Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

Synthesis of aryl and heteroaryl tetrafluoro-λ^6-sulfanyl chlorides from diaryl disulfides using trichloroisocyanuric acid and potassium fluoride

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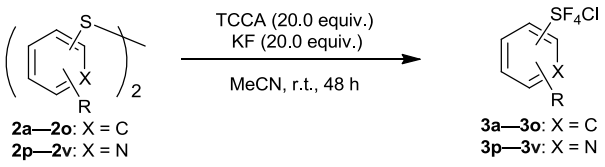
1. Experimental Section

1.1 General Methods

All reactions were performed in oven-dried FEP bottle (or tube) under a positive pressure of nitrogen. All solvents were dried and distilled using standard methods, transferred via syringe and were introduced into the reaction vessels though a rubber septum. All reagents were weighed out under N_2 atmosphere in a glove box. All reactions were monitored by thin-layer chromatography (TLC) or ^{19}F NMR. Column chromatography was carried out on a column packed with silica-gel 60N spherical neutral size 63-210 μm. The ^{1}H-NMR (300 MHz), ^{19}F-NMR (282 MHz) spectra for solution in $CDCl_3$ or CD_3CN were recorded on a Varian Mercury 300. Chemical shifts (δ) are expressed in ppm downfield from internal TMS (δ = 0.00). The C_6F_6 [δ = −162.2 ($CDCl_3$)] was used as internal standard for ^{19}F NMR. The chemical yields were determined by ^{19}F NMR, Fluorobenzene was used internal standard.

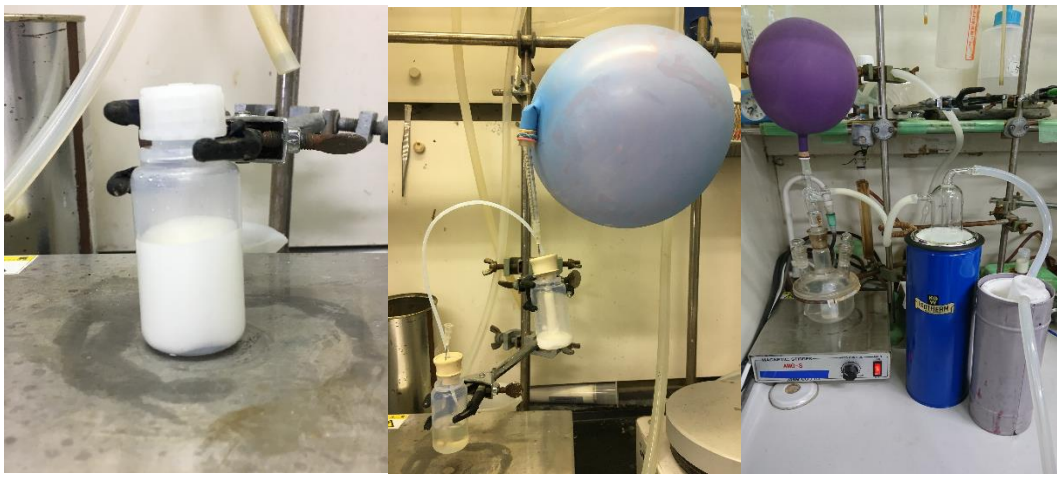
2. General procedure for the oxidative chlorotetrafluorination of diaryl disulfide (0.1 mmol scale and 0.5 mmol scale).



0.1 mmol scale: Inside a glove box, an oven-dried narrow-mouth FEP tube (Nalgene®) (10.0 mL) equipped with a magnetic stirrer bar was charged with diaryl disulfide (0.1 mmol, 1.0 equiv.), anhydrous spray-dried KF (0.12 g, 2.0 mmol, 20.0 equiv.), TCCA (0.46 g, 2.0 mmol, 20.0 equiv.), and anhydrous MeCN (2.0 mL, 0.05 M). The tube was tightly sealed and taken out of the glove box. The reaction mixture was stirred vigorously for 48 hours at room temperature. Yields were directly determined by ^{19}F NMR analysis of the crude products using C_6H_5F (37.5 μL, 0.4 mmol, 4.0 equiv.)

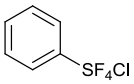
as an internal standard.

0.5 mmol scale: Inside a glove box, an oven-dried narrow-mouth FEP bottle (Nalgene®) (30.0 mL) equipped with a magnetic stirrer bar was charged with diaryl disulfide (0.5 mmol, 1.0 equiv.), anhydrous spray-dried KF (10.0 mmol, 20.0 equiv.), TCCA (10.0 mmol, 20.0 equiv.), and anhydrous MeCN (10.0 mL, 0.05 M). The bottle was tightly sealed and taken out of the glove box. The reaction mixture were stirred for 48 hours at room temperature. Thereafter, the supernatant was decanted and filtered through a PP/ETFE suction filter (Flom Cat. # 8800) under a stream of N_2 into another FEP bottle (30 mL). The residue was washed with anhydrous MeCN (3.0 mL) and the combined liquid phases were evaporated carefully *in vacuo* to furnish the desired crude products. All the products were characterized by NMRs (see the next part) and they were also confirmed by comparisons of previously reported data. Photographs of the used synthetic apparatus were shown below.



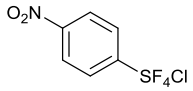
(1) Reaction mixture **(2) Filtration** **(3) Evaporation *in vacuo***

2.1 Chlorotetrafluoro(phenyl)-λ^6-sulfane (3a);



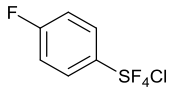
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76 – 7.72 (m, 2H), 7.53 – 7.42 (m, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 136.64 (s, 4F) ppm.

2.2 Chlorotetrafluoro(4-nitrophenyl)- λ^6-sulfane (3b);



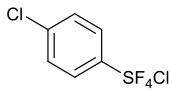
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.33 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 9.1 Hz, 2H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 134.95 (s, 4F) ppm.

2.3 Chlorotetrafluoro(4-fluorophenyl)- λ^6-sulfane (3c);



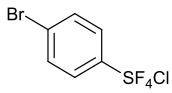
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 73%. ^{1}H NMR (300 MHz, CD_3CN) δ: 7.89 – 7.84 (m, 2H), 7.29 – 7.23 (m, 2H) ppm. ^{19}F NMR (282 MHz, CD_3CN) δ: 137.54 (s, 4F), -108.21 – -108.31 (m, 1F) ppm.

2.4 Chlorotetrafluoro(4-chlorophenyl)- λ^6-sulfane (3d);



The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 84%. ^{1}H NMR (300 MHz, CD_3CN) δ: 7.79 (d, *J* = 9.1 Hz, 2H), 7.54 (d, *J* = 8.7 Hz, 2H) ppm. ^{19}F NMR (282 MHz, CD_3CN) δ: 136.62 (s, 4F) ppm.

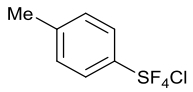
2.5 Chlorotetrafluoro(4-bromophenyl)- λ^6-sulfane (3e);



The reaction was run according to the general procedure, and the product is consistent with

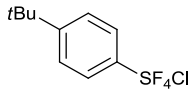
previously reported characterization data.[1] ^{19}F NMR yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60 (s, 4H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 136.59 (s, 4F) ppm.

2.6 Chlorotetrafluoro(*p*-tolyl)- λ^6-sulfane (3f);



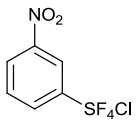
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 2.40 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 137.62 (s, 4F) ppm.

2.7 Chlorotetrafluoro(4-(*tert*-butyl)phenyl)- λ^6-sulfane (3g);



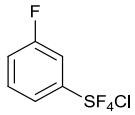
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 1.33 (s, 9H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 137.61 (s, 4F) ppm.

2.8 Chlorotetrafluoro(3-nitrophenyl)- λ^6-sulfane (3h);



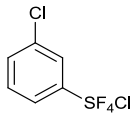
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[2] ^{19}F NMR yield: 84%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.63 (t, *J* = 2.1 Hz, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 8.11 – 8.07 (m, 1H), 7.71 (t, *J* = 8.2 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 135.19 (s, 4F) ppm.

2.9 Chlorotetrafluoro(3-fluorophenyl)- λ^6-sulfane (3i);



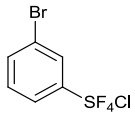
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 74%. ^{1}H NMR (300 MHz, CD_3CN) δ: 7.72 – 7.53 (m, 3H), 7.40 – 7.35 (m, 1H) ppm. ^{19}F NMR (282 MHz, CD_3CN) δ 138.07 (s, 4F), -109.20 – -109.46 (m, 1F) ppm.

2.10 Chlorotetrafluoro(3-chlorophenyl)- λ^6-sulfane (3j);



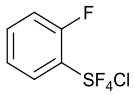
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data. [2] ^{19}F NMR yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.89 (t, *J* = 2.0 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.34 (t, *J* = 8.1 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 136.05 (s, 4F) ppm.

2.11 Chlorotetrafluoro(3-bromophenyl)- λ^6-sulfane (3k);



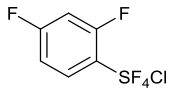
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.75 (t, *J* = 2.1 Hz, 1H), 7.70 – 7.58 (m, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 8.2 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 136.02 (s, 4F) ppm.

2.12 Chlorotetrafluoro(2-fluorophenyl)- λ^6-sulfane (3l);



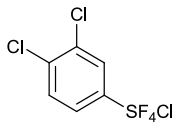
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data. [2] ^{19}F NMR yield: 77%. ^{1}H NMR (300 MHz, CD_3CN) δ: 7.87 – 7.81 (m, 1H), 7.67 – 7.60 (m, 1H), 7.39 – 7.29 (m, 2H) ppm. ^{19}F NMR (282 MHz, CD_3CN) δ: 142.23 (d, *J* = 24.4 Hz, 4F), -107.92 – -108.18 (m, 1F) ppm.

2.13 Chlorotetrafluoro(2,4-difluorophenyl)- λ^6-sulfane (3m);



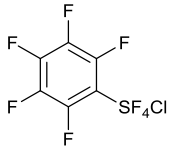
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[2] ^{19}F NMR yield: 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.94 – 7.86 (m, 1H), 7.19 – 7.08 (m, 2H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 142.14 (d, *J* = 23.9 Hz, 4F), -102.05 – -102.17 (m, 1F), -102.79 – -103.07 (m, 1F) ppm.

2.14 Chlorotetrafluoro(3,4-dichlorophenyl)- λ^6-sulfane (3n);



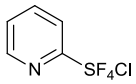
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[2] ^{19}F NMR yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 2.4 Hz, 1H), 7.61 – 7.52 (m, 2H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ 136.21 (s, 4F) ppm.

2.15 Chlorotetrafluoro(perfluorophenyl)- λ^6-sulfane (3o);



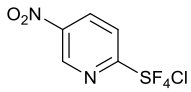
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[1] ^{19}F NMR yield: 72%. ^{19}F NMR (282 MHz, CD_3CN): trans-isomer: δ: 141.87 (t, *J* = 27.1 Hz, 4F), -136.28 – -136.80 (m, 2F), -149.98 – -150.90 (m, 1F), -162.13 – -162.25 (m, 2F) ppm; cis-isomer: δ: 151.81 (q, *J* = 158.2, 1F), 122.01 – 120.83 (m, 2F), 78.55 – 77.68 (m, 1F), -136.28 – -136.80 (m, 2F), -149.98 – -150.90 (m, 1F), -162.13 – -162.25 (m, 2F) ppm. trans:cis ratio: 1.8:1.

2.16 2-(Chlorotetrafluoro-λ^6-sulfaneyl)pyridine (3p);



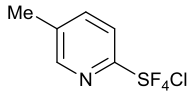
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[3] ^{19}F NMR yield: 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.58 (d, *J* = 3.5 Hz, 1H), 7.95 (t, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.52 (dd, *J* = 7.5, 4.7 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 124.04 (s, 4F) ppm.

2.17 2-(Chlorotetrafluoro-λ^6-sulfaneyl)-5-nitropyridine (3q);



The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[2] ^{19}F NMR yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.38 (s, 1H), 8.71 (d, *J* = 8.9 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 123.55 (s, 4F) ppm.

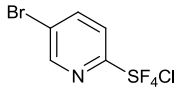
2.18 2-(Chlorotetrafluoro-λ^6-sulfaneyl)-5-methylpyridine (3r);



The reaction was run according to the general procedure, and the product is consistent with

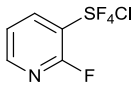
previously reported characterization data.[3] ^{19}F NMR yield: 52%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.38 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 1H), 2.44 (s, 3H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 125.14 (s, 4F) ppm.

2.19 2-(Chlorotetrafluoro-λ^6-sulfaneyl)-5-bromopyridine (3s);



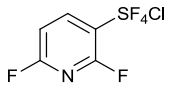
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[2] ^{19}F NMR yield: 81%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.63 (s, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 124.73 (s, 4F) ppm.

2.20 3-(Chlorotetrafluoro-λ^6-sulfaneyl)-2-fluorolpyridine (3t);



The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[4] ^{19}F NMR yield: 80%. ^{1}H NMR (300 MHz, CD_3CN) δ: 8.41 (d, *J* = 4.8 Hz, 1H), 8.37 – 8.31 (m, 1H), 7.49 – 7.46 (m, 1H) ppm. ^{19}F NMR (282 MHz, CD_3CN) δ: 137.95 (d, *J* = 21.5 Hz, 4F), -63.16 – -63.29 (m, 1F) ppm.

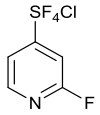
2.21 3-(Chlorotetrafluoro-λ^6-sulfaneyl)-2,6-difluorolpyridine (3u);



The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[4] ^{19}F NMR yield: 75%. ^{1}H NMR (300 MHz, CD_3CN) trans-isomer: δ: 8.48 (d, *J* = 8.2 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H) ppm. ^{19}F NMR (282 MHz, CD_3CN): trans-isomer: δ: 138.65 (d, *J* = 21.4 Hz, 4F), -61.88 – -62.02 (m, 1F), -62.84 – -63.27 (m, 1F) ppm; cis-isomer: δ: 158.49 (q, *J* = 159.9, 1F), 111.70 – 110.70 (m, 2F), 71.49 – 69.78 (m, 1F),

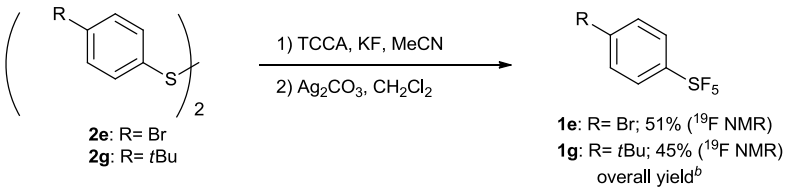
-61.88 – -62.02 (m, 1F), -62.84 – -63.27 (m, 1F) ppm. trans:cis ratio: 5.2:1.

2.22 4-(Chlorotetrafluoro-λ^6-sulfaneyl)-2-fluorolpyridine (3v);



The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[4] ^{19}F NMR yield: 72%. ^{1}H NMR (300 MHz, CD_3CN) δ: 8.44 (s, 1H), 7.67 (s, 1H), 7.49 (s, 1H) ppm. ^{19}F NMR (282 MHz, CD_3CN) δ: 132.24 (s, 4F), -65.79 (s, 1F) ppm.

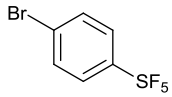
3. Two-step synthetic procedure for the formation of arylsulfur pentafluorides and product characterization data for Scheme 3.



Inside a glove box, an oven-dried narrow-mouth FEP bottle (Nalgene®) (30 mL), equipped with a magnetic stirrer bar, was charged with diaryl disulfide (**2e** or **2g**, 0.5 mmol, 1.0 equiv.), anhydrous spray-dried KF (0.58 g, 10.0 mmol, 20.0 equiv.), TCCA (2.3 g, 10.0 mmol, 20.0 equiv.) and anhydrous MeCN (10.0 mL, 0.05 M). The bottle was tightly sealed and taken out of the glove box. The reaction mixture was stirred vigorously for 48 hours at room temperature. Thereafter, the supernatant was decanted and filtered through a PP/ETFE suction filter (Flom Cat. # 8800) under a stream of N_2 into another FEP bottle (30 mL). The residue was washed with anhydrous MeCN (3.0 mL) and the combined liquid phases were evaporated carefully *in vacuo*. Then, the residue was washed with anhydrous *n*-hexane (5.0 mL×2), filtered into a FEP bottle under N_2 atmosphere, and concenrated *in vacuo*. The FEP bottle was transferred into a glove box under an N_2 atmosphere, before Ag_2CO_3 (0.14 g, 0.5 mmol, 1.0 equiv.) and anhydrous DCM (10.0 mL) were added. The bottle was tightly sealed, removed from the glove box and stirred vigorously for 24 hours at room temperature. Thereafter, the reaction mixture was filtered through a pad of Kieselguhr and washed

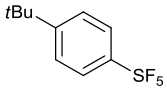
with DCM. The combined filtrates were concentrated under vacuum in an ice bath. The yield was determined by ^{19}F NMR analysis of the crude reaction mixture using C_6H_5F (0.188 mL, 2.0 mmol, 4.0 equiv.) as an internal standard. The crude product was purified by column chromatography on silica gel (eluent: pentane) to give pure **1e** or **1g**.

3.1 (4-bromophenyl)pentafluoro-λ^6-sulfane (1e);



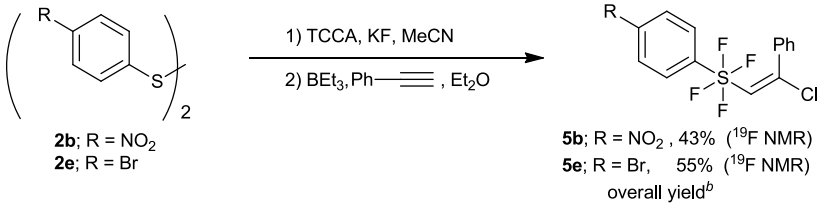
The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[3] Isolated yield: 81.2 mg, 29% (51%). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.62 (s, 4H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 84.07 – 81.94 (m, 1F), 62.51 (d, *J* = 150.5 Hz, 4F) ppm.

3.2 (4-(*tert*-butyl)phenyl)pentafluoro-λ^6-sulfane (1g);



The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[3] Isolated yield: 72.9 mg, 28% (45%). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 9.1 Hz, 2H), 1.33 (s, 9H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 86.46 – 83.43 (m,1F), 62.78 (d, *J* = 149.8 Hz, 4F) ppm.

4. Two-step synthetic procedure for the formation of SF_4-alkene and product characterization data for Scheme 4.

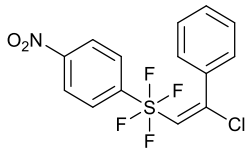


2b; R = NO_2
2e; R = Br

5b; R = NO_2 , 43% (^{19}F NMR)
5e; R = Br, 55% (^{19}F NMR)
overall yield[b]

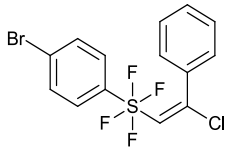
Inside a glove box, an oven-dried narrow-mouth FEP bottle (Nalgene®) (30 mL), equipped with a magnetic stirrer bar, was charged with diaryl disulfide (**2b** or **2e**, 0.5 mmol, 1.0 equiv.), anhydrous spray-dried KF (0.58 g, 10.0 mmol, 20.0 equiv.), TCCA (2.3 g, 10.0 mmol, 20.0 equiv.), and anhydrous MeCN (10.0 mL, 0.05 M). The bottle was tightly and taken out of the glove box. The reaction mixture was stirred vigorously for 48 hours at room temperature. Thereafter, the supernatant was decanted and filtered through a PP/ETFE suction filter (Flom Cat. # 8800) under a stream of N_2 into another FEP bottle (30 mL). The residue was washed with anhydrous MeCN (3.0 mL) and the combined liquid phases were evaporated carefully *in vacuo*. Then, the residue was washed with anhydrous *n*-hexane (5.0 mL×2), filtered into a FEP bottle (30 mL) under N_2 atmosphere, and concenrated *in vacuo*. The product was dissolved in dry Et_2O (2.0 mL). Phenylacetylene (PhC≡CH, 164.7 μL, 1.5 mmol, 3.0 equiv.) was added to the combined ether layers, and the reaction mixture was cooled to 0 °C, before Et_3B (88.0 μL, 1.0 M in hexane, 0.088 mmol, 0.176 equiv.) was added by dropwise. Thereafter, the reaction mixture was warmed to room temperature, where stirring was continued for 30 min. Then, the reaction mixture was quenched with aqueous $NaHCO_3$, extracted with Et_2O (20.0 mL x 3), washed with brine (20.0 mL), and concentrated under reduced pressure. The yield was determined by ^{19}F NMR analysis of the crude reaction mixture using C_6H_5F (0.188 mL, 2.0 mmol, 4.0 equiv.) as an internal standard. The crude product was purified by column chromatography on silica gel (eluent: hexane/EtOAc; 20:1; v/v) to afford pure SF_4-alkene **5b** or **5e**.

4.1 [(*E*)-2-(4-nitrophenyltetrafluoro- λ^6-sulfanyl)-1-chloroethenyl]benzene (5b).



The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[5] Isolated yield: 139.4 mg, 38% (43%). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 9.2 Hz, 2H), 7.44 – 7.38 (m, 5H), 7.22 – 7.13 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: *E*-isomer: 70.80 (d, *J* = 8.2 Hz, 4F) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ: *Z*-isomer: 69.44 (d, *J* = 9.4 Hz, 4F) ppm.

