

Supporting Information

Synthesis of Electron-deficient Oxacalix[2]arene[2]triazines and Their Isomeric Analogs from One-pot Reaction of Perfluorinated Dihydroxybenzenes with Dichlorotriazines

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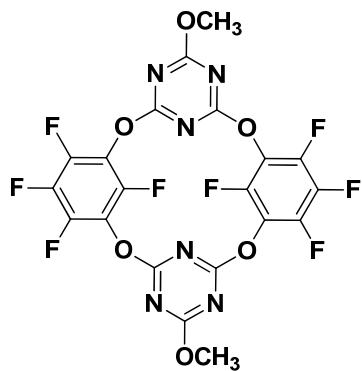
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1. General Information

¹H and ¹³C NMR spectra were recorded on 400MHz NMR spectrometers. Chemical shifts are reported in ppm versus tetramethylsilane with either tetramethylsilane or the residual solvent resonance used as an internal standard. ¹⁹F NMR chemical shifts were reported relative to residual benzotrifluoride (-63.80 ppm) as an outer standard. Abbreviations are used in the description of NMR data as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constant (J , Hz). Melting points are uncorrected. All solvents were dried according to standard procedures prior to use. All other major chemicals were obtained from commercial sources and used without further purification. Compound **1**, **2**, **8** was synthesized according to published procedure.^[1] Unless otherwise noted, all reactions were carried out in oven dried glasswares.

2. Synthesis of 4, 7 and 10

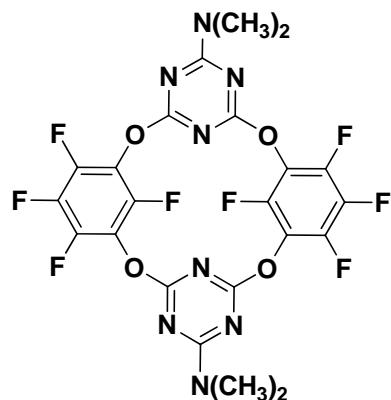
2.1 Synthesis of 4a.



A mixture of 2,4-Dichloro-6-methoxy-1,3,5-triazine **2a** (1.803 g, 10.0 mol), 2,4,5,6-tetrafluorobenzene-1,3-diol **1** (0.912 g, 5.0 mmol) and dried potassium carbonate powder (1.383 g, 10.0 mmol) in anhydrous acetone (30 ml) was stirred for 0.5 h at room temperature. A further portion of anhydrous acetone (120 ml) was added followed by the addition of **1** (0.910 g, 5.0 mmol) and potassium carbonate (1.656 g, 12 mmol). The resulting mixture was refluxed for 1.5 h. When the starting material

was consumed, which was monitored by TLC analysis, the reaction mixture was cooled down to room temperature. The insoluble substance was removed by filtration and the filtrate was concentrated to dryness. Dichloromethane (50 mL) was added and the organic solution was washed with water and brine (2×15 mL), and dried over anhydrous MgSO₄. After filtration and concentration under vacuum, the residue was recrystallized in a mixture of dichloromethane and methanol to give pure **4a** (2.690 g, yield: 93 %) as white solid: mp 205 - 209 °C; ¹H NMR (400 MHz, CDCl₃) δ 4.20 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 175.2 (s), 172.1 (s), 146.0 - 145.9 (m), 144.2 - 144.1 (m), 143.5 - 143.4 (m), 141.7 - 141.5 (m), 139.0 - 138.9 (m), 136.6 - 136.3 (m), 125.8 - 125.4 (m), 56.8 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ -144.5 (d, *J* = 5.6 Hz, 2F), -150.3 (d, *J* = 20.3 Hz, 4F), -162.3 (dt, *J* = 20.4 Hz, 5.6 Hz, 2F); IR (KBr, cm⁻¹) ν 1607, 1559, 1517, 1509; MS (CI) *m/z* (%) 578.0 [M]⁺ (100), 579.0 [M+H]⁺ (54). Anal. Calcd. for C₂₀H₆F₈N₆O₆: C, 41.54; H, 1.05; N, 14.53. Found: C, 41.29; H, 1.20; N, 14.57.

2.2 Synthesis of **4b**.



To a solution of reactant **2b** (0.384 g, 2.0 mmol) in anhydrous acetone (6 ml) was added 2,4,5,6-tetrafluorobenzene-1,3-diol **1** (0.182 g, 1.0 mmol) and dried cesium carbonate powder (0.326 g, 1.0 mmol) with stirring. The mixture was kept stirring at 30 °C for 8 h. A further portion of anhydrous acetone (24 ml) was added followed by the addition of compound **1** (0.182 g, 1.0 mmol) and cesium carbonate (0.456 g, 1.4 mmol). The reaction mixture was refluxed for 38 h until the starting materials were

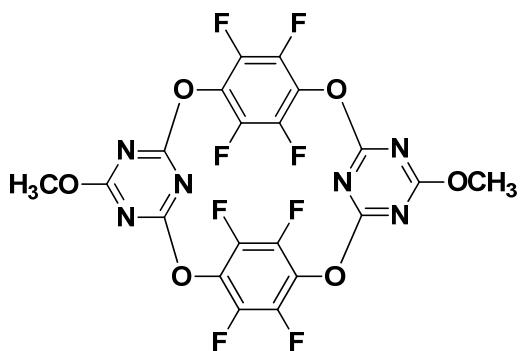
consumed, which was monitored by TLC, analysis. The reaction mixture was cooled down to room temperature and the solvent was removed using a rotary evaporator. Water (25 ml) was added and aqueous phase was extracted with dichloromethane (15 ml × 3). The organic phase was then washed by water and brine, dried over anhydrous MgSO₄. After filtration and concentration under vacuum, the residue was subjected to flash chromatography on silica gel (petroleum ether / ethyl acetate = 4: 1) to afford **4b** (0.326 g, yield: 54 %) as white solid: mp > 300 °C (sublimation); ¹H NMR (400 MHz, CDCl₃) δ 3.30 (s, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 170.5 (s), 167.9 (s), 146.5 - 146.4 (m), 144.1 - 143.9 (m), 141.6 - 141.4 (m), 138.8 - 138.5 (m), 136.3 - 136.0 (m), 126.0 - 125.7 (m), 37.2 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ -145.7 (d, *J* = 6.0 Hz, 2F), -152.0 (d, *J* = 23.3 Hz, 4F), -164.4 (dt, *J* = 23.1 Hz, 6.0 Hz, 2F); IR (KBr, cm⁻¹) ν 1655, 1617, 1514, 1507; MS (ESI) *m/z* (%) 605.6 [M+H]⁺ (100), 627.5 [M+Na]⁺ (9). Anal. Calcd. for C₂₂H₁₂F₈N₈O₄: C, 43.72; H, 2.00; N, 18.54. Found: C, 43.95; H, 2.18; N, 18.52.

Table S1 Optimization for the synthesis of **4b**

entry ^a	base	1 : 2b : base	Temp (°C).	t ₁ + t ₂ (h)	yield (%)
1	K ₂ CO ₃	1 : 1 : 2	rt	24 + —	trace
2	K ₂ CO ₃	1 : 1 : 2	reflux	48 + —	—
3	Cs ₂ CO ₃	1 : 1 : 1	rt	8 + 30	10
4	Cs ₂ CO ₃	1 : 1 : 1.1	rt	8 + 30	13
5	Cs ₂ CO ₃	1 : 1 : 1.2	rt	8 + 30	29
6	Cs ₂ CO ₃	1 : 1 : 1.5	rt	8 + 30	28
7	Cs ₂ CO ₃	1 : 1 : 2.0	rt	8 + 30	22
8	DIPEA	1 : 1 : 1.2	rt	4h + 48	10
9	DBU	1 : 1 : 1.2	rt	4h + 48	11
10	Et ₃ N	1 : 1 : 1.2	rt	2h + 48	—
11	Cs ₂ CO ₃	1 : 1 : 1.2	30	8 h + 30	54
12	Cs ₂ CO ₃	1 : 1 : 1.2	40	8 h + 30	47

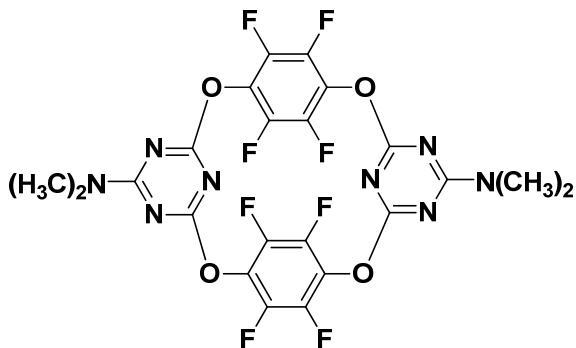
13	Cs_2CO_3	1 : 1 : 1.2	reflux	8 h + 28	30
^a Acetone was dried					

2.3 Synthesis of 7a.



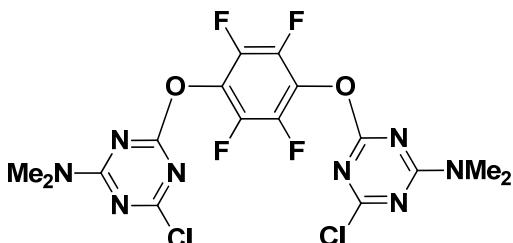
A mixture of 2,4-dichloro-6-methoxy-1,3,5-triazine **2a** (1.807 g, 10.0 mol), 2,3,5,6-tetrafluorobenzene-1,4-diol **5** (0.911 g, 5.0 mmol), dried potassium carbonate powder (1.381 g, 10.0 mmol) in anhydrous acetone (30 ml) was stirred at room temperature for 0.5 h. Another portion of anhydrous acetone (120 ml) was added followed by the addition of **5** (0.914 g, 5.0 mmol) and potassium carbonate (1.660 g, 12 mmol). The resulting mixture was refluxed for 2 h. The reaction mixture was cooled down to room temperature and insoluble substance was removed by filtration. The filtrate was concentrated to dryness and dichloromethane (40 mL) was added. The organic solution was washed by water (10 mL × 2) and brine (10 mL × 2), dried over with anhydrous MgSO_4 . After filtration and concentration, the residue was recrystallized in a mixture of dichloromethane and methanol to give pure **7a** (2.515 g, yield: 87 %) as white solid: mp > 300 °C (sublimation); ^1H NMR (400 MHz, CDCl_3) δ 4.02 (s, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.5 (s), 171.8 (s), 142.1 - 142.0 (m), 139.6 - 139.4 (m), 128.3 - 128.0 (m), 56.9 (s); ^{19}F NMR (376 MHz, CDCl_3) δ -154.1 (8F); IR (KBr, cm^{-1}) ν 1609, 1551, 1516, 1503; MS (CI) m/z (%) 577.9 [$\text{M}]^+$ (100), 578.9 [$\text{M+H}]^+$ (40). Anal. Calcd. for $\text{C}_{20}\text{H}_6\text{F}_8\text{N}_6\text{O}_6$: C, 41.54; H, 1.05; N, 14.53. Found: C, 41.24; H, 1.19; N, 14.58.

2.5 Synthesis of 7b.



Method A: One-pot macrocyclic condensation reaction of 2b with 5. A mixture of **2b** (0.386 g, 2.0 mmol), 2,3,5,6-tetrafluorobenzene-1,4-diol **5** (0.182 g, 1.0 mmol) and dried cesium carbonate powder (0.329 g, 1.0 mmol) in dried acetone (6 ml) was stirred at 30 °C for 8 h. Another portion of dried acetone (24 ml) was added followed by the addition of **5** (0.184 g, 1.0 mmol), cesium carbonate (0.458 g, 1.4 mmol) and deionized water (2 ml). The resulting mixture was refluxed for 38 h. When all the starting materials were consumed (monitored by TLC), the reaction mixture was cooled down to room temperature. The insoluble substance was removed by filtration and the filtrate was concentrated to dryness. Dichloromethane (50 ml) and water (25 ml) were added, and organic phase was separated. The aqueous phase was extracted with dichloromethane (15 ml × 3). The combined organic phase was washed with brine, dried over with anhydrous MgSO₄. After filtration and concentration, the residue was flash chromatographed on a silica gel column (petroleum ether / ethyl acetate = 5: 1) to afford **7b** (0.247 g, yield: 41 %).

Method B: Synthesis from fragment coupling reaction of 6b with 5



Preparation of 6b. A mixture of **2b** (0.385 g, 2.0 mmol), 2,3,5,6-tetrafluorobenzene-1,4-diol **5** (0.183 g, 1.0 mmol) and dried cesium carbonate

powder (0.329 g, 1.0 mmol) in dried acetone (6 ml) was stirred for 9 h at room temperature. The insoluble substance was removed by filtration and the filtrate was concentrated to dryness. The residue was flash chromatographed on a silica gel column (petroleum ether / ethyl acetate = 6: 1) to afford **6b** (0.149 g, yield: 30 %) as pale yellow solid: ¹H NMR (400 MHz, CDCl₃) δ 3.23 (s, 6 H), 3.08 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 171.2 (s), 169.0 (s), 165.9 (s), 142.5 - 142.3 (m), 139.9 - 139.7 (m), 128.1 - 128.0 (m), 37.0 (s), 36.8 (s); ¹⁹F NMR (376MHz, CDCl₃) δ -154.4 (4F); IR (KBr, cm⁻¹) v 1603, 1577, 1495; MS (CI) *m/z* (%) 459.2 [M-Cl]⁺ (100), 495.1 [M]⁺ (47), 497.1 [M+2]⁺ (31), 499.1 [M+4]⁺ (6). Intermediate **6b** is not stable and undergoes decomposition at room temperature. It was used directly for the next macrocyclization step without further purification.

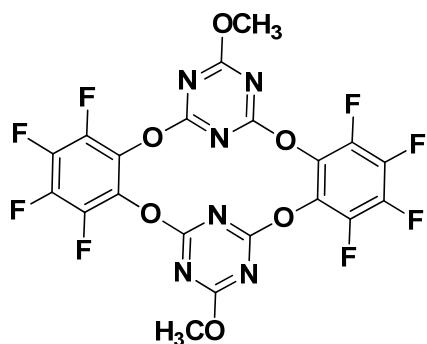
Synthesis of 7b. Under the atmosphere of Ar, a mixture of **6b** (0.248 g, 0.5 mmol), **5** (0.110 g, 0.6 mmol) and cesium carbonate powder (0.327 g, 1.0 mmol) in dried acetone (20 ml) was refluxed for 18 h until the complete consumption **6b**, which was monitored by TLC. The resulting mixture was cooled down to room temperature. The insoluble substance was removed by filtration and the filtrate was concentrated to dryness. Dichloromethane (50 ml) and water (25 ml) were added, and organic phase was separated. The aqueous phase was extracted with dichloromethane (15 ml × 3). The combined organic phase was washed with brine (10 mL × 2) and dried over with anhydrous MgSO₄. After filtration and concentration, the residue was flash chromatographed on a silica gel column (petroleum ether / ethyl acetate = 5: 1) to afford **7b** (0.196 g, yield: 65 %): white solid, mp > 300 °C (sublimation); ¹H NMR (400 MHz, CDCl₃) δ 3.30 (s, 12 H); ¹³C NMR (100 MHz, CDCl₃) δ 169.7 (s), 164.6 (s), 139.6 - 139.3 (m), 137.1 - 136.9 (m), 127.9 - 127.7 (m), 37.1 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ -154.0 (8F); IR (KBr, cm⁻¹) v 1600, 1583, 1501; MS (ESI) *m/z* (%) 605.3 [M+H]⁺ (100). Anal. Calcd. for C₂₂H₁₂F₈N₈O₄: C, 43.72; H, 2.00; N, 18.54. Found: C, 43.70; H, 2.21; N, 18.49.

