Lewis Base Activation of Lewis Acids – Group 13. Catalytic Generation and Reaction of Borenium Ions

Scott E. Denmark* and Yusuke Ueki

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, IL 61801

SUPPORTING INFORMATION

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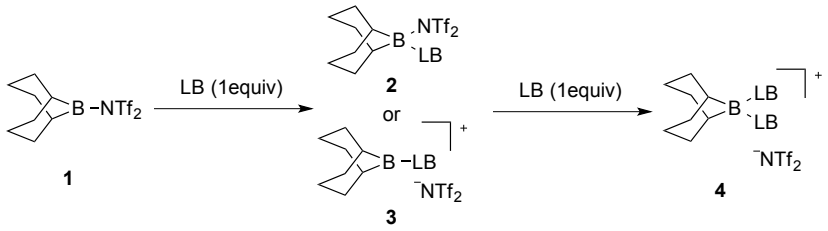
General Experimental. All reactions which boron species was used were performed in oven-dried quartz NMR tube at room temperature, under an atmosphere of dry argon, either in a glove box. ^{1}H NMR spectra were recorded on a Varian Unity 400 (400 MHz) or Unity Inova 400 (400 MHz). Chemical shifts are reported in ppm from the tetramethylsilane (0.0 ppm) or residual chloroform (7.26 ppm) resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet) and coupling constants (Hz). No-D NMR: no-deuterium ^{1}H-NMR was executed according to Hoye.[6] ^{11}B NMR spectra were recorded on a Varian Unity Inova 400 (128 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $BF_3 \cdot OEt_2$ (0.0 ppm) as the external

standard. ^{19}F NMR spectra were recorded on a Varian Unity Inova 400 (376 MHz) or Unity 400 (376 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from $CFCl_3$ (0.0 ppm) as the external standard. ^{31}P NMR spectra were recorded on a Varian Unity Inova 400 (162 MHz) or Unity 400 (U400, 162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 (0.0 ppm) as the external standard. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on Merck silica gel 60 230–400 mesh (60–63 μm, 60Å pore size).

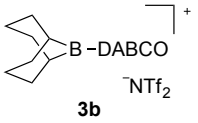
Toluene, tetrahydrofuran (THF), diethyl ether (Et_2O), and dichloromethane (CH_2Cl_2) (Fisher, HPLC grade) were dried by percolation through neutral alumina in a solvent dispensing system. 9-BBN-NTf_2,[1] Tf_2NH,[2] 9-borabicyclo[3.3.1]nonane dimer,[3] $Ph_3P{=}S$,[4] and $TMSNTf_2$[5] were prepared by following the literature procedures. 3-Methylbenzophenone **5b**, 4-bromobenzophenone **5d**, isobutyrophenone **5h** and other commercially available chemicals were purified by distillation or crystallization before used. Dichloromethane and the amines were dried by storing over activated 3Å molecular sieves in a glove box.

NMR Study for the Combination of 9-BBN-NTf_2 with Various Lewis Bases



Representative Procedure for the Preparation of the NMR Samples. In a glove box, to a solution of 9-BBN-NTf_2 (**1**) in CH_2Cl_2 in oven-dried, 5-mm, quartz NMR tube was added the Lewis base in varying molar ratios (**1**/Lewis base = 1:0.5 to 1:2). After sealing the NMR tube with a rubber septum cap, the tube was shaken. The NMR samples were analyzed by ^{1}H, ^{11}B, ^{19}F, and ^{31}P NMR spectroscopy at room temperature.

<u>9-BBN-DABCO borenium bistriflimide complex (**3b**)</u>



<u>Data for **3b** (under the condition of **1**/Lewis base = 1:1)</u>

^{1}<u>H NMR</u>: (400 MHz, CH_2Cl_2, No-D NMR)

3.20 (4 H, s), 1.98-1.72 (10 H, m), 1.43-1.30 (2 H, m), 1.16-1.04 (2 H, m)

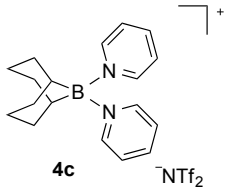
^{11}<u>B NMR</u>: (128 MHz, CH_2Cl_2)

56.9

^{19}<u>F NMR</u>: (376 MHz, CH_2Cl_2)

–80.0

9-BBN-bis-pyridine boronium bistriflimide complex (**4c**)



4c

Data for **4c** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

8.82 (4 H, d, *J* = 7.6 Hz), 8.24 (2 H, t, *J* = 7.6 Hz), 7.88 (2 H, t, *J* = 7.6 Hz), 2.04-1.82 (8 H, m), 1.60-1.43 (4 H, m), 1.40-1.29 (2 H, m)

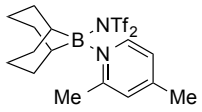
^{11}B NMR: (128 MHz, CH_2Cl_2)

5.2

^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.0

9-BBN-NTf_2-2,4-lutidine complex (**2d**)



2d

Data for **2d** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

8.56 (1 H, d, *J* = 6.4 Hz), 7.54 (1 H, d, *J* = 6.4 Hz), 7.51 (1 H, s), 2.83 (3 H, s), 2.58 (3 H, s), 2.08-1.80 (10 H, m), 1.77-1.68 (2 H, m), 1.53-1.42 (2 H, m)

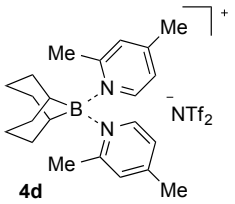
^{11}B NMR: (128 MHz, CH_2Cl_2)

39.4

^{19}F NMR: (376 MHz, CH_2Cl_2)

–79.3

9-BBN-bis-2,4-lutidine boronium bistriflimide complex (**4d**)



Data for **4d** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

8.90 (2 H, d, *J* = 6.4 Hz), 7.53 (2 H, d, *J* = 6.4 Hz), 7.35 (2 H, s), 2.52 (6 H, s), 2.44 (6 H, s), 2.22-1.66 (10 H, m), 1.50-1.38 (2 H, m), 1.00-0.87 (2 H, m)

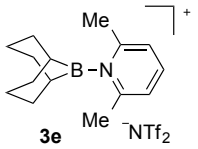
^{11}B NMR: (128 MHz, CH_2Cl_2)

9.7

^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.1

9-BBN-2,6-lutidine borenium bistriflimide complex (**3e**)



Data for **3e** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

8.29 (1 H, t, *J* = 8.0 Hz), 7.74 (2 H, d, *J* = 8.0 Hz), 2.79 (6 H, s), 2.46-2.20 (10 H, m),

1.90-1.78 (4 H, m)

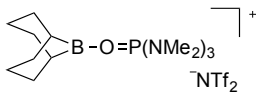
^{11}B NMR: (128 MHz, CH_2Cl_2)

84.4

^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.1

9-BBN-HMPA borenium bistriflimide complex (**3h**)



3e

Data for **3h** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

2.81 (18 H, d, J = 10.4 Hz), 2.10-1.80 (10 H, m), 1.45-1.24 (4 H, m)

^{11}B NMR: (128 MHz, CH_2Cl_2)

64.9

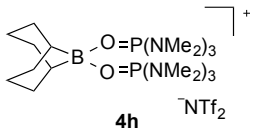
^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.0

^{31}P NMR: (162 MHz, CH_2Cl_2)

30.3

9-BBN-bis-HMPA boronium bistriflimide complex (**4h**)



4h

Data for **4h** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

2.71 (36 H, d, J = 10.0 Hz), 1.96-1.82 (2 H, m), 1.78-1.62 (8 H, m), 1.48-1.38 (2 H, m), 0.76-0.68 (2 H, m)

^{11}B NMR: (128 MHz, CH_2Cl_2)

17.8

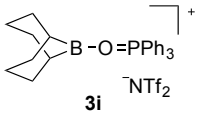
^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.1

^{31}P NMR: (162 MHz, CH_2Cl_2)

21.8

9-BBN-triphenylphosphine oxide boronium bistriflimide complex (**3i**)



3i

Data for **3i** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

8.00-7.90 (3 H, m), 7.85-7.71 (12 H, m), 1.96-1.82 (6 H, m), 1.76-1.62 (4 H, m), 1.36-1.17 (4 H, m)

^{11}B NMR: (128 MHz, CH_2Cl_2)

67.4

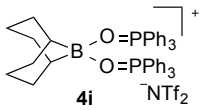
^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.0

^{31}P NMR: (162 MHz, CH_2Cl_2)

57.7

9-BBN-bis(triphenylphosphine oxide) boronium bistriflimide complex (**4i**)



4i

Data for **4i** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

7.74-7.66 (6 H, m), 7.66-7.43 (24 H, m), 1.94-1.44 (10 H, m), 1.34-1.18 (2 H, m), 0.92-0.80 (2 H, m)

^{11}B NMR: (128 MHz, CH_2Cl_2)

17.3

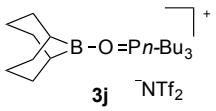
^{19}F NMR: (376 MHz, CH_2Cl

–80.1

^{31}P NMR: (162 MHz, CH_2Cl_2)

42.0

9-BBN-tri-*n*-butylphosphine oxide borenium bistriflimide complex (**3j**)



Data for **3j** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

2.46-1.20 (32 H, m), 0.99 (9 H, t, J = 7.6 Hz)

^{11}B NMR: (128 MHz, CH_2Cl_2)

65.1

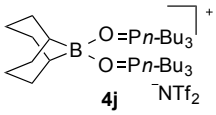
^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.1

^{31}P NMR: (162 MHz, CH_2Cl_2)

–105.4

9-BBN-bis(tri-*n*-butylphosphine oxide) boronium bistriflimide complex (**4j**)



Data for **4j** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

2.04-1.40 (48 H, m), 0.97 (18 H, t, J = 7.6 Hz), 0.52-0.46 (2 H, m)

^{11}B NMR: (128 MHz, CH_2Cl_2)

14.5

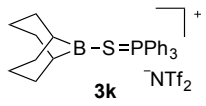
^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.1

^{31}P NMR: (162 MHz, CH_2Cl_2)

71.9

9-BBN-triphenylphosphine sulfide borenium bistriflimide complex (**3k**)



3k

Data for **3k** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

7.83-7.64 (15 H, m), 1.94-1.77 (6 H, m), 1.70-1.62 (2 H, m), 1.62-1.48 (4 H, m), 1.34-1.20 (2 H, m)

^{11}B NMR: (128 MHz, CH_2Cl_2)

80.4

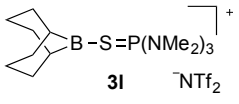
^{19}F NMR: (376 MHz, CH_2Cl_2)

–79.9

^{31}P NMR: (162 MHz, CH_2Cl_2)

40.0

9-BBN-hexamethylthiophosphoramide borenium bistriflimide complex (**3l**)



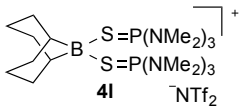
3l

Data for **3l** (under the condition of **1**/Lewis base = 1:1)

^{11}B NMR: (128 MHz, CH_2Cl_2)

80.9

9-BBN-bis(hexamethylthiophosphoramide) boronium bistriflimide complex (**4l**)



Data for **4l** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

2.83 (18 H, d, *J* = 11.2 Hz), 2.81 (18 H, d, *J* = 14.0 Hz), 1.92-1.56 (10 H, m), 1.50-1.40 (2 H, m), 1.35-1.21 (2 H, m)

^{11}B NMR: (128 MHz, CH_2Cl_2)

46.9

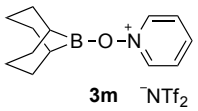
^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.1

^{31}P NMR: (162 MHz, CH_2Cl_2)

89.0 (d, *J* = 11.7 Hz), 60.6 (d, *J* = 11.7 Hz)

9-BBN-pyridine-*N*-oxide borenium bistriflimide complex (**3m**)



Data for **3m** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

8.92 (2 H, d, *J* = 6.0 Hz), 8.61 (1 H, brs), 8.24 (2 H, brs), 2.10-1.72 (10 H, m), 1.56-1.44 (2 H, m), 1.24-1.04 (2 H, m)

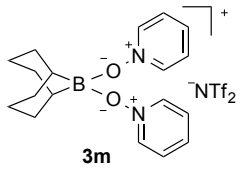
^{11}B NMR: (128 MHz, CH_2Cl_2)

64.2

^{19}F NMR: (376 MHz, CH_2Cl_2)

–79.9

9-BBN-bis(pyridine-*N*-oxide) boronium bistriflimide complex (**4m**)



3m

Data for **4m** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

8.98 (4 H, d, *J* = 7.6 Hz), 8.20 (2 H, t, *J* = 7.6 Hz), 7.88 (4 H, t, *J* = 7.6 Hz), 1.83-1.74 (2 H, m), 1.68-1.46 (10 H, m), 0.72-0.62 (2 H, m)

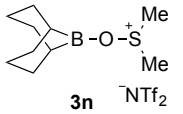
^{11}B NMR: (128 MHz, CH_2Cl_2)

14.4

^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.1

9-BBN-(dimethyl sulfoxide) borenium bistriflimide complex (**3n**)



3n

Data for **3n** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

3.44 (6 H, s), 2.08-1.76 (10 H, m), 1.60-1.34 (4 H, m)

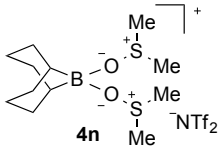
^{11}B NMR: (128 MHz, CH_2Cl_2)

66.1

^{19}F NMR: (376 MHz, CH_2Cl_2)

–79.7

9-BBN-bis(dimethyl sulfoxide) boronium bistriflimide complex (**4n**)



4n

Data for **4n** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

3.04 (12 H, s), 1.90-1.68 (6 H, m), 1.67-1.54 (4 H, m), 1.52-1.42 (2 H, m), 0.86-0.76 (2 H, m)

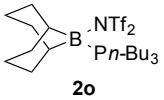
^{11}B NMR: (128 MHz, CH_2Cl_2)

15.0

^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.0

9-BBN-NTf_2-(tri-*n*-butylphosphine) complex (**2o**)



2o

Data for **2o** (under the condition of **1**/Lewis base = 1:1)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

2.04-1.78 (16 H, m), 1.58-1.40 (18 H, m), 0.96 (9 H, t, J = 7.2 Hz)

^{11}B NMR: (128 MHz, CH_2Cl_2)

33.1

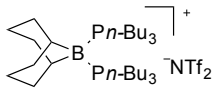
^{19}F NMR: (376 MHz, CH_2Cl_2)

–79.2

^{31}P NMR: (162MHz, CH_2Cl_2)

–6.3

9-BBN-bis(tri-*n*-butylphosphine) boronium bistriflimide complex (**4o**)



4o

Data for **4o** (under the condition of **1**/Lewis base = 1:2)

^{1}H NMR: (400 MHz, CH_2Cl_2, No-D NMR)

2.16-1.32 (50 H, m), 0.99 (18 H, t, J = 7.2 Hz)

^{11}B NMR: (128 MHz, CH_2Cl_2)

–5.4

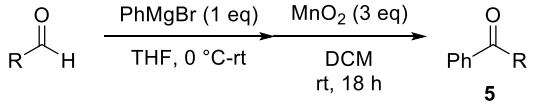
^{19}F NMR: (376 MHz, CH_2Cl_2)

–80.1

^{31}P NMR: (162 MHz, CH_2Cl_2)

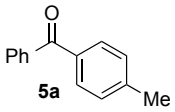
–4.1

General Procedure for the Preparation of Ketones 5



To the solution of aldehyde (5 mmol) in THF (10 mL) was added a solution of phenylmagnesium bromide in THF (1.1 equiv, 1.0 M) at 0 °C. Then, the reaction mixture was allowed to warm to room temperature. The progress of the reaction was monitored with TLC. When the reaction was complete, the mixture was poured into sat. aq. ammonium chloride solution at 0 °C. The aqueous phase was extracted with Et_2O (3 X 15 mL) and the organic phases were washed with brine (50 mL). The combined organic extracts were dried over Na_2SO_4 and filtered. All volatiles were removed by rotary evaporation, then the residue was dissolved in CH_2Cl_2 (0.2 M) and MnO_2 (3 equiv) was added portion wise to the solution at room temperature. The resulting slurry was stirred for 18 h whereupon the solid was removed by filtration and the solvent was removed by rotary evaporation. Purification of the residue by silica gel column chromatography and distillation or recrystallization by following the literature procedure afforded the corresponding ketones **5**.

4-Methylbenzophenone (5a)

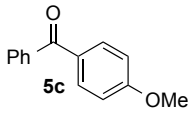


Data for **5a**[7]

^{1}H NMR: (400 MHz, $CDCl_3$)

7.78 (2 H, d, *J* = 7.2 Hz), 7.72 (2 H, d, *J* = 8.0 Hz), 7.58 (1 H, t, *J* = 7.2 Hz), 7.48 (2 H, t, *J* = 7.2 Hz), 7.28 (2 H, d, *J* = 8.0 Hz), 2.43 (3 H, s)

4-Methoxybenzophenone (5c)

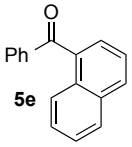


Data for **5c**[7]

^{1}H NMR: (400 MHz)

7.84 (2 H, d, *J* = 8.8 Hz), 7.76 (2 H, d, *J* = 7.6 Hz), 7.57 (1 H, t, *J* = 7.6 Hz), 7.48 (2 H, t, *J* = 7.6 Hz), 6.97 (2 H, d, *J* = 8.8 Hz), 3.89 (3 H, s)

1-Naphthyl Phenyl Ketone (5e)

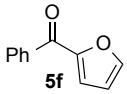


Data for **5e**[7]

^{1}H NMR: (400 MHz)

8.09 (1 H, d, *J* = 7.6 Hz), 8.10 (1 H, d, *J* = 7.6 Hz), 7.93 (1 H, d, *J* = 7.6 Hz), 7.87 (2 H, d, *J* = 7.6 Hz), 7.64-7.49 (5 H, m), 7.47 (2 H, t, *J* = 7.6 Hz)

2-Furyl Phenyl Ketone (5f)

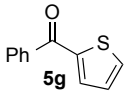


Data for **5f**[7]

^{1}H NMR: (400 MHz)

7.97 (2 H, d, *J* = 7.2 Hz), 7.72 (1 H, d, *J* = 1.6 Hz), 7.60 (1 H, t, *J* = 7.2 Hz), 7.50 (2 H, t, *J* = 7.2 Hz), 7.24 (1 H, d, *J* = 3.2 Hz), 6.60 (1 H, dd, *J* = 3.2, 1.6 Hz)

2-Thienyl Phenyl Ketone (5g)

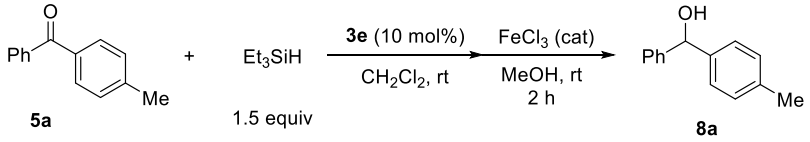


Data for **5g**[7]

^{1}H NMR: (400 MHz, $CDCl_3$)

7.87 (2 H, d, *J* = 7.2 Hz), 7.73 (1 H, d, *J* = 4.8 Hz), 7.65 (1 H, dd, *J* = 4.8, 4.0 Hz), 7.60 (1 H, t, *J* = 7.2 Hz), 7.53 (2 H, t, *J* = 7.2 Hz), 7.17 (1 H, dd, *J* = 4.8, 4.0 Hz)

Representative Procedure for Complex 3e Catalyzed Hydrosilylation of Ketones.



In a glove box, a solution of 9-BBN-2,6-lutidine borenium bistriflimide (**3e**) in CH_2Cl_2 (100 μL, 0.1 M, 0.01 mmol) was placed in oven-dried, 5-mm NMR tube and was diluted with CH_2Cl_2 (900 μL). To the solution was introduced 4-methylbenzophenone **5a** (19.6 mg, 0.1 mmol). The NMR tube was sealed with a rubber septum and shaken. Triethylsilane (24 μL, 0.15 mmol) was introduced dropwise via syringe (NMR tube was shaken after each drop) at room temperature. The progress of the reaction was monitored by No-D ^{1}H NMR. After the reaction was complete, the mixture was directly poured onto a short path filtration (silica gel/celite in a disposable pasteur pipette) and was eluted with pentane/Et_3N, 49:1. All the volatiles were removed under reduced pressure. To the residue was added a solution of $FeCl_3$ in methanol (200 μL, 0.05 M) at room temperature. The progress of the reaction was monitored with TLC. When the cleavage of the silyl protecting group was complete, the reaction mixture was diluted with water and the aqueous phase was extracted with Et_2O (3 X 5 mL). The combined organic

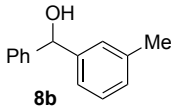
extracts were washed with brine (10 mL) then were dried over Na_2SO_4 and filtered. The solvent was removed by evaporation and the residue was purified by column chromatography onto silica gel (hexanes/Et_2O, 10-5:1) to afford 18.2 mg of alcohol **8a** (92%).

Data for **8a**[8]

^{1}H NMR: (400 MHz)

7.38 (2 H, d, *J* = 7.6 Hz), 7.33 (1 H, t, *J* = 7.6 Hz), 7.30-7.23 (4 H, m), 7.15 (2 H, d, *J* = 7.6 Hz), 5.82 (1 H, d, *J* = 4.0 Hz), 2.33 (3 H, s), 2.17 (1 H, d, *J* = 4.0 Hz)

Phenyl(3-tolyl)methanol (8b)



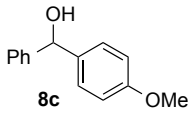
8b

Data for **8b**[9]

^{1}H NMR: (400 MHz)

7.41-7.31 (4 H, m), 7.29-7.15 (4 H, m), 7.08 (1 H, d, *J* = 7.6 Hz), 5.82 (1 H, d, *J* = 3.6 Hz), 2.34 (3 H, s), 2.18 (1 H, d, *J* = 3.6 Hz)

Phenyl(4-methoxyphenyl)methanol (8c)



8c

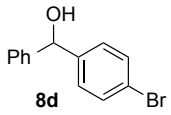
Data for **8c**[8]

^{1}H NMR: (400 MHz)

7.40-7.24 (7 H, m), 6.87 (2 H, d, *J* = 8.8 Hz), 5.82 (1 H, d, *J* = 3.6 Hz), 3.79 (3 H, s),

2.14 (1 H, d, *J* = 3.6 Hz)

Phenyl(4-bromophenyl)methanol (8d)



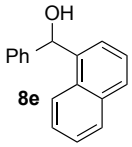
8d

Data for **8d**[8]

^{1}H NMR: (400 MHz)

7.46 (2 H, d, *J* = 8.0 Hz), 7.41-7.24 (7 H, m), 5.81 (1 H, d, *J* = 3.2 Hz), 2.20 (1 H, d, *J* = 3.2 Hz)

Phenyl(1-naphthyl)methanol (8e)



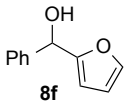
8e

Data for **8e**[8]

^{1}H NMR: (400 MHz)

8.04 (1 H, d, *J* = 7.6 Hz), 7.87 (1 H, d, *J* = 7.6 Hz), 7.83 (1 H, d, *J* = 7.6 Hz), 7.65 (1 H, d, *J* = 7.6 Hz), 7.50 (1 H, t, *J* = 7.6 Hz), 7.47-7.39 (4 H, m), 7.34 (2 H, t, *J* = 7.6 Hz), 7.28 (1 H, d, *J* = 7.6 Hz), 6.56 (1 H, d, *J* = 4.0 Hz), 2.33 (1 H, d, *J* = 4.0 Hz)

Phenyl(2-furyl)methanol (8f)



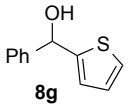
8f

Data for **8f**[8]

^{1}H NMR: (400 MHz)

7.47-7.30 (6 H, m), 6.32 (1 H, dd, *J* = 3.2, 2.0 Hz), 6.12 (1 H, d, *J* = 3.2 Hz), 5.84 (1 H, d, *J* = 4.4 Hz), 2.36 (1 H, d, *J* = 4.4 Hz)

Phenyl(2-thienyl)methanol (8g)



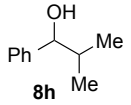
8g

Data for **8g**[8]

^{1}H NMR: (400 MHz)

7.46 (2 H, d, *J* = 7.2 Hz), 7.38 (2 H, t, *J* = 7.2 Hz), 7.34-7.24 (2 H, m), 6.95 (1 H, dd, *J* = 4.8, 3.6 Hz), 6.89 (1 H, d, *J* = 3.6 Hz), 6.07 (1 H, d, *J* = 4.4 Hz), 2.37 (1 H, d, *J* = 4.4 Hz)

2-Methyl-1-phenylpropan-1-ol (8h)



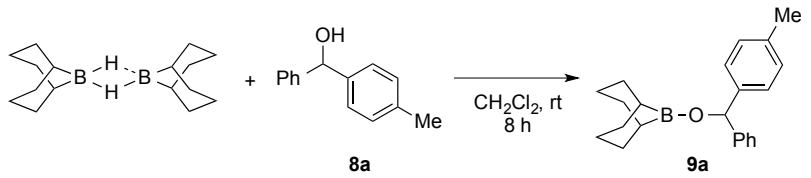
8h

Data for **8h**[10]

^{1}H NMR: (400 MHz)

7.37-7.24 (5 H, m), 4.37 (1 H, dd, *J* = 6.8, 3.2 Hz), 1.96 (1 H, octet, *J* = 6.8 Hz), 1.80 (1 H, d, *J* = 3.2 Hz), 1.00 (3 H, d, *J* = 6.8 Hz), 0.80 (1 H, d, *J* = 6.8 Hz)

Control Experiments and Kinetic Data.



