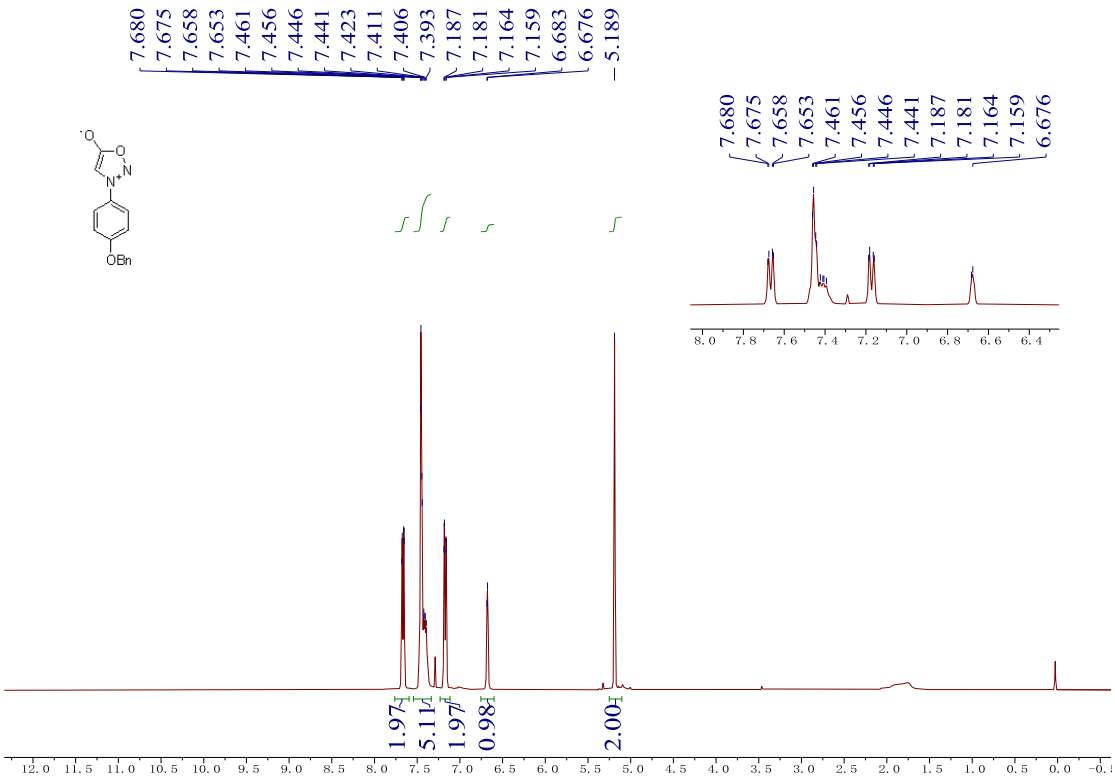
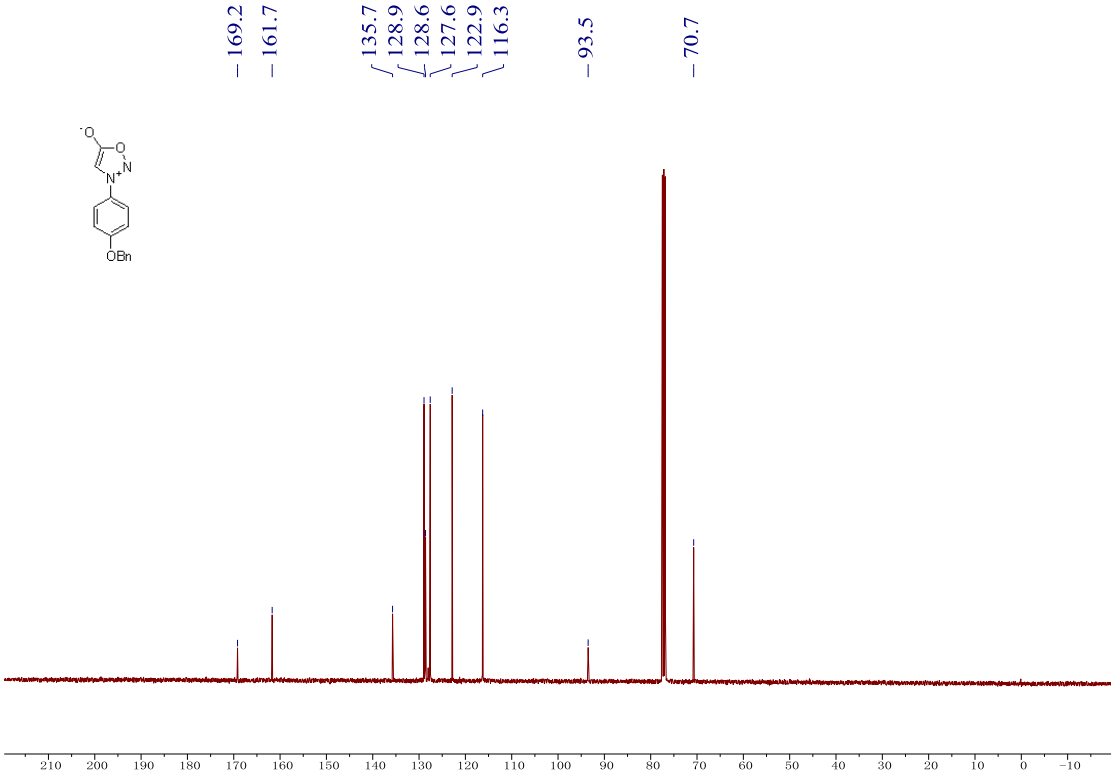


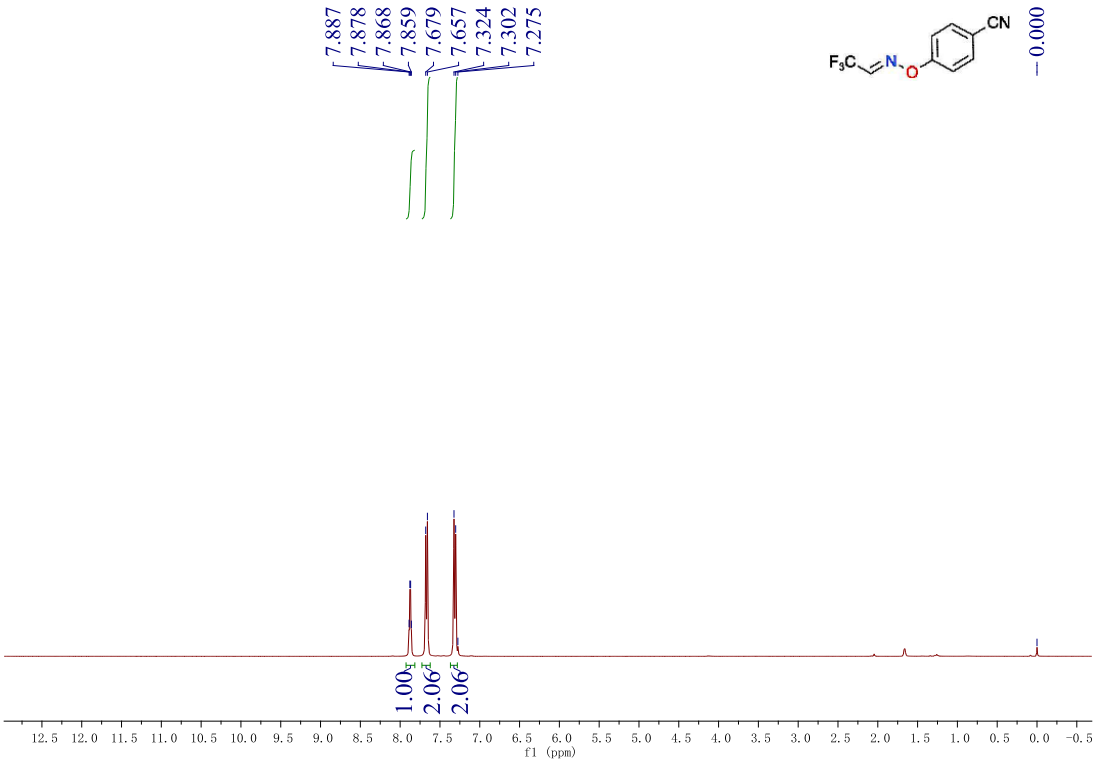
^{1}H NMR spectra of 2p (400 MHz, $CDCl_3$)



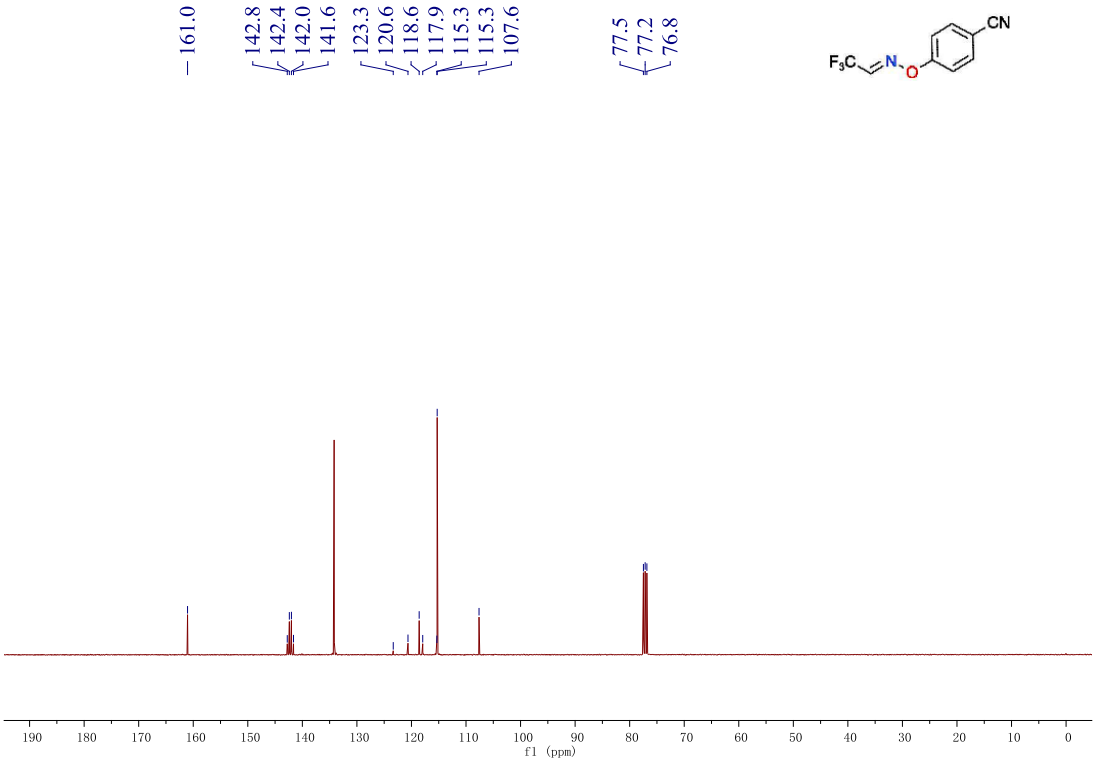
^{13}C{^{1}H} NMR spectra of 2p (101 MHz, $CDCl_3$)



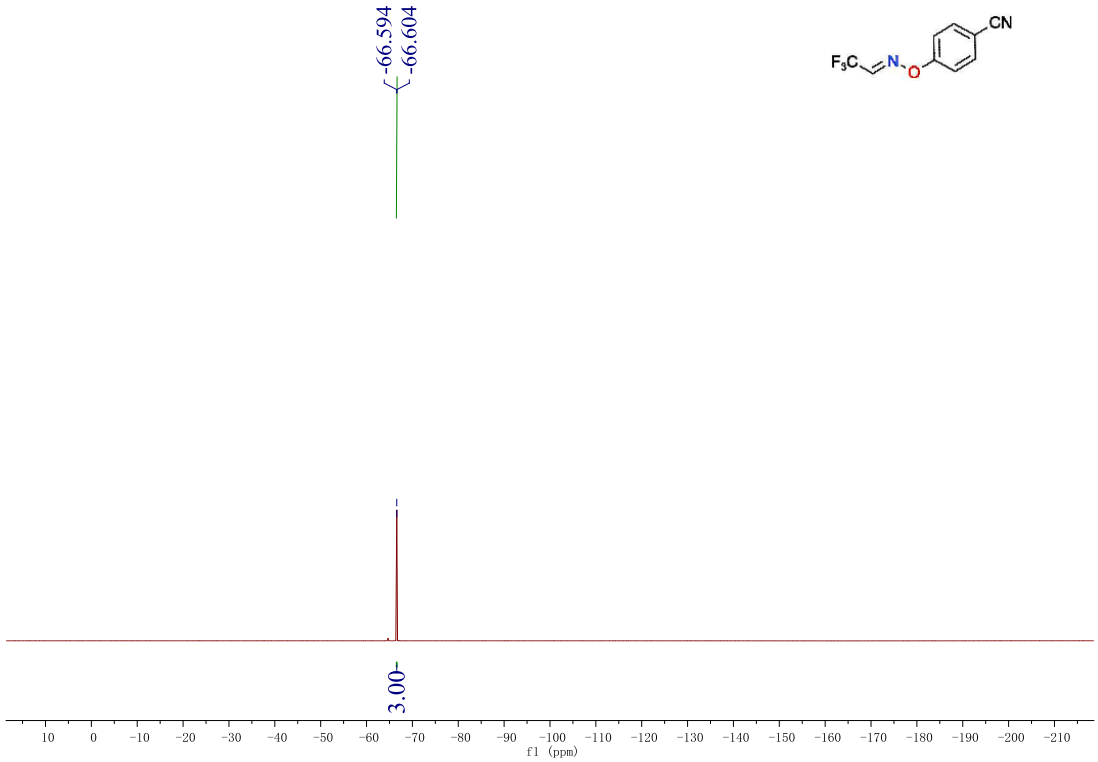
^{1}H NMR spectra of 1b (400 MHz, $CDCl_3$)



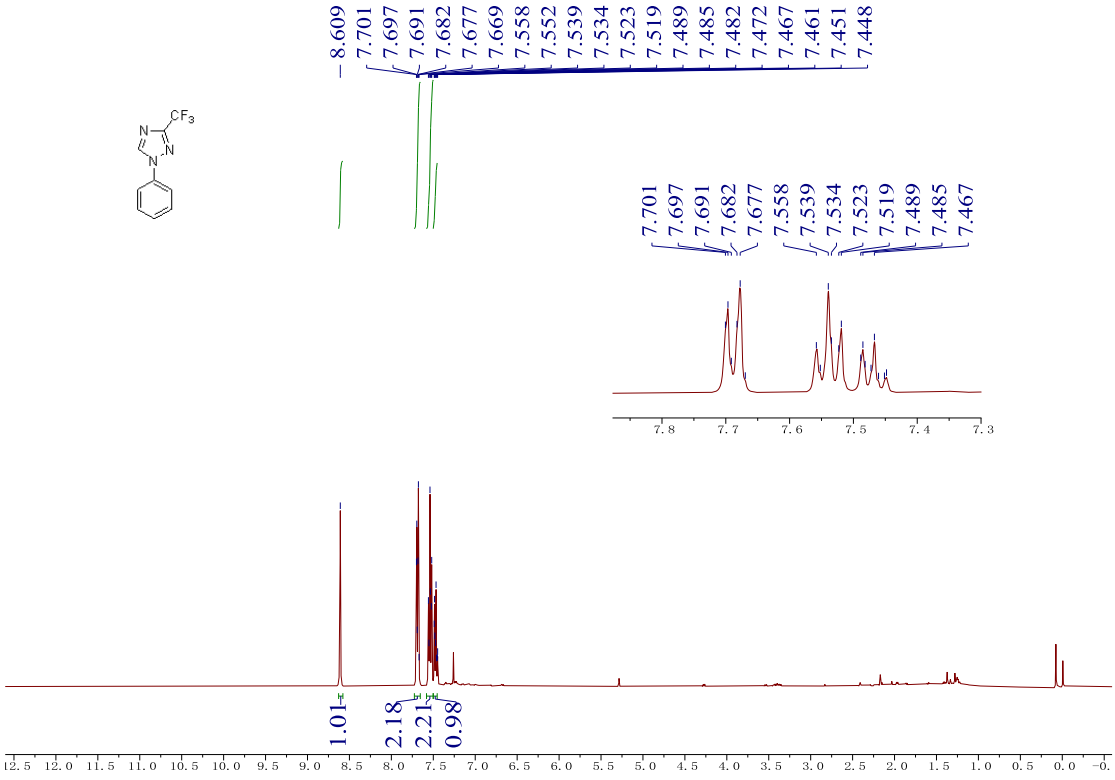
^{13}C{^{1}H} NMR spectra of 1b (101 MHz, $CDCl_3$)



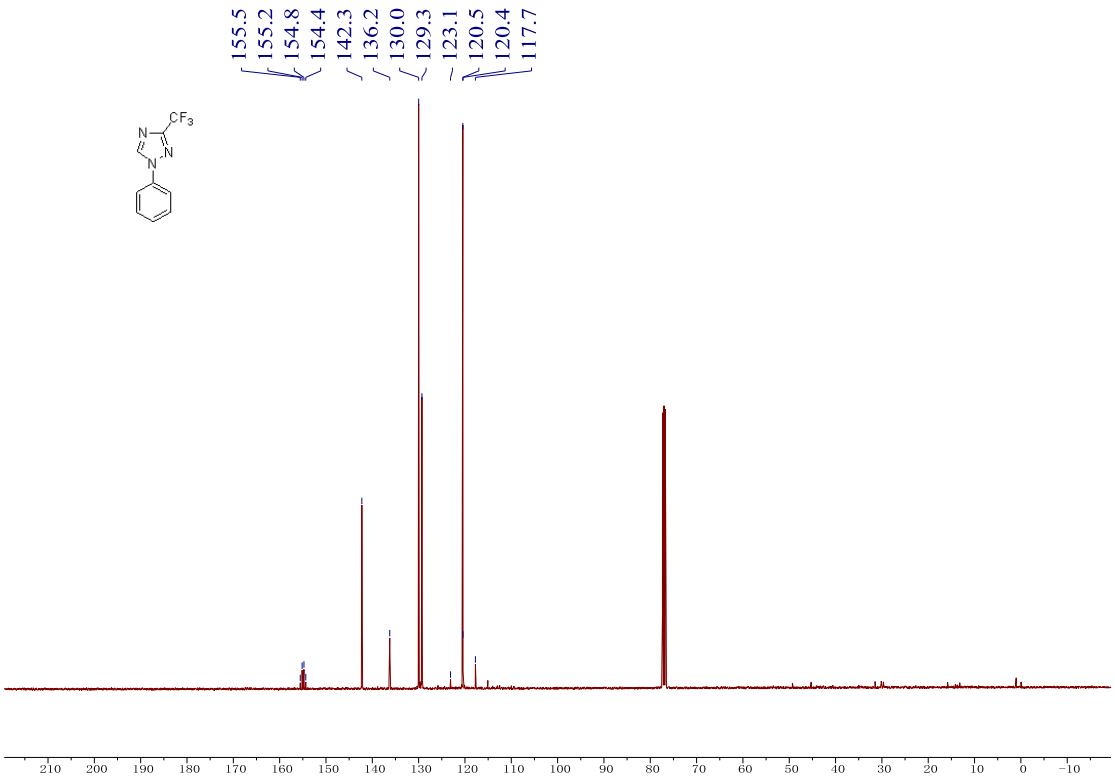
^{19}F NMR spectra of 1b (376 MHz, $CDCl_3$)



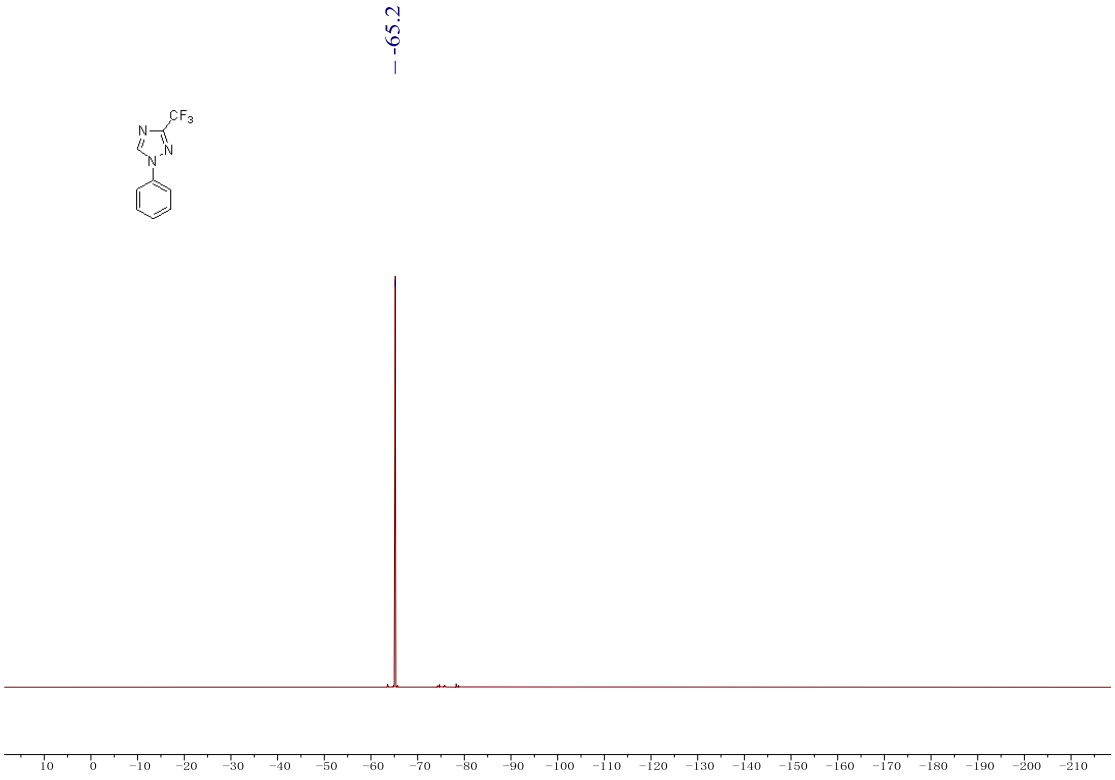
^{1}H NMR spectra of 3a (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectra of 3a (101 MHz, $CDCl_3$)



^{19}F NMR spectra of 3a (376 MHz, $CDCl_3$)



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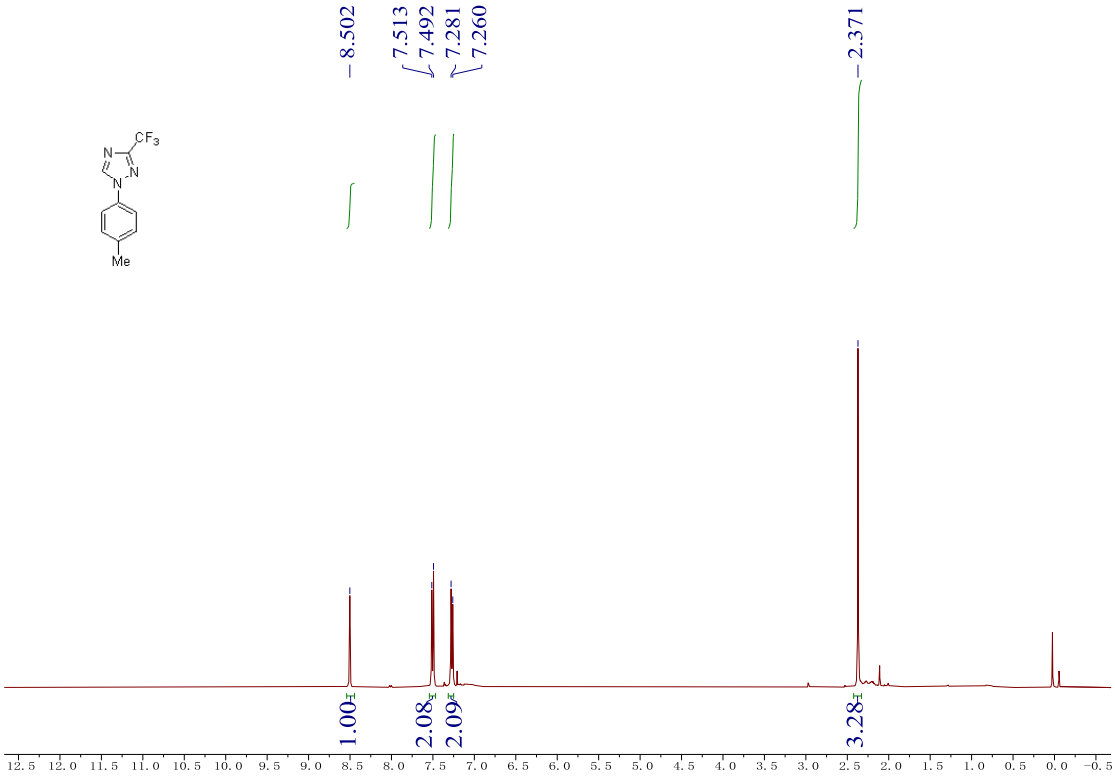

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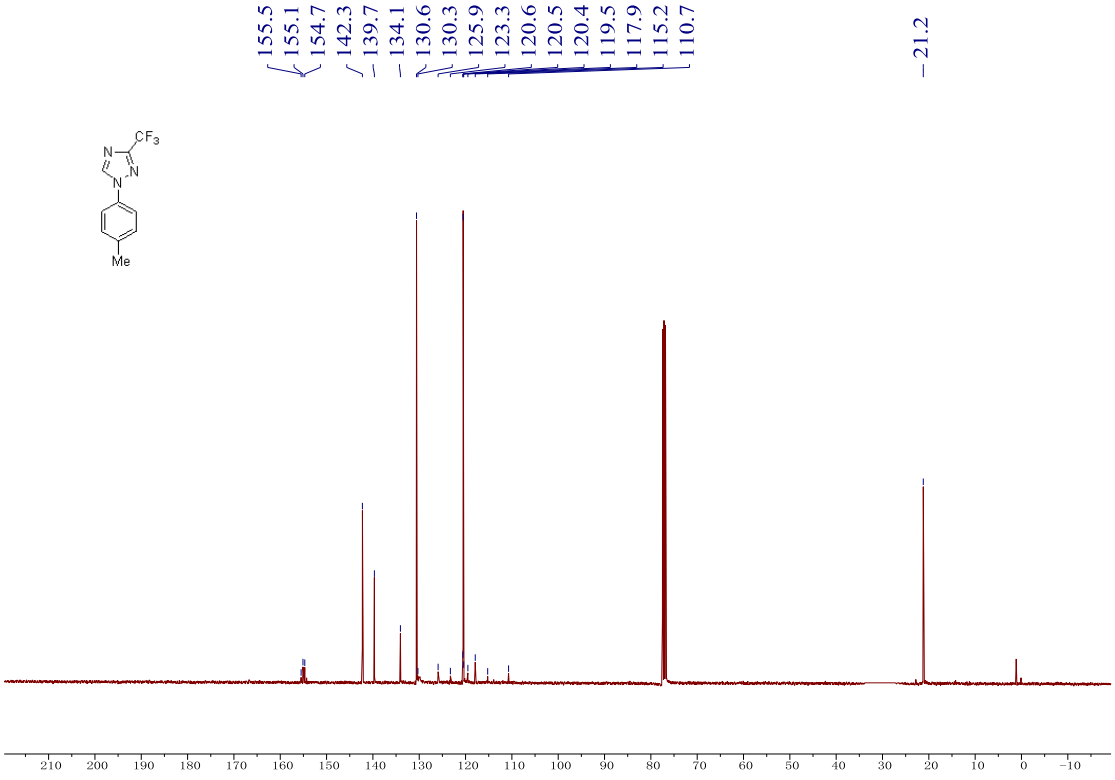

