

## Supporting Information

### **Photoinduced selective perfluoroalkylation of terminal alkynes via electron donor-acceptor complexes**

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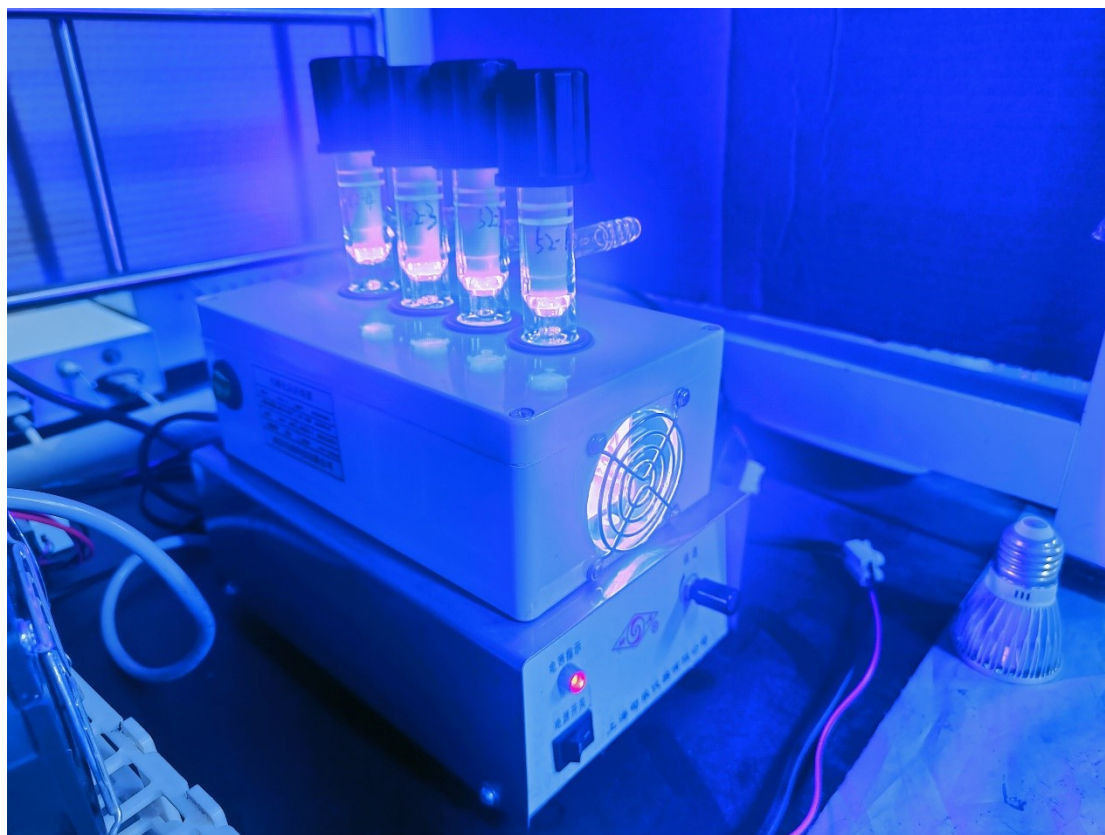
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## 1. General information

All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere in a sealed tube. Unless otherwise noted, all the solvents and reagents were obtained from commercial suppliers (Strem, Alfa, Aldrich, Adamas-beta®, Innochem, Aladdin, Acros, TCI, bidepharm and so on) and used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (bp. 60-90 °C). Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using helium as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5 capillary column using helium carrier gas. The absorbance data were obtained by a UV-vis spectrophotometer (Lamba 25, PerkinElmer). <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR data were recorded with Bruker DRX-400 spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. Singlet (s), doublet (d), doublet of doublet (dd), triplet (t), doublet of triplet (dt), triplet of doublet (td), quartet (q), multiplet (m), doublet of doublet of doublet (ddd) were used to express the signal. All chemical shifts were reported relative to tetramethylsilane (0 ppm for <sup>1</sup>H), CDCl<sub>3</sub> (77.0 ppm for <sup>13</sup>C), respectively. High resolution mass spectra (HRMS) were recorded on an Agilent 6210 Series 1969A ESI-TOF (time of flight) mass spectrometer using ESI (electrospray ionization) or EI (electron ionization).

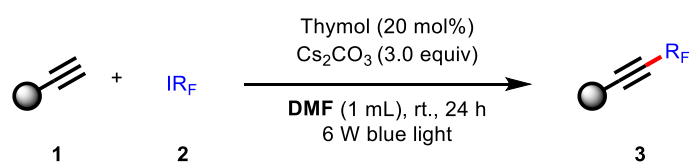
## 2. Photographs of the photochemical reaction set-ups



**Figure S1.** Photographs of the photochemical reaction set-up. The 10 mL reaction vials were illuminated from both sides of the bottom with LEDs (2×3W LEDs and wavelength 400-410 nm, 420-430 nm, or 460-470 nm), and cooled by fans on the front and rear sides of the photoreactor.

## 3. General synthetic procedure

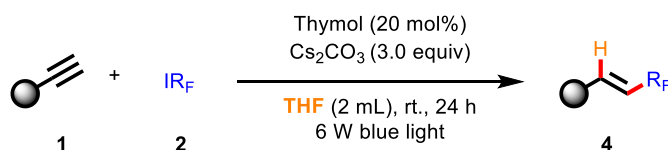
### 3.1 General procedure A



To a 10 mL glass tube was added alkyne **1** (0.2 mmol), iodoperfluoroalkane **2** (0.6 mmol, 3.0 equiv),  $\text{Cs}_2\text{CO}_3$  (0.6 mmol, 3.0 equiv), thymol (20 mol%) and anhydrous DMF (1.0

mL) under argon atmosphere. And the mixture was first stirred at rt. for 10 min. Then, the mixture was irradiated by 6 W 420-430 nm blue LEDs at rt. for 24 h. After completion, the reaction mixture was washed with brine solution (3×10 mL) and the water layer was extracted again with ethyl ether (2×10 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated, and concentrated in vacuo. Purification by column chromatography on silica gel afforded the desired products **3**.

### 3.2 General procedure B



To a 10 mL glass tube was added alkyne **1** (0.2 mmol), iodoperfluoroalkane **2** (0.6 mmol, 3.0 equiv), Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol, 3.0 equiv), thymol (20 mol%) and anhydrous THF (2.0 mL) under argon atmosphere. And the mixture was first stirred at rt. for 10 min. Then, the mixture was irradiated by 6 W 420-430 nm blue LEDs at rt. for 24 h. After completion, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel afforded the desired products **4**.

## 4. Optimization of the reaction conditions

**Table S1.** Additional optimizations <sup>a</sup>.

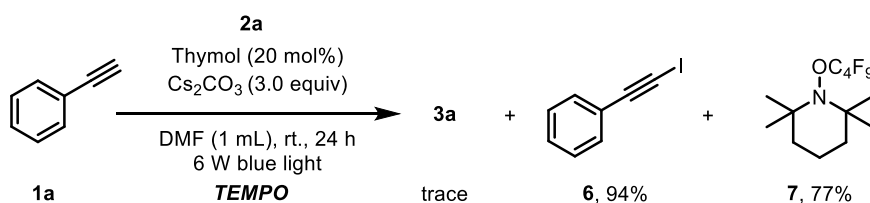
entry	solvent	<b>3a</b> (%)	<b>4a</b> (%)	<b>5a</b> (%)	<b>6</b> (%)
1	DMSO	79	n.d.	n.d.	18
2	DCM	n.d.	n.d.	35	20
3	EA	n.d.	n.d.	41	28
4	acetone	n.d.	n.d.	32	13
5	dioxane	n.d.	n.d.	21	n.d.

6	toluene	n.d.	n.d.	11	n.d.
7	MeOH	n.d.	n.d.	30	n.d.

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), IC<sub>4</sub>F<sub>9</sub> (**2a**, 3.0 equiv.), thymol (20 mol%), Cs<sub>2</sub>CO<sub>3</sub> (3.0 equiv.), solvent (1 mL), room temperature, blue LEDs (6 W, 420-430 nm), 24 h, GC yields. n.d. = not detected.

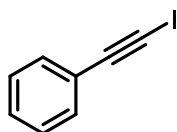
## 5. Mechanistic studies

### 5.1 Radical trapping experiment



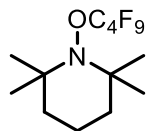
To a 10 mL glass tube was added alkyne **1a** (0.2 mmol), **2a** (0.6 mmol, 3.0 equiv), Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol, 3.0 equiv), thymol (20 mol%), TEMPO (0.2 mmol, 1.0 equiv) and anhydrous DMF (1.0 mL) under argon atmosphere. And the mixture was first stirred at rt. for 10 min. Then, the mixture was irradiated by 6 W 420-430 nm blue LEDs at rt. for 24 h. After completion, the reaction mixture purified by column chromatography on silica gel afforded the products (**6**, **7**).

#### (Iodoethynyl)benzene (**6**)



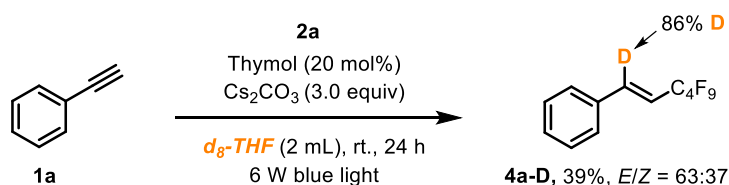
The reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **6** (43 mg, 94%) as a yellow oil. This compound is known. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.41 (m, 2H), 7.37 – 7.28 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 132.3, 128.8, 128.2, 123.4, 94.1, 6.1.

#### 2,2,6,6-tetramethyl-1-(perfluorobutoxy)piperidine (**7**)

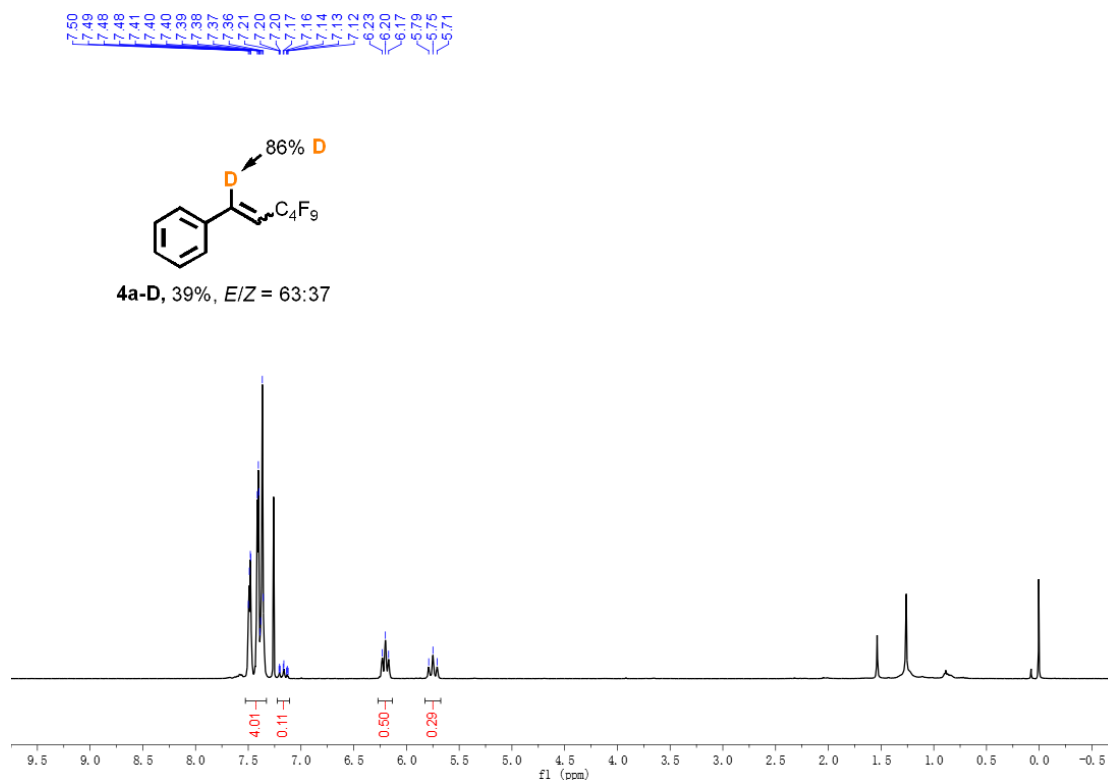


The reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **7** (58 mg, 77%) as a colorless oil. This compound is known.<sup>2</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.66 – 1.53 (m, 5H), 1.42 – 1.32 (m, 1H), 1.18 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 61.9, 40.5, 33.5 (t, *J* = 5.4 Hz), 20.7, 16.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -78.8 (m, 2F), -81.0 (t, *J* = 9.5 Hz, 3F), -124.5 (dd, *J* = 9.8, 4.9 Hz, 2F), -126.1 (m, 2F).

## 5.2 Deuterium experiment



To a 10 mL glass tube was added alkyne **1a** (0.2 mmol), **2a** (0.6 mmol, 3.0 equiv), Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol, 3.0 equiv), thymol (20 mol%) and anhydrous *d*<sub>8</sub>-THF (2.0 mL) under argon atmosphere. And the mixture was first stirred at rt. for 10 min. Then the mixture was irradiated by 6 W 420-430 nm blue LEDs at rt. for 24 h. After completion, the reaction mixture was concentrated in vacuo. Purification by column chromatography on silica gel afforded the desired products **4a-D** in 39% yield. As shown in the <sup>1</sup>H NMR, the integration of one hydrogen atom on the double bond (*E*+*Z*) is 0.50+0.29 = 0.79, and the other is 0.11 (*E*+*Z*). Therefore, the deuteration rate is (0.79-0.11)/0.79 = 0.86.



### 5.3 UV-vis spectroscopic measurement in DMF

Solution 1 (IC<sub>4</sub>F<sub>9</sub>): **2a** (103  $\mu$ L, 0.6 mmol) was added in DMF (4 mL). The mixture was stirred for 20 minutes and filtered.

Solution 2 (thymol): thymol (6.0 mg, 0.04 mmol) was added in DMF (4 mL). The mixture was stirred for 20 minutes and filtered.

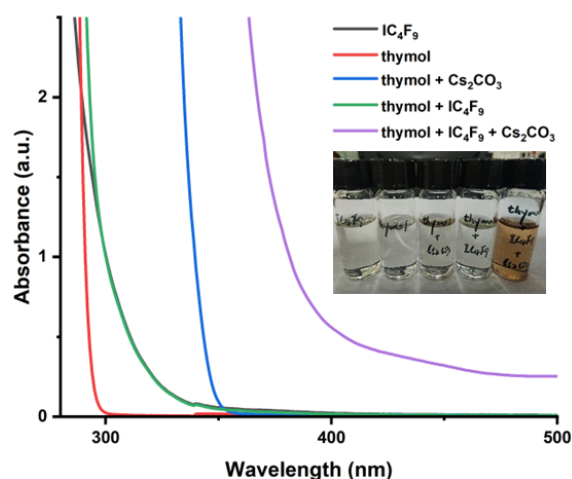
Solution 3 (thymol + Cs<sub>2</sub>CO<sub>3</sub>): thymol (6.0 mg, 0.04 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) were added in DMF (4 mL). The mixture was stirred for 20 minutes and filtered.

Solution 4 (thymol + IC<sub>4</sub>F<sub>9</sub>): thymol (6.0 mg, 0.04 mmol), and **2a** (103  $\mu$ L, 0.6 mmol) was added in DMF (4 mL). The mixture was stirred for 20 minutes and filtered.

Solution 5 (thymol + IC<sub>4</sub>F<sub>9</sub> + Cs<sub>2</sub>CO<sub>3</sub>): thymol (6.0 mg, 0.04 mmol), **2a** (103  $\mu$ L, 0.6 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) were added in DMF (4 mL). The mixture was stirred for 20 minutes and filtered.

Performed on UV-vis spectrophotometer (Lamba 25, PerkinElmer), recorded in 1 cm path quartz cuvettes, pure DMF as blank sample.





#### 5.4 UV-vis spectroscopic measurement in THF

Solution 1 (IC<sub>4</sub>F<sub>9</sub>): **2a** (103  $\mu$ L, 0.6 mmol) was added in THF (4 mL). The mixture was stirred for 20 minutes and filtered.

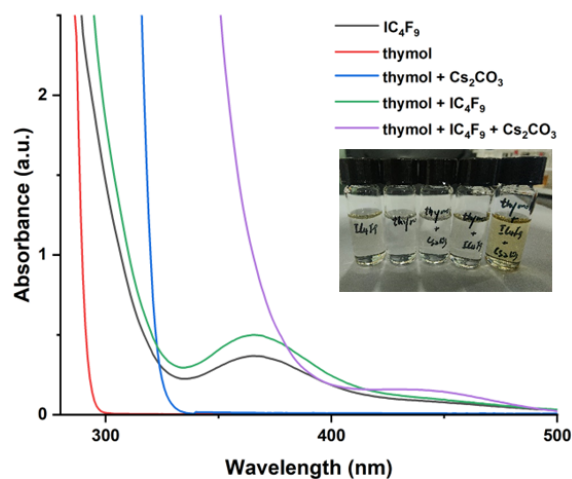
Solution 2 (thymol): thymol (6.0 mg, 0.04 mmol) was added in THF (4 mL). The mixture was stirred for 20 minutes and filtered.

Solution 3 (thymol + Cs<sub>2</sub>CO<sub>3</sub>): thymol (6.0 mg, 0.04 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) were added in THF (4 mL). The mixture was stirred for 20 minutes and filtered.

Solution 4 (thymol + IC<sub>4</sub>F<sub>9</sub>): thymol (6.0 mg, 0.04 mmol), and **2a** (103  $\mu$ L, 0.6 mmol) was added in THF (4 mL). The mixture was stirred for 20 minutes and filtered.

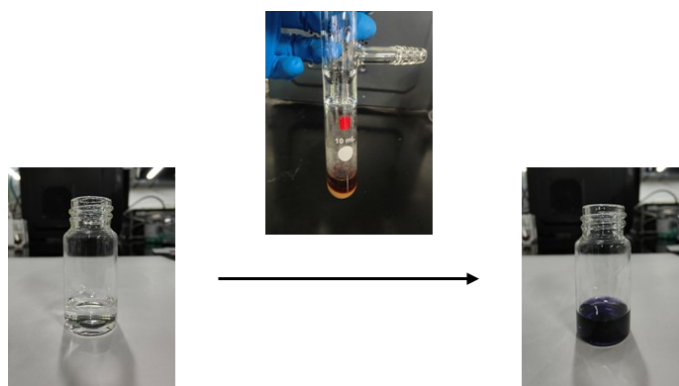
Solution 5 (thymol + IC<sub>4</sub>F<sub>9</sub> + Cs<sub>2</sub>CO<sub>3</sub>): thymol (6.0 mg, 0.04 mmol), **2a** (103  $\mu$ L, 0.6 mmol), and Cs<sub>2</sub>CO<sub>3</sub> (195.5 mg, 0.6 mmol) were added in THF (4 mL). The mixture was stirred for 20 minutes and filtered.

Performed on UV-vis spectrophotometer (Lamba 25, PerkinElmer), recorded in 1 cm path quartz cuvettes, pure THF as blank sample.



### 5.5 Starch indicator experiment

To a 10 mL glass tube was added alkyne **1a** (0.2 mmol), iodoperfluoroalkane **2c** (0.6 mmol, 3.0 equiv), Cs<sub>2</sub>CO<sub>3</sub> (0.6 mmol, 3.0 equiv), thymol (20 mol%) and anhydrous DMF (1.0 mL) under argon atmosphere. And the mixture was first stirred at rt. for 10 min. Then, the mixture was irradiated by 6 W 420-430 nm blue LEDs at rt. for 24 h. After completion, the reaction mixture was diluted with 2 mL ethyl acetate. Then the mixture was dropped into the starch indicator solution and the solution turned blue.



**Figure S2.** Starch indicator experiment

## 5.6 GC-MS of iodo-tetrahydrofuran

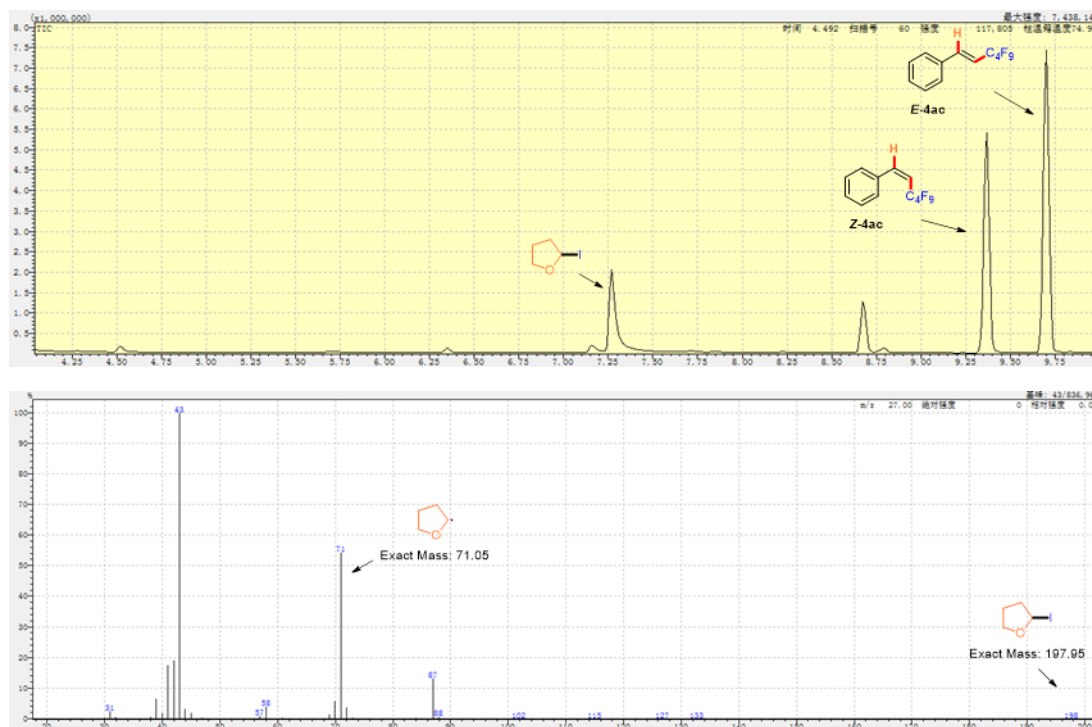
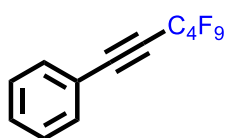


Figure S3. GC-MS of iodo-tetrahydrofuran

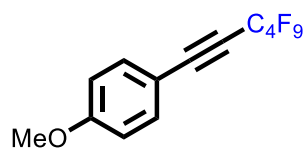
## 6. Characterization data of products

### (Perfluorohex-1-yn-1-yl)benzene (**3a**)



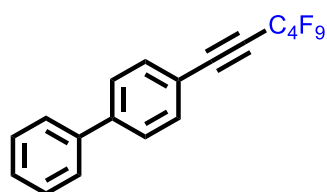
Following the **General Procedure A**, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3a** (59 mg, 92%) as a yellow oil. This compound is known.<sup>3</sup> **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.57 (d,  $J = 7.3$  Hz, 2H), 7.49 (t,  $J = 7.5$  Hz, 1H), 7.41 (t,  $J = 7.5$  Hz, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  132.5 (t,  $J = 2.3$  Hz), 131.1 (s), 128.7 (s), 118.5 (t,  $J = 2.9$  Hz), 92.3 (t,  $J = 6.3$  Hz), 74.6 (t,  $J = 36.0$  Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -81.0 (t,  $J = 9.8$  Hz, 3F), -97.4 (m, 2F), -123.4 (m, 2F), -125.4 (m, 2F).

### 1-methoxy-4-(perfluorohex-1-yn-1-yl)benzene (3b)



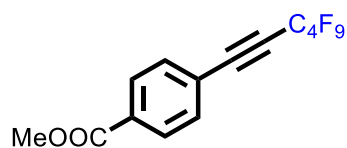
Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3b** (60 mg, 86%) as a colorless oil. This compound is known.<sup>3</sup> **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.50 (d,  $J$  = 8.8 Hz, 2H), 6.90 (d,  $J$  = 8.9 Hz, 2H), 3.84 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  161.7, 134.3 (t,  $J$  = 2.4 Hz), 114.4, 110.3 (t,  $J$  = 3.0 Hz), 92.9 (t,  $J$  = 6.4 Hz), 73.7 (t,  $J$  = 36.1 Hz), 55.4. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -81.1 (m, 3F), -96.8 (m, 2F), -123.4 (m, 2F), -125.4 (m, 2F).

### 4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexa-1-yn-1-yl)-1-phenyl benzene (3c)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3b** (69 mg, 87%) as a white solid. This compound is known.<sup>3</sup> **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.64 (s, 4H), 7.62 – 7.57 (m, 2H), 7.52 – 7.45 (m, 2H), 7.41 (ddd,  $J$  = 7.3, 3.7, 1.2 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  144.0, 139.7, 132.9 (t,  $J$  = 2.4 Hz), 129.0, 128.3, 127.3, 127.2, 117.1 (t,  $J$  = 2.9 Hz), 92.4 (t,  $J$  = 6.3 Hz), 75.1 (t,  $J$  = 36.2 Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -81.0 (t,  $J$  = 9.5 Hz, 3F), -97.3 (dt,  $J$  = 6.6, 6.0 Hz, 2F), -123.4 (m, 2F), -125.4 (m, 2F).

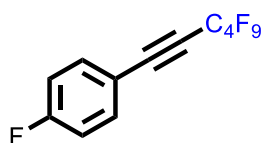
### methyl 4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexa-1-yn-1-yl)benzoate (3d)



Following the General Procedure A, the reaction mixture was purified by column

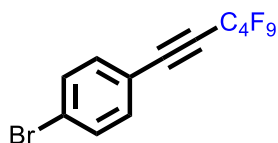
chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **3d** (61 mg, 81%) as a colorless oil. This compound is known.<sup>3</sup> **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.12 – 8.03 (m, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 3.94 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 165.9, 132.5 (t, *J* = 2.1 Hz), 132.3, 129.7, 122.7 (t, *J* = 3.0 Hz), 90.9 (t, *J* = 6.4 Hz), 76.8 (t, *J* = 38.4 Hz), 52.5. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -81.0 (t, *J* = 9.5 Hz, 3F), -98.0 (m, 2F), -123.3 (m, 2F), -125.5 (m, 2F).

#### 1-fluoro-4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexa-1-yn-1-yl)benzene (**3e**)



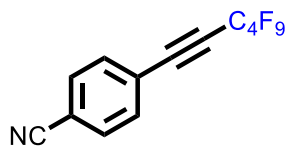
Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3e** (57 mg, 84%) as a colorless oil. This compound is known.<sup>3</sup> **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.57 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.16 – 7.04 (m, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 164.2 (d, *J* = 254.1 Hz), 134.8 (dt, *J* = 8.9, 2.3 Hz), 116.3 (d, *J* = 22.5 Hz), 114.6 (dd, *J* = 6.3, 3.2 Hz), 91.3 (t, *J* = 6.5 Hz), 74.6 (t, *J* = 36.3 Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -81.0 (t, *J* = 9.7 Hz, 3F), -97.5 (d, *J* = 1.7 Hz, 2F), -105.6 (m, 1F), -123.4 (m, 2F), -125.5 (m, 2F).

#### 1-bromo-4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexa-1-yn-1-yl)benzene (**3f**)



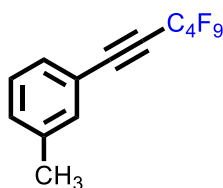
Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3f** (67 mg, 84%) as a colorless oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 133.8 (t, *J* = 2.3 Hz), 132.1, 126.0, 117.4 (d, *J* = 3.0 Hz), 91.1 (t, *J* = 6.3 Hz), 75.60 (t, *J* = 36.2 Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -81.0 (t, *J* = 8.4 Hz, 3F), -97.8 (m, 2F), -123.4 (m, 2F), -125.5 (m, 2F). **HRMS (ESI):** calcd for C<sub>12</sub>H<sub>5</sub>BrF<sub>9</sub><sup>+</sup> [M+H]<sup>+</sup> 398.9425; found 398.9418.

#### 4-(3,3,4,4,5,5,6,6,6-nonafluoro-hexa-1-yn-1-yl)benzotrile (3g)



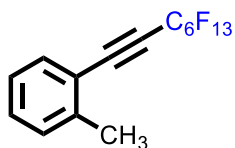
Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **3g** (54 mg, 78%) as a yellow oil. This compound is known.<sup>4</sup> **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.70 (q,  $J$  = 8.5 Hz, 4H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  133.0 (t,  $J$  = 2.3 Hz), 132.3, 123.0 (t,  $J$  = 2.9 Hz), 117.6, 114.8, 89.6 (t,  $J$  = 6.4 Hz), 77.8 (t,  $J$  = 36.6 Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -81.0 (t,  $J$  = 9.6 Hz, 3F), -98.5 (m, 2F), -123.3 (m, 2F), -125.4 (m, 2F).

#### 1-methyl-3-(perfluorohex-1-yn-1-yl)benzene (3h)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3h** (51 mg, 76%) as a colorless oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.41 – 7.34 (m, 2H), 7.29 (m, 2H), 2.37 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  138.6, 132.9 (t,  $J$  = 2.4 Hz), 132.0, 129.6 (t,  $J$  = 2.4 Hz), 128.6, 118.3 (t,  $J$  = 2.9 Hz), 92.7 (t,  $J$  = 6.4 Hz), 74.3 (t,  $J$  = 36.1 Hz), 21.1. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -81.03 (t,  $J$  = 9.5 Hz, 3F), -97.3 (m, 2F), -123.4 (m, 2F), -125.4 (m, 2F). **HRMS (ESI):** calcd for C<sub>13</sub>H<sub>8</sub>F<sub>9</sub><sup>+</sup> [M+H]<sup>+</sup> 335.0477; found 335.0470.

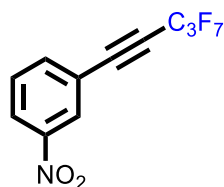
#### 1-methyl-2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octa-1-yn-1-yl)benzene (3i)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3i** (71 mg, 82%) as a yellow oil.

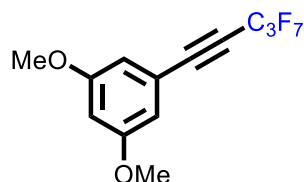
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.52 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 5.8 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 2.46 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 141.9 (d, *J* = 1.9 Hz), 132.9 (t, *J* = 2.1 Hz), 131.1, 129.9, 125.9, 118.4 (t, *J* = 3.0 Hz), 91.5 (t, *J* = 6.3 Hz), 78.4 (t, *J* = 36.0 Hz), 20.2. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -80.9 (t, *J* = 9.8 Hz, 3F), -96.8 (dd, *J* = 13.4, 5.5 Hz, 2F), -121.2 (m, 2F), -122.4 (dd, *J* = 16.2, 12.1 Hz, 2F), -122.8 (m, 2F), -126.2 (m, 2F). **HRMS (ESI):** calcd for C<sub>15</sub>H<sub>8</sub>F<sub>13</sub><sup>+</sup> [M+H]<sup>+</sup> 435.0413; found 435.0408.

### 1-(3,3,4,4,5,5,5-heptafluoro-penta-1-yn-1-yl)-3-nitrobenzene (**3j**)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **3j** (45 mg, 71%) as a yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.43 (s, 1H), 8.36 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 148.2, 138.0 (t, *J* = 2.1 Hz), 130.0, 127.4 (t, *J* = 2.3 Hz), 125.8, 120.2 (t, *J* = 2.9 Hz), 88.9 (t, *J* = 6.3 Hz), 76.5 (t, *J* = 36.4 Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -80.1 (t, *J* = 8.5 Hz, 3F), -99.2 (m, 2F), -126.7 (t, *J* = 5.3 Hz, 2F). **HRMS (ESI):** calcd for C<sub>11</sub>H<sub>5</sub>F<sub>7</sub>NO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> 316.0203; found 316.0199.

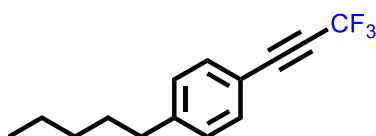
### 1-(3,3,4,4,5,5,5-heptafluoro-penta-1-yn-1-yl)-3,5-dimethoxybenzene (**3k**)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **3k** (40 mg, 61%) as a yellow oil. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 6.69 (d, *J* = 2.2 Hz, 2H), 6.58 (t, *J* = 2.2 Hz, 1H), 3.80 (s, 6H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 160.7, 119.6 (t, *J* = 2.9

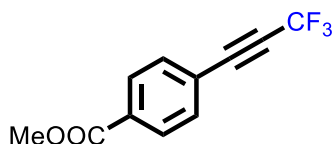
Hz), 110.2 (t,  $J = 2.4$  Hz), 104.4, 92.2 (t,  $J = 6.3$  Hz), 73.8 (t,  $J = 36.4$  Hz), 55.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.1 (t,  $J = 8.3$  Hz, 3F), -98.2 (m, 2F), -126.8 (t,  $J = 5.9$  Hz, 2F). HRMS (ESI): calcd for  $\text{C}_{13}\text{H}_{10}\text{F}_7\text{O}_2^+$   $[\text{M}+\text{H}]^+$  331.0564; found 331.0559.

### 1-pentyl-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (3l)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3l** (37 mg, 77%) as a yellow oil. This compound is known.<sup>5</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 8.1$  Hz, 2H), 7.20 (d,  $J = 8.1$  Hz, 2H), 2.69 – 2.57 (m, 2H), 1.61 (dt,  $J = 15.0, 7.6$  Hz, 2H), 1.39 – 1.27 (m, 4H), 0.89 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.4, 132.4 (d,  $J = 1.1$  Hz), 128.8, 115.6 (d,  $J = 1.5$  Hz), 114.9 (q,  $J = 257.6$  Hz), 87.0 (q,  $J = 6.4$  Hz), 75.2 (q,  $J = 52.3$  Hz), 36.0, 31.4, 30.7, 22.5, 14.0.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -49.6.

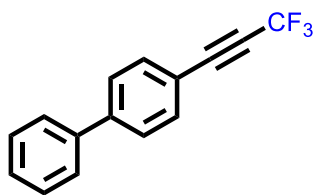
### methyl 4-(3,3,3-trifluoroprop-1-yn-1-yl)benzoate (3m)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) yielded **3m** (30 mg, 66%) as a yellow oil. This compound is known.<sup>6</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.4$  Hz, 2H), 7.63 (d,  $J = 8.3$  Hz, 2H), 3.94 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 132.4 (d,  $J = 1.2$  Hz), 132.1, 129.7, 122.8 (d,  $J = 1.8$  Hz), 114.6 (q,  $J = 257.6$  Hz), 85.2 (q,  $J = 6.6$  Hz), 77.7 (q,  $J = 52.9$  Hz), 52.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -50.2.

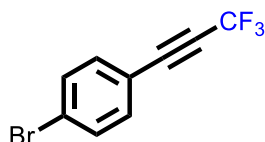
### 4-(3,3,3-trifluoroprop-1-yn-1-yl)-1,1'-biphenyl (3n)





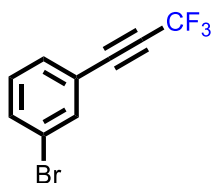
Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3n** (37 mg, 75%) as a white solid. This compound is known.<sup>4</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 – 7.57 (m, 6H), 7.48 (t,  $J = 7.4$  Hz, 2H), 7.44 – 7.37 (m, 1H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.7, 139.7, 132.9 (d,  $J = 1.2$  Hz), 129.0, 128.2, 127.3, 127.1, 117.2 (d,  $J = 1.8$  Hz), 114.9 (q,  $J = 256.7$  Hz), 86.5 (q,  $J = 6.5$  Hz), 76.2 (q,  $J = 52.5$  Hz).  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -49.7.

#### 1-bromo-4-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**3o**)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3o** (31 mg, 62%) as a yellow oil. This compound is known.<sup>6</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 8.5$  Hz, 2H), 7.42 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.7, 132.1, 125.7, 117.4 (d,  $J = 1.5$  Hz), 114.7 (q,  $J = 257.2$  Hz), 85.4 (q,  $J = 6.4$  Hz), 76.7 (q,  $J = 53.0$  Hz).  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -50.0.

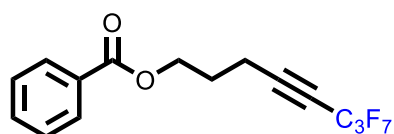
#### 1-bromo-3-(3,3,3-trifluoroprop-1-yn-1-yl)benzene (**3p**)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **3p** (37 mg, 74%) as a yellow oil. This compound is known.<sup>6</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (s, 1H), 7.58 (d,  $J$

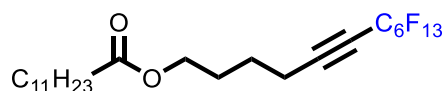
= 8.1 Hz, 1H), 7.46 (d,  $J = 7.8$  Hz, 1H), 7.23 (d,  $J = 7.6$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.1, 134.1, 131.0, 130.1, 122.5, 120.4 (d,  $J = 1.7$  Hz), 114.6 (q,  $J = 257.4$  Hz), 84.6 (q,  $J = 6.5$  Hz), 76.6 (q,  $J = 53.1$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -50.1.

### 6,6,7,7,8,8,8-heptafluoro-octa-4-yn-1-yl benzoate (3q)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) yielded **3q** (30 mg, 42%) as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 – 7.99 (m, 2H), 7.59 – 7.54 (m, 1H), 7.47 – 7.42 (m, 2H), 4.41 (t,  $J = 6.2$  Hz, 2H), 2.62 – 2.53 (m, 2H), 2.12 – 1.96 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 132.9, 130.2, 129.6 (d,  $J = 2.4$  Hz), 128.4 (d,  $J = 4.9$  Hz), 93.6 (t,  $J = 6.0$  Hz), 67.8 (t,  $J = 36.2$  Hz), 63.5, 27.7, 17.8.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.1 (t,  $J = 8.5$  Hz, 3F), -97.7 (m, 2F), -126.9 (t,  $J = 5.4$  Hz, 2F). HRMS (ESI): calcd for  $\text{C}_{15}\text{H}_{12}\text{F}_7\text{O}_2^+$   $[\text{M}+\text{H}]^+$  357.0720; found 357.0712.

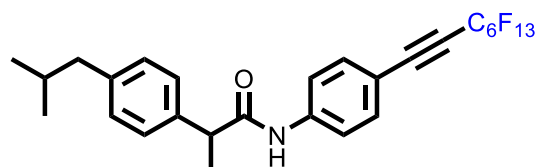
### 7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-dodeca-5-yn-1-yl dodecanoate (3r)



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) yielded **3r** (55 mg, 46%) as a colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.09 (dd,  $J = 11.3, 6.1$  Hz, 2H), 2.50 – 2.34 (m, 2H), 2.29 (t,  $J = 7.5$  Hz, 2H), 1.79 – 1.68 (m, 2H), 1.66 – 1.54 (m, 4H), 1.43 – 1.17 (m, 16H), 0.88 (t,  $J = 6.7$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9 (d,  $J = 7.2$  Hz), 94.4 (t,  $J = 6.6$  Hz), 67.8 (t,  $J = 35.0$  Hz), 63.4 (d,  $J = 40.0$  Hz), 34.3 (d,  $J = 8.1$  Hz), 31.9, 29.6 (d,  $J = 1.4$  Hz), 29.5 (d,  $J = 1.8$  Hz), 29.3, 29.2 (d,  $J = 2.3$  Hz), 29.2 (d,  $J = 1.9$  Hz), 27.7 (d,  $J = 13.9$  Hz), 25.0, 23.9, 22.7, 20.5, 18.2, 14.1 (d,  $J = 2.2$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.8 (t,  $J = 9.9$  Hz, 3F), -96.4 (m, 2F), -121.3 (m, 2F), -122.7 (d,  $J = 106.6$  Hz, 4F), -126.1 (td,  $J = 14.3, 6.5$  Hz, 2F). HRMS (ESI): calcd

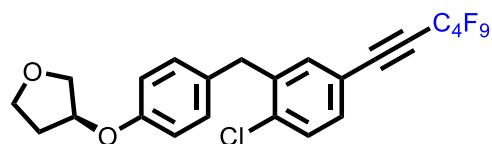
for  $C_{24}H_{32}F_{13}O_2^+$   $[M+H]^+$  599.2189; found 599.2176.

**2-(4-isobutylphenyl)-*N*-(4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octa-1-yn-1-yl)phenyl)propenamide (3s)**



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **3s** (77 mg, 62%) as a yellow solid.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.54 – 7.44 (m, 4H), 7.27 (d,  $J$  = 8.8 Hz, 2H), 7.19 (d,  $J$  = 8.0 Hz, 2H), 3.73 (q,  $J$  = 7.1 Hz, 1H), 2.50 (d,  $J$  = 7.2 Hz, 2H), 1.89 (dp,  $J$  = 13.5, 6.7 Hz, 1H), 1.61 (d,  $J$  = 7.1 Hz, 3H), 0.93 (d,  $J$  = 6.6 Hz, 6H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  172.8, 141.4, 140.4, 137.5, 133.4, 130., 127.4, 119.2, 113.5, 92.2 (t,  $J$  = 6.3 Hz), 74.3 (t,  $J$  = 36.0 Hz), 47.9, 45.0, 30.2, 22.3, 18.4.  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -80.8 (t,  $J$  = 9.4 Hz, 3F), -96.8 (d,  $J$  = 3.0 Hz, 2F), -121.3 (m, 2F), -122.4 (dd,  $J$  = 10.5, 5.3 Hz, 2F), -122.8 (m, 2F), -126.1 (dd,  $J$  = 14.3, 8.2 Hz, 2F). HRMS (ESI): calcd for  $C_{27}H_{23}F_{13}NO^+$   $[M+H]^+$  624.1567; found 624.1556.

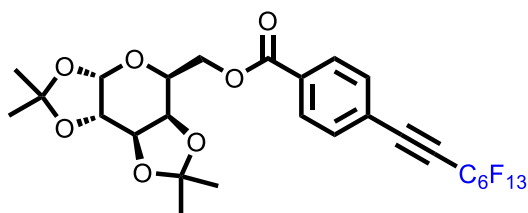
**(*S*)-3-(4-((2-chloro-5-(3,3,4,4,5,5,6,6,6-nonafluoro-hexa-1-yn-1-yl)phenyl)methyl)phenoxy)tetrahydrofuran (3t)**



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **3t** (56 mg, 53%) as a yellow oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.41 (d,  $J$  = 8.1 Hz, 1H), 7.35 (dd,  $J$  = 10.6, 2.3 Hz, 2H), 7.09 (d,  $J$  = 8.6 Hz, 2H), 6.86 – 6.77 (m, 2H), 4.90 (qd,  $J$  = 4.6, 2.3 Hz, 1H), 4.06 – 3.85 (m, 6H), 2.27 – 2.08 (m, 2H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  156.1, 140.1, 137.6, 134.5 (t,  $J$  = 2.3 Hz), 131.5 (t,  $J$  = 2.1 Hz), 130.6, 130.1, 130.0, 117.1 (t,  $J$  = 3.0 Hz), 115.5, 91.3 (t,  $J$  = 6.3 Hz), 75.2 (t,  $J$  = 36.2 Hz), 73.1, 67.2, 38.1,

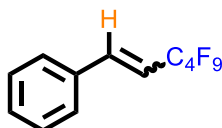
33.0, 29.7.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.0 (t,  $J = 9.6$  Hz, 3F), -97.5 (m, 2F), -123.3 (m, 2F), -125.4 (m, 2F). HRMS (ESI): calcd for  $\text{C}_{23}\text{H}_{16}\text{ClF}_9\text{O}_2\text{Na}^+$   $[\text{M}+\text{Na}]^+$  553.0587; found 553.0579.

**((5*S*,5*aR*,8*aR*,8*bS*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octa-1-yn-1-yl)benzoate (3u)**



Following the General Procedure A, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) yielded **3u** (76 mg, 54%) as a yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 8.3$  Hz, 2H), 7.63 (d,  $J = 8.3$  Hz, 2H), 5.56 (d,  $J = 5.0$  Hz, 1H), 4.66 (dd,  $J = 7.9, 2.5$  Hz, 1H), 4.55 (dd,  $J = 11.6, 4.5$  Hz, 1H), 4.45 (dd,  $J = 11.6, 7.7$  Hz, 1H), 4.33 (ddd,  $J = 9.7, 6.4, 2.2$  Hz, 2H), 4.23 – 4.12 (m, 1H), 1.49 (d,  $J = 12.3$  Hz, 6H), 1.34 (d,  $J = 8.3$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 132.5 (t,  $J = 1.7$  Hz), 132.3, 129.8, 122.8 (t,  $J = 3.0$  Hz), 109.8, 108.8, 96.3, 91.0 (t,  $J = 6.0$  Hz), 76.8 (t,  $J = 36.4$  Hz), 71.1, 70.8, 70.5, 66.1, 64.5, 26.0 (d,  $J = 3.1$  Hz), 24.9, 24.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.8 (m, 3F), -97.7 (m, 2F), -121.3 (m, 2F), -122.4 (m, 2F), -122.8 (m, 2F), -126.1 (m, 2F). HRMS (ESI): calcd for  $\text{C}_{27}\text{H}_{23}\text{F}_{13}\text{O}_7\text{Na}^+$   $[\text{M}+\text{Na}]^+$  729.1128; found 729.1114.

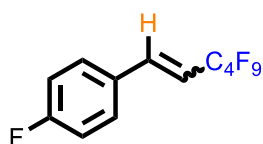
**(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)benzene (4a)**



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4a** (47 mg, 73%) as a yellow oil. The ratio of *E/Z* is **56:44** by  $^1\text{H}$  NMR. This compound is known.<sup>7</sup>  $^1\text{H}$  NMR (400

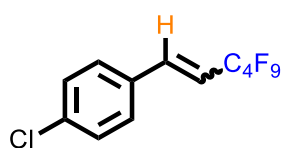
**MHz, CDCl<sub>3</sub>**)  $\delta$  7.53 – 7.31 (m, 10H, *E+Z*), 7.17 (ddd,  $J = 16.9, 5.2, 2.6$  Hz, 2H, *E+Z*), 6.21 (dt,  $J = 16.0, 12.2$  Hz, 1H, *E*), 5.75 (dd,  $J = 29.0, 15.7$  Hz, 1H, *Z*). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  142.1 (t,  $J = 5.1$  Hz), 139.8 (t,  $J = 9.6$  Hz), 134.0, 133.6, 130.2, 129.0, 128.8, 128.7 (t,  $J = 3.5$  Hz), 128.1, 127.7, 115.7 (t,  $J = 22.0$  Hz), 114.3 (t,  $J = 23.1$  Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -81.0 (m, 6F, *E+Z*), -105.5 (dd,  $J = 24.8, 12.1$  Hz, *Z*, 2F), -111.31 (q,  $J = 11.8$  Hz, *E*, 2F), -124.1 (dd,  $J = 17.1, 8.5$  Hz, *E+Z*, 4F), -125.7 (dd,  $J = 19.9, 9.1$  Hz, *E+Z*, 4F).

#### 1-fluoro-4-(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)benzene (**4b**)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4b** (40 mg, 59%) as a yellow oil. The ratio of *E/Z* is **58:42** by <sup>1</sup>H NMR. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.52 – 7.43 (m, 2H, *E*), 7.36 (dd,  $J = 8.3, 5.4$  Hz, 2H, *Z*), 7.19 – 7.01 (m, 6H, *E+Z*), 6.13 (dt,  $J = 16.0, 12.1$  Hz, 1H, *E*), 5.74 (dd,  $J = 28.9, 15.8$  Hz, 1H, *Z*). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  163.8 (d,  $J = 251.0$  Hz), 163.0 (d,  $J = 249.4$  Hz), 141.0 (t,  $J = 5.1$  Hz), 138.6 (t,  $J = 9.6$  Hz), 130.9 – 130.6 (m), 129.5 (d,  $J = 8.6$  Hz), 116.1 (d,  $J = 22.0$  Hz), 115.8 (t,  $J = 21.9$  Hz), 115.3 (d,  $J = 21.8$  Hz), 114.0 (t,  $J = 23.0$  Hz). **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)**  $\delta$  -81.1 (d,  $J = 7.8$  Hz, 6F, *E+Z*), -105.5 (dd,  $J = 25.7, 13.4$  Hz, 2F, *Z*), -109.9 (m, 1F, *E*), -111.3 (q,  $J = 11.7$  Hz, 2F, *E*), -112.0 (m, 1F, *Z*), -124.1 (m, 4F, *E+Z*), -125.7 (m, 4F, *E+Z*). **HRMS (ESI):** calcd for C<sub>12</sub>H<sub>7</sub>F<sub>10</sub><sup>+</sup> [M+H]<sup>+</sup> 341.0383; found 341.0380.