Table S2 Optimization for the synthesis of **7b**

Entry	solvent 1 ^a	solvent 2	Ratio of	t (h)	yield (%)
			solvent 1 : solvent2		
1	acetone	acetone	—	40	30
2	THF	THF	—	36	21
3	acetonitrile	acetonitrile	—	24	25
4	1,4-dioxane	1,4-dioxane	—	17	13
5	DMSO	DMSO	—	15	15
6	acetone	acetone + H ₂ O	15 : 1	36	41
7	THF	THF + H ₂ O	15 : 1	34	27
8	acetonitrile	acetonitrile + H ₂ O	15 : 1	24	33
9	1,4-dioxane	1,4-dioxane + H ₂ O	15 : 1	28	25
10	acetone	acetone + H ₂ O	5 : 1	26	18
11	acetone	acetone + H ₂ O	6 : 1	30	20
12	acetone	acetone + H ₂ O	7.5 : 1	33	30
13	acetone	acetone + H ₂ O	10 : 1	36	37
14	acetone	acetone + H ₂ O	12 : 1	36	37
15	acetone	acetone + H ₂ O	15 : 1	36	41
16	acetone	acetone + H ₂ O	30 : 1	40	35
17	acetone	acetone + H ₂ O	20 : 1 ^b	36	40
18	acetone	acetone + H ₂ O	30 : 1 ^c	36	36

^aDry solvents were used. ^bAcetone (20 mL) and water (1 mL) were used. ^cAcetone (30 mL) and water (1 mL) were used.

2.6 Synthesis of **10a**.



Under the atmosphere of Ar, a mixture of 2,4-dichloro-6-methoxy-1,3,5-triazine **2a** (1.803 g, 10.0 mol), 3,4,5,6-tetrafluorobenzene-1,2-diol **8** (0.912 g, 5.0 mmol) and dried potassium carbonate powder (1.383 g, 10.0 mmol) in anhydrous acetone (30 ml) was stirred for 1 h at room temperature. Another portion of dried acetone (120 ml) was added followed by the addition of **8** (0.911 g, 6 mmol), potassium carbonate (1.659 g, 12 mmol) and deionized water (10 ml). The resulting mixture was refluxed for 3 h. When **2a** was consumed (monitored by TLC), the reaction mixture was cooled down to room temperature. The insoluble substance was removed by filtration and the filtrate was concentrated to dark brown oil which was directly flash chromatographed on a silica gel column (petroleum ether / ethyl acetate = 3: 1) to afford **10a** (1.360 g, 47 %) as white solid: mp 196 - 199 °C; ¹H NMR (400 MHz, CDCl₃) δ 4.22 (s, 6 H); ¹³C NMR (100 MHz, CDCl₃) δ 172.6 (s), 171.5 (s), 138.9 - 138.7 (m), 136.8 - 136.3 (m), 134.3 - 134.0 (m), 130.2 - 130.0 (m), 57.7 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ -152.5 - -153.0 (m, 4F), -157.7 - -157.8 (m, 4F); IR (KBr, cm⁻¹) ν 1608, 1551, 1518, 1503; MS (ESI) *m/z* 579.1 [M+H]⁺. Anal. Calcd. for C₂₀H₆F₈N₆O₆: C, 41.54; H, 1.05; N, 14.53. Found: C, 41.88; H, 1.32; N, 14.36.

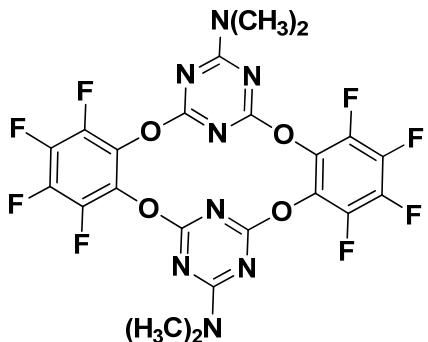
Table S3 Optimization for the synthesis of **10a**

entry	solvent	atmosphere	t ^a (h)	yield (%)
1	acetone	air	2.5	25
2	acetone (dried)	air	2.5	29
3 ^b	Acetone (dried) : H ₂ O ^c	air	3	16

4 ^d	Acetone (dried) : H ₂ O ^c	air	3	40
5	acetone	Ar	2.5	37
6	acetone (dried)	Ar	2.5	36
7 ^b	Acetone (dried) : H ₂ O ^c	Ar	3	20
8 ^d	Acetone (dried) : H ₂ O ^c	Ar	3	47

^a Time used for the complete conversion of **2a**, which was monitored by TLC analysis. ^b Water was used in the first step reaction. ^c Acetone (150 mL) and water (10 mL) were used. ^d Water was added in the second step reaction.

2.7 Synthesis of **10b**.



Under the atmosphere of Ar, a mixture of **2b** (0.387 g, 2.0 mmol), 3,4,5,6-tetrafluorobenzene-1,2-diol **8** (0.183 g, 1.0 mmol) and dried cesium carbonate powder (0.326 g, 1.0 mmol) in dried acetone (6 ml) was stirred at 30 °C for 8 h. Another portion of dried acetone (24 ml) was added followed by the addition of **8** (0.200 g, 1.1 mmol), cesium carbonate (0.458 g, 1.4 mmol) and deionized water (2 ml). The resulting mixture was refluxed for 40 h. When **2b** was consumed (monitored by TLC), the reaction mixture was cooled down to room temperature. The insoluble substance was removed by filtration and the filtrate was concentrated to dark brown oil. The dark brown oil was firstly flash chromatographed on a silica gel (100 - 200 mesh) column (petroleum ether / ethyl acetate = 4: 1) to obtain yellow oil, which was again flash chromatographed on a silica gel (200 - 300 mesh) column (petroleum ether / ethyl acetate = 8: 1) to afford **10b** (0.181 g, 30%) as white solid: mp >300 °C (sublimation); ¹H NMR (400 MHz, CDCl₃) δ 3.30 (s, 12 H); ¹³C NMR (100 MHz,

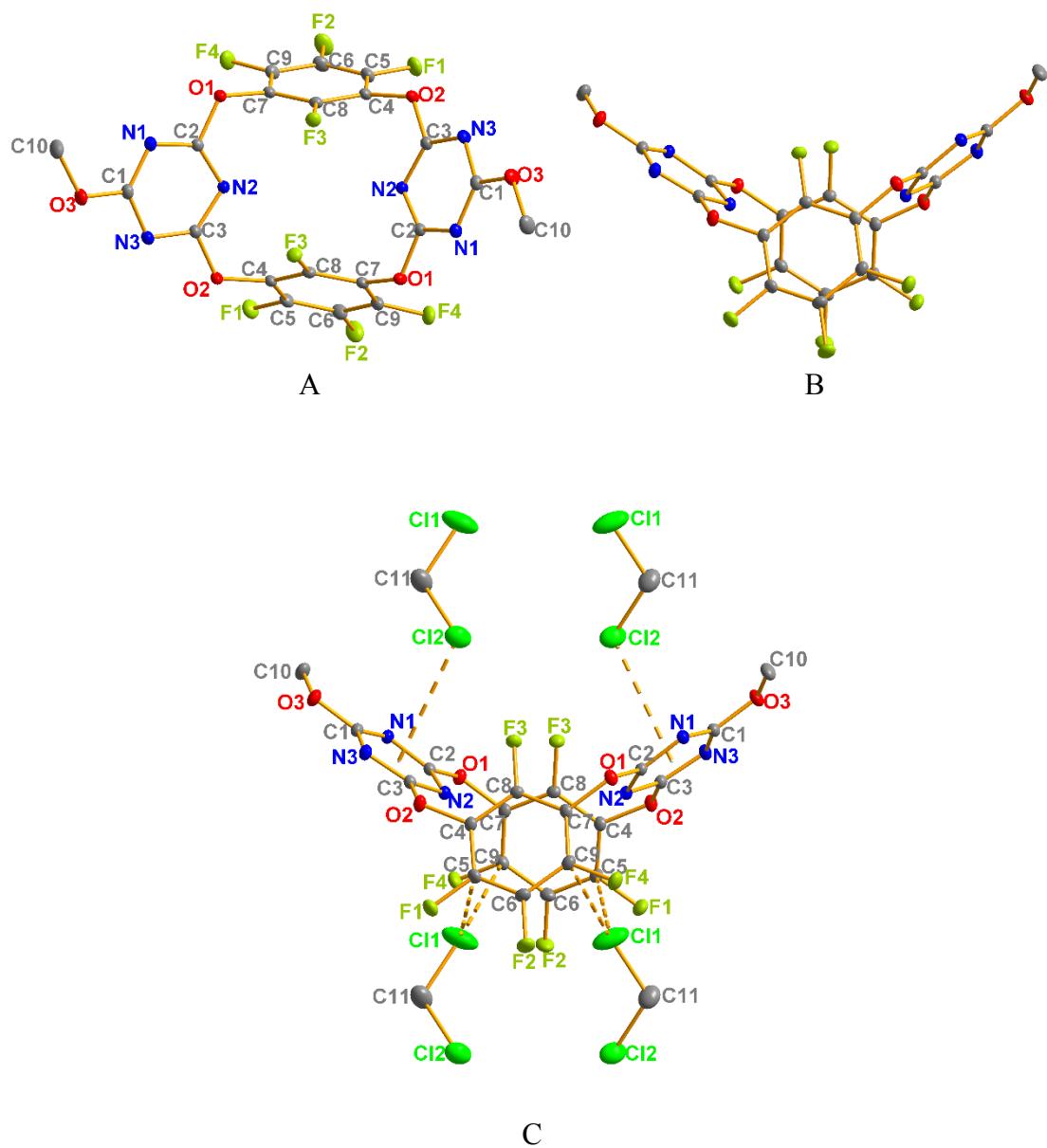
CDCl_3) δ 169.5 (s), 164.5 (s), 138.9 - 138.7 (m), 136.7 - 136.4 (m), 134.3 - 133.9 (m), 130.5 - 130.2 (m), 37.2 (s); ^{19}F NMR (376 MHz, CDCl_3) δ -152.9 - -153.0 (m, 4F), -157.7 - -157.8 (m, 4F); IR (KBr, cm^{-1}) ν 1602, 1576, 1505; MS (ESI) m/z (%) 605.9 [$\text{M}+\text{H}]^+$ (100), 627.8 [$\text{M}+\text{Na}]^+$ (12). Anal. Calcd. for $\text{C}_{22}\text{H}_{12}\text{F}_8\text{N}_8\text{O}_4$: C, 43.72; H, 2.00; N, 18.54. Found: C, 43.80; H, 2.24; N, 18.14.

3. X-ray Crystallographic Data

Compound	4a·(CH₂Cl₂)₂	4b	7a	10a
empirical formula	$\text{C}_{22}\text{H}_{10}\text{Cl}_4\text{F}_8\text{N}_6\text{O}_6$	$\text{C}_{22}\text{H}_{12}\text{F}_8\text{N}_8\text{O}_4$	$\text{C}_{20}\text{H}_6\text{F}_8\text{N}_6\text{O}_6$	$\text{C}_{20}\text{H}_6\text{F}_8\text{N}_6\text{O}_6$
M_r	748.16	604.4	578.31	578.31
crystal size [mm ³]	0.50×0.50×0.30	0.34×0.20×0.14	0.32×0.19×0.11	0.60×0.50×0.20
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	C2/c	P-1	P-1	P-1
a [Å]	23.108(2)	8.6780(17)	7.1595(14)	8.3306(17)
b [Å]	10.2900(7)	16.031(3)	8.7231(17)	13.589(3)
c [Å]	15.5912(14)	17.808(4)	9.2770(19)	19.417(4)
α [deg]	90.00	75.13(3)	90.88(3)	92.70(3)
β [deg]	131.567(3)	80.07(3)	100.91(3)	94.67(3)
γ [deg]	90.00	77.81(3)	114.13(3)	97.19(3)
V [Å ³]	2773.8(4)	2321.9(8)	516.41(21)	2169.9(8)
d [g/cm ³]	1.792	1.729	1.860	1.770
Z	4	4	1	4
T [K]	173(2)	173(2)	173(2)	173(2)
R factor [I>2σ(I)]	0.0560	0.1395	0.0472	0.0381

R factor (all data)	0.0564	0.1611	0.0531	0.0536
quality of fit	1.149	2.334	1.143	1.074

4. X-Ray Molecule Structure of 4, 7a and 10a.



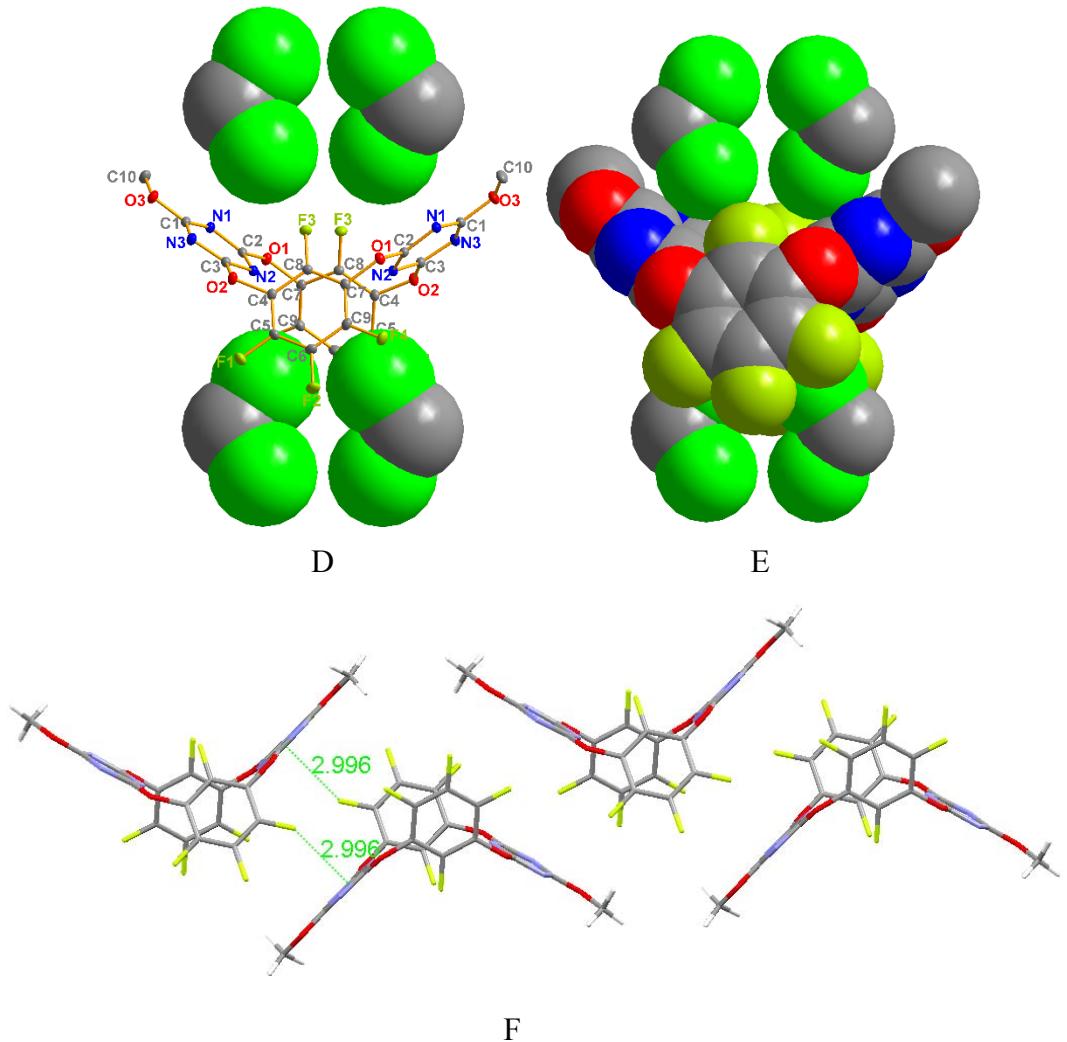
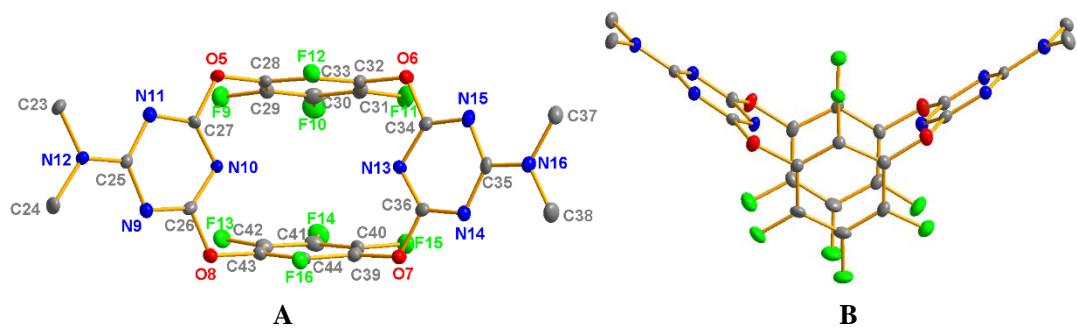


Figure S1 Crystal structure of **4a** (A) top view, (B) side view, (C to E) complex of **4a** and dichloromethane molecules and (F) self assembly in solid state. Selected bond length [Å]: C4-O2 1.383, O2-C3 1.359, C2-O1 1.356, O1-C7 1.387. Selected distances [Å]: C1···C1 8.871, N2···N2 4.535, C8···C8 4.248, C6···C6 6.224. Hydrogens are omitted for clarity. The probability is 25 percent.



