Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


*Electronic Supplementary Information*

# Electrochemical multicomponent reaction toward vicinal sulfenyltetrazolation of unactivated alkenes

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## 1. General Information

All reactions were performed under an atmosphere of nitrogen using standard undivided three-necked glassware, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with potassium permanganate. Yields refer to products isolated after purification by column chromatography, unless otherwise stated. Proton nuclear magnetic resonance ($^{1}$H NMR) spectra, carbon nuclear magnetic resonance ($^{13}$C NMR) spectra and fluorine nuclear magnetic resonance ($^{19}$F NMR) were recorded on Bruker AV-400 (400 MHz), and JEOL-500 (500 MHz) spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR. HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer and Aglient 1290-6545xt with the use of quadrupole analyzer. All chemcials were purchased from *TCI Shanghai* or *Energy Chemical* and used as received.

Electrolysis experiments were performed using MESTEK DC power supply. Electrode clips (PT-3) and platinum plate (99.99%, 15*15*0.3 mm) was purchased from Gaoss Union. The graphite was cut into 15 x 15 x 1 mm pieces before use, and was clamped between electrode clips.

*CAUTION:* Organic azides are known to be potentially explosive compounds. While we did not encounter any issues during their synthesis, proper precautions were taken. All azidation reactions and subsequent workups should be performed behind a blast shield. Once isolated, organic azides should be stored below room temperature and away from sources of heat, light, pressure and shock.

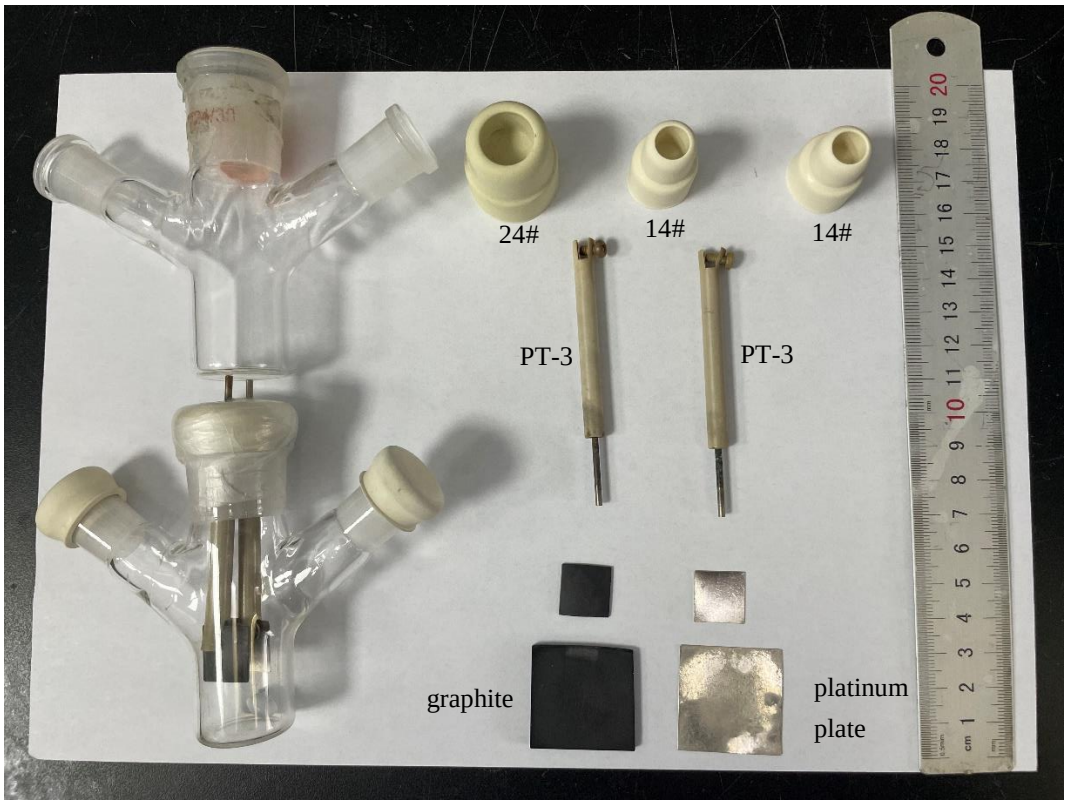



Figure 1. Electrolysis devices


Figure 2. Reaction devices

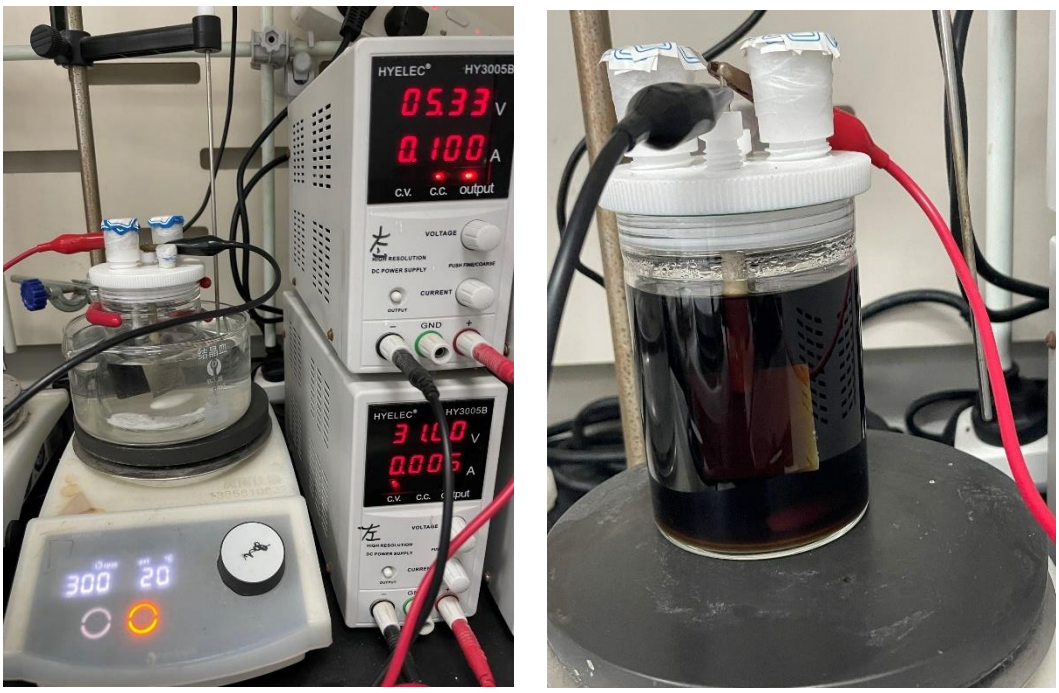
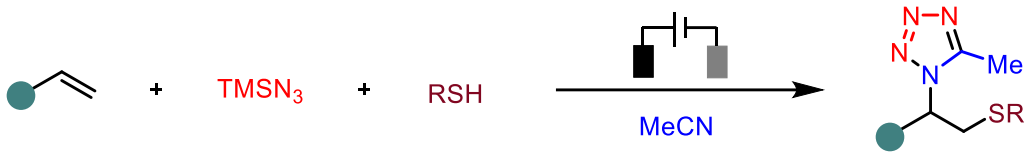



Figure 3. Scale-up reaction devices

## 2. General Procedures

**General procedure for the electrochemical thioeher-tetrazolialition**



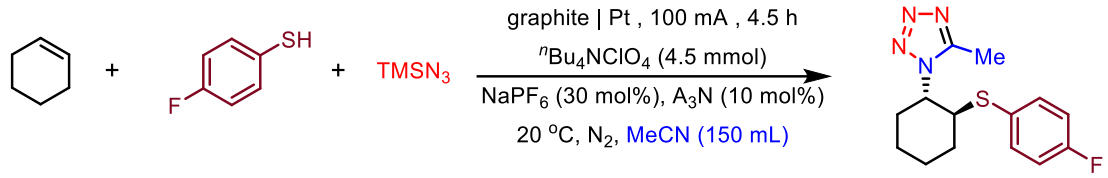

**Method A:** In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, $^{n}Bu_4NClO_4$ (0.3 mmol), tris(2,4-dibromophenyl)amine (10 mol%) and $NaPF_6$ (30 mol%) were added. The glassware was equipped with graphite (15 mm × 15 mm × 1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of $N_2$, alkene (2.0 equiv.), thiol (1.5 equiv.), $TMSN_3$ (0.3 mmol) and $CH_3CN$ (10 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA at 20 ℃ for 1.5 hours. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

**Method B:** In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, $^{n}Bu_4NClO_4$ (0.3 mmol), tris(2,4-dibromophenyl)amine (5 mol%) were added. The glassware was equipped with graphite (15 mm × 15 mm × 1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of $N_2$, alkene (2.0 equiv.), thiophenol/thiol (1.5 equiv.), $TMSN_3$ (0.3 mmol) and $CH_3CN$ (10 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 20 mA at 20 ℃ for 1.5 hours. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

**Method C:** In an oven-dried undivided three-necked glassware (25 mL) equipped with a stirring bar, $^{n}Bu_4NClO_4$ (0.3 mmol), tris(2,4-dibromophenyl)amine (5 mol%) were added. The glassware was equipped with graphite (15 mm × 15 mm × 1 mm) as the anode and platinum plate (15 mm × 15 mm × 0.3 mm) as the cathode. Under the protection of $N_2$, cyclohexene (2.4 equiv.), 1,2-diphenyldiselenide (0.25 mmol), $TMSN_3$ (1.2 equiv.) and $CH_3CN$ (10 mL) were injected respectively into the glassware

via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 15 mA at 20 ℃ for 2 hours. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

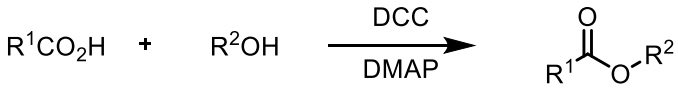
**Method D (Scale-up synthesis):**




2.0 equiv. 1.5 equiv. 4.5 mmol **4**, 51%, 0.6654g

In an oven-dried undivided cylindrical glassware (150 mL) equipped with a stirring bar, $^{n}Bu_4NClO_4$ (4.5 mmol), tris(2,4-dibromophenyl)amine (10 mol%) and $NaPF_6$ (30 mol%) were added. The glassware was equipped with graphite (30 mm × 30 mm × 0.1 mm) as the anode and platinum plate (30 mm × 30 mm × 1 mm) as the cathode. cyclohexene (2.0 equiv.), 4-fluorobenzenethiol (1.5 equiv.), $TMSN_3$ (4.5 mmol) and $CH_3CN$ (150 mL) were injected respectively into the glassware via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 100 mA at 20 ℃ for 4.5 hours. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired products.

**General procedure the synthesis of esters**

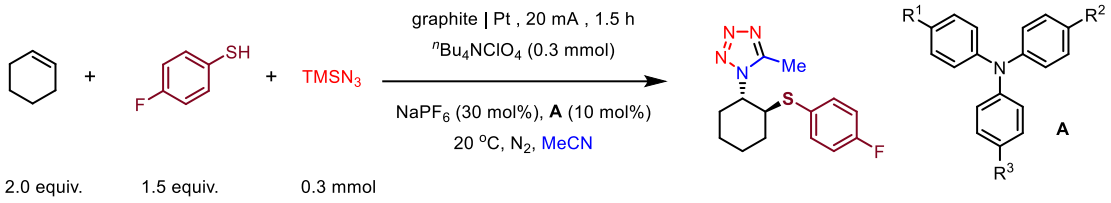



In an oven-dried 50 mL round-bottomed flask, DCC (6.5 mmol, 1.3 equiv.) and DMAP (2.5 mmol, 0.5 equiv.) were added sequentially to an ice-cold solution of the corresponding alcohol (5 mmol, 1.0 equiv.) and acid (5 mmol, 1.0 equiv.) in DCM (30 mL). After 30 min, the ice-water cooling bath was removed, and the resulting suspension was stirred vigorously at room temperature overnight. Then, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel (n-hexane/EtOAc) afforded the desired esters.

# 3. Optimization of reaction conditions

## 3.1 Optimization of conditions

Table 1. Screening of catalyst

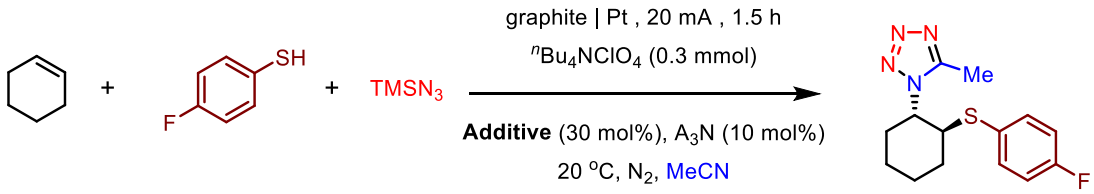



2.0 equiv. 1.5 equiv. 0.3 mmol

| Entry | Catalyst | $R^1$ | $R^2$ | $R^3$ | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | $A_1$ | I | I | I | 38 |
| 2 | $A_2$ | H | H | H | 30 |
| 3 | $A_3$ | Me | Me | Me | 40 |
| 4 | $A_4$ | H | H | Br | 45 |
| 5 | $A_5$ | Br | H | H | 35 |
| 6 | $A_6$ | H | Me | Me | 25 |
| 7 | $A_7$ | Br | Me | Me | 33 |
| 8 | $A_8$ | Br | Br | Br | 38 |

[a] Yield was determined by $^1$H NMR with 1,3,5-trimethoxybenzene as the internal standard.

Table 2. Screening of additive

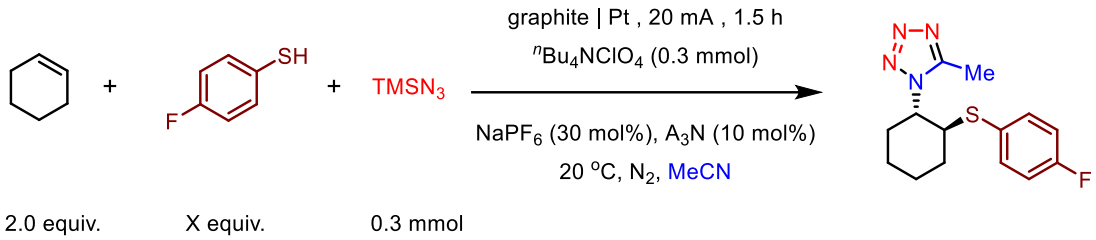



2.0 equiv. 1.5 equiv. 0.3 mmol

| Entry | Additive | Yield (%)[a] |
|---|---|---|
| 1 | $KPF_6$ | 45 |
| 2 | $AgPF_6$ | 42 |
| 3 | $NaBF_4$ | 53 |
| 4 | $NH_4PF_6$ | 39 |

[a] Yield was determined by $^1$H NMR with 1,3,5-trimethoxybenzene as the internal standard.

Table 3. Screening of the amount of thiophenol

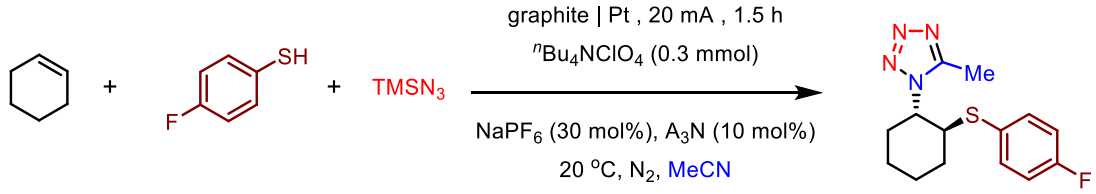



2.0 equiv. X equiv. 0.3 mmol

| Entry | X equiv. | Yield (%)[a] |
|---|---|---|
| 1 | 1.0 | 36 |
| 2 | 1.3 | 35 |
| 3 | 1.7 | 48 |
| 4 | 2.0 | 38 |

[a] Yield was determined by $^1$H NMR with 1,3,5-trimethoxybenzene as the internal standard.

Table 4. Screening of the amount of cyclohexene

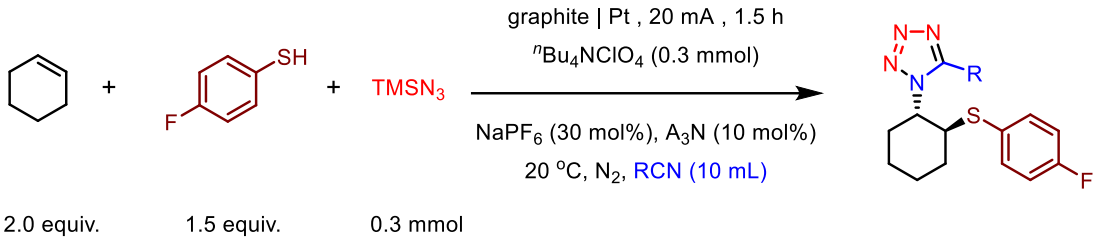



X equiv. 1.5 equiv. 0.3 mmol

| Entry | X equiv. | Yield (%)[a] |
|---|---|---|
| 1 | 1.0 | 25 |
| 2 | 1.3 | 32 |
| 3 | 1.7 | 36 |
| 4 | 2.3 | 30 |

[a] Yield was determined by $^1$H NMR with 1,3,5-trimethoxybenzene as the internal standard.

Table 5. Screening of nitrile sources



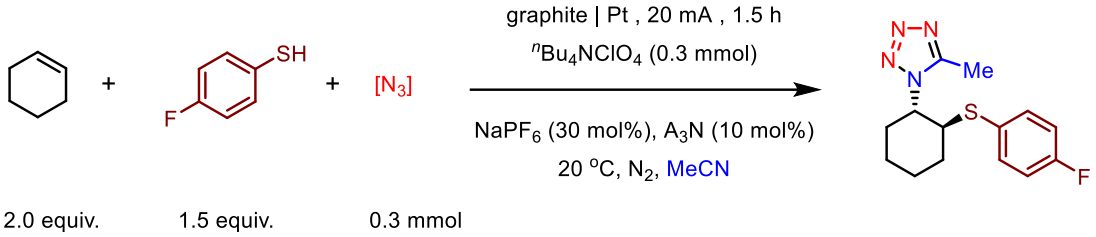

2.0 equiv. 1.5 equiv. 0.3 mmol

| Entry | R | Yield (%)[a] |
|---|---|---|
| 1 | Ph | n.d. |
| 2 | Bn | n.d. |
| 3 | $^{n}Pr$ | 28 |
| 4 | $^{i}Pr$ | 28 |

[a] isolated yleid. n.d. = not detected.

Under the standard conditions, the use of benzonitrile rendered the reaction mixture almost non-conductive and thus did not give any of the anticipated vicinal sulfenyltetrazole. Additionally, we also investigated other organonitriles, including phenylacetonitrile, butyronitrile, and isobutyronitrile. While butyronitrile and isobutyronitrile are compatible albeit with in low yield (28%), phenylacetonitrile was completely not reactive.

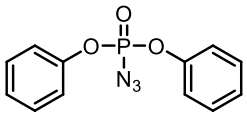
Table 6. Screening of $N_3$ sources




2.0 equiv. 1.5 equiv. 0.3 mmol

| Entry | [$N_3$] | Yield (%)[a] |
|---|---|---|
| 1 | $NaN_3$ | 8 |
| 2 | DPPA | n.d. |

[a] Yield was determined by $^1$H NMR with 1,3,5-trimethoxybenzene as the internal standard. n.d. = not detected.




DPPA

Employing $NaN_3$ in lieu of $TMSN_3$ under standard conditions only resulted in 8% yield of product. Despite the low yield, we anticipate a thorough optimization of reaction conditions using $NaN_3$ should be fruitful, especially when the reaction is used in APIs or large-scale processes. Another azide reagent, such as diphenylphosphoryl azide (DPPA), was found to be not compatible with the reaction.

Unfortunately, alkyne was not compatible under the electrochemical multicomponent reaction conditions yet as only the formation of disulfide was observed. Increasing the current did not change the situation but only further disrupted the alkyne to benzaldehyde.

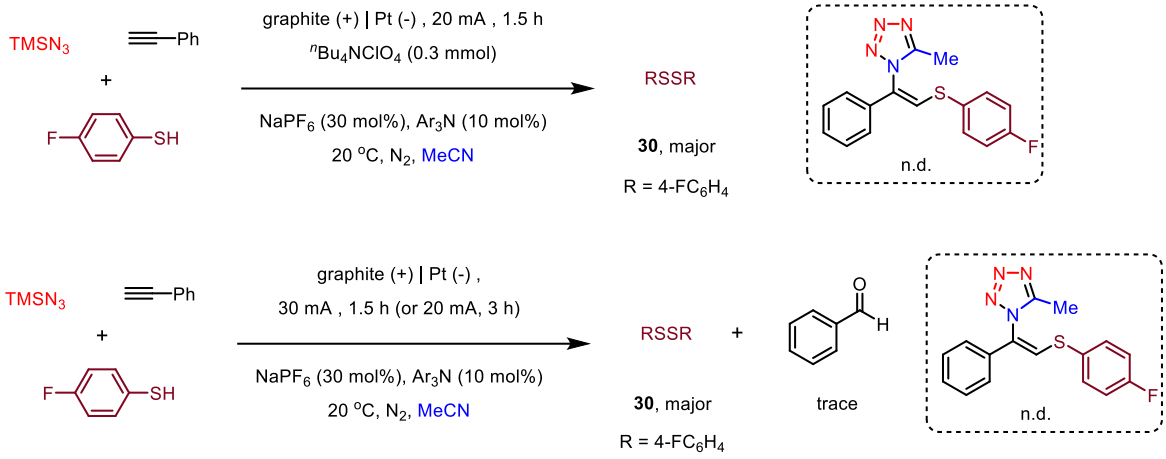



Figure 4. Reactivity of alkynes

## 3.2 Analysis of low reactivity

Two side reactions are responsible for the low yields for some substrates. First, besides the desired vicinal sulfenyltetrazolation of alkenes, we also observed a concomitant formation of vicinal azidosulfide byproduct. For instance, we isolated 10% yield of compound **6b** and 16% yield of compound **14b**, respectively. Second, the oxidation potential of the product ($E_{p/2}$ = 1.96 V vs SCE) is close to that of the 4-(trifluoromethyl)benzenethiol **7a** ($E_{p/2}$ = 1.69 V vs SCE) resulting in the unproductive overoxidation.

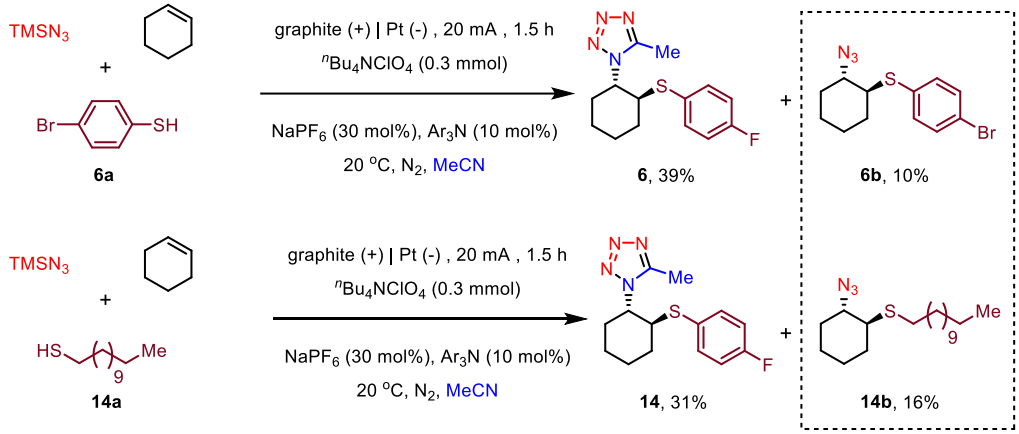



Figure 5. Analysis of by-products

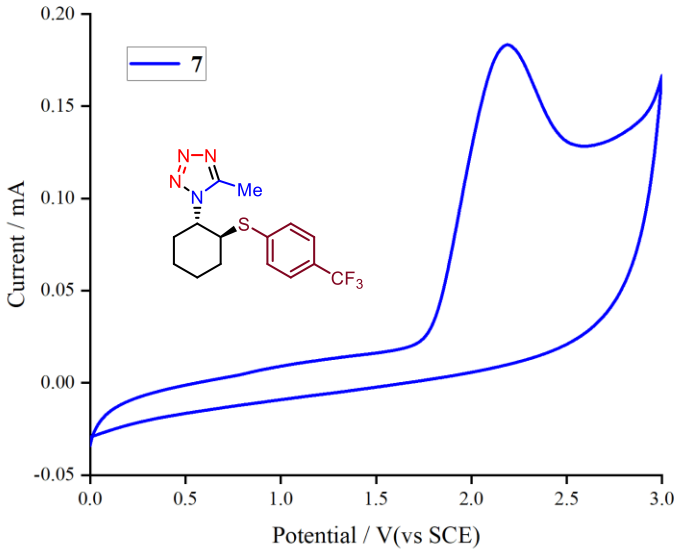



Figure 6. Cyclic voltammograms recorded in MeCN with $^{n}Bu_4NClO_4$ as the supporting electrolyte. **7** (3 mM).

## 3.3 Analysis of chemical oxidant

Analysing the reactivity of chemical oxidants using Selectfluor as an example: The use of selectfluor as the oxidant still failed to replicate the e-MCR reactivity. Despite achieving an exceptionally high conversion, the desired products were not detected. Instead, the major product of this reaction was disulfide **30** along with a trace amount of fluorosulfide **4b** (<5%).

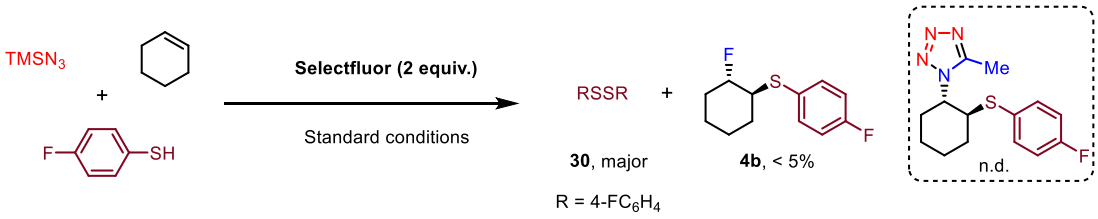
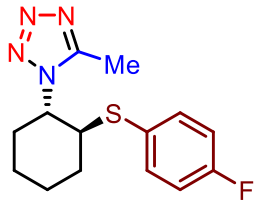



Figure 7. Reactivity of selectfluor

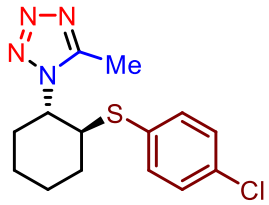
## 4. Characterization of products




**1-(2-((4-fluorophenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (4)**

Following **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 52.6 mg (60% yield) of **4** as a yellow oil.

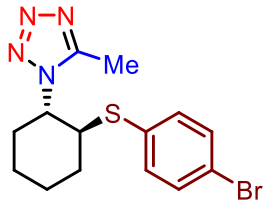
IR (neat, $cm^{-1}$): 2941(w), 2105(s), 1511(s), 1228(m), 838(m), 749(m), 535(m). $^{1}H$ NMR (400 MHz, Chloroform-d) δ 7.05 (dd, *J* = 8.6, 5.5 Hz, 2H), 6.86 (t, *J* = 8.6 Hz, 2H), 4.03 (td, *J* = 11.2, 4.4 Hz, 1H), 3.43 (td, *J* = 11.6, 4.2 Hz, 1H), 2.57 (s, 3H), 2.34 – 2.26 (m, 1H), 2.15 – 2.00 (m, 2H), 2.00 – 1.80 (m, 2H), 1.58 – 1.35 (m, 3H). $^{13}C$ NMR (101 MHz, Chloroform-d) δ 162.7 (d, *J* = 248.7 Hz), 151.6, 135.2 (d, *J* = 8.4 Hz), 127.9 (d, *J* = 3.4 Hz), 116.2 (d, *J* = 22.0 Hz), 62.2, 54.0, 34.3, 33.7, 25.7, 24.9, 9.4. $^{19}F$ NMR (471 MHz, Chloroform-d) δ -114.0. HRMS (ESI) calculated for $C_{14}H_{18}FN_4S^+$ $[M+H]^+$: 293.1231; found: 293.1226.




**1-(2-((4-chlorophenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (5)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 44.4 mg (48% yield) of **5** as a yellow oil.

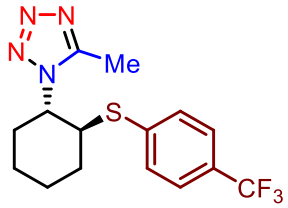
IR (neat, $cm^{-1}$): 3077(w), 2936(m), 1523(m), 1476(s), 1405(s), 1284(m), 820 (m). $^{1}H$ NMR (400 MHz, Chloroform-d) δ 7.16 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H), 4.04 (td, *J* = 11.3, 4.3 Hz, 1H), 3.52 (td, *J* = 11.5, 4.1 Hz, 1H), 2.59 (s, 3H), 2.33 (d, *J* = 13.7 Hz, 1H), 2.18 – 2.00 (m, 2H), 1.97 – 1.83 (m, 2H), 1.63 – 1.37 (m, 3H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 151.6, 134.2, 133.8, 131.4, 129.3, 62.2, 53.7, 34.3, 33.7, 25.8, 24.9, 9.5. HRMS (ESI) calculated for $C_{14}H_{18}ClN_4S^+$ $[M+H]^+$:309.0935; found: 309.0930.




**1-(2-((4-bromophenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (6)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 41.2 mg (39% yield) of **6** as a yellow oil.

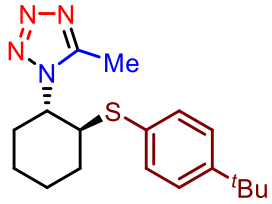
IR (neat, $cm^{-1}$): 3058(w), 2938(m), 1523(m), 1473(s), 1404(m), 1247(m), 818 (m).$^{1}$H NMR (500 MHz, Chloroform-d) δ 7.31 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 4.04 (td, *J* = 11.4, 4.3 Hz, 1H), 3.58 – 3.47 (td, *J* = 11.7, 4.1 Hz, 1H), 2.58 (s, 3H), 2.36 – 2.29 (m, 1H), 2.20 – 2.08 (m, 1H), 2.07 – 2.00 (m, 1H), 1.95 – 1.83 (m, 2H), 1.61 – 1.36 (m, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 151.6, 134.0, 132.2, 132.0, 122.3, 62.2, 53.6, 34.3, 33.7, 25.8, 24.9, 9.5. HRMS (ESI) calculated for $C_{14}H_{18}BrN_4S^+$ $[M+H]^+$: 353.0430; found: 353.0424.




**5-methyl-1-(2-((4-(trifluoromethyl)phenyl)thio)cyclohexyl)-1H-tetrazole (7)**

Followed **Method B**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 47.2 mg (46% yield) of **7** as a yellow oil.

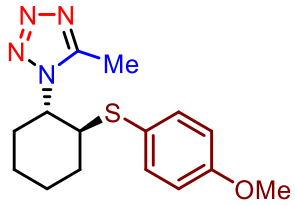
IR (neat, $cm^{-1}$): 3069(w), 2941(m), 1524(m), 1402(m), 1325(s), 1282(m), 832 (m). $^{1}$H NMR (400 MHz, Chloroform-d) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 4.07 (td, *J* = 11.4, 4.3 Hz, 1H), 3.72 – 3.61 (td, *J* = 11.6, 4.1 Hz, 1H), 2.58 (s, 3H), 2.36 (d, *J* = 14.9 Hz, 1H), 2.23 – 1.86 (m, 4H), 1.72 – 1.32 (m, 3H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 151.6, 138.3, 131.1, 129.4 (q, *J* = 32.8 Hz), 125.9 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.2 Hz), 62.2, 52.9, 34.3, 33.7, 25.8, 24.9, 9.4. $^{19}$F NMR (376 MHz, Chloroform-d) δ -62.7. HRMS (ESI) calculated for $C_{15}H_{18}F_3N_4S^+$ $[M+H]^+$: 343.1199; found: 343.1196.



**1-(2-((4-(tert-butyl)phenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (8)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 52.4 mg (53% yield) of **8** as a yellow oil.

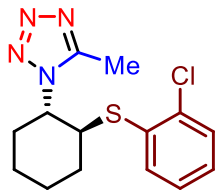
IR (neat, $cm^{-1}$): 3025(w), 2949(m), 1523(m), 1489(m), 1402(s), 1268(m), 829 (m). $^{1}H$ NMR (500 MHz, Chloroform-d) δ 7.20 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 4.04 (td, *J* = 11.3, 4.3 Hz, 1H), 3.47 (td, *J* = 11.6, 4.1 Hz, 1H), 2.57 (s, 3H), 2.38 – 2.30 (m, 1H), 2.17 – 1.98 (m, 2H), 1.97 – 1.77 (m, 2H), 1.56 (d, *J* = 10.0 Hz, 1H), 1.48 – 1.33 (m, 2H), 1.25 (s, 9H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 151.6, 151.3, 132.9, 129.1, 126.1, 62.0, 53.3, 34.6, 34.5, 33.6, 31.2, 25.7, 24.9, 9.5. HRMS (ESI) calculated for $C_{18}H_{27}N_4S^+$ $[M+H]^+$: 331.1951; found: 331.1944.



**1-(2-((4-methoxyphenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (9)**

Followed **Method B**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 45.4 mg (50% yield) of **9** as a yellow oil.

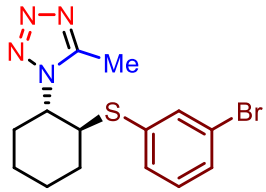
IR (neat, $cm^{-1}$): 3004(w), 2937(m), 1493(m), 1406(m), 1245(s), 1029(m), 830 (m).$^{1}H$ NMR (400 MHz, Chloroform-d) δ 7.04 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 2H), 4.02 (td, *J* = 11.3, 4.4 Hz, 1H), 3.76 (s, 3H), 3.39 (td, *J* = 11.5, 4.2 Hz, 1H), 2.60 (s, 3H), 2.34 – 2.30 (m, 1H), 2.13 – 2.00 (m, 2H), 1.93 – 1.83 (m, 2H), 1.56 – 1.38 (m, 3H). $^{13}C$ NMR (101 MHz, Chloroform-d) δ 160.0, 151.6, 135.6, 123.0, 114.7, 62.0, 55.4, 53.9, 34.3, 33.7, 25.7, 24.9, 9.5. HRMS (ESI) calculated for $C_{15}H_{21}N_4OS^+$ $[M+H]^+$: 305.1431; found: 305.1425.




**1-(2-((2-chlorophenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (10)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 37.2 mg (41% yield) of **10** as a yellow oil.

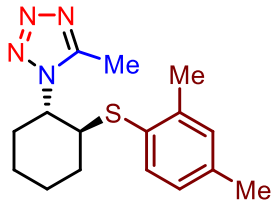
IR (neat, $cm^{-1}$): 3056(w), 2938(m), 1524(m), 1450(s), 1405(m), 1249(m), 755 (m). $^{1}H$ NMR (500 MHz, Chloroform-d) δ 7.30 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.12 (td, *J* = 7.6, 1.8 Hz, 1H), 7.07 (td, *J* = 7.5, 1.5 Hz, 1H), 7.00 (dd, *J* = 7.7, 1.7 Hz, 1H), 4.14 (td, *J* = 11.3, 4.2 Hz, 1H), 3.73 (ddd, *J* = 12.3, 10.7, 4.2 Hz, 1H), 2.62 (s, 3H), 2.27 – 2.13 (m, 1H), 2.05 – 2.00 (m, 1H), 1.99 – 1.88 (m, 2H), 1.67 – 1.56 (m, 2H), 1.53 – 1.40 (m, 2H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 151.5, 136.3, 133.2, 132.0, 130.1, 129.0, 127.3, 63.1, 52.0, 33.7, 33.6, 25.8, 25.0, 9.5. HRMS (ESI) calculated for $C_{14}H_{18}ClN_4S^+$ $[M+H]^+$: 309.0935; found: 309.0930.




**1-(2-((3-bromophenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (11)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 42.5 mg (40% yield) of **11** as a yellow oil.

