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Supporting Information

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A General Strategy for the Perfluoroalkylation of Arenes and Arylbromides by Using Arylboronate Esters and [(phen)CuR^F]**

*Nichole D. Litvinas, Patrick S. Fier, and John F. Hartwig**

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General Experimental Details

All manipulations were conducted under an inert atmosphere with a nitrogen-filled glovebox (Innovative Technologies, Newburyport, Massachusetts) equipped with an oxygen sensor (working oxygen level <20.0 ppm) and low-temperature refrigeration unit (–30 °C), unless otherwise noted. All reactions were conducted in oven-dried 4-mL or 20-mL vials fitted with a Teflon-lined screw cap under an atmosphere of nitrogen unless otherwise noted.

$[Ir(cod)OMe]_2$ was obtained from Johnson-Matthey and used as received. 2-Mesitylmagnesium bromide was purchased as a 1.0M THF solution from Sigma-Aldrich. Copper(I) chloride (99.999%) was purchased from Strem and used as received. 4,4'-Di-tert-butylbipyridine was obtained from Sigma-Aldrich and used as received. B_2pin_2 was obtained from Allychem and used as received. Arenes and aryl bromides were purchased from Sigma-Aldrich and used as received, except 4-butyliodobenzene and 3-iodopyridine, which were purchased from Alfa Aesar and used as received. (Pentafluoroethyl)trimethylsilane ($TMSCF_2CF_3$) was purchased from Combi-Blocks. (Perfluoropropyl)trimethylsilane ($TMSCF_2CF_2CF_3$), and 4-(trifluoromethoxy)anisole (internal standard for ^{19}F NMR analysis) were purchased from Aldrich. (Trifluoromethyl)trimethylsilane ($TMSCF_3$, Ruppert's reagent) was purchased from Matrix Scientific. KF and KOAc were purchased from Sigma-Aldrich and dried in a vacuum oven overnight before use. Mesitylcopper was prepared according to the literature

procedure.[1] (1,10-phenanthroline)(heptafluoropropyl)copper(I) [(phen)$CuCF_2CF_2CF_3$] was prepared according to the published procedure.[2] Phen$CuCF_3$ was synthesized as described below, but it can now be purchased from Sigma-Aldrich.

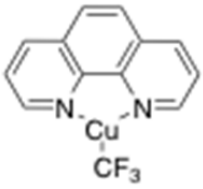
Organic solutions were concentrated by rotary evaporation. Flash column chromatography was performed on Silicylce Siala-P silica gel or on a Teledyne Isco CombiFlash Rf automated chromatography system with 4 g RediSep Rf Gold normal-phase silica columns. The products were visualized by UV light and stained with ceric ammonium molybdate (CAM) or potassium permanganate ($KMnO_4$).

NMR spectra were acquired on 400 MHz and 500 MHz Varian Unity or Innova instruments at the University of Illinois VOICE NMR facility. NMR spectra were processed with MestReNova 5.0 (Mestrelab Research SL). Chemical shifts are reported in ppm and referenced to residual solvent peaks ($CHCl_3$ in $CDCl_3$: 7.26 ppm for ^1H and 77.0 ppm for ^{13}C; DMF-d_6 in DMF-d_7: 2.91 ppm for ^1H and 162.7 ppm for ^{13}C) or to an external standard (1% $CFCl_3$ in $CDCl_3$: 0 ppm for ^{19}F). Coupling constants are reported in hertz.

All GC-MS analyses were conducted with an Agilent 6890N GC equipped with an HP-5 column (25 m x 0.20 mm ID x 0.33 μm film) and an Agilent 5973 Mass Selective Detector. The temperature for each run was held at 50 °C for 2 min, ramped from 50 °C to 300 °C at 40 °C/min, and held at 300 °C for 5 min.

Elemental analyses were performed by the University of Illinois at Urbana-Champaign Microanalysis Laboratory and by Robertson Microlit Laboratories, Inc. (Madison, NJ).

Preparation of (1,10-phenanthroline)(trifluoromethyl)copper(I) [(phen)$CuCF_3$]



To an oven-dried 500-mL round-bottomed flask equipped with a stir bar was added $[Cu(Mesityl)]_5$ (9.14 g, 12.5 mmol, 50.0 mmol of monomeric [Cu(Mesityl)] units), and benzene (160 mL). The resulting light yellow solution was stirred vigorously while anhydrous ^{t}BuOH (5.3

[1] Tsuda, T., Yazawa, T. and Watanabe, K. Preparation of thermally stable and soluble mesitylcopper(I) and its application in organic synthesis. *J. Org. Chem.* **1981**, *46*, 192-194.
[2] Morimoto, H., Tsubogo, T., Litvinas, N. D. and Hartwig, J. F. A Broadly Applicable Copper Reagent for Trifluoromethylations and Perfluoroalkylations of Aryl Iodides and Bromides. *Angew. Chem. Int. Ed*. **2011**, *50*, 3793–3798.

mL, 55.0 mmol, 1.1 equiv) was added dropwise. The flask was sealed with a septum, and the light yellow solution was stirred at room temperature for 1 h. 1,10-phenanthroline (9.01 g, 50.0 mmol, 1.0 equiv) was added with an additional 170 mL of benzene. The dark purple solution was stirred at room temperature for 30 min. $TMSCF_3$ (8.1 mL, 55.0 mmol, 1.1 equiv) was then added dropwise. The mixture was stirred at room temperature for 18 h to give a red-orange suspension. The suspension was filtered through a medium fritted funnel, and the solid was washed with Et_2O (50 mL) and dried under vacuum to give (1,10-phenanthroline)(trifluoromethyl)copper(I) as an orange solid (12.63 g, 40.4 mmol, 81% yield). The product consists of a 21:79 ratio of isomers $(Phen)CuCF_3$ and $[(Phen)_2Cu][Cu(CF_3)_2]$.

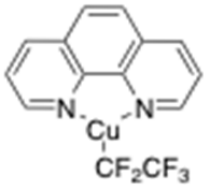
Major isomer: ^1H NMR (400 MHz, DMF-d_7, -25 ºC) δ 9.23 (s, 4H), 8.93 (s, 4H), 8.79 (s, 2H), 8.36 (s, 4H), 8.11 (br s, 4H).

Minor isomer: ^1H NMR (400 MHz, DMF-d_7, -25 ºC) δ 9.10 (s, 2H), 8.79 (s, 2H), 8.11 (br s, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, DMF-d_7) δ 150.4, 144.2, 138.3, 130.0, 127.8, 126.5 (note that a carbon resonance for CF_3 was not observed due to (1) dynamic behavior of the complex (see below), (2) broadening of the resonance by Cu-C coupling and (3) splitting of the resonance by C-F coupling).

^{19}F NMR (376 MHz, DMF-d_7): δ –22.6 (br), –30.9 (s).

Anal. Calcd for $C_{13}H_8CuN_2F_3$: C, 49.92; H, 2.58; N, 8.96; F, 18.22; Found: C, 49.74; H, 2.52; N, 8.99; F, 18.17.

Preparation of (1,10-phenanthroline)(pentafluoroethyl)copper(I) [(phen)CuCF$_2$CF$_3$]



To an oven-dried 50-mL round-bottomed flask equipped with a stir bar was added $[Cu(Mesityl)]_5$ (859 mg, 0.94 mmol, 4.7 mmol of the monomeric [Cu(Mesityl)] unit), and benzene (16 mL). The resulting light yellow solution was stirred vigorously while anhydrous ^{t}BuOH (500 µL, 5.2 mmol, 1.1 equiv) was added dropwise. The flask was sealed with a septum, and the light yellow solution was stirred at room temperature for 1 h. 1,10-phenanthroline (847 mg, 4.7 mmol, 1.0 equiv) was added with an additional 16 mL of benzene. The dark purple solution was stirred at room temperature for 30min. $TMSCF_2CF_3$ (1.0 g, 5.2 mmol, 1.1 equiv) was then added dropwise. The mixture was stirred at room temperature for 18 h to give a red-orange suspension. The suspension was filtered through a medium fritted funnel, and the solid was washed with Et_2O (5 mL) and dried under vacuum to give (1,10-phenanthroline)(pentafluoroethyl)copper(I) as an orange solid (1.33 g, 3.67 mmol, 78% yield). As for $(Phen)CuCF_3$, neutral (Phen)CuCF2CF3 equilibrates with its anionic

form. Two sets of ^{19}F NMR peaks for the pentafluoroethyl group were observed in a 52:48 ratio, reflecting a 69:31 ratio of the neutral to anionic form after correcting for the number of equivalent fluorine resonances in the ionic form.

Major Isomer: ^{1}H NMR (500 MHz, DMF) δ 9.19 (d, *J* = 4.6, 2H), 8.89 (d, *J* = 8.2 Hz, 2H), 8.30 (s, 2H), 8.10 (dd, *J* = 8.2, 4.6 Hz, 2H).

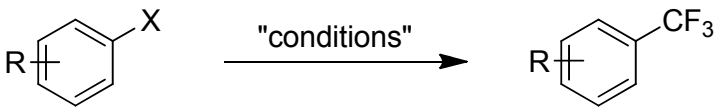
^{19}F NMR (470 MHz, DMF) δ -84.01 (s), -117.31 (s).

Minor Isomer: ^{1}H NMR (500 MHz, DMF) δ 9.19 (d, *J* = 4.6 Hz, 2H), 8.89 (d, *J* = 8.1 Hz, 2H), 8.30 (s, 2H), 8.10 (dd, *J* = 8.1, 4.6 Hz, 2H).

^{19}F NMR (470 MHz, DMF) δ -84.03 (s), -110.01 (br s).

Anal. Calcd. for $C_{14}H_8CuF_5N_2$: C, 46.35; H, 2.22; N, 7.72; Found: C, 46.42; H, 2,42; N, 8.05.

Screening Conditions for Trifluoromethylation of Aryl Boronic Acids and Boronate Esters



entry	X	R	conditions	yield (%)[a]
1	Bpin	4-F	CuI, phen, KOtBu, CF_3TMS, KF, air	49
2	Bpin	4-F	$PhenCuCF_3$, KF, air	77
3	$B(OH)_2$	4-F	"	36
4	$B(OH)_2$	4-Br	"	60
5	$B(OH)_2$	3-NO_2	"	56
6	Bnpg	4-F	"	67
7	Bcat	4-F	"	16
8	BMIDA	4-F	"	10
9	BF_3K	4-F	"	np
10	Bpin	4-F	20 mol % $PhenCuCF_3$ 1.2 equiv CF_3TMS, KF, air	42

[a] Reactions run on a 0.1 mmol scale; yields determined by ^{19}F NMR spectroscopy with 4-trifluoromethoxyanisole as an internal standard.

General Procedure for One-Pot Generation of Perfluoroalkyl Arenes via Ir-Catalyzed C–H Borylation

In a nitrogen-filled glove box, the arene (0.500 mmol, 1 equiv) and a stock solution of B_2Pin_2, $[Ir(cod)OMe]_2$, and dtbpy were combined in a 20 mL vial. The stock solution contained B_2Pin_2 (95.3 mg, 0.375 mmol, 0.75 equiv), $[Ir(cod)OMe]_2$ (0.1 – 3.0 mol%) and dtbpy (0.2 – 6.0 mol%) per 1 mL of THF (0.5M) (See specific catalyst and ligand loadings below). The reaction mixture was heated in a sealed vessel at 80 ºC for 18 h. The dark red solution was then cooled to room temperature, and the volatile materials were evaporated under reduced pressure for 2-4 h. The reaction vessel was returned to the glove box where (Phen)$CuCF_3$ (188 mg, 0.600 mmol, 1.2 equiv) or (Phen)$CuCF_2CF_3$ (218 mg, 0.600 mmol, 1.2 equiv) or (Phen)$CuCF_2CF_2CF_3$ (248 mg, 0.600 mmol, 1.2 equiv), KF (29.1 mg, 0.500 mmol, 1.0 equiv) and DMF (5 mL, 0.1M) were added, and the vial was sealed with a screw cap fitted with a septum. Outside of the glove box, air from a balloon was bubbled into the DMF solution or 5-10 min. The balloon was removed, and the vial was placed in a 50 ºC heating bath. After 18 h, the reaction mixture was cooled to room temperature and diluted with 5 mL of Et_2O. The mixture was filtered over Celite, washed with an additional 20 mL of Et_2O, and transferred to a separatory funnel. The mixture was washed with 4 x 40 mL of H_2O and 1 x 25 mL brine, dried with $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with pentane or pentane/Et_2O mixtures as the eluent.

General Procedure for One-Pot Generation of Perfluoroalkyl Arenes via Palladium-Catalyzed C–Br Borylation

In a nitrogen-filled glove box, the aryl bromide (0.500 mmol, 1 equiv), B_2Pin_2 (139 mg, 0.550 mmol, 1.1 equiv), KOAc (147 mg, 1.50 mmol, 3 equiv), $PdCl_2$•dppf (12.2 mg, 0.015 mmol, 3 mol%), and 2.5 mL dioxane (0.2M) were combined in a 20 mL vial. The reaction vessel was sealed with a Teflon-lined cap and heated at 80 ºC for 18 h, or until the starting material was consumed, as determined by GC-MS. The solution was then allowed to cool to room temperature and filtered through a plug of Celite. The Celite plug was rinsed with a minimal volume of EtOAc (~2 mL), and the resulting solution was concentrated under vacuum for 2-4 h. The reaction vessel was returned to the glove box where (Phen)$CuCF_3$ (188 mg, 0.600 mmol, 1.2 equiv) or (Phen)$CuCF_2CF_3$ (218 mg, 0.600 mmol, 1.2 equiv) or (Phen)$CuCF_2CF_2CF_3$ (248 mg, 0.600 mmol, 1.2 equiv), KF (29

mg, 0.500 mmol, 1.0 equiv) and DMF (5 mL, 0.1M) were added, and the vial was sealed with a screw cap fitted with a septum. Outside of the glove box, air from a balloon was bubbled into the DMF solution for 5-10 min. The balloon was removed, and the vial was placed in a 50 ºC heating bath. After 18 h, the reaction mixture was cooled to room temperature and diluted with 5 mL of Et_2O. The mixture was filtered over Celite, washed with an additional 20 mL of Et_2O, and transferred to a separatory funnel. The mixture was washed with 4 x 40 mL of H_2O and 1 x 25 mL brine, dried with $MgSO_4$, filtered, and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with pentane or pentane/Et_2O mixtures as the eluent.

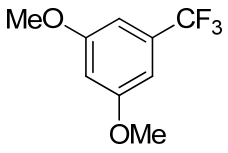
Characterization of Known Products.

3-(trifluoromethyl)benzonitrile, 1-nitro-4-(trifluoromethyl)benzene, 1,3-bis(trifluoromethyl)-5-bromobenzene, and 4-(trifluoromethyl)benzaldehyde are available from Aldrich. 1-methoxy-4-(trifluoromethyl)benzene and 1-methoxy-2-(trifluoromethyl)benzene are available from Ryan Scientific. 4-(trifluoromethyl)-1,1'-biphenyl is available from Matrix Scientific. 1,2-dibromo-4-(trifluoromethyl)benzene, 1-butyl-4-(trifluoromethyl)benzene, and ethyl 4-(trifluoromethyl)benzoate have been previously reported.[3,4]

Specific Procedures and Characterization of Perfluoroalkyl Arenes not Previously Reported

1,3-dimethoxy-5-(trifluoromethyl)benzene (5a)

The reaction was performed according to the general procedure for the trifluoromethylation of arenes on a 0.500 mmol scale (65.8 μL **4a**) with 1.0 mol % $[Ir(COD)OMe]_2$ and 2.0 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **5a** (56.4 mg, 55% yield) (Average isolated yield: 55%).



R_f = 0.47 (8:1 hexanes:EtOAc)

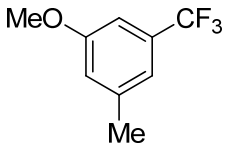
[3] Menzel,K., Fisher, E.L., DiMechele, L., Frantz,D.E., Nelson, T.D. and Kress, M.H. **"**An Improved Method for the Bromination of Metalated Haloarenes via Lithium, Zinc Transmetalation: A Convenient Synthesis of 1,2-Dibromoarenes." *J. Org. Chem.* **2006** *71*, 2188-2191.

[4] Morimoto, H., Tsubogo, T., Litvinas, N.D., Hartwig, J.F. "A Broadly Applicable Copper Reagent for Trifluoromethylations and Perfluoroalkylations of Aryl Iodides and Bromides." *Angew. Chem. Int. Ed.* **2011** 50, 3793-3798.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.74 (d, *J* = 2.3 Hz, 2H), 6.60 (t, *J* = 2.2 Hz, 1H), 3.83 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 161.20 (s), 132.58 (q, *J* = 32.3 Hz), 124.10 (q, *J* = 272.5 Hz), 103.83 (s), 103.47 (dd, *J* = 7.5, 3.7 Hz), 55.77 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.35 (s).

1-methoxy-3-methyl-5-(trifluoromethyl)benzene (5b)



The reaction was performed according to the general procedure for the trifluoromethylation of arenes on a 0.500 mmol scale (63.1 μL **4b**) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **5b** (60.0 mg, 63% yield) (Average isolated yield: 52%).

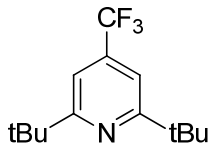
R_f = 0.63 (8:1 hexanes:EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H), 6.94 (s, 1H), 6.88 (s, 1H), 3.83 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.67 (s), 140.33 (s), 131.54 (q, *J* = 32.0 Hz), 124.07 (q, *J* = 272.4 Hz), 120.57 (s), 118.11 (q, *J* = 3.9 Hz), 107.63 (q, *J* = 3.8 Hz), 55.34 (s), 21.41 (s).

^{19}F NMR (470 MHz, $CDCl_3$) δ -63.09 (s).

2,6-di-tert-butyl-4-(trifluoromethyl)pyridine (5c)



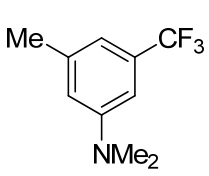
The reaction was performed according to the general procedure for the trifluoromethylation of arenes on a 0.500 mmol scale (108.1 μL **4c**) with 3.0 mol % $[Ir(COD)OMe]_2$ and 6.0 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **5c** (88.5 mg, 68% yield) (Average isolated yield: 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 2H), 1.37 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.29 (s), 138.48 (q, *J* = 32.6 Hz), 123.63 (q, *J* = 273.4 Hz), 111.22 (q, *J* = 2.8 Hz), 38.01 (s), 29.98 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.68 (s).

***N*,*N*,3-trimethyl-5-(trifluoromethyl)aniline (5d)**



The reaction was performed according to the general procedure for the trifluoromethylation of arenes on a 0.500 mmol scale (72.7 μL **4d**) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **5d** (36.3 mg, 35% yield) (Average isolated yield: 35%).

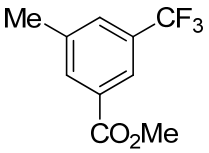
R_f = 0.60 (8:1 hexanes:EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.79 (s, 1H), 6.74 (s, 1H), 6.68 (s, 1H), 2.99 (s, 6H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.76 (s), 139.64 (s), 131.43 (q, *J* = 31.0 Hz), 124.85 (q, *J* = 272.6 Hz), 116.06 (s), 113.83 (q, *J* = 3.8 Hz), 106.17 (q, *J* = 4.0 Hz), 40.65 (s), 22.04 (s).

^{19}F NMR (470 MHz, $CDCl_3$) δ -63.08 (s).

methyl 3-methyl-5-(trifluoromethyl)benzoate (5e)



The reaction was performed according to the general procedure for the trifluoromethylation of arenes on a 0.500 mmol scale (70.8 μL **4e**) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **5e** (58.8 mg, 54% yield) (Average isolated yield: 52%).

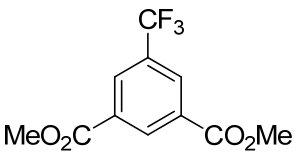
R_f = 0.52 (8:1 hexanes:EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.03 (s, 1H), 7.61 (s, 1H), 3.94 (s, 3H), 2.47 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.95 (s), 139.32 (s), 133.36 (s), 130.92 (q, *J* = 32.6 Hz), 130.82 (s), 130.02 (s), 123.71 (q, *J* = 272.3 Hz), 123.66 (s), 52.41 (s), 21.18 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.22 (s).

dimethyl 5-(trifluoromethyl)isophthalate (5f)



The reaction was performed according to the general procedure for the trifluoromethylation of arenes on a 0.500 mmol scale (97.1 mg **4f**) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the

first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **5f** (85.0 mg, 65% yield) (Average isolated yield: 54%).

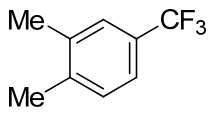
R_f = 0.39 (8:1 hexanes:EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.46 (s, 2H), 3.98 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.87 (s), 133.63 (s), 131.62 (s), 131.59 (q, *J* = 33.8 Hz), 130.40 (q, *J* = 3.6 Hz), 123.13 (q, *J* = 272.9 Hz), 52.75 (s).

^{19}F NMR (470 MHz, $CDCl_3$) δ -63.36 (s).

1,2-dimethyl-4-(trifluoromethyl)benzene (5i)



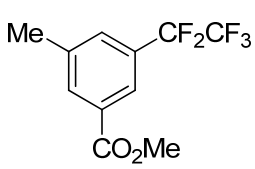
The reaction was performed according to the general procedure for the trifluoromethylation of arenes on a 0.500 mmol scale (60.3 μL **4i**) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **5i** (34.0 mg, 39% yield) (Average isolated yield: 36%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 2.33 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 140.87 (s), 137.43 (s), 130.02 (s), 128.34 (q, *J* = 32.1 Hz), 126.40 (q, *J* = 3.8 Hz), 124.66 (q, *J* = 271.8 Hz), 122.80 (q, *J* = 3.9 Hz), 19.99 (s), 19.97 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.68 (s).

methyl 3-methyl-5-(perfluoroethyl)benzoate (6a)

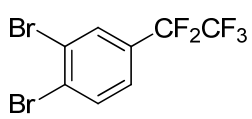


The reaction was performed according to the general procedure for the perfluoroalkylation of arenes on a 0.500 mmol scale (70.6 μL methyl 3-methylbenzoate) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **6a** (55.2 mg, 41% yield) (Average isolated yield: 39%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.06 (s, 1H), 7.58 (s, 1H), 3.95 (s, 3H), 2.48 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.14 (s), -115.31 (s).

1,2-dibromo-4-(perfluoroethyl)benzene (6b)

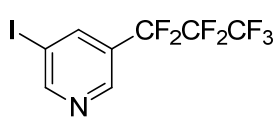


The reaction was performed according to the general procedure for the perfluoroalkylation of arenes on a 0.500 mmol scale (60.5 µL 1,2-dibromobenzene) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **6b** (90.3 mg, 51% yield) (Average isolated yield: 51%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.40 (dd, *J* = 8.4, 1.9 Hz, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.13 (s), -115.58 (s).

3-iodo-5-(perfluoropropyl)pyridine (7a)

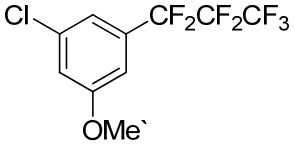


The reaction was performed according to the general procedure for the perfluoroalkylation of arenes on a 0.500 mmol scale (102.5 mg 3-iodopyridine) with 3.0 mol % $[Ir(COD)OMe]_2$ and 6.0 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **7a** (70.9 mg, 38% yield) (Average isolated yield: 39%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.77 (s, 1H), 8.21 (s, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -80.21 (t, *J* = 8.8 Hz), -112.89 (m), -126.52 (s).

