^{19}F CEST imaging probes for metal ions detection

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1. ^{19}F NMR spectra of 1-4 in the presence of Cu^{2+} and Fe^{3+}

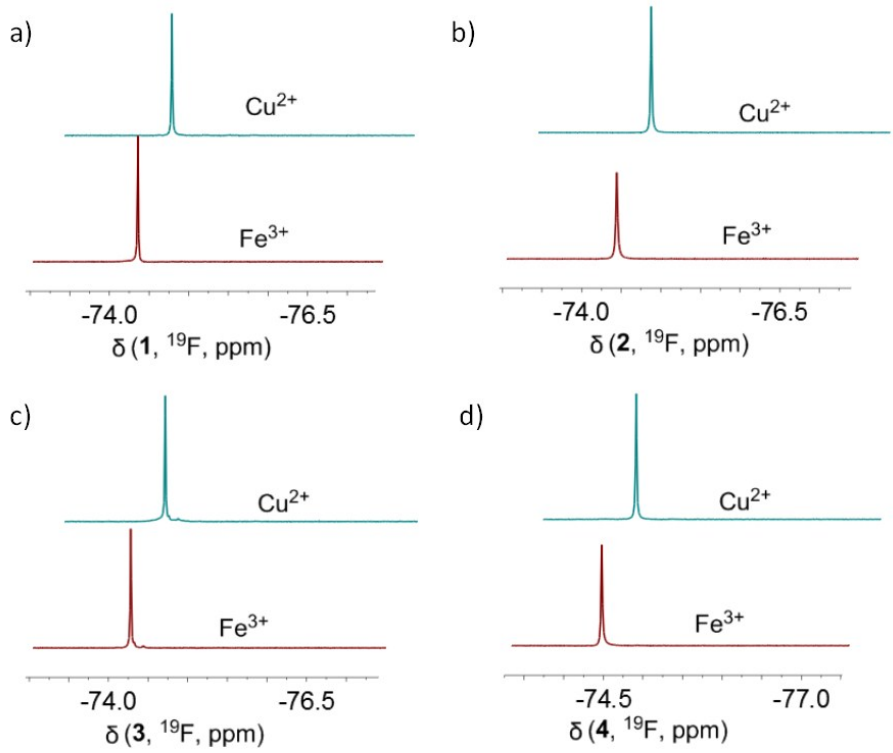


Figure S1 ^{19}F NMR spectra of **1-4** in the presence of Cu^{2+} (blue) and Fe^{3+} (red).

2. ^{19}F NMR spectra of 4(+Ca^{2+}/Zn^{2+}) in the presence of EDTA/DTPA

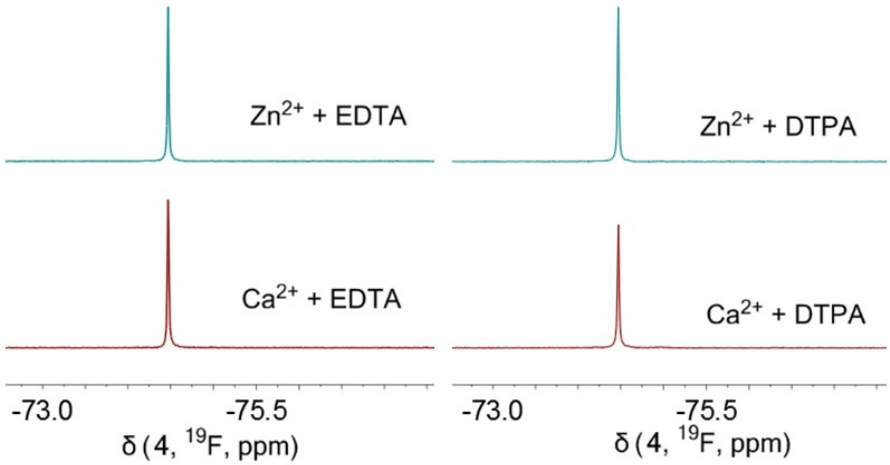


Figure S2 ^{19}F NMR spectra of **4**(+Ca^{2+}/Zn^{2+}) in the presence of EDTA/DTPA.

3. Association constants of chelators 1-4 with metal ions.

$$M+L \rightleftharpoons ML$$

$$K=\frac{[ML]}{[M][L]}$$

The experimental method consisted of potentiometric titration of the each chelator in the absence of and in the presence of the metal ion being investigated. The ionic strength was maintained constant by using 0.1 M KCl as a supporting electrolyte and by employing relatively very low concentrations of metal and chelator. The pH readings were then taken after the addition of small increments of 0.02 M KOH until the pH reached 10 (chelators **2** and **4** were adjusted by KOH initially until dissolved). All measurements were carried out at 25 °C.

The results of the experimental measurements are presented in Fig. S3. These titration curves indicate qualitatively the formulas of the metal chelates formed. The association constants of chelators **1-4** with Ca^{2+}, Mg^{2+} and Zn^{2+} were determined from the titration curves (Fig. S3) by a direct algebraic method, and by an adaptation of Bjerrum's method[11] (Table S1).

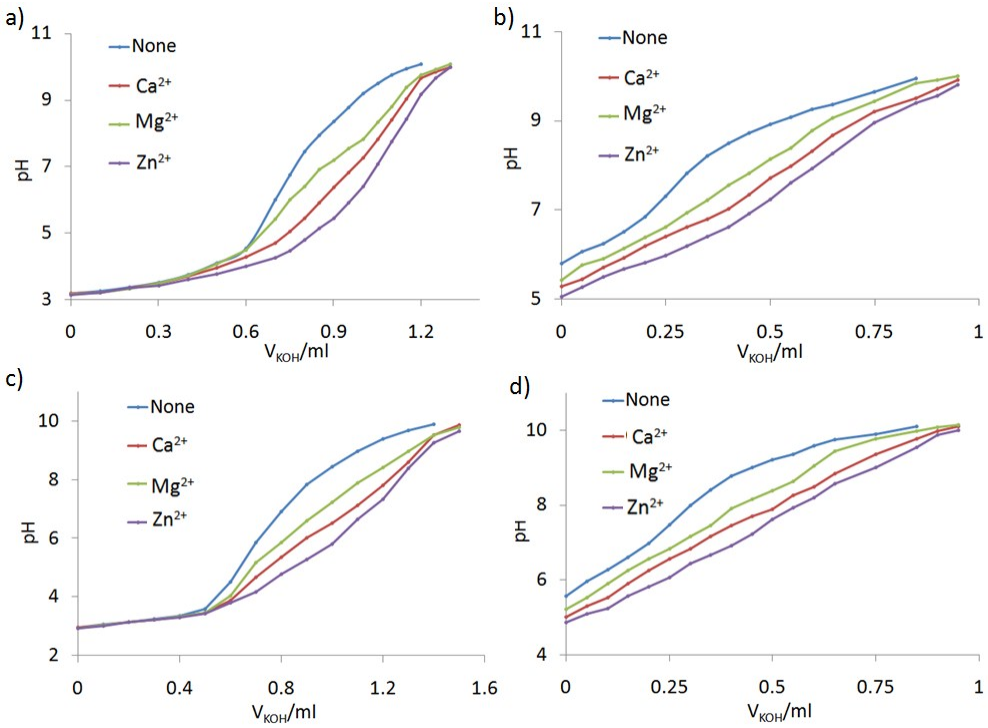


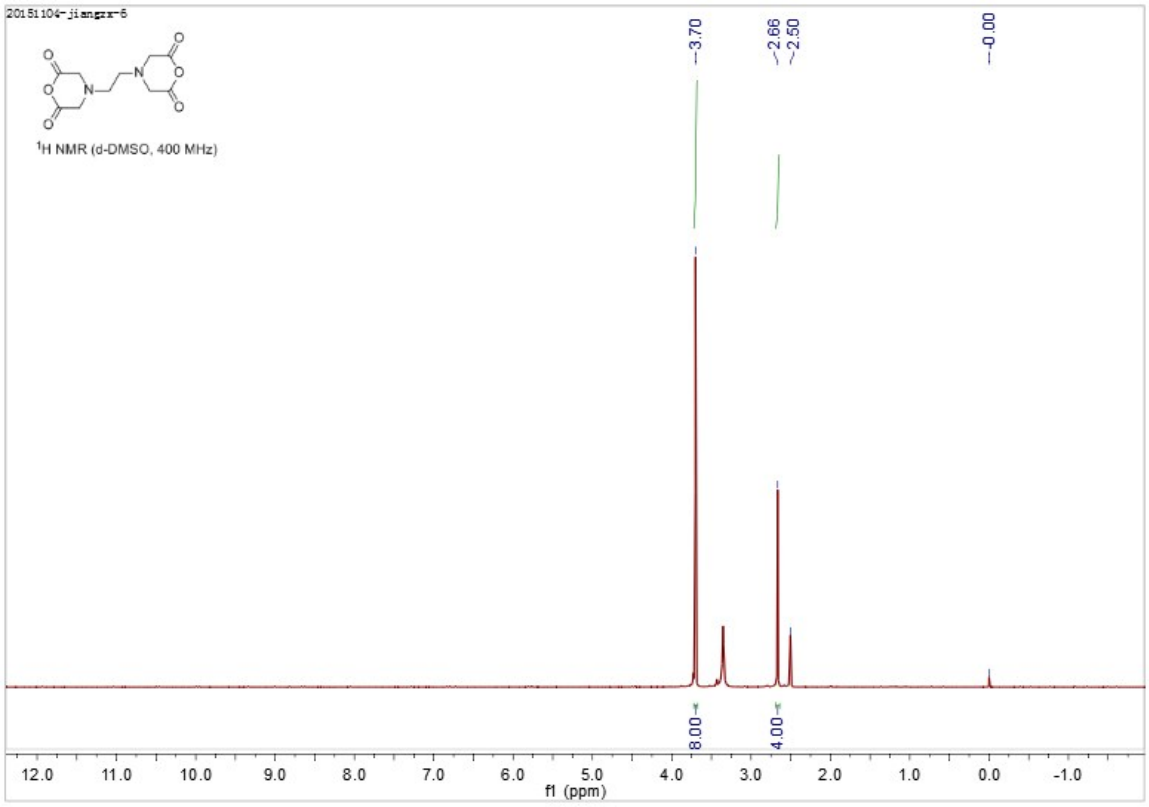
Figure S3 Titration curves of chelators **1-4.** C^0 = 0.0004 M, V^0 = 10 mL, C_M^{2+} = 0.0002 M, C_{KOH} = 0.02 M, C_{KCl} = 0.1 M, T = 25 °C.

Table S1 The association constants of chelators **1-4** with Ca^{2+}, Mg^{2+} and Zn^{2+}.

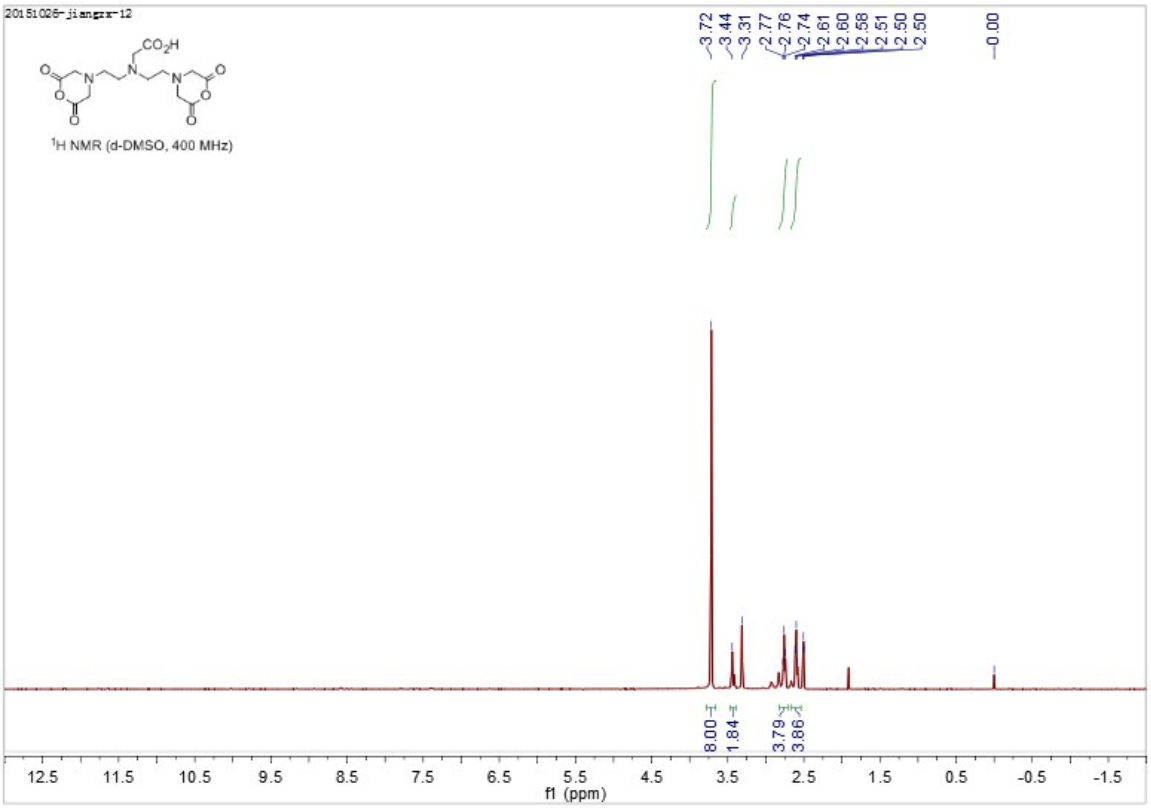
	lgK (T = 25 °C, I = 0.1 M)		
	Mg^{2+}	Ca^{2+}	Zn^{2+}
1	8.45	10.02	13.14
2	7.91	9.36	12.03
3	8.63	10.17	13.55
4	8.07	9.39	12.54