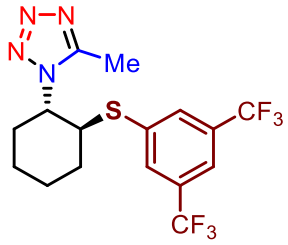
IR (neat, $cm^{-1}$): 3059(w), 2938(m), 1523(m), 1459(s), 1404(s), 1285(m), 755 (m), 680(m). $^{1}H$ NMR (500 MHz, Chloroform-d) δ 7.32 (ddd, *J* = 7.9, 1.9, 1.1 Hz, 1H), 7.29 (t, *J* = 1.8 Hz, 1H), 7.06 (t, *J* = 7.8 Hz, 1H), 6.99 (ddd, *J* = 7.8, 1.8, 1.1 Hz, 1H), 4.05 (td, *J* = 11.5, 4.3 Hz, 1H), 3.60 (ddd, *J* = 12.3, 10.8, 4.2 Hz, 1H), 2.59 (s, 3H), 2.40 – 2.31 (m, 1H), 2.23 – 2.13 (m, 1H), 2.07 – 2.00 (m, 1H), 1.99 – 1.85 (m, 2H), 1.57 – 1.39 (m, 3H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 151.6, 135.1, 134.7, 131.0, 130.7, 130.5, 122.7, 62.4, 53.2, 34.2, 33.7, 25.8, 25.0, 9.5. HRMS (ESI) calculated for $C_{14}H_{18}BrN_4S^+$ $[M+H]^+$: 353.0430; found: 353.0423.



**1-(2-((2,4-dimethylphenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (12)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 38.2 mg (42% yield) of **12** as a yellow oil.

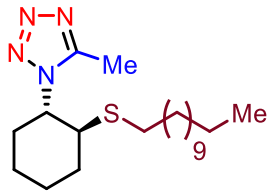
IR (neat, $cm^{-1}$): 3006(w), 2937(m), 1524(m), 1477(m), 1404(s), 1283(m), 877 (m), 816(s). $^{1}H$ NMR (500 MHz, Chloroform-d) δ 6.96 (d, *J* = 7.9 Hz, 2H), 6.88 – 6.81 (m, 1H), 4.07 (td, *J* = 11.4, 4.3 Hz, 1H), 3.41 (ddd, *J* = 12.2, 10.9, 4.3 Hz, 1H), 2.60 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 2.08 – 1.78 (m, 4H), 1.64 – 1.52 (m, 1H), 1.53 – 1.31 (m, 2H), 1.29 – 1.23 (m, 1H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 151.7, 140.9, 138.6, 134.4, 131.5, 128.3, 127.4, 61.9, 52.8, 34.4, 33.7, 25.7, 25.1, 21.1, 20.8, 9.5. HRMS (ESI) calculated for $C_{16}H_{23}N_4^+$ $[M+H]^+$: 303.1638; found: 303.1632.



**1-(2-((3,5-bis(trifluoromethyl)phenyl)thio)cyclohexyl)-5-methyl-1H-tetrazole (13)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 38.1 mg (31% yield) of **13** as a yellow oil.

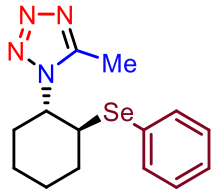
IR (neat, $cm^{-1}$): 3077(w), 2942(m), 1523(m), 1451(m), 1405(m), 1275(s), 844 (m), 713(m). $^{1}H$ NMR (400 MHz, Chloroform-d) δ 7.64 (s, 1H), 7.50 (s, 2H), 4.10 (td, *J* = 11.3, 4.2 Hz, 1H), 3.75 (td, *J* = 11.4, 4.0 Hz, 1H), 2.58 (s, 3H), 2.38 – 2.35 (m, 1H), 2.21 – 1.91 (m, 4H), 1.64 – 1.45 (m, 3H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 151.5, 136.6, 132.3 (q, *J* = 33.6 Hz), 130.9 (d, *J* = 3.7 Hz), 122.8 (q, *J* = 273.3 Hz), 121.3 (dt, *J* = 7.6, 3.7 Hz), 62.5, 53.0, 33.9, 33.7, 25.6, 24.8, 9.2. $^{19}F$ NMR (471 MHz, Chloroform-d) δ -63.0. HRMS (ESI) calculated for $C_{16}H_{17}F_6N_4S^+$ $[M+H]^+$: 411.1073; found: 411.1065.




**1-(2-(dodecylthio)cyclohexyl)-5-methyl-1H-tetrazole (14)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 33.9 mg (31% yield) of **14** as a yellow oil.

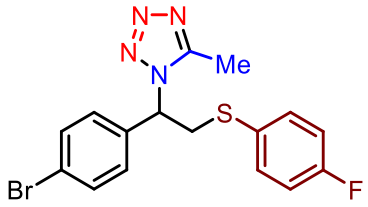
IR (neat, $cm^{-1}$): 2923(s), 1524(m), 1489(m), 1405(m), 1277(m), 820 (m), 713(m). $^{1}H$ NMR (500 MHz, Chloroform-d) δ 3.93 (td, 1H), 3.05 (td, 1H), 2.61 (s, 3H), 2.36 – 2.26 (m, 1H), 2.26 – 2.14 (m, 1H), 2.07 – 1.98 (m, 2H), 1.98 – 1.82 (m, 3H), 1.55 – 1.34 (m, 2H), 1.31 – 1.14 (m, 21H), 0.87 (t, *J* = 7.0 Hz, 3H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 152.0, 63.4, 49.8, 34.8, 33.5, 32.0, 29.9, 29.8, 29.75, 29.74 29.7, 29.6, 29.5, 29.2, 28.7, 26.0, 25.1, 22.8, 14.3, 9.6. HRMS (ESI) calculated for $C_{20}H_{39}N_4S^+$ $[M+H]^+$: 367.2890; found: 367.2885.




**5-methyl-1-(2-(phenylselanyl)cyclohexyl)-1H-tetrazole (15)**

Followed **Method C**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 26.1 mg (32% yield) of **15** as a yellow oil.

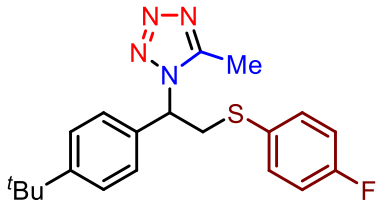
IR (neat, $cm^{-1}$): 2936(w), 1523(s), 1403(m), 741(m), 692(m). $^{1}H$ NMR (400 MHz, Chloroform-d) δ 7.26 (d, *J* = 7.8 Hz, 3H), 7.22 – 7.16 (m, 2H), 4.15 (td, *J* = 11.3, 4.4 Hz, 1H), 3.68 (td, *J* = 11.0, 4.3 Hz, 1H), 2.57 (s, 3H), 2.50 – 2.42 (m, 1H), 2.13 – 1.94 (m, 3H), 1.71 – 1.57 (m, 2H), 1.56 – 1.31 (m, 2H). $^{13}C$ NMR (101 MHz, Chloroform-d) δ 151.2, 135.0, 129.3, 128.4, 127.2, 63.0, 47.8, 34.7, 34.2, 26.5, 25.1, 9.5. HRMS (ESI) calculated for $C_{14}H_{19}N_4Se^+$ $[M+H]^+$: 323.0769; found: 323.0773.




**1-(1-(4-bromophenyl)-2-((4-fluorophenyl)thio)ethyl)-5-methyl-1H-tetrazole (16)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 43.8 mg (37% yield) of **16** as a yellow oil.

IR (neat, $cm^{-1}$): 2977(w), 1524(m), 1489(s), 1398(m), 1224(m), 828 (m). $^{1}H$ NMR (400 MHz, Chloroform-d) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.24 (m, 2H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.22 (dd, *J* = 9.3, 5.5 Hz, 1H), 3.96 (dd, *J* = 14.3, 9.3 Hz, 1H), 3.66 (dd, *J* = 14.3, 5.6 Hz, 1H), 2.38 (s, 3H). $^{13}C$ NMR (101 MHz, Chloroform-d) δ 162.6 (d, *J* = 249.0 Hz), 151.8, 135.3, 133.8 (d, *J* = 8.2 Hz), 132.6, 128.8, 128.7, 123.8, 116.8 (d, *J* = 22.0 Hz), 61.6, 41.1, 9.1. $^{19}F$ NMR (376 MHz, Chloroform-d) δ -112.7 (ddd, *J* = 13.4, 8.5, 5.0 Hz). HRMS (ESI) calculated for $C_{16}H_{14}BrFN_4NaS^+$ $[M+Na]^+$: 414.9999; found: 414.9990.

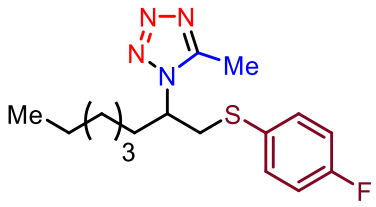



**1-(1-(4-(tert-butyl)phenyl)-2-((4-fluorophenyl)thio)ethyl)-5-methyl-1H-tetrazole (17)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 46.9 mg (43% yield) of **17** as a yellow oil.

$^{1}H$ NMR (400 MHz, Chloroform-d) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.03 (t, *J* = 8.6 Hz, 2H), 5.28 (dd, *J* = 9.6, 5.1 Hz, 1H), 4.03 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.71 (dd, *J* = 14.3, 5.1 Hz, 1H), 2.40 (s, 3H), 1.30 (s, 9H). $^{13}C$ NMR (101 MHz, Chloroform-d) δ 162.5 (d, *J* = 248.5 Hz), 152.7, 151.8, 133.7 (d, *J* = 8.3 Hz), 133.3, 129.1 (d, *J* = 3.4 Hz), 126.7, 126.3, 116.7 (d, *J* = 22.0 Hz), 62.0, 41.0, 34.8, 31.3, 9.2. $^{19}F$ NMR (376 MHz, Chloroform-d) δ -113.3 (ddd, *J* = 13.7, 8.6,

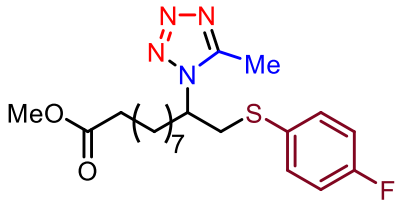
5.1 Hz). HRMS (ESI) calculated for $C_{20}H_{23}FN_4NaS^+$ $[M+Na]^+$: 393.1520; found: 393.1511.



**1-(1-((4-fluorophenyl)thio)octan-2-yl)-5-methyl-1H-tetrazole (18)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 41.4 mg (42% yield) of **18** as a yellow oil.

IR (neat, $cm^{-1}$): 3066(w), 2928(m), 1524(m), 1491(s), 1405(m), 1228(m), 830 (m). $^1H$ NMR (400 MHz, Chloroform-d) δ 7.22 (dd, *J* = 8.6, 5.3 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.28 – 4.16 (m, 1H), 3.40 (d, *J* = 7.5 Hz, 2H), 2.42 (s, 3H), 2.17 – 2.03 (m, 1H), 2.03 – 1.90 (m, 1H), 1.29 – 1.08 (m, 8H), 0.83 (t, *J* = 6.8 Hz, 3H).$^{13}C$ NMR (101 MHz, Chloroform-d) δ 162.4 (d, *J* = 248.4 Hz), 152.2, 132.9 (d, *J* = 8.2 Hz), 129.2 (d, *J* = 3.4 Hz)., 116.7 (d, *J* = 22.0 Hz), 59.3, 40.6, 34.8, 31.5, 28.7, 25.9, 22.5, 14.1, 9.2. $^{19}F$ NMR (376 MHz, Chloroform-d) δ -113.5 (td, *J* = 8.6, 4.2 Hz). HRMS (ESI) calculated for $C_{16}H_{24}FN_4S^+$ $[M+H]^+$: 323.1700; found: 323.1694.

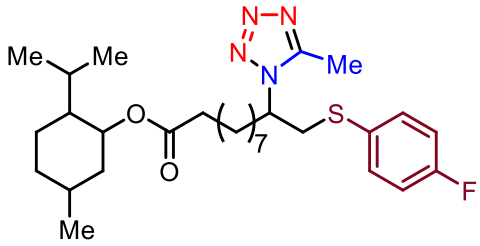


**methyl 5-((4-fluorophenyl)thio)-4-(5-methyl-1H-tetrazol-1-yl)pentanoate (19)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 48.0 mg (40% yield) of **19** as a yellow oil.

IR (neat, $cm^{-1}$): 3067(w), 2928(m), 1733(m), 1524(m), 1490(s), 1404(m), 1223(s), 830 (m). $^1H$ NMR (400 MHz, Chloroform-d) δ 7.20 (dd, *J* = 8.4, 5.2 Hz, 2H), 6.97 (t, *J* = 8.5 Hz, 2H), 4.21 (dq, *J* = 11.6, 6.7 Hz, 1H), 3.63 (s, 3H), 3.39 (d, *J* = 7.0 Hz, 2H), 2.41 (s, 3H), 2.25 (t, *J* = 7.5 Hz, 2H), 2.14 – 2.02 (m, 1H), , 2.00 – 1.88 (m,1H), 1.61 – 1.50 (m, 2H), 1.29 – 1.06 (m, 10H). $^{13}C$ NMR (101 MHz, Chloroform-d) δ 174.3, 162.3 (d, *J* = 248.4 Hz), 152.2, 132.8 (d, *J* = 8.1 Hz), 129.1 (d, *J* = 3.5 Hz), 116.6 (d, *J* = 22.0

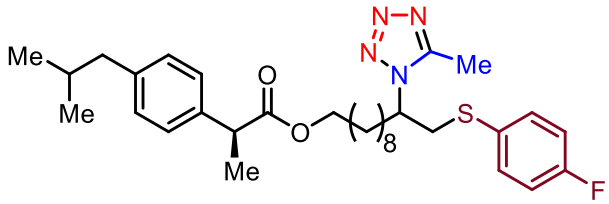
Hz), 59.2, 51.5, 40.5, 34.7, 34.1, 29.08, 29.05, 29.0, 28.9, 25.9, 24.9, 9.1. $^{19}$F NMR (376 MHz, Chloroform-d) δ -113.5 (dt, *J* = 8.9, 3.9 Hz). HRMS (ESI) calculated for $C_{20}H_{30}FN_4O_2S^+$ $[M+H]^+$: 409.2068; found: 409.2063.




**2-isopropyl-5-methylcyclohexyl 11-((4-fluorophenyl)thio)-10-(5-methyl-1H-tetrazol-1-yl)undecanoate (20)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 67.5 mg (42% yield) of **20** as a yellow oil.

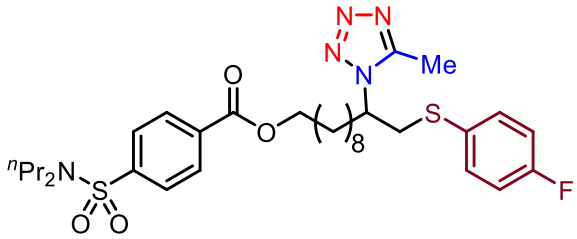
IR (neat, $cm^{-1}$): 3068(w), 2926(s), 1725(s), 1524(m), 1491(s), 1227(m), 830(m), 728(m). $^1$H NMR (500 MHz, Chloroform-d) δ 7.21 (dd, *J* = 8.8, 5.1 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.65 (td, *J* = 10.9, 4.4 Hz, 1H), 4.26 – 4.17 (m, 1H), 3.42 – 3.37 (m, 2H), 2.41 (s, 3H), 2.23 (t, *J* = 7.6 Hz, 2H), 2.14 – 2.03 (m, 1H), 2.00 – 1.91 (m, 2H), 1.88 – 1.78 (m, 1H), 1.66 (m, 2H), 1.65 – 1.48 (m, 2H), 1.51 – 1.40 (m, 1H), 1.39 – 1.29 (m, 1H), 1.28 – 1.17 (m, 10H), 0.96 – 0.84 (m, 9H), 0.75 – 0.70 (m, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 173.5, 162.3 (d, *J* = 248.5 Hz), 152.2, 132.9 (d, *J* = 8.1 Hz), 129.2 (d, *J* = 3.4 Hz), 116.7 (d, *J* = 21.8 Hz), 74.0, 59.2, 47.1, 41.1, 40.6, 34.8, 34.4, 31.5, 29.14, 29.06, 29.0, 26.4, 26.0, 25.1, 23.5, 22.1, 20.9, 16.4, 9.2. $^{19}$F NMR (471 MHz, Chloroform-d) δ -113.4. HRMS (ESI) calculated for $C_{29}H_{46}FN_4O_2S^+$ $[M+H]^+$: 533.3320; found: 533.3311.




**11-((4-fluorophenyl)thio)-10-(5-methyl-1H-tetrazol-1-yl)undecyl (2S)-2-(4-isobutylphenyl)propanoate (21)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 4:1) to give 79.8 mg (45% yield) of **21** as a yellow oil.

IR (neat, $cm^{-1}$): 3010(w), 2925(m), 1725(s), 1512(m), 1491(s), 1491(m), 1228(m), 829(m). $^{1}H$ NMR (500 MHz, Chloroform-d) δ 7.24 – 7.17 (m, 4H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.27 – 4.17 (m, 1H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.66 (d, *J* = 7.2 Hz, 1H), 3.43 – 3.36 (m, 2H), 2.43 (d, *J* = 7.1 Hz, 5H), 2.15 – 2.04 (m, 1H), 2.01 – 1.90 (m, 1H), 1.88 – 1.77 (m, 1H), 1.57 – 1.50 (m, 2H), 1.47 (d, *J* = 7.2 Hz, 3H), 1.20 – 1.13 (m, 12H), 0.88 (d, *J* = 6.6 Hz, 6H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 175.0, 162.3 (d, *J* = 248.4 Hz), 152.2, 140.5, 138.0, 132.9 (d, *J* = 8.1 Hz), 129.4, 129.2 (d, *J* = 3.5 Hz), 127.3, 116.7 (d, *J* = 22.1 Hz), 64.8, 59.3, 45.3, 45.1, 40.6, 34.8, 30.3, 29.3, 29.2, 29.1, 29.0, 28.6, 26.0, 25.8, 22.5, 18.6, 9.2. $^{19}F$ NMR (471 MHz, Chloroform-d) δ -113.3. HRMS (ESI) calculated for $C_{32}H_{46}FN_4O_2S^+$ $[M+H]^+$: 569.3320; found: 569.3308.

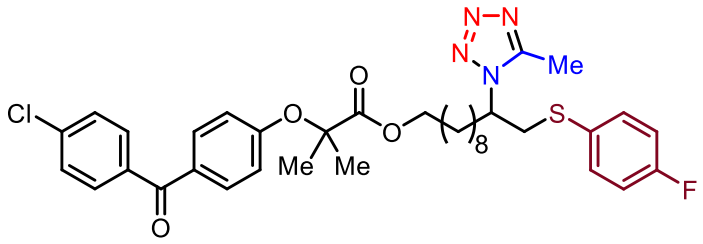



**11-((4-fluorophenyl)thio)-10-(5-methyl-1H-tetrazol-1-yl)undecyl 4-(N,N-dipropylsulfamoyl)benzoate (22)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 78.8 mg (40% yield) of **22** as a yellow oil.

IR (neat, $cm^{-1}$): 3066(w), 2928(m), 1719(s), 1490(s), 1273(m), 830(m), 739(m). $^{1}H$ NMR (400 MHz, Chloroform-d) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.21 (dd, *J* = 8.6, 5.3 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 4.28 – 4.18 (m, 1H), 3.40 (d, *J* = 7.0 Hz, 2H), 3.12 – 3.04 (m, 4H), 2.41 (s, 3H), 2.17 – 2.02 (m, 1H), 2.02 – 1.89 (m, 1H), 1.79 – 1.68 (m, 3H), 1.58 – 1.46 (m, 4H), 1.44 – 1.32 (m, 2H), 1.33 – 1.26 (m, 2H), 1.25 – 1.15 (m, 7H), 0.85 (t, *J* = 7.4 Hz, 6H). $^{13}C$ NMR (101 MHz, Chloroform-d) δ 165.4, 162.3 (d, *J* = 248.4 Hz), 152.2, 144.3, 133.9, 132.9 (d, *J* = 8.2 Hz), 130.3, 129.2 (d, *J* = 3.5 Hz), 127.1, 116.6 (d, *J* = 22.0 Hz), 65.8, 59.3, 50.0,

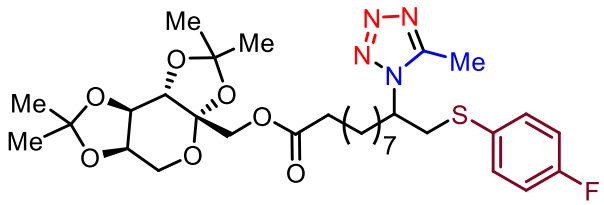
40.6, 34.7, 29.4, 29.24, 29.22, 29.0, 28.7, 26.0, 25.9, 22.0, 11.3, 9.2. $^{19}$F NMR (376 MHz, Chloroform-d) δ -113.5 (ddd, *J* = 13.2, 8.4, 4.9 Hz). HRMS (ESI) calculated for $C_{32}H_{47}FN_5O_4S_2^+$ $[M+H]^+$: 648.3048; found: 648.3035.



**11-((4-fluorophenyl)thio)-10-(5-methyl-1H-tetrazol-1-yl)undecyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (23)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 60.6 mg (30% yield) of **23** as a yellow oil.

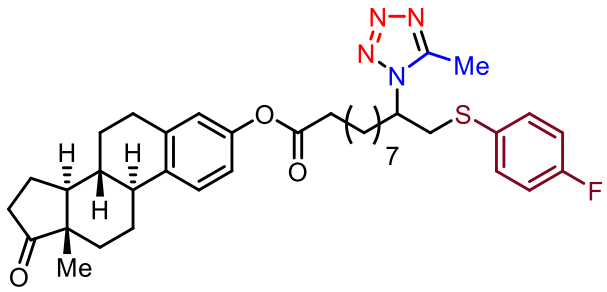
IR (neat, $cm^{-1}$): 2993(w), 2927(m), 1736(s), 1653(s), 1598(s), 1491(m), 1250(m), 834(m), 726(m). $^1$H NMR (500 MHz, Chloroform-d) δ 7.69 (dd, *J* = 15.5, 8.7 Hz, 4H), 7.46 – 7.41 (m, 2H), 7.21 (dd, *J* = 8.8, 5.1 Hz, 2H), 7.01 – 6.94 (m, 2H), 6.87 – 6.81 (m, 2H), 4.27 – 4.17 (m, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 3.39 (d, *J* = 6.7 Hz, 2H), 2.41 (s, 3H), 2.16 – 2.01 (m, 1H), 1.98 – 1.88 (m, 1H), 1.66 (s, 6H), 1.60 – 1.51 (m, 2H), 1.19 – 1.06 (m, 12H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 194.3, 173.9, 162.3 (d, *J* = 248.4 Hz), 159.8, 152.2, 138.5, 136.5, 132.8, 132.1, 131.3, 130.3, 129.2 (d, *J* = 3.4 Hz), 128.7, 117.3, 116.7 (d, *J* = 22.3 Hz), 79.5, 65.9, 59.3, 40.6, 34.7, 29.3, 29.2, 29.1, 29.0, 28.4, 25.9, 25.8, 25.6, 25.5, 9.2. $^{19}$F NMR (471 MHz, Chloroform-d) δ -114.9. HRMS (ESI) calculated for $C_{36}H_{43}ClFN_4O_4S^+$ $[M+H]^+$: 681.2672; found: 681.2661.



**((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 11-((4-fluorophenyl)thio)-10-(5-methyl-1H-tetrazol-1-yl)undecanoate (24)**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 73.2 mg (38% yield) of **24** as a yellow oil.

IR (neat, $cm^{-1}$): 3069(w), 2936(m), 1745(s), 1524(w), 1491(m), 1491(m), 1251(m), 832(m), 731(m).$^{1}$H NMR (500 MHz, Chloroform-d) δ 7.23 – 7.16 (m, 2H), 6.96 (t, *J* = 8.6 Hz, 2H), 4.57 (dd, *J* = 7.9, 2.6 Hz, 1H), 4.36 (d, *J* = 11.6 Hz, 1H), 4.27 (d, *J* = 2.6 Hz, 1H), 4.25 – 4.16 (m, 2H), 3.99 (d, *J* = 11.7 Hz, 1H), 3.87 (dd, *J* = 12.9, 1.9 Hz, 1H), 3.73 (d, *J* = 12.8 Hz, 1H), 3.38 (d, *J* = 7.0 Hz, 2H), 2.40 (s, 3H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.13 – 2.01 (m, 1H), 1.99 – 1.84 (m, 1H), 1.57 (t, *J* = 7.5 Hz, 2H), 1.51 (s, 3H), 1.44 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H), 1.24 – 1.16 (m, 10H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 173.0, 162.3 (d, *J* = 248.4 Hz), 152.2, 132.8 (d, *J* = 8.1 Hz), 129.1 (d, *J* = 3.4 Hz), 116.6 (d, *J* = 22.1 Hz), 109.2, 108.8, 101.6, 70.8, 70.6, 70.1, 65.2, 61.3, 59.2, 40.5, 34.7, 34.1, 29.1, 29.03, 28.99, 28.9, 26.6, 25.9, 25.9, 25.3, 24.7, 24.1, 9.1. $^{19}$F NMR (471 MHz, Chloroform-d) δ -113.4 (t, *J* = 6.9 Hz). HRMS (ESI) calculated for $C_{31}H_{46}FN_4O_7S^+$ $[M+H]^+$: 637.3066; found: 637.3052.



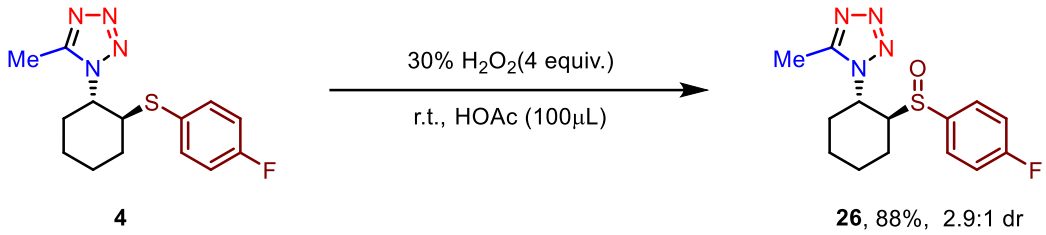

**(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 11-((4-fluorophenyl)thio)-10-(5-methyl-1H-tetrazol-1-yl)undecanoate (25)**

Followed **Method B**, the desired pure product was purified using silica gel chromatography (PE:EA = 2:1) to give 79.4 mg (41% yield) of **25** as a yellow oil.

IR (neat, $cm^{-1}$): 3061(w), 2927(m), 1736(s), 1524(m), 1491(s), 1223(m), 823(m), 729(m). $^{1}$H NMR (400 MHz, Chloroform-d) δ 7.32 – 7.20 (m, 3H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.88 – 6.78 (m, 2H), 4.30 – 4.19 (m, 1H), 3.42 (d, *J* = 6.9 Hz, 2H), 2.94 – 2.88 (m, 2H), 2.52 (q, *J* = 8.9, 8.1 Hz, 3H), 2.44 (s, 3H), 2.32 – 1.93 (m, 8H), 1.72 – 1.16 (m, 18H), 0.92 (s, 3H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 220.9, 172.6, 162.3 (d, *J* =

248.5 Hz), 152.2, 148.7, 138.1, 137.4, 132.8 (d, *J* = 8.1 Hz), 129.1 (d, *J* = 3.3 Hz), 126.5, 121.7, 118.8, 116.6 (d, *J* = 21.9 Hz), 59.2, 50.5, 48.0, 44.2, 40.5, 38.1, 35.9, 34.7, 34.4, 31.6, 29.5, 29.08, 29.06, 28.99, 28.96, 26.4, 25.9, 25.8, 24.9, 21.7, 13.9, 9.2. $^{19}$F NMR (376 MHz, Chloroform-d) δ -113.4 (ddd, J = 13.5, 8.6, 5.0 Hz). HRMS (ESI) calculated for $C_{37}H_{48}FN_4O_3S^+$ $[M+H]^+$: 647.3426; found: 647.3412.

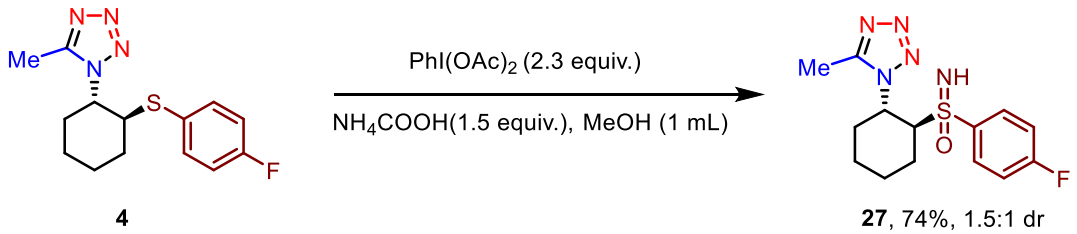
## 5. Derivatization of the products




The mixture solution of **4** ( 0.1 mmol, 1.0 equiv.) , hydrogen peroxide (0.4 mmol) and glacial acetic acid (100 μL) was stirred at room temperature for 1.5 h.[1] The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (PE:EA=1:2) to give the desired product (**26**, 27 mg, 88% yield, dr = 2.9:1) as a white solid.

**1-(2-((4-fluorophenyl)sulfinyl)cyclohexyl)-5-methyl-1H-tetrazole (26)**

IR (neat, $cm^{-1}$): 2934(w), 1588(s), 1492(s), 1224(m), 836(m), 729(m), 534(m). $^{1}H$ NMR (500 MHz, Chloroform-d) δ 7.43 (dd, *J* = 8.8, 5.0 Hz, 8.5H), 7.25 – 7.17 (m, 9.2H), 7.06 – 7.01 (m, 3.7H), 4.64 (ddd, *J* = 11.9, 10.2, 4.7 Hz, 1H), 4.55 (td, *J* = 11.5, 4.8 Hz, 4.3H), 3.76 – 3.57 (m, 1H), 3.26 – 3.17 (m, 4.3H), 2.71 (s, 12.9H), 2.64 (s, 3H), 2.26 – 1.86 (m, 18.4H), 1.49 – 1.17 (m, 24H). $^{13}C$ NMR (126 MHz, Chloroform-d) δ 164.5 (d, *J* = 250.9 Hz), 152.9, 152.3, 136.0(d, *J* = 3.0 Hz), 134.8 (d, *J* = 2.8 Hz), 126.5 (d, *J* = 8.9 Hz), 124.6 (d, *J* = 8.8 Hz), 116.9 (d, *J* = 22.6 Hz), 116.8 (d, *J* = 22.7 Hz), 65.9, 64.2, 56.3, 51.9, 33.7, 29.0, 24.9, 24.5, 24.3, 24.0, 19.4, 9.3, 9.0. $^{19}F$ NMR (471 MHz, Chloroform-d) δ -108.3 (t, *J* = 6.7 Hz), -108.5 (t, *J* = 10.1 Hz). HRMS (ESI) calculated for $C_{14}H_{18}FN_4OS^+$ $[M+H]^+$: 309.1180; found: 309.1182.

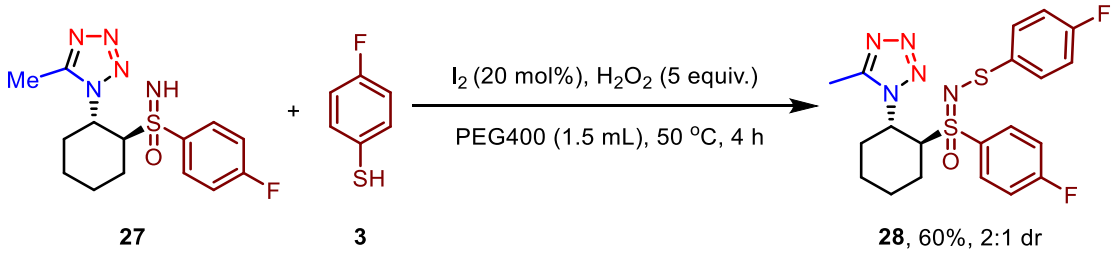



The mixture solution of **4** ( 0.1 mmol, 1.0 equiv.) , $NH_4COOH$ (1.5 equiv.), $PhI(OAC)_2$ (2.3 equiv.) and MeOH (1 mL) was stirred at room temperature for 1.5 h.[2]

The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (PE : EA=1:3) to give the desired product (**27**, 24 mg, 74% yield, dr = 1.5:1) as a yellow solid.

**(4-fluorophenyl)(imino)(2-(5-methyl-1*H*-tetrazol-1-yl)cyclohexyl)-λ$^6$-sulfanone (27)**

IR (neat, cm$^{-1}$): 3262(m), 2941(w), 1588(s), 1490(s), 1229(m), 841(m), 734(m), 563(m). $^1$H NMR (400 MHz, Chloroform-d) δ 7.57 – 7.49 (m, 1.8H), 7.46 – 7.37 (m, 0.2H), 7.07 (d, *J* = 8.5 Hz, 2H), 4.76 – 4.64 (m, 1H), 3.95 – 3.86 (m, 0.1H), 3.85 – 3.76 (m, 0.9H), 2.64 (s, 3H), 2.31 (d, *J* = 10.9 Hz, 1H), 2.11 – 1.88 (m, 4H), 1.80 – 1.66 (m, 1H), 1.52 – 1.33 (m, 2H). $^{13}$C NMR (101 MHz, Chloroform-d) δ 165.53 (d, *J* = 256.4 Hz), 151.5, 138.4, 136.8, 130.5 (d, *J* = 9.6 Hz), 130.0 (d, *J* = 9.5 Hz), 116.5 (d, *J* = 22.7 Hz), 65.9, 65.8, 56.7, 55.9, 34.0, 33.9, 26.3, 25.5, 24.5, 24.4, 9.2. $^{19}$F NMR (376 MHz, Chloroform-d) δ -104.1 (td, *J* = 8.2, 4.1 Hz), -104.2 (tt, *J* = 8.6, 5.0 Hz). HRMS (ESI) calculated for $C_{14}H_{19}FN_5OS^+$ $[M+H]^+$: 324.1289; found: 324.1284.



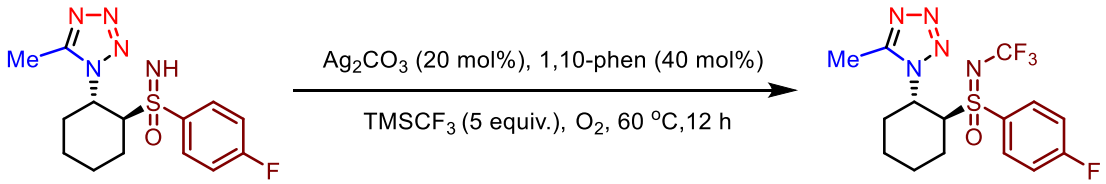

**27** **3** **28**, 60%, 2:1 dr

To a 25 mL round-bottom flask equipped with a stir bar were added **27** (0.1 mmol), **3** (0.2 mmol), and PEG400 (1.5 mL). Then the flask was immersed in a pre-heated oil bath set at 50 ℃ for 4 h. Iodine (0.02 mmol) and hydrogen peroxide (0.5 mmol) were then added to the flask. After the flask was stirring for a set time, a saturated solution of $Na_2S_2O_3$ (5 mL) and ethyl acetate (15 mL) was added to the reaction mixture.[3] The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with saturated solution of $Na_2CO_3$, and then dried over anhydrous $MgSO_4$. The organic solvent was then evaporated under reduced pressure and the residue was

purified by flash column chromatography on silica gel (PE/EA=1:1) to give the desired product (**28**, 27 mg, 60% yield, dr = 2:1) as a yellow solid.