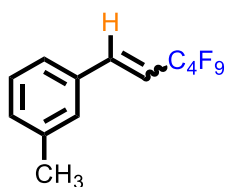
#### 1-chloro-4-(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)benzene (**4c**)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) yielded **4c** (48 mg,

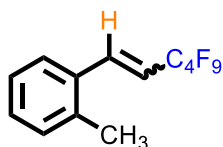
67%) as a yellow oil. The ratio of *E/Z* is **47:53** by  $^1\text{H}$  NMR. This compound is known.<sup>7</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.18 (m, 8H, *E+Z*), 7.11 – 6.97 (m, 2H, *E+Z*), 6.11 (dt,  $J = 16.1, 12.1$  Hz, 1H, *E*), 5.70 (dd,  $J = 28.7, 15.7$  Hz, 1H, *Z*).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 138.5 (t,  $J = 9.7$  Hz), 136.2, 135.0, 132.4, 132.0, 130.1 (t,  $J = 3.6$  Hz), 129.3, 128.9, 128.4, 116.4 (t,  $J = 22.0$  Hz), 114.9 (t,  $J = 23.1$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.0 (m, 6F, *E+Z*), -105.6 (m, 2F, *Z*), -111.5 (m, 2F, *E*), -124.1 (m, 4F, *E+Z*), -125.7 (m, 4F, *E+Z*).

#### 1-methyl-3-(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)benzene (4d)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4d** (52 mg, 77%) as a yellow oil. The ratio of *E/Z* is **43:57** by  $^1\text{H}$  NMR. This compound is known.<sup>8</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.16 (m, 8H, *E+Z*), 7.16 – 7.08 (m, 2H, *E+Z*), 6.19 (dt,  $J = 16.0, 12.2$  Hz, 1H, *E*), 5.73 (dd,  $J = 28.9, 15.8$  Hz, 1H, *Z*), 2.38 (d,  $J = 8.0$  Hz, 6H, *E+Z*).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3 (t,  $J = 5.0$  Hz), 139.9 (t,  $J = 9.5$  Hz), 138.7, 137.7, 134.0, 133.5, 131.0, 129.6, 129.4 (t,  $J = 3.3$  Hz), 128.8, 128.3, 128.0, 125.8 (t,  $J = 3.8$  Hz), 124.9, 115.4 (t,  $J = 21.8$  Hz), 114.0 (t,  $J = 23.0$  Hz), 29.7, 21.3 (d,  $J = 3.3$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (ddd,  $J = 9.3, 8.1, 3.2$  Hz, 6F, *E+Z*), -105.5 (dd,  $J = 25.0, 12.4$  Hz, 2F, *Z*), -111.3 (dt,  $J = 20.0, 11.3$  Hz, 2F, *E*), -124.1 (m, 4F, *E+Z*), -125.7 (m, 4F, *E+Z*).

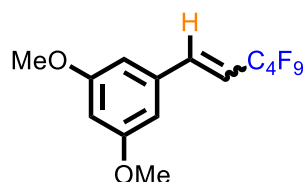
#### 1-methyl-2-(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)benzene (4e)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4e** (48 mg, 71%) as a yellow

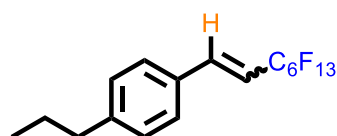
oil. The ratio of *E/Z* is **43:57** by  $^1\text{H NMR}$ . This compound is known.<sup>9</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.35 (m, 2H, *E+Z*), 7.33 – 7.15 (m, 8H, *E+Z*), 6.11 (dt,  $J = 15.9, 12.2$  Hz, 1H, *E*), 5.84 (dd,  $J = 27.9, 15.1$  Hz, 1H, *Z*), 2.41 (s, 3H, *E*), 2.27 (s, 3H, *Z*).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.7 (t,  $J = 5.5$  Hz), 137.8 (t,  $J = 9.1$  Hz), 137.0, 135.4, 133.9, 132.8, 130.7, 129.9, 129.5, 128.5, 128.3 (t,  $J = 4.2$  Hz), 126.5, 126.3, 125.4, 116.9 (t,  $J = 21.4$  Hz), 115.6 (t,  $J = 22.9$  Hz), 19.8, 19.6.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (m, 6F, *E+Z*), -106.5 (dd,  $J = 25.0, 12.5$  Hz, 2F, *Z*), -111.27 (q,  $J = 11.5$  Hz, 2F, *E*), -124.2 (m, 2F, *E+Z*), -125.7 (m, 2F, *E+Z*).

#### 1,3-dimethoxy-5-(3,3,4,4,5,5,6,6,6-nonafluoro-hexa-1-en-1-yl)benzene (**4f**)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4f** (52 mg, 68%) as a yellow oil. The ratio of *E/Z* is **57:43** by  $^1\text{H NMR}$ . This compound is known.<sup>4</sup>  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.16 – 7.02 (m, 2H, *E+Z*), 6.61 (d,  $J = 2.2$  Hz, 2H, *E+Z*), 6.54 – 6.44 (m, 3H, *E+Z*), 6.17 (dt,  $J = 15.9, 12.2$  Hz, 1H, *E*), 5.74 (dd,  $J = 28.8, 15.6$  Hz, 1H, *Z*), 3.82 (s, 6H, *E*), 3.79 (s, 6H, *Z*).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 160.5, 142.0 (t,  $J = 5.0$  Hz), 139.8 (t,  $J = 9.5$  Hz), 135.8, 135.4, 116.0 (t,  $J = 22.1$  Hz), 114.8 (t,  $J = 23.0$  Hz), 106.7 (t,  $J = 3.6$  Hz), 105.7, 102.3, 101.1, 55.4, 55.3.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.1 (m, 6F, *E+Z*), -105.55 (dt,  $J = 15.3, 7.7$  Hz, 2F, *Z*), -111.36 (q,  $J = 12.1$  Hz, 2F, *E*), -124.1 (m, 4F, *E+Z*), -125.7 (m, 4F, *E+Z*).

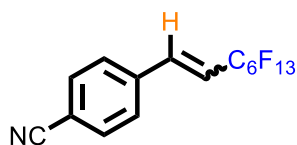
#### 1-propyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octa-1-en-1-yl)benzene (**4g**)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4g** (74 mg, 80%) as a yellow

oil. The ratio of *E/Z* is **43:57** by  $^1\text{H NMR}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 8.0$  Hz, 2H, *E*), 7.32 (d,  $J = 7.9$  Hz, 2H, *Z*), 7.20 (dd,  $J = 15.4, 8.0$  Hz, 4H, *E+Z*), 7.16 – 7.05 (m, 2H, *E+Z*), 6.25 – 6.09 (m, 1H, *E*), 5.70 (dd,  $J = 29.3, 15.9$  Hz, 1H, *Z*), 2.70 – 2.54 (m, 4H, *E+Z*), 1.76 – 1.59 (m, 4H, *E+Z*), 0.96 (t,  $J = 7.3$  Hz, 6H, *E+Z*).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 143.9, 142.1 (t,  $J = 4.9$  Hz), 139.7 (t,  $J = 9.5$  Hz), 131.3, 131.1, 129.1, 129.0 (t,  $J = 3.7$  Hz), 128.3, 127.6, 114.7 (t,  $J = 21.9$  Hz), 113.2 (t,  $J = 23.1$  Hz), 37.8 (d,  $J = 5.2$  Hz), 24.4 (d,  $J = 6.0$  Hz), 13.7 (d,  $J = 5.2$  Hz).  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.9 (dd,  $J = 8.9, 6.3$  Hz, 6F, *E+Z*), -105.2 (q,  $J = 13.8$  Hz, 2F, *Z*), -110.9 (m, 2F, *E*), -121.6 (d,  $J = 10.4$  Hz, 4F, *E+Z*), -122.9 (m, 4F, *E+Z*), -123.3 (m, 4F, *E+Z*), -126.2 (m, 4F, *E+Z*). **HRMS** (ESI): calcd for  $\text{C}_{17}\text{H}_{14}\text{F}_{13}^+$   $[\text{M}+\text{H}]^+$  465.0882; found 465.0873.

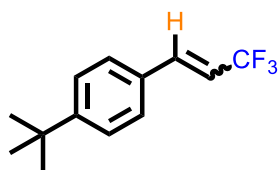
#### 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octa-1-en-1-yl)benzotrile (4h)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) yielded **4h** (47 mg, 53%) as a yellow oil. The ratio of *E/Z* is **33:67** by isolated yields. **E isomers:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 8.3$  Hz, 2H), 7.58 (d,  $J = 8.3$  Hz, 2H), 7.20 (d,  $J = 16.2$  Hz, 1H), 6.32 (dt,  $J = 16.0, 11.8$  Hz, 1H). **E isomers:**  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.9 (t,  $J = 9.8$  Hz), 137.7, 132.8, 128.1, 118.1 (t,  $J = 23.2$  Hz), 118.1, 113.7. **E isomers:**  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.76 (dd,  $J = 13.4, 6.1$  Hz, 3F), -111.7 (m, 2F), -121.55 (m, 2F), -122.81 (m, 2F), -123.0 (m, 2F), -126.1 (m, 2F). **Z isomers:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 8.2$  Hz, 2H), 7.43 (d,  $J = 8.1$  Hz, 2H), 7.16 (d,  $J = 12.8$  Hz, 1H), 5.91 (dd,  $J = 28.6, 15.1$  Hz, 1H). **Z isomers:**  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9 (t,  $J = 5.2$  Hz), 138.7, 131.9, 129.1 (t,  $J = 3.4$  Hz), 118.8 (t,  $J = 22.1$  Hz), 118.3, 112.5. **Z isomers:**  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.8 (t,  $J = 10.0$  Hz, 3F), -105.7 (m, 2F), -121.6 (m, 2F), -122.9 (m, 2F), -123.1 (m, 2F), -126.1 (m, 2F). **HRMS** (ESI): calcd for  $\text{C}_{15}\text{H}_7\text{F}_{13}\text{N}^+$   $[\text{M}+\text{H}]^+$  448.0365; found 448.0357.

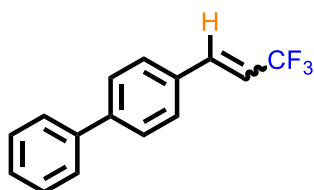


#### 1-(tert-butyl)-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (4i)



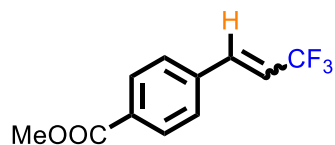
Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4i** (31 mg, 68%) as a yellow oil. The ratio of *E/Z* is **63:37** by  $^1\text{H}$  NMR. This compound is known.<sup>4</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.33 (m, 8H, *E+Z*), 7.14 (dd,  $J = 16.1, 2.1$  Hz, 1H, *E*), 6.88 (d,  $J = 12.7$  Hz, 1H, *Z*), 6.17 (dq,  $J = 16.1, 6.6$  Hz, 1H, *E*), 5.71 (dq,  $J = 12.6, 9.2$  Hz, 1H, *Z*), 1.34 (s, 18H, *E+Z*).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.5, 152.4, 139.5 (q,  $J = 5.9$  Hz), 137.4 (q,  $J = 6.8$  Hz), 130.6, 129.0 (dd,  $J = 5.0, 2.6$  Hz), 127.3, 125.9, 125.3, 117.0 (q,  $J = 35.1$  Hz), 115.0 (q,  $J = 33.7$  Hz), 34.8, 34.7, 31.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.6 (d,  $J = 8.9$  Hz, *Z*), -63.1 (d,  $J = 7.1$  Hz, *E*).

#### 4-(3,3,3-trifluoroprop-1-en-1-yl)-1,1'-biphenyl (4j)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4j** (25 mg, 50%) as a white solid. The ratio of *E/Z* is **71:29** by  $^1\text{H}$  NMR. This compound is known.<sup>10</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.36 (m, 18H, *E+Z*), 7.20 (d,  $J = 16.1$  Hz, 1H, *E*), 6.96 (d,  $J = 12.6$  Hz, 1H, *Z*), 6.25 (dq,  $J = 16.0, 6.5$  Hz, 1H, *E*), 5.80 (dq,  $J = 12.6, 9.1$  Hz, 1H, *Z*).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 141.9, 141.6, 140.2, 140.1, 139.2 (q,  $J = 5.8$  Hz), 137.2 (q,  $J = 6.8$  Hz), 132.5, 132.3, 129.6 (q,  $J = 2.6$  Hz), 128.9, 128.9, 128.0, 127.8, 127.7, 127.6, 127.0 (t,  $J = 4.0$  Hz), 117.8 (q,  $J = 35.0$  Hz), 115.7 (q,  $J = 33.8$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.5 (d,  $J = 9.6$  Hz, *Z*), -63.2 (d,  $J = 6.0$  Hz, *E*).

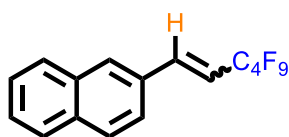
#### methyl 4-(3,3,3-trifluoroprop-1-en-1-yl)benzoate (**4k**)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) yielded **4k** (24 mg, 52%) as a white solid. The ratio of *E/Z* is **50:50** by  $^1\text{H}$  NMR. This compound is known.<sup>8</sup>

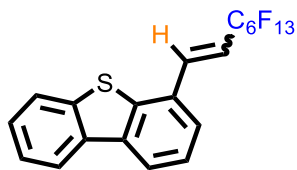
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (t,  $J = 8.6$  Hz, 4H, *E+Z*), 7.48 (dd,  $J = 31.1, 8.3$  Hz, 4H, *E+Z*), 7.19 (dd,  $J = 16.1, 2.0$  Hz, 1H, *E*), 6.97 (d,  $J = 12.6$  Hz, 1H, *Z*), 6.30 (dq,  $J = 16.1, 6.4$  Hz, 1H, *E*), 5.87 (dq,  $J = 12.6, 8.8$  Hz, 1H, *Z*), 3.93 (d,  $J = 2.7$  Hz, 6H, *E+Z*).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 166.4, 138.6 (q,  $J = 5.8$  Hz), 138.1, 137.6, 136.6 (q,  $J = 6.7$  Hz), 131.3, 130.4, 130.2, 129.5, 128.8 (dd,  $J = 4.9, 2.3$  Hz), 127.5, 119.9 (q,  $J = 34.9$  Hz), 118.2 (q,  $J = 34.1$  Hz), 52.3, 52.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.7 (d,  $J = 8.5$  Hz, *Z*), -63.7 (dd,  $J = 6.6, 1.9$  Hz, *E*).

#### 2-(3,3,4,4,5,5,6,6,6-nonafluoro-hexa-1-en-1-yl)naphthalene (**4l**)



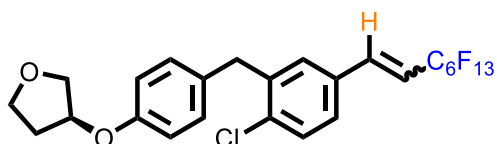
Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4l** (38 mg, 51%) as a yellow solid. The ratio of *E/Z* is **93:7** by  $^1\text{H}$  NMR. **E isomers:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 – 7.79 (m, 4H), 7.62 (dd,  $J = 8.6, 1.6$  Hz, 1H), 7.59 – 7.49 (m, 2H), 7.35 (dt,  $J = 16.1, 2.1$  Hz, 1H), 6.32 (dt,  $J = 15.9, 12.2$  Hz, 1H). **E isomers:**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8 (t,  $J = 9.6$  Hz), 134.1, 133.2, 130.9, 129.3, 128.8, 128.5, 127.8, 127.3, 126.8, 123.1, 114.3 (t,  $J = 23.1$  Hz). **E isomers:**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.0 (m, 3F), -111.10 (q,  $J = 12.2$  Hz, 2F), -124.01 (td,  $J = 18.2, 9.2$  Hz, 2F), -125.6 (m, 2F). **HRMS** (ESI): calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_9$ <sup>+</sup> [M+H]<sup>+</sup> 373.0633; found 373.0629.

#### 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-en-1-yl)dibenzo[*b,d*]thiophene (**4m**)



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether) yielded **4j** (59 mg, 56%) as a yellow solid. The ratio of *E/Z* is **54:46** by  $^1\text{H NMR}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 – 8.09 (m, 4H, *E+Z*), 7.95 – 7.81 (m, 2H, *E+Z*), 7.59 (d,  $J = 7.4$  Hz, 1H, *E*), 7.56 – 7.42 (m, 8H, *E+Z*), 7.33 (d,  $J = 12.5$  Hz, 1H, *Z*), 6.50 (dt,  $J = 16.0, 12.0$  Hz, 1H, *E*), 6.00 (dd,  $J = 28.2, 14.8$  Hz, 1H, *Z*).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.0, 138.7 (m), 137.6 (t,  $J = 9.8$  Hz), 136.8, 135.5 (d,  $J = 3.4$  Hz), 135.1, 129.0, 128.5, 127.3, 127.0, 126.7, 126.6 (t,  $J = 5.1$  Hz), 124.9 (d,  $J = 1.6$  Hz), 124.7, 124.4, 123.0, 122.8 (d,  $J = 4.5$  Hz), 121.8 (m), 118.3 (t,  $J = 22.0$  Hz), 116.7 (t,  $J = 23.0$  Hz).  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.8 (m, 6F, *E+Z*), -106.2 (m, 2F, *Z*), -111.2 (m, 2F, *E*), -121.5 (dd,  $J = 24.5, 13.0$  Hz, 4F, *E+Z*), -122.82 (m, 4F, *E+Z*), -123.0 (m, 4F, *E+Z*), -126.1 (m, 4F, *E+Z*). **HRMS** (ESI): calcd for  $\text{C}_{20}\text{H}_{10}\text{F}_{13}\text{S}^+$   $[\text{M}+\text{H}]^+$  529.0290; found 529.0281.

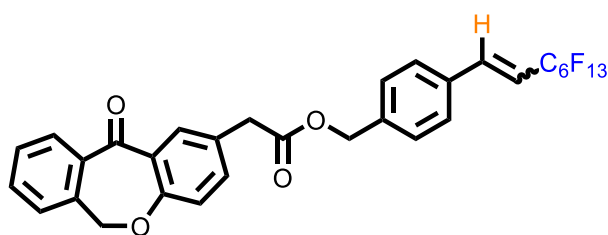
**(S)-3-(4-((2-chloro-5-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-en-1-yl)phenyl)methyl)phenoxy)tetrahydrofuran (4n)**



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **4k** (52 mg, 41%) as a yellow oil. The ratio of *E/Z* is **67:33** by isolated yields. **E isomers:**  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (d,  $J = 8.3$  Hz, 1H), 7.30 (dd,  $J = 8.3, 2.1$  Hz, 1H), 7.22 (d,  $J = 1.9$  Hz, 1H), 7.16 – 7.02 (m, 3H), 6.87 – 6.76 (m, 2H), 6.13 (dt,  $J = 16.0, 12.1$  Hz, 1H), 4.90 (ddd,  $J = 8.0, 5.6, 2.4$  Hz, 1H), 4.06 – 3.87 (m, 6H), 2.26 – 2.09 (m, 2H). **E isomers:**  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.1, 139.8, 138.7 (t,  $J = 9.6$  Hz), 136.1, 132.3, 131.2, 130.4, 130.2, 130.0, 126.2, 115.5, 114.8 (t,  $J = 23.2$  Hz), 77.3, 73.1, 67.2, 38.3, 33.0. **E isomers:**  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.8 (t,  $J = 8.2$  Hz, 3F), -111.1

(q,  $J = 12.3$  Hz, 2F), -121.6 (m, 2F), -122.9 (m, 2F), -123.1 (dd,  $J = 13.4, 9.6$  Hz, 2F), -126.1 (m, 2F). **Z isomers:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 8.2$  Hz, 1H), 7.15 (d,  $J = 8.3$  Hz, 1H), 7.13 – 7.06 (m, 3H), 7.02 (dt,  $J = 12.9, 2.9$  Hz, 1H), 6.89 – 6.71 (m, 2H), 5.72 (dd,  $J = 28.8, 15.7$  Hz, 1H), 4.97 – 4.81 (m, 1H), 4.03 – 3.86 (m, 6H), 2.21 – 2.09 (m, 2H). **Z isomers:**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.0, 140.9 (t,  $J = 5.1$  Hz), 138.9, 134.9, 132.6, 131.3, 131.2 (t,  $J = 3.5$  Hz), 130.0, 129.3, 127.8 (t,  $J = 3.7$  Hz), 116.3 (t,  $J = 22.1$  Hz), 115.4, 77.3, 73.1, 67.2, 38.3, 33.0. **Z isomers:**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.7 (t,  $J = 9.9$  Hz, 3F), -105.4 (m, 2F), -121.6 (m, 2F), -123.0 (m, 2F), -123.2 (m, 2F), -126.1 (m, 2F). **HRMS** (ESI): calcd for  $\text{C}_{25}\text{H}_{18}\text{ClF}_{13}\text{O}_2\text{Na}^+$   $[\text{M}+\text{Na}]^+$  655.0680; found 655.0669.

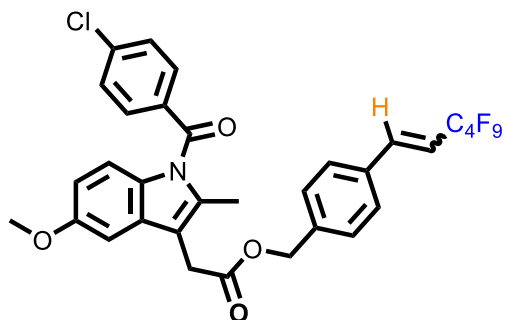
**(4-(3,3,4,4,5,5,6,6,7,7,8,8,8--tridecafluorooct-1-en-1-yl)phenyl)methyl 2-(11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetate (4o)**



Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **4l** (56 mg, 40%) as a yellow oil. The ratio of *E/Z* is **49:51** by  $^1\text{H}$  NMR.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (s, 2H, *E*), 7.89 (d,  $J = 7.7$  Hz, 2H, *Z*), 7.56 (tt,  $J = 7.4, 1.5$  Hz, 2H, *E+Z*), 7.51 – 7.40 (m, 6H, *E+Z*), 7.34 (dd,  $J = 13.4, 8.3$  Hz, 8H, *E+Z*), 7.21 – 7.07 (m, 2H, *E+Z*), 7.03 (d,  $J = 8.4$  Hz, 2H, *E+Z*), 6.21 (dt,  $J = 16.0, 12.1$  Hz, 1H, *E*), 5.77 (dd,  $J = 28.9, 15.7$  Hz, 1H, *Z*), 5.18 (s, 4H, *E*), 5.16 (s, 4H, *Z*), 3.71 (s, 4H, *E+Z*).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8, 171.1 (d,  $J = 6.7$  Hz), 160.5, 141.5 (t,  $J = 5.0$  Hz), 140.4, 139.2 (t,  $J = 9.5$  Hz), 137.9, 136.4, 136.3, 135.5 (d,  $J = 2.3$  Hz), 133.9, 133.4, 132.8 (d,  $J = 3.9$  Hz), 132.5, 129.4 (d,  $J = 2.0$  Hz), 129.2, 128.9 (t,  $J = 3.6$  Hz), 128.6, 127.8 (d,  $J = 3.8$  Hz), 127.5 (d,  $J = 7.0$  Hz), 125.2, 121.1 (d,  $J = 1.5$  Hz), 116.1 (t,  $J = 22.0$  Hz), 114.7 (t,  $J = 23.1$  Hz), 73.6, 66.1 (d,  $J = 12.9$  Hz), 40.1 (d,  $J = 0.9$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -80.8 (m, 6F, *E+Z*), -105.3 (m, 2F, *Z*), -111.1 (m, 2F, *E*), -121.6 (m, 4F,

*E+Z*), -122.9 (m, 4F, *E+Z*), -123.2 (m, 4F, *E+Z*), -126.1 (m, 4F, *E+Z*). **HRMS** (ESI): calcd for C<sub>31</sub>H<sub>19</sub>F<sub>13</sub>O<sub>4</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> 725.0968; found 725.0951.

**4-(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)phenyl)methyl** **2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (4p)**

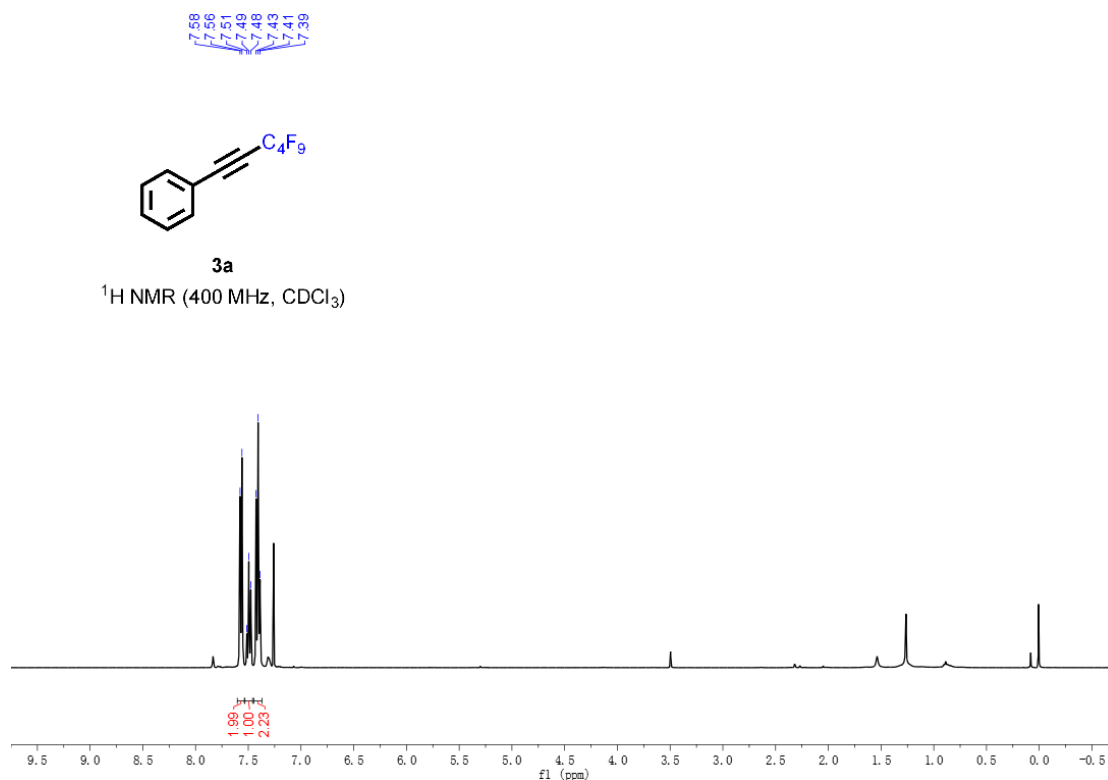


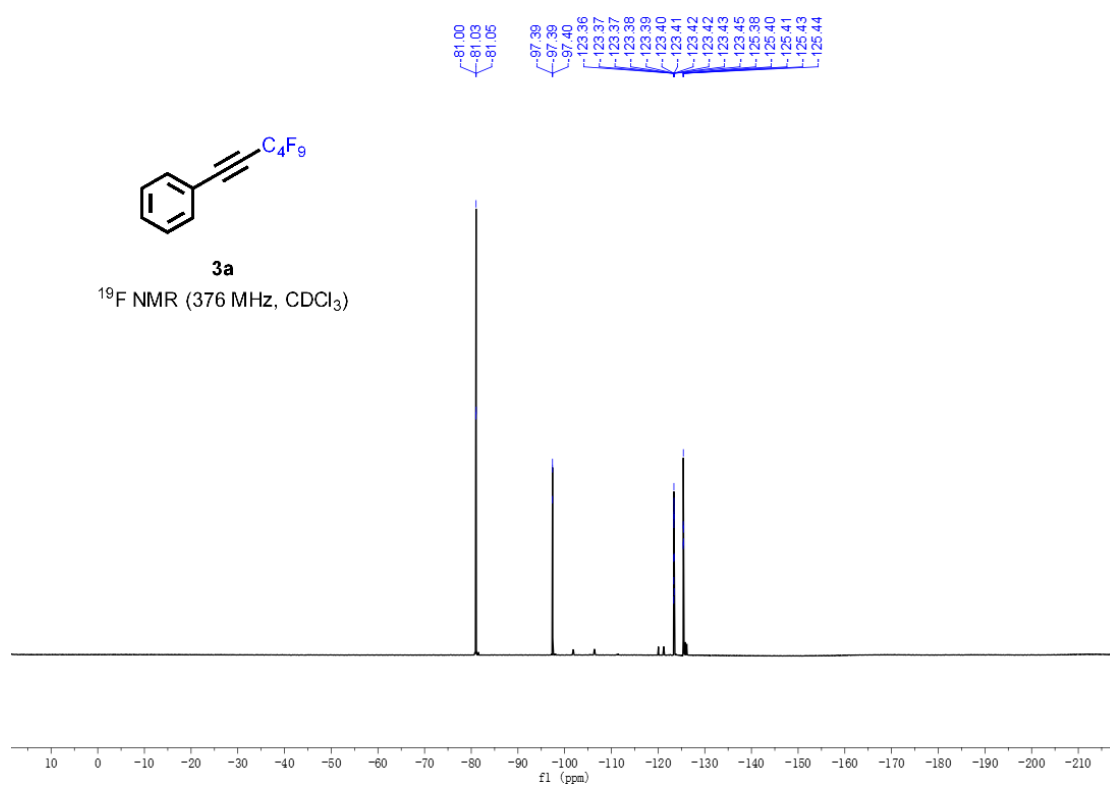
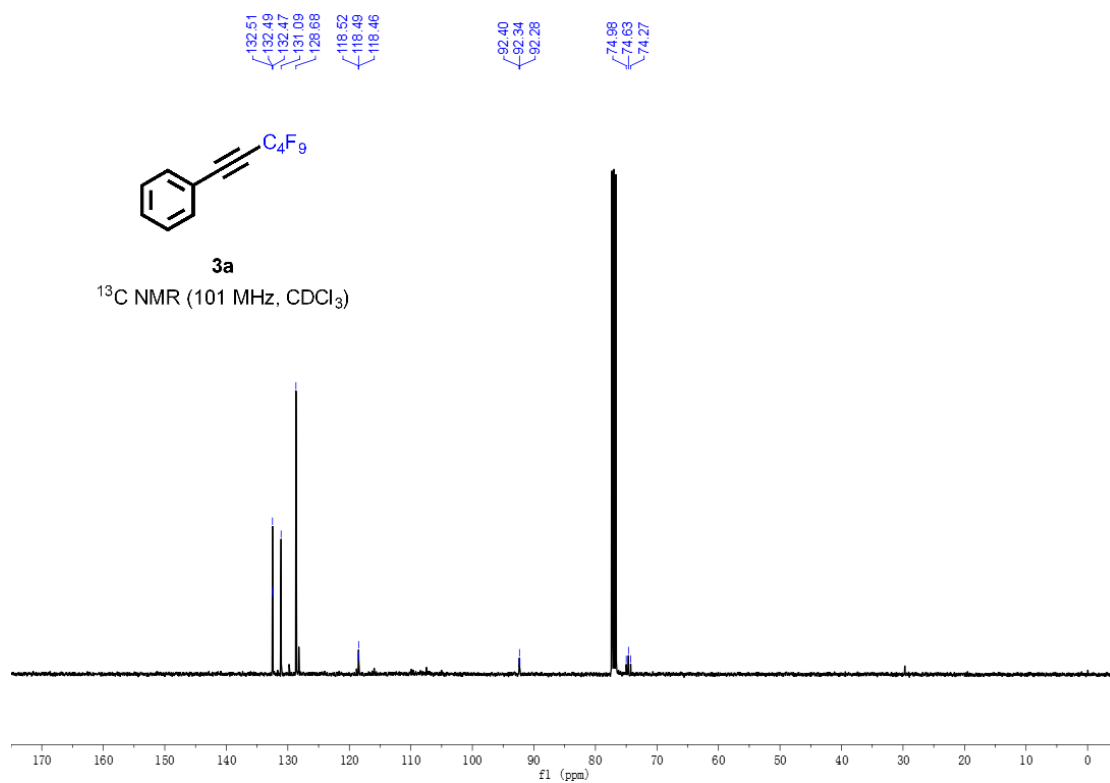
Following the General Procedure B, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) yielded **4m** (59 mg, 43%) as a yellow solid. The ratio of *E/Z* is **41:59** by <sup>1</sup>H NMR. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.65 (d, *J* = 8.6 Hz, 4H, *E+Z*), 7.51 – 7.40 (m, 6H, *E+Z*), 7.32 (dt, *J* = 12.1, 7.0 Hz, 6H, *E+Z*), 7.21 – 7.06 (m, 2H, *E+Z*), 6.94 (dd, *J* = 7.2, 2.4 Hz, 2H, *E+Z*), 6.89 (d, *J* = 9.0 Hz, 2H, *E+Z*), 6.68 (dd, *J* = 9.0, 2.4 Hz, 2H, *E+Z*), 6.21 (dt, *J* = 15.9, 12.1 Hz, 1H, *E*), 5.77 (dd, *J* = 28.9, 15.8 Hz, 1H, *Z*), 5.15 (s, 4H, *E+Z*), 3.77 (s, 6H, *E+Z*), 3.73 (d, *J* = 1.5 Hz, 4H, *E+Z*), 2.38 (s, 6H, *E+Z*). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.5 (d, *J* = 5.2 Hz), 168.2, 156.0 (d, *J* = 1.7 Hz), 141.5 (t, *J* = 5.0 Hz), 139.3 (d, *J* = 4.4 Hz), 139.1 (t, *J* = 9.3 Hz), 137.9, 136.5, 136.0 (d, *J* = 1.9 Hz), 133.9, 133.8 (d, *J* = 3.7 Hz), 133.4, 131.1, 130.8, 130.5 (d, *J* = 2.4 Hz), 129.1, 128.9 (t, *J* = 3.5 Hz), 128.5, 127.7 (d, *J* = 7.9 Hz), 116.0 (t, *J* = 21.9 Hz), 114.7 (t, *J* = 23.2 Hz), 112.3 (d, *J* = 7.5 Hz), 111.7 (d, *J* = 11.1 Hz), 101.2 (d, *J* = 10.4 Hz), 100.0, 66.1 (d, *J* = 11.2 Hz), 55.5 (d, *J* = 2.8 Hz), 30.3, 13.3. **<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -81.0 (td, *J* = 9.6, 2.2 Hz, 6F, *E+Z*), -105.6 (dd, *J* = 25.3, 12.8 Hz, 2F, *Z*), -111.4 (q, *J* = 11.6 Hz, 2F, *E*), -124.1 (ddd, *J* = 27.7, 18.5, 9.0 Hz, 4F, *E+Z*), -125.7 (dt, *J* = 8.9, 7.6 Hz, 4F, *E+Z*). **HRMS** (ESI): calcd for C<sub>32</sub>H<sub>23</sub>ClF<sub>9</sub>NO<sub>4</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> 714.1064; found 714.1051.

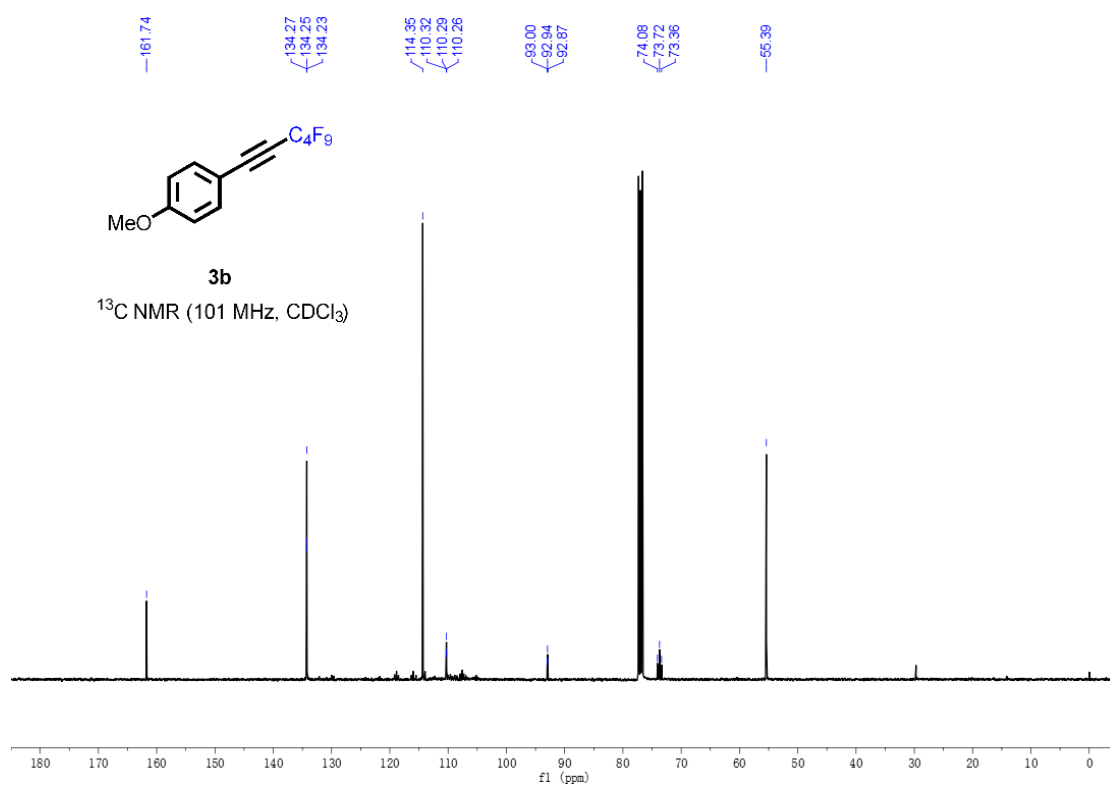
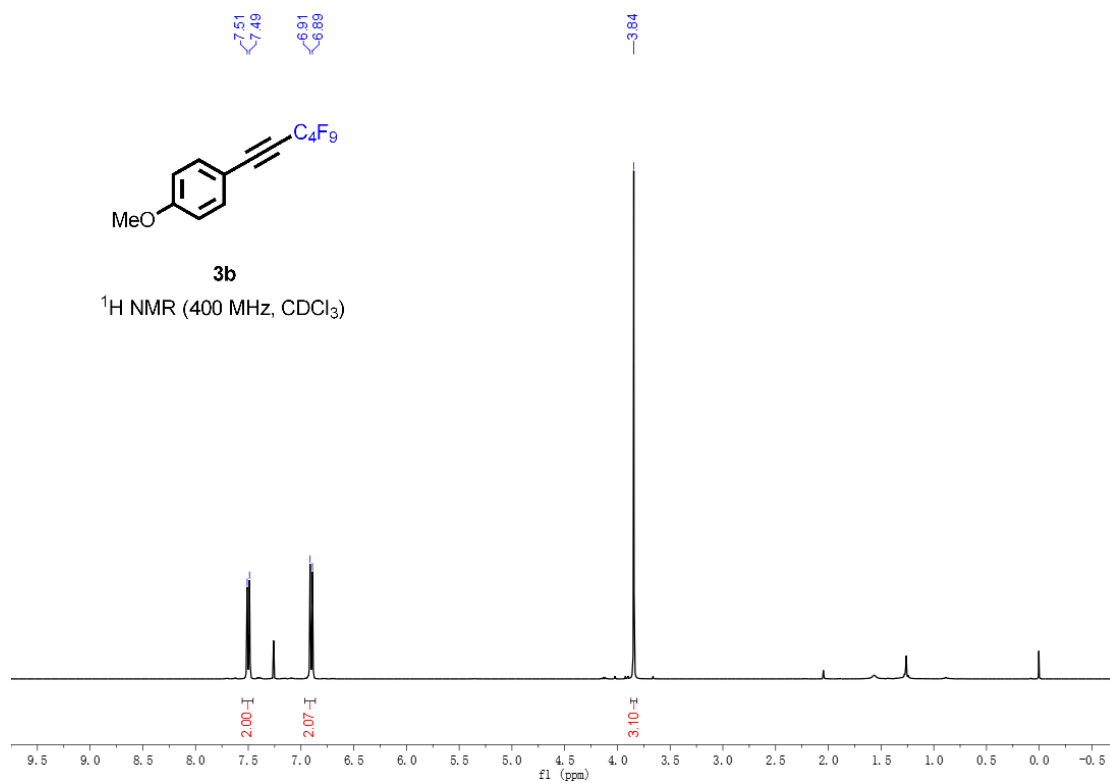
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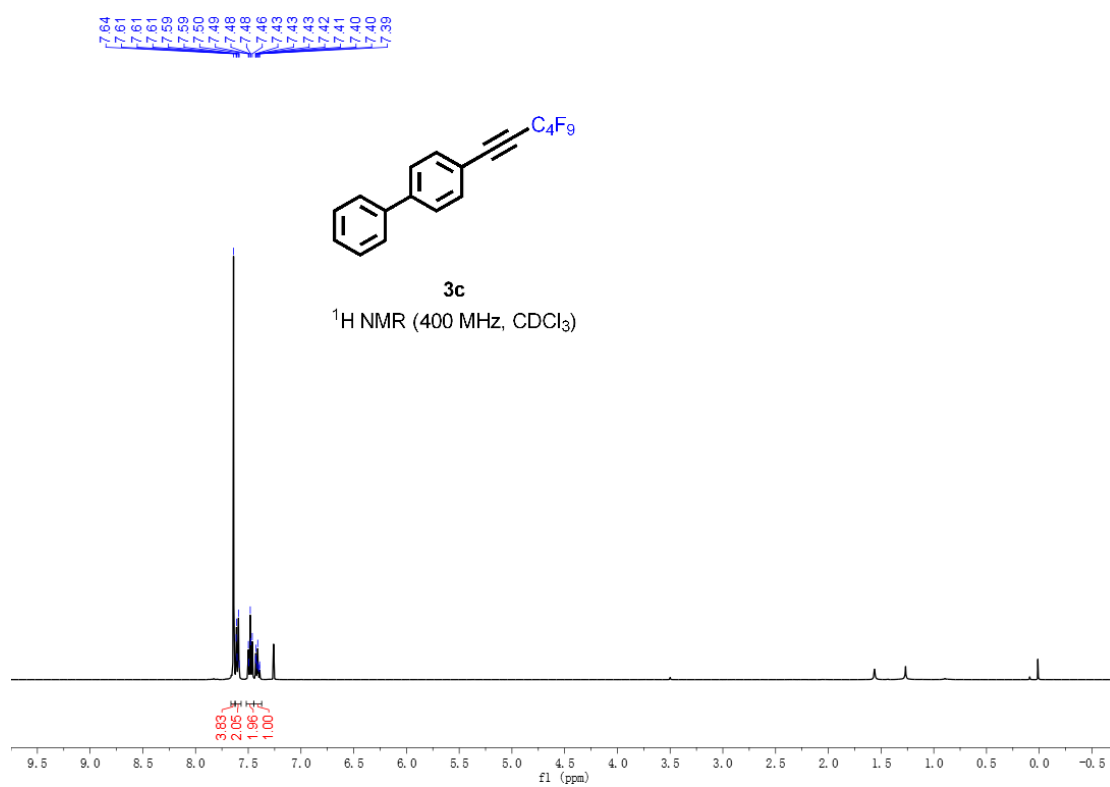
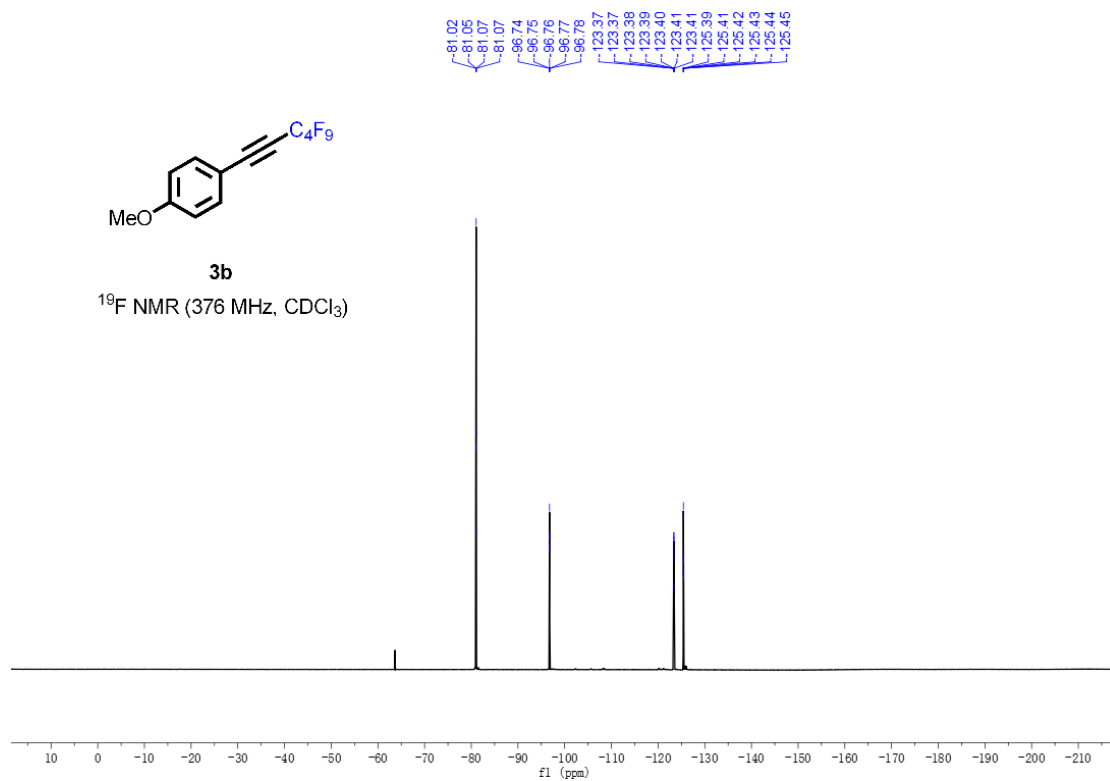
## 8. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR and $^{19}\text{F}$ NMR spectra

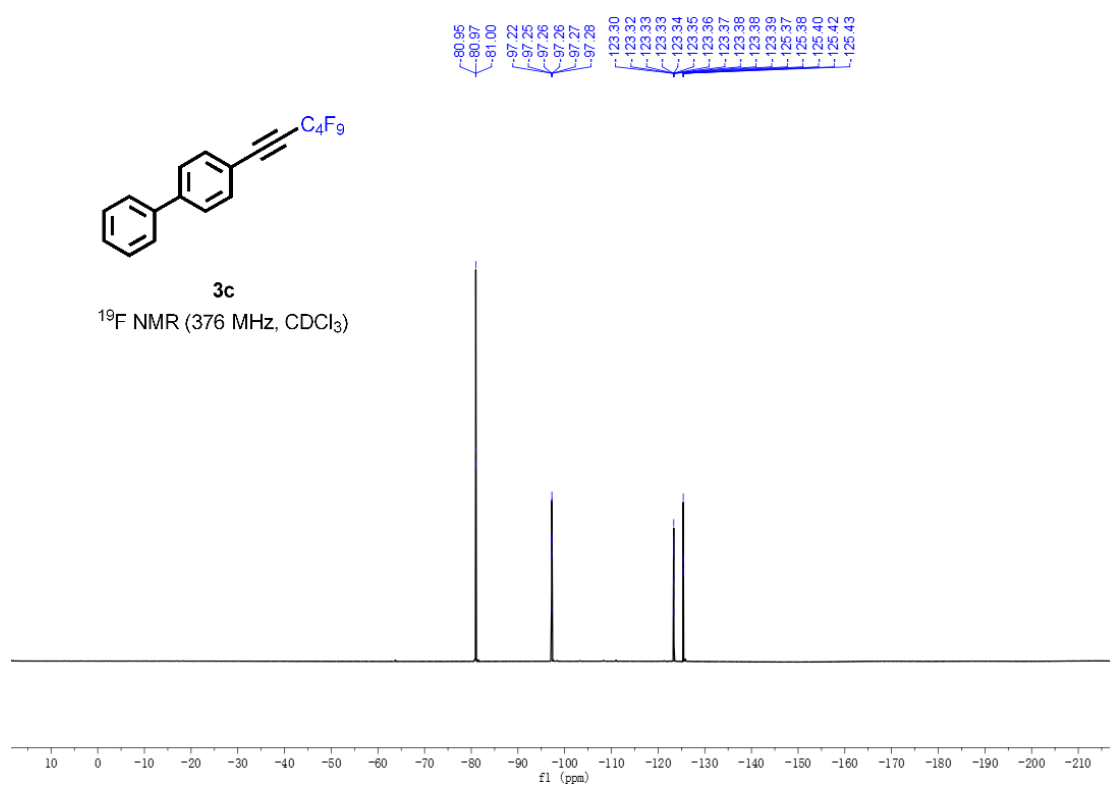
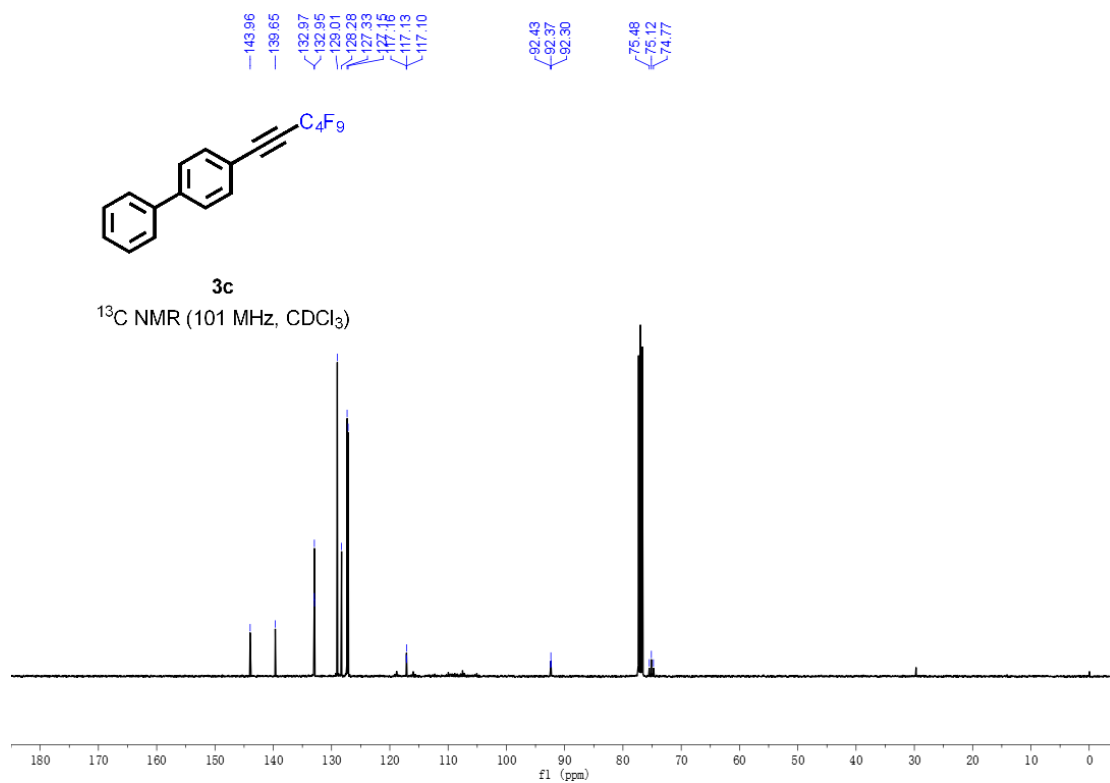


