

Electronic Supplementary Information

Ni(0) or Cu(0) catalyzed cleavage of carbon-chlorine bond of 2-chloro-1,1,1-trifluoroethane (HCFC-133a) via Single Electron Transfer (SET) process

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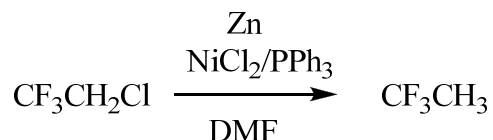
I, General Procedure

All reactions were carried out under the N₂ atmosphere, DMF, DMSO and MeCN were distilled prior to use. Reagents were purchased at the commercial quality and used without further purification, unless otherwise stated. 2-chloro-1,1,1-trifluoroethane(HCFC-133a) was used in the form of fresh DMF solution.

¹H NMR were recorded on a Bruker 300MHz or Varian 300MHz spectrometer. Chemical shifts are reported in ppm relative to TMS as a reference (CDCl₃ = 7.26 ppm) The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ¹⁹F NMR spectra were recorded on a Bruker 300 MHz or Varian 300MHz spectrometer without proton decoupling. Chemical shifts are reported in ppm relative to CFC1₃. ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm relative to TMS as a reference (CDCl₃ = 77.0 ppm). GC/MS analysis was performed using a Agilent 7890A Network GC system coupled to a 5975C Network mass selective detector.

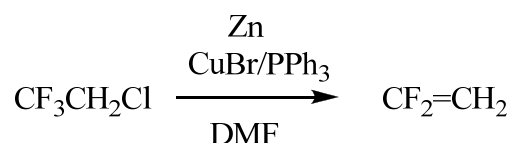
II, Experimental Procedures

II-1. Prepare of 1,1,1-trifluoroethane(HFC-143a) **1b**



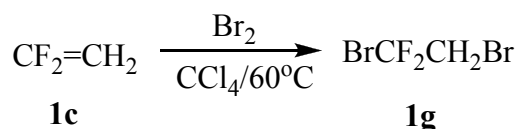
A 3 mL sealed tube was charged with zinc powder (423 mg, 6.5 mmol), NiCl₂ (65 mg, 0.5 mmol) and PPh₃ (530 mg, 2.0 mmol). The sealed tube was filled with nitrogen and the nitrogen purged solvent DMF (1.5 mL) was then added. The mixture was heated to 120 °C for 30 min to form a brown catalyst and cooled to room temperature. The solution of HCFC-133a **1a** (5M in DMF, 1 mL) was added, then the valve of the sealed tube was screwed down. The sealed mixture was stirred at 90 °C for 5 h, then cooled to room temperature. The gas phase was collected using a condensate trap in the liquid nitrogen. About 400 mg product was collected, which contained about 96% CF₃CH₃ **1b**. The yield was about 92% based on HCFC-133a. GC-MS showed the peak: 84, 83, 69, 65, 64. ¹⁹F NMR (CDCl₃): -61.0 ppm (q, J = 12 Hz), ¹H NMR: 1.87 ppm (q, J = 12 Hz). Spectra data reported in literature¹: ¹⁹F NMR: -61.2 ppm (q, J = 13.1 Hz). ¹H NMR: 1.87 ppm (q, J = 12.8 Hz).

II-2. Prepare of 1,1-trifluoroethane(VDF) **1c**



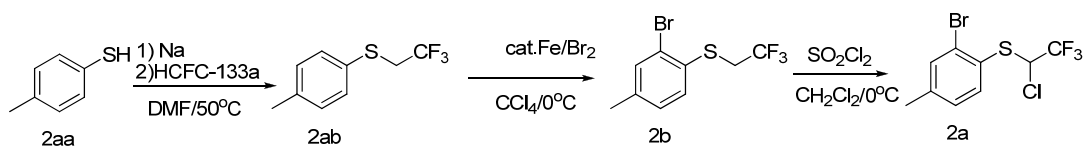
A 3 mL sealed tube was charged with CuBr (72 mg, 0.5 mmol) and PPh₃ (530 mg, 2 mmol). The sealed tube was filled with nitrogen and the nitrogen purged solvent DMF (1.5 mL) was then added. The mixture was heated to 100 °C about 30 min until it was colorless, then cooled to room temperature. Zinc powder (489 mg, 7.5 mmol) and the solution of HCFC-133a **1a** (5M in DMF, 1 mL) was added, then the valve of the sealed tube was screwed down. The sealed mixture was heated at 150 °C for 6 h and cooled to room temperature. The gas phase was obtained with a gasometer. About 103 mL gas (4.6 mmol, converted to standard state: 273.15 K, 1 atm). The GC-MS showed only CF₂=CH₂ **1c** was contained in the gas phase. The yield was about 92% based on HCFC-133a. GC-MS showed the peak: 64, 45, 44, 43. ¹⁹F NMR: (CDCl₃): -81.0 ppm (m), ¹H NMR: 3.84 ppm (dd, J = 25, 10 Hz) Spectra data reported in literature²: ¹⁹F NMR: (CDCl₃): -81.9 ppm.

II-3. Absorption of VDF using Br₂



A 3mL sealed tube was charged with CuBr(72mg, 0.5mmol) and PPh₃(530mg, 2mmol). The sealed tube was filled with nitrogen and the nitrogen purged solvent DMF (1.5 mL) was then added. The mixture was heated to 100°C about 30min until it was colorless, then cooled to room temperature. Zinc powder (489mg, 7.5mmol) and the solution of HCFC-133a **1a** (5M in DMF, 1mL) was added. The mixture was heated at 150°C for 6h and cooled to room temperature. The gas phase was bubbled into Br₂ (1.2g, 7.5mmol) in the 5mL CCl₄ in a 10mL schlenk tube at 60°C for 2h slowly. The mixture was washed with the saturated aqueous solution of Na₂S₂O₃ and water, dried over Na₂SO₄. The mixture was distilled at atmospheric pressure to give BrCF₂CH₂Br 0.649g (2.9mmol, 58%). ¹⁹FNMR: -50.4ppm (t, J=13Hz), ¹HNMR: 4.03 ppm (t, J=13Hz). Spectra data reported in literature³: ¹⁹FNMR: -49.1ppm (t, J=13Hz), ¹HNMR: 4.10ppm (t, J=13Hz).