1-chloro-3-methoxy-5-(perfluoropropyl)benzene (7b)



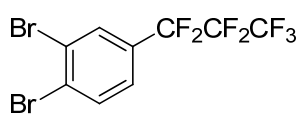
The reaction was performed according to the general procedure for the perfluoroalkylation of arenes on a 0.500 mmol scale (61.5 µL 3-chloroanisole) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **7b** (71.4 mg, 46% yield) (Average isolated yield: 42%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (s, 1H), 7.11 (t, *J* = 2.0 Hz, 1H), 7.01 (s, 1H), 3.87 (s, 3H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -80.52 (t, *J* = 9.8 Hz), -112.27 (q, *J* = 9.8 Hz), -126.82 (s).

1,2-dibromo-4-(perfluoropropyl)benzene (7c)

The reaction was performed according to the general procedure for the perfluoroalkylation of arenes on a 0.500 mmol scale (60.5 μL 1,2-dibromobenzene) with 0.1 mol % $[Ir(COD)OMe]_2$ and 0.2 mol % dtbpy in the first step. The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **7c** (115.1 mg, 57% yield) (Average isolated yield: 55%).

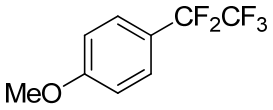


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.0 Hz, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -80.41 (t, *J* = 9.6 Hz), -112.43 (q, *J* = 9.5 Hz), -126.71 (s).

1-methoxy-4-(perfluoroethyl)benzene (6c)

The reaction was performed according to the general procedure for the perfluoroalkylation of aryl bromides on a 0.500 mmol scale (62.8 μL 4-bromoanisole). The crude mixture was purified by silica gel chromatography (4g silica, 100% pentane) to give **6c** (34.5 mg, 31% yield) (Average isolated yield: 30%).



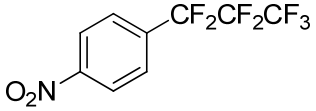
R_f = 0.58 (8:1 hexanes:EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.8 Hz, 2 H), 7.03 (d, *J* = 8.9 Hz, 2 H), 3.90 (s, 3 H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -85.41 (s), -114.29 (s).

1-nitro-4-(perfluoropropyl)benzene (7d)

The reaction was performed according to the general procedure for the perfluoroalkylation of aryl bromides on a 0.500 mmol scale (101.0 mg 1-bromo-4-nitrobenzene). The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **7d** (83.1 mg, 57% yield) (Average isolated yield: 56%).

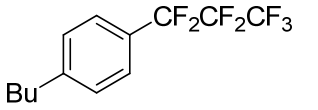


^{1}H NMR (376 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 8.7 Hz, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.26 (t, *J* = 9.8 Hz), -112.63 (q, *J* = 9.7 Hz), -126.51 (s).

1-butyl-4-(perfluoropropyl)benzene (7e)

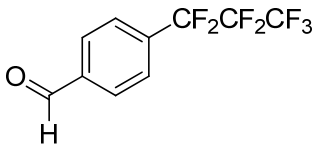
The reaction was performed according to the general procedure for the perfluoroalkylation of aryl bromides on a 0.500 mmol scale (88.2 µL 1-bromo-4-butylbenzene). The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **7f** (86.3 mg, 57% yield) (Average isolated yield: 54%).



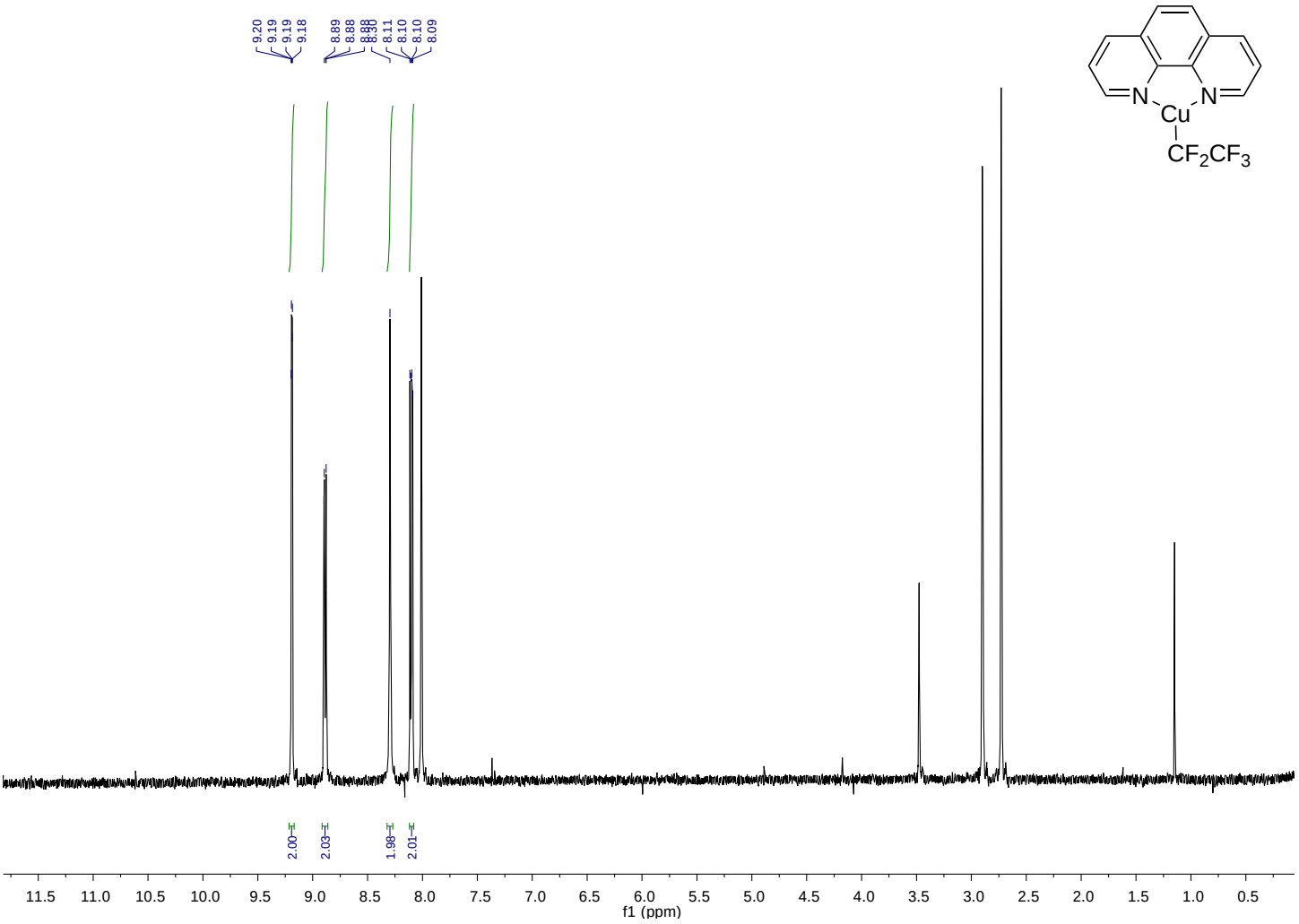
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H), 1.62 (m, 2H), 1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -80.43 (t, *J* = 9.9 Hz), -111.79 (q, *J* = 9.8 Hz), -126.93 (s).

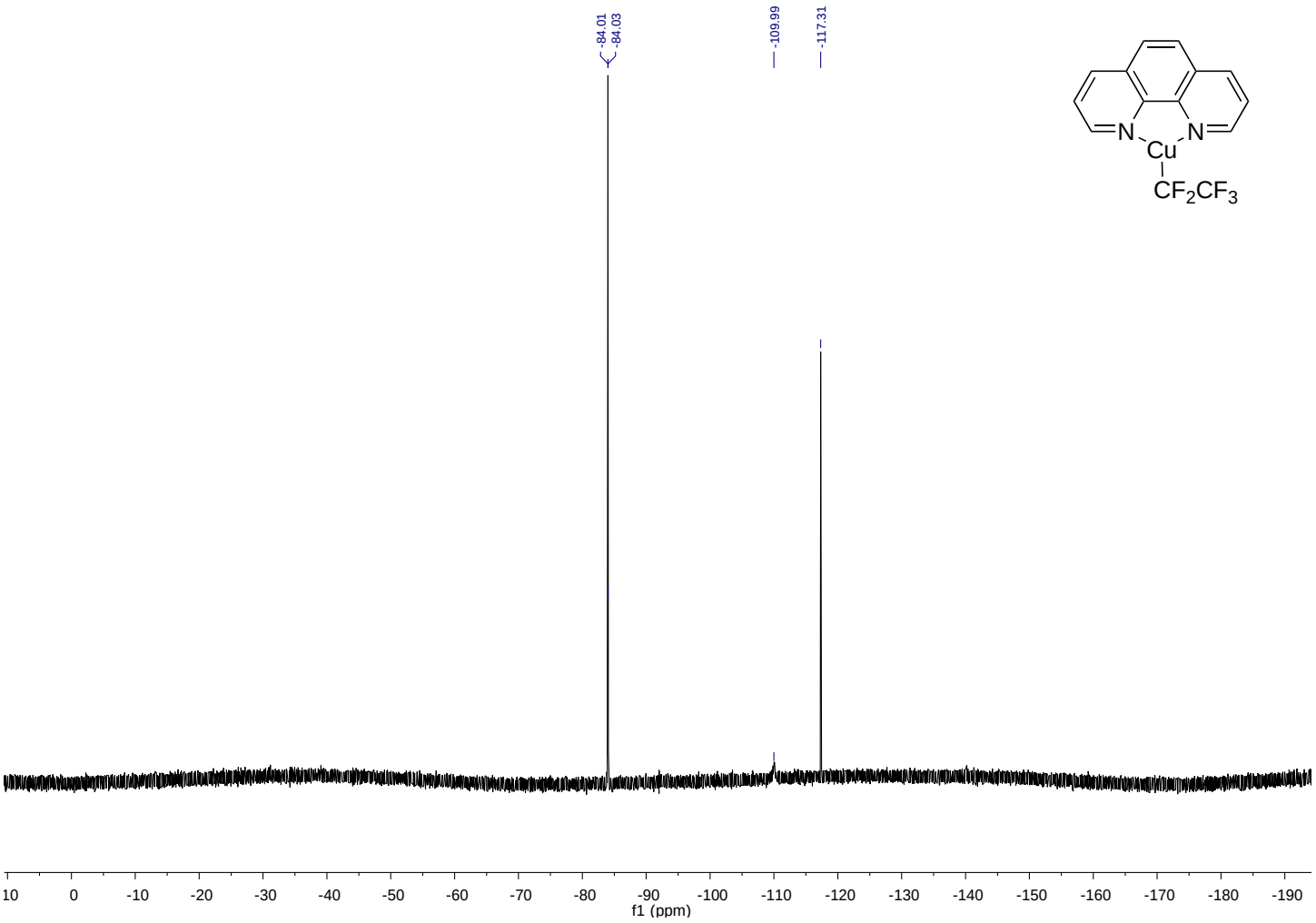
4-(perfluoropropyl)benzaldehyde (7f)

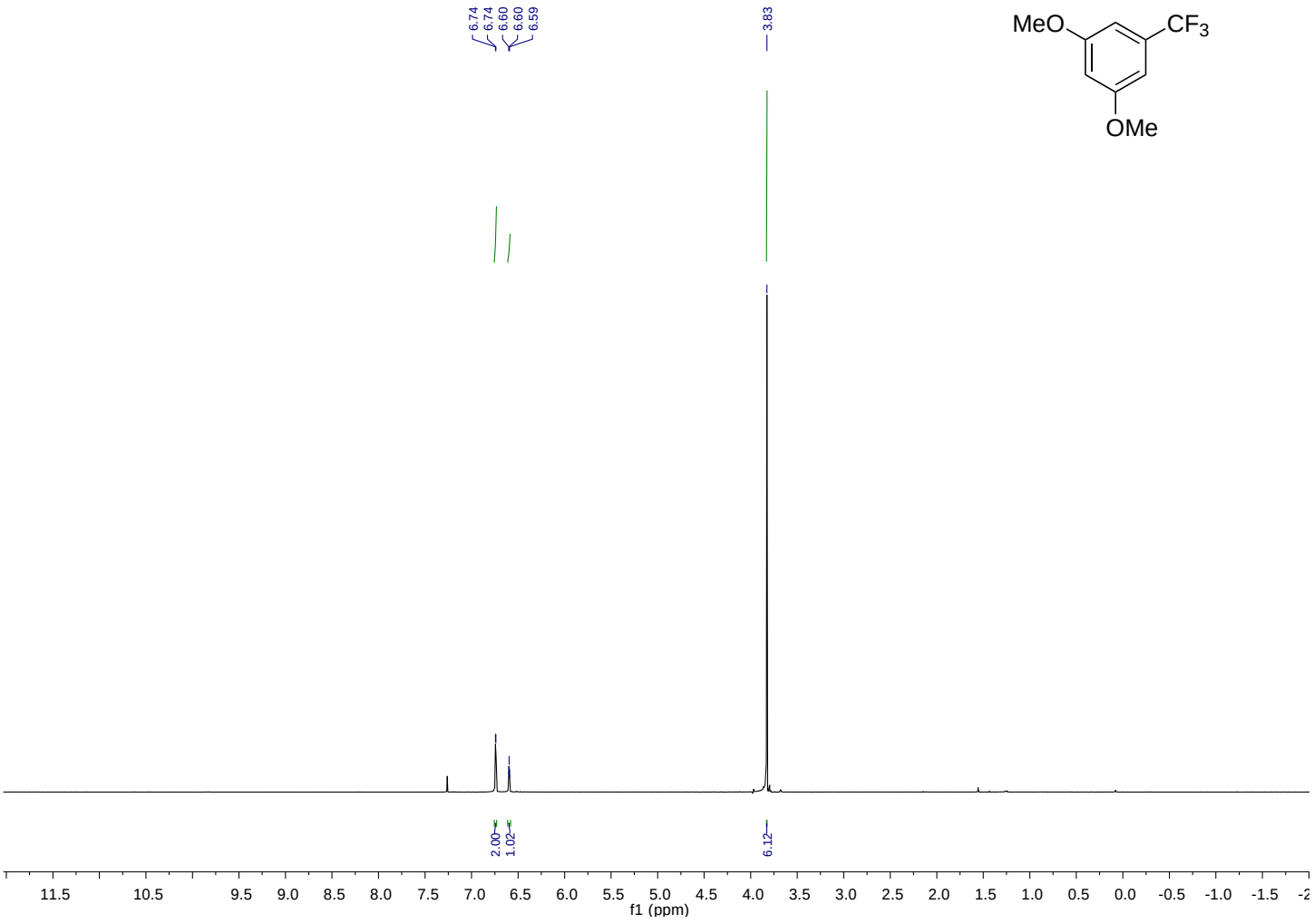
The reaction was performed according to the general procedure for the perfluoroalkylation of aryl bromides on a 0.500 mmol scale (92.5 mg 4-bromobenzaldehyde). The crude mixture was purified by silica gel chromatography (4 g of silica, 100:0 → 90:10 pentane:Et_2O) to give **7g** (93.4 mg, 68% yield) (Average isolated yield: 64%).

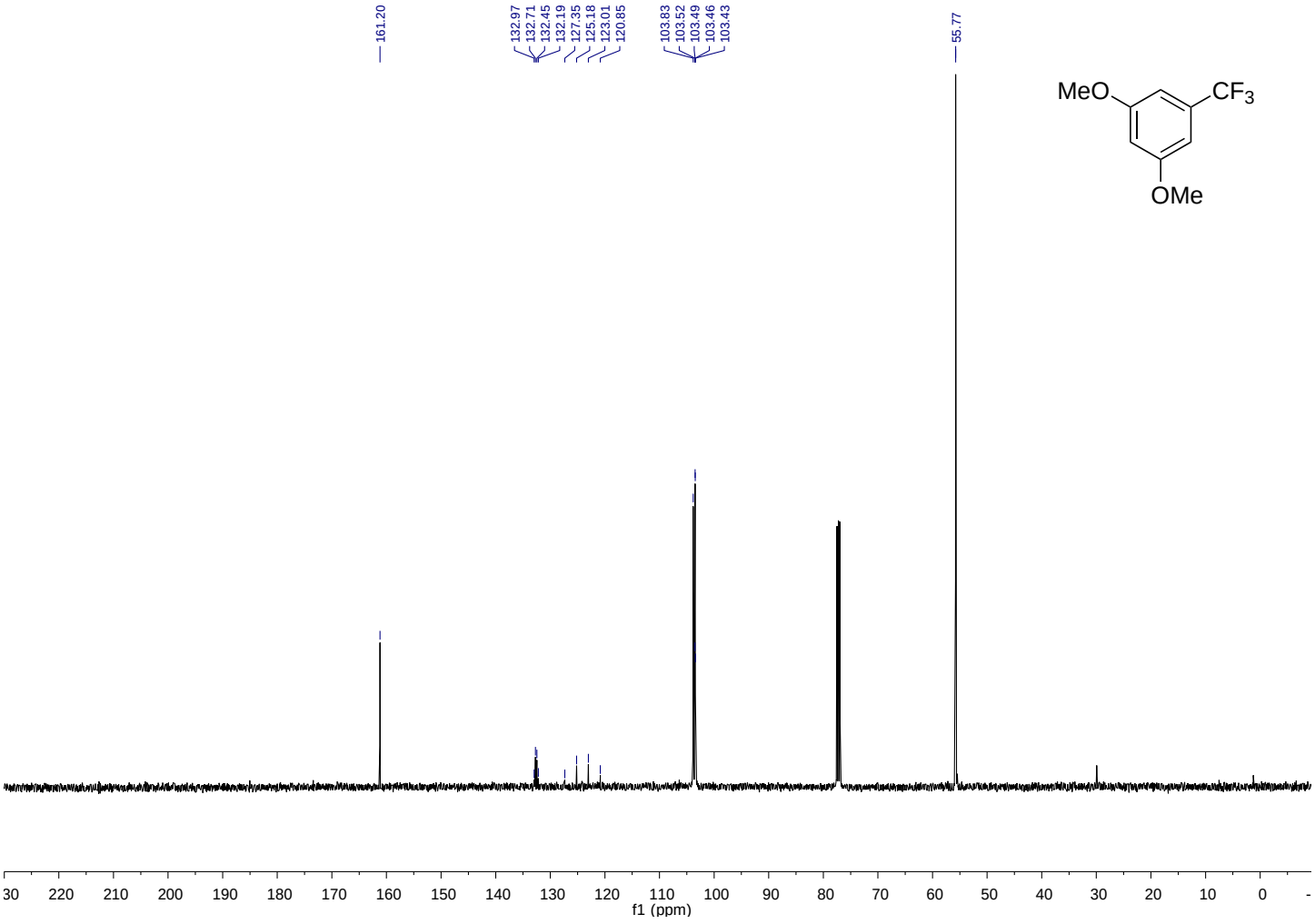


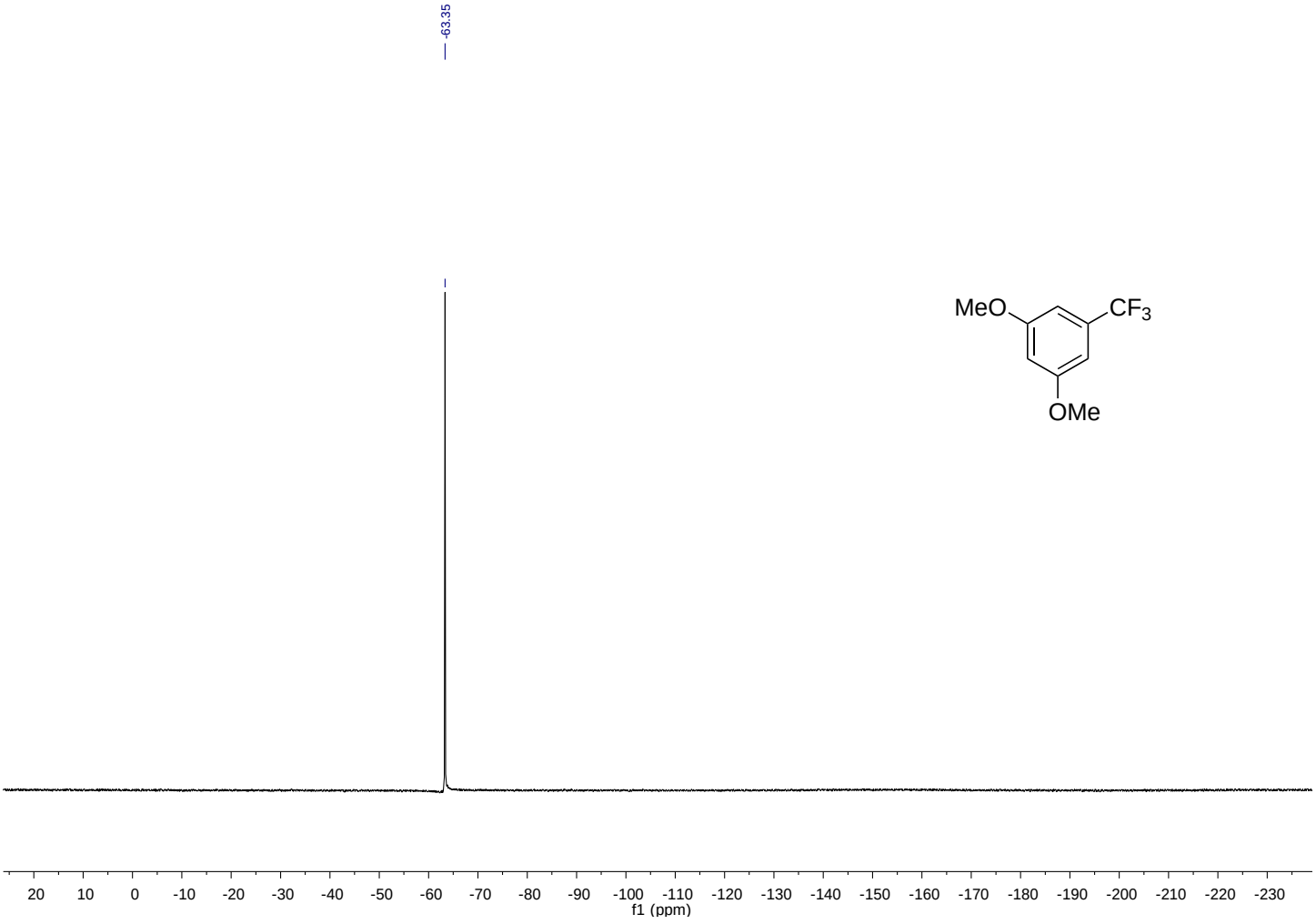
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -80.34 (t, *J* = 9.7 Hz), -112.71 (q, *J* = 9.7 Hz), -126.68 (s).

