

## Supporting Information

# One-pot synthesis of monodisperse dual-functionalized polyethylene glycols through macrocyclic sulfates

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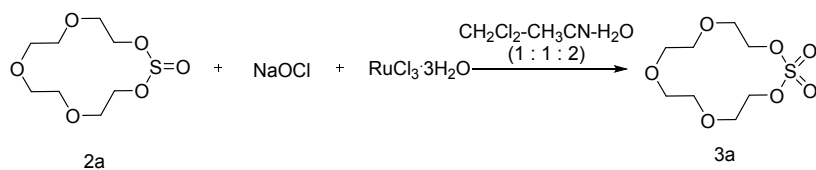
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## Table of contents

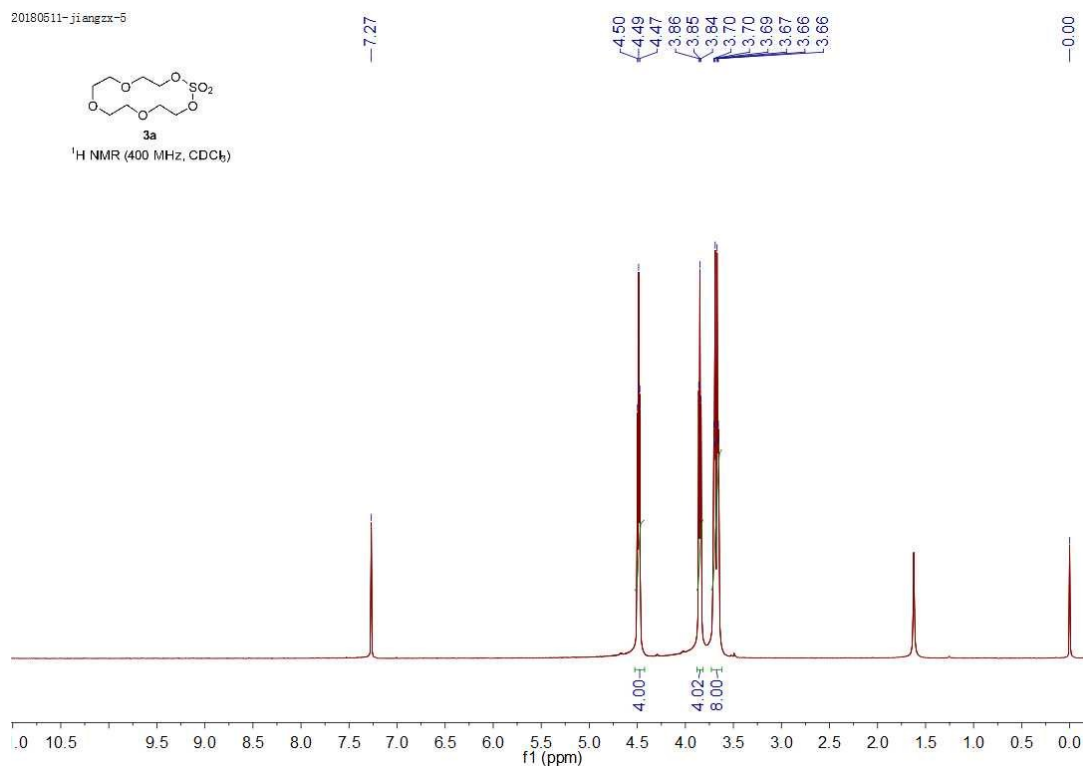
|                                                                                                                    |         |
|--------------------------------------------------------------------------------------------------------------------|---------|
| 1. Optimization of oxidation conditions of macrocyclic sulfites <b>3a</b> .....                                    | S2      |
| 2. Copies of <sup>1</sup> H NMR spectra of compounds <b>3a-3e</b> .....                                            | S2-S4   |
| 3. Copies of <sup>1</sup> H, <sup>13</sup> C, <sup>19</sup> F NMR and HRMS spectra of compounds <b>4a-4h</b> ..... | S5-S14  |
| 4. Copies of <sup>1</sup> H, <sup>13</sup> C, <sup>19</sup> F NMR and HRMS spectra of compounds <b>5a-5h</b> ..... | S14-S25 |
| 5. Copies of <sup>1</sup> H, <sup>13</sup> C, <sup>19</sup> F NMR and HRMS spectra of compounds <b>6a-6j</b> ..... | S26-S41 |
| 6. Copies of <sup>1</sup> H, <sup>13</sup> C, <sup>19</sup> F NMR and HRMS spectra of compounds <b>7a-7j</b> ..... | S41-S57 |
| 7. Copies of <sup>1</sup> H, <sup>13</sup> C, <sup>19</sup> F NMR and HRMS spectra of compounds <b>8a-8b</b> ..... | S58-S60 |

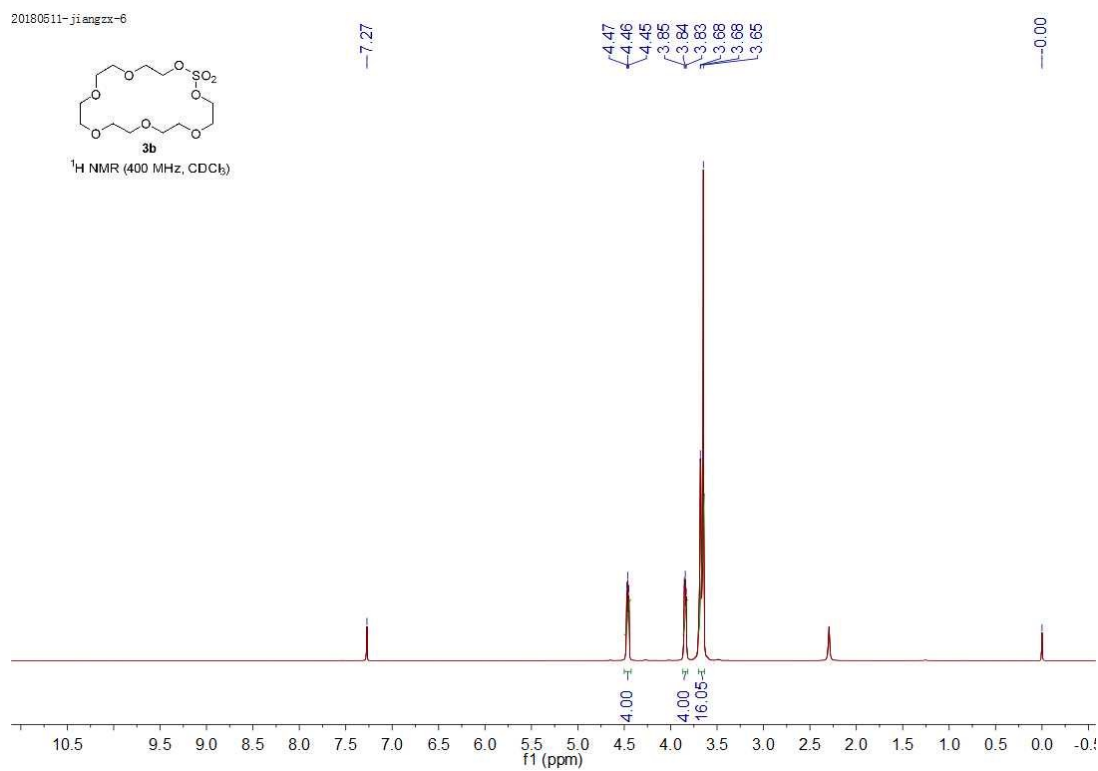
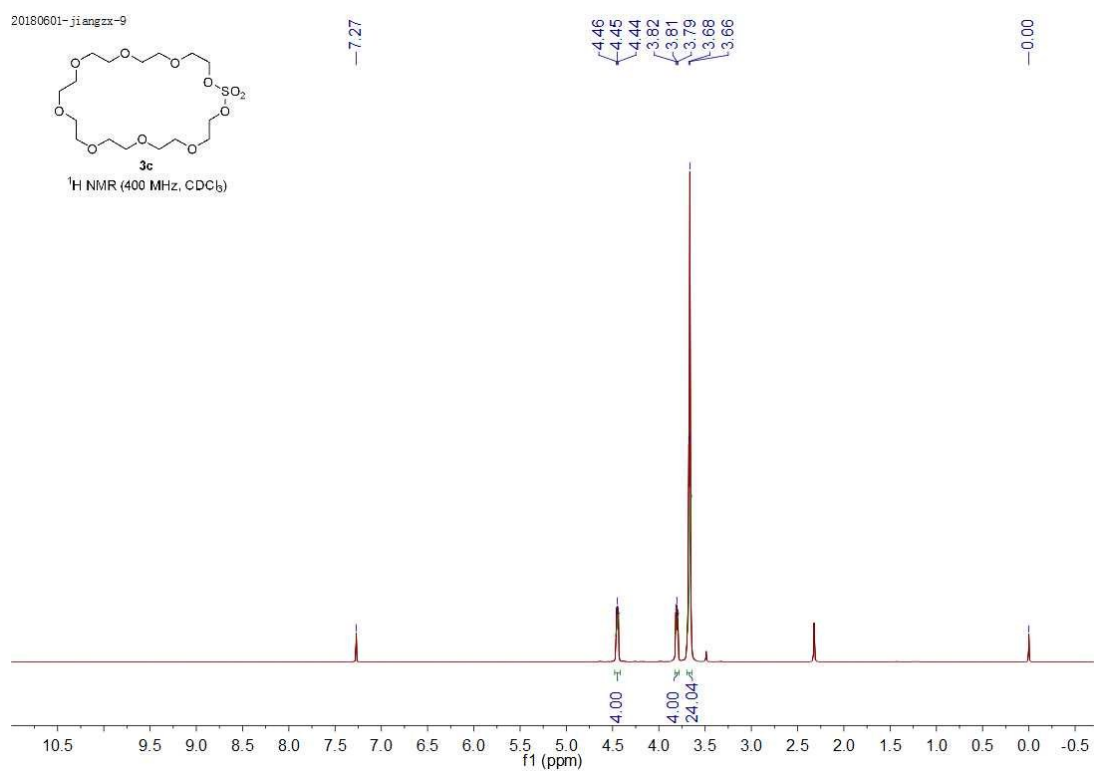
**Table S1** Optimization of reaction conditions

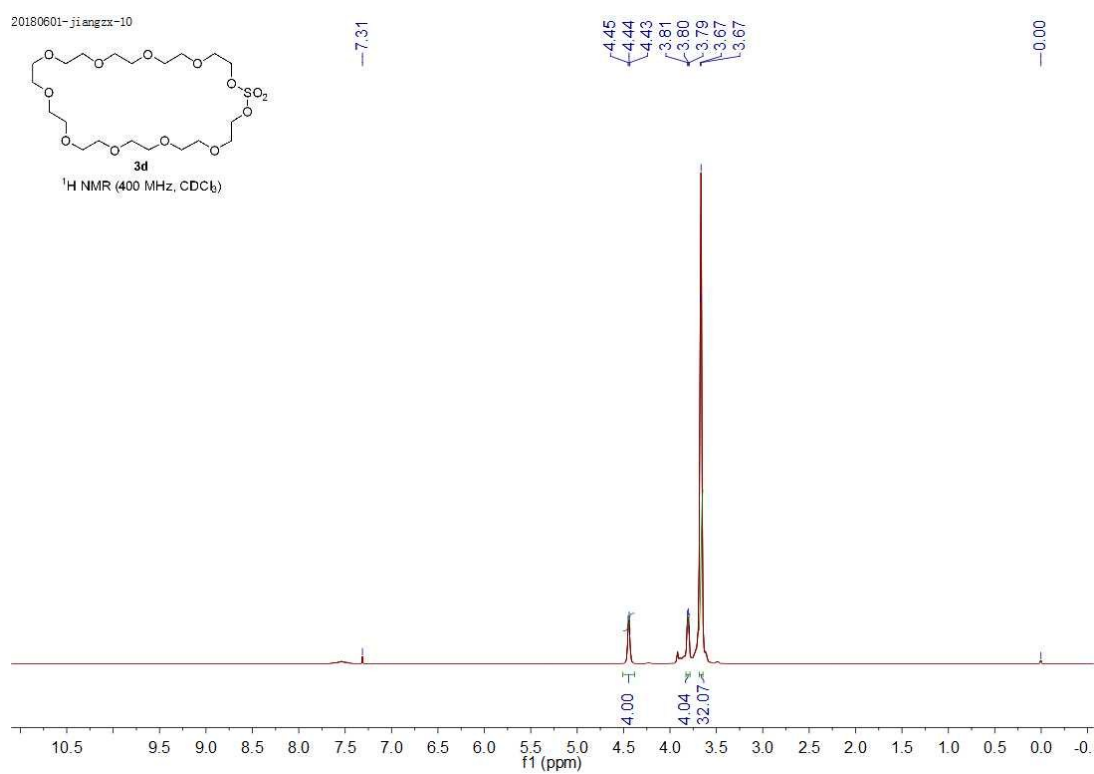
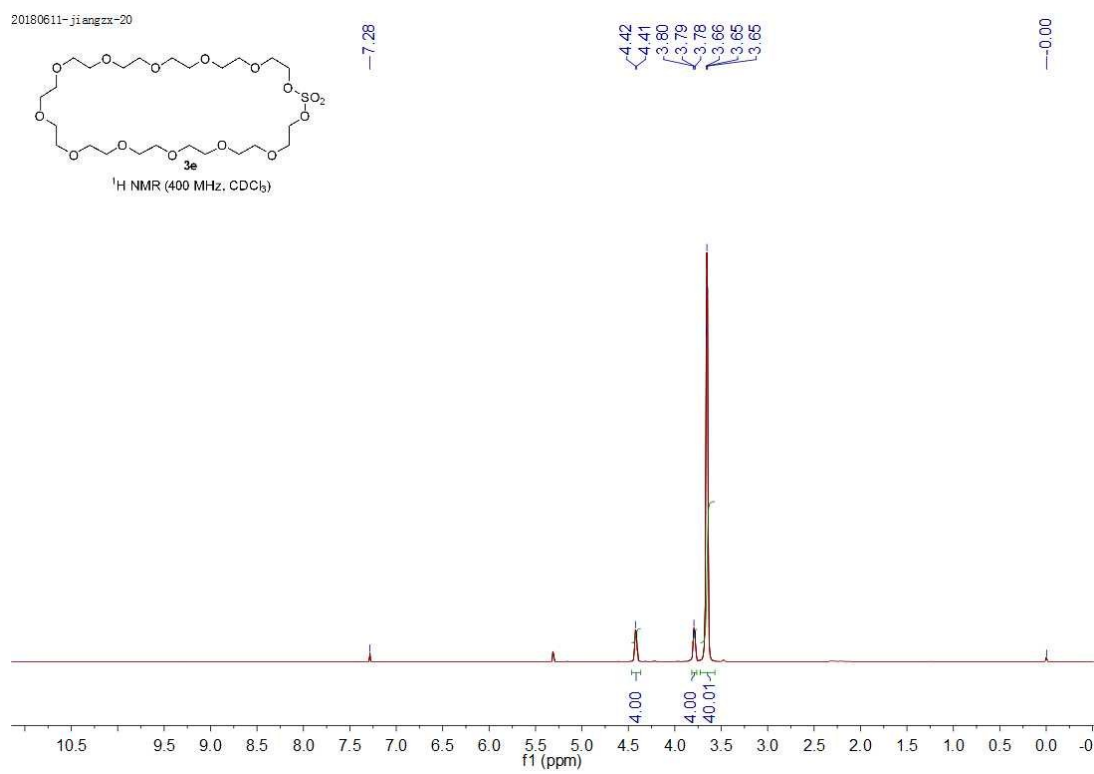


| Entry | NaClO (equiv.) | $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (equiv.) | Concentration (mmol/mL) | Yield (%) |
|-------|----------------|----------------------------------------------------|-------------------------|-----------|
| 1     | 4.0            | 0.001                                              | 0.20                    | 89        |
| 2     | 4.0            | 0.005                                              | 0.20                    | 92        |
| 3     | 4.0            | 0.01                                               | 0.20                    | 92        |
| 4     | 1.0            | 0.005                                              | 0.20                    | 11        |
| 5     | 2.0            | 0.005                                              | 0.20                    | 20        |
| 6     | 3.0            | 0.005                                              | 0.20                    | 55        |
| 7     | 5.0            | 0.005                                              | 0.20                    | 92        |
| 8     | 6.0            | 0.005                                              | 0.20                    | 92        |
| 9     | 4.0            | 0.005                                              | 0.11                    | 90        |
| 10    | 4.0            | 0.005                                              | 0.08                    | 88        |
| 11    | 4.0            | 0.005                                              | 0.06                    | 82        |

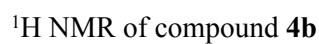
**$^1\text{H}$  NMR of compound **3a****



<sup>1</sup>H NMR of compound **3b**<sup>1</sup>H NMR of compound **3c**

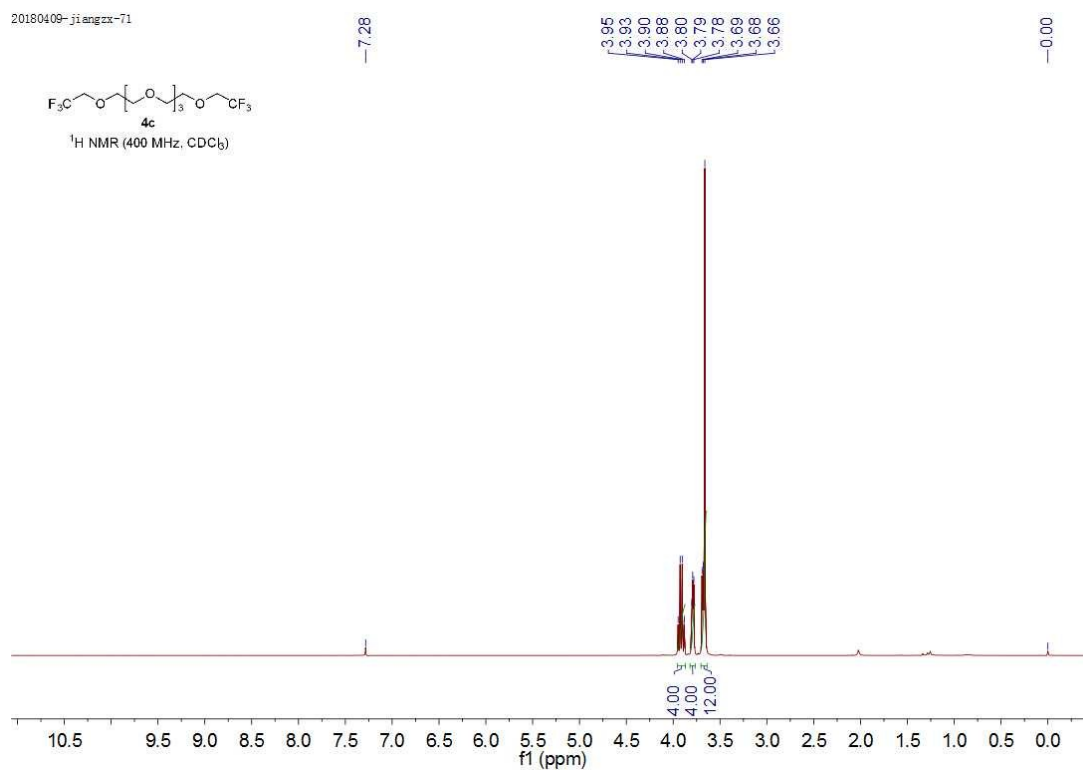
<sup>1</sup>H NMR of compound **3d**<sup>1</sup>H NMR of compound **3e**

20170913-jiangzx-12



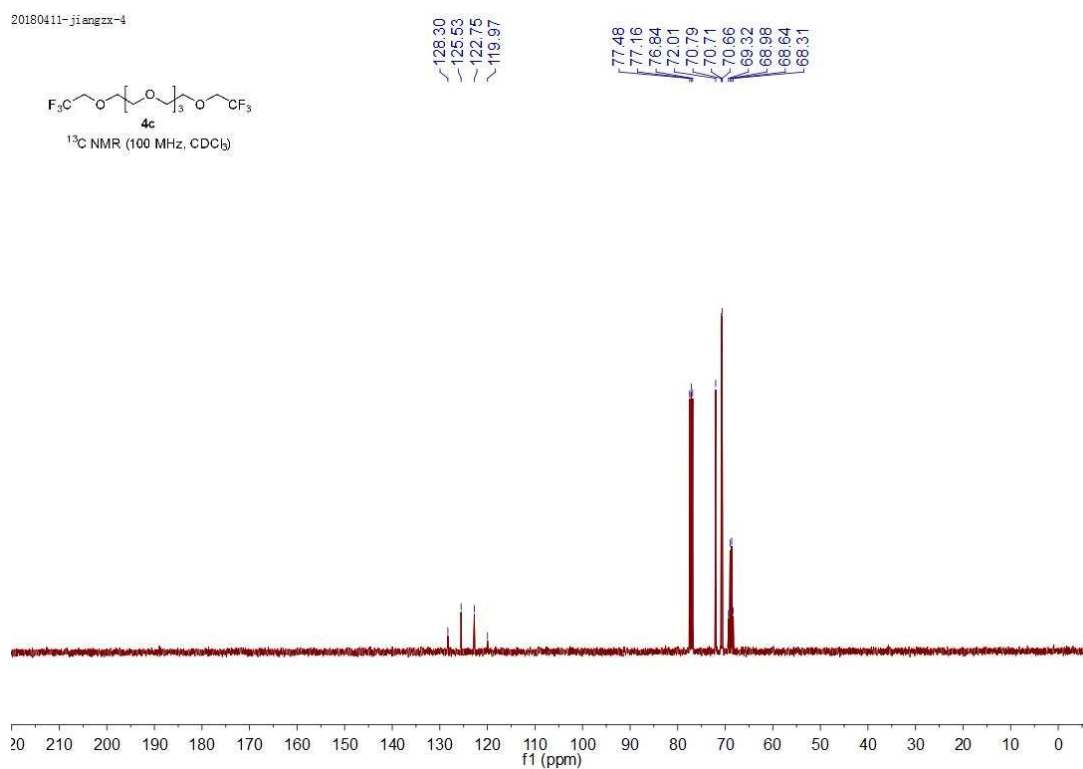
# <sup>1</sup>H NMR of compound **4c**

20180409-jiangzx-71

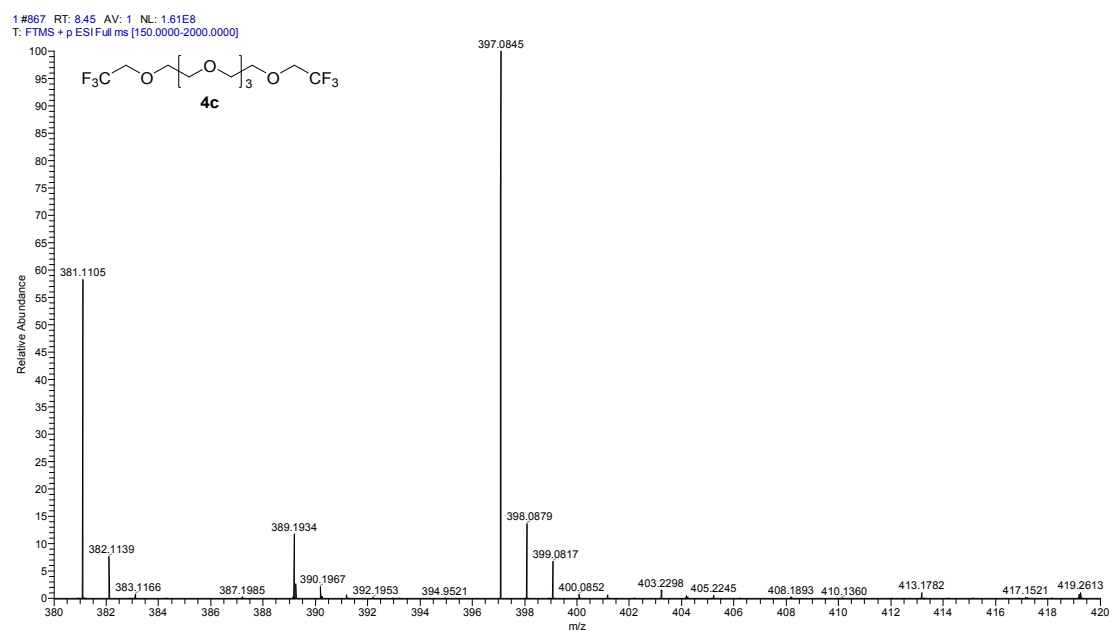
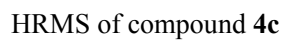