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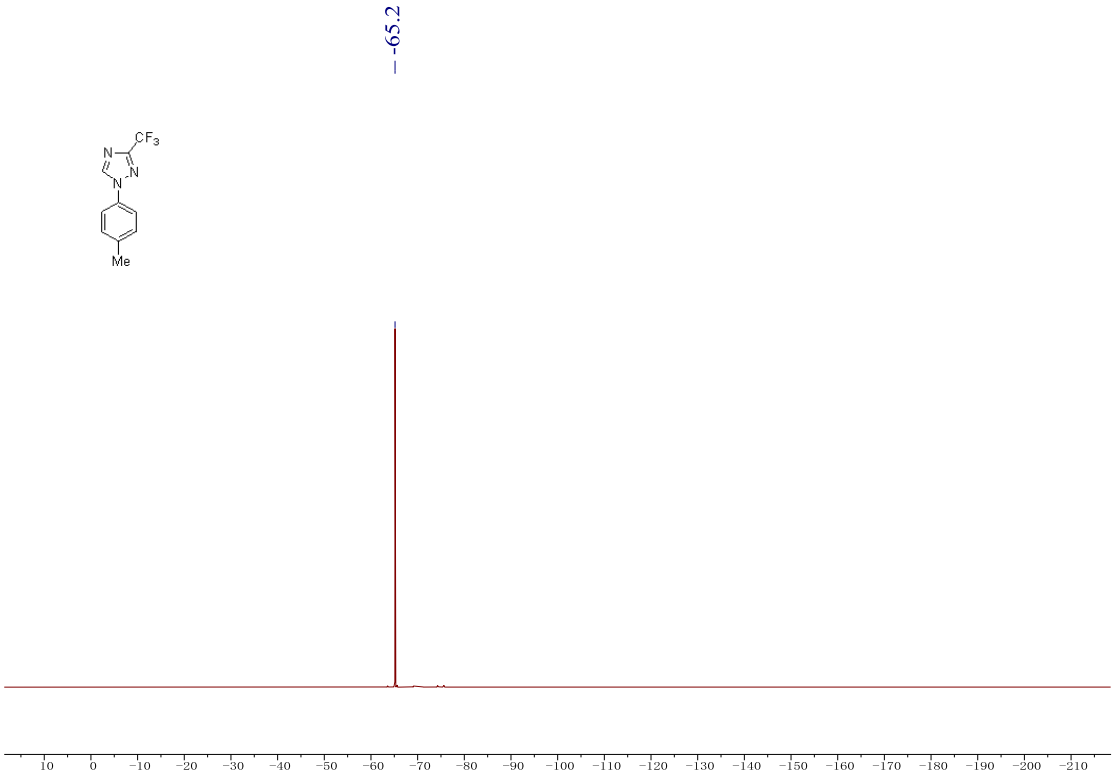
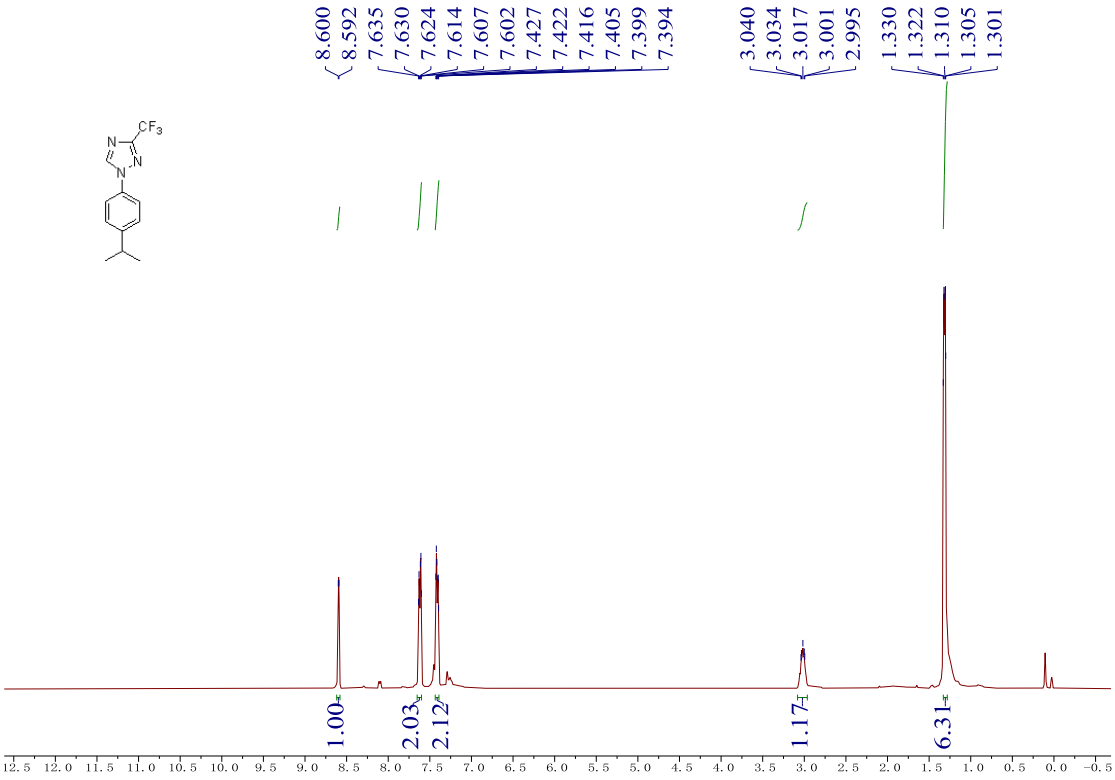
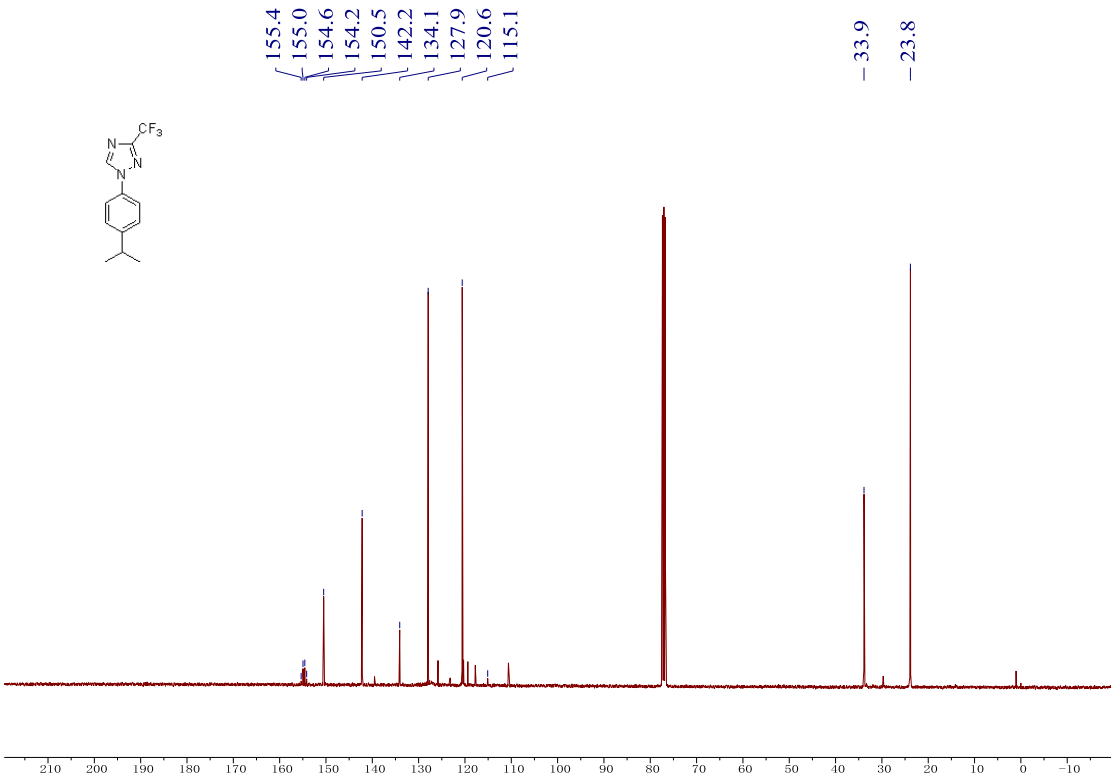


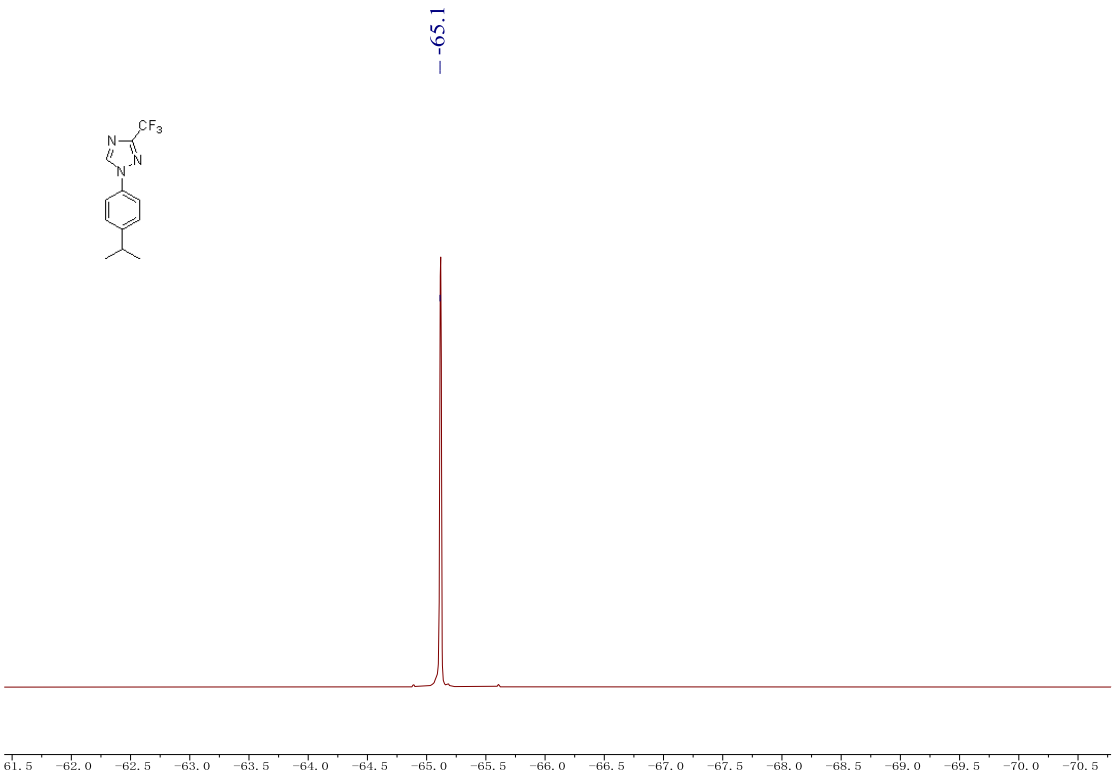
^{1}H NMR spectra of 3c (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectra of 3c (101 MHz, $CDCl_3$)



^{19}F NMR spectra of 3c (376 MHz, $CDCl_3$)



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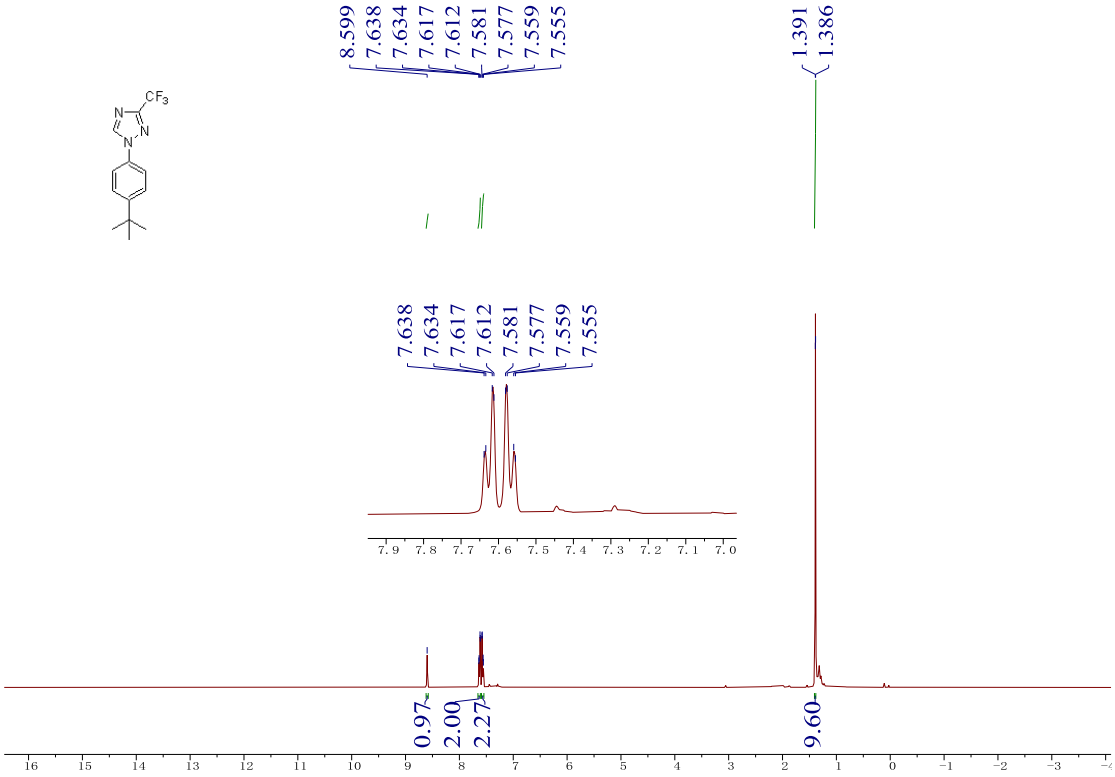

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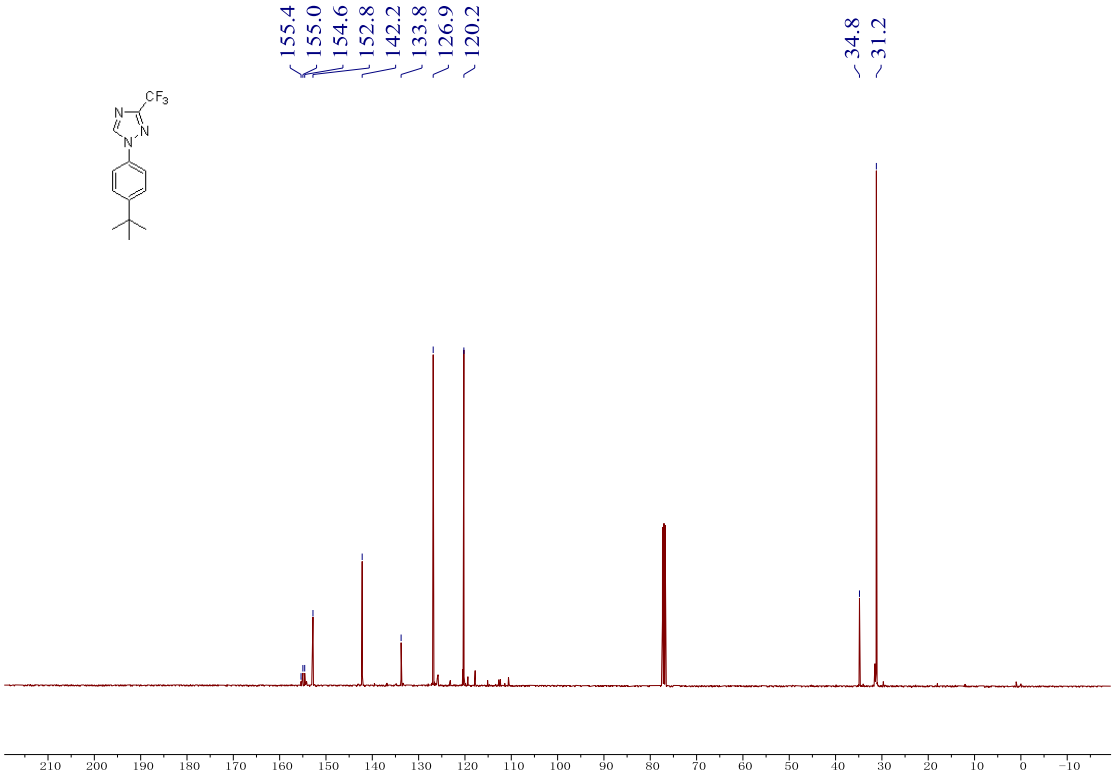

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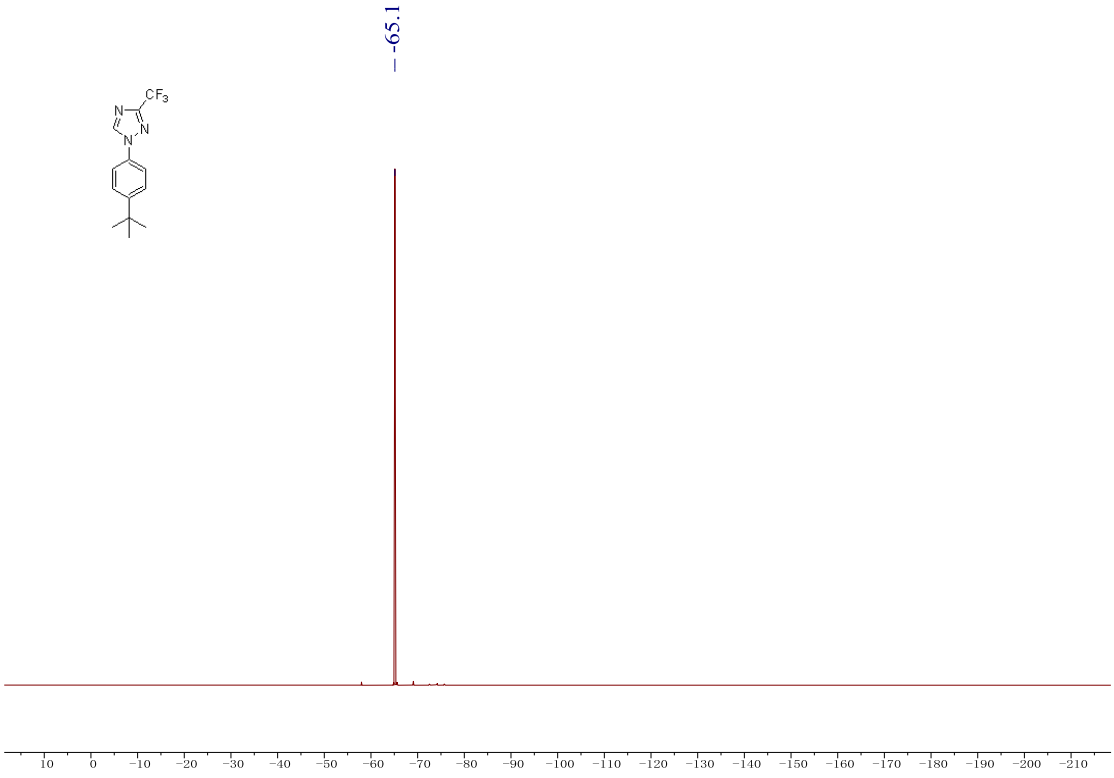

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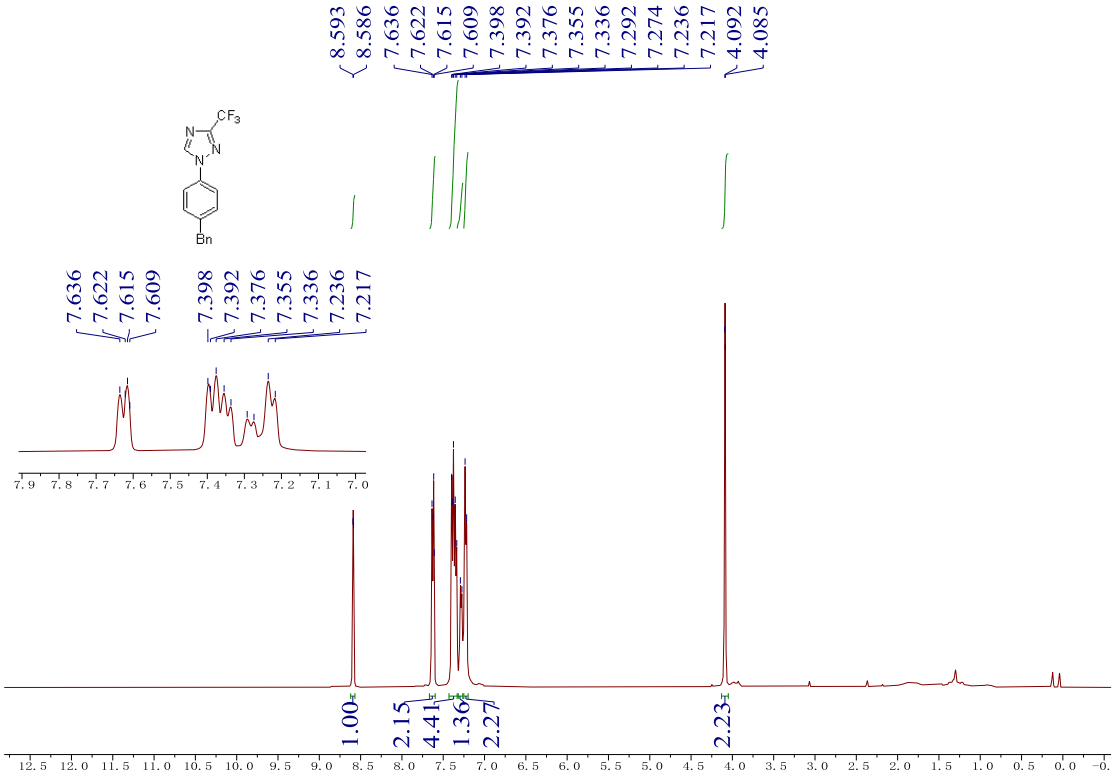

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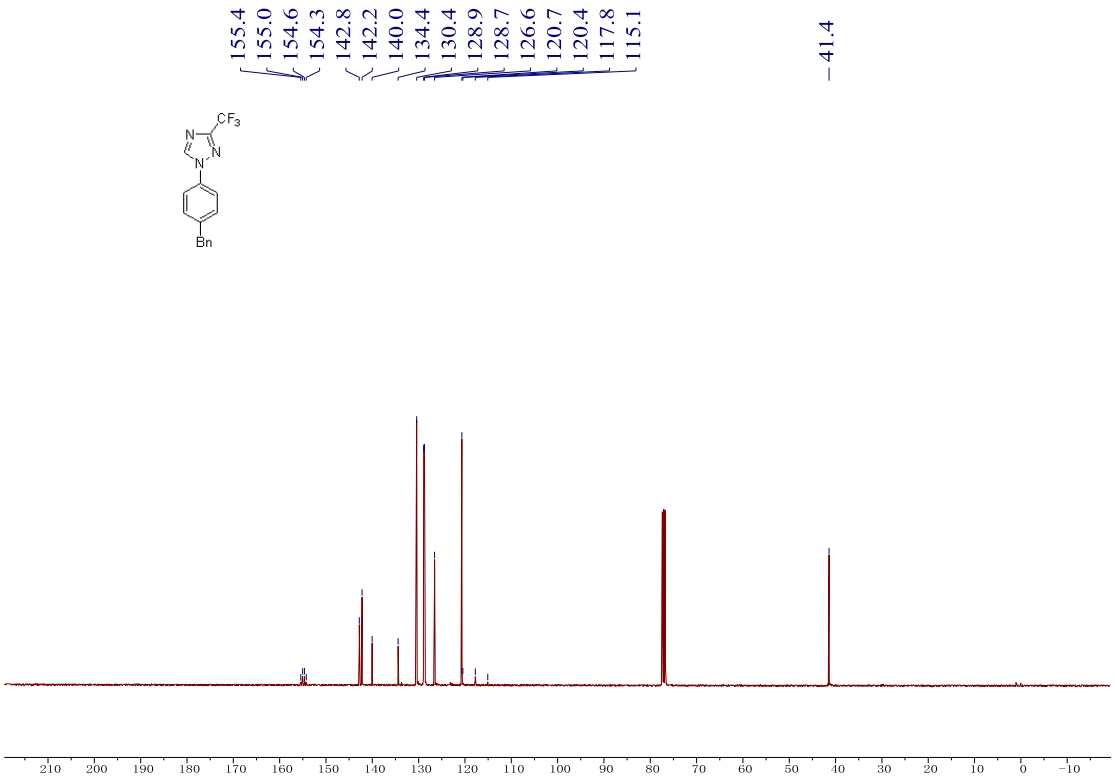
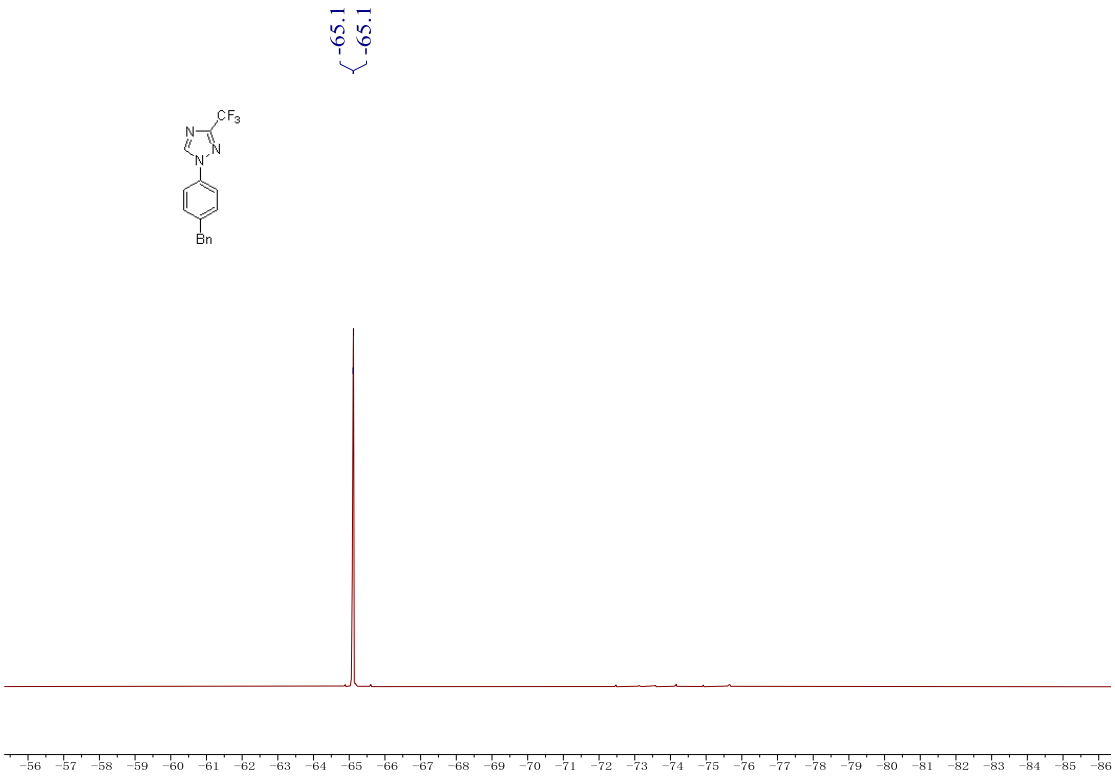


^{19}F NMR spectra of 3e (376 MHz, $CDCl_3$)



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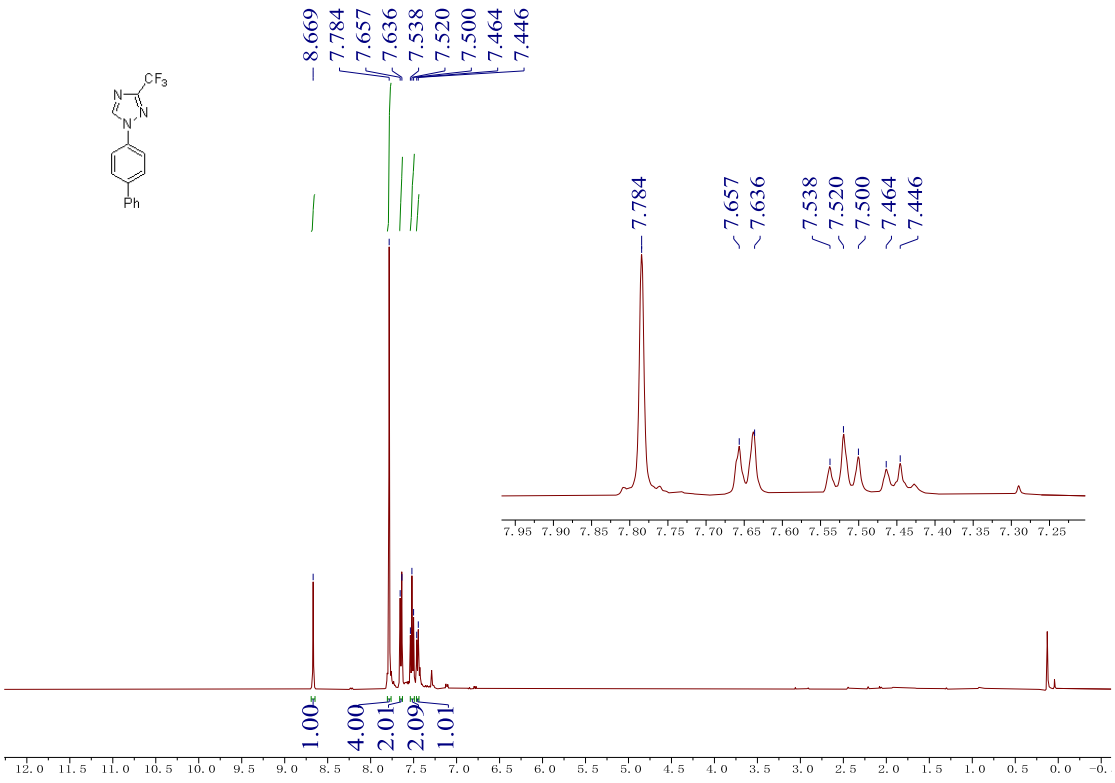

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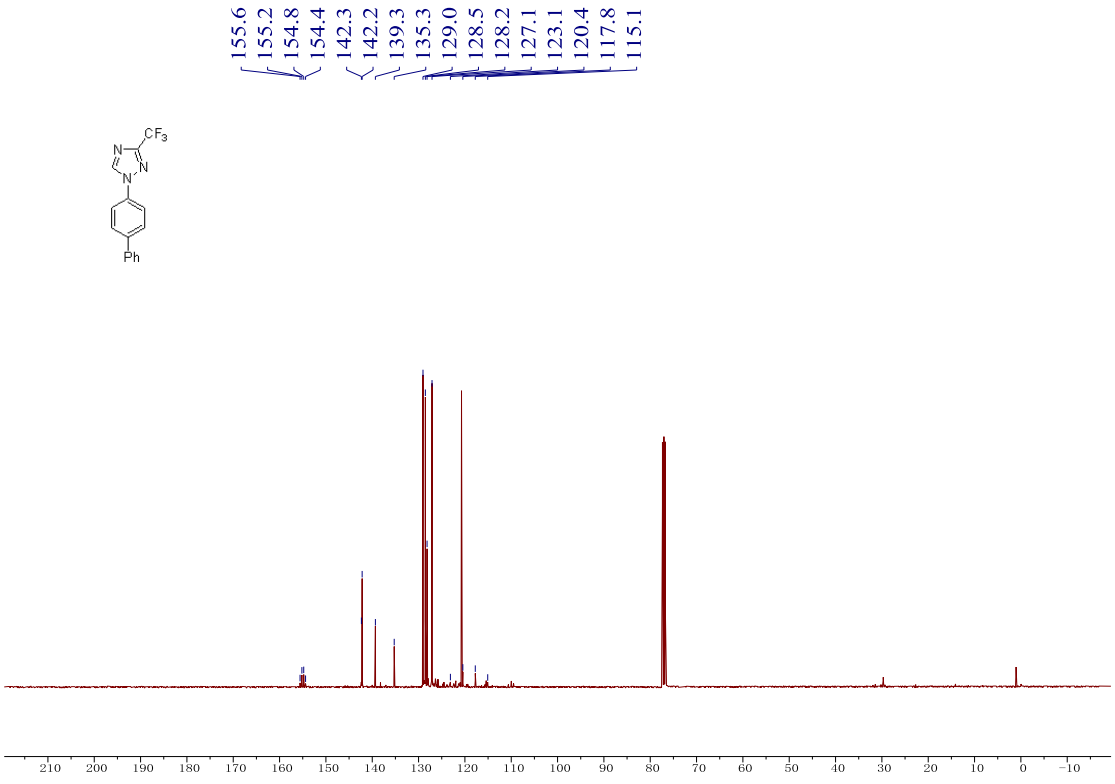