4.2 [(*E*)-2-(4-bromophenyltetrafluoro- λ^6-sulfanyl)-1-chloroethenyl]benzene (**5e**).



The reaction was run according to the general procedure, and the product is consistent with previously reported characterization data.[5] Isolated yield: 192.8 mg, 48% (55%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.49 – 7.39 (m, 9H), 7.20 – 7.12 (m, 1H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ: 71.00 (d, *J* = 8.5 Hz, 4F) ppm.

5. References

[1]. T. Umemoto, L. M. Garrick, N. Saito, *Beilstein J. Org. Chem.* 2012, **8**, 461.

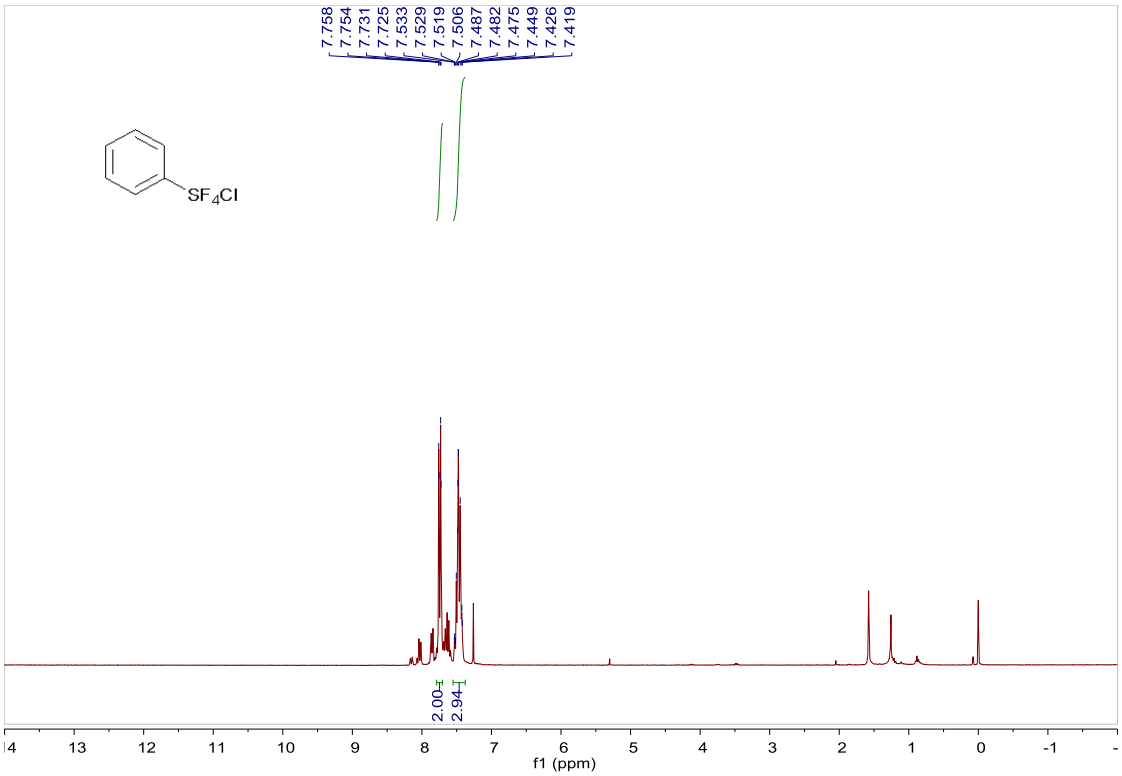
[2]. B. Cui, S. Jia, E. Tokunaga, N. Saito, N. Shibata, *Chem. Commun.* 2017, **53**, 12738.

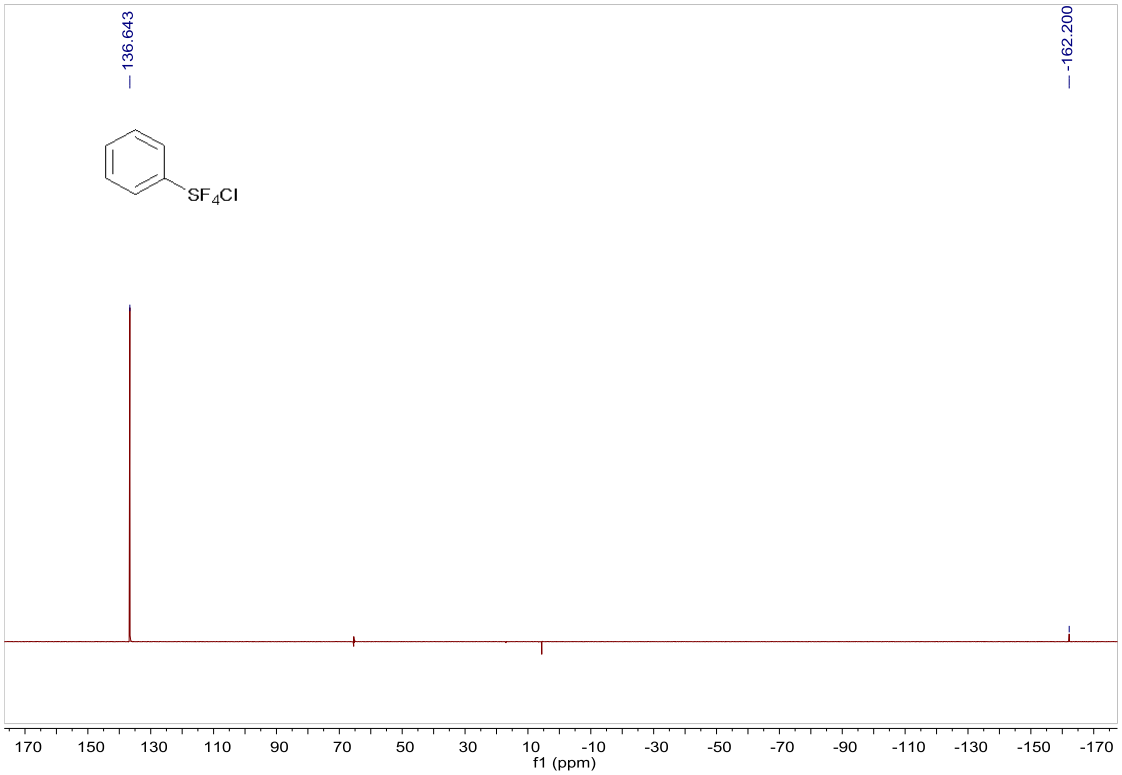
[3]. O. S. Kanishchev, W. R. Dolbier, Jr., *Angew. Chem. Int. Ed.* 2015, **54**, 280.

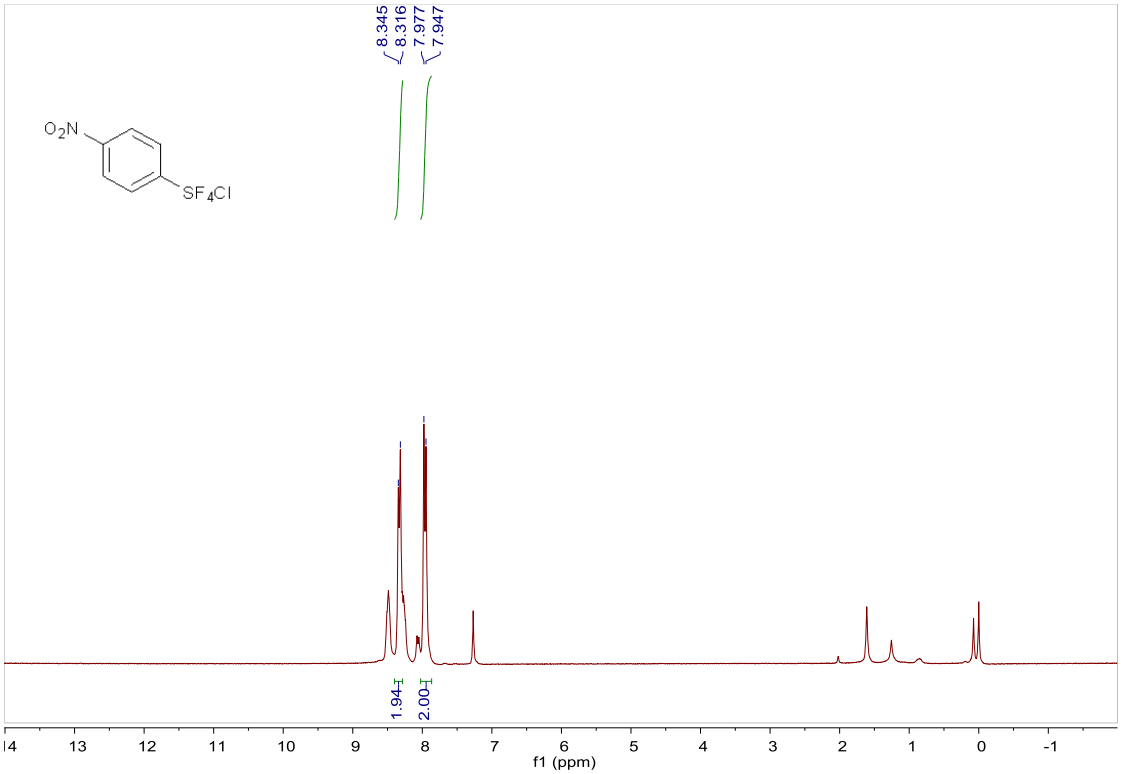
[4]. M. Kosobokov, B. Cui, A. Balia, K. Matsuzaki, E. Tokunaga, N. Saito and N. Shibata, *Angew. Chem., Int. Ed*., 2016, **55**, 10781.

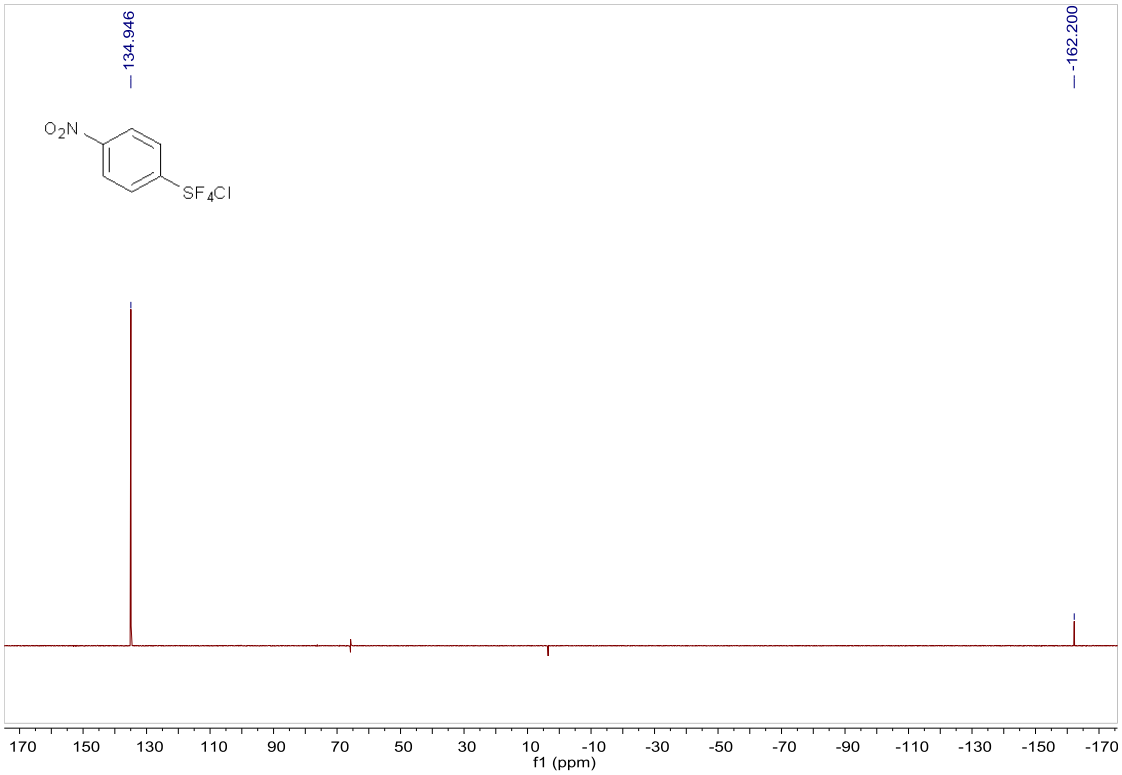
[5]. L. Zhong, P. R. Savoie, A. S. Filatov and J. T. Welch, *Angew. Chem. Int. Ed.*, 2014, **53**, 526.

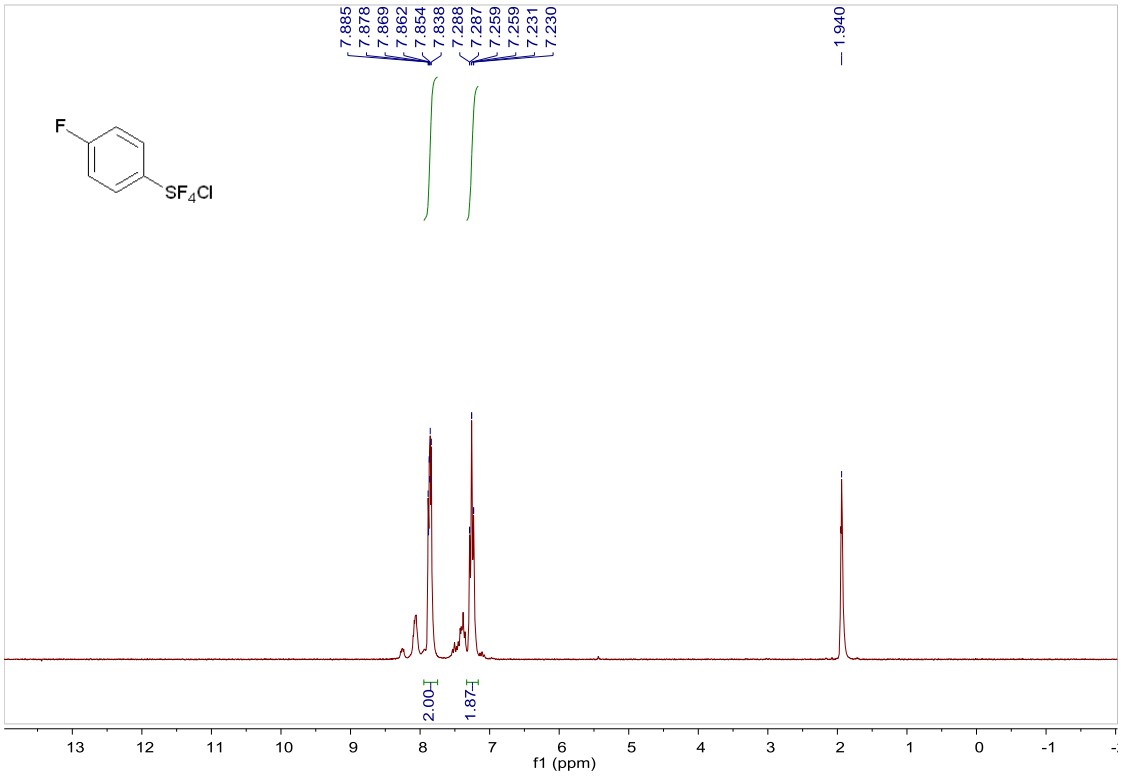
6. ^{1}H NMR and ^{19}F NMR spectra for desired compounds

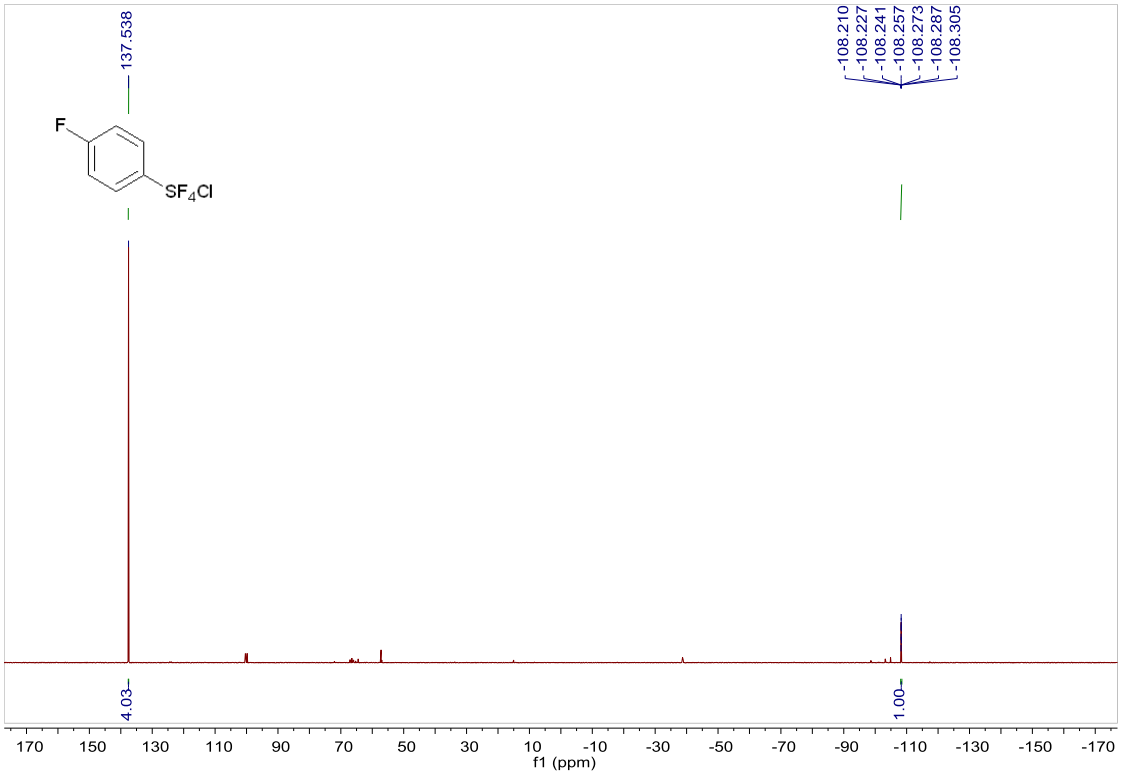





8.345
8.316
7.977
7.947
O2N
SF4Cl
1.94
2.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


134.946
-162.200
O2N
SF4Cl
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)


7.885
7.878
7.869
7.862
7.854
7.838
7.288
7.287
7.259
7.259
7.231
7.230
1.940
F
SF4Cl
2.00
1.87
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


137.538
-108.210
-108.227
-108.241
-108.257
-108.273
-108.287
-108.305
F
SF4Cl
4.03
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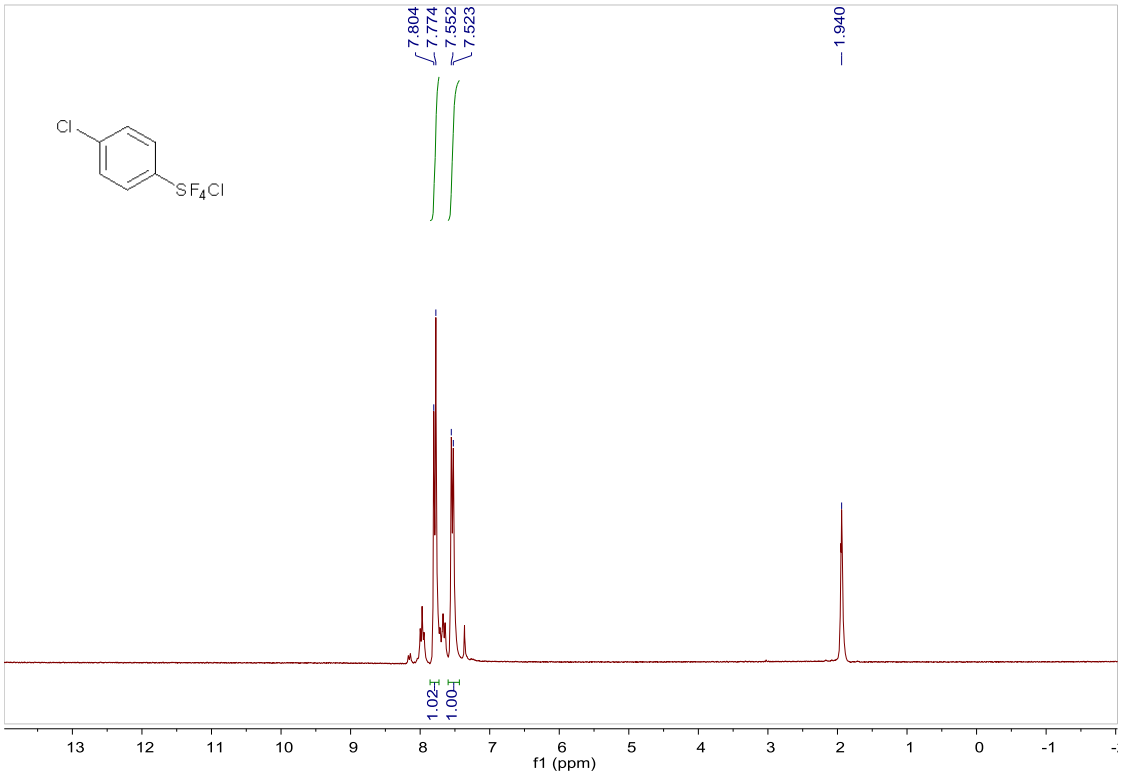
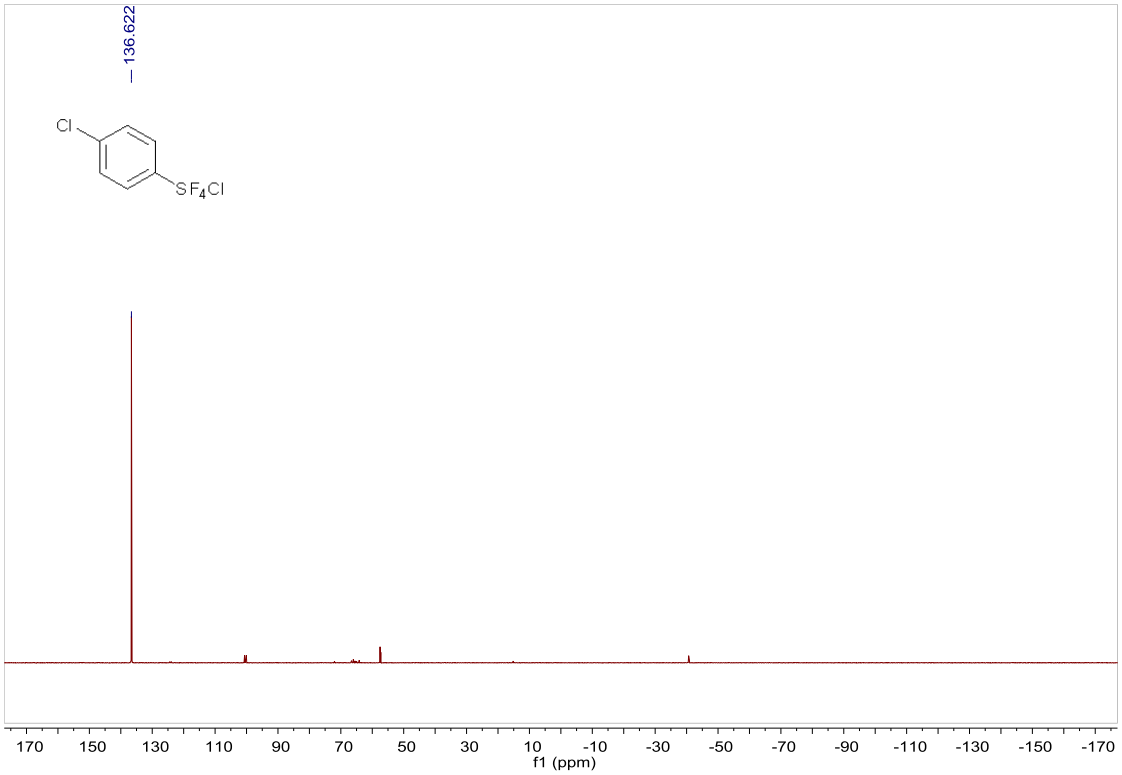
f1 (ppm)


