Copper-Mediated Fluorination of Arylboronate Esters. Identification of a Copper(III) Fluoride Complex.

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Supporting Information

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General Experimental Details

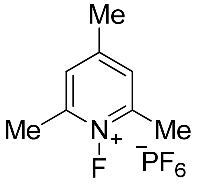
All manipulations were conducted under an inert atmosphere with a nitrogen-filled glovebox unless otherwise noted. All reactions were conducted in oven-dried 4-mL vials fitted with a Teflon-lined screw cap under an atmosphere of nitrogen unless otherwise noted.

Silver fluoride (>99%) was purchased from Acros and used as received. THF was sparged with N_2, passed through activated alumina and stored over 3 Å molecular sieves prior to use. $(^tBuCN)_2CuOTf$ was prepared according to our previously published procedure (*J. Am. Chem. Soc.* **2012**, 134, 10795). Unless otherwise noted, all other reagents were purchased from commercial suppliers and used as received.

NMR spectra were acquired on 400 MHz, 500 MHz, or 600 MHz Bruker instruments at the University of California. 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) 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.

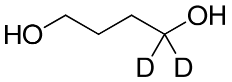
Preparation of 1-fluoro-2,4,6-trimethylpyridinium hexafluorophosphate, [Me$_3$pyF]PF$_6$



1-fluoro-2,4,6-trimethylpyridinium tetrafluoroborate ($[Me_3pyF]BF_4$, 4.54 g, 20.0 mmol) was dissolved in water (80 mL), and ammonium hexafluorophosphate (19.56 g, 120.0 mmol) was added to the resulting solution at once. A white precipitant formed quickly, and the resulting suspension was stirred at room temperature for 2 h. The white solid was collected on a funnel, washed with 3 x 15 mL of water, 2 x 15 mL of ether, and dried in vacuo (20 mtorr). 5.00 g (17.5 mmol) of a white powder was obtained, 88% yield.

^1H NMR (400 MHz, CD_3CN) δ 7.65 (d, *J* = 6.4 Hz, 2H), 2.74 (d, *J* = 4.0 Hz, 6H), 2.55 (s, 3H).
^{19}F NMR (376 MHz, CD_3CN) δ 17.48 (s), -71.40 (d, *J* = 706.4 Hz).

Preparation of 1,1-dideuterio-1,4-butanediol

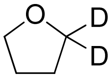


1,1-dideuterio-1,4-butanediol was prepared by the reduction of γ-butyrolactone according to a similar procedure as that reported in *J. Org. Chem.* **1982**, 47, 4702. Sodium borodeuteride ($NaBD_4$, 576 mg, 13.8 mmol) and LiCl (583 mg, 13.8 mmol) were suspended in THF (10 mL) and stirred at room temperature for 1 h. γ-butyrolactone (1.9 mL, 25 mmol) and toluene (4 mL) were added and the resulting mixture was heated at 80 °C for 12 hours. The bulk of the solvent was distilled off at 120 °C and the remaining liquid was removed by vacuum distillation at 120 °C. The flask was allowed to cool to room temperature and the white solid was hydrolyzed with 1 M HCl (20 mL) over 3 hours. K_2CO_3 was added to saturate the aqueous layer followed by extraction with THF (3 x 20 mL). The THF was dried over anhydrous K_2CO_3, concentrated and dried *in-vacuo* (20 mtorr) overnight to afford the title compound as a viscous oil (1.52 g, 16.5 mmol, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.68 (t, J = 5.8 Hz, 2H), 2.52 (s, 2H), 1.68 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 62.52 (s), 61.85 (m), 29.72 (s), 29.58 (s).

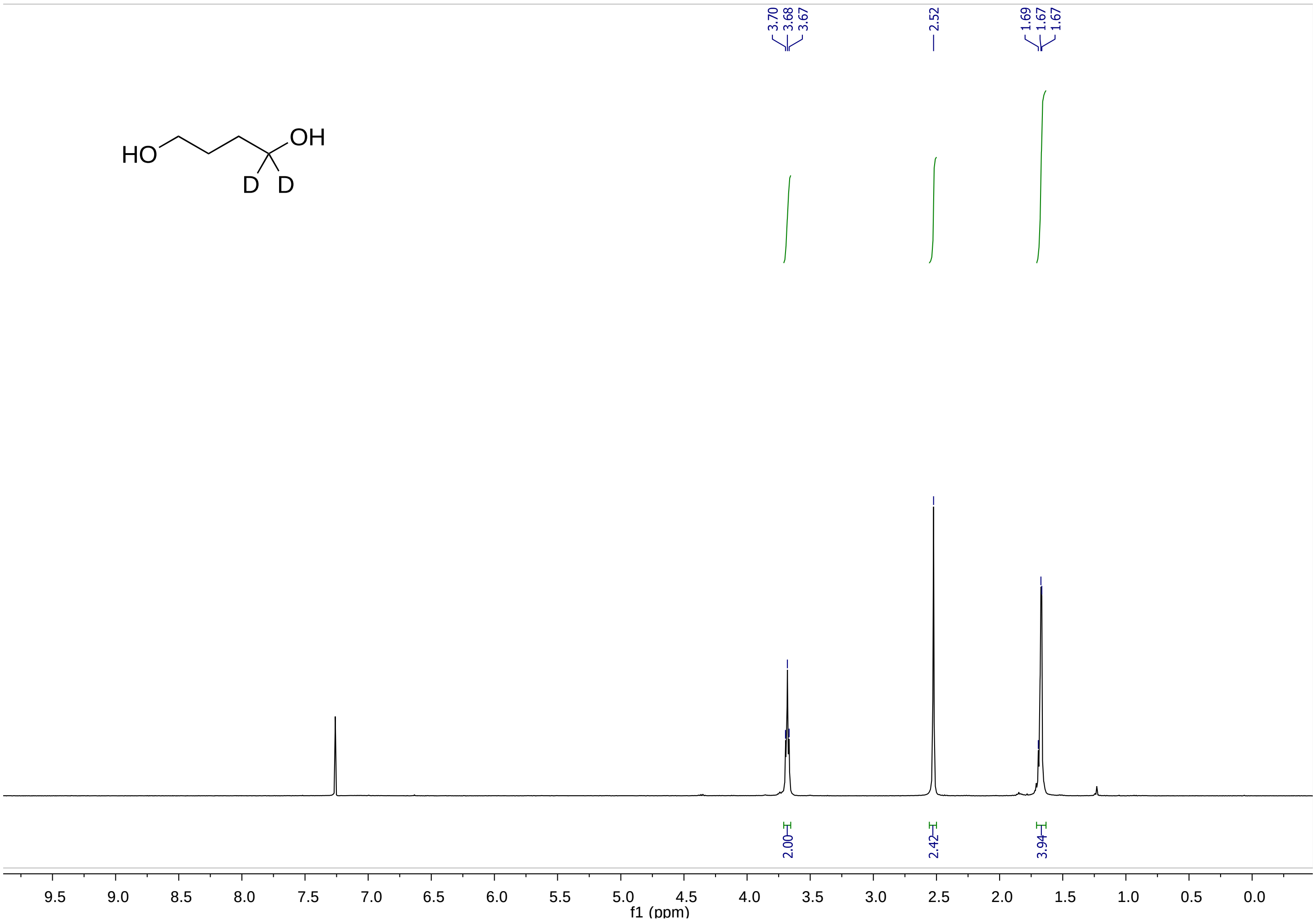
Preparation of 2,2-dideuteriotetrahydrofuran (THF-d_2)



A similar procedure was used as that reported in *J. Org, Chem.***1959**, 24, 1259. To a Schlenk flask was added 1,1-dideuterio-1,4-butanediol (1.5 g, 16 mmol) and 85% aqueous phosphoric acid (400 μL). The resulting solution was heated at 125 °C for 24 hours. The reaction was cooled to room temperature and the THF-d_2 formed was vacuum transferred to a separate Schlenk flask. The THF-d_2 was dried over sodium metal with benzophenone as an indicator. Once the THF-d_2 was dry (3 days), it was vacuum transferred to an oven dried flask to afford the title compound as a clear liquid (ca. 900 μL). Note: the THF initially contains a large amount of water and the sodium metal should be added carefully.

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.73 (t, J = 6.5 Hz, 2H), 1.84 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 67.94 (s), 67.32 (m), 25.59 (s), 25.36 (s).



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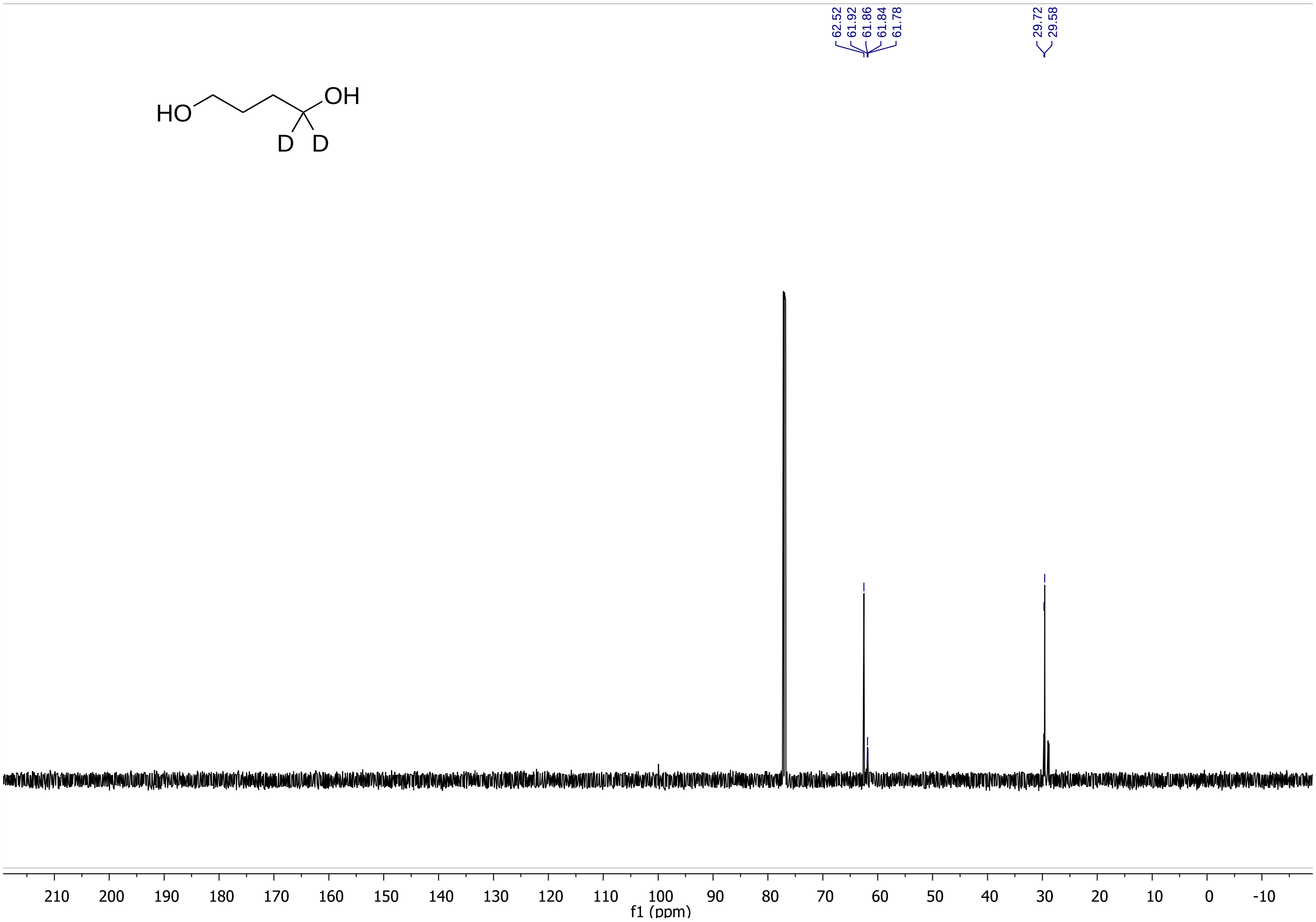
OH
D D
3.70
3.68
3.67
2.52
1.69
1.67
1.67
2.00
2.42
3.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