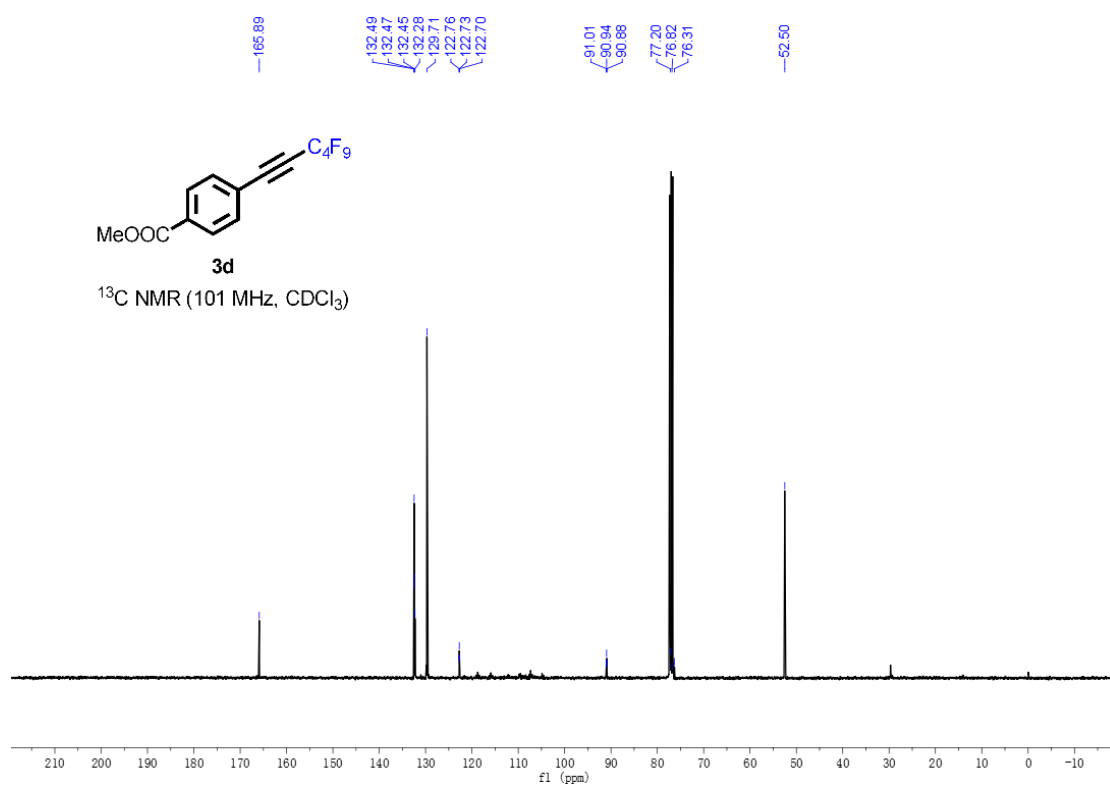
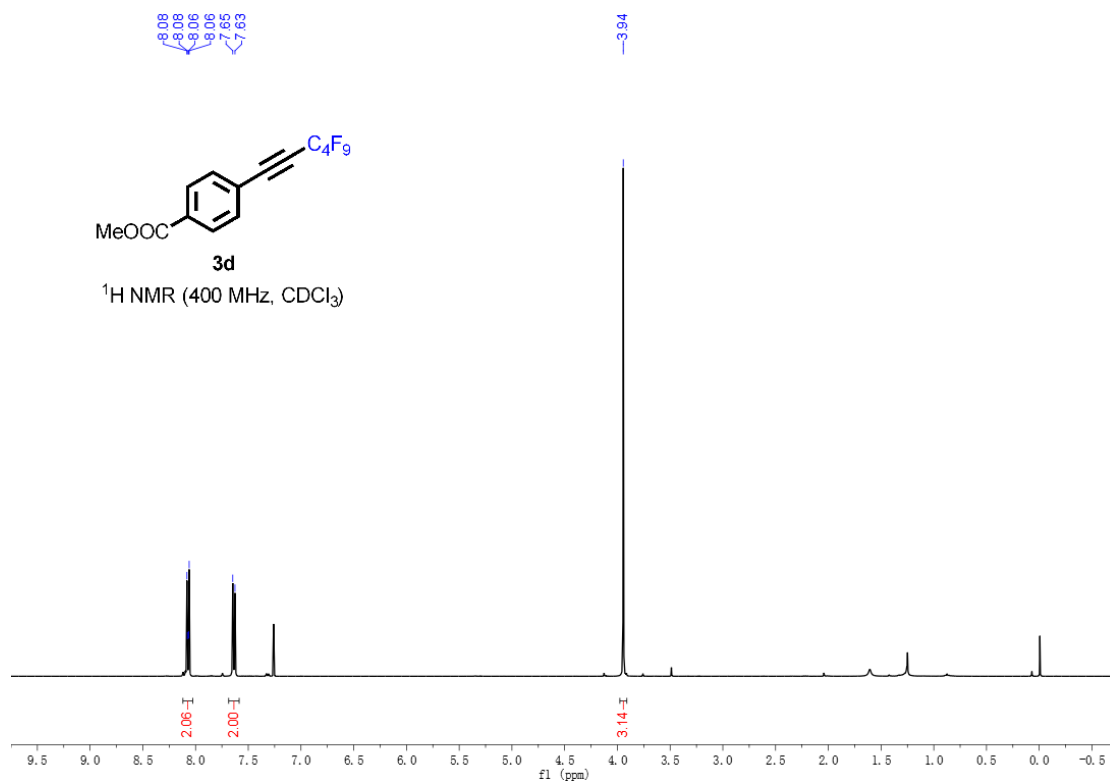


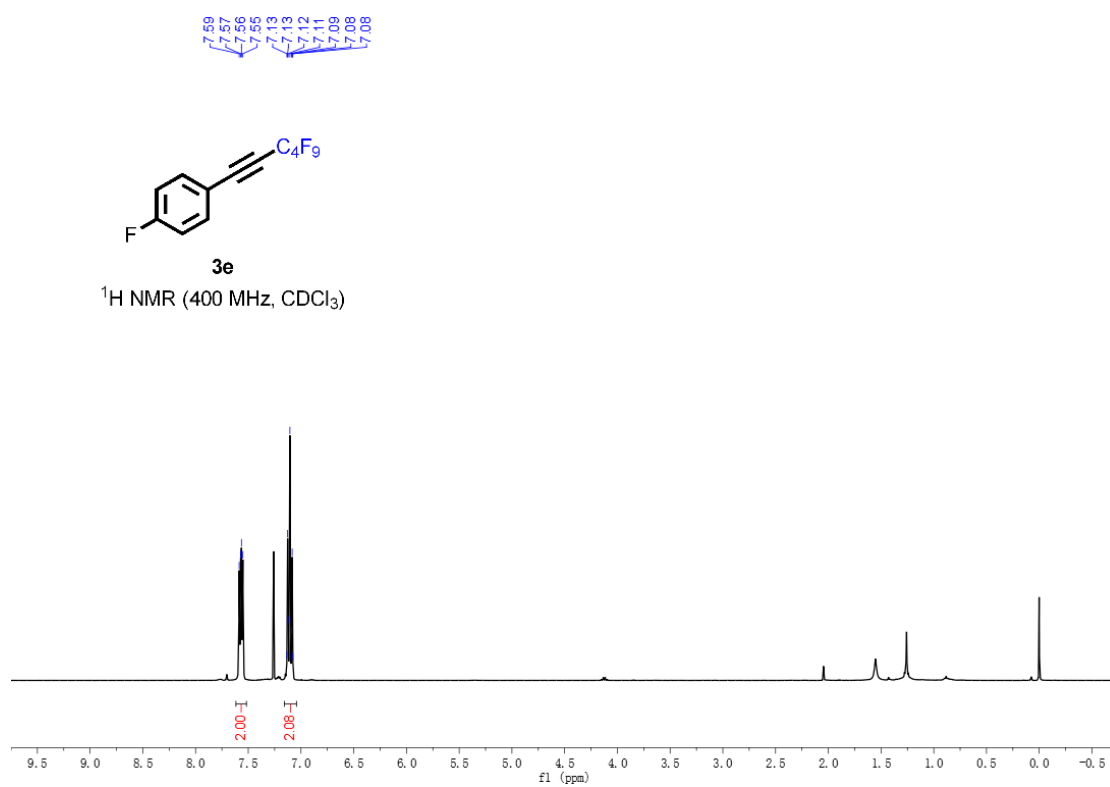
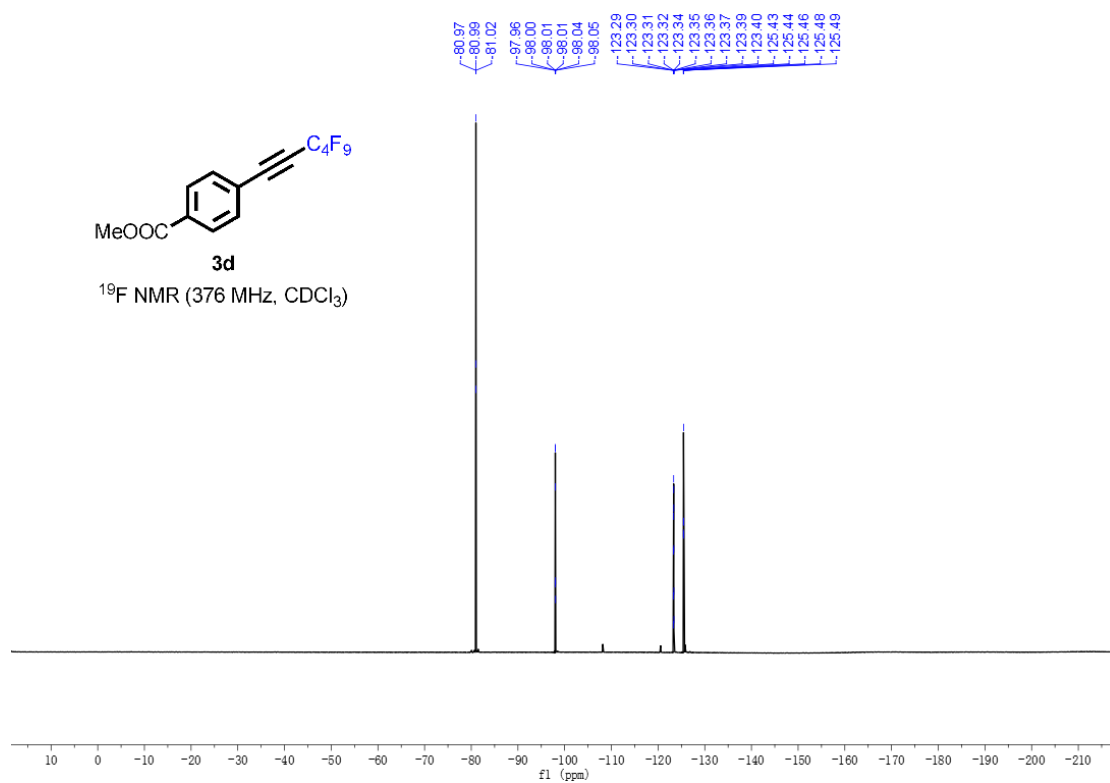


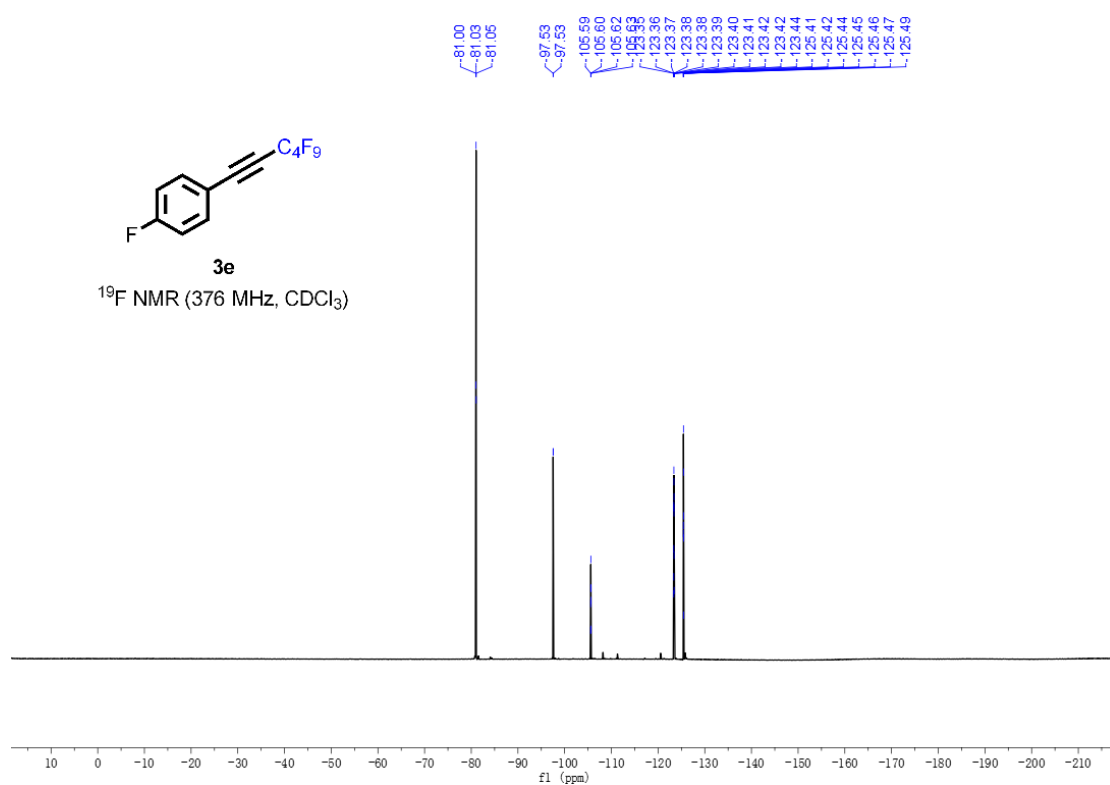
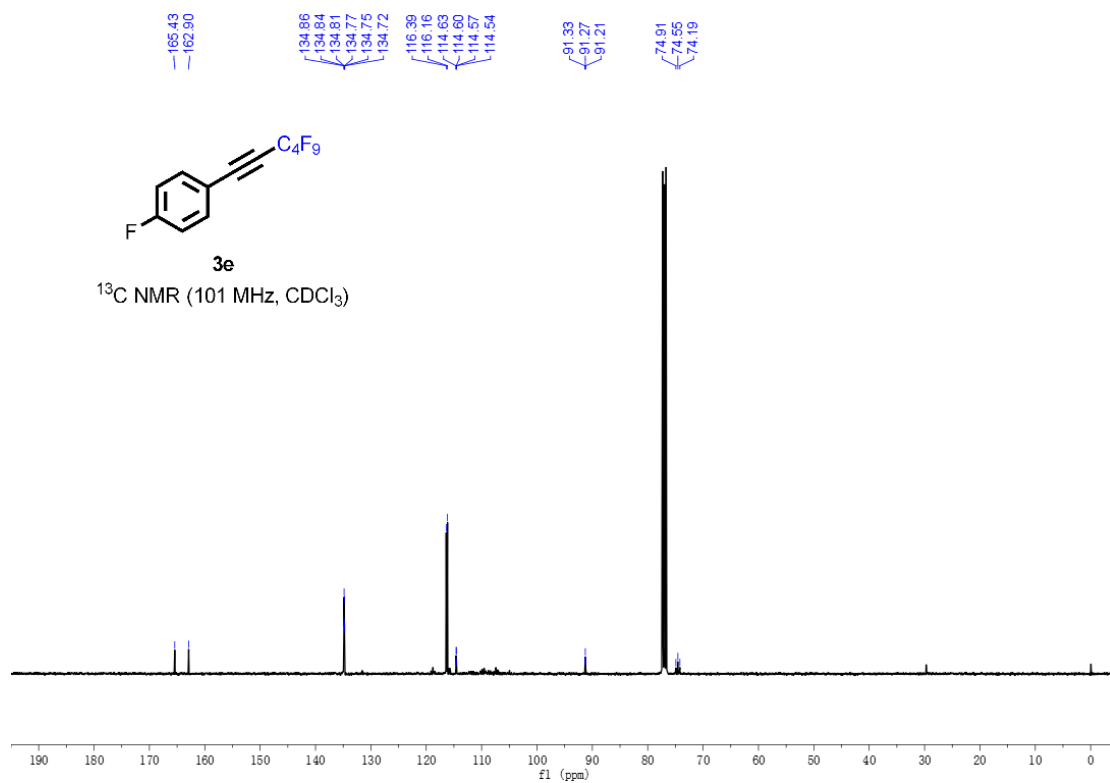


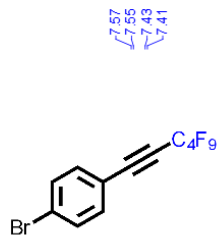






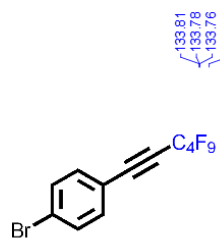
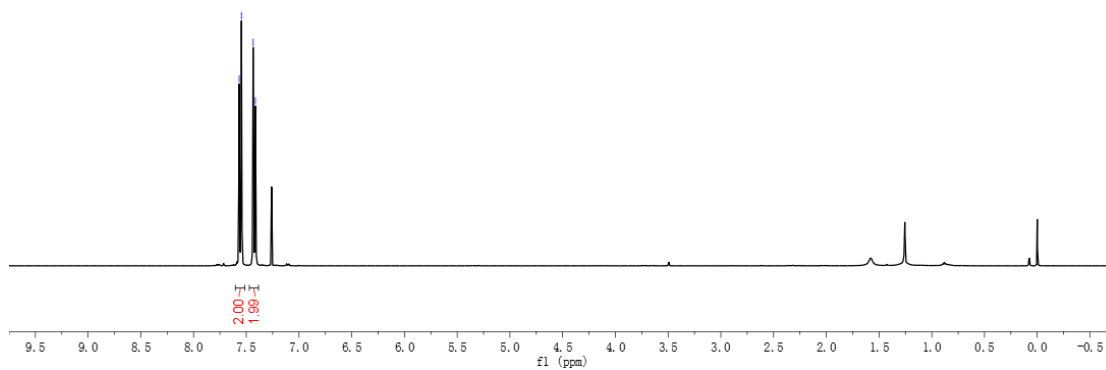






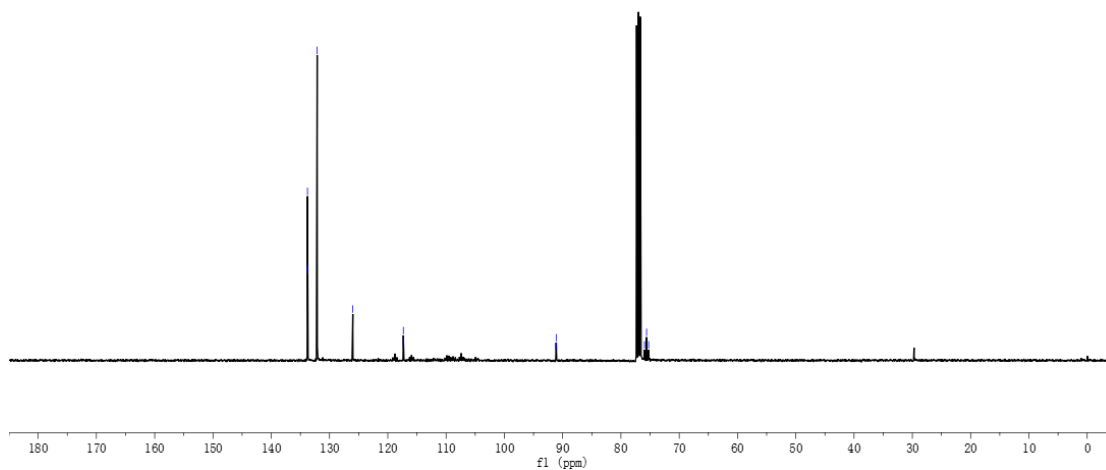
**3f**

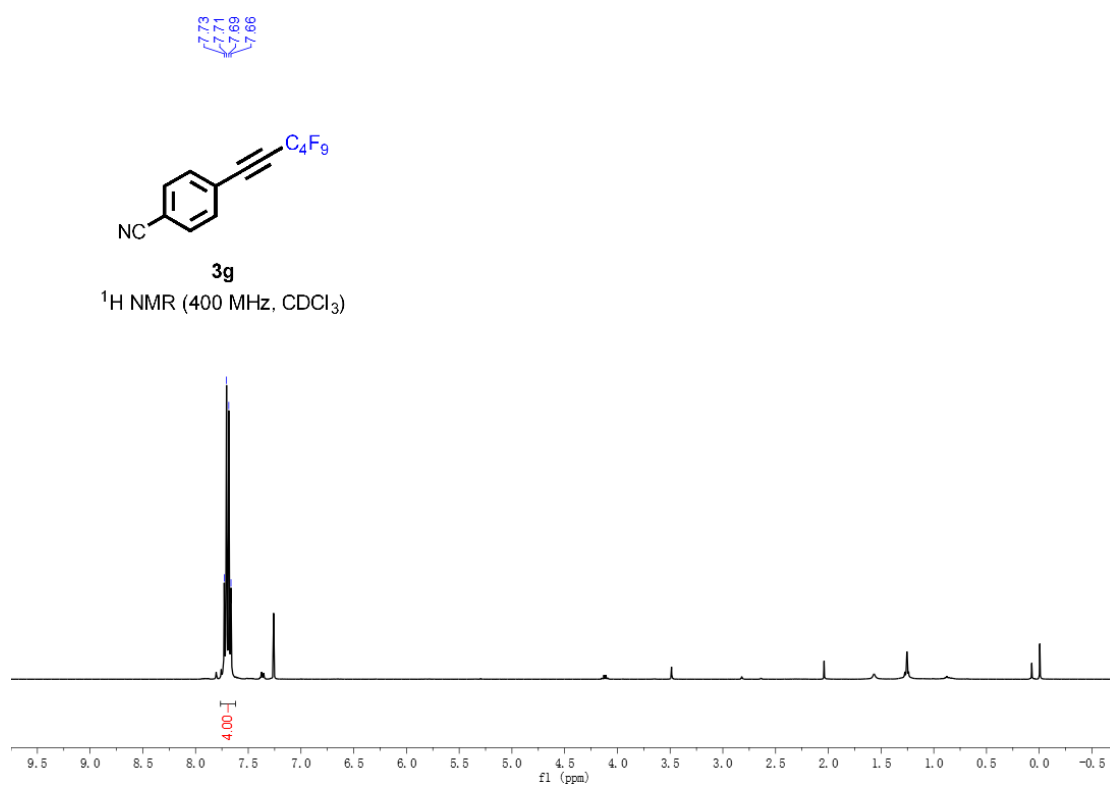
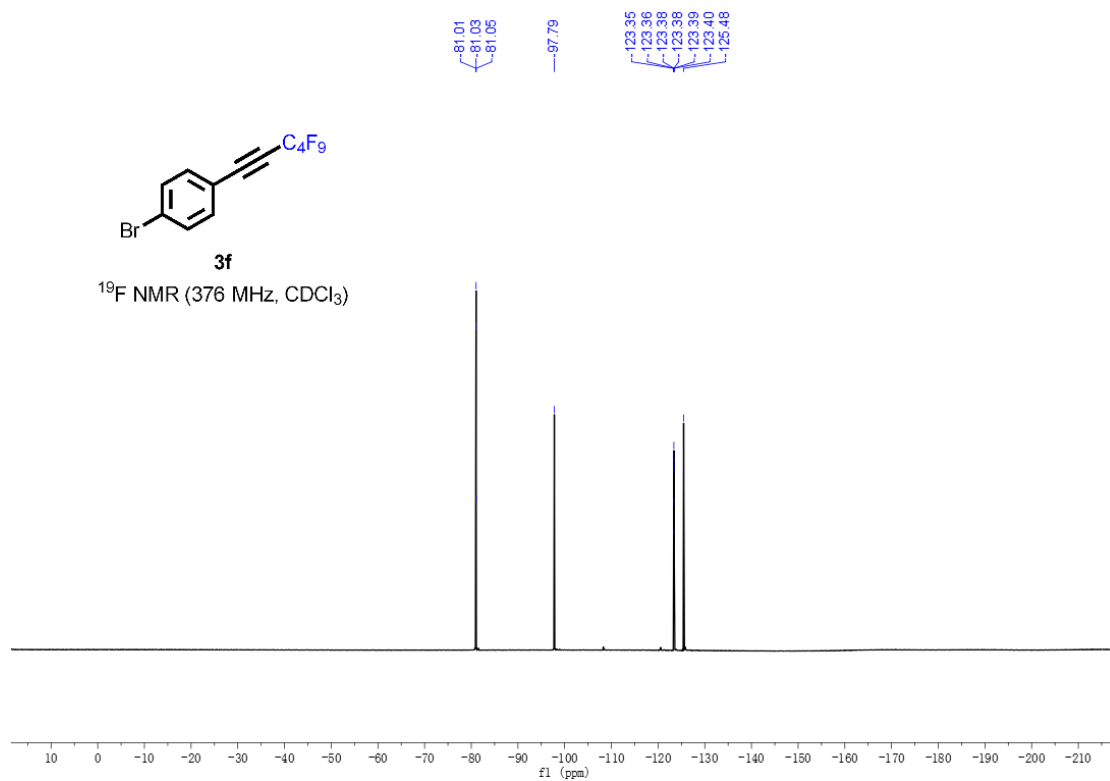
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

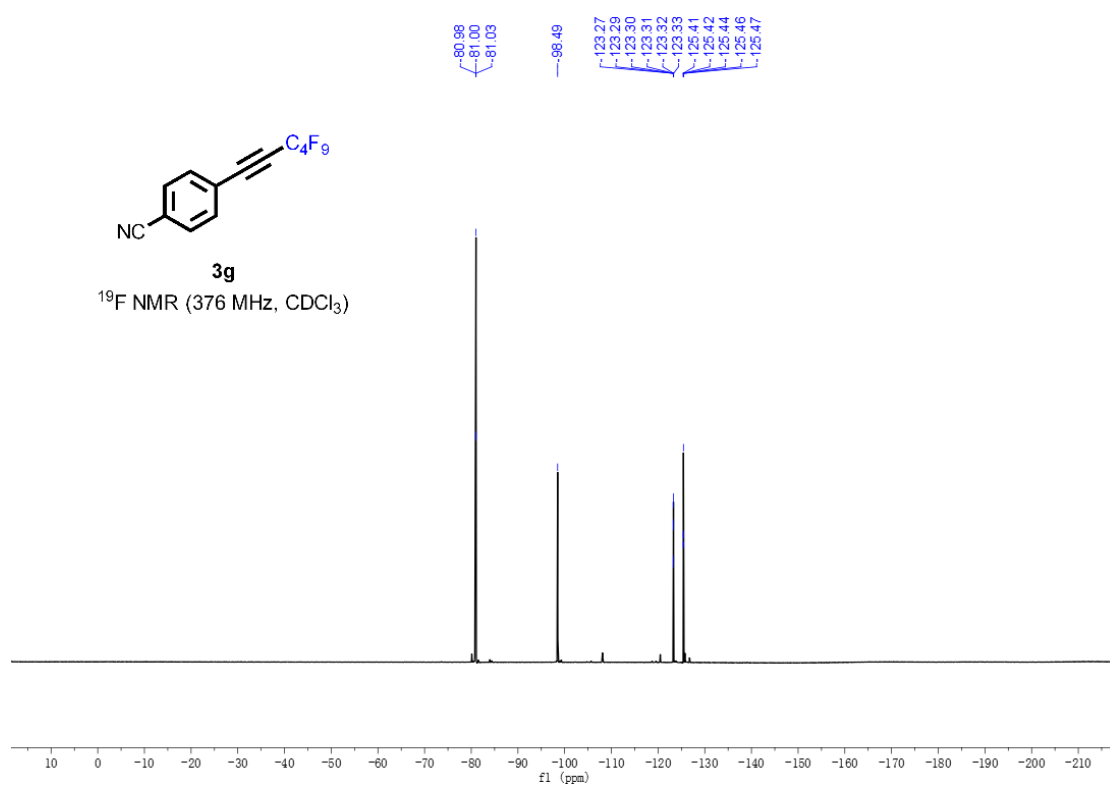
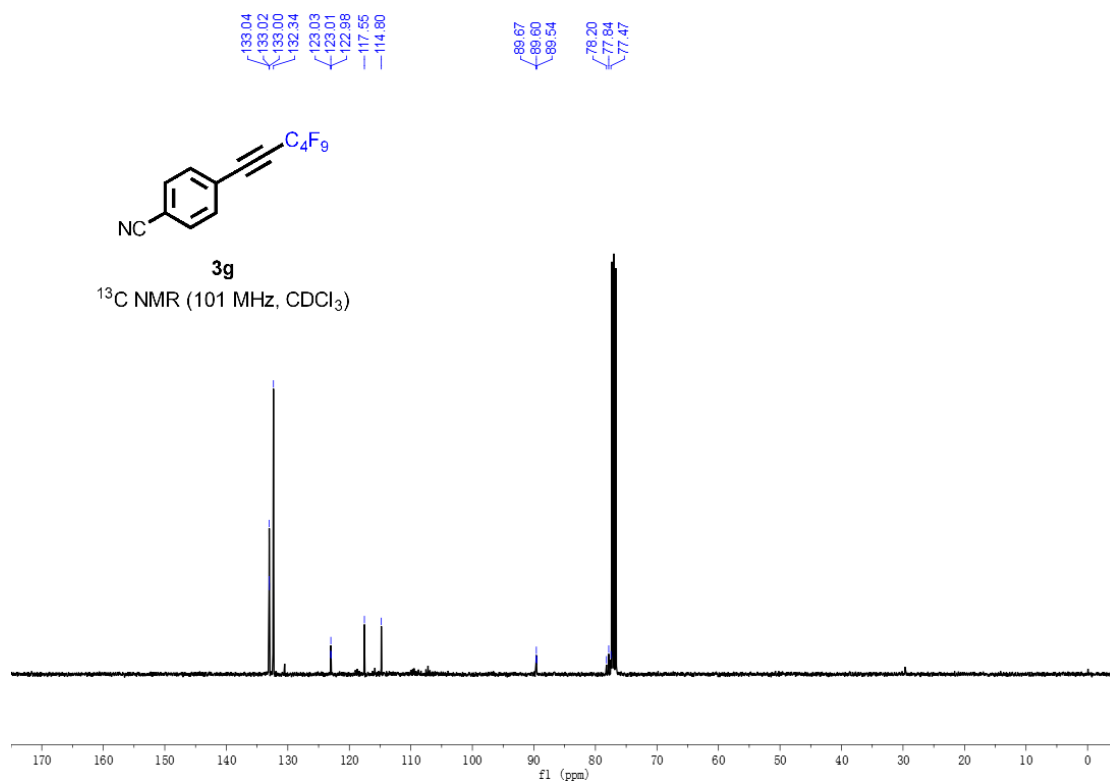


**3f**

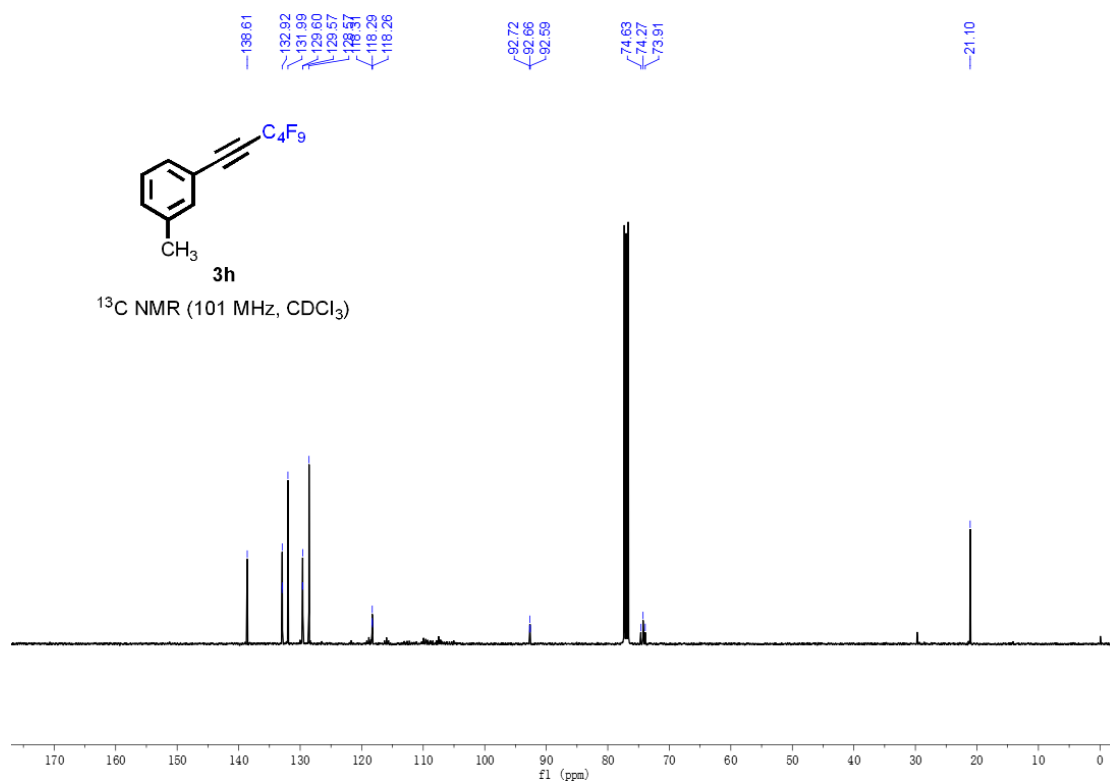
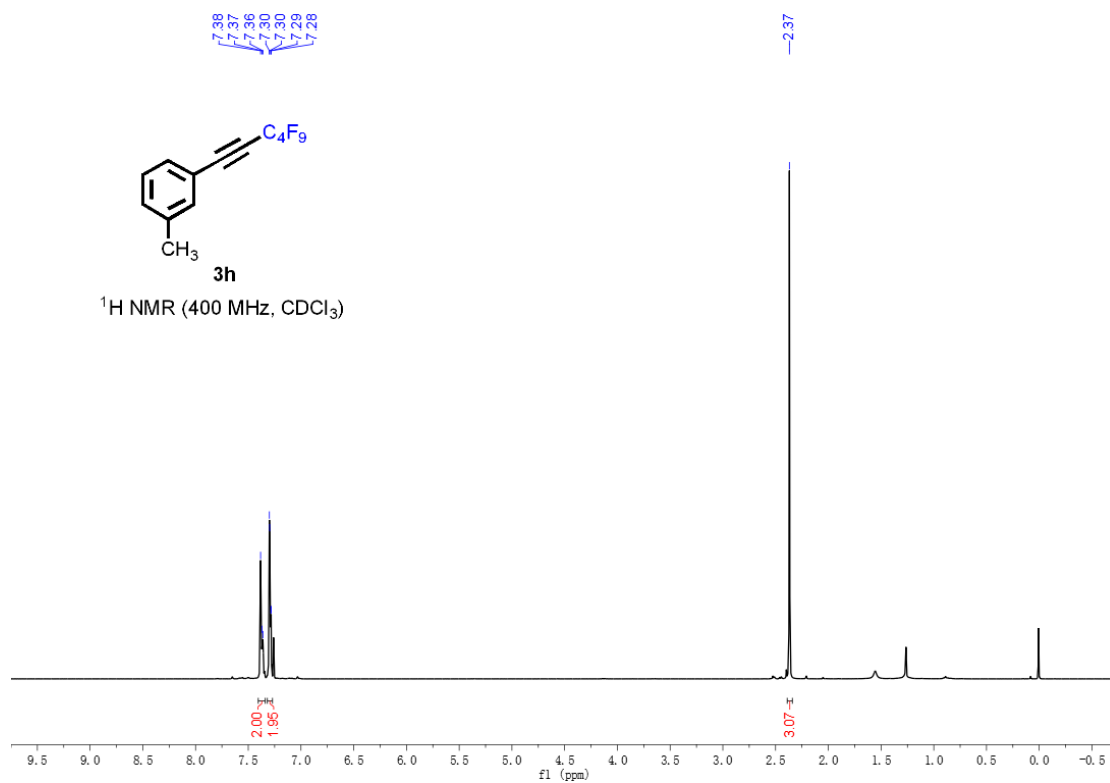
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

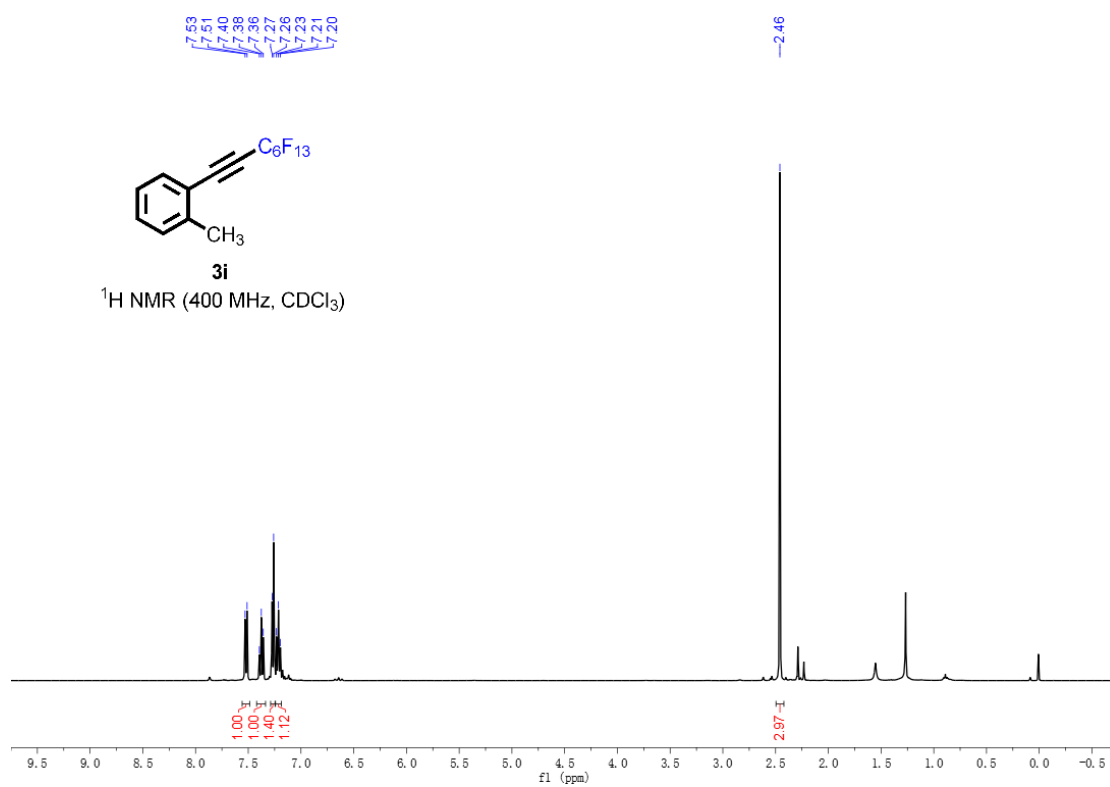
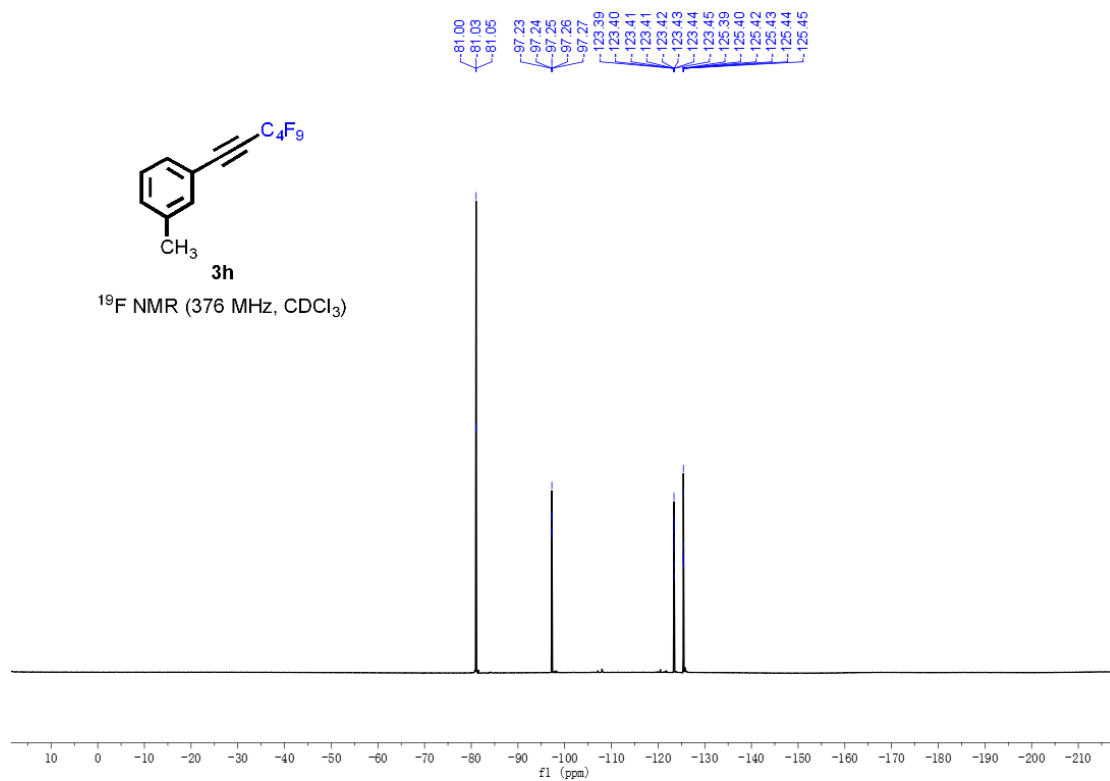


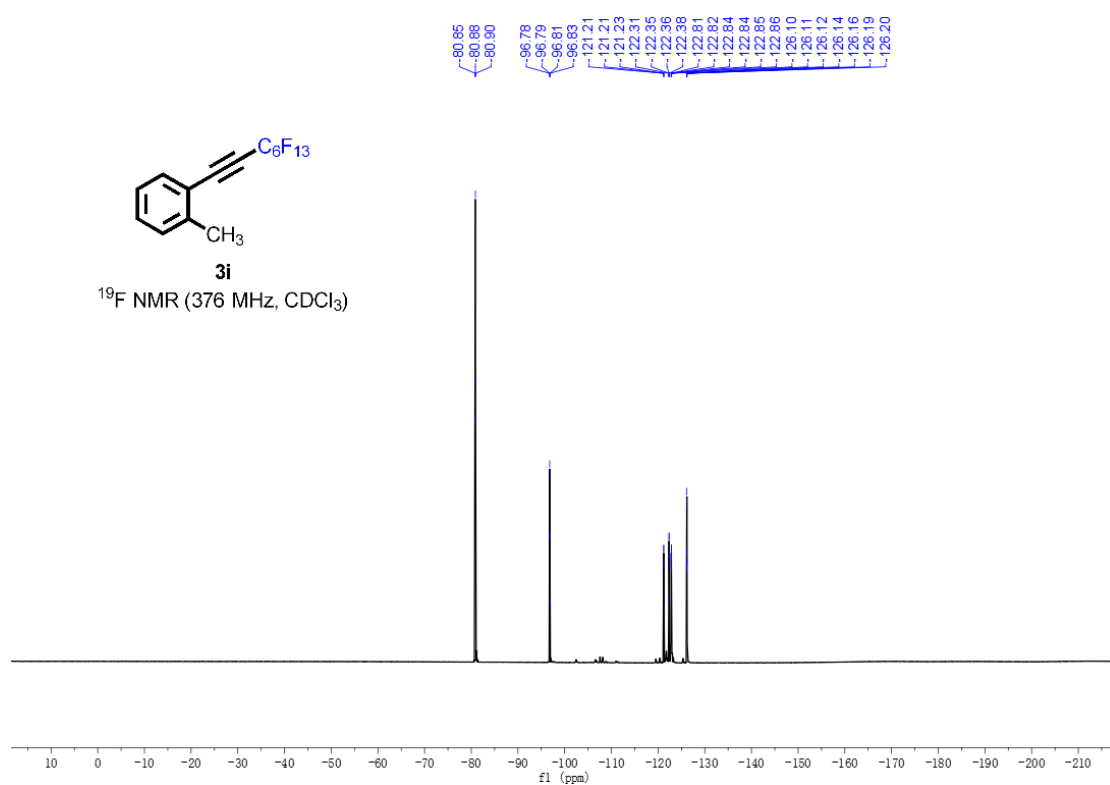
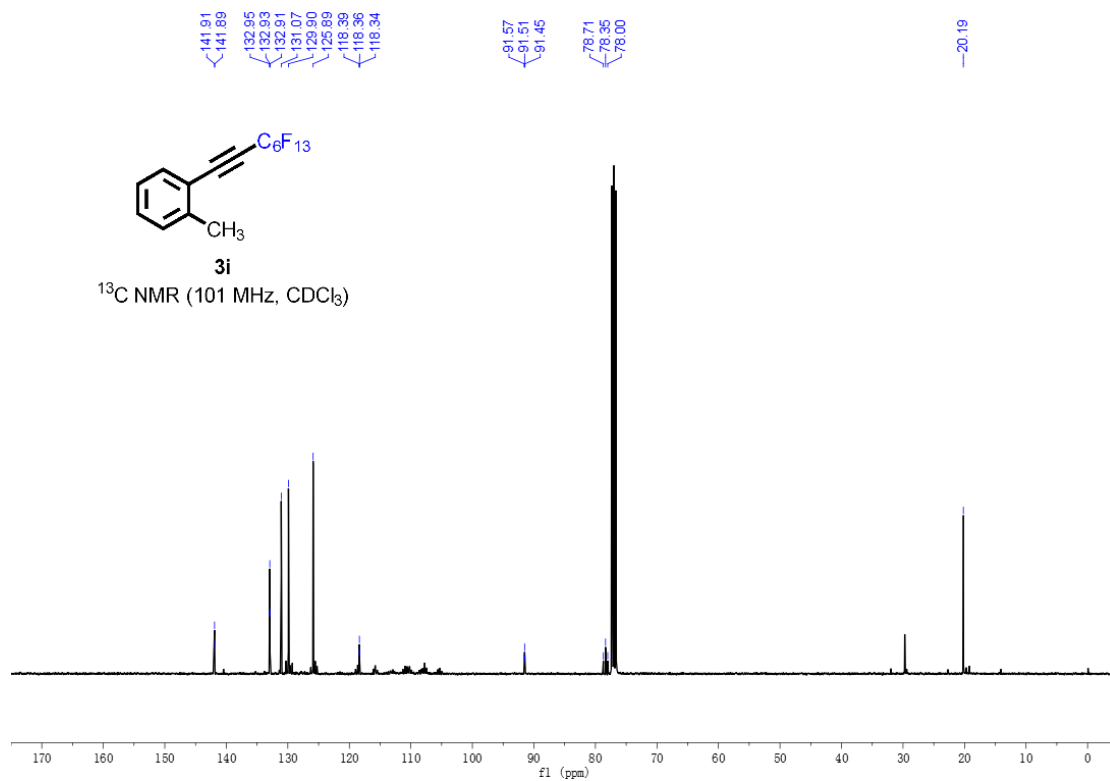