7.804
7.774
7.552
7.523
1.940
Cl
SF4Cl
1.02
1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


136.622
Cl
SF4Cl
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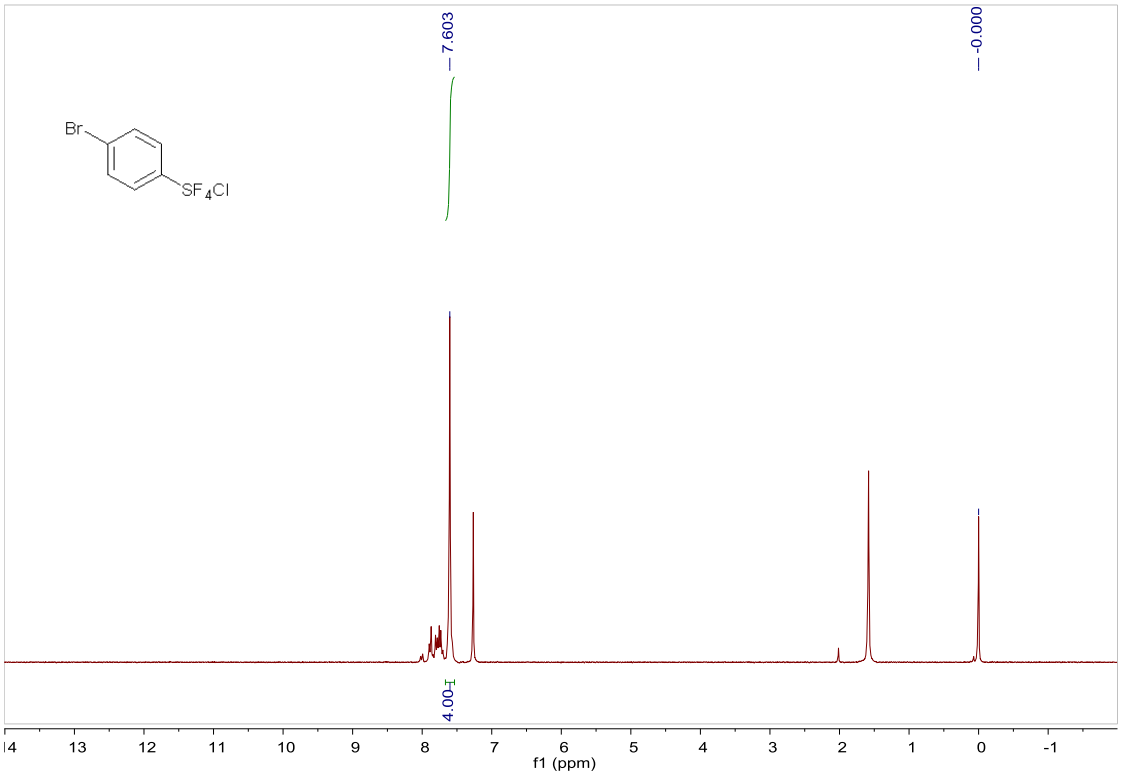
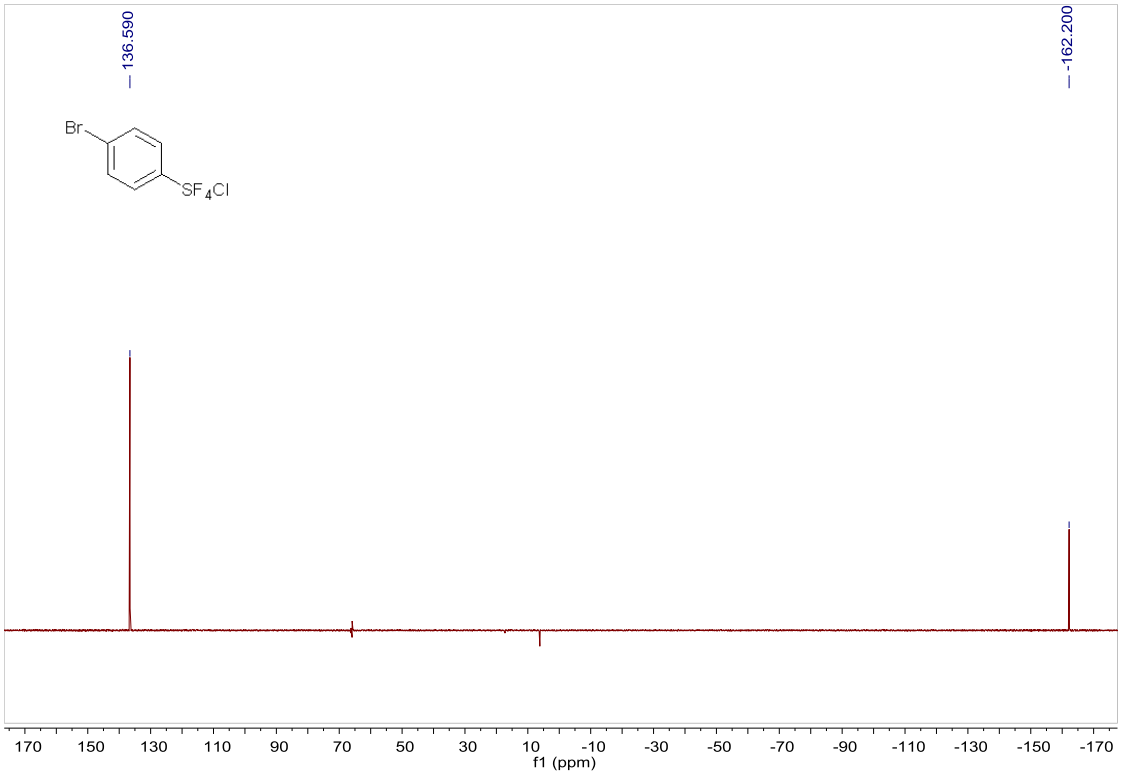
f1 (ppm)


7.603
-0.000
Br
SF4Cl
4.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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-162.200
Br
SF4Cl
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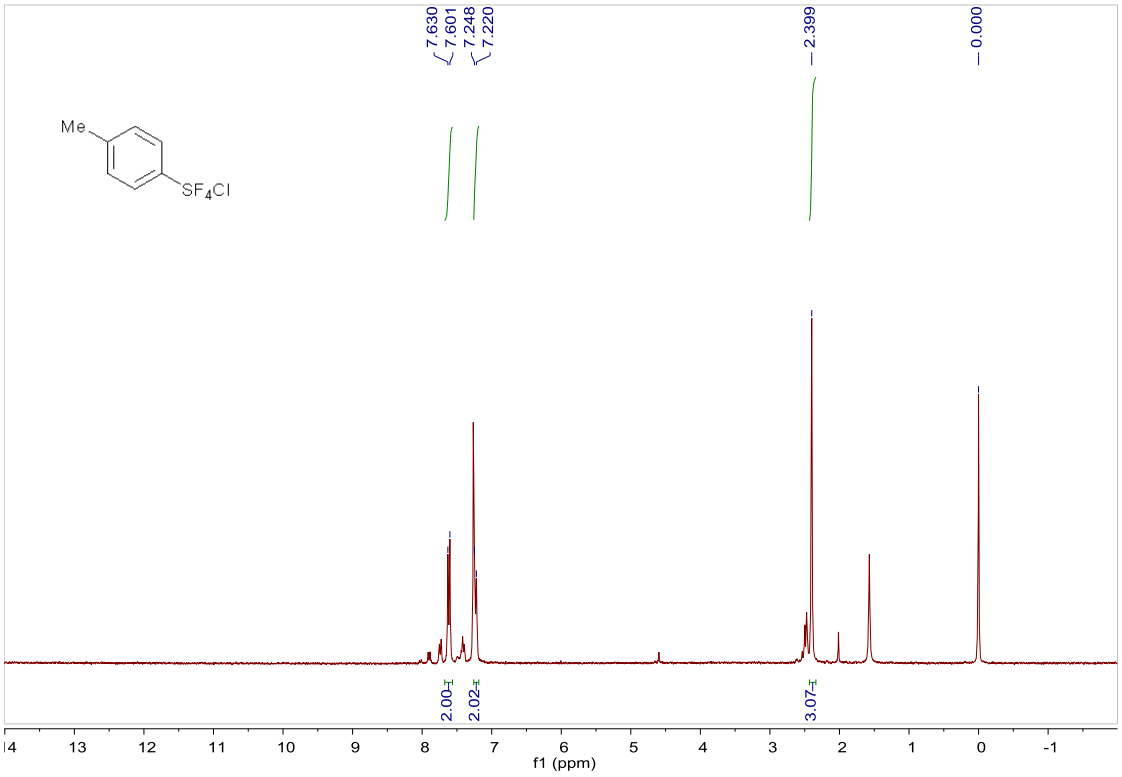
f1 (ppm)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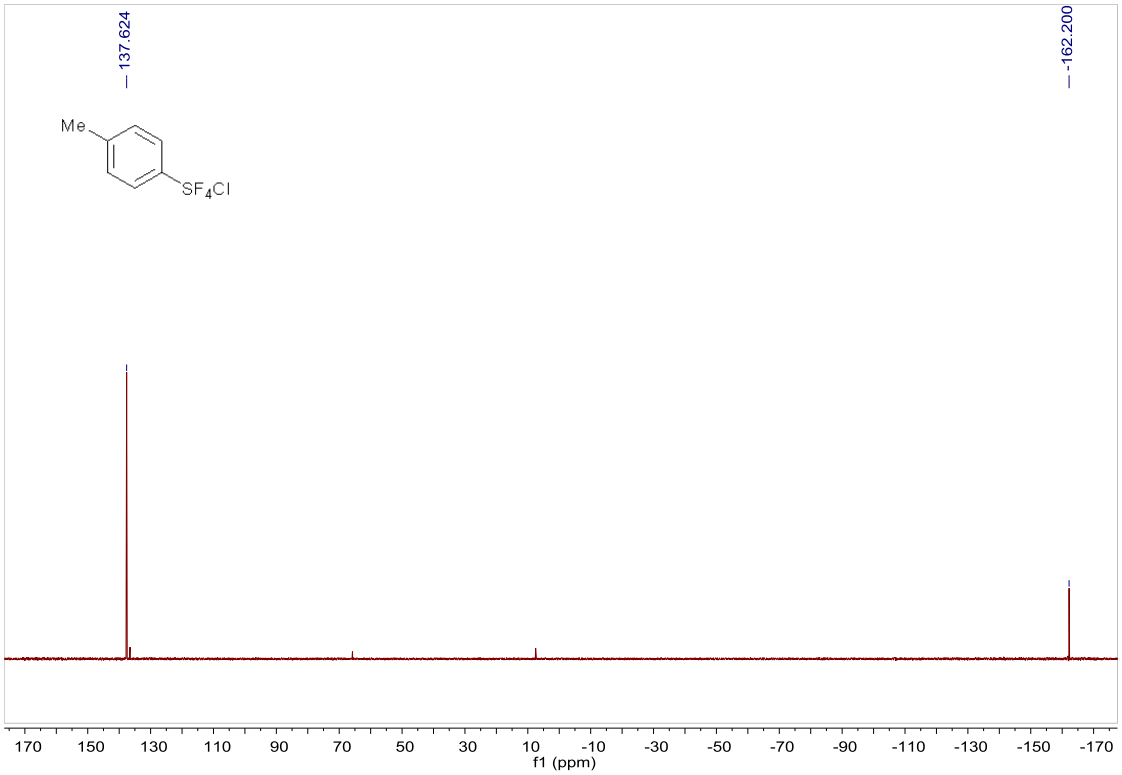
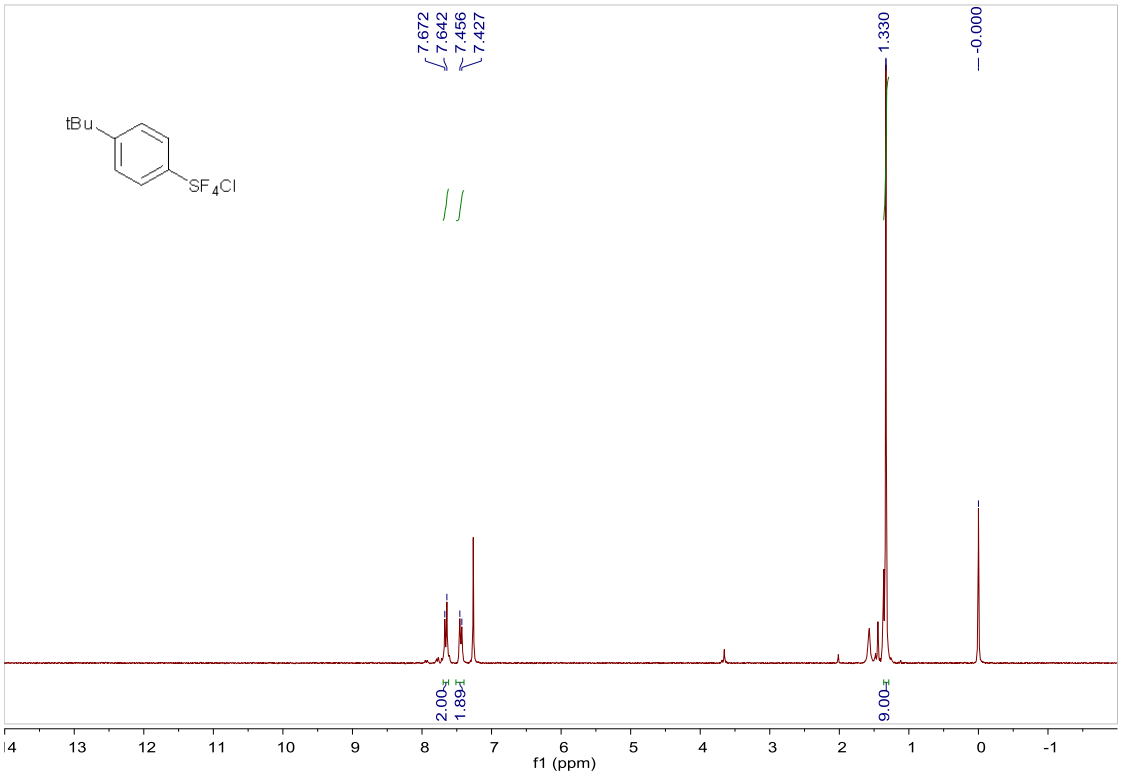
7.601
7.248
7.220
2.399
0.000
Me
SF4Cl
2.00
2.02
3.07
f1 (ppm)


