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Supporting Information

Continuous flow synthesis of aryl aldehydes by Pd-catalyzed formylation of phenol-derived aryl fluorosulfonates using syngas

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Contents

1. Materials and Methods

All solvents and chemicals were obtained from standard commercial vendors (Sigma-Aldrich/Merck or VWR) and were used without any further purification, unless otherwise noted.

NMR spectra: ^{1}H NMR spectra were recorded on a Bruker 300 MHz or 500 MHz instrument. ^{13}C NMR spectra were recorded on a 300 MHz instrument at 75 MHz. ^{19}F NMR spectra were recorded on the 300 MHz instrument at 282 MHz. Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard. The letters s, d, dd, t, q, and m are used to indicate singlet, doublet, doublet of doublets, triplet, quadruplet, and multiplet.

GC-MS spectra were recorded using a Shimadzu GCMS-QP 2010 SE coupled with a DSQ II (EI, 70 eV). A RTX-5MS column (30 m × 0.25 mm × 0.25 µm) was used, with helium as carrier gas (40 cm/sec linear velocity). The injector temperature was set at 280 °C. Within the GC oven, after 1 min at 50 °C, the temperature was increased by 25 °C/min to 300 °C and kept at 300 °C for 3 min.

GC-FID analysis was performed on a Shimadzu GCFID 2030 with a flame ionization detector, using a RTX -5MS column (30 m × 0.25 mm ID × 0.25 µm) and helium as carrier gas (40 cm/sec linear velocity). The injector temperature was set at 280 °C. Within the GC oven, after 1 min at 50 °C, the temperature was increased by 25 °C/min to 300 °C and kept constant at 300 °C for 4 min. The detector gases used for flame ionization were hydrogen and synthetic air (5.0 quality).

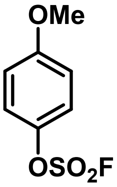
Identity and purity of compounds (**2a** – **2u**) after reductive carbonylation reaction was established via GC-MS and GC-FID with internal standard respectively. Isolation, with exception of **2a**, **2b**, **2c** and **2p**, was not attempted due to volatility of the products.

CAUTION NOTE: CO is an odorless, toxic, and flammable gas. All of the experiments must be performed in a well-ventilated fume cupboard with a fitted CO detector. H_2 is extremely flammable. A N_2 purge should be used at the outlet. Care should be taken when operating pressurized equipment. A thorough safety assessment should be made before conducting any experiments.

2. General Procedure A for the Preparation of Sulfurofluoridates 1a-1u

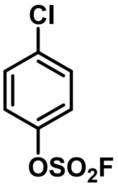
A 20 mL microwave vial equipped with stirrer bar and charged with phenol (10 mmol, 1 equiv), Et_3N (2.79 mL, 20 mmol) and CH_2Cl_2 (12.5 mL). After sealing of the reaction vessel with a septum, a slight vacuum was applied. Subsequently a balloon filled with SO_2F_2 was attached to the reaction vessel via a syringe. The reaction mixture was stirred (1-16 h). The reaction mixture was concentrated under reduced pressure after complete conversion of starting material was observed via GC-FID. The crude product was diluted with EtOAc (20 mL) and washed with 1 M HCl (2 x 30 mL) and brine (30 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure.

2.1. 4-Methoxyphenyl Sulfurofluoridate (1a)



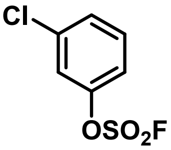
Product **1a** was obtained as a colorless oil (2.04 g, 99% yield). ^1H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[2] MS EI (m/z): $[M]^+$ calcd. for $C_7H_7FO_4S$, 206; found, 206.

2.2. 4- Chlorophenyl Sulfurofluoridate (1b)



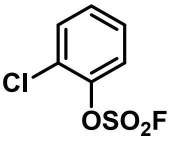
Product **1b** was obtained as a colorless oil (2.10 g, 98% yield). ^1H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[3] MS EI (m/z): $[M]^+$ calcd. for $C_6H_4ClFO_3S$, 210; found, 210.

2.3. 3- Chlorophenyl Sulfurofluoridate (1c)



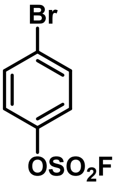
Product **1c** was obtained as an orange oil (2.06 g, 98% yield). ^1H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[6] MS EI (m/z): $[M]^+$ calcd. for $C_6H_4ClFO_3S$, 210; found, 210.

2.4. 2-Chlorophenyl Sulfurofluoridate (1d)



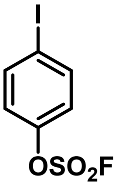
Product **1d** was obtained as a colorless oil (1.81 g, 86% yield). ^1H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[5] MS EI (m/z): $[M]^+$ calcd. for $C_6H_4ClFO_3S$, 210; found, 210.

2.5. 4-Bromophenyl Sulfurofluoridate (1e)



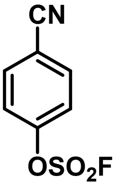
Product **1e** was obtained as a colorless oil (2.54 g, 99% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[7] MS EI (m/z): [M]$^+$ calcd. for $C_6H_4BrFO_3S$, 254; found, 254.

2.6. 4-Iodophenyl Sulfurofluoridate (1f)



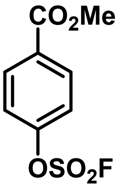
Product **1f** was obtained as a beige crystalline solid (2.96 g, 98% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[9] MS EI (m/z): [M]$^+$ calcd. for $C_6H_4FIO_3S$, 302; found, 302.

2.7. 4-Cyanophenyl Sulfurofluoridate (1g)



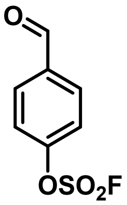
Product **1g** was obtained as a white solid (2.01 g, 99% yield, mp = 37.7–39.5 °C). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[3] MS EI (m/z): [M]$^+$ calcd. for $C_7H_4FNO_3S$, 201; found, 201.

2.8. Methyl 4-((fluorosulfonyl)oxy)benzoate (1h)



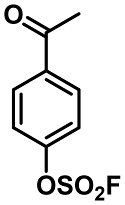
Product **1h** was obtained as a colorless oil (2.17 g, 93% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[8] MS EI (m/z): [M]$^+$ calcd. for $C_8H_7FO_5S$, 234; found, 234.

2.9. 4-Formylphenyl Sulfurofluoridate (1i)



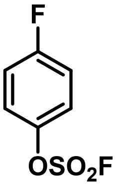
Product **1i** was obtained as a yellow oil (2.03 g, 99% yield). ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[10] MS EI (m/z): $[M]^+$ calcd. for $C_7H_5FO_4S$, 204; found, 204.

2.10. 4-Acetylphenyl Sulfurofluoridate (1j)



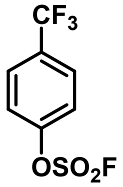
Product **1j** was obtained as a yellow oil (2.17 g, 99% yield). The ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[8] MS EI (m/z): $[M]^+$ calcd. for $C_8H_7FO_4S$, 218; found, 218.

2.11. 4-Fluorophenyl Sulfurofluoridate (1k)



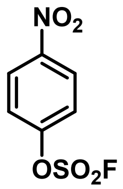
Product **1k** was obtained as a colorless oil (1.45 g, 75% yield). ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[7] MS EI (m/z): $[M]^+$ calcd. for $C_6H_4F_2NO_3S$, 194; found, 194.

2.12. 4-(Trifluoromethyl)phenyl Sulfurofluoridate (1l)



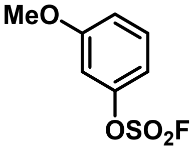
Product **1l** was obtained as a colorless oil (2.17 g, 89% yield). ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[3] MS EI (m/z): $[M]^+$ calcd. for $C_7H_4F_4O_3S$, 244; found, 244.

2.13. 4-Nitrophenyl Sulfurofluoridate (1m)



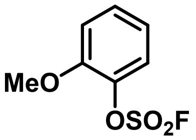
Product **1m** was obtained as a yellow oil (2.11 g, 95% yield). ^{1}H NMR ($CDCl_3$), ^{19}F NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) spectra matched those previously reported in the literature.[3] MS EI (m/z): $[M]^+$ calcd. for $C_6H_4FNO_5S$, 221; found, 221.

2.14. 3-Methoxyphenyl Sulfurofluoridate (1n)



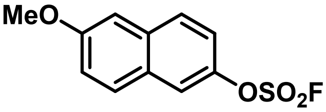
Product 1n was obtained as a colorless oil (2.04 g, 99% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[4] MS EI (m/z): [M]$^+$ calcd. for $C_7H_7FO_4S$, 206; found, 206.

2.15. 2-Methoxyphenyl Sulfurofluoridate (1o)



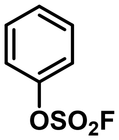
Product **1o** was obtained as a colorless oil (1.77 g, 86% yield). The ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[2] MS EI (m/z): [M]$^+$ calcd. for $C_7H_7FO_4S$, 206; found, 206.

2.16. 6-Methoxynaphthalen-2-yl Sulfurofluoridate (1p)



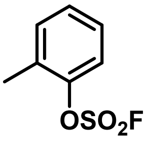
Product **1p** was obtained as a brown solid (2.14 g, 84% yield). ^{1}H NMR (300.36 MHz, CDCl$_3$): δ = 7.90 – 7.71 (m, 3H), 7.41 (ddd, J = 9.0, 2.6, 1.0 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.19 (d, J = 2.5 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (75 MHz, CDCl$_3$) δ = 158.8, 146.2, 134.1, 129.6, 129.4, 128.7, 120.8, 119.6, 118.9, 105.9, 55.6. ^{19}F NMR (282 MHz, CDCl$_3$) δ = 37.28 ppm. MS EI (m/z): [M]$^+$ calcd. for $C_{11}H_9FO_4S$, 256; found, 256.

2.17. Phenyl Sulfurofluoridate (1q)



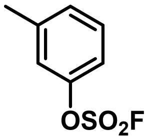
Product **1q** was obtained as a colorless oil (0.704 g, 40% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[1] MS EI (m/z): [M]$^+$ calcd. for $C_6H_5FO_3S$, 176; found, 176.

2.18. *o*-Tolyl Sulfurofluoridate (1r)



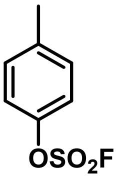
Product **1r** was obtained as a colorless oil (1.58 g, 83% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[2] MS EI (m/z): [M]$^+$ calcd. for $C_7H_7FO_3S$, 190; found, 190.

2.19. *m*-Tolyl Sulfurofluoridate (1s)



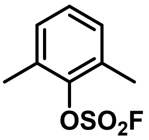
Product **1s** was obtained as a colorless oil (1.73 g, 91% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[3] MS EI (m/z): [M]$^+$ calcd. for $C_7H_7FO_3S$, 190; found, 190.

2.20. *p*-Tolyl Sulfurofluoridate (1t)



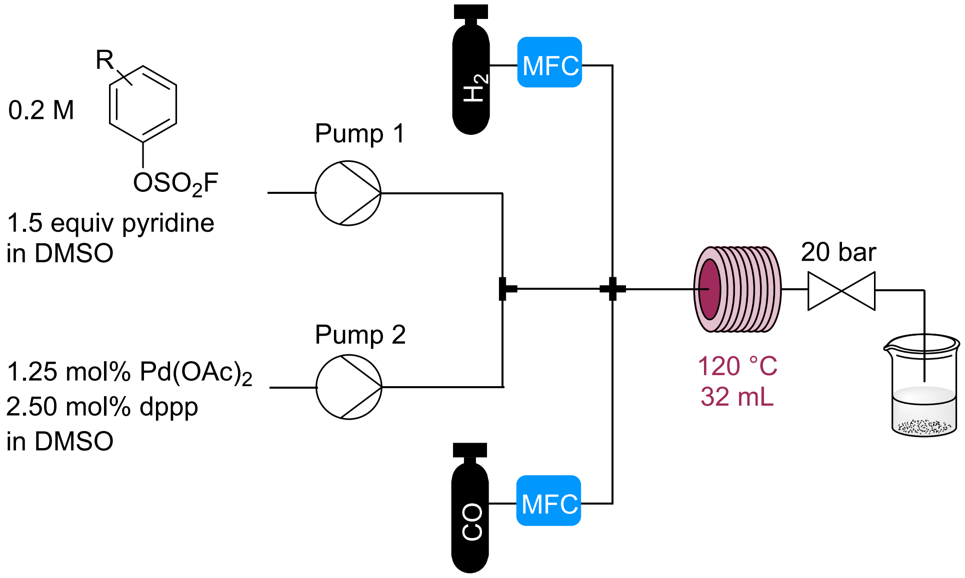
Product **1t** was obtained as a colorless oil (1.62 g, 85% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[3] MS EI (m/z): [M]$^+$ calcd. for $C_7H_7FO_3S$, 190; found, 190.

2.21. 2,6-Dimethylphenyl Sulfurofluoridate (1u)



Product **1u** was obtained as a colorless oil (1.82 g, 89% yield). ^{1}H NMR (CDCl$_3$), ^{19}F NMR (CDCl$_3$), and ^{13}C NMR (CDCl$_3$) spectra matched those previously reported in the literature.[4] MS EI (m/z): [M]$^+$ calcd. for $C_8H_9FO_3S$, 204; found, 204.

3. General Procedure B for the Formylation of EWG Containing Aryl Fluorosulfonates 2a-2m



The flow setup consisted of two HPLC pumps (Uniqsis FlowSyn, Feed 1 and 2). Input solutions for feeds 1 and 2 were prepared with DMSO, in oven-dried volumetric flasks as follows:

Feed 1: 0.2 M fluorosulfonates (2 mmol, 1 equiv) and pyridine (3 mmol, 1.5 equiv) in DMSO within a 10 mL volumetric flask.

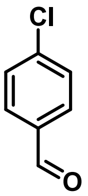
Feed 2: 0.0025 M $Pd(OAc)_2$ (14 mg, 62.5 µmol) and 0.005 M dppp (48 mg, 0.125 mmol) in DMSO within a 25 mL volumetric flask.

Feeds 1 and 2 were introduced through sample loops (Feed 1, 2 mL, 0.4 mmol, Feed 2, 3 mL) using DMSO as carrier solvent.

Before commencing the experiment, the reactor setup was flushed by pumping DMSO with a flow rate of 0.30 mL/min; using the pump for feed 1; and 0.30 mL/min using the pump for feed 2. Gas flow rates were measured in units of $mL_n\ min^{-1}$, where n represents measurement under standard conditions, i.e., T_n = 0 °C, P_n = 1.01 bar. Hydrogen was introduced into the reactor with a flow rate of 1.87 mL_n/min (1.4 equiv) using a calibrated mass flow controller (MFC, Bronkhorst, EL-FLOW). Carbon monoxide was introduced into the reactor with a flow rate of 1.87 mL_n/min (1.4 equiv) using a calibrated mass flow controller (MFC, Bronkhorst, EL-FLOW). To commence the experiment, the pumping of DMSO at pumps 1 and 2 was switched to their respective input solution whilst maintaining their flow rate. Feed 1 and 2 were combined within an arrowhead mixer at room temperature. The combined reaction feed was mixed with CO and H_2 in a four-way mixer. The biphasic gas liquid mixture was passed through a stainless-steel reaction coil before exiting the system through a back-pressure regulator (Zaiput BPR-10). The system was maintained at 120 °C and 20 bar pressure to provide ~43 min residence time. The residence time was measured from the three streams combining at the mixer until color was observed at the BPR. The liquid pump flow rates, temperature, and pressure were measured and monitored by the control platform of the pumping system. Once color was observed at the BPR, a fraction was collected until there was no color observed.

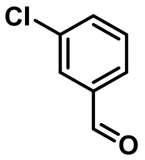
The collected process stream was diluted with Et_2O (1/1 = v/v) and washed (2x 1/1 = v/v) with aqueous 5 wt% LiCl solution. The organic phase was dried over $NaSO_4$ and concentrated under reduced pressure.

3.1. 4- Chlorobenzaldehyde (2b)



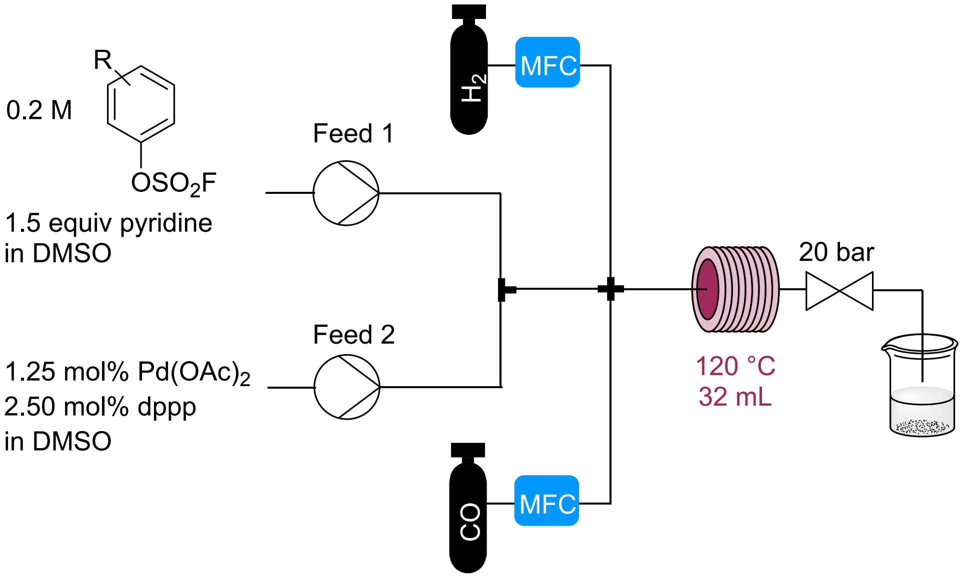
Product **2b** was obtained as after flash column chromatography (EtOAc/petroleum ether a colorless crystalline solid (50 mg, 89% yield, Mp. = 46 °C). ^{1}H NMR (300.36 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H) ppm. MS EI (m/z): $[M]^+$ calcd. for C_7H_5ClO, 140; found, 140.

3.2. 3- Chlorobenzaldehyde (2c)



Product **2c** was obtained as after flash column chromatography (EtOAc/petroleum ether a colorless oil (49 mg, 88% yield). ^{1}H NMR (300.36 MHz, $CDCl_3$): δ = 9.98 (s, 1H), 7.89 – 7.83 (m, 1H), 7.77 (dt, *J* = 7.5, 1.4 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 1H). MS EI (m/z): $[M]^+$ calcd. for C_7H_5ClO, 140; found, 140.

4. General Procedure C for the Formylation of EWG Containing Aryl Fluorosulfonates 2k-2u



The flow setup consisted of two HPLC pumps (Uniqsis FlowSyn, Feed 1 and 2). Input solutions for feeds 1 and 2 were prepared with DMSO, in oven-dried volumetric flasks as follows:

Feed 1: 0.2 M fluorosulfonate (2 mmol, 1 equiv) and pyridine (3 mmol, 1.5 equiv) in DMSO within a 10 mL volumetric flask.

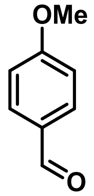
Feed 2: 0.0025 M Pd(OAc)$_2$ (14 mg, 62.5 µmol) and 0.005 M dppp (48 mg, 0.125 mmol) in DMSO within a 25 mL volumetric flask.

Feeds 1 and 2 were introduced through sample loops (Feed 1, 2 mL, 0.4 mmol; Feed 2, 3 mL) using DMSO as carrier solvent.

Before commencing the experiment, the reactor setup was flushed by pumping DMSO with a flow rate of 0.08 mL/min; using the pump for feed 1; and 0.08 mL/min using the pump for feed 2. Hydrogen was introduced into the reactor with a flow rate of 1.5 mL/min (4.5 equiv) using a calibrated mass flow controller (MFC, Bronkhorst, EL-FLOW). Carbon monoxide was introduced into the reactor with a flow rate of 0.5 mL/min (1.5 equiv) using a calibrated mass flow controller (MFC, Bronkhorst, EL-FLOW). To commence the experiment, the pumping of DMSO at pumps 1 and 2 was switched to their respective input solution whilst maintaining their flow rate. Feed 1 and 2 were combined within an arrowhead mixer at room temperature. The combined reaction feed was mixed with CO and H_2 in a four-way mixer. The biphasic gas liquid mixture was passed through a stainless-steel reaction coil before exiting the system through a back-pressure regulator (Zaiput BPR-10). The system was maintained at 120 °C and 20 bar pressure to provide ~120 min residence time. The residence time was measured from the three streams mixing at the mixer until colour was observed at the BPR. The liquid pump flow rates, temperature, and pressure were measured and monitored by the control platform of the pumping system. Once colour was observed at the BPR, a fraction was collected until there was no colour observed.

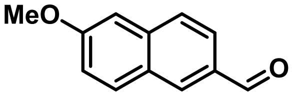
The collected process stream was diluted with Et$_2$O (1/1 = v/v) and washed (2x 1/1 = v/v) with an aqueous 5 wt% LiCl solution. The organic phase was dried over NaSO$_4$ and concentrated under reduced pressure.

4.1. 4-Anisaldehyde (2a)



Product **2a** was obtained as a colorless oil (49 mg, 90% yield). ^{1}H NMR (300.36 MHz, CDCl$_3$): δ = 9.88 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H) ppm. MS EI (m/z): [M]$^+$ calcd. for $C_8H_8O_2$, 136; found, 136.

4.2. 6-Methoxy-2-naphthaldehyde (2p)



Product **2p** was obtained after flash column chromatography (EtOAc/petroleum ether) as a colorless solid (61 mg, 82% yield, mp = 82 °C). ^{1}H NMR (300.36 MHz, $CDCl_3$): δ = 10.10 (d, *J* = 0.7 Hz, 1H), 8.35 – 8.17 (m, 1H), 8.01 – 7.71 (m, 3H), 7.31 – 7.14 (m, 2H), 3.96 (s, 3H) ppm. MS EI (m/z): $[M]^+$ calcd. for $C_{12}H_{10}O_2$, 186; found, 186.

5. Optimization of Reaction Parameters

5.1. Pressure

Increasing the pressure to 20 bar suppressed the formation of the defunctionalized product. The GC yield of obtained 4-methoxybenzaldehyde (**2a**) remained similar.

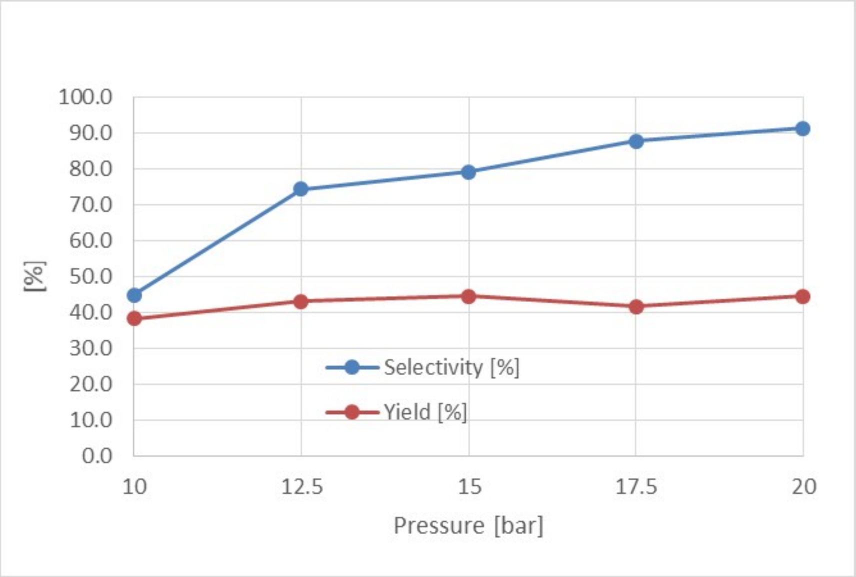


Figure S1 Influence of pressure on 4-methoxybenzaldehyde (**2a**) GC yield. Conditions: Feed 1: 0.2 M 4-methoxy sulfurofluoridate (1a), 1.5 equiv pyridine and 0.15 equiv Ph_2O in DMF/DMSO = 40/60; Feed 2: 1.25 mol% $Pd(OAc)_2$ and 2.5 mol% dppp in DMSO. H_2 and CO were introduced via mass flow controller with flow rates for Feed 1/Feed 2/H_2/CO = 0.3:0.3:1.5:1.5 mL/min. System pressure was gradually increased for 2.5 bar every run, the residence time varied accordingly.

5.2. Catalyst Loading

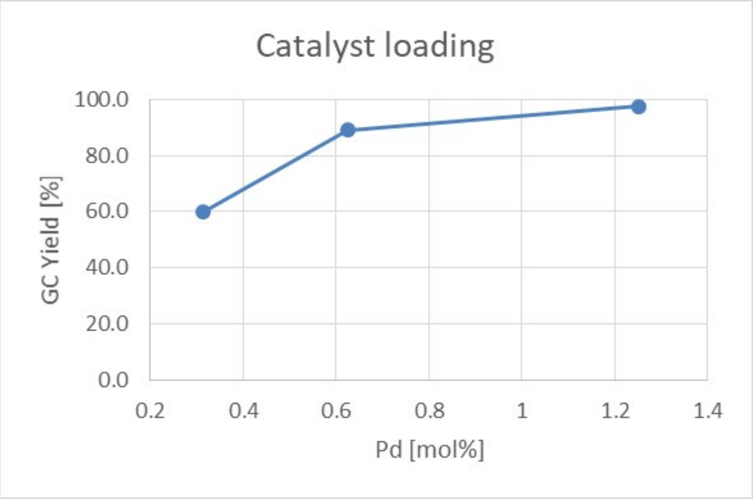


Figure S2 Influence of catalyst loading on 4-chlorobenzaldehyde (**2b**) GC yield. Conditions: Feed 1: 0.2 M 4-chloro sulfurofluoridate (1b), 1.5 equiv pyridine and 0.15 equiv Ph_2O in DMSO; Feed 2: $Pd(OAc)_2$ and dppp in DMSO. Feed 1/Feed 2/H_2/CO = 0.3:0.3:1.5:1.5 mL/min resulting in a residence time of 43 min. System pressure was maintained at 20 bar.

5.3. Residence Time EWG

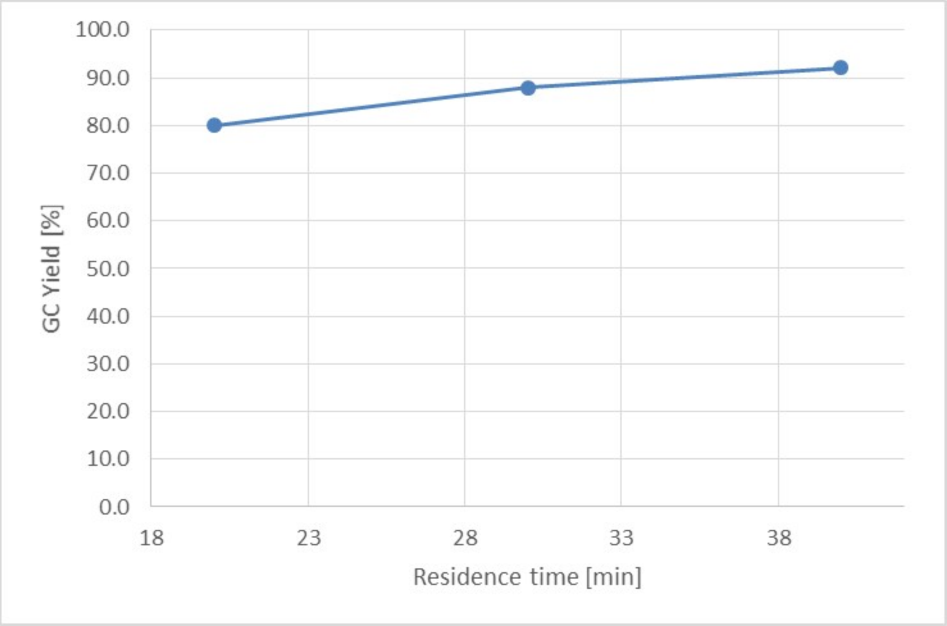


Figure S3 Influence of residence time on 4-chlorobenzaldehyde (**2b**). Conditions: Feed 1: 0.2 M 4-chloro sulfurofluoridate (**1b**), 1.5 equiv pyridine and 0.15 equiv Ph_2O in DMSO; Feed 2: 1.25 mol% $Pd(OAc)_2$ and 2.5 mol% dppp in DMSO. Flow rate ratio of H_2/CO = 1/1. System pressure was maintained at 20 bar.

5.4. Residence Time EDG

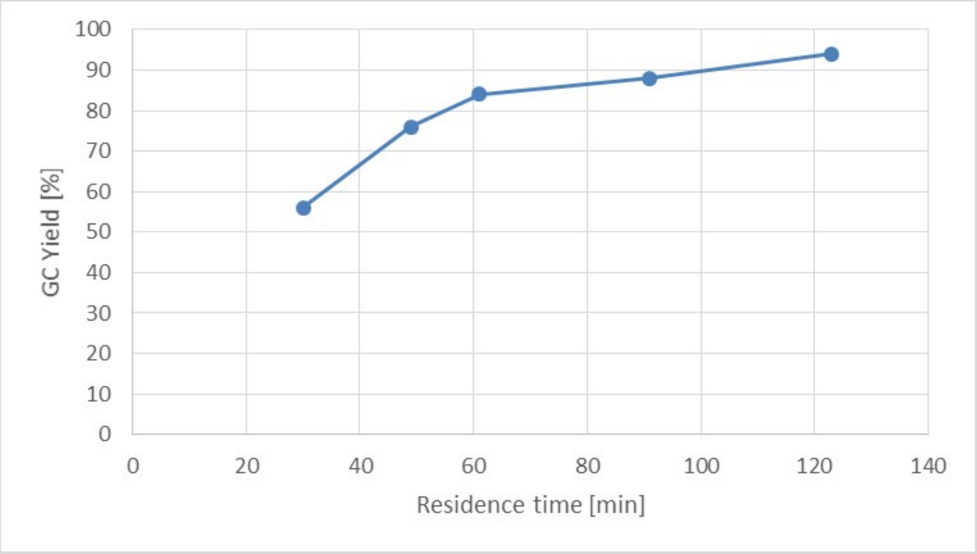


Figure S4 Influence of residence time on 4-methoxybenzaldehyde (**2a**) GC yield. Conditions: Feed 1: 0.2 M 4-methoxy sulfurofluoridate (**1a**), 1.5 equiv pyridine and 0.15 equiv Ph_2O in DMSO; Feed 2: 1.25 mol% $Pd(OAc)_2$ and 2.5 mol% dppp in DMSO. H_2/CO = 1/3. System pressure was maintained at 20 bar.

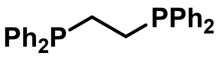
5.5. Ligand Screening

Table S1 4-Chlorobenzaldehyde (**2b**) for different ligand systems. Conditions: Feed 1: 0.2 M 4-chloro sulfurofluoridate (**1b**), 1.5 equiv pyridine and 0.15 equiv Ph_2O in DMSO; Feed 2: 1.25 mol% $Pd(OAc)_2$ and 2.5 mol%

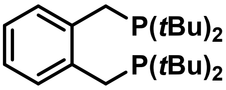
ligand in DMSO. Feed 1/Feed 2/H_2/CO = 0.6:0.6:3:3 mL/min resulting in a residence time of 21 min. System pressure was maintained at 20 bar.

