

## Cu-mediated 2,2,2-Trifluoroethylation of Terminal Alkynes using

### 1,1-Dichloro-2,2,2-trifluoroethane (HCFC-123)

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## Support Information

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**General information:** NMR spectra were obtained on 300 or 400 MHz spectrometers and recorded at 25 °C. Chemical shifts for <sup>1</sup>H NMR spectra are reported in ppm downfield from TMS, chemical shifts for <sup>13</sup>C NMR spectra are recorded in ppm relative to internal chloroform (δ 77.0 ppm for <sup>13</sup>C), and chemical shifts for <sup>19</sup>F NMR are reported in ppm downfield from fluorotrichloromethane (CFCl<sub>3</sub>). Coupling constants (*J*) are reported in hertz. The terms m, s, d, t, q and br refer to multiplet, singlet, doublet, triplet, quartet and broad, respectively. <sup>13</sup>C NMR was broad-band

decoupled from hydrogen nuclei.  $^{19}\text{F}$  NMR yield was determined by  $^{19}\text{F}$  NMR using benzotrifluoride as an internal standard before working up the reaction. Infrared spectra (IR) were recorded with an infrared spectrometer; absorbance frequencies are given at maximum intensity in  $\text{cm}^{-1}$ . The mass analyzer type used for the HRMS is time-of-flight mass spectrometry (TOF-MS) or Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). Column chromatography was performed using silica gel (mesh 300–400).

**Screening conditions for reactions of phenylacetylene **2a** with 1,1-Dichloro-2,2,2-trifluoroethane (HCFC-123) in the presence of various metals and salts (Table 1S and 2S).**

**Table 1S:** Screening of conditions for copper-mediated 2,2,2-trifluoroethylation of **2a** with **1**<sup>a</sup>

$$\text{Ph}-\text{C}\equiv\text{C}-\text{H} + \text{CF}_3\text{CHCl}_2 \xrightarrow[\text{solvent}]{\substack{x \text{ mmol Cu} \\ z \text{ mmol amine}}} \text{Ph}-\text{C}\equiv\text{C}-\text{CH}_2\text{CF}_3$$

$\underset{1 \text{ mmol}}{\mathbf{2a}}$        $\underset{y \text{ mmol}}{\mathbf{1}}$        $\mathbf{3a}$

Entry	amine	<b>2a</b> : <b>1</b> :Cu:amine	Solvent	Temp. (°C)	Yield (%) <sup>b</sup>
1	Et <sub>2</sub> NH	1:1:2:2	DMF	70	N.R
2	Et <sub>2</sub> NH	1:1:2:2	THF	70	N.R
3	Et <sub>2</sub> NH	1:1:2:2	CH <sub>3</sub> NO <sub>2</sub>	70	N.R
4	Et <sub>2</sub> NH	1:1:2:2	CH <sub>3</sub> CN	70	5
5	Et <sub>2</sub> NH	1:1:2:2	DCE	70	10
6	Et <sub>2</sub> NH	1:1:3:3	DCE	70	65
7	Et <sub>2</sub> NH	1:1:4:4	DCE	70	63
8	Et <sub>2</sub> NH	1:2:3:3	DCE	70	73
9	Et <sub>2</sub> NH	1:2:1:3	DCE	70	74
10	Et <sub>2</sub> NH	1:2:1:3	DCE	60	42
11	Et <sub>2</sub> NH	1:2:1:3	DCE	80	46
12	Et <sub>2</sub> NH	1:-:1:3 <sup>c</sup>	CF <sub>3</sub> CHCl <sub>2</sub>	70	55
<b>13</b>	<b>Et<sub>2</sub>NH</b>	<b>1:2:2:3</b>	<b>DCE</b>	<b>70</b>	<b>77</b>
14	<sup>n</sup> Pr <sub>2</sub> NH	1:2:2:3	DCE	70	64

15	<sup>n</sup> Bu <sub>2</sub> NH	1:2:2:3	DCE	70	63
16	diallylamine	1:2:2:3	DCE	70	30
17	DMEA	1:2:2:3	DCE	70	44 <sup>d</sup>
18	piperidine	1:2:2:3	DCE	70	7
19	azolidine	1:2:2:3	DCE	70	trace
20	<sup>i</sup> Pr <sub>2</sub> NH	1:2:2:3	DCE	70	N.R
21	Ph <sub>2</sub> NH	1:2:2:3	DCE	70	N.R
22	EtNH <sub>2</sub>	1:2:2:3	DCE	70	N.R
23	Et <sub>3</sub> N	1:2:2:3	DCE	70	N.R
24	TEDA	1:2:2:3	DCE	70	N.R

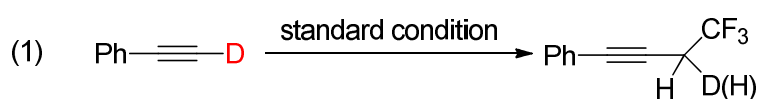
<sup>a</sup>The reactions were carried out with **2** (1 mmol) and **1** (x mmol) in the presence of Cu powder (y mmol) and amine (z mmol) in 2 mL of solvent in a sealed tube under a nitrogen atmosphere. <sup>b</sup>Yields were determined by <sup>19</sup>F NMR spectroscopy using benzotrifluoride as an internal standard. <sup>c</sup>**1** was used as reactant and also as a sole solvent. <sup>d</sup>An allene product was found with the alkyne product.

**Table 2S:** Screening conditions for the reactions of **2a** with **1** mediated by various metals and salts<sup>a</sup>

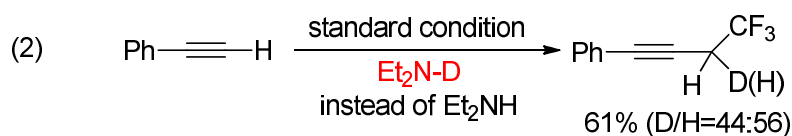
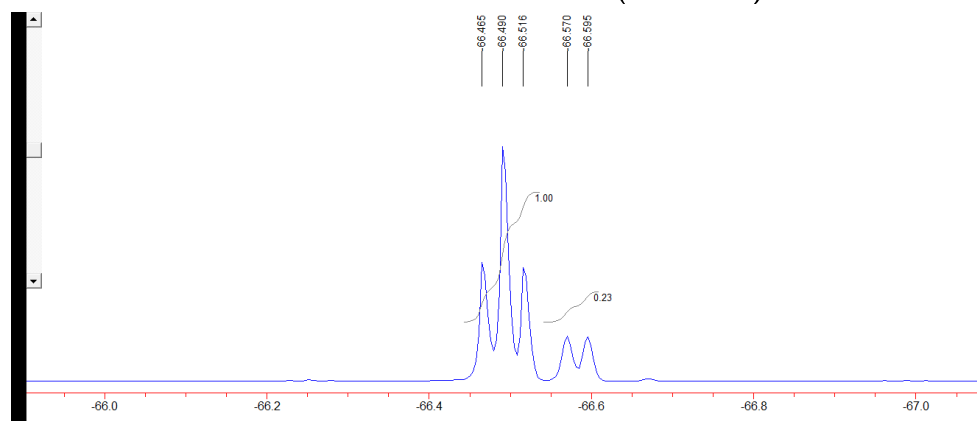
$\text{Ph}-\text{C}\equiv\text{C}-\text{H} + \text{CF}_3\text{CHCl}_2 \xrightarrow[\text{DCE, 70}^\circ\text{C}]{\substack{2 \text{ mmol metal} \\ 3 \text{ mmol Et}_2\text{NH}}} \text{Ph}-\text{C}\equiv\text{C}-\text{CH}_2\text{CF}_3$		
entry	Metal	Yield (%) <sup>b</sup>
1	Zn	NR
2	Mg	NR
3	Fe	NR
4 <sup>c</sup>	CuI/Zn	<10
5	CuCl	<10
6	CuI	<10
7	CuBr <sub>2</sub>	<10
8	FeCl <sub>2</sub>	NR

<sup>a</sup>The reactions were carried out with **2a** (102 mg, 1 mmol), **1** (306 mg, 2 mmol), metal (1 mmol), and Et<sub>2</sub>NH (219 mg, 3 mmol) in 2 mL of DCE at 70 °C for 8h in a sealed tube under a nitrogen atmosphere. <sup>b</sup>Yields were determined by <sup>19</sup>F NMR spectroscopy using benzotrifluoride as an internal standard. <sup>c</sup>CuI (19.1 mg, 10% mol), Zn (65 mg, 1 mmol).

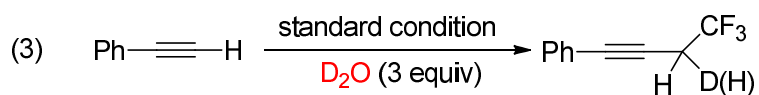
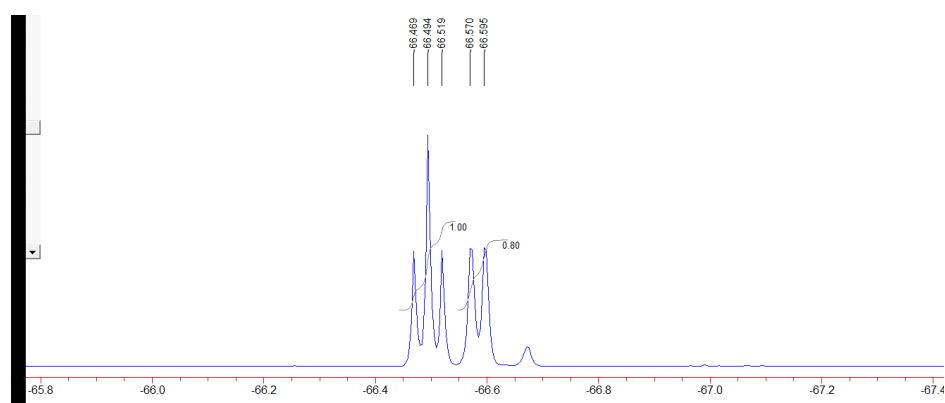
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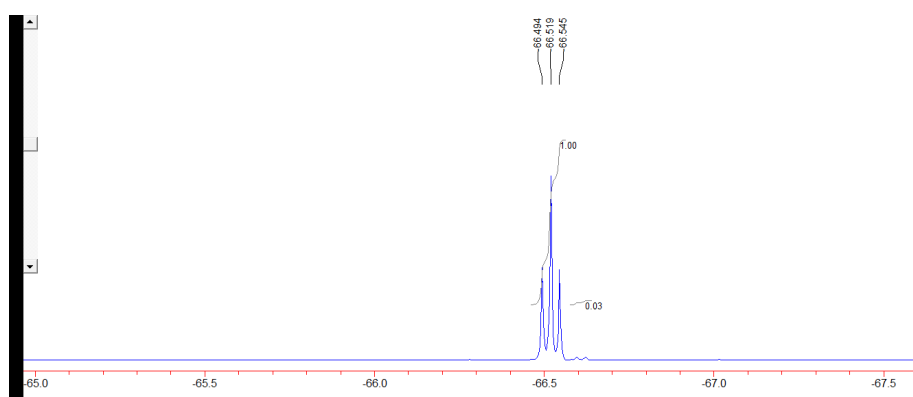
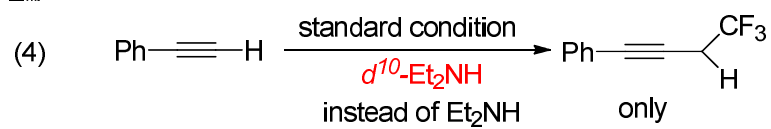
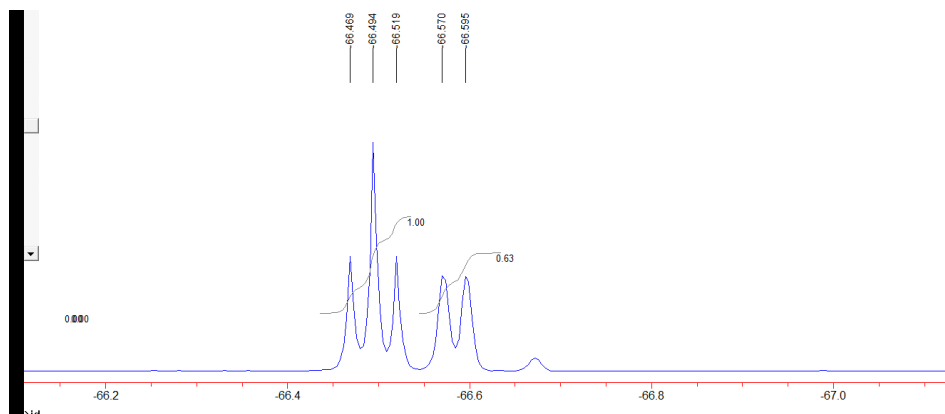
64% (D/H=18:82)



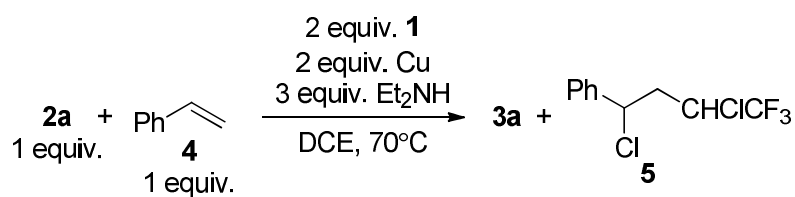
61% (D/H=44:56)



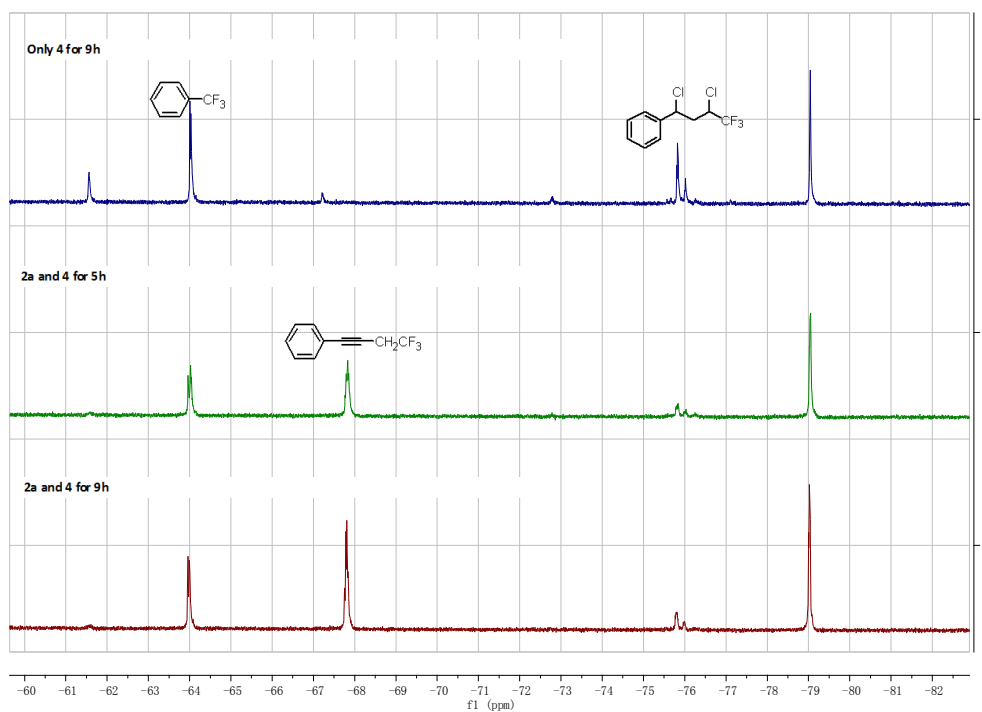
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## Competitive reaction between alkyne 2a and alkene 4