Procedure for the Preparation of Intermediate 9a from 8a: 9-BBN-dimer (12.2 mg, 0.05 mmol) and **8a** (19.8 mg, 0.1 mmol) were dissolved in CH_2Cl_2 (1 mL) in oven dried quartz-NMR tube. After the NMR tube was well shaken, the reaction mixture was kept stand at room temperature. The reaction progress was monitored by ^{11}B NMR. After completion of the reaction, all volatiles were removed under vacuum gave the corresponding pure intermediate **9a**. The intermediate **9a** was used next reaction without further purification.

Data for **9a**

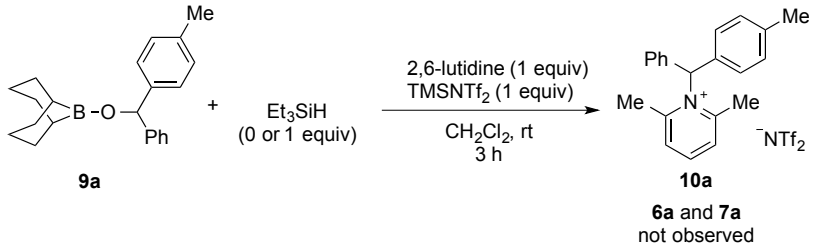
^{1}H NMR: (400 MHz, CD_2Cl_2, No-D NMR)

7.39 (2 H, d, *J* = 8.0 Hz), 7.32 (2 H, t, *J* = 8.0 Hz), 7.27 (2 H, d, *J* = 8.0 Hz), 7.23 (2 H, t, *J* = 8.0 Hz), 7.13 (1 H, d, *J* = 8.0 Hz), 6.27 (1 H, s), 1.90-1.55 (10 H, m), 1.42-1.28 (4 H, m)

^{11}B NMR: (128 MHz, CH_2Cl_2)

57.5

Control Experiment 1 (Scheme 3). Conversion of Putative Intermediate 9a to 6a or 7a. Catalyst Turnover Step in Mechanism I.



Procedure for Control Experiment 1: In a glove box, **9a** was diluted with CH_2Cl_2 (0.9 mL) and a solution of Cl_3CCH_2Cl in CH_2Cl_2 (100 μL, 1.0 M, 0.1 mmol). Then, triethylsilane (12 μL, 0.1 mol), 2,6-lutidine (11.6 μL, 0.1 mmol), $TMSNTf_2$ (23 μL, 0.1 mmol) were added to the solution. The reaction progress was monitored by No-D ^{1}H NMR and the yields were determined by integration of product signals versus internal standard. Product **10a** was isolated after purification by flash column chromatography on silica gel (CH_2Cl_2/ methanol, 50:1).

Data for **10a**

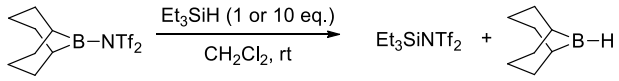
^{1}H NMR: (400 MHz, $CDCl_3$)

8.36 (1 H, t *J* = 8.0 Hz), 7.83 (2 H, d, *J* = 8.0 Hz), 7.61 (1 H, s), 7.52-7.40 (3 H, m), 7.26 (2 H, d, *J* = 8.0 Hz), 7.10 (2 H, d, *J* = 8.0 Hz), 6.98 (2 H, d, *J* = 8.0 Hz), 2.58 (6 H, s), 2.39 (3 H, s)

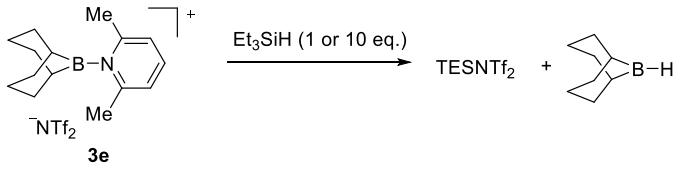
^{19}F NMR: (376 MHz, $CDCl_3$)

–79.3

Procedure for NMR Kinetic Experiment 1 (Scheme 4). In a glove box, a CH_2Cl_2 solution of 9-BBN-NTf_2 (100 μL, 0.1M, 0.01 mmol) or **3e** (100 μL, 0.1M, 0.01 mmol) was placed into oven-dried, 5-mm quartz NMR tube and was diluted in CH_2Cl_2 (900 μL). To the solution was added a solution of triethylsilane in CH_2Cl_2 (10 or 100 μL, 1M, 0.01 or 0.1 mmol). ^{11}B NMR was monitored every 10 min to 1 h. The amount of 9-BBN-dimer formed was determined by integration of versus 9-BBN-NTf_2 or **3e**.

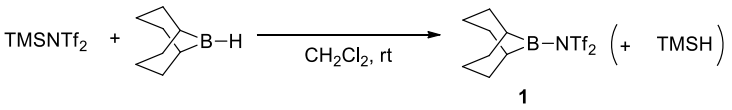


	Amount of 9-BBN dimer formed (%) at time (min)			
Et_3SiH	10 min	20 min	30 min	40 min
1.0 equiv	5%	6%	7%	8%
10 equiv	9%	9%	13%	18%



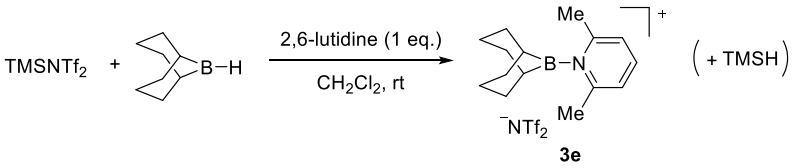
	Amount of 9-BBN dimer formed (%) at time (min)			
Et_3SiH	10 min	20 min	30 min	40 min
1.0 equiv	8.5%	10.4%	12.4%	13.9%
10 equiv	12.2%	17.7%	21.9%	24.6%

Procedure for NMR Kinetic Experiment 2 (Scheme 4). In a glove box, 9-BBN-dimer (12.2 mg, 0.05 mmol) was placed into oven-dried, 5-mm quartz NMR tube and was dissolved in CH_2Cl_2 (1 mL). Then, 2,6-lutidine (0 or 11.6 μL, 0 or 0.1 mmol) and $TMSNTf_2$ (23 μL, 0.1 mmol) was added to the solution. ^{11}B NMR was monitored every 10 min to 40 min. The amount of 9-BBN-NTf_2 or **3e** formed was determined by integration of **1** or **3e** versus 9-BBN-dimer.



1

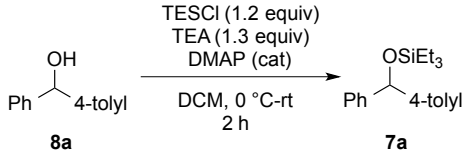
Amount of **1** formed (%) at time				
10 min	20 min	30 min	40 min	12 h
1	3	3	4	18



3e

Amount of **3e** formed (%) at time				
10 min	20 min	30 min	40 min	12 h
4	7	8	10	36

Phenyl(4-methylphenyl)methyl Triethylsilyl Ether (7a).



8a **7a**

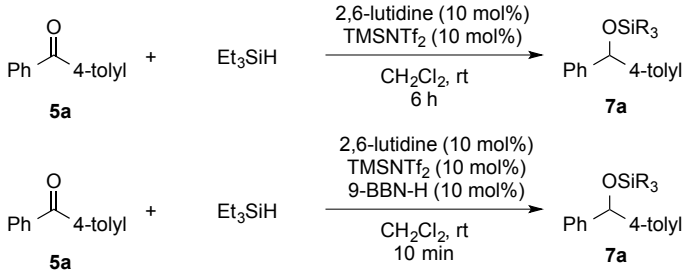
To a solution of **8a** (0.4 g, 2.0 mmol) in CH_2Cl_2 (7 mL) was added triethylamine (0.36 mL, 2.6 mmol) and of 4-(*N*,*N*-dimethylamino)pyridine (24 mg, 10 mol%) at room temperature. Then the reaction mixture was cooled to 0 °C. After the addition of chlorotriethylsilane (0.4 mL, 2.4 mmol), the reaction mixture was allowed to warm to rt and was stirred for 2 h. The resulting solution was poured onto ice cold sat. aq. ammonium chloride solution and the aqueous phase was extracted with CH_2Cl_2 (2 X 15 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and evaporated to afford a yellowish oil that was purified by column chromatography on deactivated silica gel (pentane/Et_3N, 49:1) to afford 0.56 g (90%) of **7a** as a colorless oil.

Data for **7a**[11]

^{1}H NMR: (400 MHz, $CDCl_3$)

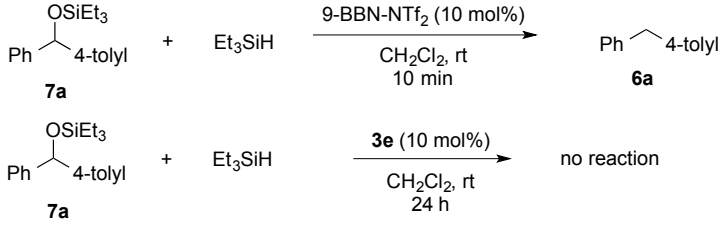
7.35 (2 H, d, *J* = 7.2 Hz), 7.27 (2 H, t, *J* = 7.2 Hz), 7.24 (1 H, d, *J* = 7.2 Hz), 7.19 (1 H, t, *J* = 7.2 Hz), 7.09 (2 H, d, *J* = 7.2 Hz), 5.73 (1 H, s), 2.30 (3 H, s), 0.88 (9 H, t, *J* = 7.6 Hz), 0.56 (6 H, q, *J* = 7.6 Hz)

Control Experiment 2 (Scheme 6). Differentiating Mechanisms II and III.



Procedure for Control Experiment 2: In a glove box, a solution of $TMSNTf_2$ or $TMSNTf_2$ and 2,6-lutidine (1:1) in CH_2Cl_2 (100 μL, 0.1 M, 0.01 mmol) was placed in oven dried NMR tube and diluted with CH_2Cl_2 (800 μL) and a solution of Cl_3CCH_2Cl in CH_2Cl_2 (100 μL, 1.0 M, 0.1 mmol). To the solution was introduced 4-methylbenzophenone **5a** (23.0 mg, 0.1 mmol). The NMR tube was capped with a rubber septum as was shaken. Triethylsilane (24 μL, 0.15 mmol) was added dropwise via syringe (the tube was shaken after each drop) at room temperature. The reaction progress was monitored by No-D ^1H NMR and the yields were determined by integration of product signals versus the internal standard.

Control Experiment 3 (Scheme 7). Testing the Stability of 7a in the Presence of 9-BBN-NTf_2 and 3e.



Procedure for Control Experiment 3. In a glove box, **1** or **3a** (100 μL, 0.1 M, 0.01 mmol) was placed in an oven-dried, 5-mm NMR tube. Then CH_2Cl_2 (0.8 mL), a solution of Cl_3CCH_2Cl in CH_2Cl_2 (100 μL, 1.0 M, 0.1 mmol), and triethylsilane (12 μL, 0.1 mmol) were added to the NMR tube and resulting reaction mixture was shaken. To the solution was added a

solution of 9-BBN-NTf_2 (100 μL, 0.1M, 0.01 mmol) or **3e** (100 μL, 0.1 M, 0.01 mmol) in CH_2Cl_2. The reaction progress was monitored by No-D ^{1}H NMR and the yields were determined by integration of product signals versus the internal standard. Product **6a** was isolated after purification by flash column chromatography on silica gel (pentane/Et_2O, 20:1).

Data for **6a**[12]

^{1}H NMR: (400 MHz, $CDCl_3$)

7.31-7.25 (2 H, m), 7.22-7.16 (3 H, m), 7.12-7.06 (4 H, m), 3.95 (2 H, s), 2.32 (3 H, s)

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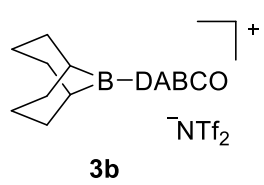
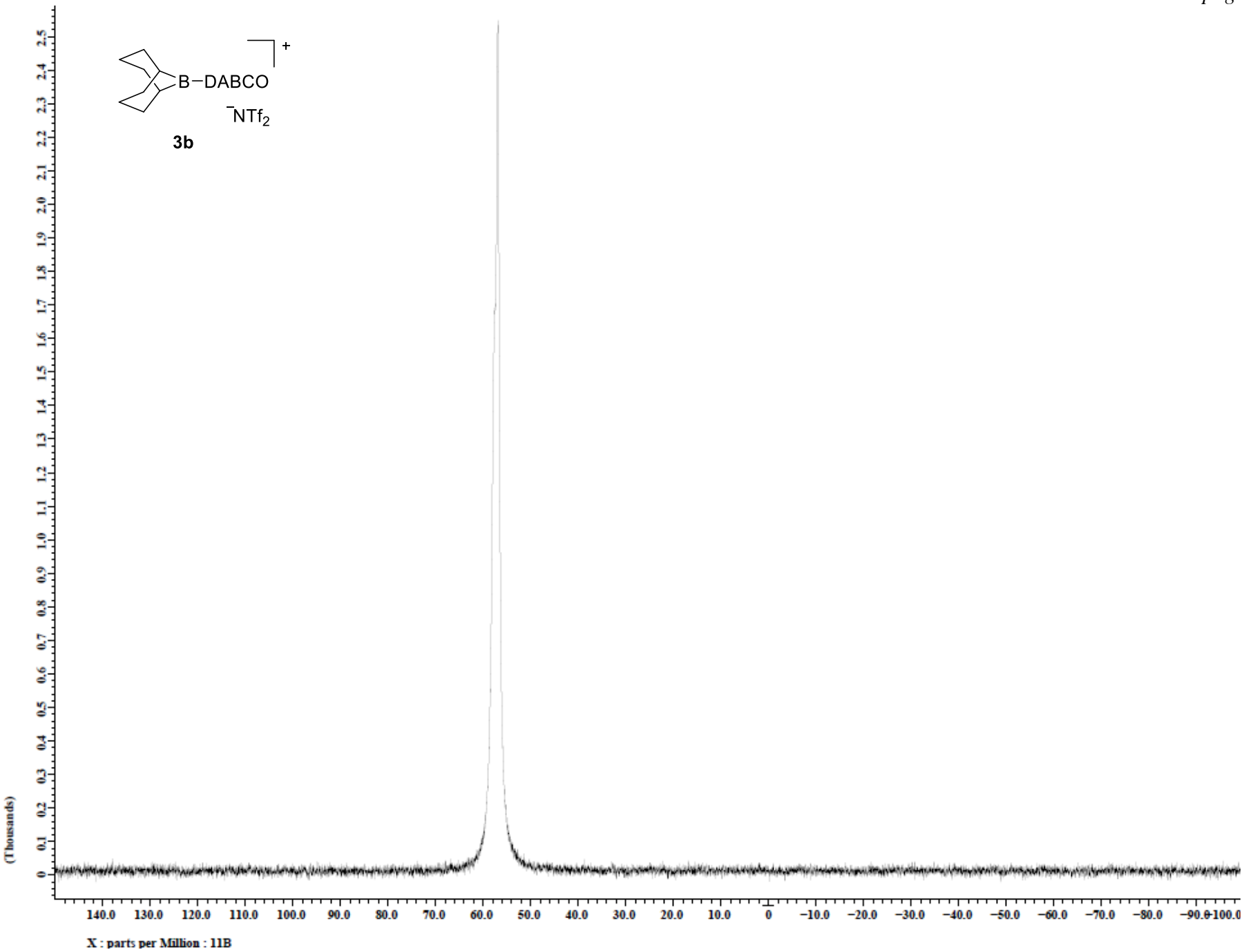
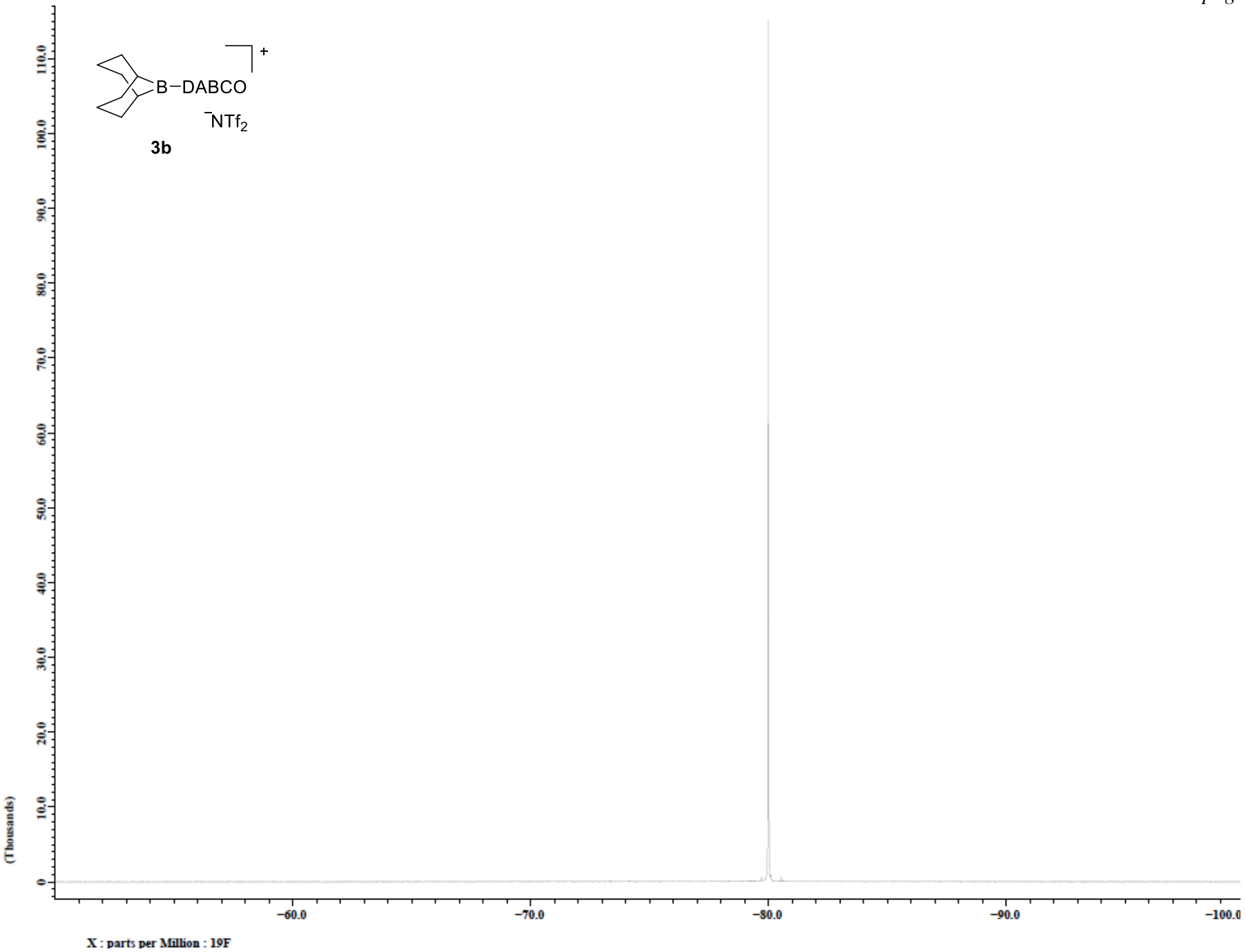
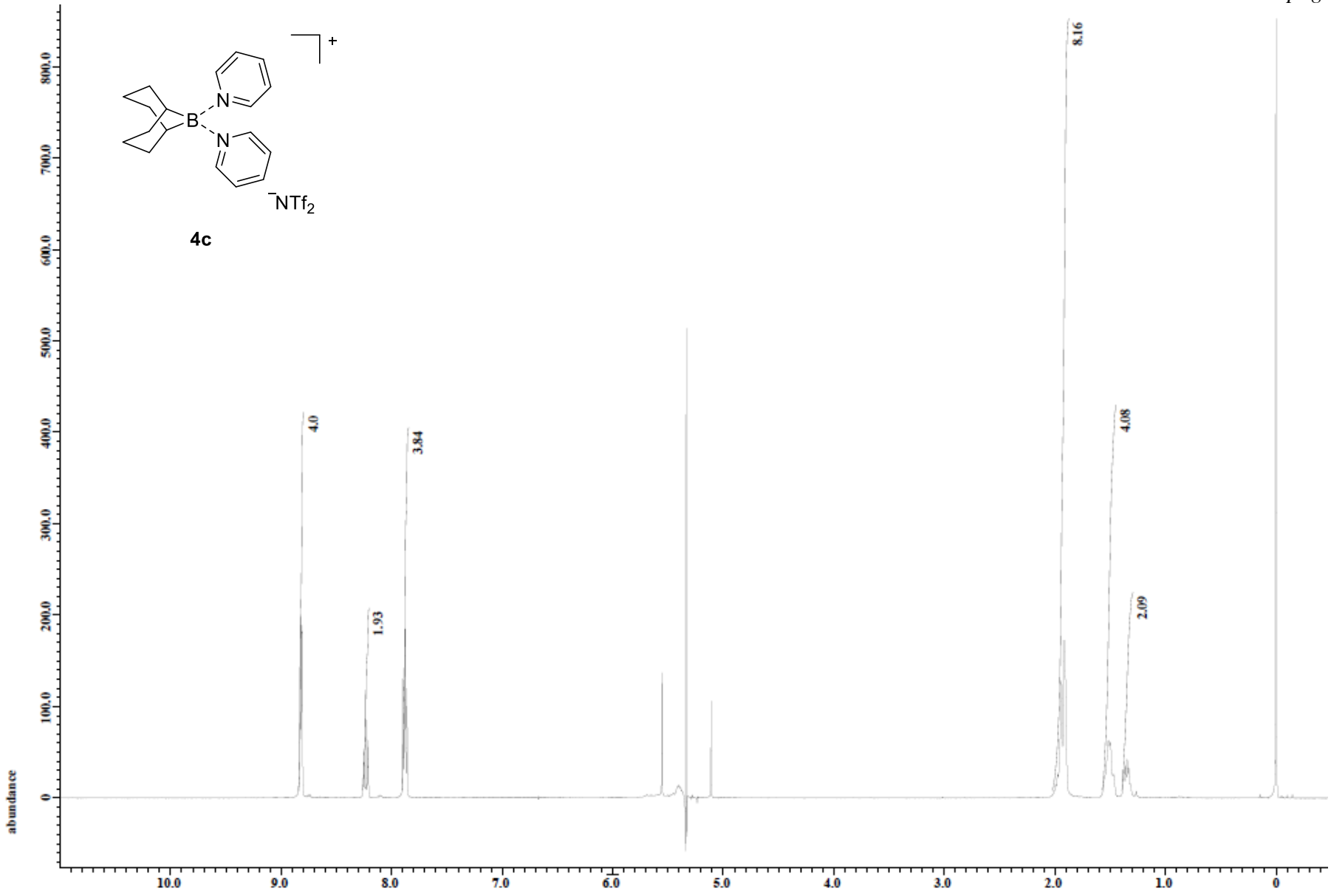

