Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Fluorinated Paramagnetic Chelates as Potential Agents for Multi-chromic ^{19}F Magnetic Resonance Spectroscopy and Imaging

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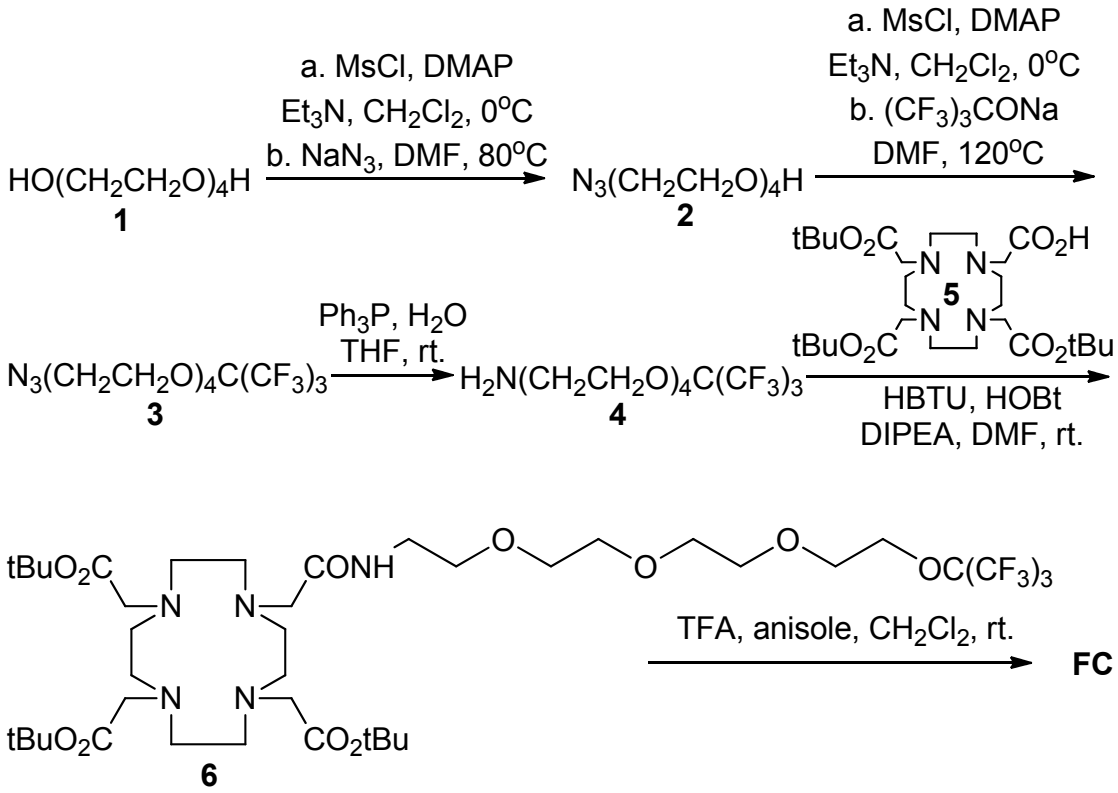
General information

Commercially available reagents and solvents were used without further purification. ^{1}H NMR ^{19}F NMR and ^{13}C NMR spectra were recorded on a Varian 500 MHz NMR spectrometer. ^{1}H NMR spectra were referenced to tetramethylsilane (δ, 0.00 ppm) using $CDCl_3$ as solvent. ^{13}C NMR spectra were referenced to solvent carbon (77.23 ppm for $CDCl_3$). ^{19}F NMR spectra were referenced to 2% perfluorobenzene (s, -164.9 ppm) in $CDCl_3$ or 5% trifluroacetic acid (s, -76.55ppm) in D_2O. PBS or human sera were used as NMR solvents. A capillary filled with 2% perfluorobenzene in $CDCl_3$ or 5% of trifluoroacetic acid in D_2O was inserted into the NMR tube as the internal ^{19}F chemical shift standard. Before each NMR measurement, the sample was bubbled with a stream of nitrogen or oxygen gas for 10 minutes on an ice bath. High resolution mass spectra (HRMS) were recorded on a Micromass GCT (GC-EI/CI Time of Flight Mass Spectrometer) with Electron Ionization (EI) resource. HPLC purification and analysis was performed on Aglient 1100 chromatograph systems using FlouroFlash® columns. Water and methanol were used as eluents; the flow rate for analytical and preparative runs was 1 and 5 mL/min respectively. The free fluorinated chelator is denoted as **FC** and fluorinated metal chelates are denoted as **FC**-M^{x+}, with $x+$ representing the valence of the metal ion, such as **FC**-Tb^{3+}.

Synthesis of fluorinated chelates

Compound **1** is from Sigma-Aldrich; compound **5** is from Macrocyclics. They were used without further purification. The synthesis route is depicted in the following scheme. From tetraethylene glycol **1**, its two hydroxyl groups were sequentially transformed into an azido group and a perfluoro-*tert*-butoxyl group, respectively, to give fluorinated azide **3**. After reduction of the azido group in **3**, amine **4** was then coupled with DOTA-tri-*tert*-Butyl-ester **5** yielded **6**. Finally, the fluorinated chelator **FC** was prepared on a 5-gram scale after removal of its three *tert*-butyl groups in **6**.



Compound 2 To a stirred solution of tetraethylene glycol **1** (45.6 mL, 264.0 mmol) in dicholoromethane (DCM, 500 mL) was added 4-*N,N*-dimethylaminopyridine (5.0 g, 4.1 mmol) and triethylamine (44.5 mL, 317.0 mmol). After cooling to 0°C, methanesulfonyl chloride (16.5 mL, 211.2 mmol) was added dropwise to the solution and the resulting mixture was stirred for an additional hour at room temperature. The reaction mixture was washed with 2N HCl (100 mL, twice), brine (100 mL, twice), dried over anhydrous sodium sulfate and concentrated under

vacuum. The resulting residue was dissolved in dimethylformamide (DMF, 150 mL) and sodium azide (15.5 g, 238.5 mmol) was added. The resulting mixture was stirred at 80°C overnight. After removal of solvent under vacuum, the residue was purified by flash chromatography on silica gel to give the azide **2** (45.1 g, yield 78%) as clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36-3.38 (m, 2H), 3.57-3.59 (m, 2H), 3.6-3.7 (m, 12H).

Compound 3 At 0°C, methanesulfonyl chloride (12.4 mL, 159.5 mmol) was added dropwise to a stirred solution of compound **2** (29.1 g, 109.7 mmol), 4-*N,N*-dimethylaminopyridine (1.3 g, 10.7 mmol) and triethylamine (37.3 mL, 265.5 mmol) in dichloromethane (DCM, 400 mL). Afterwards, the mixture was stirred for one hour at room temperature. The reaction mixture was washed with 2N HCl (100 mL, twice), brine (100 mL, twice), dried and concentrated under vacuum. The residue was dissolved in DMF (300 mL); and sodium perfluoro-*tert*-butoxide (60.1 g, 167.9 mmol) was added in one portion. The mixture was stirred at 120°C overnight. After cooled to room temperature, the reaction mixture was diluted with brine (1,200 mL) and extracted with ethyl acetate (300 mL, five times). The combined organic layers were dried over anhydrous sodium sulfate, concentrated, purified by flash chromatography on silica gel to give compound **3** (30.9 g, yield 63%) as clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.39 (t, J = 4.5 Hz,, 2H), 3.65-3.69 (m, 10H), 3.74 (t, J = 4.5 Hz, 2H), 4.16 (t, J = 4.5 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.45 (s); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 50.9, 69.5, 69.6, 70.2, 70.9, 71.3, 79.8-80.3 (m), 120.5 (q, J = 291.5 Hz); MS (ESI) *m/z* 460.2 ($(M+Na)^+$) ; HRMS (ESI) calcd for $C_{12}H_{16}F_9N_3NaO_4$, 460.08948; found, 460.08975.

Compound 4 Triphenyl phosphine (19.9 g, 76.0 mmol) was added in portions to a stirred solution of compound **3** (30.3 g, 69.3 mmol) in tetrahydrofuran (THF, 250 mL) at 0°C and the resulting mixture was stirred at room temperature for 10 hours. Then, water (3.7 mL, 207.5 mmol) was added and the mixture was stirred overnight. The reaction mixture was concentrated and purified by flash chromatography on silica gel to give compound **4** (27.4 g, yield 96%) as clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.83-2.92 (m, 2H), 3.50-3.55 (m, 2H), 3.62-3.75 (m, 10H), 4.10-4.20 (m, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.53 (s); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 41.9, 69.5, 69.6, 70.5, 70.8, 71.3, 73.4, 79.6-80.5 (m), 120.5 (q, J = 292.9 Hz); MS (ESI) *m/z* 412.3 ($(M+H)^+$) ; HRMS (ESI) calcd for $C_{12}H_{19}F_9NO_4$, 412.11704; found, 412.11245.

Compound 6 At room temperature, HBTU (11.4g, 30.0 mmol) and HOBt (2.0 g, 15.0 mmol) were added sequentially to a stirred solution of DOTA-tri-*tert*-Butyl-ester (5.73 g, 10.0 mmol) in DMF (25 mL) and the resulting mixture was stirred for 30 min. Then compound **4** (4.94 g, 12.0 mmol) was added in one portion followed by *N*,*N*-Diisopropylethylamine (DIPEA, 10.9 mL, 60.0 mmol). The reaction mixture was stirred overnight, dilluted with water (100 mL), extracted with ethyl acetate (50 mL, 5 times). The combined organic layers were dried, concentrated under vacuum, purified by flash chromatoraphy on silica gel to give compound **6** (8.8 g, yiled 91%) as clear oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45-1.46 (m, 27H), 2.07-3.18 (m, 22H), 3.39-3.42 (m, 2H), 3.52-3.55 (m, 2H), 1.59-1.61 (m, 2H), 3.63-3.69 (m, 6H), 3.73 (t, J = 4.5 Hz, 2H), 4.16 (t, J = 4.5 Hz, 2H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.52 (s); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 28.5, 28.54, 39.0, 40.2, 53.7, 56.85, 56.9, 57.3, 70.6, 70.8, 71.2, 71.3, 71.6, 71.64, 71.9, 80.5-81.8 (m), 82.8, 82.84, 121.9 (q, J = 290.9), 167.5, 173.6, 174.2, 174.5; MS (ESI) *m/z* 988.4 ($(M+Na)^+$) ; HRMS (ESI) calcd for $C_{40}H_{69}F_9N_5O_{11}$, 966.48499; found, 966.48755.

Compound FC To a stirred solution of compoud **6** (6.4 g, 6.6 mmol) was added anisole (3.6 mL, 33.2 mmol), trifluoroacetic acid (20 mL, 260.0 mmol) and water (1.2 mL, 66.2 mmol) at room temperature. Afterwards, the mixture was stirred for additional 2 hours, concentrated under vacuum. The residue was purified by preparative HPLC on FlouroFlash® column to give chelator **FC** (3.4 g, yield 64%) as a white solid. ^{1}H NMR (500 MHz, D_2O) δ 2.70-3.60 (m, 20H), 3.69-3.84 (m, 14H), 3.83-4.37 (m, 6H); ^{19}F NMR (470 MHz, D_2O) δ -72.46 (s), (470 MHz, PBS, pH 7.0, N_2) δ -71.20 (s); ^{13}C NMR (125.7 MHz, D_2O) δ 41.2, 50.9, 51.0, 53.9, 54.5, 57.7, 58.7, 59.3, 71.6, 71.7, 72.0, 72.3, 72.4, 72.9, 81.7-82.7 (m), 122.9 (q, J = 293.0), 172.8, 174.5, 180.6; MS (ESI) *m/z* 798.3 ($(M+H)^+$); HRMS (ESI) calcd for $C_{28}H_{45}F_9N_5O_{11}$, 798.29719; found, 798.29652.