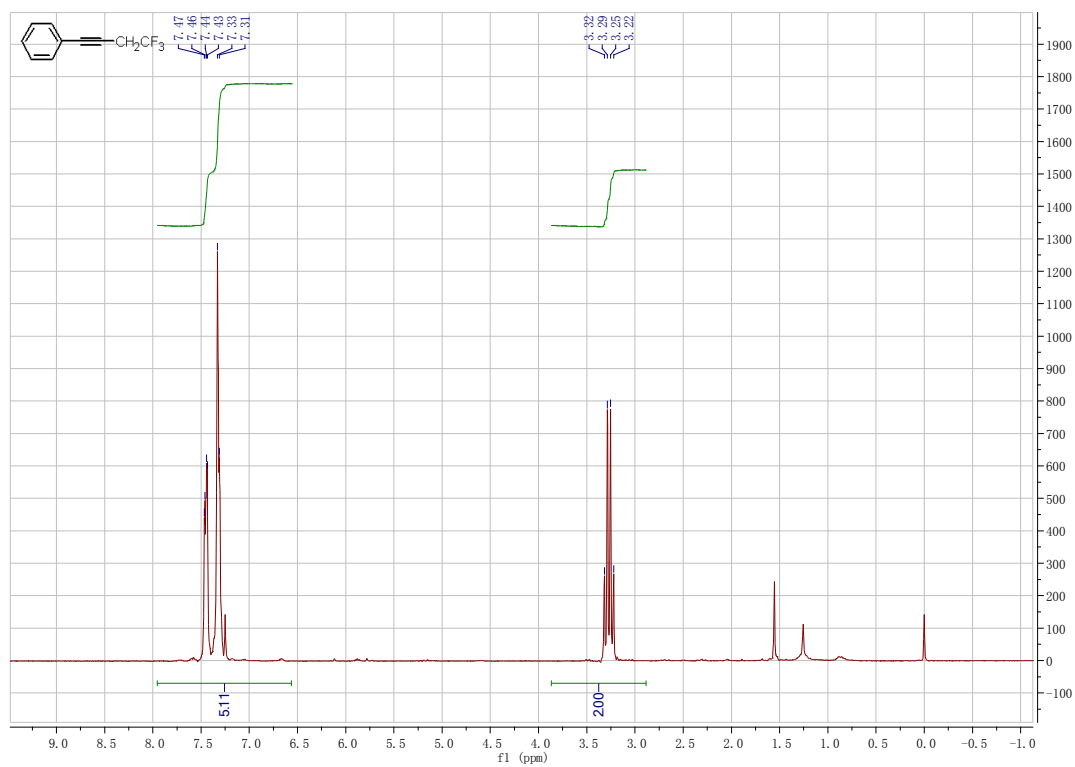
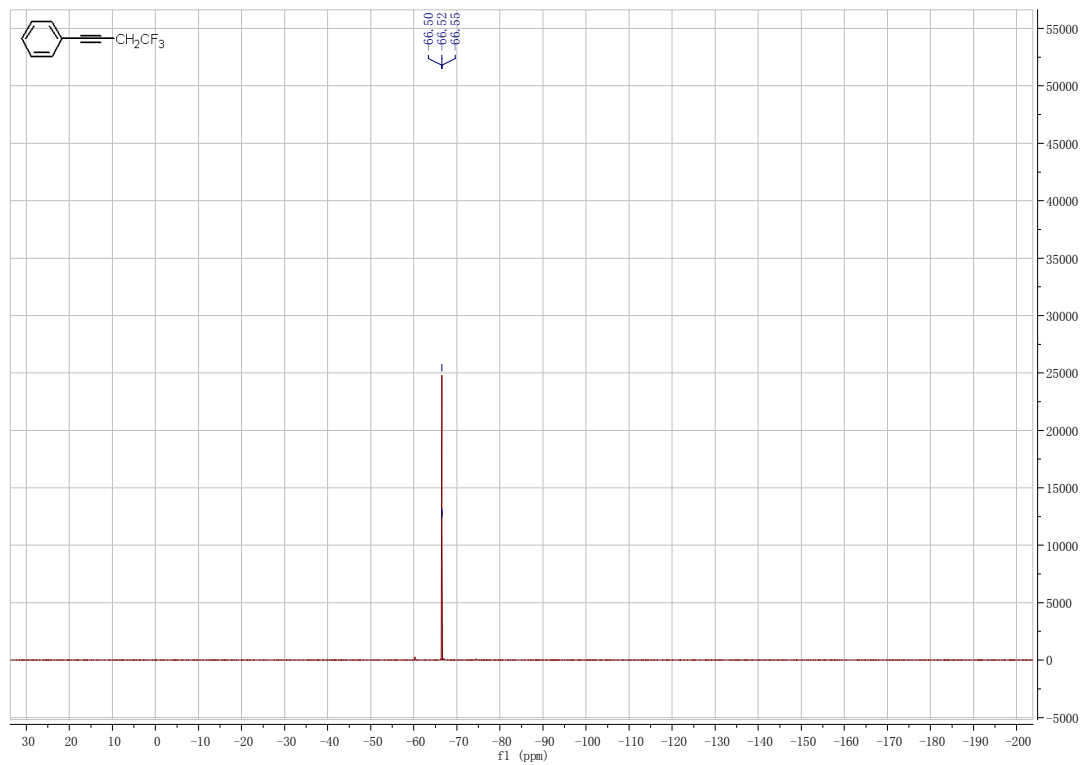


entry	condition	yield (%)	
		3a	5
1	only 4 for 8h	0	24
2	2a and 4 for 5h	57	7
3	2a and 4 for 9h	63	9

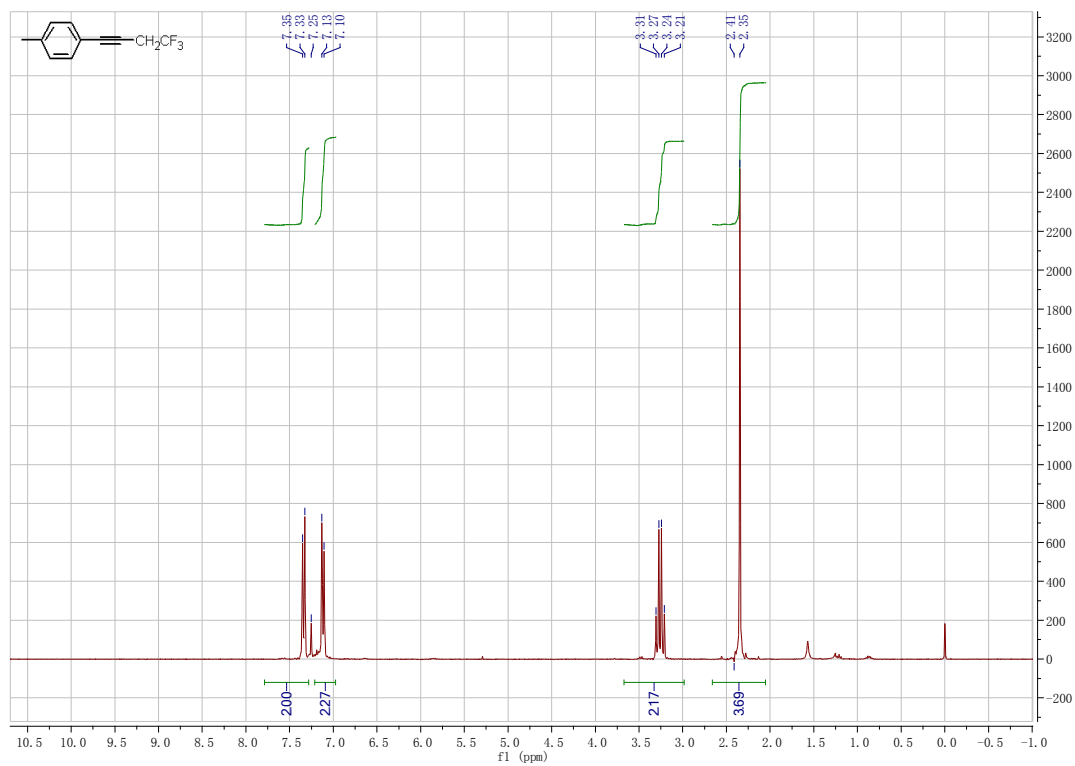
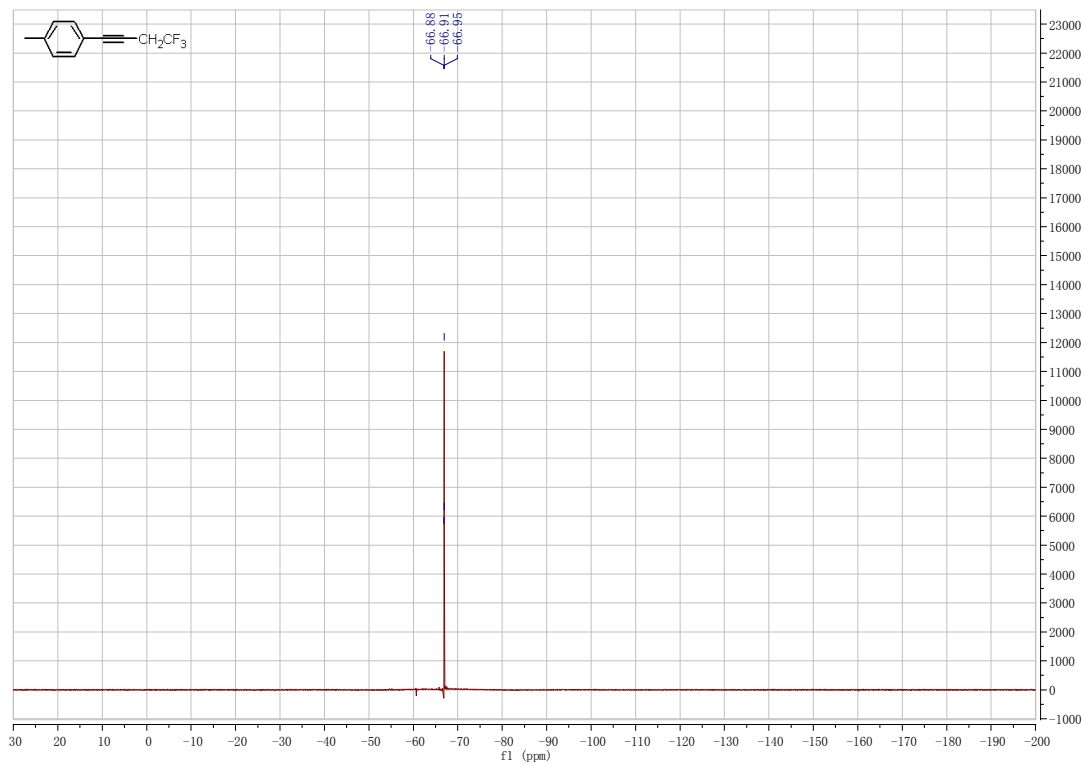


## Spectroscopic data for products

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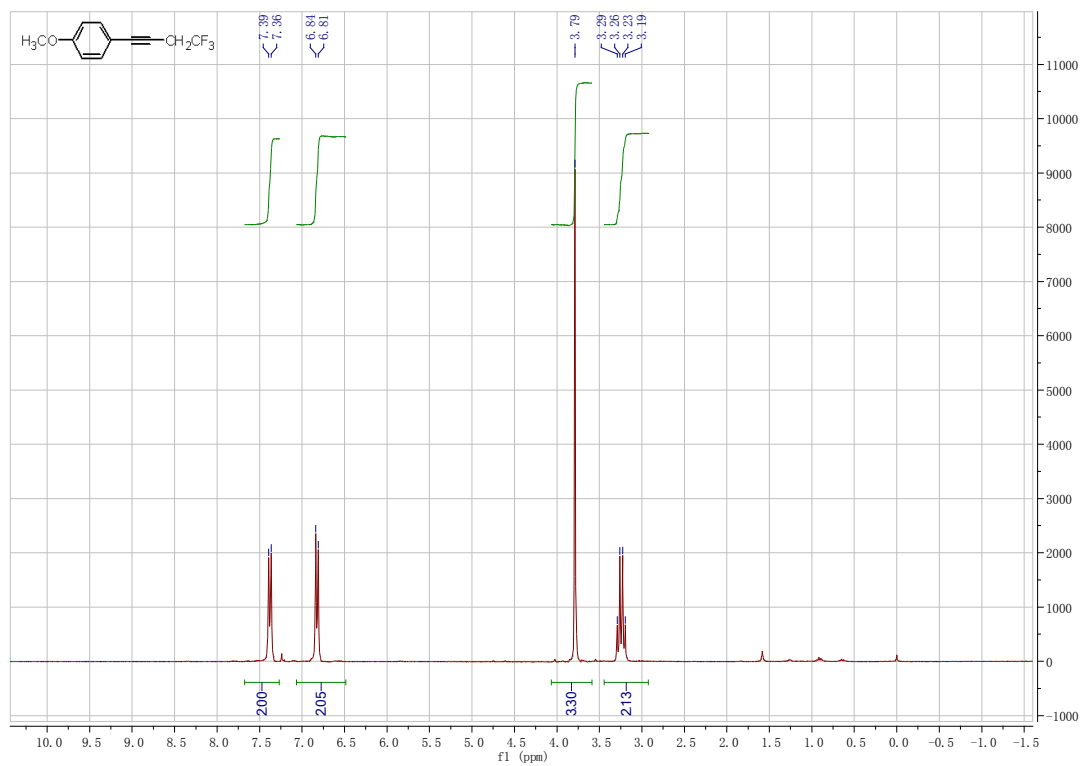
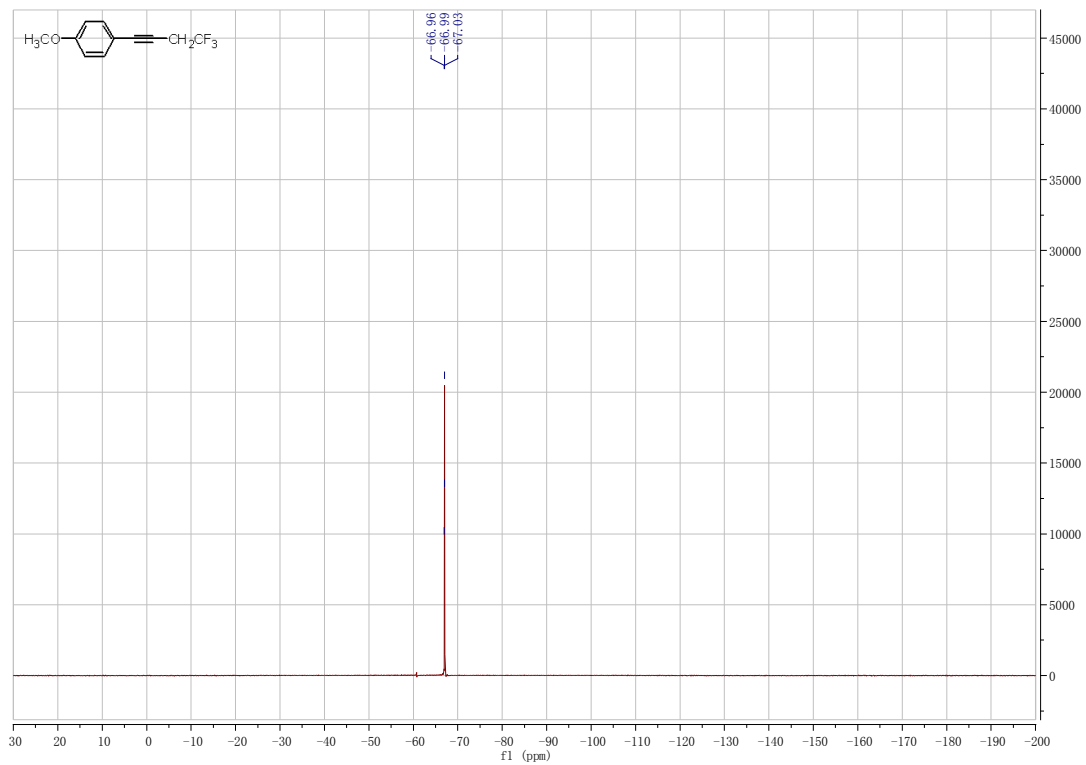