HO
OH
D
D
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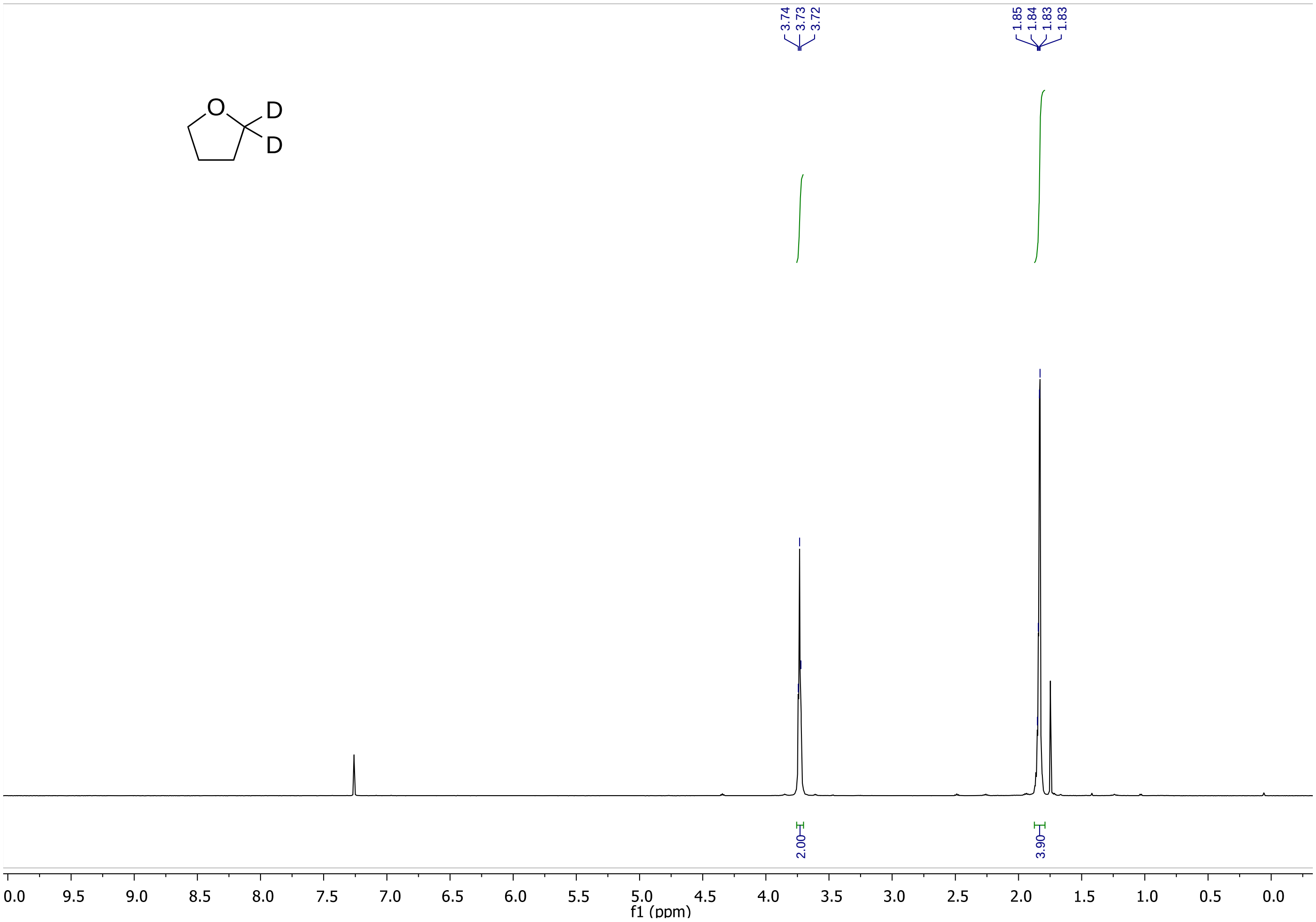
61.92
61.86
61.84
61.78
29.72
29.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3.74
3.73
3.72
1.85
1.84
1.83
1.83
O
D
D
2.00
3.90
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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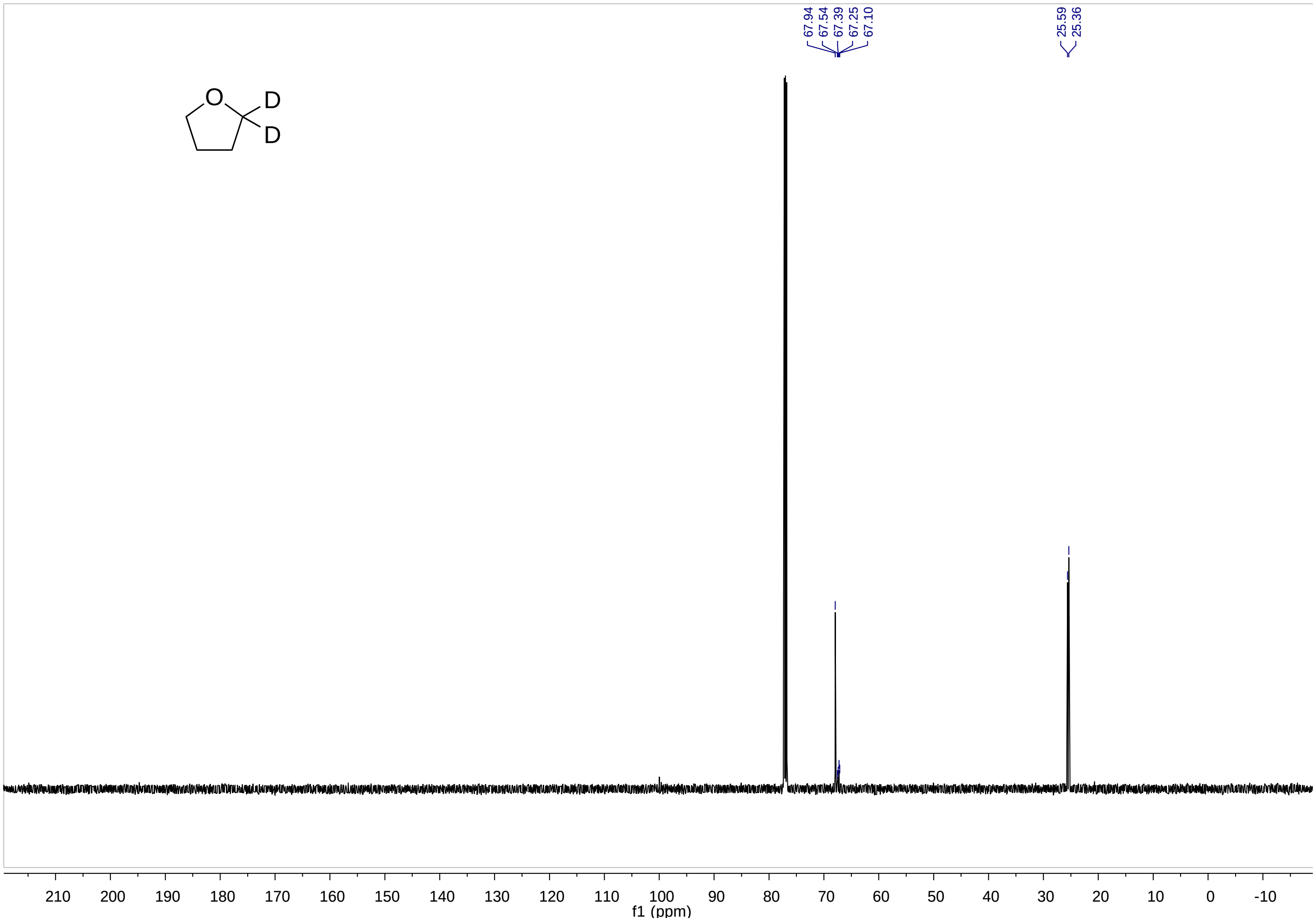
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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67.25
67.10
25.59
25.36
O
D
D
210
200
190
180
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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

General Procedure for the Synthesis of Aryl Pinacol Boronate Esters

Into a 20 mL vial was placed the aryl boronic acid (2.00 mmol, 1.00 equiv), pinacol (236 mg, 2.00 mmol, 1.00 equiv), powdered 4 Å molecular sieves (~300 mg), and 5 mL of ether. The mixture was stirred at room temperature overnight. The molecular sieves were removed by filtration, and the filtrate was concentrated to afford aryl pinacol boronate esters as colorless solids or oils. Further purification of the aryl boronate ester was rarely needed.

General Procedure for the Fluorination of Aryl Boronate Esters

To an oven-dried 4 mL vial was added AgF (25 mg, 0.20 mmol, 2.0 equiv), $(^tBuCN)_2CuOTf$ (76 mg, 0.20 mmol, 2.0 equiv), $[Me_3pyF]PF_6$ (86 mg, 0.30 mmol, 3.0 equiv) and THF (2.0 mL). The aryl boronate ester (0.10 mmol, 1.0 equiv) was added (solid aryl boronate esters were weighed in the vial prior to adding THF, and liquid aryl boronate esters were added neat by syringe after the addition of THF). The vial was sealed with a Teflon-lined cap and heated at 50 ^oC with vigorous stirring for 18 h. The solution was allowed to cool to room temperature, and 11.0 µL (0.100 mmol, 1.00 equiv) of 1-bromo-4-fluorobenzene was added as an internal standard. The crude reaction mixture was analyzed by ^{19}F NMR spectroscopy to determine the yield of aryl fluoride. ^{19}F NMR chemical shifts were compared to authentic samples of the aryl fluoride product to confirm the identity of the product, and the identities of the products were further assessed by GC/MS.

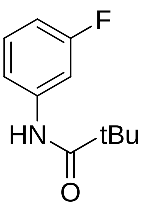
General Procedure for the Fluorination of Arenes through Ir-Catalyzed C-H Borylation

To an oven-dried 4 mL vial was added arene (0.10 mmol, 1.0 equiv), and 0.2 mL of a stock solution containing 0.1 mol% $[Ir(COD)OMe]_2$, 0.2 mol% 4,4'-di-*tert*-butyl bipyridine (dtbpy), and 0.75 equiv of B_2Pin_2. The vial was sealed with a Teflon-lined cap and heated at 80 ^oC for 18 h. The solution was allowed to cool, and the volatile components were removed in vacuo. To the crude ArBPin was added AgF (25 mg, 0.20 mmol, 2.0 equiv), $(^tBuCN)_2CuOTf$ (76 mg, 0.20 mmol, 2.0 equiv), $[Me_3pyF]PF_6$ (86 mg, 0.30 mmol, 3.0 equiv) and THF (2.0 mL). The vial was sealed with a Teflon-lined cap and heated at 50 ^oC with vigorous stirring for 18 h. The solution was allowed to cool to room temperature, and 11.0 µL (0.100 mmol, 1.00 equiv) of 1-bromo-4-fluorobenzene was added as an internal standard. The crude reaction mixture was analyzed by ^{19}F NMR spectroscopy to determine the yield of aryl fluoride. ^{19}F NMR chemical shifts were compared to authentic samples of the aryl fluoride product to confirm the identity of the product, and the identities of the products were further confirmed by GC/MS.

General Procedure for the Fluorination of Aryl Bromides through Pd-Catalyzed C-Br Borylation

To an oven-dried 4 mL vial was added (dppf)$PdCl_2$ (2.2 mg, .0030 mmol, 3.0 mol%), KOAc (29 mg, 0.30 mmol, 3.0 equiv), B_2Pin_2 (28 mg, 0.11 mmol, 1.1 equiv) and dioxane (0.5 mL). The aryl bromide (0.10 mmol, 1.0 equiv) was added (solid aryl bromides were weighed in the vial prior to adding dioxane, and liquid aryl bromides were added neat by syringe after the addition of dioxane). The vial was sealed with a Teflon-lined cap and heated at 80 °C for 18 h. The solution was allowed to cool and filtered through a short plug of Celite with EtOAc, and the volatile components were removed in vacuo. To the crude ArBPin was added AgF (25 mg, 0.20 mmol, 2.0 equiv), $(^tBuCN)_2CuOTf$ (76 mg, 0.20 mmol, 2.0 equiv), $[Me_3pyF]PF_6$ (86 mg, 0.30 mmol, 3.0 equiv) and THF (2.0 mL). The vial was sealed with a Teflon-lined cap and heated at 50 °C with vigorous stirring for 18 h. The solution was allowed to cool to room temperature, and 11.0 µL (0.100 mmol, 1.00 equiv) of 1-bromo-4-fluorobenzene was added as an internal standard. The crude reaction mixture was analyzed by ^{19}F NMR spectroscopy to determine the yield of aryl fluoride. ^{19}F NMR chemical shifts were compared to authentic samples of the aryl fluoride product to confirm the identity of the product. The identities of the products were further confirmed by GC/MS.

Synthesis of N-(3-fluorophenyl)pivalamide (2o)

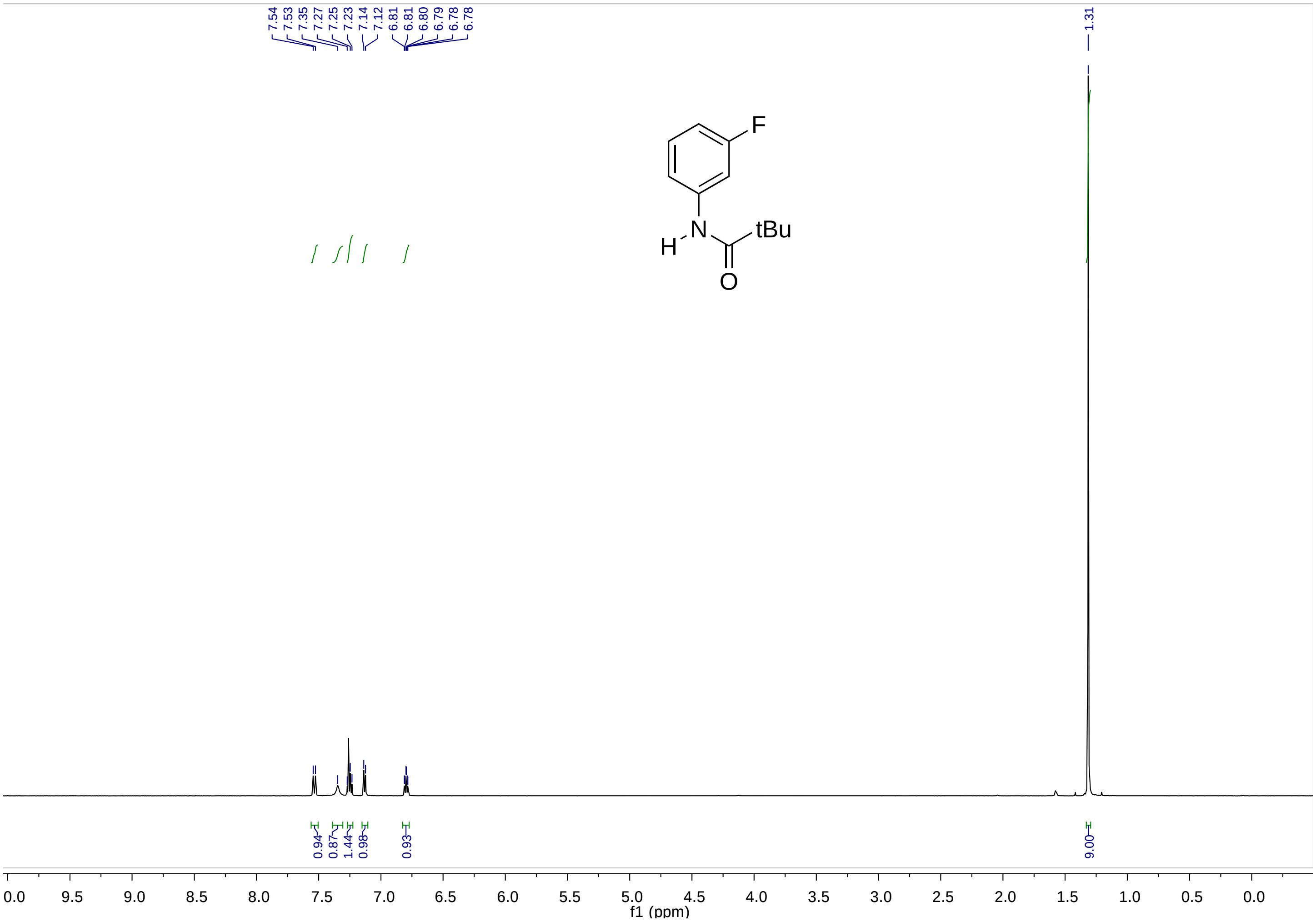


To an oven-dried 20 mL vial was added AgF (127 mg, 1.00 mmol, 2.00 equiv), $(^tBuCN)_2CuOTf$ (379 mg, 1.00 mmol, 2.00 equiv), 1-fluoro-2,4,6-trimethylpyridinium hexafluorophosphate (428 mg, 1.50 mmol, 3.00 equiv), **1o** (152 mg, 0.500 mmol, 1.00 equiv) and THF (10 mL). The vial was sealed with a Teflon-lined cap, and the reaction was heated at 50 °C for 18 h. The reaction was cooled, diluted with 15 mL of ether, and filtered through Celite. The filtrate was concentrated and purified by silica gel chromatography eluting with 9:1 hexanes:ethyl acetate (R_f=0.18) to afford a white solid (63 mg, 0.32 mmol, 64% yield).