4. Copies of $^{1}H/^{13}C/^{19}F$ NMR, HPLC and HRMS spectra of compounds

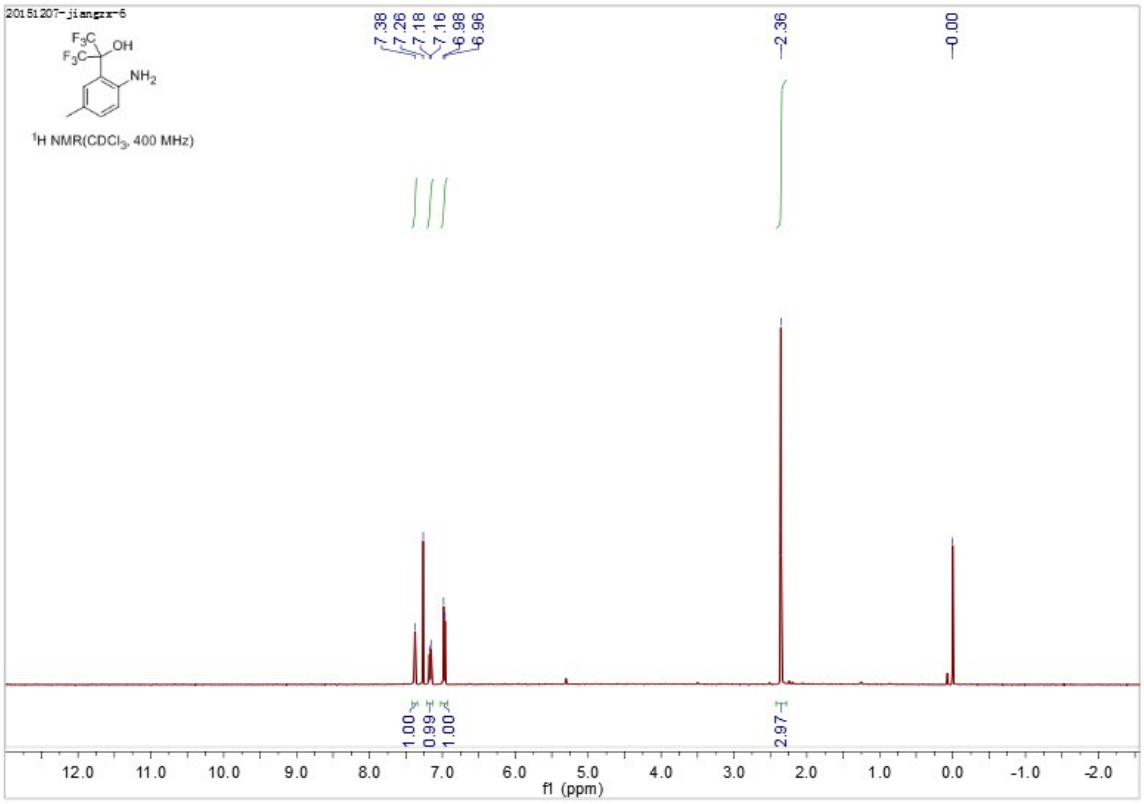
^{1}H NMR of compound **5**



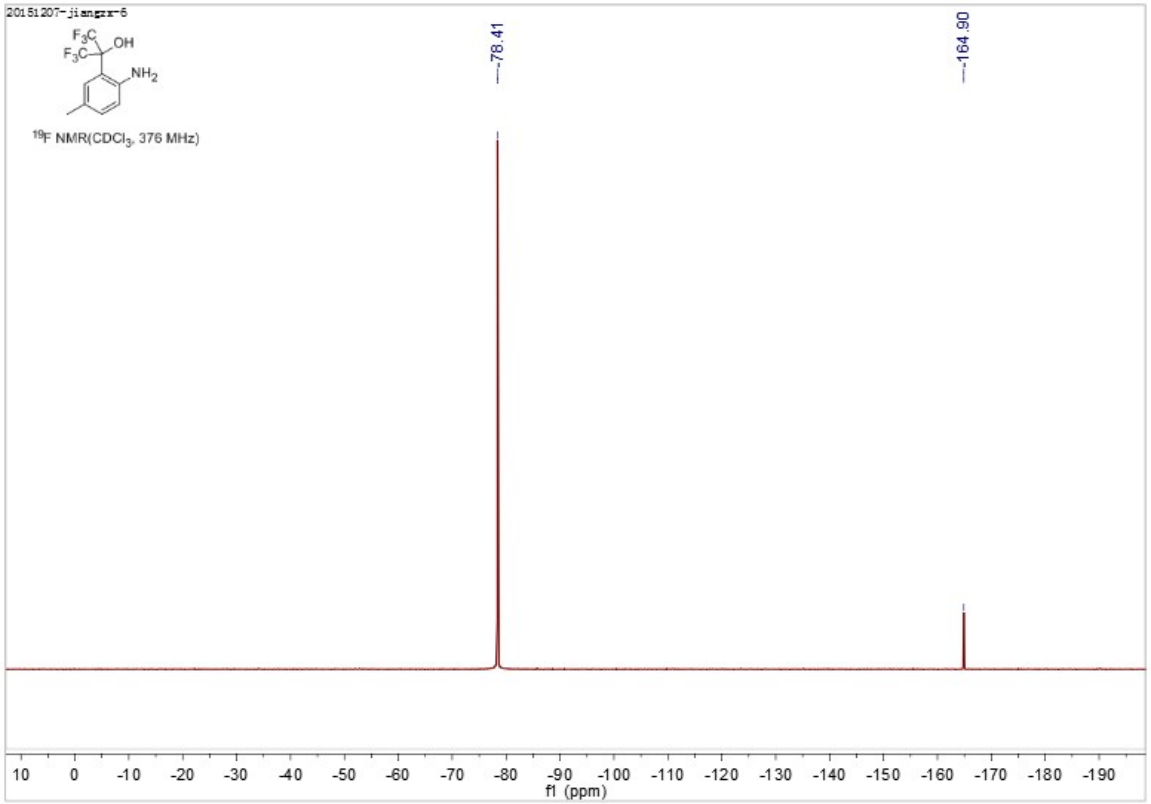
^{1}H NMR of compound **6**



^{1}H NMR of compound **7**

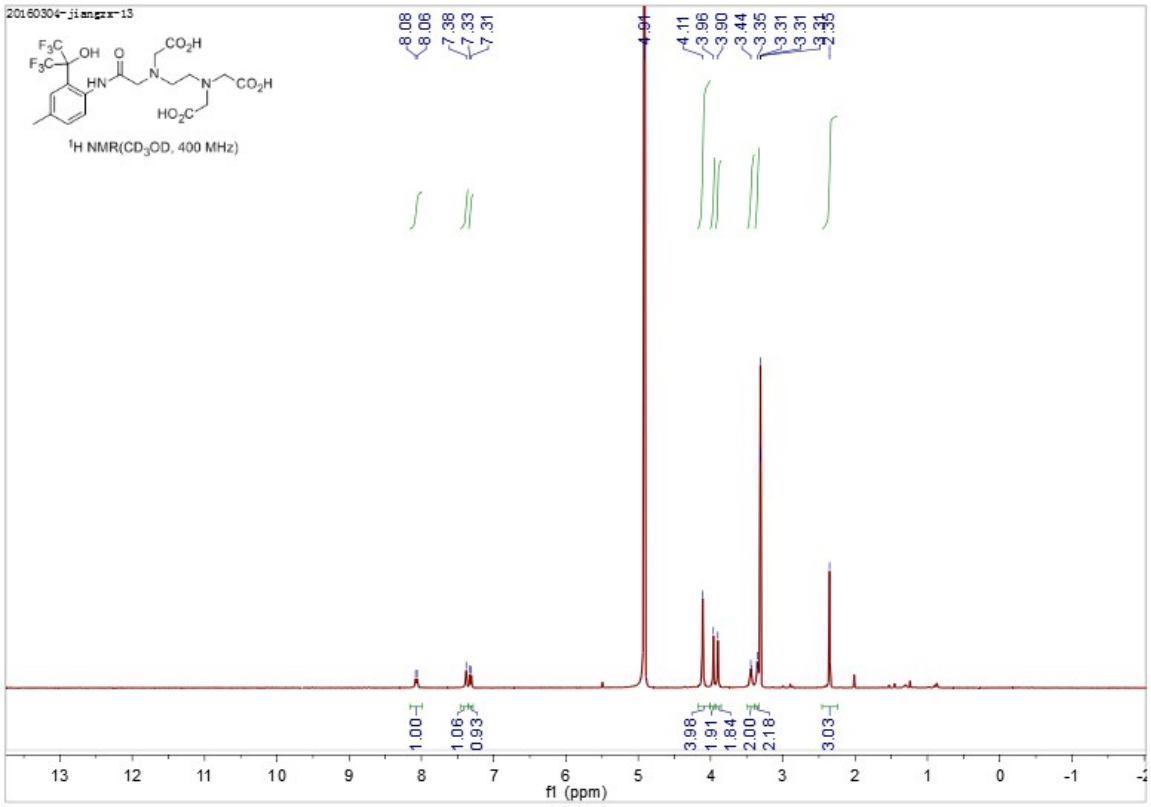


^{19}F NMR of compound **7**

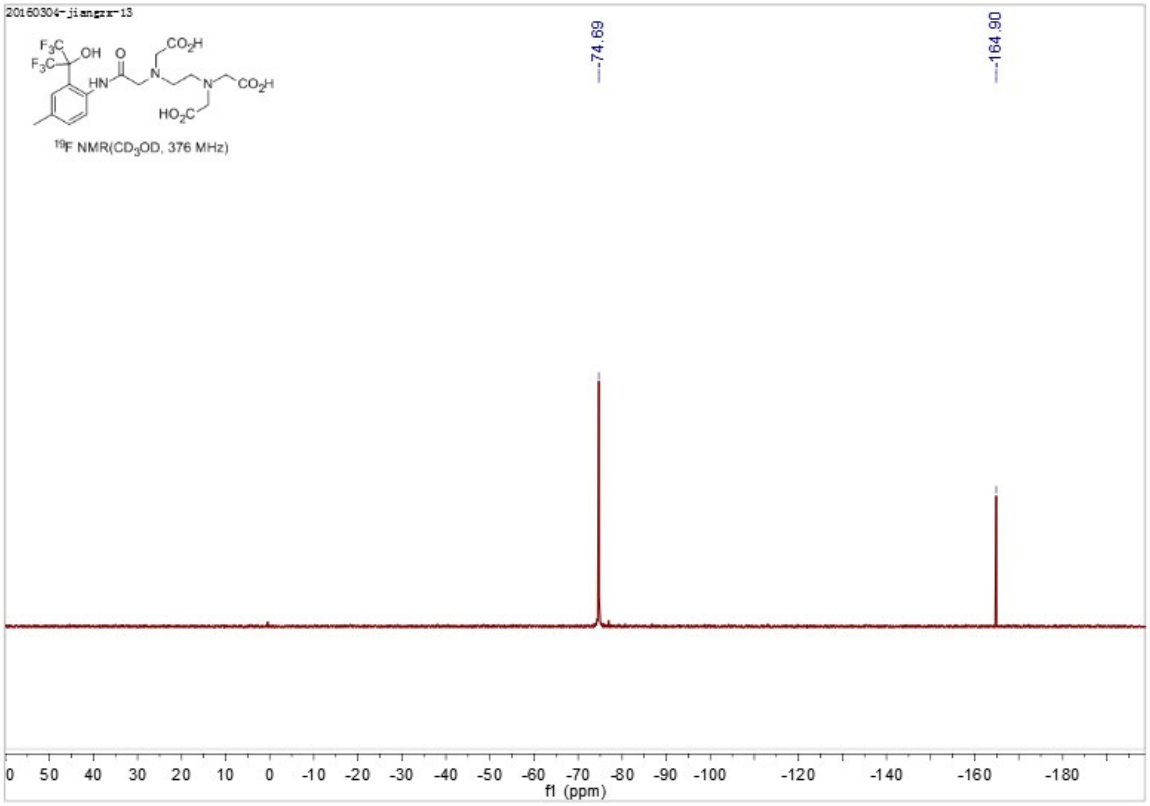


1

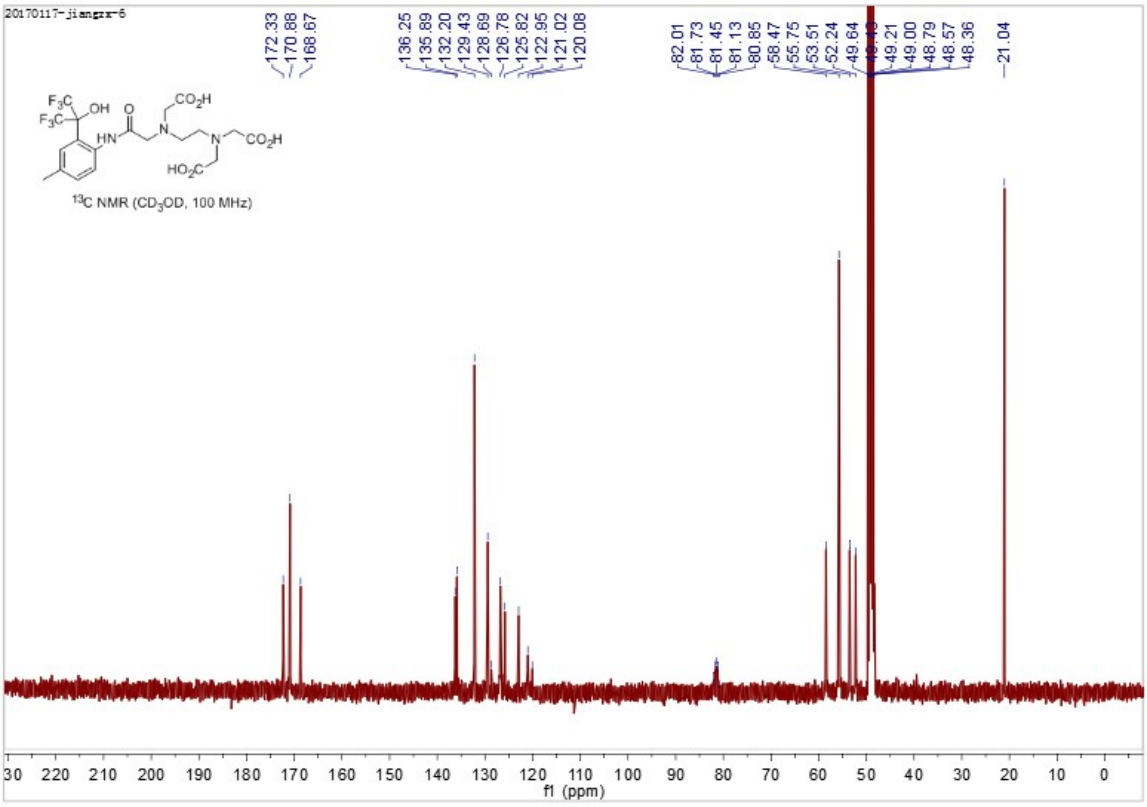
H NMR of compound **1**



^{19}F NMR of compound **1**



^{13}C NMR of compound **1**



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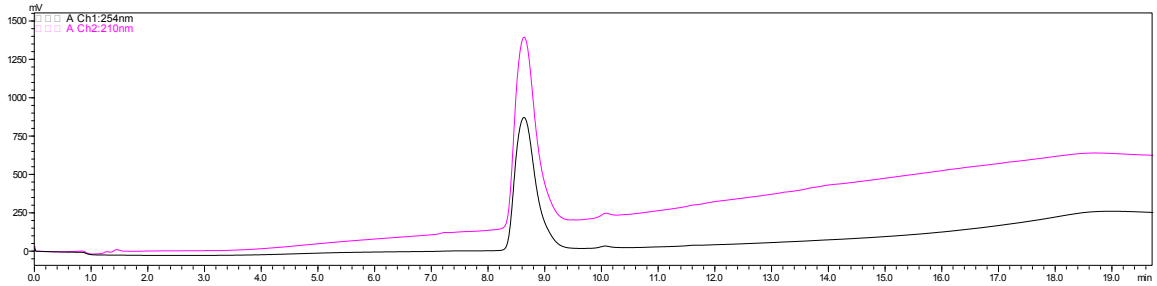
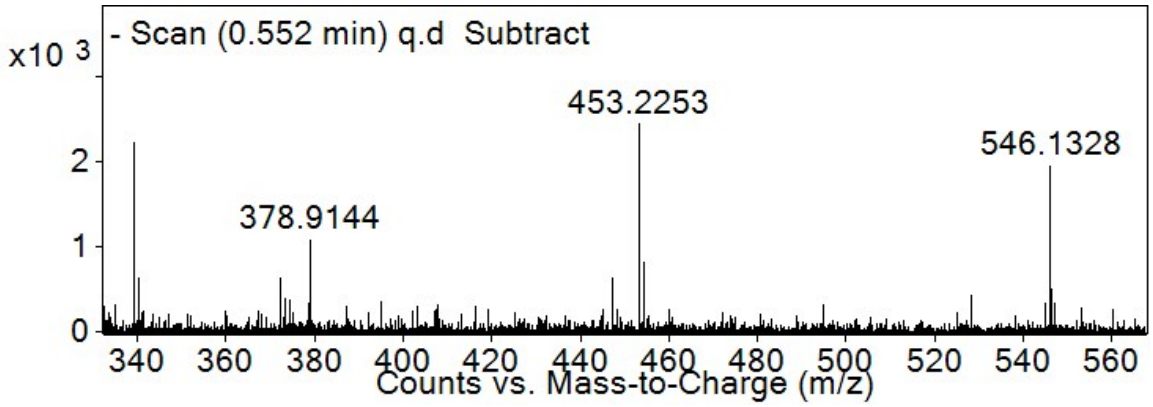
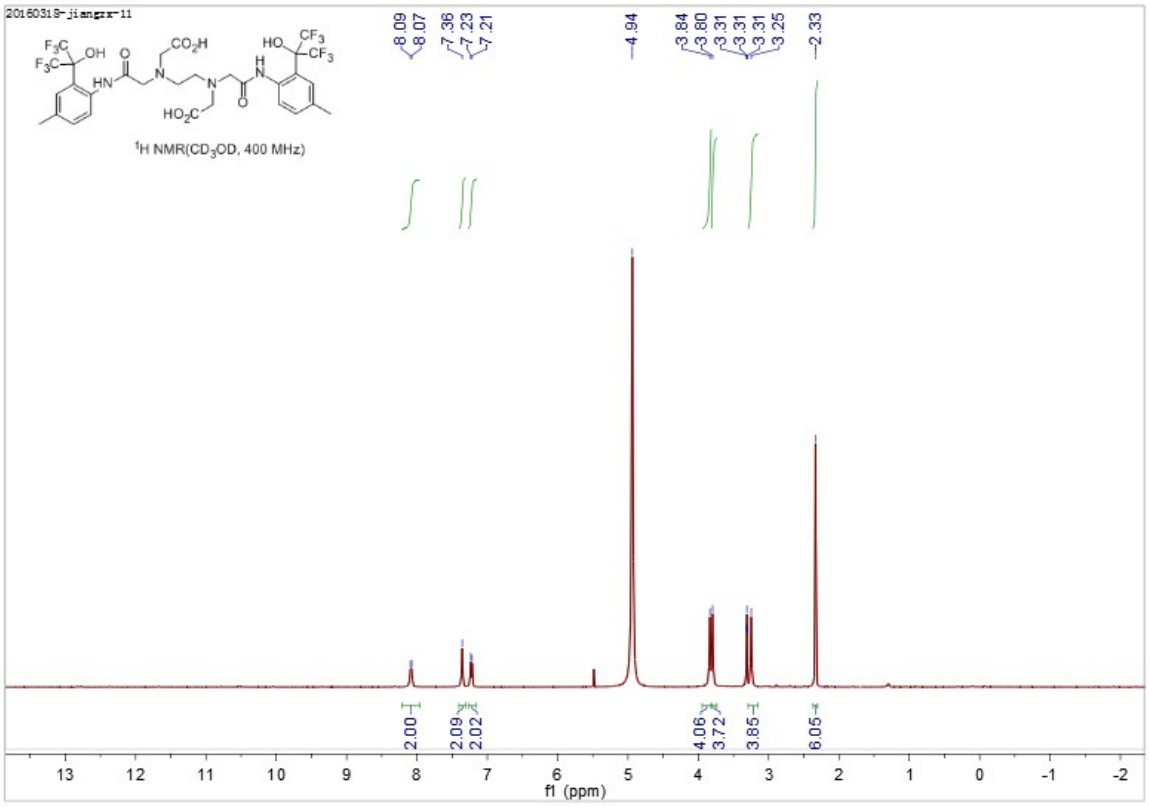


