

*Supporting Information*

**Metal-Free Intramolecular Trifluoromethylthiolation/Selenolation of  
Alkynes**

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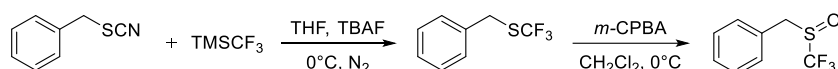
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## 1. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed on silica gel GF254. Visualization was accomplished by irradiation with UV light at 254 nm or KMnO<sub>4</sub> stain solution. Column chromatography was performed on silica gel (200 - 300 mesh). <sup>1</sup>H NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz). Chemical shifts were reported in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. <sup>13</sup>C NMR spectra were recorded on a Bruker DRX-400 spectrometer (100 MHz) and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in parts per million (ppm) referenced to 77.16 ppm for CDCl<sub>3</sub>. High resolution mass spectra (HRMS) were recorded on a waters LCT Premierxe™ (USA) (with Electron Spray Ionization as mass analyzer). Low reactions were carried out with low reaction reactor.

## 2. Experimental Procedures and Spectroscopic Data

### 2.1 Typical Procedure for the Synthesis of Benzyl Trifluoromethyl Sulfoxide (2a)

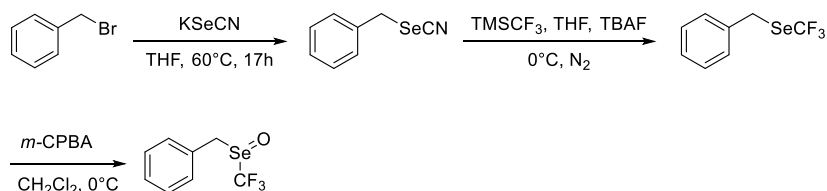


Benzyl Trifluoromethyl Sulfoxide (**2a**) was prepared according to the literature method.<sup>[1-2]</sup> To a solution of benzyl thiocyanate (10.0 g, 33.5 mmol, 1.0 equiv) in THF (100 mL), TMSCF<sub>3</sub> (9.0 mL, 81.9 mmol, 2.44 equiv) in ice-water bath was added under the N<sub>2</sub> atmosphere. Then TBAF (1 M, 1.5 mL, 8.4 mmol, 0.25 equiv) was added dropwise within 15 min. The mixture was allowed to stir for about 2 h and TLC was used to monitor the reaction process. When the reaction was completed, the mixture was concentrated in vacuo. The residue was purified by column chromatography over silica gel (hexane) to give benzyl trifluoromethyl sulfide (5.6 g, 87%) as colorless liquid.

To a solution of benzyl trifluoromethyl sulfide (5.0 g, 26.0 mmol, 1.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) in ice-water bath was added m-CPBA (85% w/w, 5.8 g, 28.6 mmol, 1.1 equiv) in a portionwise manner. The mixture was stirred for about 6 h and detected by TLC. When the reaction was completed, the reaction was quenched with saturated aqueous Na<sub>2</sub>CO<sub>3</sub> (10 mL) at 0 °C and the

aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 50$  mL). The combined organic layers were dried with  $\text{MgSO}_4$  and concentrated in vacuo. The residue was purified by column chromatography (EA/ PE = 1:1) to give the desired product **2a** as a white solid (3.7 g, 68%).

## 2.2 Typical Procedure for the Synthesis of Benzyl Trifluoromethyl Selenium Sulfoxide (**2b**)



Benzyl Trifluoromethyl Selenium Sulfoxide (**2b**) was prepared according to the literature method.<sup>[3]</sup> To a dry round-bottom flask equipped with a magnetic stirrer were added potassium selenocyanate (4.6 g, 32.2 mmol, 1.1 equiv), dry THF (50 mL), and benzylbromide (5.0 g, 29.2 mmol, 1.0 equiv). The reaction mixture was then stirred at 60 °C for 17 h. When the reaction was completed (monitored by TLC), the reaction mixture was then partitioned between water and EtOAc ( $3 \times 60$  mL). The organic layer was dried over  $\text{MgSO}_4$ , filtered, and concentrated to afford the desired (selenocyanatomethyl)benzene, which was used for next step without further purification.

To a dry roundbottom flask equipped with a magnetic stirrer were added (benzylselanyl)carbonitrile (5.0 g, 25.5 mmol, 1.0 equiv) and dry THF (100 mL). The flask was evacuated and refilled with nitrogen three times, and then  $\text{TMSCF}_3$  (7.5 mL, 51.0 mmol, 2.0 equiv) was added. The reaction mixture was cooled to 0 °C, and TBAF in 1 M THF (5.1 mL, 5.1 mmol, 0.2 equiv) was added dropwise. After 10 min at 0 °C under nitrogen, the reaction was allowed to warm to 25 °C and stirred for 7 h. The reaction mixture was then concentrated in vacuo. The crude residue was purified by chromatography (hexane) to afford the desired product benzyl(trifluoromethyl)selane as colorless liquid.

To a solution of benzyl(trifluoromethyl)selane (4.0 g, 16.73 mmol, 1.0 equiv) in  $\text{CH}_2\text{Cl}_2$  (100 mL) in ice-water bath was added m-CPBA (85% w/w, 3.18 g, 18.40 mmol, 1.1 equiv) in a portionwise manner. The mixture was stirred for about 6 h and detected by TLC. When the reaction was completed, the reaction was quenched with saturated aqueous  $\text{Na}_2\text{CO}_3$  (10 mL) at 0 °C and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 60$  mL). The combined organic layers were

dried with MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography (EA/ PE = 1:1) to give the desired product **b** as a white solid (2.9 g, 68%).

### 2.3 Optimization of Trifluoromethylthiolation Reaction Conditions

At the beginning of the study, **1a** was used as a model substrate to test the feasibility of our hypothesis. By consulting the relevant literature, we know that, **1a** was first treated with BnS(O)CF<sub>3</sub> and SOCl<sub>2</sub> (1.0 equiv) in DCM at 0 °C for 12 h (Table S1, entry 1). However, the reaction did not occur and no desired product was detected at all. Then the other additives including AcCl, TFAA and Tf<sub>2</sub>O were applied, and the results revealed that Tf<sub>2</sub>O could enable the formation of **3a** in 85% yield (Table S1, entry 2). Solvent screening showed that DCM was the most favorable solvent in comparison to THF, MeCN, DCE and toluene (Table S1, entries 5-8). Further dosage screening of the additives indicated that with the use of more Tf<sub>2</sub>O, the yield of product **3a** was also improved with need of shorter reaction time. A highest yield of 96% was achieved when 2 equiv of Tf<sub>2</sub>O was applied, with the reaction time shortened to 2 h (Table S1, entries 9-11). Furthermore, all the above reactions were operated at 0 °C, as the reaction conducted at room temperature afforded product **3a** with even lower yield (Table S1, entry 12). Carrying out the reaction at an even lower temperature is not necessary as the reaction operated at -10 °C delivered **3a** with relatively lower yield (Table S1, entry 13). Eventually, the optimized conditions were confirmed to be: 1.0 equiv of **1a**, 2.0 equiv of **2a** and 2.0 equiv of Tf<sub>2</sub>O in DCM stirred at 0 °C for 2 h (Table S1, entry 10).

**Table S1. Optimization of Reaction Conditions** <sup>[a]</sup>

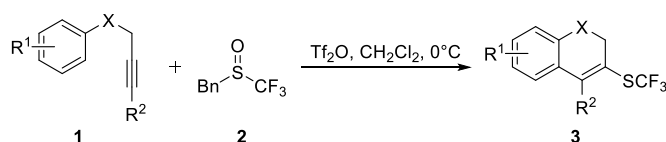
C#CC1=CC=C(C=C1)N(C2=CC=C(C=C2)S(=O)(=O)C3=CC=CC=C3) + C4=CC=CC=C4S(=O)(=O)SC(F)(F)F >> C#CC1=CC=C(C=C1)N(C2=CC=C(C=C2)S(=O)(=O)C3=CC=CC=C3)C4=CC=CC=C4SC(F)(F)F

Entry	Solvent	Additive (equiv)	Temp. (°C)	Time (h)	Yield(%) <sup>[b]</sup>
1	DCM	SOCl <sub>2</sub> (1.0)	0	12	NR <sup>[c]</sup>
2	DCM	Tf <sub>2</sub> O(1.0)	0	12	85
3	DCM	TFAA(1.0)	0	12	ND <sup>[d]</sup>
4	DCM	AcCl(1.0)	0	12	ND <sup>[d]</sup>
5	THF	Tf <sub>2</sub> O(1.0)	0	12	67

6	toluene	Tf <sub>2</sub> O(1.0)	0	12	83
7	MeCN	Tf <sub>2</sub> O(1.0)	0	12	58
8	DCE	Tf <sub>2</sub> O(1.0)	0	12	82
9	DCM	Tf <sub>2</sub> O(1.5)	0	6	90
10	DCM	Tf <sub>2</sub> O(2.0)	0	2	96
11	DCM	Tf <sub>2</sub> O(3.0)	0	1	83
12	DCM	Tf <sub>2</sub> O(2.0)	rt	0.5	80
13	DCM	Tf <sub>2</sub> O(2.0)	-10	5	91

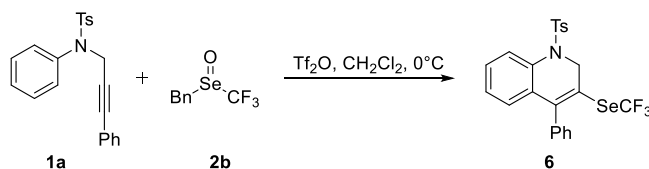
<sup>[a]</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol) and additive (0.4 mmol) in solvent (2 mL) for 12 h, unless otherwise stated. <sup>[b]</sup> Yield determined by <sup>1</sup>H NMR of crude sample. <sup>[c]</sup> NR = no reaction. <sup>[d]</sup> ND = not detected.

#### 2.4 General Procedure for Trifluoromethylthiolation



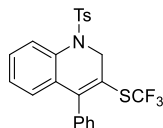
To a solution of **2a** (0.4 mmol, 2.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was slowly added triflic anhydride (0.4 mmol, 2.0 equiv) at 0 °C, then **1** (0.2 mmol, 1.0 equiv) was added and the mixture was kept stirring until TLC indicated the total consumption of substrate **1**. Then the reaction mixture was washed with saturated aq. NaHCO<sub>3</sub> solution (4 mL) and water (20 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the product.

#### 2.5 Typical Synthetic Procedure for Trifluoromethylselenolation



To a solution of **2b** (102.0 mg, 0.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was slowly added triflic anhydride (113 mg, 0.4 mmol) at 0 °C, then **1a** (72.0 mg, 0.2 mmol) was added and the mixture was kept stirring until TLC indicated the total consumption of substrate **1a**. Then the reaction mixture was washed with saturated aq. NaHCO<sub>3</sub> solution (4 mL) and water (20 mL), extracted

with CH<sub>2</sub>Cl<sub>2</sub> (3 × 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the product.



#### 4-phenyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3a)

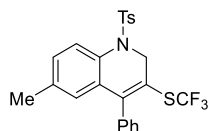
Compound **3a** was prepared according to the general procedure and was isolated as a white solid (84.0 mg, 91% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 12.6, 4.6 Hz, 3H), 7.29 (m, 3H), 7.20 – 7.07 (m, 3H), 6.61 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.48 (d, *J* = 6.9 Hz, 2H), 4.83 (s, 2H), 2.39 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.9, 144.2, 135.9, 135.7, 134.7, 131.1, 129.8, 129.5, 129.2, 128.3, 128.2, 127.7, 127.4, 127.2, 126.9, 115.6, 51.0, 21.4.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -38.6.

HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>23</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>2</sub>S<sub>2</sub> 462.0809, found: 462.0812.



#### 6-methyl-4-phenyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3b)

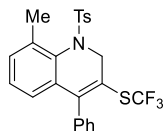
Compound **3b** was prepared according to the general procedure and was isolated as a white solid (76.0 mg, 80% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.21 – 7.11 (m, 3H), 6.46 (d, *J* = 7.0 Hz, 2H), 6.42 – 6.33 (m, 1H), 4.80 (s, 2H), 2.39 (s, 3H), 2.19 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.1, 144.0, 136.8, 136.0, 135.9, 132.1, 130.8, 130.6, 129.4, 129.2, 128.2, 128.1, 127.9, 127.4, 127.0, 115.6, 51.1, 21.4, 21.1.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -38.7.

HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>21</sub>F<sub>3</sub>NO<sub>2</sub>S<sub>2</sub> 476.0966, found: 476.0942.



**8-methyl-4-phenyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3c)**

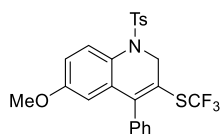
Compound **3c** was prepared according to the general procedure and was isolated as a white solid (72.3 mg, 76% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.41 (m, 3H), 7.35 – 7.14 (m, 7H), 7.06 (t,  $J = 7.7$  Hz, 1H), 6.45 (d,  $J = 7.7$  Hz, 1H), 5.15 (d,  $J = 17.8$  Hz, 1H), 4.39 (d,  $J = 17.8$  Hz, 1H), 2.64 (s, 3H), 2.40 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.5, 144.2, 138.2, 136.2, 135.7, 133.3, 132.9, 132.4, 131.0, 129.6, 128.2, 128.1, 128.0, 127.1, 125.2, 117.3, 51.8, 21.5, 19.9.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.5.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_2\text{S}_2$  476.0966, found:476.0984.



**6-methoxy-4-phenyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3d)**

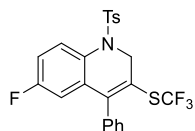
Compound **3d** was prepared according to the general procedure and was isolated as a white solid (93.4 mg, 95% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 8.8$  Hz, 1H), 7.39 (d,  $J = 8.2$  Hz, 2H), 7.28 (m, 3H), 7.17 (d,  $J = 8.1$  Hz, 2H), 6.92 (dd,  $J = 8.9, 2.9$  Hz, 1H), 6.45 (d,  $J = 6.9$  Hz, 2H), 6.11 (d,  $J = 2.9$  Hz, 1H), 4.80 (s, 2H), 3.65 (s, 3H), 2.39 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.0, 146.6, 144.0, 135.8, 135.6, 132.1, 131.0, 129.5, 129.2, 128.5, 128.3, 128.2, 127.5, 116.4, 114.6, 113.2, 55.4, 51.1, 21.4.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_3\text{S}_2$  492.0915, found: 492.0933.



**6-fluoro-4-phenyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3e)**

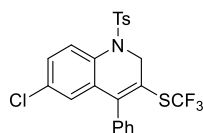
Compound **3e** was prepared according to the general procedure and was isolated as a white solid (79.6 mg, 83% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (dd,  $J = 8.9, 5.2$  Hz, 1H), 7.51 – 7.37 (m, 2H), 7.36 – 7.24 (m, 3H), 7.19 (d,  $J = 8.1$  Hz, 2H), 7.08 (m, 1H), 6.45 (d,  $J = 7.0$  Hz, 2H), 6.30 (dd,  $J = 9.3, 2.9$  Hz, 1H), 4.83 (s, 2H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.1, 159.7, 145.5, 144.3, 135.7, 135.1, 132.7 (d,  $J = 8.5$  Hz), 130.5 (d,  $J = 2.9$  Hz), 129.6, 129.1, 129.1, 128.6, 128.4, 127.4, 117.6, 115.3 (dd,  $J = 258.1, 23.7$  Hz), 50.8, 21.4.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.3.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{F}_4\text{NO}_2\text{S}_2$  480.0715, found: 480.0736.



#### **6-chloro-4-phenyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3f)**

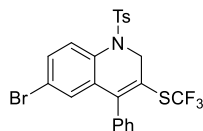
Compound **3f** was prepared according to the general procedure and was isolated as a white solid (85.0 mg, 86% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.6$  Hz, 1H), 7.41 (d,  $J = 8.2$  Hz, 2H), 7.32 (m, 4H), 7.20 (d,  $J = 8.1$  Hz, 2H), 6.57 (d,  $J = 2.4$  Hz, 1H), 6.45 (d,  $J = 6.9$  Hz, 2H), 4.82 (s, 2H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.3, 144.4, 135.7, 135.0, 133.1, 132.7, 132.3, 129.6, 129.6, 129.1, 128.6, 128.6, 128.4, 127.4, 127.2, 117.6, 50.7, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.3.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{ClF}_3\text{NO}_2\text{S}_2$  496.0420, found: 496.0426.



#### **6-bromo-4-phenyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3g)**

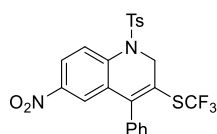
Compound **3g** was prepared according to the general procedure and was isolated as a white solid (80.0 mg, 74% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 8.6$  Hz, 1H), 7.51 – 7.47 (m, 1H), 7.42 (d,  $J = 8.2$  Hz, 2H), 7.36 – 7.27 (m, 3H), 7.20 (d,  $J = 8.0$  Hz, 2H), 6.73 (m, 1H), 6.46 (d,  $J = 7.6$  Hz, 2H), 4.81 (s, 2H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.2, 144.4, 135.7, 134.9, 133.6, 132.6, 132.6, 130.1, 129.7, 129.1, 128.8, 128.7, 128.5, 127.4, 120.6, 117.6, 50.7, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.3.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{BrF}_3\text{NO}_2\text{S}_2$  539.9914, found: 539.9931.



### 6-nitro-4-phenyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3h)

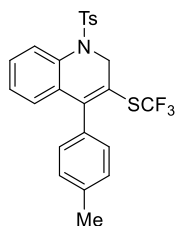
Compound **3h** was prepared according to the general procedure and was isolated as a white solid (79.0 mg, 78% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (dd,  $J = 8.9, 2.4$  Hz, 1H), 8.03 (d,  $J = 8.9$  Hz, 1H), 7.49 (d,  $J = 2.6$  Hz, 1H), 7.44 (d,  $J = 8.3$  Hz, 2H), 7.39 – 7.28 (m, 3H), 7.22 (d,  $J = 8.1$  Hz, 2H), 6.52 (d,  $J = 7.0$  Hz, 2H), 4.88 (s, 2H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.8, 145.0, 140.1, 135.6, 134.3, 131.6, 129.9, 129.1, 128.9, 128.8, 128.5, 127.8 (q,  $J_{\text{C-F}} = 350.2$  Hz) 127.7, 127.2, 124.2, 122.5, 119.1, 50.4, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.0.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_4\text{S}_2$  507.0660, found: 507.0684.



### 4-(p-tolyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3i)

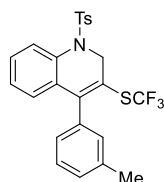
Compound **3i** was prepared according to the general procedure and was isolated as a white solid (87.5 mg, 92% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 – 7.73 (m, 1H), 7.37 (dd,  $J = 11.5, 4.8$  Hz, 3H), 7.21 – 7.03 (m, 5H), 6.63 (dd,  $J = 7.8, 1.1$  Hz, 1H), 6.37 (d,  $J = 7.9$  Hz, 2H), 4.82 (s, 2H), 2.39 (s, 3H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 144.1, 138.2, 135.9, 134.7, 132.7, 131.2, 129.69, 129.4, 129.1, 128.9, 127.7, 127.4, 127.2, 126.8, 115.4, 51.0, 21.5, 21.3.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.7.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_2\text{S}_2$  476.0966, found: 476.0944.



#### 4-(m-tolyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3j)

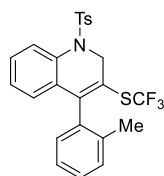
Compound **3j** was prepared according to the general procedure and was isolated as a white solid (82.0 mg, 86% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J$  = 8.0 Hz, 1H), 7.51 – 7.33 (m, 3H), 7.22 – 7.05 (m, 5H), 6.62 (dd,  $J$  = 7.8, 1.1 Hz, 1H), 6.35 (d,  $J$  = 7.3 Hz, 1H), 6.21 (s, 1H), 4.82 (s, 2H), 2.39 (s, 3H), 2.29 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 143.9, 137.8, 136.0, 135.7, 134.6, 131.1, 129.7, 129.6, 129.5, 129.0, 128.1, 127.7, 127.4, 127.2, 126.9, 126.3, 115.5, 50.9, 21.5, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.7.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_2\text{S}_2$  476.0966, found: 476.0976.



#### 4-(o-tolyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3k)

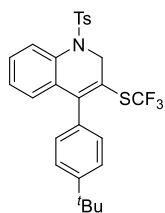
Compound **3k** was prepared according to the general procedure and was isolated as a white solid (76.0 mg, 80% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J$  = 8.0 Hz, 1H), 7.45 (d,  $J$  = 8.2 Hz, 2H), 7.37 (dd,  $J$  = 11.3, 4.3 Hz, 1H), 7.24 (d,  $J$  = 7.3 Hz, 1H), 7.19 (d,  $J$  = 8.0 Hz, 3H), 7.07 (m, 2H), 6.54 – 6.45 (m, 1H), 5.92 (d,  $J$  = 7.5 Hz, 1H), 5.05 (d,  $J$  = 17.6 Hz, 1H), 4.73 (d,  $J$  = 17.6 Hz, 1H), 2.41 (s, 3H), 1.75 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.4, 144.1, 136.3, 135.9, 135.2, 134.1, 130.2, 129.8, 129.6, 129.6, 129.0, 128.5, 127.4, 126.8, 126.8, 126.7, 125.7, 117.4, 49.6, 21.4, 18.8.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -37.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_2\text{S}_2$  476.0966, found: 476.0981.



#### 4-(4-(tert-butyl)phenyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (**3l**)

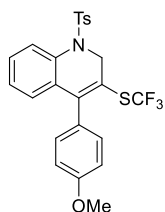
Compound **3l** was prepared according to the general procedure and was isolated as a white solid (86.0 mg, 83% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 8.0$  Hz, 1H), 7.37 (dd,  $J = 13.2, 4.7$  Hz, 3H), 7.27 (d,  $J = 8.0$  Hz, 2H), 7.20 – 7.05 (m, 3H), 6.63 (dd,  $J = 7.8, 1.0$  Hz, 1H), 6.41 (d,  $J = 8.2$  Hz, 2H), 4.82 (s, 2H), 2.40 (s, 3H), 1.33 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.2, 146.7, 144.0, 135.9, 134.6, 132.6, 131.3, 129.6, 129.5, 128.9, 127.7, 127.4, 127.1, 126.8, 125.0, 115.5, 51.0, 34.6, 31.3, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{27}\text{H}_{27}\text{F}_3\text{NO}_2\text{S}_2$  518.1435, found: 518.1444.



#### 4-(4-methoxyphenyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (**3m**)

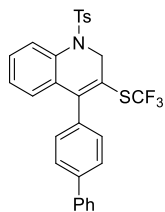
Compound **3m** was prepared according to the general procedure and was isolated as a white solid (83.5 mg, 85% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 7.8$  Hz, 1H), 7.49 – 7.32 (m, 3H), 7.19 – 7.08 (m, 3H), 6.80 (d,  $J = 8.7$  Hz, 2H), 6.65 (d,  $J = 7.8$  Hz, 1H), 6.43 (d,  $J = 8.6$  Hz, 2H), 4.81 (s, 2H), 3.82 (s, 3H), 2.37 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  159.4, 146.5, 144.1, 135.9, 134.8, 131.4, 130.6, 129.7, 129.4, 128.3, 127.8, 127.7, 127.4, 127.2, 126.8, 115.3, 113.5, 55.2, 51.1, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_3\text{S}_2$  492.0915, found: 492.0928.



**4-([1,1'-biphenyl]-4-yl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3n)**

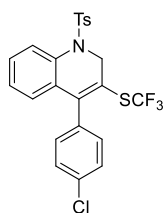
Compound **3n** was prepared according to the general procedure and was isolated as a white solid (92.5mg, 86% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.1$  Hz, 1H), 7.60 (d,  $J = 7.6$  Hz, 2H), 7.52 – 7.44 (m, 3H), 7.43 – 7.37 (m, 4H), 7.20 – 7.14 (m, 4H), 6.70 (d,  $J = 7.8$  Hz, 1H), 6.56 (d,  $J = 8.1$  Hz, 2H), 4.85 (s, 2H), 2.40 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.6, 144.1, 141.1, 140.2, 136.0, 134.7, 134.6, 131.1, 129.8, 129.8, 129.5, 128.9, 127.7, 127.4, 127.3, 127.1, 126.9, 126.8, 115.7, 51.1, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{29}\text{H}_{23}\text{F}_3\text{NO}_2\text{S}_2$  538.1122, found:538.1132.



**4-(4-chlorophenyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3o)**

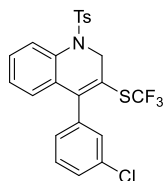
Compound **3o** was prepared according to the general procedure and was isolated as a white solid (85.3 mg, 86% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.1$  Hz, 1H), 7.40 (dd,  $J = 12.1, 7.9$  Hz, 3H), 7.25 (dd,  $J = 10.5, 7.0$  Hz, 2H), 7.21 – 7.08 (m, 3H), 6.59 (d,  $J = 7.8$  Hz, 1H), 6.42 (d,  $J = 8.3$  Hz, 2H), 4.82 (s, 2H), 2.39 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 144.1, 135.9, 134.7, 134.4, 134.1, 130.7, 130.7, 130.0, 129.5, 128.5, 127.8, 127.4, 127.3, 127.0, 116.1, 51.0, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{ClF}_3\text{NO}_2\text{S}_2$  496.0420, found: 496.0433.



#### 4-(3-chlorophenyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3p)

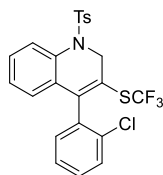
Compound **3p** was prepared according to the general procedure and was isolated as a white solid (83.0 mg, 84% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.0$  Hz, 1H), 7.47 – 7.35 (m, 3H), 7.28 (m, 2H), 7.17 (dd,  $J = 15.7, 8.0$  Hz, 3H), 6.67 (d,  $J = 7.2$  Hz, 1H), 6.59 (dd,  $J = 7.8, 0.9$  Hz, 1H), 6.13 (s, 1H), 4.83 (d,  $J = 132.0$  Hz, 2H), 2.43 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.7, 144.5, 137.5, 135.8, 134.6, 134.1, 130.6, 130.1, 129.6, 129.6, 129.0, 128.5, 127.8, 127.6, 127.4, 127.4, 127.1, 116.4, 50.9, 21.6.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{ClF}_3\text{NO}_2\text{S}_2$  496.0420, found: 496.0418.



#### 4-(2-chlorophenyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3q)

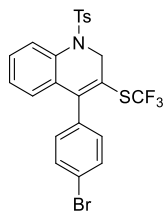
Compound **3q** was prepared according to the general procedure and was isolated as a white solid (71.5 mg, 72% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 8.3$  Hz, 1H), 7.44 (d,  $J = 8.3$  Hz, 2H), 7.40 – 7.37 (m, 2H), 7.31 – 7.28 (m, 1H), 7.18 (d,  $J = 8.1$  Hz, 2H), 7.15 – 7.10 (m, 2H), 6.52 (dd,  $J = 7.8, 1.2$  Hz, 1H), 6.09 (dd,  $J = 7.6, 1.4$  Hz, 1H), 5.05 (d,  $J = 17.7$  Hz, 1H), 4.74 (d,  $J = 17.7$  Hz, 1H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 143.1, 136.2, 134.7, 134.3, 133.3, 130.6, 129.9, 129.8, 129.6, 129.6, 129.2, 127.5, 126.8, 126.7, 126.7, 126.2, 118.7, 49.9, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -37.7.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{ClF}_3\text{NO}_2\text{S}_2$  496.0420, found: 496.0442.



#### 4-(4-bromophenyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3r)

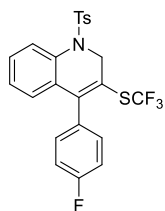
Compound **3r** was prepared according to the general procedure and was isolated as a white solid (92.0 mg, 85% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 – 7.79 (m, 1H), 7.48 – 7.32 (m, 5H), 7.21 – 7.06 (m, 3H), 6.59 (dd,  $J = 7.8, 1.1$  Hz, 1H), 6.35 (d,  $J = 8.3$  Hz, 2H), 4.82 (s, 2H), 2.39 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 144.1, 135.9, 134.7, 134.6, 131.5, 130.9, 130.6, 130.0, 129.5, 127.8, 127.4, 127.3, 127.0, 122.6, 116.1, 51.0, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{BrF}_3\text{NO}_2\text{S}_2$  539.9914, found: 539.9912.



#### 4-(4-fluorophenyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3s)

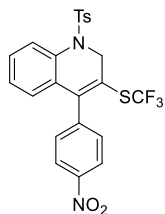
Compound **3s** was prepared according to the general procedure and was isolated as a white solid (80.5 mg, 84% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.0$  Hz, 1H), 7.40 (dd,  $J = 12.7, 4.7$  Hz, 3H), 7.21 – 7.08 (m, 3H), 6.98 (t,  $J = 8.7$  Hz, 2H), 6.60 (dd,  $J = 7.8, 1.0$  Hz, 1H), 6.46 (dd,  $J = 8.4, 5.4$  Hz, 2H), 4.82 (s, 2H), 2.38 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d,  $J = 248.6$  Hz), 146.0, 144.1, 136.0, 134.7, 131.6 (d,  $J = 3.6$  Hz), 131.1 (d,  $J = 8.1$  Hz), 130.0, 129.4, 127.5, 127.4, 127.3, 126.9, 116.1, 115.4, 115.2, 51.0, 21.4.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.2.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{F}_4\text{NO}_2\text{S}_2$  480.0715, found: 480.0725.



#### 4-(4-nitrophenyl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3t)

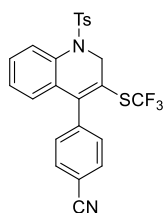
Compound **3t** was prepared according to the general procedure and was isolated as a white solid (77.0 mg, 76% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J = 8.8$  Hz, 2H), 7.88 (d,  $J = 7.7$  Hz, 1H), 7.56 – 7.33 (m, 3H), 7.26 – 7.07 (m, 3H), 6.67 (d,  $J = 8.6$  Hz, 2H), 6.51 (dd,  $J = 7.8, 0.9$  Hz, 1H), 4.85 (s, 2H), 2.43 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.7, 145.4, 144.3, 142.5, 136.0, 134.7, 130.5, 130.4, 129.9, 129.5, 127.5, 127.5, 127.1, 127.1, 123.5, 116.9, 51.0, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_4\text{S}_2$  507.0660, found: 507.0684.



#### 4-(1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinolin-4-yl)benzonitrile (3u)

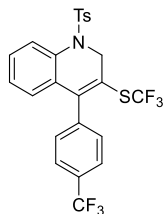
Compound **3u** was prepared according to the general procedure and was isolated as a white solid (76.0 mg, 78% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.0$  Hz, 1H), 7.59 (d,  $J = 8.3$  Hz, 2H), 7.47 – 7.34 (m, 3H), 7.16 (dd,  $J = 13.8, 7.6$  Hz, 3H), 6.61 (d,  $J = 8.1$  Hz, 2H), 6.50 (d,  $J = 7.8$  Hz, 1H), 4.84 (s, 2H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.6, 144.2, 140.6, 136.0, 134.7, 132.0, 130.4, 130.1, 130.0, 129.5, 127.5, 127.4, 127.2, 127.1, 118.2, 116.7, 112.5, 51.0, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI ( $m/z$ ):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_2\text{S}_2$  487.0762, found: 587.0752.



**1-tosyl-4-(4-(trifluoromethyl)phenyl)-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3v)**

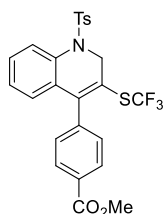
Compound **3v** was prepared according to the general procedure and was isolated as a white solid (84.5 mg, 80% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 (d,  $J = 8.1$  Hz, 1H), 7.55 (d,  $J = 8.1$  Hz, 2H), 7.49 – 7.35 (m, 3H), 7.23 – 7.09 (m, 3H), 6.61 (d,  $J = 8.0$  Hz, 2H), 6.53 (dd,  $J = 7.9, 1.1$  Hz, 1H), 4.84 (s, 2H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.2, 142.7 (d,  $J = 641.7$  Hz), 136.0, 132.5 (d,  $J = 433.8$  Hz), 130.8, 130.7, 130.2, 129.7, 129.5, 127.7, 127.4, 127.4, 127.2 (d,  $J = 27.1$  Hz), 125.3, 125.2, 122.5, 116.5, 51.0, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6, -62.7.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{24}\text{H}_{18}\text{F}_6\text{NO}_2\text{S}_2$  530.0683, found: 530.0687.



**methyl 4-(1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinolin-4-yl)benzoate (3w)**

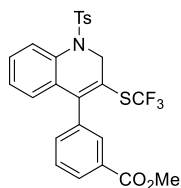
Compound **3w** was prepared according to the general procedure and was isolated as a white solid (85.2 mg, 82% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.3$  Hz, 2H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.49 – 7.33 (m, 3H), 7.20 – 7.06 (m, 3H), 6.61 – 6.51 (m, 3H), 4.84 (s, 2H), 3.93 (s, 3H), 2.41 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 146.3, 144.3, 140.5, 135.9, 134.6, 130.8, 130.4, 130.1, 129.5, 129.5, 129.4, 127.8, 127.4, 127.4, 127.0, 116.2, 52.3, 51.0, 21.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{21}\text{F}_3\text{NO}_4\text{S}_2$  520.0864, found: 520.0842.



**methyl 3-(1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinolin-4-yl)benzoate (3x)**

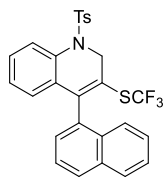
Compound **3x** was prepared according to the general procedure and was isolated as a white solid (84.0 mg, 81% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 7.9$  Hz, 1H), 7.86 (d,  $J = 8.0$  Hz, 1H), 7.40 (m, 4H), 7.25 – 7.17 (m, 3H), 7.13 (m, 1H), 6.85 (d,  $J = 7.6$  Hz, 1H), 6.55 (d,  $J = 7.8$  Hz, 1H), 4.83 (dd,  $J = 26.3, 9.9$  Hz, 2H), 3.93 (s, 3H), 2.37 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 146.2, 144.5, 136.0, 135.8, 134.8, 133.9, 130.7, 130.4, 130.3, 130.1, 129.6, 129.5, 128.4, 127.5, 127.4, 127.2, 127.0, 116.1, 52.3, 51.0, 21.4.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.6.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{25}\text{H}_{21}\text{F}_3\text{NO}_4\text{S}_2$  520.0864, found: 520.0868.



**4-(naphthalen-1-yl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3y)**

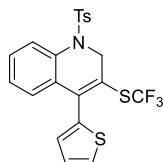
Compound **3y** was prepared according to the general procedure and was isolated as a white solid (74.5 mg, 73% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.1$  Hz, 1H), 7.85 (dd,  $J = 8.2, 2.4$  Hz, 2H), 7.54 (d,  $J = 8.2$  Hz, 2H), 7.45 (t,  $J = 7.4$  Hz, 1H), 7.34 (t,  $J = 7.7$  Hz, 3H), 7.25 – 7.16 (m, 2H), 7.00 – 6.87 (m, 2H), 6.46 – 6.32 (m, 1H), 6.26 (d,  $J = 7.0$  Hz, 1H), 5.10 (d,  $J = 17.6$  Hz, 1H), 4.90 (d,  $J = 17.6$  Hz, 1H), 2.47 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 136.5, 134.0, 133.4, 131.2, 130.4, 129.7, 129.6, 129.5, 128.9, 128.6, 128.4, 127.5, 127.4, 127.1, 126.8, 126.7, 126.6, 126.2, 125.1, 125.0, 118.8, 50.1, 21.6.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.0.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{27}\text{H}_{21}\text{F}_3\text{NO}_2\text{S}_2$  512.0966, found: 512.0952.



#### 4-(thiophen-2-yl)-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (**3z**)

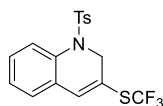
Compound **3z** was prepared according to the general procedure and was isolated as a white solid (80.5 mg, 86% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 8.1$  Hz, 1H), 7.49 – 7.30 (m, 4H), 7.17 (dd,  $J = 17.8$ , 7.8 Hz, 3H), 6.99 (dd,  $J = 5.0$ , 3.6 Hz, 1H), 6.82 (d,  $J = 7.8$  Hz, 1H), 6.51 (d,  $J = 3.4$  Hz, 1H), 4.80 (s, 2H), 2.37 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 139.5, 135.5, 135.3, 134.5, 131.0, 130.0, 129.6, 129.3, 127.3, 127.2, 127.2, 127.1, 127.0, 126.8, 119.2, 50.9, 21.6.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -38.5.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{21}\text{H}_{17}\text{F}_3\text{NO}_2\text{S}_3$  468.0374, found: 468.0377.



#### 1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (**3aa**)

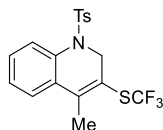
Compound **3aa** was prepared according to the general procedure and was isolated as a white solid (65.5 mg, 85% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.3$  Hz, 2H), 7.32 – 7.29 (m, 2H), 7.29 – 7.26 (m, 2H), 7.05 (s, 1H), 7.04 – 6.98 (m, 2H), 4.50 (s, 2H), 2.44 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.53, 144.18, 138.52, 134.49, 129.64, 129.30, 128.60, 128.53, 127.84, 123.50 (q,  $J_{\text{C-F}} = 315.7$  Hz), 115.79, 48.98, 21.59.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -41.7.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{17}\text{H}_{15}\text{F}_3\text{NO}_2\text{S}_2$  386.0496, found: 386.0484.



#### 4-methyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (**3ab**)

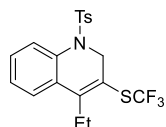
Compound **3ab** was prepared according to the general procedure and was isolated as a white solid (60.7 mg, 76% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.2$  Hz, 2H), 7.34 – 7.22 (m, 4H), 7.00 (dd,  $J = 6.6, 2.9$  Hz, 2H), 4.52 (s, 2H), 2.44 (s, 3H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.0, 144.1, 139.1, 134.3, 129.6, 129.2, 128.6, 128.4, 127.9, 127.1, 123.5 (q,  $J_{\text{C-F}} = 366.2$  Hz), 118.9, 51.1, 21.6, 19.0.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.8.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{18}\text{H}_{17}\text{F}_3\text{NO}_2\text{S}_2$  400.0653, found: 400.0646.