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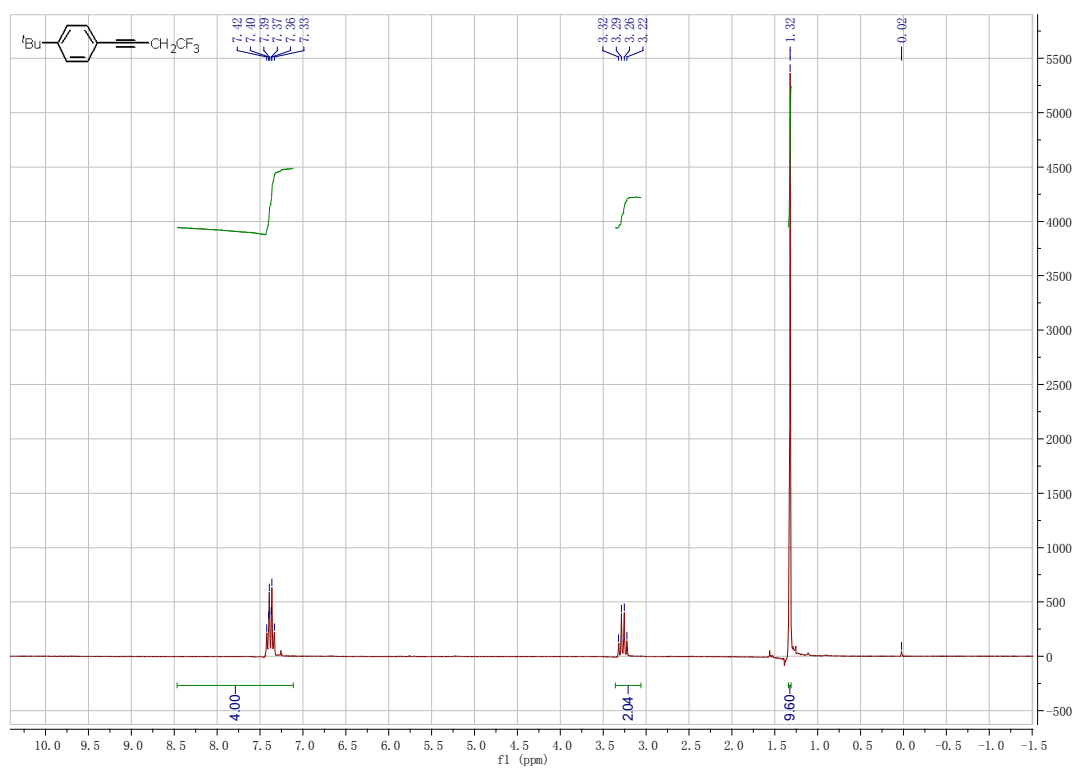
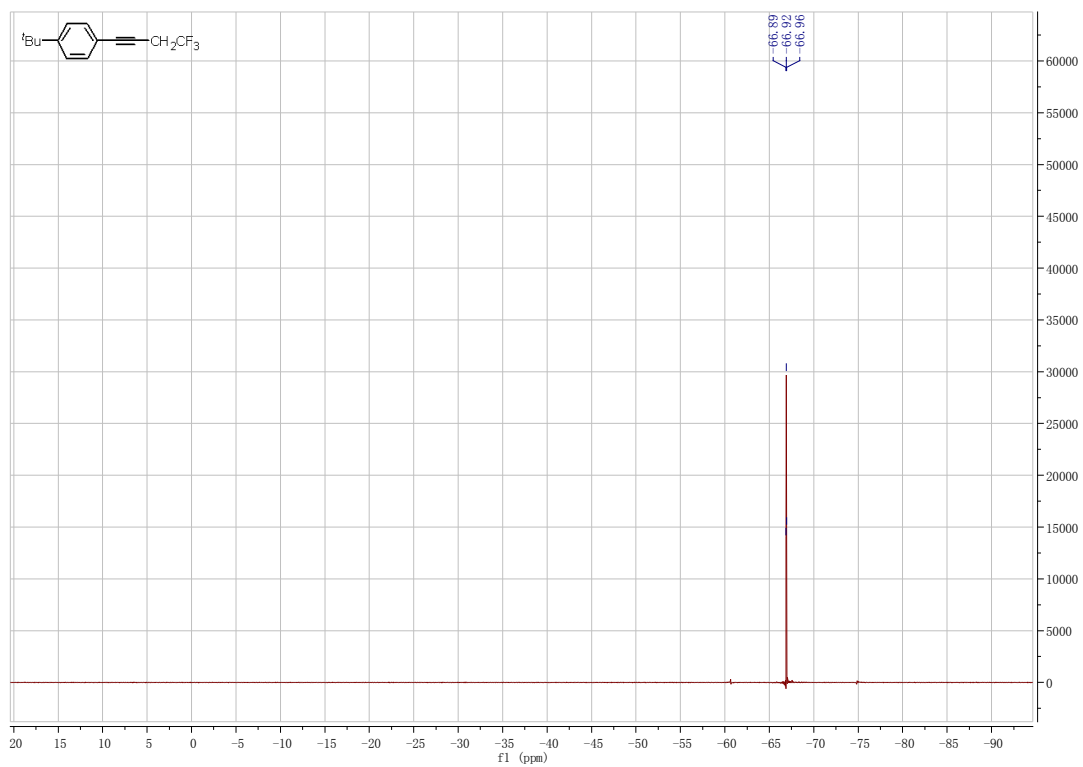