II-4. Prepare of (2-bromo-4-methylphenyl)(1-chloro-2,2,2-trifluoroethyl)sulfane **2a**



II-4-1 Prepare of p-tolyl(2,2,2-trifluoroethyl)sulfane⁴ **2ab**

A 100mL schlenk tube was charged with **2aa**(100mmol, 12.4g) and filled with N₂, then nitrogen purged solvent DMF (60 mL) and sodium(106mmol, 2.44g) was added. The mixture was stirred at room temperature until the sodium disappeared. The solution of HCFC-133a (150mmol, 5M in DMF) was added to the tube. The mixture was stirred at 50°C for 10h. After the reaction was over, the mixture was poured into 500mL of Et₂O. The resulted solution was washed with water, dried over Na₂SO₄ and evaporated in a vacuo. The mixture was distilled at reduced pressure to afford **2ab**⁵ (77mmol, 15.8g, 77%yield). ¹⁹FNMR: (CDCl₃): -65.8ppm (t, J=10Hz), ¹HNMR: 2.34ppm (s, 3H), 3.37(q, J=10Hz, 2H), 7.40(d, J=8Hz, 2H), 7.13(d, J=8Hz, 2H).

II-4-2 Prepare of (2-bromo-4-methylphenyl)(2,2,2-trifluoroethyl)sulfane **2b**

A 50mL schlenk tube was charged with Fe power (2mmol, 0.112g) and filled with N₂, then 10mL CCl₄ and **2ab** (20mmol, 5.12g) was added. The mixture was cooled to 0°C and Br₂ (23mmol, 3.68g in 5mL CCl₄) was dropped slowly. The mixture was stirred vigorously at 0°C for about 2h detected by TLC. After the reaction was over, the mixture was poured into 100mL CH₂Cl₂, washed with the saturated aqueous solution of Na₂S₂O₃ and water, dried over Na₂SO₄. The solvent was removed and the residue was purified by flash chromatography on a silica gel column using n-hexane

as the eluent. **2b** (17.8mmol, 5.07g, 89%yield) was obtained as colorless oil.

IR (KBr):2947, 2924, 1590, 1464, 1380, 1266, 1241, 1126, 1081, 848, 817, 638 cm^{-1} .

^{19}F NMR (282MHz, CDCl_3): -66.3 (q, $J=10\text{Hz}$).

^1H NMR(400MHz, CDCl_3): 2.32 (s, 3H), 3.44(q, $J=10\text{Hz}$, 2H),7.09(d, $J=8\text{Hz}$,1H), 7.46- 7.48 (m, 2H).

^{13}C NMR(100MHz, CCl_3): 140.52, 134.09, 134.06, 130.29, 128.96, 127.46, 125.42(q, $J=278\text{Hz}$), 37.15(q, $J=33\text{Hz}$), 20.66.

MS(EI): $m/z=286(\text{M}^+)$. HRMS (EI) M^+ calcd for $\text{C}_{19}\text{H}_8\text{F}_3\text{SBr}$: 283.9482, found 283.9484.

II-4-3 Prepare of ((2-bromo-4-methylphenyl)(1-chloro-2,2,2-trifluoroethyl)sulfane)⁶ **2a**

A 10mL schlenk tube was filled with N_2 , then 7mL CH_2Cl_2 and **2b** (10mmol, 2.86g) was added. The mixture was cooled to 0°C and SO_2Cl_2 (10.5mmol, 1.31g in 3mL CH_2Cl_2) was dropped slowly. The mixture was stirred vigorously at 0°C for about 2h detected by TLC. After the reaction was over, the mixture was poured into 80mL CH_2Cl_2 , washed with washed with the saturated aqueous solution of Na_2CO_3 and water, dried over Na_2SO_4 . The solvent was removed and the residue was purified by flash chromatography on a silica gel column using n-hexane as the eluent. **2a** (9.1mmol, 2.91g, 91% yield) was obtained as the colorless oil.

IR (KBr):2969, 2952, 1590, 1463, 1380, 1315, 1260, 1208, 1176, 1116, 830, 809, 786, 673 cm^{-1} .

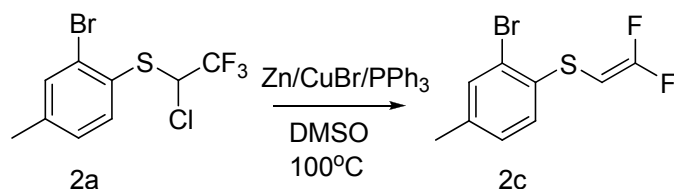
^{19}F NMR (282MHz, CDCl_3): -72.7 (d, $J=7\text{Hz}$).

^1H NMR (400MHz, CDCl_3): 2.38 (s, 3H), 5.38(q, $J=7\text{Hz}$, 1H), 7.17(d, $J=8\text{Hz}$,1H), 7.55- 7.60 (m, 2H).

^{13}C NMR (100MHz, CCl_3): 142.61, 136.76, 134.94, 129.43, 129.24, 127.08, 122.92(q, $J=280\text{Hz}$), 64.23(q, $J=34\text{Hz}$), 20.90.

MS (EI): $m/z=320(\text{M}^+)$. HRMS (EI) M^+ calcd for $\text{C}_{19}\text{H}_8\text{F}_3\text{SBr}$: 317.9092, found 317.9094.

II-4-4: The cleavage C-Cl of ((2-bromo-4-methylphenyl)(1-chloro-2,2,2-trifluoroethyl)sulfane **2a** using $\text{Cu}(0)$ catalyzation



A 10mL schlenk tube was charged with CuBr (7.2mg, 0.1mmol) and PPh_3 (104mg, 0.4mmol). The sealed tube was filled with nitrogen and the nitrogen purged solvent DMSO (4 mL)was then added. The mixture was heated to 100°C about 30min until it was colorless. Zinc powder (195mg, 3mmol) and **2a**(2mmol, 0.64g) was added. The mixture was heated at 100°C for 1.5h detected by TLC. After the reaction was over, the mixture was poured into 30mL Et_2O , washed with water, dried over Na_2SO_4 . The

solvent was removed and the residue was purified by flash chromatography on a silica gel column using n-hexane as the eluent. **2c** (1.76mmol, 0.466g, 88% yield) was obtained as straw yellow oil.

IR (KBr): 3062, 2922, 1705, 1463, 1381, 1315, 1260, 1208, 1176, 1116, 1023, 961, 809, 786, 673, 536 cm^{-1} .

^{19}F NMR (282MHz, CDCl_3): -74.3 (d, $J=13\text{Hz}$, 1F), -77.9(dd, $J=20, 13\text{Hz}$, 1F).

^1H NMR (300MHz, CDCl_3): 2.30 (s, 3H), 5.11(d, $J=20\text{Hz}$, 1H), 7.07-7.14(m, 2H), 7.37 (s, 1H).