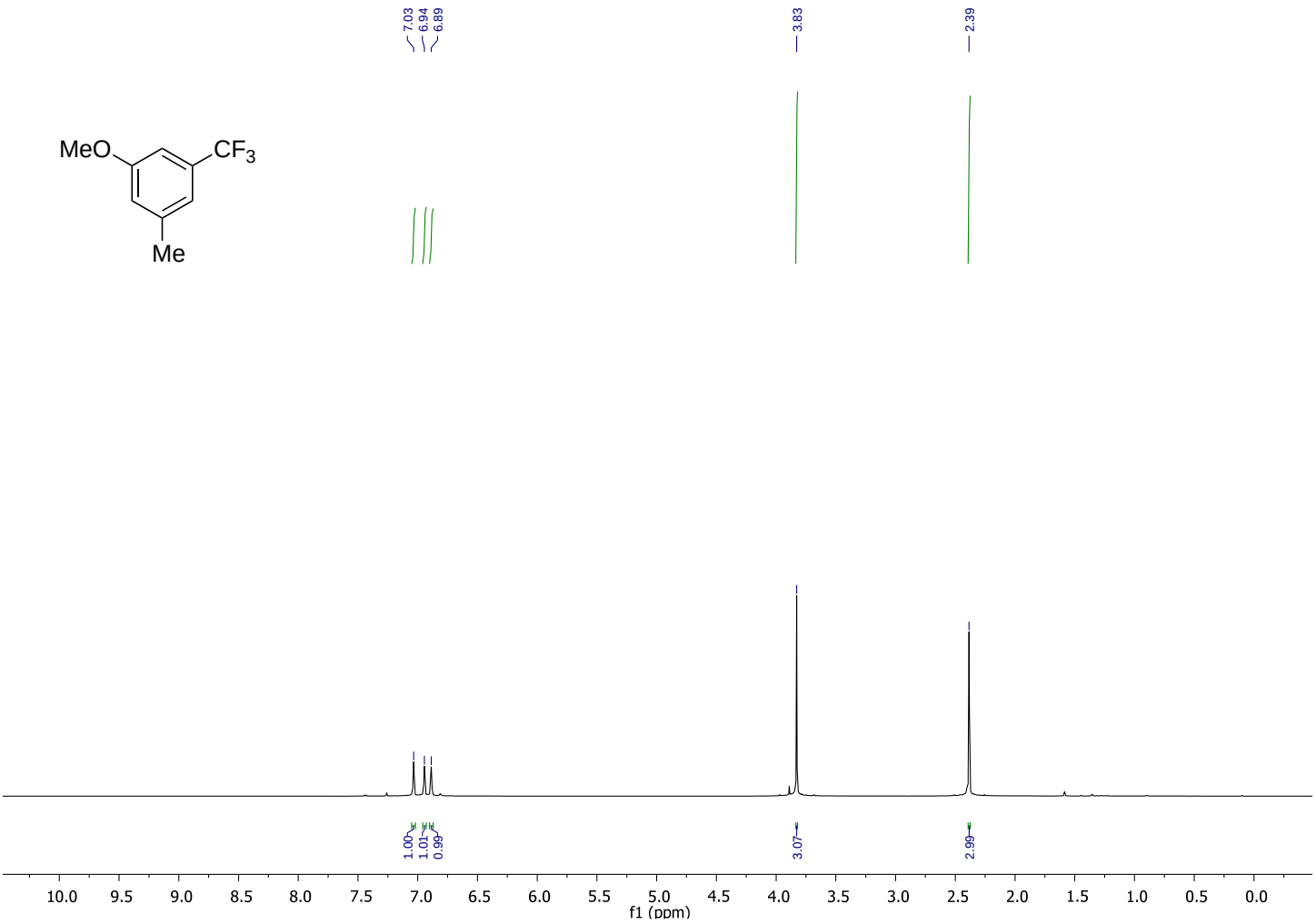

9.20
9.19
9.19
9.18
8.89
8.88
8.88
8.88
8.11
8.10
8.10
8.09
N
Cu
N
CF2CF3
2.00
2.03
1.98
2.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


-84.01
-84.03
-109.99
-117.31
N
Cu
N
CF2CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)


6.74
6.74
6.60
6.60
6.59
3.83
MeO
CF3
OMe
2.00
1.02
6.12
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


161.20
132.97
132.71
132.45
132.19
127.35
125.18
123.01
120.85
103.83
103.52
103.49
103.46
103.43
55.77
MeO
CF3
OMe
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -
f1 (ppm)


-63.35
MeO
CF3
OMe
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)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CF3
Me
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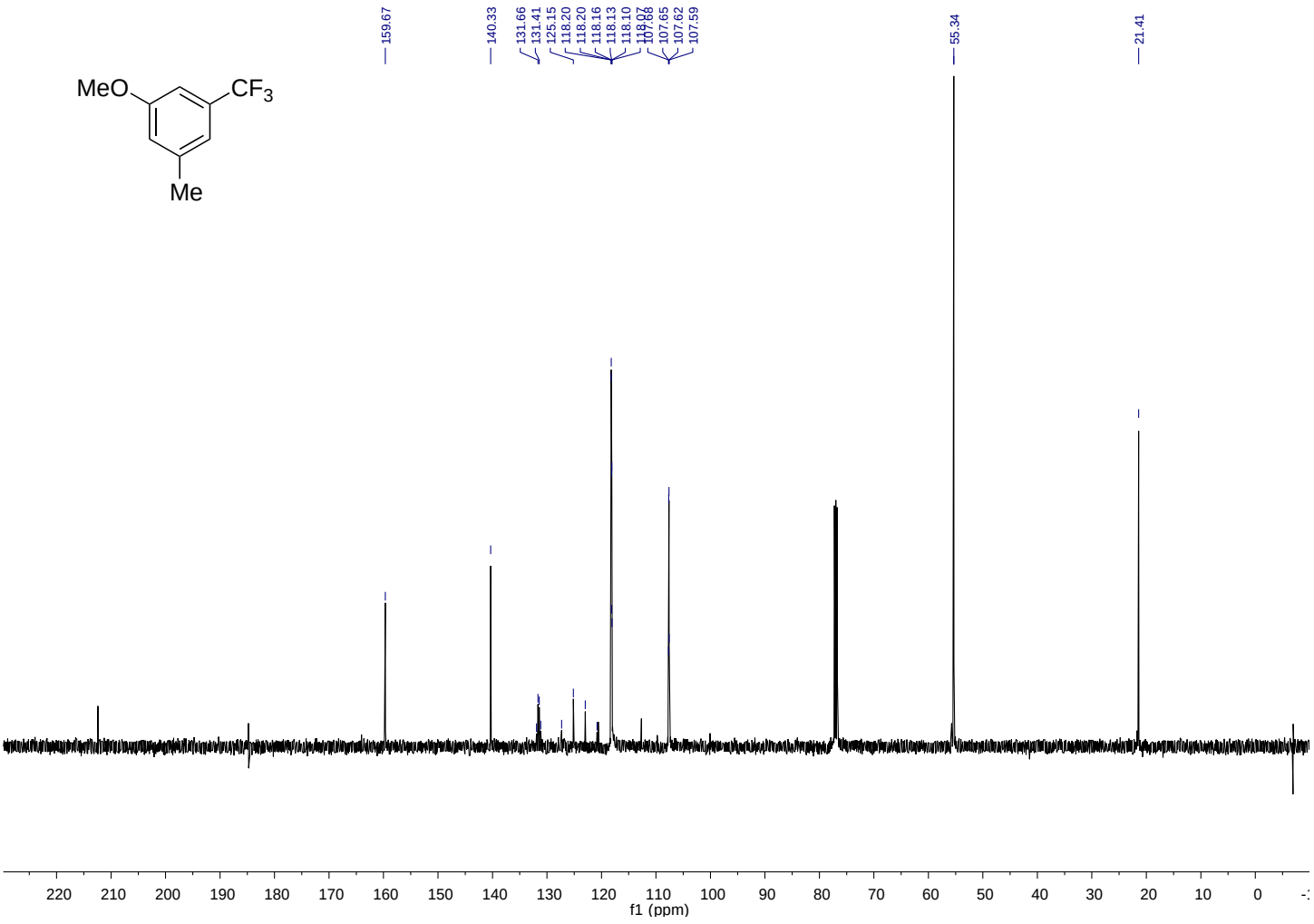
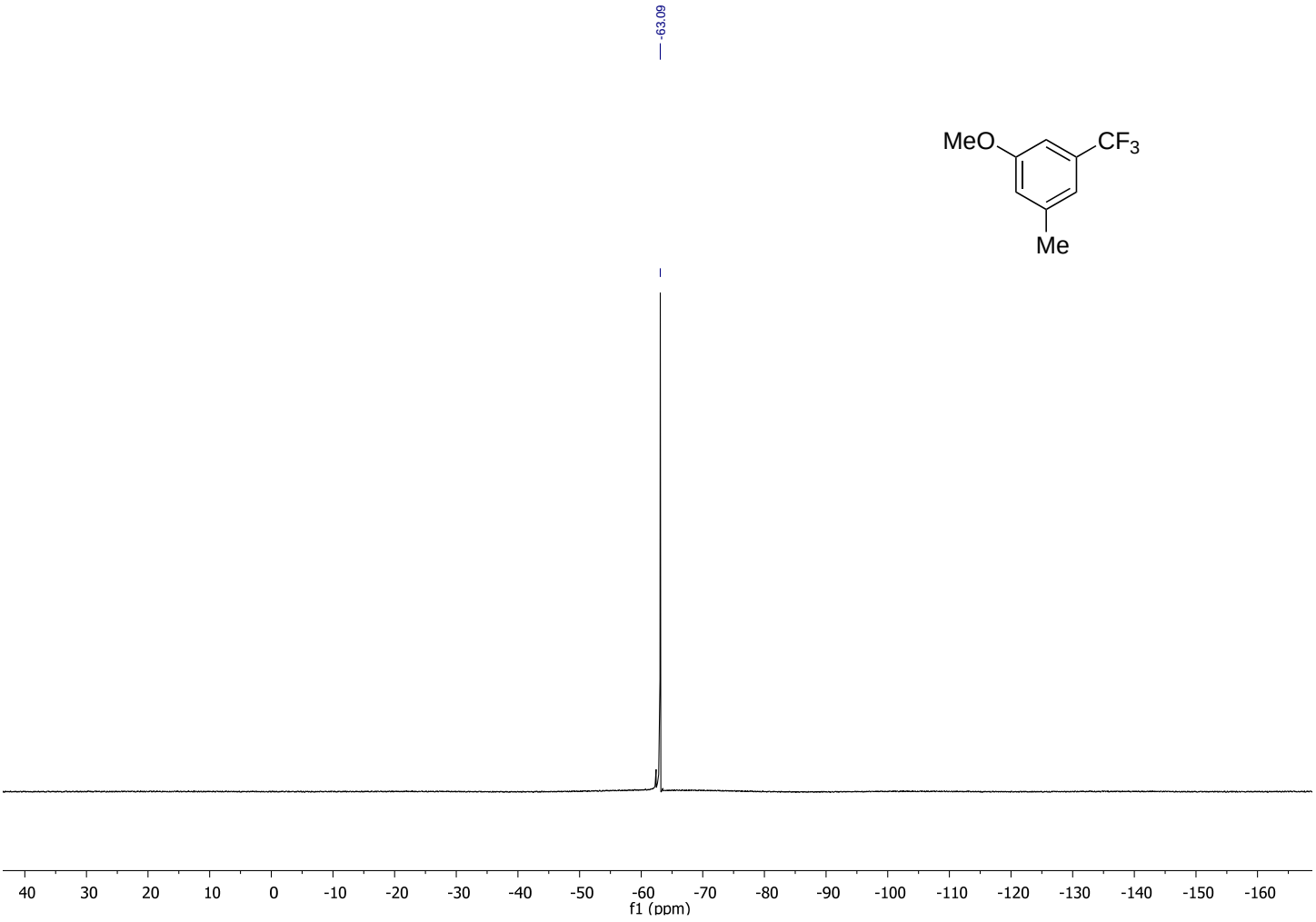
6.94
6.89
3.83
2.39
1.00
1.01
0.99
3.07
2.99
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


MeO
CF3
Me
159.67
140.33
131.66
131.41
125.15
118.20
118.16
118.13
118.10
107.65
107.62
107.59
55.34
21.41
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.09
MeO
CF3
Me
40
30
20
10
0
-10
-20
-30
-40
-50
-60
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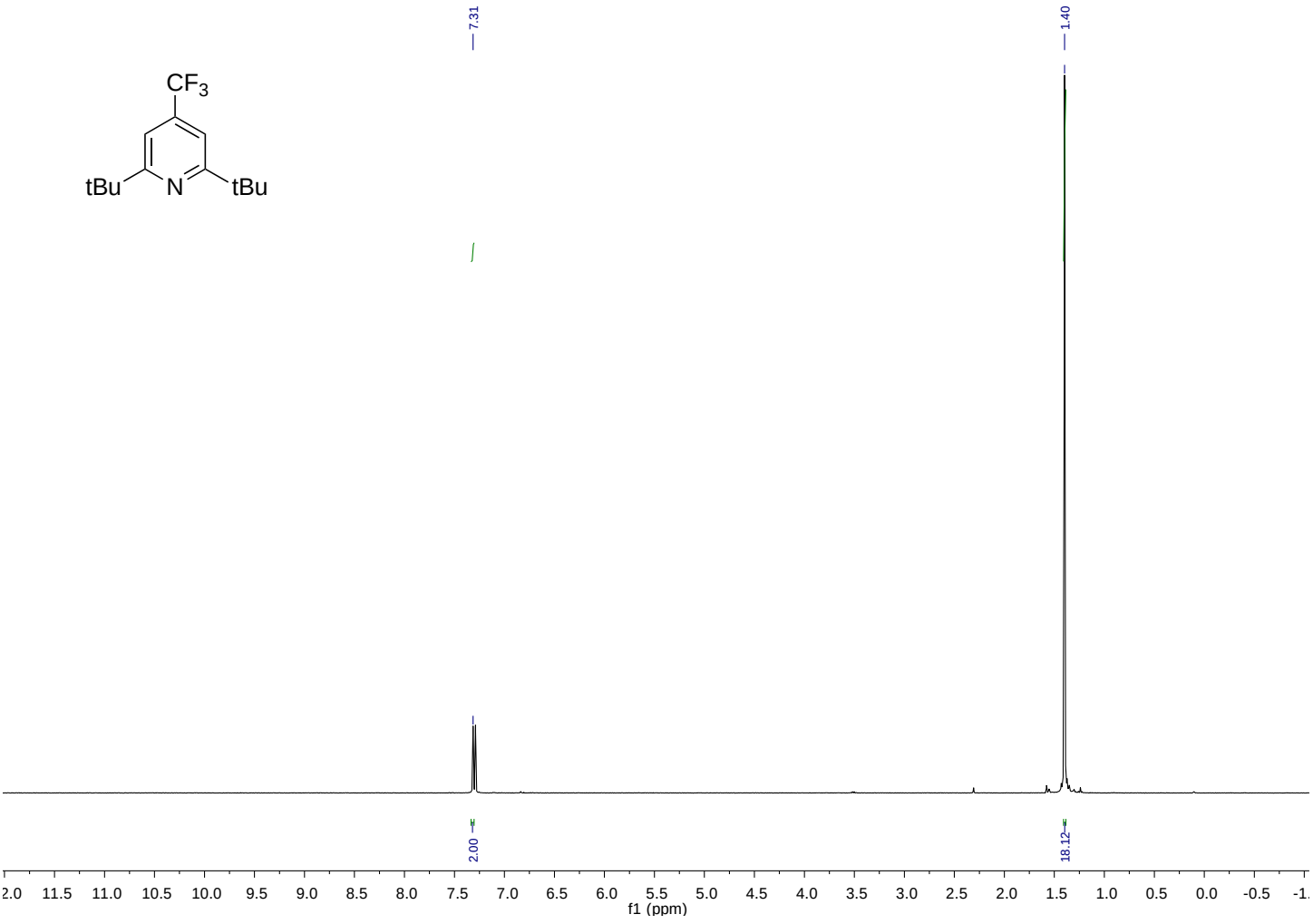
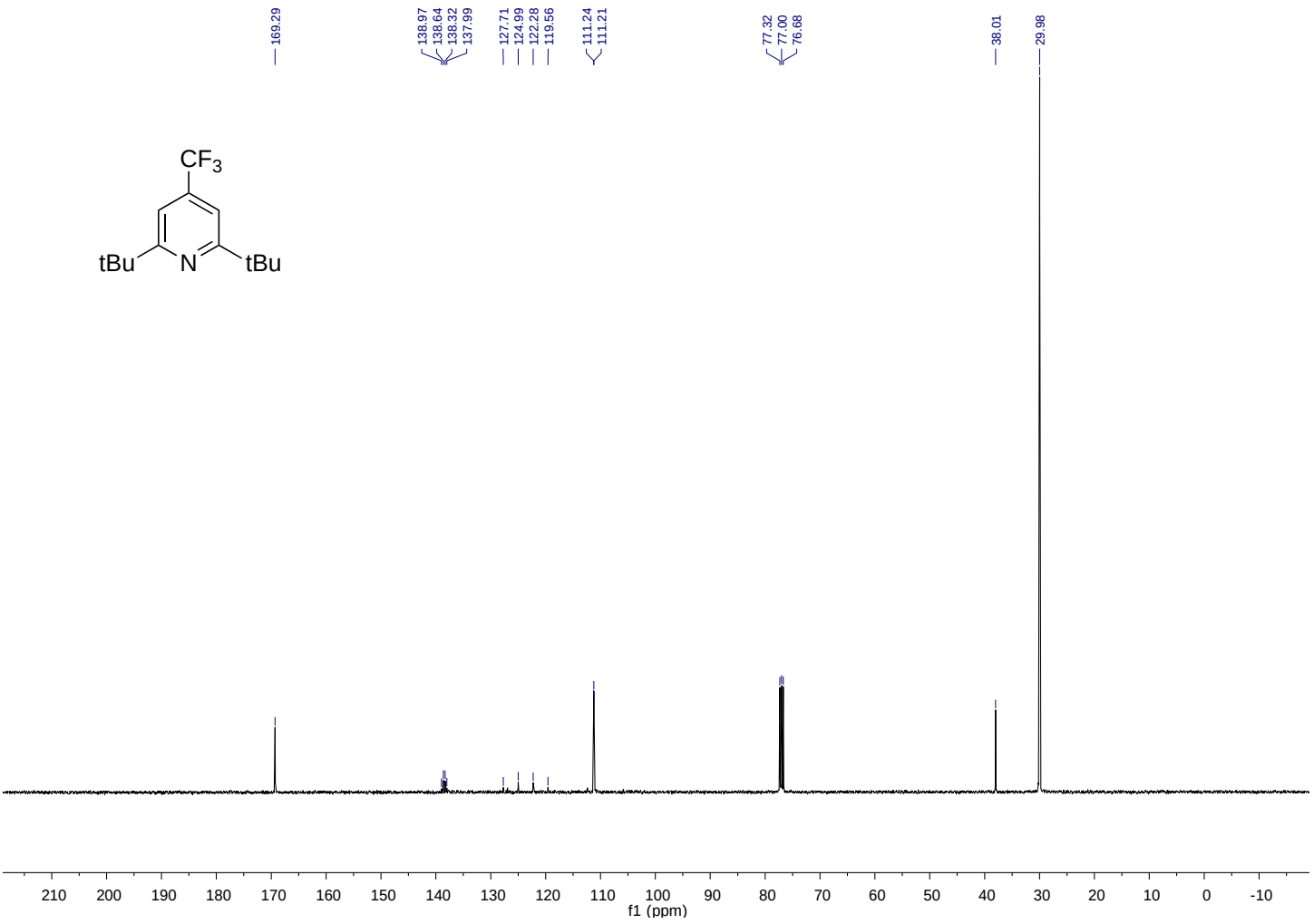
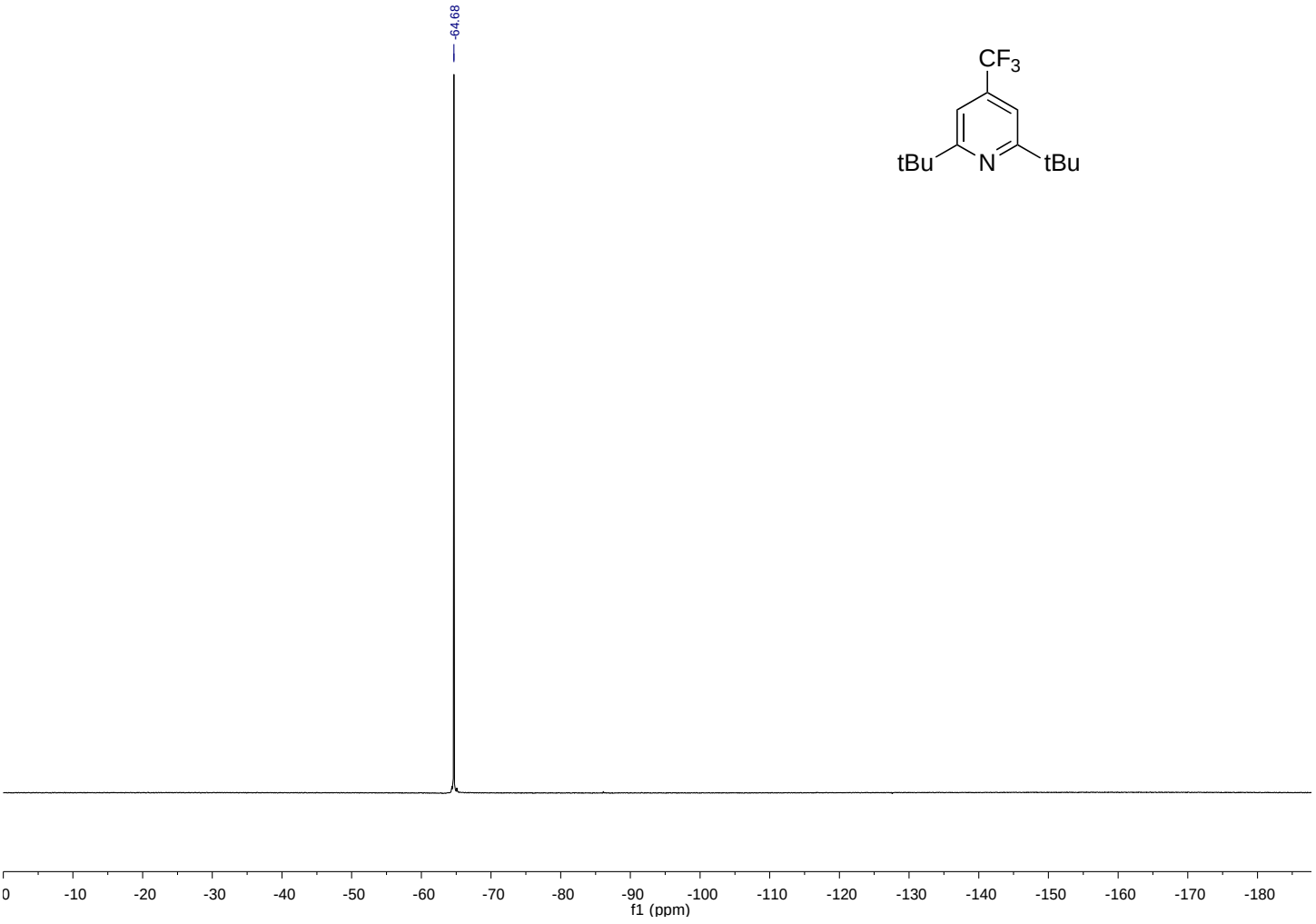
-110
-120
-130
-140
-150
-160
f1 (ppm)


7.31
1.40
CF3
tBu
N
tBu
2.00
18.12
f1 (ppm)


169.29
138.97
138.64
138.32
137.99
127.71
124.99
122.28
119.56
111.24
111.21
77.32
77.00
76.68
38.01
29.98
CF3
tBu
N
tBu
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)