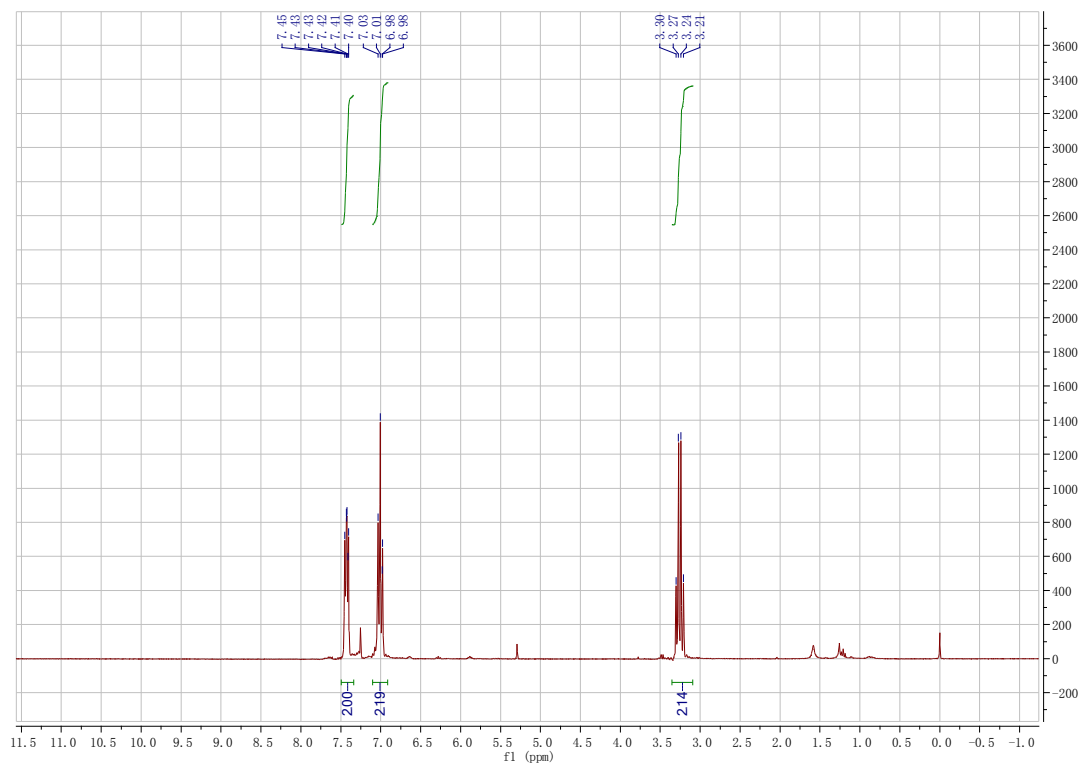
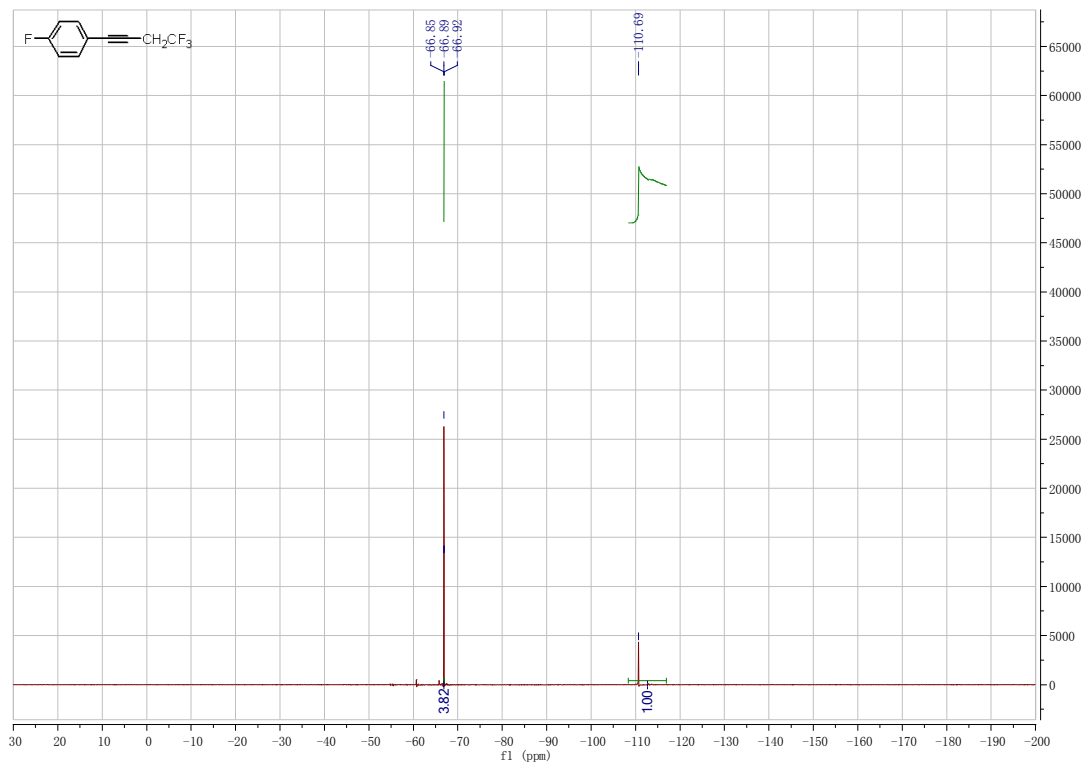
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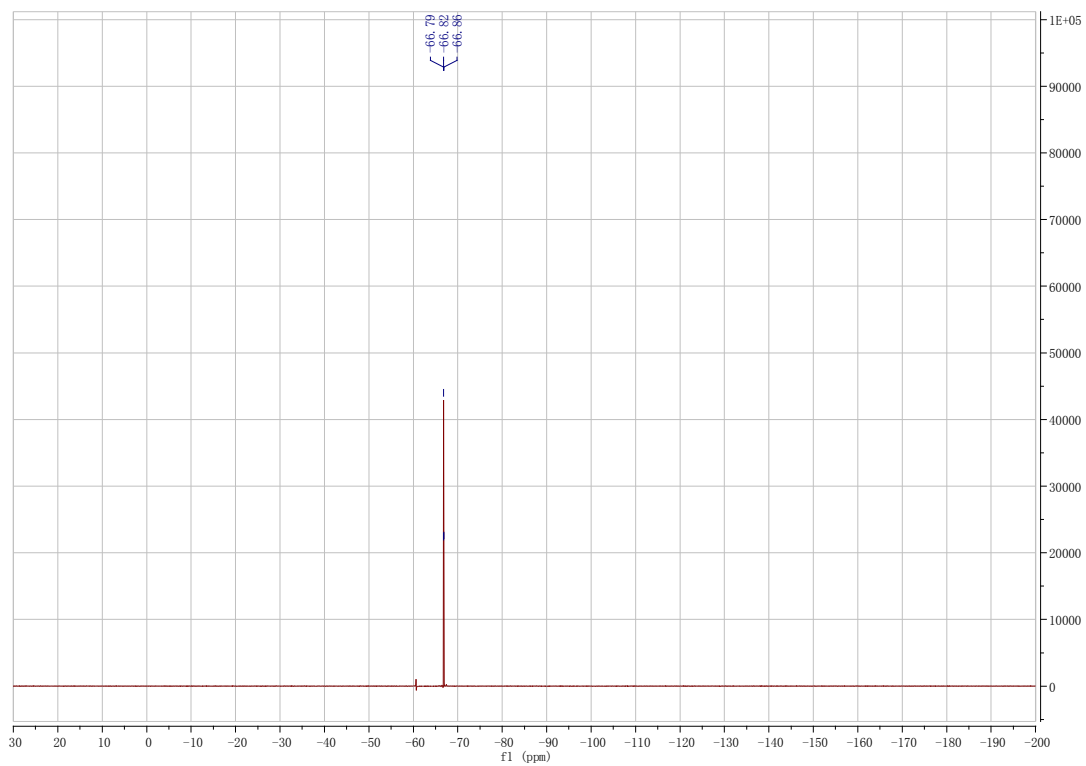
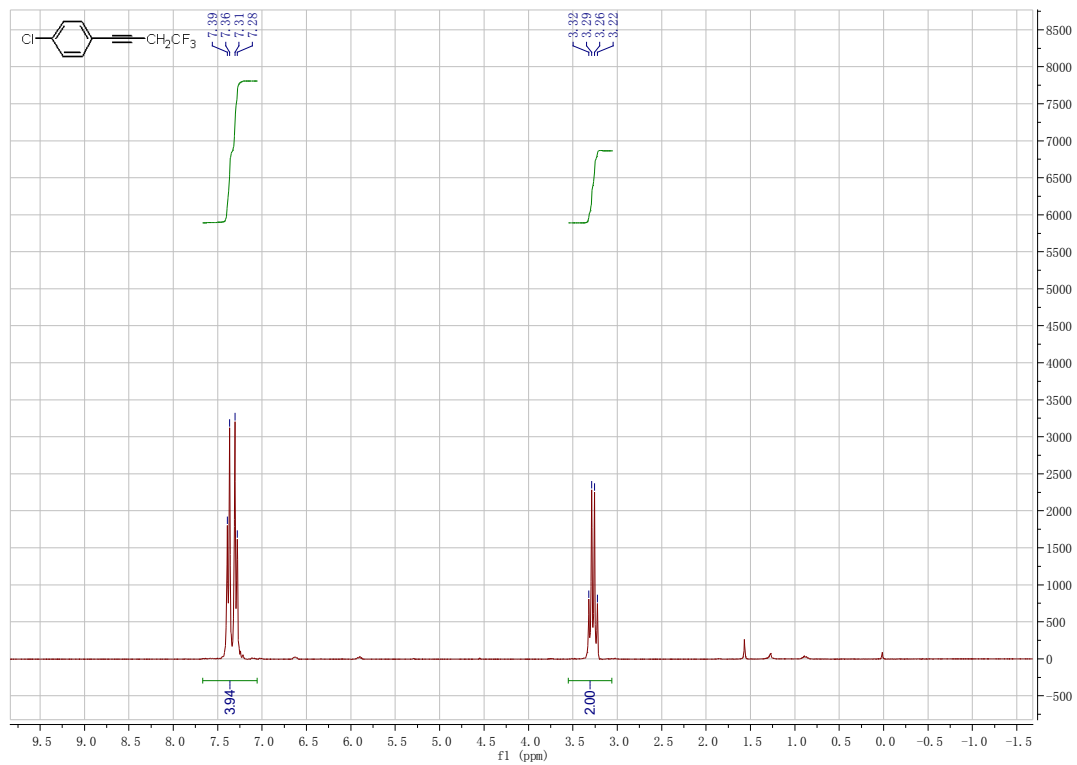
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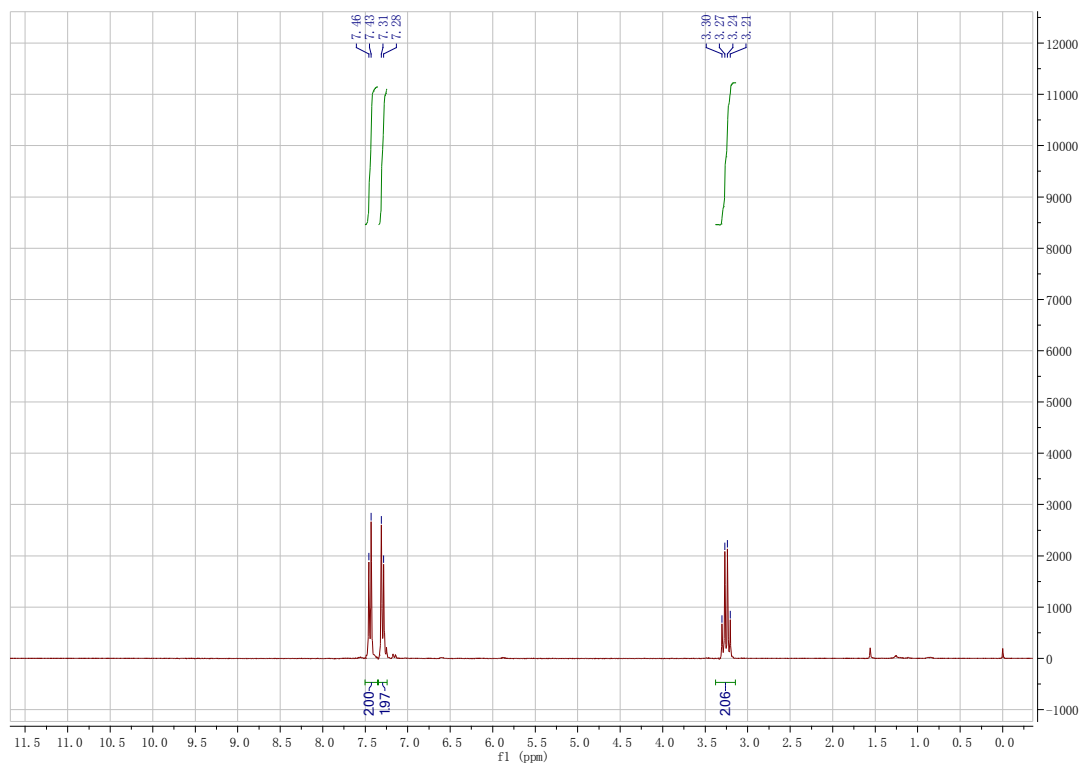
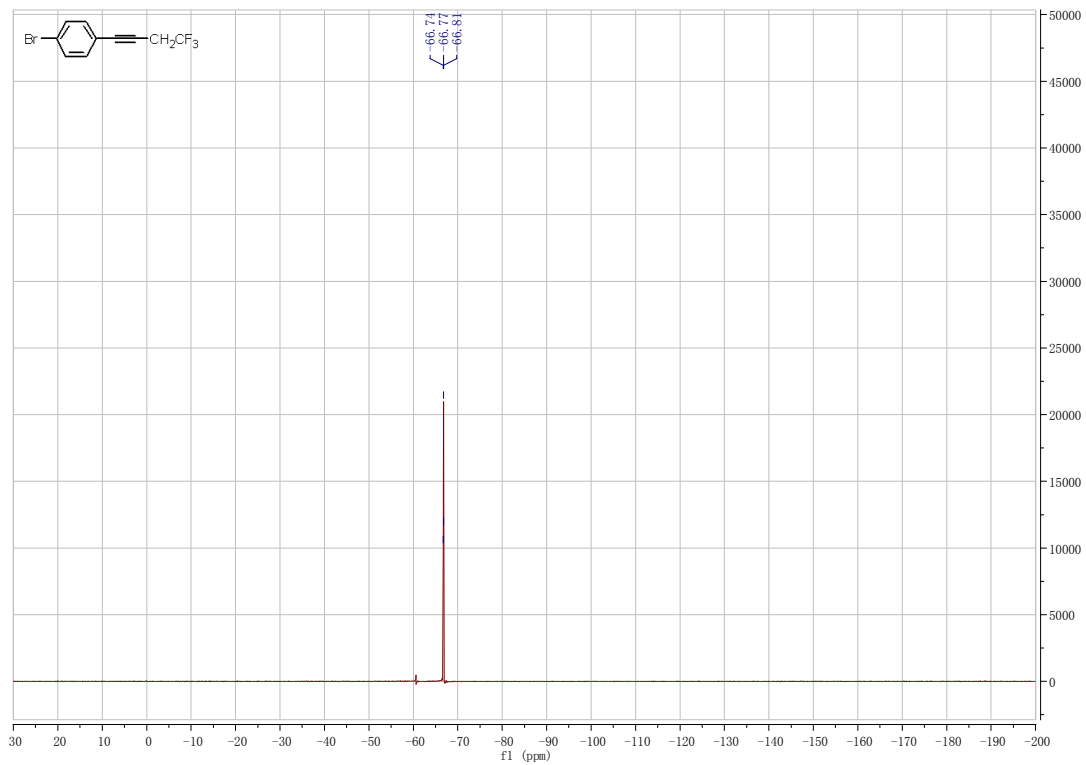
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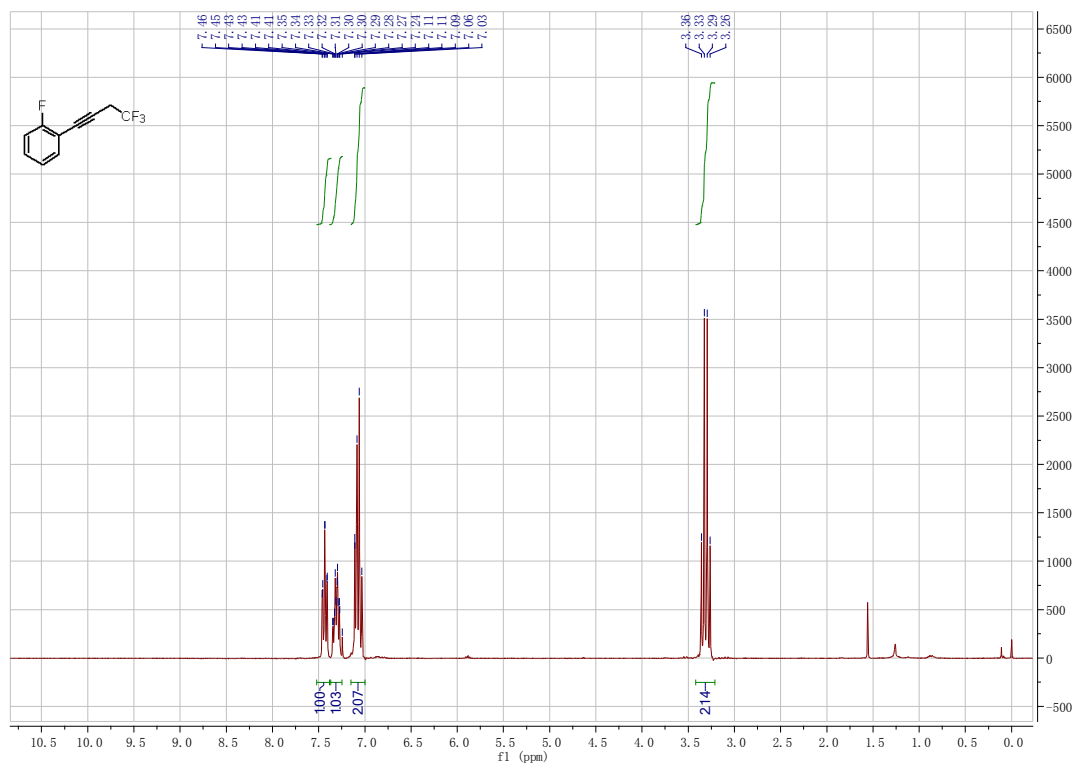
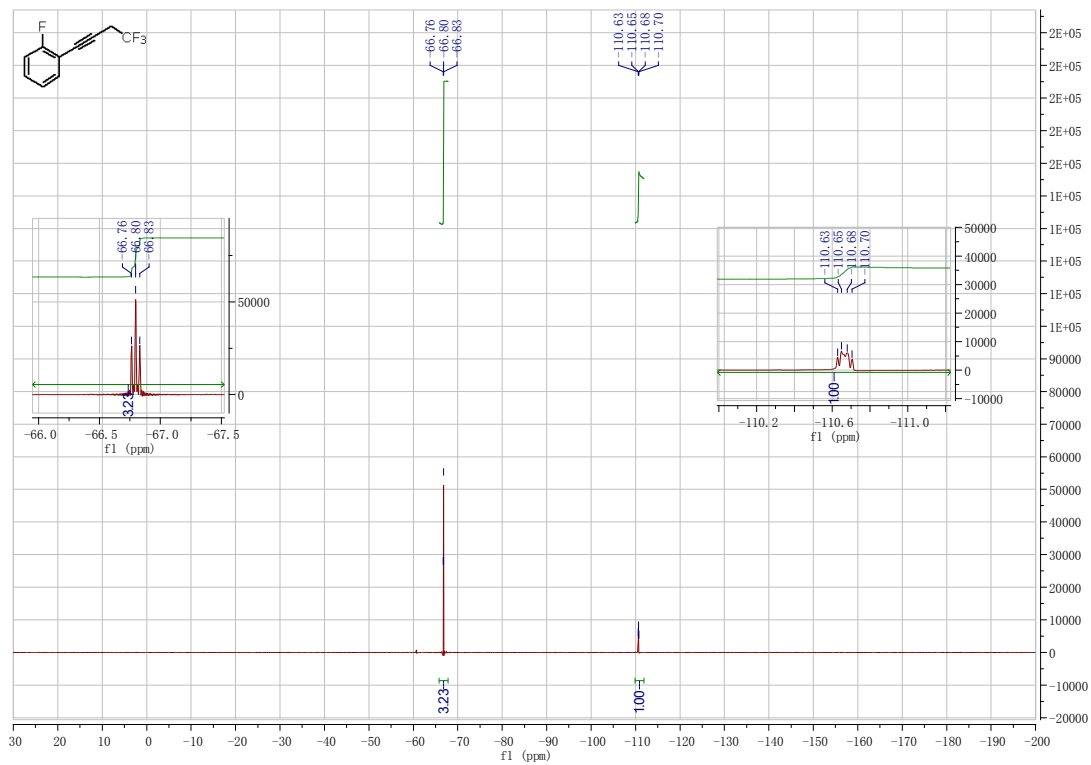
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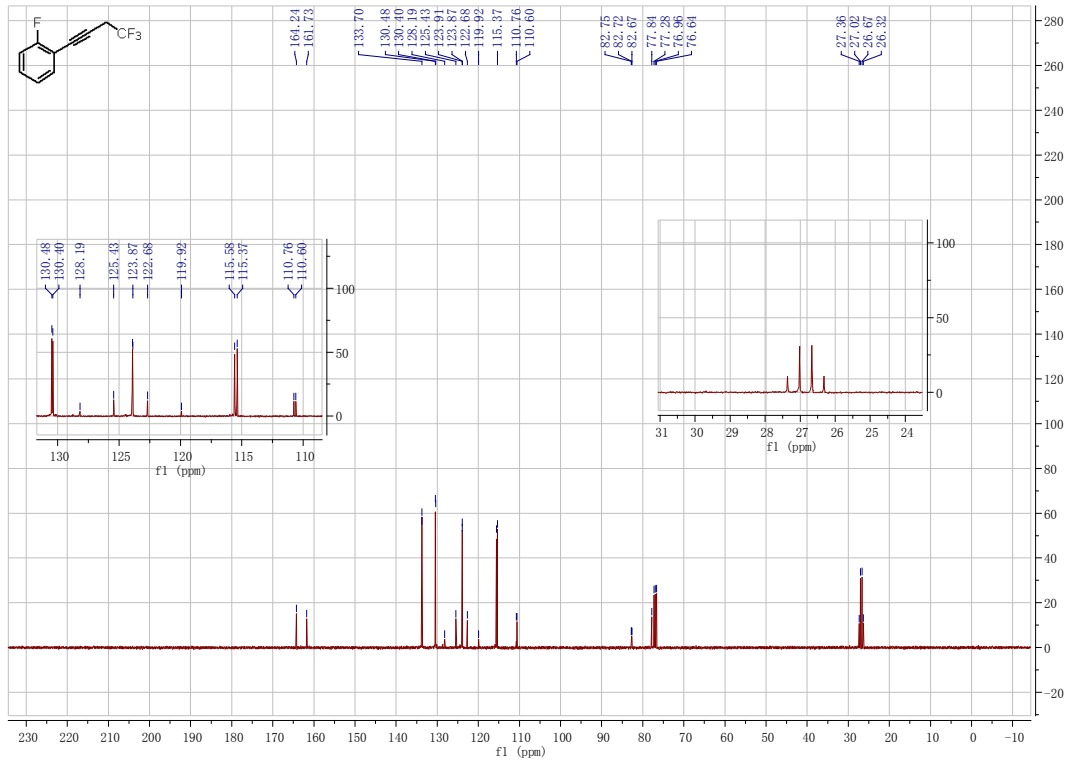


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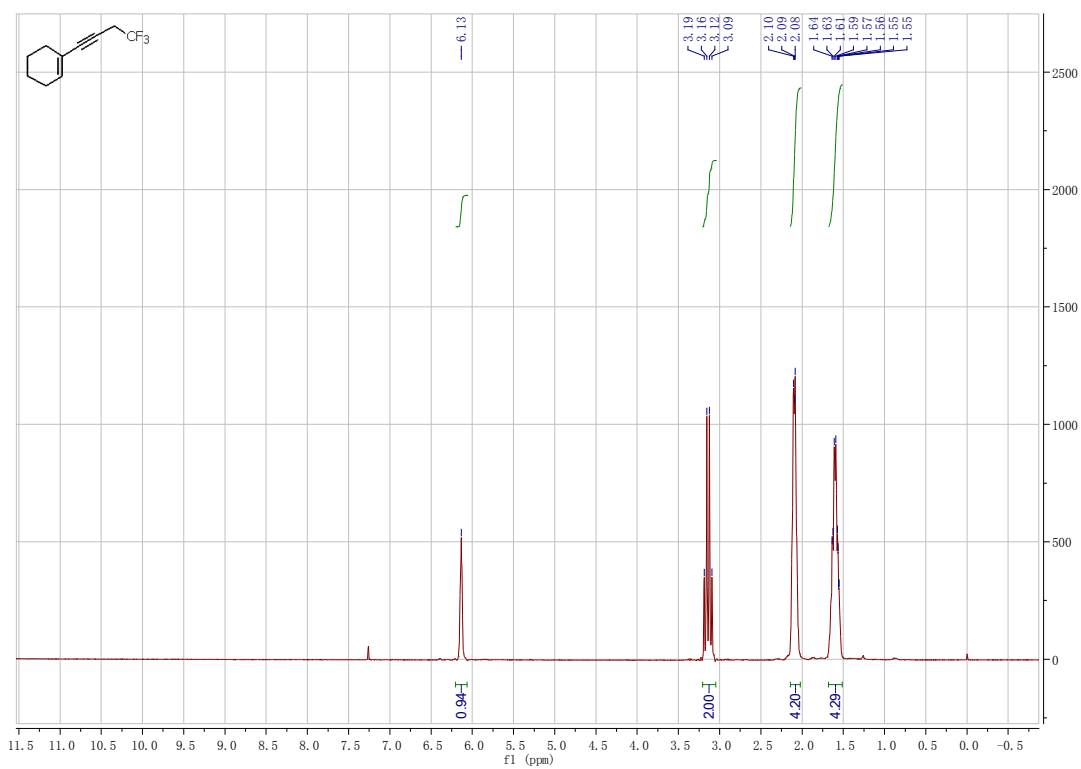
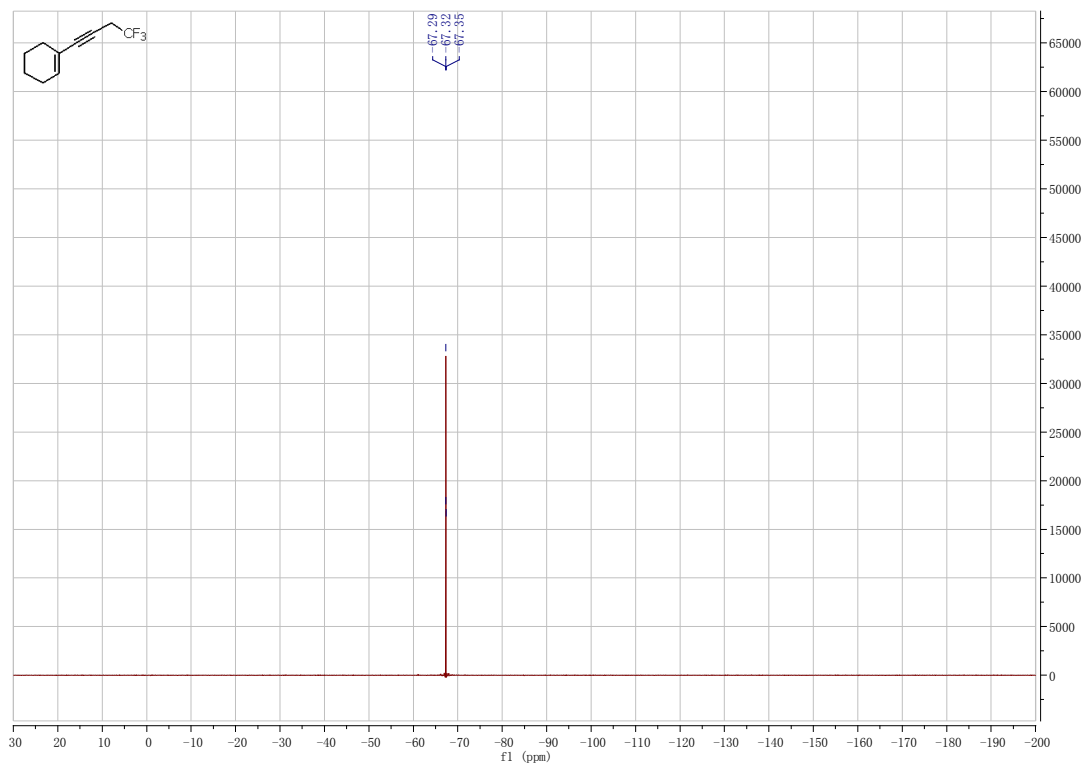