# <sup>13</sup>C NMR of compound **4c**

20180411-jiangzx-4

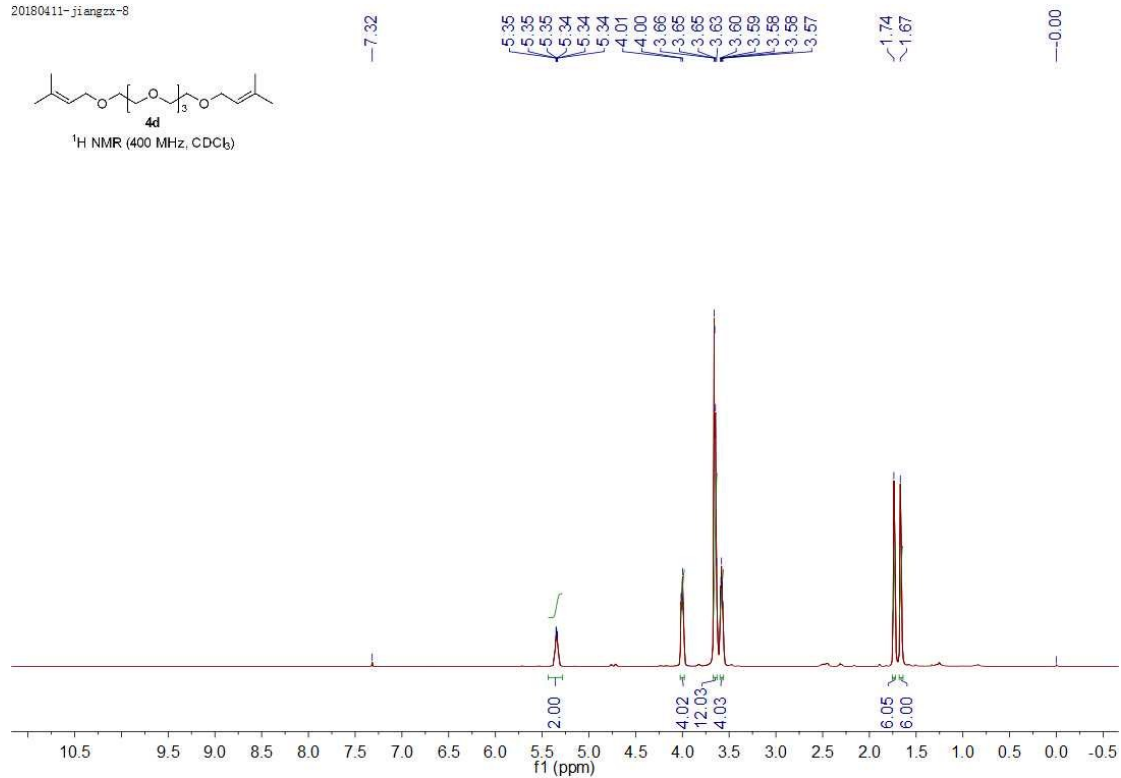


20180409-jiangzx-71



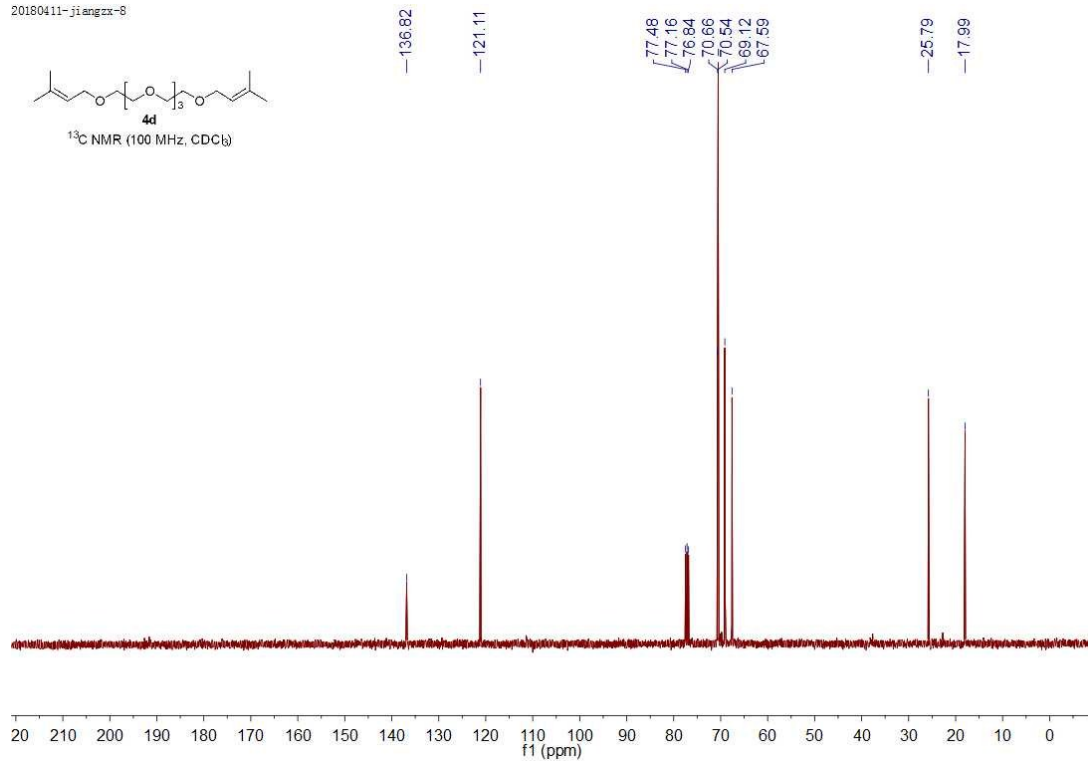
# <sup>1</sup>H NMR of compound **4d**

20180411-jiangzx-8

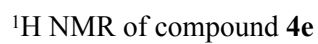


## <sup>13</sup>C NMR of compound **4d**

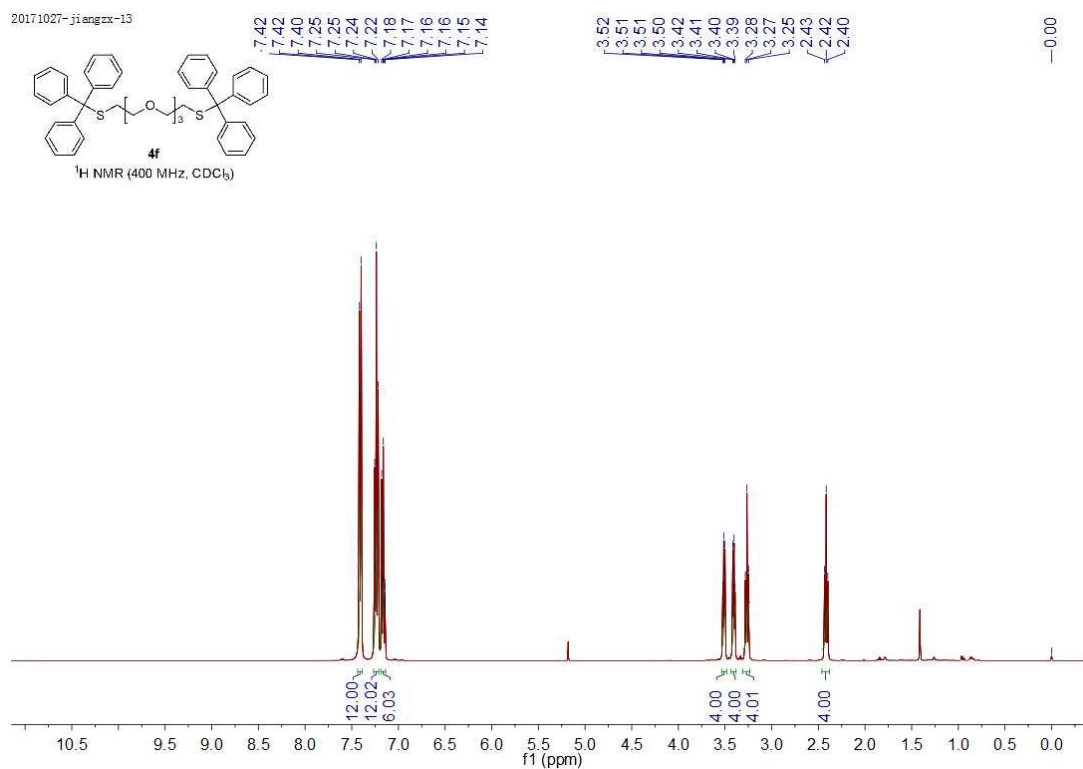
20180411-jiangzx-8



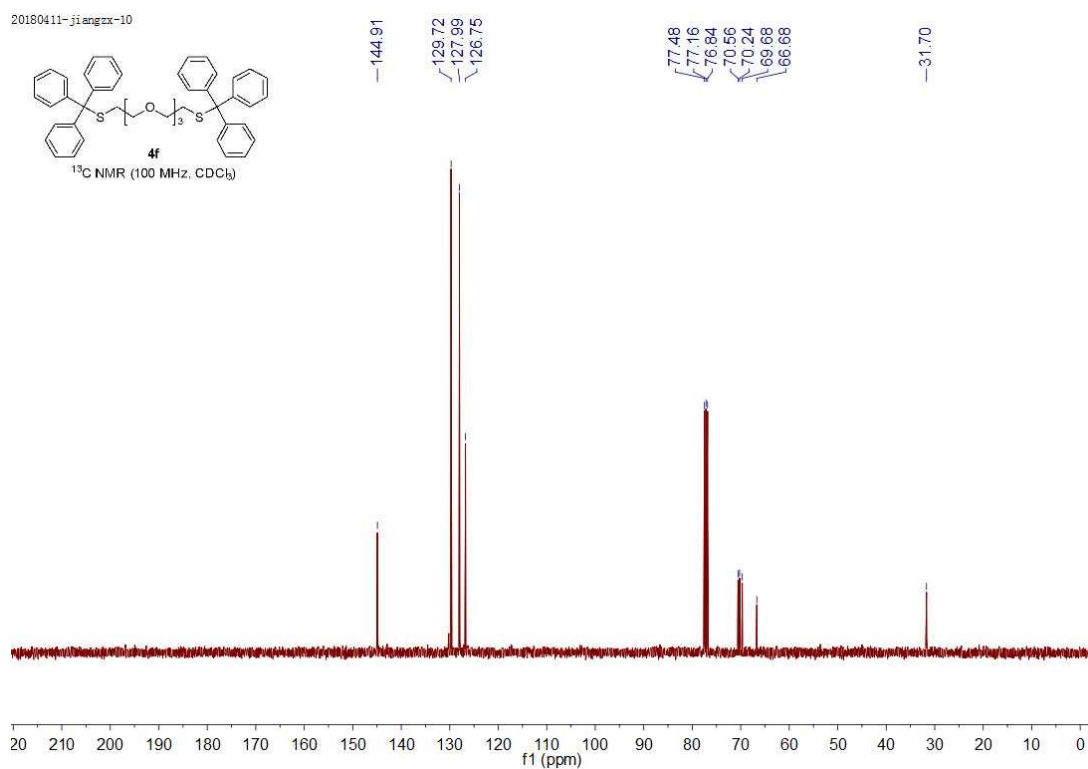
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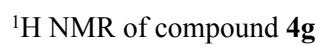
# <sup>1</sup>H NMR of compound **4f**



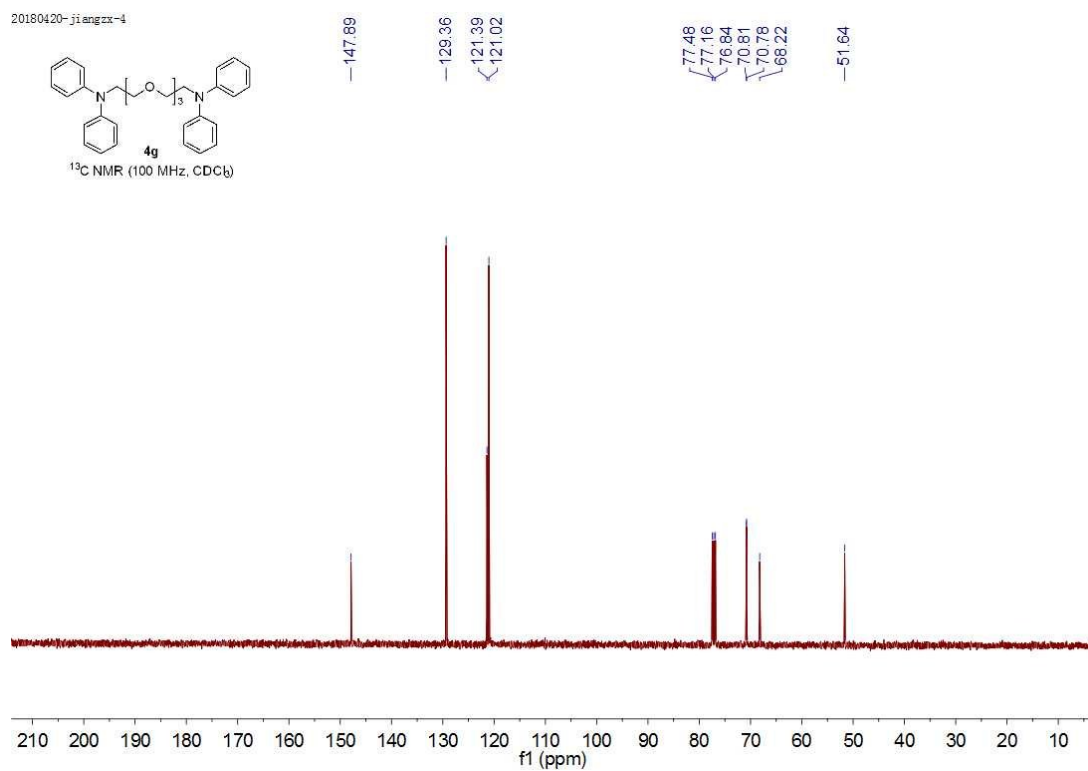
# <sup>13</sup>C NMR of compound **4f**



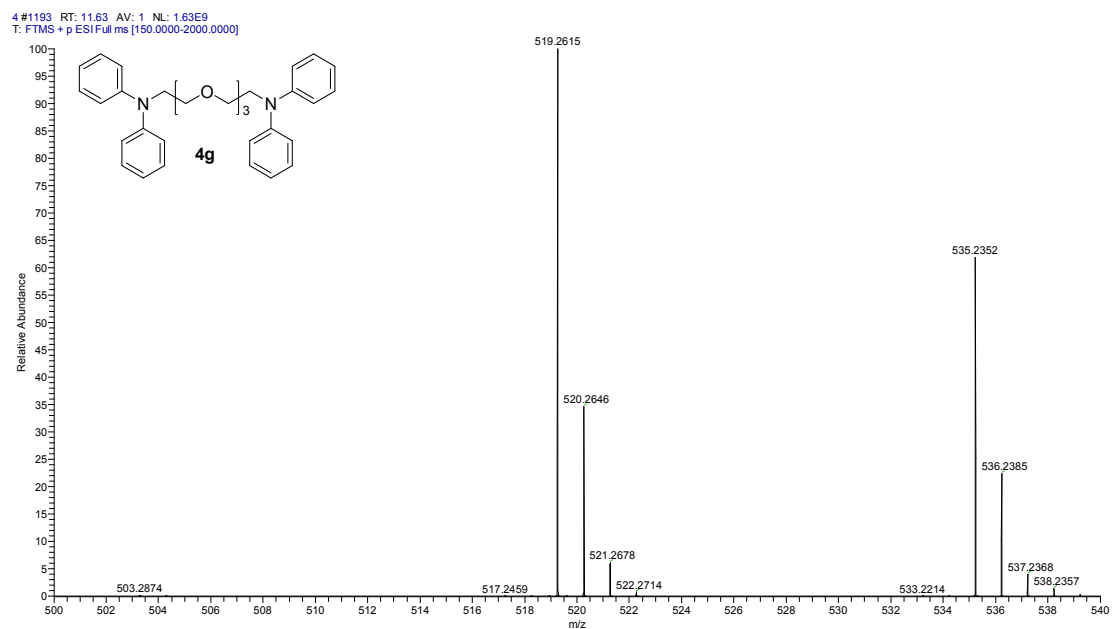
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## <sup>13</sup>C NMR of compound **4g**

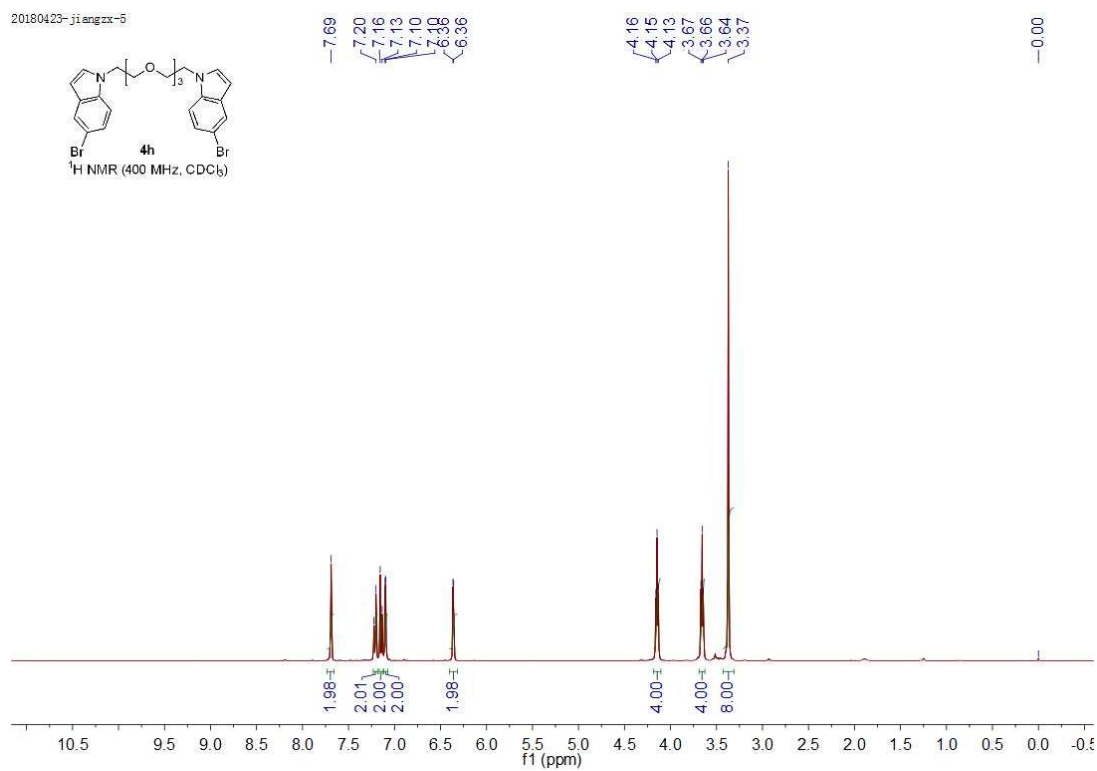


## HRMS of compound **4g**



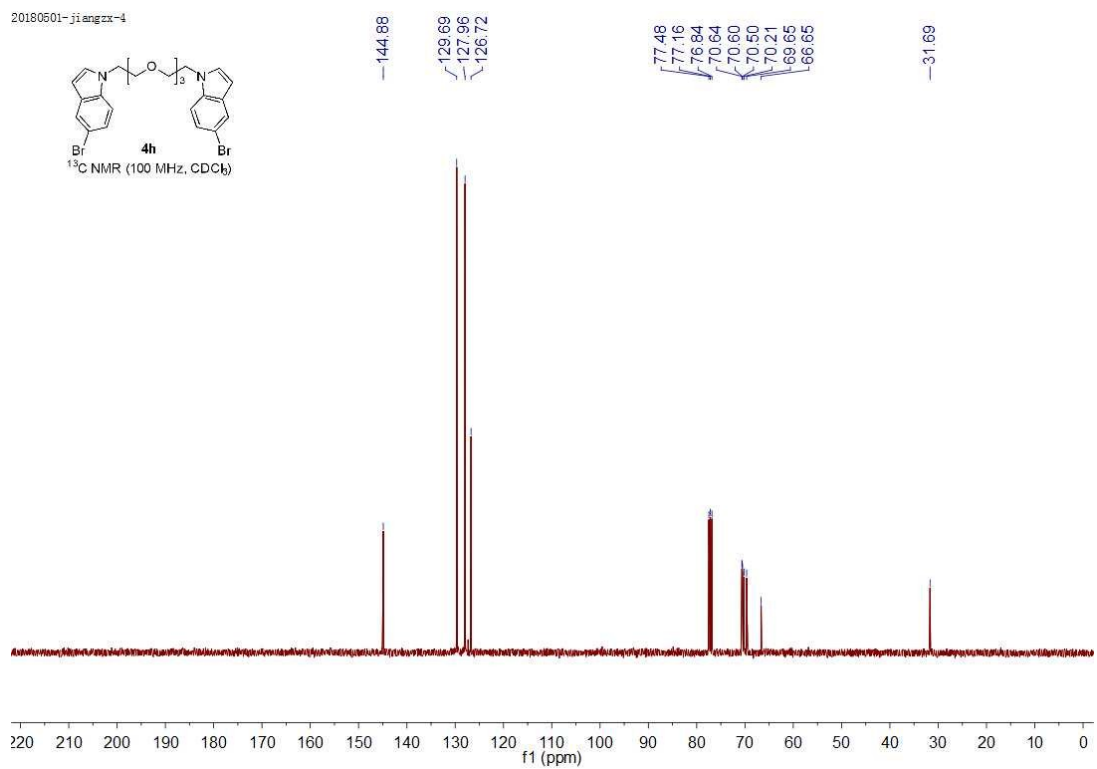
# <sup>1</sup>H NMR of compound **4h**

20180423-jiangzx-5

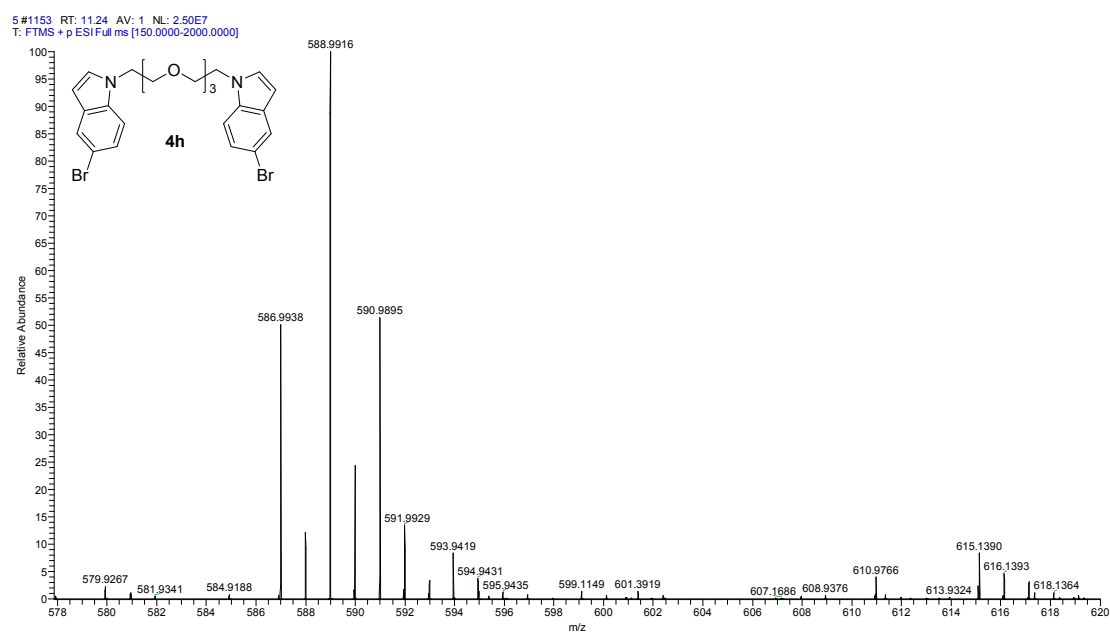


# <sup>13</sup>C NMR of compound **4h**

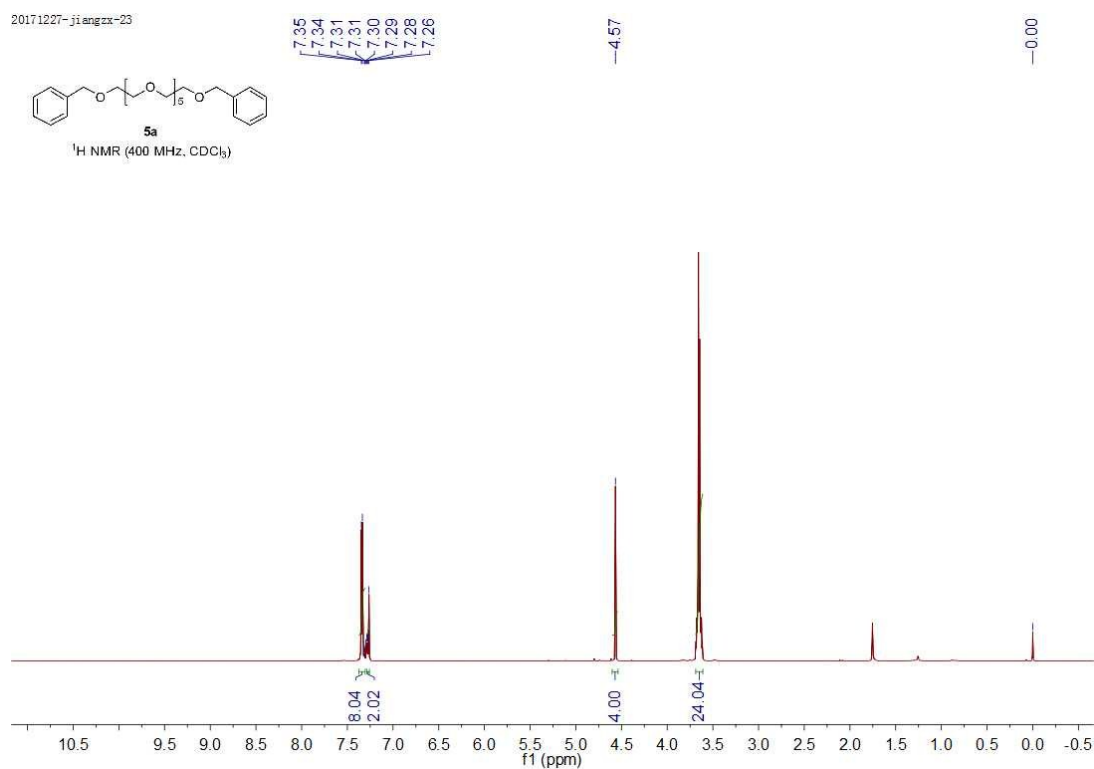
20180501-jiangzx-4



## HRMS of compound **4h**

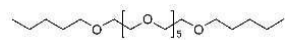


## $^1\text{H}$ NMR of compound **5a**

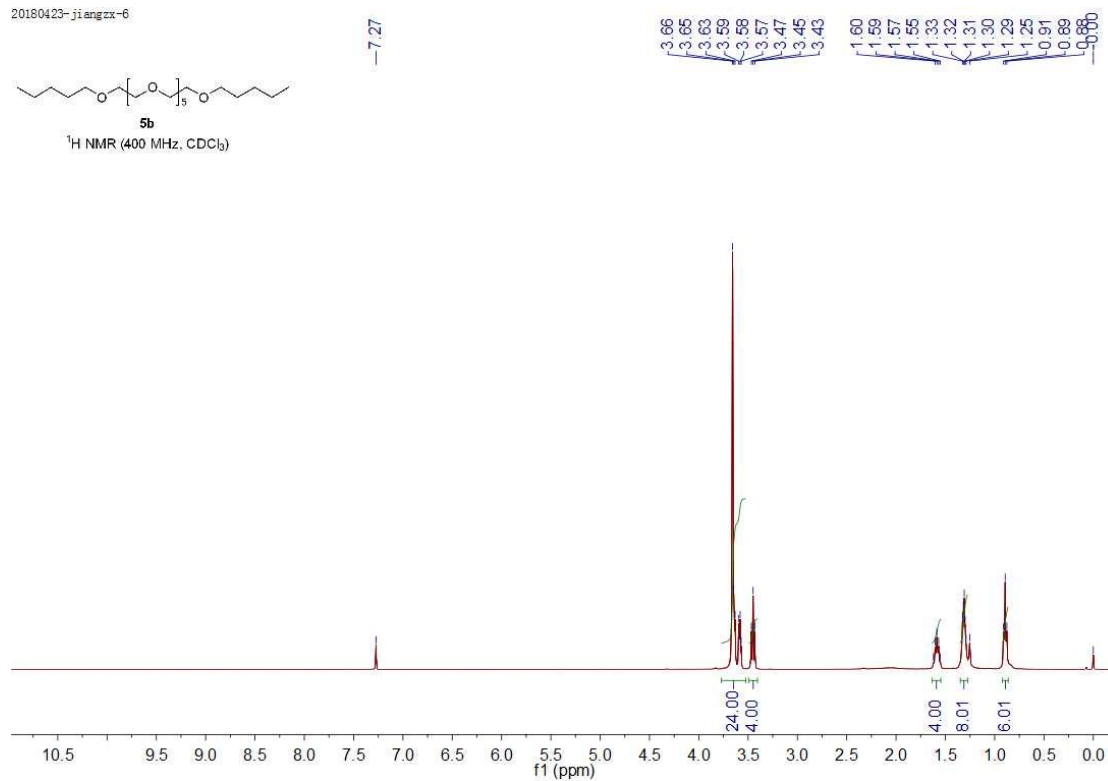


# <sup>1</sup>H NMR of compound **5b**

20180423-jiangzx-6

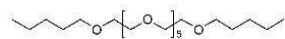


**5b**  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

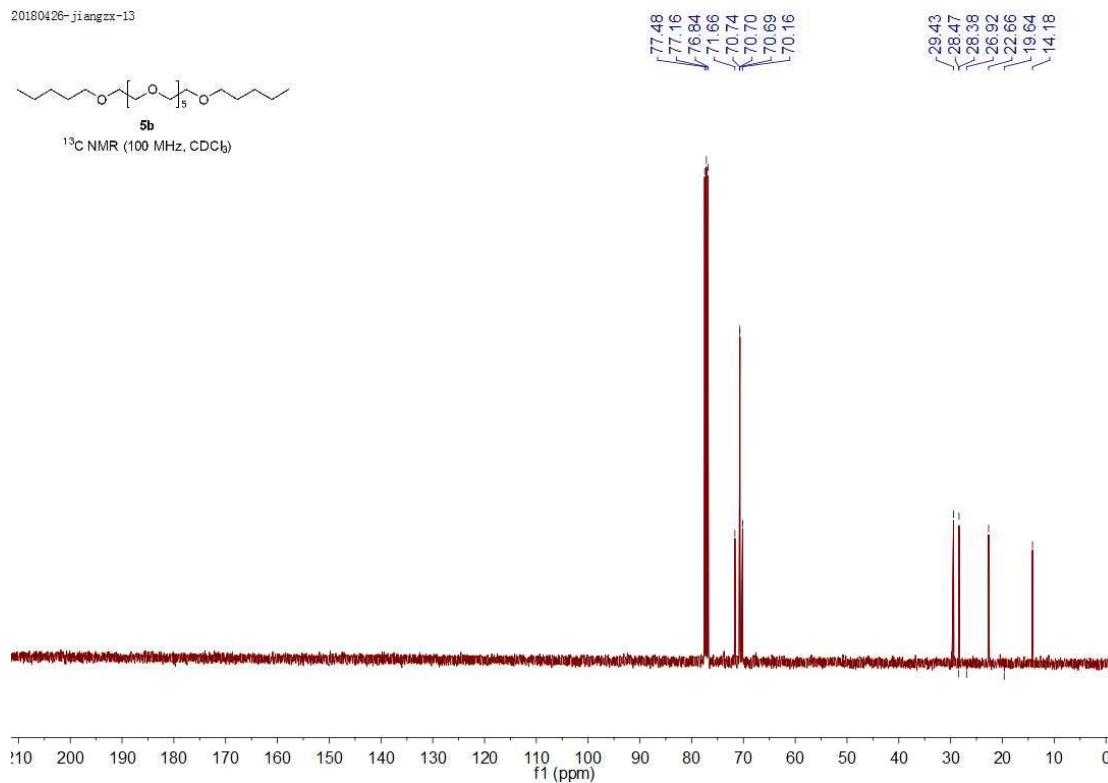


# <sup>13</sup>C NMR of compound **5b**

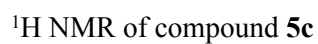
20180426-jiangzx-13



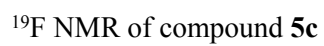
**5b**  
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