General procedure for chelation of chelator FC with metal ions (Gd^{3+} as an examples) Chelator **FC** (500 mg, 0.63 mmol) was dissolved in water (10 mL). After adjusting to pH 7.0 by addition of sodium hydroxide solution (1 mmol/mL), gadolinium chloride hexahydride (467 mg, 1.26 mmol) was added and the resulting mixture was stirred for 2 hours at 80^{o}C. During this time, sodium hydroxide solution (1 mmol/mL) was added to maintain pH 7.0. If needed, the pH was adjusted to 10 to remove exccess ions. The reaction mixture was centrifuged and the aquoues layer was subjected to HLPC purification to give the pure chelate **FC**-Gd^{3+}.

Compound **FC**-Tb^{3+} HPLC T_R = 10.85 min; ^{19}F NMR (470 MHz, PBS, pH 7, N_2) δ -63.32 (s); (470 MHz, PBS, pH 7.0, O_2) δ -63.30 (s); MS (ESI) *m/z* 954.2 $((M+H)^+)$.

Compound **FC**-Ho^{3+} HPLC T_R = 10.89 min; ^{19}F NMR (470 MHz, PBS, pH 7, N_2) δ -63.51 (s); (470 MHz, PBS, pH 7.0, O_2) δ -63.46 (s); MS (ESI) *m/z* 960.2 $((M+H)^+)$.

Compound **FC**-Dy^{3+} HPLC T_R = 10.84 min; ^{19}F NMR (470 MHz, PBS, pH 7, N_2) δ -63.55 (s); (470 MHz, PBS, pH 7.0, O_2) δ -63.45 (s); MS (ESI) *m/z* 959.2 $((M+H)^+)$.

Compound **FC**-Er^{3+} HPLC T_R = 10.85 min; ^{19}F NMR (470 MHz, PBS, pH 7, N_2) δ -65.41 (s); (470 MHz, PBS, pH 7.0, O_2) δ -65.39 (s); MS (ESI) *m/z* 962.2 $((M+H)^+)$.

Compound **FC**-Gd^{3+} HPLC T_R = 10.88 min; ^{19}F NMR (470 MHz, PBS, pH 7, N_2) δ -66.61 (s); (470 MHz, PBS, pH 7.0, O_2) δ -66.61 (s); MS (ESI) *m/z* 953.2 $((M+H)^+)$, HRMS (ESI) calcd for $C_{28}H_{42}F_9GdN_5O_{11}$, 953.19946 found 953.20167**.**

Compound **FC**-Fe^{3+} HPLC T_R = 11.20 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -68.71 (s); (470 MHz, PBS, pH 7.0, O_2) δ -68.88 (s); MS (ESI) *m/z* 851.1 $((M+H)^+)$.

Compound **FC**-Yb^{3+} HPLC T_R = 10.85 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -70.21 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.16 (s); MS (ESI) *m/z* 969.2 $((M+H)^+)$.

Compound **FC**-Ni^{3+} HPLC T_R = 10.57 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -70.25 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.22 (s); MS (ESI) *m/z* 854.2 $((M+H)^+)$.

Compound **FC**-Nd^{3+} HPLC T_R = 10.86 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -70.30 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.26 (s); MS (ESI) *m/z* 937.2 $((M+H)^+)$.

Compound **FC**-Pr^{3+} HPLC T_R = 10.89 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -70.33 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.29 (s); MS (ESI) *m/z* 936.1 $((M+H)^+)$.

Compound **FC**-Eu^{3+} HPLC T_R = 10.87 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -70.47 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.43 (s); MS (ESI) *m/z* 948.2 $((M+H)^+)$.

Compound **FC**-Cu^{2+} HPLC T_R = 10.67 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -70.74 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.70 (s); MS (ESI) *m/z* 859.1 $((M+H)^+)$.

Compound **FC**-Ce^{3+} HPLC T_R = 10.89 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -70.77 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.72 (s); MS (ESI) *m/z* 935.2 $((M+H)^+)$.

Compound **FC**-Sm^{3+} HPLC T_R = 10.87 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) -70.97 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.94 (s); MS (ESI) *m/z* 947.2 $((M+H)^+)$.

Compound **FC**-Cd^{2+} HPLC T_R = 10.66 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -71.12 (s); (470 MHz, PBS, pH 7.0, O_2) δ -71.08 (s); MS (ESI) *m/z* 910.3 $((M+H)^+)$.

Compound **FC**-Ca^{2+} HPLC T_R = 10.67 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -71.12 (s); (470 MHz, PBS, pH 7.0, O_2) δ -71.08 (s); MS (ESI) *m/z* 836.4 $((M+H)^+)$.

Compound **FC**-La^{3+} HPLC T_R = 10.91 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -71.13 (s); (470 MHz, PBS, pH 7.0, O_2) δ -71.09 (s); MS (ESI) *m/z* 934.2 $((M+H)^+)$.

Compound **FC**-Pb^{2+} HPLC T_R = 10.45 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -71.13 (s); (470 MHz, PBS, pH 7.0, O_2) δ -70.09 (s); MS (ESI) *m/z* 1004.3 $((M+H)^+)$.

Compound **FC**-Y^{3+} HPLC T_R = 10.55 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -71.13 (s); (470 MHz, PBS, pH 7.0, O_2) δ -71.09 (s); MS (ESI) *m/z* 884.2 $((M+H)^+)$.

Compound **FC**-Hg^{2+} HPLC T_R = 10.59 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -71.15 (s); (470 MHz, PBS, pH 7.0, O_2) δ -71.10 (s); MS (ESI) *m/z* 998.2 $((M+H)^+)$.

Compound **FC**-Bi^{3+} HPLC T_R = 10.65 min; ^{19}F NMR (470 MHz, PBS, pH 7.0, N_2) δ -71.17 (s); (470 MHz, PBS, pH 7.0, O_2) δ -71.06 (s); MS (ESI) *m/z* 1004.2 $((M+H)^+)$.

* All the HPLC retention times were collected using a FluoroFlash® colmn (4.6 mm × 150 mm) with water and MeOH as eluents, 1 mL/min, from 100% water to 100% methanol in 15 min then 100% methanol for 5 min.

General Information of NMR experiments:

All the NMR experiments were conducted on Varian INOVA 500 spectrometer equipped with a $^{1}H/^{19}F\{^{13}C/^{15}N\}$ 5mm Triple resonance PFG probe.

Calibrated 90° pulse was used as the transmitter pulse. The relaxation delay varied according to the different samples, but larger than $5\times T_1$. Inversion-Recovery[1] and CPMG (Carr-Purcell-Meiboom-Gill)[2] sequences were used to measure the relaxation times T_1 and T_2, respectively. The parameters of T_1 and T_2 measurements are optimized according to the different relaxation time of these samples. All the ^{19}F chemical shifts were referenced to TFA (a capillary filled with 5% of trifluoroacetic acid in D_2O was inserted into the NMR tube) at δ -76.55 ppm.

1. Vold, R. L.; Waugh, J. S.; Klein, M. P.; Phelps, D. E. J. Chem. Phys. 1968, 48, 3831-3832.

2. Meiboom, S.; Gill, D. Rev. Sci. Instr. 1958, 29, 688-691

Table S1. Effects of pH and temperature on the ^{19}F chemical shift (δ) and relaxation times (T_1 & T_2) of fluorinated chelates. All measurements were conducted in PBS saturated with N_2.

Parameters	Chelates	pH6	pH8	**pH7 25°C**	10°C	35°C	45°C
δ (ppm)	**FC**-Tb^{3+}	-63.075	-63.105	**-63.315**	-62.755	-63.690	-64.113
	FC-Gd^{3+}	-66.531	-66.022	**-66.611**	-66.110	-66.687	-66.713
	FC-Y^{3+}	-71.126	-71.126	**-71.134**	-71.114	-71.150	-71.175
	FC	-71.201	-71.201	**-71.203**	-71.134	-71.287	-71.325
T_1 (ms)	**FC**-Tb^{3+}	73.24	71.67	**72.56**	65.92	75.81	81.25
	FC-Gd^{3+}	3.917	4.076	**4.235**	4.119	4.06	3.973
	FC-Y^{3+}	1431	1498	**1514**	1052	1753	2133
	FC	1431	1440	**1330**	982.3	1315	1380
T_2 (ms)	**FC**-Tb^{3+}	46.58	46.81	**41.74**	37.0	42.9	46.0
	FC-Gd^{3+}	1.071	1.07	**1.661**	1.41	1.28	1.22
	FC-Y^{3+}	1234	1196	**783**	720.2	1531	1511
	FC	789.9	825.6	**701**	671	708.3	618.6

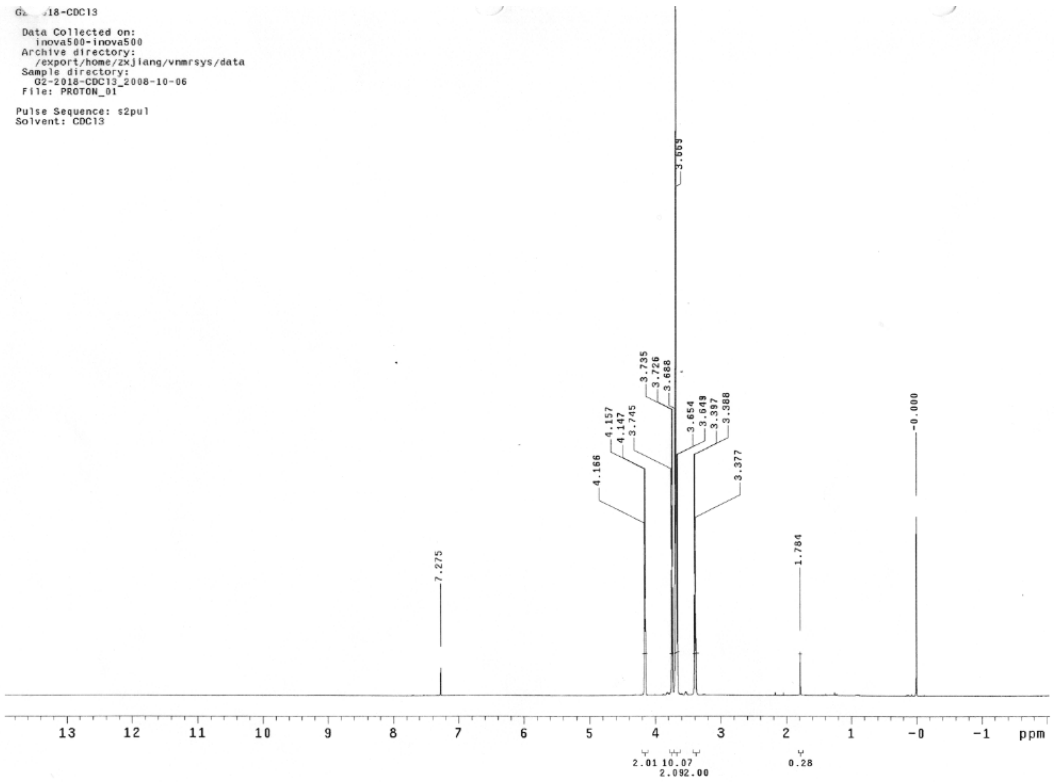
Notes on experimental error estimate in relaxation time determination:

1. T_1 of FC-Y^{3+} was measured 5 times at pH 6, 25°C to give the experimental error. 1431 ± 5 ms
2. T_2 of FC-Y^{3+} was measured 10 times at pH 6, 25°C to give the experimental error. 1234 ± 34 ms
3. T_1 of FC-Gd^{3+} was measured 12 times at pH 6, 25°C to give the experimental error. 3.917 ± 0.030 ms
4. T_2 of FC-Gd^{3+} was measured 12 times at pH 6, 25°C to give the experimental error. 1.071 ± 0.030 ms