-64.68
CF3
tBu
N
tBu
0
-10
-20
-30
-40
-50
-60
-70
-80
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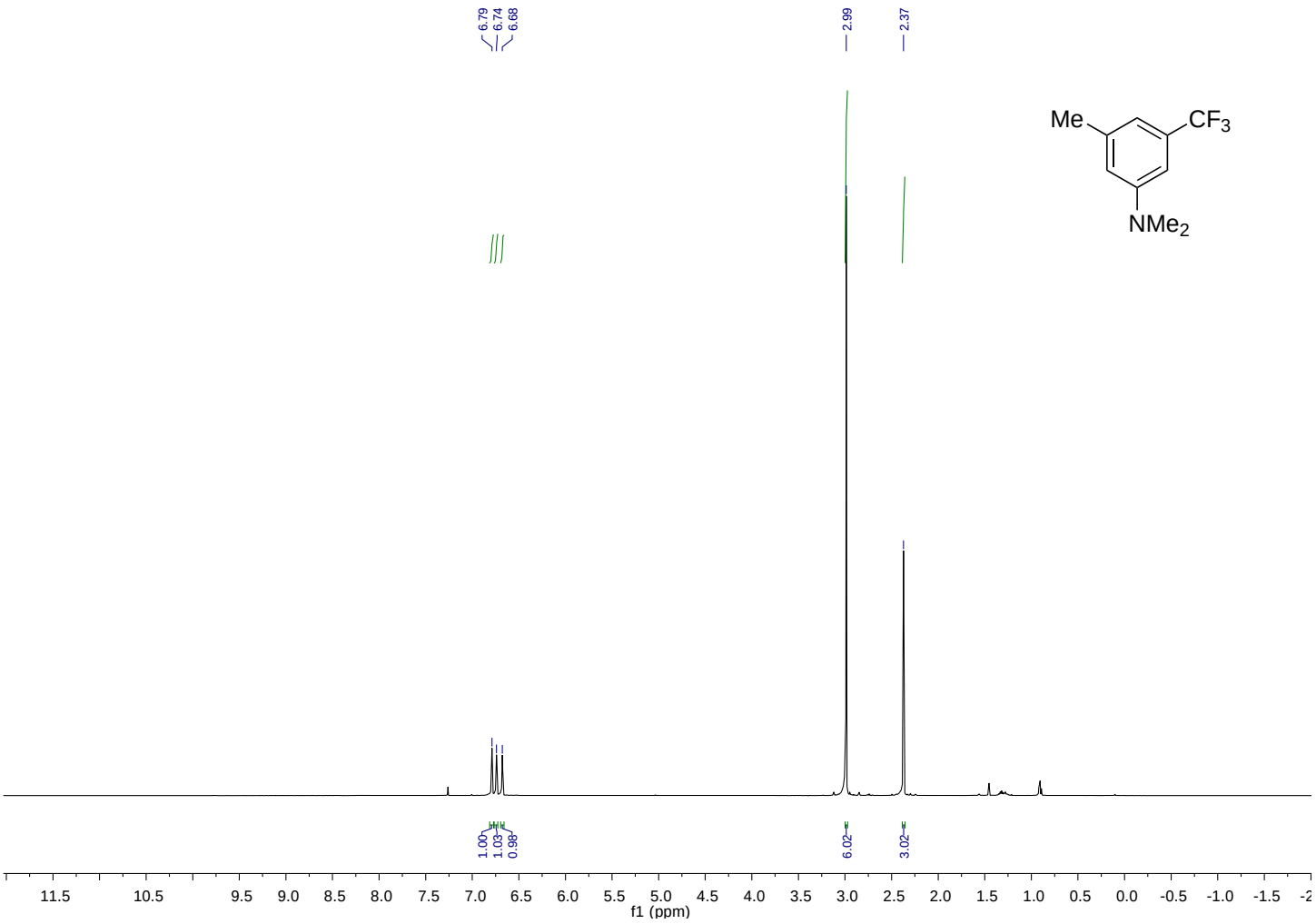
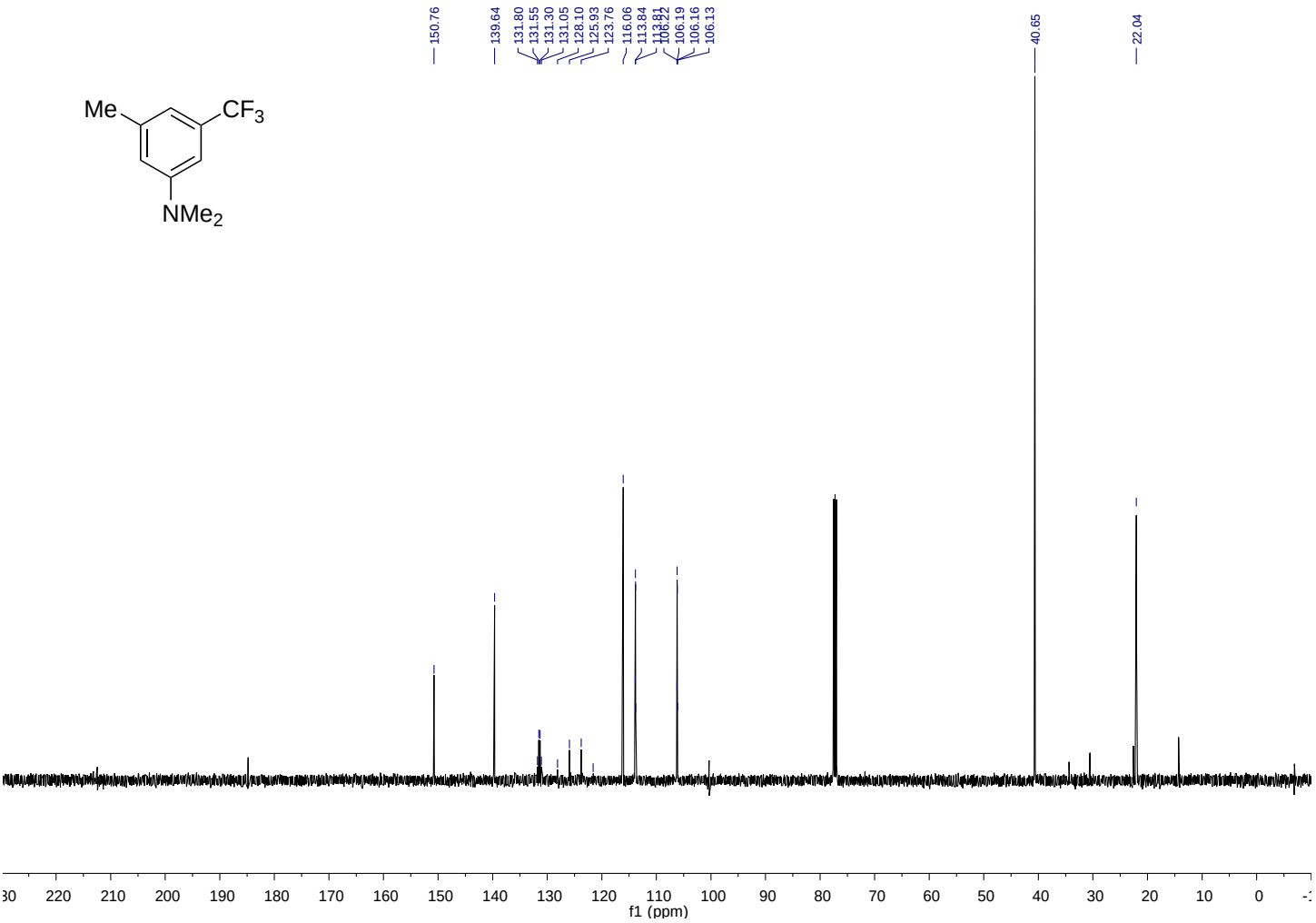
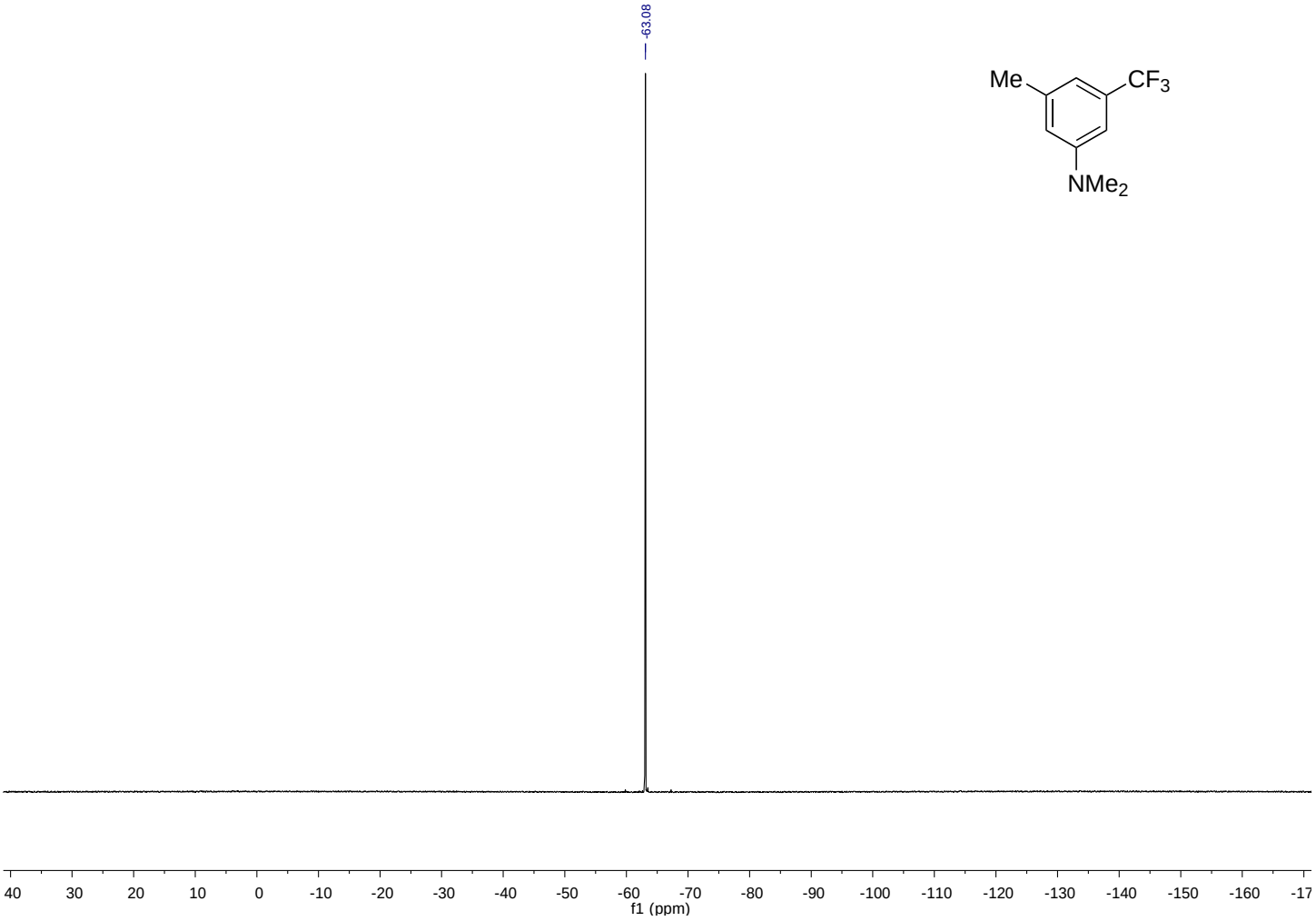
-140
-150
-160
-170
-180
f1 (ppm)


6.79
6.74
6.68
2.99
2.37
Me
CF3
NMe2
1.00
1.03
0.98
6.02
3.02
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


150.76
139.64
131.80
131.55
131.30
131.05
128.10
125.93
123.76
116.06
113.84
106.19
106.16
106.13
40.65
22.04
Me
CF3
NMe2
f1 (ppm)


-63.08
Me
CF3
NMe2
40
30
20
10
0
-10
-20
-30
-40
-50
-60
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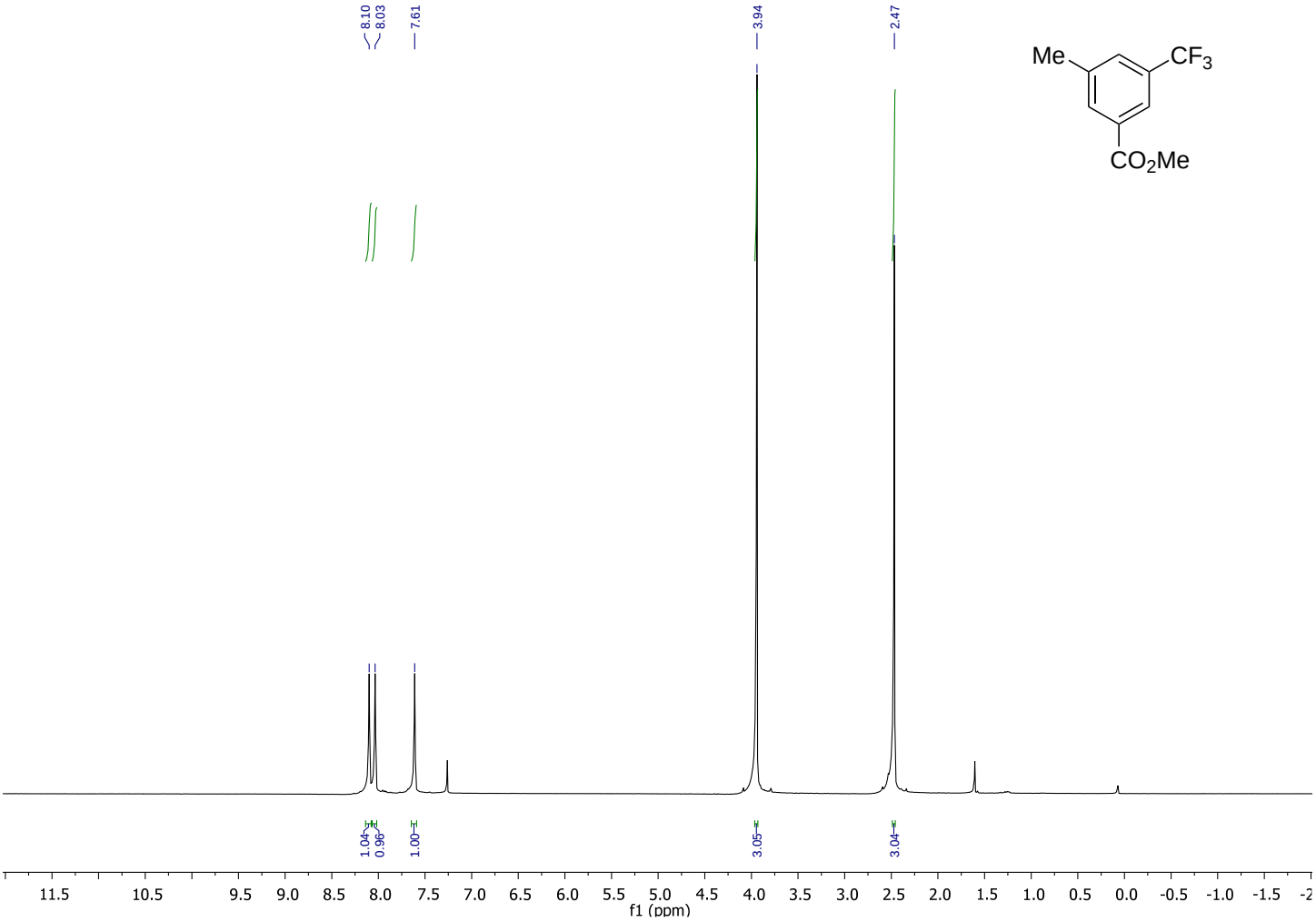
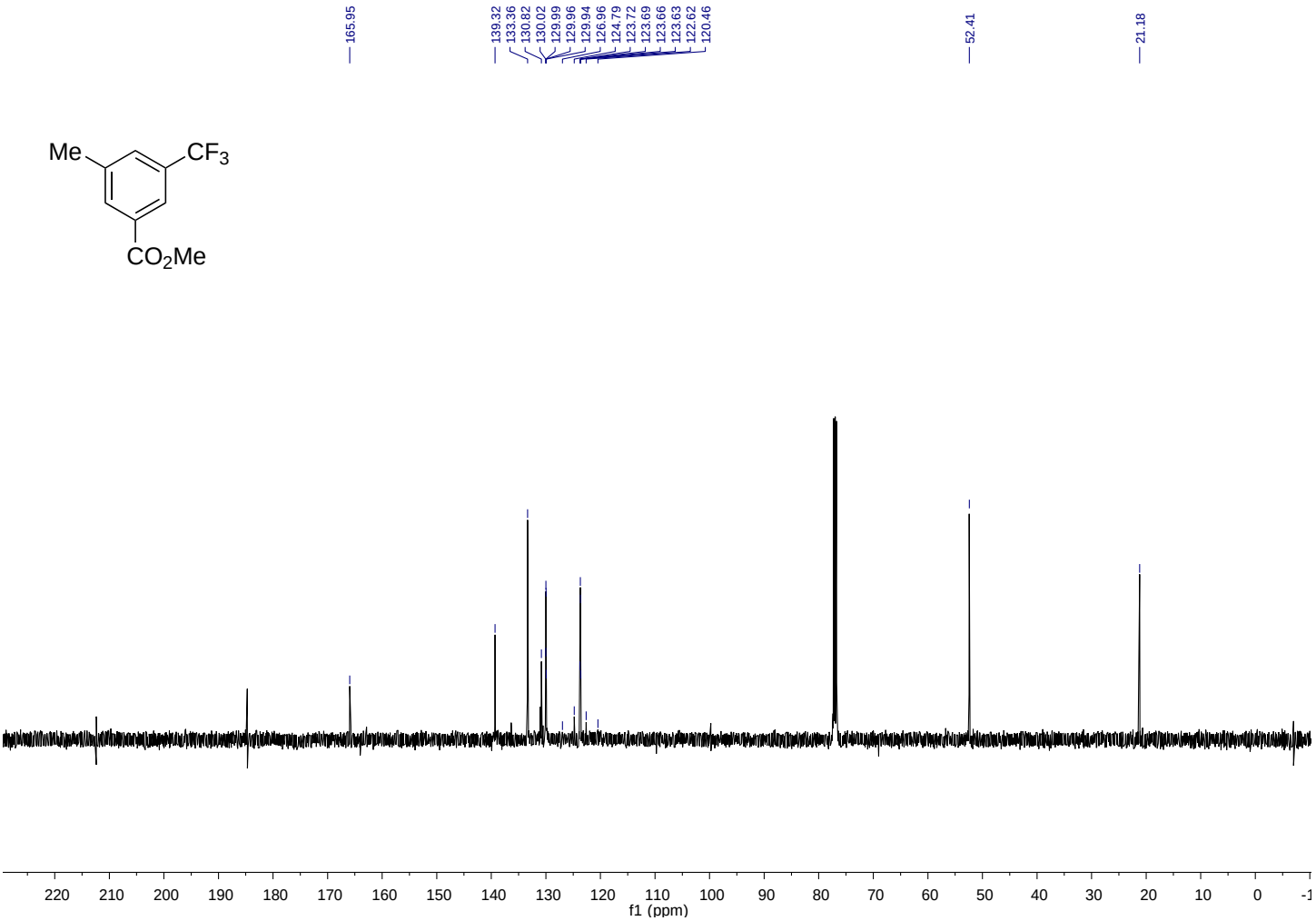
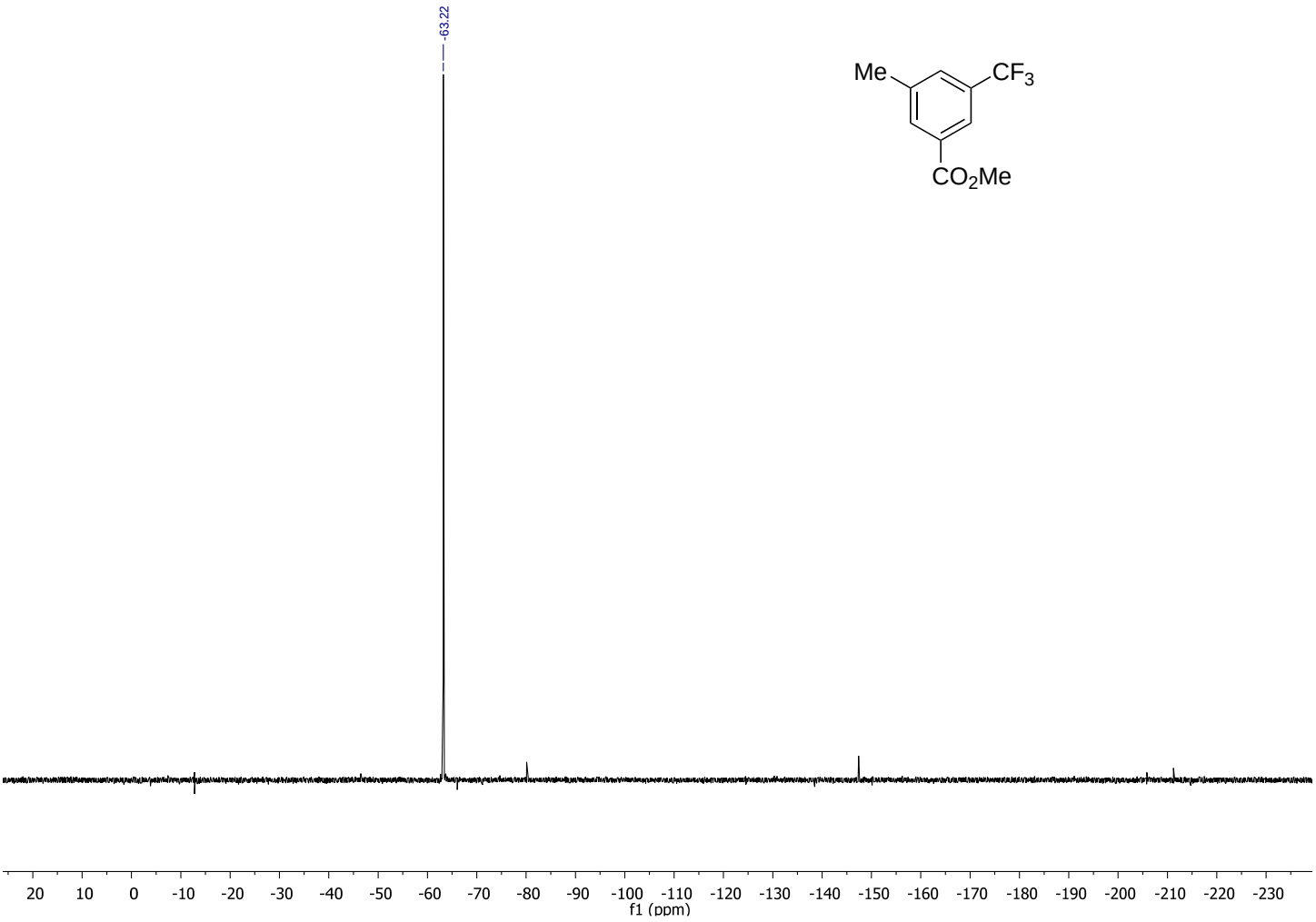
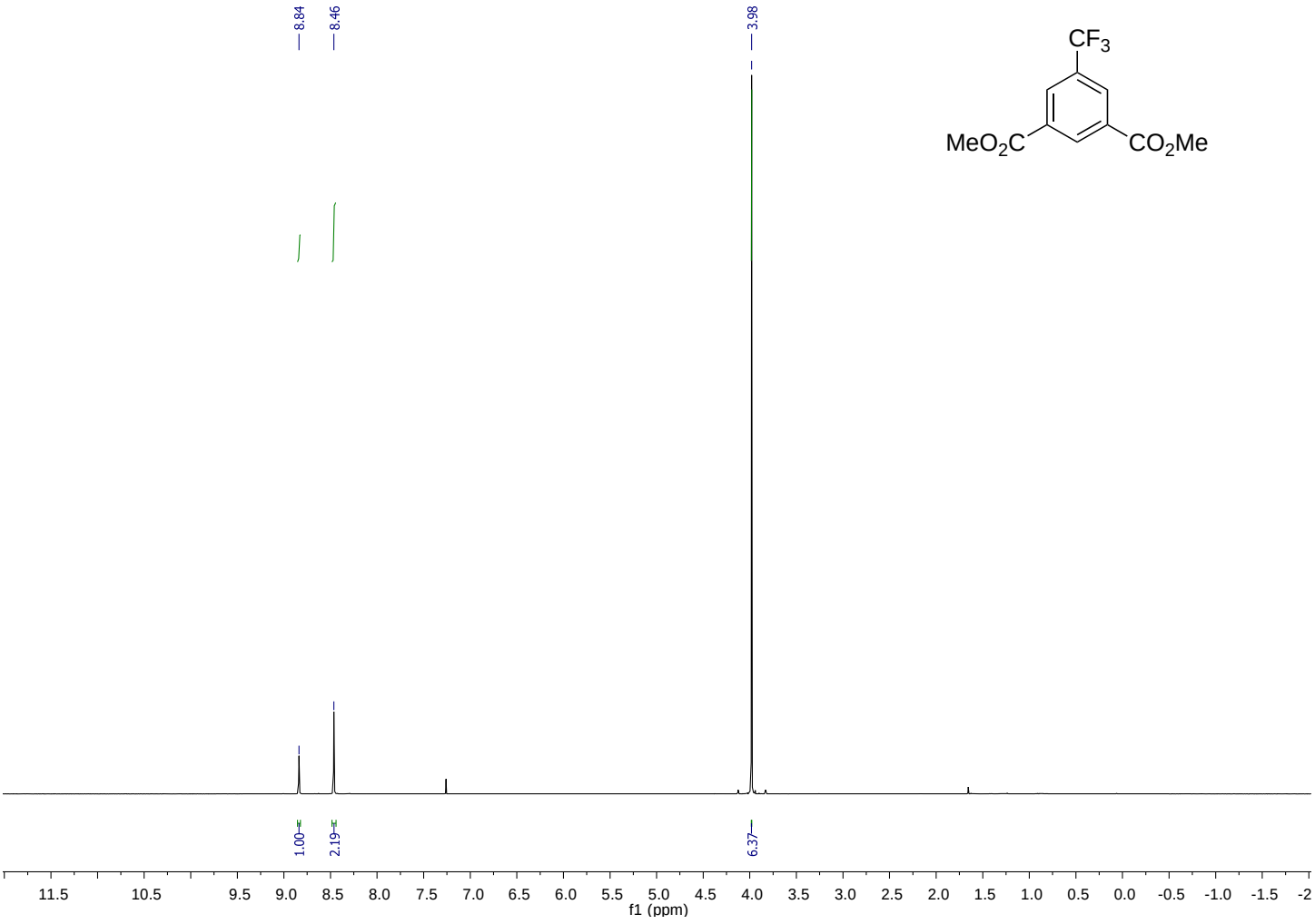
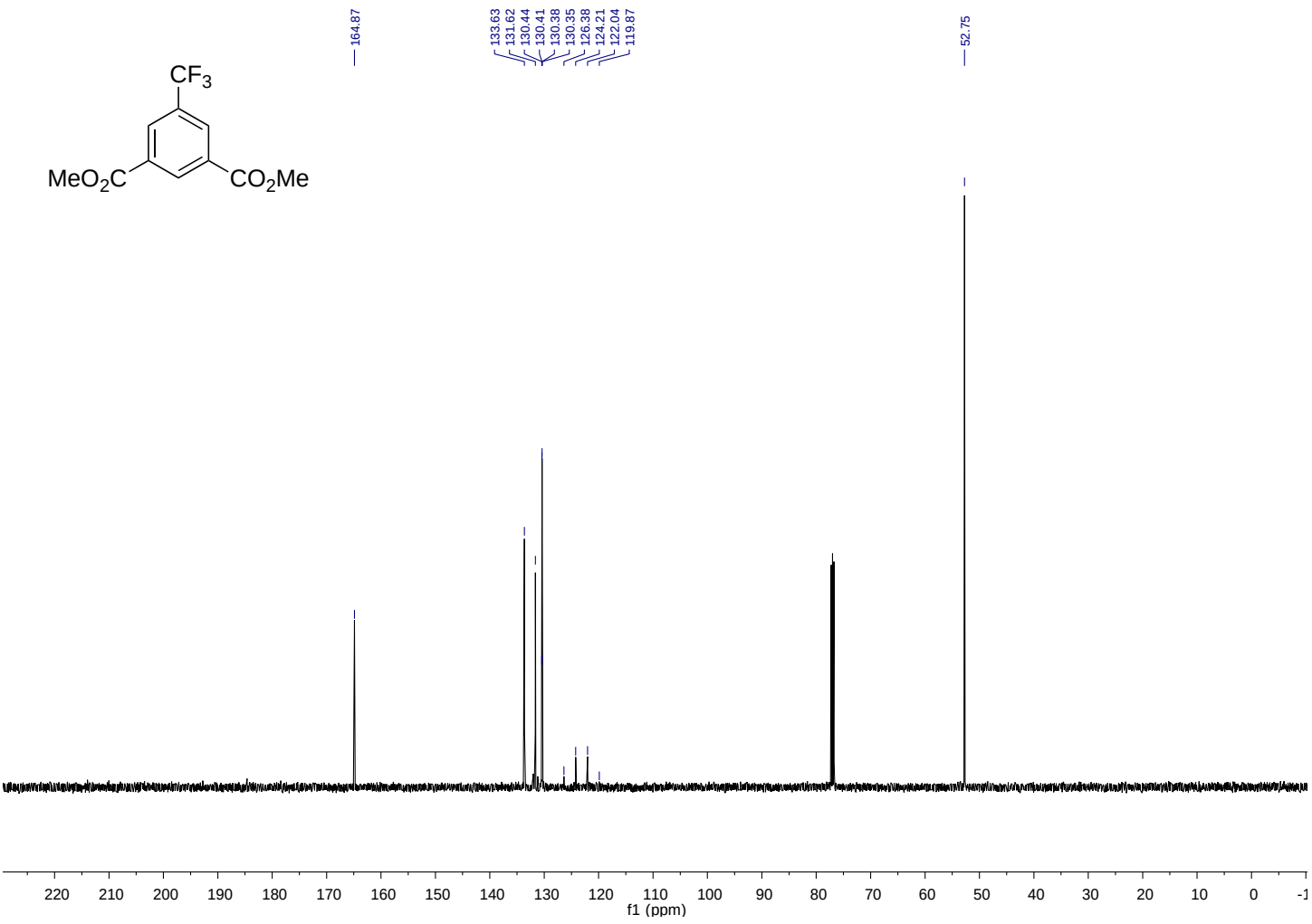
-130
-140
-150
-160
-17
f1 (ppm)