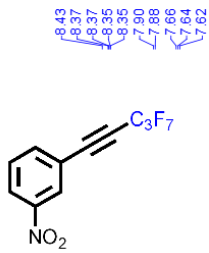






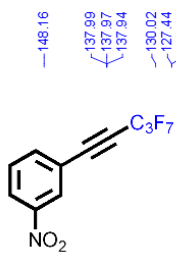
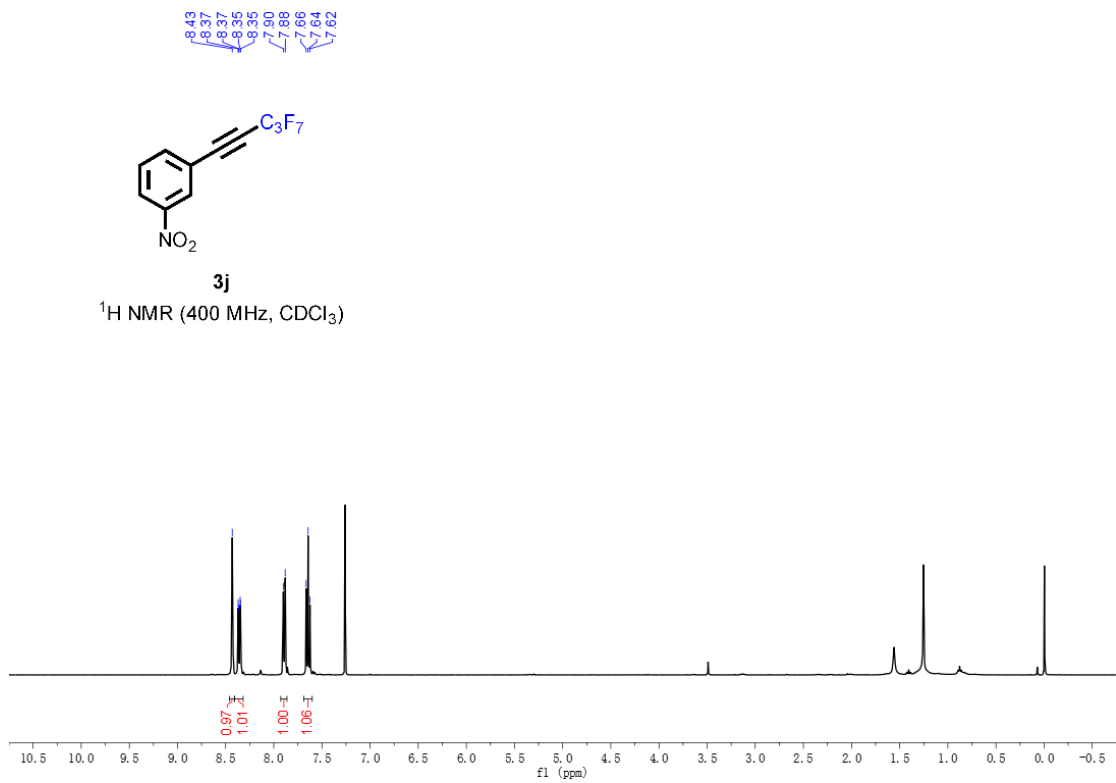






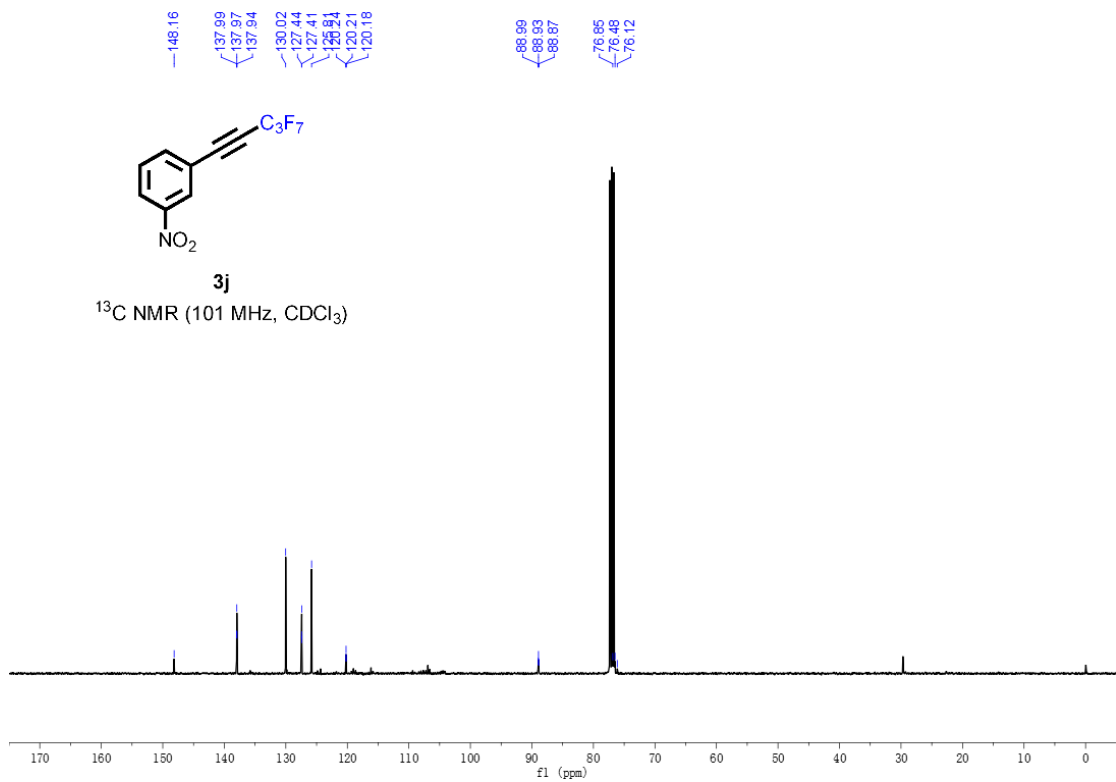
**3j**

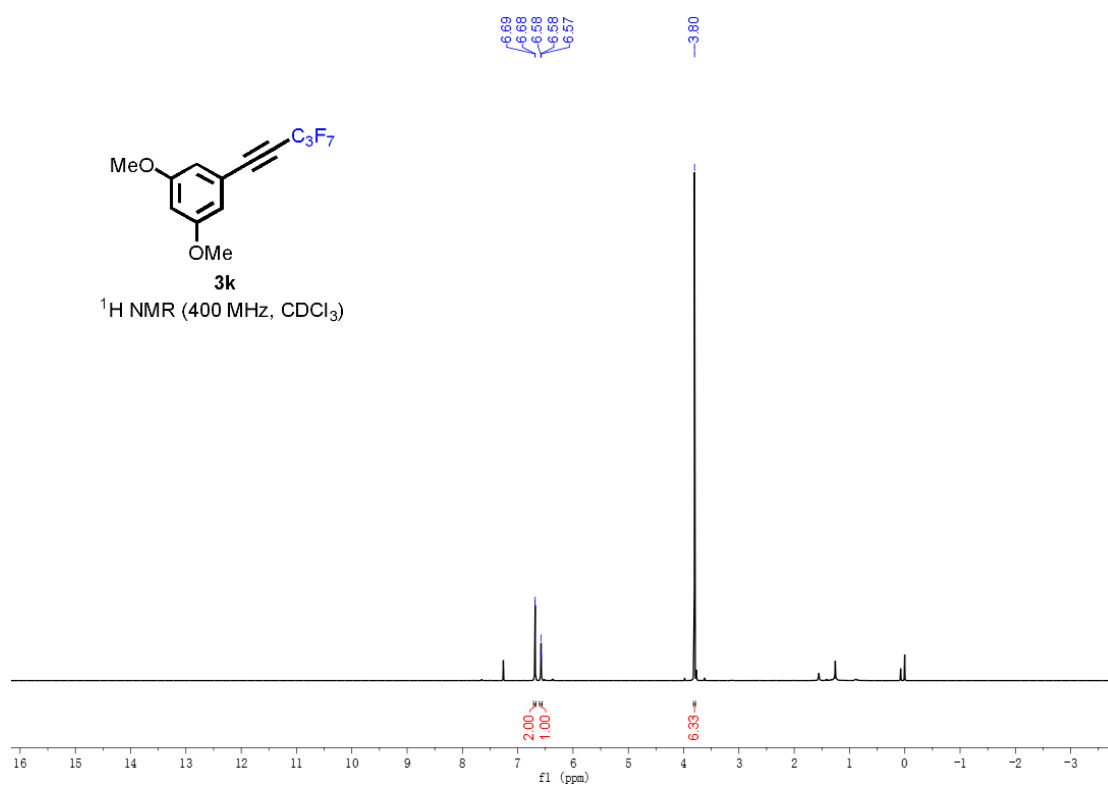
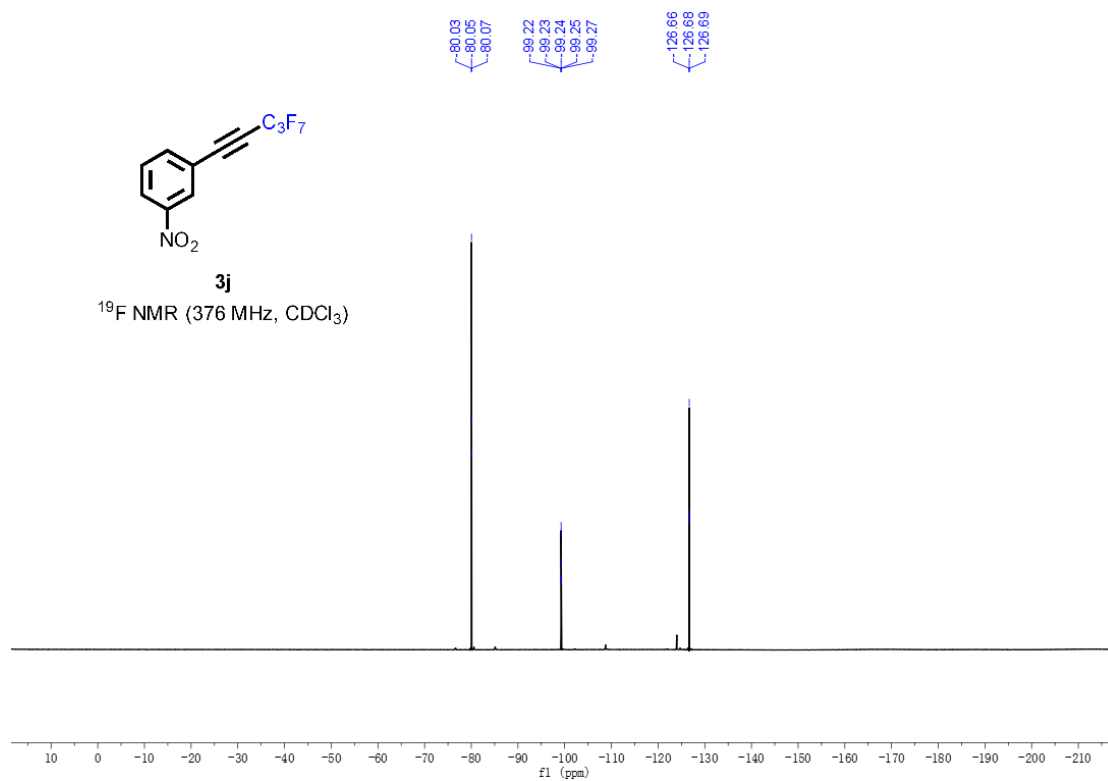
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

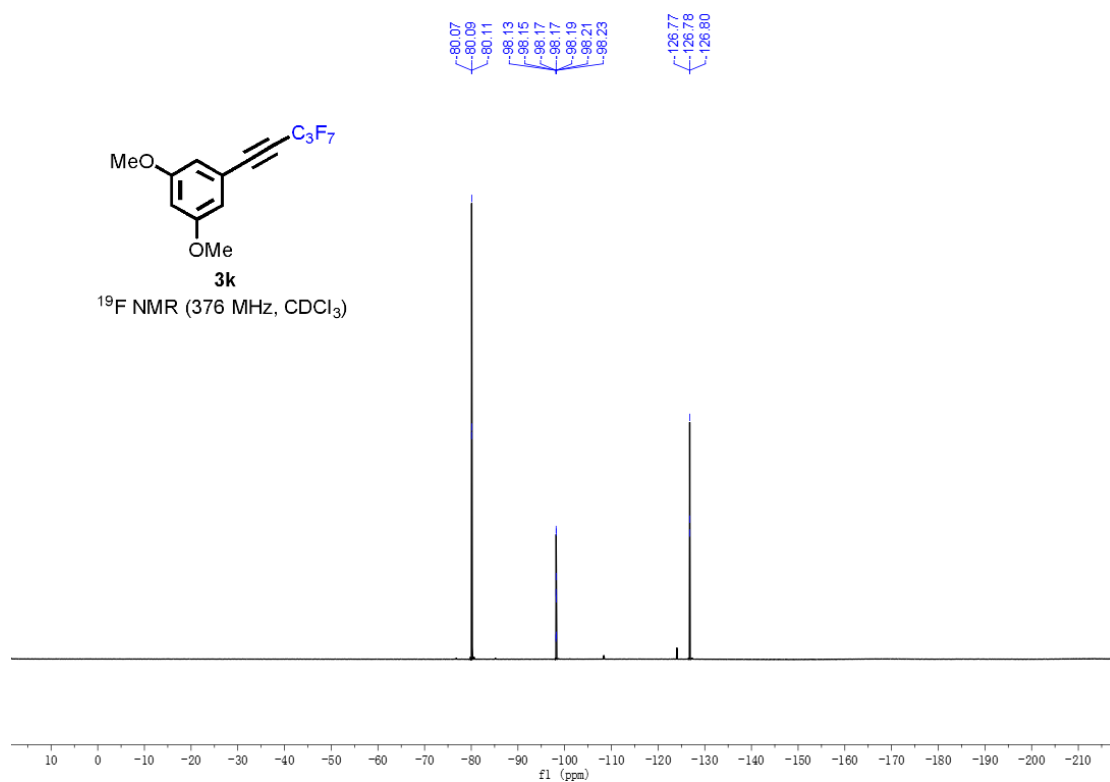
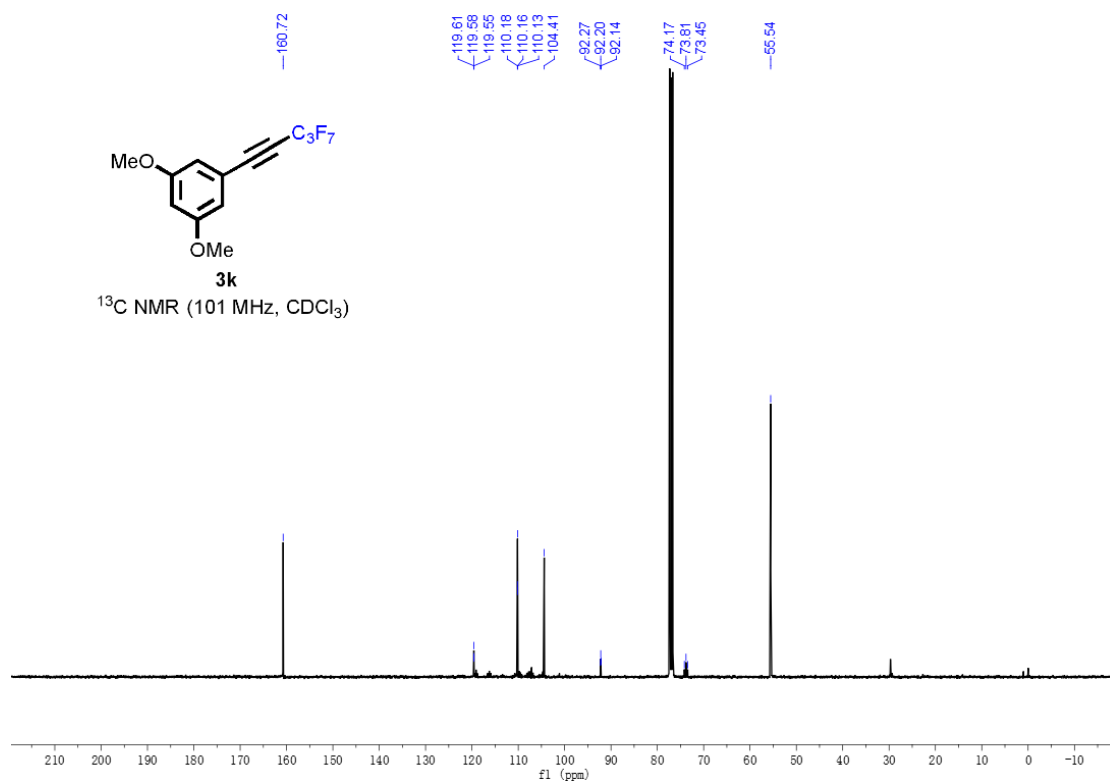


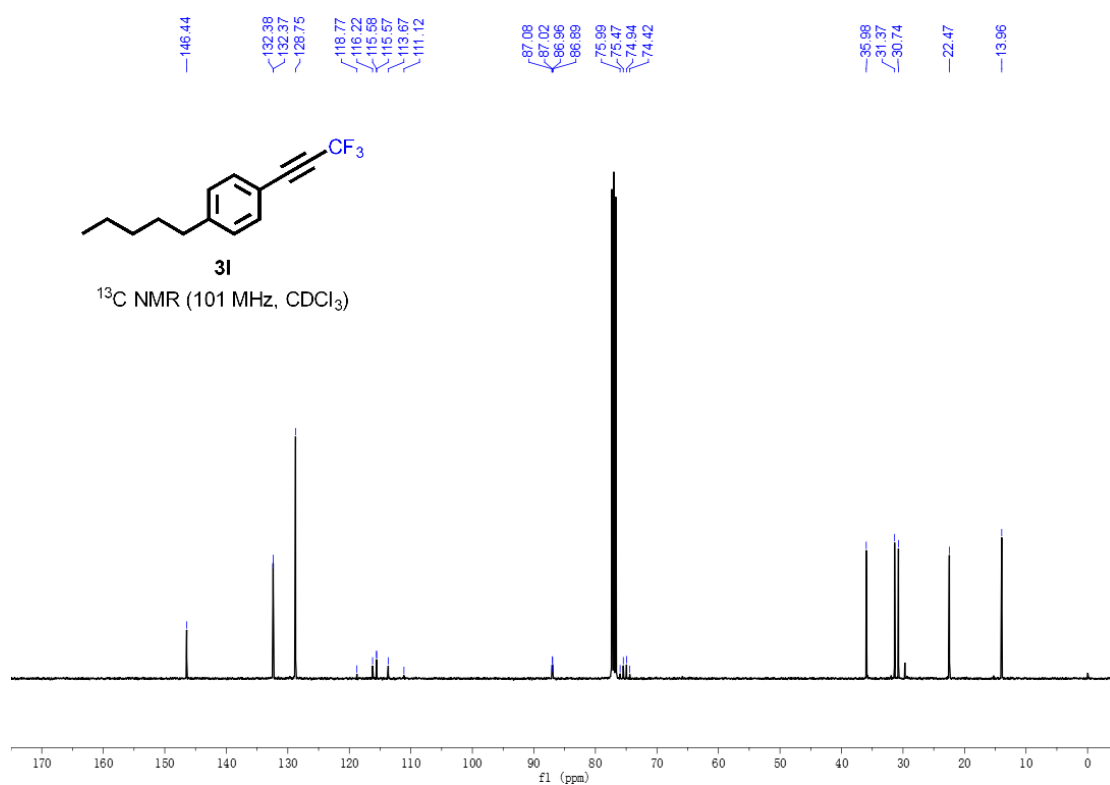
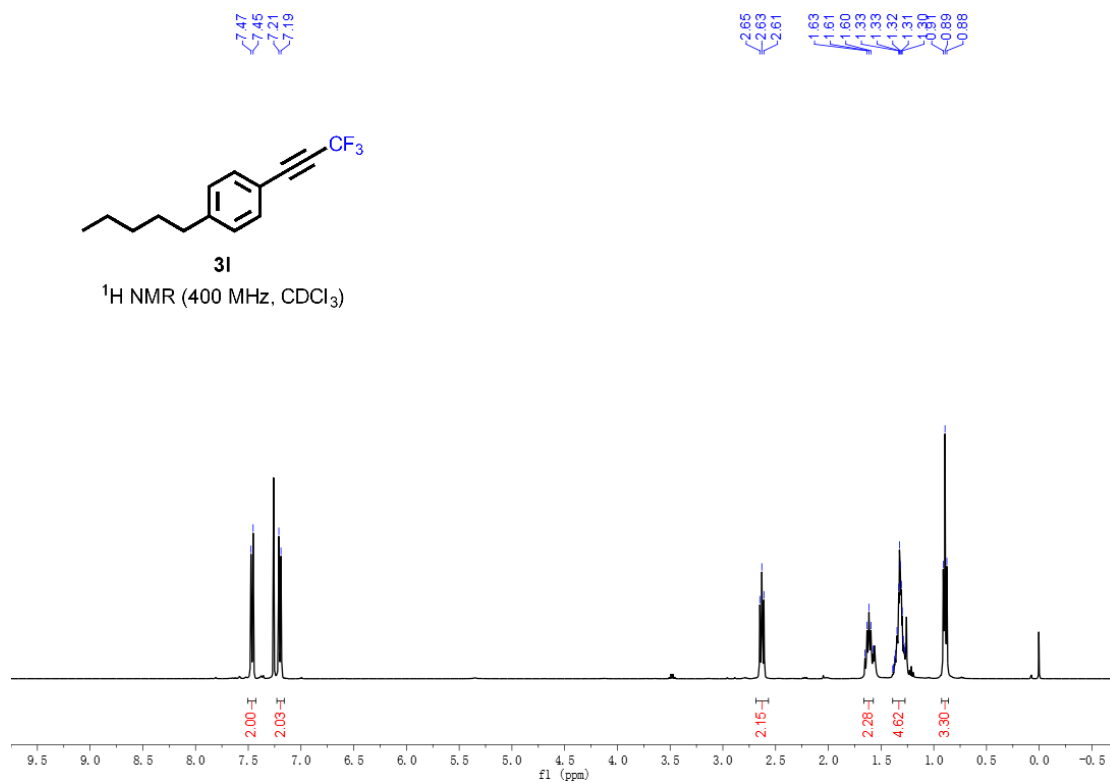
**3j**

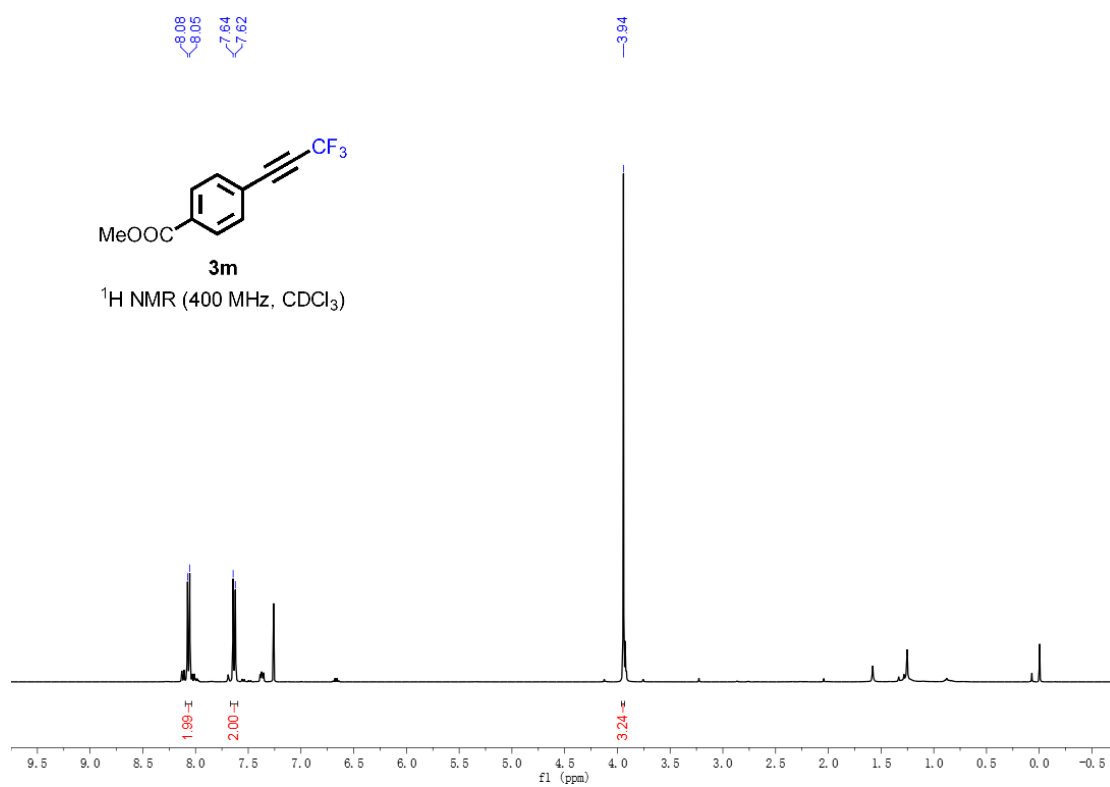
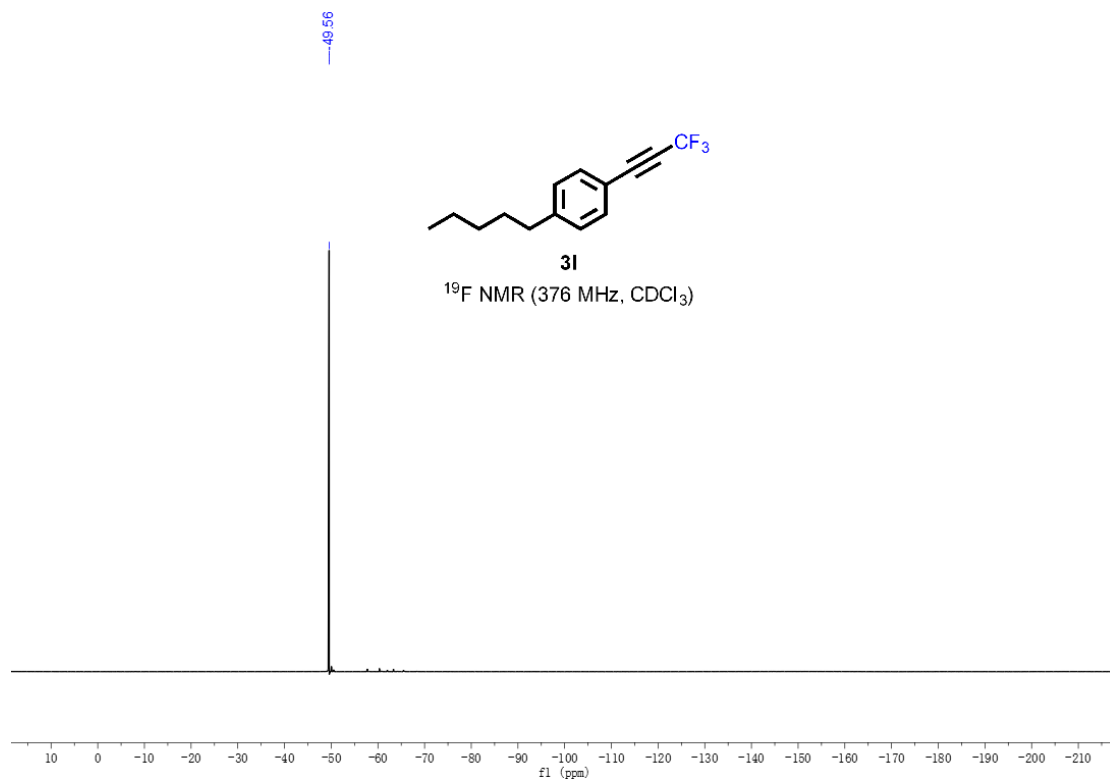
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



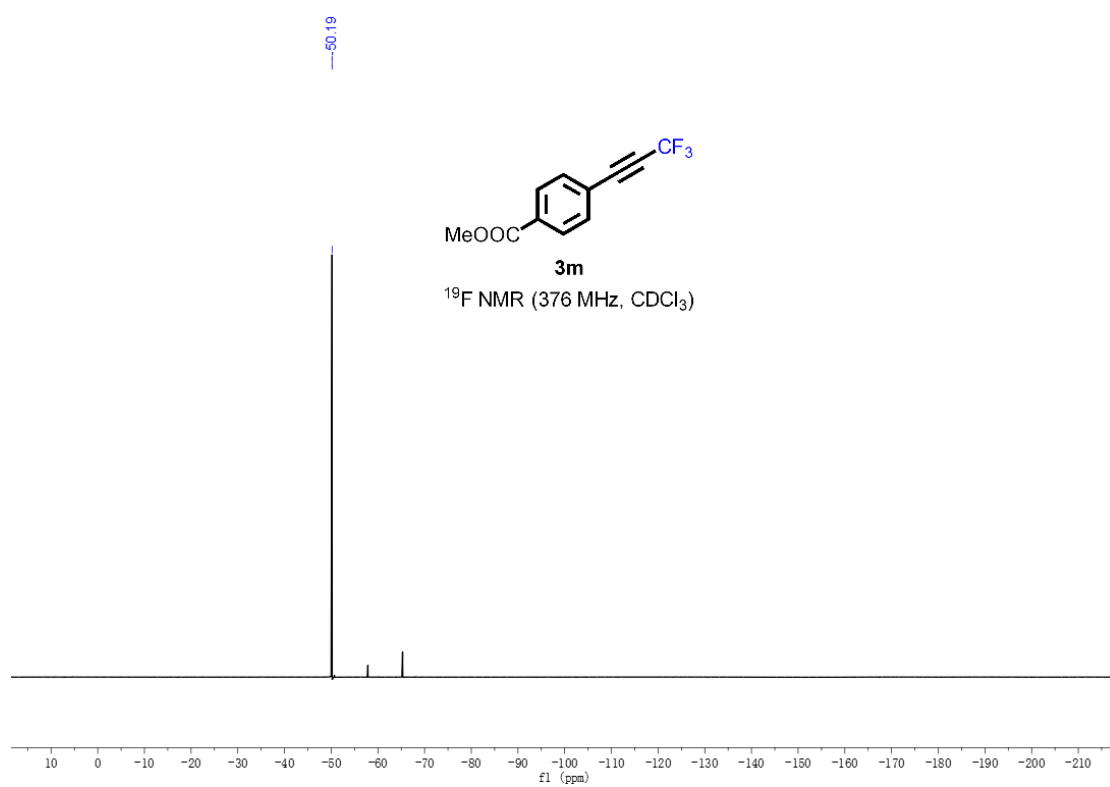
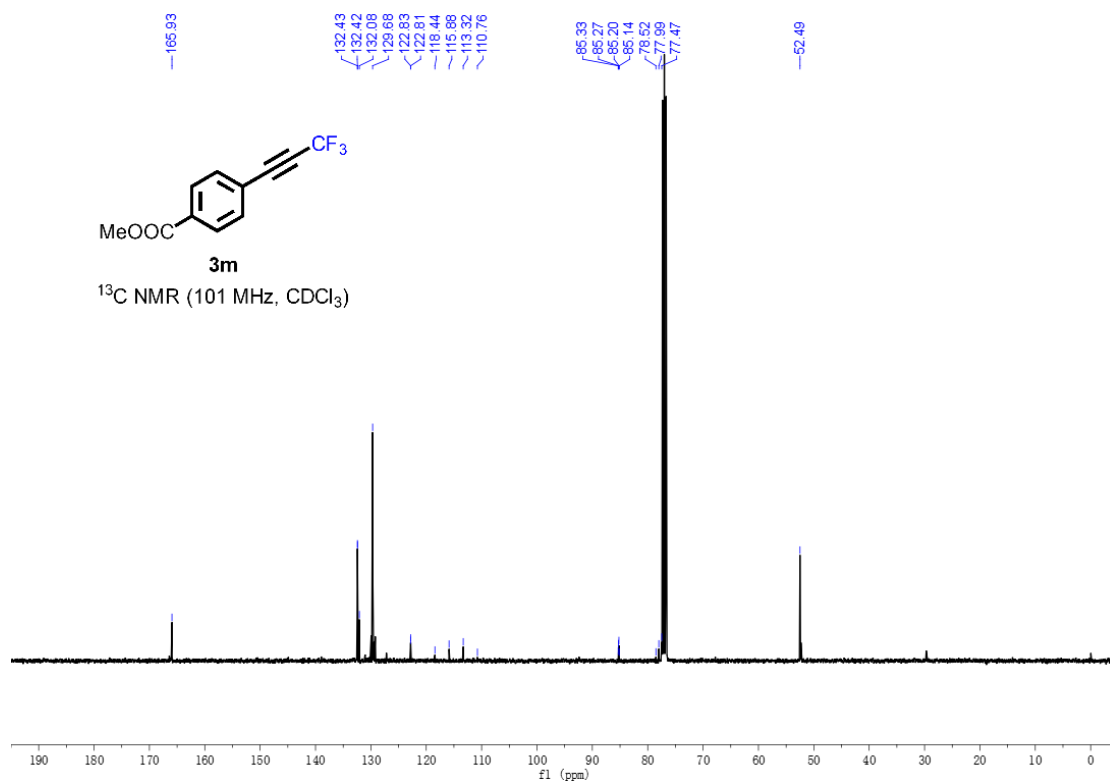


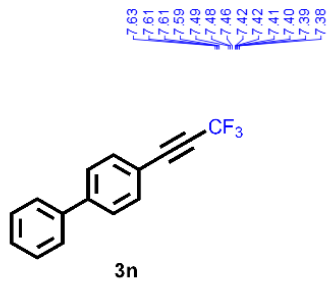




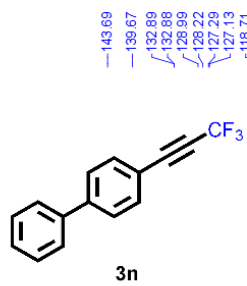
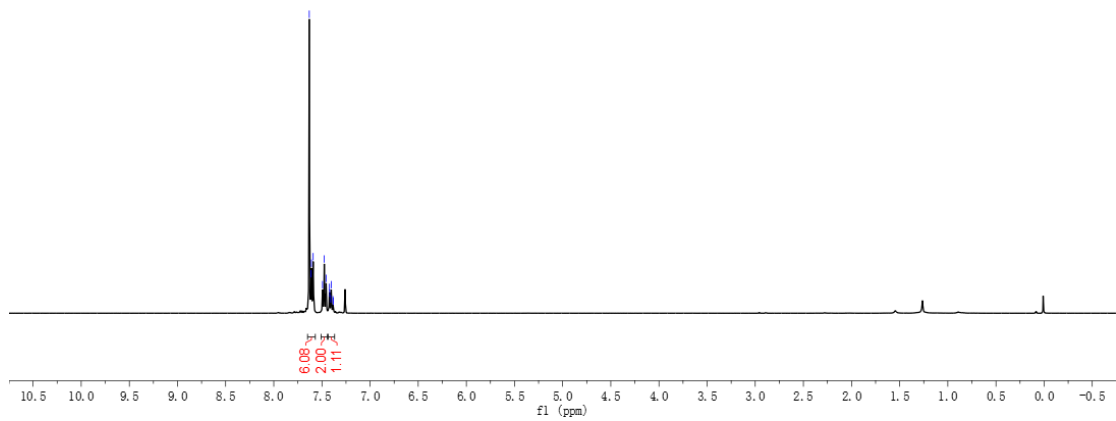




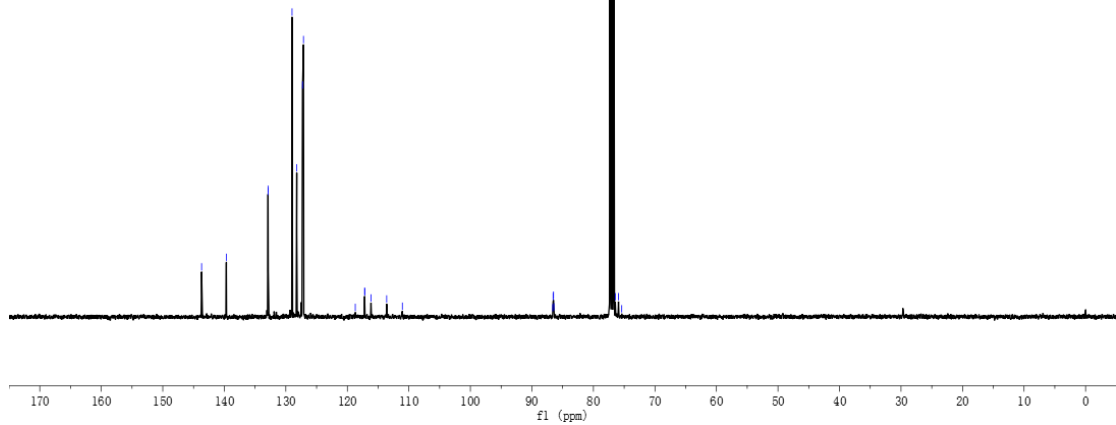


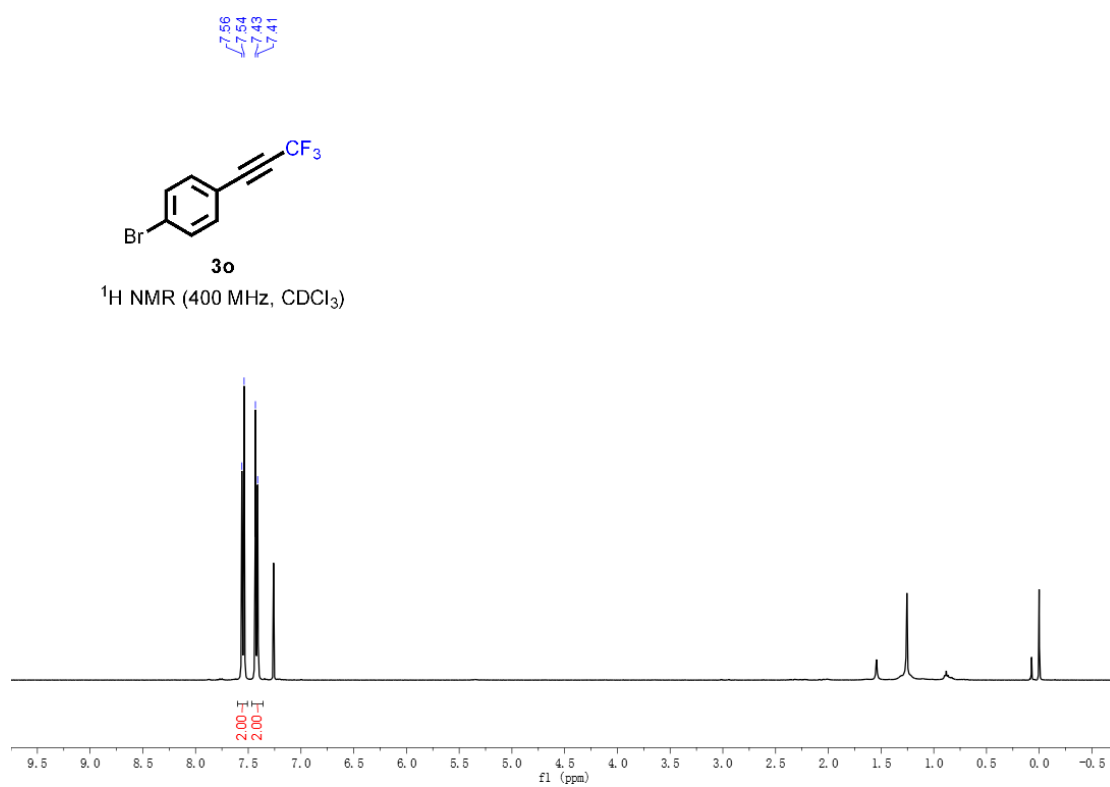
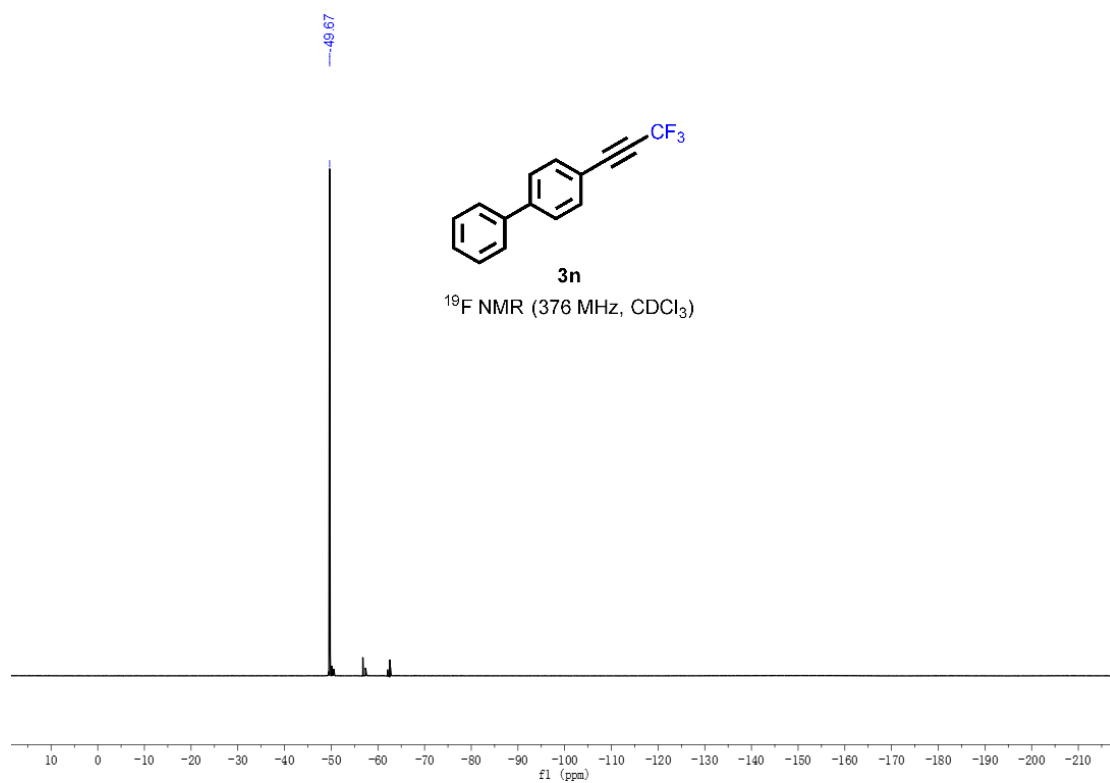


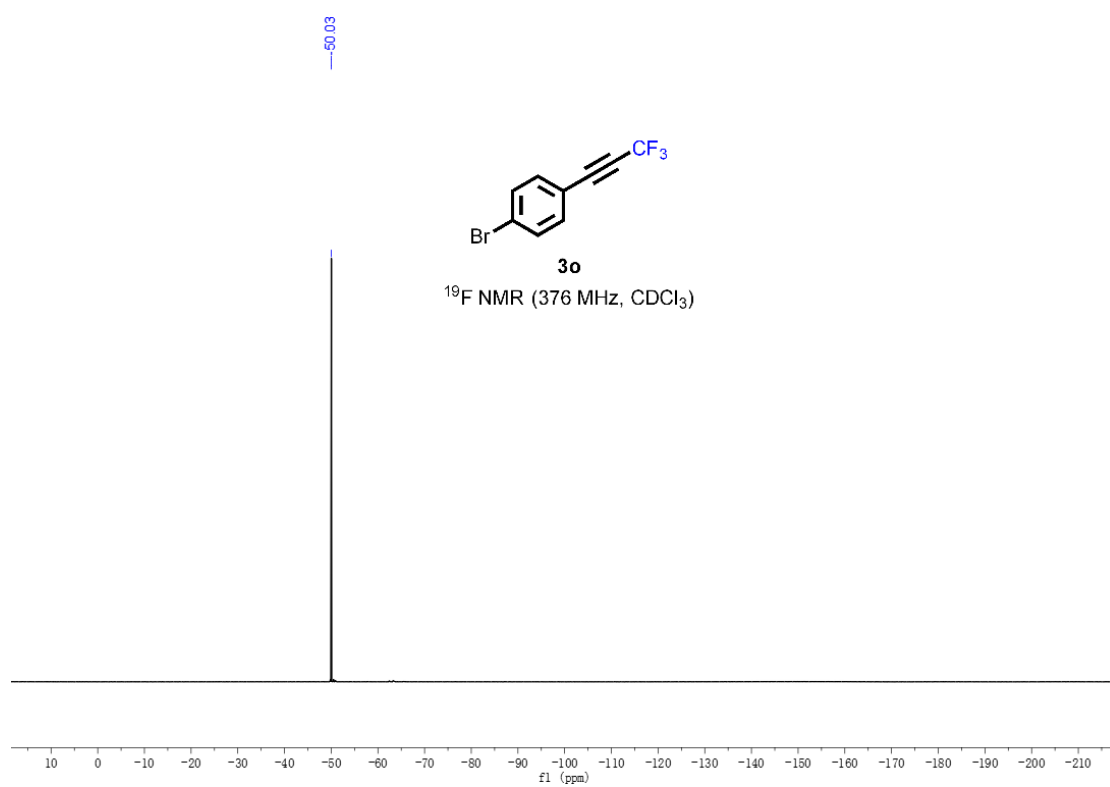
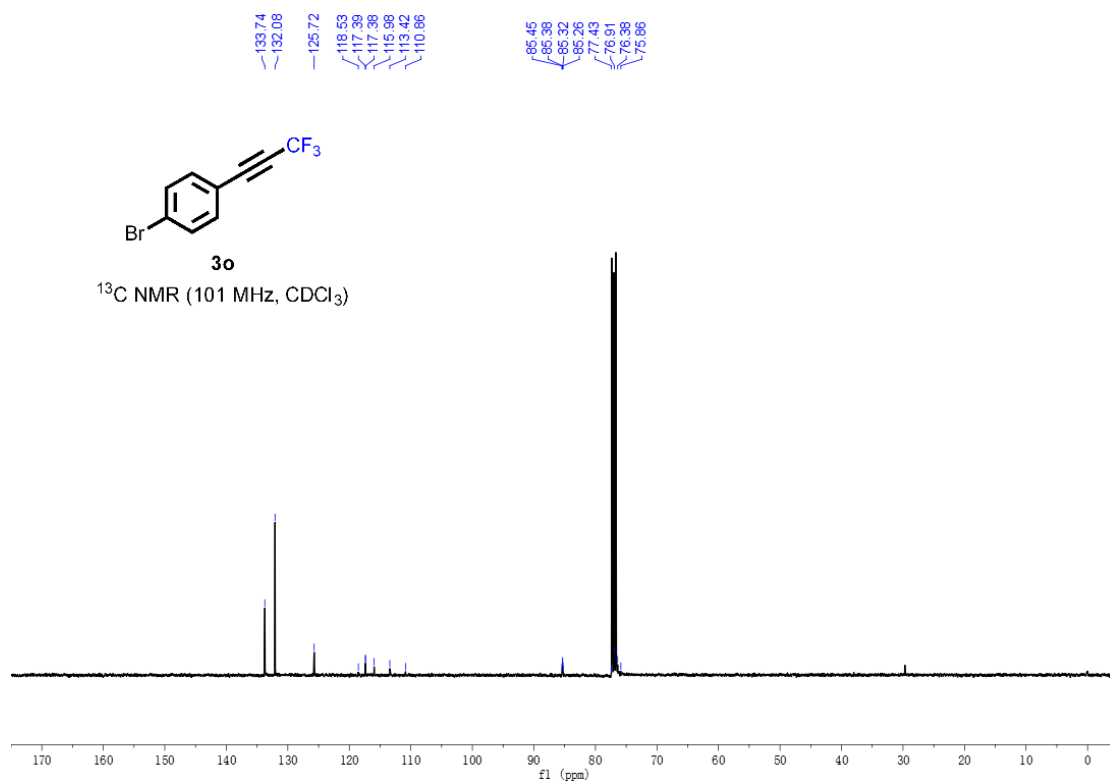
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



