# Supporting information

## Copper-mediated [3+2] cycloaddition of trifluoroacetimidoyl chlorides and *N*-isocyanoiminotriphenylphosphorane for the synthesis of 3-trifluoromethyl-1,2,4-triazoles

Hefei Yang,[a] Shu-Ning Lu,[a] Yufei Song,[a] Zhengkai Chen,*[,a] and Xiao-Feng Wu*[,b,c,]

[a] Department of Chemistry, Key Laboratory of Surface & Interface Science of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou 310018, China

[b] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

[c] Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Straβe 29a, 18059 Rostock, Germany

**E-mail**: *zkchen@zstu.edu.cn*

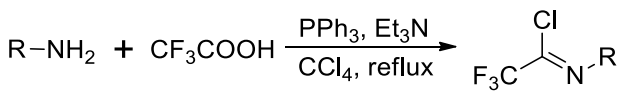
*xiao-feng.wu@catalysis.de*

## *Contents*

# 1. General Information

Unless otherwise noted, all reactions were carried out under $N_2$ atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. $^1$NMR spectra were recorded on a Bruker Avance operating at for $^1$H NMR at 400 MHz, $^{13}$C NMR at 100 MHz and $^{19}$F NMR at 377 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ ($^1$H NMR δ 7.26, $^{13}$C NMR δ 77.16) as solvent. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014C chromatograph equipped with a FID detector. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier using EI or ESI ionization. Melting points were measured with WRR digital point apparatus and not corrected.

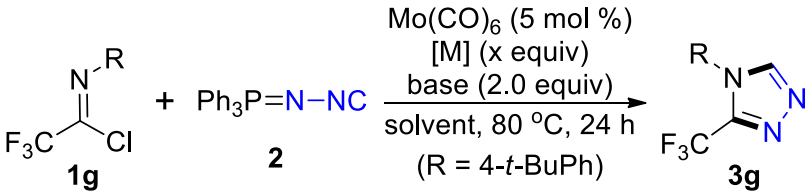
1.1 **Preparation of Fluorinated Imidoyl Chlorides**[1]




A 200 mL two-necked flask equipped with a septum cap, a condenser, and a Tefloncoated magnetic stir bar was charged with $PPh_3$ (34.5 g, 132 mmol), $Et_3N$ (7.3 mL, 53 mmol), $CCl_4$ (21.1 mL, 220 mmol), and TFA (3.4 mL, 44 mmol). After the solution was stirred for about 10 min (ice bath), amine (53 mmol) dissolved in $CCl_4$ (21.1 mL, 220 mmol) was added. The mixture was then refluxed under stirring for 3 h. After the reaction was completed, residual solid $Ph_3PO$, $PPh_3$ and $Et_3N$-HC1 were washed with hexane several times. Then the hexane was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel or neutral alumina to afford the corresponding product.

## 2. Experimental Procedures

### 2.1 Optimization of the Reaction Conditions




#### 2.1.1 Screening of Solvent[a]

| Entry | Solvent | Yield (%)[b] |
|---|---|---|
| 1 | Dioxane | 14 |
| 2 | MeCN | 25 |
| 3 | DMF | 13 |
| 4 | DMSO | trace |
| **5** | **THF** | **33** |
| 6 | DCM | 12 |

[a]Reaction conditions: **1g** (0.2 mmol, 1.0 equiv.), **2** (1.5 equiv.), $Mo(CO)_6$ (5 mol %), CuO (1.5 equiv.), $Na_2CO_3$ (2.0 equiv.), Solvent (2 mL), 4 Å MS (40 mg), 80 °C, 24 h. [b]Yields determined by GC analysis using dodecane as an internal standard.

#### 2.1.2 Screening of Catalyst[a]

| Entry | [M] | Yield (%)[b] |
|---|---|---|
| 1 | \ | trace |
| 2 | $CuCl_2$ | 12 |
| 3 | CuO | 33 |
| 4 | $Cu(CF_3COO)_2$ | trace |
| 5 | $Cu(OAc)_2$ | 10 |
| **6** | **CuOAc** | **64** |
| 7 | CuBr | trace |
| 8 | $Cu(CF_3SO_3)_2$ | trace |

| | | |
|---|---|---|
| **9** | $Ag_2CO_3$ | 9 |

[a]Reaction conditions: **1g** (0.2 mmol, 1.0 equiv.), **2** (1.5 equiv.), $Mo(CO)_6$ (5 mol %), [M] (1.5 equiv.), $Na_2CO_3$ (2.0 equiv.), THF (2 mL), 4 Å MS (40 mg), 80 ℃, 24 h. [b]Yields determined by GC analysis using dodecane as an internal standard.

### 2.1.3 Screening of CuOAc[a]

| Entry | CuOAc | Yield (%)[b] |
|---|---|---|
| 1 | 1 equiv. | 63 |
| **2** | **0.5 equiv.** | **68** |

[a]Reaction conditions: **1g** (0.2 mmol, 1.0 equiv.), **2** (1.5 equiv.), $Mo(CO)_6$ (5 mol %), CuOAc (1.5 equiv.), $Na_2CO_3$ (2.0 equiv.), THF (2 mL), 4 Å MS (40 mg), 80 ℃, 24 h. [b]Yields determined by GC analysis using dodecane as an internal standard.

### 2.1.4 Screening of Base[a]

| Entry | Base | Yield (%)[b] |
|---|---|---|
| 1 | DBU | trace |
| **2** | **$Et_3N$** | **97[b], 89[c]** |
| 3 | $Cs_2CO_3$ | 39 |
| 4 | $K_2CO_3$ | 37 |
| 5 | $NaHCO_3$ | 38 |
| 6 | $NaPO_4$ | 46 |
| 7 | DIPEA | 76 |

[a]Reaction conditions: **1g** (0.2 mmol, 1.0 equiv.), **2** (1.5 equiv.), $Mo(CO)_6$ (5 mol %), CuOAc (0.5 equiv.), Base (2.0 equiv.), THF (2 mL), 4 Å MS (40 mg), 80 ℃, 24 h. [b]Yields determined by GC analysis using dodecane as an internal standard. [c] Isolated Yield.

### 2.1.5 Screening of Additive[a]

| Entry | $X(CO)_6$ | Yield (%)[b] |
|---|---|---|
| 1 | / | trace |
| 2 | $Cr(CO)_6$ | 11 |
| 3 | $W(CO)_6$ | 66 |

[a]Reaction conditions: **1g** (0.2 mmol, 1.0 equiv.), **2** (1.5 equiv.), $X(CO)_6$ (5 mol %), CuOAc (0.5 equiv.), $Et_3N$ (2.0 equiv.), THF (2 mL), 4 Å MS (40 mg), 80 °C, 24 h. [b]Yields determined by GC analysis using dodecane as an internal standard. [c]Yield by Isolated.

### 2.1.6 Screening of Temperature[a]

| Entry | T/°C | Yield (%)[b] |
|---|---|---|
| 1 | 30 | 78 |
| 2 | 60 | 90 |
| 3 | 100 | 78 |

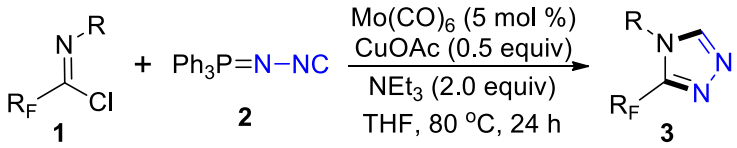
[a]Reaction conditions: **1g** (0.2 mmol, 1.0 equiv.), **2** (1.5 equiv.), $Mo(CO)_6$ (5 mol %), CuOAc (0.5 equiv.), $Et_3N$ (2.0 equiv.), THF (2 mL), 4 Å MS (40 mg), T °C, 24 h. [b]Yields determined by GC analysis using dodecane as an internal standard.

### 2.1.7 Screening of Time[a]

| Entry | Time (h) | Yield (%)[b] |
|---|---|---|
| 1 | 12 | 80 |
| **2** | **24** | **97[b],89[c]** |

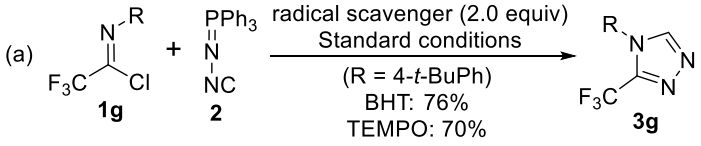
[a]Reaction conditions: **1g** (0.2 mmol, 1.0 equiv.), **2** (1.5 equiv.), $Mo(CO)_6$ (5 mol %), CuOAc (0.5 equiv.), $Et_3N$ (2.0 equiv.), THF (2 mL), 4 Å MS (40 mg), 80 °C, Time. [b]Yields determined by GC analysis using dodecane as an internal standard. [c]Isolated Yield.

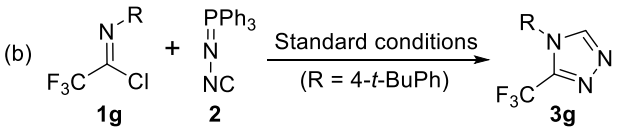
### 2.2 General Procedure for the Synthesis of 3-Trifluoromethyl-1,2,4-triazoles



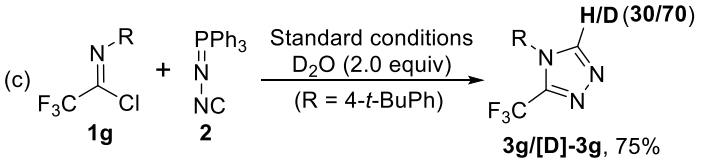

Under nitrogen atmosphere, **1** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), 4 Å MS (40 mg), $Mo(CO)_6$ (5 mol %, 2.7 mg), CuOAc (0.1 mmol, 0.5 equiv, 12.3 mg), $NEt_3$ (0.4 mmol, 2.0 equiv, 40.5 mg), THF (2 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 80 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the 3-trifluoromethyl-1,2,4-triazole product **3**.

## 3 Control Experiments




| | 4 Å MS | $H_2O$ | Yield |
|---|---|---|---|
| 1) | √ | × | 97% |
| 2) | × | × | 42% |
| 3) | × | √ | 73% |
| 4) | √ | √ | 79% |

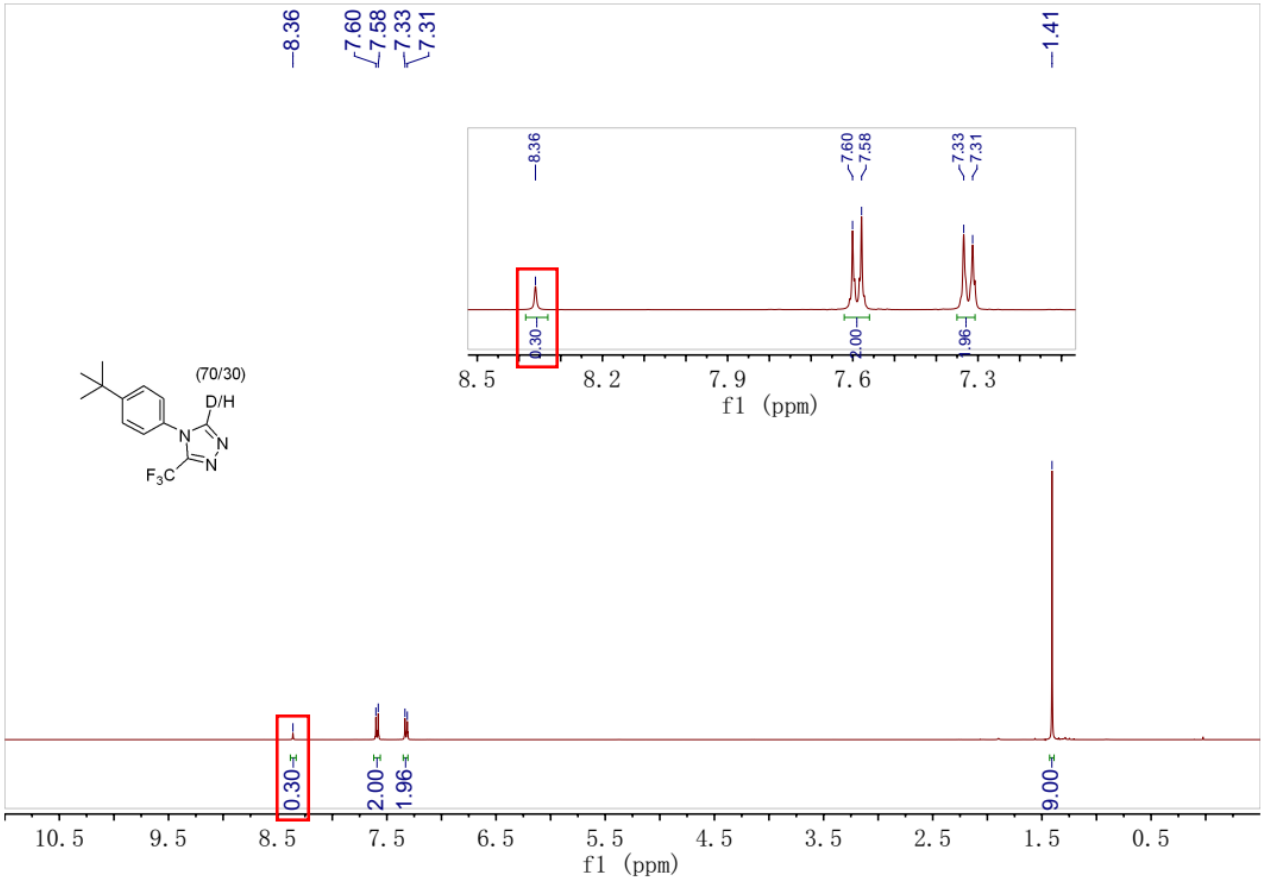



**Eq a**: Under nitrogen atmosphere, **1g** (0.2 mmol, 1.0 equiv, 52.6 mg), **2** (0.3 mmol, 1.5 equiv, 90.7 mg), 4 Å MS (40 mg), $Mo(CO)_6$ (5 mol %, 2.7 mg), CuOAc (0.1 mmol, 0.5 equiv, 12.3 mg), $NEt_3$ (0.4 mmol, 2.0 equiv, 40.5 mg), TEMPO (0.4 mmol, 2.0 equiv, 62.5 mg) or BHT (0.4 mmol, 2.0 equiv, 88.1 mg) and THF (2 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then

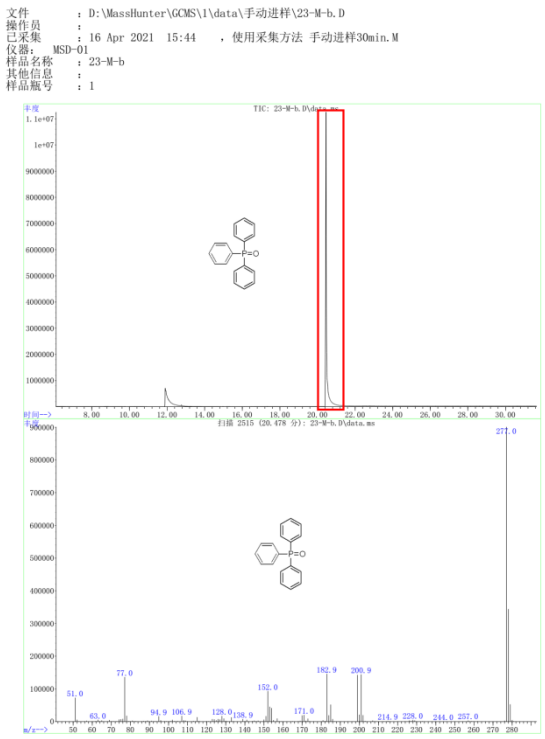
the tube was sealed and the mixture was stirred at 80 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **3g** as a white solid in 76% or 76% yield, respectively.

**Eq b**: Under nitrogen atmosphere, **1g** (0.2 mmol, 1.0 equiv, 52.6 mg), **2** (0.3 mmol, 1.5 equiv, 90.7 mg), $Mo(CO)_6$ (5 mol %, 2.7 mg), CuOAc (0.1 mmol, 0.5 equiv, 12.3 mg), $NEt_3$ (0.4 mmol, 2.0 equiv, 40.5 mg), and THF (2 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Four parallel experiments were conducted using the following additional conditions: 1) 4 Å MS (40 mg) without $H_2O$; 2) without 4 Å MS and $H_2O$; 3) $H_2O$ (2.0 equiv, 7.2 mg) without 4 Å MS; 4) 4 Å MS (40 mg) and $H_2O$ (2.0 equiv, 7.2 mg). Then these tubes were sealed and the mixture was stirred at 80 °C (oil bath) for 24 h. After the reactions were completed, the mixtures were tested by GC analysis using dodecane as an internal standard. The corresponding GC yield of the product **3g** was 97%, 42%, 73% or 79% yield, respectively.

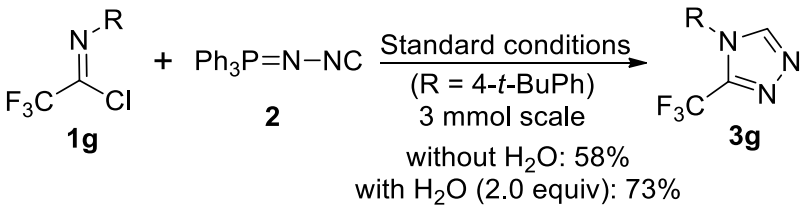
**Eq c**: Under nitrogen atmosphere, **1g** (0.2 mmol, 1.0 equiv, 52.6 mg), **2** (0.3 mmol, 1.5 equiv, 90.7 mg), $Mo(CO)_6$ (5 mol %, 2.7 mg), CuOAc (0.1 mmol, 0.5 equiv, 12.3 mg), $NEt_3$ (0.4 mmol, 2 equiv, 40.5 mg), $D_2O$ (0.4 mmol, 2.0 equiv, 8 mg), THF (2 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 80 °C (oil bath) for 24 h. After the reaction was completed, the mixture was slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **3**. The sample of the reaction was tested by $^1$H NMR and the H/D ratio of the product **3g** was successfully determined by $^1$H NMR.




**Note (the detection of byproduct $Ph_3P=O$)**: Under nitrogen atmosphere, **1g** (0.2 mmol, 1.0 equiv, 52.6 mg), **2** (0.3 mmol, 1.5 equiv, 90.7 mg), 4 Å MS (40 mg), $Mo(CO)_6$ (5 mol %, 2.7 mg), CuOAc (0.1 mmol, 0.5 equiv, 12.3 mg), $NEt_3$ (0.4 mmol, 2 equiv, 40.5 mg), THF (2 mL) (extra dry) were added to an oven-dried 15 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 80 °C (oil bath) for 24 h. The sample of the reaction was tested by GC-MS and the byproduct triphenylphosphine oxide generated in the reaction was successfully detected.

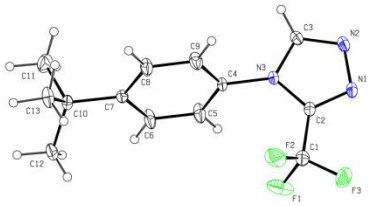


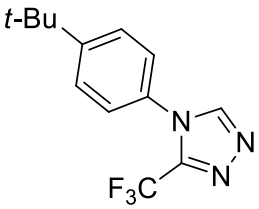

## 4 Scale-up Reaction




Under nitrogen atmosphere, **1g** (3 mmol, 1.0 equiv, 789 mg), **2** (4.5 mmol, 1.5 equiv, 1.36 g), 4 Å MS (600 mg), $Mo(CO)_6$ (5 mol %, 40.5 mg), CuOAc (1.5 mmol, 0.5 equiv, 184.5 mg), $NEt_3$ (6 mmol, 2.0 equiv, 608 mg), and THF (20 mL) (extra dry) were added to an oven-dried 100 mL *In-Ex* tube. Then the tube was sealed and the mixture was stirred at 80 °C (oil bath) for 24 h. Another experiment was conducted by the addition of 2.0 equiv. of $H_2O$ (6 mmol, 108 mg). After the reactions were completed, the mixtures were slowly cooled to room temperature, and extracted with EtOAc for three times (3×10 mL). The extract was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield the product **3g** as a white solid in 58% (468 mg) or 73% (589 mg) yield, respectively.

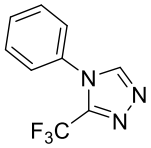
## 5 The Crystal Structure of Product 3g






**3g** **CCDC: 2087515**

## 6 Characterization Data of the Corresponding Products




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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.2) to give the titled product **3a** as a yellow solid (26.9 mg, 64%).

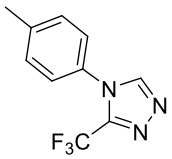
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.64 – 7.51 (m, 3H), 7.37 (d, *J* = 6.8 Hz, 2H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 146.2, 144.6 (C-F, q, $^{2}J_{(C-F)}$ = 34.6 Hz), 132.3, 130.8, 130.0, 125.9, 118.2 (C-F, q, $^{1}J_{(C-F)}$ = 271.2 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.5.

**M.p.** 67.4 - 69.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_9H_7F_3N_3$ 214.0587, found 214.0595.




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

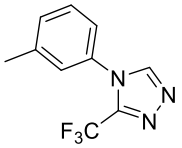
Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3b** as a yellow oily liquid (41.1 mg, 91%).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 2.45 (s, 3H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 146.4, 144.6 (C-F, q, $^2J_{(C-F)}$ = 39.1 Hz), 141.2, 130.5, 129.7, 125.6, 118.2 (C-F, q, $^1J_{(C-F)}$ = 271.2 Hz), 21.2 (C-F, q, $^1J_{(C-F)}$ = 9.8 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.6.

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{10}H_9F_3N_3$ 228.0743, found 228.0744.



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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3c** as a yellow solid (40.2 mg, 89%).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.32 (s, 1H), 7.46 – 7.36 (m, 2H), 7.16 (s, 2H), 2.44 (s, 3H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 146.2, 144.5 (C-F, q, $^2J_{(C-F)}$ = 41.1 Hz), 140.4, 132.2, 131.5, 129.7, 126.3, 122.9, 118.2 (C-F, q, $^1J_{(C-F)}$ = 271.1 Hz), 21.2.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.5.

**M.p.** 70.4 - 72.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{10}H_9F_3N_3$ 228.0743, found 228.0751.

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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product **3d** as a white solid (38.9 mg, 86%).

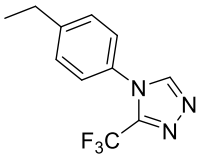
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.27 (s, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.31 (m, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 2.06 (s, 3H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 146.2, 144.7 (C-F, q, $^2J_{(C-F)}$ 38.2 Hz), 135.2, 131.5, 131.2, 131.2, 127.4, 127.2, 118.1 (C-F, q, $^1J_{(C-F)}$ = 271.2 Hz), 16.9 (C-F, q, $^1J_{(C-F)}$ = 14.8 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -61.8.

**M.p.** 76.4 - 77.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{10}H_9F_3N_3$ 228.0743, found 228.0750.



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

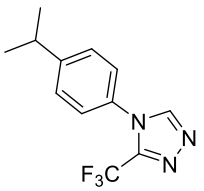
Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3e** as a yellow oily liquid (47.7 mg, 99%).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.34 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.76 (q, *J* = 7.6 Hz, 2H), 1.30 (t, *J* = 7.6 Hz, 3H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 147.4, 146.4, 144.6 (C-F, q, $^2J_{(C-F)}$ 40.2 Hz), 129.8, 129.3, 125.7, 118.2 (C-F, q, $^1J_{(C-F)}$ = 271.1 Hz), 28.5, 15.2.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.6.

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{11}H_{11}F_3N_3$ 242.0900, found 242.0906.



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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3f** as a yellow solid (35.7 mg, 70%).

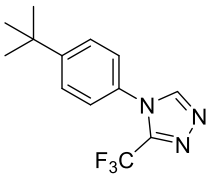
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.34 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.08 – 2.97 (m, 1H), 1.31 (d, *J* = 6.9 Hz, 6H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 152.0, 146.4, 144.6 (C-F, q, $^{2}J_{(C-F)}$ = 39.0 Hz), 129.9, 127.9, 125.7, 118.2 (C-F, q, $^{1}J_{(C-F)}$ = 271.1 Hz), 34.0, 23.8.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.6.

**M.p.** 67.4 - 69.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{12}H_{13}F_3N_3$ 256.1056, found 256.1063.




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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3g** as a white solid (47.9 mg, 89%).

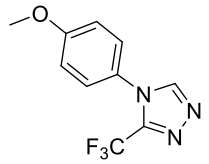
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.34 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 1.38 (s, 9H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 154.3, 146.4 (C-F, q, $^{2}J_{(C-F)}$ = 35.6 Hz), 129.6, 126.9, 125.4, 118.2 (C-F, q, $^{1}J_{(C-F)}$ = 271.2 Hz), 35.0, 31.2.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.6.

**M.p.** 130.4 - 131.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{13}H_{15}F_3N_3$ 270.1213, found 270.1219.



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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3h** as a yellow solid (47.4 mg, 98%).

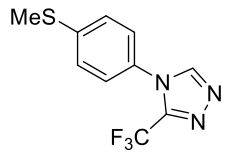
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.32 (s, 1H), 7.29 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.89 (s, 3H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 161.1, 146.6, 144.8 (C-F, q, $^{2}J_{(C-F)}$ = 39.3 Hz), 127.2, 124.7, 118.2 (C-F, q, $^{1}J_{(C-F)}$ = 271.1 Hz), 115.0, 55.7.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.7.

**M.p.** 75.1 - 77.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{10}H_9F_3N_3O$ 244.0692, found 244.0699.



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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3i** as a yellow solid (37.2 mg, 72%).

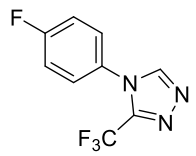
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.33 (s, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 2.55 (s, 3H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 146.3, 144.6 (C-F, q, $^{2}J_{(C-F)}$ = 41.2 Hz), 143.1, 128.6, 126.6, 126.1, 118.2 (C-F, q, $^{1}J_{(C-F)}$ = 271.2 Hz), 15.2.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.6.

**M.p.** 94.8 - 96.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{10}H_9F_3N_3S$ 260.0464, found 260.0470.



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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3j** as a yellow solid (35.5 mg, 77%).

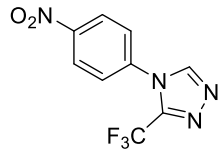
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.43 – 7.37 (m, 2H), 7.31 – 7.24 (m, 2H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 163.6 (C-F, d, $^{3}J_{(C-F)}$ = 252.7 Hz), 146.3, 144.7 (C-F, q, $^{2}J_{(C-F)}$ = 39.5 Hz), 128.1 (C-F, d, $^{2}J_{(C-F)}$ = 9.2 Hz), 118.1 (C-F, q, $^{1}J_{(C-F)}$ = 271.2 Hz), 117.2 (C-F, d, $^{1}J_{(C-F)}$ = 23.4 Hz), 117.2.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.6, -108.3.

**M.p.** 91.6 - 93.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_9H_6F_4N_3$ 232.0492, found 232.0499.



4-(4-nitrophenyl)-3-(trifluoromethyl)-4*H*-1,2,4-triazole (**3k**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3k** as a yellow solid (22.6 mg, 44%).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, *J* = 8.9 Hz, 2H), 8.42 (s, 1H), 7.63 (d, *J* = 8.9 Hz, 2H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 149.0, 145.7 (C-F, q, $^{2}J_{(C-F)}$ = 39.5 Hz), 137.2, 127.1, 125.5, 118.0 (C-F, q, $^{1}J_{(C-F)}$ = 271.3 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.1.

**M.p.** 143.9 - 145.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_9H_6F_3N_4O_2$ 259.0437, found 259.0446.

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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.2) to give the titled product **3l** as a yellow solid (27.2 mg, 55%).

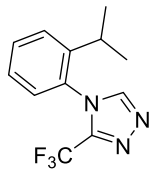
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.48 (t, *J* = 6.8 Hz, 1H), 7.43 (d, *J* = 9.1 Hz, 1H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 146.1, 141.7 (C-F, q, $^{2}J_{(C-F)}$ = 37.1 Hz), 132.4, 131.9, 130.8, 130.0, 128.8, 128.1, 117.9 (C-F, q, $^{1}J_{(C-F)}$ = 271.4 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -61.6.

**M.p.** 86.9 - 88.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_9H_6ClF_3N_3$ 248.0197, found 248.0206.



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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3m** as a yellow oily liquid (39.1 mg, 77%).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.25 (s, 1H), 7.56 (t, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 6.6 Hz, 1H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 2.48 – 2.29 (m, 1H), 1.18 – 1.13 (m, 6H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 146.7, 145.9, 145.1 (C-F, q, $^{2}J_{(C-F)}$ = 38.6 Hz), 131.6, 129.6, 127.4, 127.3, 126.9, 118.1 (C-F, q, $^{1}J_{(C-F)}$ = 271.4 Hz), 28.0, 25.0, 22.5.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -61.3.

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{12}H_{13}F_3N_3$ 256.1056, found 256.1065.

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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3n** as a yellow oily liquid (33.5 mg, 69%).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.24 (s, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.11 – 7.04 (m, 2H), 3.79 (s, 3H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 154.3, 146.7, 145.0 (C-F, q, $^{2}J_{(C-F)}$ = 40.2 Hz), 132.3, 127.8, 121.0, 120.8, 118.2 (C-F, q, $^{1}J_{(C-F)}$ = 271.3 Hz), 112.1, 55.8.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -61.9.

**HRMS (ESI)**: $[M+Na]^+$ calcd. for $C_{10}H_8F_3N_3NaO$ 266.0512, found 266.0515.

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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3o** as a yellow solid (47.9 mg, 83%).

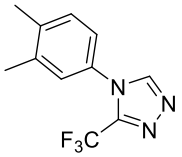
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.97 (s, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.08 – 7.02 (m, 2H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 146.7, 144.8 (C-F, q, $^{2}J_{(C-F)}$ = 36.2 Hz), 139.5, 136.2, 131.5, 131.1, 130.0, 128.9, 128.7, 128.5, 128.1, 127.4, 118.2 (C-F, q, $^{1}J_{(C-F)}$ = 271.3 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.4.

**M.p.** 125.9 - 127.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{15}H_{11}F_3N_3$ 290.0900, found 290.0908.



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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3p** as a white solid (46.5 mg, 96%).

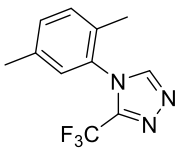
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.14 – 7.06 (m, 2H), 2.36 (s, 3H), 2.34 (s, 3H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 146.4, 144.6 (C-F, q, $^{2}J_{(C-F)}$ = 39.3 Hz), 139.9, 138.8, 130.8, 129.9, 126.6, 123.1, 118.3 (C-F, q, $^{1}J_{(C-F)}$ = 271.1 Hz), 19.8, 19.7.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.6.

**M.p.** 104.2 - 106.6 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{11}H_{11}F_3N_3$ 242.0900, found 242.0908.



4-(2,5-dimethylphenyl)-3-(trifluoromethyl)-4*H*-1,2,4-triazole (**3q**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3q** as a white solid (37.3 mg, 78%).

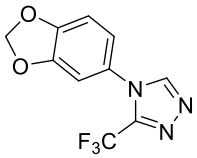
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.26 (s, 1H), 7.28 (s, 2H), 7.06 (s, 1H), 2.39 (s, 3H), 2.02 (s, 3H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 146.3, 144.8 (C-F, q, $^{2}J_{(C-F)}$ = 36.1 Hz), 137.4, 131.9, 131.2, 131.1, 127.7, 118.1 (C-F, q, $^{1}J_{(C-F)}$ = 271.6 Hz), 20.6, 16.5.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -61.8.

**M.p.** 95.4 - 97.8 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{11}H_{11}F_3N_3$ 242.0900, found 242.0909.



4-(benzo[*d*][1,3]dioxol-5-yl)-3-(trifluoromethyl)-4*H*-1,2,4-triazole (**3r**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product **3r** as a yellow solid (44.1 mg, 86%).

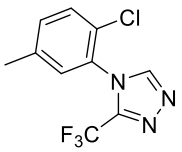
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.87 – 6.80 (m, 2H), 6.13 (s, 2H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 149.6, 148.6, 146.5, 144.7 (C-F, q, $^2J_{(C-F)}$ = 37.8 Hz), 125.6, 120.0, 118.2 (C-F, q, $^1J_{(C-F)}$ = 271.2 Hz), 108.6, 106.9, 102.6.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -60.7.

**M.p.** 111.3 - 113.6 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{10}H_7F_3N_3O_2$ 258.0485, found 258.0493.



4-(2-chloro-5-methylphenyl)-3-(trifluoromethyl)-4*H*-1,2,4-triazole (**3s**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product **3s** as a white solid (31.9 mg, 62%).

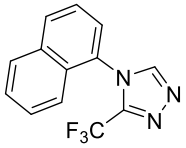
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.28 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 9.7 Hz, 1H), 7.22 (s, 1H), 2.42 (s, 3H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 146.1, 144.5 (C-F, q, $^2J_{(C-F)}$ = 39.4 Hz), 138.7, 133.1, 130.3, 129.6, 129.2, 128.6, 118.0 (C-F, q, $^1J_{(C-F)}$ = 271.4 Hz), 20.7.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -61.6.

**M.p.** 78.6 - 80.2 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{10}H_8ClF_3N_3$ 262.0353, found 262.0361.



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

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3t** as a yellow solid (32.3 mg, 62%).

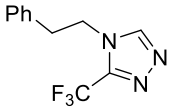
**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.41 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 147.1, 145.6 (C-F, q, $^{2}J_{(C-F)}$ = 39.5 Hz), 134.0, 131.6, 129.5, 128.6, 128.6, 128.3, 127.6, 125.4, 124.9, 120.9, 118.1 (C-F, q, $^{1}J_{(C-F)}$ = 271.6 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -61.4.

**M.p.** 132.4 - 134.6 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{13}H_9F_3N_3$ 264.0743, found 264.0748.



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

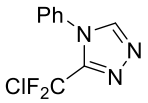
Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3u** as a yellow oily liquid (17.4 mg, 36%).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 7.36 – 7.27 (m, 3H), 7.06 (d, *J* = 6.3 Hz, 2H), 4.36 (t, *J* = 7.1 Hz, 2H), 3.10 (t, *J* = 7.1 Hz, 2H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 146.0 (C-F, q, $^{2}J_{(C-F)}$ = 41.5 Hz), 135.6, 129.2, 128.6, 127.7, 118.6 (C-F, q, $^{1}J_{(C-F)}$ = 270.1 Hz), 47.4, 36.8.

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -61.9.

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{11}H_{11}F_3N_3$ 242.0900, found 242.0905.



