

Supporting Information
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Supporting Information

CsF-catalyzed Fluoroacylation of Tetrafluoroethylene Using Acyl Fluorides for the Synthesis of Pentafluoroethyl Ketones

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Table of Contents

1. Experimental Section.	S3
1-1. Preparation of anhydrous Me ₄ N•F.	S3
1-2. Synthesis of Me ₄ N•SCF ₃ .	S3
1-3. Procedures of preparation of acyl fluoride 1 .	S3
1-4. Characterization of acyl fluoride 1 .	S4
1-5. A picture of a reaction vessel for catalytic pentafluoroethylation of acyl fluorides.	S10
1-6. Stoichiometric reaction at 80 °C and isolation of ester 3b .	S11
1-7. CsF-catalyzed fluoroacylation of HFP or TFE with acyl fluoride 1a at room temperature.	S12
1-8. Investigation of reactivity of ester 3b under CsF catalytic system.	S12
1-9. Yield change of perfluoroalkylation of 1a at 80 °C over reaction time.	S13
2. Computational Section.	S14
2-1. Calculation method details.	S14
2-2. DFT calculation of formation of pentafluoroethyl cesium (B).	S14
2-3. DFT calculation of pentafluoroethylation of acyl fluoride 1a .	S15
2-4. Calculated Properties and Geometries.	S16
3. References.	S21
4. NMR Spectra.	S23

1. Experimental Section.

1-1. Preparation of anhydrous Me₄N•F.

According to a following the previously reported method, under air, Me₄NF•4H₂O was dried.^{S1} Me₄NF•4H₂O was placed in a round bottom flask. The solid was heated at 150 °C for 2 days under reduced pressure. After heating, the flask was brought into grove box. The resulting solid was recrystallized from 2-propanol. After removal of solvents, anhydrous Me₄N•F was obtained as a white powder.

1-2. Synthesis of Me₄N•SCF₃.

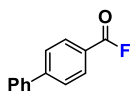
Me₄N•SCF₃ was synthesized by a following the previously reported method.^{S2} Elemental sulfur (160 mg, 5.00 mmol) was added to a 100 mL round bottom flask followed by THF (40 mL) at room temperature. TMSCF₃ (0.800 mL, 5.41 mmol) was added to the mixture. Then, the reaction mixture was cooled to -60 °C. Me₄N•F (0.500 g, 5.37 mmol) was added slowly over 30 min. The reaction mixture was stirred at -60 °C for 30 min and then allowed to warm to room temperature. Additionally, the mixture was stirred for 16 hours. A precipitation was filtered off. Then, the resulting crude material was washed with diethyl ether to give the desired product Me₄N•SCF₃ as a pale orange solid in 82% yield (718 mg, 4.10 mmol). ¹H NMR (CD₃CN, 400 MHz): δ = 3.14 (s, 12H). ¹⁹F NMR (CD₃CN, 376 MHz): δ = -10.8. ¹³C NMR (CD₃CN, 100 MHz): δ = 56.1 (m), 145.4 (q, J_{CF} = 293.1 Hz).

1-3. Procedures of preparation of acyl fluoride 1.

Method A^{S3}: Under N₂ atmosphere, the corresponding carboxylic acid (3.00 mmol) was transferred to a PFA bottle equipped with a stirrer bar. After addition of CH₂Cl₂ (5.00 mL) to the bottle, the reaction mixture was cooled at 0 °C in ice bath. Then, Deoxo-fluor® (0.560 mL, 3.04 mmol) was added to the solution. The bottle was capped, and the reaction mixture was stirred at 0 °C for 5–30 min (written at each substrate in parentheses). The reaction was quenched by addition of aqueous NaHCO₃. The mixture was extracted with CH₂Cl₂ (10.0 mL) three times. The combined organic layer was dried over Na₂SO₄. Solvents were removed under reduced pressure. The crude material was purified by silica gel column chromatography (hexane/AcOEt = 97:3) to give the corresponding acid fluoride.

Method B^{S4}: Under N₂ atmosphere, the corresponding carboxylic acid (1.00 mmol) was transferred to a PFA bottle equipped with a stirrer bar. To the reaction vessel, Me₄N•SCF₃ (230 mg, 1.31 mmol) and CH₂Cl₂ (5.00 mL) were added. Then, the reaction mixture was stirred until completely consumption of Me₄N•SCF₃. The resulting suspension was filtered through a silica gel pad. Solvents were removed under reduced pressure. The crude material was purified by silica gel column chromatography (hexane/AcOEt = 97:3) to give the corresponding acid fluoride.

1-4. Characterization of acyl fluoride **1**.



Biphenyl-4-carboxylic acid fluoride (1b): Method A (5 min) with biphenyl-4-carboxylic acid (595 mg, 3.00 mmol) gave the title compound **1b** as a white solid in 73% yield (439 mg, 2.19 mmol).

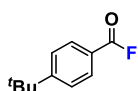
^1H NMR (CDCl_3 , 400 MHz): δ = 8.12 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.64 (d, J_{HH} = 7.1 Hz, 2H), 7.50 (dd, J = 7.2, 7.2 Hz, 2H), 7.44 (dd, J = 7.2, 7.2 Hz, 1H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 15.4 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 157.3 (d, J = 343.3 Hz), 148.0 (s), 139.2 (s), 131.9 (d, J = 3.9 Hz), 129.1 (s), 128.8 (s), 127.6 (s), 127.3 (s), 123.4 (d, J = 61.2 Hz).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{13}\text{H}_9\text{FO}$: 200.0637; Found: 200.0638.

The analytical data are in agreement with those reported previously in the literature.^{S5}



4-tert-Butylbenzoyl fluoride (1c): Method A (10 min) with *p*-tert-butylbenzoic acid (890 mg, 4.99 mmol) gave the title compound **1c** as a colorless oil in 70% yield (632 mg, 3.51 mmol).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.97 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 1.36 (s, 9H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 15.0 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 159.5 (s), 157.4 (d, J = 342.8 Hz), 131.3 (d, J = 3.9 Hz), 126.1 (s), 122.0 (d, $^2J_{\text{CF}}$ = 61.0 Hz), 35.4 (s), 30.9 (s).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{11}\text{H}_{13}\text{FO}$: 180.0950; Found: 180.0953.

The analytical data are in agreement with those reported previously in the literature.^{S6}



Biphenyl-2-carboxylic acid fluoride (1d): Method B with biphenyl-2-carboxylic acid (198 mg, 0.999 mmol) gave the title compound **1d** as a colorless oil in 62% yield (124 mg, 0.619 mmol).

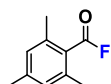
^1H NMR (CDCl_3 , 400 MHz): δ = 8.05 (d, J = 7.9 Hz, 1H), 7.68 (ddd, J = 7.6, 7.6 1.3 Hz, 1H), 7.53–7.40 (m, 5H), 7.33–7.36 (m, 2H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 32.3 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 157.5 (d, $^1J_{\text{CF}}$ = 347.9 Hz), 145.5 (d, J_{CF} = 2.3 Hz), 140.1 (s), 133.9 (s), 132.1 (d, J = 2.9 Hz), 131.7 (d, J = 2.7 Hz), 128.4 (s), 128.2 (s), 127.9 (s), 127.6 (s), 124.1 (d, J = 56.9 Hz).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{13}\text{H}_9\text{FO}$: 200.0637; Found: 200.0637.

The analytical data are in agreement with those reported previously in the literature.^{S5}



2,4,6-Trimethylbenzoyl fluoride (1e): Method A (10 min) with 2,4,6-trimethylbenzoic acid (499 mg, 3.04 mmol) gave the title compound **1e** as a white solid in 68% yield (342 mg, 2.06 mmol).

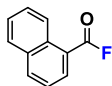
^1H NMR (CDCl_3 , 400 MHz): δ = 6.94 (s, 2H), 2.45 (d, J = 3.4 Hz, 6H), 2.32 (s, 3H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 49.6 (m, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 158.5 (d, J = 352.4 Hz), 142.7 (s), 139.5 (s), 129.6 (d, J = 1.5 Hz), 123.4 (d, J_{CF} = 53.9 Hz), 21.2(s), 21.1 (d, J = 3.1 Hz).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{FO}$: 166.0794; Found: 166.0796.

The analytical data are in agreement with those reported previously in the literature.^{S7}



1-Naphthoic acid fluoride (1f): Method A (5 min) with 1-naphthoic acid (517 mg, 3.00 mmol) gave the title compound **1f** as a white solid in 59% yield (306 mg, 1.76 mmol).

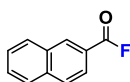
^1H NMR (CDCl_3 , 400 MHz): δ = 9.01 (d, J = 8.7 Hz, 1H), 8.33 (d, J = 7.3 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.71 (dd, J_{HH} = 7.5, 7.5 Hz, 1H), 7.60 (dd, J_{HH} = 7.4, 7.4 Hz, 1H), 7.54 (dd, J_{HH} = 7.8, 7.8 Hz, 1H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 27.3 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ =: 156.3 (d, J = 344.6 Hz), 136.6 (s), 133.7 (d, J_{CF} = 4.0 Hz), 133.6 (d, J_{CF} = 1.7 Hz), 132.0 (d, J_{CF} = 7.3 Hz), 129.1 (s), 128.9 (s), 126.9 (s), 125.1 (s), 124.4 (s), 120.2 (d, J = 56.0 Hz).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{11}\text{H}_7\text{FO}$: 174.0481; Found: 174.0484.

The analytical data are in agreement with those reported previously in the literature.^{S8}



2-Naphthoic acid fluoride (1g): Method A (10 min) with 2-naphthoic acid (517 mg, 3.00 mmol) gave the title compound **1g** as a white solid in 49% yield (257 mg, 1.48 mmol).

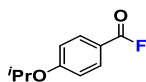
^1H NMR (CDCl_3 , 400 MHz): δ = 8.65 (s, 1H), 8.02-7.92 (m, 4H), 7.69 (dd, J = 7.4, 7.4 Hz, 1H), 7.62 (dd, J = 7.4, 7.4 Hz, 1H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 15.4 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 157.6 (d, J = 343.6 Hz), 136.4 (s), 134.0 (d, J_{CF} = 3.2 Hz), 132.3 (s), 129.7 (s), 129.6 (s), 129.1 (s), 128.0 (s), 127.4 (s), 125.6 (d, J = 4.2 Hz), 122.0 (d, J = 60.4 Hz).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{11}\text{H}_7\text{FO}$: 174.0481; Found: 174.0480.

The analytical data are in agreement with those reported previously in the literature.^{S6}



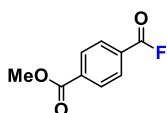
4-Isopropoxybenzoyl fluoride (1h): Method A (10 min) with 4-isopropoxybenzoic acid (547 mg, 3.04 mmol) gave the title compound **1h** as a colorless oil in 62% yield (342 mg, 1.88 mmol).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.97 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 4.67 (septet, J = 6.1 Hz, 1H), 1.38 (d, J_{HH} = 6.0 Hz, 6H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 13.0 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 163.8 (s), 157.2 (d, J = 339.5 Hz), 133.7 (d, J = 4.1 Hz), 116.1 (d, J = 61.7 Hz), 115.6 (s), 70.5 (s), 21.7 (s).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{FO}_2$: 182.0743; Found: 182.0740.



Methyl 4-(fluorocarbonyl)benzoate (1i): Method B with monomethyl terephthalate (181 mg, 1.00 mmol) gave the title compound **1i** as a white solid in 40% yield (72.5 mg, 0.398 mmol).

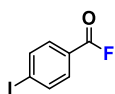
^1H NMR (CDCl_3 , 400 MHz): δ = 8.18 (d, J = 8.4 Hz, 2H), 8.11 (d, J = 8.4 Hz, 2H), 3.97 (s, 3H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 17.4 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 165.6 (s), 156.5 (d, J = 345.8 Hz), 136.0 (s), 131.4 (d, J = 3.7 Hz), 130.1 (s), 128.6 (d, J = 61.8 Hz), 52.7 (s).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_9\text{H}_7\text{FO}_3$: 182.0379; Found: 182.0381.

The analytical data are in agreement with those reported previously in the literature.^{S9}



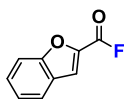
4-Iodobenzoyl fluoride (1j): Method A (15 min) with 4-iodobenzoic acid (744 mg, 3.00 mmol) gave the title compound **1j** as a white solid in 68% yield (513 mg, 2.05 mmol).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.90 (dd, J = 8.5, 0.96 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 15.6 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 157.0 (d, J = 344.0 Hz), 138.5 (s), 132.4 (d, J = 3.8 Hz), 124.3 (d, J = 62.4 Hz), 104.0 (s).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_7\text{H}_4\text{FIO}$: 249.9291; Found: 249.9293.



Benzofuran-2-carbonyl fluoride (1k): Method B with benzofuran-2-carboxylic acid (162 mg, 0.999 mmol) gave the title compound **1k** as a yellow solid in 75% yield (123 mg, 0.749 mmol).

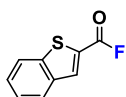
^1H NMR (CDCl_3 , 400 MHz): δ = 7.77 (s, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.62 (dd, J = 8.4, 0.64 Hz, 1H), 7.56 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.38 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 14.7 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 156.9 (d, J = 2.2 Hz), 149.4 (d, J = 329.9 Hz), 139.8 (d, J = 89.4 Hz), 129.5 (s), 126.3 (s), 124.6 (s), 123.5 (s), 119.3 (s), 112.6 (s).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_9\text{H}_5\text{FO}_2$: 164.0274; Found: 164.0272.

The analytical data are in agreement with those reported previously in the literature.^{S9}



Benzo[b]thiophene-2-carbonyl fluoride (1l): Method B with benzo[b]thiophene-2-carboxylic acid (179 mg, 1.00 mmol) gave the title compound **1l** as a yellow solid in 86% yield (155 mg, 0.860 mmol).

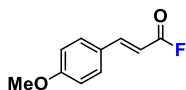
^1H NMR (CDCl_3 , 400 MHz): δ = 8.22 (s, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.91 (dd, J = 8.3, 0.76 Hz, 1H), 7.56 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.48 (ddd, J = 8.1, 7.1, 1.0 Hz, 1H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 21.9 (s, 1F).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz): δ = 153.1 (d, J = 335.2 Hz), 143.6 (s), 138.1 (s), 135.1 (d, J = 2.3 Hz), 128.4 (s), 126.7 (d, J = 74.8 Hz), 126.3 (s), 125.6 (s), 122.9 (s).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_9\text{H}_5\text{FO}_2$: 180.0045; Found: 180.0046.

The analytical data are in agreement with those reported previously in the literature.^{S10}



(E)-3-(4-Methoxyphenyl)acryloyl fluoride (1m): Method A (30 min) with 4-methoxycinnamic acid (535 mg, 3.00 mmol) gave the title compound **1m** as a white solid in 70% yield (381 mg, 2.11 mmol).

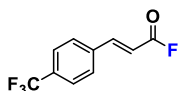
^1H NMR (CDCl_3 , 400 MHz): δ = 7.78 (d, J = 15.9 Hz, 1H), 7.51 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 6.21 (dd, J = 15.9, J = 7.3 Hz, 1H), 3.86 (s, 3H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 21.7 (s, 1F).

^{13}C { ^1H } NMR (CDCl_3 , 100 MHz): δ = 162.6 (s), 157.5 (d, J = 336.6 Hz), 151.1 (d, J = 6.3 Hz), 130.6 (s), 125.9 (s), 114.6 (s), 109.1 (d, J = 67.2 Hz), 55.4 (s).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{10}\text{H}_9\text{FO}_2$: 180.0587; Found: 180.0587.

The analytical data are in agreement with those reported previously in the literature.^{S11}



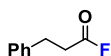
(E)-3-(4-Trifluoromethylphenyl)acryloyl fluoride (1n): Method A (30 min) with 4-trifluoromethylcinnamic acid (649 mg, 3.00 mmol) gave the title compound **1n** as a white solid in 42% yield (273 mg, 1.25 mmol).

^1H NMR (CDCl_3 , 400 MHz): δ = 7.85 (d, J = 16.0 Hz, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 6.46 (dd, J = 16.0 Hz, J = 7.0 Hz, 1H),.

^{19}F NMR (CDCl_3 , 376 MHz): δ = 24.8 (d, J = 6.7 Hz, 1F), -65.0 (s).

^{13}C { ^1H } NMR (CDCl_3 , 100 MHz): δ = 156.4 (d, J = 339.7 Hz), 149.3 (d, J = 5.9 Hz), 136.3 (s), 133.1 (q, J = 32.9 Hz), 128.8 (s), 126.1 (q, J = 3.8 Hz), 123.6 (q, J = 272.4 Hz), 114.8 (d, J = 68.1 Hz).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_{10}\text{H}_6\text{F}_4\text{O}$: 218.0355; Found: 218.0357.



3-Phenylpropanoic acid fluoride (1o): Method A (10 min) with 3-phenylpropanoic acid (451 mg, 3.00 mmol) gave the title compound **1o** as a colorless oil in 32% yield (144 mg, 0.946 mmol).

^1H NMR (CDCl_3 , 400 MHz): 7.33 (d, J = 7.3 Hz, 2H), 7.27–7.21 (m, 3H), 3.01 (t, J = 7.6 Hz, 2H), 2.84 (t, J = 7.6 Hz, 2H).

^{19}F NMR (CDCl_3 , 376 MHz): δ = 42.6 (s, 1F).

^{13}C { ^1H } NMR (CDCl_3 , 100 MHz): 162.8 (d, J = 360.4 Hz), 138.9 (s), 128.7 (s), 128.2 (s), 126.8 (s), 33.8 (d, J = 50.4 Hz), 29.9 (d, J = 2.2 Hz).

HRMS (EI): m/z [M] $^+$ calcd for $\text{C}_9\text{H}_9\text{FO}$: 152.0637; Found: 152.0636.

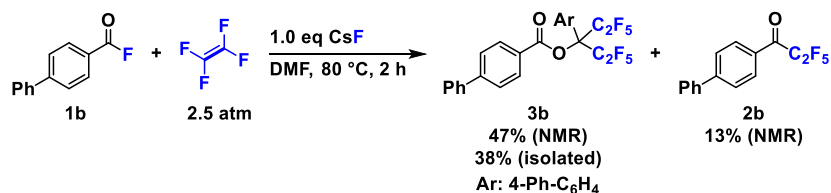
The analytical data are in agreement with those reported previously in the literature.^{S12}

1-5. A picture of a reaction vessel for catalytic pentafluoroethylation of acyl fluorides.

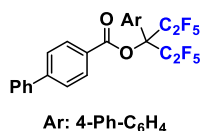


Figure S1. A reaction vessel for catalytic pentafluoroethylation of acyl fluorides (Wilmad-LabGlass 513-7PVM-9).

1-6. Stoichiometric reaction at 80 °C and Isolation of ester 3b.



Biphenyl-4-carboxylic acid fluoride (100 mg, 0.499 mmol) was dissolved into DMF (2.50 mL) as a solvent. After addition of CsF (76.0 mg, 0.500 mmol) to a pressure-tight reaction vessel (total volume is 12 mL) as a reactor, the resulting solution was transferred to the tube. Then, TFE (2.5 atm) was charged into the reactor. The reaction mixture was heated at 80 °C for 2 h. After, the remaining TFE was purged from the reactor, the reaction mixture was quenched by addition of water (10.0 mL). The resulting mixture was extracted with ether (10 mL) three times. The solvents were removed under reduced pressure. The yields of the ketone **2b** and ester **3b** were estimated by ¹⁹F NMR measurement of the crude material (**2b**: 13%, **3b**: 47%). The crude material was purified by preparative HPLC to give the corresponding ester **3b** as colorless oil in 38% yield (56.7 mg, 0.0944 mmol).



3-(4-Biphenyl)-1,1,1,2,2,4,4,5,5,5-decafluoropentyl biphenyl-4-carboxylate (**3b**):

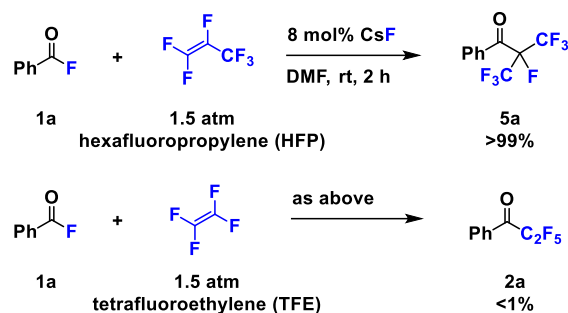
¹H NMR (CDCl₃, 400 MHz): δ = 8.22 (d, *J*_{HH} = 8.3 Hz, 2H), 7.78 (d, *J*_{HH} = 8.1 Hz, 2H), 7.69–7.62 (m, 6H), 7.55–7.46 (m, 7H), 7.40 (dd, *J*_{HH} = 7.2, 7.2 Hz, 1H).

¹⁹F NMR (CDCl₃, 376 MHz): δ = -80.2 (s, 3F), -80.3 (s, 3F), -110.6 (d, ¹*J*_{CF} = 295.4 Hz, 2F), -114.9 (d, ¹*J*_{CF} = 296.0 Hz, 2F).

¹³C{¹H} NMR (CDCl₃, 100 MHz): δ = 161.9 (s), 147.4 (s), 142.8 (s), 139.6 (s), 139.5 (s), 130.8 (s), 129.1 (s), 128.9 (s), 128.6 (s), 128.3 (s), 128.0 (s), 127.6 (s), 127.3 (s), 127.2 (s), 126.7 (s), 126.4 (s), 125.0 (s), 118.6 (qt, ¹*J*_{CF} = 289.8 Hz, ²*J*_{CF} = 35.3 Hz, -CF₃), 113.2 (tq, ¹*J*_{CF} = 272.8 Hz, ²*J*_{CF} = 37.7 Hz, -CF₂-), 86.3 (t, *J*_{CF} = 26.7 Hz).

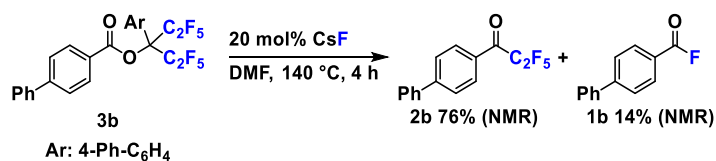
HRMS (EI): *m/z* [M]⁺ calcd for C₃₀H₁₈F₁₀O₂: 600.1147; Found: 600.1146.

1-7. CsF-catalyzed fluoroacylation of HFP or TFE with acyl fluoride 1a at room temperature.



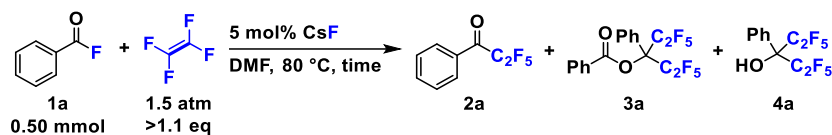
These reactions were performed according to the reported reaction conditions.^{S13} Under N_2 atmosphere, benzoyl fluoride (0.500 g, 4.00 mmol) was dissolved to DMF (0.500 mL). After addition of CsF (50.0 mg, 0.330 mmol) to an autoclave reactor equipped with a stirrer bar, the solution was transferred to the reactor. Then, HFP or TFE (1.5 atm) was charged into the reactor. The reaction mixture was stirred at room temperature for 2 h. After the remaining gas was purged from the reactor, α,α,α -trifluorotoluene (100 μL , 0.815 mmol) was added as an internal standard. Yields were determined by ^{19}F NMR measurement of the crude materials respectively.

1-8. Investigation of reactivity of ester 3b under CsF catalytic system.



3b (30.0 mg, 0.0500 mmol) and α,α,α -trifluorotoluene (5.0 μL , 0.041 mmol) were dissolved to a mix solvent of DMF and C_6D_6 (0.500 mL, $v/v' = 4/1$). After addition of CsF (1.55 mg, 0.0102 mmol) to a pressure-tight NMR tube (Wilmad-LabGlass, 524-PV-7; total volume: 2 mL), the solution was transferred to the tube. The reaction tube was heated at 140 $^\circ\text{C}$ for 4 h. The yields of the ketone **2b** and acyl fluoride **1b** were determined by ^{19}F NMR measurement of the crude material using an internal standard.

1-9. Yield change of perfluoroalkylation of **1a** at 80 °C over reaction time.



Under N₂ atmosphere, benzoyl fluoride (**1a**) (62.1 mg, 0.500 mmol) was dissolved into DMF (0.500 mL). After addition of CsF (3.8 mg, 0.025 mmol) to a pressure-tight tube (Wilmad-LabGlass 513-7PVM-9; total volume; 12 mL), the solution was transferred to the tube. After further addition of DMF (2.0 mL), TFE (1.5 atm, > ca. 1.1 eq) was charged into the reactors. The reaction mixtures were respectively heated at 80 °C for 2, 4, 8 or 20 h. After the unreacted gas was purged from the reactor, α,α,α -trifluorotoluene was added as an internal standard to each reaction mixture. The yields of **1a**, **2a**, **3a** and **4a** were determined by ¹⁹F NMR measurement of the crude materials. The results are summarized in Table S1 and Figure S2.

Table S1. Yields of each product at 80 °C.

time/h	1a /%	2a /% (max 100%)	3a /% (max 100%)	4a /% (max 100%)
0	100	0	0	0
2	67	21	10	0
4	37	27	30	<1
8	15	31	44	3
20	10	42	35	3

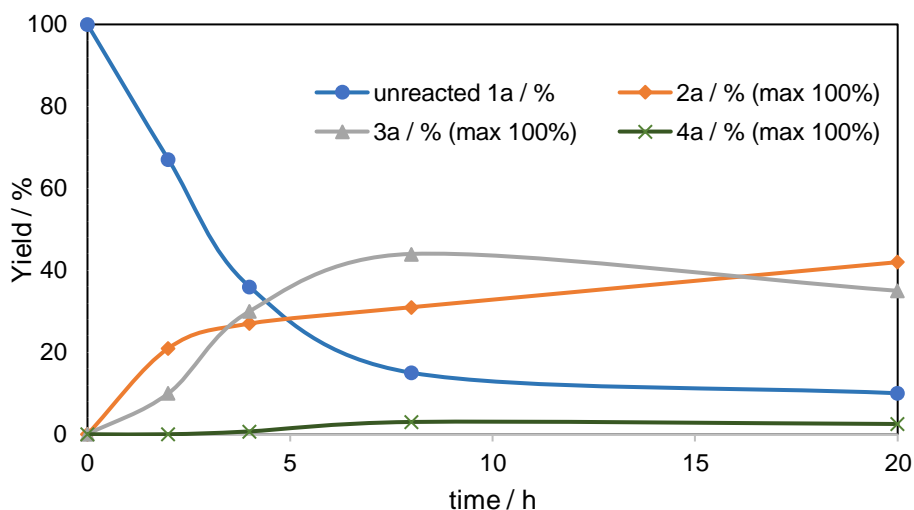


Figure S2. Time-course change of yields at 80 °C.

2. Computational Study

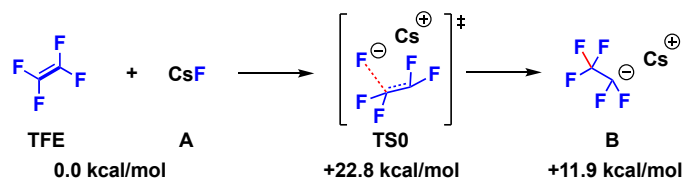
2-1. Calculation method details.

All geometry optimizations for the pentafluoroethylation reaction pathways using density functional theory (DFT) were performed with Gaussian 09 (revision D.01)^{S14} suite of programs at B3LYP level^{S15,S16} combined with Grimme's dispersion correlation^{S17} of theory using SMD solvation model ($\epsilon = 37.219$, DMF)^{S18} and an effective core potential, Lanl2DZ^{S19} for cesium atom and 6-31+G(d,p) as double-zeta quality basis sets. Harmonic frequency calculations were conducted at the same level of theory on the optimized geometries to check all the stationary points as either minima or first-order saddle points. Intrinsic reaction coordinate (IRC)^{S20} calculations were carried out to confirm the transition states connecting the correct reactants and products on the potential energy surface. The thermal energy corrections were calculated for the optimized geometry at B3LYP level combined with Grimme's dispersion correlation of theory using SMD solvation model ($\epsilon = 37.219$, DMF) and an effective core potential, SDD^{S21} for cesium atom and 6-311++G(d,p) as triple-zeta quality basis sets.

Summary: B3LYP-D3/6-311++G(d,p), SDD for Cs atom/SMD($\epsilon = 3.7219$, DMF)//B3LYP-D3/6-31+G(d,p), Lanl2DZ for Cs/SMD($\epsilon = 3.7219$, DMF).

2-2. DFT calculation of formation of pentafluoroethyl cesium (B).

The calculation of the formation of pentafluoroethyl cesium (**B**) was conducted. The related Gibbs activation energy value of the transition state (TS0) of the nucleophilic attack of a fluoride anion of CsF (**A**) to a C–C double bond of TFE was reasonable to proceed at 140 °C ($\Delta G^\ddagger = +22.8$ kcal/mol). This process was predicted as an endothermic step by the DFT calculation. The resulting pentafluoroethyl cesium (**B**) was highly unstable compared to CsF (**A**) and TFE [ΔG (**B**) = +11.9 kcal/mol]. This calculation was agreed with the experimental result which pentafluoroethyl cesium (**B**) was not observed in the reaction mixture.



Scheme S1. DFT calculation of formation of pentafluoroethyl cesium (**B**).

2-3. DFT calculation of pentafluoroethylation of acyl fluoride 1a.

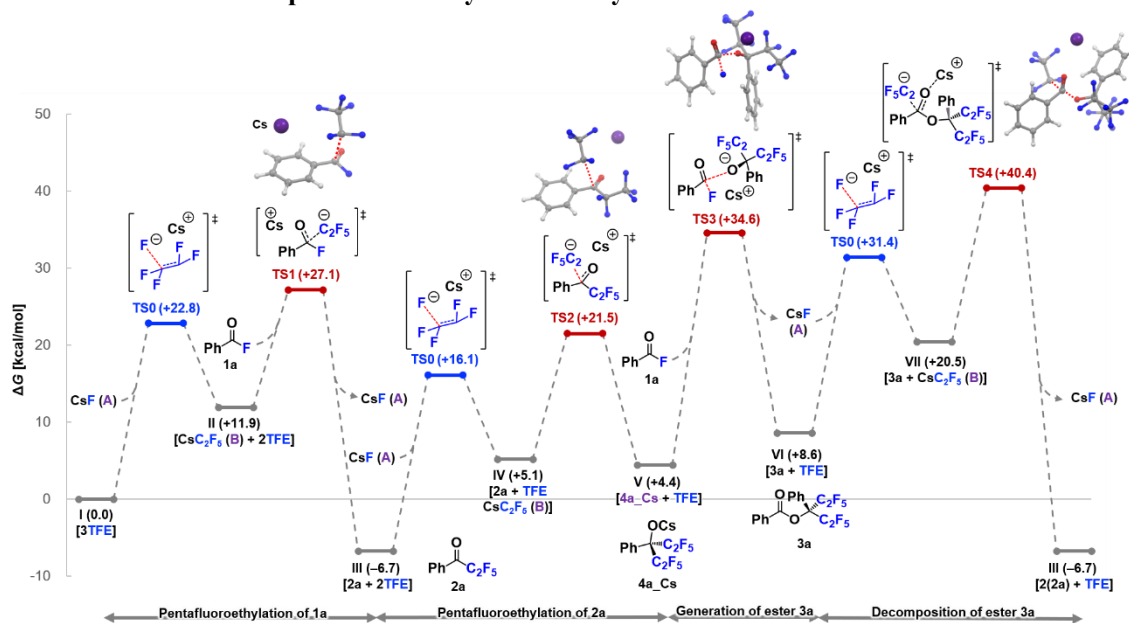


Figure S3. Computational study for the entire reaction pathway; all calculations were carried out at the B3LYP-D3/6-311++G(d,p), SDD for Cs/SMD(DMF,ε=37.219)//B3LYP-D3/6-31+G(d,p), LanL2DZ for Cs/SMD(DMF,ε=37.219), 413.15 K levels of theory.

In order to investigate the reaction mechanism, we carried out density functional theory (DFT) calculations (Figure S3). The calculations relating to the change from state **I** to state **II**, i.e., the reaction between TFE and CsF (**A**) to give pentafluoroethyl cesium (**B**), indicated that this process should be endothermic, as **B** is significantly less stable than state **I** (**II**: $\Delta G = +11.9$ kcal/mol). Furthermore, the estimated activation energy (**TS0**) for the formation of **B** was reasonable for a reaction that proceeds at 140 °C (**TS0**: $\Delta G^\ddagger = +22.8$ kcal/mol). The results of these calculations agree well with the experimentally observed results, i.e., that **B** was not observed in the reaction mixture. Subsequently, we calculated the activation energy for the nucleophilic addition of **B** to acyl fluoride **1a** and found it sufficiently low to proceed at 140 °C (**TS1**: $\Delta G^\ddagger = +27.1$ kcal/mol). The elimination of **A** from the resulting intermediate furnishes pentafluoroethyl ketone **2a** via an almost barrierless process. The DFT calculations also suggested that the activation energy for the pentafluoroethylation of ketone **2a** to give the cesium *tert*-alkoxide **4a-Cs** should be slightly higher than that of the nucleophilic attack on acyl fluoride **1a** [**TS2**: $\Delta G^\ddagger = +28.2$ kcal/mol; **TS1**: $\Delta G^\ddagger = +27.1$ kcal/mol; $\Delta\Delta G^\ddagger(\text{TS2-TS1}) = +1.1$ kcal/mol]. However, this extra addition step would be disfavored with respect to the thermodynamic stability of **4a-Cs** as the formation of cesium *tert*-alkoxide **4a-Cs** is an endothermic process (**V**: $\Delta G = +4.4$ kcal/mol). Furthermore, the calculated pathway for the formation of ester **3a** revealed that the activation energy for the nucleophilic attack of **4a-Cs** onto the acyl fluoride **1a** (**TS3**) is significantly higher than that of the transition state (**TS1**) for the generation of the ketone **2a** [**TS3**: $\Delta G^\ddagger = +34.6$ kcal/mol; **TS1**: $\Delta G^\ddagger = +27.1$ kcal/mol; $\Delta\Delta G^\ddagger(\text{TS3-TS1}) = +7.5$ kcal/mol]. Moreover, the formation

of the ester is thermodynamically disfavored (**VI**: $\Delta G = +8.6$ kcal/mol), which suggests that the equilibrium between ketone **2a** and ester **3a** is extremely imbalanced and would provide ketone **2a** as the major product in the reaction mixture. This result is also in agreement with the experimental results that ester **3** is not detected at high reaction temperatures (140 °C; Table 1, entries 6 and 7) and decomposes into ketone **2** and acyl fluoride **1** under the optimized conditions (Scheme 2). The energetic analysis of the decomposition of ester **3a** (**TS4**), where the nucleophilic attack of **B** to ester **3a** furnishes ketone **2a** and cesium alkoxide **4a_Cs**, was also examined. The activation energy was found to be extremely high compared to other transition states (**TS1–3**) (**TS4**: $\Delta G^\ddagger = +40.4$ kcal/mol). A series of the DFT calculations on the reaction pathway suggested that the reaction between acyl fluoride **1a** and TFE in the presence of CsF at 140 °C should generate only pentafluoroethyl ketone **2a**.

2-4. Calculated Properties and Geometries

Table S2. Calculated energies and thermochemical parameters of the optimized structures.