137.624
-162.200
Me
SF4Cl
f1 (ppm)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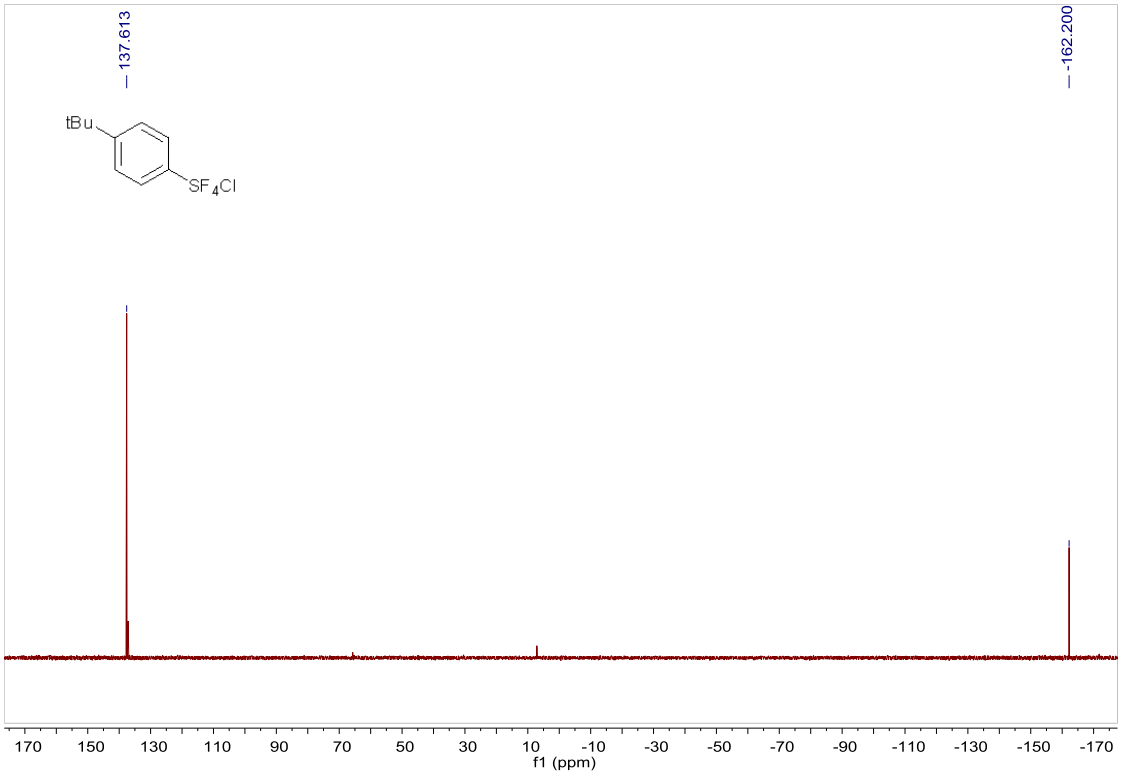
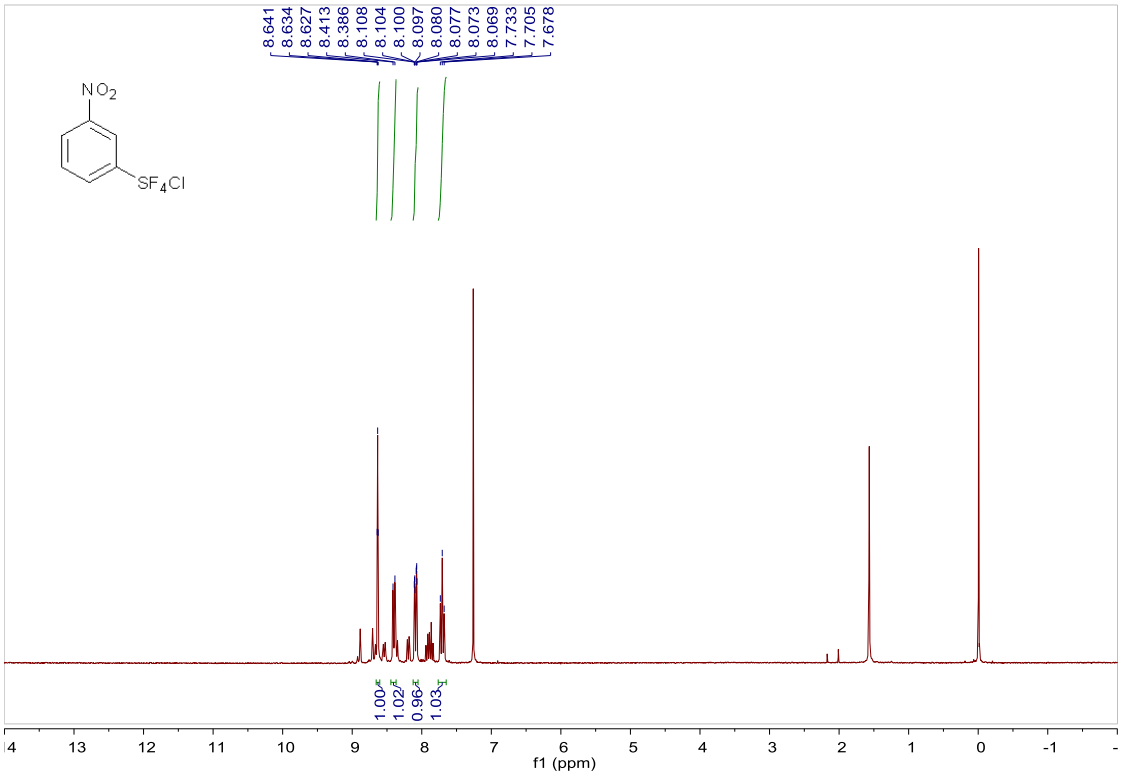
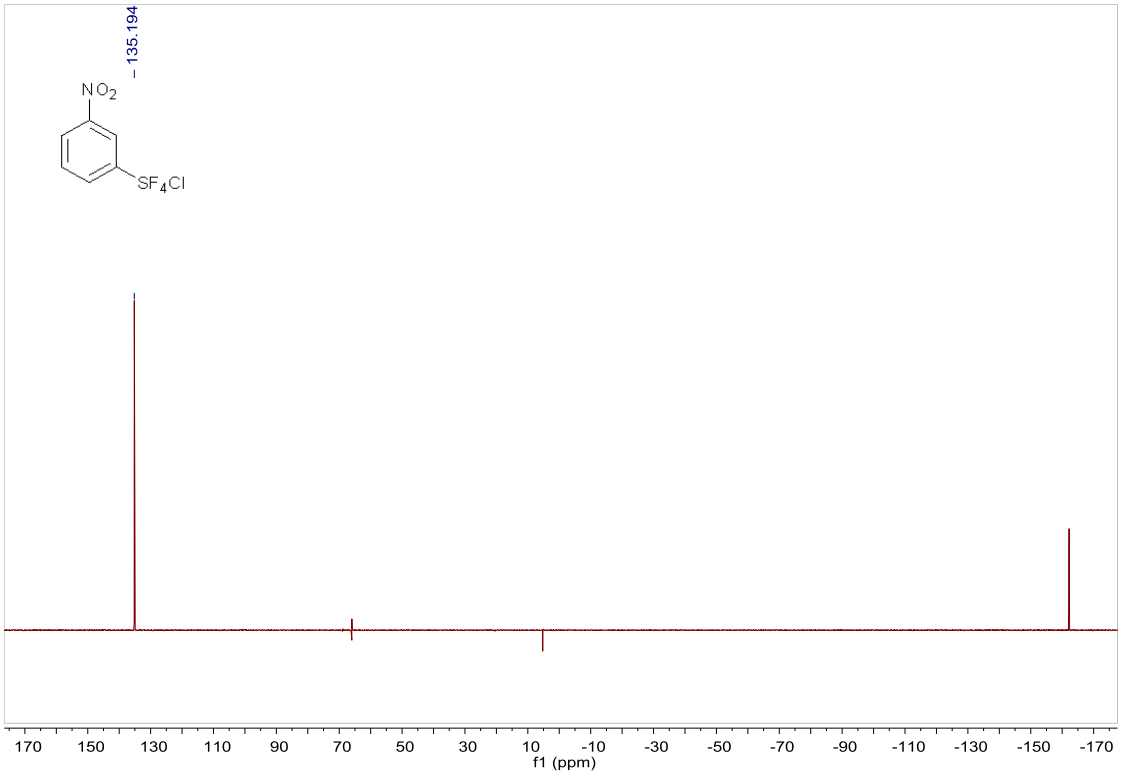
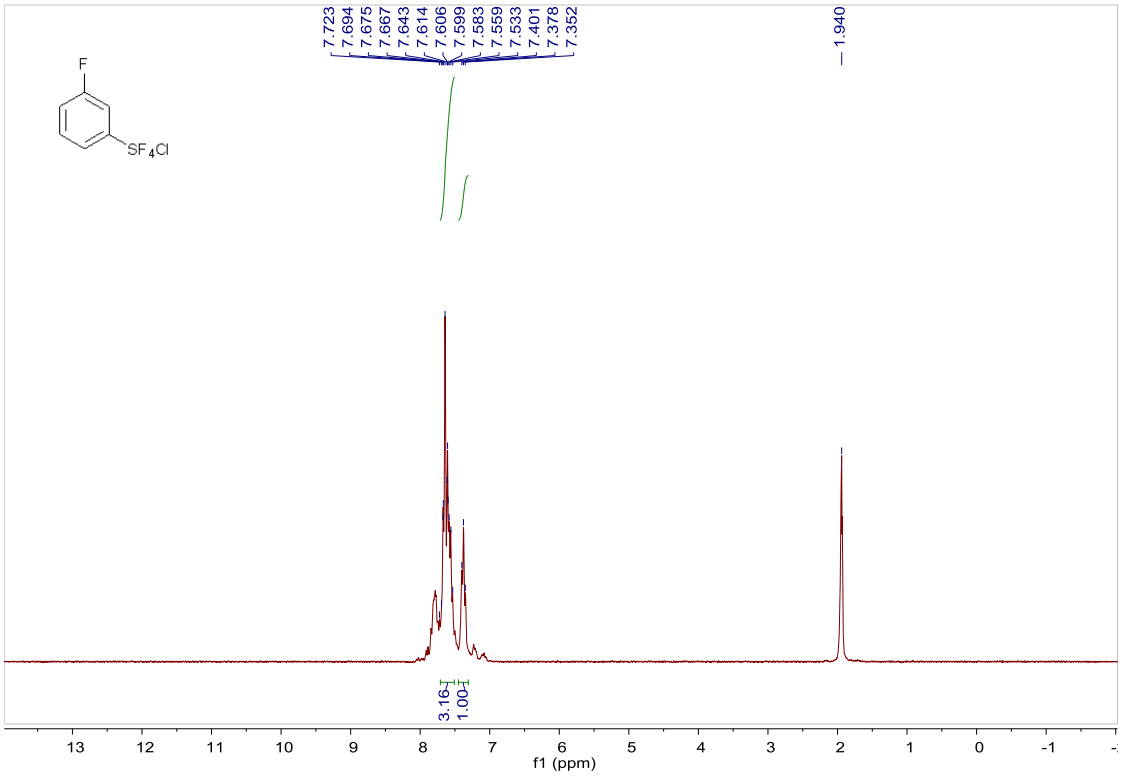
7.642
7.456
7.427
1.330
-0.000
tBu
SF4Cl
2.00
1.89
9.00
f1 (ppm)


137.613
-162.200
tBu
SF4Cl
f1 (ppm)


8.641
8.634
8.627
8.413
8.386
8.108
8.104
8.100
8.097
8.080
8.077
8.073
8.069
7.733
7.705
7.678
NO2
SF4Cl
1.00
1.02
0.96
1.03
f1 (ppm)


135.194
NO2
SF4Cl
f1 (ppm)


7.723
7.694
7.675
7.667
7.643
7.614
7.606
7.599
7.583
7.559
7.533
7.401
7.378
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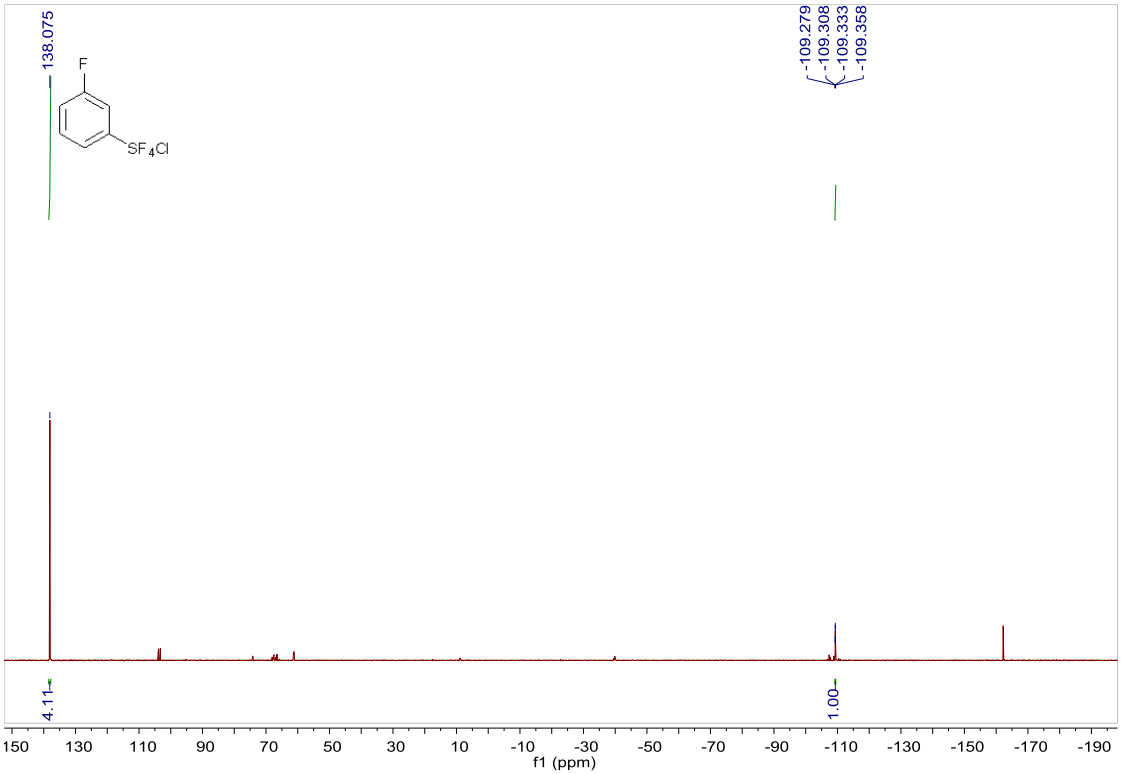
1.940
F
SF4Cl
3.16
1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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-109.308
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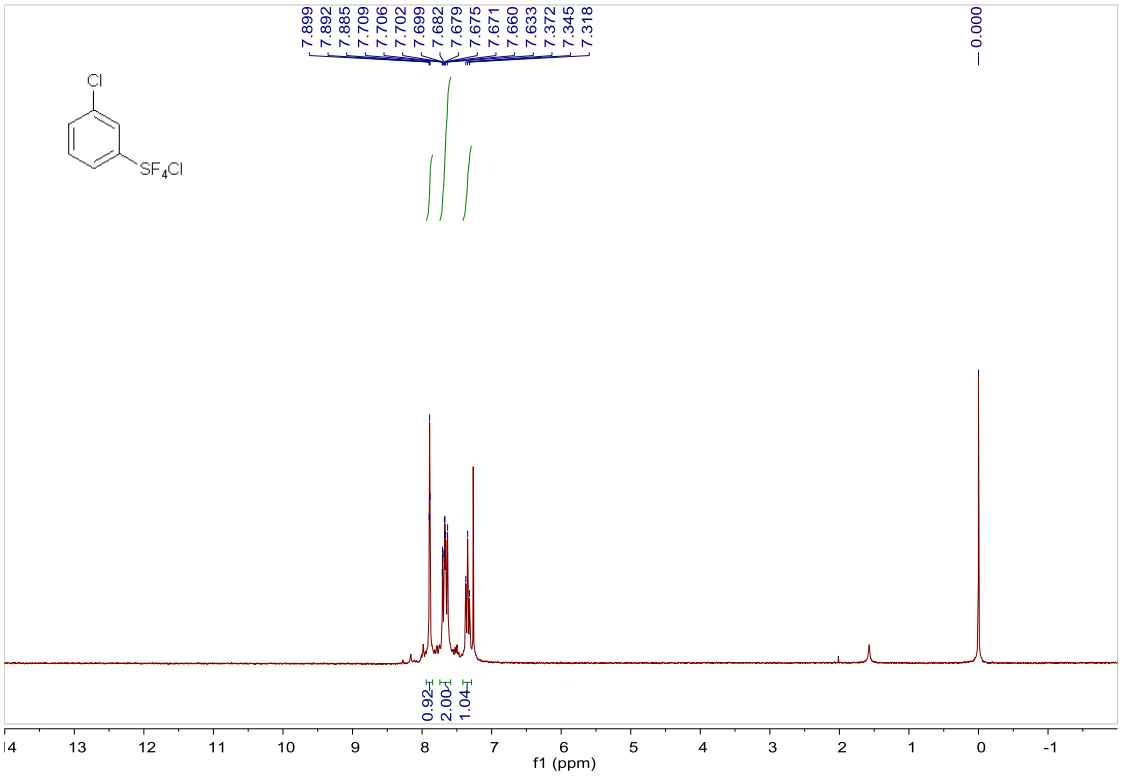
4.11
1.00
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)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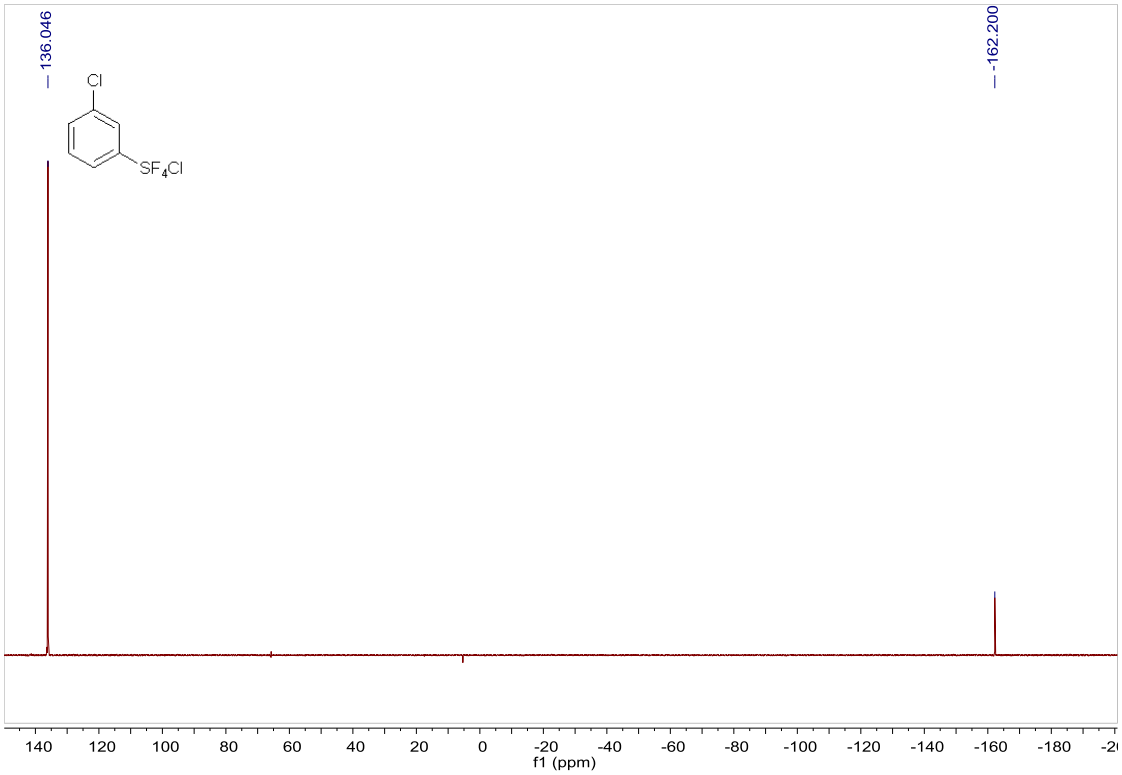
7.892
7.885
7.709
7.706
7.702
7.699
7.682
7.679
7.675
7.671
7.660
7.633
7.372
7.345
7.318
0.000
Cl
SF4Cl
0.92
2.00
1.04
f1 (ppm)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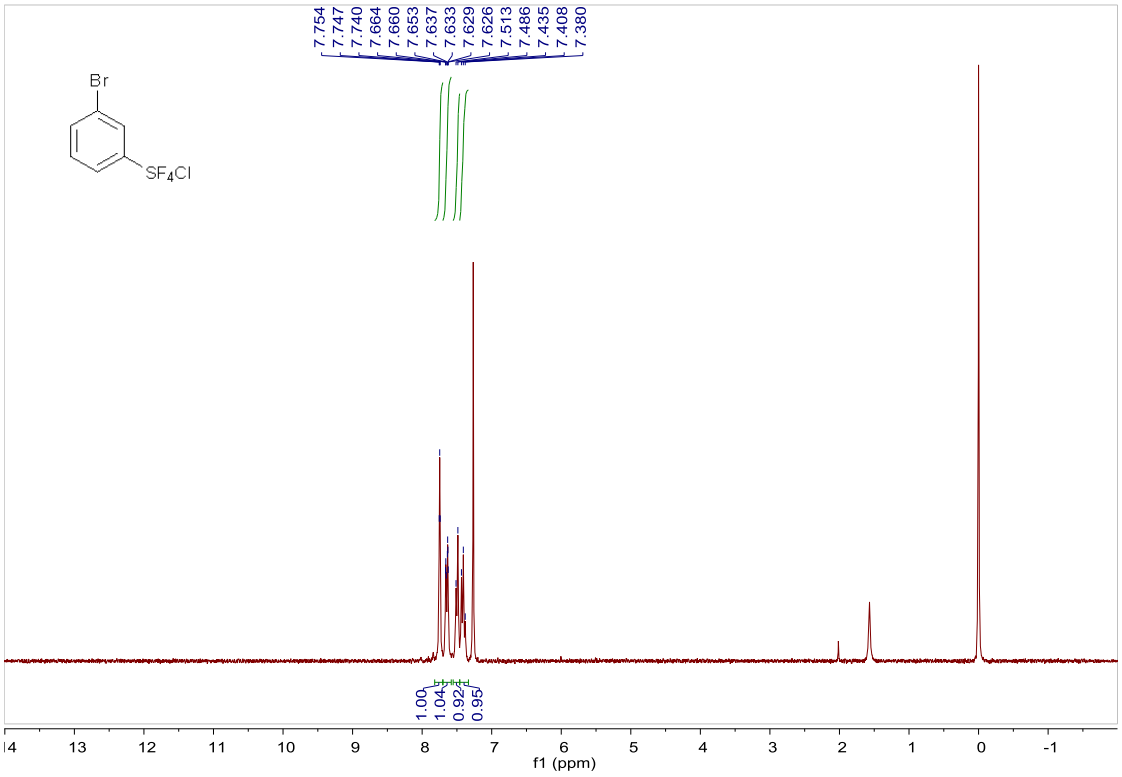
-162.200
Cl
SF4Cl
f1 (ppm)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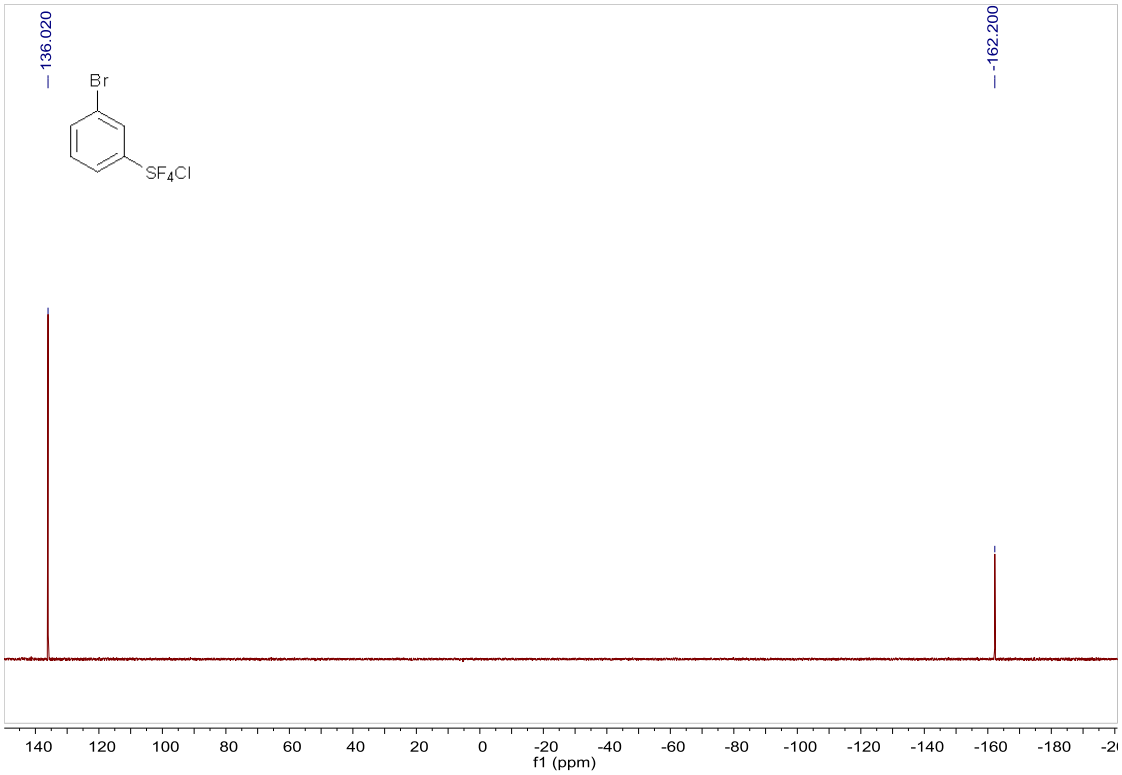
7.747
7.740
7.664
7.660
7.653
7.637
7.633
7.629
7.626
7.513
7.486
7.435
7.408
7.380
Br
SF4Cl
1.00
1.04
0.92
0.95
f1 (ppm)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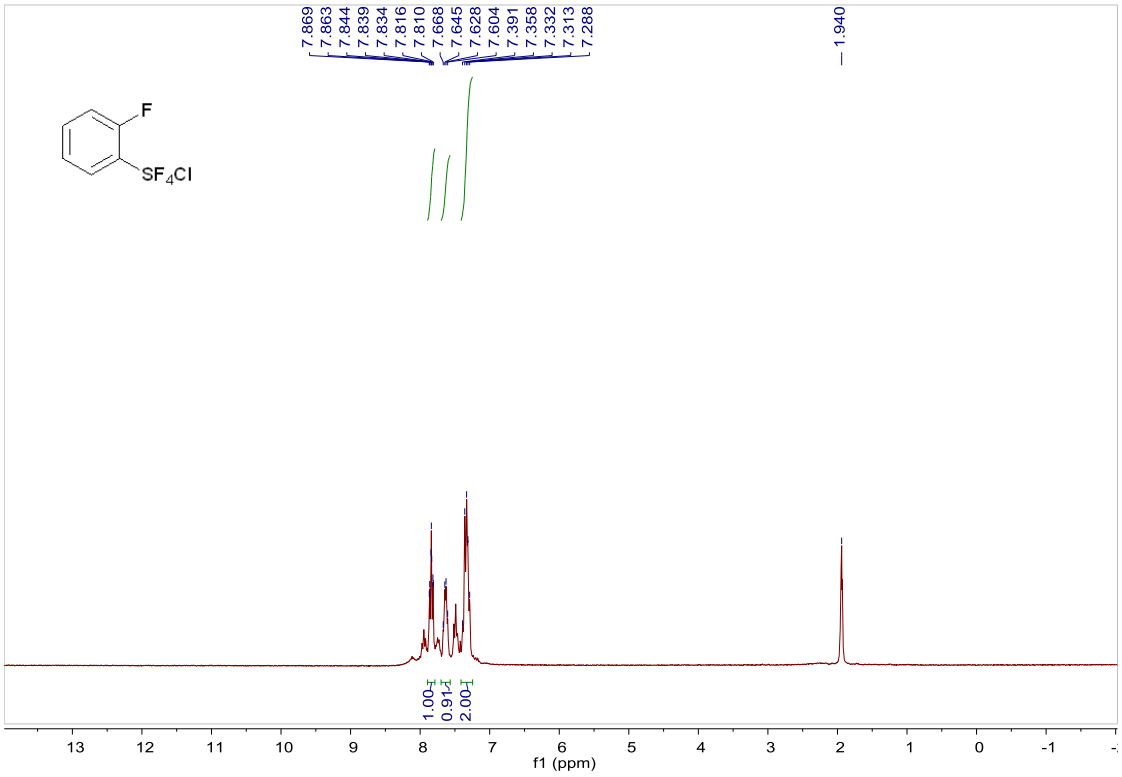
-162.200
Br
SF4Cl
f1 (ppm)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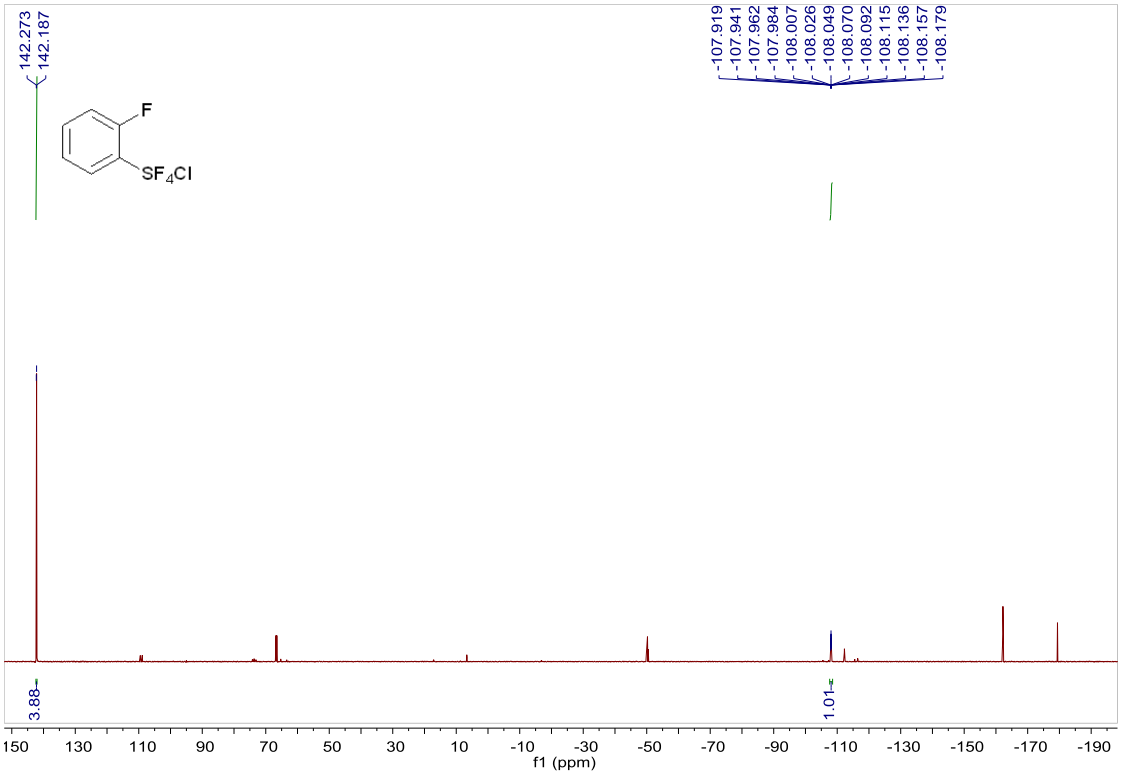
7.863
7.844
7.839
7.834
7.816
7.810
7.668
7.645
7.628
7.604
7.391
7.358
7.332
7.313
7.288
1.940
F
SF4Cl
1.00
0.91
2.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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142.187
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-107.941
-107.962
-107.984
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-108.026
-108.049
-108.070
-108.092
-108.115
-108.136
-108.157
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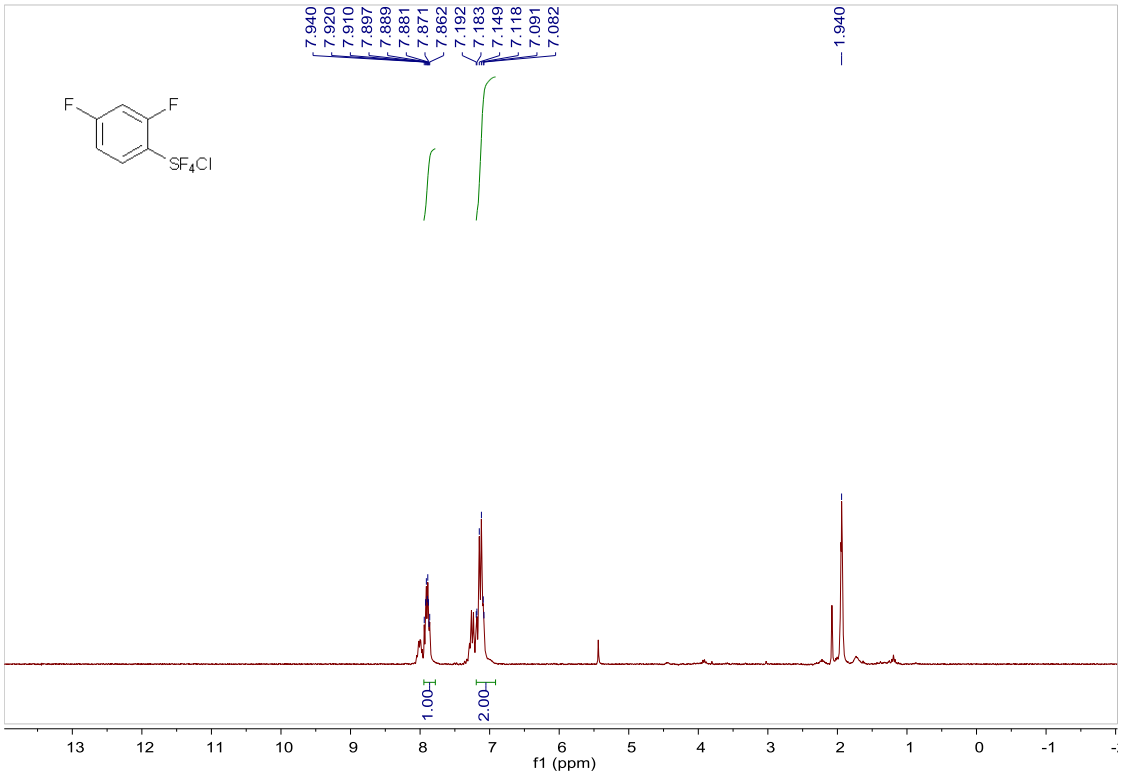
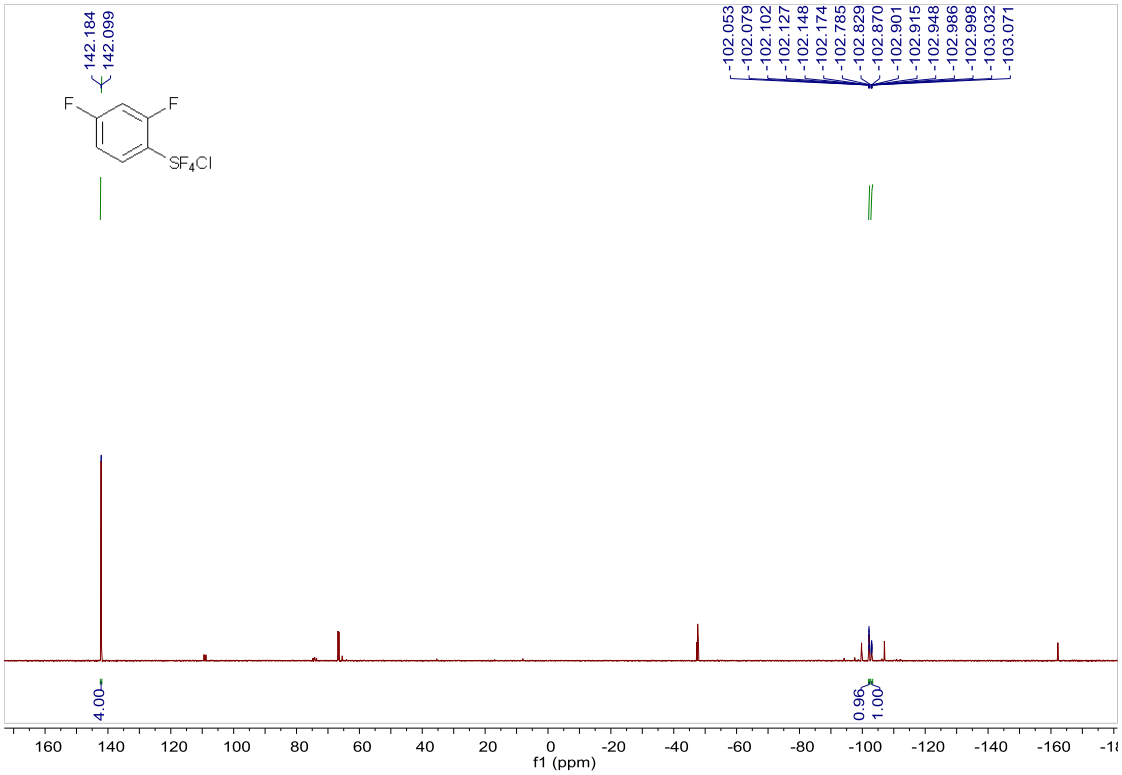
3.88
1.01
150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)