#### 4-ethyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3ac)

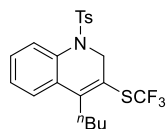
Compound **3ac** was prepared according to the general procedure and was isolated as a white solid (74.0 mg, 89% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 8.3$  Hz, 2H), 7.29 – 7.25 (m, 5H), 7.00 – 6.94 (m, 2H), 4.52 (s, 2H), 2.74 (q,  $J = 7.5$  Hz, 2H), 2.43 (s, 3H), 0.85 (t,  $J = 7.5$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.02, 162.01, 144.14, 138.71, 134.39, 129.57, 129.08, 128.77, 128.47, 127.84, 123.65 (q,  $J_{\text{C-F}} = 315.4$  Hz), 118.01, 50.90, 25.77, 21.54, 10.58.

$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -41.03.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NO}_2\text{S}_2$  436.0629, found: 436.0621.



#### 4-butyl-1-tosyl-3-((trifluoromethyl)thio)-1,2-dihydroquinoline (3ad)

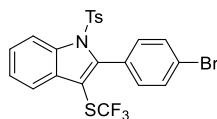
Compound **3ad** was prepared according to the general procedure and was isolated as a white solid (81.0 mg, 92% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 8.3$  Hz, 2H), 7.20 – 7.16 (m, 5H), 6.89 (dd,  $J = 6.8, 2.9$  Hz, 2H), 4.46 (s, 2H), 2.65 (t,  $J = 7.3$  Hz, 2H), 2.34 (s, 3H), 1.18 – 1.08 (m, 2H), 0.87 – 0.75 (m, 2H), 0.64 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  160.95, 144.11, 138.46, 134.32, 129.55, 129.09, 128.66, 128.44, 127.81, 123.65 (q,  $J_{\text{C-F}} = 315.5$  Hz), 118.70, 50.67, 31.67, 28.00, 21.53, 21.07, 13.47.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -41.02.

HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>21</sub>H<sub>22</sub>F<sub>3</sub>NO<sub>2</sub>S<sub>2</sub> 441.1044, found: 441.1046.



### 3-phenyl-1-tosyl-2-((trifluoromethyl)thio)-1H-indole (3ae)

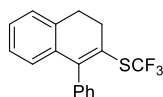
Compound **3ac** was prepared according to the general procedure and was isolated as a white solid (84.0 mg, 80% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.14 (dd, *J* = 8.2, 3.8 Hz, 4H), 2.35 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.6, 142.0, 136.6, 135.2, 133.2, 130.7, 129.7, 129.5, 126.9, 126.3, 124.9, 124.3, 120.1, 115.7, 21.6.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -42.0.

HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>16</sub>BrF<sub>3</sub>NO<sub>2</sub>S<sub>2</sub> 525.9758, found: 525.9738.



### (1-phenyl-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (5a)

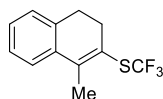
Compound **5a** was prepared according to the general procedure and was isolated as a white solid (53.3 mg, 87% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53 – 7.46 (m, 1H), 7.44 – 7.41 (m, 2H), 7.19 (d, *J* = 4.1 Hz, 2H), 7.17 – 7.13 (m, 2H), 7.08 – 7.04 (m, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 3.06 – 2.97 (m, 2H), 2.90 – 2.82 (m, 2H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.8, 138.2, 135.6, 135.4, 130.1, 129.7, 128.5, 128.30, 127.8, 127.3, 126.5, 123.1, 31.1, 28.7.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -39.5.

HRMS-ESI (m/z): [M+Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>F<sub>3</sub>S 307.0768, found: 307.0772.



### (1-methyl-3,4-dihydronaphthalen-2-yl)(trifluoromethyl)sulfane (5b)

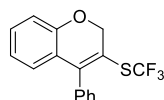
Compound **5b** was prepared according to the general procedure and was isolated as a white solid (36.6 mg, 75% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (dd,  $J = 9.4, 3.3$  Hz, 1H), 7.31 – 7.20 (m, 2H), 7.19 – 7.11 (m, 1H), 2.95 – 2.78 (m, 2H), 2.69 (m, 2H), 2.40 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 136.3, 135.1, 128.5, 127.4, 126.6, 124.7, 120.6, 32.5, 28.8, 17.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.7.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{12}\text{H}_{12}\text{F}_3\text{S}$  245.0612, found: 245.0615.



#### 4-phenyl-3-((trifluoromethyl)thio)-2H-chromene (5c)

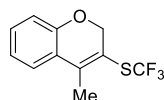
Compound **5c** was prepared according to the general procedure and was isolated as a white solid (57.4 mg, 93% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.37 (m, 3H), 7.22 (m, 3H), 6.93 (d,  $J = 8.1$  Hz, 1H), 6.83 (dd,  $J = 11.0, 4.1$  Hz, 1H), 6.70 (dd,  $J = 7.8, 1.3$  Hz, 1H), 5.02 (s, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.1, 147.5, 135.6, 131.1, 129.5, 128.4, 127.9, 127.7, 124.3, 121.7, 116.2, 113.3, 69.7.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -39.6.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{16}\text{H}_{11}\text{F}_3\text{NaOS}$  331.0380, found: 331.0388.



#### 4-methyl-3-((trifluoromethyl)thio)-2H-chromene (5d)

Compound **5d** was prepared according to the general procedure and was isolated as a white solid (44.3 mg, 90% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

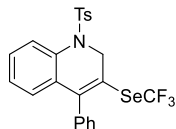
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 7.4$  Hz, 1H), 7.28 – 7.20 (m, 1H), 6.98 (t,  $J = 7.5$  Hz, 1H), 6.88 (d,  $J = 8.1$  Hz, 1H), 4.84 (s, 2H), 2.36 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.31, 144.03, 130.97, 125.12, 123.81, 121.72, 116.37, 111.98, 70.04, 15.88.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.3, 144.0, 131.0, 130.6, 125.1, 123.8, 121.7, 116.4, 112.0, 70.0, 15.9.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -40.7.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{11}\text{H}_9\text{F}_3\text{NaOS}$  269.0224, found: 269.0232.



### 4-phenyl-1-tosyl-3-((trifluoromethyl)selanyl)-1,2-dihydroquinoline (**6**)

Compound **6** was prepared according to the general procedure and was isolated as a white solid (81.5 mg, 80% yield) after short column chromatography (10%-20% EtOAc/Petroleum).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (dd,  $J = 8.1, 1.2$  Hz, 1H), 7.42 – 7.36 (m, 2H), 7.36 – 7.21 (m, 4H), 7.17 (d,  $J = 8.0$  Hz, 2H), 7.12 (m, 1H), 6.60 (dd,  $J = 7.8, 1.5$  Hz, 1H), 6.52 – 6.41 (m, 2H), 4.91 (s, 2H), 2.40 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 144.0, 137.0, 136.1, 134.4, 130.9, 129.4, 129.4, 129.0, 128.3, 127.5, 127.3, 127.1, 126.9, 124.3, 117.2, 51.9, 21.4.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -31.5.

HRMS-ESI (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{23}\text{H}_{19}\text{F}_3\text{NO}_2\text{SSe}$  510.0254, found: 510.0262.

## 3. Mechanism study

### 3.1 Calculation results

#### Computation details

All the geometrical structures were optimized at the pbe0 level with the Grimme's dispersion correction at the D3BJ level including conductor-like polarizable continuum model by the ORCA package<sup>[4-7]</sup>. The 6-31+G\*\* basis set was used for all atoms. Frequency analyses were done at the same level. For all the reactants, products and mediums, there are no imaginary frequencies. While, for transition states, there are only one imaginary frequency. The single point energies were revised at the M06-2X-D3/def2-TZVP level with RIJCOSX approximation containing SMD solvation model<sup>[8-11]</sup>. Thermal corrections to Gibbs free energies are corrected by Minenkov's quasi-RRHO model<sup>[12]</sup>. Relative energies include electronic energies and thermal corrections to Gibbs free energies.

To elucidate the possible reaction mechanisms, we performed theoretical calculations. The computational details and the calculated results are presented in Figure S1. First,  $\text{F}_3\text{C-S-OTf}$  attacks  $\text{C}\equiv\text{C}$  bond of **1a** via **TS1** to form a zwitterionic intermediate **B**. Subsequently, C-S bond of **B** easily cleaves, generating a carbocation **C**. This intermediate then undergoes an intramolecular cyclization,

wherein the positively charged carbon of **C** attacks the phenyl ring to form the intermediate **D**. Finally, **D** undergoes deprotonation to yield the final product **3a**. In conclusion, the theoretical results confirm that the proposed reaction pathway is feasible under the experimental conditions.

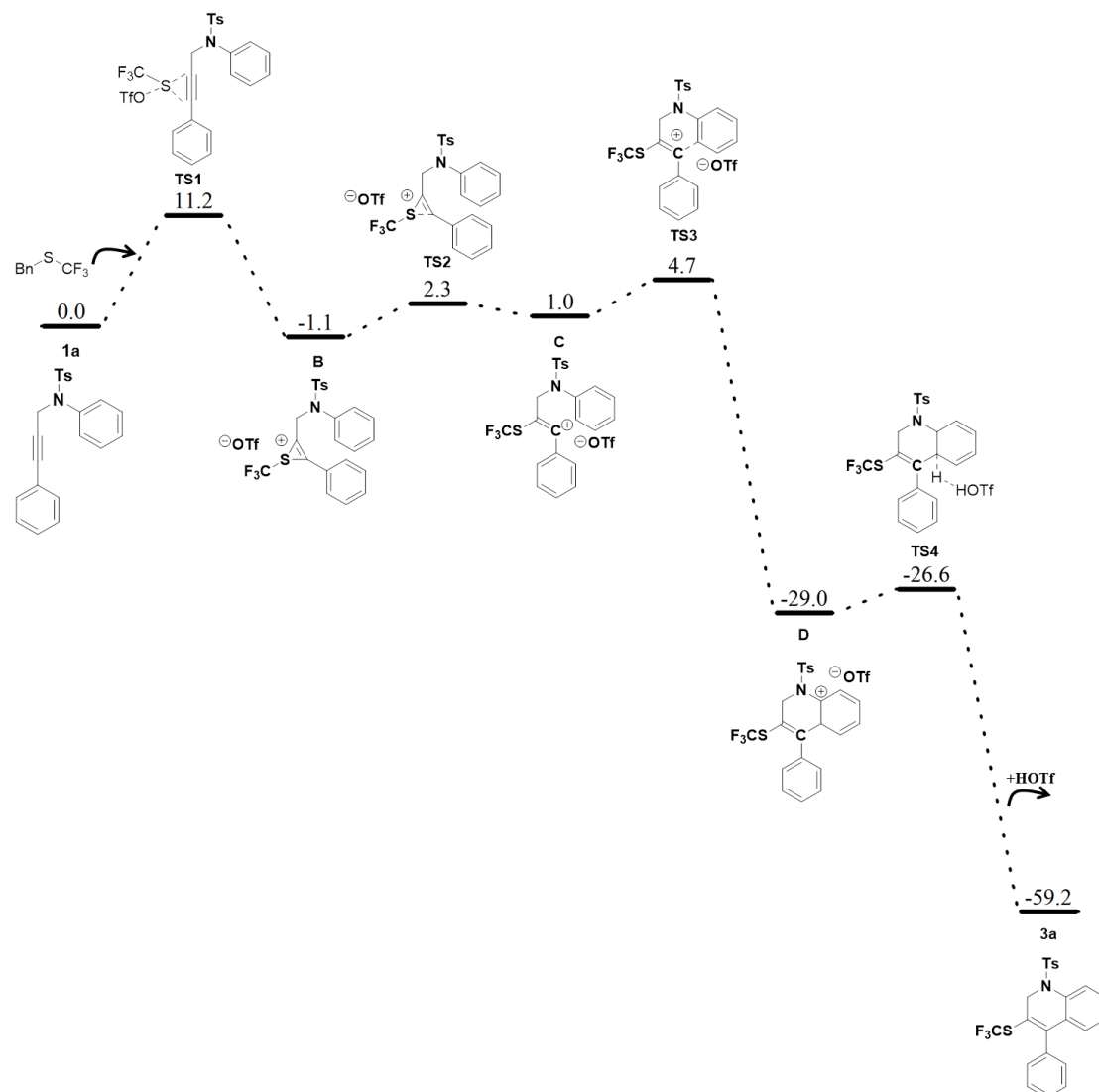
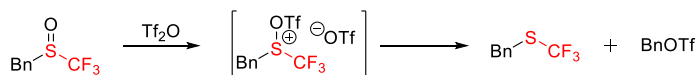
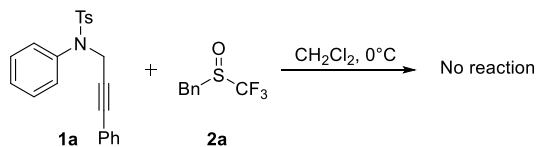
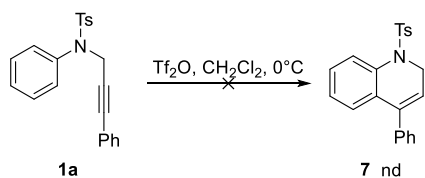


Figure S2. Simplified potential energy surface for reactant **1a**.

The unit of relative energy is kcal/mol.

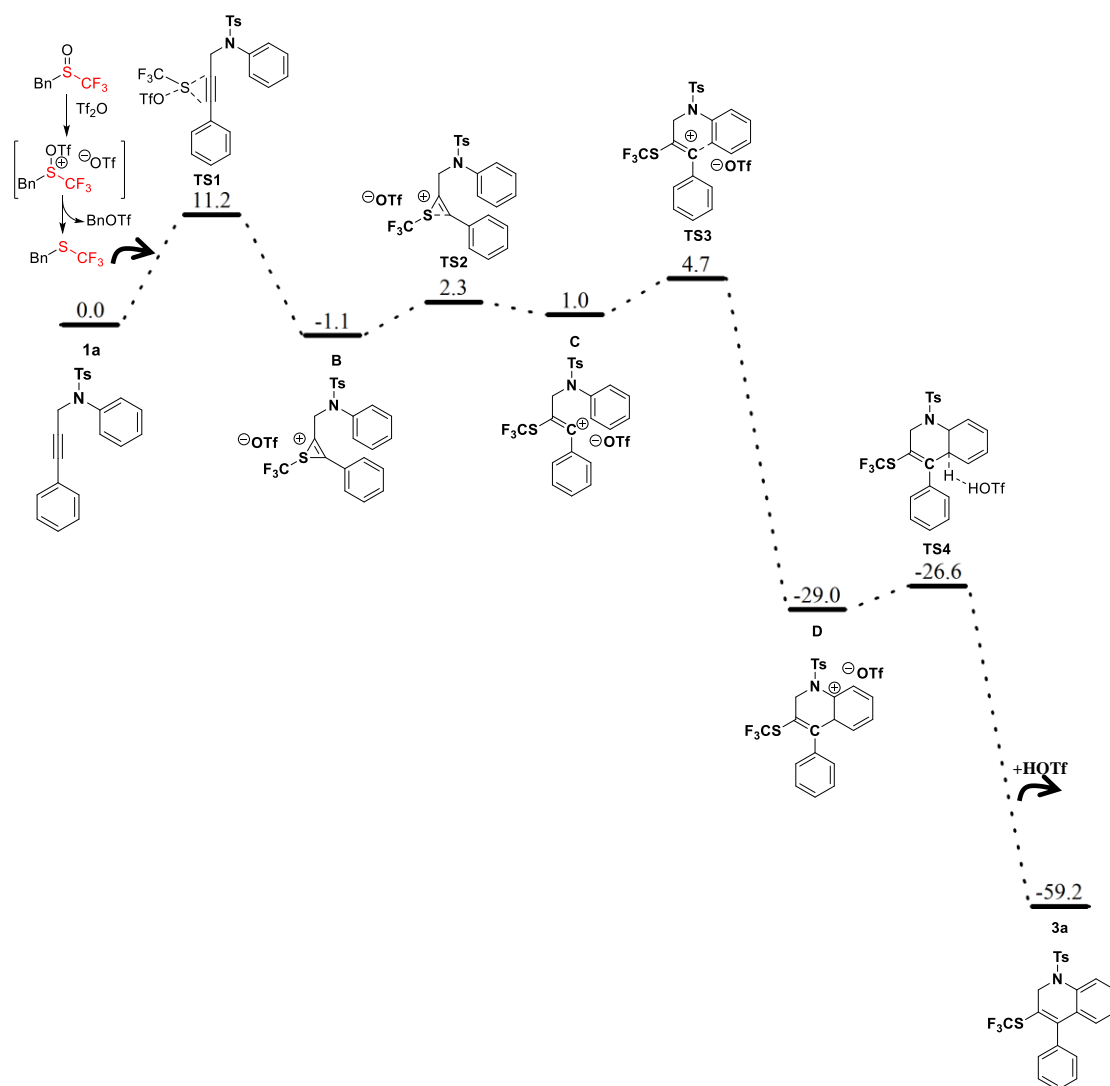
### 3.2 Control experimental results

Based on the previous reports<sup>[13-14]</sup>, in order to understand the mechanism of this process, control experiments were conducted. When substrate **1a** was treated solely with Tf<sub>2</sub>O, 1,2-Dihydroquinolines **7** was not detected. When substrate **1a** was treated solely with BnSOSCF<sub>3</sub>, no reaction was observed. These results might indicate that the reaction undergoes an interrupted Pummerer reaction of trifluoromethyl sulfoxide with Tf<sub>2</sub>O to produce first the sulfonium salt, which was converted to the electrophilic intermediate **A**.



### 3.3 Possible Mechanism

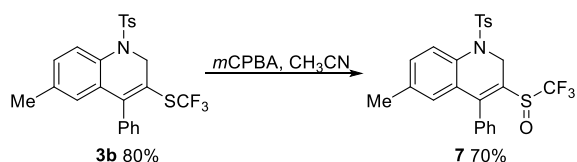
Based on the previous reports<sup>[13-16]</sup>, control experimental results and the calculation results (Figure S3), a tentative mechanism is proposed and is shown in Scheme 8. First, the electrophilic sulfur species **A** generates from the sulfonium salt, which was formed from **2a** and Tf<sub>2</sub>O through interrupted Pummerer reaction. The electrophilic sulfur species **A** attacks C≡C bond of **1a** via **TS1** to form a zwitterionic intermediate **B**. Subsequently, C-S bond of **B** easily cleaves, generating a carbocation **C**. This intermediate then undergoes an intramolecular cyclization, wherein the positively charged carbon of **C** attacks the phenyl ring to form the intermediate **D**. Finally, **D** undergoes deprotonation to yield the final product **3a**.



**Figure S3. Computational study of a possible mechanism for the trifluoromethylthiolation.**

All the geometrical structures were optimized at the pbe0 level with the Grimme's dispersion correction at the D3BJ level including conductor-like polarizable continuum model by the ORCA package

#### 4. Derivatization of trifluoromethylthiolation product



To a solution of compound **3b** (238 mg, 0.50 mmol, 1.0 equiv) in MeCN (5 mL) was added *m*CPBA (85% w/w, 107 mg, 0.62 mmol, 1.05 equiv) at 0 °C. The reaction mixture was stirred at rt and the progress of the reaction was monitored by TLC. Upon completion of the reaction, MeCN was removed in vacuo. The residue was admixed with DCM (60 mL) and the resultant solution

was washed with water (30 mL). The organic layer was further washed with aq. NaOH solution, then washed with brine, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude residue was purified by column chromatography (20% EtOAc/petroleum ether) to afford the corresponding sulfoxide **7** (172mg, 70% yield).

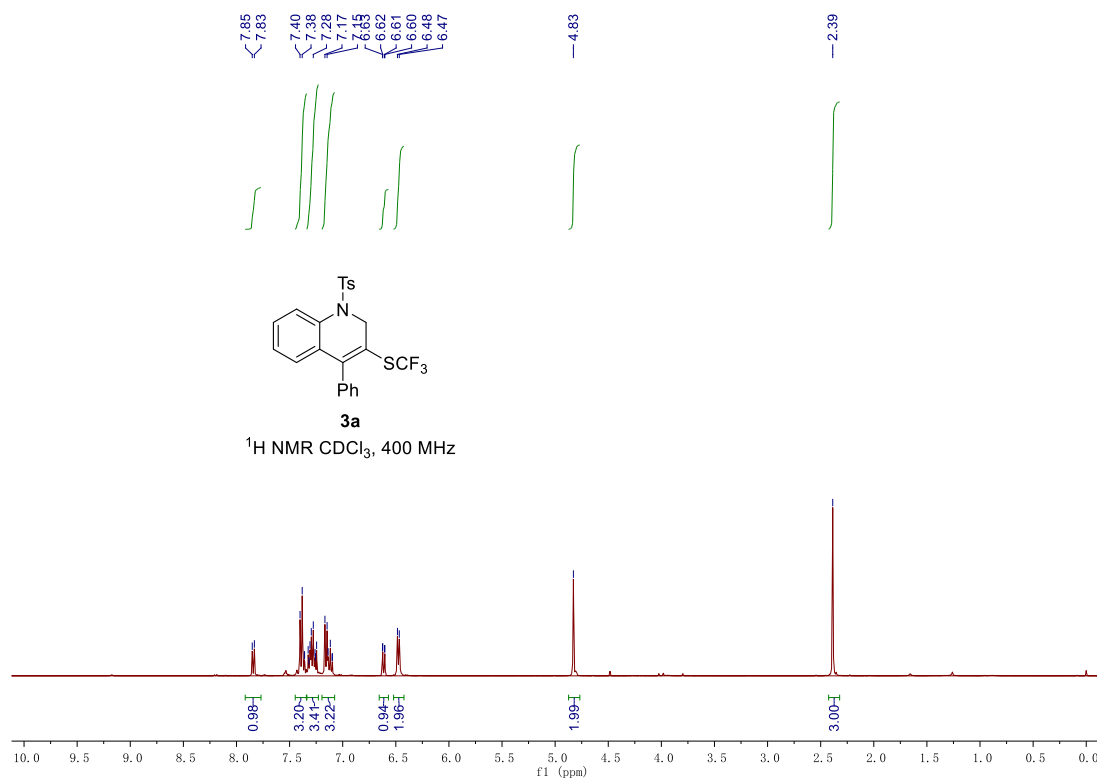
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 6.7 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.00 (s, 1H), 6.44 (s, 1H), 5.74 (d, *J* = 17.6 Hz, 1H), 4.20 (d, *J* = 17.6 Hz, 1H), 2.40 (s, 3H), 2.22 (s, 3H).

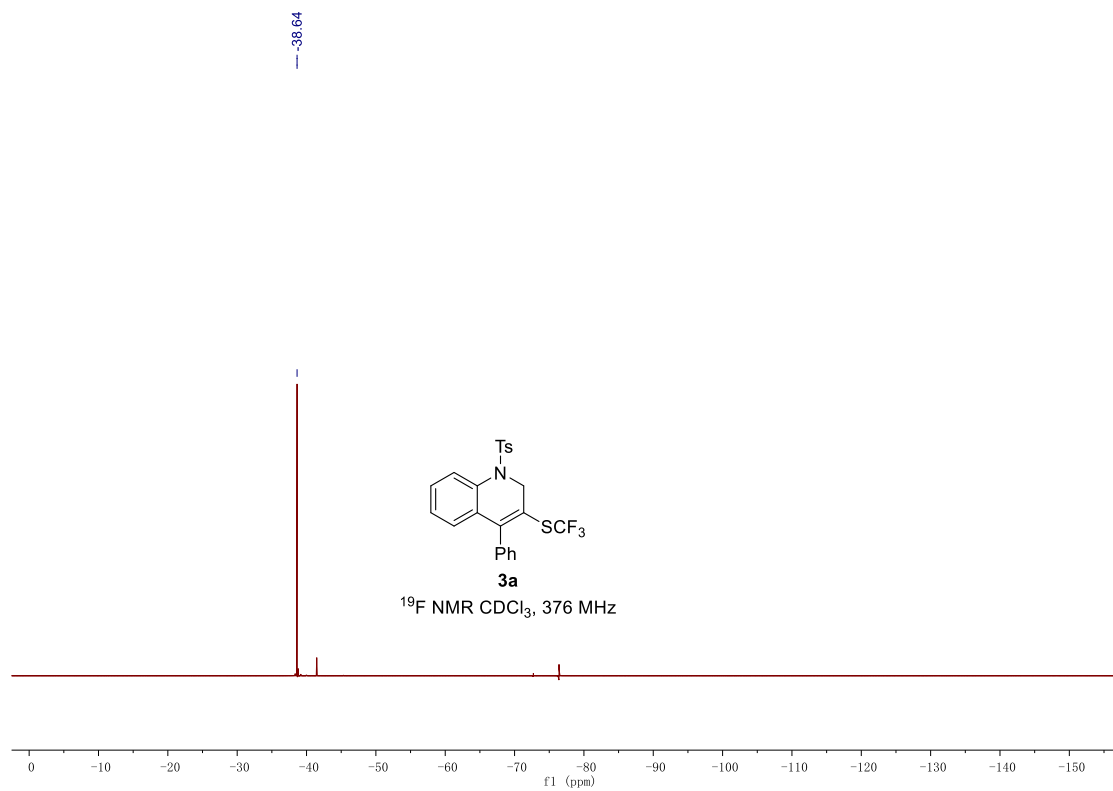
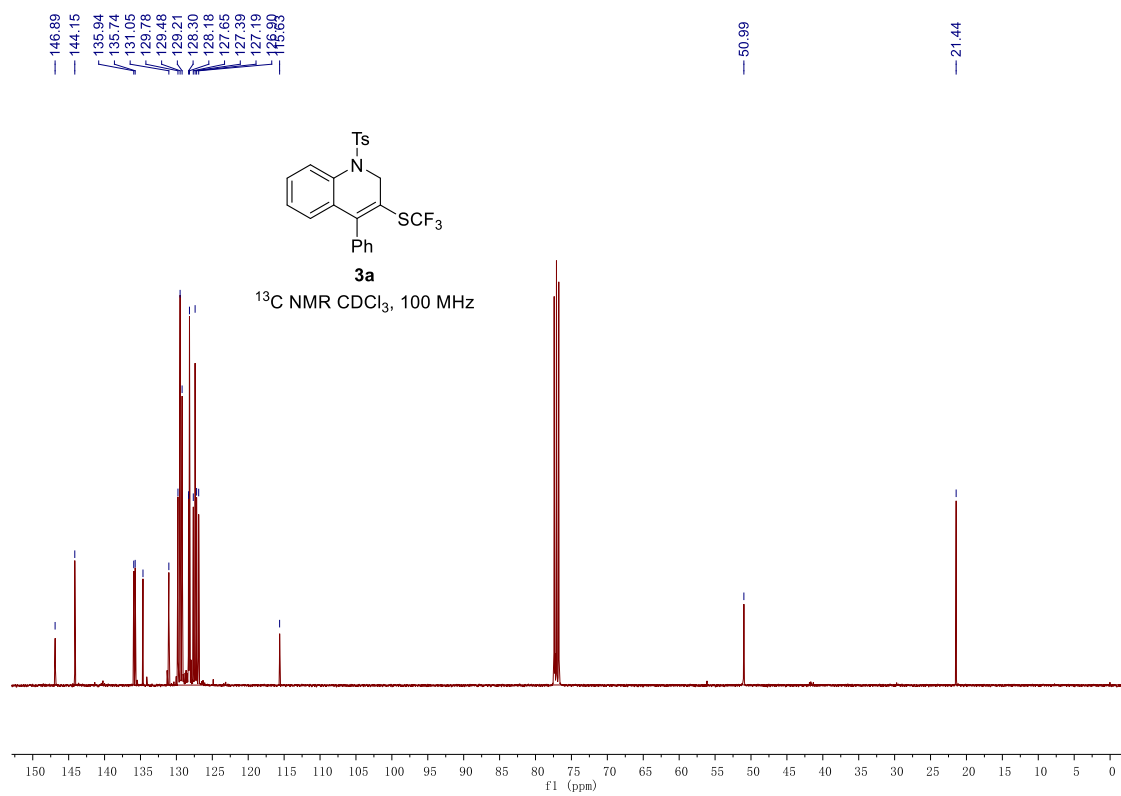
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.96, 144.02, 137.11, 135.41, 133.66, 132.67, 132.40, 129.64, 129.53, 129.36, 129.09, 128.33, 128.11, 127.65, 127.43, 127.40 (dd, *J*<sub>C-F</sub> = 369.6, 265.9 Hz), 40.29, 40.27, 21.44, 21.07.

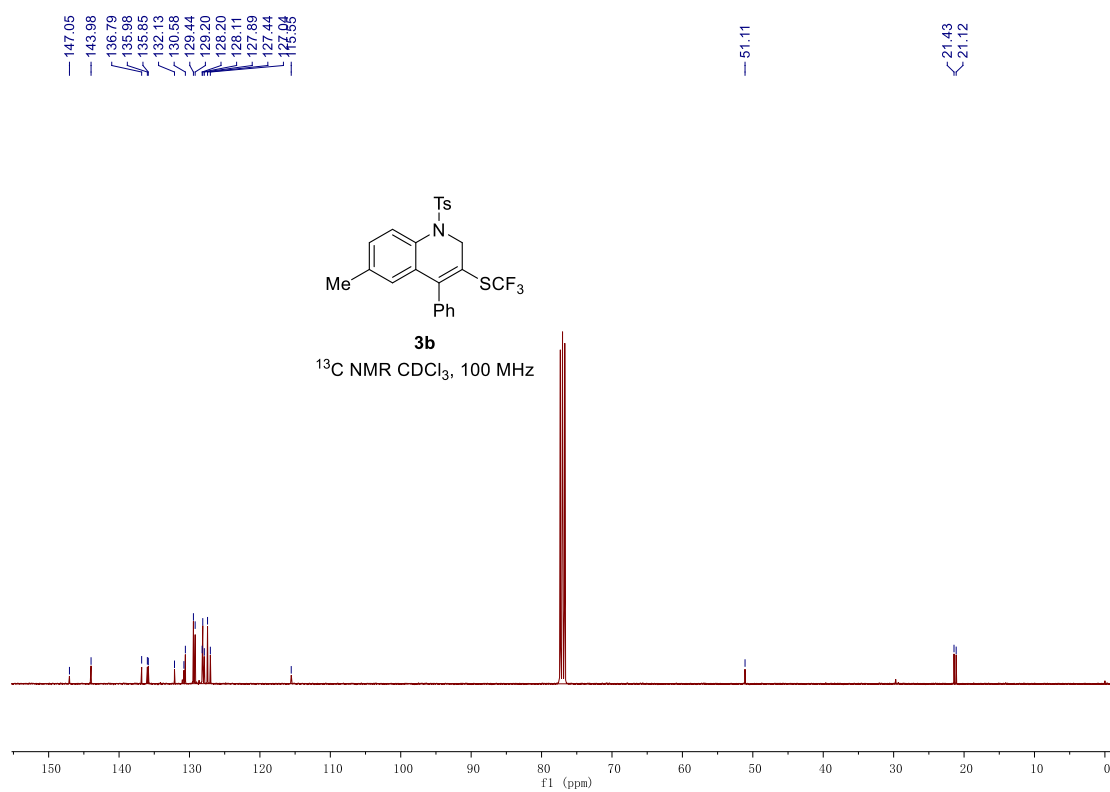
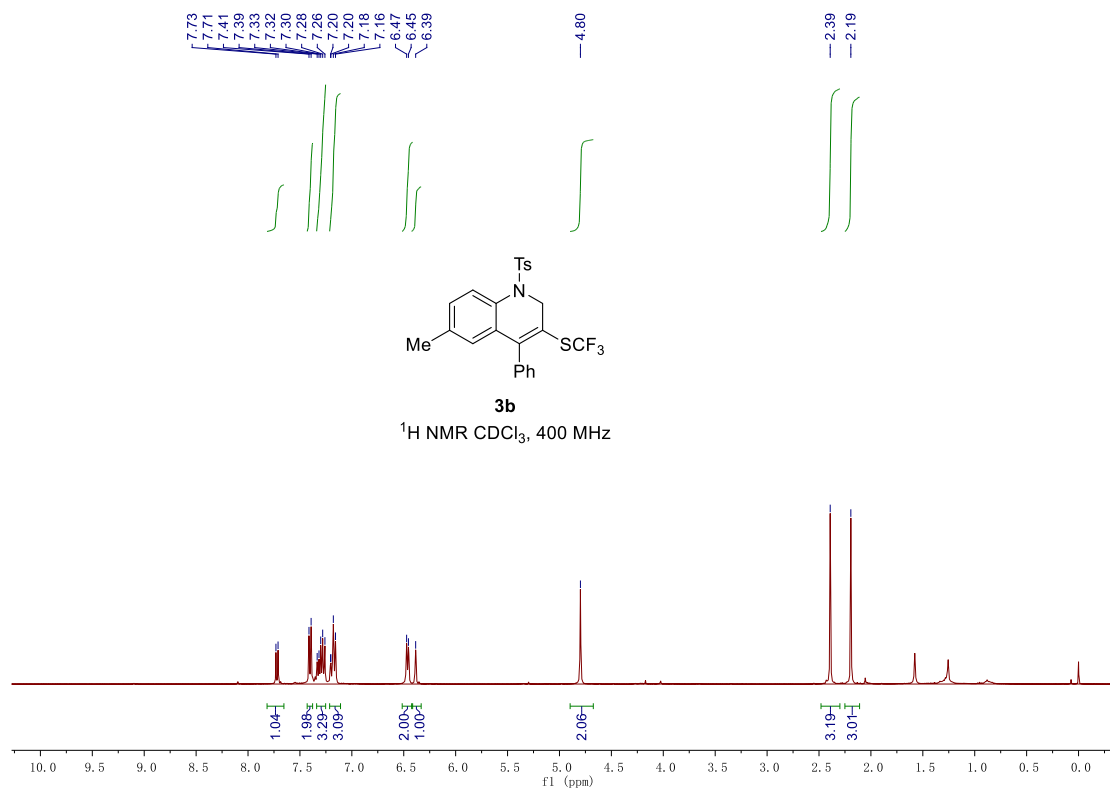
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -68.5.

HRMS-ESI (*m/z*): [M+Na]<sup>+</sup> calcd for C<sub>24</sub>H<sub>20</sub>F<sub>3</sub>NO<sub>3</sub>S<sub>2</sub> 514.0734, found: 514.0732.