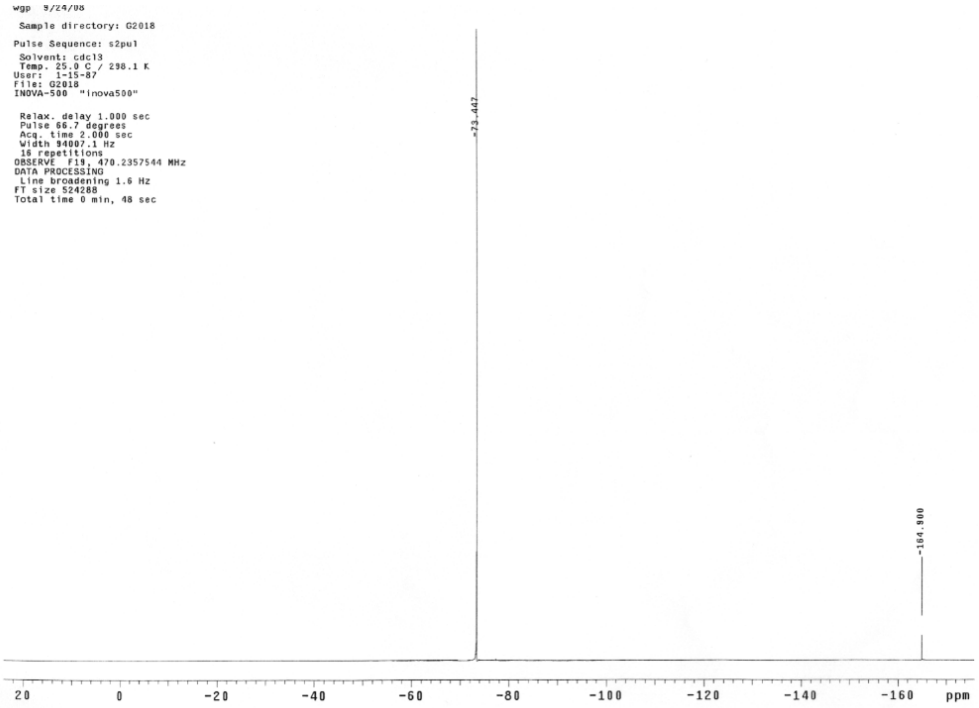
Table S2. Effects of BSA and human sera on the ^{19}F chemical shift (δ) and relaxation times (T_1 & T_2) of fluorinated chelates. For PBS and 10% BSA in PBS measurements, the solutions were saturated with N_2.

Parameters	Chelates	**PBS pH7 25°C**	10% BSA in PBS	Human sera	
				Under N_2	Under O_2
δ (ppm)	**FC**-Tb^{3+}	**-63.315**	-61.446	-63.218	-63.187
	FC-Gd^{3+}	**-66.611**	-65.808	-66.322	-63.309
	FC-Y^{3+}	**-71.134**	-71.113	-71.220	-71.170
	FC	**-71.203**	-71.238	-71.189	-71.150
T_1 (ms)	**FC**-Tb^{3+}	**72.56**	70.1	79.62	75.1
	FC-Gd^{3+}	**4.235**	4.518	4.27	4.47
	FC-Y^{3+}	**1514**	1200	1211	796
	FC	**1330**	1111	1247	840
T_2 (ms)	**FC**-Tb^{3+}	**41.74**	10.6	11.96	10.9
	FC-Gd^{3+}	**1.661**	0.55	0.87	0.62
	FC-Y^{3+}	**783**	139	213.8	189.4
	FC	**701**	100.7	209	214