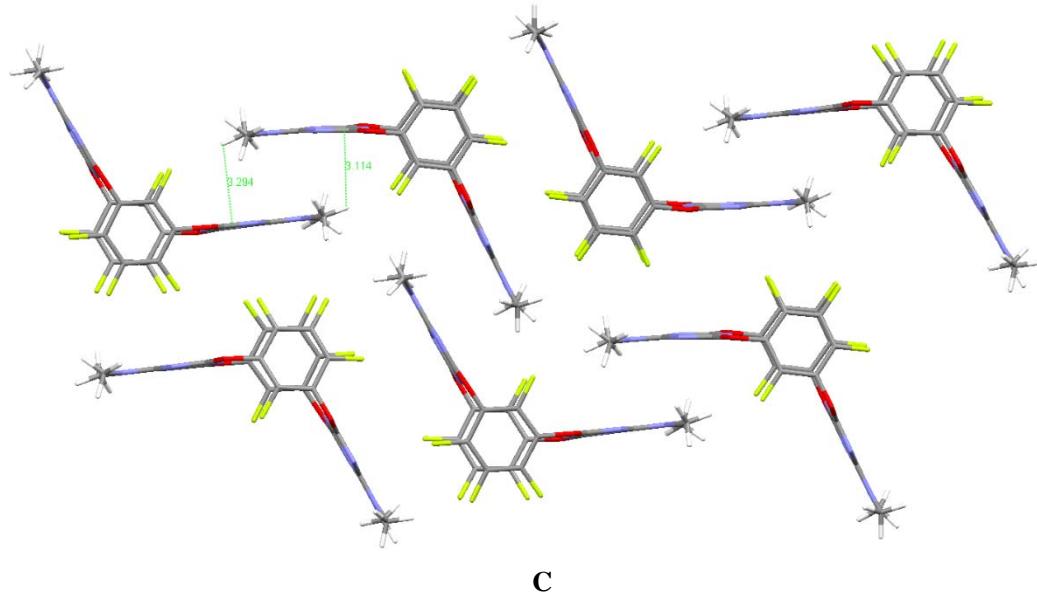


Figure S2 Crystal structure of **4b** (A) top view, (B) side view and (C) self assembly in solid state. Selected bond length [Å]: C27-O5 1.363, O5-C28 1.391, C32-O6 1.384, O6-C34 1.370, C36-O7 1.368, O7-C39 1.380, C43-O8 1.401, O8-C26 1.358. Selected distances [Å]: C25···C35 9.148, N10···N13 4.655, C33···C44 4.602, C30···C41 3.760. Hydrogens are omitted for clarity. The probability is 25 percent.

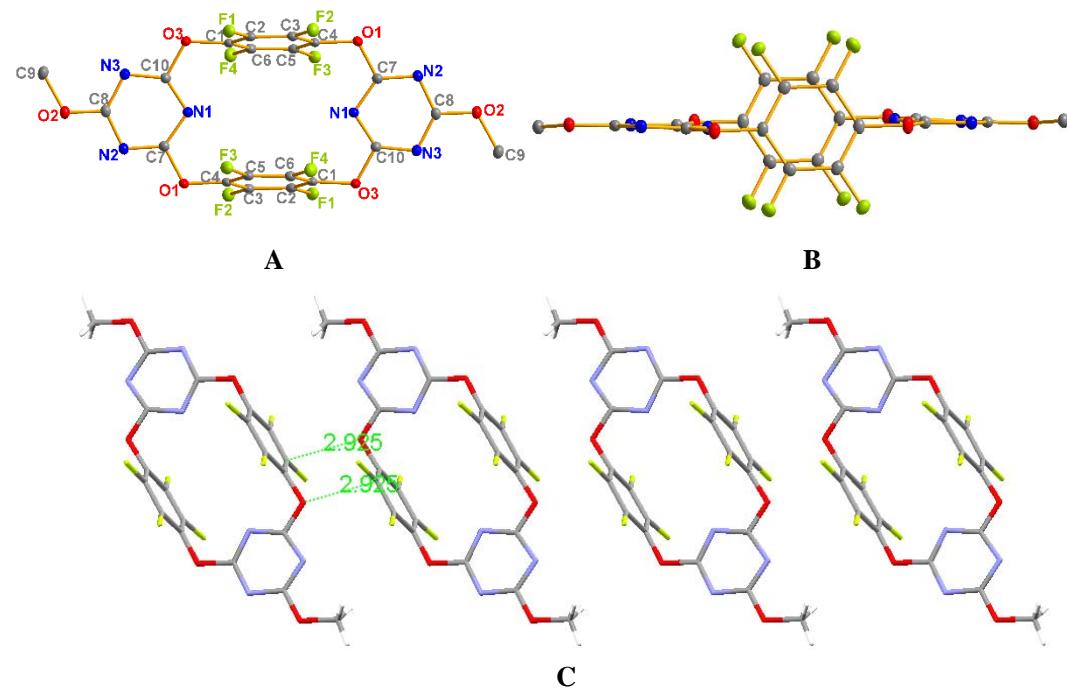


Figure S3 Crystal structure of **7a** (A) top view, (B) side view and (C) self assembly in solid state. Selected bond length [Å]: C4-O1 1.390, O1-C7 1.359, C10-O3 1.356, O3-C1 1.392. Selected distances [Å]: C8···C8 10.667, N1···N1 5.357, C2···C5 4.477, C3···C6 4.507. Hydrogens are omitted for clarity. The probability is 25 percent.

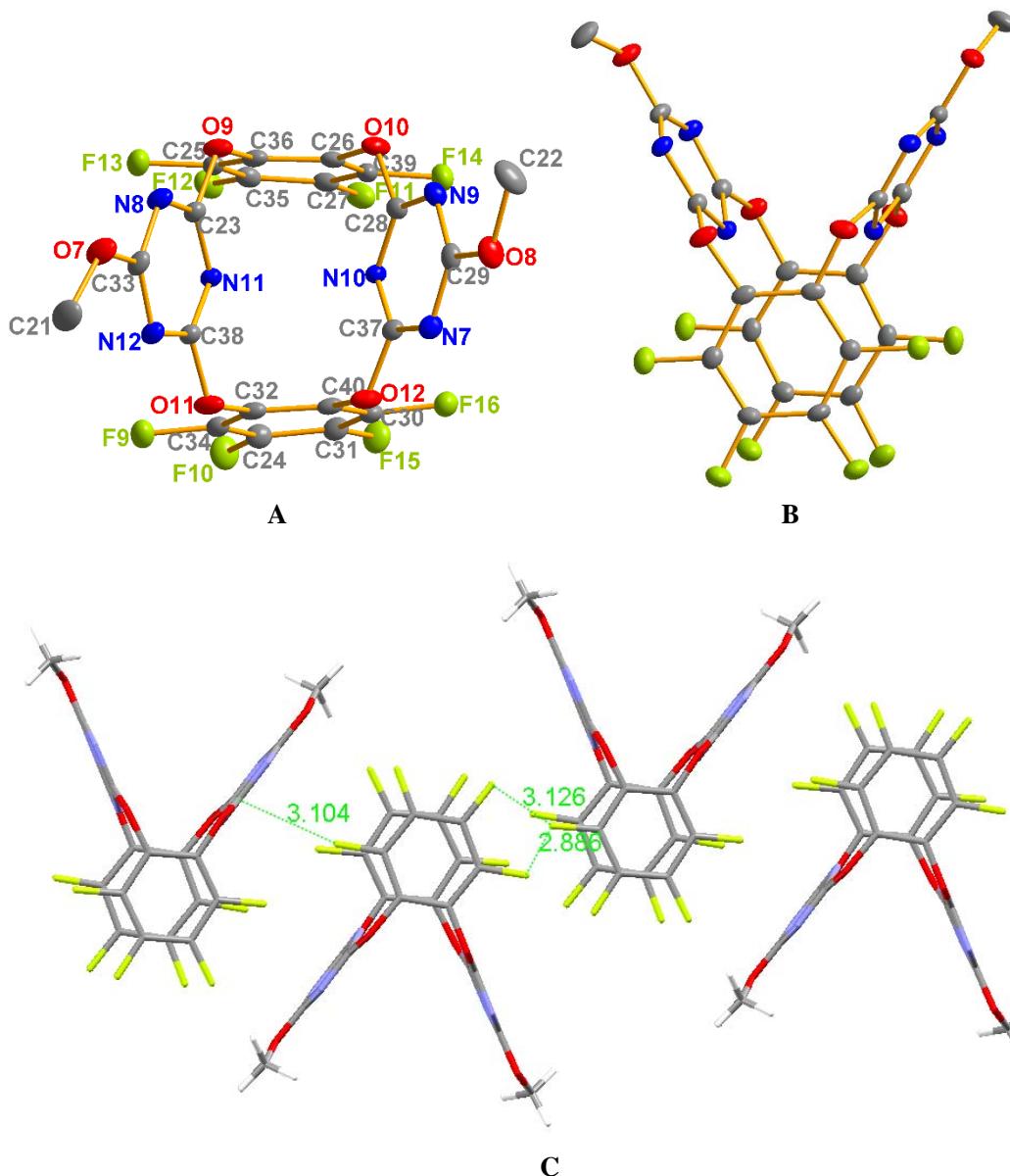


Figure S4 Crystal structure of **10a** (A) top view (B) side view and (C) self assembly in solid state. Selected bond length [Å]: C23-O9 1.368, O9-C36 1.385, C26-O10 1.387, O10-C28 1.357, C38-O11 1.359, O11-C32 1.394, C40-O12 1.388, O12-C37 1.360. Selected distances [Å]: C33···C29 5.557, N11···N10 2.932, C36···C32 4.517, C26···C40 4.427, C35···C24 4.638, C27···C31 4.432. Hydrogens are omitted for clarity. The probability is 25 percent.

5. References

- [1] (a) Mobbs, R. H. *J. Fluorine Chem.* **1971**, *1*, 365. (b) Naseer, M. N.; Wang, D.- X.; Zhao, L.; Huang, Z.- T.; Wang, M.- X. *J. Org. Chem.* **2011**, *76*, 1804. (c) Burdon, J.; Damodaran, V. A.; Tatlow, J. C. *J. Chem. Soc.* **1964**, 763. (d) Liu, J.; Wang, K.; Xu, F.; Zheng W.; Li, C.-H.; You, X.-Z.; Tang, Z.-K.; Zhang, J.-Y.; Yu, T. *Tetrahedron Lett.* **2011**, *52*, 6492.

6. Copies of ^1H , ^{13}C and ^{19}F NMR Spectra

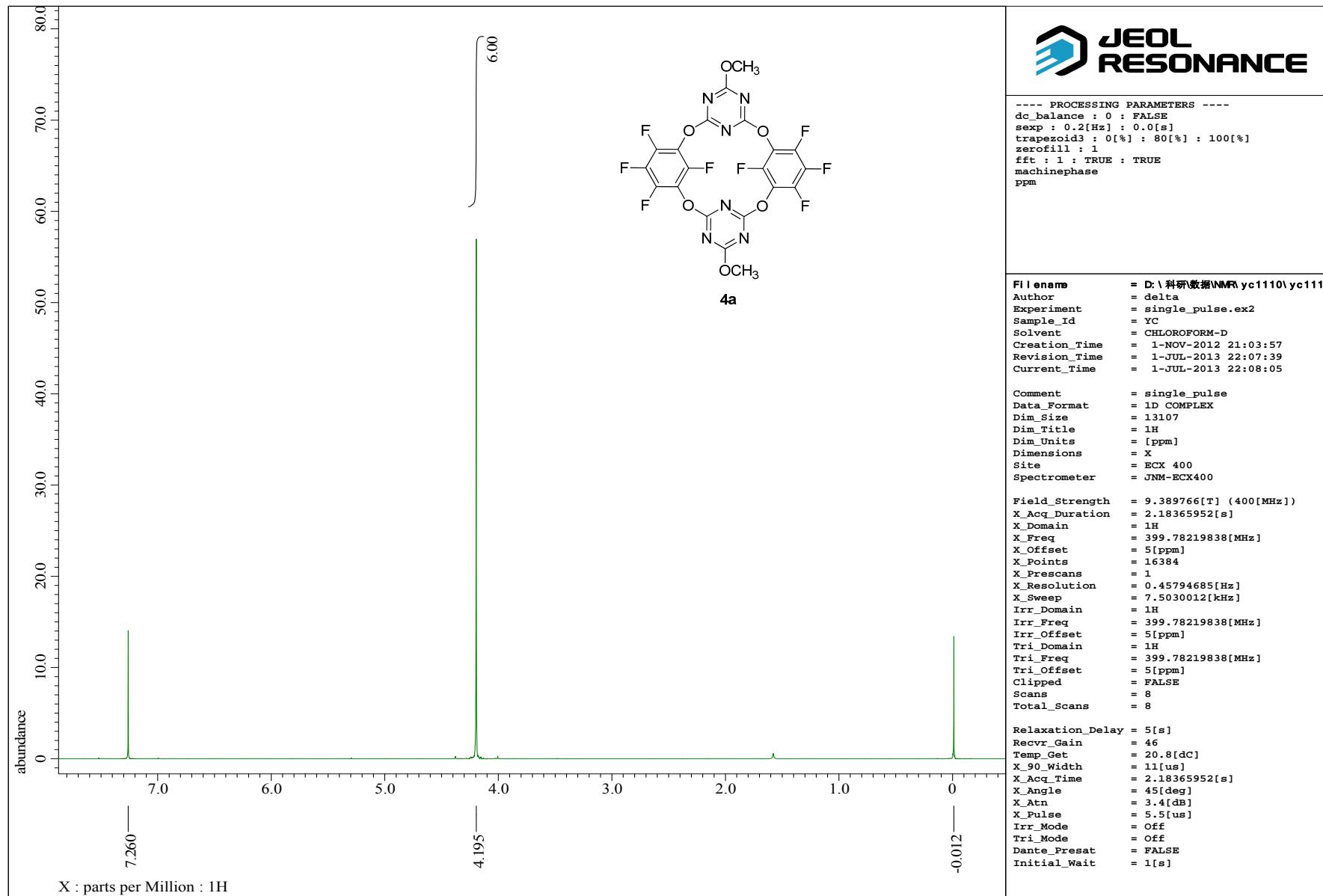


Figure S5 ^1H spectrum of **4a**.