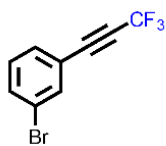
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)





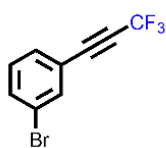
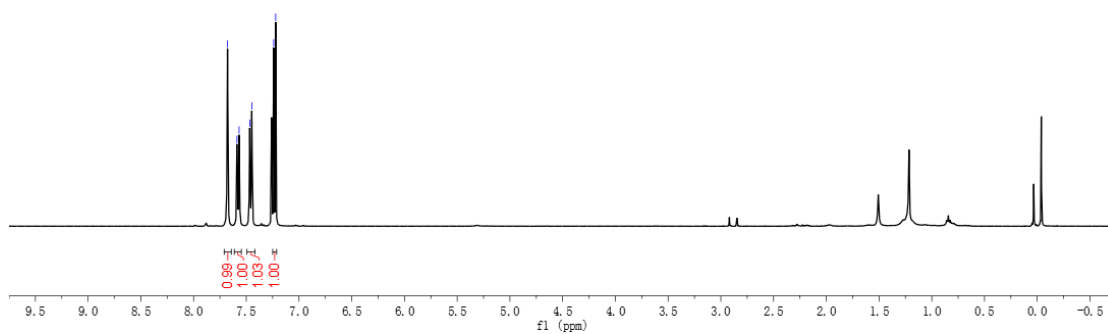


7.68  
7.59  
7.57  
7.47  
7.45  
7.24  
7.22



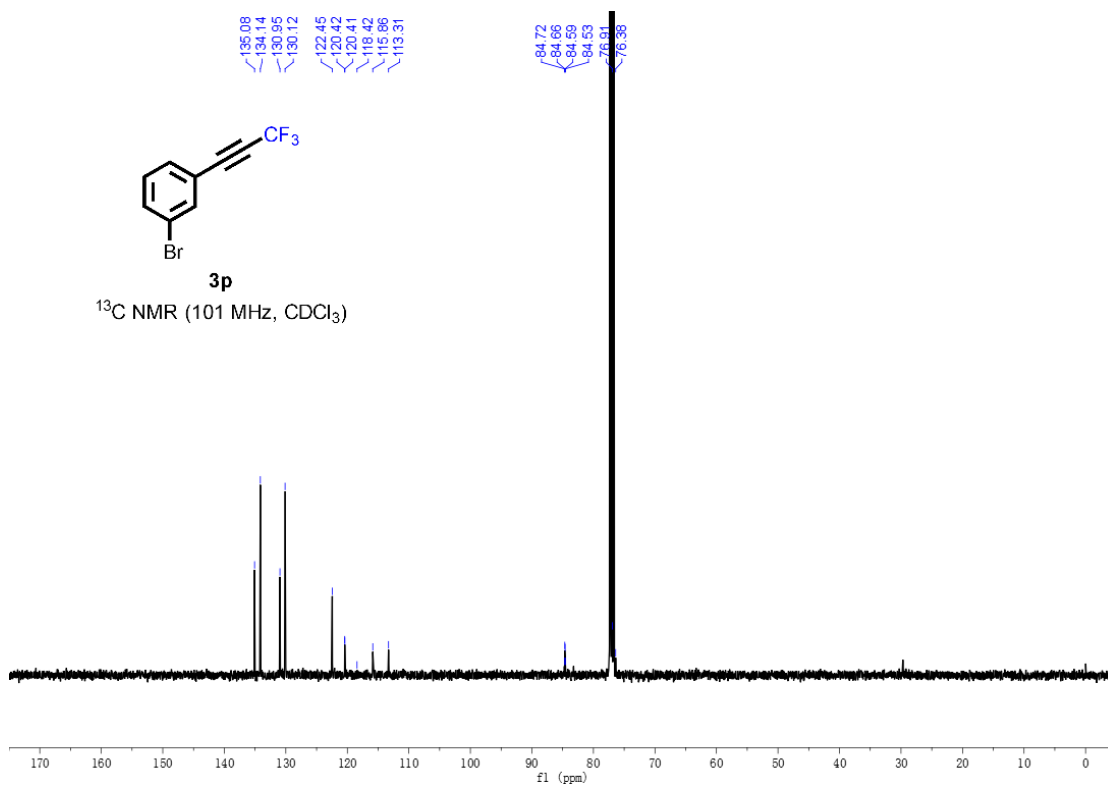
**3p**

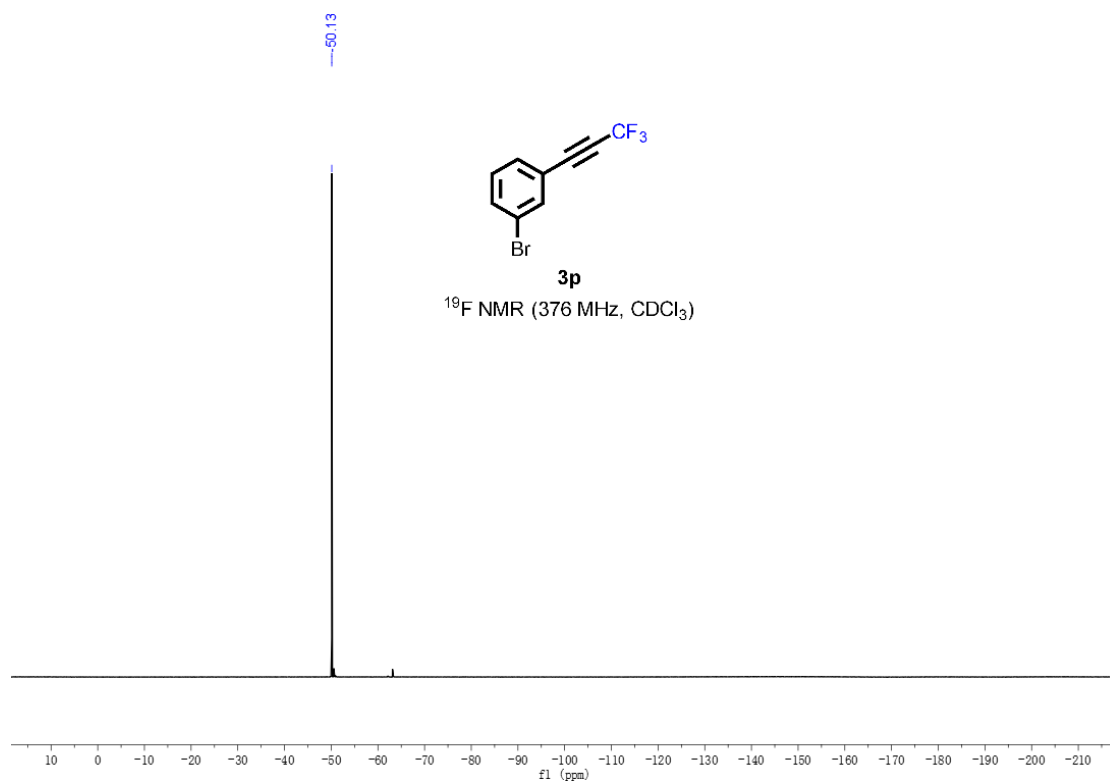
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



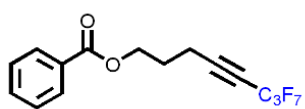
**3p**

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

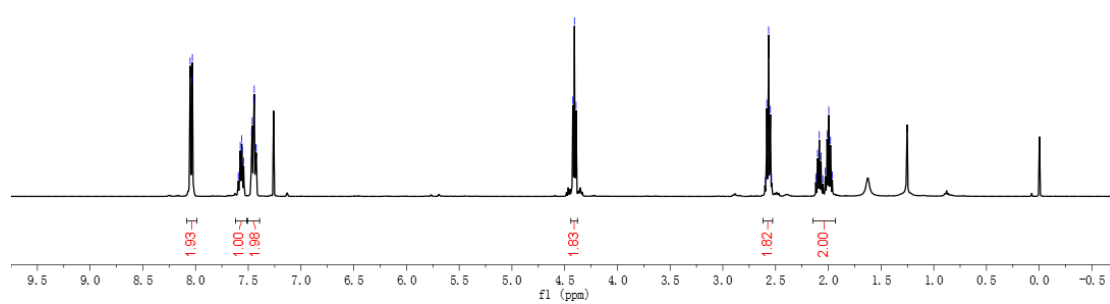


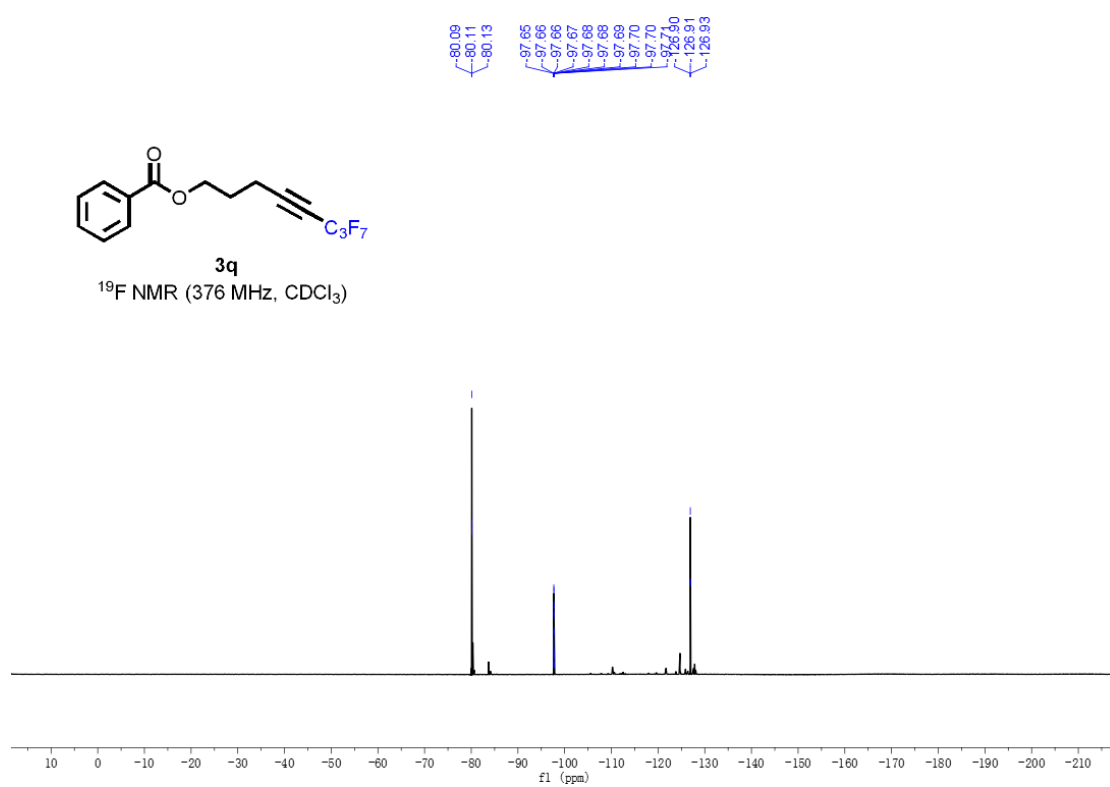
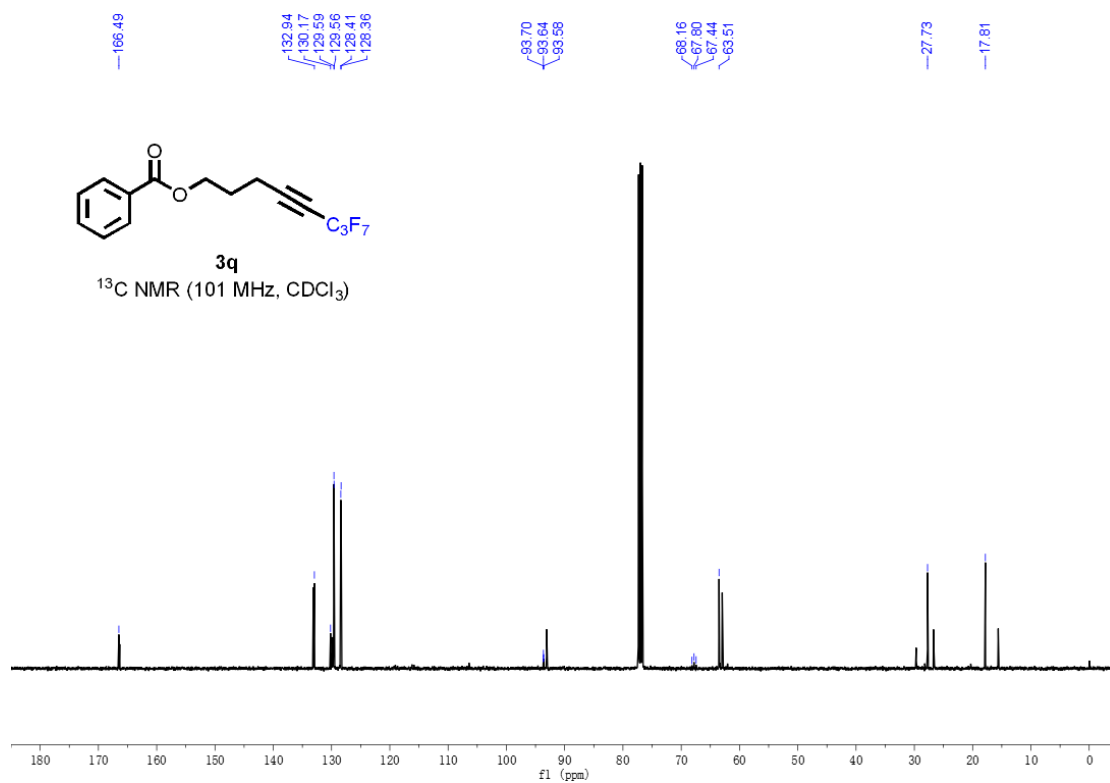


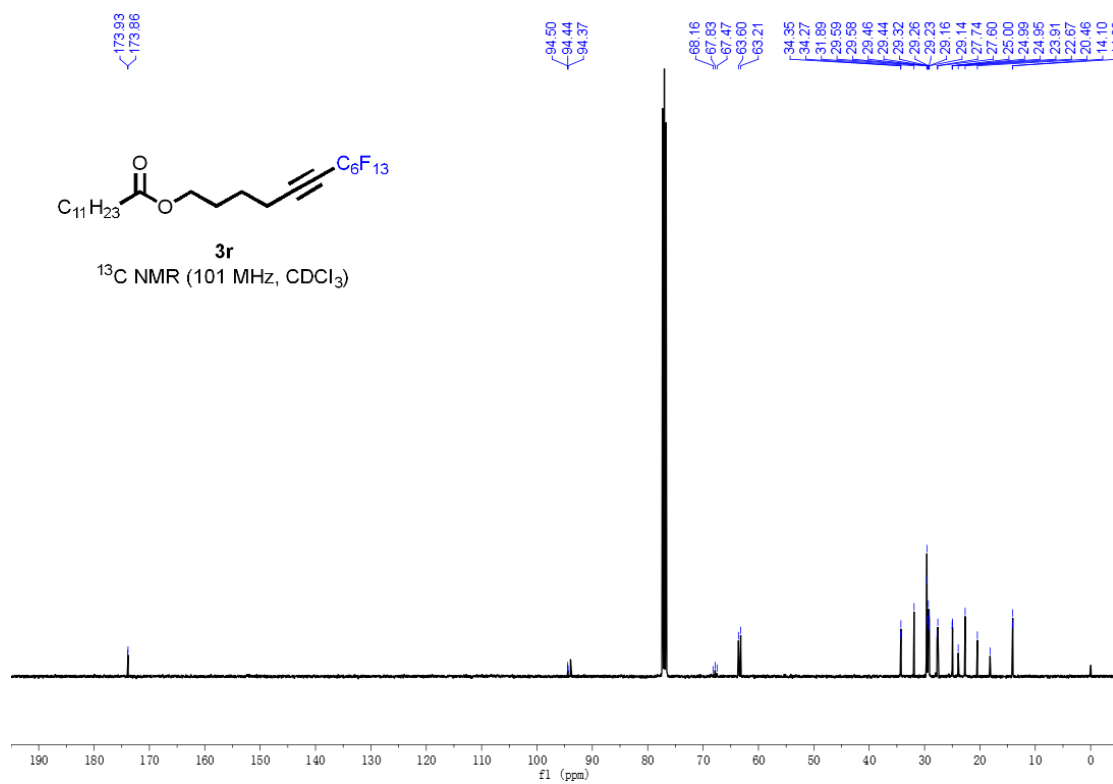
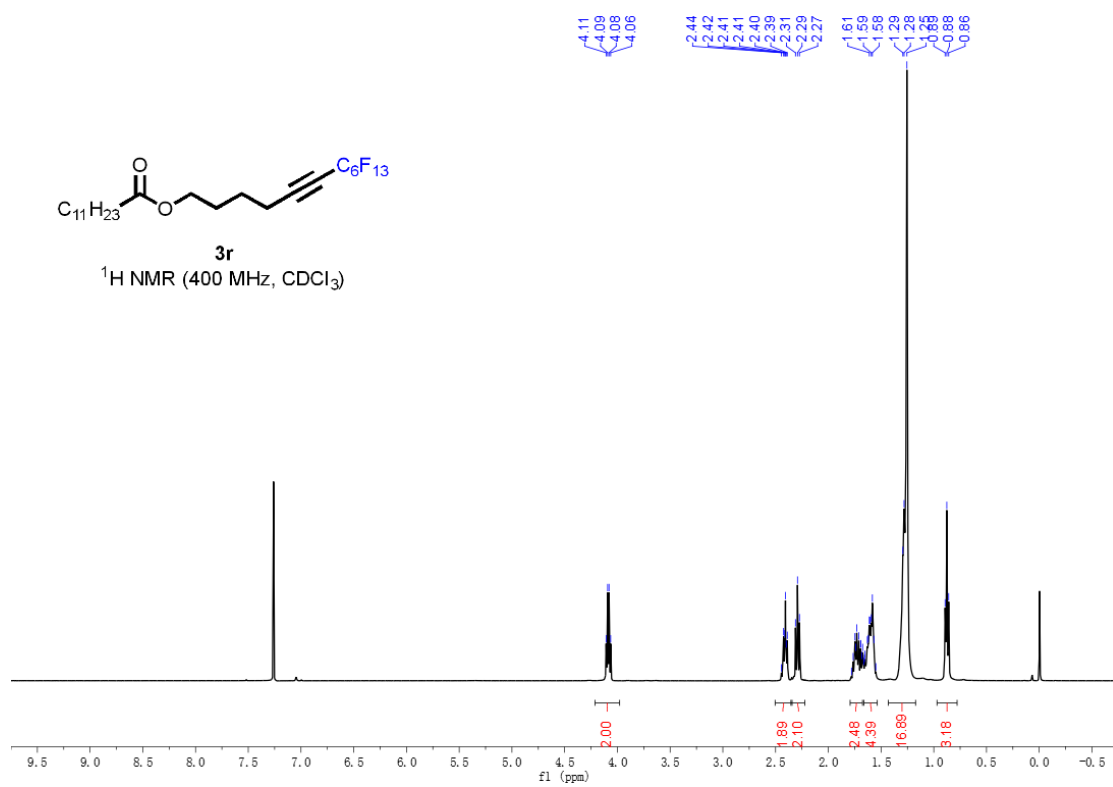
8.05, 8.03, 8.03, 7.59, 7.58, 7.58, 7.56, 7.54, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 4.42, 4.41, 4.39, 2.60, 2.58, 2.57, 2.55, 2.54, 2.12, 2.09, 2.07, 2.05, 2.03, 2.01, 2.00, 1.98, 1.96



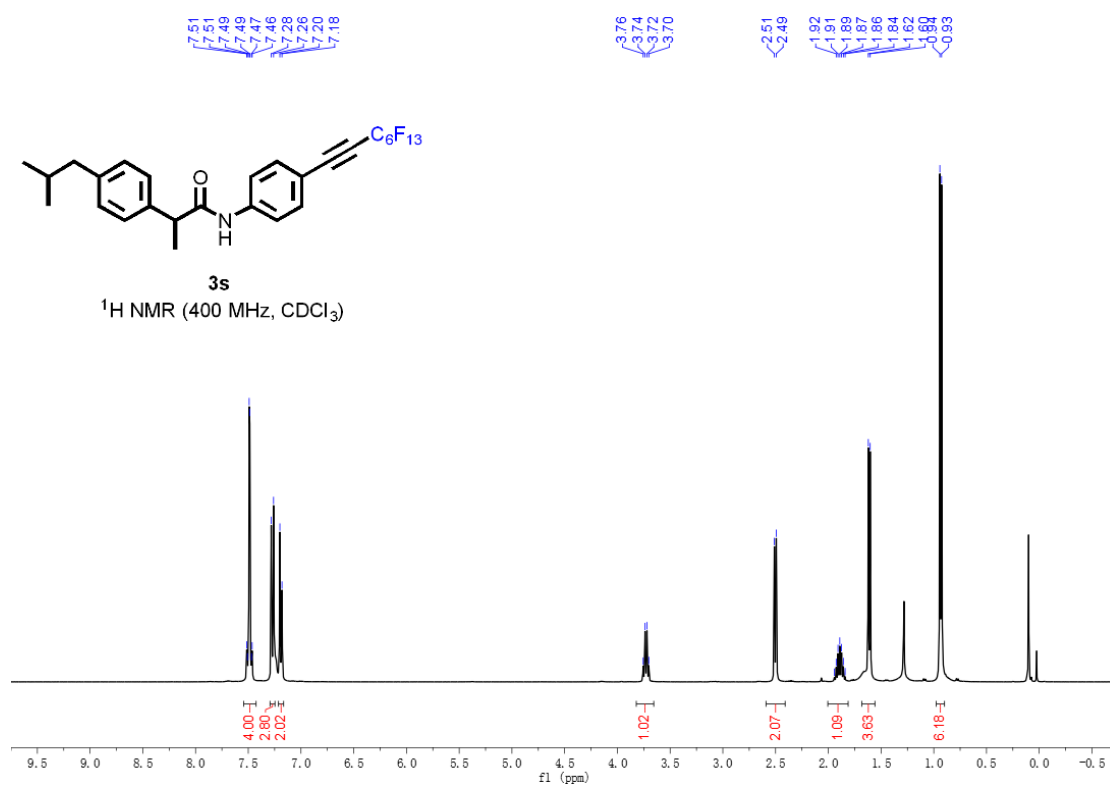
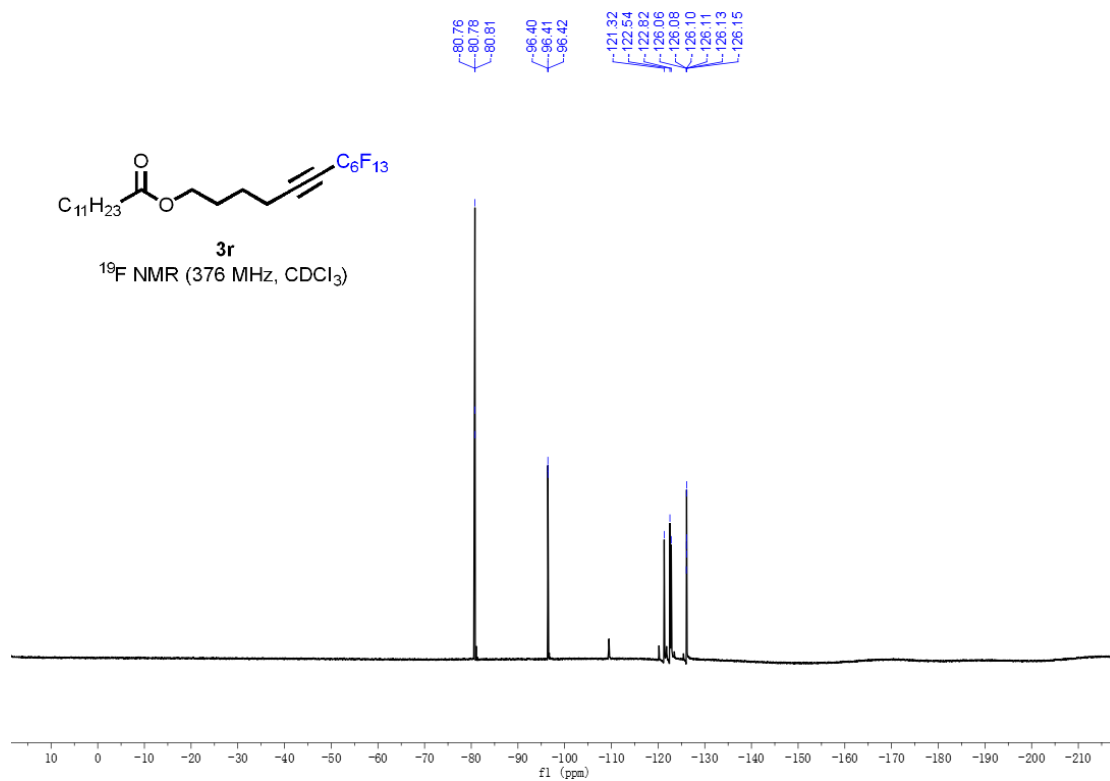
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

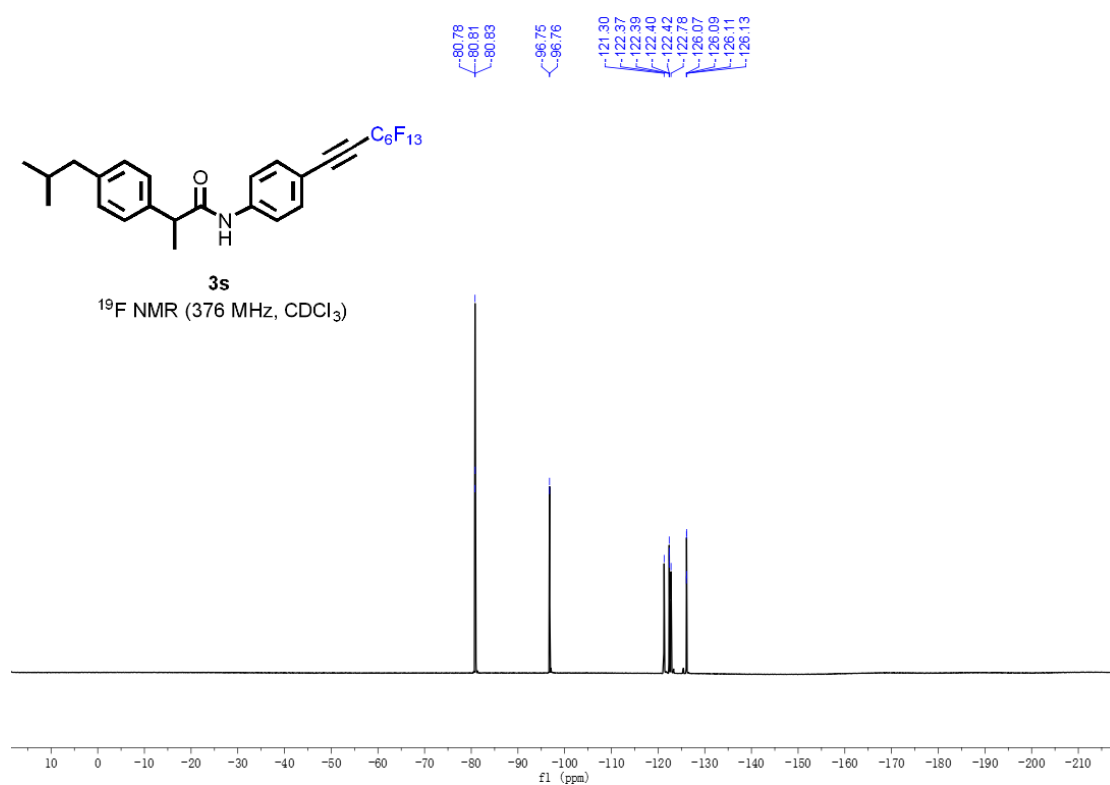
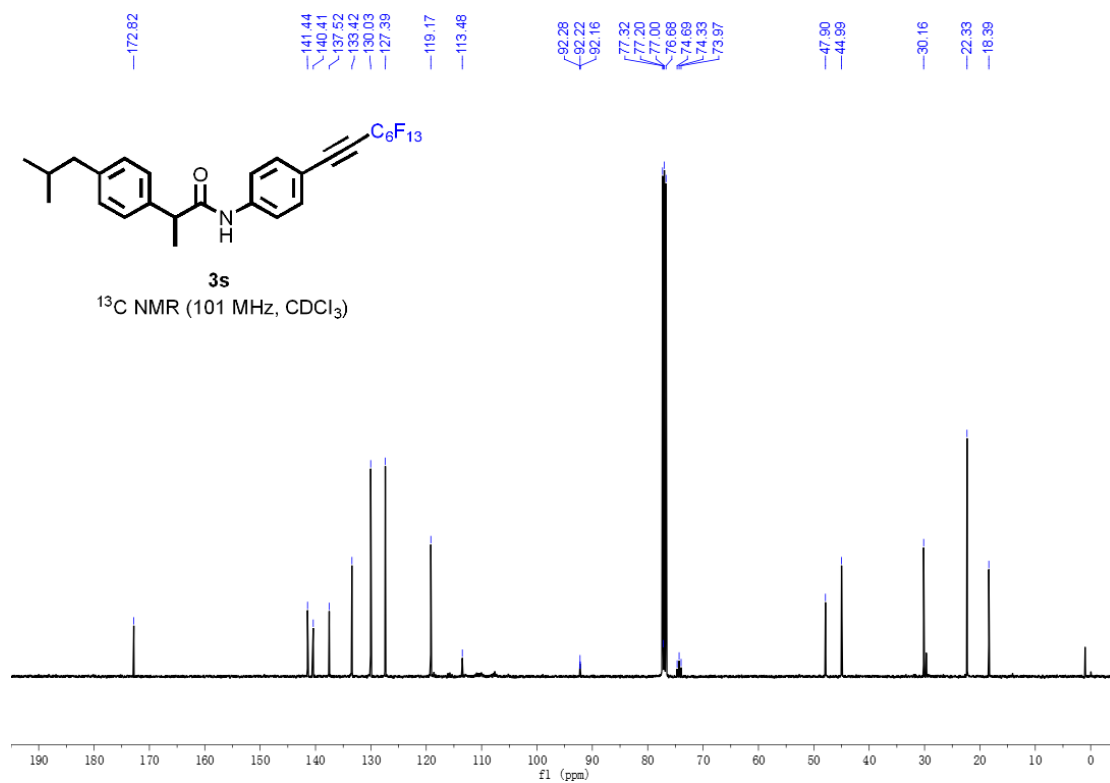


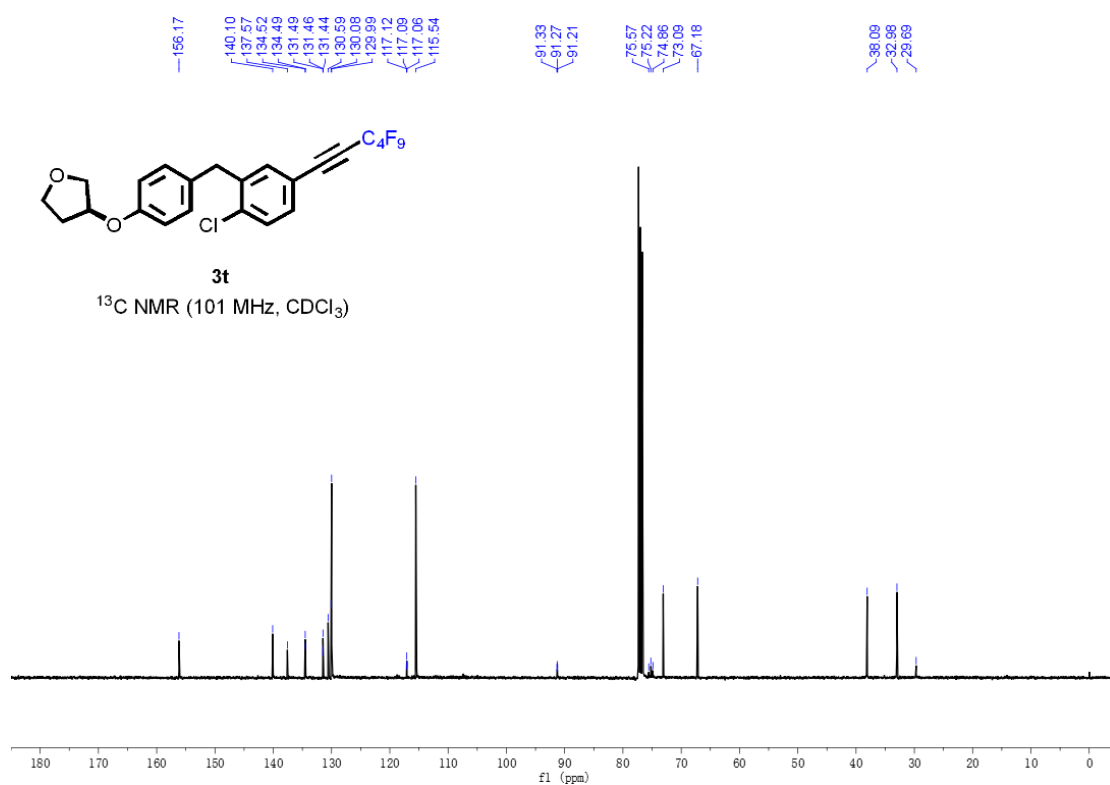
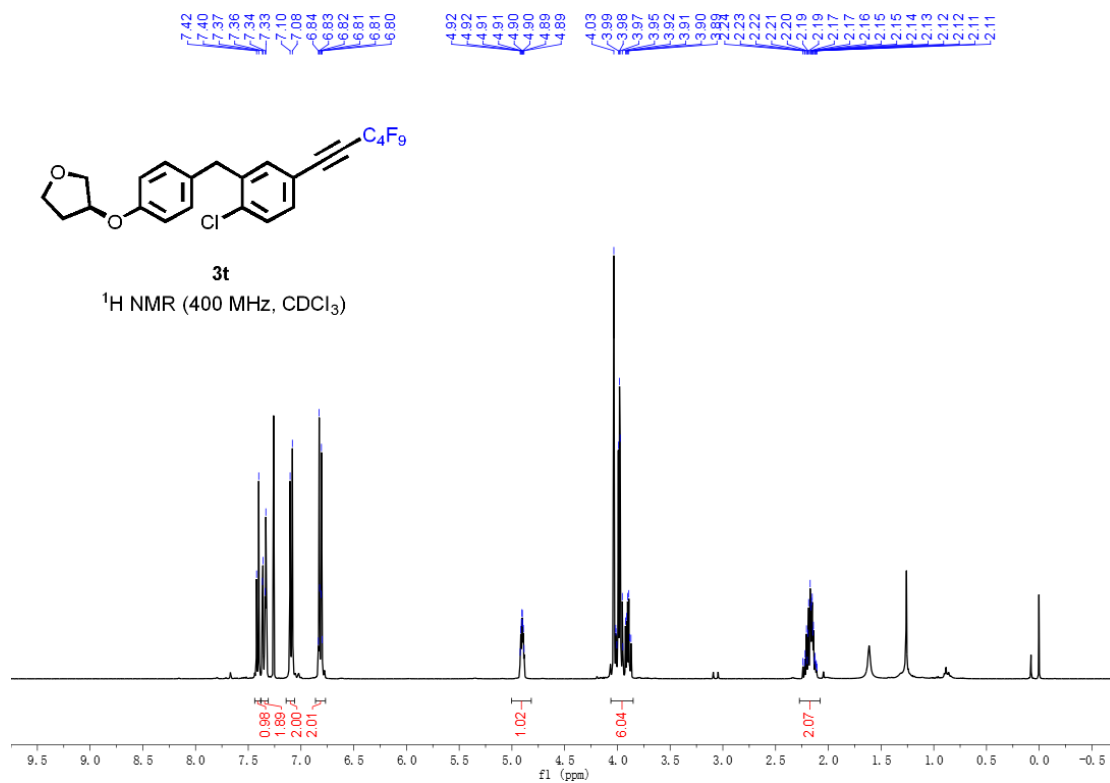


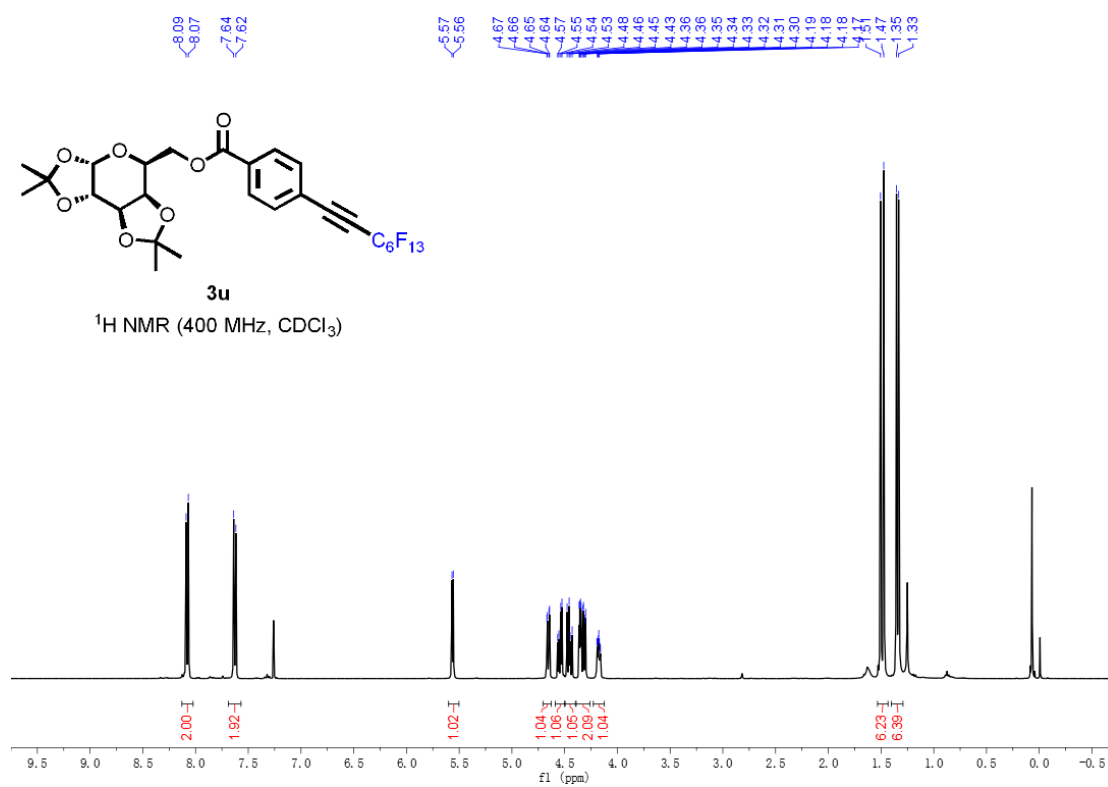
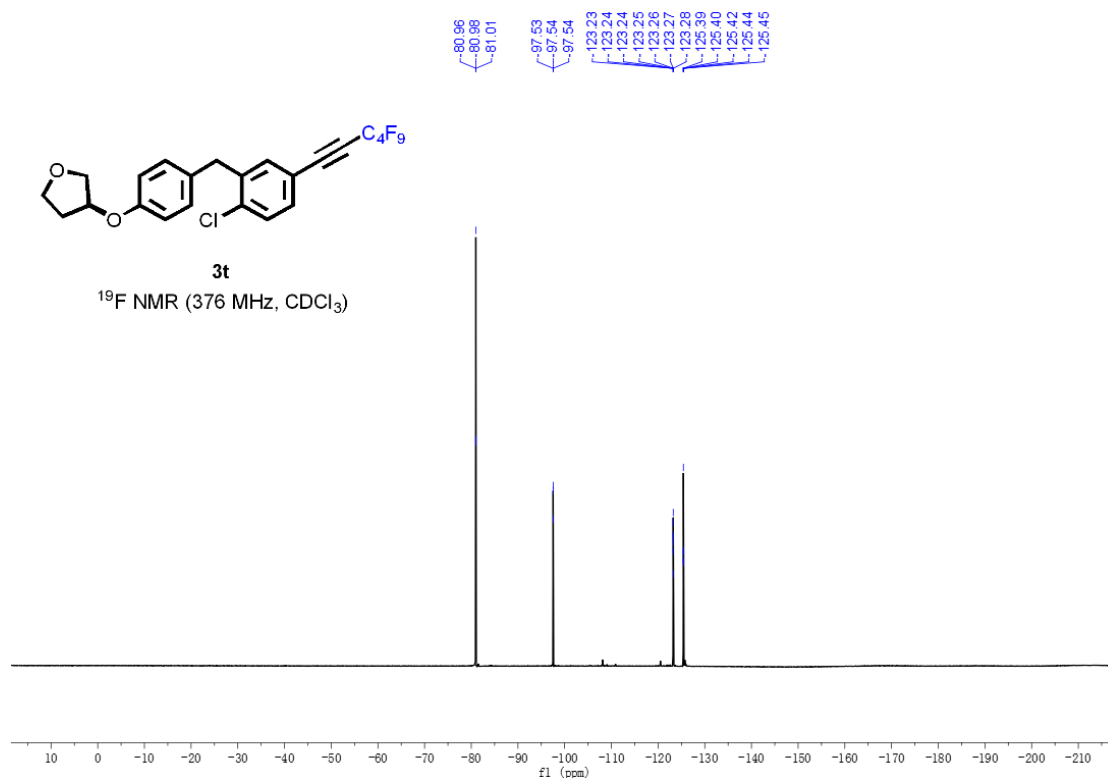


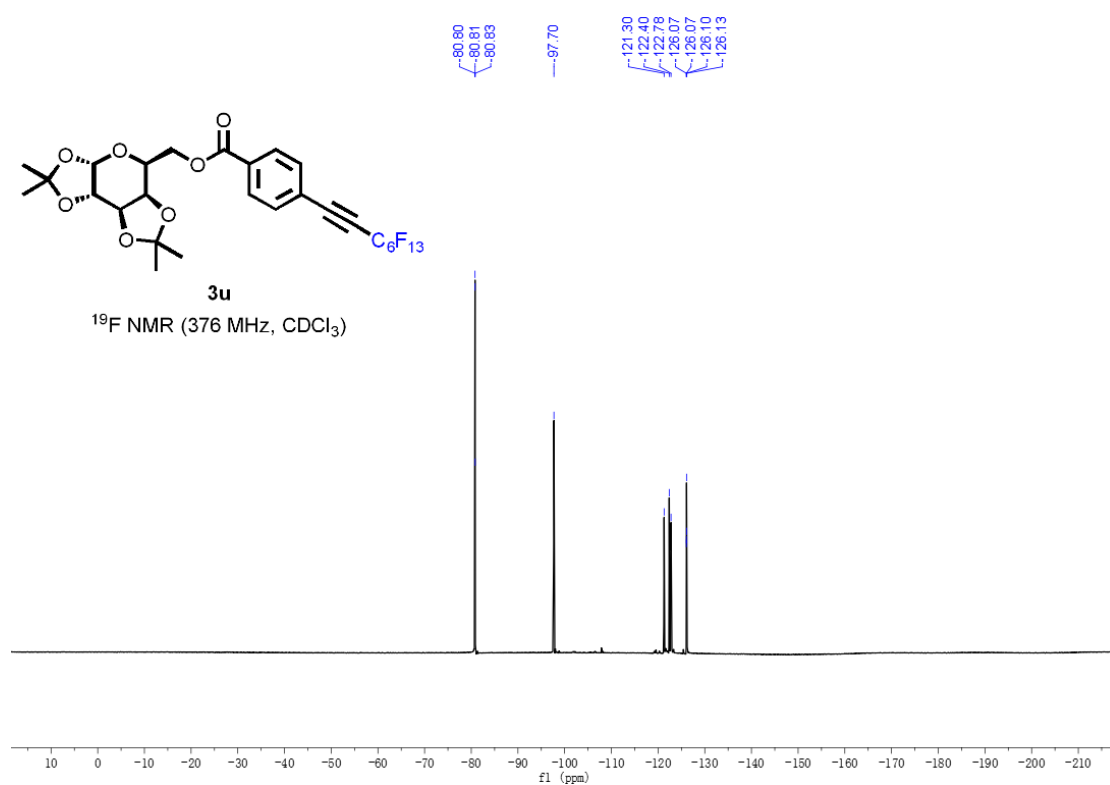
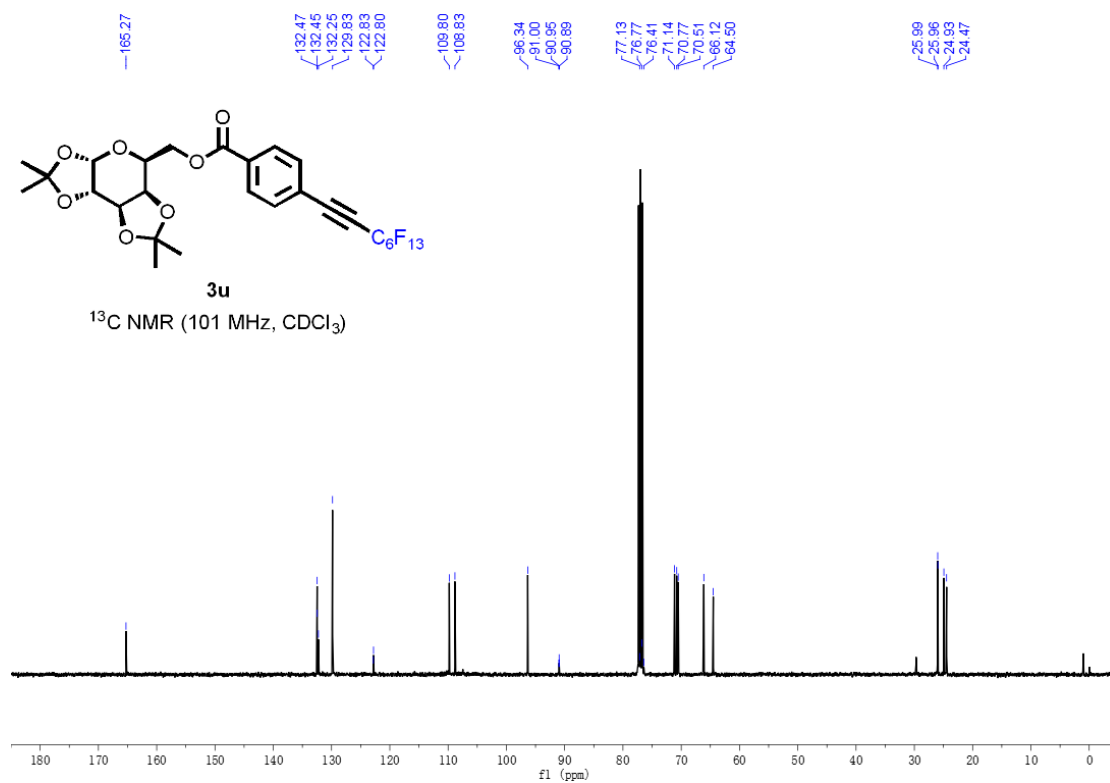