7.940
7.920
7.910
7.897
7.889
7.881
7.871
7.862
7.192
7.183
7.149
7.118
7.091
7.082
1.940
F
F
SF4Cl
1.00
2.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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142.099
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-102.127
-102.148
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-102.785
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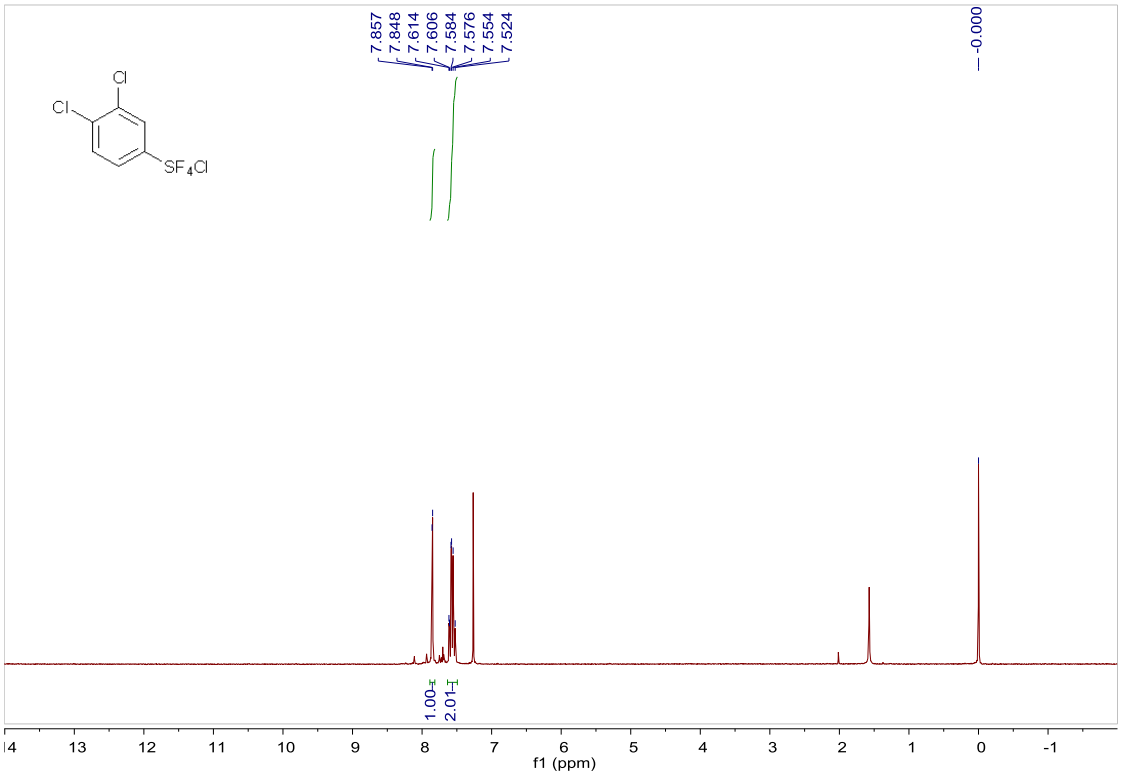
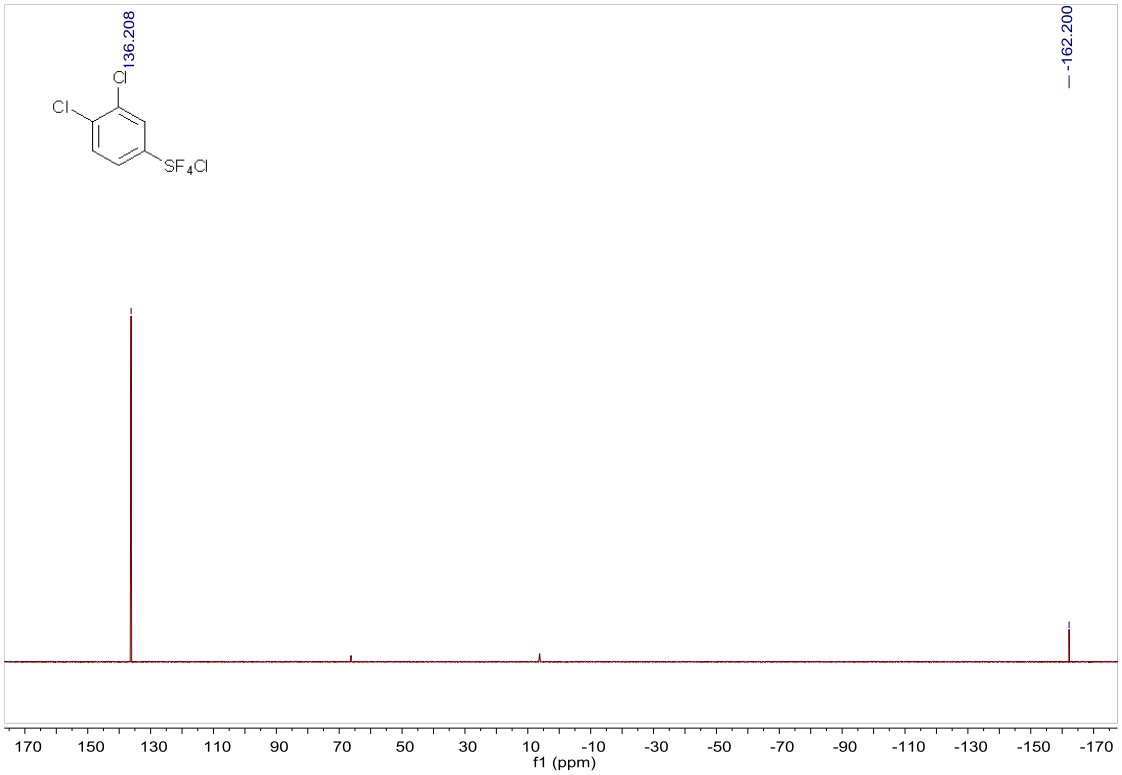
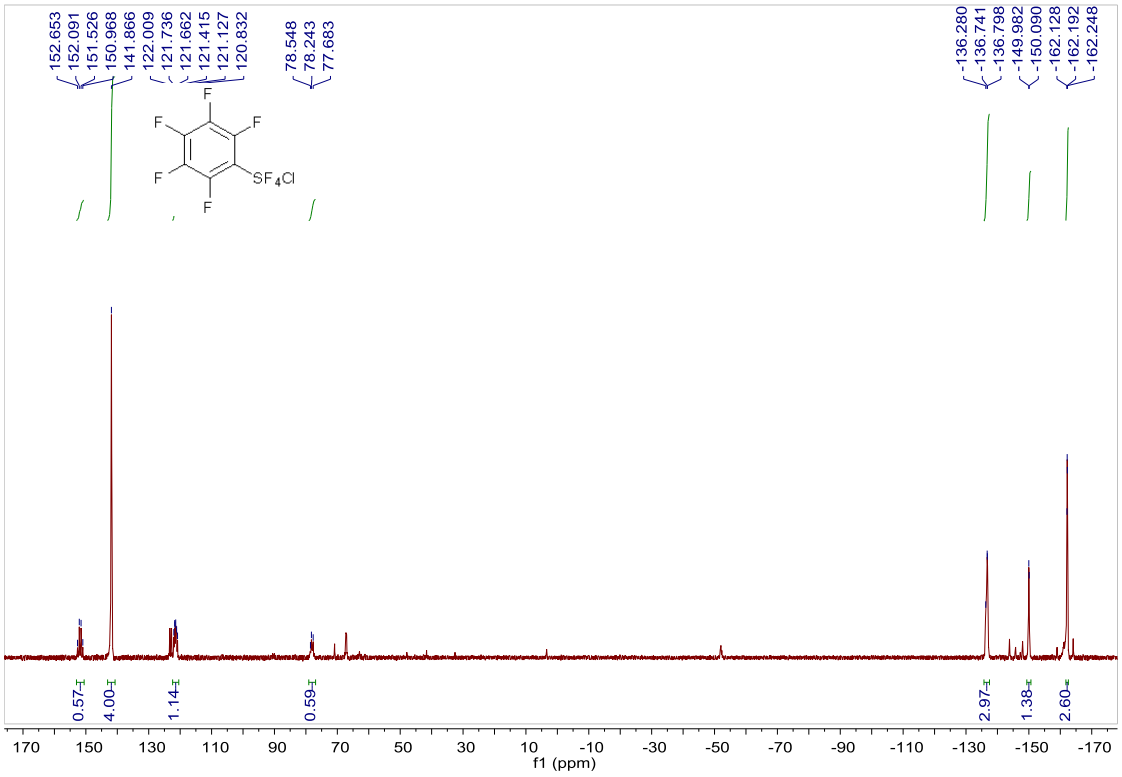
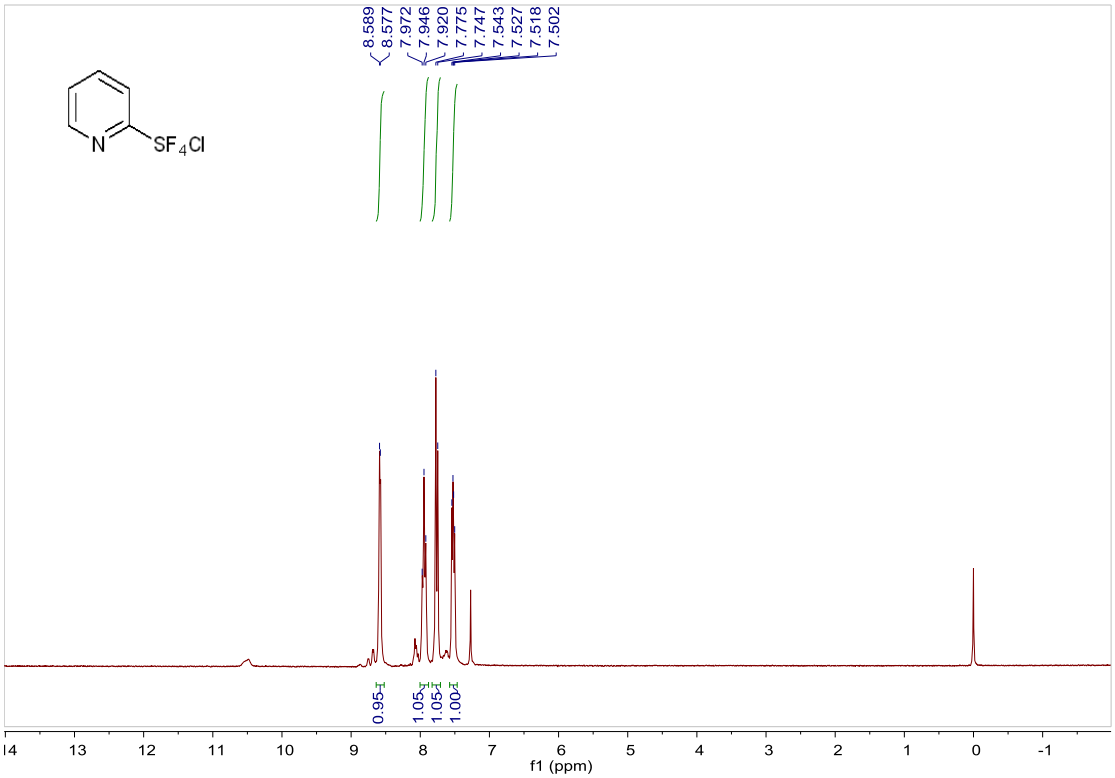
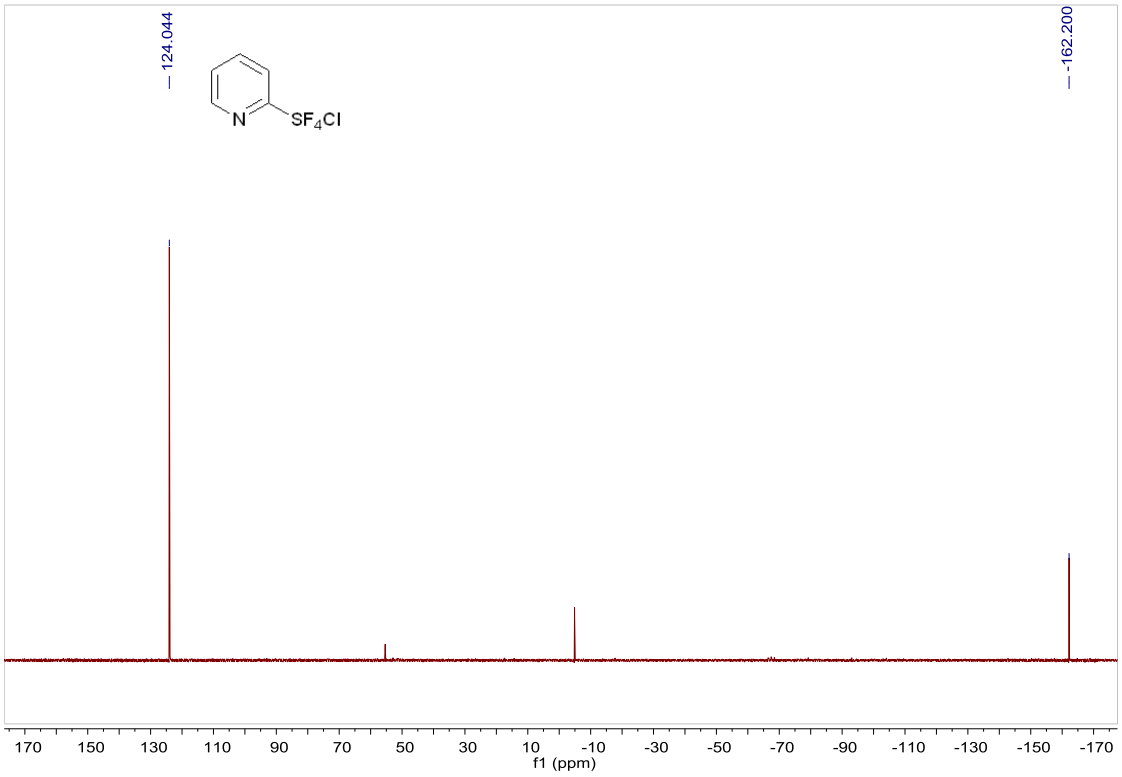
-102.901
-102.915
-102.948
-102.986
-102.998
-103.032
-103.071
F
F
SF4Cl
4.00
0.96
1.00
160
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
f1 (ppm)