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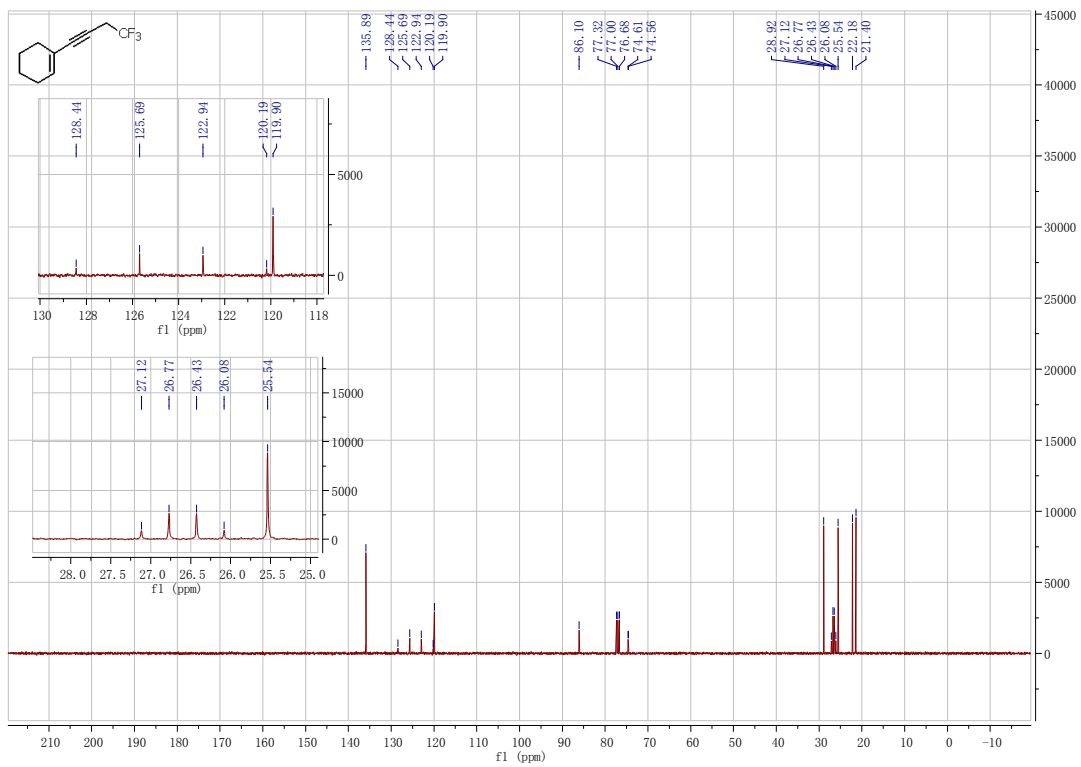




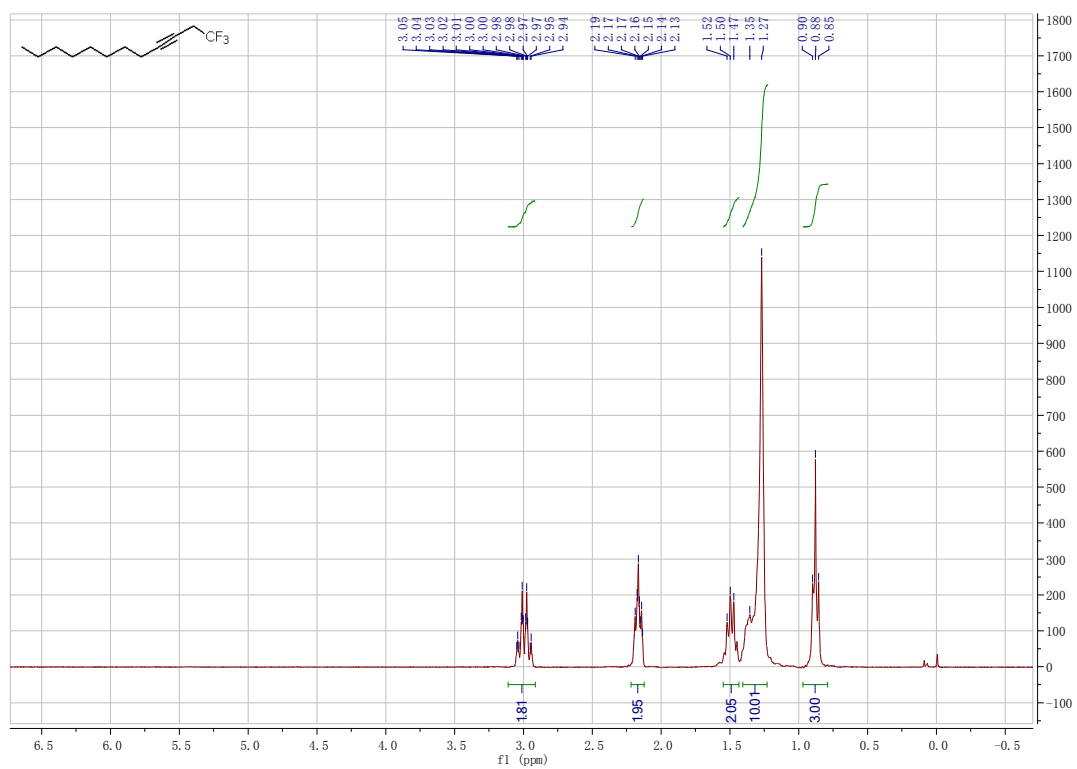
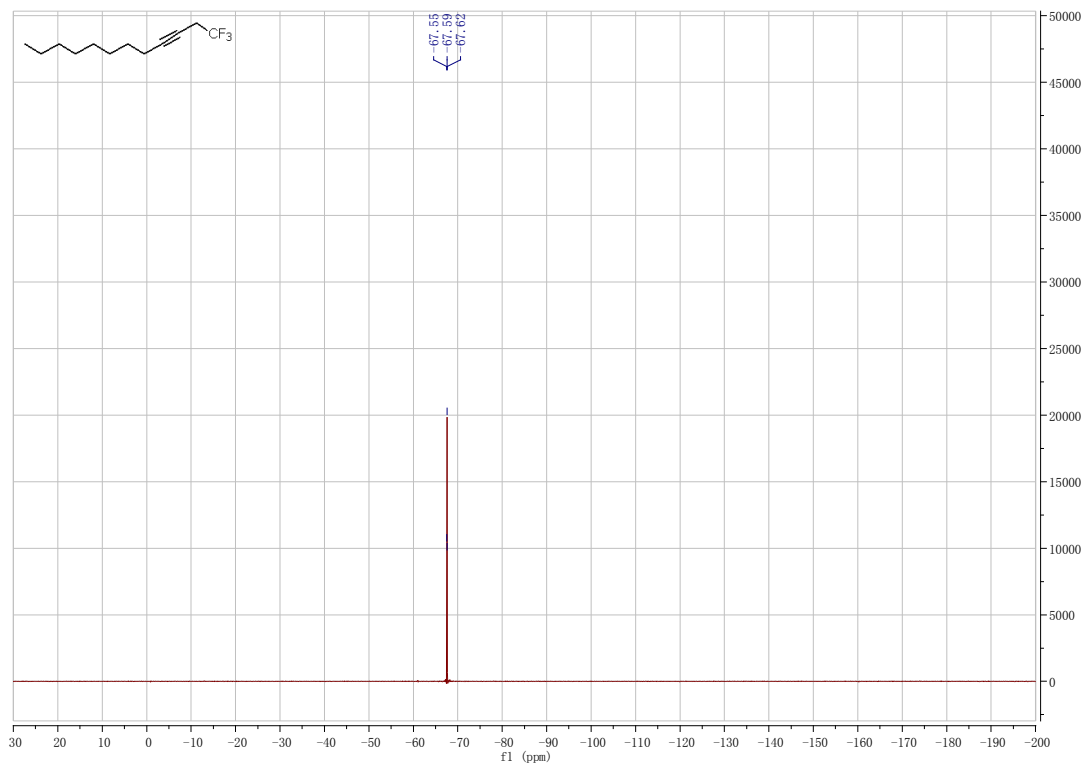
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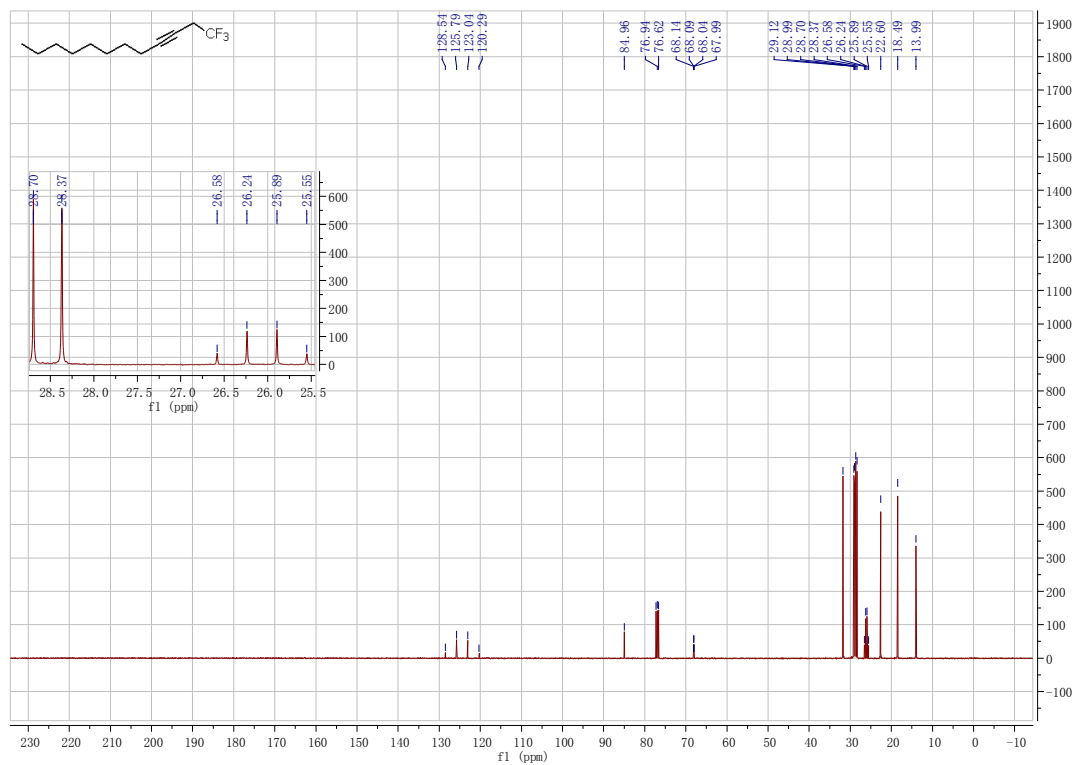




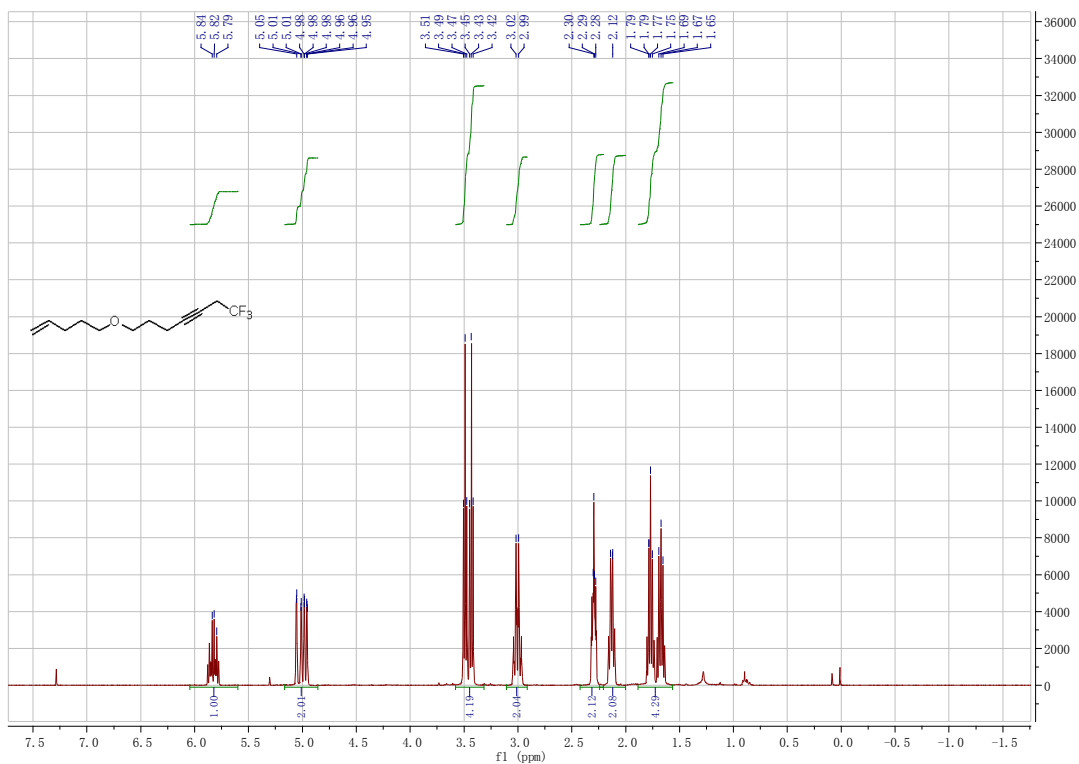
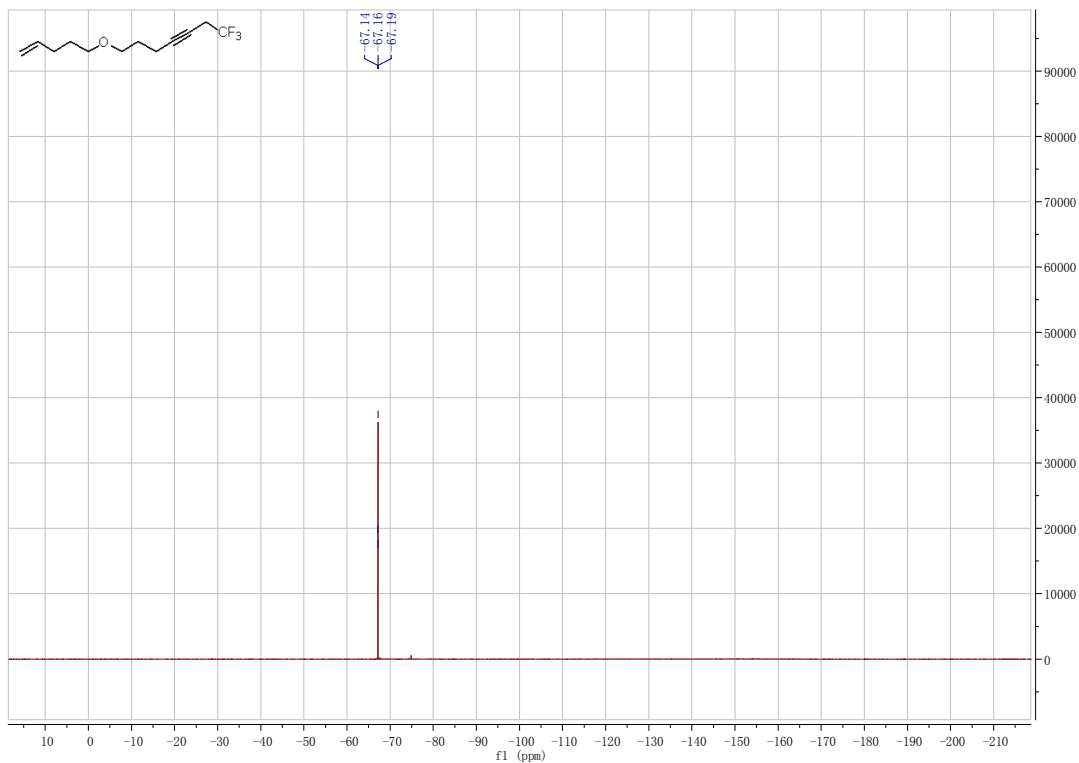