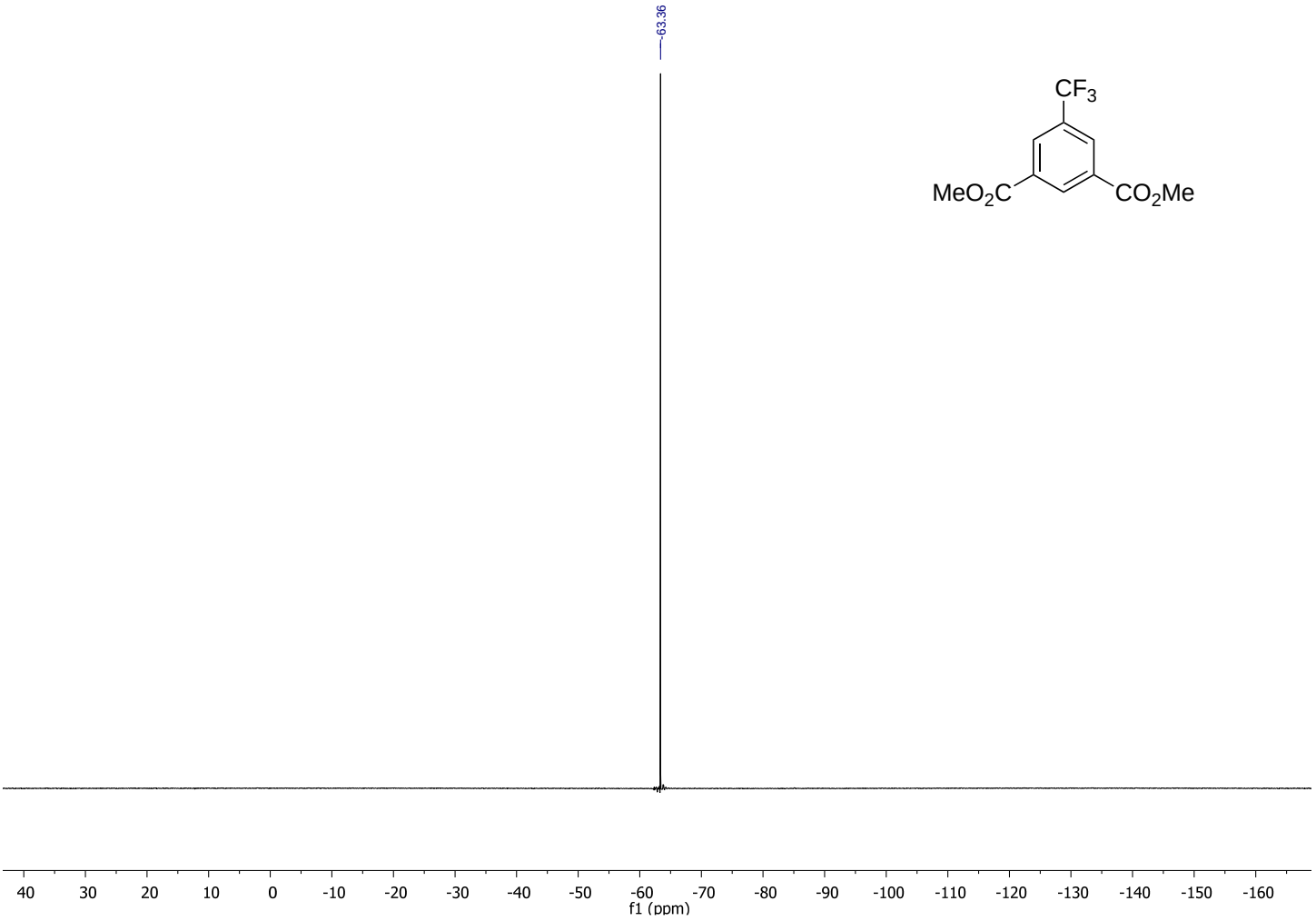

8.10
8.03
7.61
3.94
2.47
Me
CF3
CO2Me
1.04
0.96
1.00
3.05
3.04
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

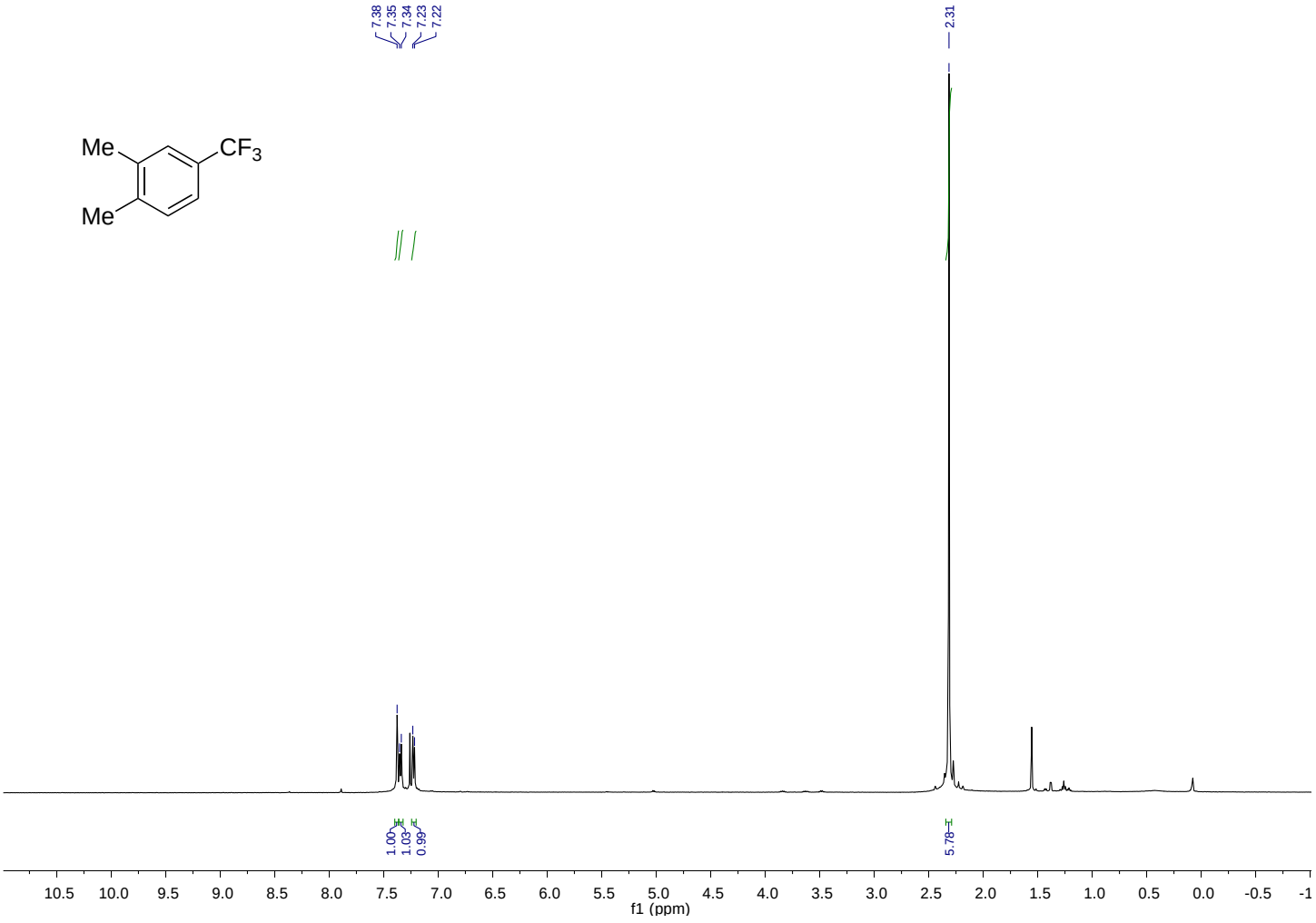

165.95
139.32
133.36
130.82
130.02
129.99
129.96
129.94
126.96
124.79
123.72
123.69
123.66
123.63
122.62
120.46
52.41
21.18
Me
CF3
CO2Me
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

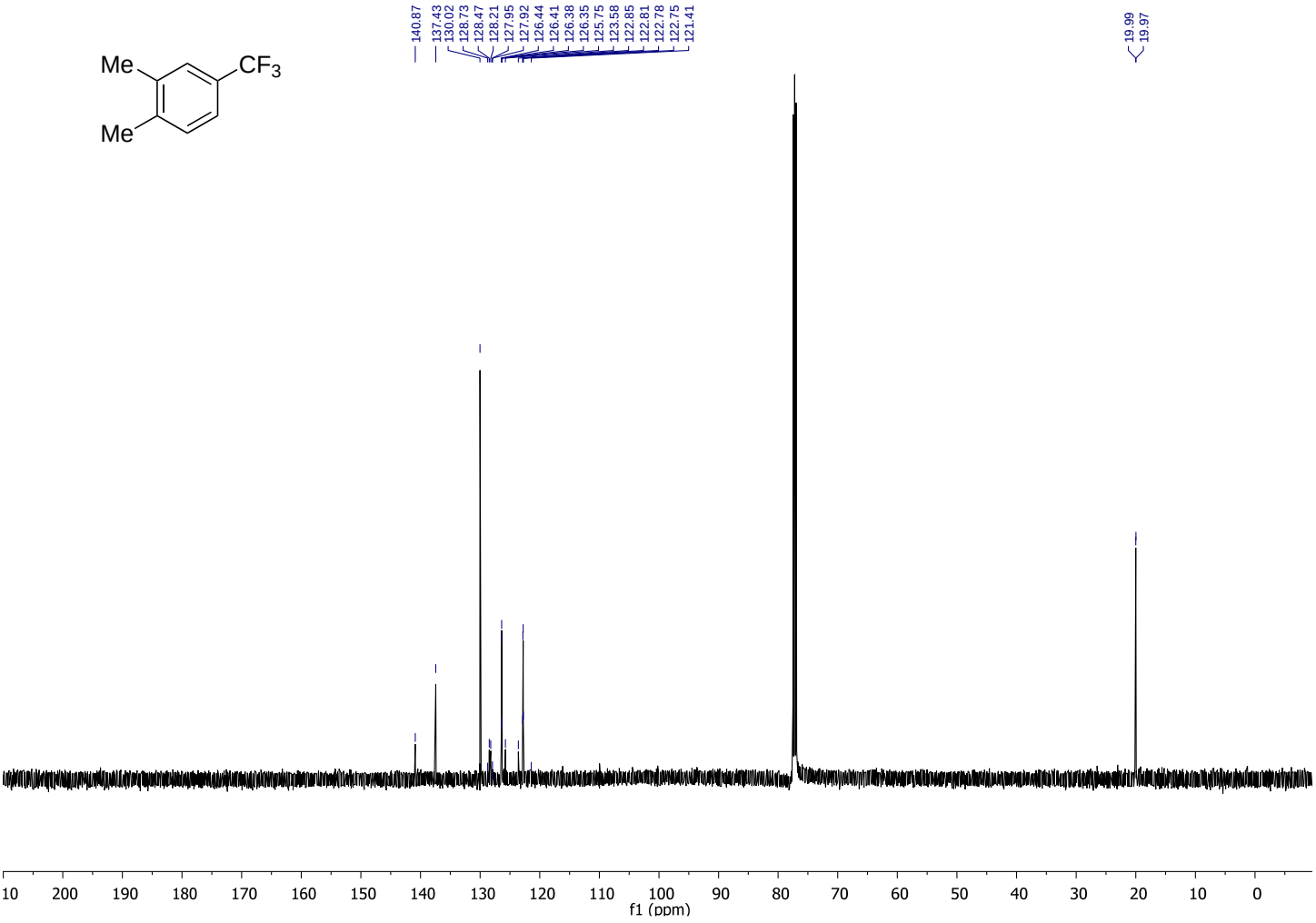

-63.22
Me
CF3
CO2Me
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

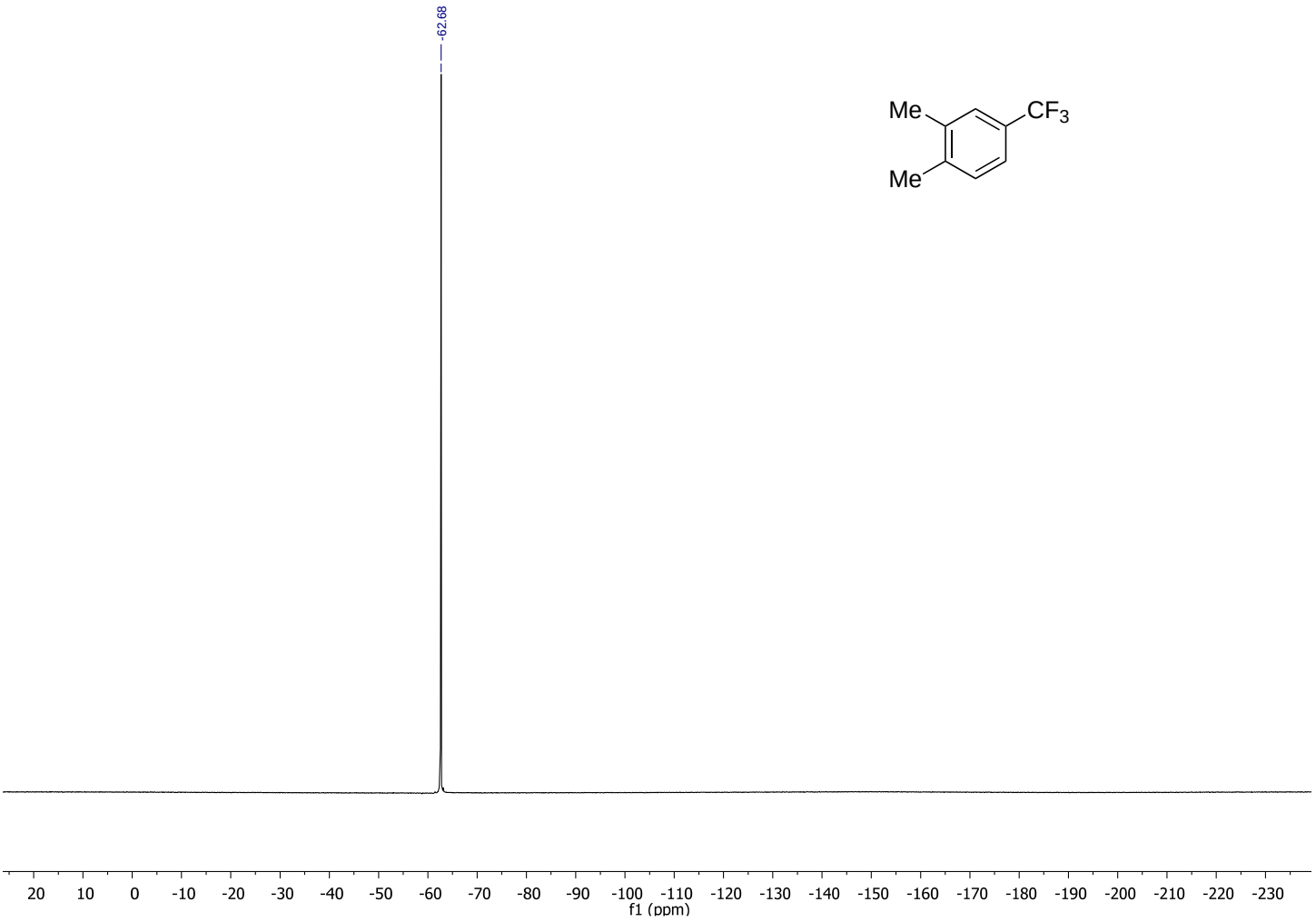

8.84
8.46
3.98
CF3
MeO2C
CO2Me
1.00
2.19
6.37
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)