Structure	<i>E</i> [hartree]	<i>H</i> [hartree]	<i>TS</i> [hartree]	<i>G</i> [hartree]
413.15 K (140 °C)				
TFE	-475.640608	-475.639300	0.053552	-475.692852
CsF (A)	-120.149357	-120.148049	0.042768	-120.190817
TS0	-595.79296	-595.775205	0.07309	-595.84732
CsC ₂ F ₅ (B)	-595.792960	-595.791652	0.07309	-595.864742
PhCOF (1a)	-444.875649	-444.874340	0.061871	-444.936211
TS1	-1040.671781	-1040.670472	0.106168	-1040.776640
PhCOC ₂ F ₅ (2a)	-920.554913	-920.553605	0.086189	-920.639794
TS2	-1516.351572	-1516.350264	0.128215	-1516.478479
PhC(C ₂ F ₅) ₂ OCs (4a_Cs)	-1516.384254	-1516.382946	0.122790	-1516.505736
TS3	-1961.244870	-1961.243562	0.150322	-1961.393884
[PhC(C ₂ F ₅) ₂ O]PhCO (3a)	-1841.108716	-1841.107408	0.137050	-1841.244458
TS4	-2436.902936	-2436.901628	0.175828	-2437.077456
353.15 K (80 °C)				
TFE	-475.642498	-475.64138	0.043855	-475.685235
CsF (A)	-120.150021	-120.148903	0.035769	-120.184672
TS0	-595.779373	-595.778254	0.058828	-595.837082
CsC ₂ F ₅ (B)	-595.795927	-595.794809	0.059562	-595.854371
PhCOF (1a)	-444.878841	-444.877722	0.049768	-444.927490
TS1	-1040.678331	-1040.677213	0.084532	-1040.761745
PhCOC ₂ F ₅ (2a)	-920.560397	-920.559279	0.068439	-920.627718

TS2	-1516.360399	-1516.359281	0.101276	-1516.460557
PhC(C ₂ F ₅) ₂ OCs(4a_Cs)	-1516.393081	-1516.391963	0.096640	-1516.488603
TS3	-1961.257250	-1961.256132	0.116899	-1961.373031
[PhC(C ₂ F ₅) ₂ O]PhCO (3a)	-1841.120089	-1841.118970	0.106485	-1841.225455
TS4	-2436.917643	-2436.916525	0.136553	-2437.053078
298.15 K (25 °C)				
TFE	-475.644065	-475.643121	0.035416	-475.678537
CsF (A)	-120.150629	-120.149685	0.029480	-120.179165
TS0	-595.781838	-595.780893	0.047246	-595.828139
CsC ₂ F ₅ (B)	-595.798425	-595.797481	0.047778	-595.845259
PhCOF (1a)	-444.881280	-444.880336	0.039678	-444.920014
TS1	-1040.683694	-1040.682750	0.065956	-1040.748706
PhCOC ₂ F ₅ (2a)	-920.564887	-920.563943	0.053160	-920.617103
TS2	-1516.367636	-1516.366692	0.078568	-1516.445260
PhC(C ₂ F ₅) ₂ OCs(4a_Cs)	-1516.400312	-1516.399367	0.074858	-1516.474225
TS3	-1961.267306	-1961.266362	0.089420	-1961.355782
[PhC(C ₂ F ₅) ₂ O]PhCO (3a)	-1841.129197	-1841.128252	0.081396	-1841.209648
TS4	-2436.929679	-2436.928735	0.104100	-2437.032835

TFE				CsC ₂ F ₅ (B)			
C	-0.662643	-0.000397	-0.000077	C	-1.798825	0.912126	0.057475
F	-1.392767	1.108786	-0.000194	C	-2.156298	-0.567915	-0.008458
C	0.661841	-0.000356	0.000103	Cs	2.375354	0.034717	0.007557
F	-1.393397	-1.108834	-0.000193	F	-2.463610	1.438090	-1.112031
F	1.394049	-1.108379	0.000185	F	-2.653345	1.384320	1.121272
F	1.392649	1.108930	0.000184	F	-1.715878	-1.217033	1.106429
				F	-1.554557	-1.159720	-1.078856
				F	-3.491914	-0.887288	-0.115675
CsF (A)				PhCOF (1a)			
F	0.000000	0.000000	-2.739658	C	-1.698317	-0.146081	-0.000017
Cs	0.000000	0.000000	0.448308	O	-2.391997	-1.123351	-0.000178
TS0				C	-0.232402	-0.046939	0.000100
C	2.048771	-0.485255	0.236685	C	0.425755	1.195486	-0.000019
C	2.149840	0.895478	0.303697	C	0.508101	-1.243379	0.000137
F	1.005250	1.569752	0.670165	C	1.819965	1.235160	-0.000035
F	2.695645	1.522857	-0.790404	H	-0.147301	2.115534	-0.000071
F	3.115742	-1.164928	-0.185965	C	1.900183	-1.193508	0.000013
F	1.438840	-1.107148	1.250178	H	-0.011569	-2.195957	0.000270
Cs	-1.955687	0.005731	-0.037216	C	2.556131	0.044604	-0.000068
F	0.896867	-1.129037	-1.076799	H	2.331642	2.192743	-0.000059

H	2.474285	-2.115029	0.000015	F	2.747831	0.837179	-1.097075
H	3.641871	0.080804	-0.000176	F	3.345863	-0.946406	0.000103
F	-2.314383	1.092962	0.000087				
				TS2			
TS1				C	1.107712	0.964337	-0.719154
C	-1.709486	2.223700	-0.440246	O	0.107914	1.037989	-1.423438
O	-2.152352	2.432464	-1.537080	C	2.264651	0.095107	-1.017177
C	-0.299278	2.287376	0.003040	C	2.082979	-0.905576	-1.992332
C	0.680021	2.579445	-0.961288	C	3.522219	0.245060	-0.403245
C	0.066181	2.127909	1.349897	C	3.135391	-1.747428	-2.338270
C	2.015729	2.716380	-0.578809	H	1.109334	-1.020590	-2.457588
H	0.387140	2.704054	-1.998991	C	4.577394	-0.595348	-0.763076
C	1.403854	2.262771	1.725631	H	3.694646	1.009978	0.344055
H	-0.689718	1.895222	2.091672	C	4.386523	-1.593922	-1.723425
C	2.379278	2.562422	0.765236	H	2.985141	-2.524401	-3.082257
H	2.770431	2.944829	-1.325948	H	5.546889	-0.470827	-0.289757
H	1.685376	2.138276	2.767415	H	5.208413	-2.251042	-1.993908
H	3.418754	2.670512	1.062760	Cs	-2.960365	-0.056232	-1.071140
F	-2.596661	2.177468	0.631161	C	0.347019	-1.301142	1.388996
Cs	2.177985	-1.306392	-0.199512	C	-0.593555	-2.487080	1.220226
C	-1.846609	-0.535910	-0.523867	F	1.637407	-1.930176	1.371067
C	-2.000590	-1.550788	0.598947	F	0.188438	-0.981359	2.785961
F	-3.070037	-0.677752	-1.250840	F	-0.516165	-2.984697	-0.046199
F	-0.896320	-1.179072	-1.403707	F	-1.889789	-2.105471	1.417881
F	-2.993750	-1.176167	1.449494	F	-0.403873	-3.568567	2.052441
F	-0.852687	-1.626037	1.335561	C	1.221169	2.000359	0.440541
F	-2.287980	-2.851873	0.242958	C	-0.110102	2.718512	0.815010
				F	1.727128	1.475665	1.587492
				F	2.084723	2.993389	0.033432
				F	0.110009	3.533750	1.867867
				F	-0.566306	3.471086	-0.199146
				F	-1.064467	1.839543	1.165990
PhCOC ₂ F ₅ (2a)				PhC(C ₂ F ₅) ₂ OCs (4a_Cs)			
C	-0.060402	0.690935	0.000455	C	0.829525	0.208436	0.009643
O	0.325770	1.849251	0.000879	O	-0.235988	-0.129168	-0.708602
C	-1.480624	0.284853	0.000018	C	2.204342	-0.047649	-0.694126
C	-2.445296	1.313914	-0.000217	C	2.166514	-0.669617	-1.945978
C	-1.900525	-1.060204	0.000029	C	3.446070	0.335295	-0.163998
C	-3.801177	1.003053	-0.000506	C	3.345366	-0.924794	-2.654768
H	-2.117238	2.347982	-0.000172	H	1.195777	-0.947668	-2.343761
C	-3.261970	-1.363782	-0.000241	C	4.627233	0.085379	-0.870806
H	-1.184689	-1.872480	0.000199	H	3.502668	0.836808	0.796375
C	-4.211832	-0.337176	-0.000552	C	4.581901	-0.549066	-2.118140
H	-4.538797	1.799931	-0.000698	H	3.297797	-1.413853	-3.624740
H	-3.579842	-2.401823	-0.000232	H	5.581247	0.389964	-0.447875
H	-5.270848	-0.579107	-0.000816	H	5.500137	-0.744129	-2.666250
C	1.034212	-0.422449	0.000893	Cs	-3.207587	-0.592779	-0.813135
C	2.497888	0.103830	-0.000743				
F	0.904423	-1.217602	1.106695				
F	0.903946	-1.220590	-1.103155				
F	2.749449	0.840046	1.093418				

C	-4.832986	-0.268539	-1.242071	H	-2.312170	5.688983	-2.691432
H	-2.716975	-0.174853	-1.625308	Cs	-1.777733	-3.139310	-1.101504
C	-5.832761	-0.366501	-0.267476	C	-2.309154	1.383857	1.307839
H	-6.264903	-0.523086	1.844220	C	-3.469085	0.403962	1.184407
H	-5.099862	-0.207214	-2.292904	F	-1.915691	1.280945	2.672341
H	-6.877955	-0.380179	-0.563382	F	-2.927886	2.656003	1.253178
				F	-4.484160	0.550310	2.105955
				F	-4.060230	0.506844	-0.032297
				F	-3.035919	-0.876932	1.319024
TS4							
C	1.477880	0.145182	0.132466				
O	0.451743	1.117126	0.181531				
C	1.152347	-1.150294	0.892867				
C	0.105606	-1.120377	1.822100				
C	1.896867	-2.329581	0.743593				
C	-0.208820	-2.253095	2.575926				
H	-0.465435	-0.214410	1.956996				
C	1.579264	-3.464079	1.496716				
H	2.719957	-2.392324	0.046285				
C	0.522624	-3.433274	2.412397				
H	-1.031210	-2.208415	3.284376				
H	2.159882	-4.371937	1.359759				
H	0.275464	-4.317937	2.992771				
C	2.635560	0.925587	0.847880				
C	2.434260	1.348128	2.344586				
F	3.774445	0.170964	0.838887				
F	2.894698	2.083398	0.174660				
F	2.386319	0.278418	3.155128				
F	1.333784	2.084917	2.532790				
F	3.502184	2.090784	2.708376				
C	1.869664	-0.123106	-1.420287				
C	3.344777	-0.310062	-1.947265				
F	1.222865	-1.241095	-1.854190				
F	1.416891	0.932430	-2.155367				
F	4.083869	0.796165	-1.787550				
F	3.983904	-1.343663	-1.377751				
F	3.267580	-0.561516	-3.270745				
O	-1.108525	-0.083149	-1.000058				
C	-0.758484	0.998508	-0.548909				
C	-1.162061	2.322052	-1.112319				
C	-2.224370	2.346510	-2.028329				
C	-0.506547	3.517173	-0.779665				
C	-2.639628	3.554589	-2.591585				
H	-2.722923	1.417480	-2.283497				
C	-0.921332	4.723930	-1.348528				
H	0.319100	3.502848	-0.077336				
C	-1.989849	4.748358	-2.252942				
H	-3.465875	3.564790	-3.297625				
H	-0.408219	5.645587	-1.086984				

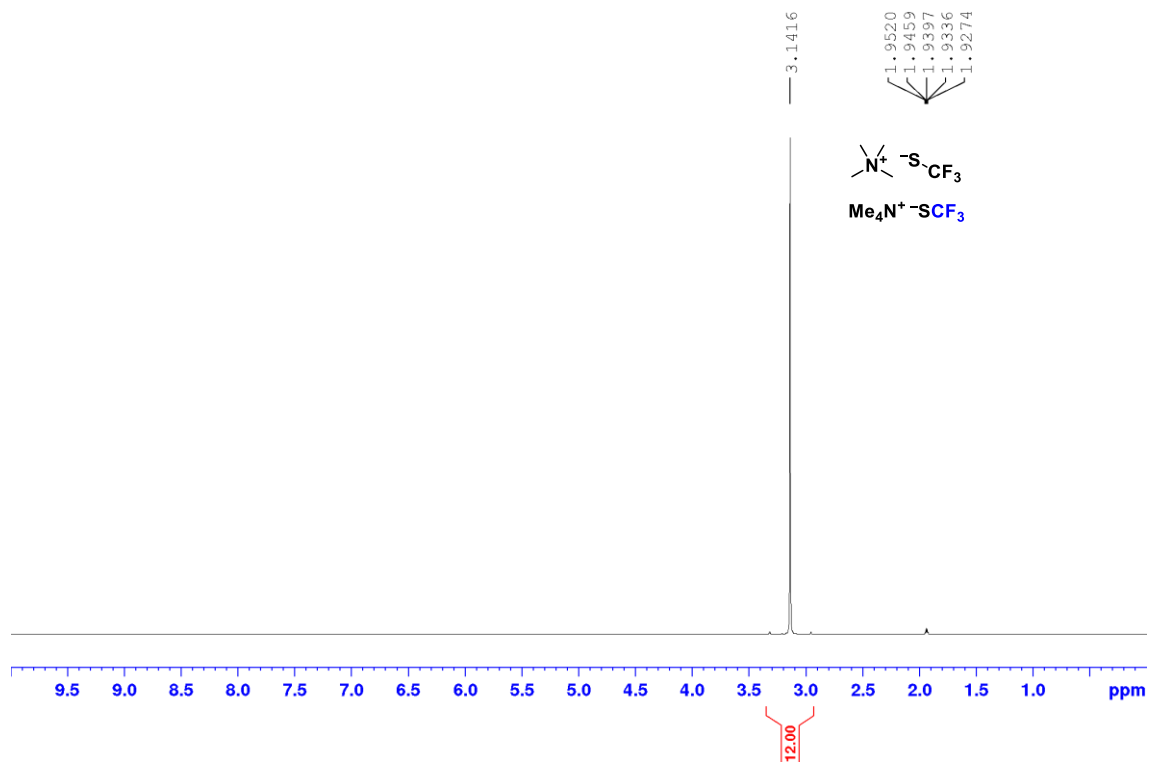
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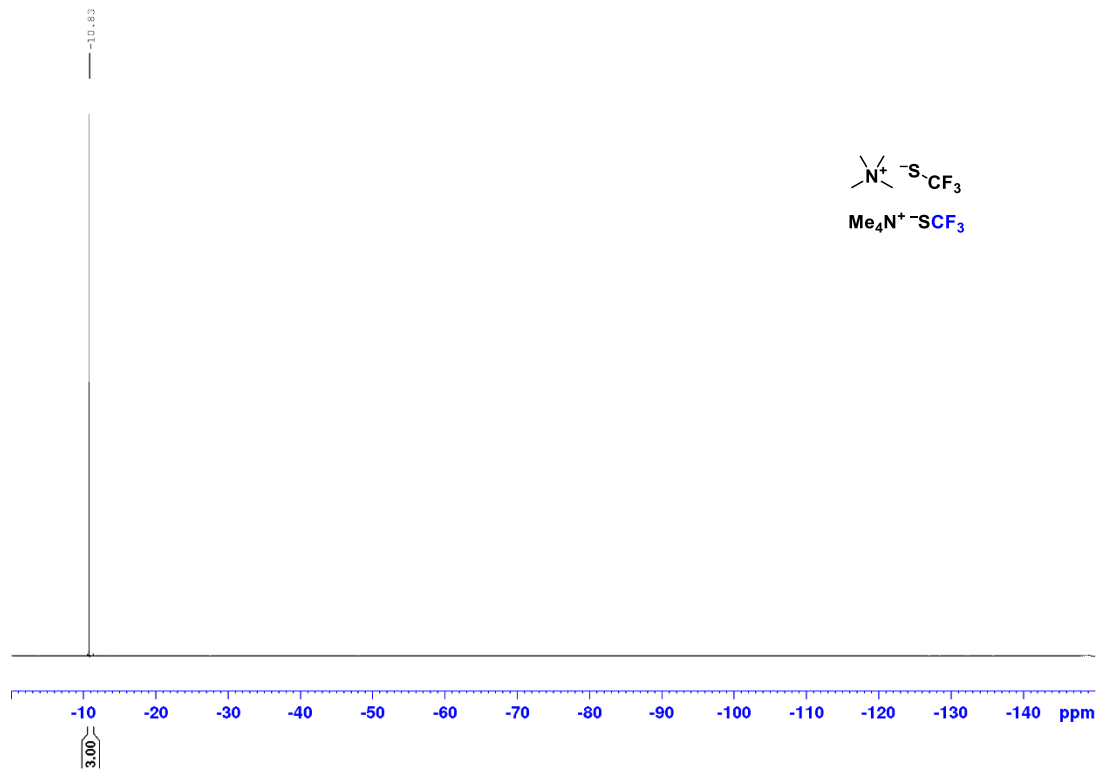
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4. NMR Spectra

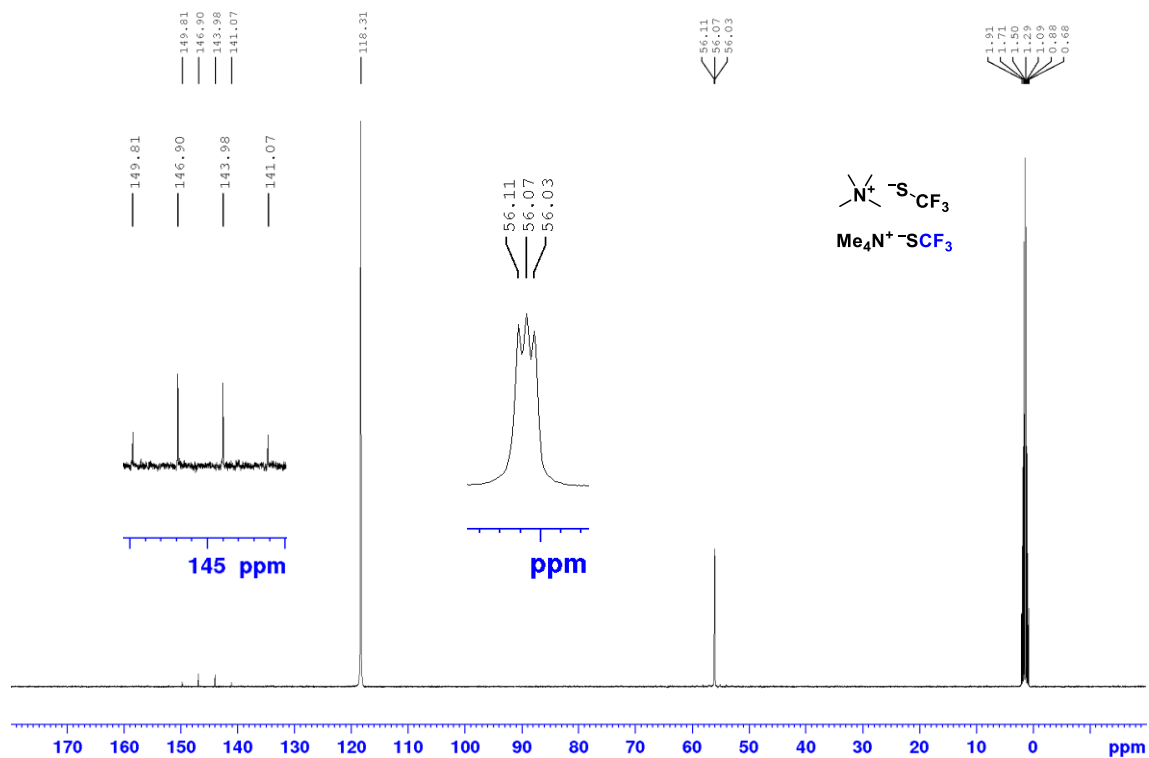
^1H NMR (400 MHz, CD_3CN , rt, δ/ppm)