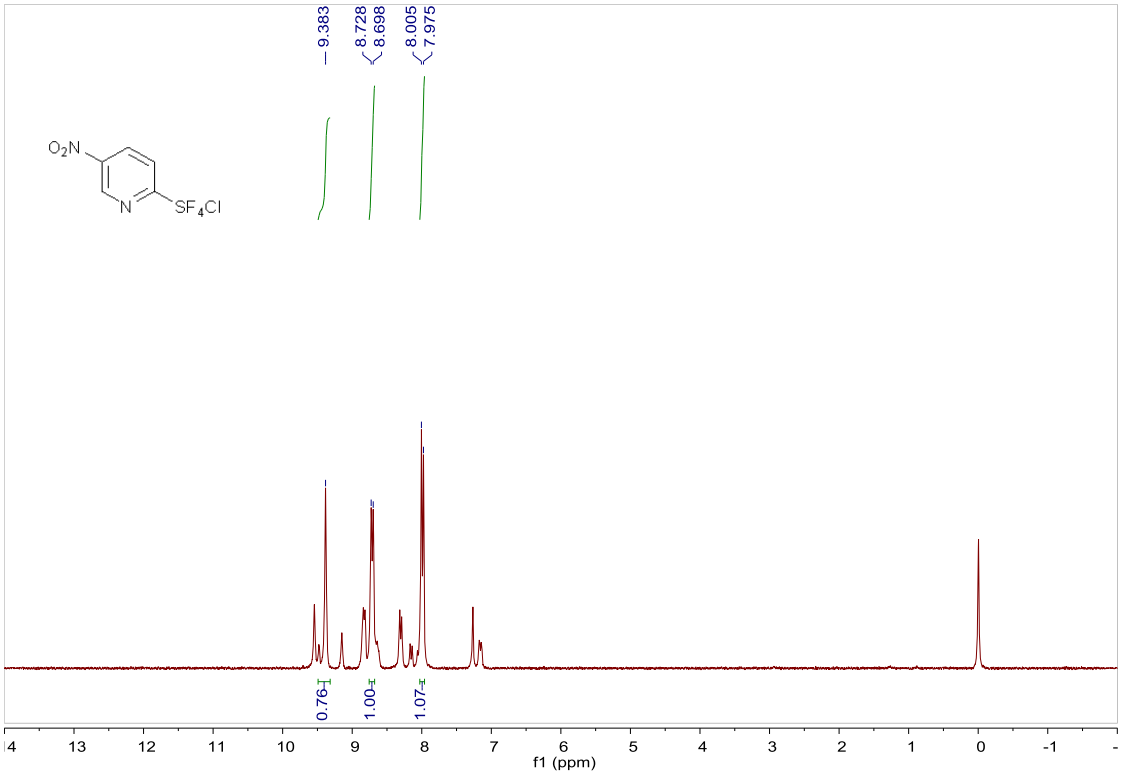

7.857
7.848
7.614
7.606
7.584
7.576
7.554
7.524
-0.000
Cl
Cl
SF4Cl
1.00
2.01
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

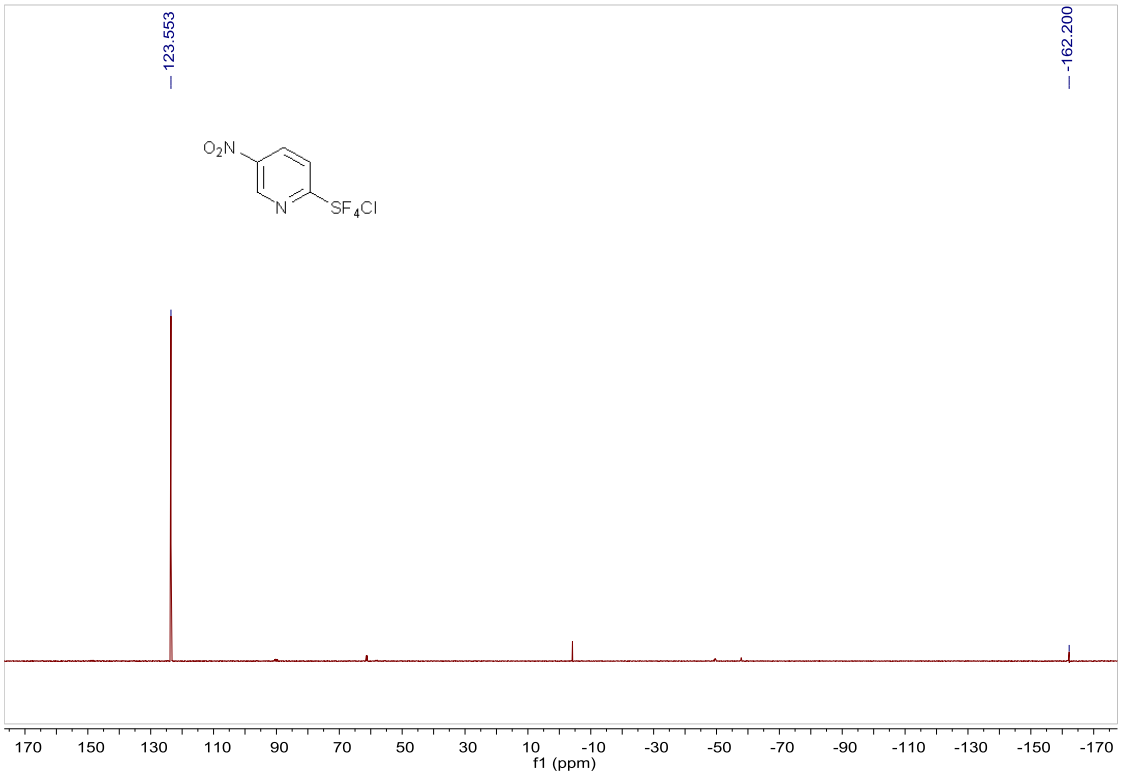

136.208
-162.200
Cl
Cl
SF4Cl
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

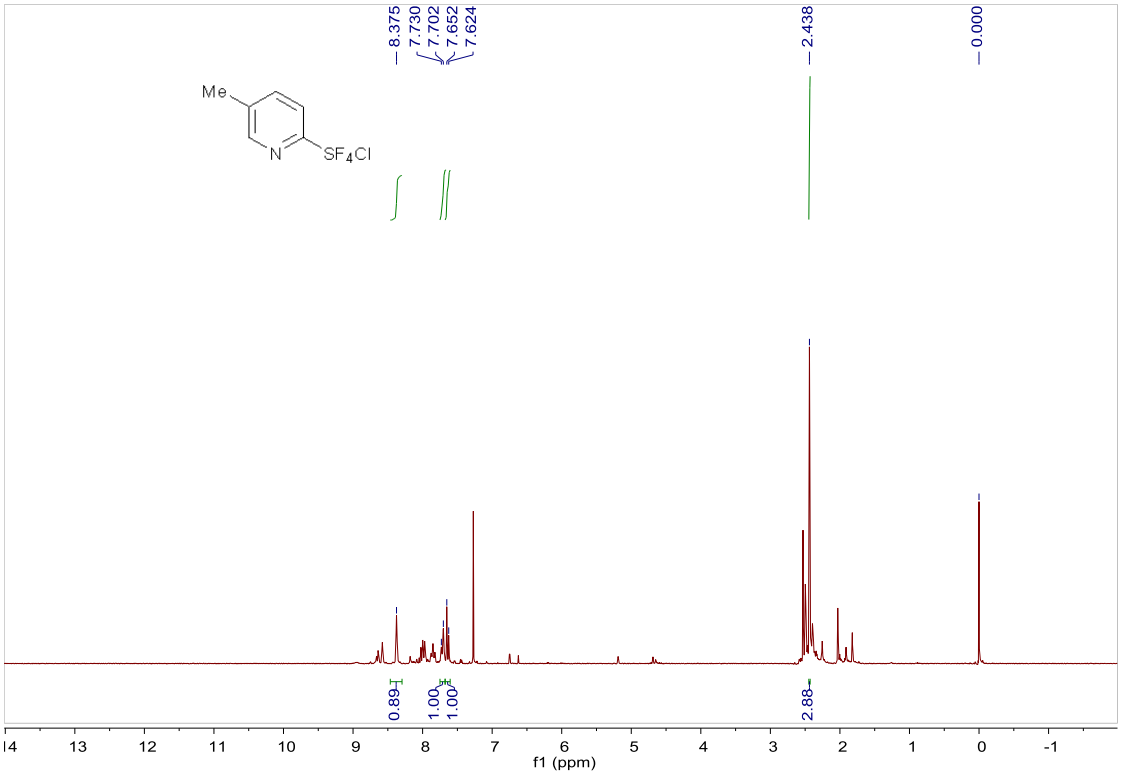

152.653
152.091
151.526
150.968
141.866
122.009
121.736
121.662
121.415
121.127
120.832
78.548
78.243
77.683
-136.280
-136.741
-136.798
-149.982
-150.090
-162.128
-162.192
-162.248
F
F
F
F
F
SF4Cl
0.57
4.00
1.14
0.59
2.97
1.38
2.60
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

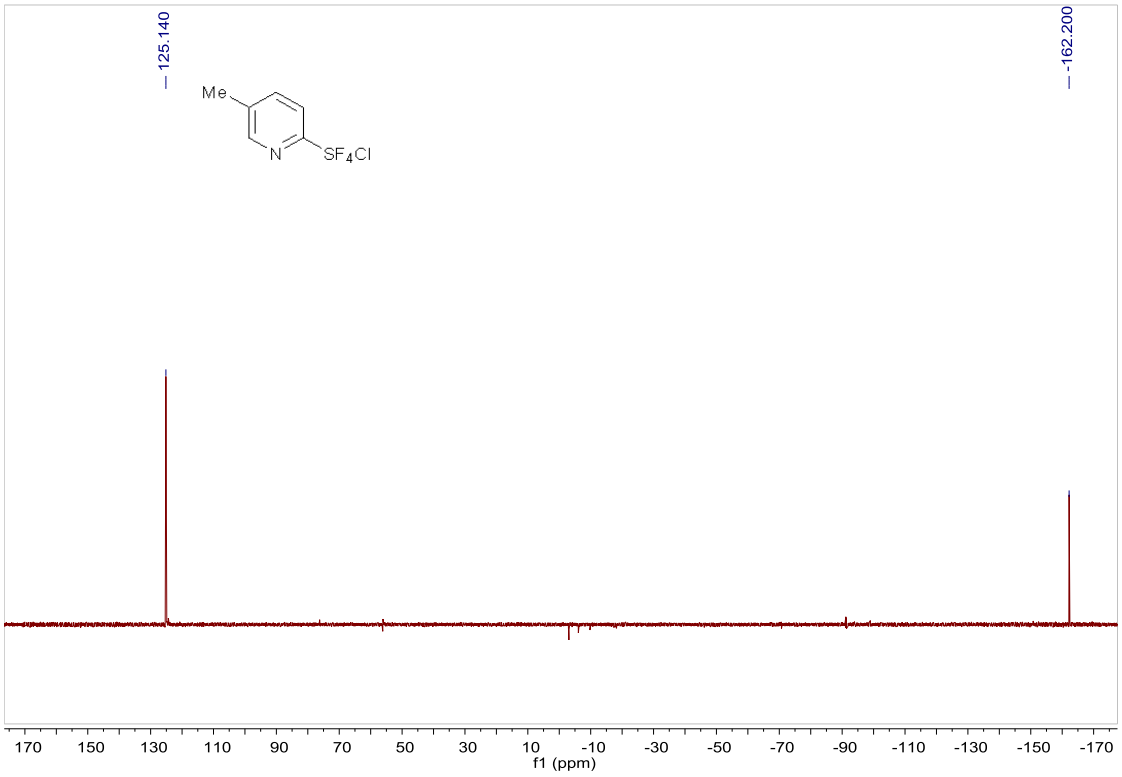

8.589
8.577
7.972
7.946
7.920
7.775
7.747
7.543
7.527
7.518
7.502
N
SF4Cl
0.95
1.05
1.05
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

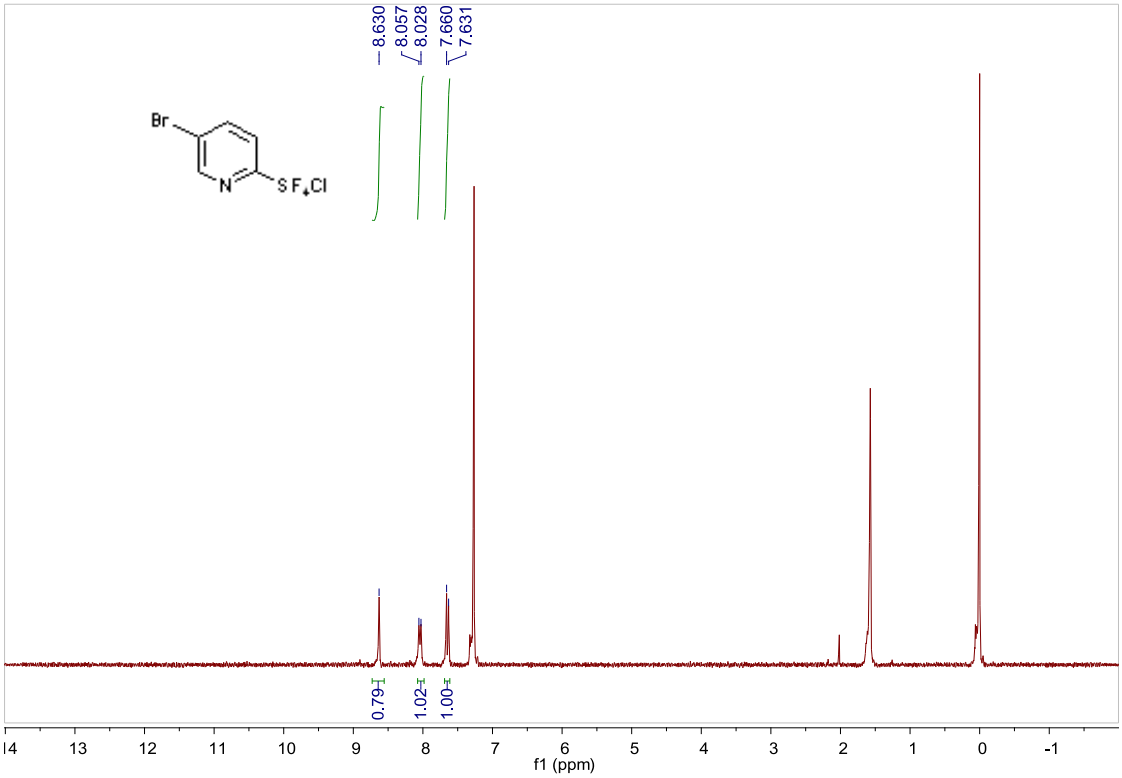

124.044
-162.200
N
SF4Cl
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

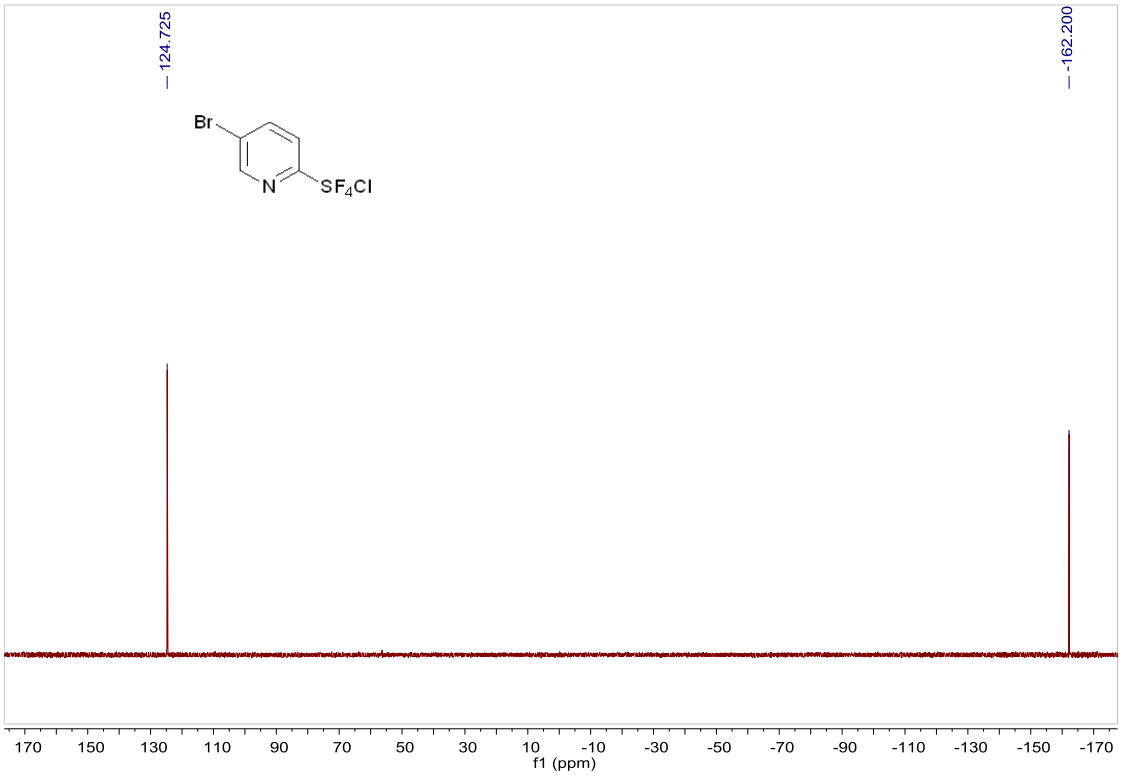

9.383
8.728
8.698
8.005
7.975
O2N
N
SF4Cl
0.76
1.00
1.07
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