^{13}C NMR (100MHz, CCl_4): 159.52(dd, $J=300, 295\text{Hz}$), 137.74, 133.61, 132.96, 128.85, 127.69, 121.88, 72.71(dd, $J=33, 20\text{Hz}$), 20.53.

MS (EI): $m/z=266(\text{M}^+)$. HRMS (EI) M^+ calcd for $\text{C}_{19}\text{H}_8\text{F}_3\text{SBr}$: 263.9420, found 263.9423.

III. Reference

- 1, Tanuma, T.; Ohnishi, K.; Okamoto, H.; Morikawa, S. *J. Fluorine Chem.* **1996**, 76, 45.
2. Prakash, G. K. Surya; Hu, Jinbo; Olah, George A. *J. Org. Chem.* **2003**, 68, 4457 .
3. Fokin, A. V.; Studnev, Yu. N.; Rapkin, A. I.; Chilikin, V. G.; Verenikin, O. V. *Bulletin of the Academy of Sciences of the USSR* , **1985**, 601.
- 4, Long, Z. -Y.; Chen, Q.-Y. *J. Fluorine Chem.* **1998**, 91, 95.
- 5, Kato, M.; Maeda, K.; Sato, K.; Omote, M.; Ando, A.; Kumadaki, I. *Chem. Pharm. Bull.*, **2000**, 48, 683.

IV. GC-MS spectral for HFC-143a and VDF

面积百分比报告
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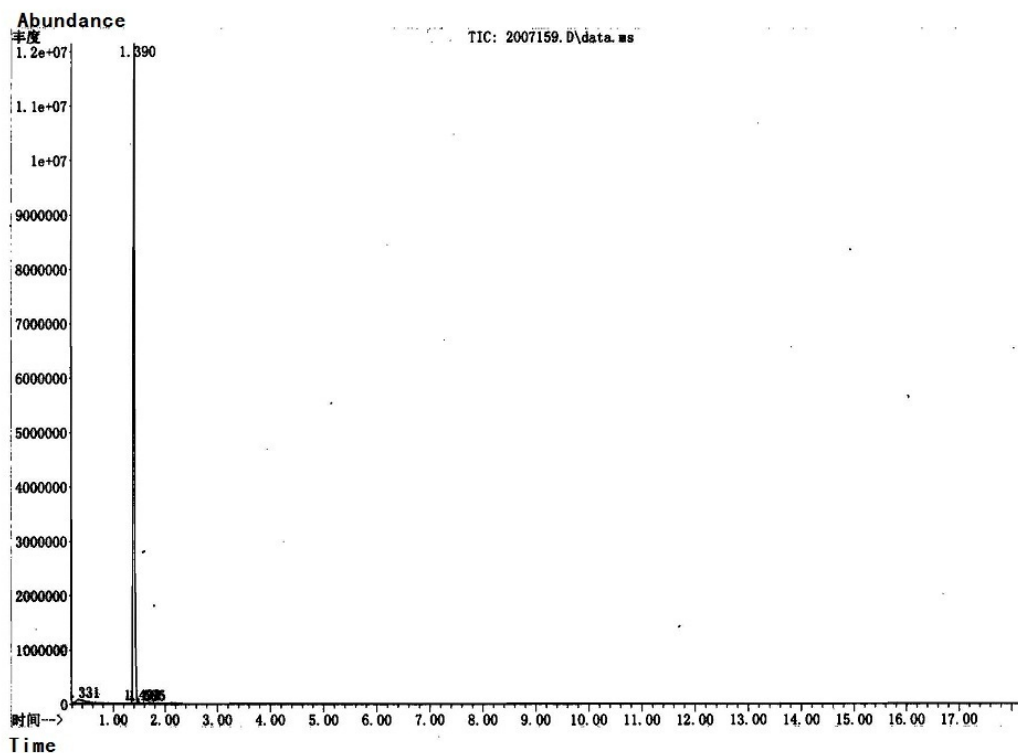
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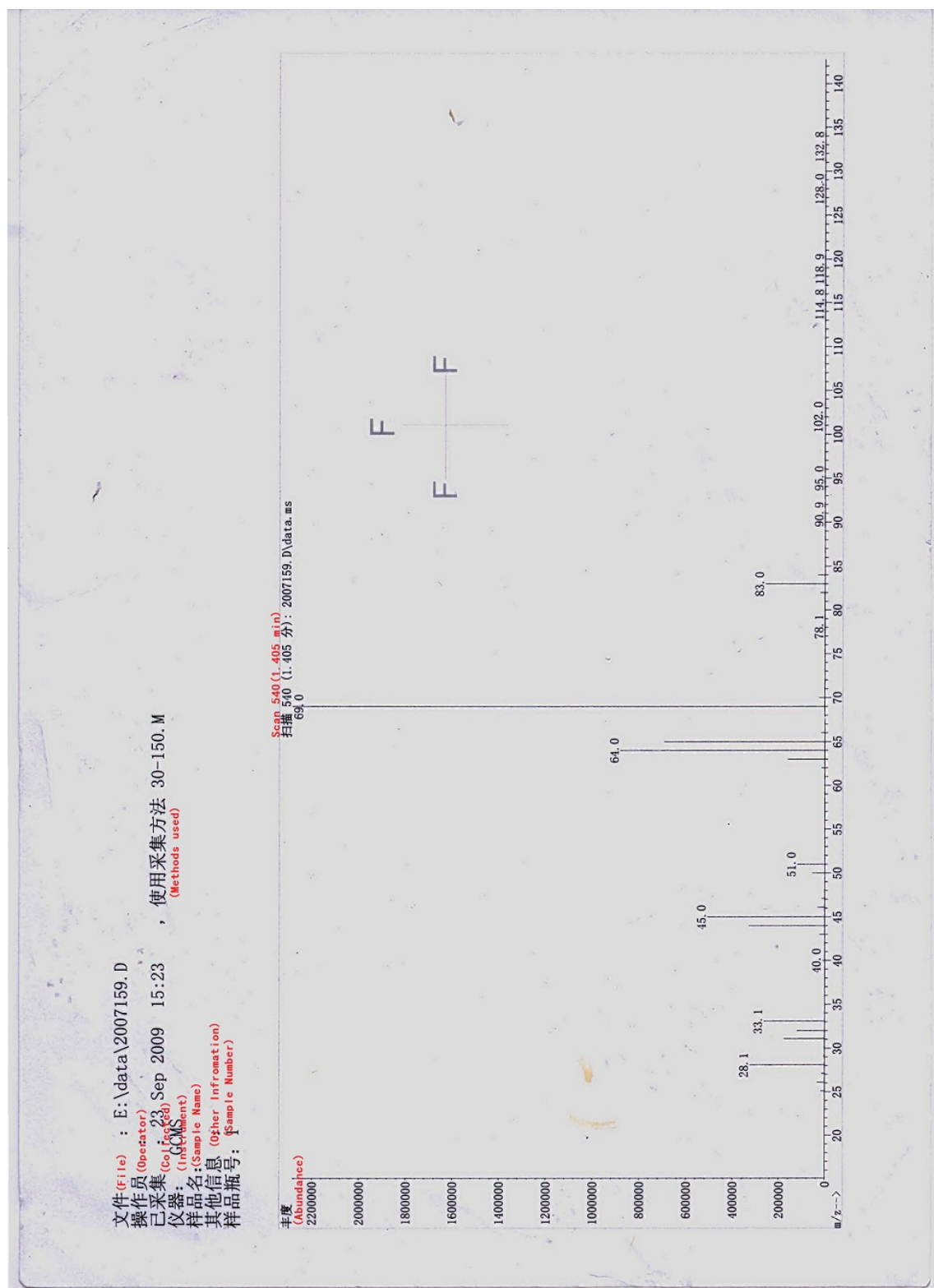
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Peak	min	Start	Top	Stop	Height of Peak	Height	Area	Area %	Percent
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2	1.390	509	534	571	M3	12175506	229596835	100.00%	96.589%
3	1.493	572	579	590	M5	14848	185185	0.08%	0.078%
4	1.585	610	620	633	M5	18450	226793	0.10%	0.095%