Ligand	Conversion [%]	Selectivity [%]	Yield [%]
Dppp	89.6	83.1	74.5
Dppe	35.2	73.9	26.0
dtbbx	54.9	2.3	1.3
2,2-bipy	1.9	0.0	0.0
cataCXium A	1.9	0.0	0.0
XantPhos	2.4	0.0	0.0

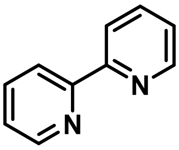
dppp



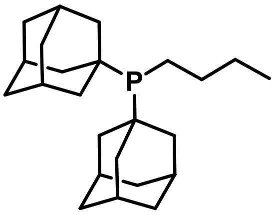
dppe



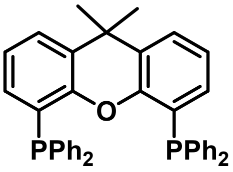
dtbpx



2,2-bipy

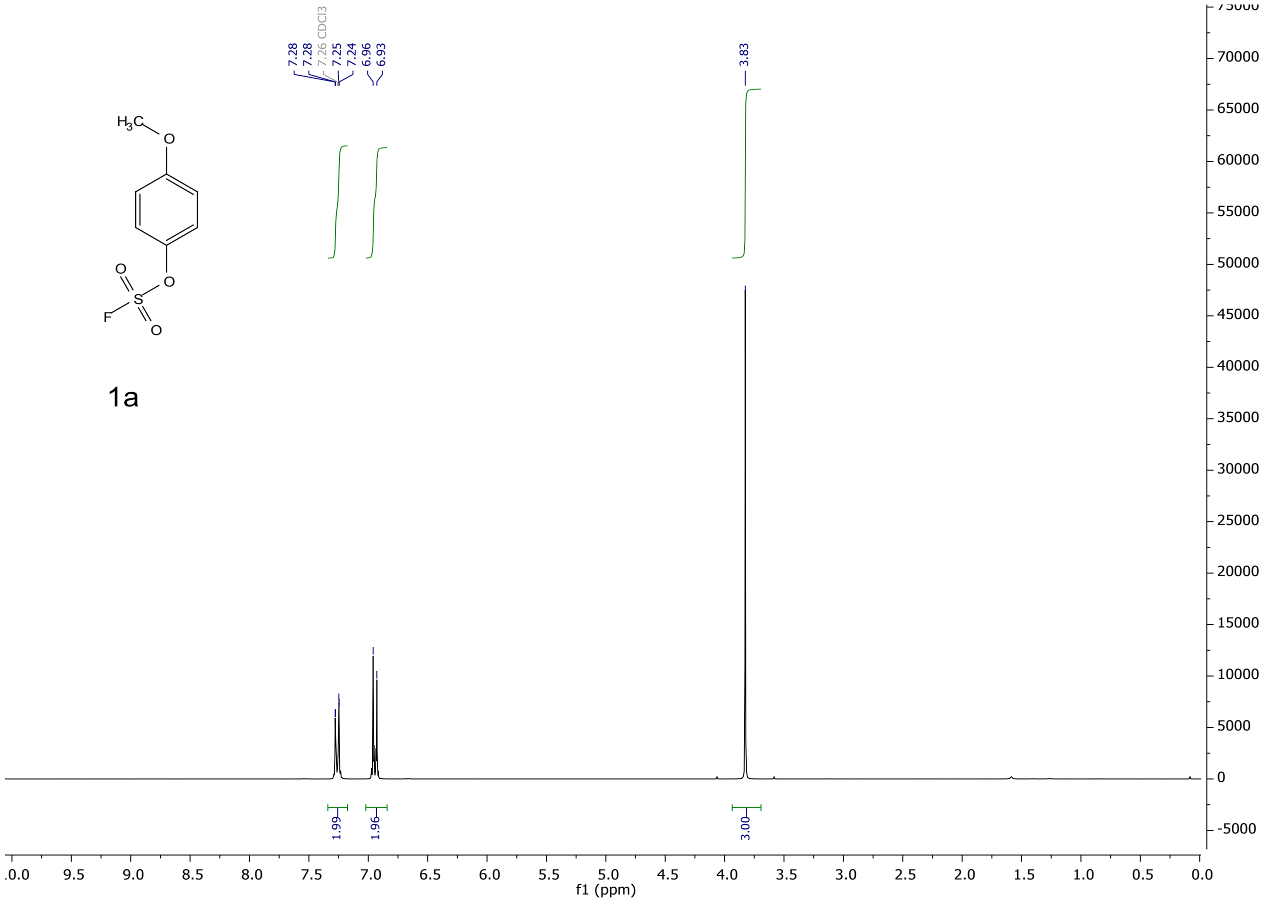


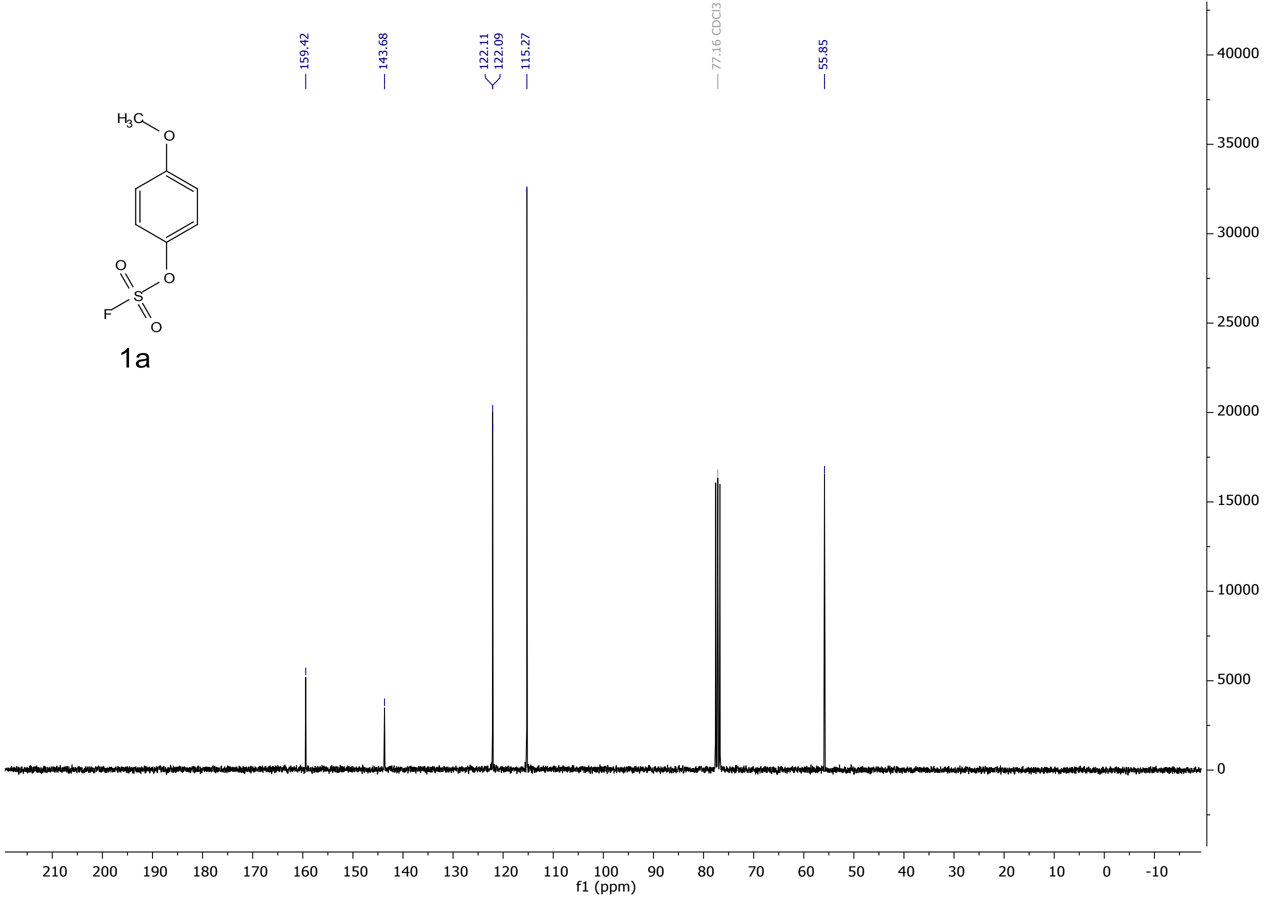
CataCXium A

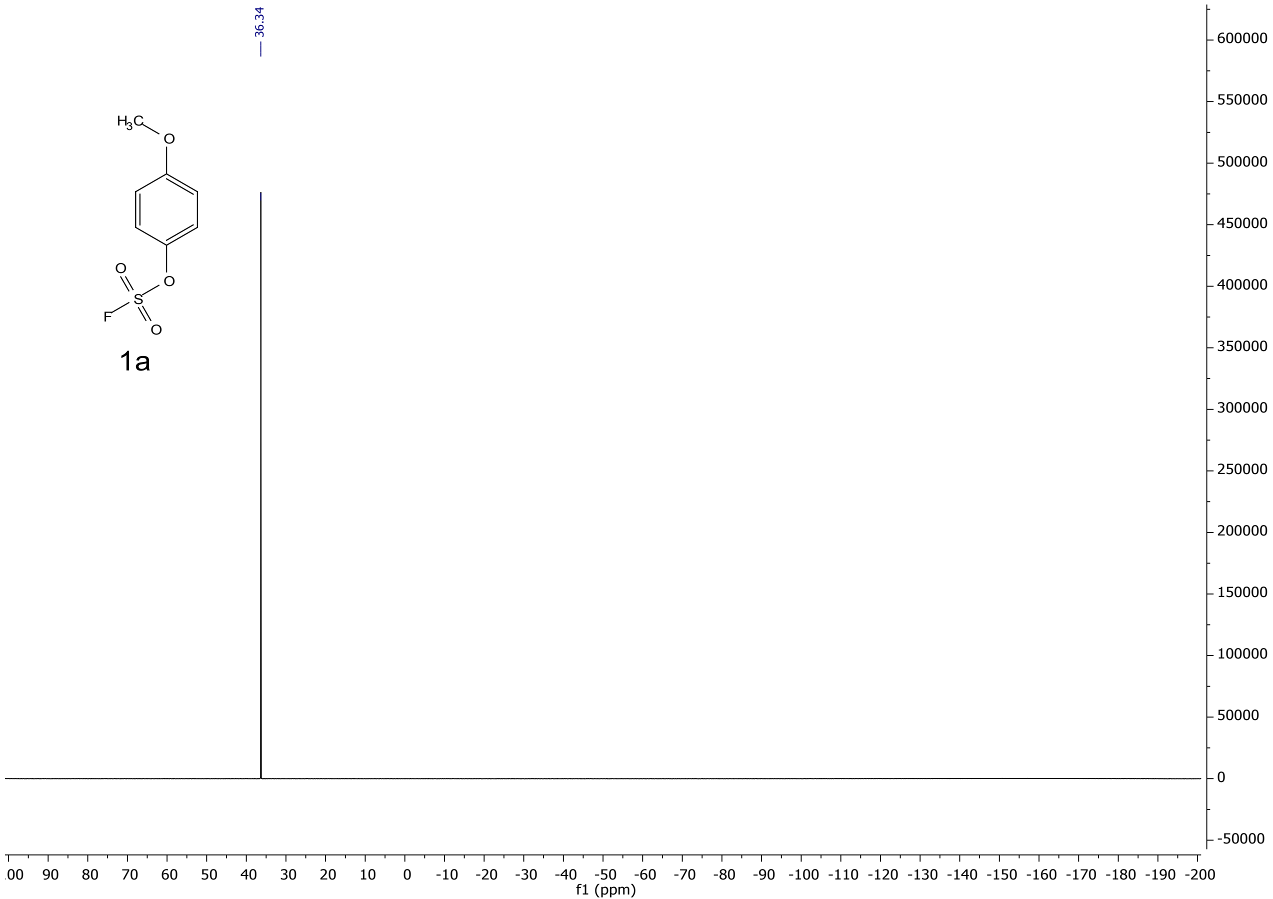


XantPhos

6. NMR spectra



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S
F
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250000
200000
150000
100000
50000
0
-50000
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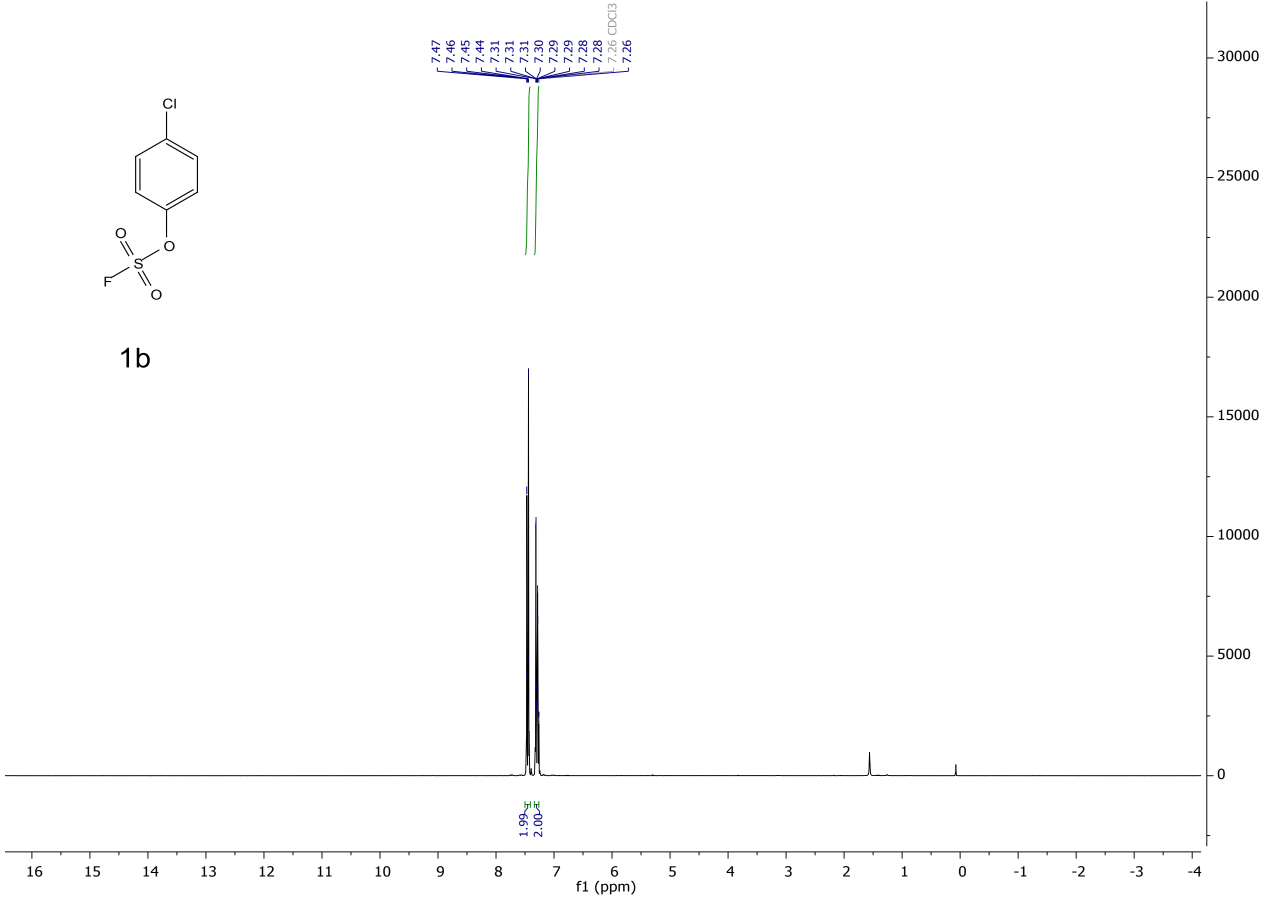
f1 (ppm)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7.45
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7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.26 CDCl3
7.26
Cl
O
O
S
F
O
30000
25000
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10000
5000
0
1.99
2.00
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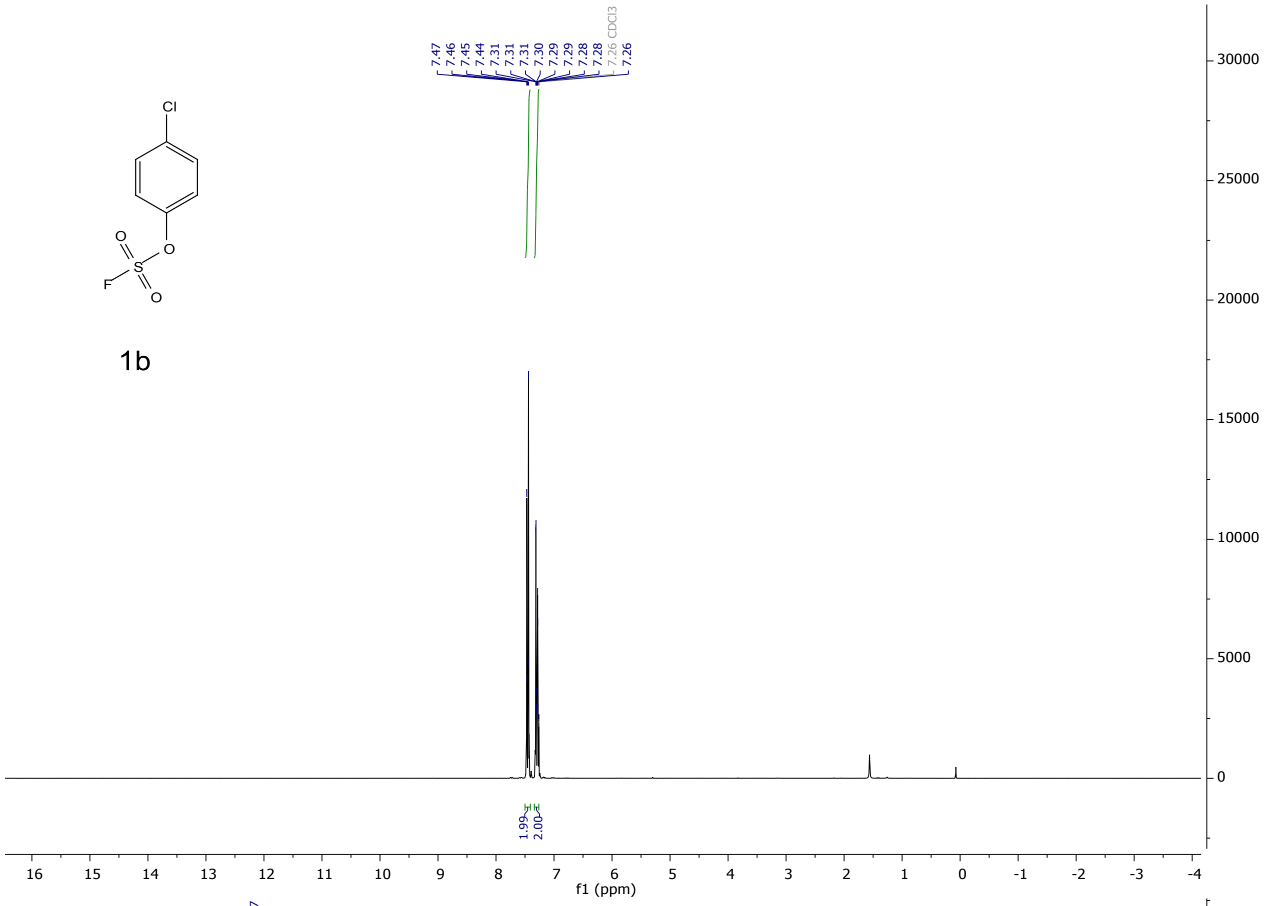
f1 (ppm)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7.26
Cl
O
S
F
O
O
1b
1.99
2.00
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10000
5000
0
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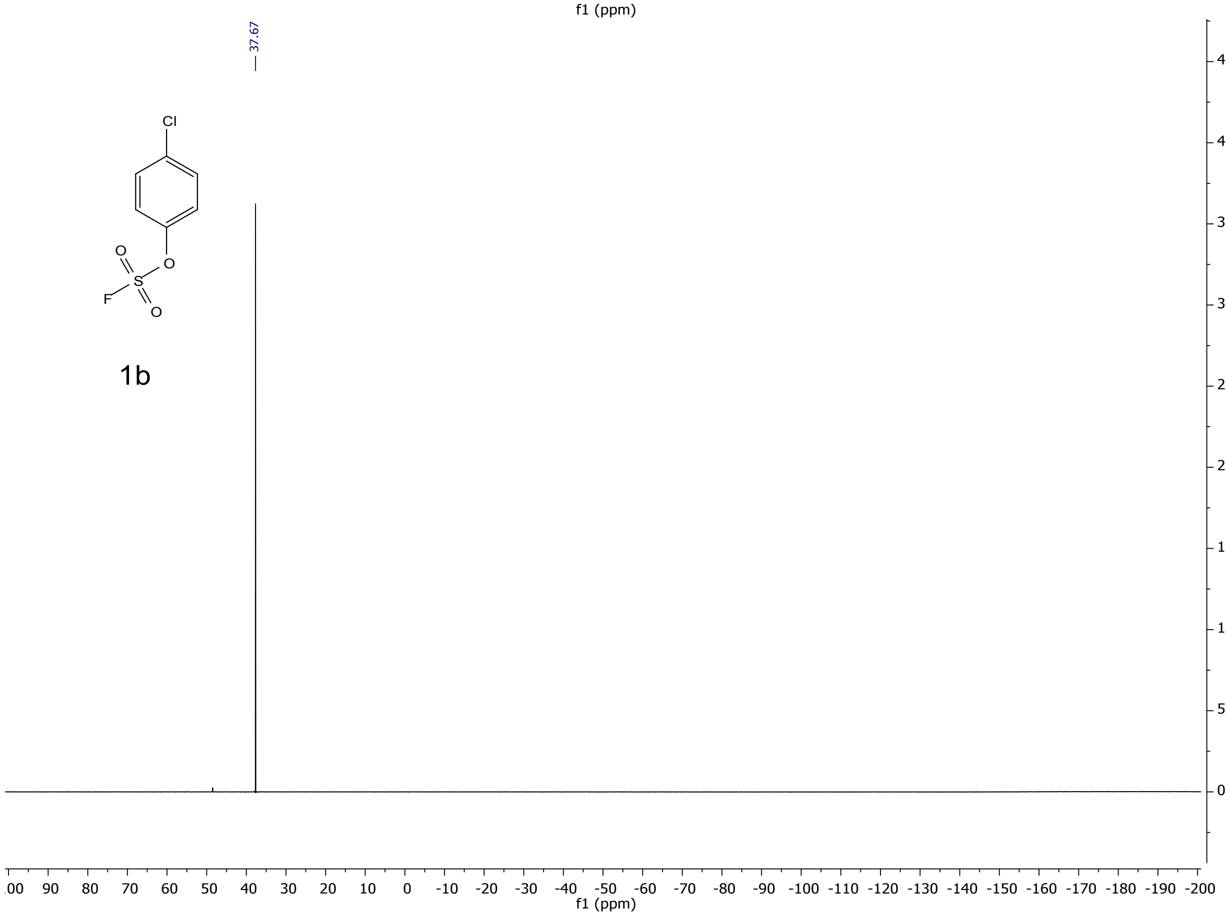
f1 (ppm)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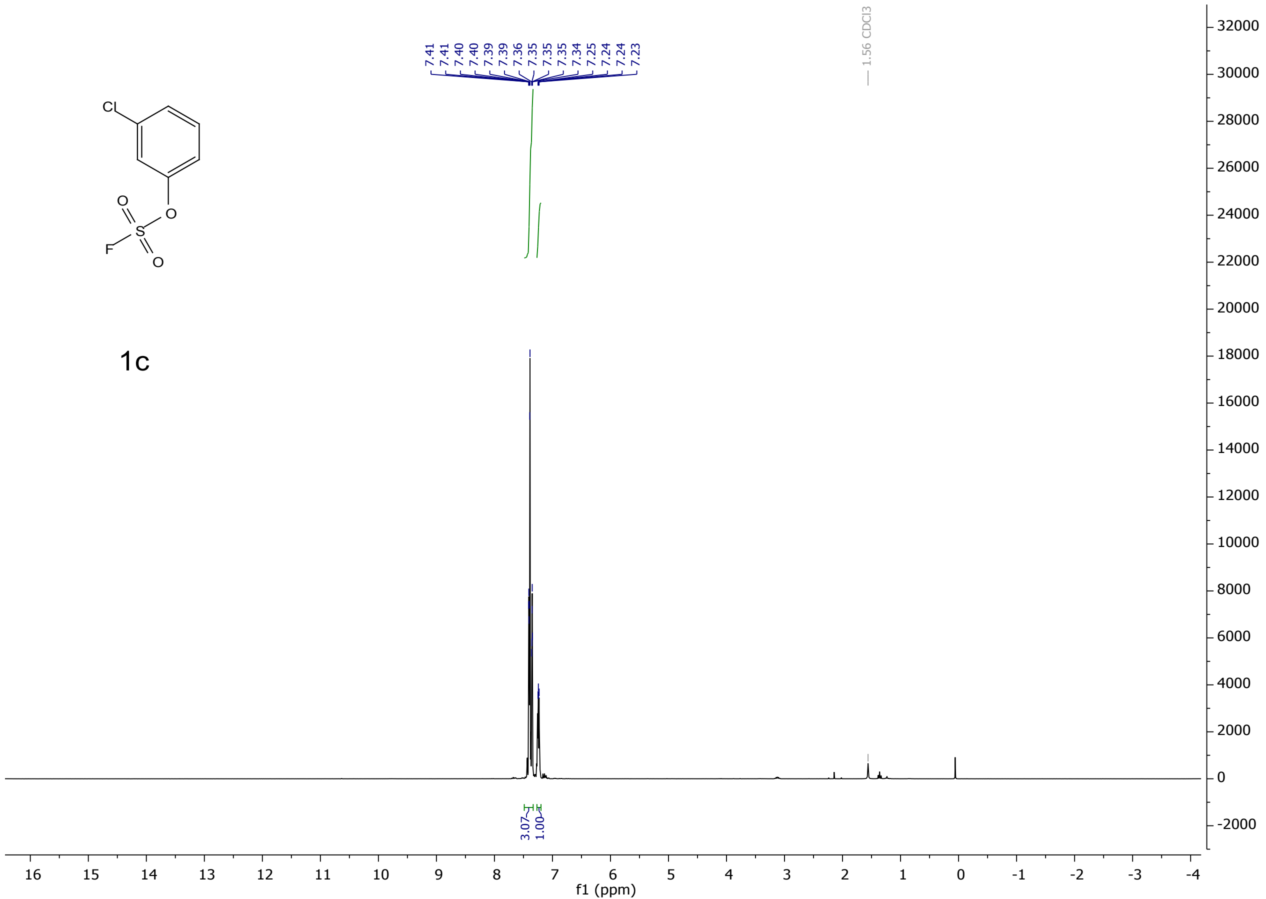
f1 (ppm)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7.39
7.36
7.35
7.35
7.35
7.34
7.25
7.24
7.24
7.23
1.56 CDCl3
Cl
O
O
S
O
F
1c
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1.00
32000
30000
28000
26000
24000
22000
20000
18000
16000
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2000
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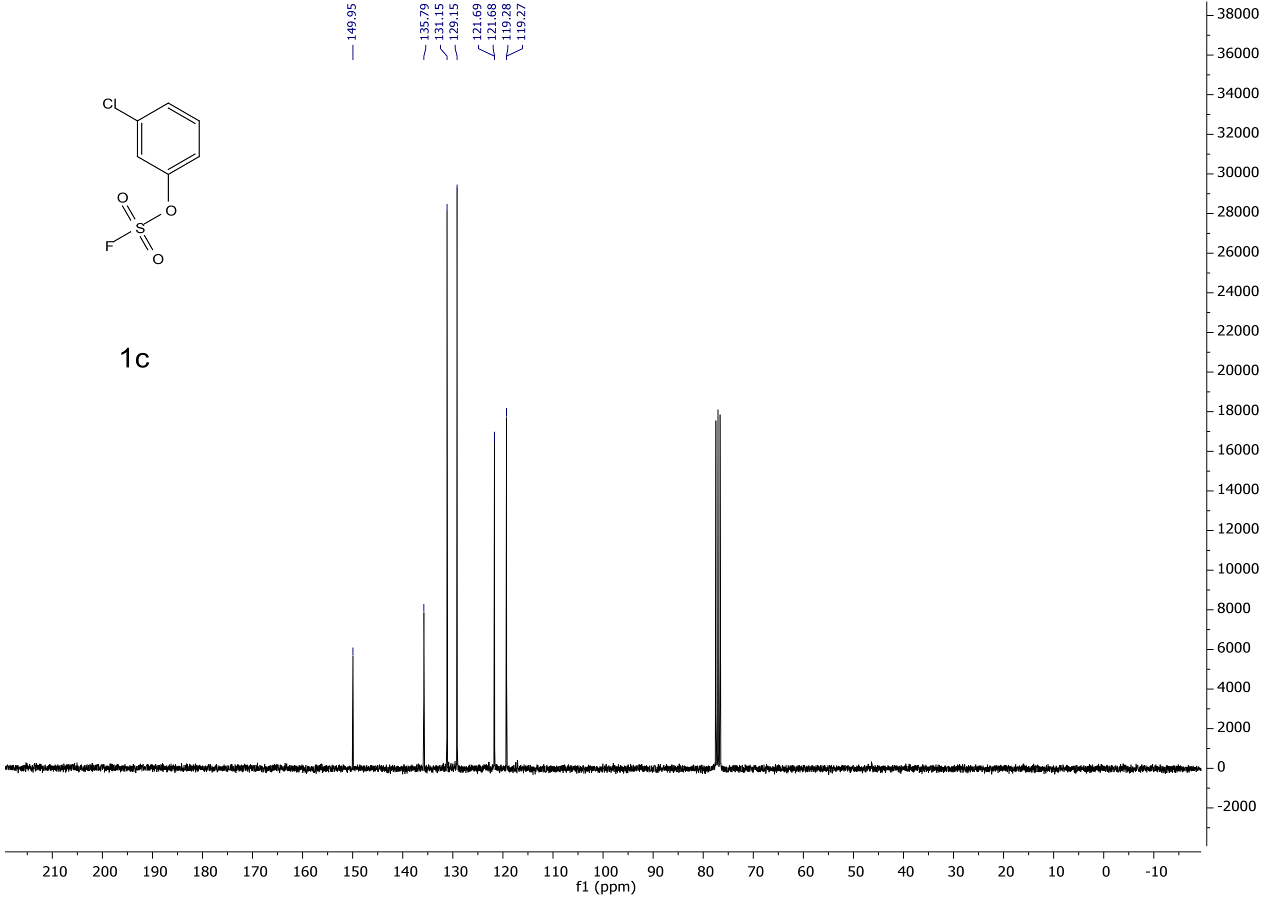
f1 (ppm)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119.27
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S
O
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32000
30000
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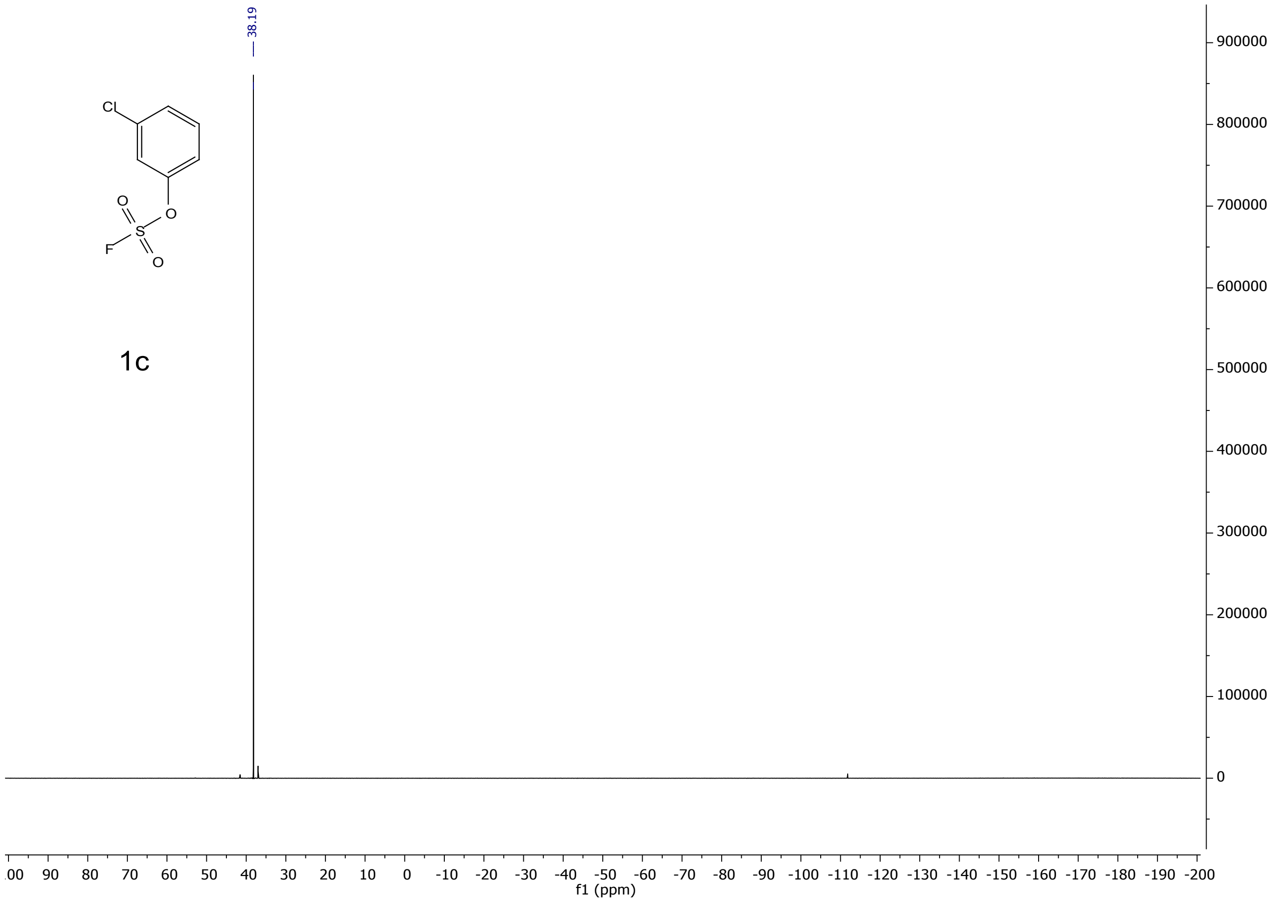
f1 (ppm)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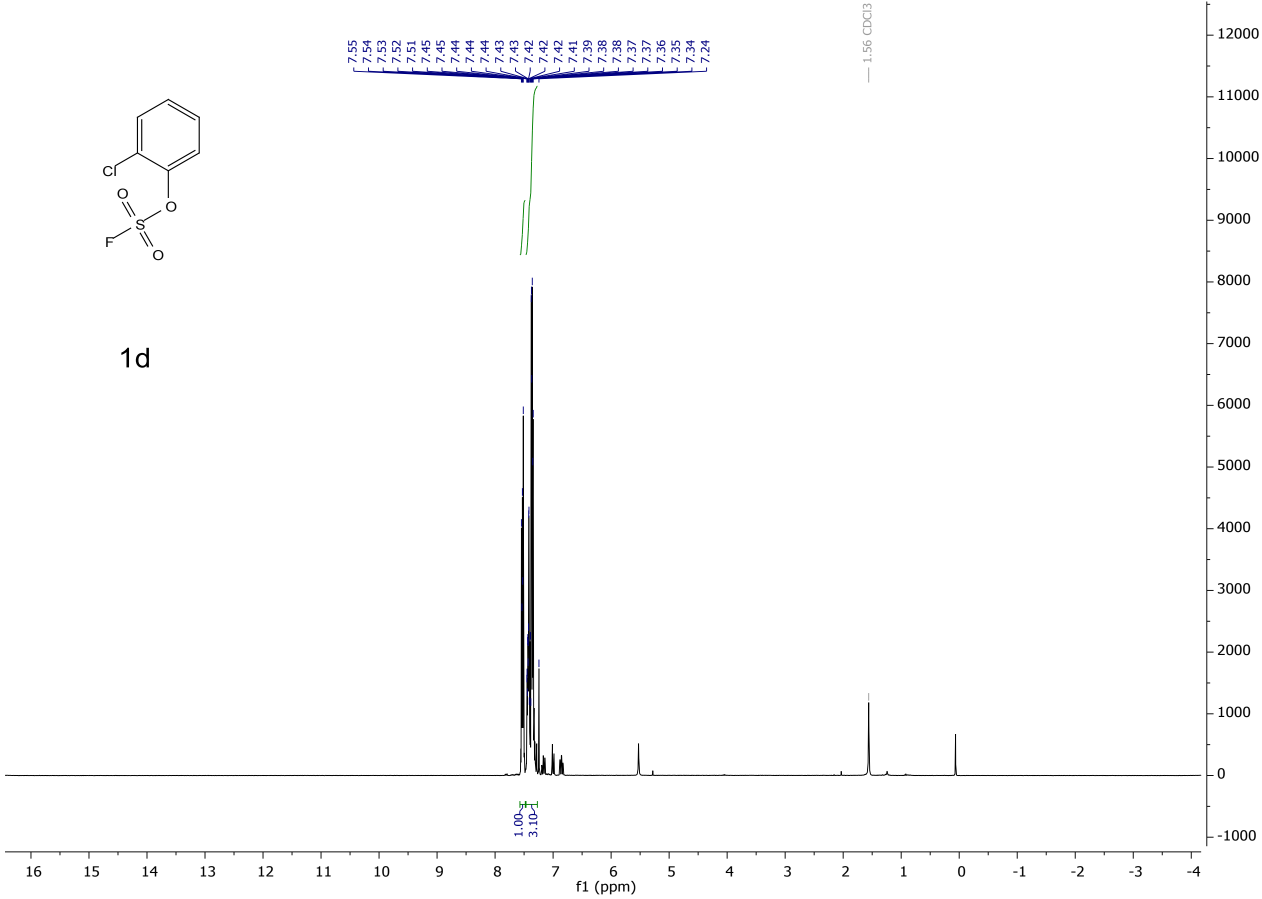
f1 (ppm)