3-(chlorodifluoromethyl)-4-phenyl-4*H*-1,2,4-triazole (**3v**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3v** as a white solid (42.0 mg, 92%).

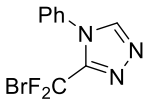
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 7.63 – 7.52 (m, 3H), 7.38 (d, *J* = 7.3 Hz, 2H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 148.1 (C-F, t, $^2J_{(C-F)}$ = 32.6 Hz), 146.5, 132.6, 130.8, 129.8, 126.4, 119.5 (C-F, t, $^1J_{(C-F)}$ = 287.4 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -48.0.

**M.p.** 74.5 - 76.5 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_8H_7ClF_2N_3$ 230.0291, found 230.0300.



3-(bromodifluoromethyl)-4-phenyl-4*H*-1,2,4-triazole (**3w**)

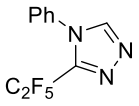
Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3w** as a yellow oily liquid (44.7 mg, 82%).

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.31 (s, 1H), 7.56 (d, *J* = 8.7 Hz, 3H), 7.39 (d, *J* = 6.8 Hz, 2H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 148.9 (C-F, t, $^2J_{(C-F)}$ = 29.2 Hz), 146.5, 132.7, 130.8, 129.8, 126.6, 109.8 (C-F, t, $^1J_{(C-F)}$ = 301.0 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -44.5.

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_8H_7BrF_2N_3$ 273.9786, found 273.9790.



3-(perfluoroethyl)-4-phenyl-4*H*-1,2,4-triazole (**3x**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product **3x** as a white solid (47.6 mg, 90%).

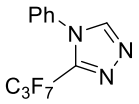
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.36 (s, 1H), 7.63 – 7.51 (m, 3H), 7.37 (d, *J* = 7.3 Hz, 2H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 146.7, 143.5 (C-F, t, $^3J_{(C-F)}$ = 27.4 Hz), 132.6, 130.8, 129.8, 126.2, 118.0 (C-F, qt, $^2J_{(C-F)}$ = 286.6, 34.7 Hz), 108.9 (C-F, tq, $^1J_{(C-F)}$ = 255.4, 40.7 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -108.6, -82.4.

**M.p.** 101.4 - 103.5 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{10}H_7F_5N_3$ 264.0555, found 264.0564.



3-(perfluoropropyl)-1-phenyl-1*H*-1,2,4-triazole (**3y**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.3) to give the titled product **3y** as a white solid (44.3 mg, 71%).

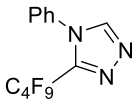
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.62 – 7.52 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 2H).

**$^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$)** δ 147.0, 143.6 (C-F, t, $^4J_{(C-F)}$ = 23.6 Hz), 132.7, 130.8, 129.7, 126.5, 117.5 (C-F, qt, $^3J_{(C-F)}$ = 288.1, 33.2 Hz), 111.0 (C-F, tt, $^2J_{(C-F)}$ = 257.1, 32.8 Hz), 108.0 (C-F, tm, $^1J_{(C-F)}$ = 229.7 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -124.9, -106.8, -79.9.

**M.p.** 86.4 - 88.5 °C

**HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{11}H_7F_7N_3$ 314.0523, found 314.0534.




3-(perfluorobutyl)-1-phenyl-1*H*-1,2,4-triazole (**3z**)

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 5:1, Rf = 0.4) to give the titled product **3z** as a yellow solid (72.4 mg, 99%).

**$^{1}$H NMR (400 MHz, $CDCl_3$)** δ 8.35 (s, 1H), 7.62 – 7.51 (m, 3H), 7.35 (d, *J* = 7.5 Hz, 2H).

**$^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$)** δ 147.0, 143.7 (C-F, t, $^{3}J_{(C-F)}$ = 28.7 Hz), 132.7, 130.8, 129.7, 126.4, 117.2 (C-F, tq, $^{2}J_{(C-F)}$ = 288.5, 32.8 Hz), 111.5 (C-F, tt, $^{1}J_{(C-F)}$ = 258.5, 33.6 Hz).

**$^{19}$F NMR (377 MHz, $CDCl_3$)** δ -125.4, -121.3, -106.2, -80.9.

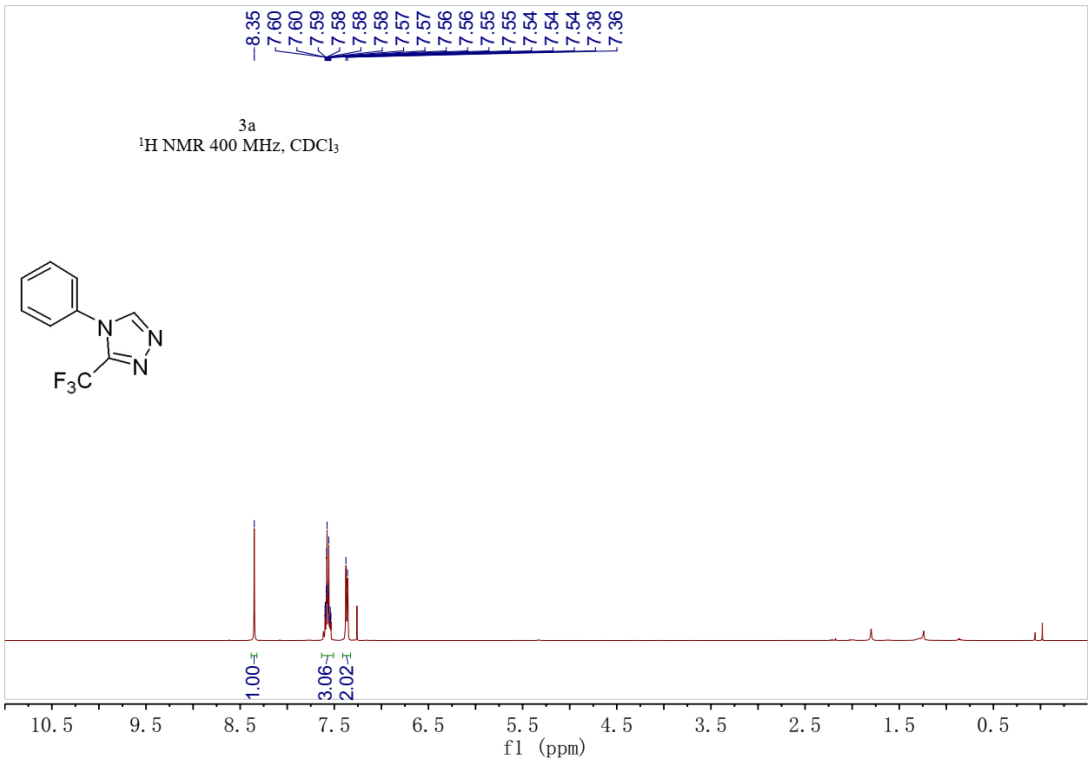
**M.p.** 78.4 - 80.5 °C

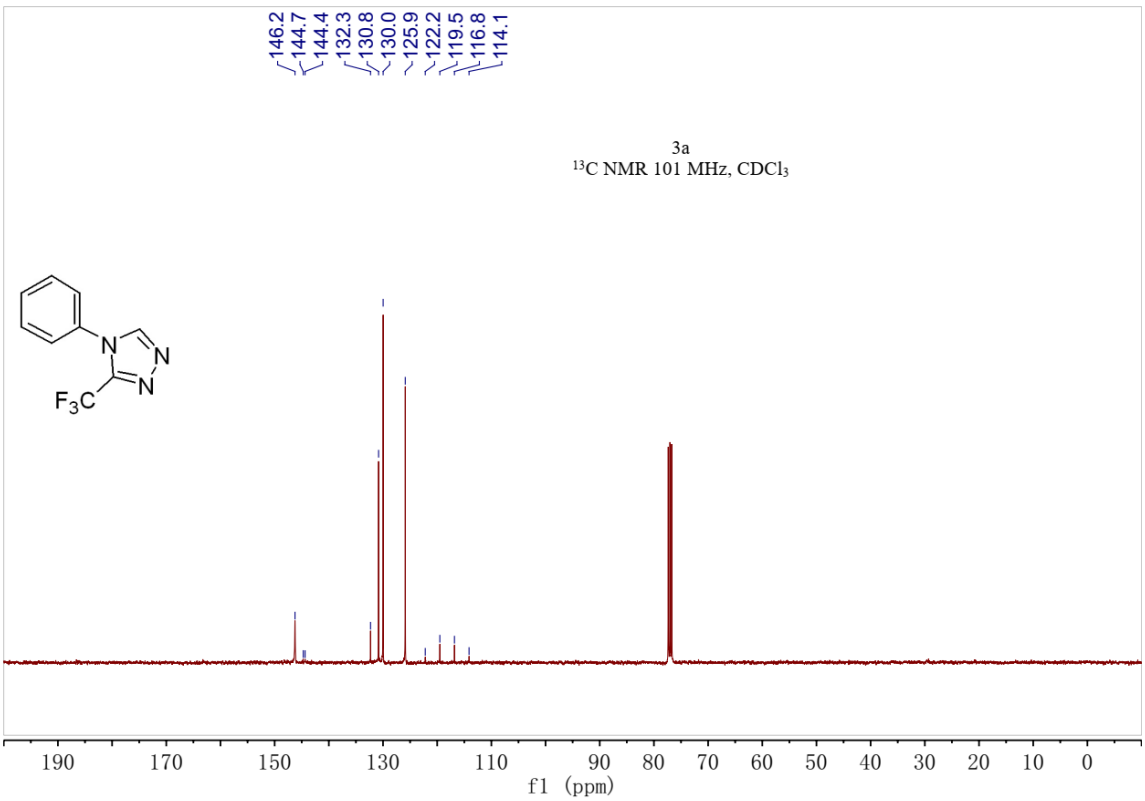
**HRMS (ESI)**: $[M+Na]^+$ calcd. for $C_{12}H_6F_9N_3Na$ 386.0310, found 386.0304.

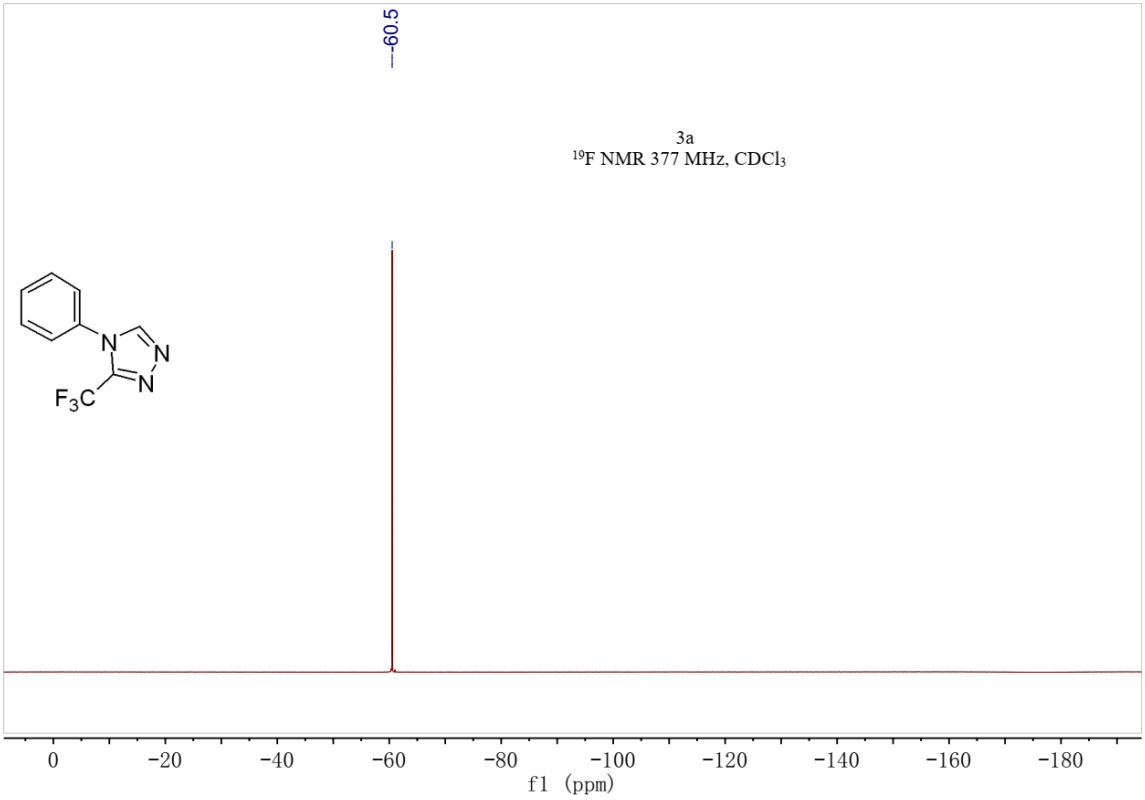
## 7 References

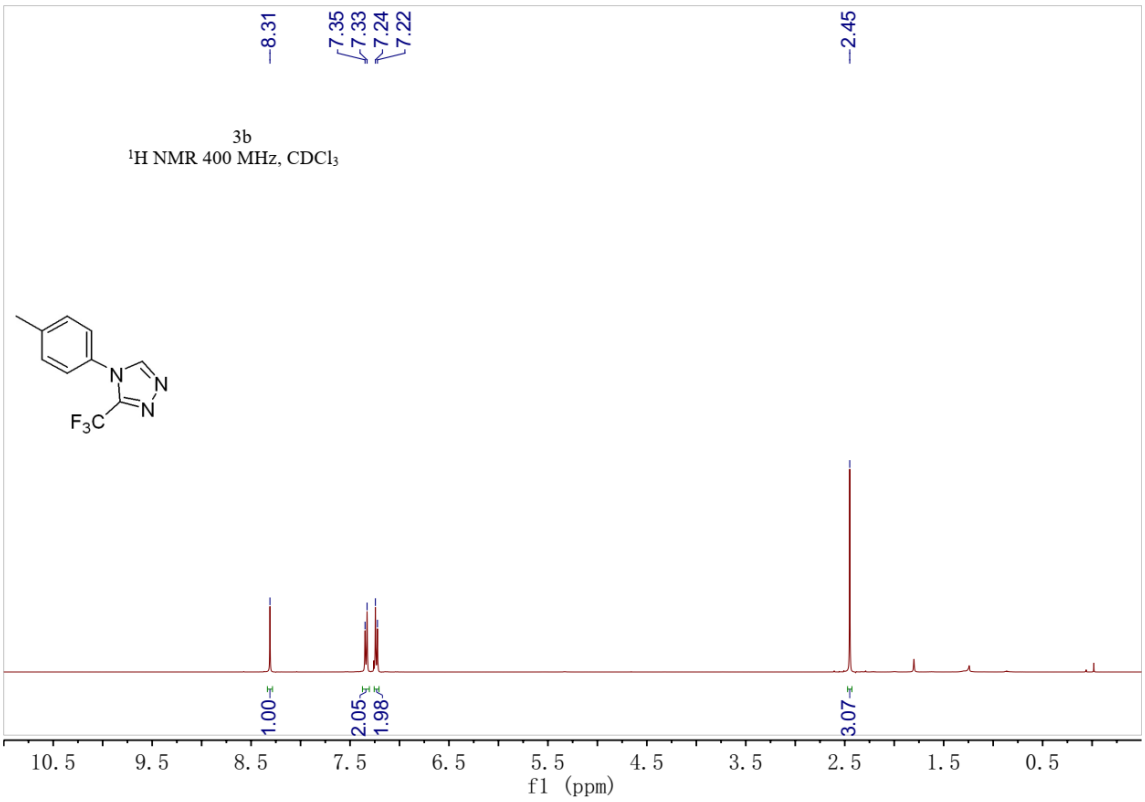
(1) K. Tamura, H. Mizukami, K. Maeda, H. Watanabe, K. Uneyama, *J. Org. Chem.* **1993**, *58*, 32-35.

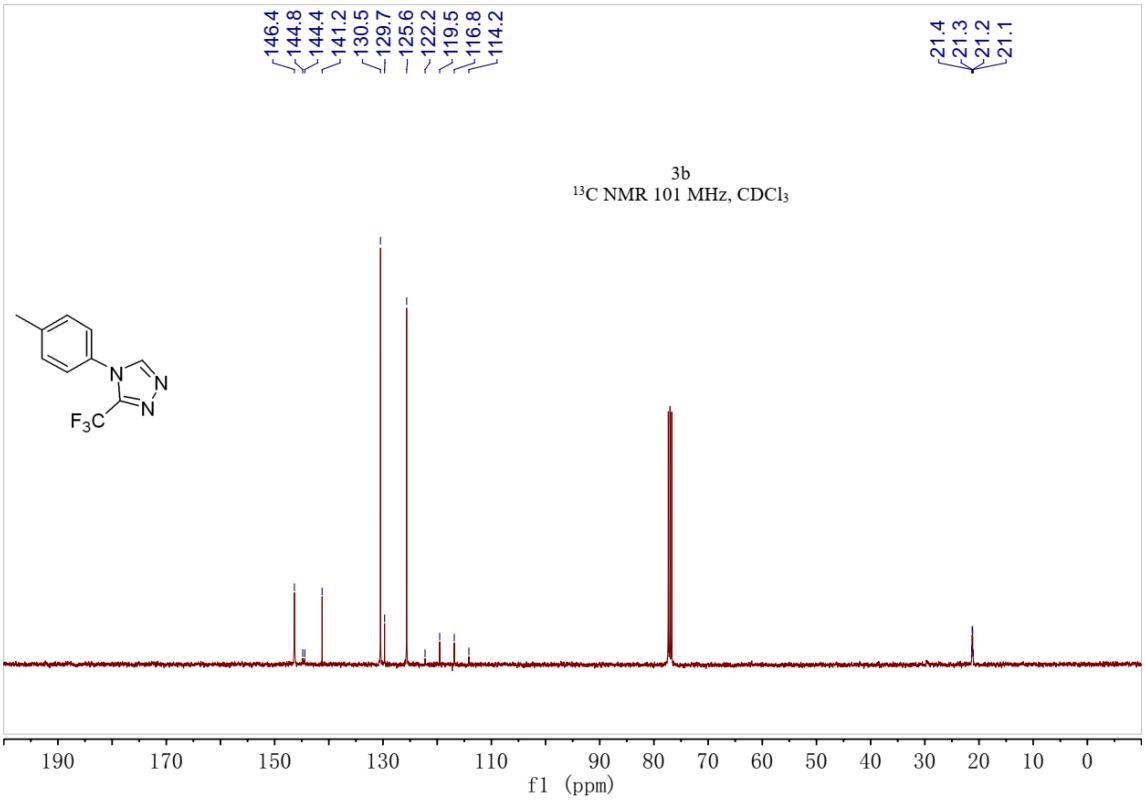
# 8 Copy of $^{1}H$, $^{13}C$ and $^{19}F$ NMR Spectra of Products

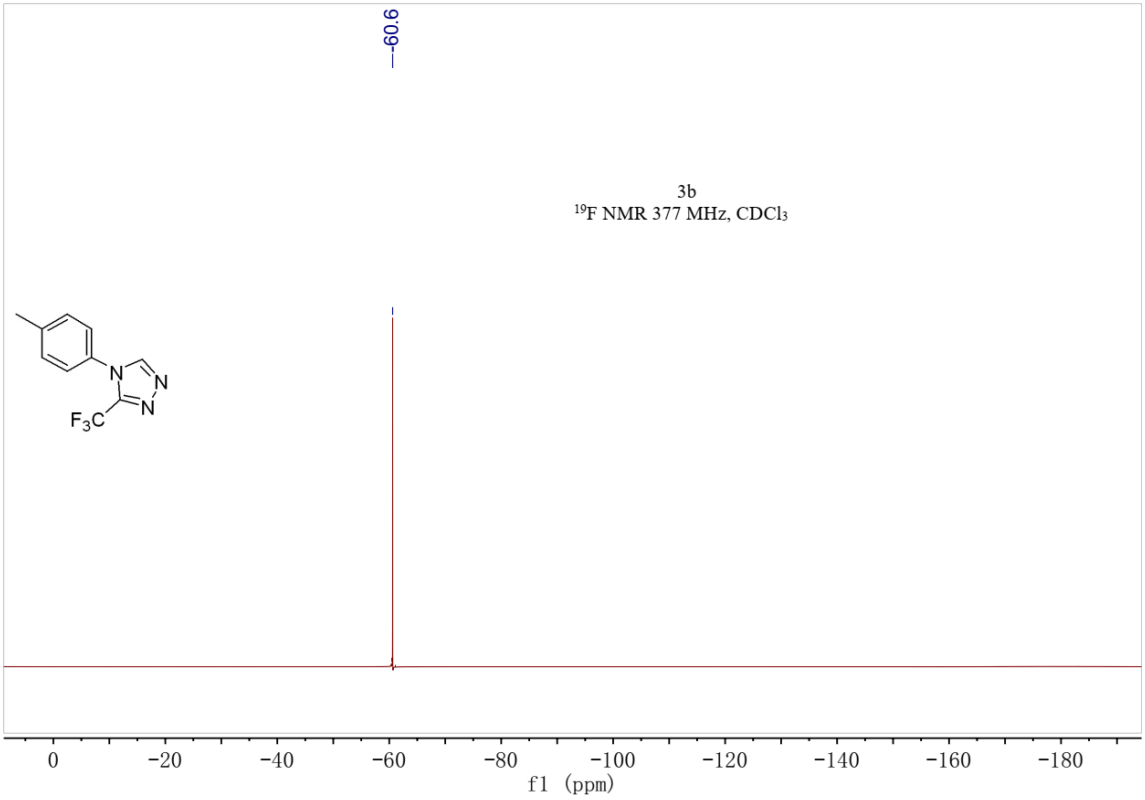


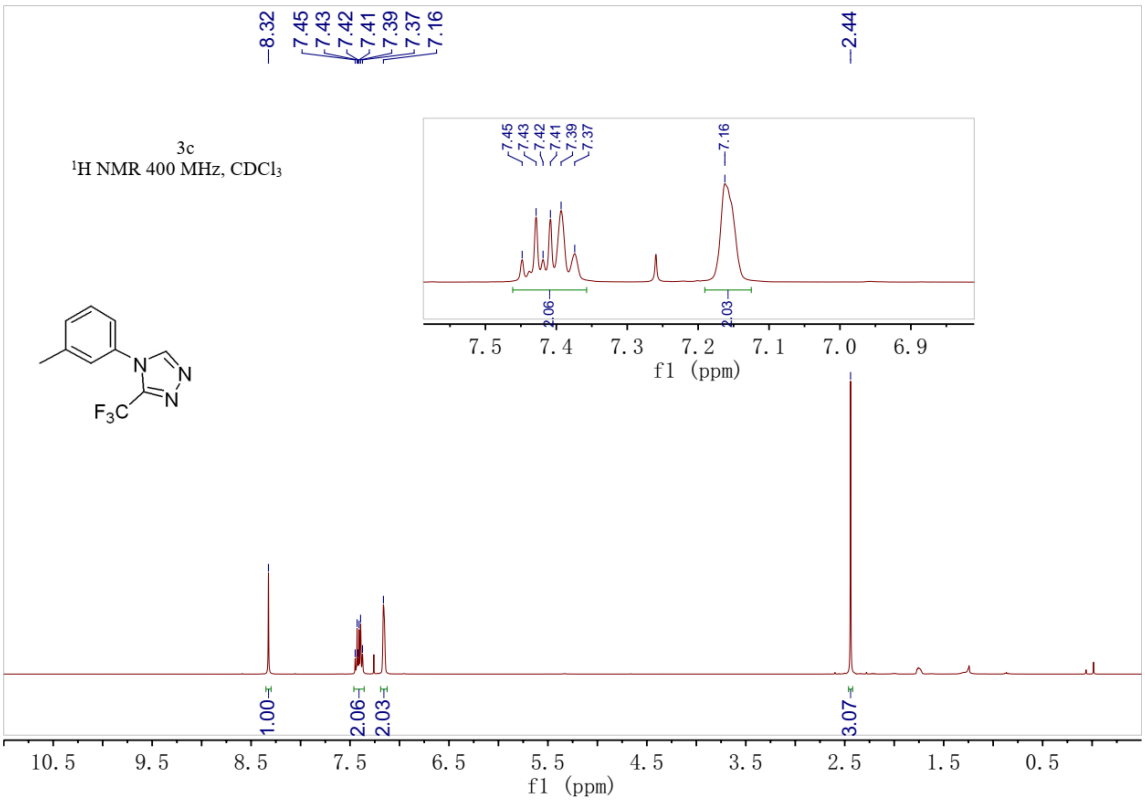



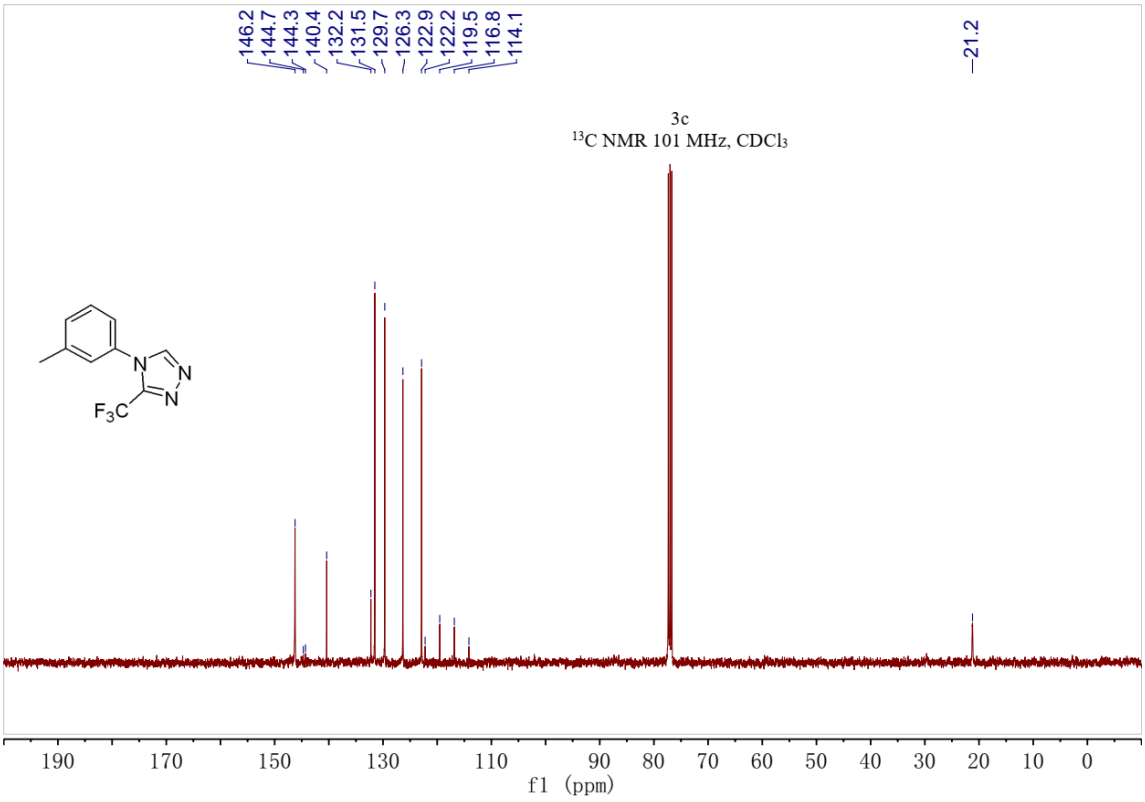

-60.5
3a
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

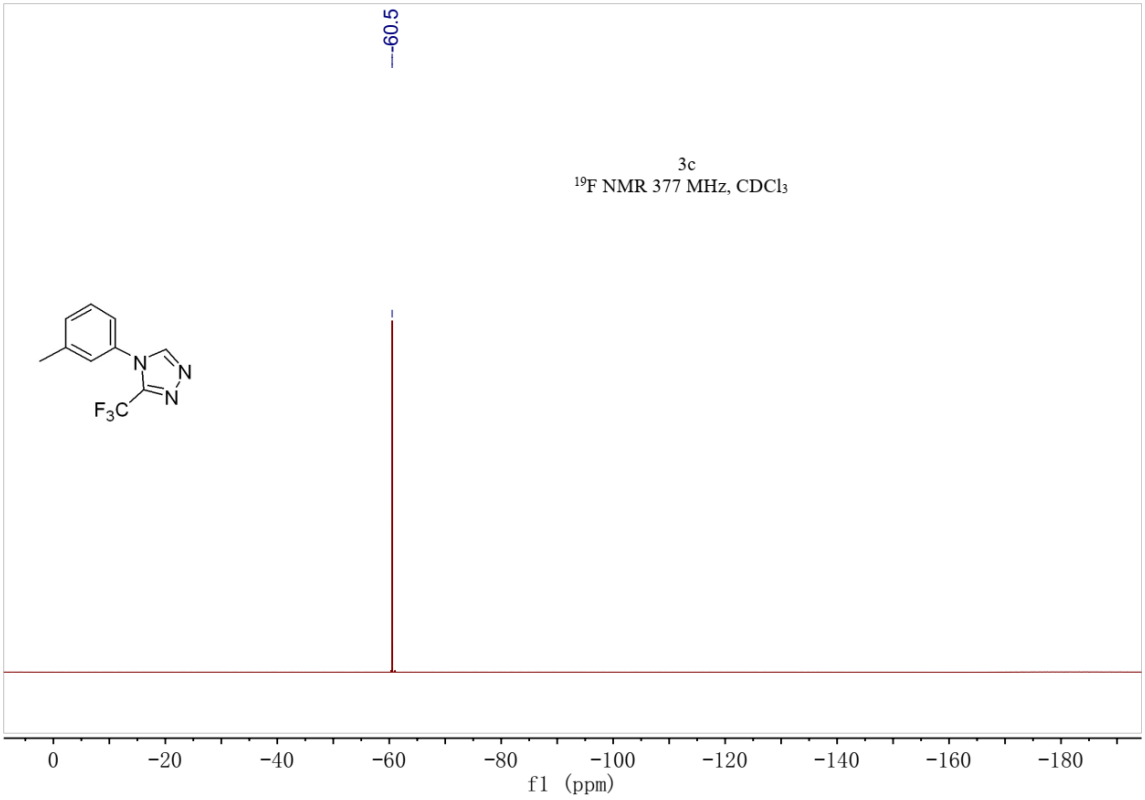

8.31
7.35
7.33
7.24
7.22
2.45
3b
1H NMR 400 MHz, CDCl3
F3C
1.00
2.05
1.98
3.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

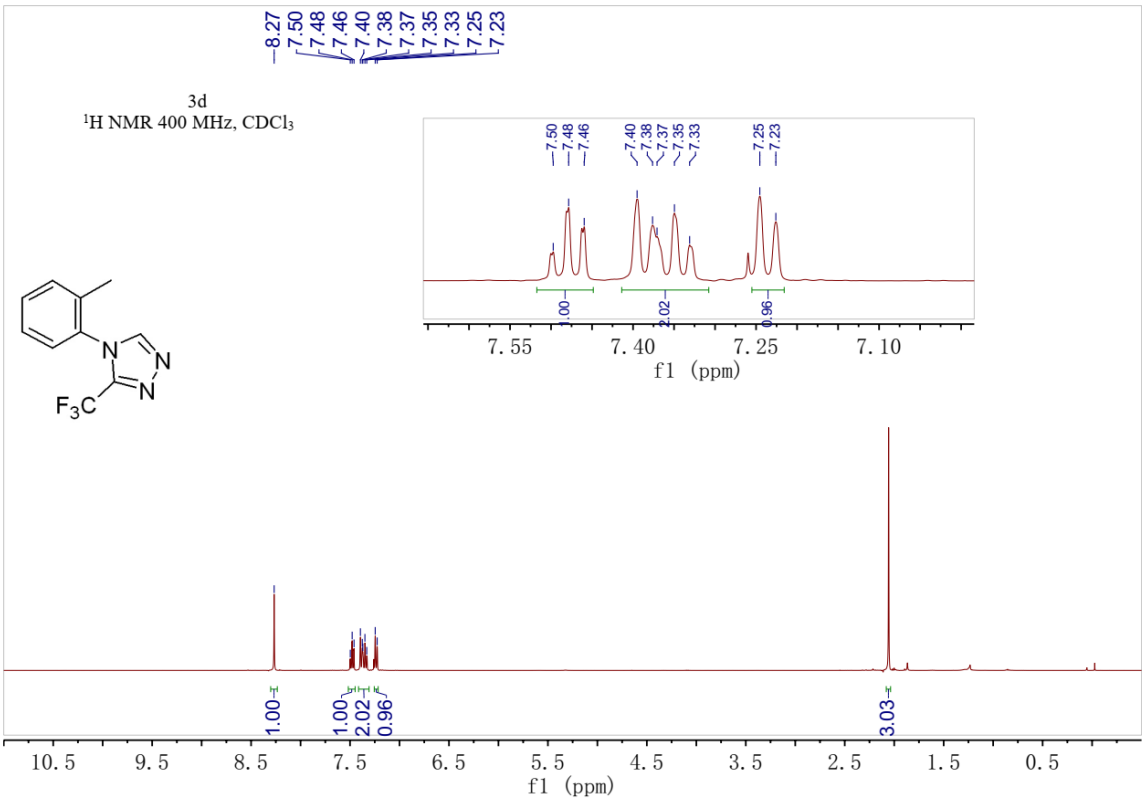

146.4
144.8
144.4
141.2
130.5
129.7
125.6
122.2
119.5
116.8
114.2
21.4
21.3
21.2
21.1
3b
13C NMR 101 MHz, CDCl3
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