**(4-fluorophenyl)(((4-fluorophenyl)thio)imino)(2-(5-methyl-1*H*-tetrazol-1-yl)cyclohexyl)- λ$^6$-sulfanone (28)**

IR (neat, cm$^{-1}$): 2926(w), 1587(s), 1488(s), 1227(m), 835(m), 727 (m), 582(m). $^1$H NMR (500 MHz, Chloroform-d) δ 7.45 – 7.35 (m, 2H), 7.30 – 7.26 (m, 2H), 7.09 (d, *J* = 6.8 Hz, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 4.82 – 4.71 (m, 1H), 4.22 – 4.08 (m, 1H), 2.58 (s, 0.27H), 2.48 (s, 2.73H), 2.11 – 1.88 (m, 4H), 1.56 – 1.22 (m, 4H). $^{13}$C NMR (126 MHz, Chloroform-d) δ 165.9 (d, *J* = 257.9 Hz), 161.7 (d, *J* = 246.1 Hz), 151.4, 136.1 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 3.5 Hz), 131.3 (d, *J* = 9.8 Hz), 129.2 (d, *J* = 8.0 Hz), 128.5 (d, *J* = 7.9 Hz), 117.0 (d, *J* = 22.9 Hz), 115.9 (d, *J* = 22.0 Hz), 67.1, 66.6, 55.9, 55.8, 34.3, 29.8, 26.5, 24.5, 24.5, 9.0. $^{19}$F NMR (471 MHz, Chloroform-d) -102.3 (t, *J* = 6.4 Hz), -102.5 (t, *J* = 6.3 Hz), -115.5 (d, *J* = 9.5 Hz), -115.8 (dd, *J* = 13.2, 8.6 Hz). HRMS (ESI) calculated for $C_{20}H_{22}F_2N_5OS_2^+$ $[M+H]^+$: 450.1228; found: 450.1223.




**27** **29**, 77%, 1.4:1 dr

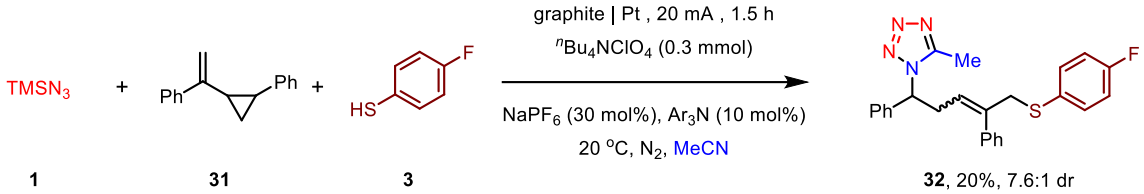
Under dioxygen, a 20 mL Schlenk tube equipped with a stir bar was charged with **27** (0.1 mmol), $TMSCF_3$ (0.5 mmol), $Ag_2CO_3$ (0.02 mmol), 1,10-phen (0.04 mmol) and 1,4-dioxane (2 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 60 ℃ for 12 h in an oil bath.[4] The organic solvent was then evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (PE:EA=1:1) to give the desired product (**29**, 30 mg, 77% yield, dr = 1.4:1) as a yellow solid.

**(4-fluorophenyl)(2-(5-methyl-1*H*-tetrazol-1-yl)cyclohexyl)((trifluoromethyl)imino)- λ$^6$-sulfanone (29)**

IR (neat, cm-1): 2946(w), 1589(m), 1491(m), 1281(s), 1239(m), 842(m), 732 (m), 584(m). $^{1}$H NMR (500 MHz, Chloroform-d) δ 7.68 – 7.62 (m, 6H), 7.53 – 7.46 (m, 2H), 7.21 – 7.13 (m, 8H), 4.84 – 4.78 (m, 3H), 4.81 – 4.69 (m, 1H), 4.07 – 3.98 (m, 1H), 3.97 – 3.88 (m, 3H), 2.68 (s, 3H), 2.65 (s, 9H), 2.26 (d, *J* = 15.3 Hz, 4H), 2.15 – 1.74 (m, 22H), 1.56 – 1.31 (m, 6H). $^{19}$F NMR (471 MHz, Chloroform-d) δ -40.7, -41.0, -101.2 (dd, *J* = 14.0, 6.4 Hz). $^{13}$C NMR (126 MHz, Chloroform-d) δ166.3 (d, *J* = 258.7 Hz), 166.2 (d, *J* = 258.4 Hz), 151.7, 151.6, 133.3, 132.1, 131.6 (dd, *J* = 9.7 Hz, *J* = 5.5 Hz), 130.9 (dd, *J* = 8.8 Hz, *J* = 3.8 Hz), 122.3 (q, *J* = 256.3 Hz), 121.6 (q, *J* = 256.7 Hz), 117.7 - 116.7 (m), 67.4, 67.1, 55.3 (d, *J* = 3.3 Hz), 54.6 (d, *J* = 9.7 Hz), 34.0, 27.0, 26.8, 24.7 - 23.8 (m), 8.9, 8.8. HRMS (ESI) calculated for $C_{20}H_{22}F_2N_5OS_2^+$ $[M+H]^+$: 392.1163; found: 392.1155.

# 6. Mechanistic Experiments

## 6.1 Radical clock experiments




**1** **31** **3** **32**, 20%, 7.6:1 dr

Following the standard procedure for the synthesis of thioeher-tetrazole using 1-(2-phenylcyclopropyl)vinyl)benzene (2.0 equiv.) as the starting material. After work-up, the crude mixture was purified using column chromatography to afford **32** (26 mg, 20% yield, dr = 7.6:1**)**.

**1-(5-((4-fluorophenyl)thio)-1,4-diphenylpent-3-en-1-yl)-5-methyl-1H-tetrazole**

Followed **Method A**, the desired pure product was purified using silica gel chromatography (PE:EA = 3:1) to give 25.8 mg (20%) of **32** as a yellow oil.

IR (neat, $cm^{-1}$): 3031(w), 1588(m), 1489(s), 1281(s), 1221(m), 829(m), 739 (m), 537(m). $^{1}H$ NMR (400 MHz, Chloroform-d) δ 7.39 (d, *J* = 7.5 Hz, 5H), 7.28 (dd, *J* = 13.2, 7.8 Hz, 7H), 7.00 (t, *J* = 8.6 Hz, 2H), 5.63 (t, *J* = 7.5 Hz, 0.94H), 5.41 (t, *J* = 7.4 Hz, 0.06H), 5.29 (dd, J = 8.8, 6.5 Hz, 0.94H), 5.11 (dd, *J* = 8.7, 6.6 Hz, 0.06H), 3.98 (d, J = 12.4 Hz, 1H), 3.84 (d, *J* = 12.4 Hz, 0.94H), 3.69 (d, *J* = 3.9 Hz, 0.06H), 3.42 – 3.30 (m, 1H), 3.04 (dt, *J* = 14.4, 6.9 Hz, 1H), 2.42 (s, 2.8H), 2.25 (s, 0.2H). $^{13}C$ NMR (101 MHz, Chloroform-d) δ 162.5 (d, *J* = 247.9 Hz), 151.8, 141.0, 139.4, 137.5, 134.2 (d, *J* = 8.1 Hz), 133.3 (d, *J* = 8.2 Hz), 130.7 (d, *J* = 3.3 Hz), 129.4, 129.23, 129.19, 128.64, 128.61, 127.9, 126.8, 126.7, 126.5, 126.0, 116.2 (d, *J* = 21.9 Hz), 63.0, 36.0, 35.2, 34.8, 9.3. $^{19}F$ NMR (376 MHz, Chloroform-d) δ -113.9 (ddd, *J* = 14.0, 8.7, 5.2 Hz), -114.7 (td, *J* = 8.7, 4.4 Hz). HRMS (ESI) calculated for $C_{25}H_{24}FN_4S^+$ $[M+H]^+$: 431.1700; found: 431.1704.

## 6.2 Radical scavenger experiments

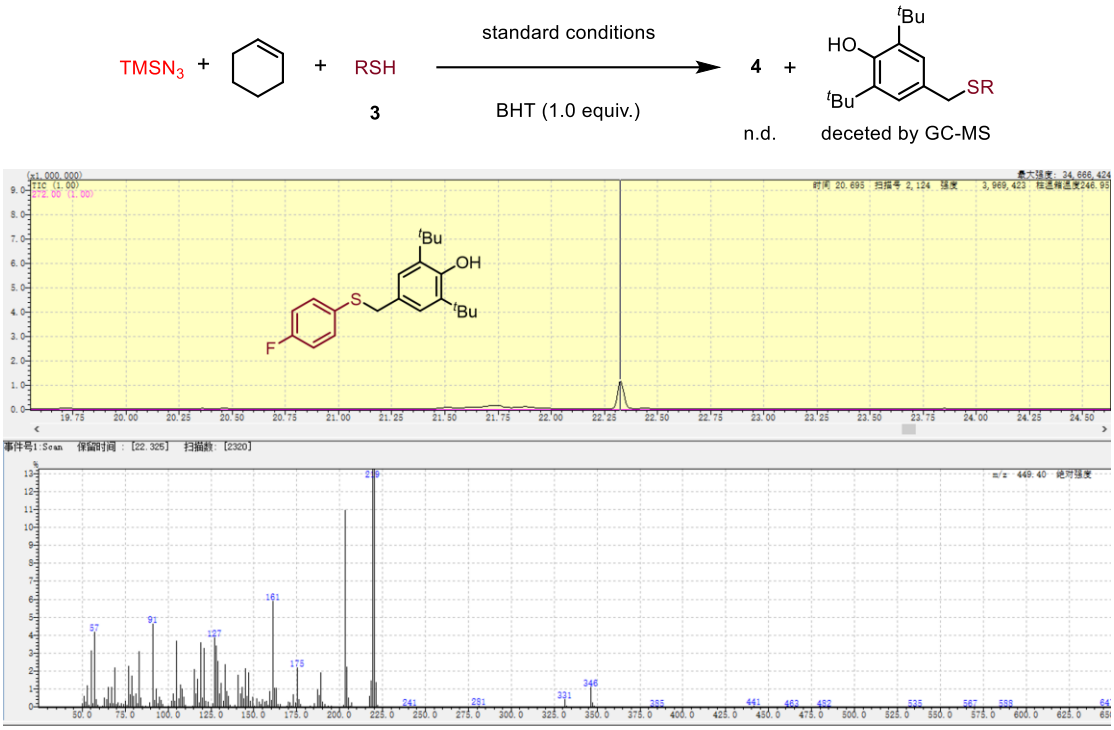



Figure 8. Verification of intermediate of radical scavenger experiment on GC-MS

## 6.3 Cyclic voltammetry studies

**General information:** Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode, and submerged in a saturated calomel reference electrode. The current was reported in mA, while all potentials were reported in V.

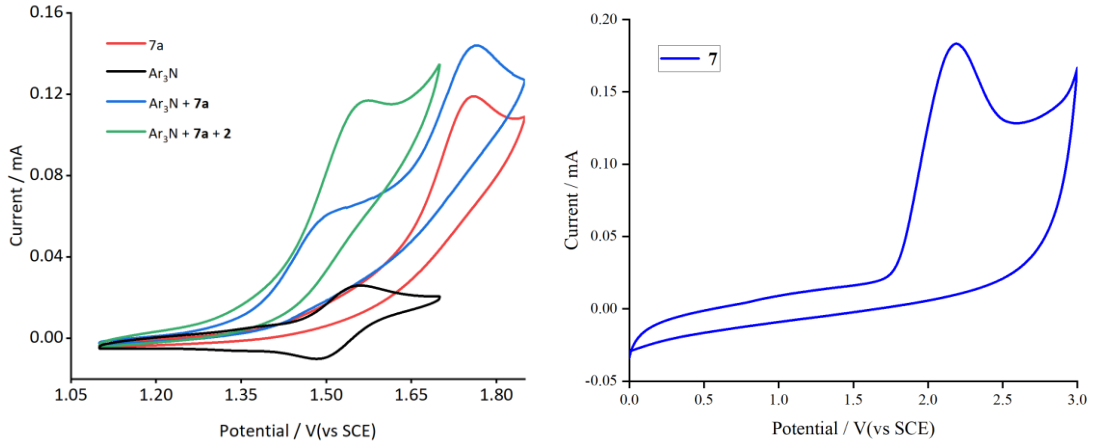
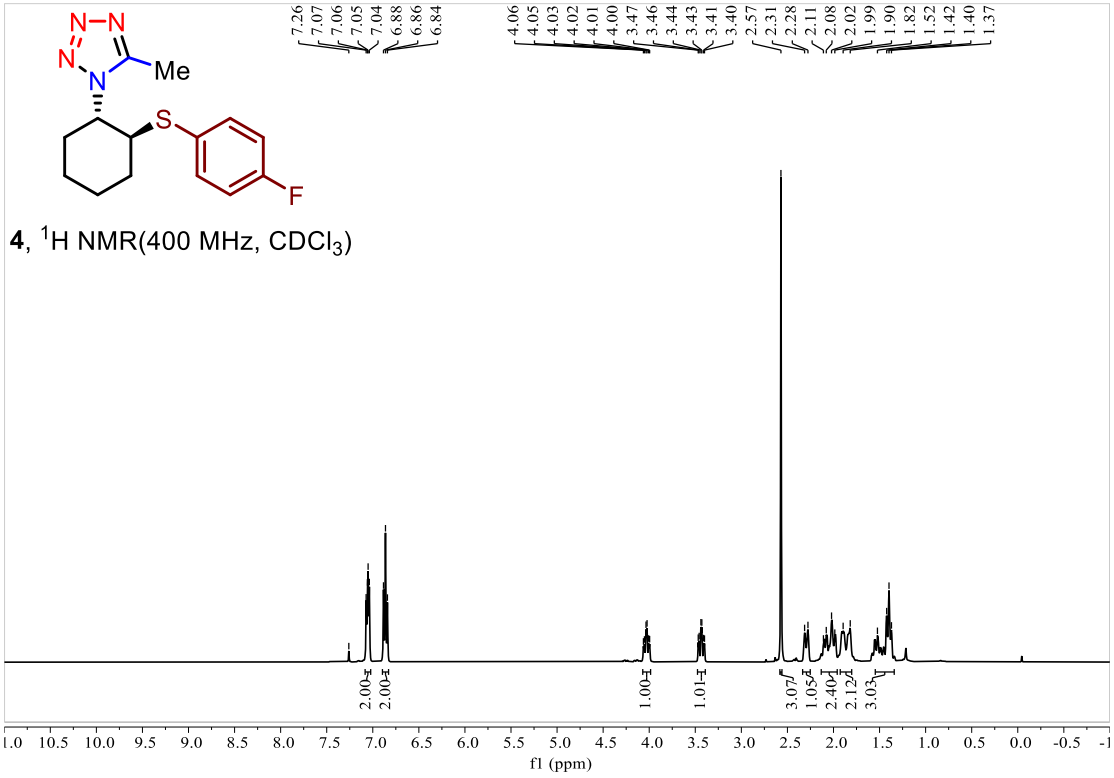



Figure 9. Cyclic voltammograms recorded in MeCN (10 mL) with 0.1M $^{n}$BuNClO$_4$ as the supporting electrolyte. scan rate: 100 mV/s. $Ar_3N$ (3 mM), **2** (4 mM), **7a** (4 mM), **7** (3 mM). **7a** = 4-(trifluoromethyl)benzenethiol.

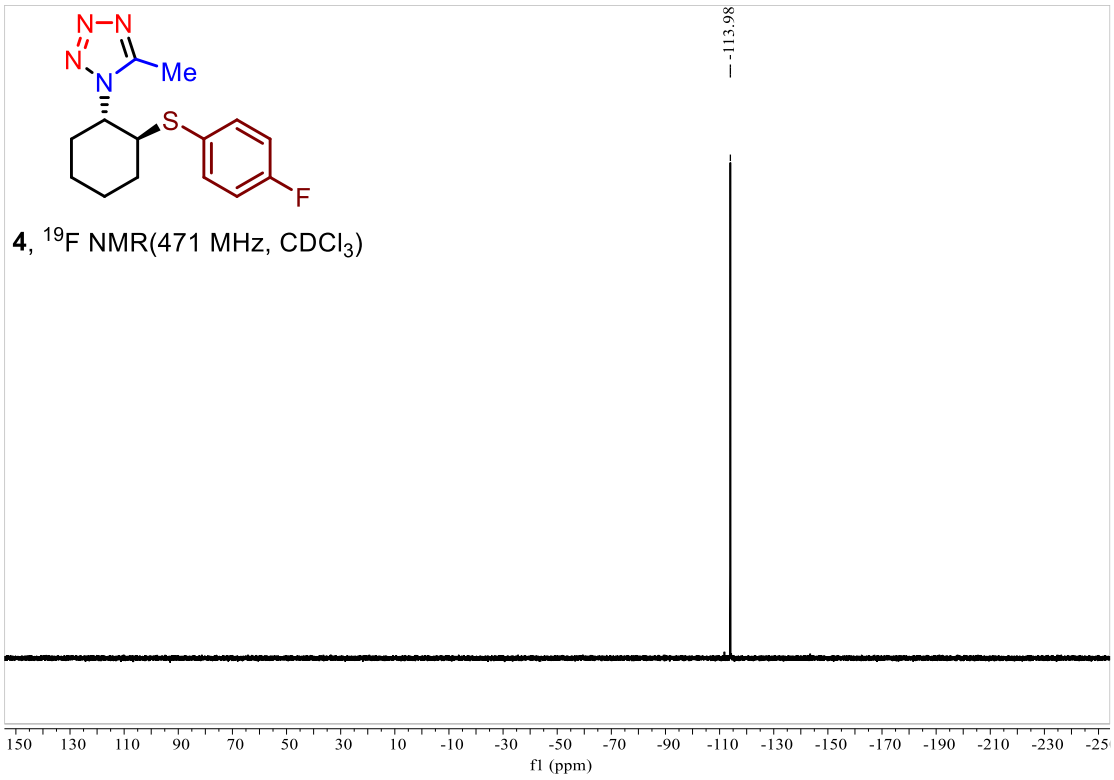
## 7. Reference


1. H. Golchoubian, F. Hosseinpoor, Effective Oxidation of Sulfides to Sulfoxides with Hydrogen Peroxide under Transition-Metal-Free Conditions, *Molecules*, 2007, **12**, 304-311.
2. Y. Xie, B. Zhou, S. Zhou, S. Zhou, W. Wei, J. Liu, Y. Zhan, D. Cheng, M. Chen, Y. Li, B. Wang, X.-S. Xue, Z. Li, Sulfimine-Promoted Fast O Transfer: One-step Synthesis of Sulfoximine from Sulfide, *ChemistrySelect*, 2017, **2**, 1620-1624.
3. L. Yang, J. Feng, M. Qiao, Q. Zeng, Synthesis of N-sulfenyl-sulfoximines and -sulfenamides through a metal-free N–H/S–H dehydrocoupling reaction, *Org. Chem. Front.*, 2018, **5**, 24-28.
4. F. Teng, J. Cheng, C. Bolm, Silver-Mediated N-Trifluoromethylation of Sulfoximines, *Org. Lett.*, 2015, **17**, 3166-3169.

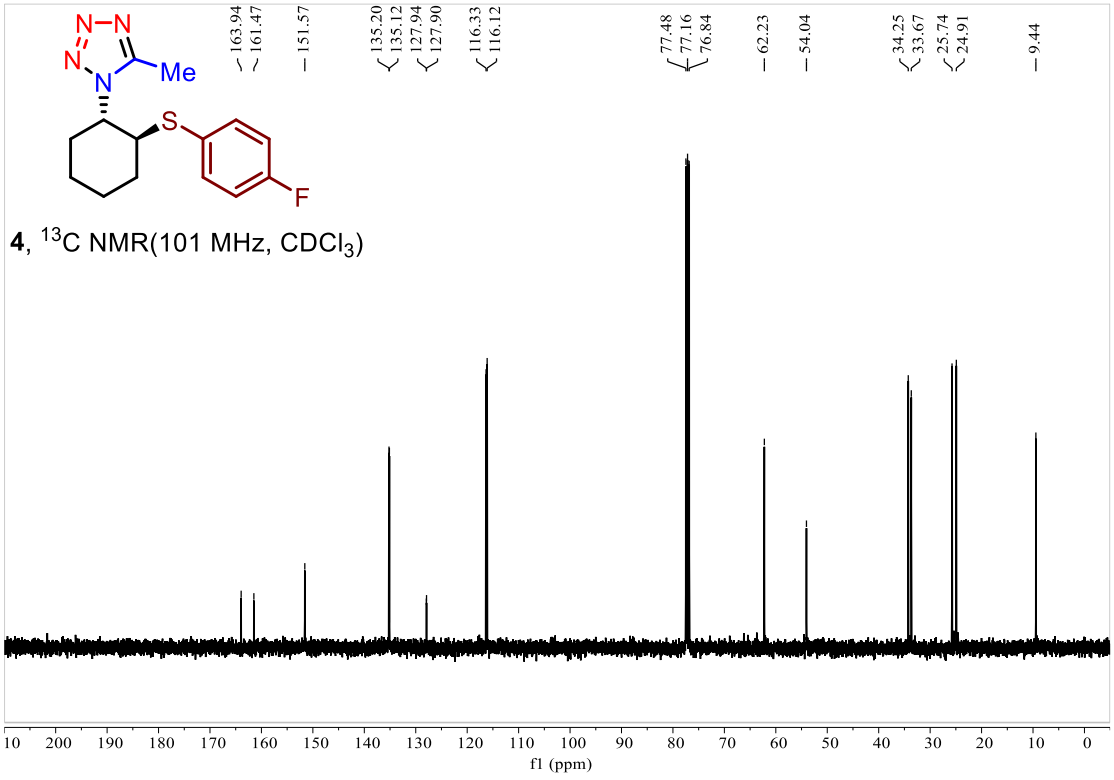
# 8. Spectral Data ( $^{1}H$, $^{19}F$ , $^{13}C$) of Products