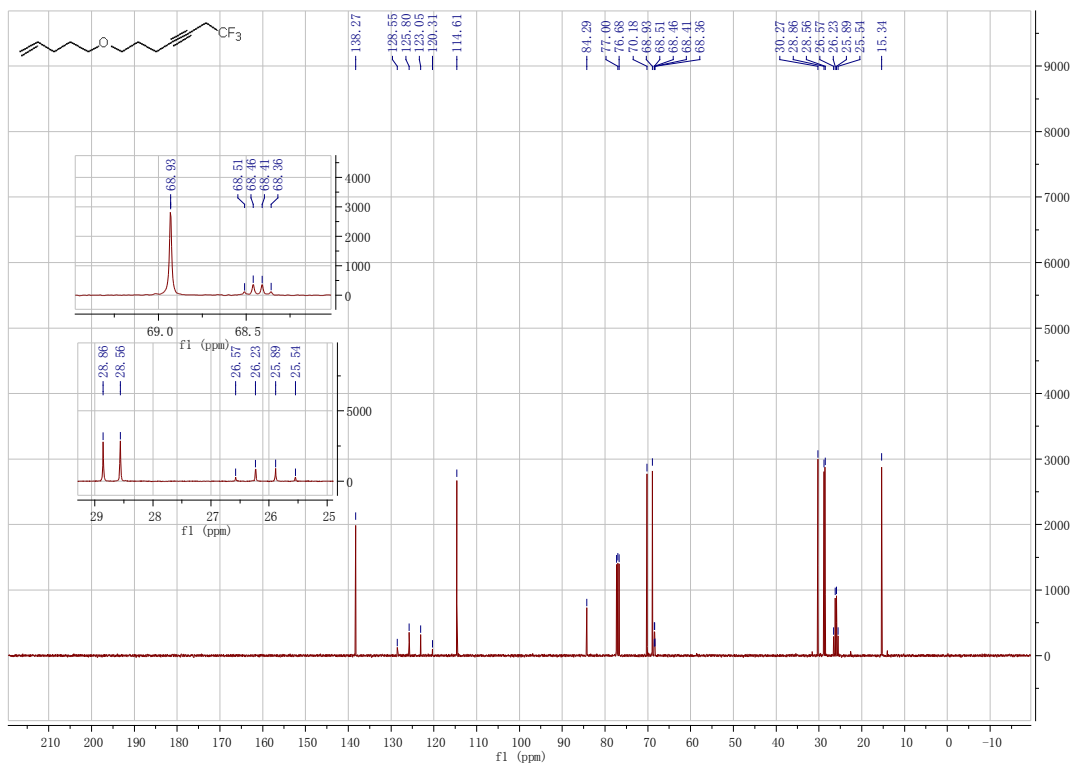
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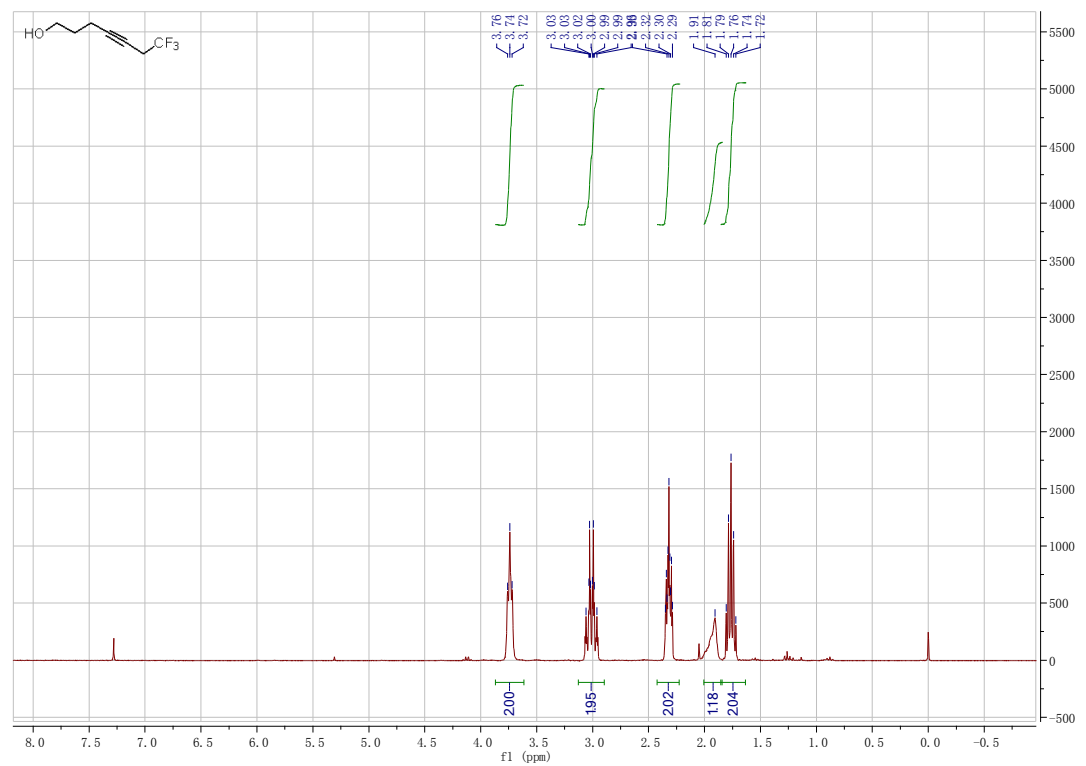
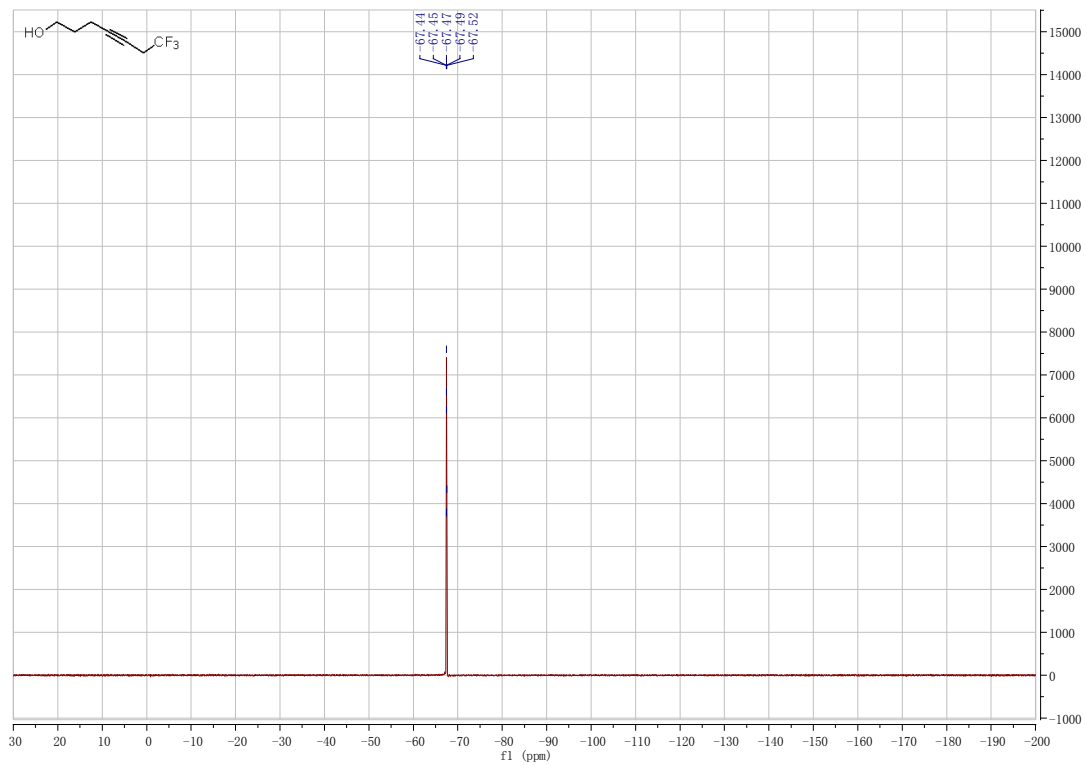


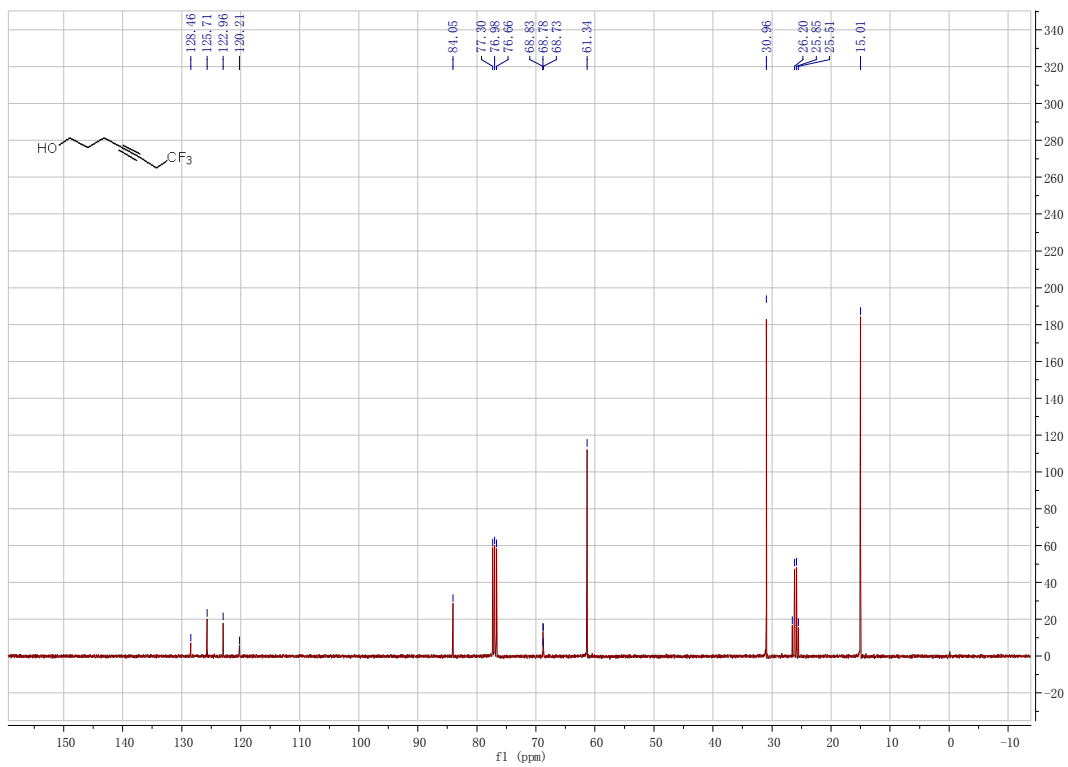
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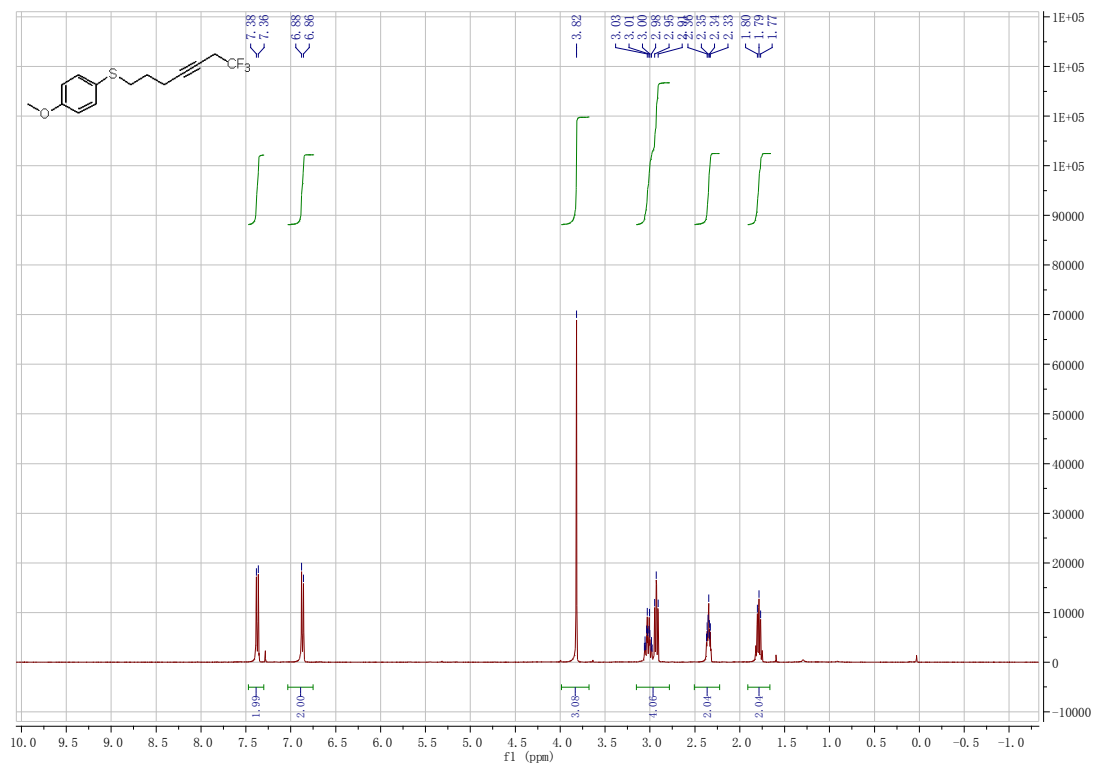
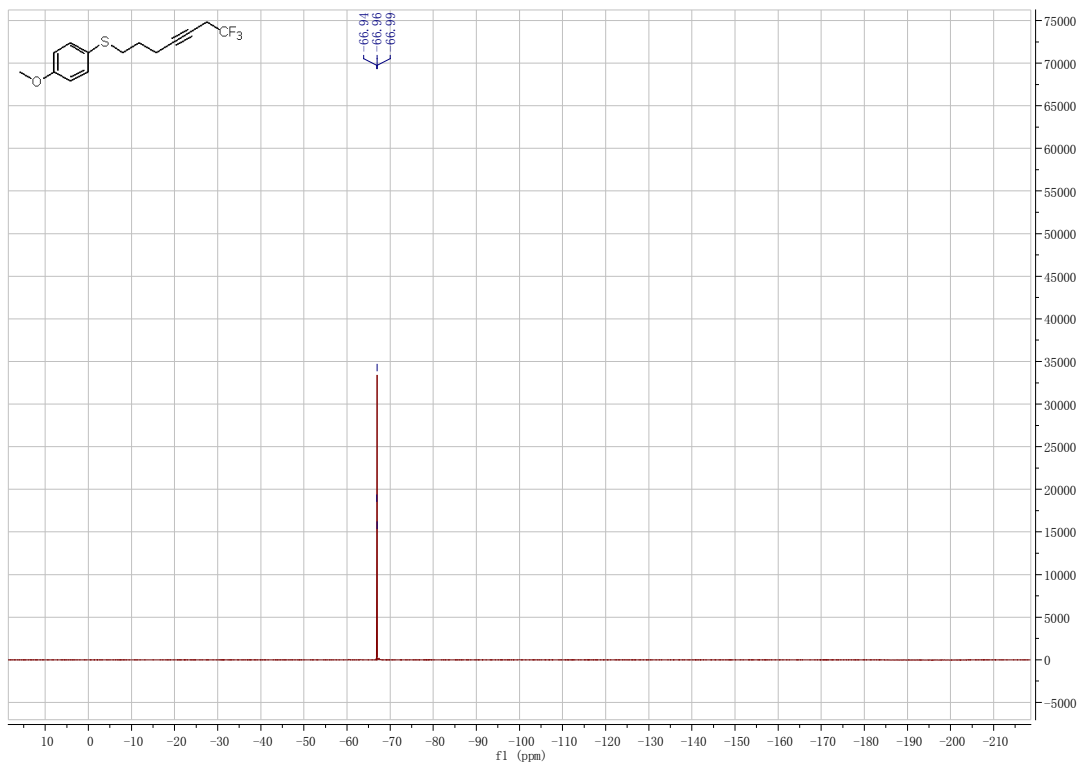