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

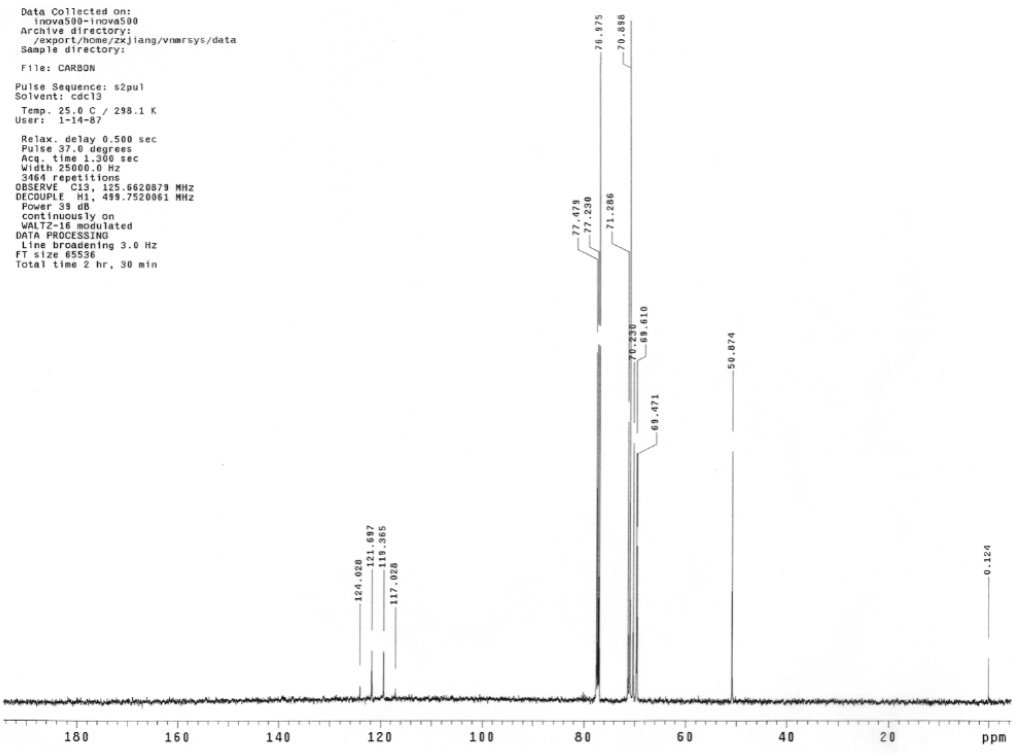


^{19}F NMR of compound

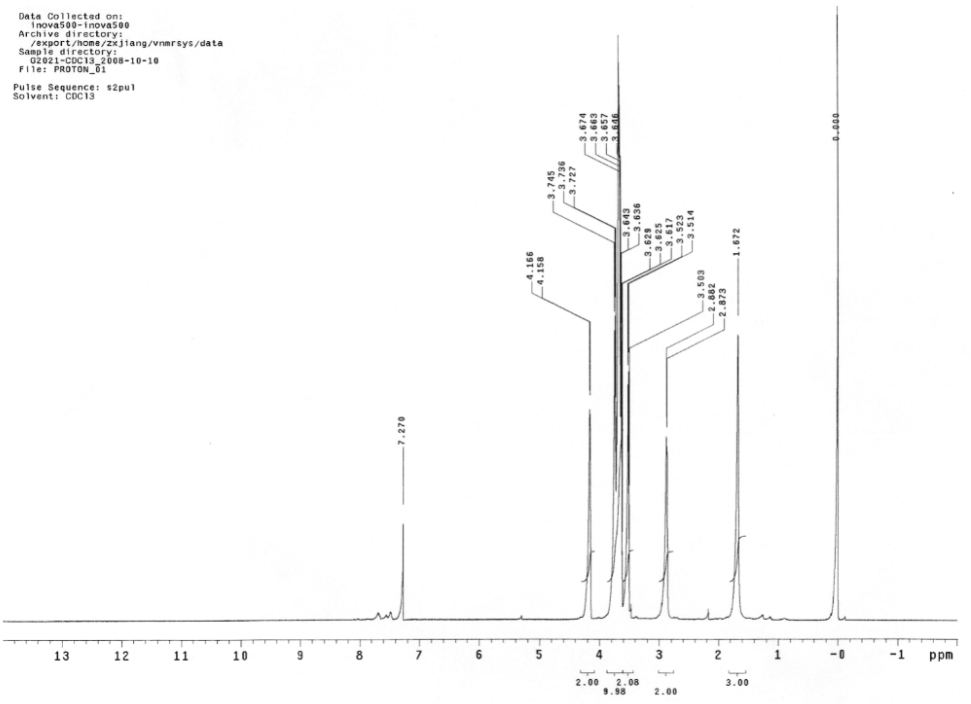


3

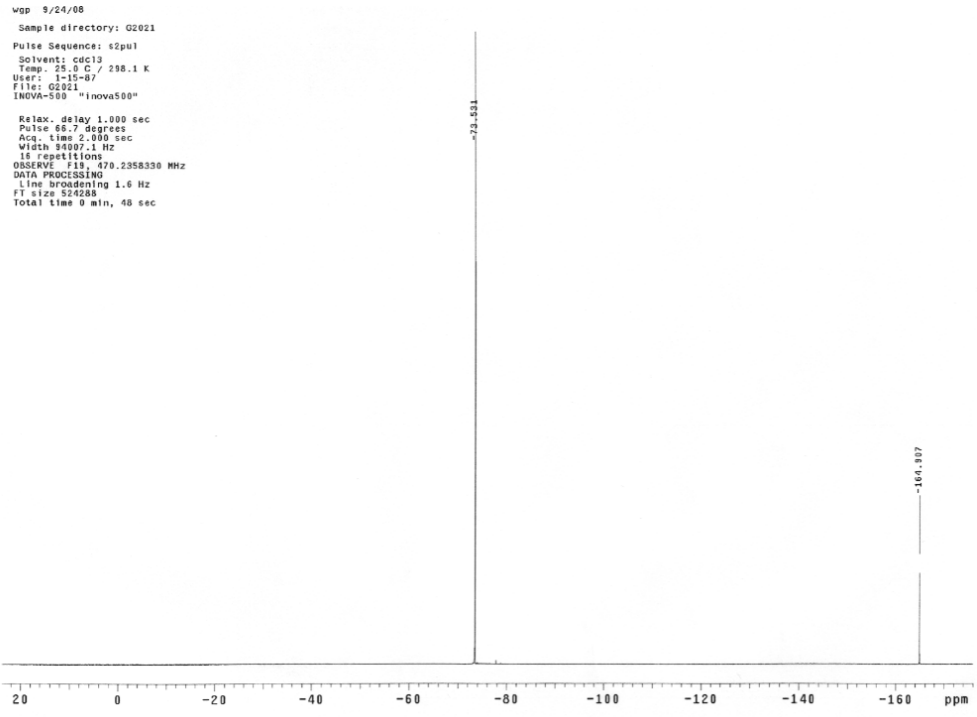
^{13}C NMR of compound **3**



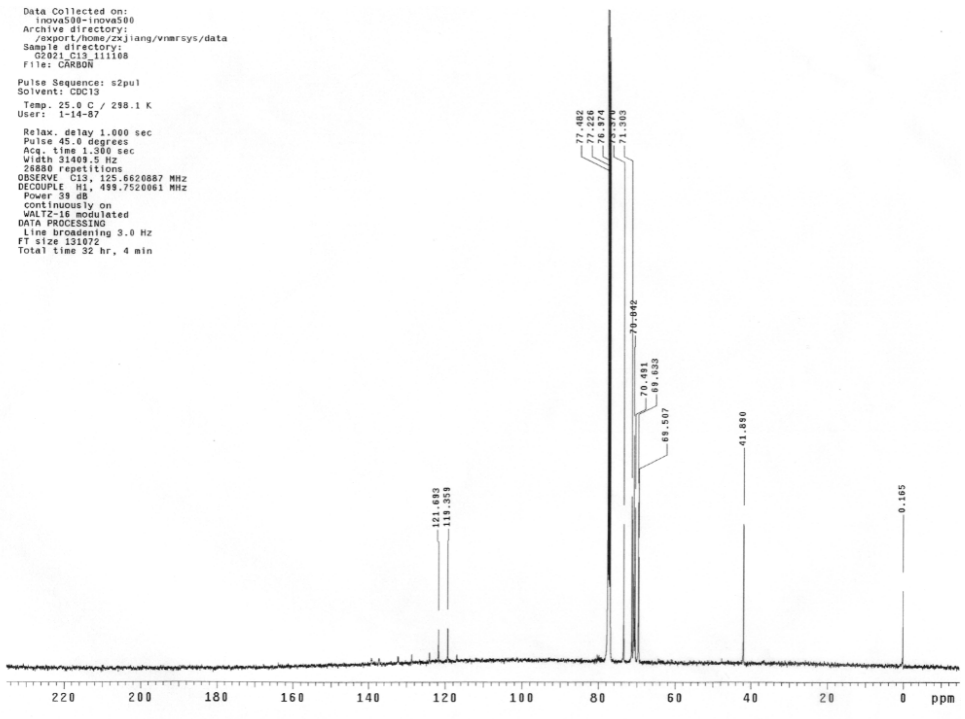
^{1}H NMR of compound **4**



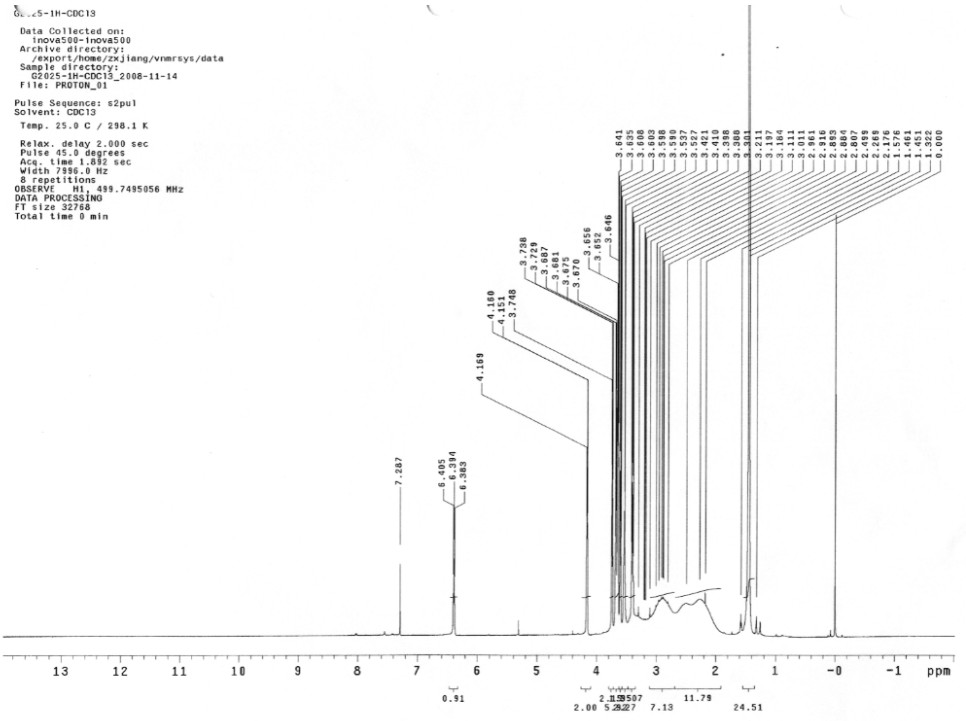
^{19}F NMR of compound **4**



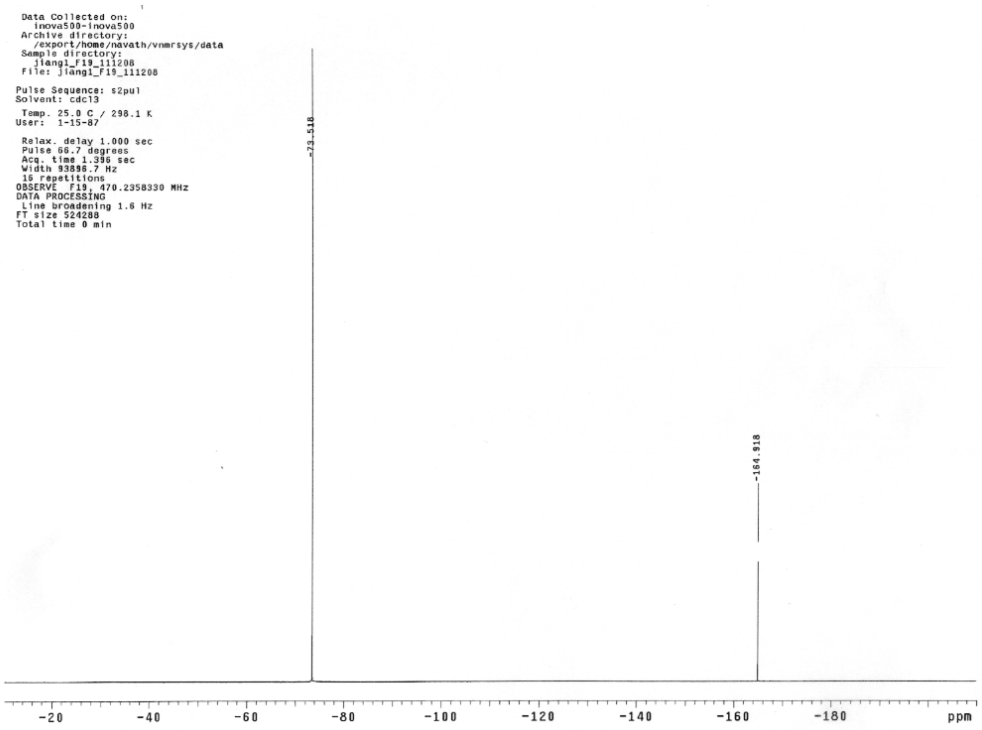
^{13}C NMR of compound **4**