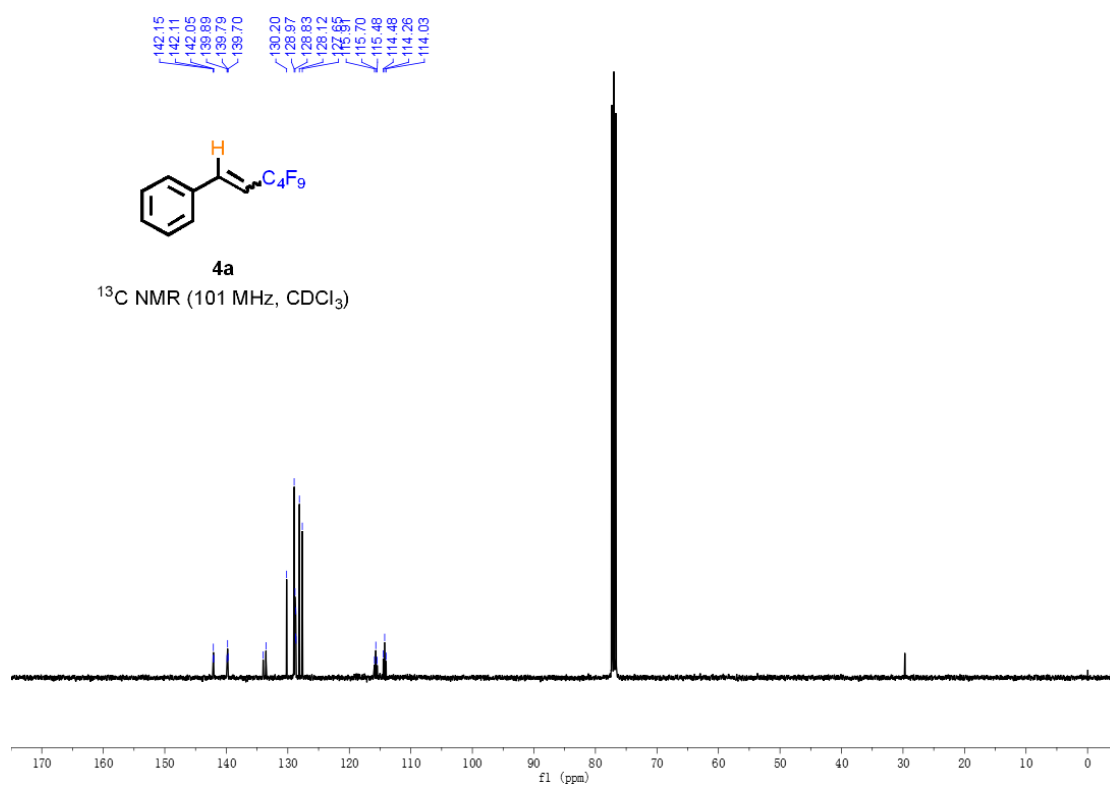
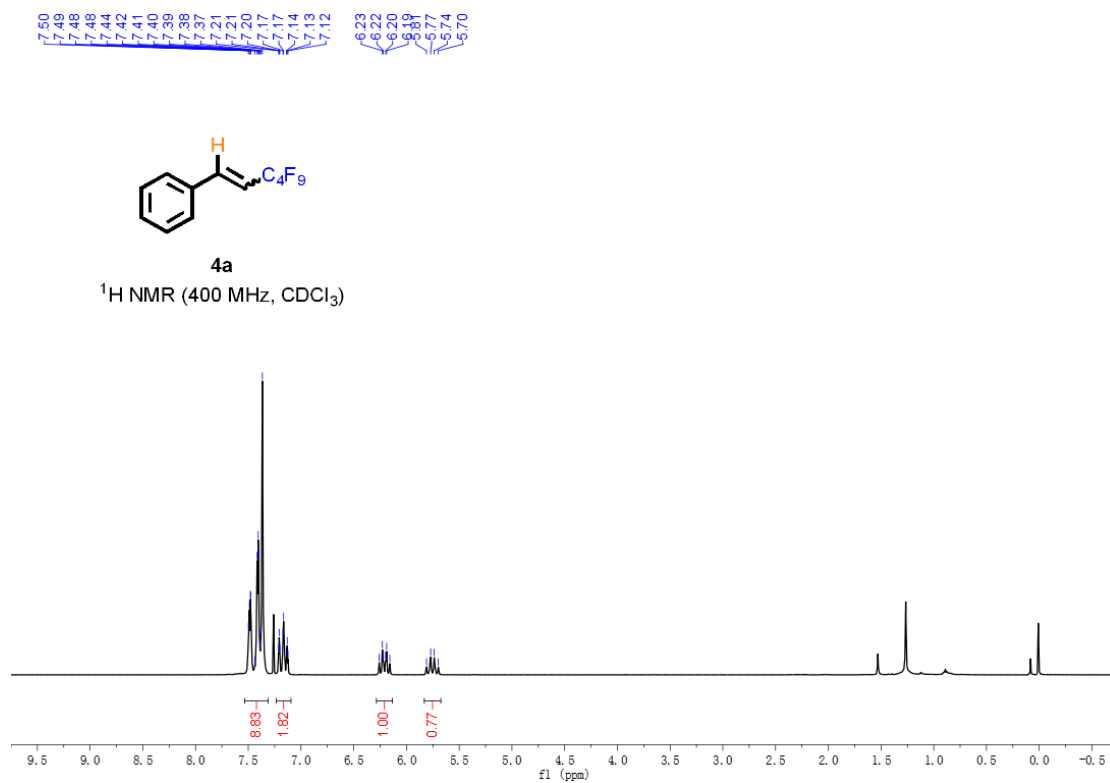


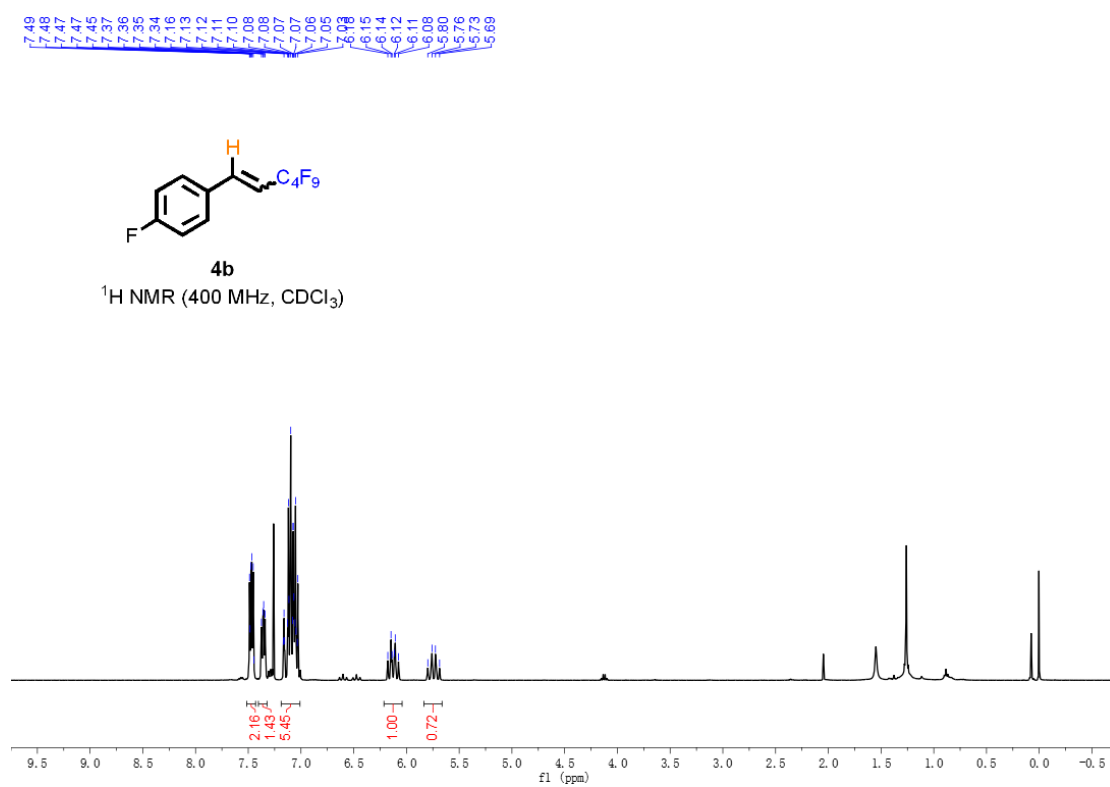
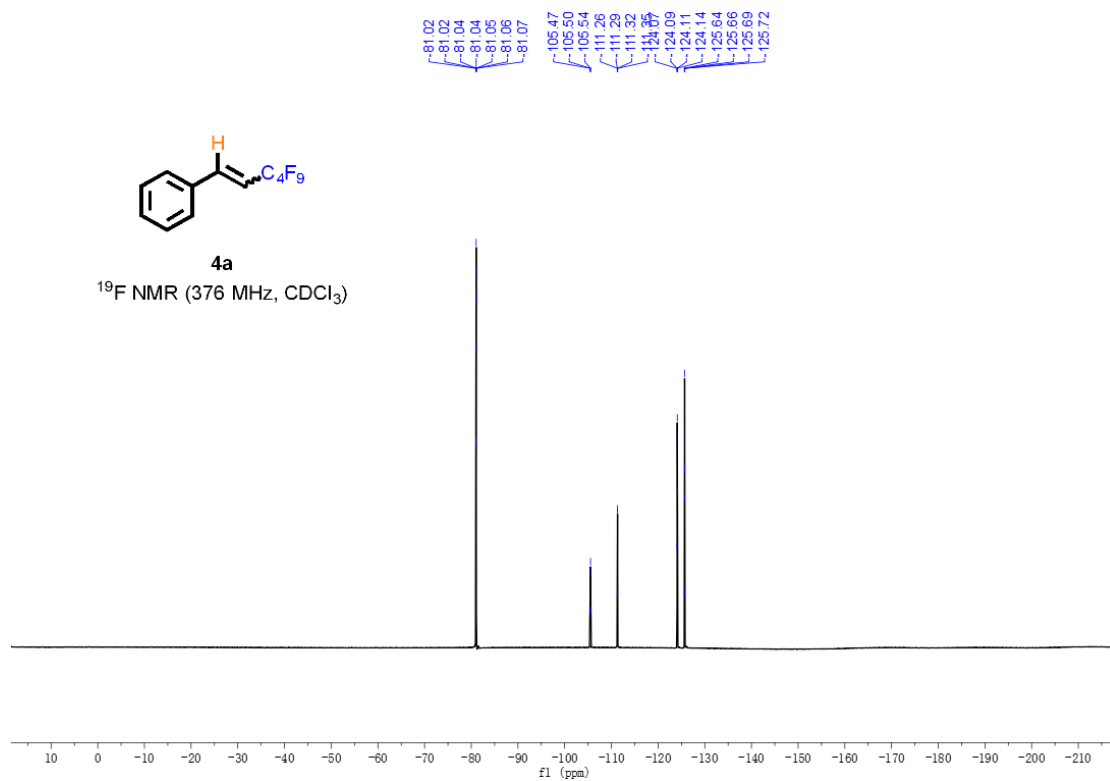


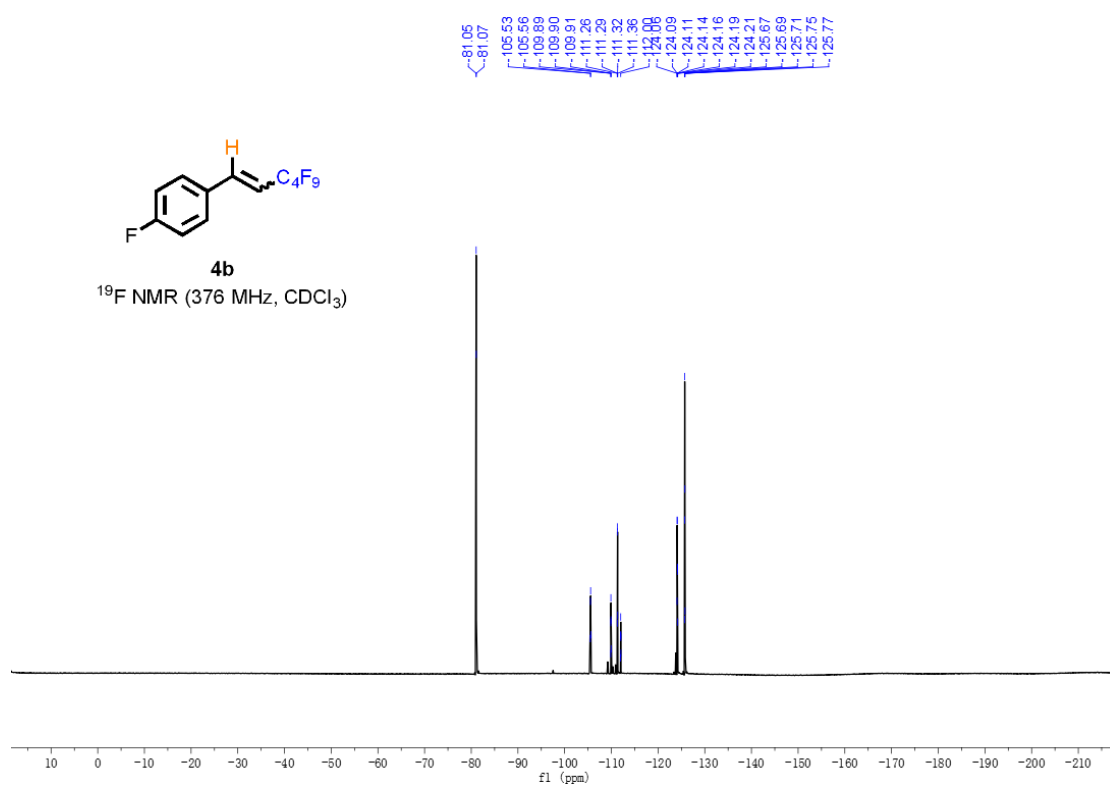
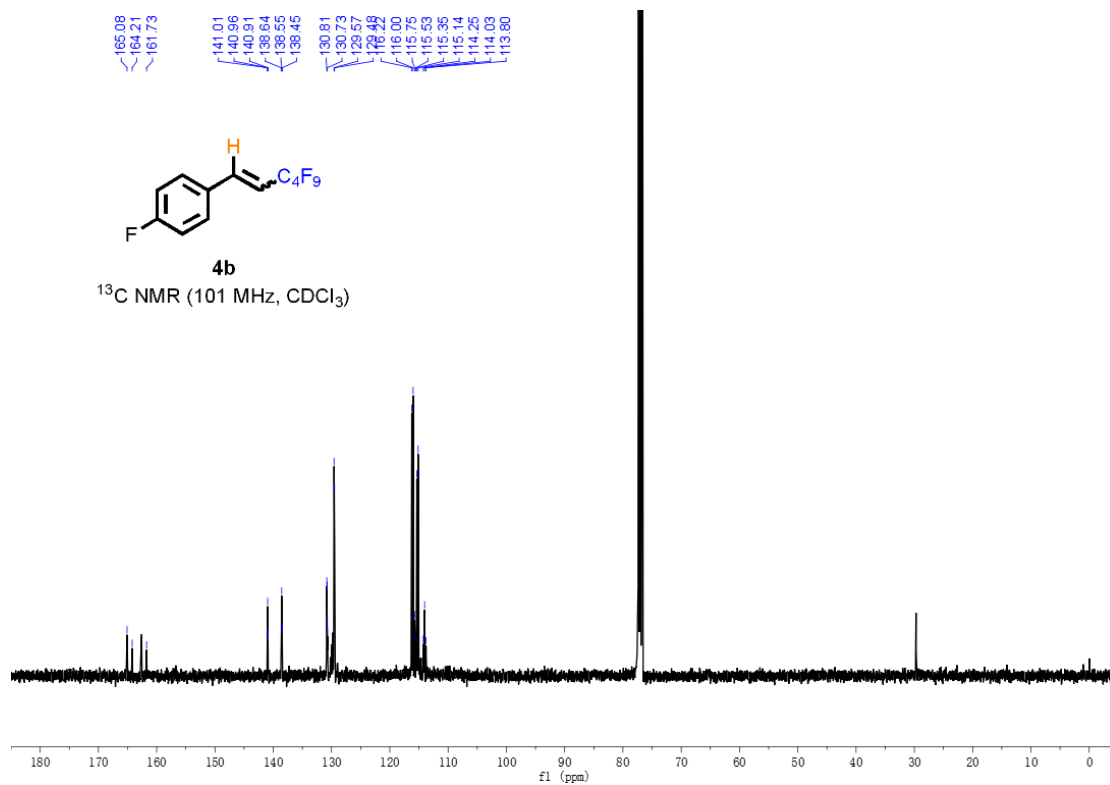






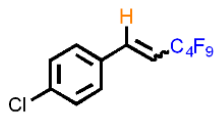






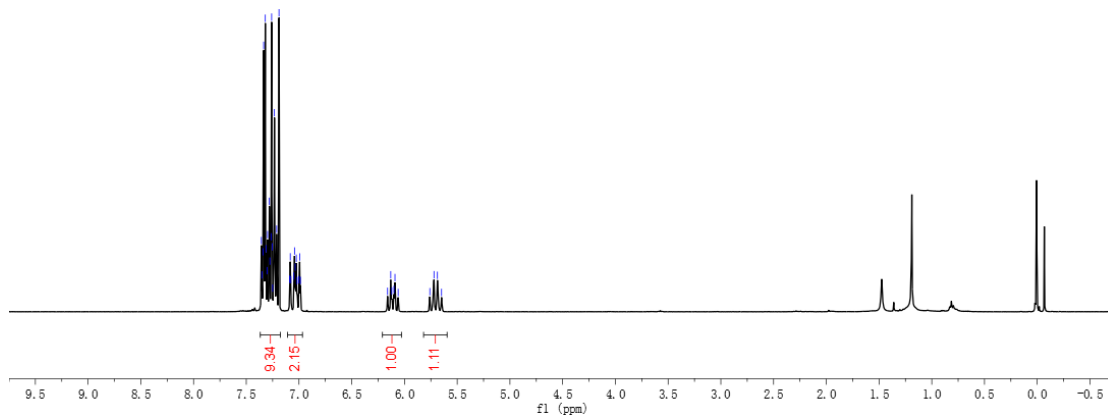


7.36  
7.35  
7.34  
7.34  
7.32  
7.31  
7.30  
7.30  
7.28  
7.28  
7.27  
7.26  
7.23  
7.21  
7.19  
7.08  
7.04  
7.03  
6.99  
6.13  
6.12  
6.10  
6.08  
5.72  
5.69

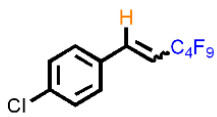


**4c**

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

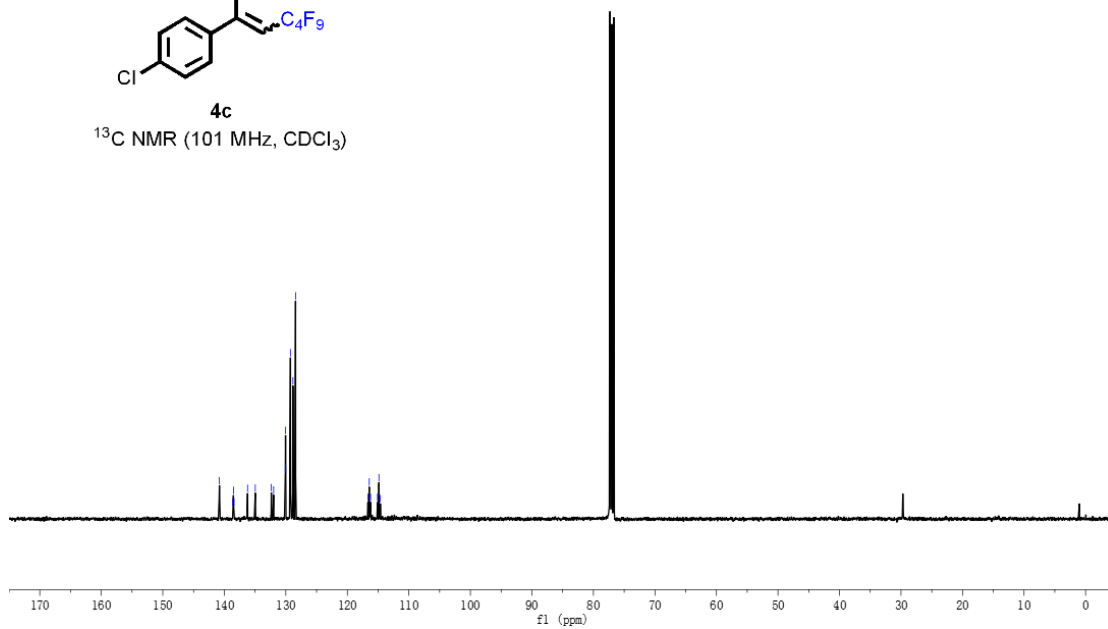


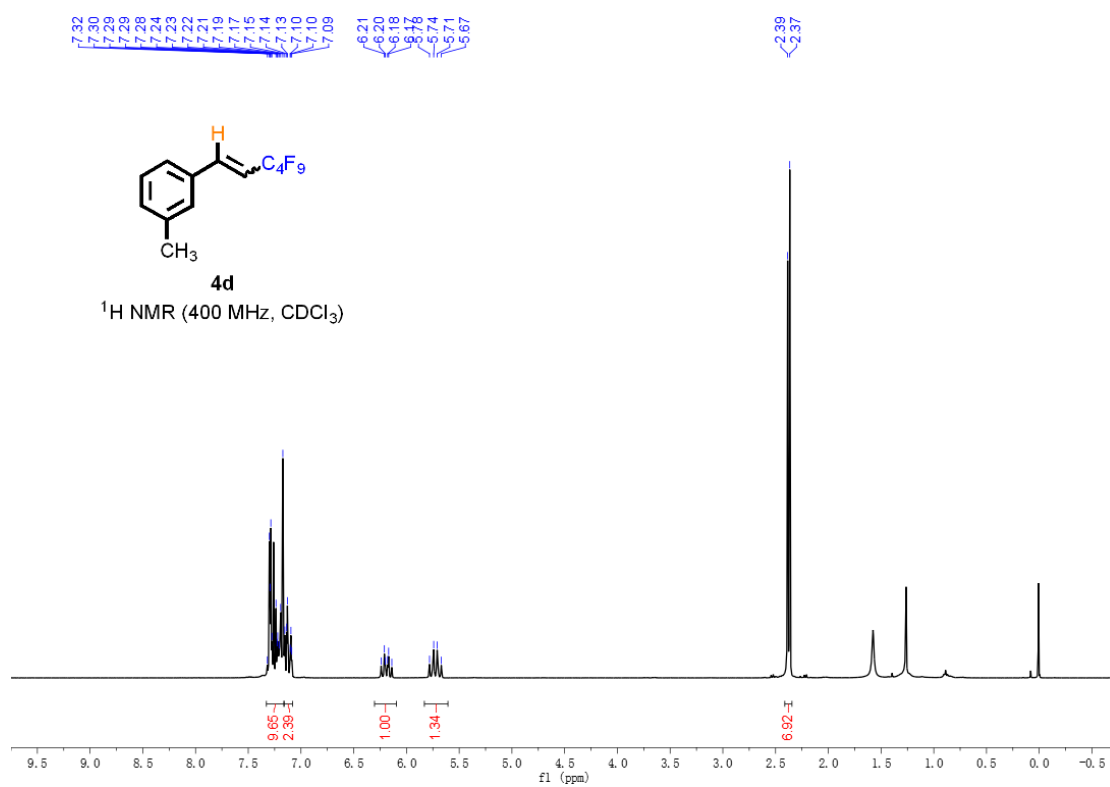
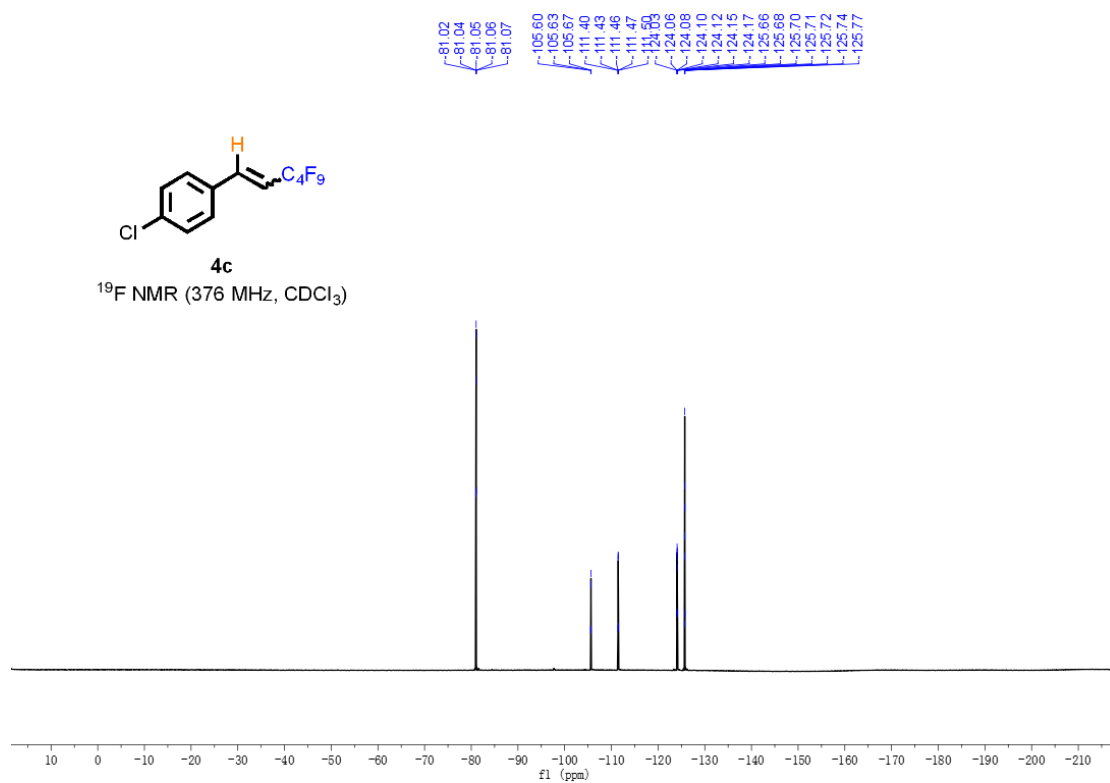
140.80  
138.91  
138.51  
138.42  
138.32  
137.56  
137.09  
130.08  
130.05  
130.01  
129.25  
128.85  
128.41  
116.65  
116.44  
116.22  
115.09  
114.87  
114.63

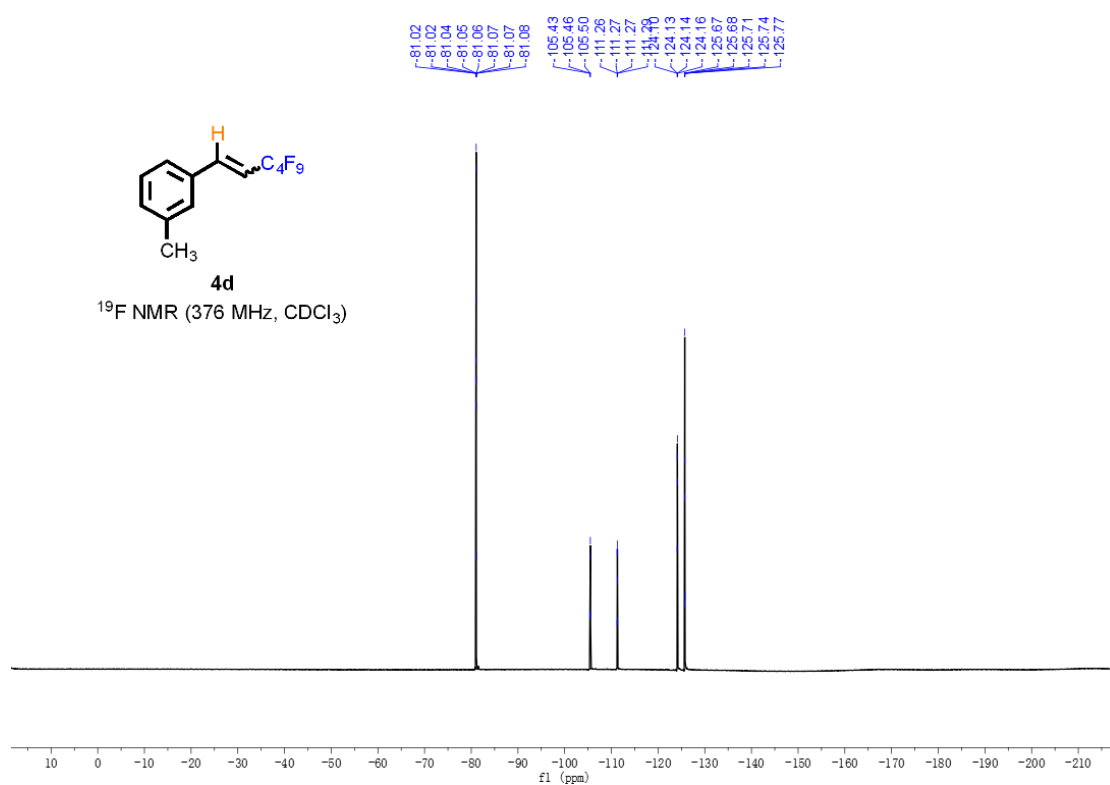
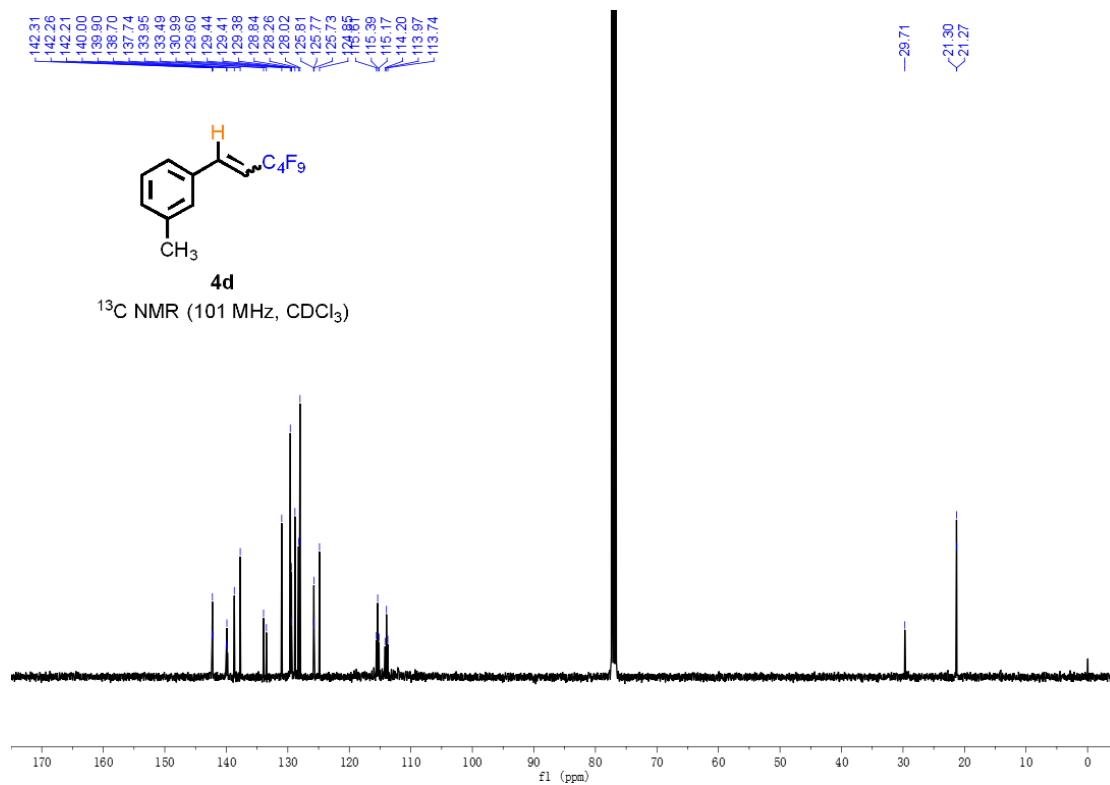


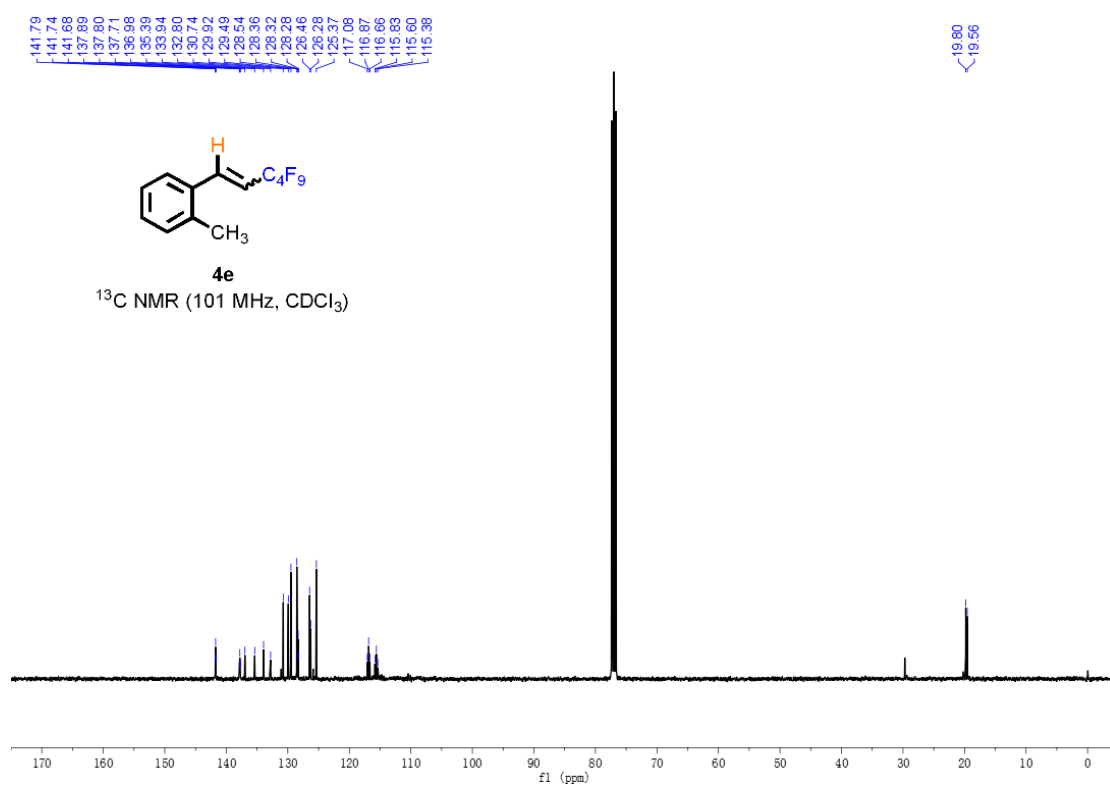
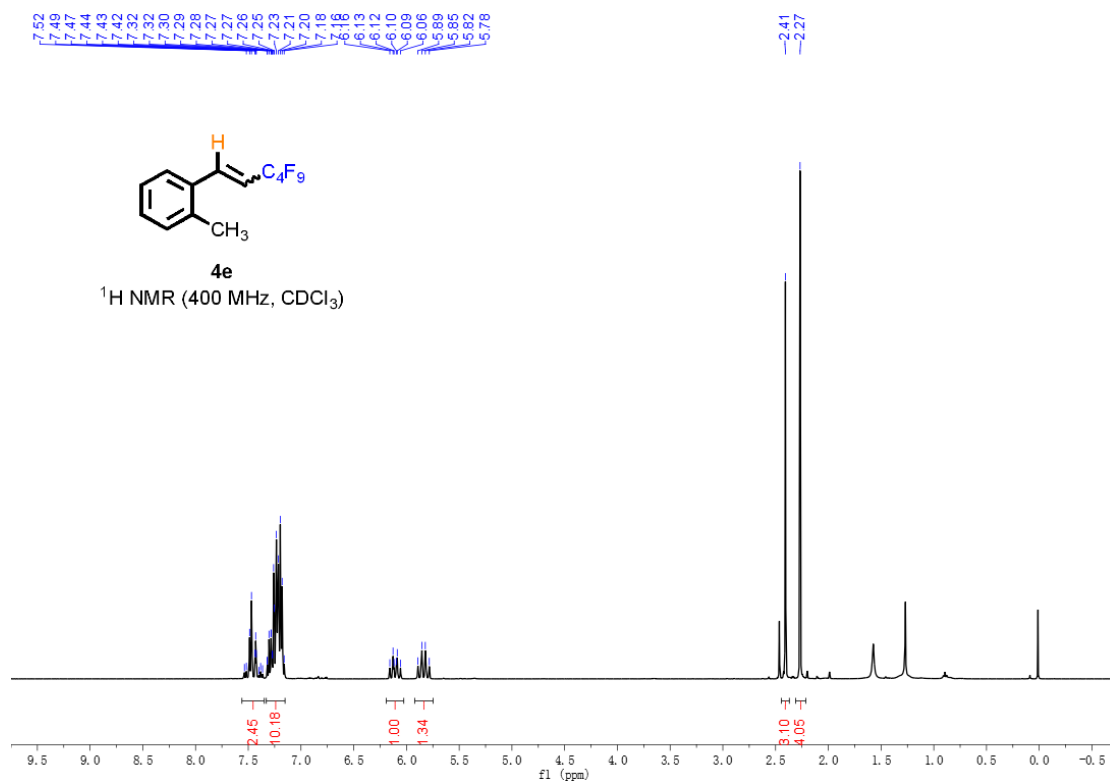
**4c**

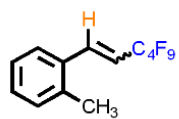
$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )







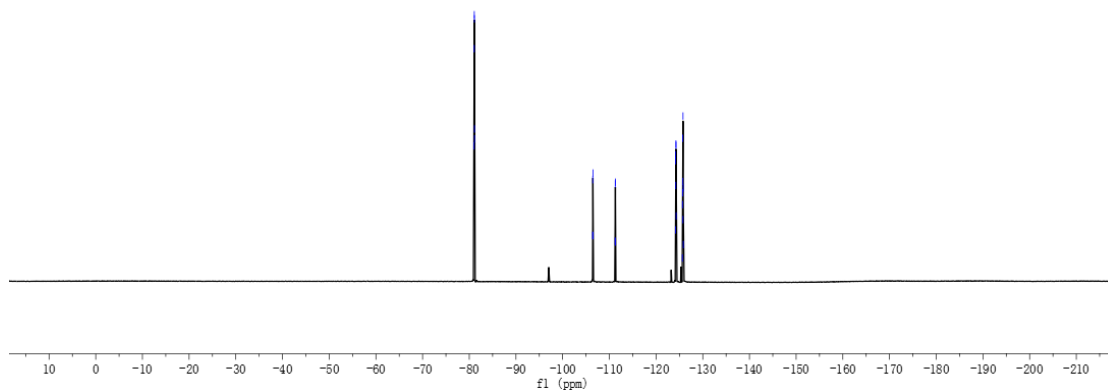




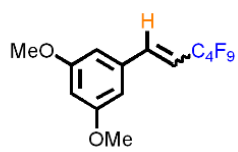
**4e**

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

-81.03  
-81.06  
-81.07  
-81.10  
-81.12  
-81.12  
106.42  
106.45  
106.48  
106.52  
111.23  
111.26  
124.15  
124.17  
124.20  
124.22  
124.25  
124.28  
124.30  
125.63  
125.65  
125.68  
125.71  
125.75  
125.76  
125.77  
125.80  
125.83

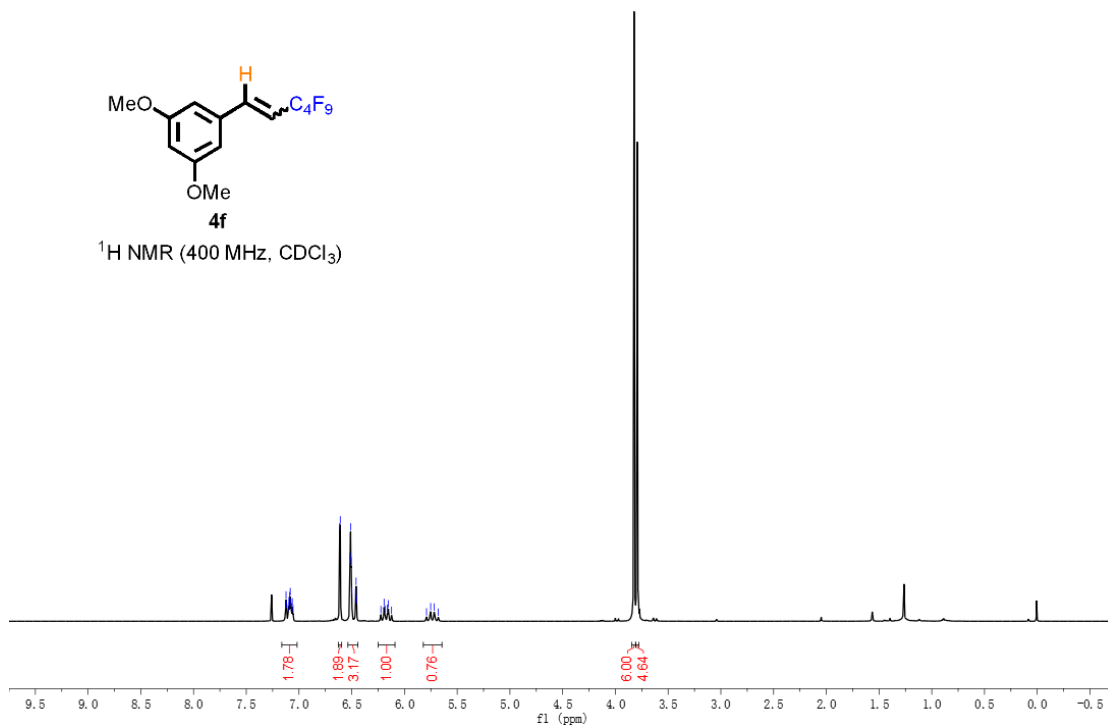


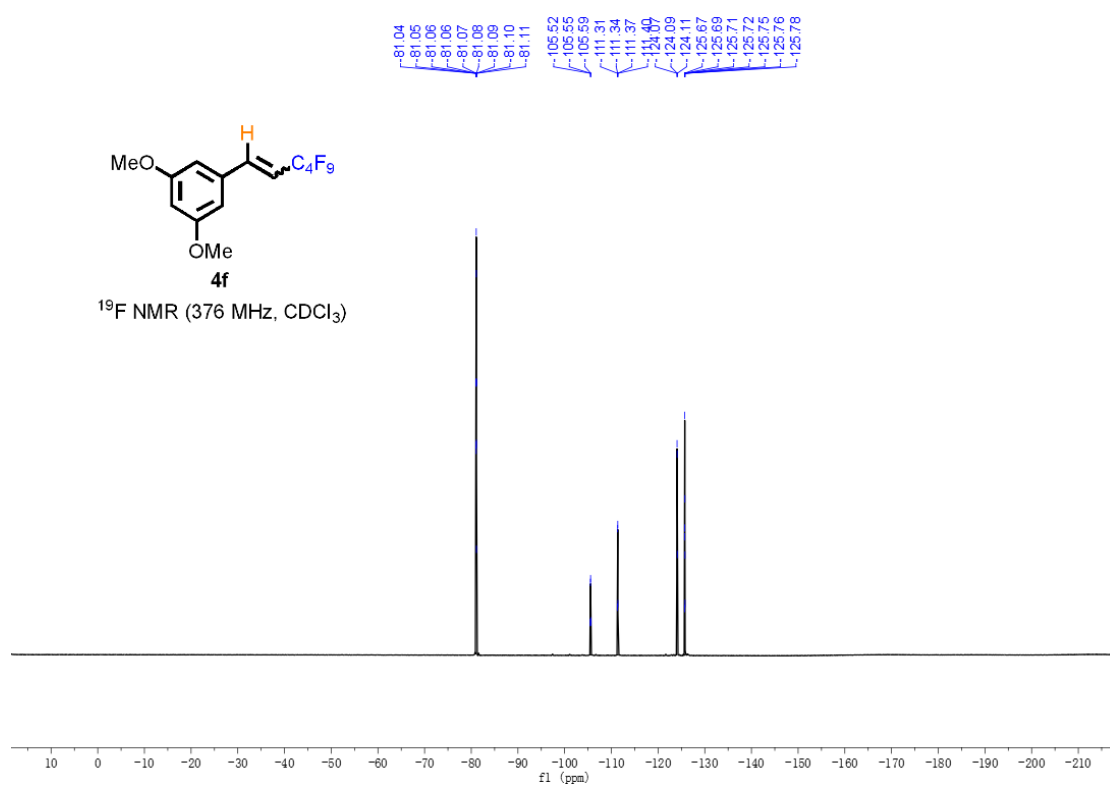
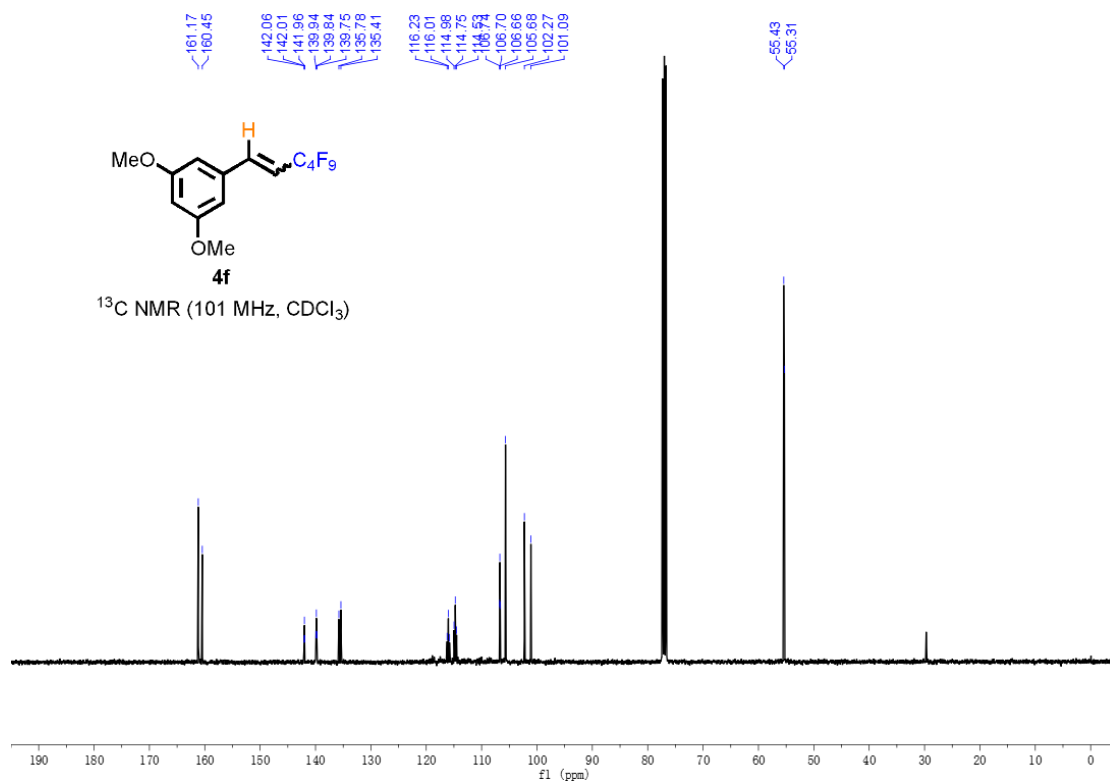
7.13  
7.12  
7.12  
7.10  
7.09  
7.08  
7.08  
7.07  
7.06  
7.06  
6.61  
6.62  
6.61  
6.59  
5.75  
5.72  
5.68