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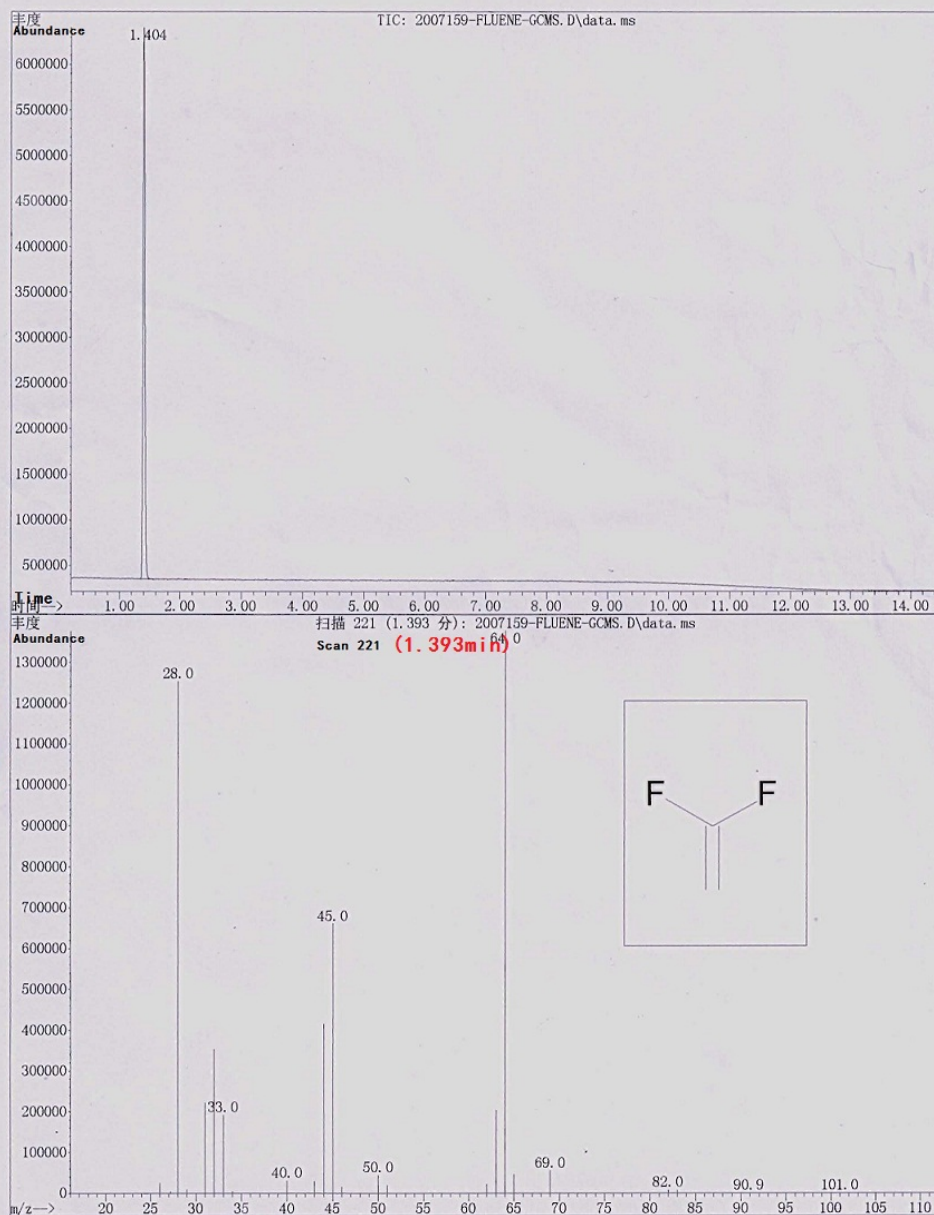


Gas phase product of Ni(0) catalytic system



Mass Spectra of HFC-143a

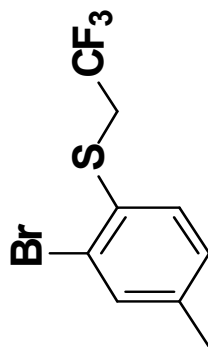
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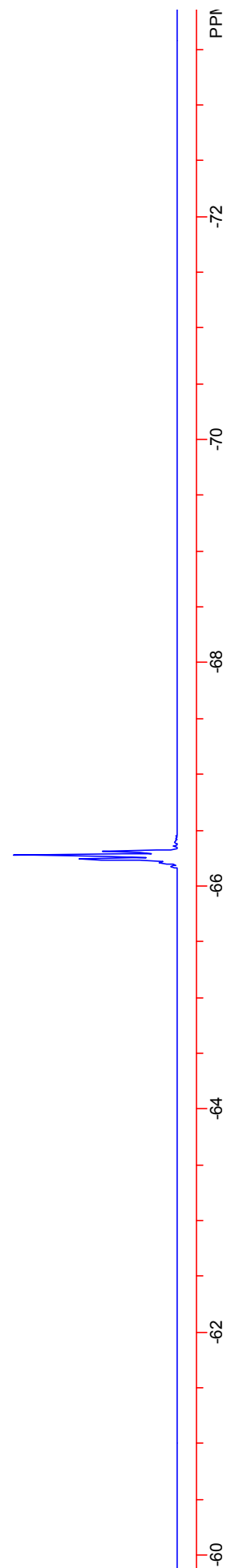
GC/MS spectra of Cu(0) catalytic system