1c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7.41
7.39
7.38
7.38
7.37
7.37
7.36
7.35
7.34
7.24
1.56 CDCl3
Cl
O
S
F
O
O
1.00
3.10
12000
11000
10000
9000
8000
7000
6000
5000
4000
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1000
0
-1000
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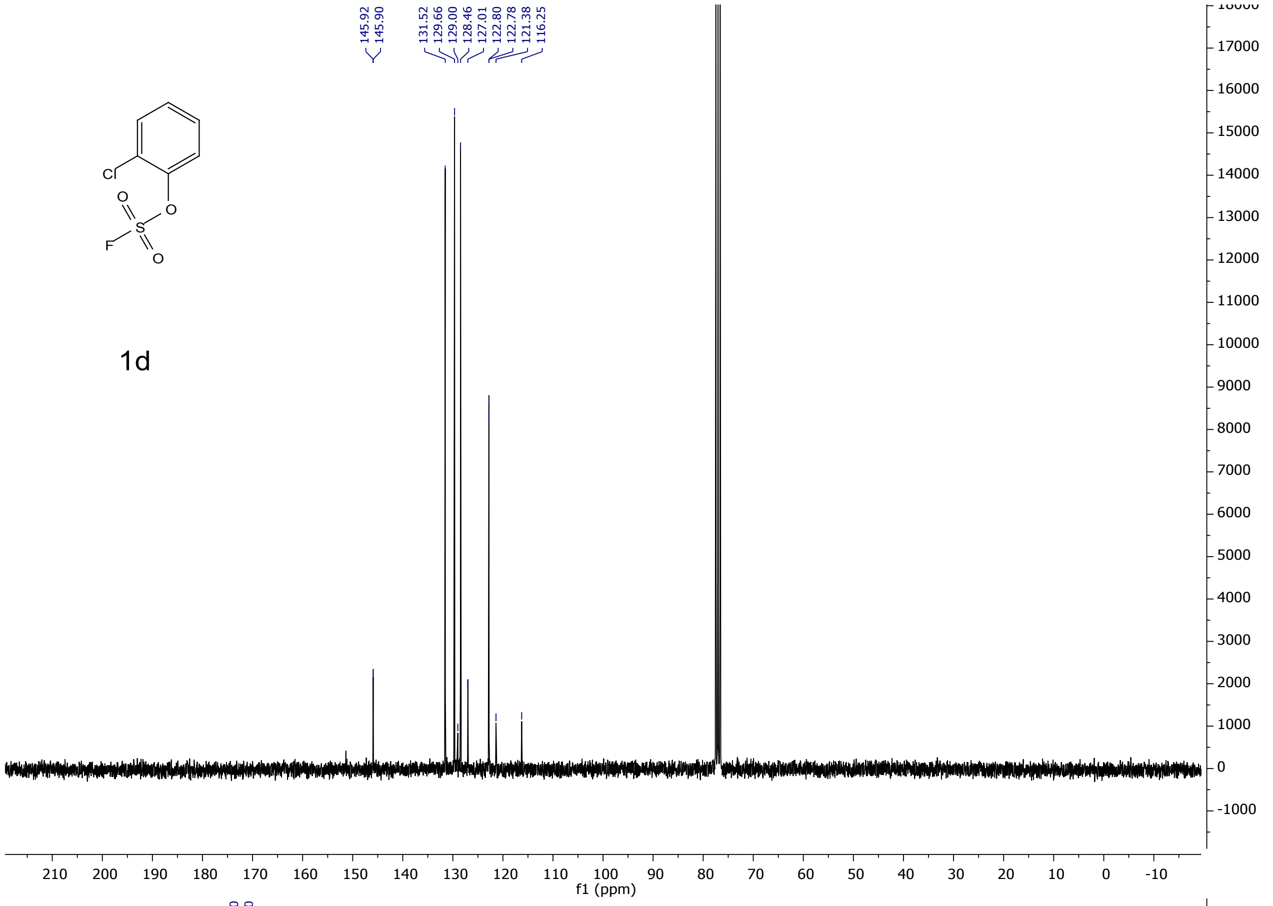
f1 (ppm)

1d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O
S
F
O
1d
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17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
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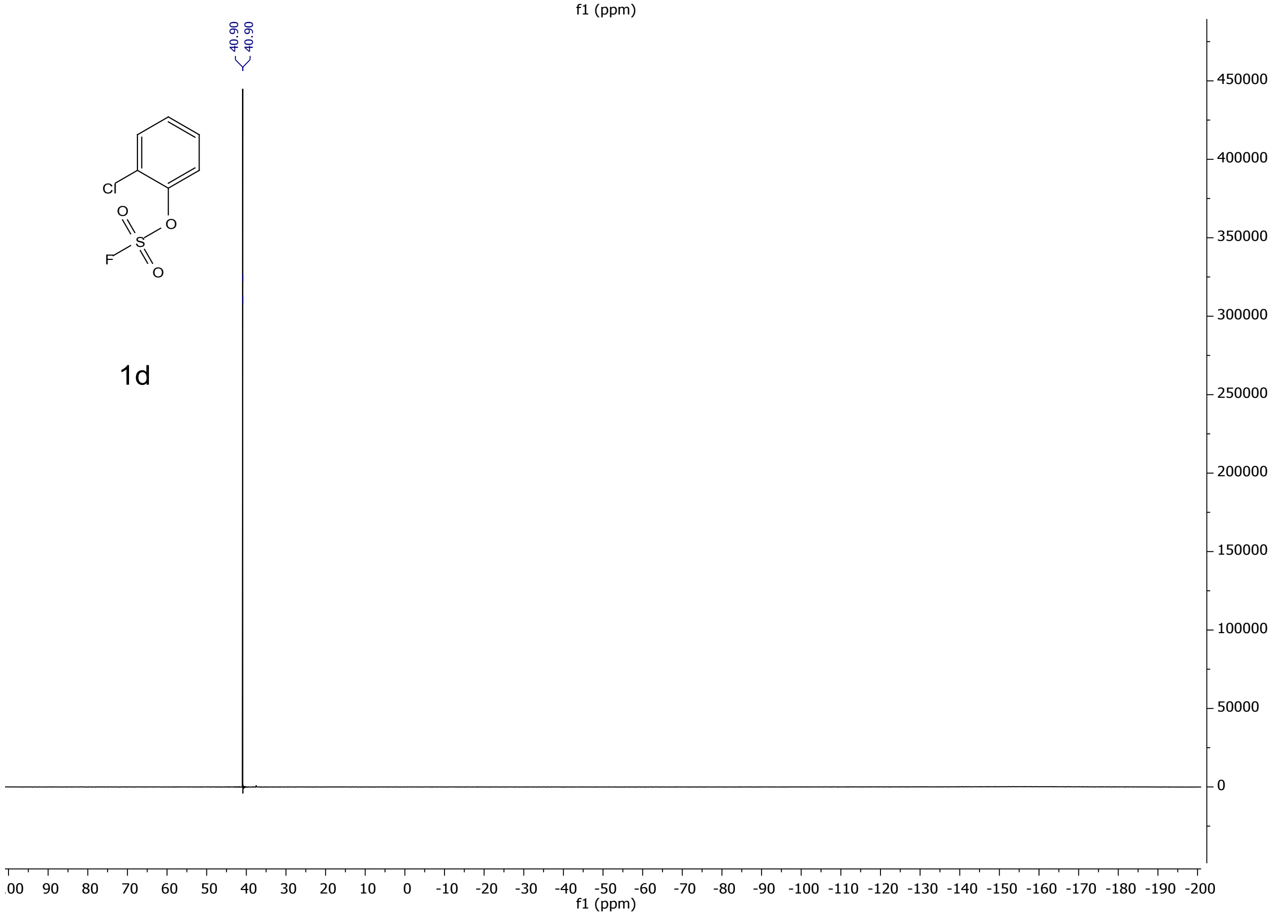
f1 (ppm)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50000
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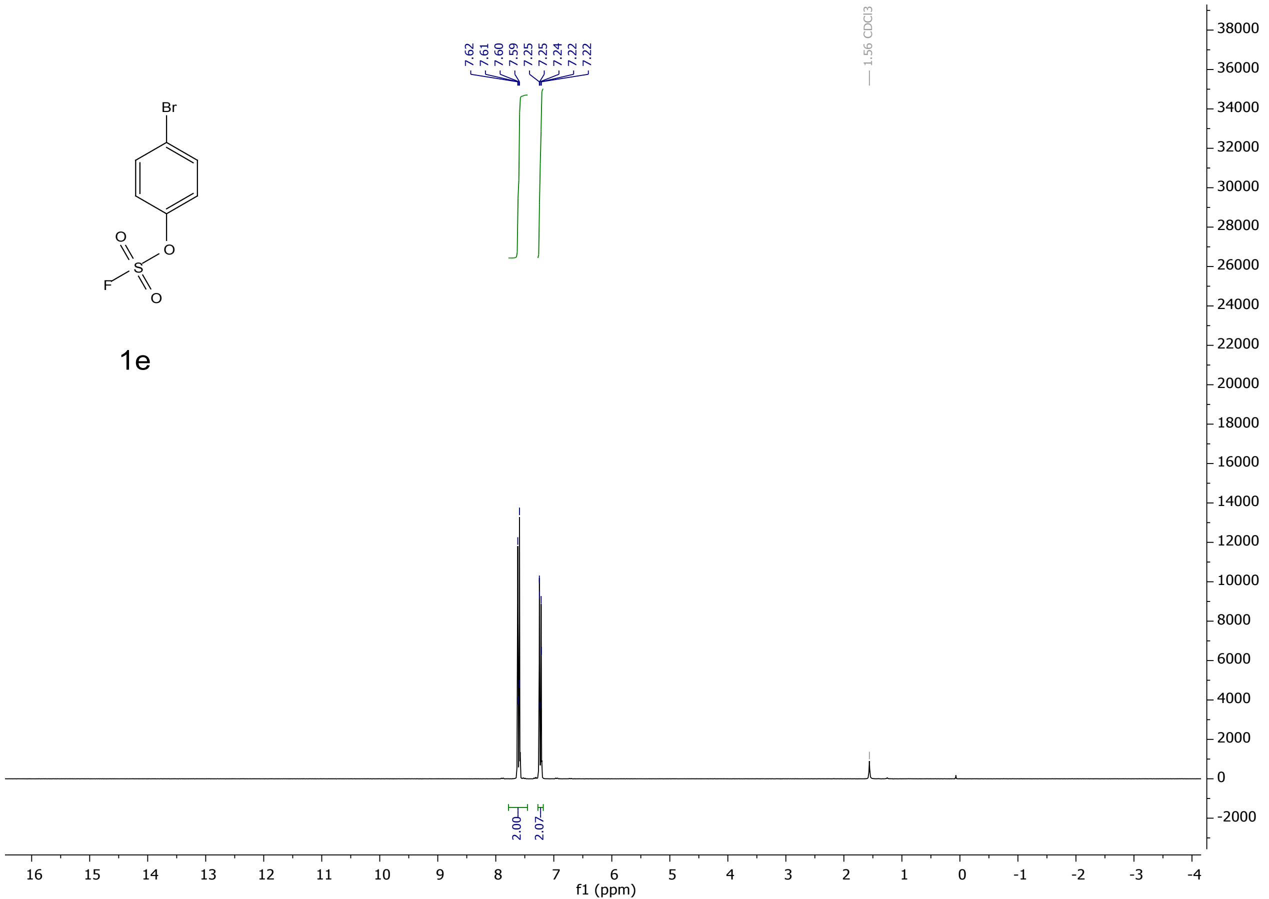
f1 (ppm)


1e

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O
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7.61
7.60
7.59
7.25
7.25
7.24
7.22
7.22
1.56 CDCl3
2.00
2.07
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f1 (ppm)
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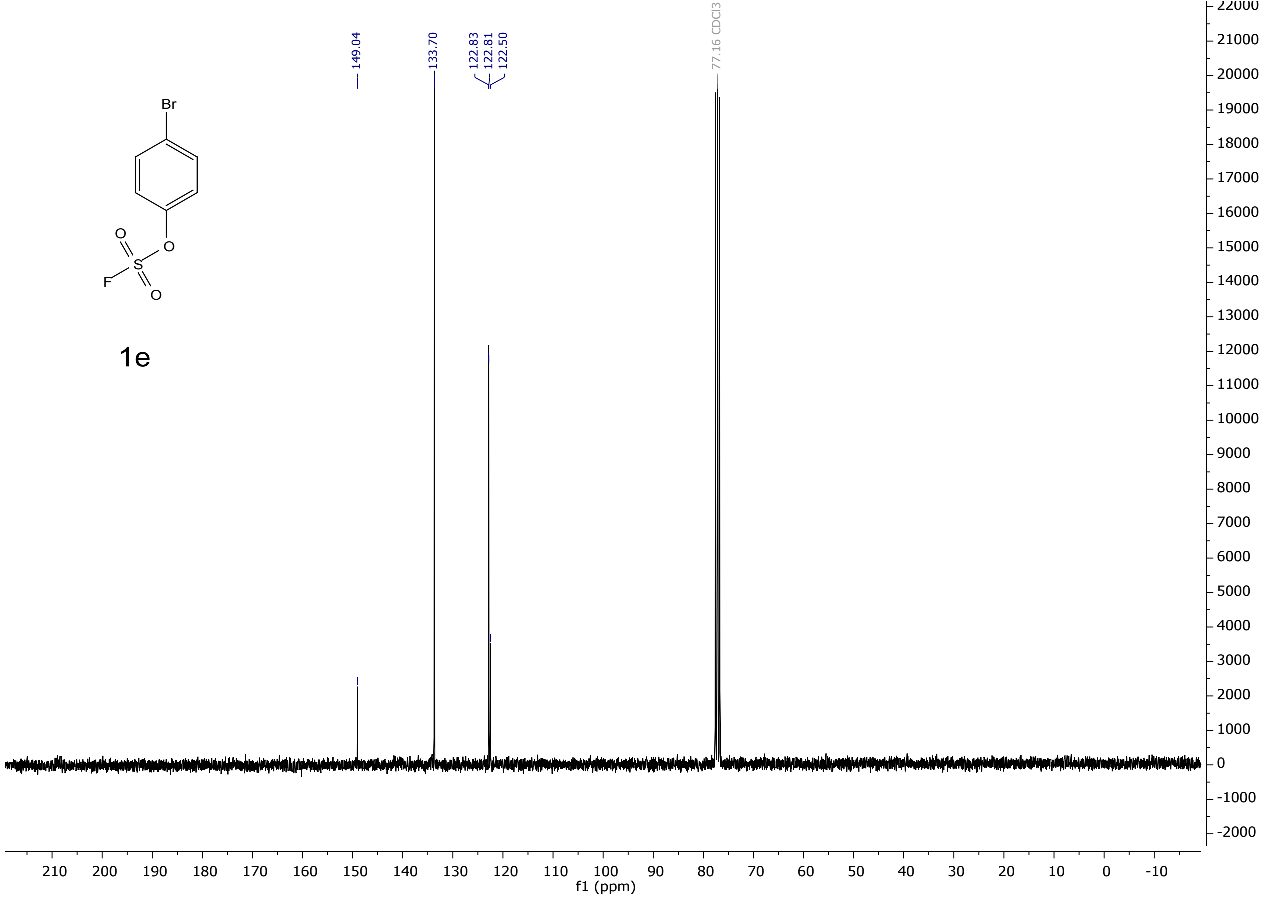
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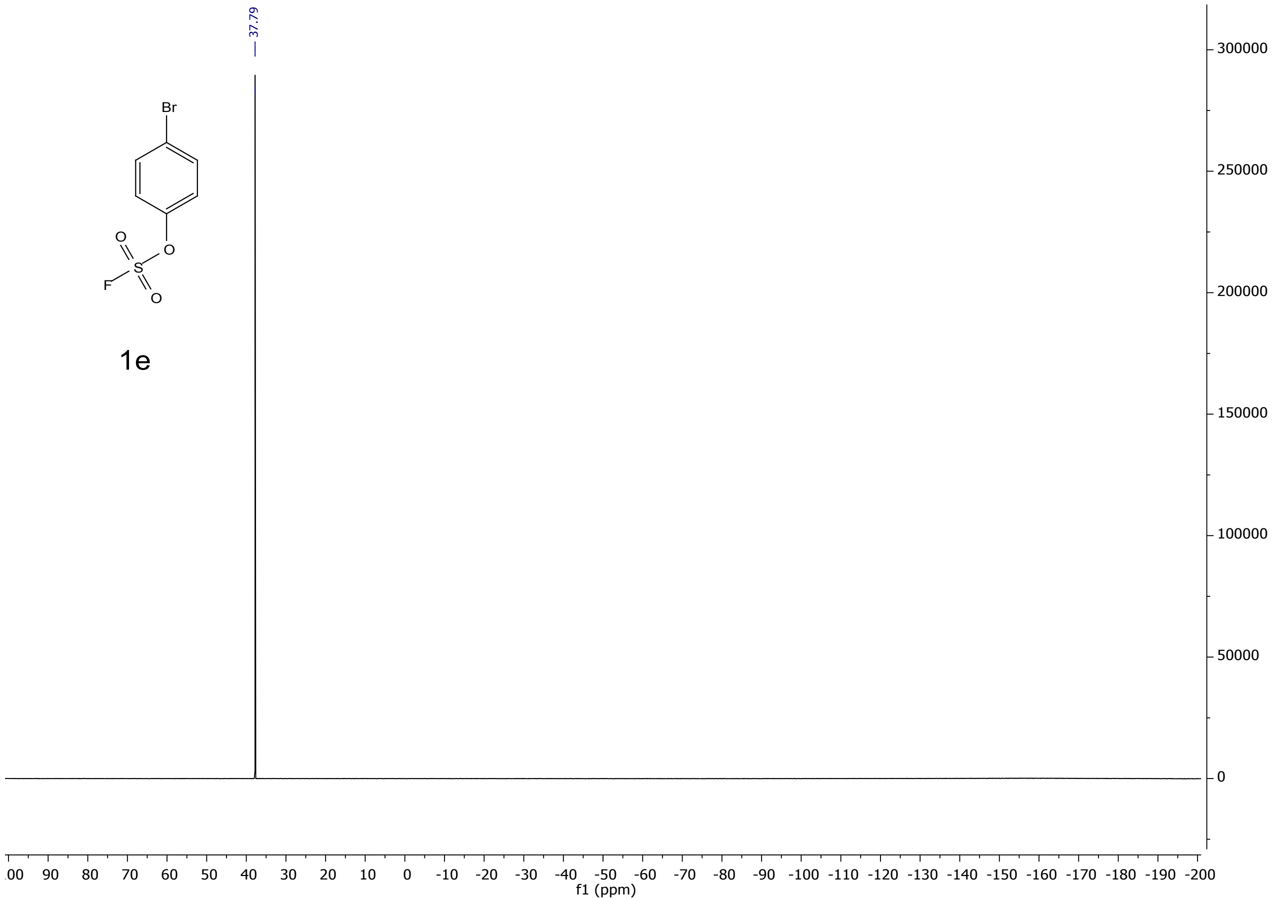

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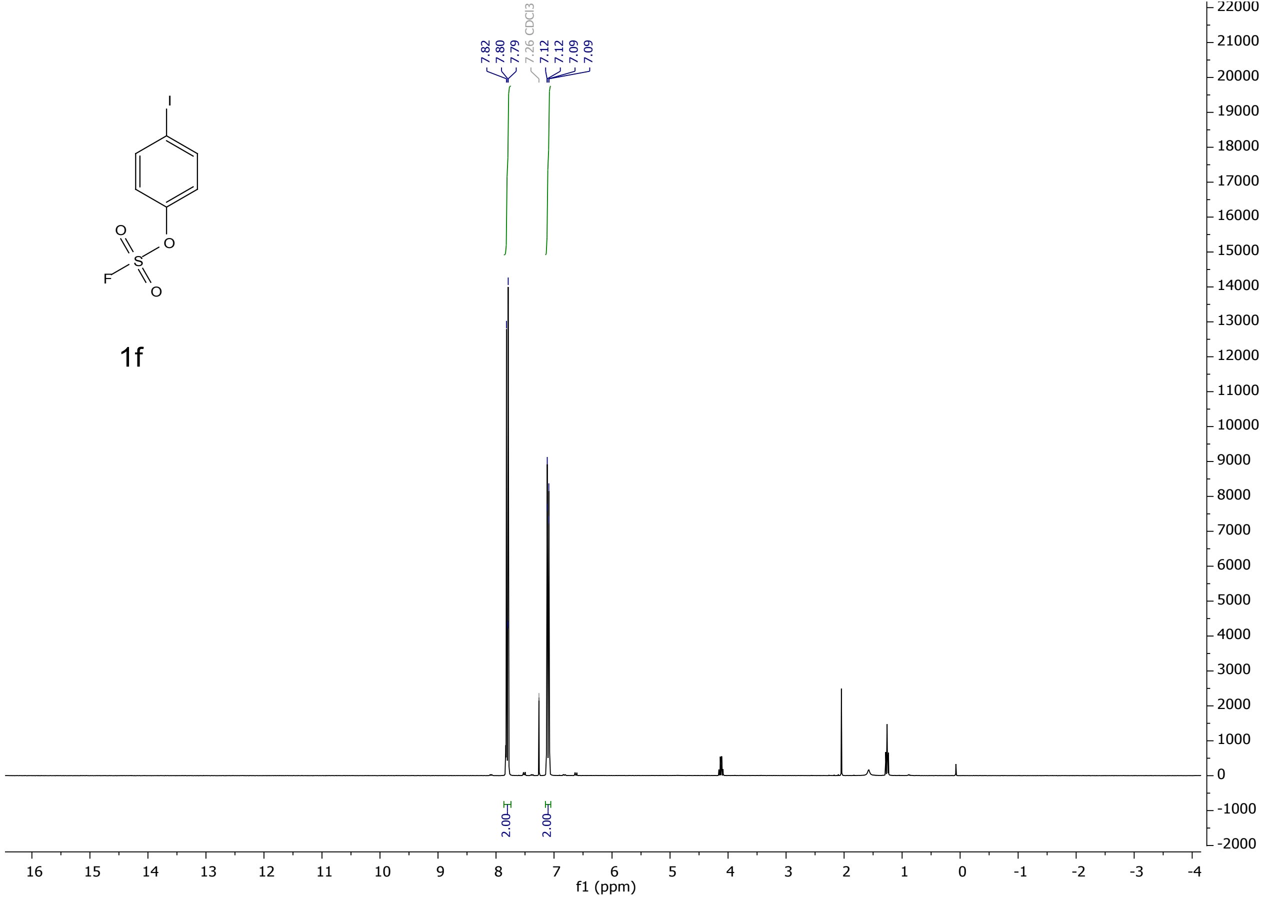
f1 (ppm)

1e



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7.09
7.09
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F
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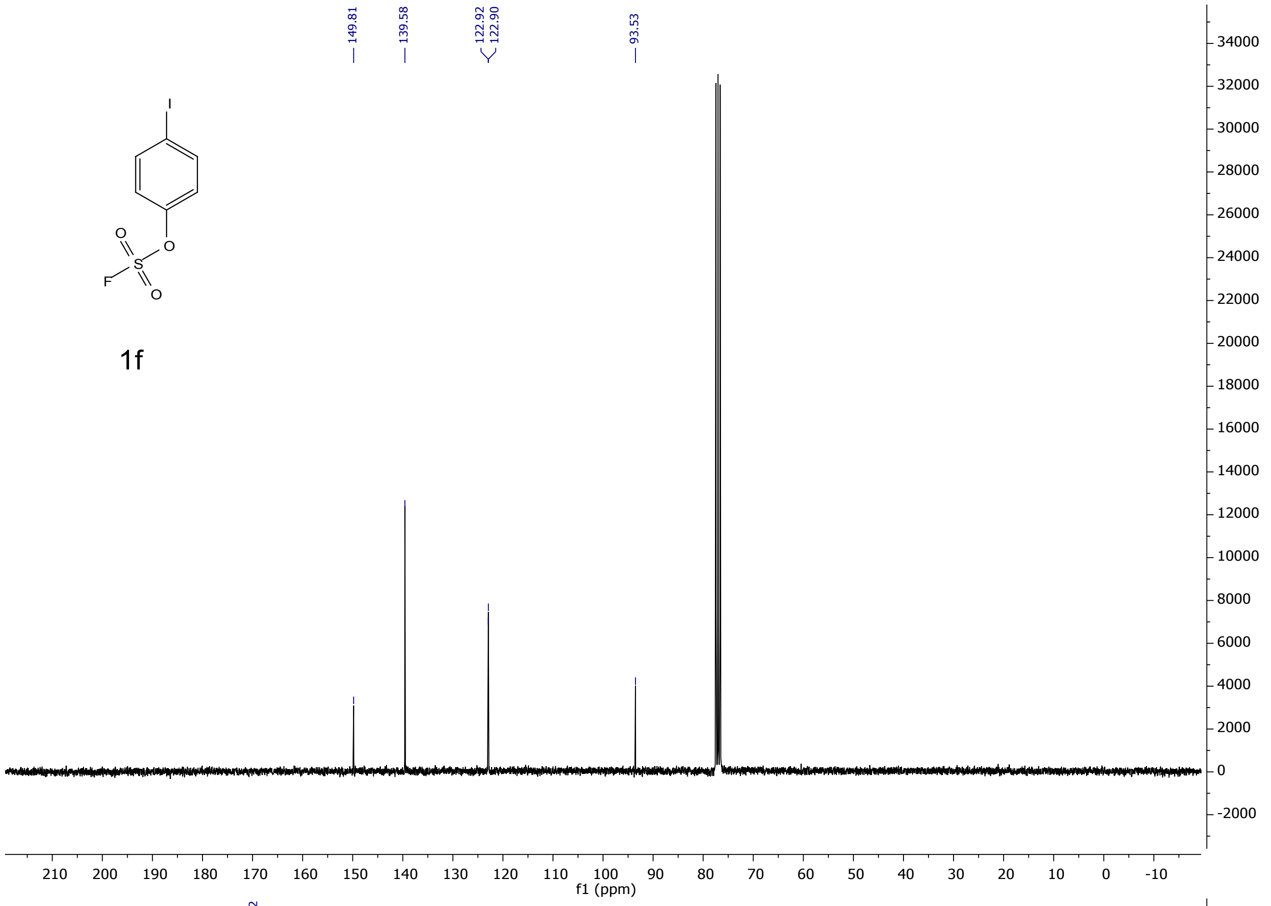
f1 (ppm)