B–DABCO
$^{-}NTf_2$
+

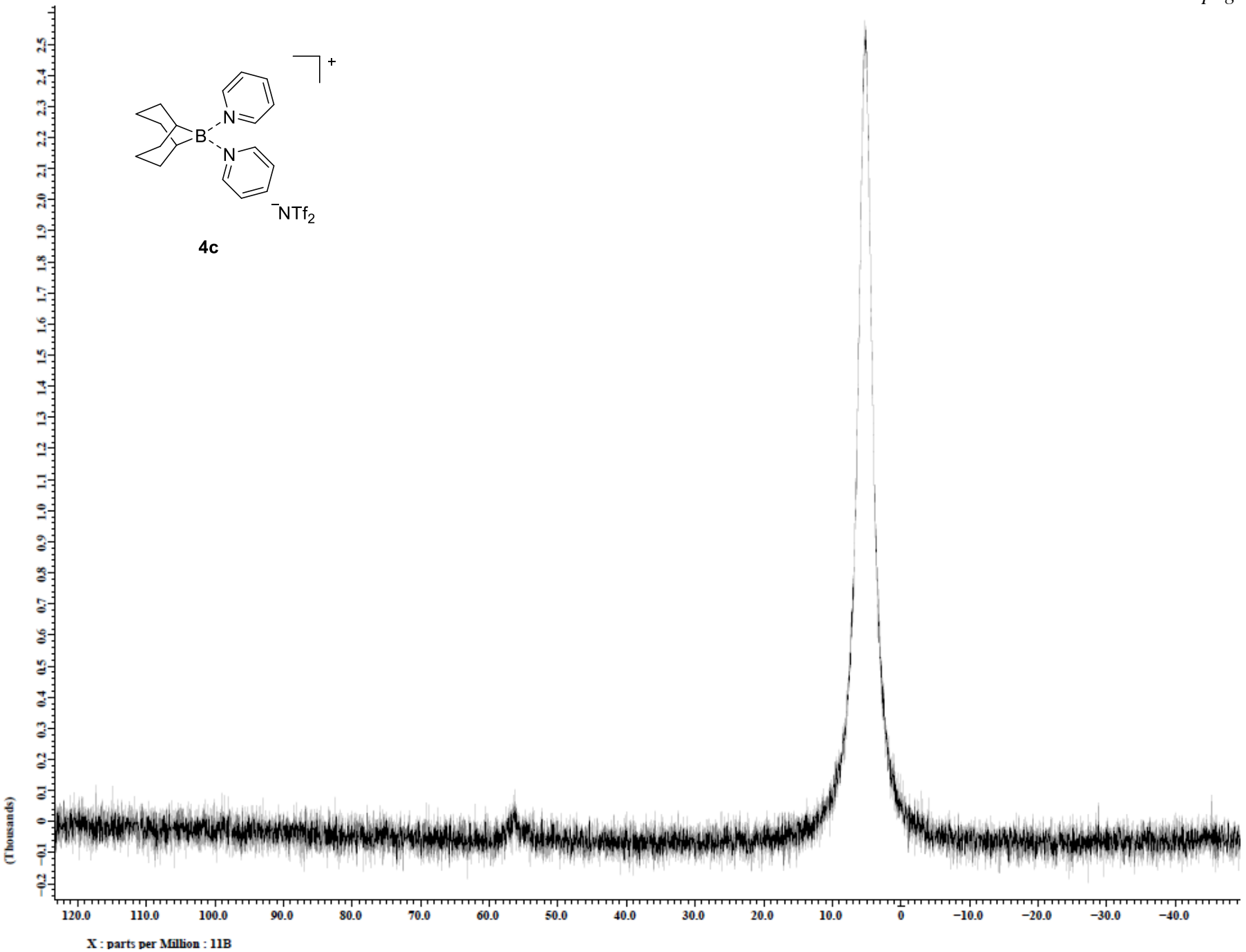
3b

12.66
3.96
2.59
1.23
abundance
600.0
500.0
400.0
300.0
200.0
100.0
0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

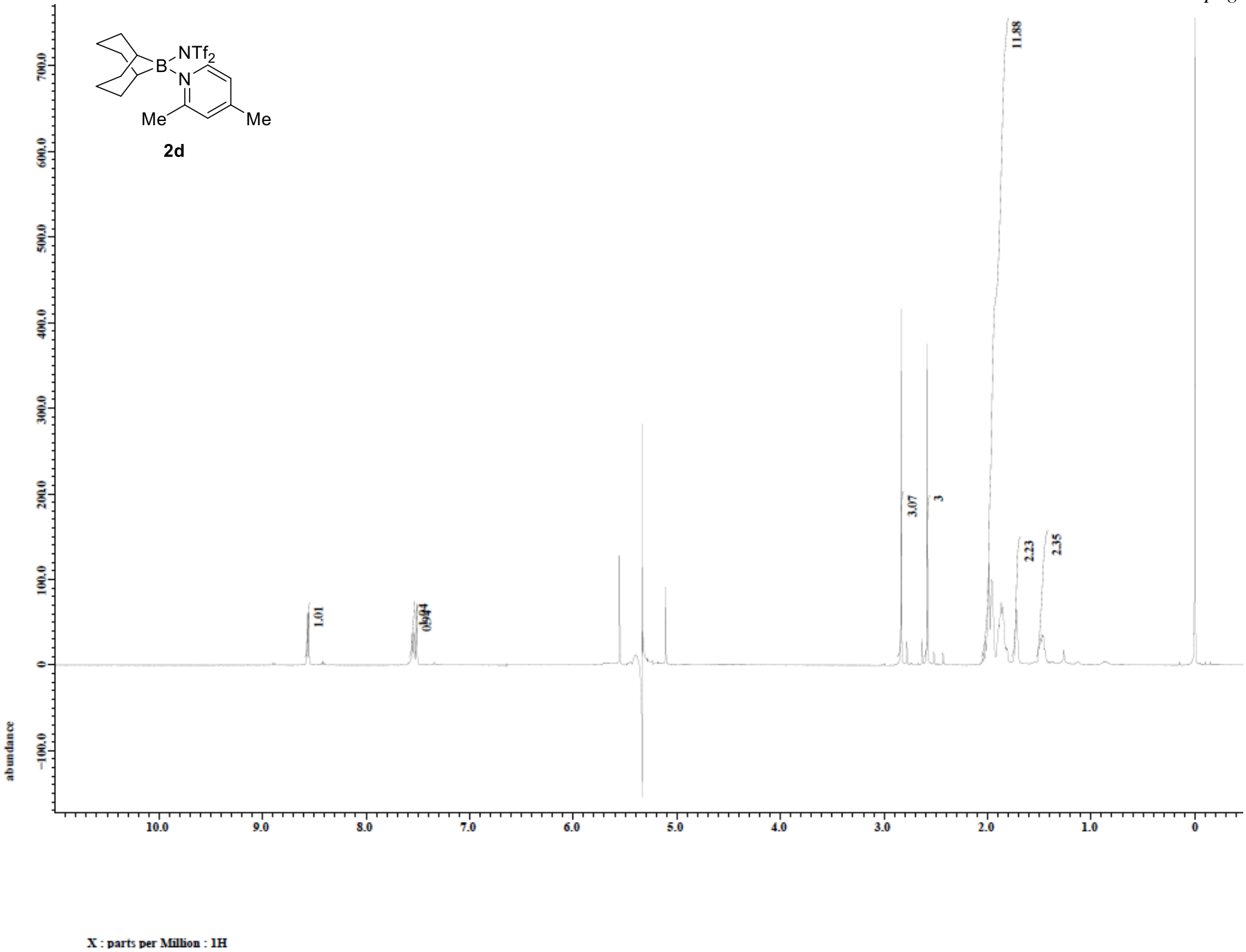

B–DABCO
NTf2
+
3b
(Thousands)
X : parts per Million : 11B

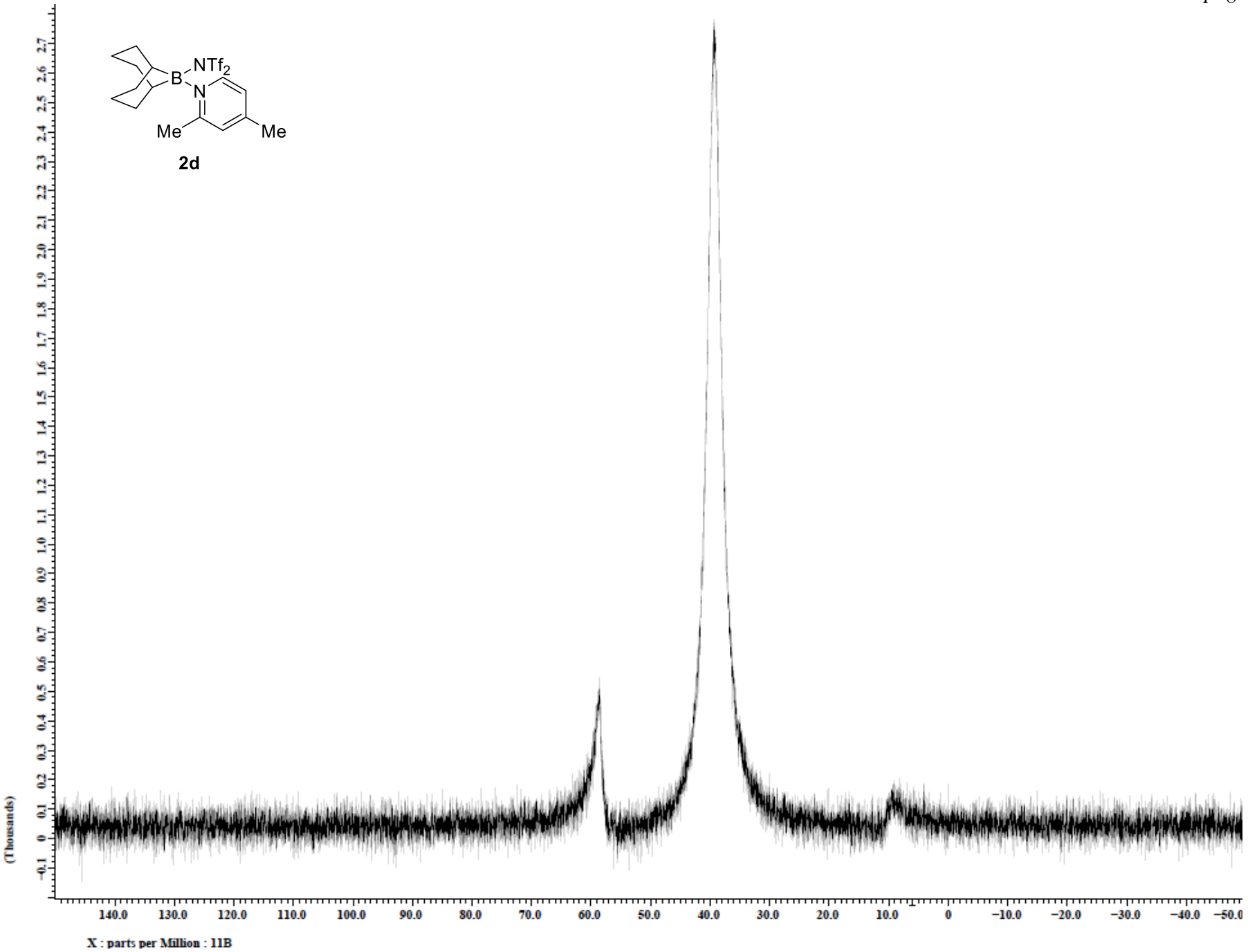

B–DABCO
$^{-}NTf_2$
+
3b
(Thousands)
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F

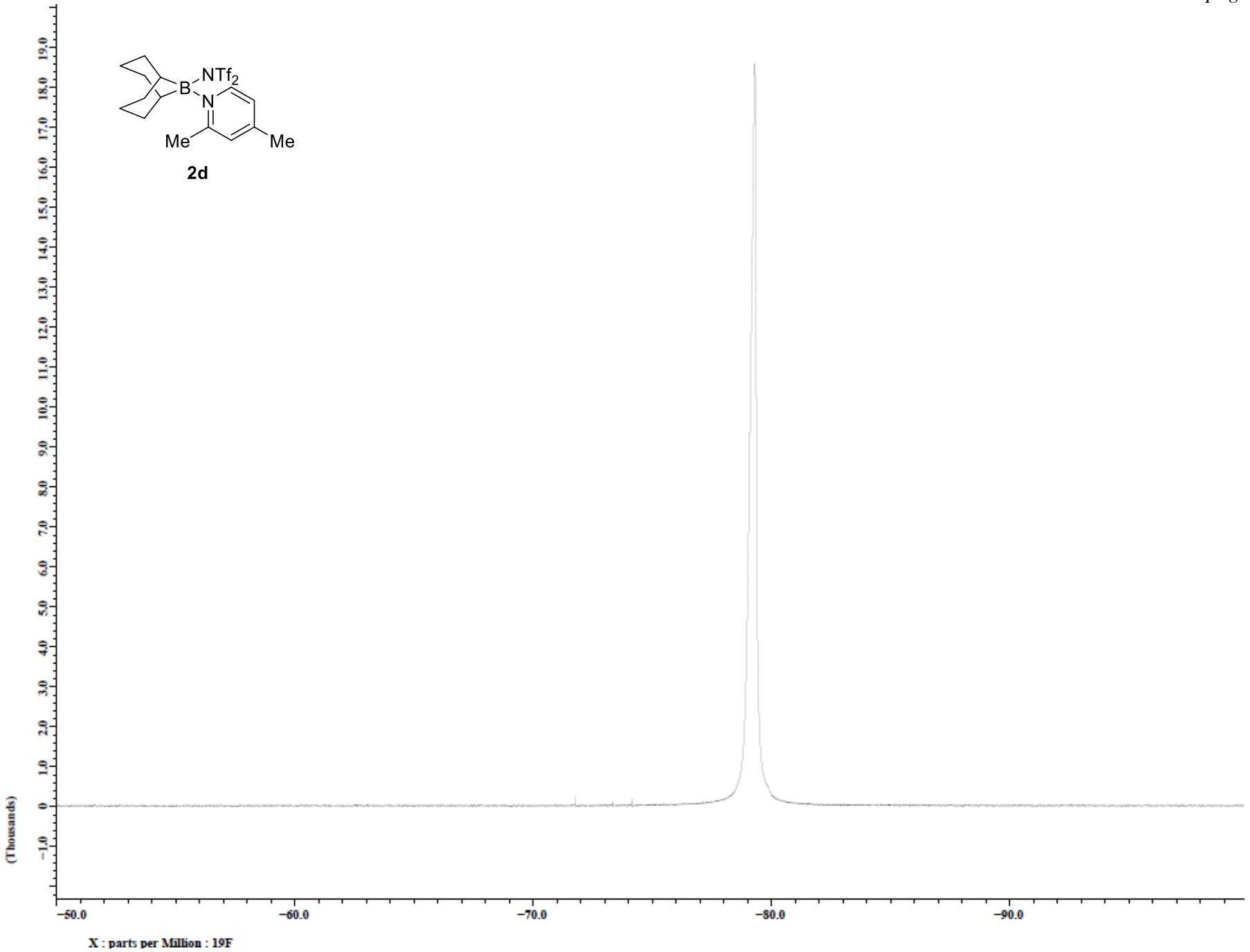

B
N
N
+
$^{-}$NTf$_2$
4c
8.16
4.08
4.0
3.84
1.93
2.09
abundance
0
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

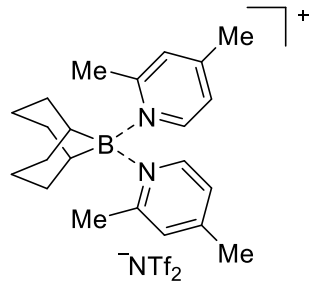


4c


NTf2
B
N
Me
Me
2d
11.88
3.07
3
2.23
2.35
1.01
0.94
abundance
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
-100.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

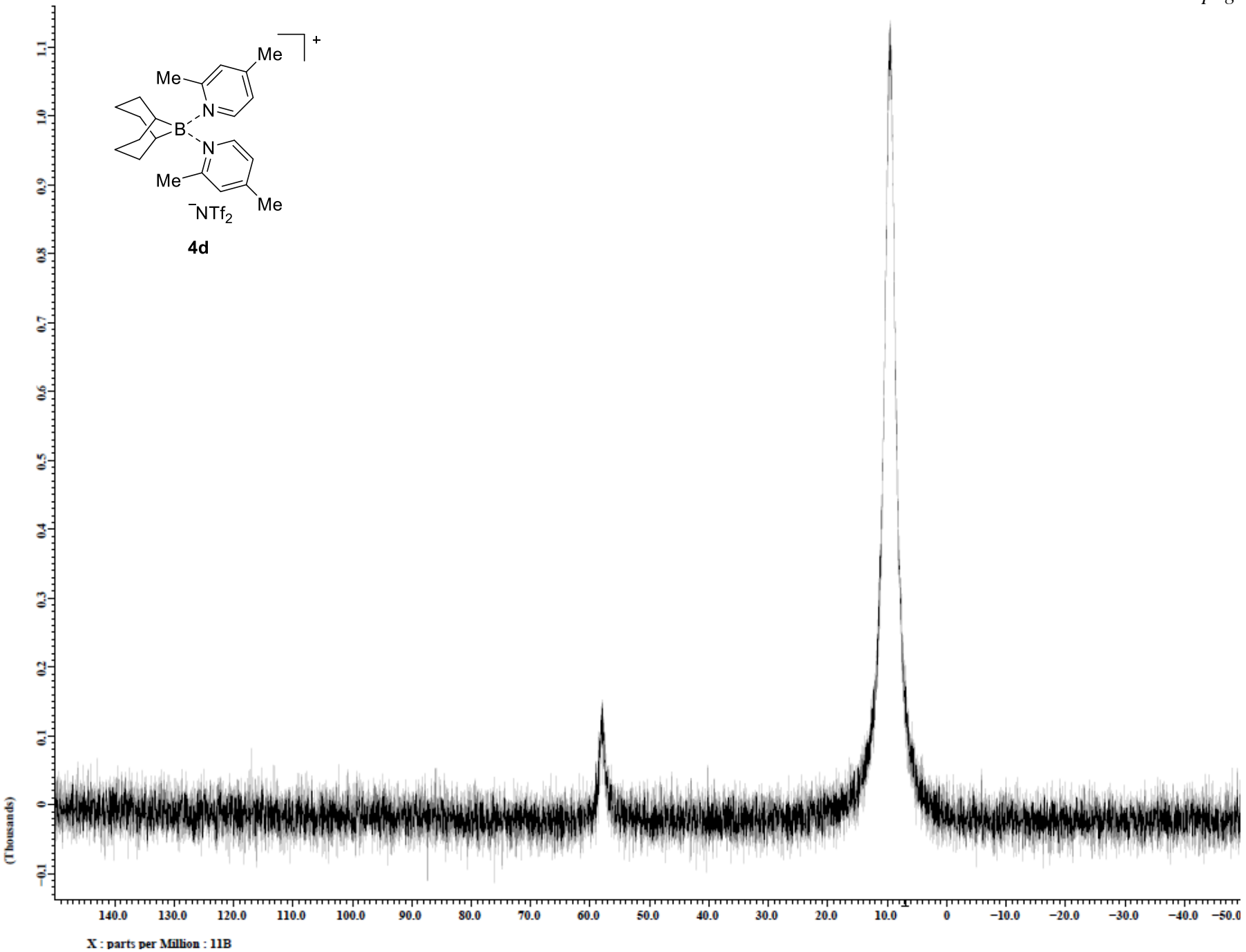

B
NTf2
N
Me
Me
2d
(Thousands)
X : parts per Million : 11B

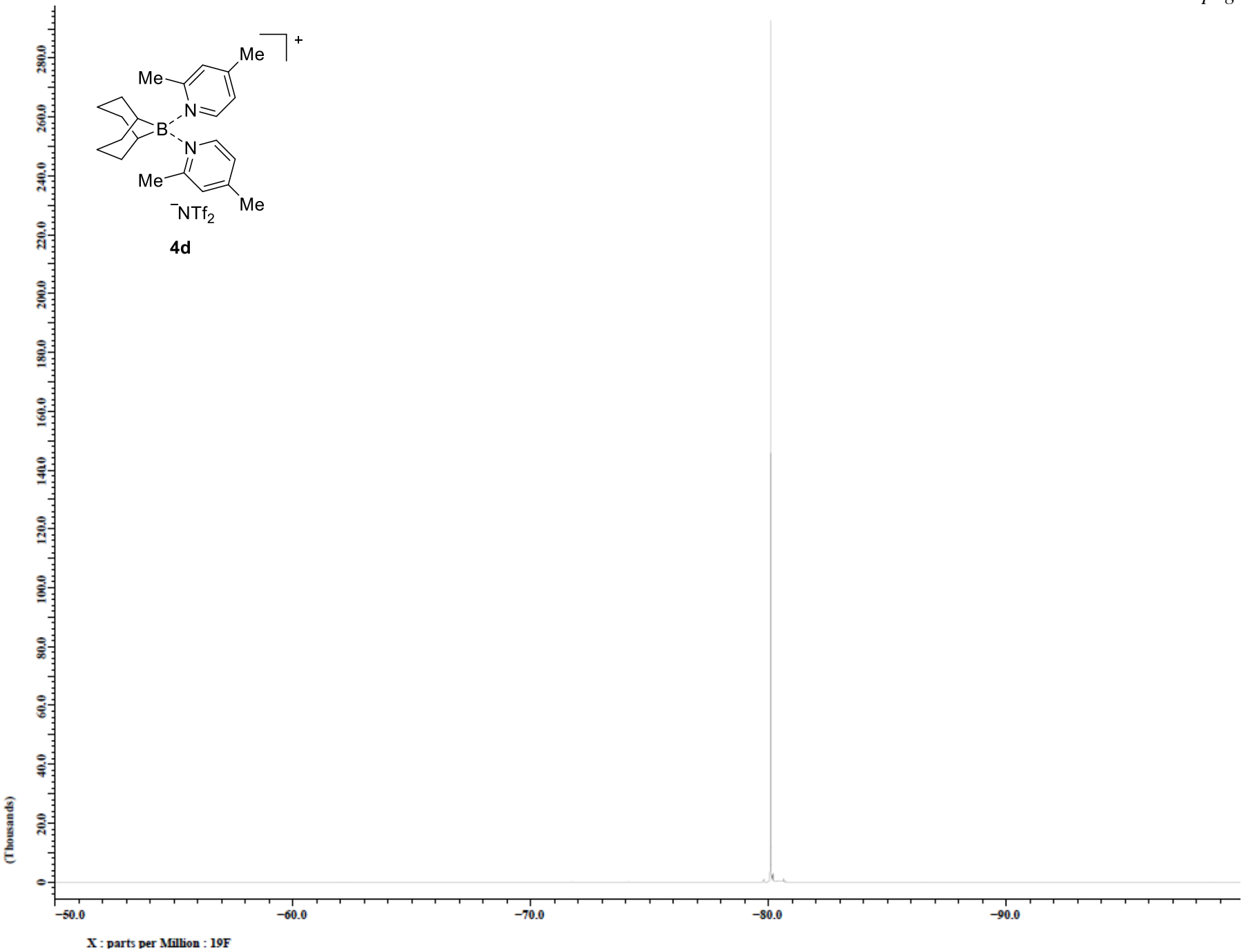

NTf2
B
N
Me
Me
2d
(Thousands)
19.0
18.0
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-50.0
-60.0
-70.0
-80.0
-90.0
X : parts per Million : 19F