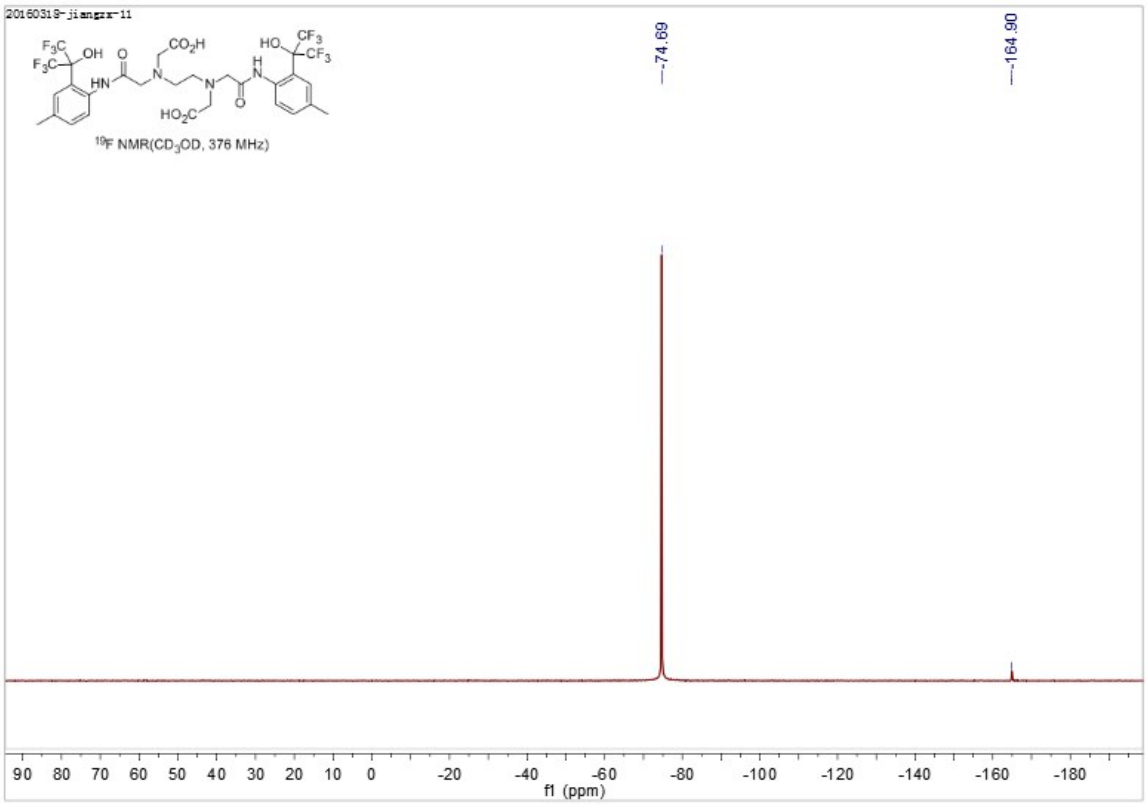
HRMS of compound **1**



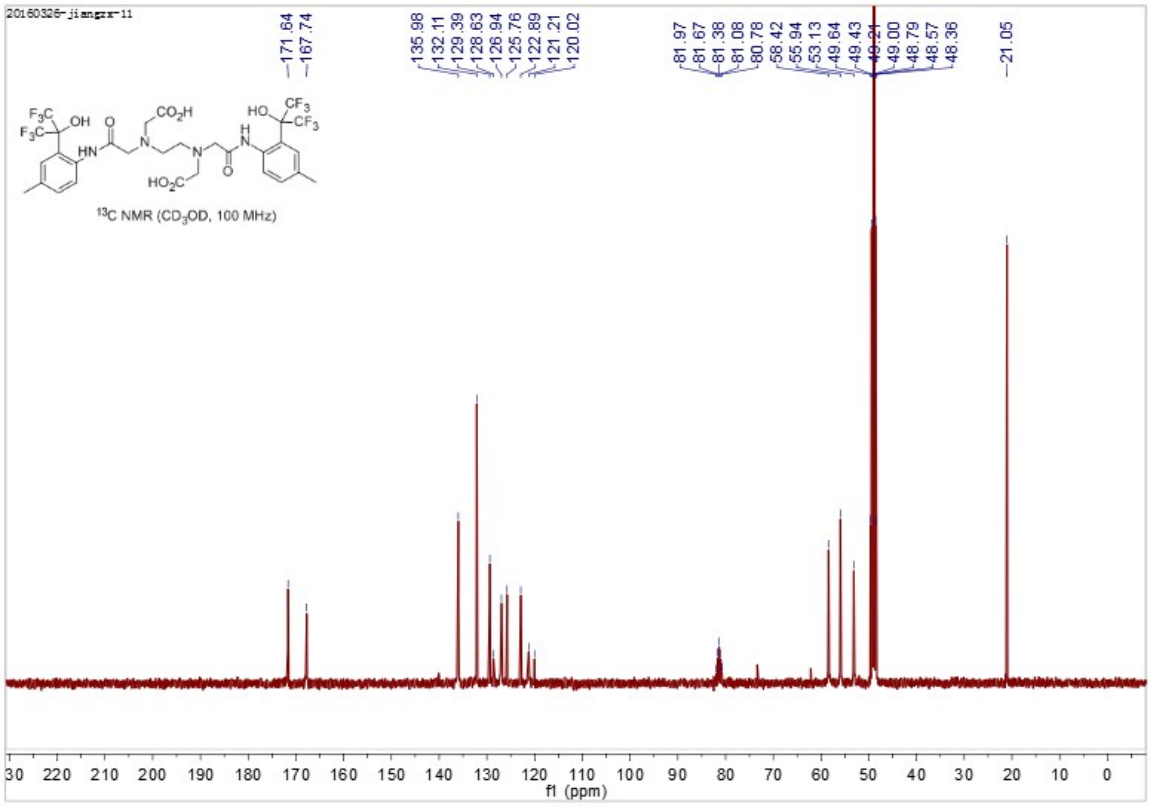
^{1}H NMR of compound **2**



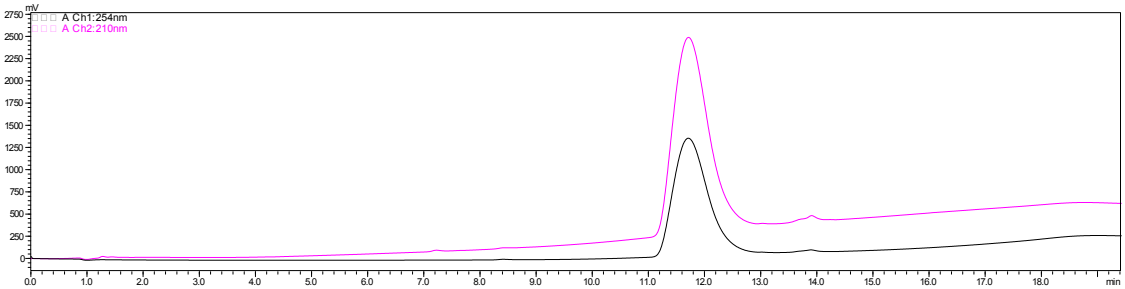
^{19}F NMR of compound **2**



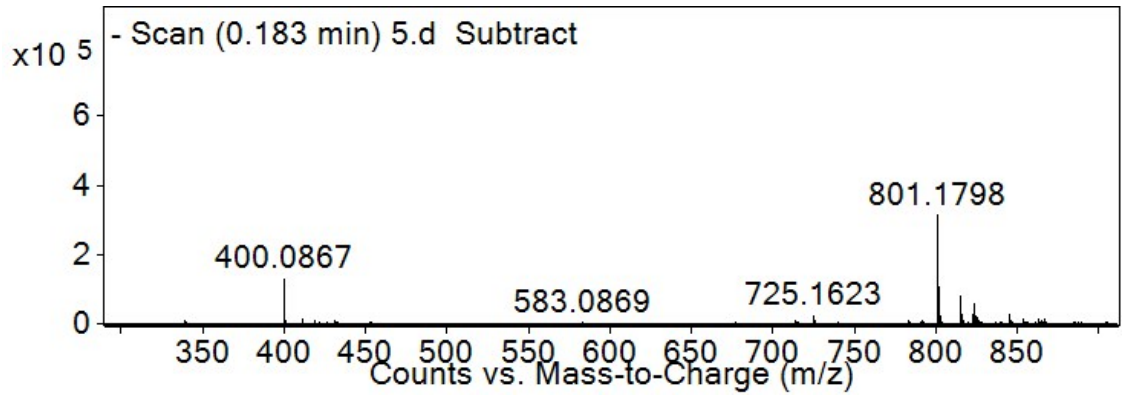
^{13}C NMR of compound **2**



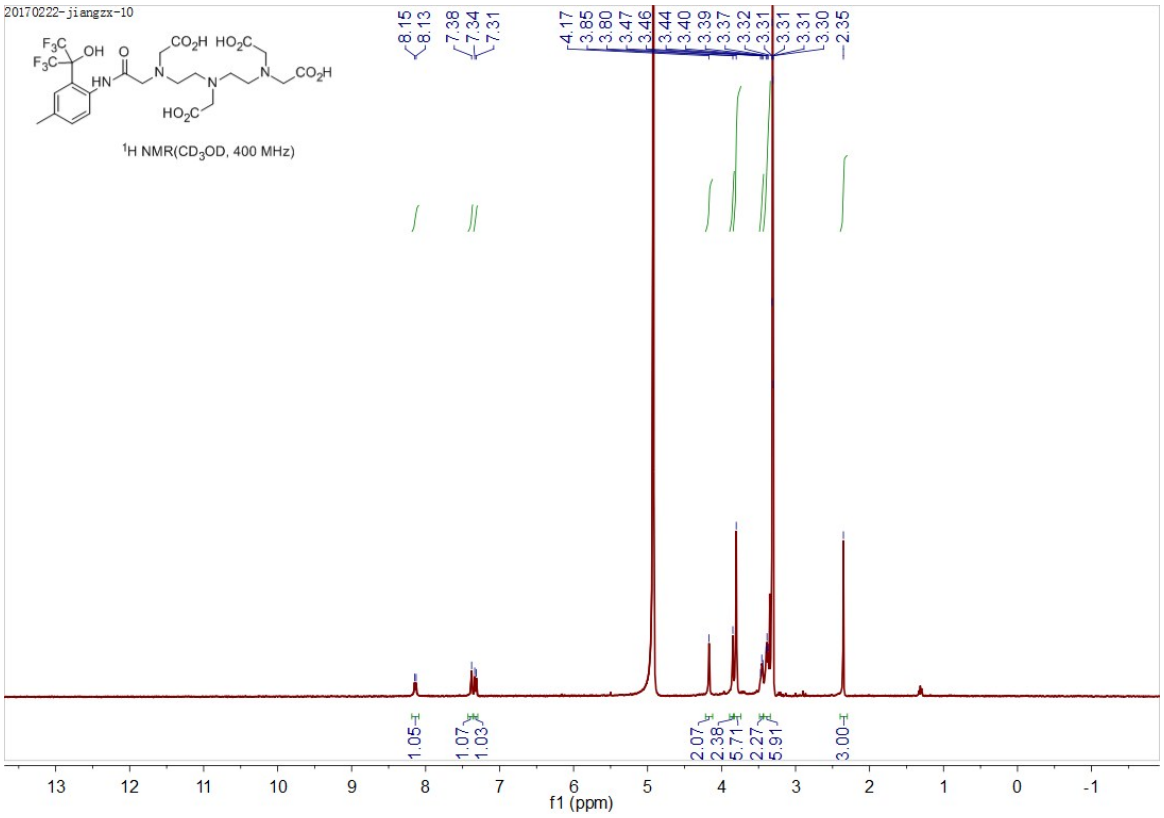
HPLC of compound **2**



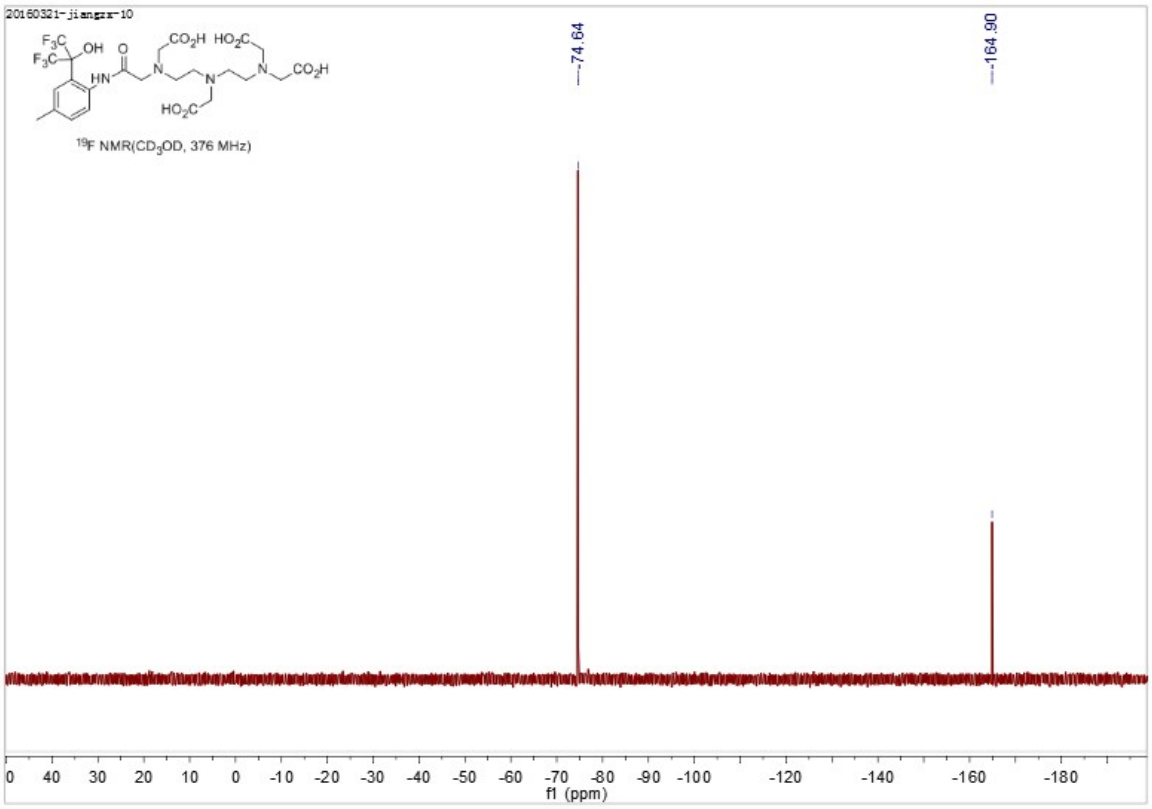
HRMS of compound **2**



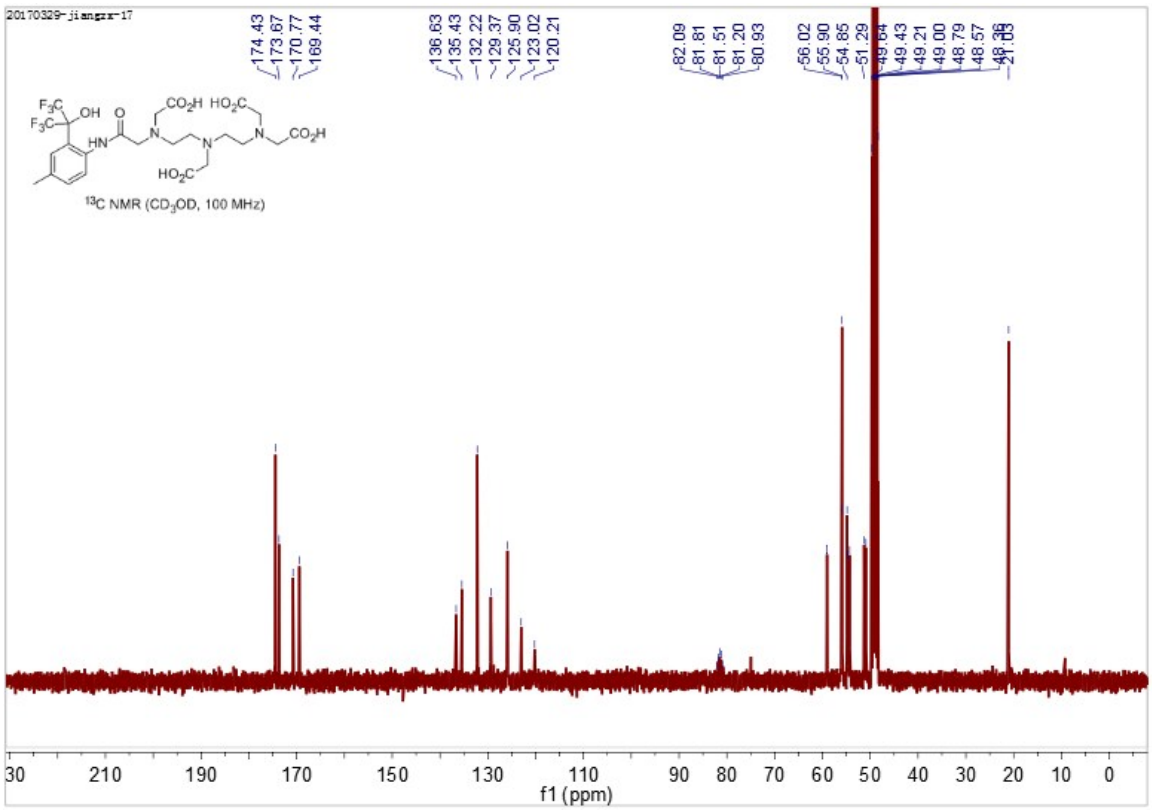
^{1}H NMR of compound **3**



^{19}F NMR of compound **3**



^{13}C NMR of compound **3**



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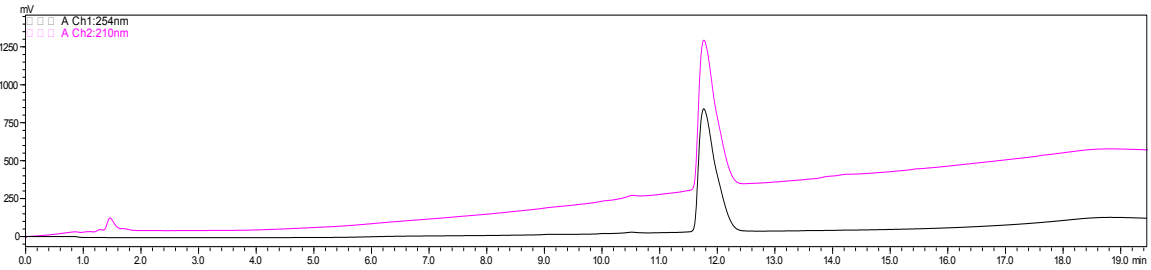

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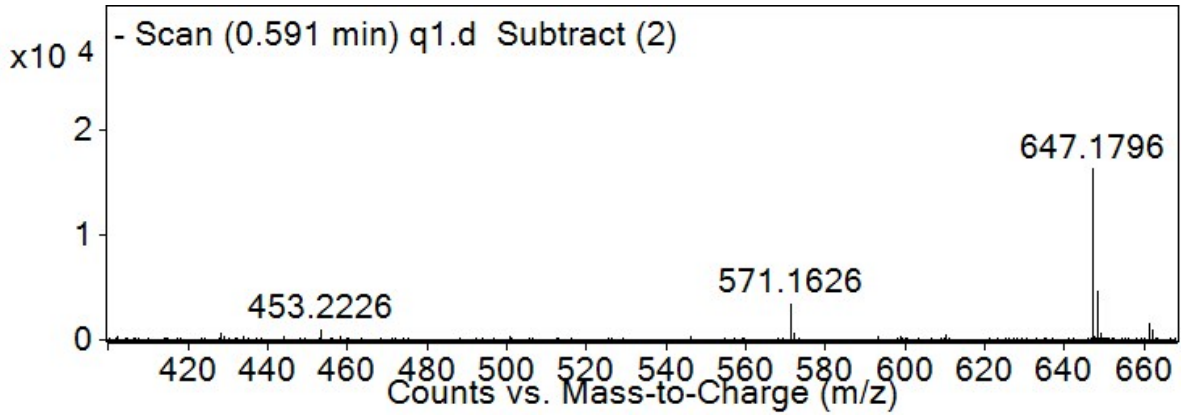
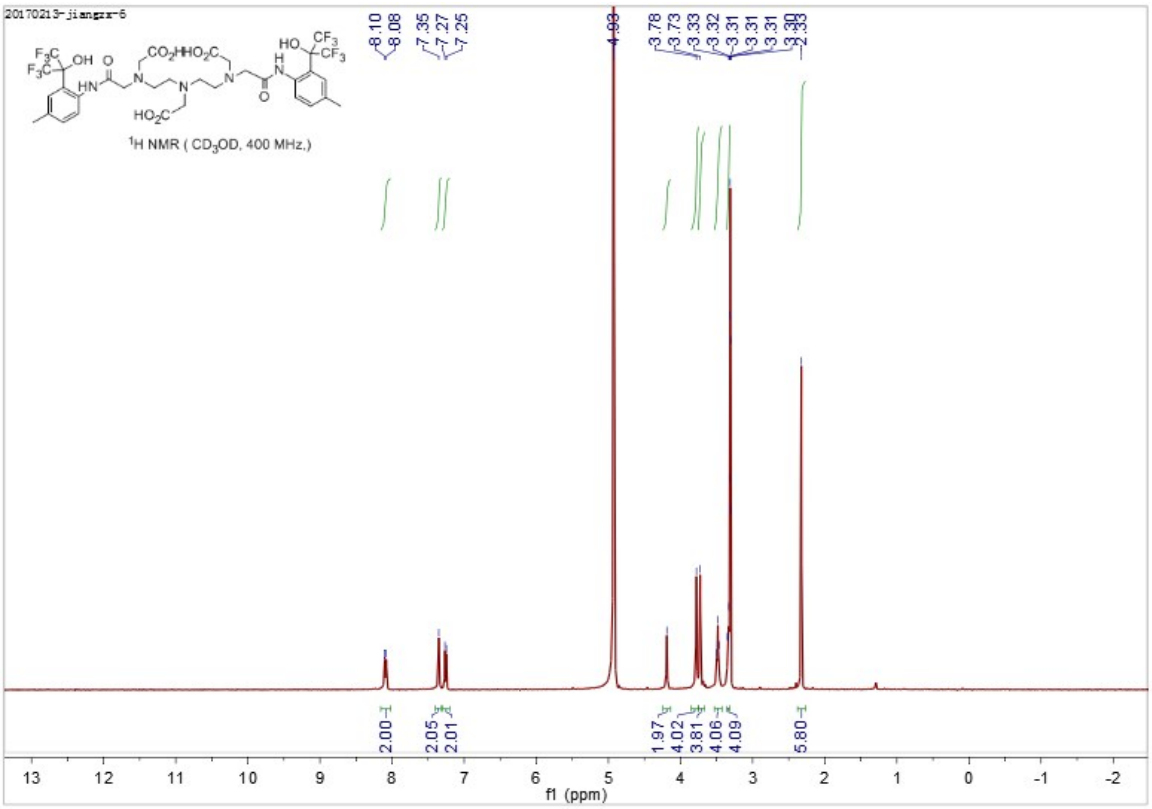


^{1}H NMR of compound **4**



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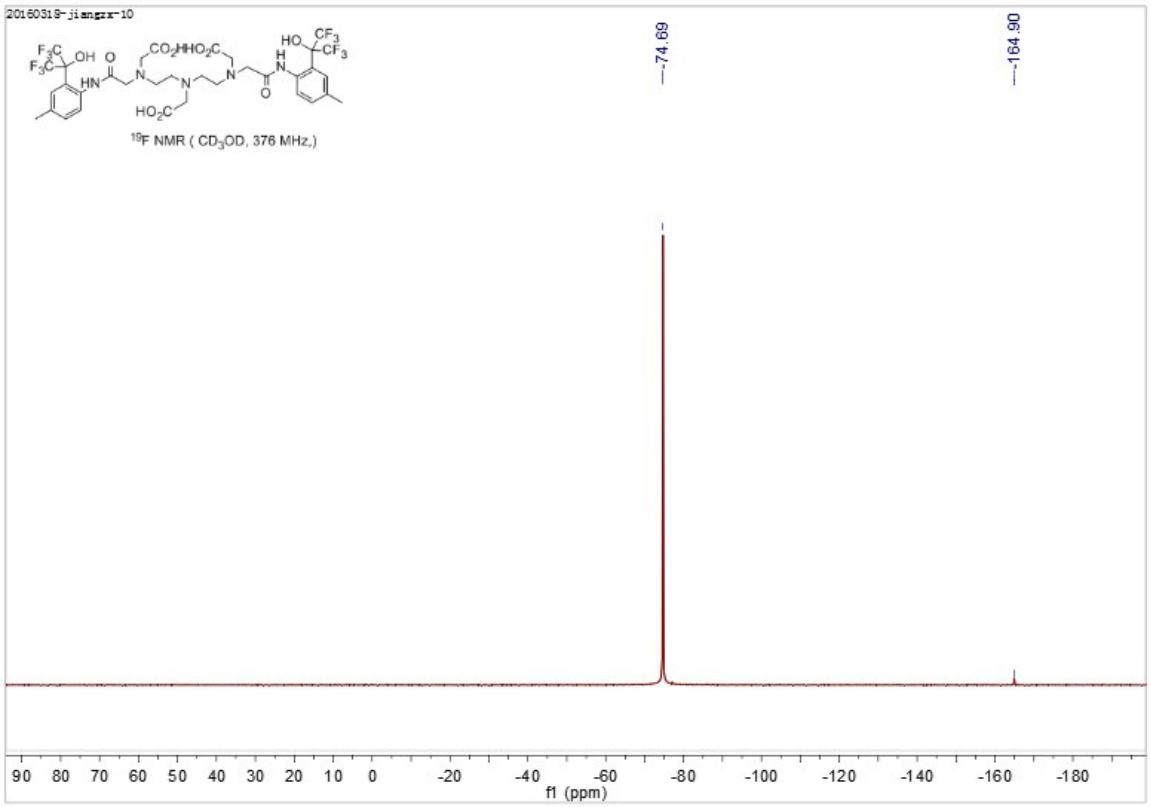

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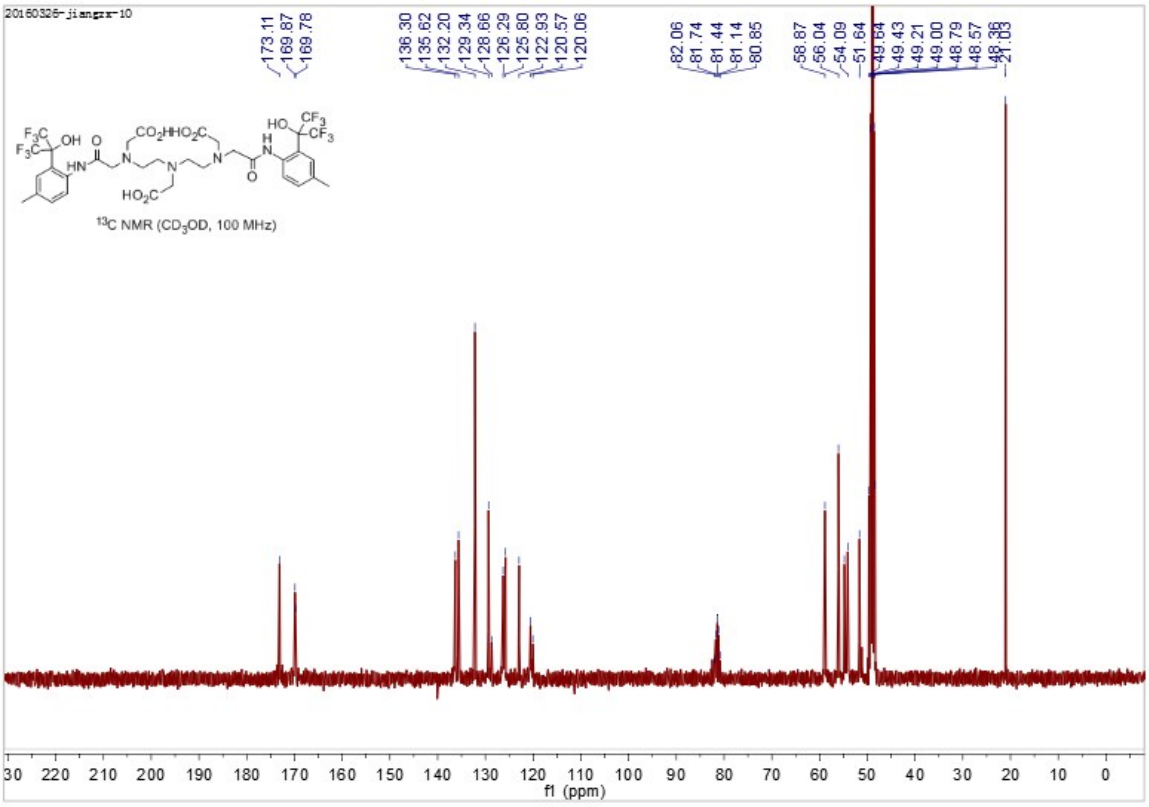

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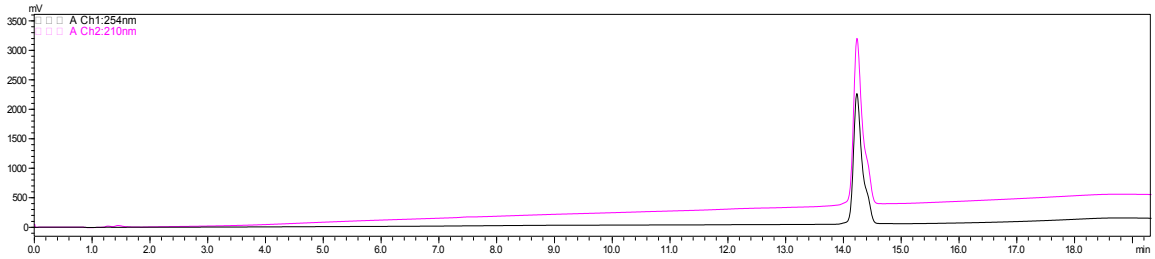

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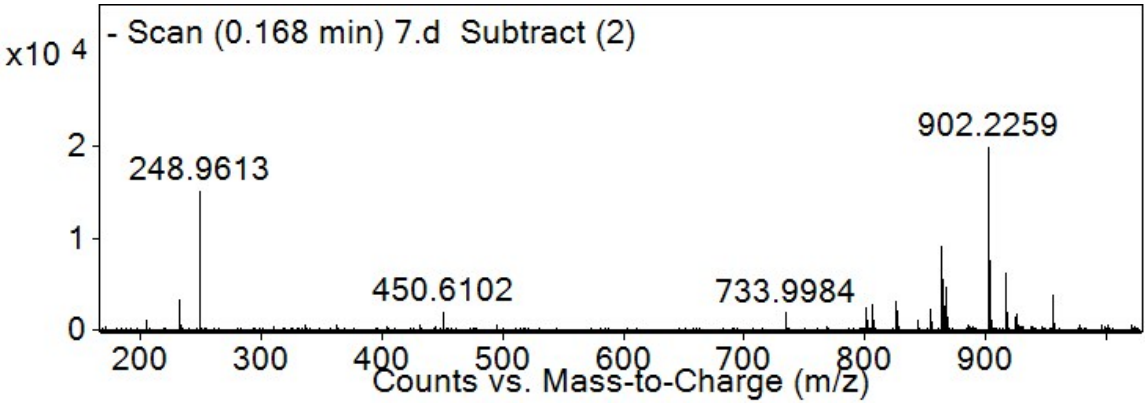
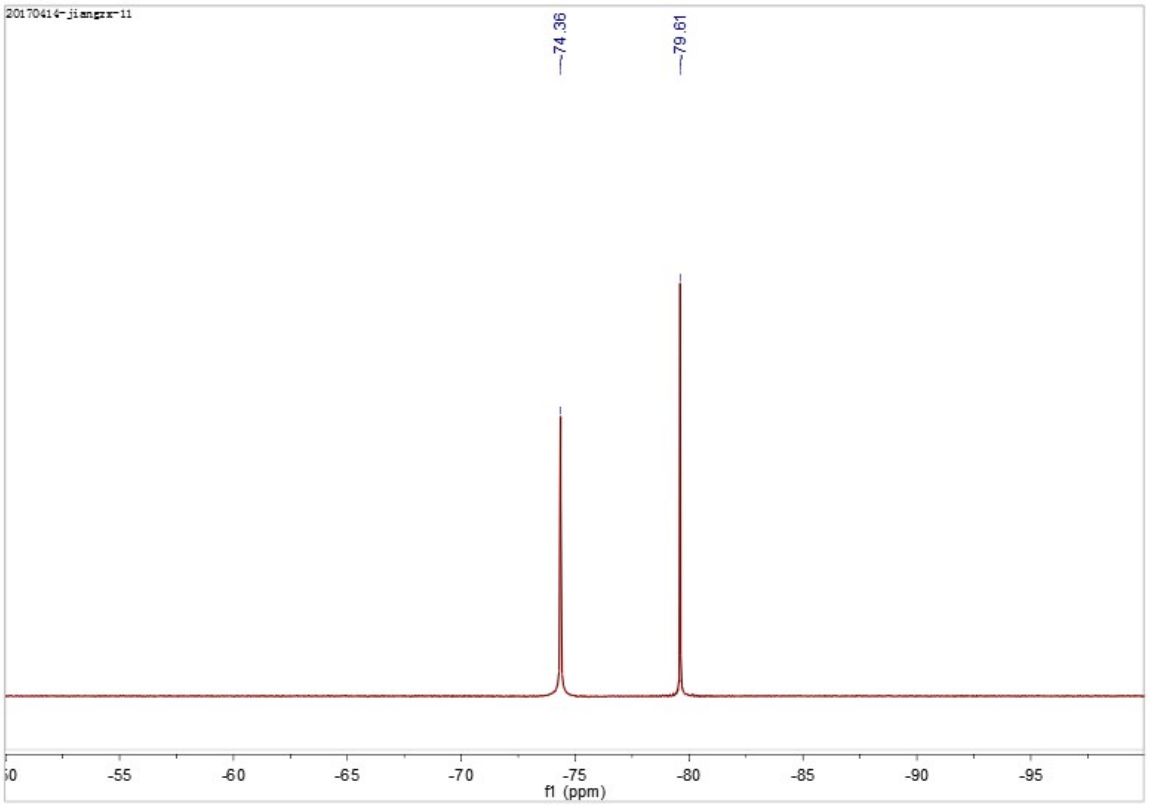
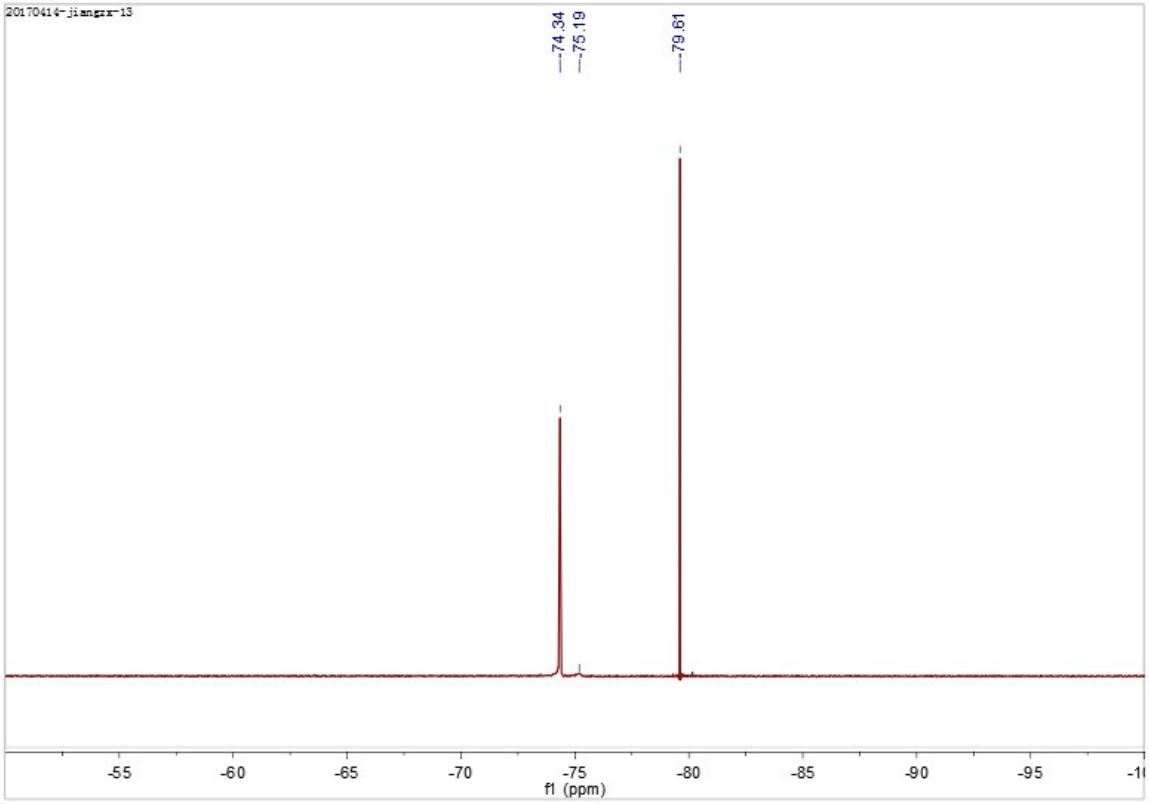