1f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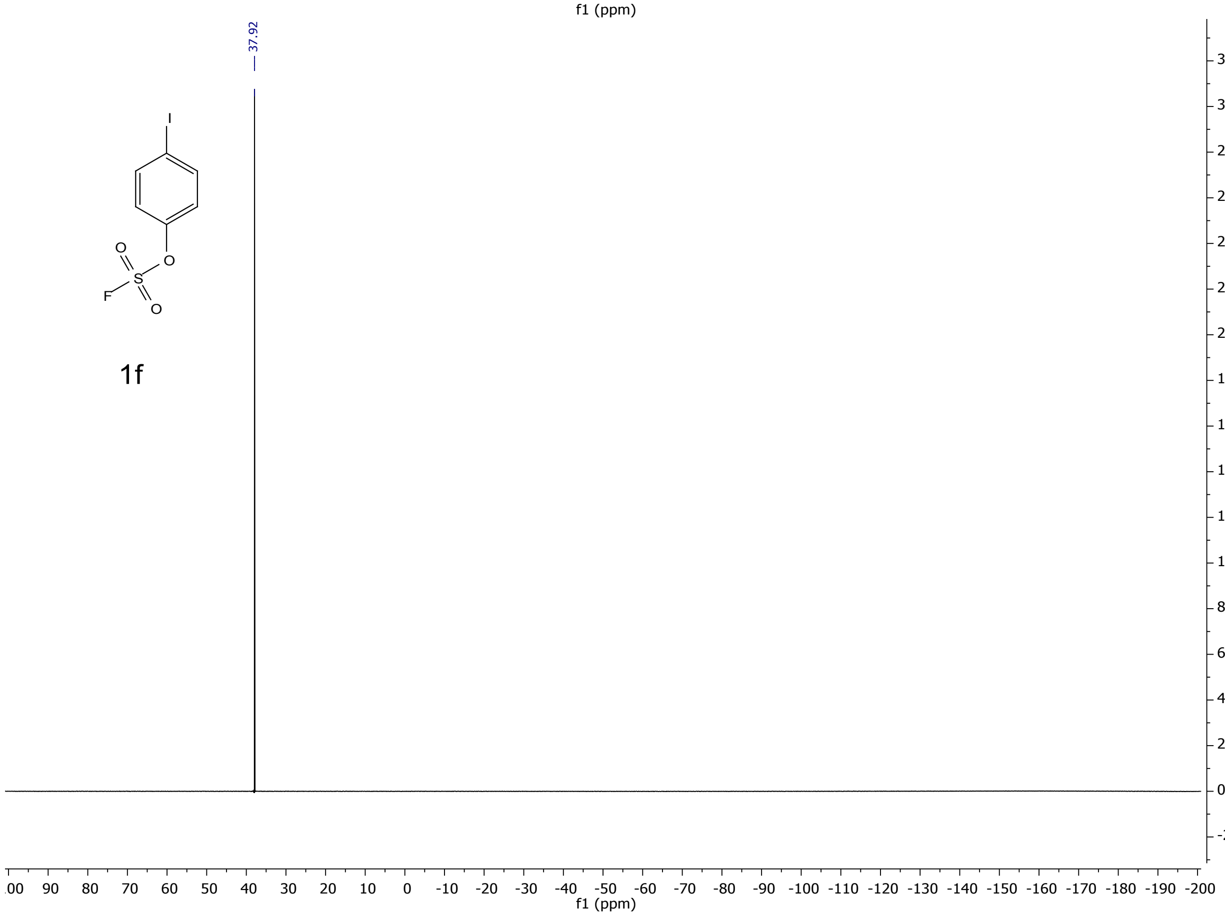
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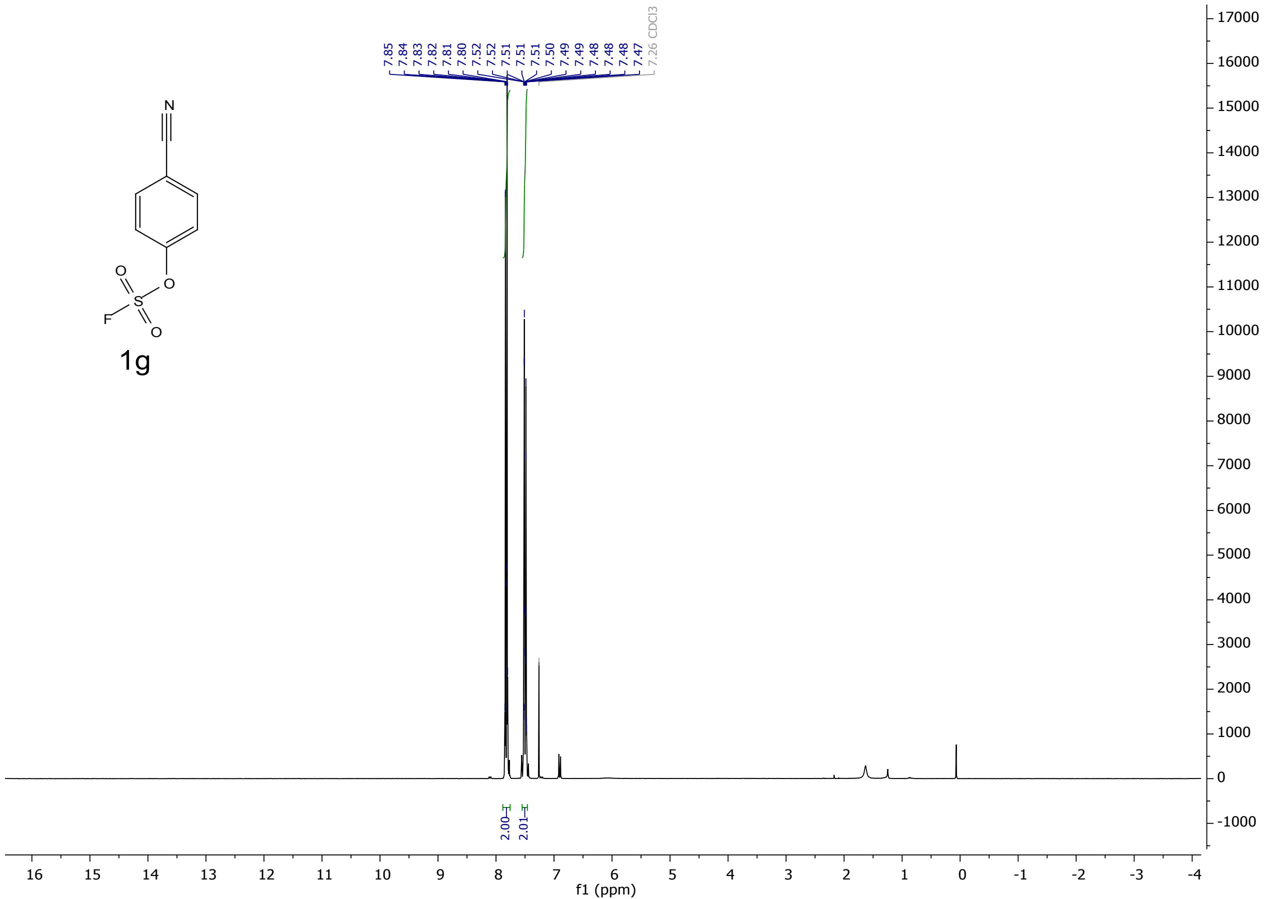
f1 (ppm)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O
1g
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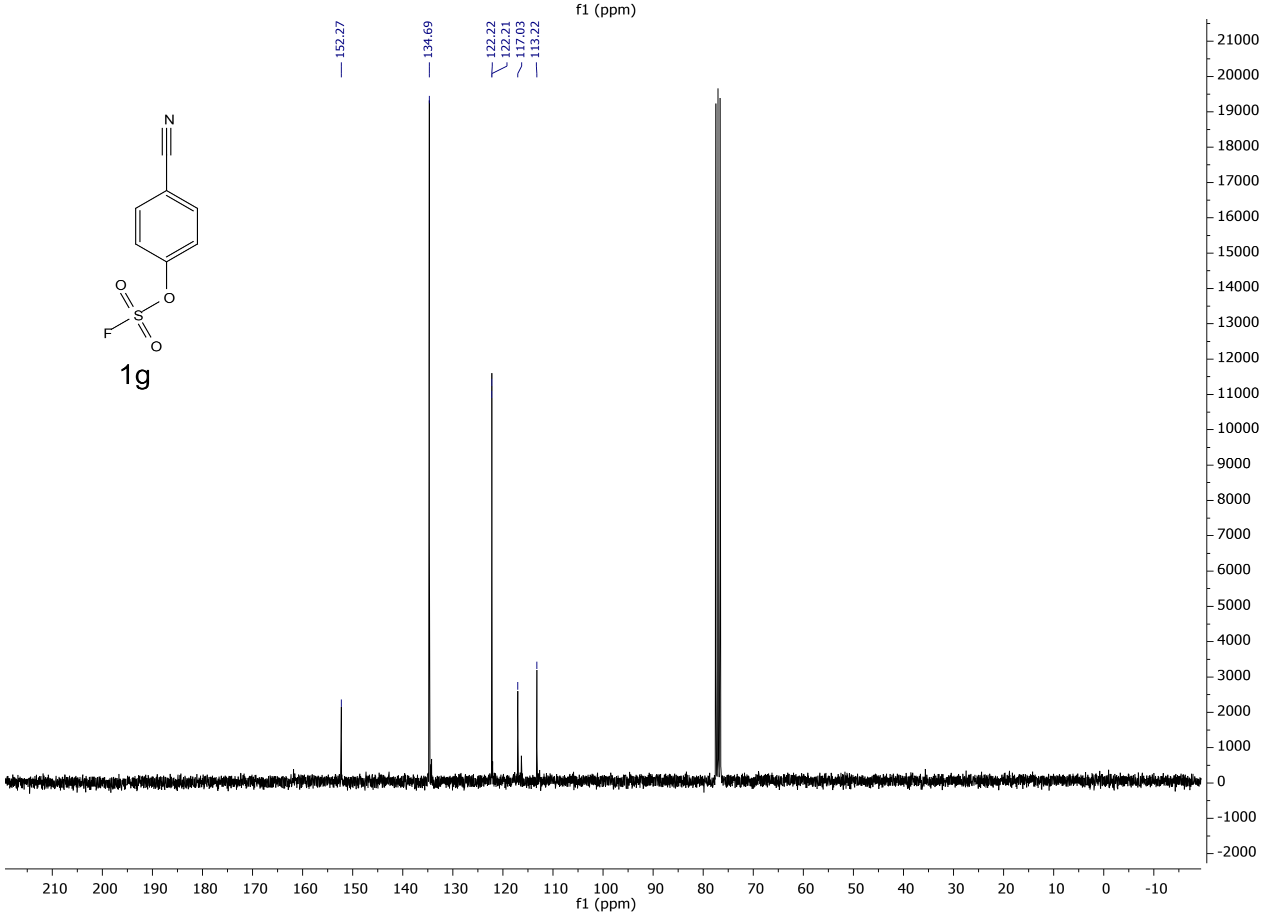
2.01
f1 (ppm)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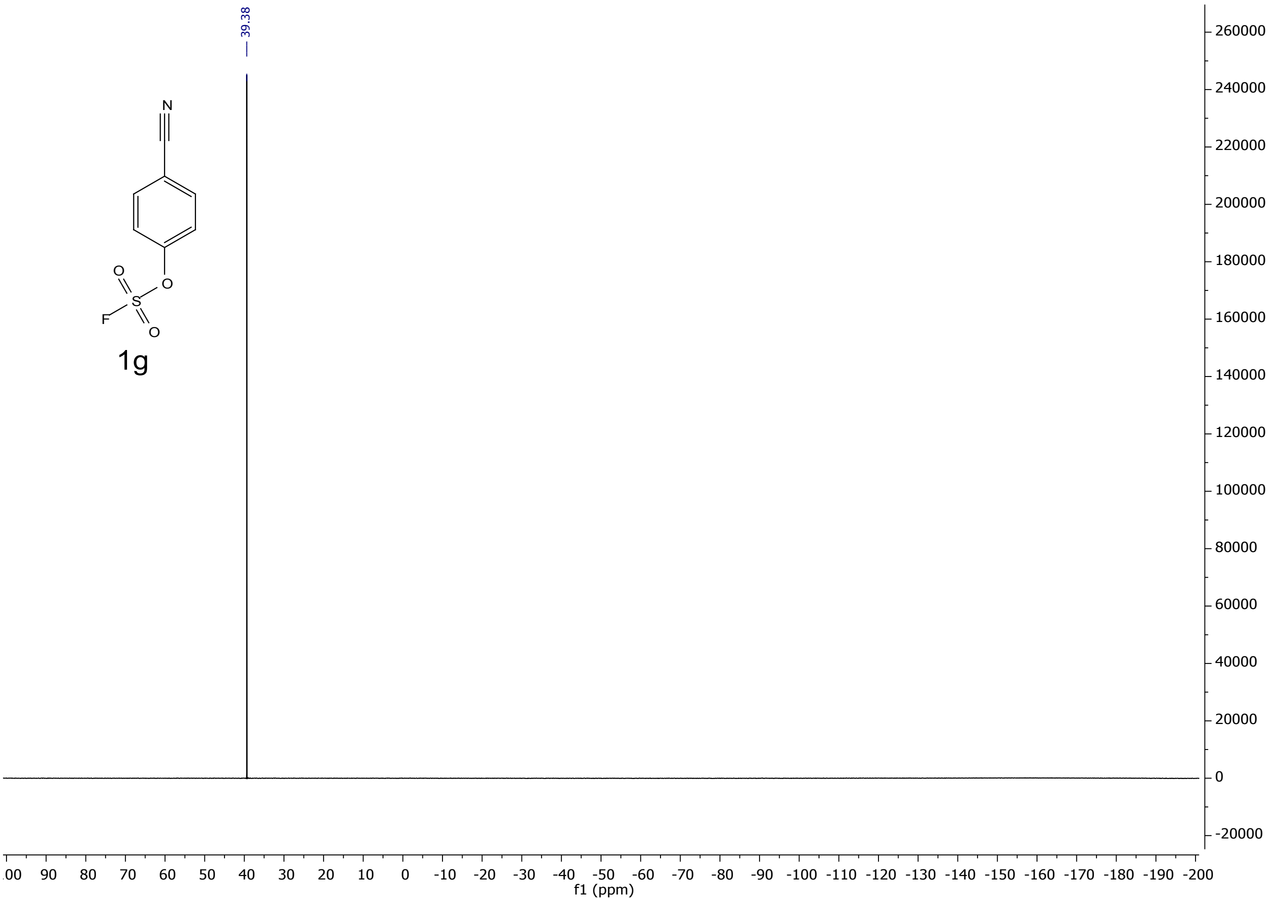
1g

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160000
140000
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100000
80000
60000
40000
20000
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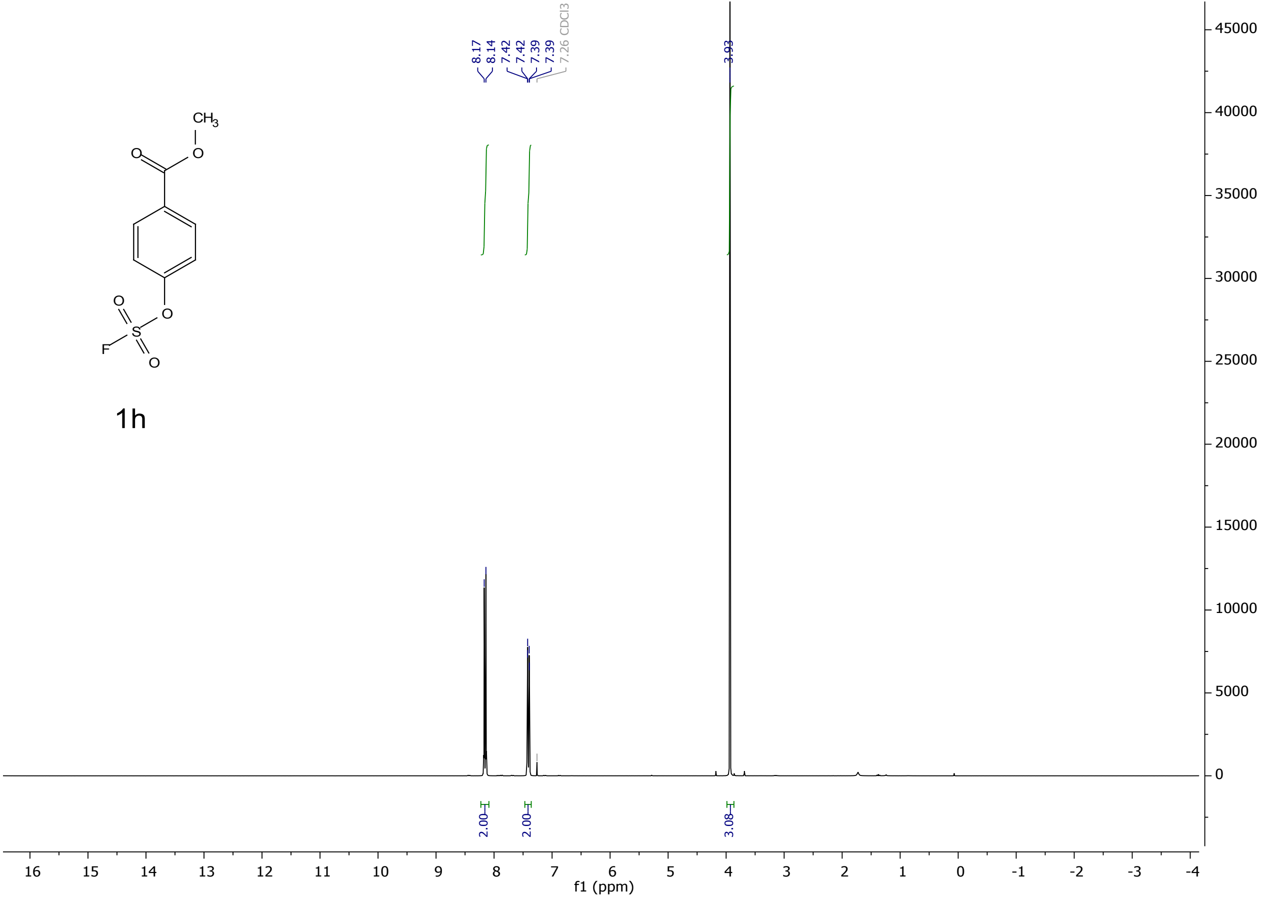
1h

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2.00
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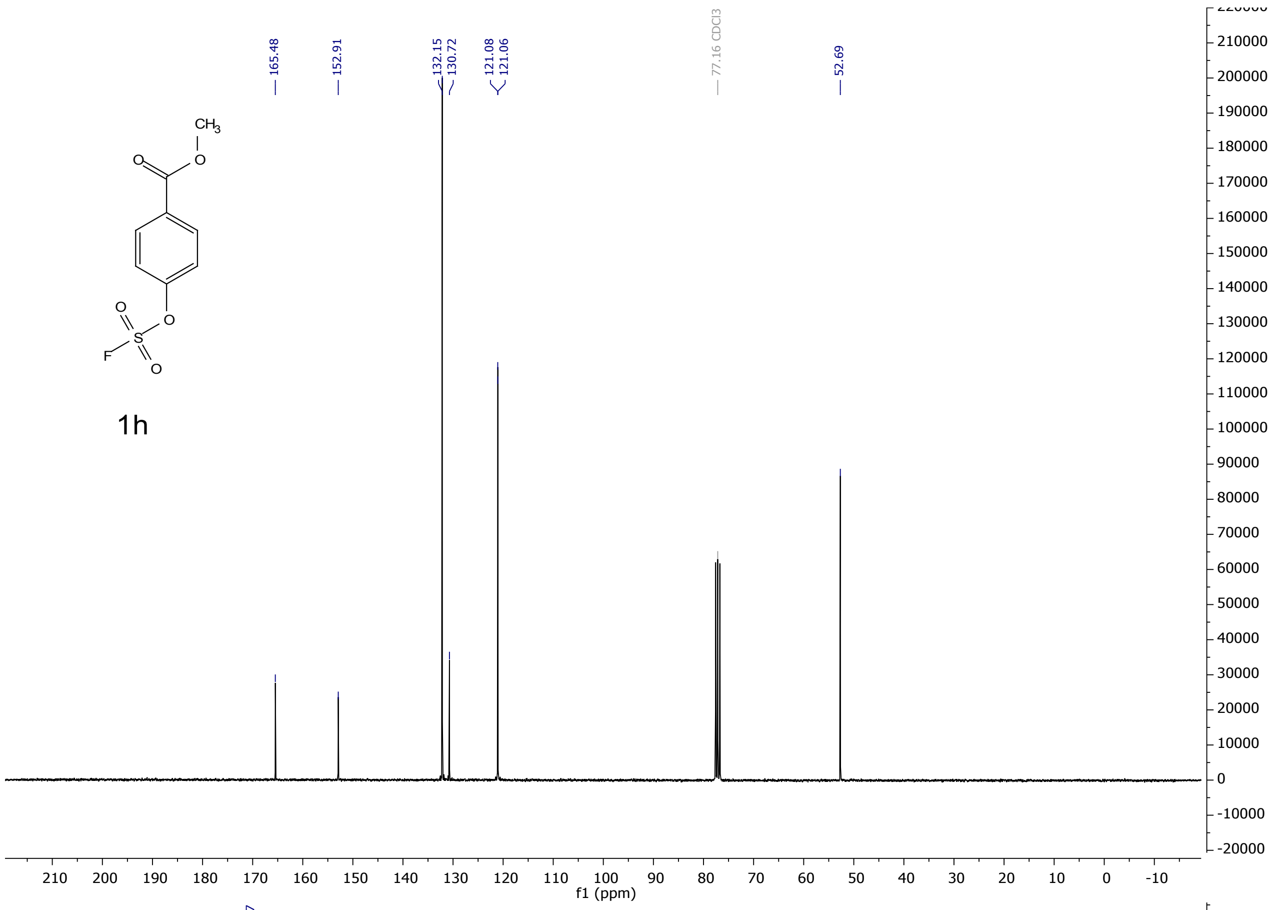
f1 (ppm)



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160000
150000
140000
130000
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110000
100000
90000
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70000
60000
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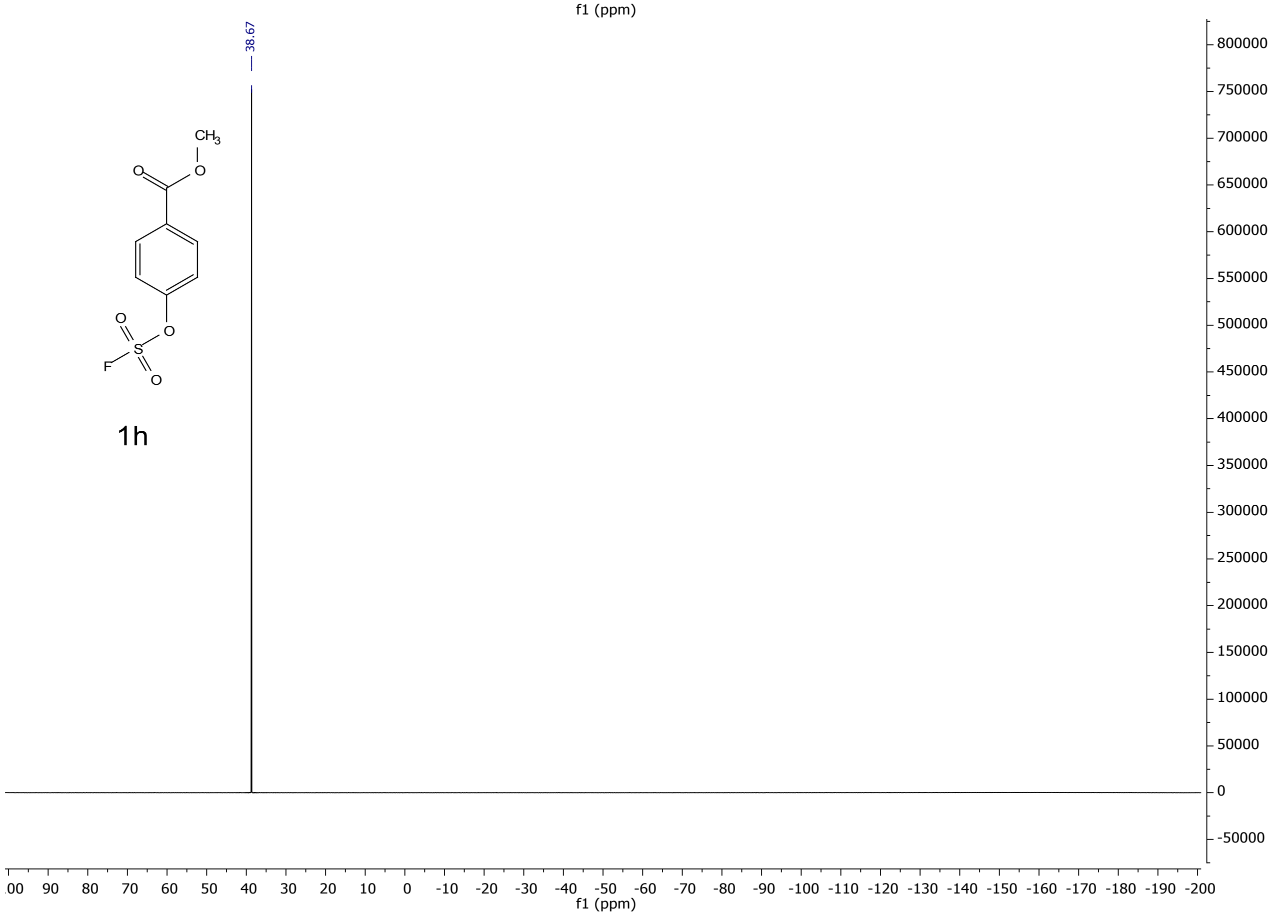
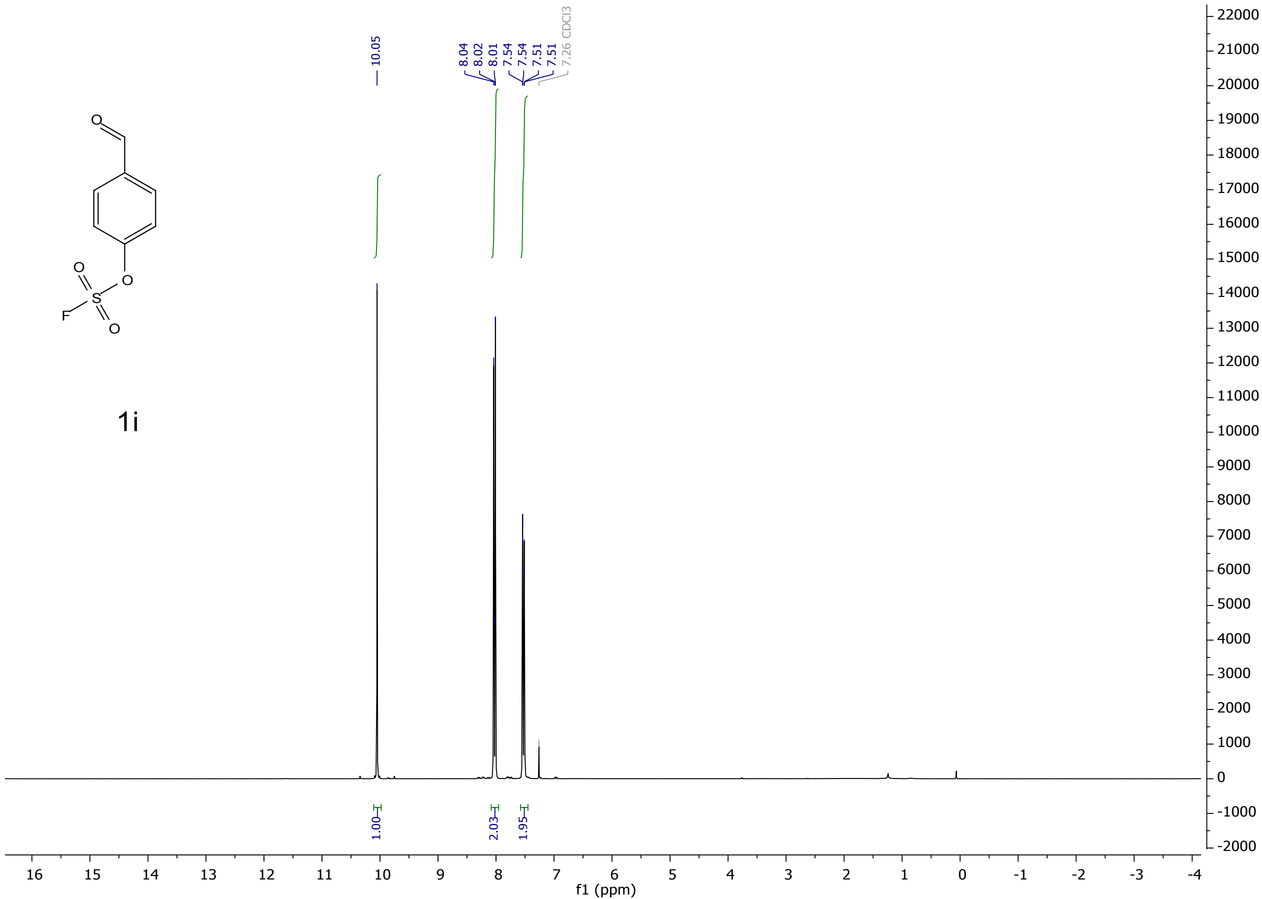
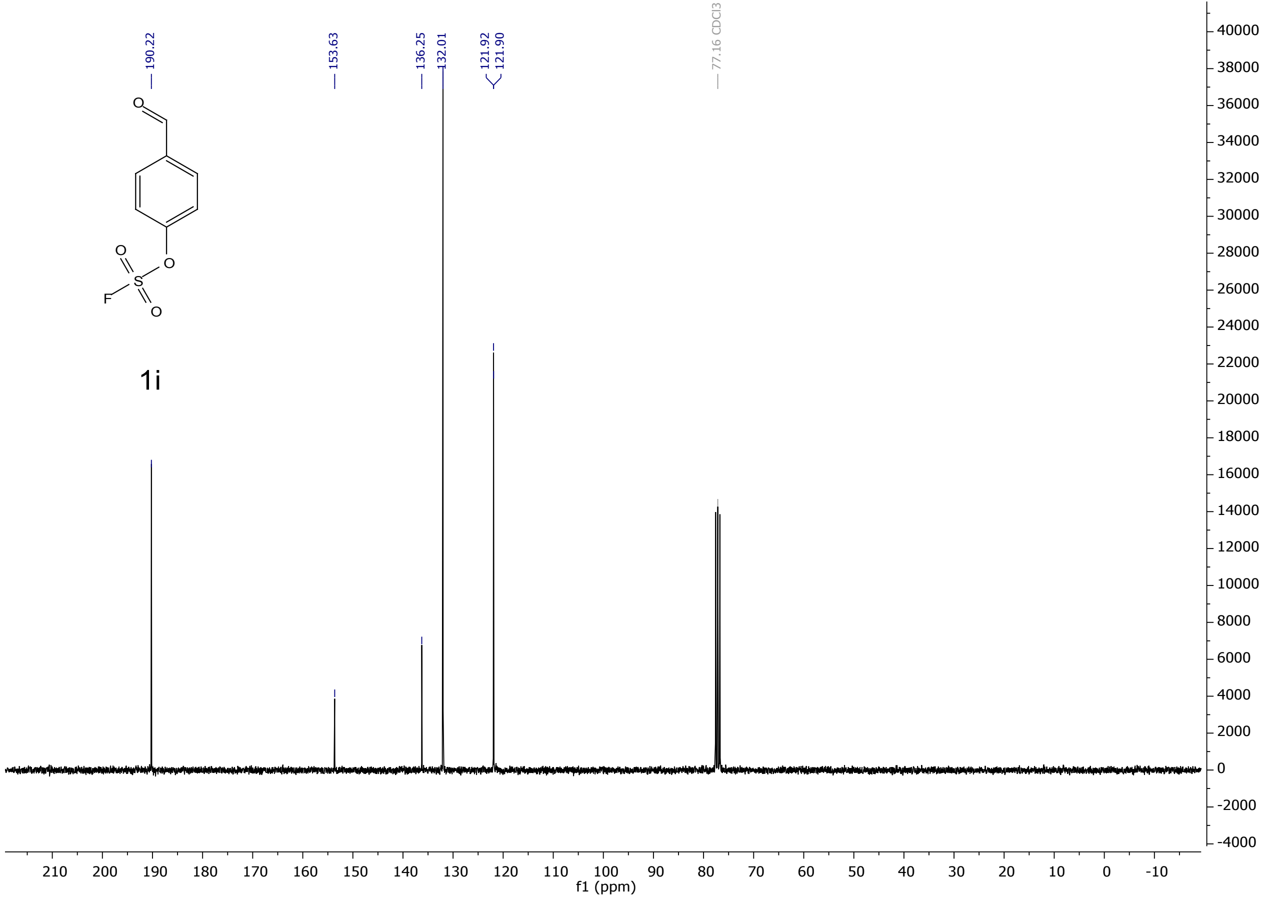
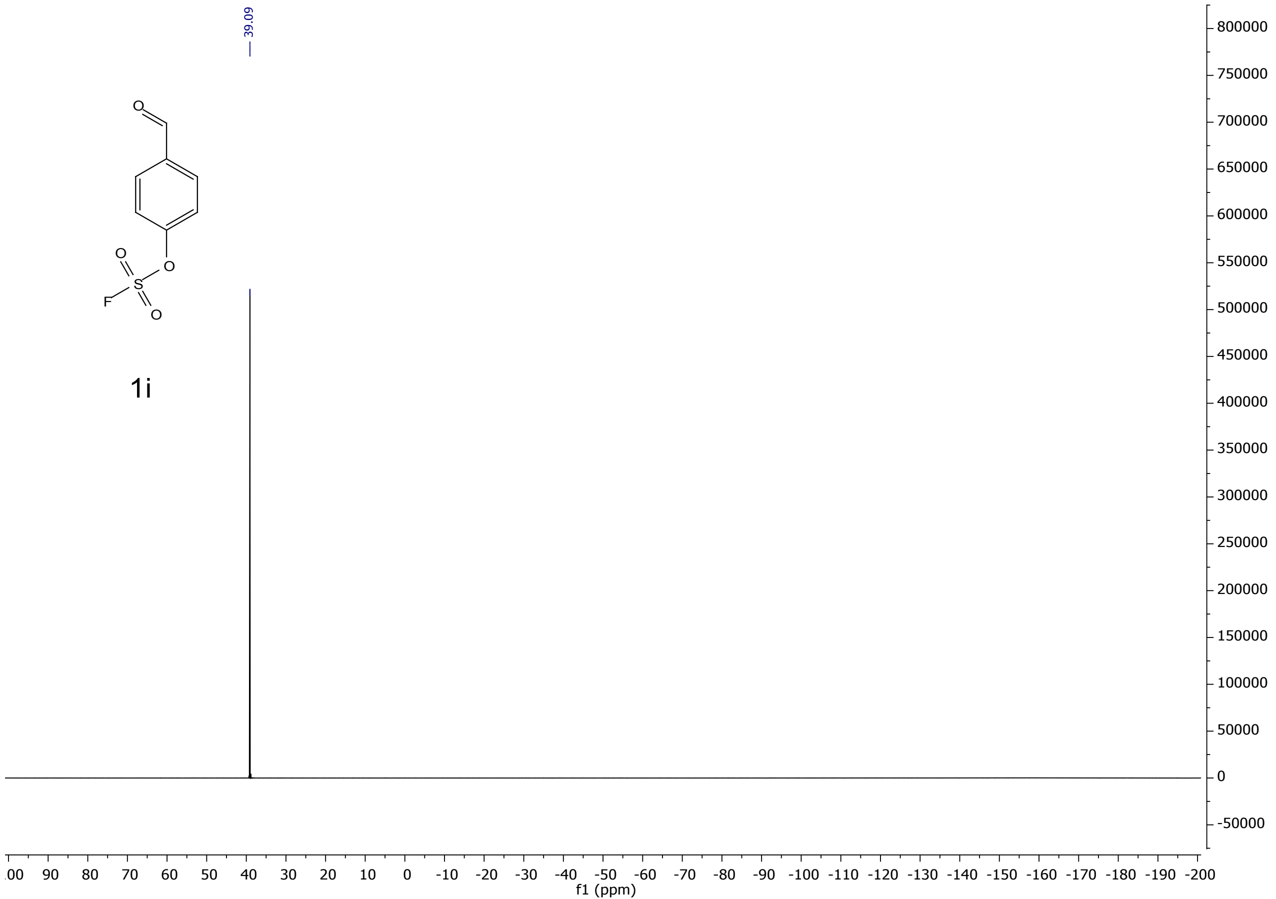
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



38.67
CH3
O
O
O
O
S
F
O
1h
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

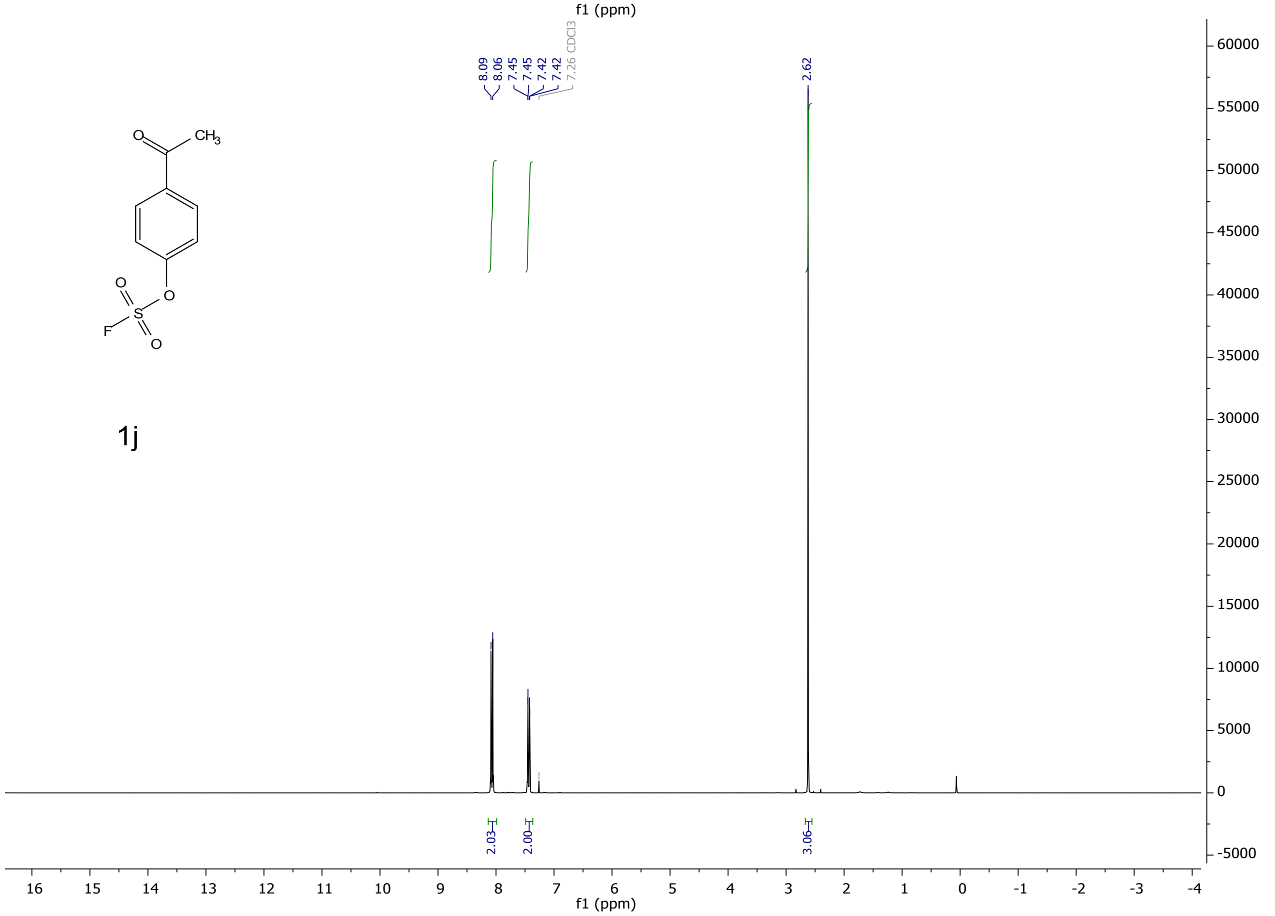

10.05
8.04
8.02
8.01
7.54
7.54
7.51
7.51
7.26 CDCl3
O
O
S
O
F
O
1i
1.00
2.03
1.95
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000


190.22
153.63
136.25
132.01
121.92
121.90
77.16 CDCl3
O
O
S
O
F
O
1i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000