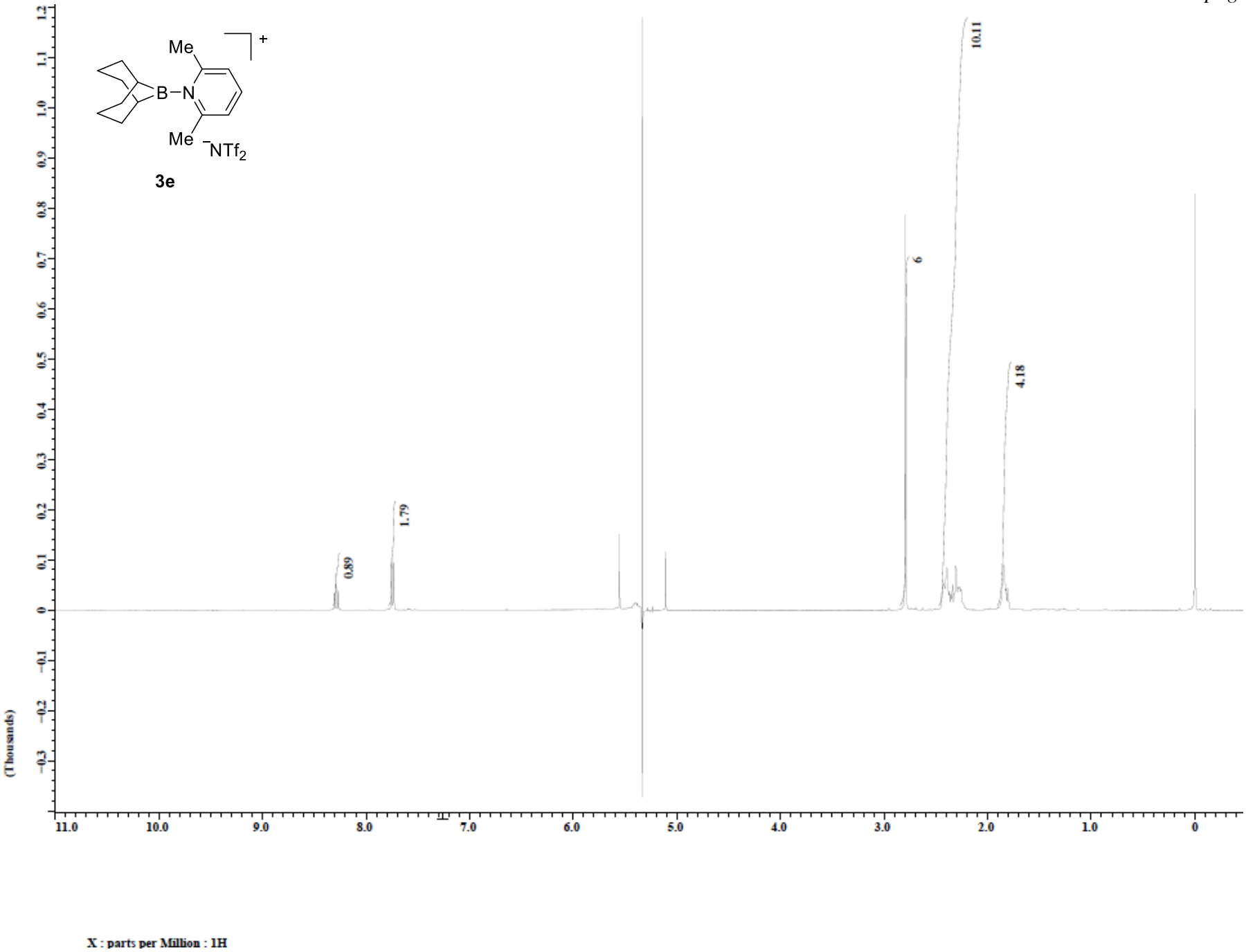


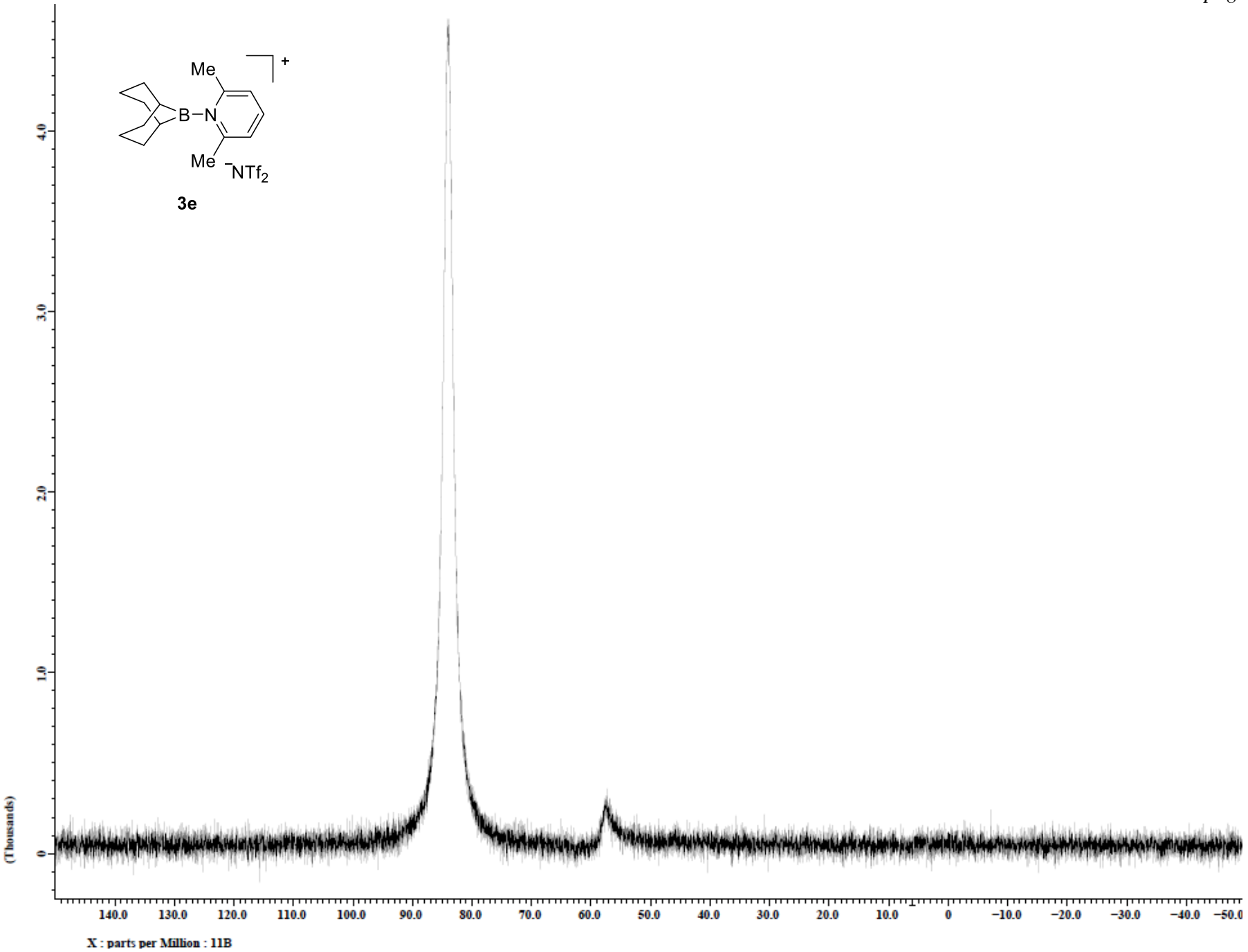
4d

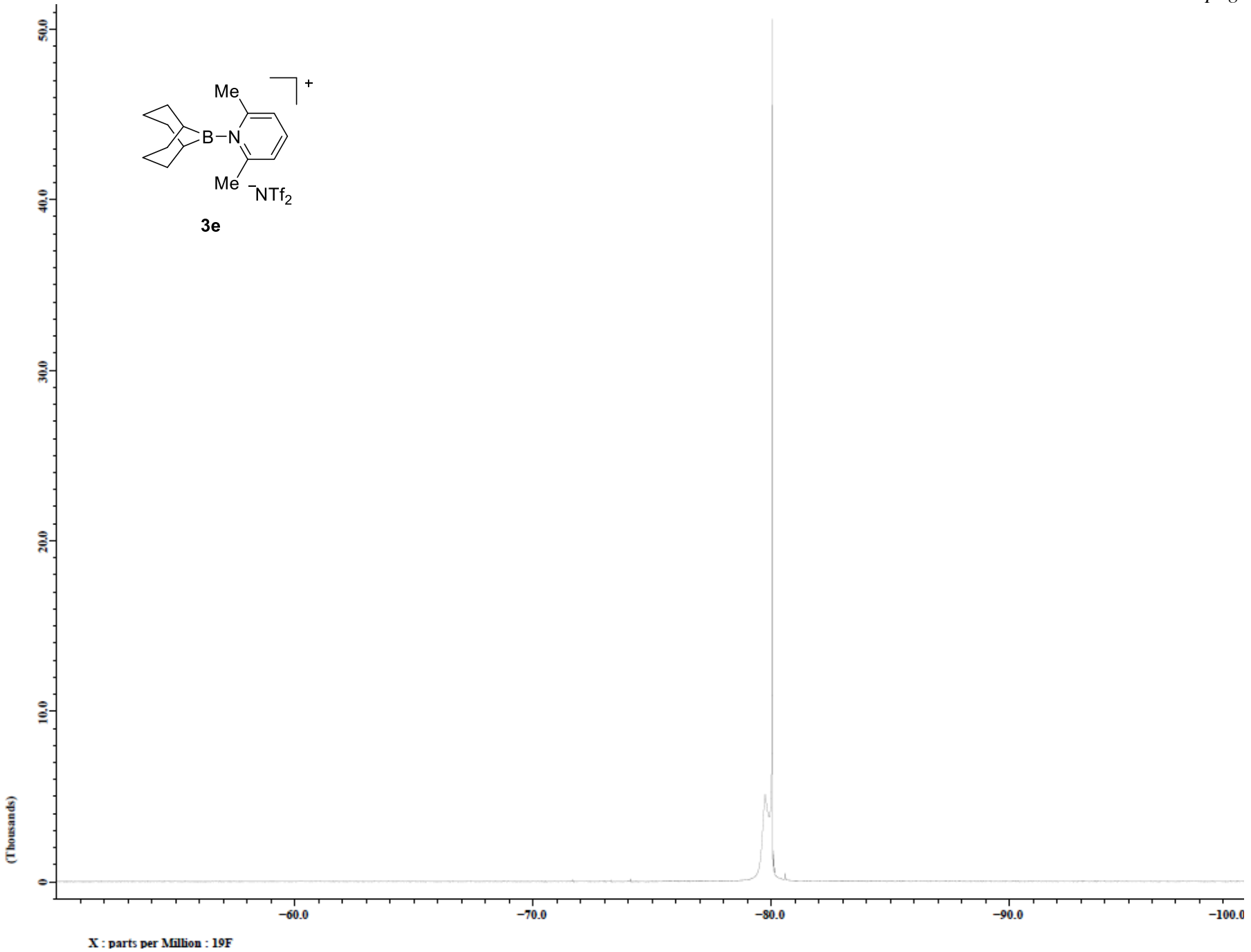
X : parts per Million : 1H

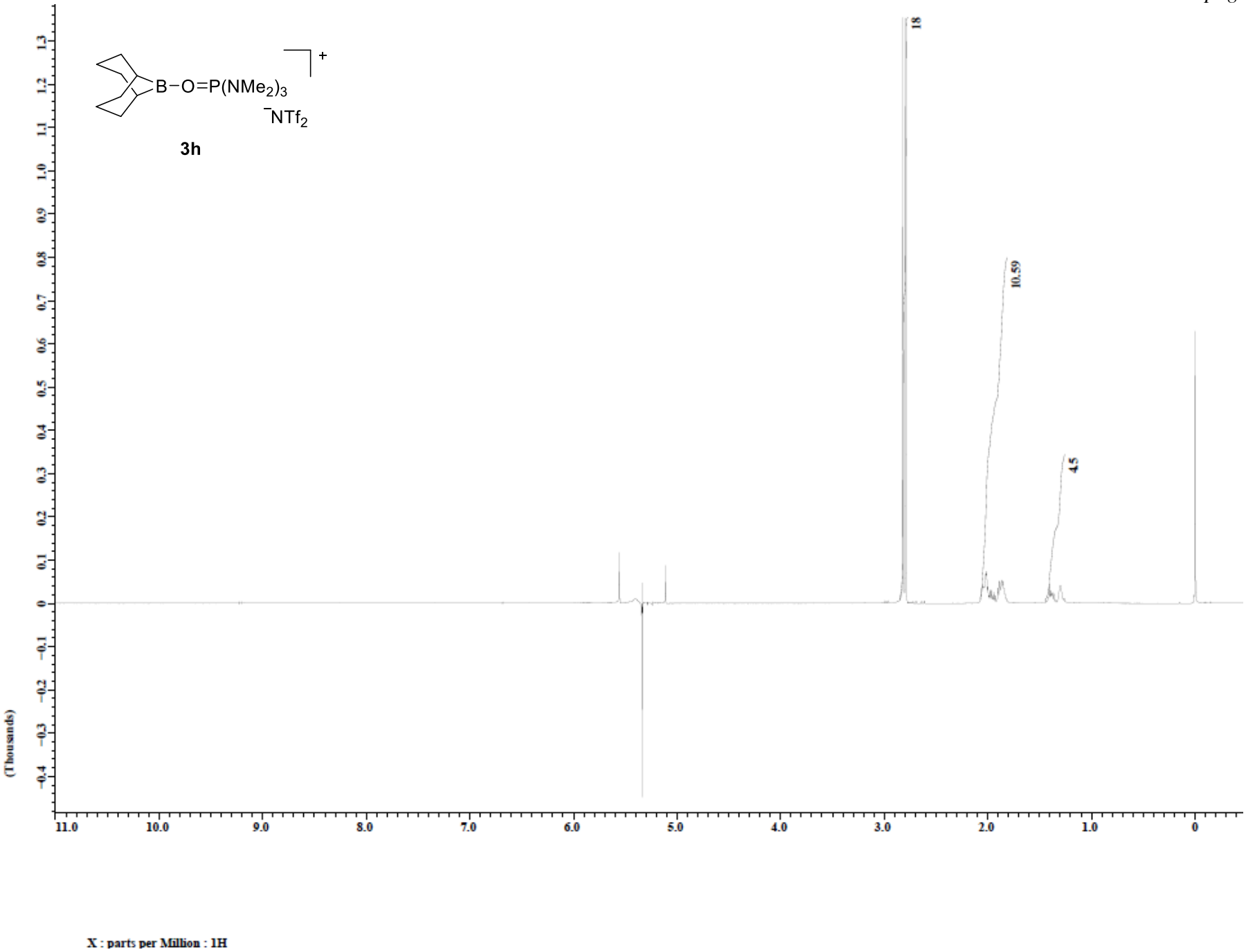

Me
Me
N
B
N
Me
Me
$^{-}NTf_2$
+
4d
(Thousands)
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
X : parts per Million : 11B

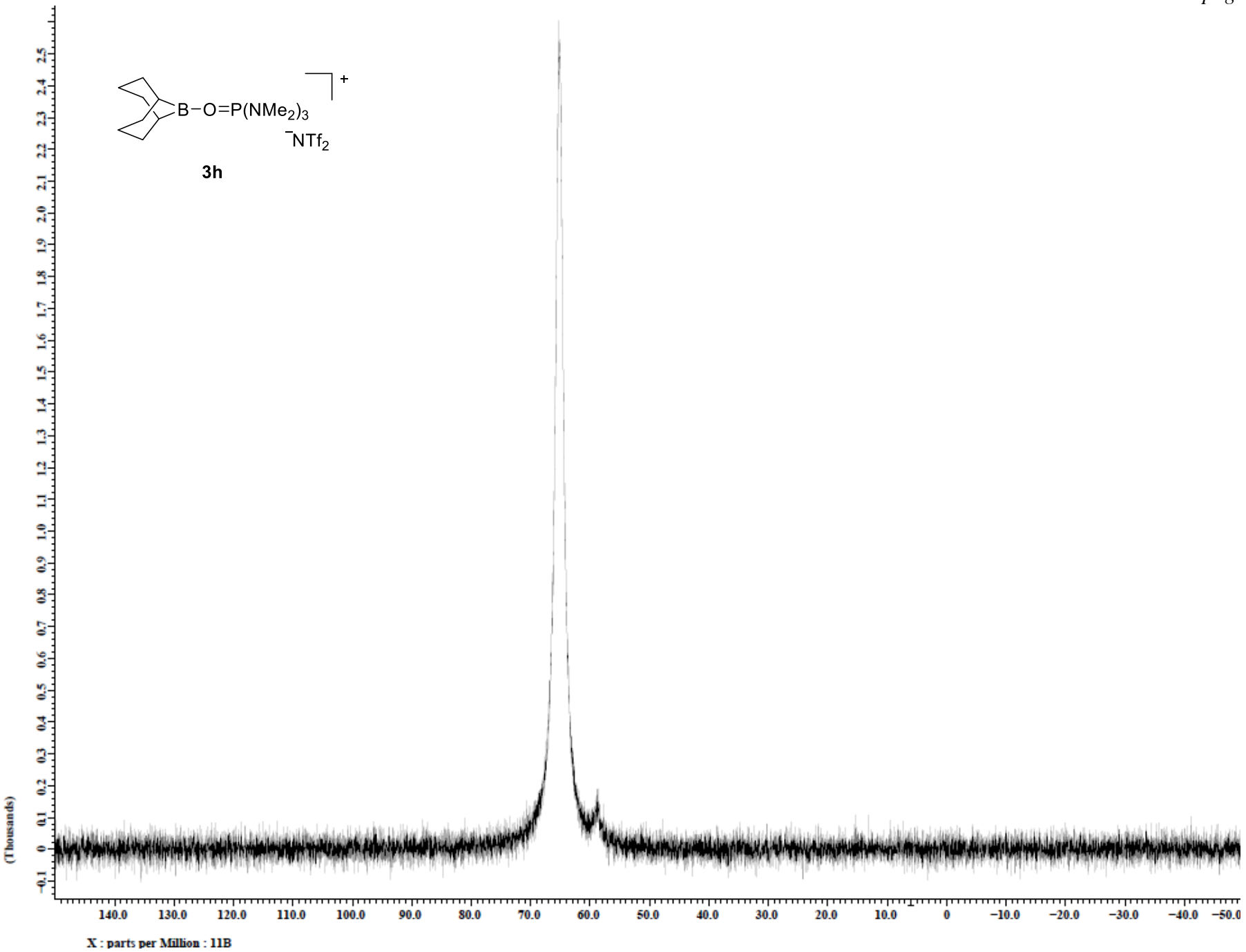

Me
Me
N
B
N
Me
Me
$^{-}NTf_2$
+
4d
(Thousands)
280.0
260.0
240.0
220.0
200.0
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
−50.0
−60.0
−70.0
−80.0
−90.0
X : parts per Million : 19F

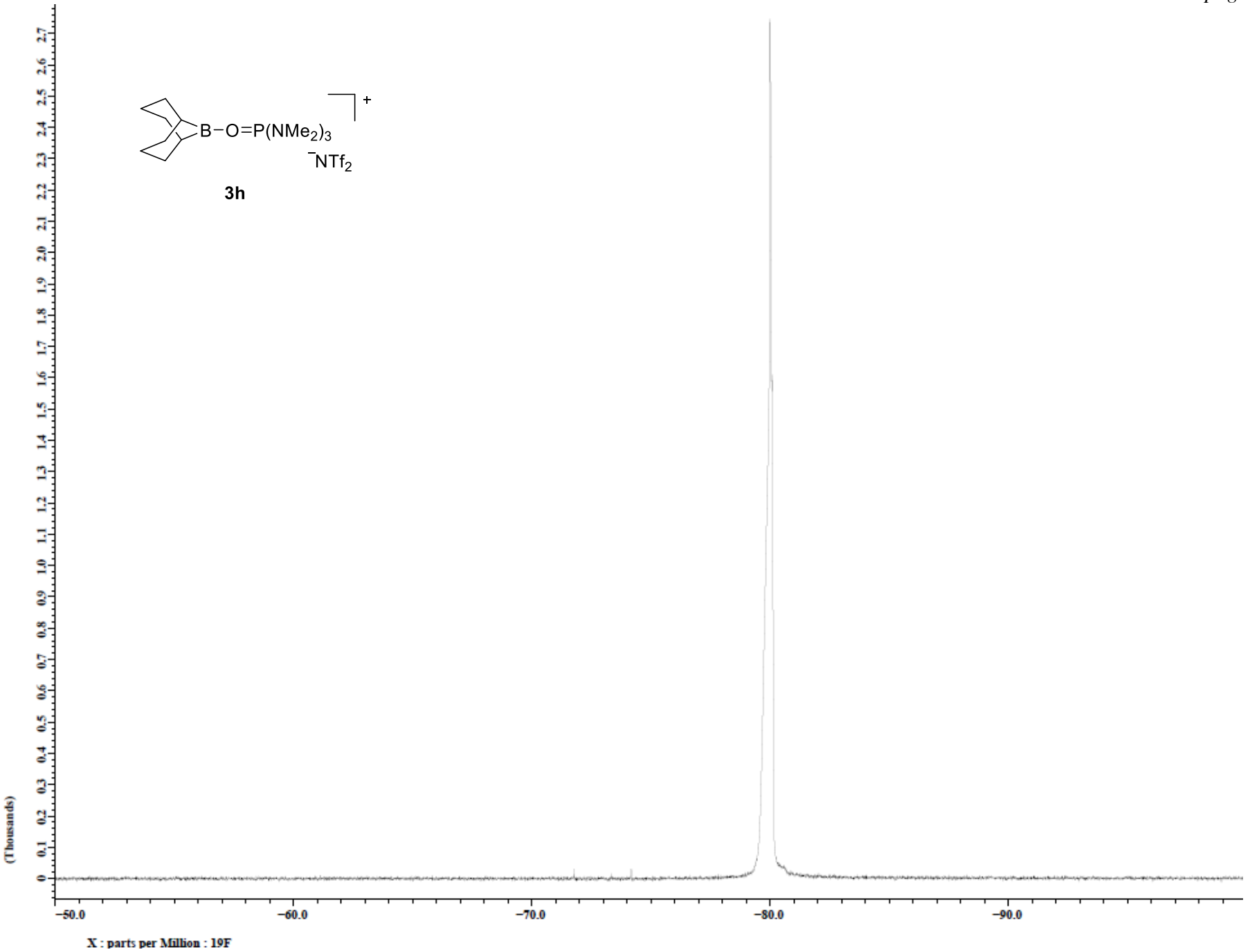

Me
B–N
Me
$^{-}NTf_2$
+
3e
10.11
6
4.18
1.79
0.89
(Thousands)
X : parts per Million : 1H