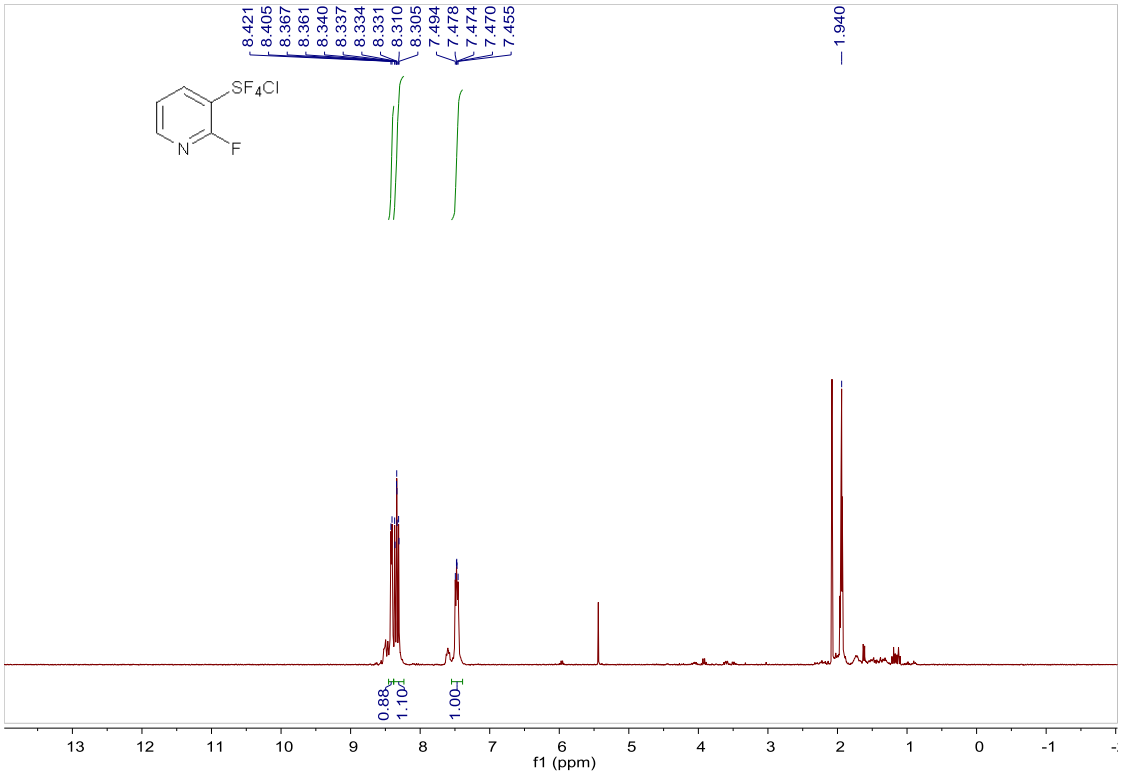

123.553
-162.200
O2N
N
SF4Cl
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

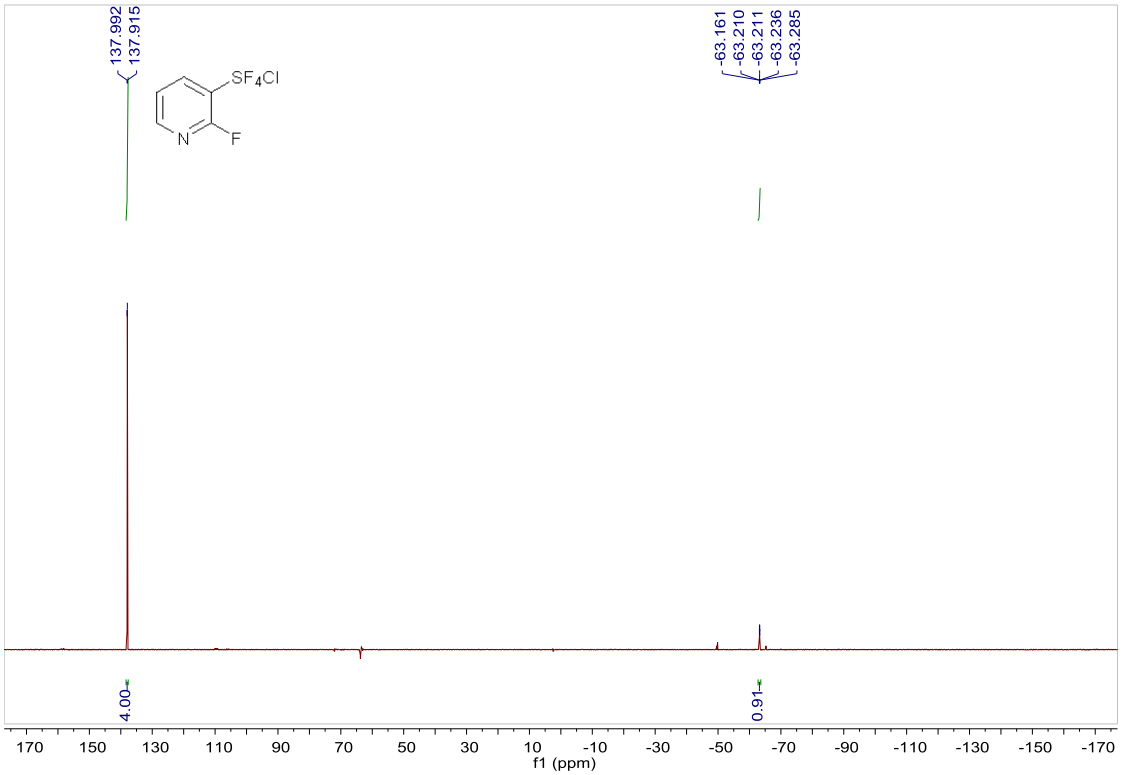

8.375
7.730
7.702
7.652
7.624
2.438
0.000
Me
N
SF4Cl
0.89
1.00
1.00
2.88
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

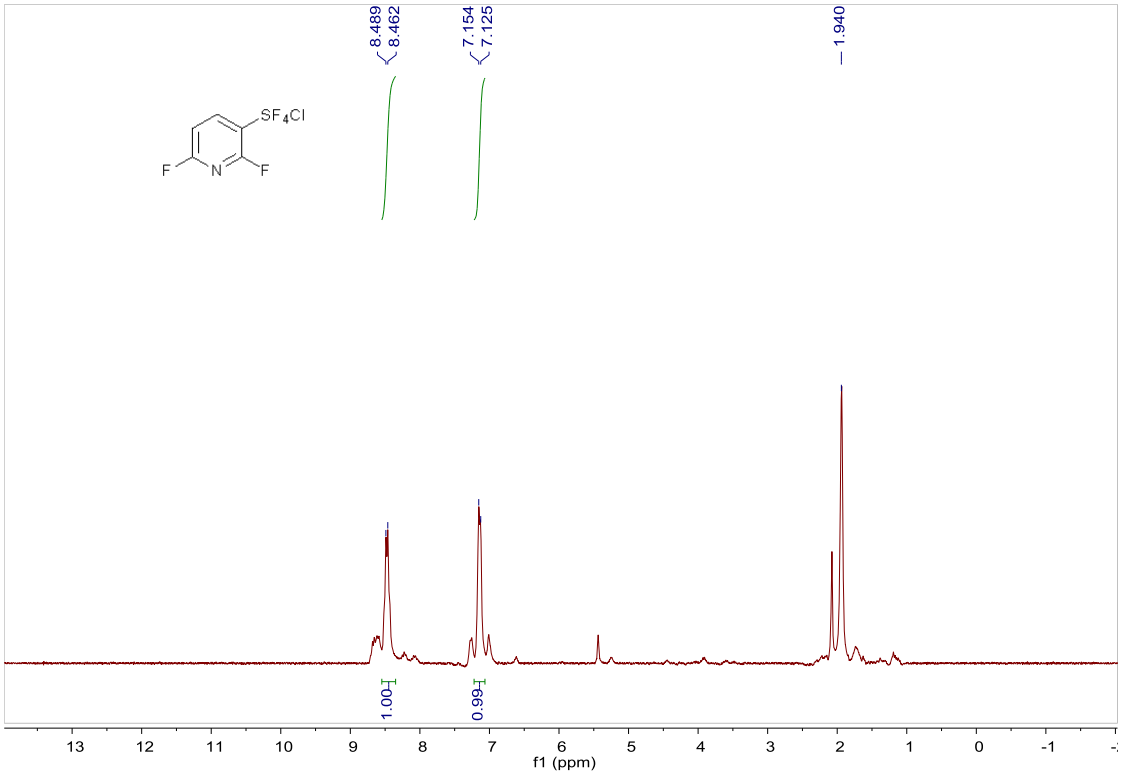

125.140
-162.200
Me
N
SF4Cl
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

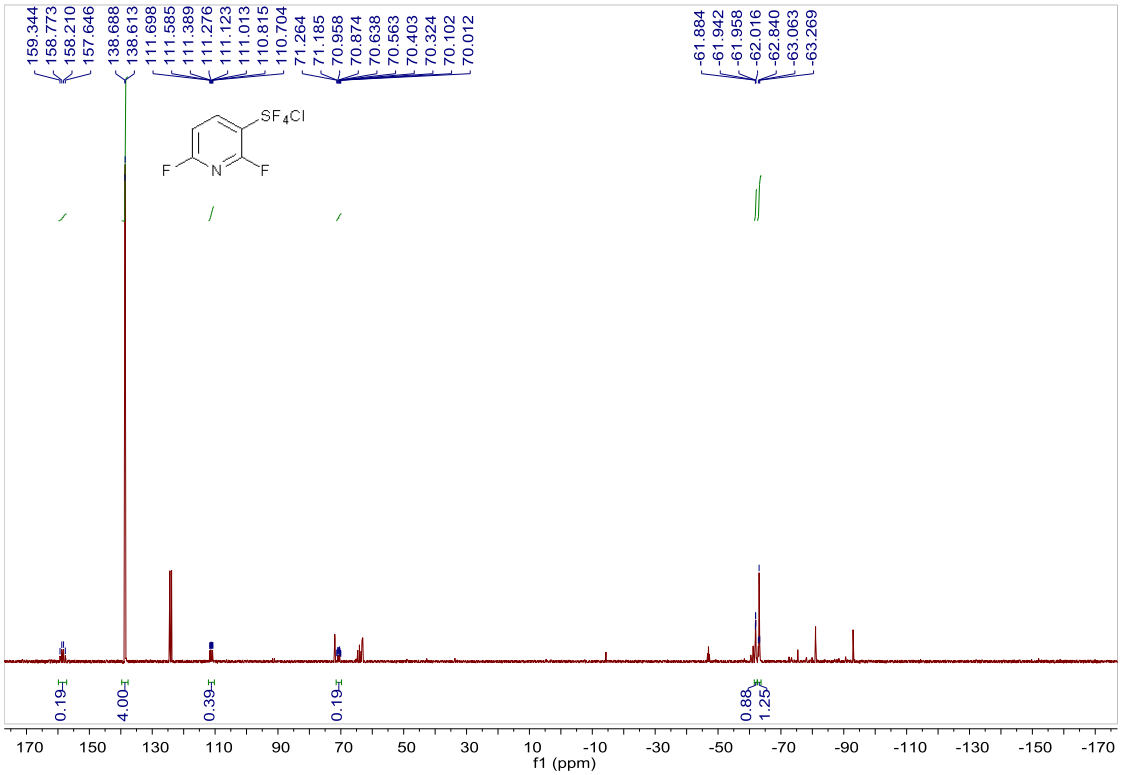

8.630
8.057
8.028
7.660
7.631
Br
N
SF4Cl
0.79
1.02
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

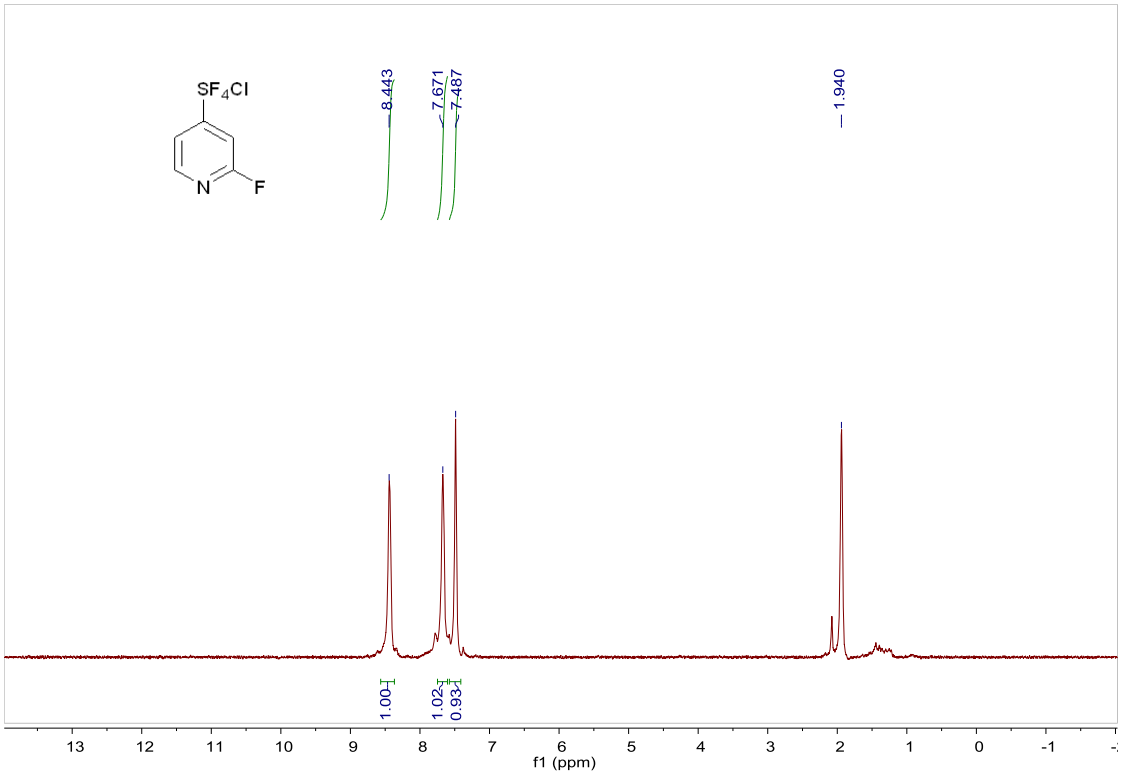

124.725
-162.200
Br
N
SF4Cl
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

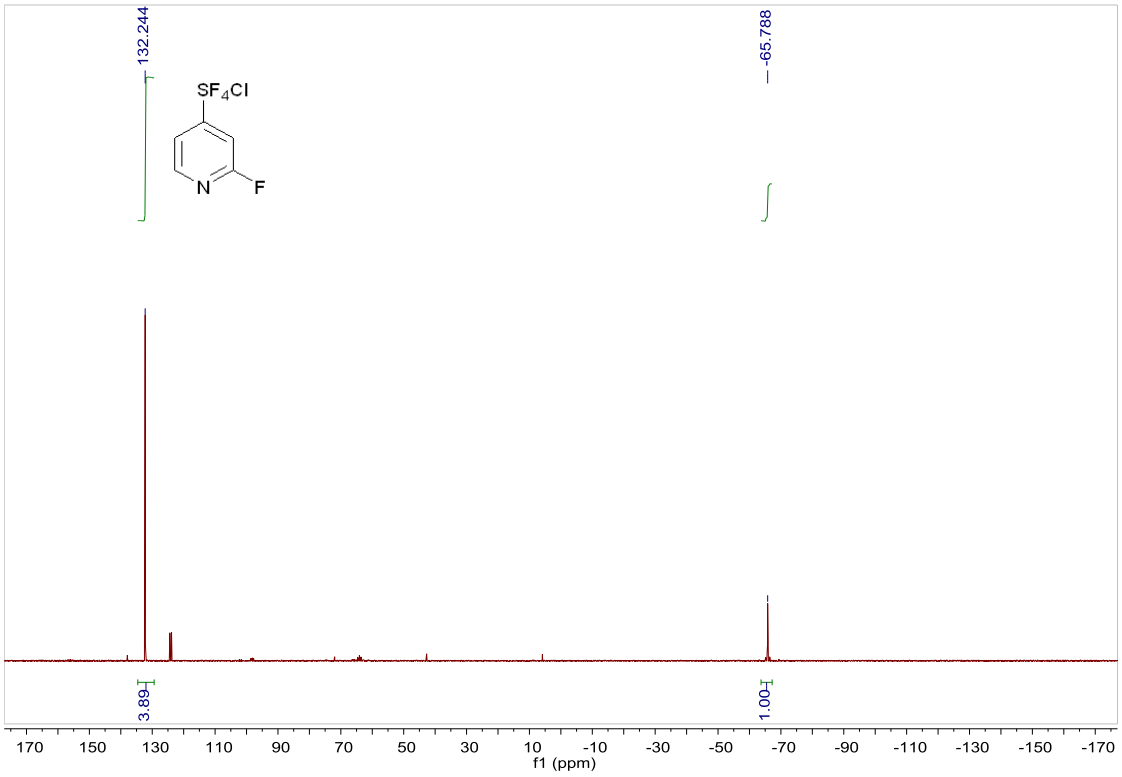

8.421
8.405
8.367
8.361
8.340
8.337
8.334
8.331
8.310
8.305
7.494
7.478
7.474
7.470
7.455
1.940
SF4Cl
N
F
0.88
1.10
1.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

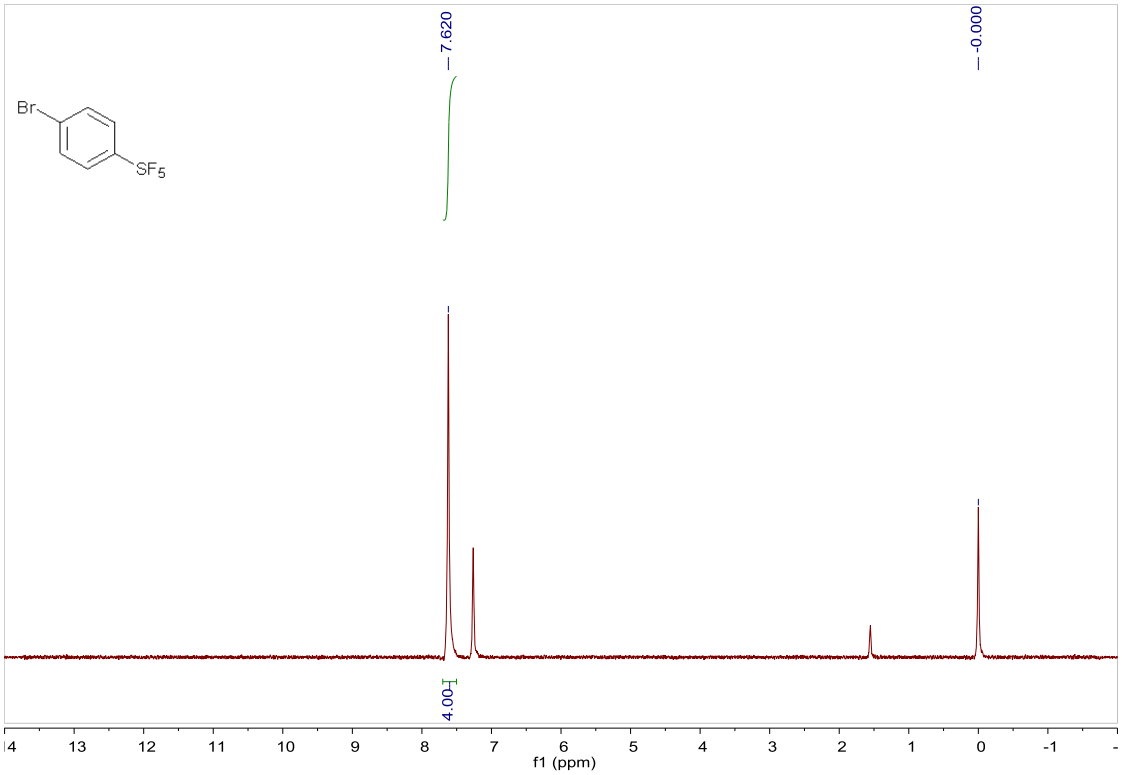

137.992
137.915
SF4Cl
N
F
-63.161
-63.210
-63.211
-63.236
-63.285
4.00
0.91
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