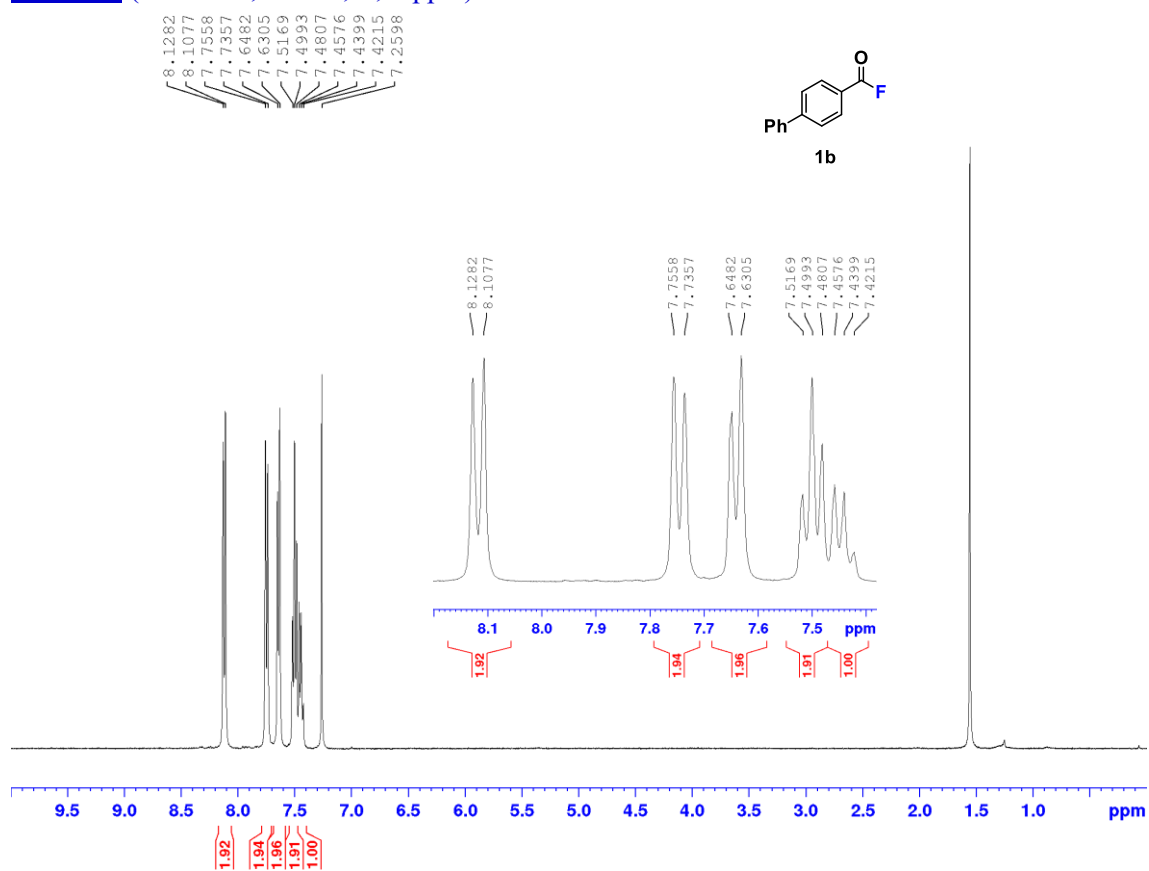
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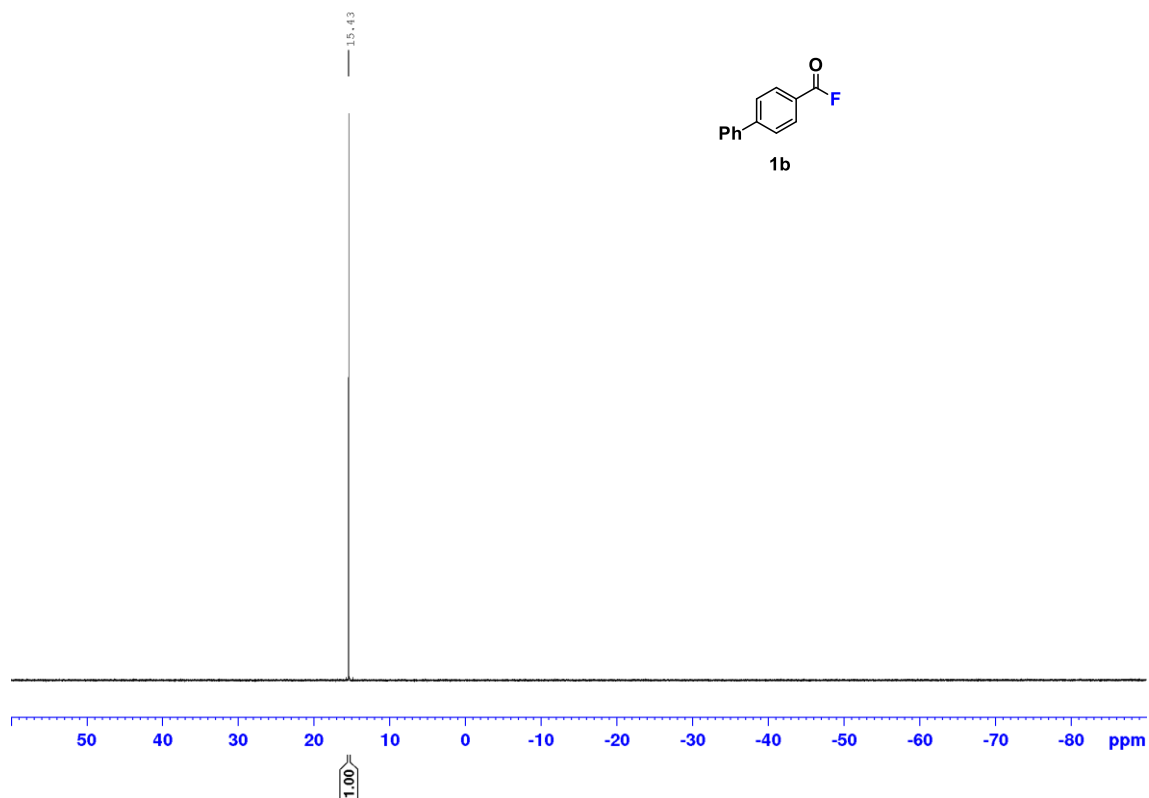
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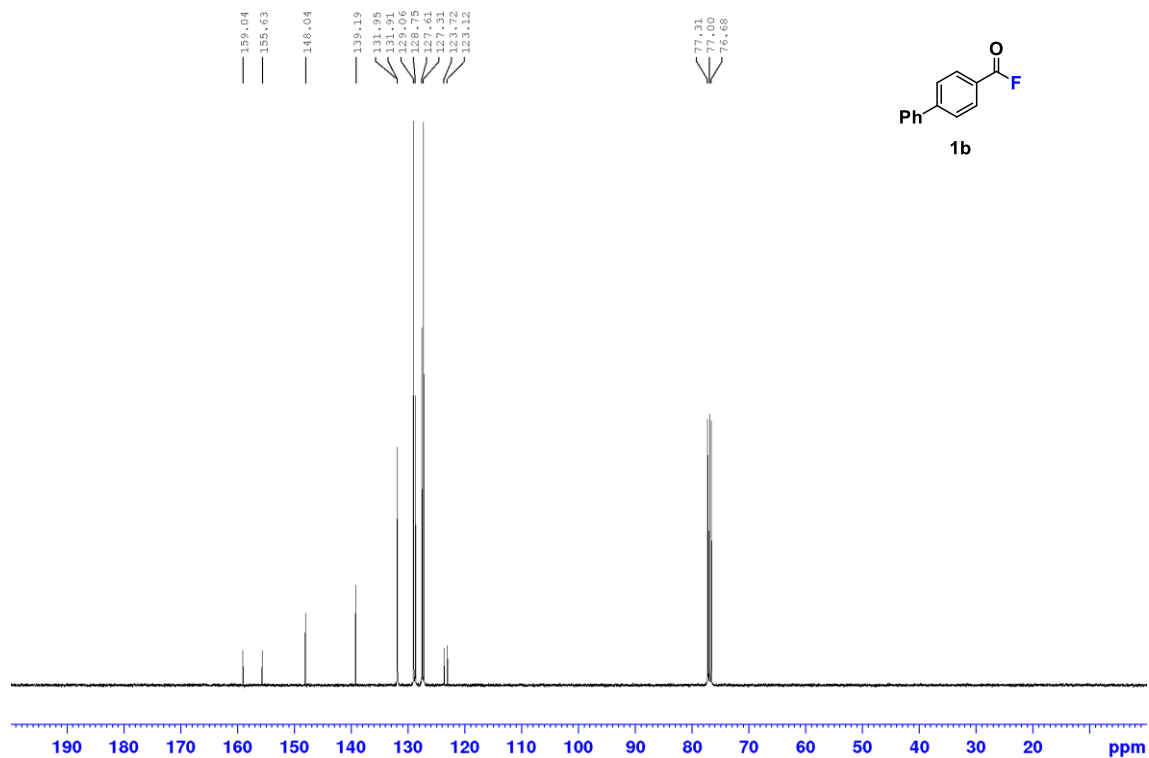
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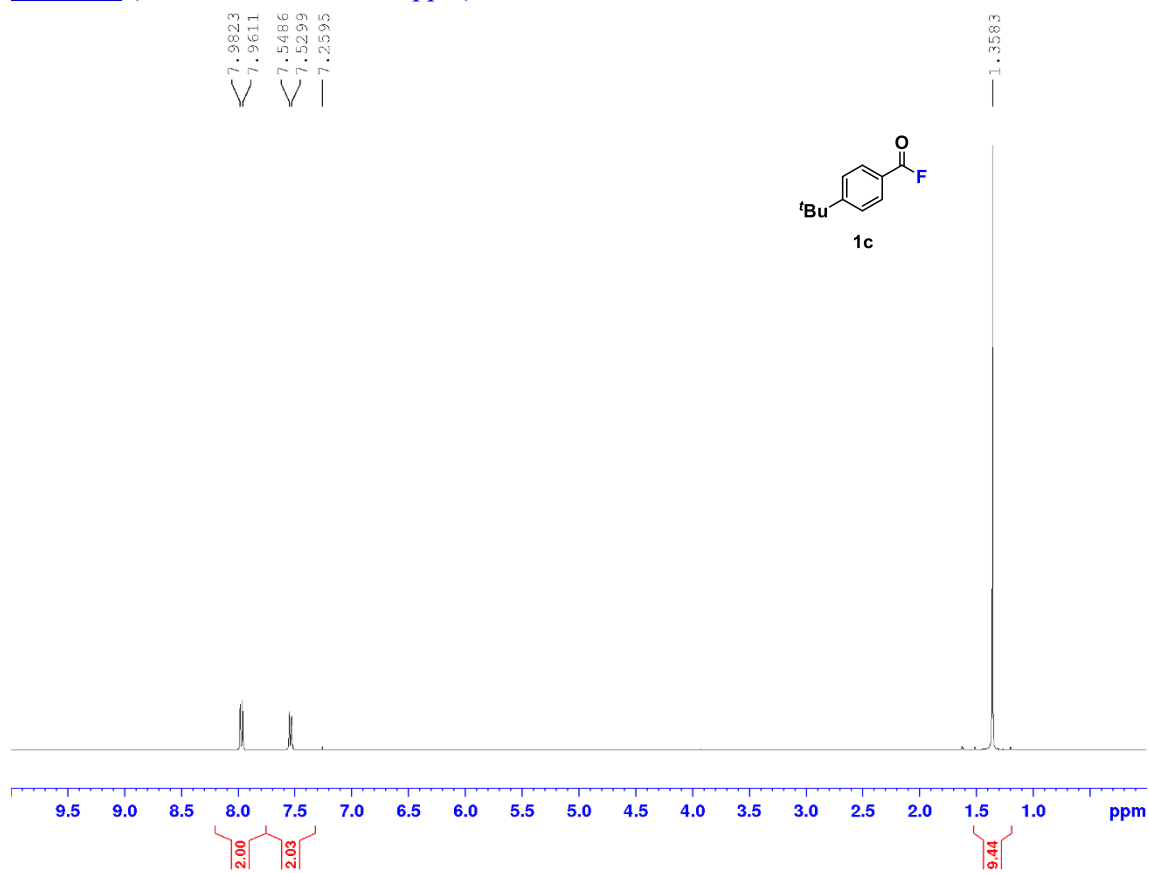
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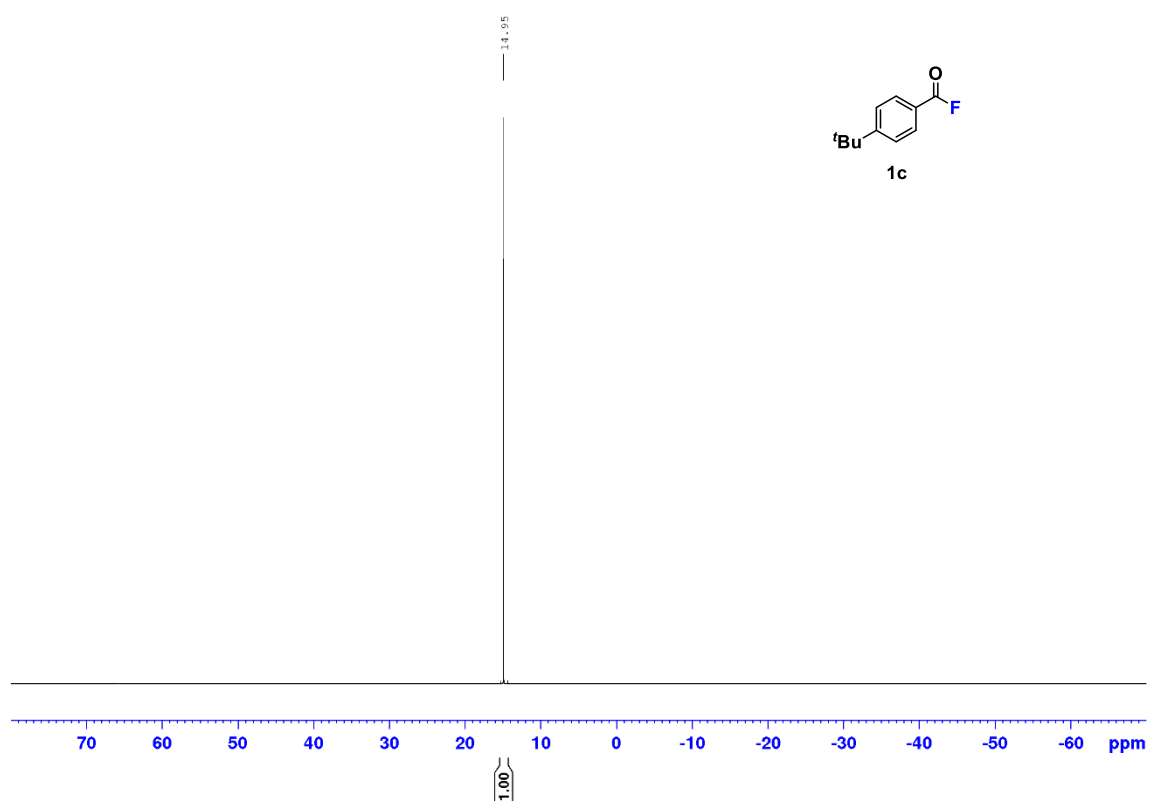
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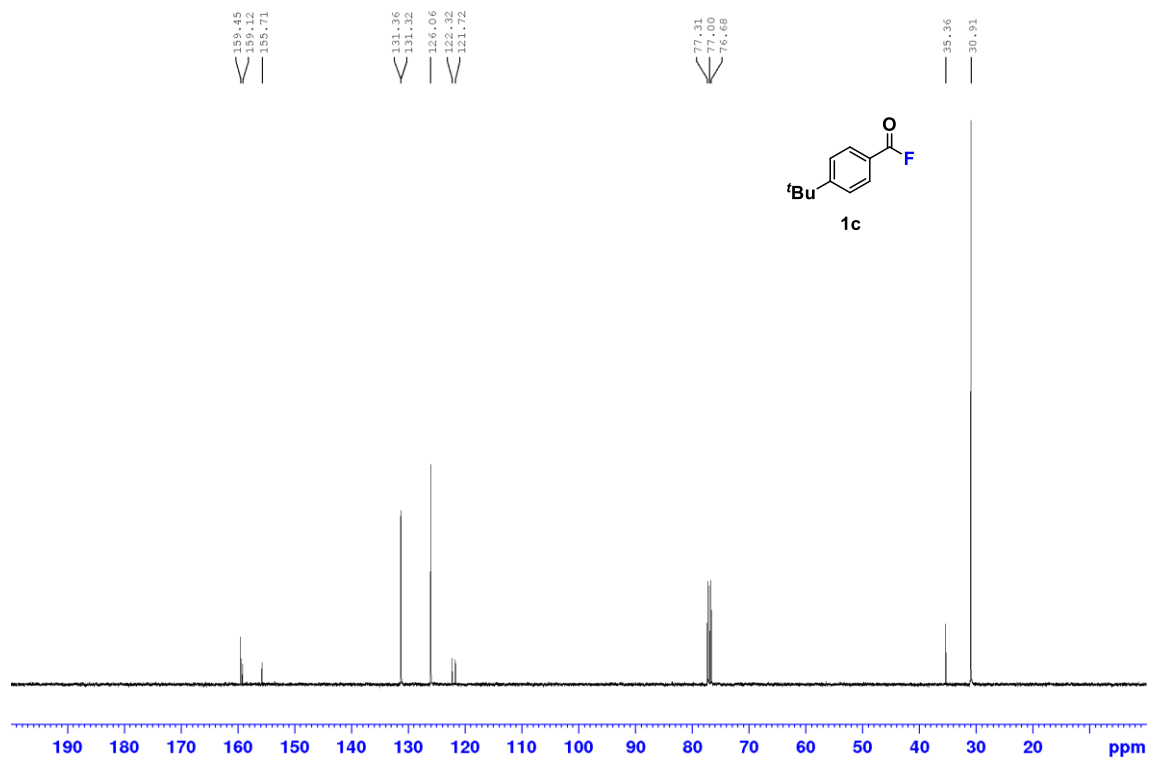
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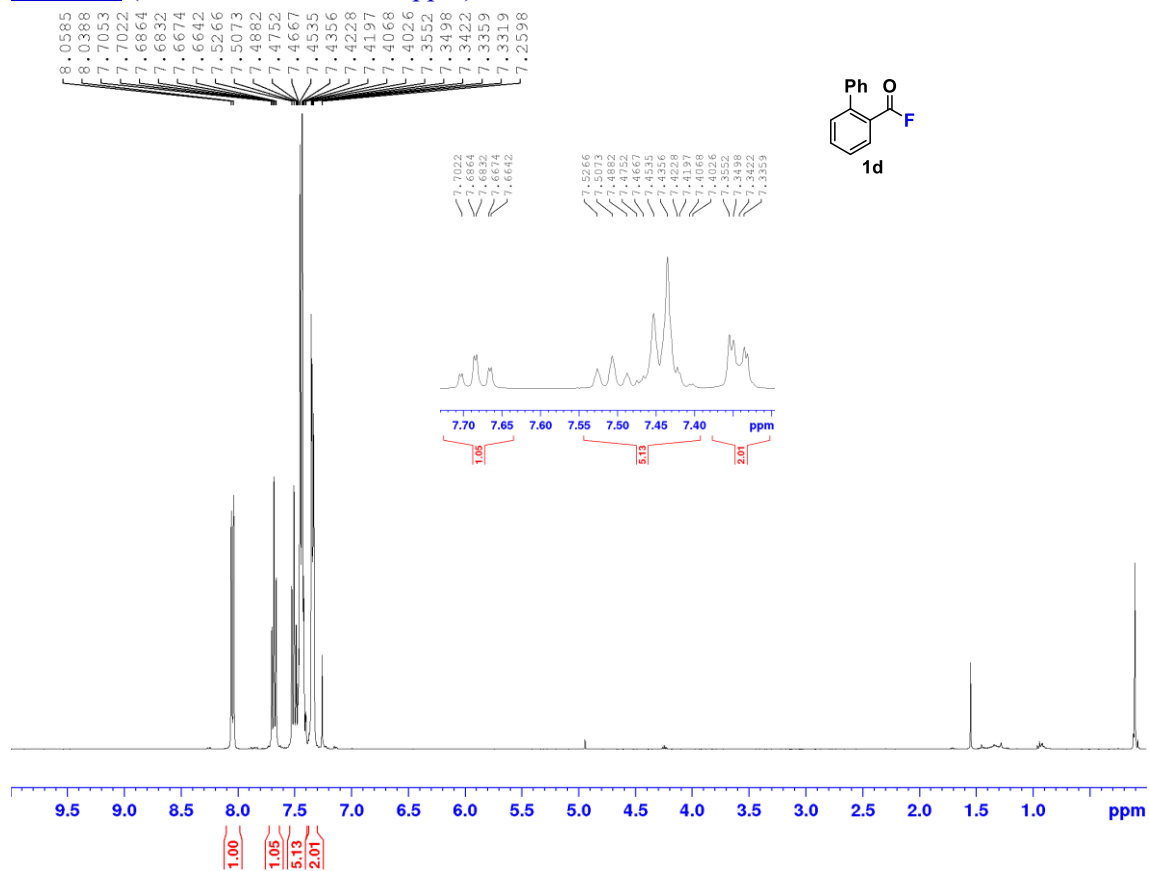
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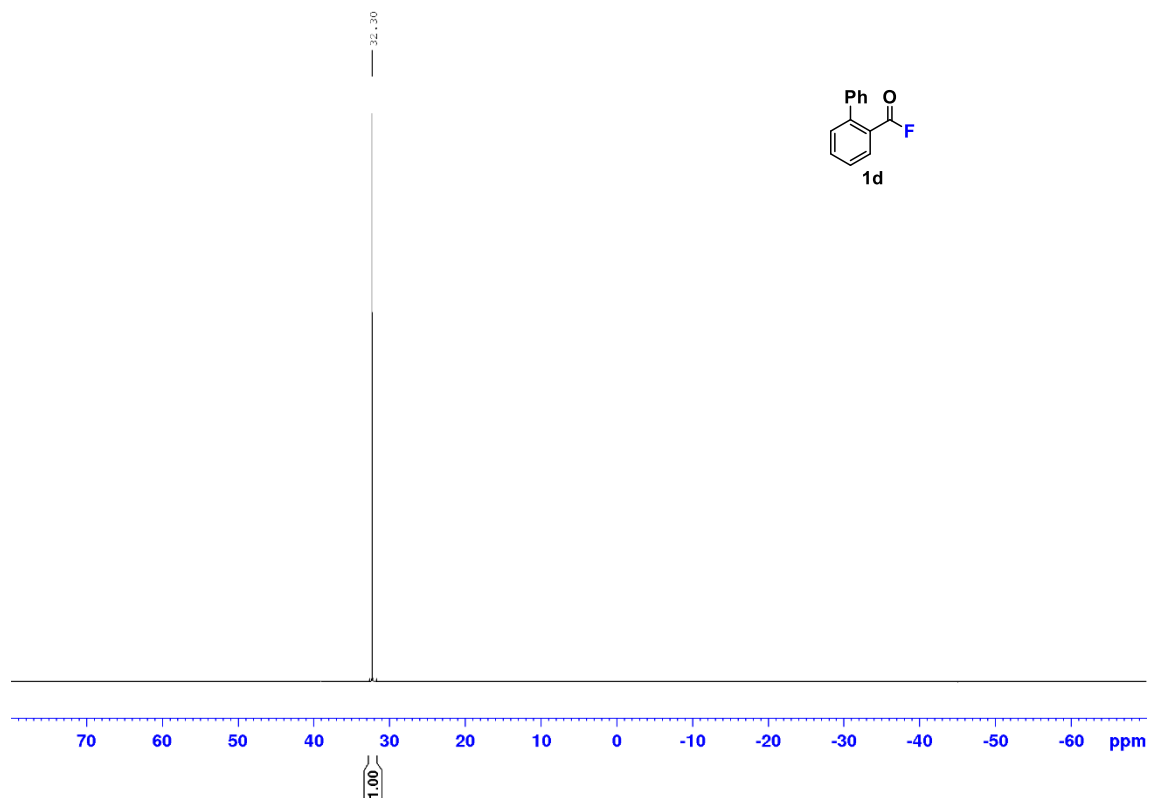
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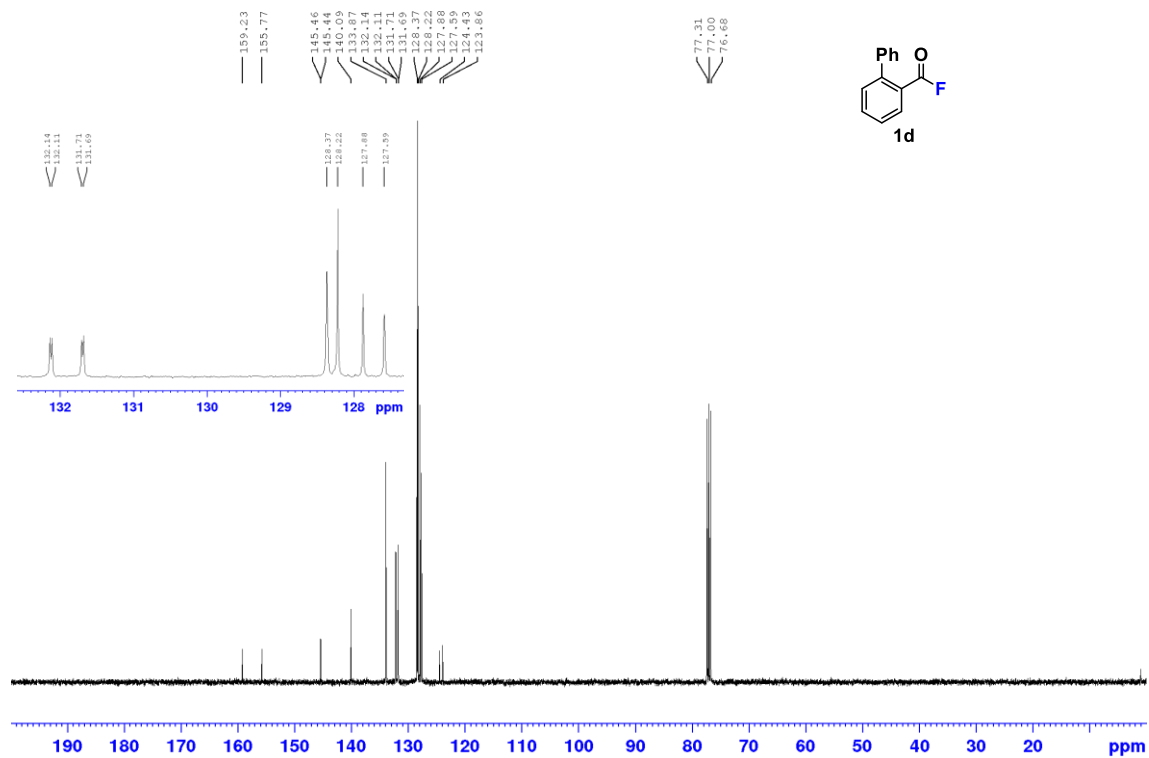
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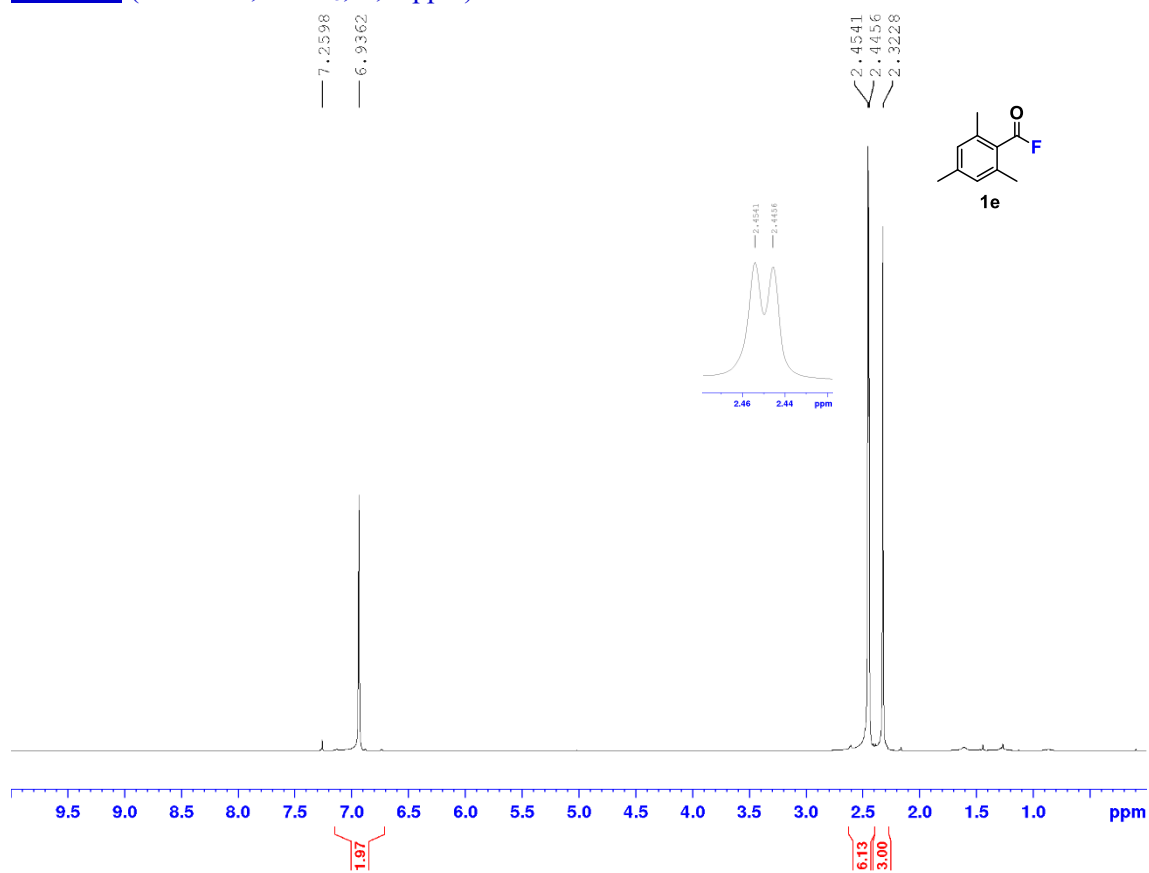
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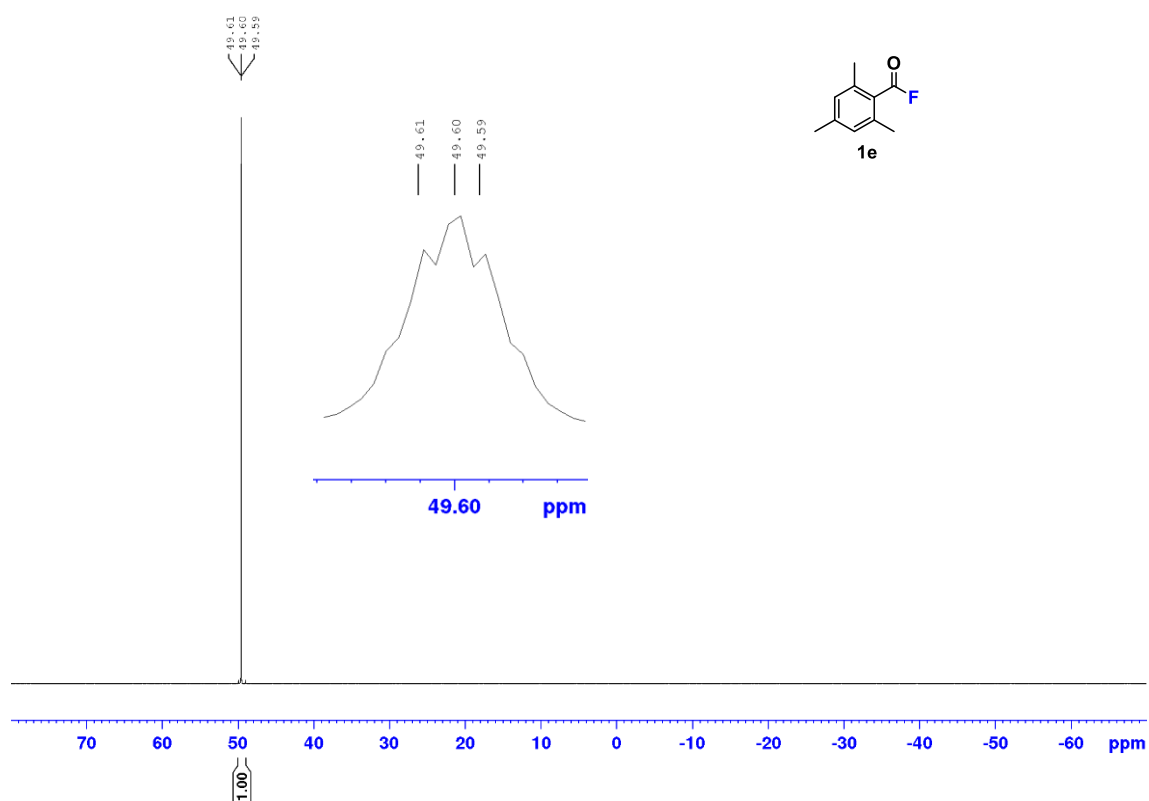
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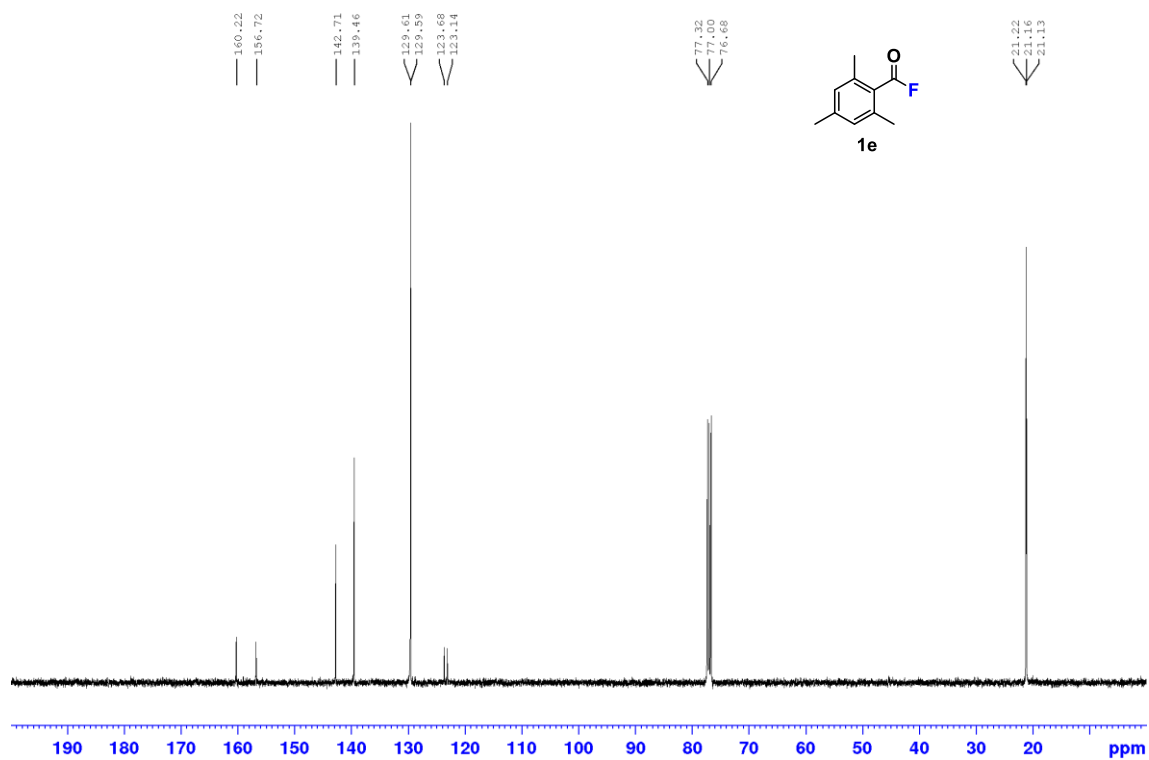
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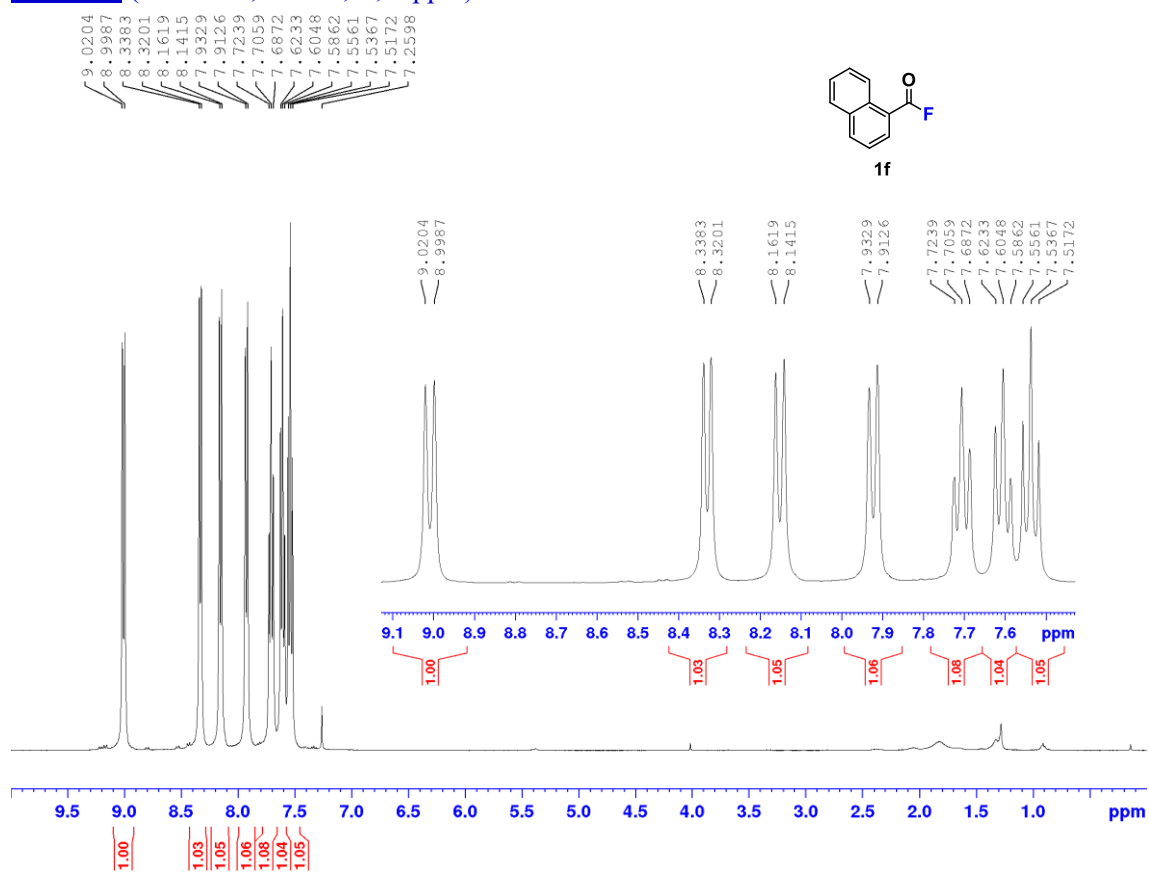
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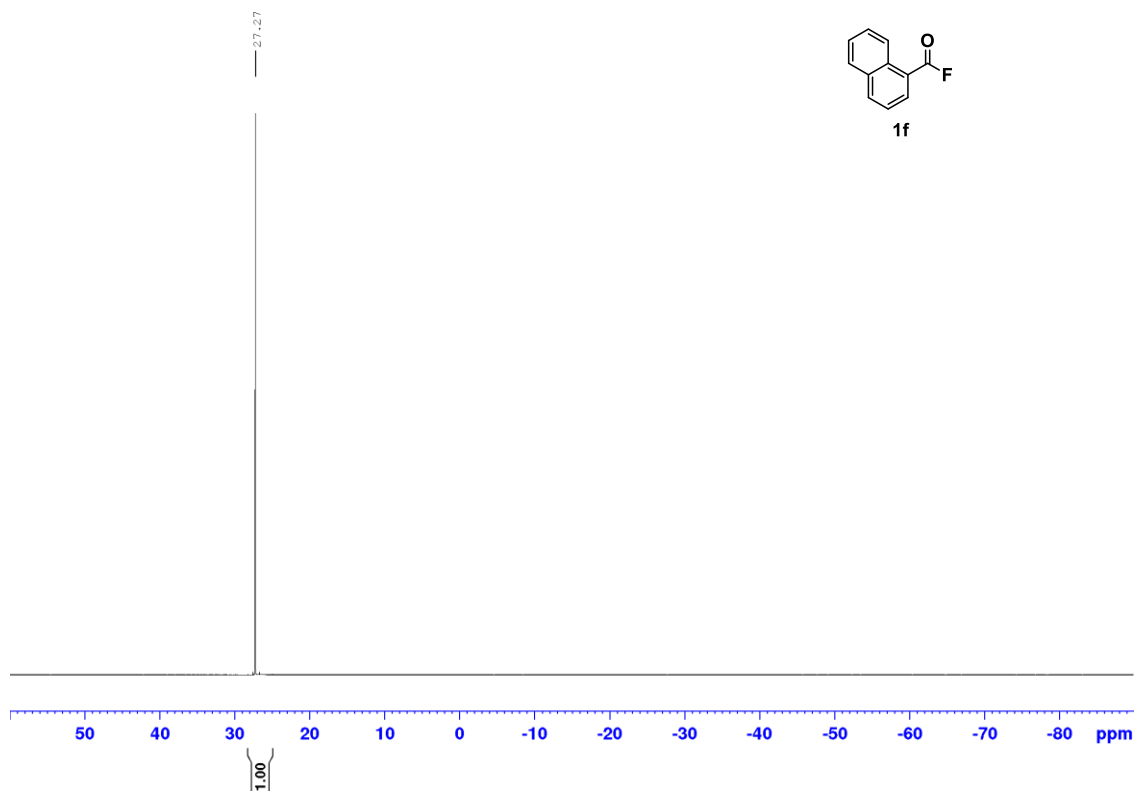
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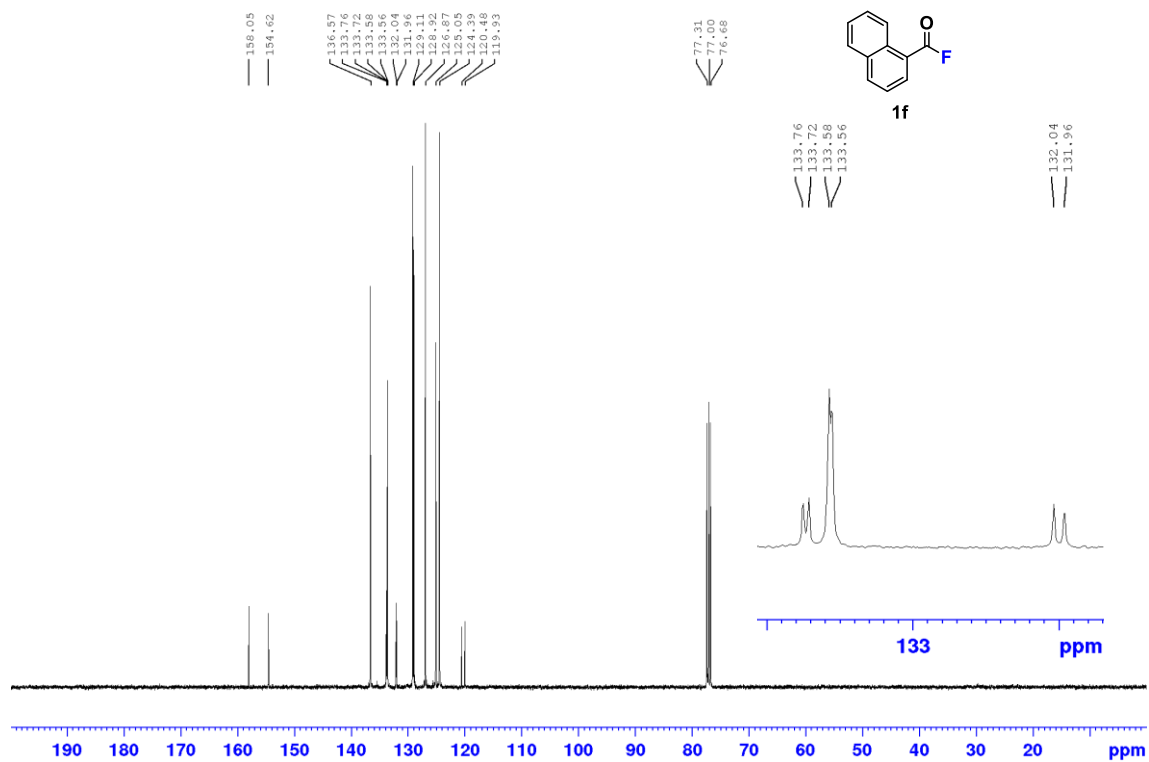
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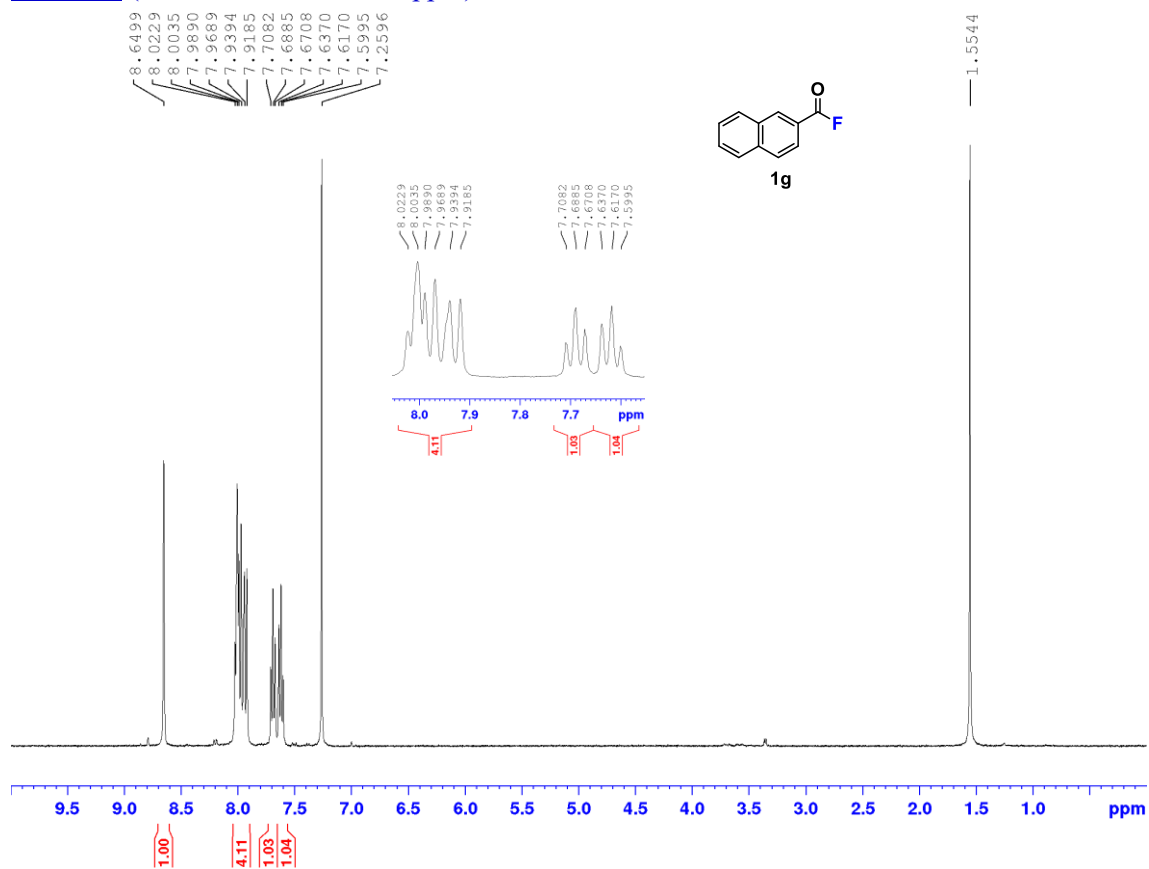
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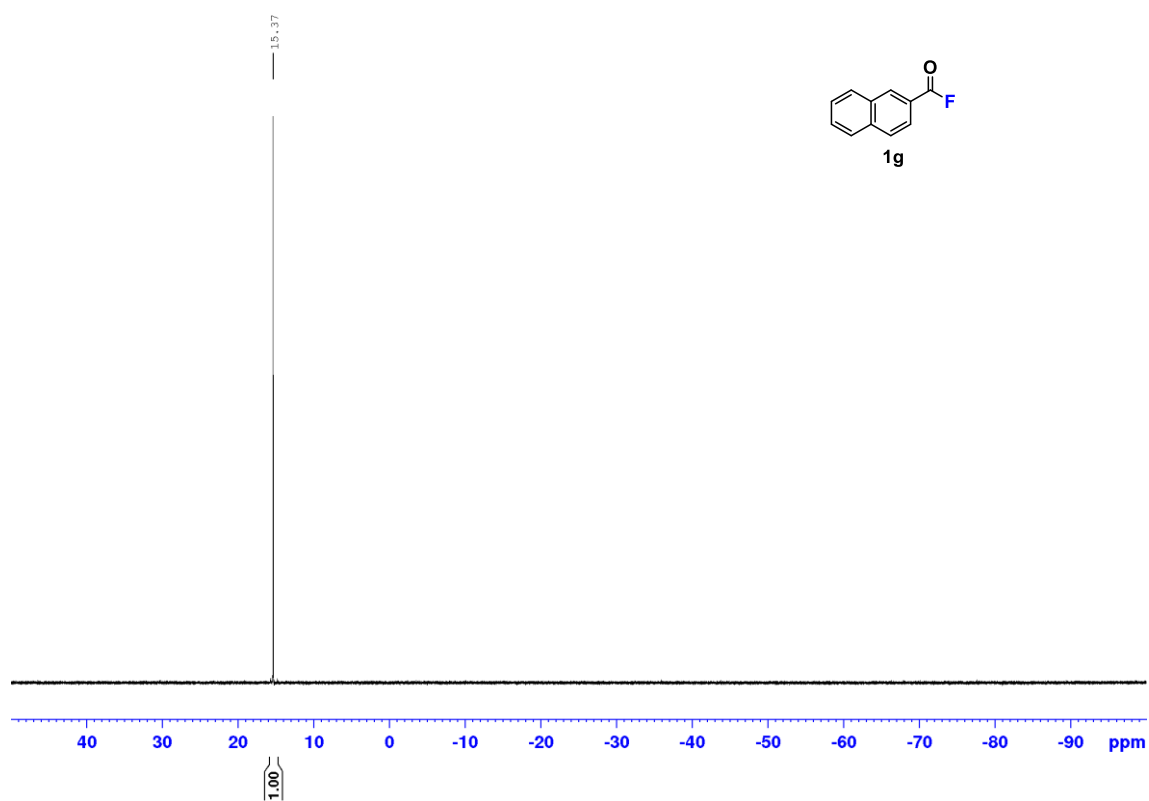
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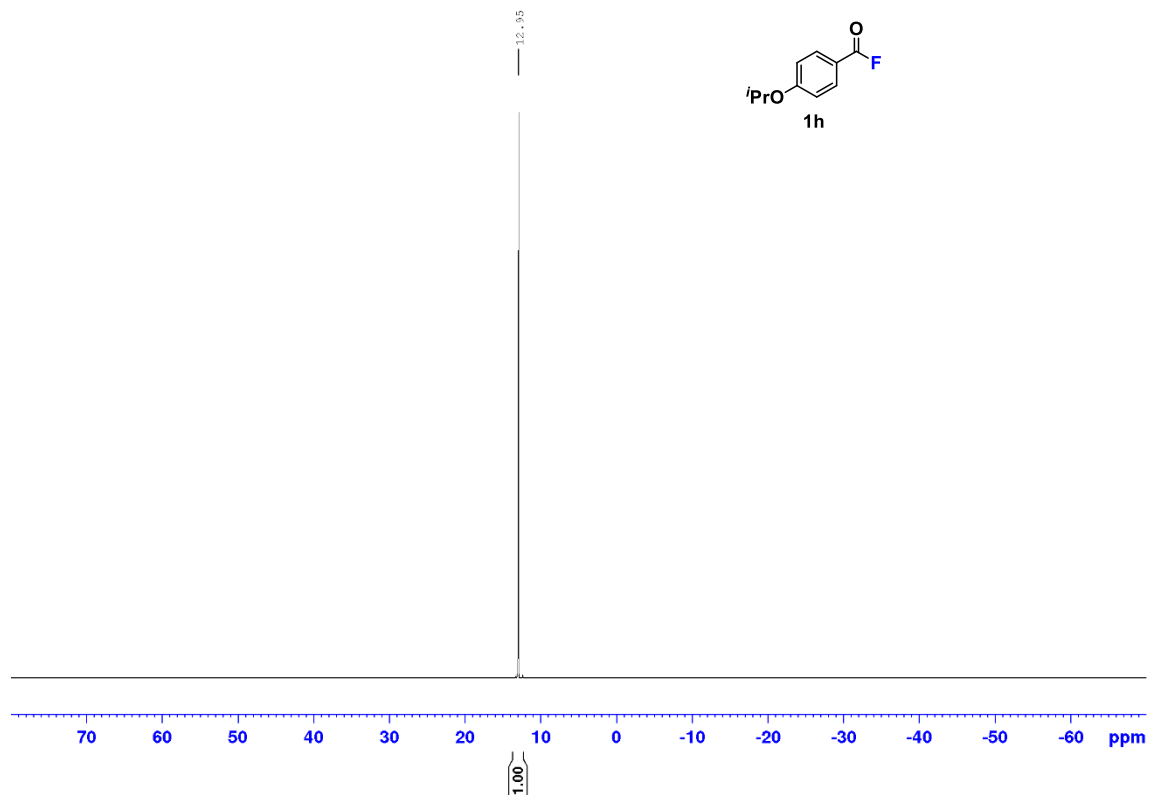
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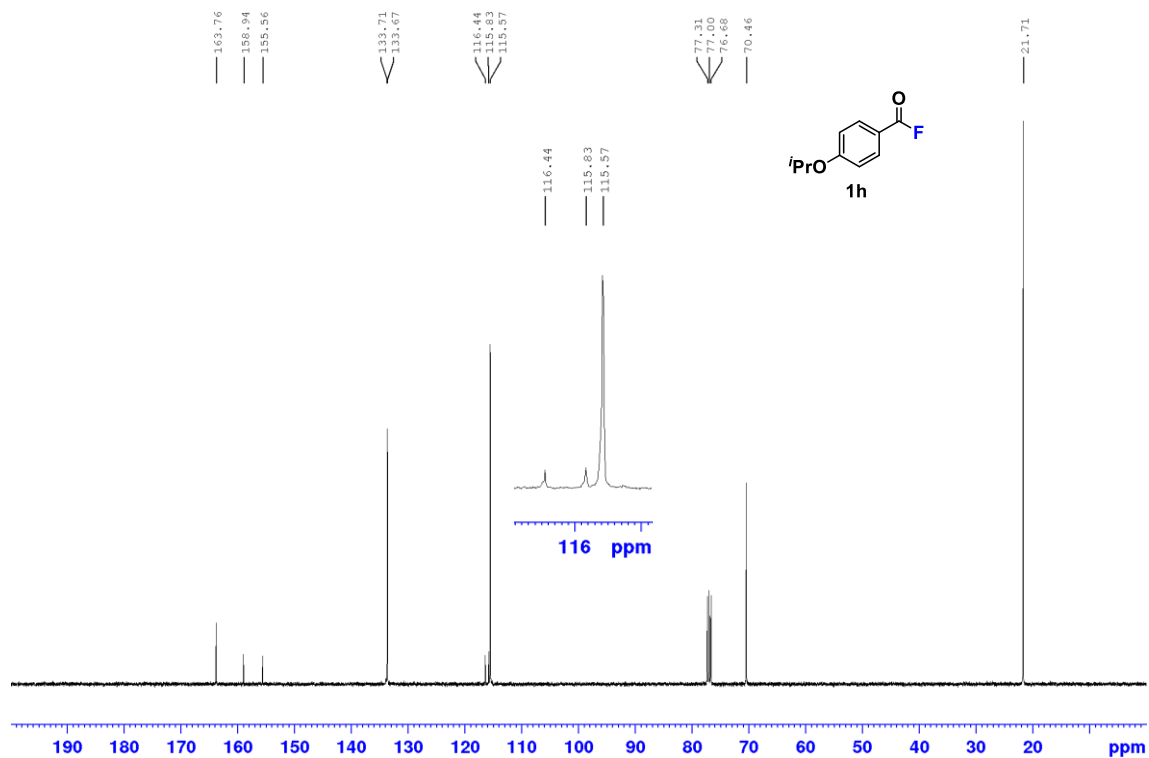
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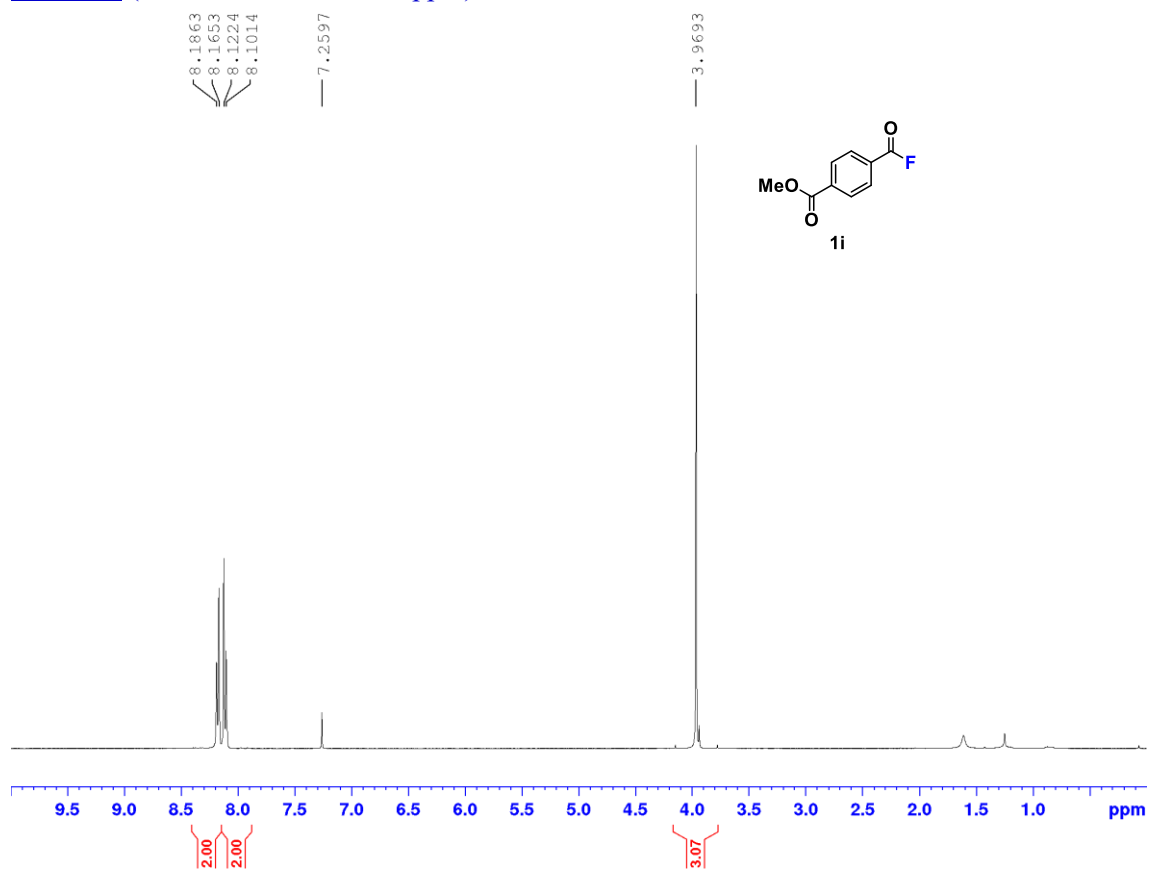
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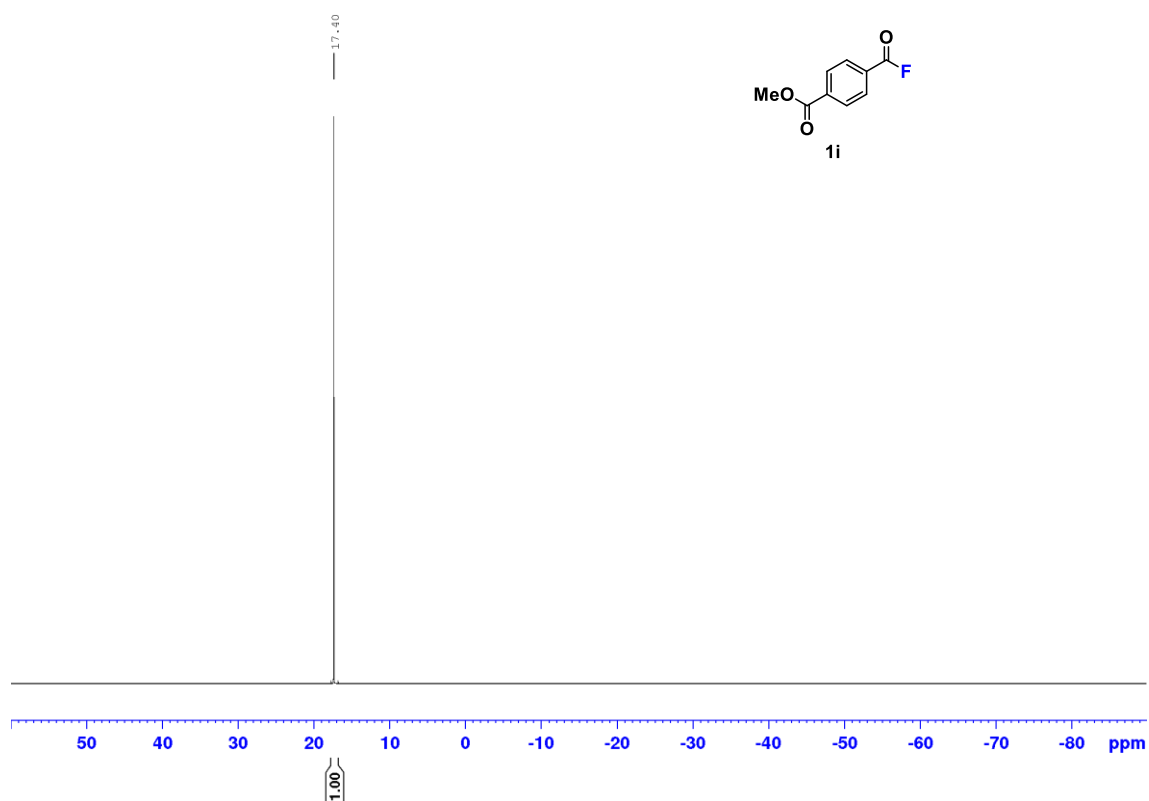
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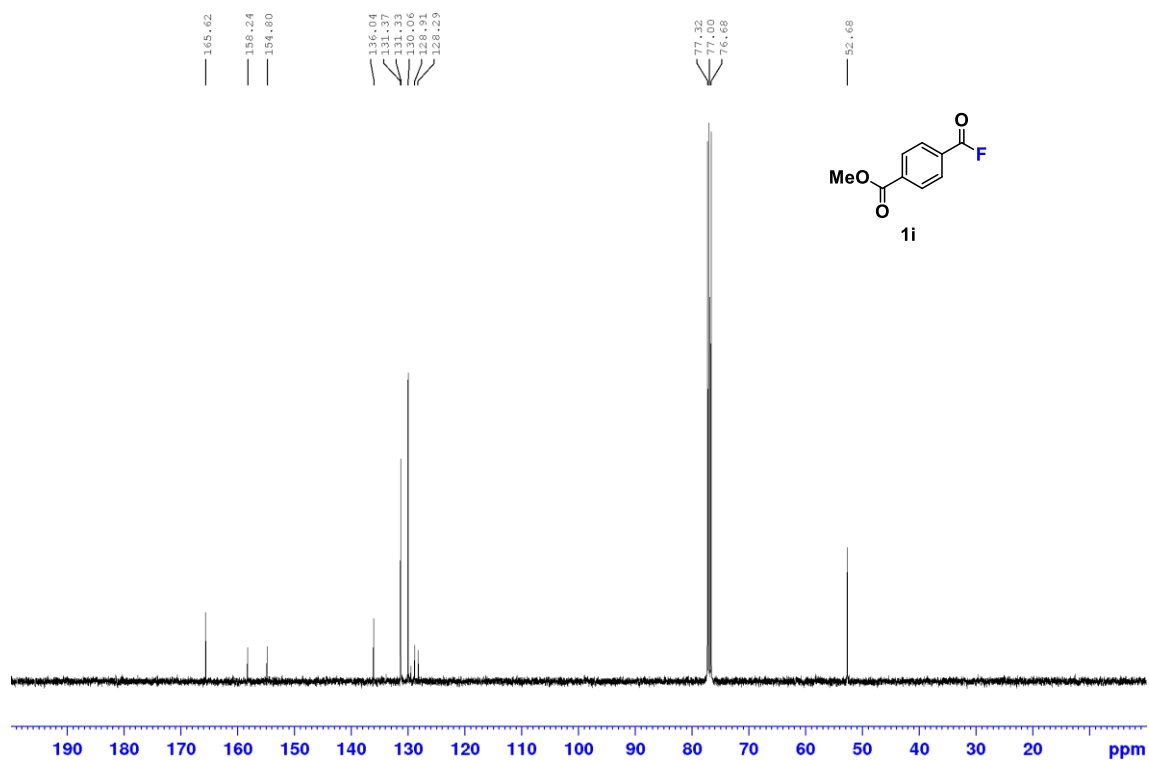
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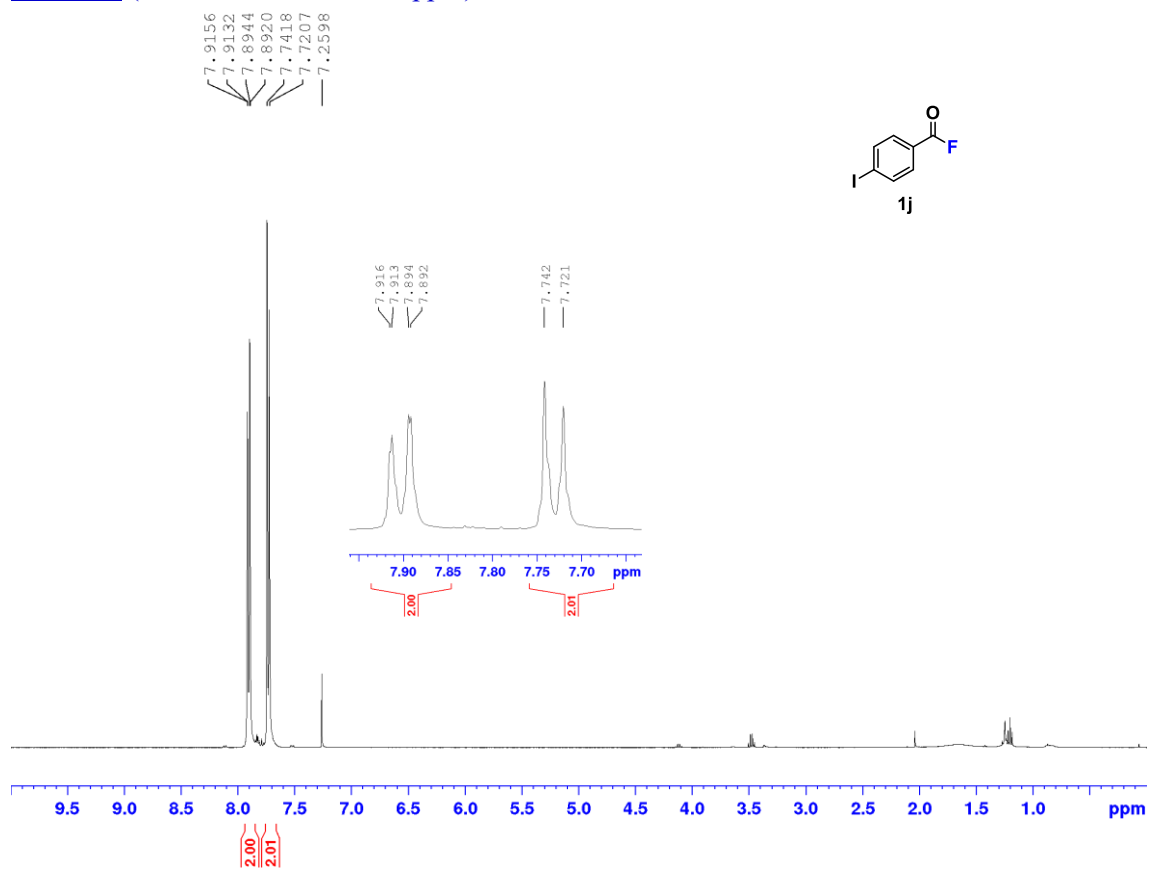
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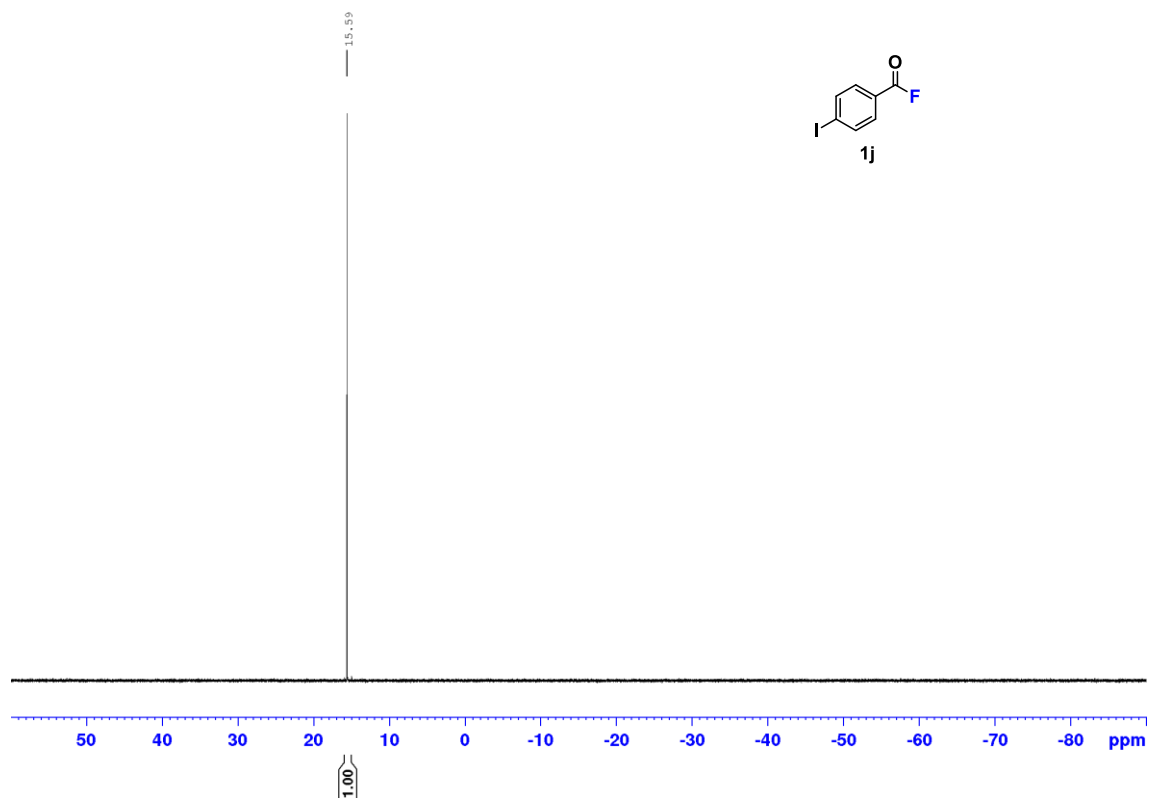