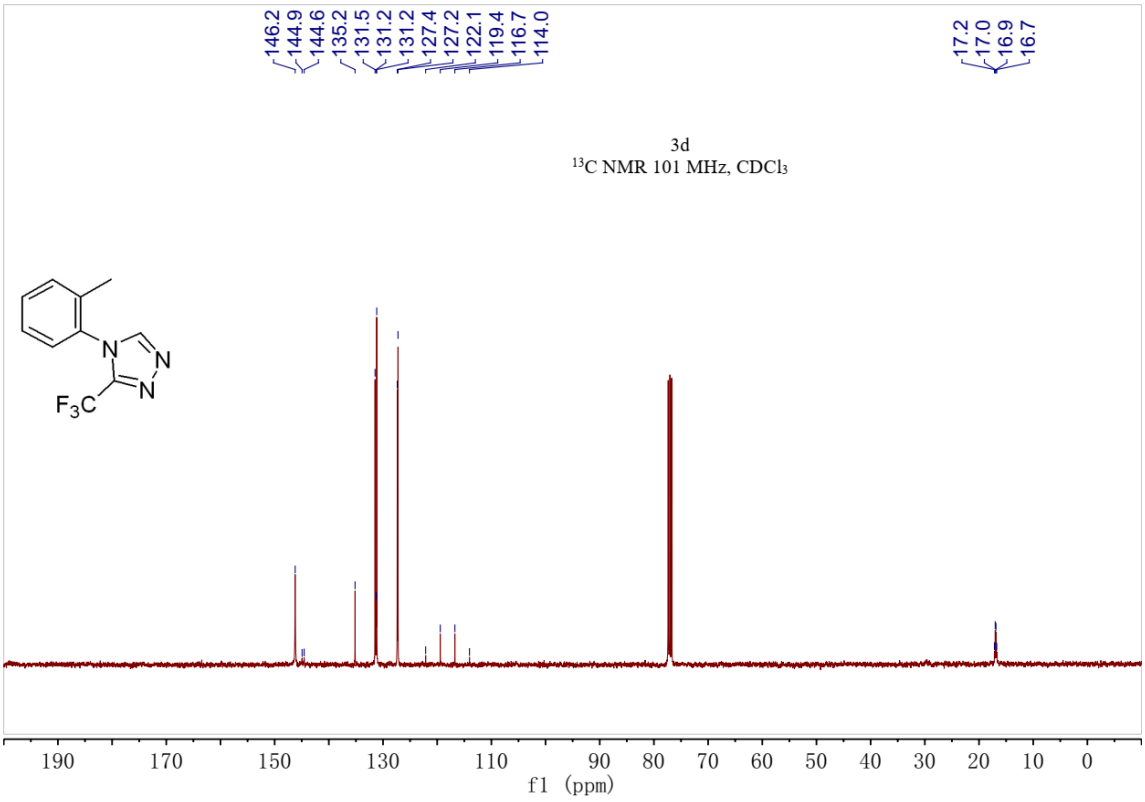

-60.6
3b
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

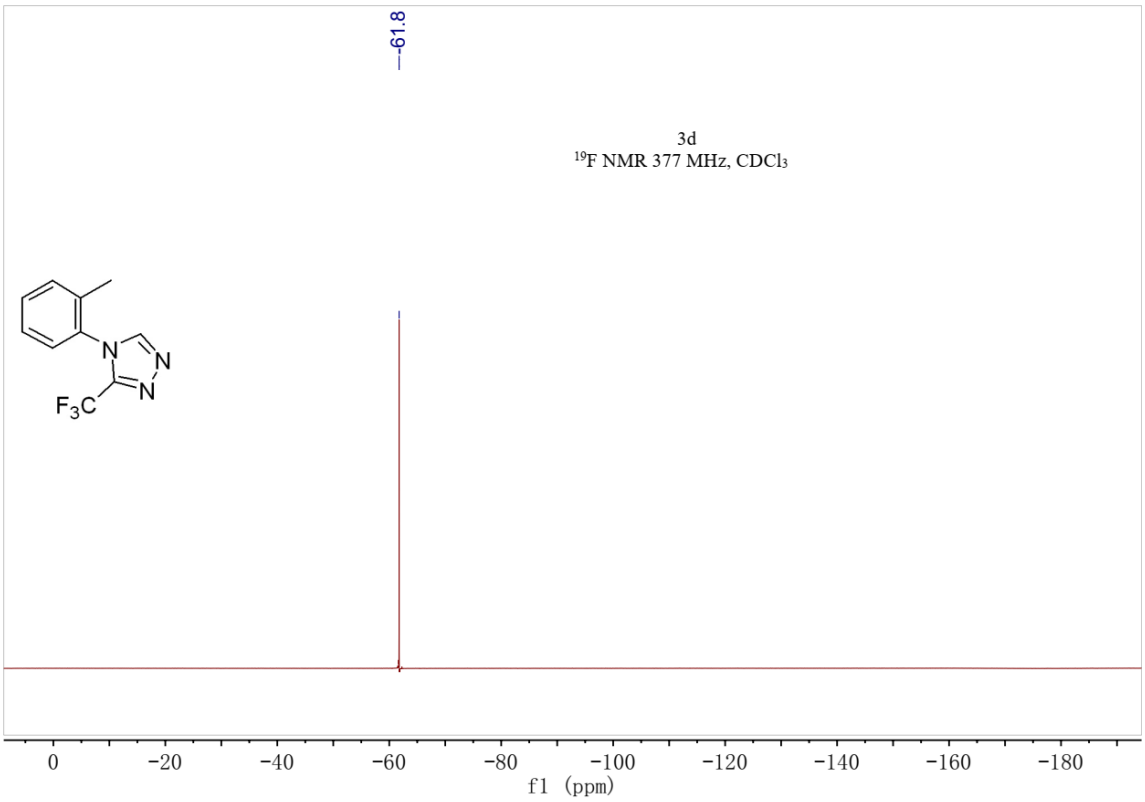

8.32
7.45
7.43
7.42
7.41
7.39
7.37
7.16
2.44
3c
1H NMR 400 MHz, CDCl3
F3C
1.00
2.06
2.03
3.07
f1 (ppm)

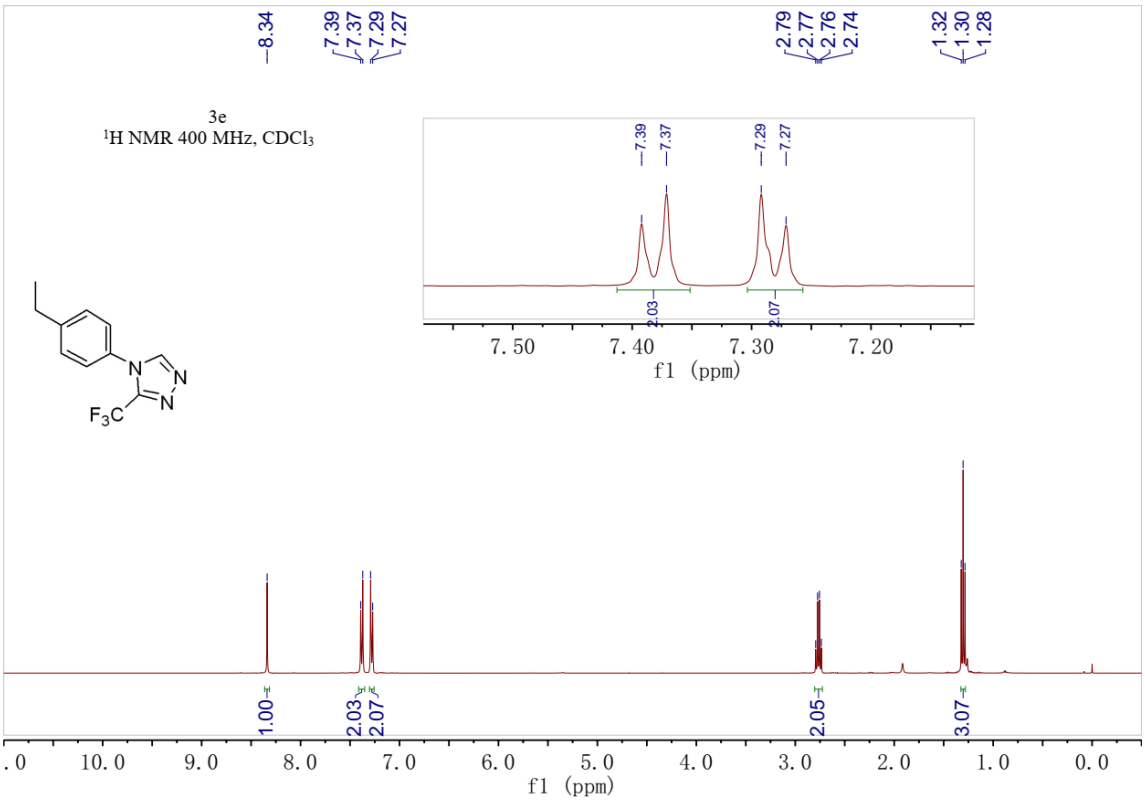

146.2
144.7
144.3
140.4
132.2
131.5
129.7
126.3
122.9
122.2
119.5
116.8
114.1
21.2
3c
13C NMR 101 MHz, CDCl3
F3C
f1 (ppm)

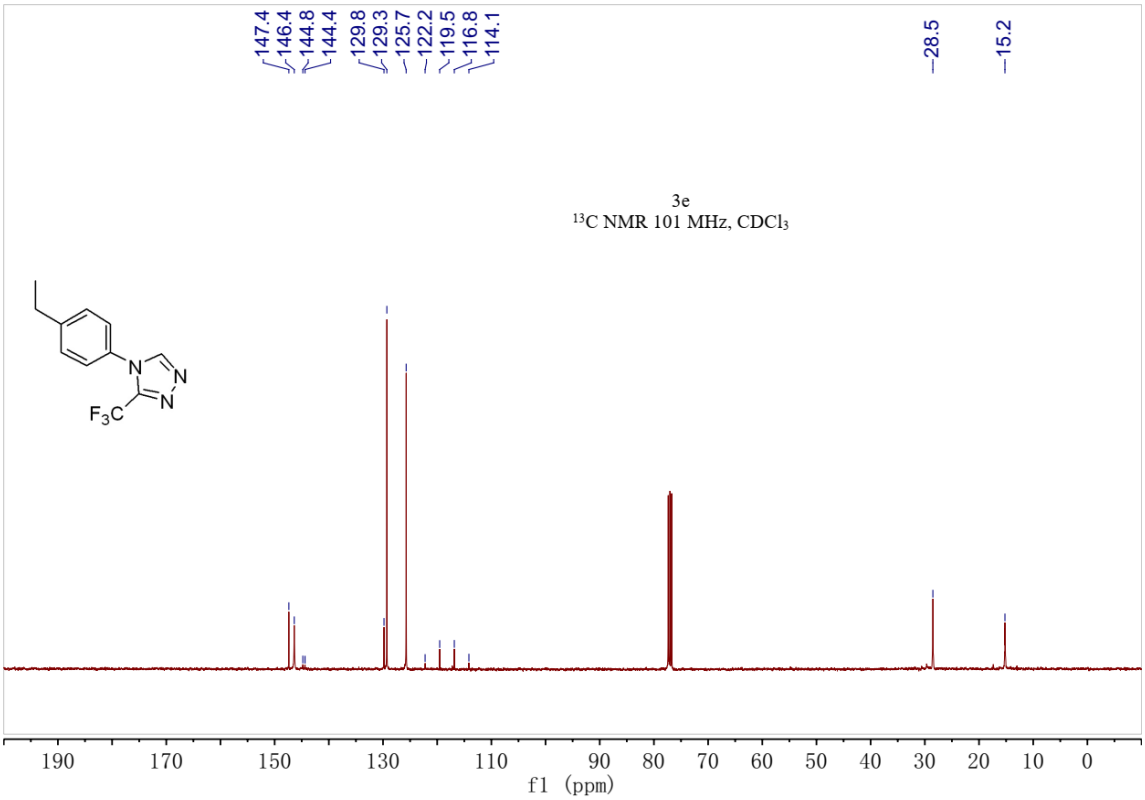

-60.5
3c
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

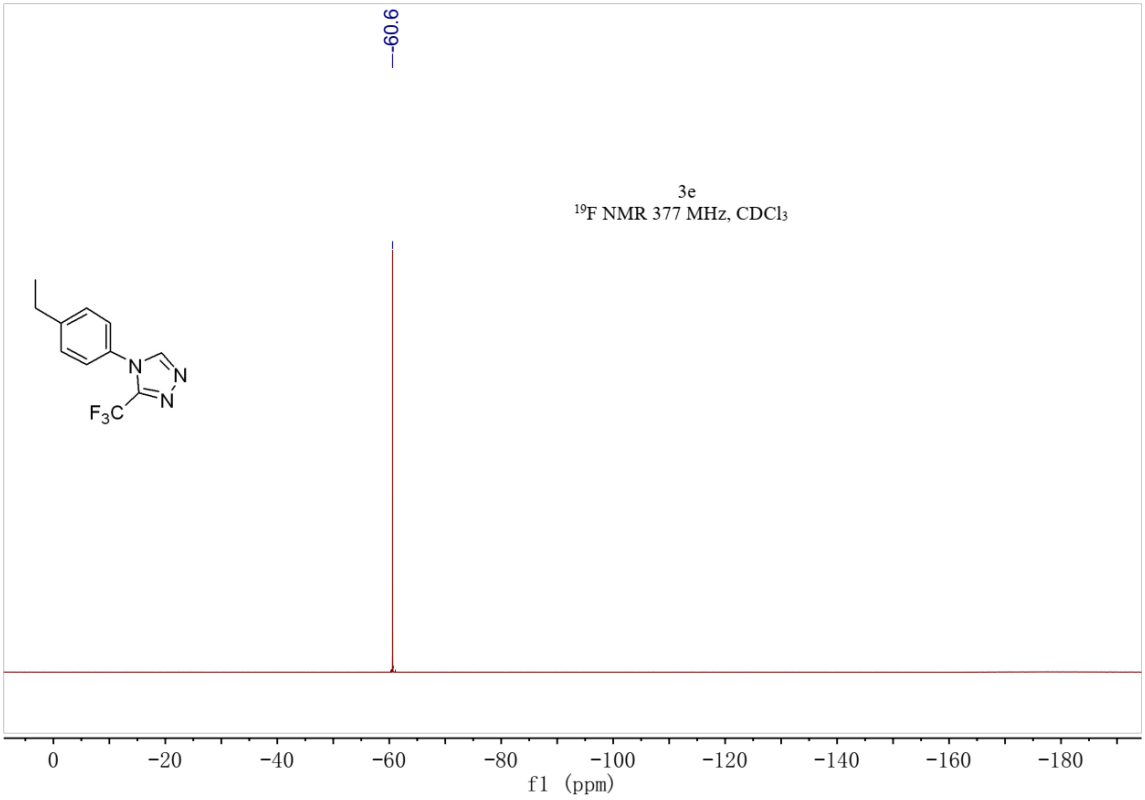

8.27
7.50
7.48
7.46
7.40
7.38
7.37
7.35
7.33
7.25
7.23
3d
1H NMR 400 MHz, CDCl3
F3C
1.00
1.00
2.02
0.96
3.03
f1 (ppm)

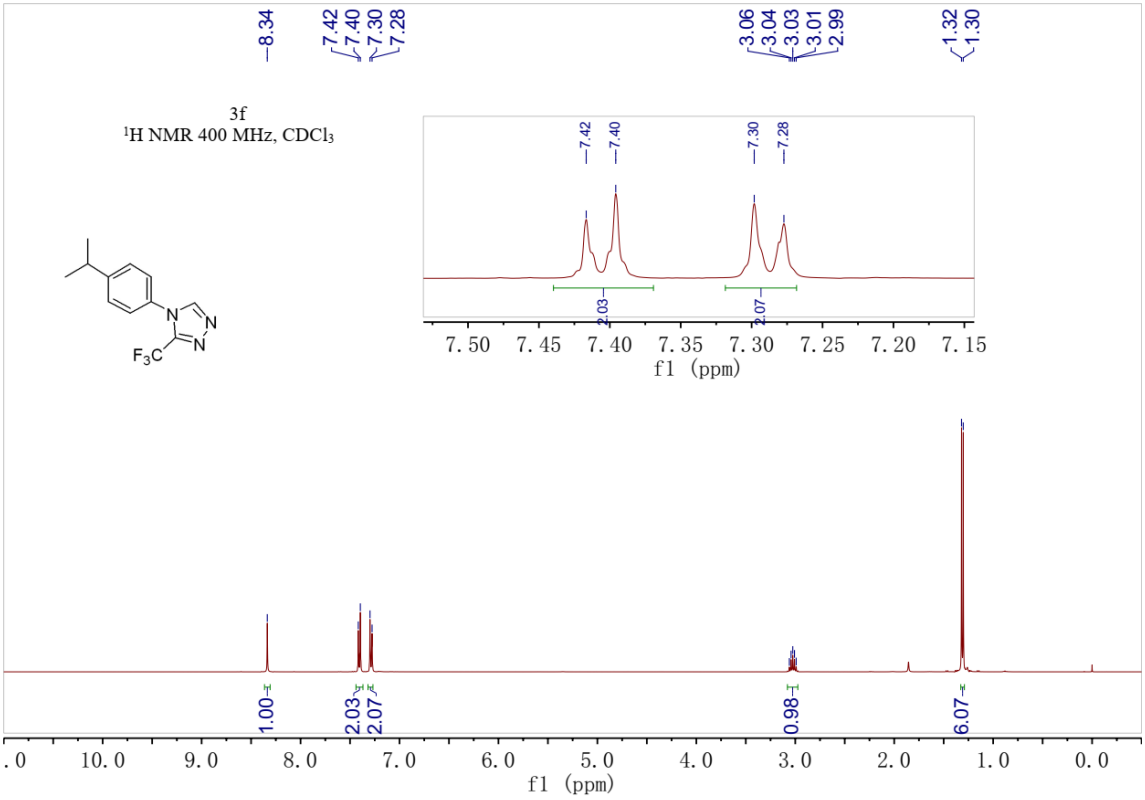

146.2
144.9
144.6
135.2
131.5
131.2
131.2
127.4
127.2
122.1
119.4
116.7
114.0
17.2
17.0
16.9
16.7
3d
13C NMR 101 MHz, CDCl3
F3C
f1 (ppm)

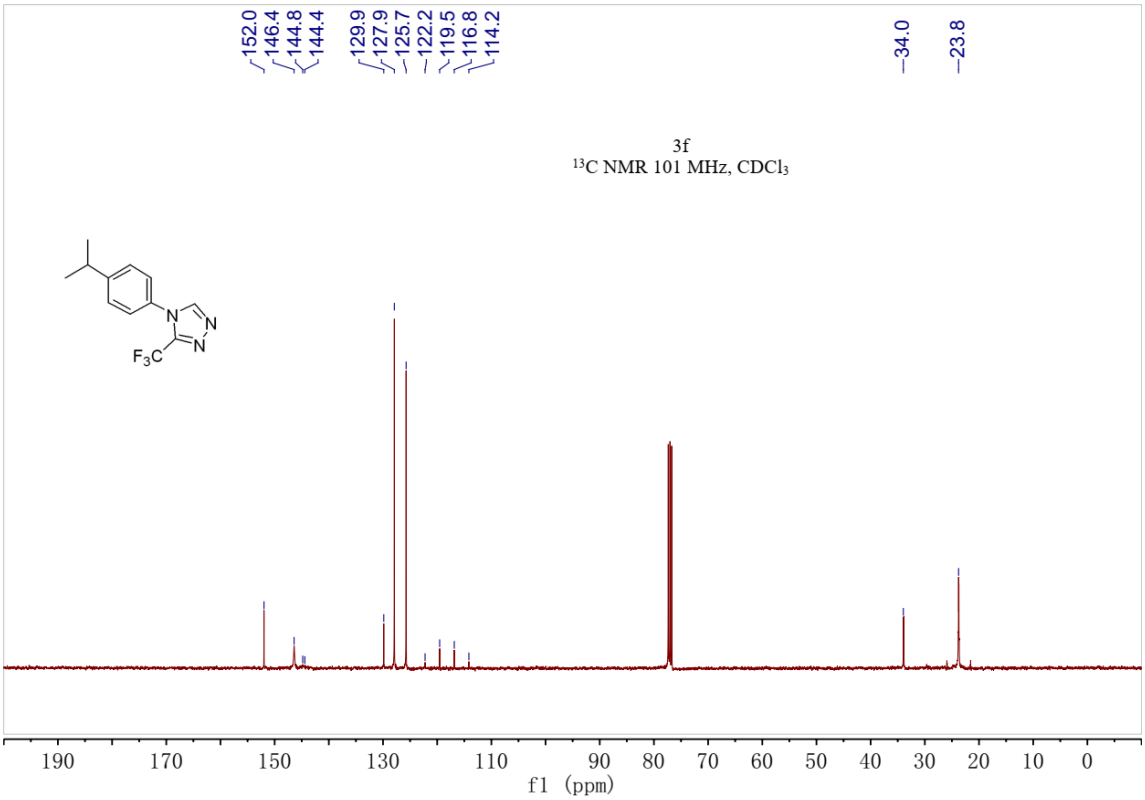

61.8
3d
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

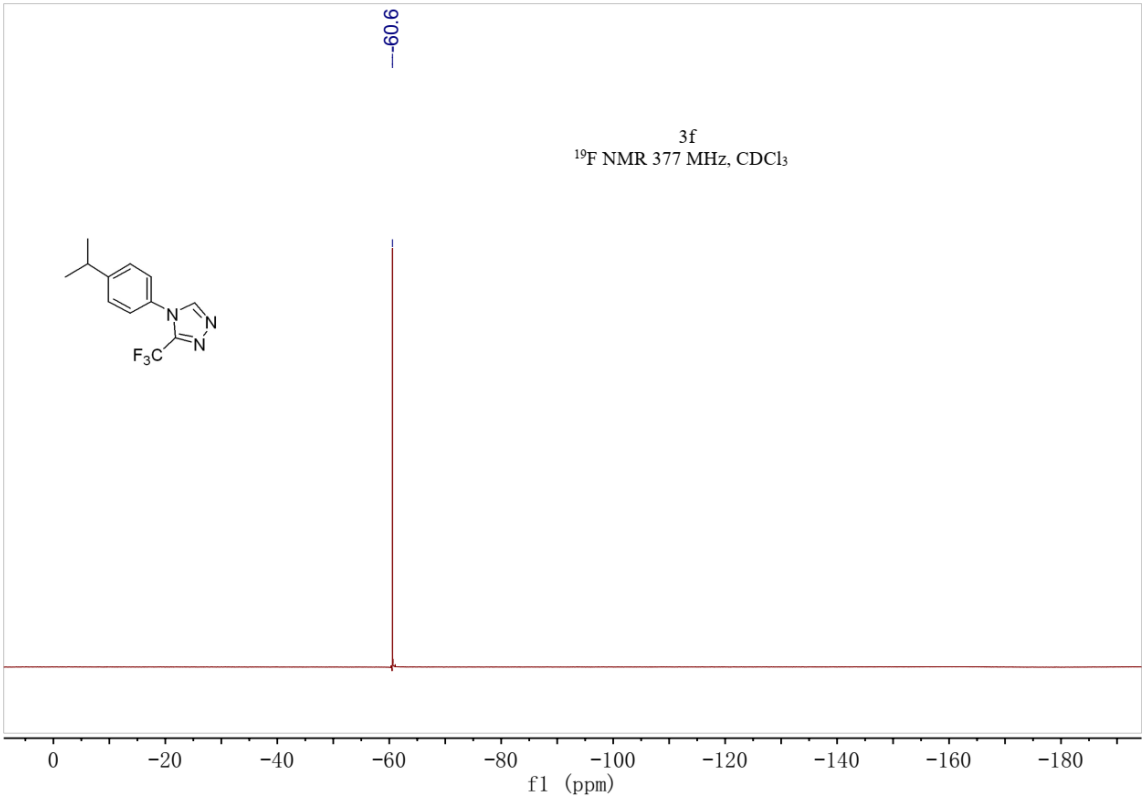

8.34
7.39
7.37
7.29
7.27
2.79
2.77
2.76
2.74
1.32
1.30
1.28
3e
1H NMR 400 MHz, CDCl3
7.39
7.37
7.29
7.27
2.03
2.07
7.50
7.40
7.30
7.20
f1 (ppm)
F3C
1.00
2.03
2.07
2.05
3.07
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

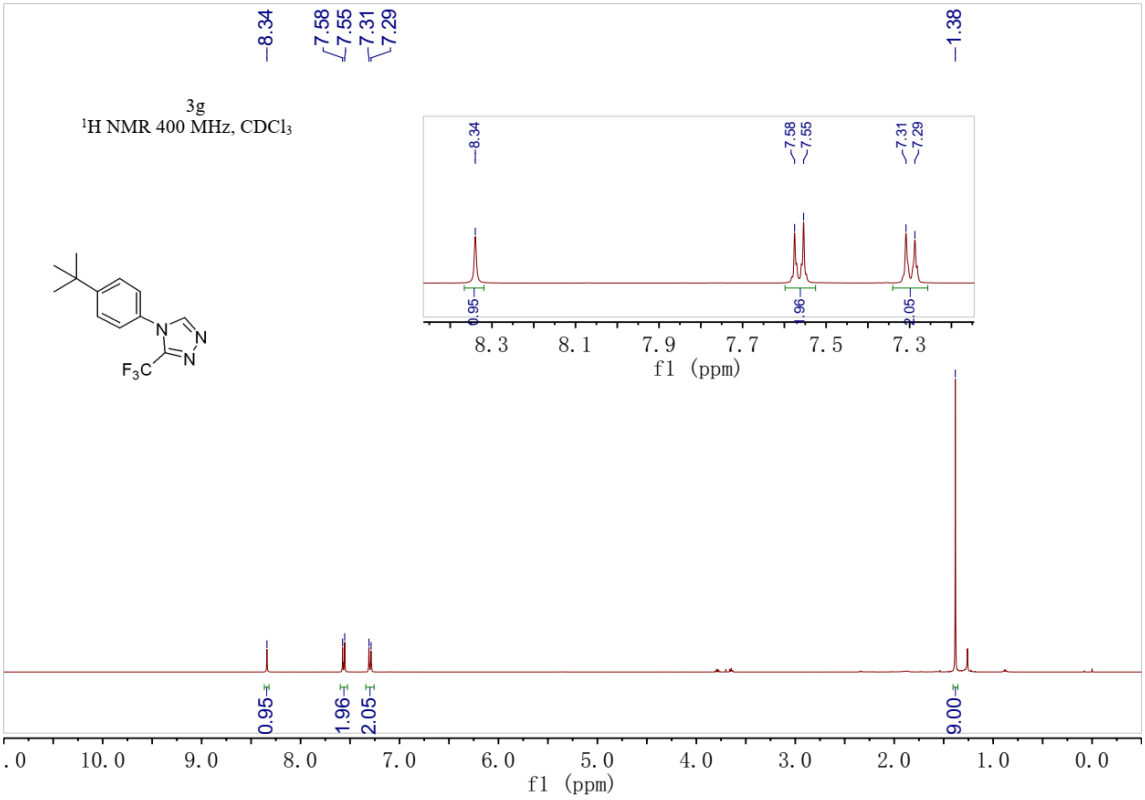

147.4
146.4
144.8
144.4
129.8
129.3
125.7
122.2
119.5
116.8
114.1
28.5
15.2
3e
13C NMR 101 MHz, CDCl3
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

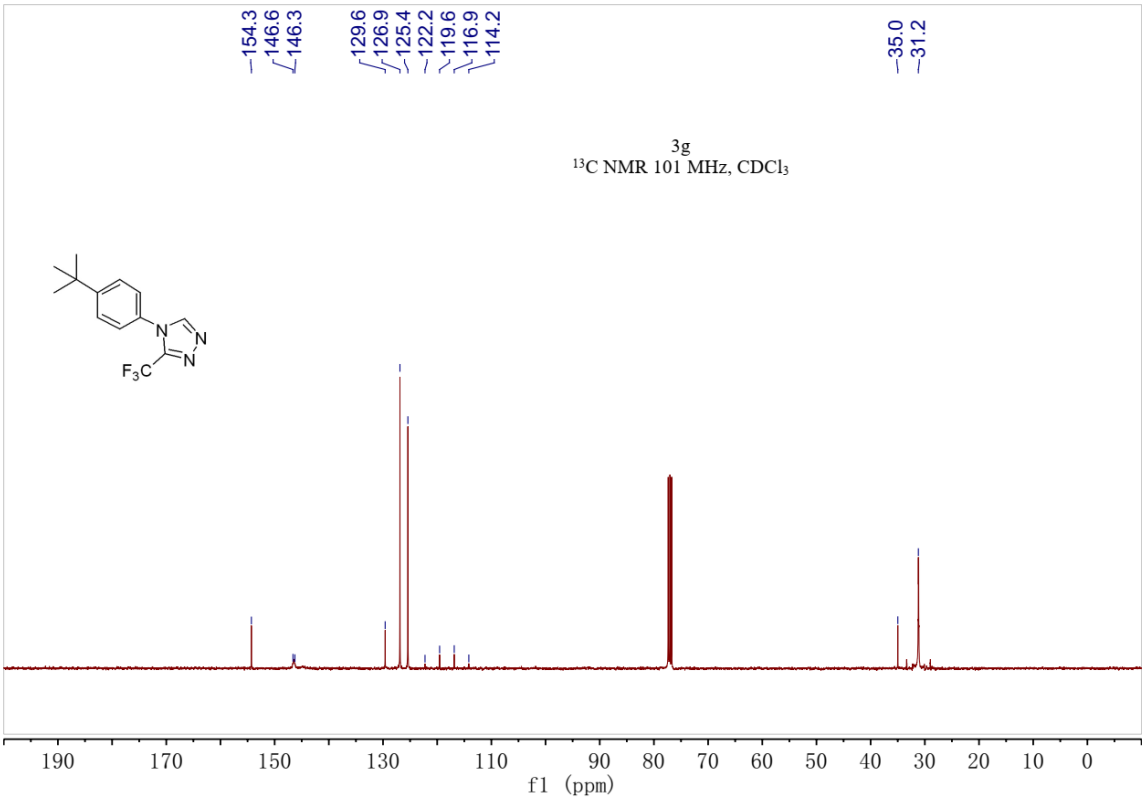

-60.6
3e
19F NMR 377 MHz, CDCl3
F3C
N
N
N
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

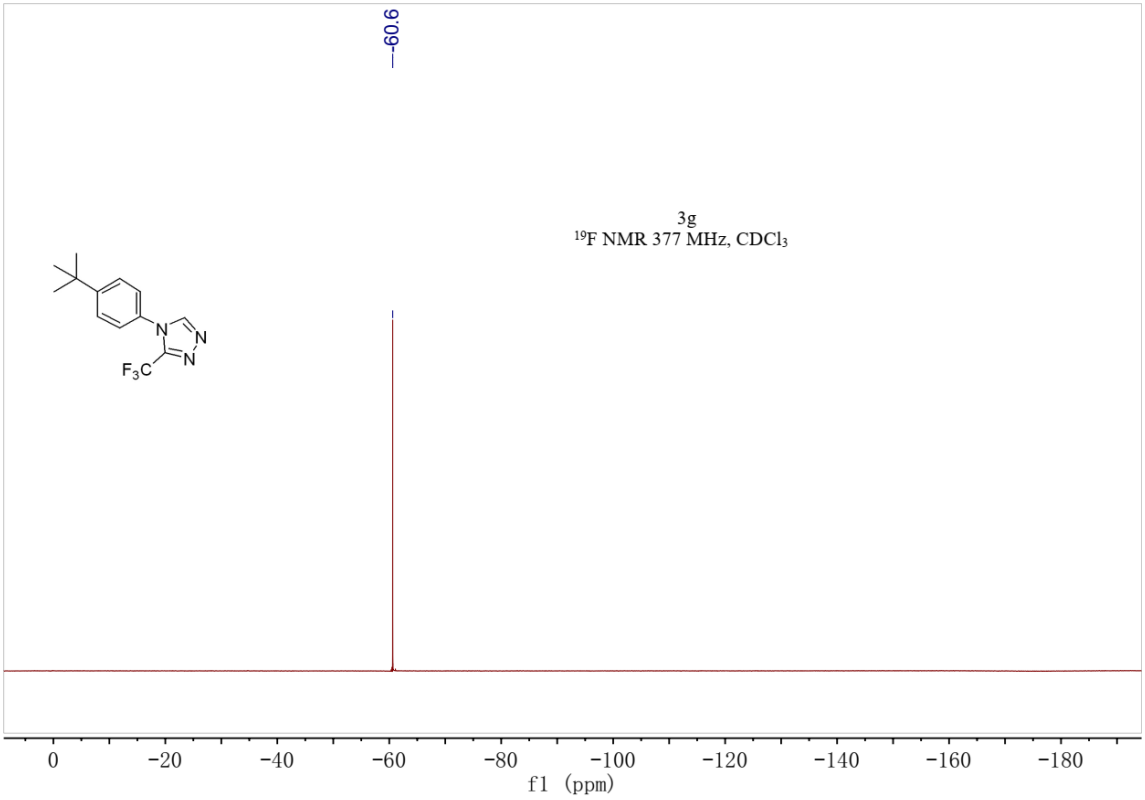

8.34
7.42
7.40
7.30
7.28
3.06
3.04
3.03
3.01
2.99
1.32
1.30
3f
1H NMR 400 MHz, CDCl3
F3C
7.42
7.40
7.30
7.28
2.03
2.07
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
f1 (ppm)
1.00
2.03
2.07
0.98
6.07
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

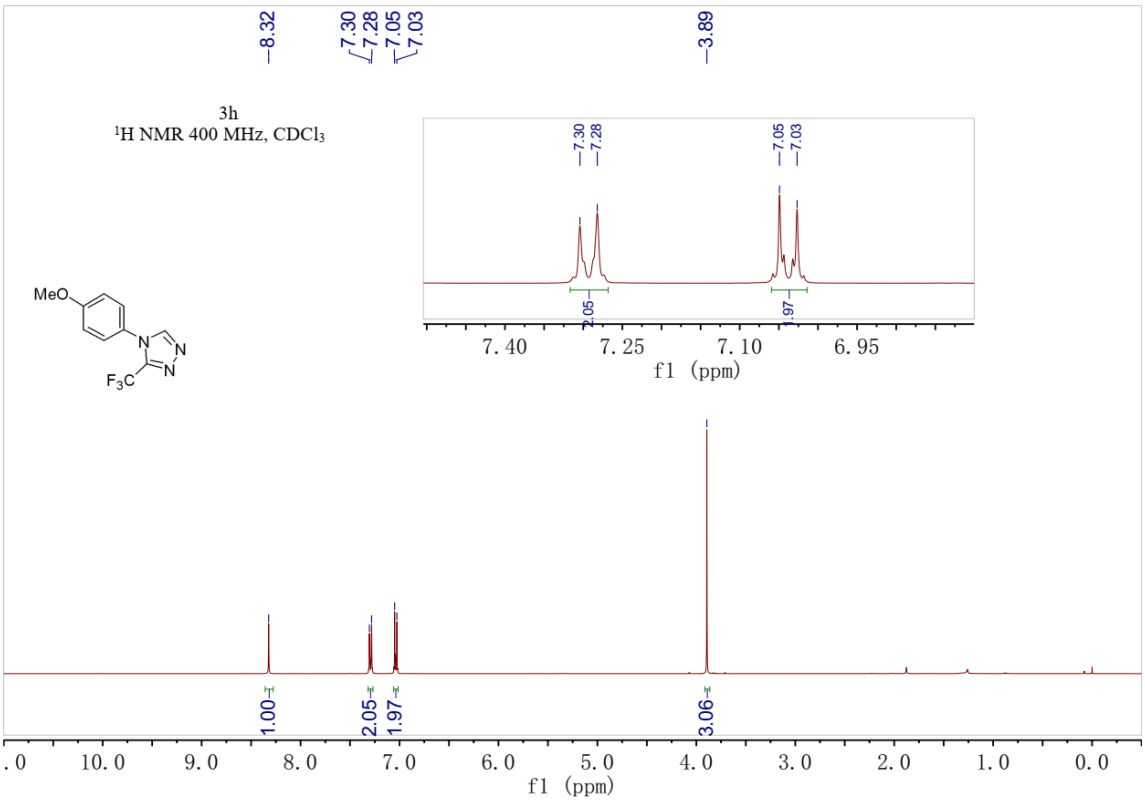

152.0
146.4
144.8
144.4
129.9
127.9
125.7
122.2
119.5
116.8
114.2
34.0
23.8
3f
13C NMR 101 MHz, CDCl3
F3C
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