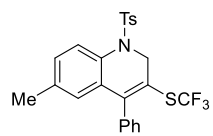
## 5. Copies of NMR Spectra



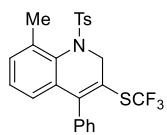
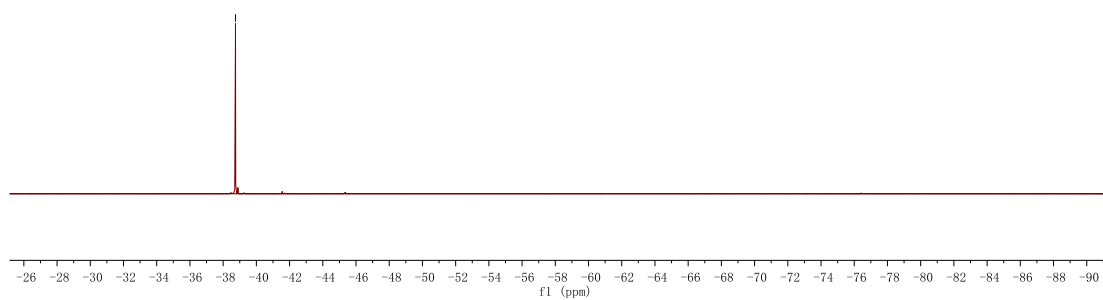




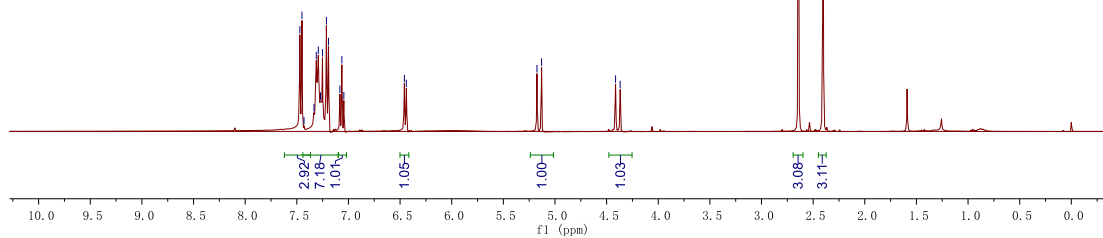
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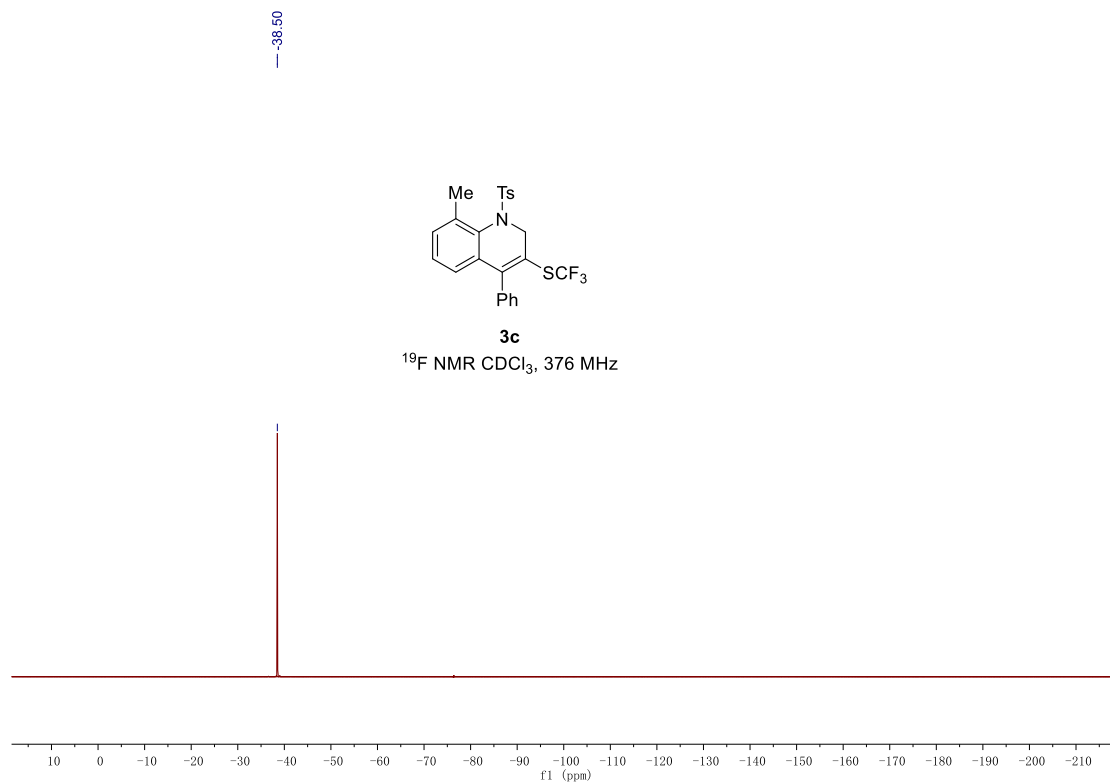
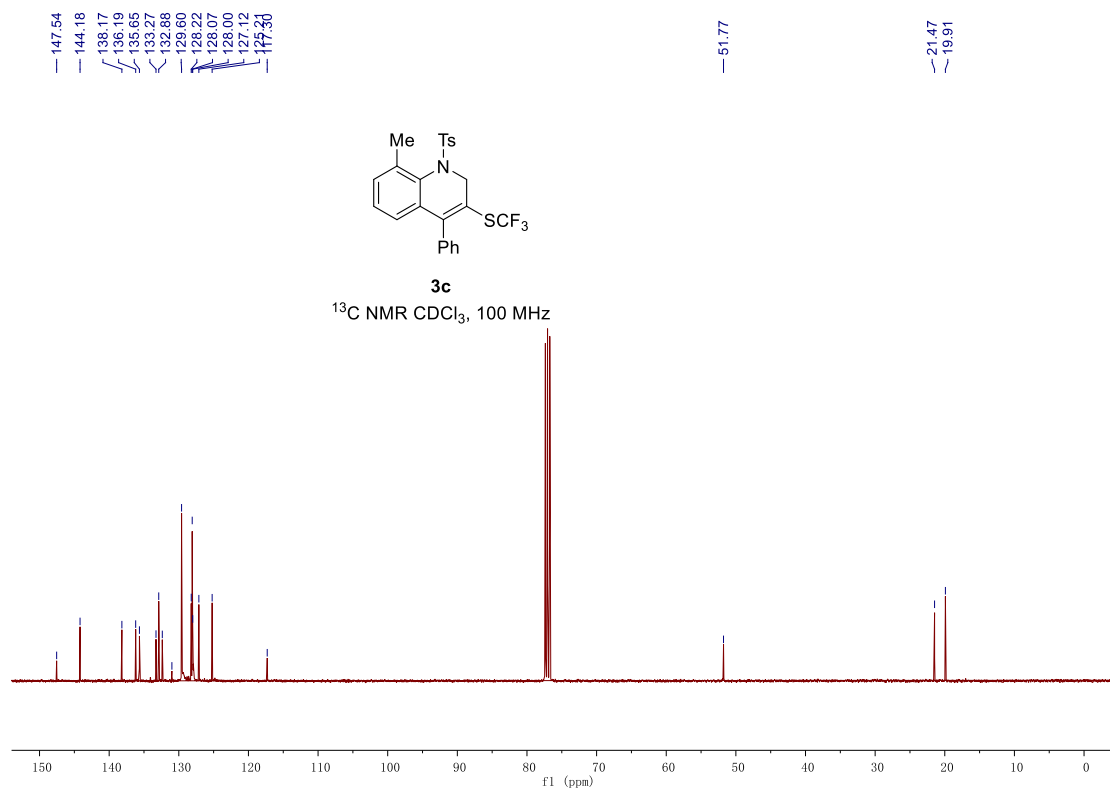


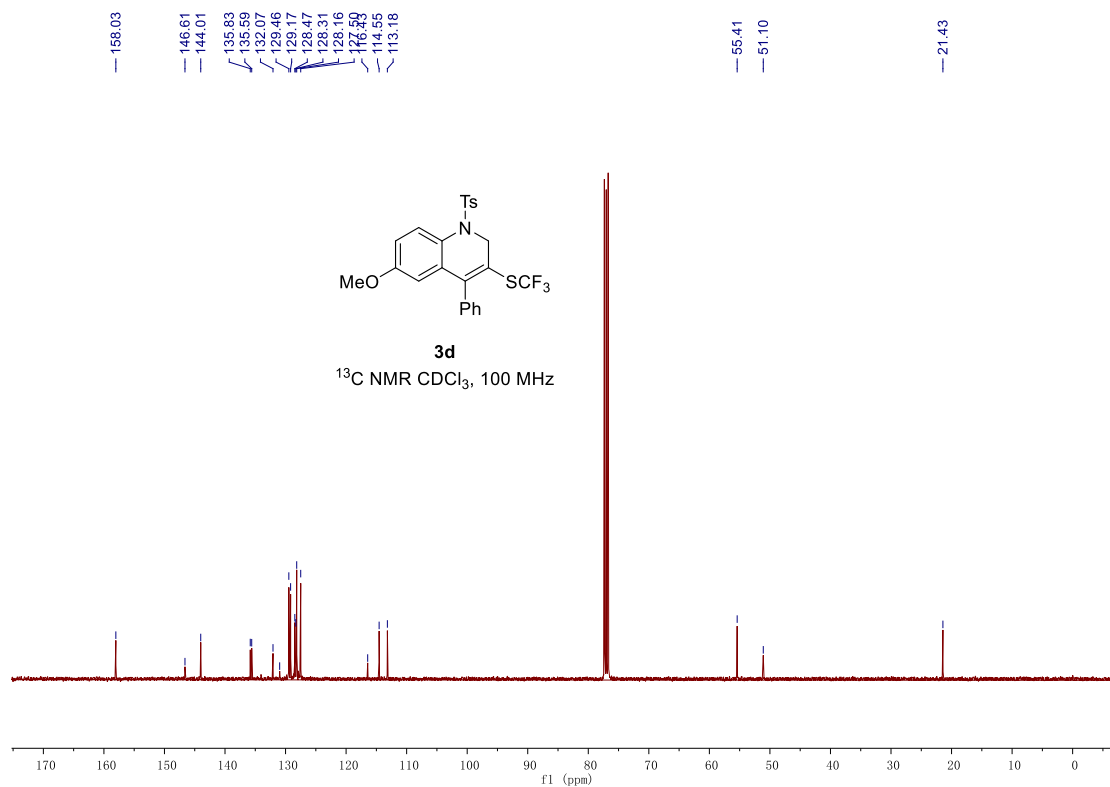
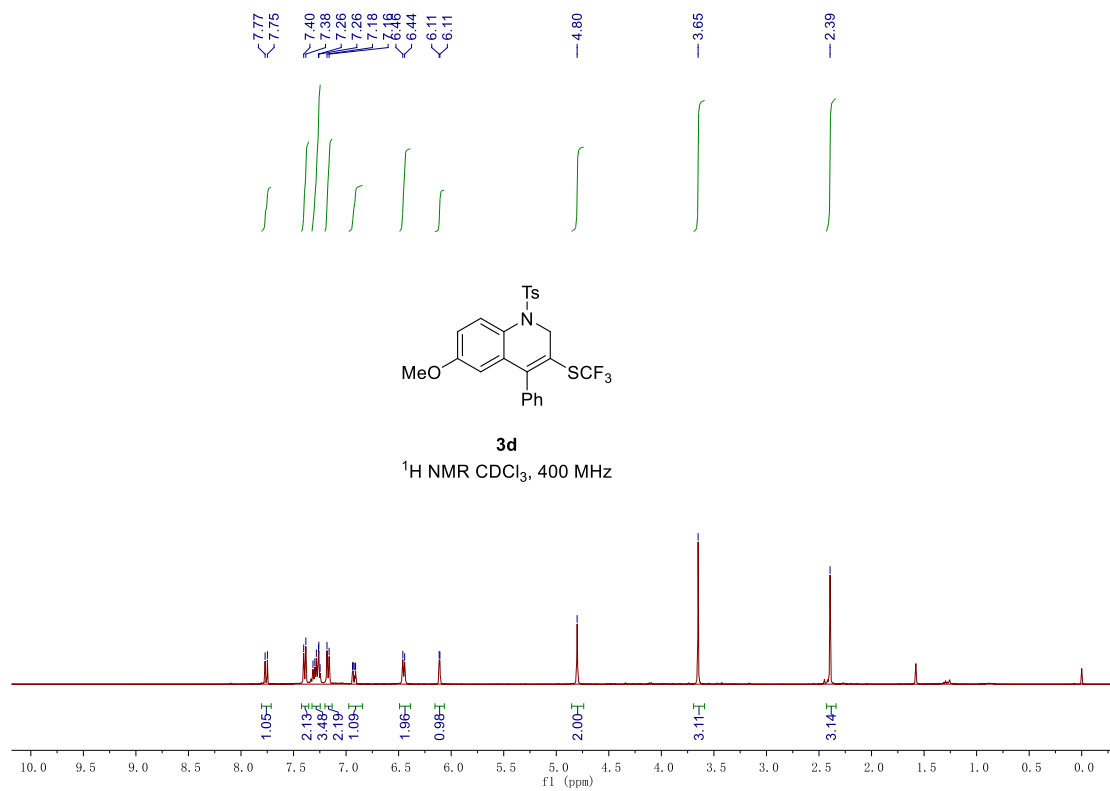
**3b**  
<sup>19</sup>F NMR CDCl<sub>3</sub>, 376 MHz



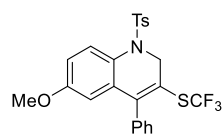
**3c**  
<sup>1</sup>H NMR CDCl<sub>3</sub>, 400 MHz





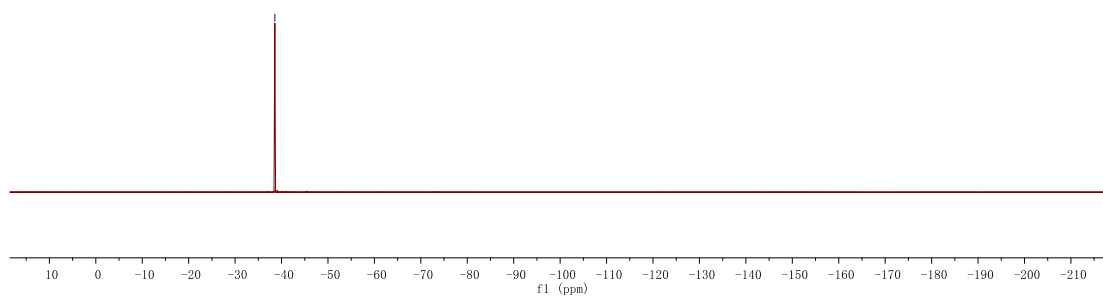


---38.56



**3d**

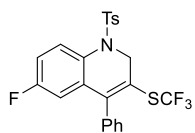
<sup>19</sup>F NMR CDCl<sub>3</sub>, 376 MHz



7.84  
7.82  
7.82  
7.80  
7.33  
7.31  
7.20  
7.20  
7.20  
6.48  
6.44  
6.32  
6.31  
6.30  
6.29

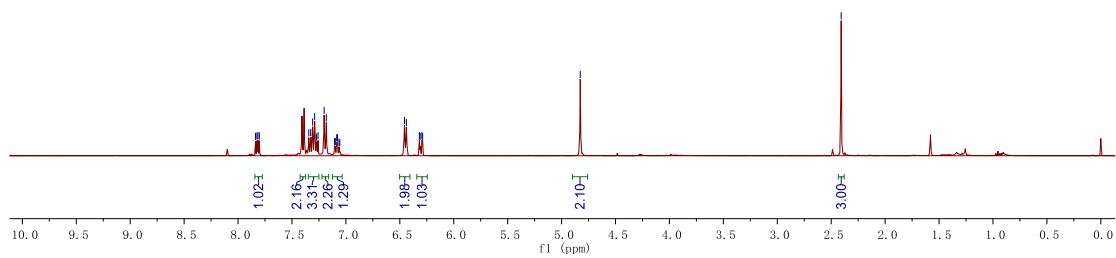
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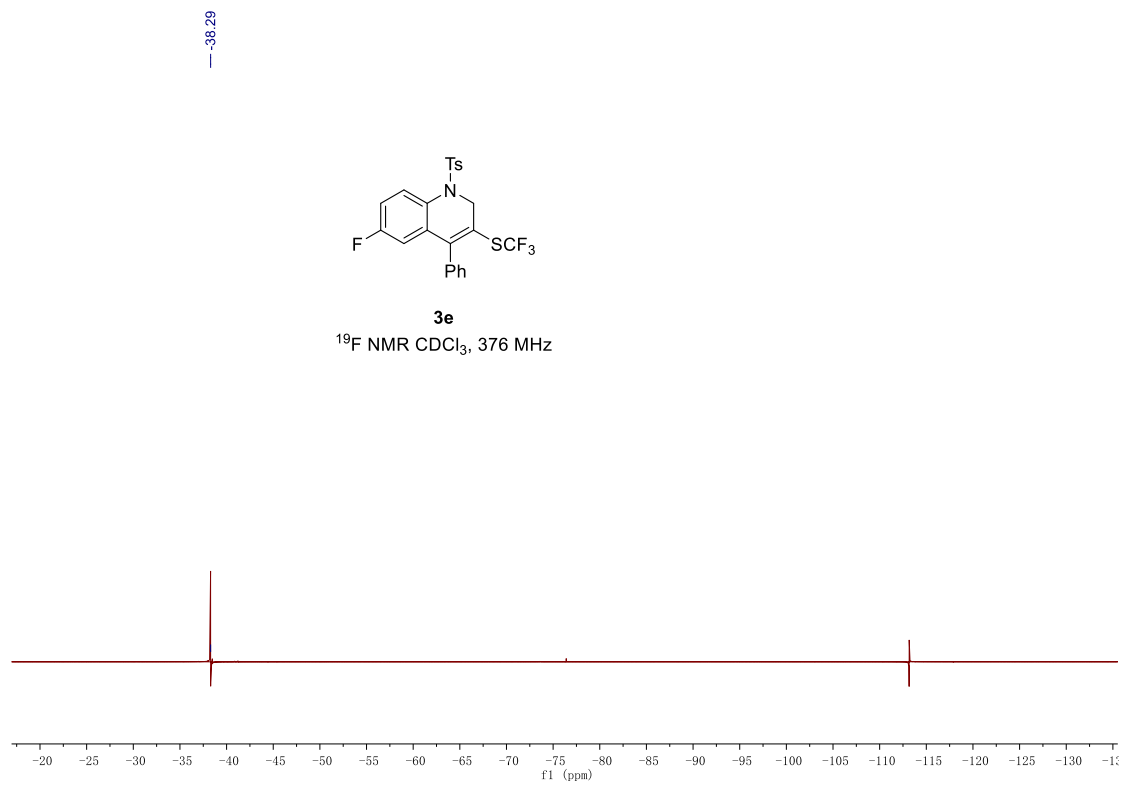
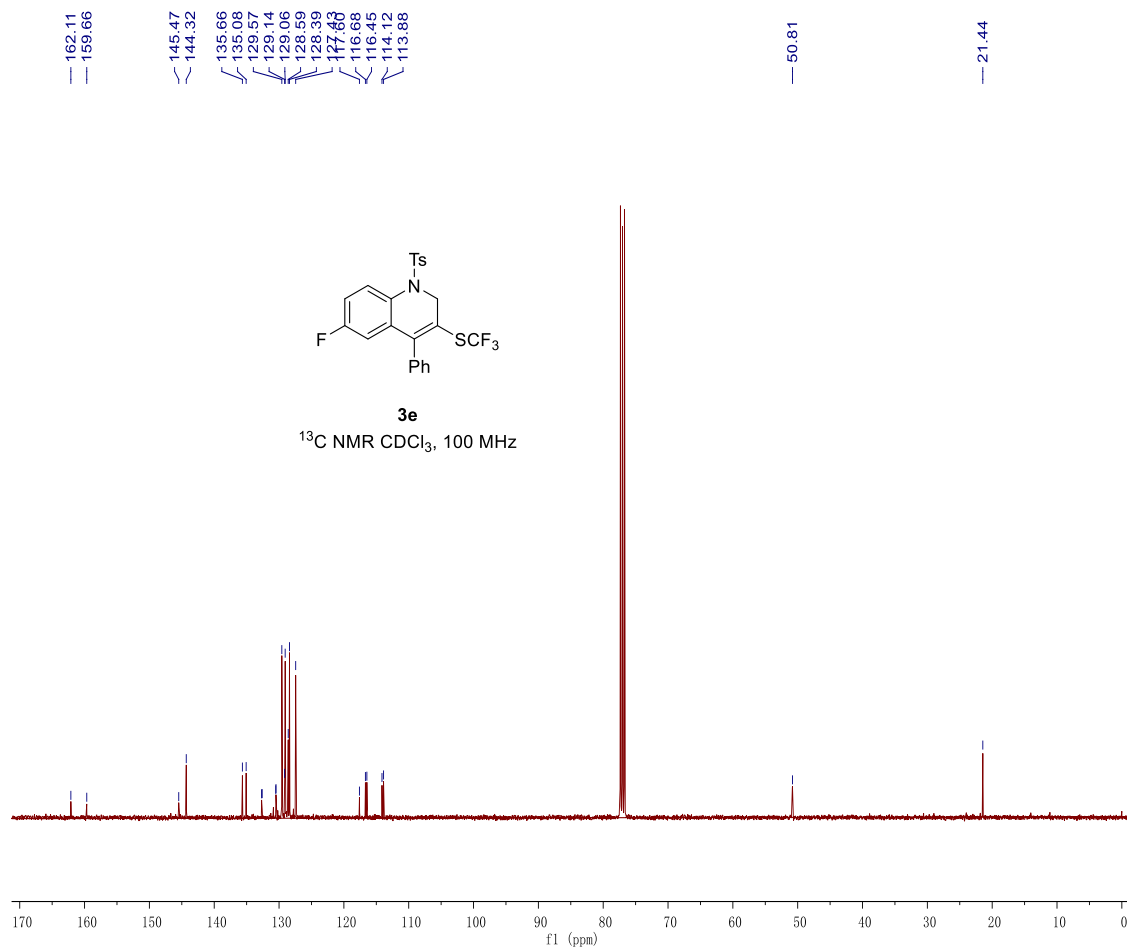
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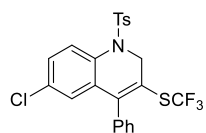
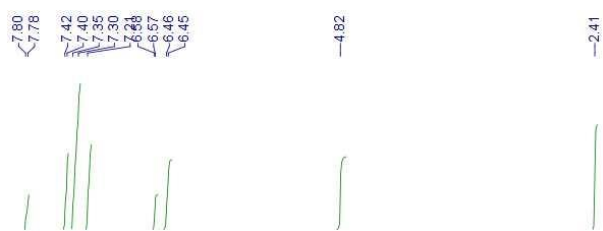


**3e**

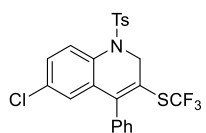
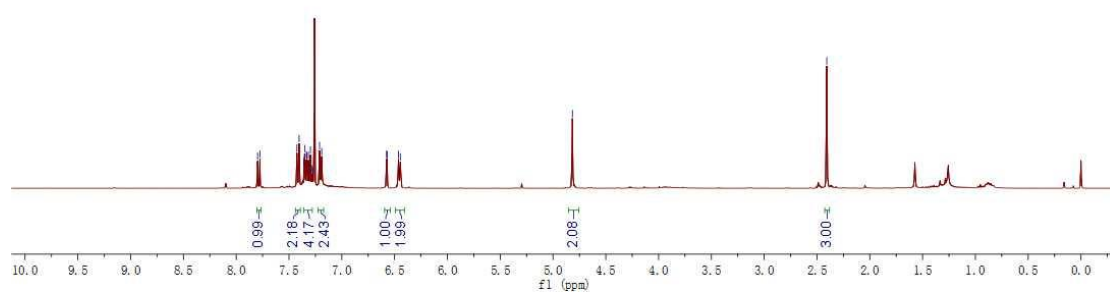
<sup>1</sup>H NMR CDCl<sub>3</sub>, 400 MHz



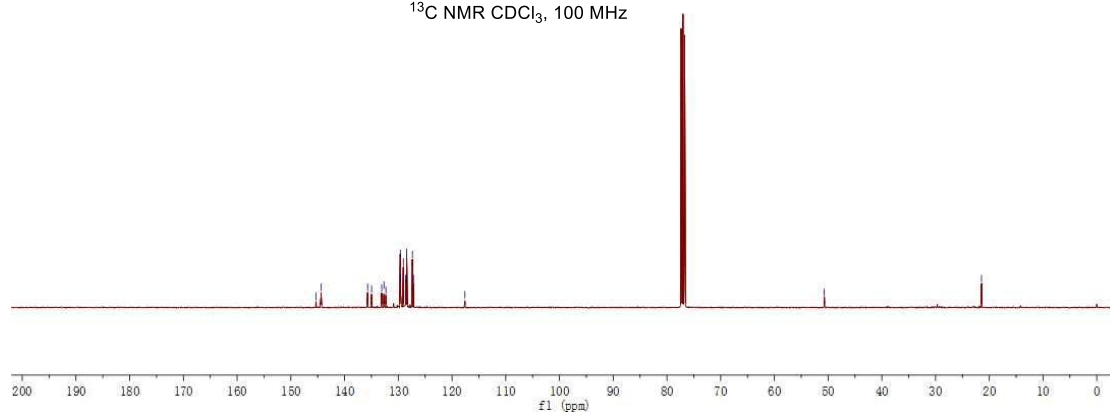


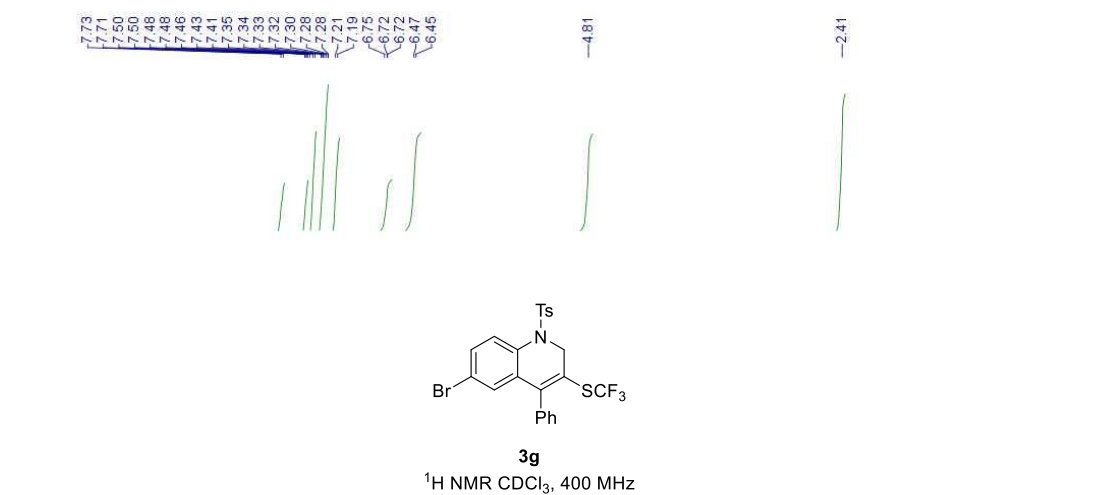
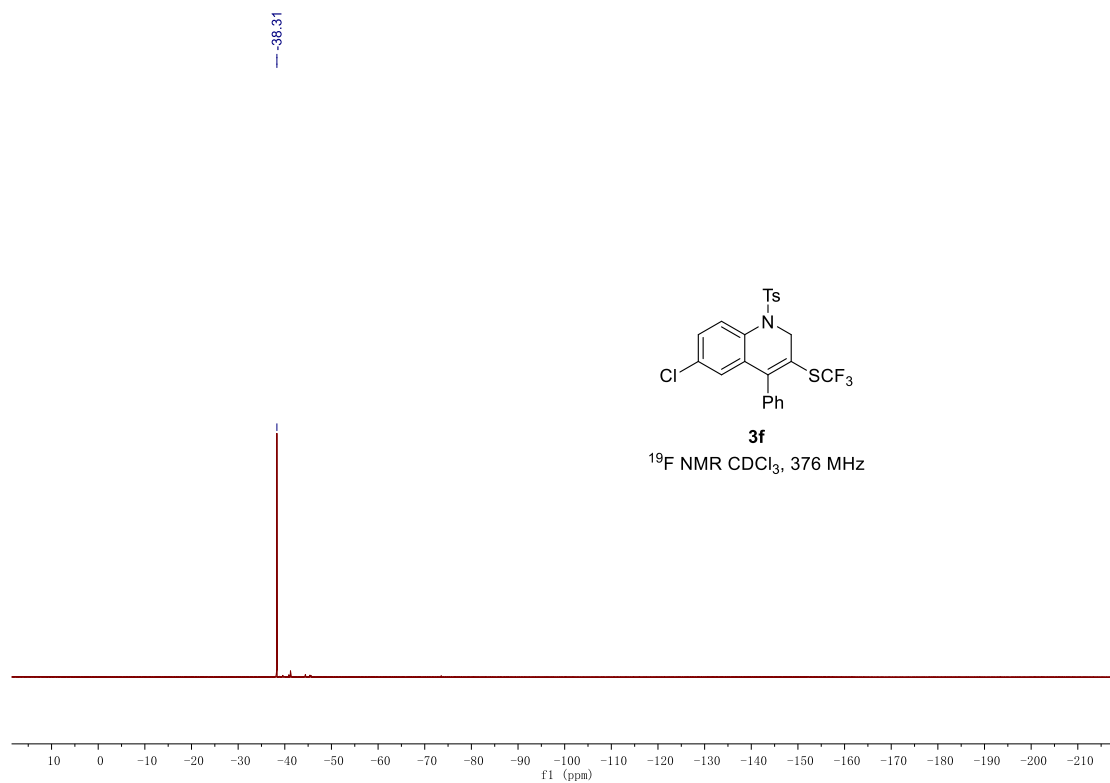


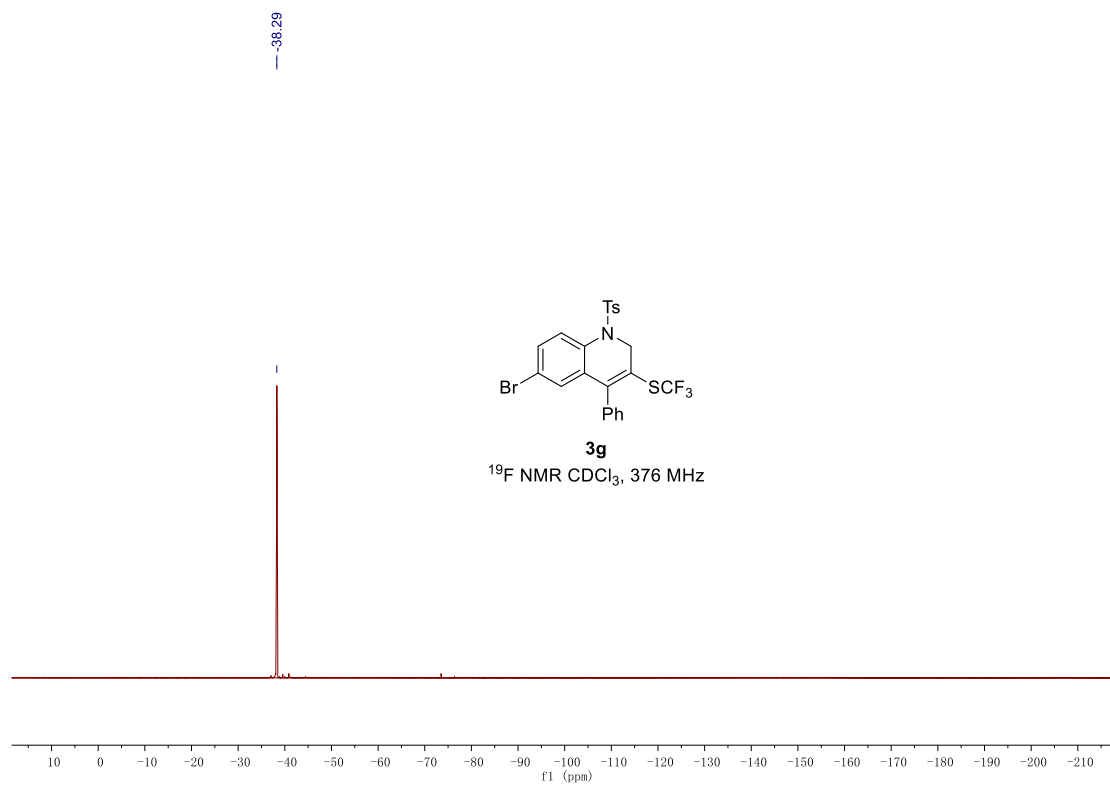
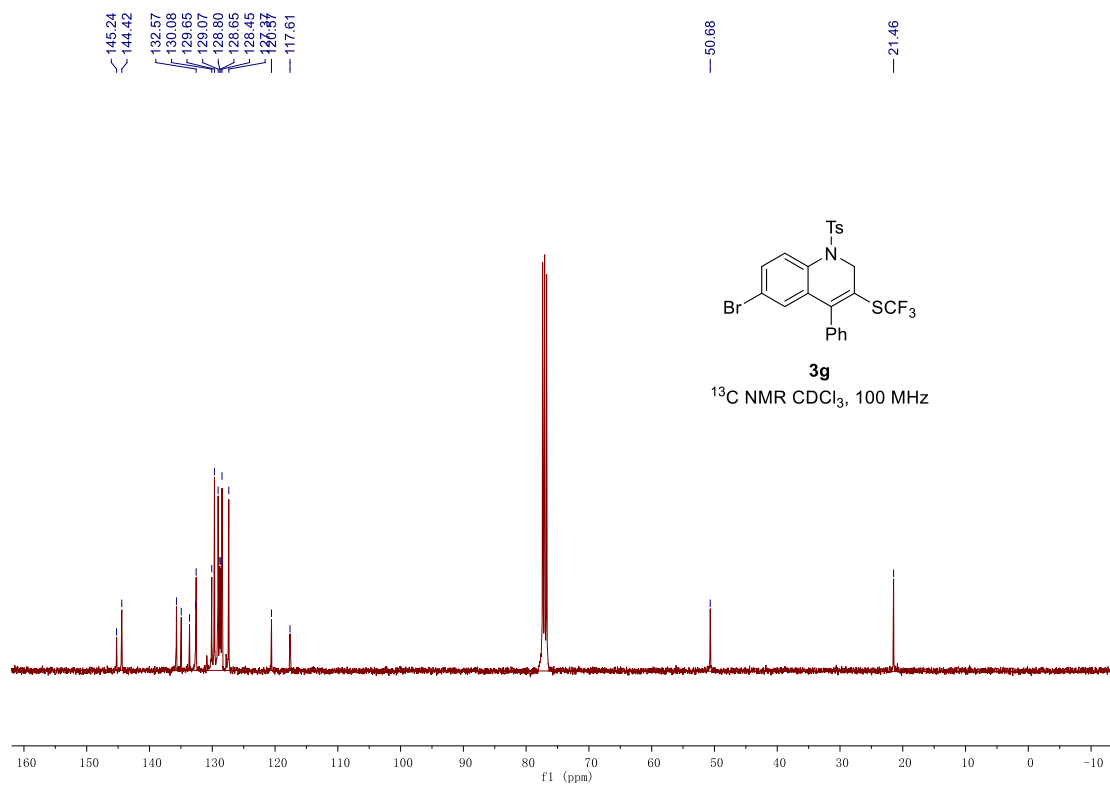
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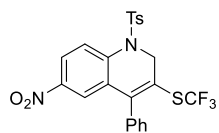
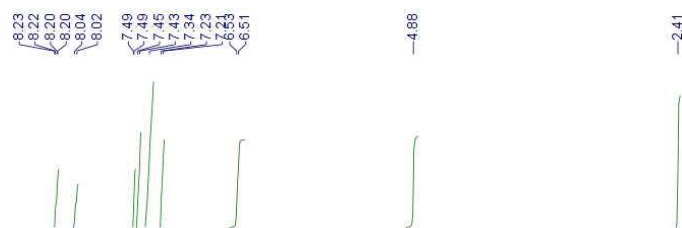


**3f**  
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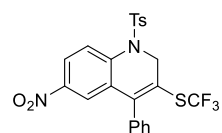
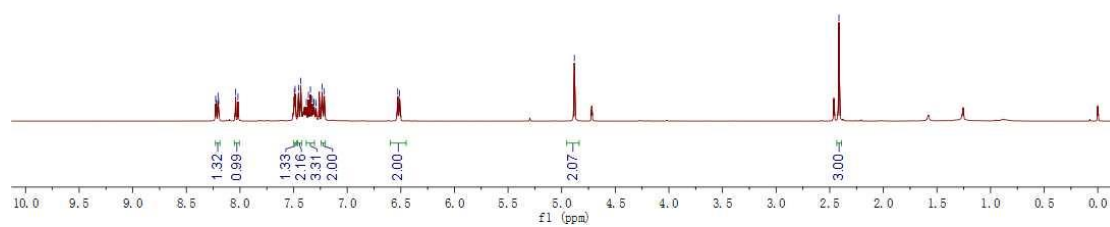




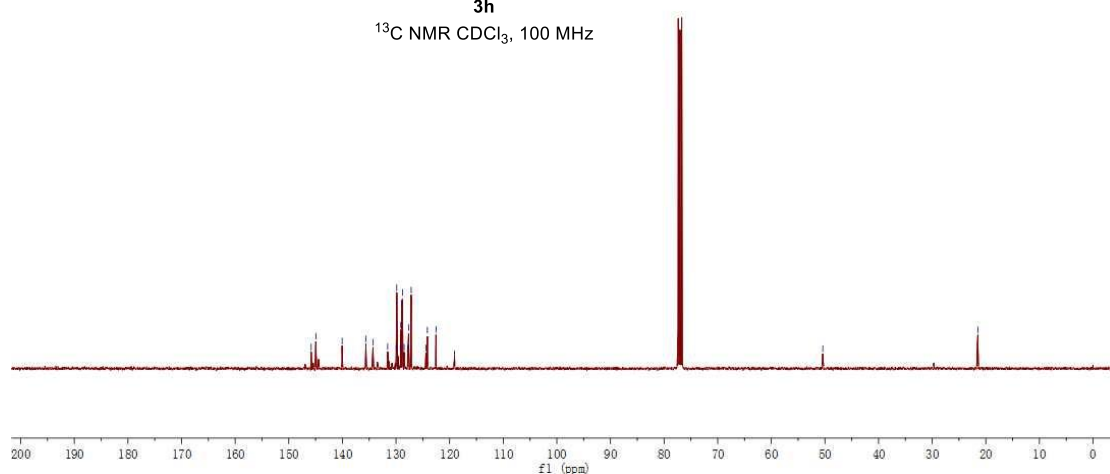




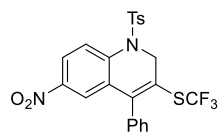
**3h**  
<sup>1</sup>H NMR CDCl<sub>3</sub>, 400 MHz



**3h**  
<sup>13</sup>C NMR CDCl<sub>3</sub>, 100 MHz

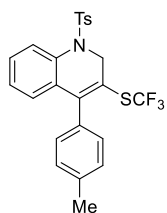
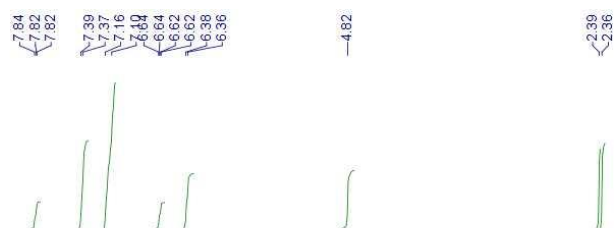
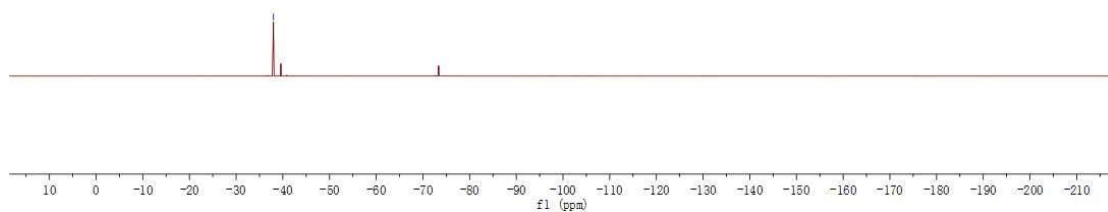


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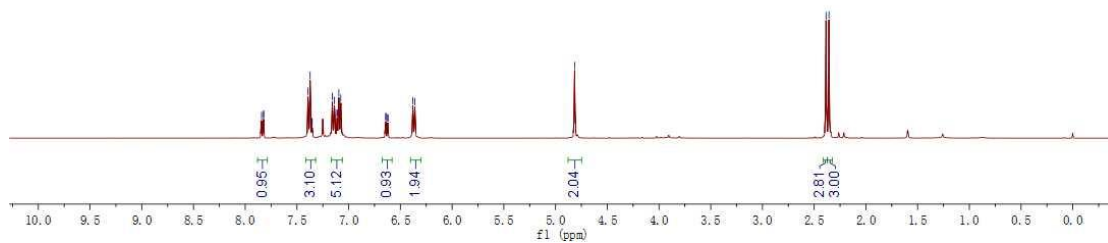
**3h**

<sup>19</sup>F NMR CDCl<sub>3</sub>, 376 MHz



**3i**

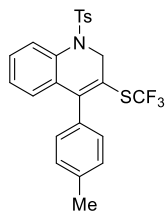
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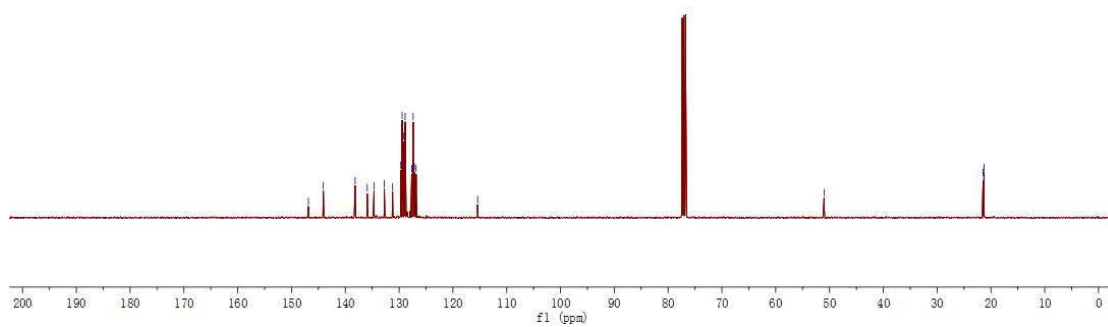
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127.66  
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127.16  
125.97