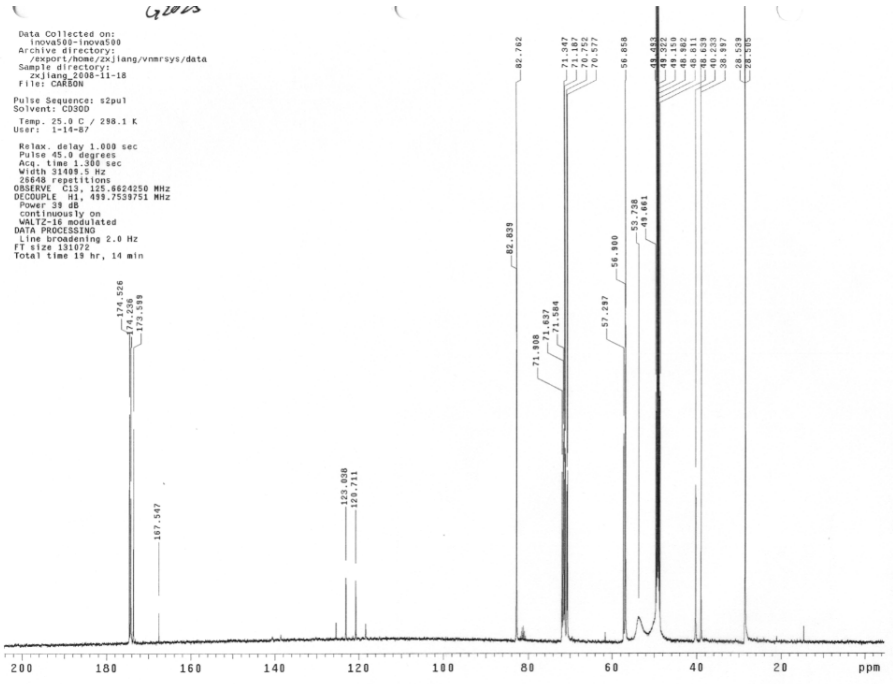
^{1}H NMR of compound **6**



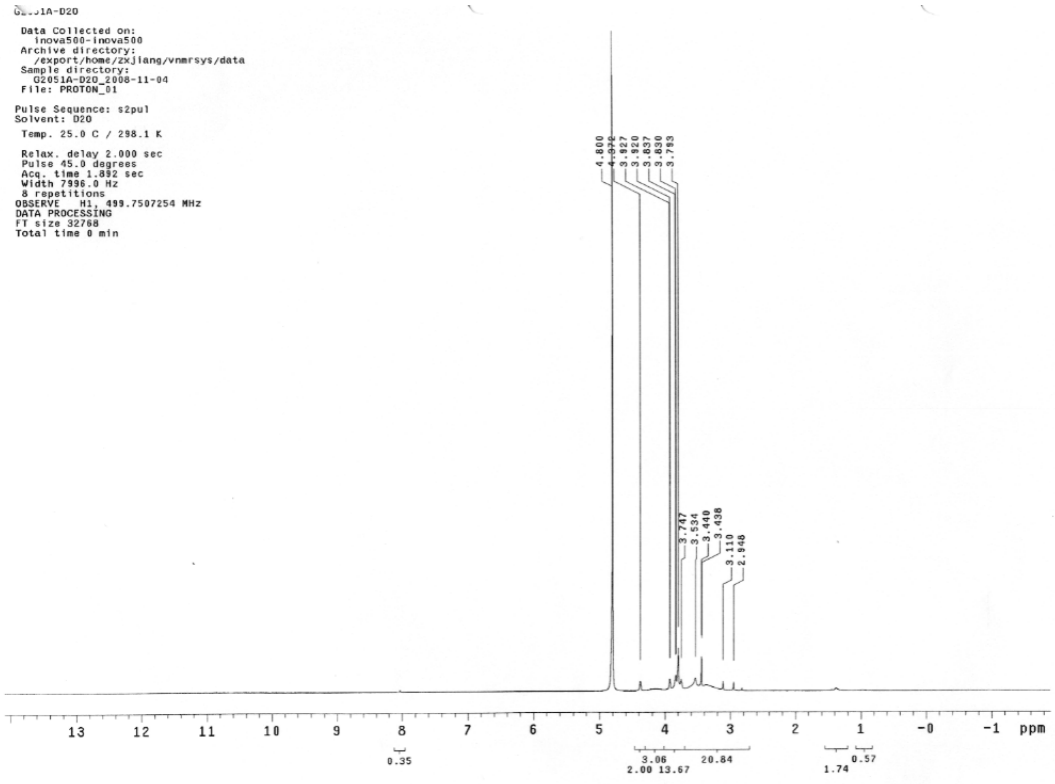
^{19}F NMR of compound **6**



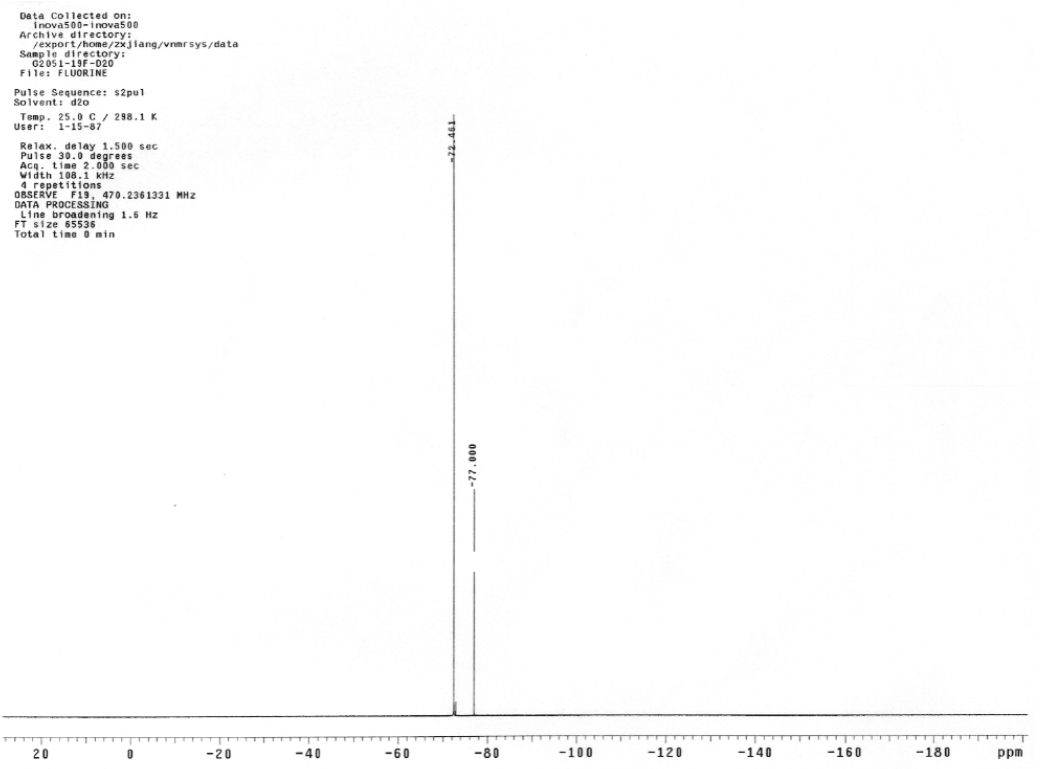
^{13}C NMR of compound **6**



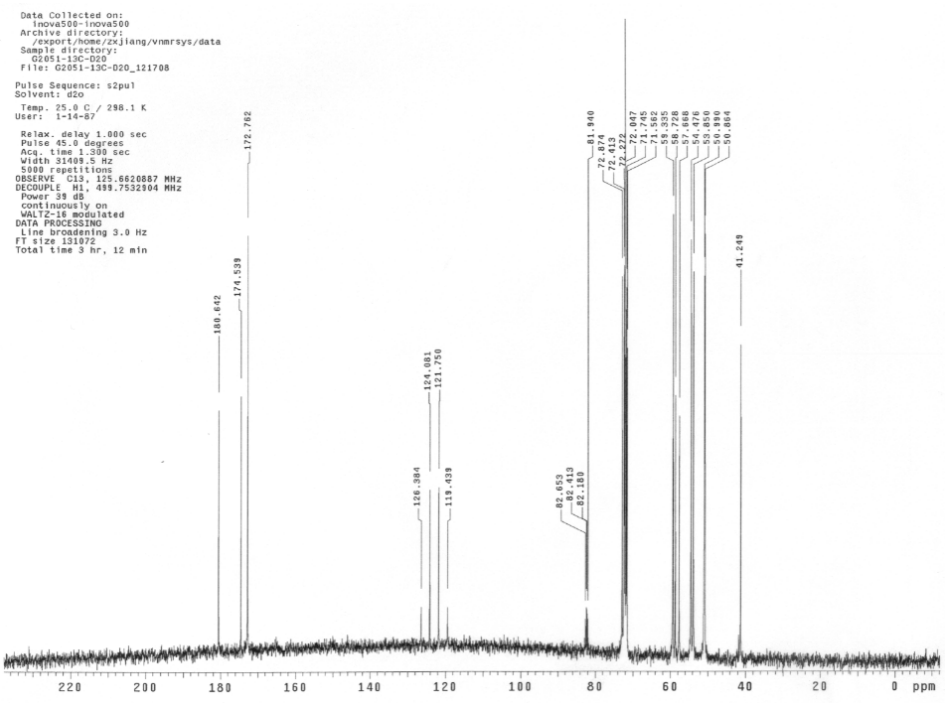
^{1}H NMR of compound **FC**



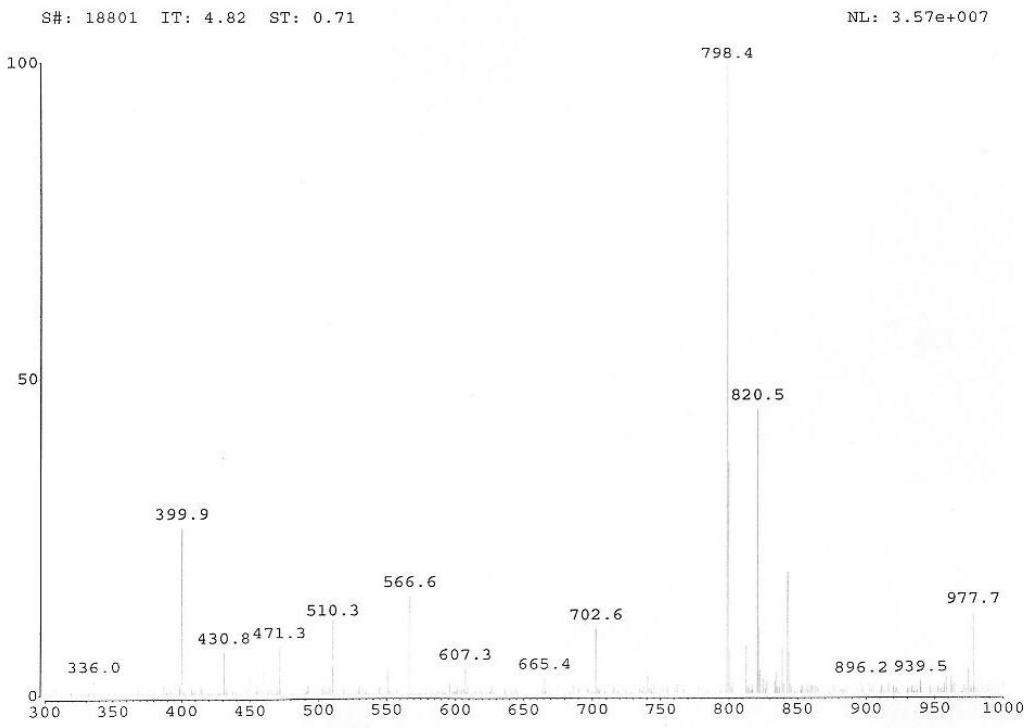
^{19}F NMR of compound **FC**



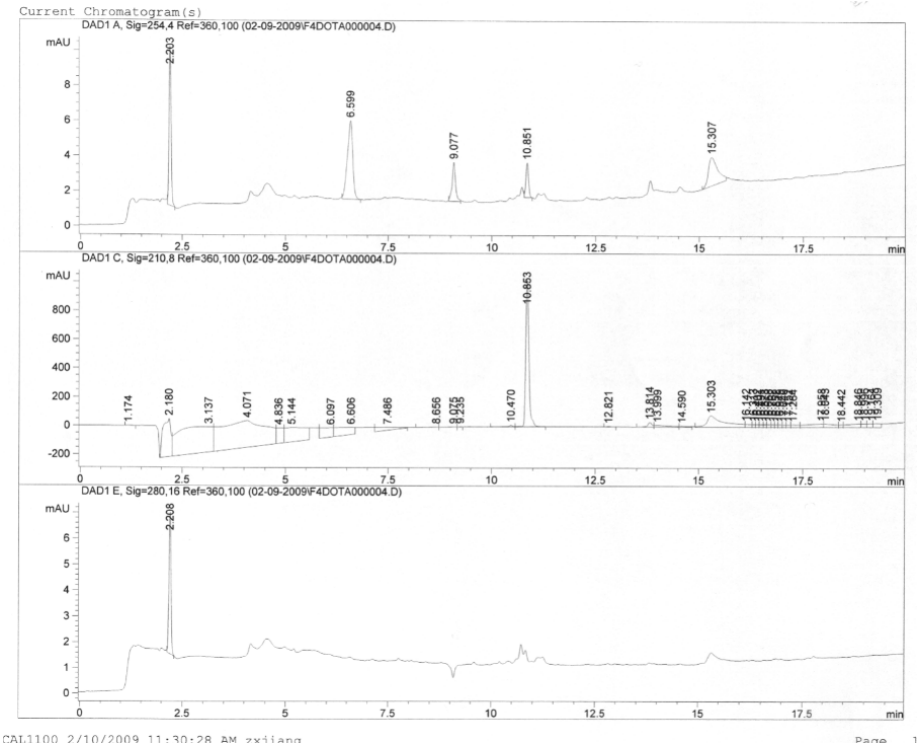
^{13}C NMR of compound **FC**



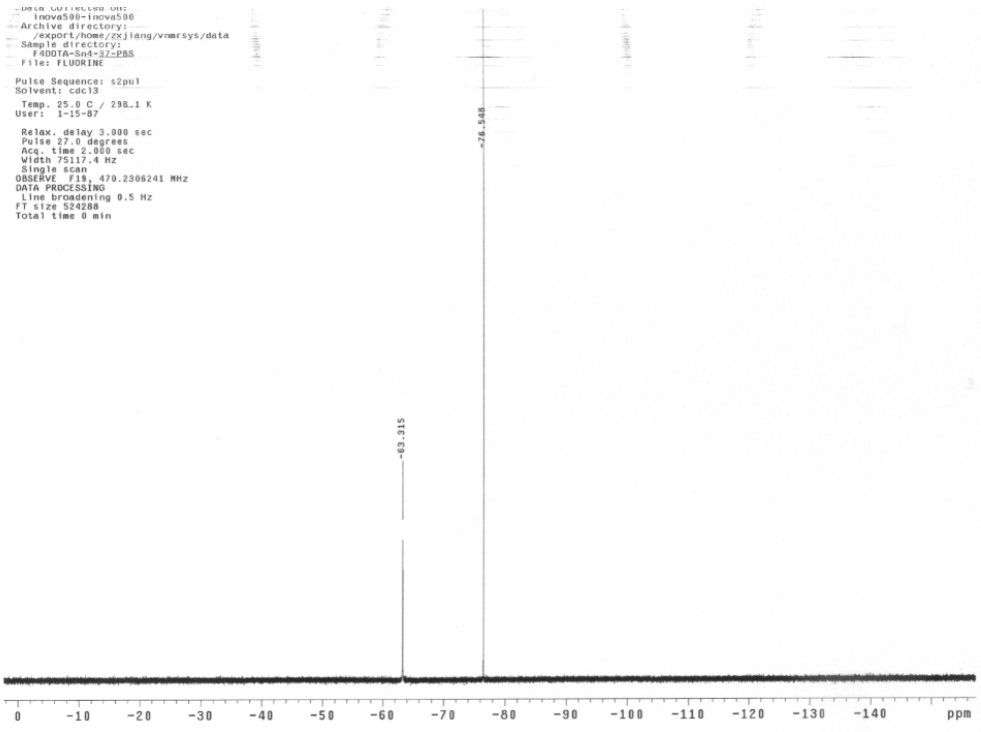