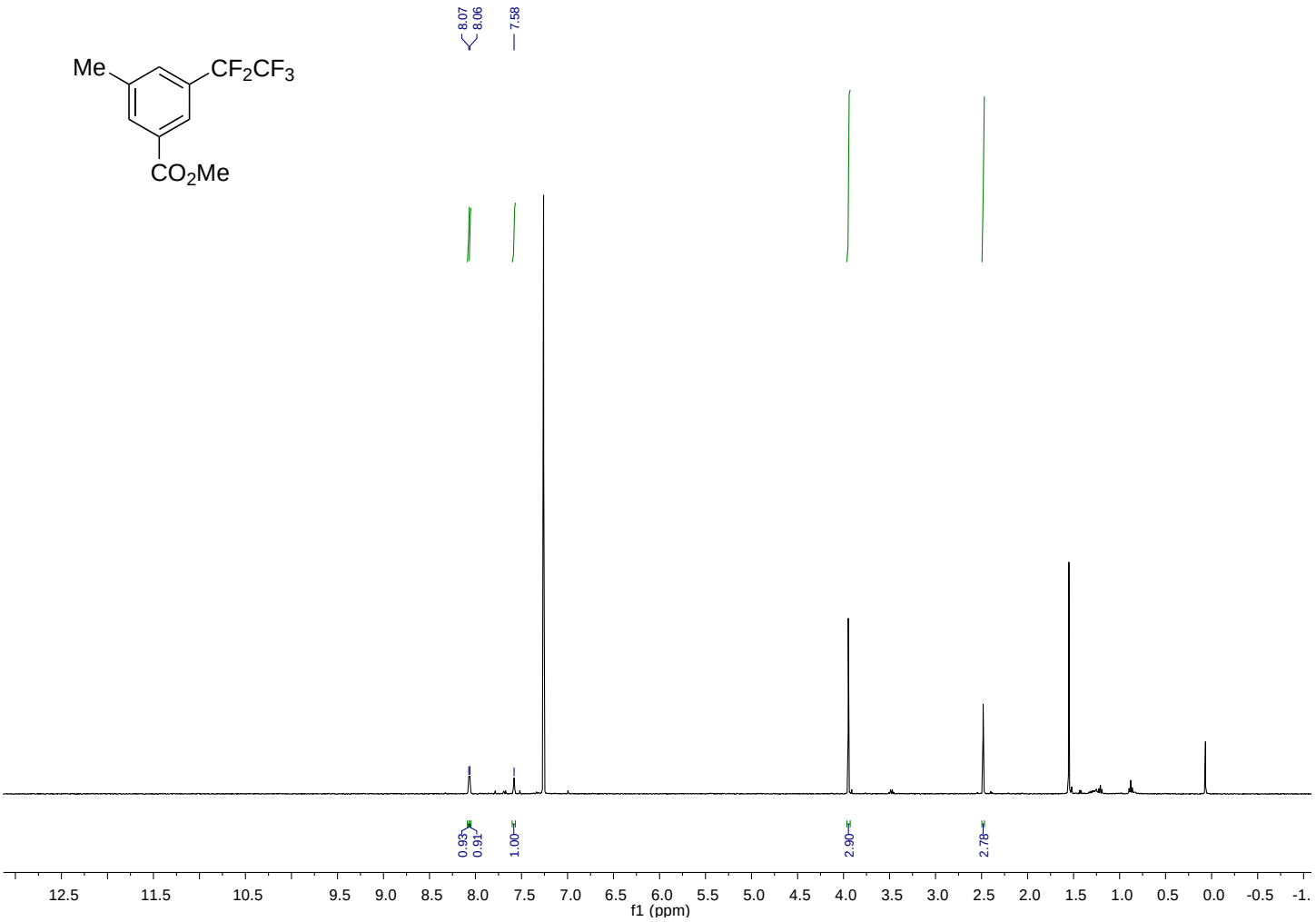

CF3
MeO2C
CO2Me
164.87
133.63
131.62
130.44
130.41
130.38
130.35
126.38
124.21
122.04
119.87
52.75
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

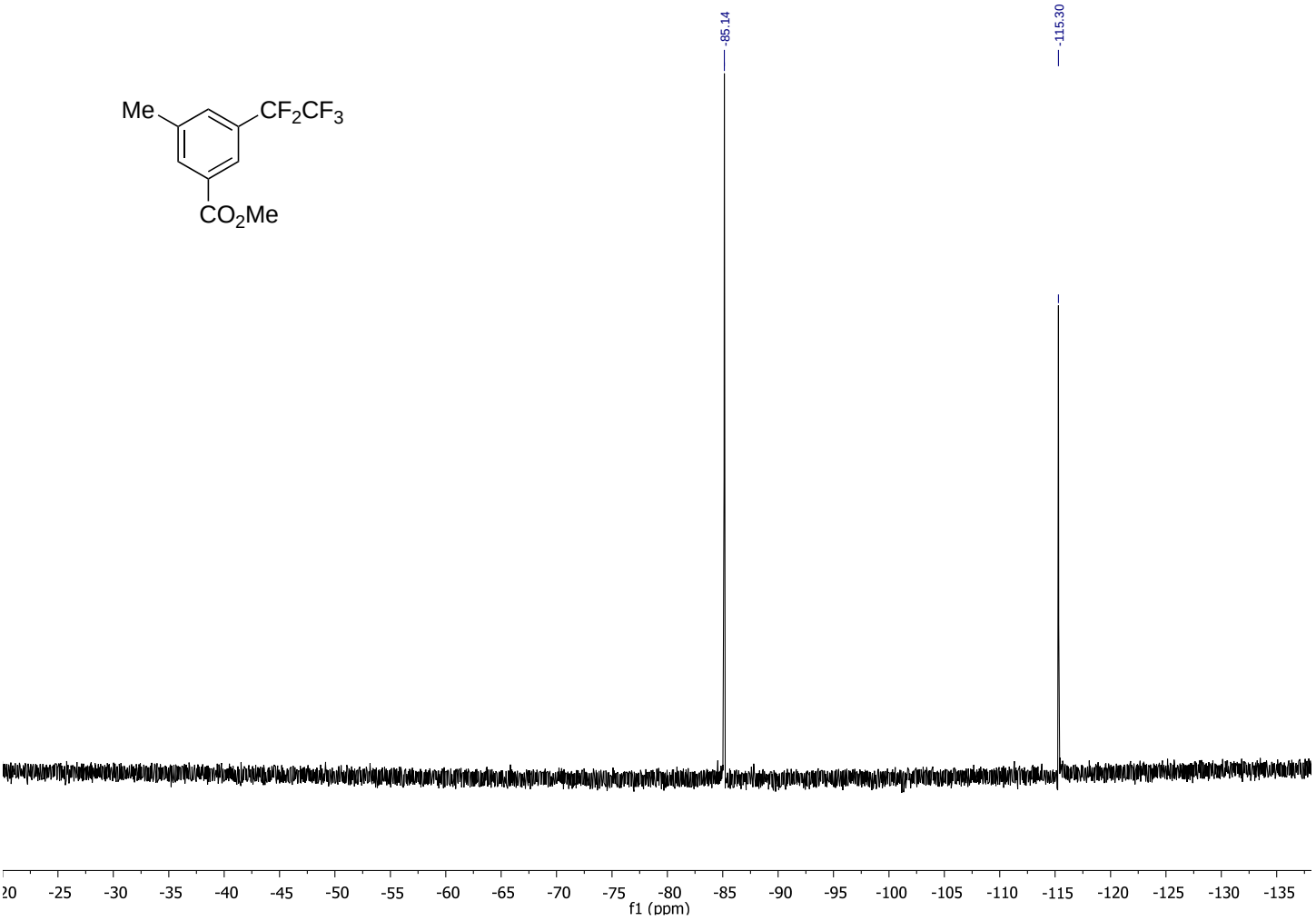

-63.36
CF3
MeO2C
CO2Me
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

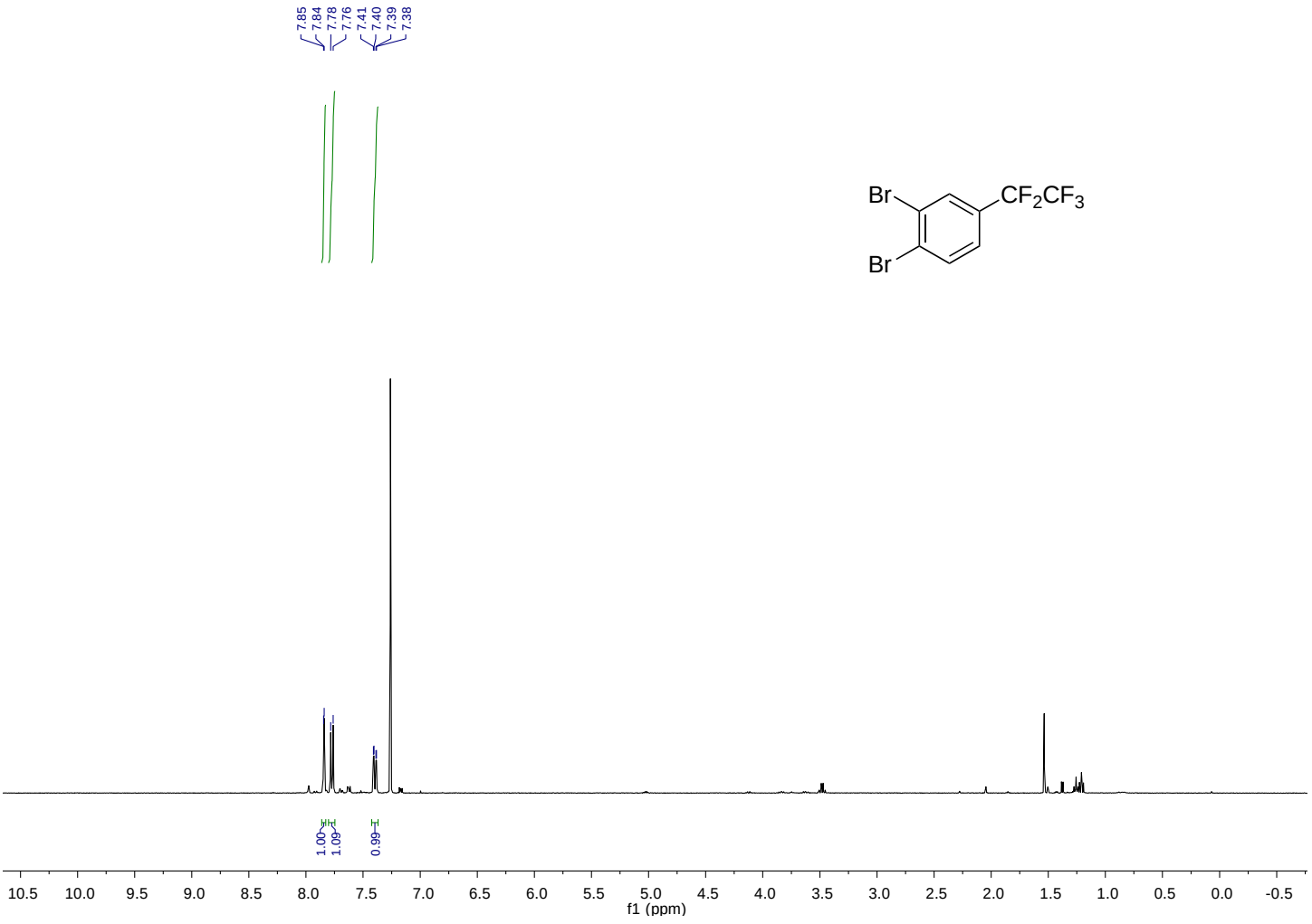

7.38
7.35
7.34
7.23
7.22
2.31
Me
CF3
Me
1.00
1.03
0.99
5.78
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

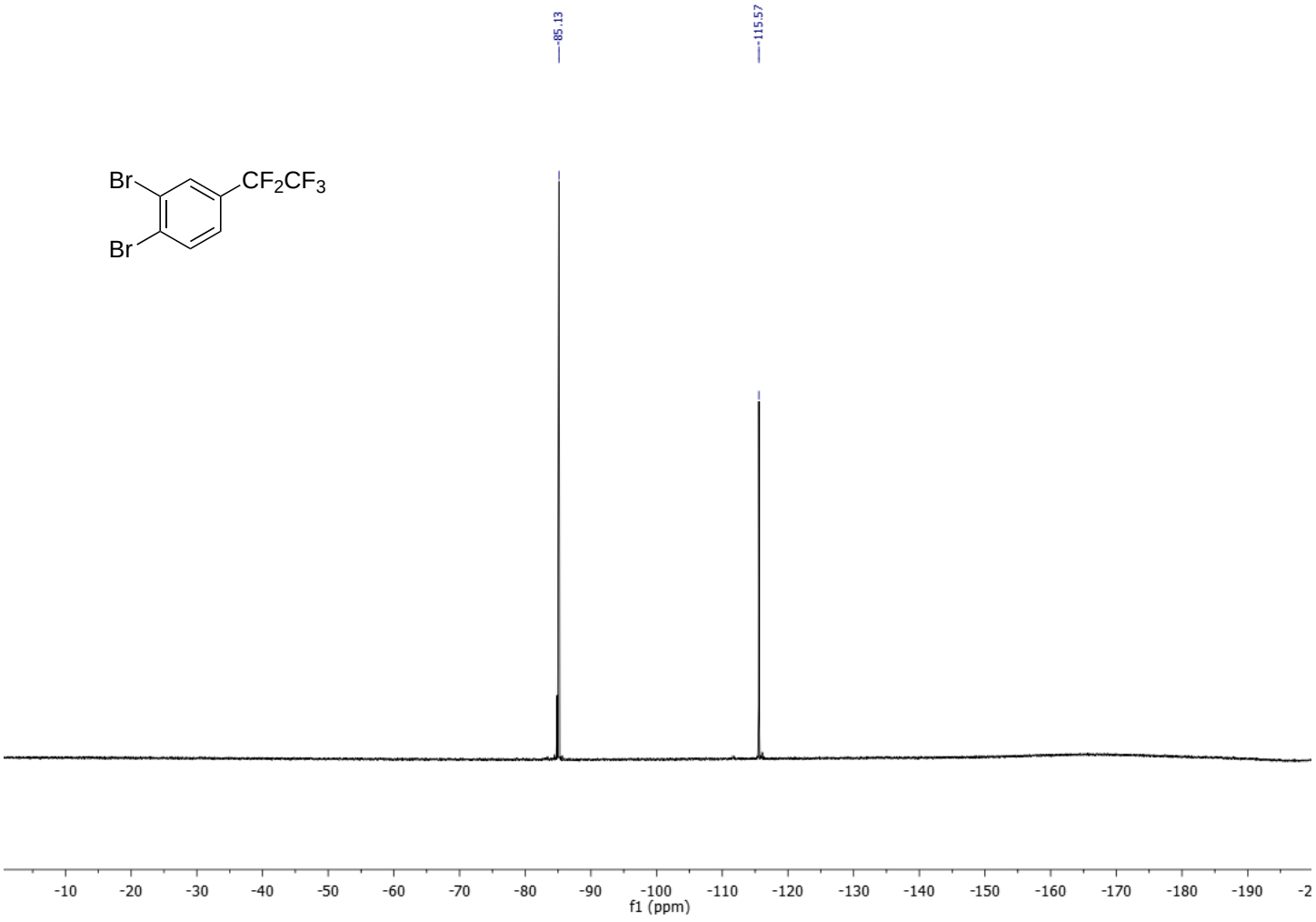

Me
CF3
Me
140.87
137.43
130.02
128.73
128.47
128.21
127.95
127.92
126.44
126.41
126.38
126.35
125.75
123.58
122.85
122.81
122.78
122.75
121.41
19.99
19.97
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

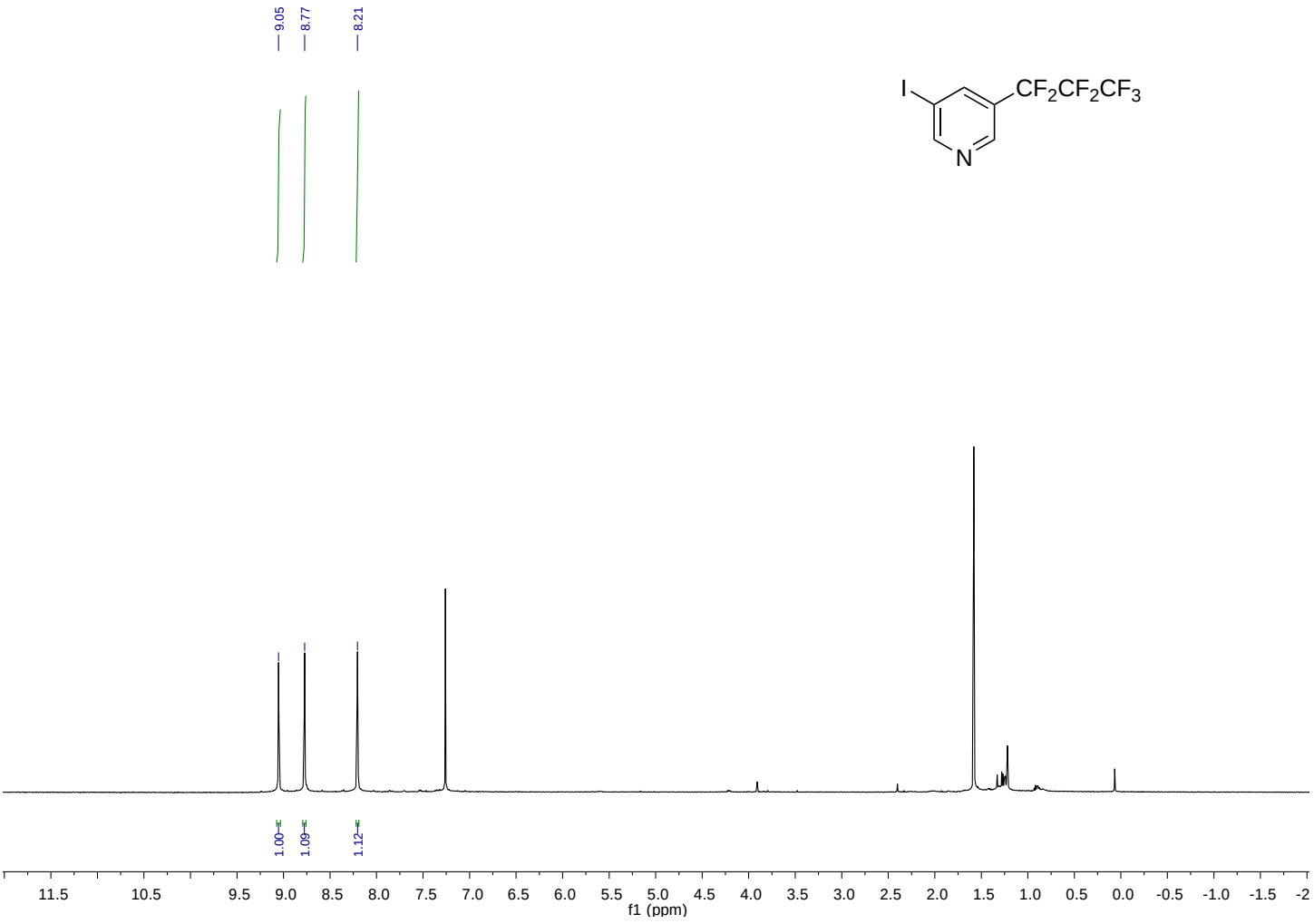

-62.68
Me
CF3
Me
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)

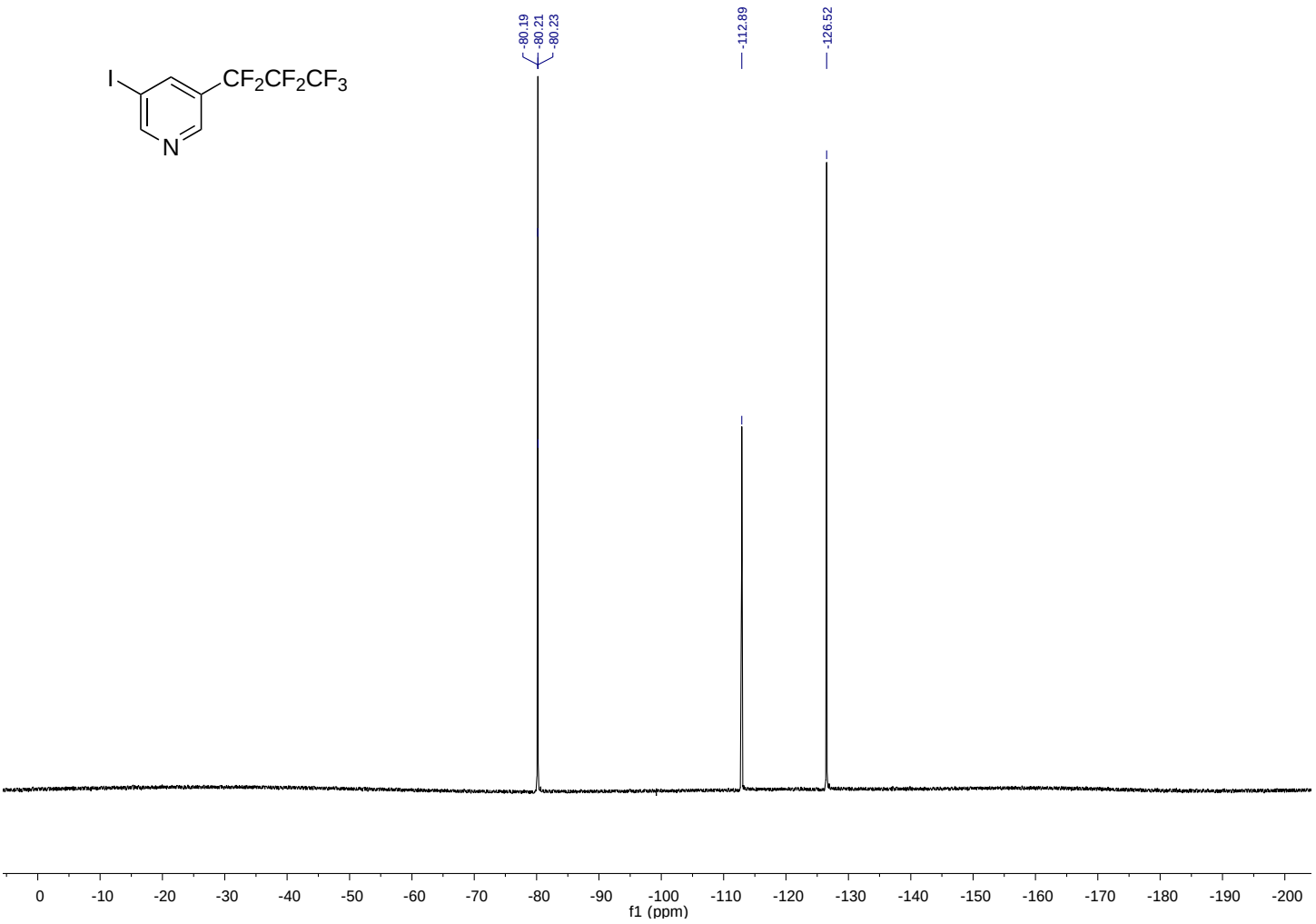

Me
CF2CF3
CO2Me
8.07
8.06
7.58
0.93
0.91
1.00
2.90
2.78
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