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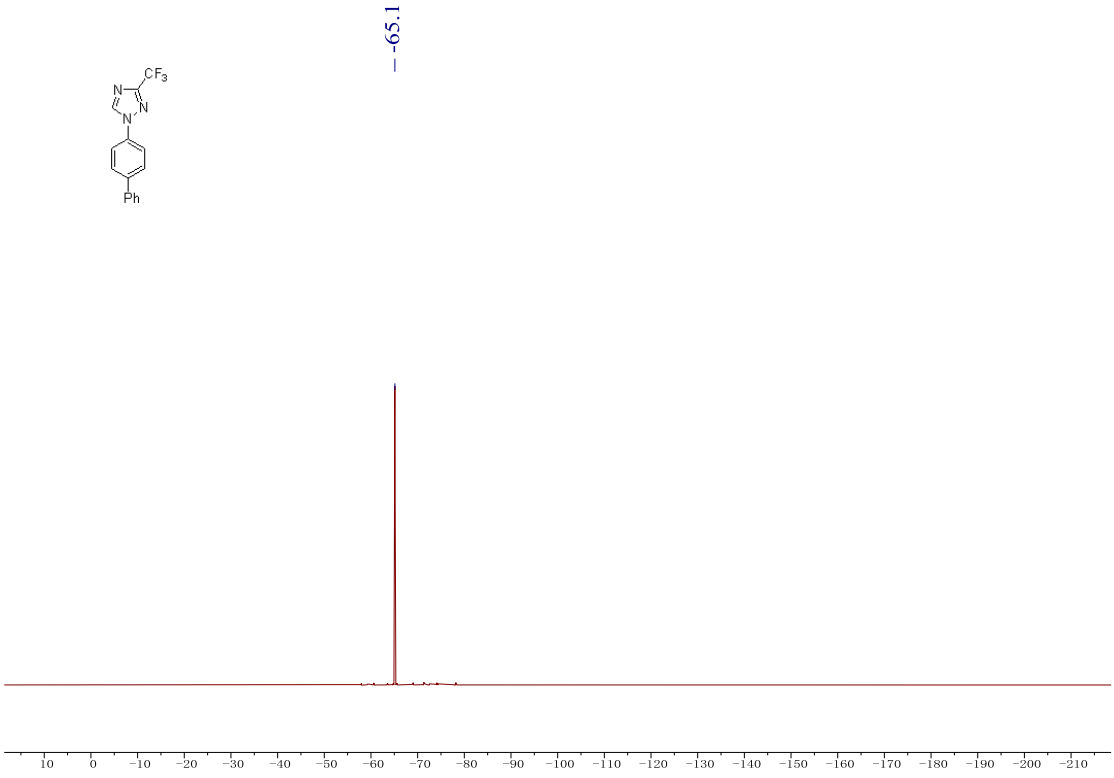
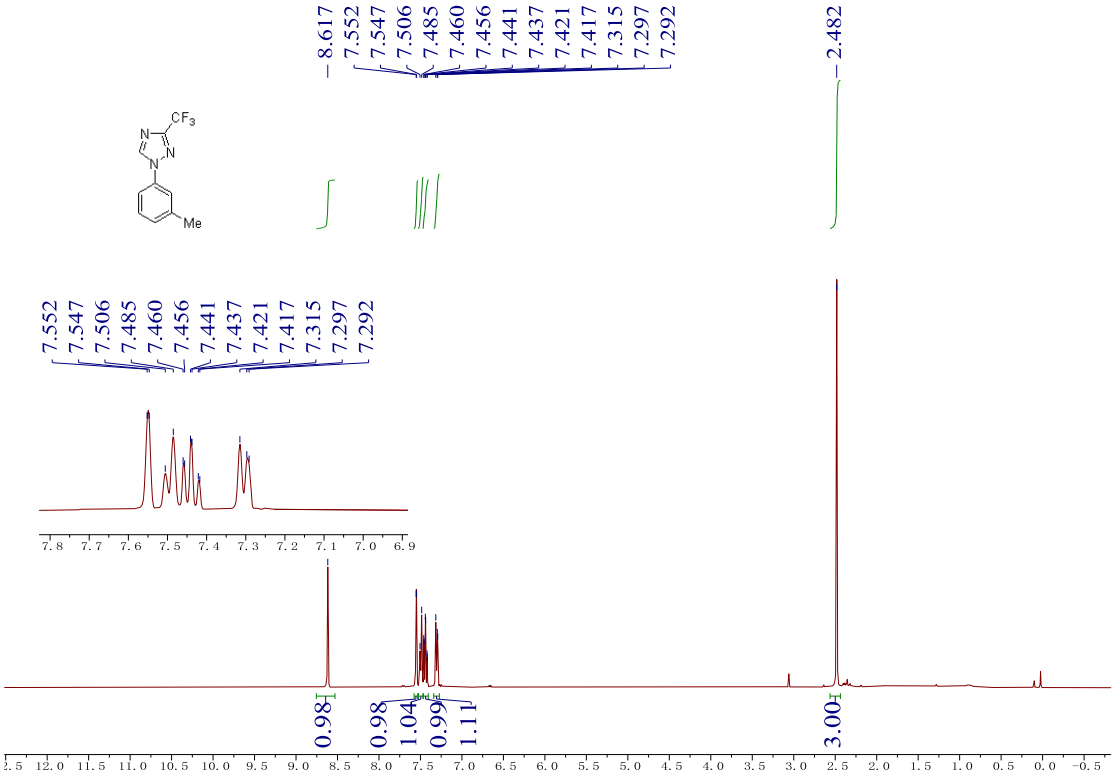
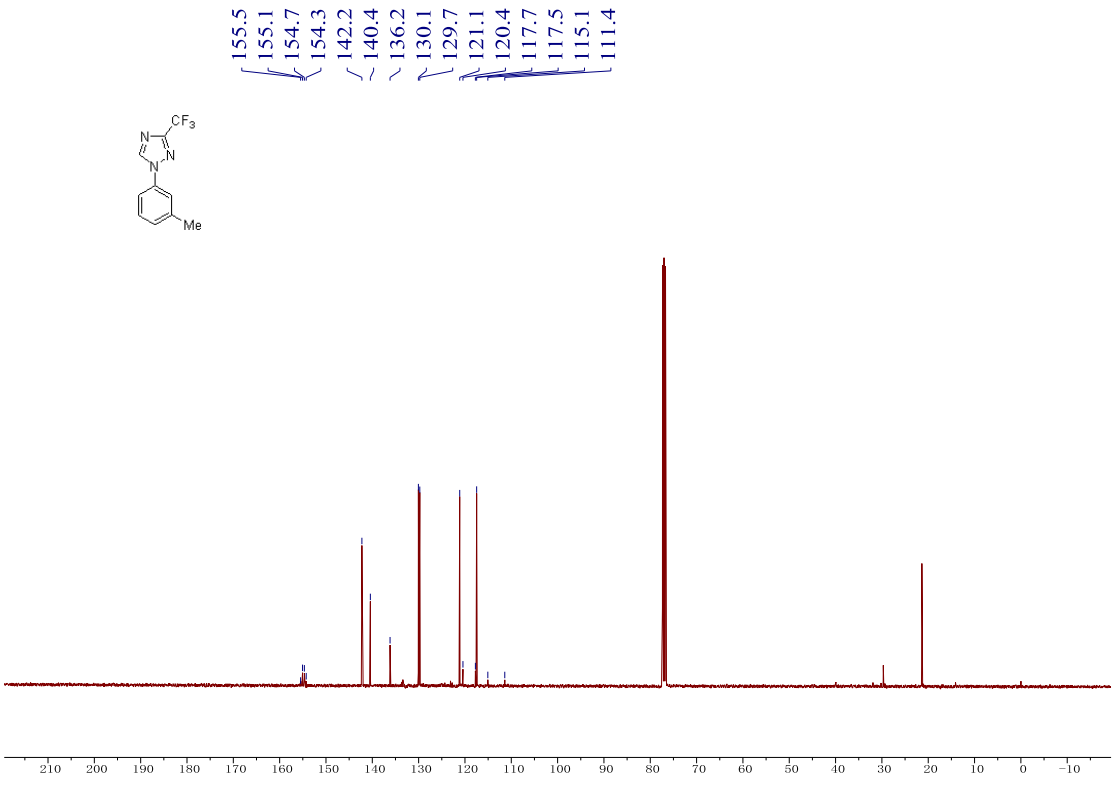


^{1}H NMR spectra of 3g (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectra of 3g (101 MHz, $CDCl_3$)



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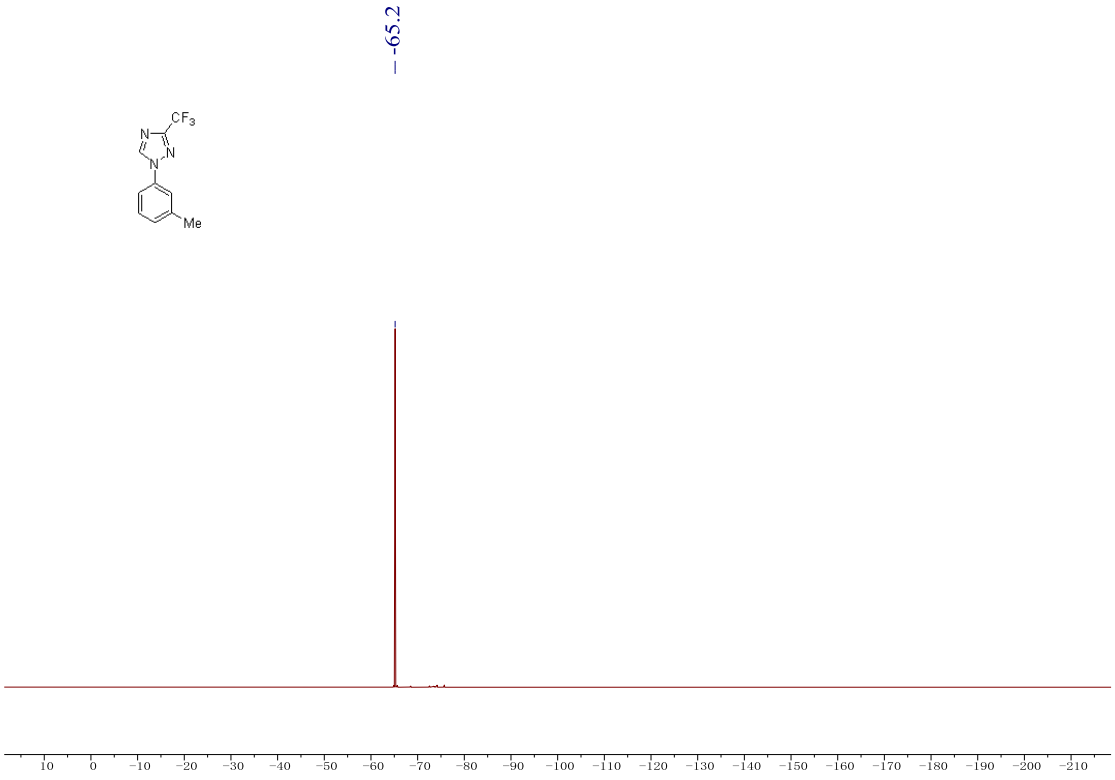
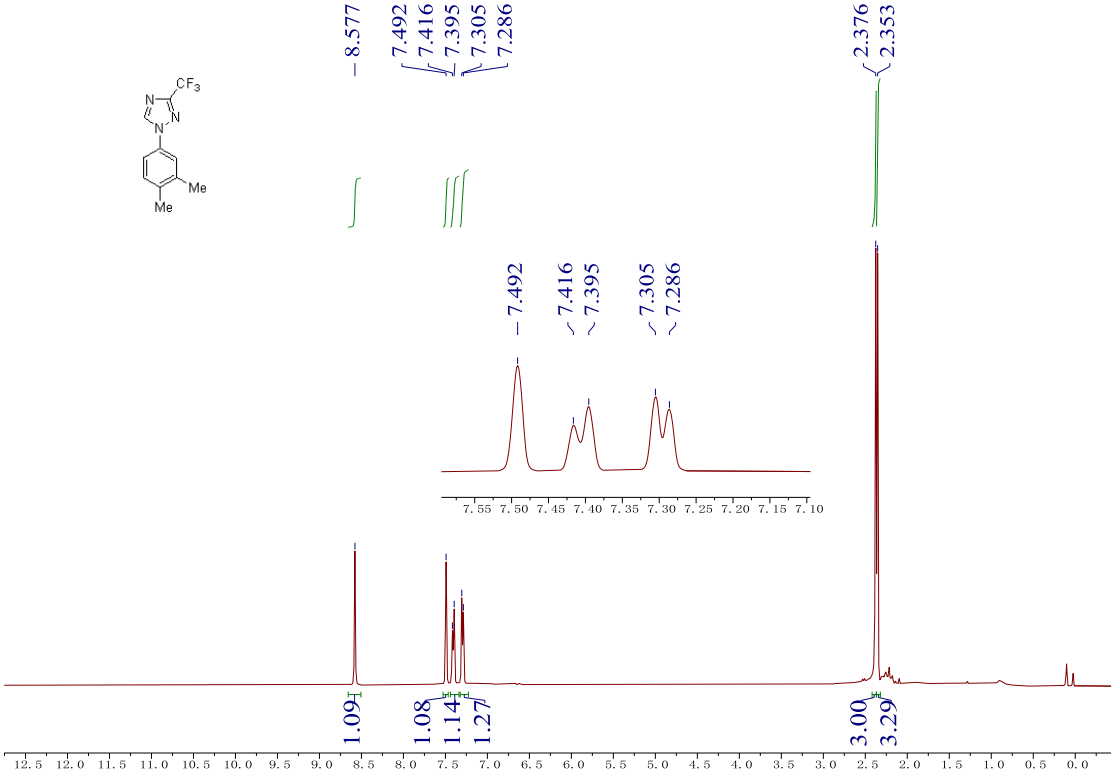


^{1}H NMR spectra of 3h (400 MHz, $CDCl_3$)



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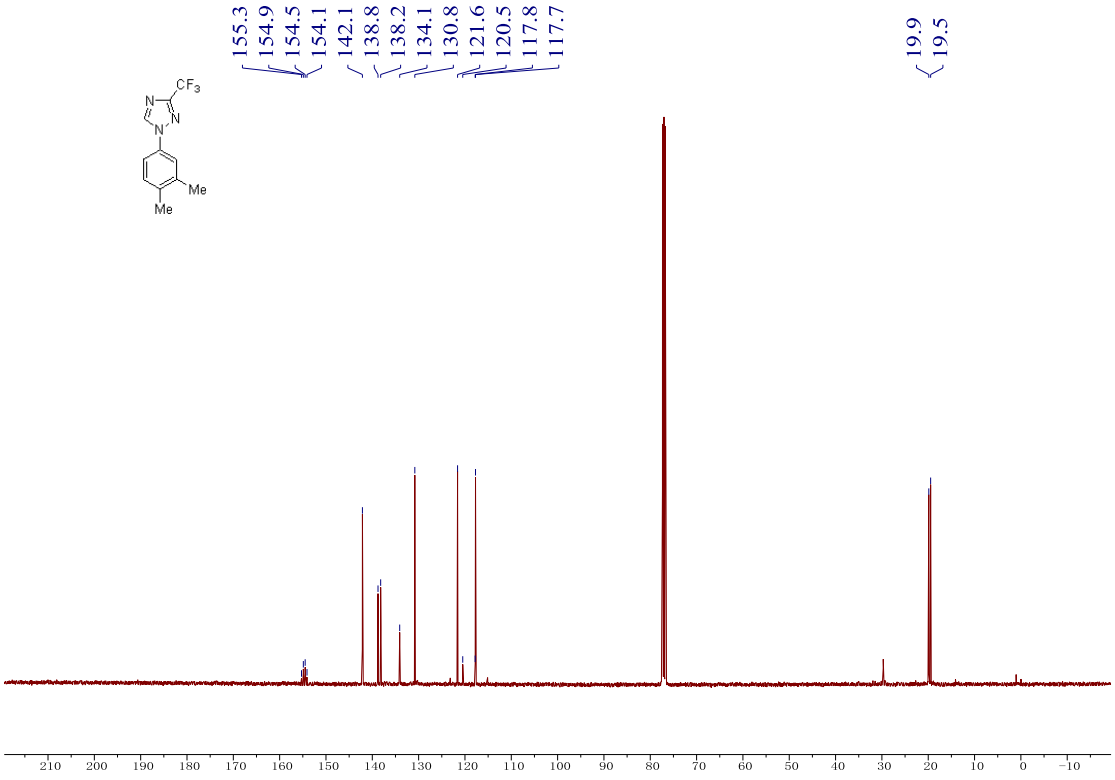
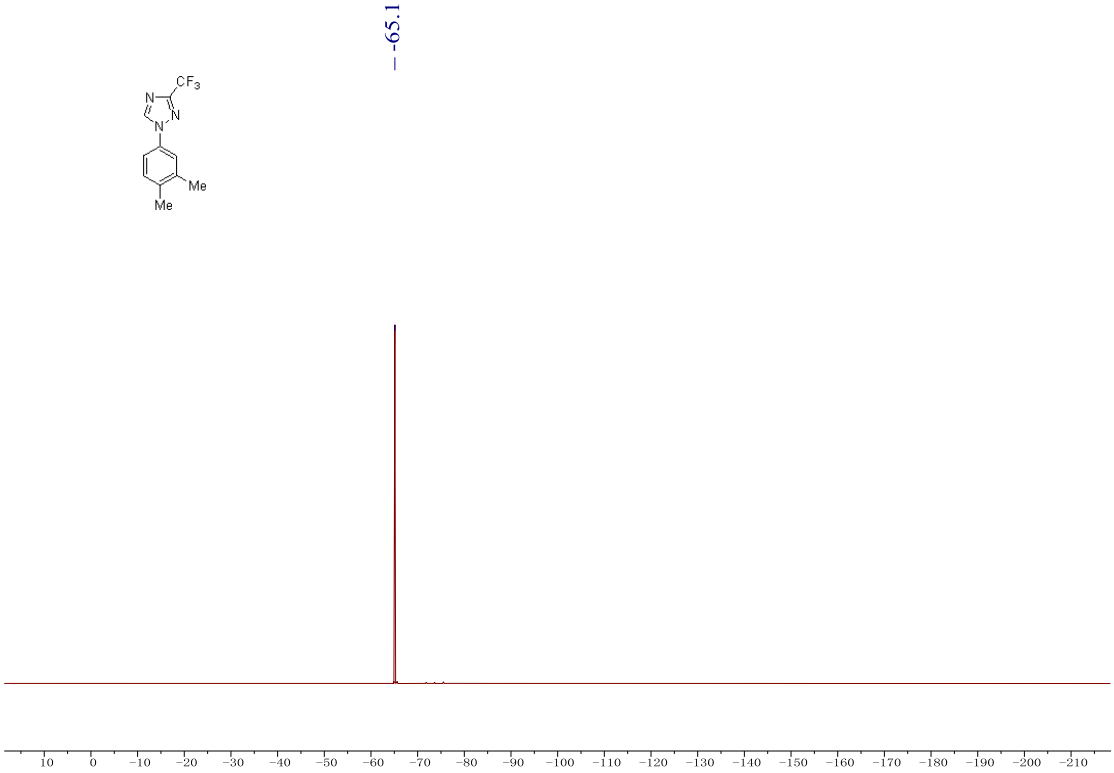
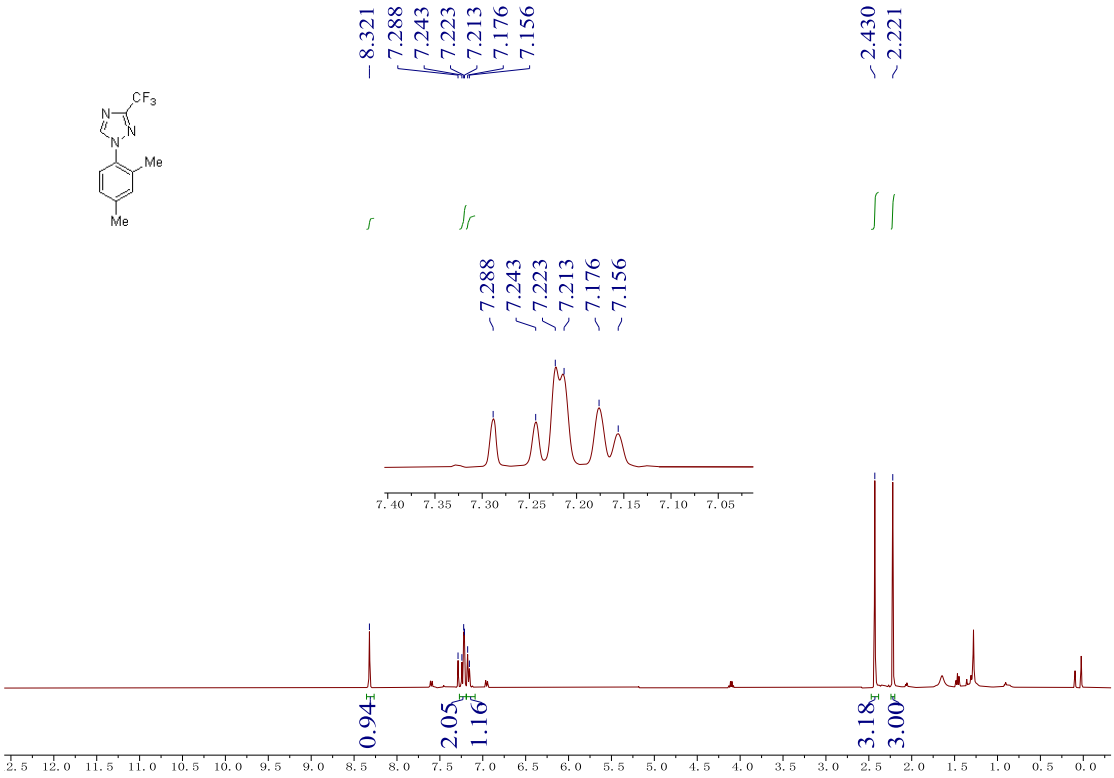


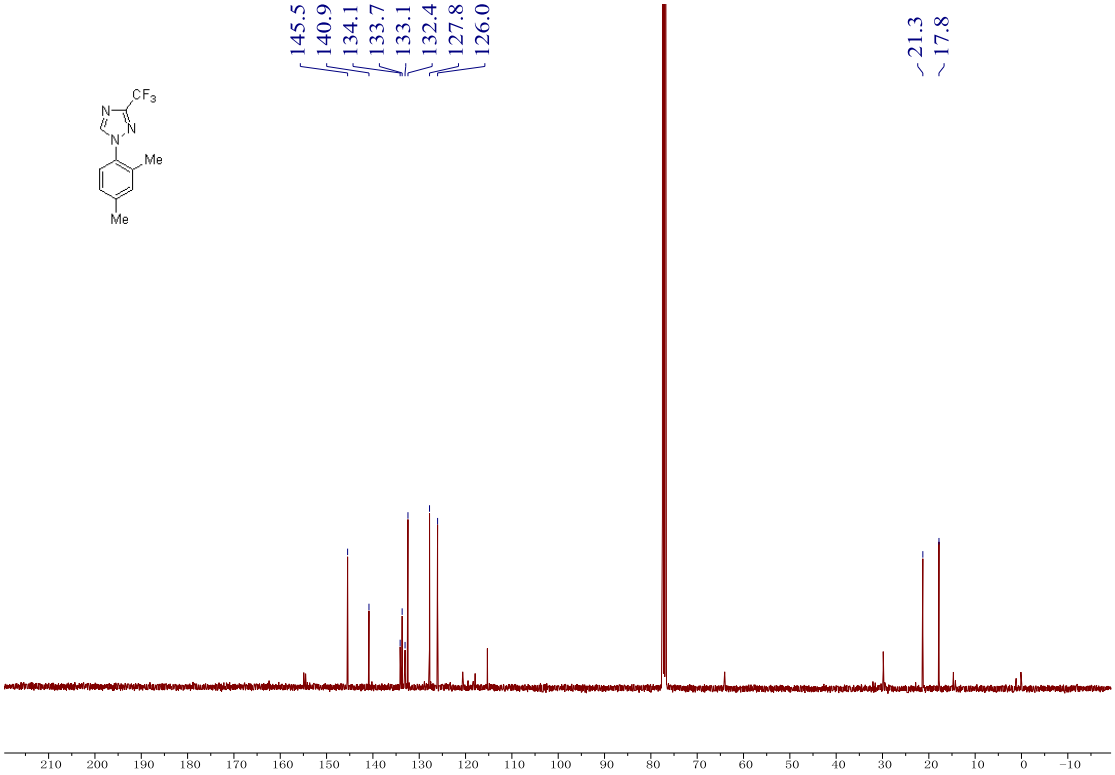
^{19}F NMR spectra of 3h (376 MHz, $CDCl_3$)



^{1}H NMR spectra of 3i (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectra of 3i (101 MHz, $CDCl_3$)



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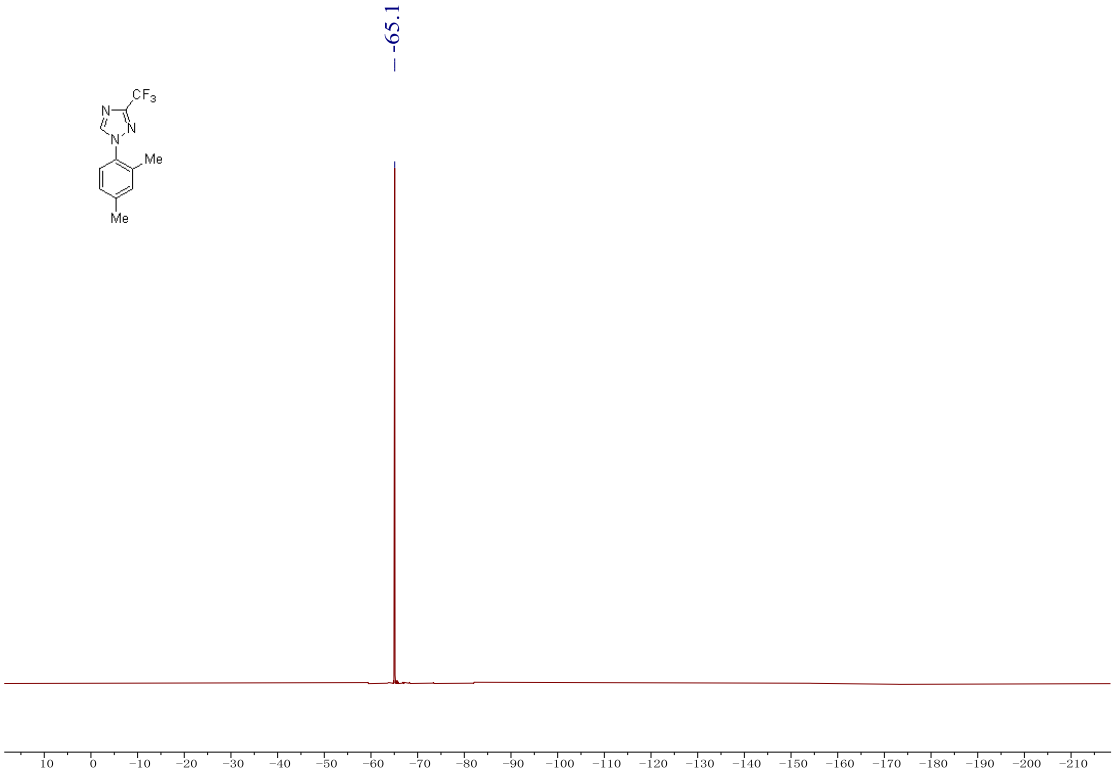
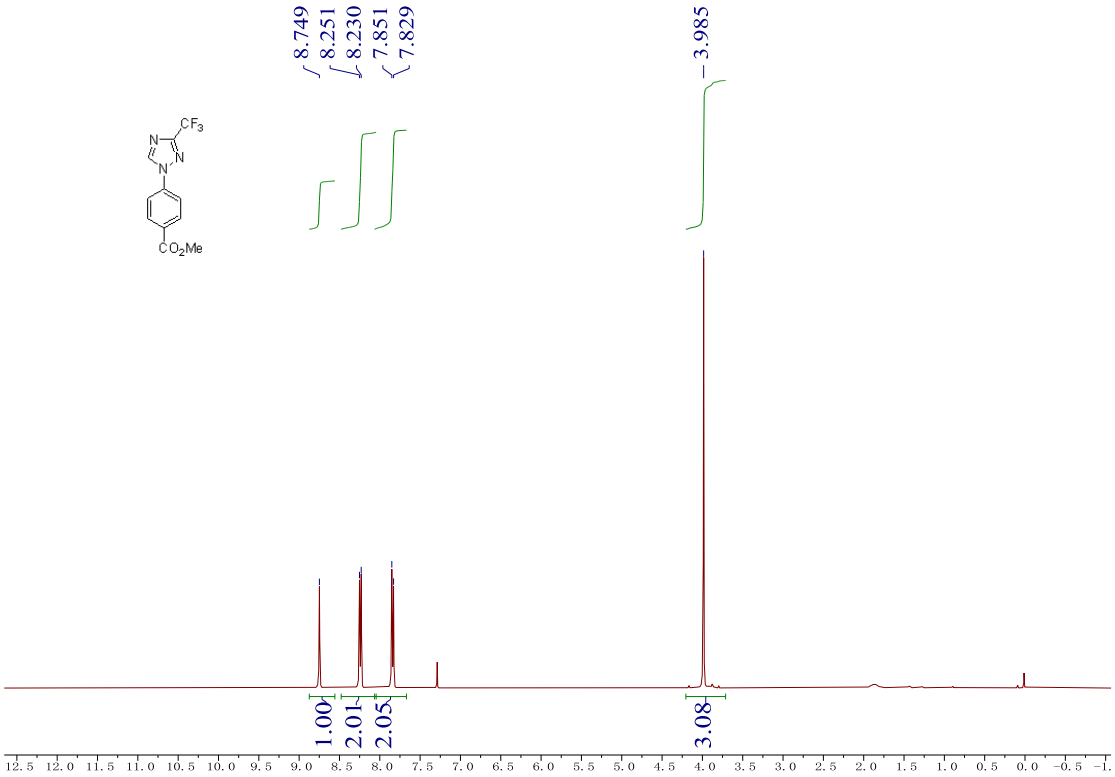
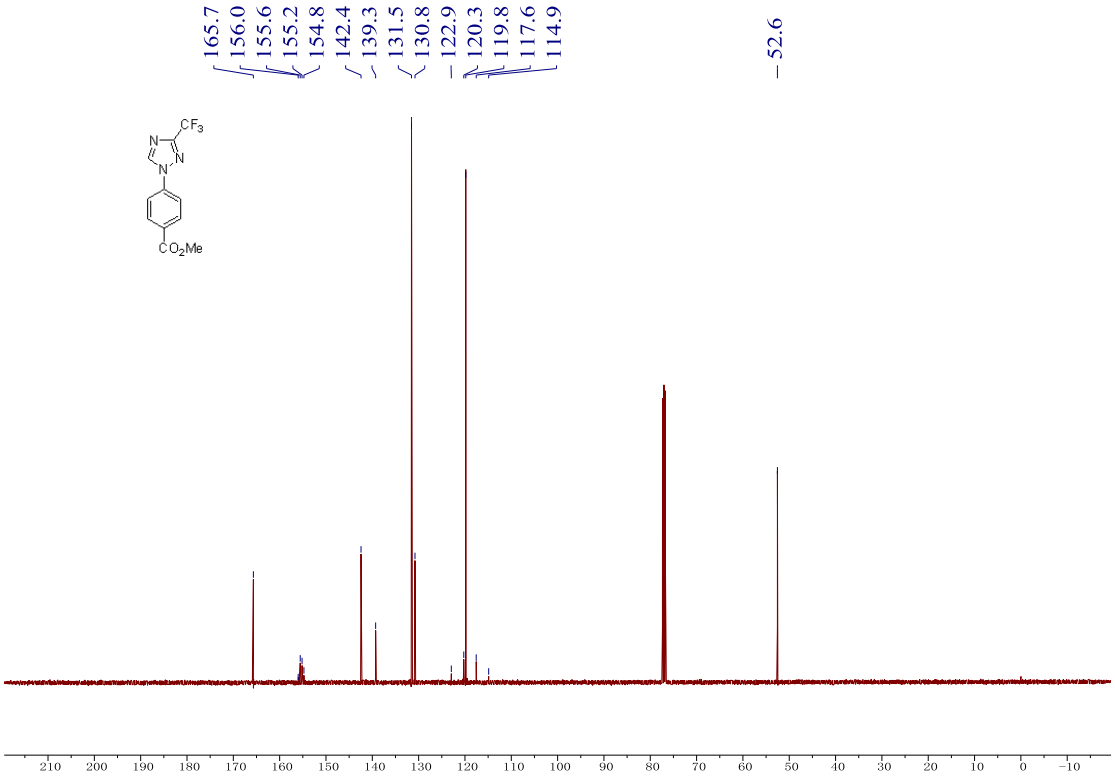