5. Original ^{19}F NMR spectra of the figures in the article

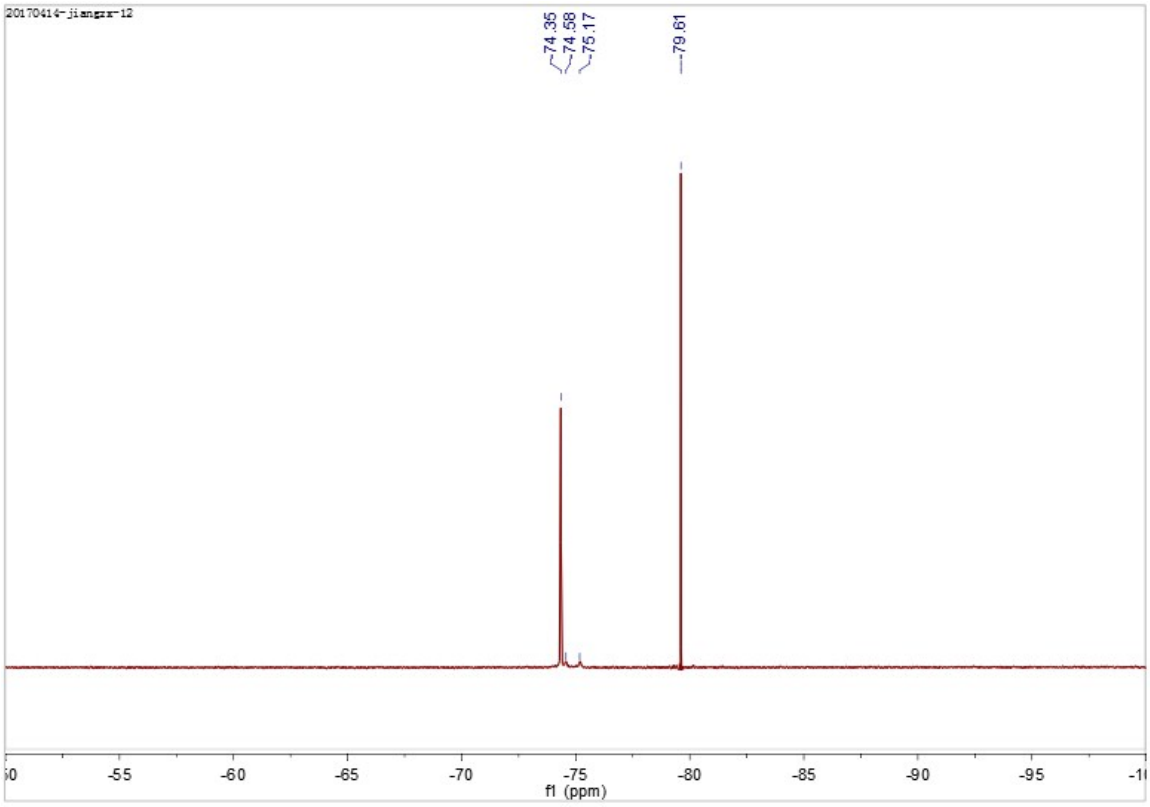
^{19}F NMR (4 mM **1**)



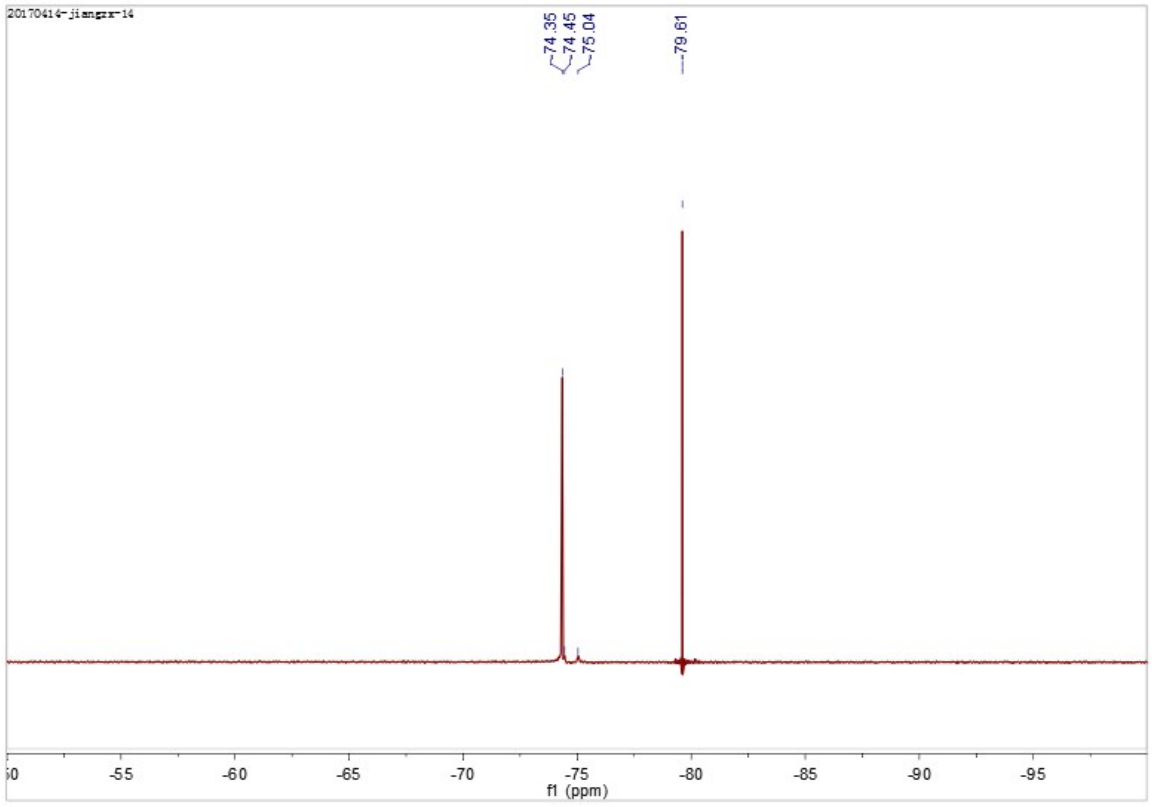
^{19}F NMR (4 mM **1** + 0.8 mM Mg^{2+})



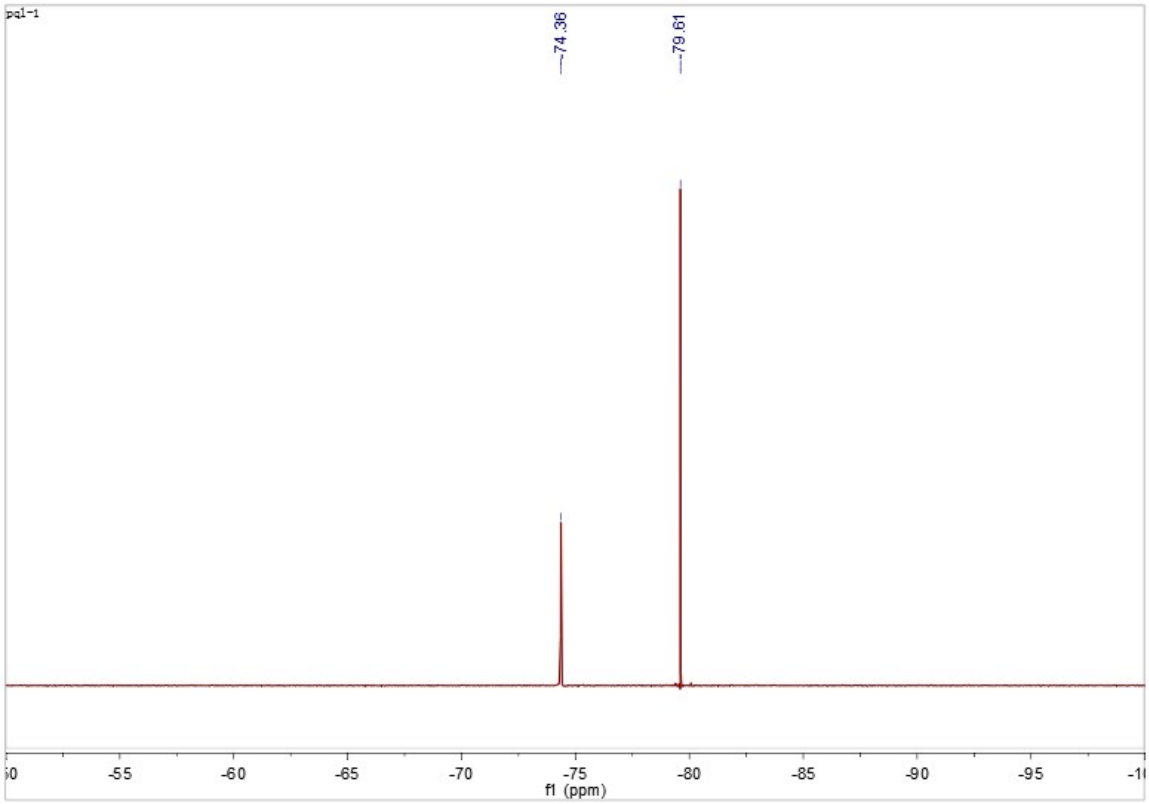
^{19}F NMR (4 mM **1** + 0.8 mM Ca^{2+})



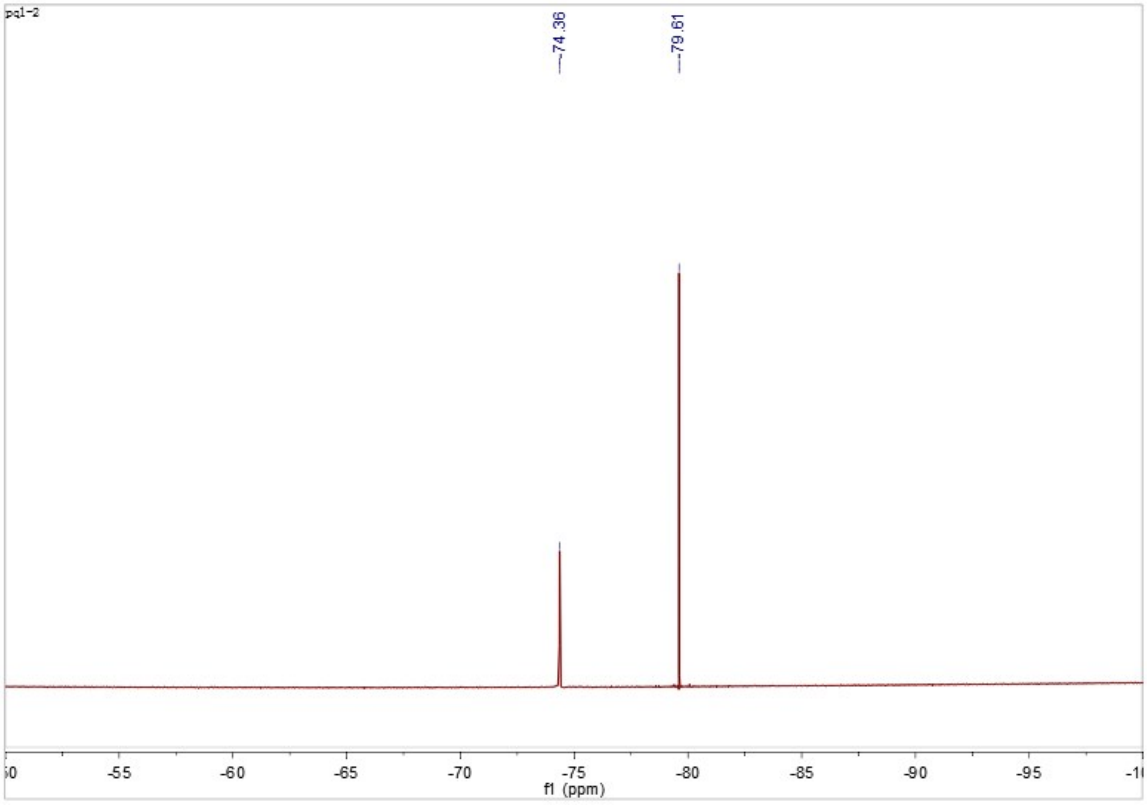
^{19}F NMR (4 mM **1** + 0.8 mM Zn^{2+})



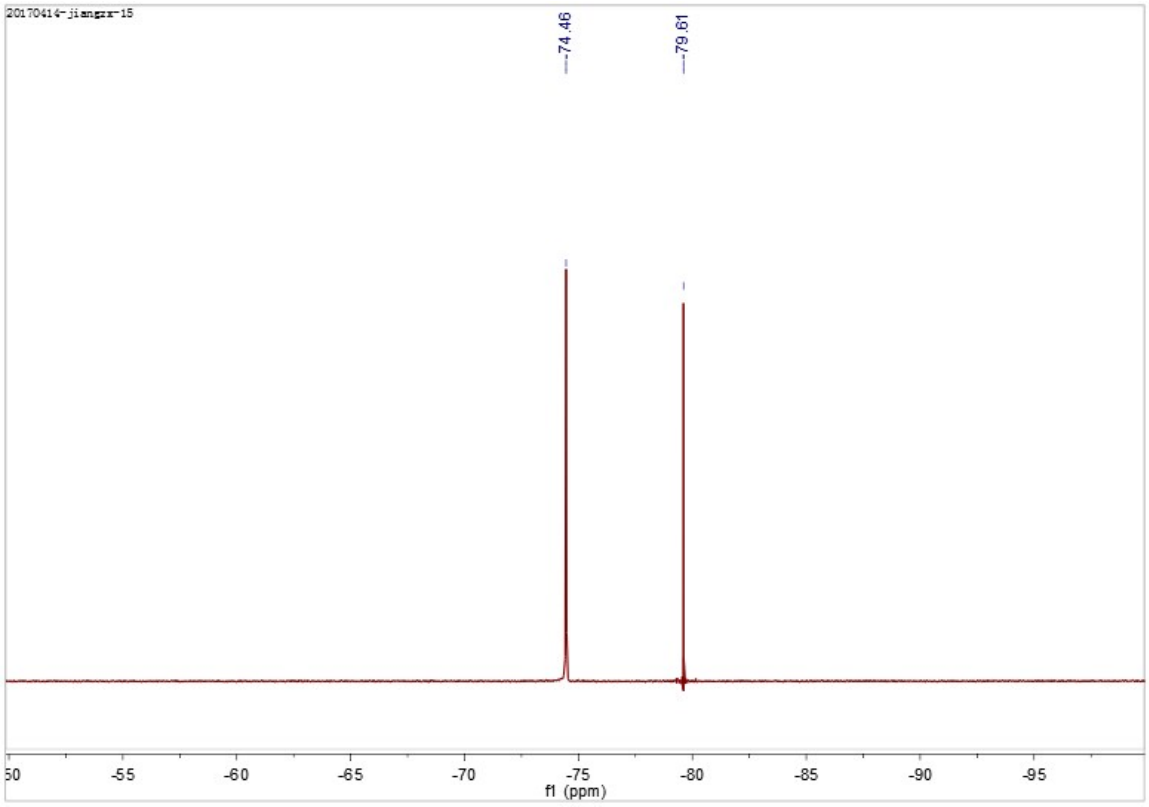
^{19}F NMR (4 mM **1** + 0.8 mM Cu^{2+})



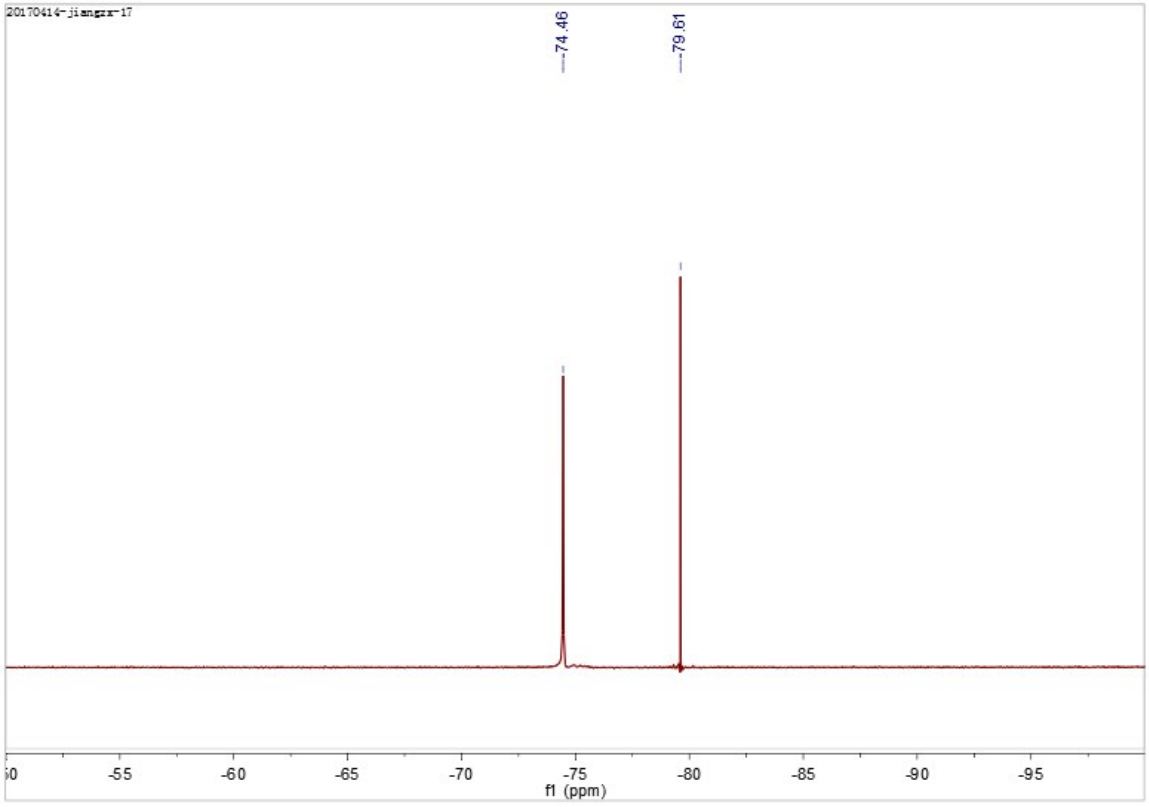
^{19}F NMR (4 mM **1** + 0.8 mM Fe^{3+})



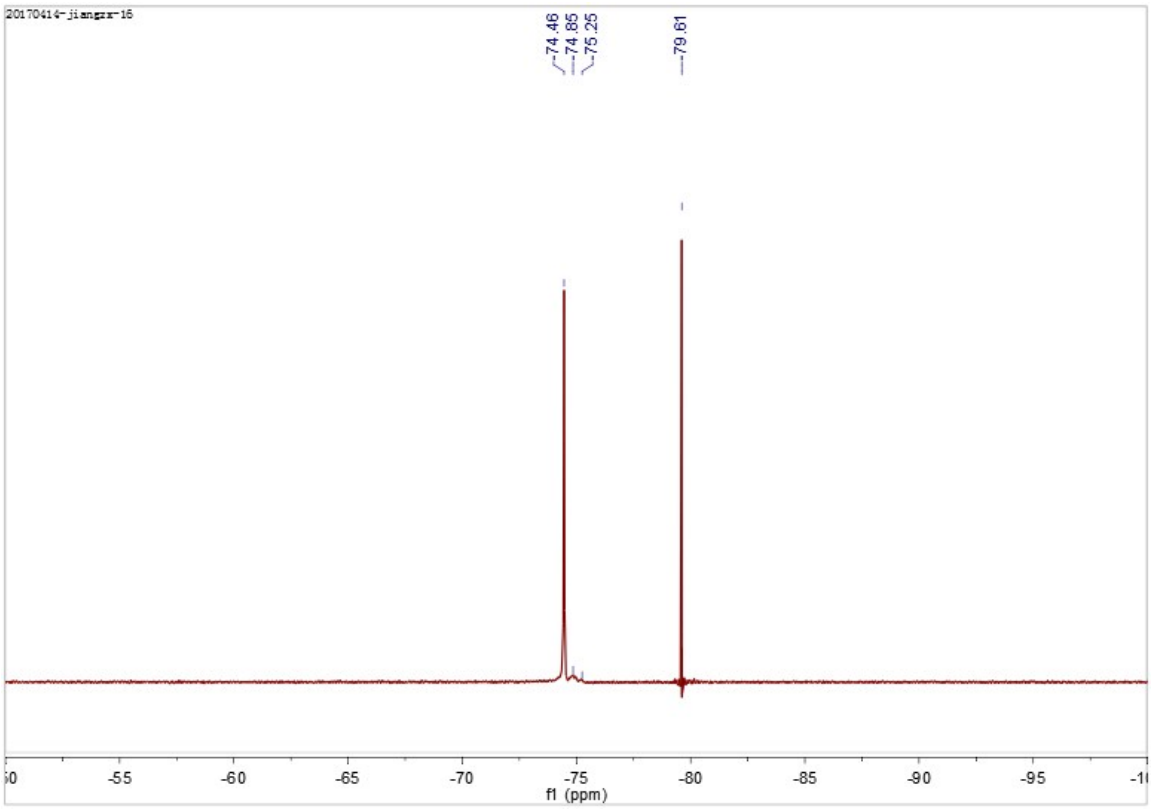
^{19}F NMR (4 mM **2**)