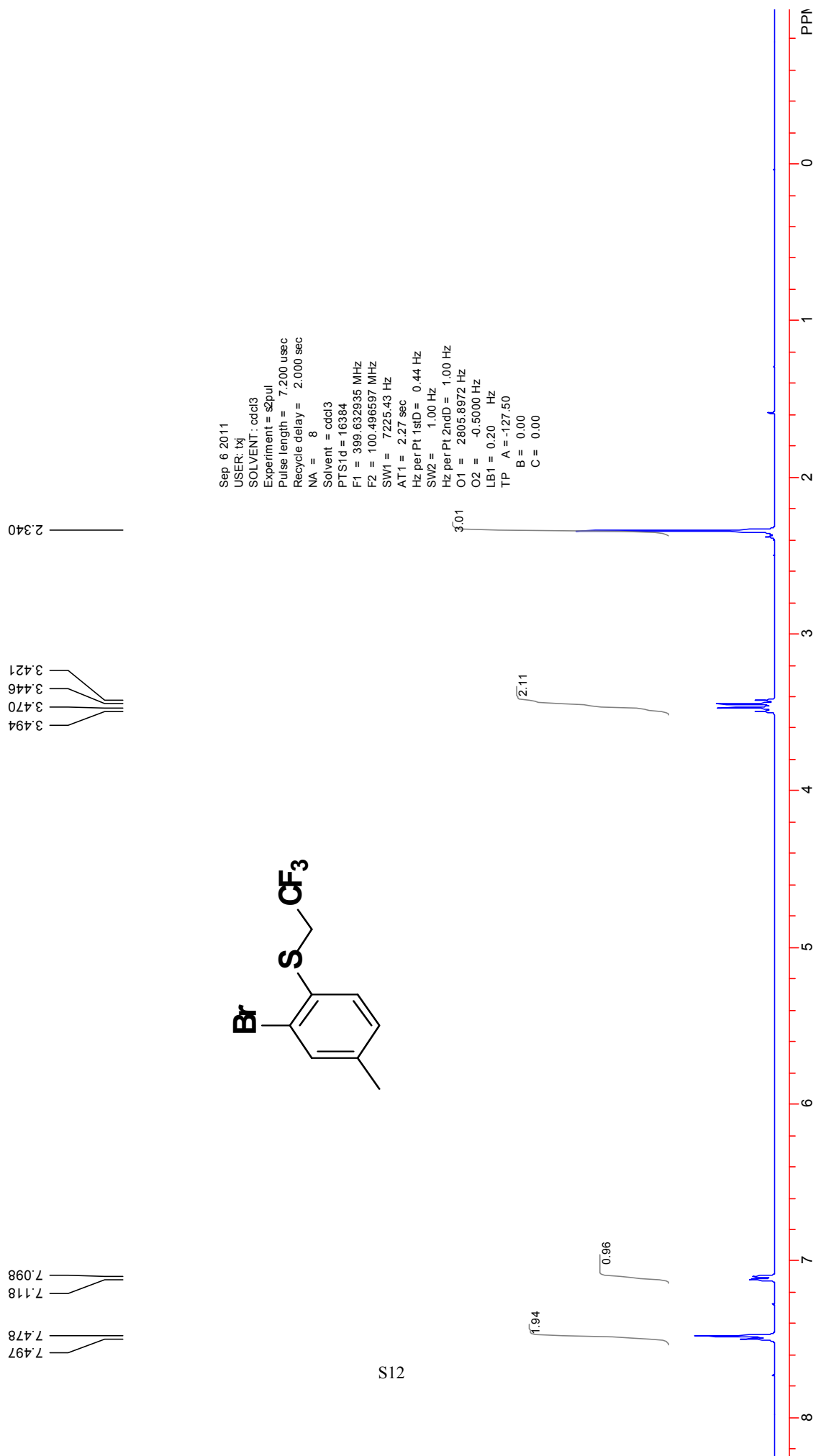
V. Spectral Data for new compounds

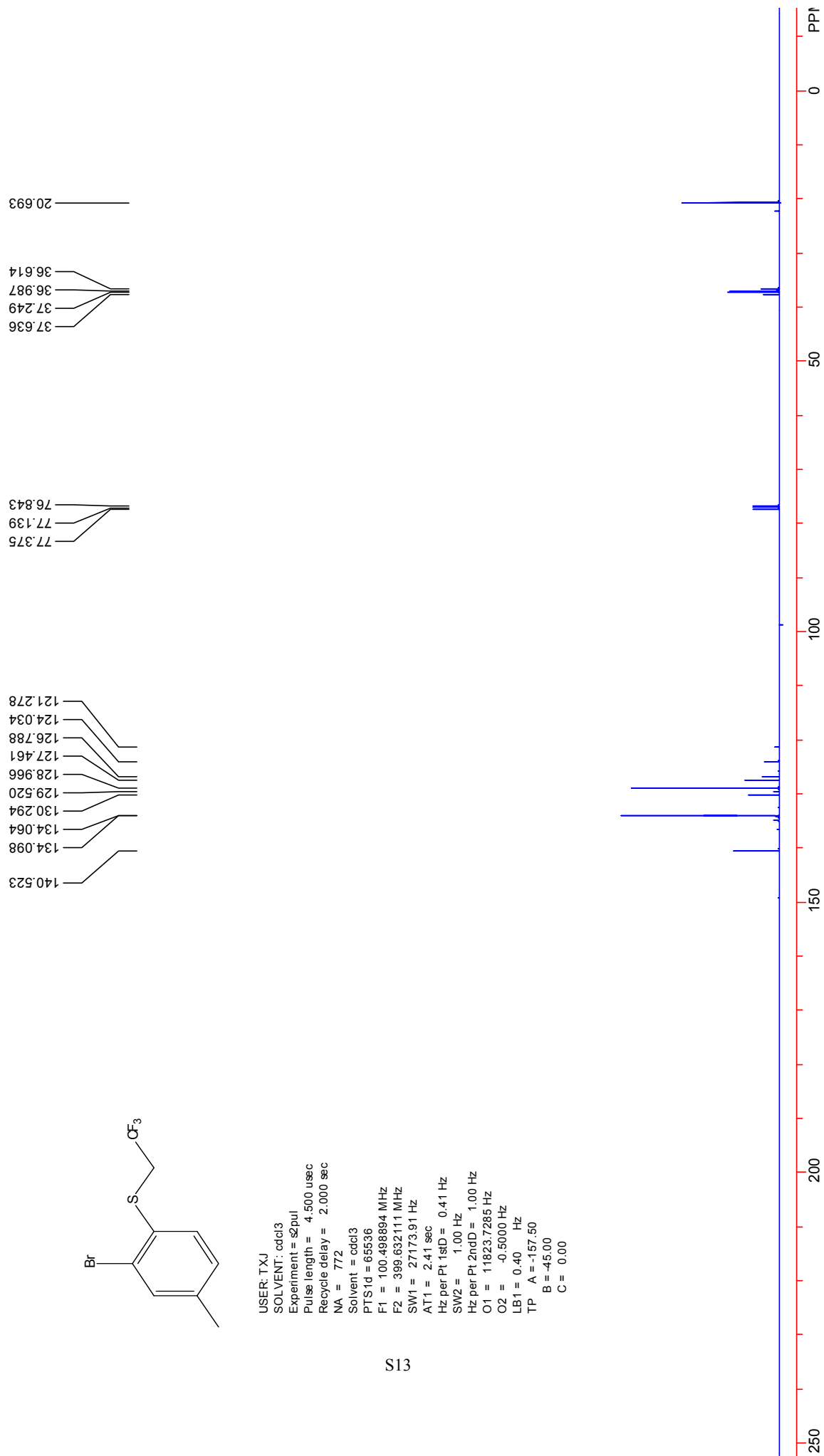
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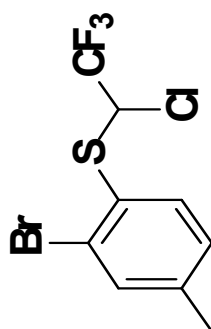
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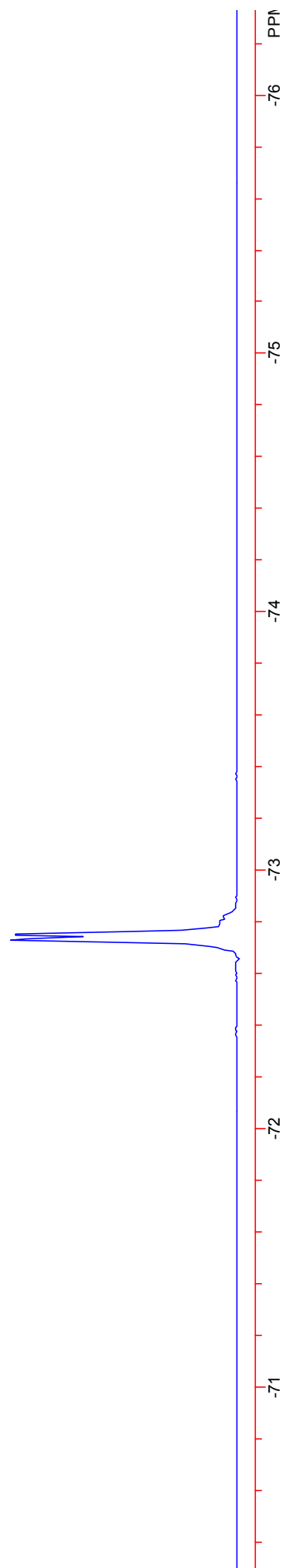