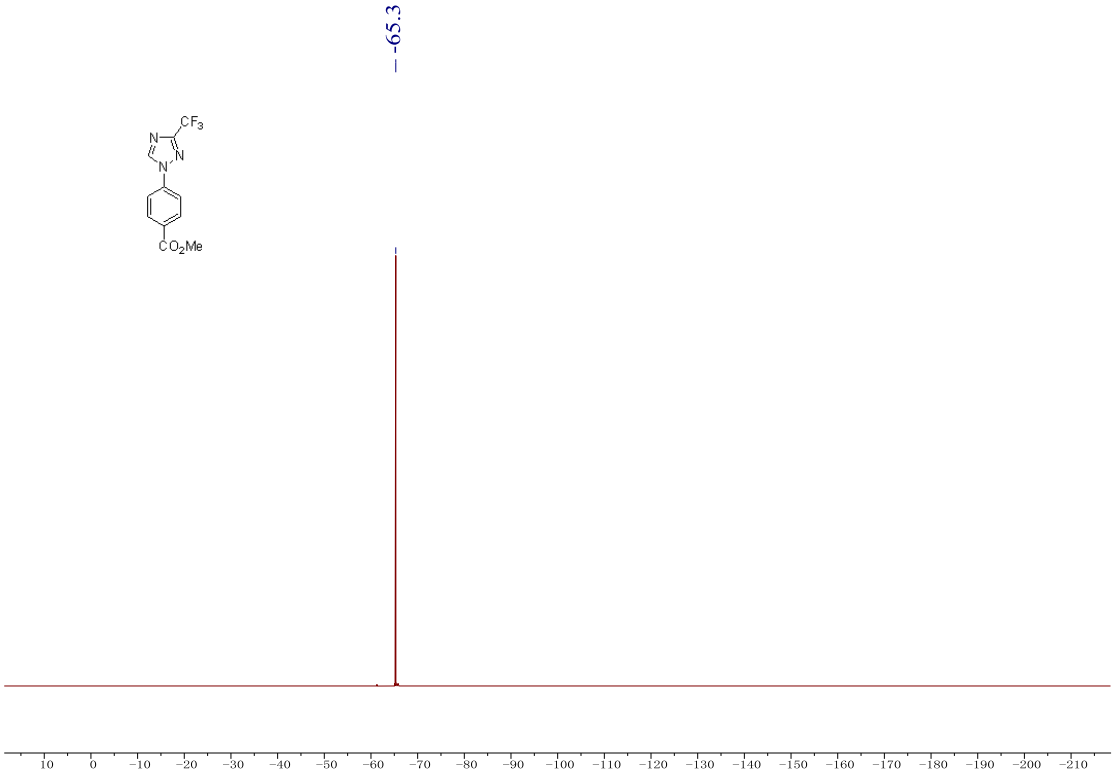
^{1}H NMR spectra of 3j (400 MHz, $CDCl_3$)



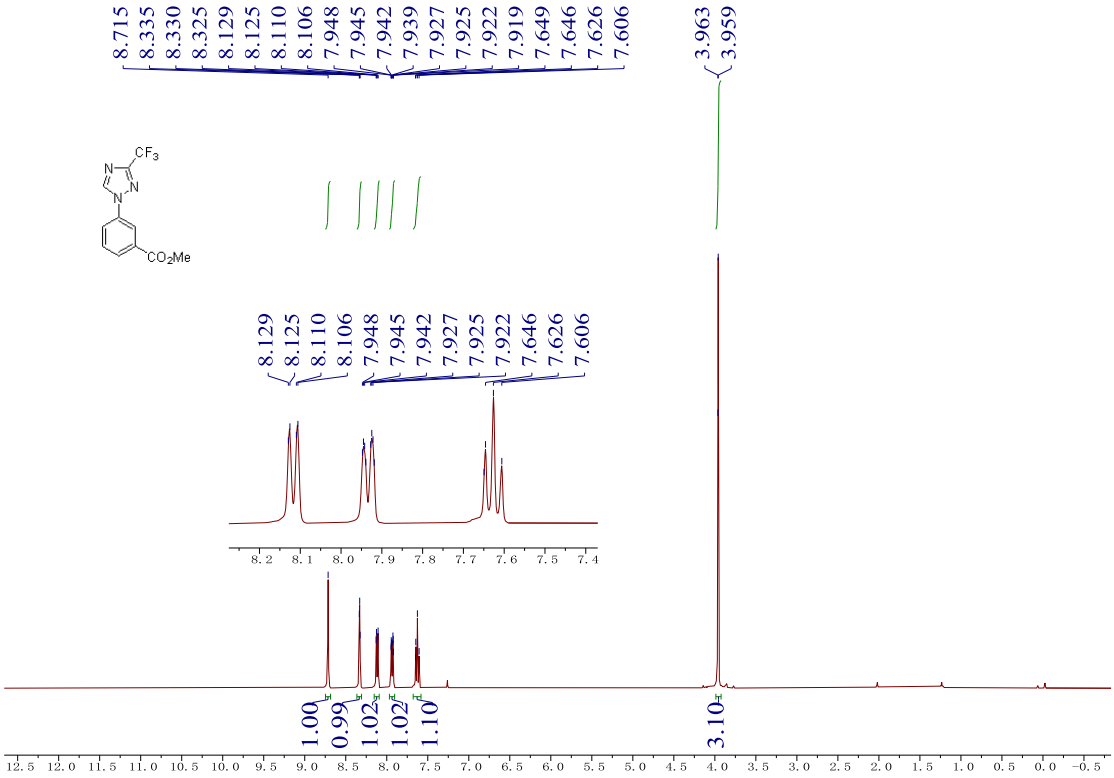
^{13}C{^{1}H} NMR spectra of 3j (101 MHz, $CDCl_3$)



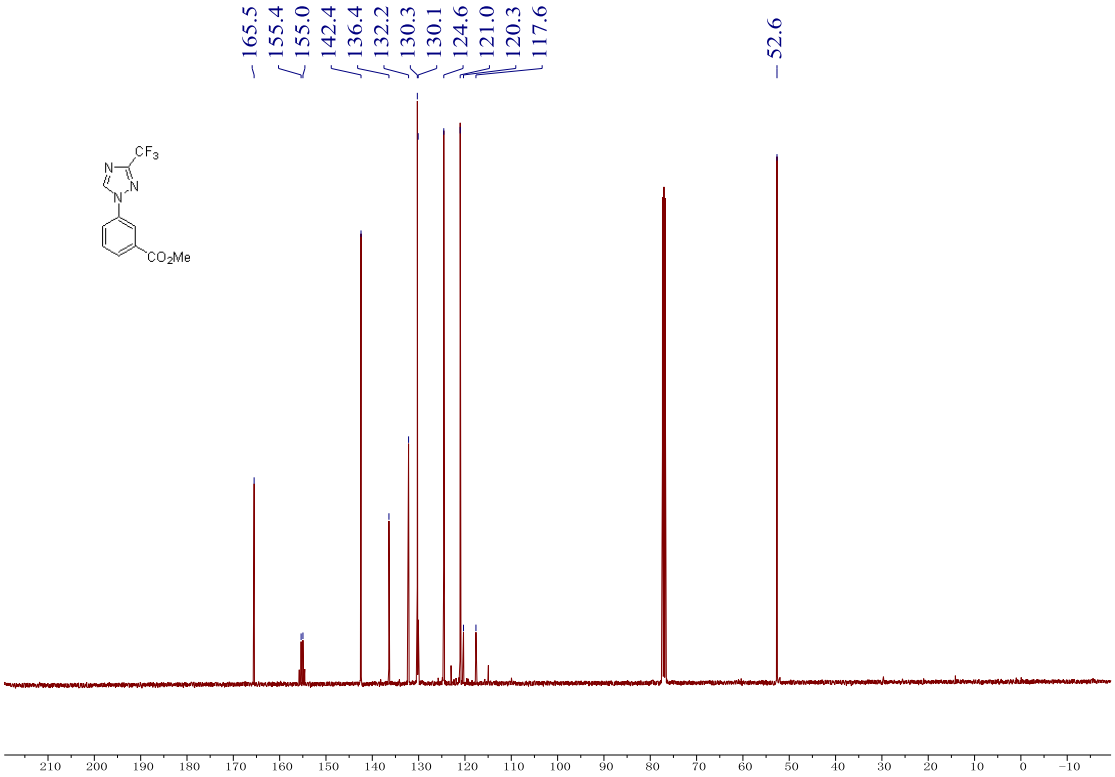
^{19}F NMR spectra of 3j (376 MHz, $CDCl_3$)



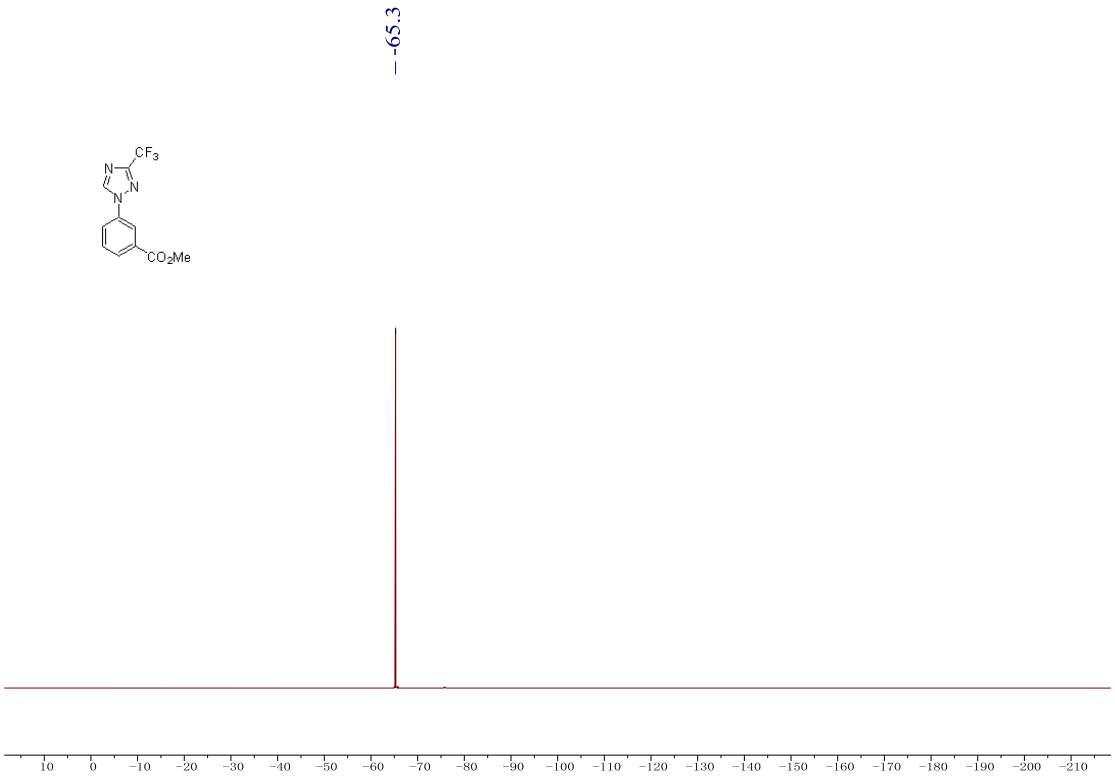
^{1}H NMR spectra of 3k (400 MHz, $CDCl_3$)



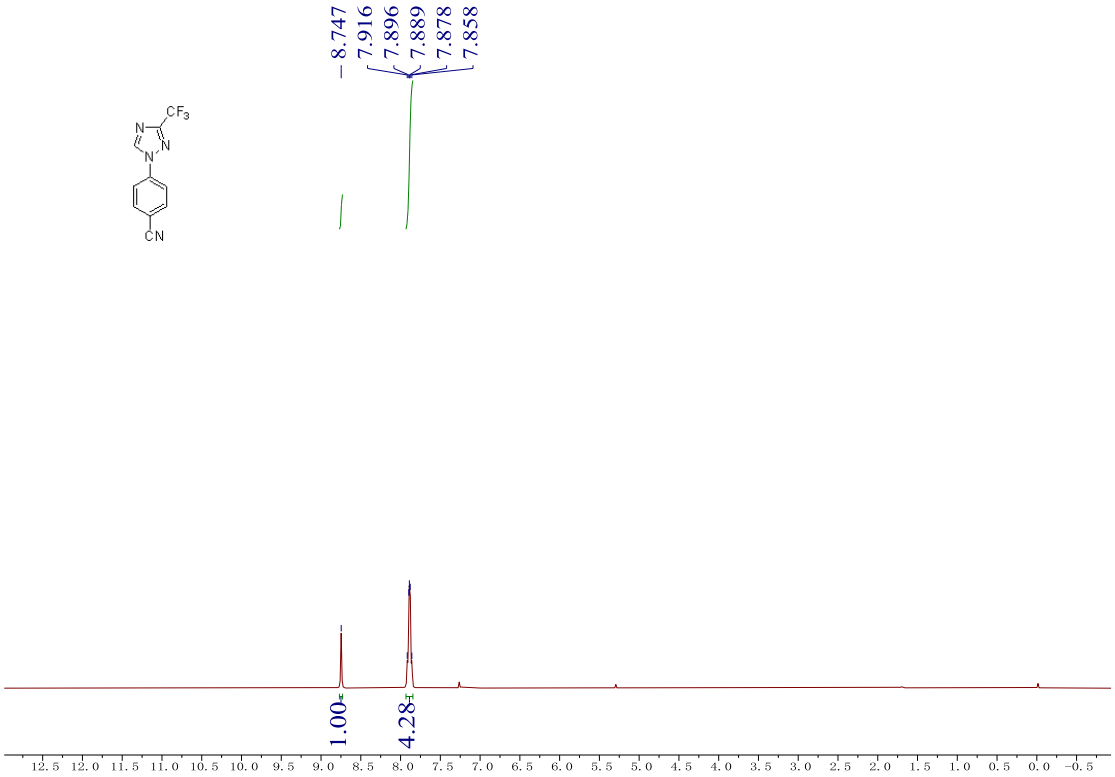
$^{13}C\{^{1}H\}$ NMR spectra of 3k (101 MHz, $CDCl_3$)



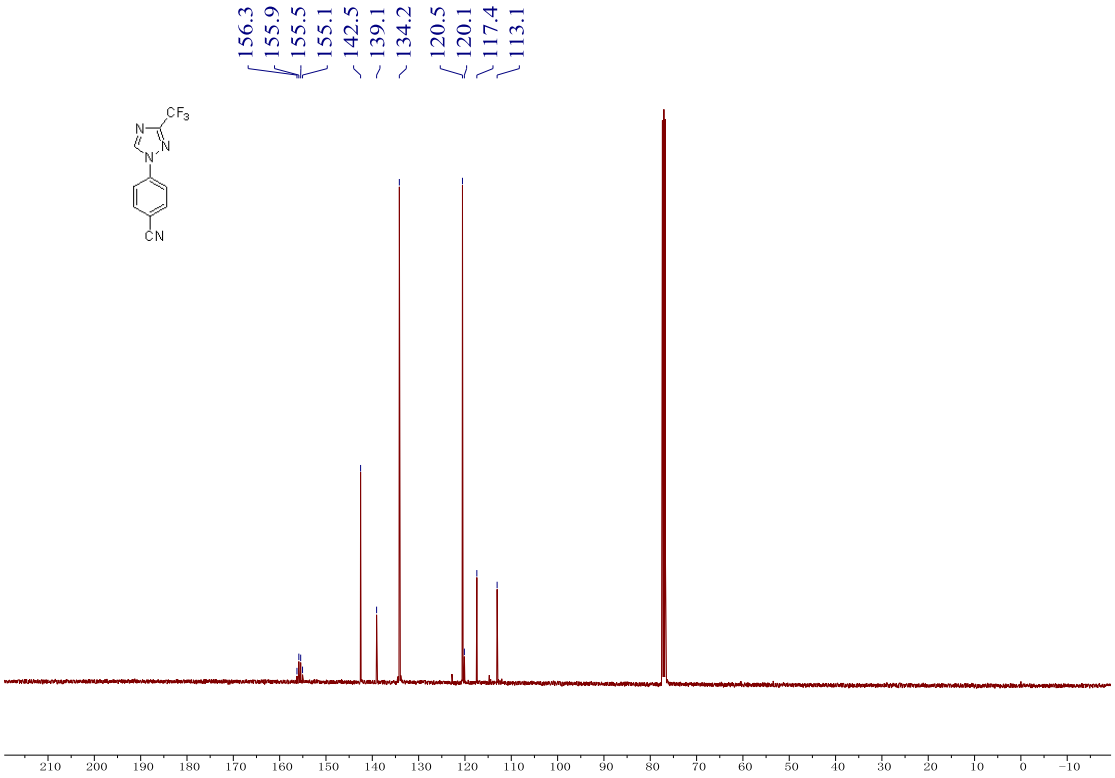
^{19}F NMR spectra of 3k (376 MHz, $CDCl_3$)



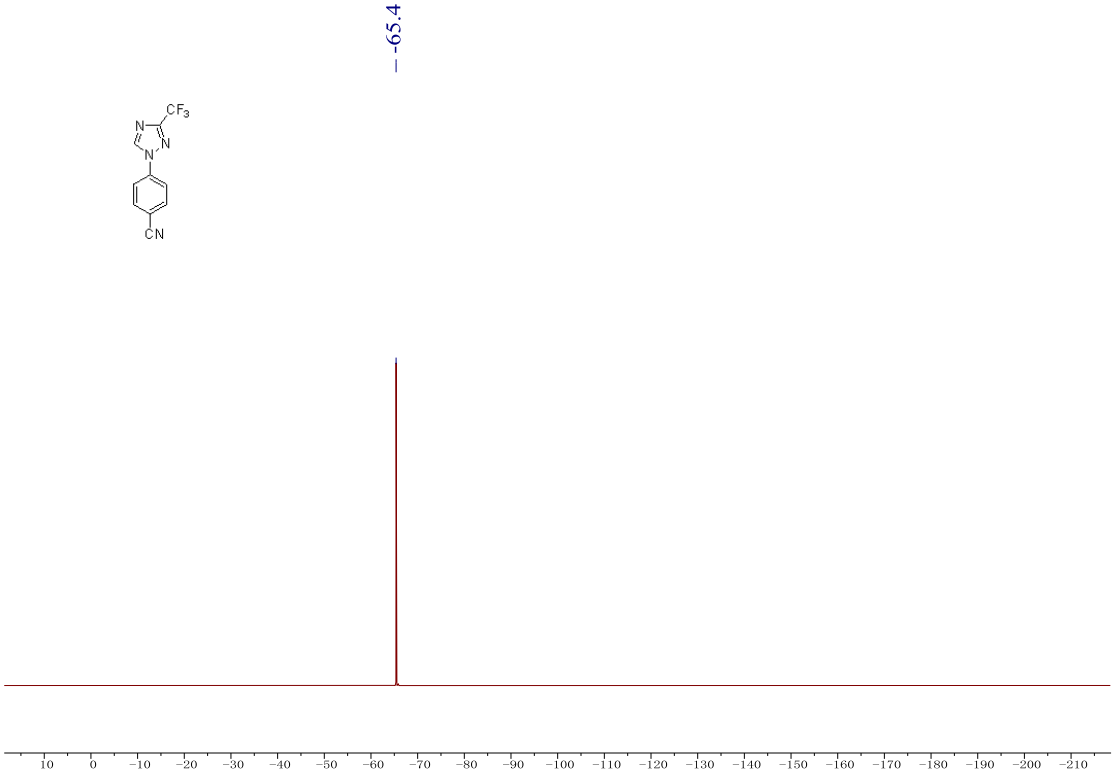
^{1}H NMR spectra of 3l (400 MHz, $CDCl_3$)



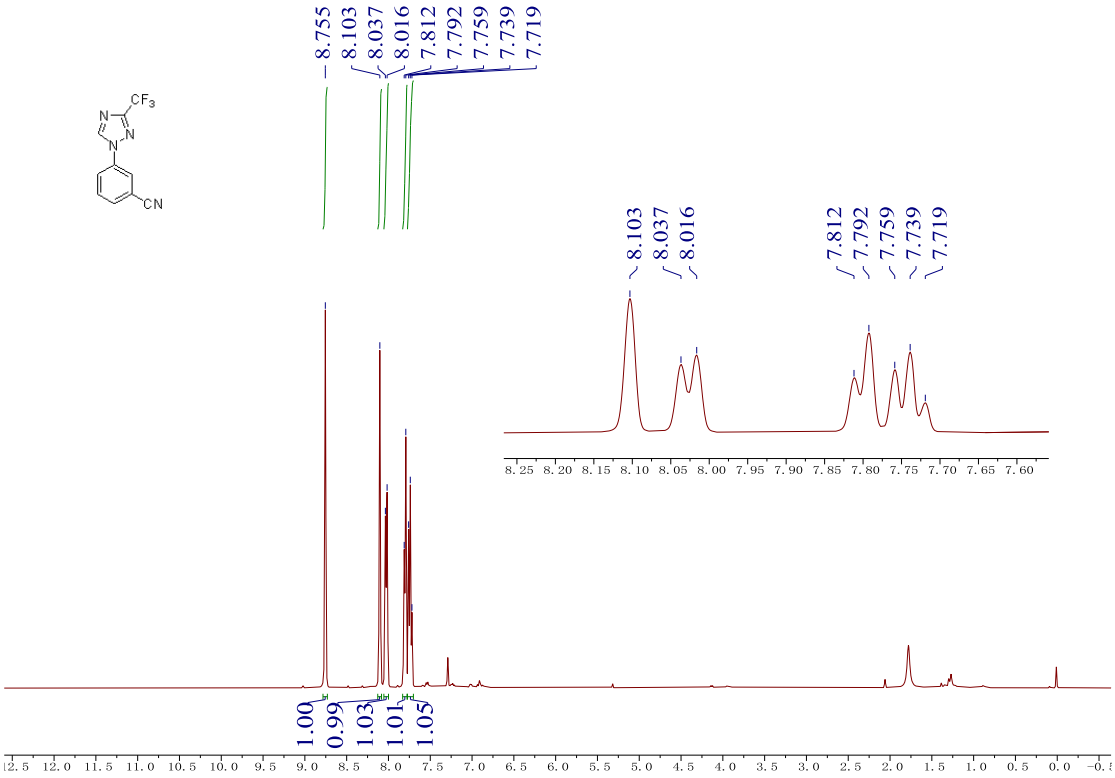
^{13}C{^{1}H} NMR spectra of 3l (101 MHz, $CDCl_3$)



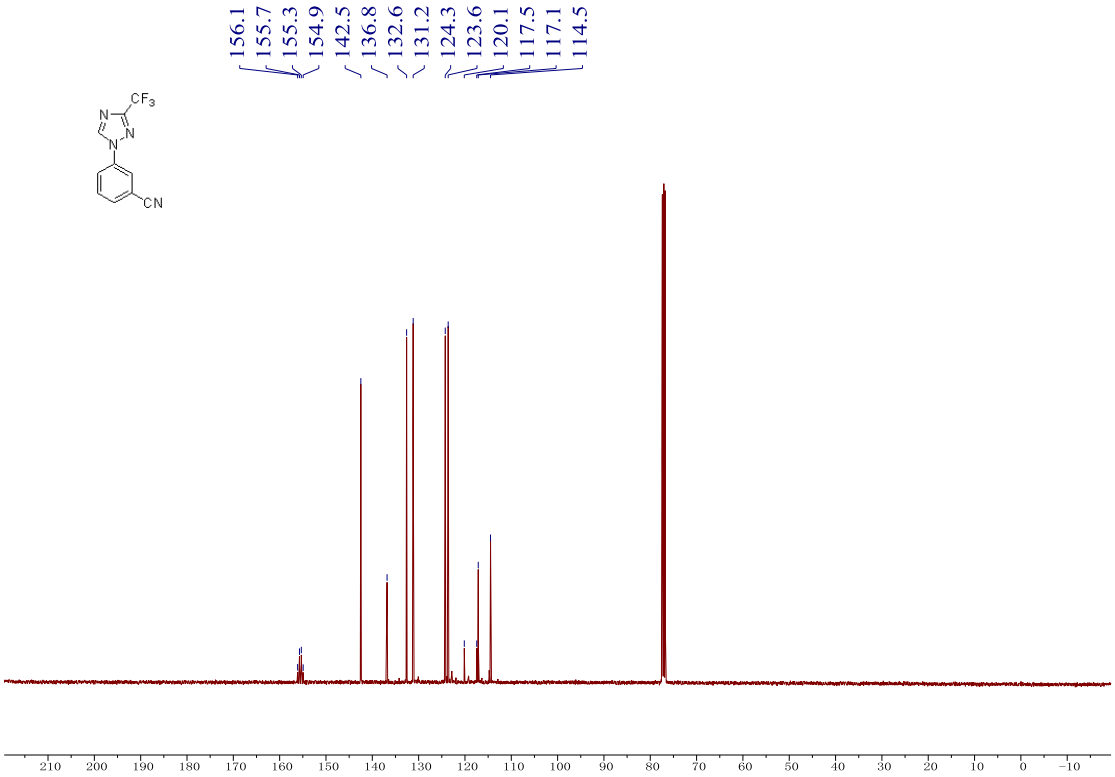
^{19}F NMR spectra of 3l (376 MHz, $CDCl_3$)



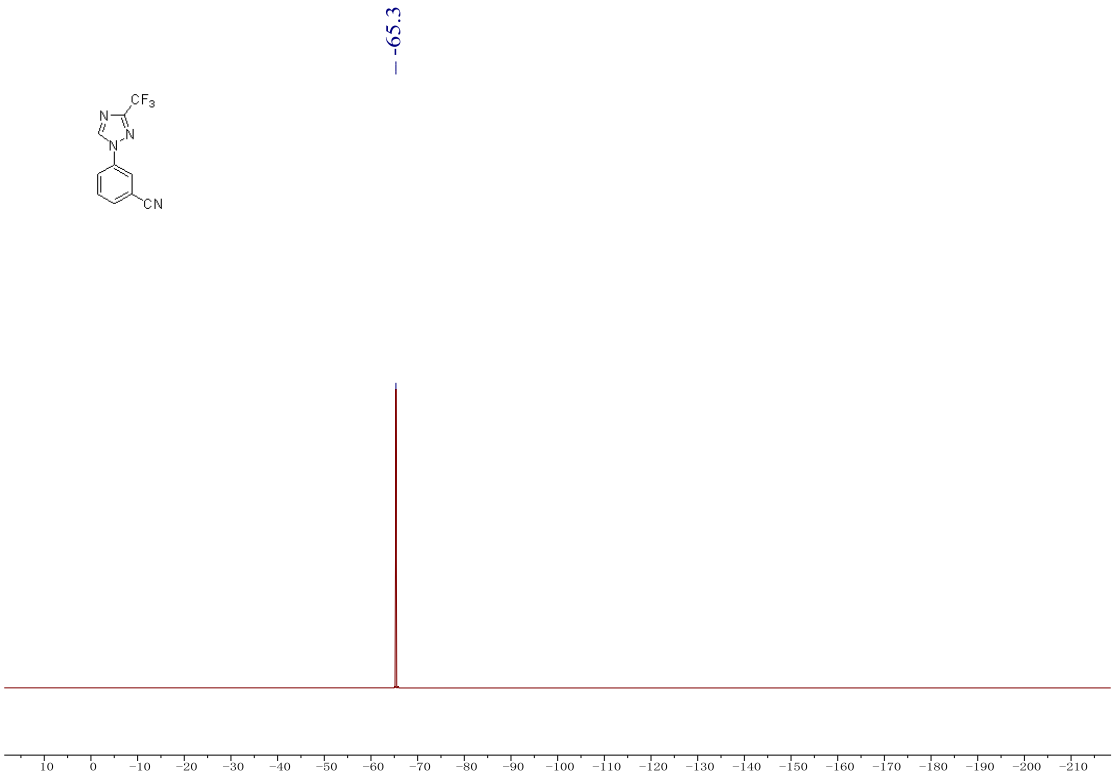
^{1}H NMR spectra of 3m (400 MHz, $CDCl_3$)



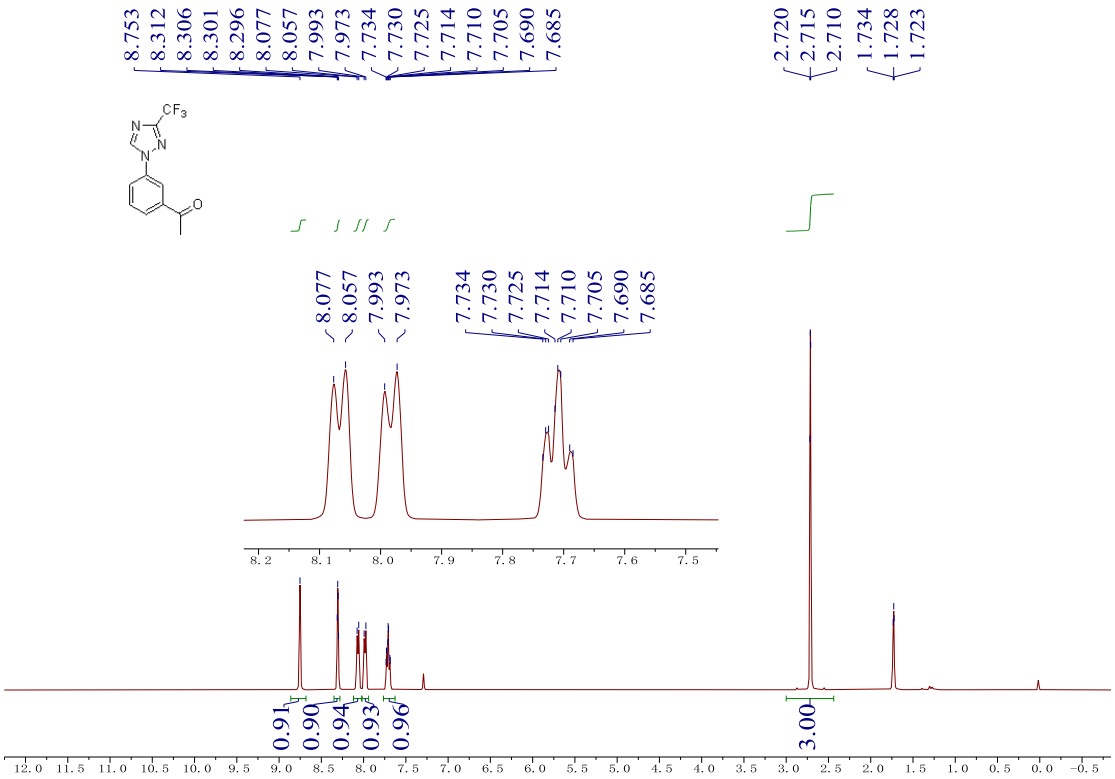
$^{13}C\{^{1}H\}$ NMR spectra of 3m (101 MHz, $CDCl_3$)