Masss pectrum of **FC**



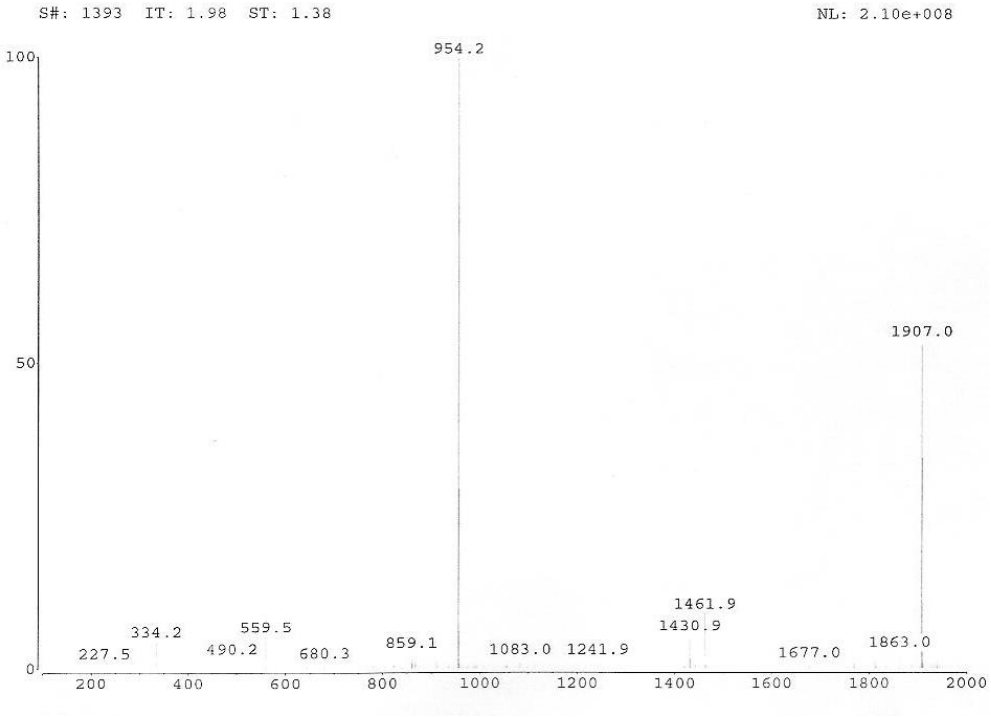
HPLC of compound **FC**-Tb^{3+}



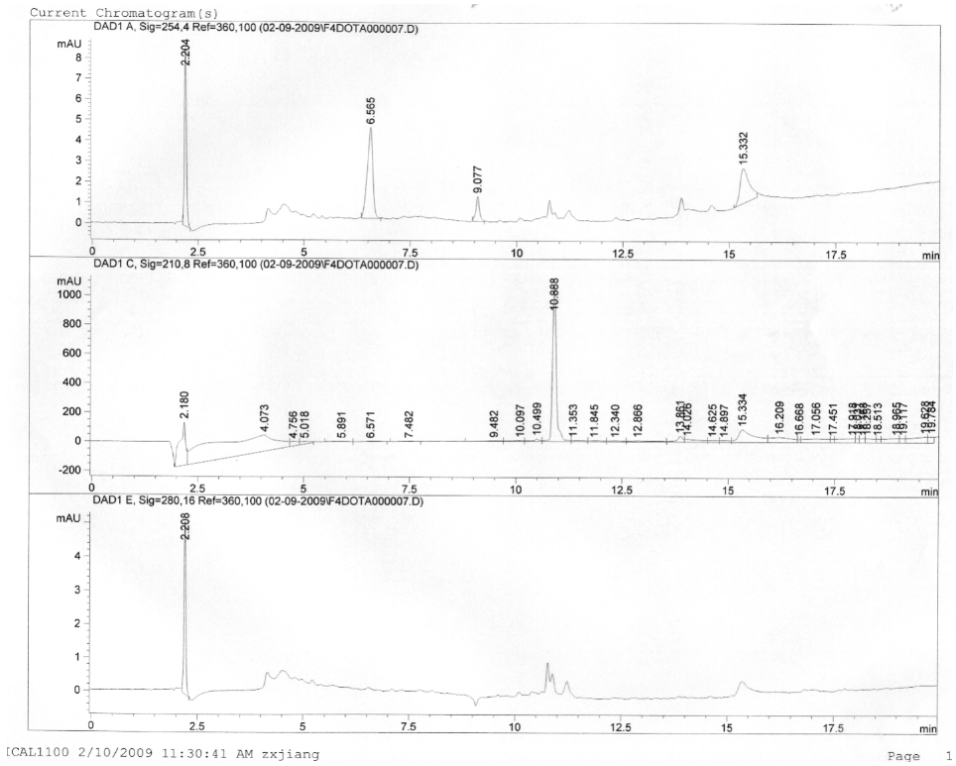
^{19}F NMR of compound **FC**-Tb^{3+}



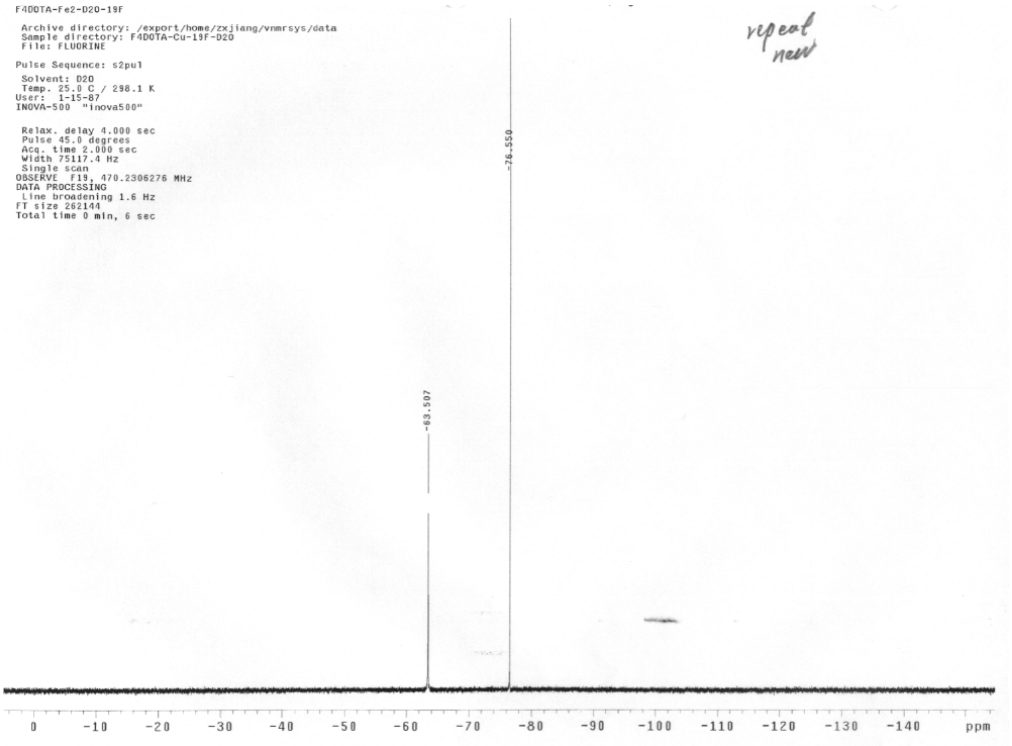
Masss pectrum of **FC**-Tb^{3+}



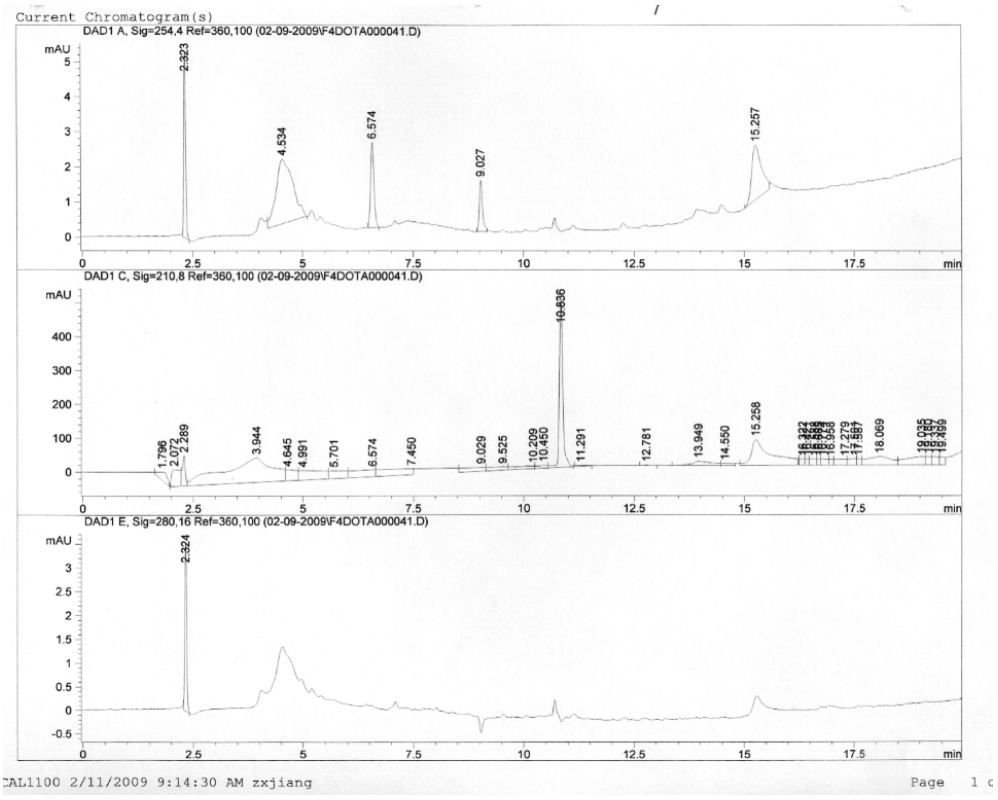
HPLC of compound **FC**-Ho^{3+}



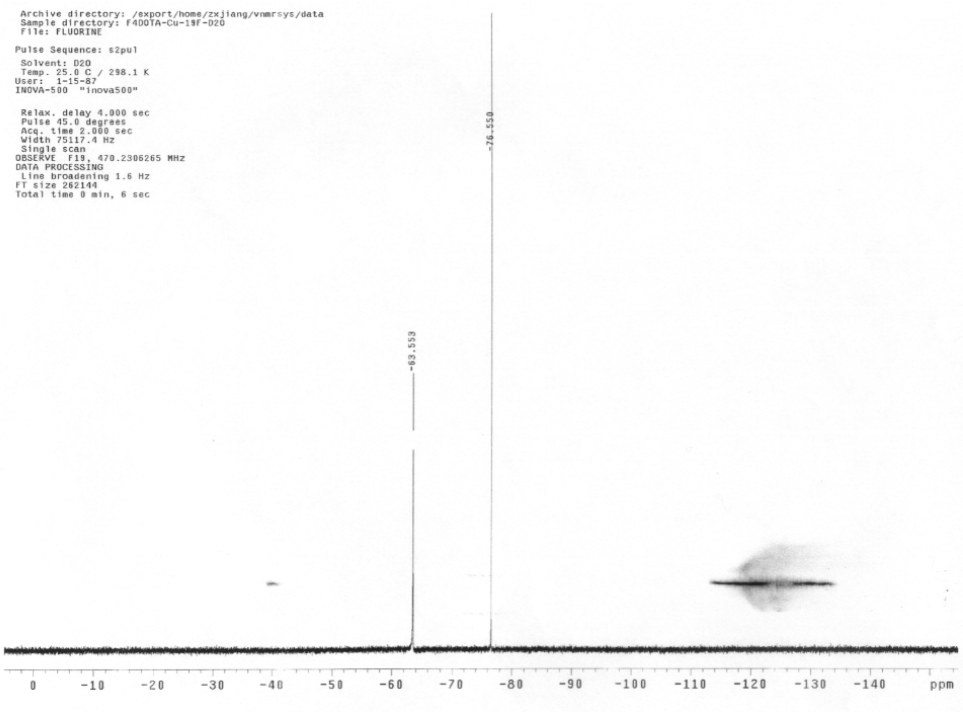
^{19}F NMR of compound **FC**-Ho^{3+}



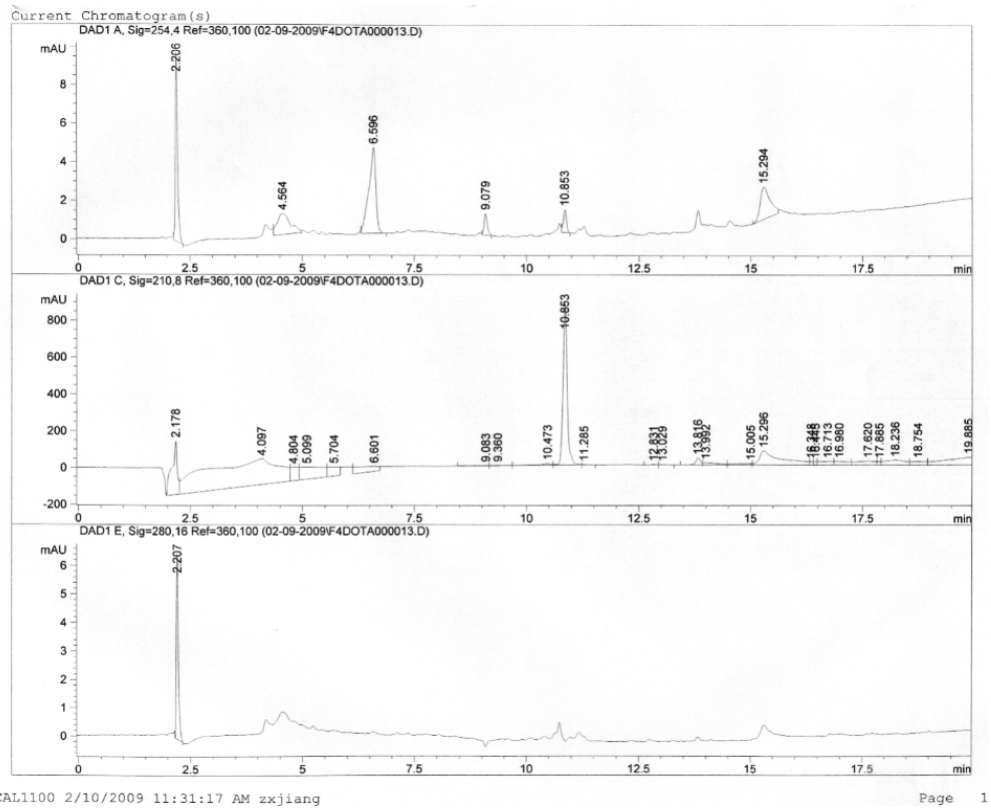