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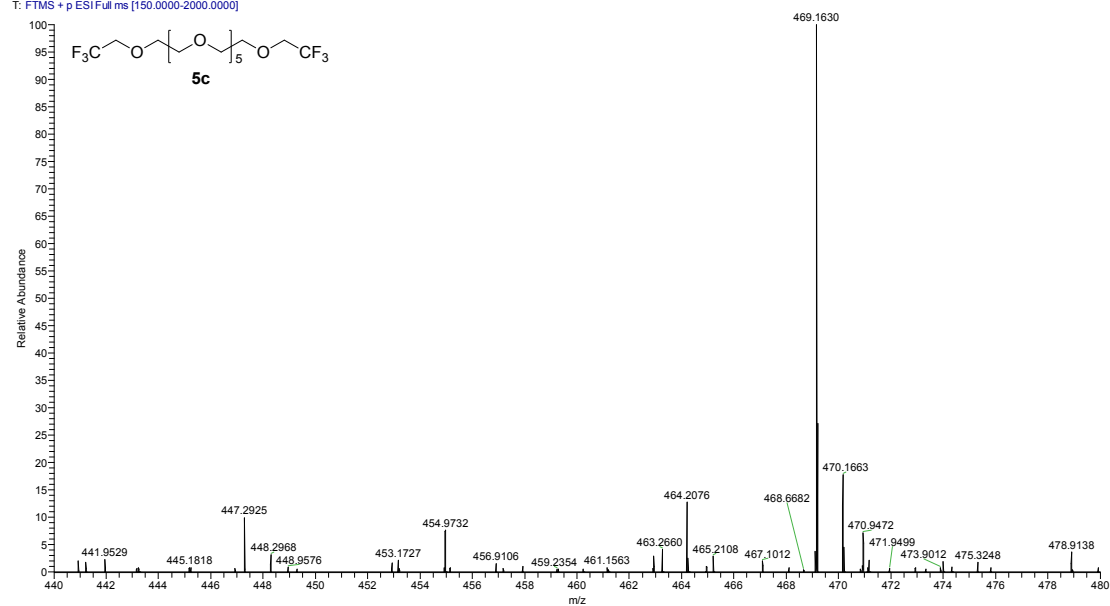


## 20180511-jiangzx-1



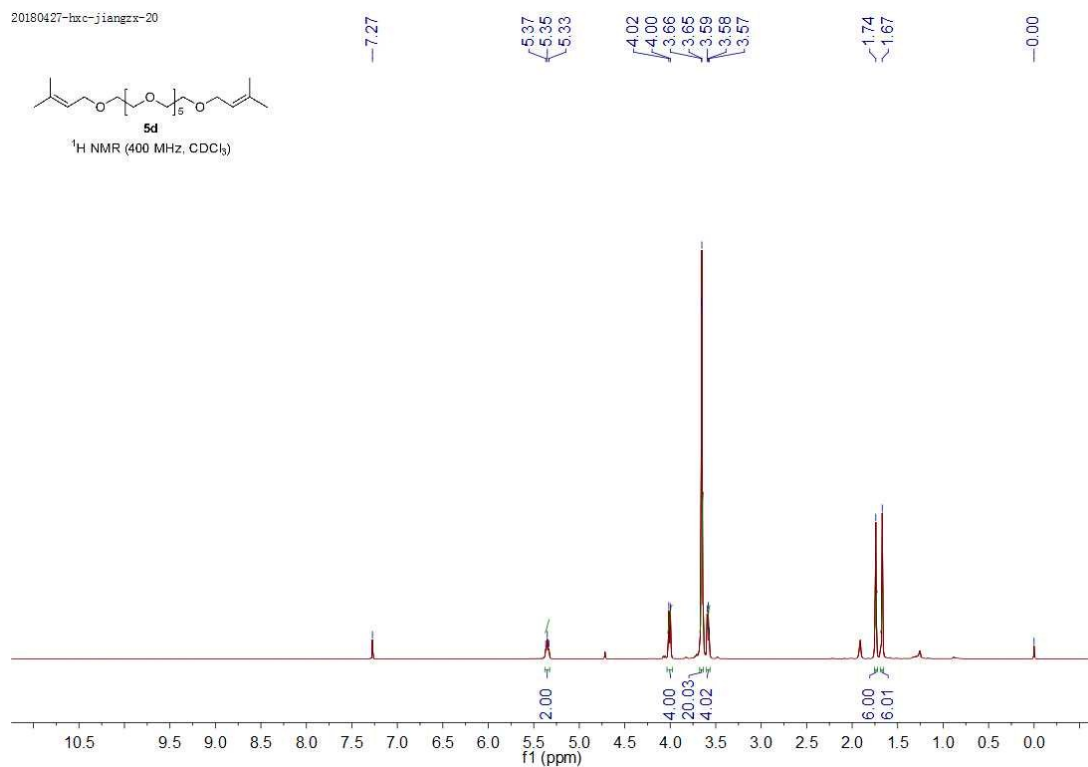
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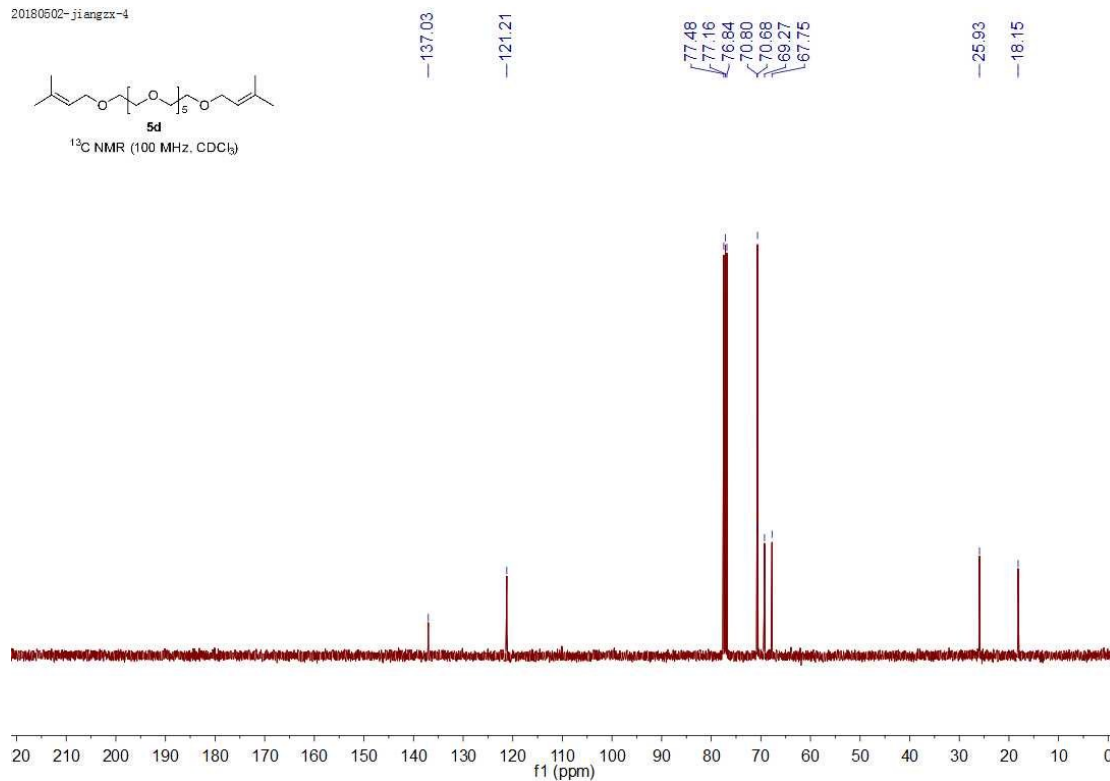
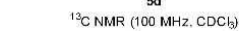


## <sup>1</sup>H NMR of compound **5d**

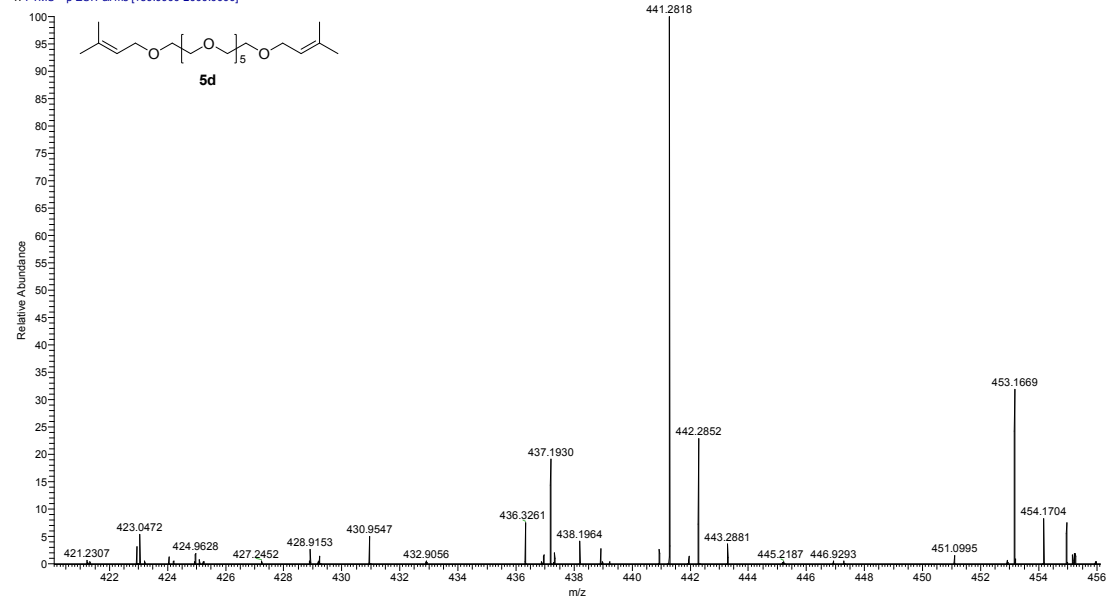
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20180502-jiangzx-4

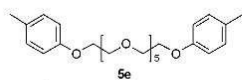


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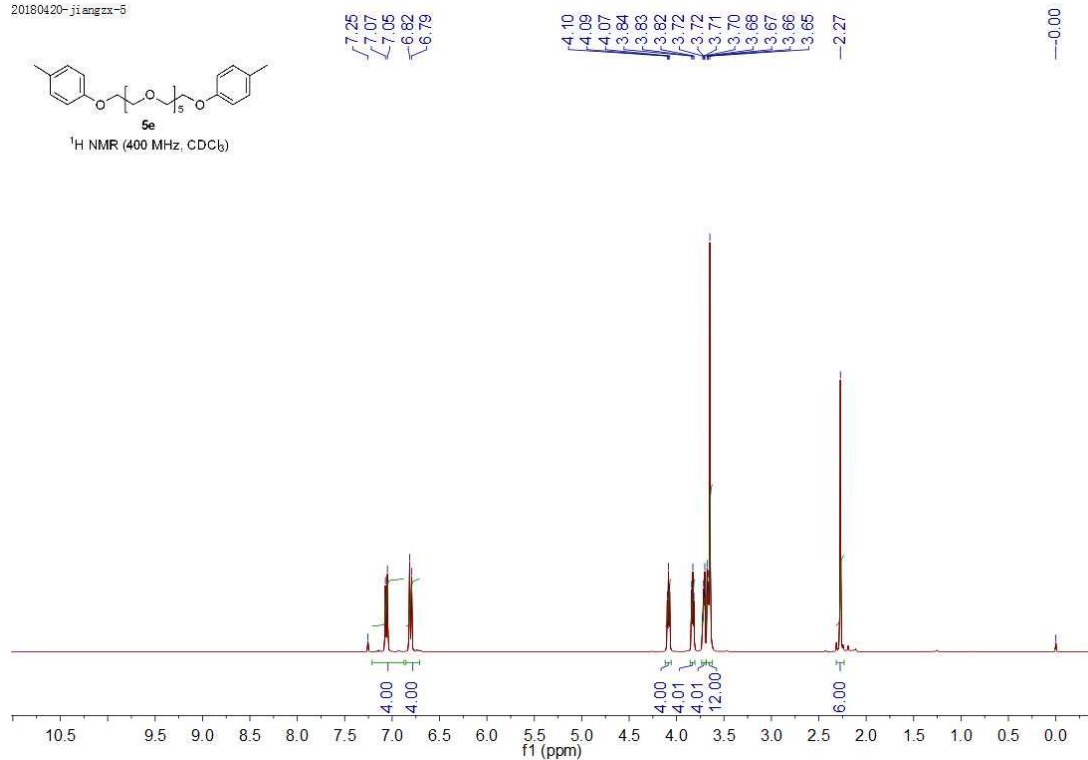


# <sup>1</sup>H NMR of compound **5e**

20180420-jiangzx-5

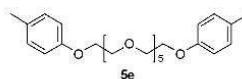


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

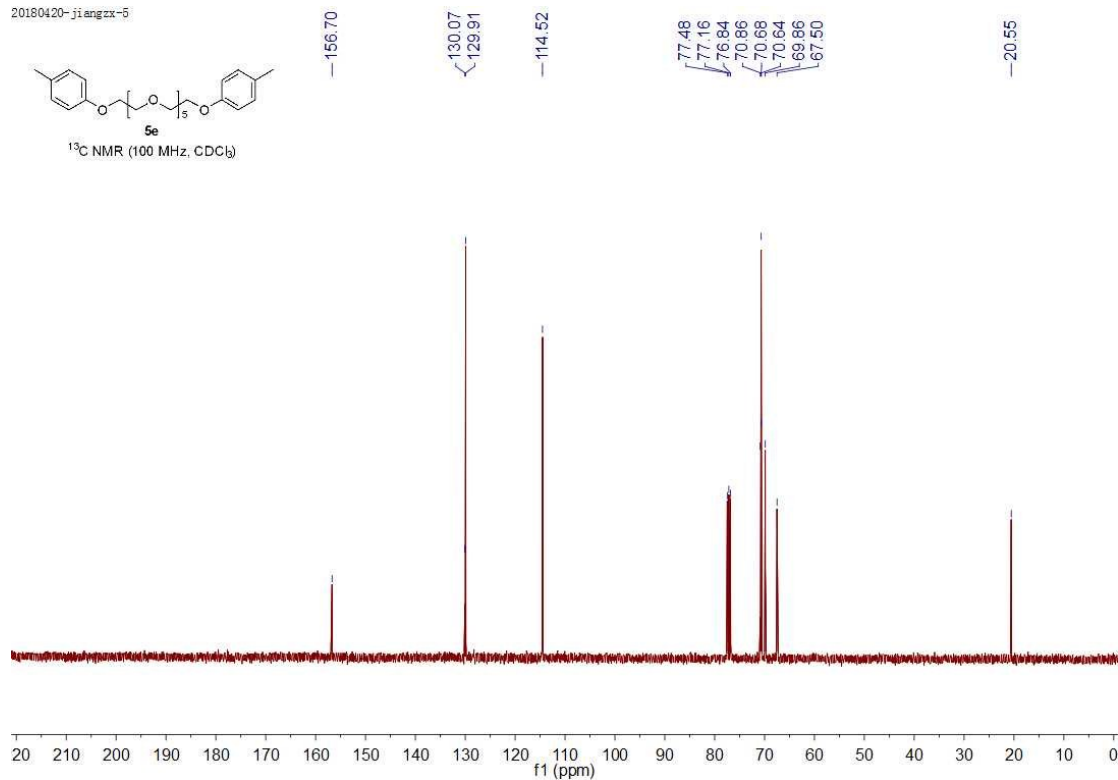


## <sup>13</sup>C NMR of compound **5e**

20180420-jiangzx-5

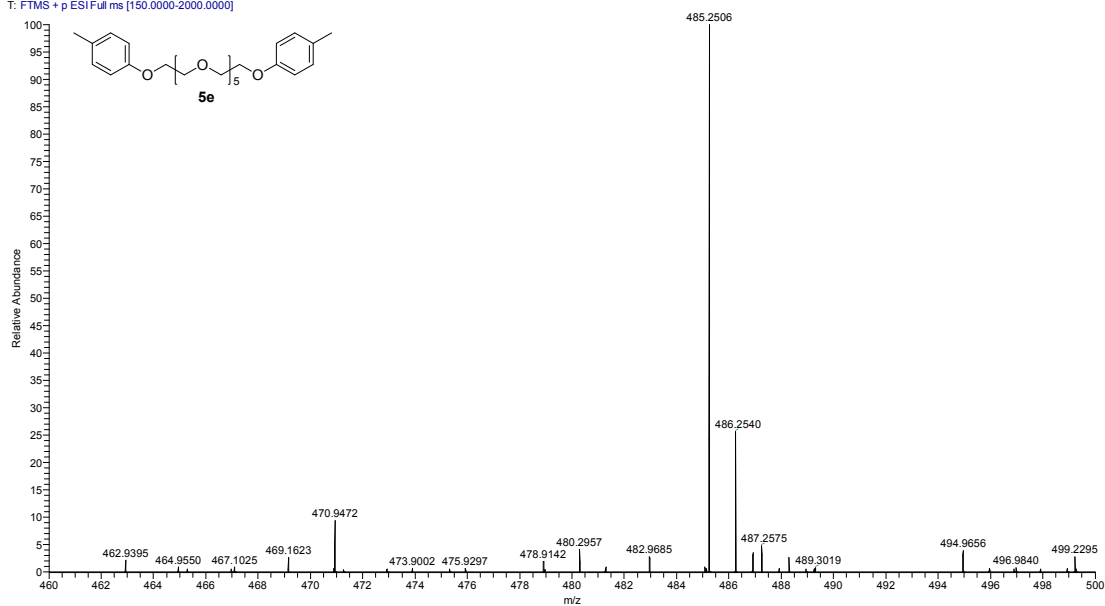


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



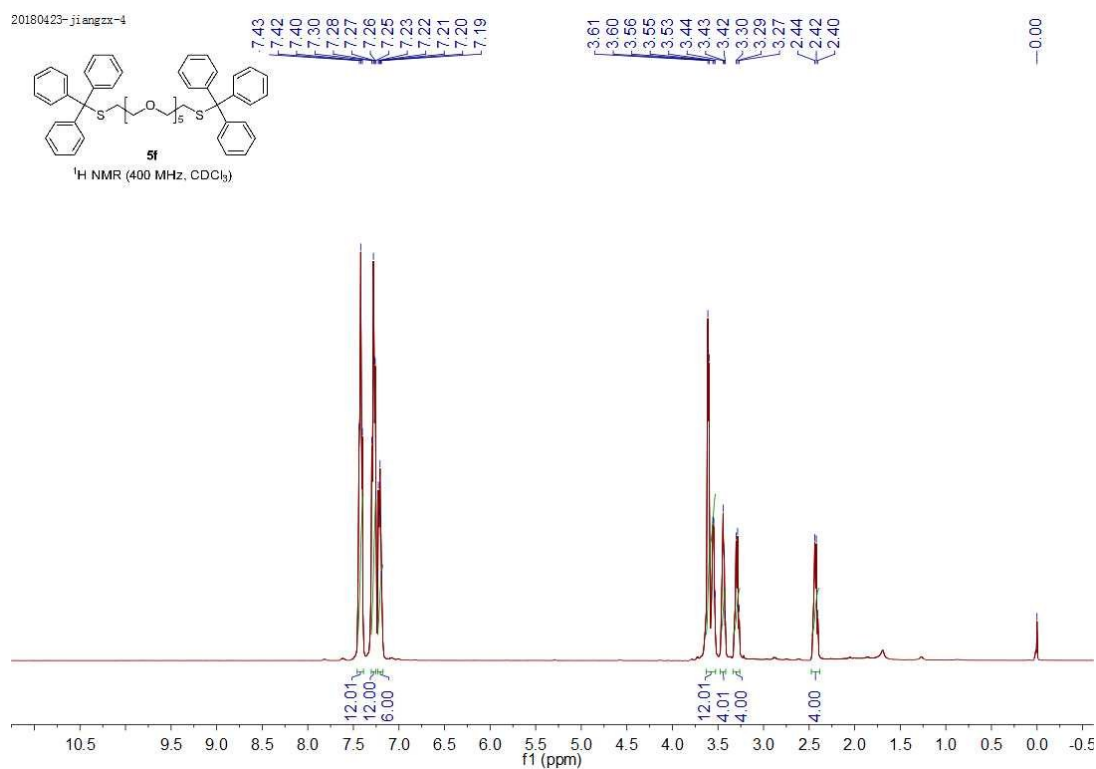
## HRMS of compound **5e**

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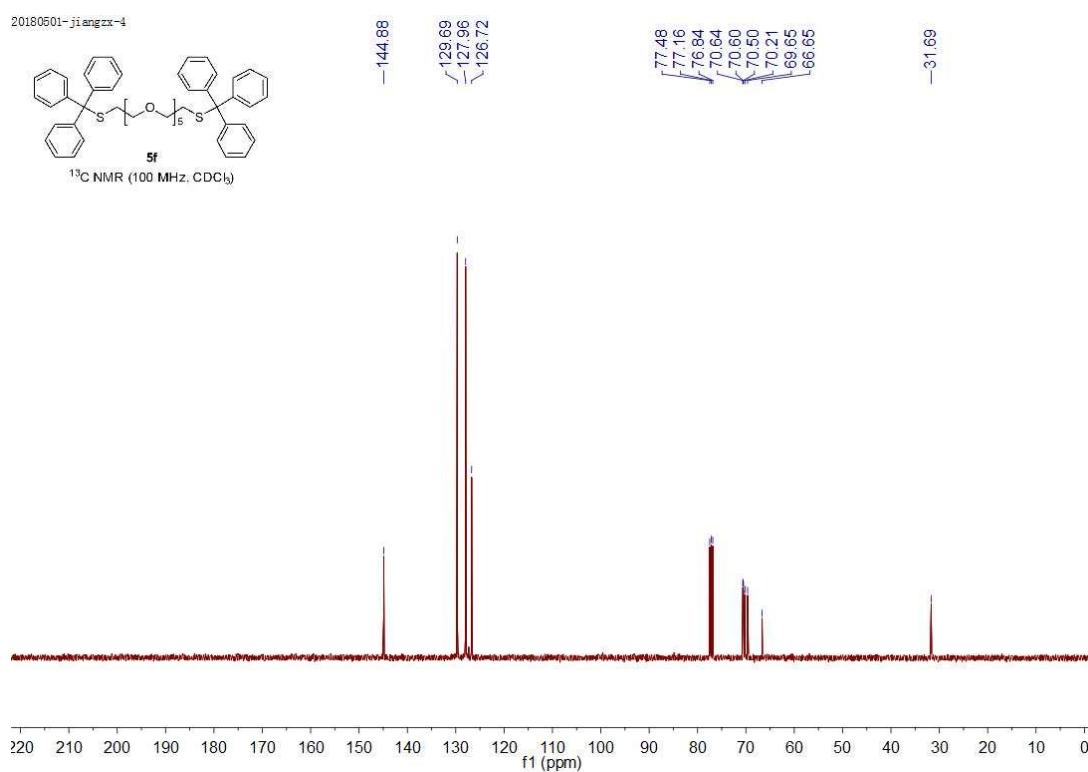
## <sup>1</sup>H NMR of compound **5f**

20180423-jj angex-4



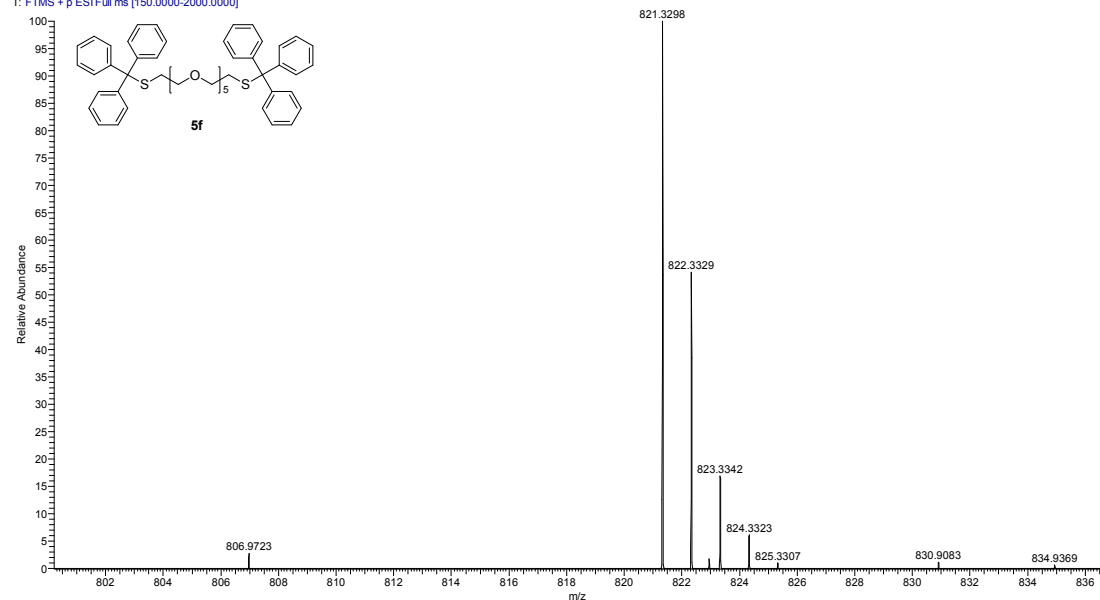
## <sup>13</sup>C NMR of compound **5f**

20180501-jiangzx-4

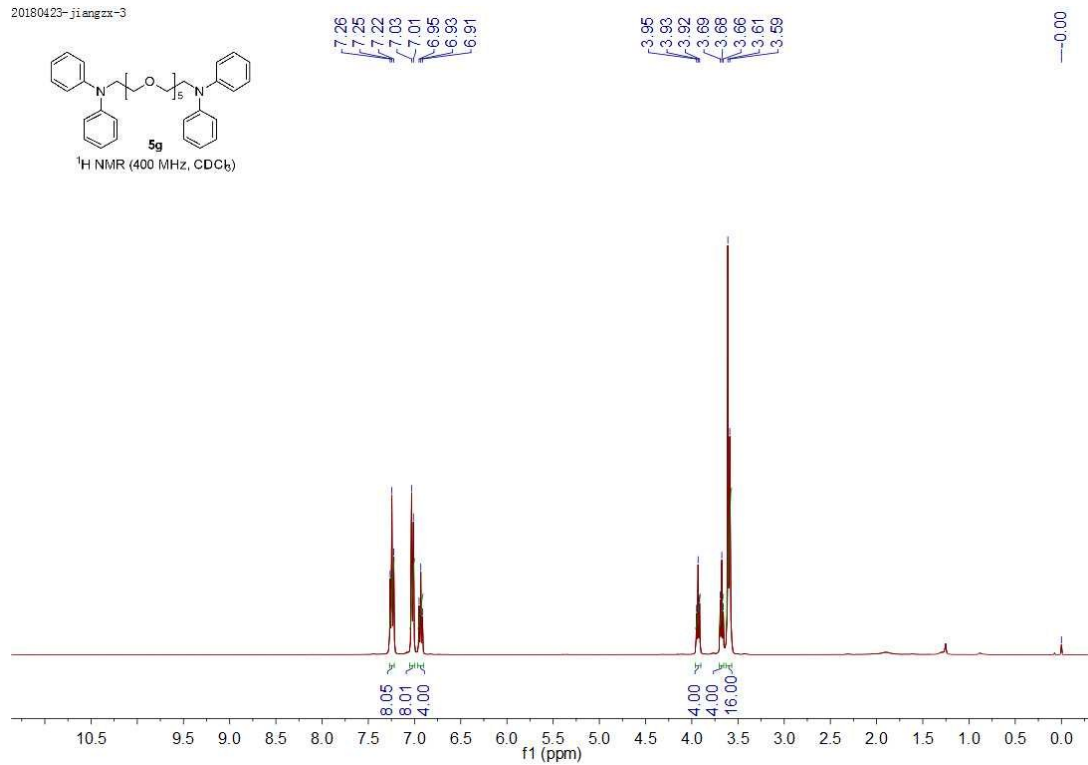


## HRMS of compound **5f**

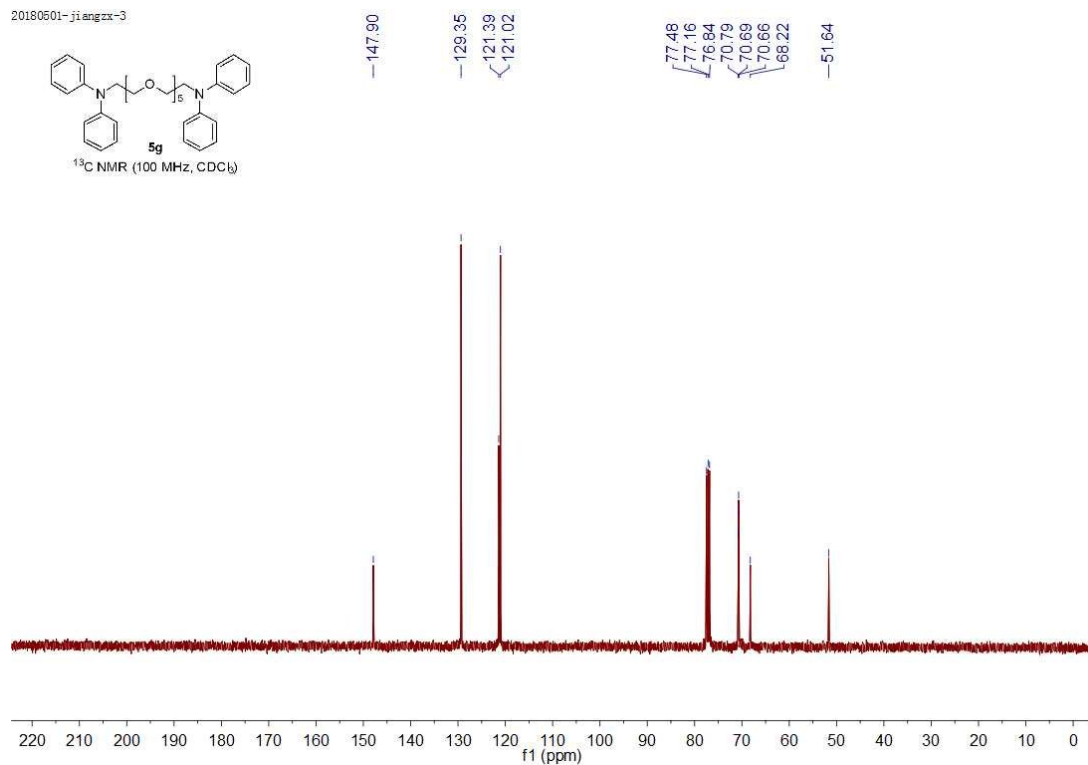
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## 20180423-jiangzx-3