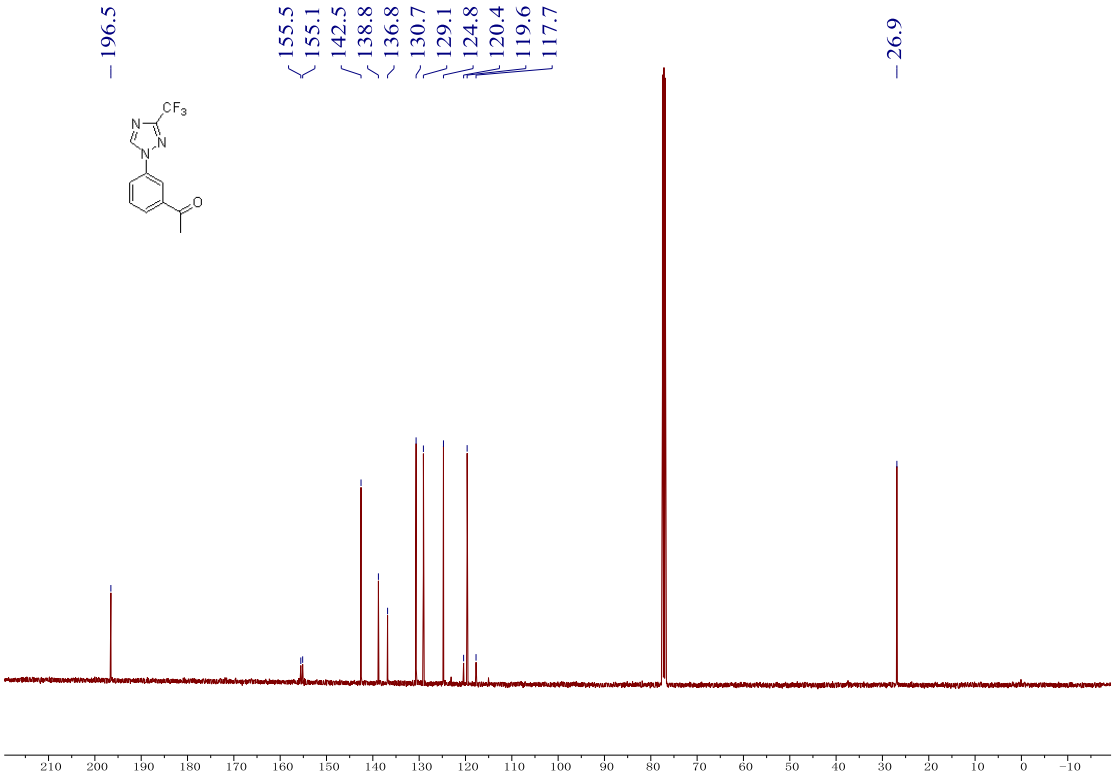
^{19}F NMR spectra of 3m (376 MHz, $CDCl_3$)



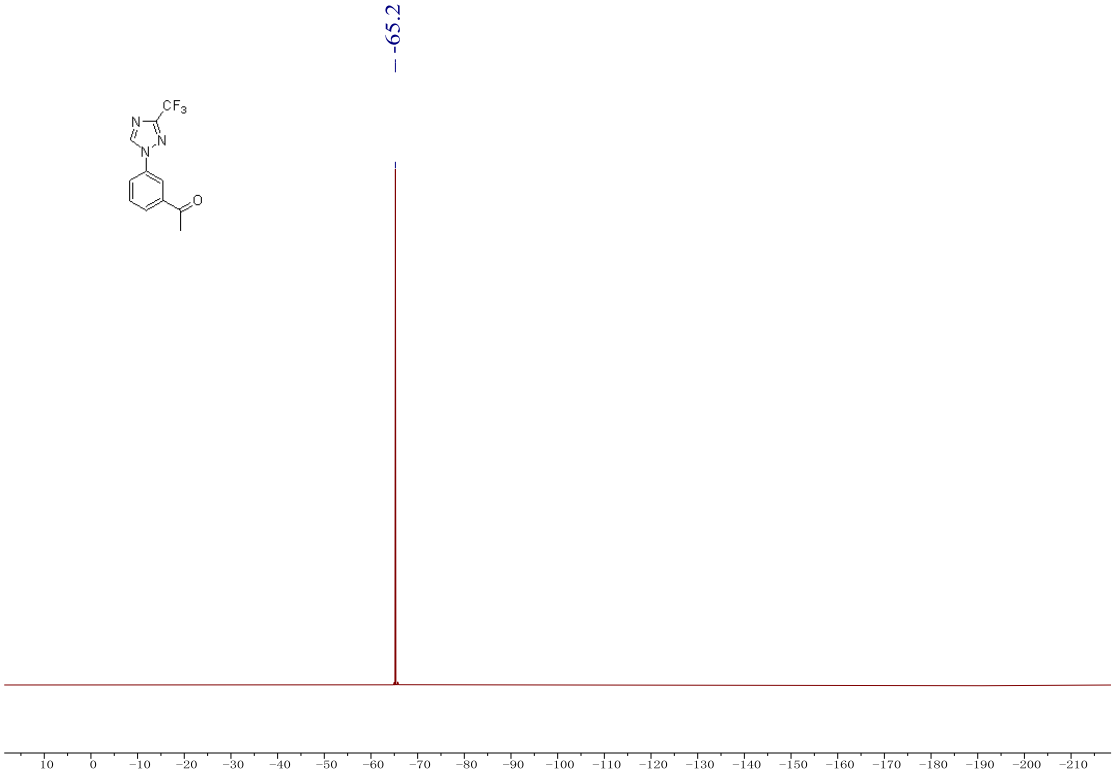
^{1}H NMR spectra of 3n (400 MHz, $CDCl_3$)



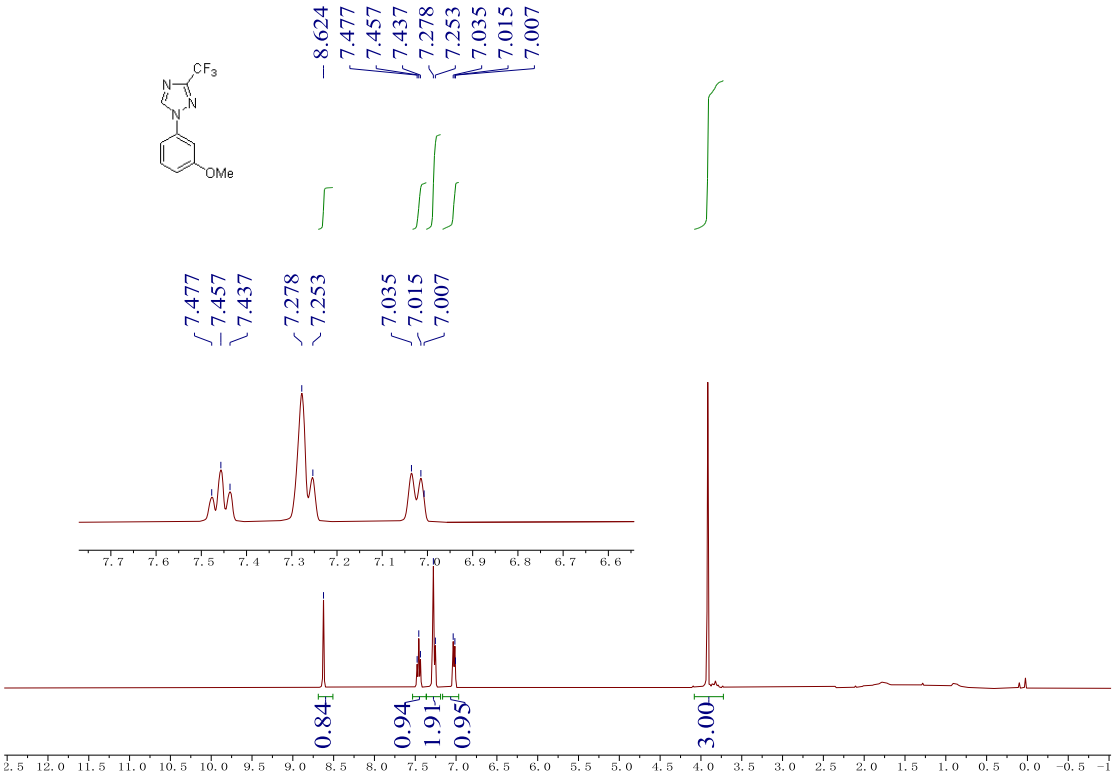
^{13}C{^{1}H} NMR spectra of 3n (101 MHz, $CDCl_3$)



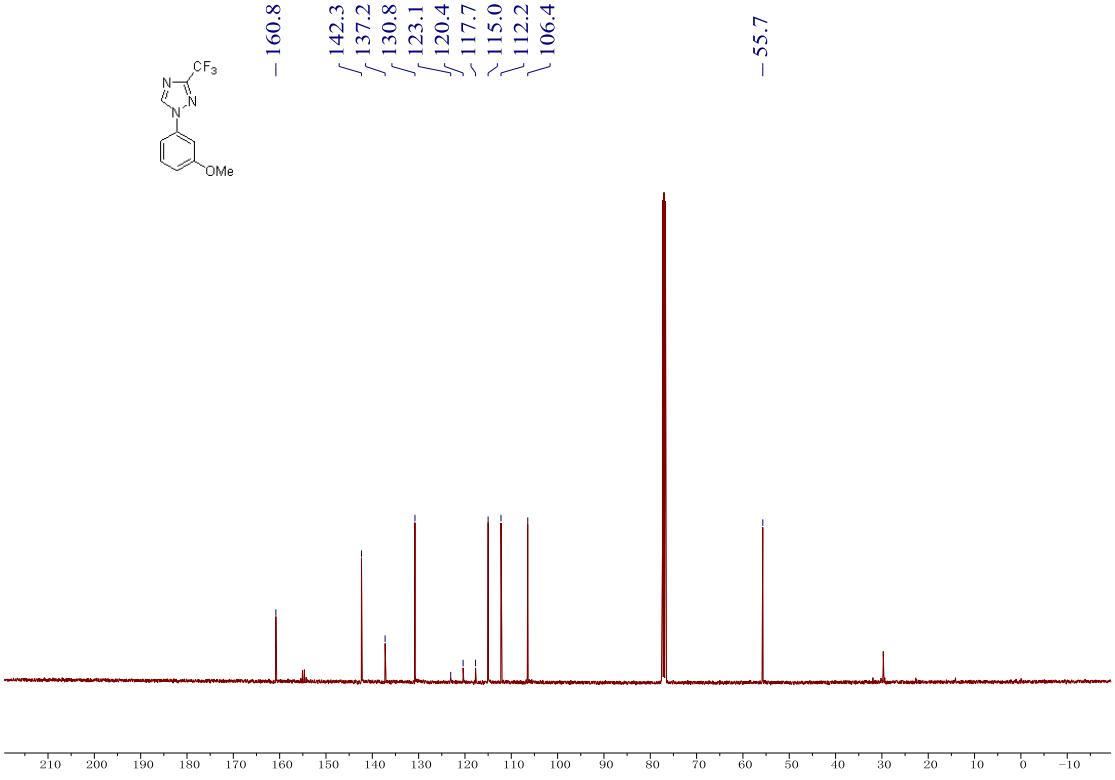
^{19}F NMR spectra of 3n (376 MHz, $CDCl_3$)



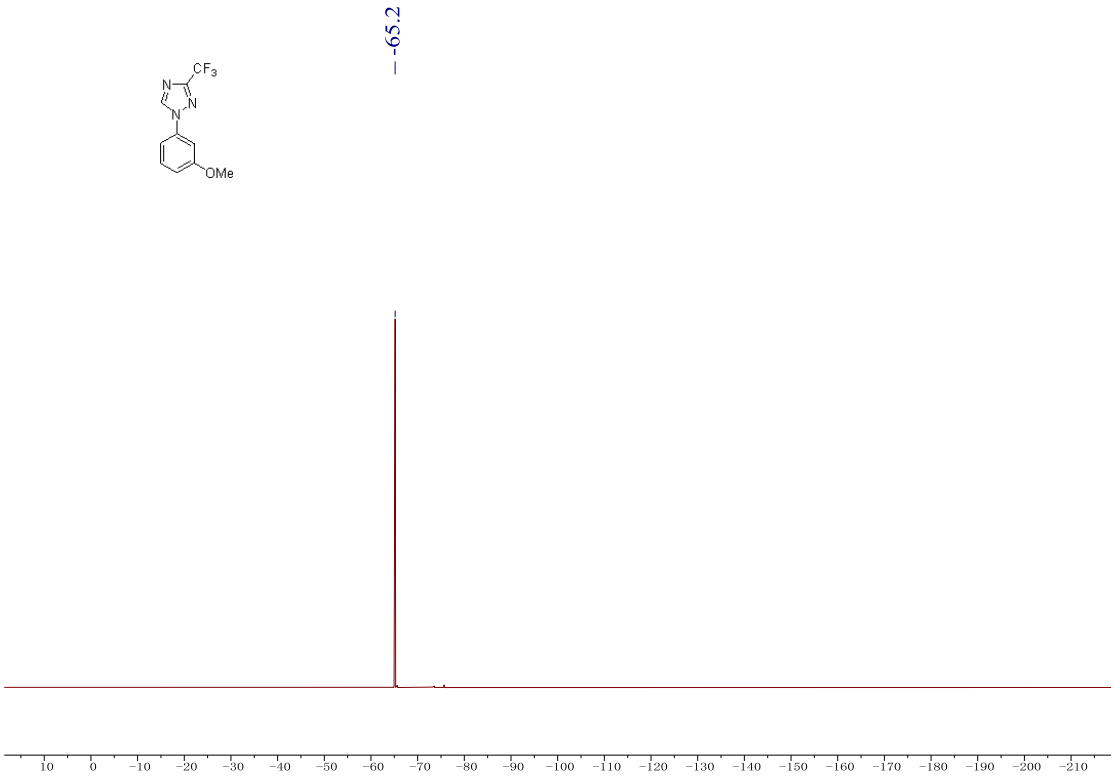
^{1}H NMR spectra of 3o (400 MHz, $CDCl_3$)



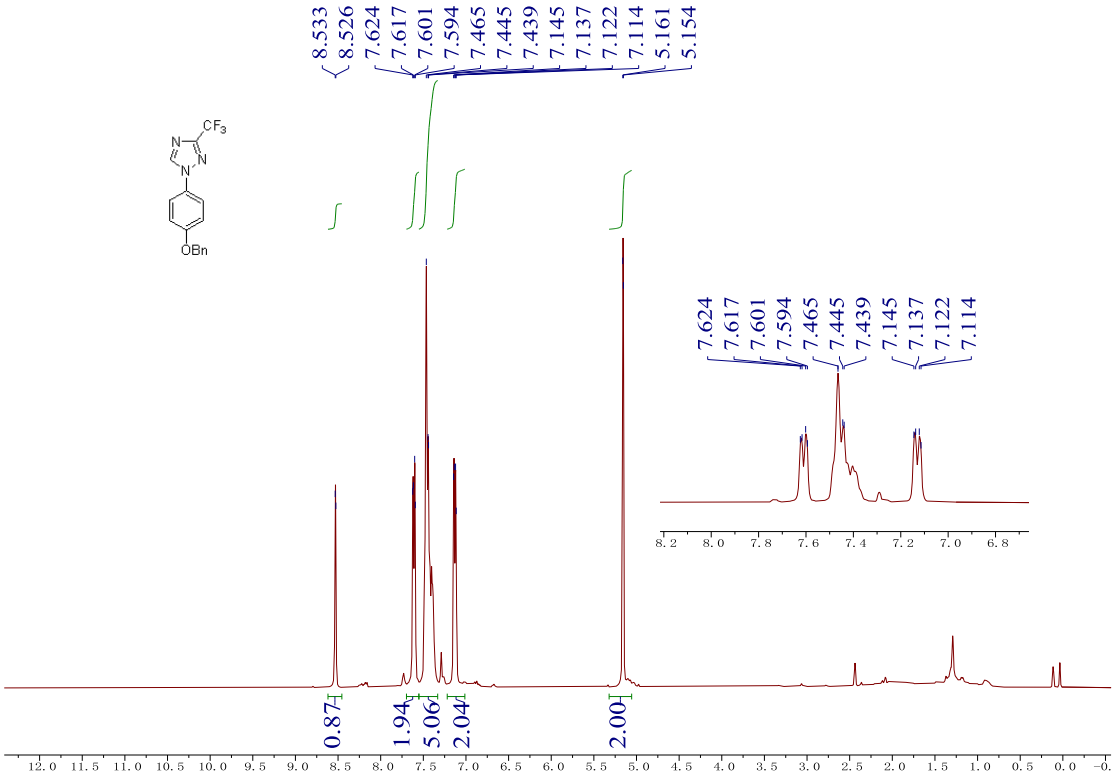
$^{13}C\{^{1}H\}$ NMR spectra of 3o (101 MHz, $CDCl_3$)



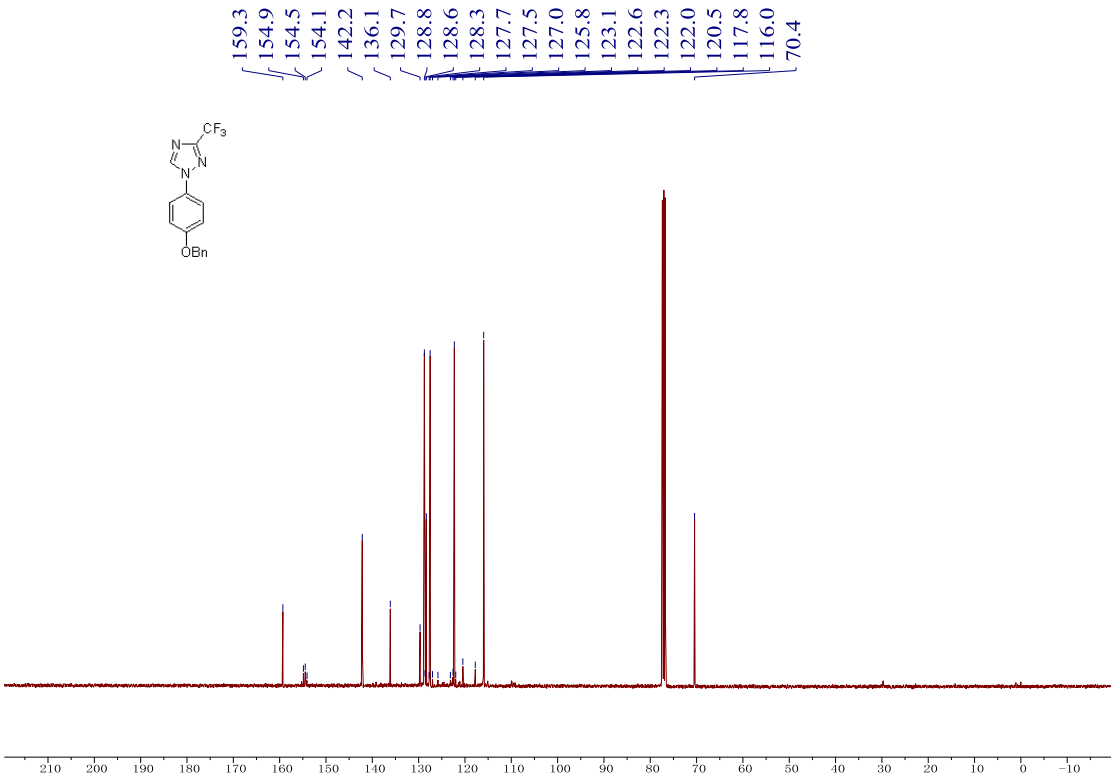
^{19}F NMR spectra of 3o (376 MHz, $CDCl_3$)



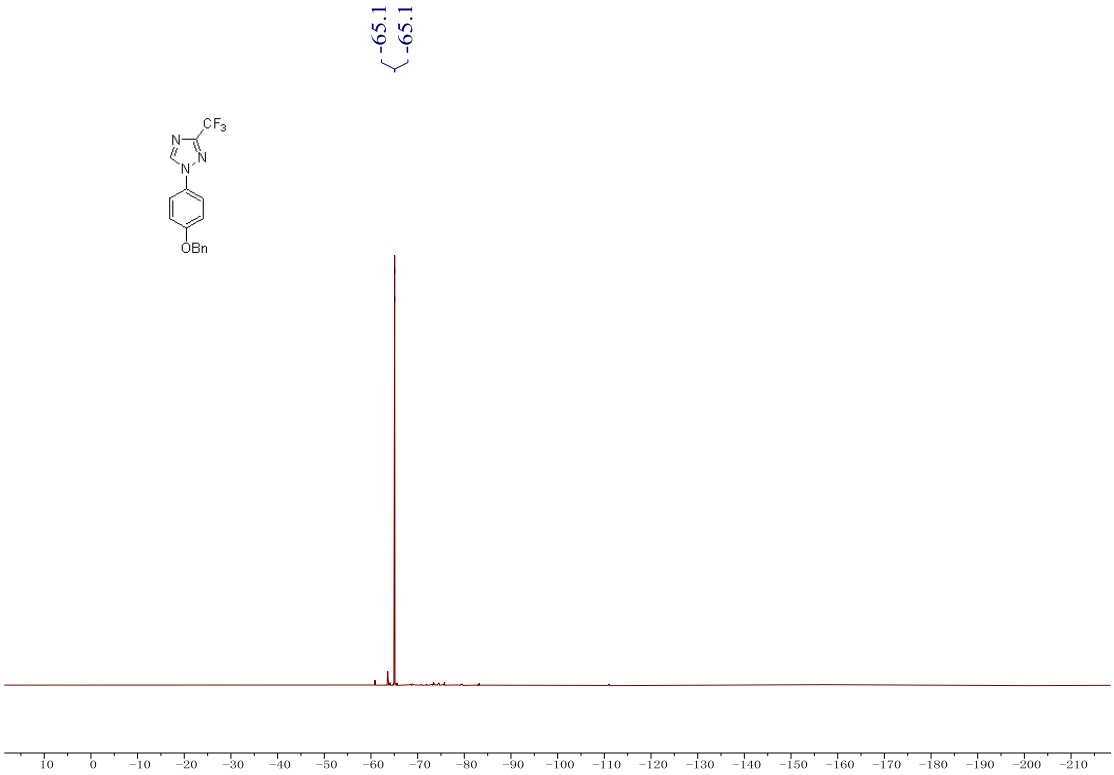
^{1}H NMR spectra of 3p (400 MHz, $CDCl_3$)



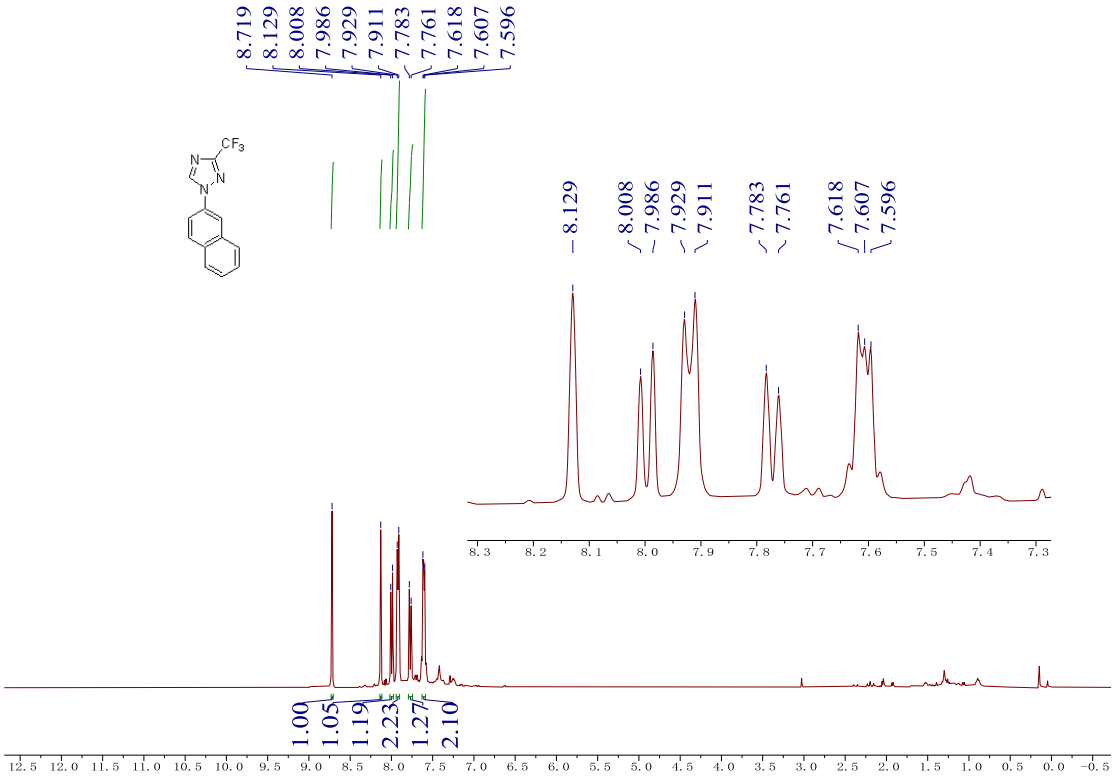
^{13}C{^{1}H} NMR spectra of 3p (101 MHz, $CDCl_3$)



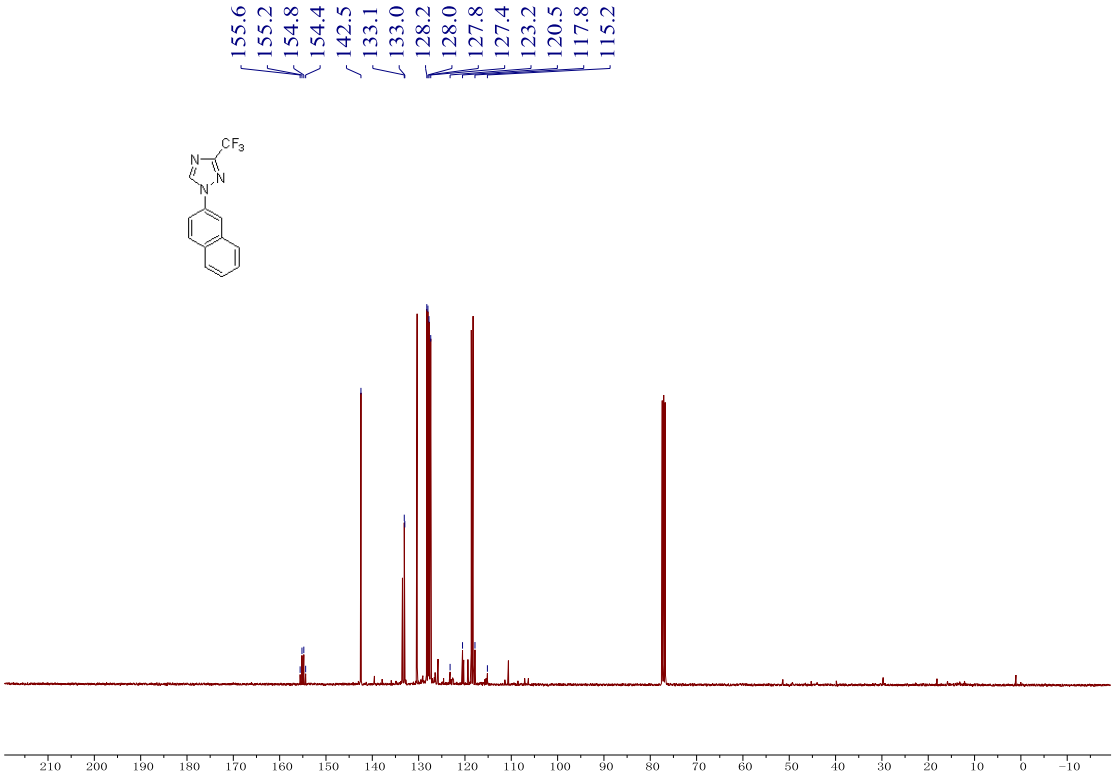
^{19}F NMR spectra of 3p (376 MHz, $CDCl_3$)



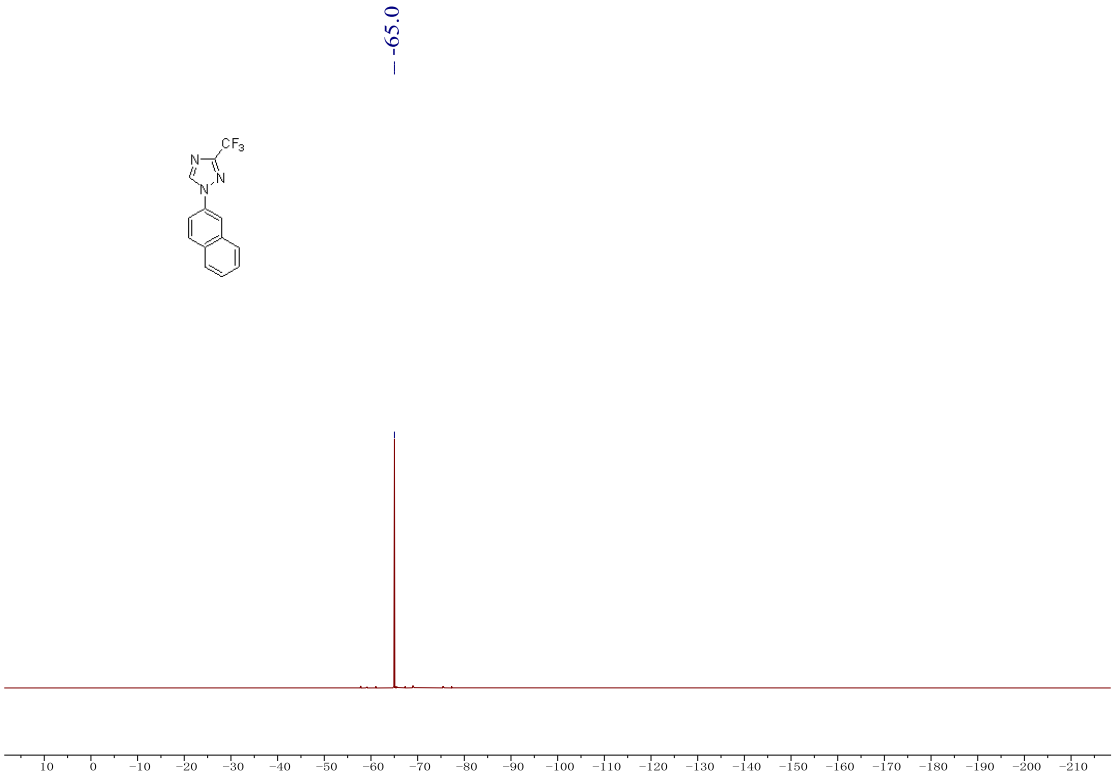
^{1}H NMR spectra of 3q (400 MHz, $CDCl_3$)



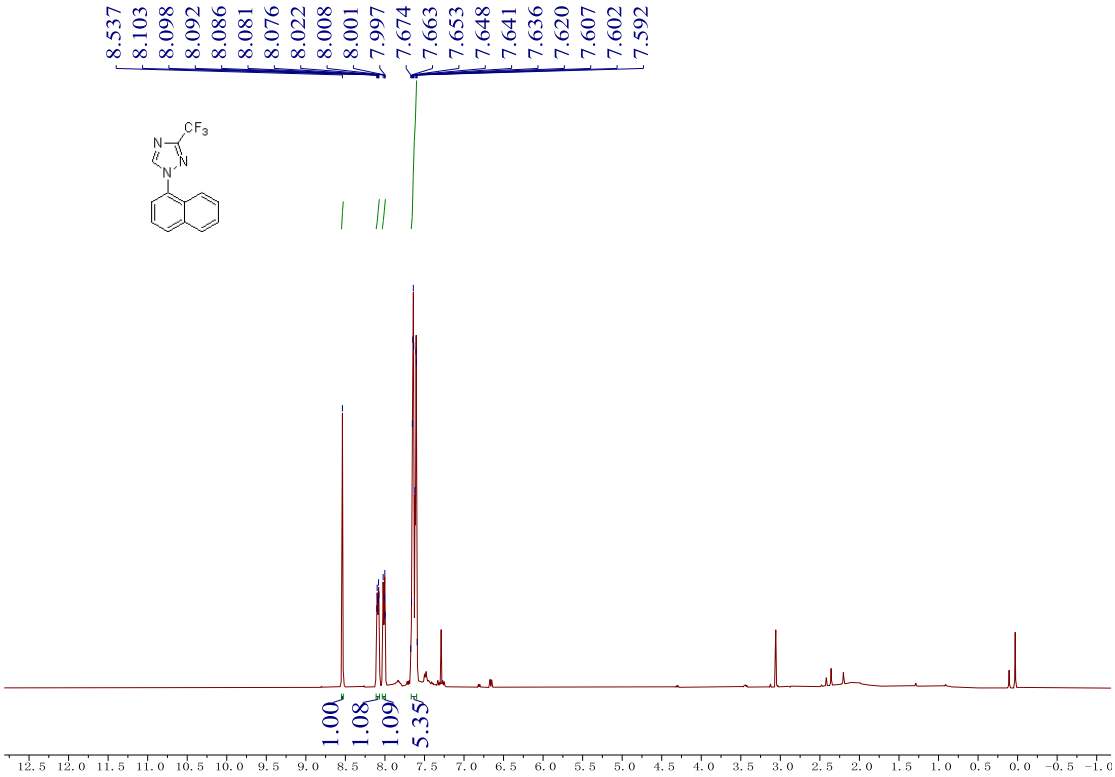
$^{13}C\{^{1}H\}$ NMR spectra of 3q (101 MHz, $CDCl_3$)