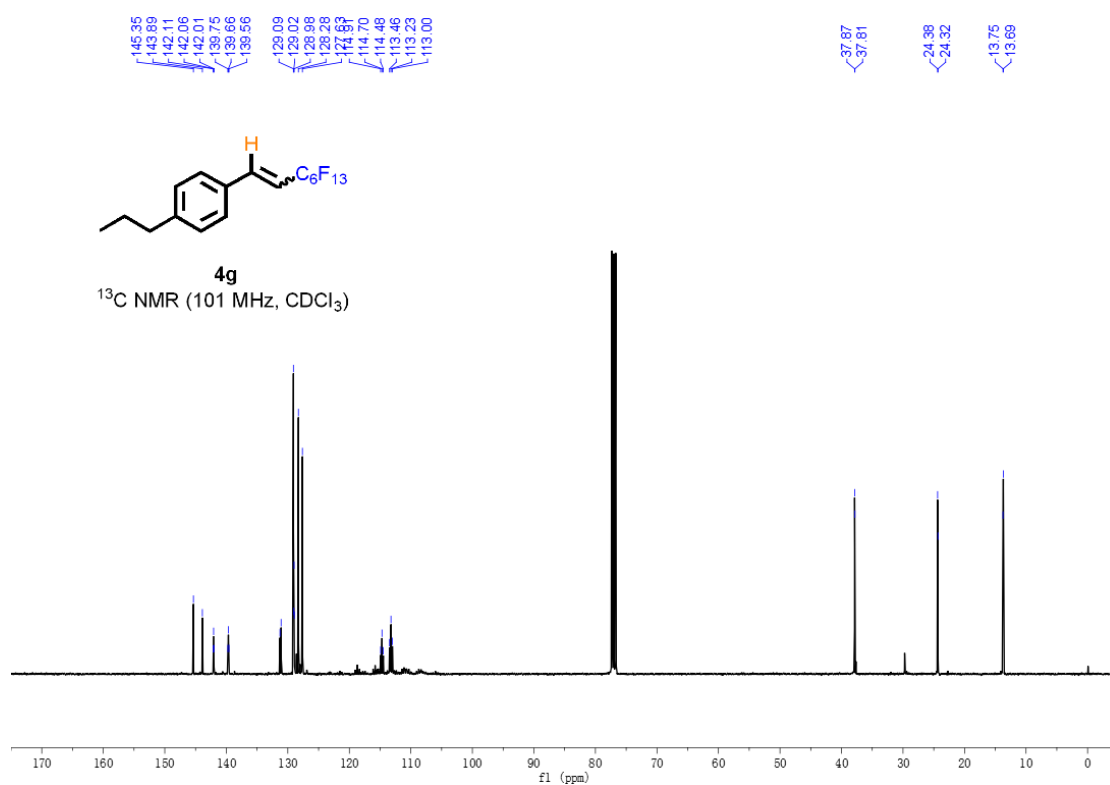
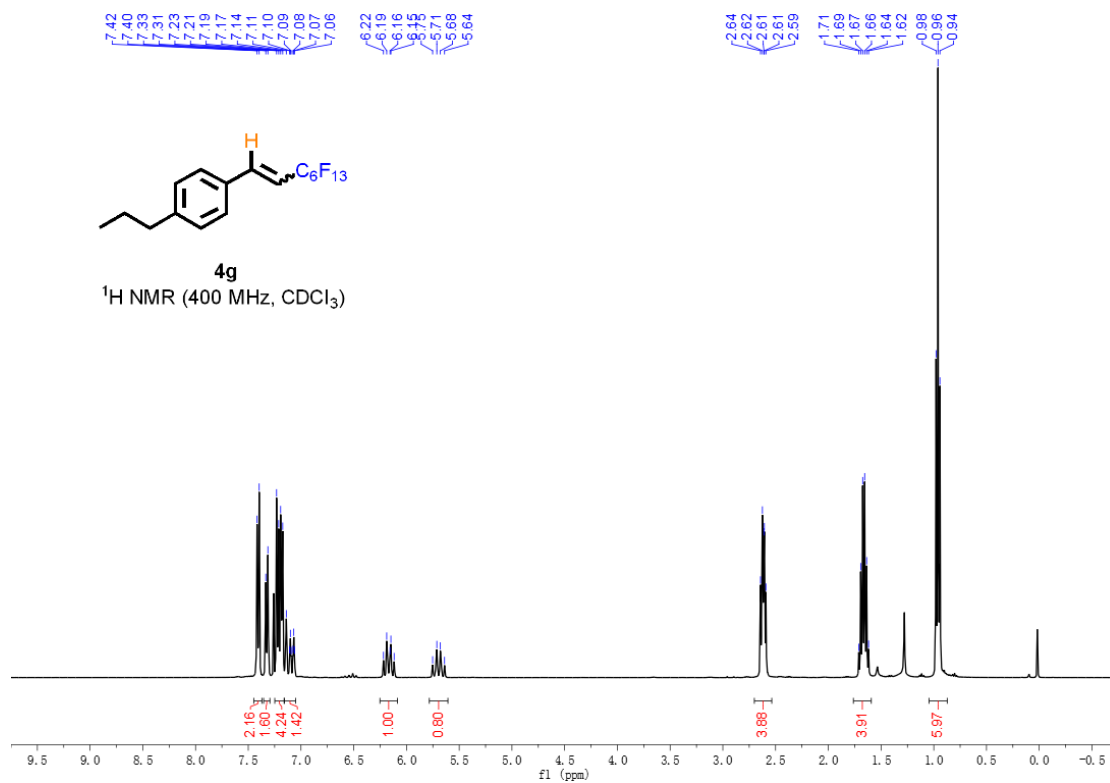


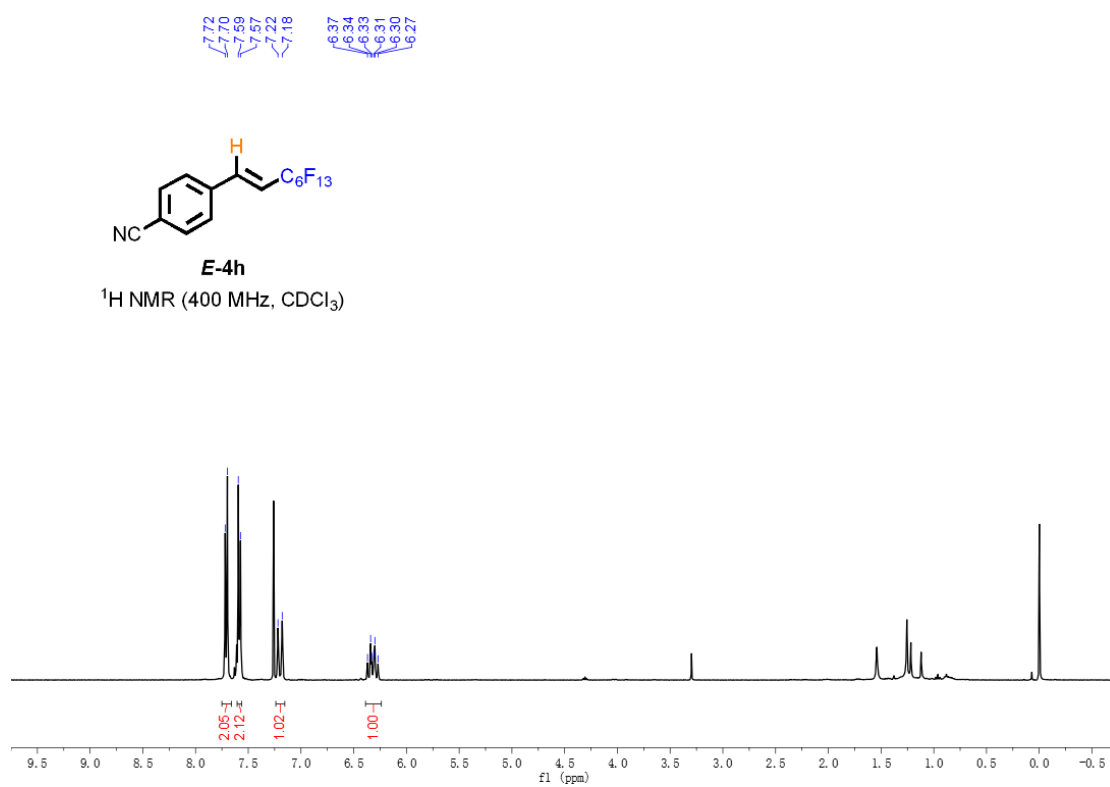
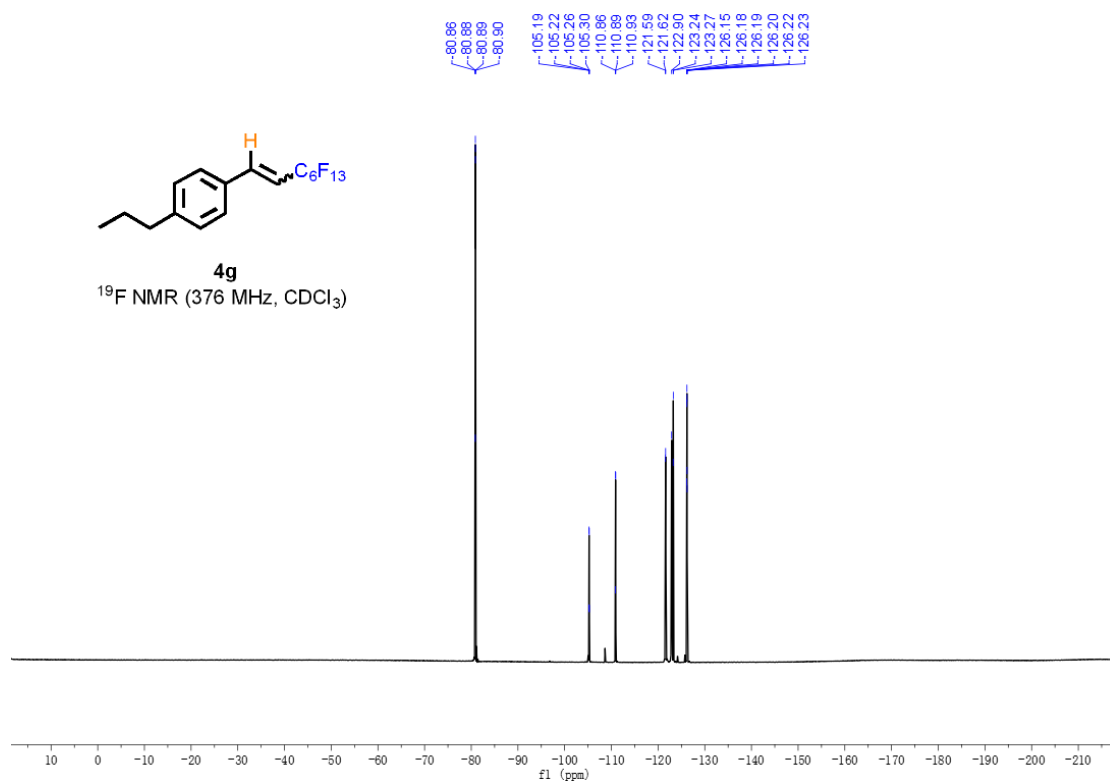
**4f**

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

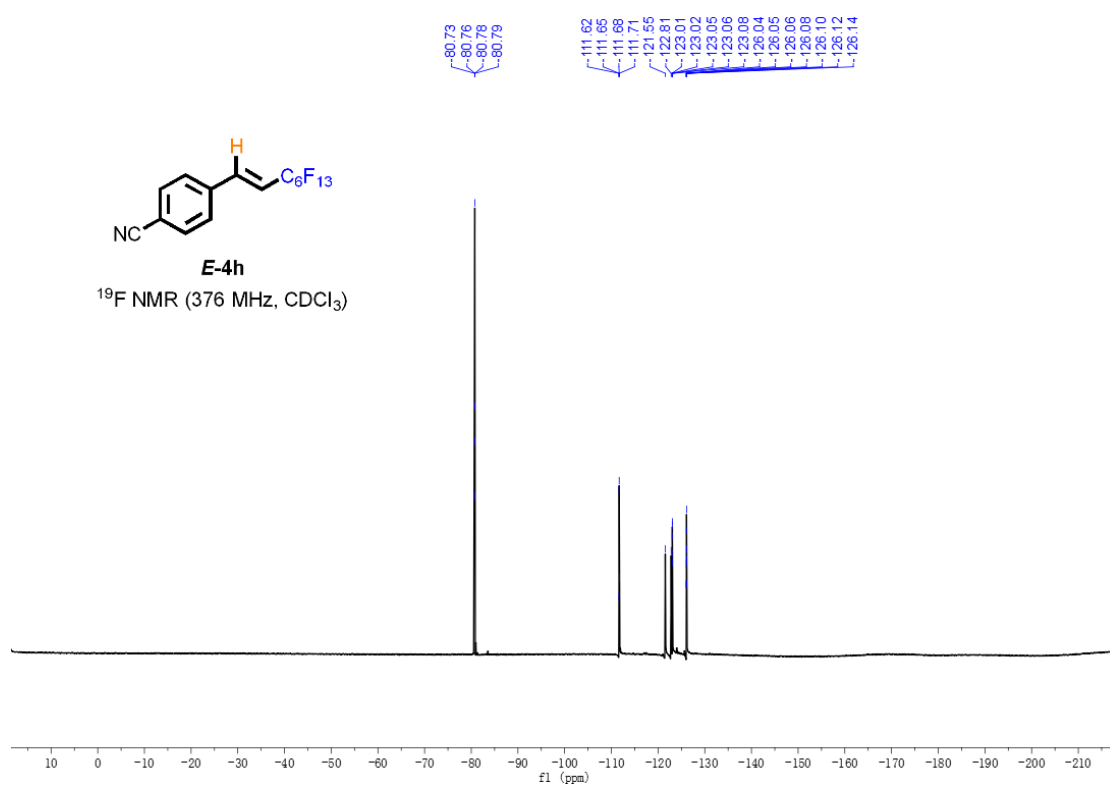
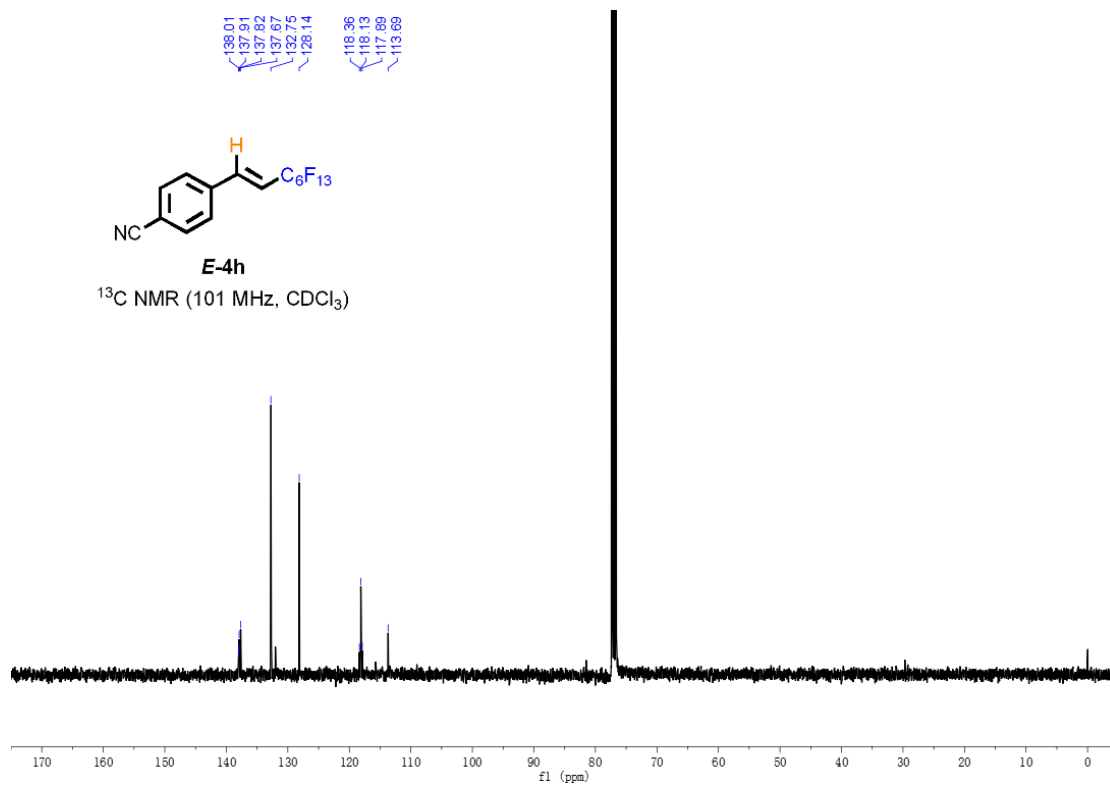




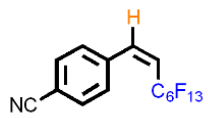






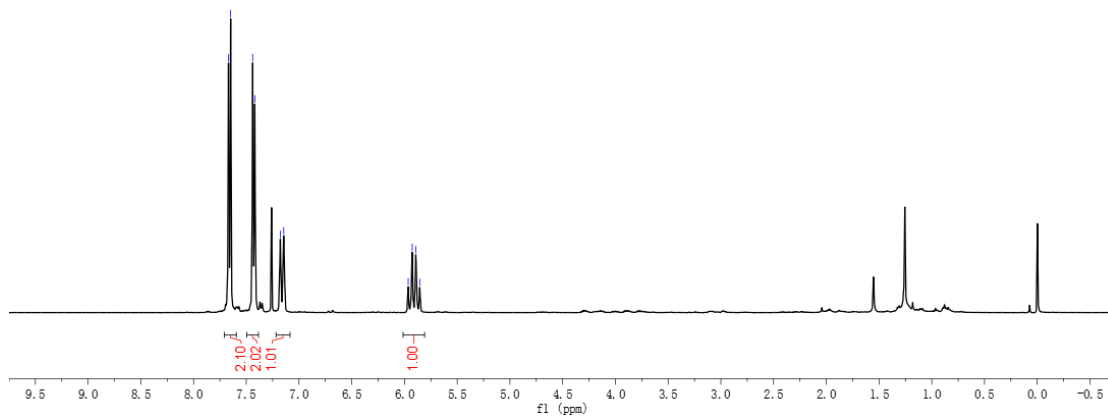


7.67  
7.65  
7.44  
7.42  
7.16  
7.14  
5.96  
5.93  
5.89  
5.86

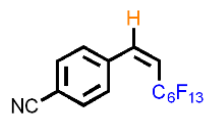


**Z-4h**

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

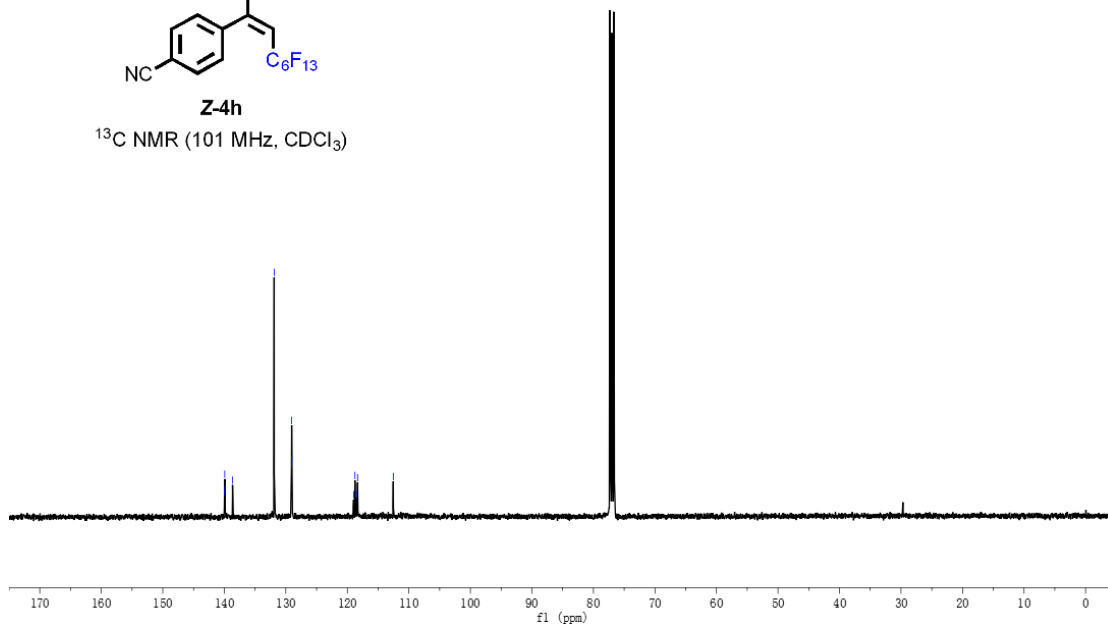


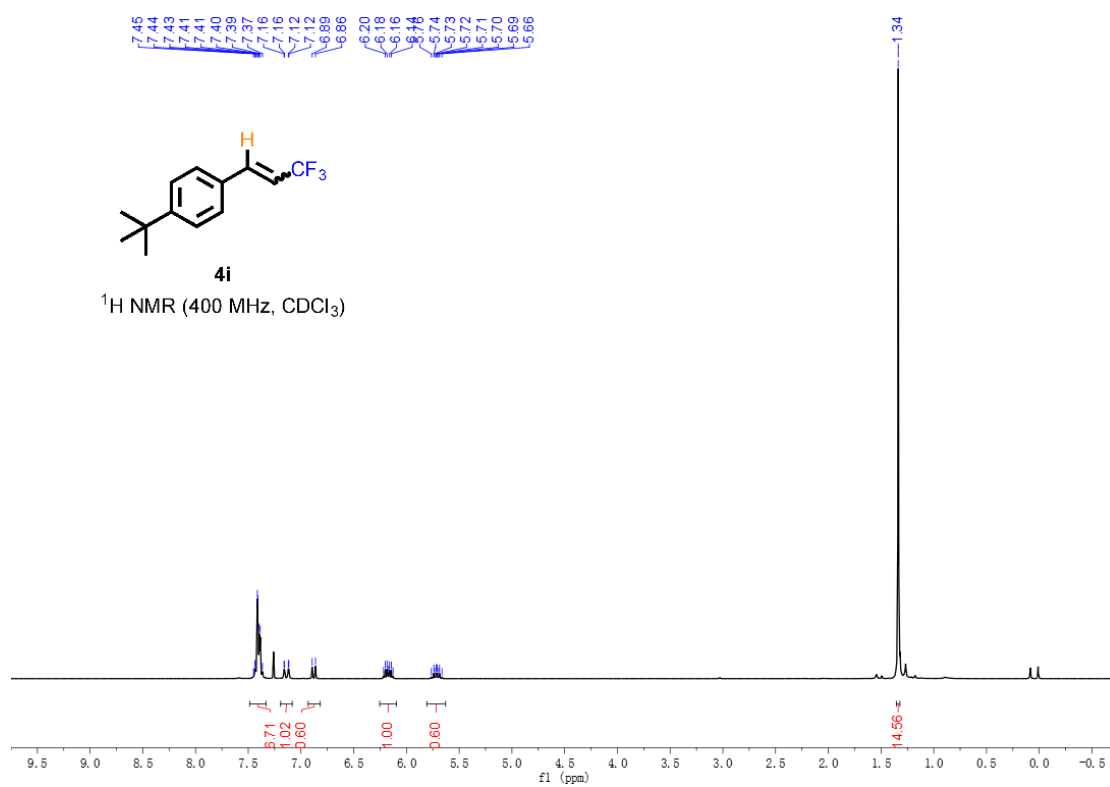
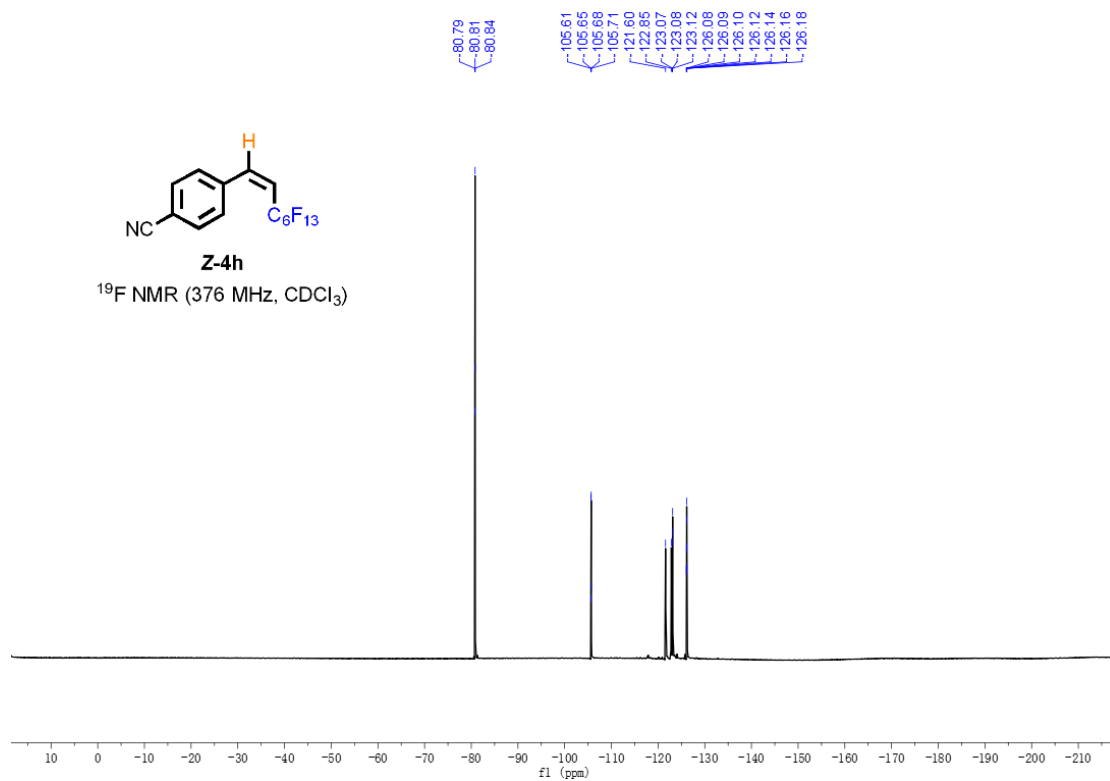
139.08  
138.93  
138.87  
138.66  
131.80  
129.08  
129.05  
129.02  
118.98  
118.76  
118.54  
118.34  
112.53

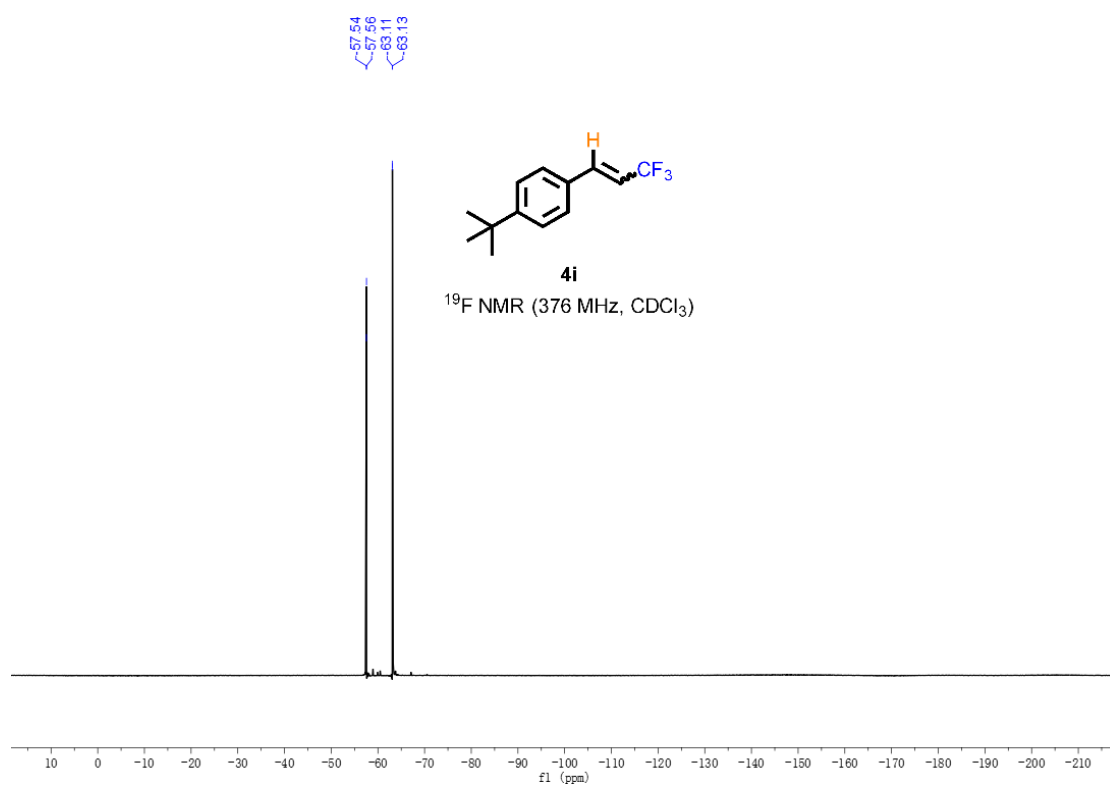
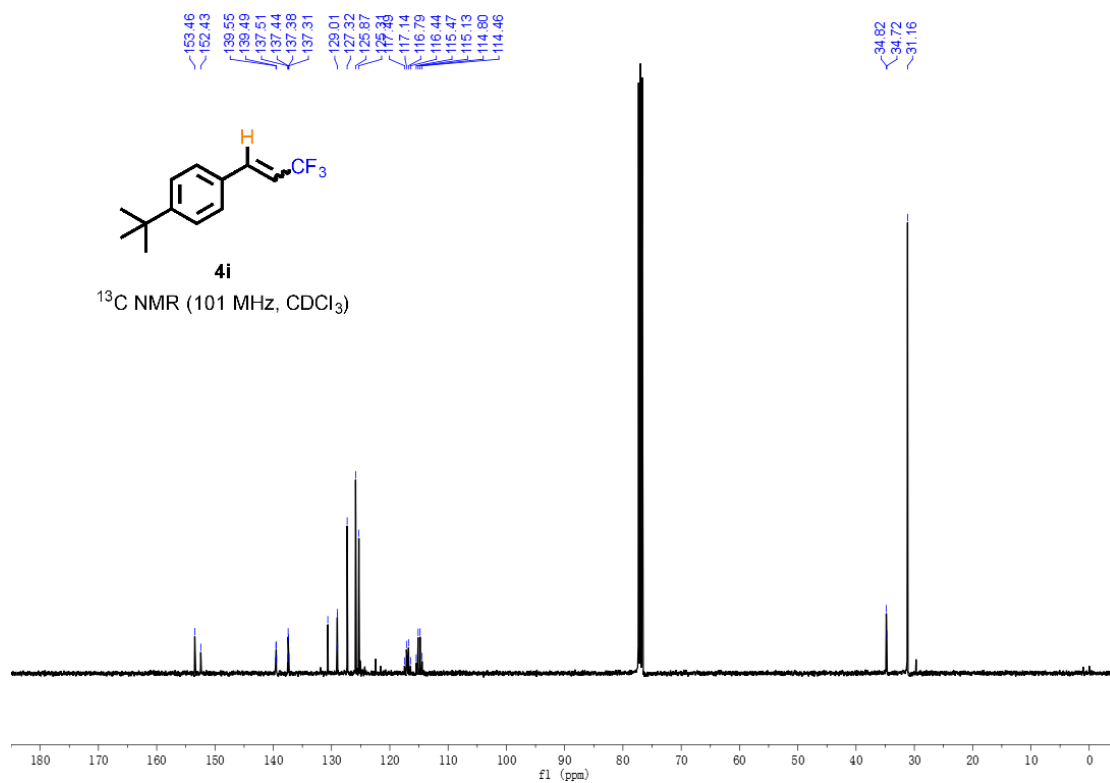


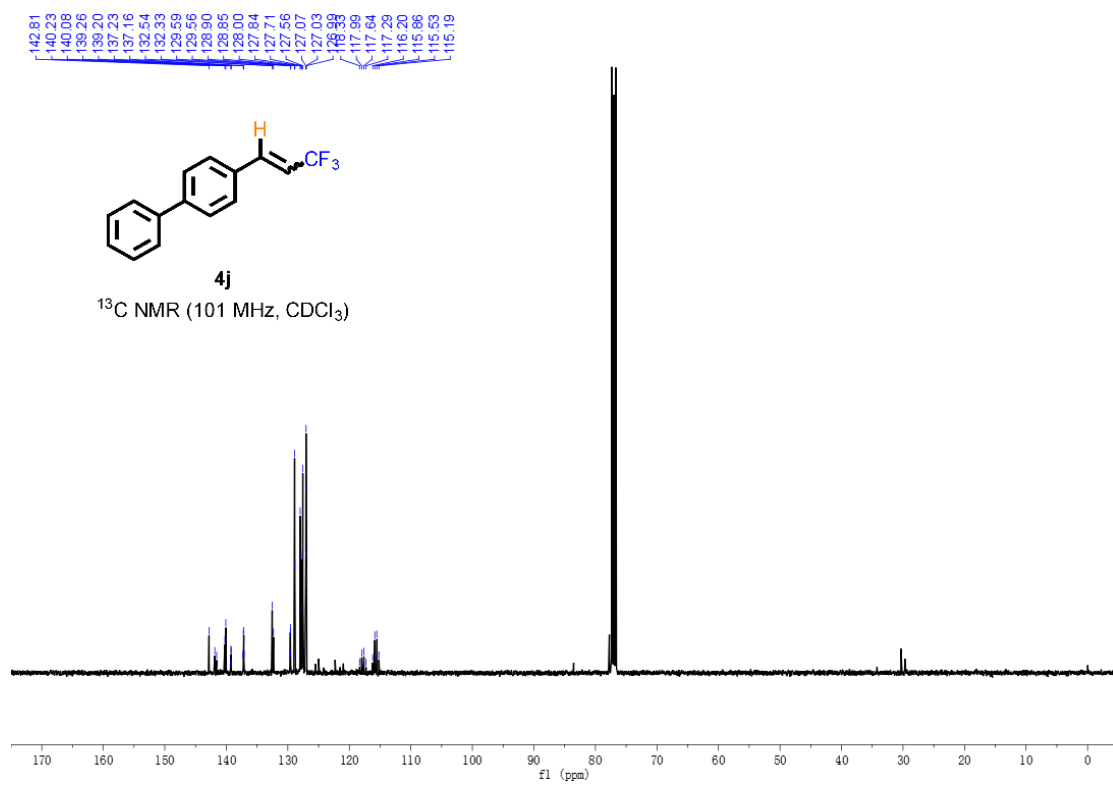
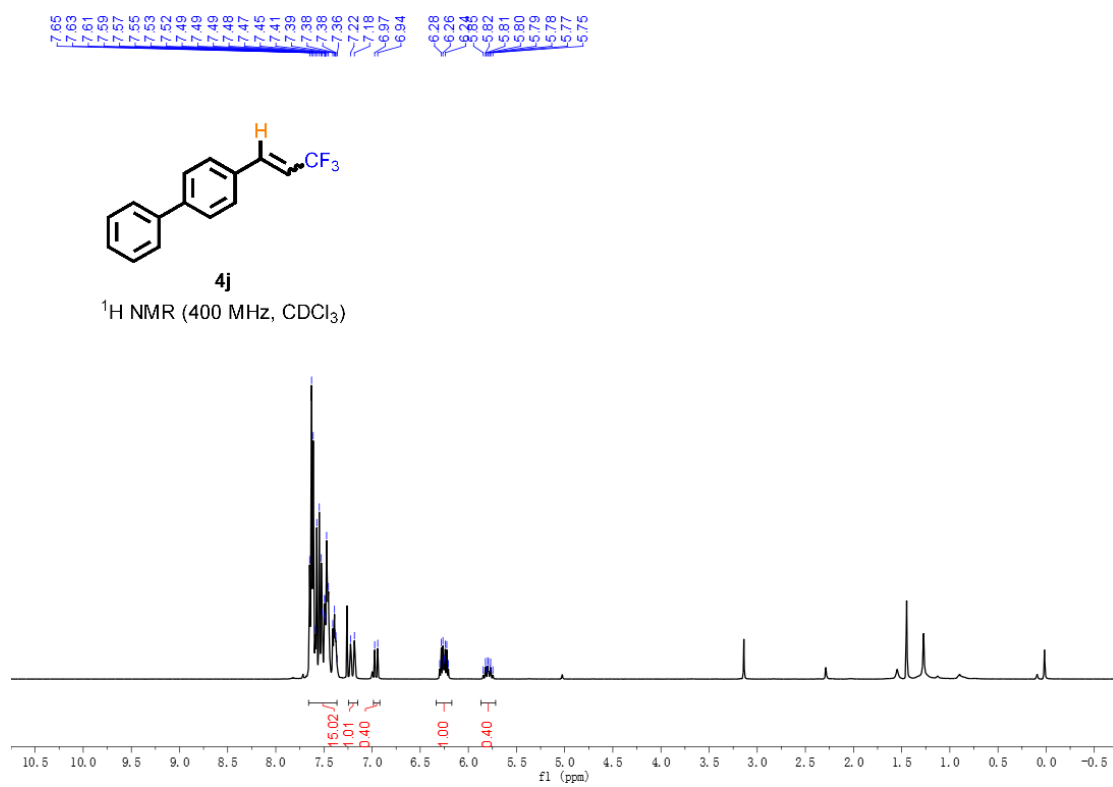
**Z-4h**

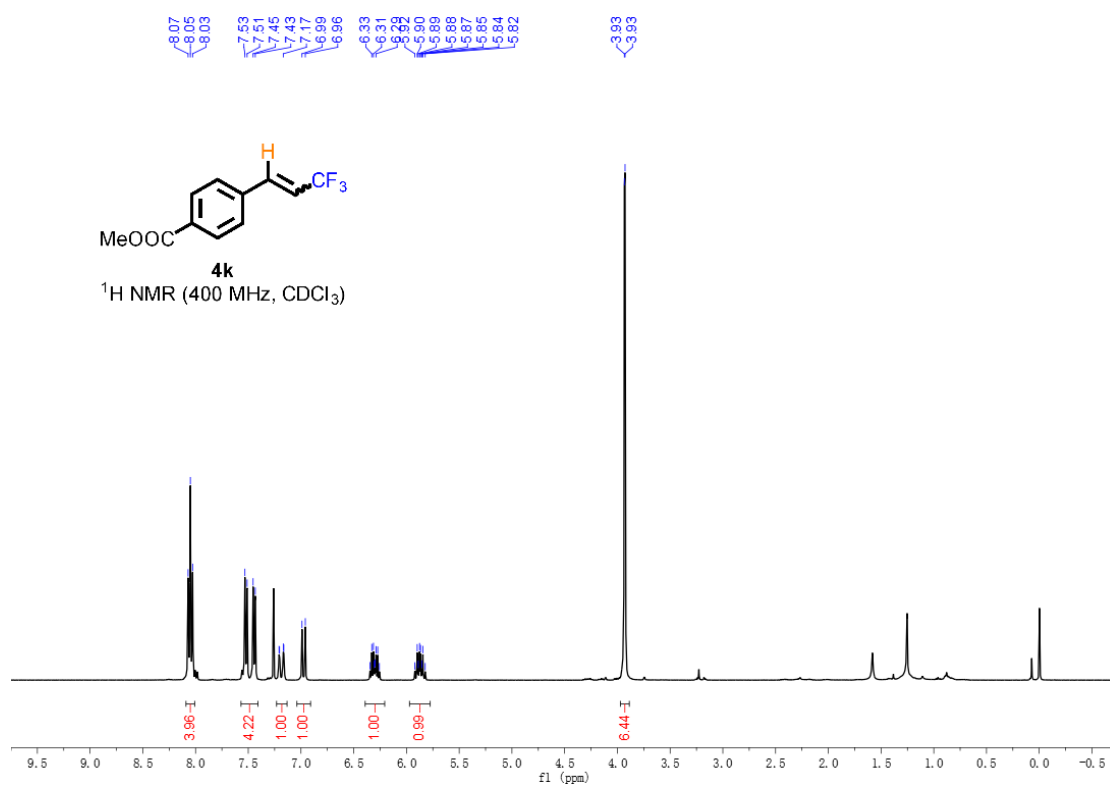
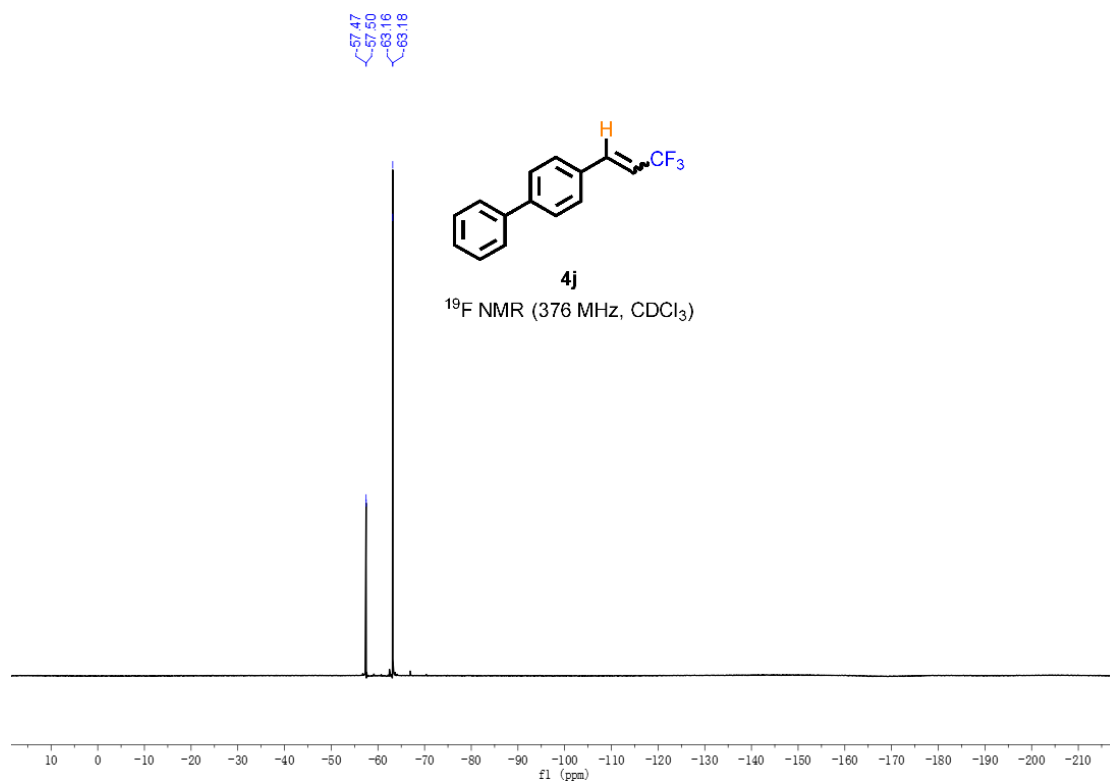
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

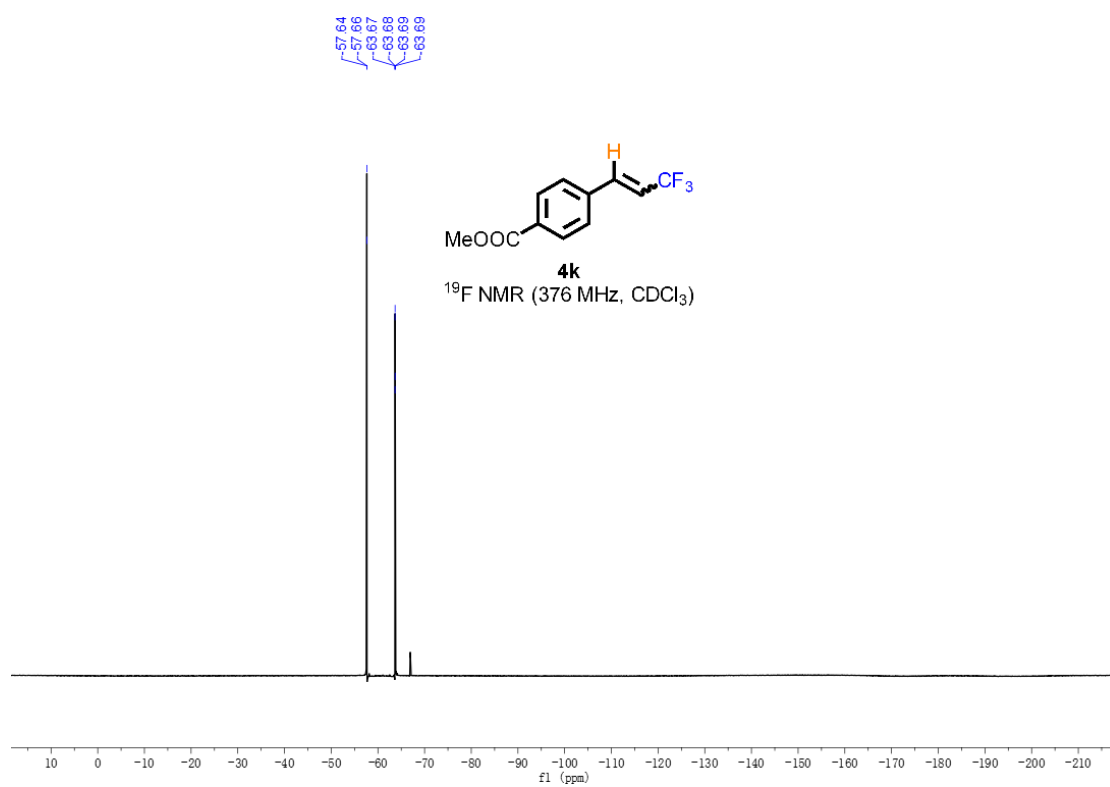
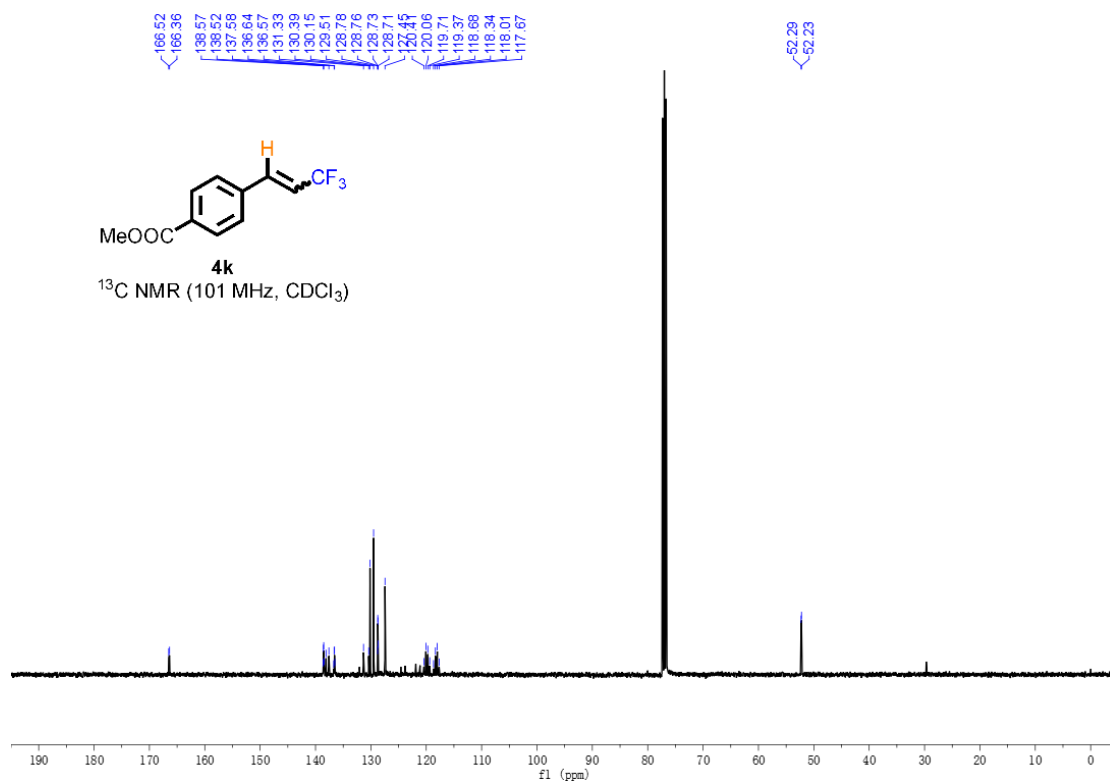




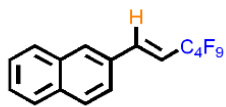






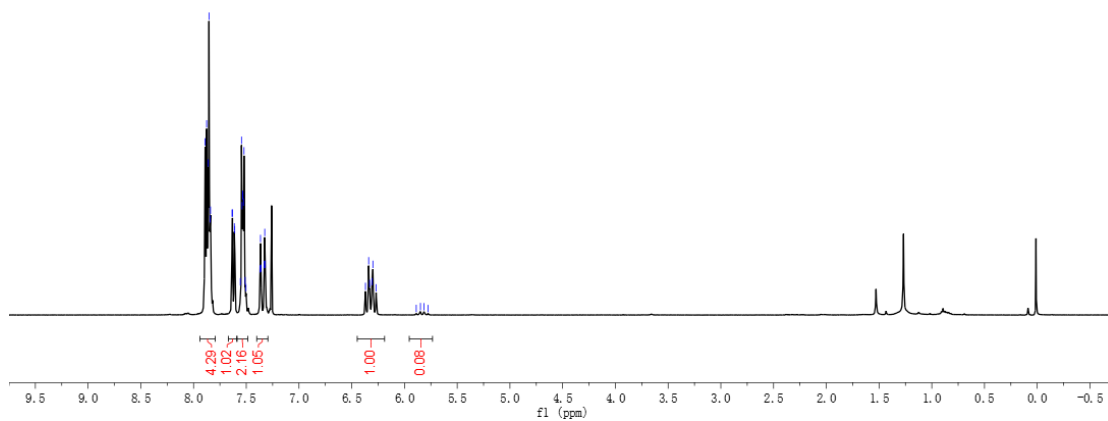


7.89  
7.88  
7.86  
7.85  
7.84  
7.63  
7.61  
7.55  
7.54  
7.53  
7.53  
7.52  
7.37  
7.32  
7.32  
6.34  
6.33  
6.31  
6.31  
5.85  
5.82  
5.78