51.01

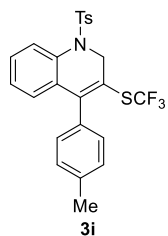
21.45  
21.29



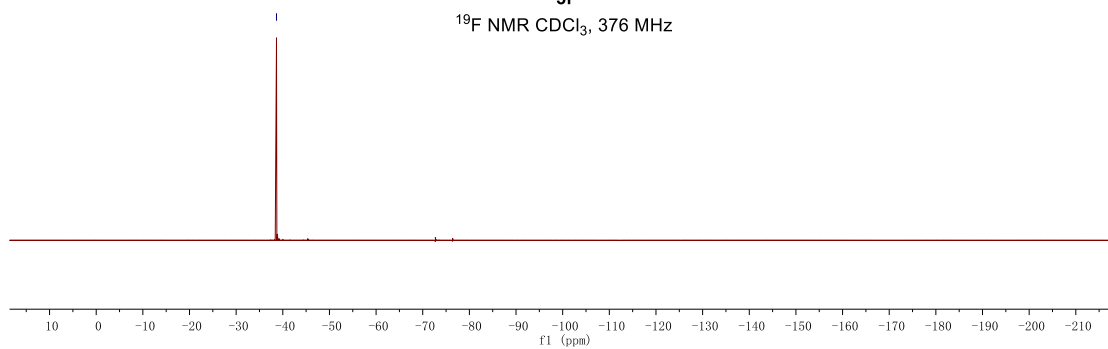
$^{13}\text{C}$  NMR  $\text{CDCl}_3$ , 100 MHz

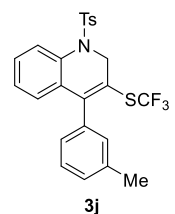
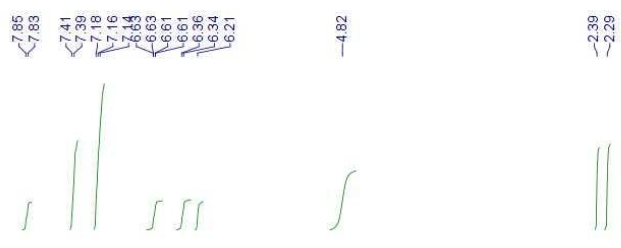


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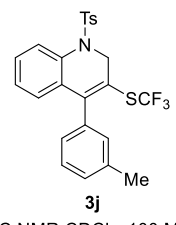
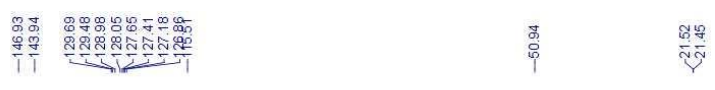
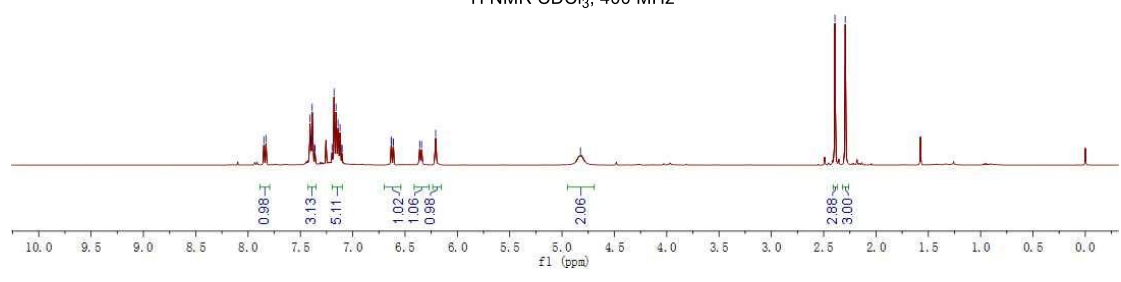


$^{19}\text{F}$  NMR  $\text{CDCl}_3$ , 376 MHz

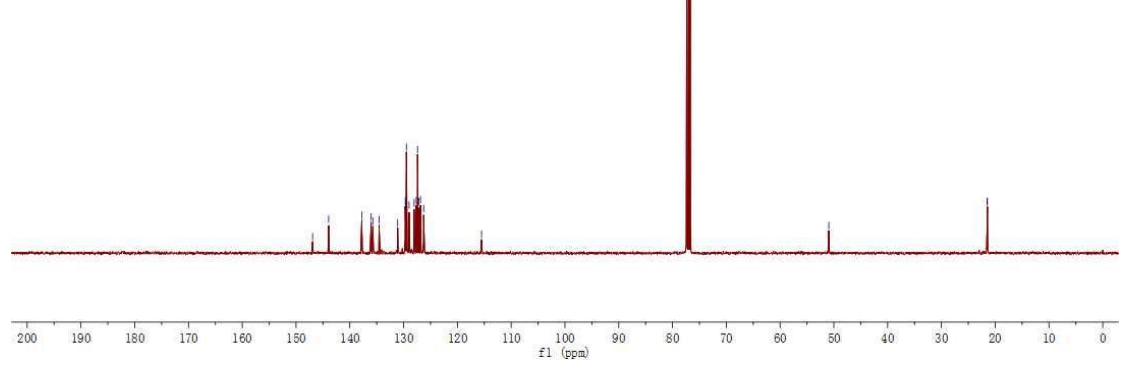


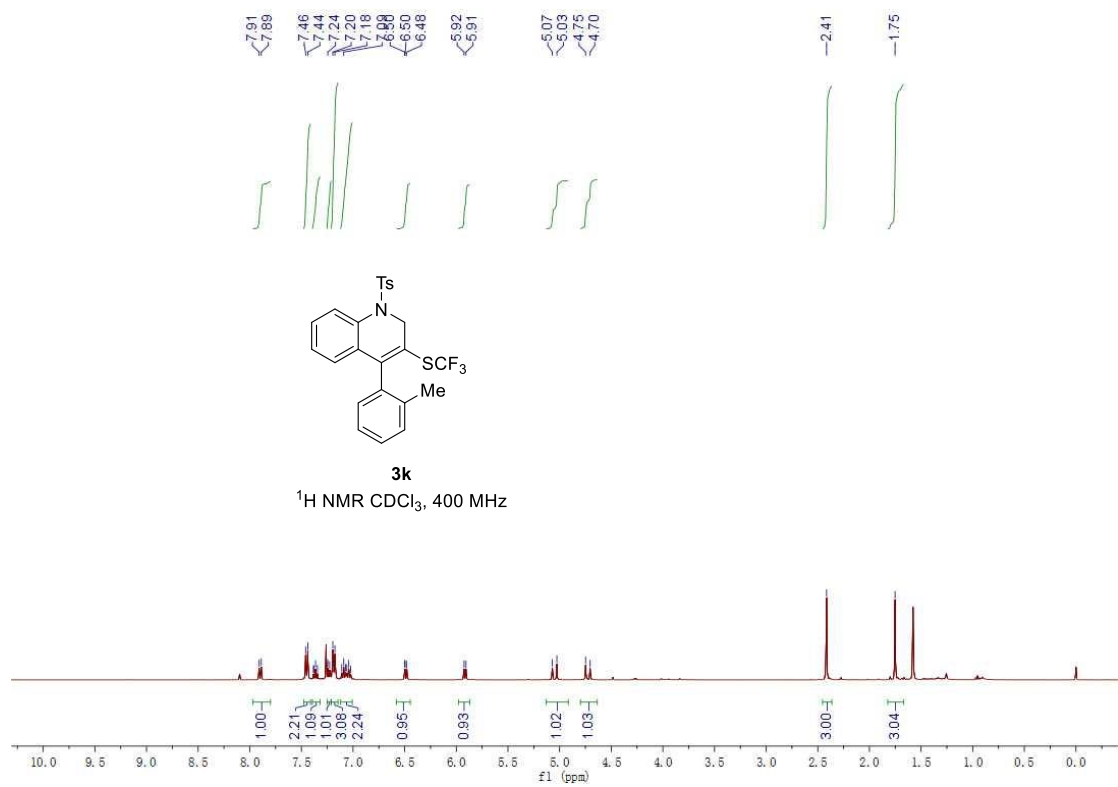
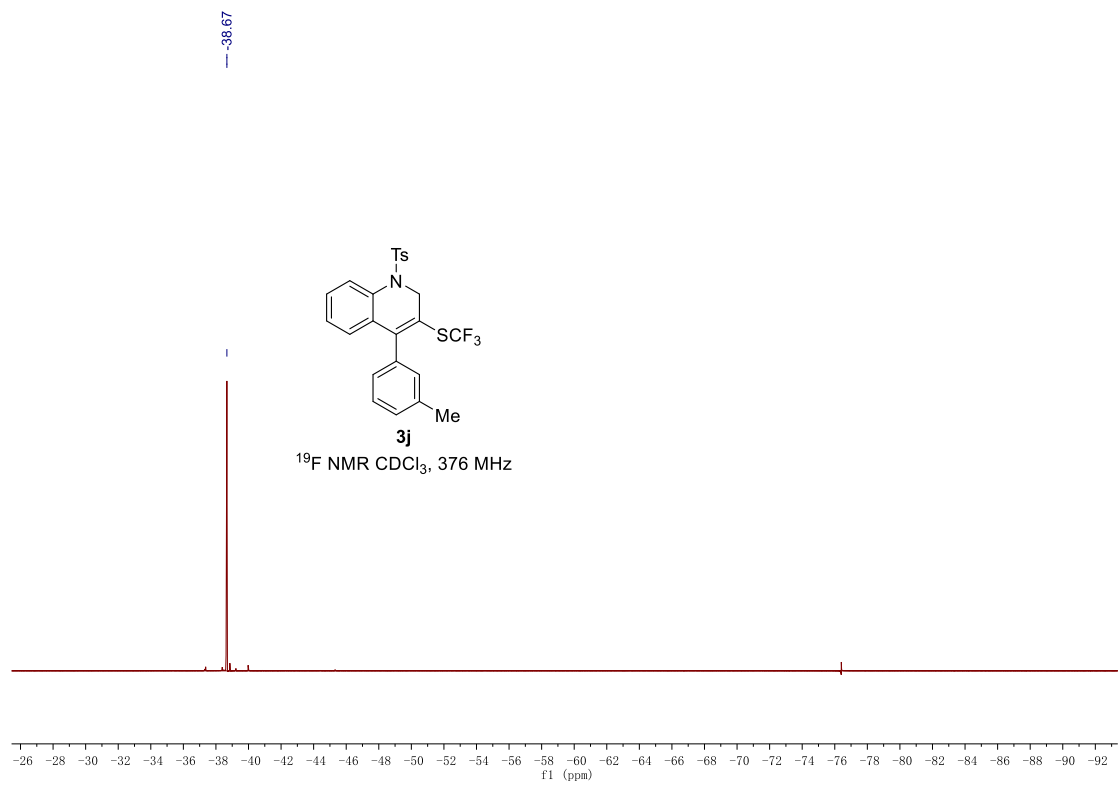


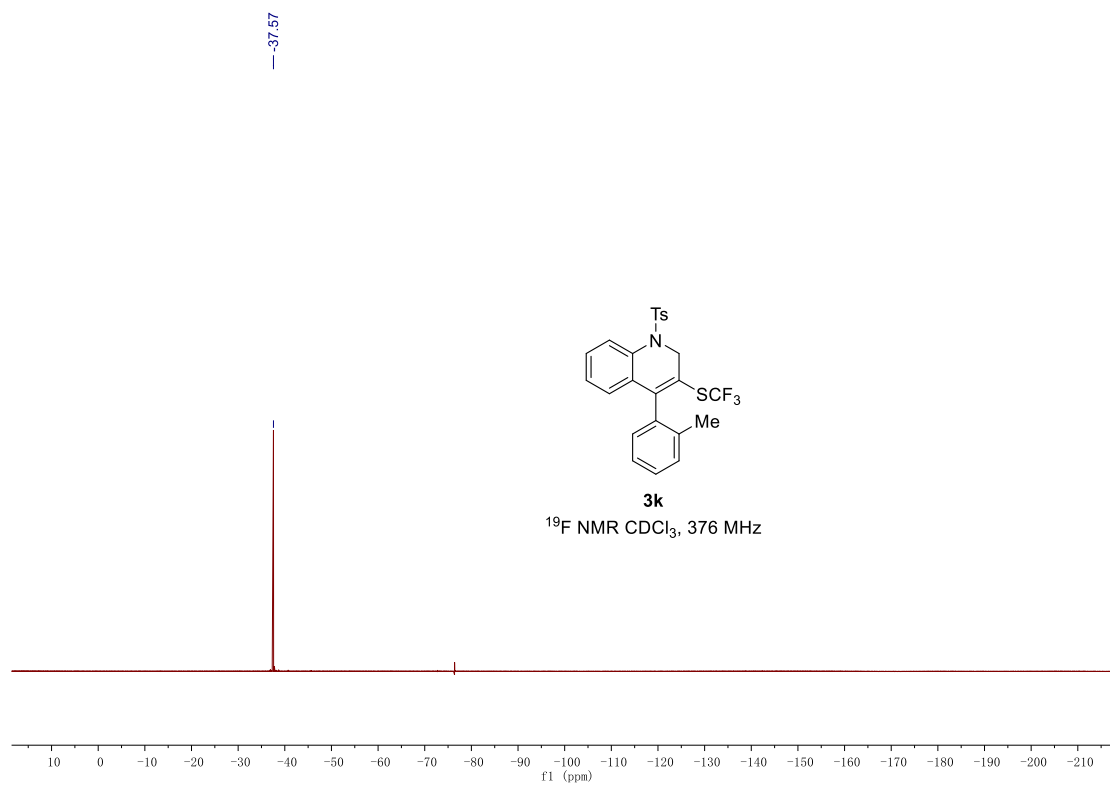
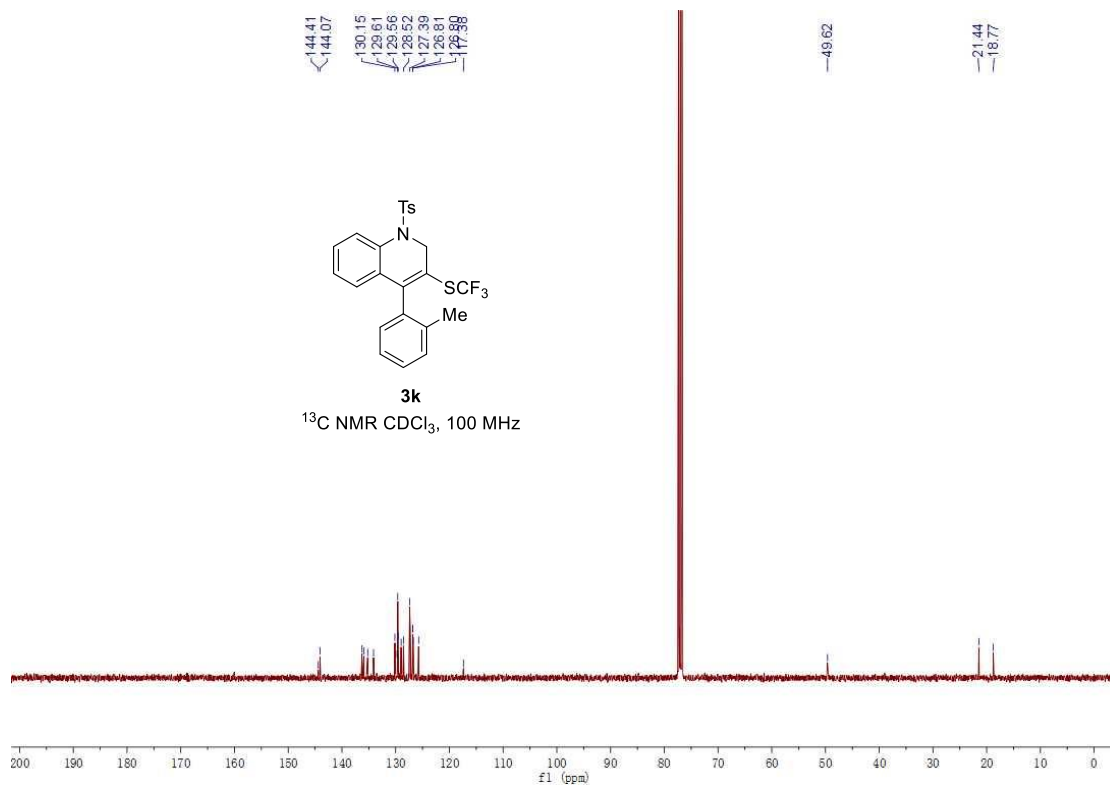
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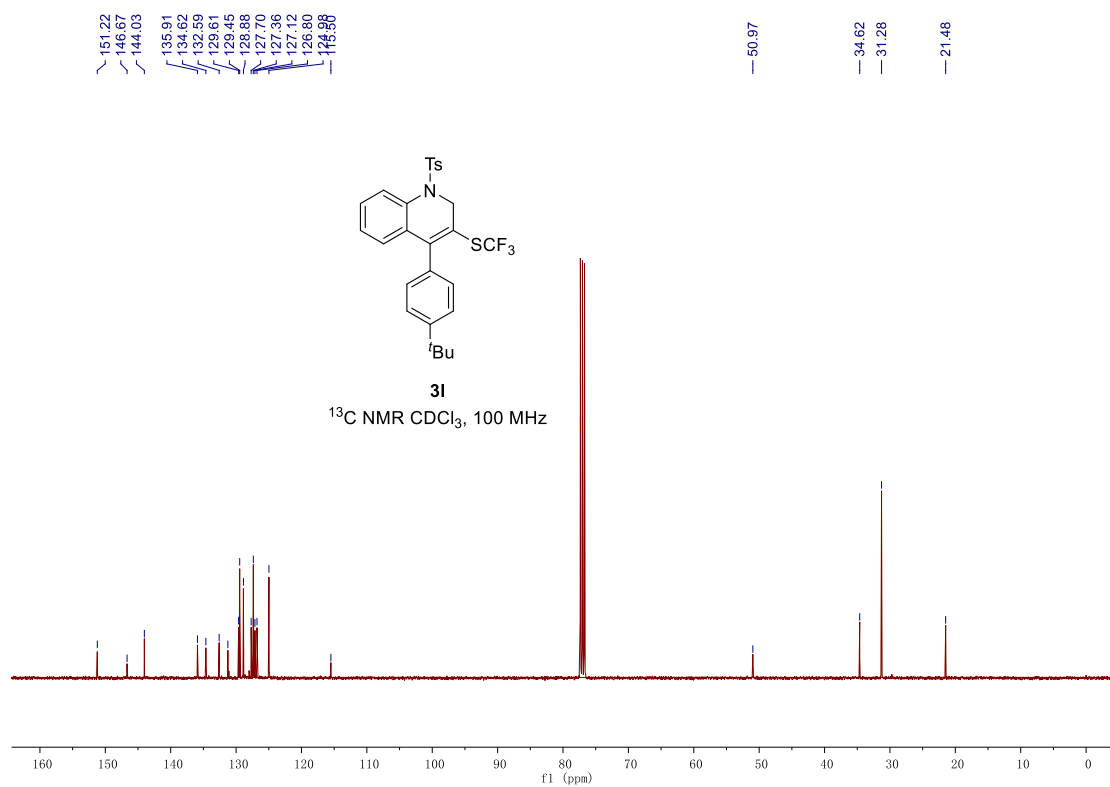
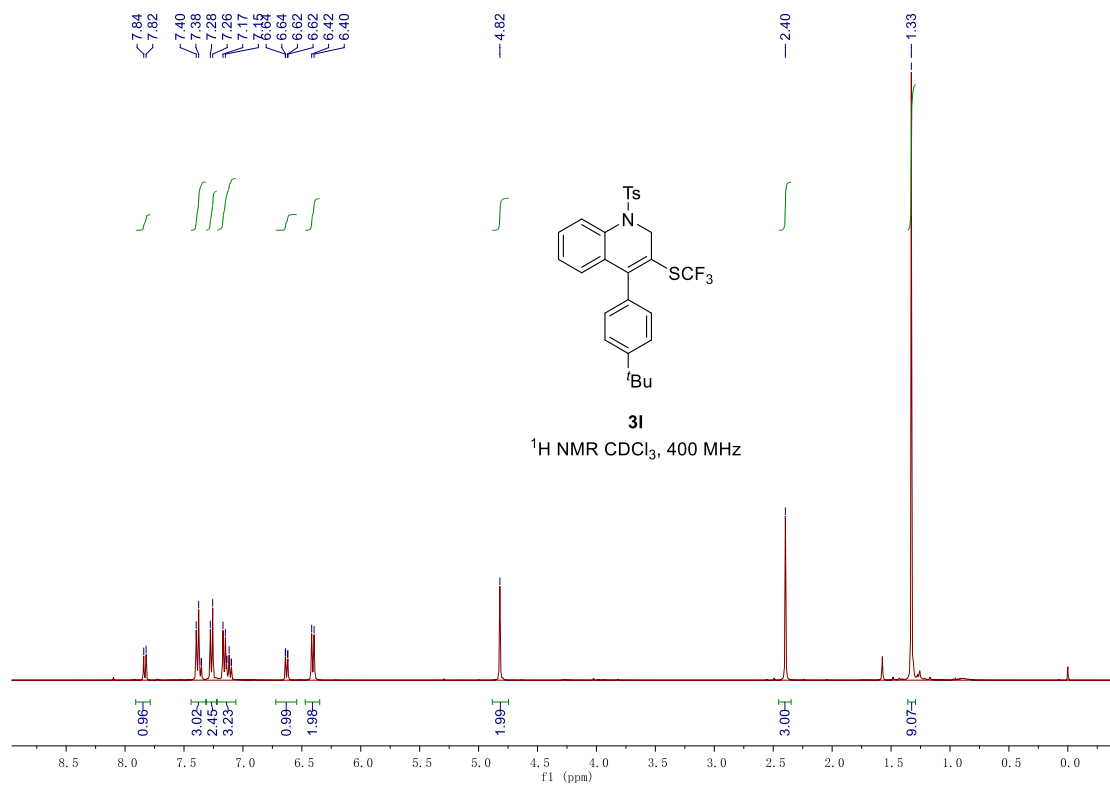


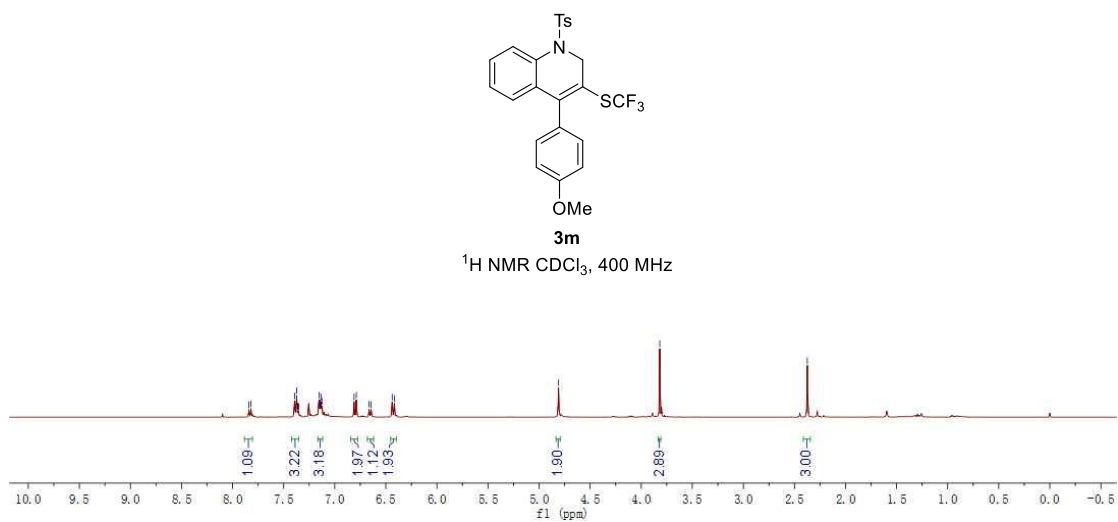
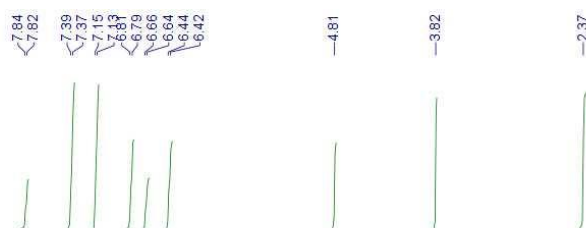
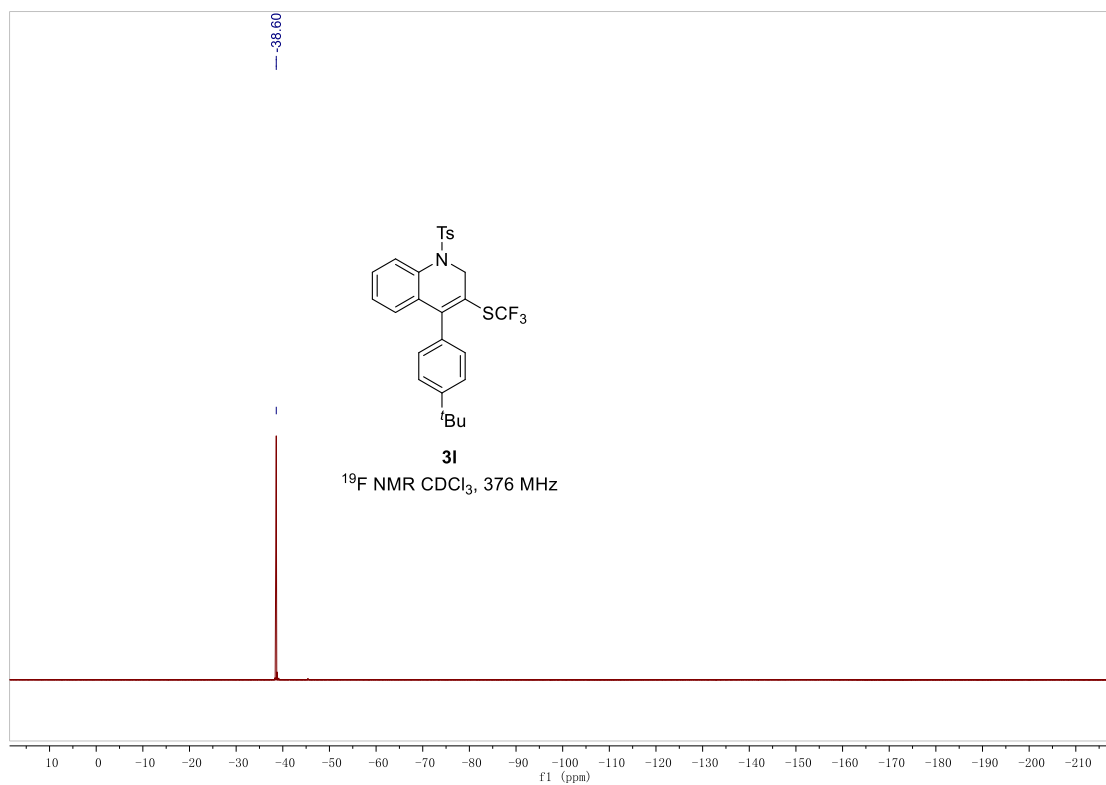
<sup>13</sup>C NMR CDCl<sub>3</sub>, 100 MHz







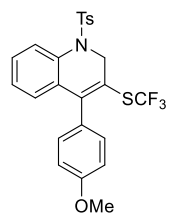




159.44  
146.54  
144.05  
130.61  
129.69  
128.41  
127.82  
127.70  
127.38  
127.17  
118.84  
113.50

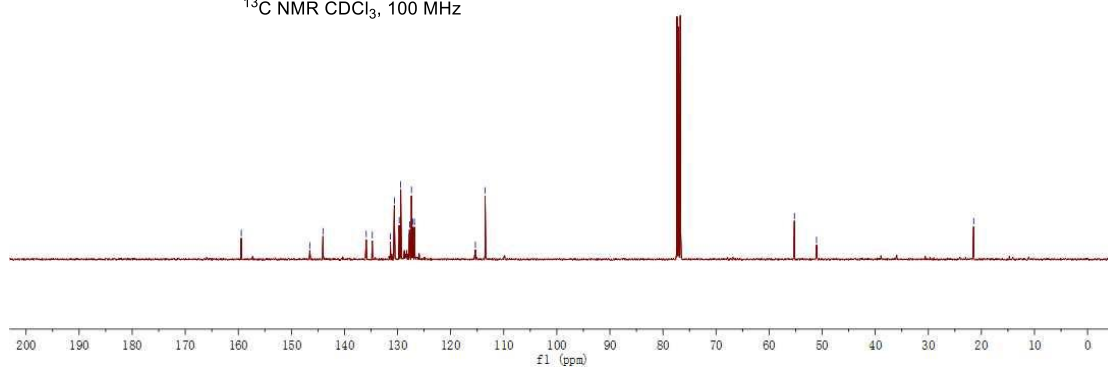
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21.45

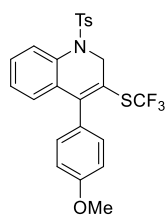


**3m**

<sup>13</sup>C NMR CDCl<sub>3</sub>, 100 MHz

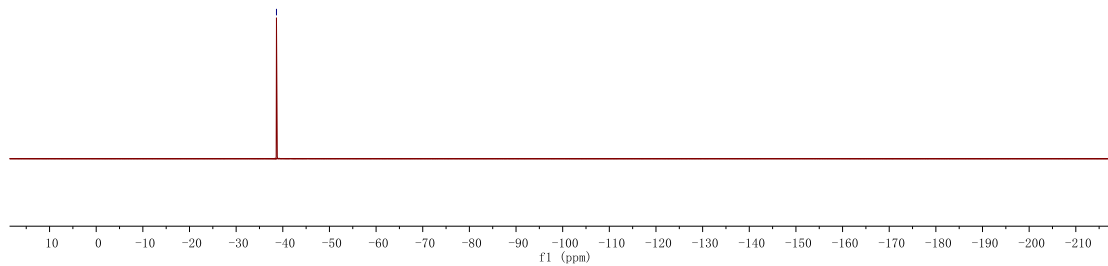


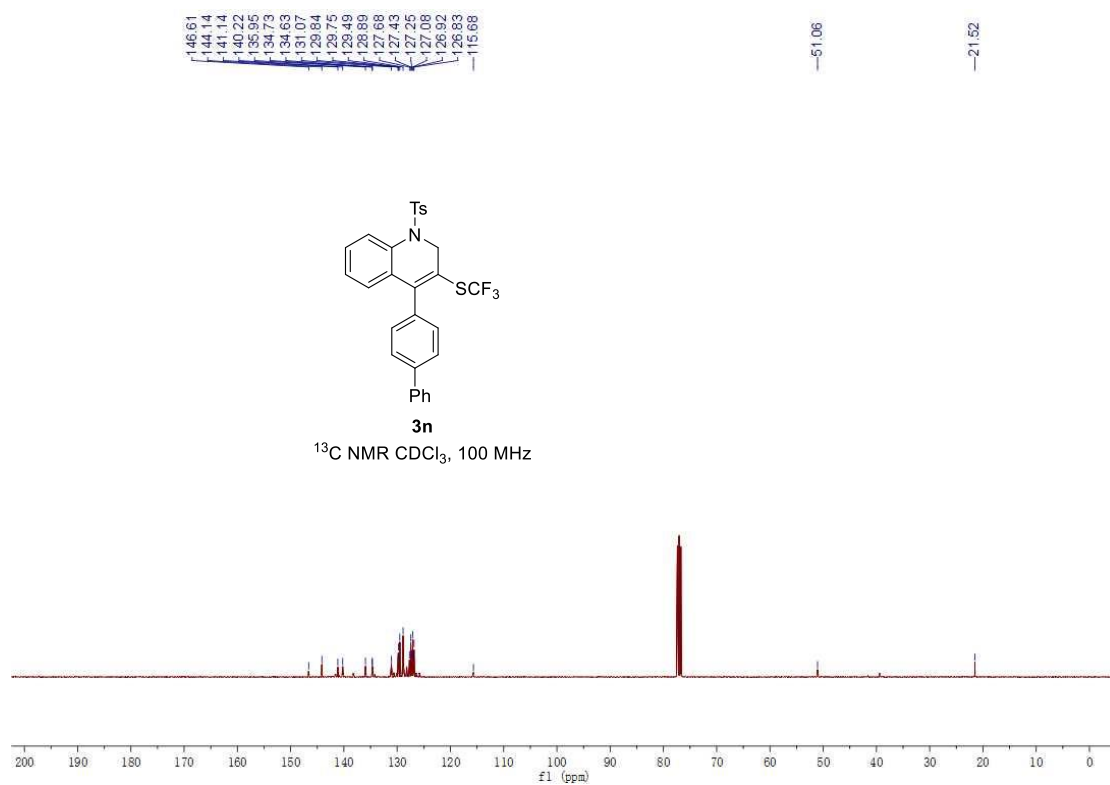
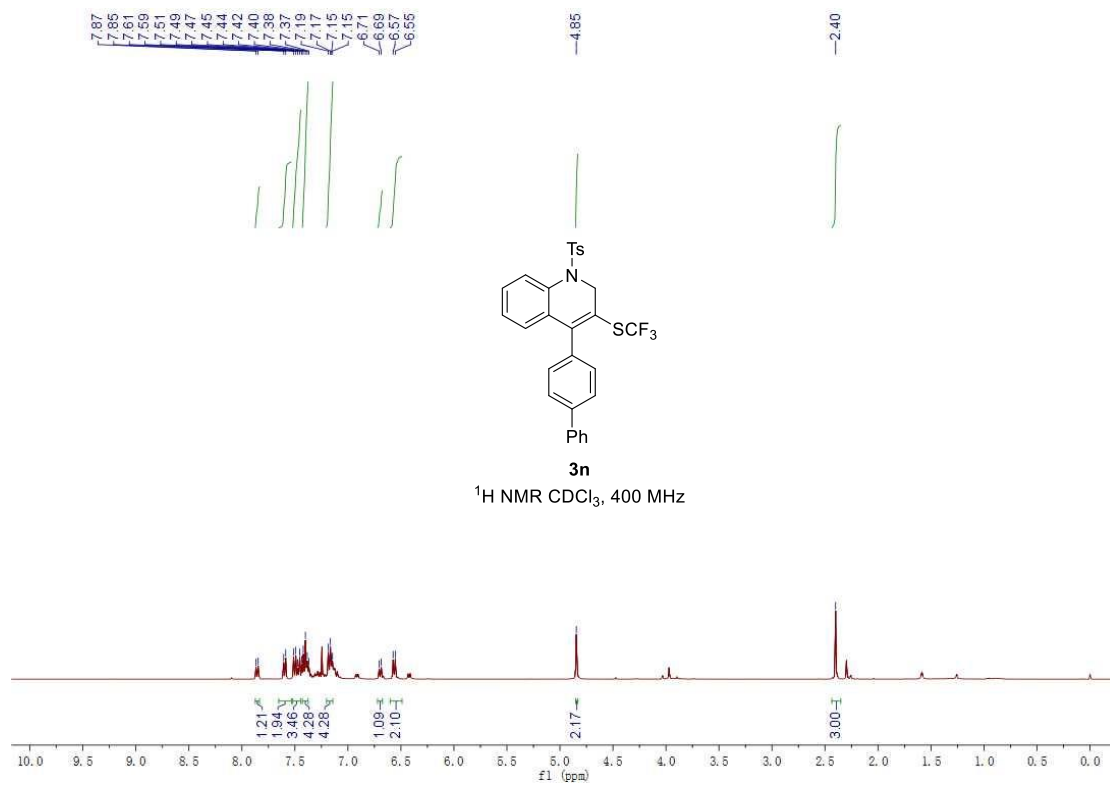
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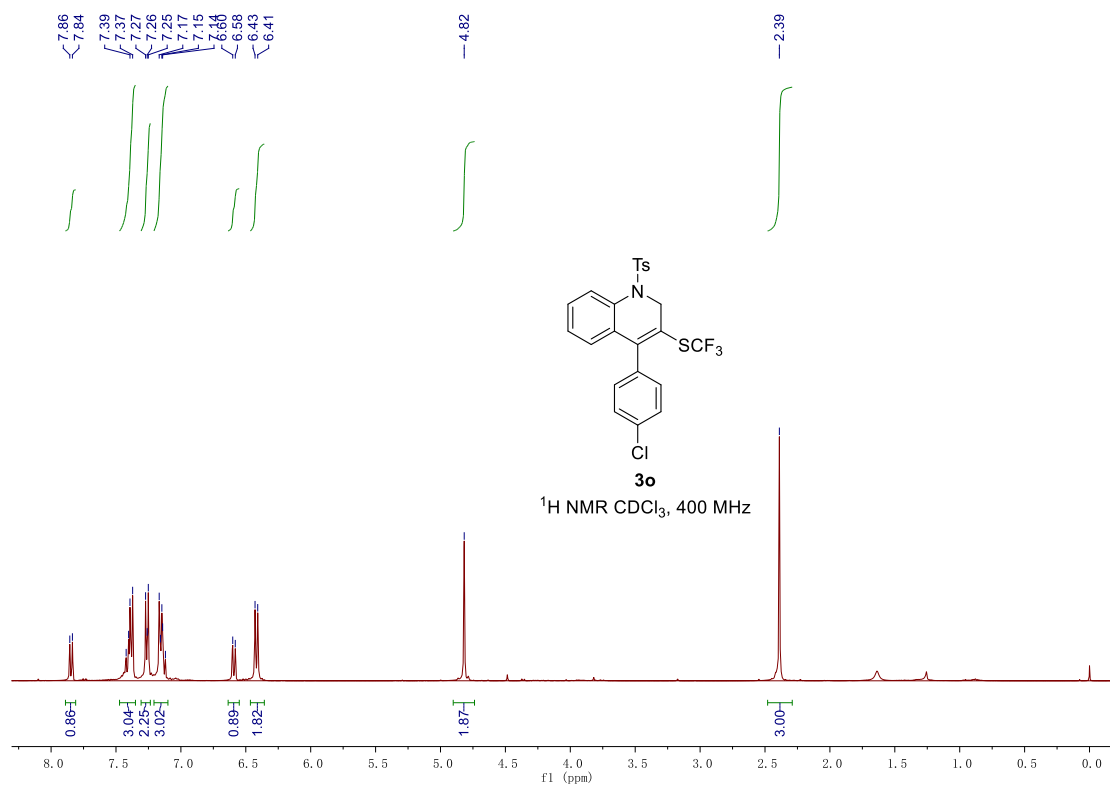
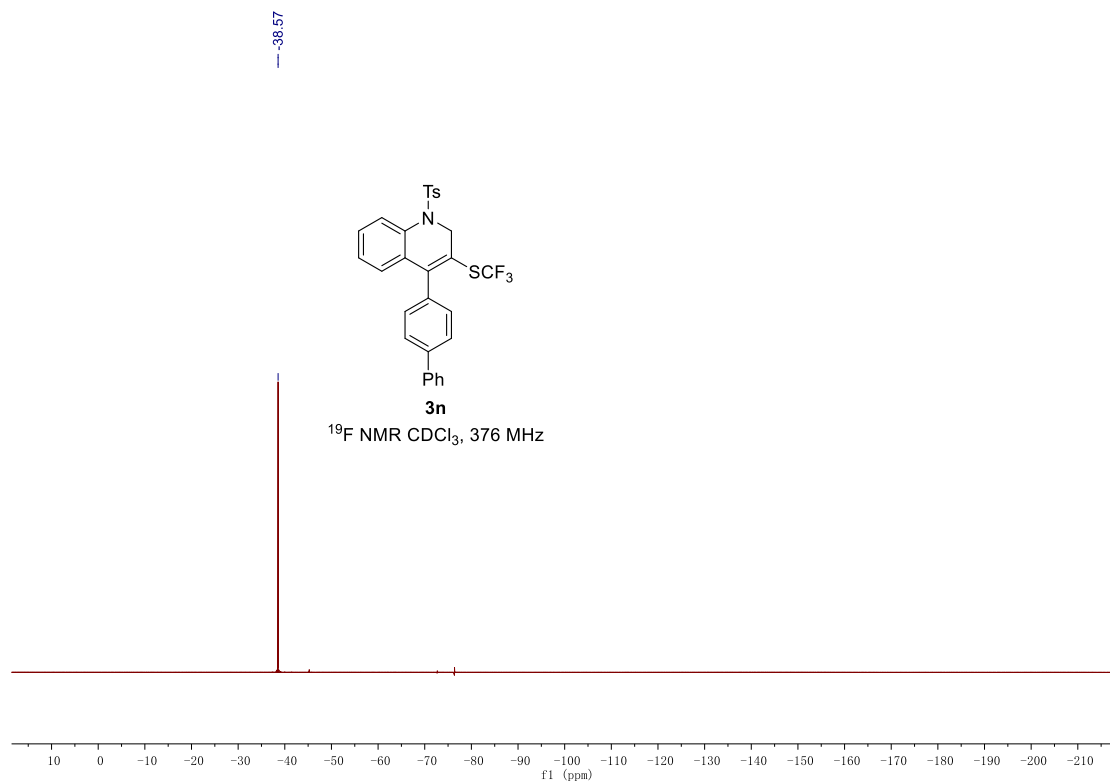