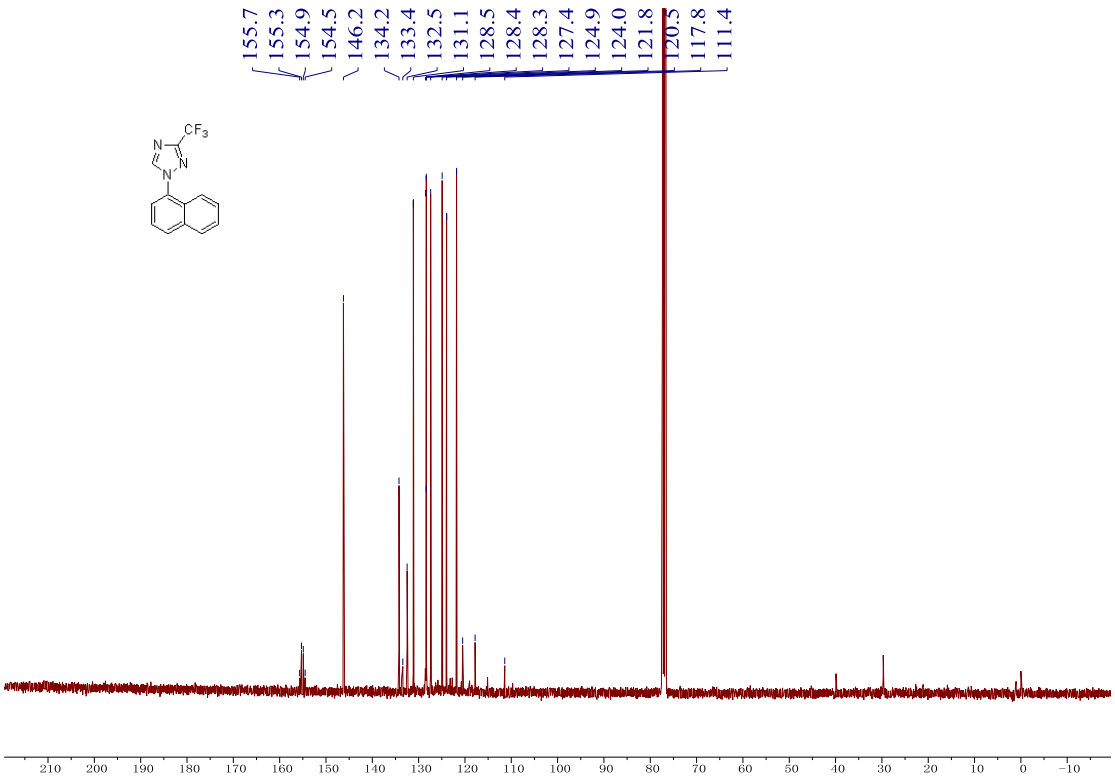
^{19}F NMR spectra of 3q (376 MHz, $CDCl_3$)



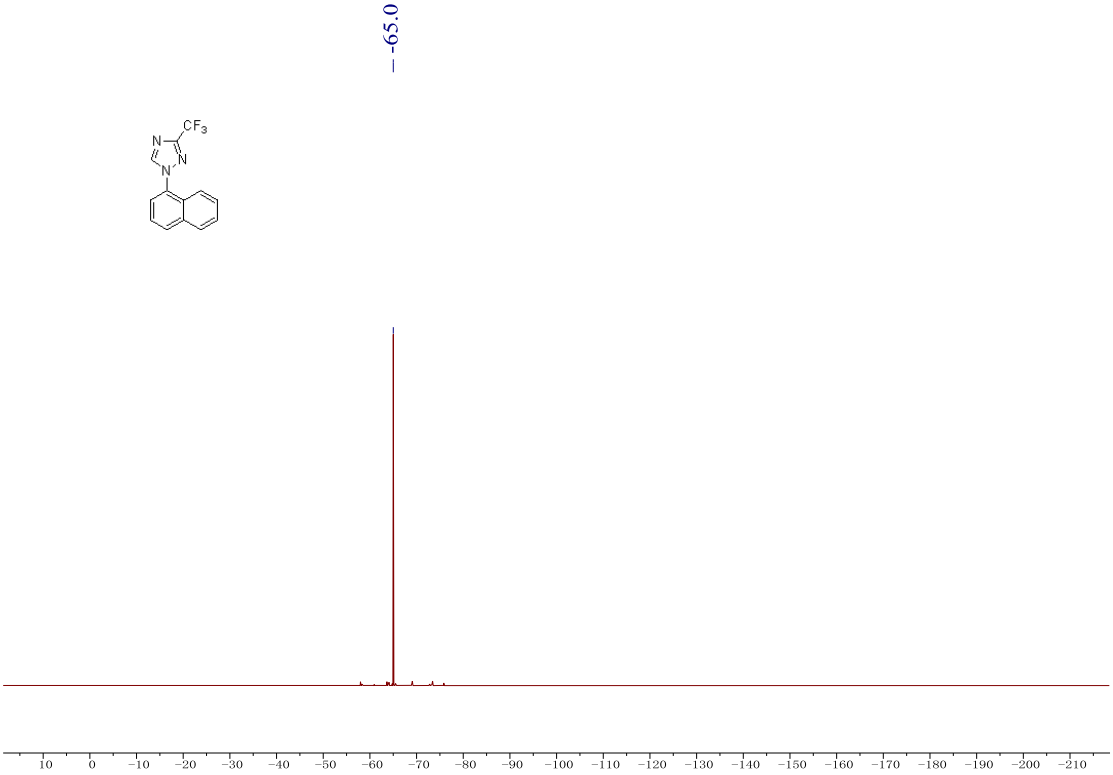
^{1}H NMR spectra of 3r (400 MHz, $CDCl_3$)



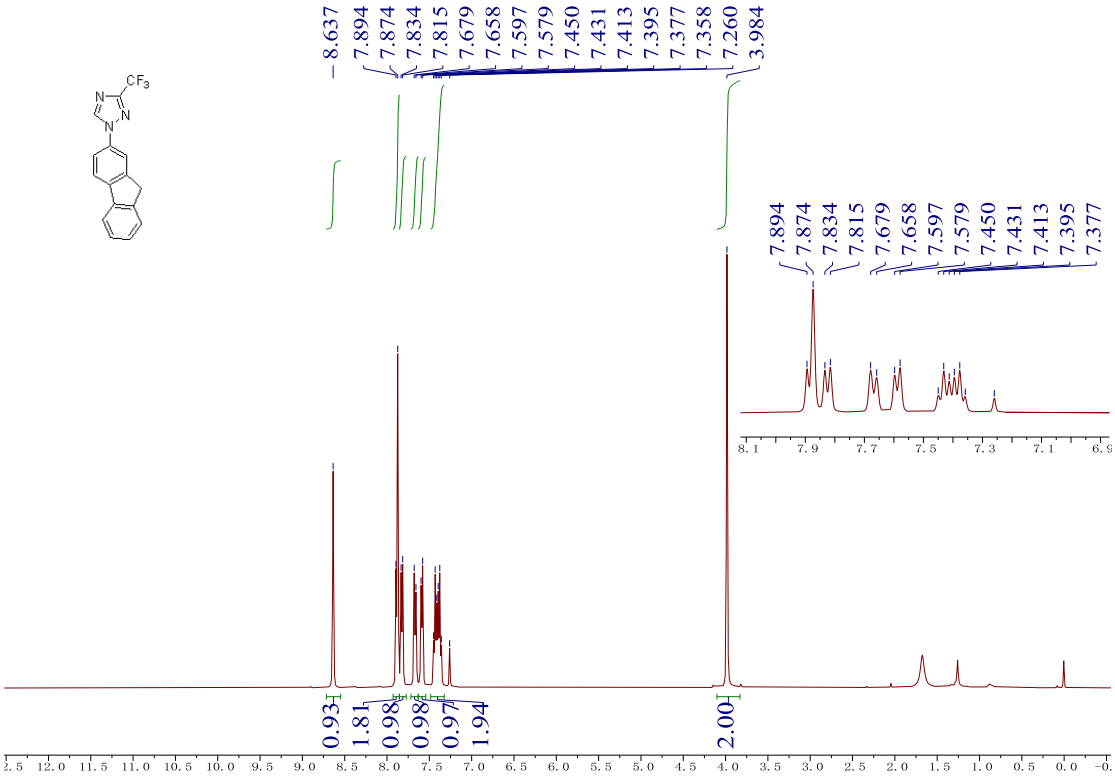
^{13}C{^{1}H} NMR spectra of 3r (101 MHz, $CDCl_3$)



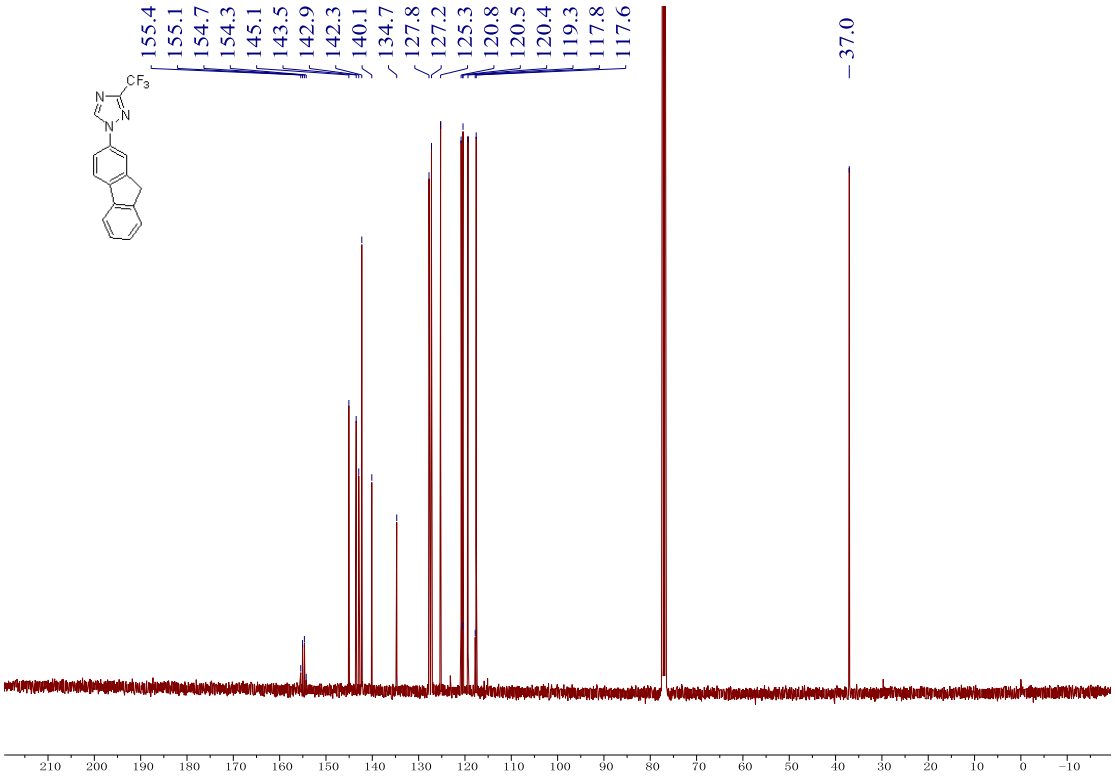
^{19}F NMR spectra of 3r (376 MHz, $CDCl_3$)



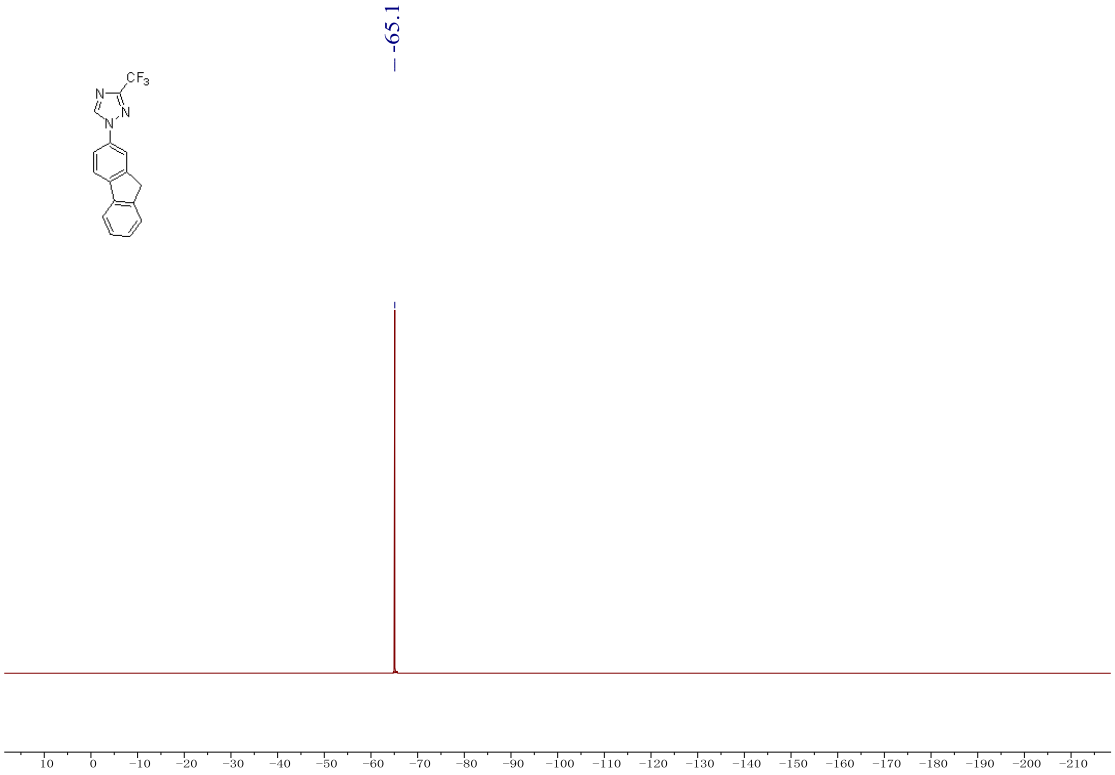
^{1}H NMR spectra of 3s (400 MHz, $CDCl_3$)



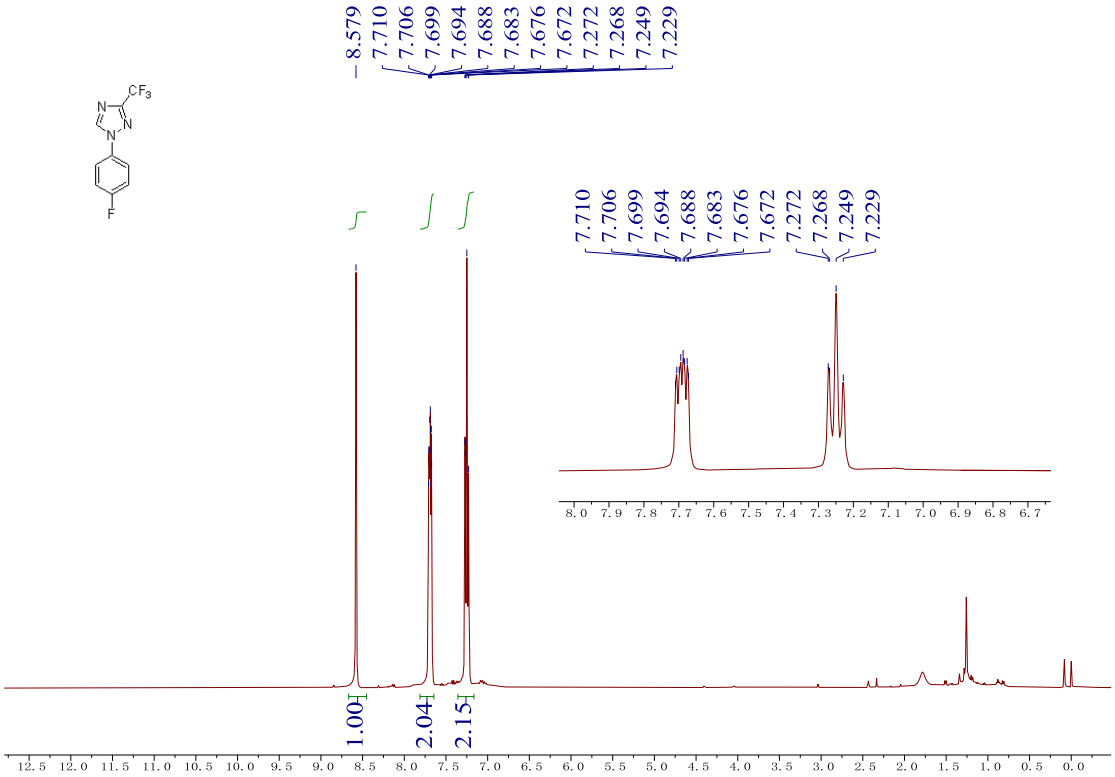
$^{13}C\{^{1}H\}$ NMR spectra of 3s (101 MHz, $CDCl_3$)



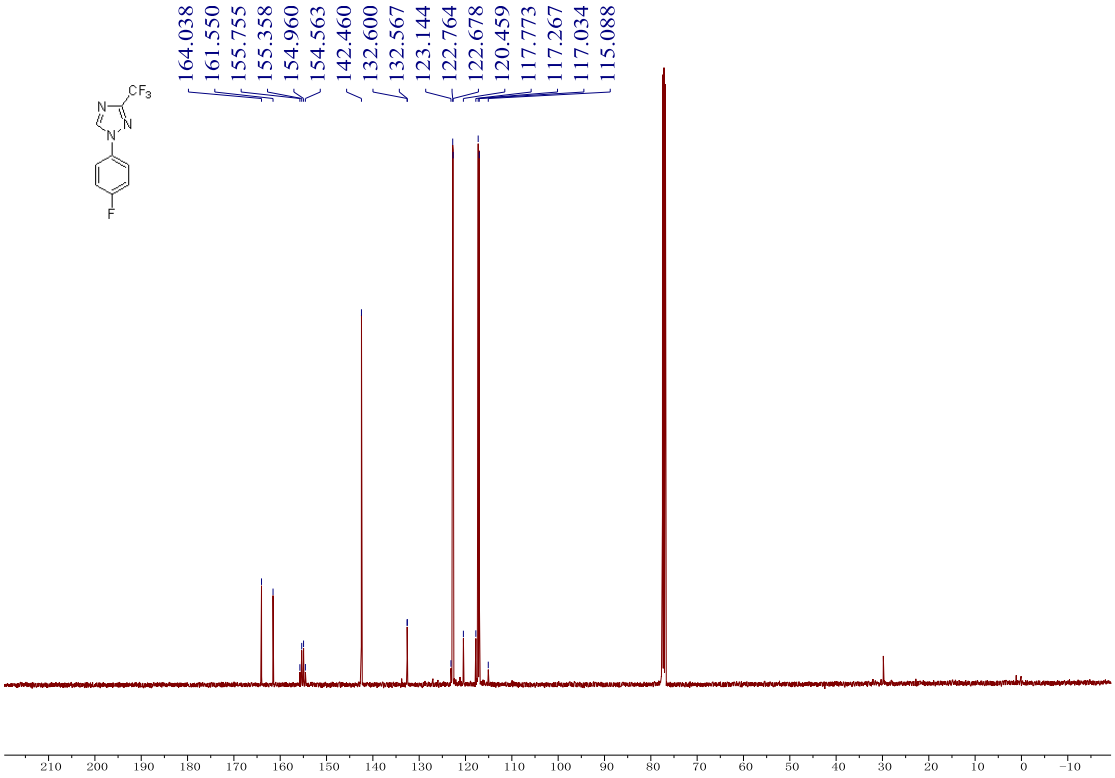
^{19}F NMR spectra of 3s (376 MHz, $CDCl_3$)



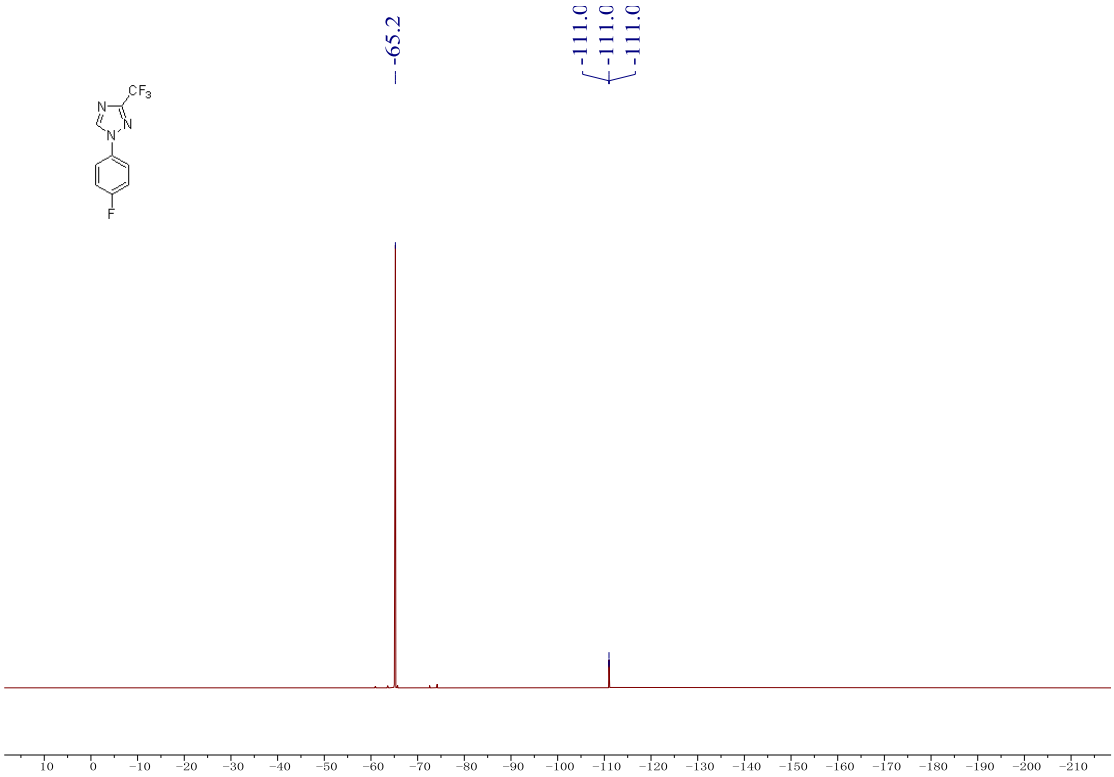
^{1}H NMR spectra of 3t (400 MHz, $CDCl_3$)



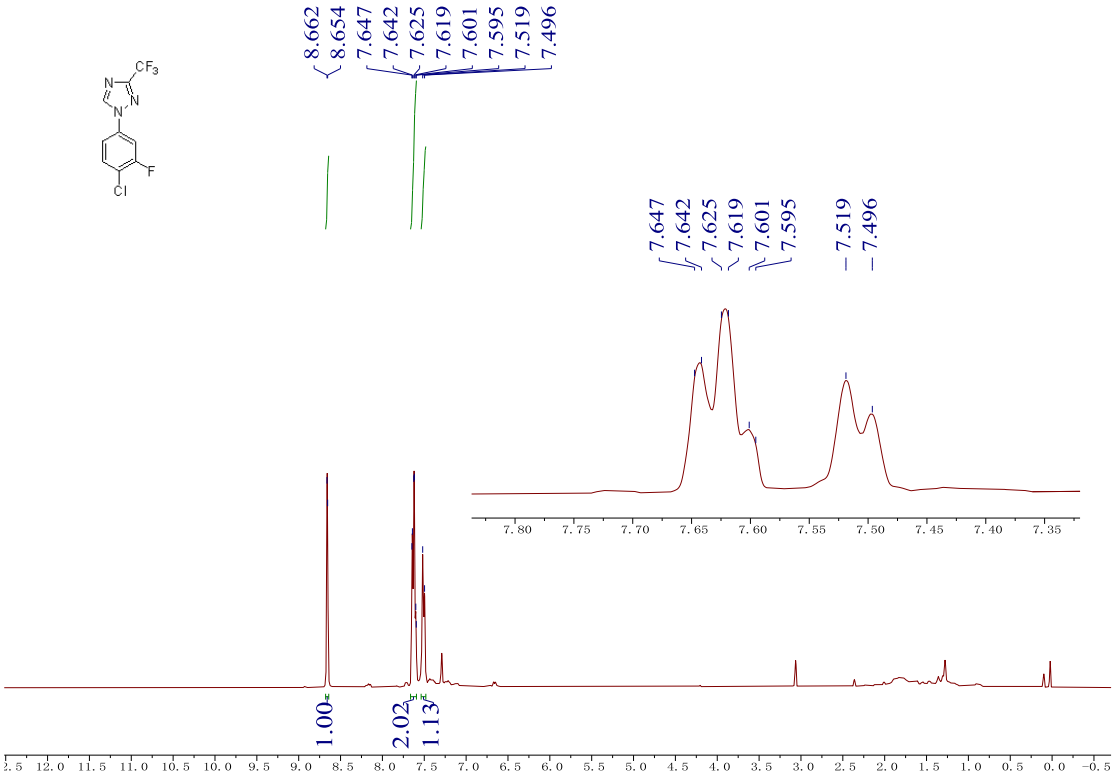
^{13}C{^{1}H} NMR spectra of 3t (101 MHz, $CDCl_3$)



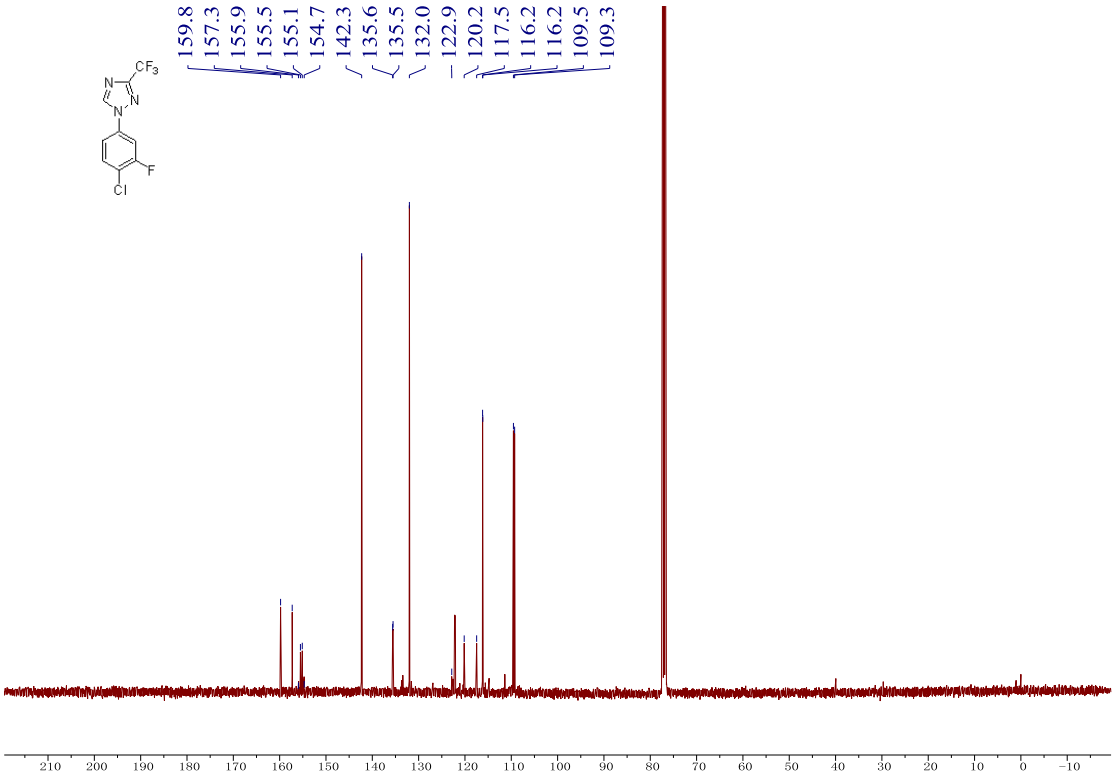
^{19}F NMR spectra of 3t (376 MHz, $CDCl_3$)



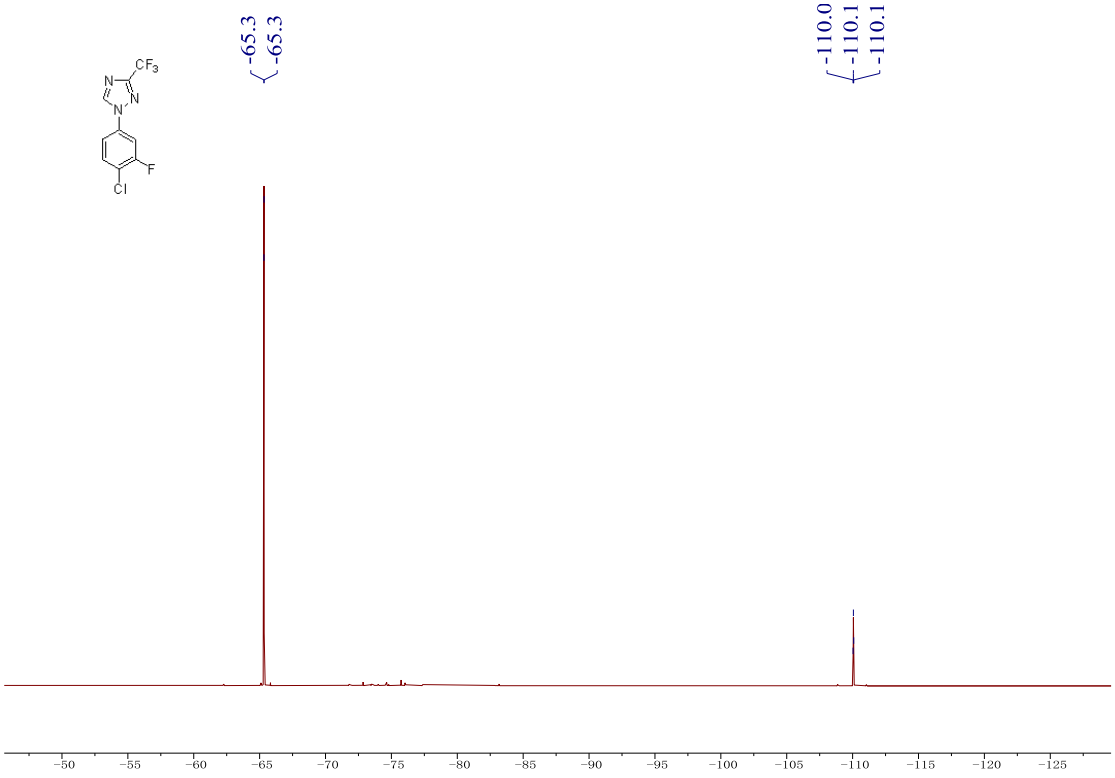
^{1}H NMR spectra of 3u (400 MHz, $CDCl_3$)