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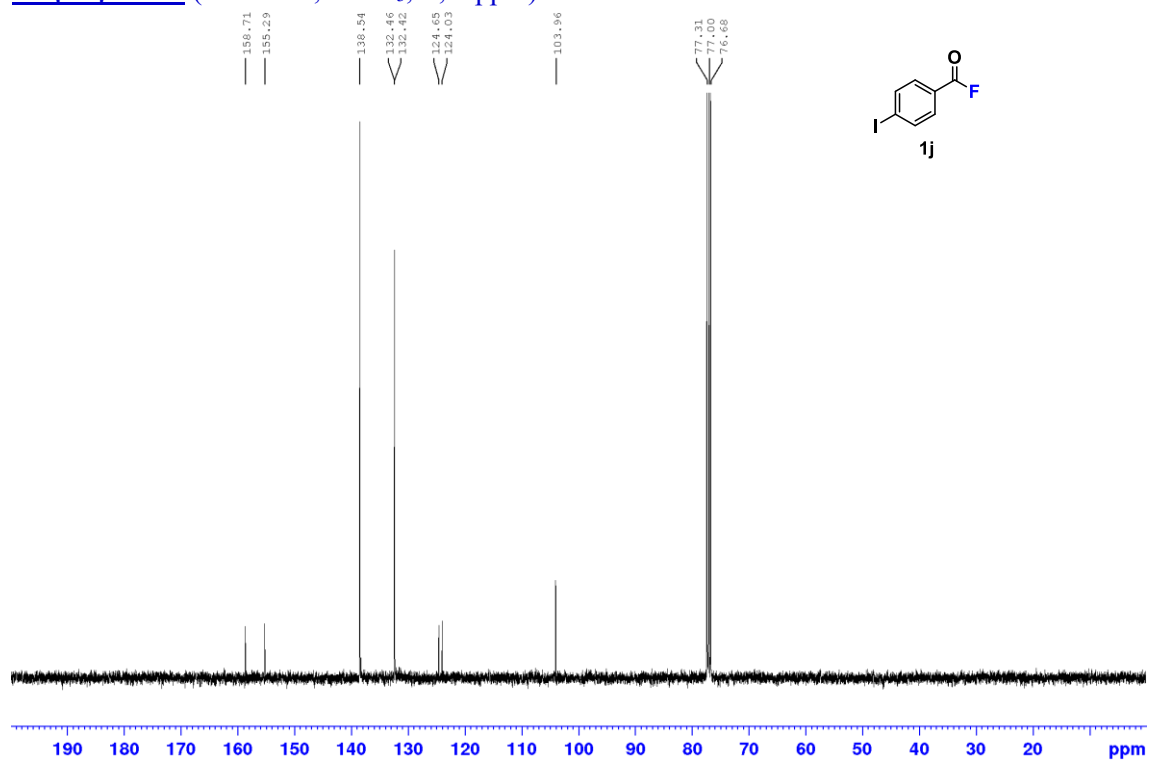