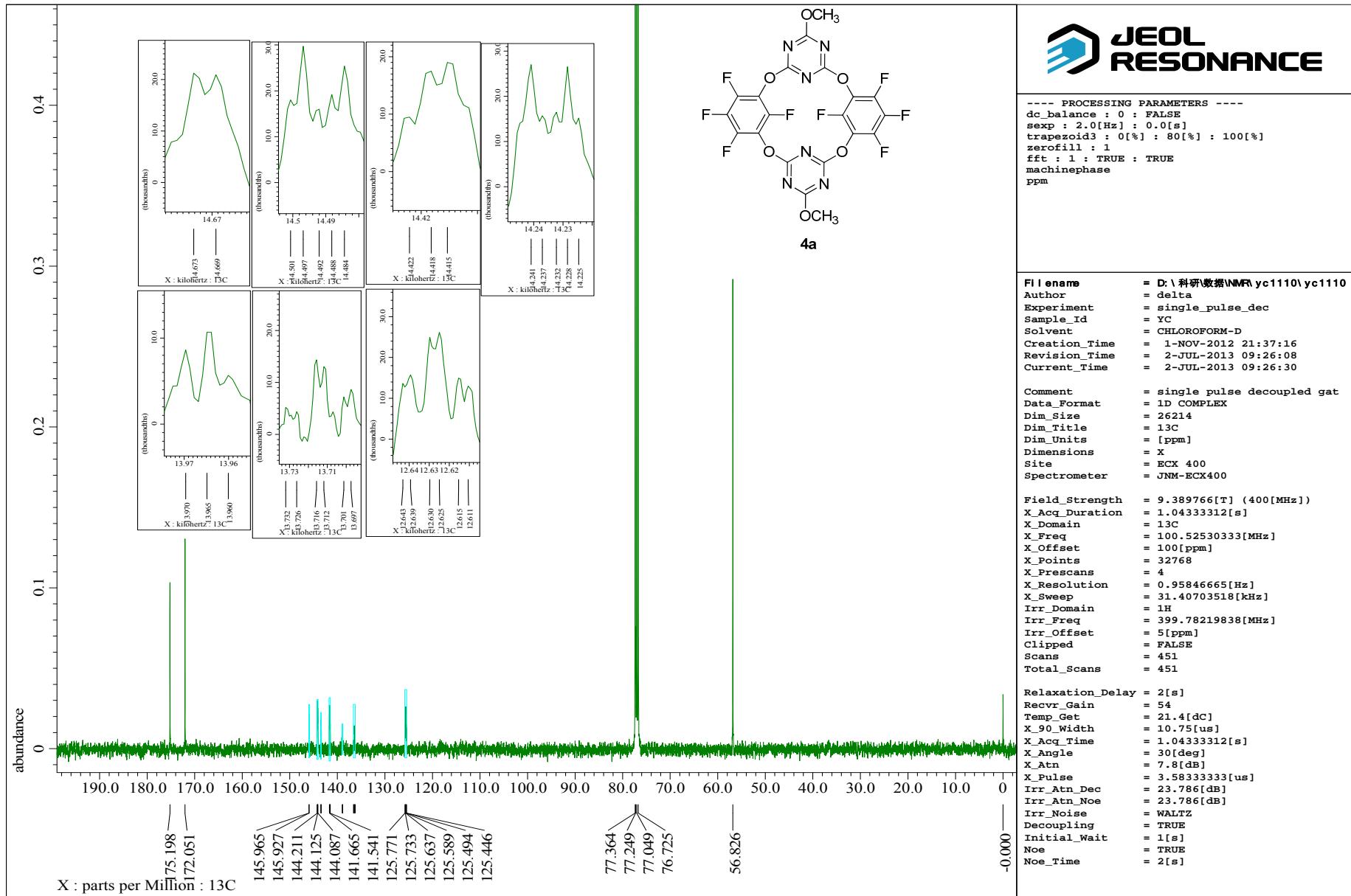


Figure S6 ^{13}C spectrum of **4a**.

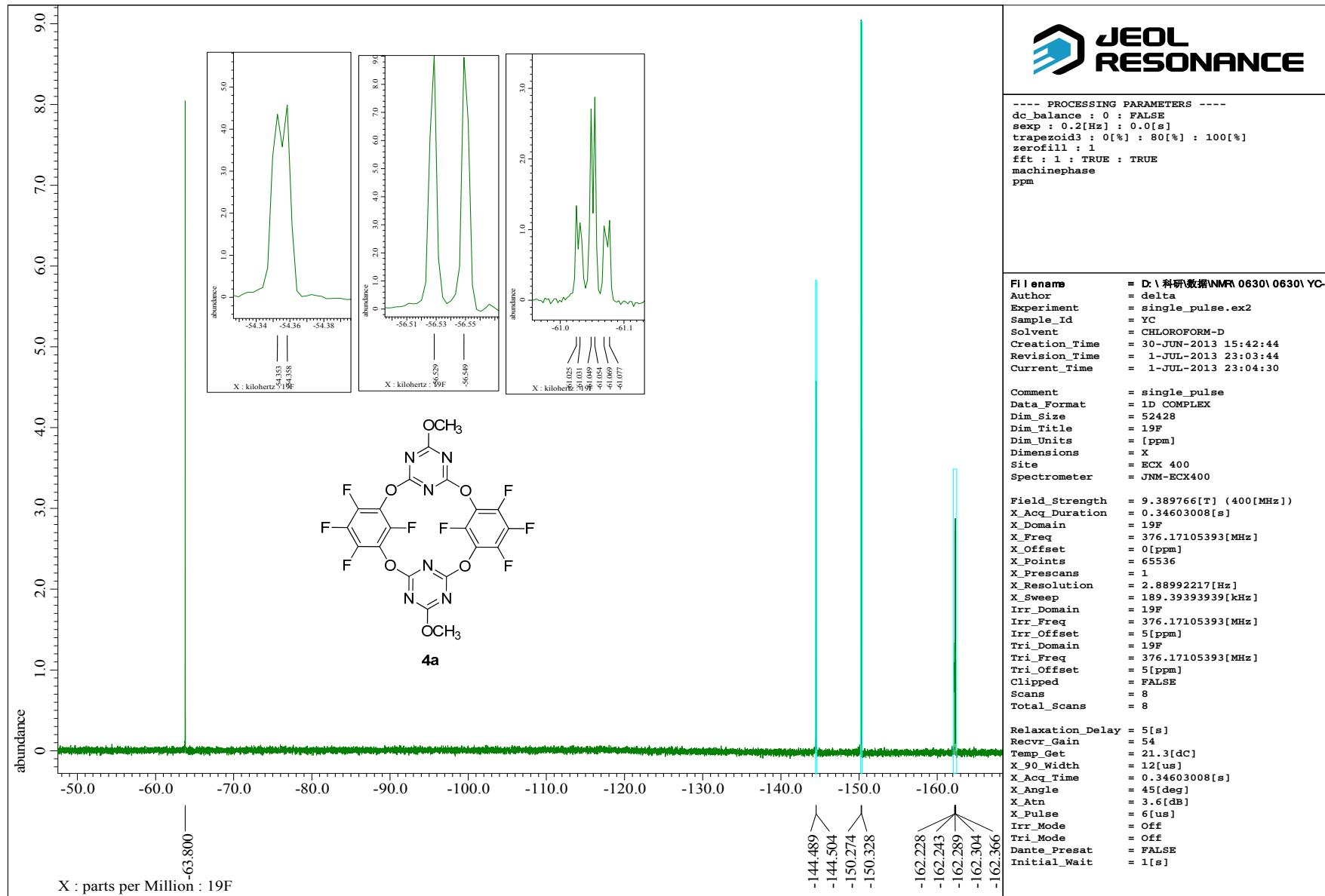


Figure S7 ^{19}F spectrum of **4a**.

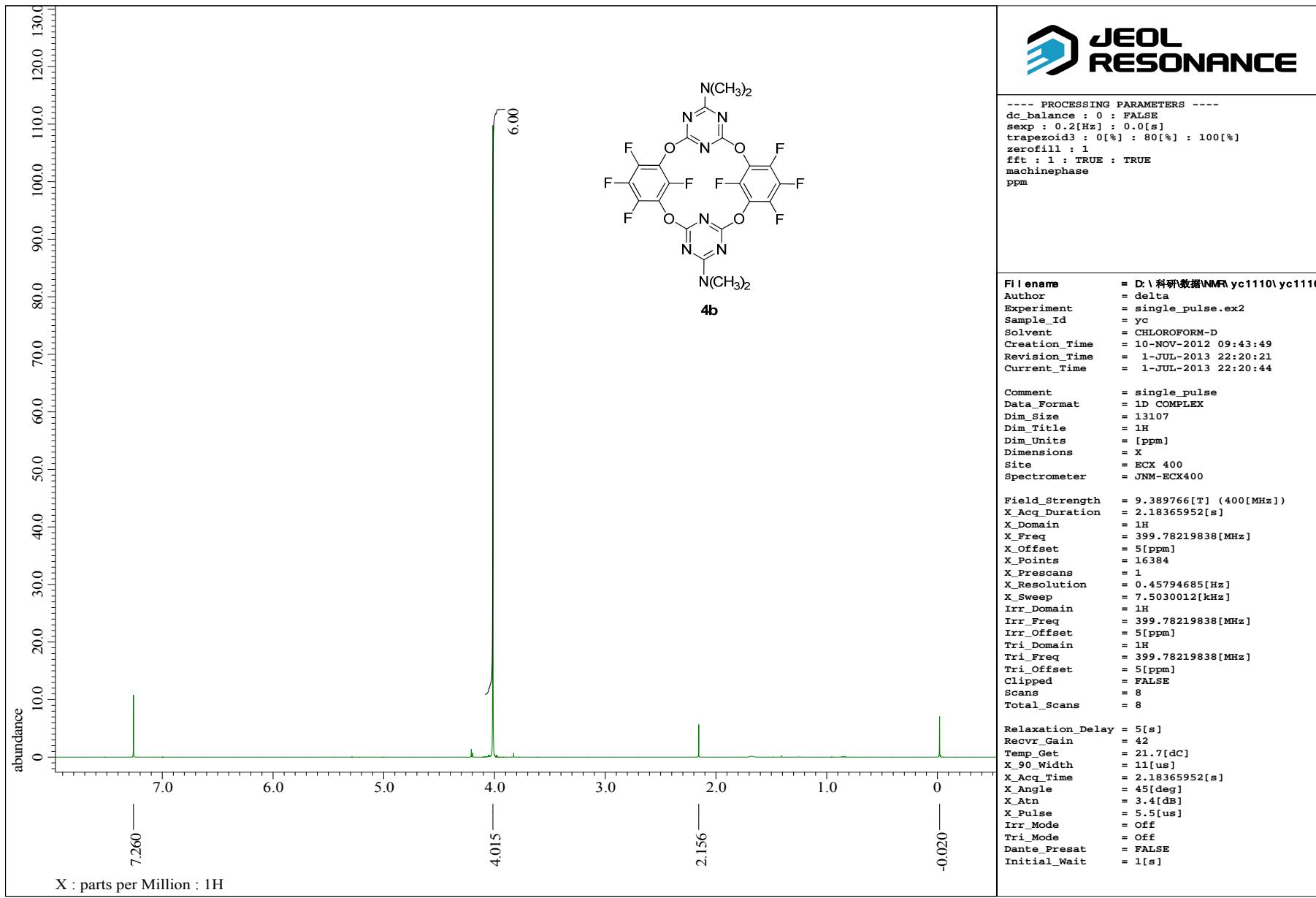


Figure S8 ¹H spectrum of **4b**.

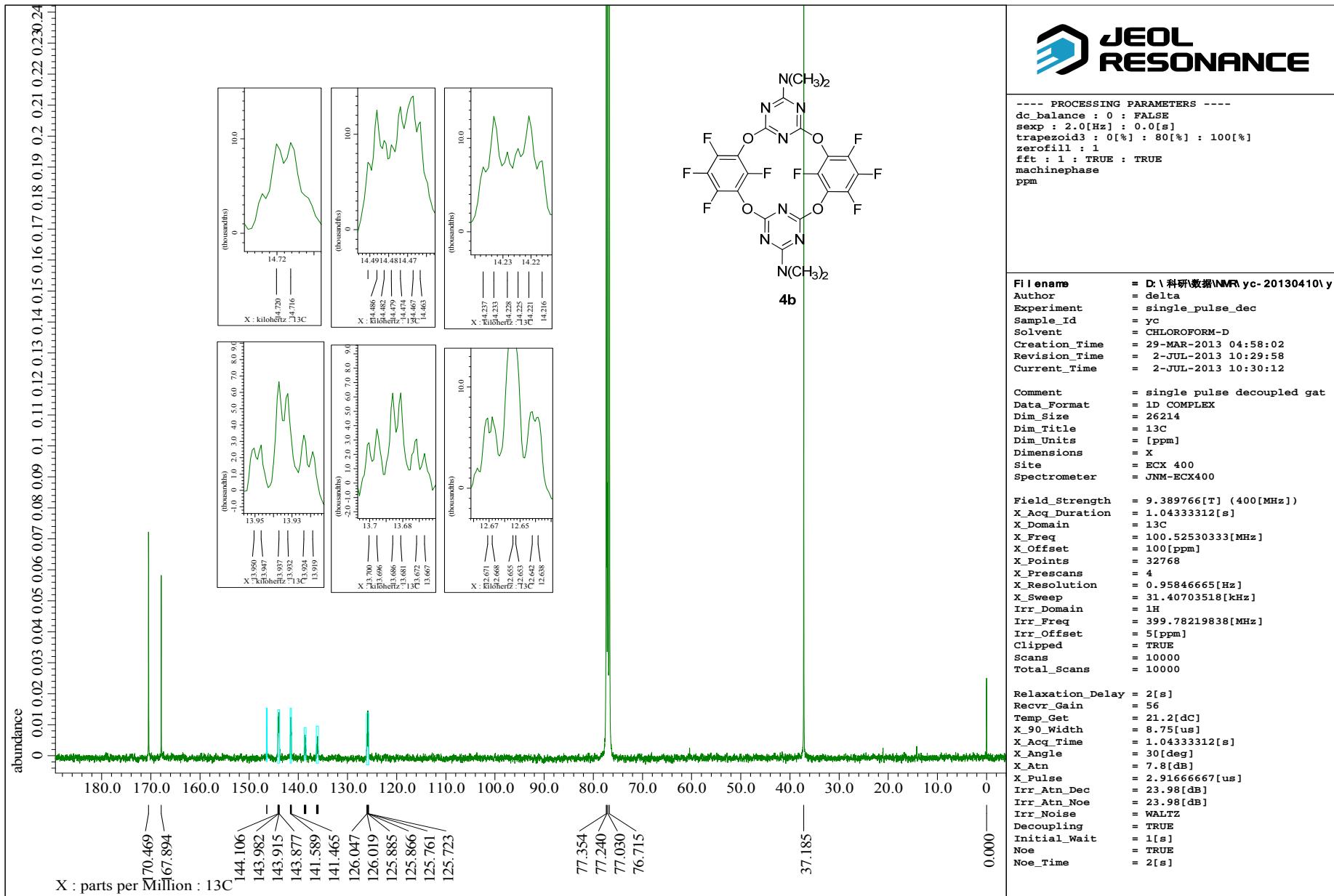


Figure S9 ¹³C spectrum of **4b**.