HPLC of compound **FC**-Dy^{3+}



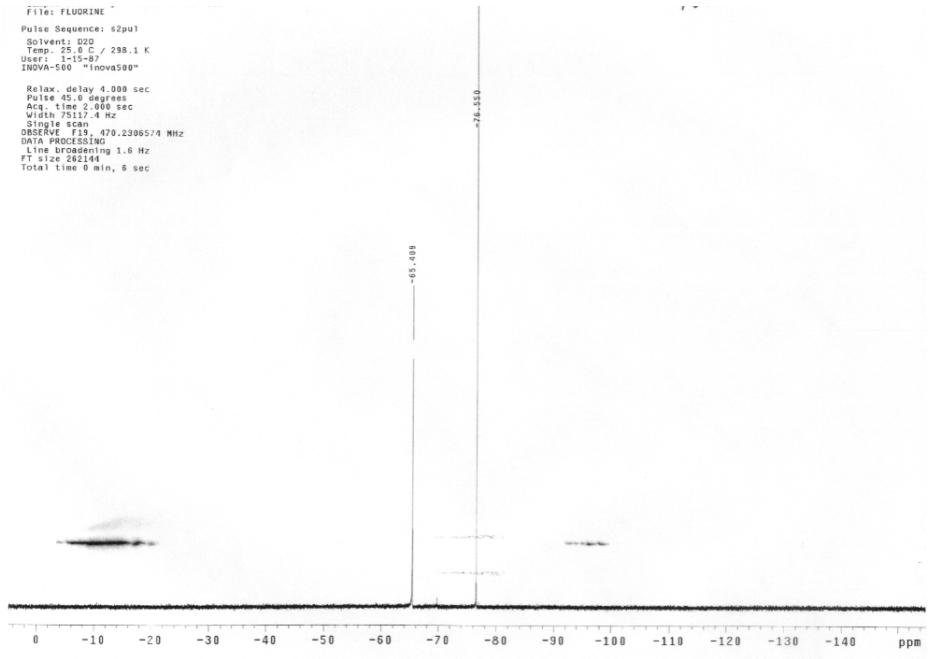
^{19}F NMR of compound **FC**-Dy^{3+}



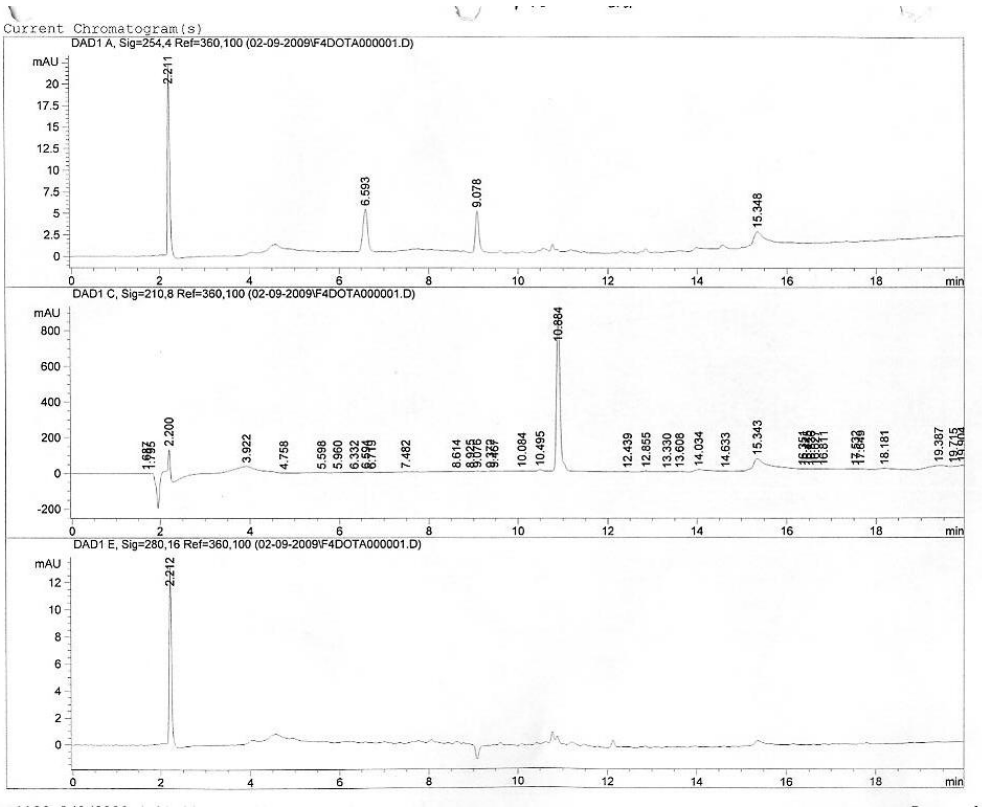
HPLC of compound **FC**-Er^{3+}



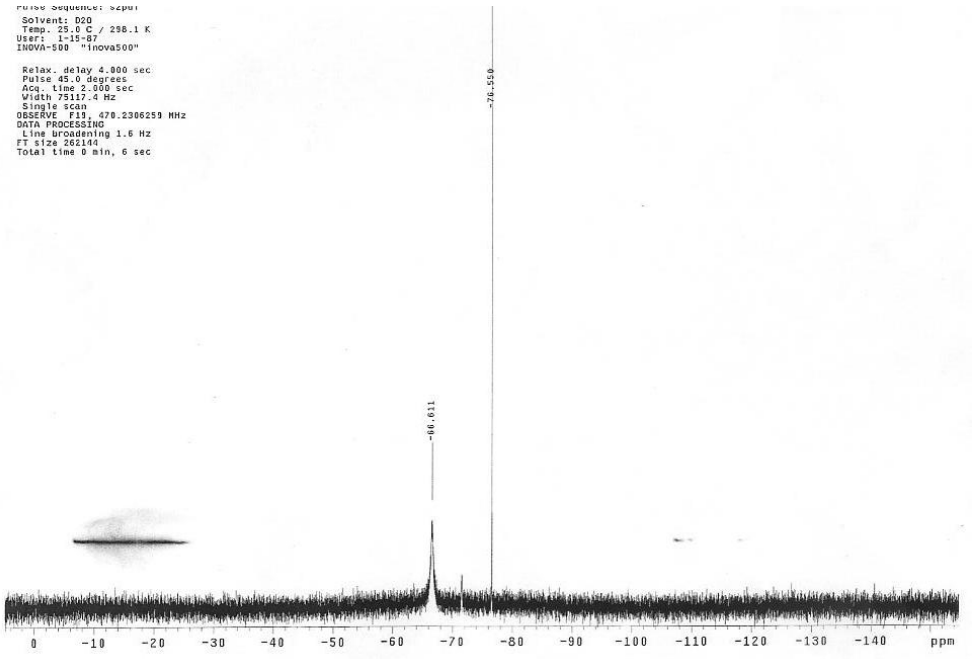
^{19}F NMR of compound **FC**-Er^{3+}



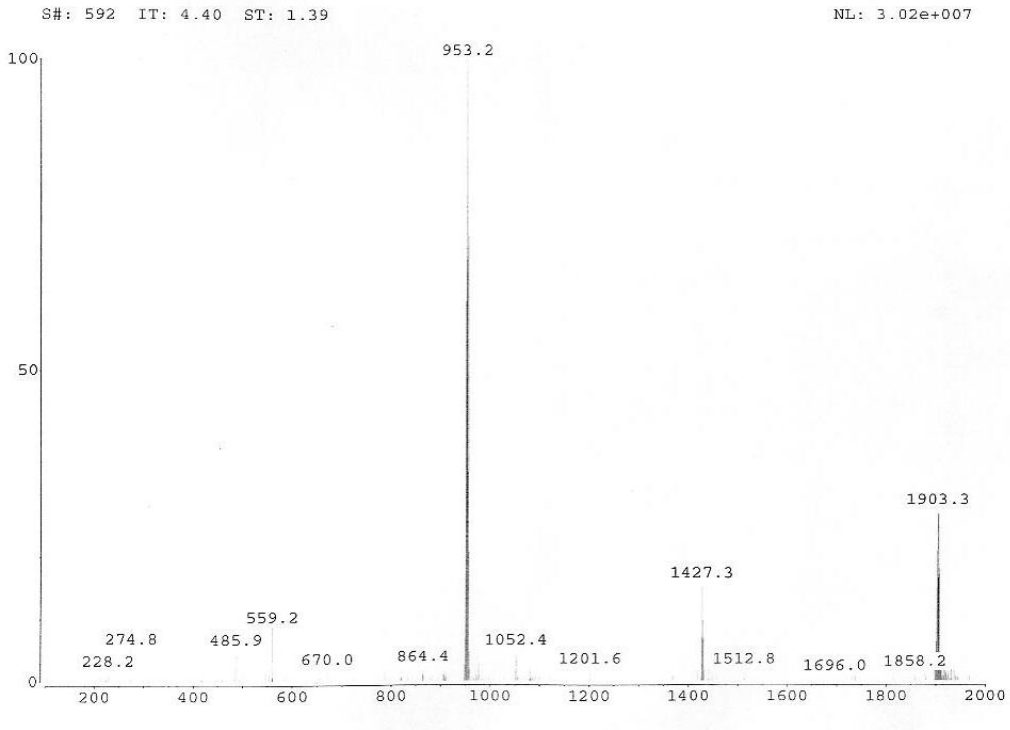
HPLC of compound **FC**-Gd^{3+}



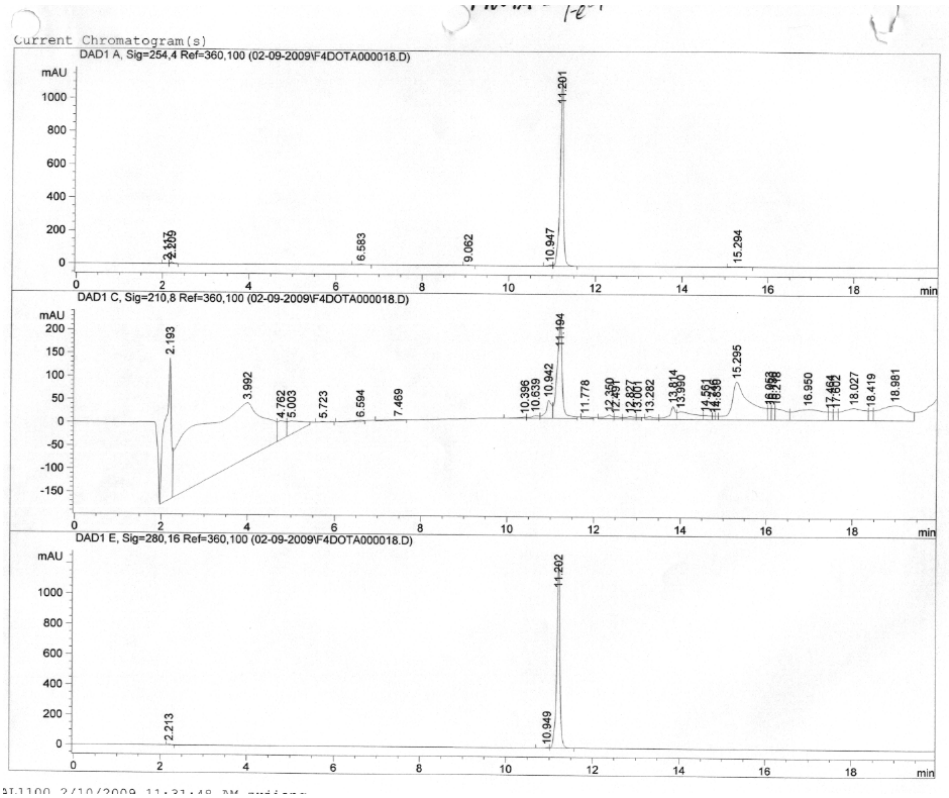
^{19}F NMR of compound **FC**-Gd^{3+}



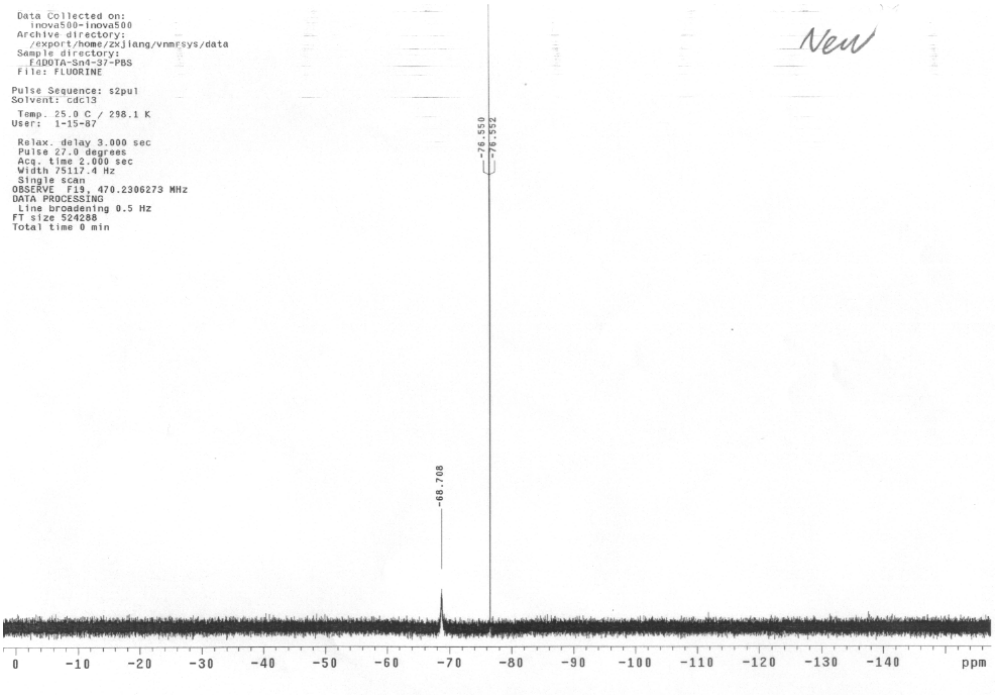