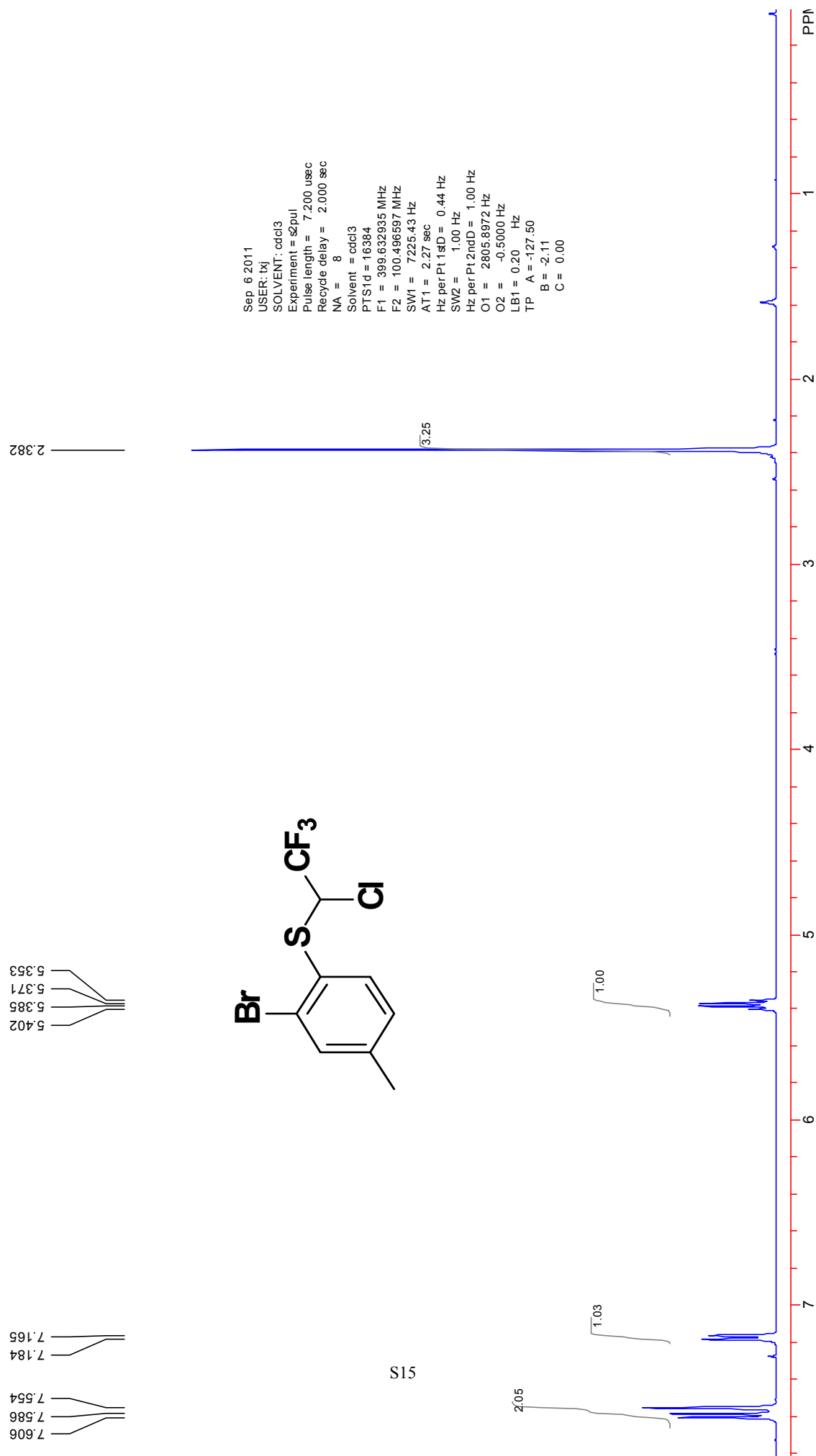


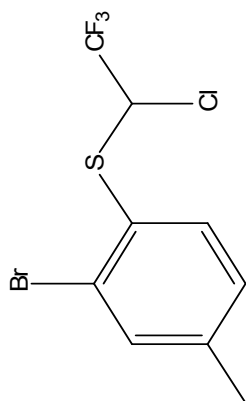
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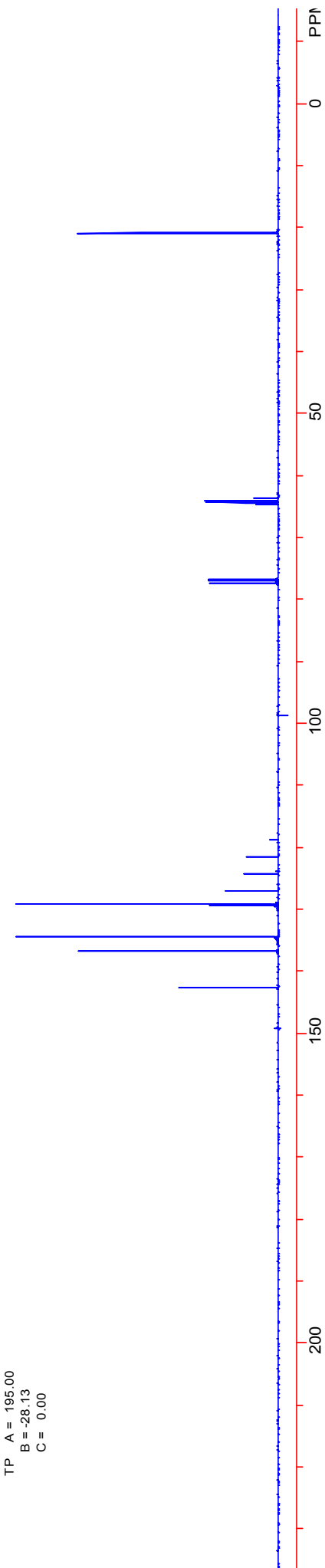
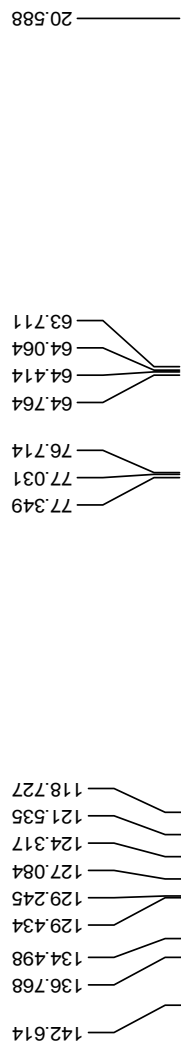