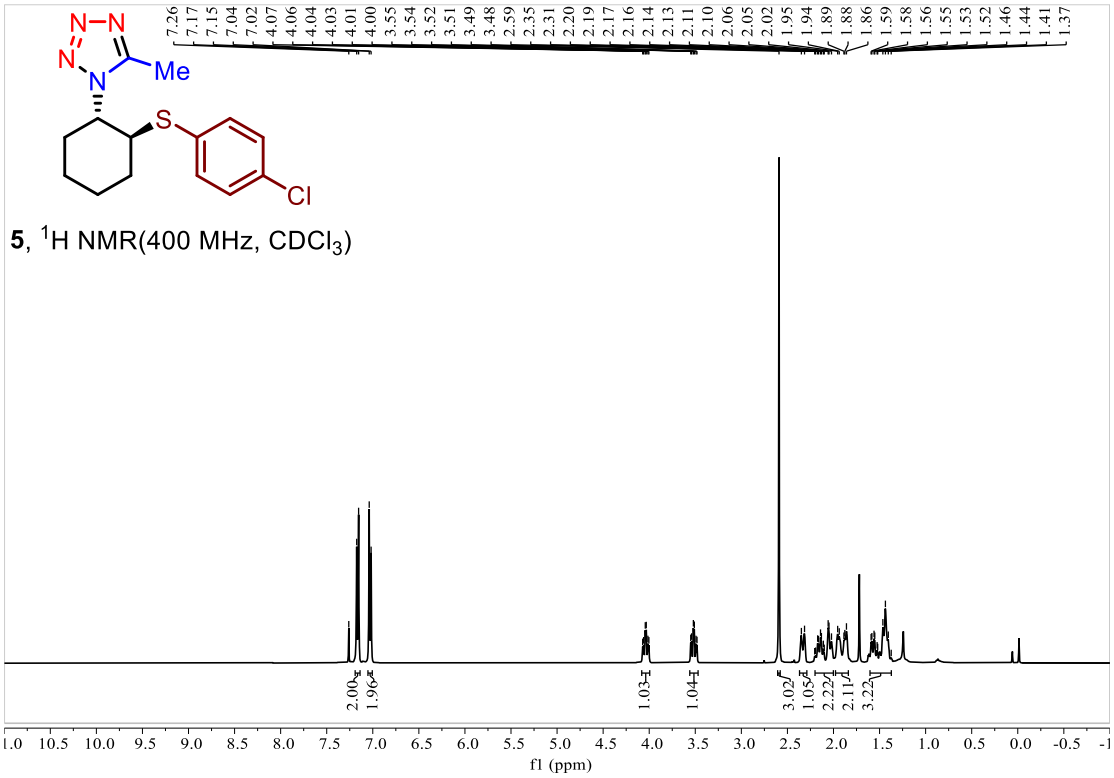

**4**, $^{1}H$ NMR(400 MHz, $CDCl_3$)



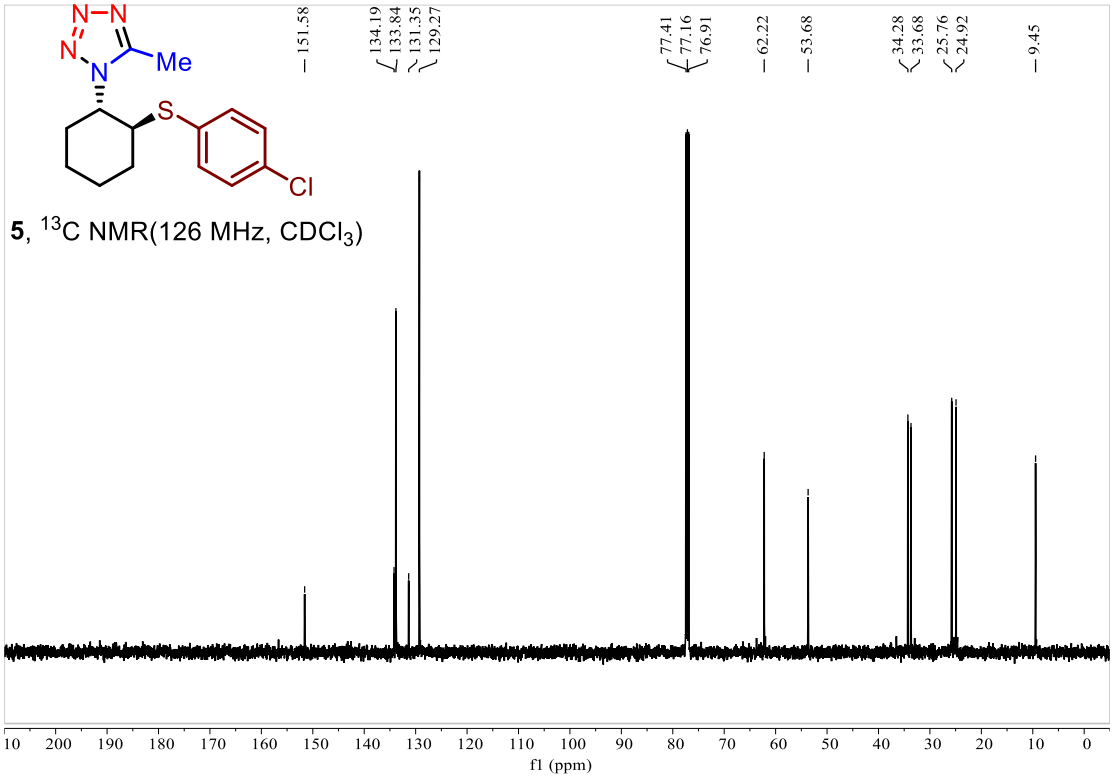

**4**, $^{19}F$ NMR(471 MHz, $CDCl_3$)



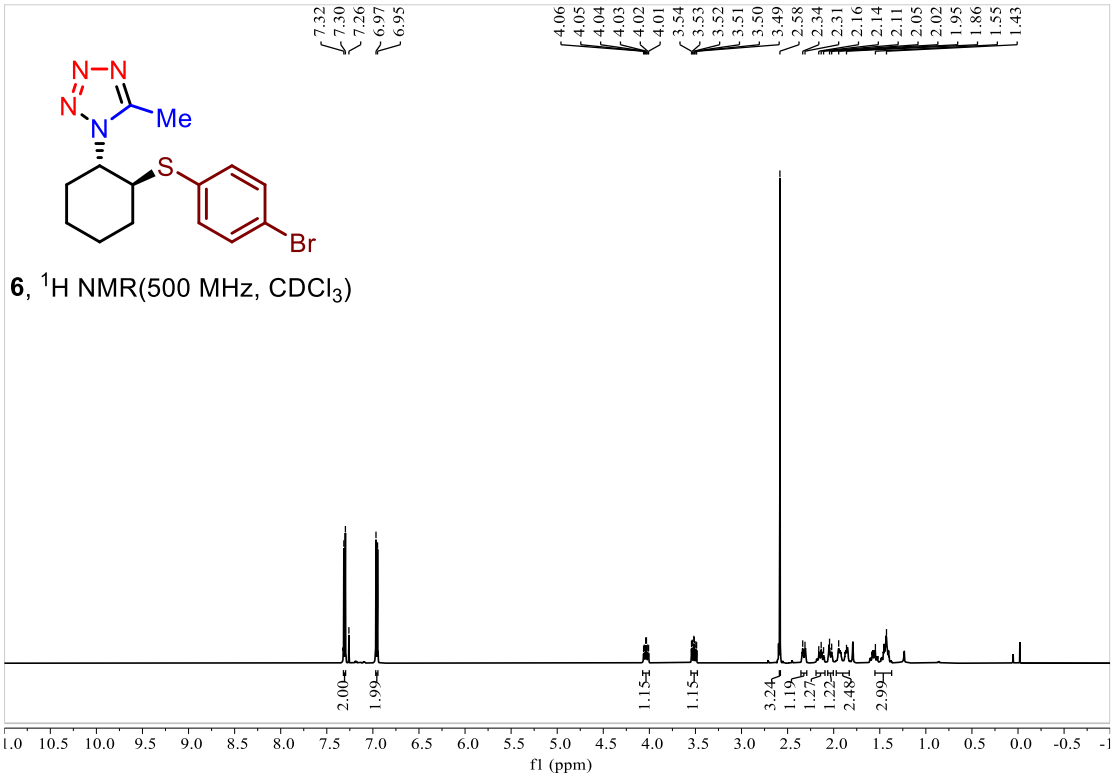

**4**, $^{13}C$ NMR(101 MHz, $CDCl_3$)



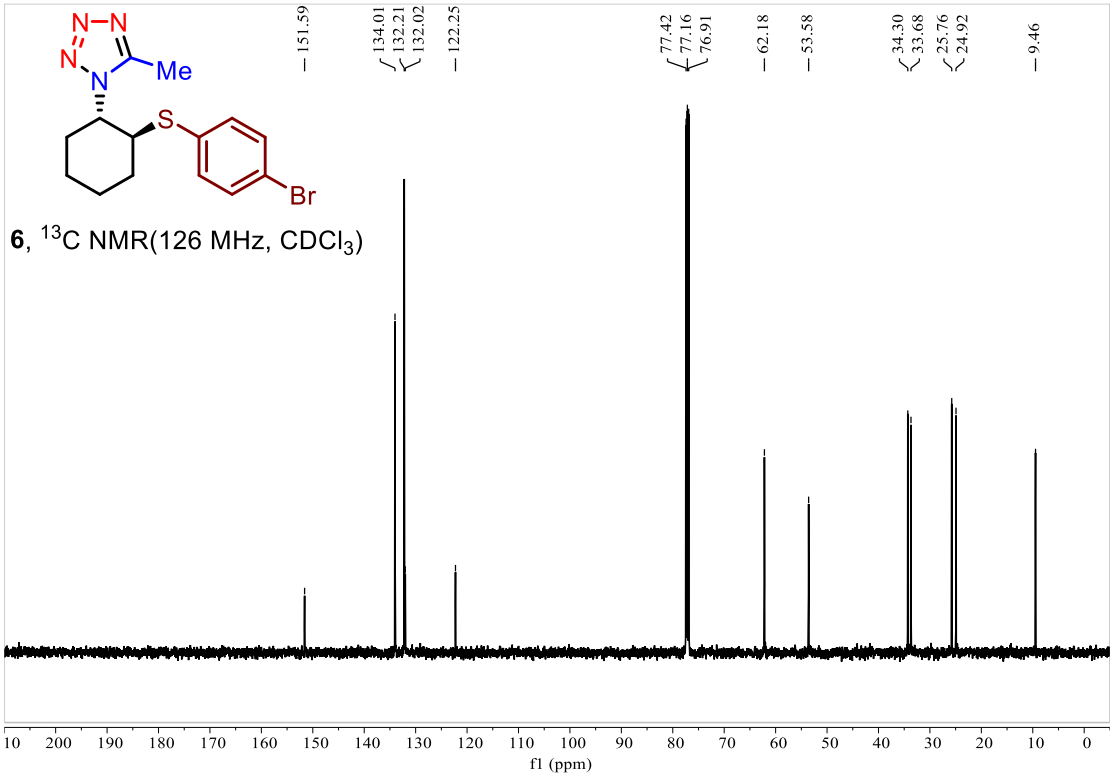

**5**, $^{1}H$ NMR(400 MHz, $CDCl_3$)



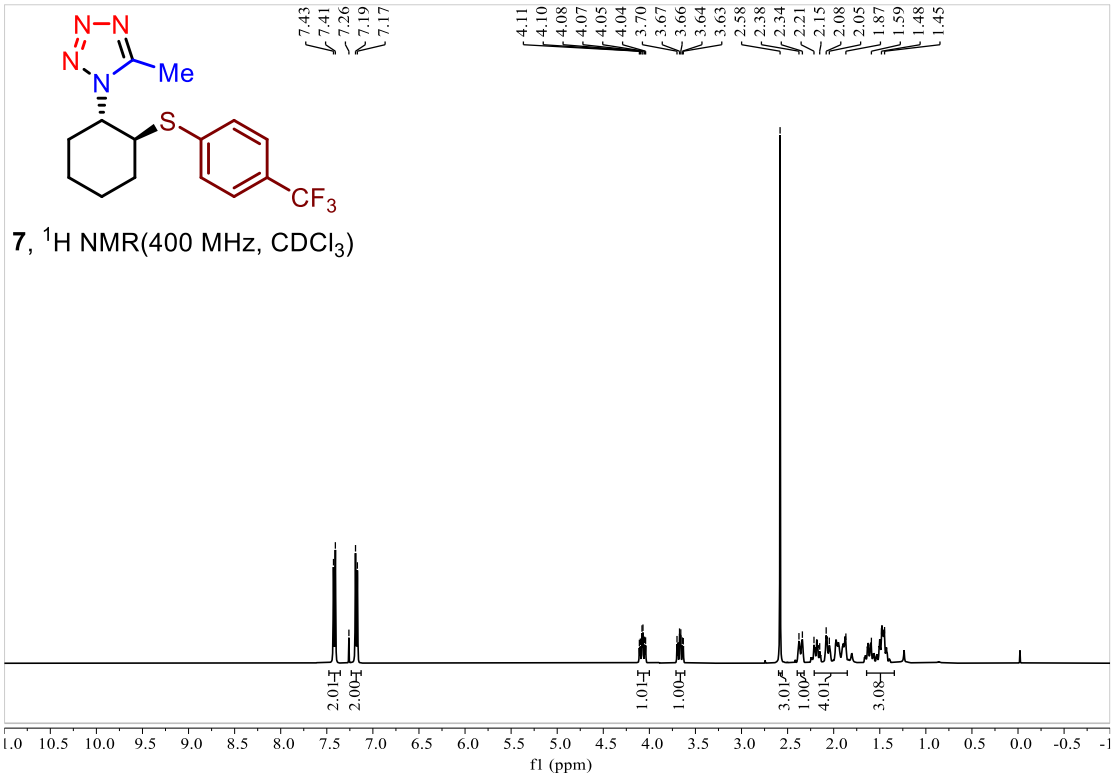

**5**, $^{13}C$ NMR(126 MHz, $CDCl_3$)



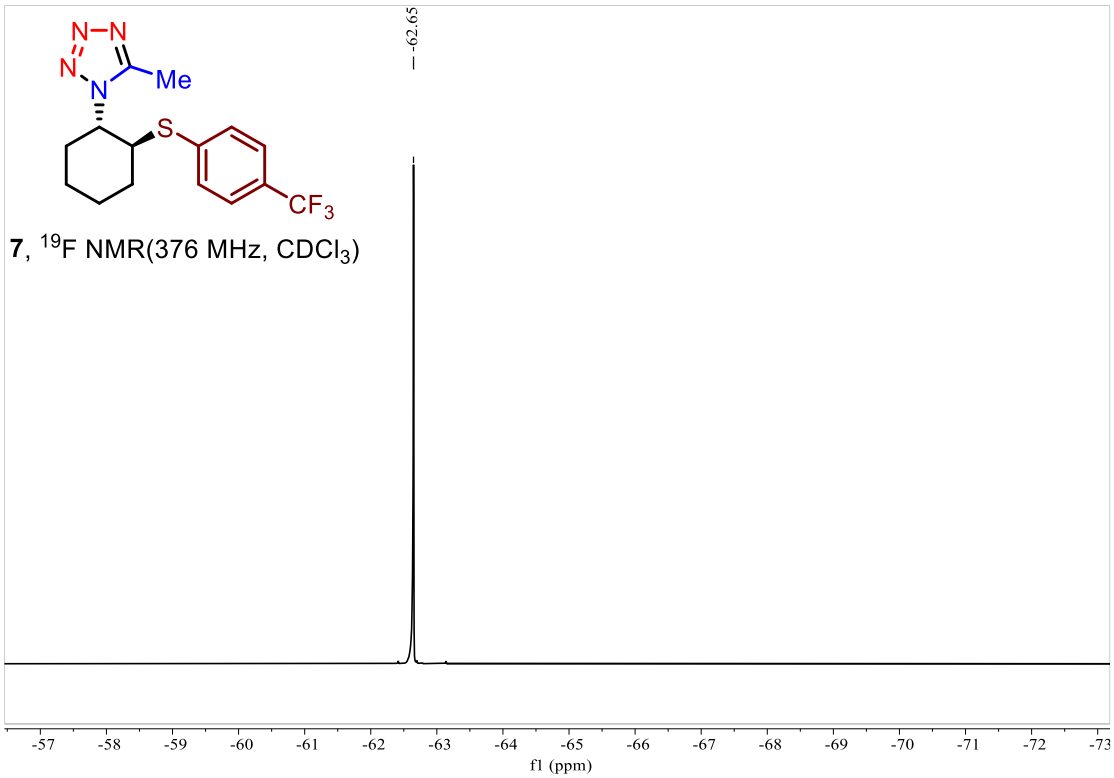

**6**, $^{1}H$ NMR(500 MHz, $CDCl_3$)



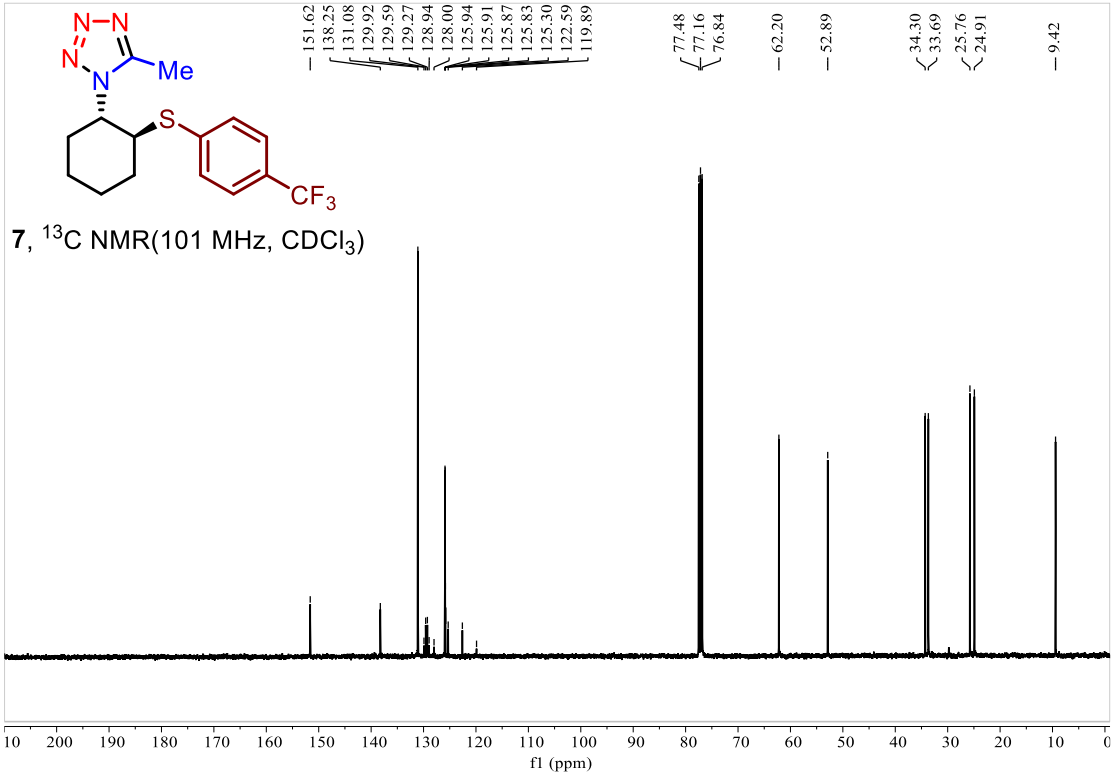

**6**, $^{13}C$ NMR(126 MHz, $CDCl_3$)



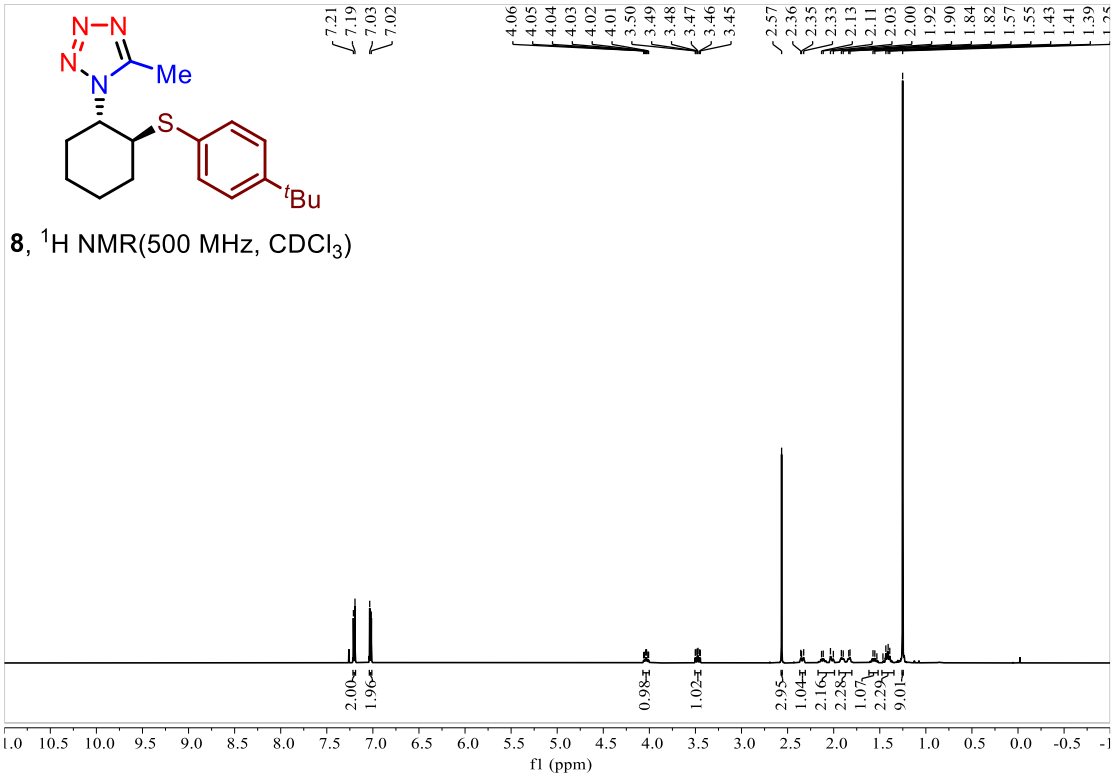

**7**, $^{1}H$ NMR(400 MHz, $CDCl_3$)



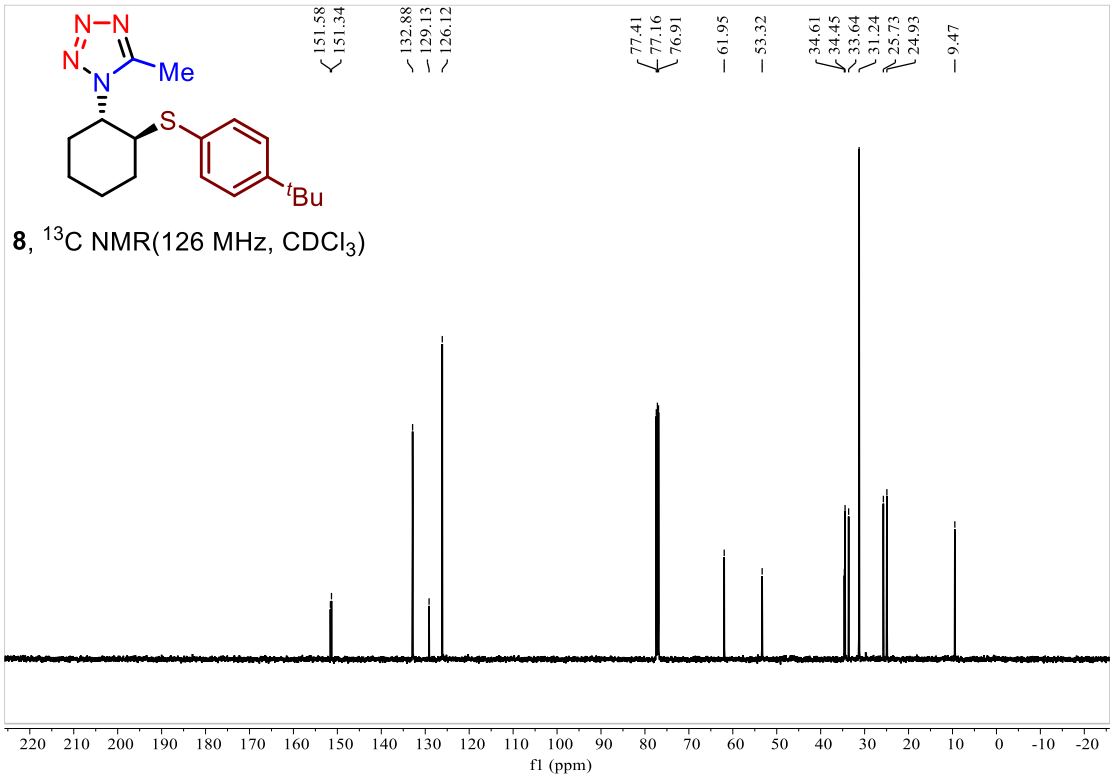

**7**, $^{19}$F NMR(376 MHz, $CDCl_3$)



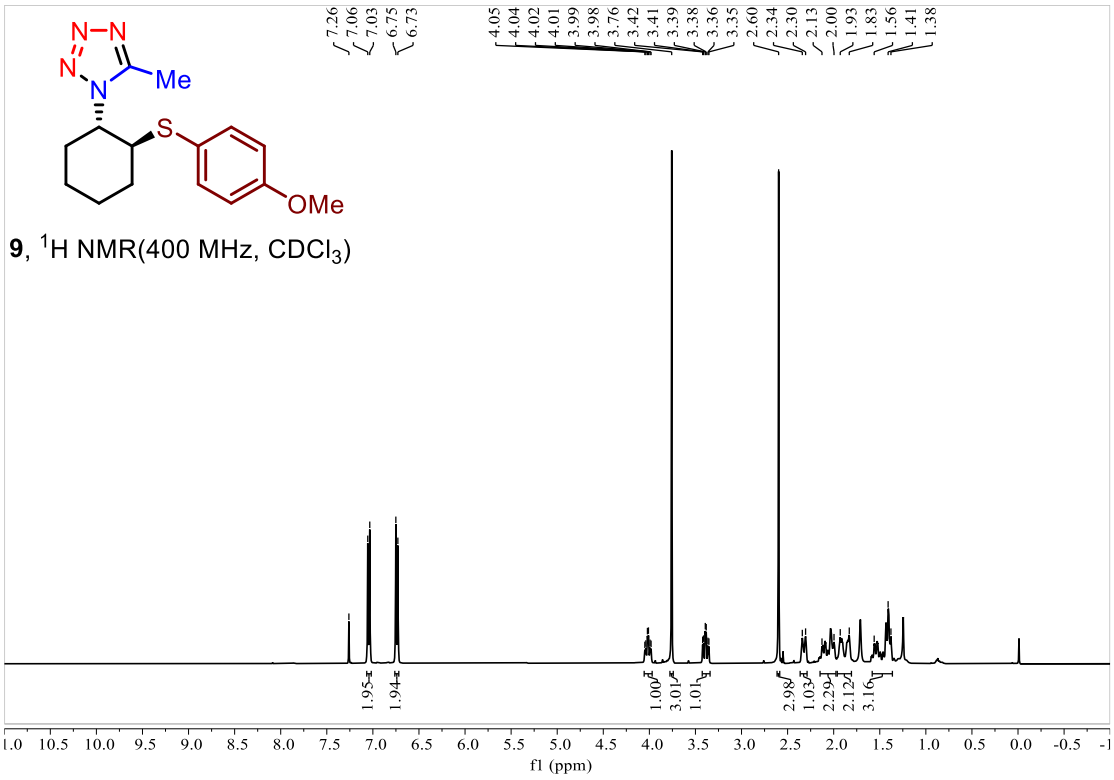

**7**, $^{13}$C NMR(101 MHz, $CDCl_3$)

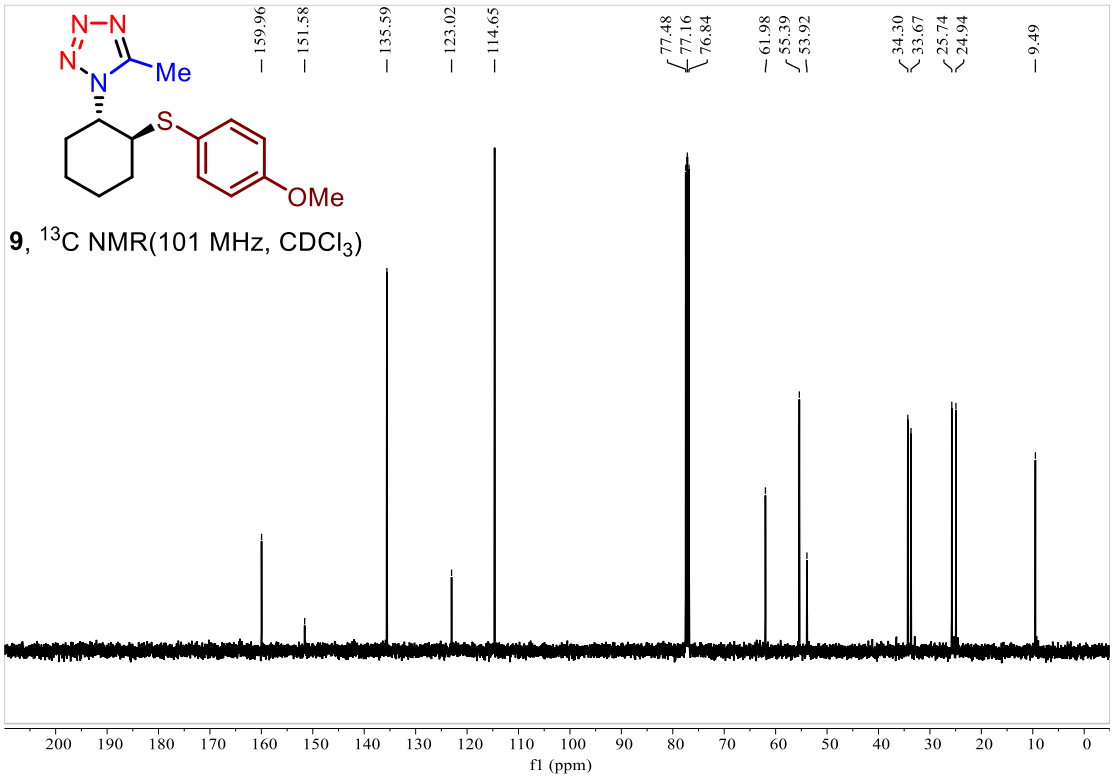


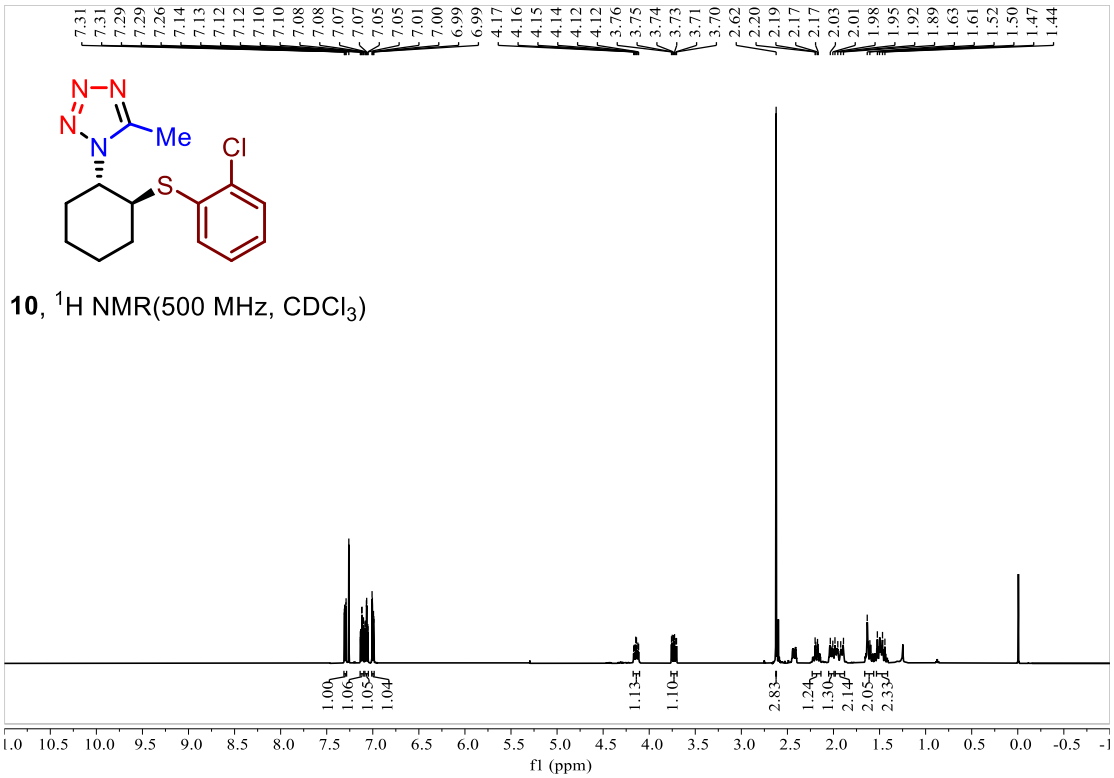

**8**, $^{1}$H NMR(500 MHz, $CDCl_3$)



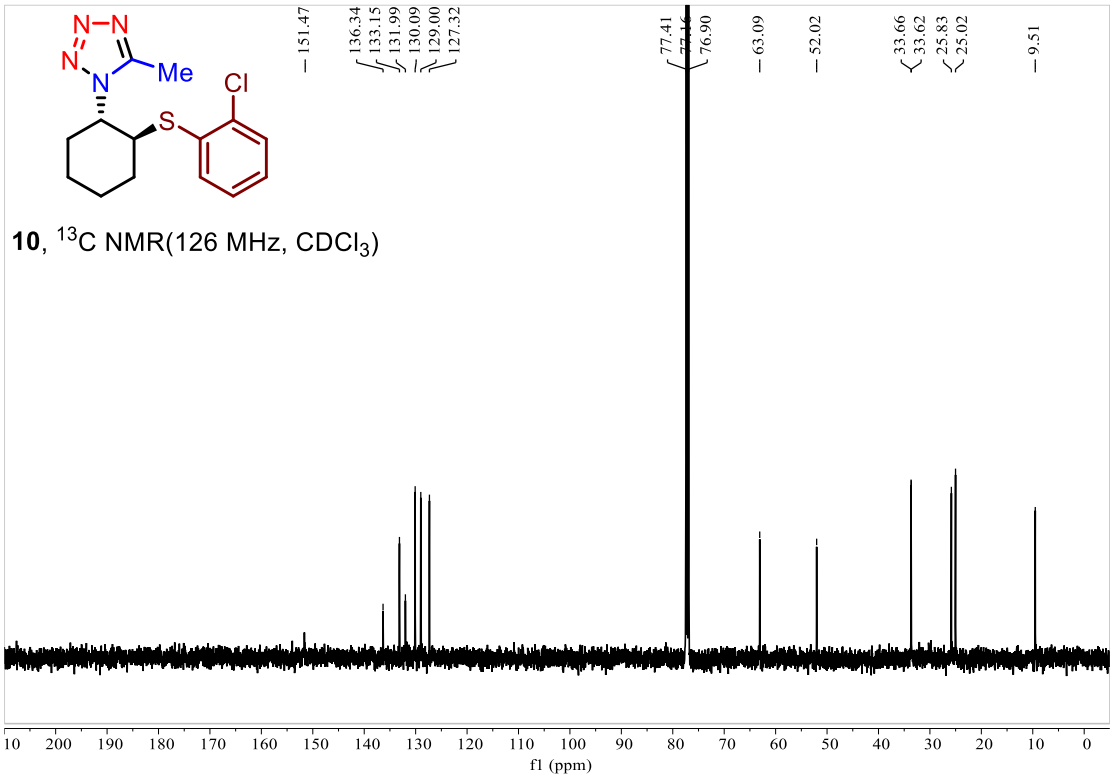

**8**, $^{13}$C NMR(126 MHz, $CDCl_3$)


Me
S
OMe
9, $^{1}$H NMR(400 MHz, $CDCl_3$)
f1 (ppm)

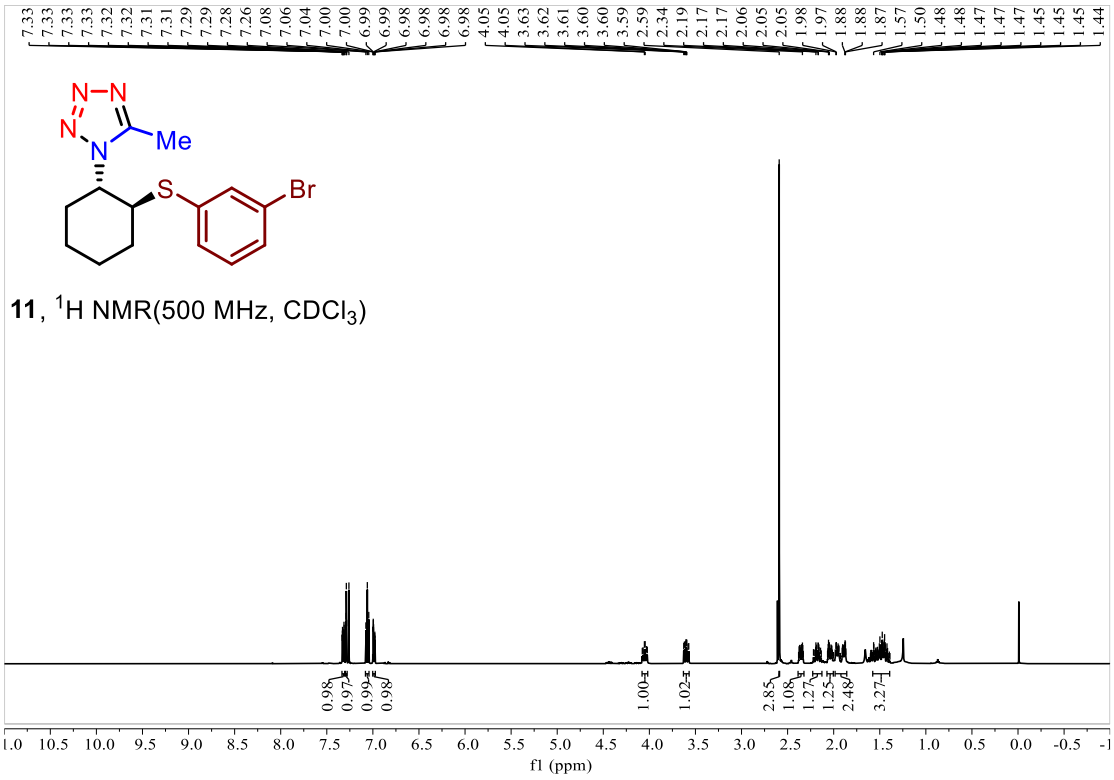

Me
S
OMe
9, $^{13}$C NMR(101 MHz, $CDCl_3$)
f1 (ppm)