^1H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, *J* = 11.0 Hz, 1H), 7.35 (s, 1H), 7.25 (t, *J* = 11.4 Hz, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.83 – 6.77 (m, 1H), 1.31 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.60 (s), 163.04 (d, *J* = 244.7 Hz), 139.58 (d, *J* = 11.0 Hz), 129.94 (d, *J* = 9.4 Hz), 115.01 (d, *J* = 2.9 Hz), 110.85 (d, *J* = 21.4 Hz), 107.44 (d, *J* = 26.4 Hz), 39.70 (s), 27.56 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.51 – -111.61 (m).


7.54
7.53
7.35
7.27
7.25
7.23
7.14
7.12
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6.81
6.80
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6.78
6.78
1.31
F
N
H
tBu
O
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0.87
1.44
0.98
0.93
9.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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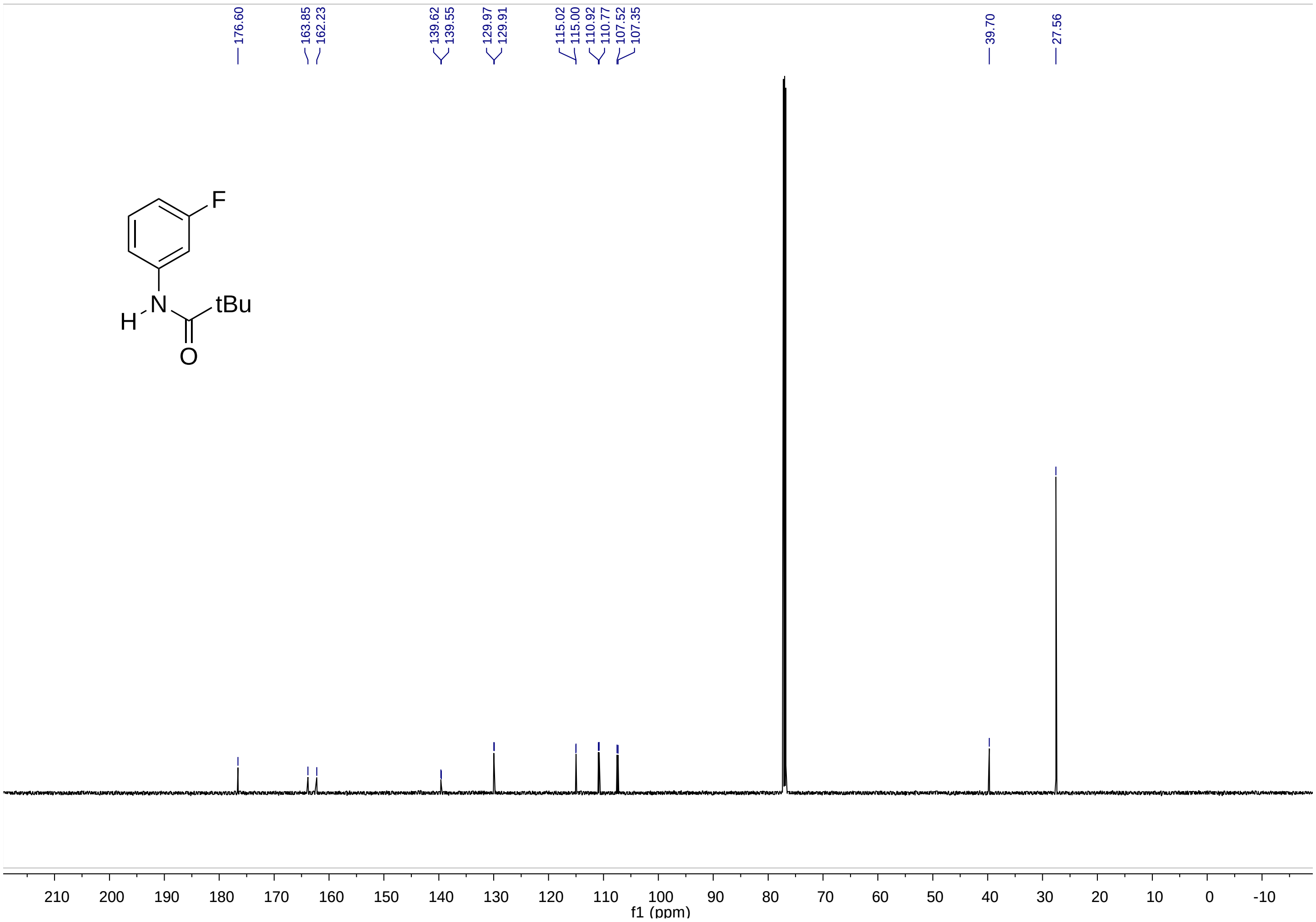
1.0
0.5
0.0
f1 (ppm)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200
190
180
170
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50
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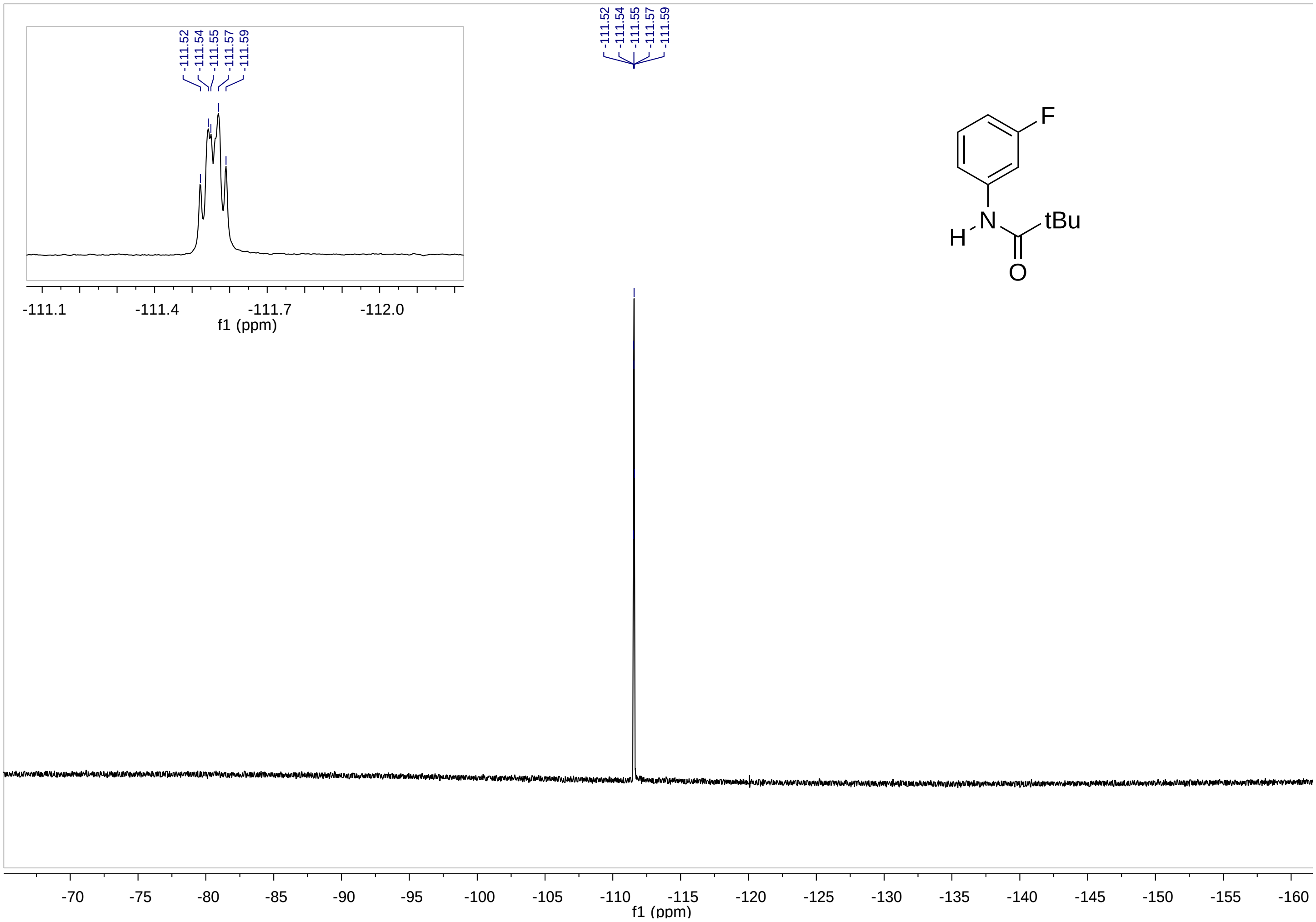
30
20
10
0
-10
f1 (ppm)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-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

Solution NMR Analysis of the Reaction Between (^{t}BuCN)$_2$CuOTf and [Me$_3$pyF]PF$_6$

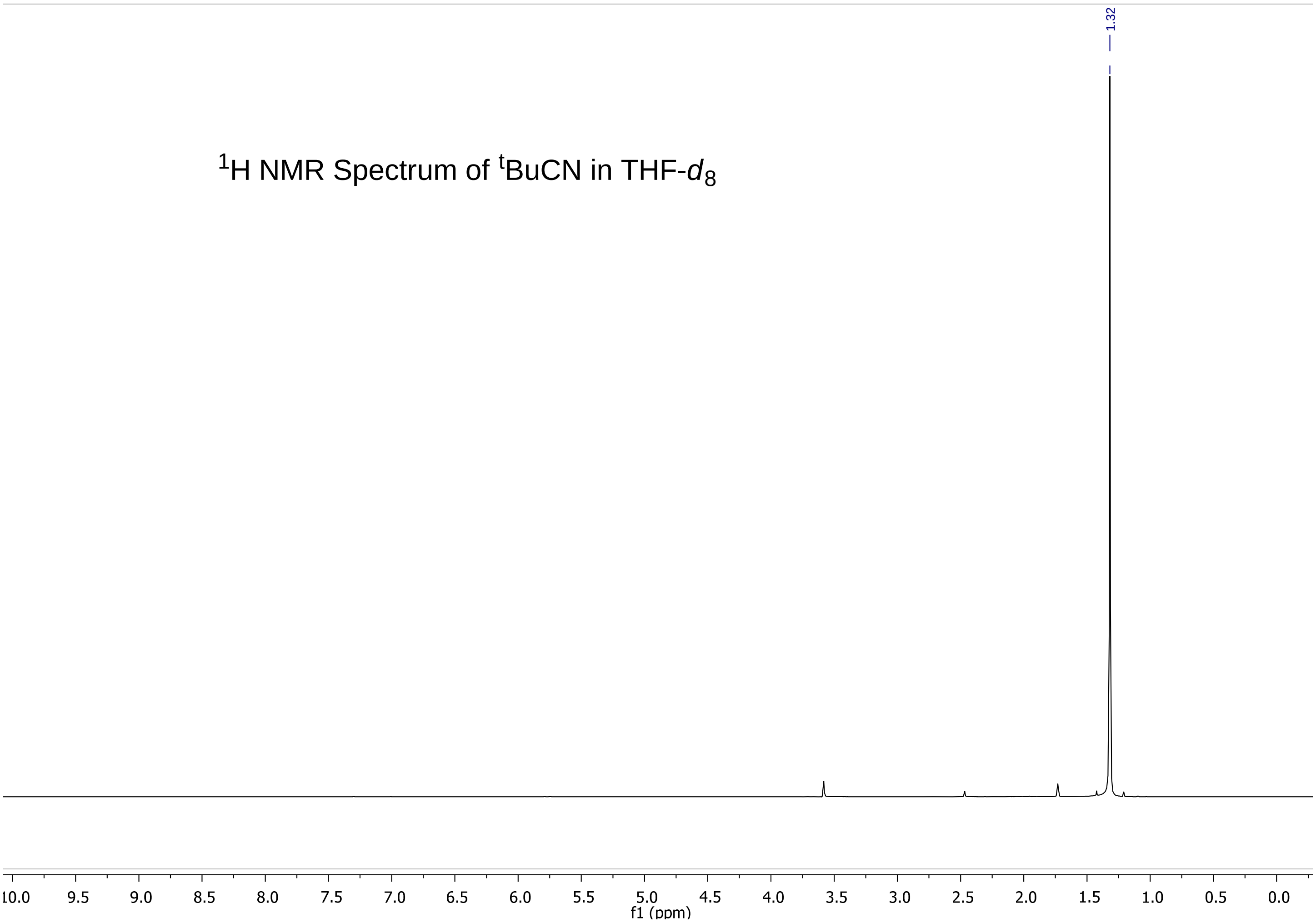
To an oven-dried 4 mL vial was added (^{t}BuCN)$_2$CuOTf (38 mg, 0.10 mmol, 1.0 equiv), [Me$_3$pyF]PF$_6$ (29 mg, 0.10 mmol, 1.0 equiv) and THF (1.0 mL) or THF-d_8 (1.0 mL). The suspension was stirred at room temperature until the solution became homogenous (5-10 min). The solution was transferred to an oven-dried NMR tube and analyzed by ^{1}H and ^{19}F NMR spectroscopy.

^{1}H NMR (600 MHz, THF-d_8) δ 7.49 (s, 2H), 2.66 (s, 6H), 2.48 (s, 3H), 1.33 (s, 18H).