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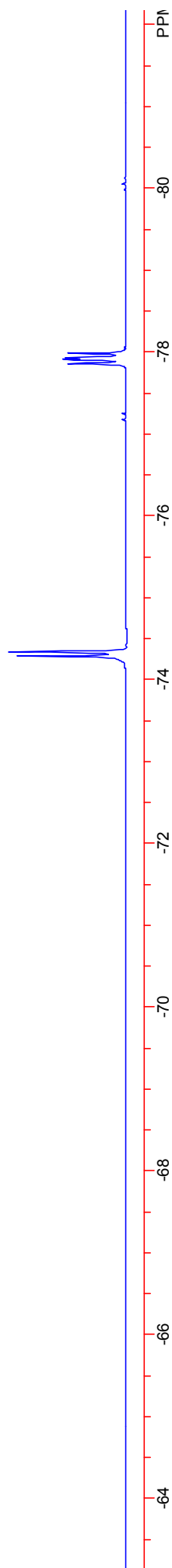
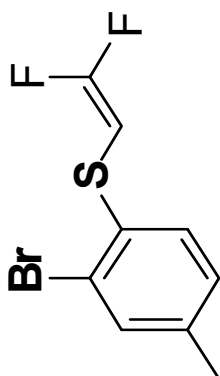
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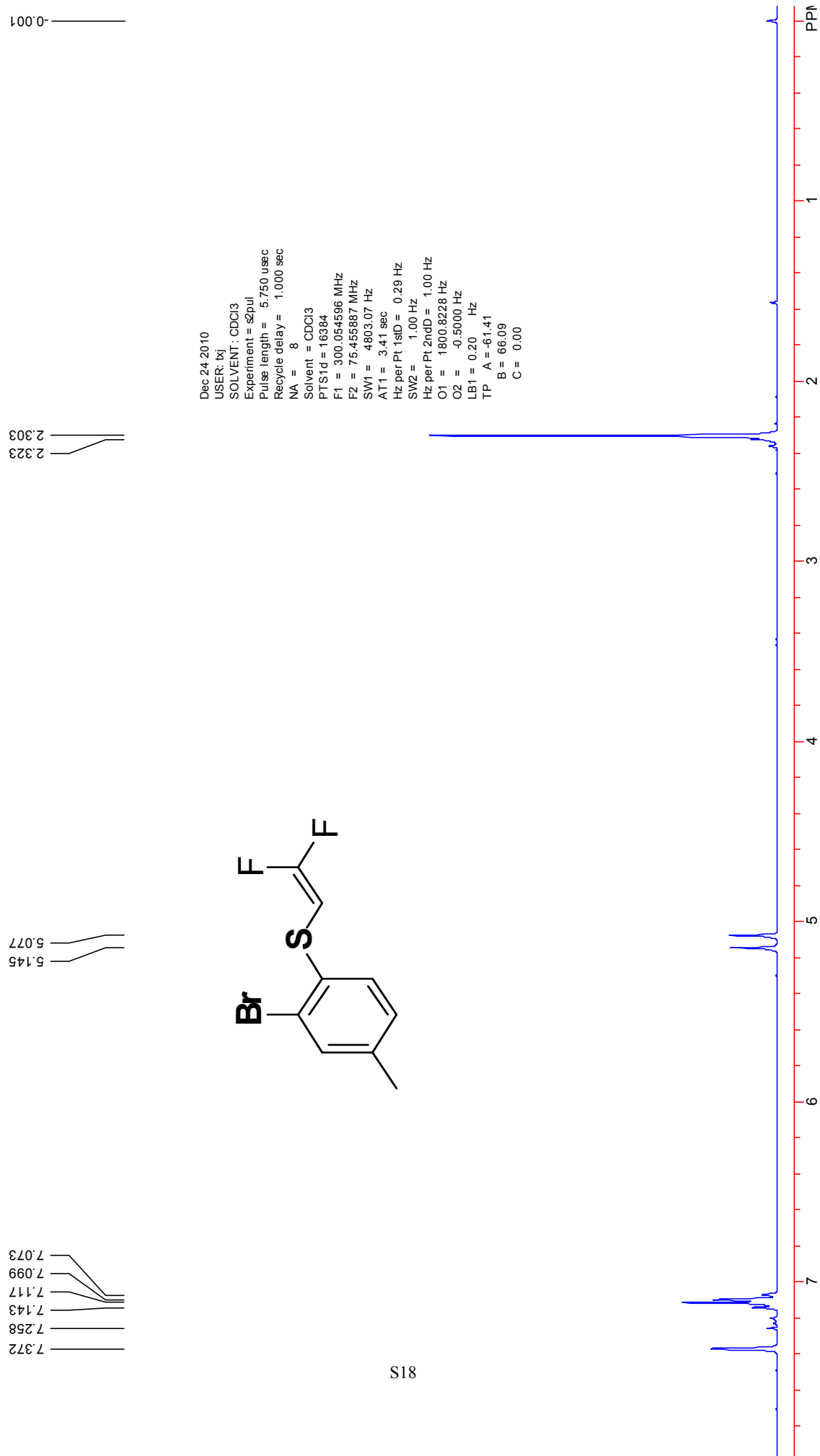