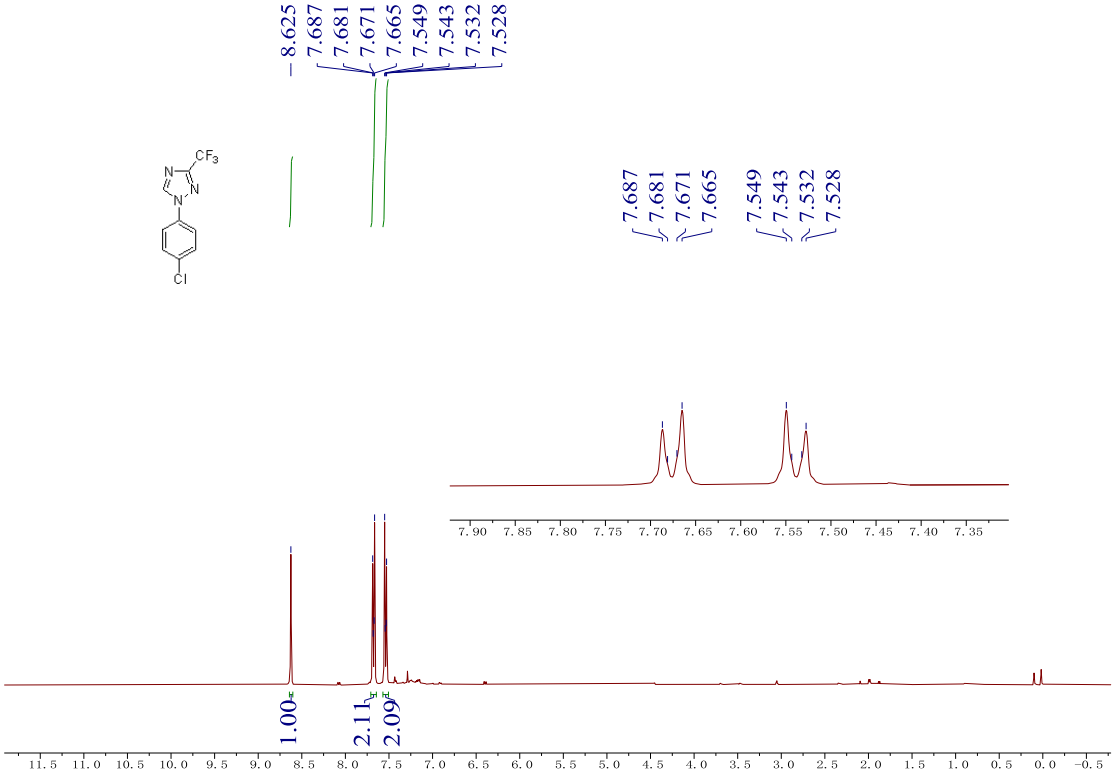
$^{13}C\{^{1}H\}$ NMR spectra of 3u (101 MHz, $CDCl_3$)



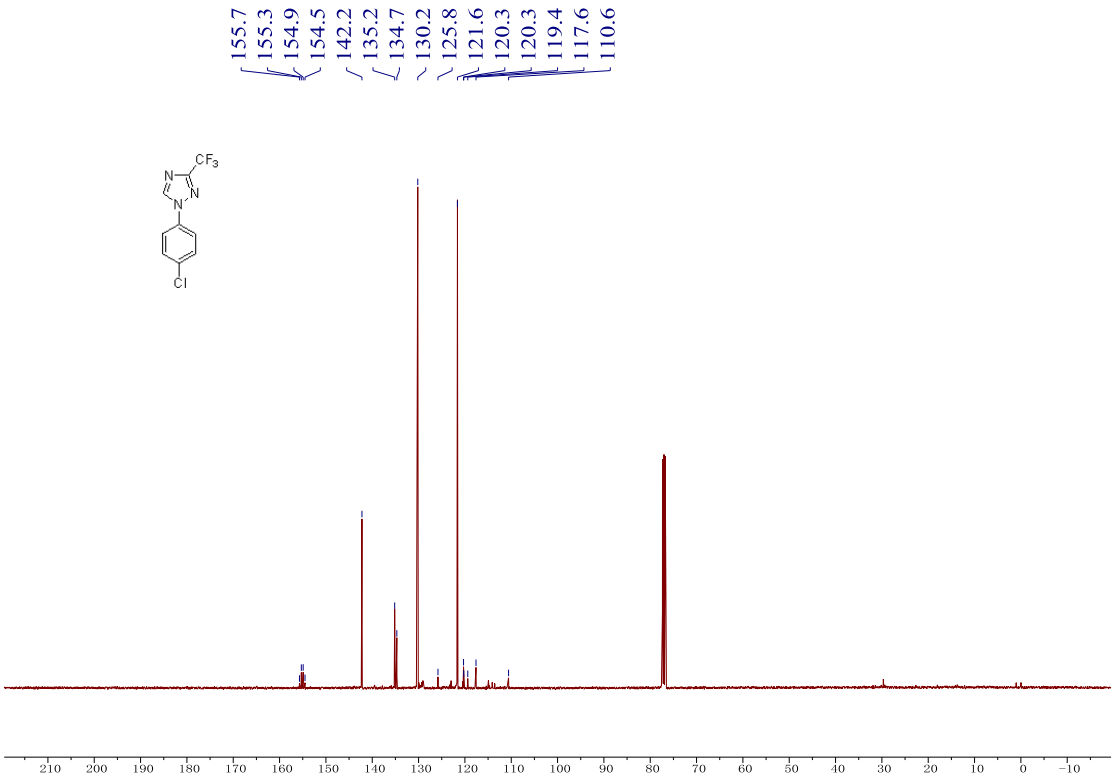
^{19}F NMR spectra of 3u (376 MHz, $CDCl_3$)



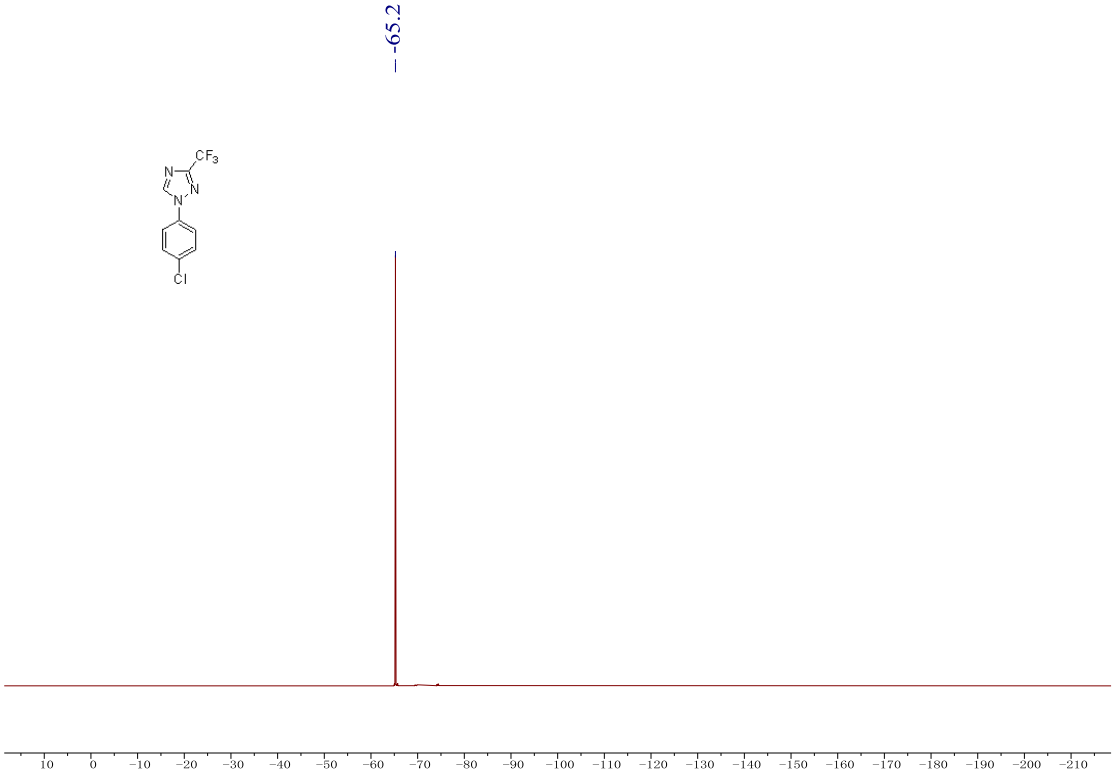
^{1}H NMR spectra of 3v (400 MHz, $CDCl_3$)



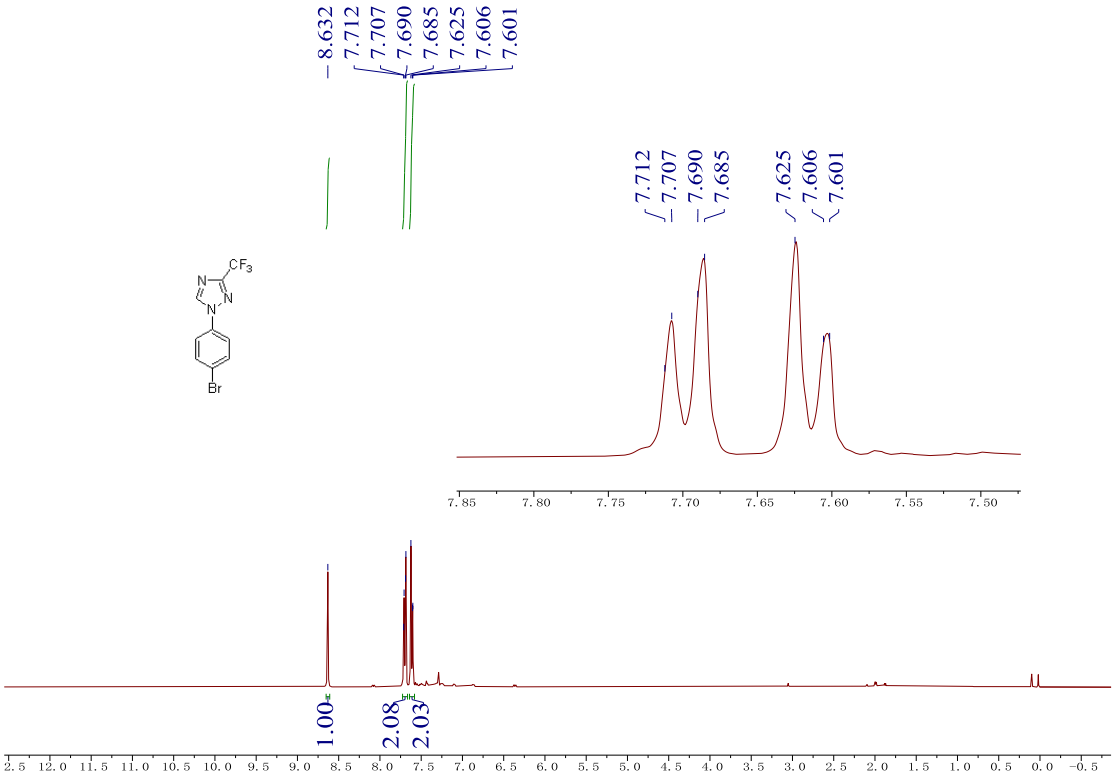
^{13}C{^{1}H} NMR spectra of 3v (101 MHz, $CDCl_3$)



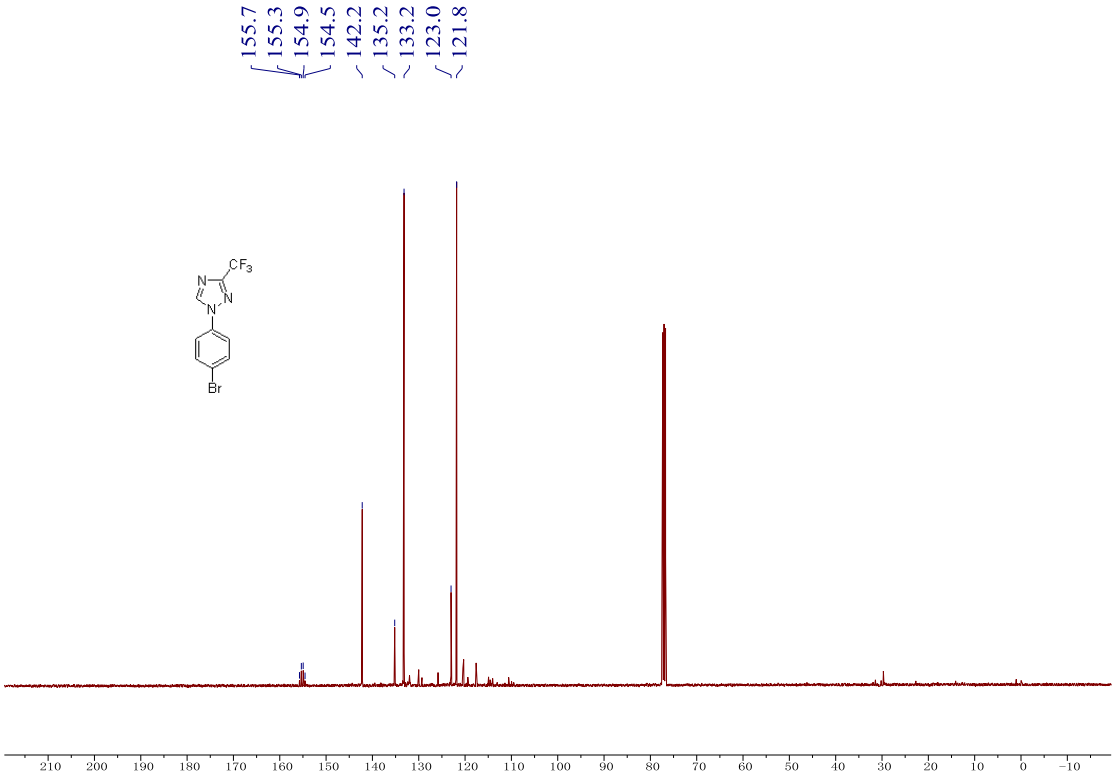
^{19}F NMR spectra of 3v (376 MHz, $CDCl_3$)



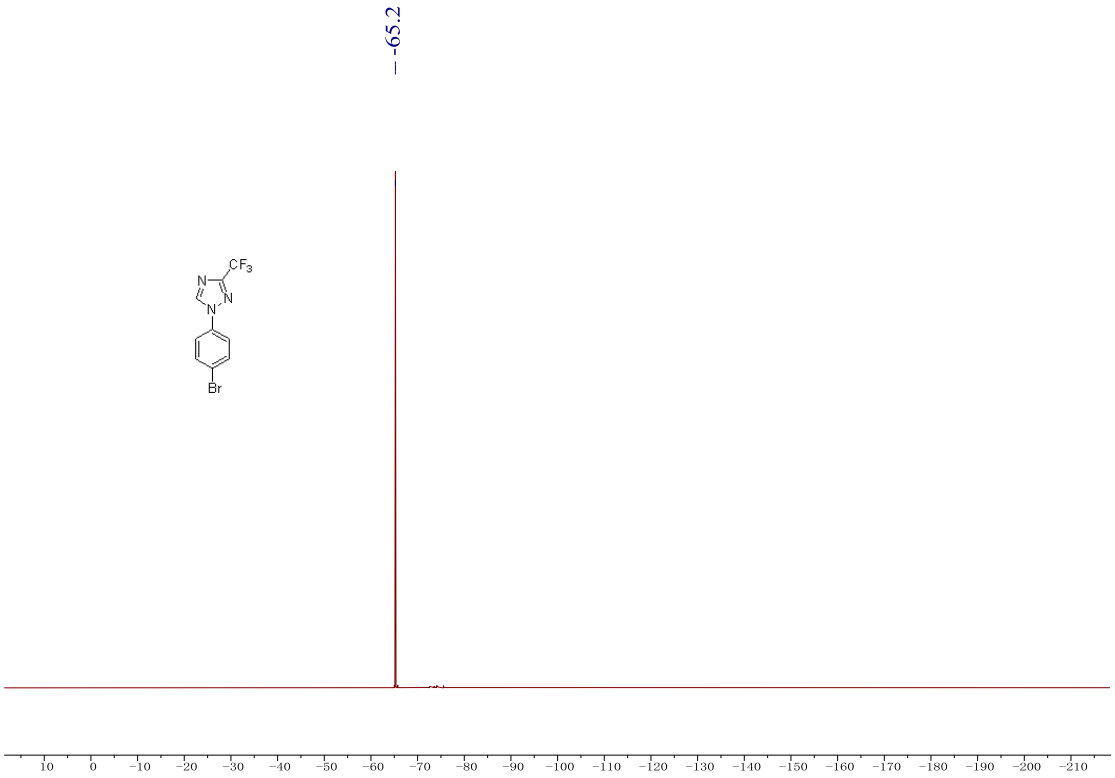
^{1}H NMR spectra of 3w (400 MHz, $CDCl_3$)



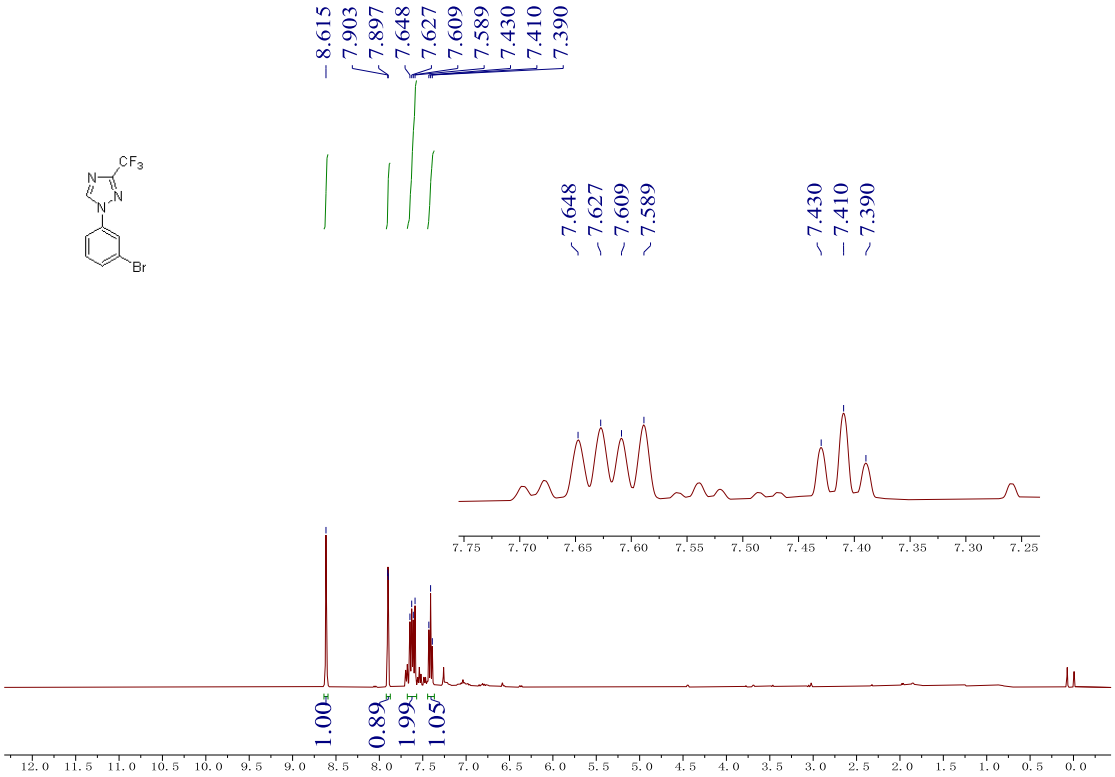
$^{13}C\{^{1}H\}$ NMR spectra of 3w (101 MHz, $CDCl_3$)



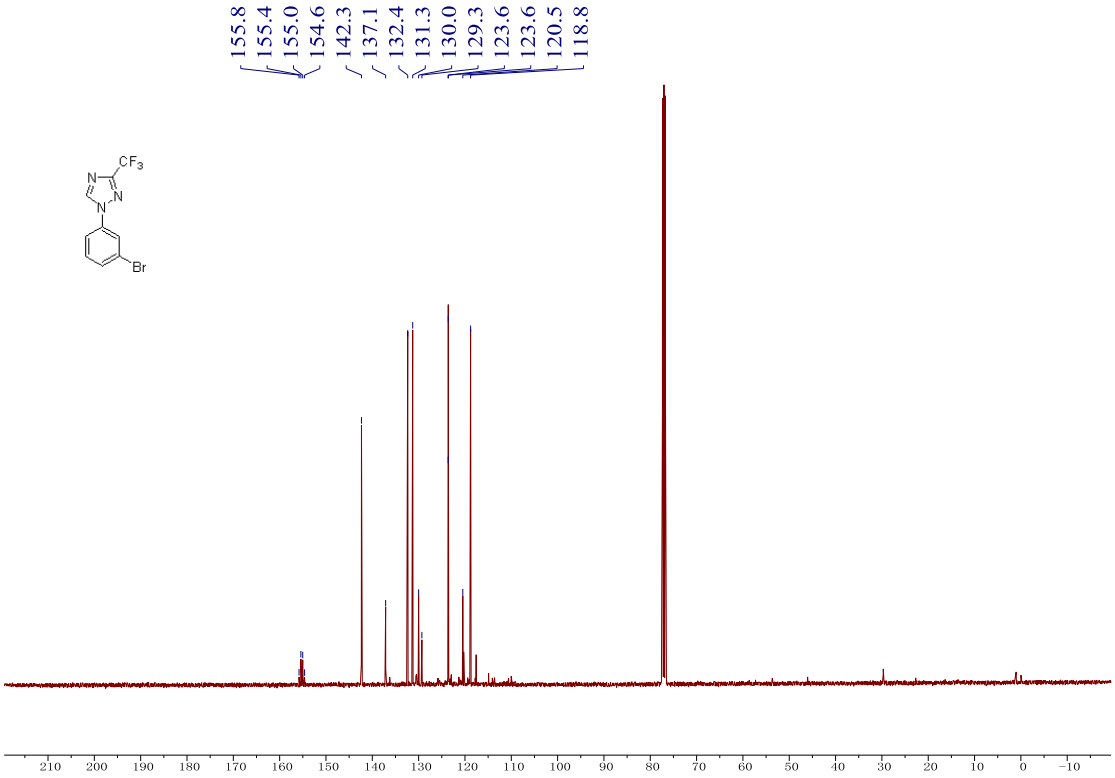
^{19}F NMR spectra of 3w (376 MHz, $CDCl_3$)



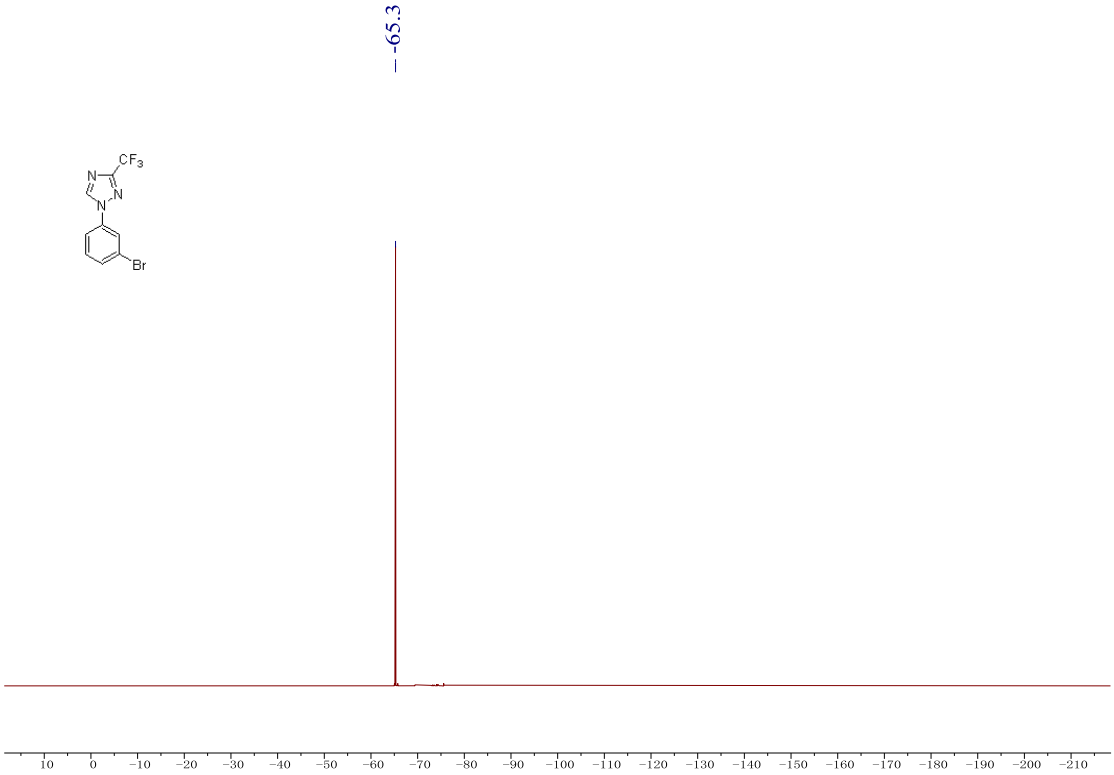
^{1}H NMR spectra of 3x (400 MHz, $CDCl_3$)



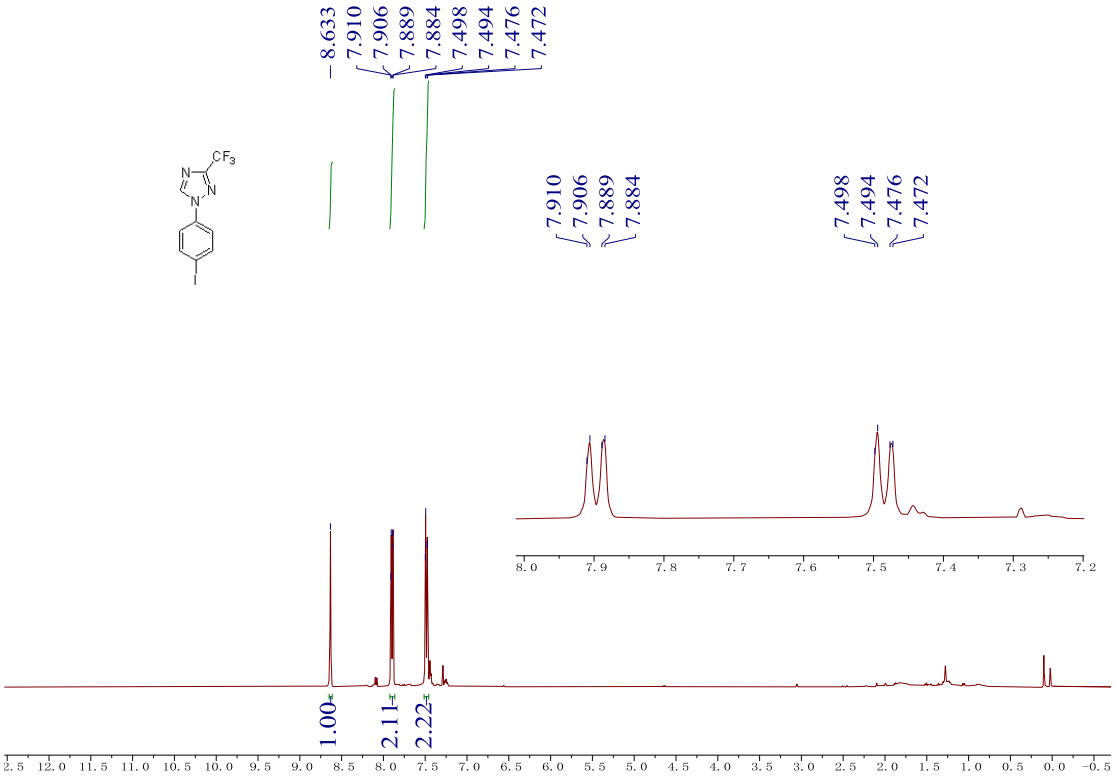
^{13}C{^{1}H} NMR spectra of 3x (101 MHz, $CDCl_3$)



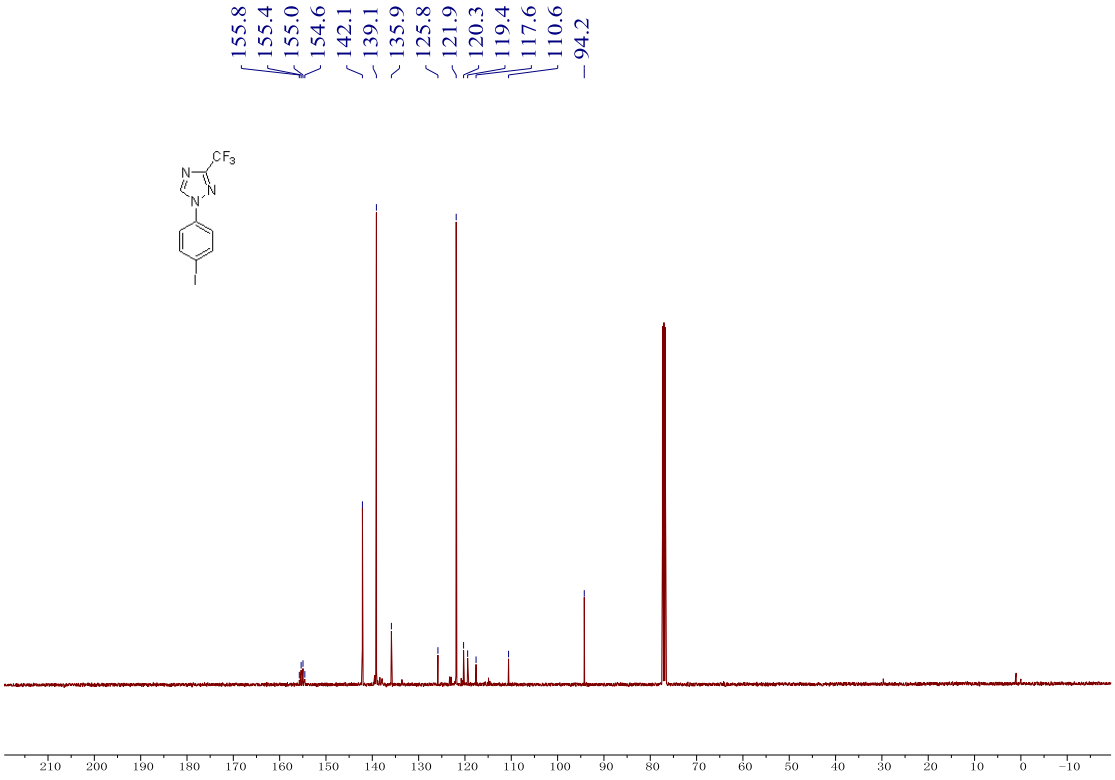
^{19}F NMR spectra of 3x (376 MHz, $CDCl_3$)