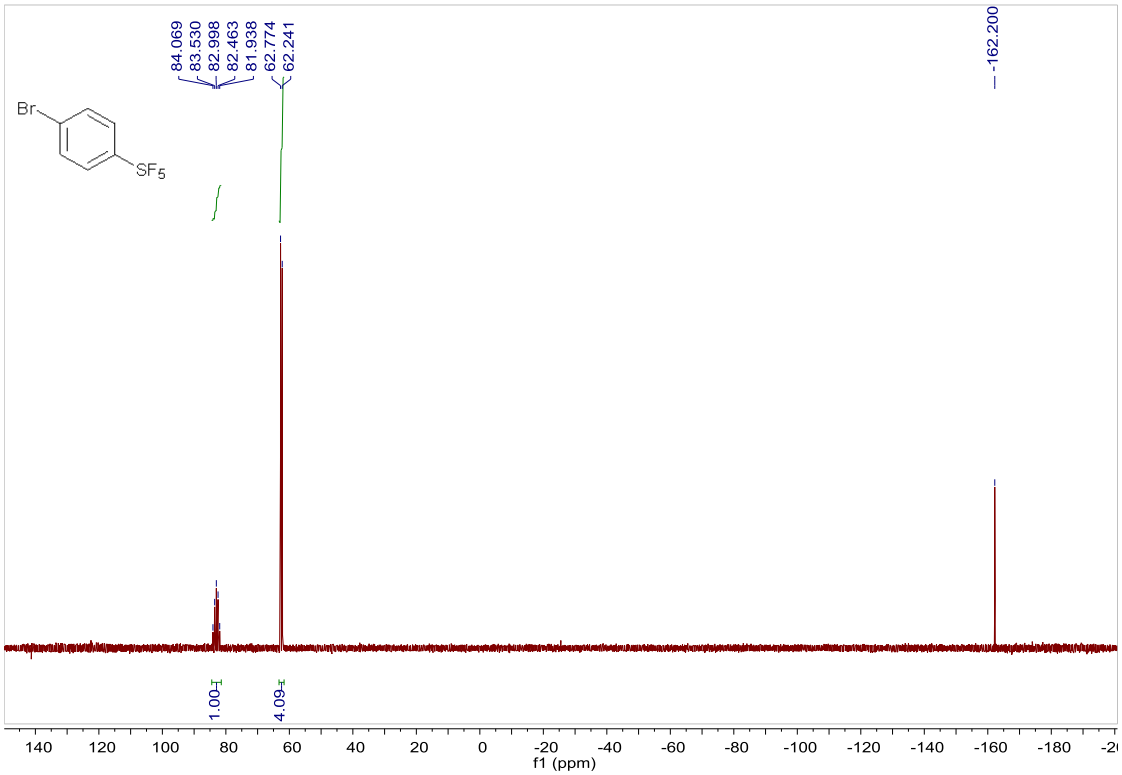

8.489
8.462
7.154
7.125
1.940
SF4Cl
F
N
F
1.00
0.99
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

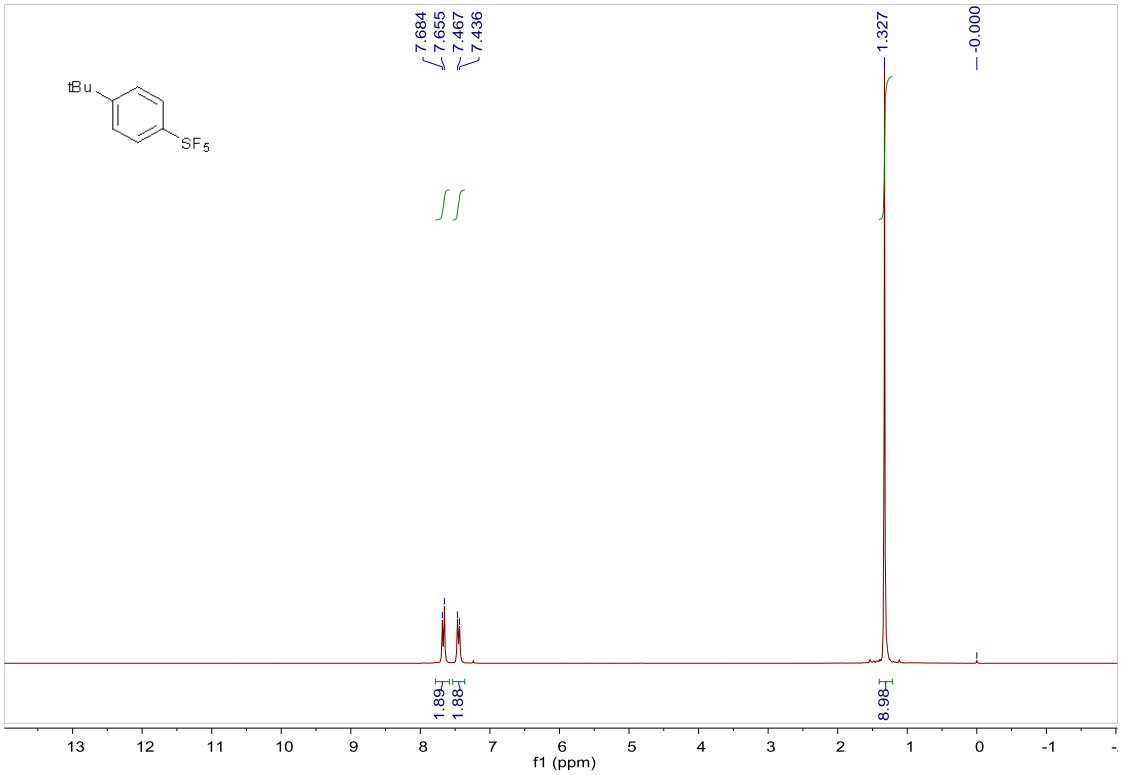

159.344
158.773
158.210
157.646
138.688
138.613
111.698
111.585
111.389
111.276
111.123
111.013
110.815
110.704
71.264
71.185
70.958
70.874
70.638
70.563
70.403
70.324
70.102
70.012
-61.884
-61.942
-61.958
-62.016
-62.840
-63.063
-63.269
SF4Cl
F
N
F
0.19
4.00
0.39
0.19
0.88
1.25
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

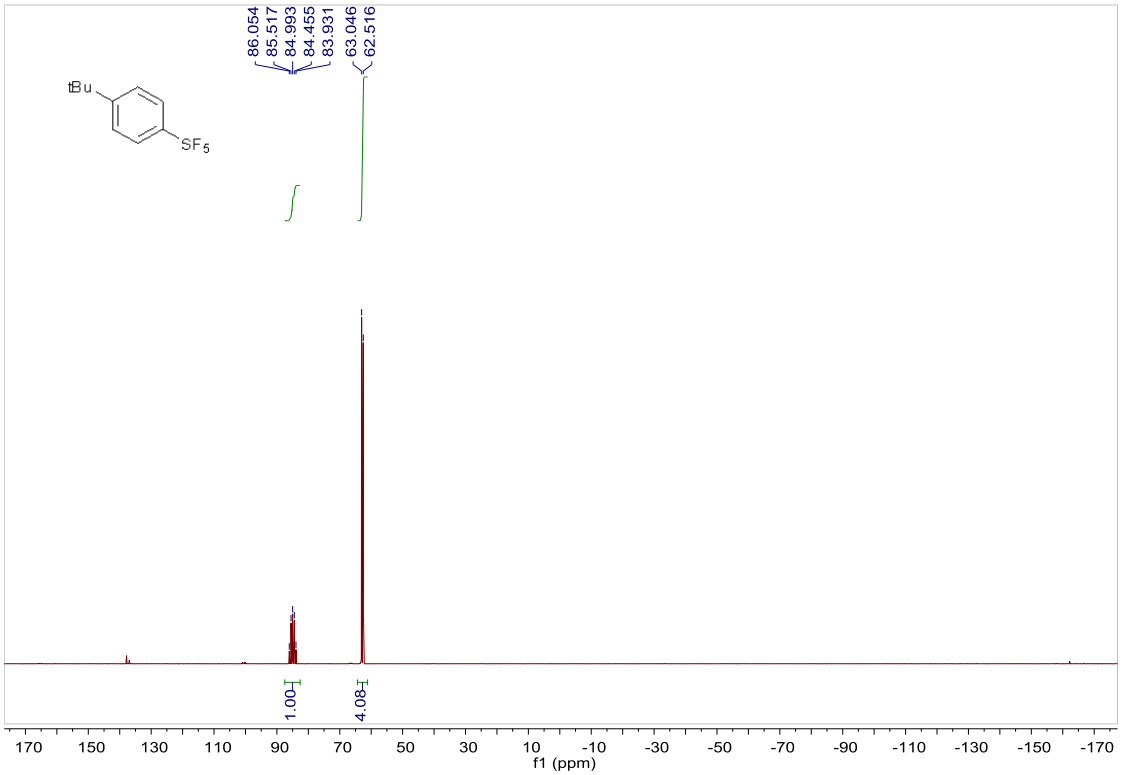

SF4Cl
N
F
8.443
7.671
7.487
1.940
1.00
1.02
0.93
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

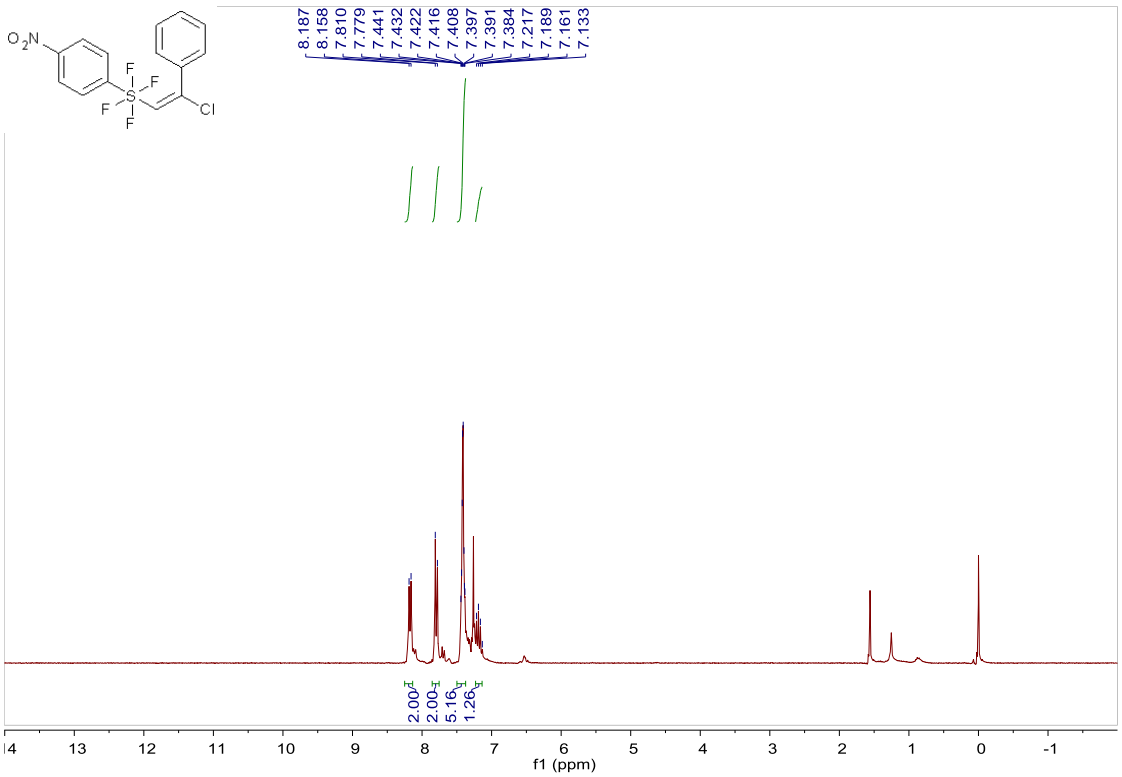

132.244
-65.788
SF4Cl
N
F
3.89
1.00
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)

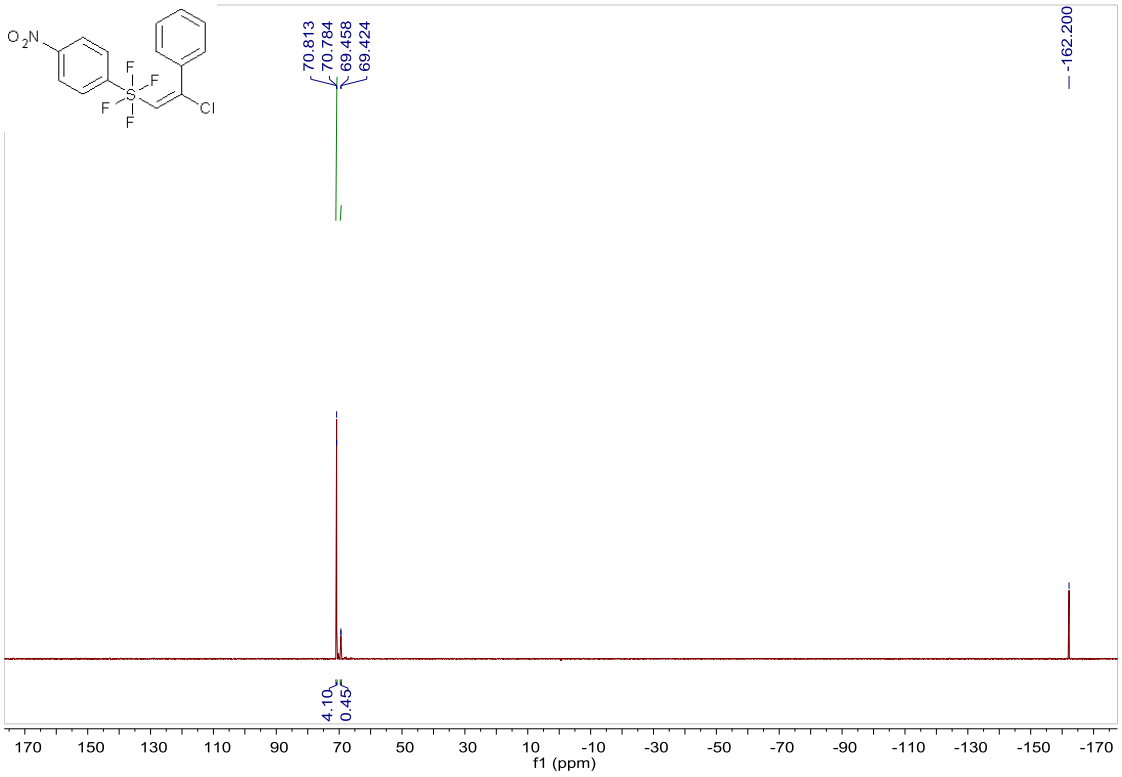

7.620
-0.000
Br
SF5
4.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

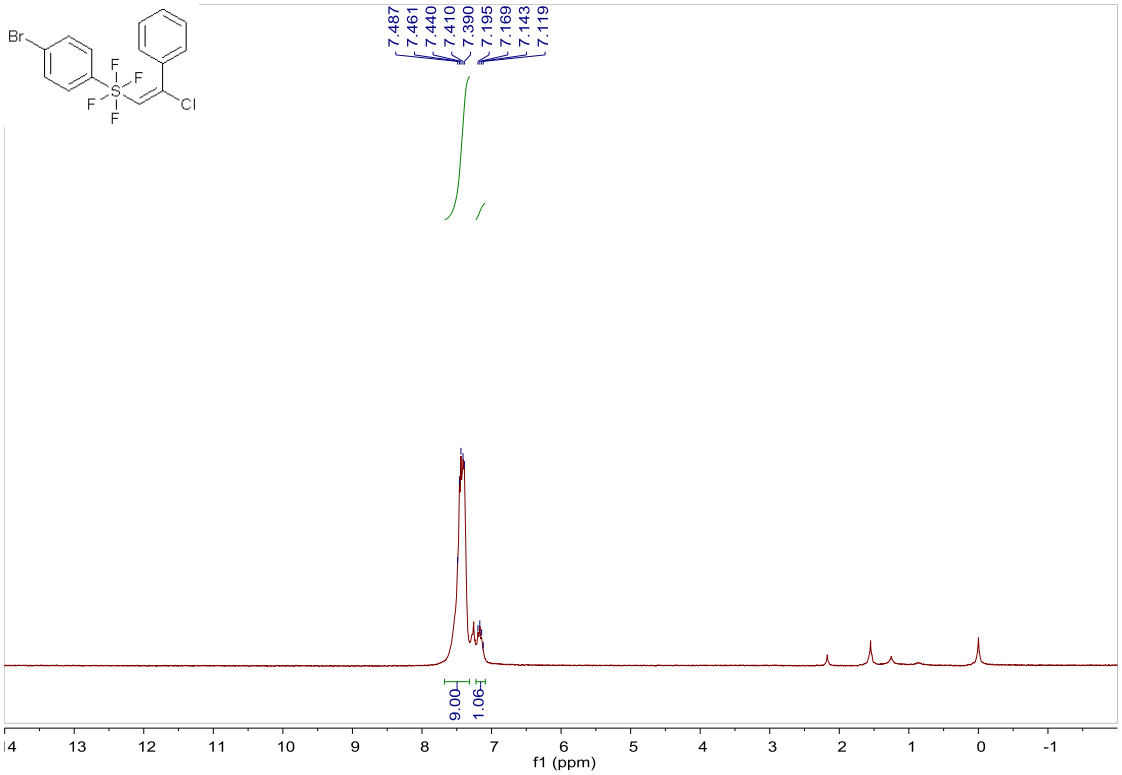

84.069
83.530
82.998
82.463
81.938
62.774
62.241
-162.200
Br
SF5
1.00
4.09
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)

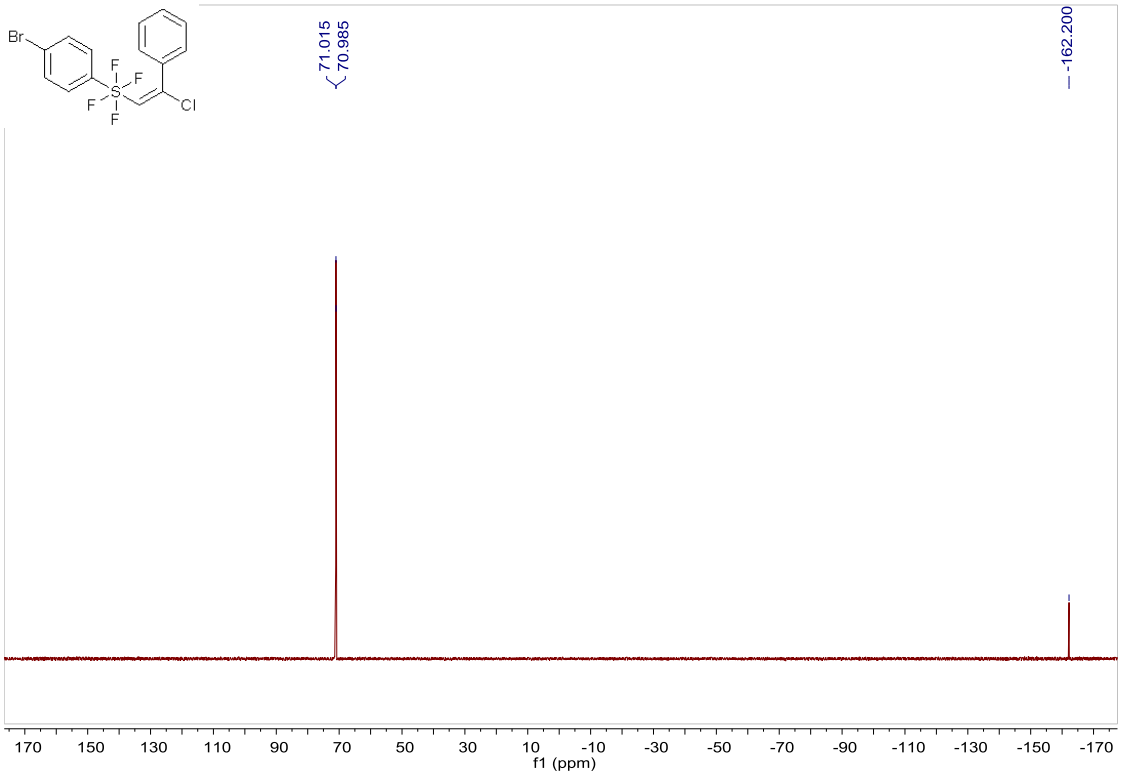

7.684
7.655
7.467
7.436
1.327
-0.000
tBu
SF5
1.89
1.88
8.98
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


86.054
85.517
84.993
84.455
83.931
63.046
62.516
tBu
SF5
1.00
4.08
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)


O2N
F
F
F
S
F
Cl
8.187
8.158
7.810
7.779
7.441
7.432
7.422
7.416
7.408
7.397
7.391
7.384
7.217
7.189
7.161
7.133
2.00
2.00
5.16
1.26
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


O2N
F
F
F
F
S
Cl
70.813
70.784
69.458
69.424
-162.200
4.10
0.45
170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)


Br
F
F
F
F
S
Cl
7.487
7.461
7.440
7.410
7.390
7.195
7.169
7.143
7.119
9.00
1.06
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


Br
F
F
S
F
F
Cl
71.015
70.985
-162.200
170
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
f1 (ppm)