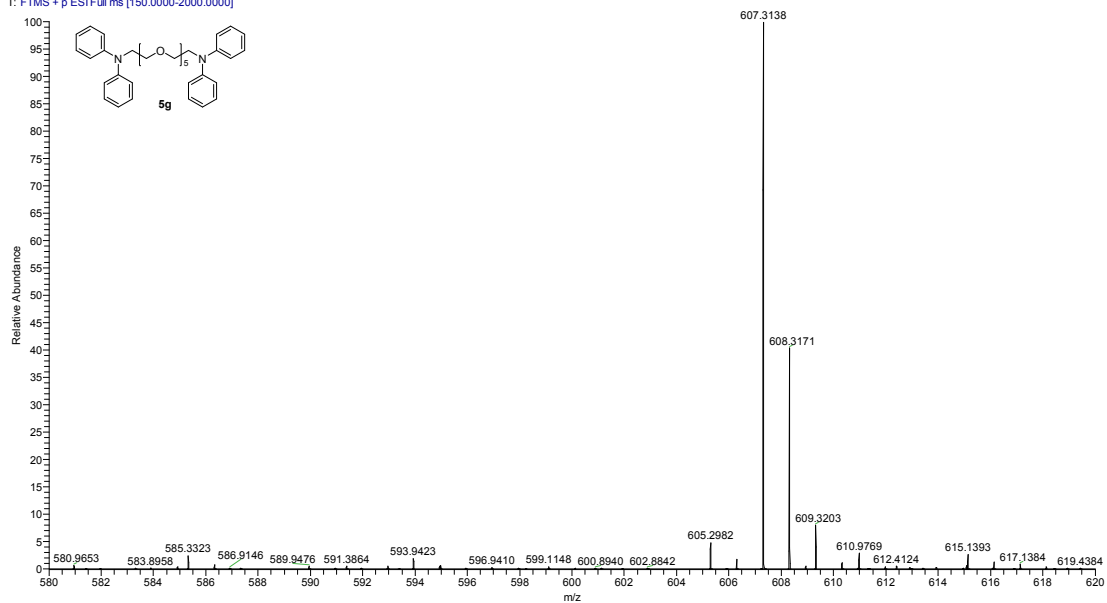


20180501-jiangzx-3



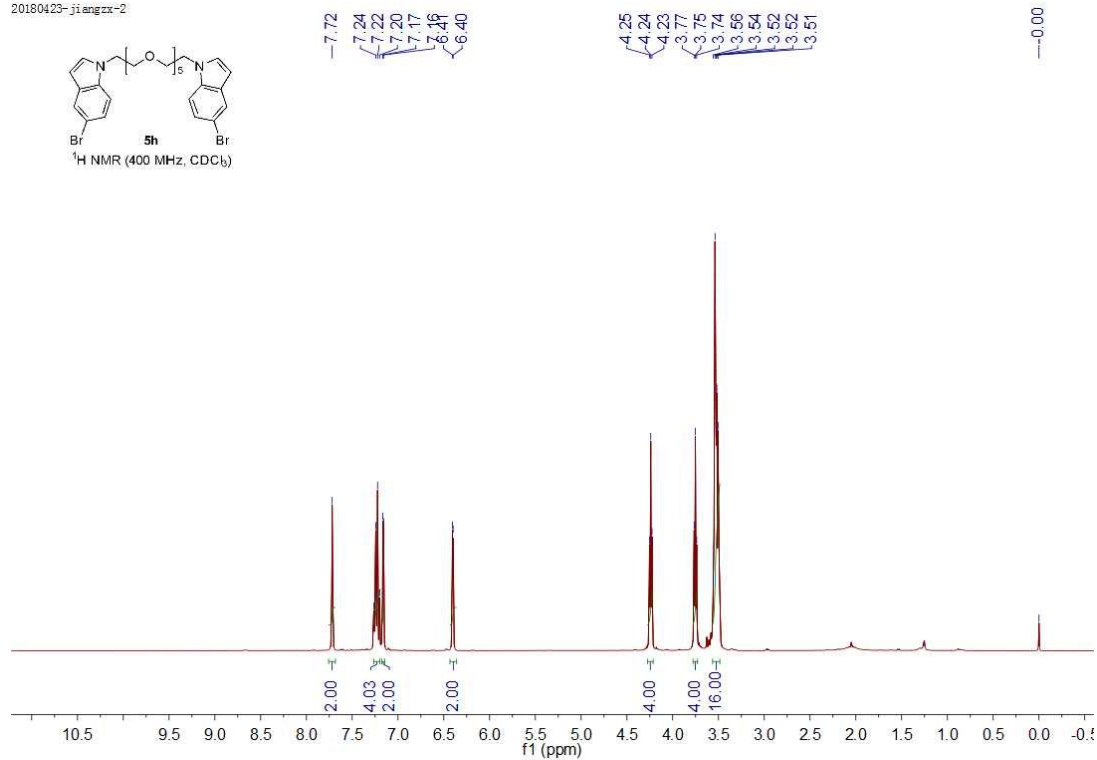
## HRMS of compound **5g**

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## <sup>1</sup>H NMR of compound **5h**

20180423-jiangsx-2

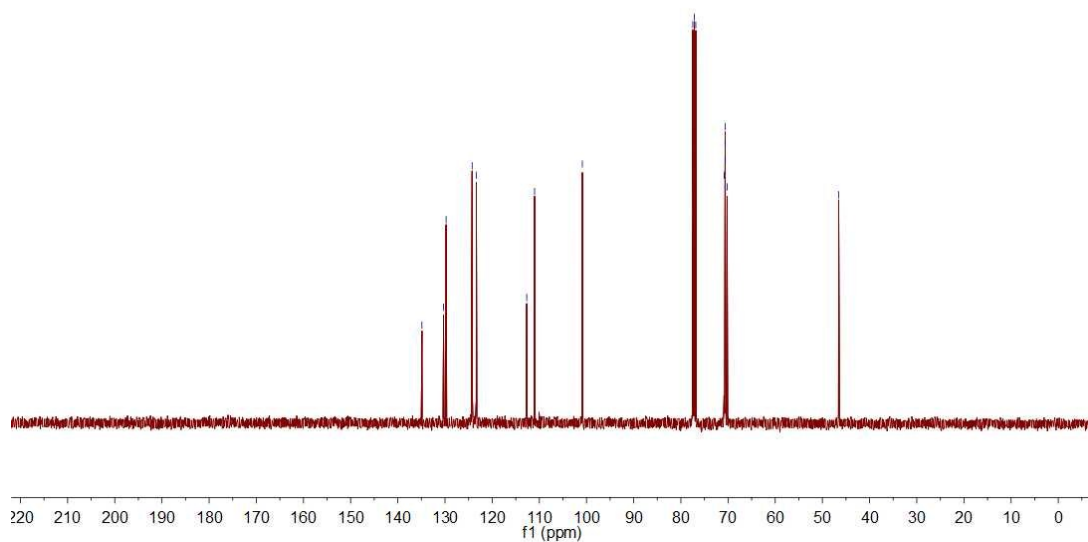


## <sup>13</sup>C NMR of compound **5h**

20180501-jiangzx-2

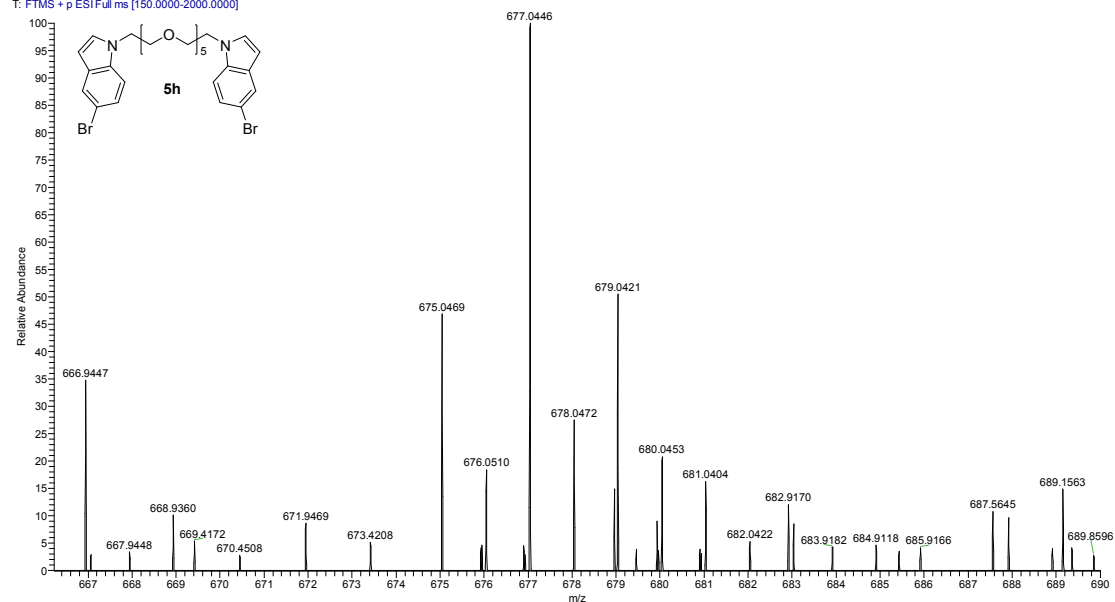


134.89, 130.31, 129.77, 124.25, 123.36, 112.88, 111.01, 100.88, 77.48, 77.16, 76.84, 70.82, 70.63, 70.61, 70.57, 70.20, 46.54

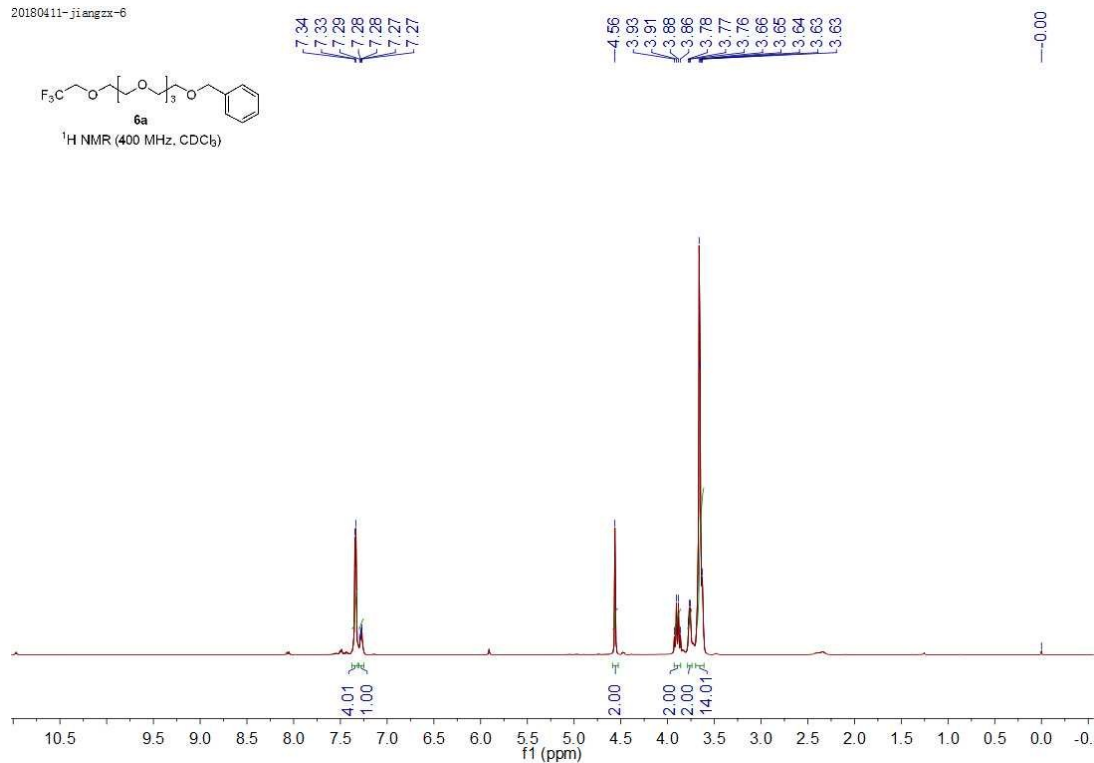
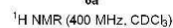


## HRMS of compound **5h**

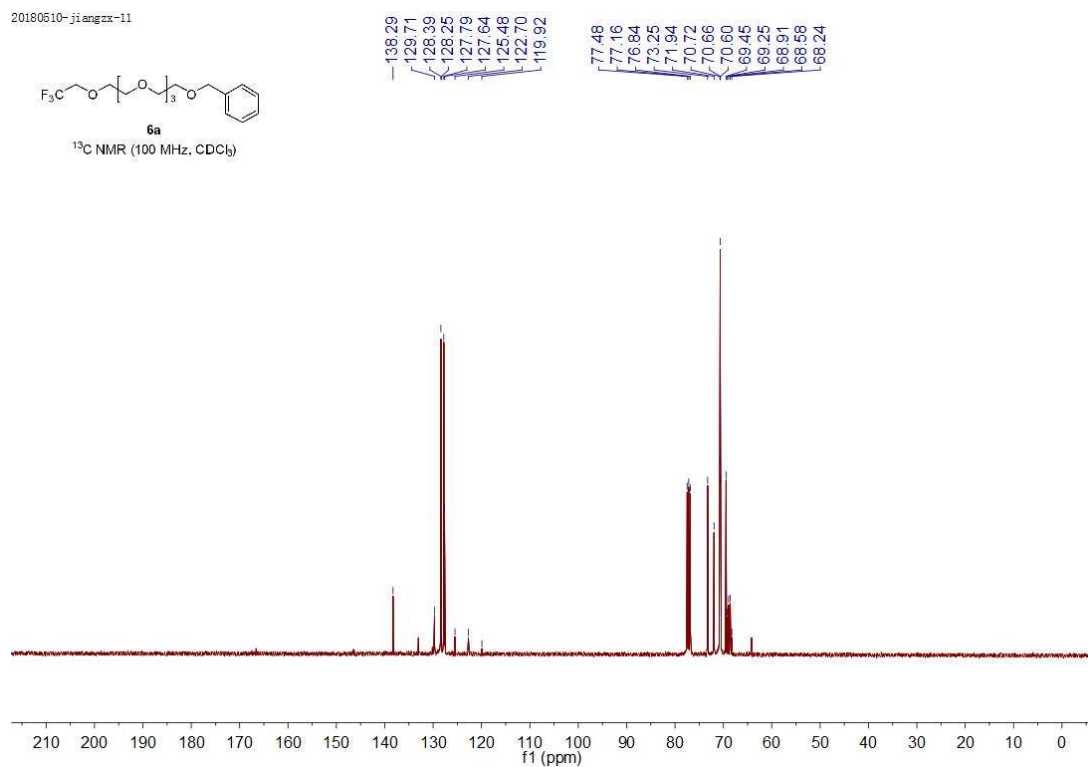
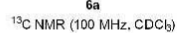
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20180411-jiangzx-6

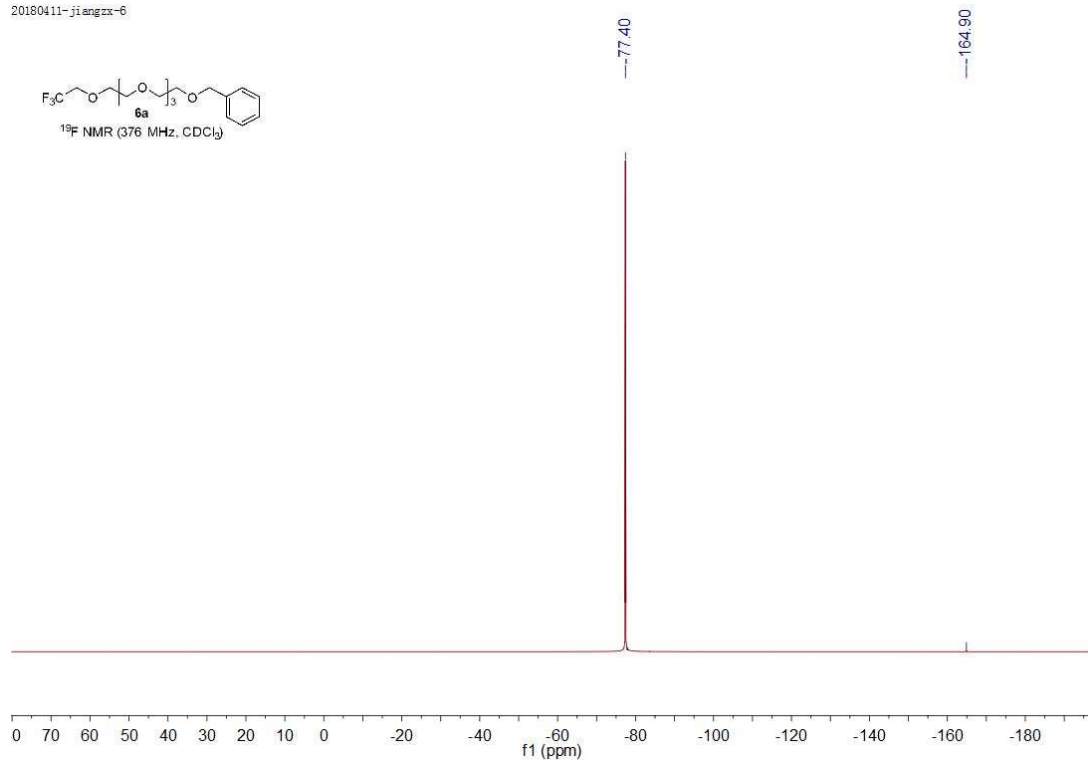


20180510-jiangzx-11



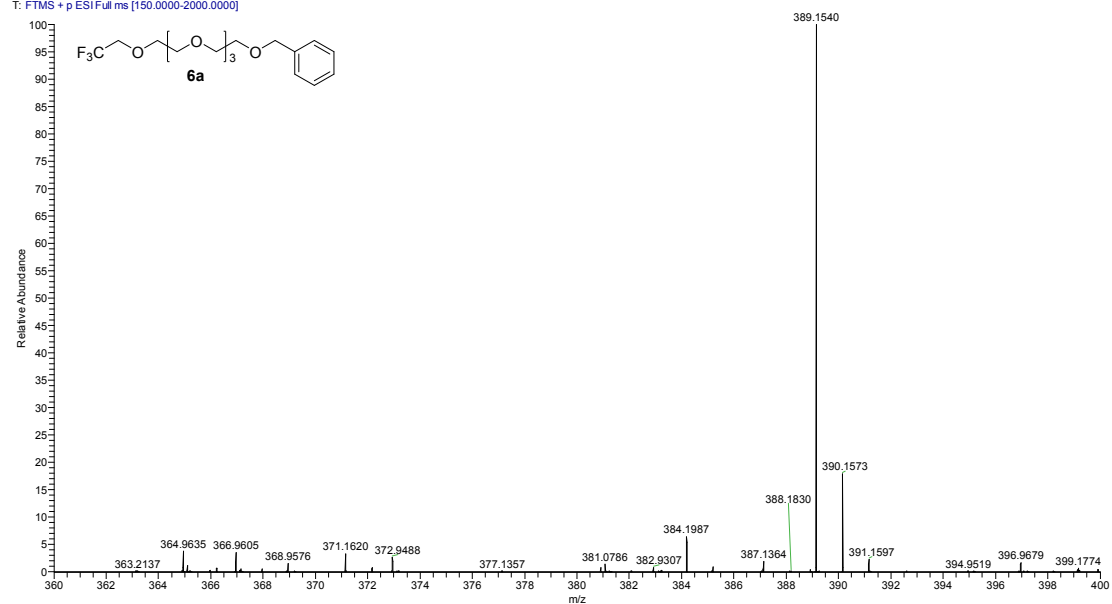
## $^{19}\text{F}$ NMR of compound **6a**

20180411-jiangzx-6



## HRMS of compound **6a**

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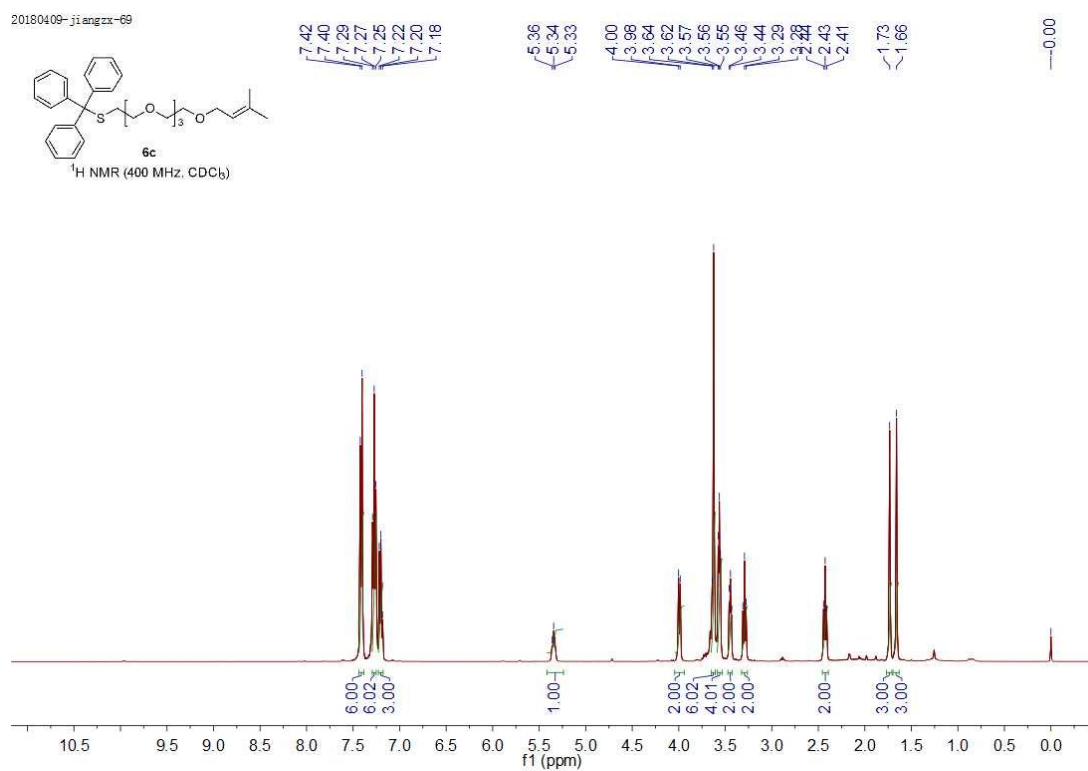
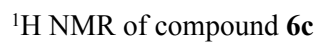
20180115-jiangzx-20



20180510-jiangzx-12

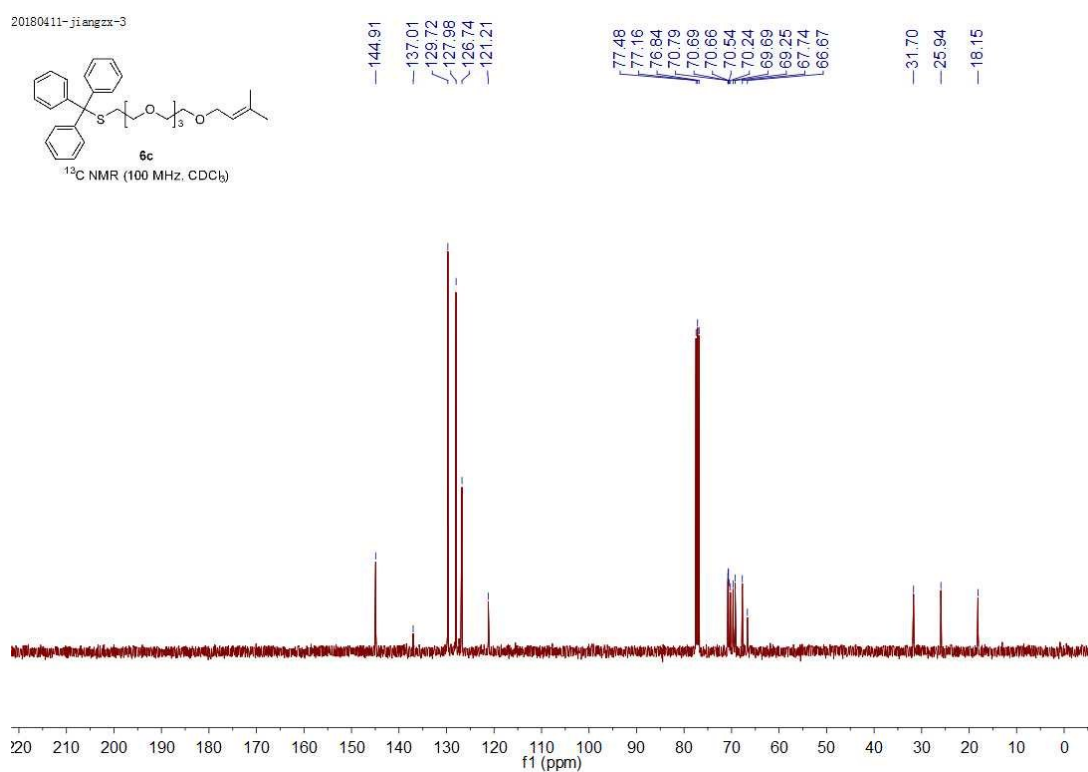


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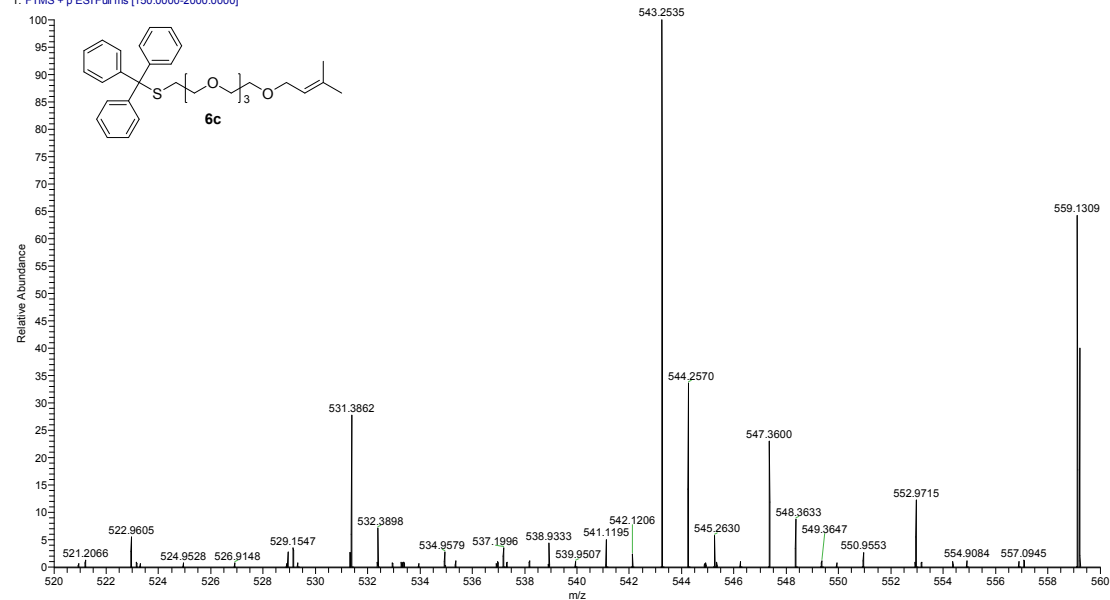
## <sup>13</sup>C NMR of compound **6c**