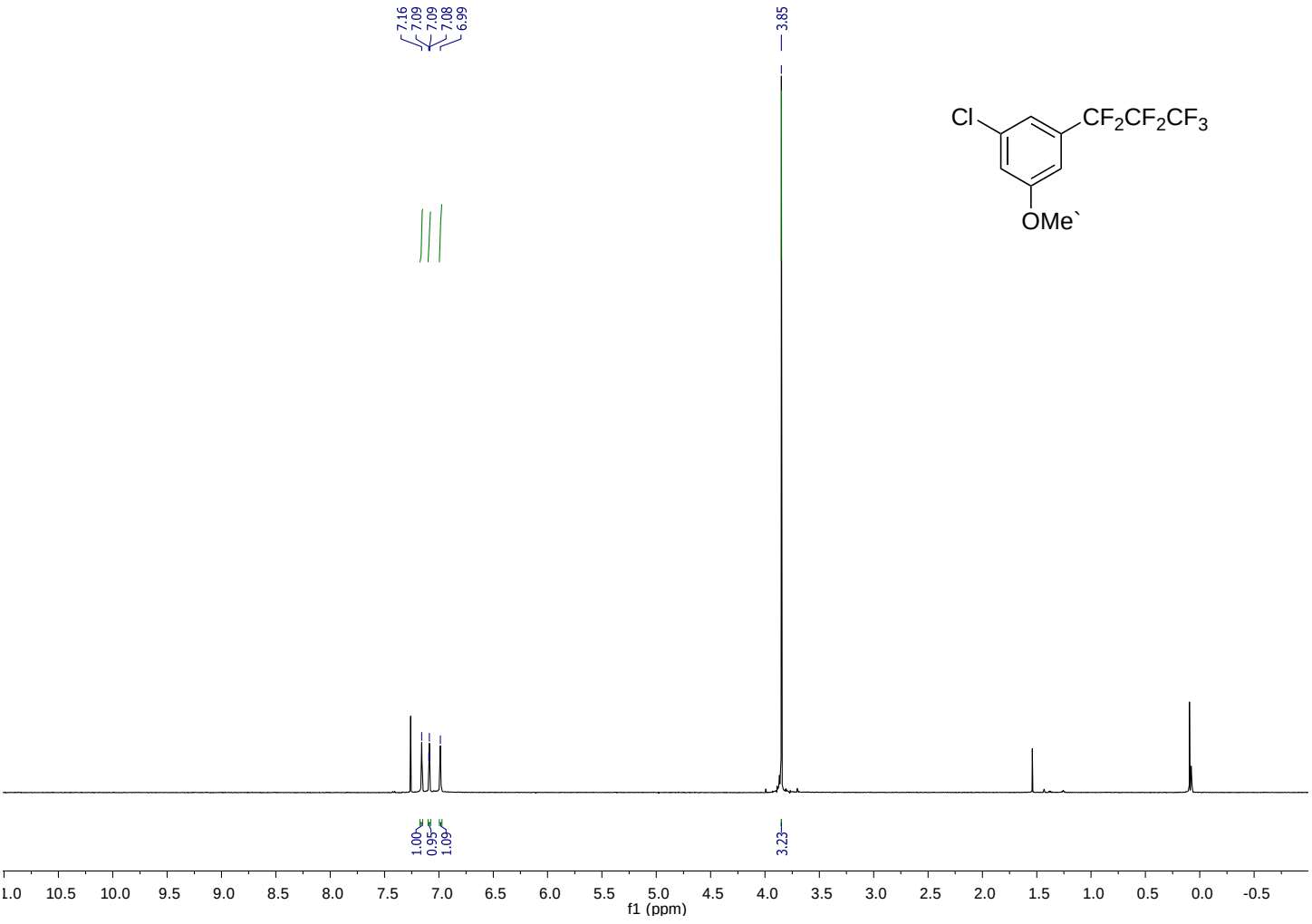

Me
CF2CF3
CO2Me
-85.14
-115.30
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
f1 (ppm)

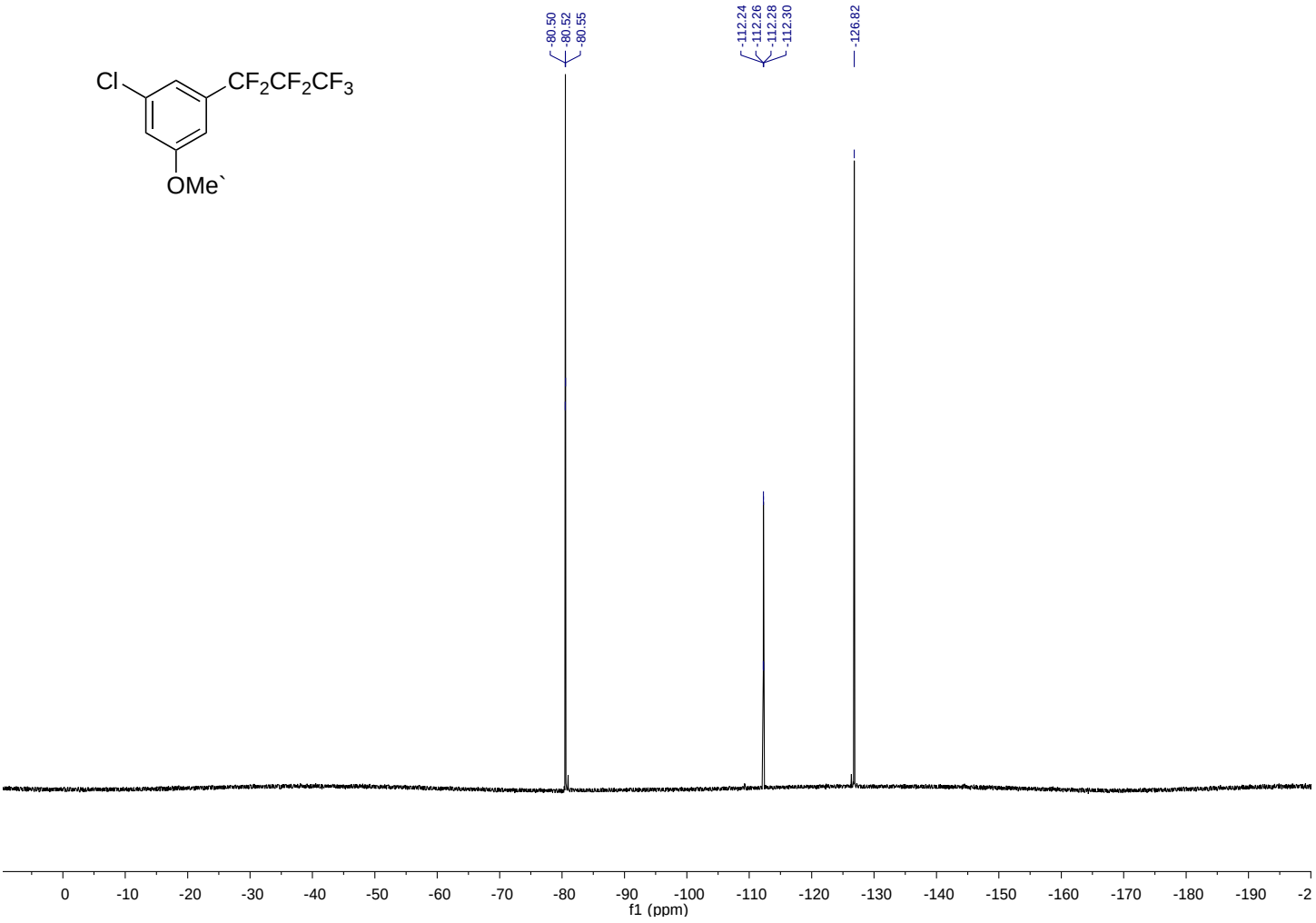

7.85
7.84
7.78
7.76
7.41
7.40
7.39
7.38
Br
Br
CF2CF3
1.00
1.09
0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

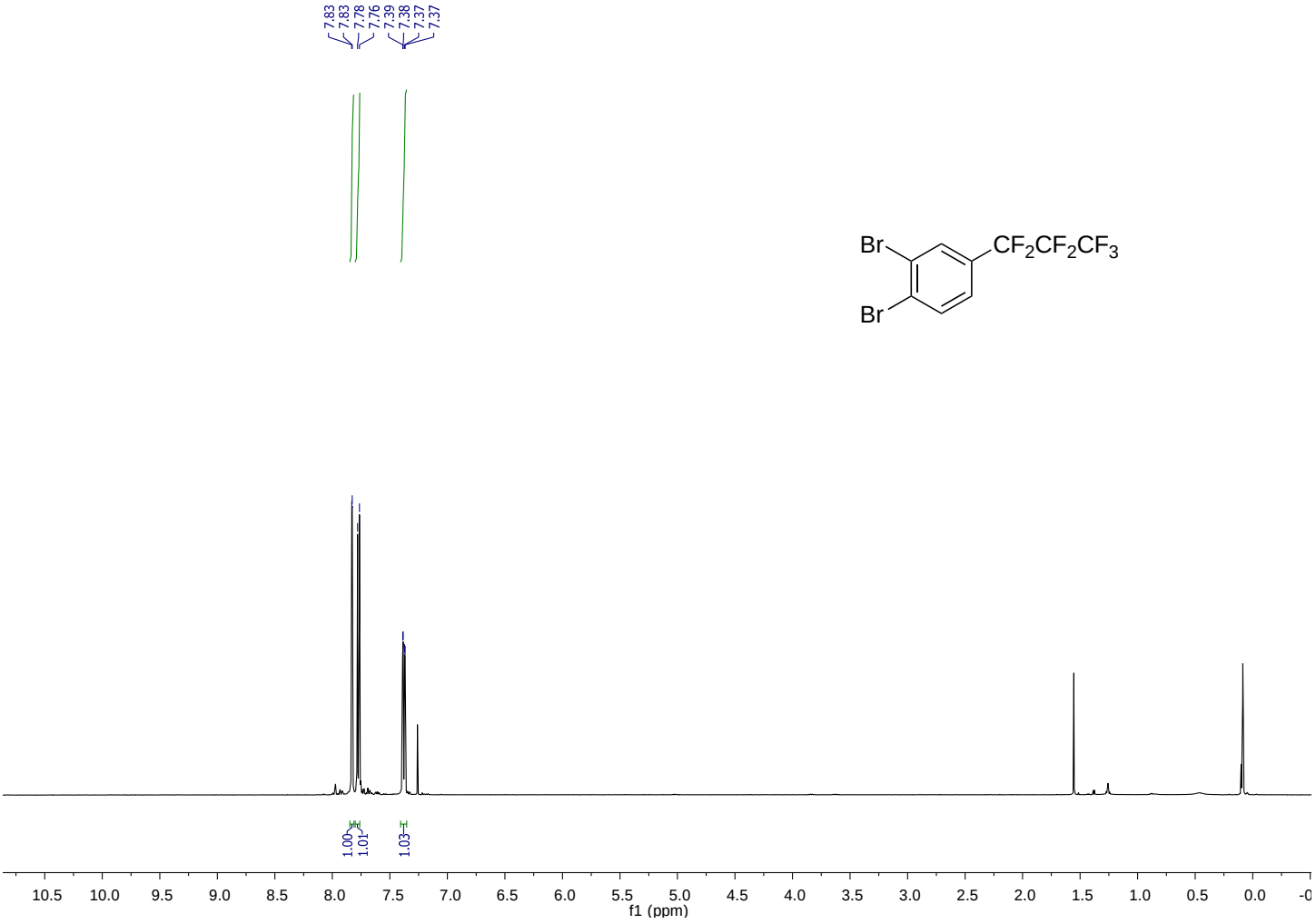

-85.13
-115.57
Br
Br
CF2CF3
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

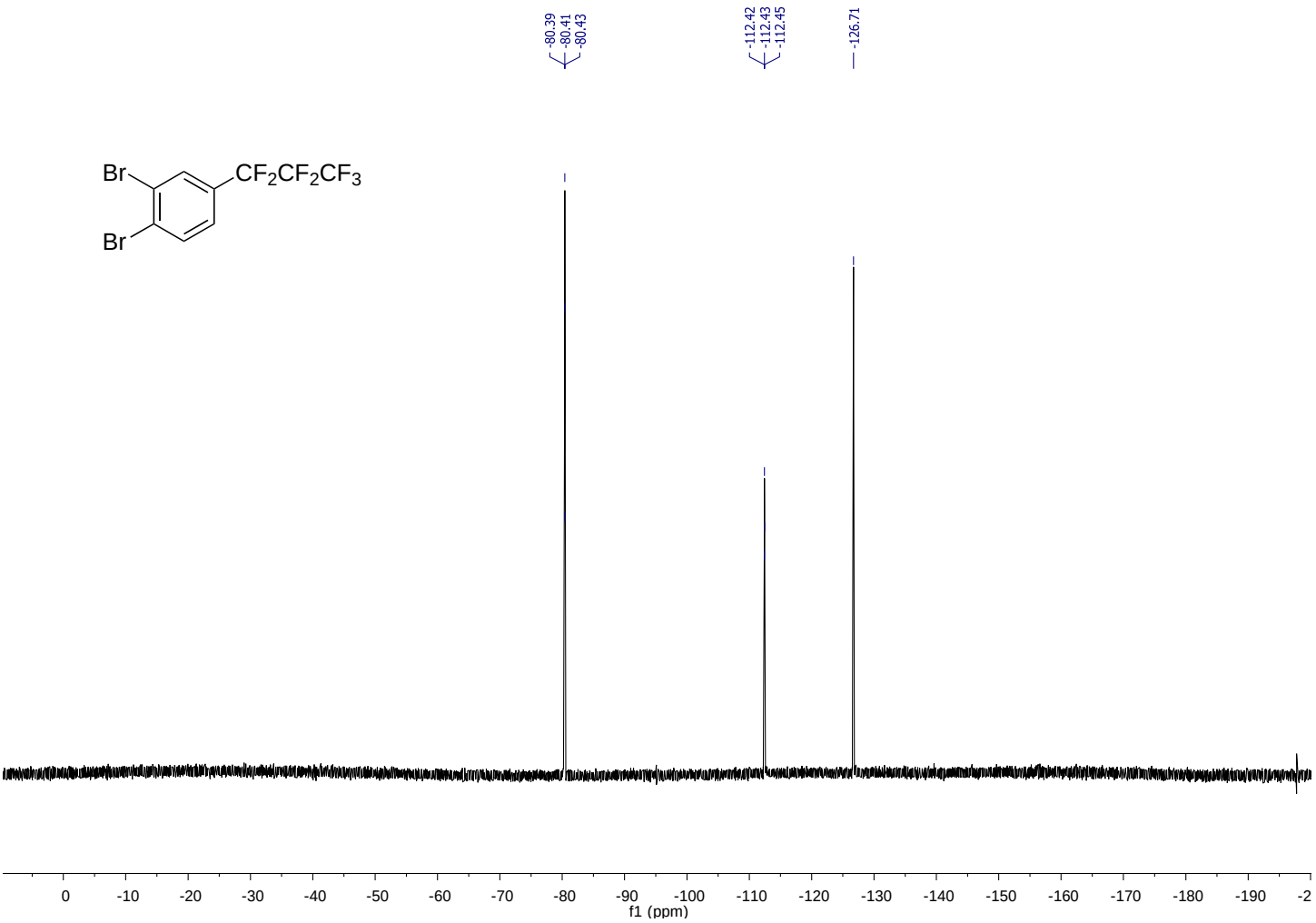

9.05
8.77
8.21
I
CF2CF2CF3
N
1.00
1.09
1.12
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)

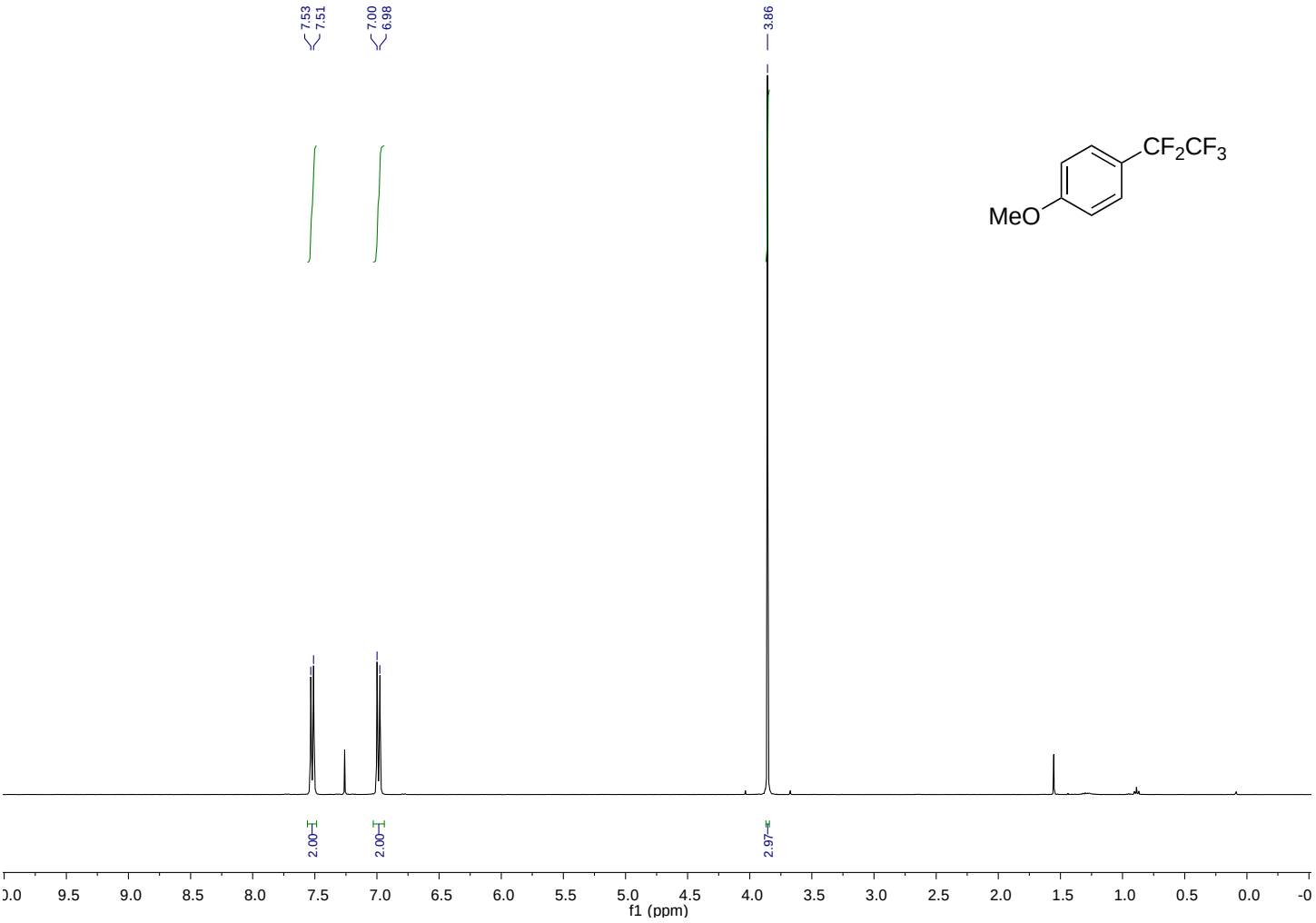

I
CF2CF2CF3
N
-80.19
-80.21
-80.23
-112.89
-126.52
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

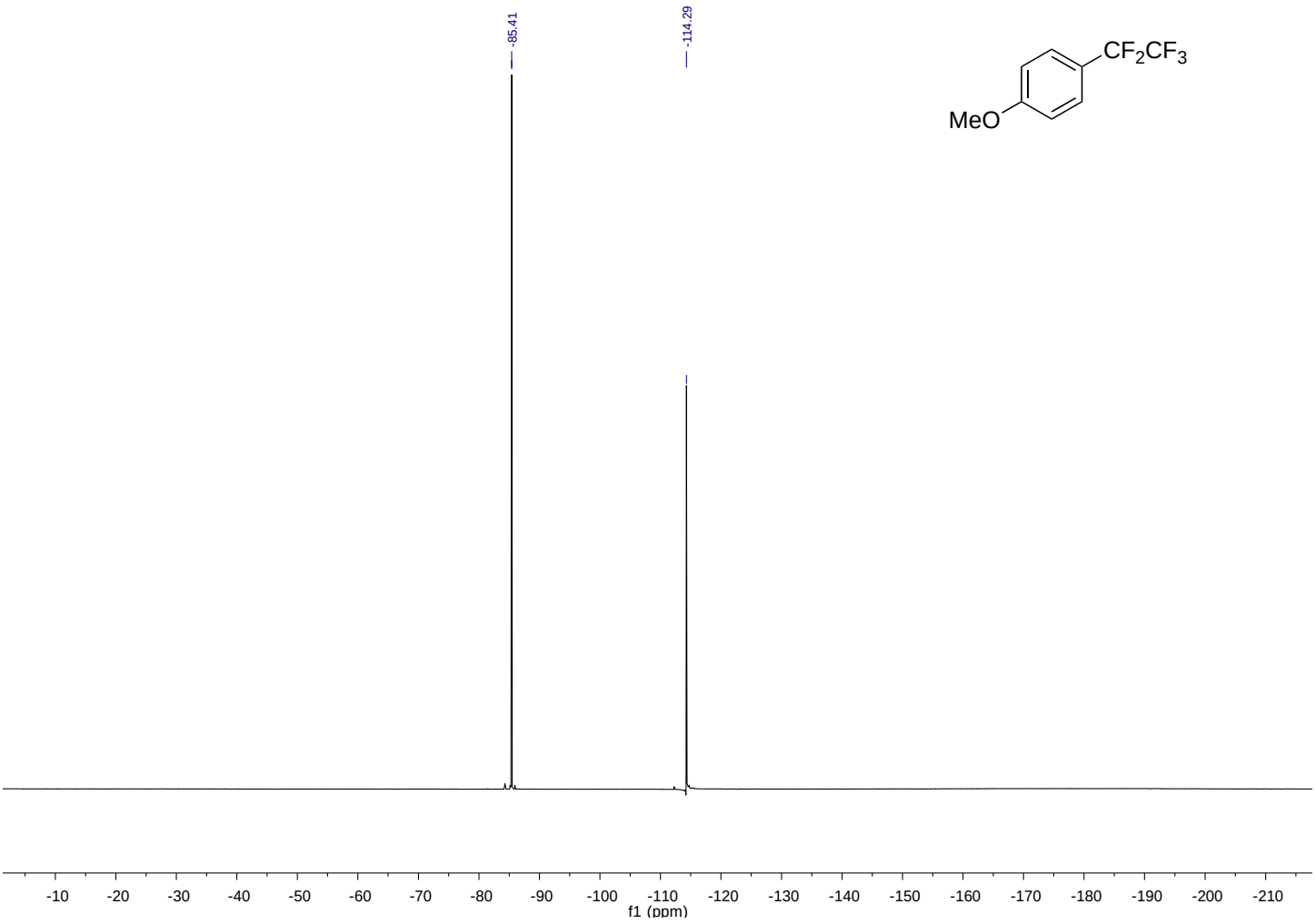

7.16
7.09
7.09
7.08
6.99
3.85
Cl
CF2CF2CF3
OMe`
1.00
0.95
1.09
3.23
f1 (ppm)