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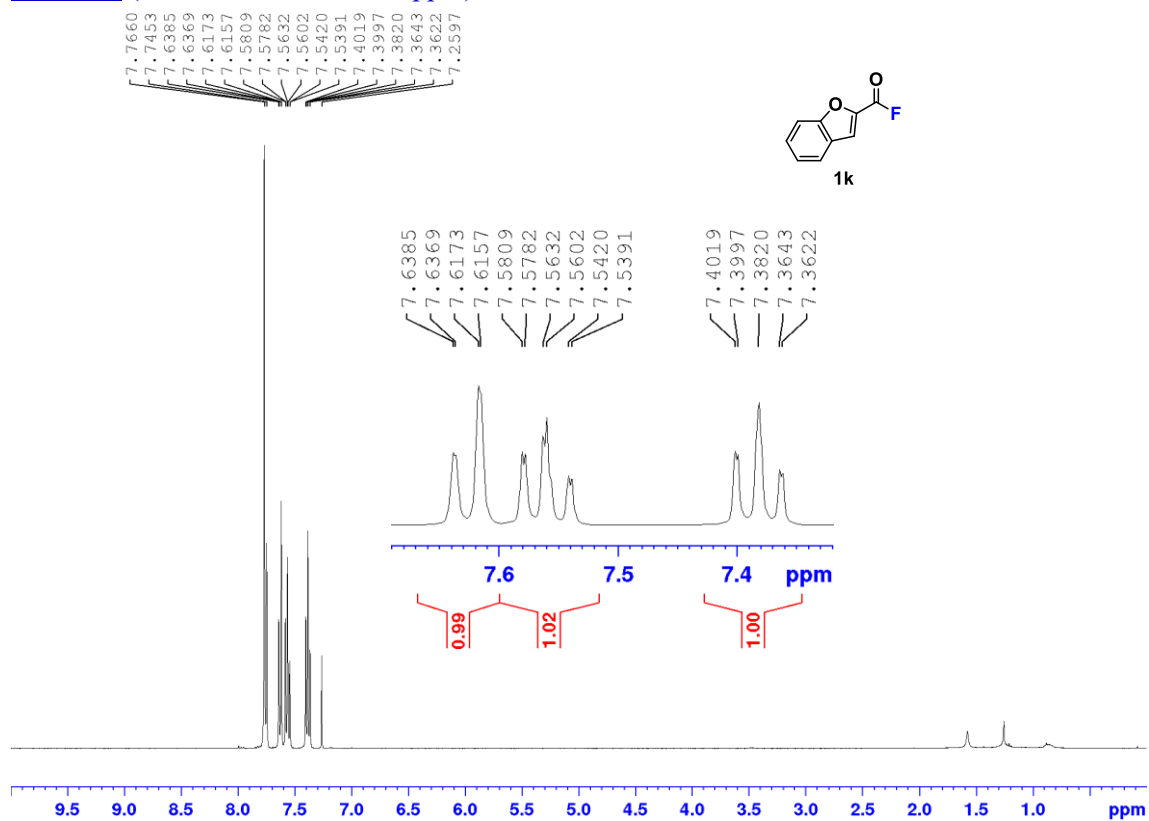
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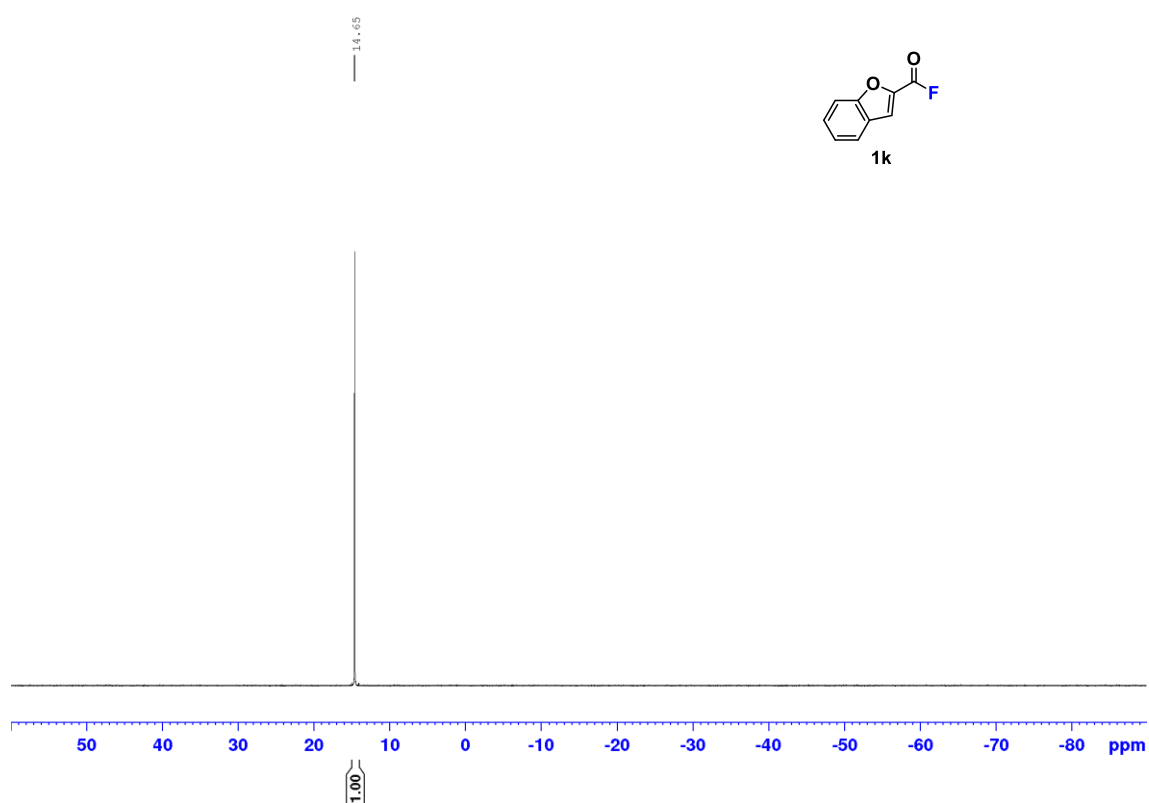
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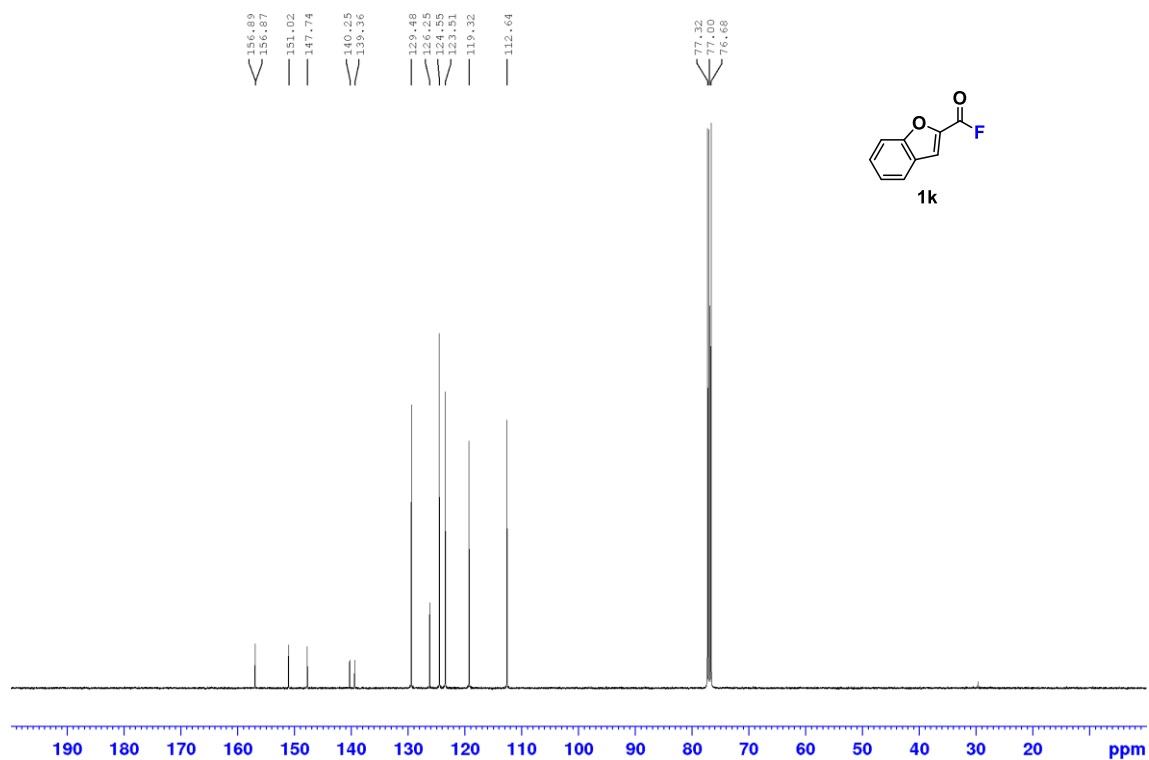
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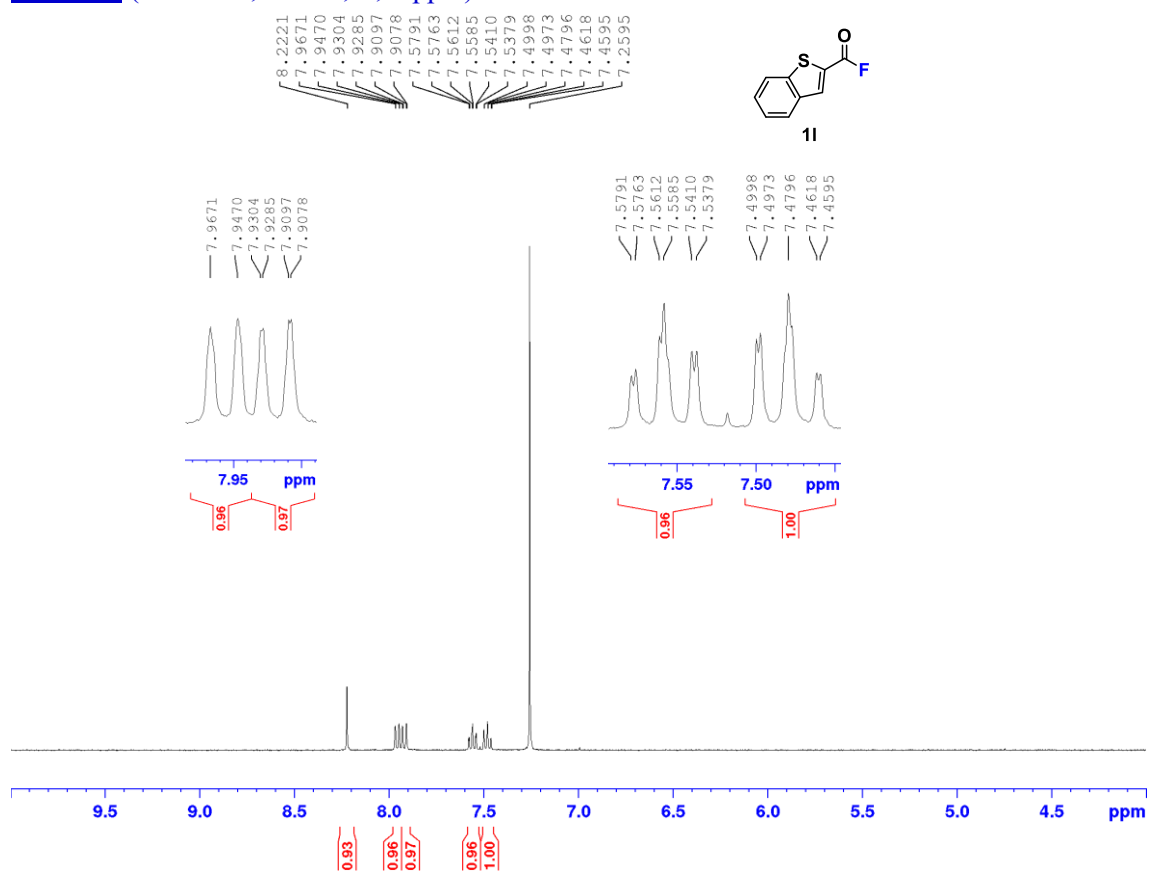
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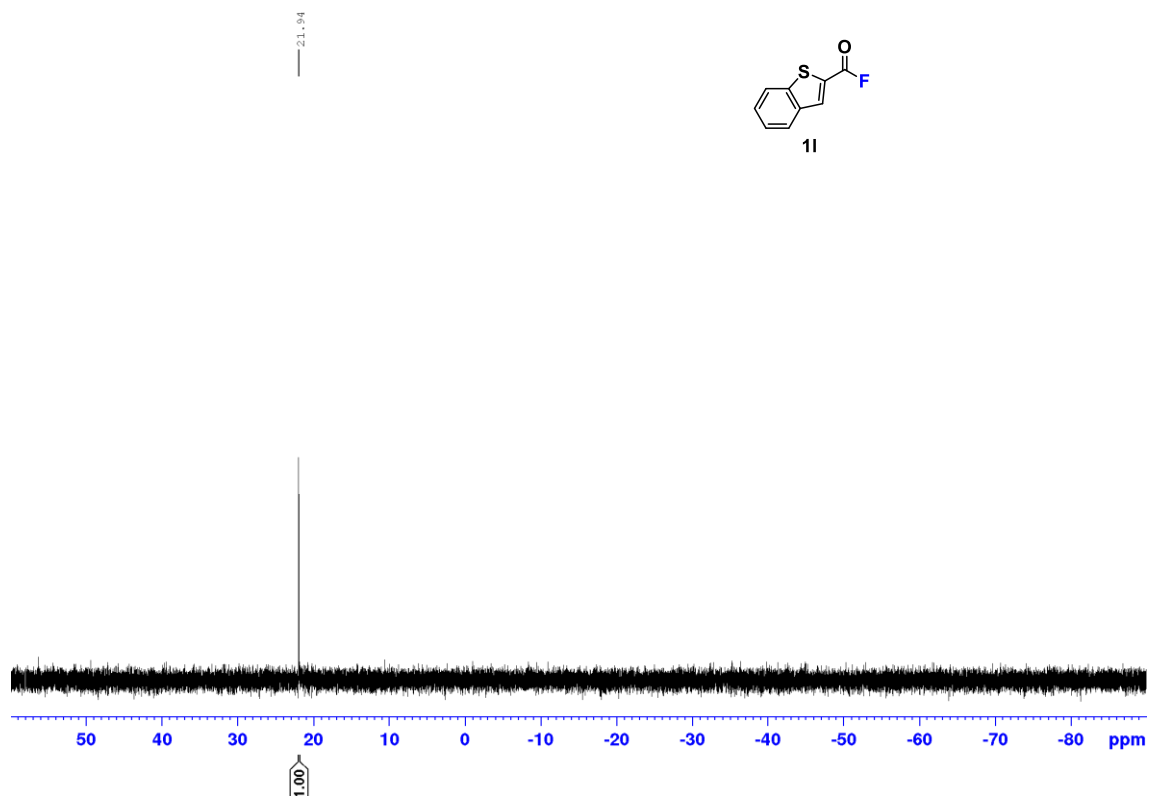
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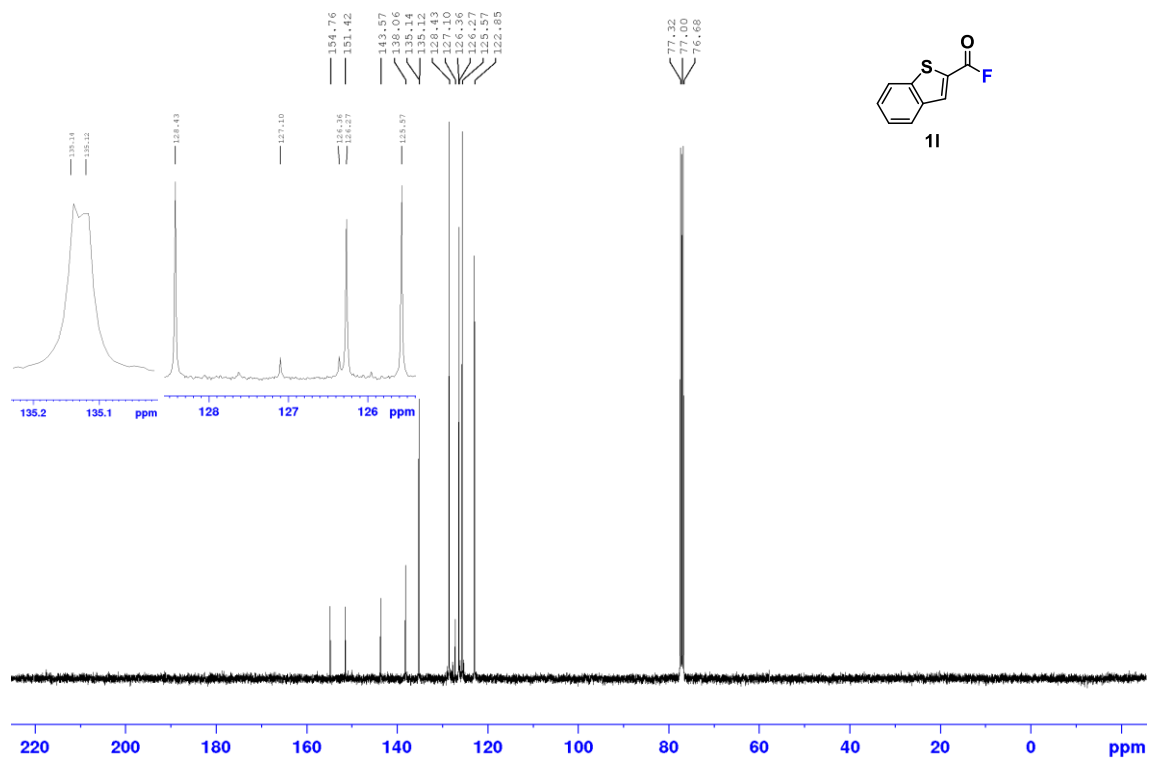
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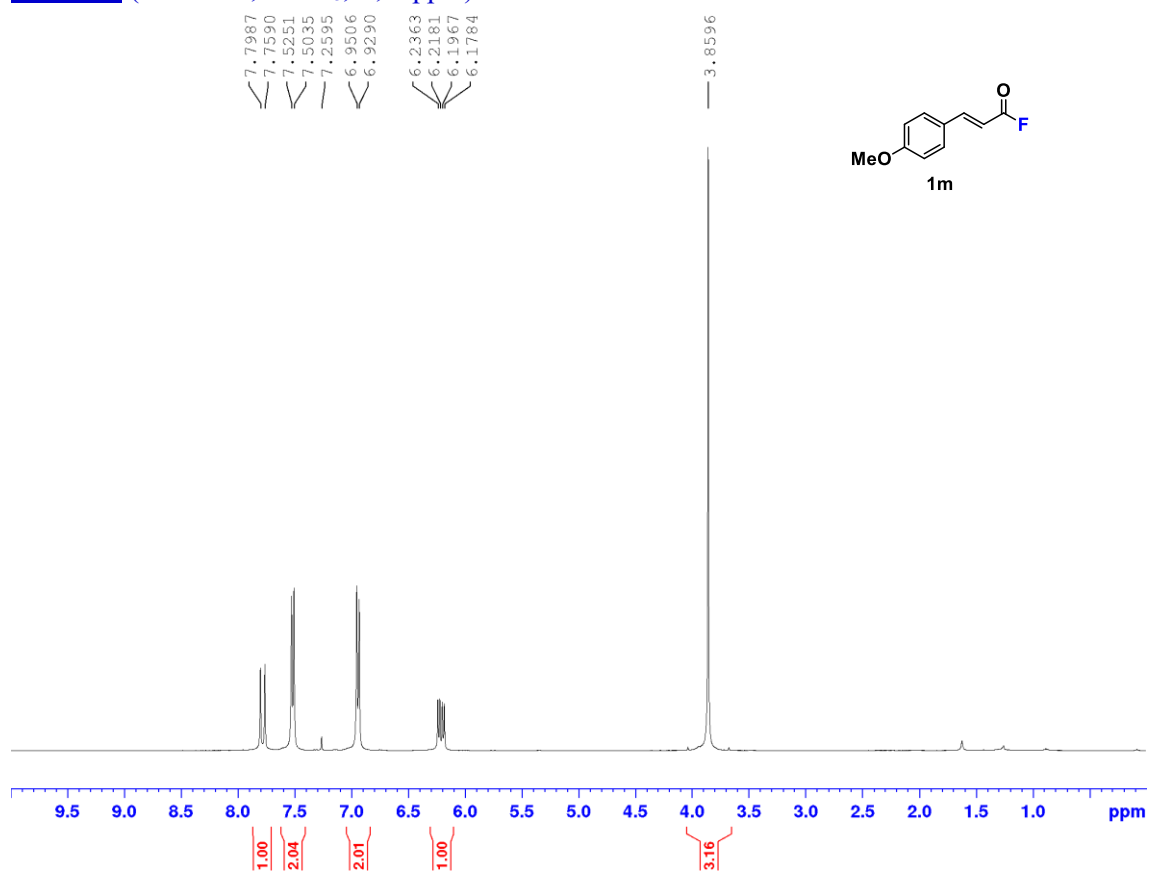
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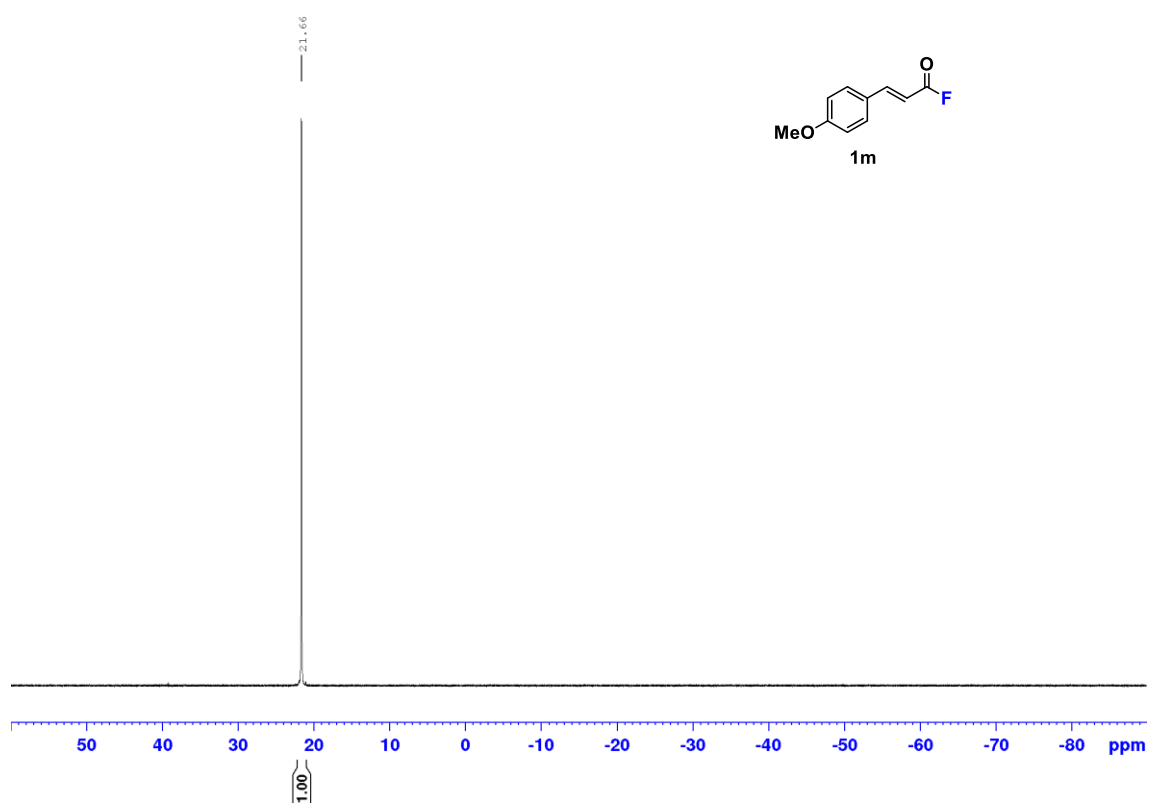
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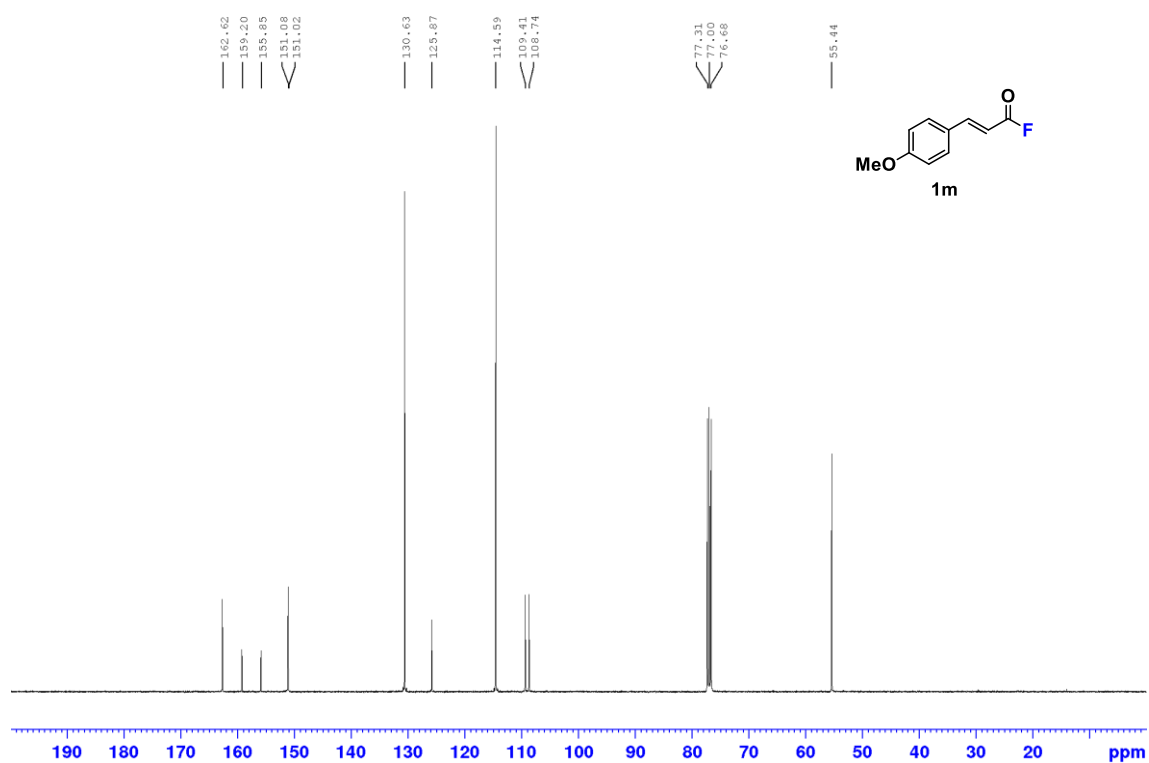
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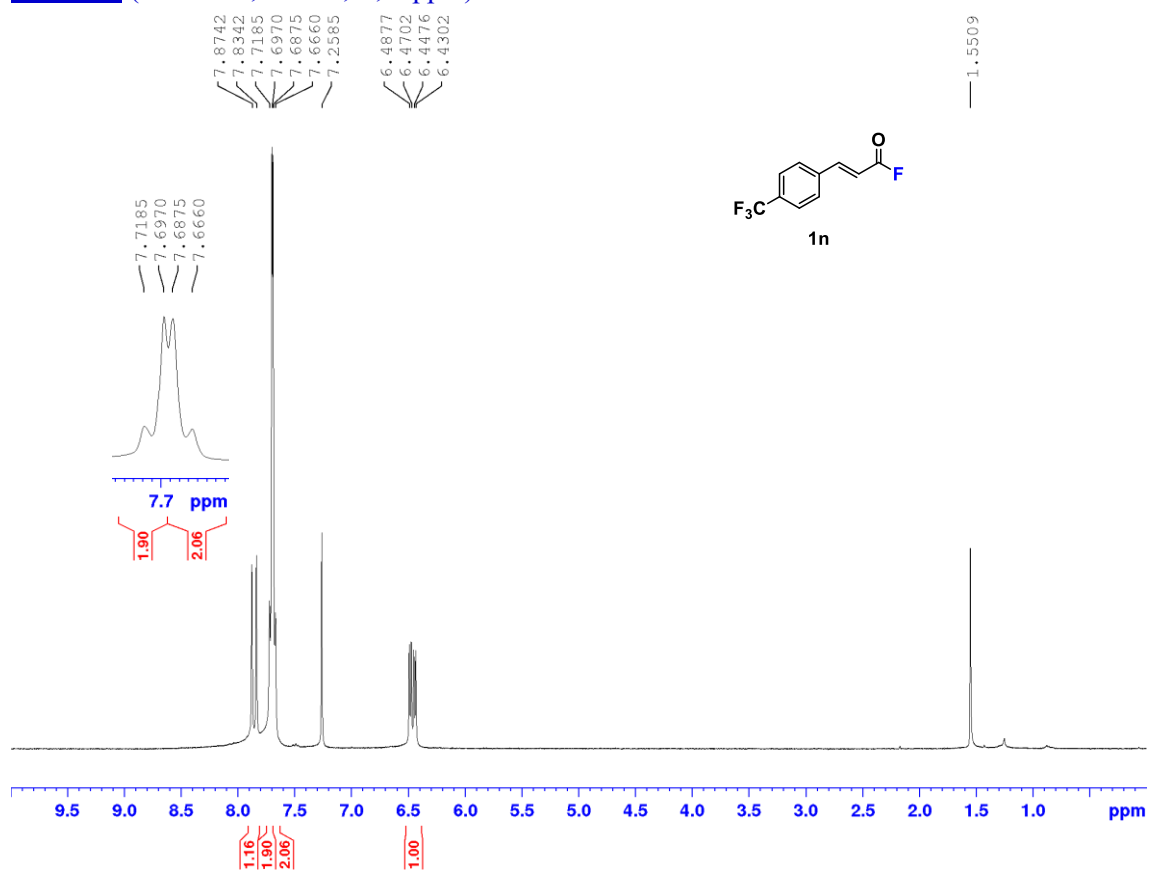
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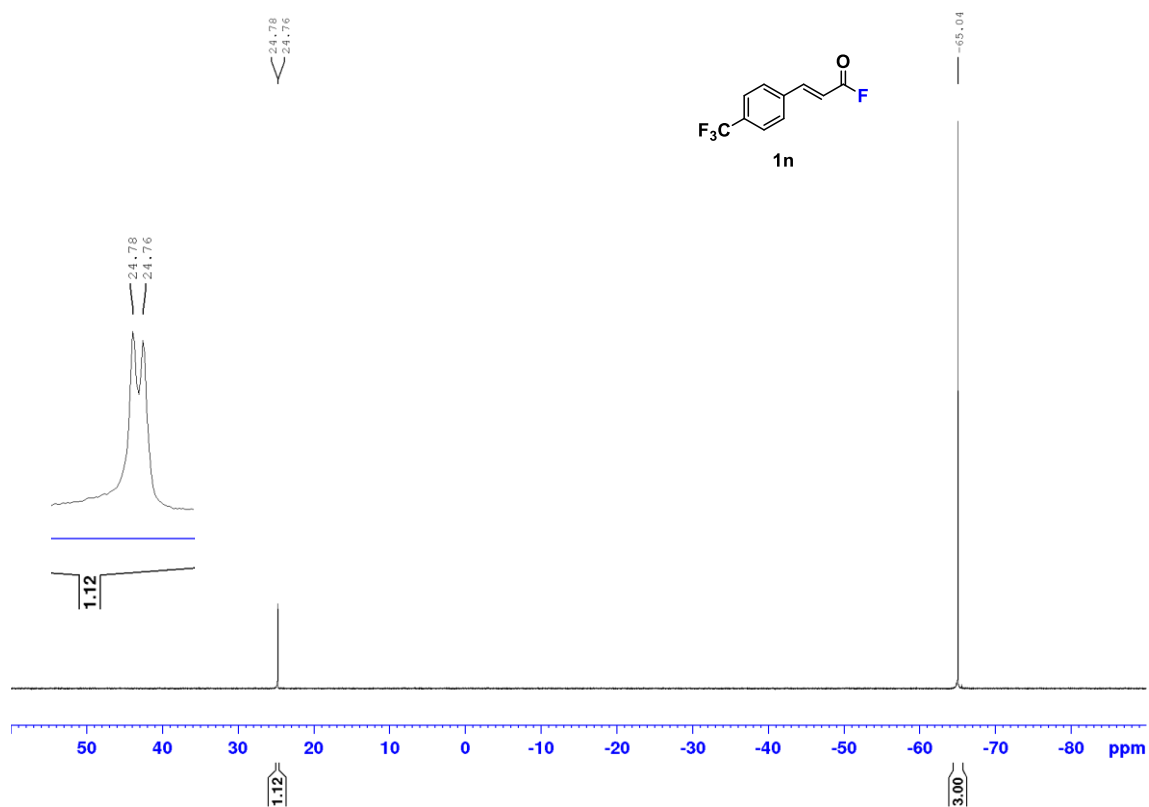
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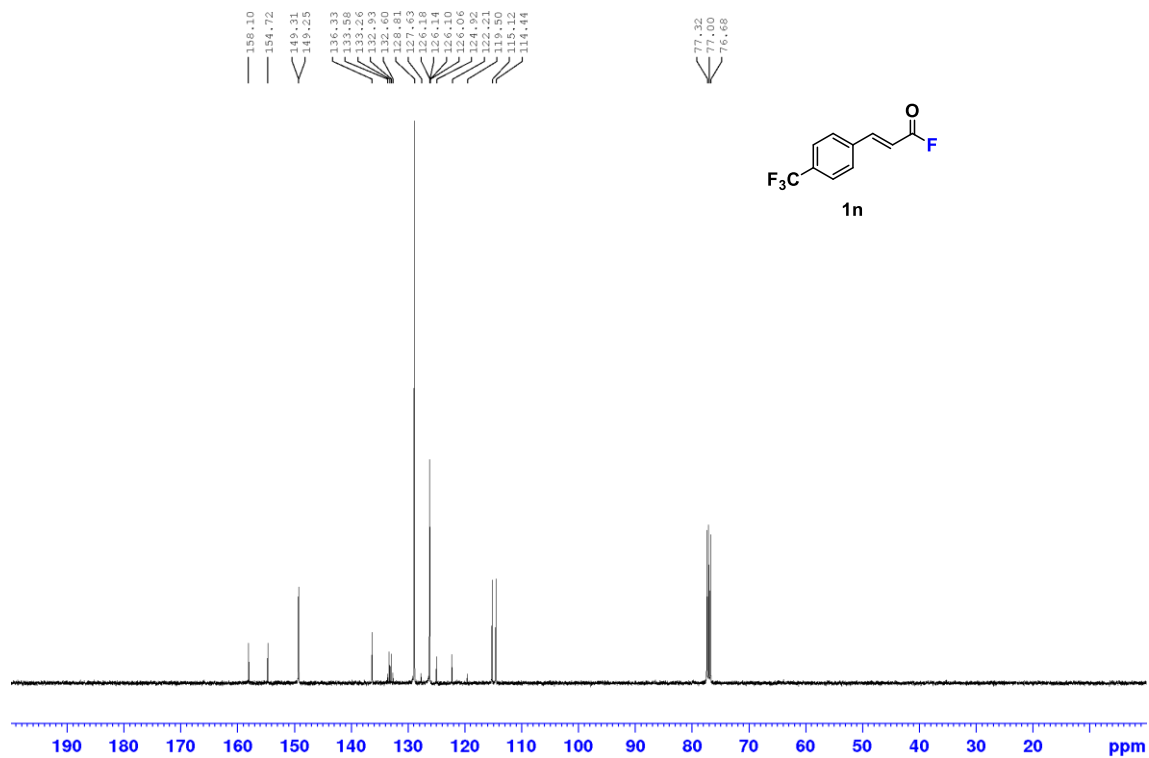
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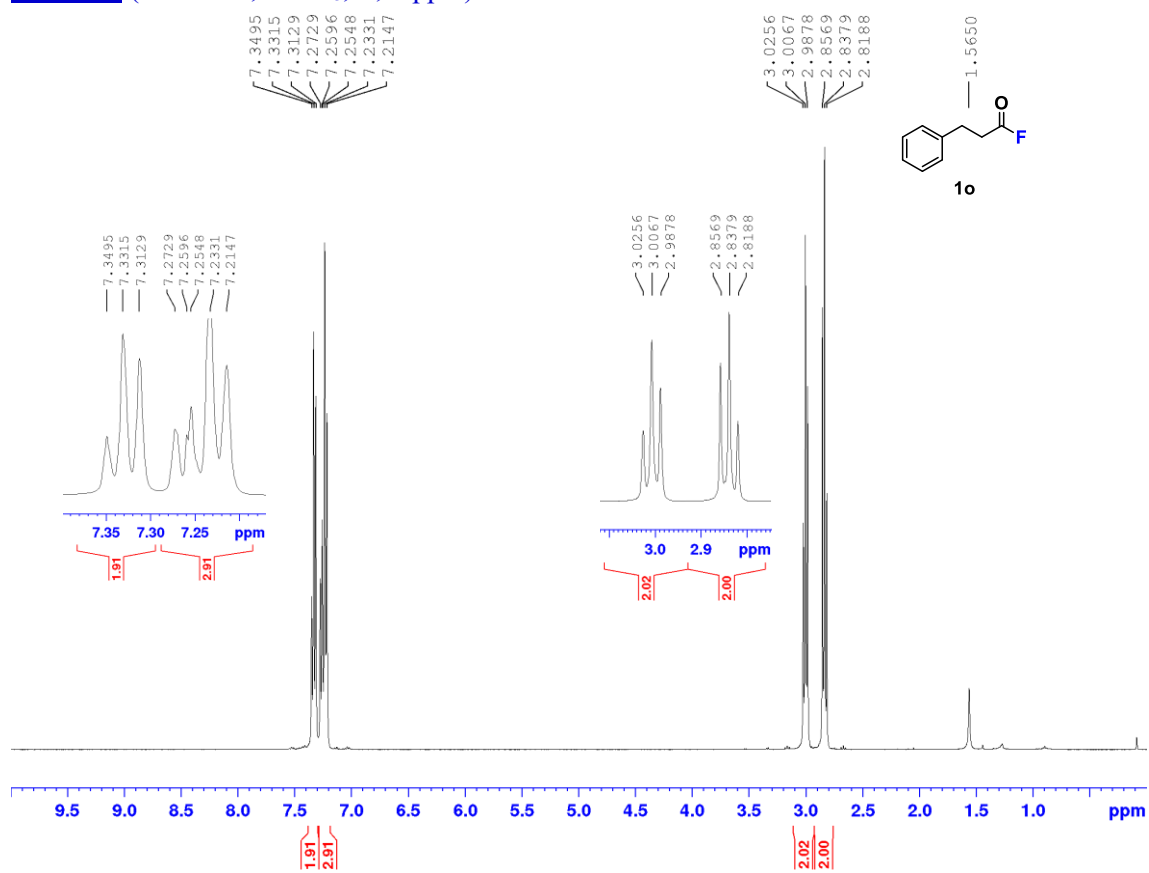
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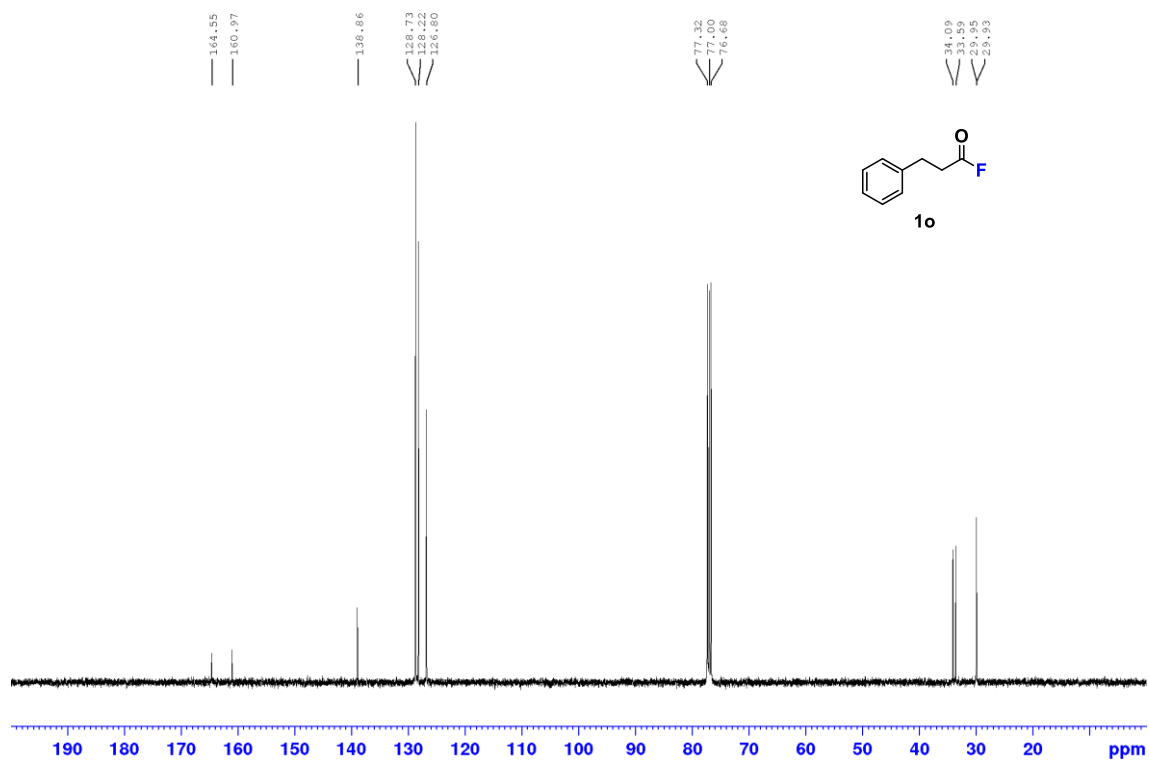
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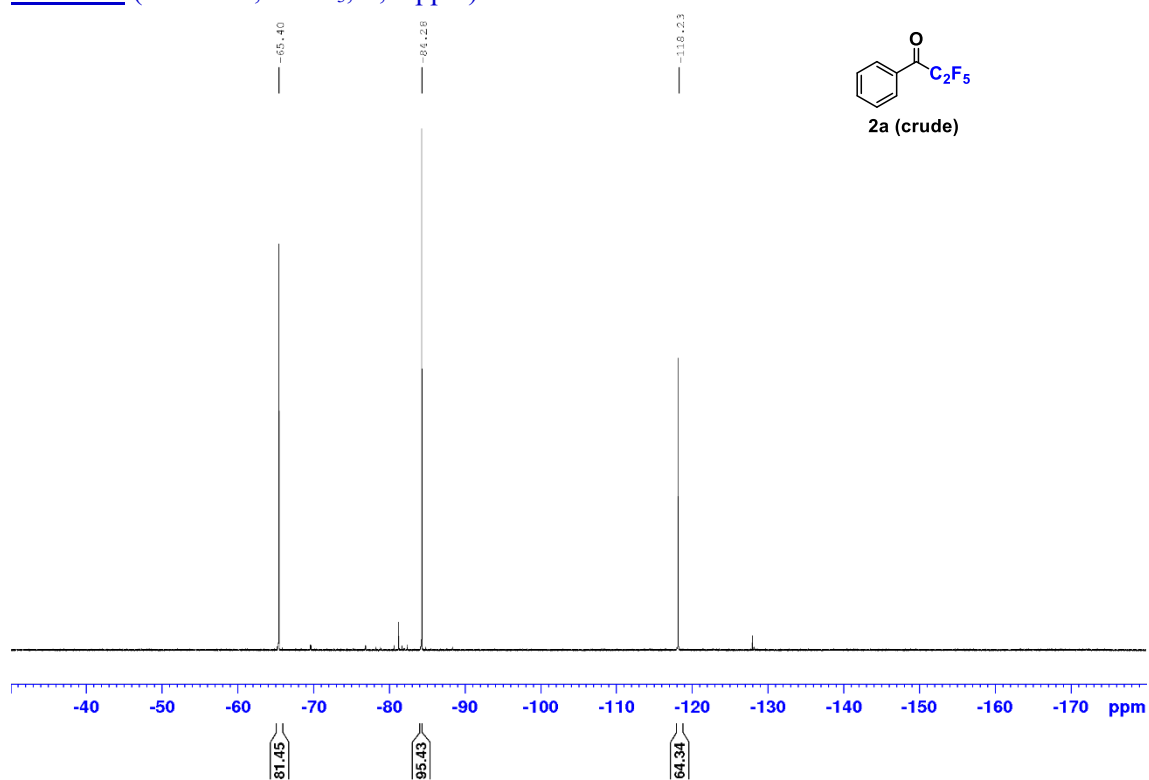
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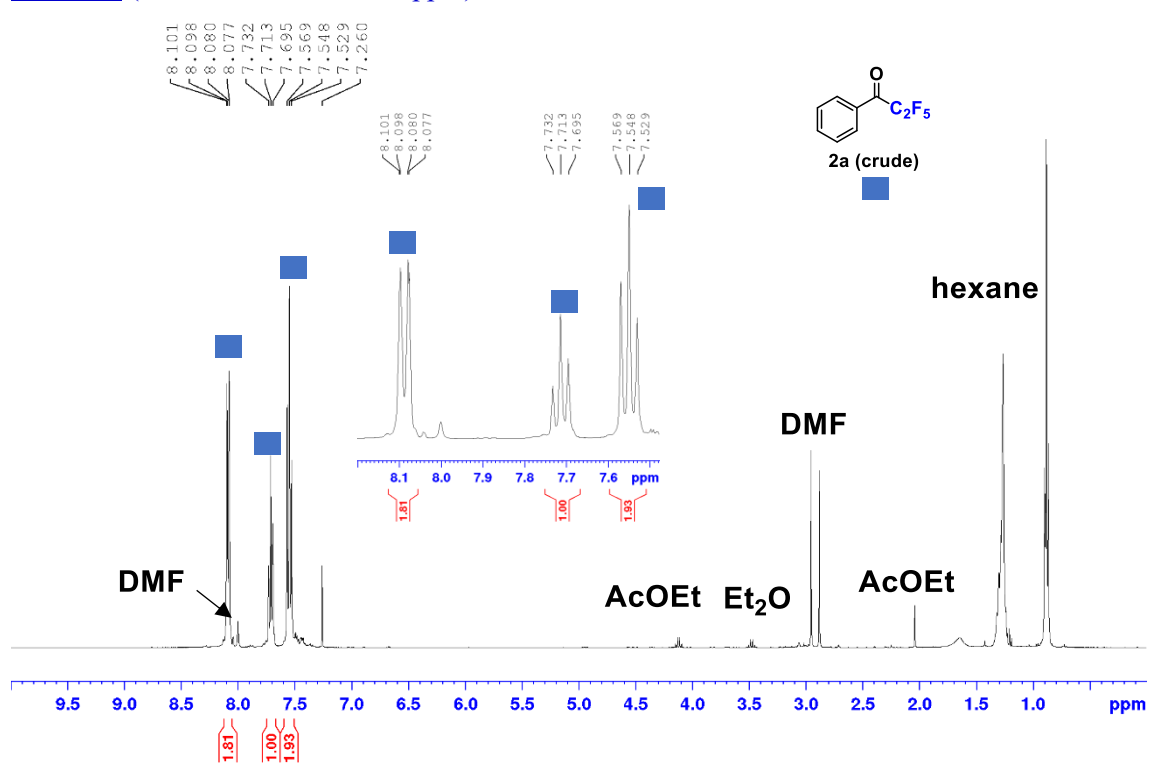
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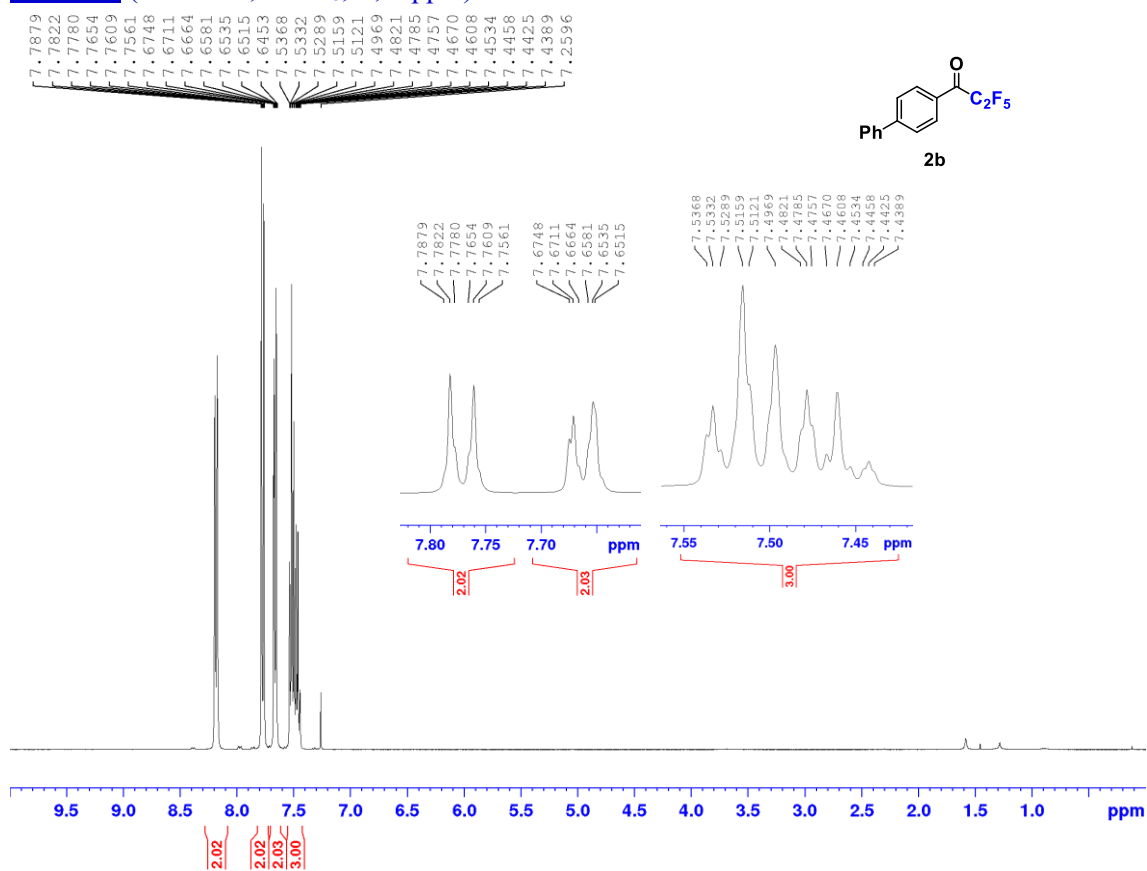
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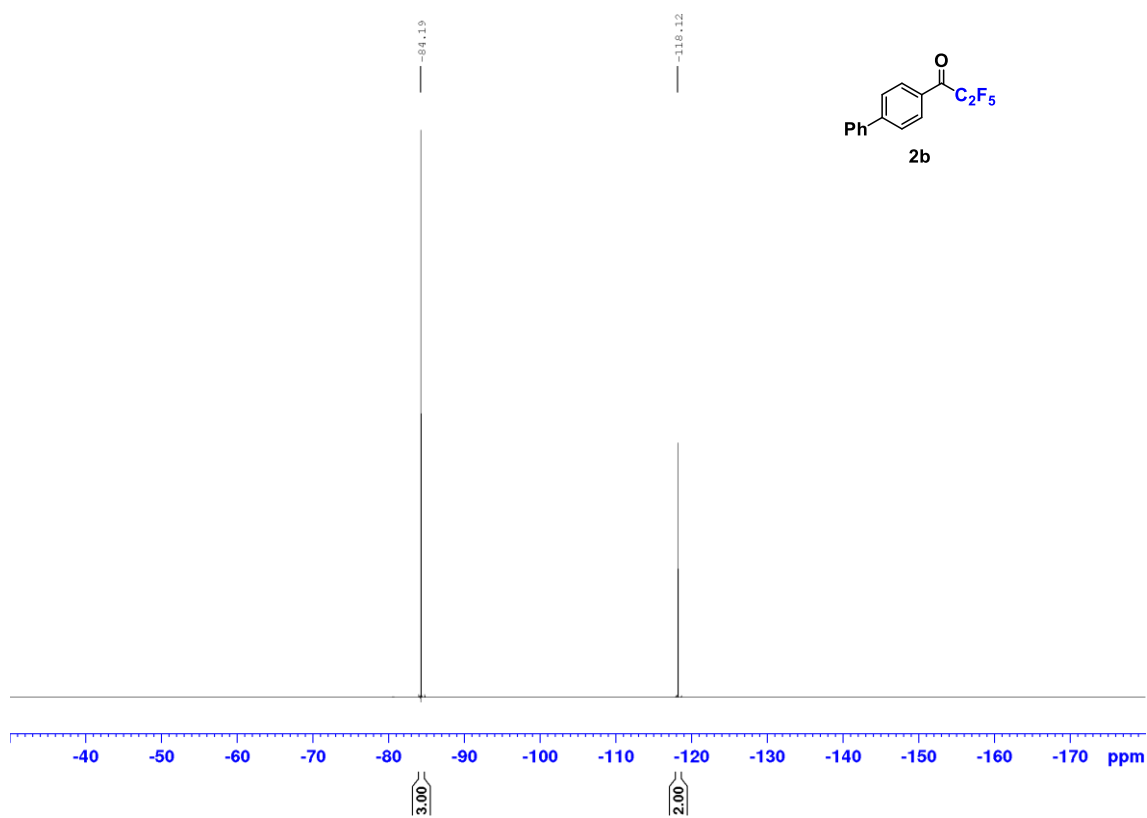
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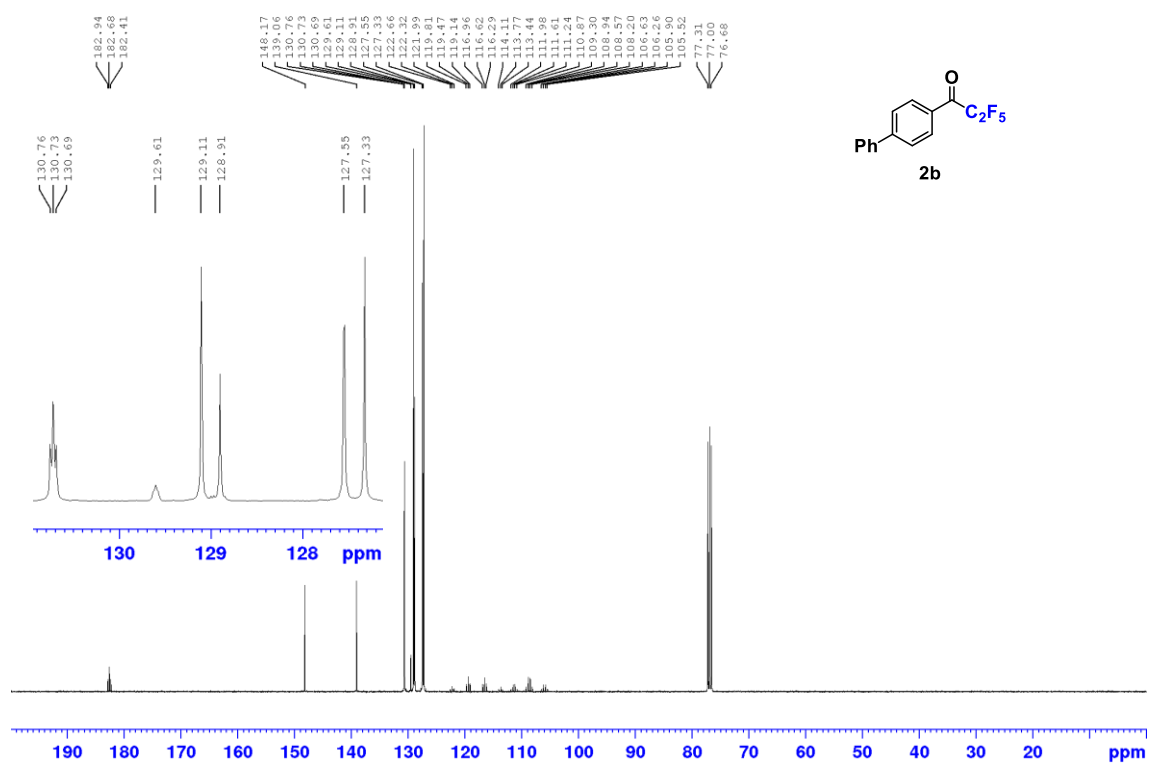
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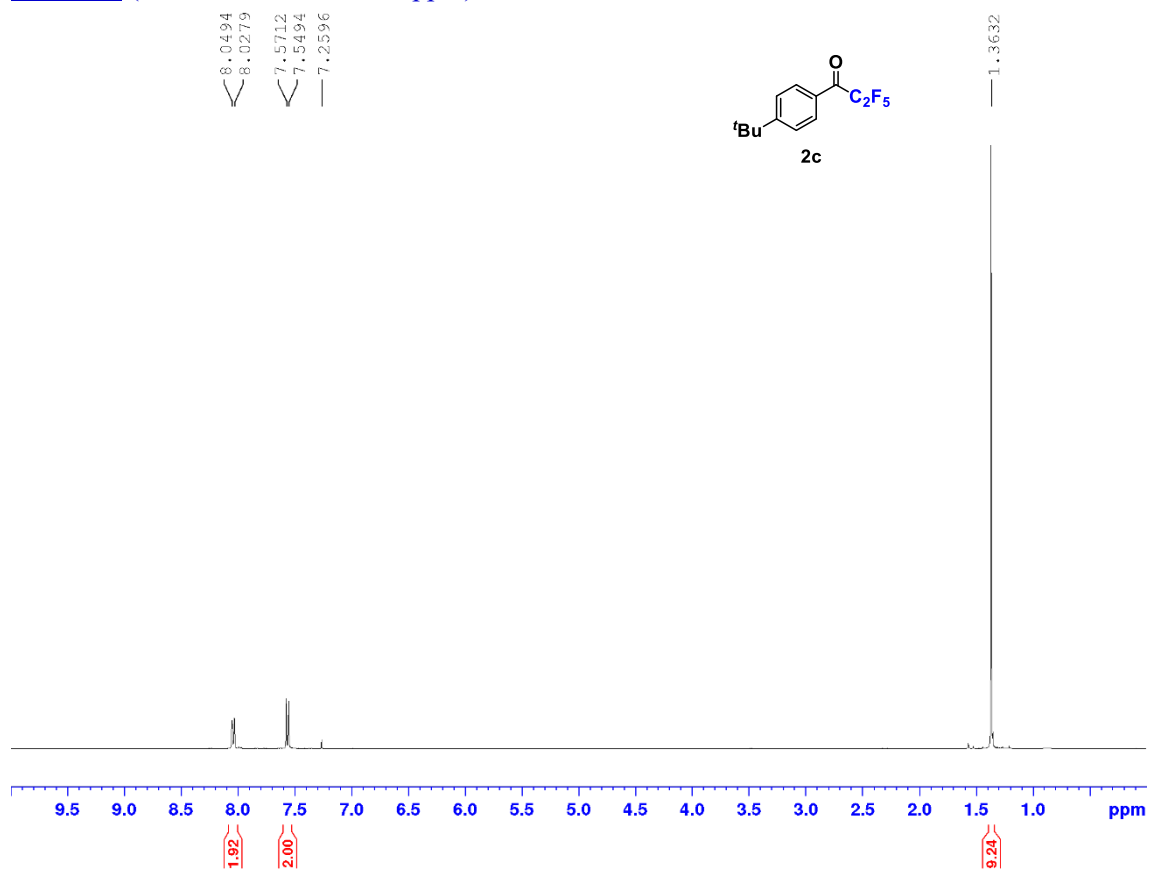
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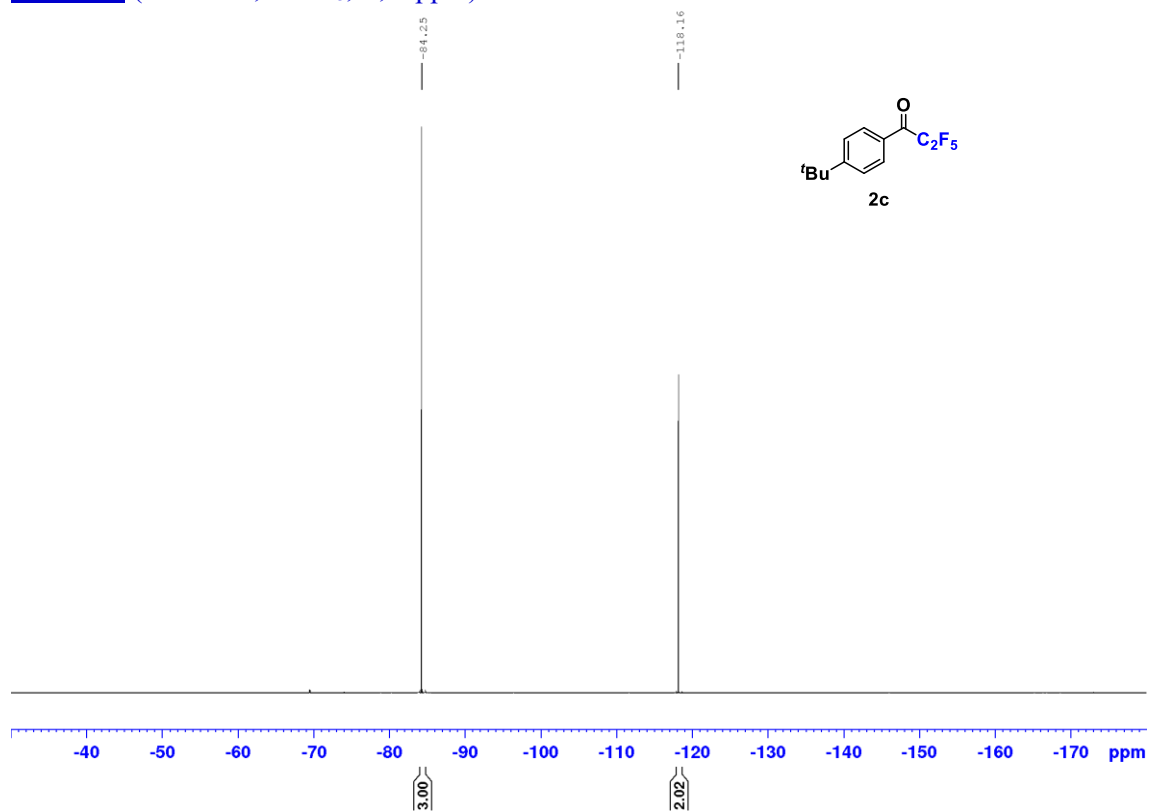
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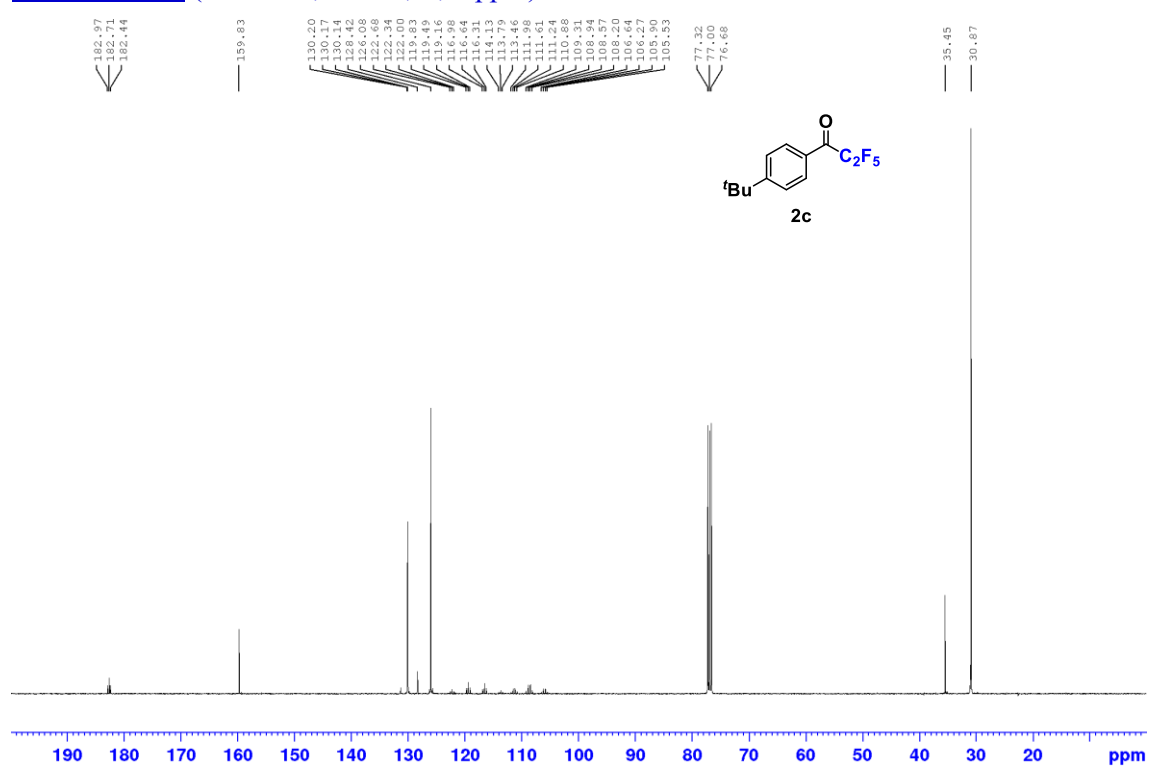
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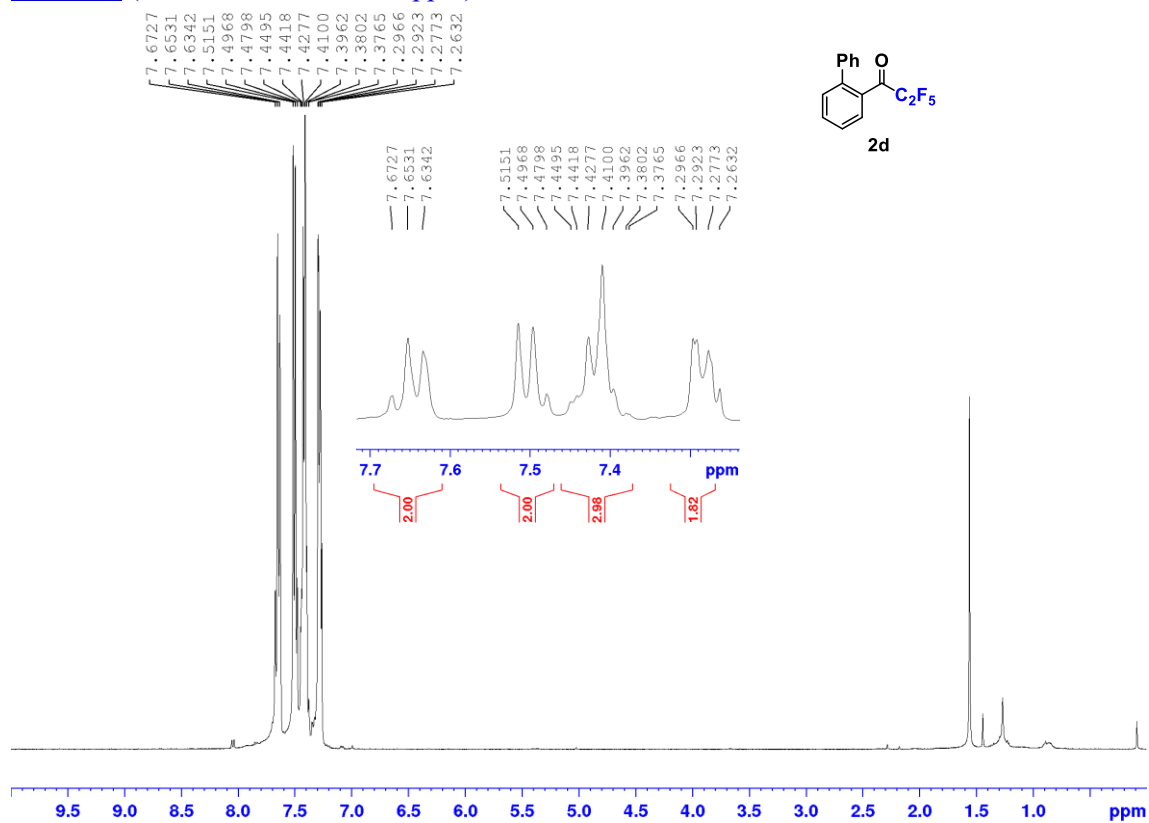
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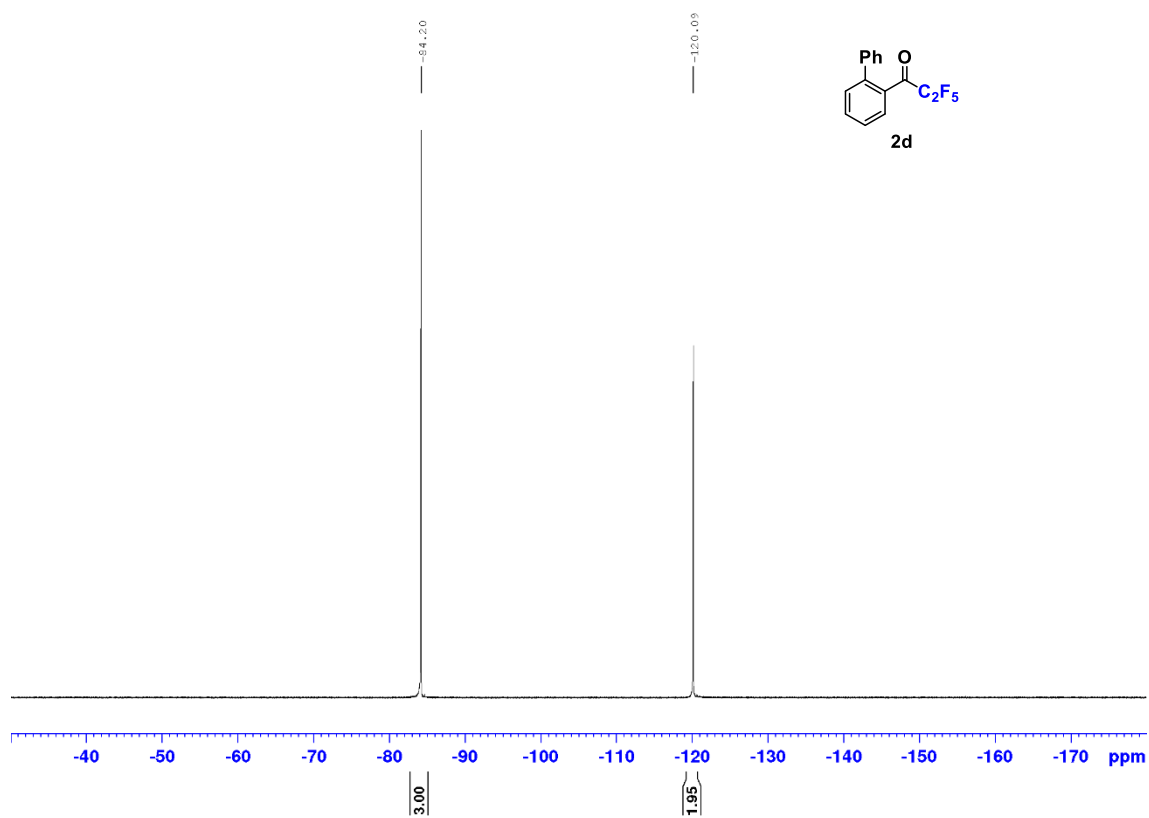
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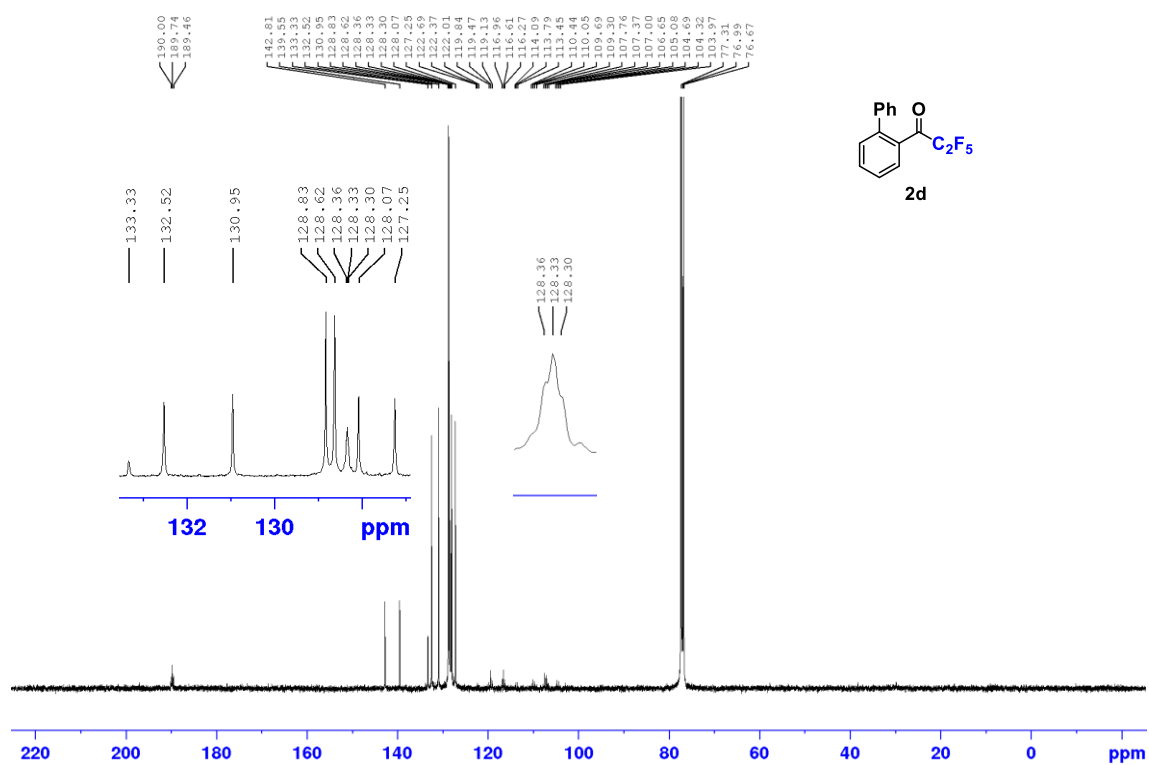
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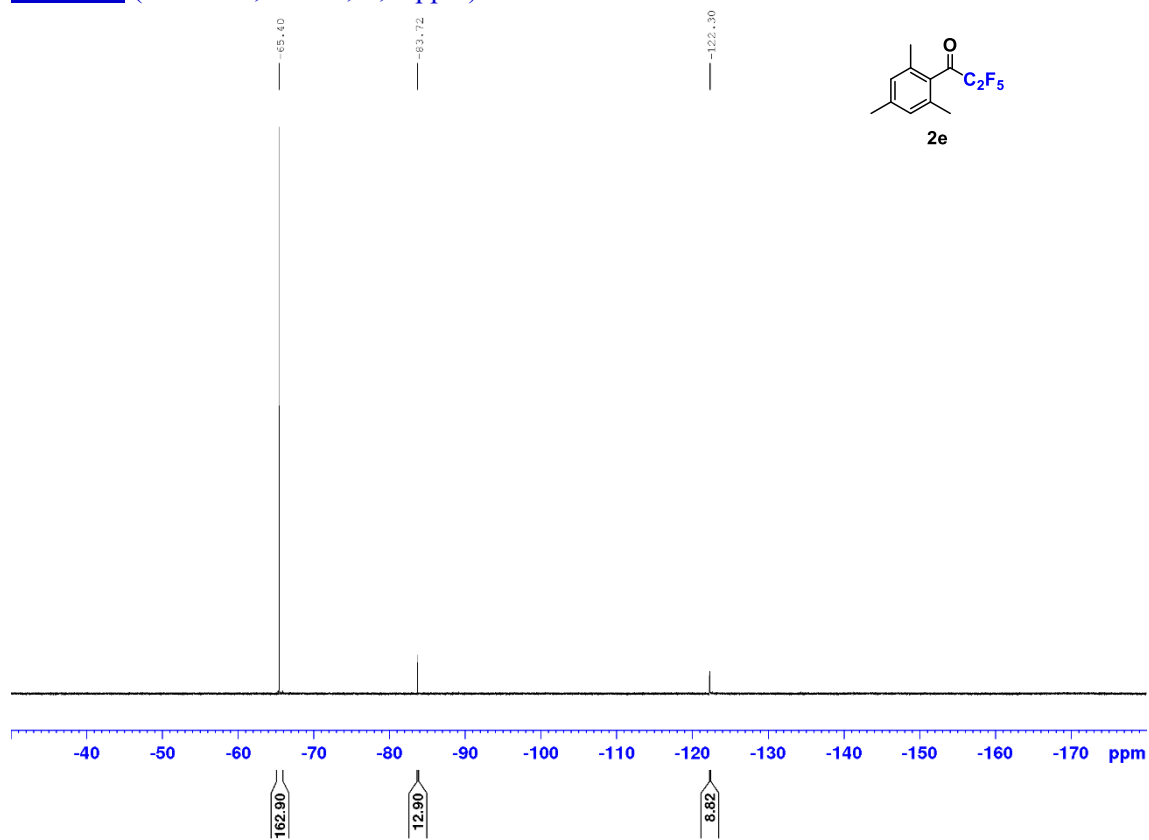
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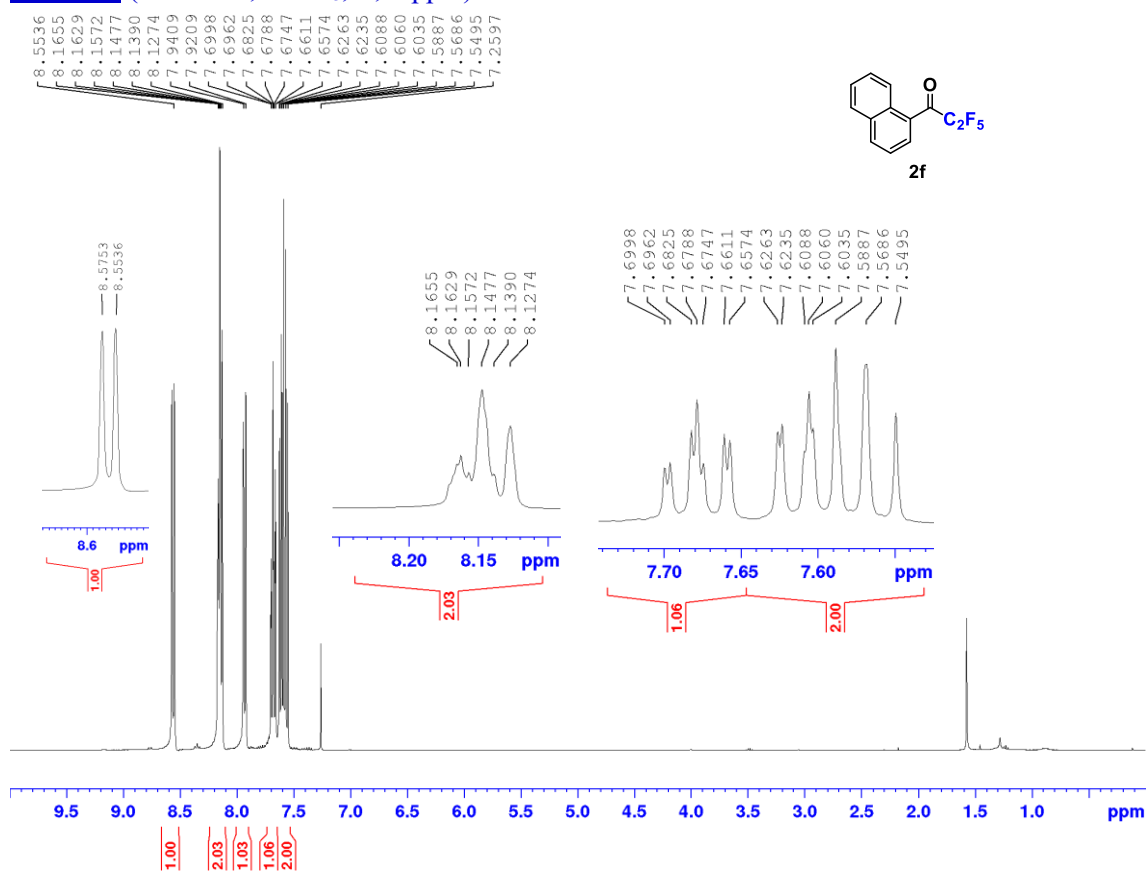
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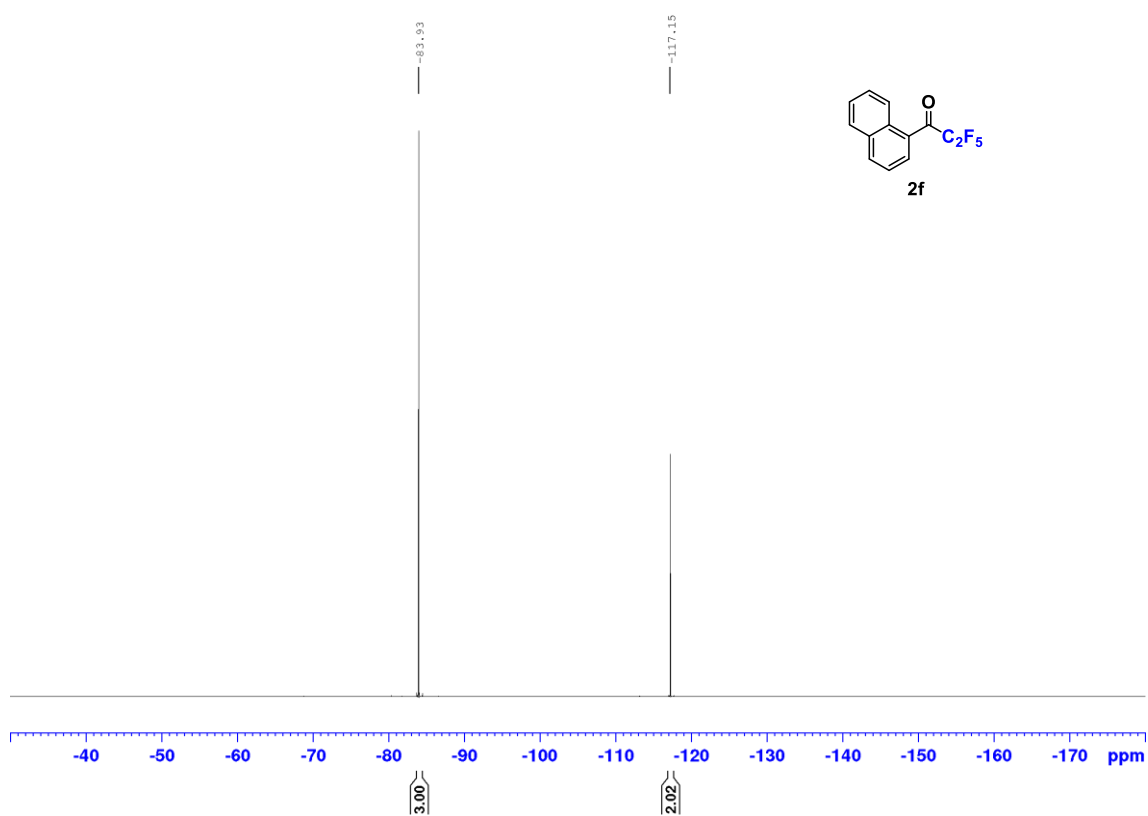
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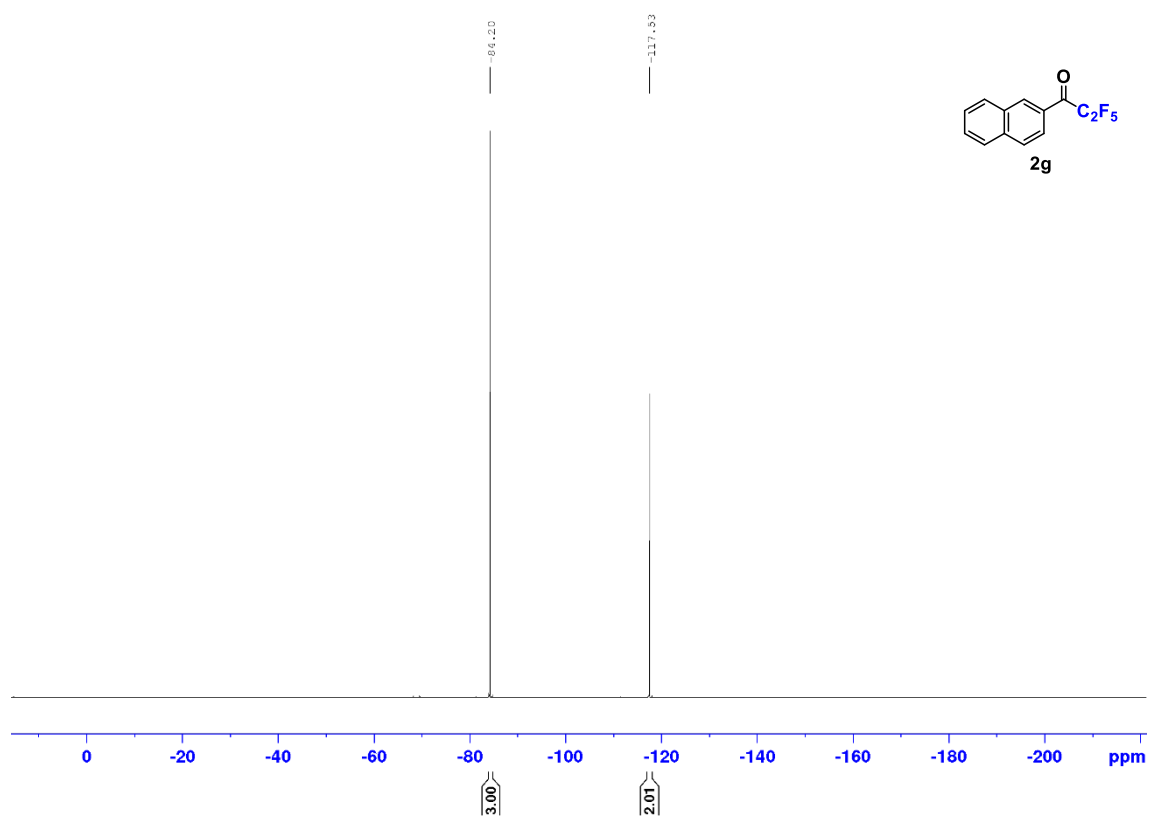
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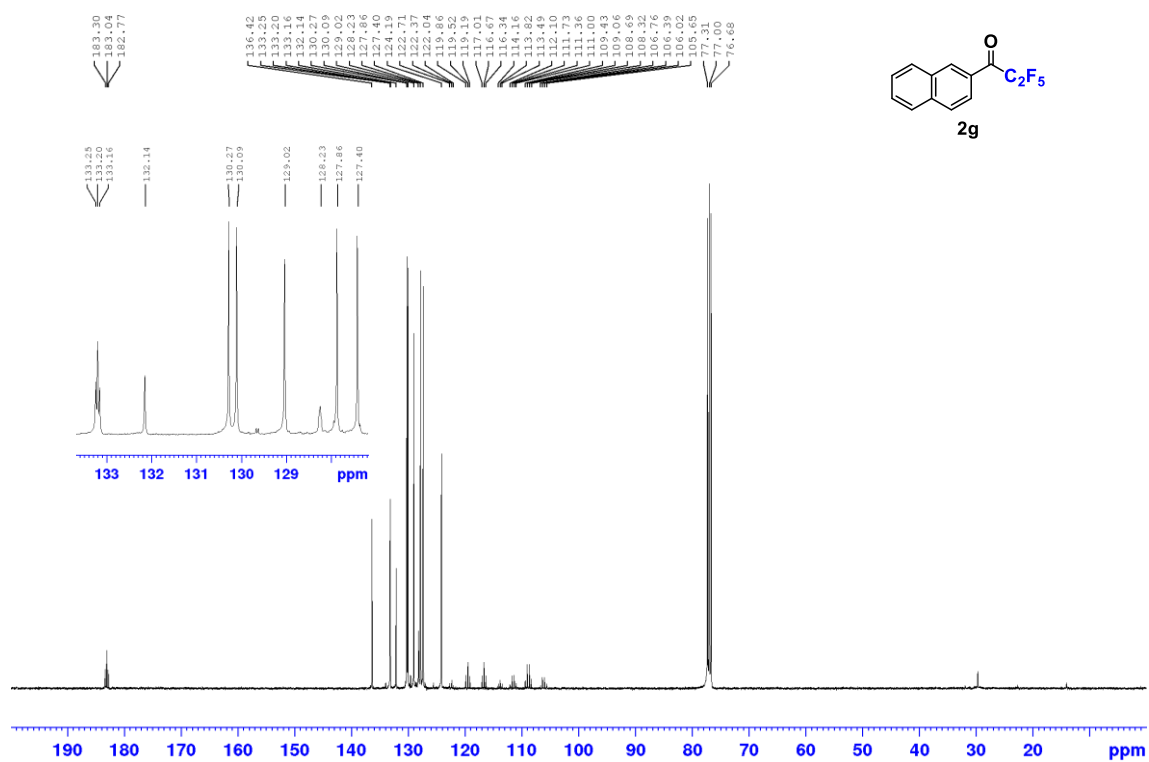
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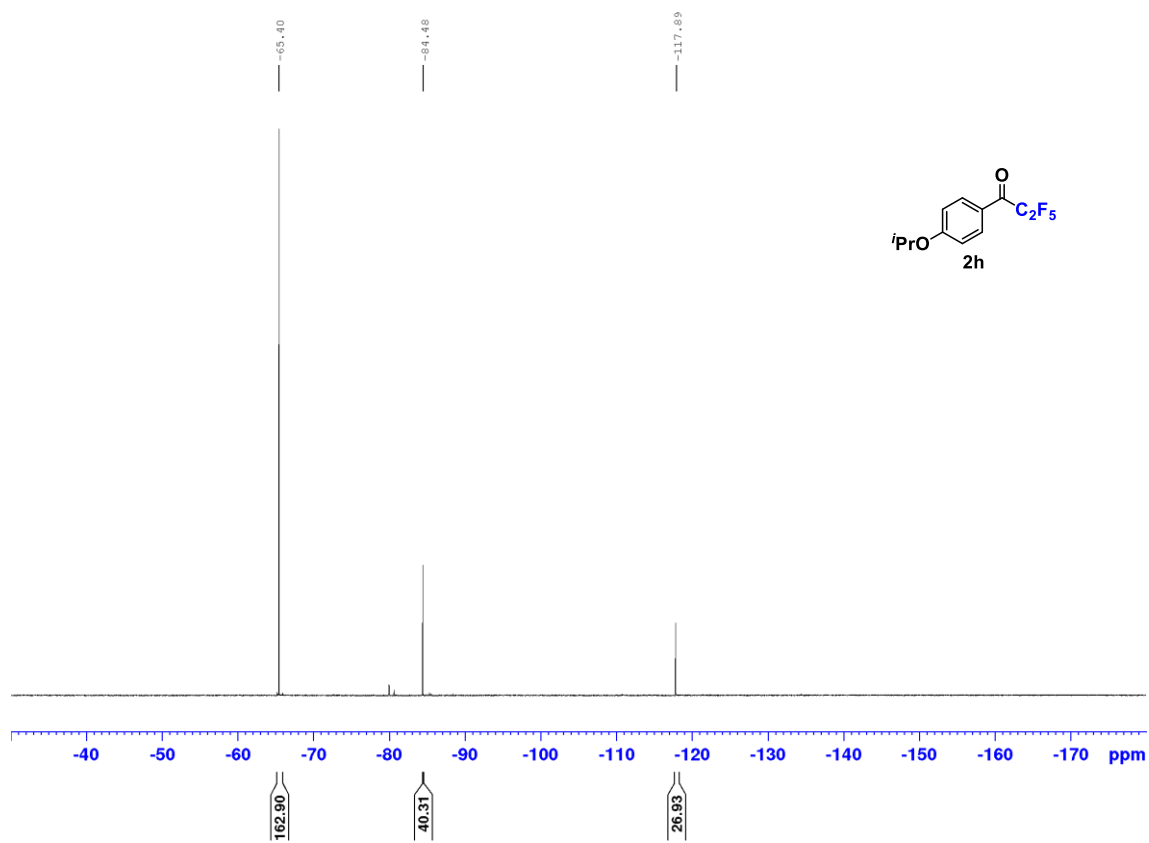
¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm)