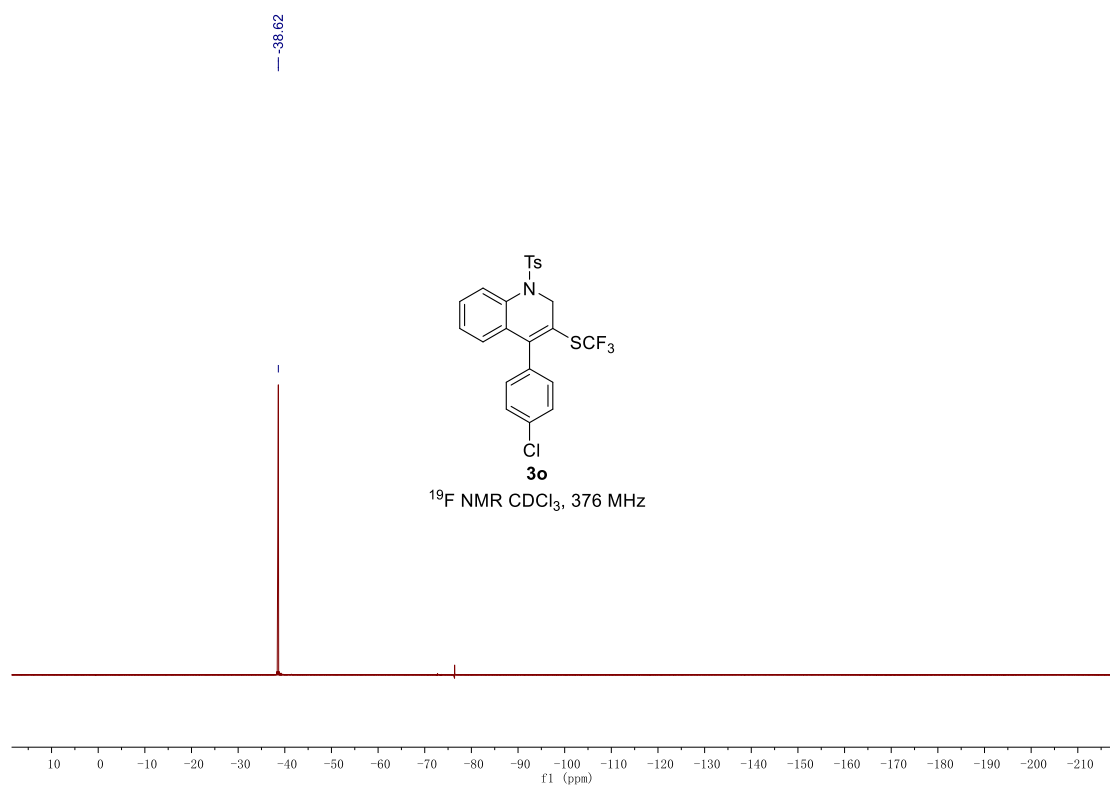
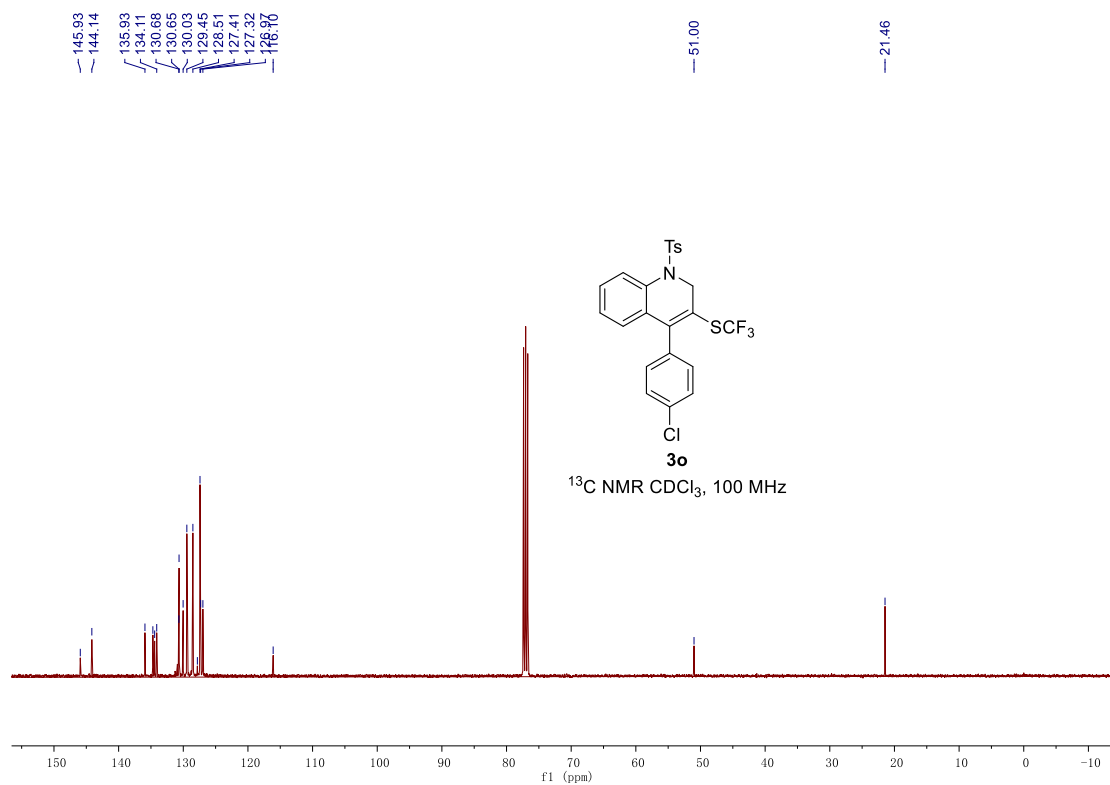
**3m**

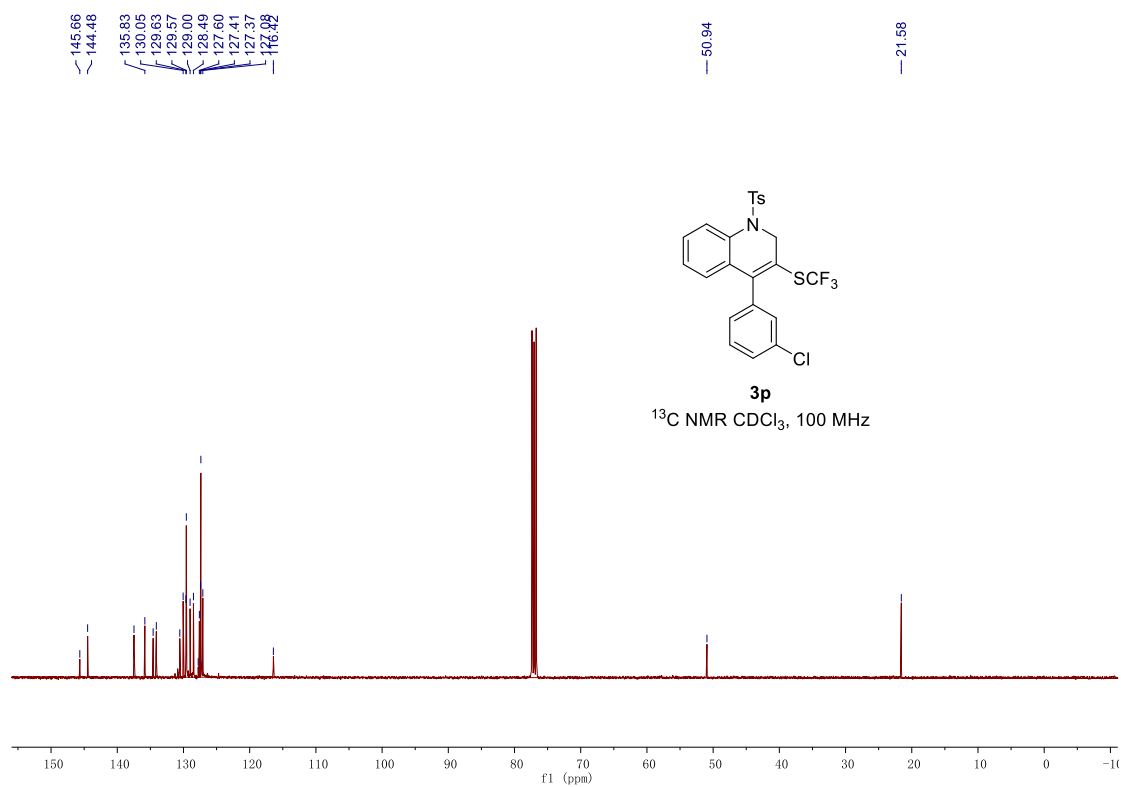
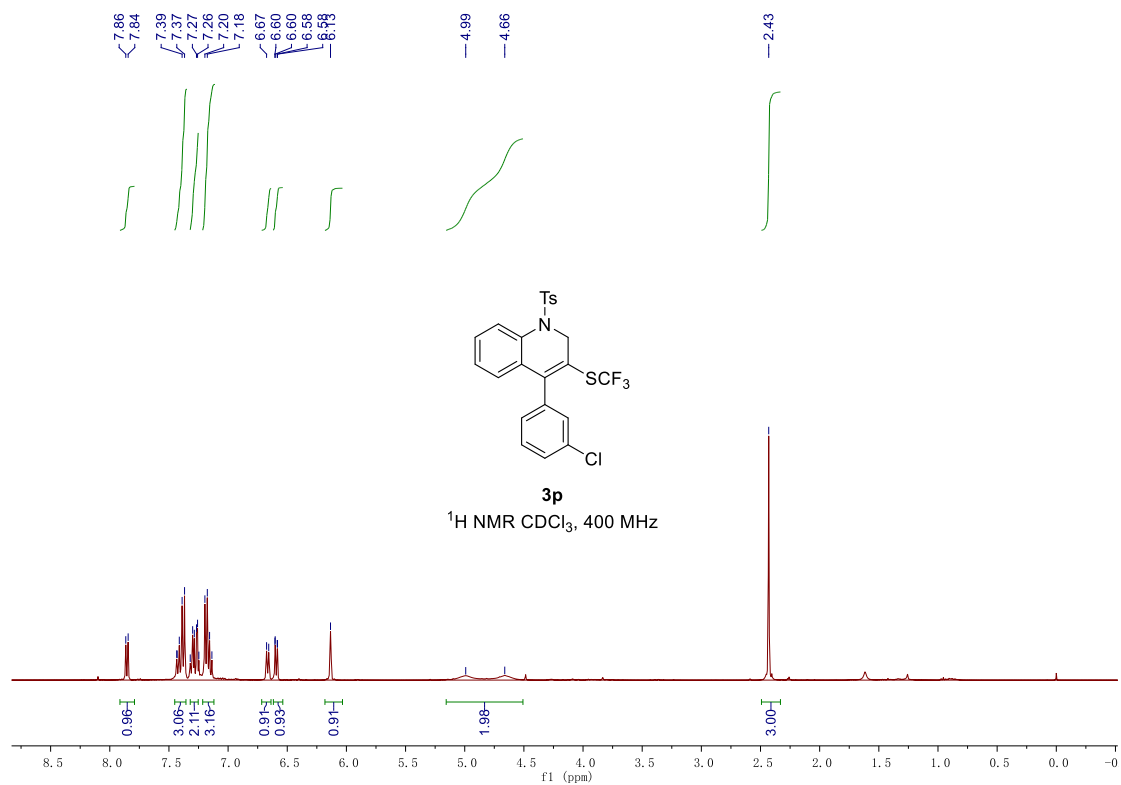
<sup>19</sup>F NMR CDCl<sub>3</sub>, 376 MHz

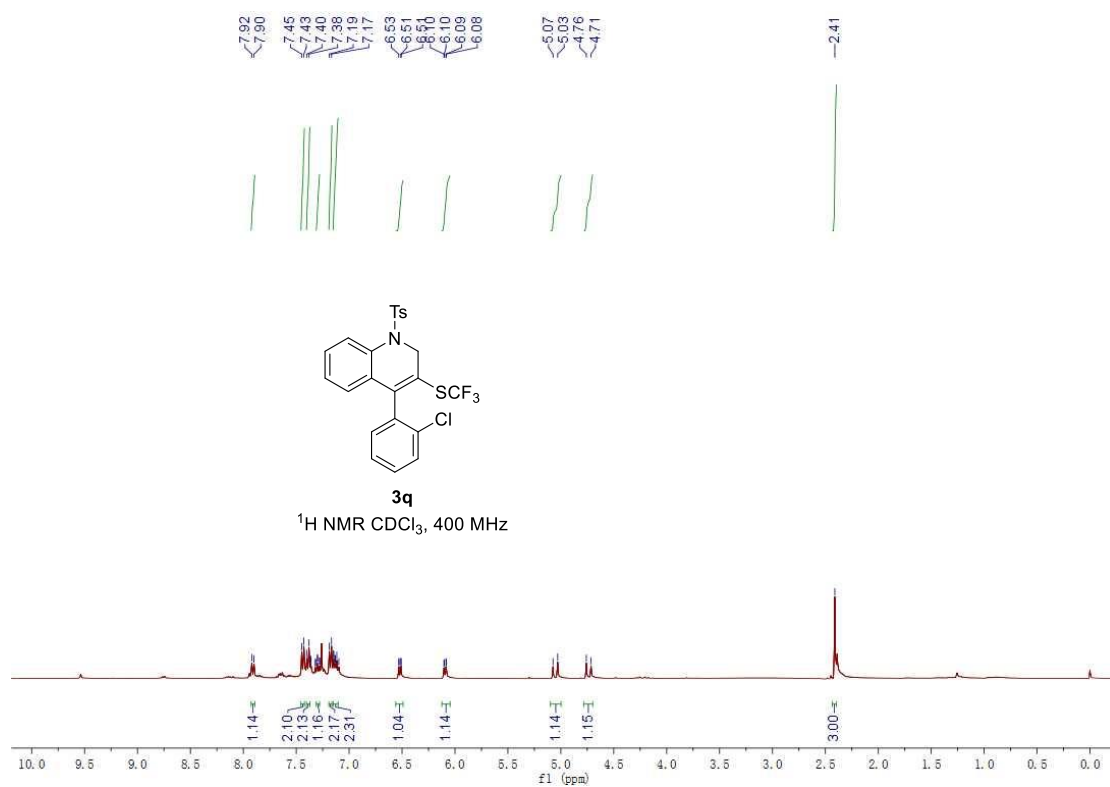
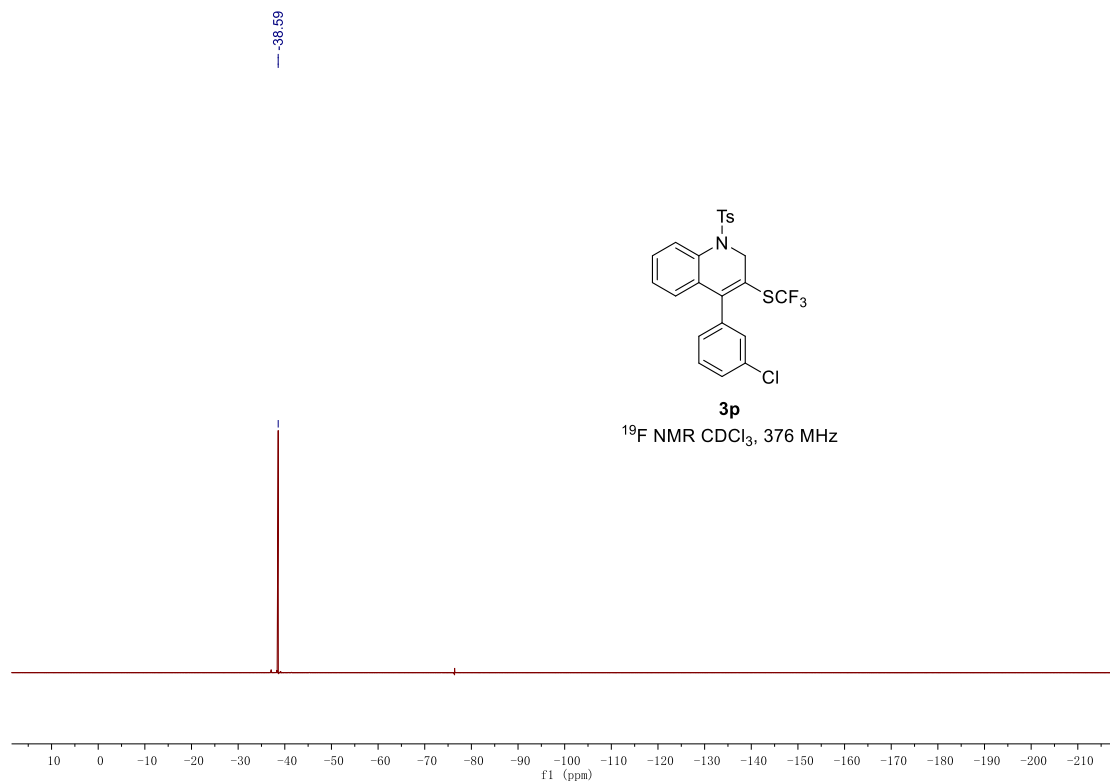








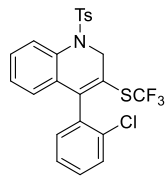




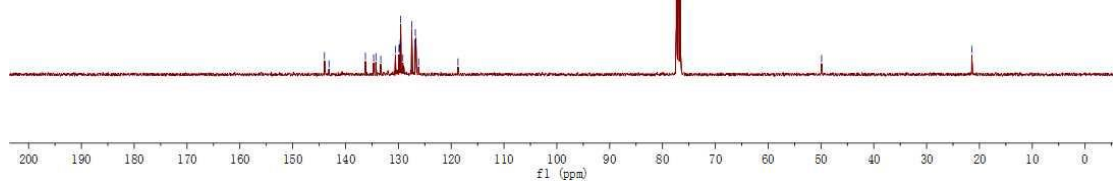
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127.46  
126.78  
126.70  
126.65

-49.88

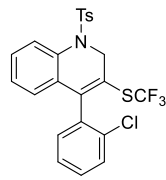
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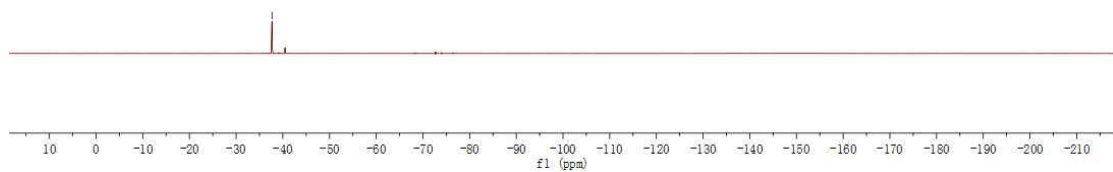
**3q**  
<sup>13</sup>C NMR CDCl<sub>3</sub>, 100 MHz

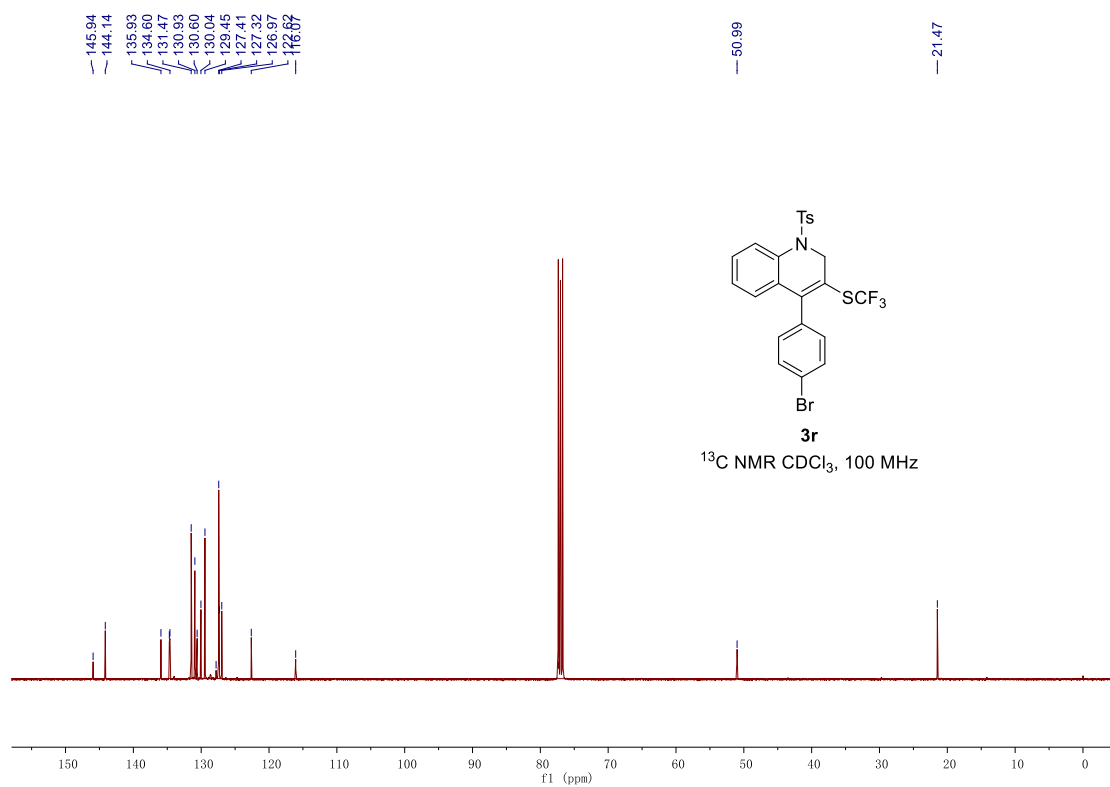
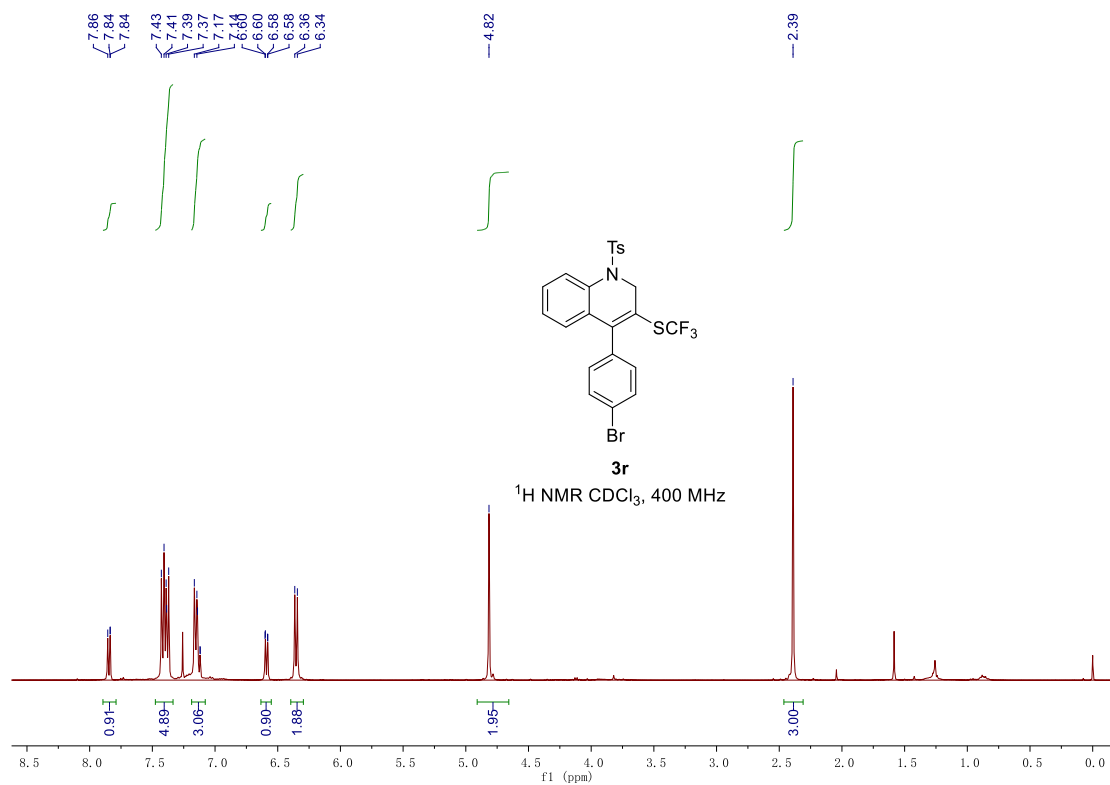


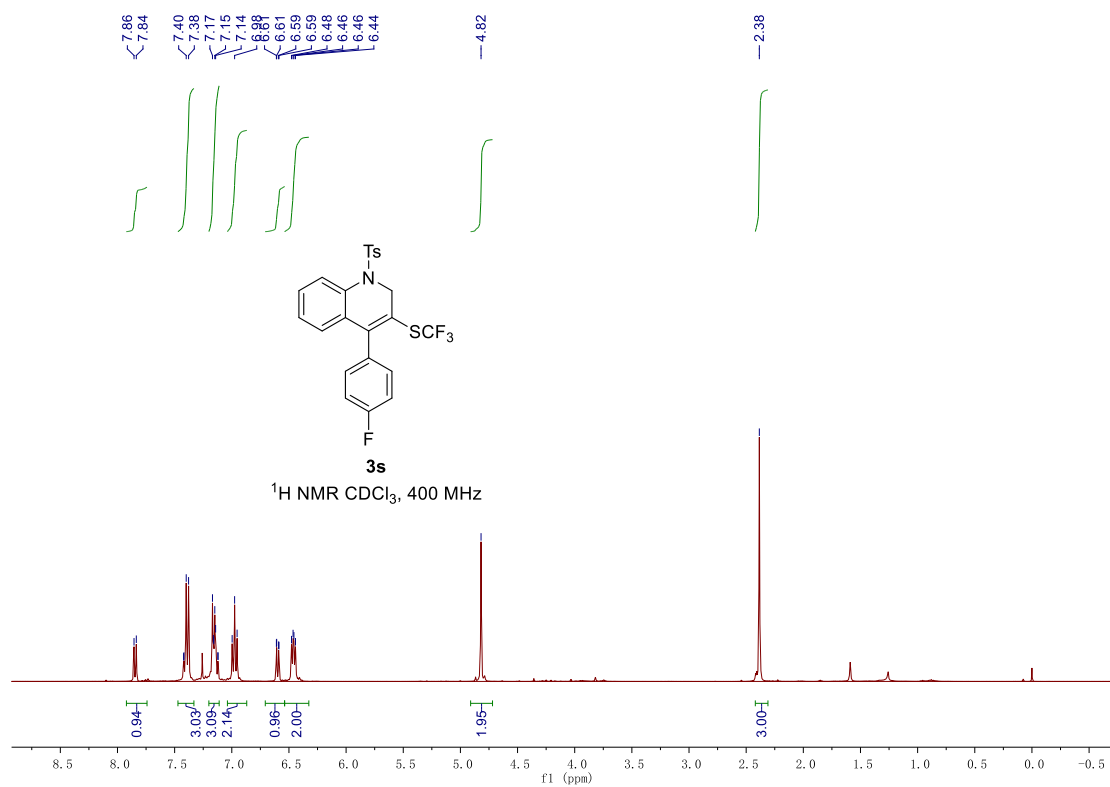
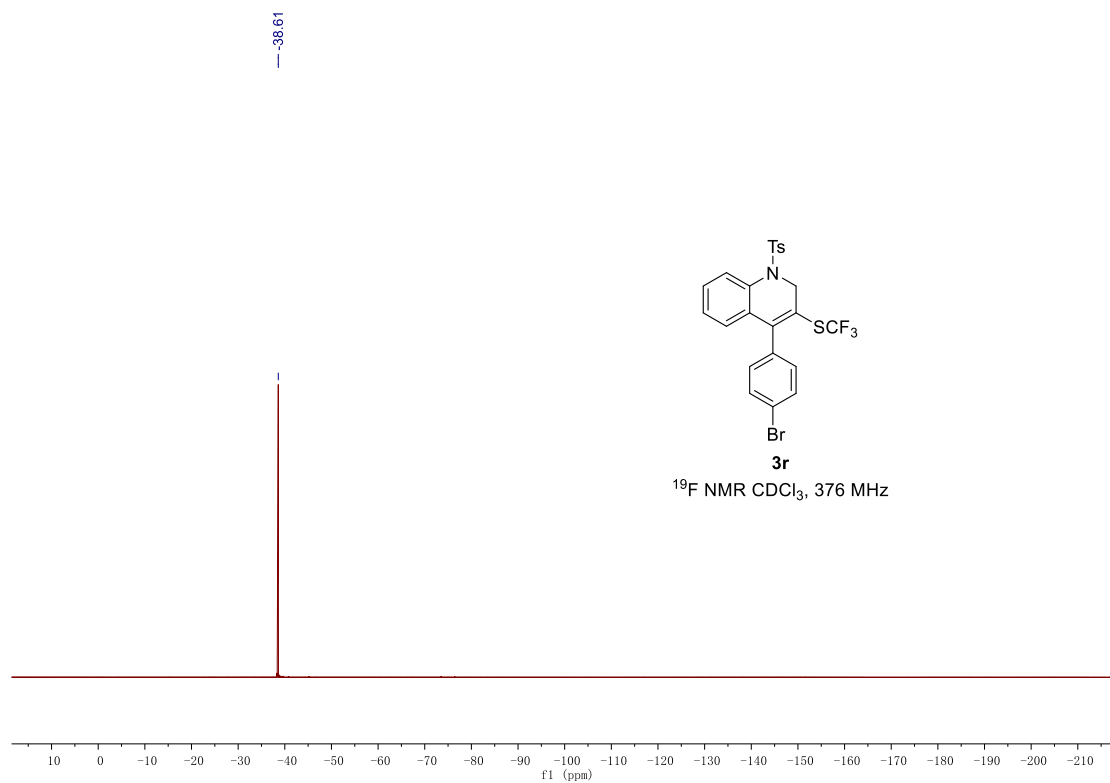
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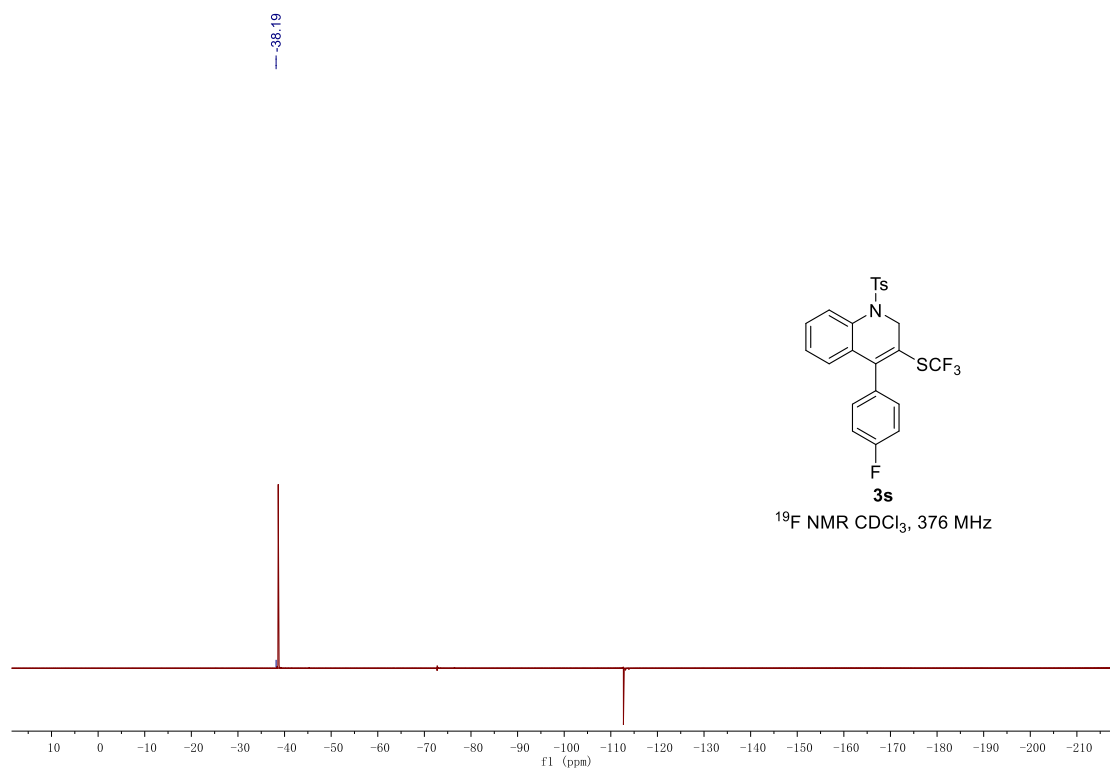
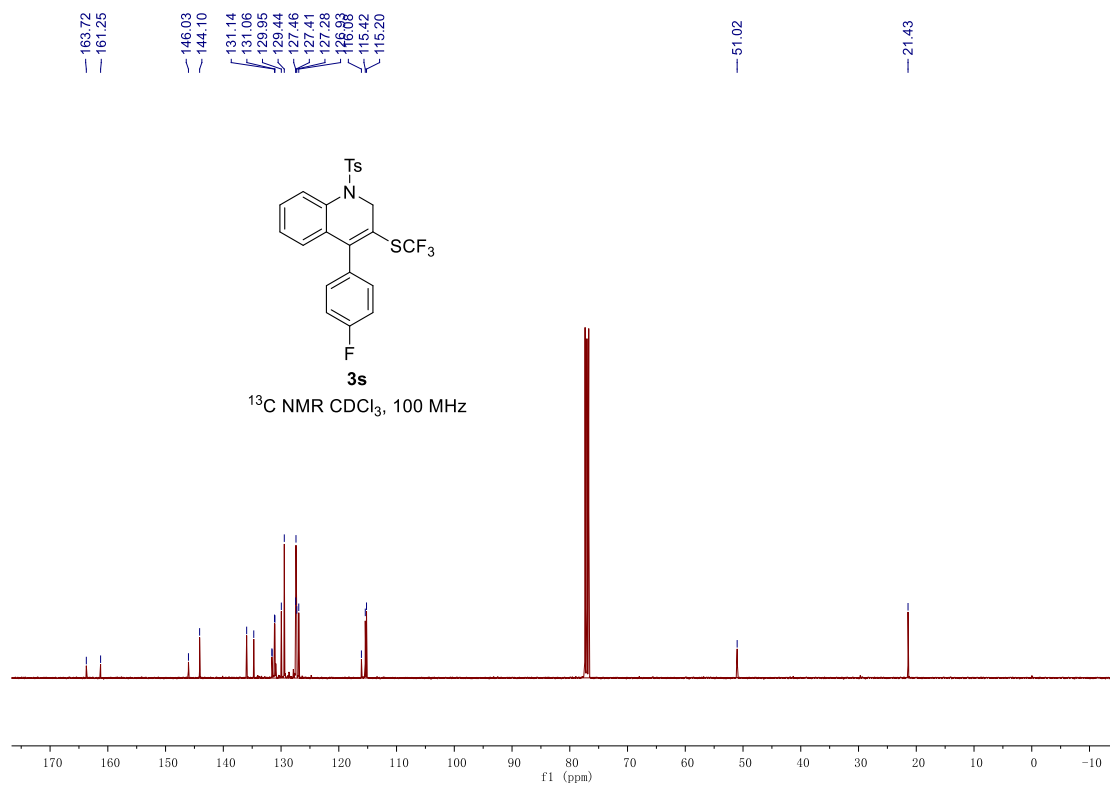