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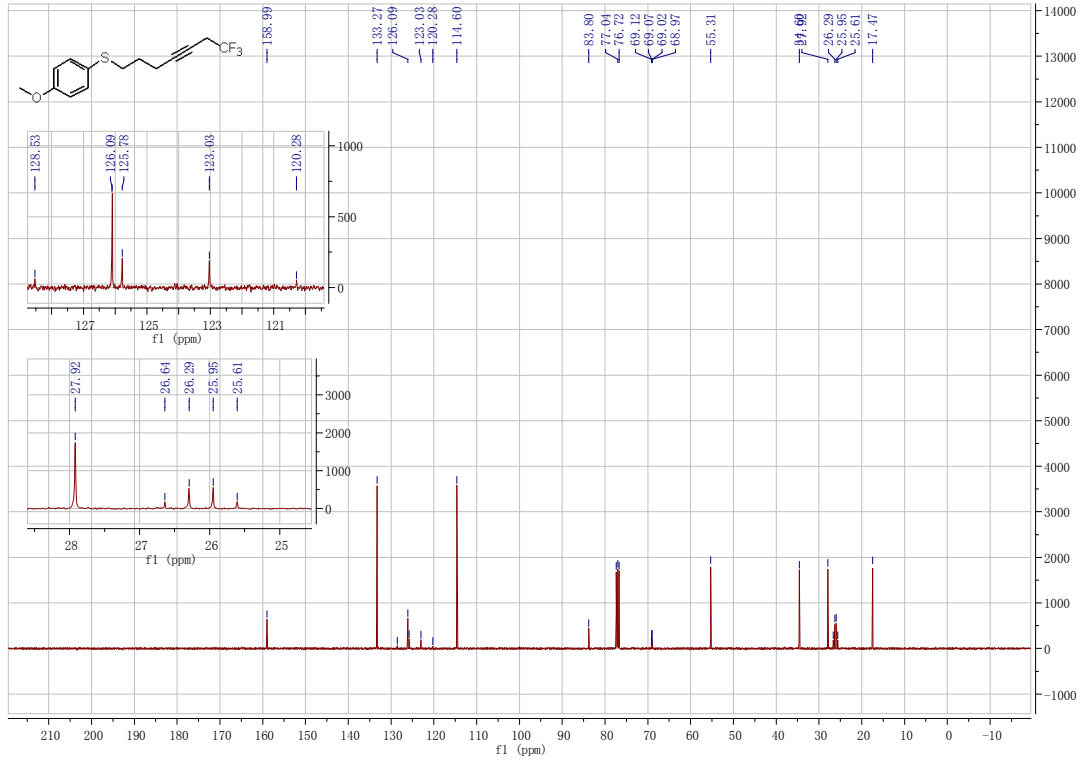




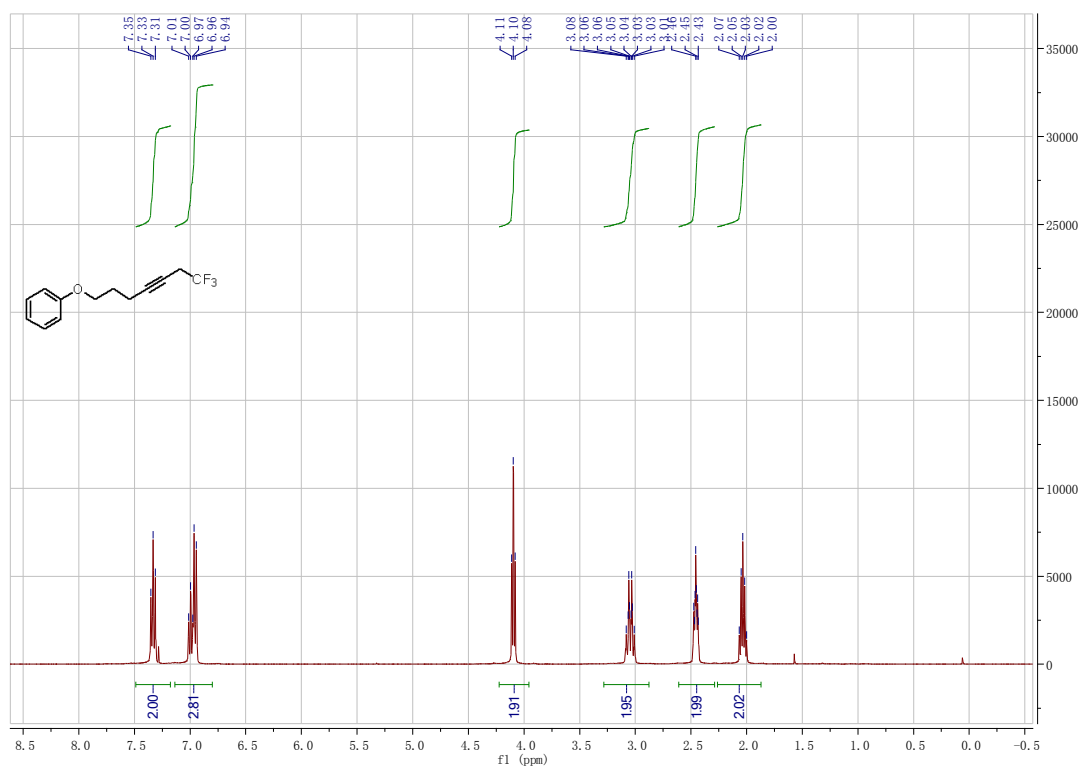
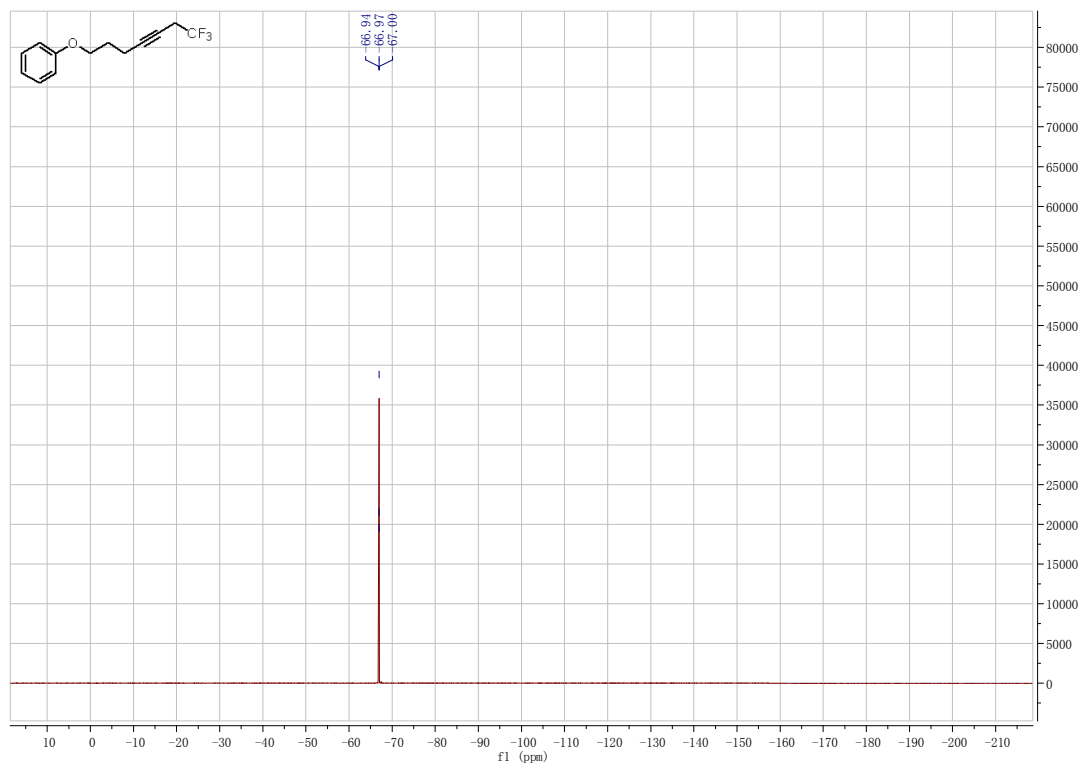
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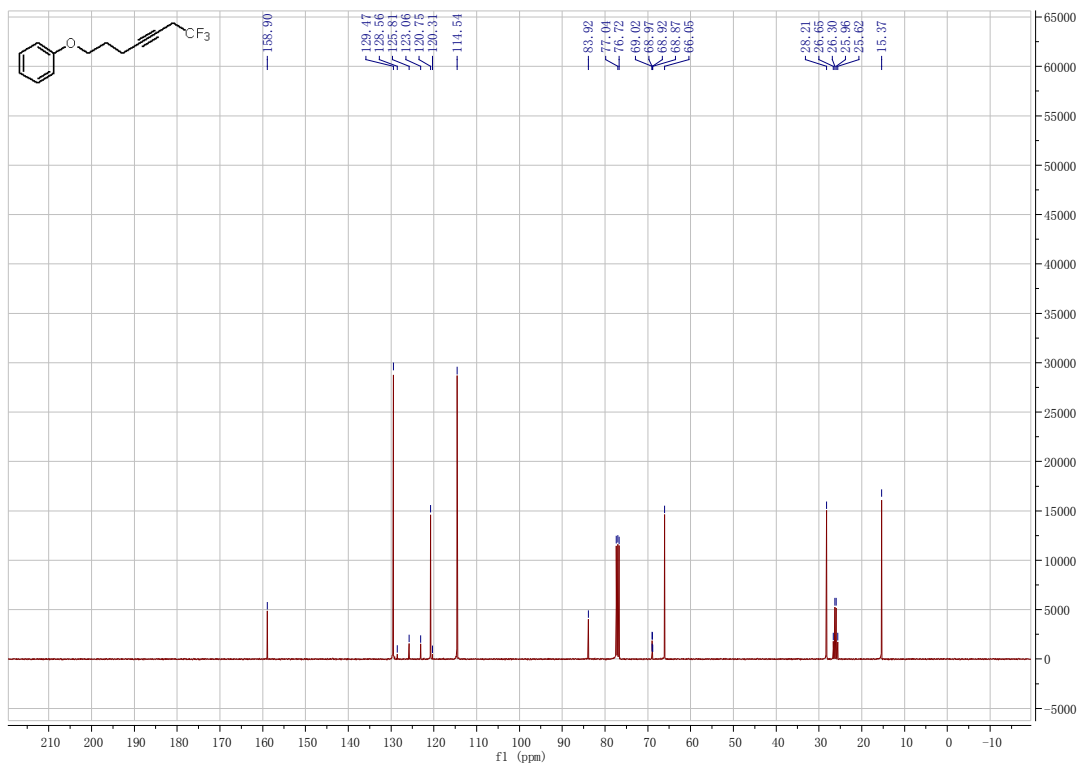




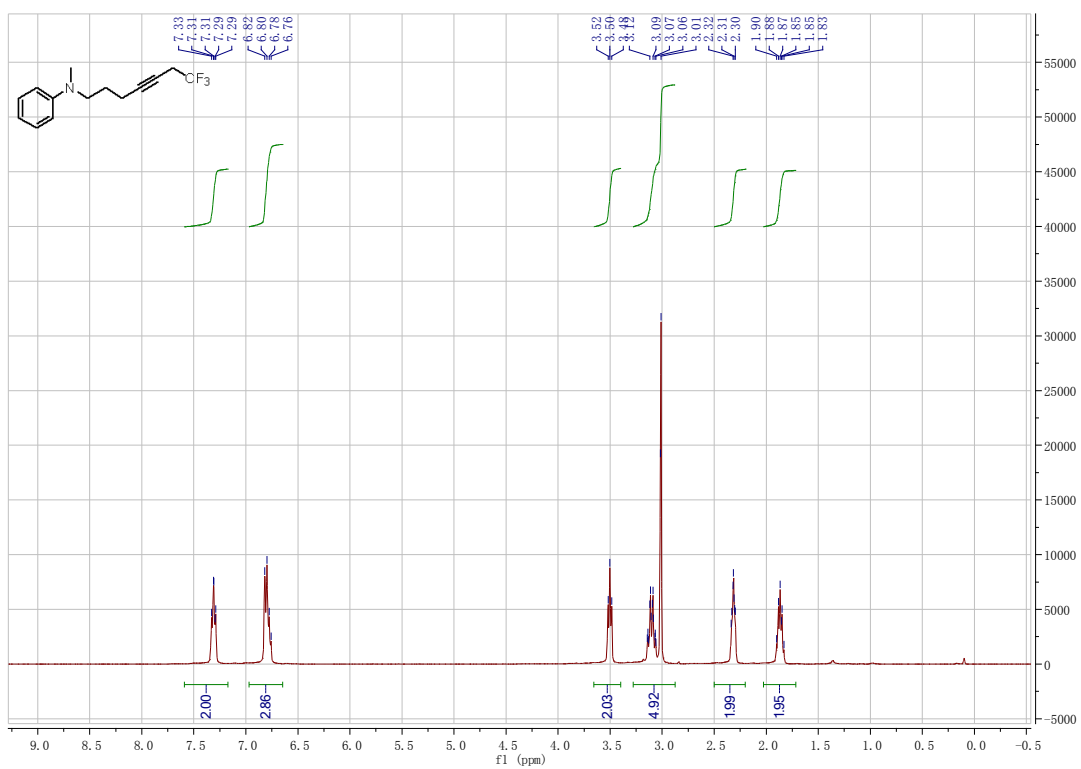
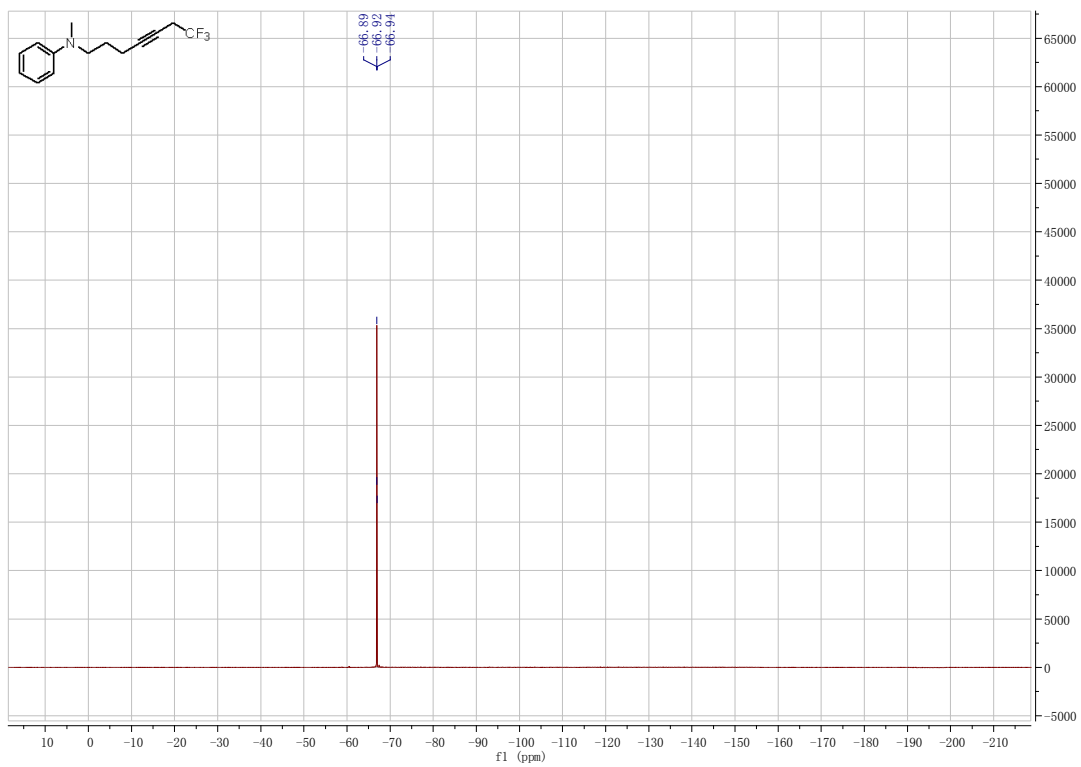