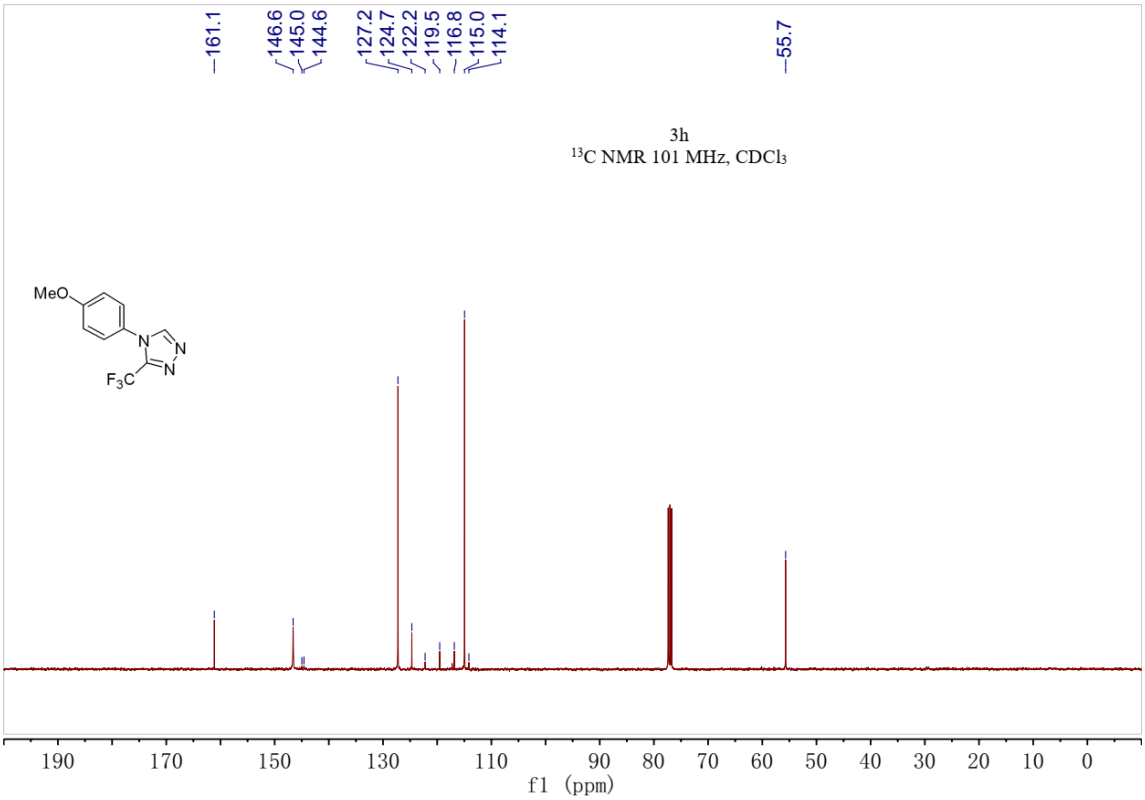

-60.6
3f
19F NMR 377 MHz, CDCl3
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

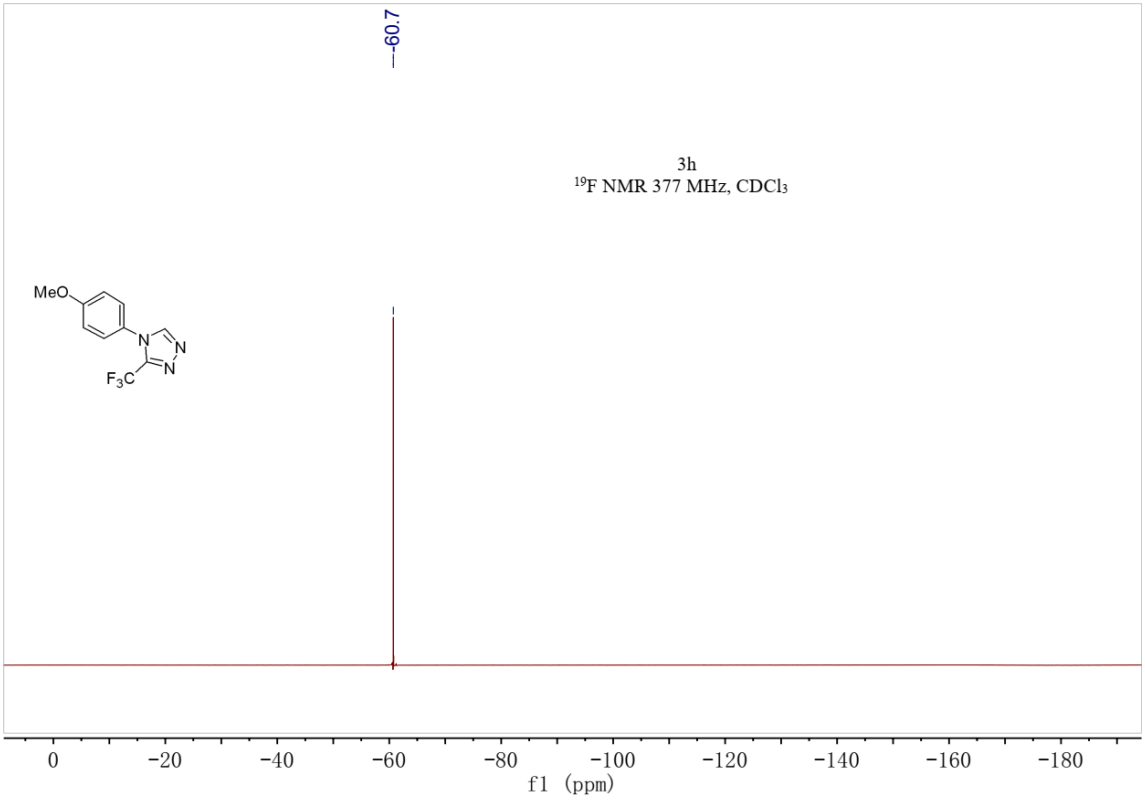

8.34
7.58
7.55
7.31
7.29
1.38
3g
1H NMR 400 MHz, CDCl3
F3C
f1 (ppm)
0.95
1.96
2.05
9.00

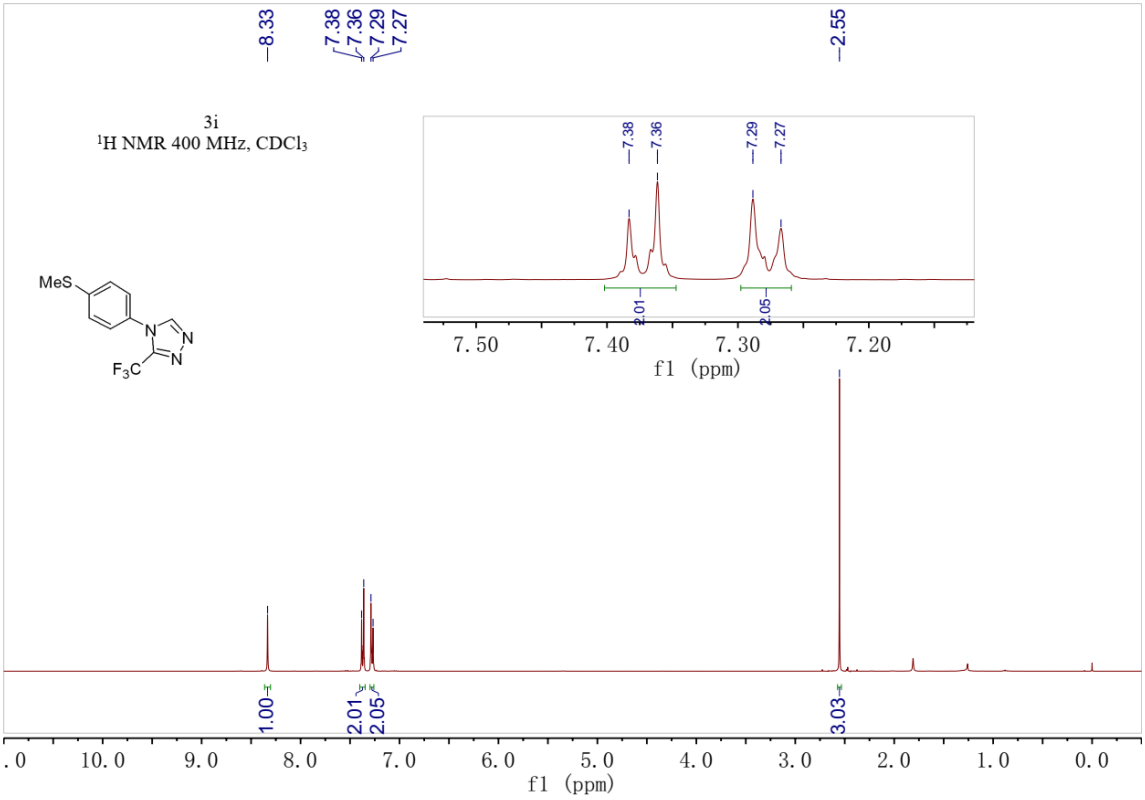

154.3
146.6
146.3
129.6
126.9
125.4
122.2
119.6
116.9
114.2
35.0
31.2
3g
13C NMR 101 MHz, CDCl3
F3C
f1 (ppm)

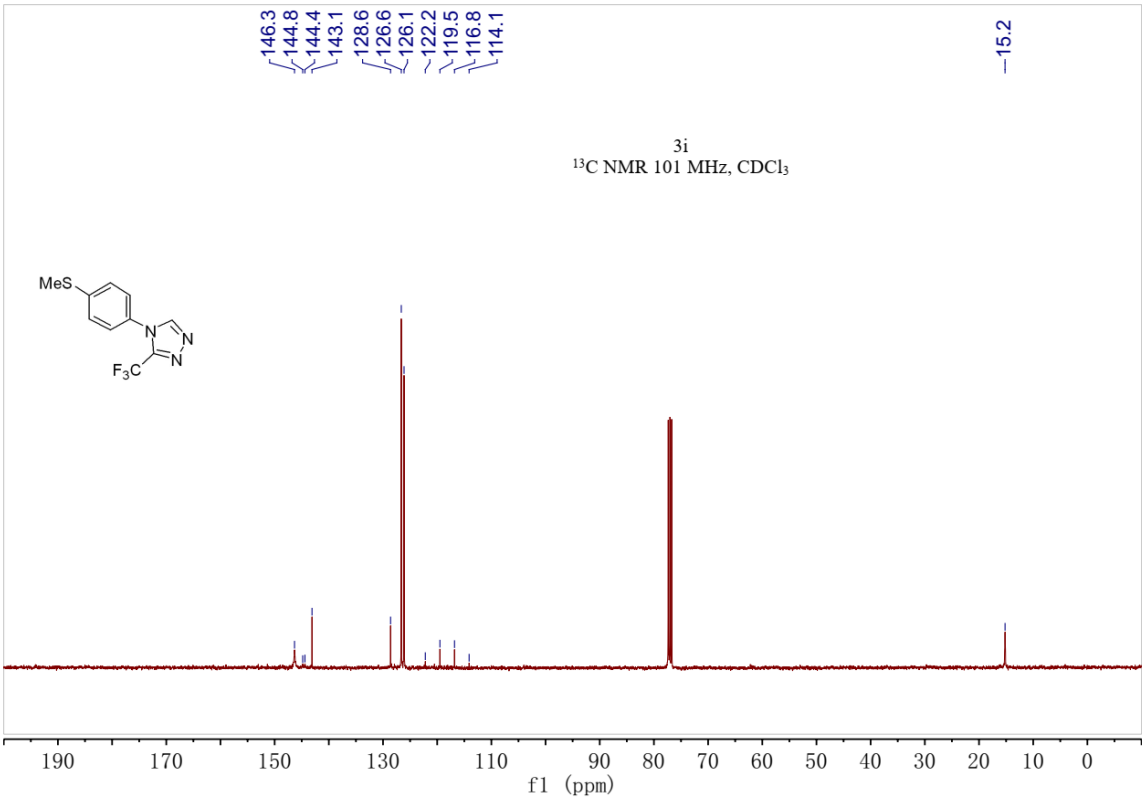

-60.6
3g
19F NMR 377 MHz, CDCl3
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

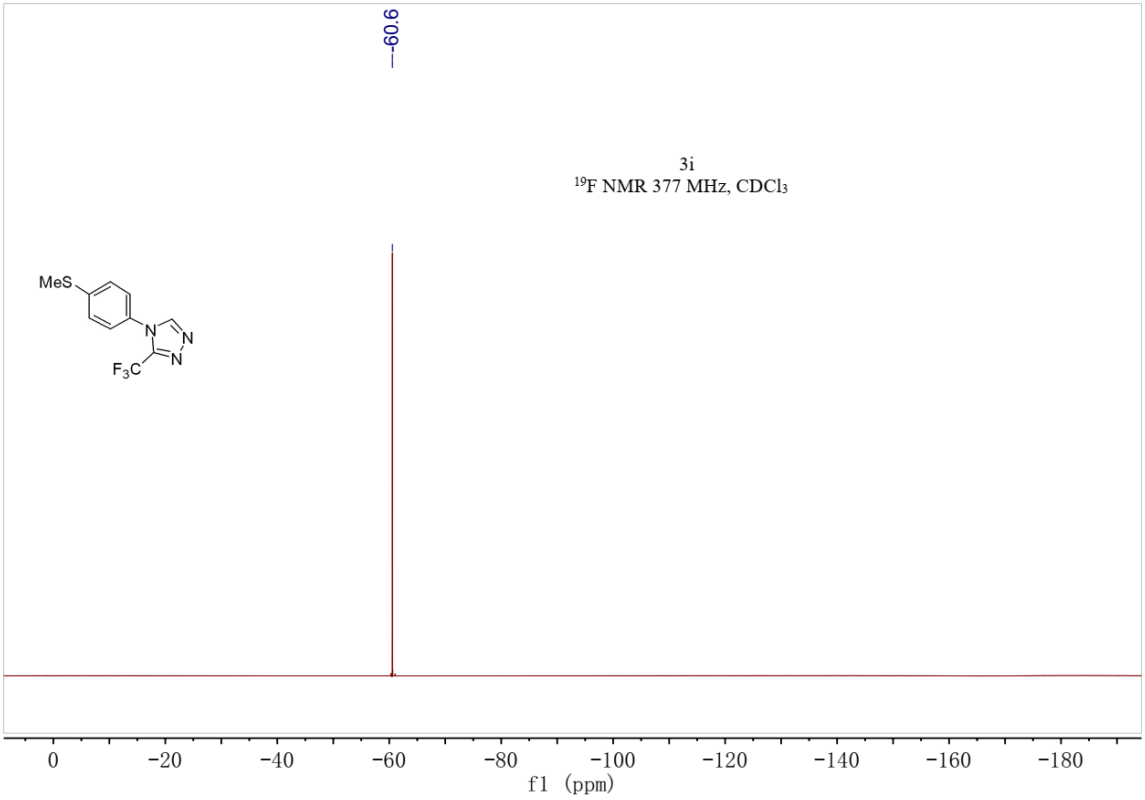

3h
1H NMR 400 MHz, CDCl3
MeO
F3C
8.32
7.30
7.28
7.05
7.03
3.89
1.00
2.05
1.97
3.06
f1 (ppm)

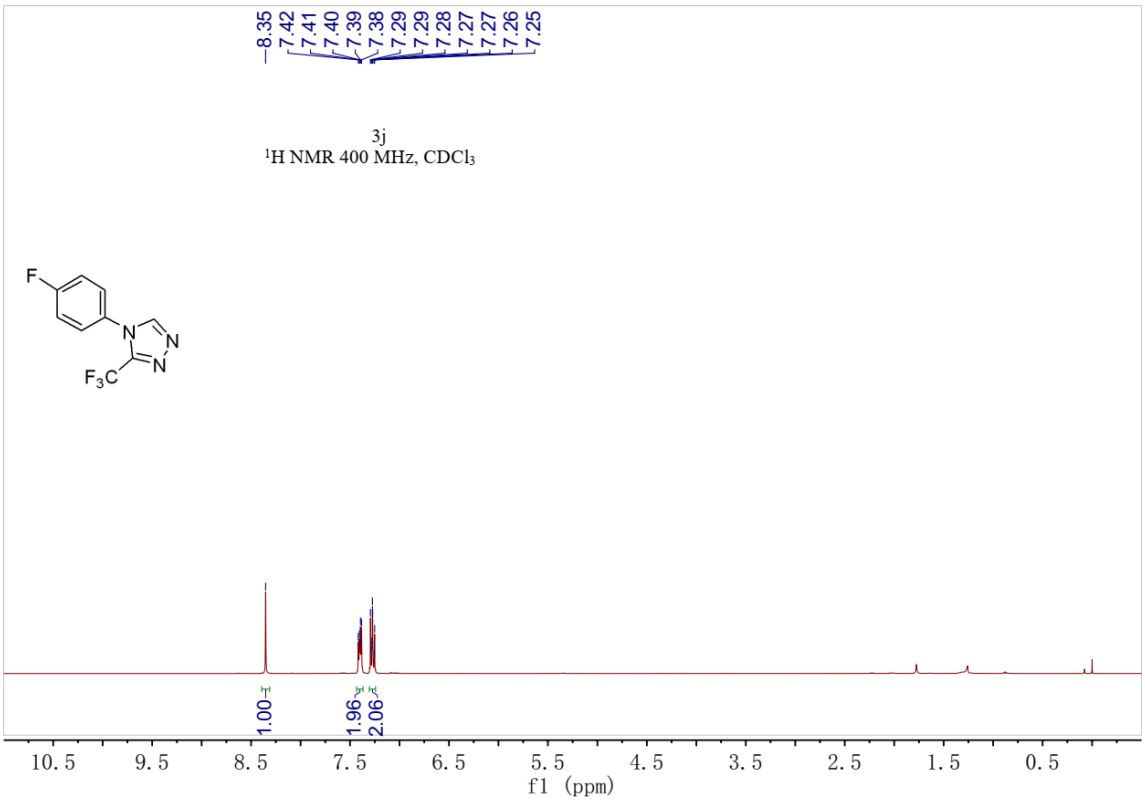

3h
13C NMR 101 MHz, CDCl3
MeO
F3C
161.1
146.6
145.0
144.6
127.2
124.7
122.2
119.5
116.8
115.0
114.1
55.7
f1 (ppm)

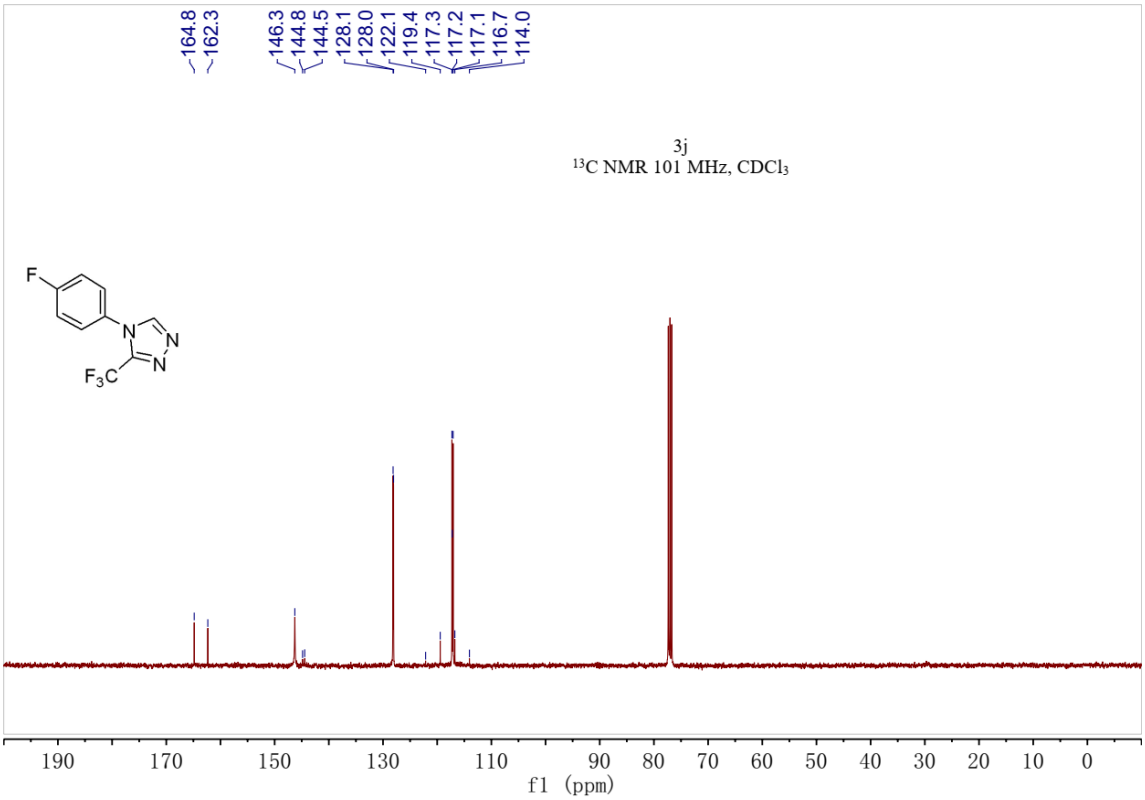

-60.7
3h
19F NMR 377 MHz, CDCl3
MeO
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

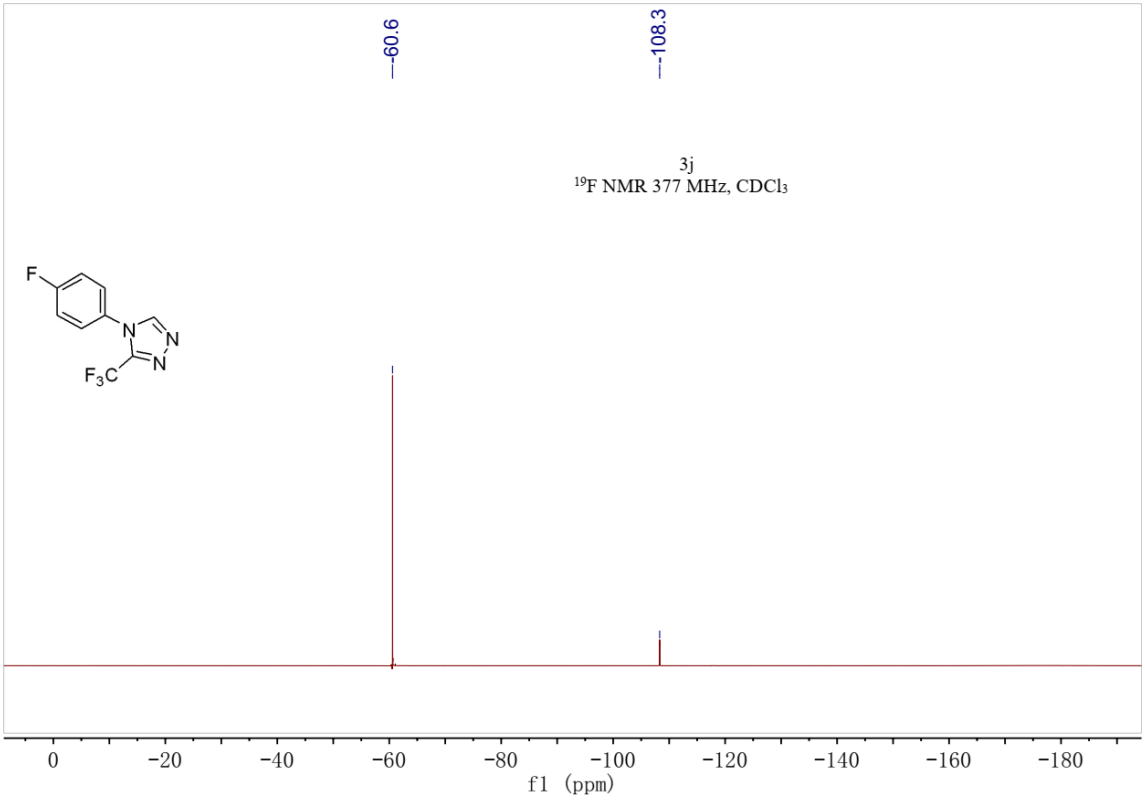

8.33
7.38
7.36
7.29
7.27
2.55
3i
1H NMR 400 MHz, CDCl3
MeS
F3C
N
N
N
7.38
7.36
7.29
7.27
2.01
2.05
7.50
7.40
7.30
7.20
f1 (ppm)
1.00
2.01
2.05
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

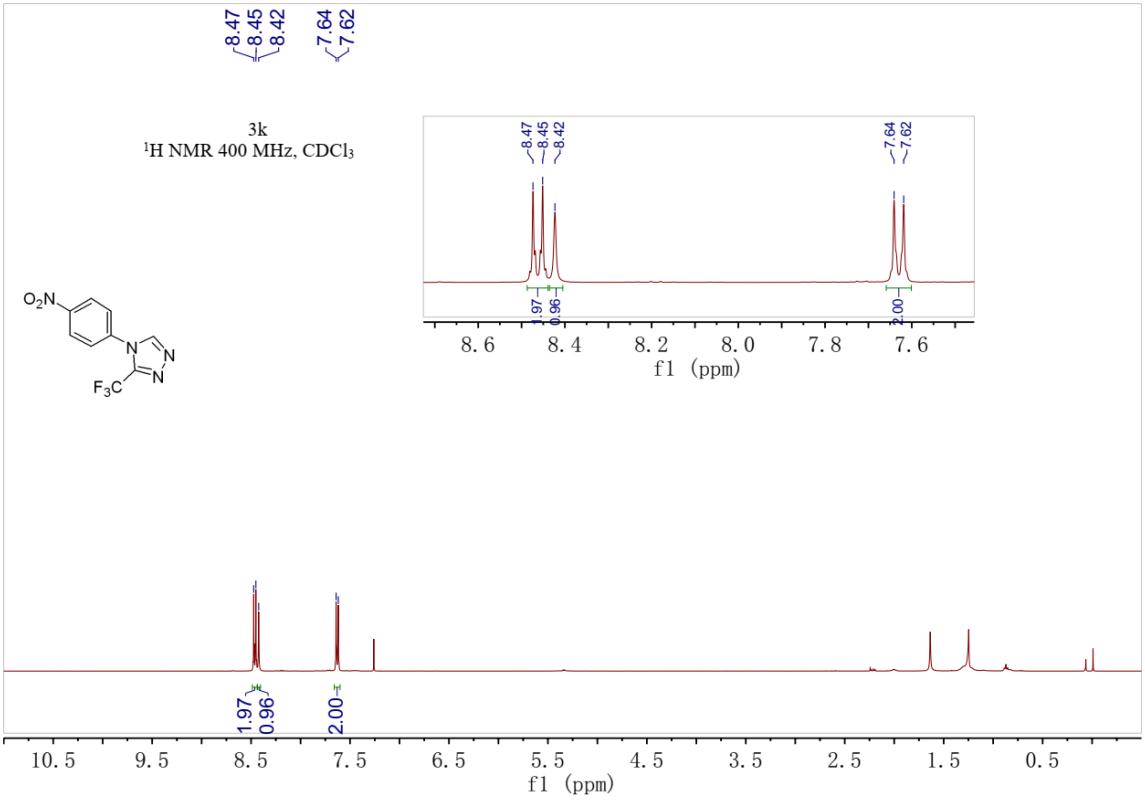

146.3
144.8
144.4
143.1
128.6
126.6
126.1
122.2
119.5
116.8
114.1
15.2
3i
13C NMR 101 MHz, CDCl3
MeS
F3C
N
N
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

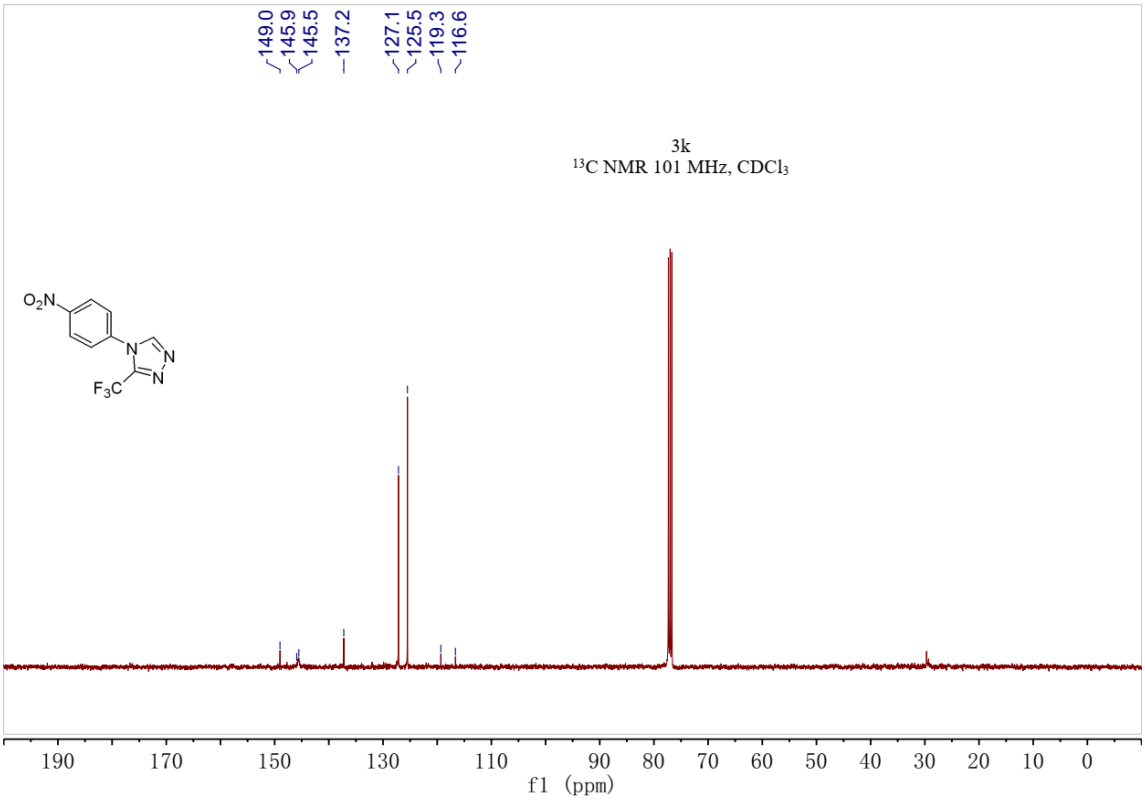

-60.6
3i
19F NMR 377 MHz, CDCl3
MeS
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

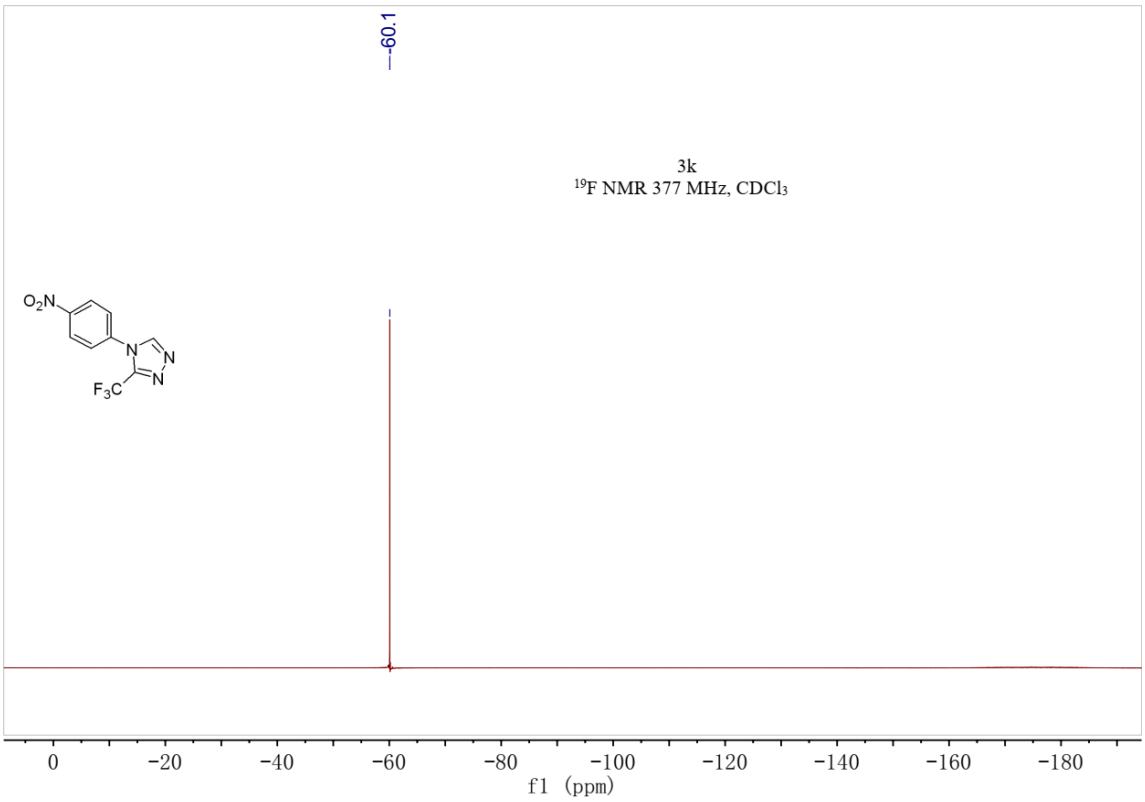

8.35
7.42
7.41
7.40
7.39
7.38
7.29
7.29
7.28
7.27
7.27
7.26
7.25
3j
1H NMR 400 MHz, CDCl3
F
N
N
N
F3C
1.00
1.96
2.06
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