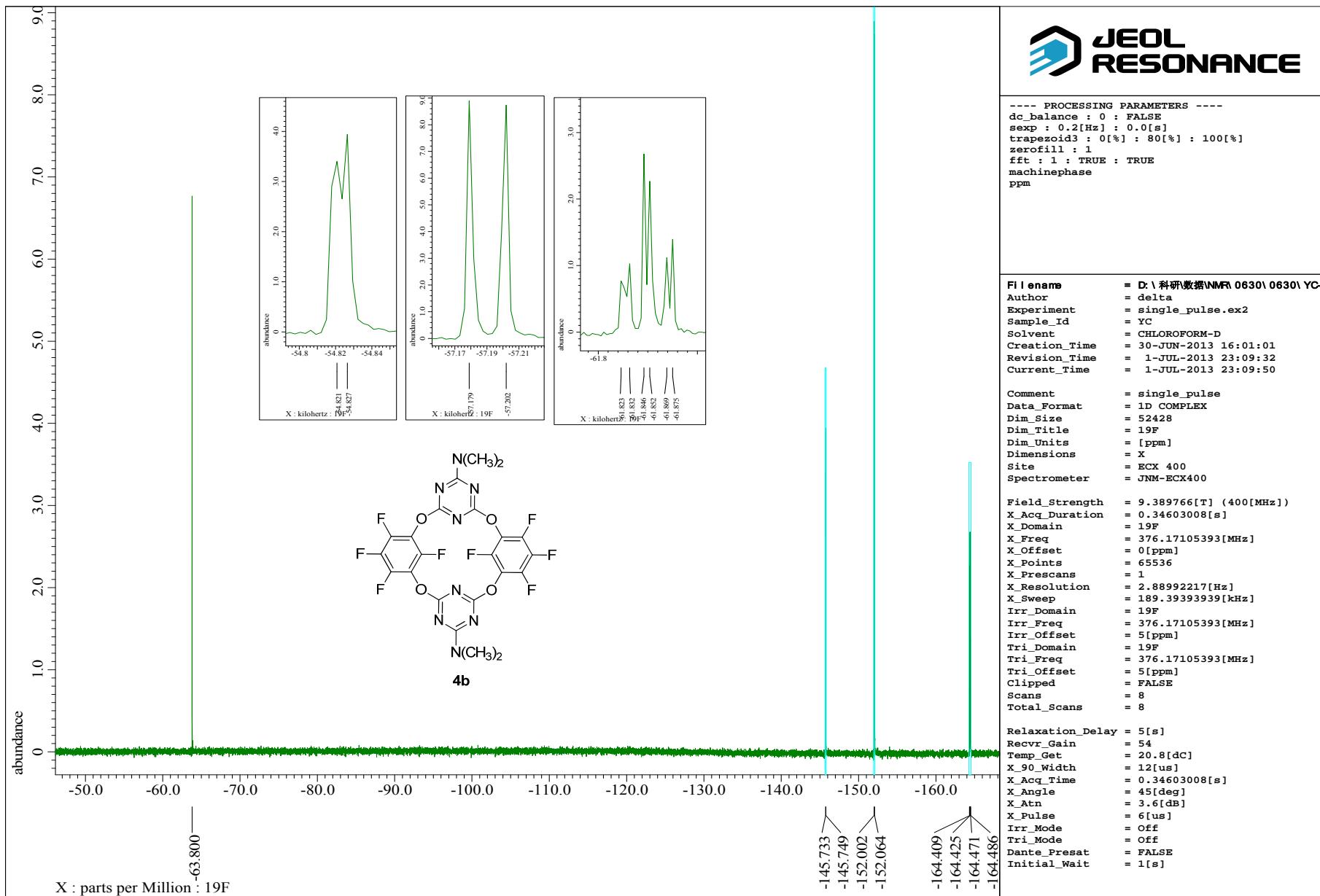


Figure S10 ^{19}F spectrum of **4b**.

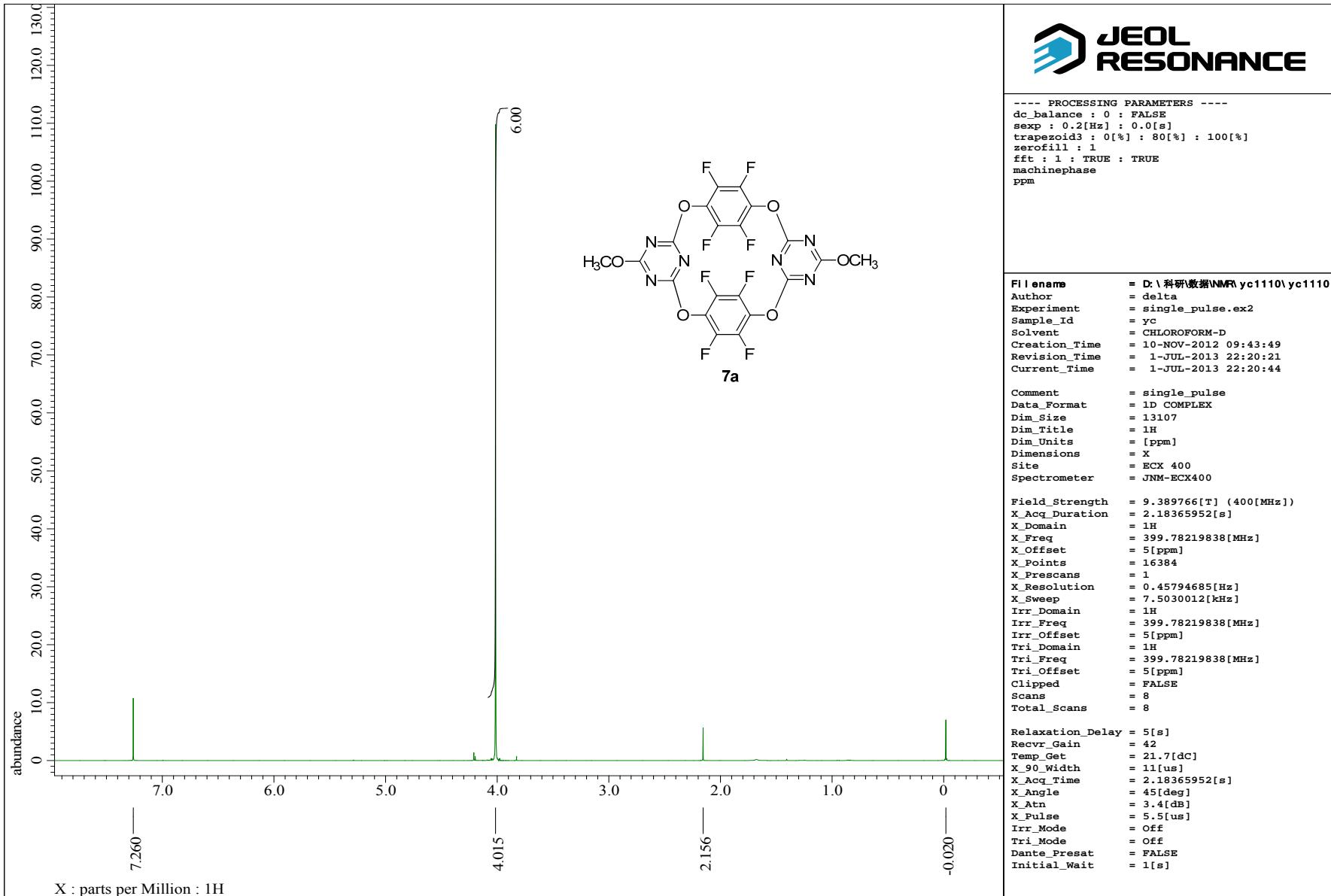


Figure SII ^1H spectrum of **7a**.

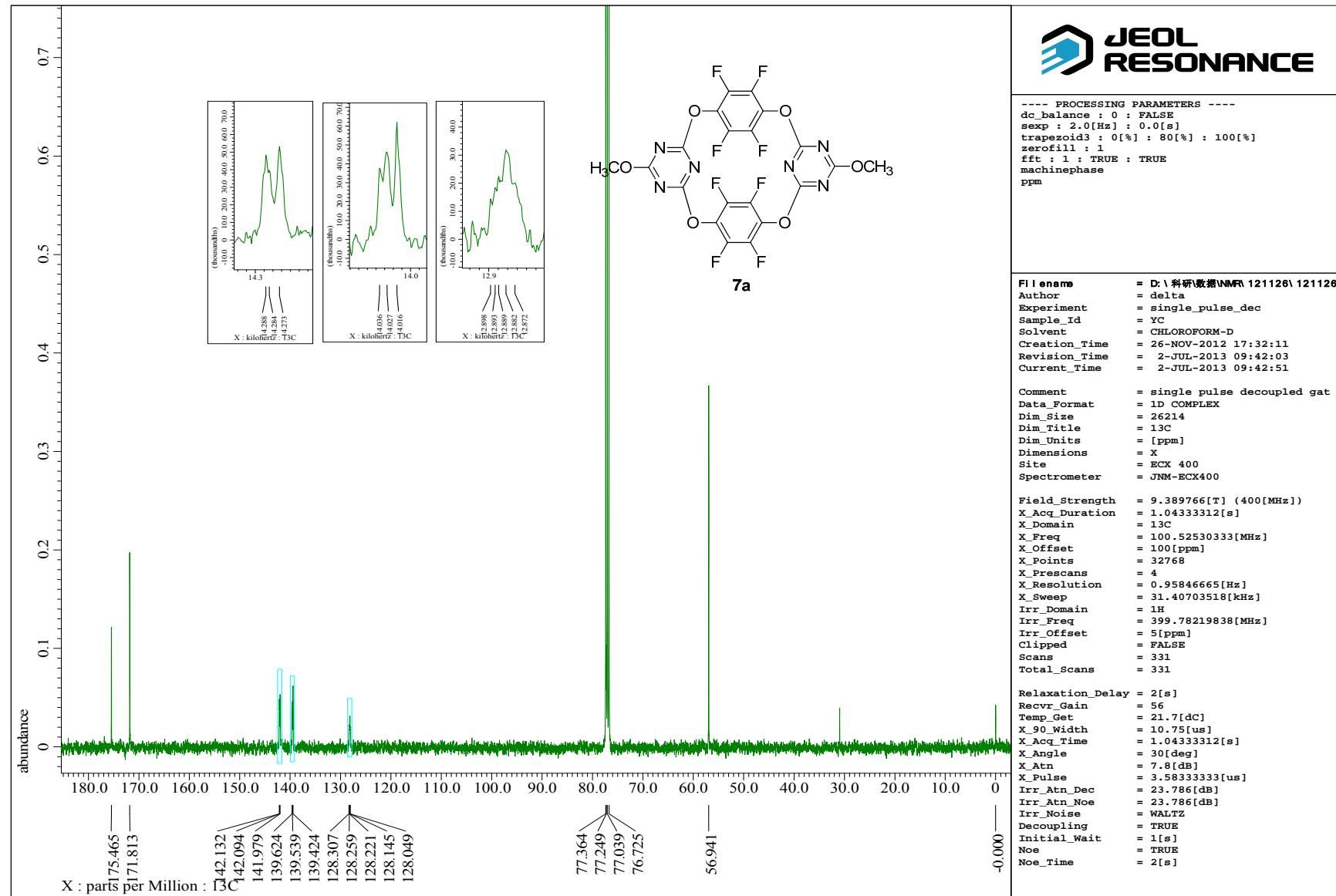


Figure S12 ^{13}C spectrum of **7a**.

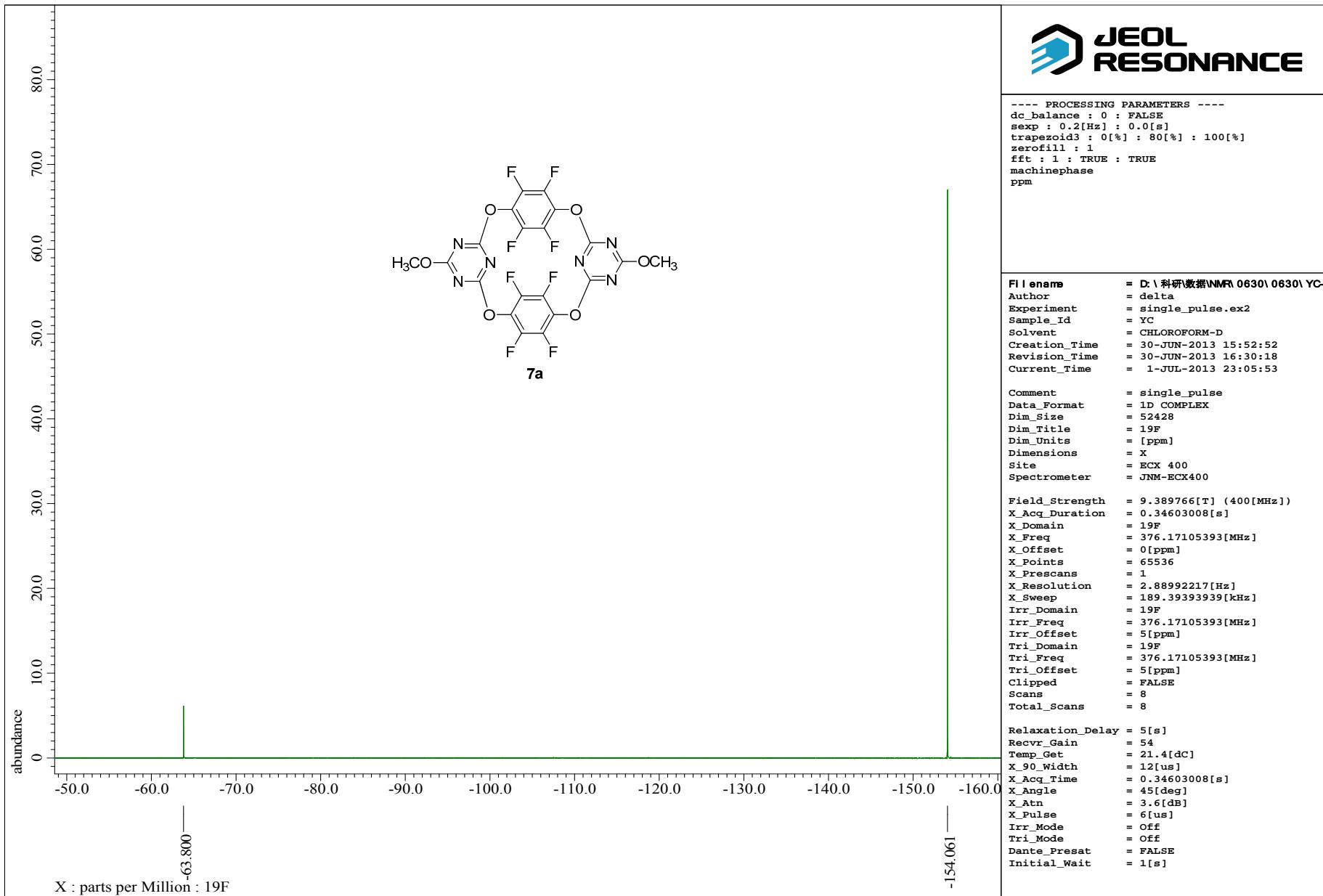


Figure S13 ^{19}F spectrum of **7a**.