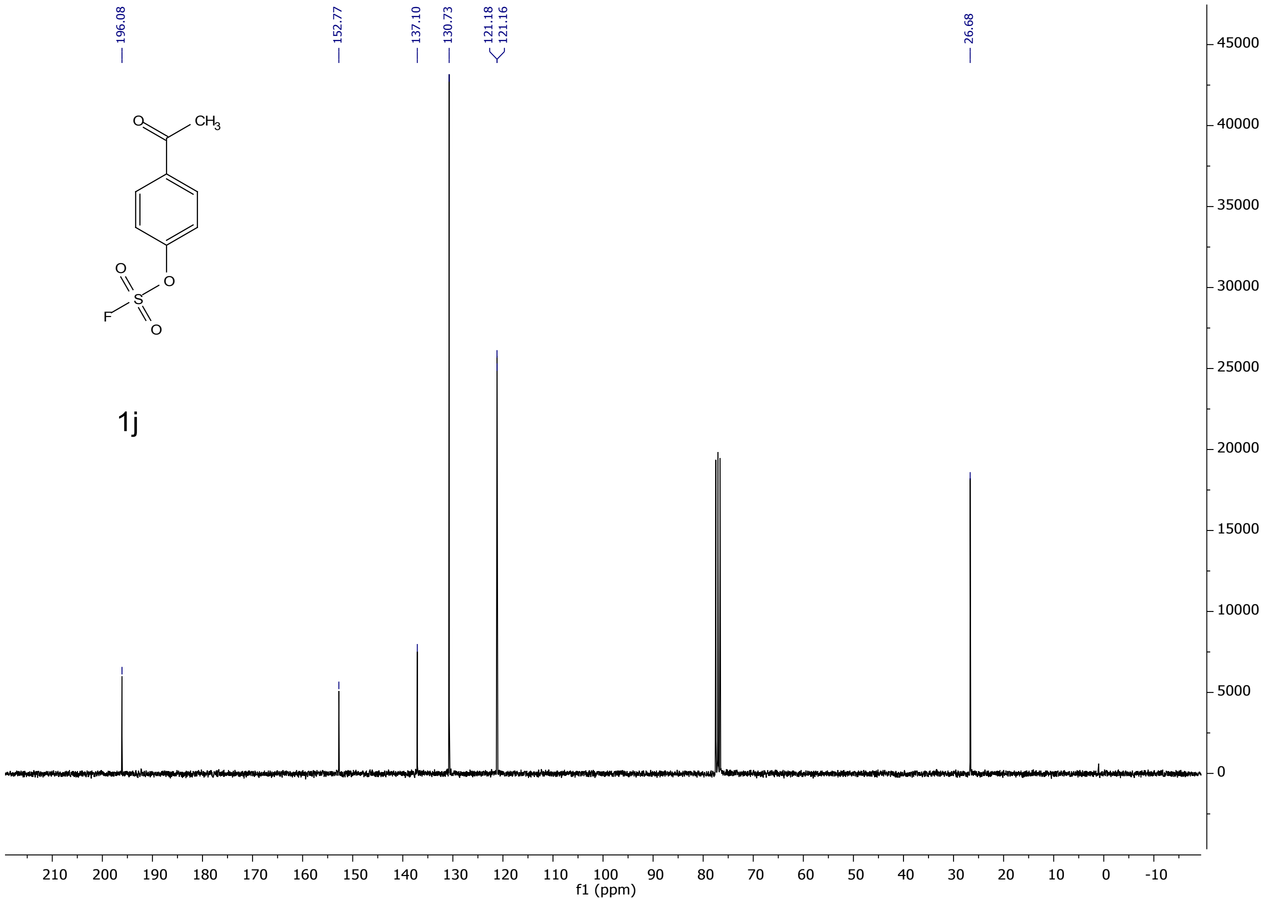
1i

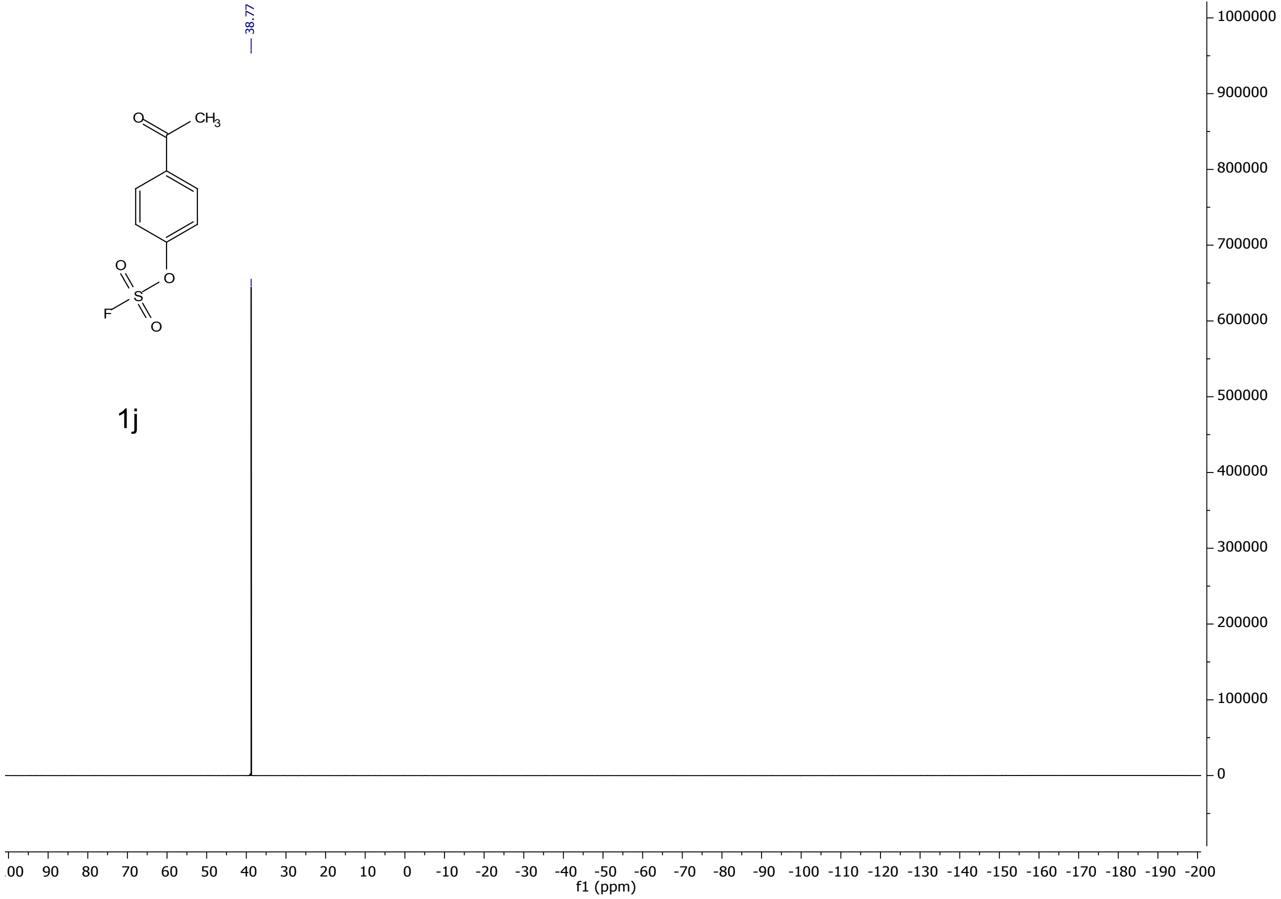
39.09
O
O
S
F
O
O
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
.00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

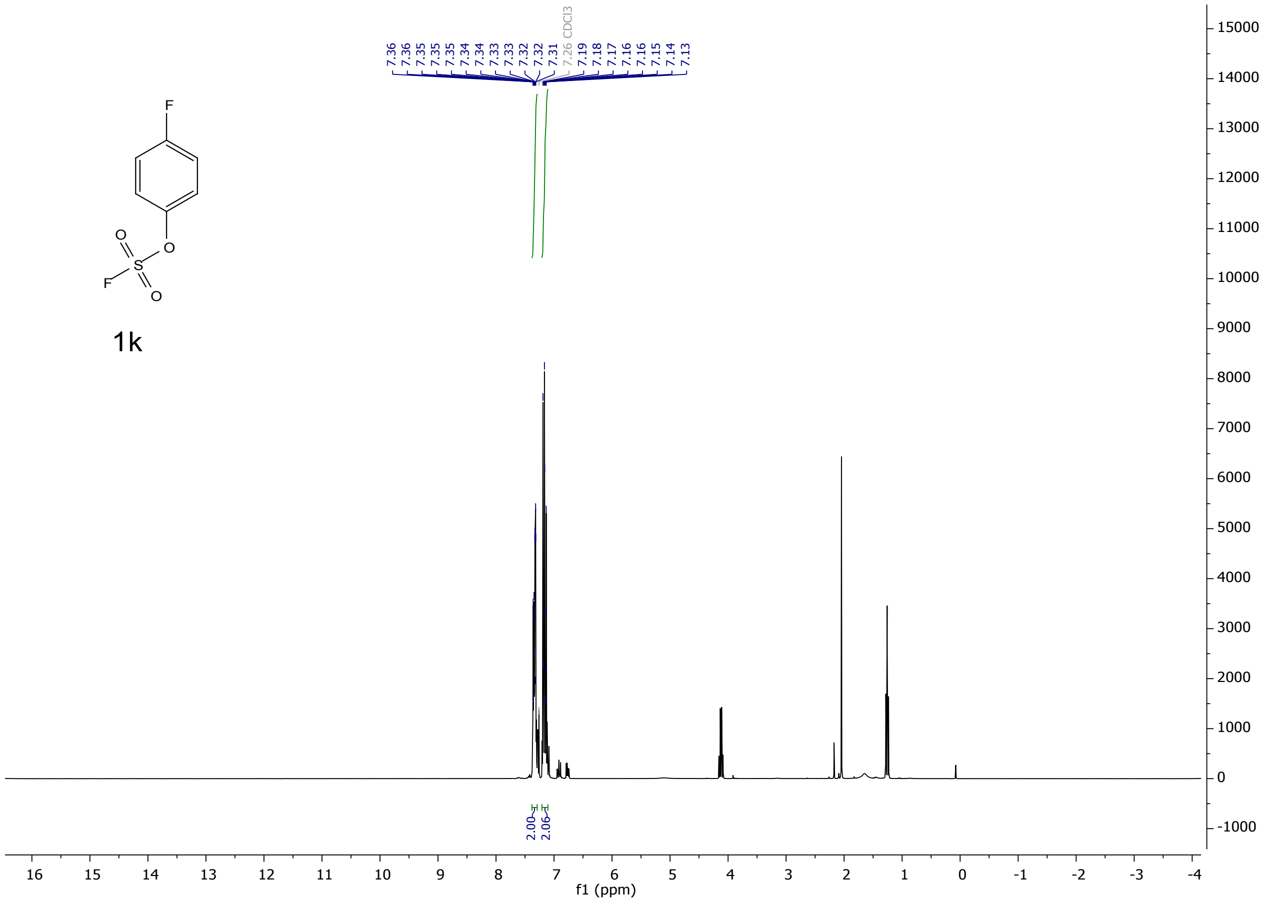


1j

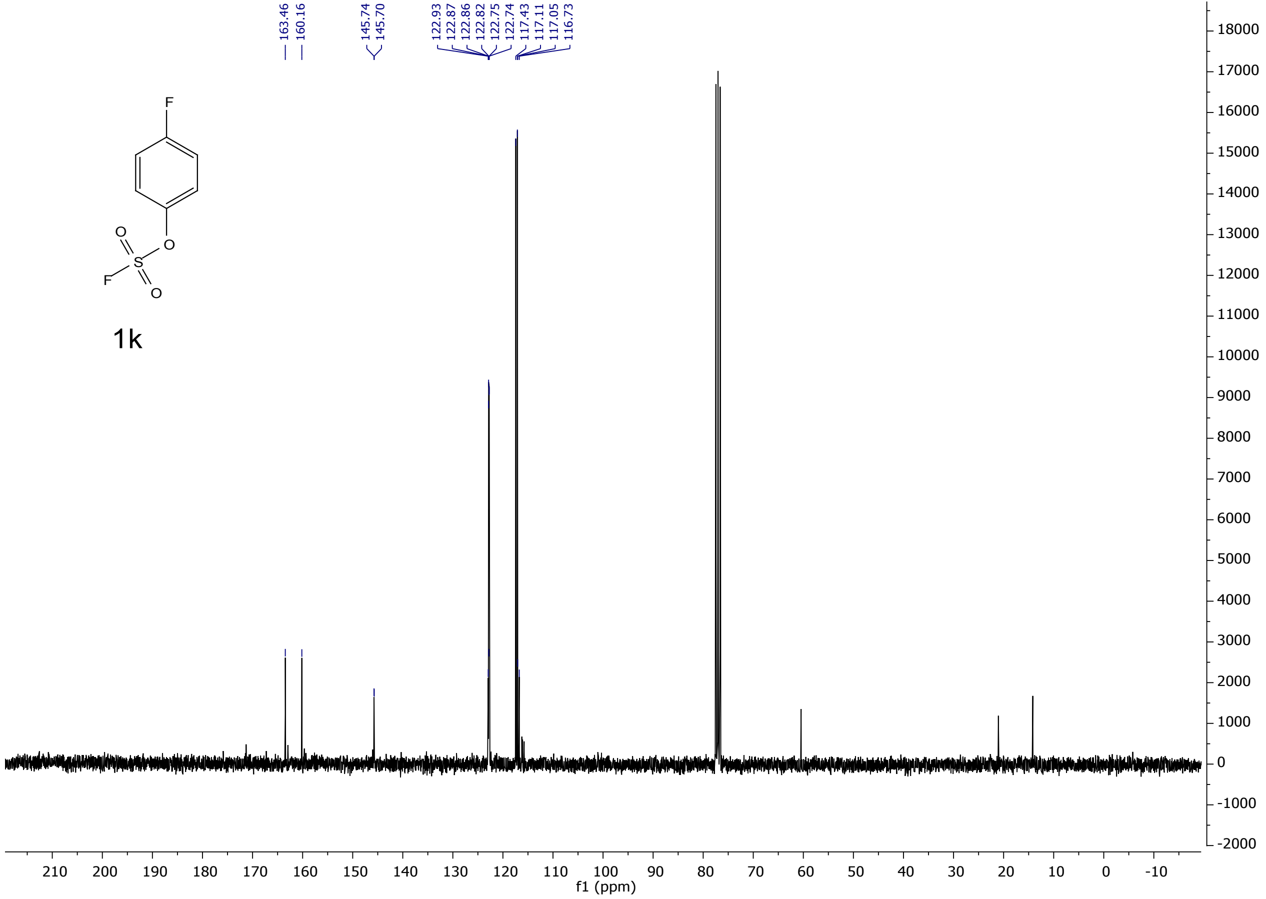
8.09
8.06
7.45
7.45
7.42
7.42
7.26 CDCl3
2.62
O
CH_3
O
S
F
O
O
2.03
2.00
3.06
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


196.08
152.77
137.10
130.73
121.18
121.16
26.68
O
CH3
O
S
O
F
O
1j
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

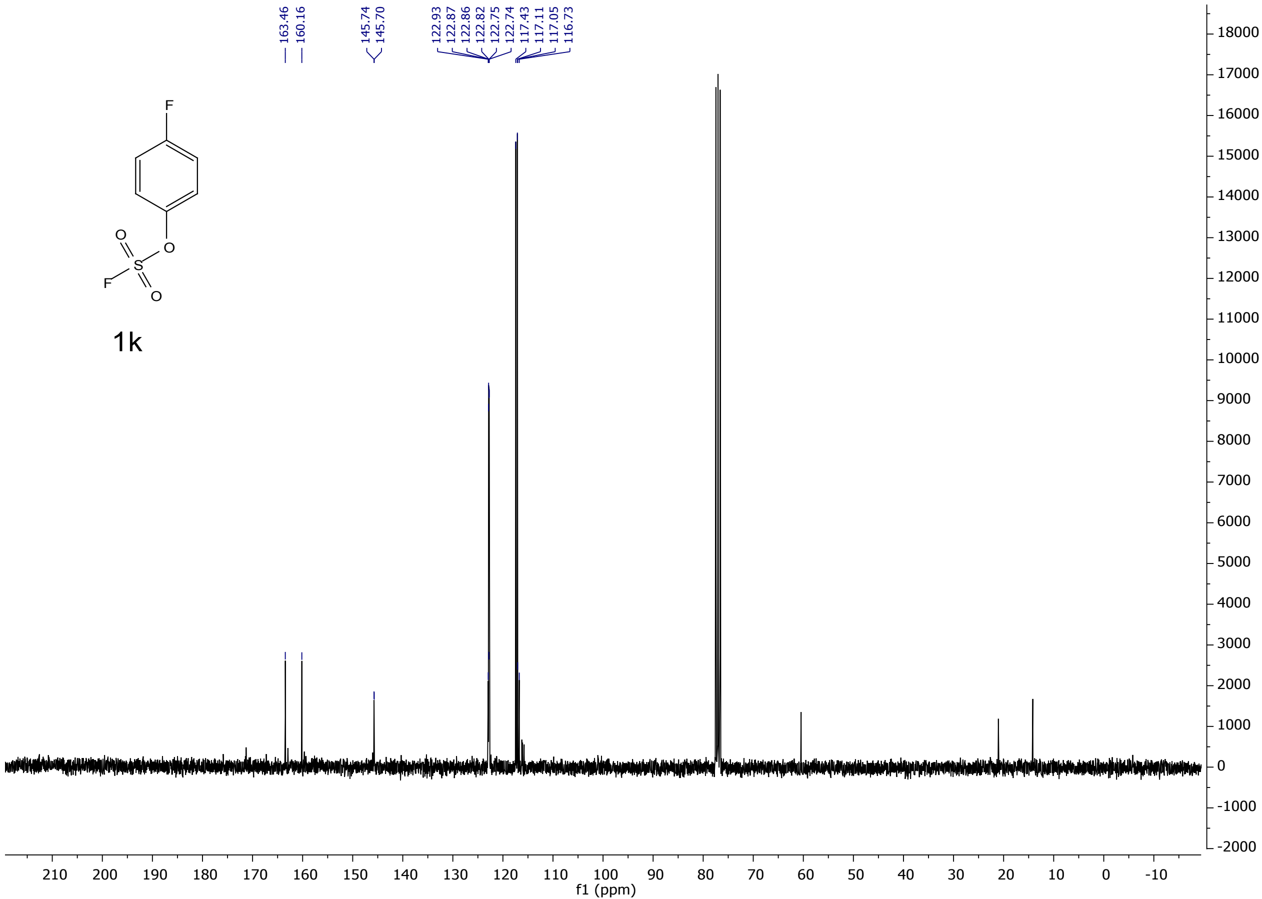

38.77
O
CH3
O
S
O
F
O
1j
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


1k

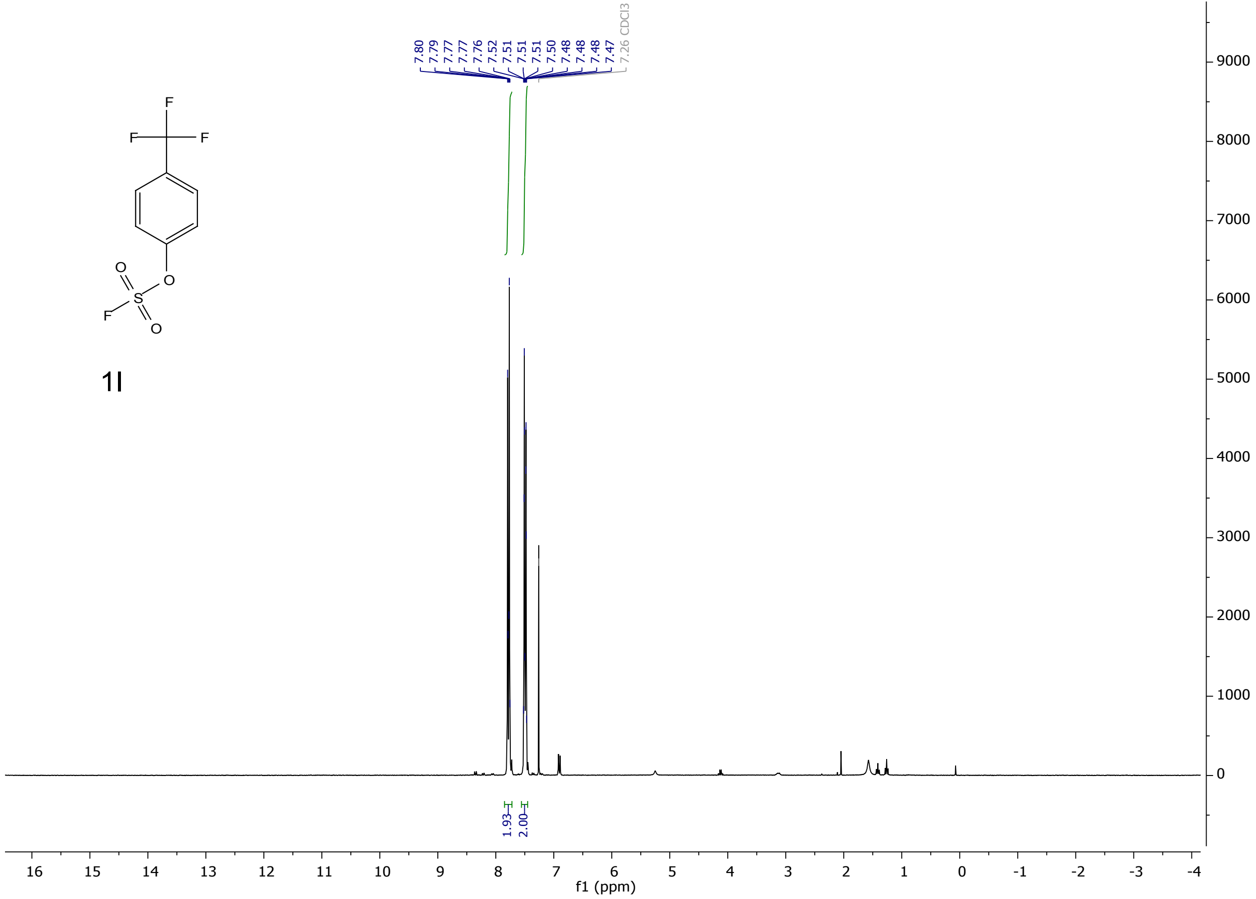
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.26 CDCl3
7.19
7.18
7.17
7.16
7.16
7.15
7.14
7.13
2.00
2.06
F
O
S
O
F
O
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


1k

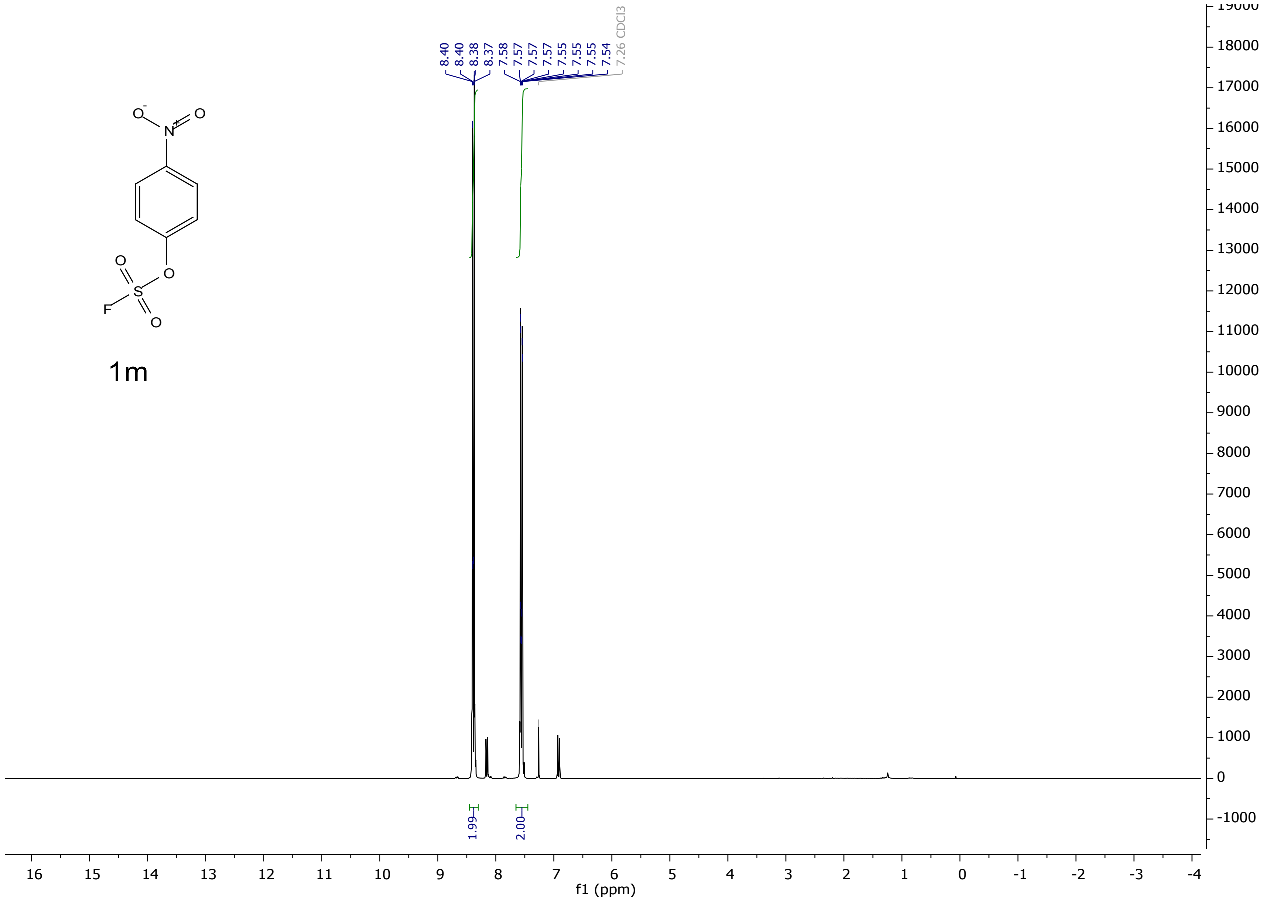
163.46
160.16
145.74
145.70
122.93
122.87
122.86
122.82
122.75
122.74
117.43
117.11
117.05
116.73
F
O
S
O
F
O
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


163.46
160.16
145.74
145.70
122.93
122.87
122.86
122.82
122.75
122.74
117.43
117.11
117.05
116.73
F
O
S
F
O
O
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

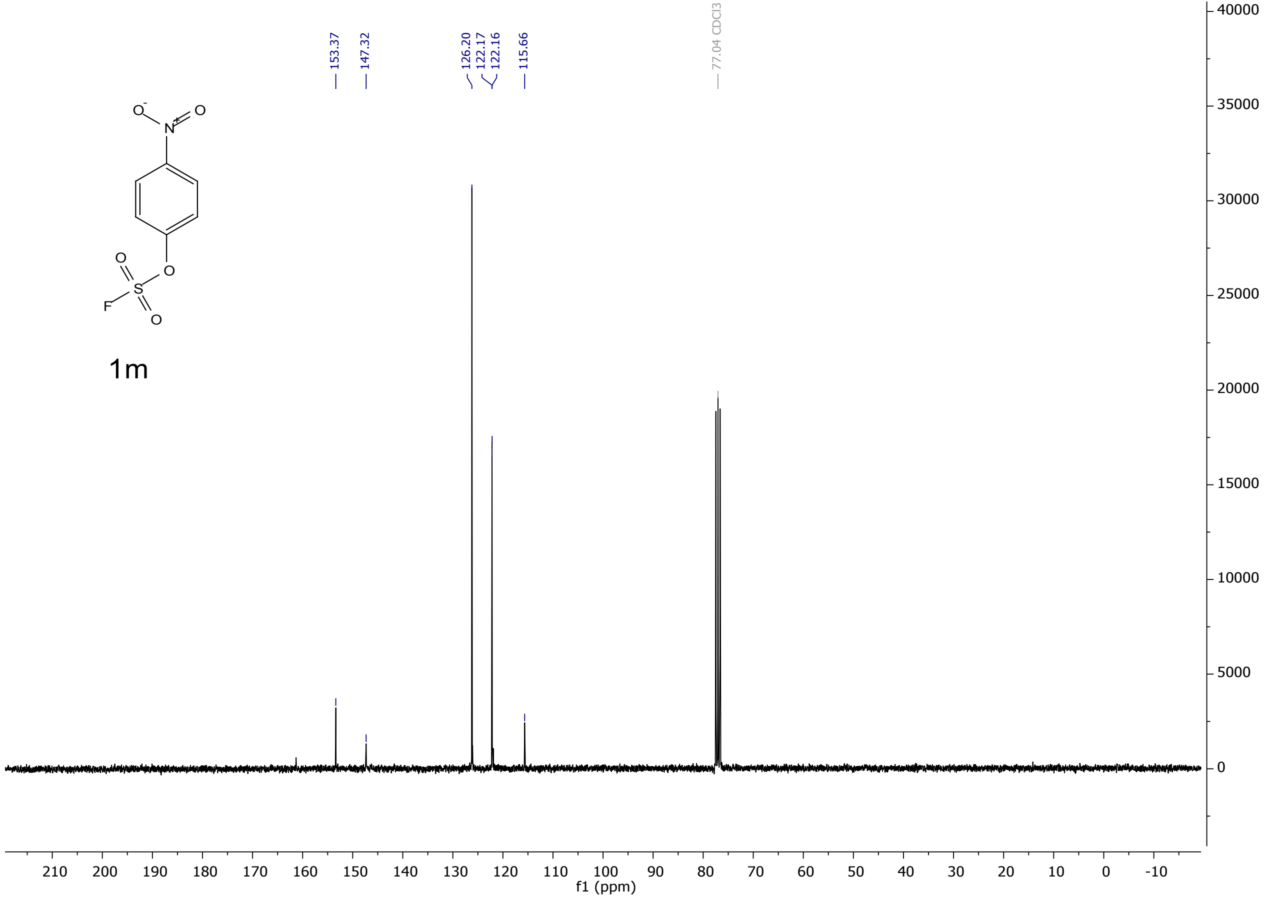
1k


7.80
7.79
7.77
7.77
7.76
7.52
7.51
7.51
7.51
7.50
7.48
7.48
7.48
7.47
7.26 CDCl3
F
F
F
O
S
F
O
O
1.93
2.00
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