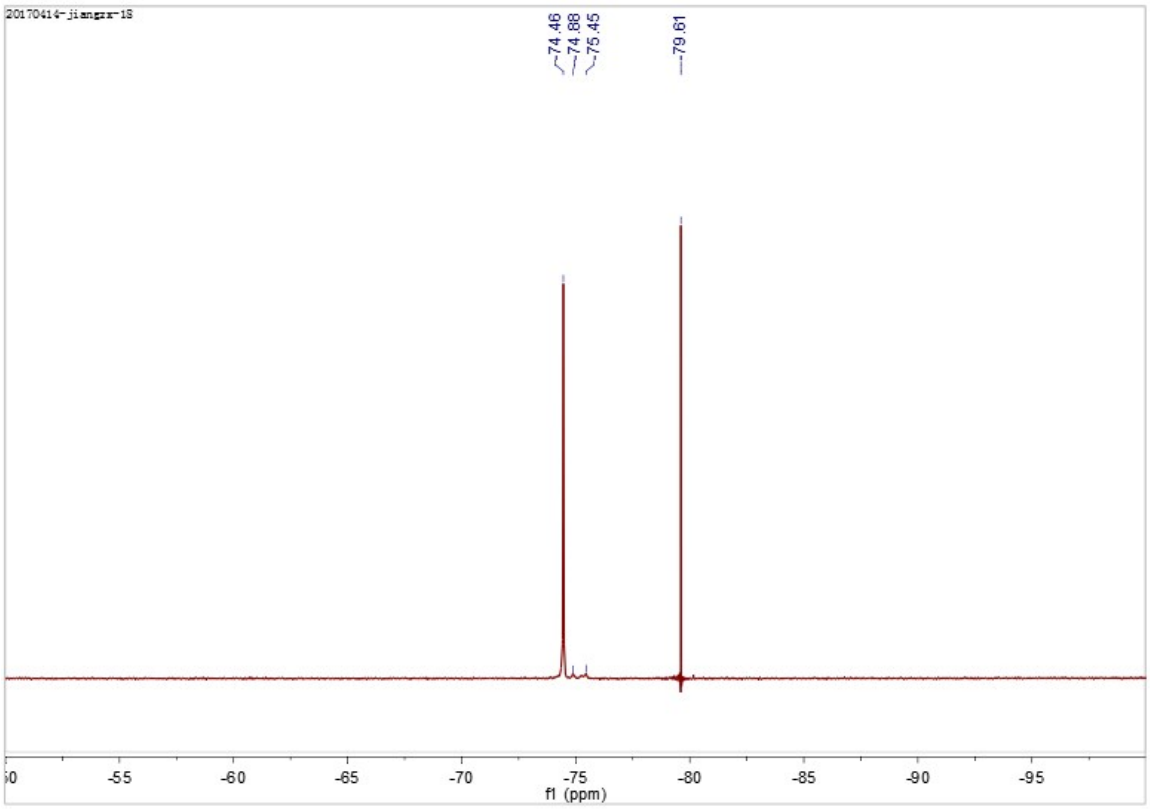
^{19}F NMR (4 mM **2** + 0.8 mM Mg^{2+})



^{19}F NMR (4 mM **2** + 0.8 mM Ca^{2+})



^{19}F NMR (4 mM **2** + 0.8 mM Zn^{2+})



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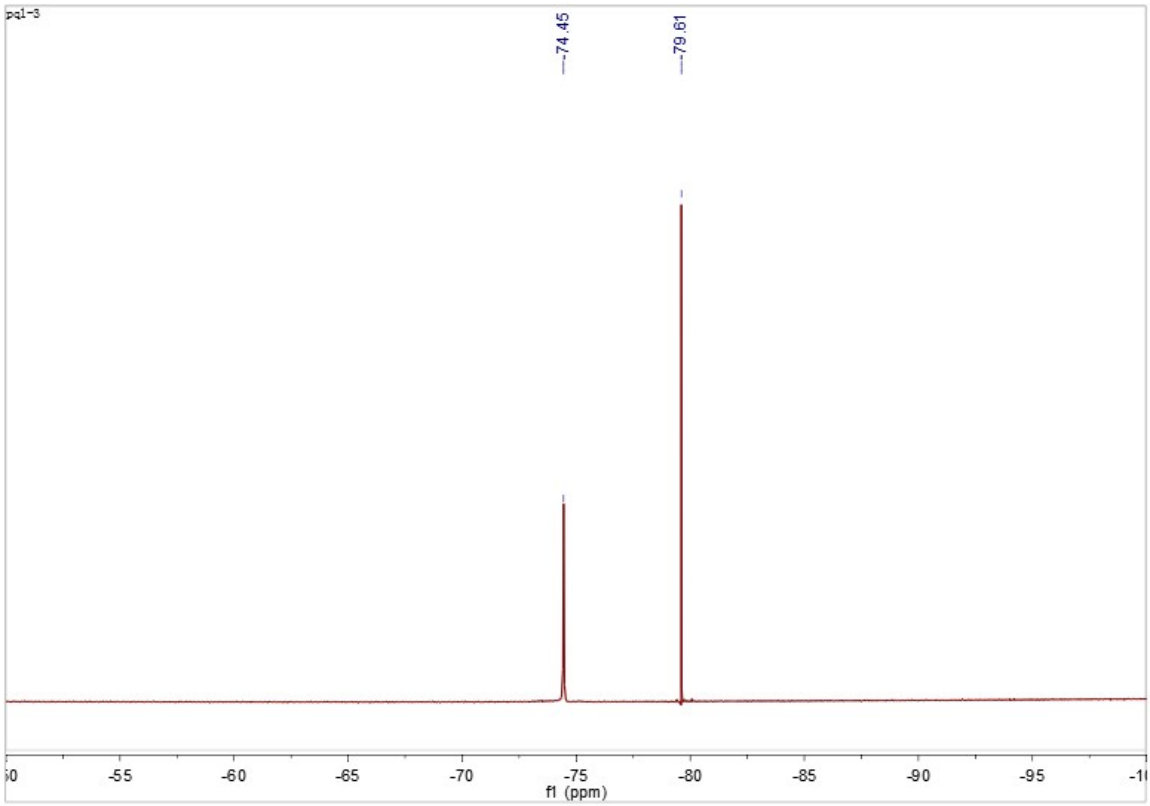
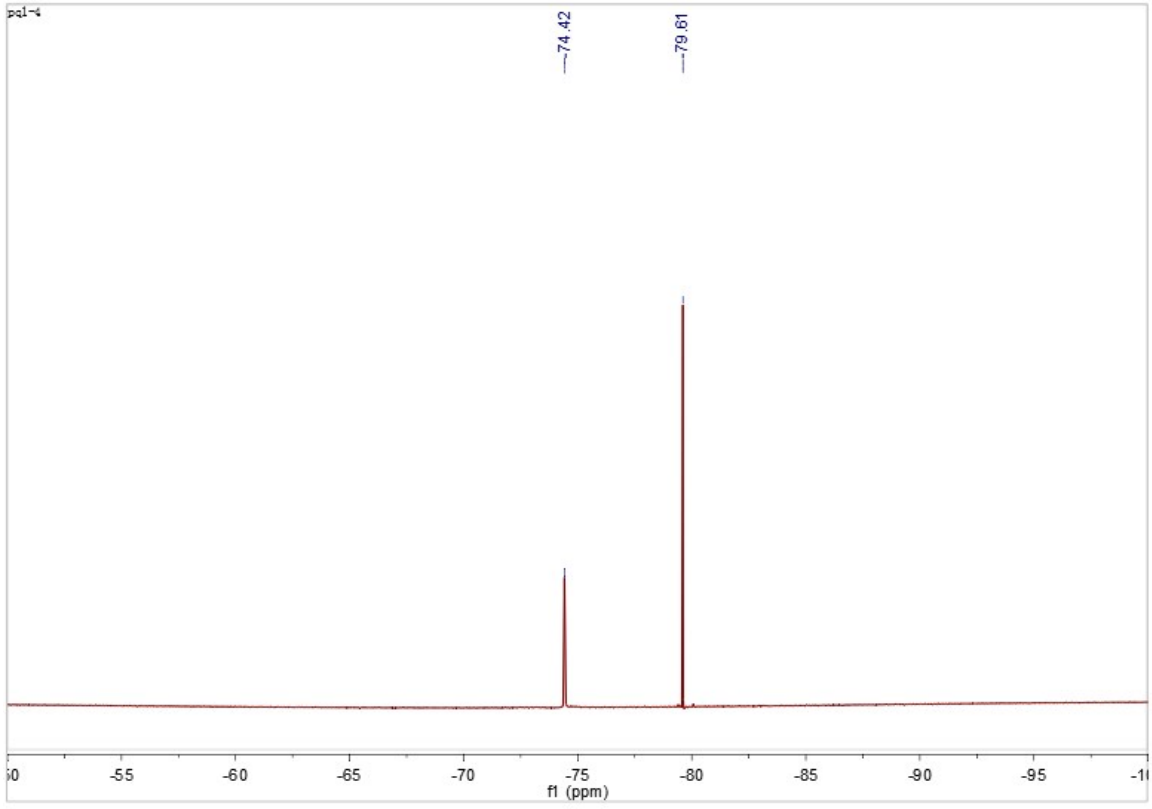
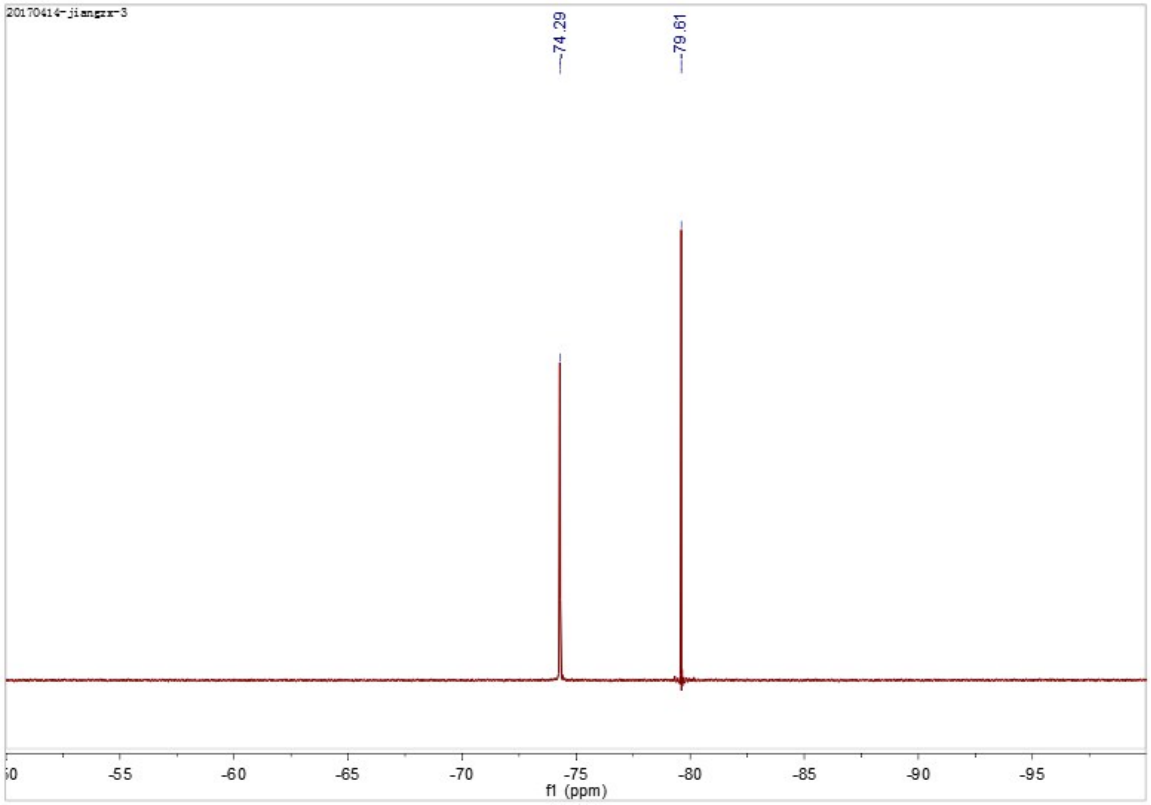


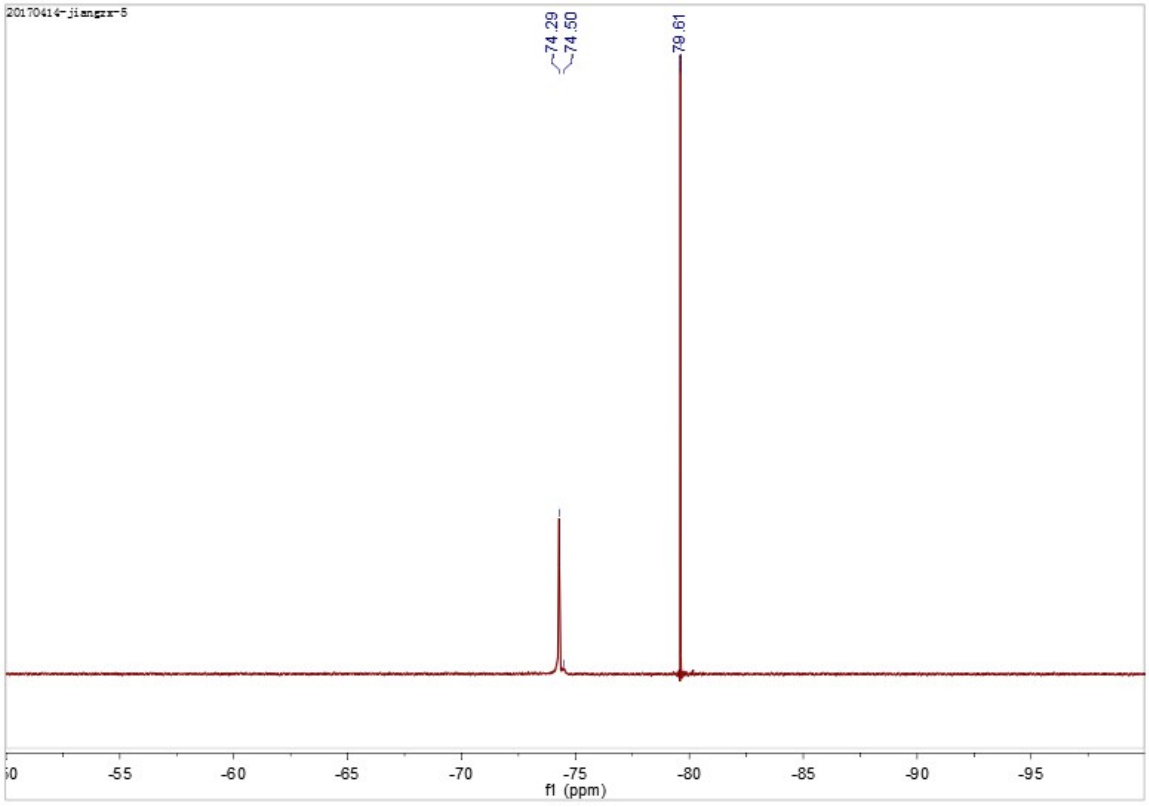
^{19}F NMR (4 mM **2** + 0.8 mM Fe^{3+})



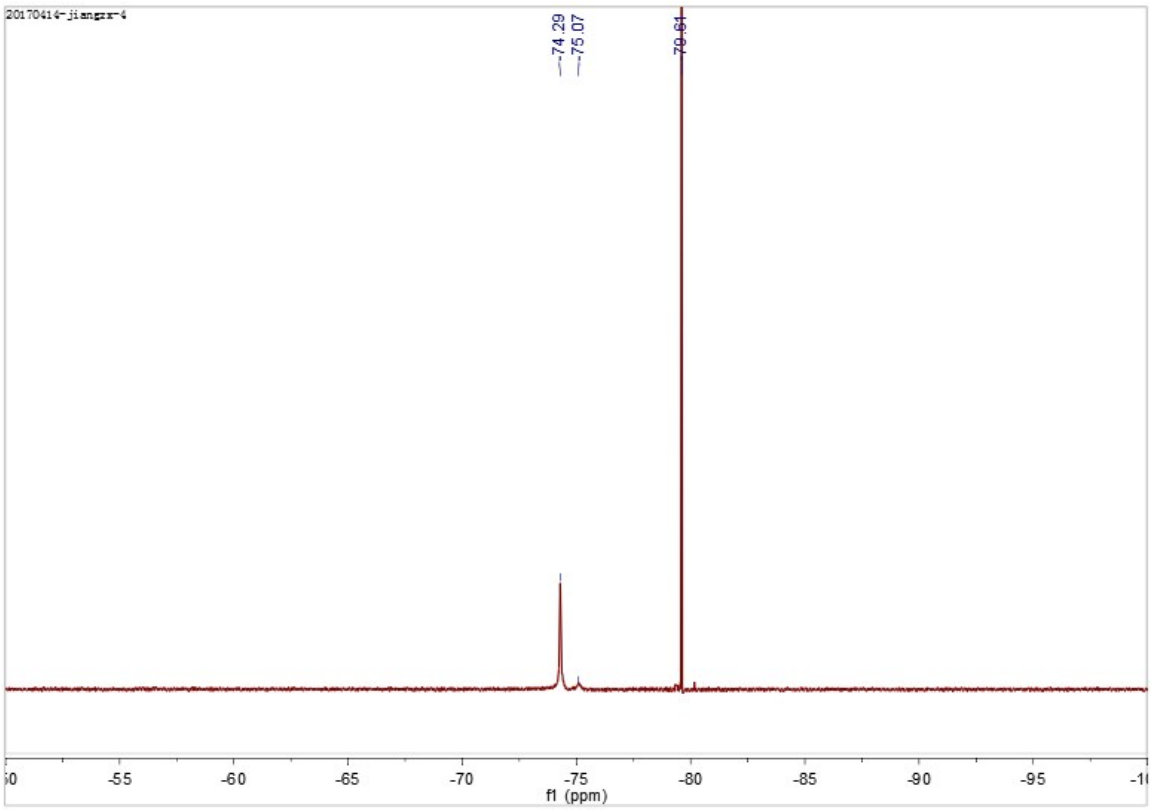
^{19}F NMR (4 mM **3**)



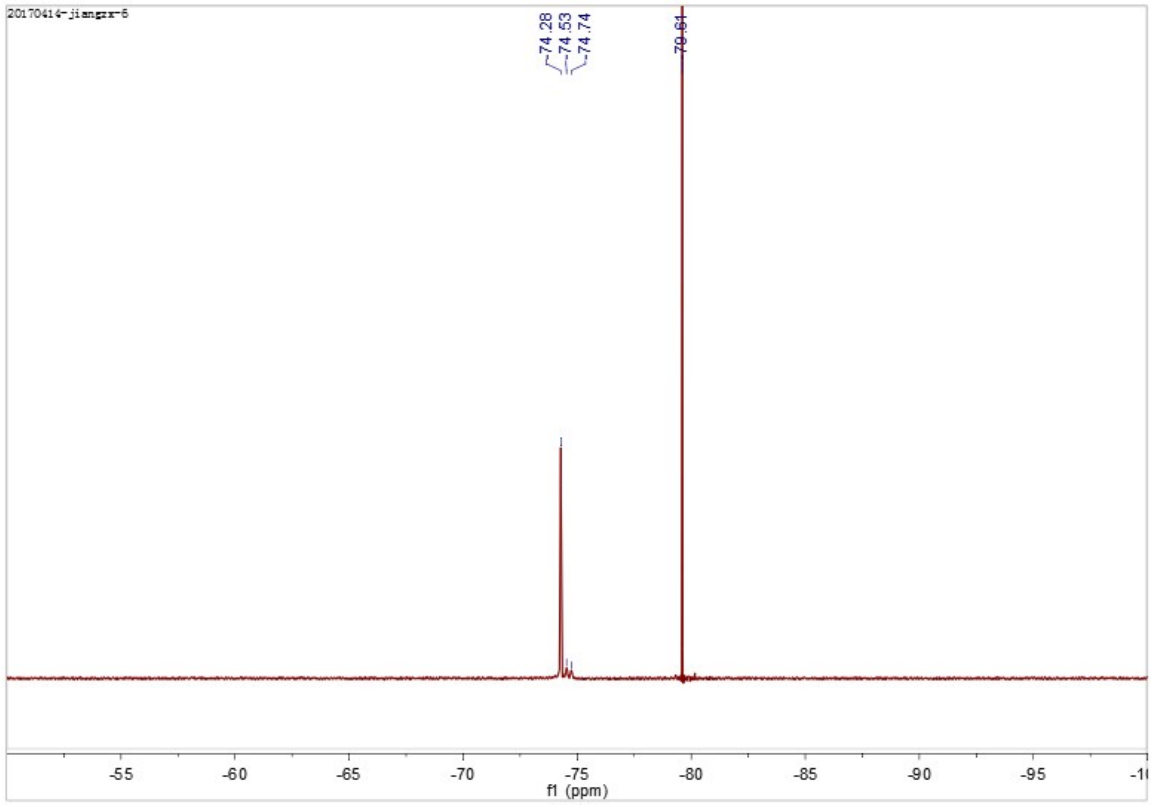
^{19}F NMR (4 mM **3** + 0.8 mM Mg^{2+})