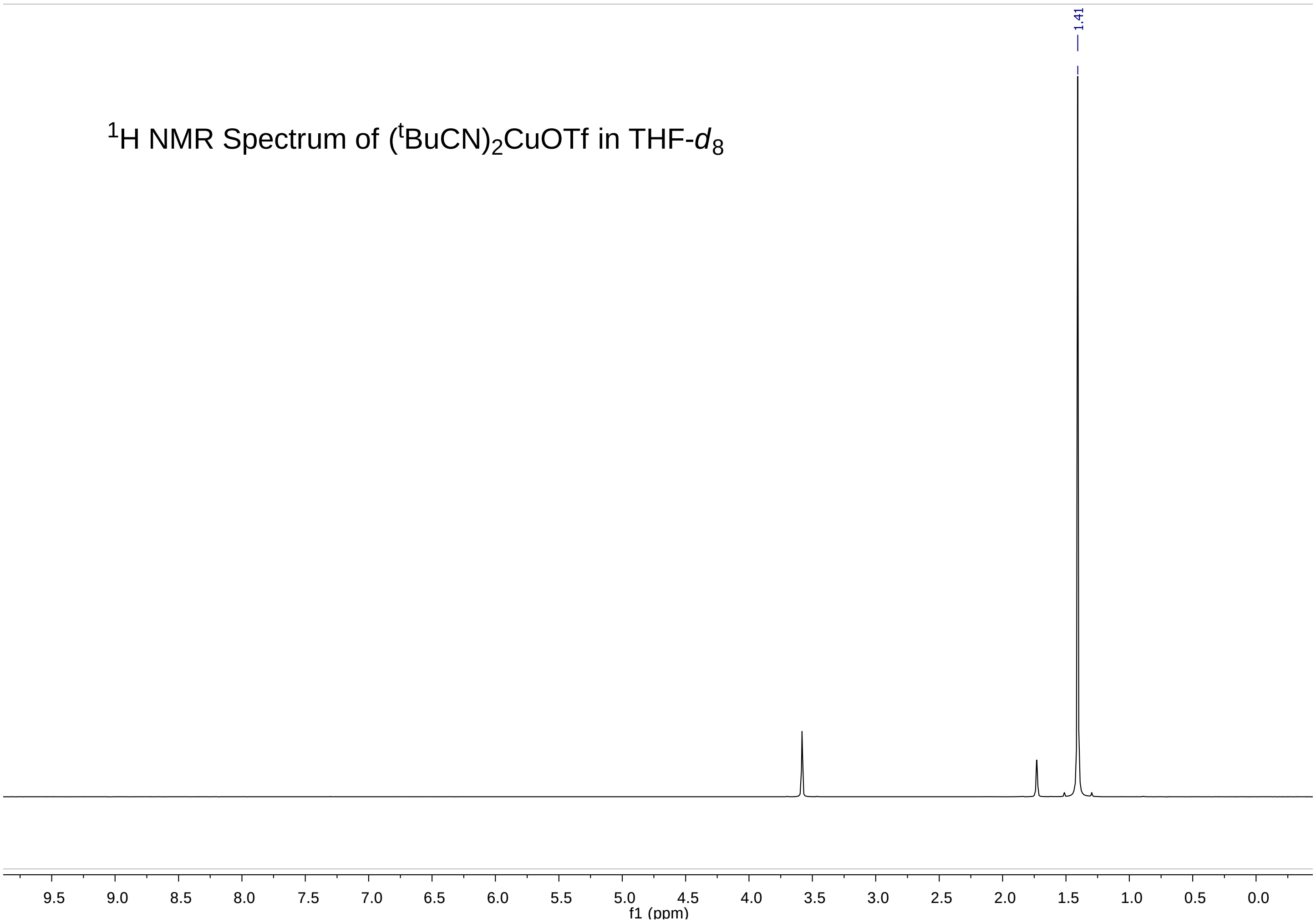
^{13}C NMR (101 MHz, THF-d_8) δ 158.86, 151.34, 124.41, 25.81, 20.03, 17.37.

^{19}F NMR (376 MHz, THF-d_8) δ -71.00 (br, s), -72.17 (d, J = 710.1 Hz), -112.12 (s).

^{19}F NMR (376 MHz, THF-H_8) δ -71.5 (br, s), -72.00 (d, J = 710.4 Hz), -110.80 (dd, J = 66.2, 26.3 Hz).



^{1}H NMR Spectrum of ^{t}BuCN in THF-d_8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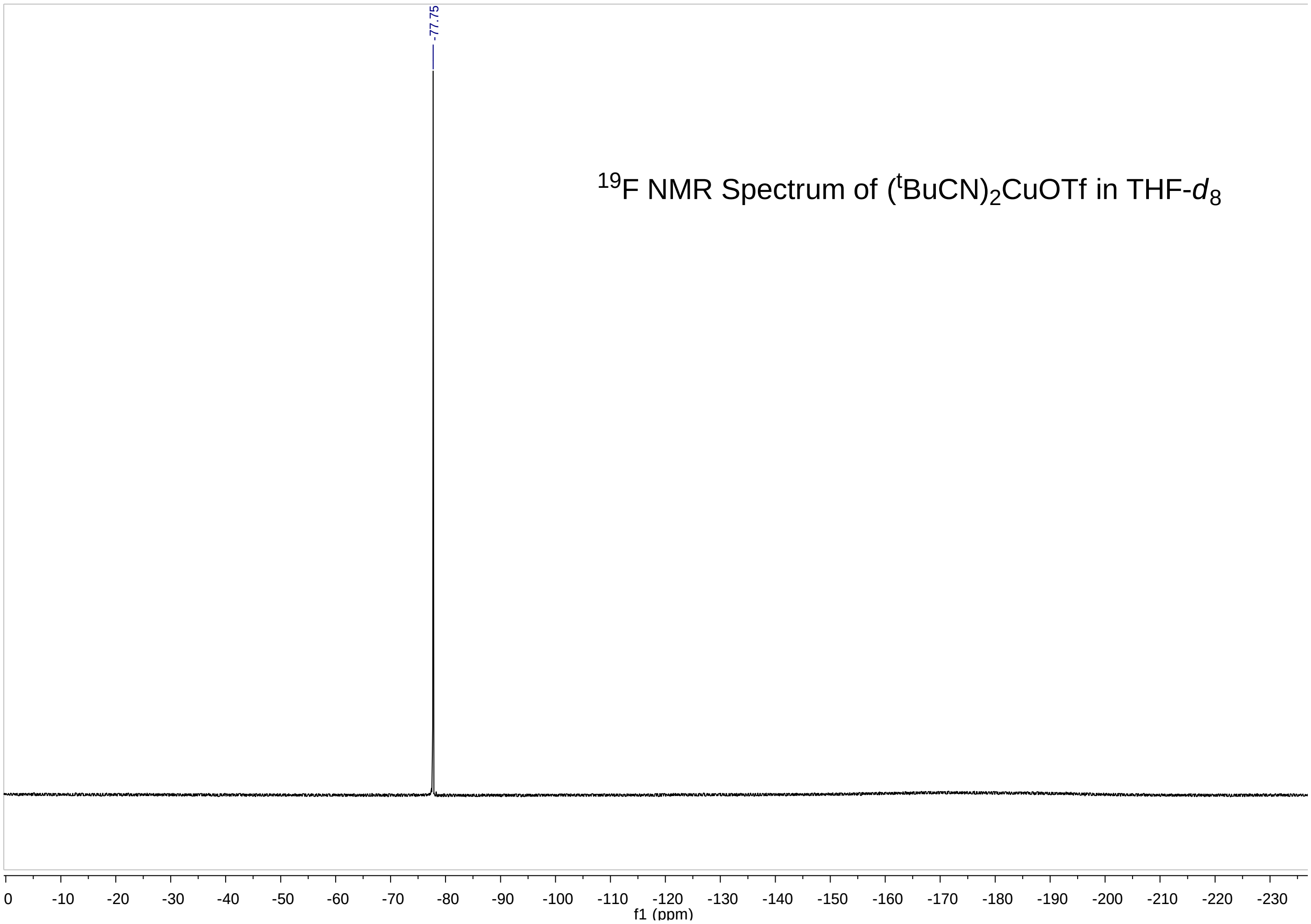
-77.75
^{19}F NMR Spectrum of (^{t}BuCN)$_2$CuOTf in THF-d_8
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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-220
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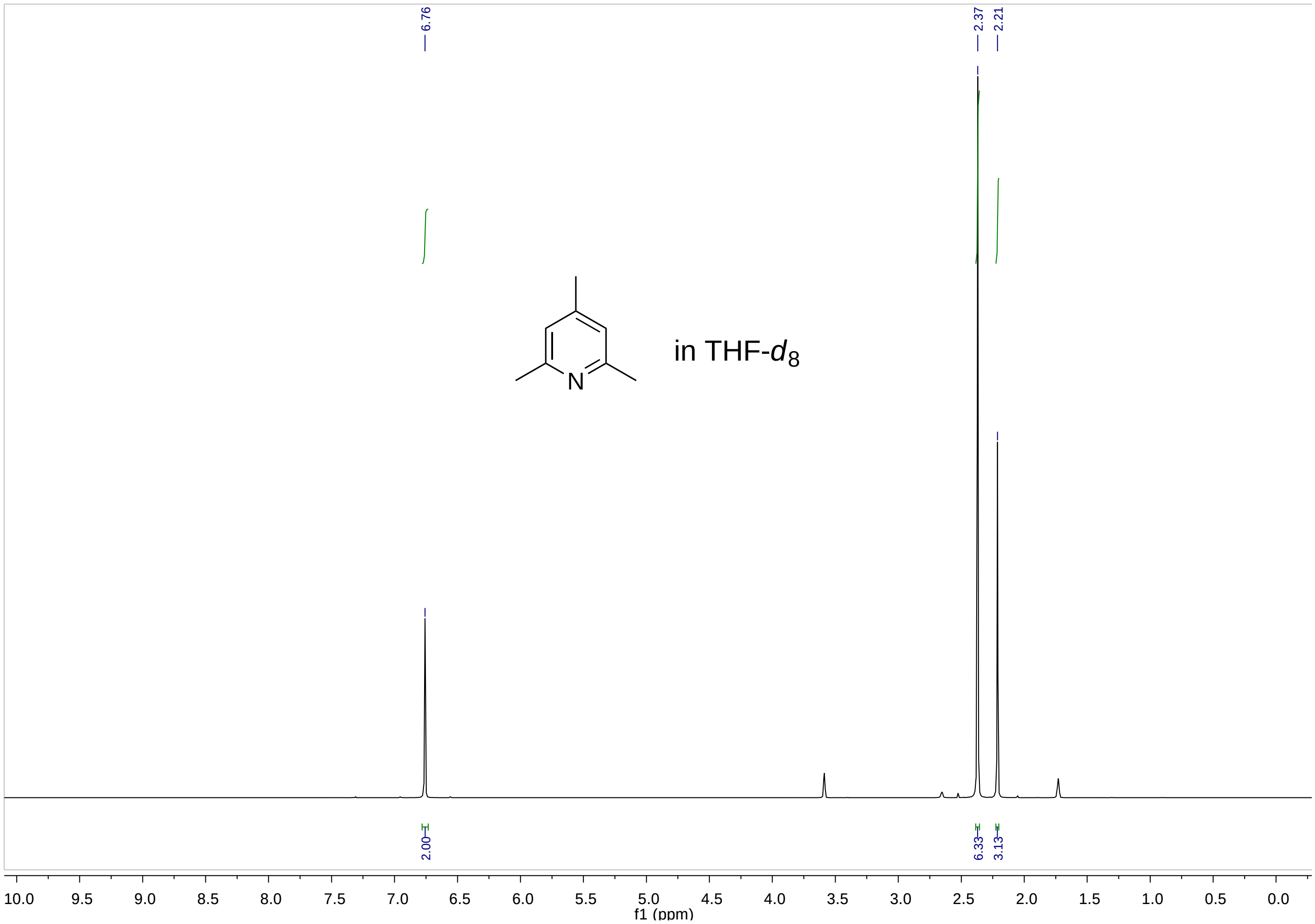
f1 (ppm)


6.76
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2.21
N
in THF-d_8
2.00
6.33
3.13
10.0
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9.0
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7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
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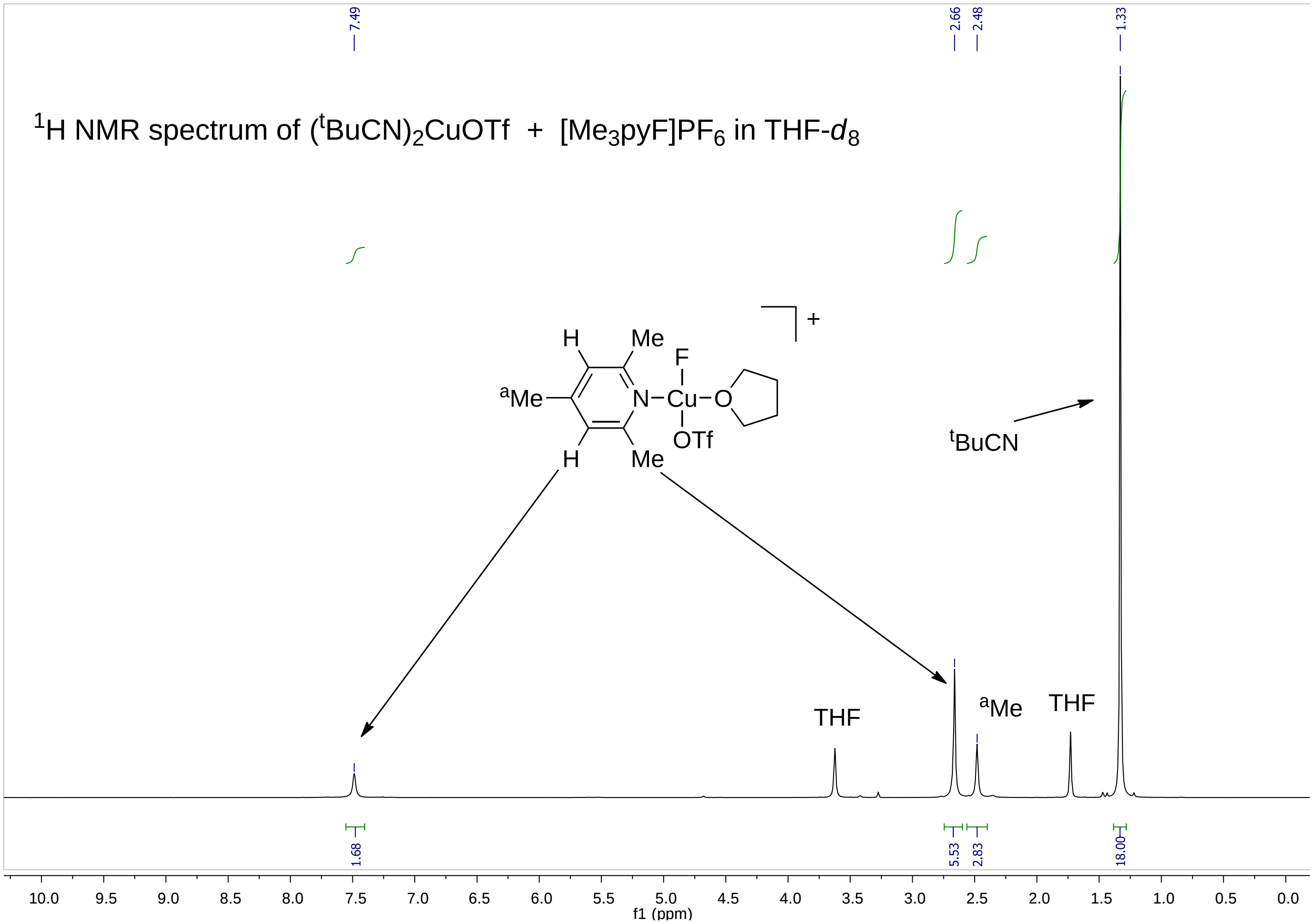
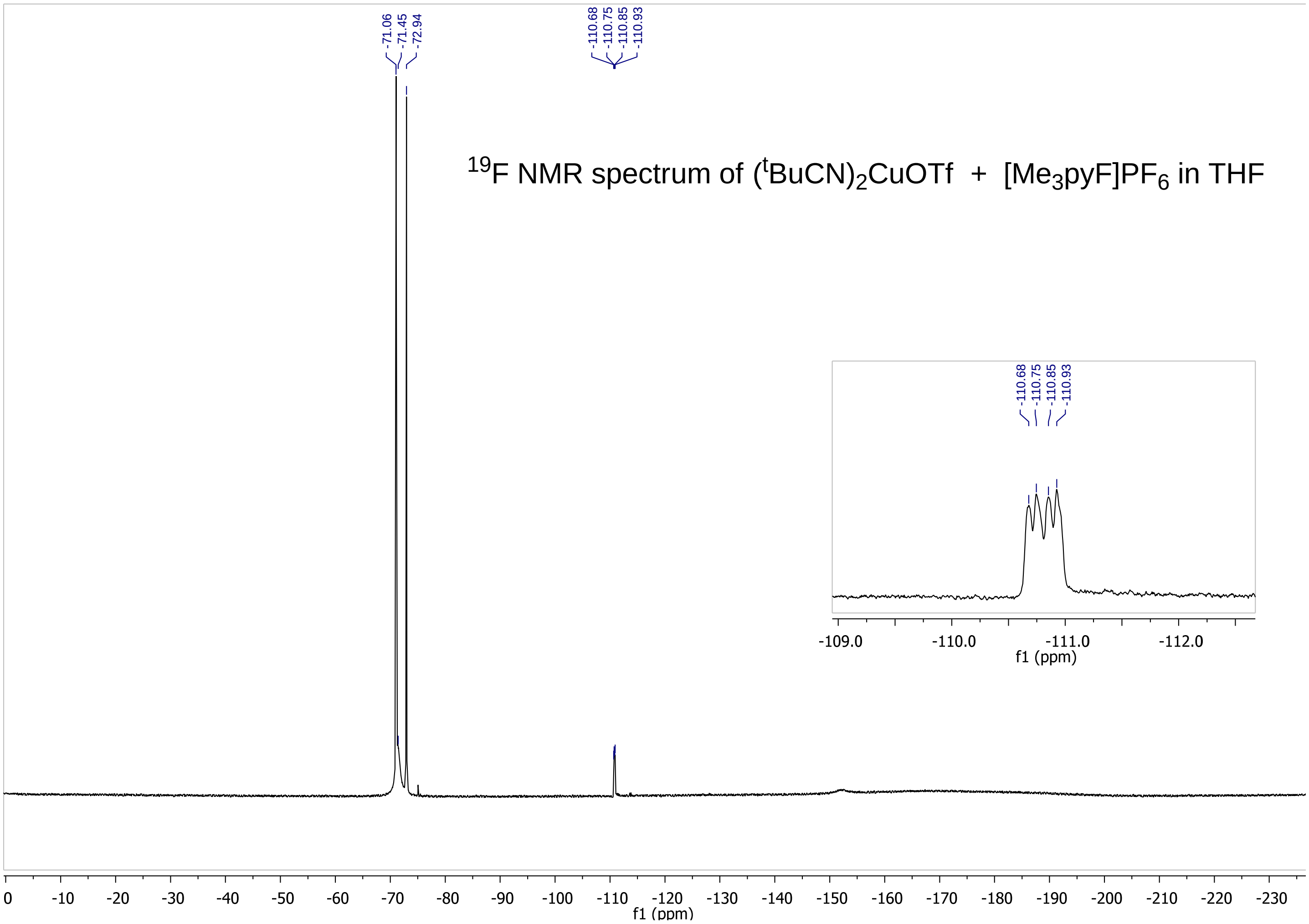
1.5
1.0
0.5
0.0
f1 (ppm)