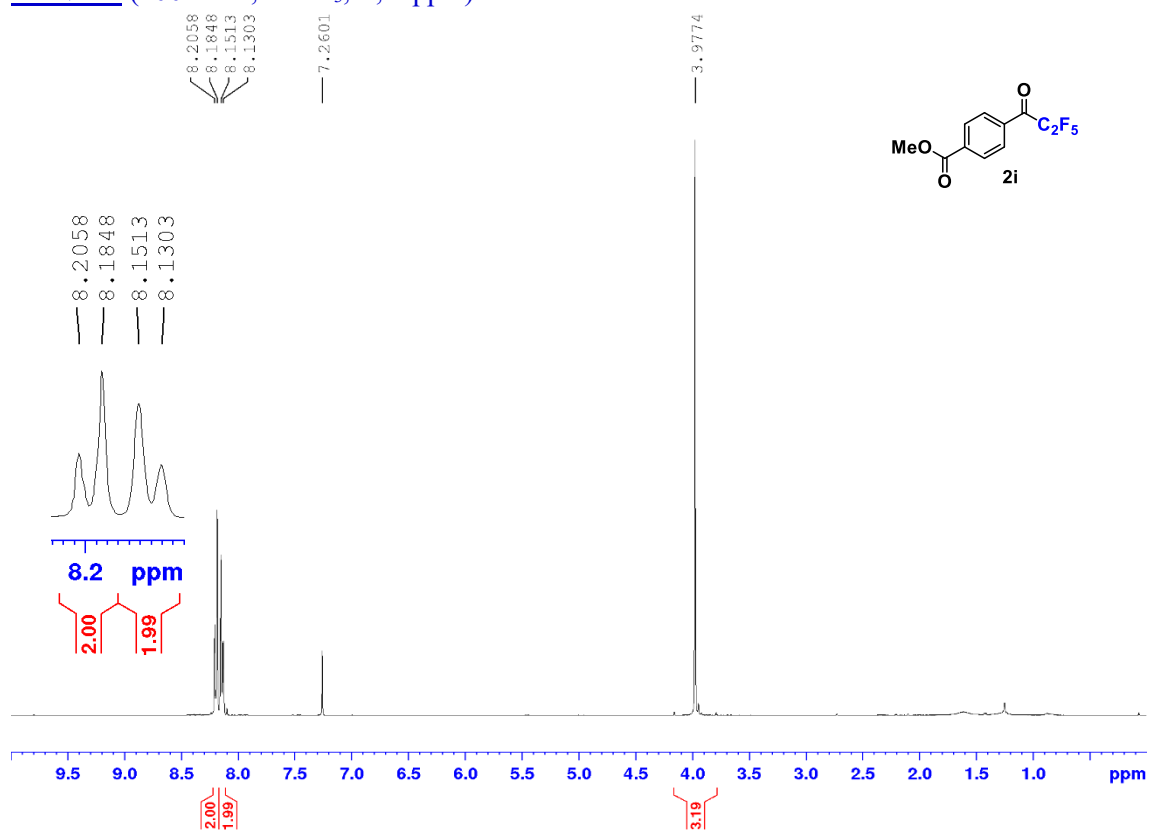
¹³C{¹H} NMR (100 MHz, CDCl₃, rt, δ/ppm)