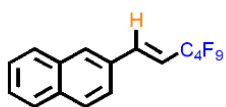


**E-4I**

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

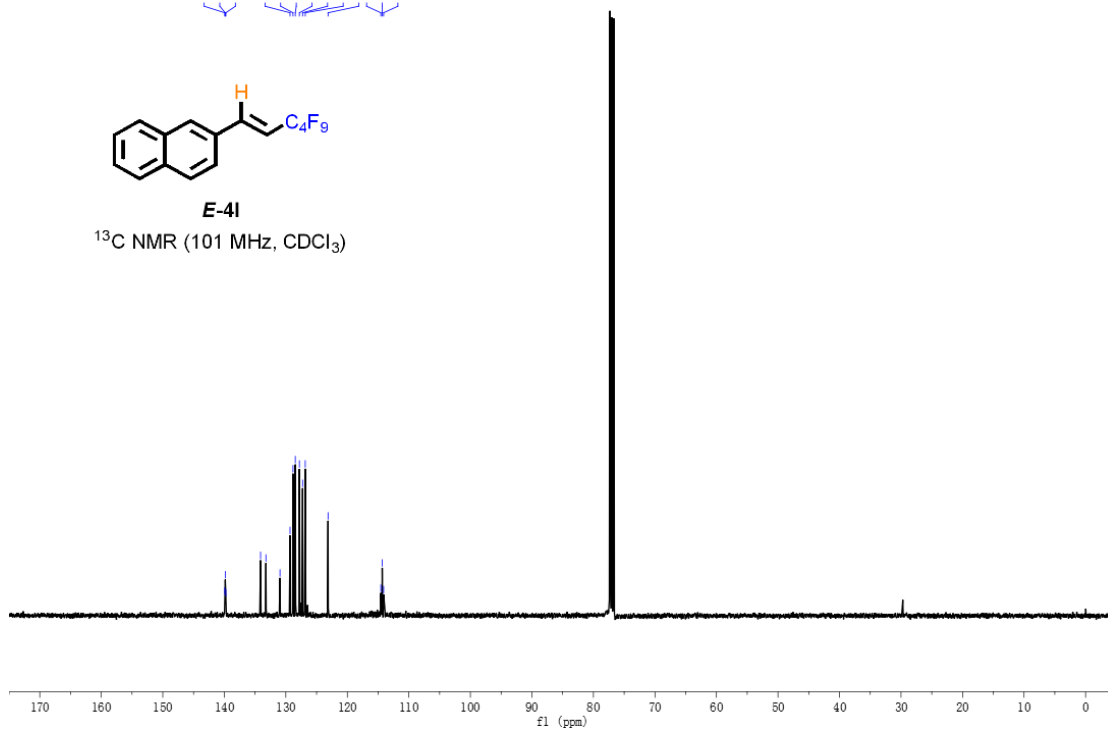


139.93  
139.84  
139.74  
129.31  
128.93  
128.46  
127.90  
126.64  
123.96  
114.33  
114.10

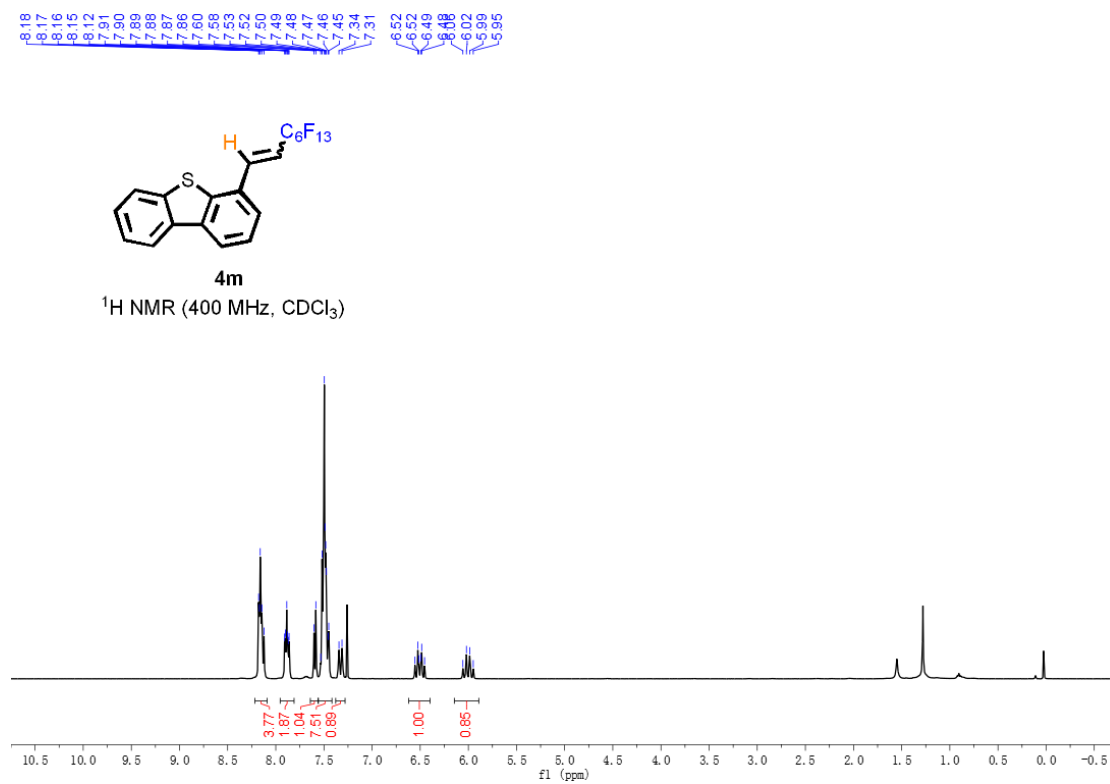
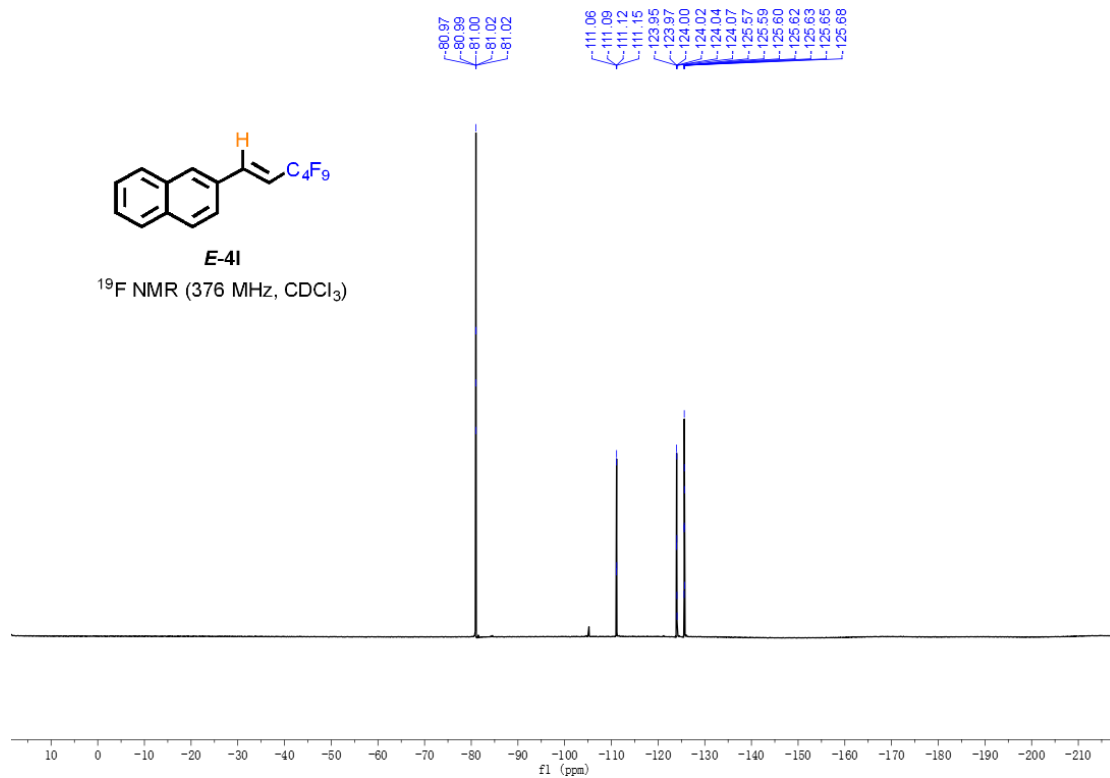


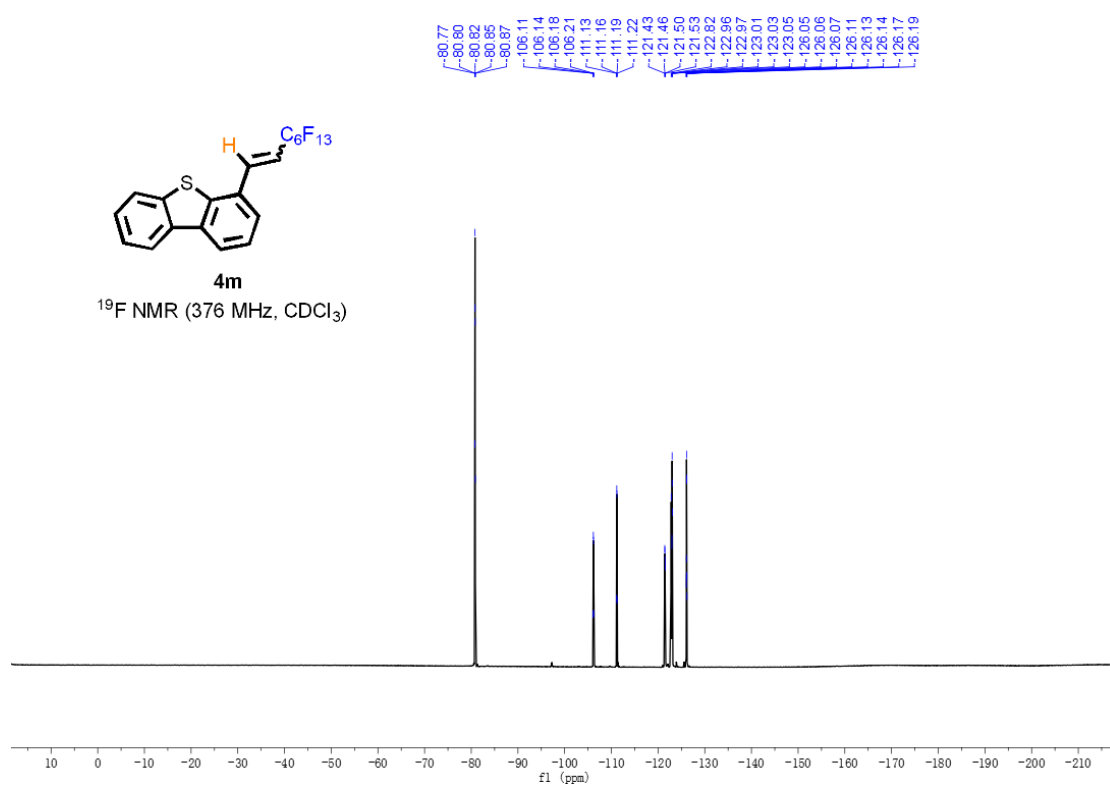
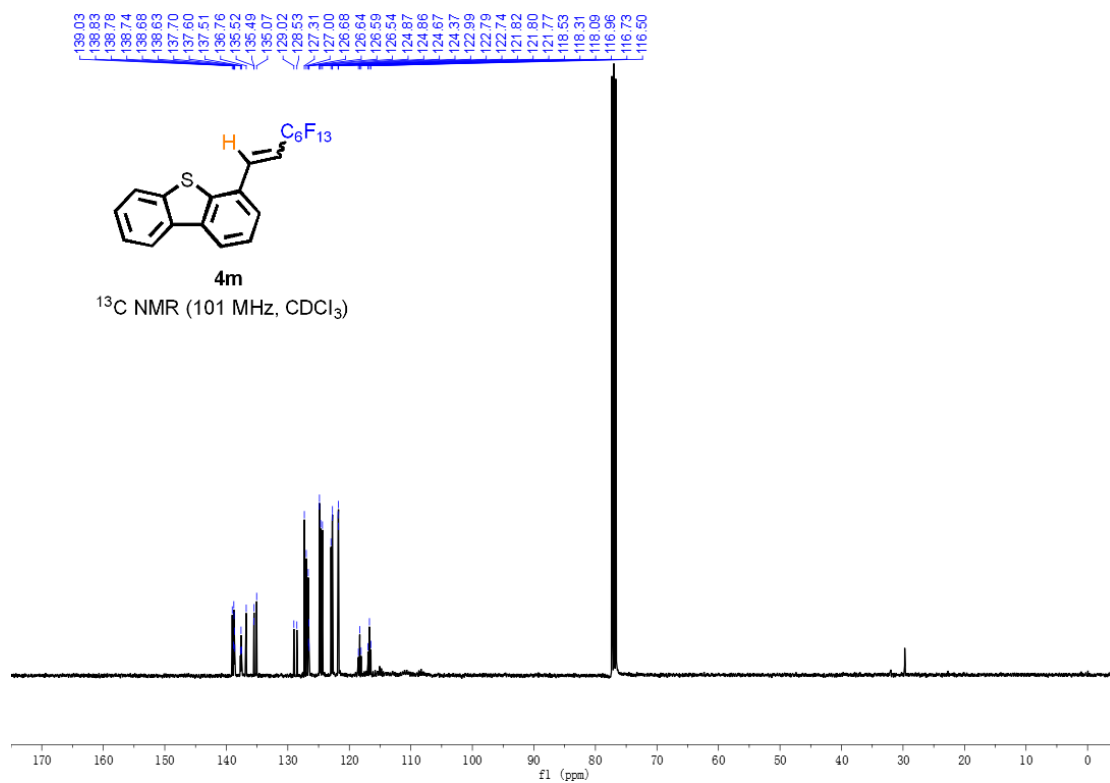
**E-4I**

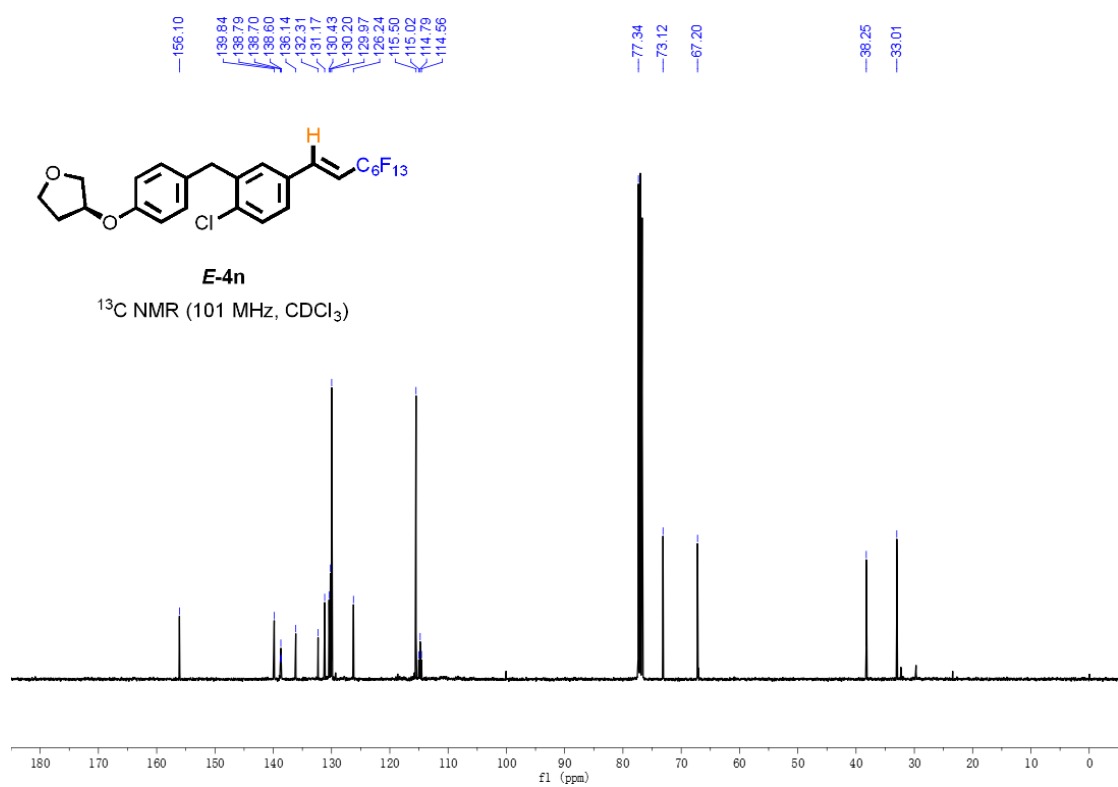
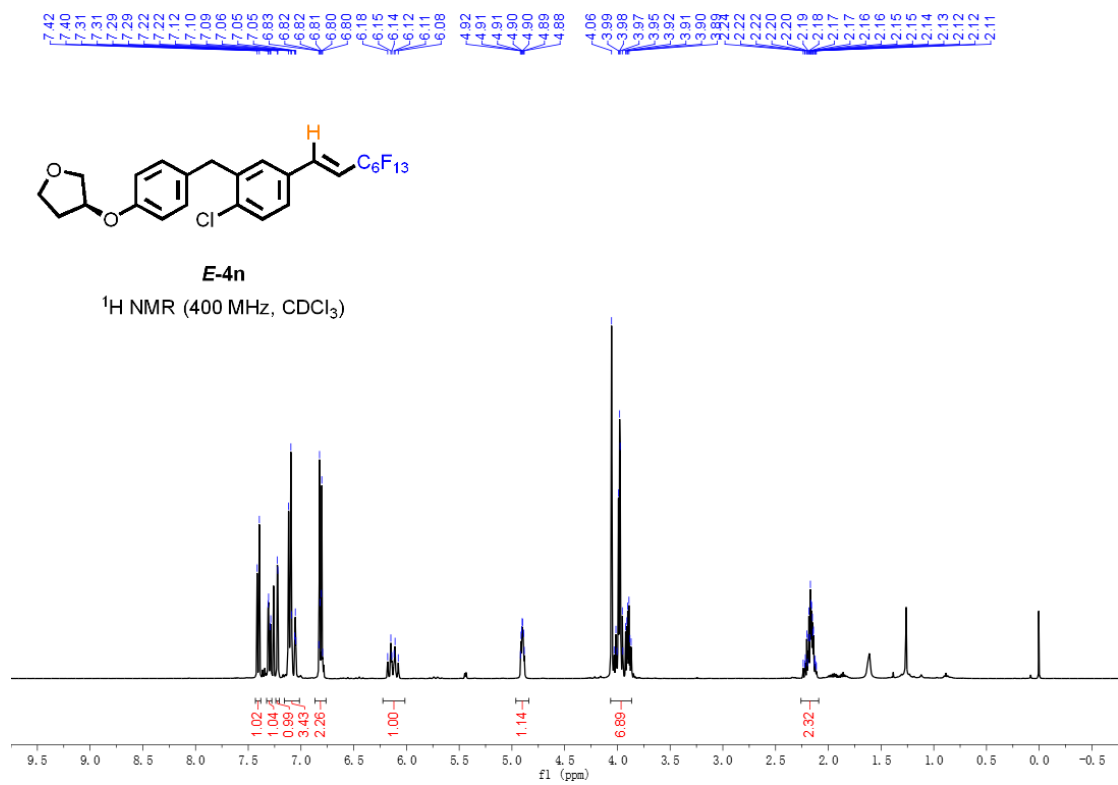
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

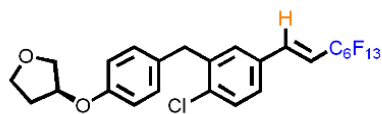






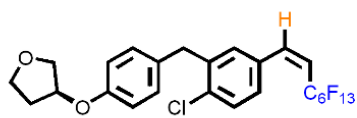
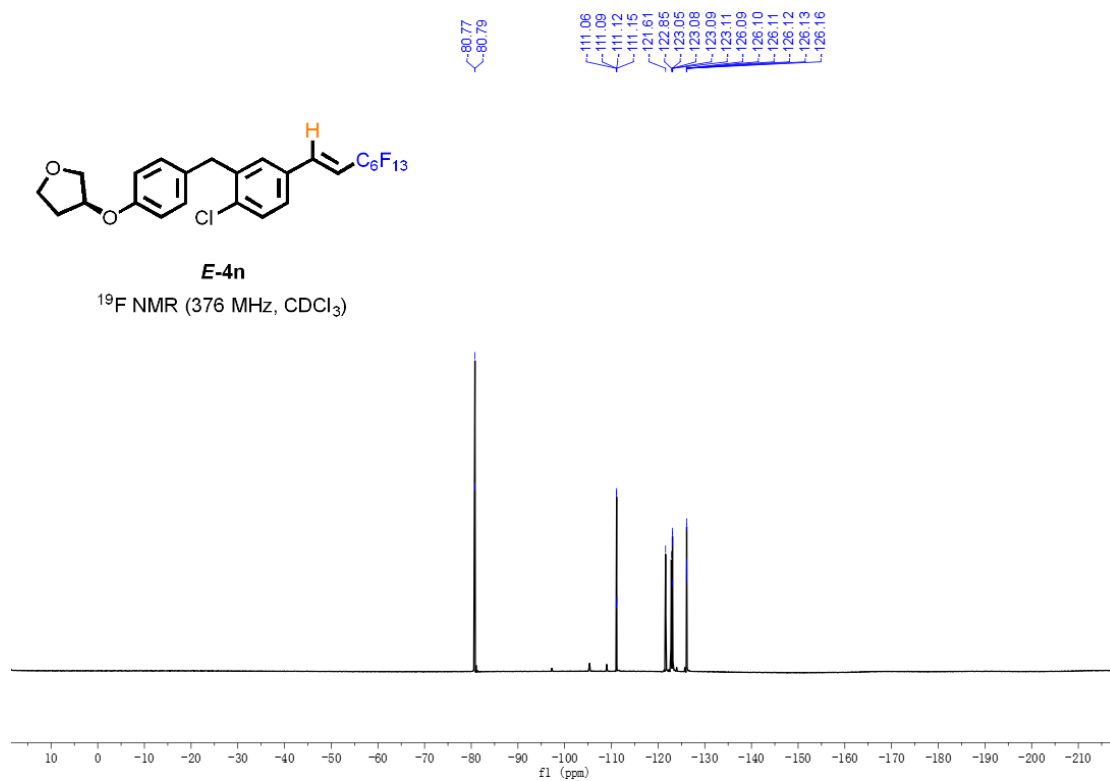






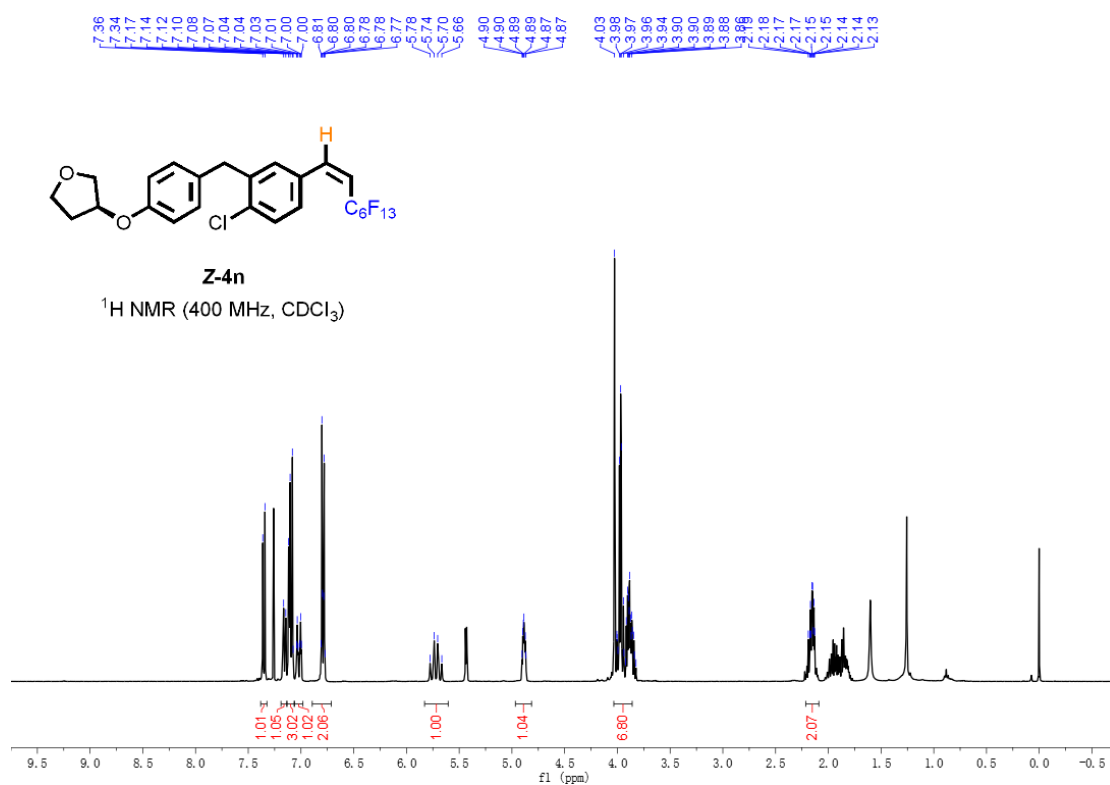
**E-4n**

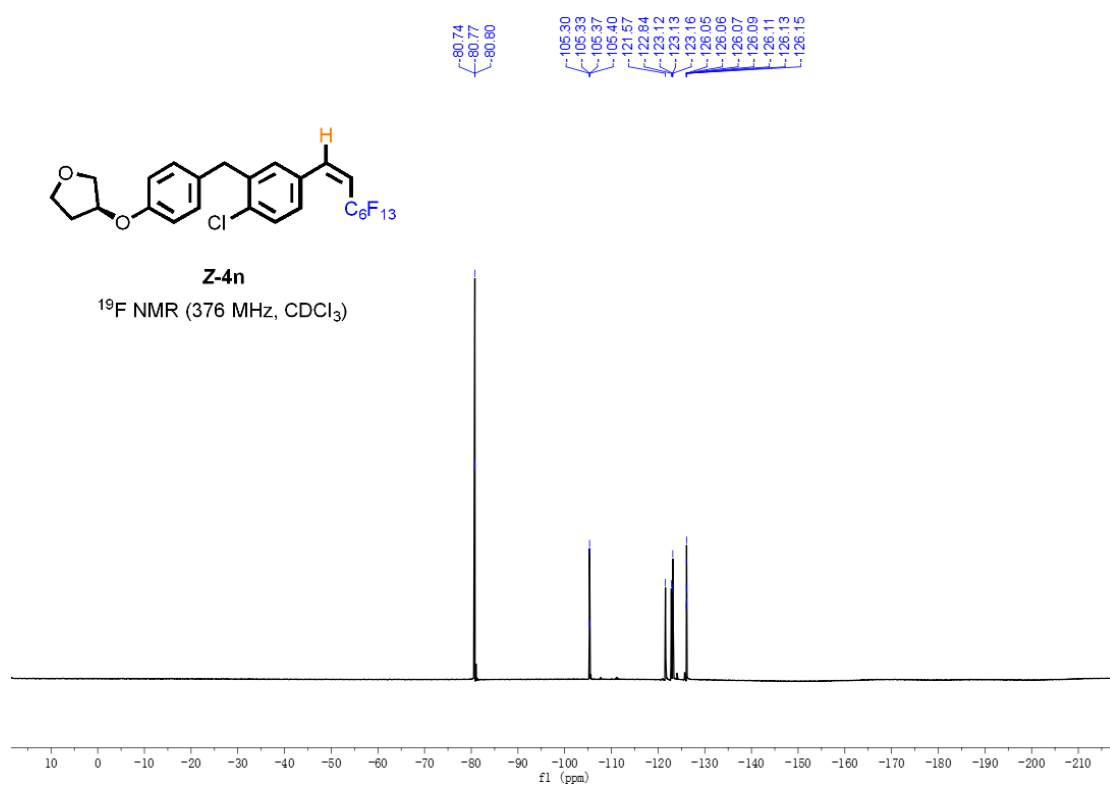
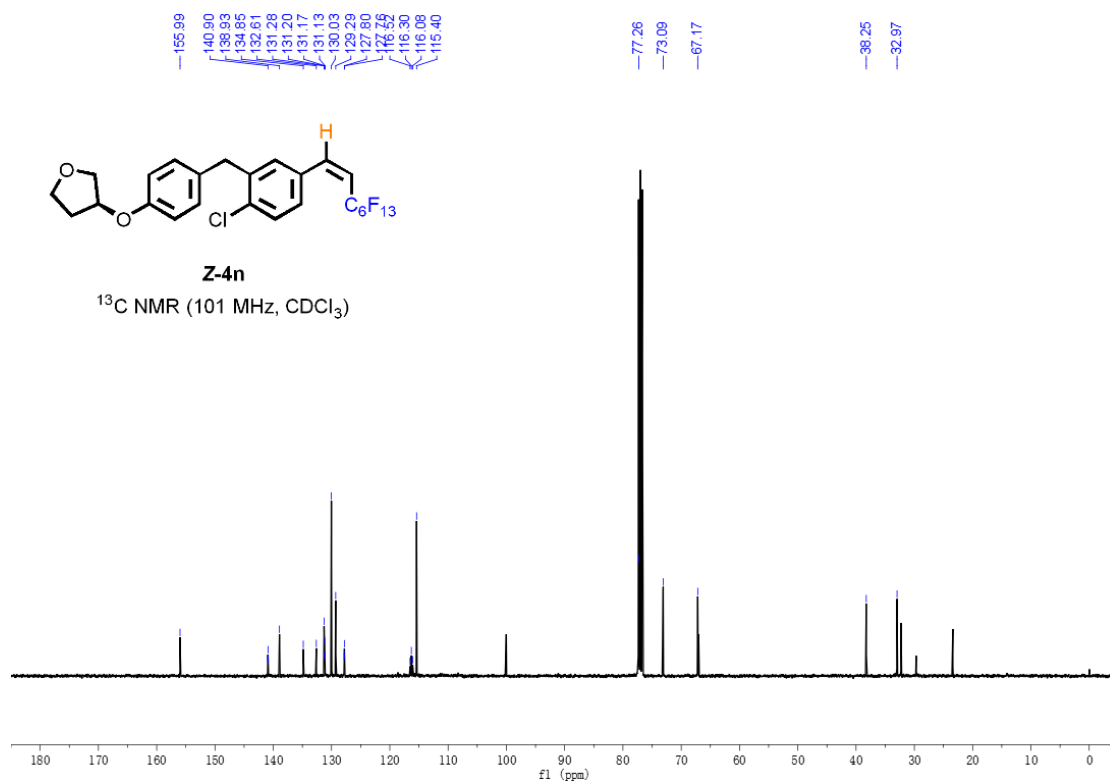
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )

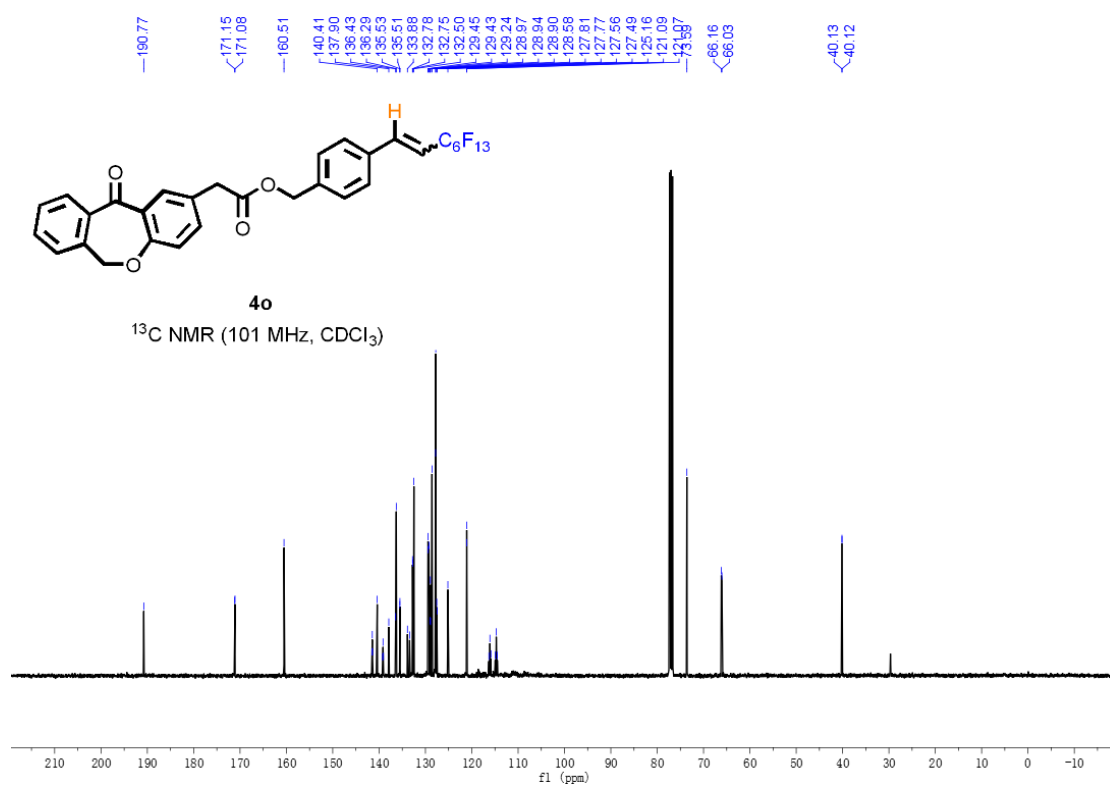
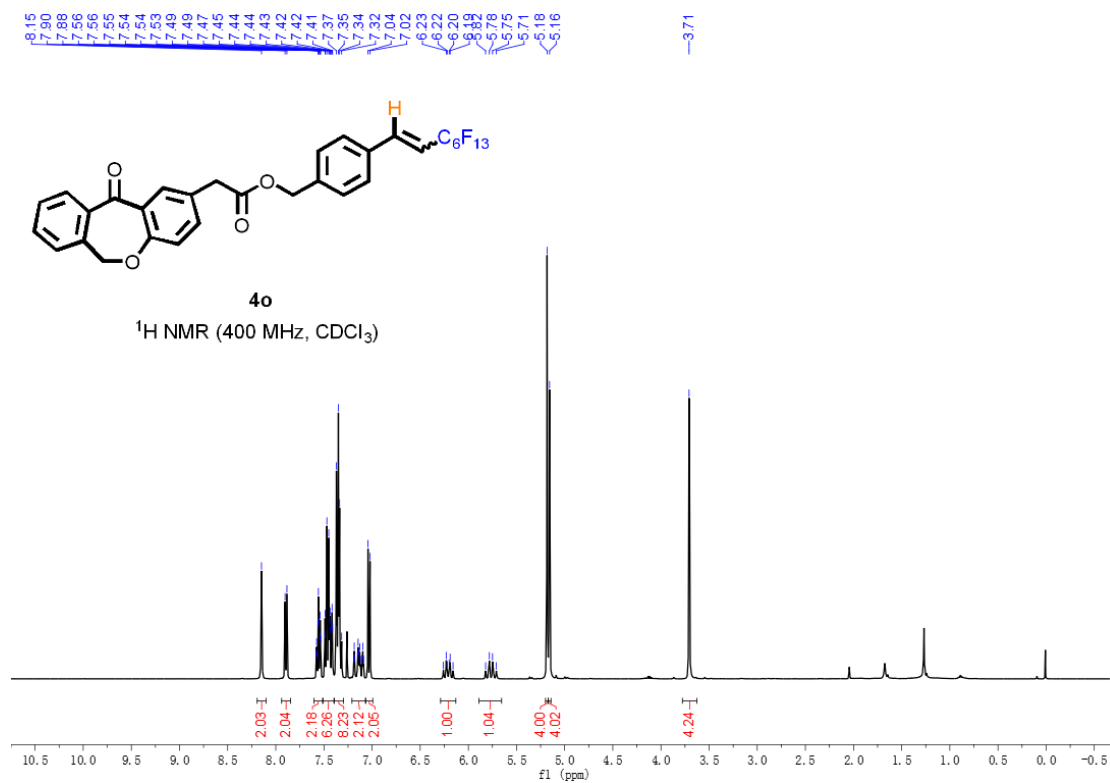


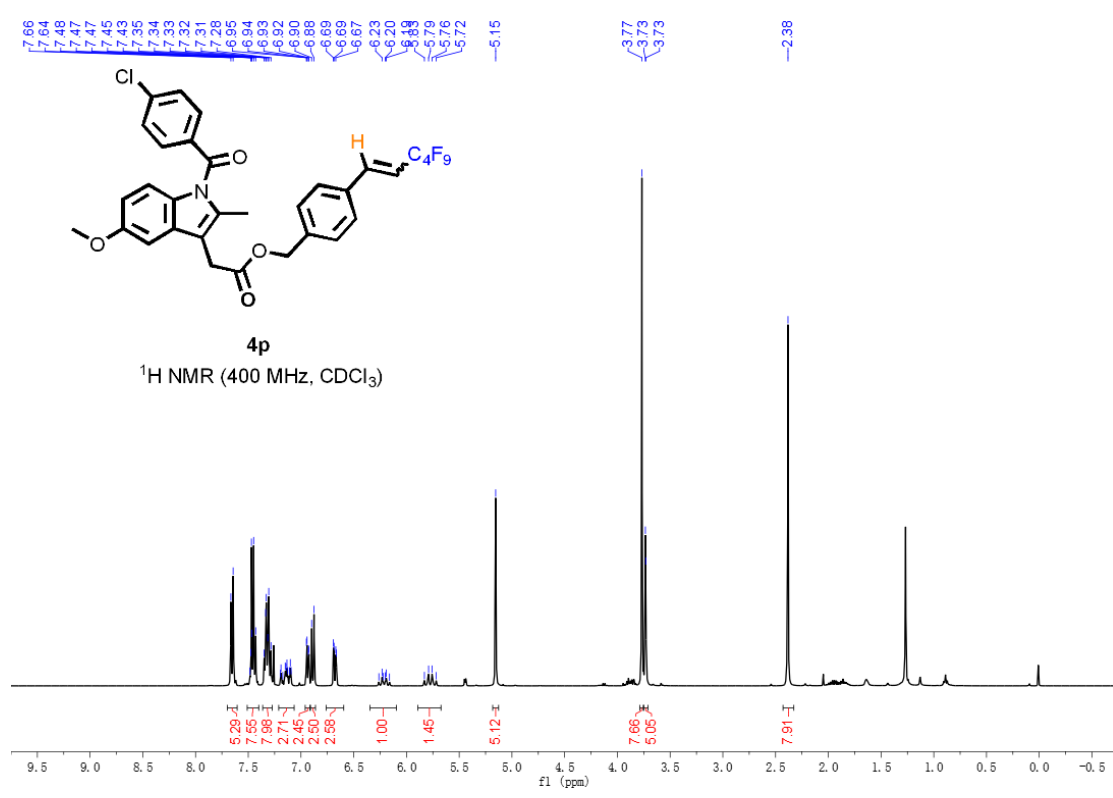
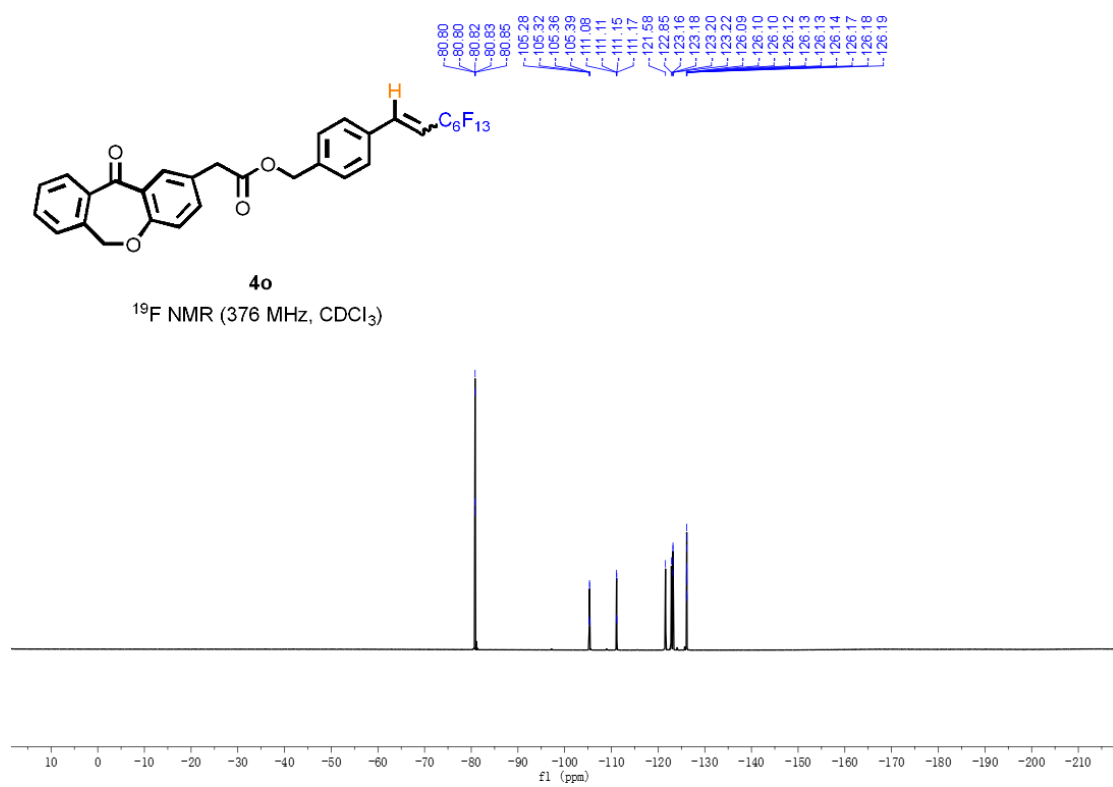
**Z-4n**

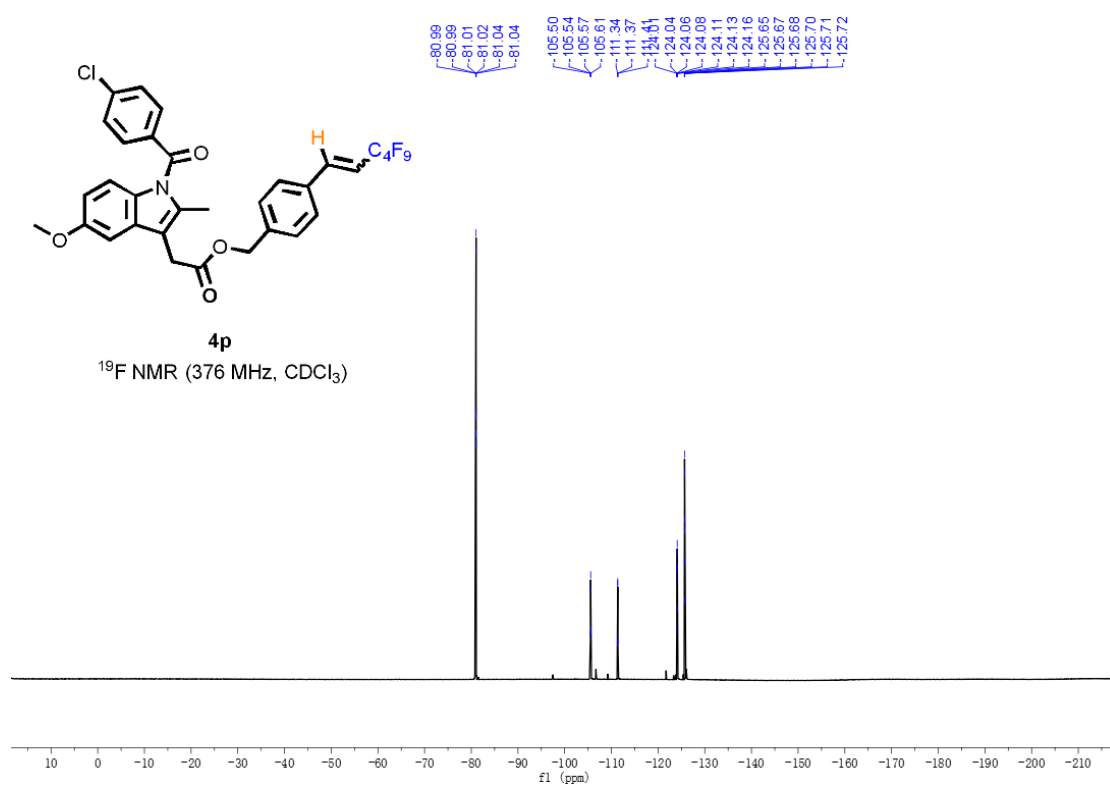
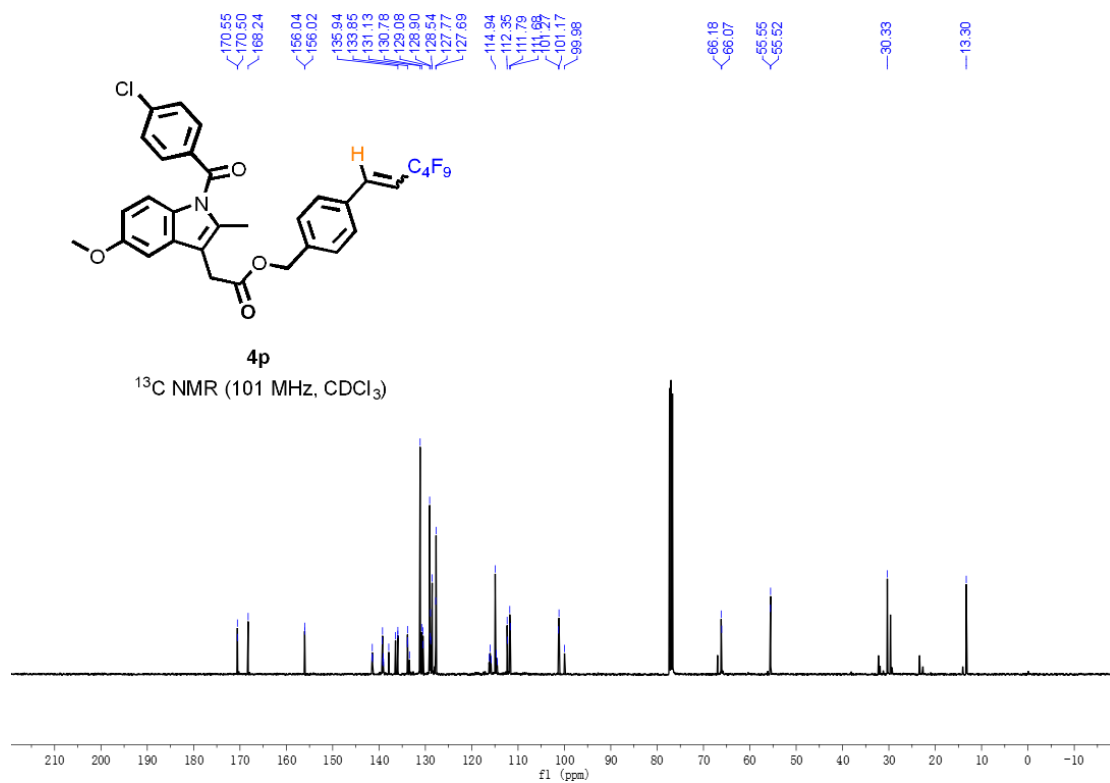
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





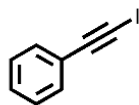




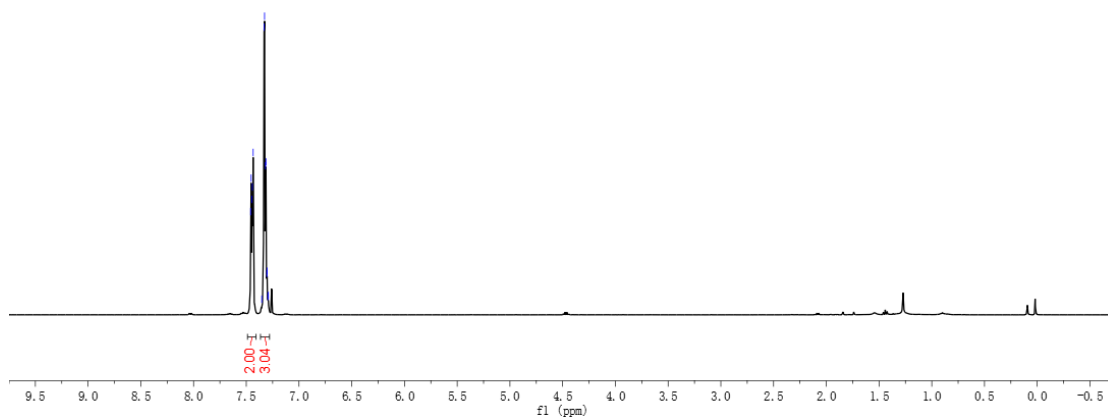




7.46  
7.45  
7.44  
7.43  
7.35  
7.33  
7.32  
7.31  
7.30  
7.29



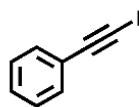
**6**  
 $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



132.31  
128.78  
128.21  
123.37

94.13

6.09



**6**  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