20180411-jiangzx-3

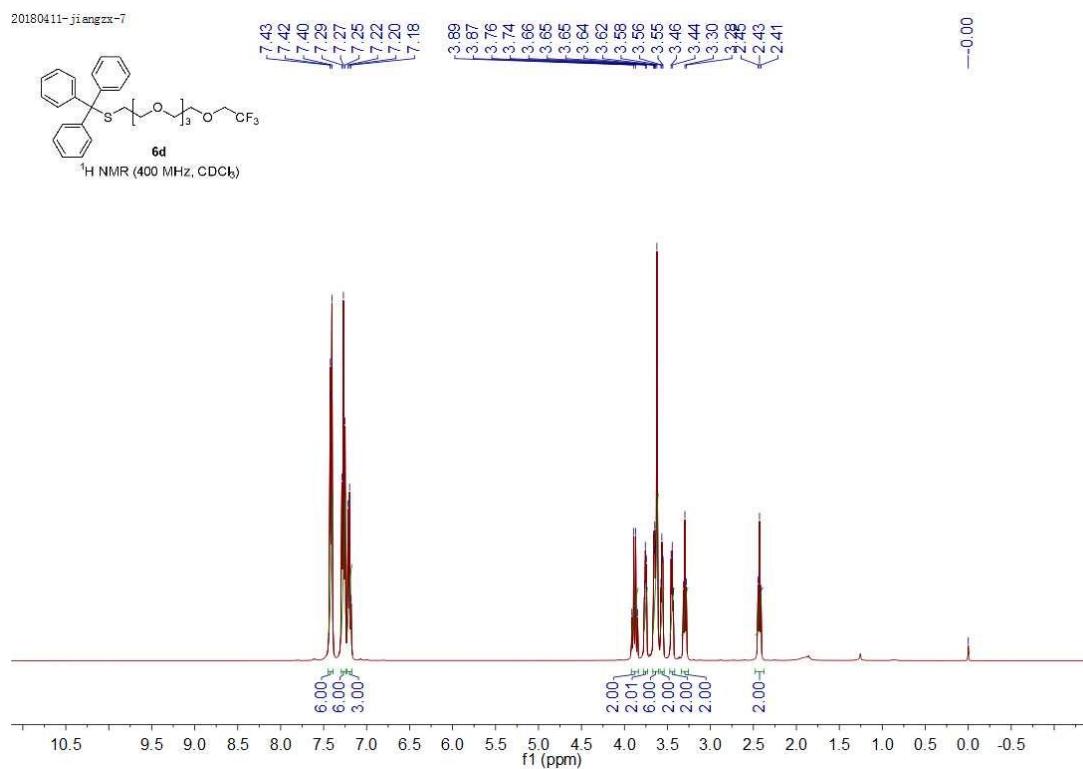


## HRMS of compound **6c**

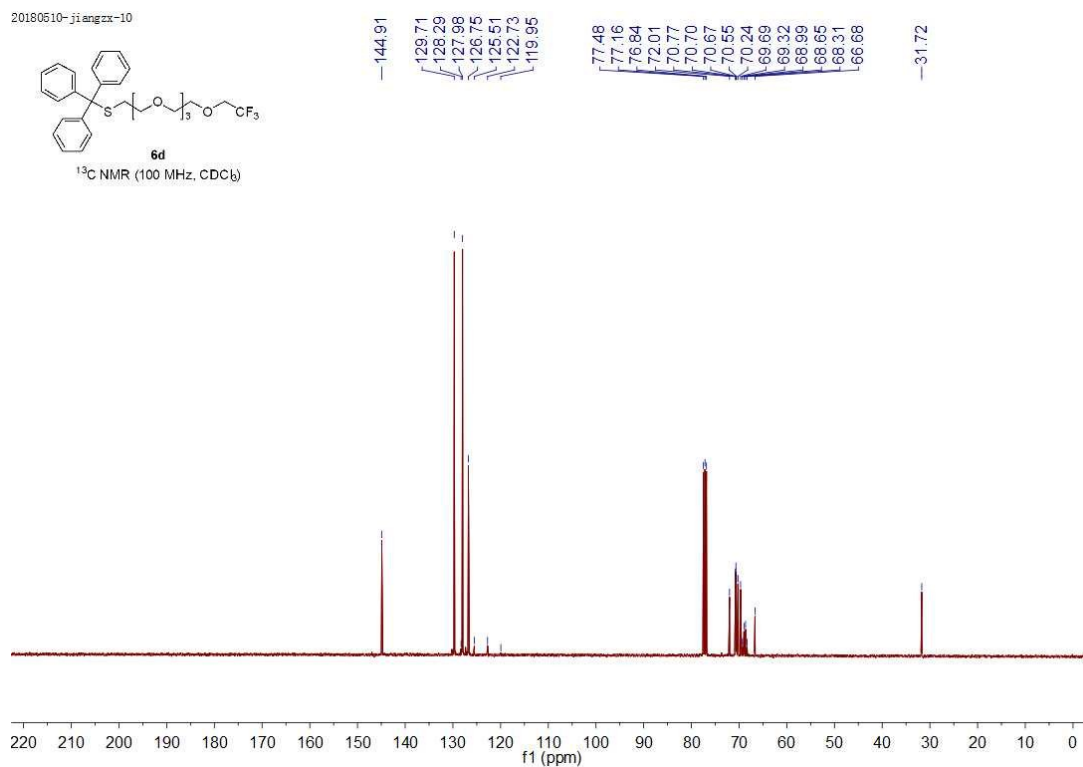
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# <sup>1</sup>H NMR of compound **6d**

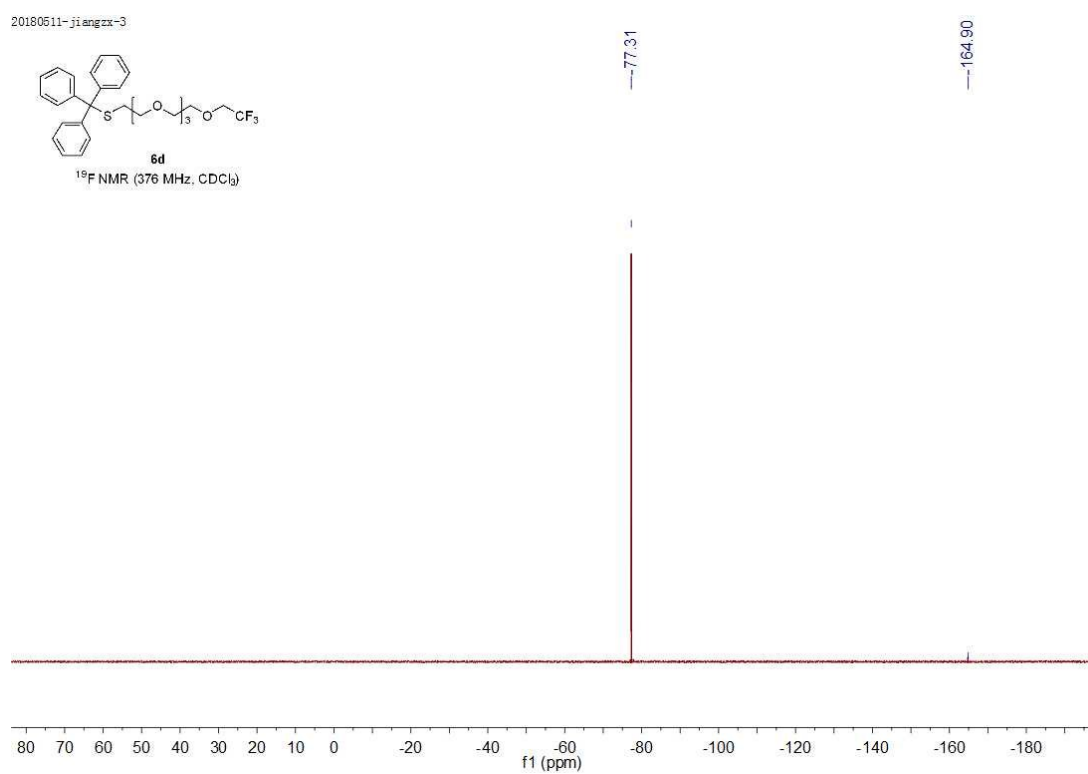


# <sup>13</sup>C NMR of compound **6d**



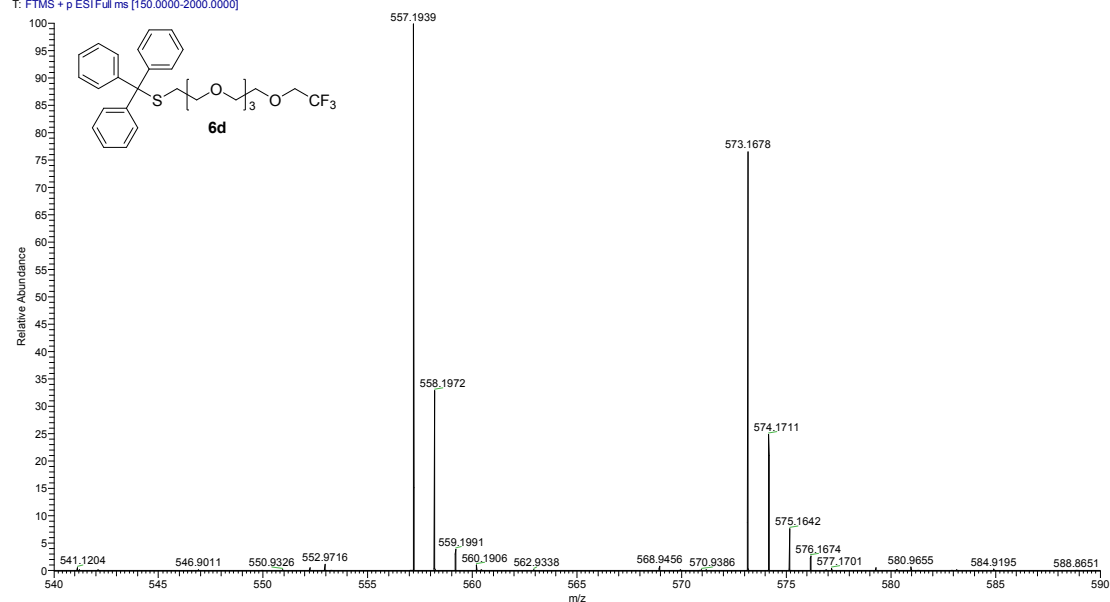
## $^{19}\text{F}$ NMR of compound **6d**

20180511-jiangzx-3

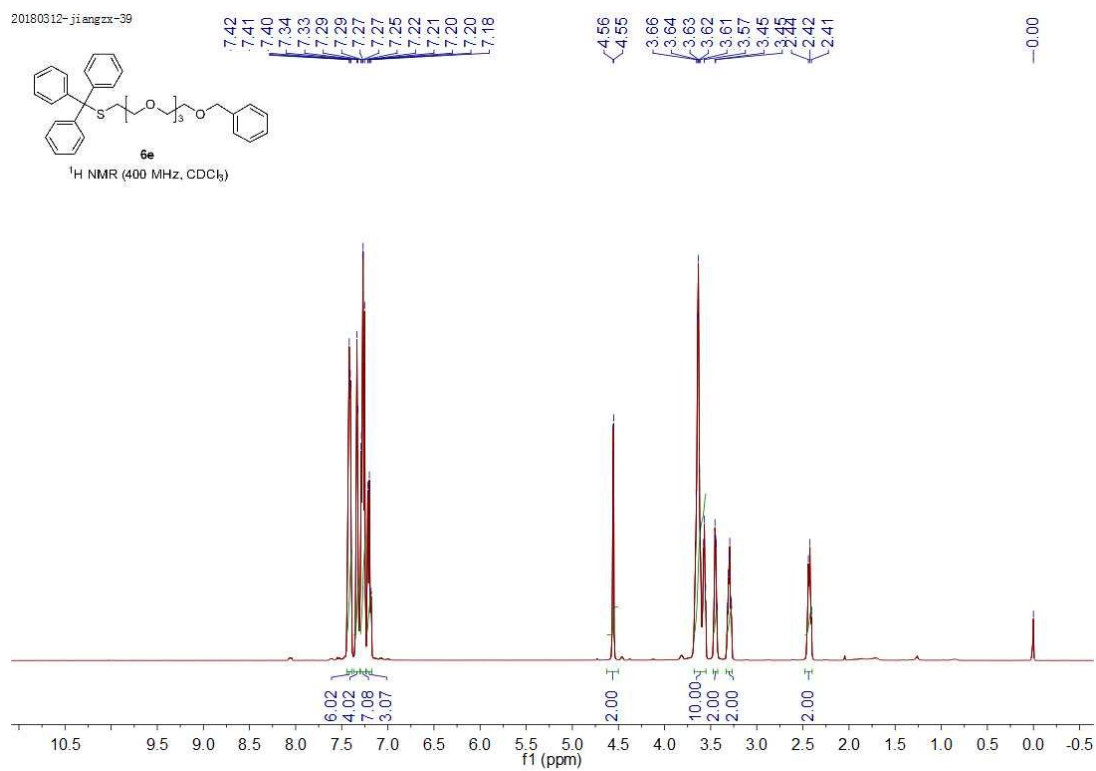


## HRMS of compound **6d**

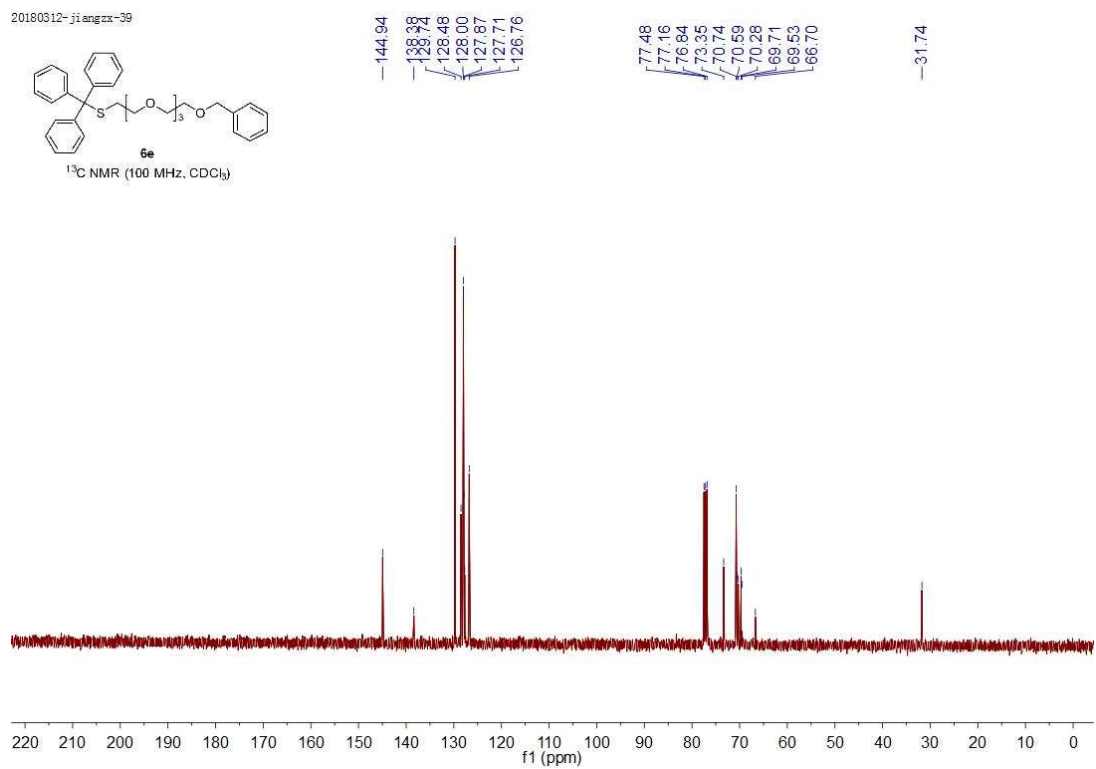
38 #1135 RT: 11.08 AV: 1 NL: 4.92E7  
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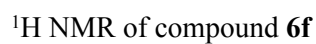
# <sup>1</sup>H NMR of compound **6e**



# <sup>13</sup>C NMR of compound **6e**

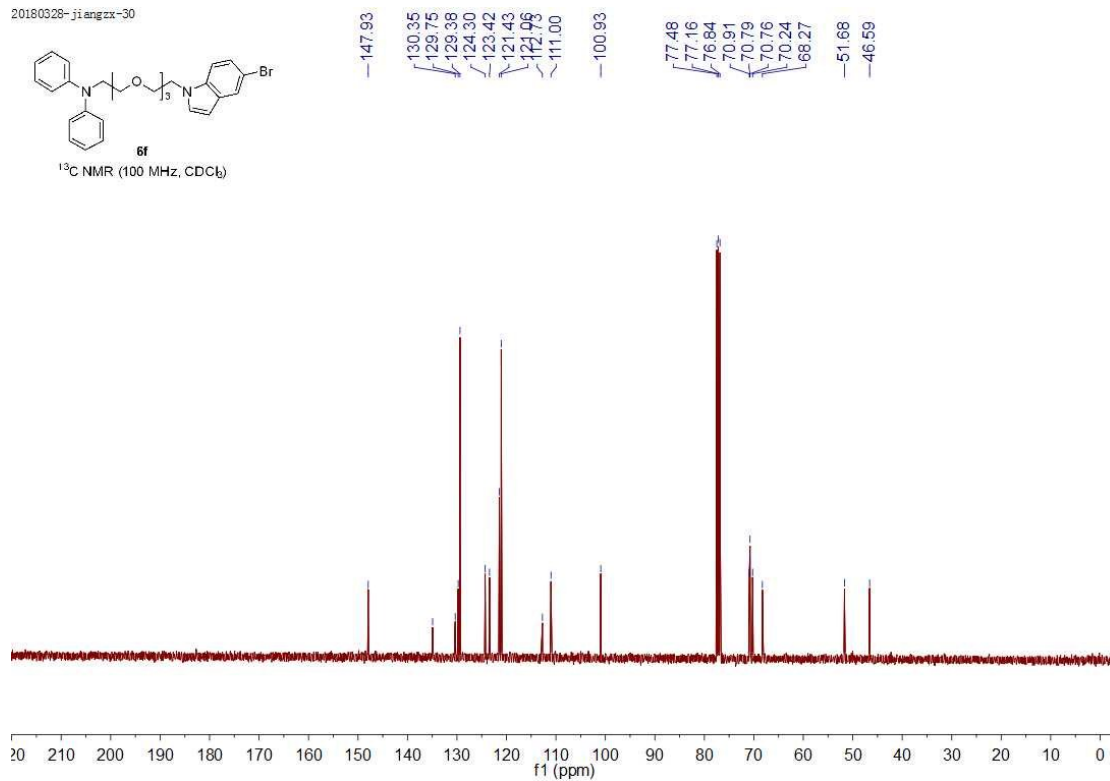


39 #1177 RT: 11.48 AV: 1 NL: 1.88E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



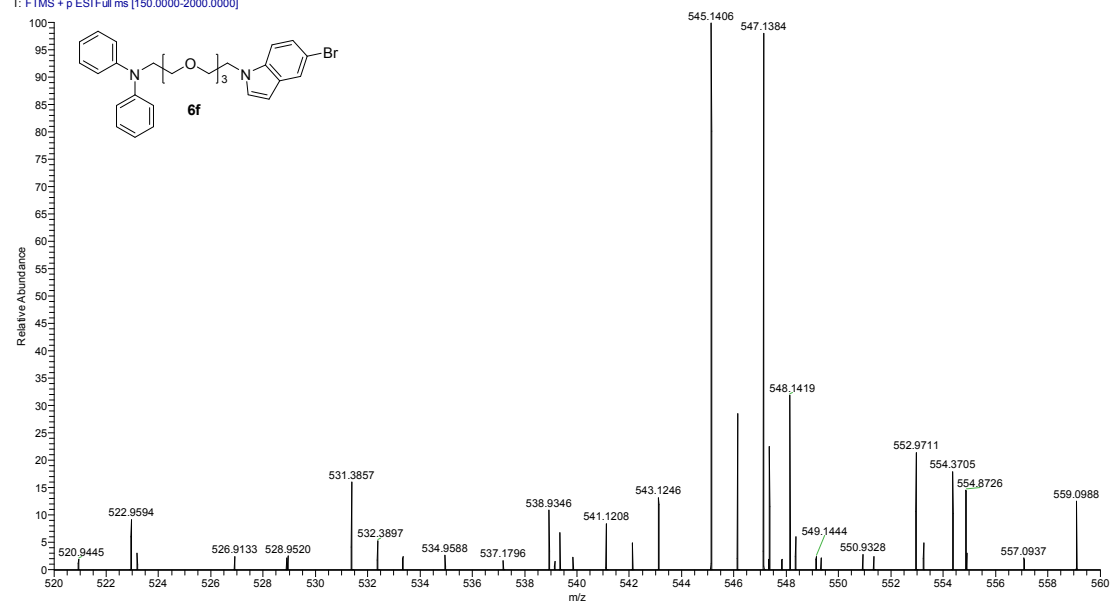
## <sup>13</sup>C NMR of compound **6f**

20180328-jiangzx-30

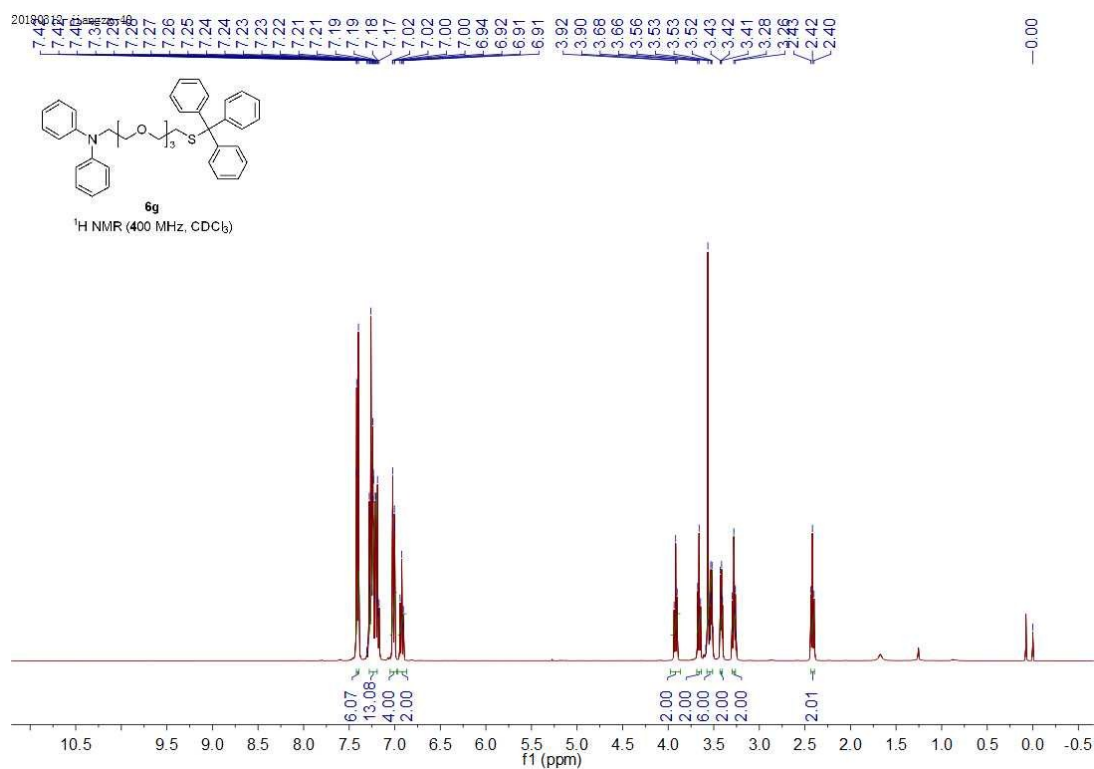


## HRMS of compound **6f**

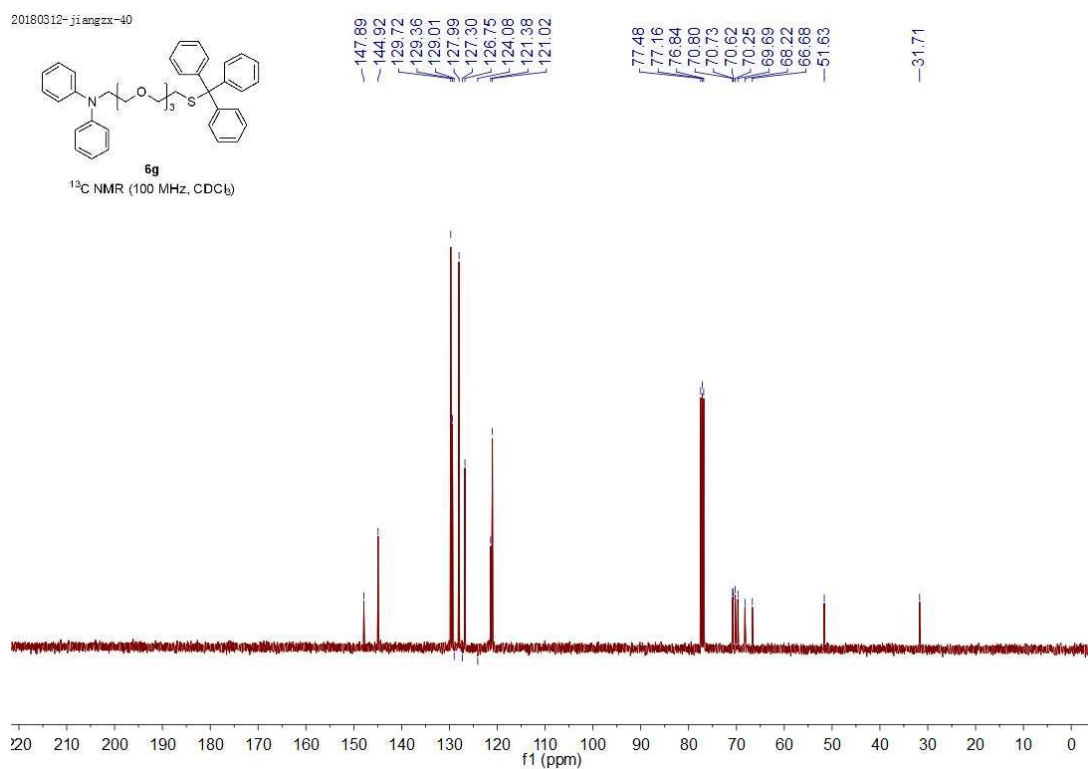
40 #1165 RT: 11.38 AV: 1 NL: 2.83E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