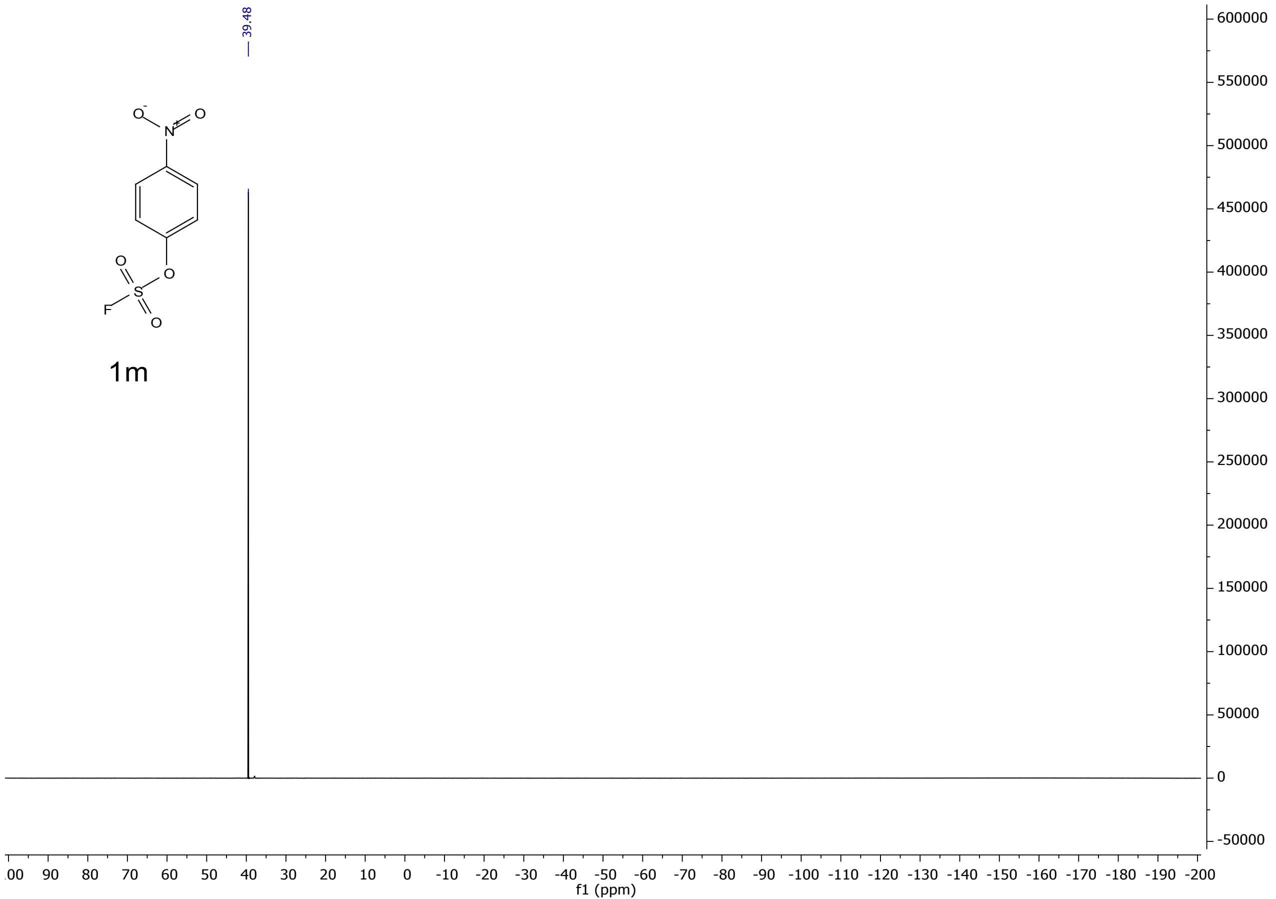
1l

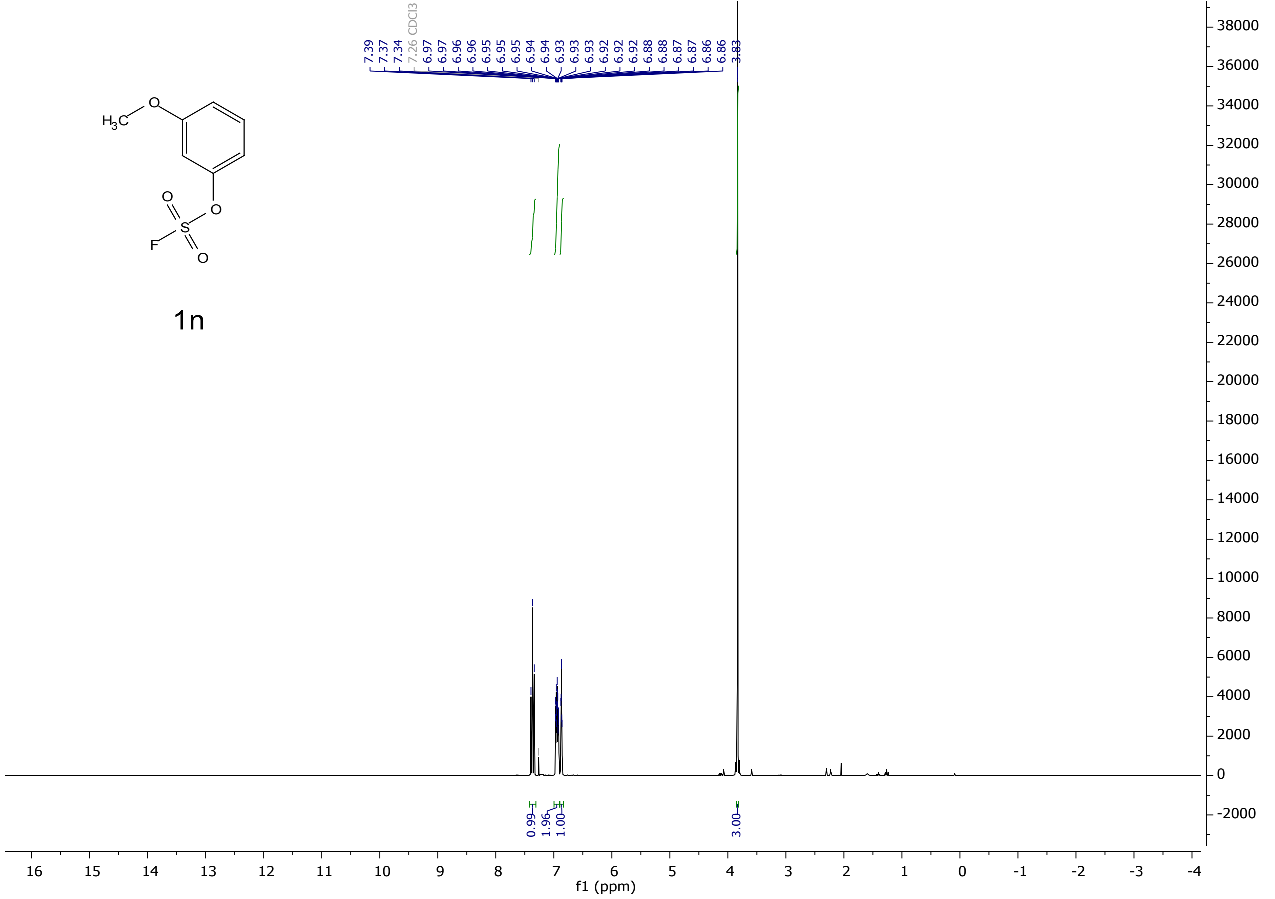


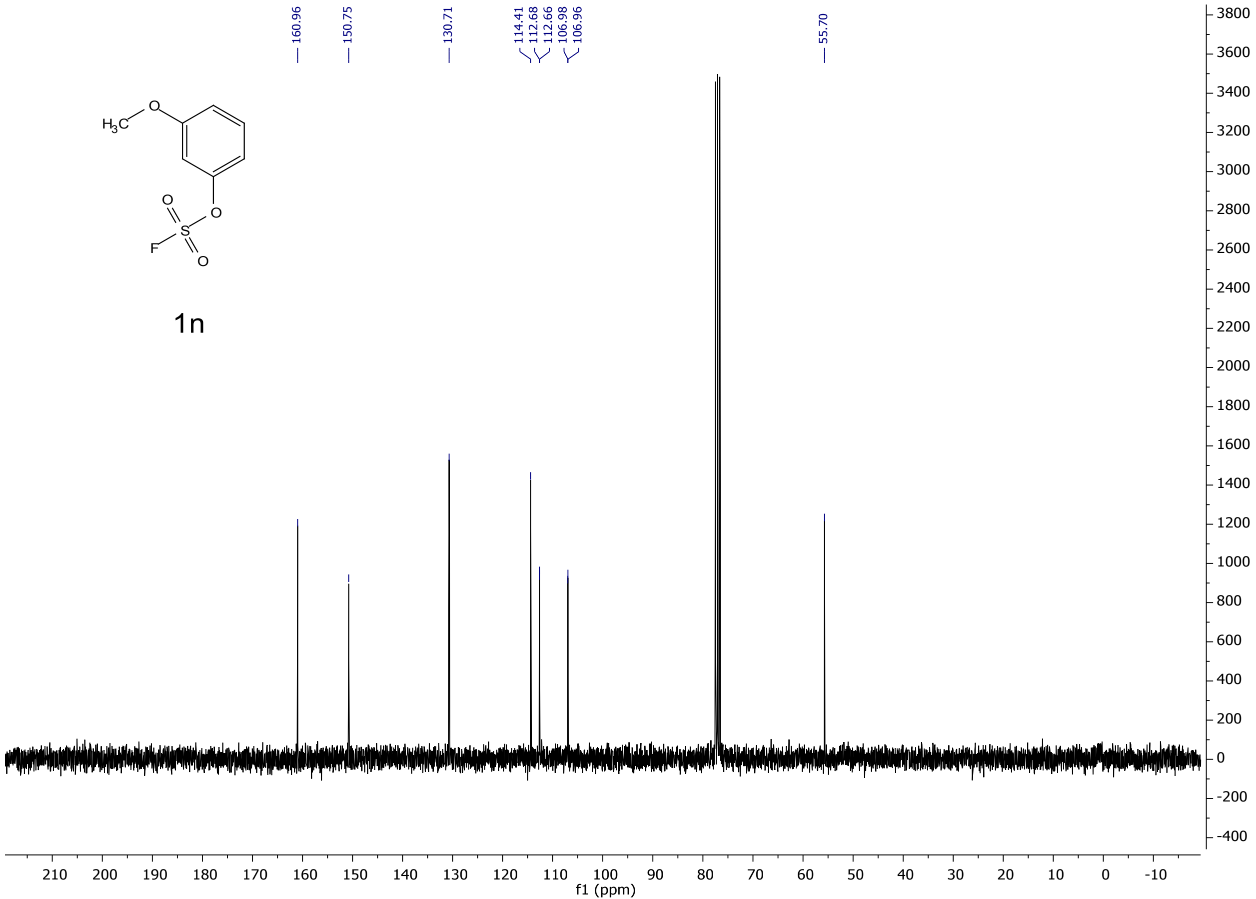
1m
O
N
O
O
S
O
F
O
8.40
8.40
8.38
8.37
7.58
7.57
7.57
7.57
7.55
7.55
7.55
7.54
7.26 CDCl3
1.99
2.00
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)



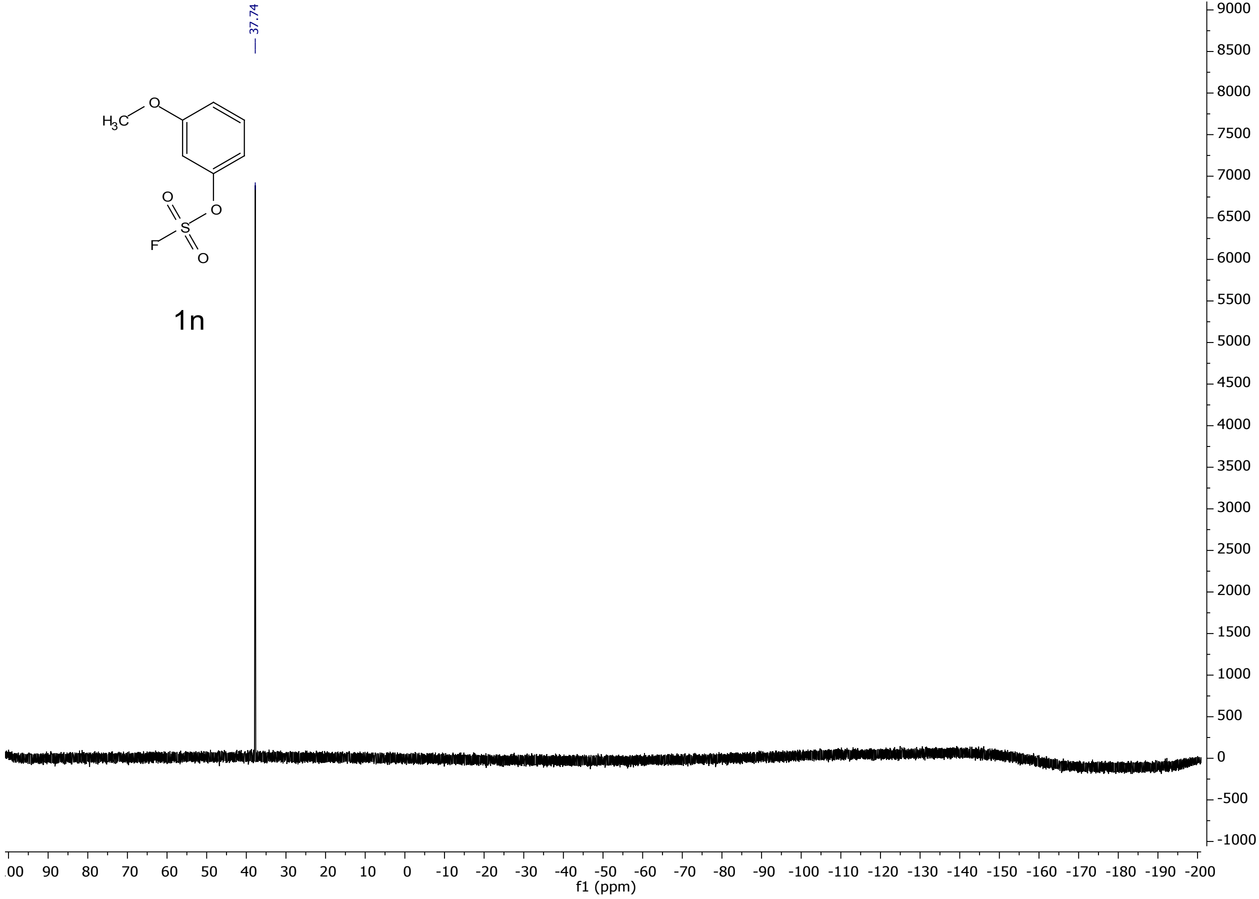
1m
O
N
O
O
S
O
F
O
153.37
147.32
126.20
122.17
122.16
115.66
77.04 CDCl3
40000
35000
30000
25000
20000
15000
10000
5000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


39.48
1m
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

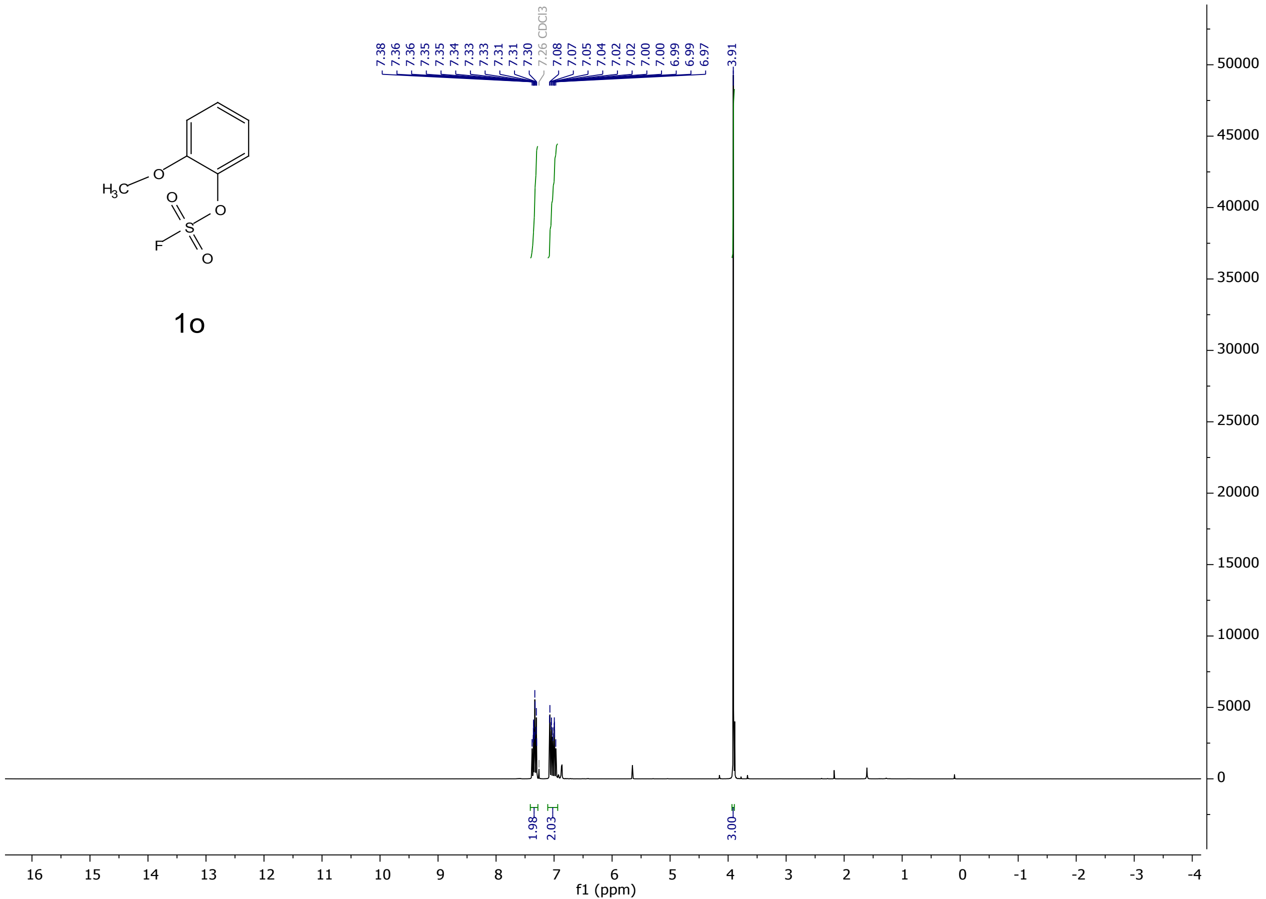

7.39
7.37
7.34
7.26 CDCl3
6.97
6.97
6.96
6.96
6.95
6.95
6.95
6.94
6.94
6.93
6.93
6.93
6.92
6.92
6.88
6.88
6.87
6.87
6.86
6.86
3.83
1n
0.99
1.96
1.00
3.00
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


1n

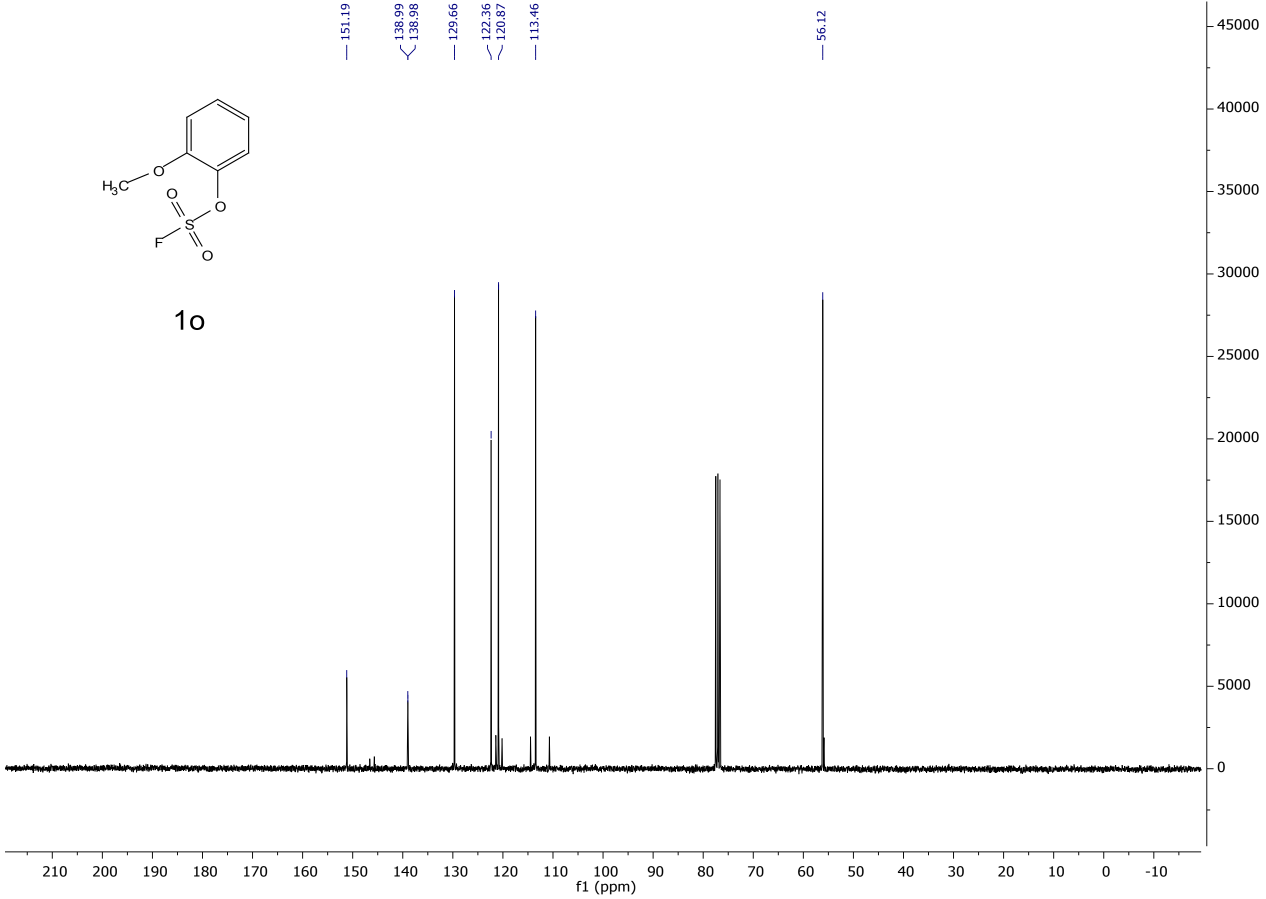
160.96
150.75
130.71
114.41
112.68
112.66
106.98
106.96
55.70
H3C
O
O
S
O
F
O
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1n

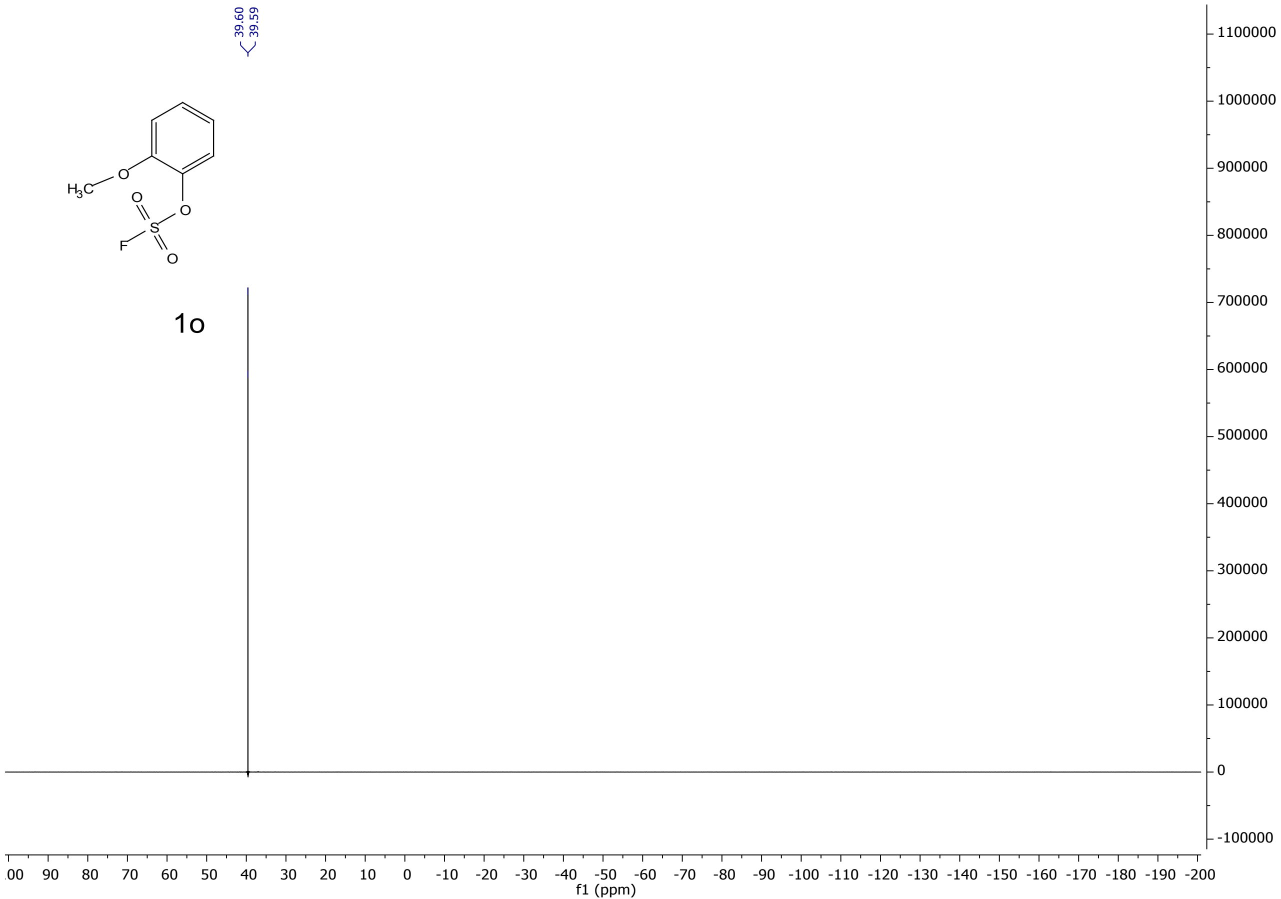
37.74
H3C
O
O
S
O
F
O
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-1000
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


7.38
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.31
7.31
7.30
7.26 CDCl3
7.08
7.07
7.05
7.04
7.02
7.02
7.00
6.99
6.99
6.97
3.91
H3C
O
O
O
S
F
O
1.98
2.03
3.00
f1 (ppm)

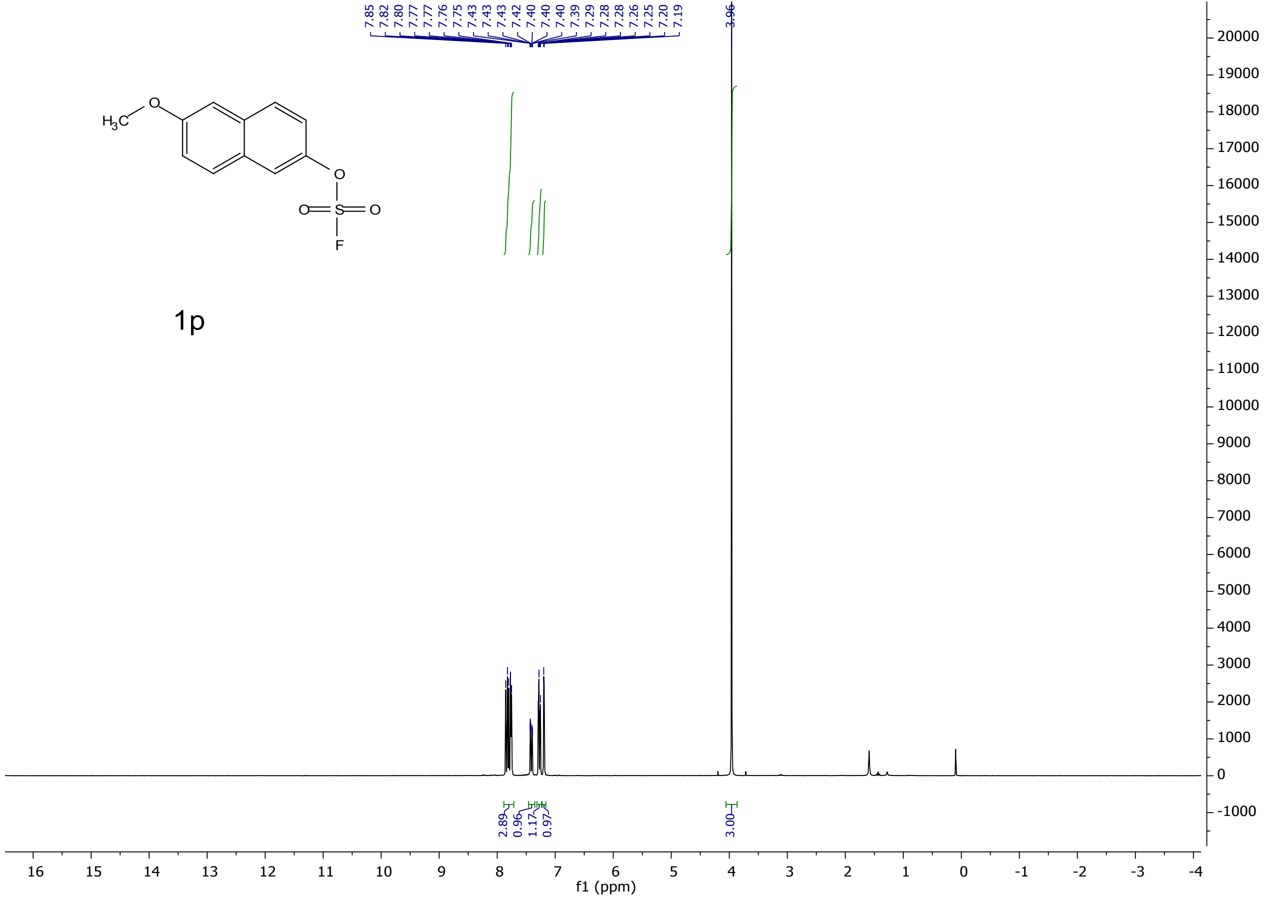
1o


151.19
138.99
138.98
129.66
122.36
120.87
113.46
56.12
H3C
O
O
O
S
F
O
f1 (ppm)

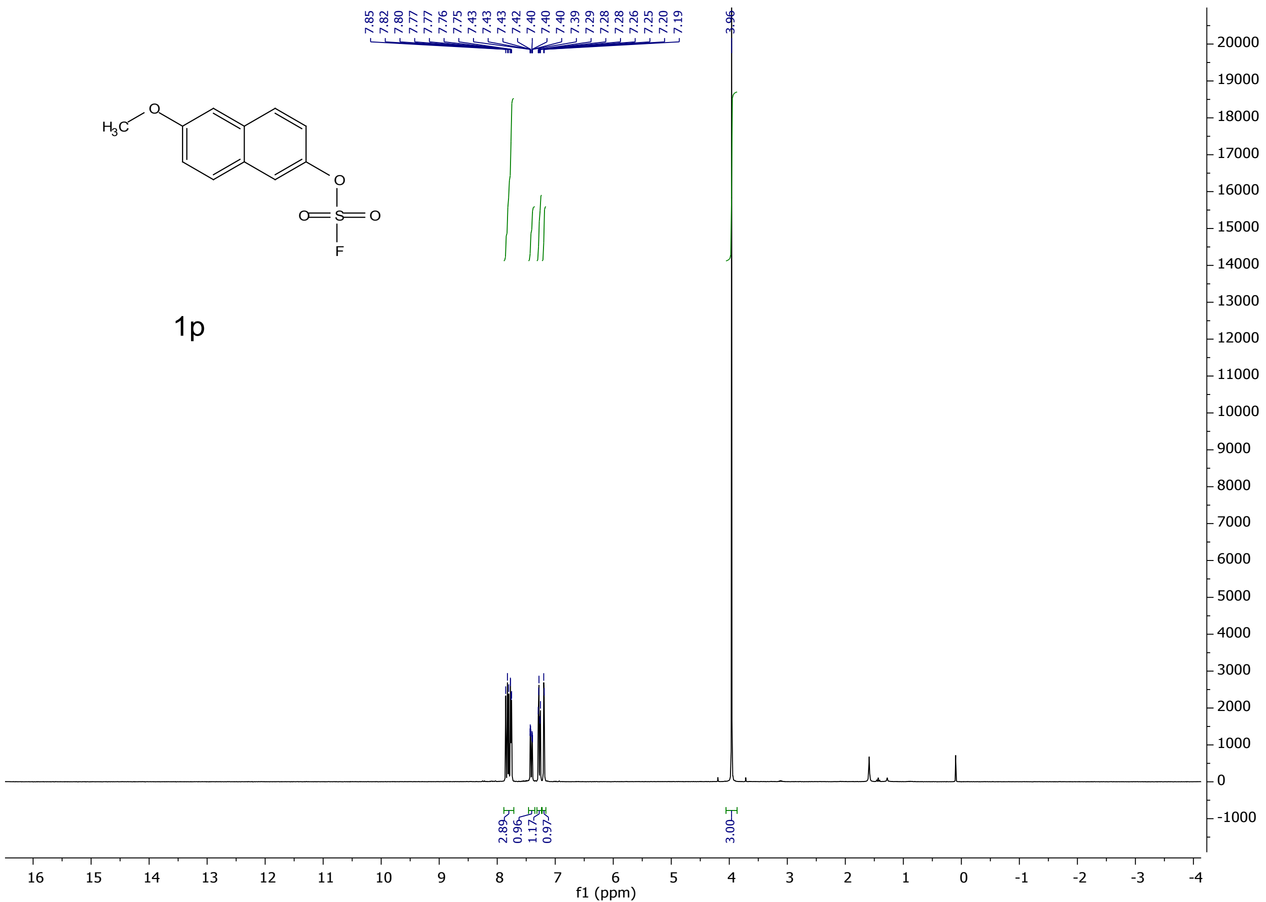
1o

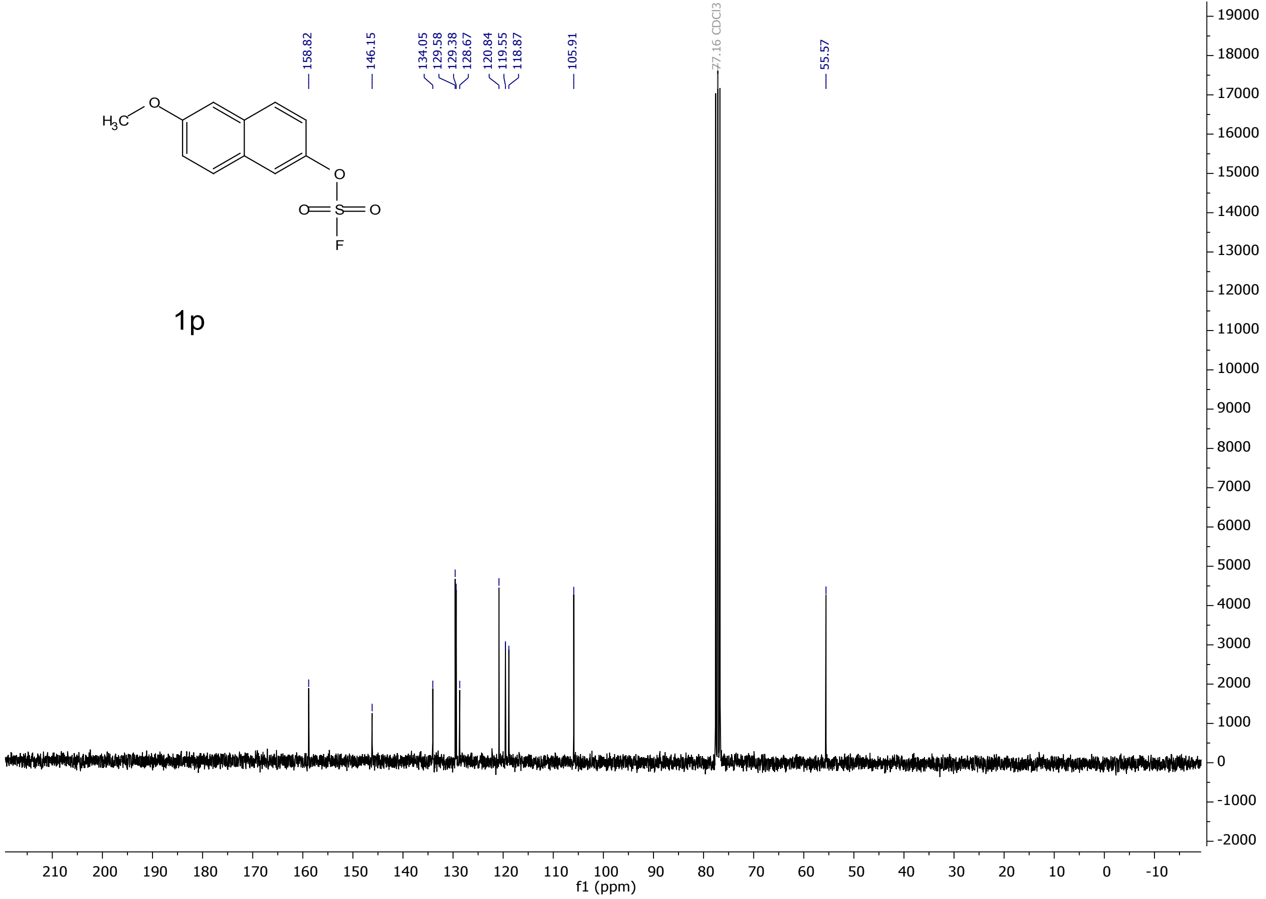

39.60
39.59
H3C
O
O
S
O
F
O
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
.00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