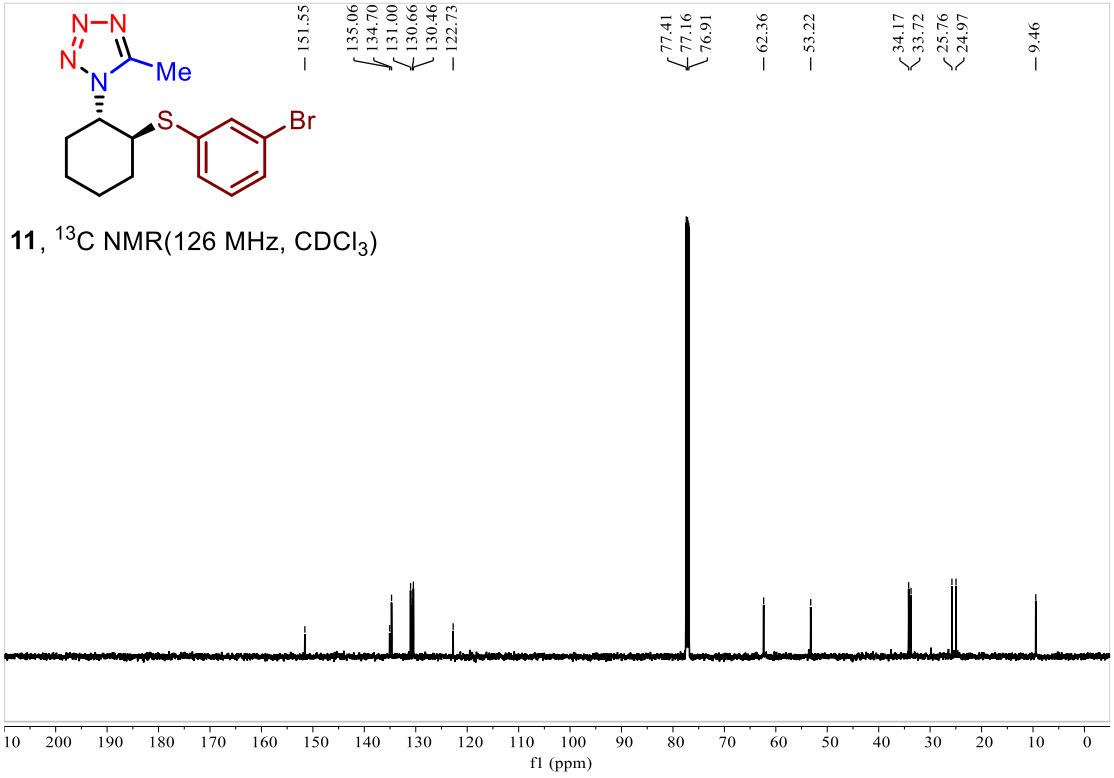

**10**, $^{1}$H NMR(500 MHz, $CDCl_3$)



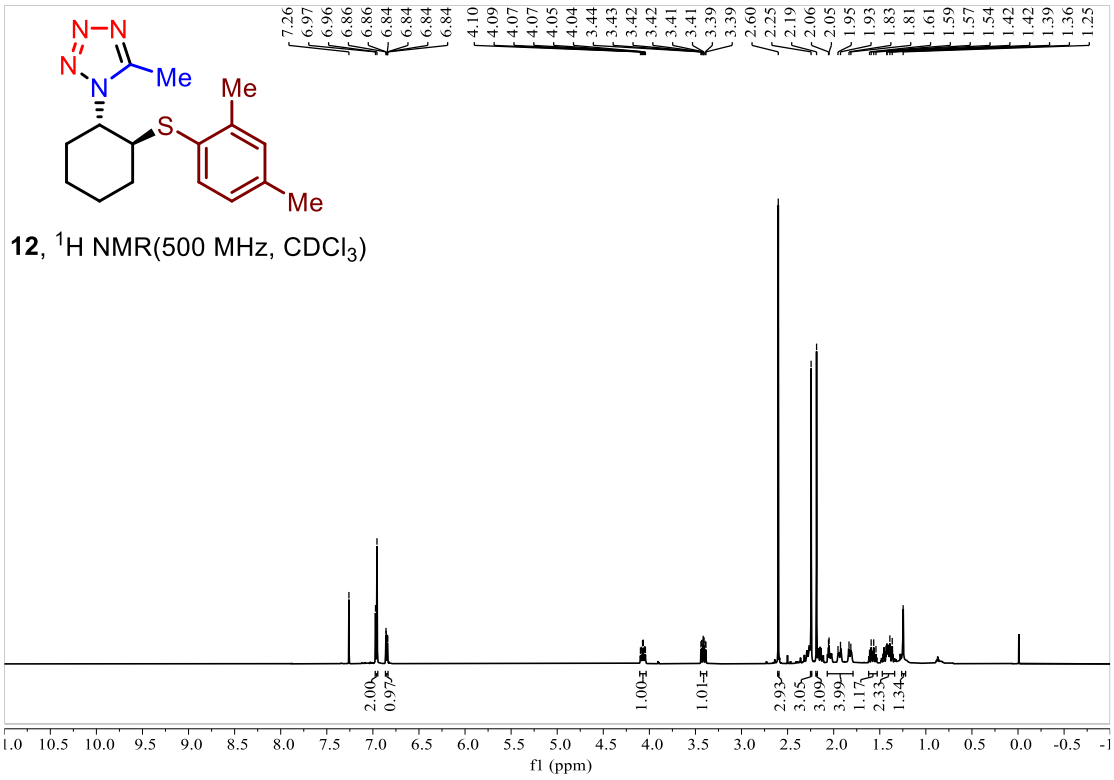

**10**, $^{13}$C NMR(126 MHz, $CDCl_3$)



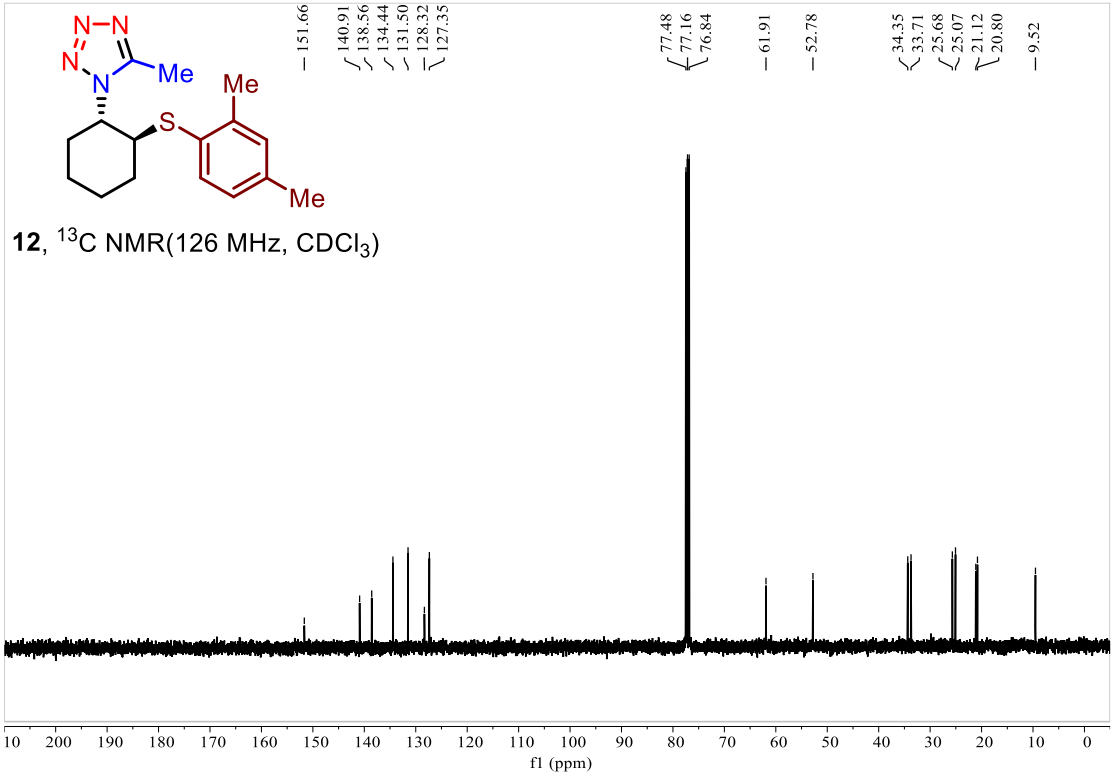

**11**, $^{1}$H NMR(500 MHz, $CDCl_3$)



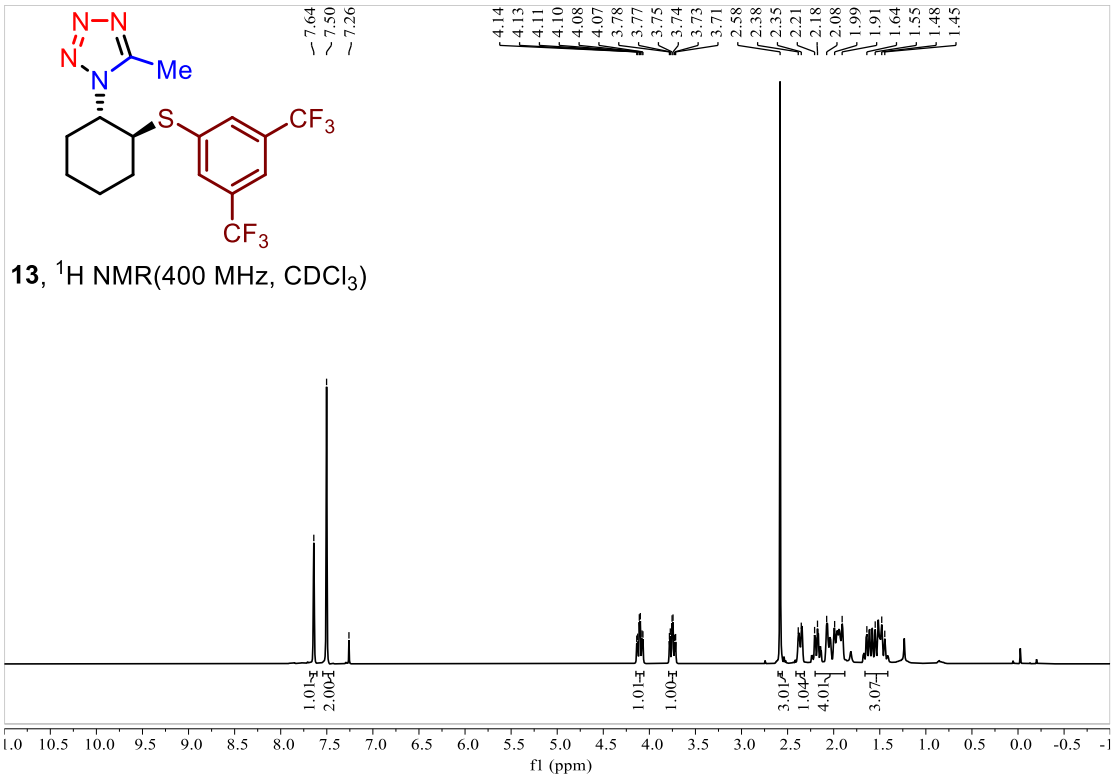

**11**, $^{13}$C NMR(126 MHz, $CDCl_3$)



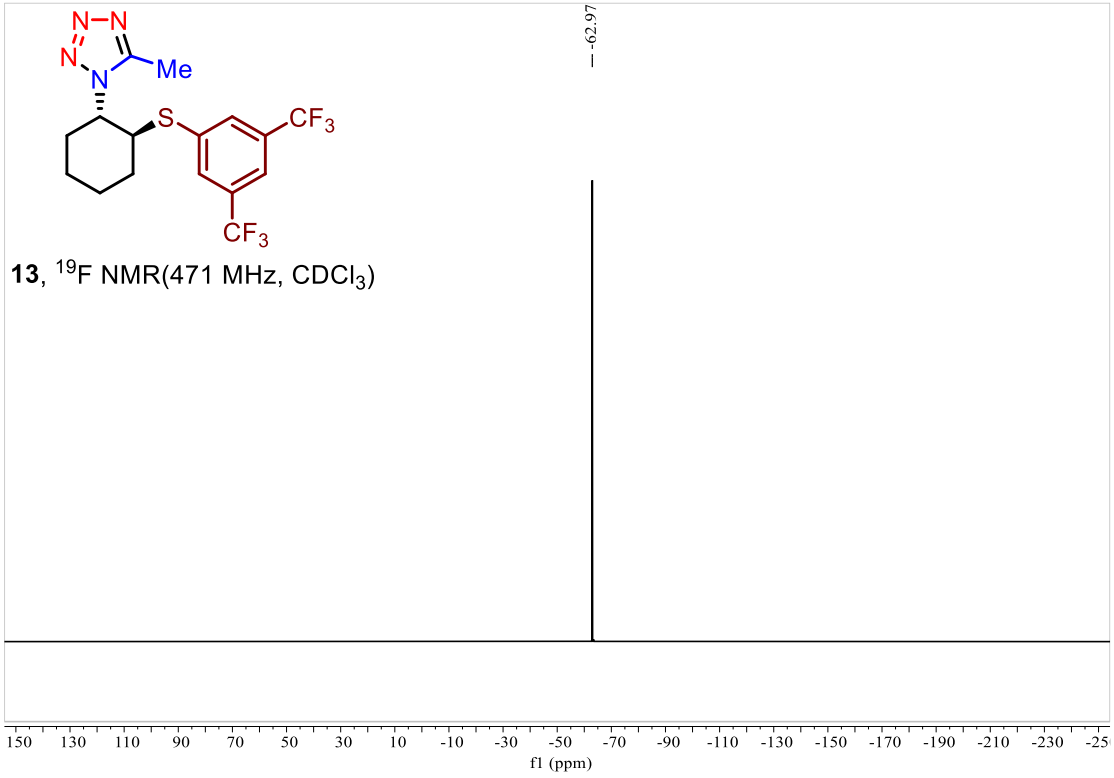

**12**, $^{1}$H NMR(500 MHz, $CDCl_3$)



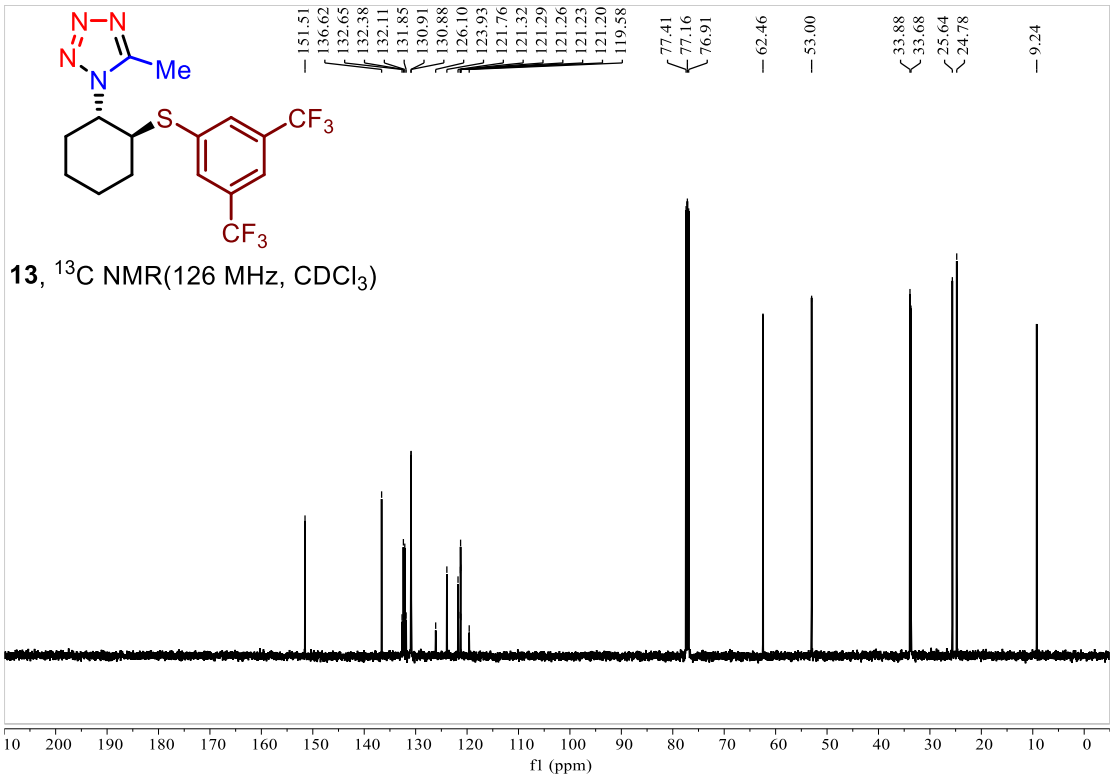

**12**, $^{13}$C NMR(126 MHz, $CDCl_3$)



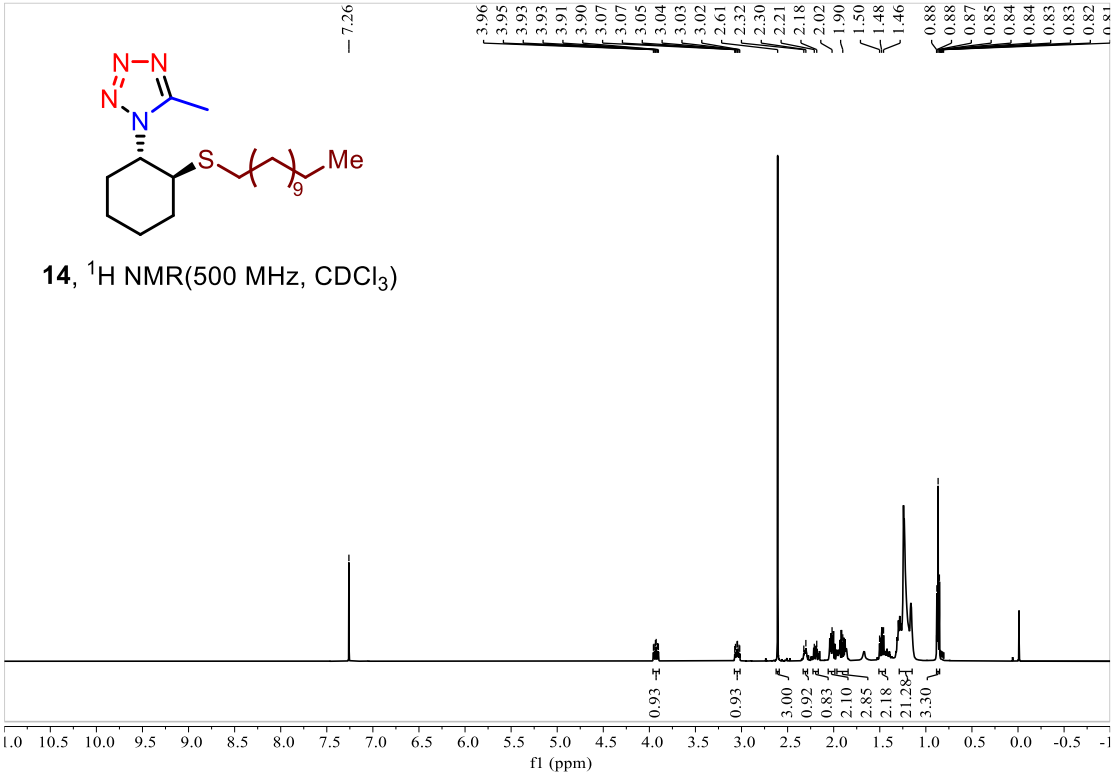

**13**, $^{1}$H NMR(400 MHz, $CDCl_3$)



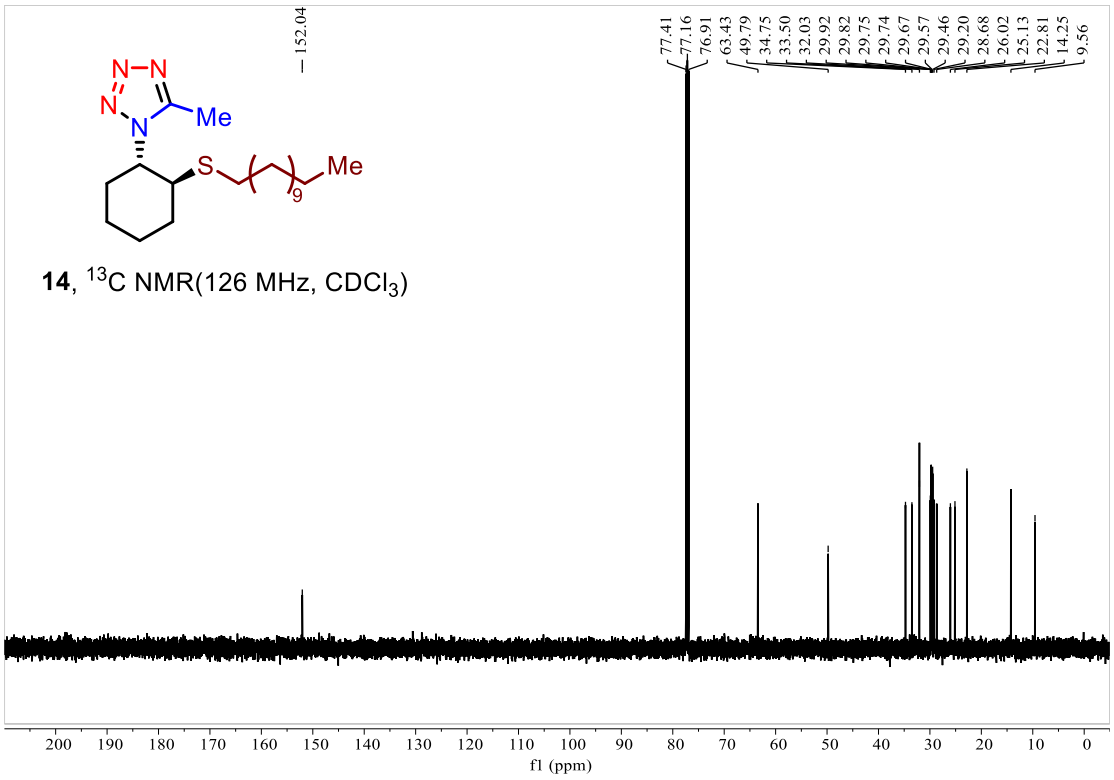

**13**, $^{19}$F NMR(471 MHz, $CDCl_3$)



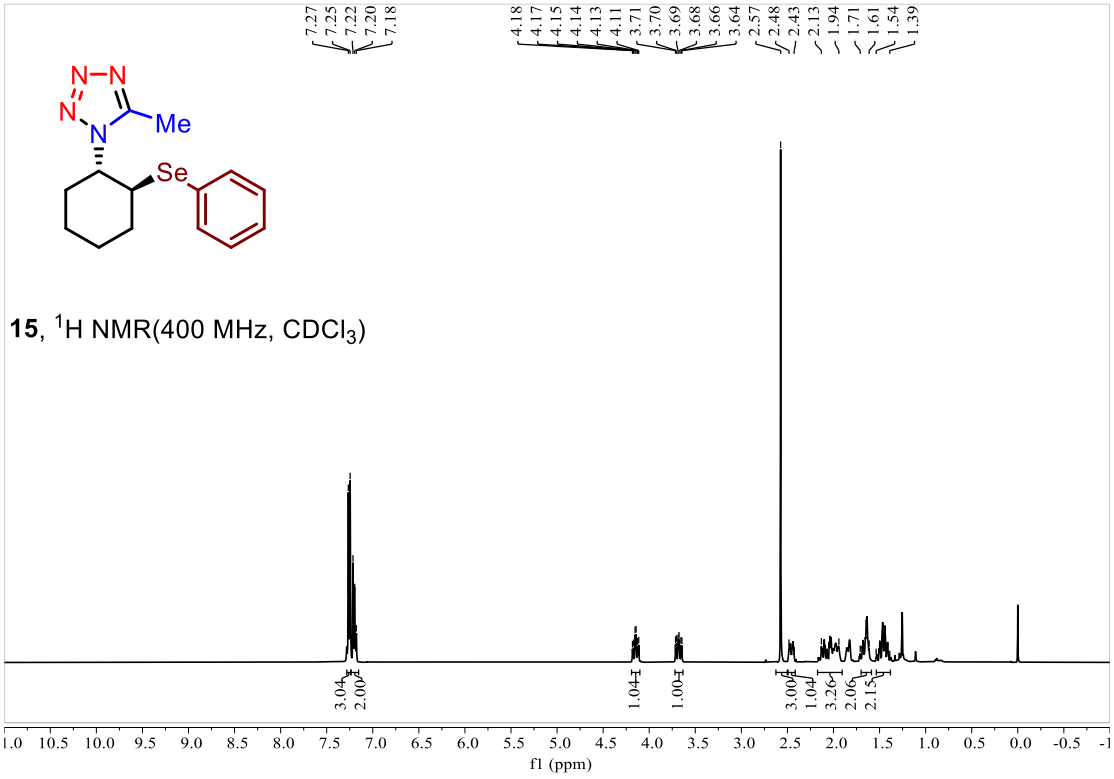

**13**, $^{13}C$ NMR(126 MHz, $CDCl_3$)



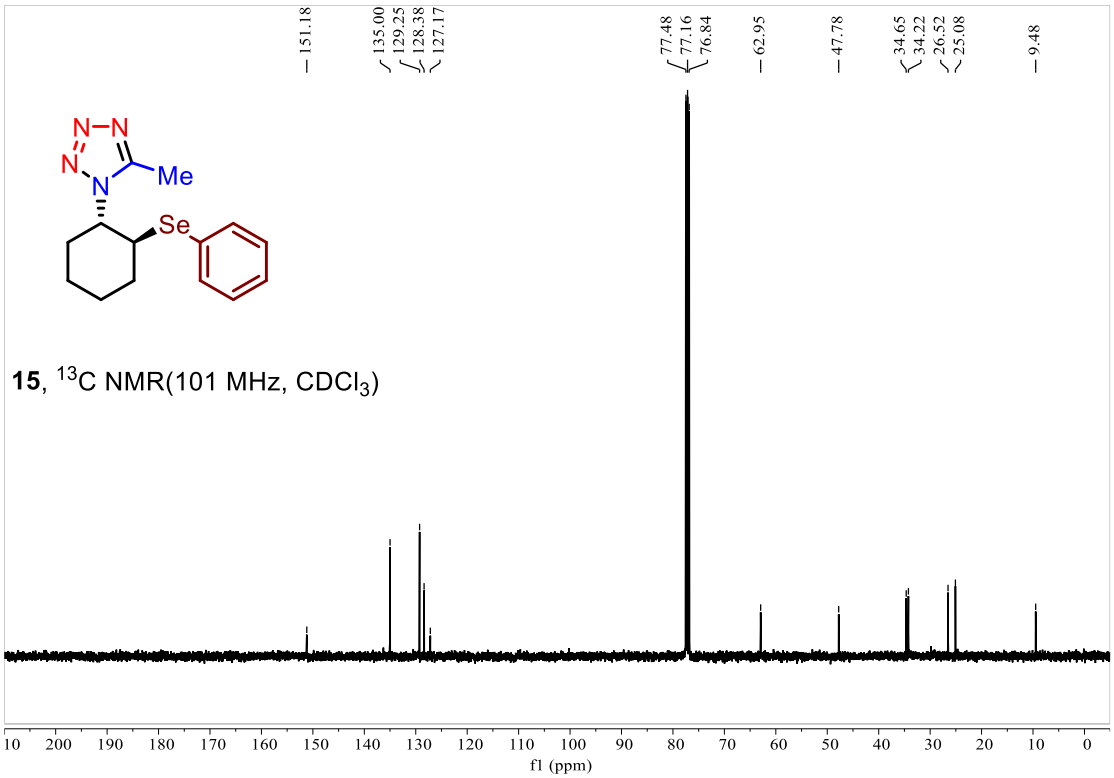

**14**, $^{1}H$ NMR(500 MHz, $CDCl_3$)



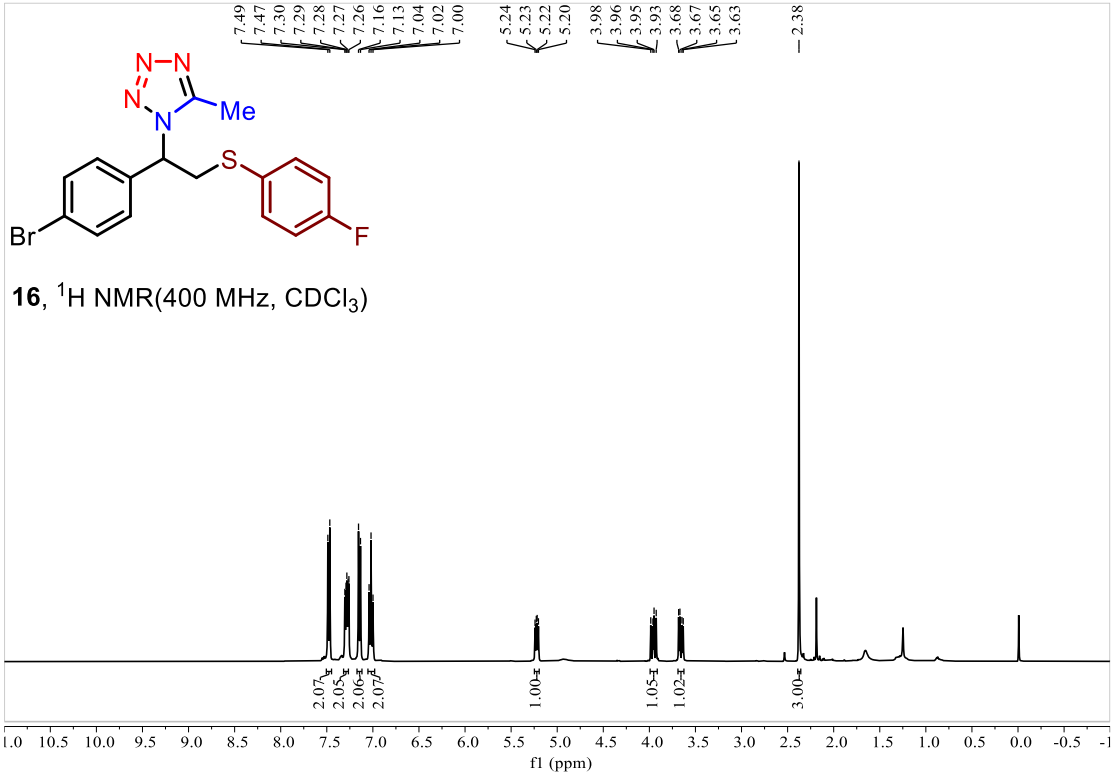

**14**, $^{13}C$ NMR(126 MHz, $CDCl_3$)



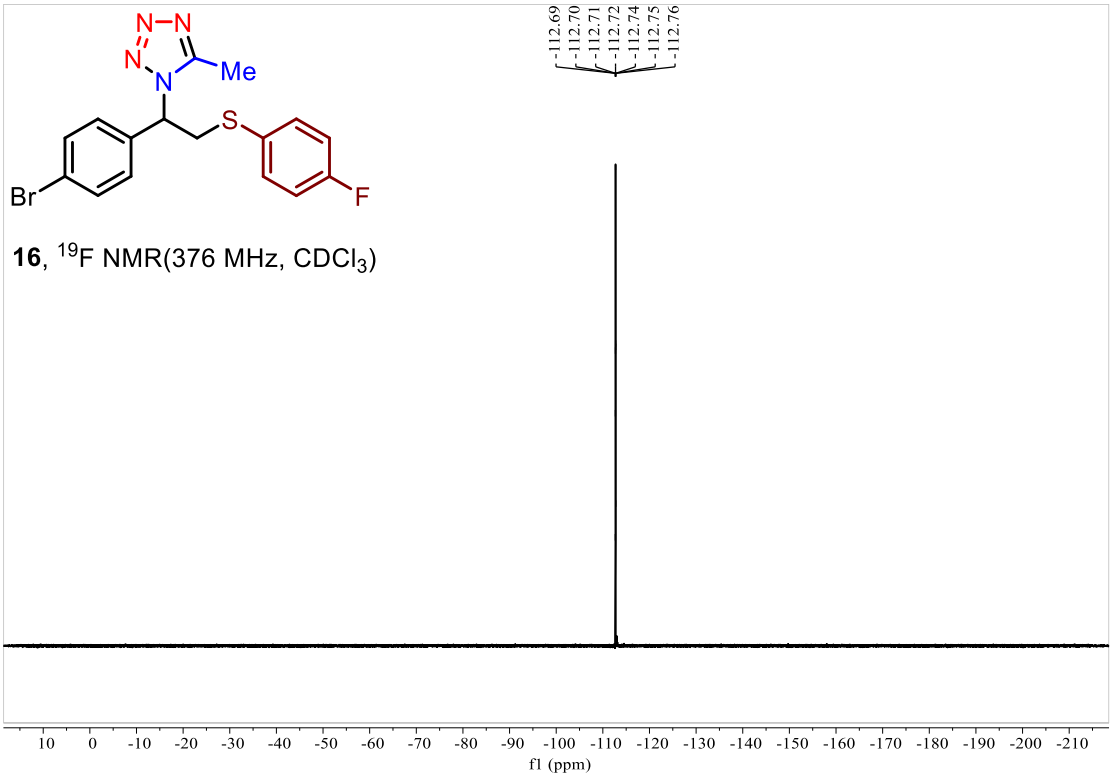

**15**, $^{1}H$ NMR(400 MHz, $CDCl_3$)



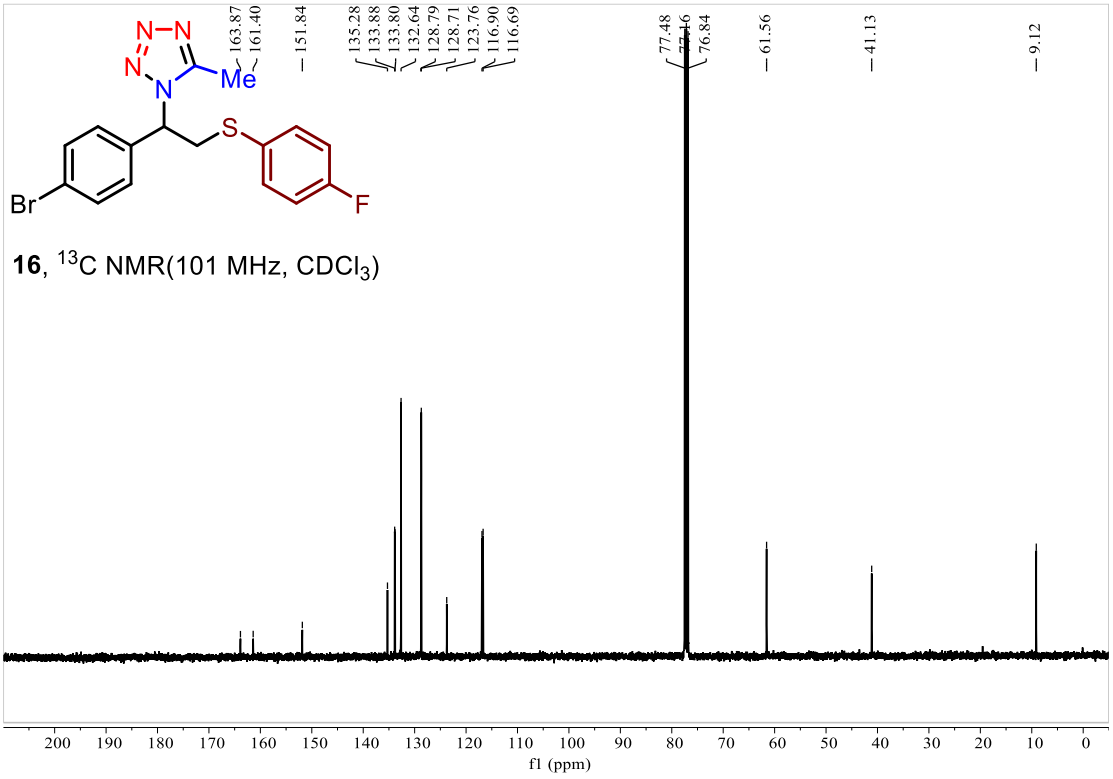

**15**, $^{13}C$ NMR(101 MHz, $CDCl_3$)



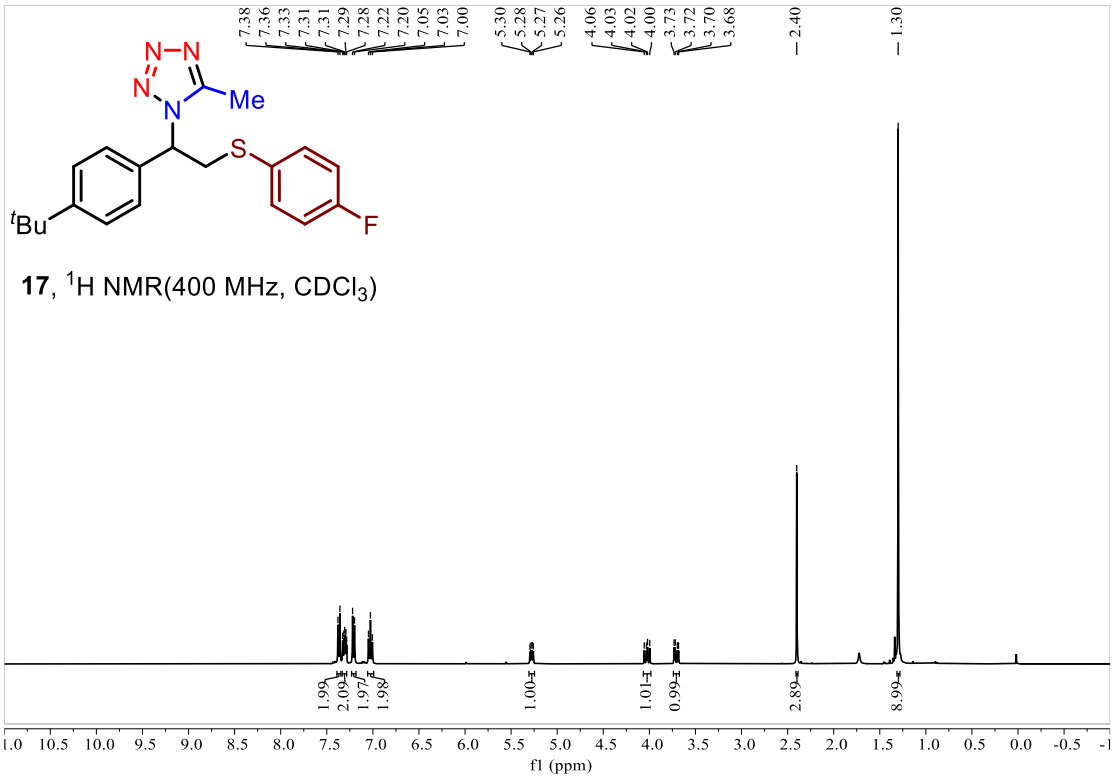

**16**, $^{1}H$ NMR(400 MHz, $CDCl_3$)



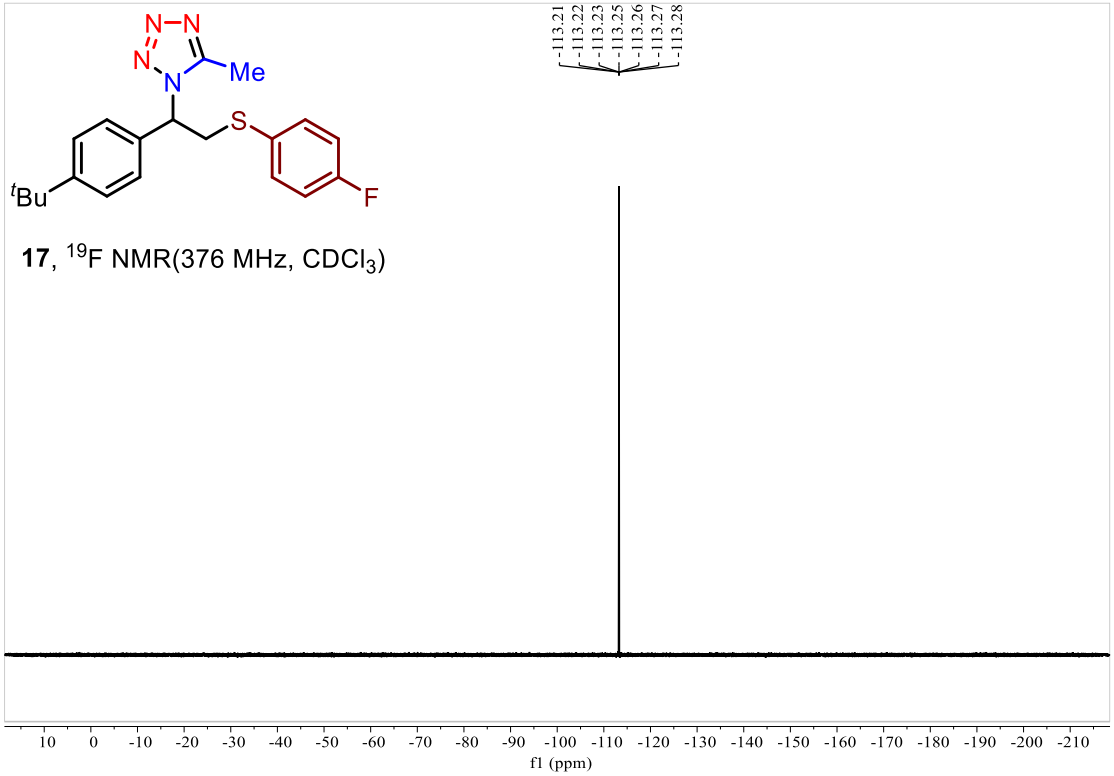

**16**, $^{19}F$ NMR(376 MHz, $CDCl_3$)



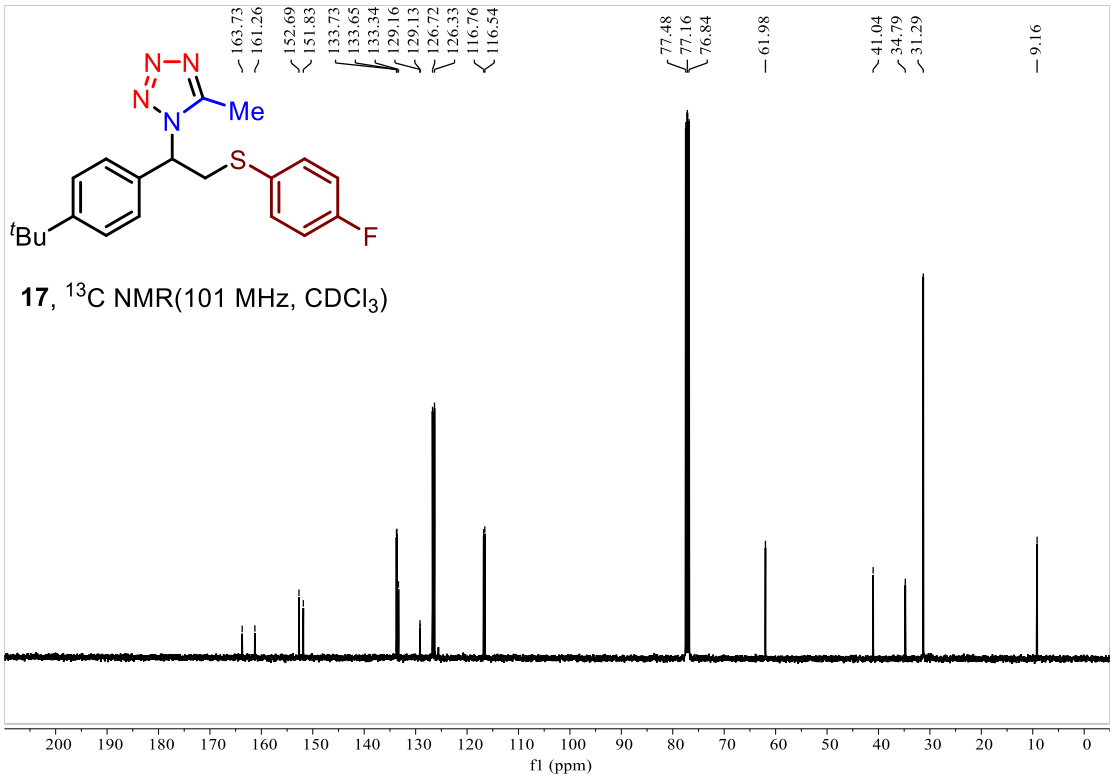

**16**, $^{13}C$ NMR(101 MHz, $CDCl_3$)

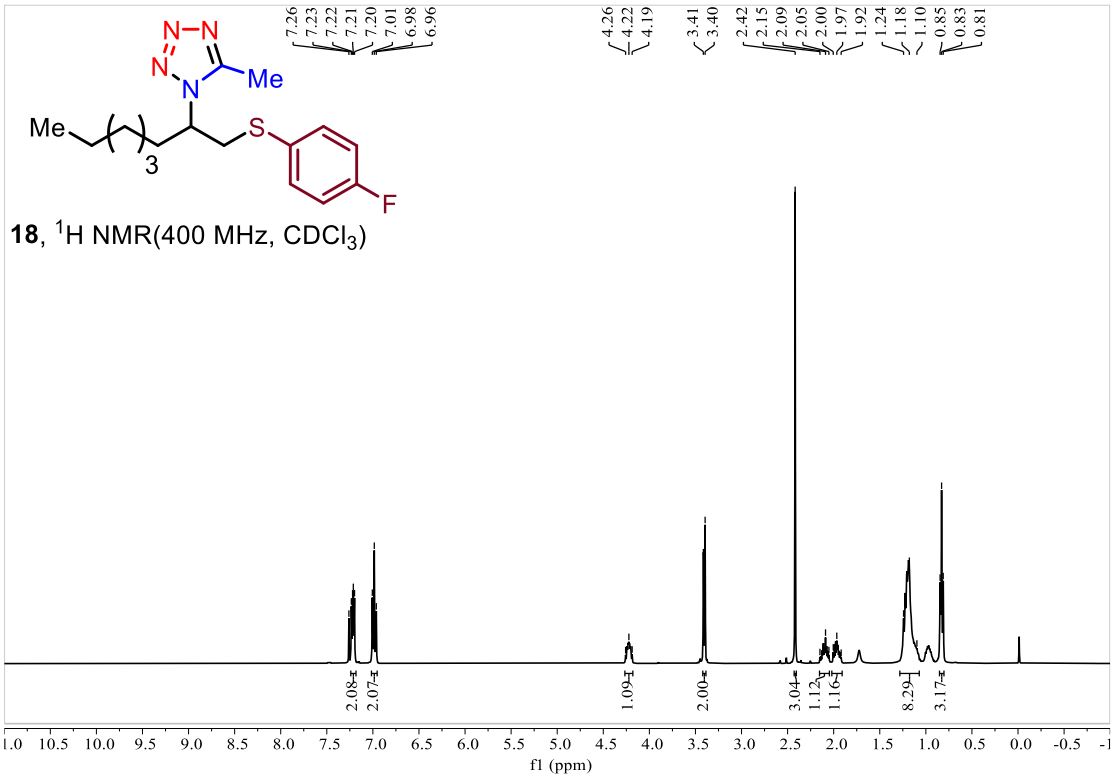


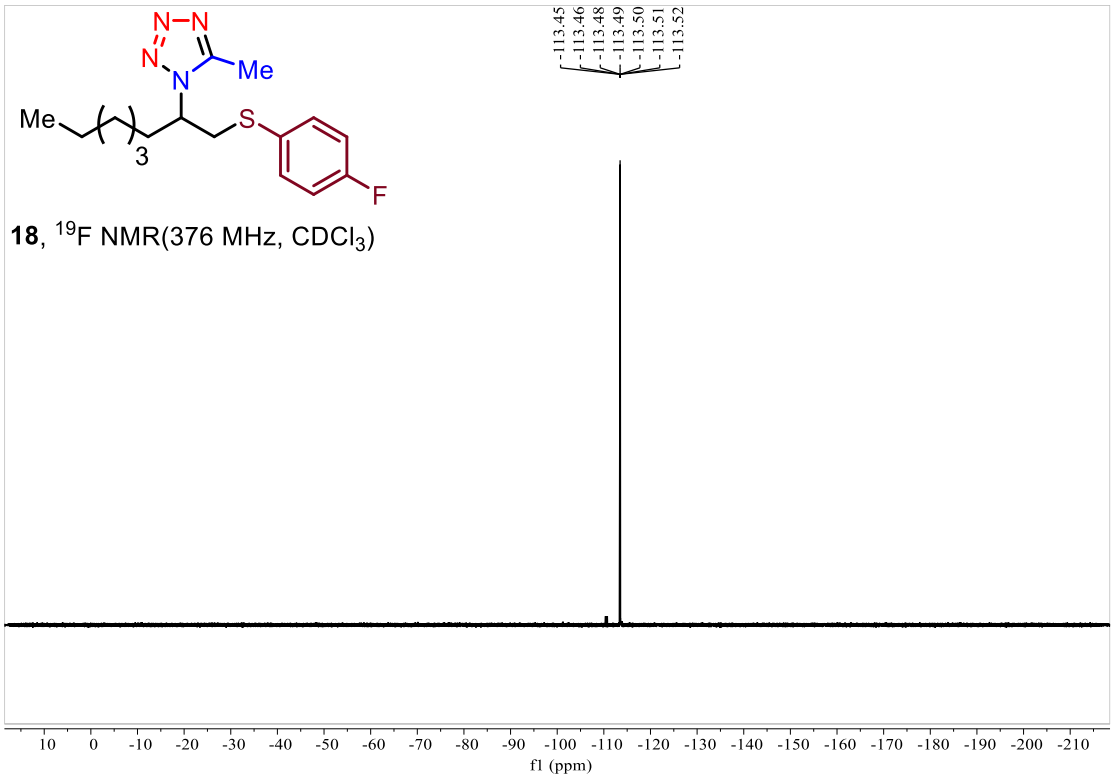

**17**, $^{1}$H NMR(400 MHz, $CDCl_3$)



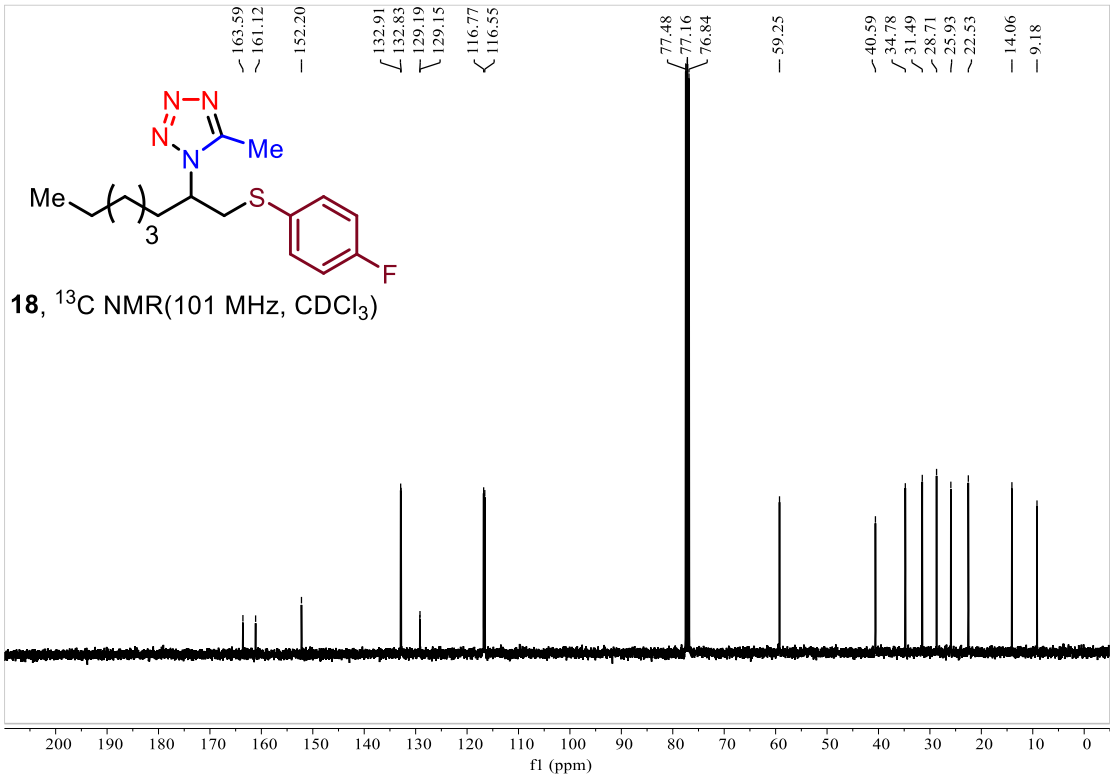

**17**, $^{19}$F NMR(376 MHz, $CDCl_3$)


163.73
161.26
152.69
151.83
133.73
133.65
133.34
129.16
129.13
126.72
126.33
116.76
116.54
77.48
77.16
76.84
61.98
41.04
34.79
31.29
9.16
N–N
N
N
Me
S
F
tBu
17, 13C NMR(101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