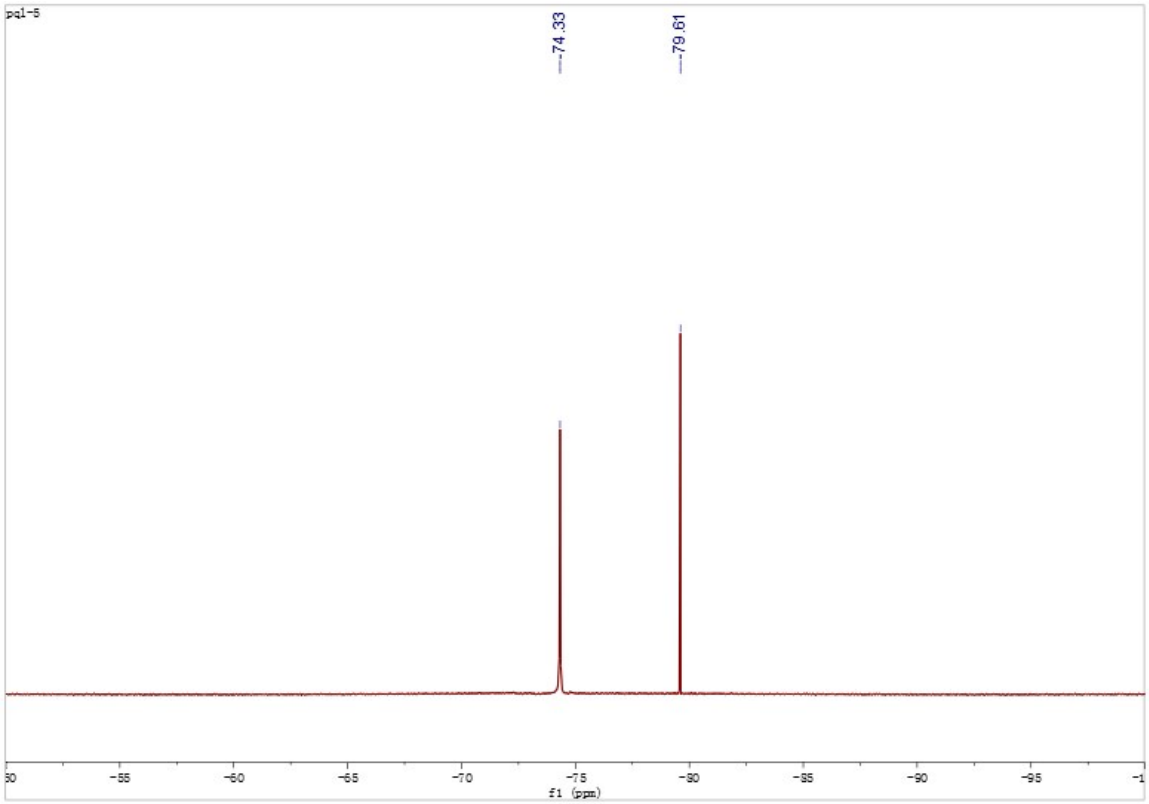
^{19}F NMR (4 mM **3** + 0.8 mM Ca^{2+})



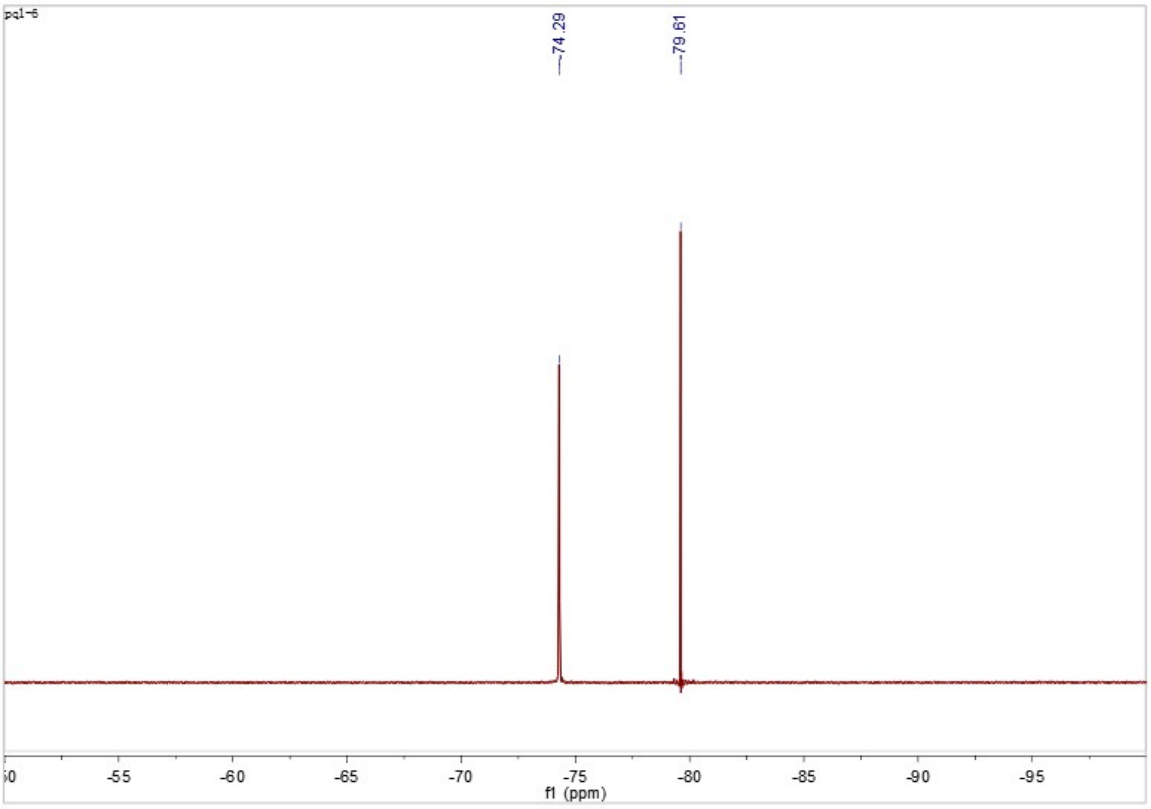
^{19}F NMR (4 mM **3** + 0.8 mM Zn^{2+})



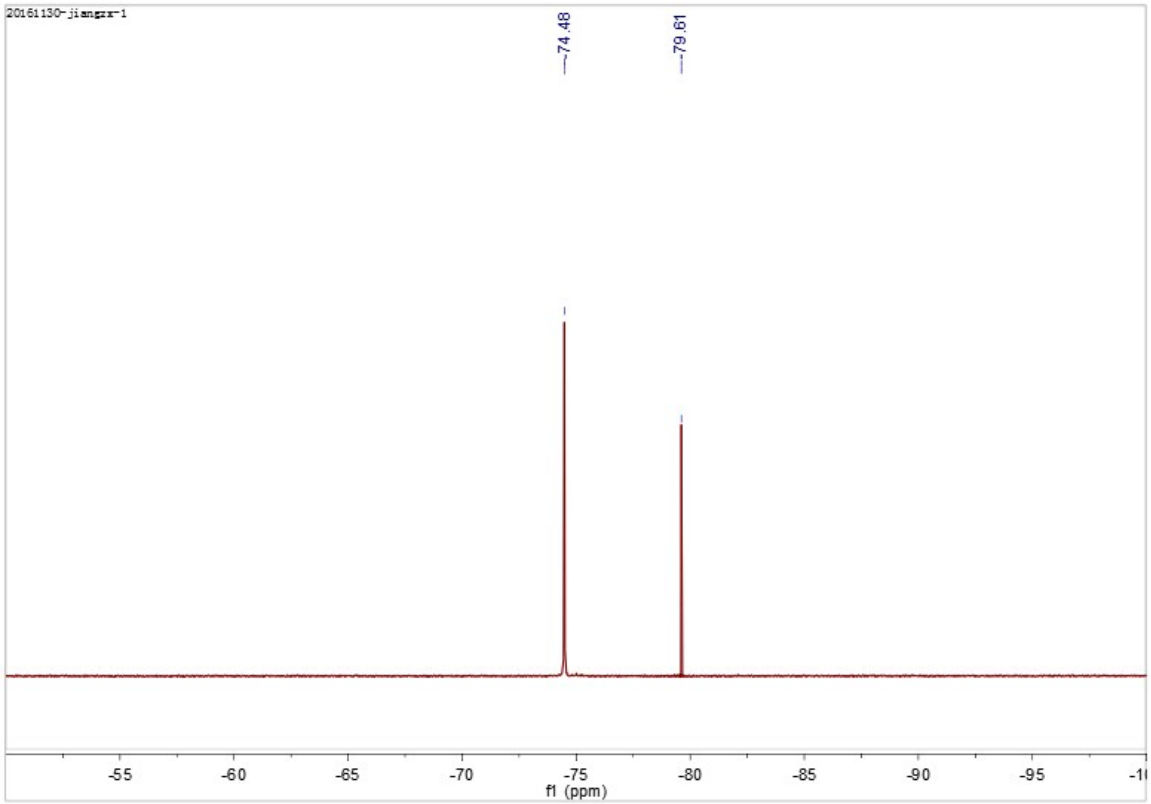
^{19}F NMR (4 mM **3** + 0.8 mM Cu^{2+})



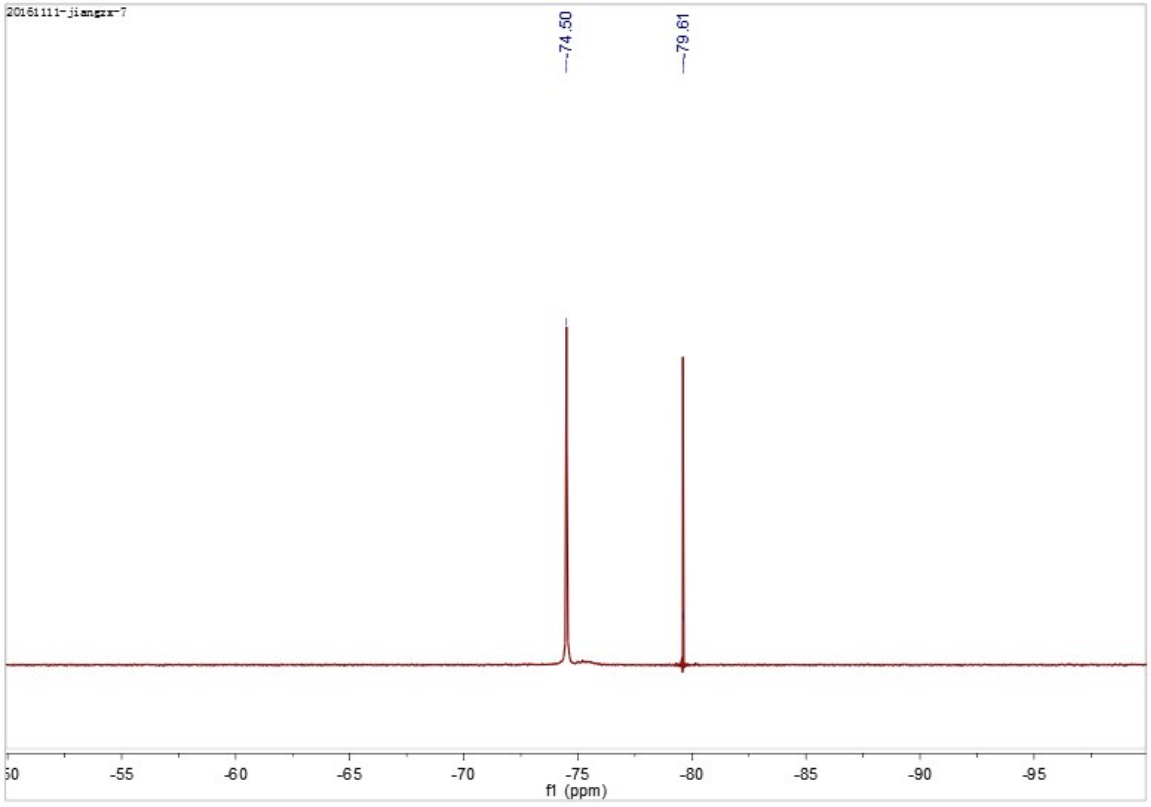
^{19}F NMR (4 mM **3** + 0.8 mM Fe^{3+})



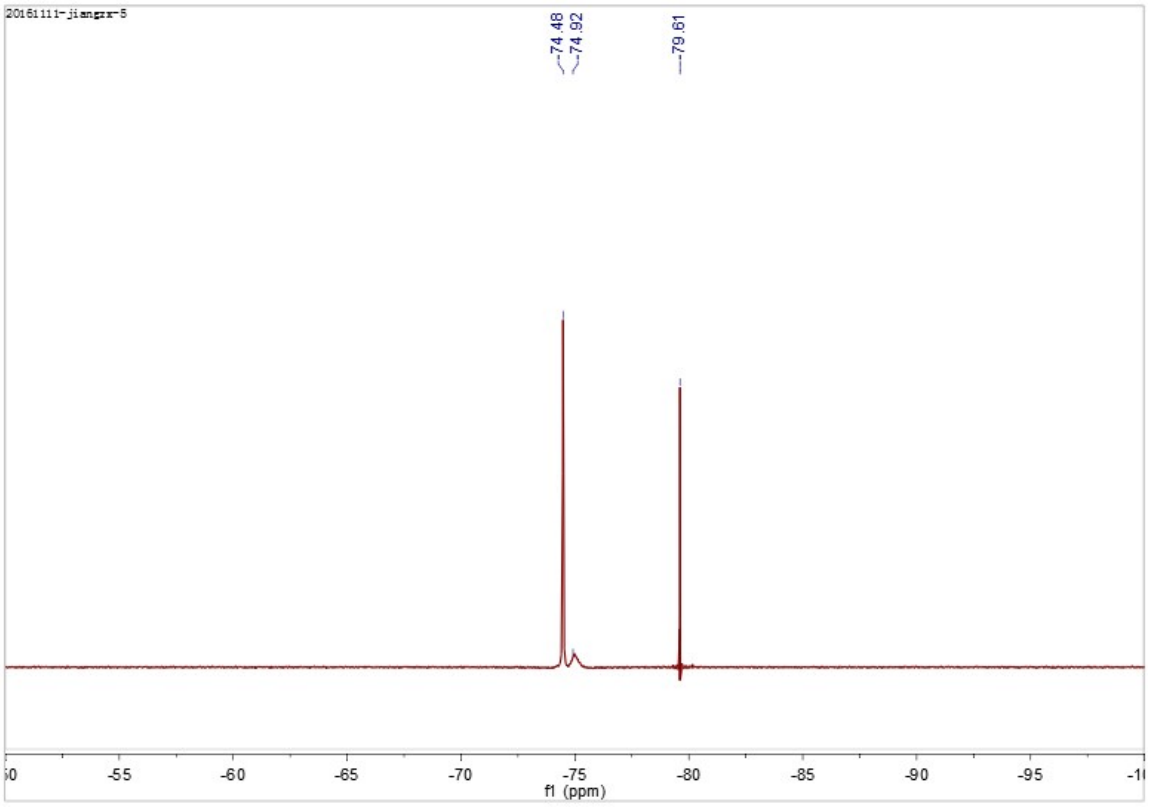
^{19}F NMR (4 mM **4**)



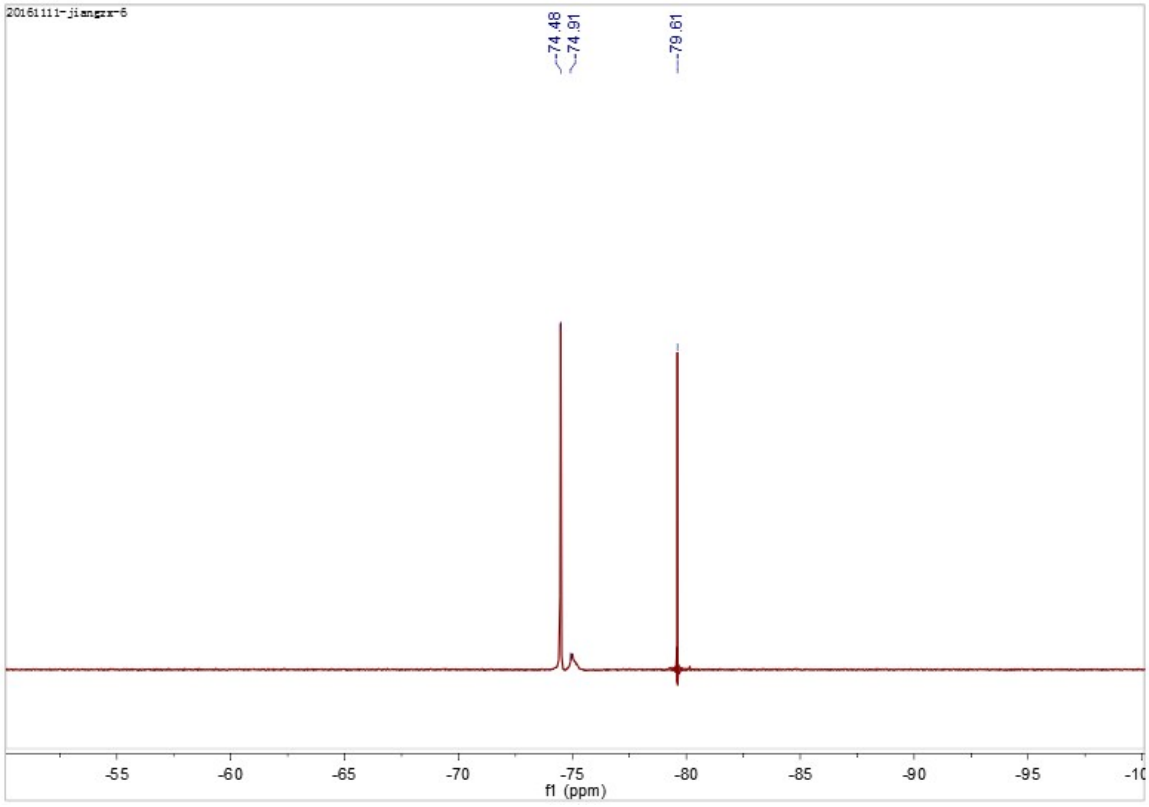
^{19}F NMR (4 mM **4** + 0.8 mM Mg^{2+})



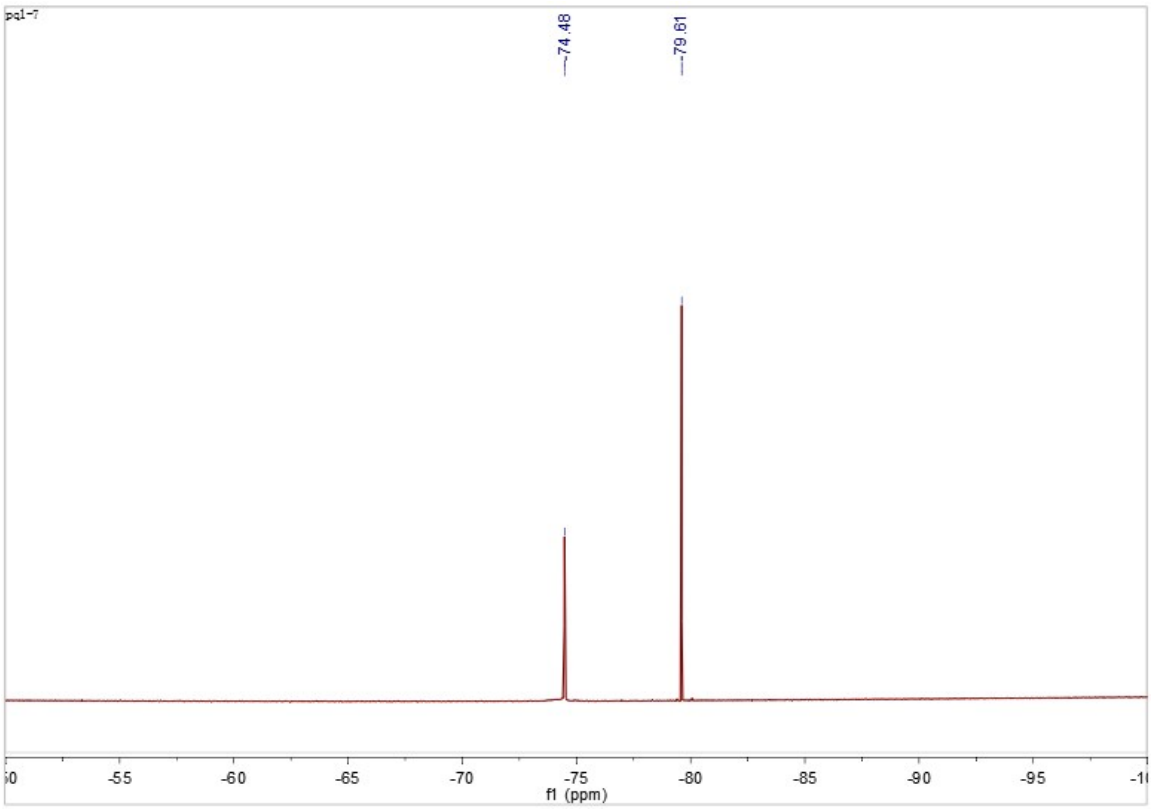
^{19}F NMR (4 mM **4** + 0.8 mM Ca^{2+})



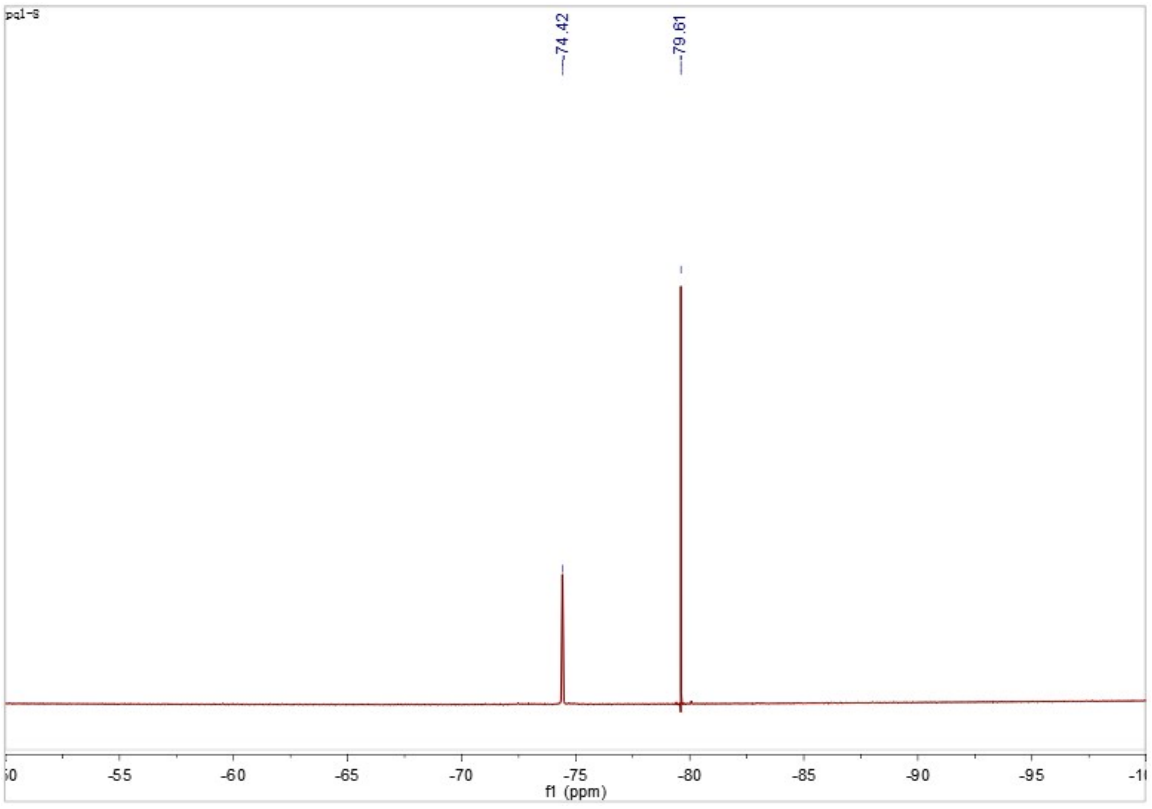
^{19}F NMR (4 mM **4** + 0.8 mM Zn^{2+})