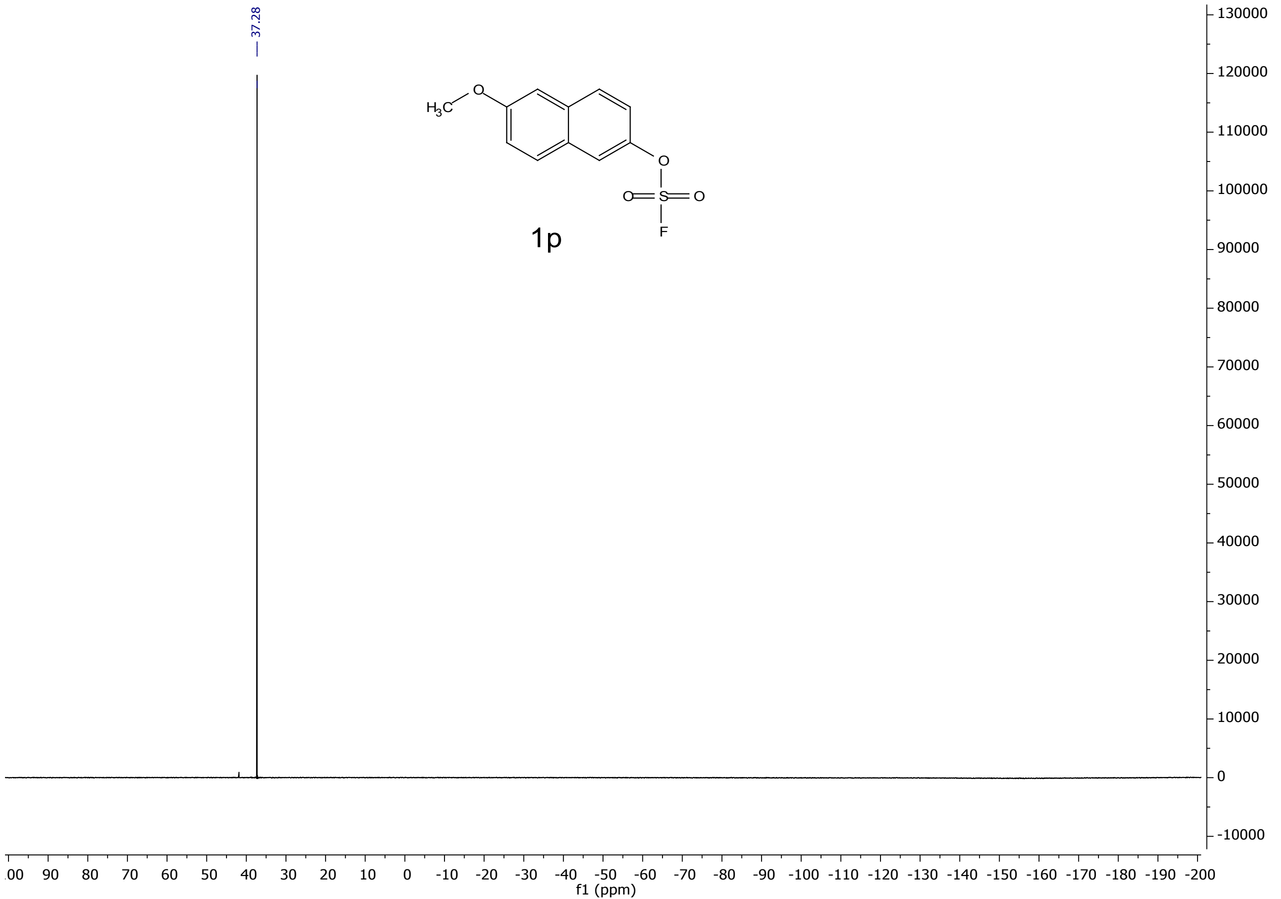
1o

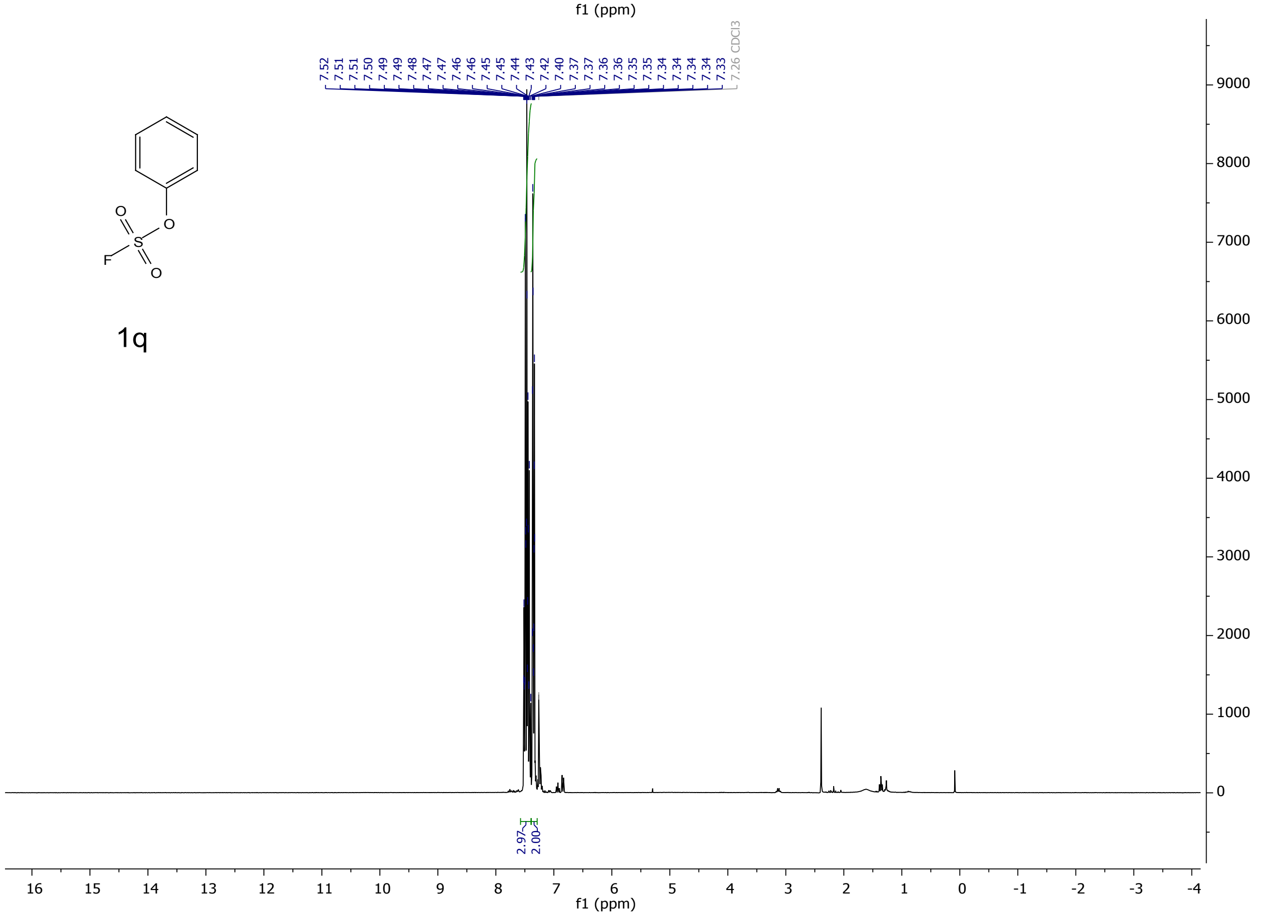

7.85
7.82
7.80
7.77
7.77
7.76
7.75
7.43
7.43
7.43
7.42
7.40
7.40
7.40
7.39
7.29
7.28
7.28
7.26
7.25
7.20
7.19
3.96
H3C
O
O
O
S
O
F
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
2.89
0.96
1.17
0.97
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

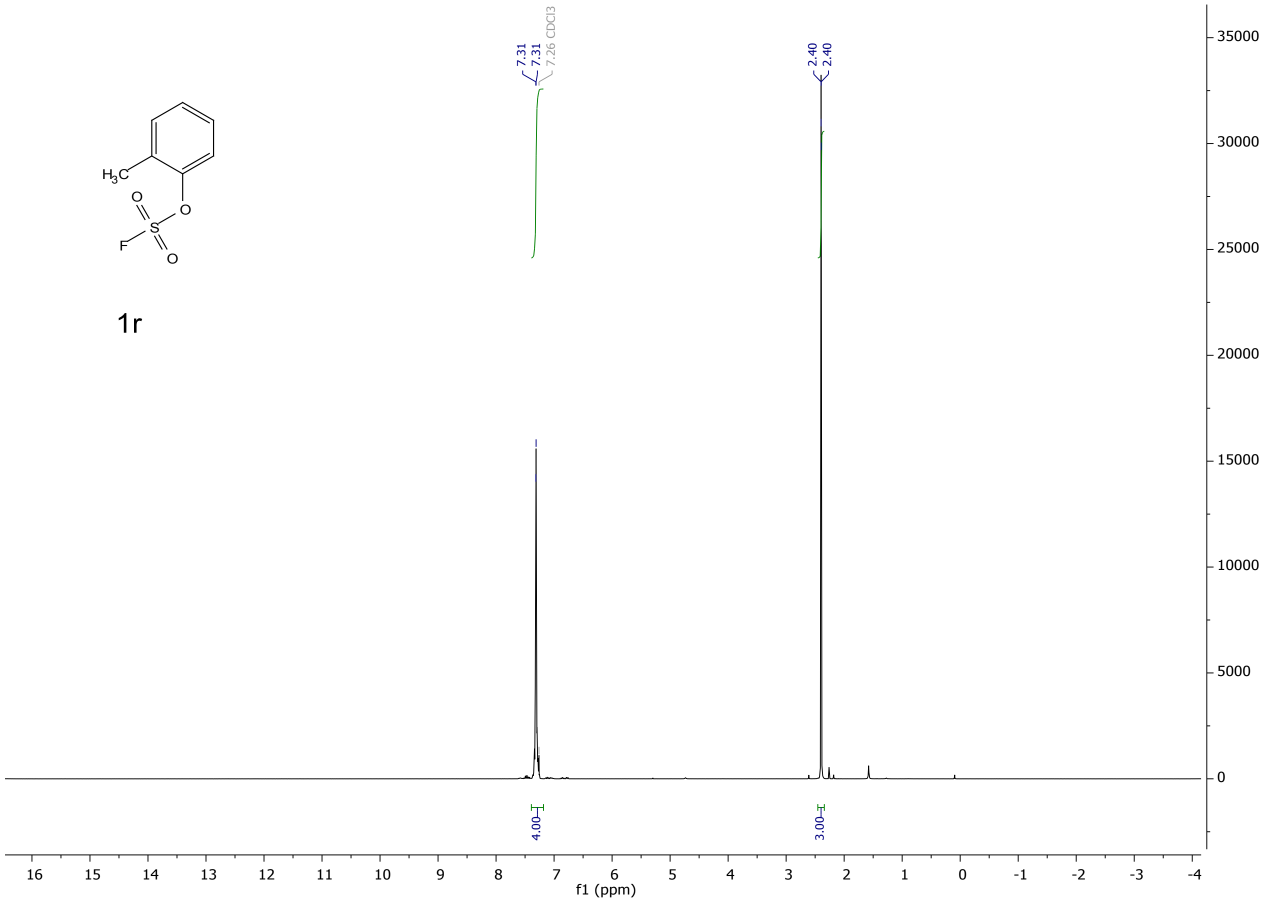
1p


7.85
7.82
7.80
7.77
7.76
7.75
7.43
7.43
7.43
7.42
7.40
7.40
7.40
7.39
7.29
7.28
7.28
7.26
7.25
7.20
7.19
3.96
H3C
O
O
O
S
O
F
1p
2.89
0.96
1.17
0.97
3.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

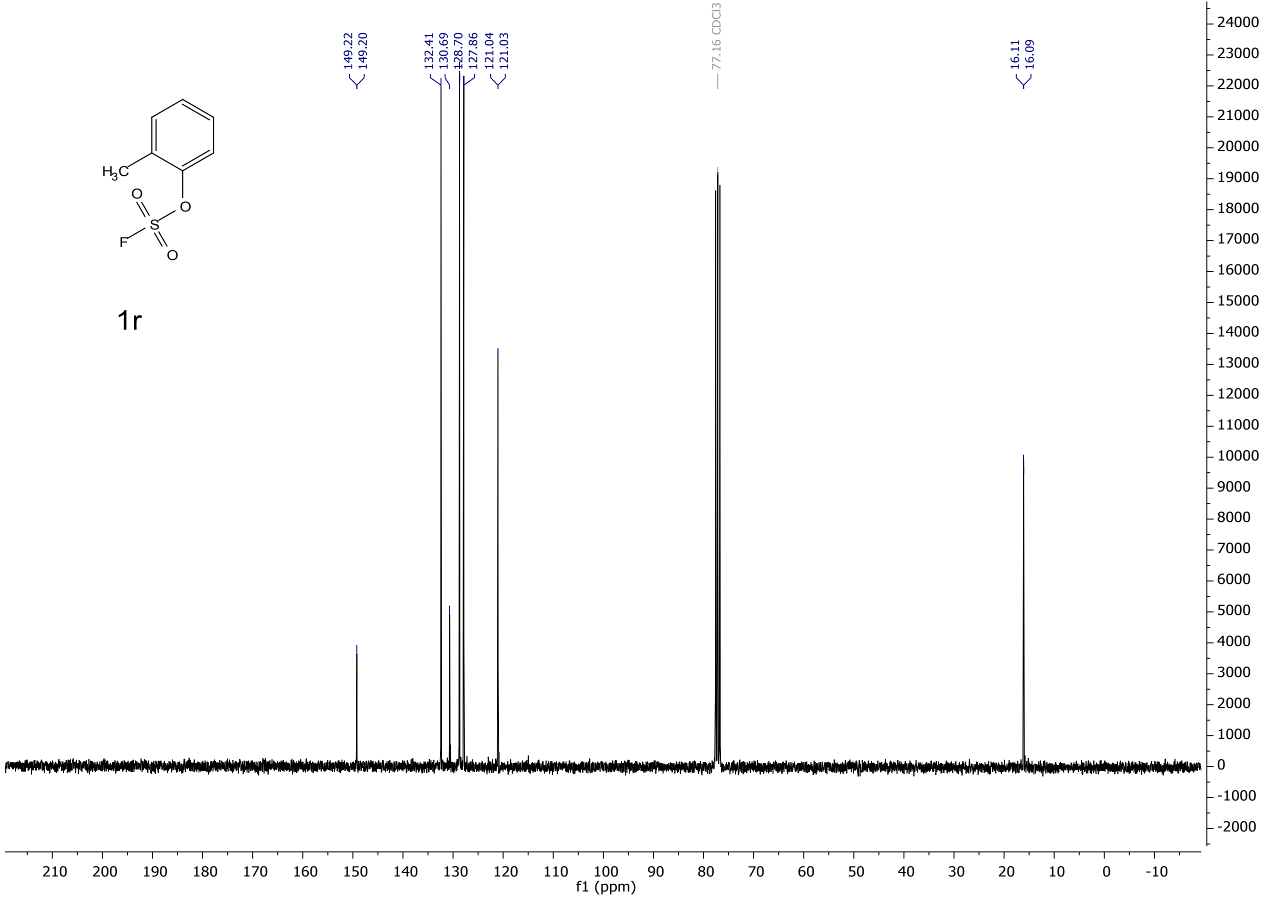

158.82
146.15
134.05
129.58
129.38
128.67
120.84
119.55
118.87
105.91
77.16 CDCl3
55.57
H3C
O
O
O
S
O
F
1p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000


37.28
H3C
O
O
O
S
O
F
1p
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

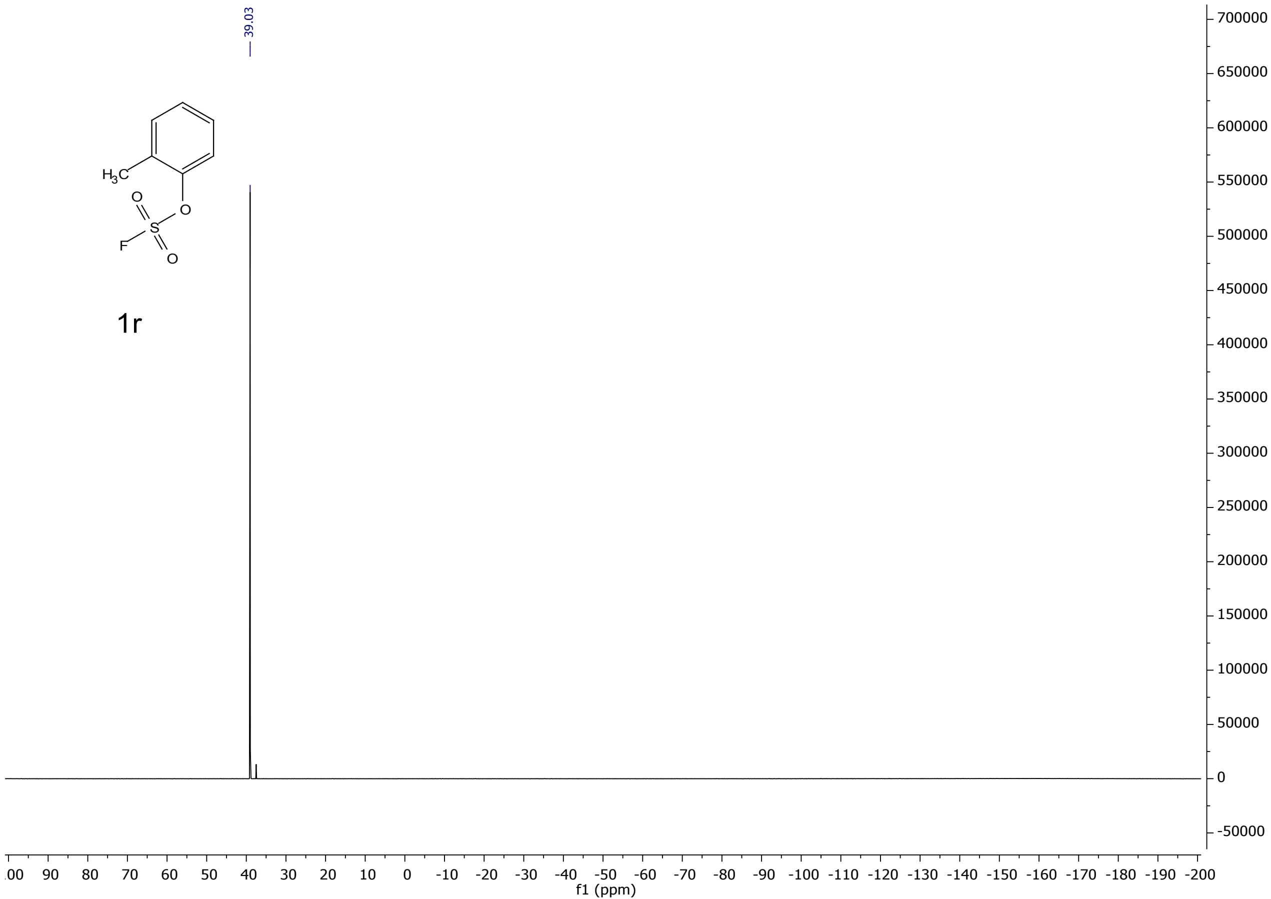

7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.43
7.42
7.40
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.34
7.33
7.26 CDCl3
O
S
O
O
F
1q
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
2.97
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)



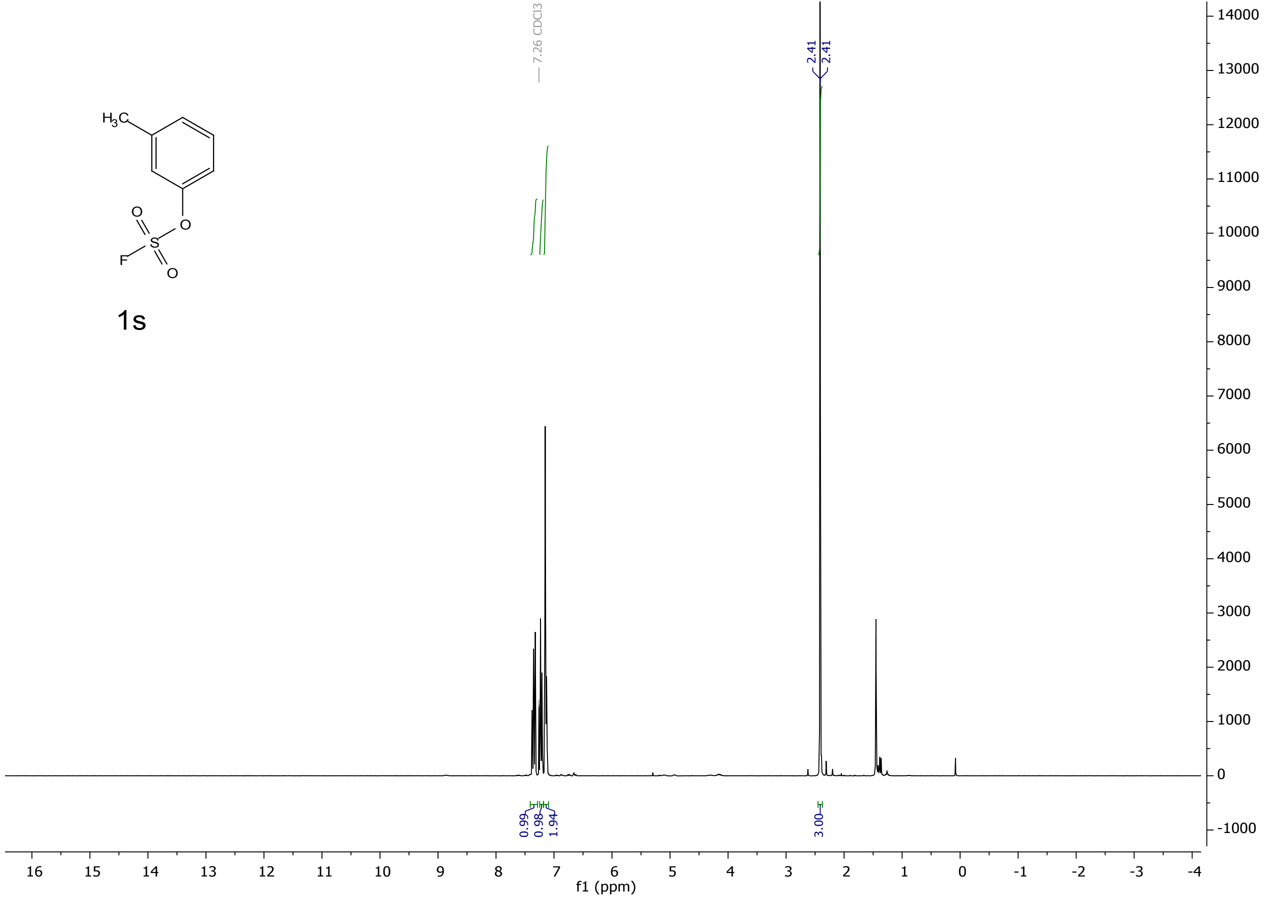
1r
H$_3$C
O
S
F
O
O
7.31
7.31
7.26 CDCl3
2.40
2.40
4.00
3.00
35000
30000
25000
20000
15000
10000
5000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)



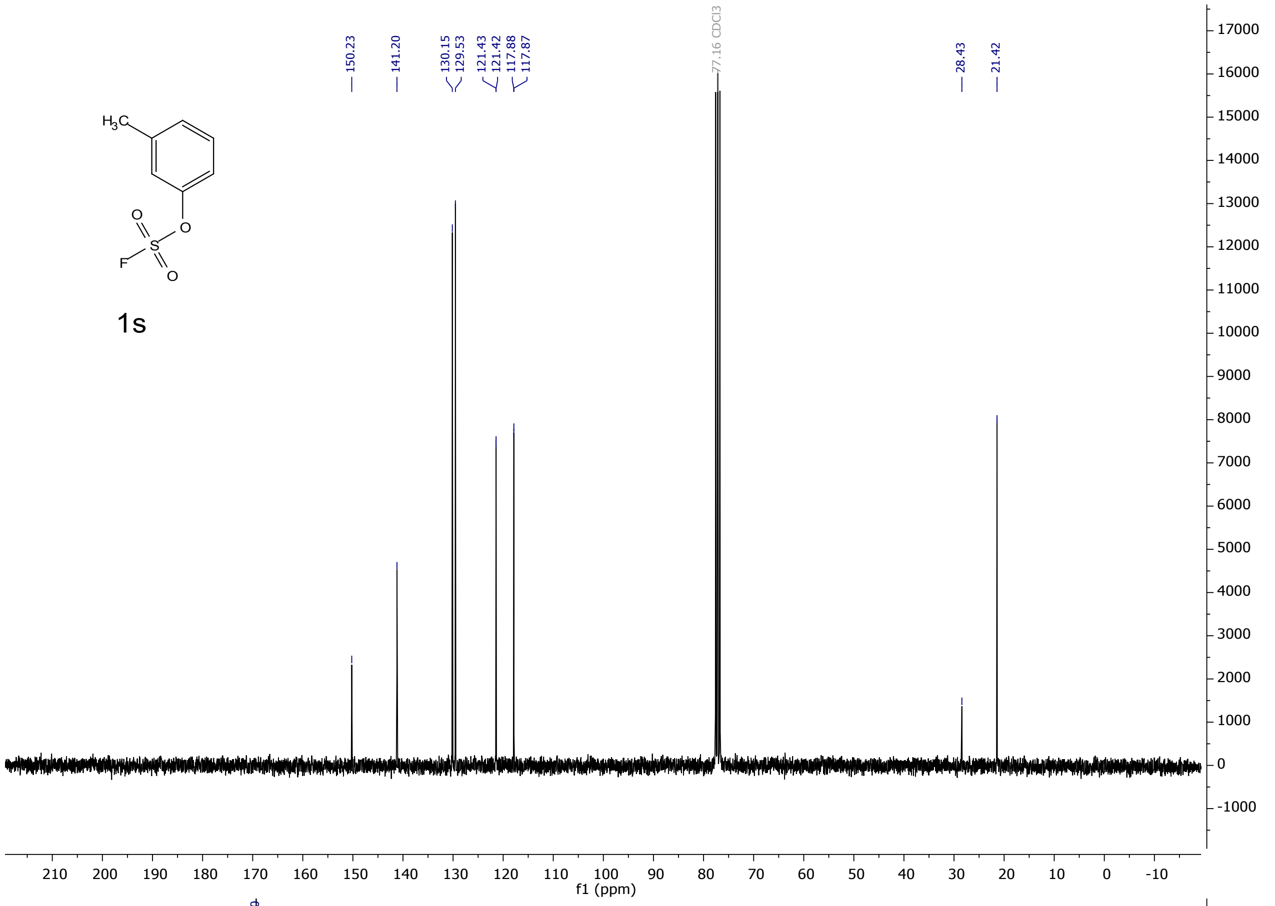
1r
H$_3$C
O
S
F
O
O
149.22
149.20
132.41
130.69
128.70
127.86
121.04
121.03
77.16 CDCl3
16.11
16.09
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


1r

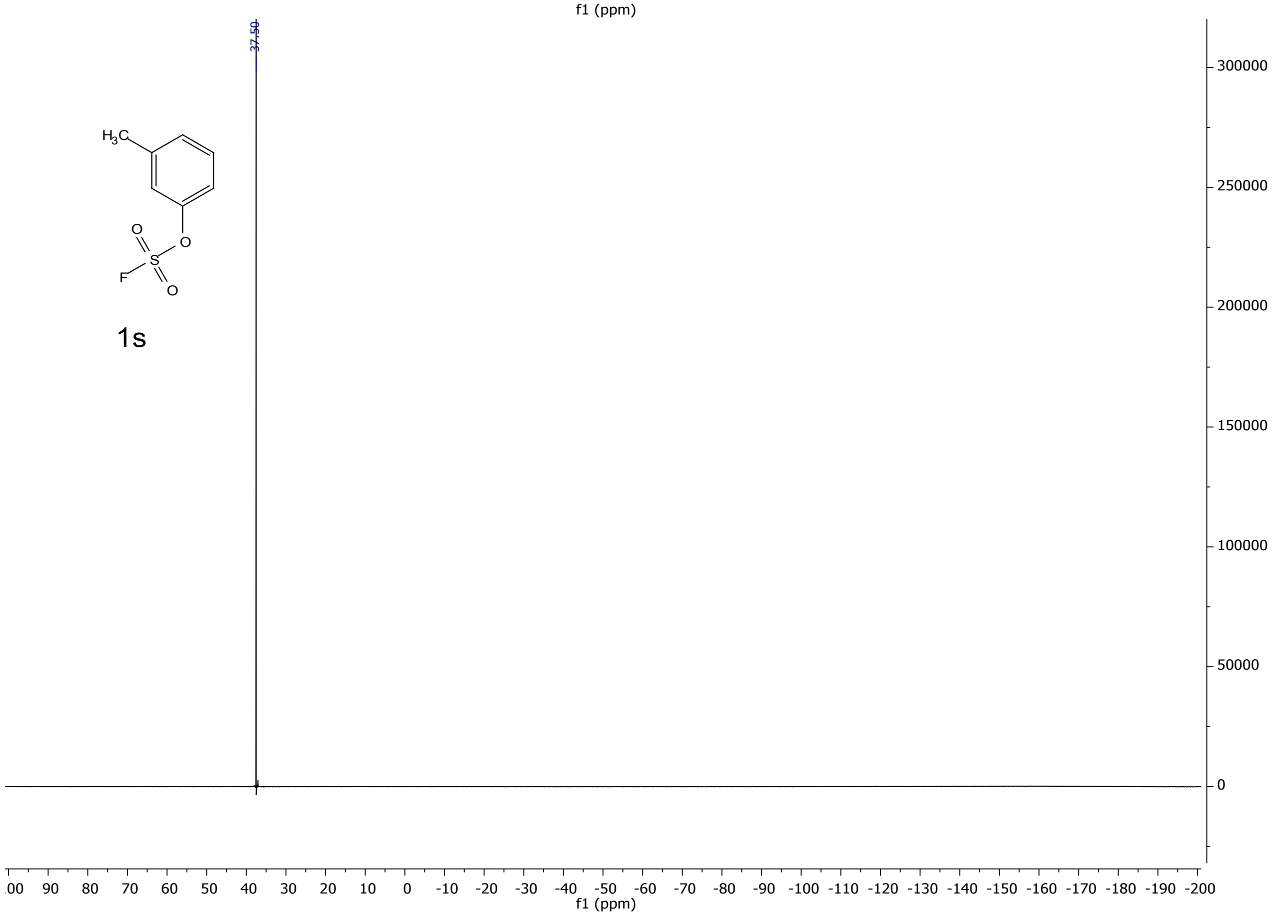
39.03
H3C
O
O
S
F
O
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
.00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


1s

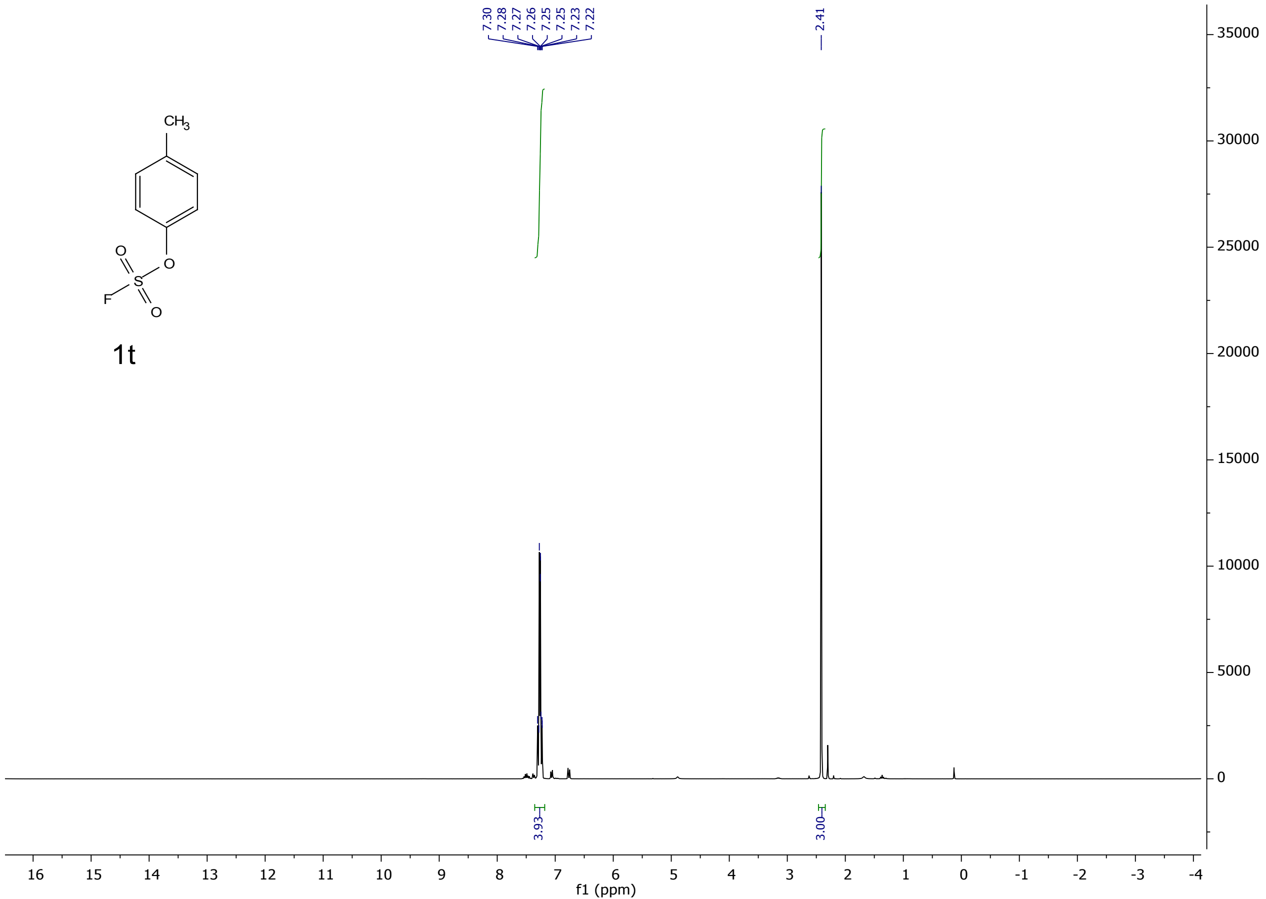
7.26 CDCl3
2.41
2.41
H3C
O
O
S
F
O
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0.99
0.98
1.94
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