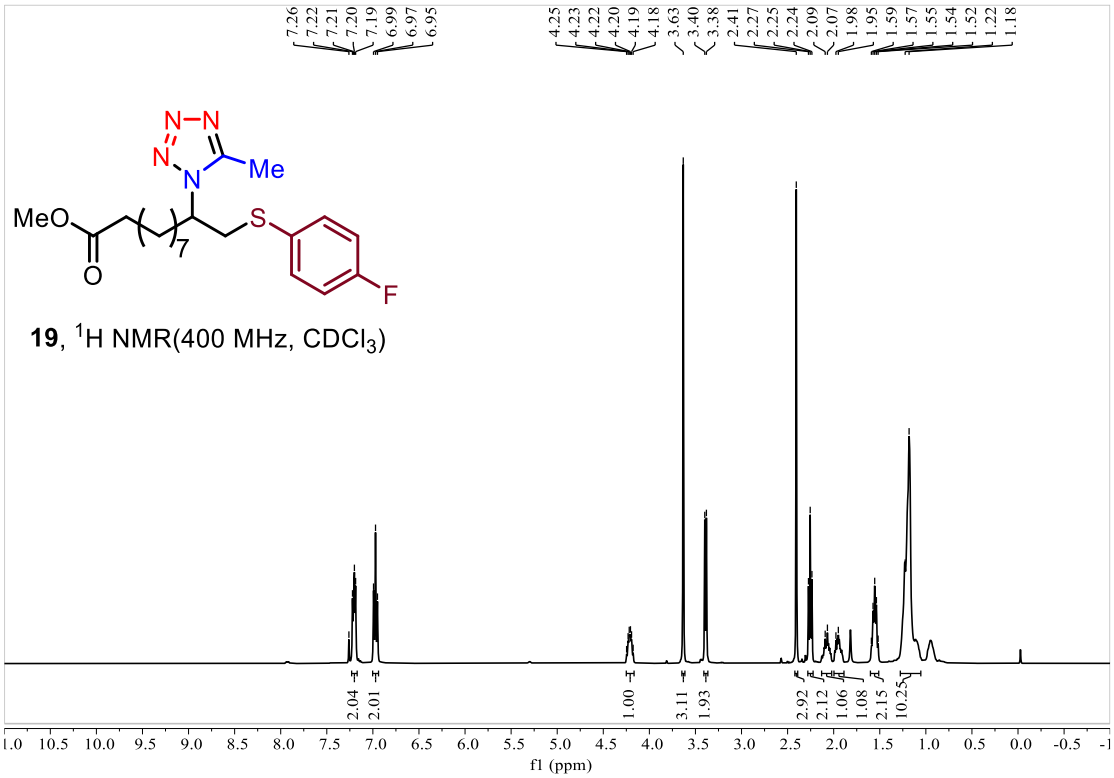

7.26
7.23
7.22
7.21
7.20
7.01
6.98
6.96
4.26
4.22
4.19
3.41
3.40
2.42
2.15
2.09
2.05
2.00
1.97
1.92
1.24
1.18
1.10
0.85
0.83
0.81
N–N
N
N
Me
Me
3
S
F
18, 1H NMR(400 MHz, CDCl3)
2.08
2.07
1.09
2.00
3.04
1.12
1.16
8.29
3.17
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



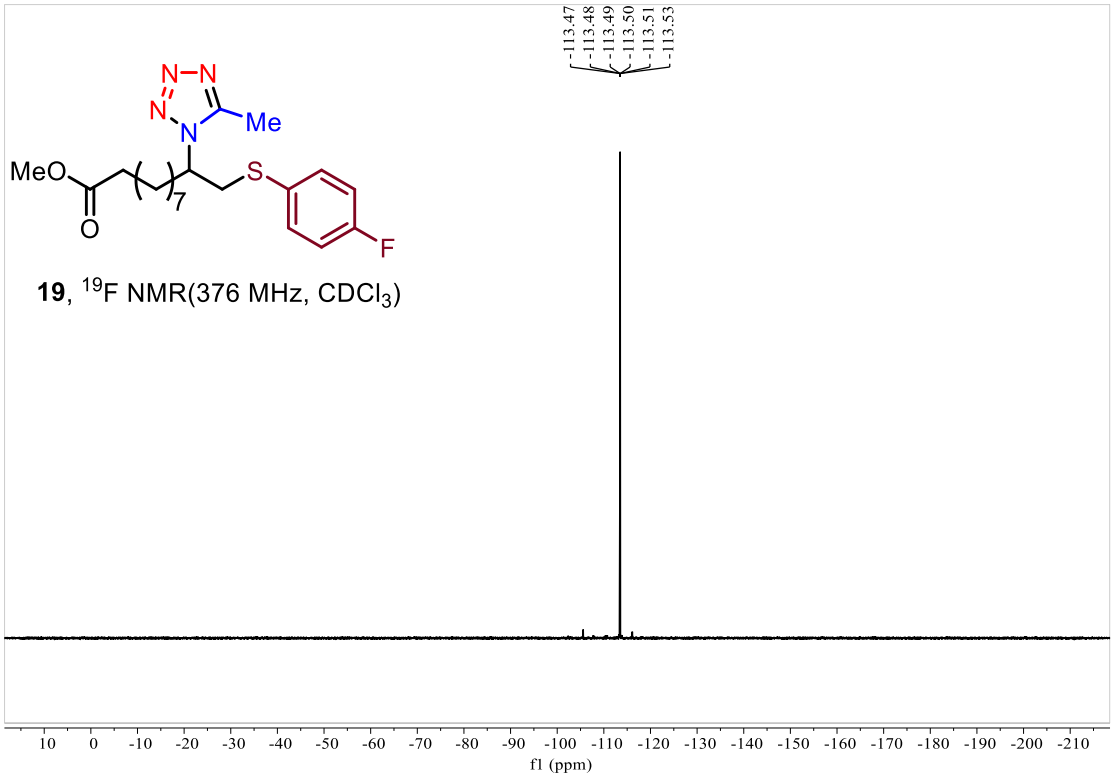

**18**, $^{19}$F NMR(376 MHz, $CDCl_3$)



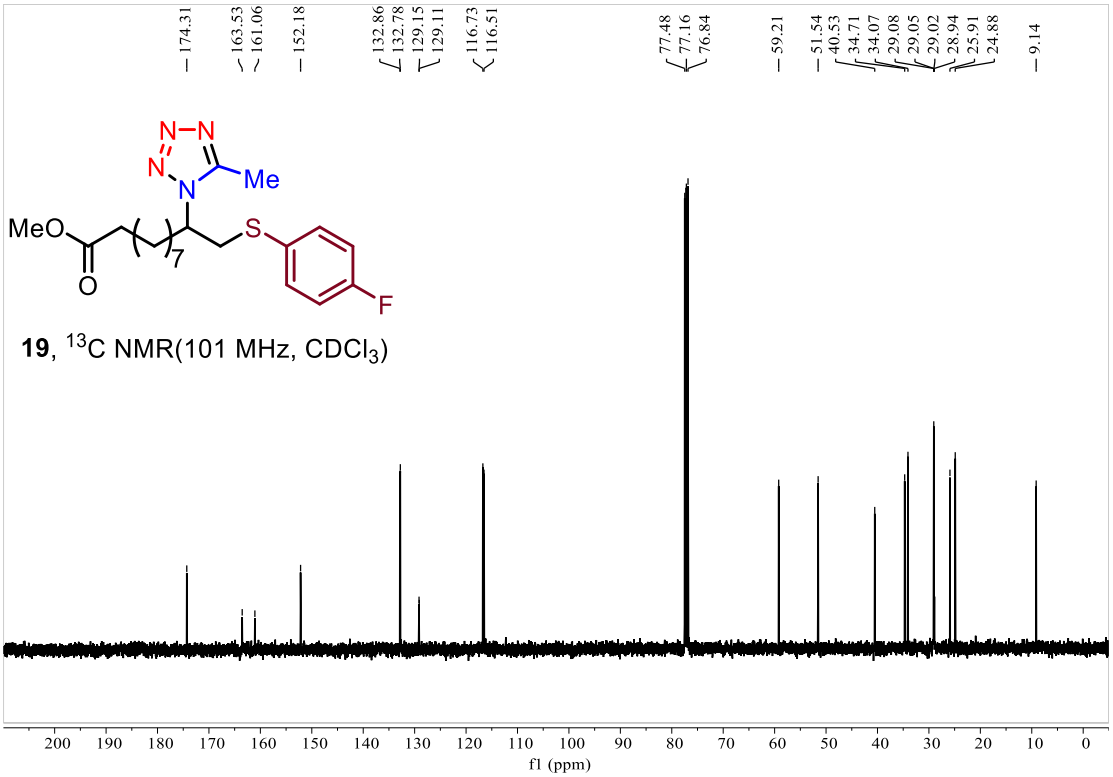

**18**, $^{13}$C NMR(101 MHz, $CDCl_3$)



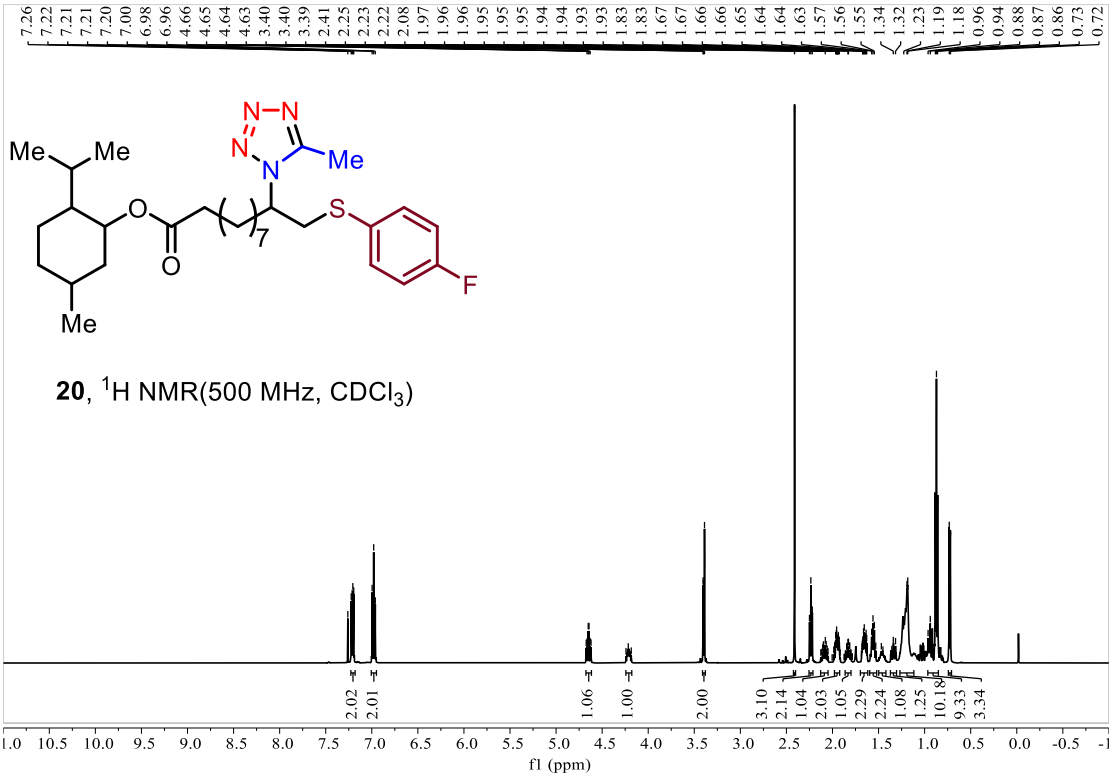

**19**, $^{1}$H NMR(400 MHz, $CDCl_3$)



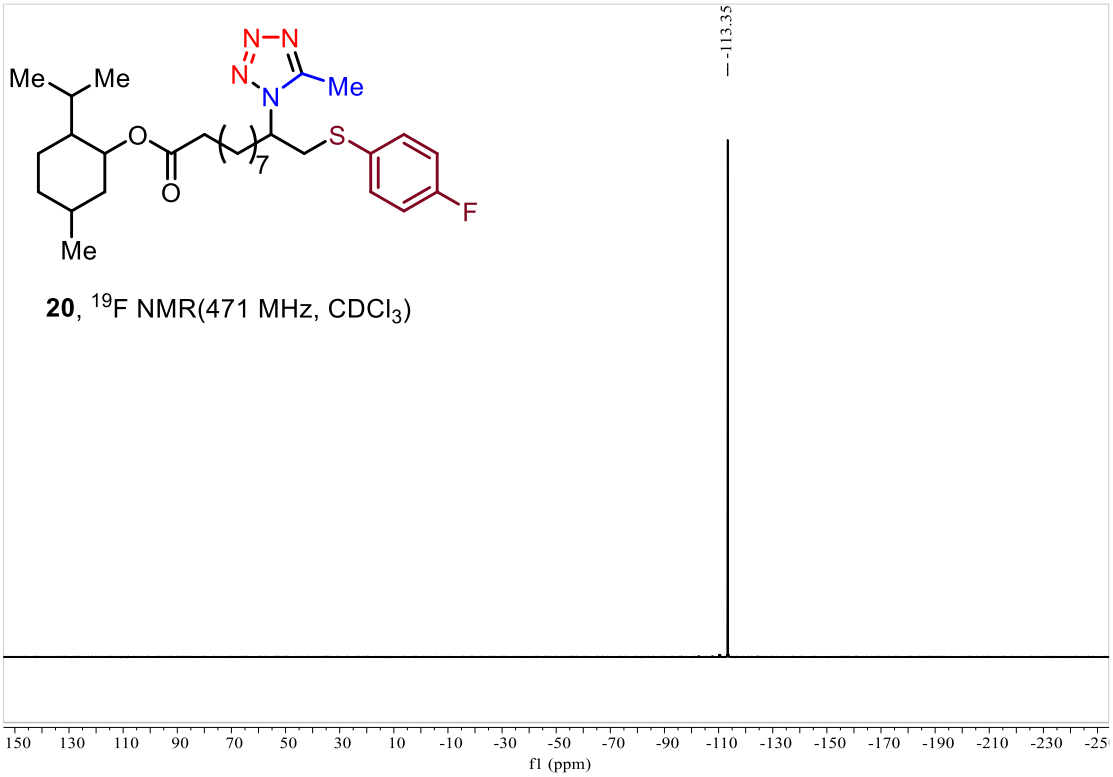

**19**, $^{19}$F NMR(376 MHz, $CDCl_3$)



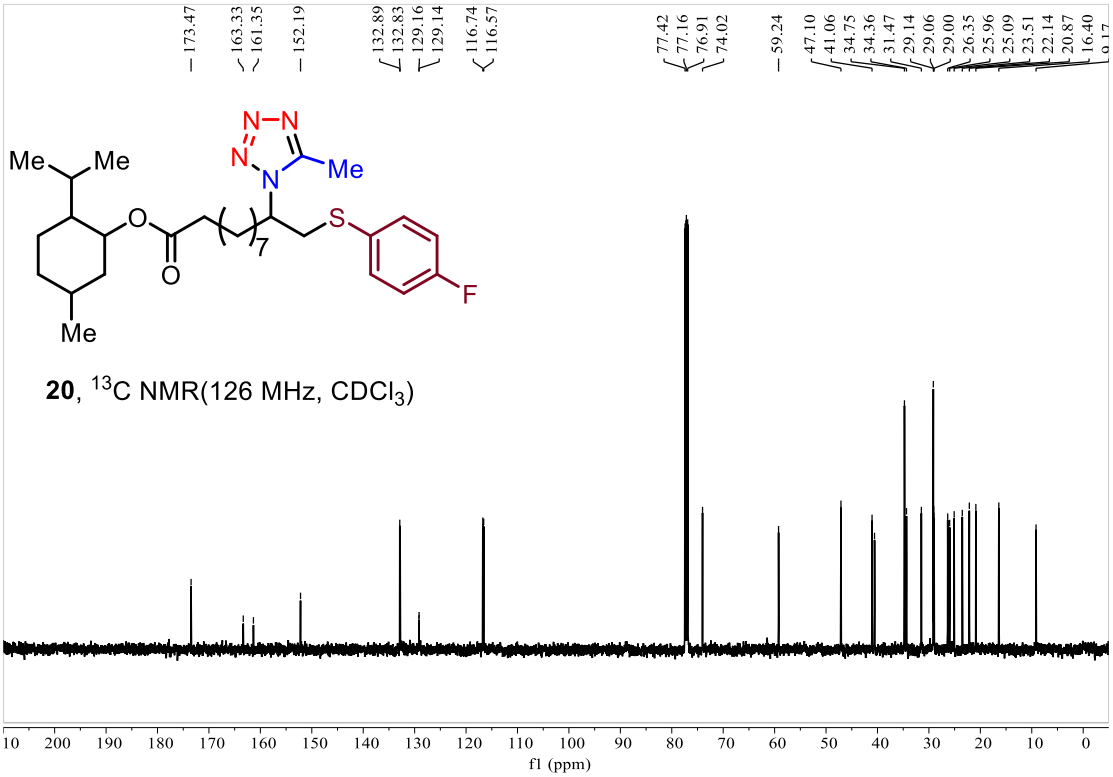

**19**, $^{13}$C NMR(101 MHz, $CDCl_3$)



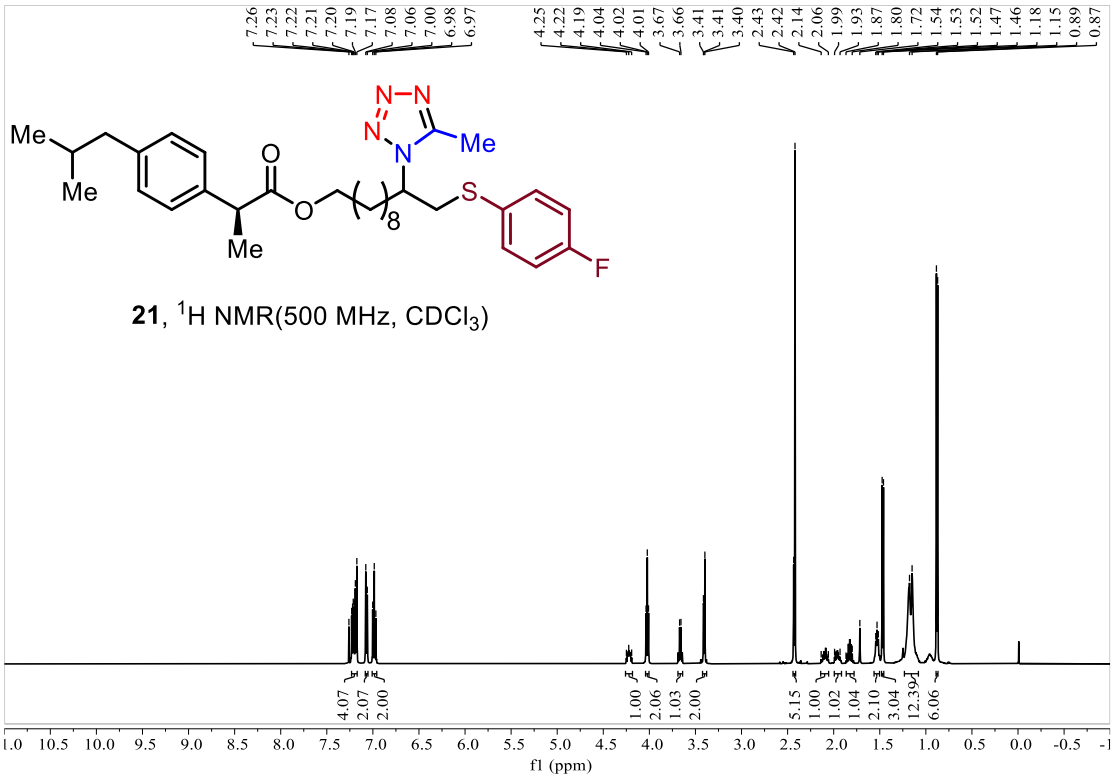

**20**, $^{1}$H NMR(500 MHz, $CDCl_3$)

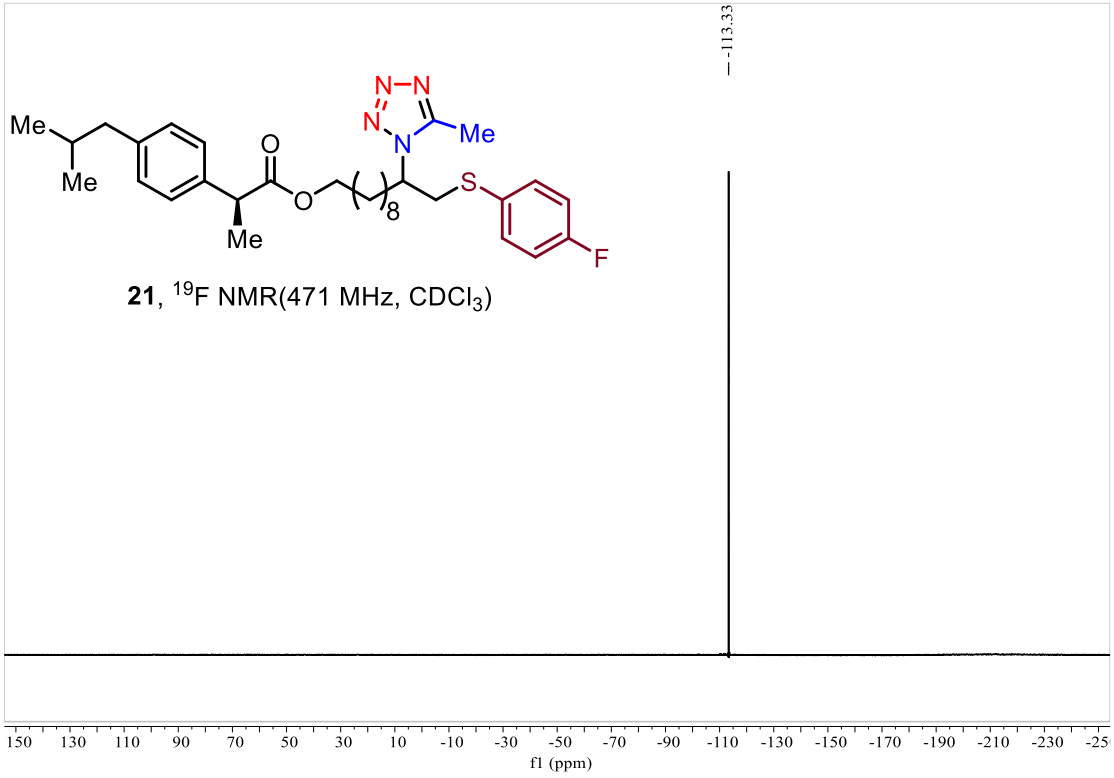


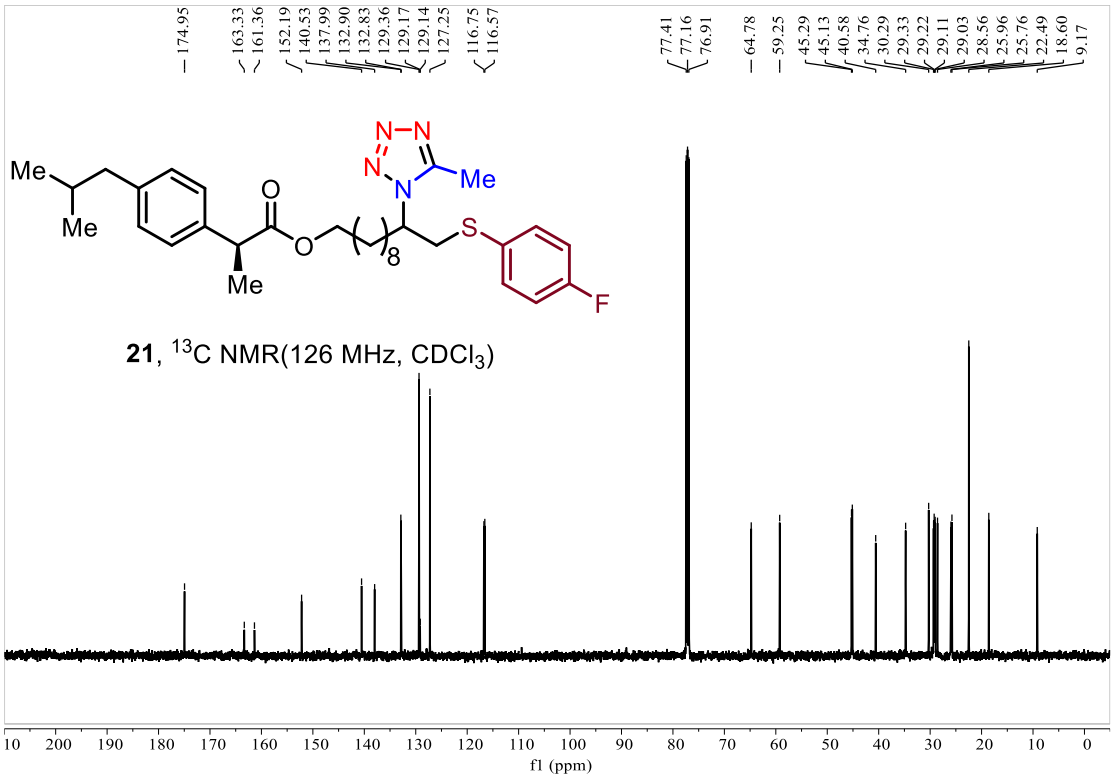

**20**, $^{19}$F NMR(471 MHz, $CDCl_3$)

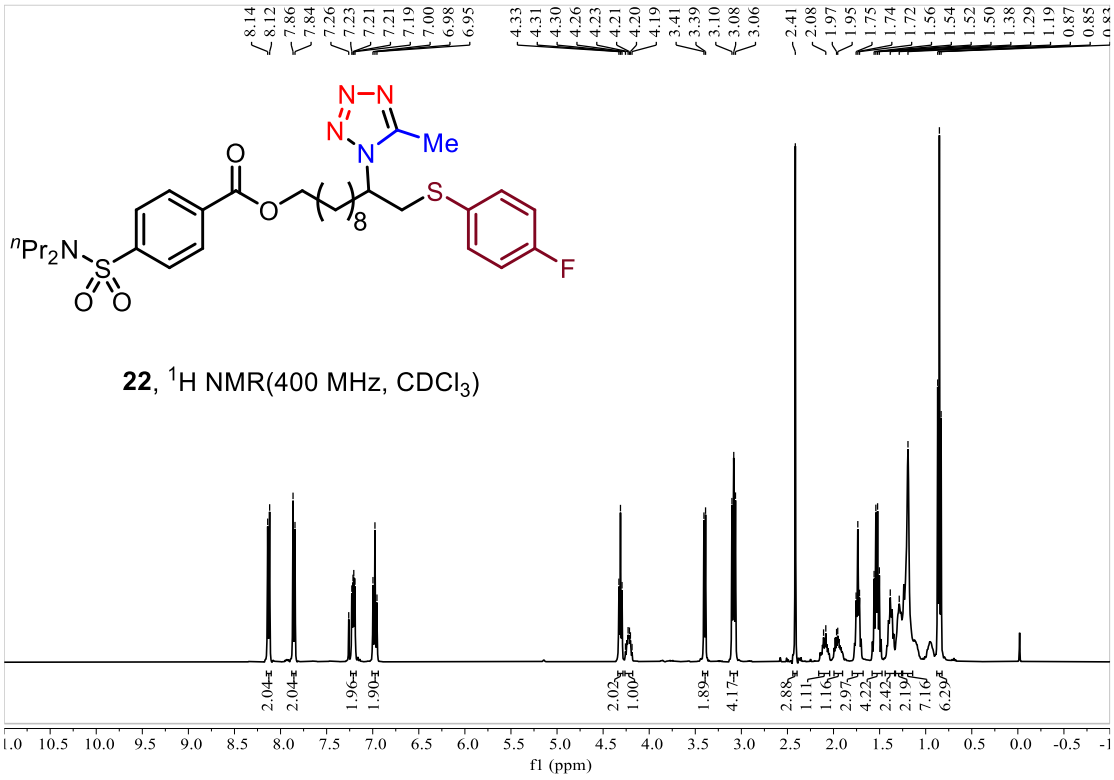


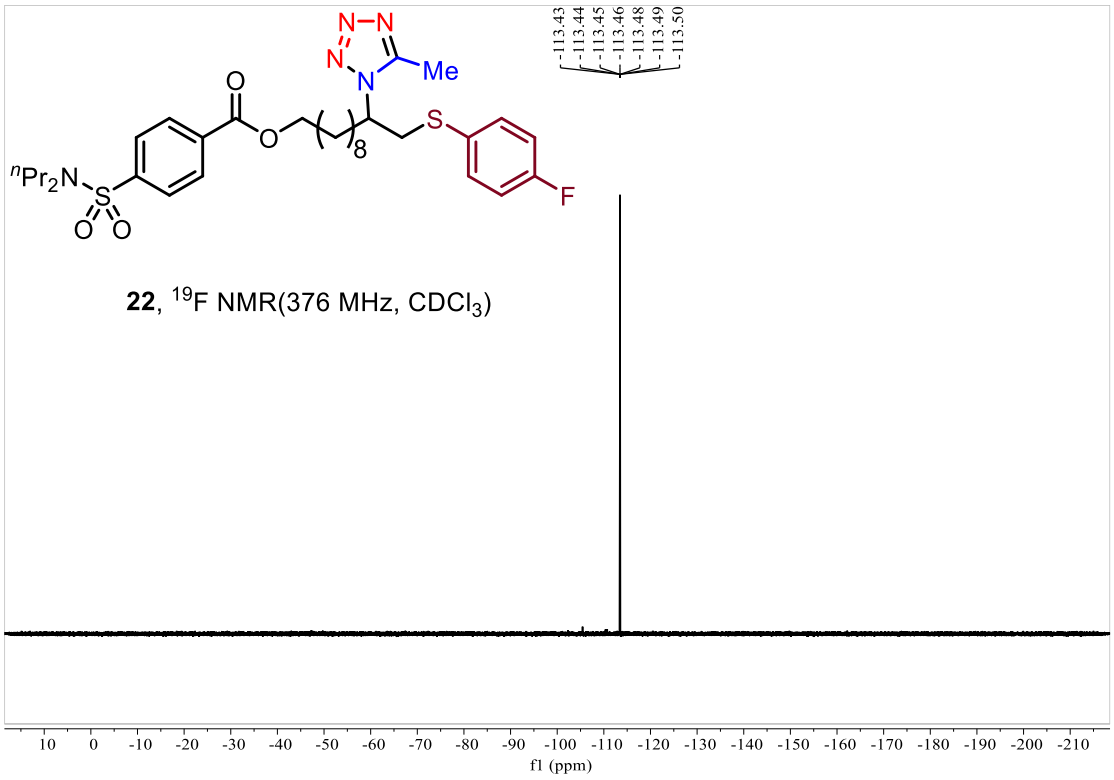

**20**, $^{13}$C NMR(126 MHz, $CDCl_3$)


Me
Me
O
O
8
N–N
N
N
Me
S
F
Me
21, $^{1}$H NMR(500 MHz, $CDCl_3$)
f1 (ppm)