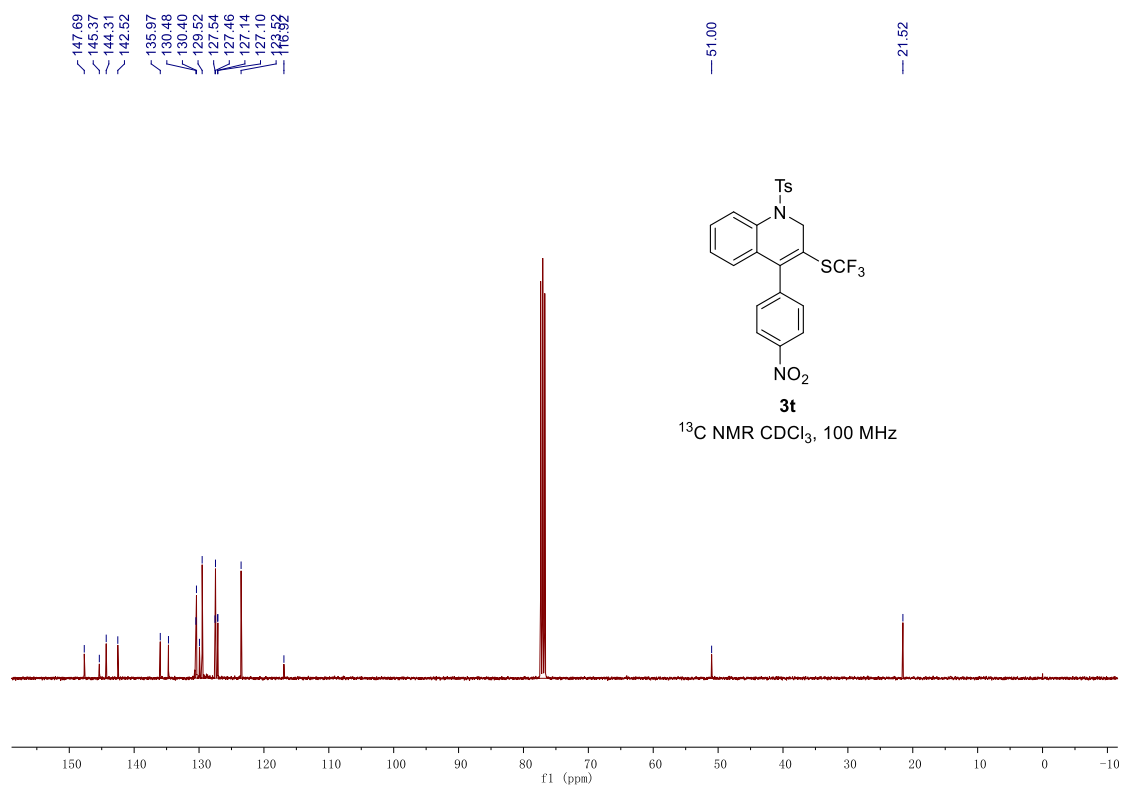
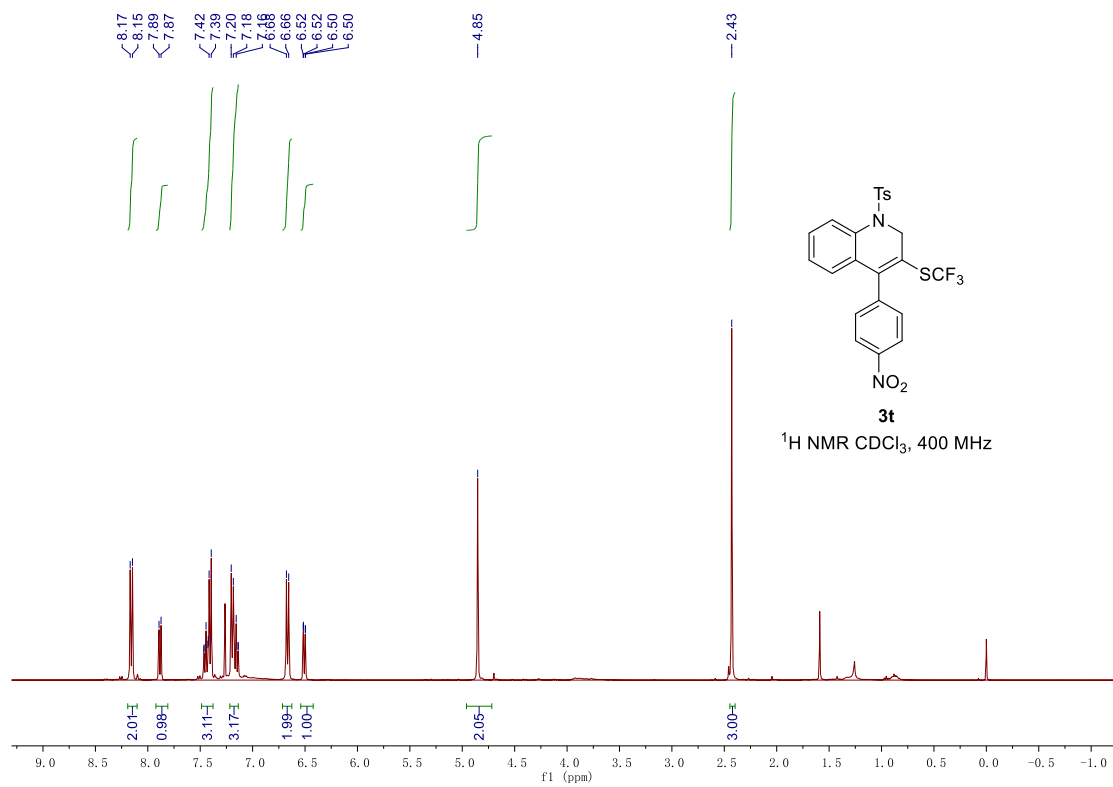
**3q**  
<sup>19</sup>F NMR CDCl<sub>3</sub>, 376 MHz

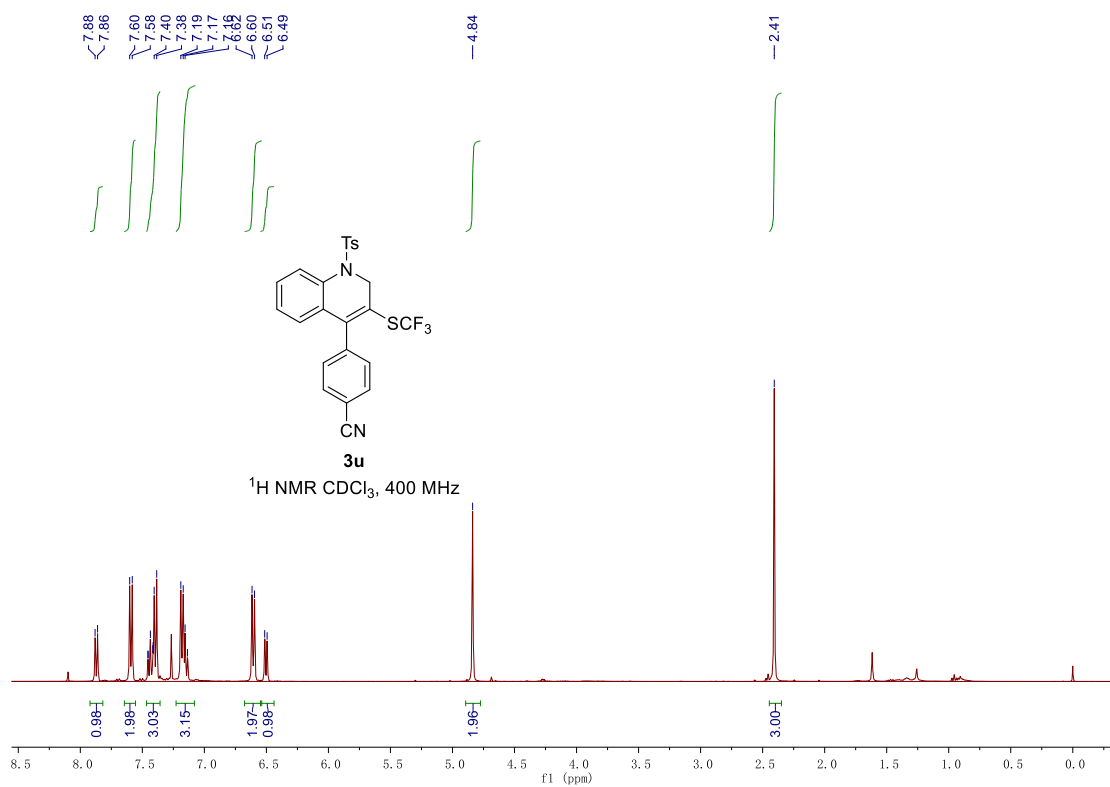
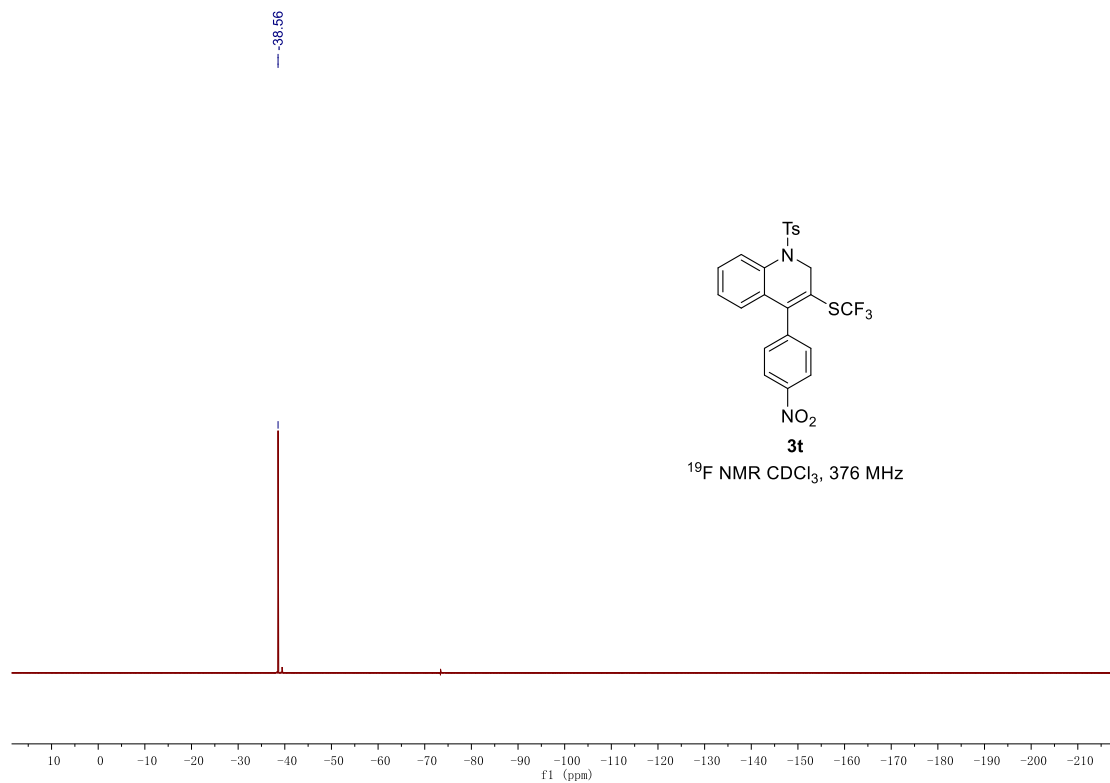


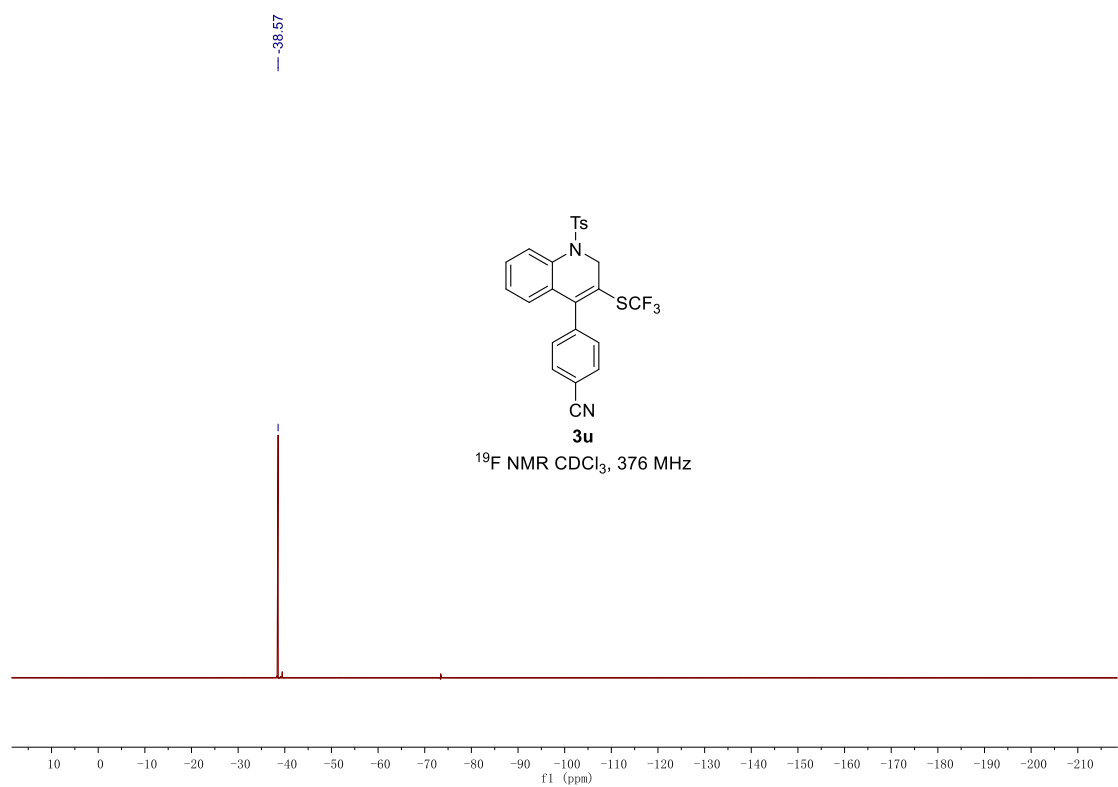
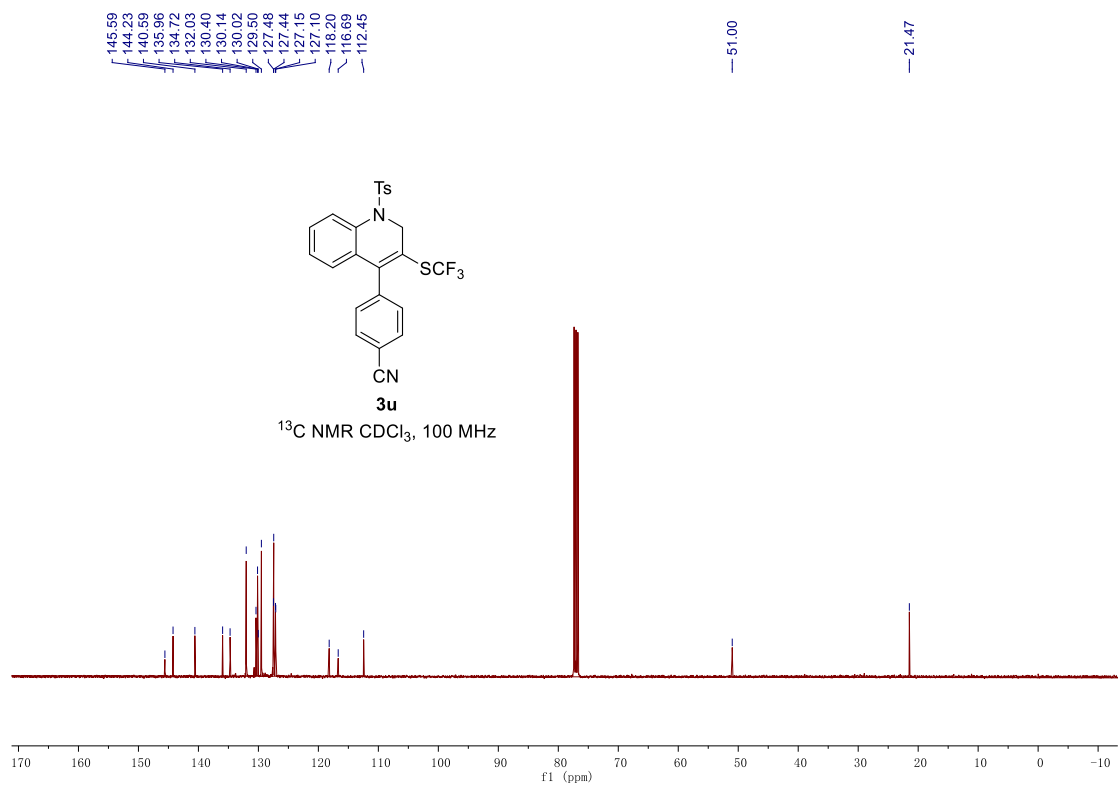


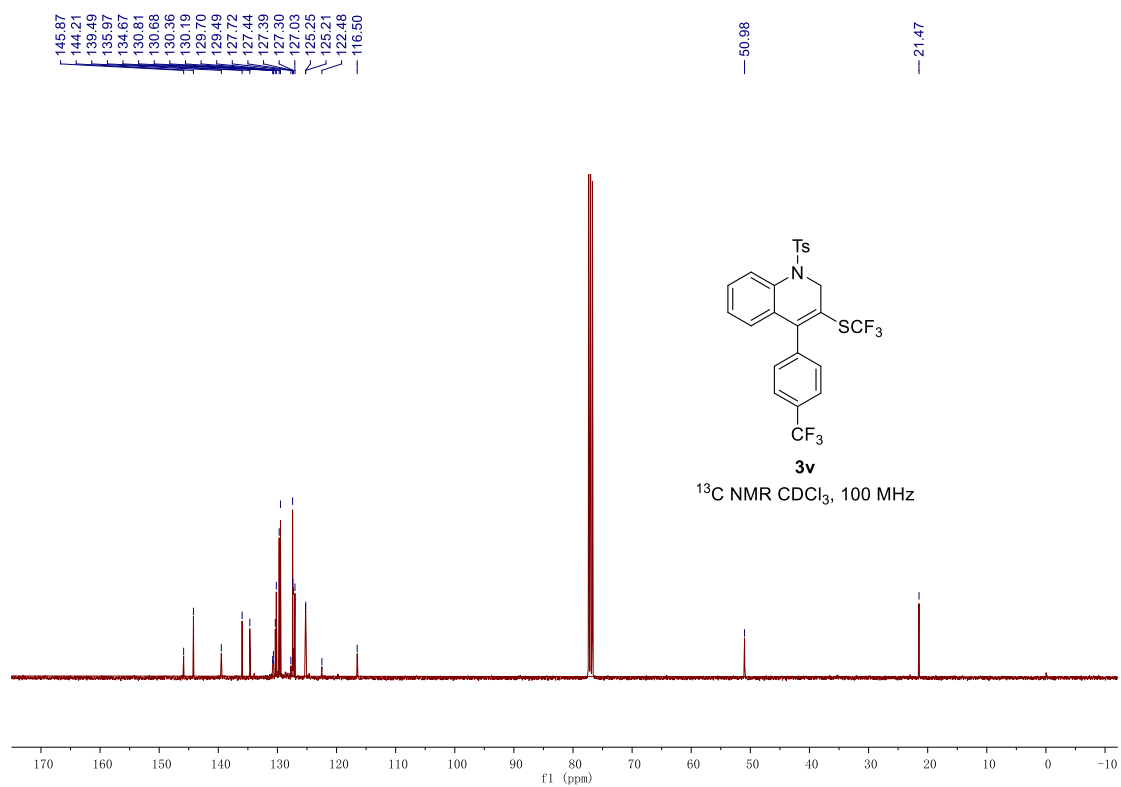
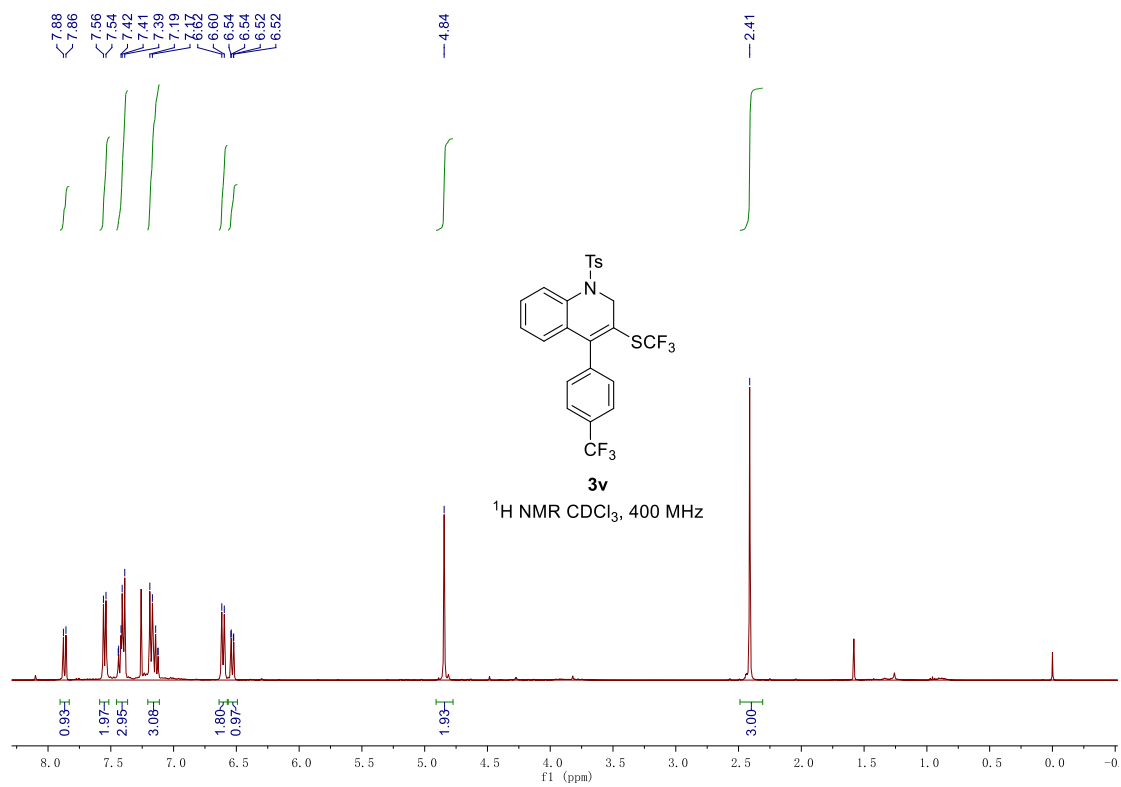


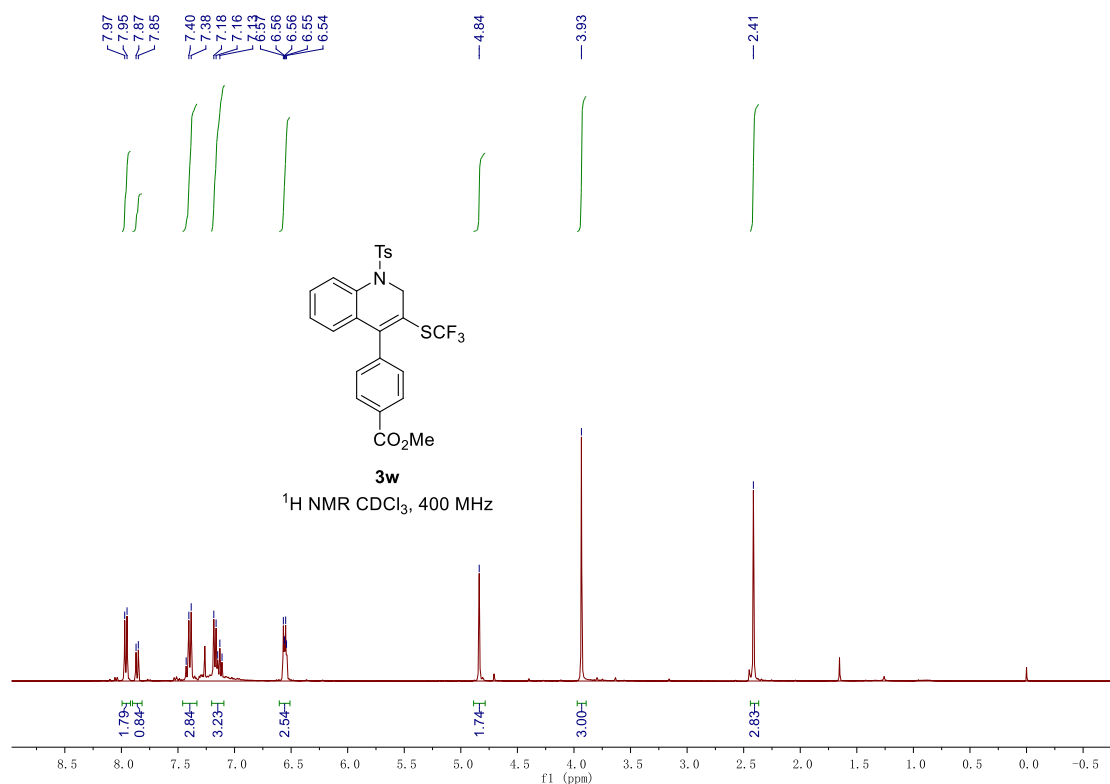
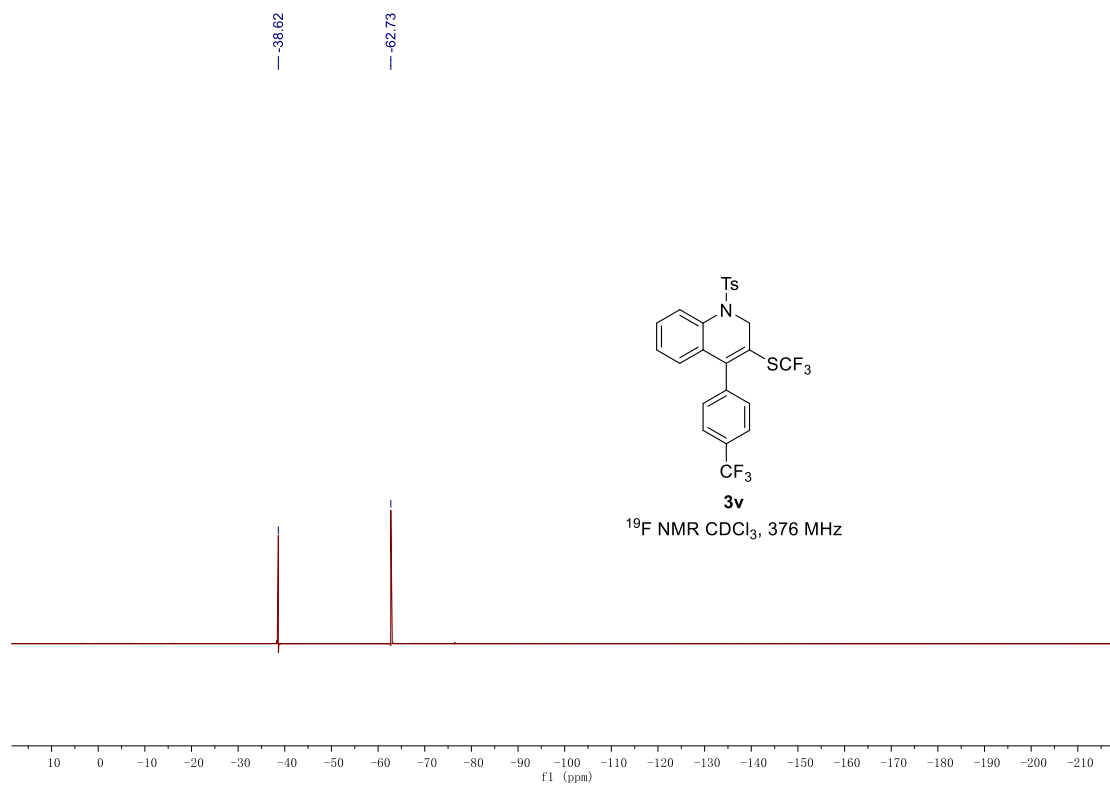


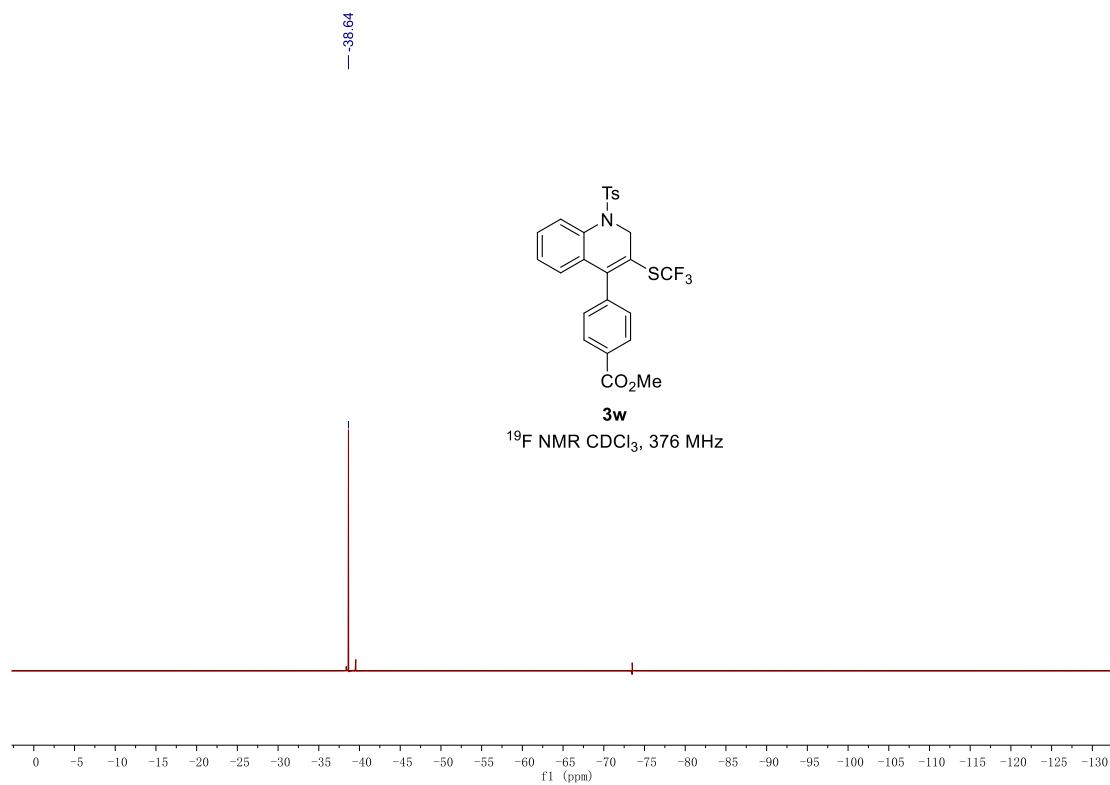
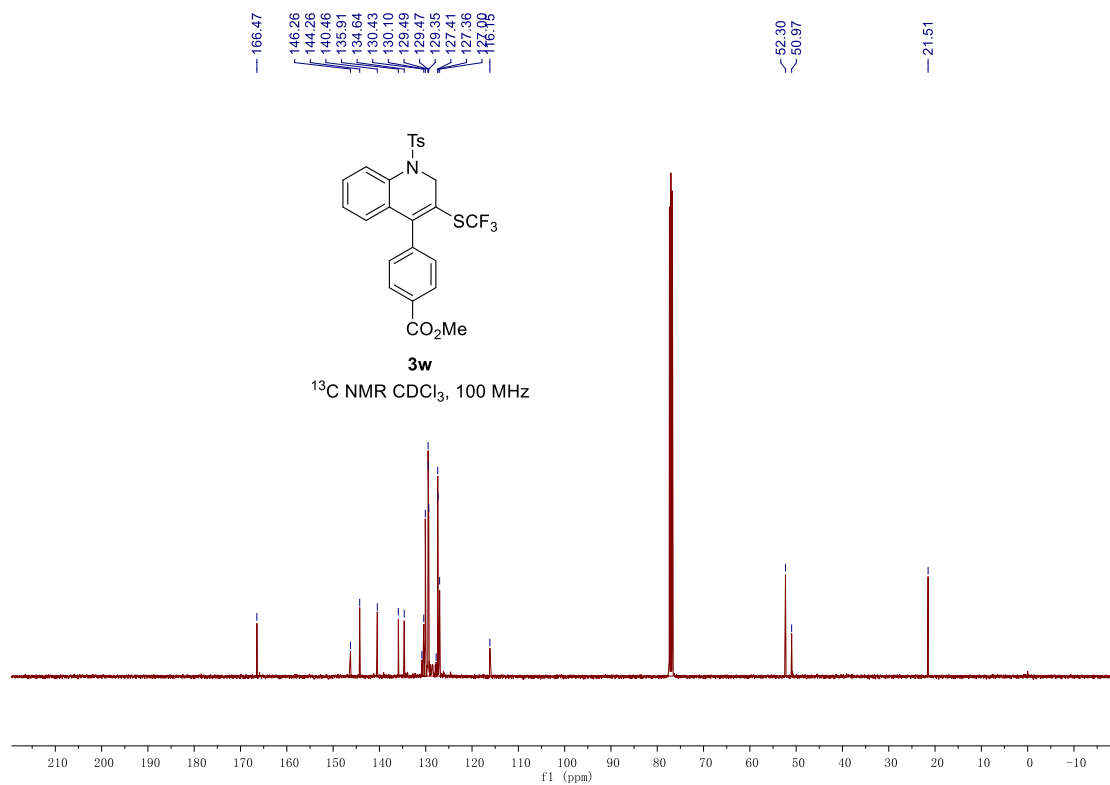


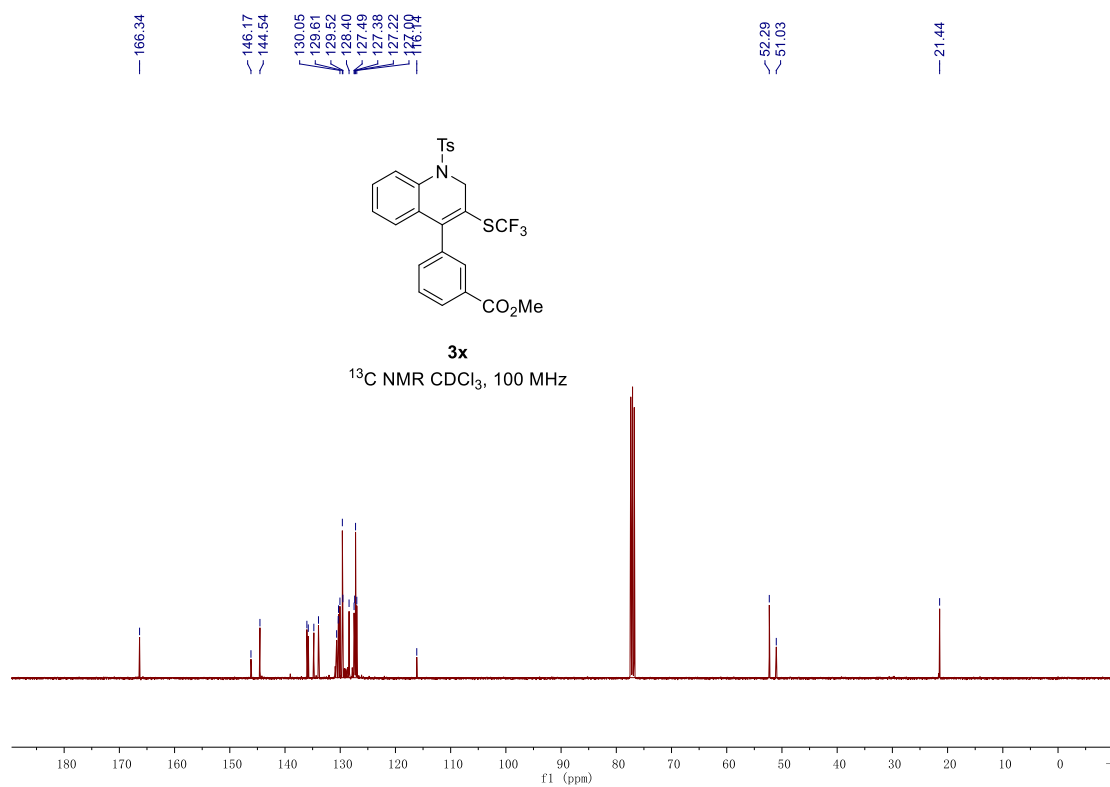
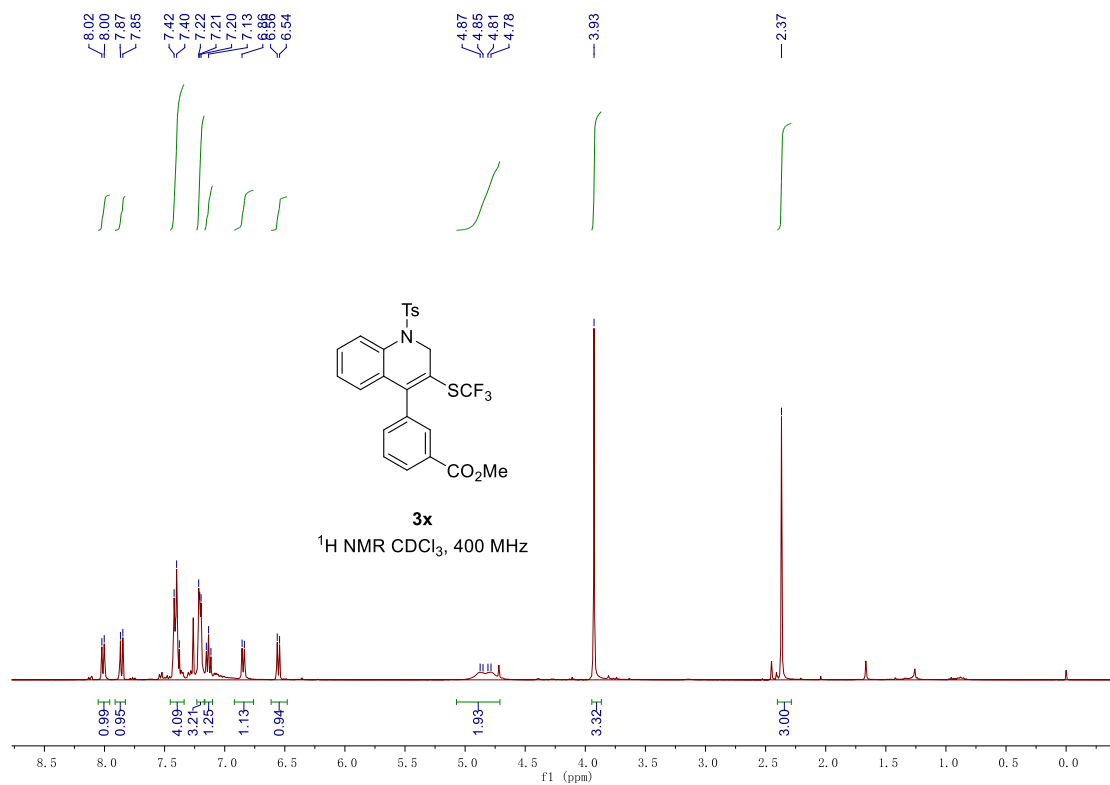