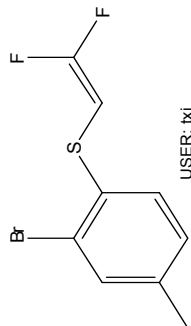
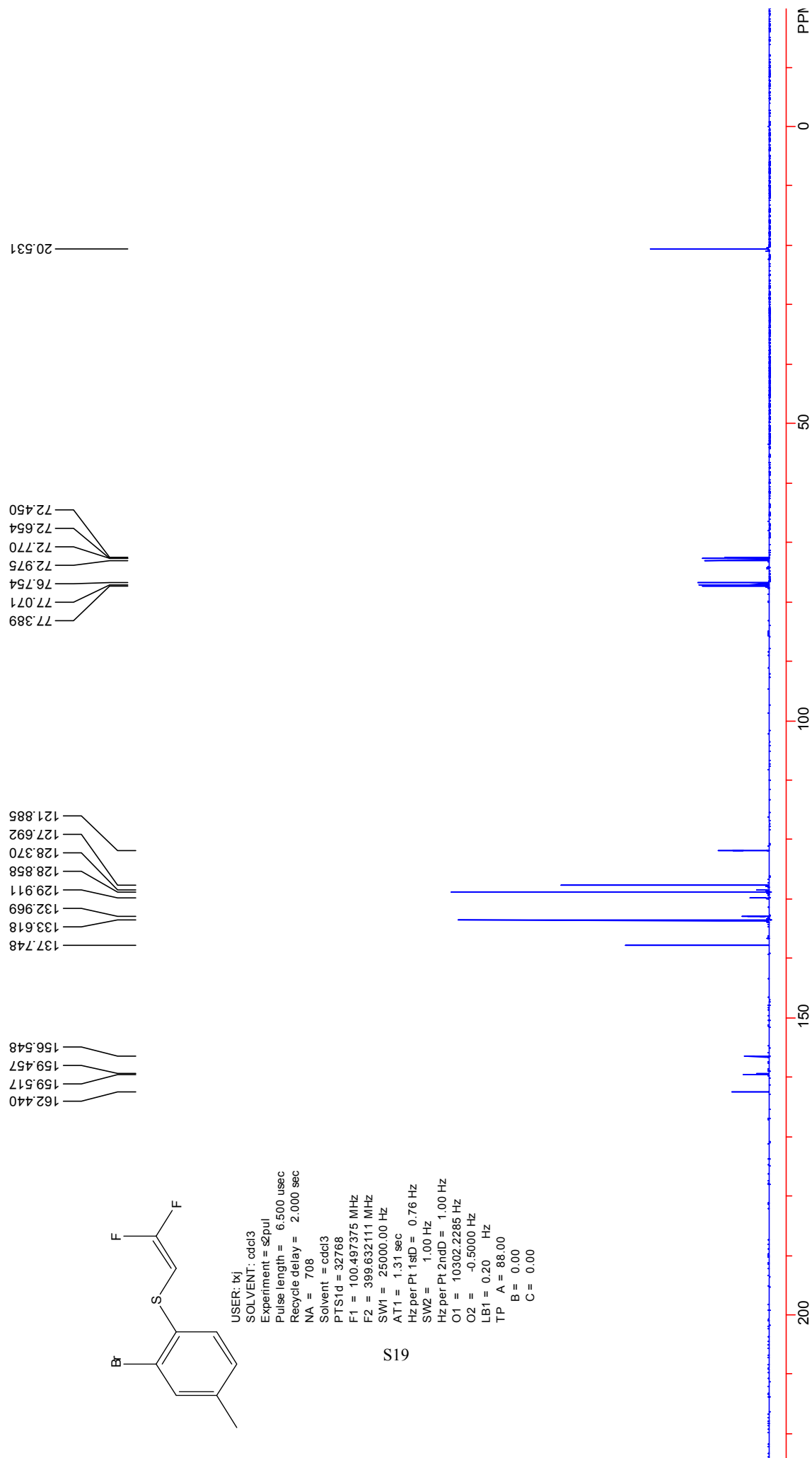
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