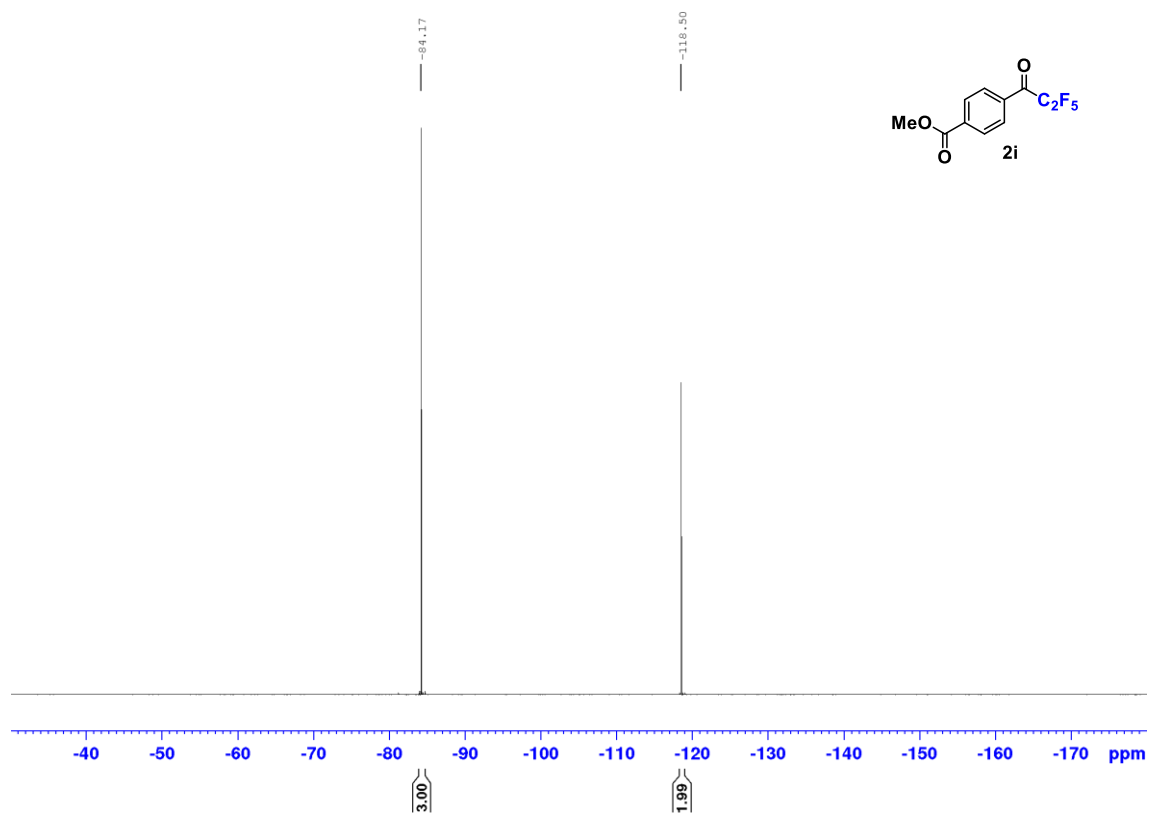
¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm)



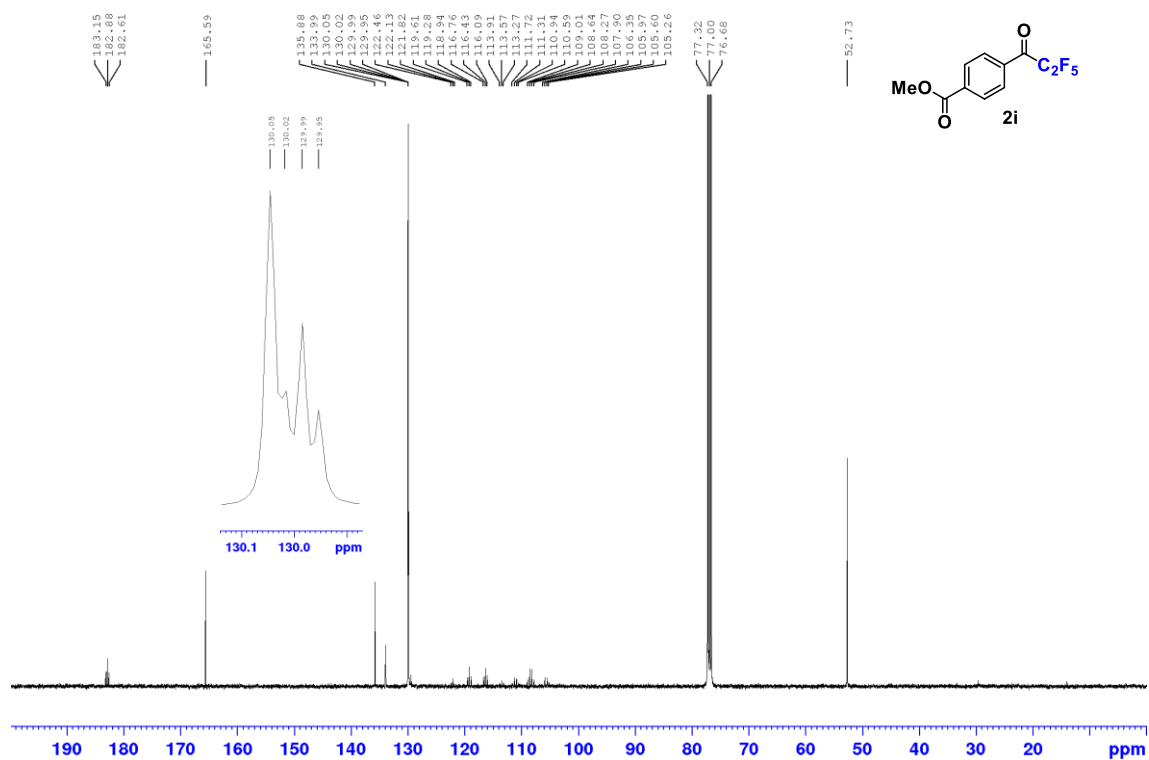
¹H NMR (400 MHz, CDCl₃, rt, δ/ppm)



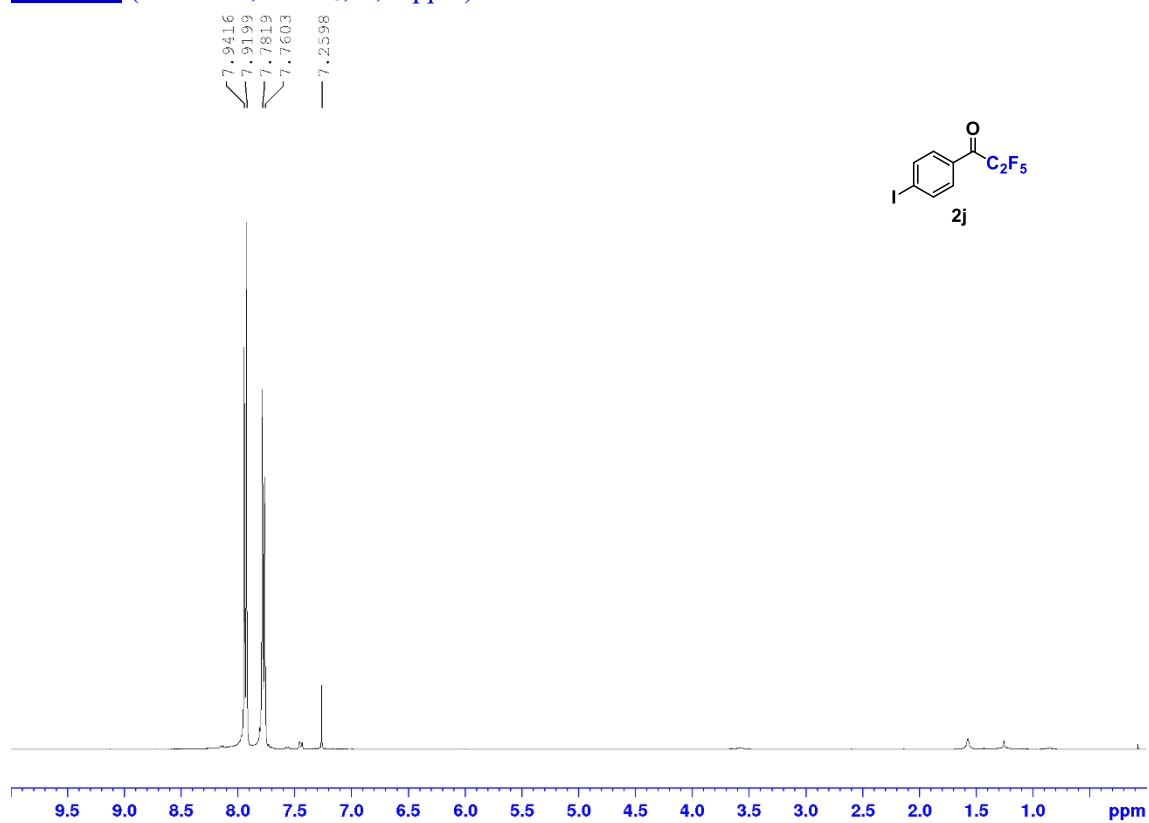
¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm)



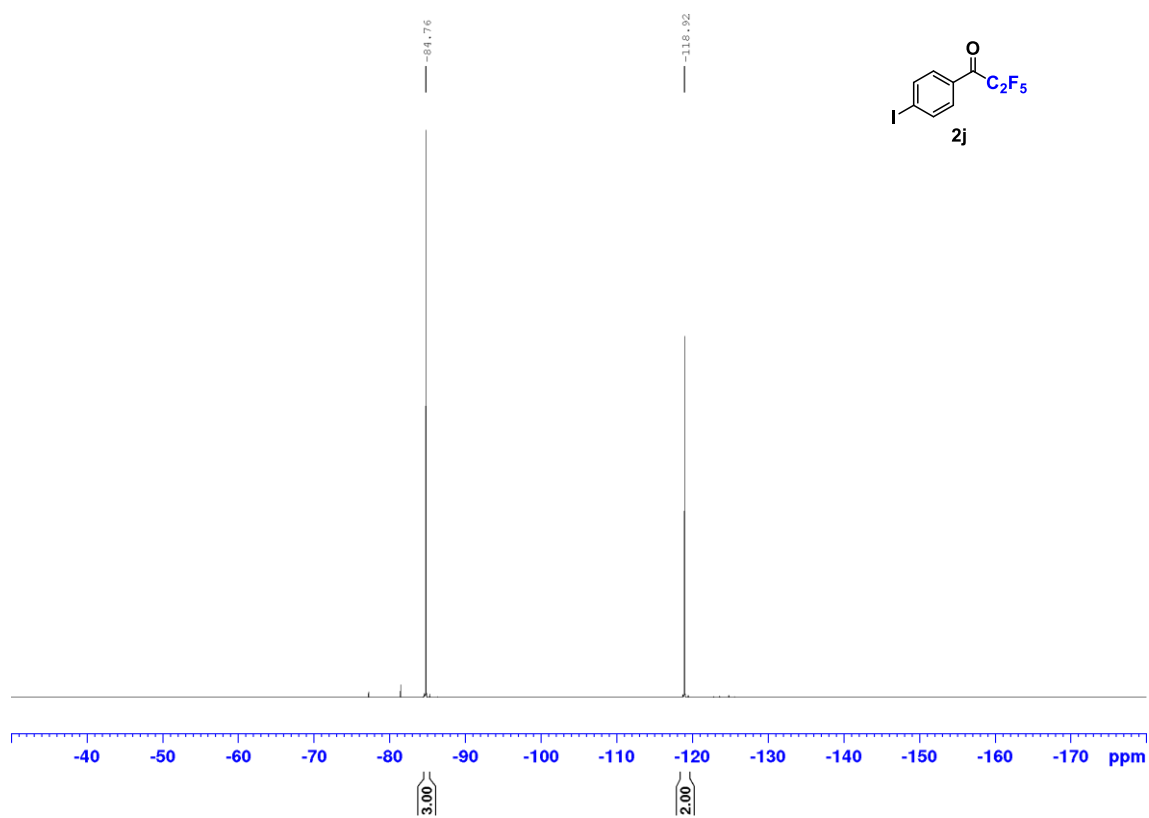
¹³C{¹H} NMR (100 MHz, CDCl₃, rt, δ/ppm)



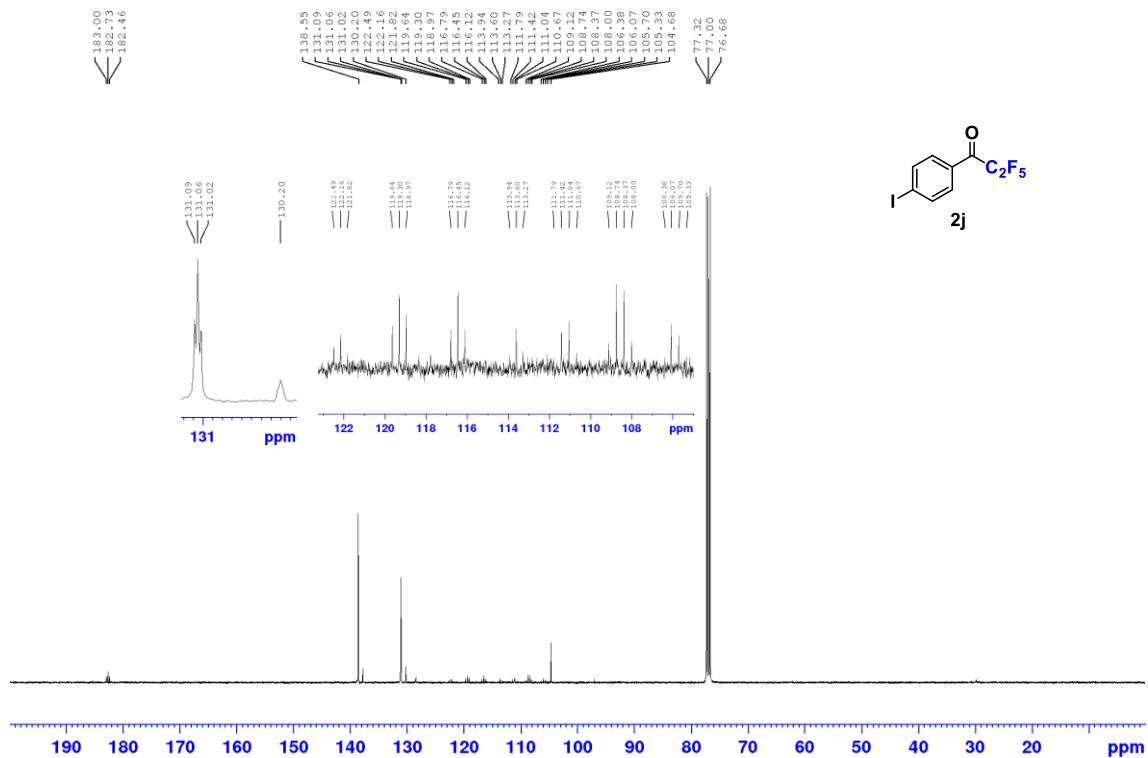
¹H NMR (400 MHz, CDCl₃, rt, δ/ppm)



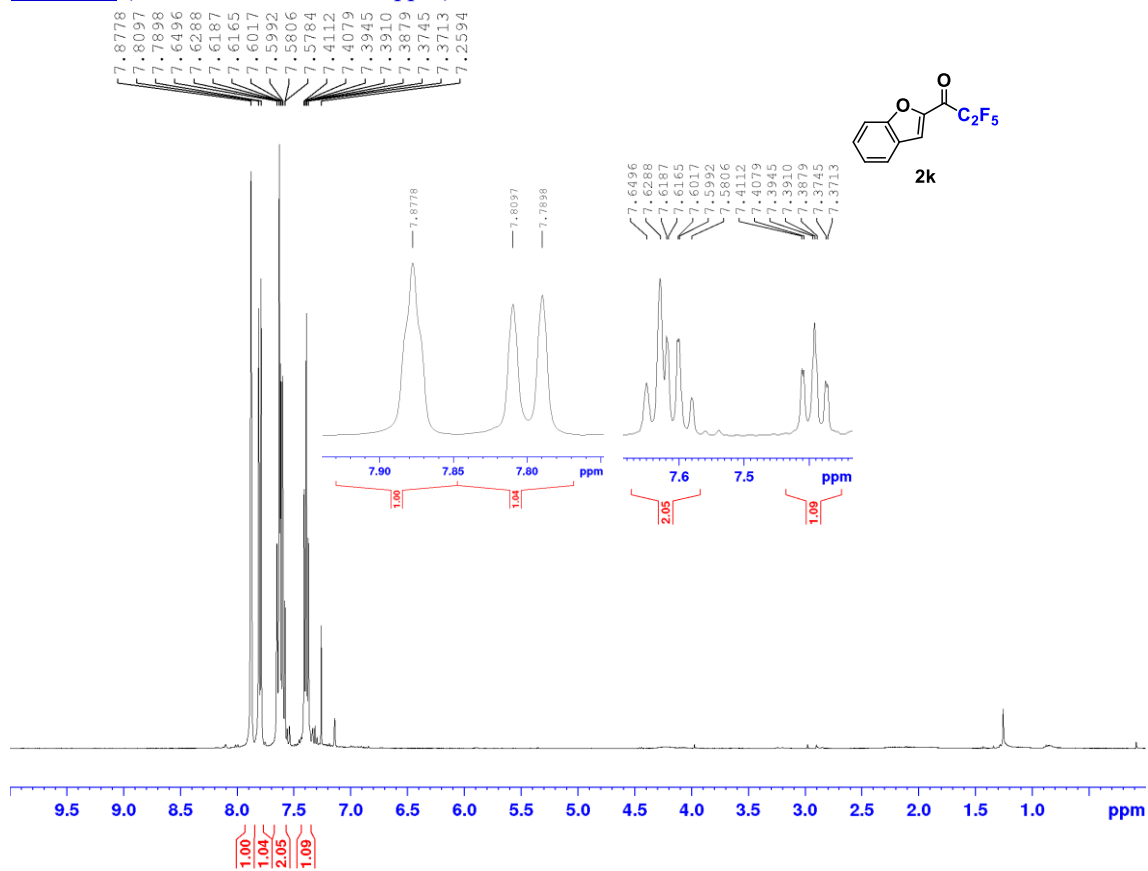
¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm)



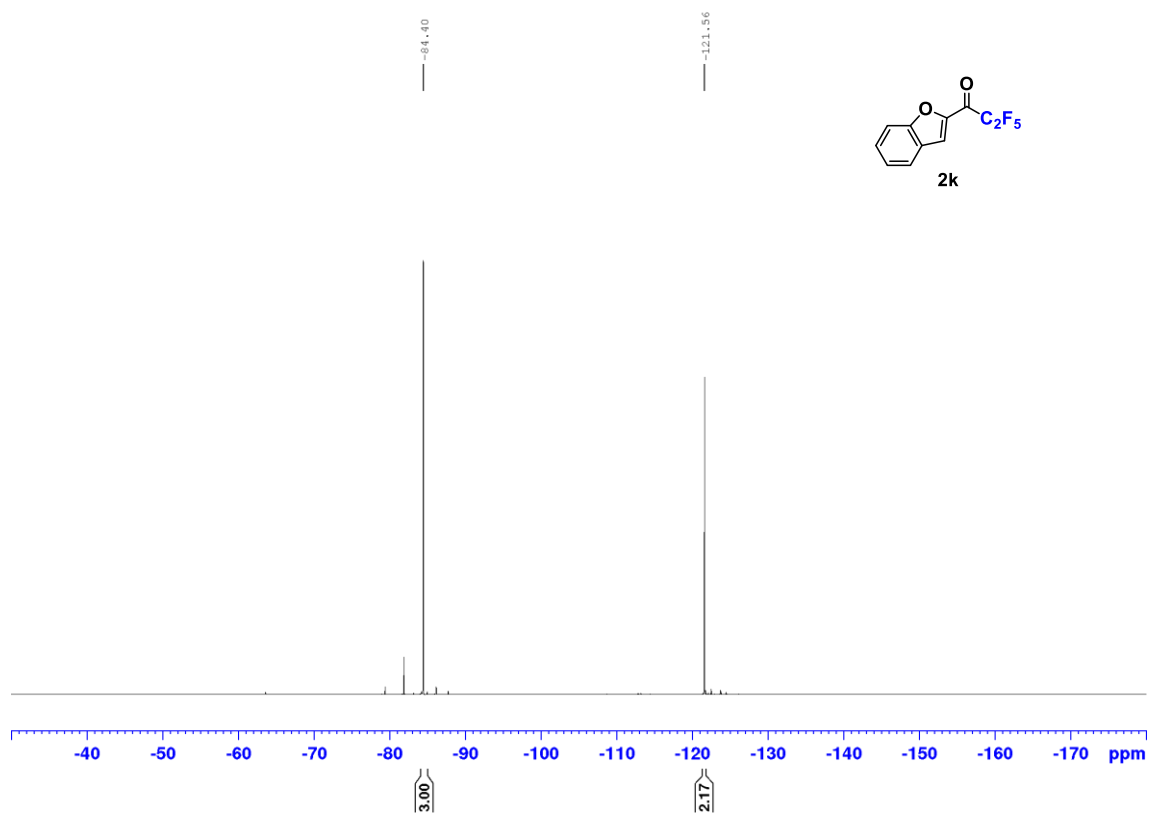
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , rt, δ/ppm)



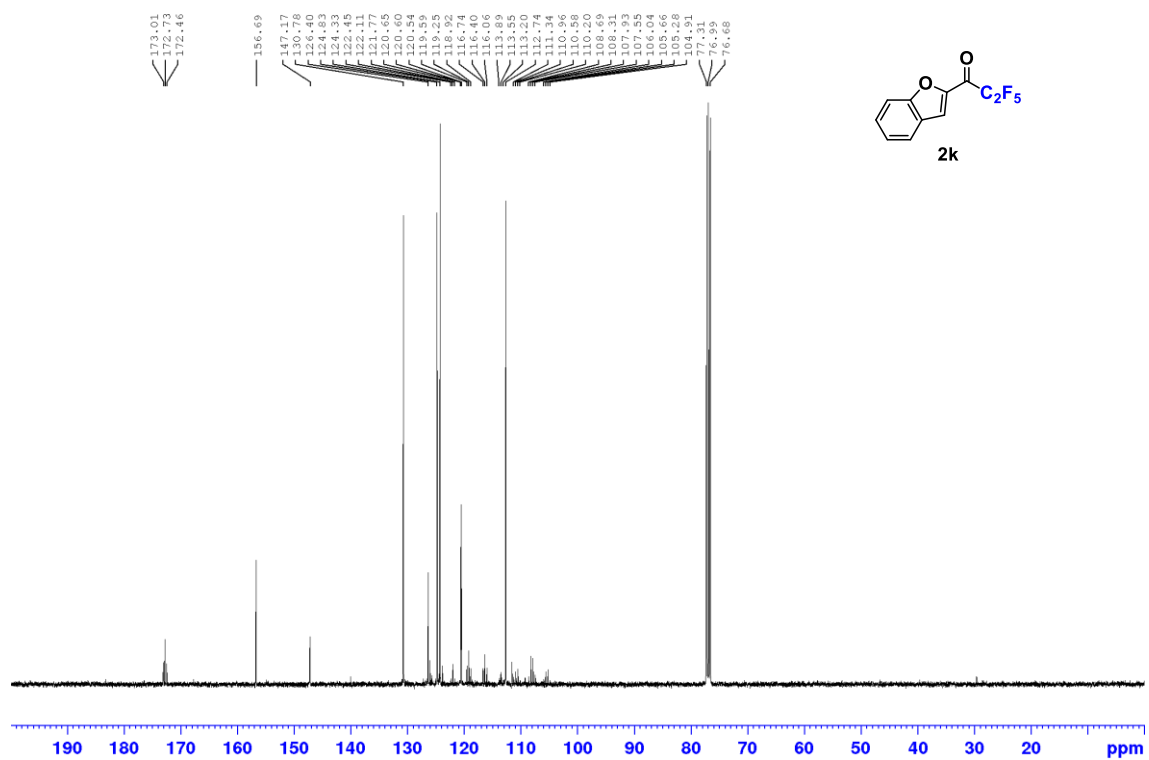
^1H NMR (400 MHz, CDCl_3 , rt, δ/ppm)



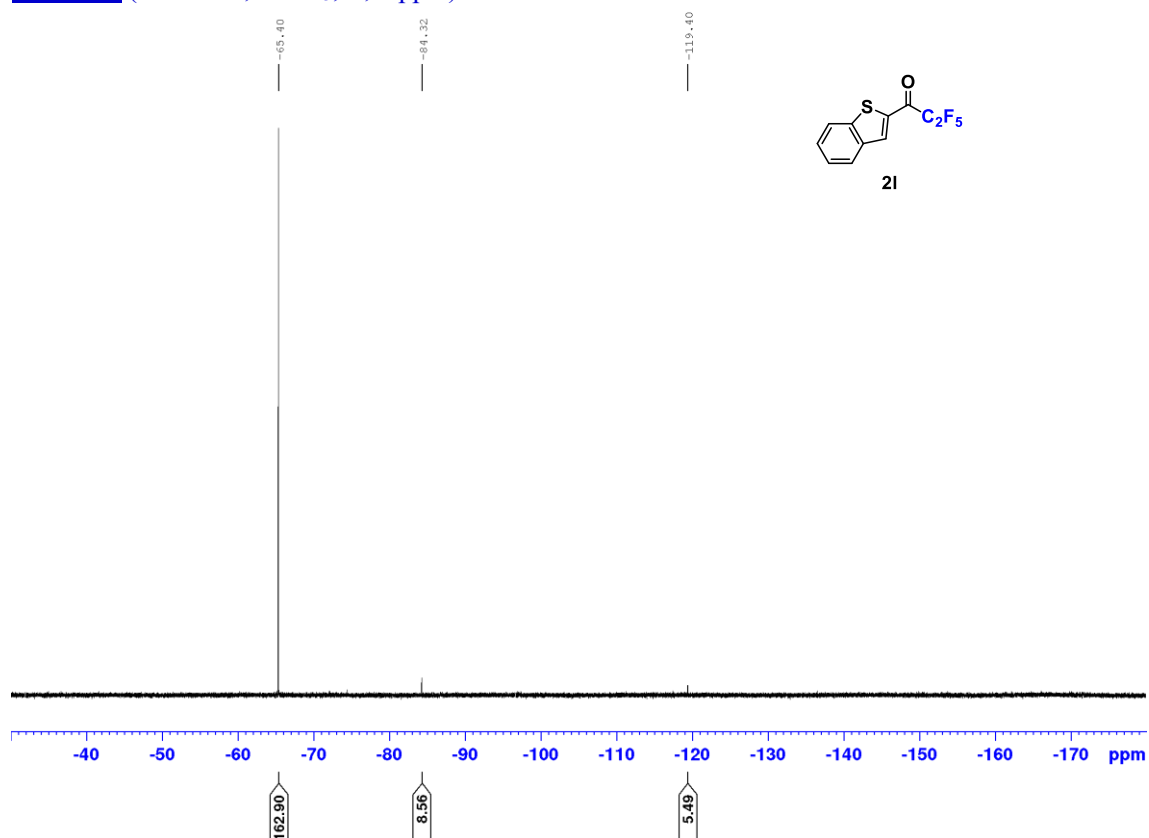
¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm)



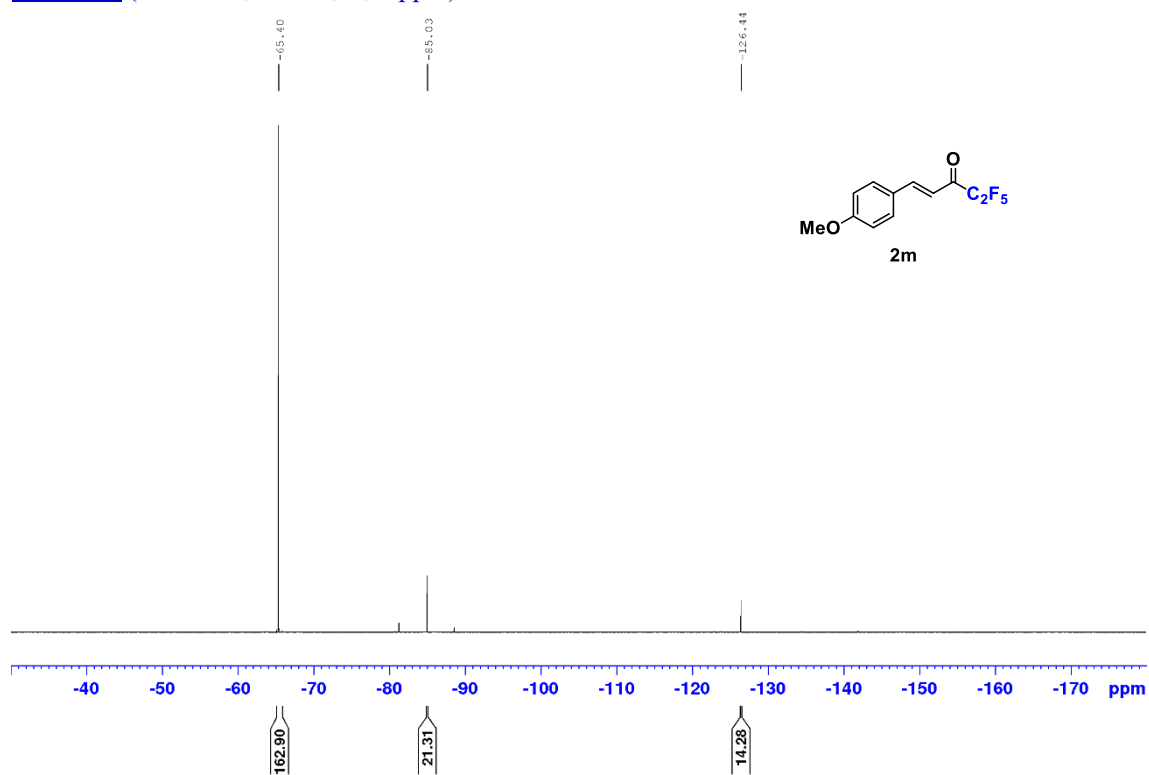
¹³C{¹H} NMR (100 MHz, CDCl₃, rt, δ/ppm)



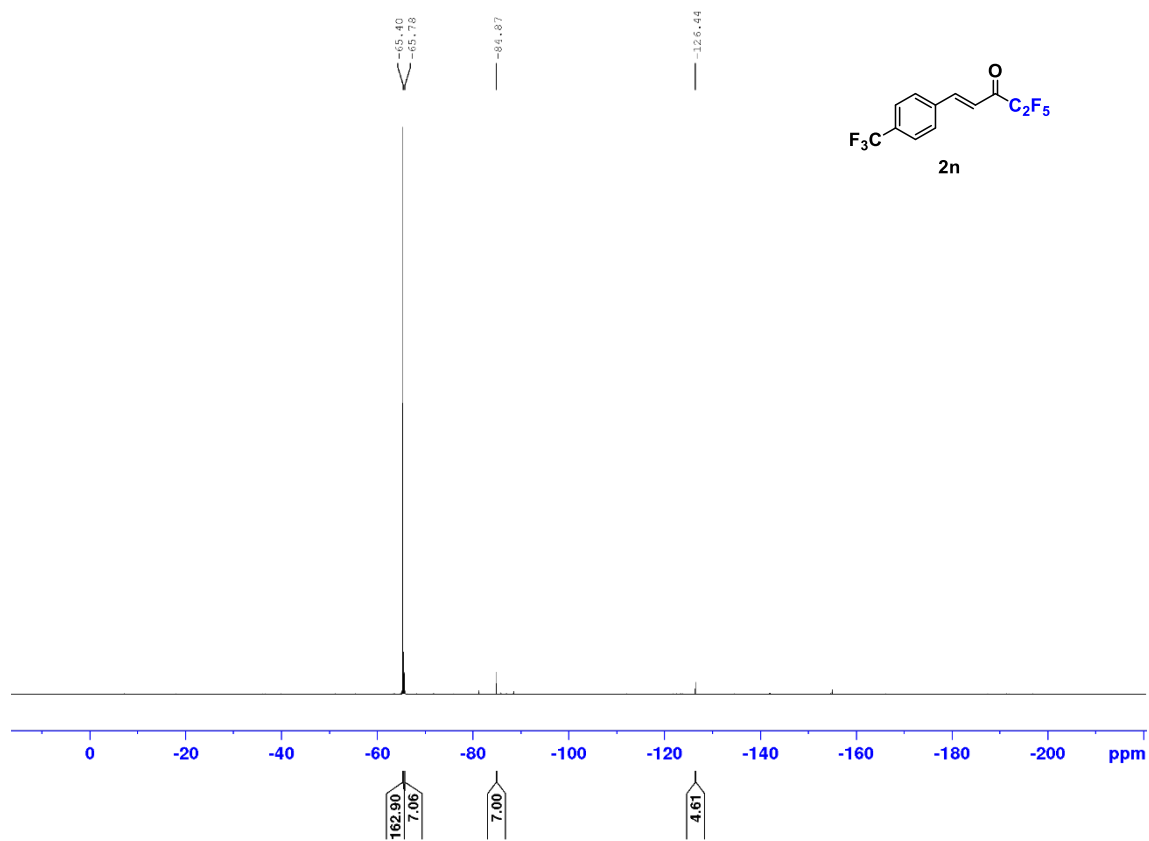
¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm)



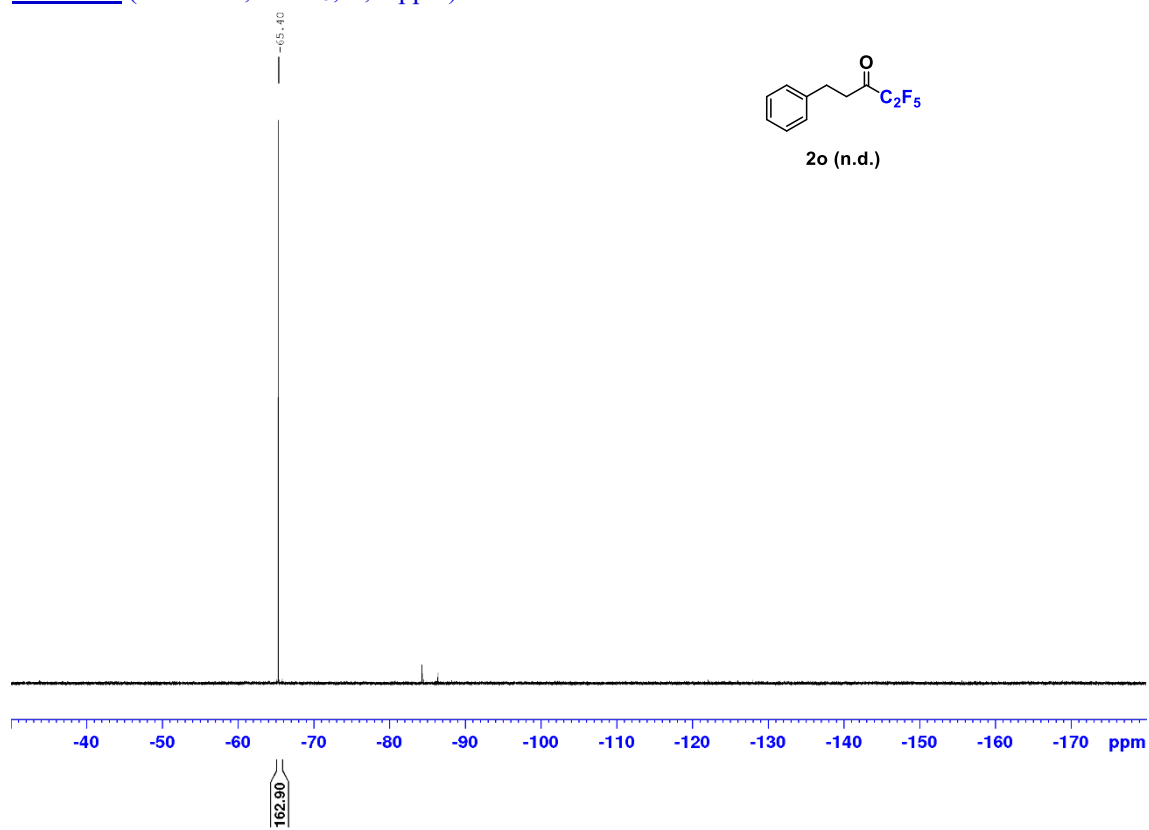
¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm)