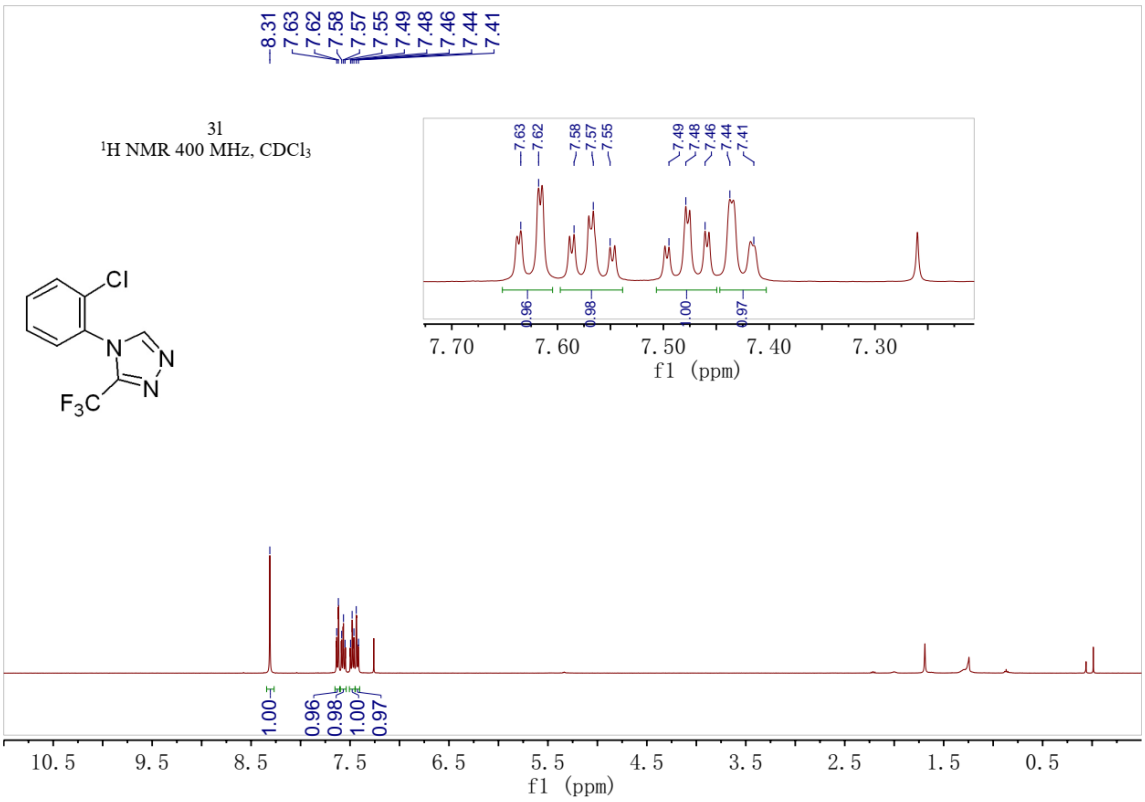

164.8
162.3
146.3
144.8
144.5
128.1
128.0
122.1
119.4
117.3
117.2
117.1
116.7
114.0
3j
13C NMR 101 MHz, CDCl3
F
N
N
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

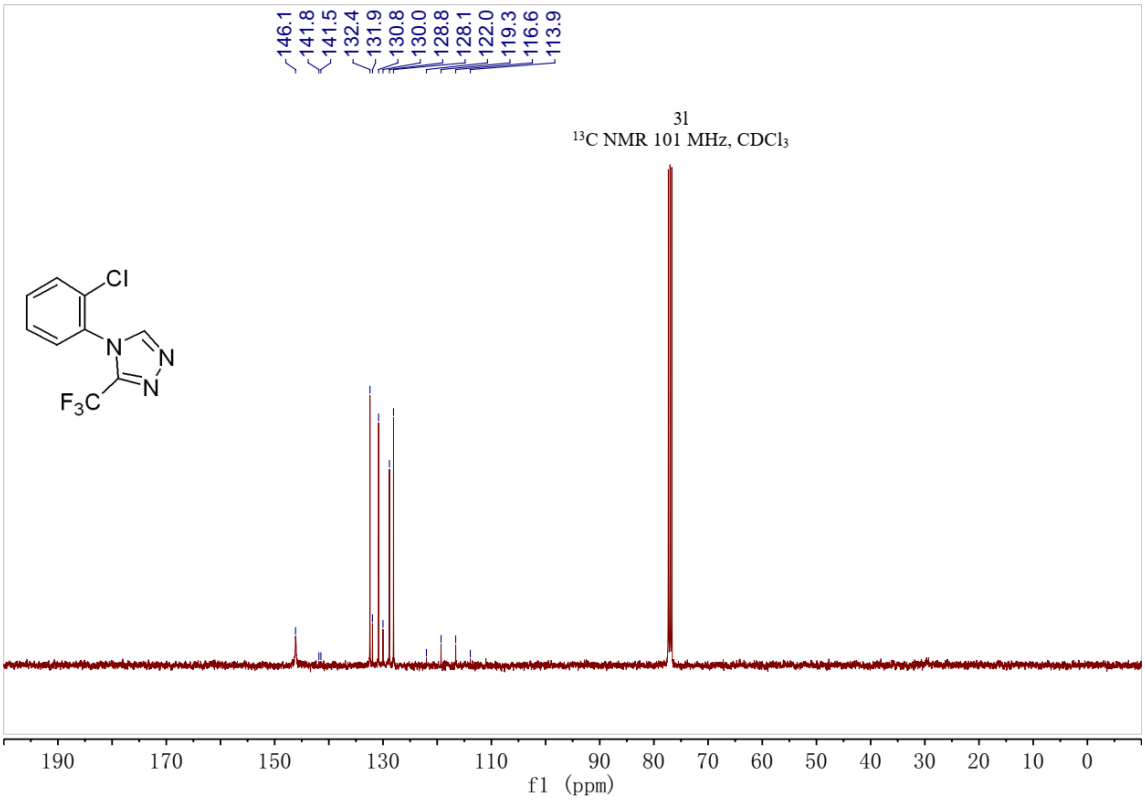

-60.6
-108.3
3j
19F NMR 377 MHz, CDCl3
F
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

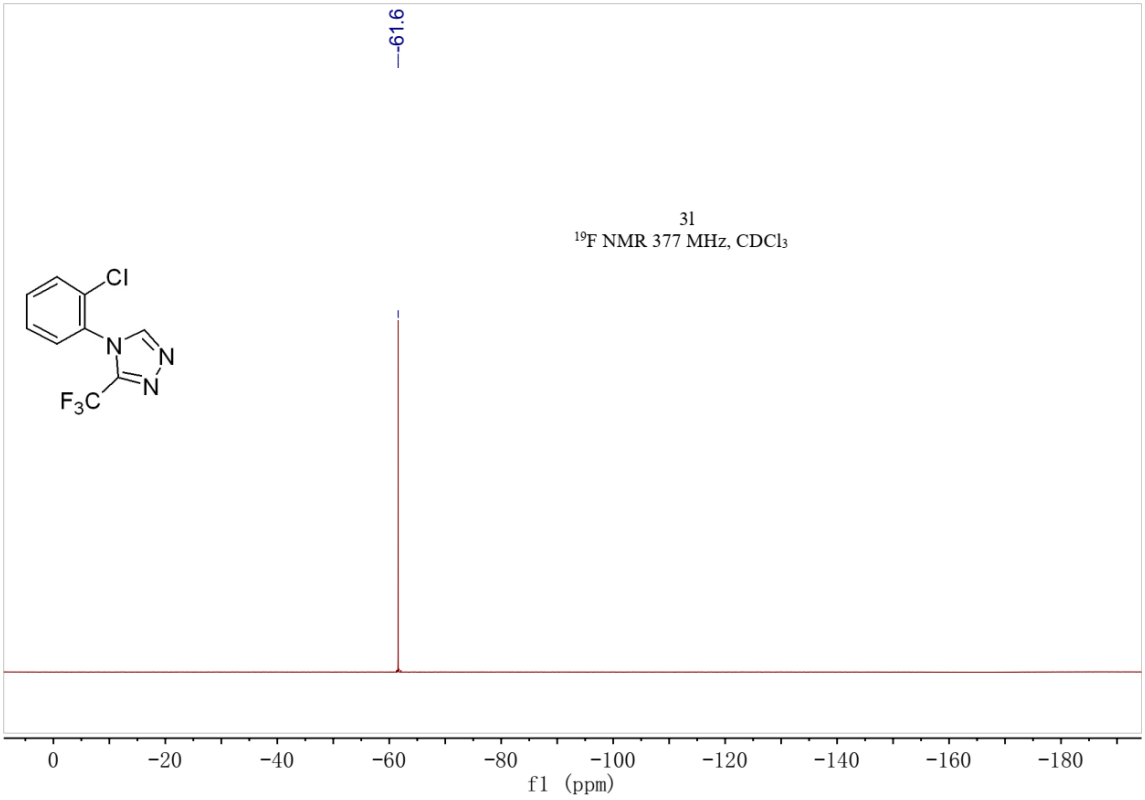

8.47
8.45
8.42
7.64
7.62
3k
1H NMR 400 MHz, CDCl3
O2N
N
N
N
F3C
1.97
0.96
2.00
8.6
8.4
8.2
8.0
7.8
7.6
f1 (ppm)
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

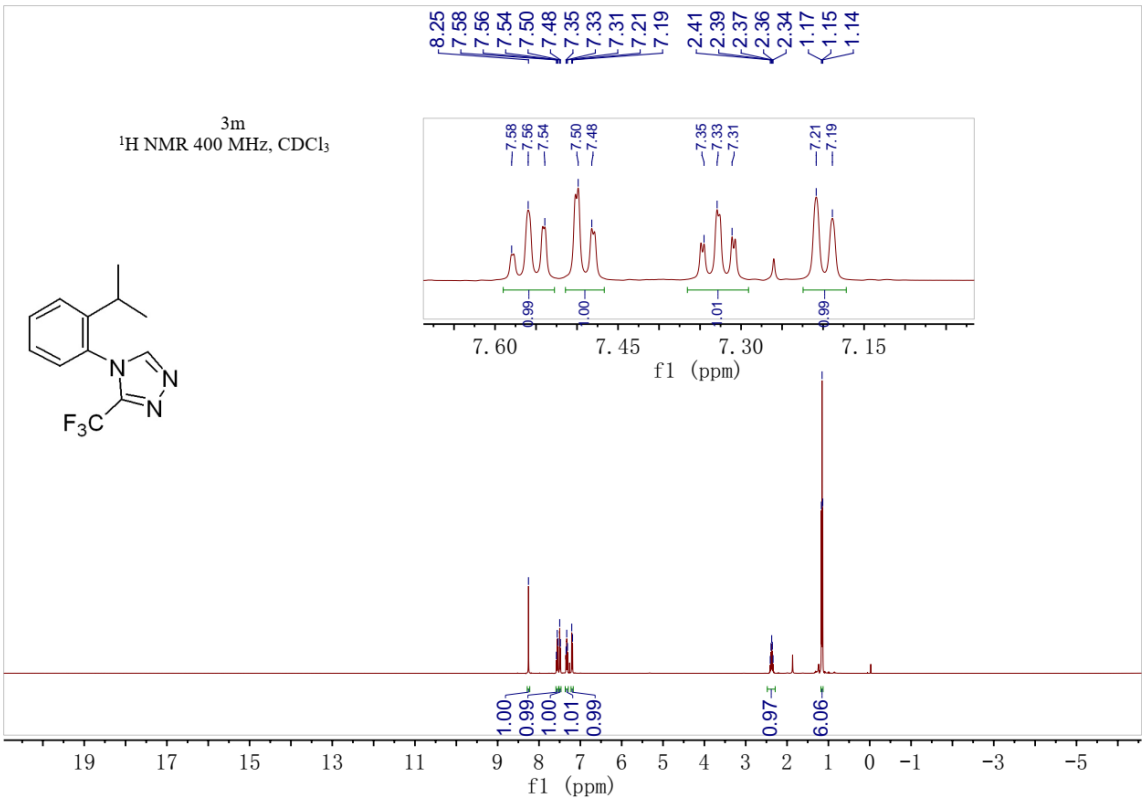

149.0
145.9
145.5
137.2
127.1
125.5
119.3
116.6
3k
13C NMR 101 MHz, CDCl3
O2N
N
N
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

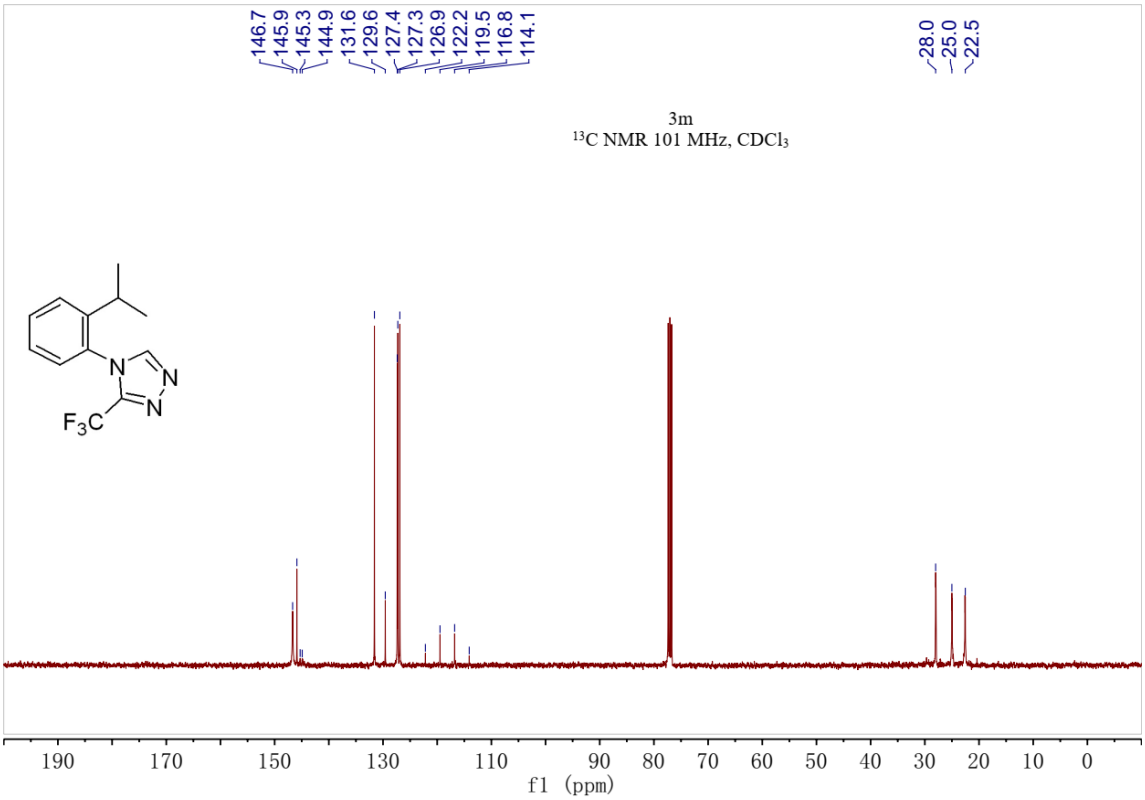

-60.1
3k
19F NMR 377 MHz, CDCl3
O2N
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

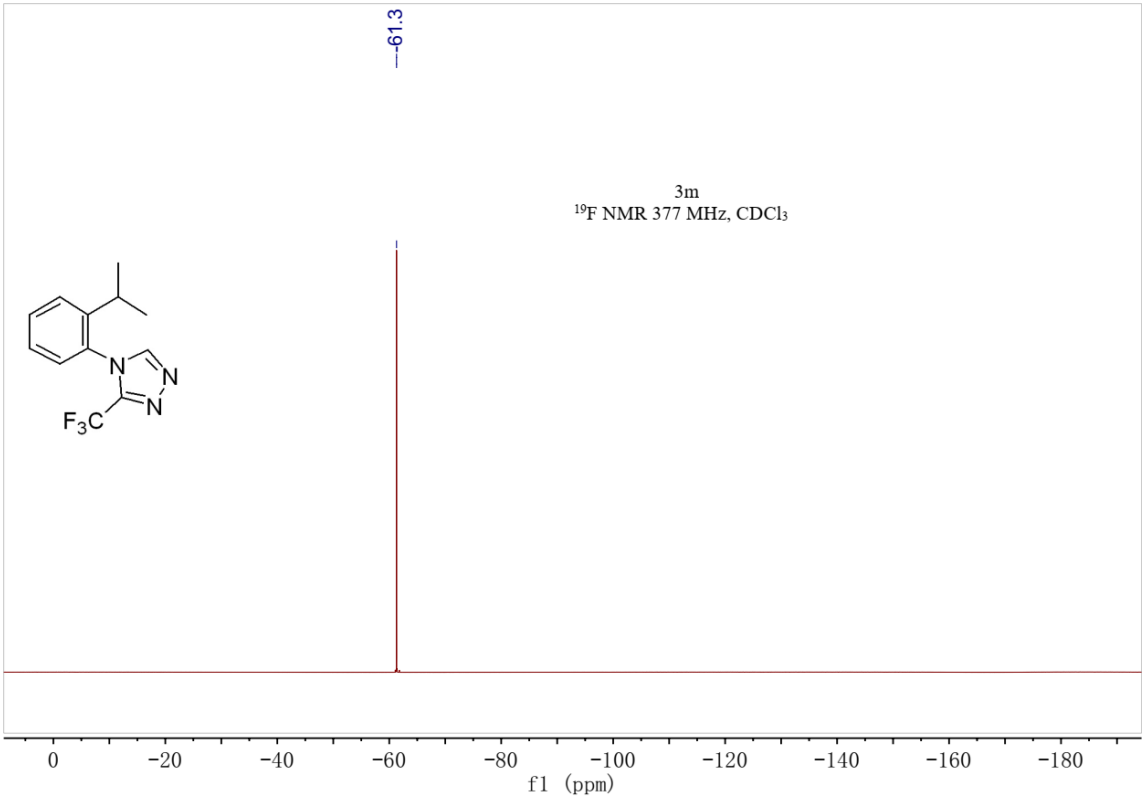

8.31
7.63
7.62
7.58
7.57
7.55
7.49
7.48
7.46
7.44
7.41
3l
1H NMR 400 MHz, CDCl3
Cl
N
N
N
F3C
1.00
0.96
0.98
1.00
0.97
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
7.70
7.60
7.50
7.40
7.30

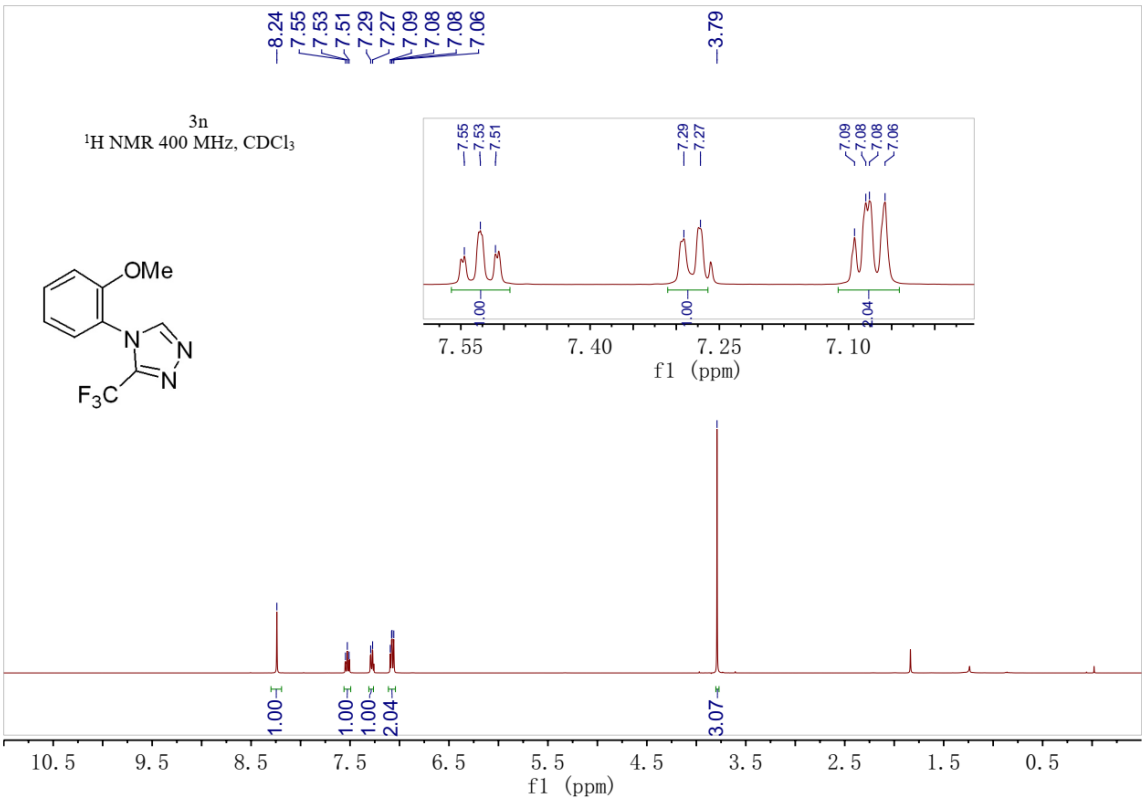

146.1
141.8
141.5
132.4
131.9
130.8
130.0
128.8
128.1
122.0
119.3
116.6
113.9
3l
13C NMR 101 MHz, CDCl3
Cl
N
N
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

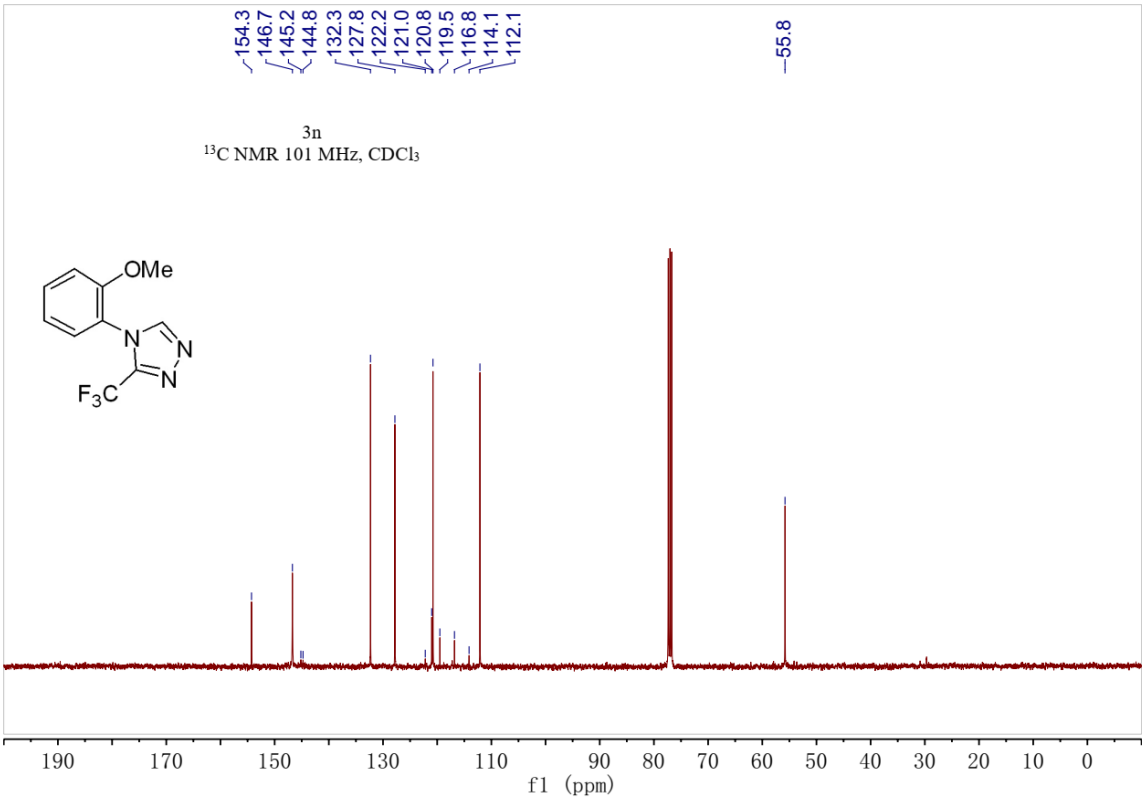

61.6
3l
19F NMR 377 MHz, CDCl3
Cl
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

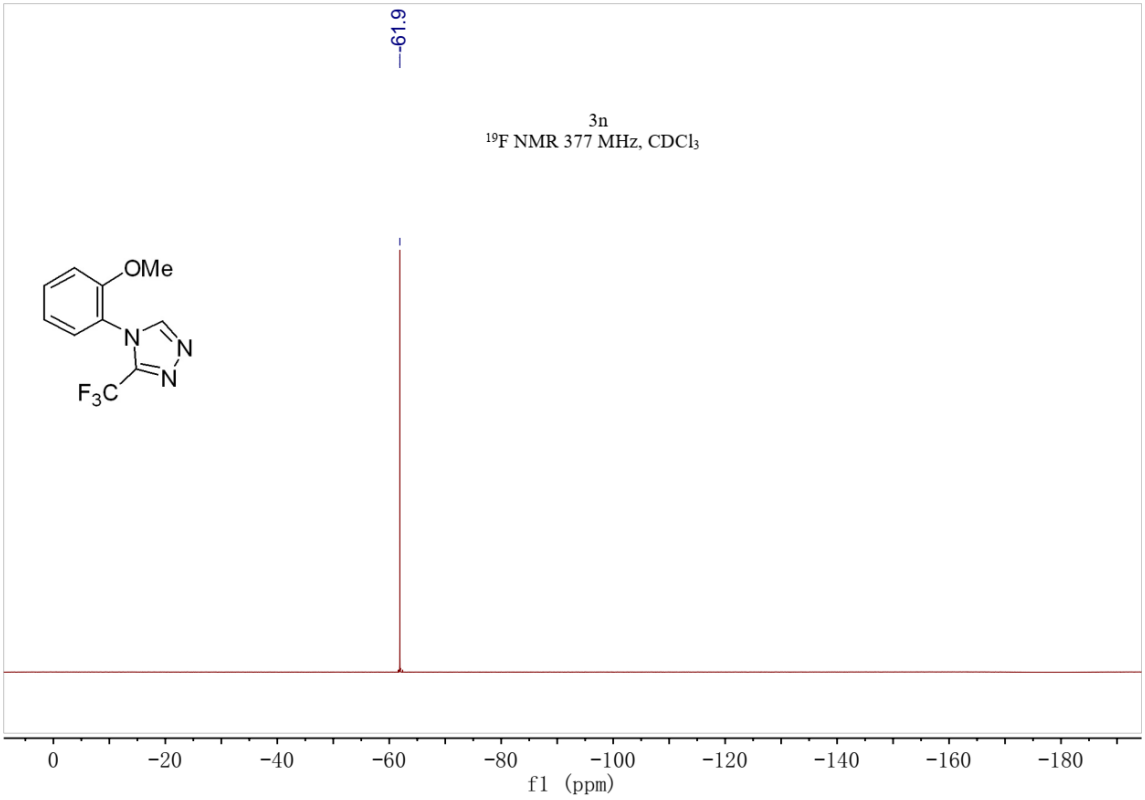

3m
1H NMR 400 MHz, CDCl3
f1 (ppm)

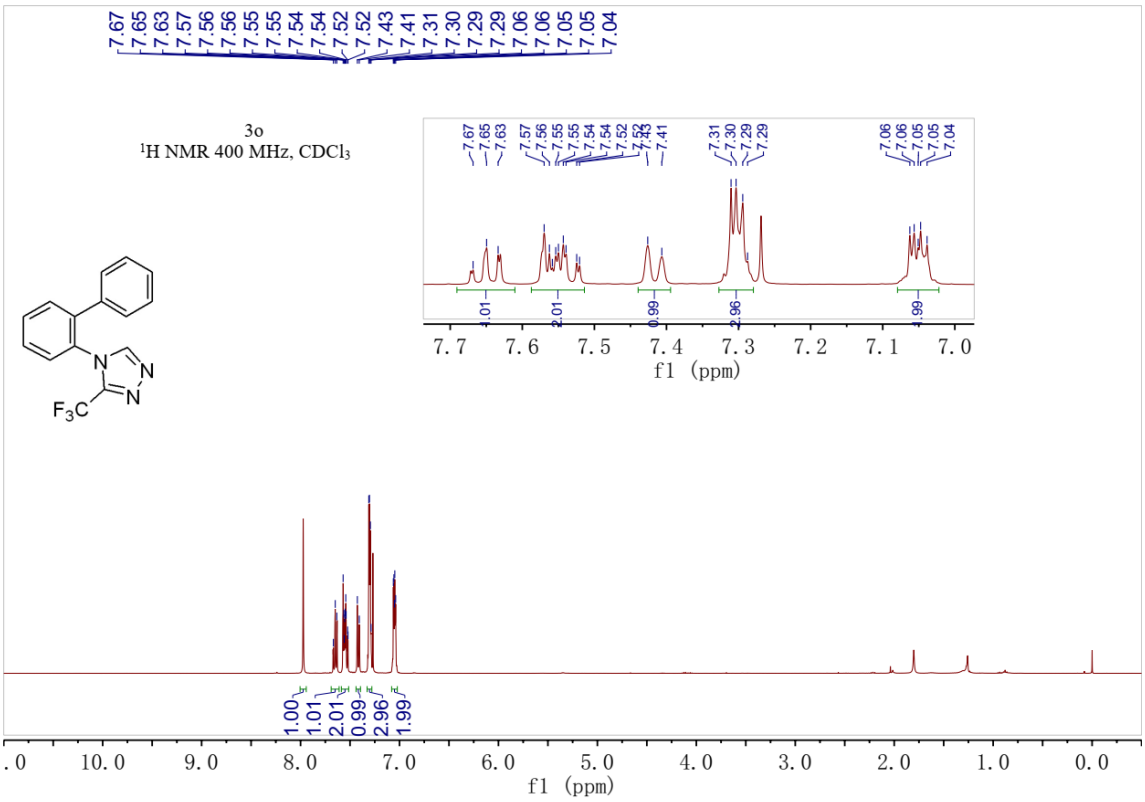

3m
13C NMR 101 MHz, CDCl3
f1 (ppm)

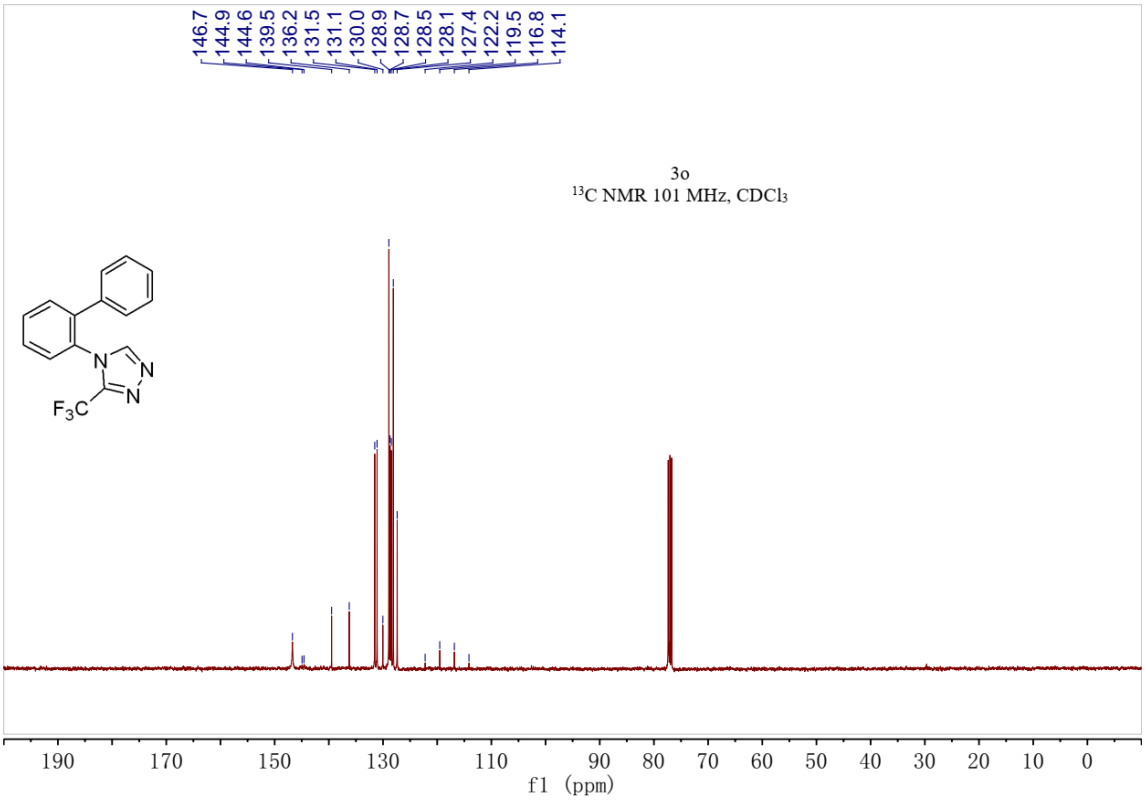

61.3
3m
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

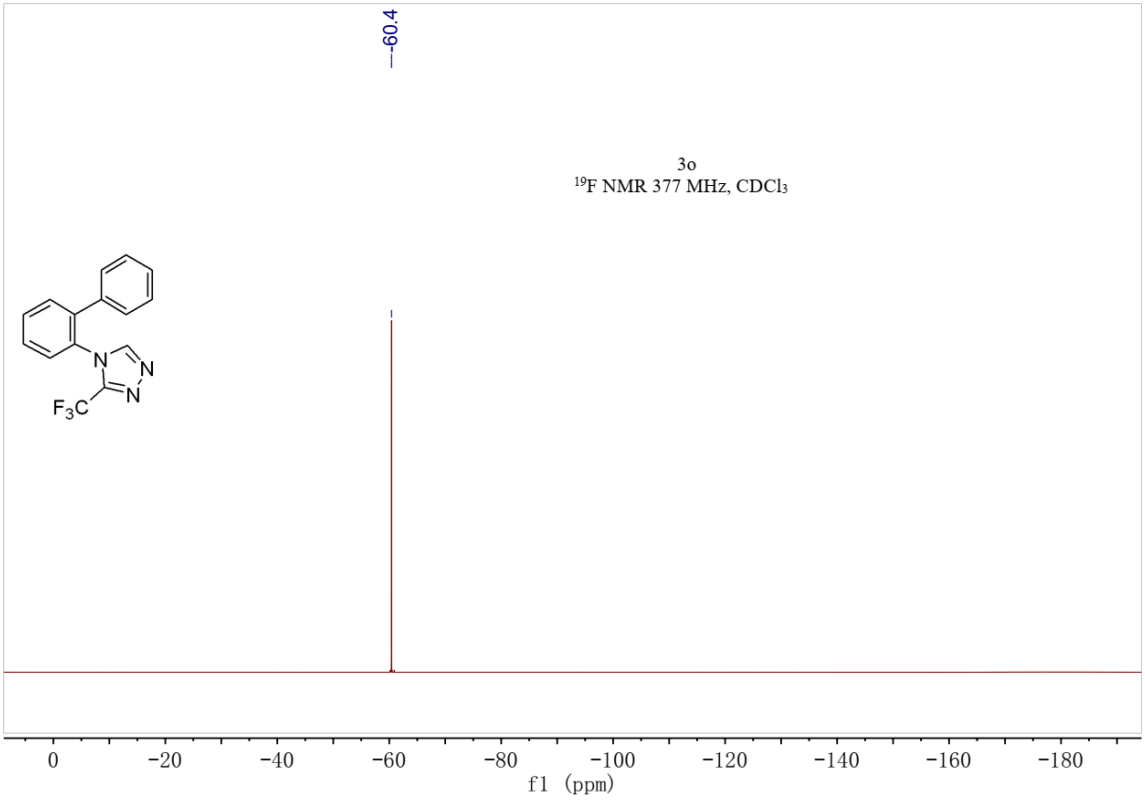

8.24
7.55
7.53
7.51
7.29
7.27
7.09
7.08
7.08
7.06
3.79
3n
1H NMR 400 MHz, CDCl3
OMe
N
N
N
F3C
1.00
1.00
2.04
7.55 7.40 7.25 7.10
f1 (ppm)
1.00
1.00
1.00
2.04
3.07
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