^{19}F NMR (4 mM **4** + 0.8 mM Cu^{2+})

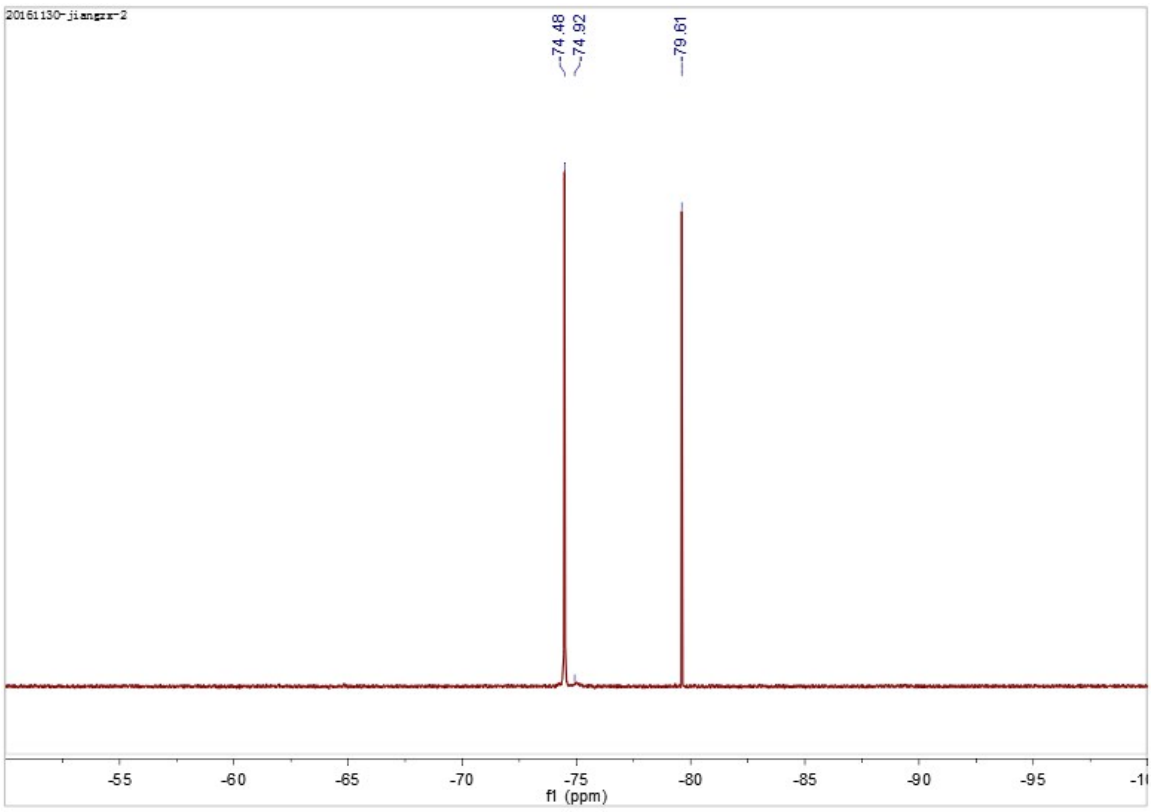


^{19}F NMR (4 mM **4** + 0.8 mM Fe^{3+})

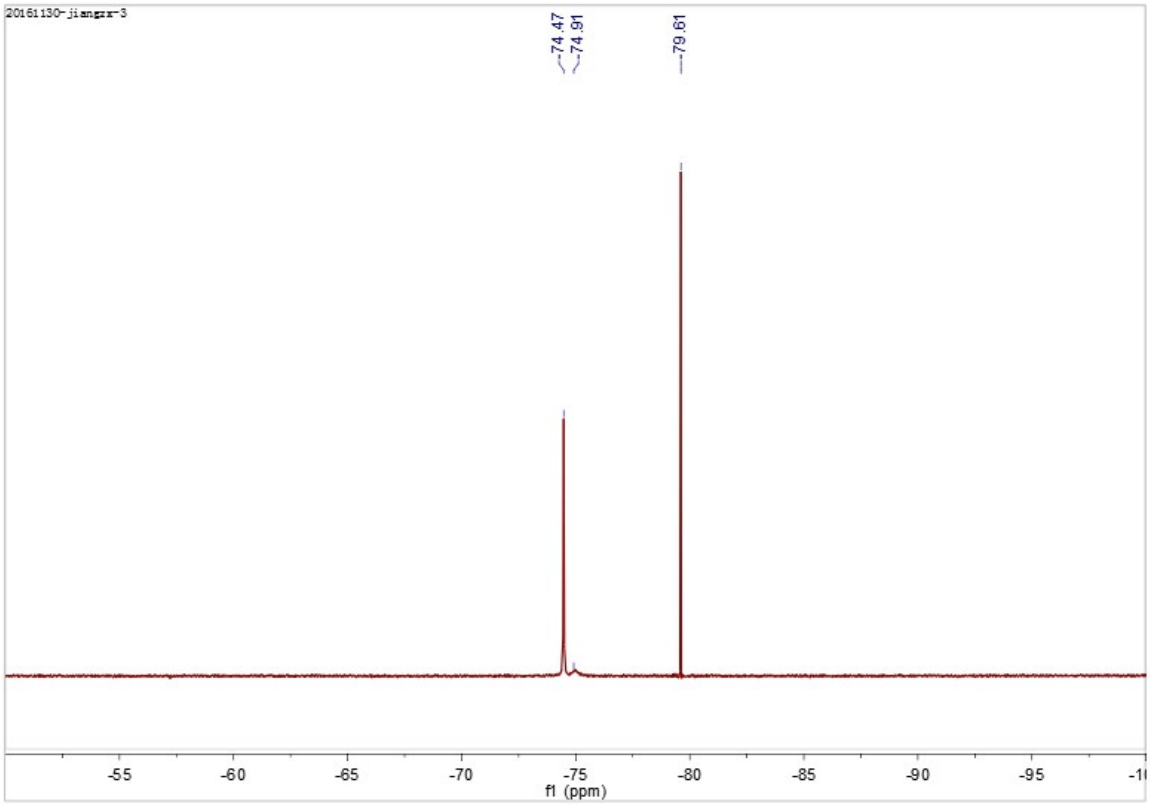


^{19}F NMR (4 mM **4**, Ca^{2+}% = 0%)

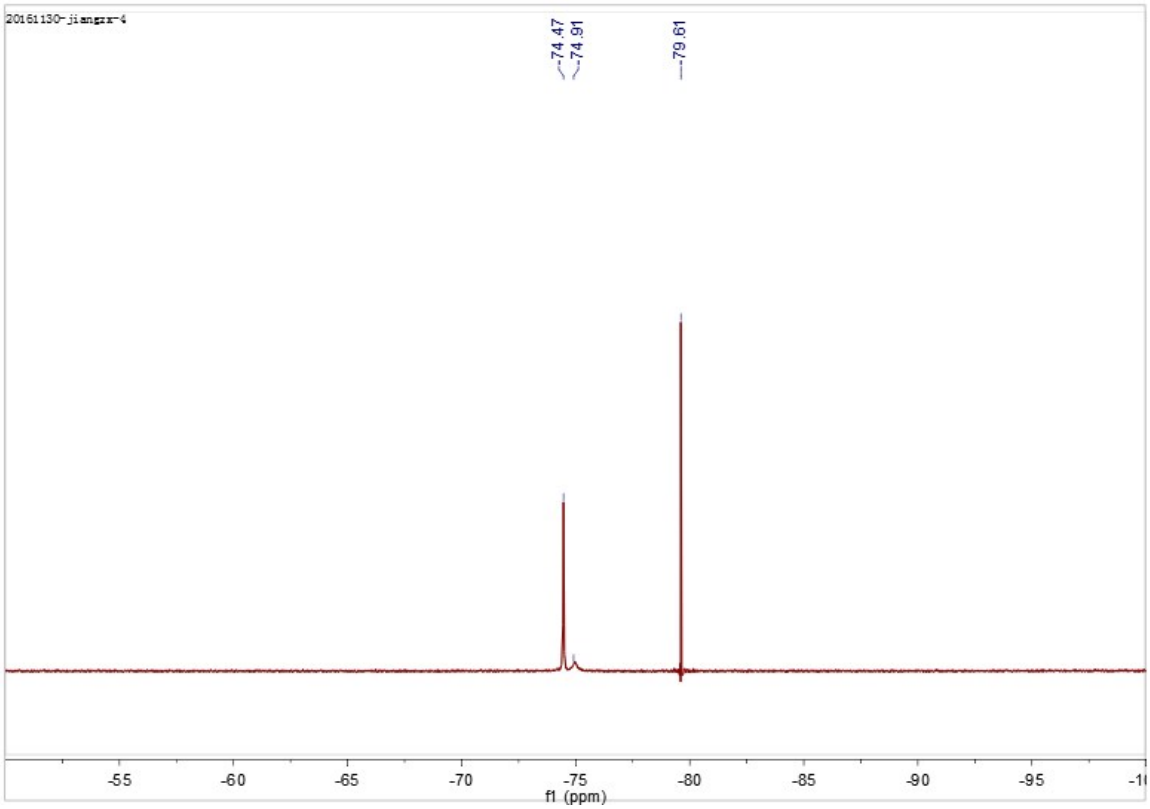
^{19}F NMR (4 mM **4** , Ca^{2+}% = 2%)



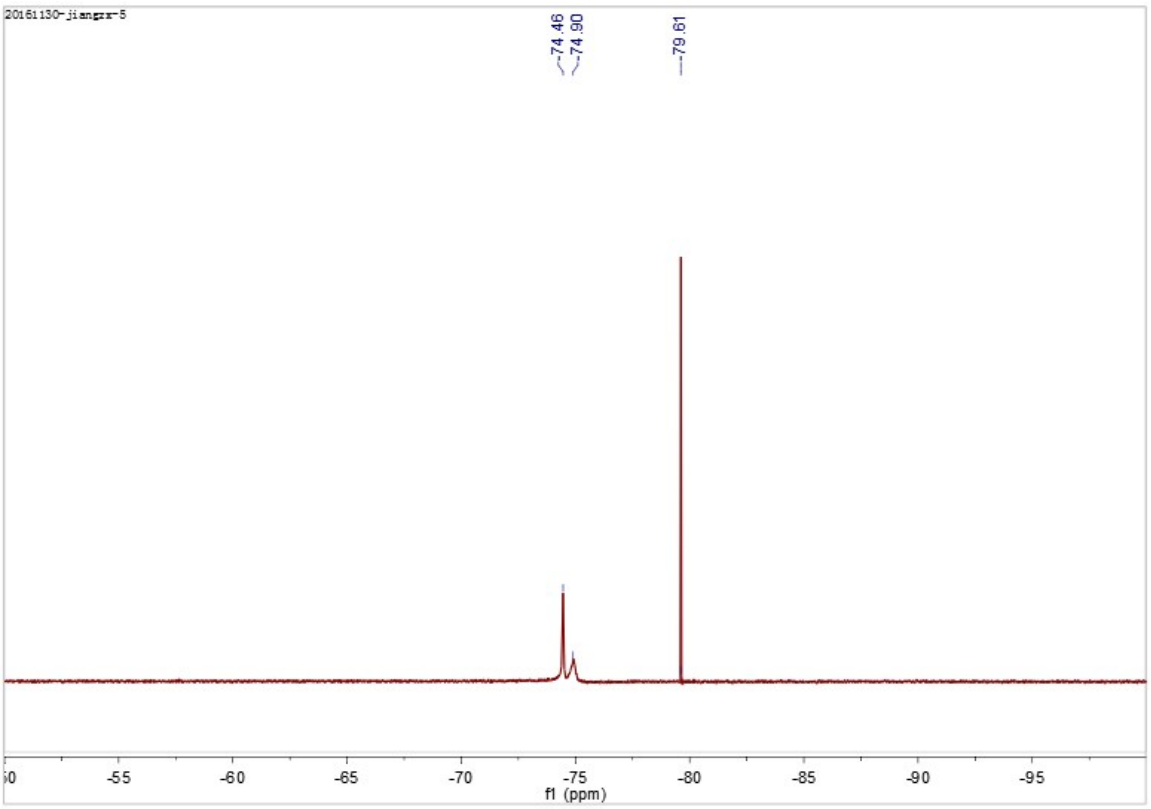
^{19}F NMR (4 mM **4**, Ca^{2+}% = 10%)



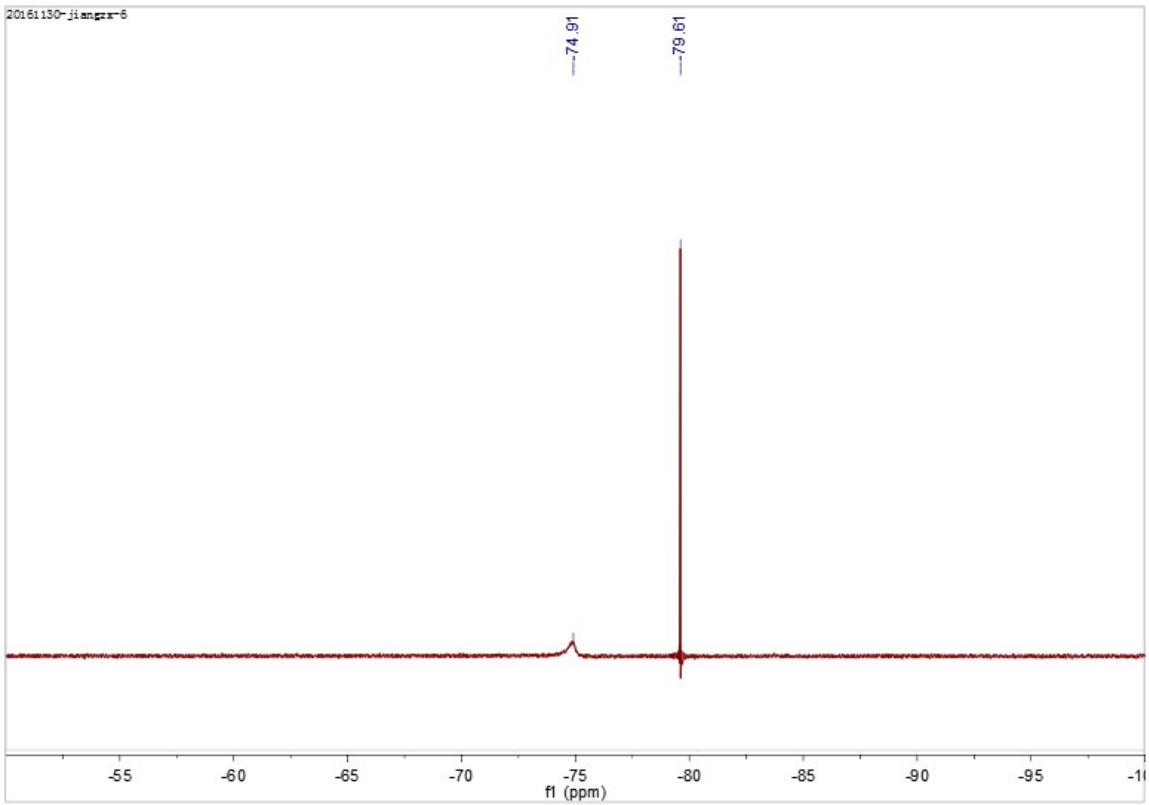
^{19}F NMR (4 mM **4**, Ca^{2+}% = 20%)



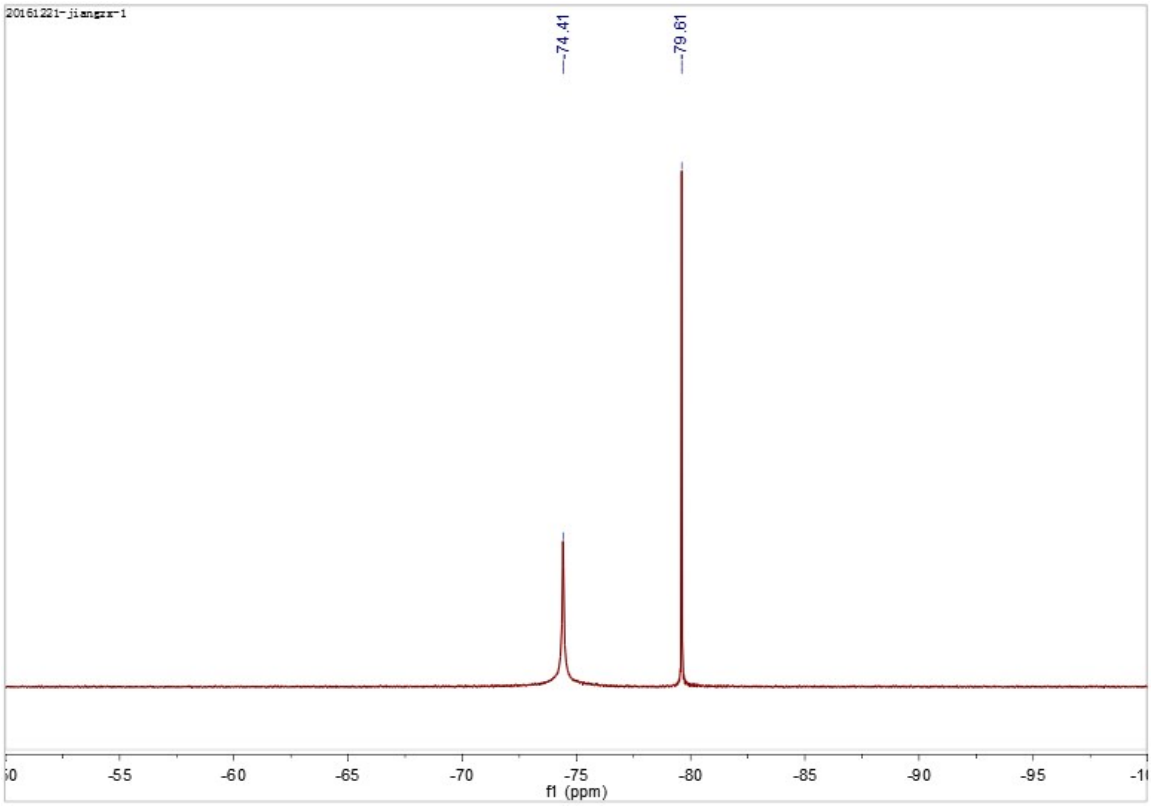
^{19}F NMR (4 mM **4**, Ca^{2+}% = 40%)



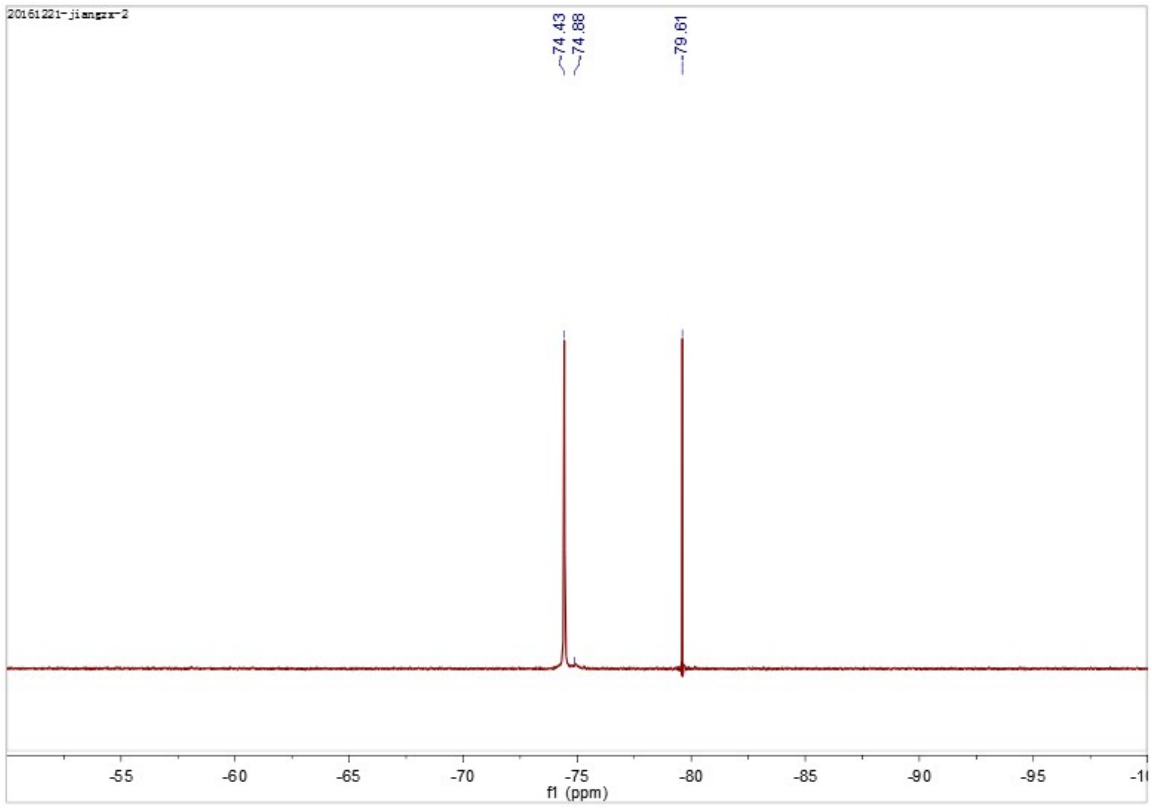
^{19}F NMR (4 mM **4**, Ca^{2+}% = 100%)



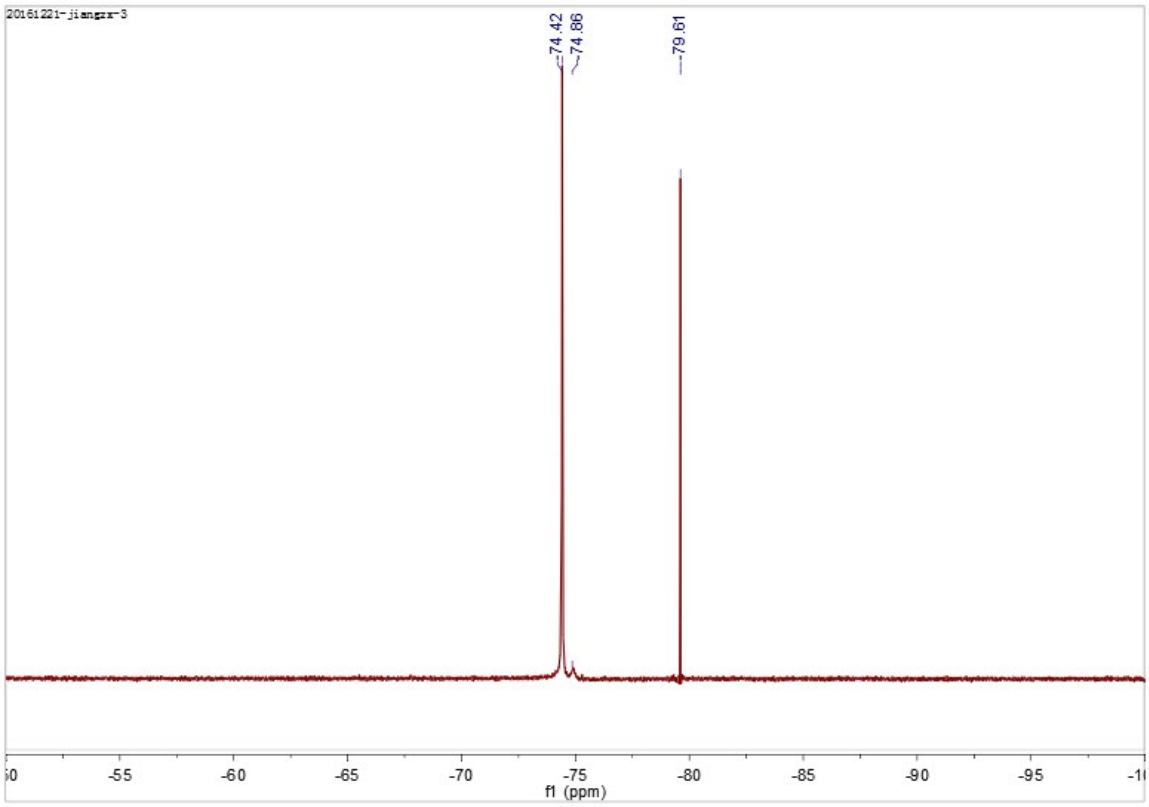
^{19}F NMR (4 mM **4** + 0.4 mM Ca^{2+}, pH 5.0)