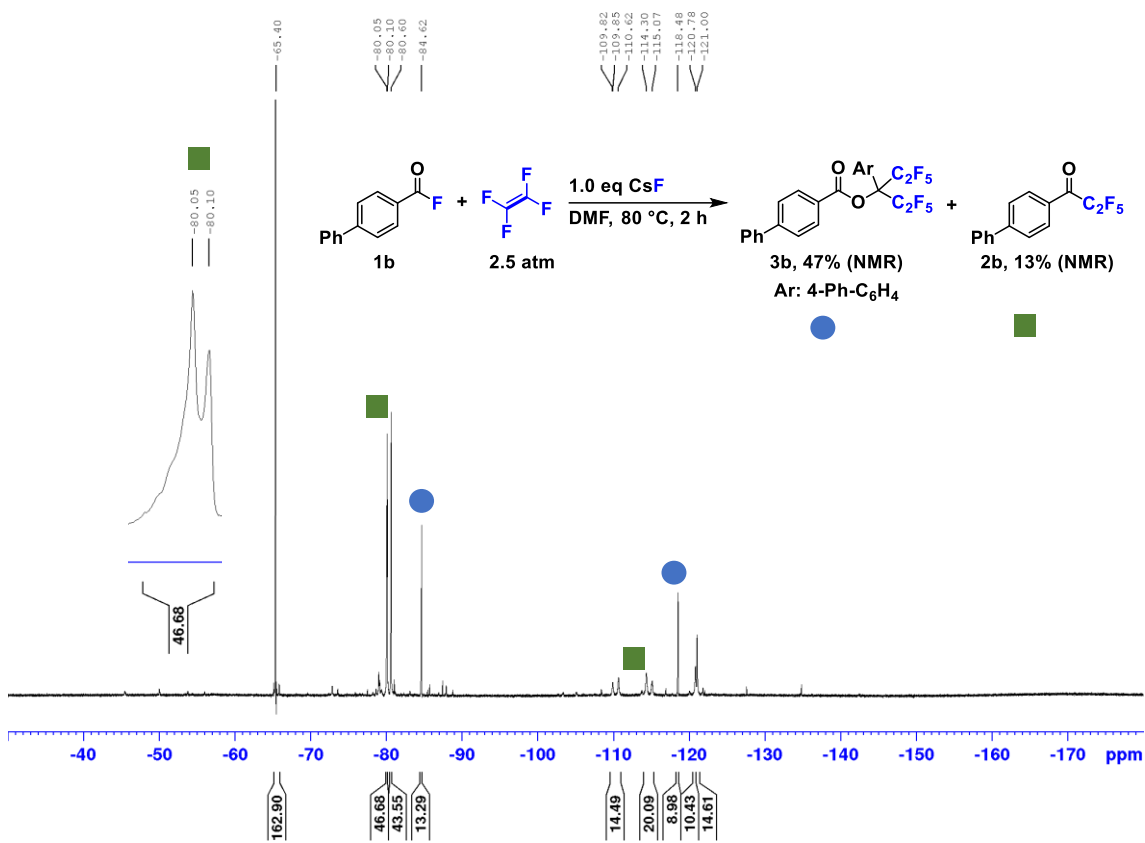
^{19}F NMR (376 MHz, CDCl_3 , rt, δ/ppm)



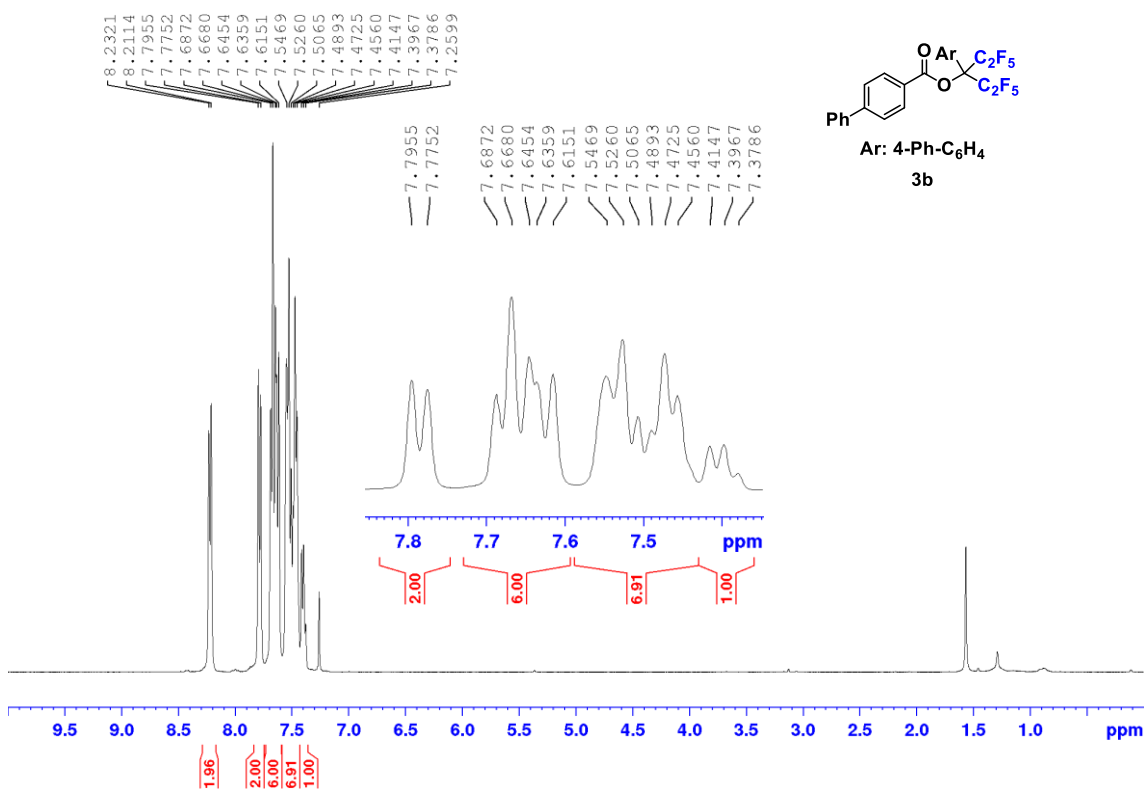
^{19}F NMR (376 MHz, CDCl_3 , rt, δ/ppm)



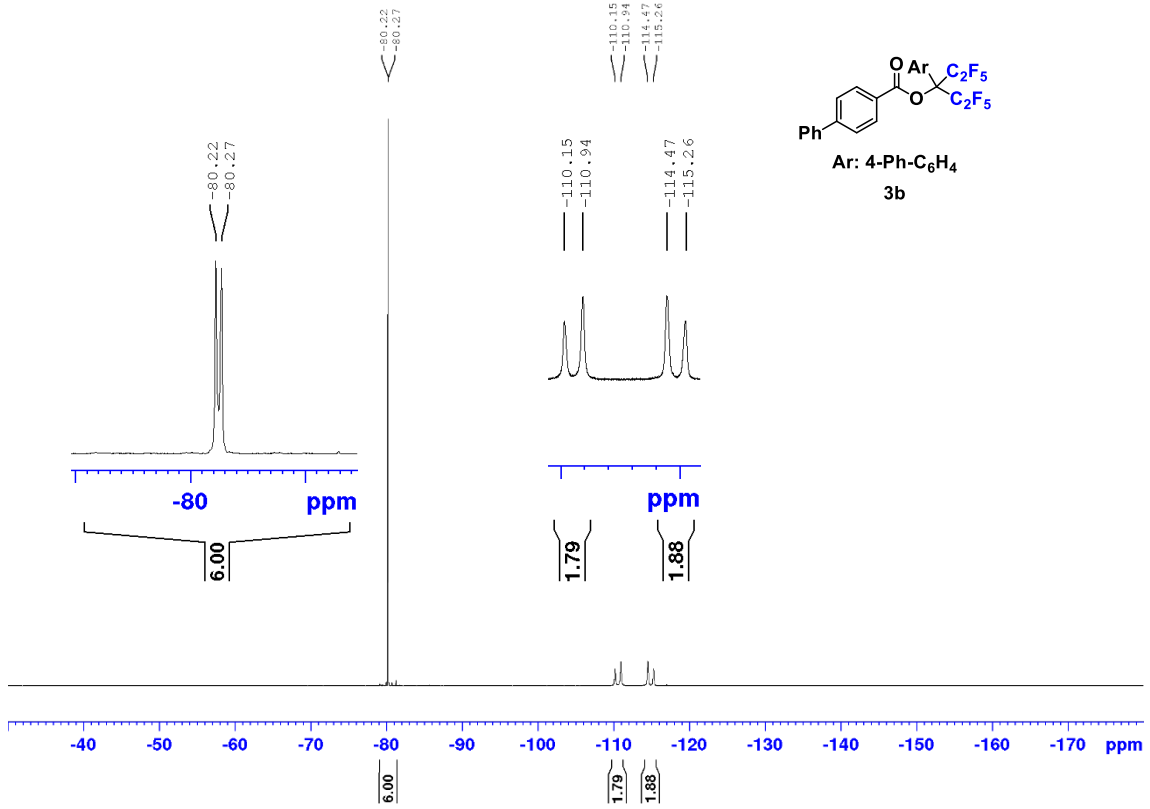
1-6 Reaction Mixture ¹⁹F NMR (376 MHz, DMF/CDCl₃, rt, δ/ppm)



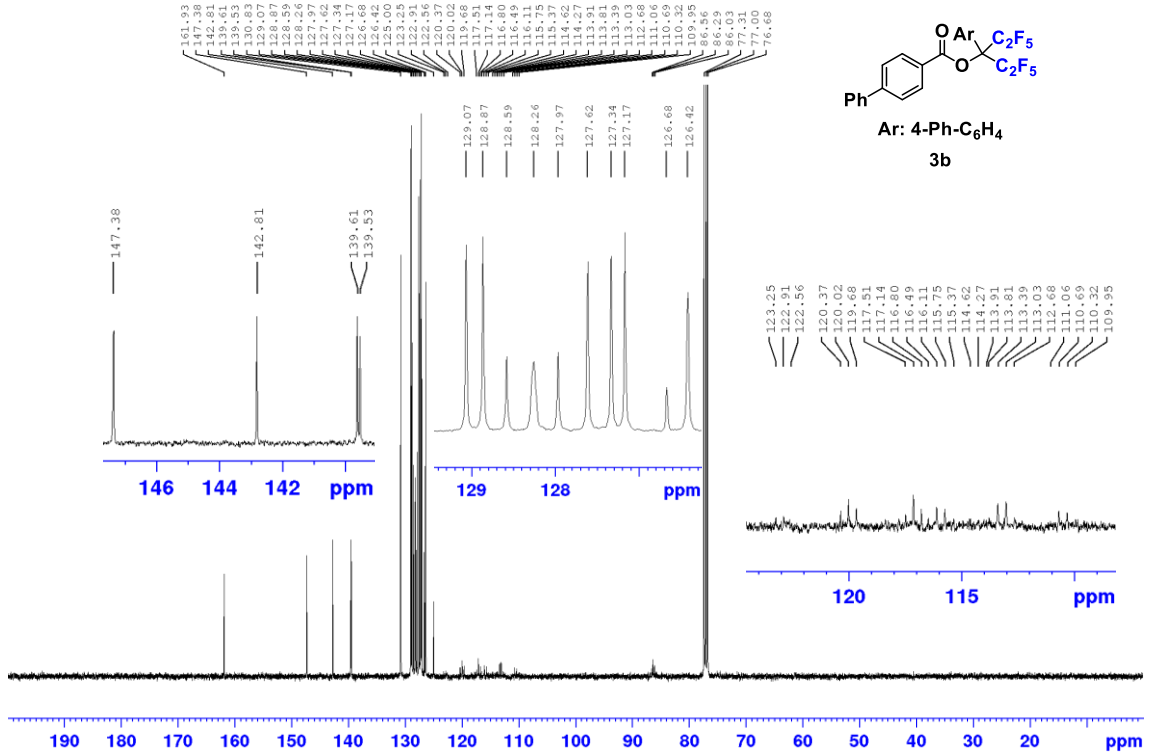
¹H NMR (400 MHz, CDCl₃, rt, δ/ppm)



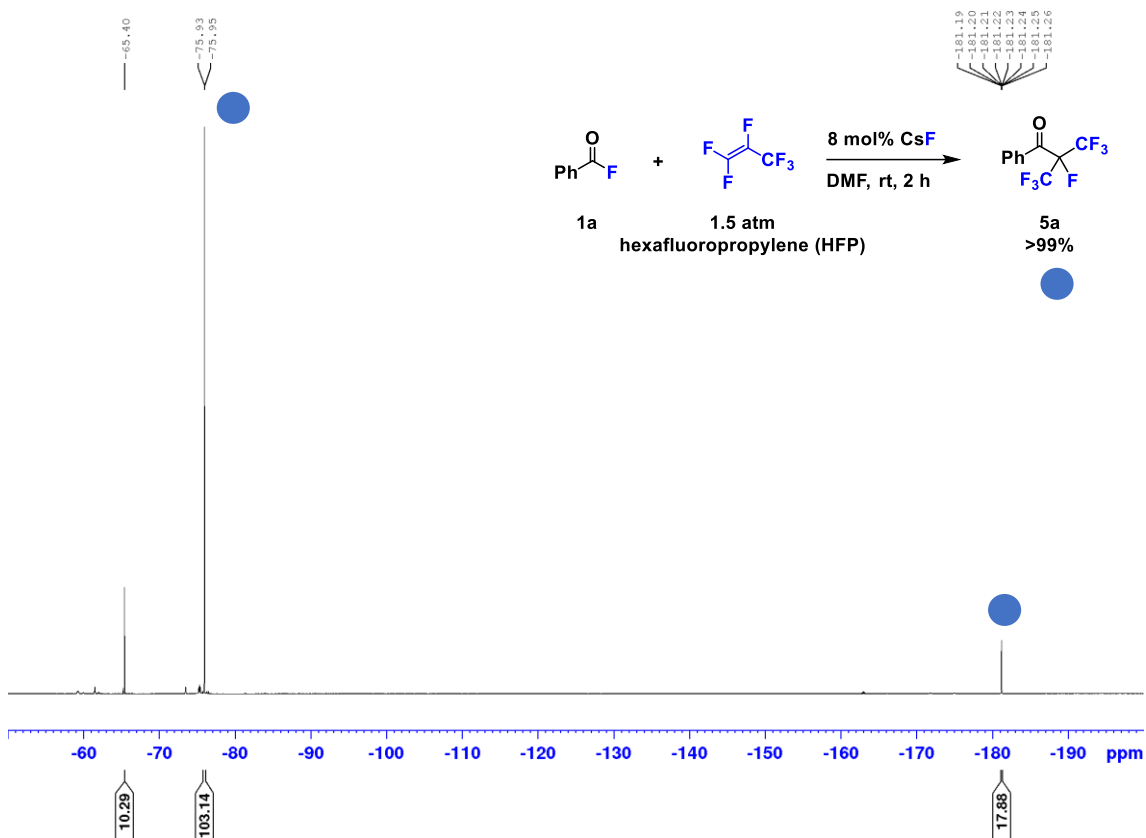
¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm)



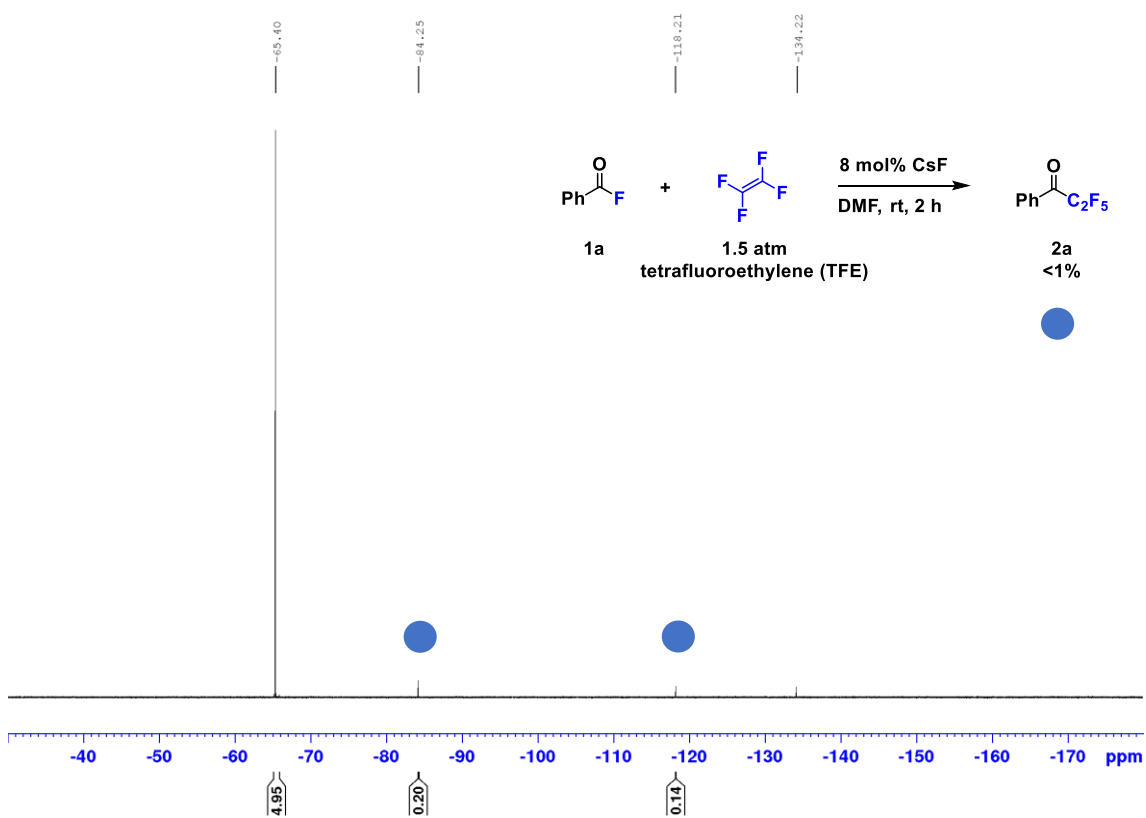
¹³C{¹H} NMR (100 MHz, CDCl₃, rt, δ/ppm)



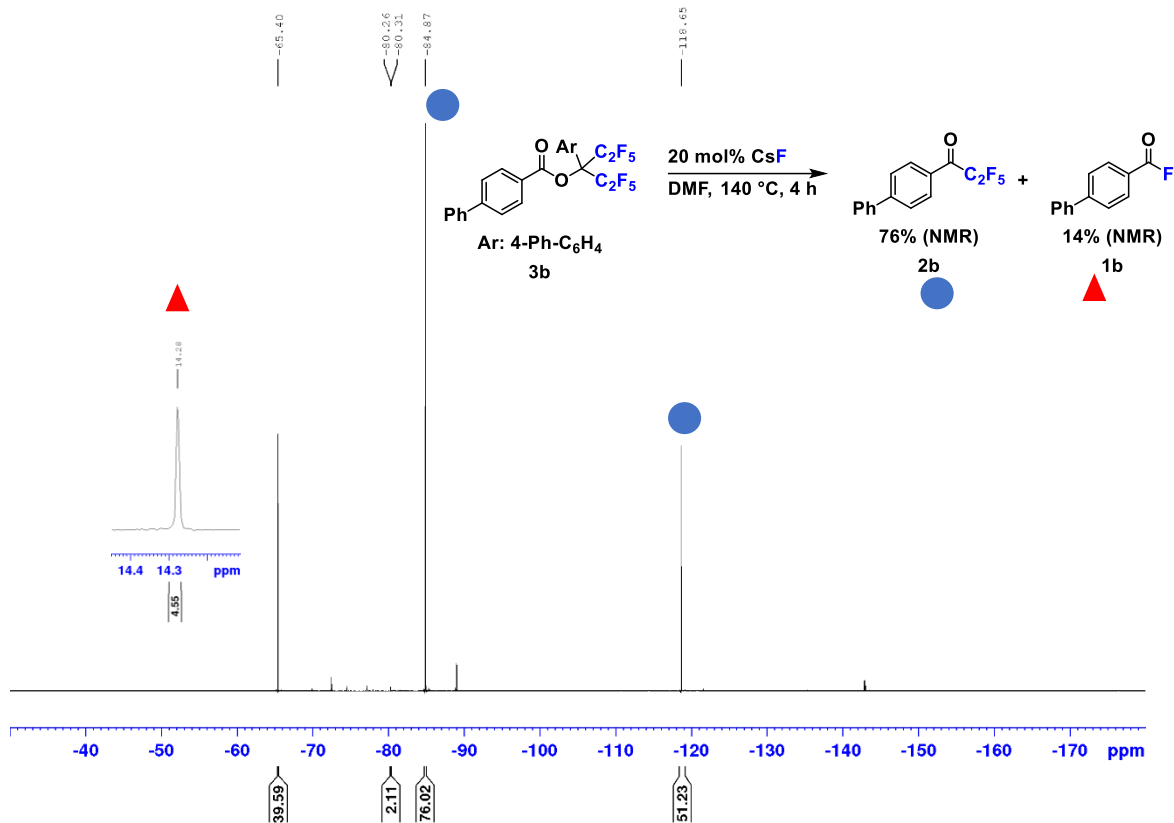
1-7 Reaction Mixture ^{19}F NMR (376 MHz, CDCl_3 , rt, δ/ppm)



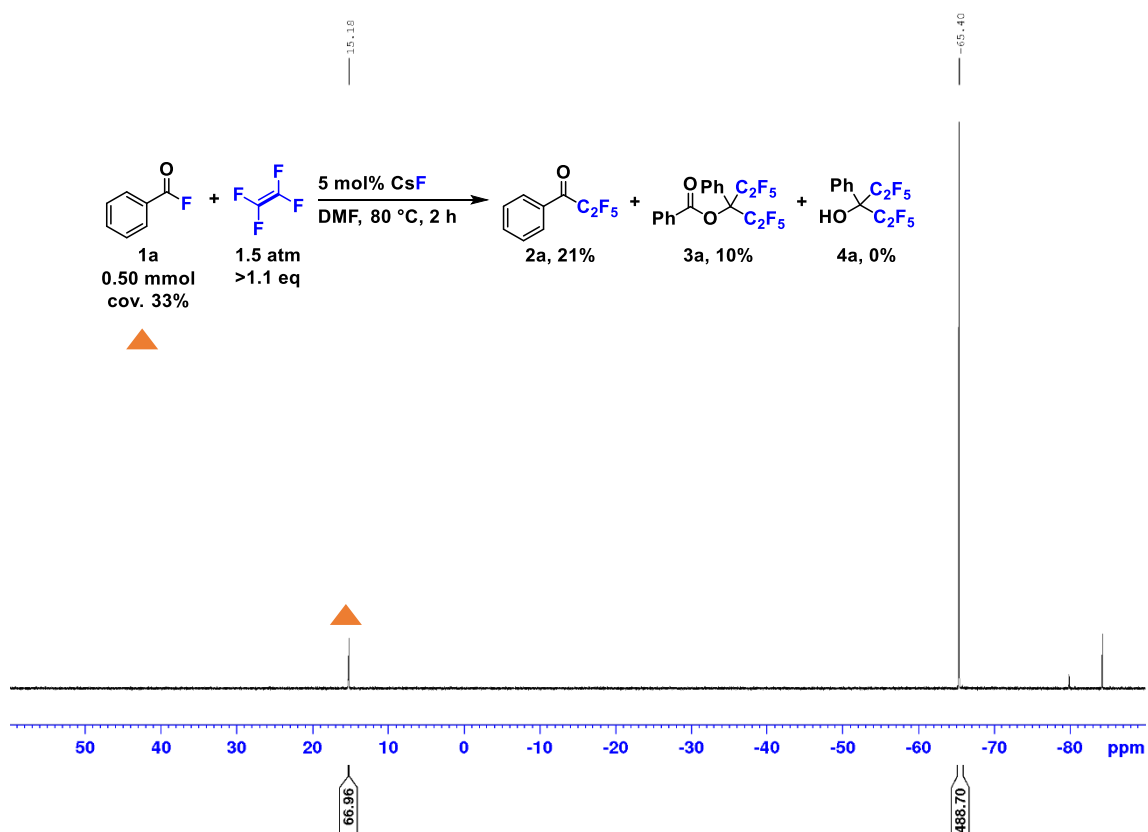
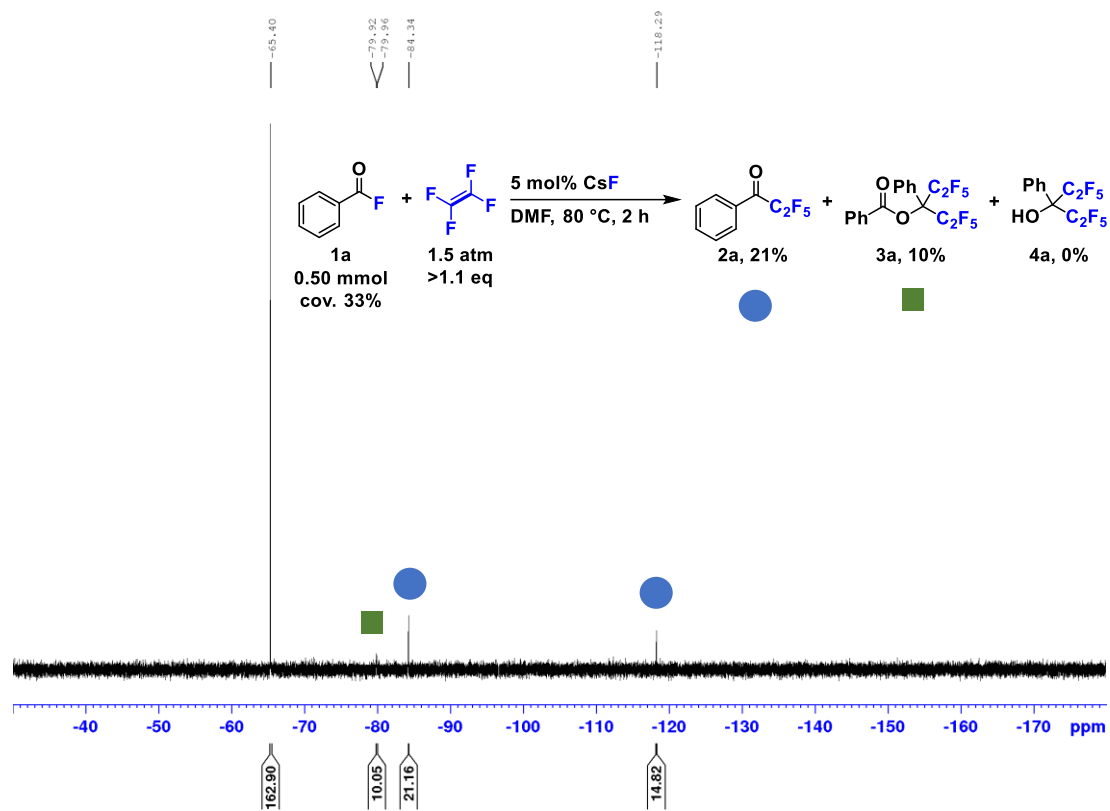
1-7 Reaction Mixture ^{19}F NMR (376 MHz, CDCl_3 , rt, δ/ppm)



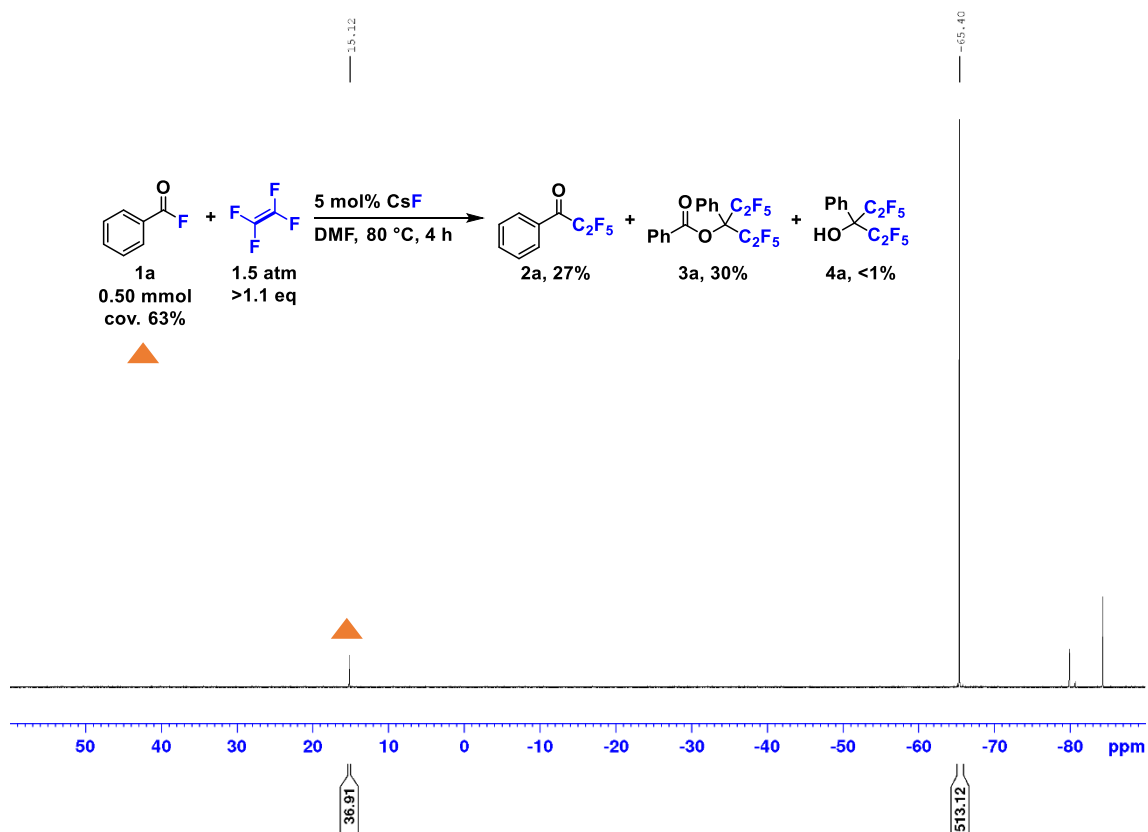
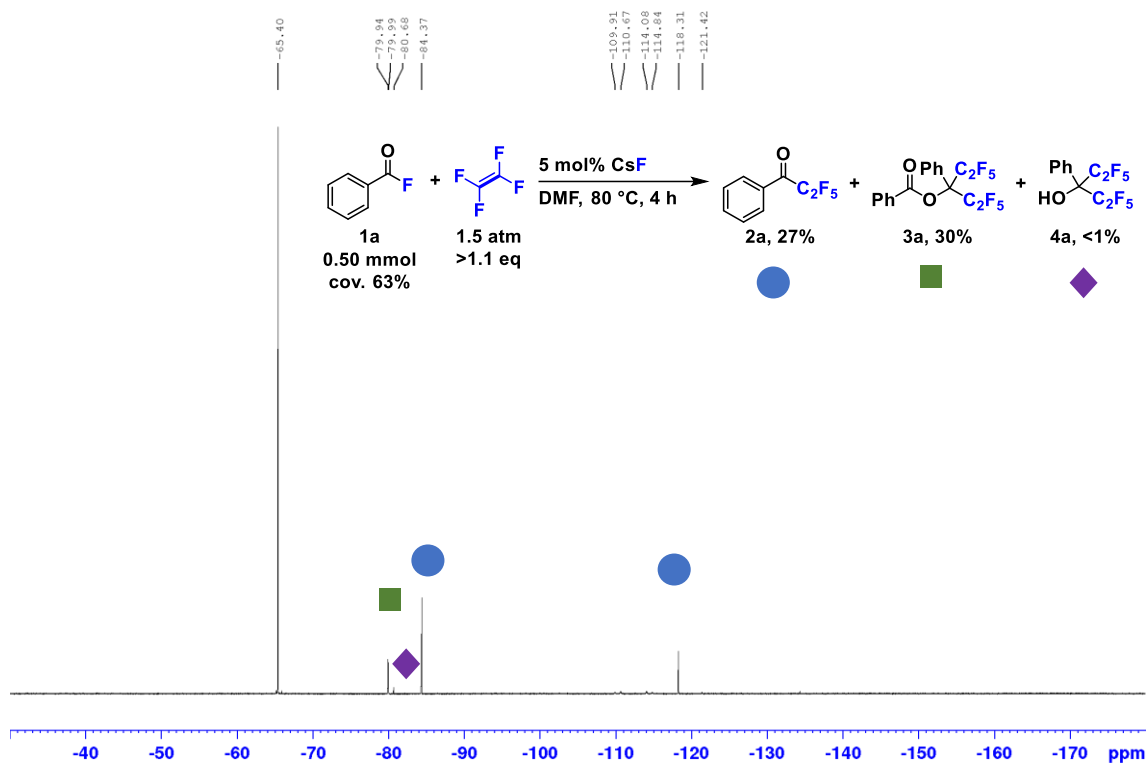
1-8 Reaction Mixture ^{19}F NMR (376 MHz, CDCl_3 , rt, δ/ppm)



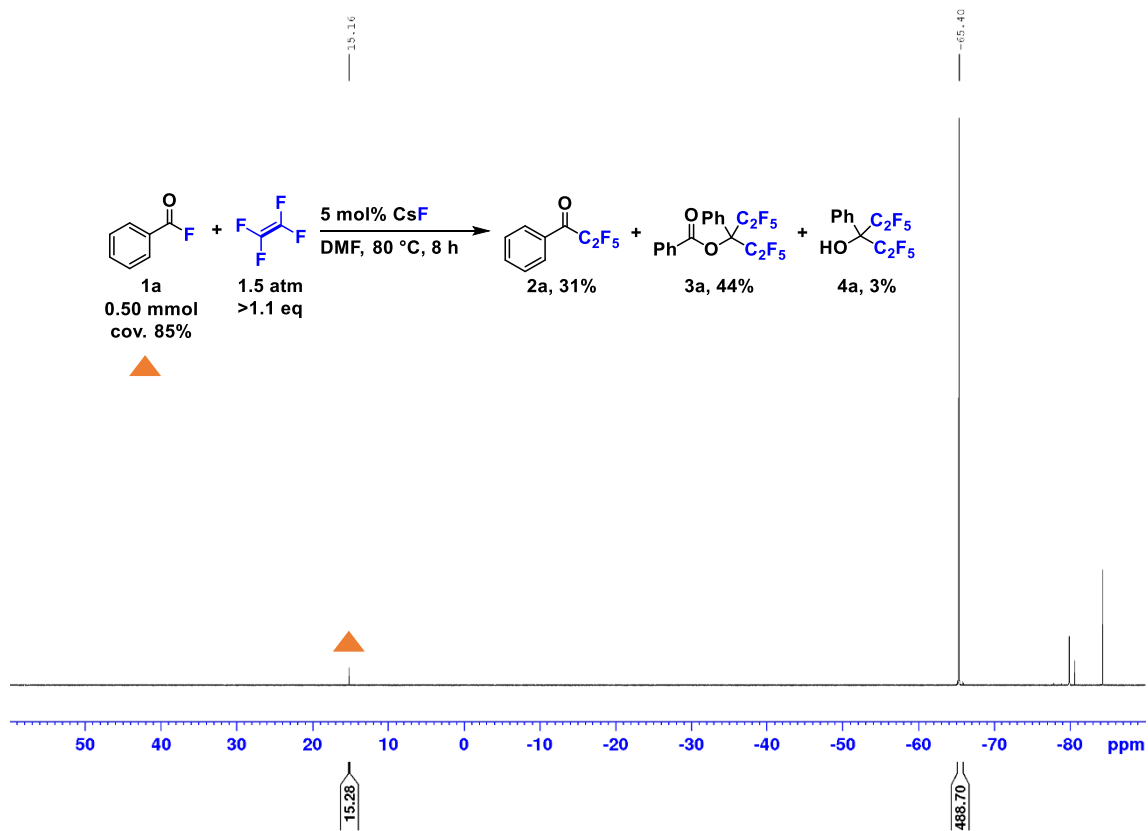
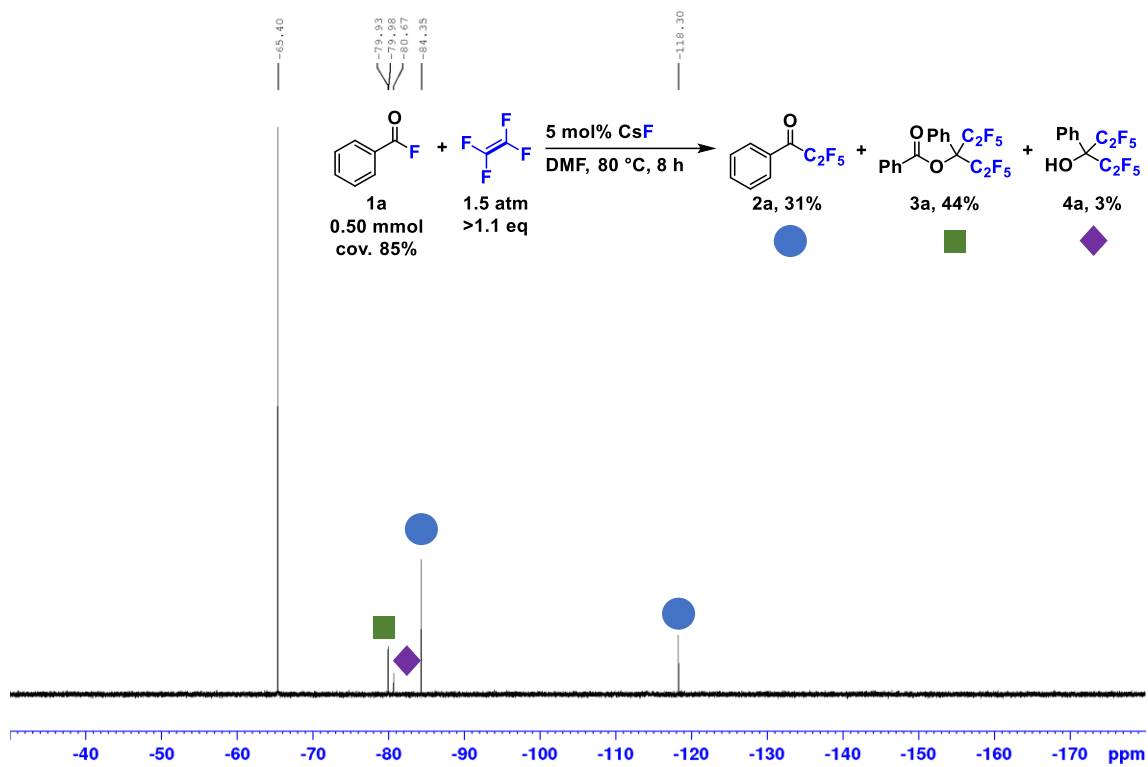
1-9 80 °C 2 h



1-9 80 °C 4 h



1-9 80 °C 8 h



1-9 80 °C 20 h