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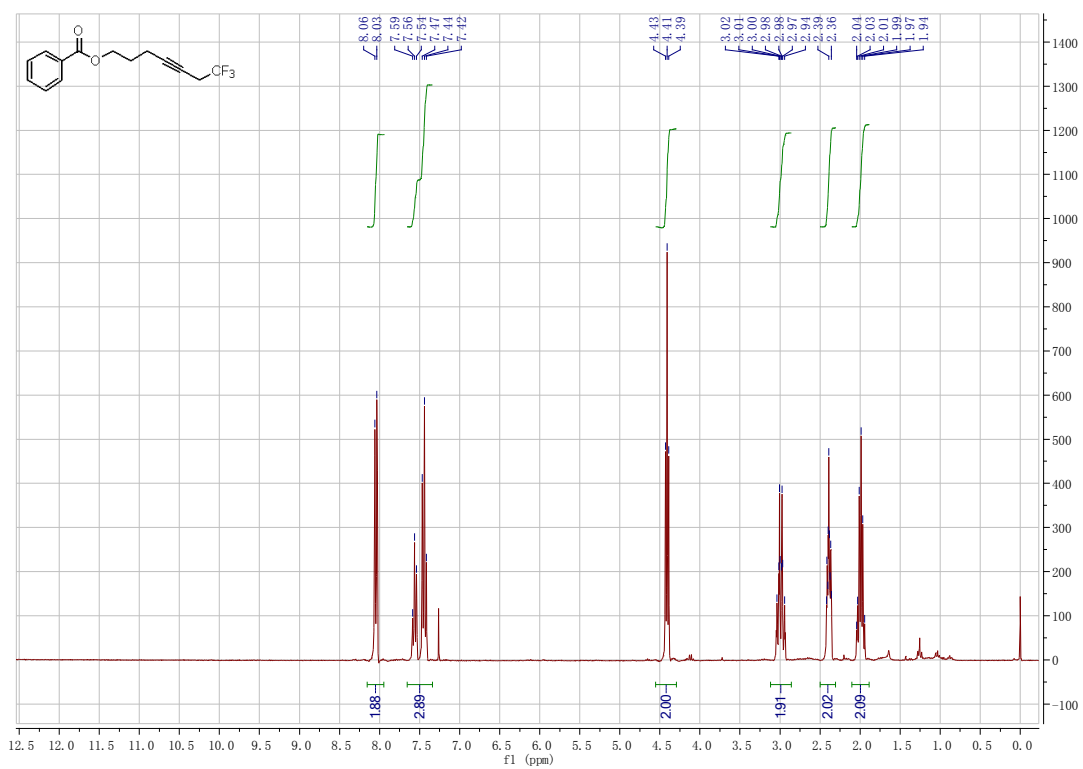
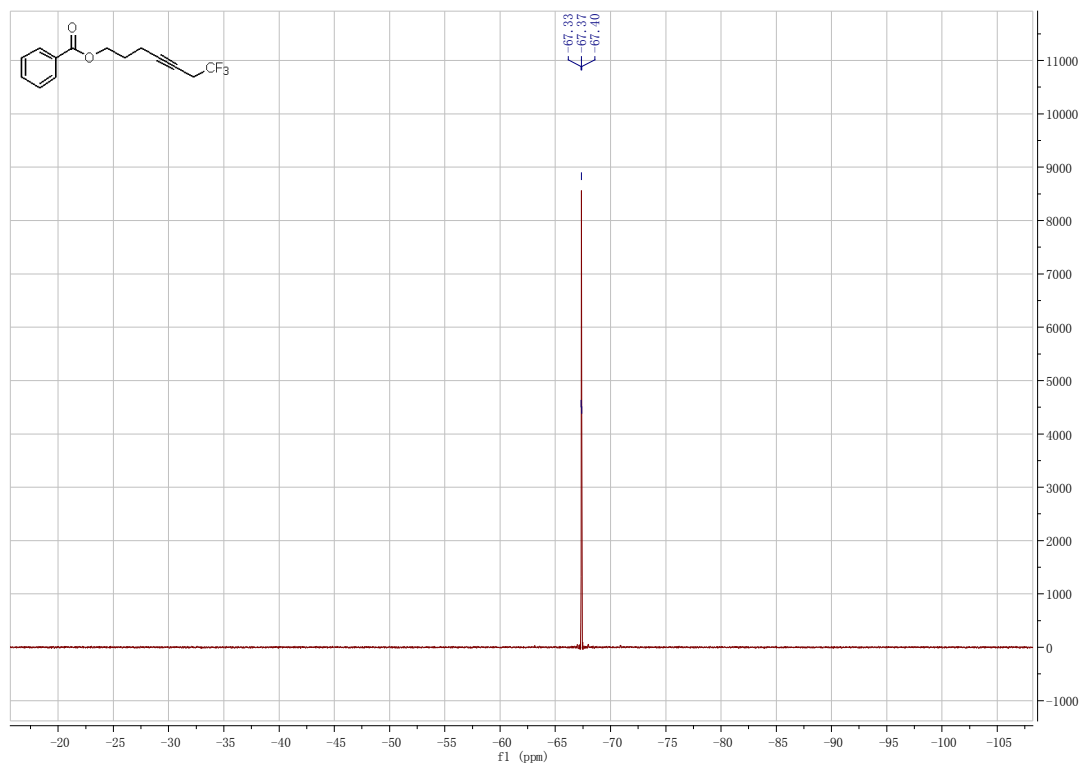


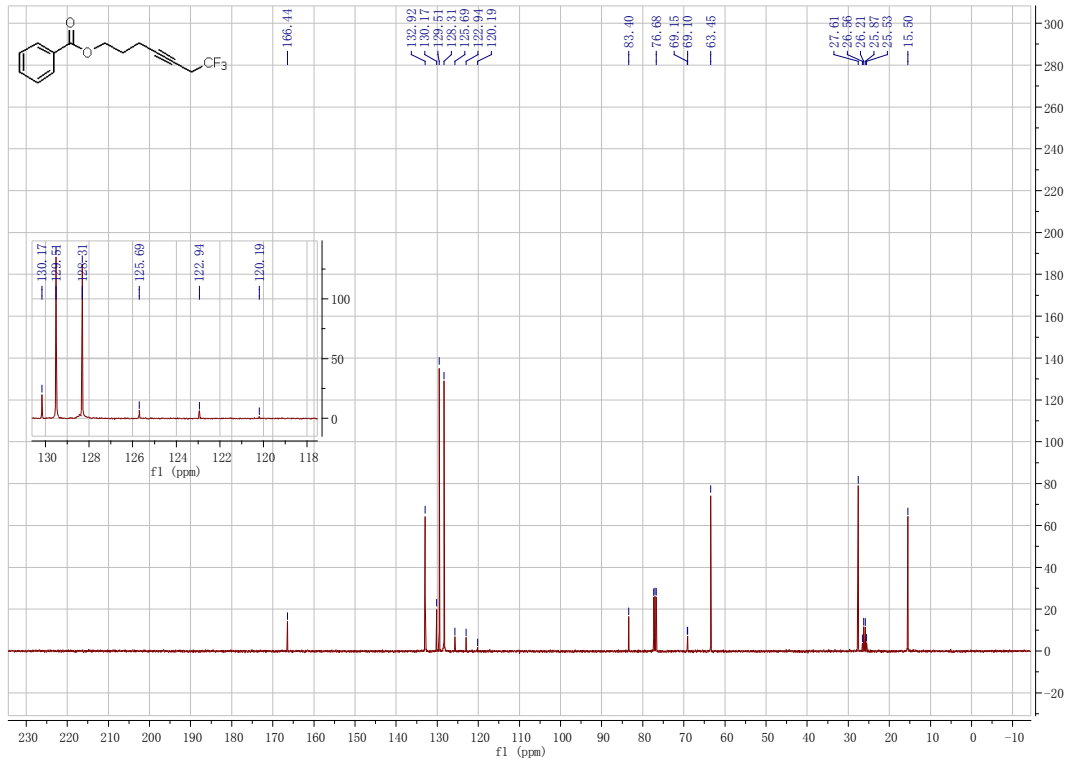
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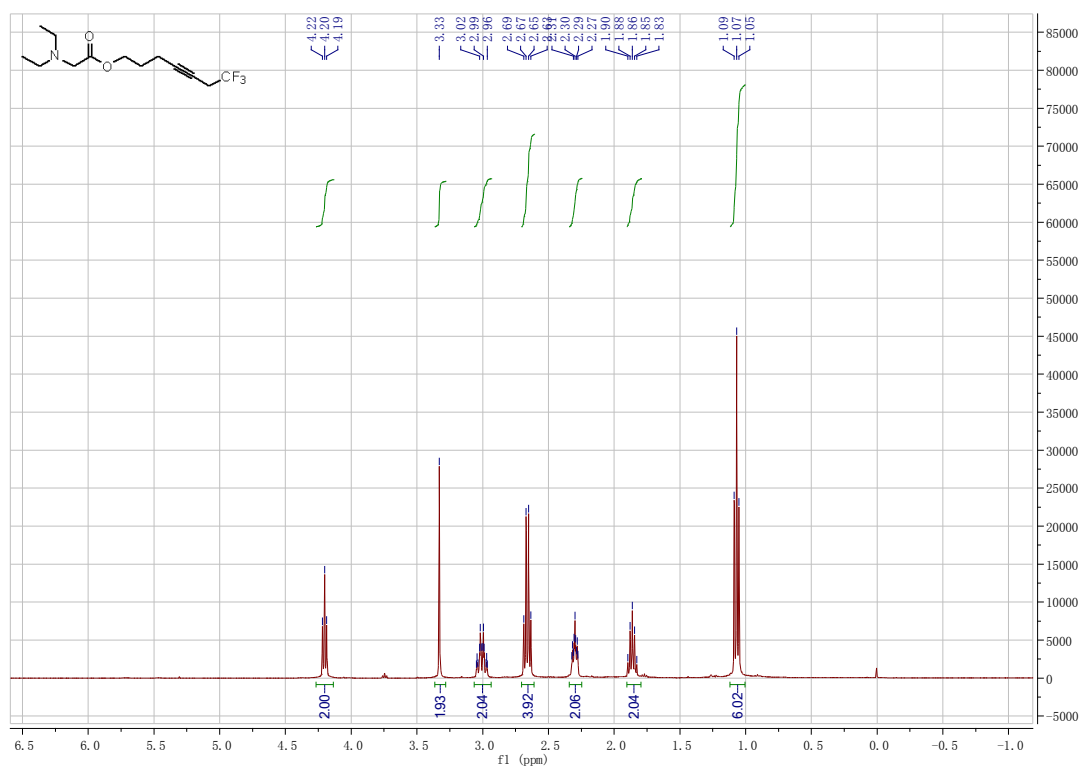
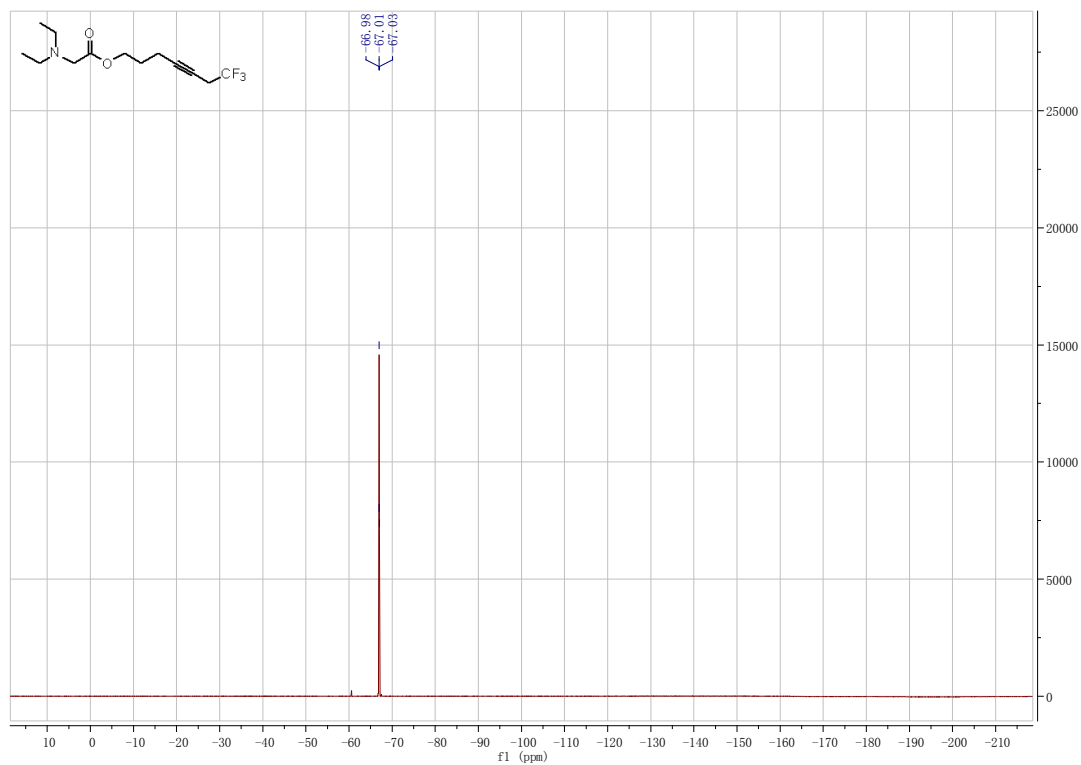


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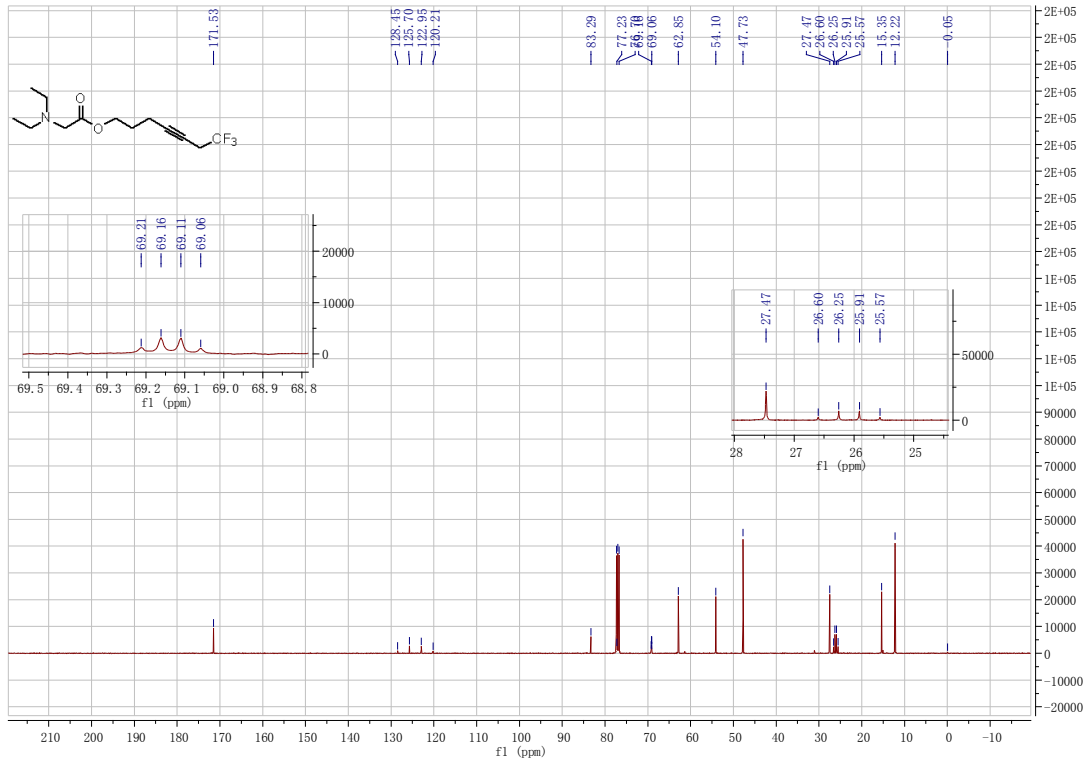




3q







3r