# <sup>1</sup>H NMR of compound **6g**

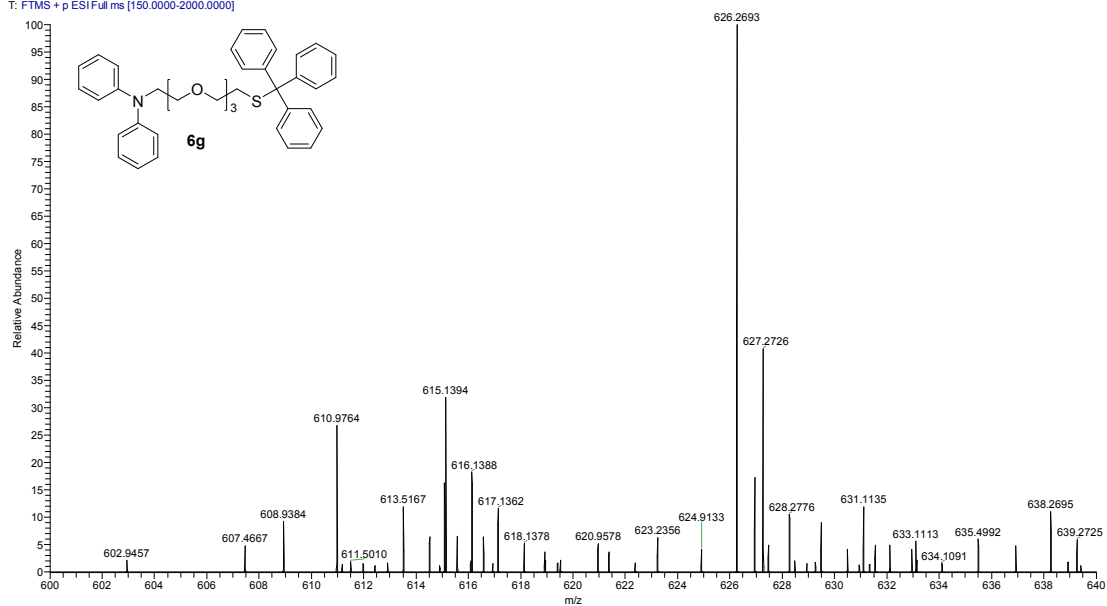


# <sup>13</sup>C NMR of compound **6g**



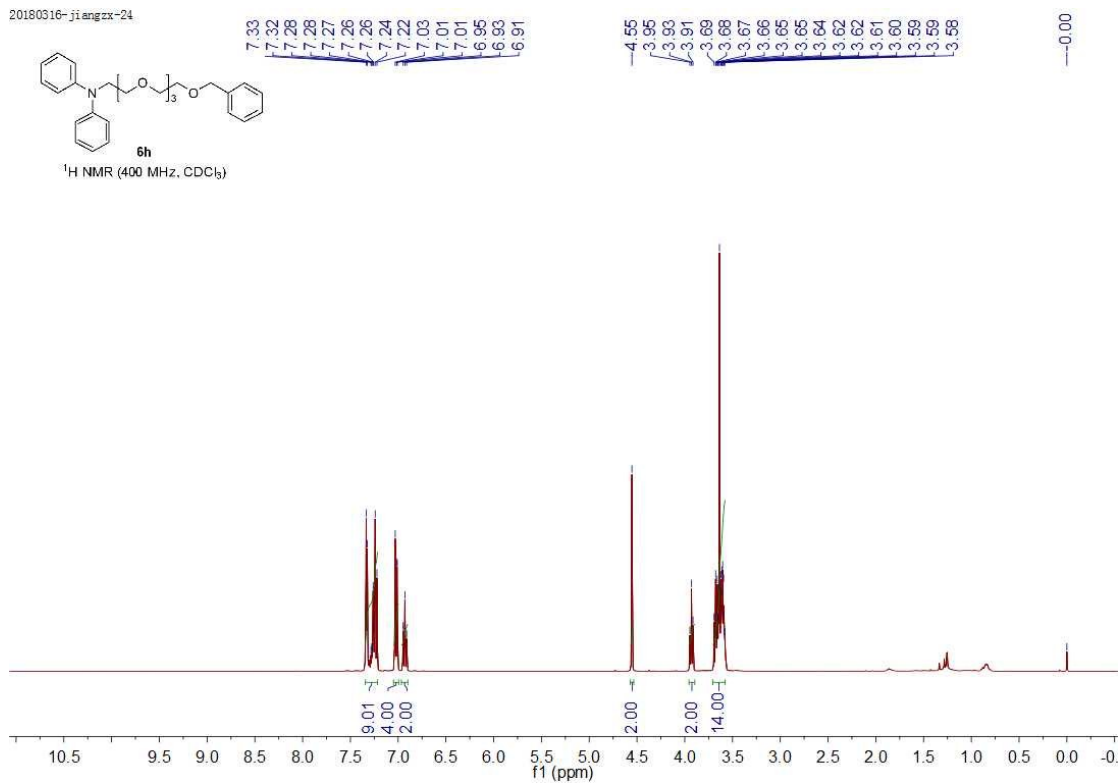
## HRMS of compound **6g**

41 #1239 RT: 12.08 AV: 1 NL: 3.47E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



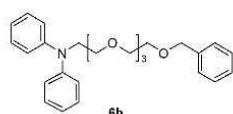
## <sup>1</sup>H NMR of compound **6h**

20180316-jiangzx-24

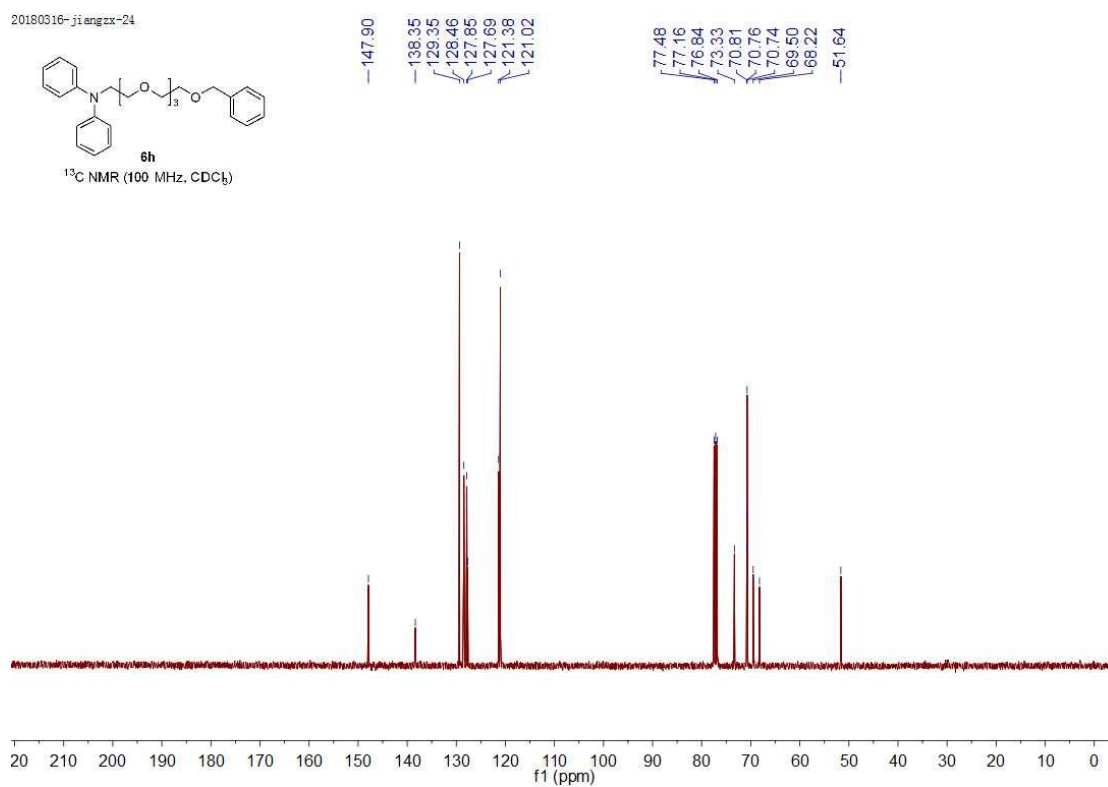


## <sup>13</sup>C NMR of compound **6h**

20180316-jiangzx-24

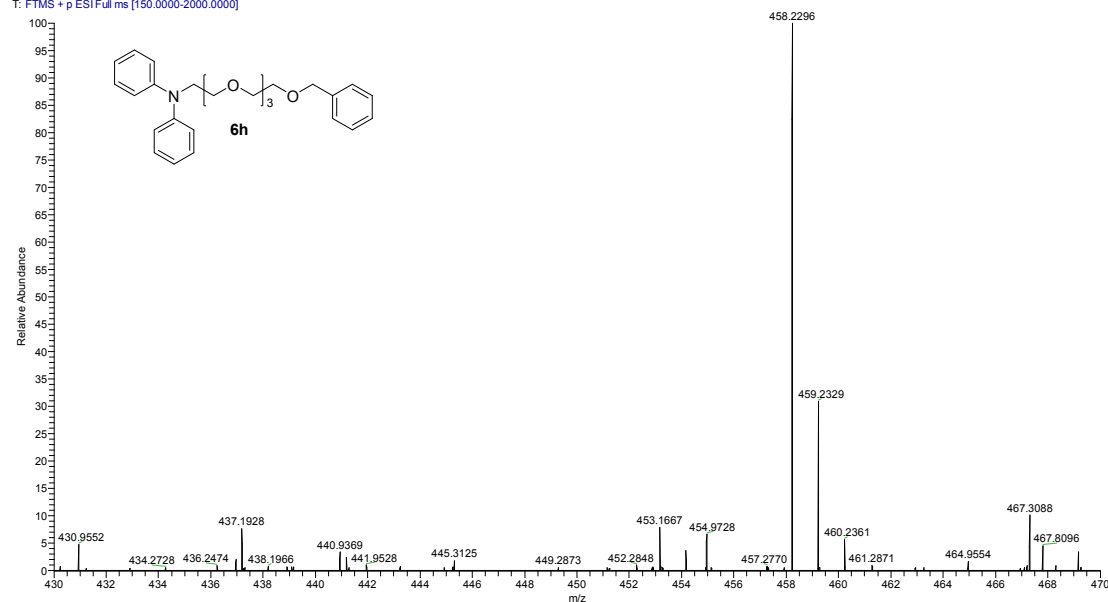


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)



## HRMS of compound **6h**

44 #1123 RT: 10.98 AV: 1 NL: 6.87E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



[illegible]

20180402-jiangzx-31

**6i**

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

Chemical structure of **6i** is shown above the spectrum. The structure is a brominated indole derivative with a polyether chain and a benzyl group.

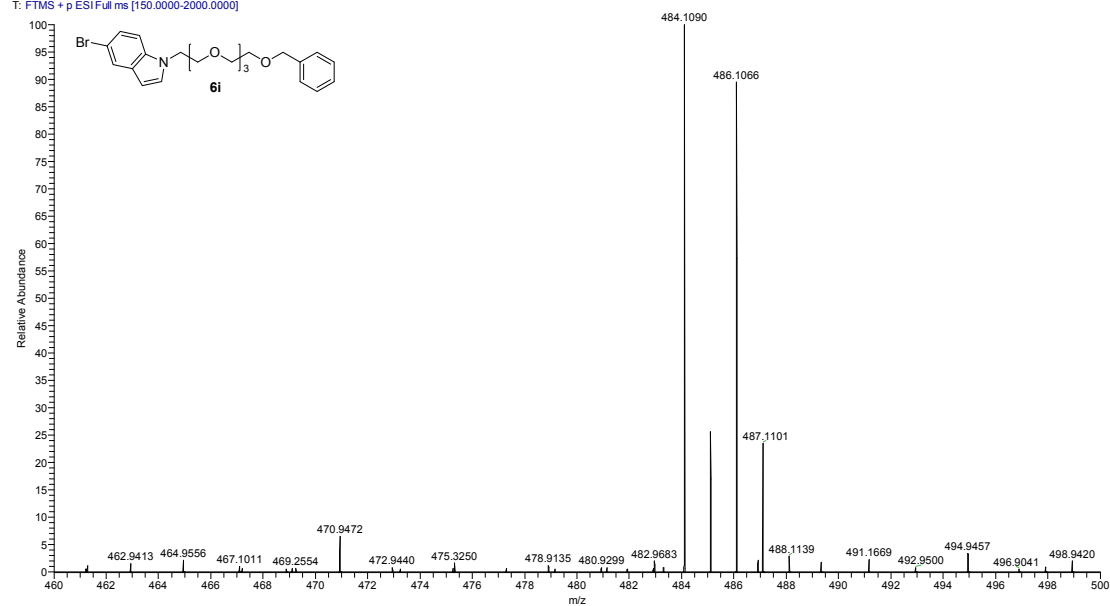
$^{13}\text{C}$  NMR peaks (ppm) are listed above the spectrum:

- 138.33, 134.92, 130.35, 129.79, 128.48, 127.88, 127.74, 124.29, 123.41, 112.72, 111.00, 100.91
- 77.48, 77.16, 76.84, 73.35, 70.88, 70.72, 70.23, 69.52
- 46.58

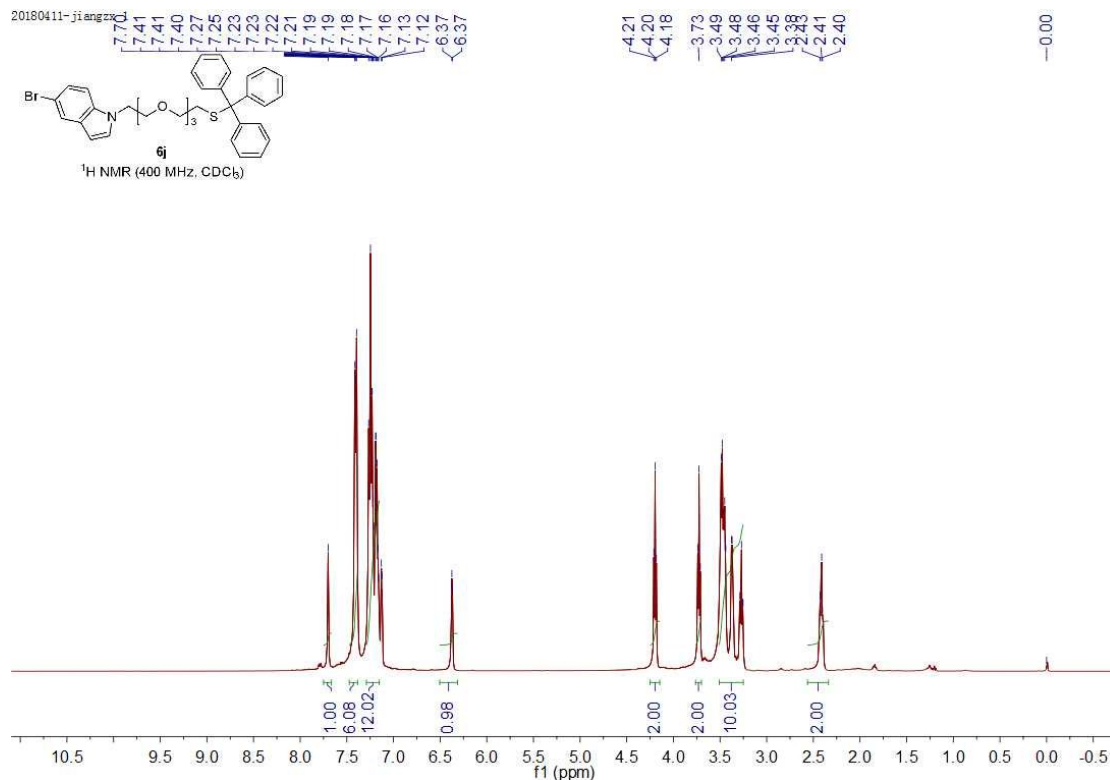
138.33, 134.92, 130.35, 129.79, 128.48, 127.88, 127.74, 124.29, 123.41, 112.72, 111.00, 100.91, 77.48, 77.16, 76.84, 73.35, 70.88, 70.72, 70.23, 69.52, 46.58

## HRMS of compound **6i**

43 #1097 RT: 10.71 AV: 1 NL: 6.76E6  
T: FTMS + p ESIFull.ms [150.0000-2000.0000]

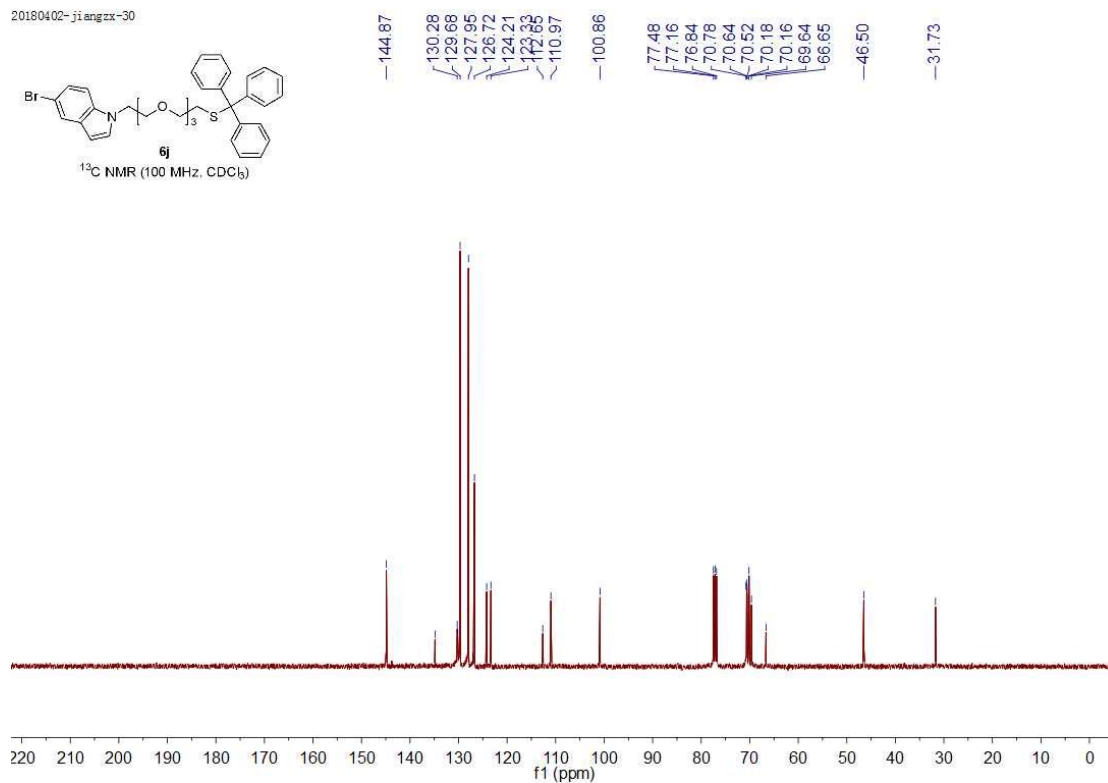


## <sup>1</sup>H NMR of compound **6j**



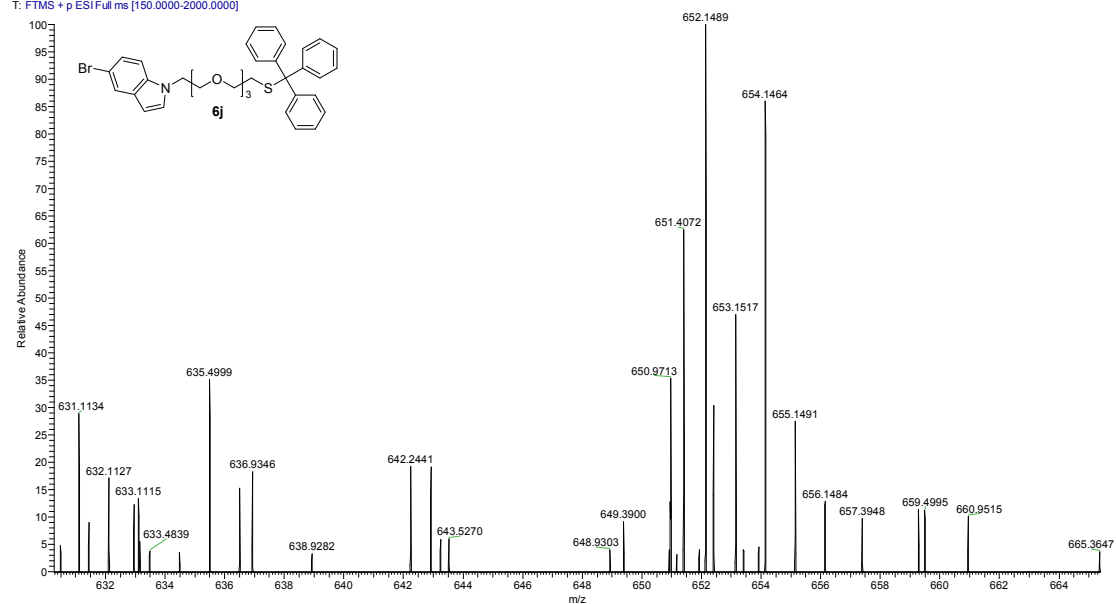
## <sup>13</sup>C NMR of compound **6j**

20180402-jiangzx-30

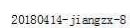
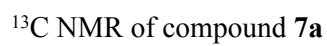


## HRMS of compound **6j**

42 #1229 RT: 11.98 AV: 1 NL: 1.30E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]

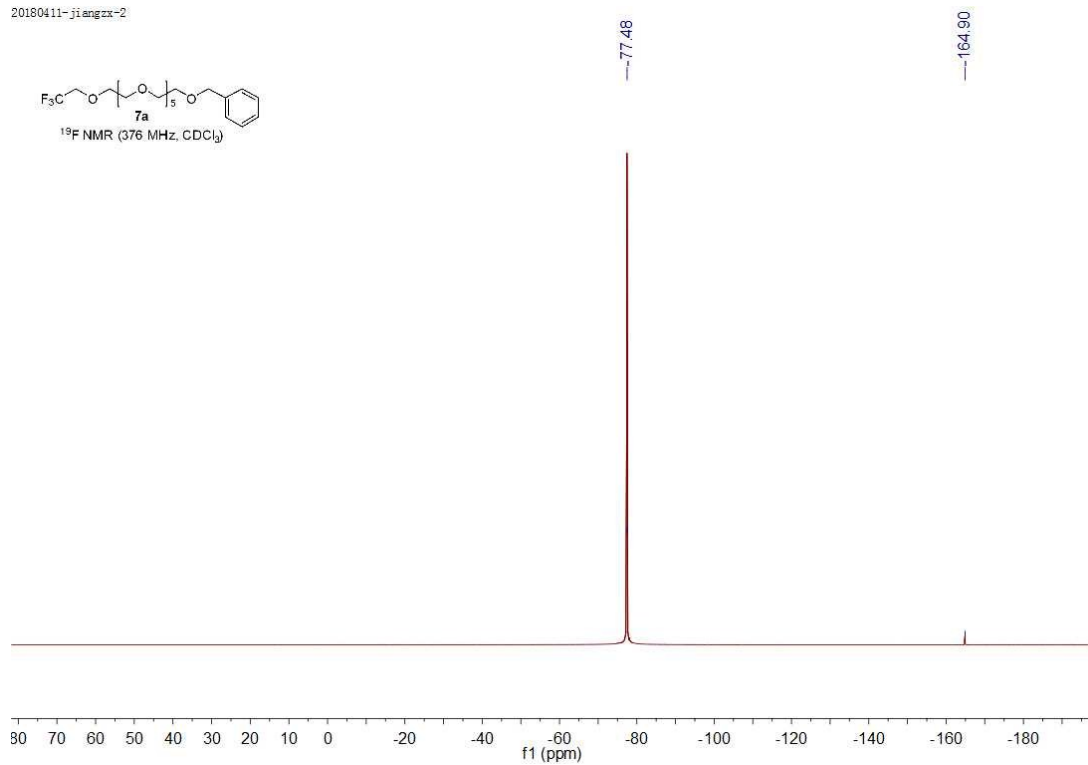


## 20180402-jiangzx-33



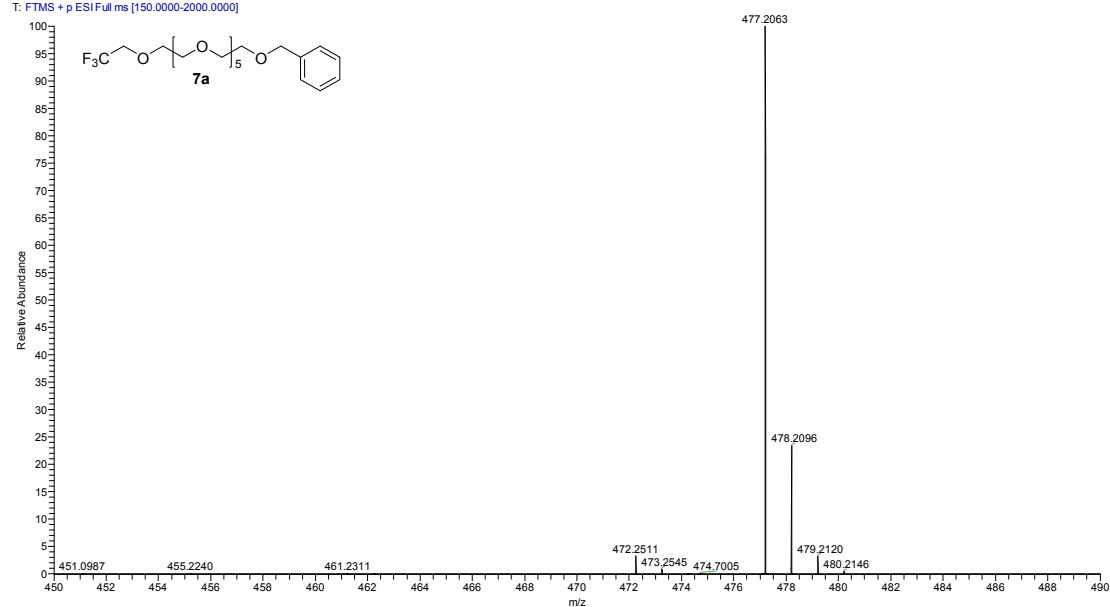
## <sup>19</sup>F NMR of compound **7a**

20180411-jiangxx-2

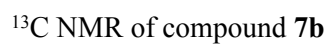


## HRMS of compound **7a**

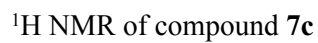
45 #943 RT: 9.23 AV: 1 NL: 3.49E9  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



20180314-jiangzx-44

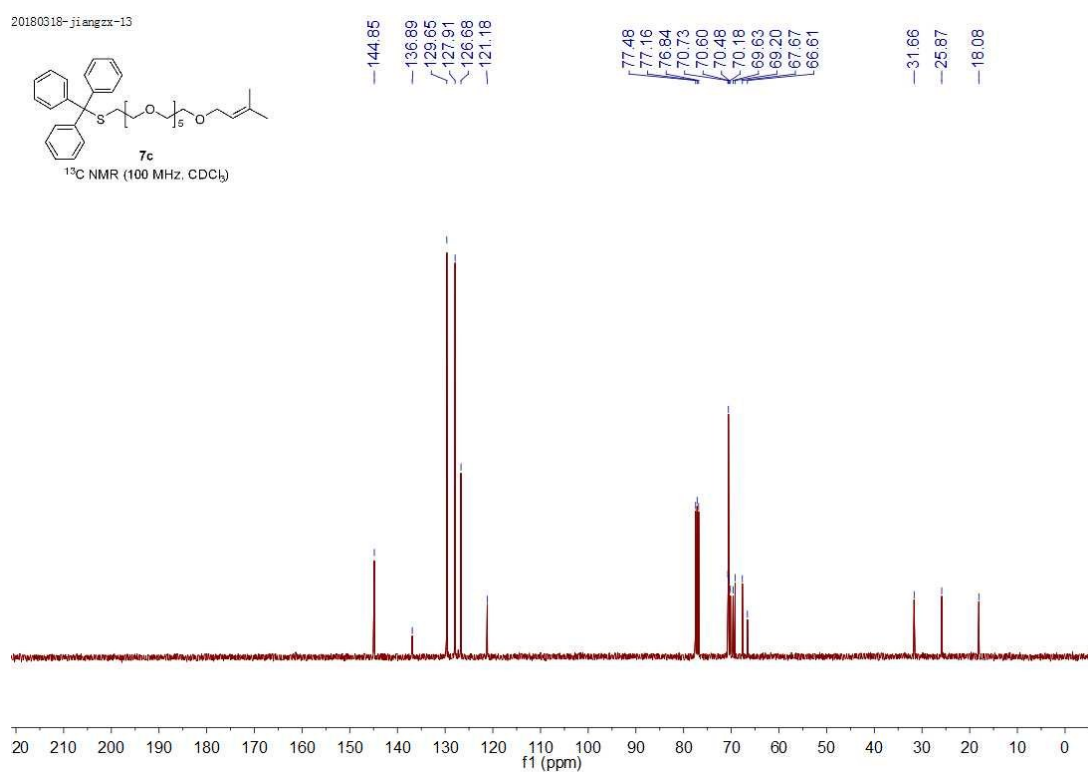


46 #1005 RT: 9.83 AV: 1 NL: 1.01E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