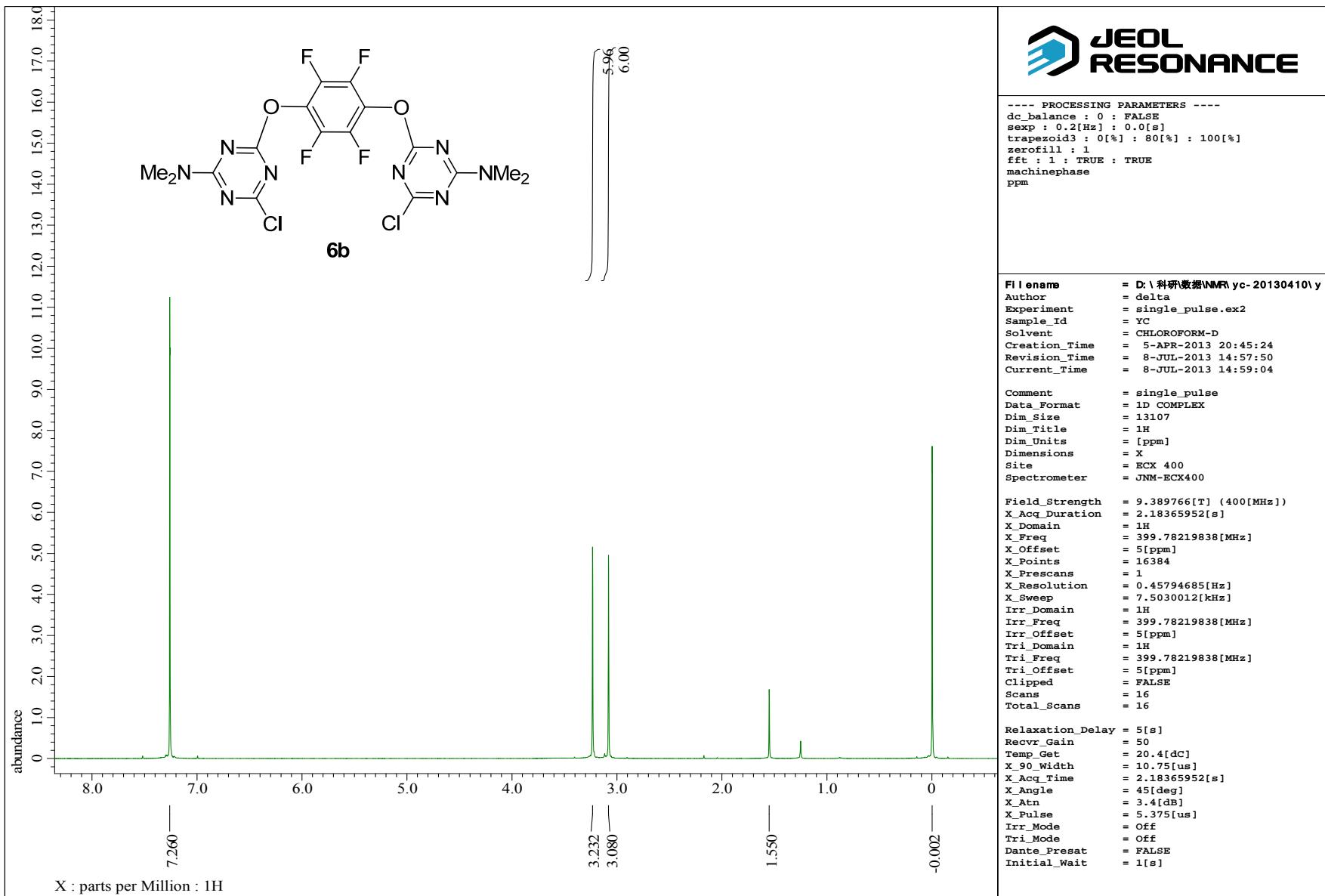


Figure S14 ^1H spectrum of **6b**.

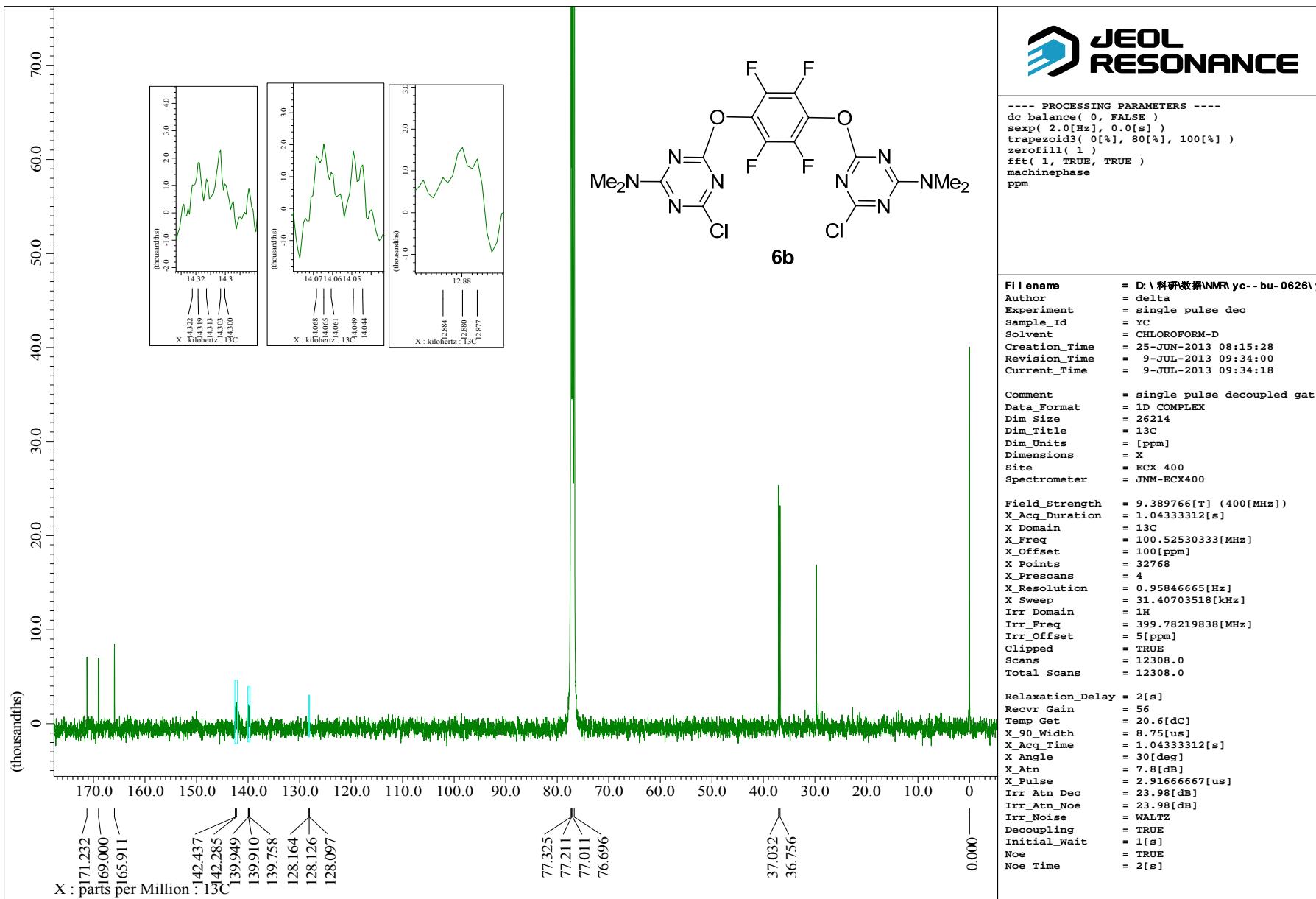


Figure S15 ^{13}C spectrum of **6b**.

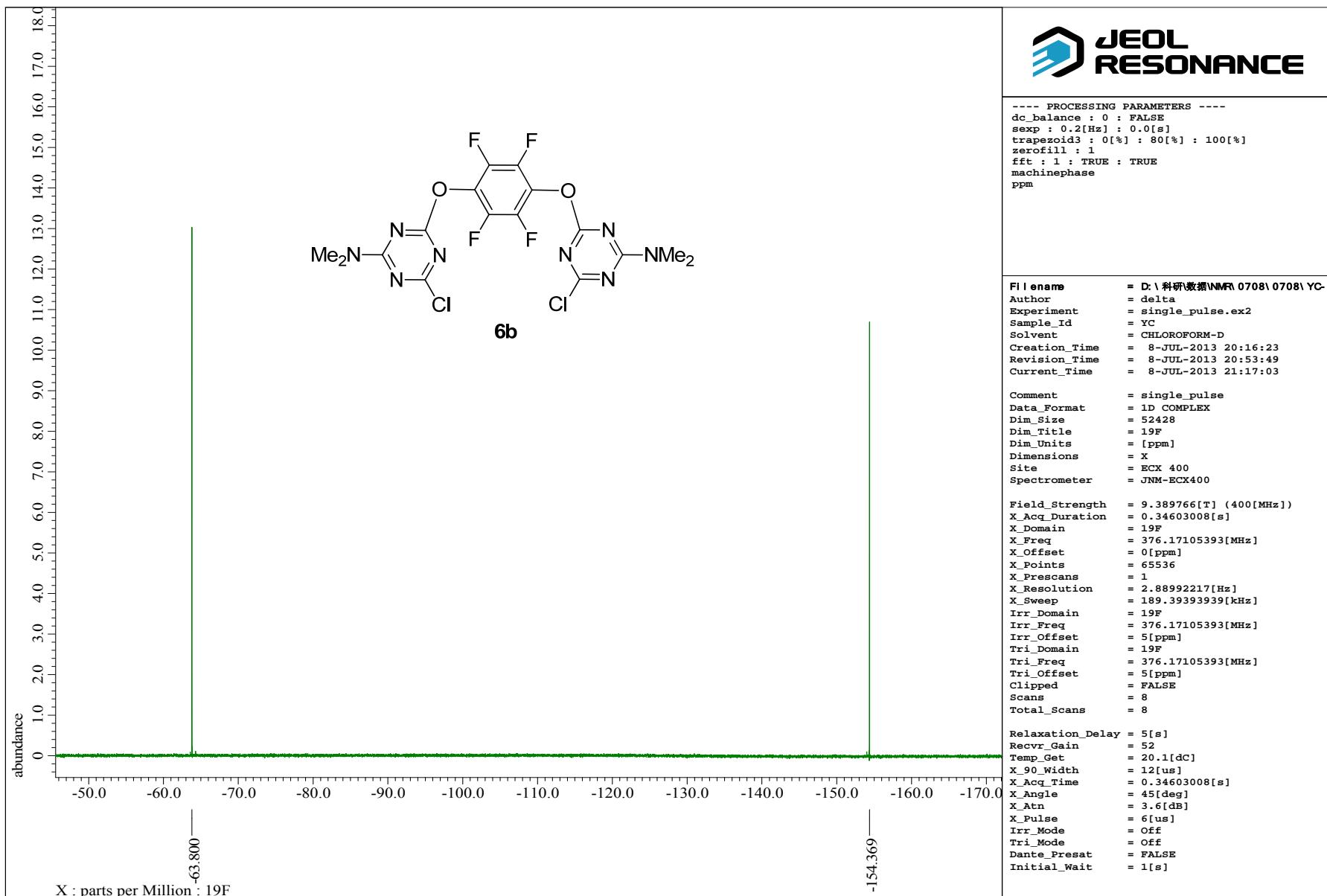


Figure S16 ^{19}F spectrum of **6b**.

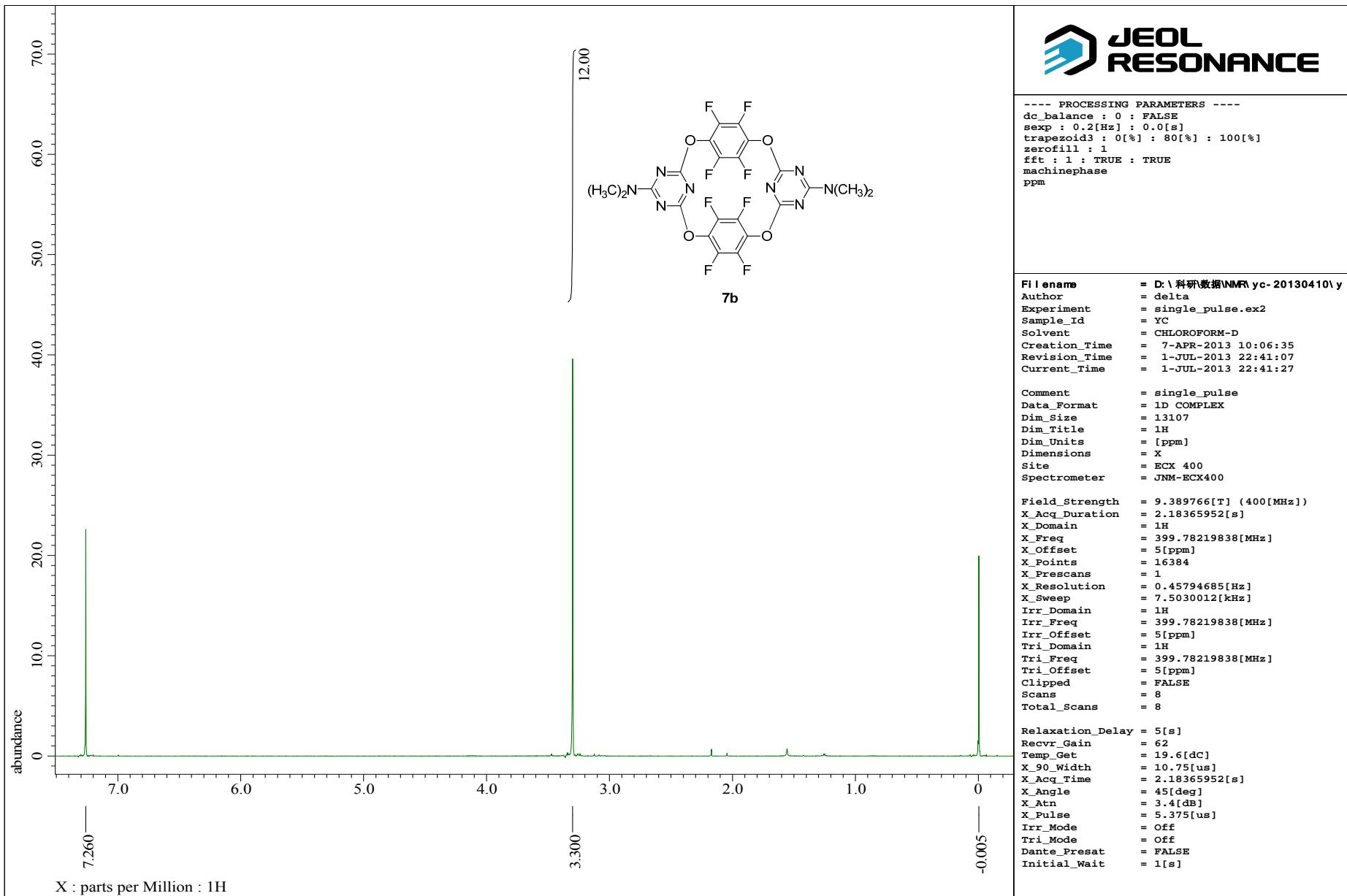


Figure S17 ^1H spectrum of 7b.