^{1}H NMR spectrum of (^{t}BuCN)$_2$CuOTf + [Me$_3$pyF]PF$_6$ in THF-d_8



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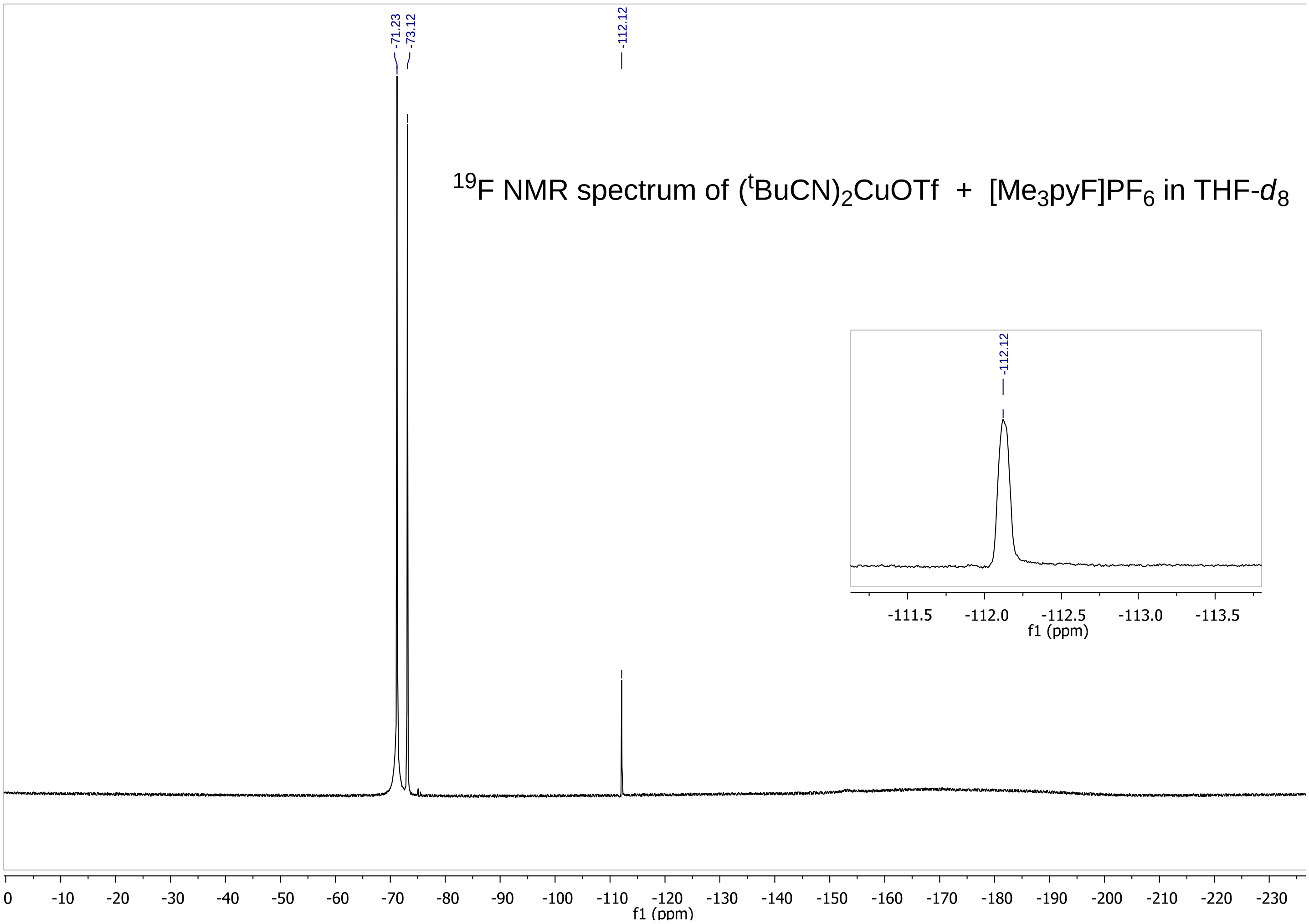
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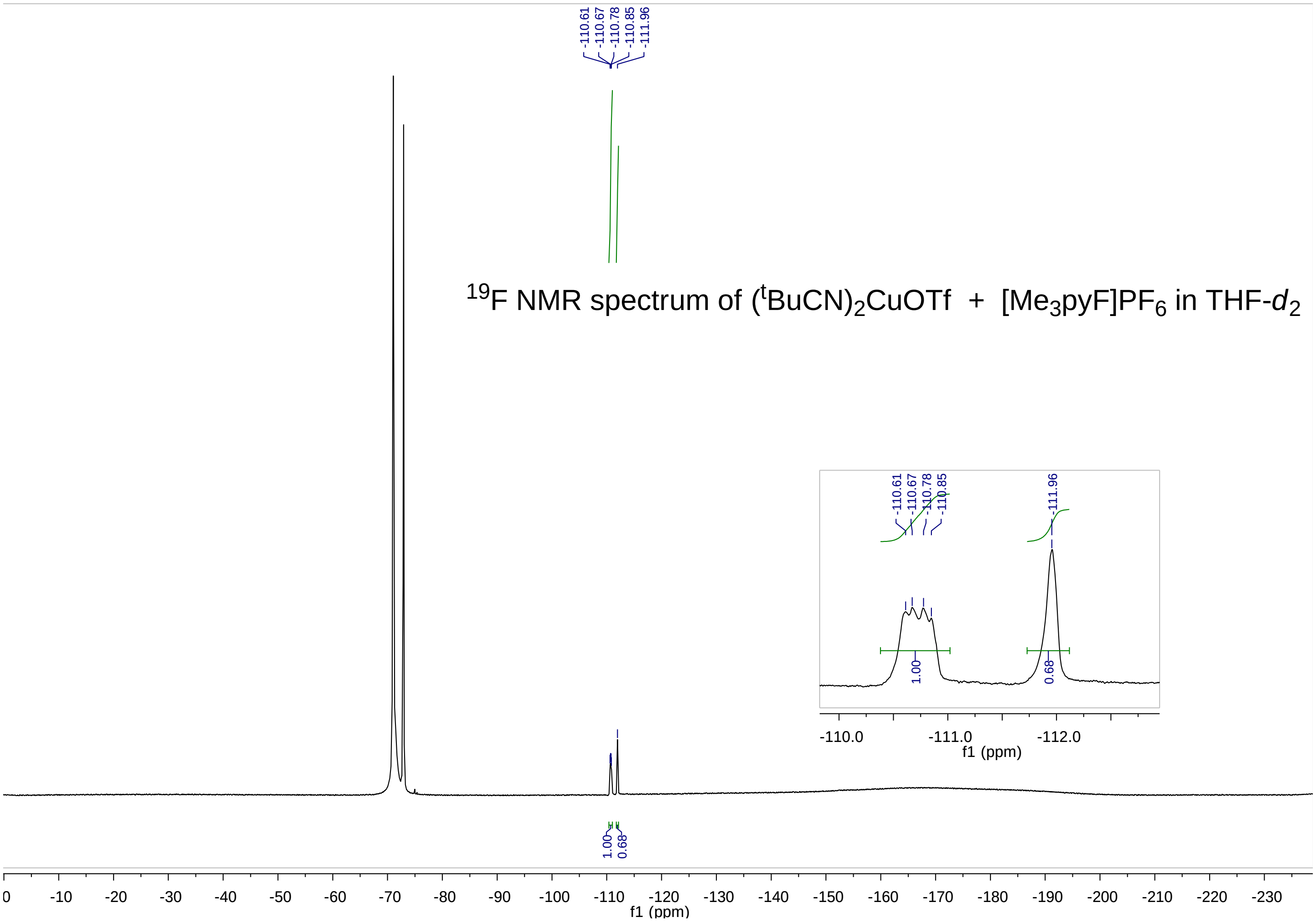
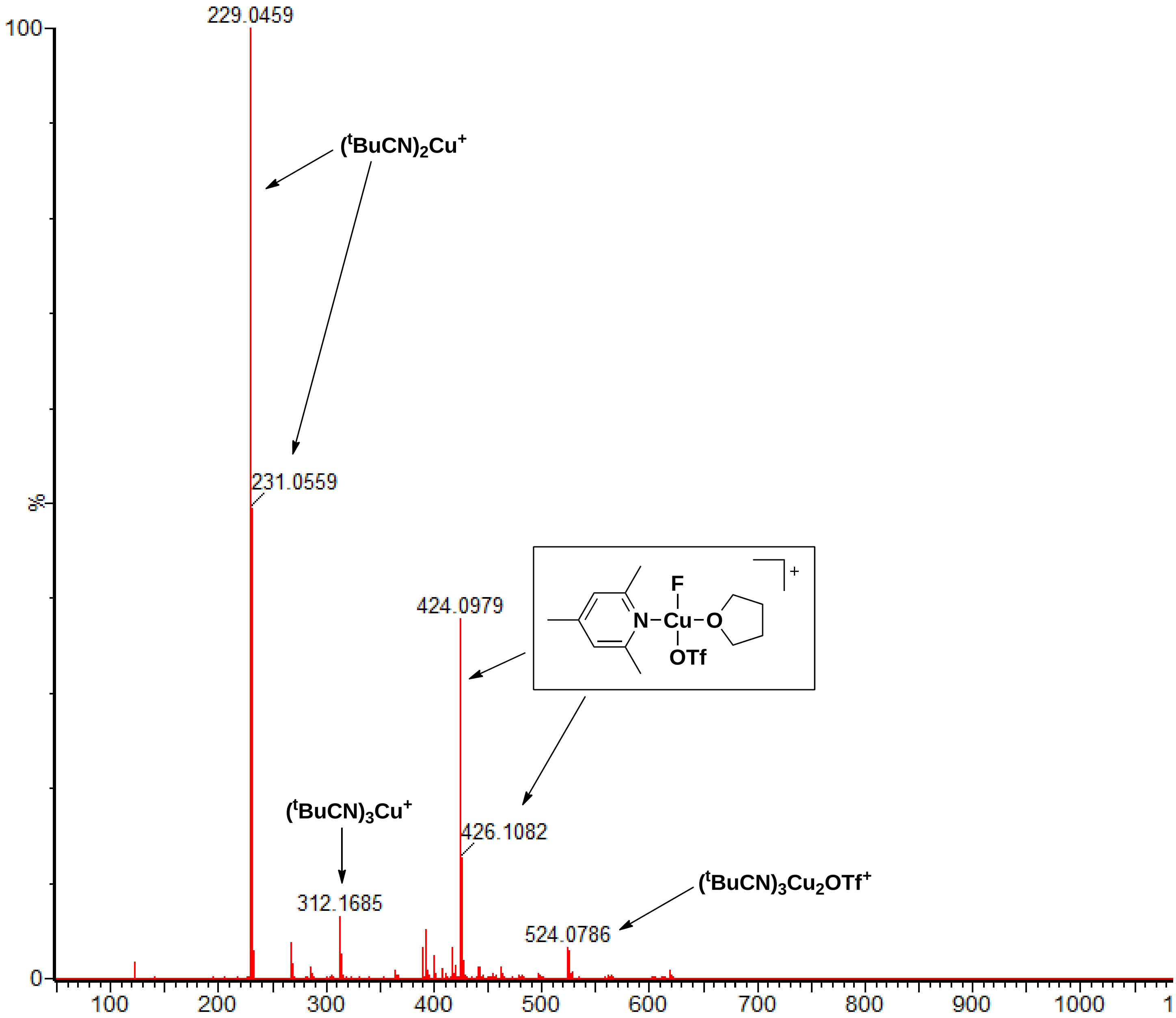