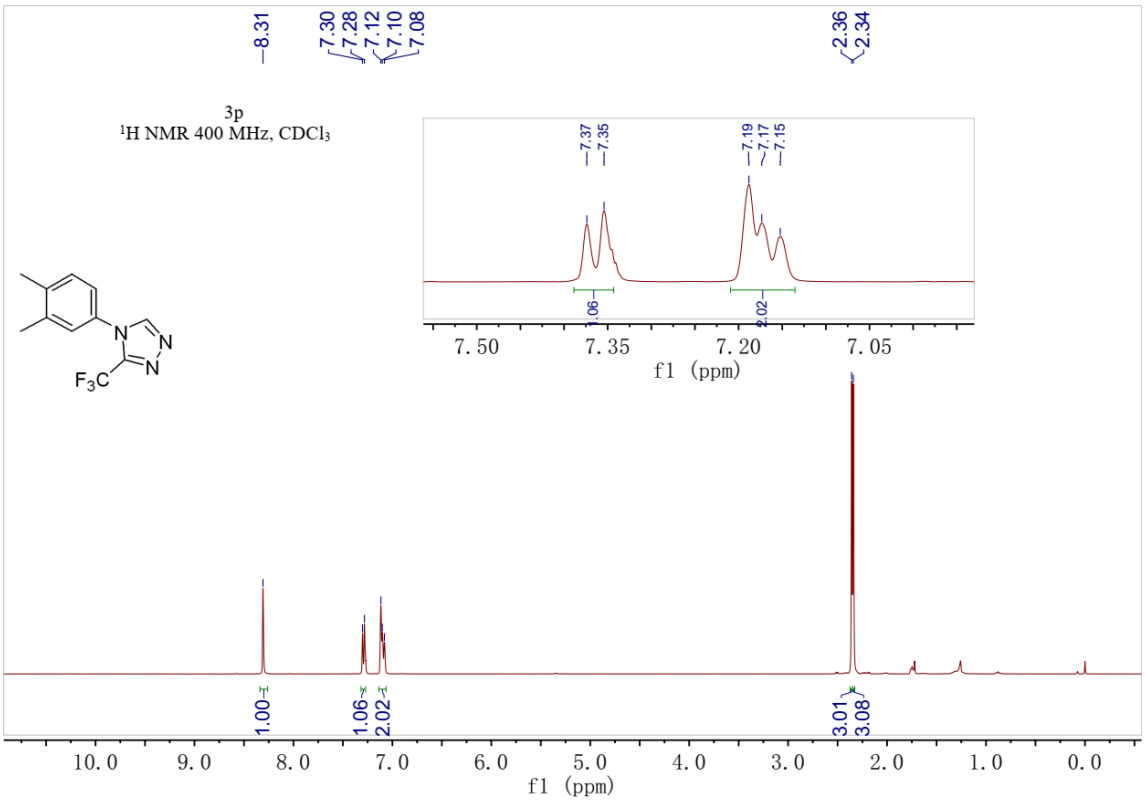

154.3
146.7
145.2
144.8
132.3
127.8
122.2
121.0
120.8
119.5
116.8
114.1
112.1
55.8
3n
13C NMR 101 MHz, CDCl3
OMe
N
N
N
F3C
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

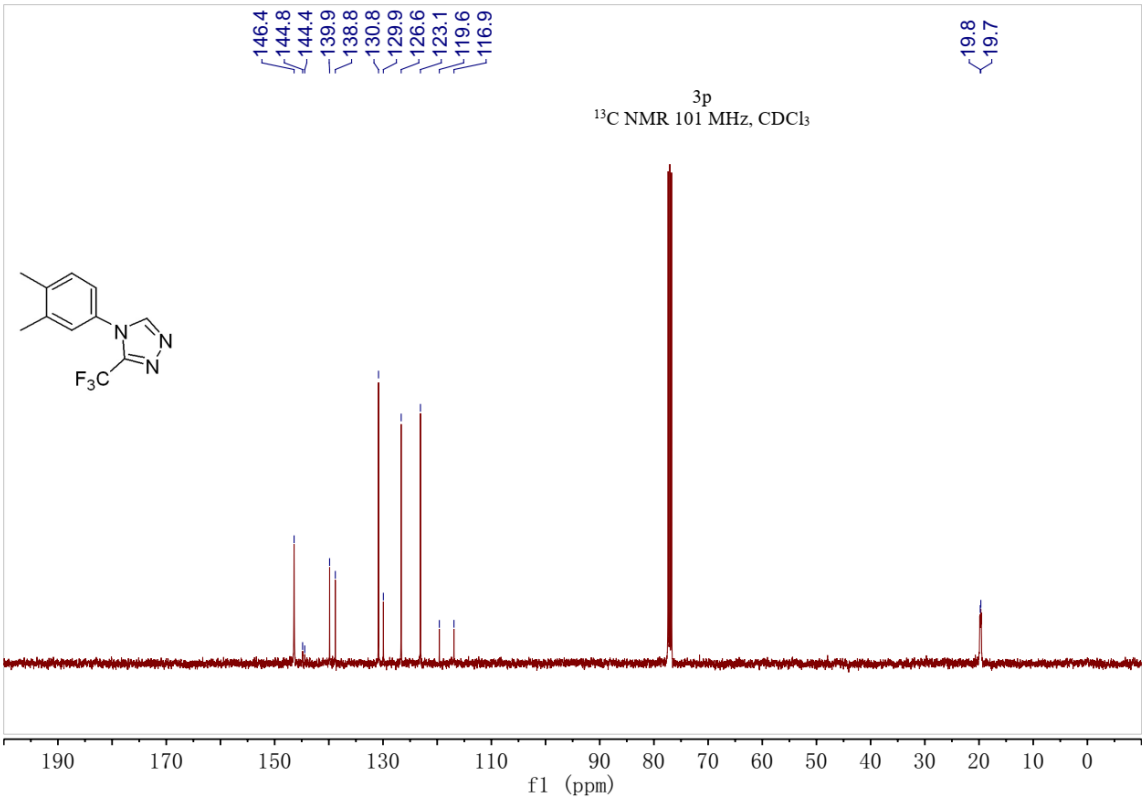

-61.9
3n
19F NMR 377 MHz, CDCl3
OMe
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

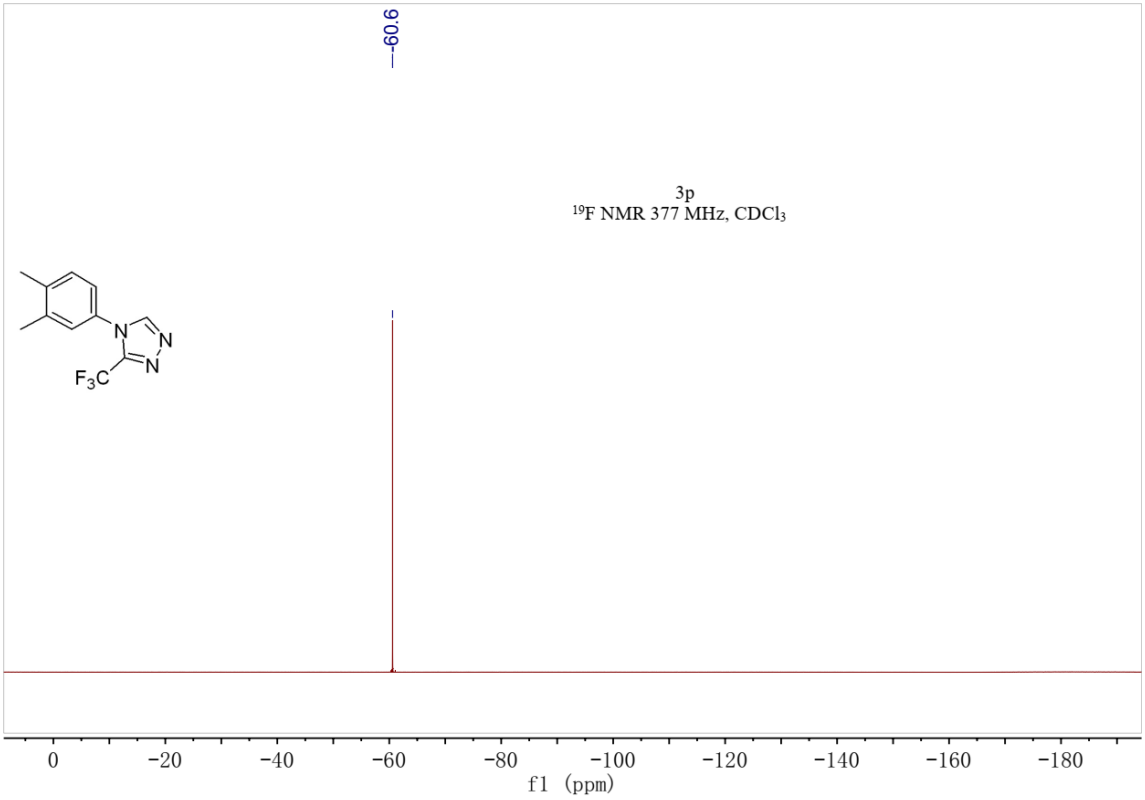

7.67
7.65
7.63
7.57
7.56
7.56
7.55
7.55
7.54
7.54
7.52
7.52
7.43
7.41
7.31
7.30
7.29
7.29
7.06
7.05
7.05
7.04
3o
1H NMR 400 MHz, CDCl3
F3C
1.00
1.01
2.01
0.99
2.96
1.99
f1 (ppm)

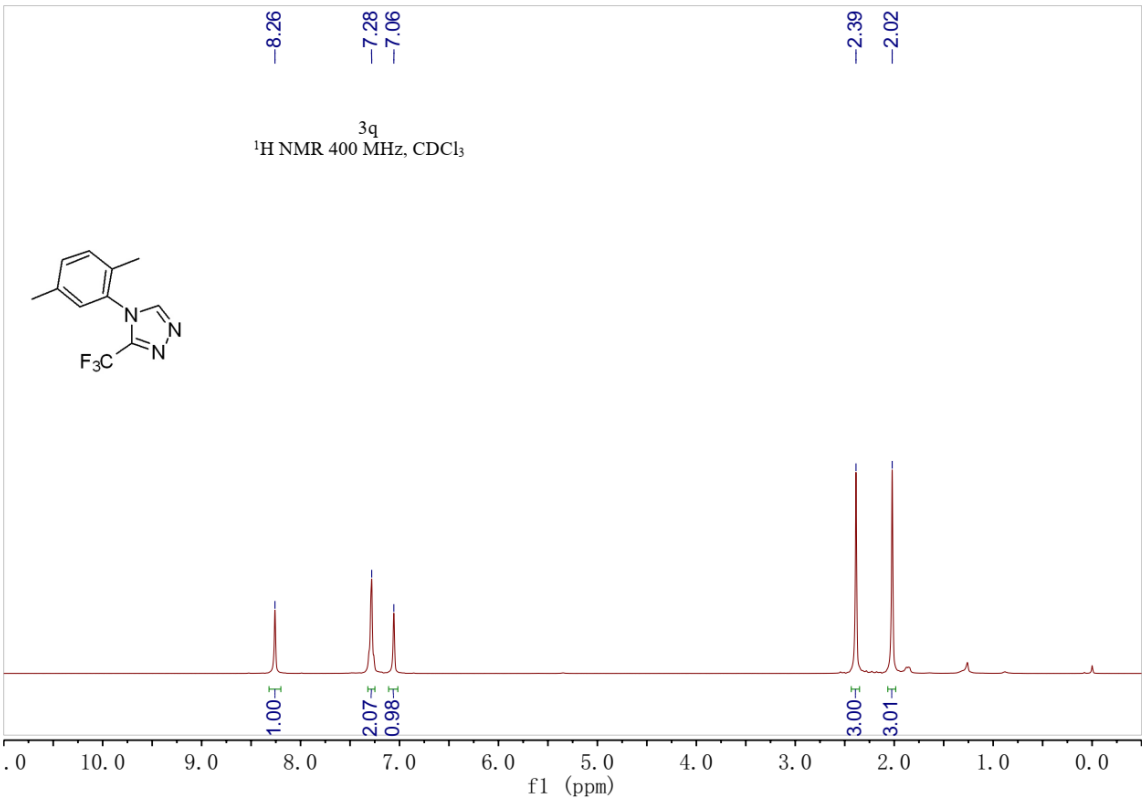

146.7
144.9
144.6
139.5
136.2
131.5
131.1
130.0
128.9
128.7
128.5
128.1
127.4
122.2
119.5
116.8
114.1
3o
13C NMR 101 MHz, CDCl3
F3C
f1 (ppm)

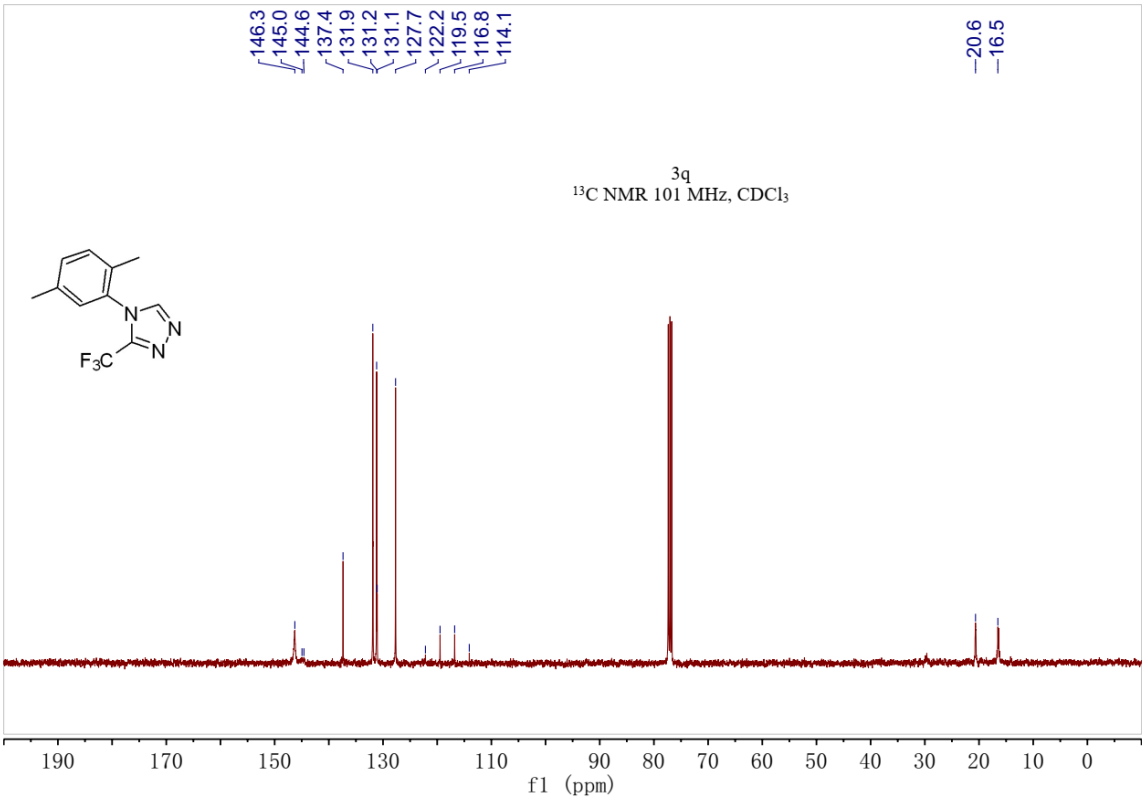

-60.4
3o
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

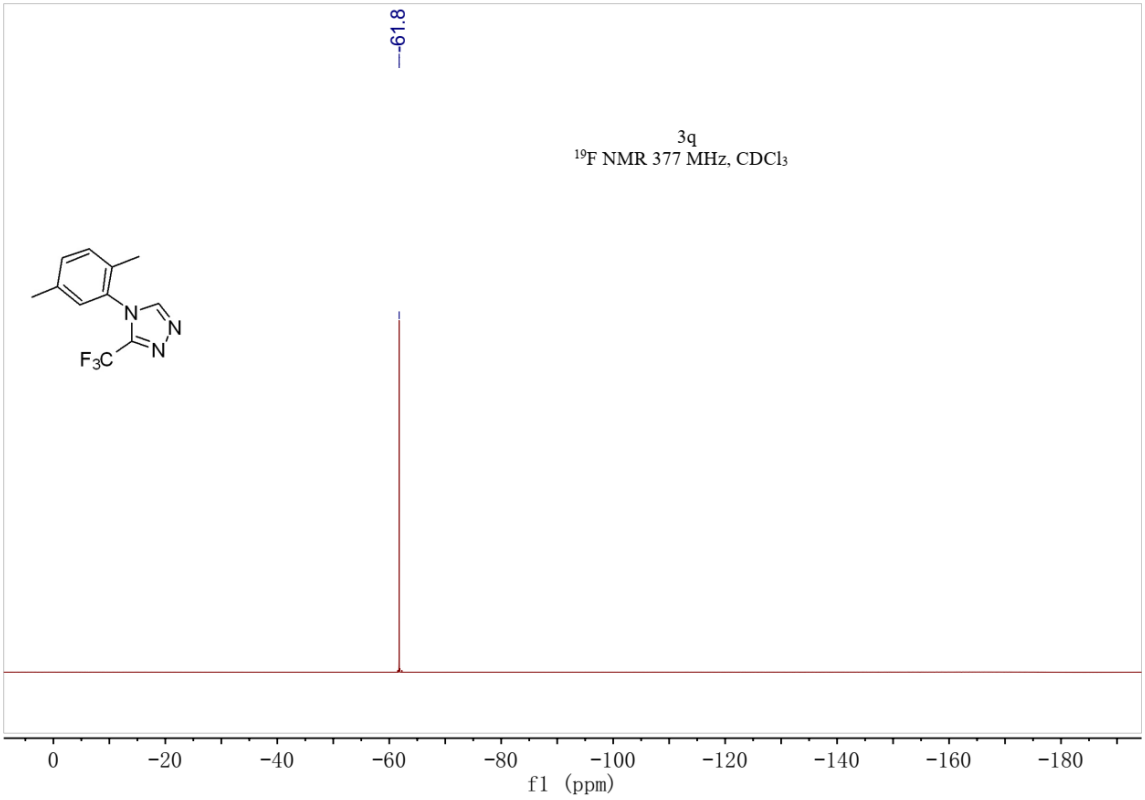

3p
1H NMR 400 MHz, CDCl3
8.31
7.30
7.28
7.12
7.10
7.08
2.36
2.34
7.37
7.35
7.19
7.17
7.15
1.00
1.06
2.02
3.01
3.08
f1 (ppm)

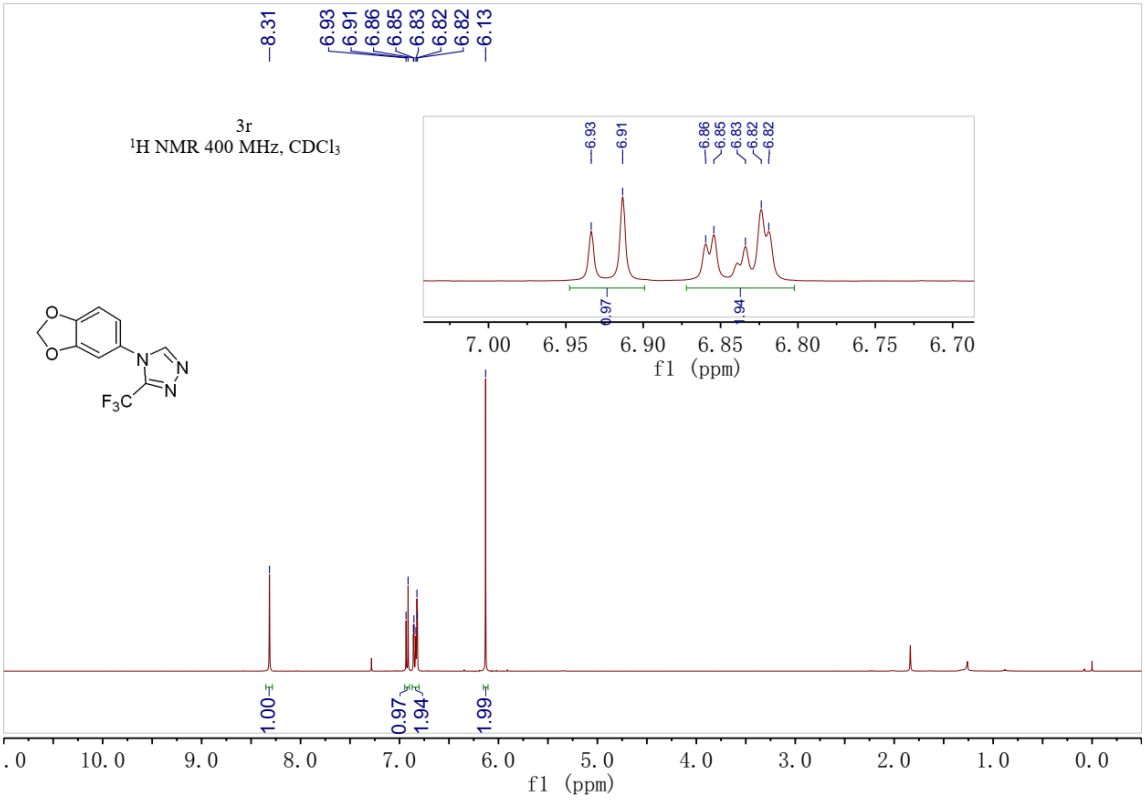

3p
13C NMR 101 MHz, CDCl3
146.4
144.8
144.4
139.9
138.8
130.8
129.9
126.6
123.1
119.6
116.9
19.8
19.7
f1 (ppm)

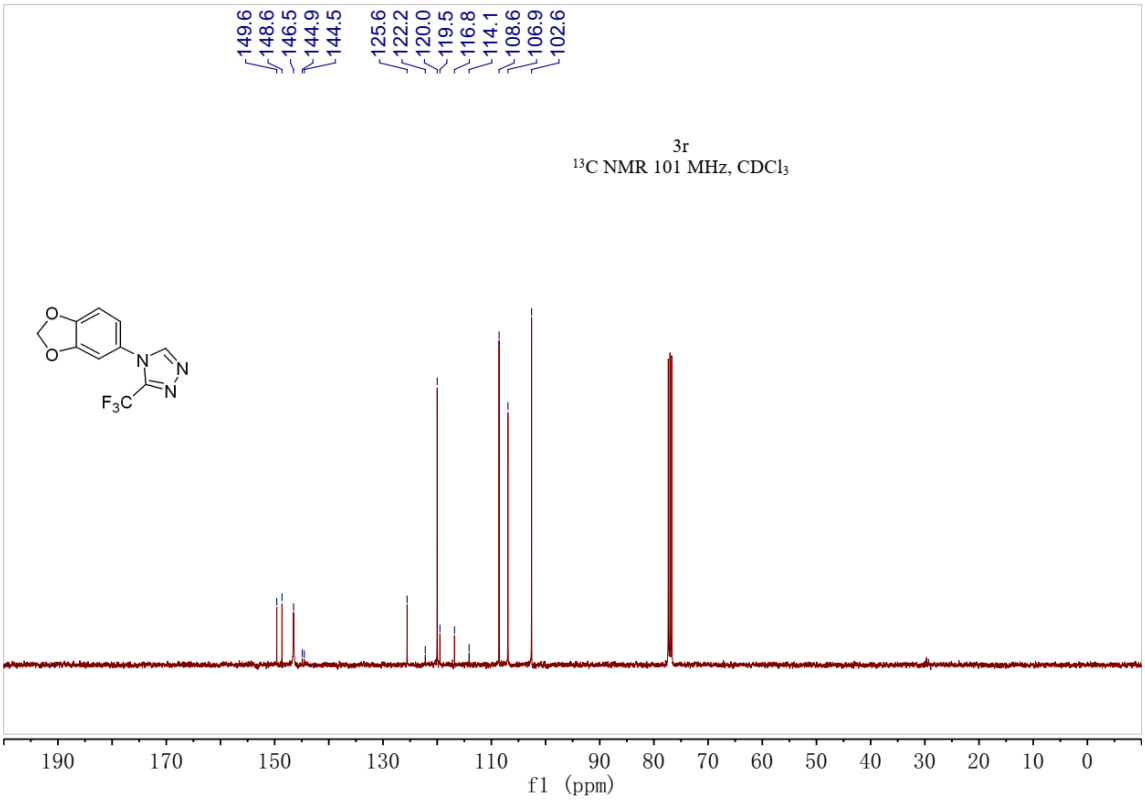

-60.6
3p
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

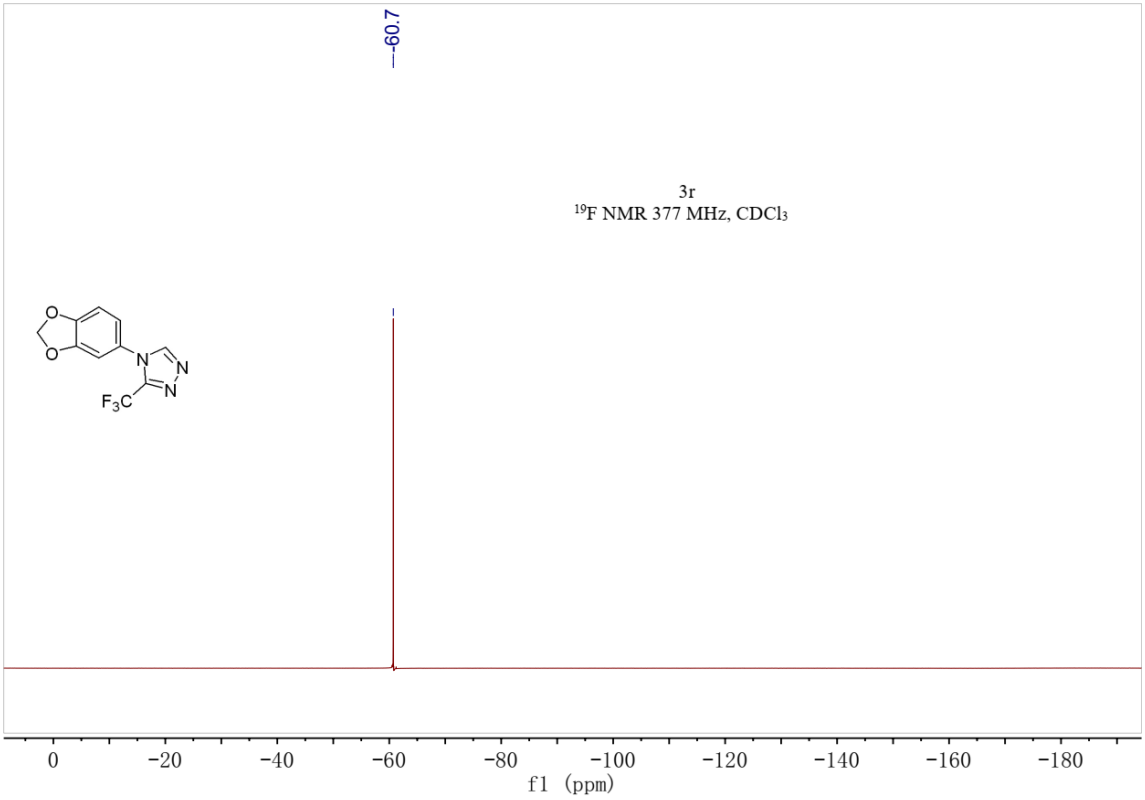

8.26
7.28
7.06
2.39
2.02
3q
1H NMR 400 MHz, CDCl3
F3C
1.00
2.07
0.98
3.00
3.01
f1 (ppm)

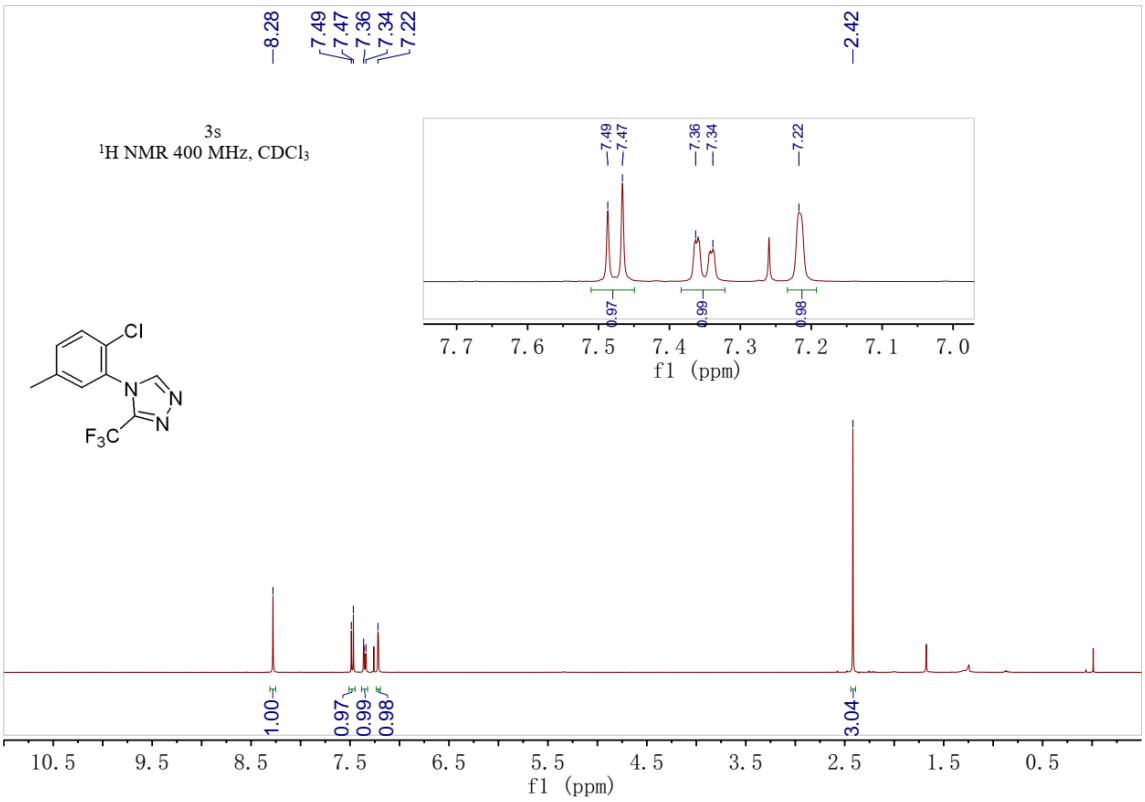

146.3
145.0
144.6
137.4
131.9
131.2
131.1
127.7
122.2
119.5
116.8
114.1
20.6
16.5
3q
13C NMR 101 MHz, CDCl3
F3C
f1 (ppm)