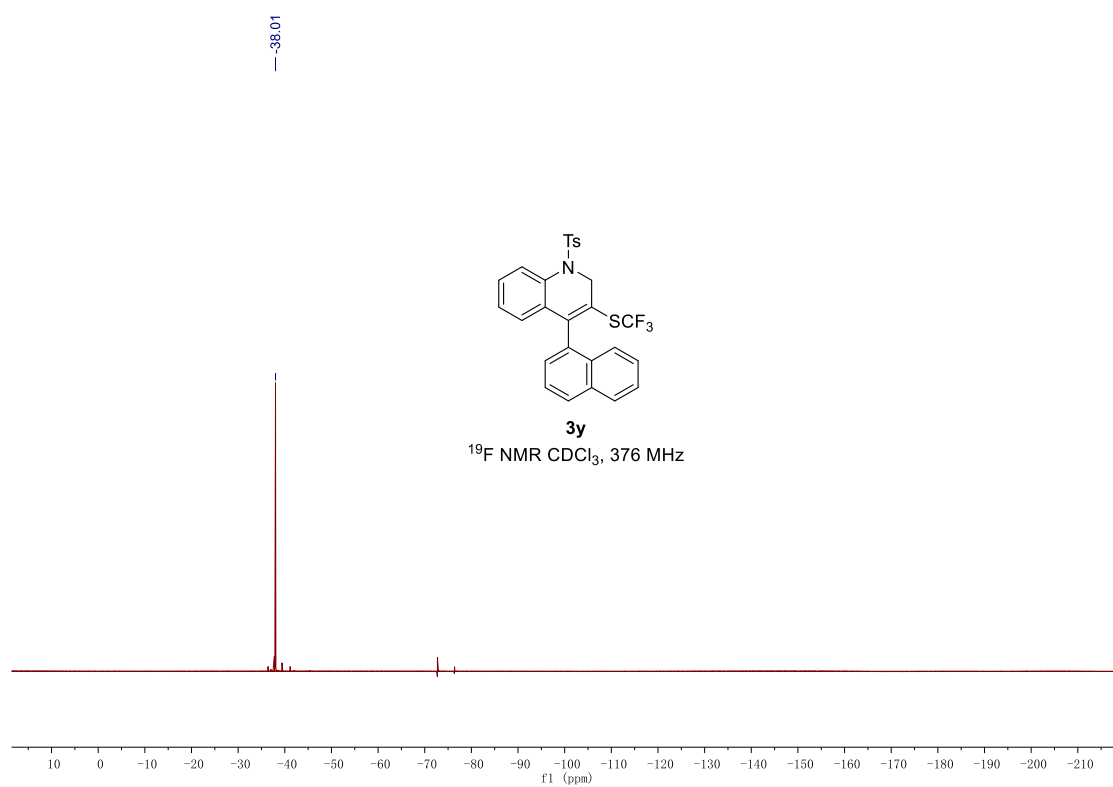
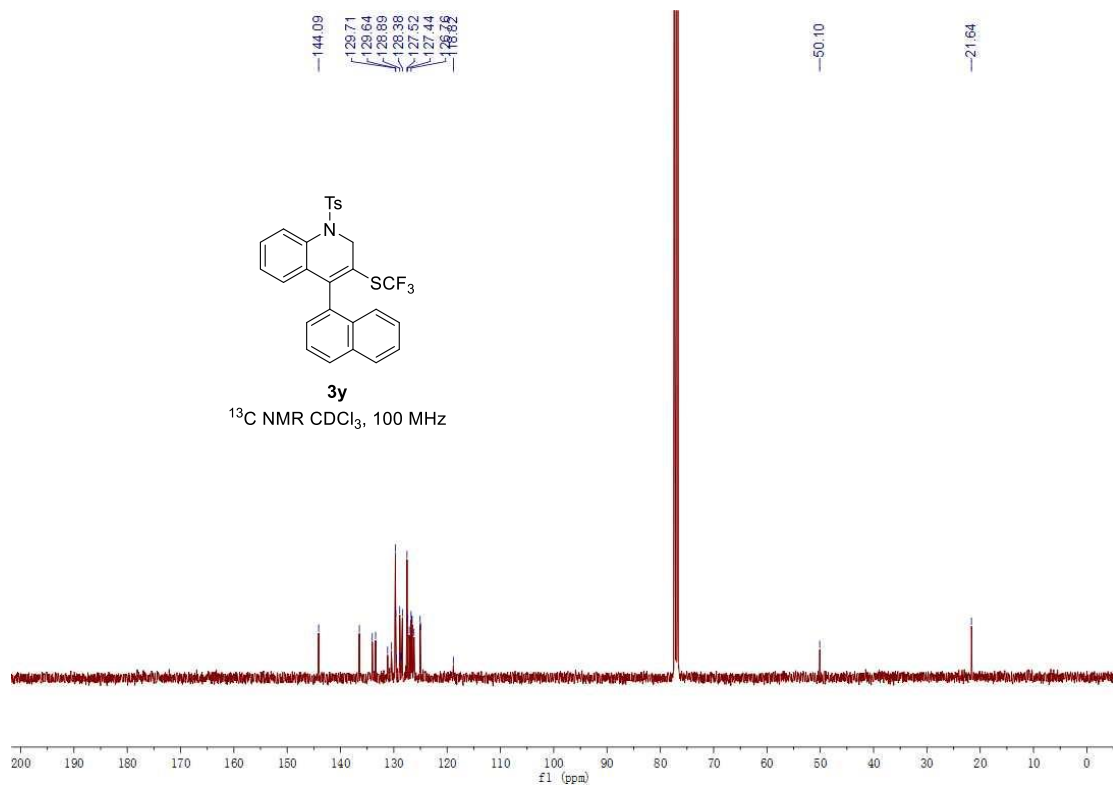


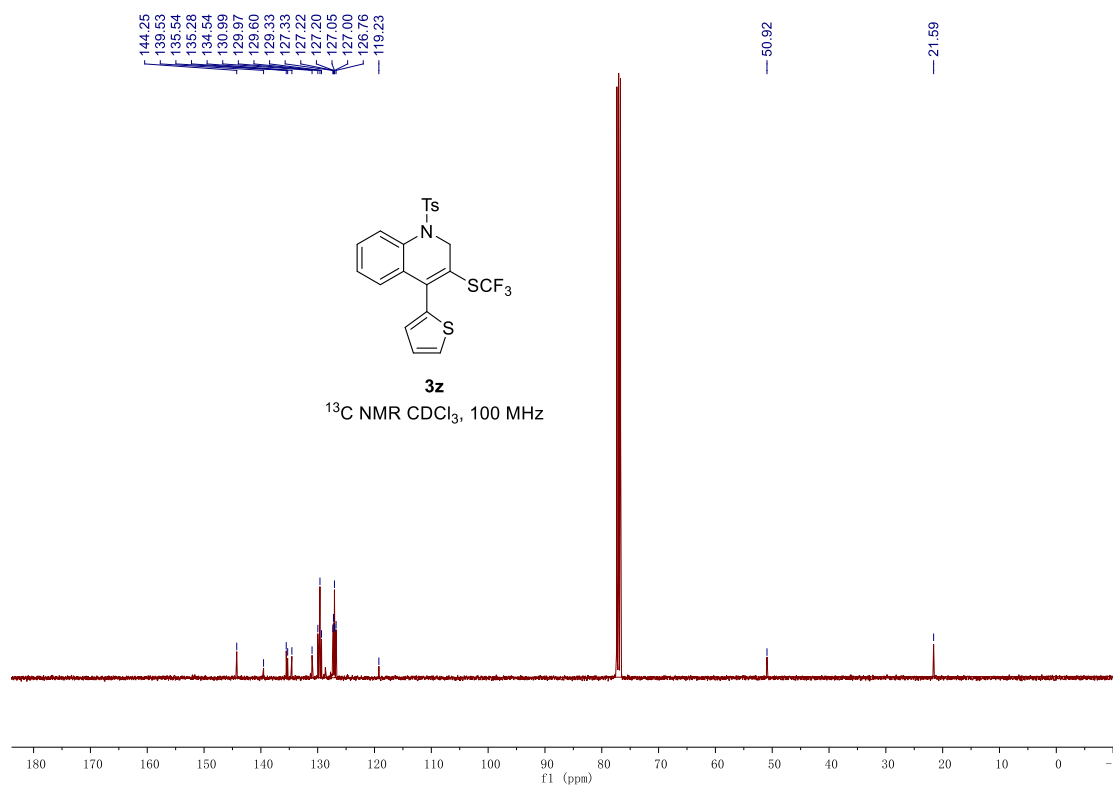
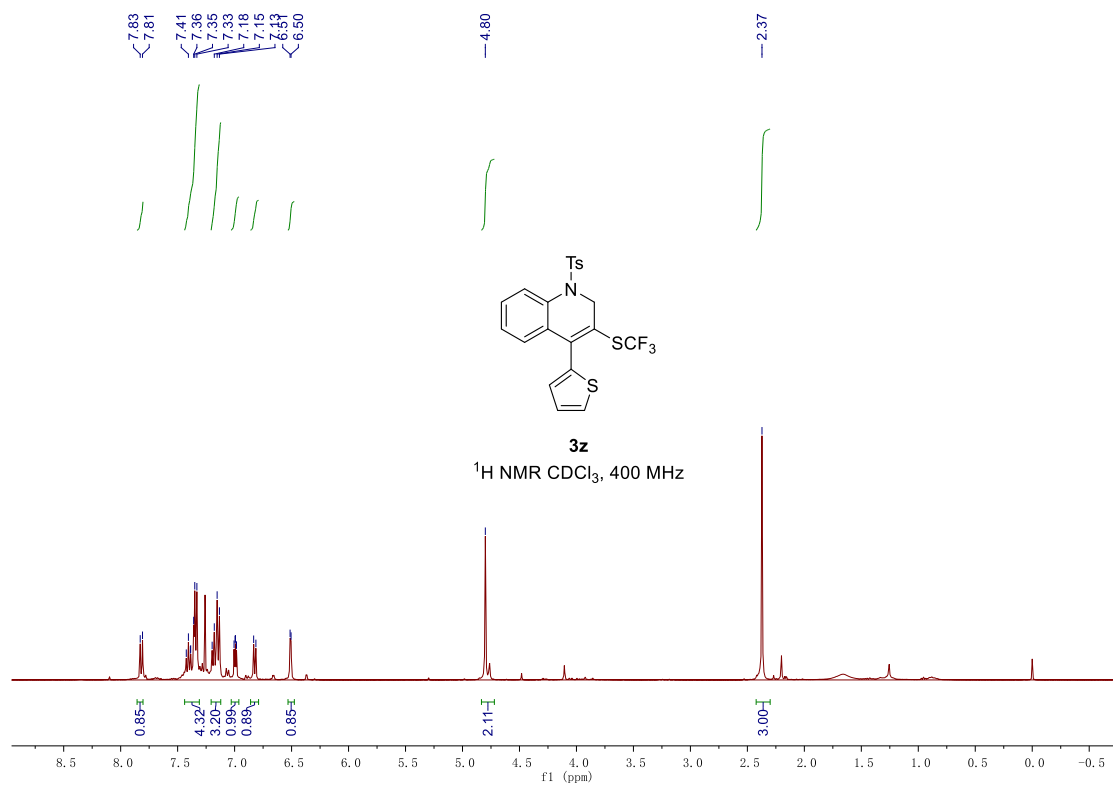


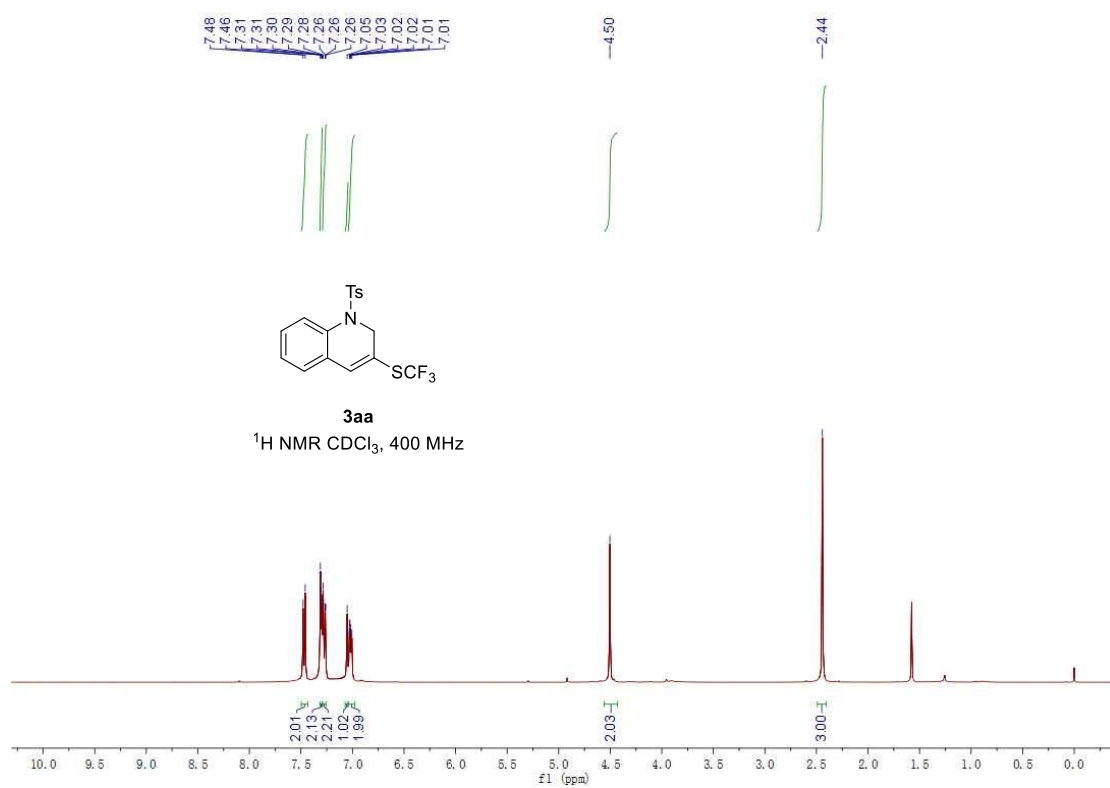
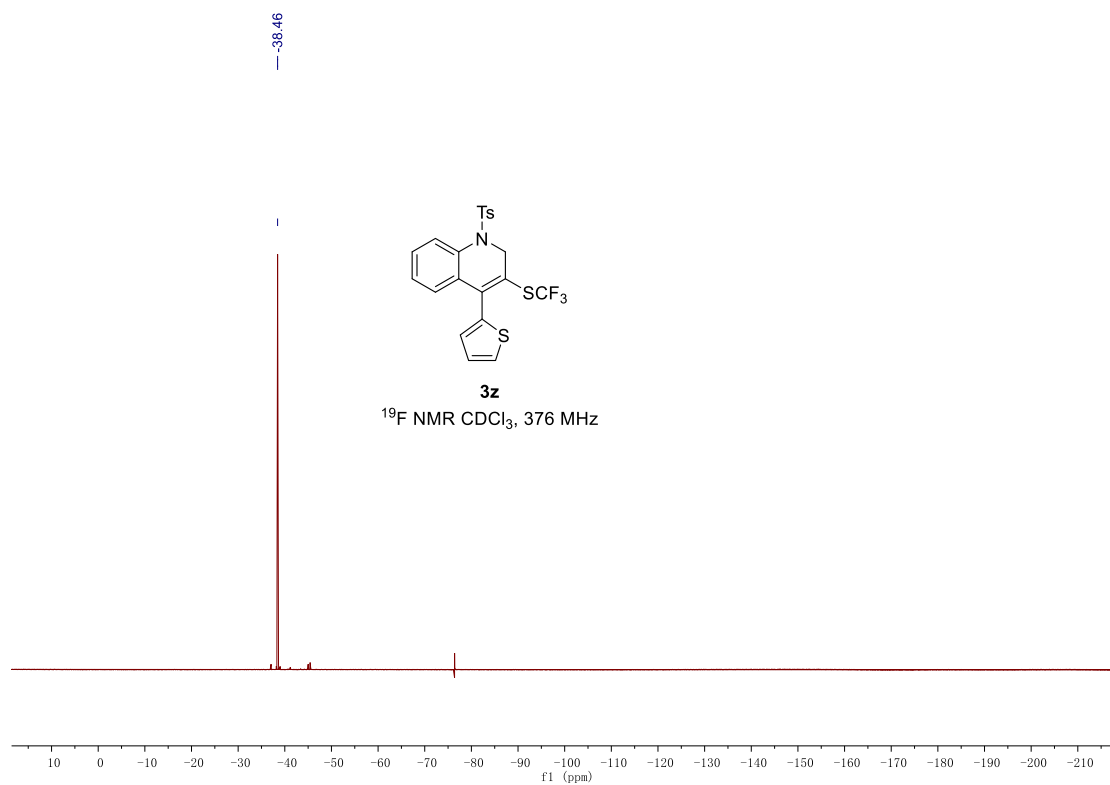


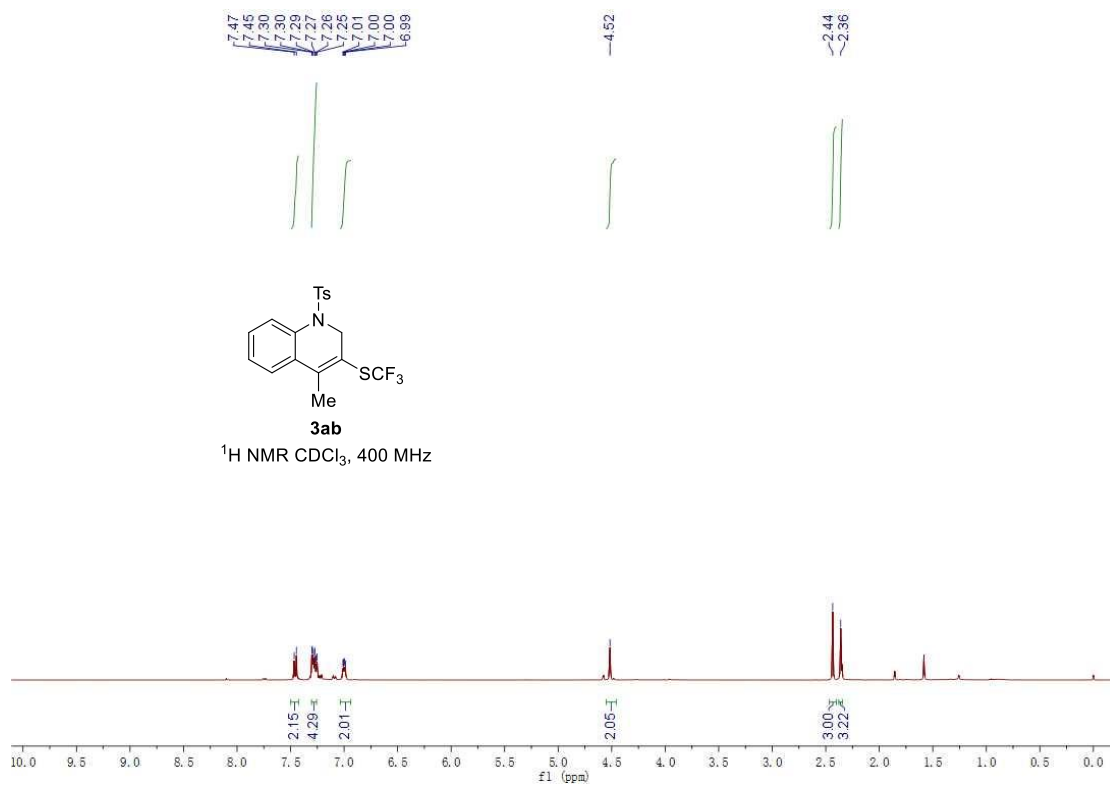
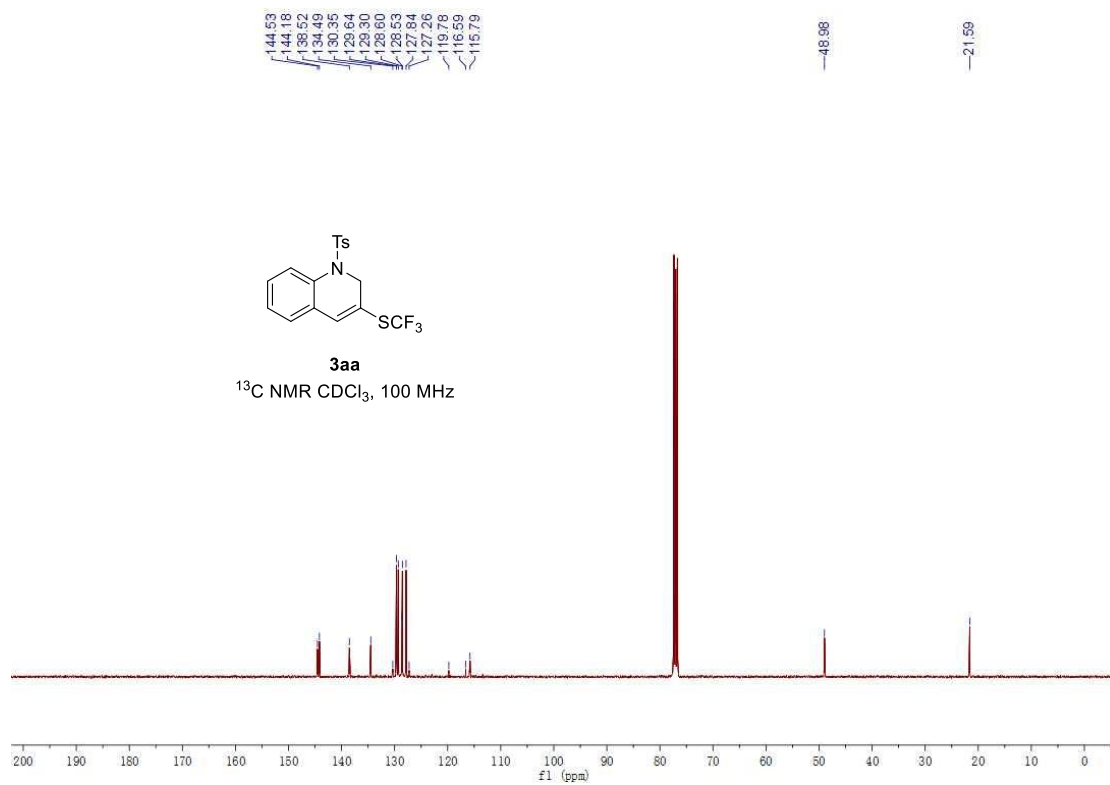








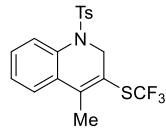




156.97  
144.09  
139.12  
134.26  
129.55  
129.16  
128.62  
128.40  
127.87  
127.07  
118.88

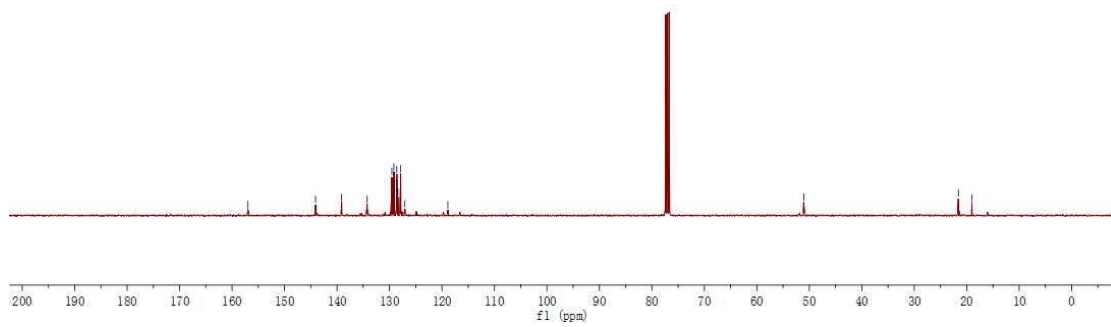
51.07

21.58  
19.02



**3ab**

$^{13}\text{C}$  NMR  $\text{CDCl}_3$ , 100 MHz

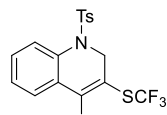


7.48  
7.46  
7.28  
7.27  
6.99  
6.98  
6.97  
6.96

4.52

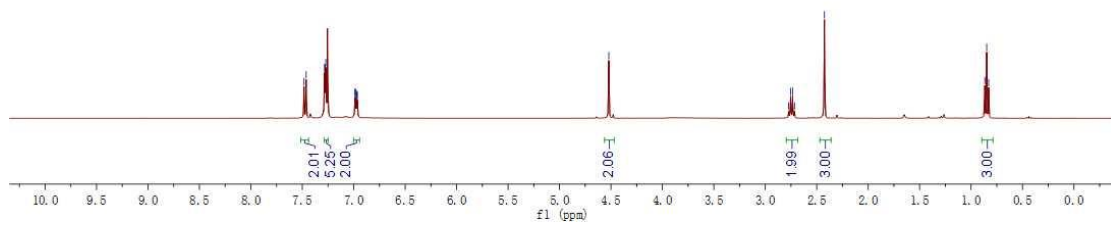
2.77  
2.75  
2.74  
2.72  
2.43

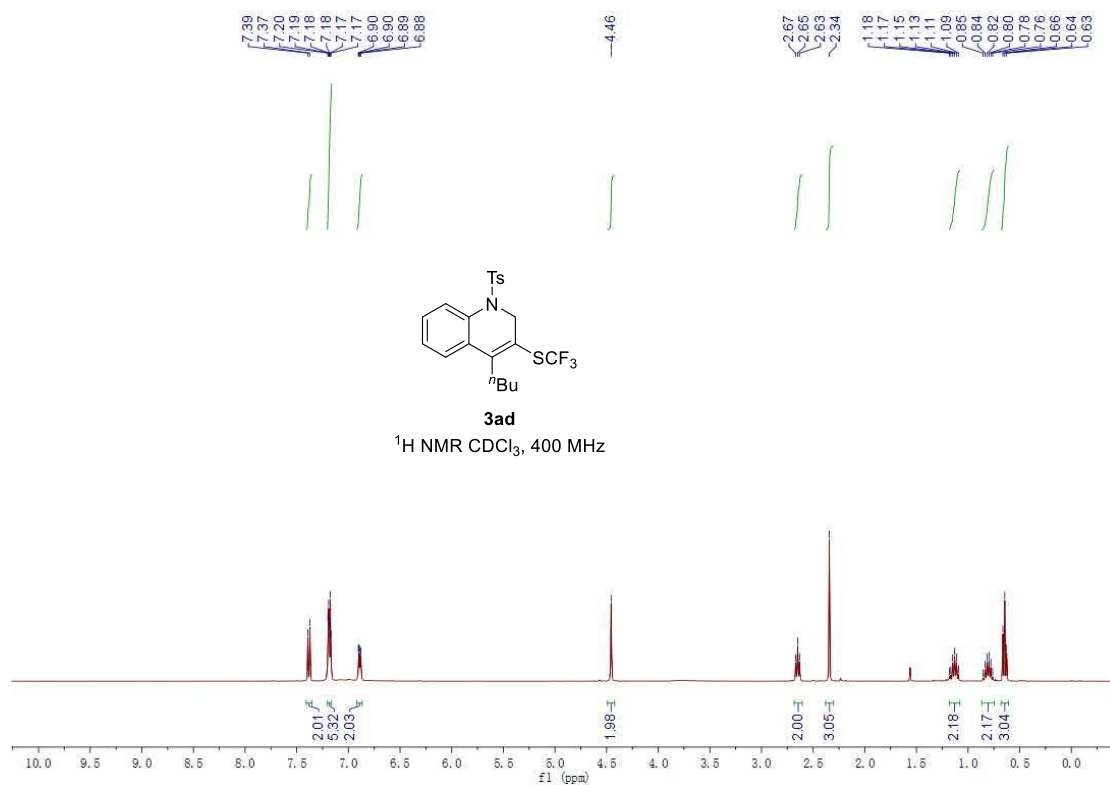
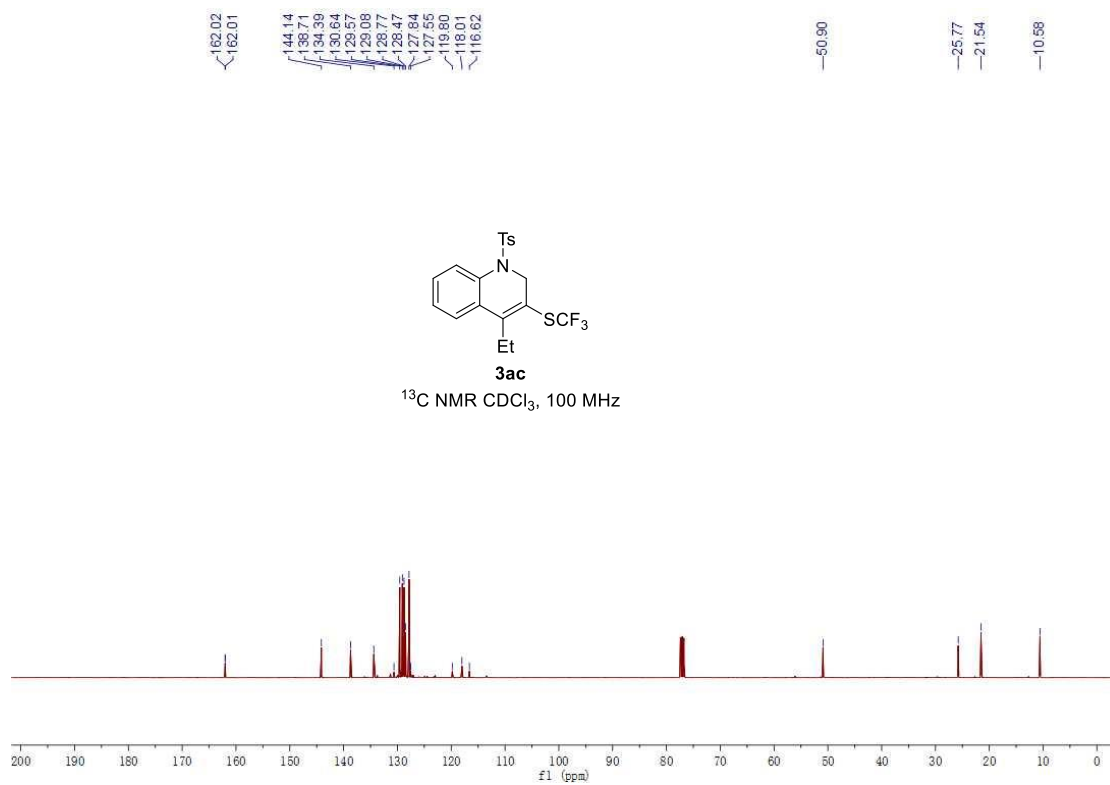
0.87  
0.85  
0.83

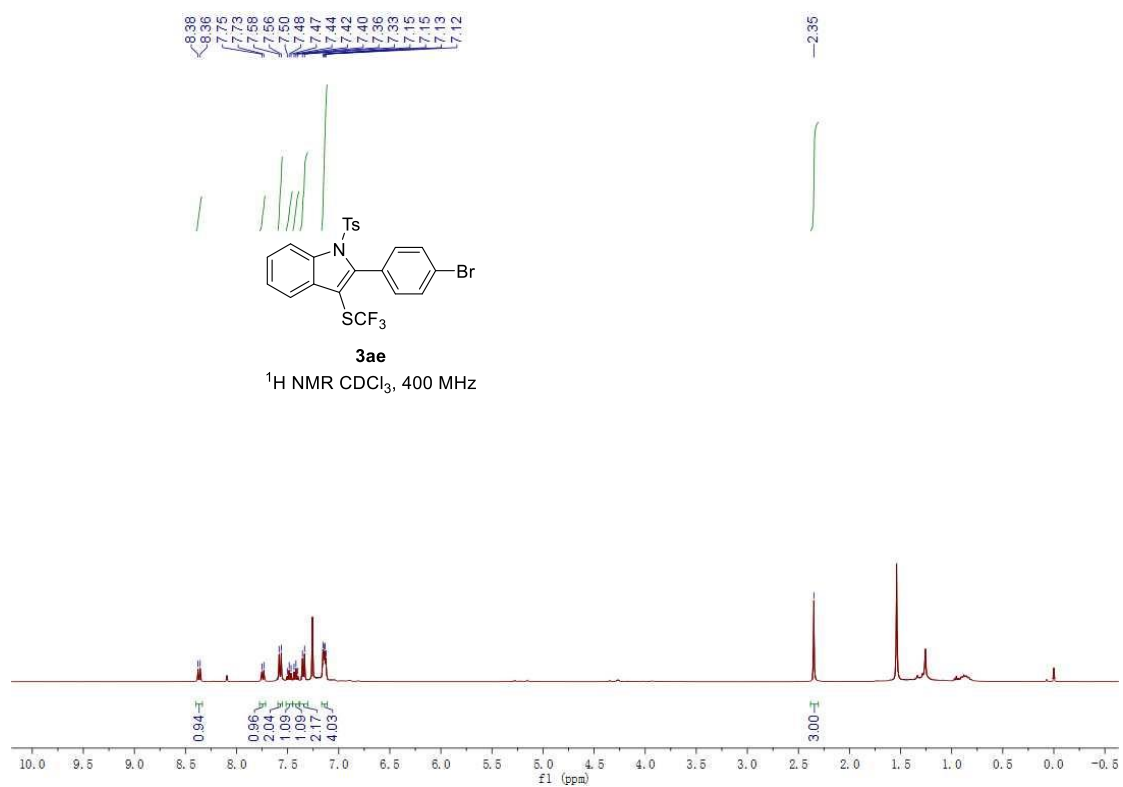
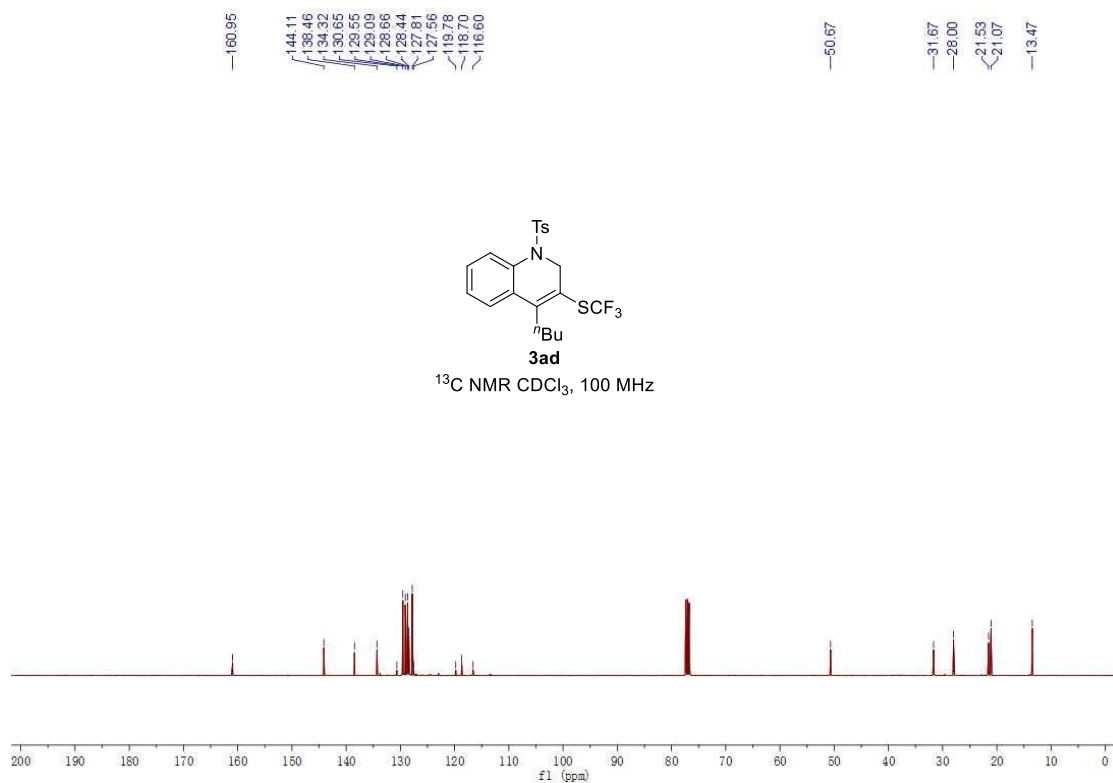