^{19}F NMR spectrum of $(^{t}BuCN)_2CuOTf$ + $[Me_3pyF]PF_6$ in THF-d_2

ESI-MS Analysis of the Reaction Between (^{t}BuCN)$_2$CuOTf and [Me$_3$pyF]PF$_6$

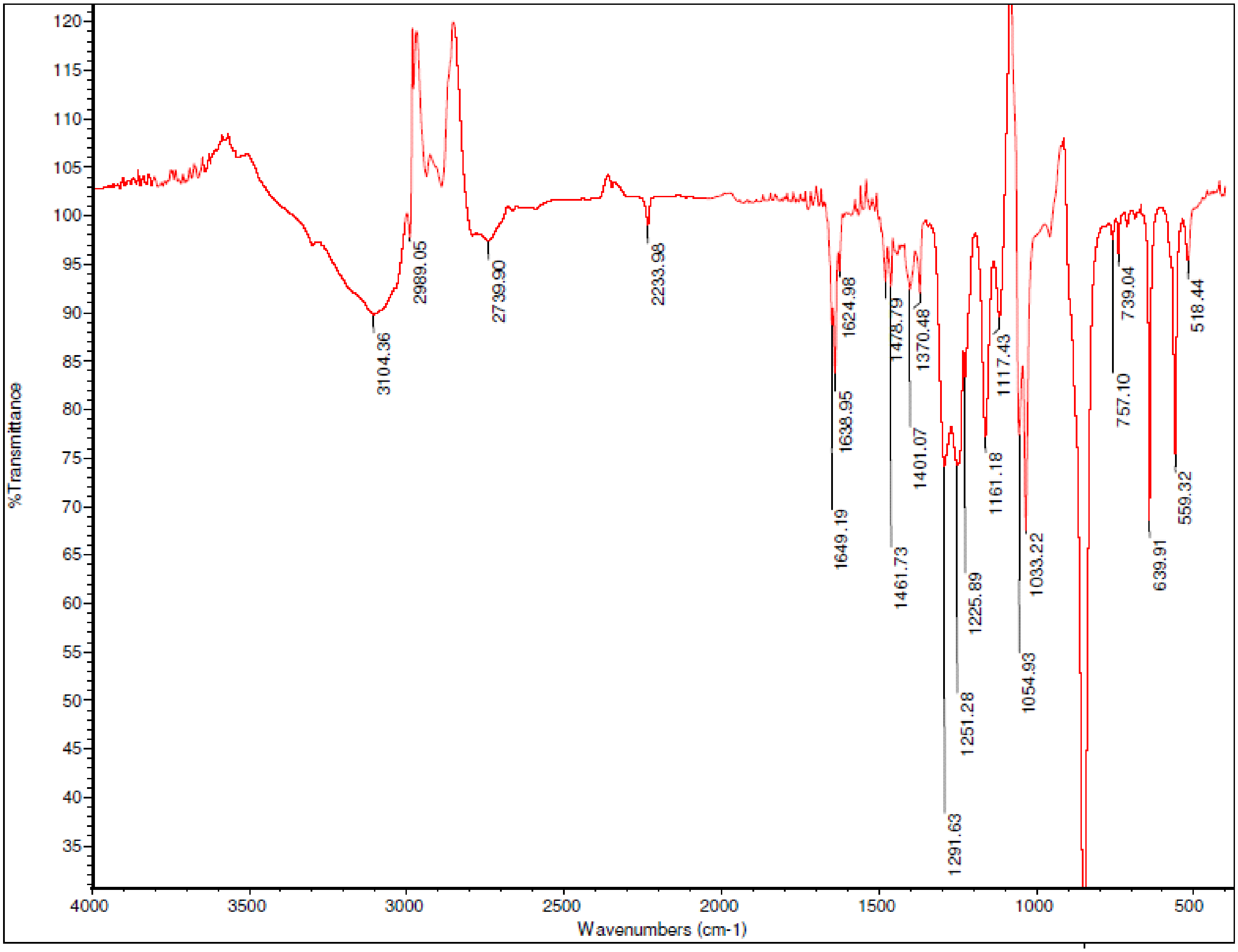
To an oven-dried flask was added (^{t}BuCN)$_2$CuOTf (38 mg, 0.10 mmol, 1.0 equiv), [Me$_3$pyF]PF$_6$ (29 mg, 0.10 mmol, 1.0 equiv),THF (1.0 mL) and fluorobenzene (1.0 mL). The reaction was stirred at room temperature, and the solution was continuously monitored on a Micromass Q-ToF micro mass spectrometer in positive-ion mode over 10 minutes under an inert atmosphere using electrospray ionization. Capillary voltage: 2900 V. Cone voltage: 15 V. Extraction voltage: 0.5 V. Source temperature: 91°C. Desolvation temperature: 191°C. cone gas flow rate, 100 L/h; desolvation gas flow, 200 L/h; collision voltage, 2 V; MCP voltage, 2700 V.



229.0459
(ᵗBuCN)₂Cu⁺
231.0559
424.0979
426.1082
F
N–Cu–O
OTf
+
(ᵗBuCN)₃Cu⁺
312.1685
(ᵗBuCN)₃Cu₂OTf⁺
524.0786
100
%
0
100
200
300
400
500
600
700
800
900
1000
1

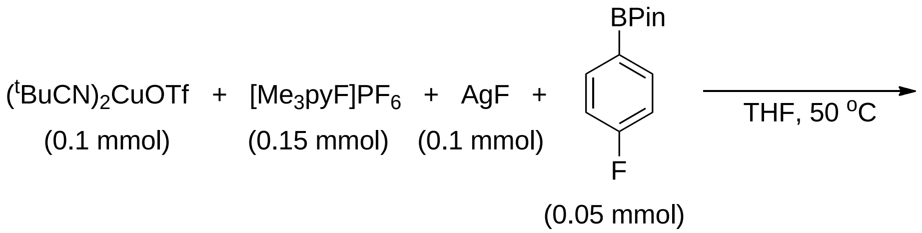
Solution IR Spectroscopy of the Reaction Between (^{t}BuCN)$_2$CuOTf and [Me$_3$pyF]PF$_6$

To an oven-dried vial was added (^{t}BuCN)$_2$CuOTf (38 mg, 0.10 mmol, 1.0 equiv), [Me$_3$pyF]PF$_6$ (29 mg, 0.10 mmol, 1.0 equiv) and THF (1.0 mL). The reaction mixture was stirred at room temperature for 5 minutes. This reaction mixture was transferred to an IR solution cell and analyzed by FT-IR spectroscopy (Thermo Scientific Nicolet iS5 FT-IR). A blank sample of THF was acquired and subtracted from the spectrum of the reaction..

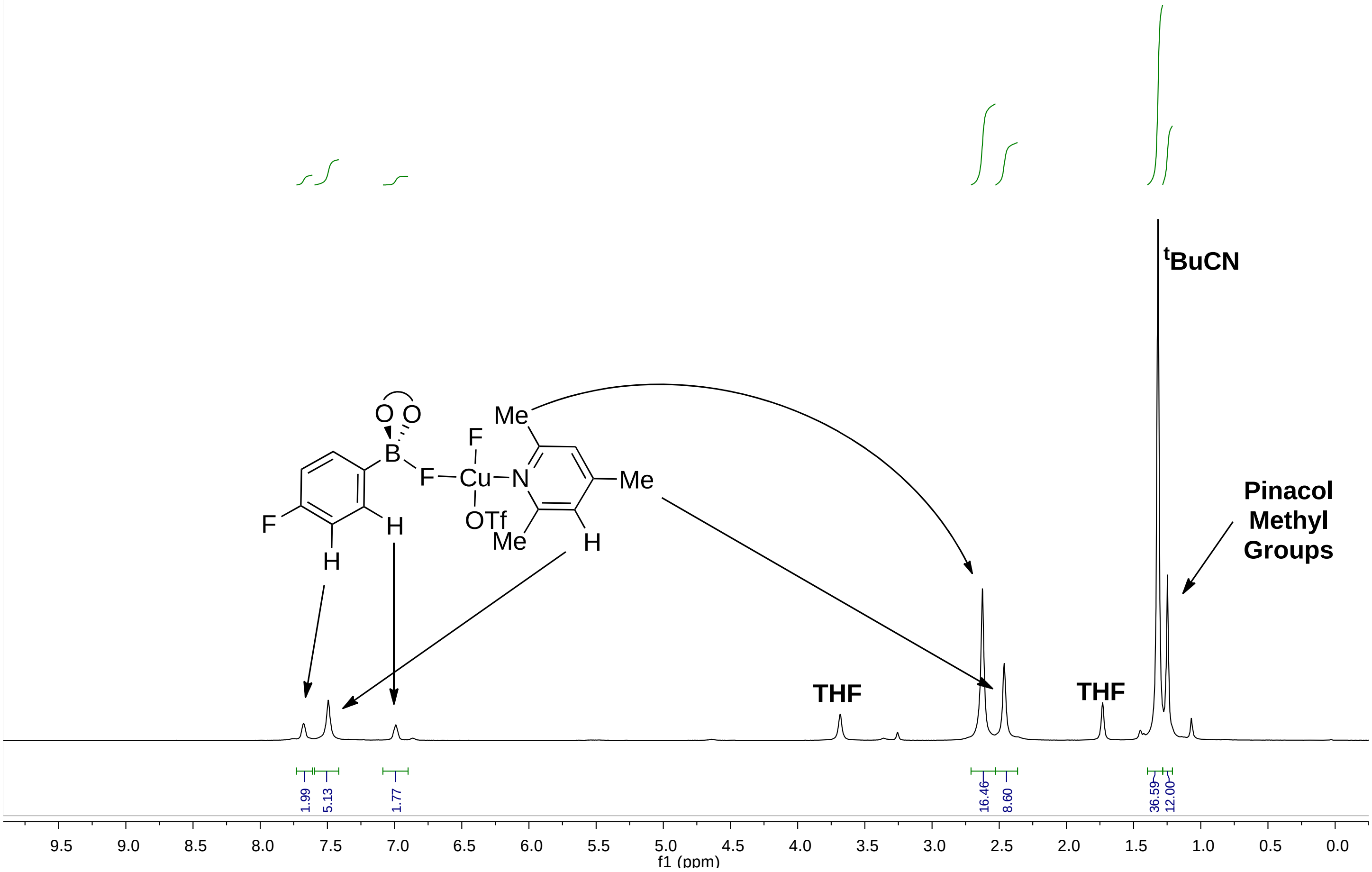

%Transmittance
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
3104.36
2989.05
2739.90
2233.98
1649.19
1638.95
1624.98
1478.79
1461.73
1401.07
1370.48
1291.63
1251.28
1225.89
1161.18
1117.43
1054.93
1033.22
757.10
739.04
639.91
559.32
518.44

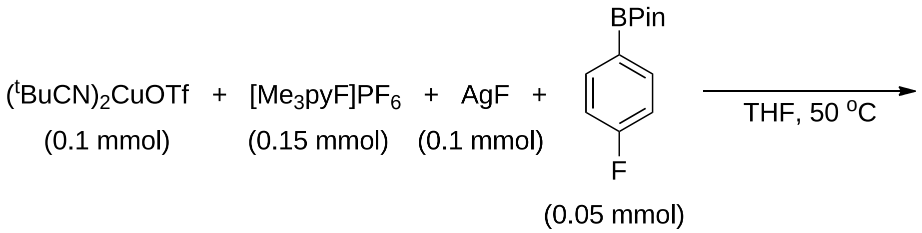
Solution NMR Analysis of the Reaction Between (^{t}BuCN)$_2$CuOTf, [Me$_3$pyF]PF$_6$, AgF and 1l

To an oven-dried 4 mL vial was added (^{t}BuCN)$_2$CuOTf (38 mg, 0.10 mmol, 2.0 equiv), [Me$_3$pyF]PF$_6$ (43 mg, 0.15 mmol, 3.0 equiv), 4-fluorophenyl pinacolboronate (**1l**, 11 mg, .050 mmol, 1.0 equiv), AgF (13 mg, 0.10 mmol, 2.0 equiv) and THF (1.0 mL) or THF-d_8 (1.0 mL). 1-bromo-4-fluorobenzne (11.0 μL, 0.100 mmol) was added as an internal standard for reactions monitored by ^{19}F NMR spectroscopy. The reaction mixture was stirred at 50 ^{o}C for the indicated time. The solution was transferred to an oven-dried NMR tube and analyzed by ^{1}H, ^{11}B and ^{19}F NMR spectroscopy.