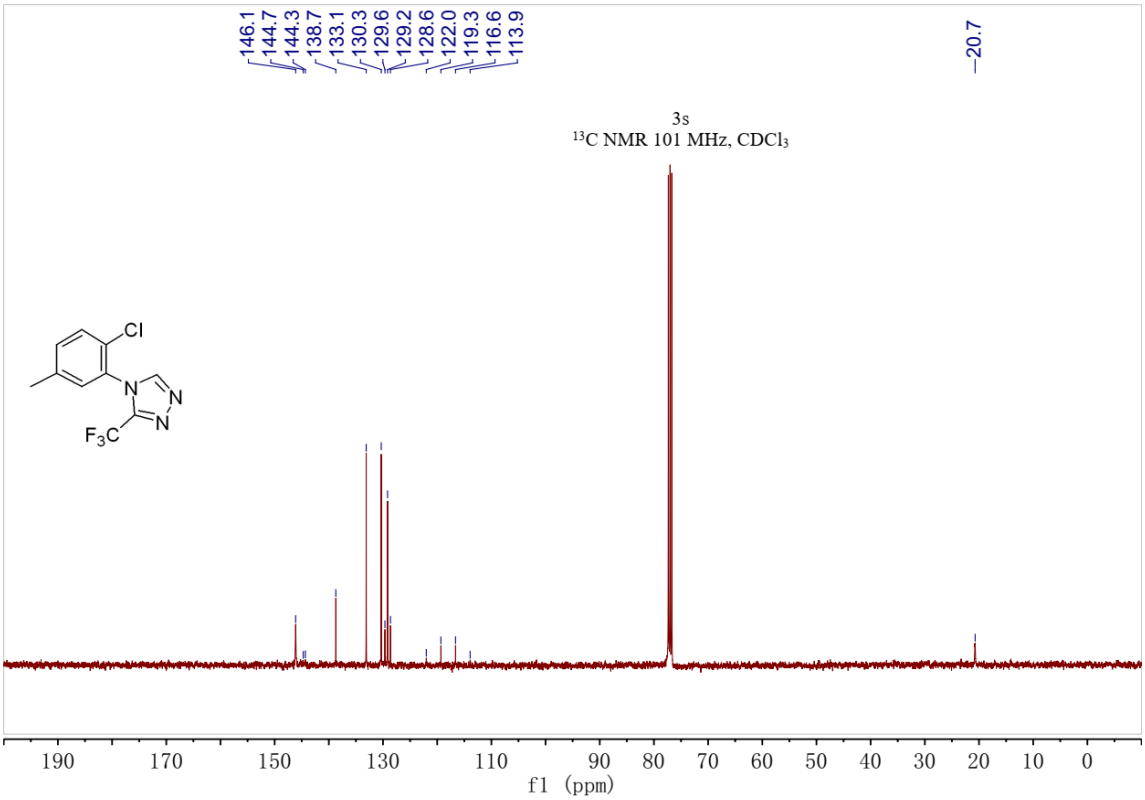

-61.8
3q
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

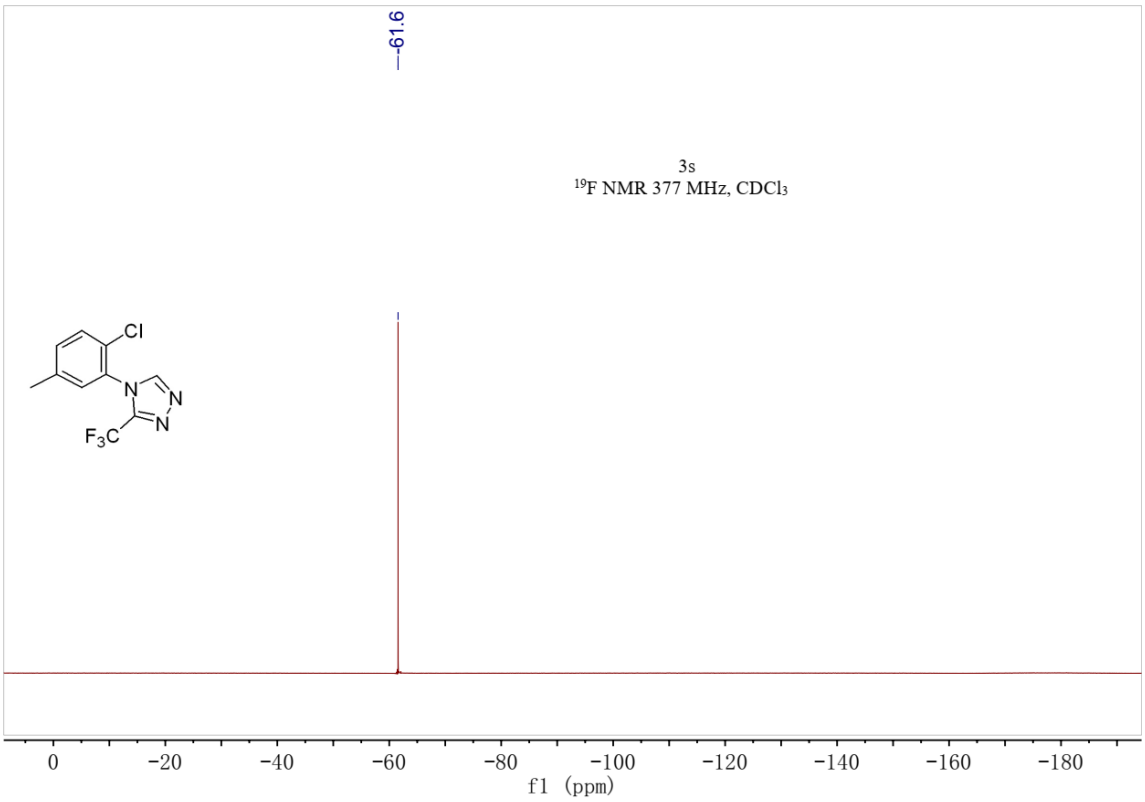

8.31
6.93
6.91
6.86
6.85
6.83
6.82
6.82
6.13
3r
1H NMR 400 MHz, CDCl3
6.93
6.91
6.86
6.85
6.83
6.82
6.82
0.97
1.94
7.00 6.95 6.90 6.85 6.80 6.75 6.70
f1 (ppm)
F3C
1.00
0.97
1.94
1.99
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)

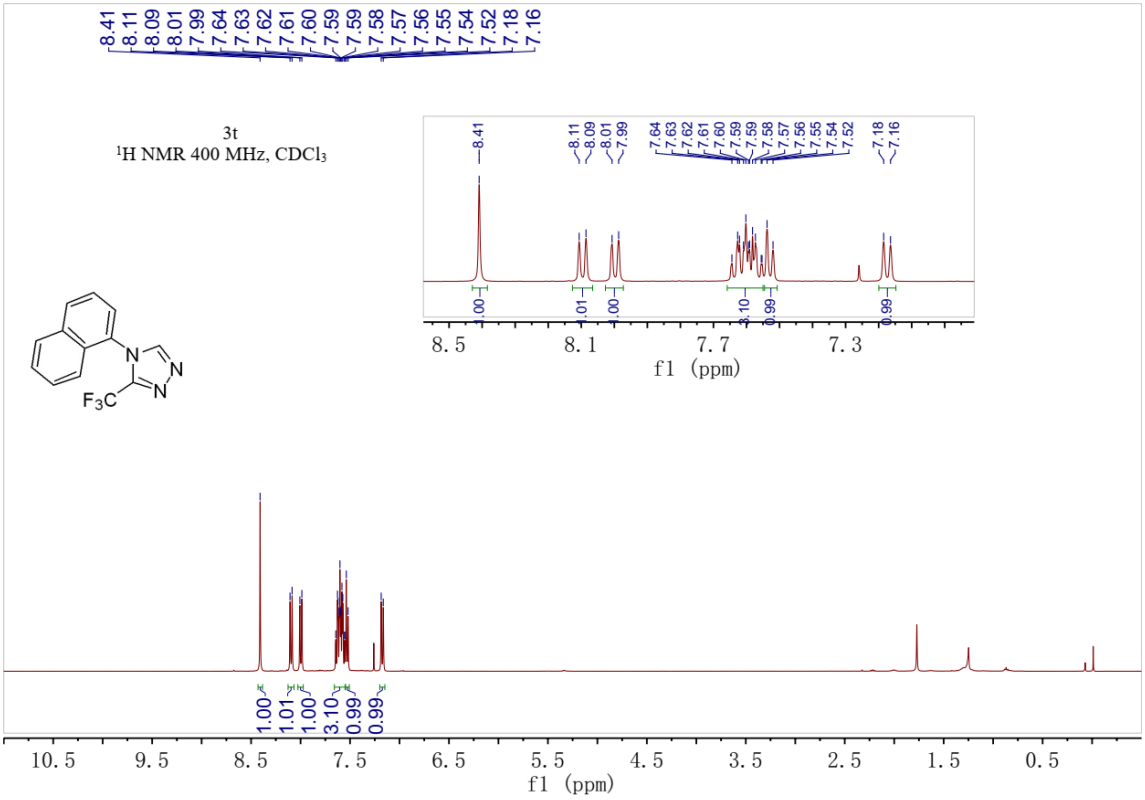

149.6
148.6
146.5
144.9
144.5
125.6
122.2
120.0
119.5
116.8
114.1
108.6
106.9
102.6
3r
13C NMR 101 MHz, CDCl3
F3C
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

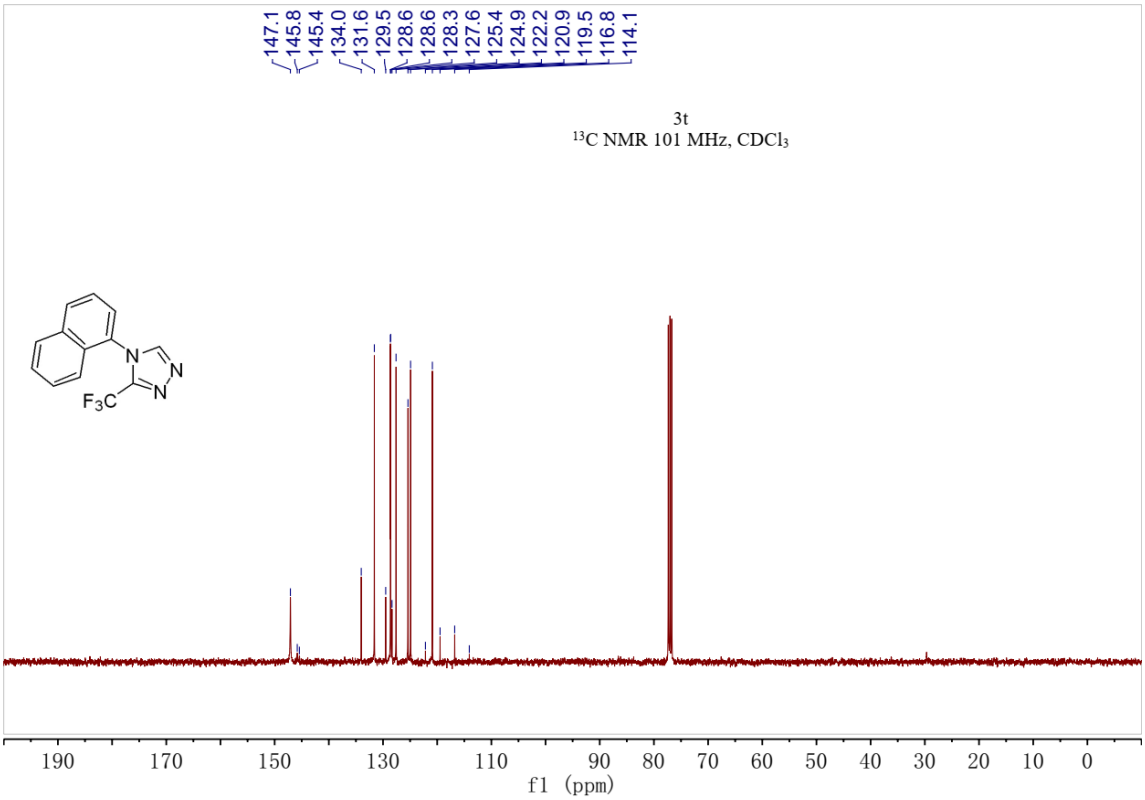

-60.7
3r
19F NMR 377 MHz, CDCl3
O
O
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

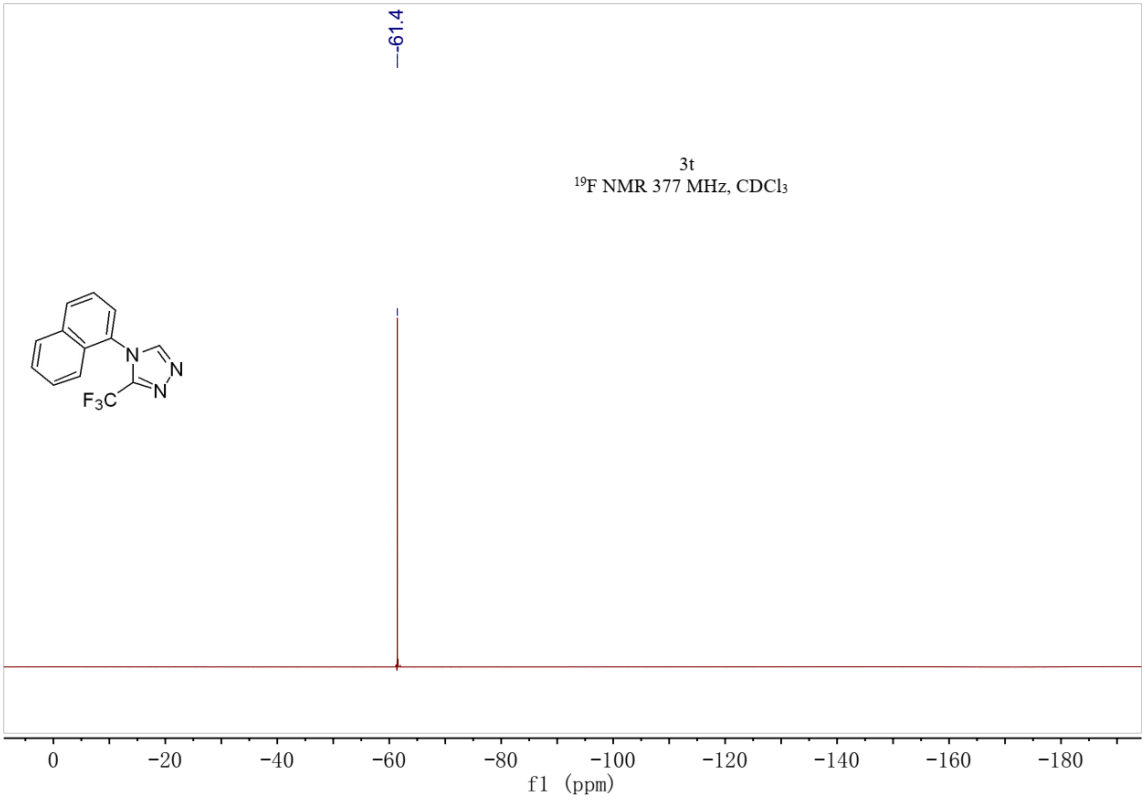

8.28
7.49
7.47
7.36
7.34
7.22
2.42
3s
1H NMR 400 MHz, CDCl3
Cl
N
N
N
F3C
0.97
0.99
0.98
f1 (ppm)
1.00
0.97
0.99
0.98
3.04
f1 (ppm)

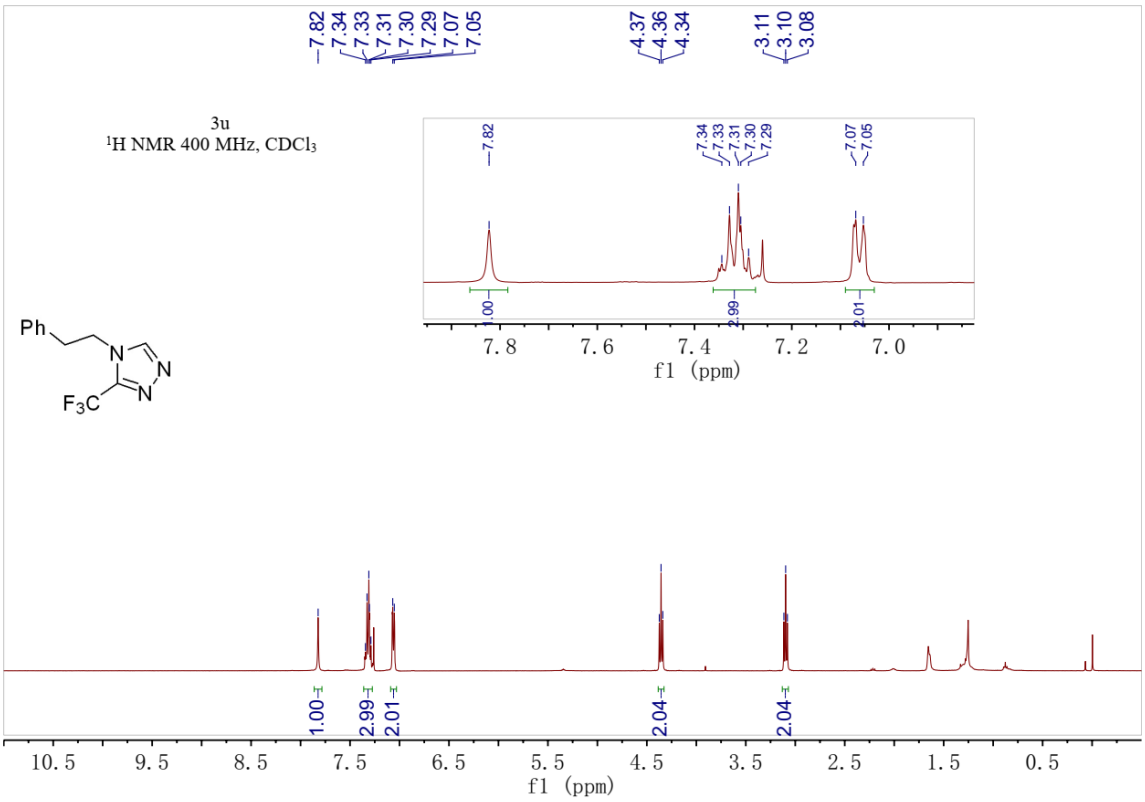

146.1
144.7
144.3
138.7
133.1
130.3
129.6
129.2
128.6
122.0
119.3
116.6
113.9
20.7
3s
13C NMR 101 MHz, CDCl3
Cl
N
N
N
F3C
f1 (ppm)

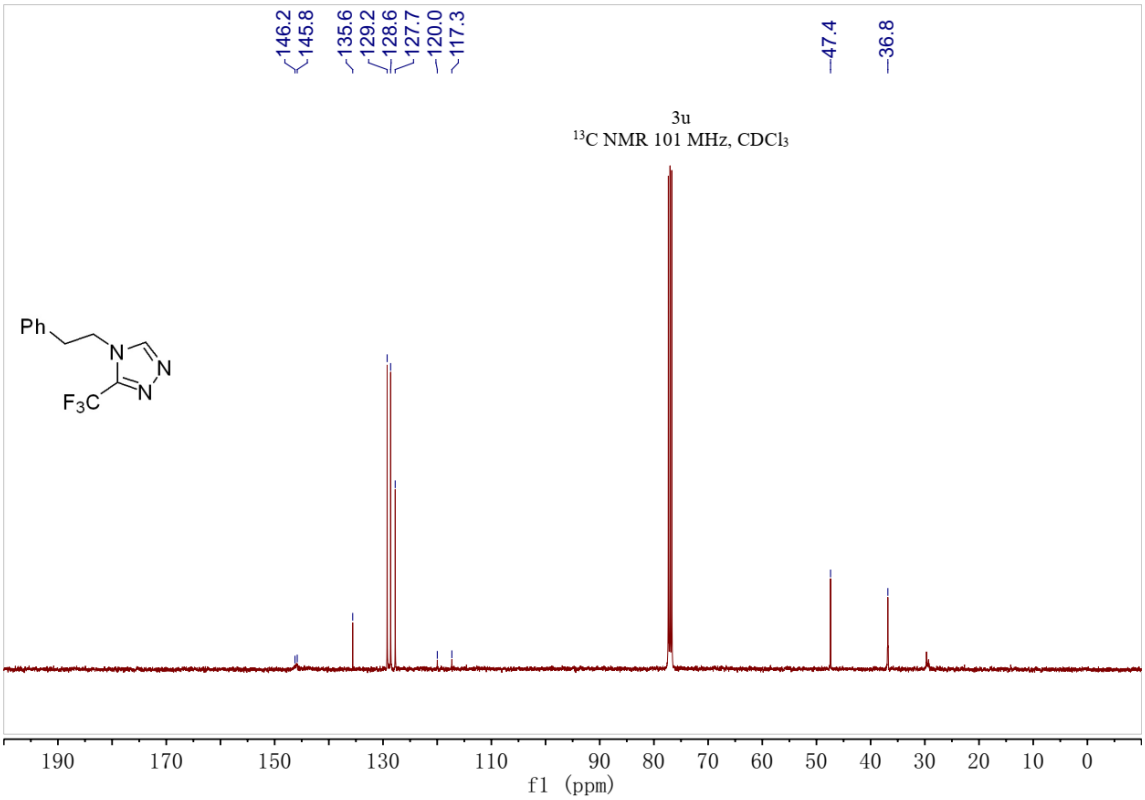

61.6
3s
19F NMR 377 MHz, CDCl3
Cl
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

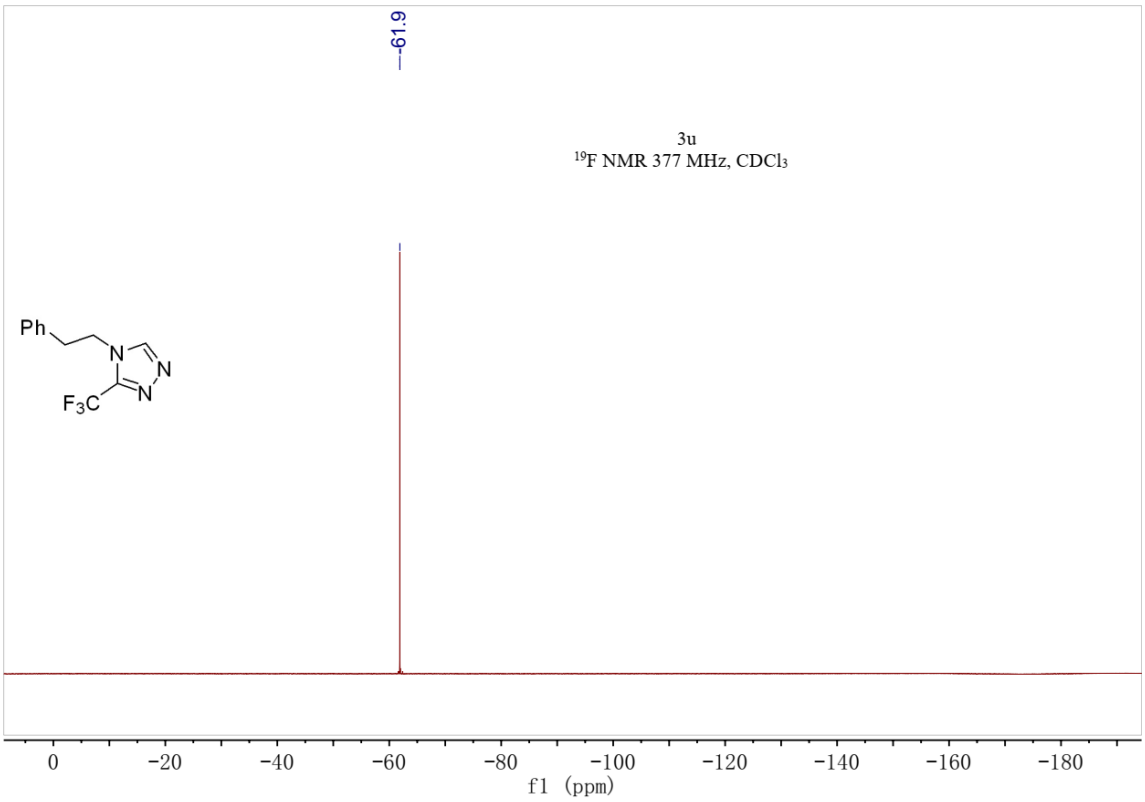

8.41
8.11
8.09
8.01
7.99
7.64
7.63
7.62
7.61
7.60
7.59
7.59
7.58
7.57
7.56
7.55
7.54
7.52
7.18
7.16
3t
1H NMR 400 MHz, CDCl3
F3C
N
N
N
1.00
1.01
1.00
3.10
0.99
0.99
8.5
8.1
7.7
7.3
f1 (ppm)
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

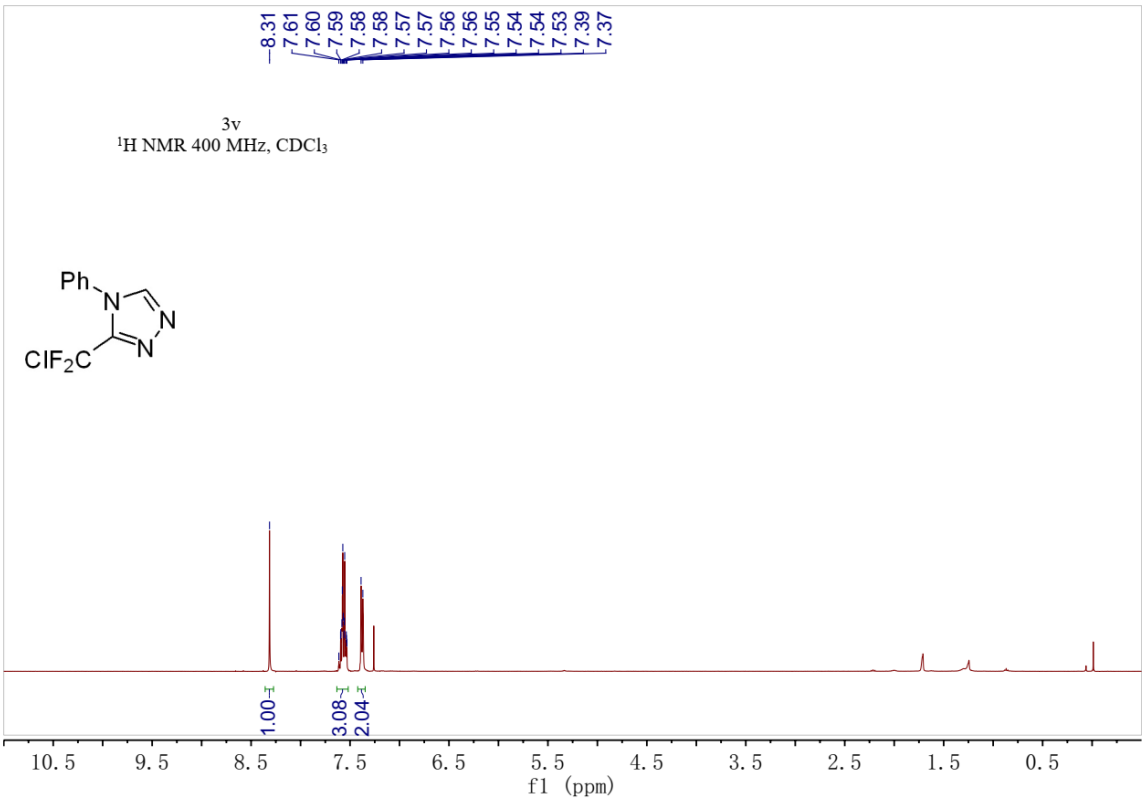

147.1
145.8
145.4
134.0
131.6
129.5
128.6
128.6
128.3
127.6
125.4
124.9
122.2
120.9
119.5
116.8
114.1
3t
13C NMR 101 MHz, CDCl3
F3C
N
N
N
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

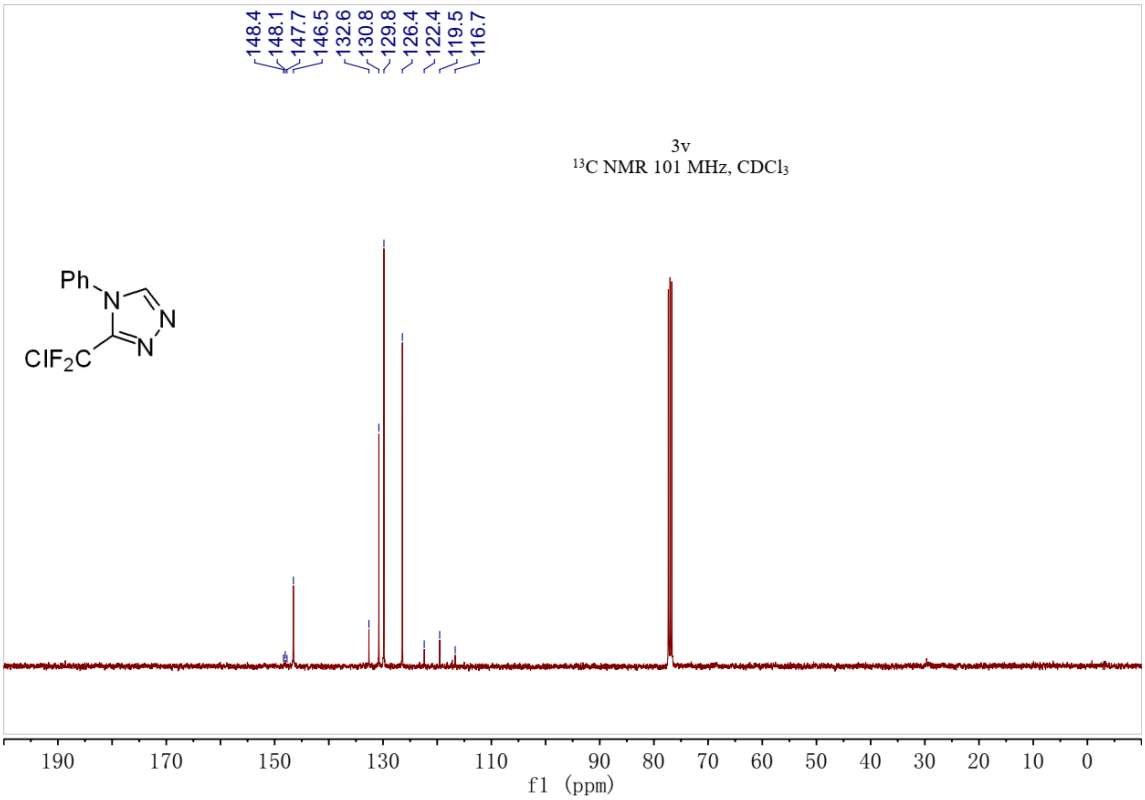

61.4
3t
19F NMR 377 MHz, CDCl3
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

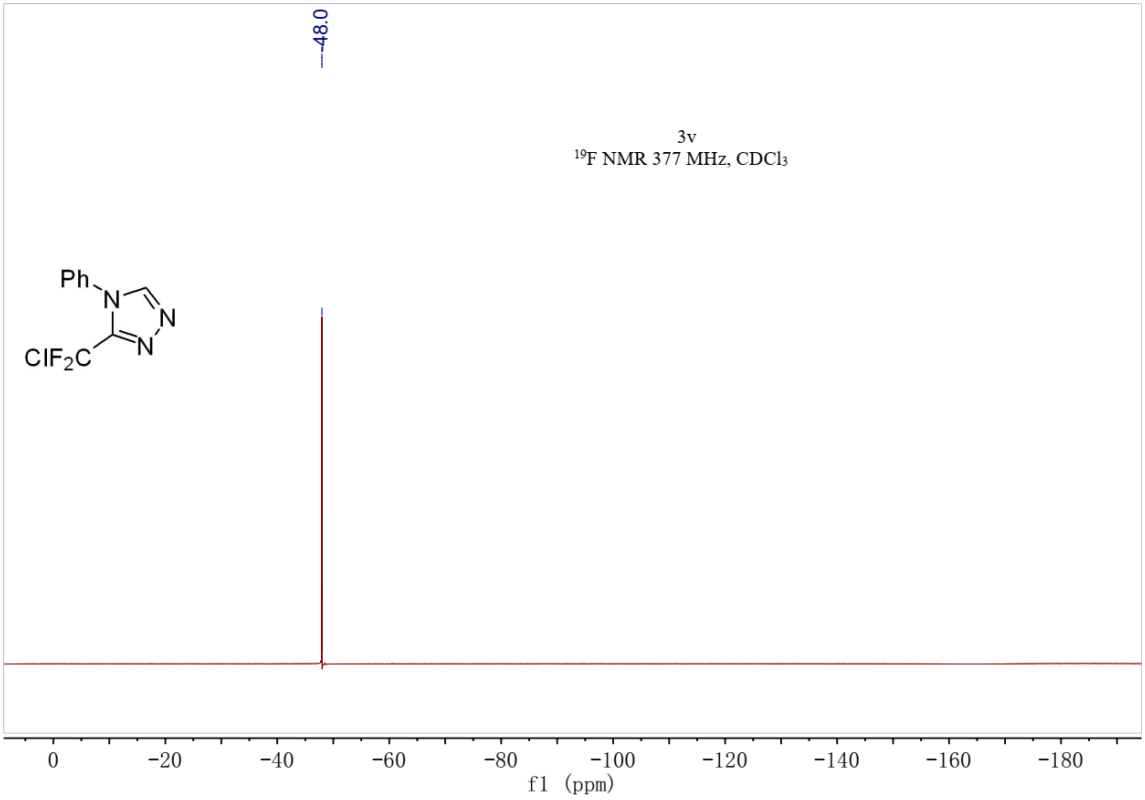

7.82
7.34
7.33
7.31
7.30
7.29
7.07
7.05
4.37
4.36
4.34
3.11
3.10
3.08
3u
1H NMR 400 MHz, CDCl3
Ph
N
N
N
F3C
1.00
2.99
2.01
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
1.00
2.99
2.01
2.04
2.04
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

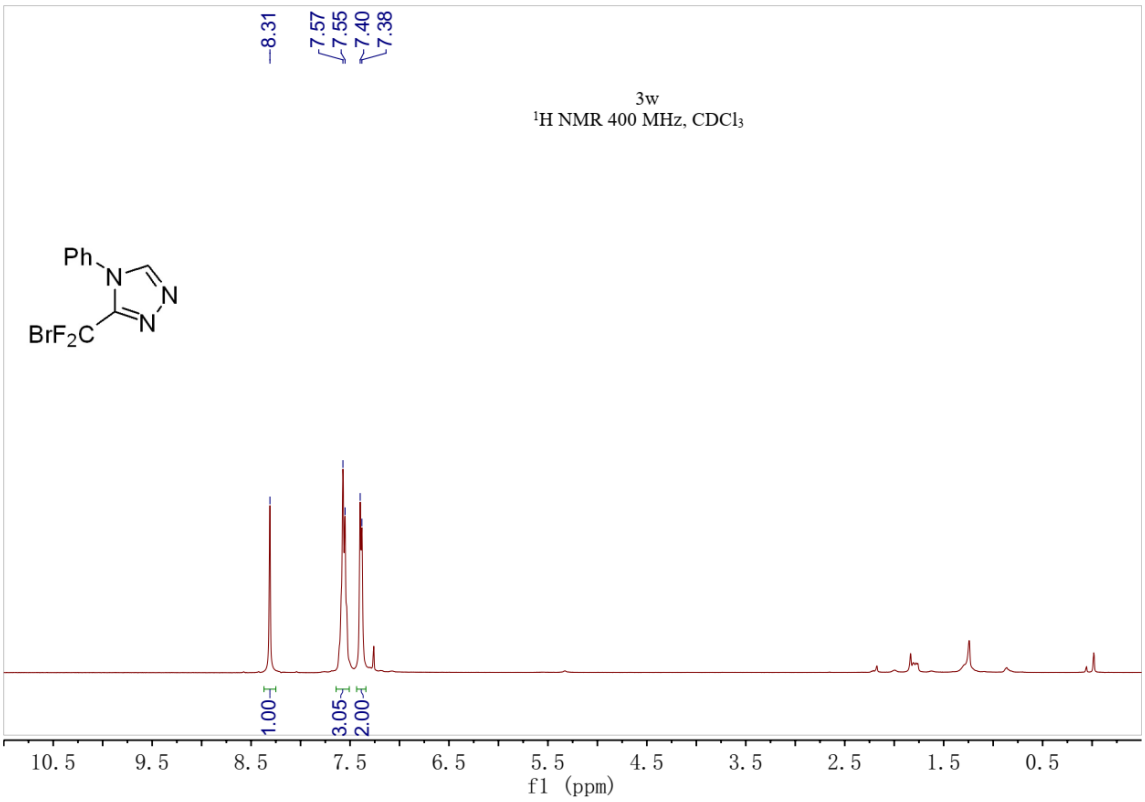

146.2
145.8
135.6
129.2
128.6
127.7
120.0
117.3
47.4
36.8
3u
13C NMR 101 MHz, CDCl3
Ph
N
N
N
F3C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