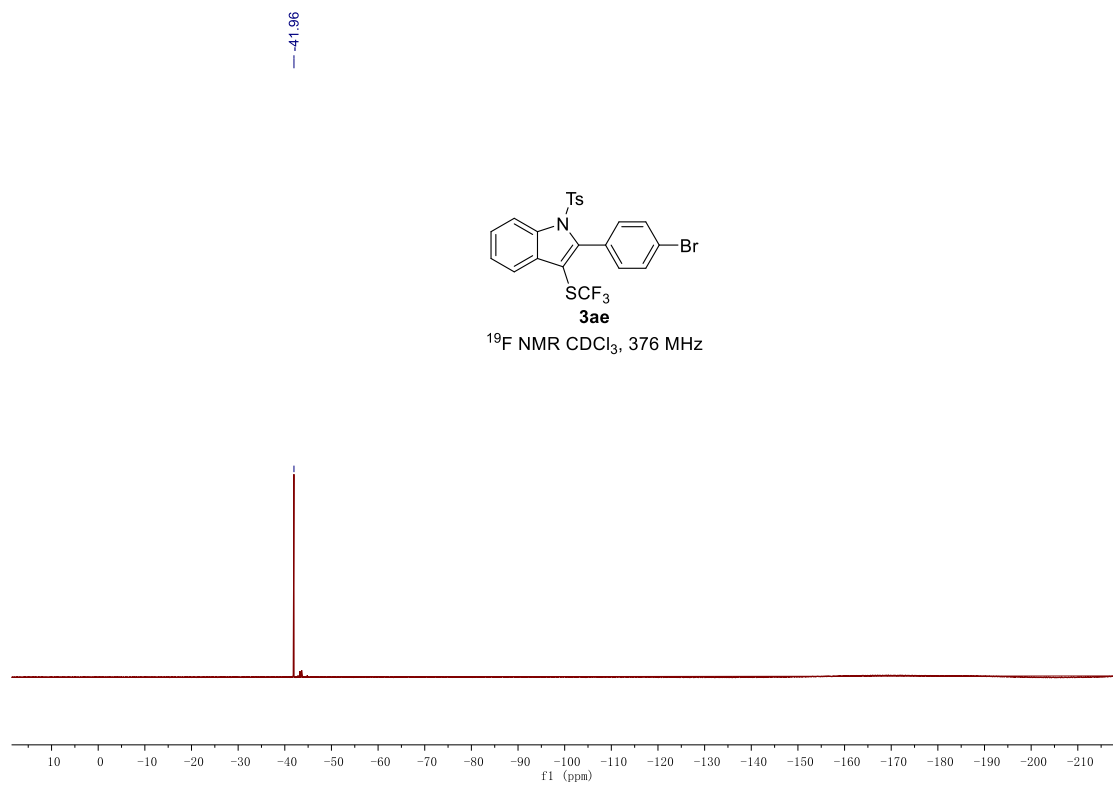
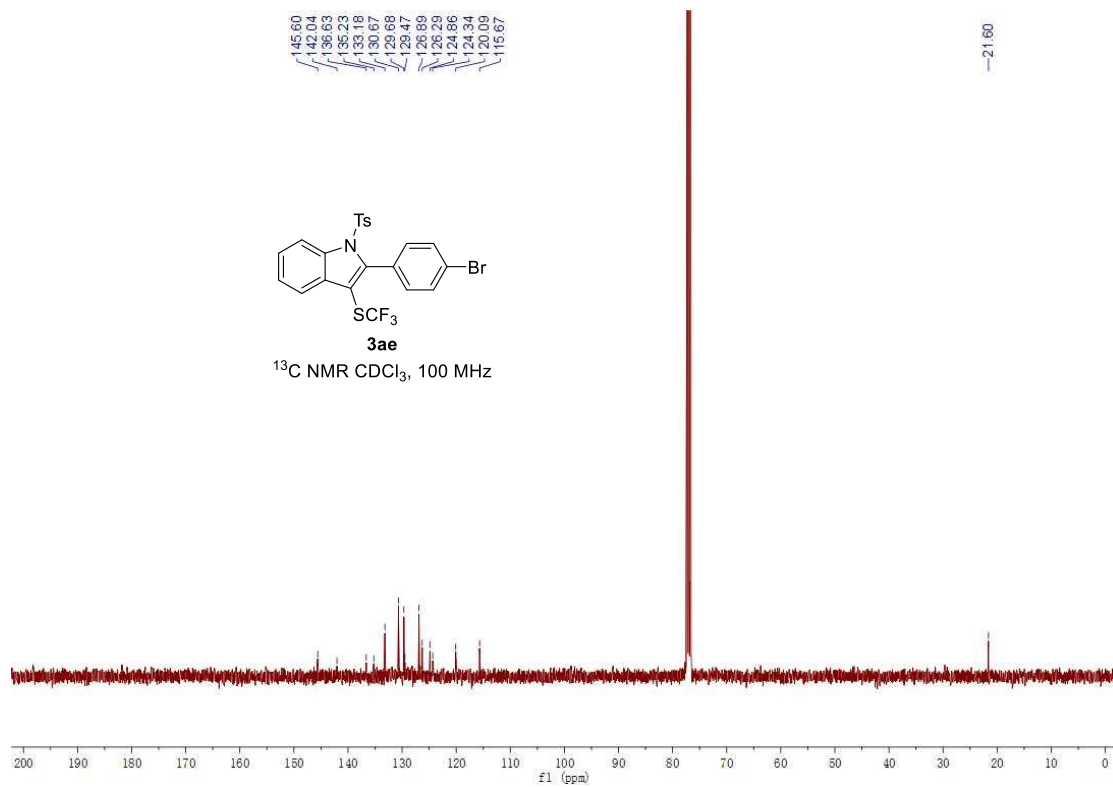
**3ac**

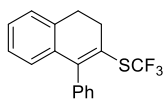
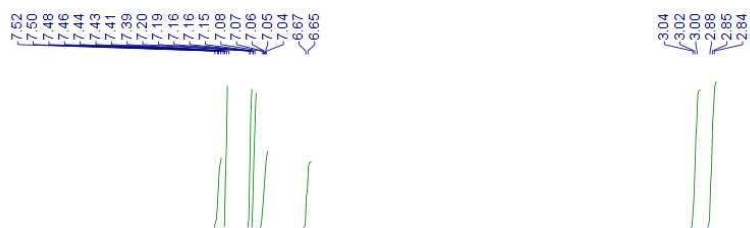
$^1\text{H}$  NMR  $\text{CDCl}_3$ , 400 MHz





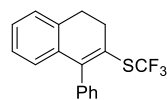
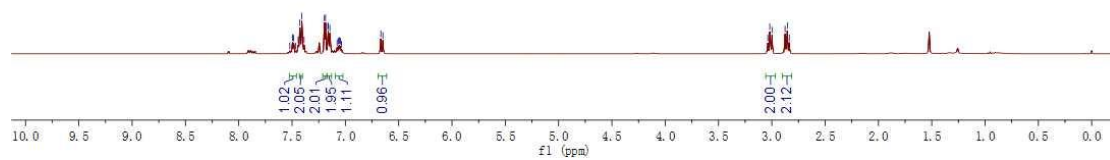






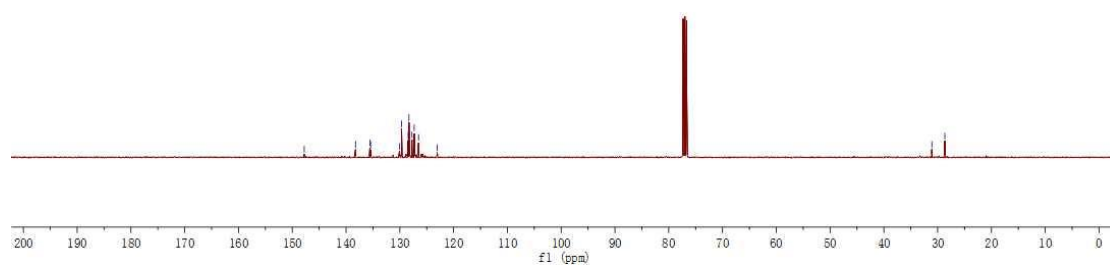
**5a**

<sup>1</sup>H NMR CDCl<sub>3</sub>, 400 MHz

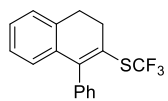


**5a**

<sup>13</sup>C NMR CDCl<sub>3</sub>, 100 MHz

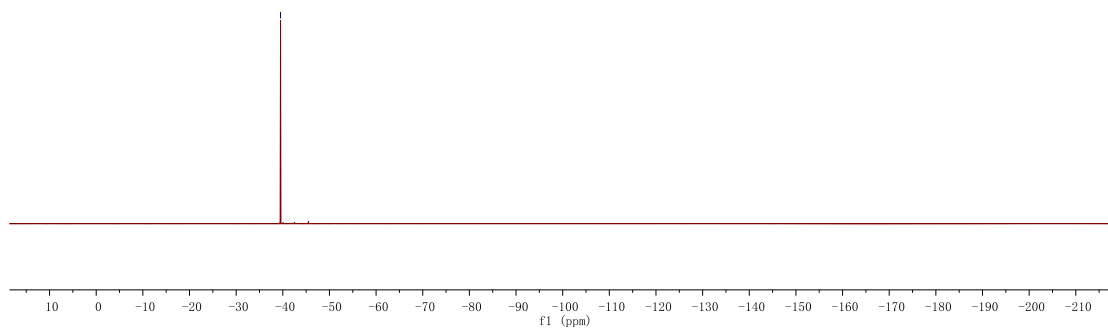


-38.51



**5a**

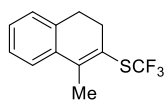
$^{19}\text{F}$  NMR  $\text{CDCl}_3$ , 376 MHz



7.38  
7.36  
7.35  
7.27  
7.25  
7.24  
7.23  
7.21  
7.17  
7.15

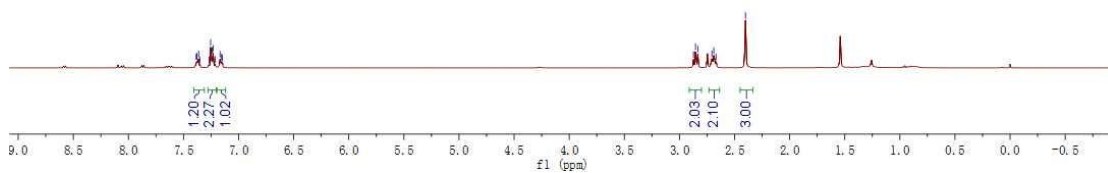


2.87  
2.85  
2.88  
2.71  
2.69  
2.40



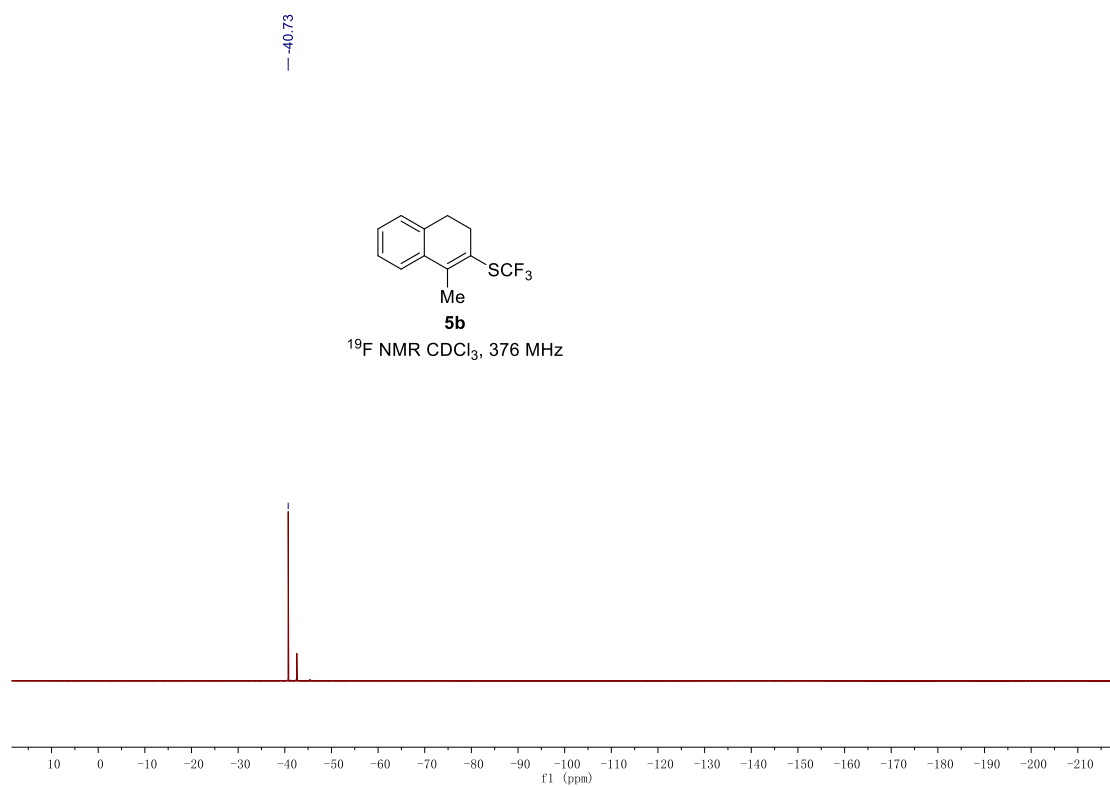
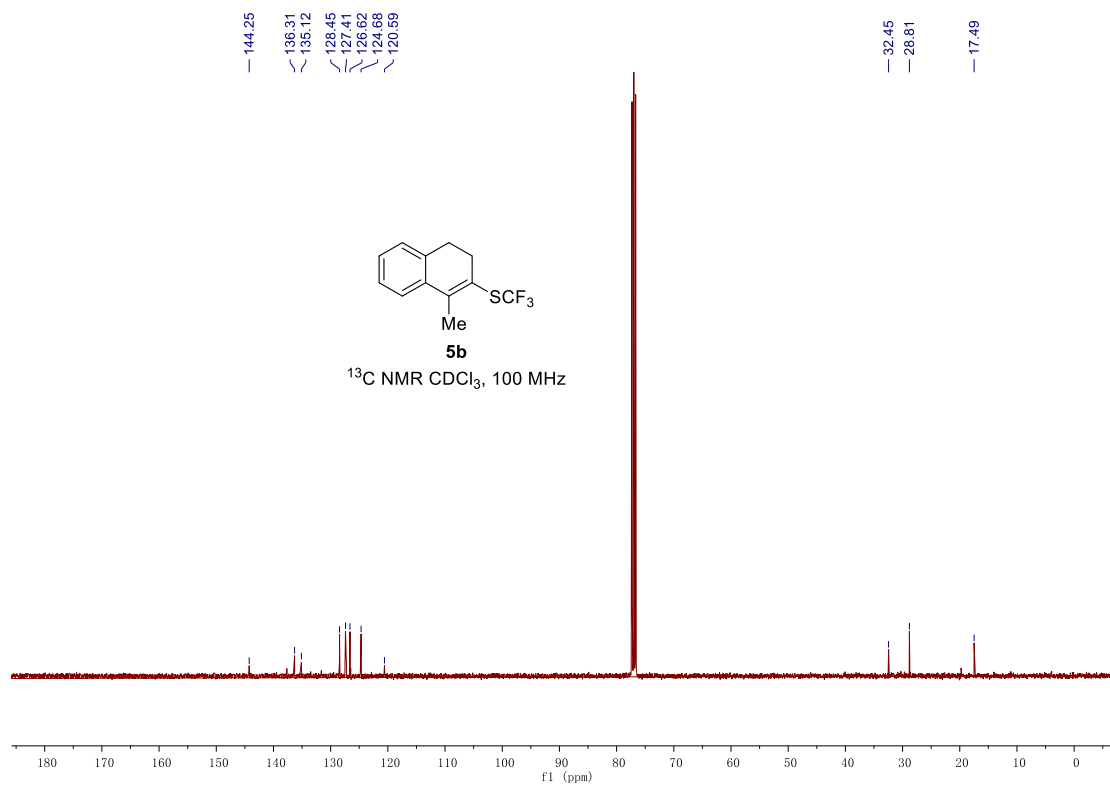
**5b**

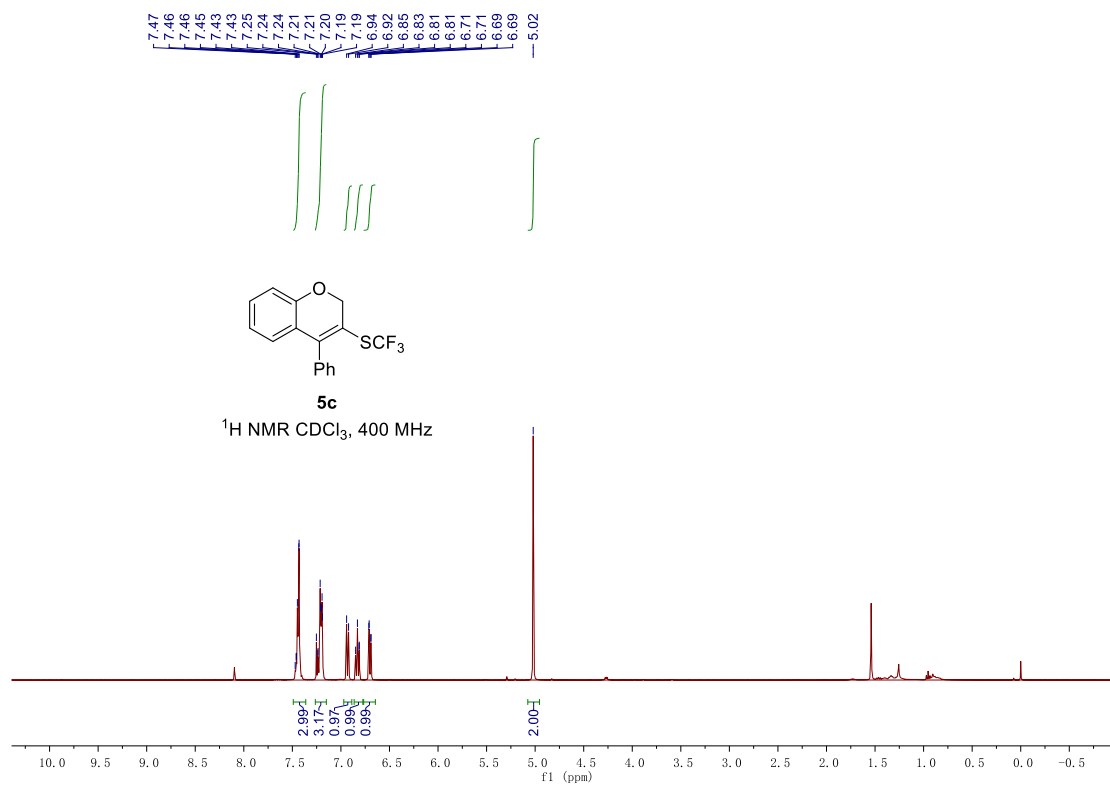
$^1\text{H}$  NMR  $\text{CDCl}_3$ , 400 MHz

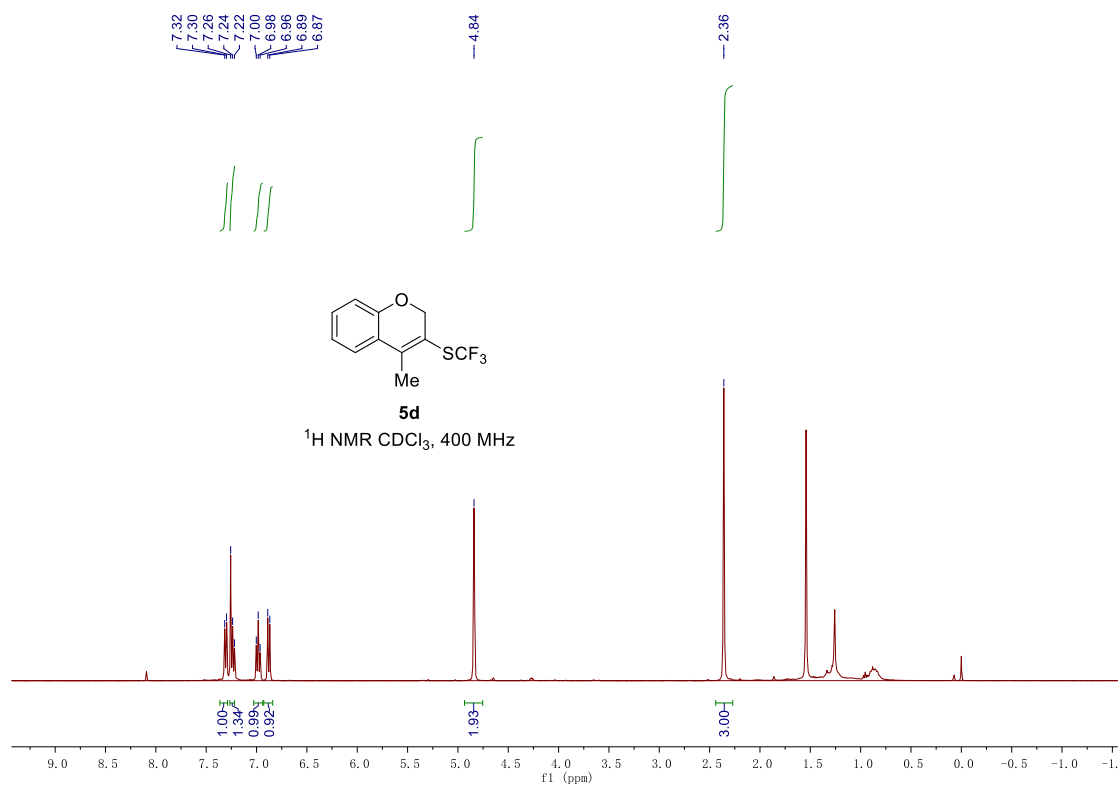
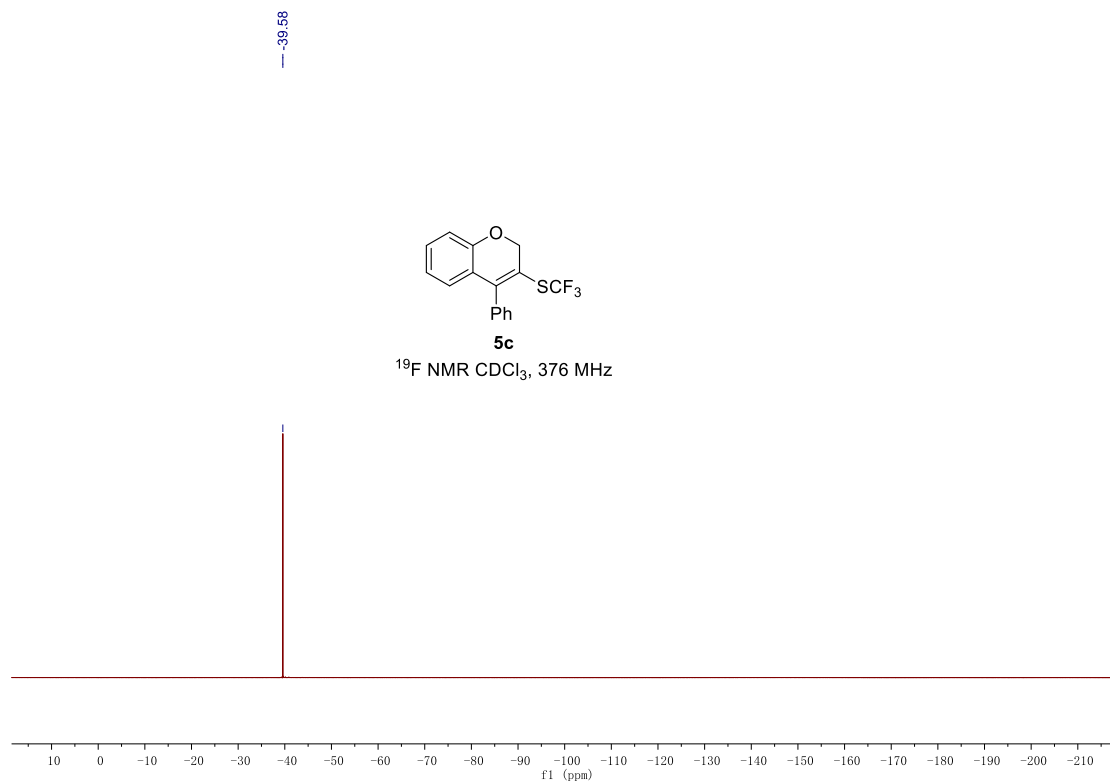


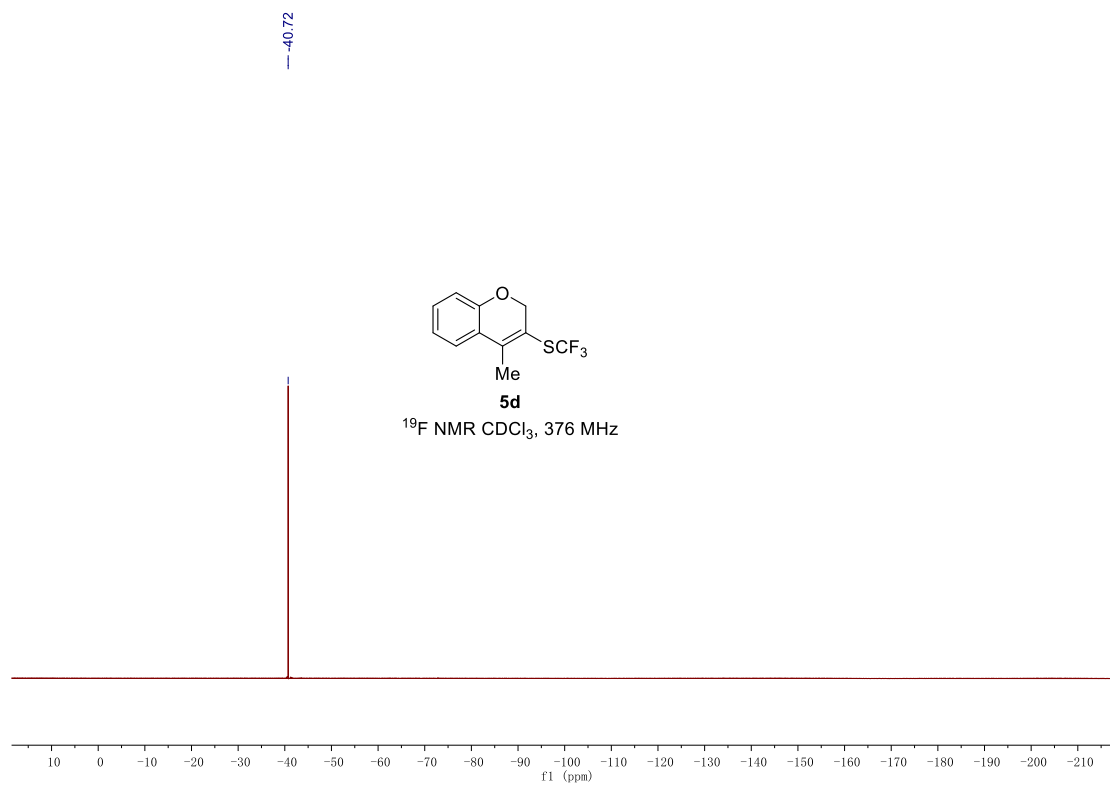
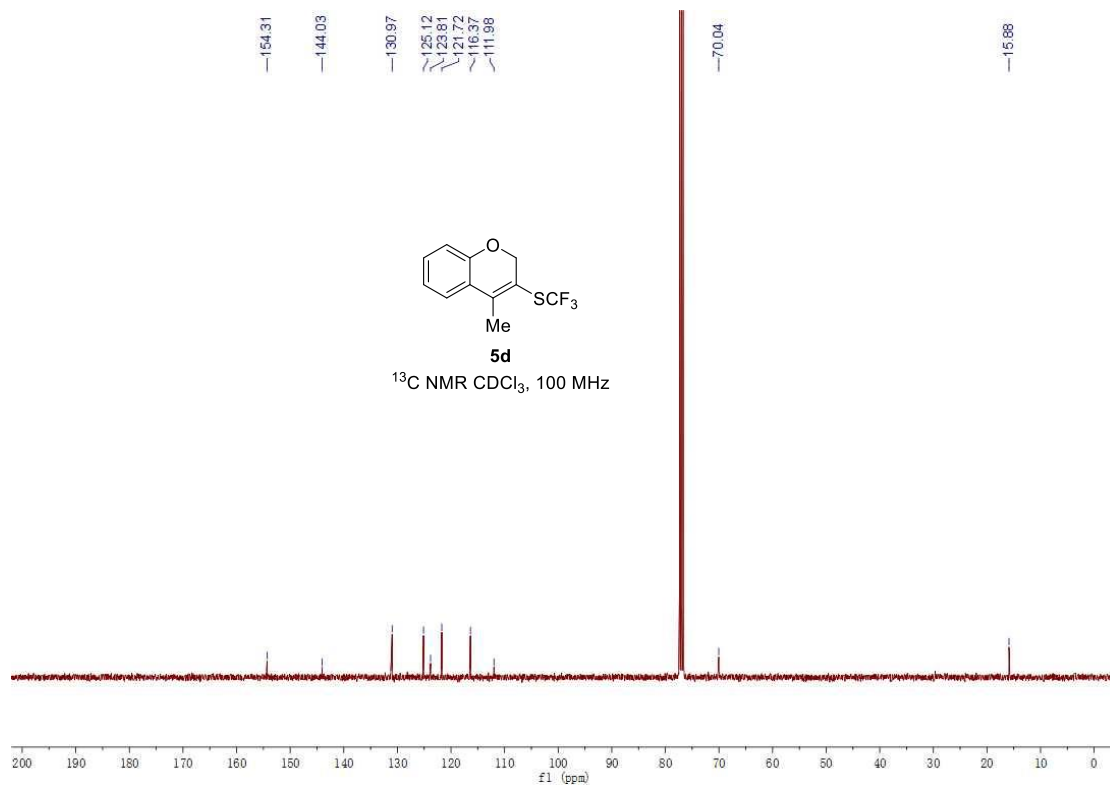
1.20  
2.27  
1.02

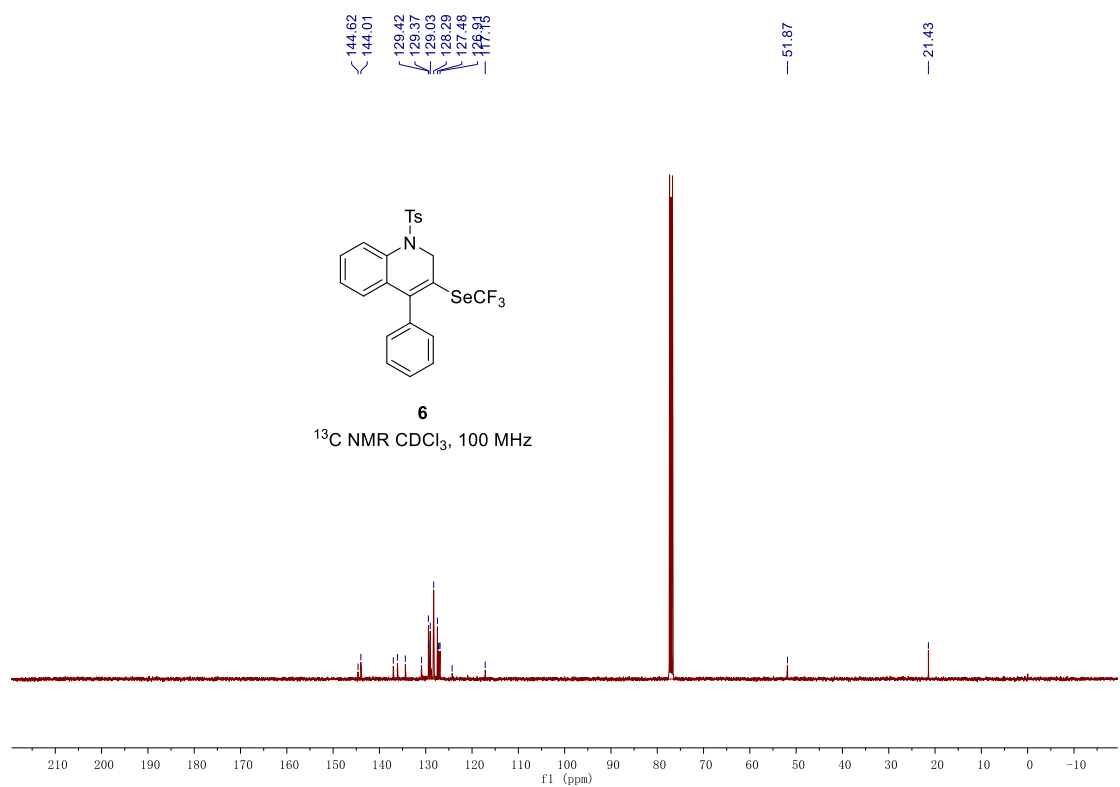
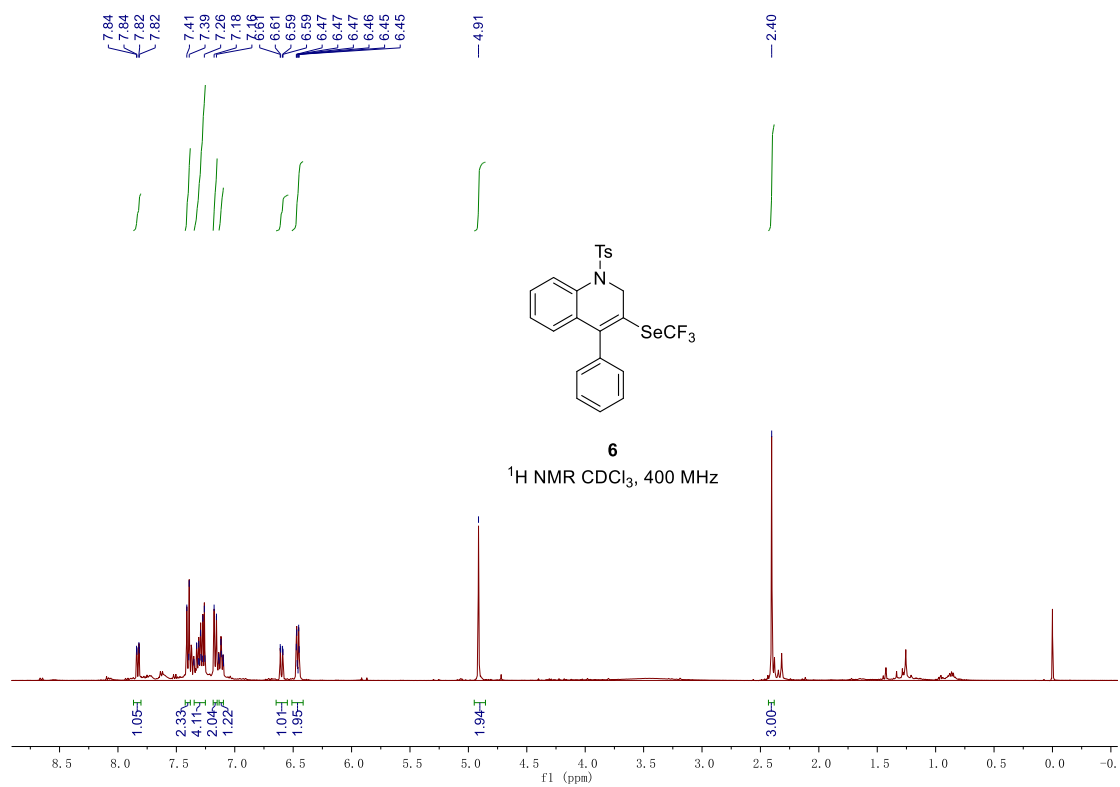
2.03  
2.10  
3.00



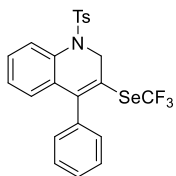






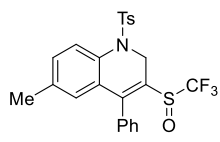
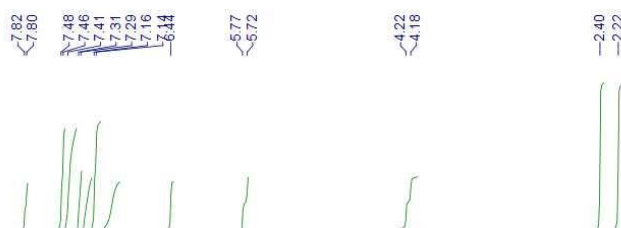
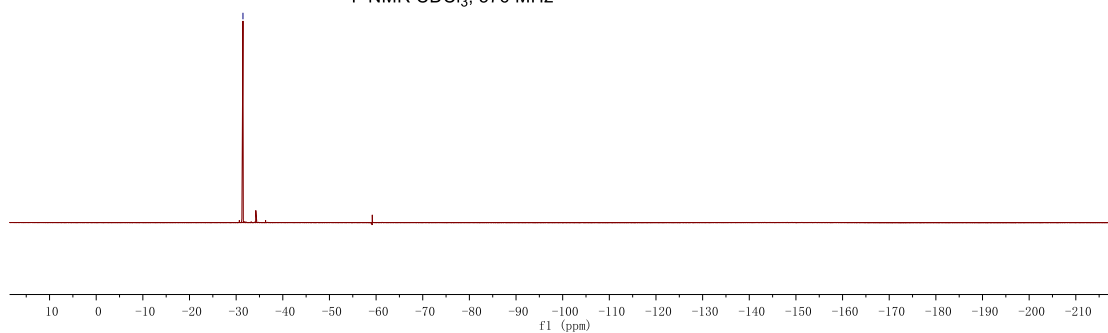


-31.46



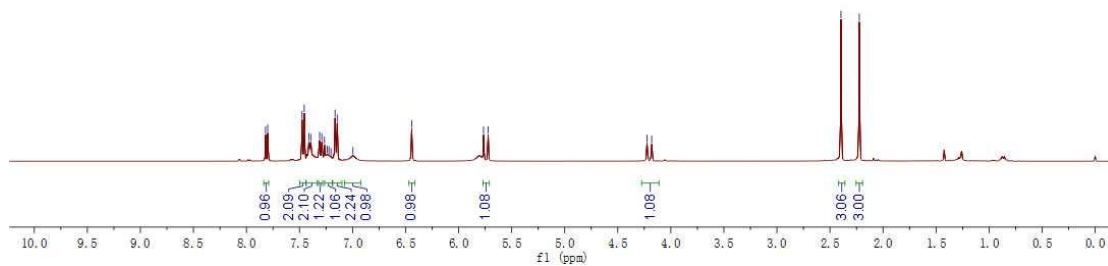
**6**

$^{19}\text{F}$  NMR  $\text{CDCl}_3$ , 376 MHz



**7**

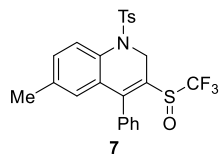
$^1\text{H}$  NMR  $\text{CDCl}_3$ , 400 MHz



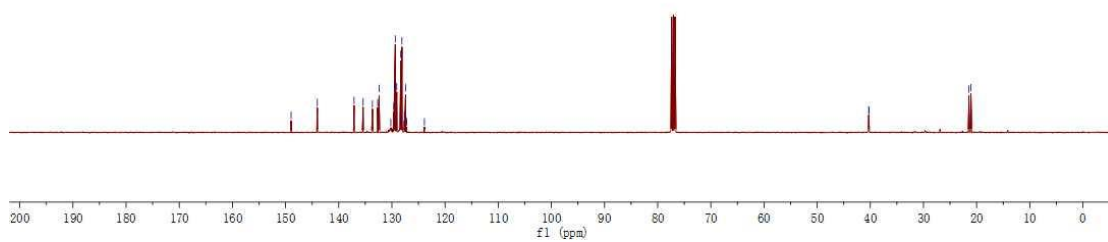
148.96  
144.07  
137.11  
135.41  
133.66  
132.67  
132.10  
130.20  
129.54  
129.36  
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127.65  
127.43  
127.24  
123.88

40.29  
40.27

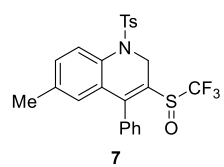
21.44  
21.07



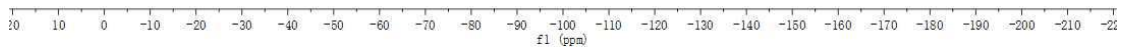
<sup>13</sup>C NMR CDCl<sub>3</sub>, 100 MHz



68.45



<sup>19</sup>F NMR CDCl<sub>3</sub>, 376 MHz



## 6. References

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