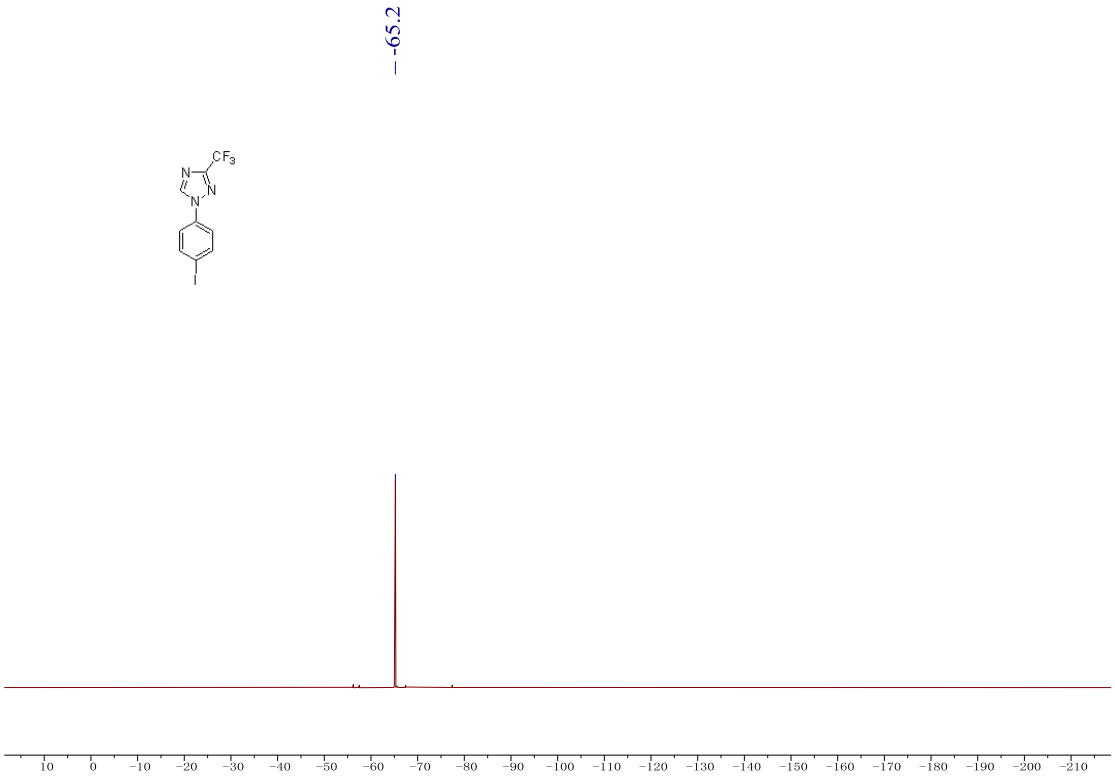
^{1}H NMR spectra of 3y (400 MHz, $CDCl_3$)



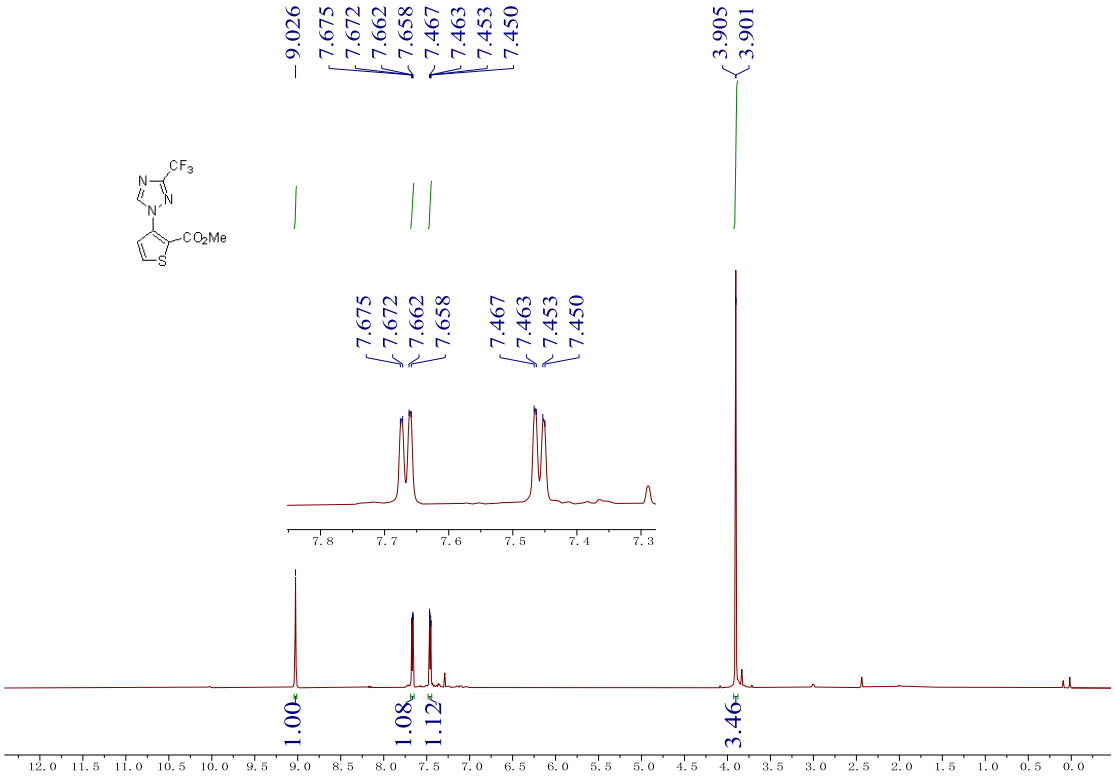
$^{13}C\{^{1}H\}$ NMR spectra of 3y (101 MHz, $CDCl_3$)



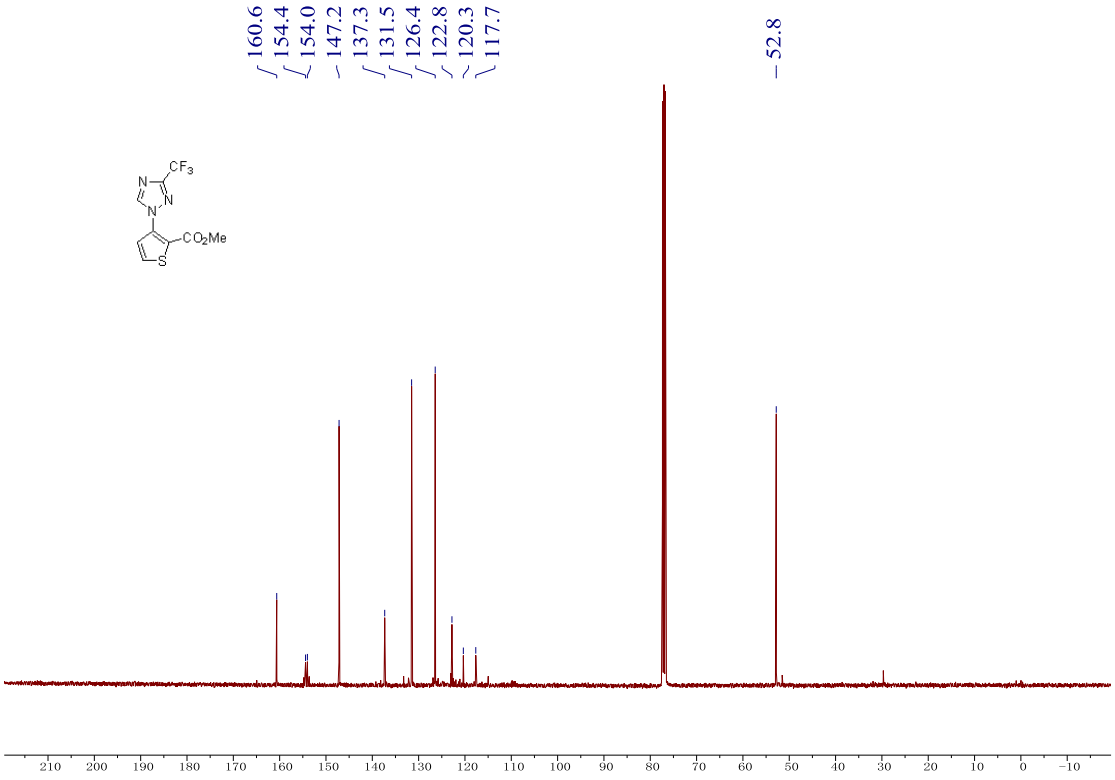
^{19}F NMR spectra of 3y (376 MHz, $CDCl_3$)



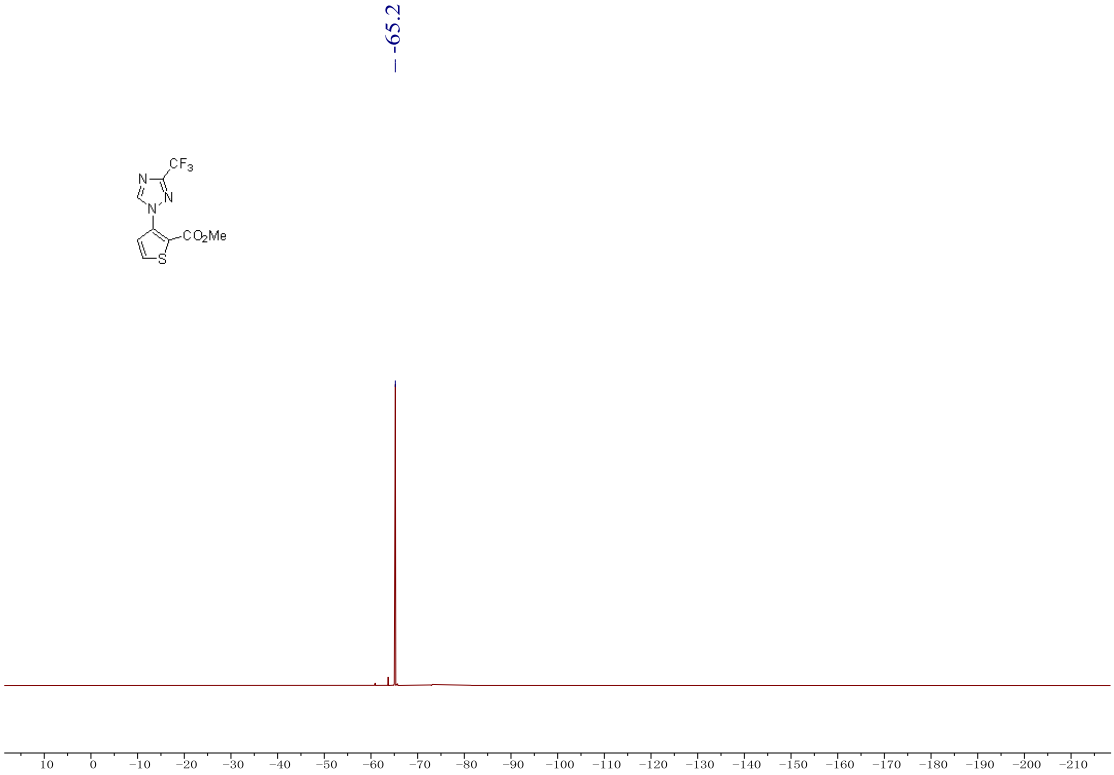
^{1}H NMR spectra of 3z (400 MHz, $CDCl_3$)



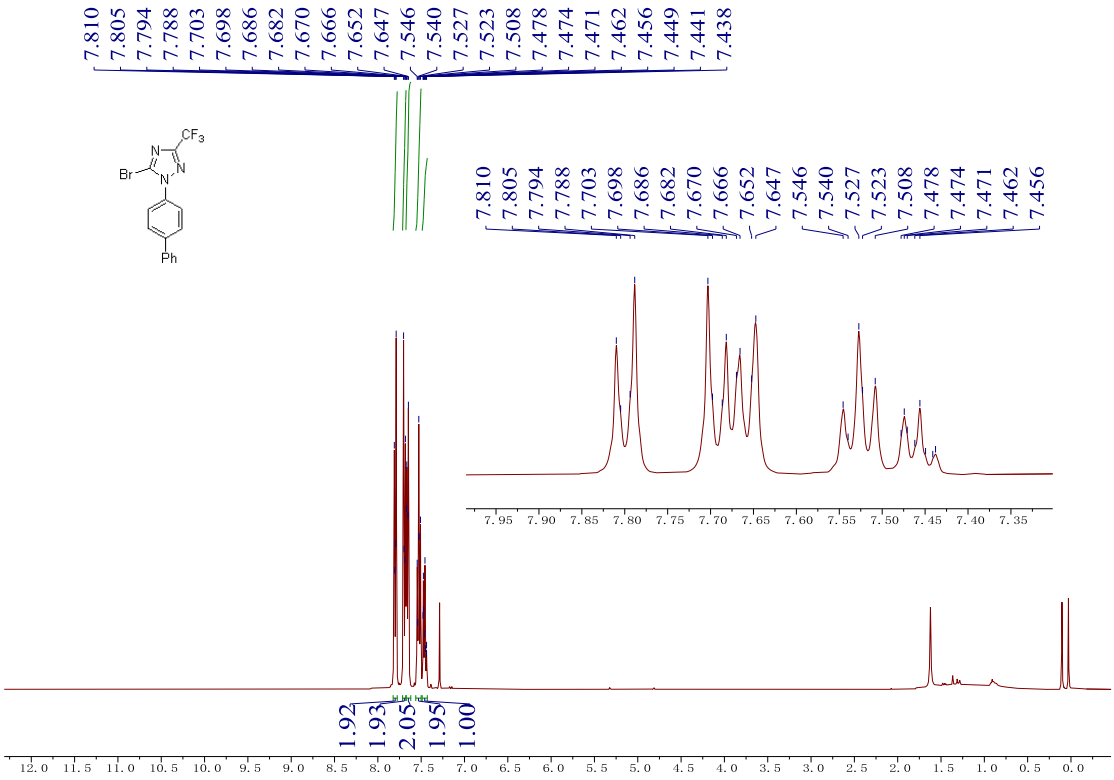
^{13}C{^{1}H} NMR spectra of 3z (101 MHz, $CDCl_3$)



^{19}F NMR spectra of 3z (376 MHz, $CDCl_3$)

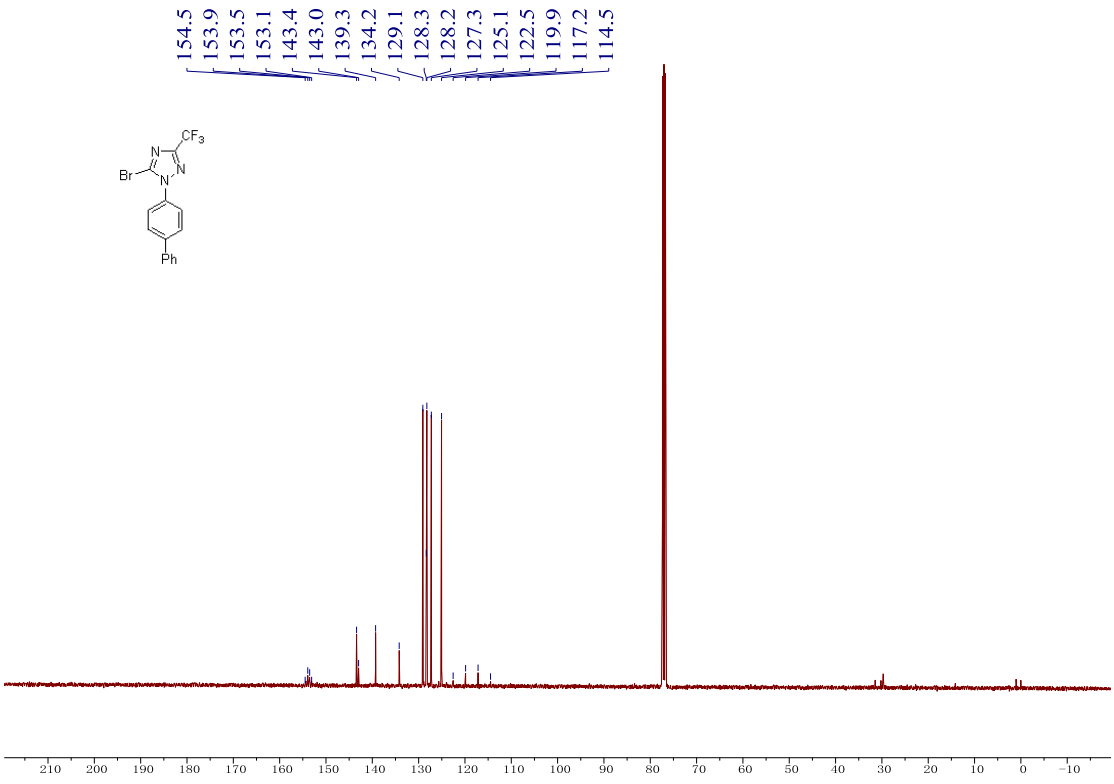


^{1}H NMR spectra of 4 (400 MHz, $CDCl_3$)

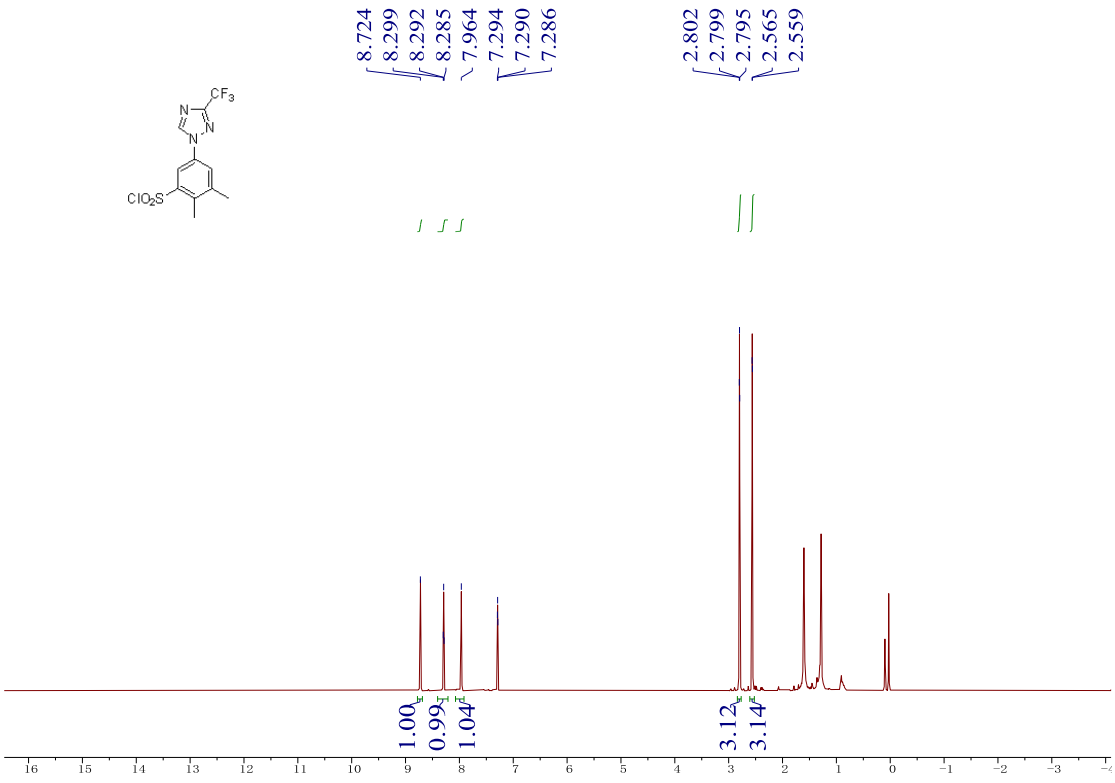


^{19}F NMR spectra of 4 (376 MHz, $CDCl_3$)

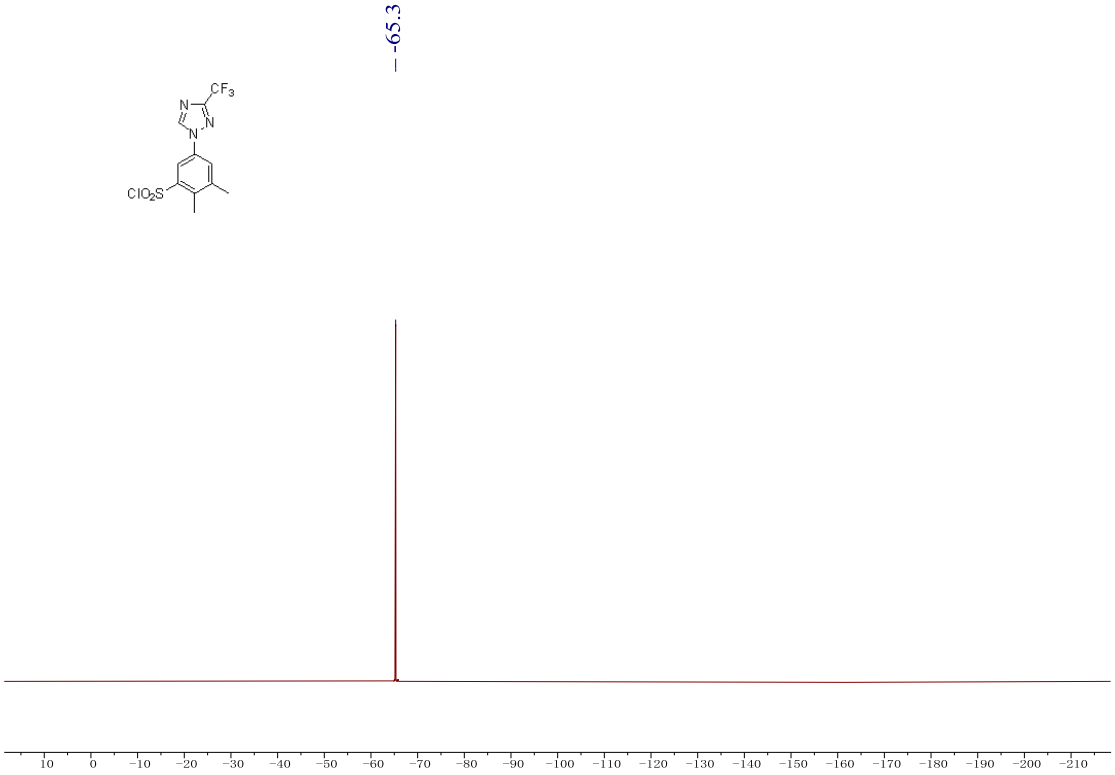
$^{13}C\{^{1}H\}$ NMR spectra of 4 (101 MHz, $CDCl_3$)



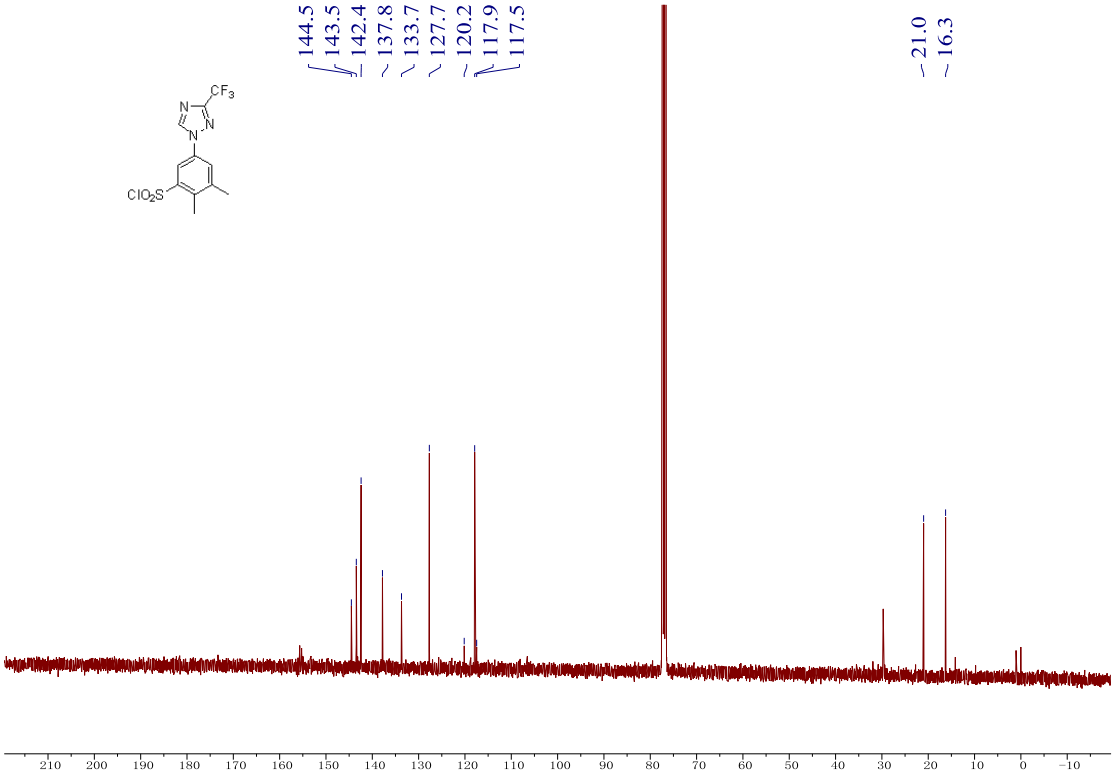
^{1}H NMR spectra of 5 (400 MHz, $CDCl_3$)



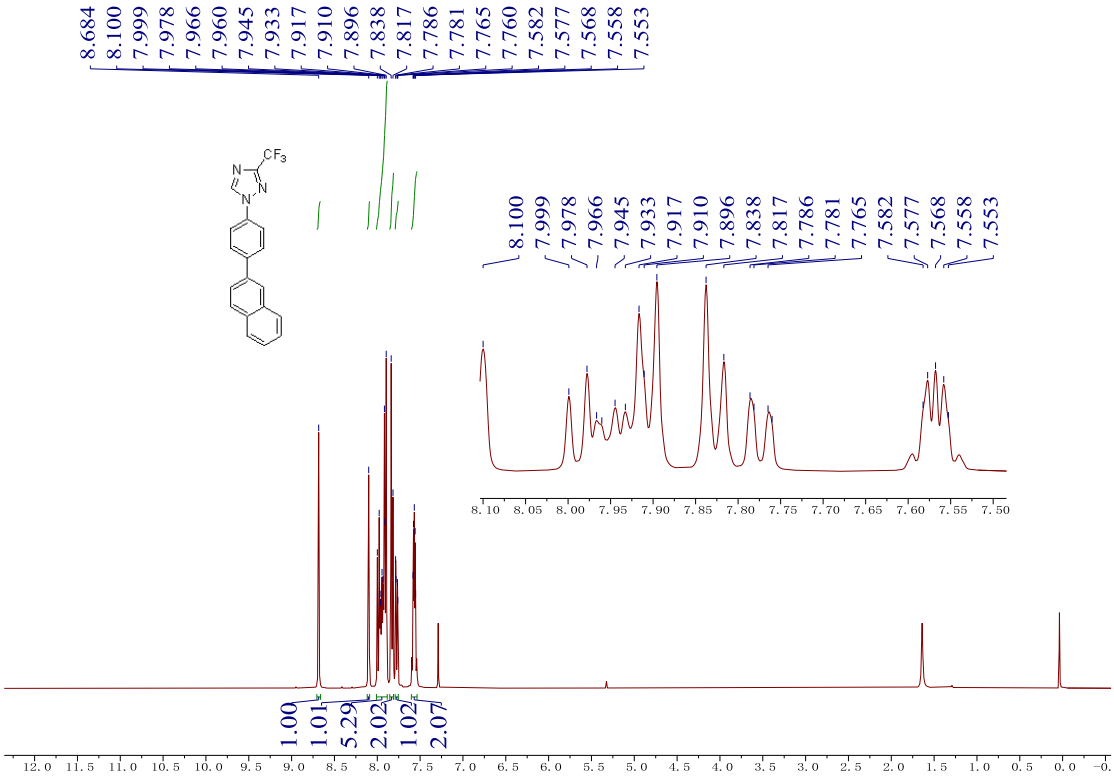
^{19}F NMR spectra of 5 (376 MHz, $CDCl_3$)



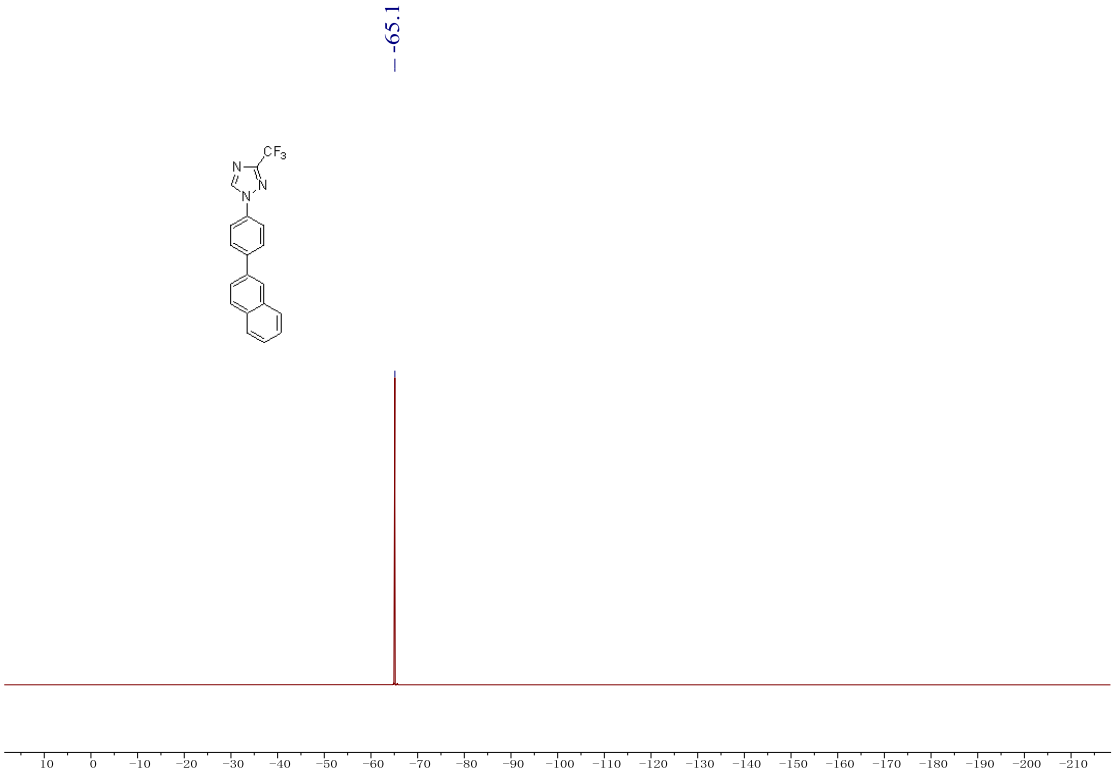
$^{13}C\{^{1}H\}$ NMR spectra of 5 (101 MHz, $CDCl_3$)



^{1}H NMR spectra of 6 (400 MHz, $CDCl_3$)



^{19}F NMR spectra of 6 (376 MHz, $CDCl_3$)



$^{13}C\{^1H\}$ NMR spectra of 6 (101 MHz, $CDCl_3$)