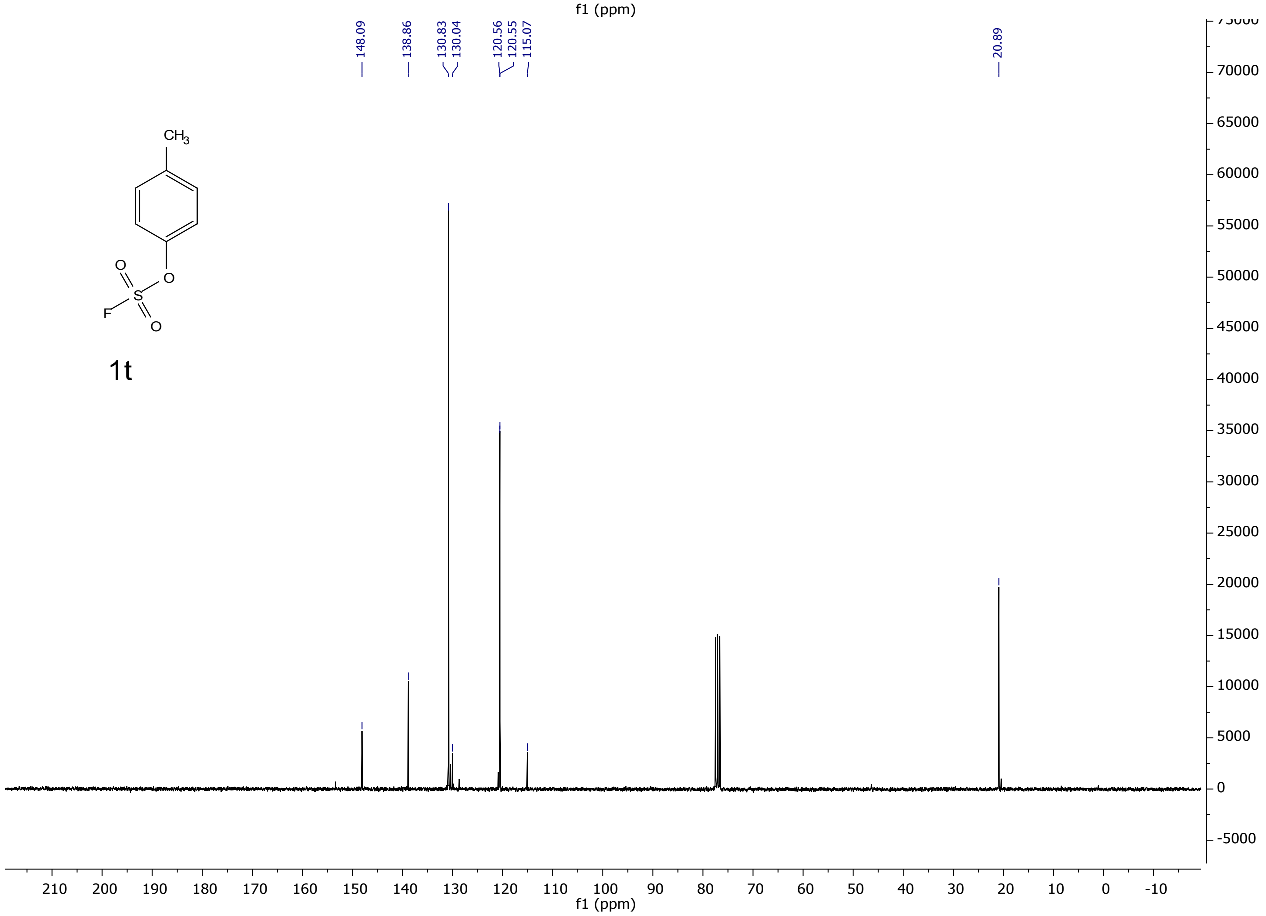

150.23
141.20
130.15
129.53
121.43
121.42
117.88
117.87
77.16 CDCl3
28.43
21.42
H$_3$C
O
S
O
F
O
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

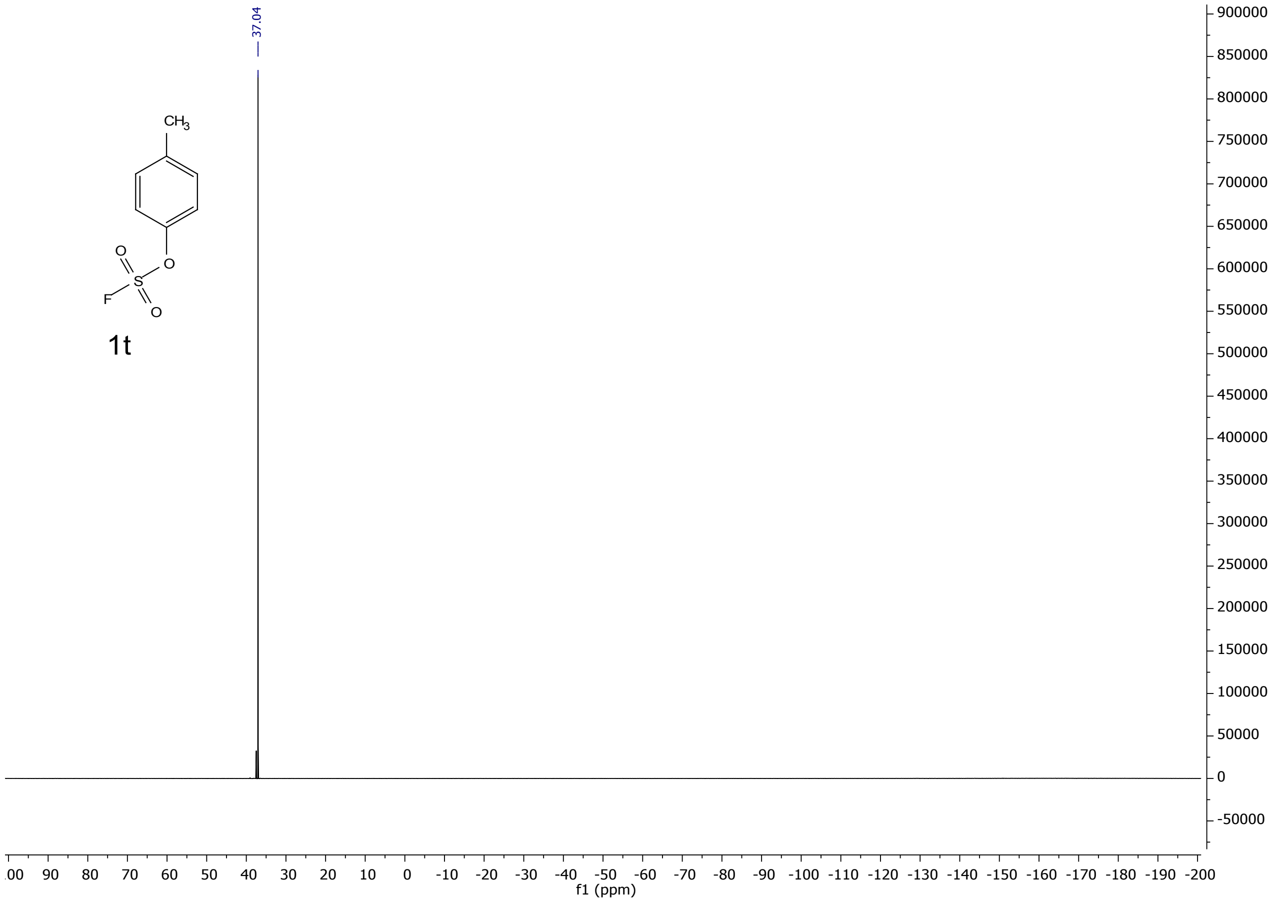
1s

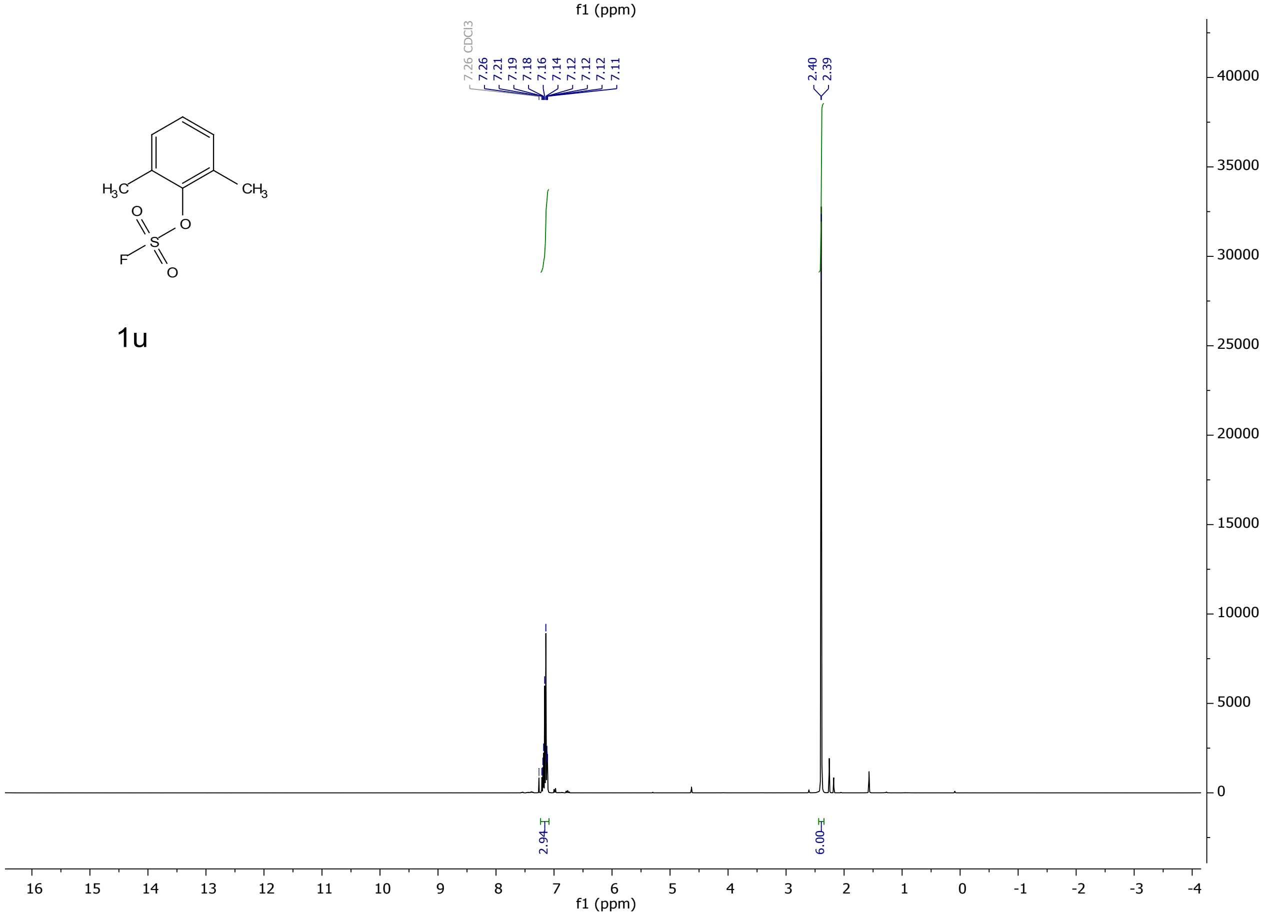

37.50
H$_3$C
O
S
O
F
O
300000
250000
200000
150000
100000
50000
0
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

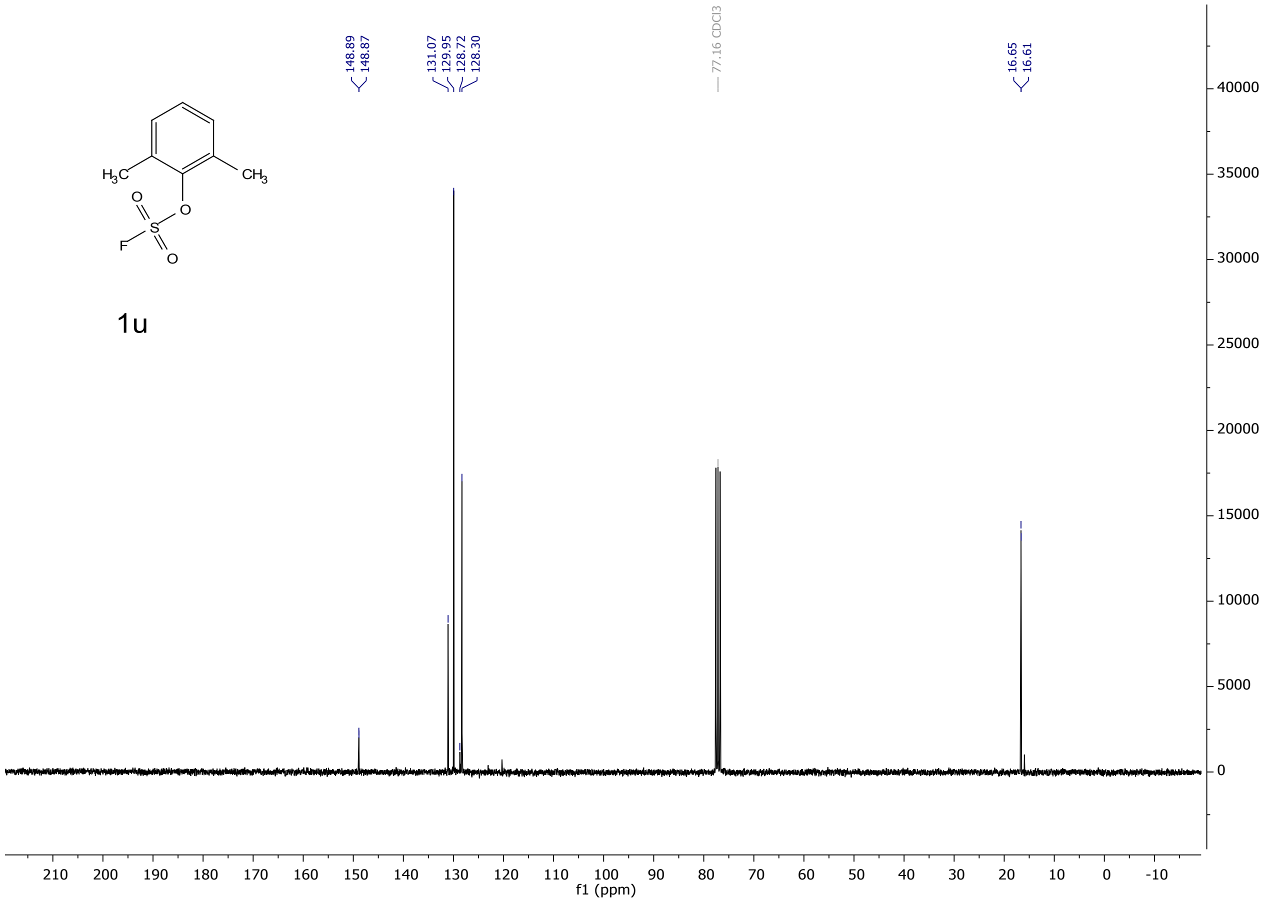
1s


7.30
7.28
7.27
7.26
7.25
7.25
7.23
7.22
2.41
CH3
O
O
S
F
O
1t
3.93
3.00
35000
30000
25000
20000
15000
10000
5000
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

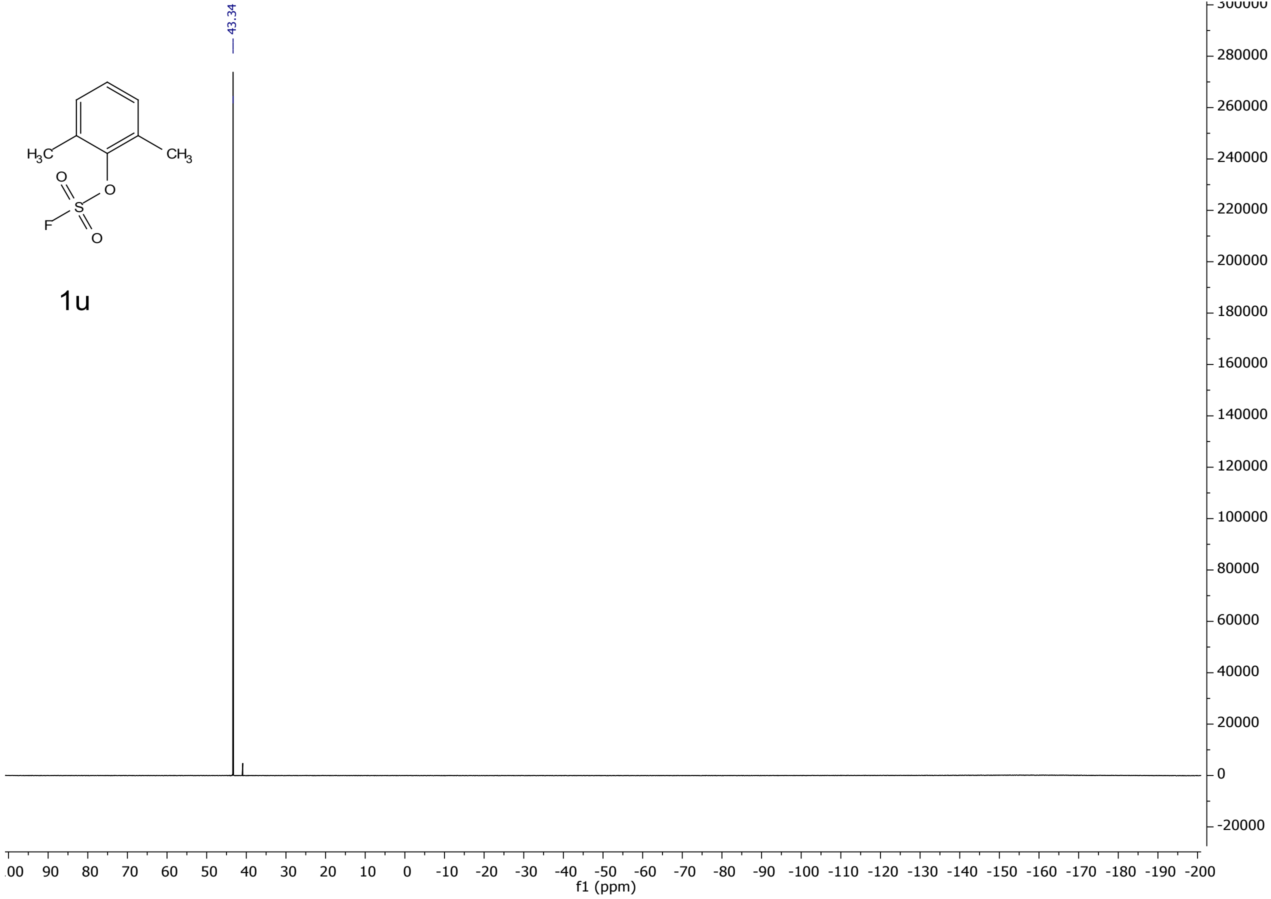

148.09
138.86
130.83
130.04
120.56
120.55
115.07
20.89
CH3
O
O
S
F
O
1t
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1t
37.04
CH3
O
S
F
O
O
900000
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
.00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

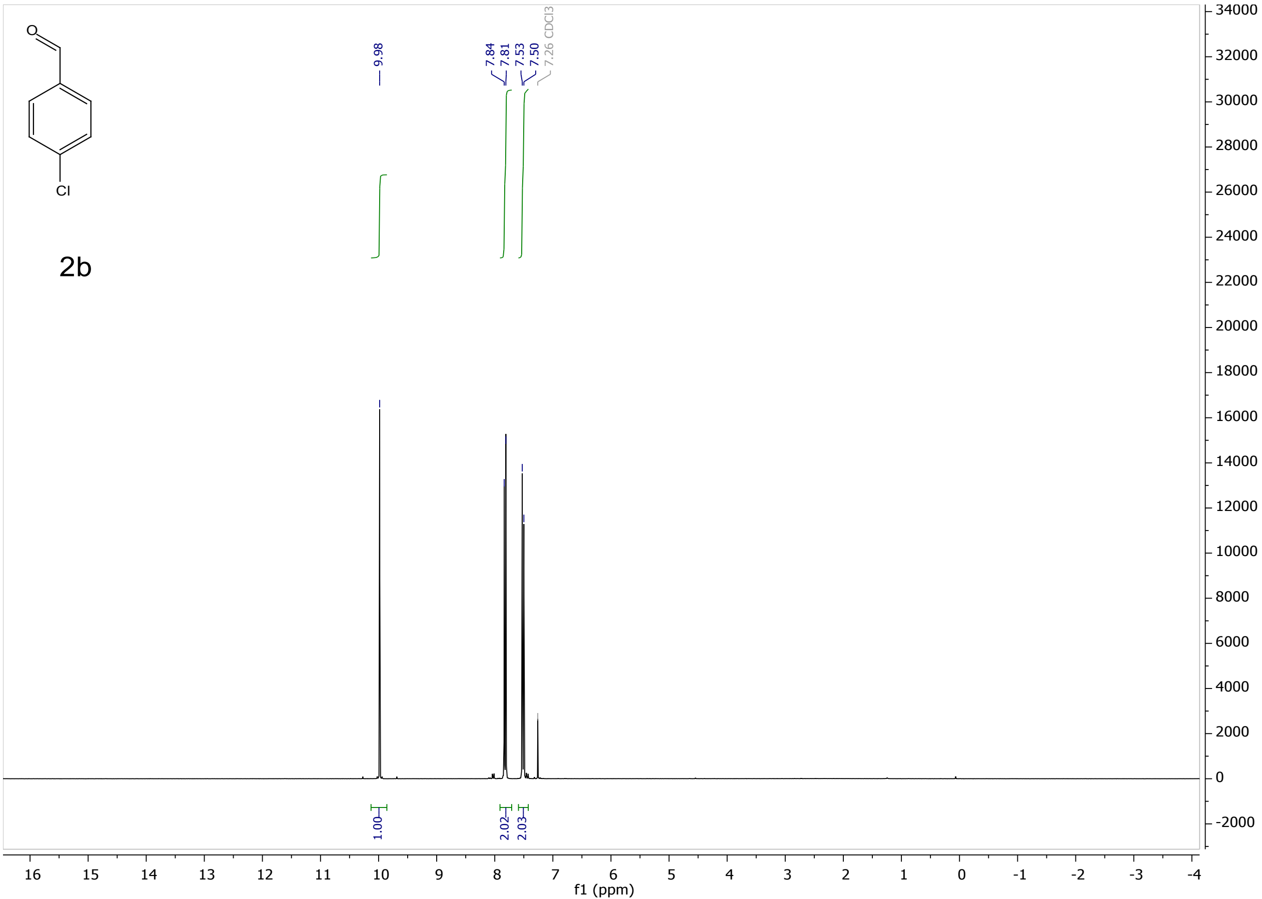

1u
7.26 CDCl3
7.26
7.21
7.19
7.18
7.16
7.14
7.12
7.12
7.12
7.11
2.40
2.39
H3C
CH3
O
S
F
O
O
2.94
6.00
40000
35000
30000
25000
20000
15000
10000
5000
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

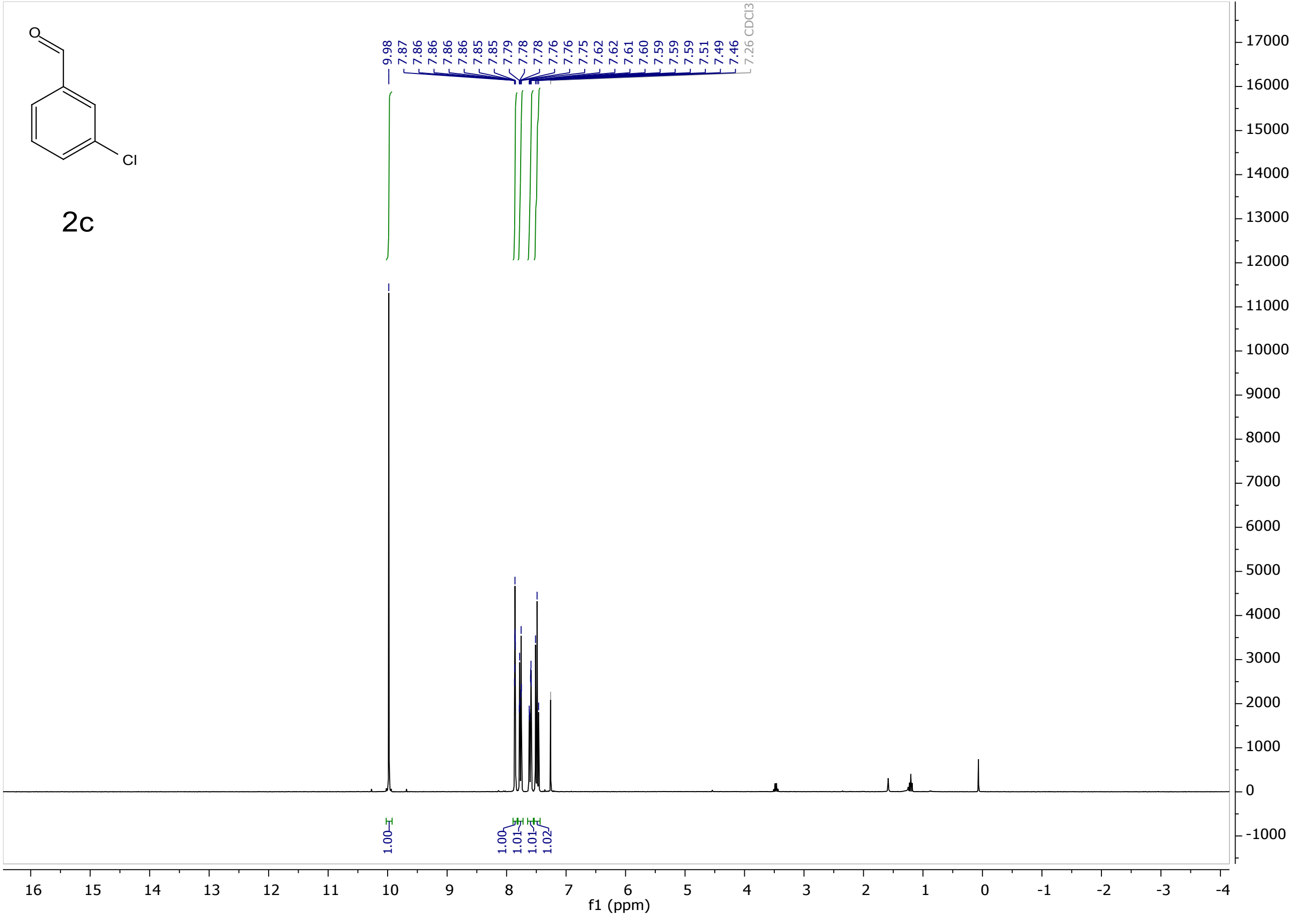

148.89
148.87
131.07
129.95
128.72
128.30
77.16 CDCl3
16.65
16.61
H3C
CH3
O
S
F
40000
35000
30000
25000
20000
15000
10000
5000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

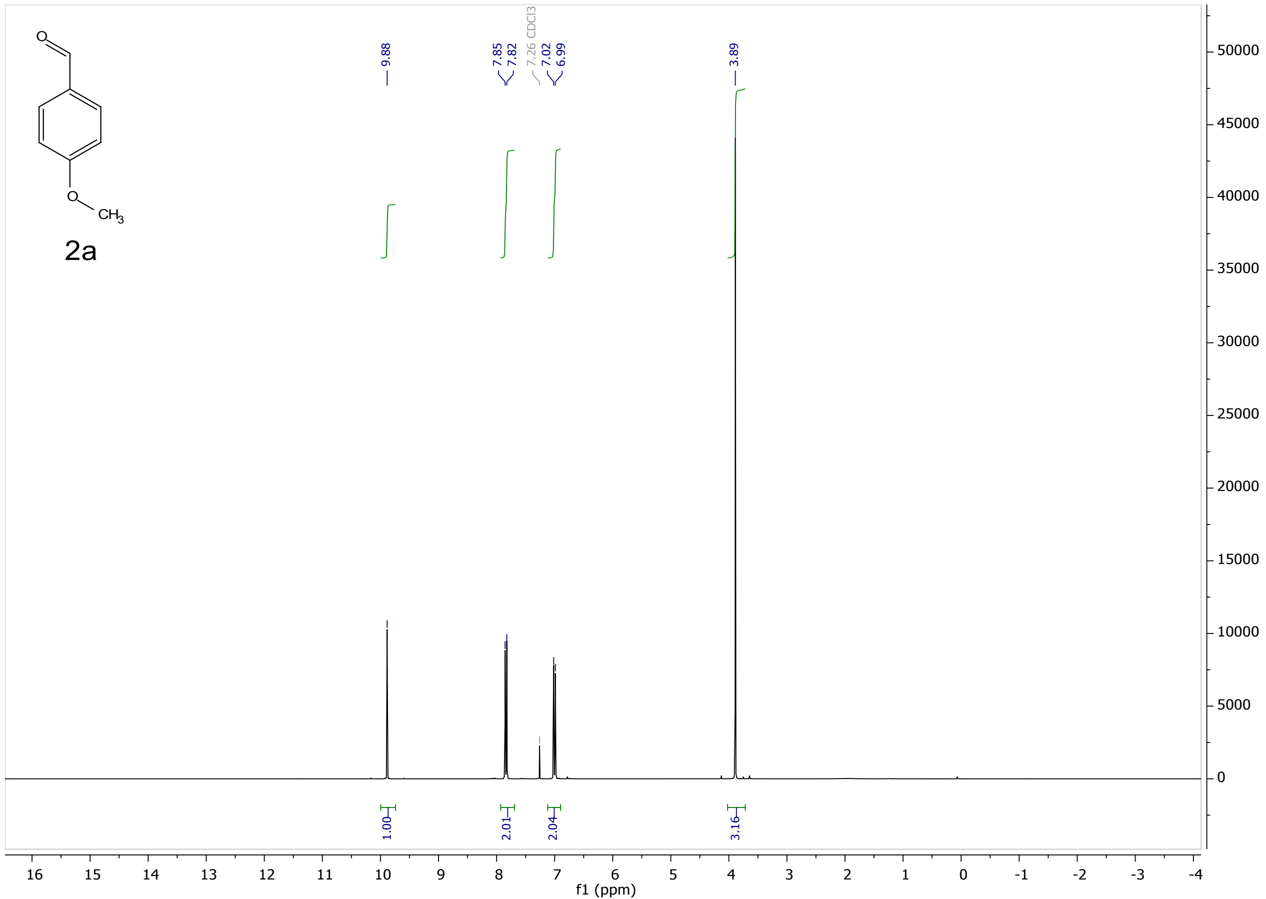
1u

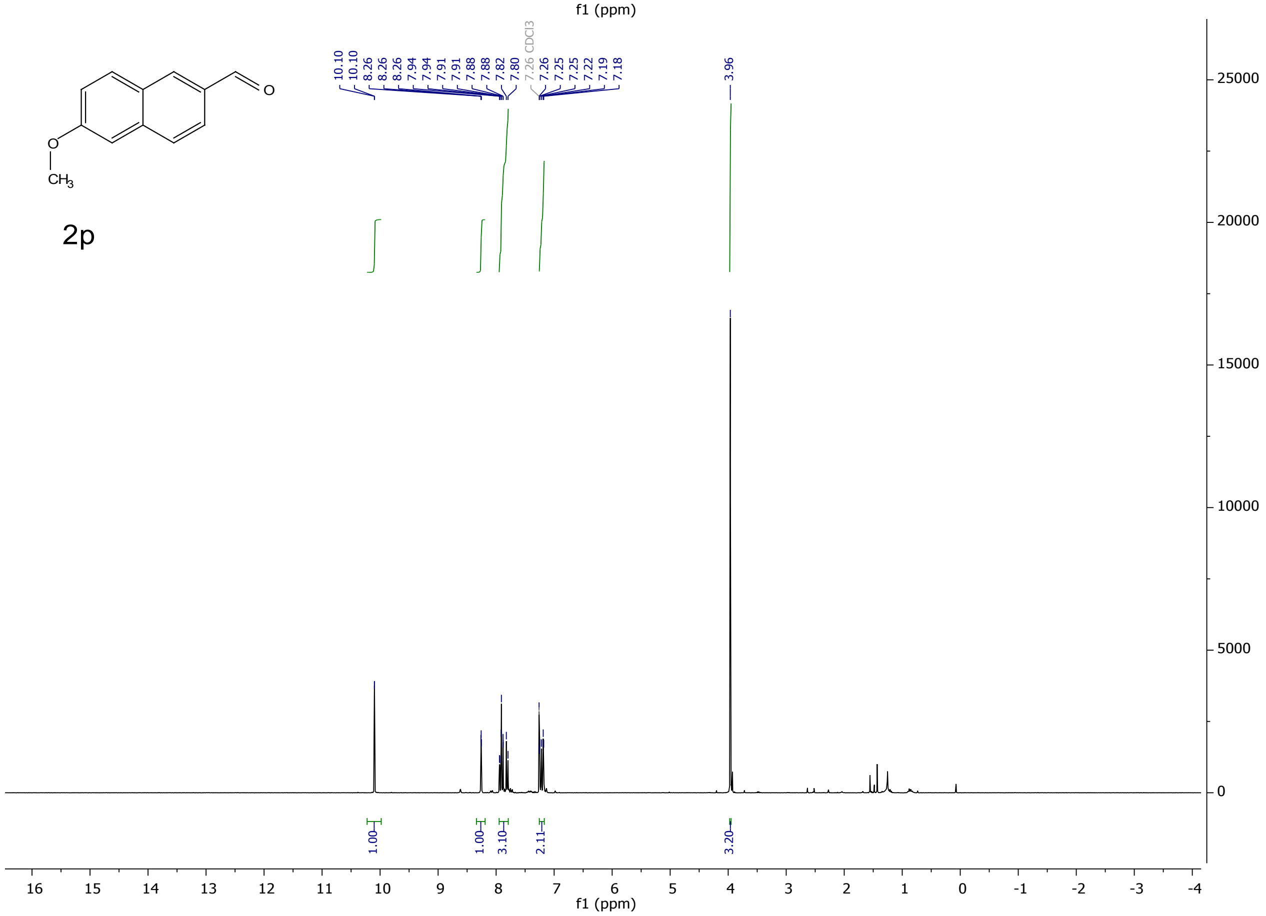

43.34
H3C
CH3
O
S
F
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

1u


2b
O
Cl
9.98
7.84
7.81
7.53
7.50
7.26 CDCl3
1.00
2.02
2.03
f1 (ppm)


2c
O
Cl
9.98
7.87
7.86
7.86
7.86
7.85
7.85
7.79
7.78
7.78
7.76
7.76
7.75
7.62
7.62
7.61
7.60
7.59
7.59
7.59
7.51
7.49
7.46
7.26 CDCl3
1.00
1.00
1.01
1.01
1.02
f1 (ppm)


2a
O
CH3
9.88
7.85
7.82
7.26 CDCl3
7.02
6.99
3.89
1.00
2.01
2.04
3.16
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


2p
O
O
CH3
10.10
10.10
8.26
8.26
7.94
7.94
7.91
7.91
7.88
7.88
7.82
7.80
7.26 CDCl3
7.26
7.25
7.25
7.22
7.19
7.18
3.96
1.00
1.00
3.10
2.11
3.20
25000
20000
15000
10000
5000
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

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