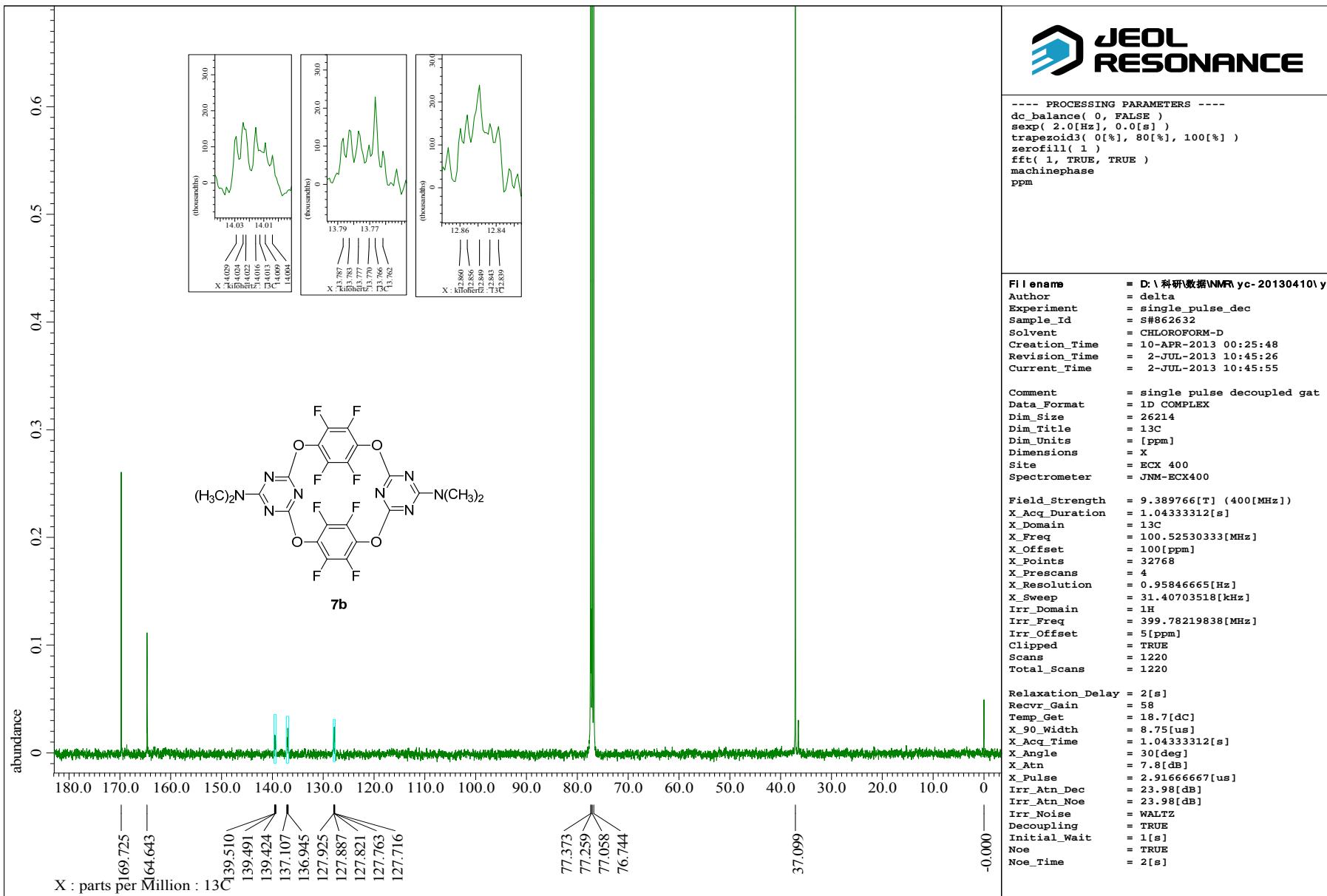


Figure S18 ^{13}C spectrum of **7b**.

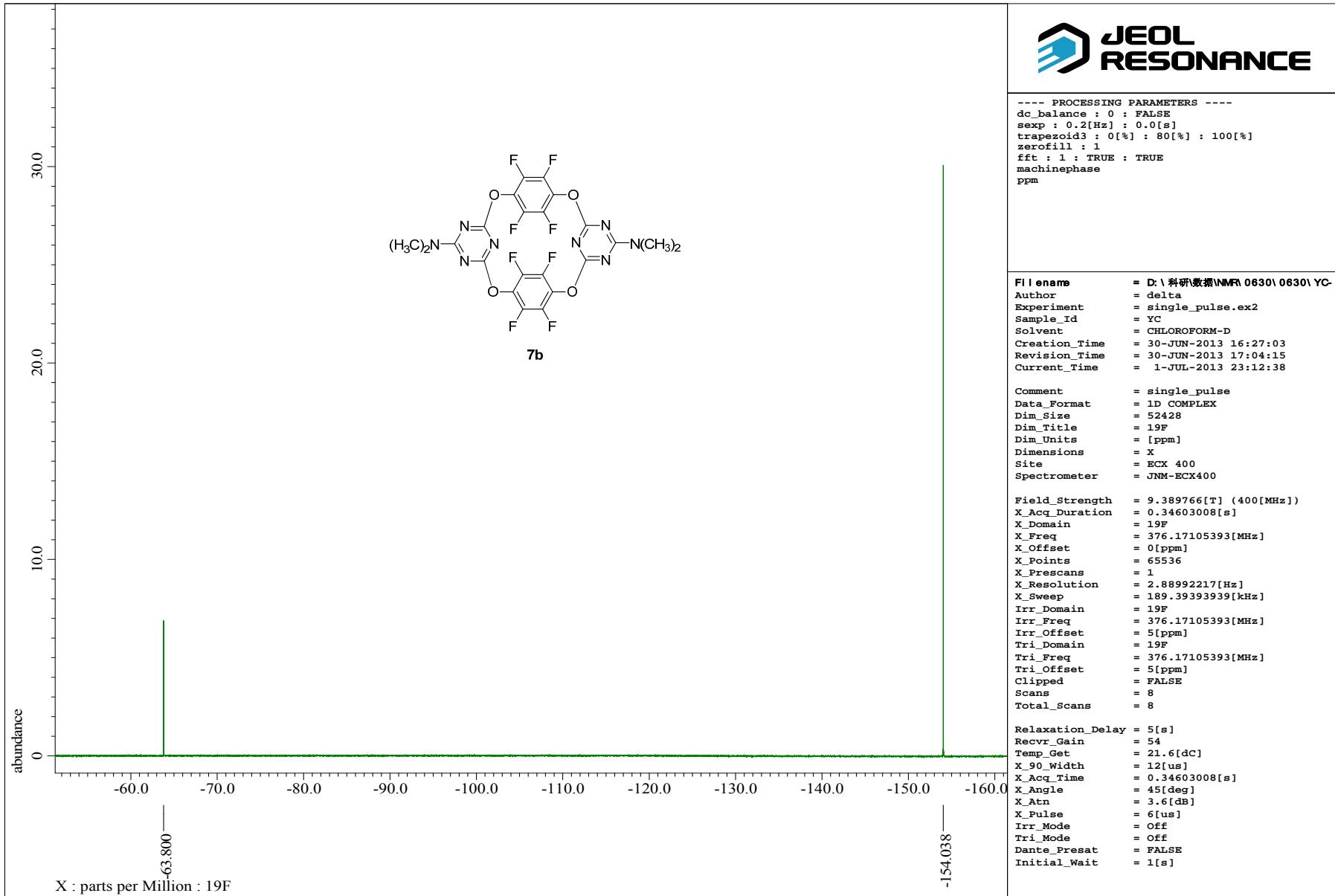


Figure S19 ^{19}F spectrum of **7b**.

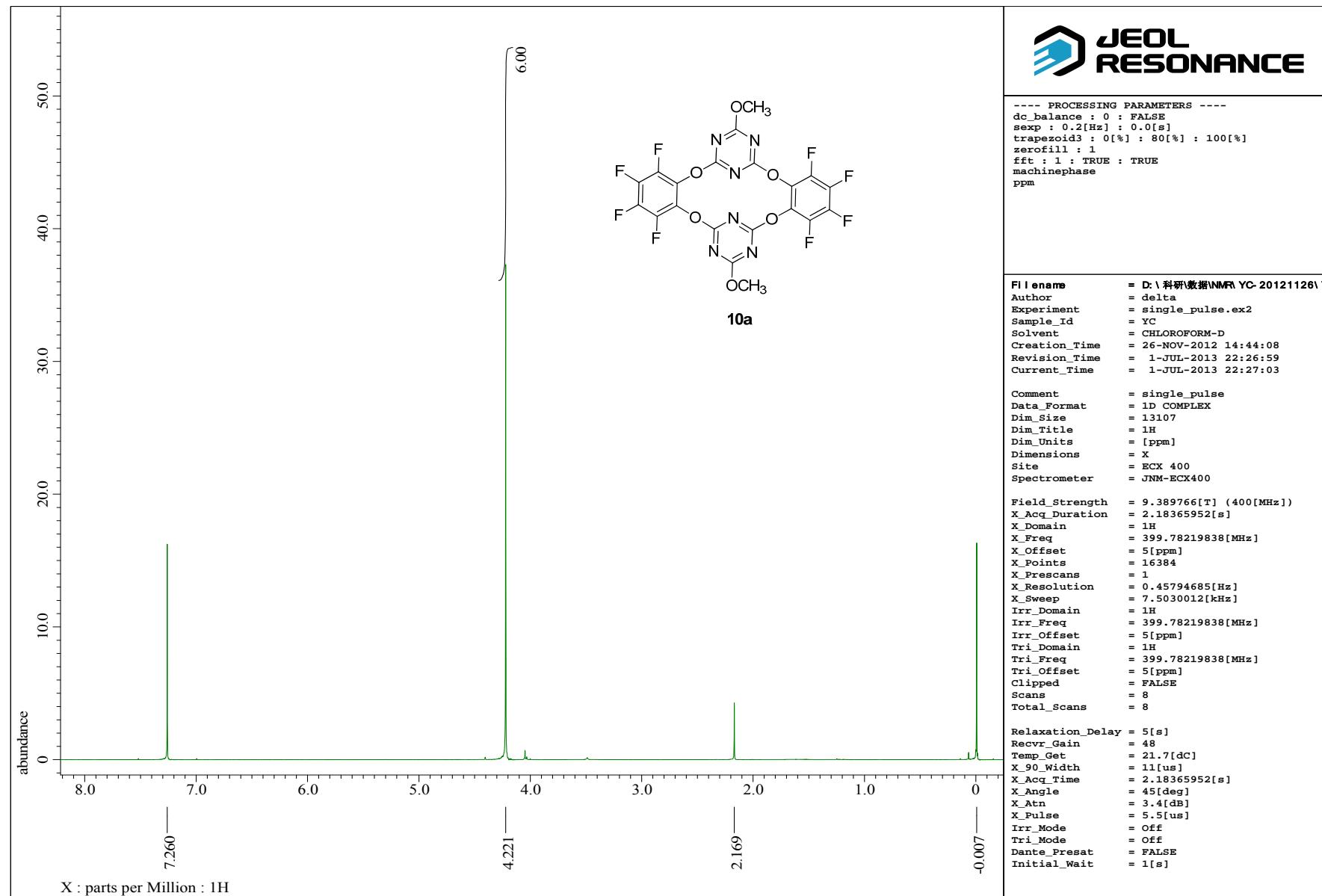


Figure S20 ^1H spectrum of **10a**.

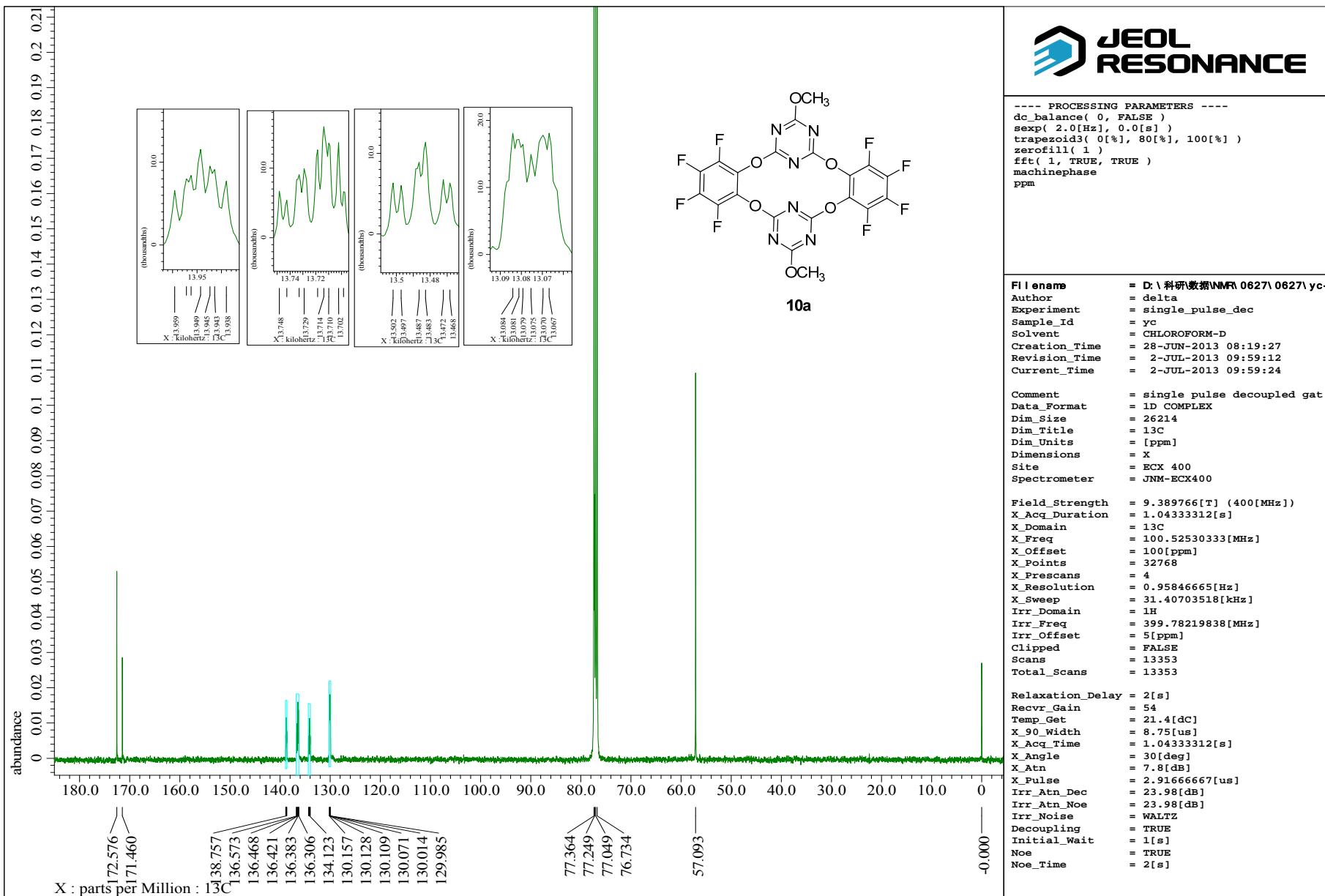


Figure S21 ^{13}C spectrum of **10a**.