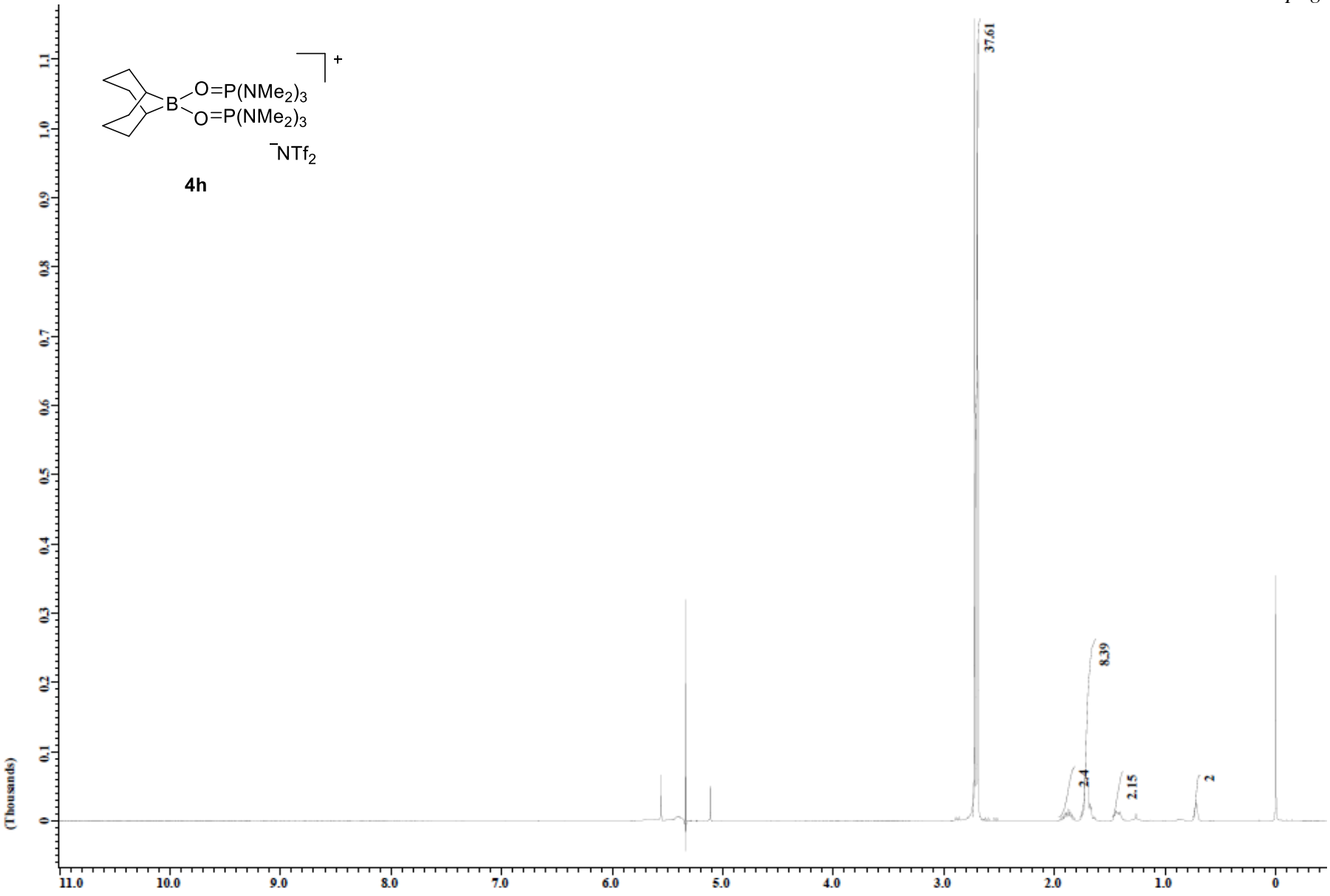

Me
B–N
Me
$^{-}$NTf$_2$
+
3e
4.0
3.0
2.0
1.0
0
(Thousands)
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
X : parts per Million : 11B


Me
B–N
Me
$^{-}NTf_2$
+
3e
50.0
40.0
30.0
20.0
10.0
0
(Thousands)
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F

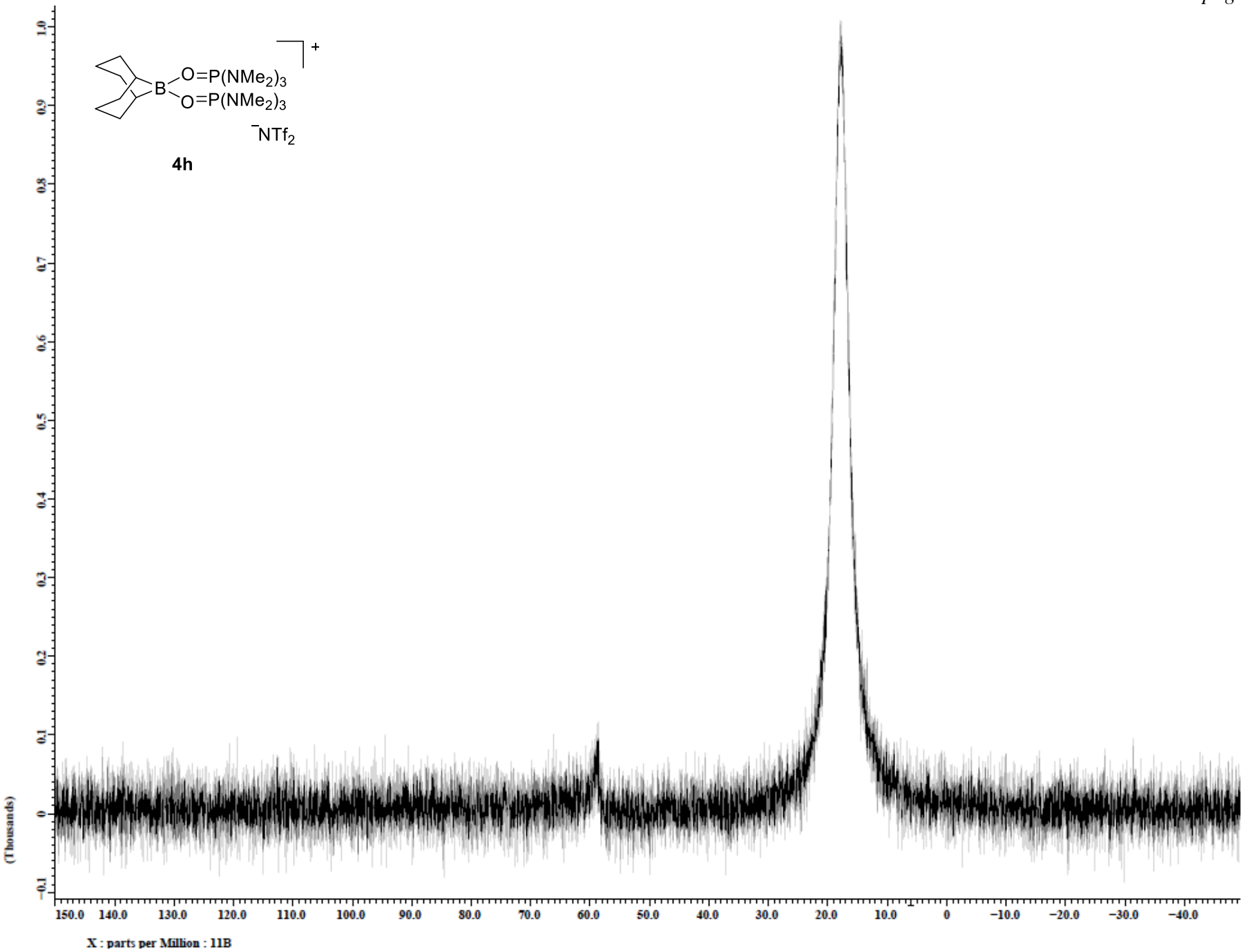

B−O=P(NMe2)3
−NTf2
+
3h
18
10.59
4.5
(Thousands)
X : parts per Million : 1H

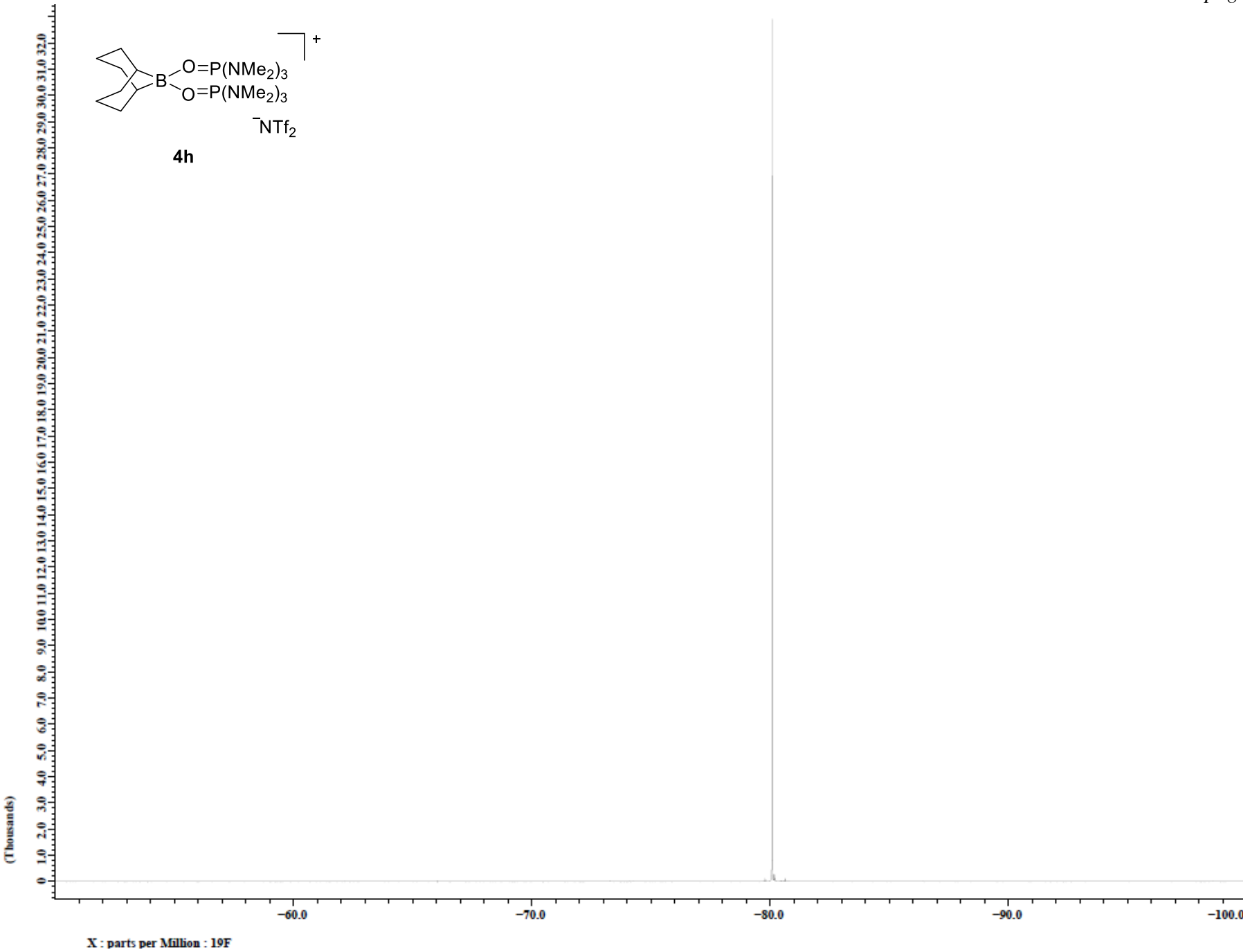

B−O=P(NMe2)3
−NTf2
+
3h
(Thousands)
X : parts per Million : 11B


B–O=P(NMe2)3
+
−NTf2
3h
(Thousands)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
−50.0
−60.0
−70.0
−80.0
−90.0
X : parts per Million : 19F

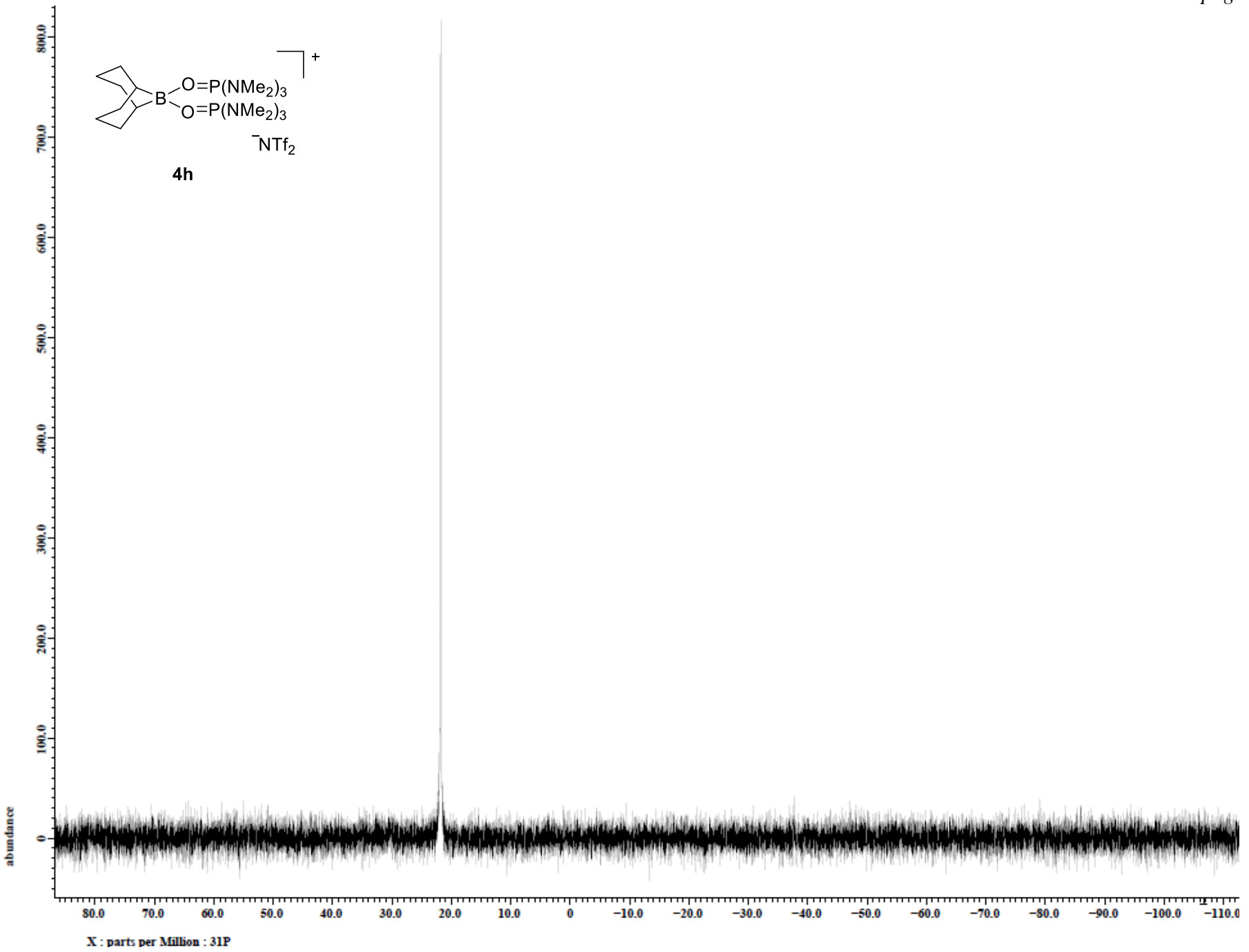


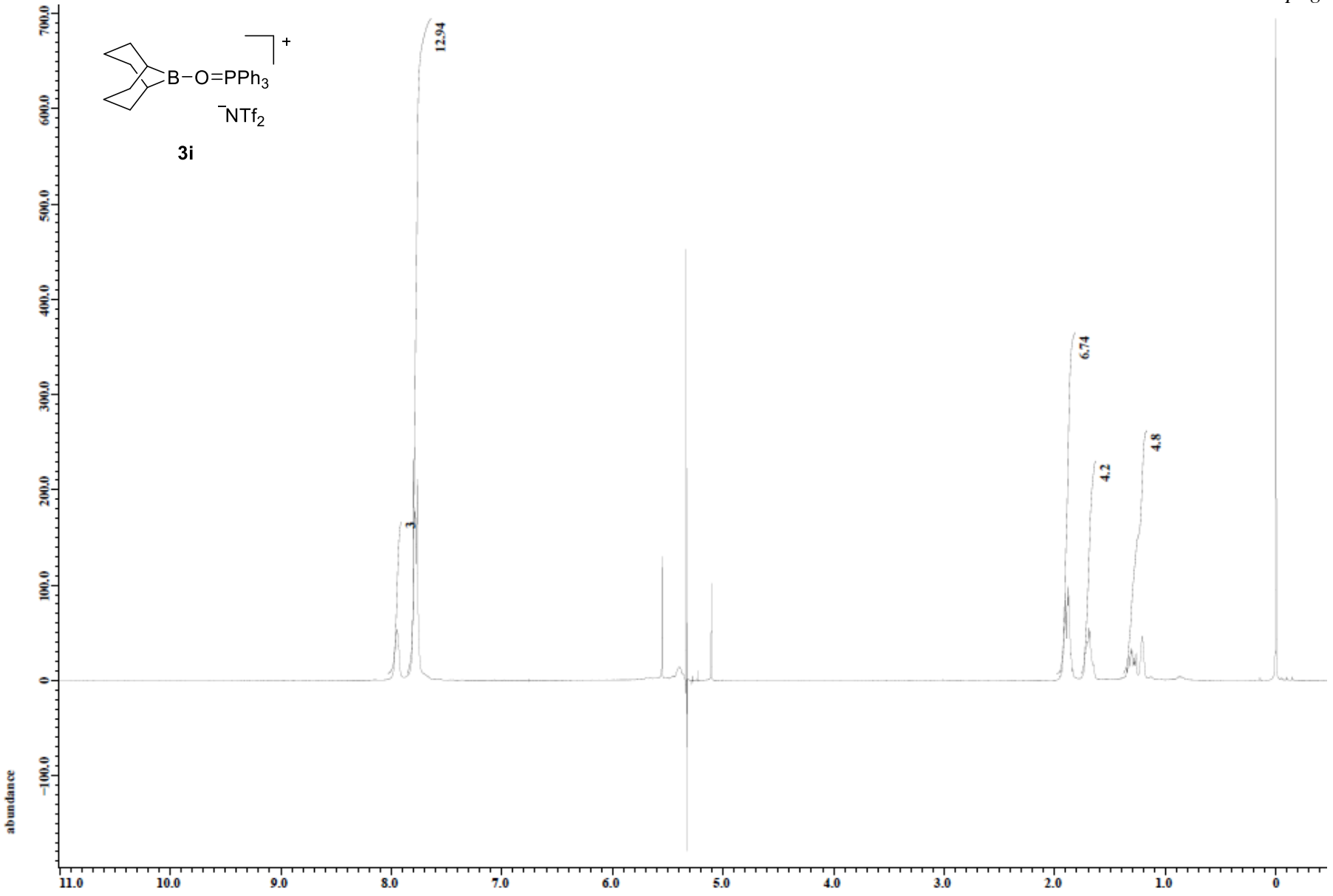
X : parts per Million : 1H

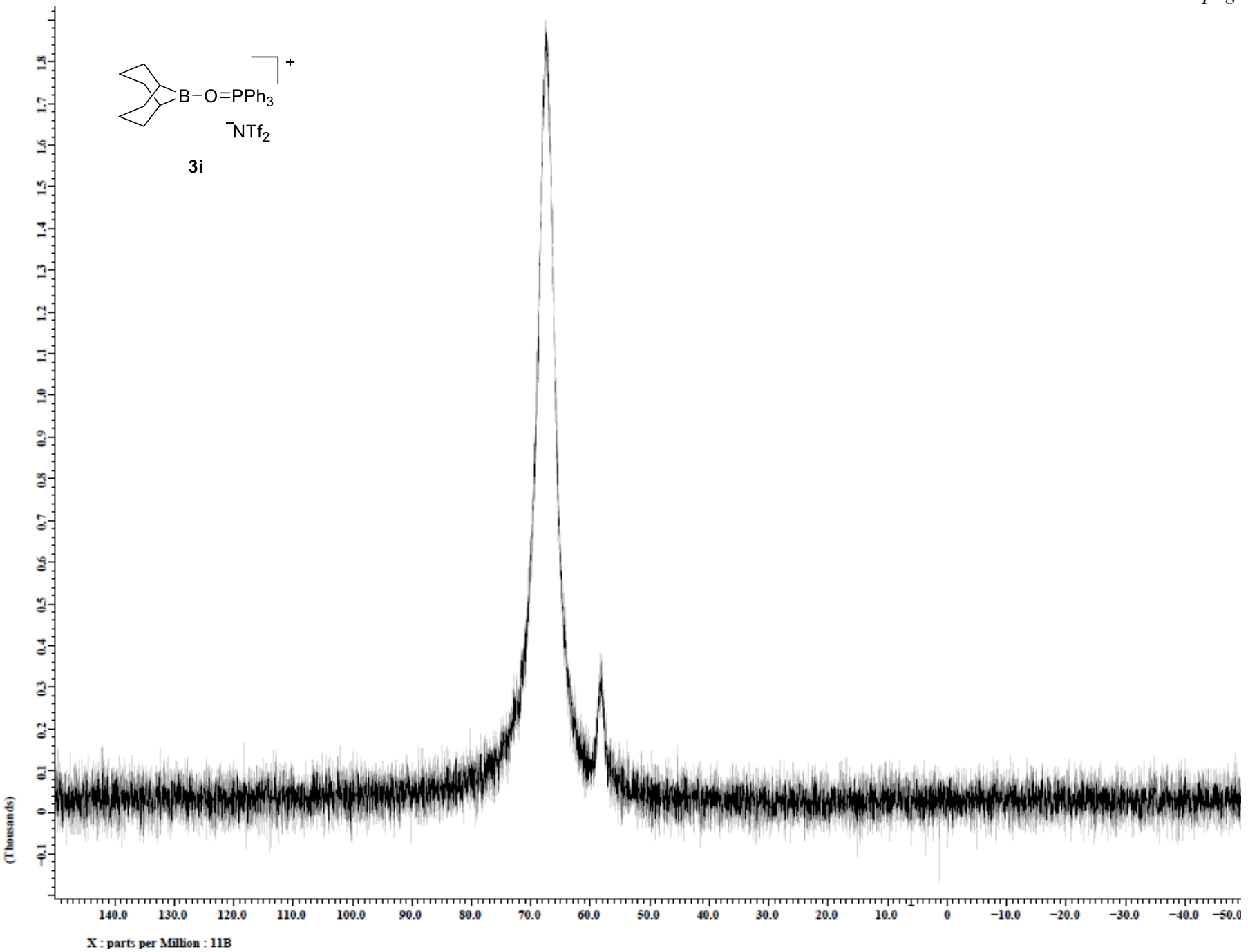

O=P(NMe2)3
B
O=P(NMe2)3
+
−NTf2
4h
(Thousands)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0
X : parts per Million : 11B

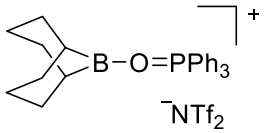

O=P(NMe2)3
O=P(NMe2)3
B
+
NTf2
(Thousands)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0 28.0 29.0 30.0 31.0 32.0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F