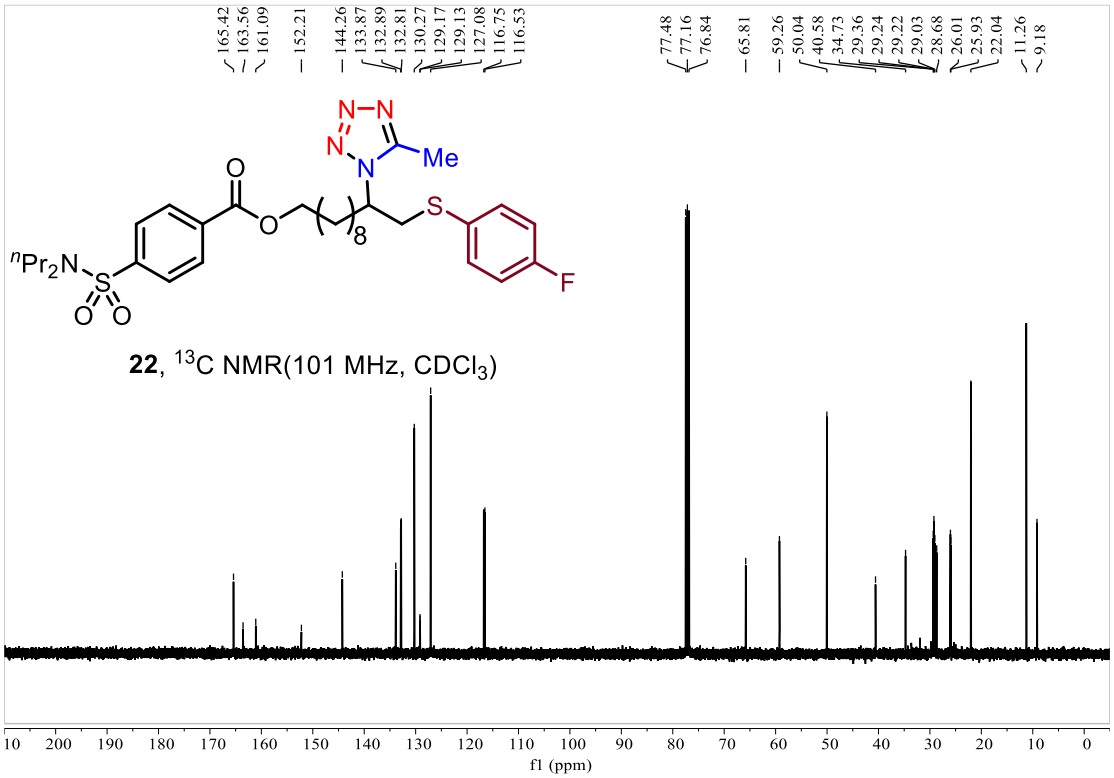

-113.33
Me
Me
O
O
8
N–N
N
N
Me
S
F
Me
21, $^{19}$F NMR(471 MHz, $CDCl_3$)
f1 (ppm)


174.95
163.33
161.36
152.19
140.53
137.99
132.90
132.83
129.36
129.17
129.14
127.25
116.75
116.57
77.41
77.16
76.91
64.78
59.25
45.29
45.13
40.58
34.76
30.29
29.33
29.22
29.11
29.03
28.56
25.96
25.76
22.49
18.60
9.17
Me
Me
Me
O
O
8
N
N
N
Me
S
F
21, 13C NMR(126 MHz, CDCl3)
f1 (ppm)

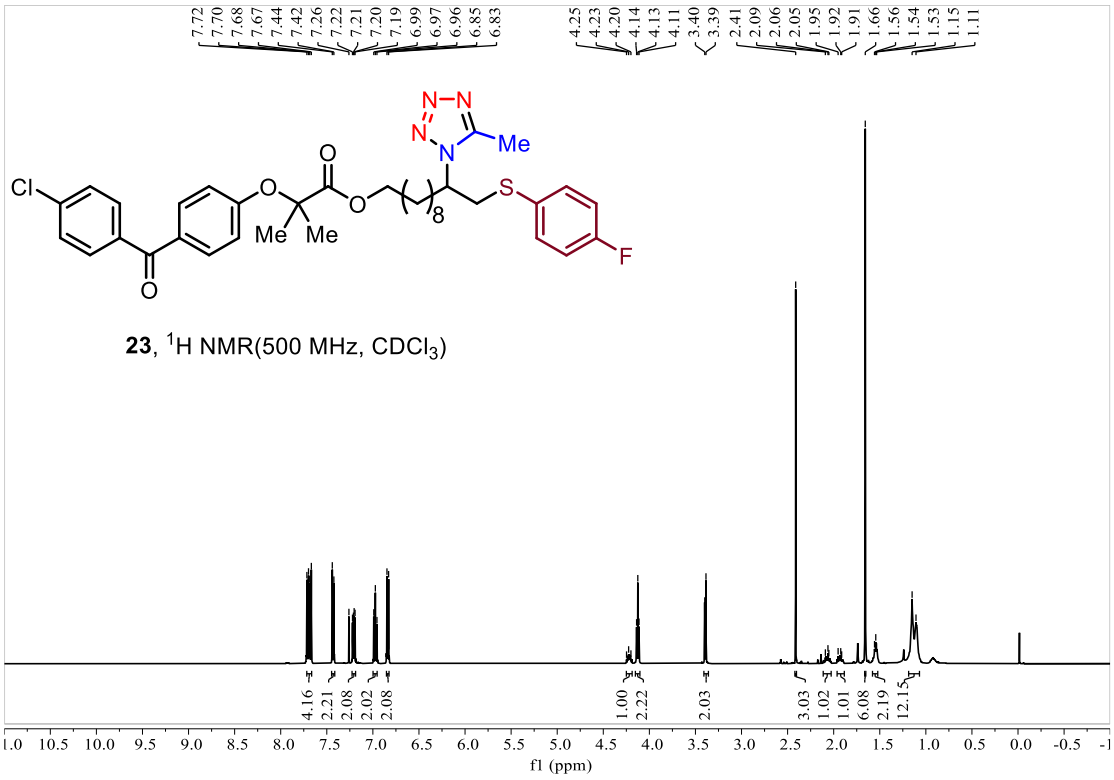

8.14
8.12
7.86
7.84
7.26
7.23
7.21
7.21
7.19
7.00
6.98
6.95
4.33
4.31
4.30
4.26
4.23
4.21
4.20
4.19
3.41
3.39
3.10
3.08
3.06
2.41
2.08
1.97
1.95
1.75
1.74
1.72
1.56
1.54
1.52
1.50
1.38
1.29
1.19
0.87
0.85
2.04
2.04
1.96
1.90
2.02
1.00
1.89
4.17
2.88
1.11
1.16
2.97
4.22
2.42
2.19
7.16
6.29
nPr2N
S
O
O
O
O
8
N
N
N
Me
S
F
22, 1H NMR(400 MHz, CDCl3)
f1 (ppm)