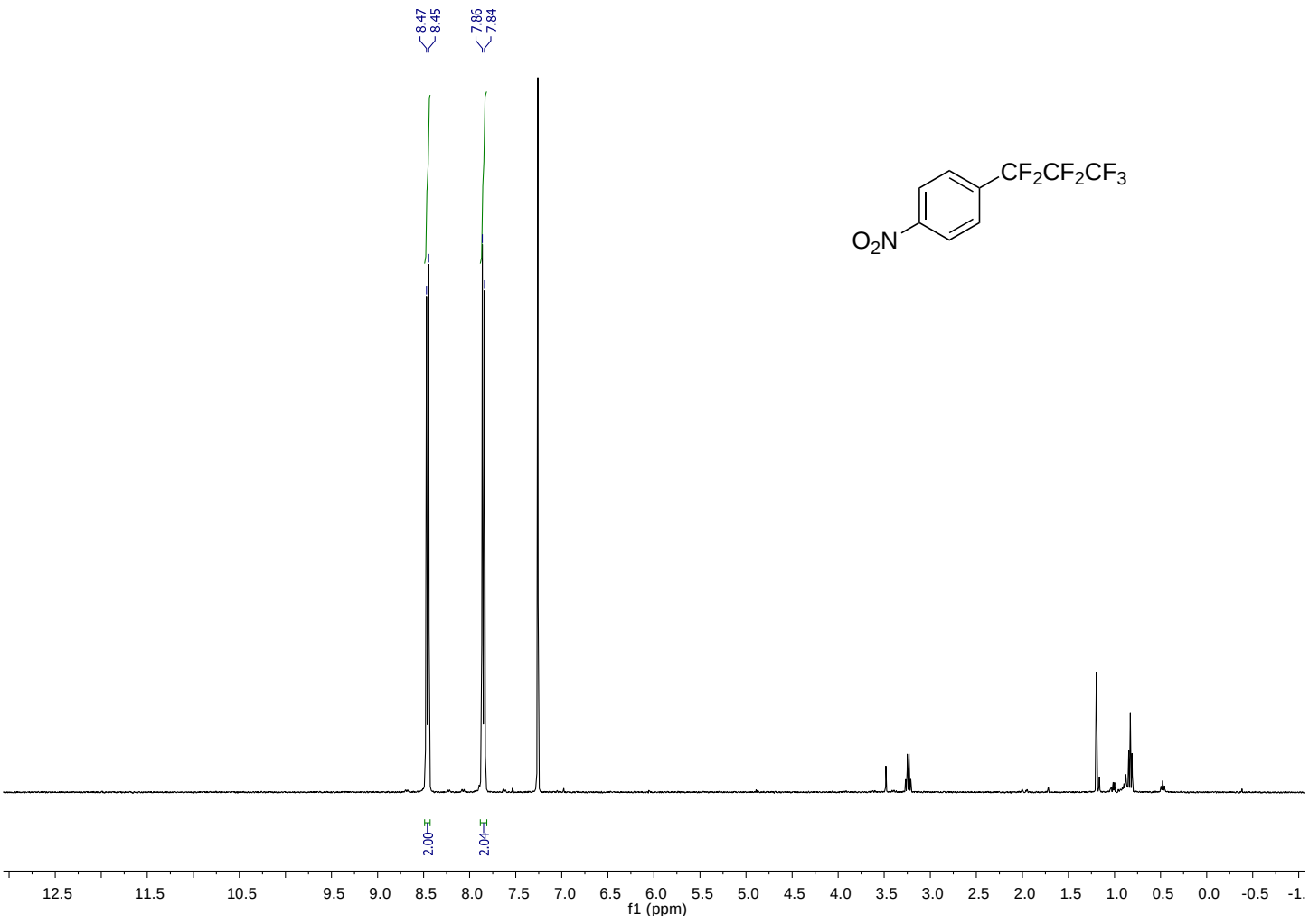

Cl
CF2CF2CF3
OMe`
-80.50
-80.52
-80.55
-112.24
-112.26
-112.28
-112.30
-126.82
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

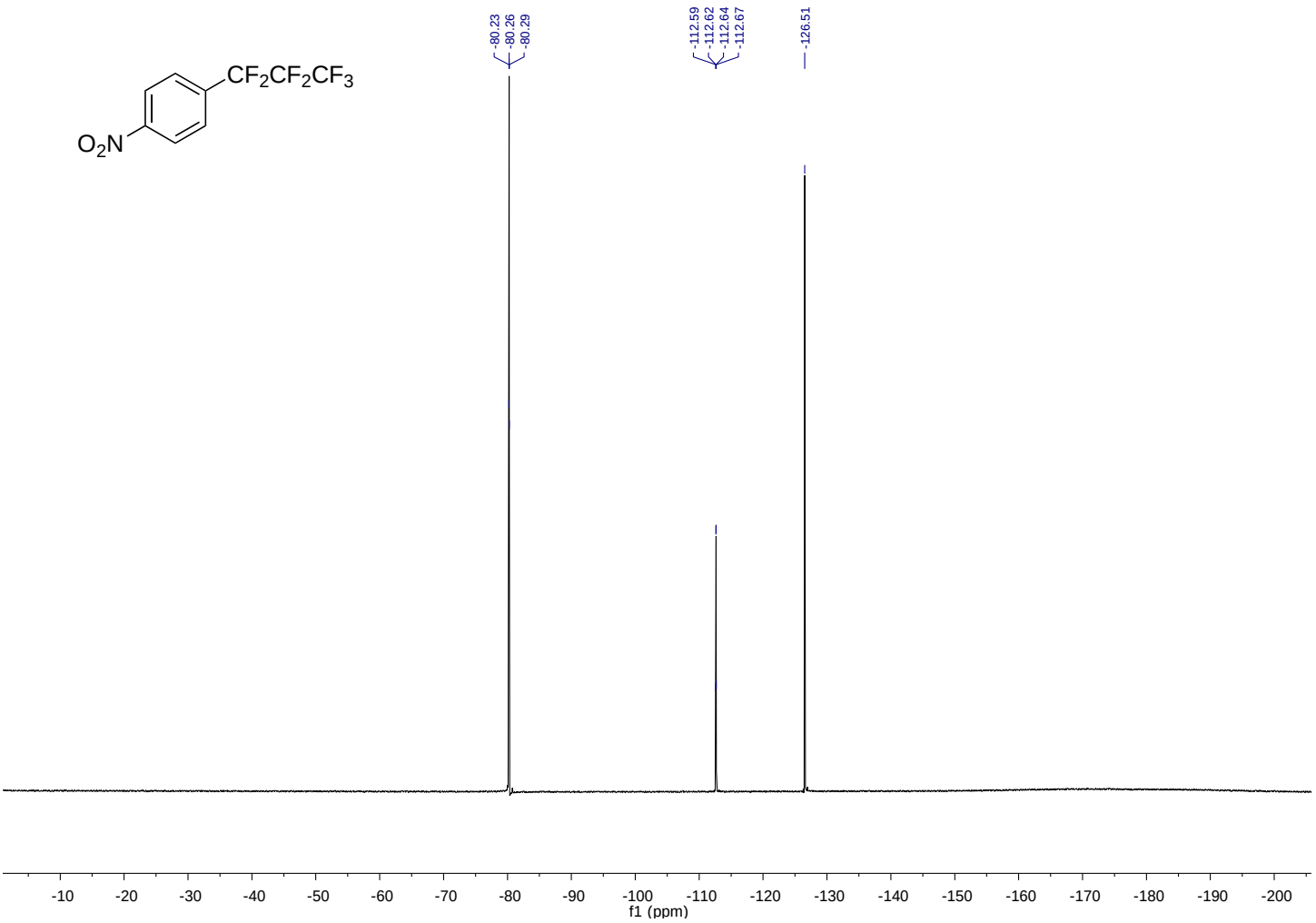

7.83
7.83
7.78
7.76
7.39
7.38
7.37
7.37
Br
Br
CF2CF2CF3
1.00
1.01
1.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

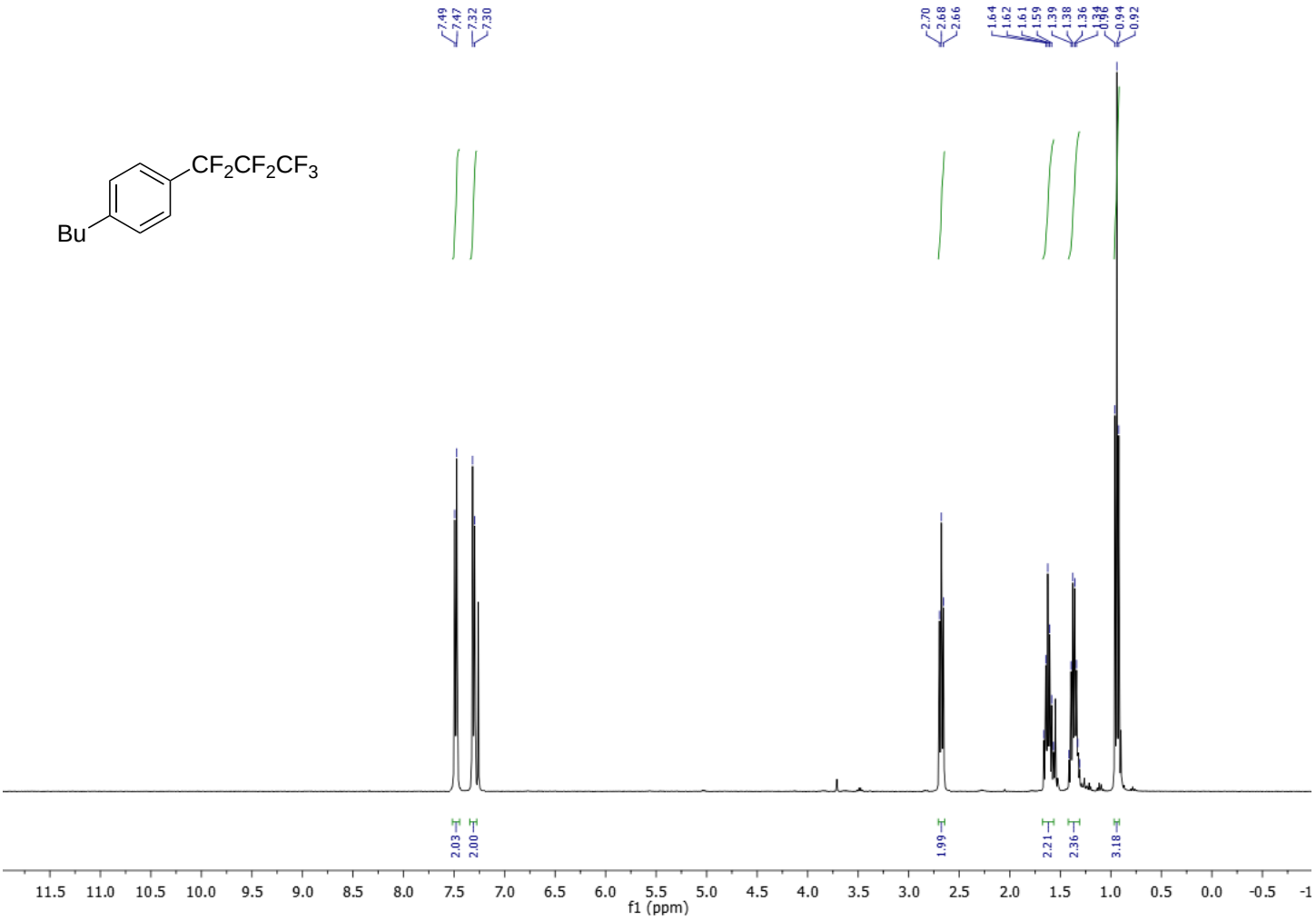

-80.39
-80.41
-80.43
-112.42
-112.43
-112.45
-126.71
Br
Br
CF2CF2CF3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

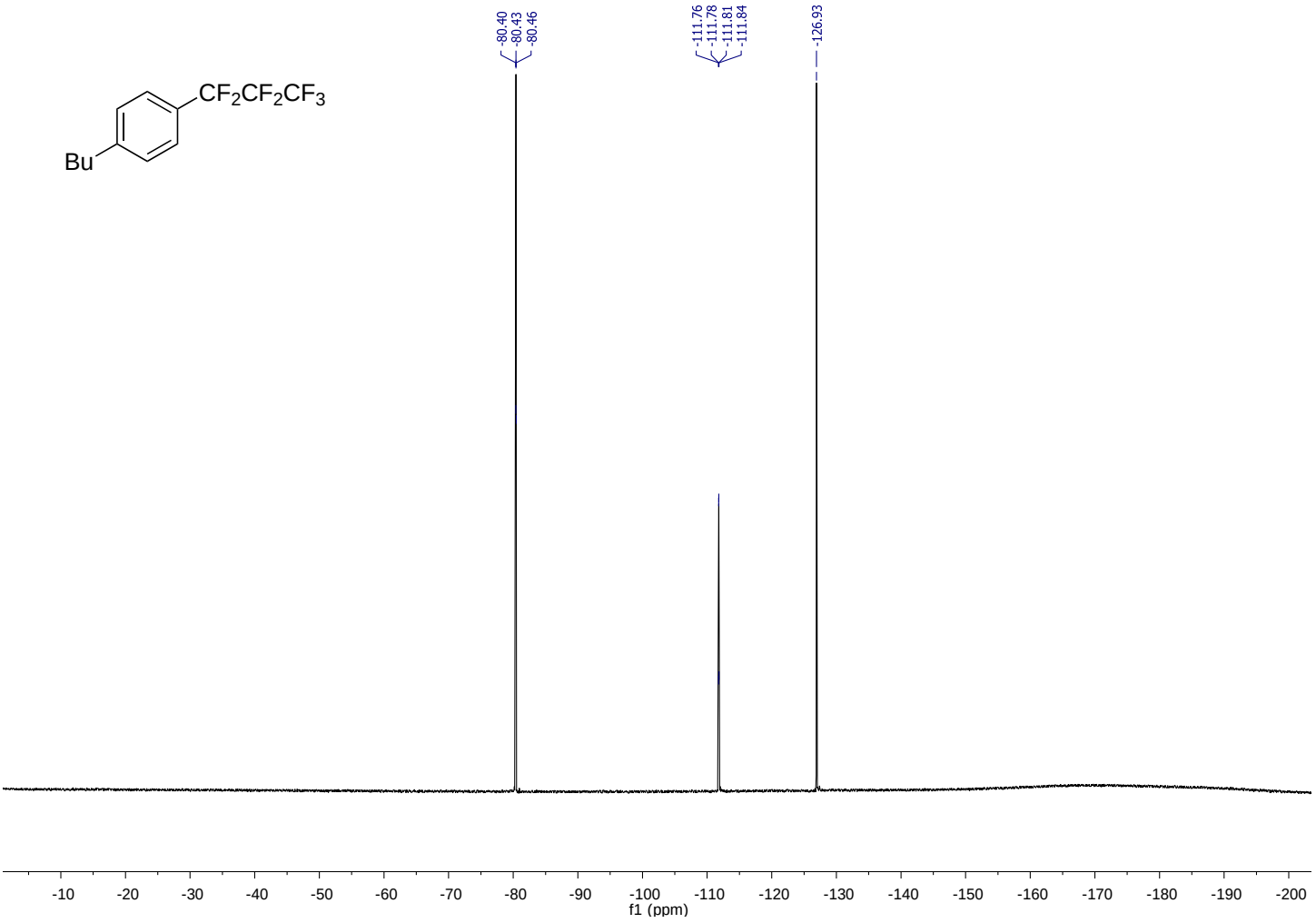

7.53
7.51
7.00
6.98
3.86
CF2CF3
MeO
2.00
2.00
2.97
f1 (ppm)

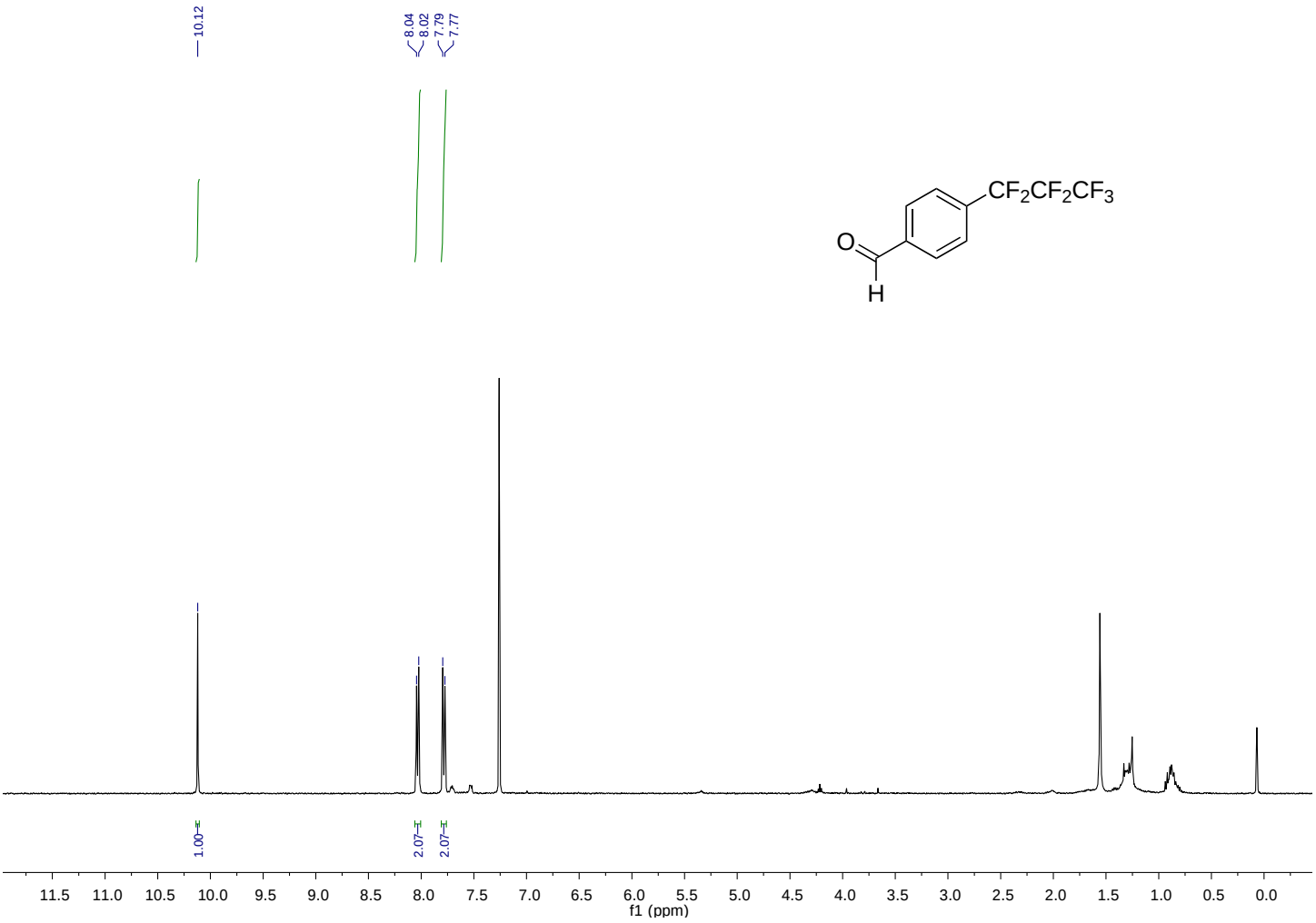

-85.41
-114.29
CF2CF3
MeO
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

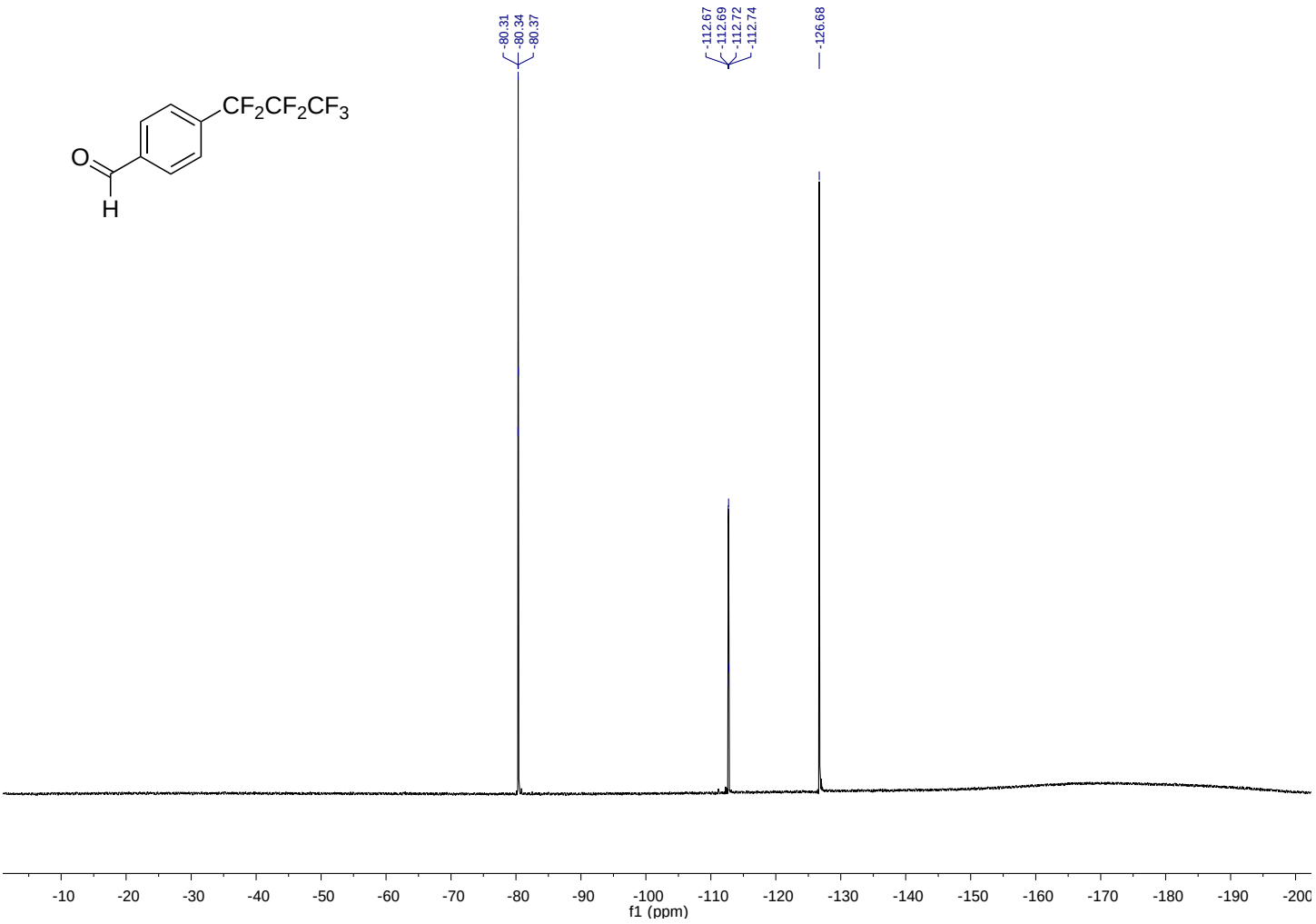

8.47
8.45
7.86
7.84
$CF_2CF_2CF_3$
O_2N
2.00
2.04
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


-80.23
-80.26
-80.29
-112.59
-112.62
-112.64
-112.67
-126.51
CF2CF2CF3
O2N
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


CF2CF2CF3
Bu
7.49
7.47
7.32
7.30
2.70
2.68
2.66
1.64
1.62
1.61
1.59
1.39
1.38
1.36
0.94
0.92
2.03
2.00
1.99
2.21
2.36
3.18
f1 (ppm)


-80.40
-80.43
-80.46
-111.76
-111.78
-111.81
-111.84
-126.93
CF2CF2CF3
Bu
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


10.12
8.04
8.02
7.79
7.77
CF2CF2CF3
O
H
1.00
2.07
2.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-80.31
-80.34
-80.37
-112.67
-112.69
-112.72
-112.74
-126.68
CF2CF2CF3
O
H
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)