4h


O=P(NMe2)3
O=P(NMe2)3
B
+
−NTf2
4h
abundance
X : parts per Million : 31P

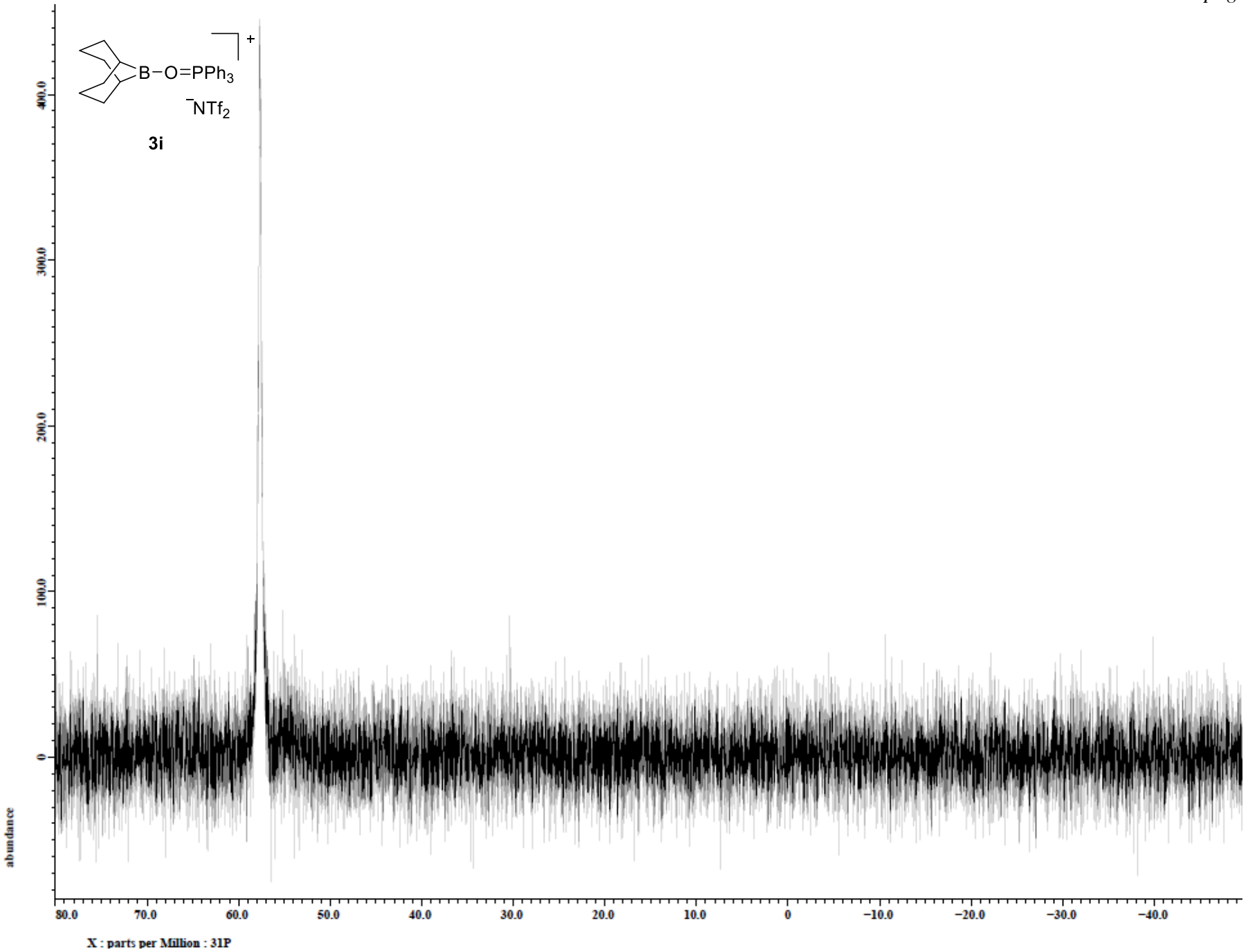

B−O=PPh3
NTf2
3i
12.94
6.74
4.2
4.8
3
abundance
X : parts per Million : 1H

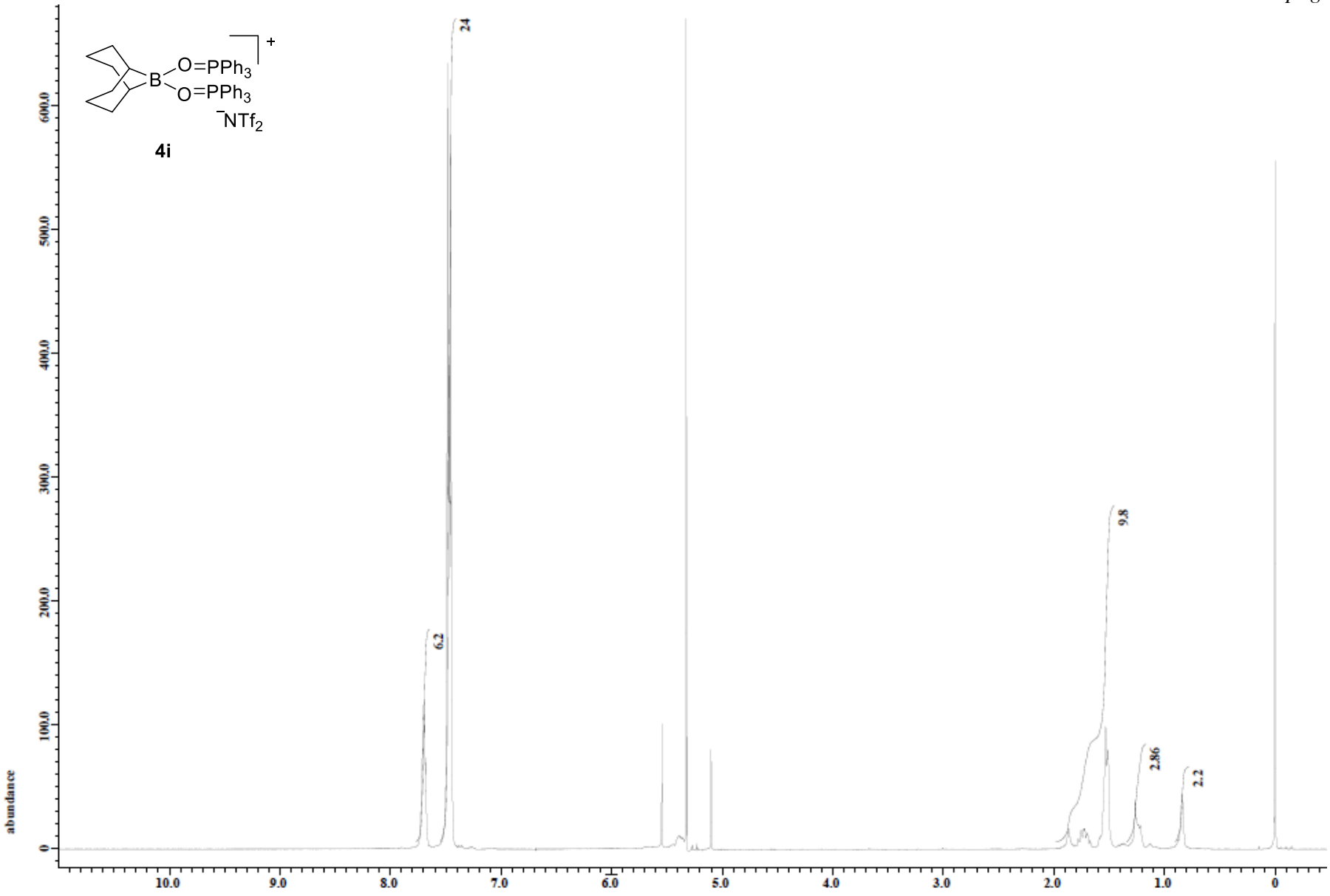

B–O=PPh3
NTf2
+
3i
(Thousands)
X : parts per Million : 11B

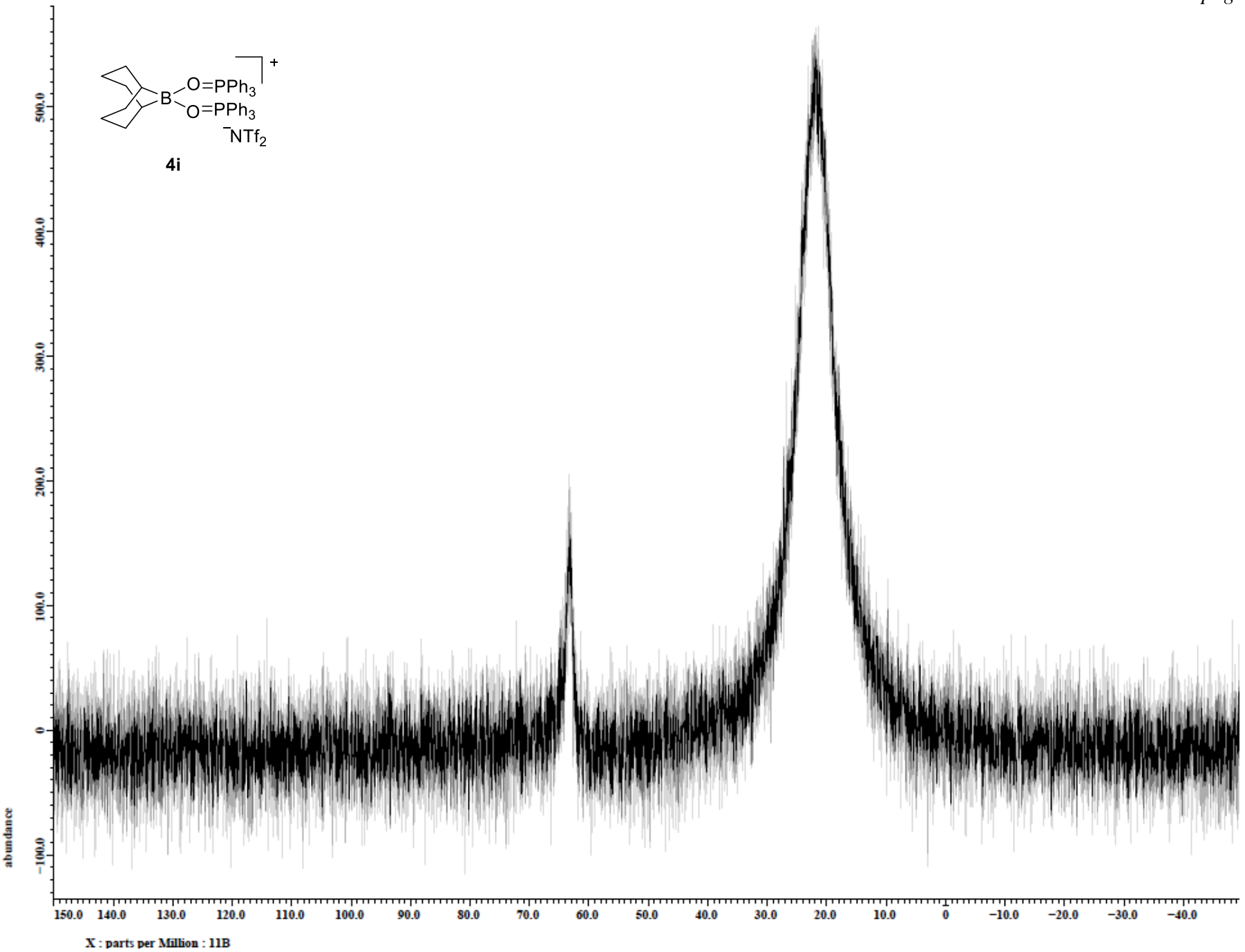

B−O=PPh3
−NTf2
+

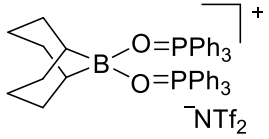
3i

(Thousands)
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F


B−O=PPh3
−NTf2
+
3i
400.0
300.0
200.0
100.0
0
abundance
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
X : parts per Million : 31P

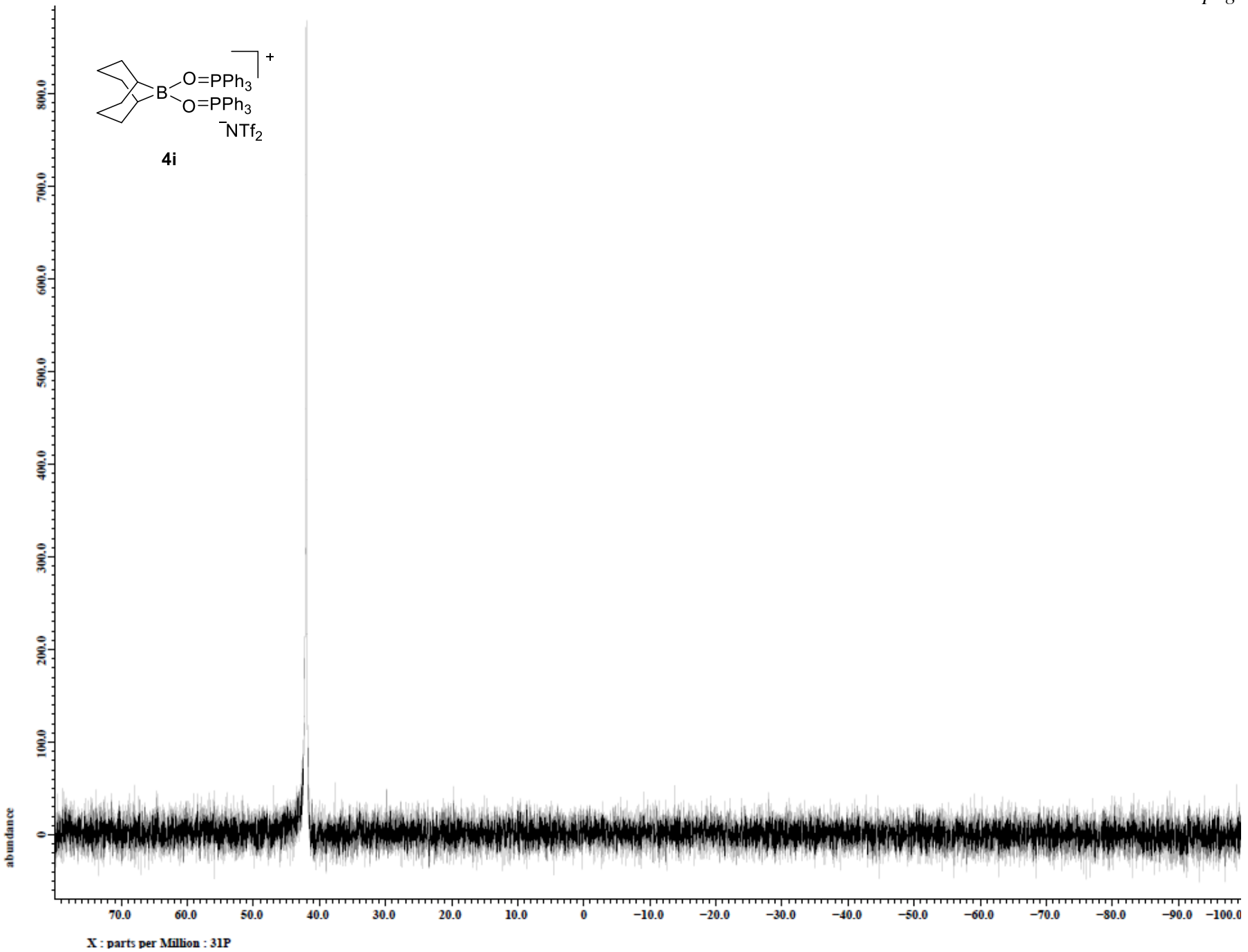

O=PPh3
O=PPh3
B
−NTf2
+
4i
24
6.2
9.8
2.86
2.2
abundance
600.0
500.0
400.0
300.0
200.0
100.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

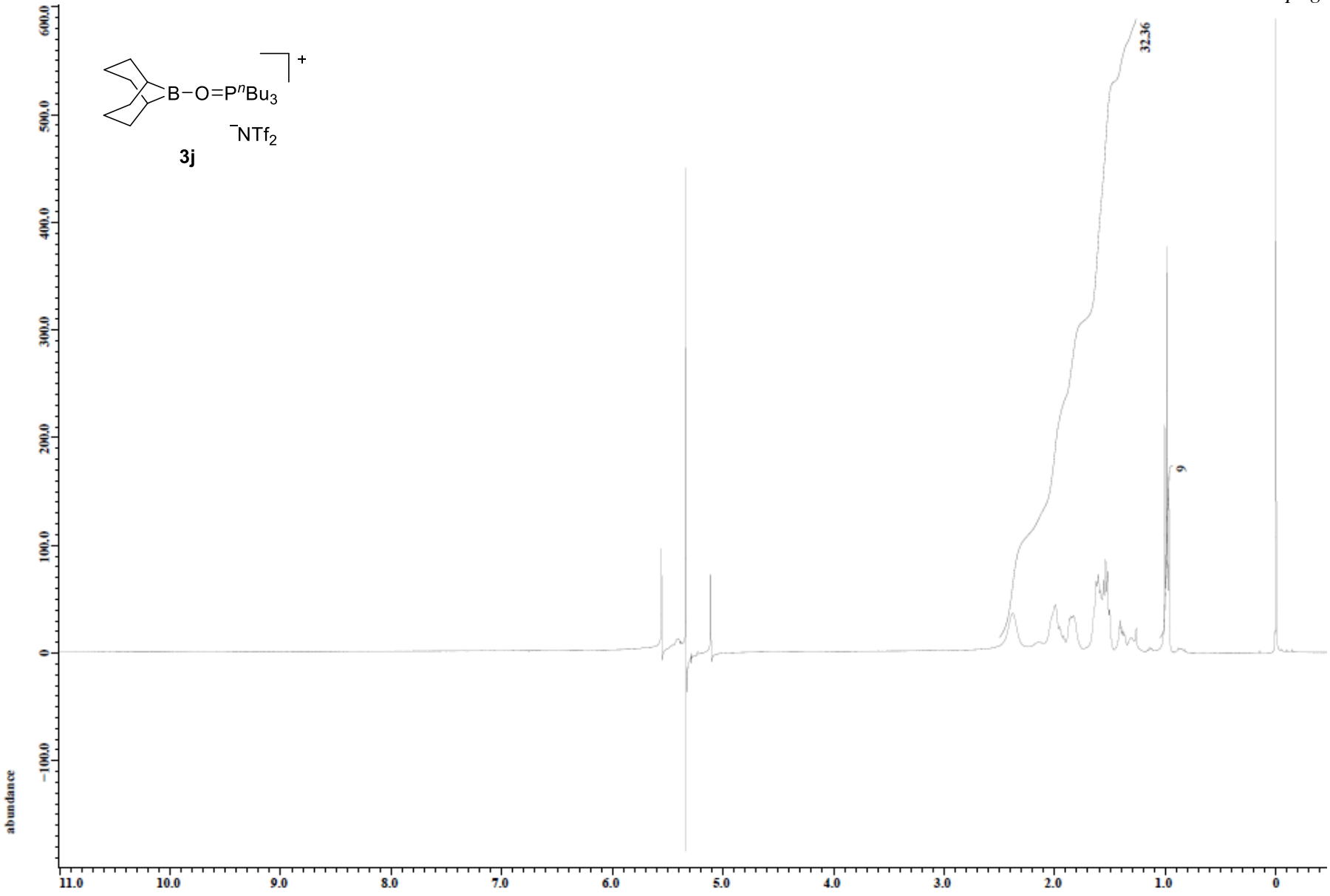

O=PPh3
B
O=PPh3
−NTf2
+
4i
500.0
400.0
300.0
200.0
100.0
0
−100.0
abundance
150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0
X : parts per Million : 11B

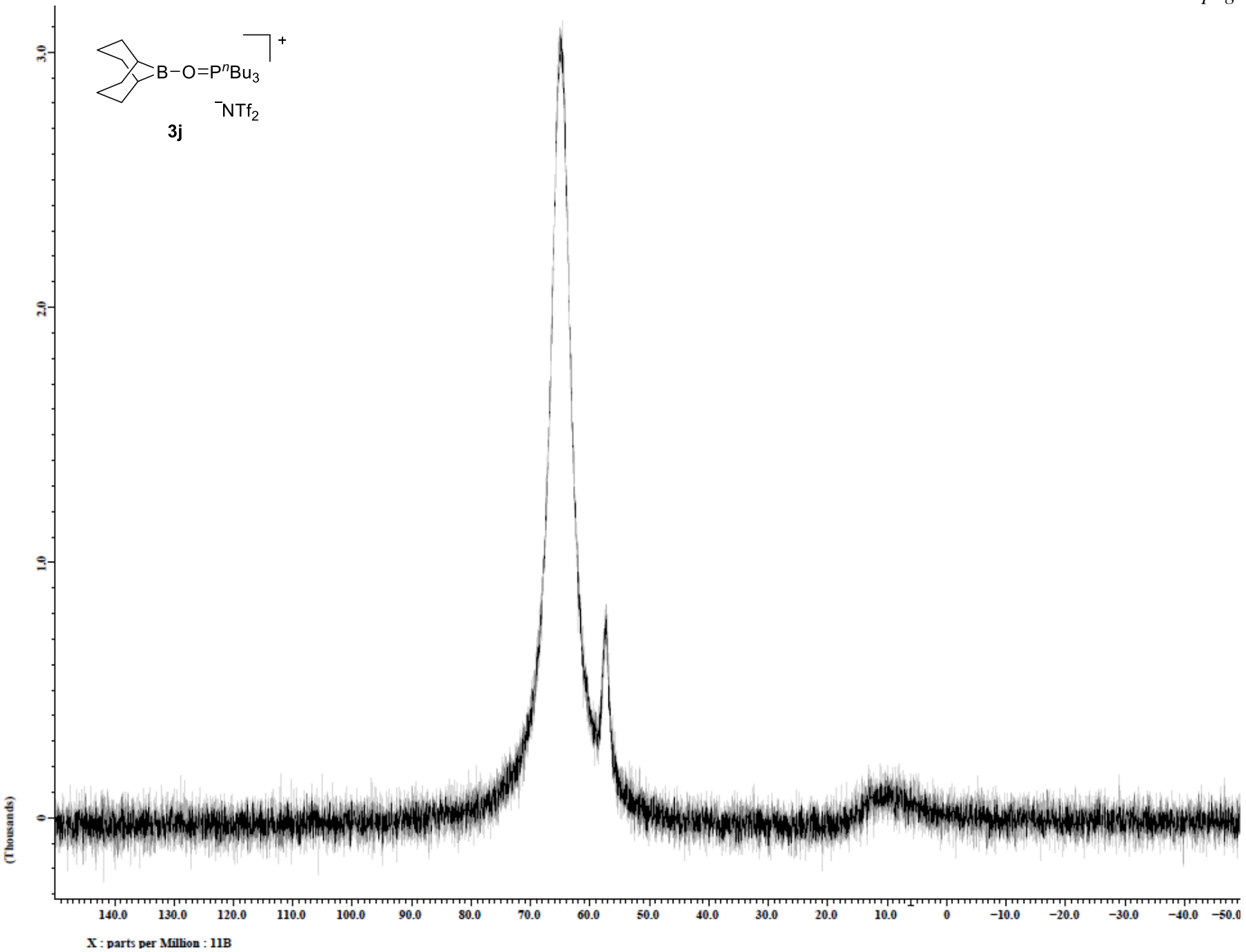

O=PPh3
B
O=PPh3
+
NTf2

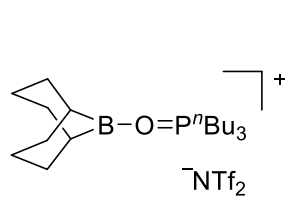
4i

(Thousands)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0 24.0 25.0 26.0 27.0 28.0 29.0 30.0 31.0 32.0
−50.0
−60.0
−70.0
−80.0
−90.0
X : parts per Million : 19F


O=PPh3
O=PPh3
B
+
−NTf2
4i
abundance
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 31P

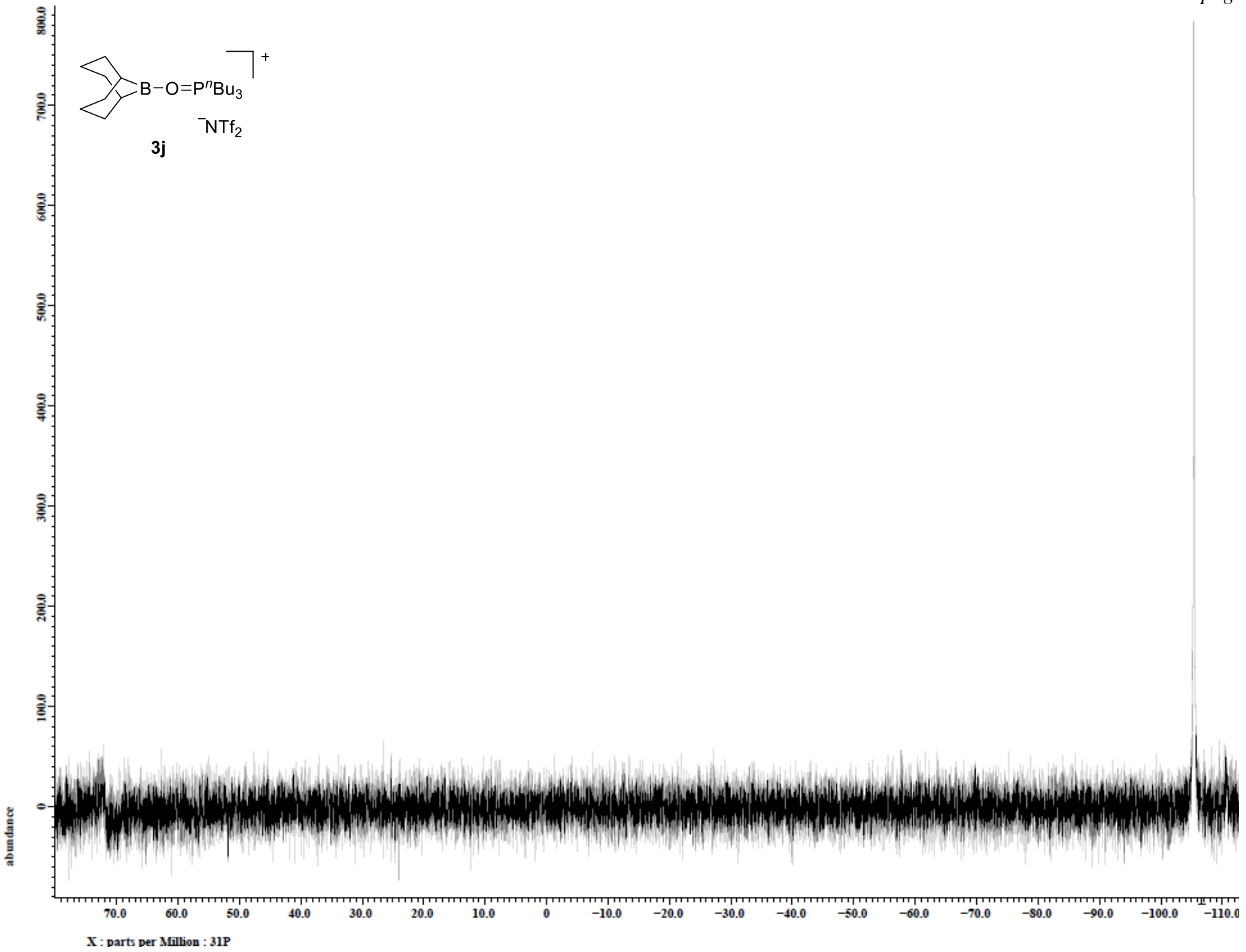

B–O=P^{n}Bu$_3$
$^-$NTf$_2$
3j
32.36
9
abundance
600.0
500.0
400.0
300.0
200.0
100.0
0
−100.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