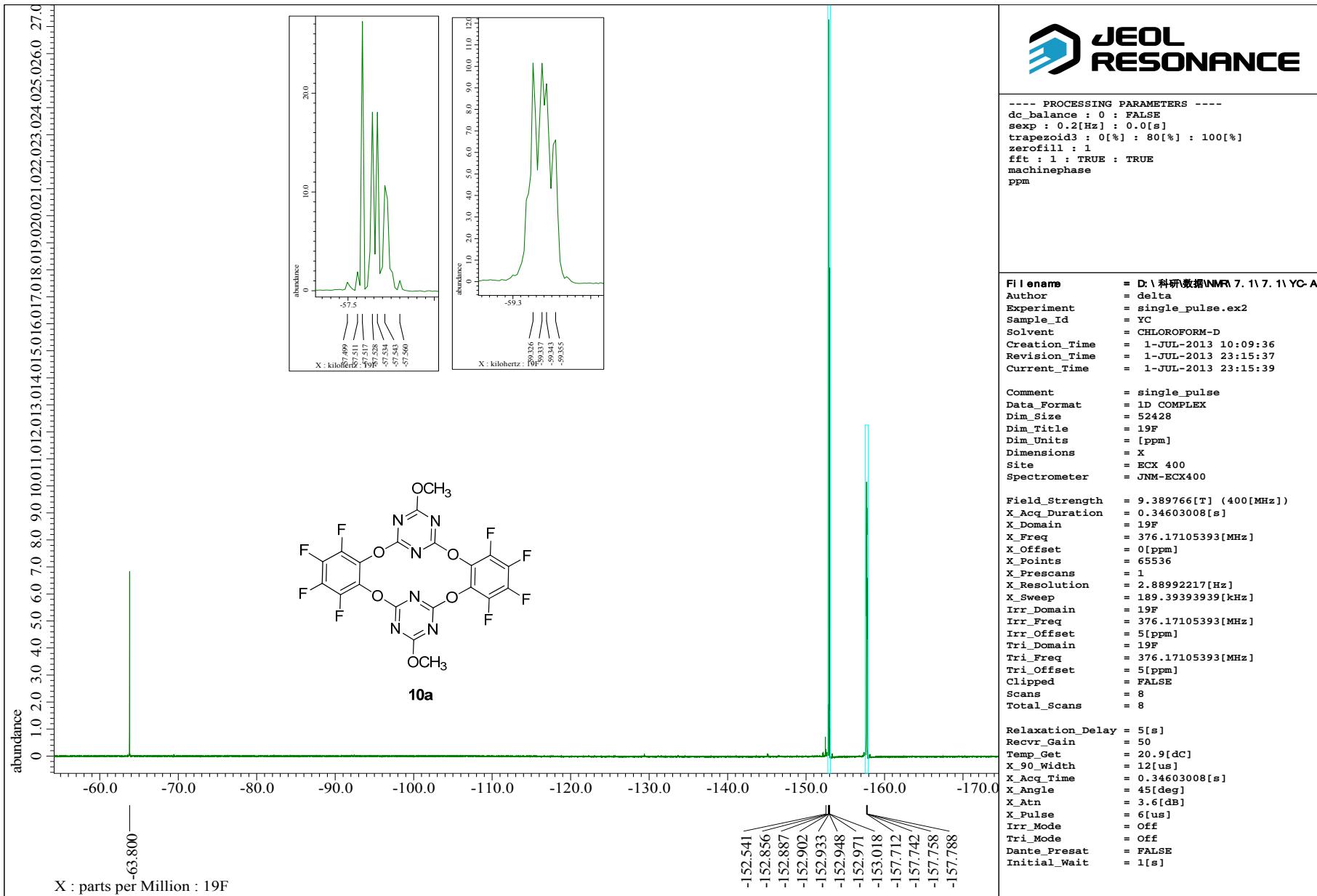


Figure S22 ^{19}F spectrum of **10a**.

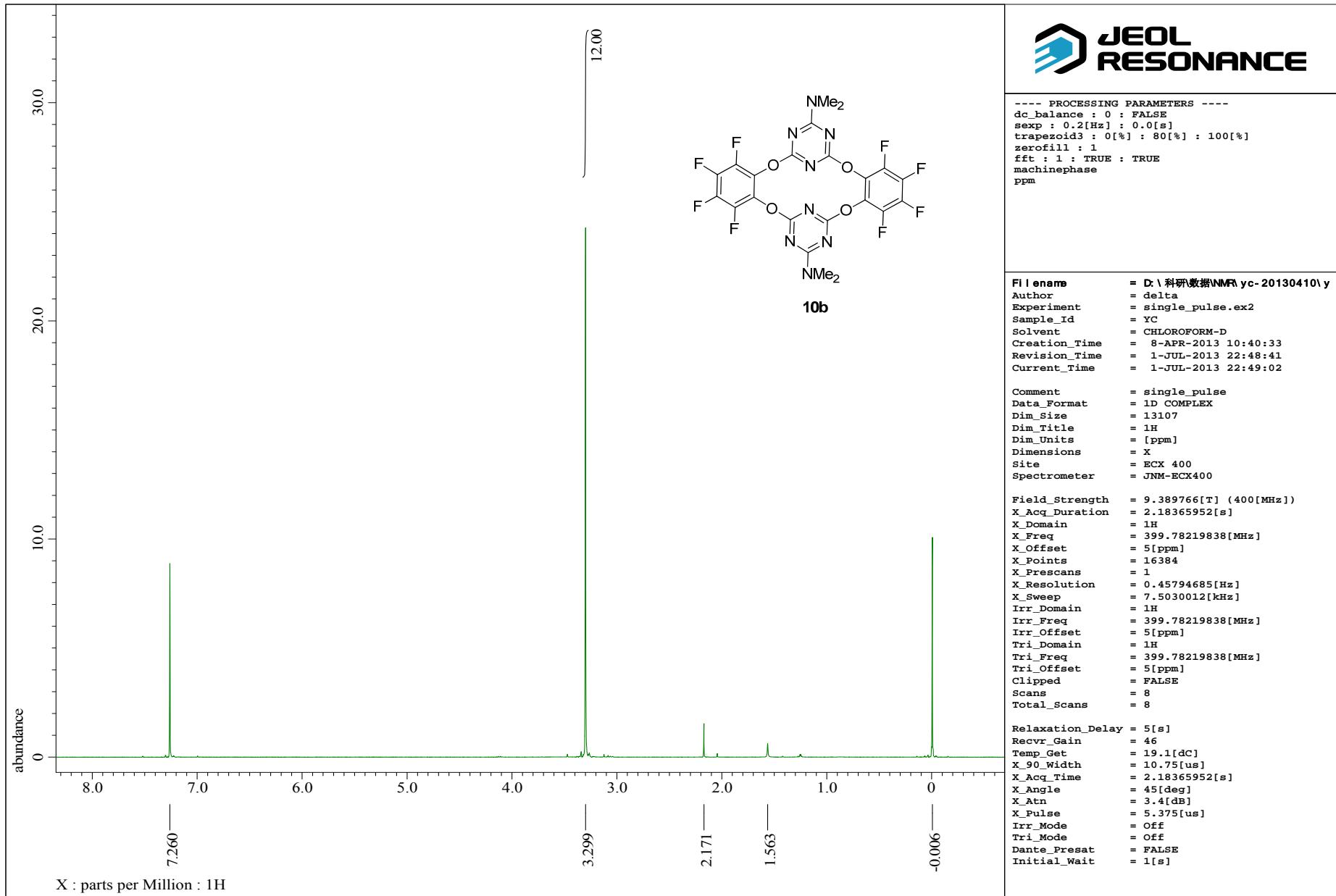


Figure S23 ^1H spectrum of **10b**.

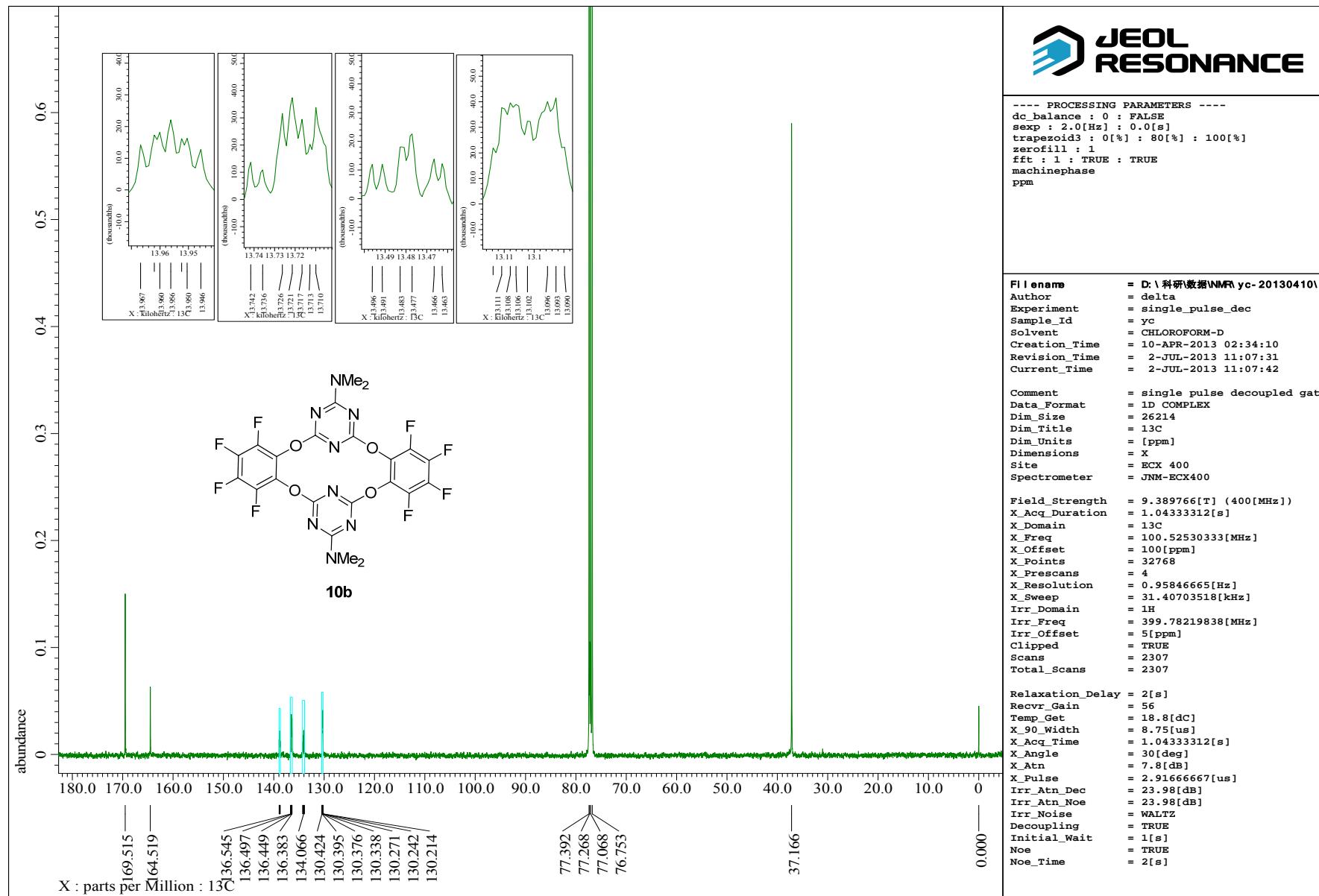


Figure S24 ^{13}C spectrum of **10b**.

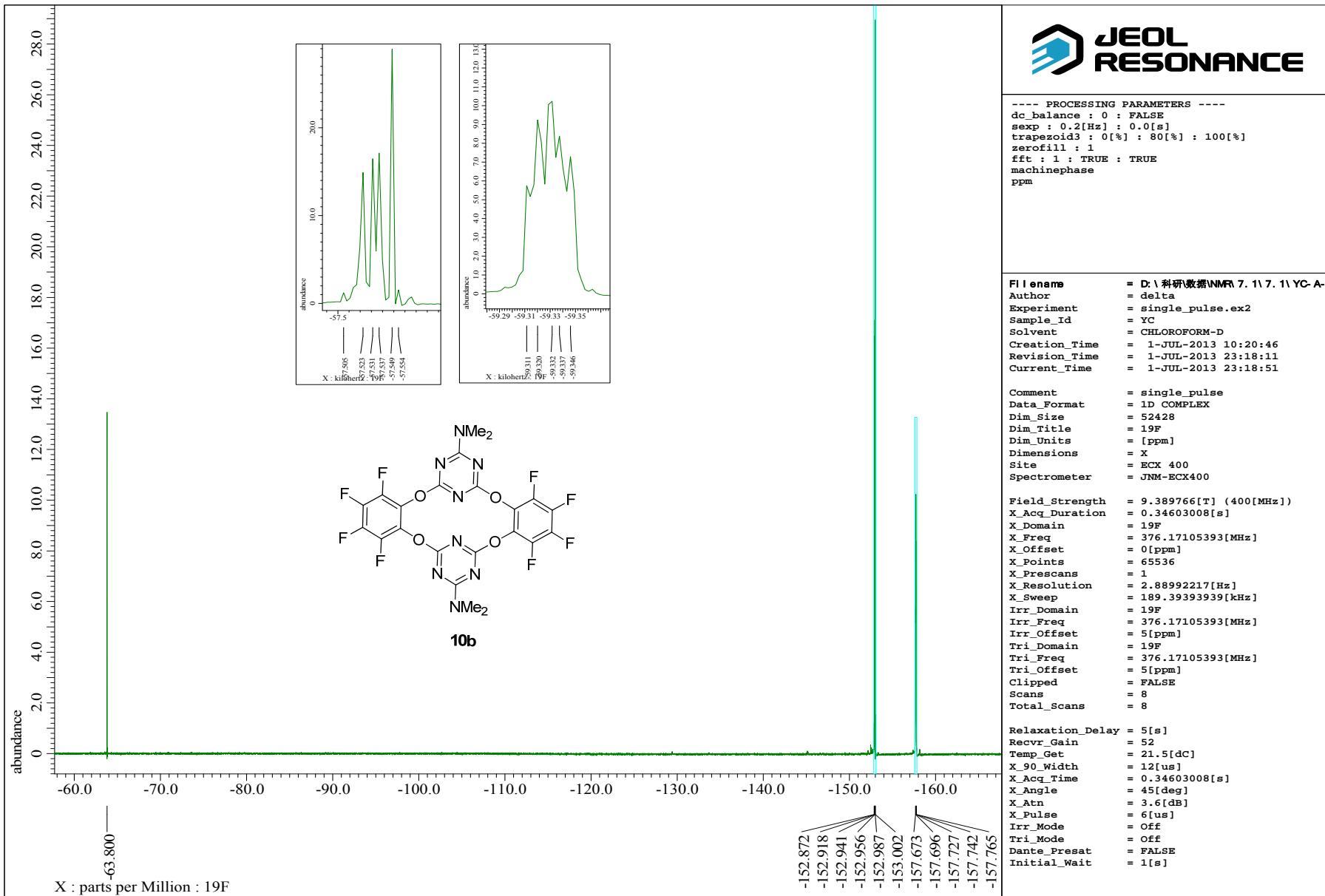


Figure S25 ^{19}F spectrum of **10b**.