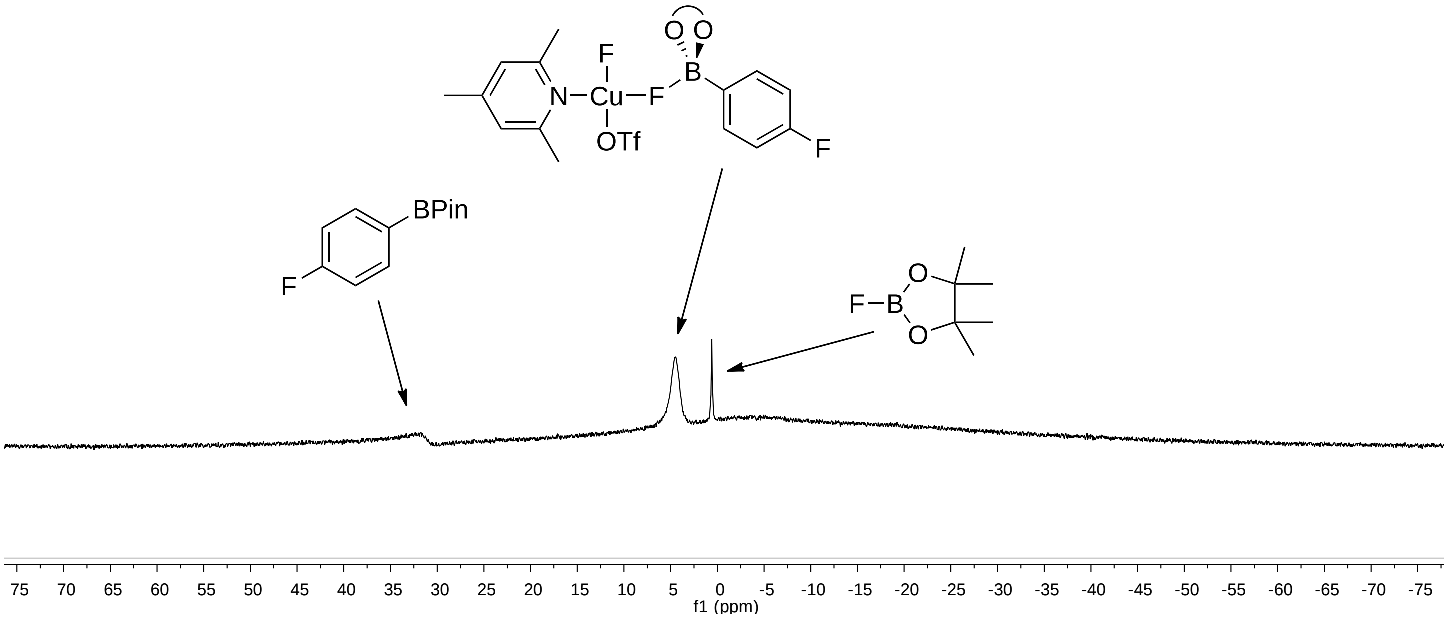


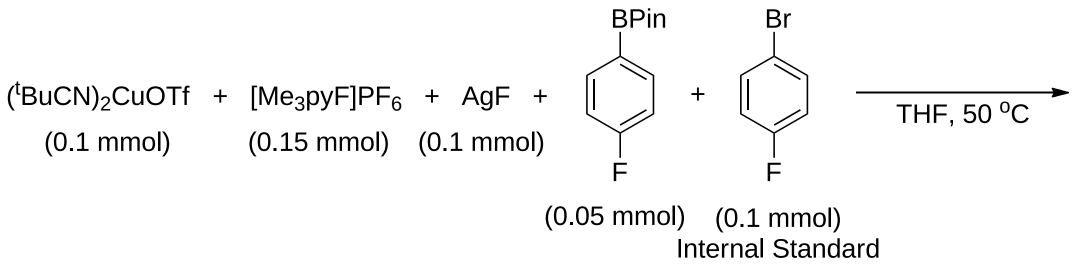
^{1}H NMR spectrum after 20 minutes at 50 ^{o}C



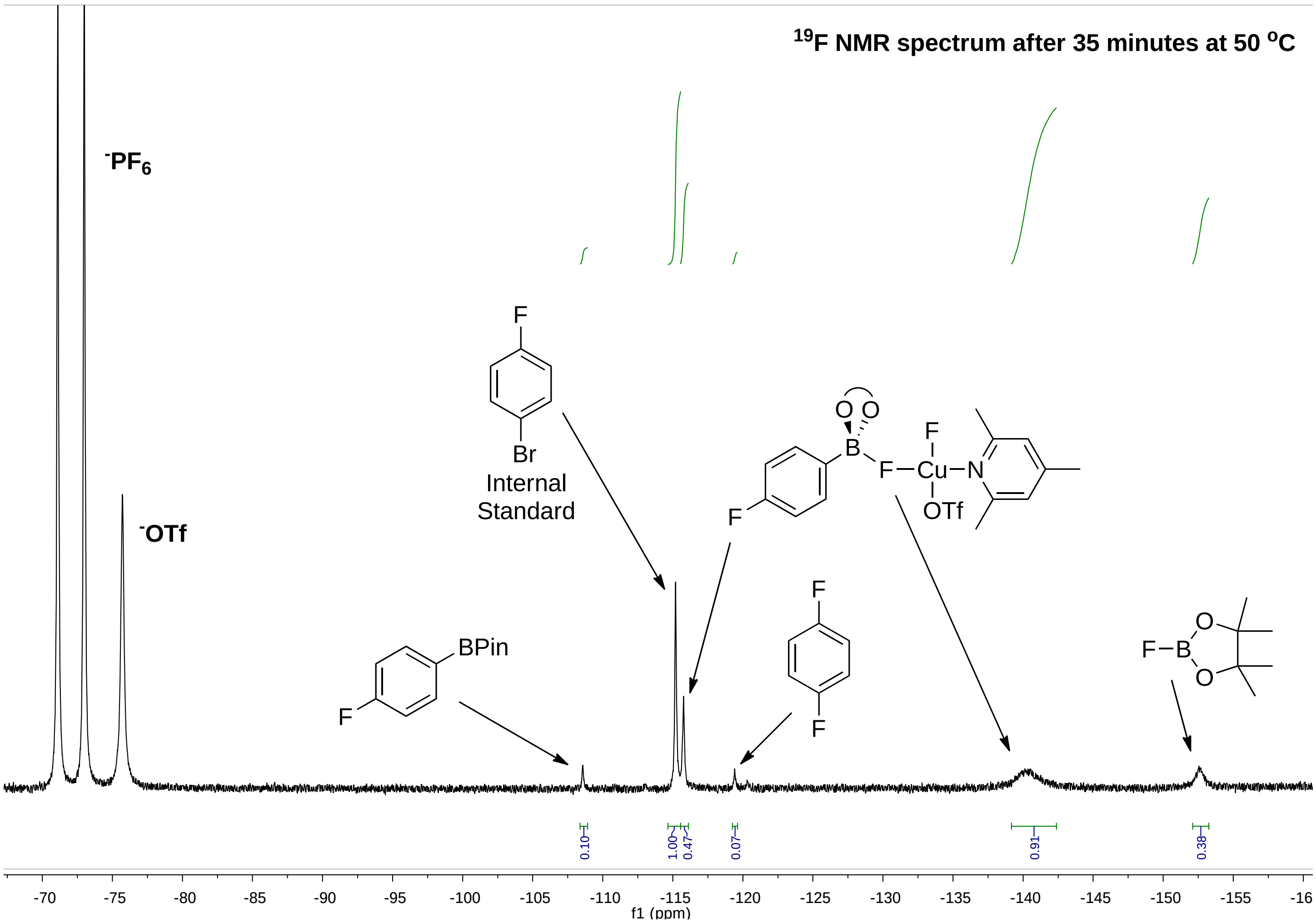


^{11}B NMR spectrum after 20 minutes at 50 ^{o}C

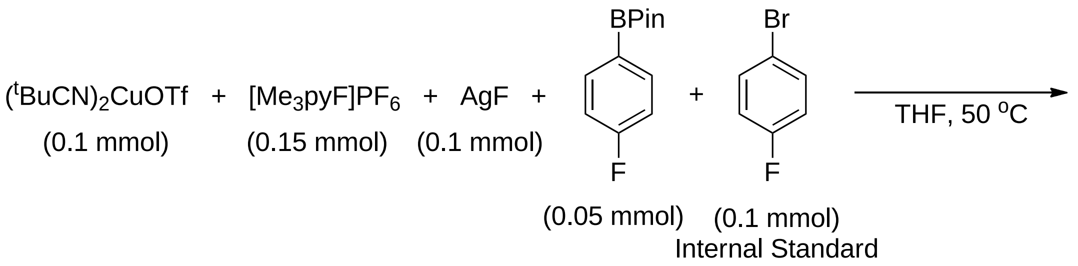


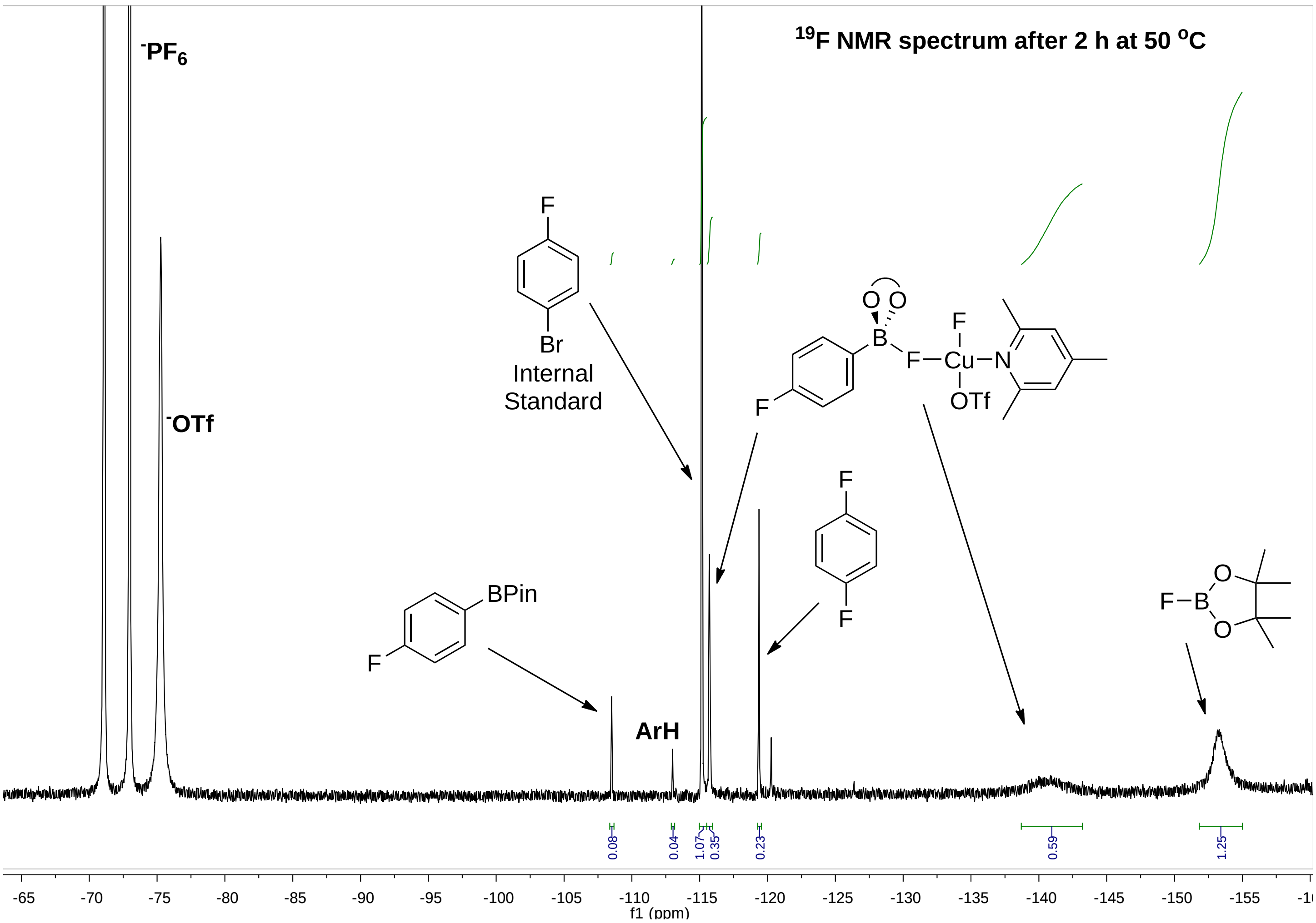


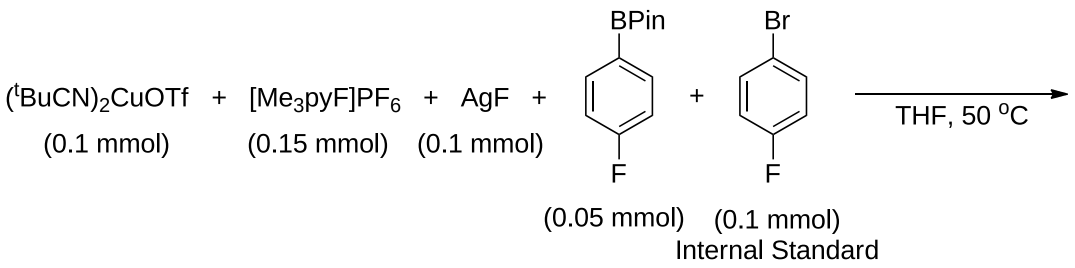
(^{t}BuCN)$_2$CuOTf (0.1 mmol)
+ [Me$_3$pyF]PF$_6$ (0.15 mmol)
+ AgF (0.1 mmol)
+ BPin, F (0.05 mmol)
+ Br, F (0.1 mmol) Internal Standard
THF, 50 ^{o}C

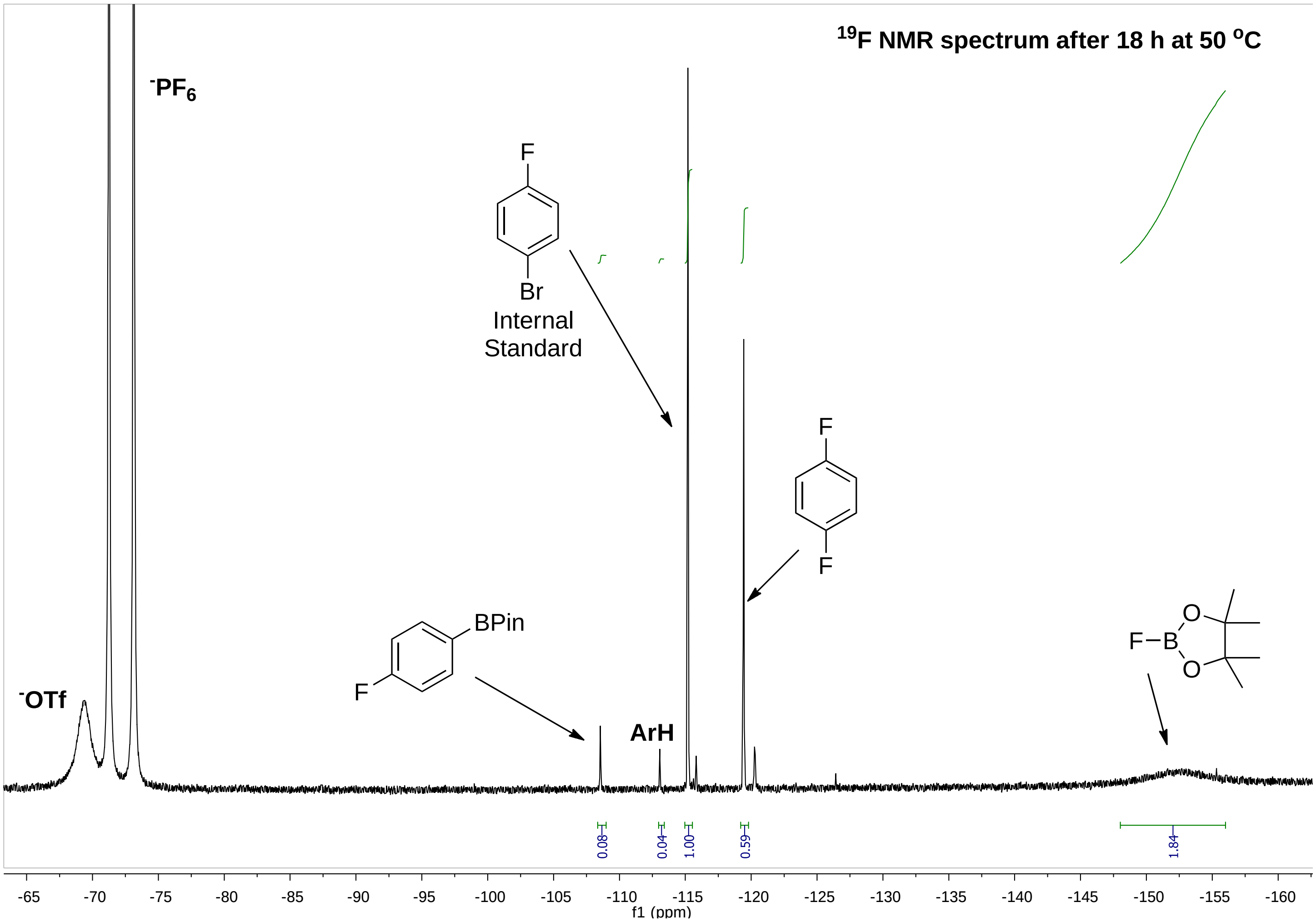


^{19}F NMR spectrum after 35 minutes at 50 ^{o}C
$^-$PF$_6$
$^-$OTf
BPin
F
Br
Internal Standard
F
O O
B
F—Cu—N
F
OTf
F
F
F—B
O
O
0.10
1.00
0.47
0.07
0.91
0.38
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-16
f1 (ppm)