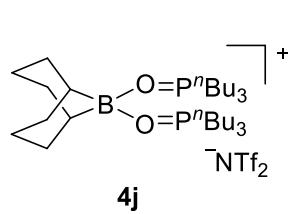

B−O=P^{n}Bu$_3$
$^-$NTf$_2$
3j
(Thousands)
3.0
2.0
1.0
0
140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0 −50.0
X : parts per Million : 11B


B−O=P^{n}Bu$_3$
$^-$NTf$_2$

3j

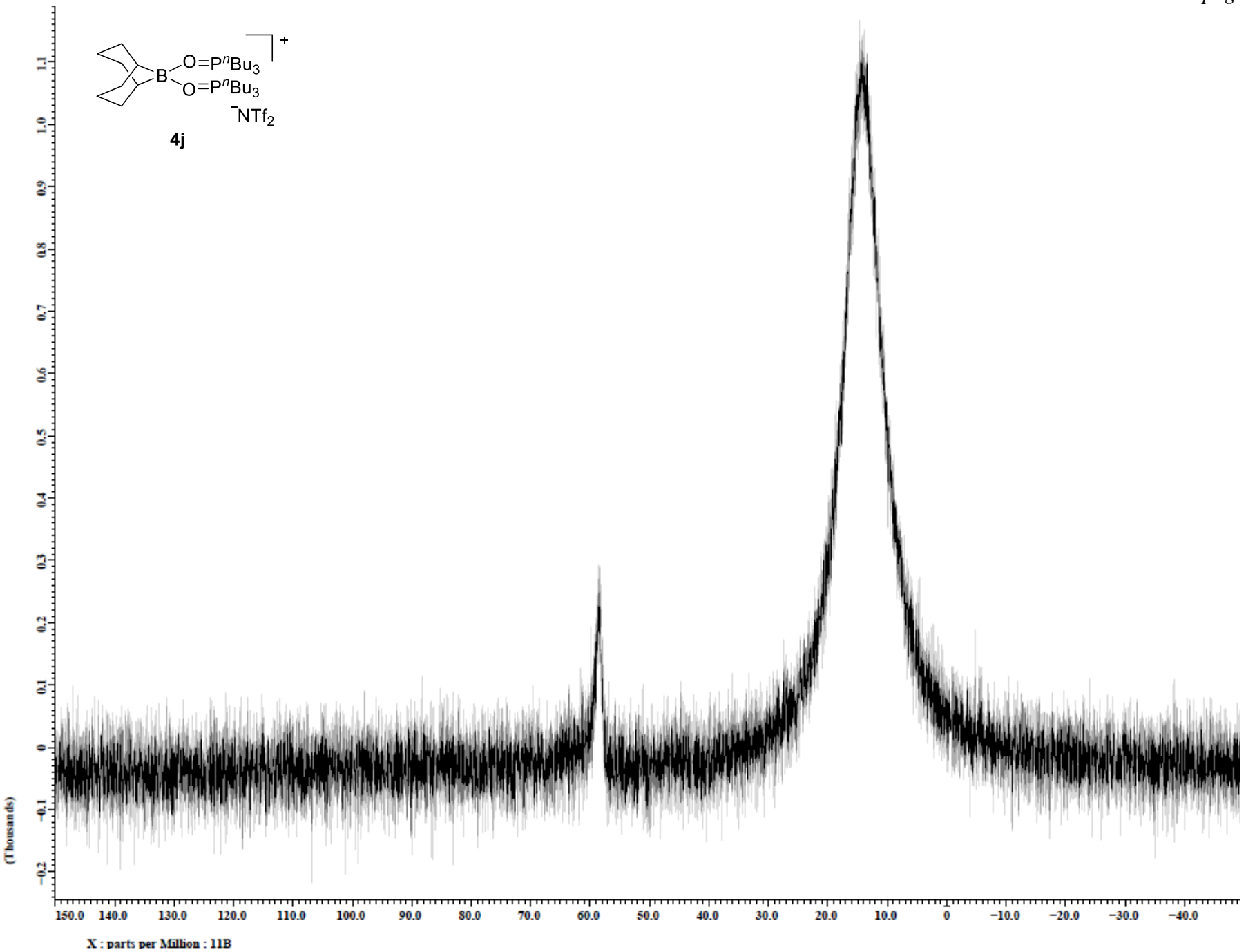
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
24.0
25.0
26.0
27.0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F

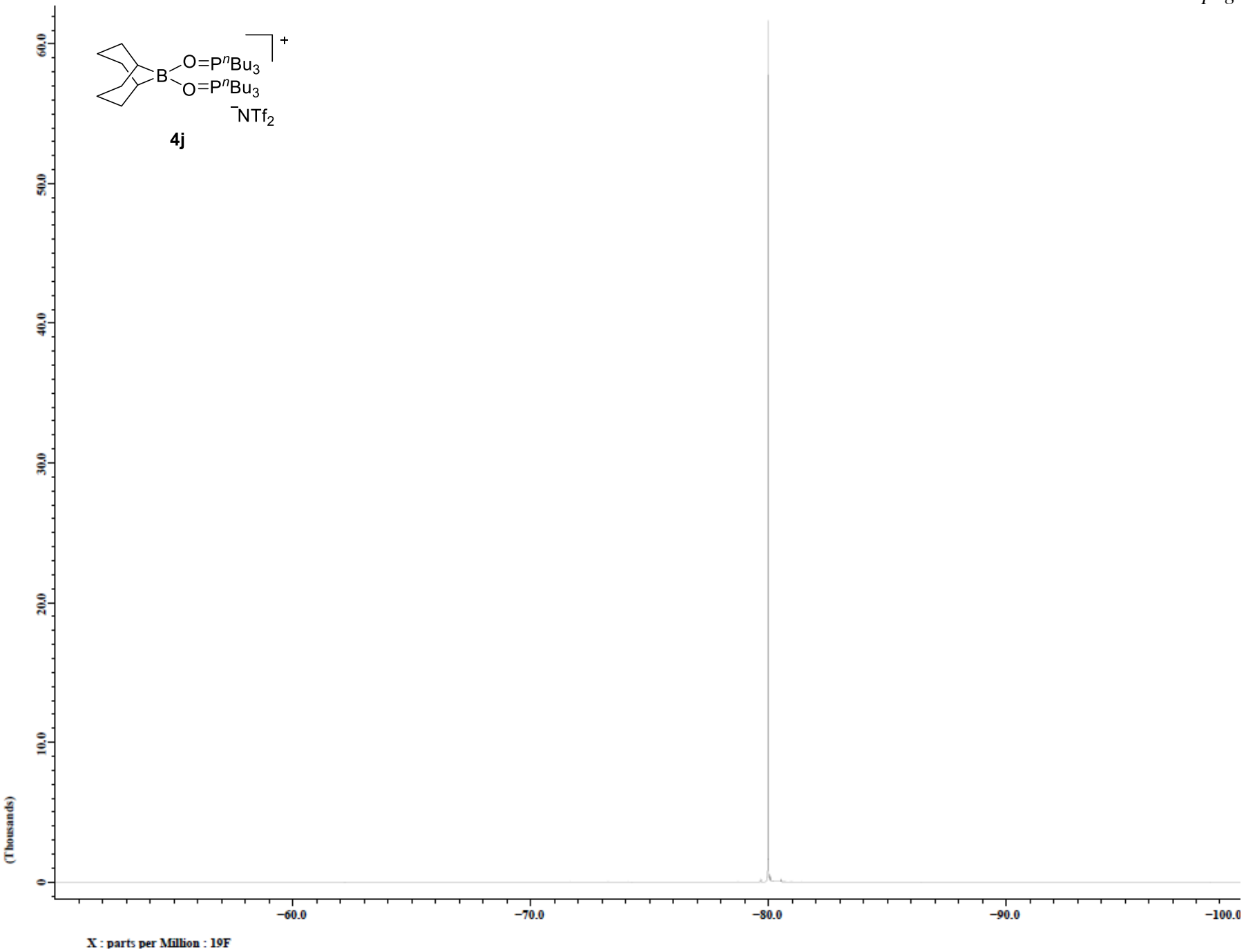

B−O=P^{n}Bu$_3$
$^-$NTf$_2$
+
3j
abundance
X : parts per Million : 31P

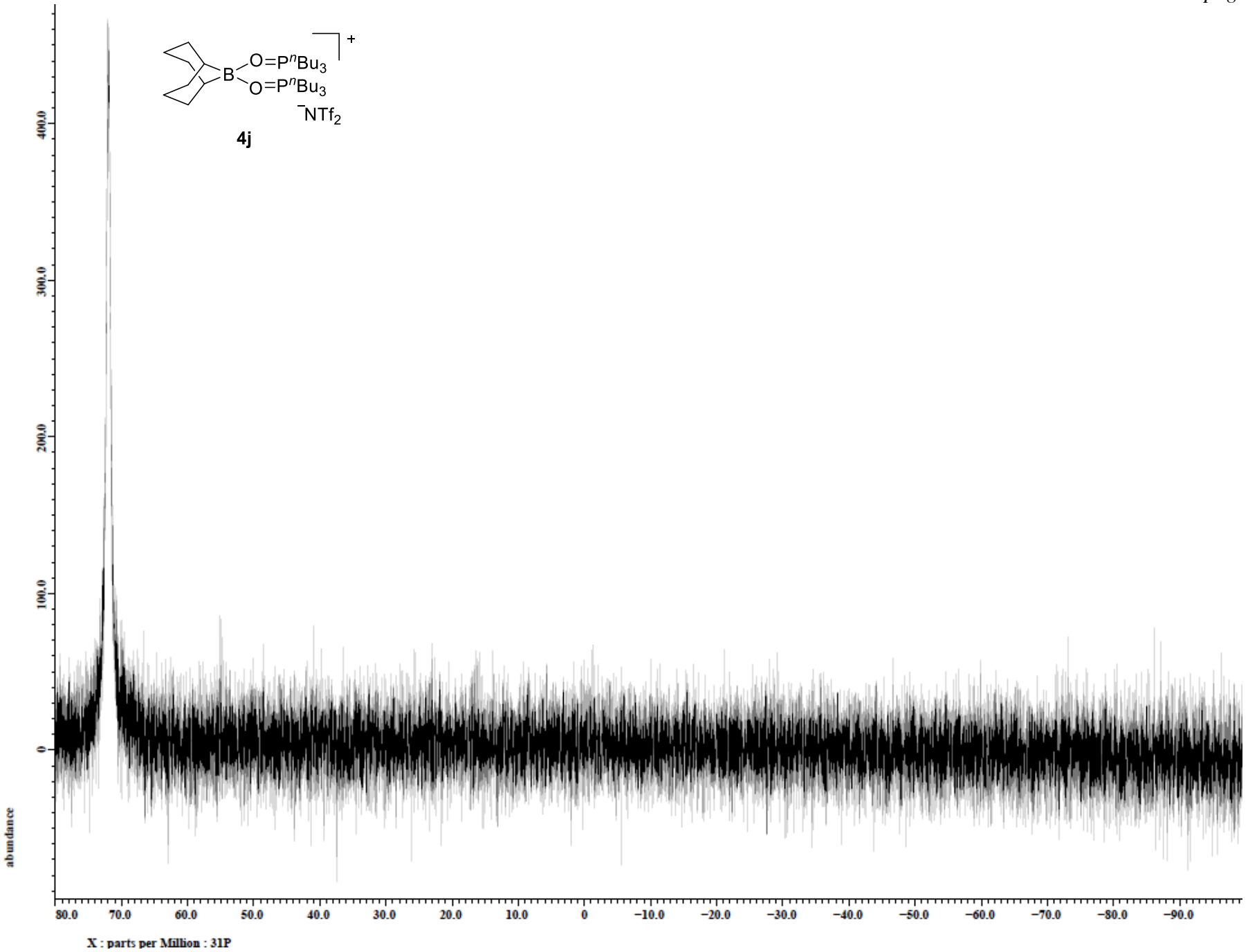

O=P^{n}Bu$_3$
B
O=P^{n}Bu$_3$
$^-$NTf$_2$
+

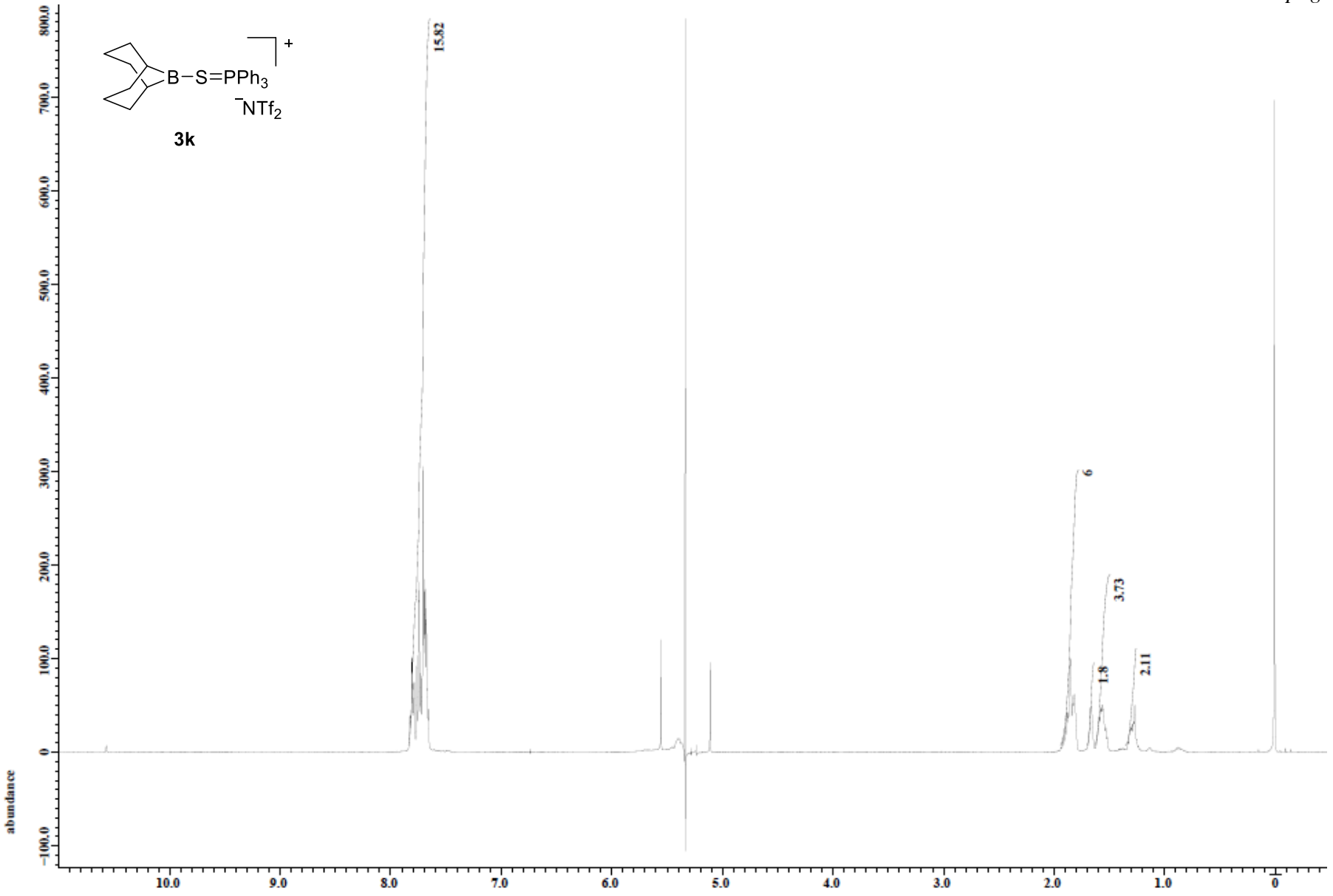
4j

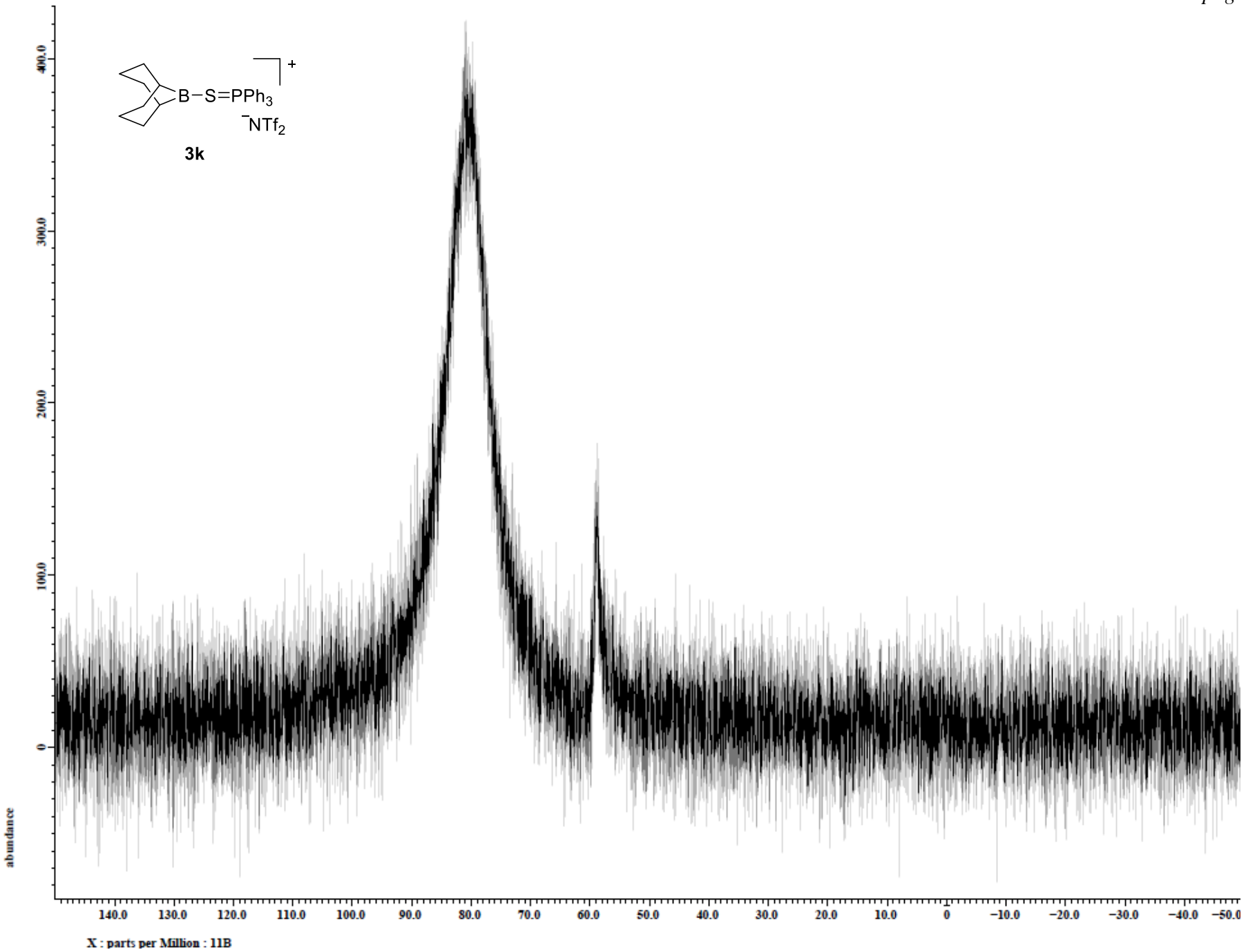
48.12
18
1.78
abundance
500.0
400.0
300.0
200.0
100.0
0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

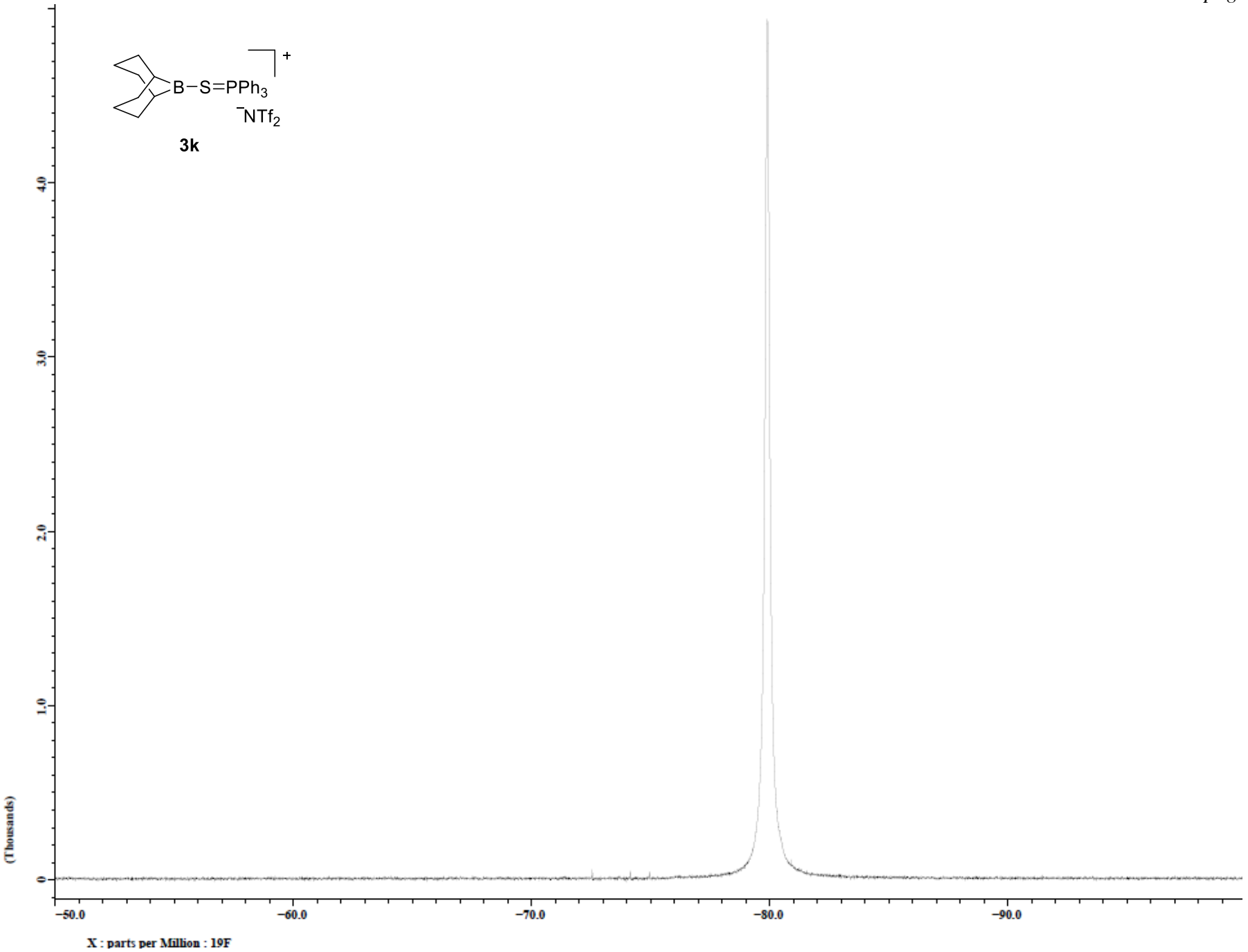

O=P^{n}Bu$_3$
O=P^{n}Bu$_3$
B
$^-$NTf$_2$
+
4j
(Thousands)
X : parts per Million : 11B