Mass spectrum of compound **FC**-Gd^{3+}



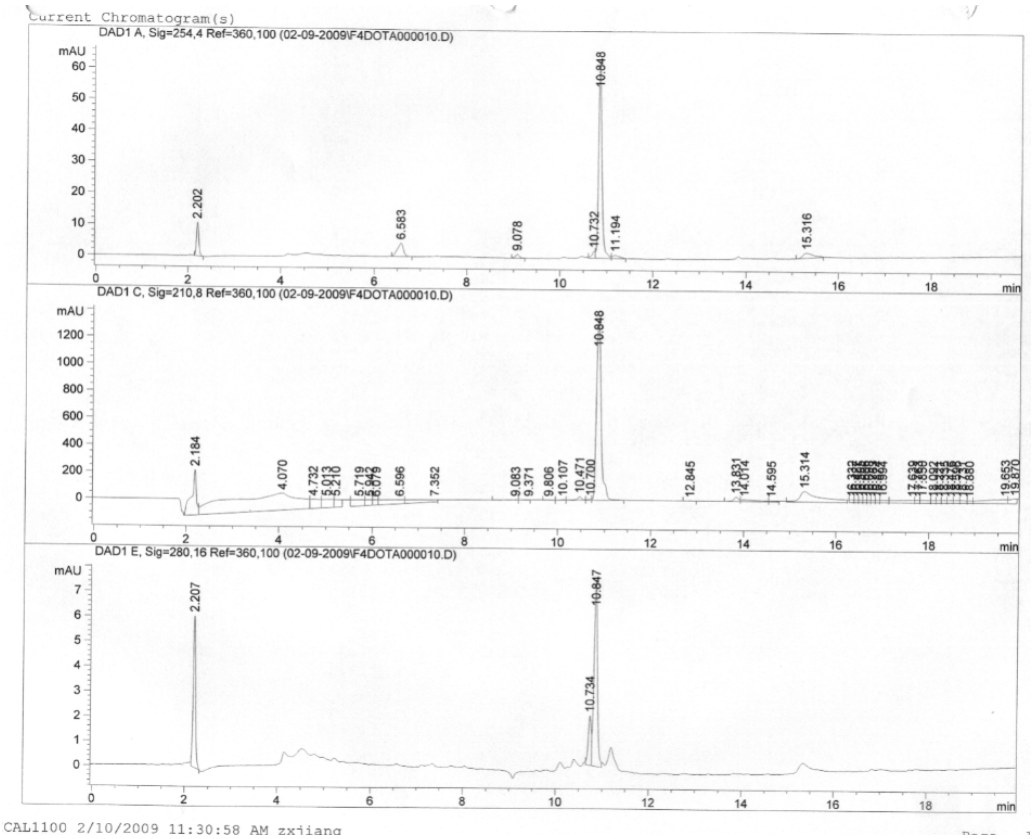
HPLC of compound **FC**-Fe^{3+}



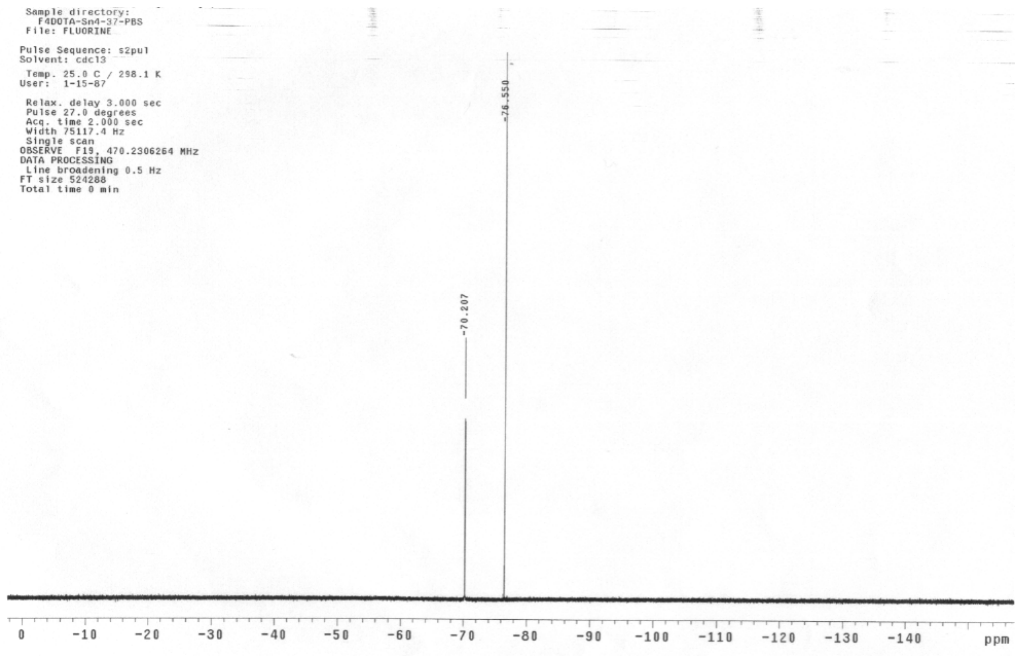
^{19}F NMR of compound **FC**-Fe^{3+}



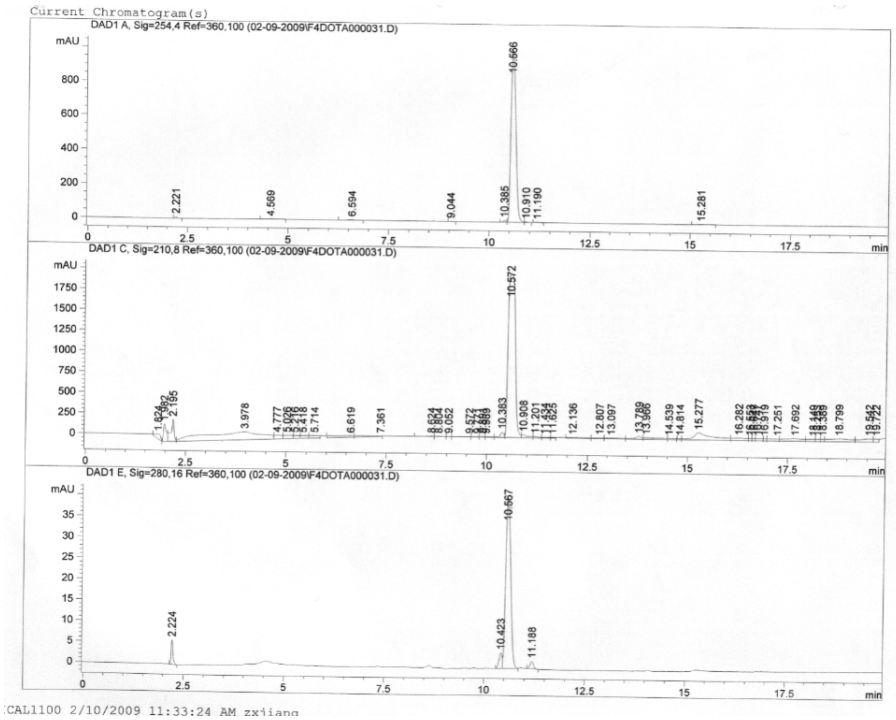
HPLC NMR of compound **FC**-Yb^{3+}



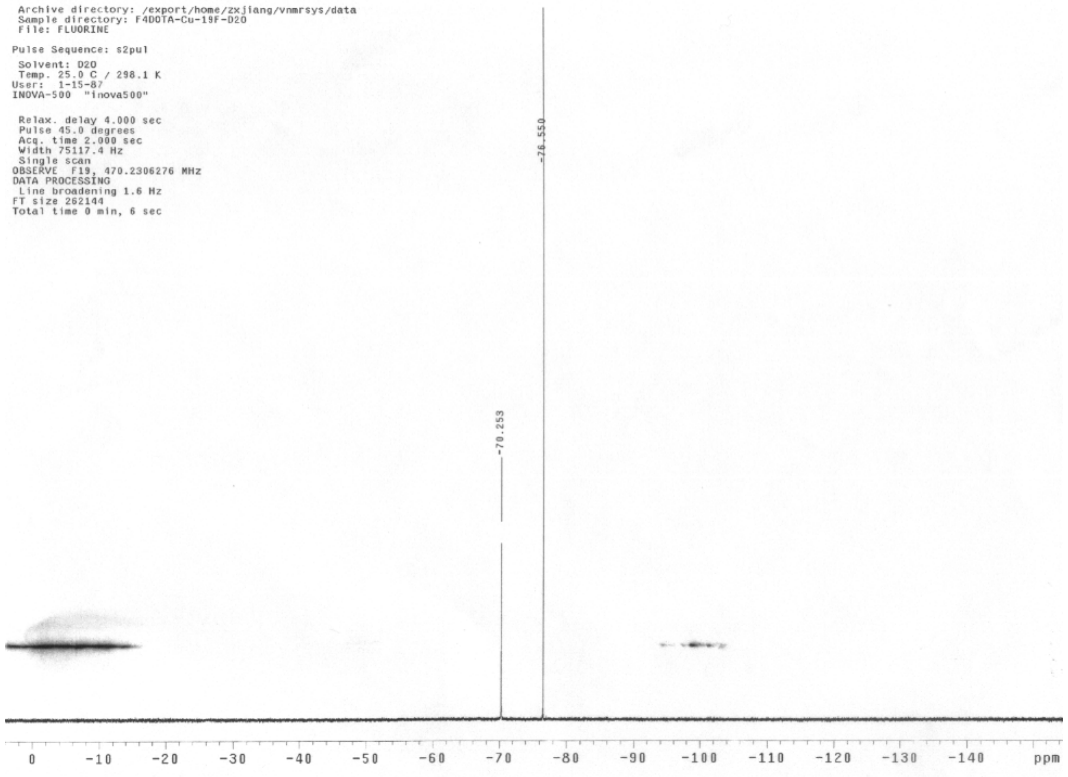
^{19}F NMR of compound **FC**-Yb^{3+}



HPLC NMR of compound **FC**-Ni^{3+}



^{19}F NMR of compound **FC**-Ni^{3+}



HPLC NMR of compound **FC**-Nd^{3+}