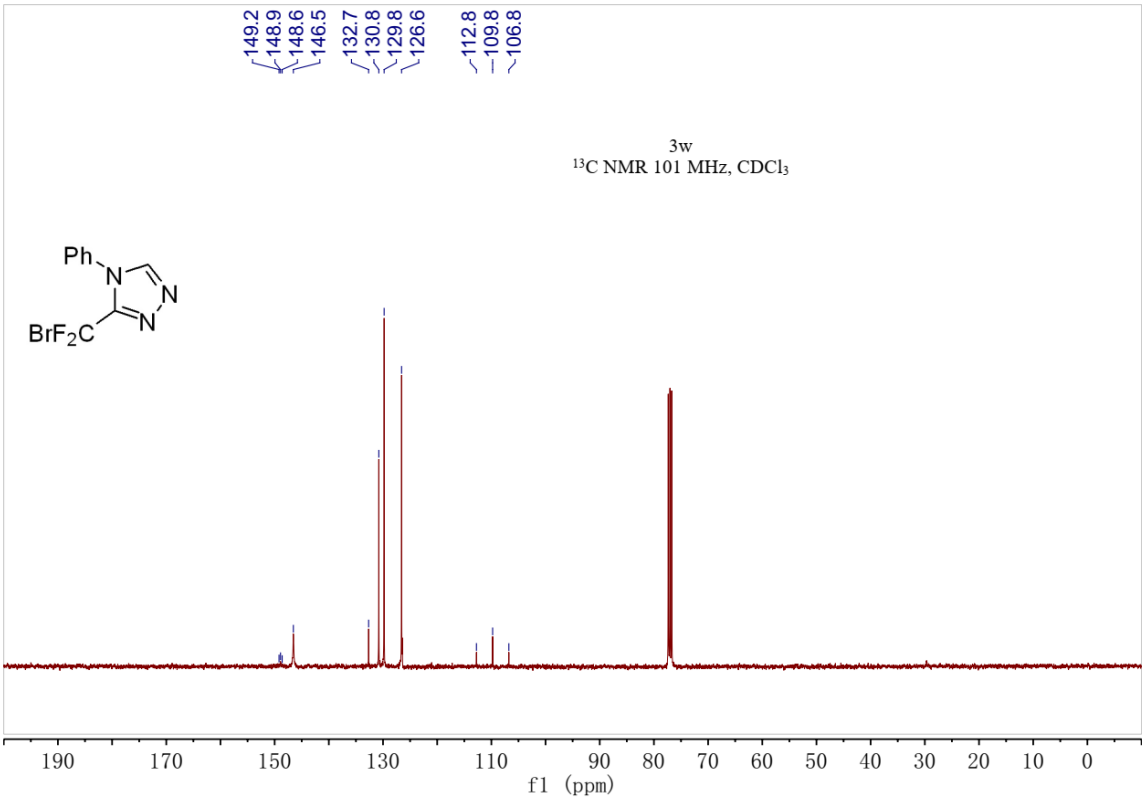

61.9
3u
19F NMR 377 MHz, CDCl3
Ph
N
N
N
F3C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

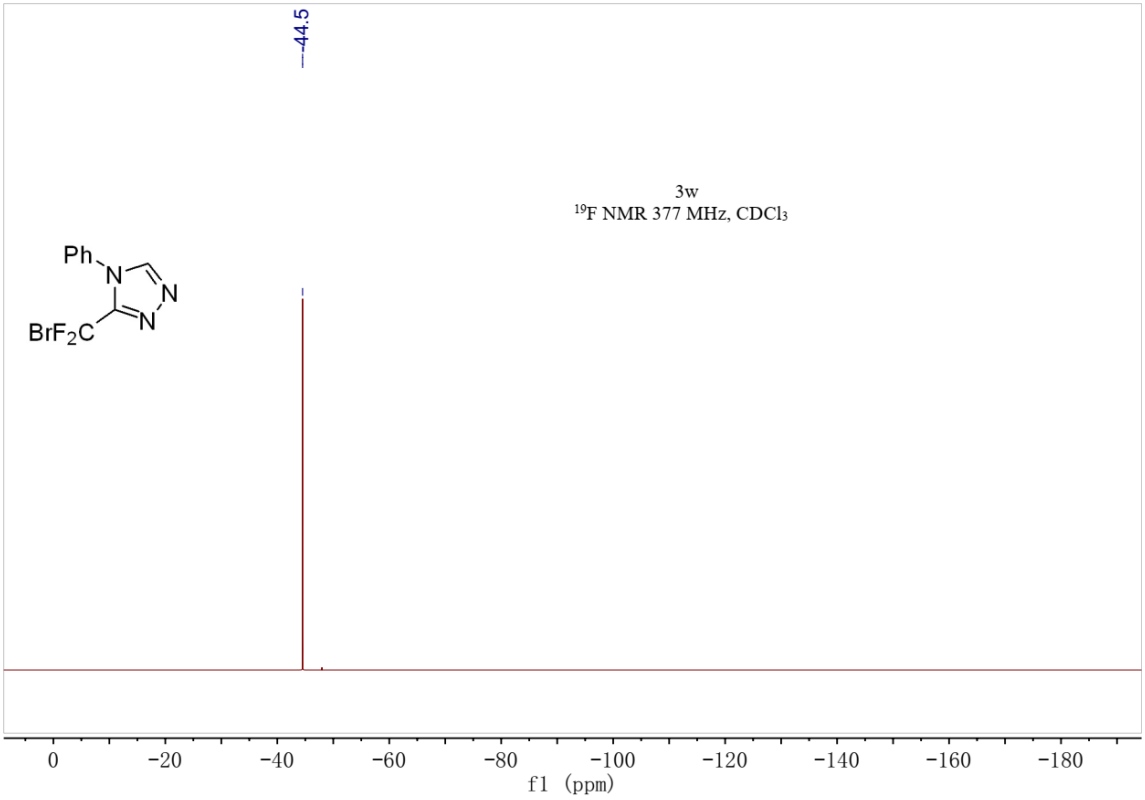

8.31
7.61
7.60
7.59
7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.54
7.54
7.53
7.39
7.37
3v
1H NMR 400 MHz, CDCl3
Ph
N
N
N
ClF2C
1.00
3.08
2.04
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

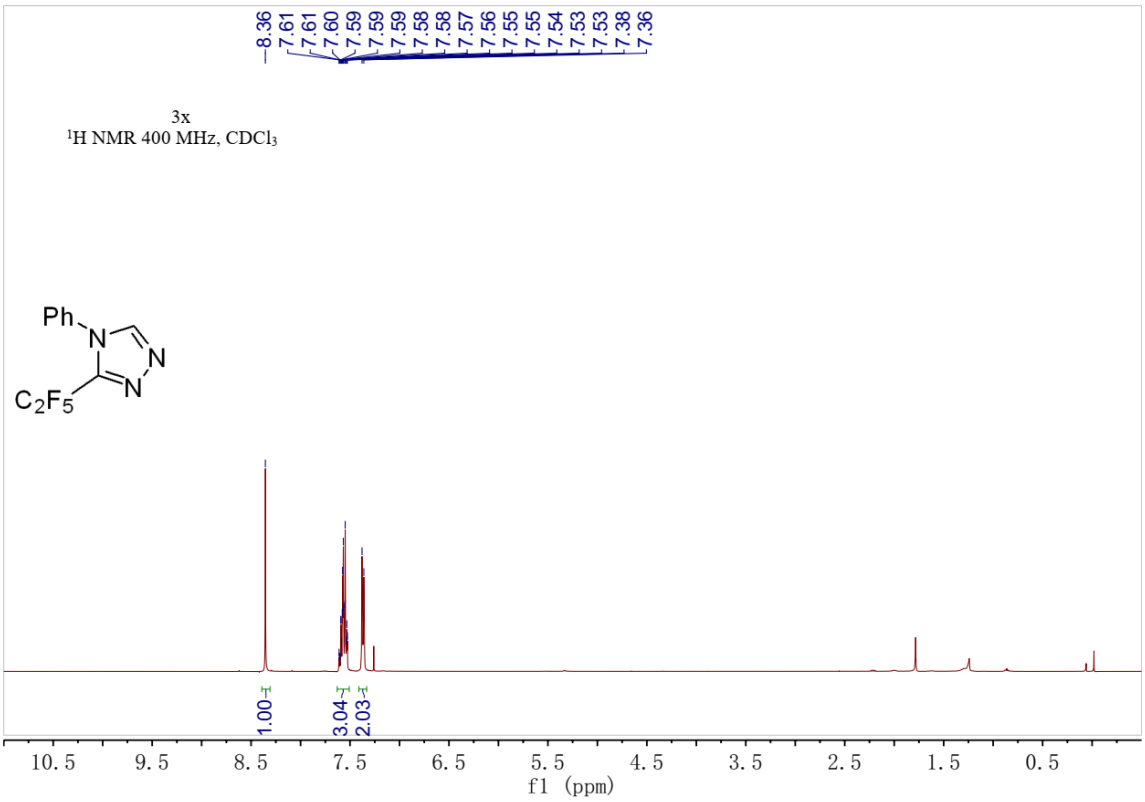

148.4
148.1
147.7
146.5
132.6
130.8
129.8
126.4
122.4
119.5
116.7
3v
13C NMR 101 MHz, CDCl3
Ph
N
N
N
ClF2C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

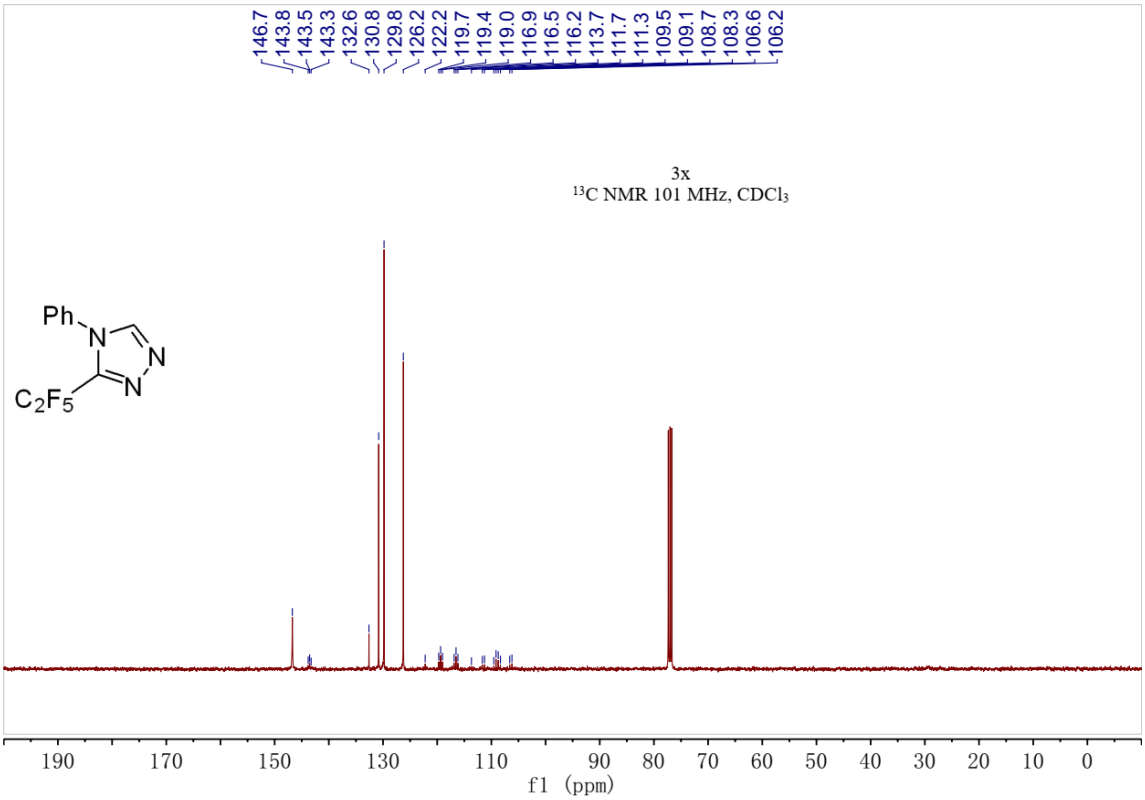

-48.0
3v
19F NMR 377 MHz, CDCl3
Ph
N
N
N
ClF2C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

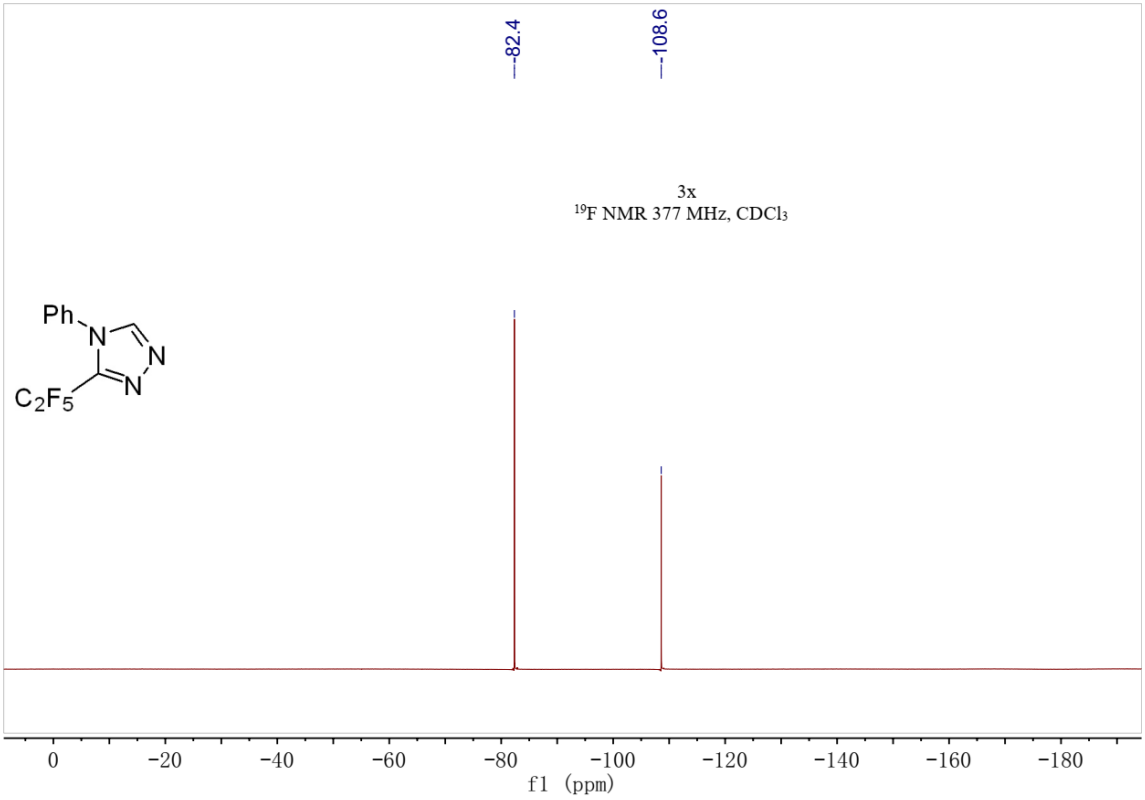

8.31
7.57
7.55
7.40
7.38
3w
1H NMR 400 MHz, CDCl3
Ph
N
N
N
BrF2C
1.00
3.05
2.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

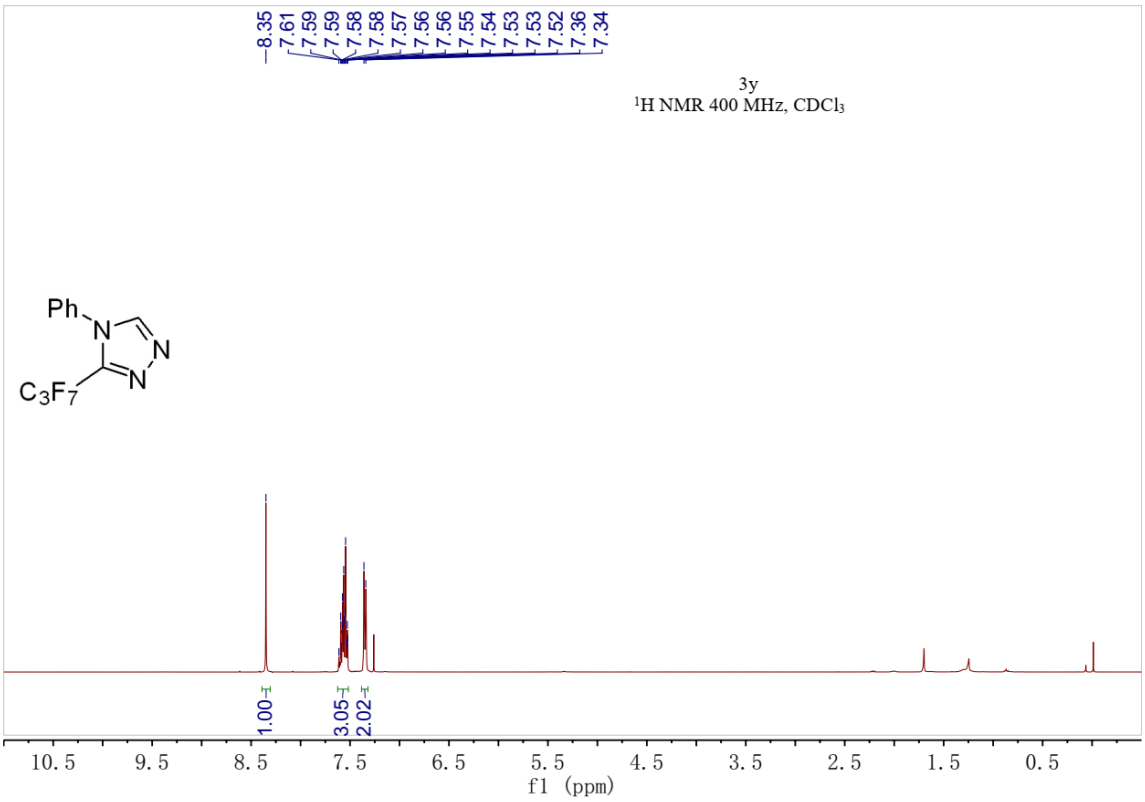

149.2
148.9
148.6
146.5
132.7
130.8
129.8
126.6
112.8
109.8
106.8
3w
13C NMR 101 MHz, CDCl3
Ph
N
N
N
BrF2C
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

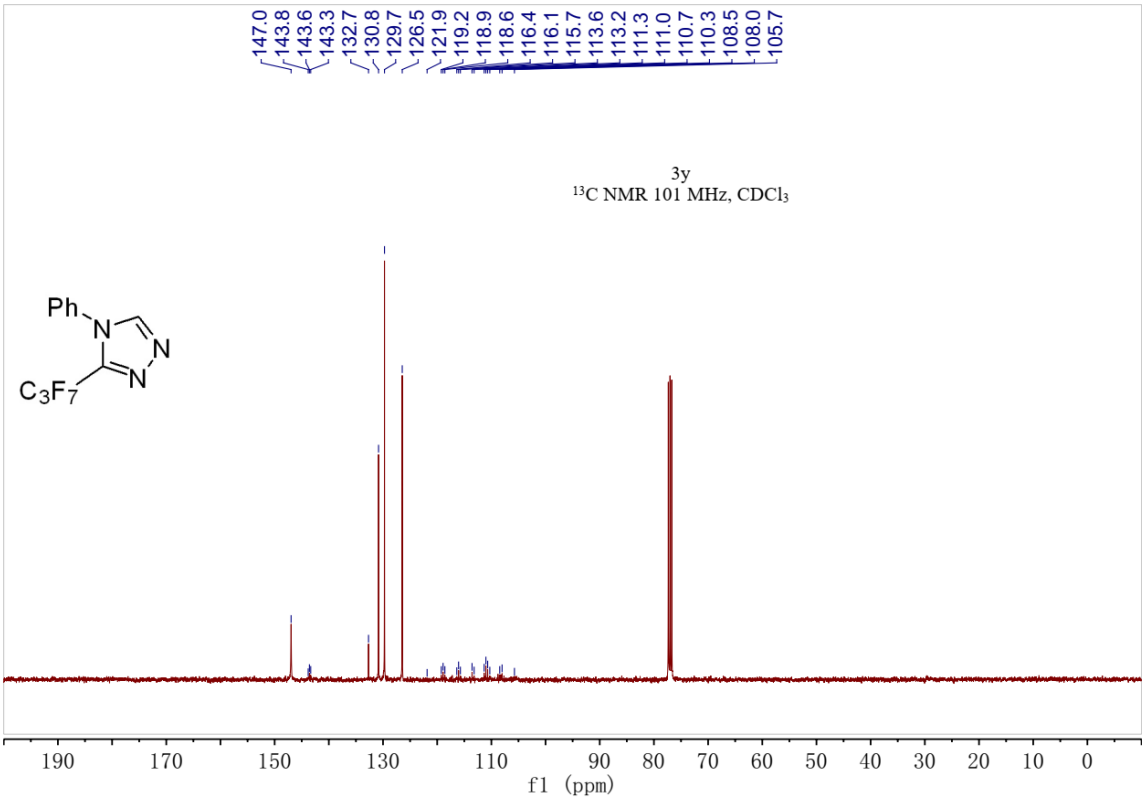

-44.5
3w
19F NMR 377 MHz, CDCl3
Ph
N
N
N
BrF2C
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

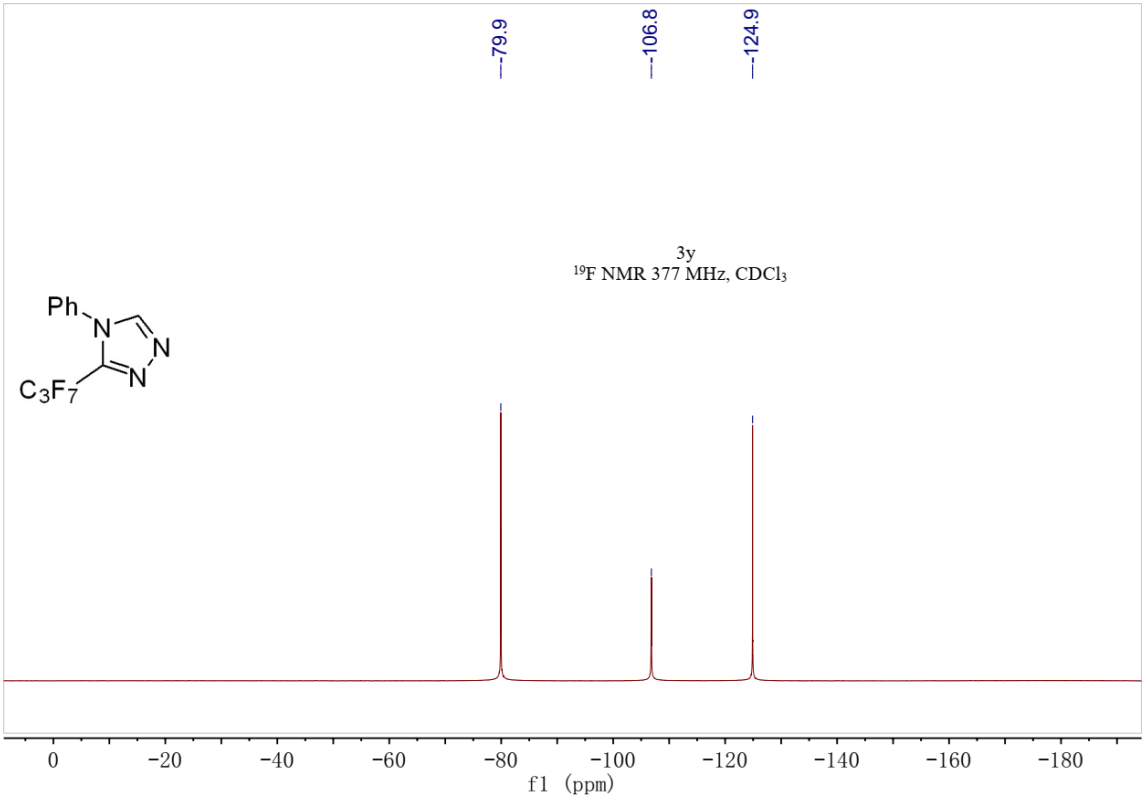

8.36
7.61
7.61
7.60
7.59
7.59
7.59
7.58
7.58
7.57
7.56
7.55
7.55
7.54
7.53
7.53
7.38
7.36
3x
1H NMR 400 MHz, CDCl3
Ph
N
N
N
C2F5
1.00
3.04
2.03
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

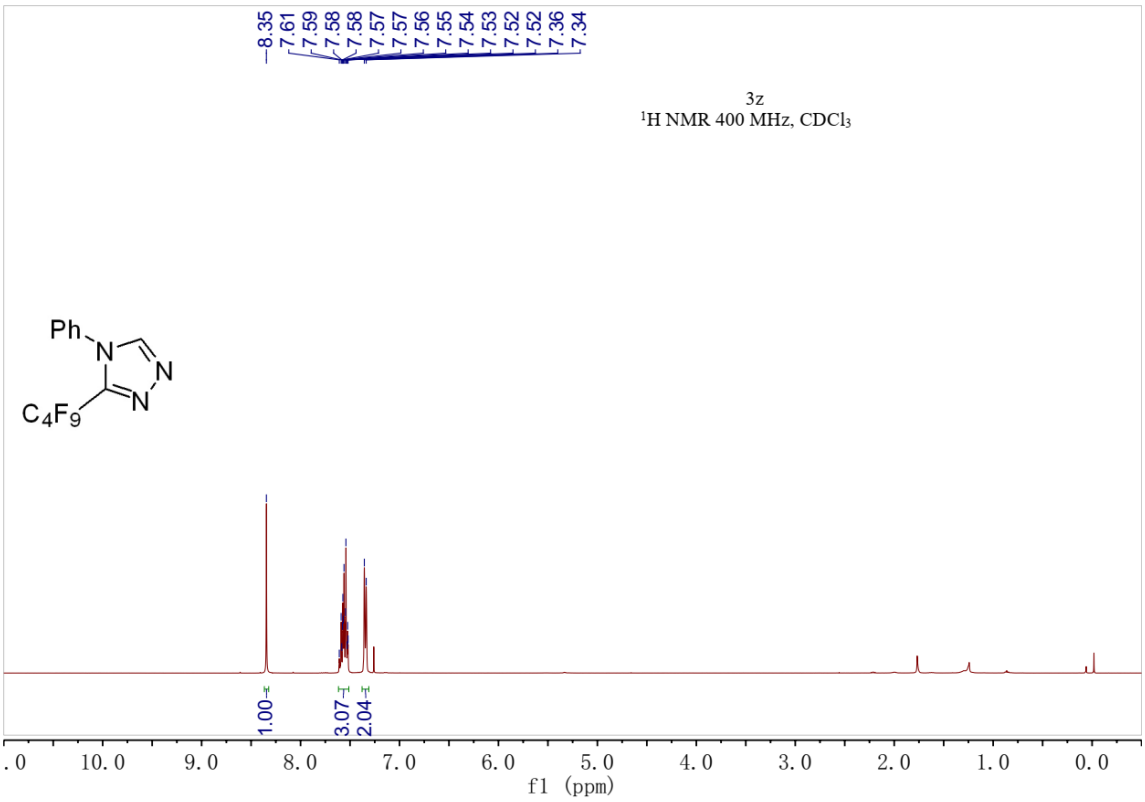

146.7
143.8
143.5
143.3
132.6
130.8
129.8
126.2
122.2
119.7
119.4
119.0
116.9
116.5
116.2
113.7
111.7
111.3
109.5
109.1
108.7
108.3
106.6
106.2
3x
13C NMR 101 MHz, CDCl3
Ph
N
N
N
C2F5
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

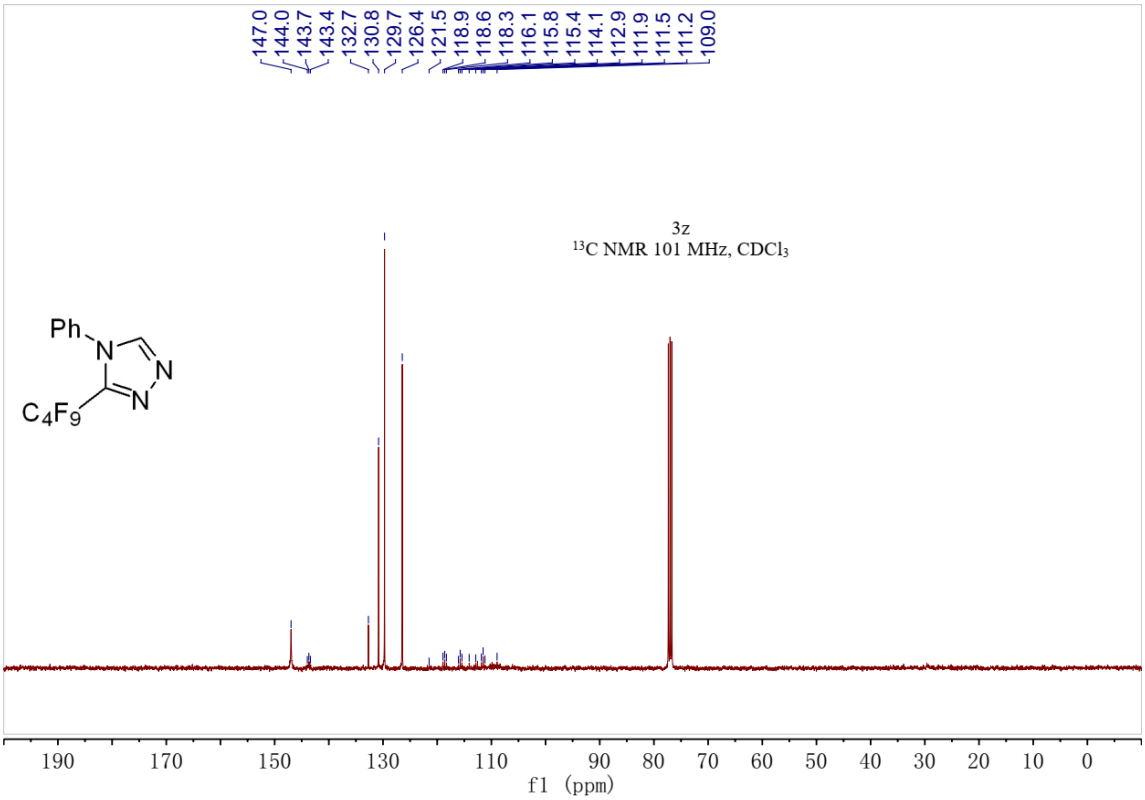

-82.4
-108.6
3x
19F NMR 377 MHz, CDCl3
Ph
N
N
N
C2F5
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

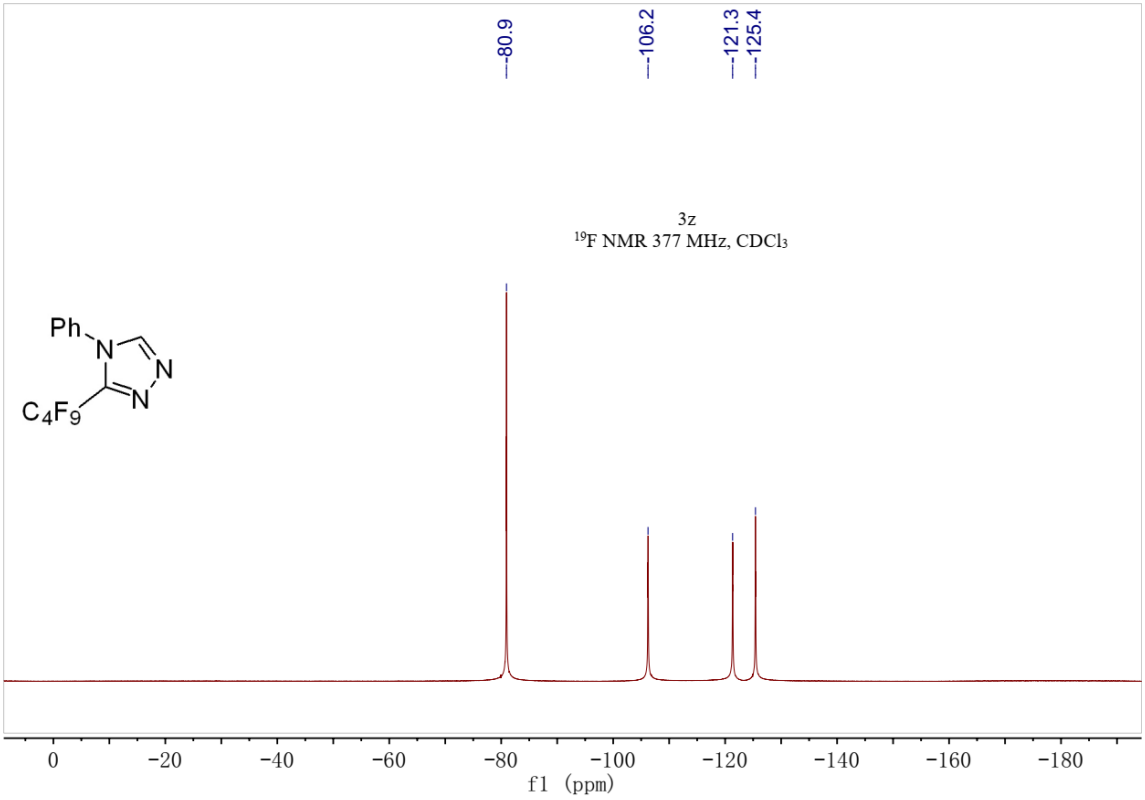

8.35
7.61
7.59
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.54
7.53
7.53
7.52
7.36
7.34
3y
1H NMR 400 MHz, CDCl3
Ph
N
N
N
C3F7
1.00
3.05
2.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


147.0
143.8
143.6
143.3
132.7
130.8
129.7
126.5
121.9
119.2
118.9
118.6
116.4
116.1
115.7
113.6
113.2
111.3
111.0
110.7
110.3
108.5
108.0
105.7
3y
13C NMR 101 MHz, CDCl3
Ph
N
N
N
C3F7
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-79.9
-106.8
-124.9
3y
19F NMR 377 MHz, CDCl3
Ph
N
N
N
C3F7
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)


8.35
7.61
7.59
7.58
7.58
7.57
7.57
7.56
7.55
7.54
7.53
7.52
7.52
7.36
7.34
3z
1H NMR 400 MHz, CDCl3
Ph
N
N
N
C4F9
1.00
3.07
2.04
f1 (ppm)


147.0
144.0
143.7
143.4
132.7
130.8
129.7
126.4
121.5
118.9
118.6
118.3
116.1
115.8
115.4
114.1
112.9
111.9
111.5
111.2
109.0
3z
13C NMR 101 MHz, CDCl3
Ph
N
N
N
C4F9
f1 (ppm)


-80.9
-106.2
-121.3
-125.4
3z
19F NMR 377 MHz, CDCl3
Ph
N
N
N
C4F9
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)