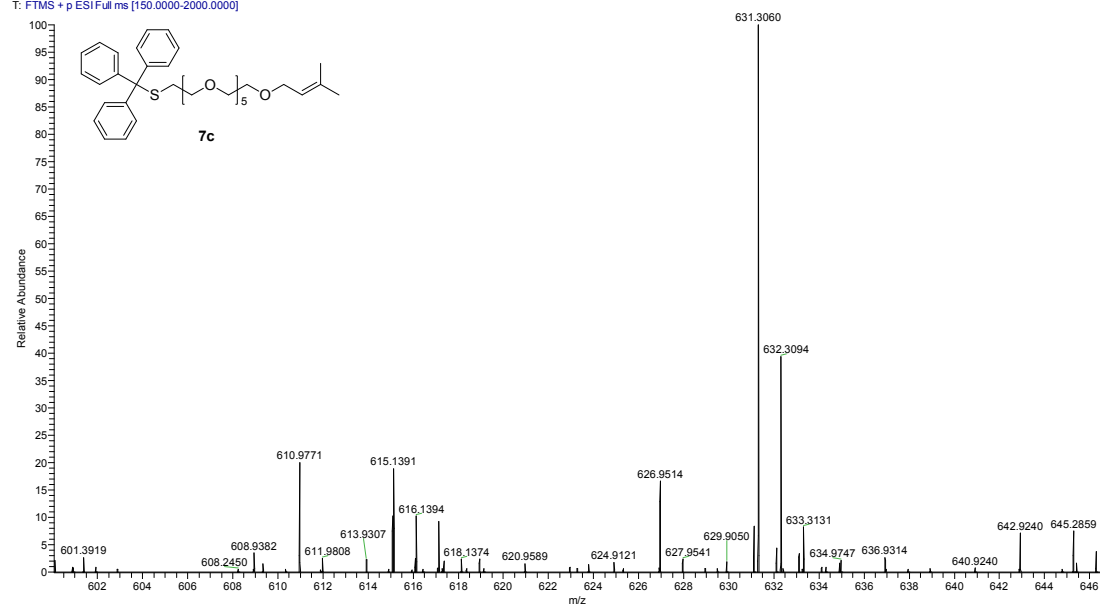
## <sup>13</sup>C NMR of compound **7c**

20180318-jiangzx-13

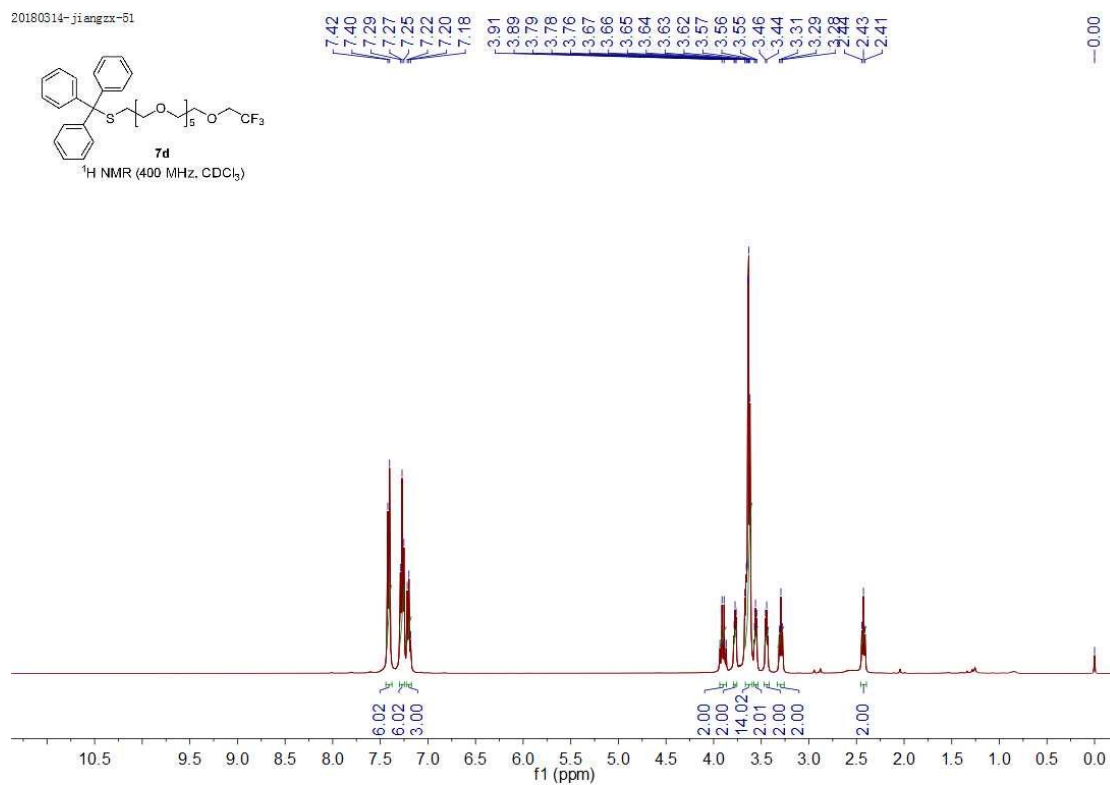


## HRMS of compound **7c**

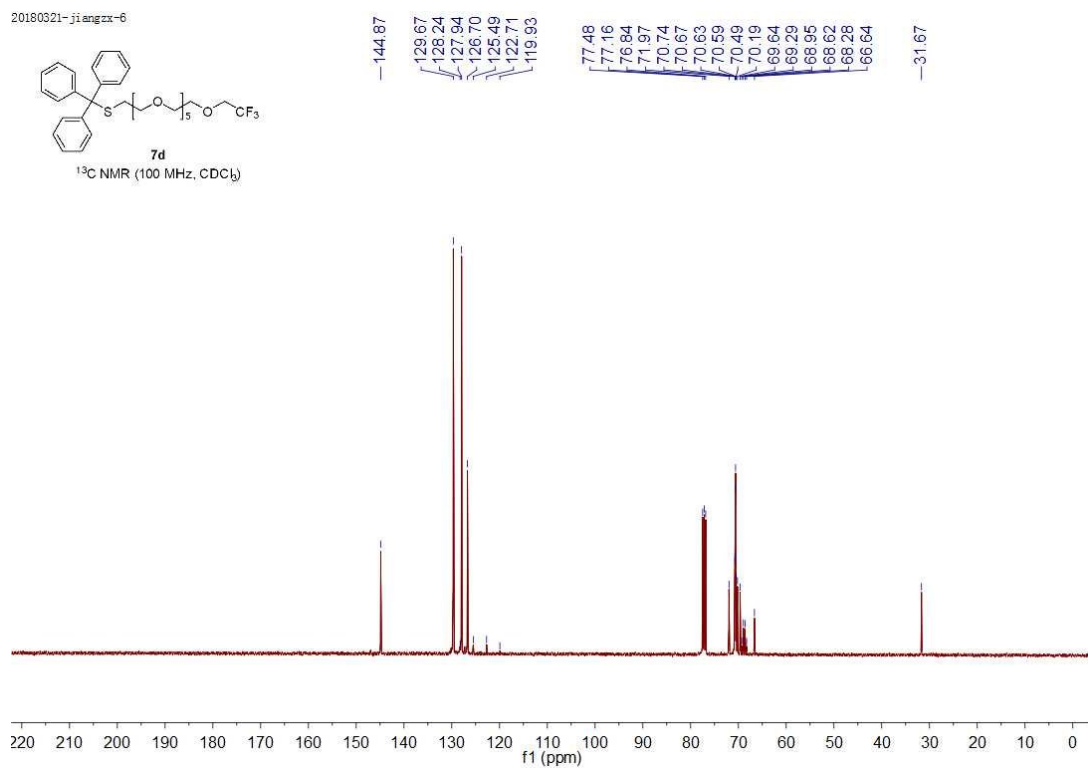
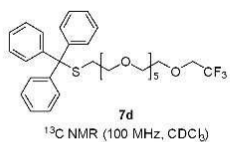
13 #1155 RT: 11.28 AV: 1 NL: 6.99E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



## 20180314-jiangzx-51

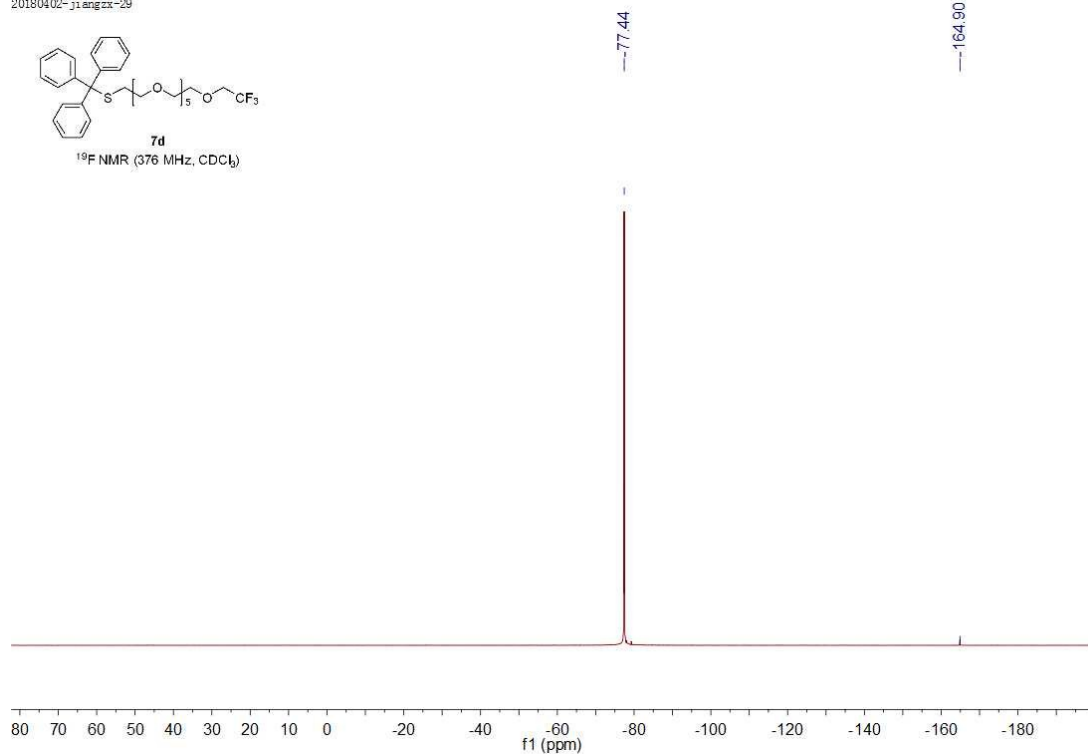


20180321-jiangzx-6



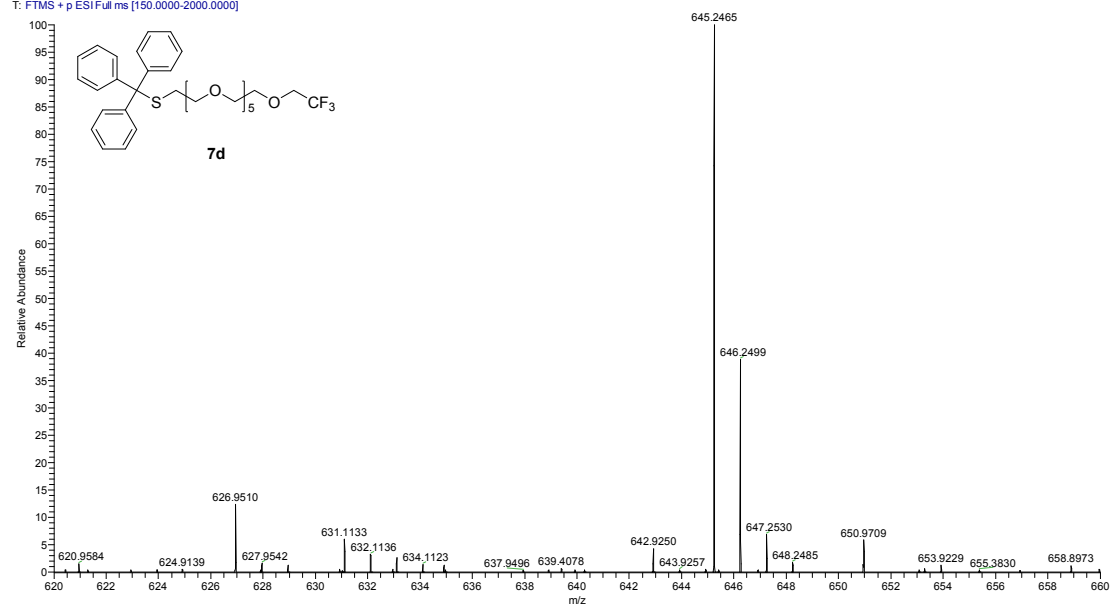
## $^{19}\text{F}$ NMR of compound **7d**

20180402-jiangxx-29

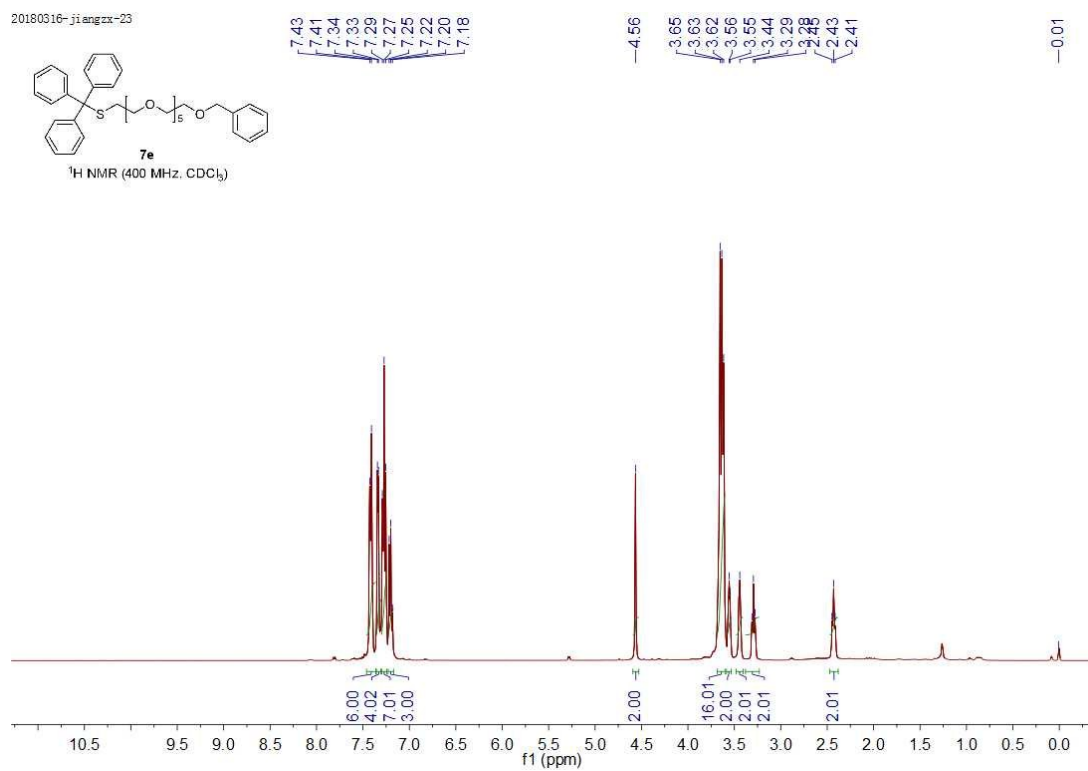


## HRMS of compound **7d**

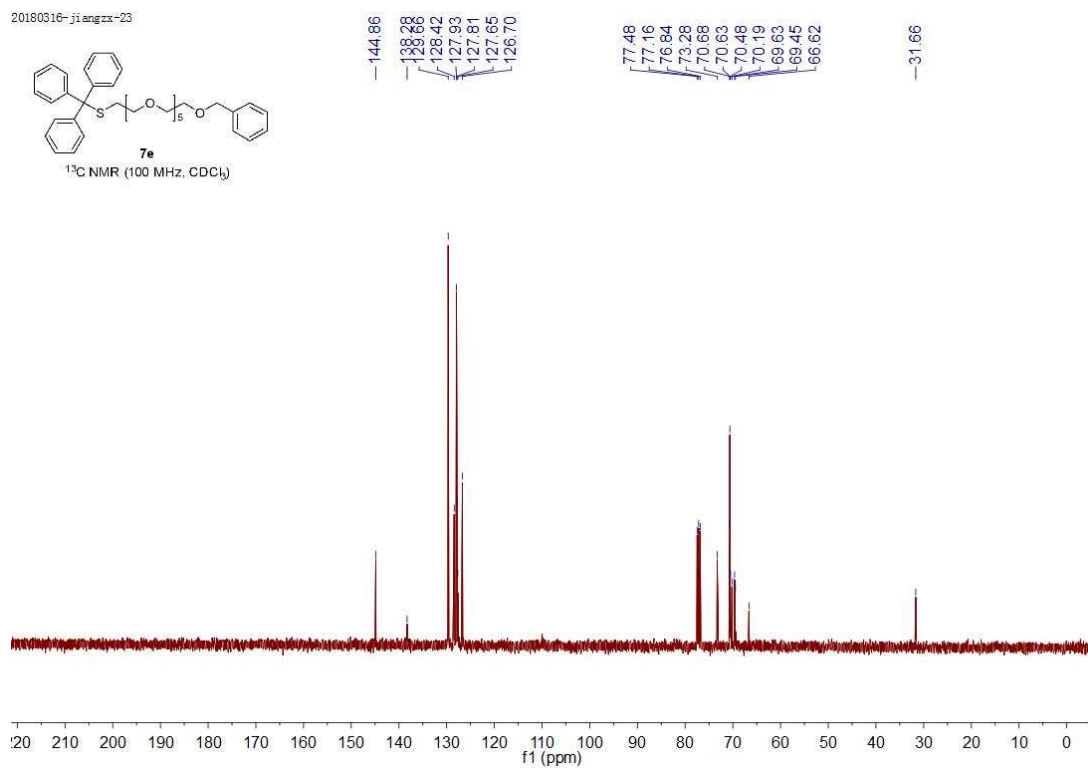
14 #1153 RT: 11.27 AV: 1 NL: 1.09E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



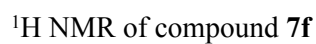
# <sup>1</sup>H NMR of compound **7e**



# <sup>13</sup>C NMR of compound **7e**

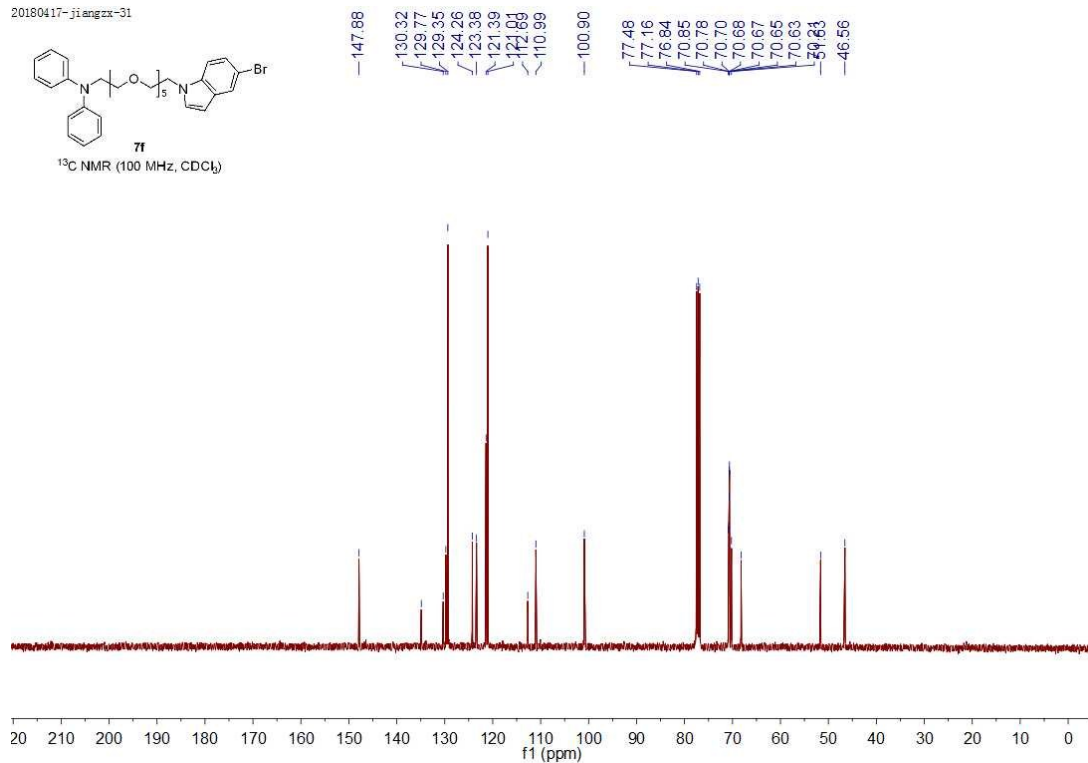


15 #1167 RT: 11.41 AV: 1 NL: 8.08E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



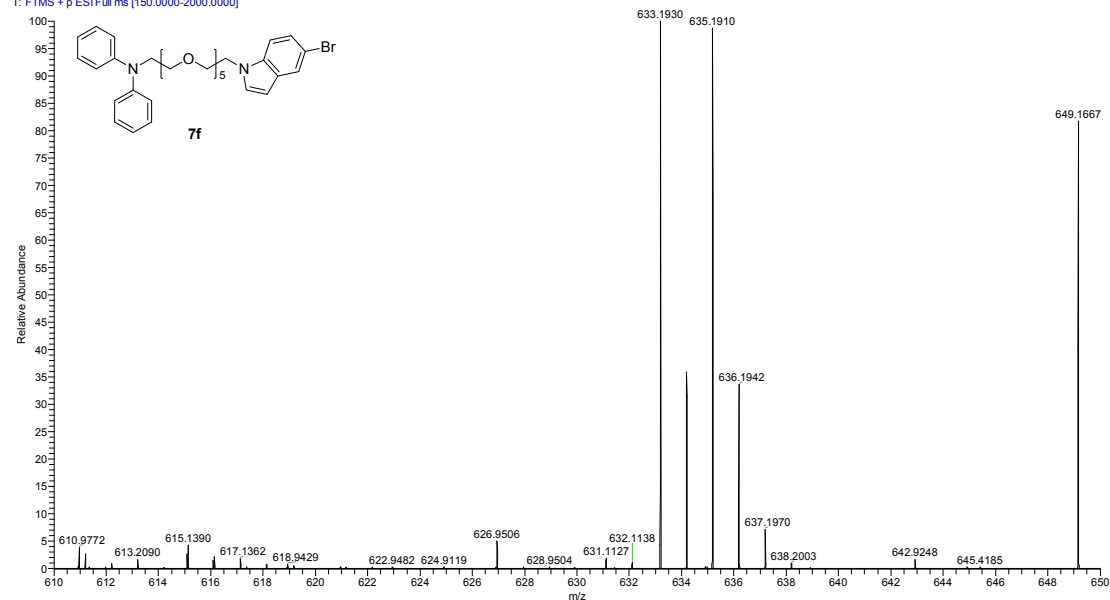
## <sup>13</sup>C NMR of compound **7f**

20180417-jiangzx-31

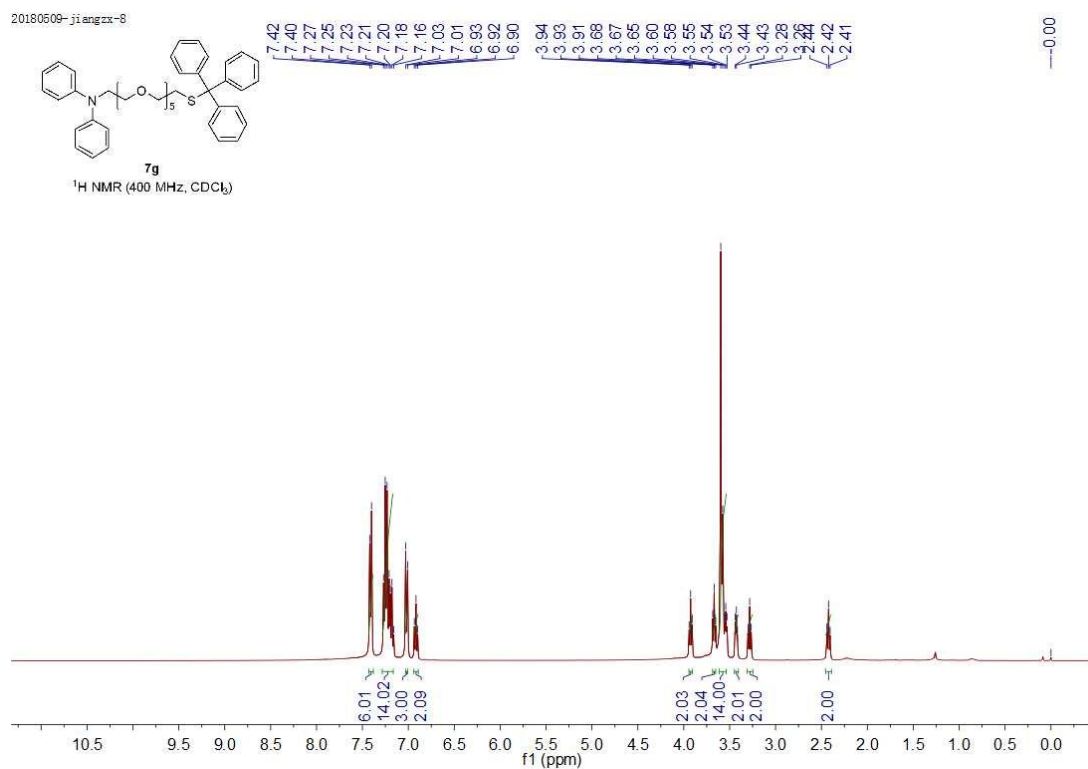


## HRMS of compound **7f**

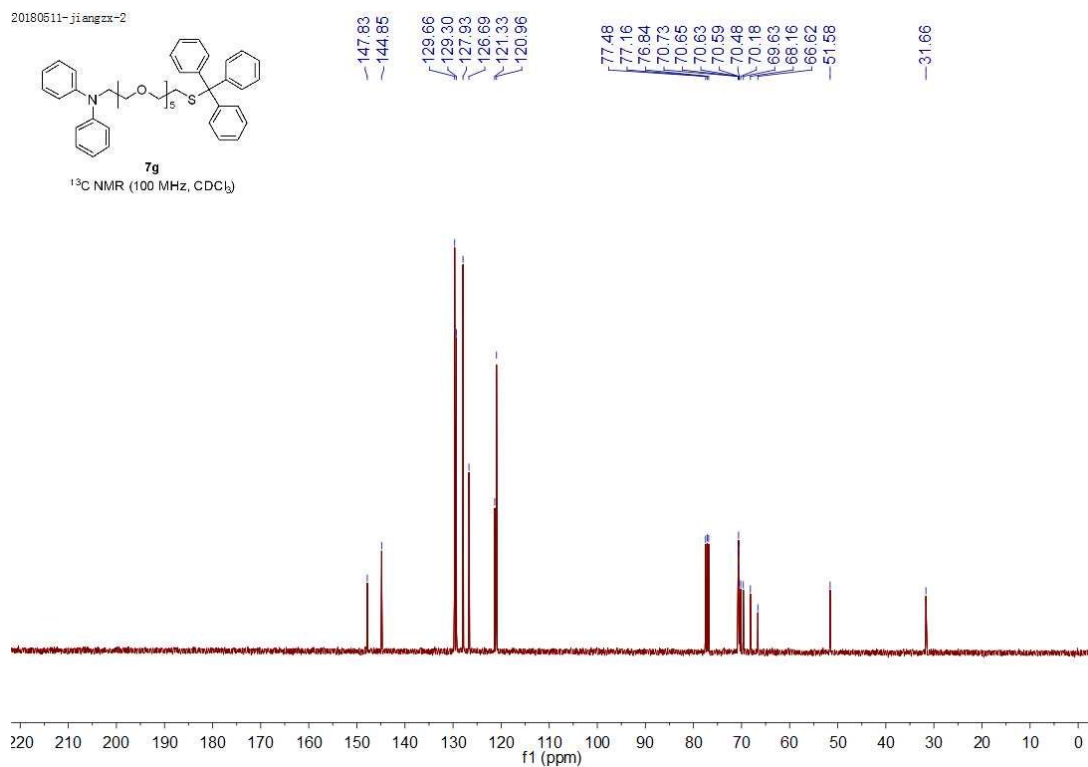
16 #1153 RT: 11.28 AV: 1 NL: 2.81E7  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