(tBuCN)2CuOTf
(0.1 mmol)
+
[Me3pyF]PF6
(0.15 mmol)
+
AgF
(0.1 mmol)
+
BPin
F
(0.05 mmol)
+
Br
F
(0.1 mmol)
Internal Standard
THF, 50 oC


19F NMR spectrum after 2 h at 50 oC
-PF6
-OTf
F
Br
Internal Standard
O O
B
F
F
Cu
N
OTf
F
F
F
BPin
F
ArH
F
B
O
O
0.08
0.04
1.07
0.35
0.23
0.59
1.25
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
f1 (ppm)


(^{t}BuCN)$_2$CuOTf + [Me$_3$pyF]PF$_6$ + AgF +
(0.1 mmol)
(0.15 mmol)
(0.1 mmol)
BPin
F
(0.05 mmol)
+
Br
F
(0.1 mmol)
Internal Standard
THF, 50 ^{o}C


^{19}F NMR spectrum after 18 h at 50 ^{o}C
$^-$PF$_6$
$^-$OTf
F
Br
Internal Standard
F
F
BPin
F
ArH
F–B O O
0.08
0.04
1.00
0.59
1.84
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

DFT Calculations

WB97XD/6-31G++(d,p) calculations were performed with Gaussian 09. Structure optimizations were performed in both the gas-phase and in a THF solvent continuum. All structures were confirmed to be stationary points by the absence of negative frequency values.

Cartesian Coordinates for WB97XD/6-31G++(d,p) optimized stationary points in the gas-phase.

$C_{13}H_{19}CuF_4NO_4S(1+)$

$[(Me_3py)(THF)Cu(F)(OTf)]^+$

	Atomic Number		***X***	***Y***	***Z***
1	29	0	-0.111435	-0.876319	-0.050266
2	8	0	1.718854	-1.311257	-0.034244
3	6	0	2.275541	-1.898616	1.201726
4	6	0	2.232782	-2.009915	-1.211820
5	6	0	3.215434	-2.993544	0.714236
6	1	0	2.770531	-1.068311	1.706099
7	1	0	1.444688	-2.269855	1.803285
8	6	0	3.554821	-2.567921	-0.720190
9	1	0	1.526604	-2.802828	-1.480892
10	1	0	2.306509	-1.262351	-2.002542
11	1	0	2.707344	-3.961408	0.715449
12	1	0	4.099633	-3.067379	1.349305
13	1	0	3.893140	-3.400816	-1.338837
14	1	0	4.321702	-1.789016	-0.731602
15	9	0	-0.527849	-2.525027	0.321518
16	7	0	-1.926774	-0.443538	-0.055183
17	6	0	-2.533969	-0.344122	-1.257910
18	6	0	-2.556658	-0.260047	1.124218
19	6	0	-3.872473	0.008042	-1.291653
20	6	0	-3.897374	0.100176	1.097882
21	6	0	-4.579073	0.251545	-0.109832
22	1	0	-4.363005	0.089354	-2.255558
23	1	0	-4.406298	0.253318	2.043145
24	6	0	-1.805461	-0.484636	2.400915
25	1	0	-1.522557	-1.539121	2.479859
26	1	0	-0.901372	0.130858	2.451213
27	1	0	-2.432797	-0.230117	3.255080
28	6	0	-1.736552	-0.637704	-2.493767
29	1	0	-0.962592	0.121217	-2.642748
30	1	0	-1.270596	-1.627459	-2.423369
31	1	0	-2.384502	-0.640574	-3.370407
32	6	0	-6.018990	0.668924	-0.144390
33	1	0	-6.082809	1.750259	-0.308268
34	1	0	-6.553240	0.178501	-0.961238
35	1	0	-6.524987	0.442333	0.795701
36	8	0	0.265570	0.813629	-0.648277
37	16	0	0.815689	1.800501	0.439357

38	8	0	1.059202	1.038703	1.658616
39	8	0	0.044737	3.015571	0.459595
40	6	0	2.478961	2.216078	-0.300290
41	9	0	3.218849	1.112231	-0.398249
42	9	0	2.308852	2.736750	-1.505589
43	9	0	3.083901	3.082787	0.492359

$F_6P(1-)$
$(PF_6)^-$

	Atomic Number		*X*	*Y*	*Z*
1	15	0	0.000069	0.000275	-0.000209
2	9	0	0.572828	0.355880	-1.493232
3	9	0	-0.999615	1.296907	-0.073233
4	9	0	1.167003	0.936752	0.669666
5	9	0	-0.573245	-0.356177	1.492786
6	9	0	0.999864	-1.297561	0.074447
7	9	0	-1.166949	-0.936258	-0.670085

$C_{13}H_{19}CuF_{10}NO_4PS$
$[(Me_3py)(THF)Cu(F)(OTf)]PF_6$

	Atomic Number		*X*	*Y*	*Z*
1	29	0	0.077445	0.245901	0.861356
2	8	0	-1.097446	-1.000291	1.728407
3	6	0	-2.088124	-0.454979	2.668134
4	6	0	-1.692318	-2.110910	0.960045
5	6	0	-3.101925	-1.574098	2.809824
6	1	0	-1.543418	-0.200982	3.576114
7	1	0	-2.525063	0.436029	2.216124
8	6	0	-3.146834	-2.152006	1.393592
9	1	0	-1.558951	-1.904345	-0.099076
10	1	0	-1.119938	-2.994792	1.250673
11	1	0	-4.067051	-1.181389	3.135820
12	1	0	-2.761484	-2.321549	3.534261
13	1	0	-3.747671	-1.517830	0.738749
14	1	0	-3.540139	-3.170262	1.359089
15	9	0	-0.431982	1.522157	1.930415
16	7	0	1.573162	1.308698	0.455320
17	6	0	1.669240	1.945004	-0.731346
18	6	0	2.532171	1.359921	1.411298
19	6	0	2.824087	2.675633	-0.989924
20	6	0	3.685517	2.079807	1.152884
21	6	0	3.856793	2.745934	-0.062395
22	1	0	2.903082	3.180055	-1.946357
23	1	0	4.456068	2.111421	1.915205

24	6	0	2.317247	0.642499	2.710377
25	1	0	1.454402	1.065320	3.230746
26	1	0	2.153323	-0.427157	2.540015
27	1	0	3.201009	0.744582	3.340510
28	6	0	0.551727	1.864131	-1.715442
29	1	0	0.301241	0.826094	-1.942804
30	1	0	-0.348467	2.340596	-1.316820
31	1	0	0.831642	2.367945	-2.640201
32	6	0	5.127571	3.486431	-0.362533
33	1	0	5.877759	2.783228	-0.740321
34	1	0	4.973344	4.254327	-1.123347
35	1	0	5.534509	3.956526	0.535930
36	8	0	0.618273	-1.047961	-0.325317
37	16	0	2.035180	-1.676766	-0.371833
38	8	0	2.463591	-2.113030	0.945944
39	8	0	2.946489	-0.918710	-1.204790
40	6	0	1.568693	-3.199395	-1.339533
41	9	0	0.702285	-3.935031	-0.646960
42	9	0	1.026872	-2.858037	-2.500205
43	9	0	2.670254	-3.910043	-1.555117
44	15	0	-3.166056	1.173606	-1.054301
45	9	0	-4.502073	1.906568	-1.562093
46	9	0	-3.758601	1.045103	0.466031
47	9	0	-2.467212	2.590729	-0.651400
48	9	0	-1.753126	0.392892	-0.506731
49	9	0	-2.484845	1.254006	-2.526227
50	9	0	-3.765417	-0.299852	-1.397810

Cartesian Coordinates for WB97XD/6-31G++(d,p) optimized stationary points in a THF solvent continuum.

$C_{13}H_{19}CuF_4NO_4S(1+)$
$[(Me_3py)(THF)Cu(F)(OTf)]^+$

	Atomic Number		***X***	***Y***	***Z***
1	29	0	0.111435	-0.876319	0.050266
2	8	0	-1.718854	-1.311257	0.034244
3	6	0	-2.275541	-1.898616	-1.201726
4	6	0	-2.232782	-2.009915	1.211820
5	6	0	-3.215434	-2.993544	-0.714236
6	1	0	-2.770531	-1.068311	-1.706099
7	1	0	-1.444688	-2.269855	-1.803285
8	6	0	-3.554821	-2.567921	0.720190
9	1	0	-1.526604	-2.802828	1.480892
10	1	0	-2.306509	-1.262351	2.002542
11	1	0	-2.707344	-3.961408	-0.715449
12	1	0	-4.099633	-3.067379	-1.349305

13	1	0	-3.893140	-3.400816	1.338837
14	1	0	-4.321702	-1.789016	0.731602
15	9	0	0.527849	-2.525027	-0.321518
16	7	0	1.926774	-0.443538	0.055183
17	6	0	2.533969	-0.344122	1.257910
18	6	0	2.556658	-0.260047	-1.124218
19	6	0	3.872473	0.008042	1.291653
20	6	0	3.897374	0.100176	-1.097882
21	6	0	4.579073	0.251545	0.109832
22	1	0	4.363005	0.089354	2.255558
23	1	0	4.406298	0.253318	-2.043145
24	6	0	1.805461	-0.484636	-2.400915
25	1	0	1.522557	-1.539121	-2.479859
26	1	0	0.901372	0.130858	-2.451213
27	1	0	2.432797	-0.230117	-3.255080
28	6	0	1.736552	-0.637704	2.493767
29	1	0	0.962592	0.121217	2.642748
30	1	0	1.270596	-1.627459	2.423369
31	1	0	2.384502	-0.640574	3.370407
32	6	0	6.018990	0.668924	0.144390
33	1	0	6.082809	1.750259	0.308268
34	1	0	6.553240	0.178501	0.961238
35	1	0	6.524987	0.442333	-0.795701
36	8	0	-0.265570	0.813629	0.648277
37	16	0	-0.815689	1.800501	-0.439357
38	8	0	-1.059202	1.038703	-1.658616
39	8	0	-0.044737	3.015571	-0.459595
40	6	0	-2.478961	2.216078	0.300290
41	9	0	-3.218849	1.112231	0.398249
42	9	0	-2.308852	2.736750	1.505589
43	9	0	-3.083901	3.082787	-0.492359

$F_6P(1-)$

$(PF_6)^-$

	Atomic Number		***X***	***Y***	***Z***
1	15	0	-0.000107	-0.000220	-0.000030
2	9	0	0.660138	0.267397	-1.476256
3	9	0	-0.810148	-1.294799	-0.596349
4	9	0	-1.263400	0.969867	-0.389254
5	9	0	-0.660310	-0.267218	1.476654
6	9	0	0.810088	1.294858	0.596197
7	9	0	1.263811	-0.969738	0.389058

$C_{13}H_{19}CuF_{10}NO_4PS$

$[(Me_3py)(THF)Cu(F)(OTf)]PF_6$

	Atomic Number		***X***	***Y***	***Z***
1	29	0	-0.077445	-0.245901	0.861356
2	8	0	1.097446	1.000291	1.728407
3	6	0	2.088124	0.454979	2.668134
4	6	0	1.692318	2.110910	0.960045
5	6	0	3.101925	1.574098	2.809824
6	1	0	1.543418	0.200982	3.576114
7	1	0	2.525063	-0.436029	2.216124
8	6	0	3.146834	2.152006	1.393592
9	1	0	1.558951	1.904345	-0.099076
10	1	0	1.119938	2.994792	1.250673
11	1	0	4.067051	1.181389	3.135820
12	1	0	2.761484	2.321549	3.534261
13	1	0	3.747671	1.517830	0.738749
14	1	0	3.540139	3.170262	1.359089
15	9	0	0.431982	-1.522157	1.930415
16	7	0	-1.573162	-1.308698	0.455320
17	6	0	-1.669240	-1.945004	-0.731346
18	6	0	-2.532171	-1.359921	1.411298
19	6	0	-2.824087	-2.675633	-0.989924
20	6	0	-3.685517	-2.079807	1.152884
21	6	0	-3.856793	-2.745934	-0.062395
22	1	0	-2.903082	-3.180055	-1.946357
23	1	0	-4.456068	-2.111421	1.915205
24	6	0	-2.317247	-0.642499	2.710377
25	1	0	-1.454402	-1.065320	3.230746
26	1	0	-2.153323	0.427157	2.540015
27	1	0	-3.201009	-0.744582	3.340510
28	6	0	-0.551727	-1.864131	-1.715442
29	1	0	-0.301241	-0.826094	-1.942804
30	1	0	0.348467	-2.340596	-1.316820
31	1	0	-0.831642	-2.367945	-2.640201
32	6	0	-5.127571	-3.486431	-0.362533
33	1	0	-5.877759	-2.783228	-0.740321
34	1	0	-4.973344	-4.254327	-1.123347
35	1	0	-5.534509	-3.956526	0.535930
36	8	0	-0.618273	1.047961	-0.325317
37	16	0	-2.035180	1.676766	-0.371833
38	8	0	-2.463591	2.113030	0.945944
39	8	0	-2.946489	0.918710	-1.204790
40	6	0	-1.568693	3.199395	-1.339533
41	9	0	-0.702285	3.935031	-0.646960
42	9	0	-1.026872	2.858037	-2.500205
43	9	0	-2.670254	3.910043	-1.555117
44	15	0	3.166056	-1.173606	-1.054301
45	9	0	4.502073	-1.906568	-1.562093
46	9	0	3.758601	-1.045103	0.466031

47	9	0	2.467212	-2.590729	-0.651400
48	9	0	1.753126	-0.392892	-0.506731
49	9	0	2.484845	-1.254006	-2.526227
50	9	0	3.765417	0.299852	-1.397810