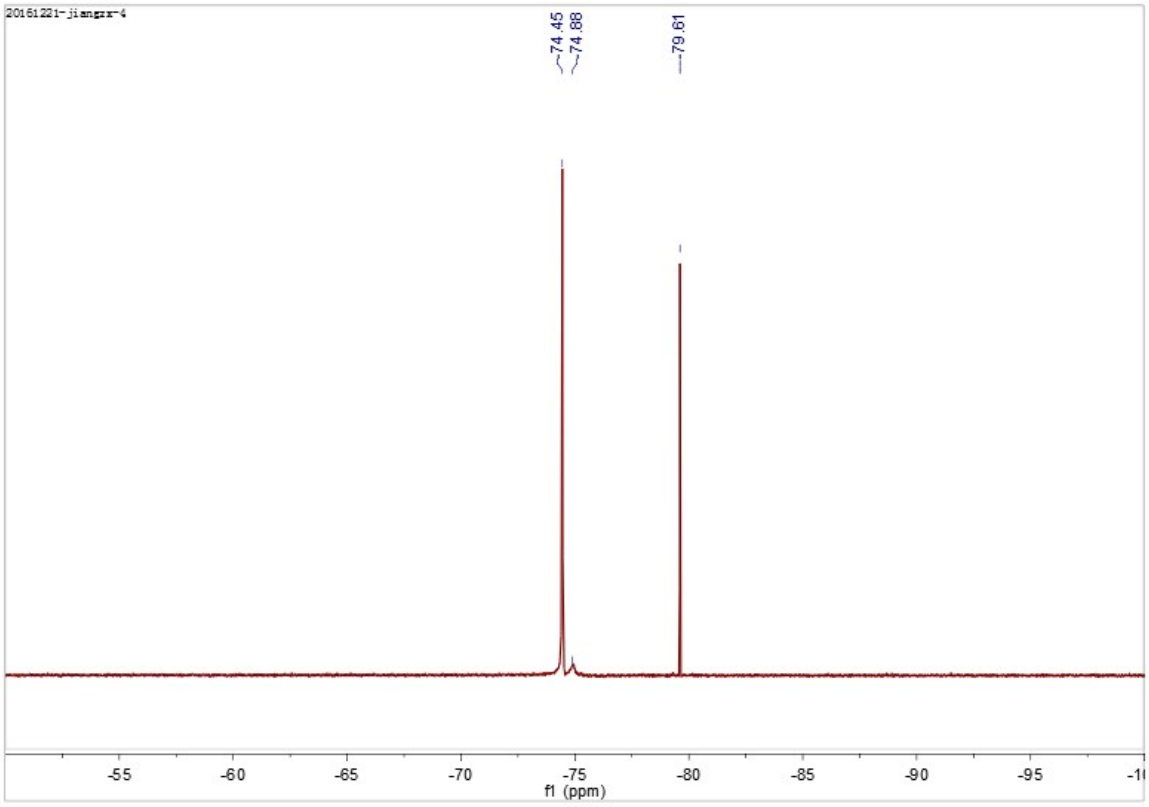
^{19}F NMR (4 mM **4** + 0.4 mM Ca^{2+}, pH 6.0)



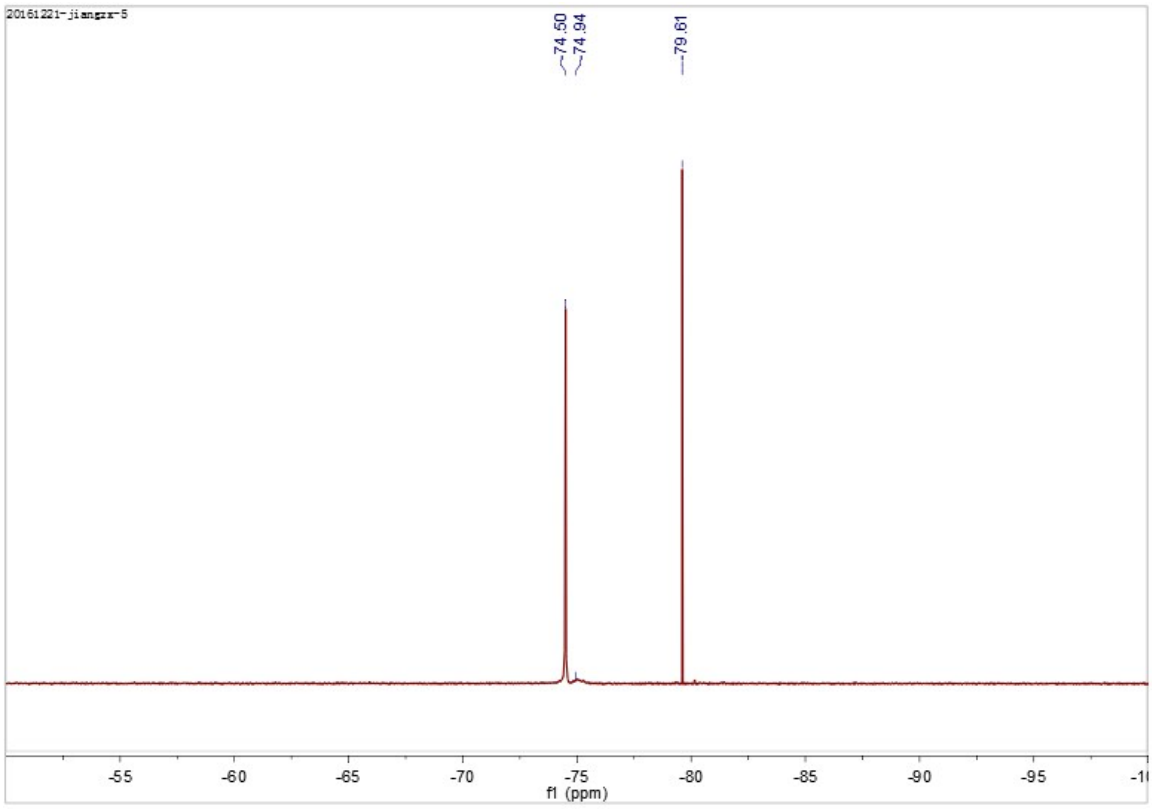
^{19}F NMR (4 mM **4** + 0.4 mM Ca^{2+}, pH 6.6)



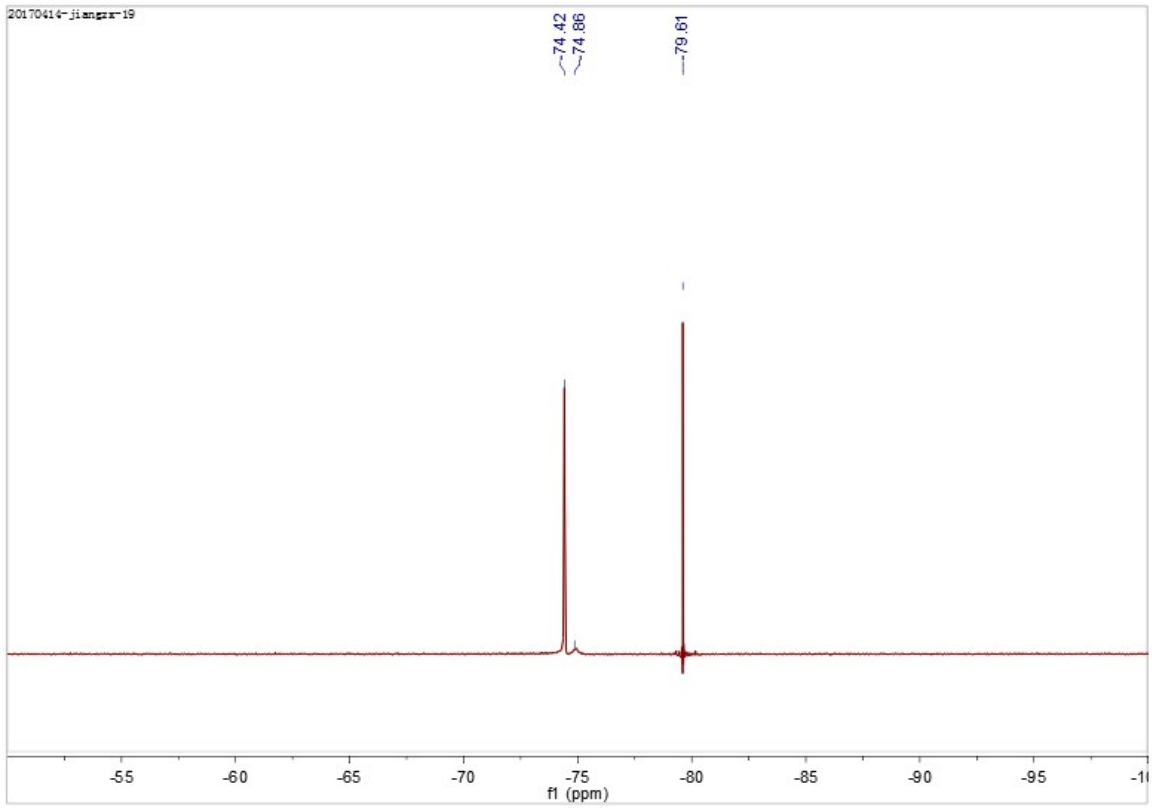
^{19}F NMR (4 mM + 0.4 mM Ca^{2+}, pH 7.1)



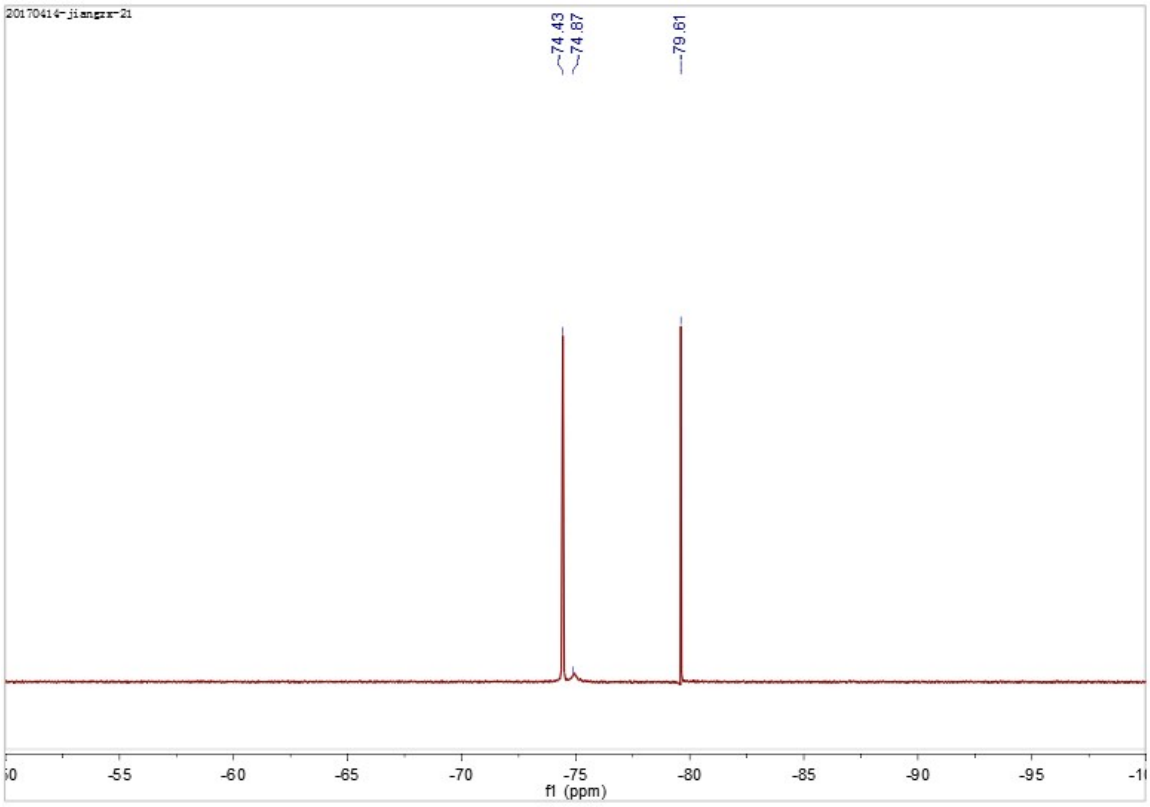
^{19}F NMR (4 mM **4** + 0.4 mM Ca^{2+}, pH 7.5)



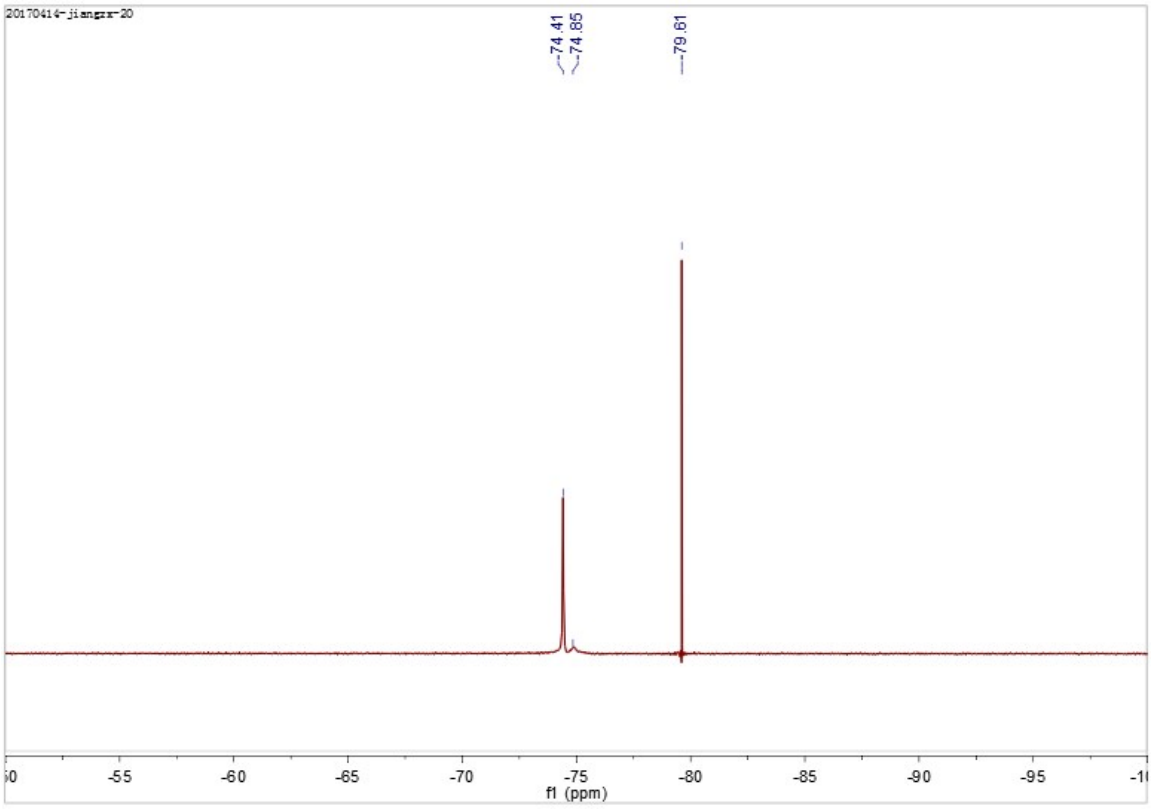
^{19}F NMR (4 mM **4** + 0.4 mM Ca^{2+})



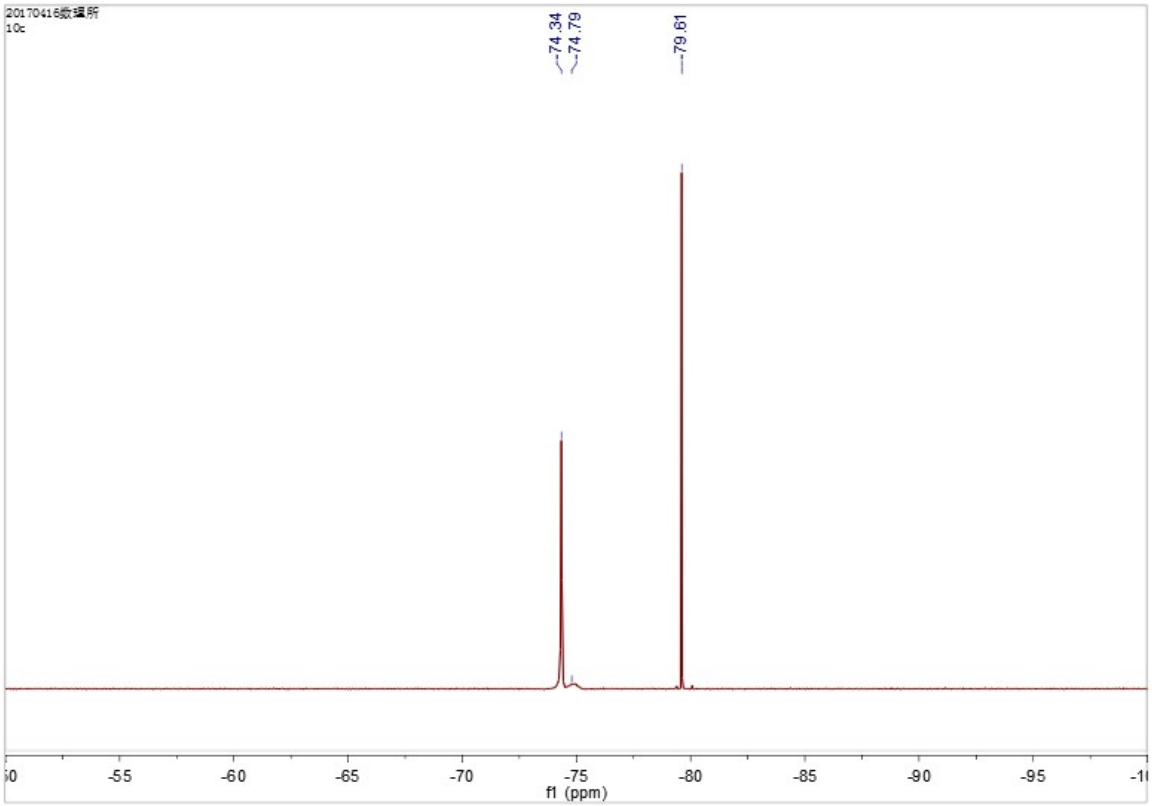
^{19}F NMR (4 mM **4** + 0.4 mM Ca^{2+} + 100 mM K^{+})



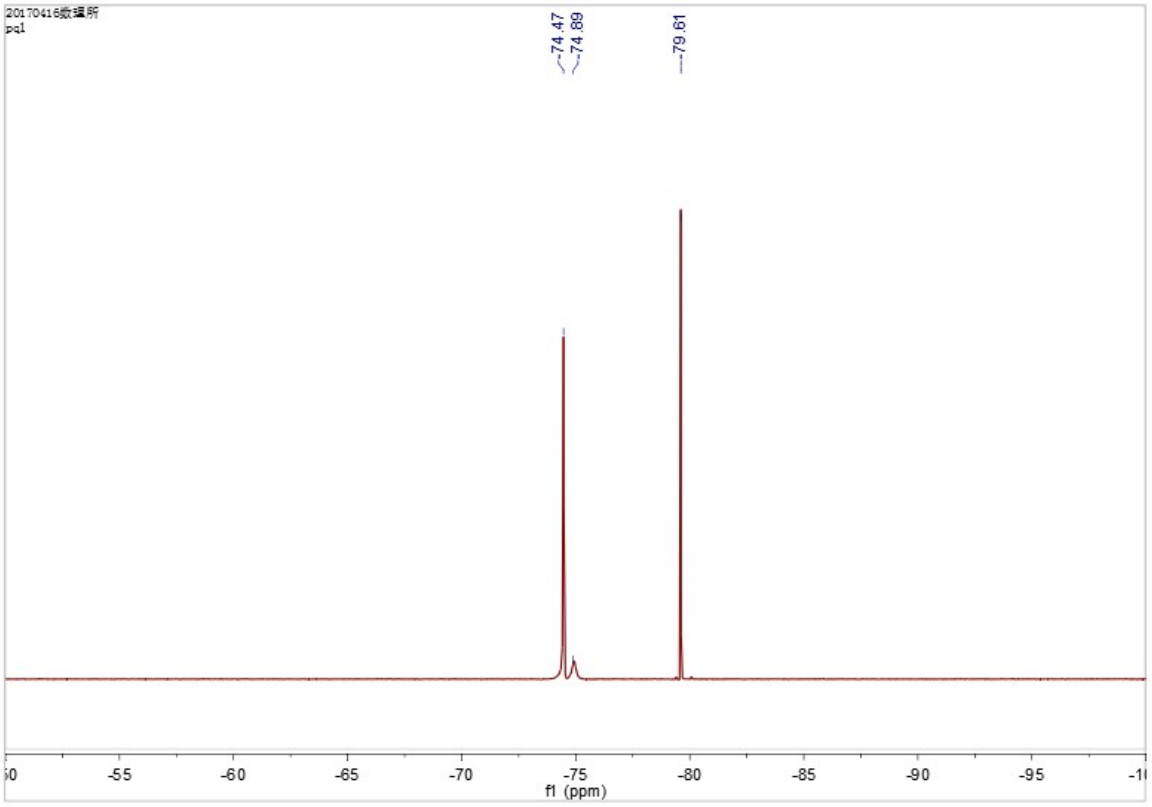
^{19}F NMR (4 mM **4** + 0.4 mM Ca^{2+} + 0.8 mM Mg^{2+})



^{19}F NMR (4 mM **4** + 0.8 mM Ca^{2+}, 283 K)



^{19}F NMR (4 mM **4** + 0.8 mM Ca^{2+}, 298 K)



^{19}F NMR (4 mM **4** + 0.8 mM Ca^{2+}, 310 K)