# <sup>1</sup>H NMR of compound **7g**

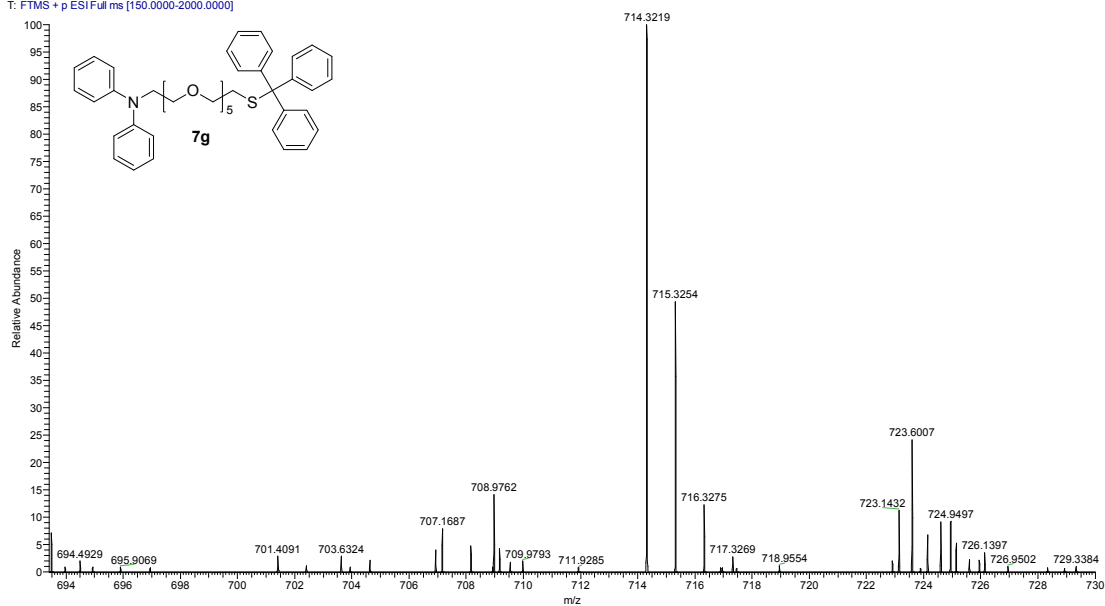


# <sup>13</sup>C NMR of compound **7g**



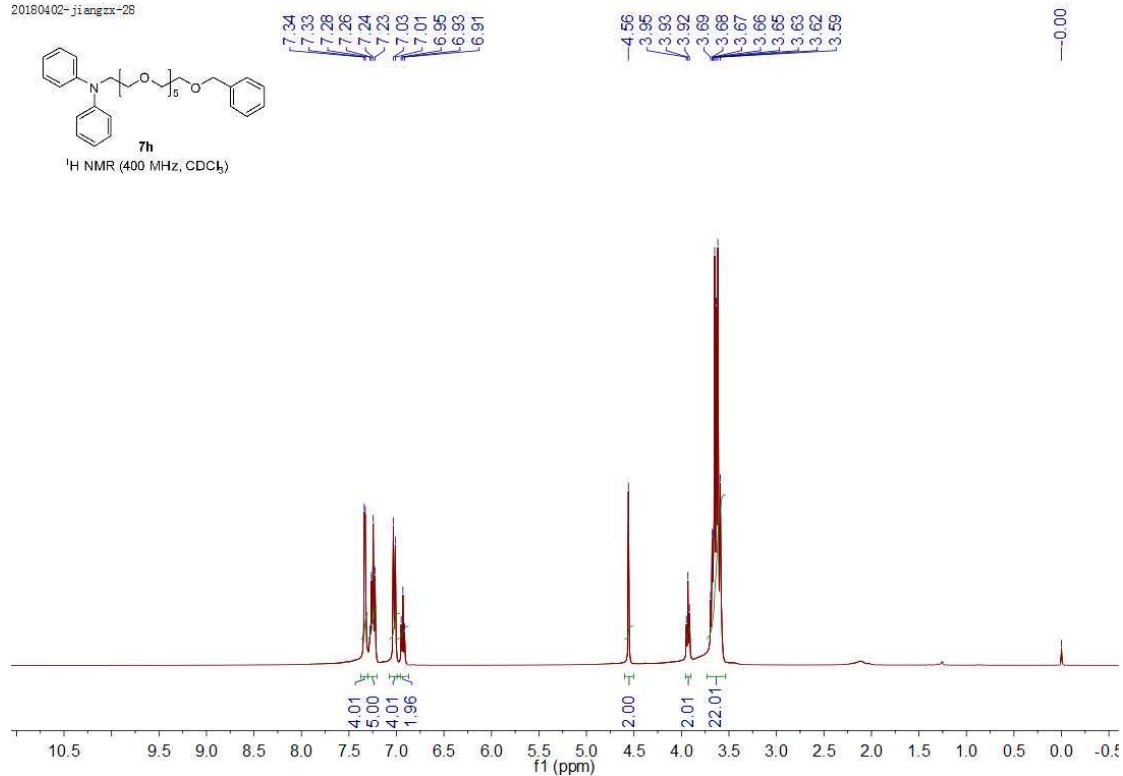
## HRMS of compound **7g**

17 #1233 RT: 12.05 AV: 1 NL: 5.79E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



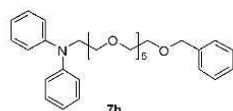
## <sup>1</sup>H NMR of compound **7h**

20180402-jiangzx-28

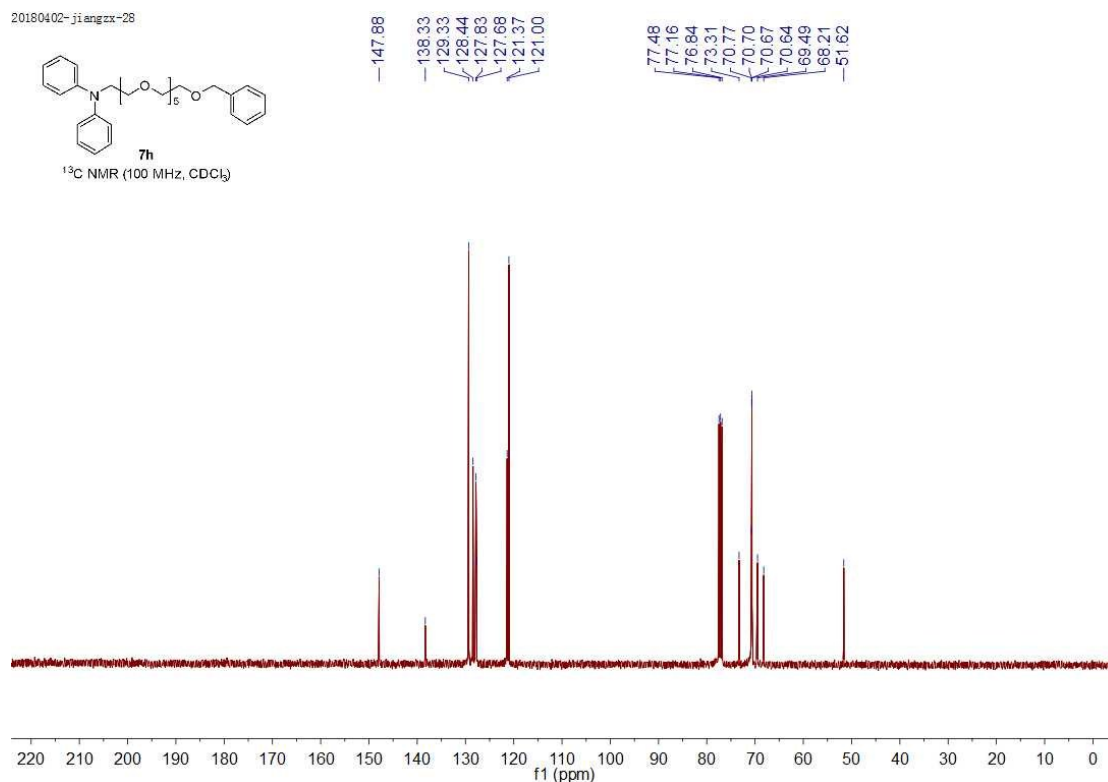


## <sup>13</sup>C NMR of compound **7h**

20180402-jiangzx-28

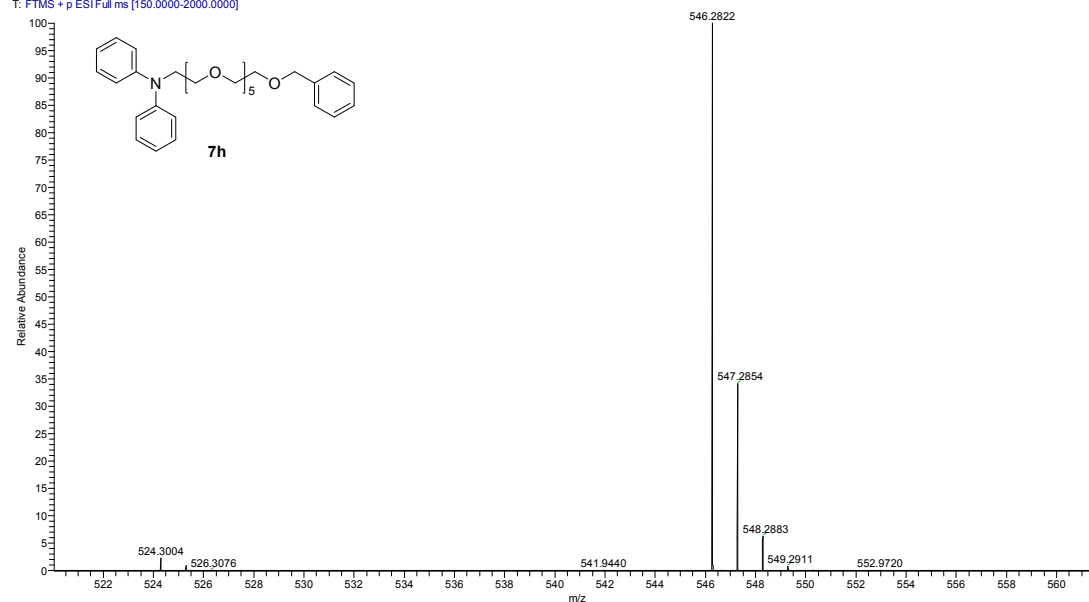


<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

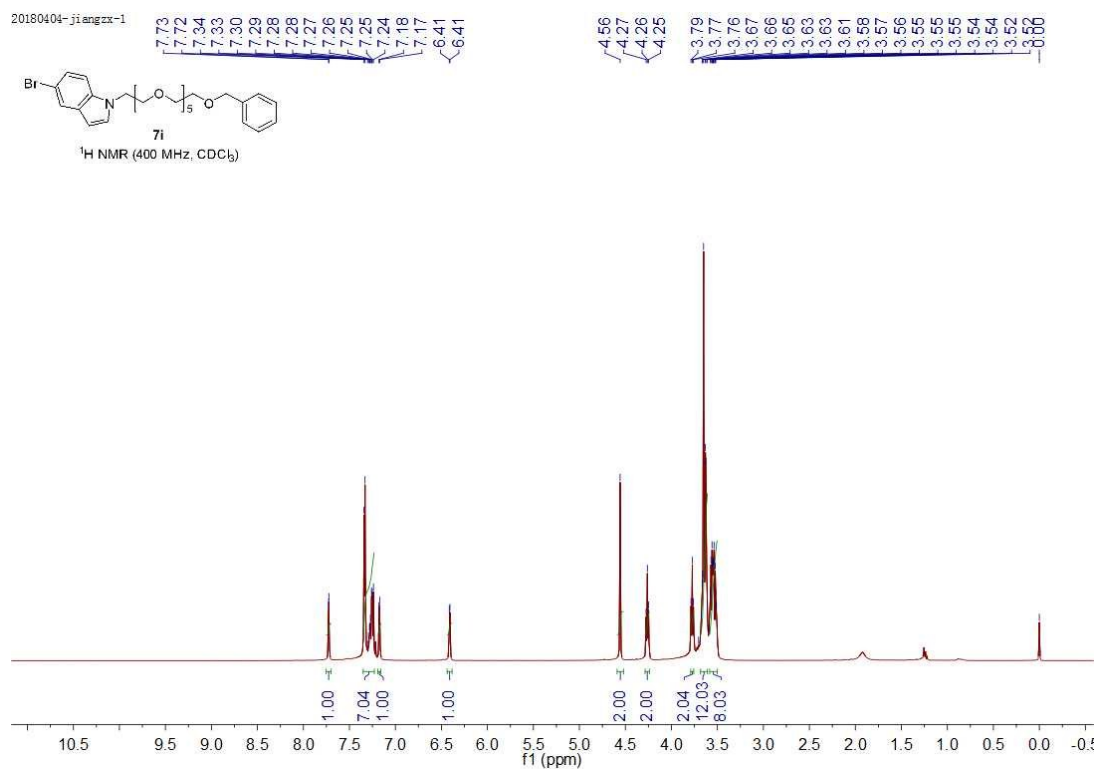


## HRMS of compound **7h**

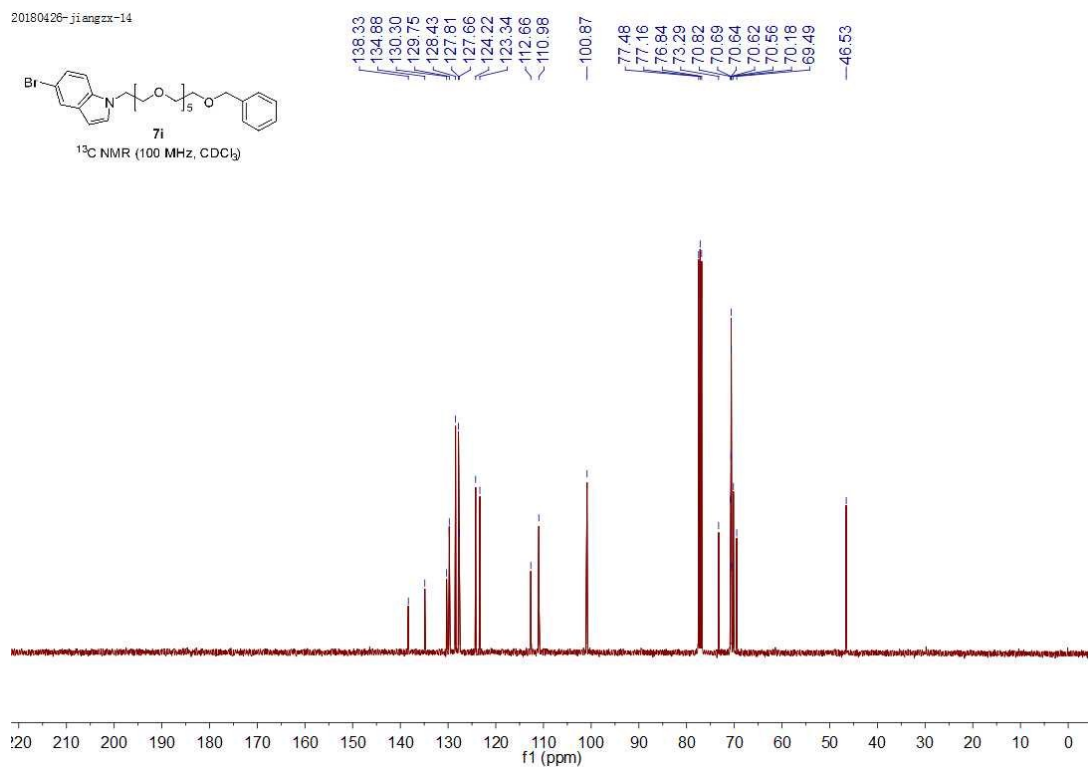
20 #1103 RT: 10.81 AV: 1 NL: 1.23E9  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



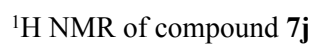
# <sup>1</sup>H NMR of compound **7i**



# <sup>13</sup>C NMR of compound **7i**



19 #1089 RT: 10.66 AV: 1 NL: 5.14E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]

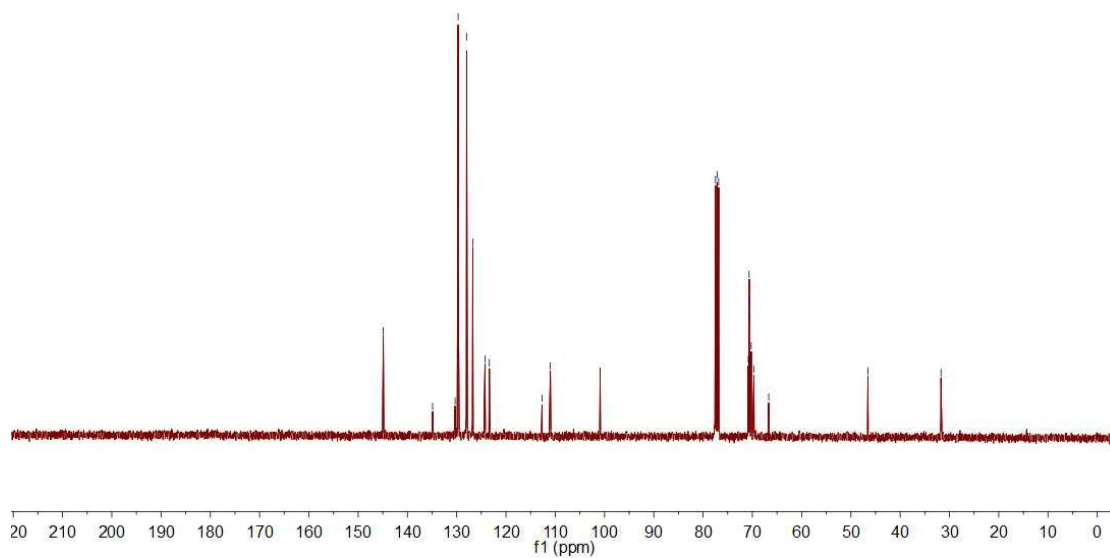


## <sup>13</sup>C NMR of compound **7j**

20180402-jiangzx-34

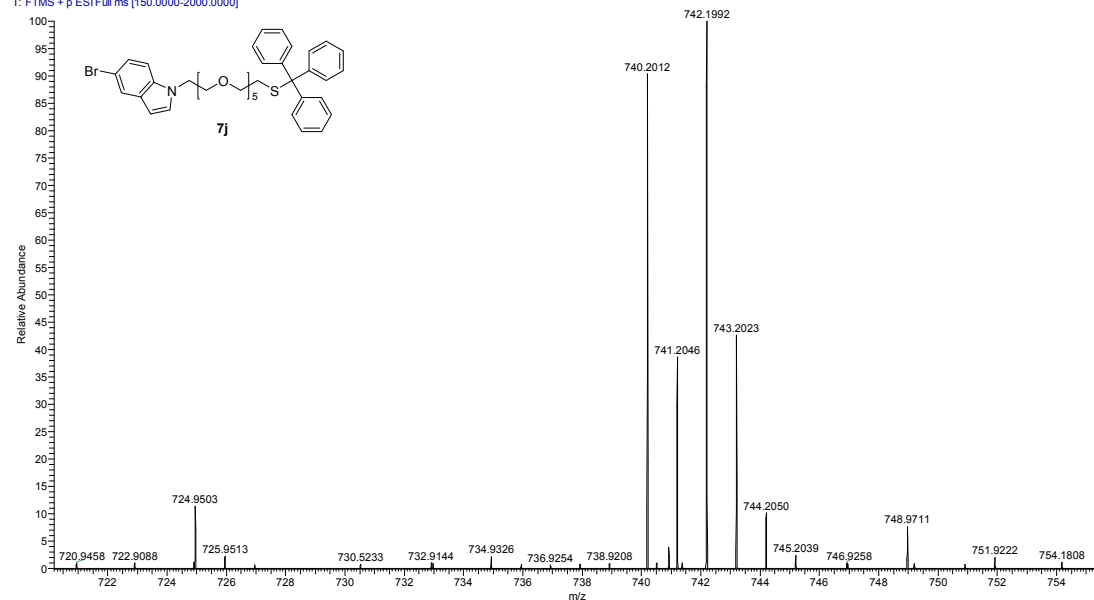


144.90, 130.32, 129.77, 129.71, 127.97, 126.74, 124.26, 123.37, 122.89, 110.99, 77.48, 77.16, 76.84, 70.83, 70.65, 70.63, 70.60, 70.51, 70.22, 69.68, 66.88, 46.55, 31.71

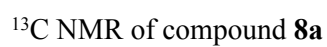


## HRMS of compound **7j**

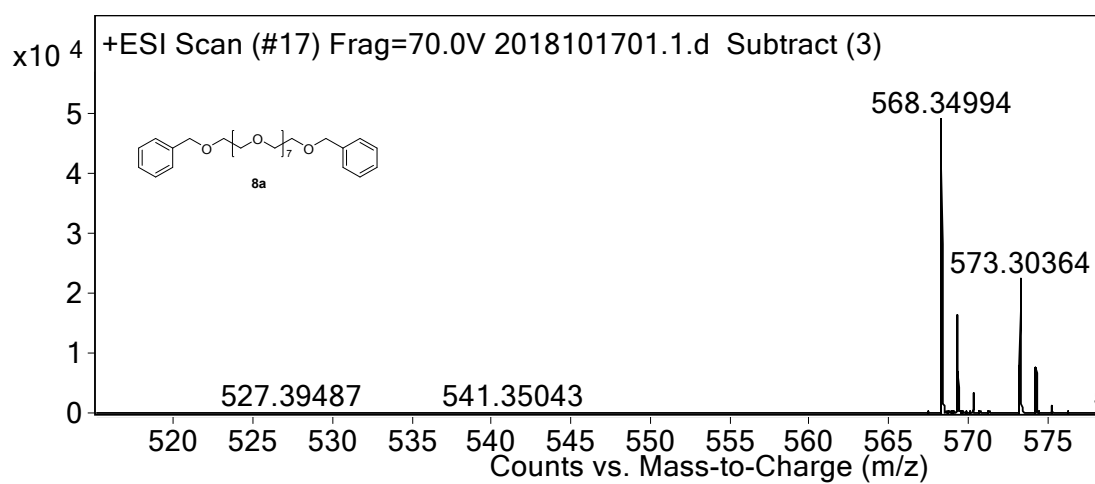
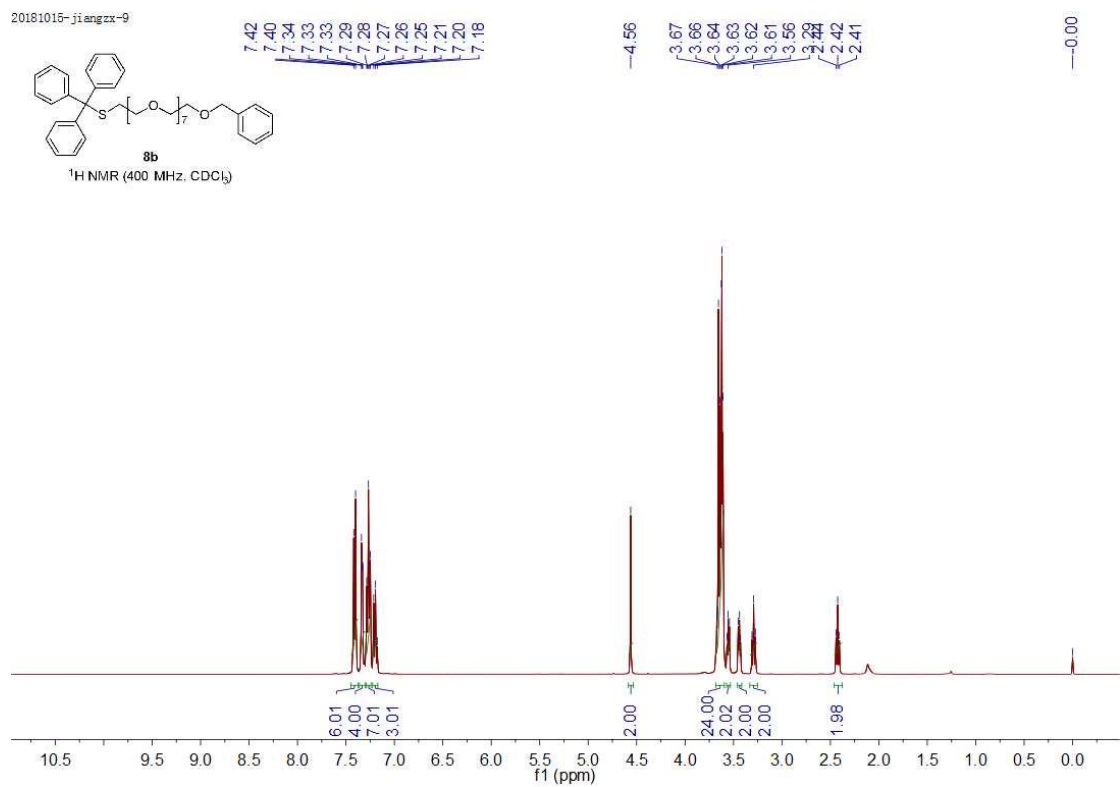
18 #1189 RT: 11.63 AV: 1 NL: 5.66E6  
T: FTMS + p ESI Full ms [150.0000-2000.0000]



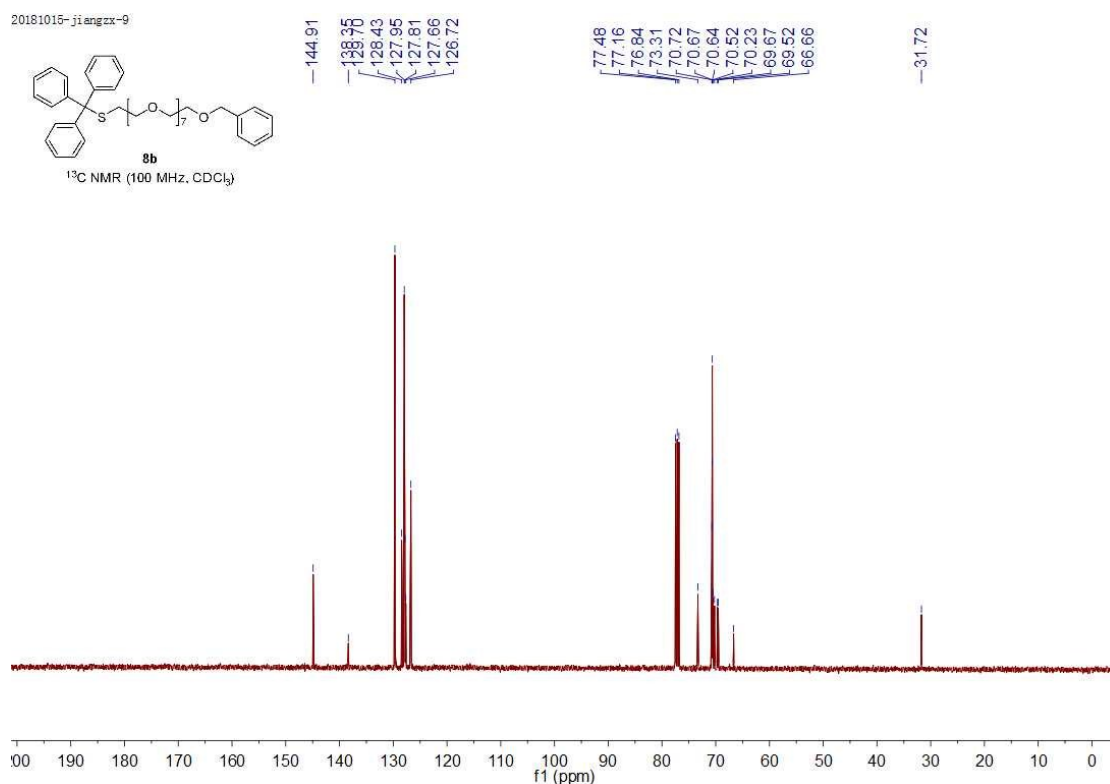
20181015-jiangzx-8



HRMS of compound **8a**

<sup>1</sup>H NMR of compound **8b**

# <sup>13</sup>C NMR of compound **8b**



# HRMS of compound **8b**