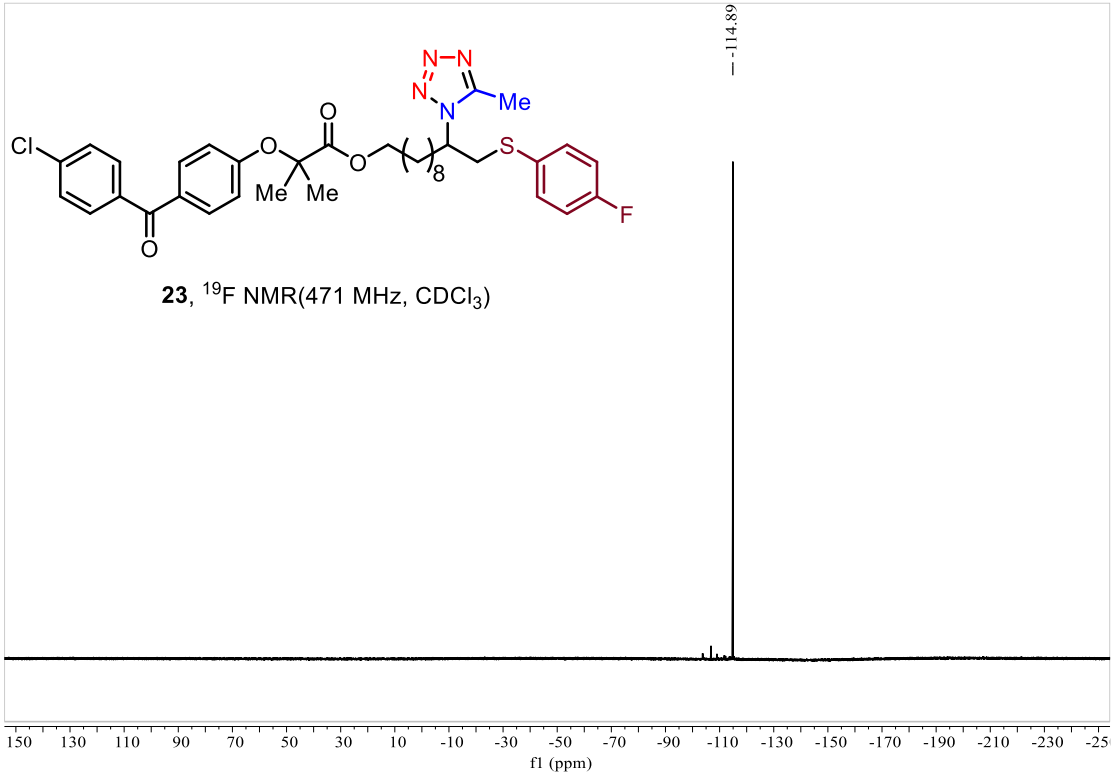

**22**, $^{19}$F NMR(376 MHz, $CDCl_3$)



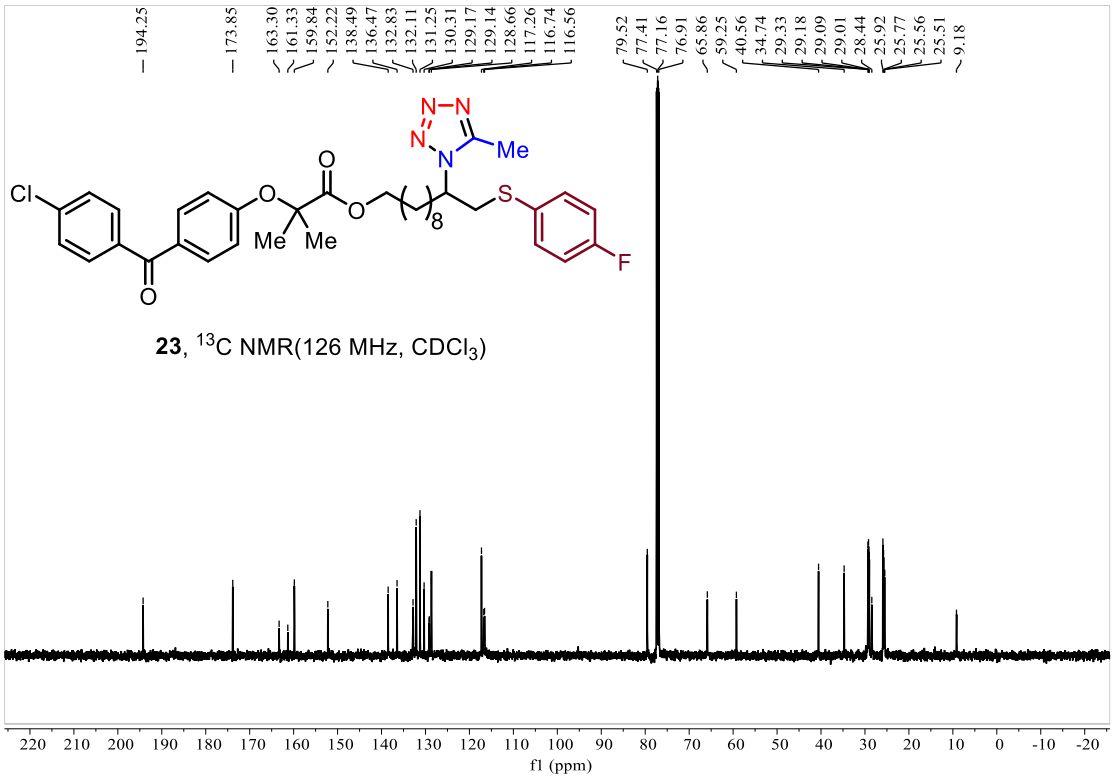

**22**, $^{13}$C NMR(101 MHz, $CDCl_3$)



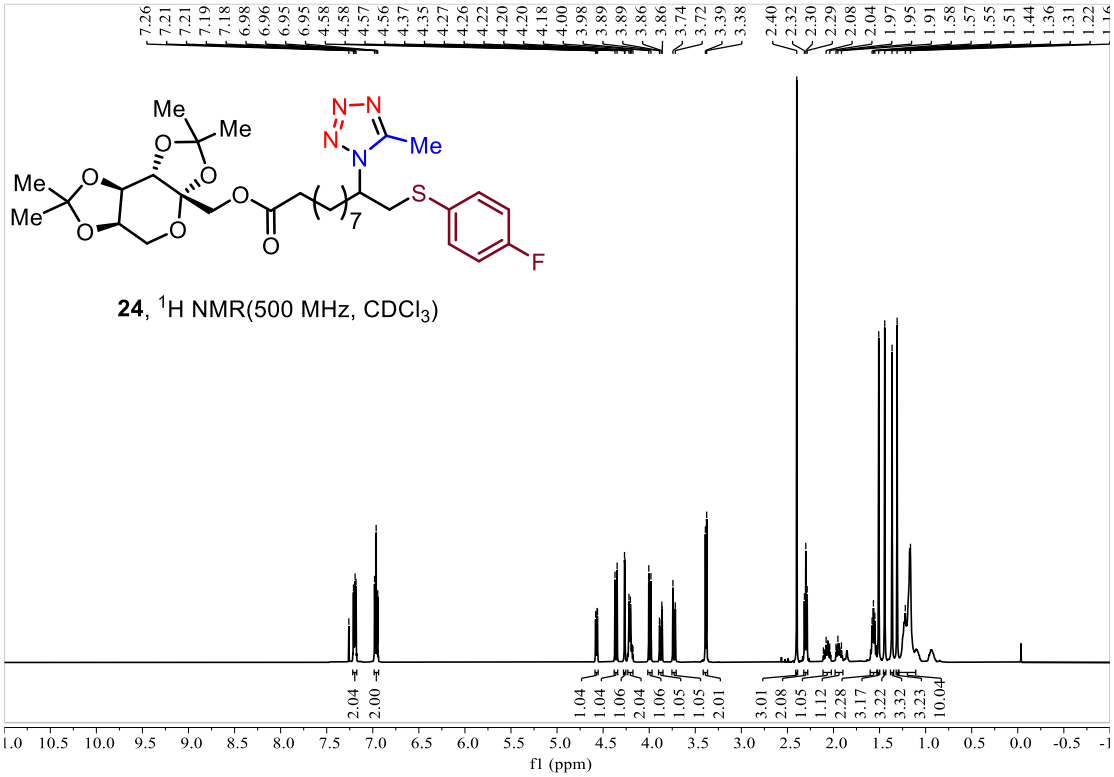

**23**, $^{1}$H NMR(500 MHz, $CDCl_3$)



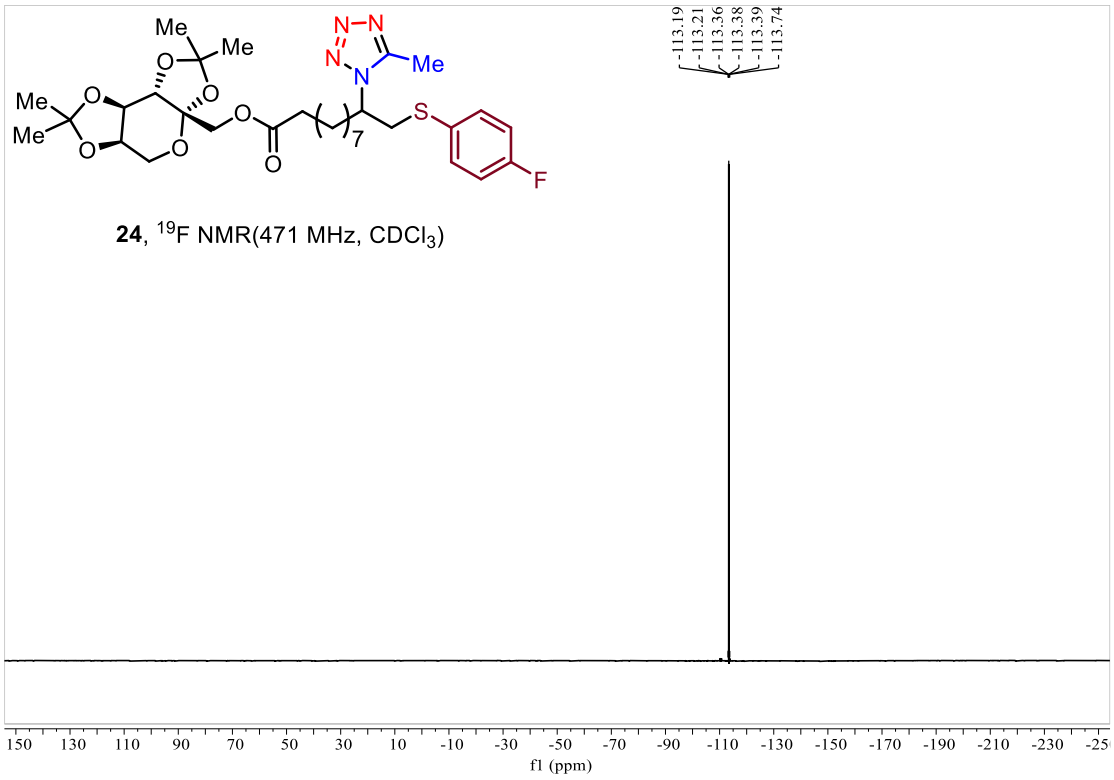

**23**, $^{19}$F NMR(471 MHz, $CDCl_3$)



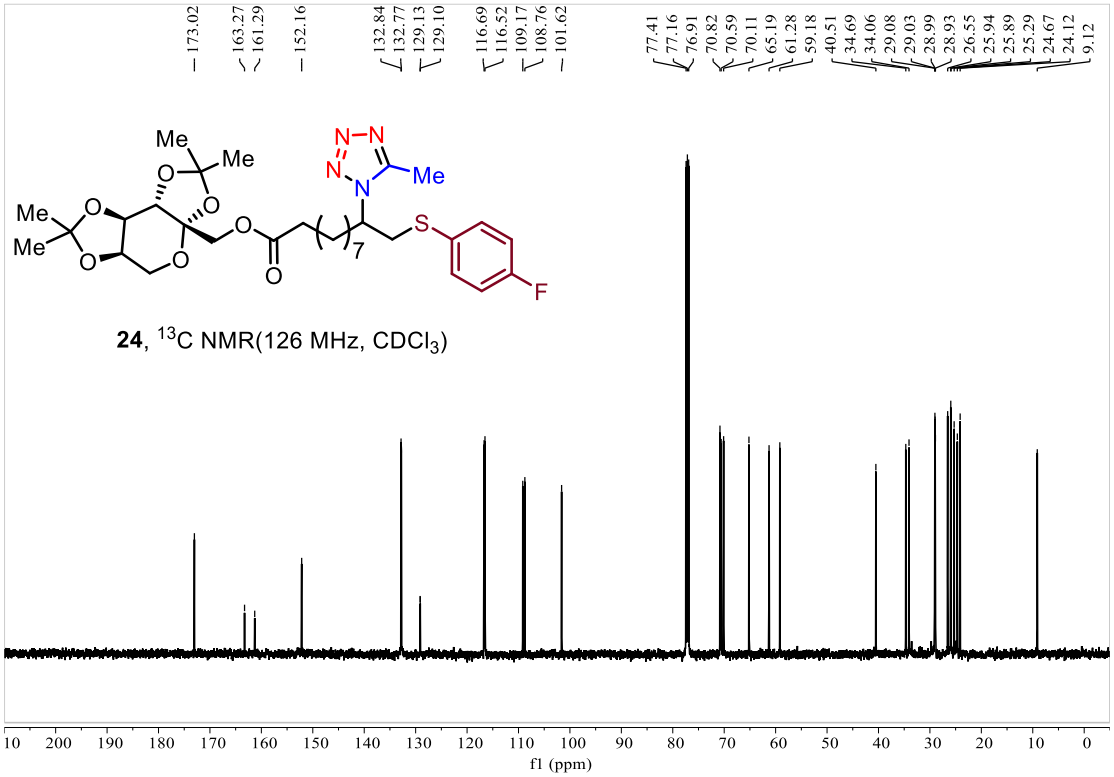

**23**, $^{13}$C NMR(126 MHz, $CDCl_3$)



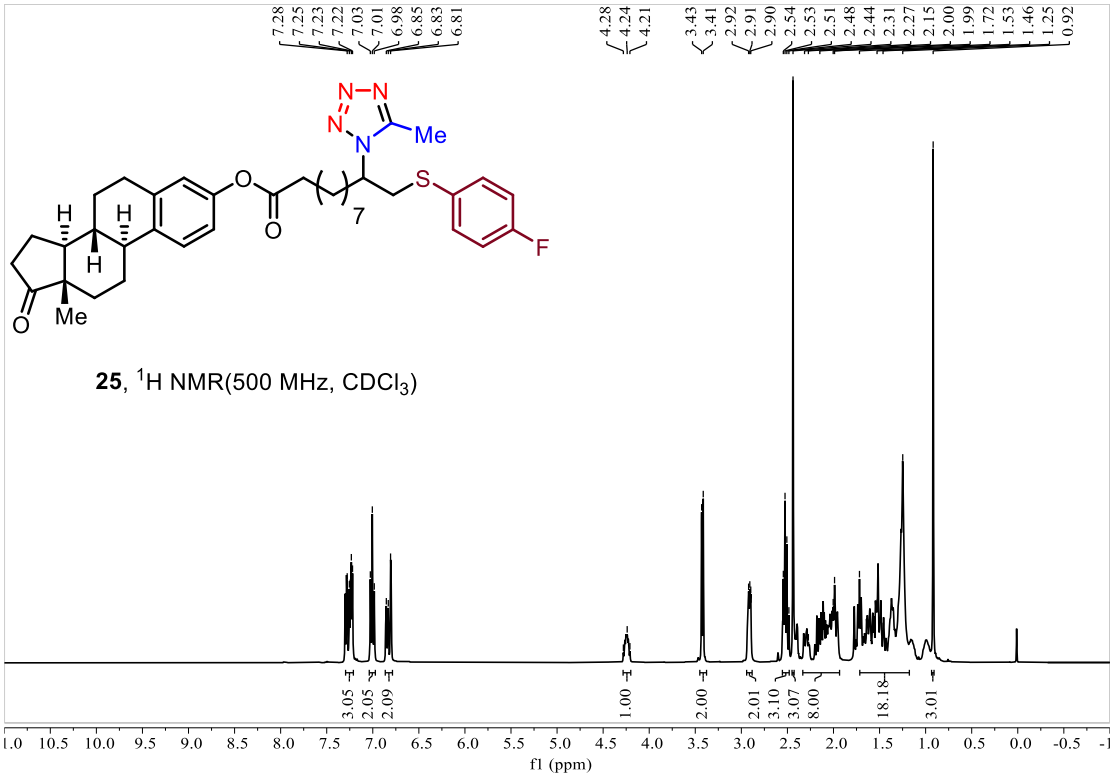

**24**, $^{1}$H NMR(500 MHz, $CDCl_3$)



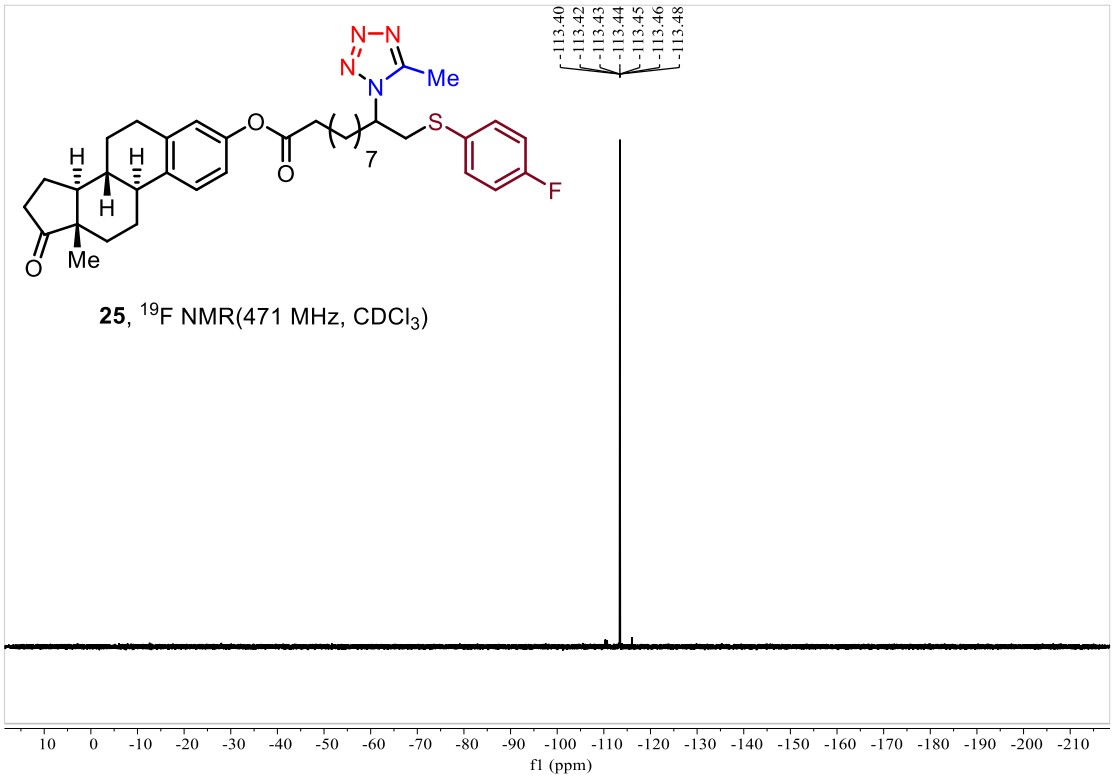

**24**, $^{19}$F NMR(471 MHz, $CDCl_3$)



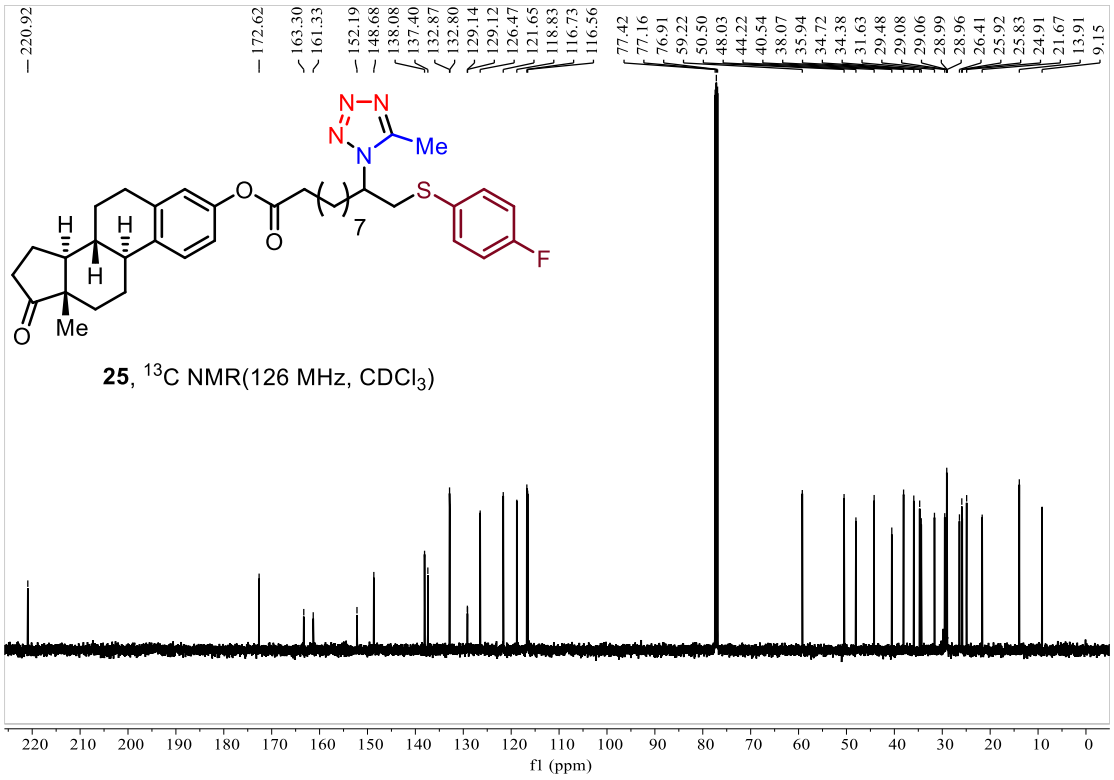

**24**, $^{13}$C NMR(126 MHz, $CDCl_3$)



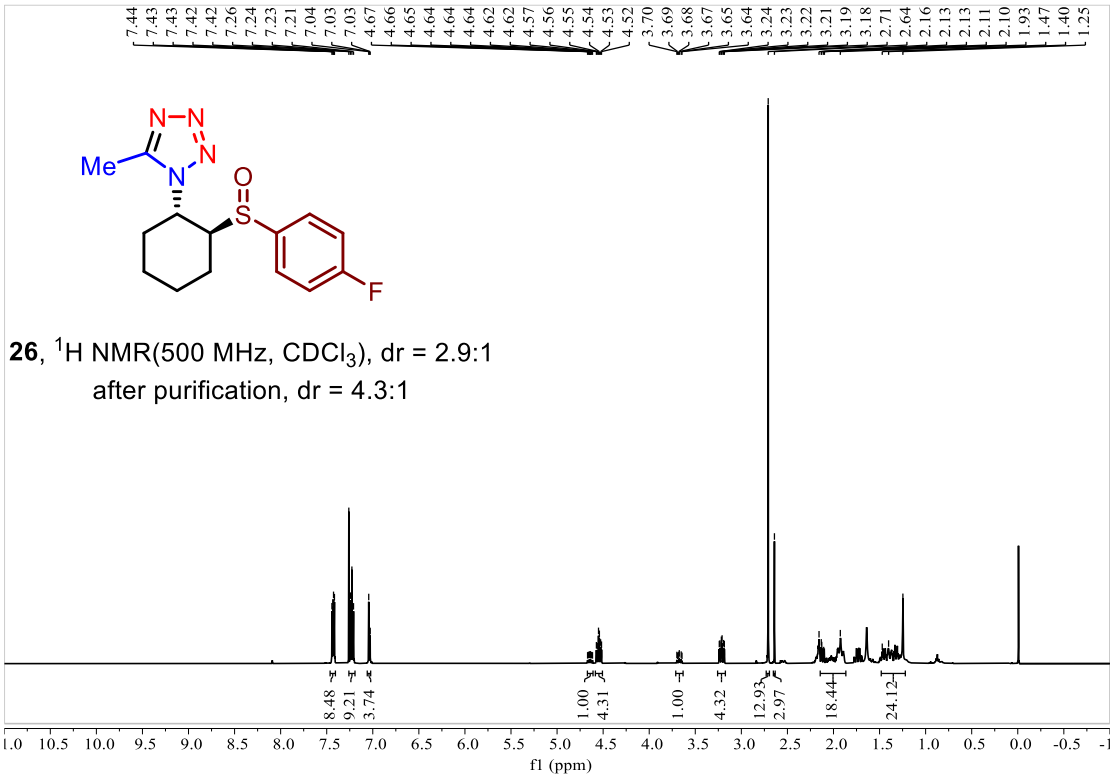

**25**, $^{1}$H NMR(500 MHz, $CDCl_3$)



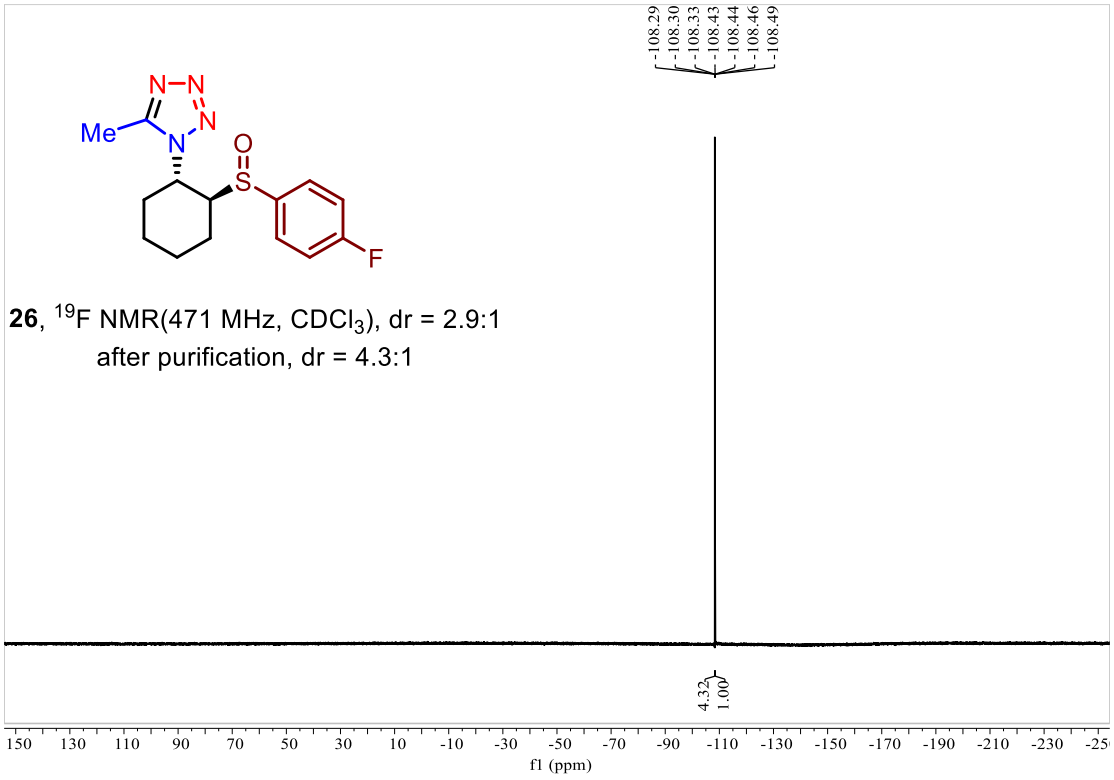

**25**, $^{19}$F NMR(471 MHz, $CDCl_3$)



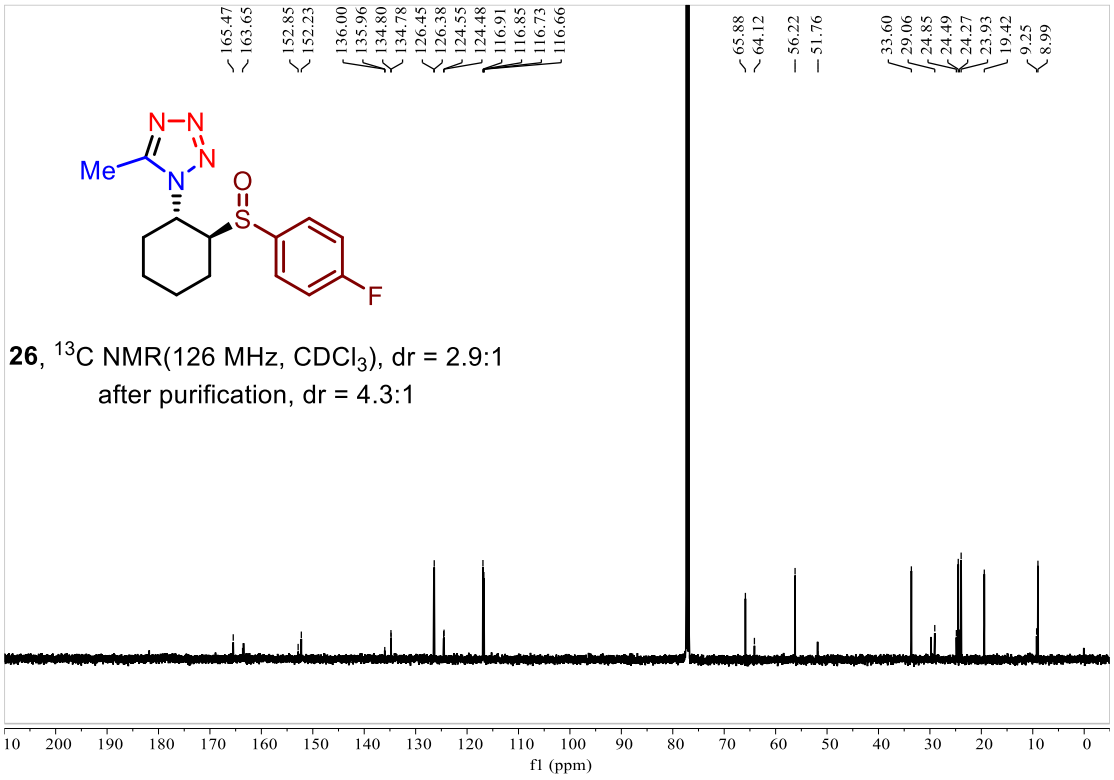

**25**, $^{13}$C NMR(126 MHz, $CDCl_3$)



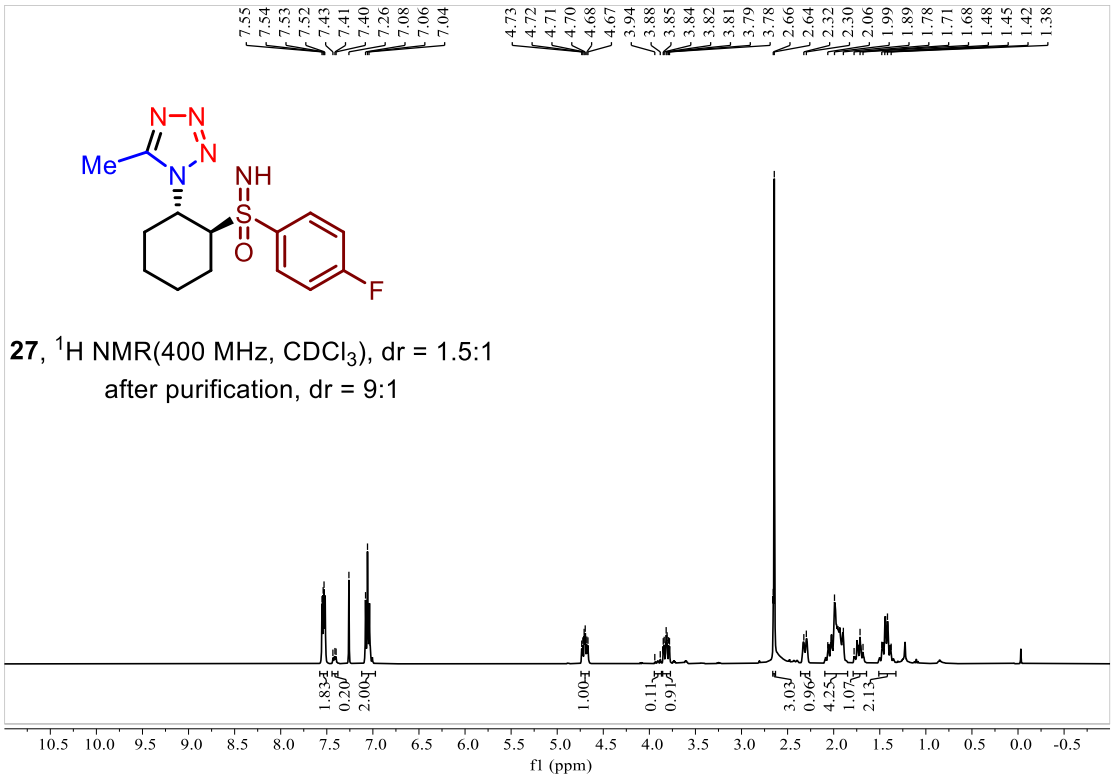

**26**, $^{1}$H NMR(500 MHz, $CDCl_3$), dr = 2.9:1
after purification, dr = 4.3:1



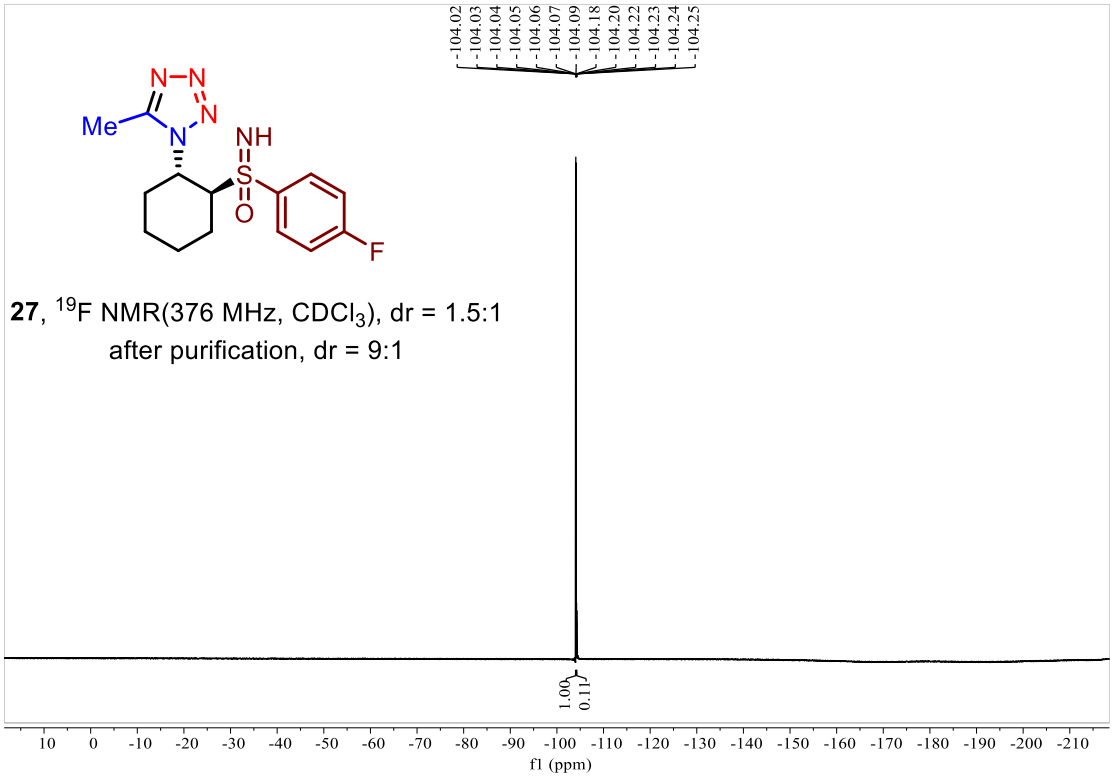

**26**, $^{19}F$ NMR(471 MHz, $CDCl_3$), dr = 2.9:1
after purification, dr = 4.3:1



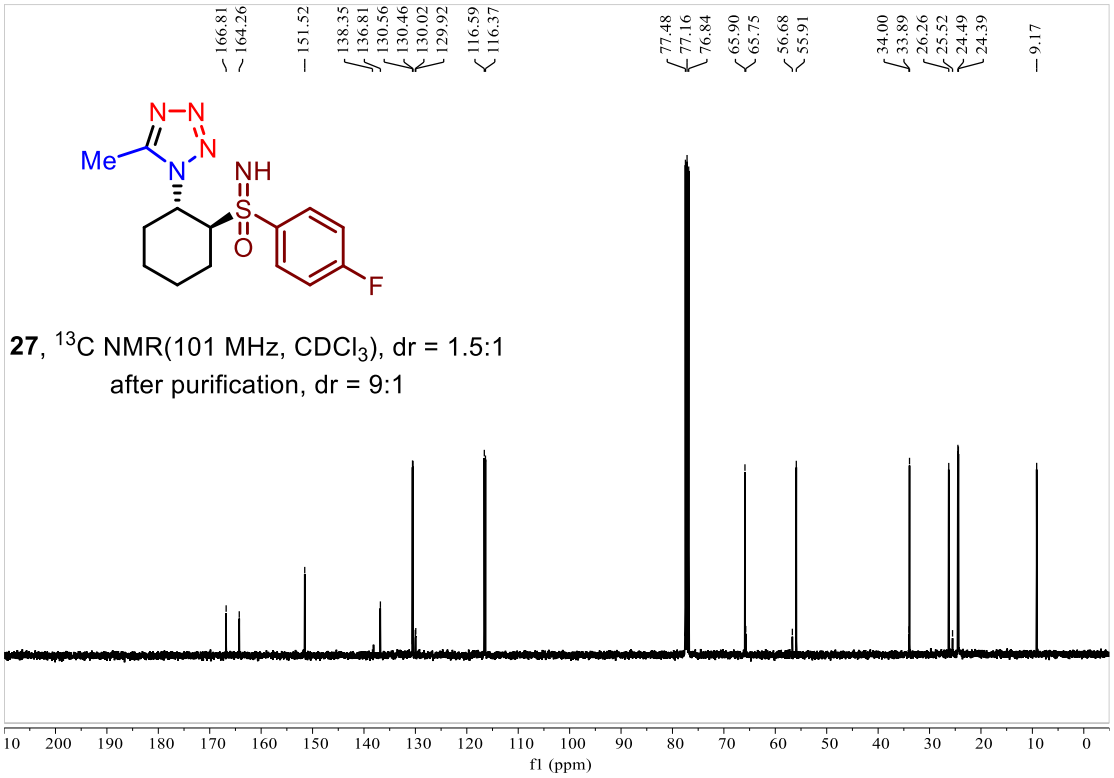

**26**, $^{13}C$ NMR(126 MHz, $CDCl_3$), dr = 2.9:1
after purification, dr = 4.3:1



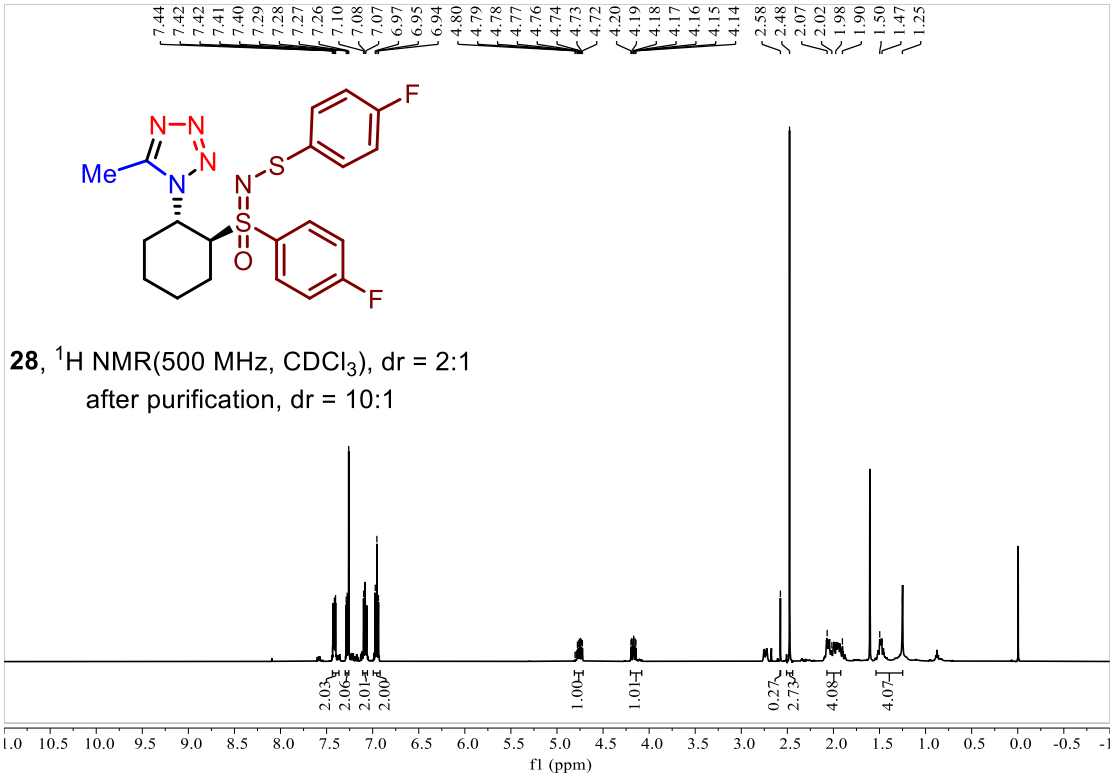

**27**, $^{1}$H NMR(400 MHz, $CDCl_3$), dr = 1.5:1
after purification, dr = 9:1



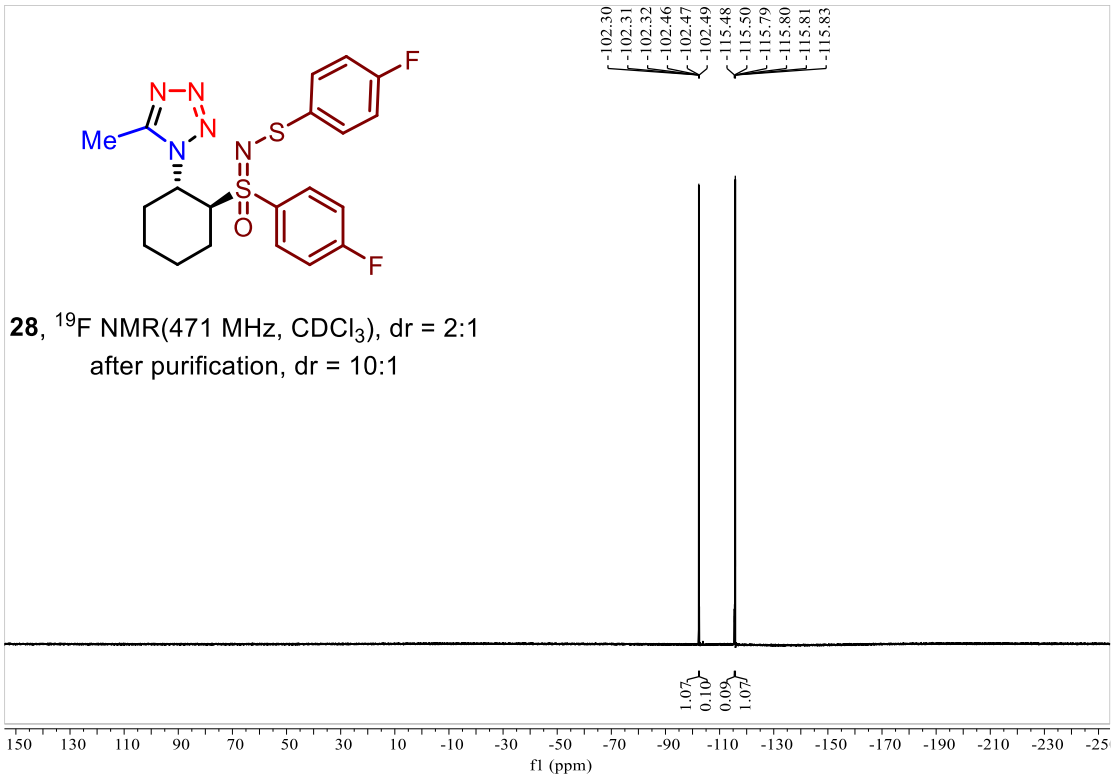

**27**, $^{19}$F NMR(376 MHz, $CDCl_3$), dr = 1.5:1
after purification, dr = 9:1



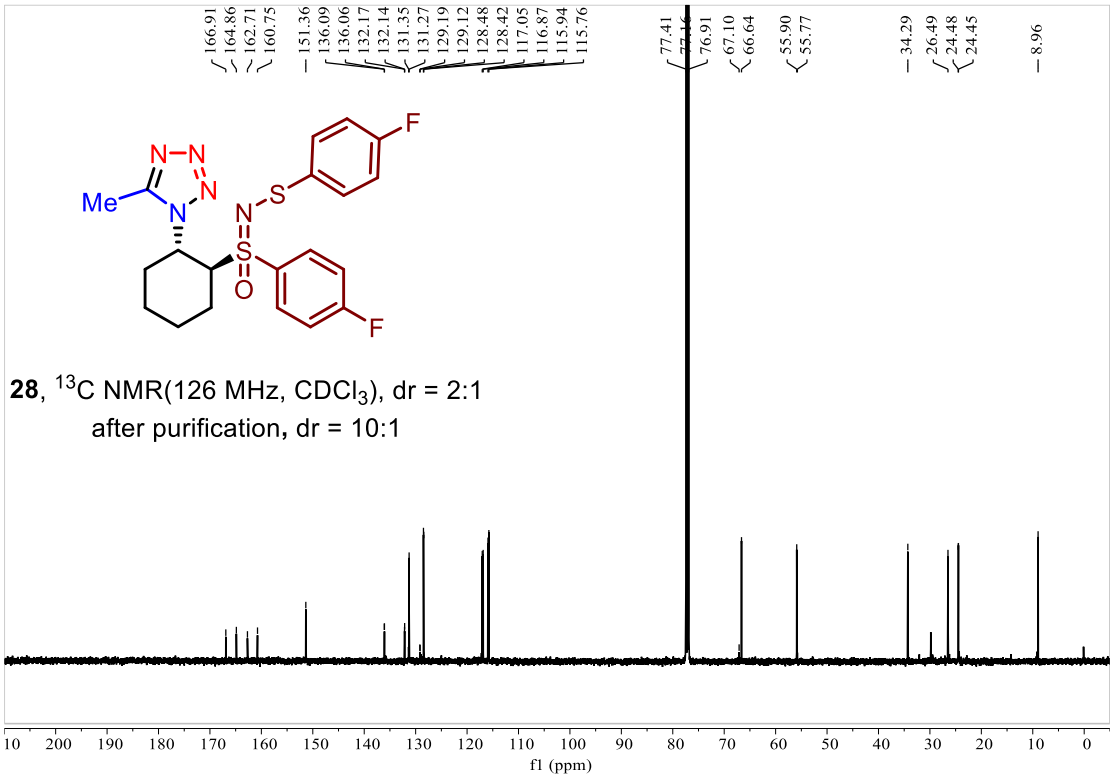

**27**, $^{13}C$ NMR(101 MHz, $CDCl_3$), dr = 1.5:1
after purification, dr = 9:1



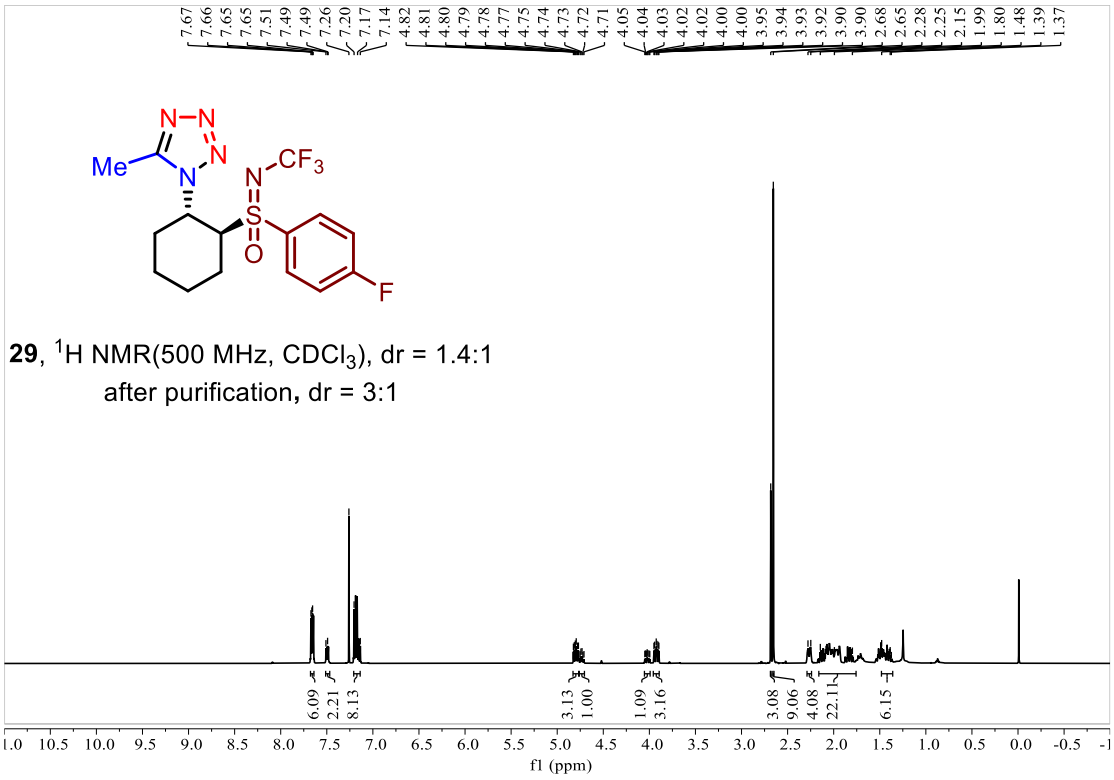

**28**, $^{1}H$ NMR(500 MHz, $CDCl_3$), dr = 2:1
after purification, dr = 10:1



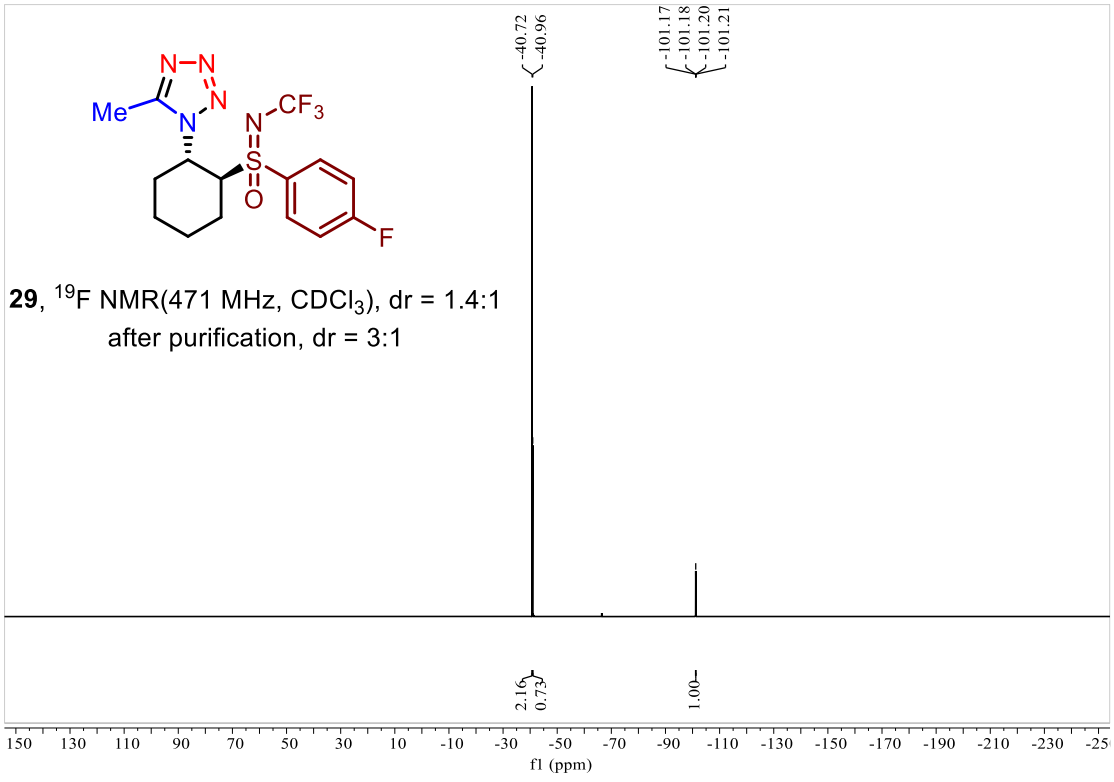

**28**, $^{19}$F NMR(471 MHz, $CDCl_3$), dr = 2:1
after purification, dr = 10:1



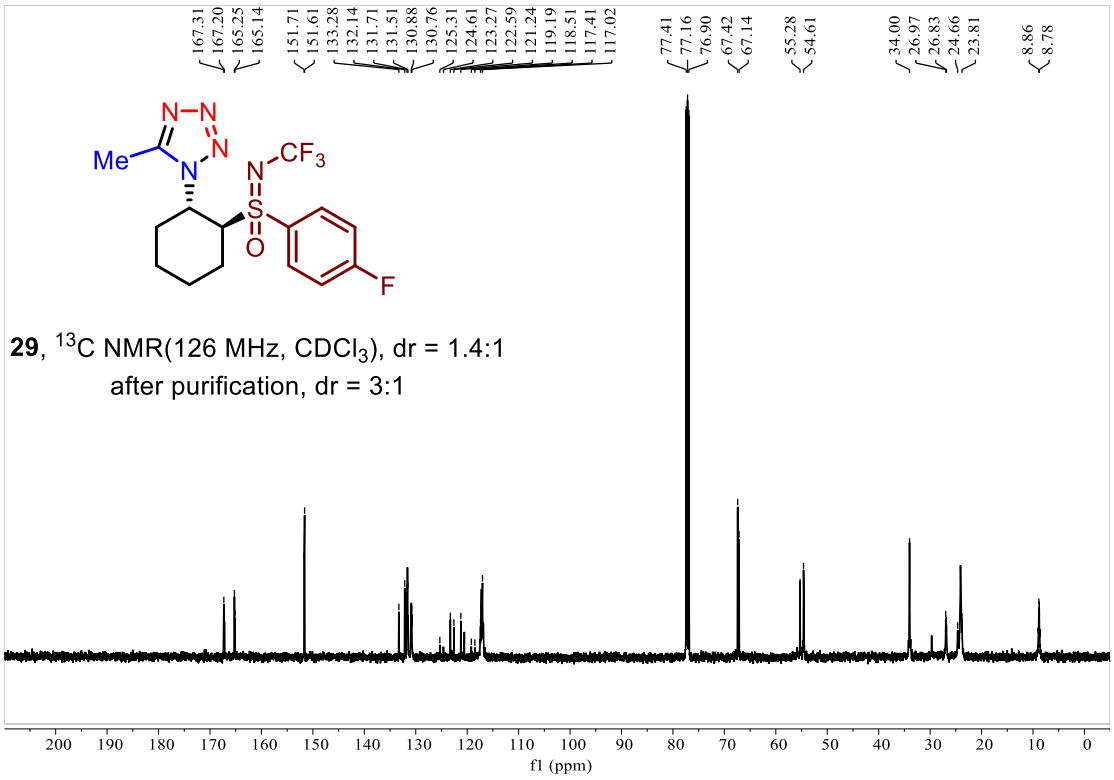

**28**, $^{13}$C NMR(126 MHz, $CDCl_3$), dr = 2:1
after purification, dr = 10:1



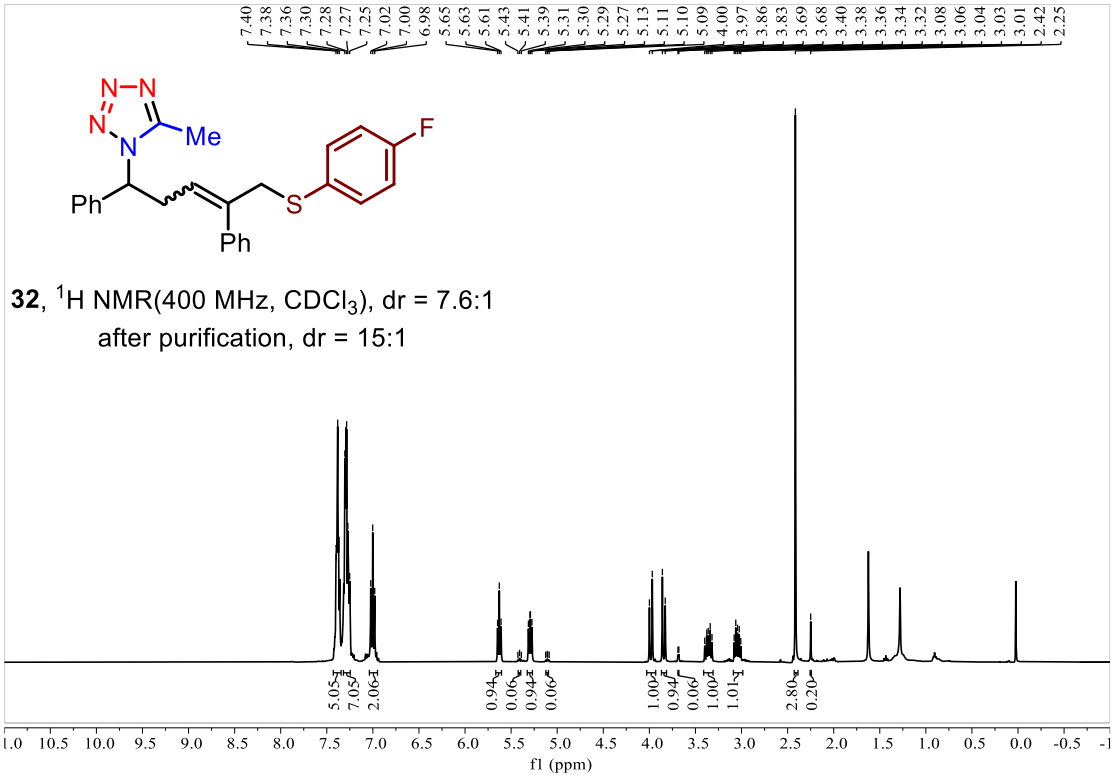

**29**, $^{1}$H NMR(500 MHz, $CDCl_3$), dr = 1.4:1
after purification, dr = 3:1



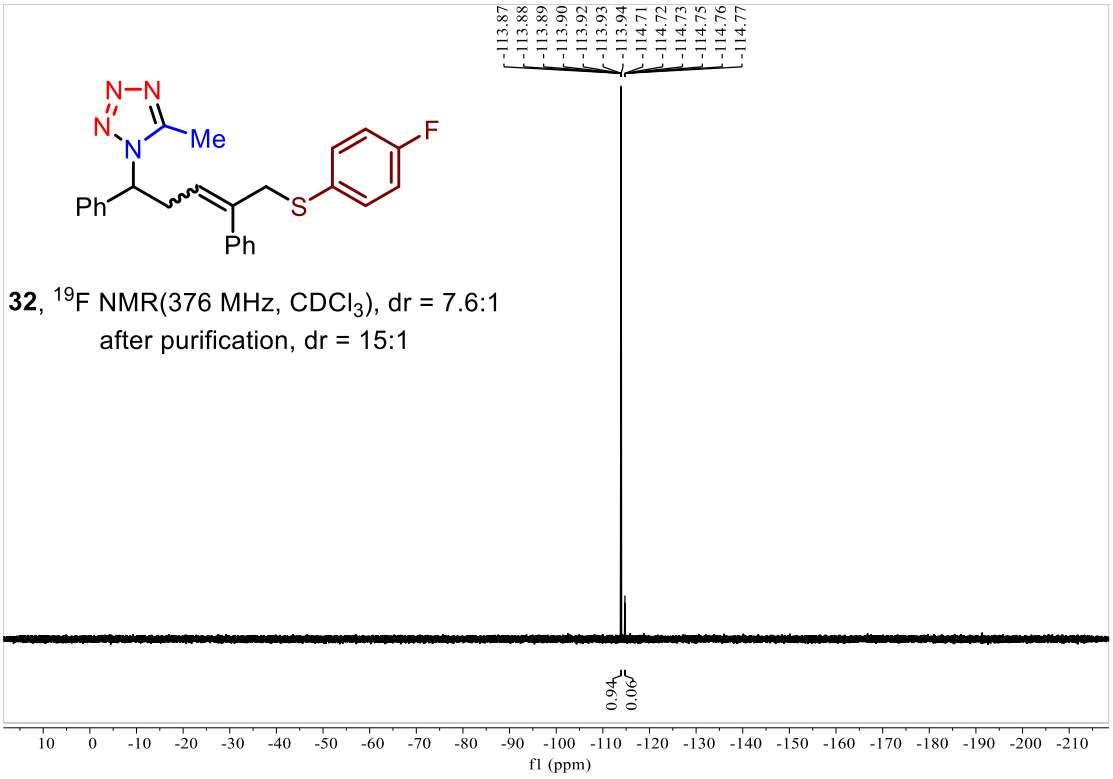

**29**, $^{19}$F NMR(471 MHz, $CDCl_3$), dr = 1.4:1
after purification, dr = 3:1



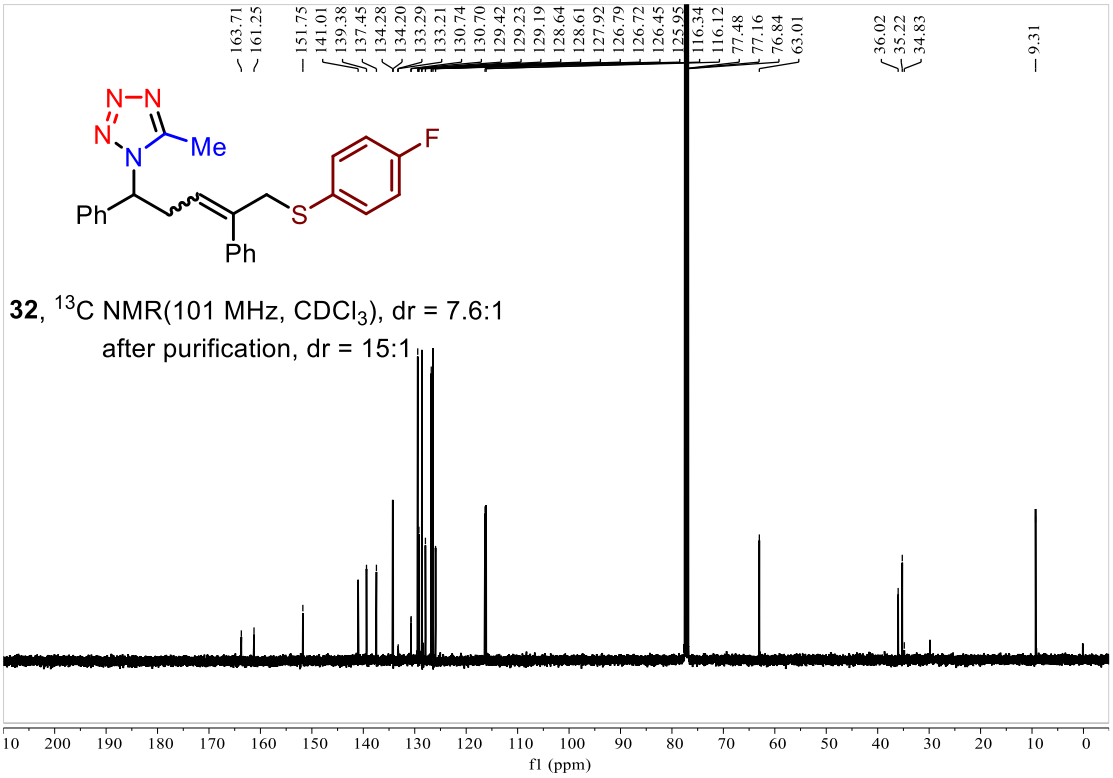

**29**, $^{13}C$ NMR(126 MHz, $CDCl_3$), dr = 1.4:1
after purification, dr = 3:1




**32**, $^{1}H$ NMR(400 MHz, $CDCl_3$), dr = 7.6:1
after purification, dr = 15:1




**32**, $^{19}$F NMR(376 MHz, $CDCl_3$), dr = 7.6:1
after purification, dr = 15:1




**32**, $^{13}$C NMR(101 MHz, $CDCl_3$), dr = 7.6:1
after purification, dr = 15:1