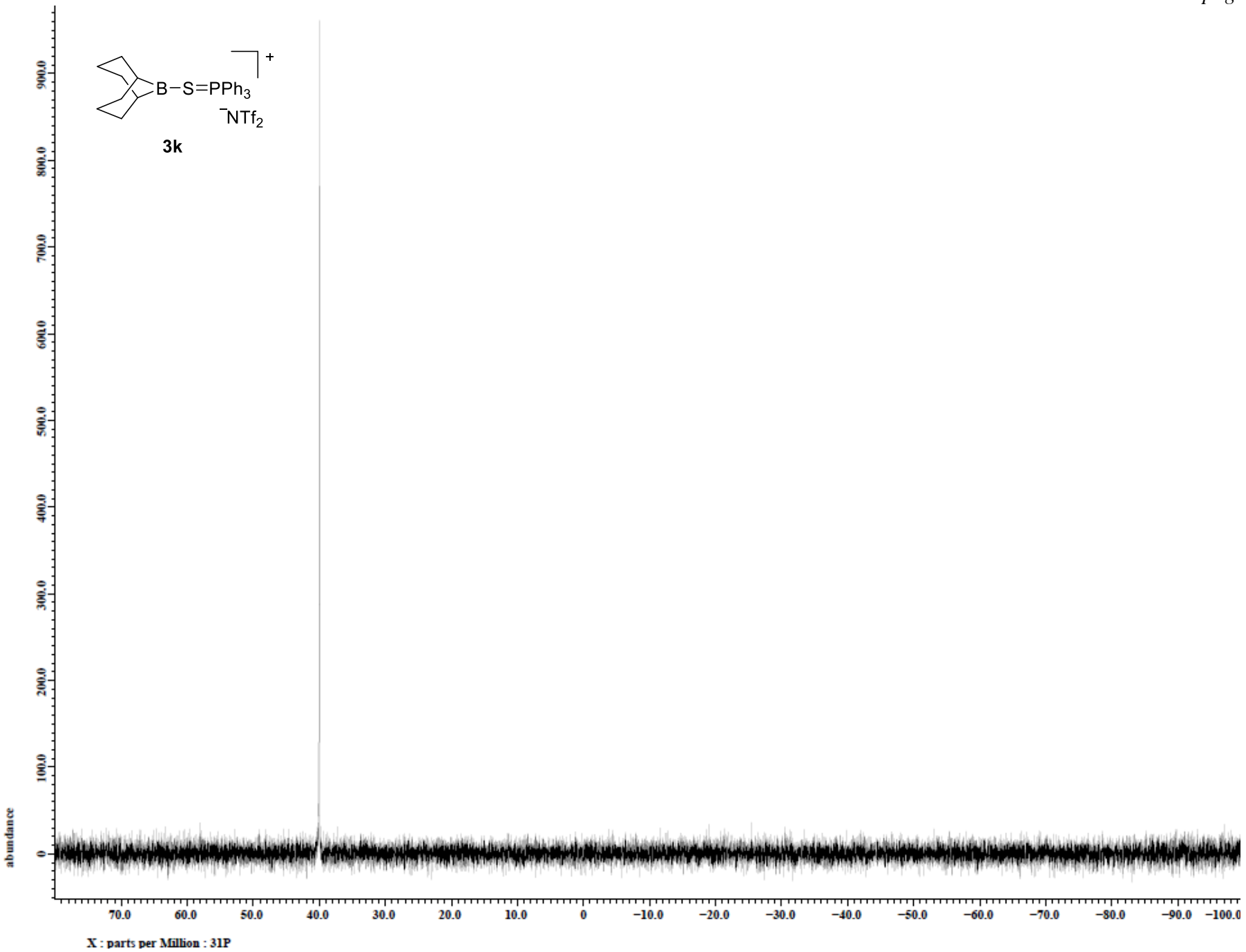

O=P^{n}Bu$_3$
O=P^{n}Bu$_3$
B
$^-$NTf$_2$
+
4j
60.0
50.0
40.0
30.0
20.0
10.0
0
(Thousands)
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F

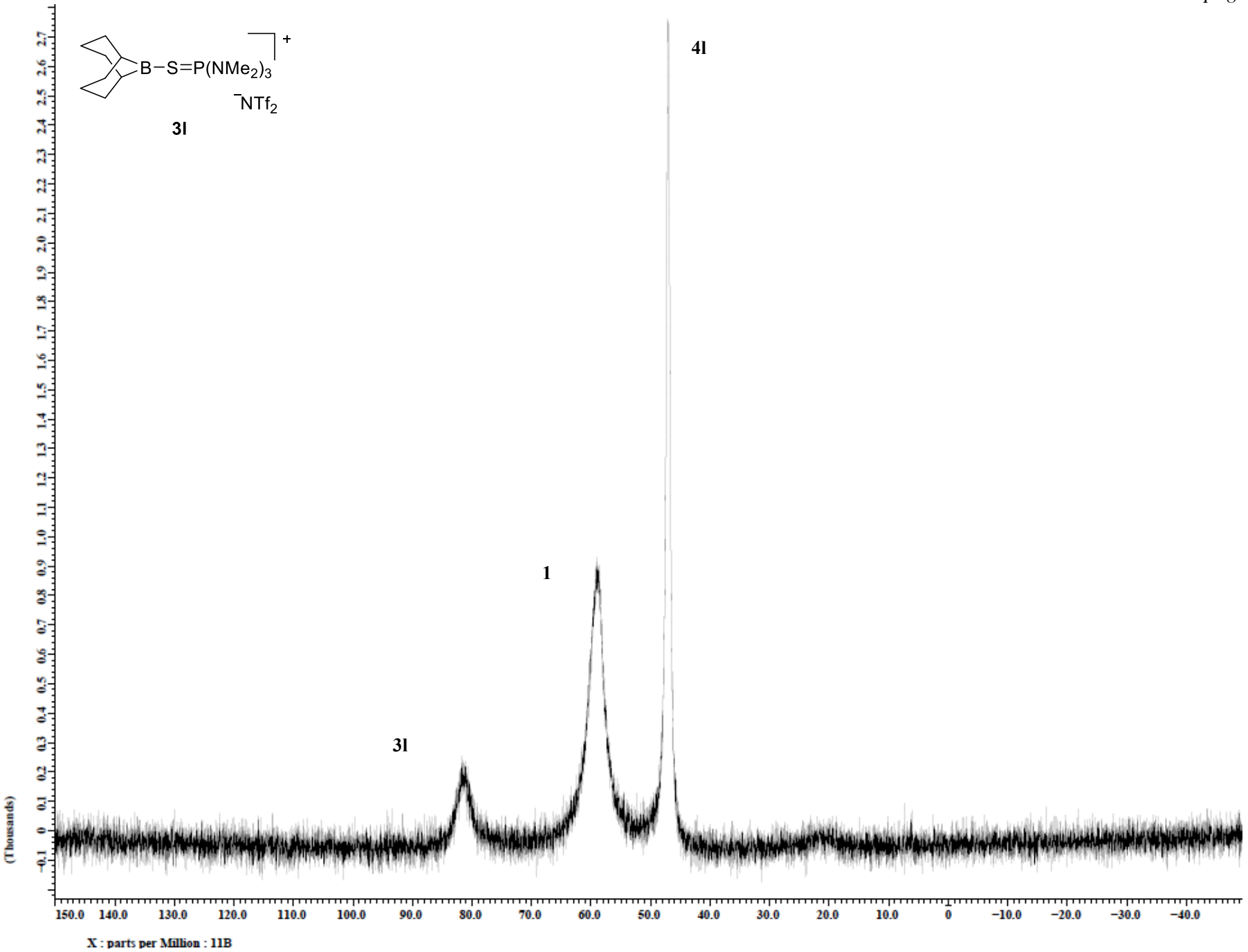

O=P^{n}Bu$_3$
O=P^{n}Bu$_3$
$^-$NTf$_2$
4j
abundance
X : parts per Million : 31P

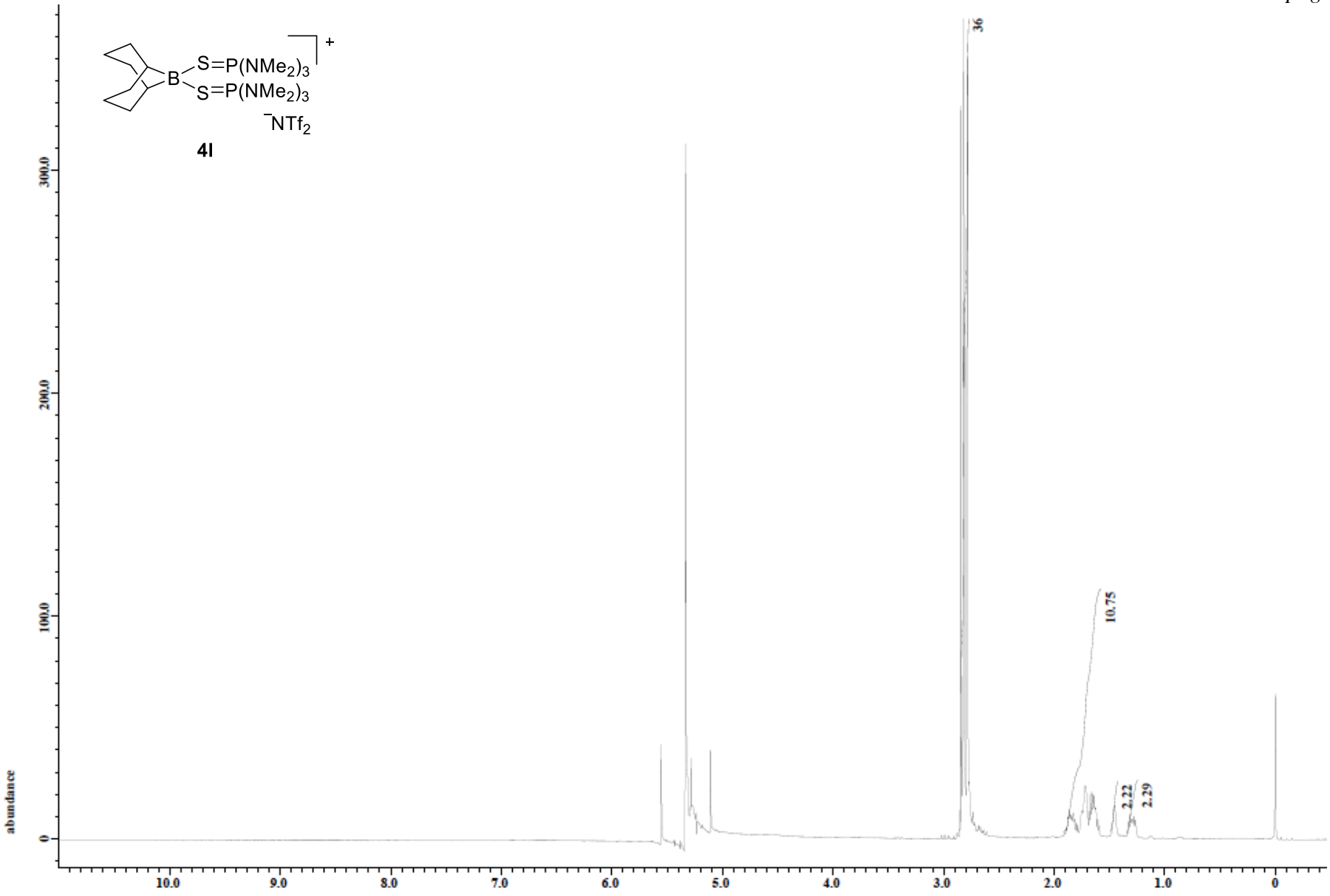

B−S=PPh3
−NTf2
+
3k
15.82
6
3.73
1.8
2.11
abundance
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
−100.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

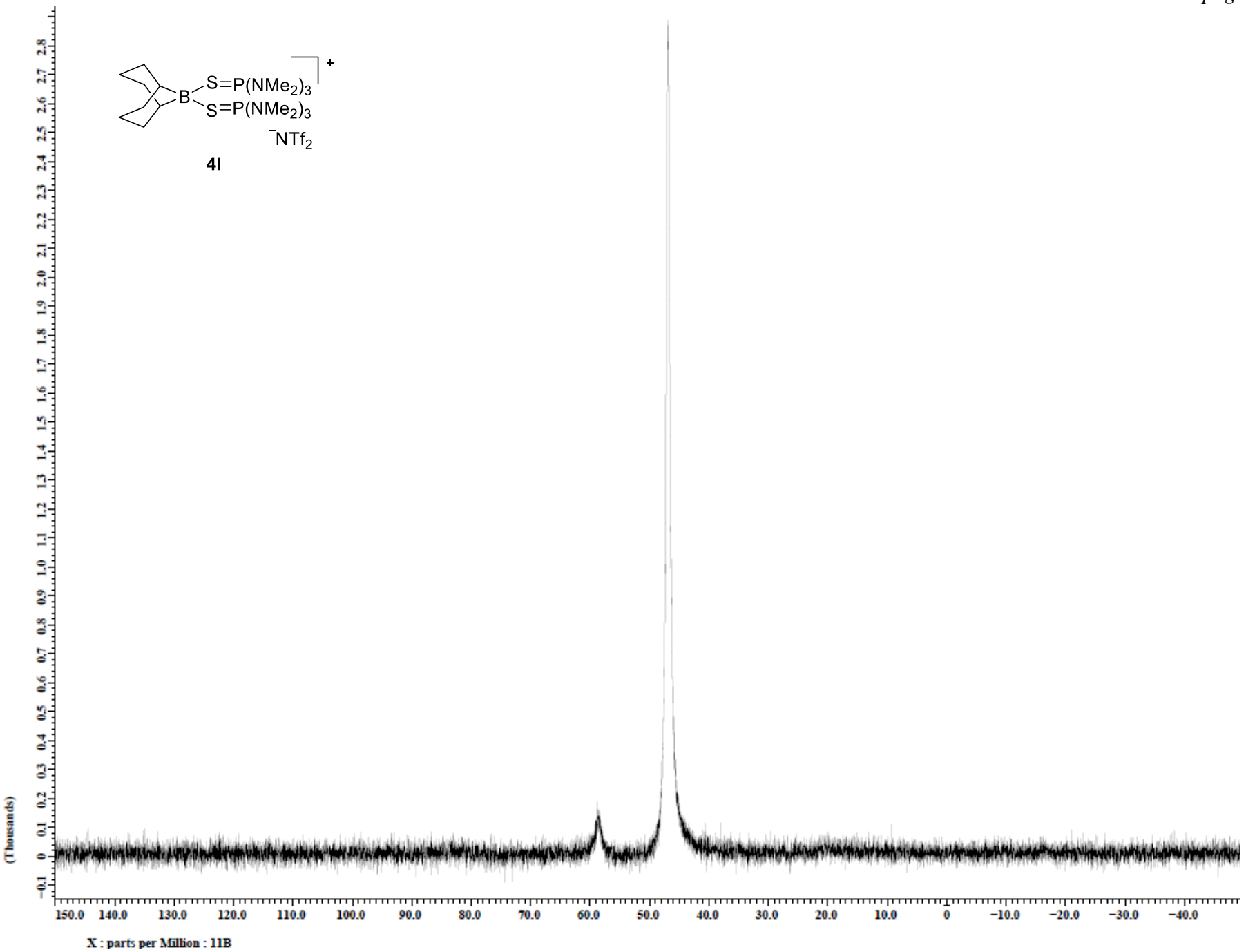

B−S=PPh3
−NTf2
+
3k
400.0
300.0
200.0
100.0
0
abundance
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
X : parts per Million : 11B

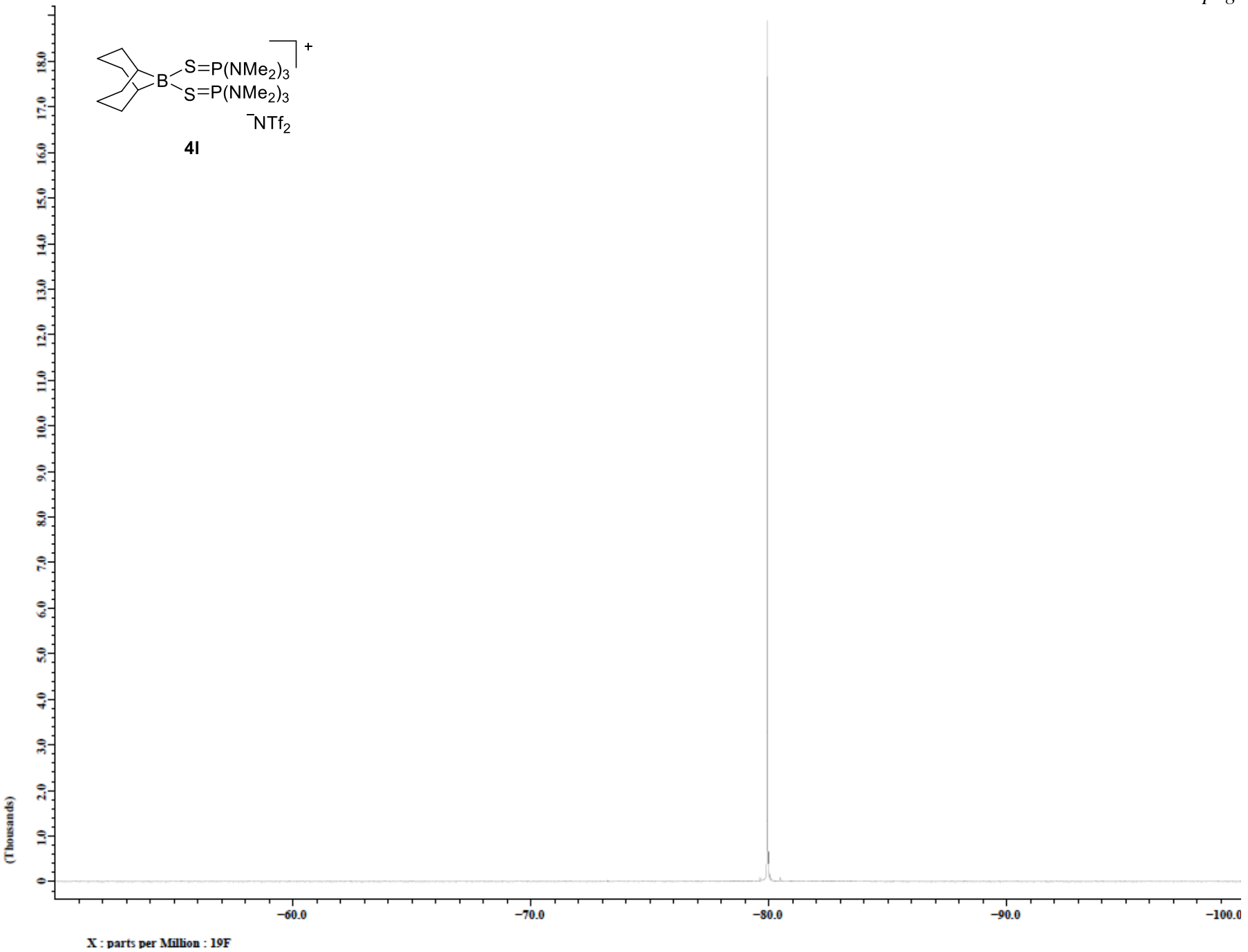

B−S=PPh3
+
−NTf2
3k
4.0
3.0
2.0
1.0
0
(Thousands)
−50.0
−60.0
−70.0
−80.0
−90.0
X : parts per Million : 19F

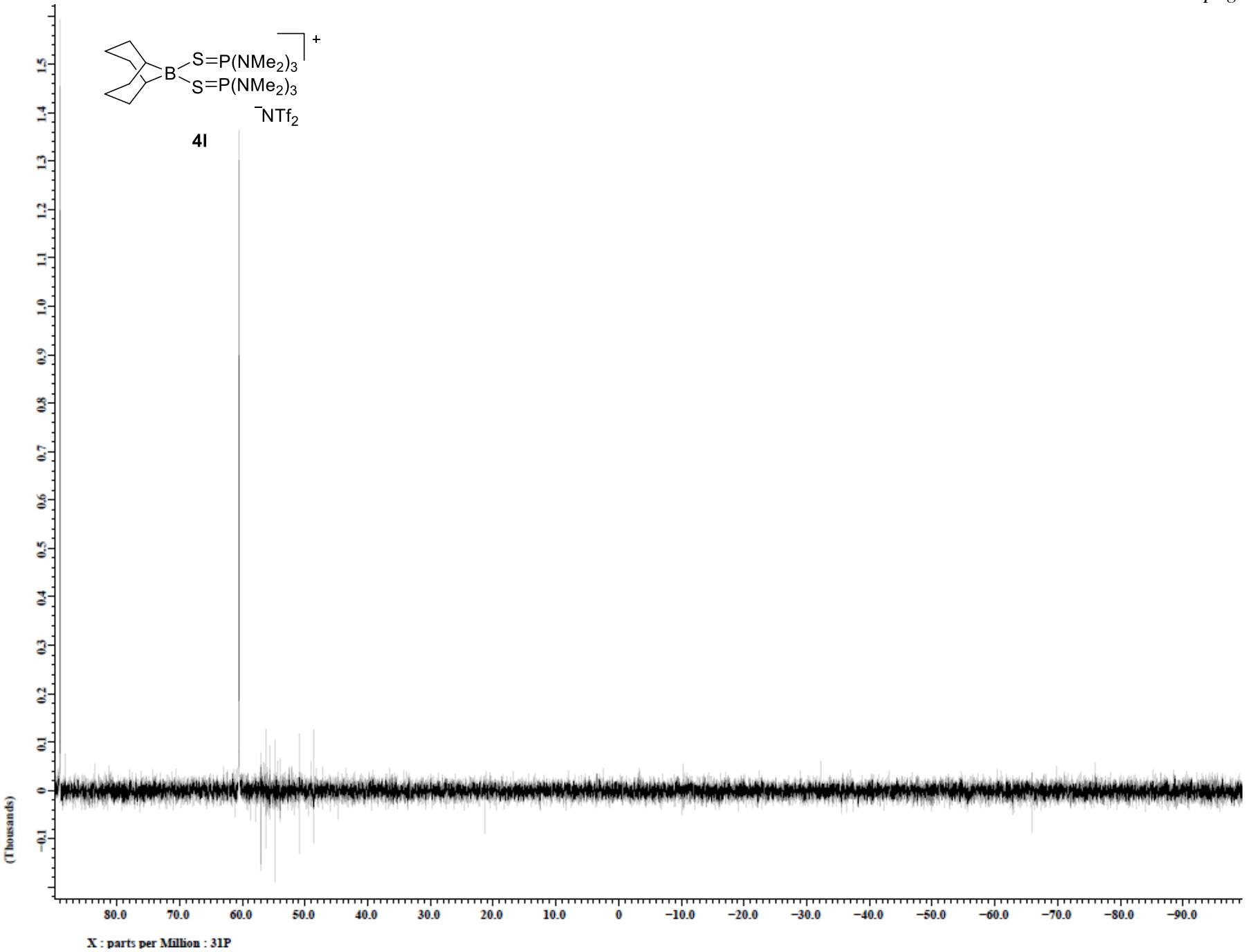

B–S=PPh3
–NTf2
+
3k
abundance
900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
–10.0
–20.0
–30.0
–40.0
–50.0
–60.0
–70.0
–80.0
–90.0
–100.0
X : parts per Million : 31P

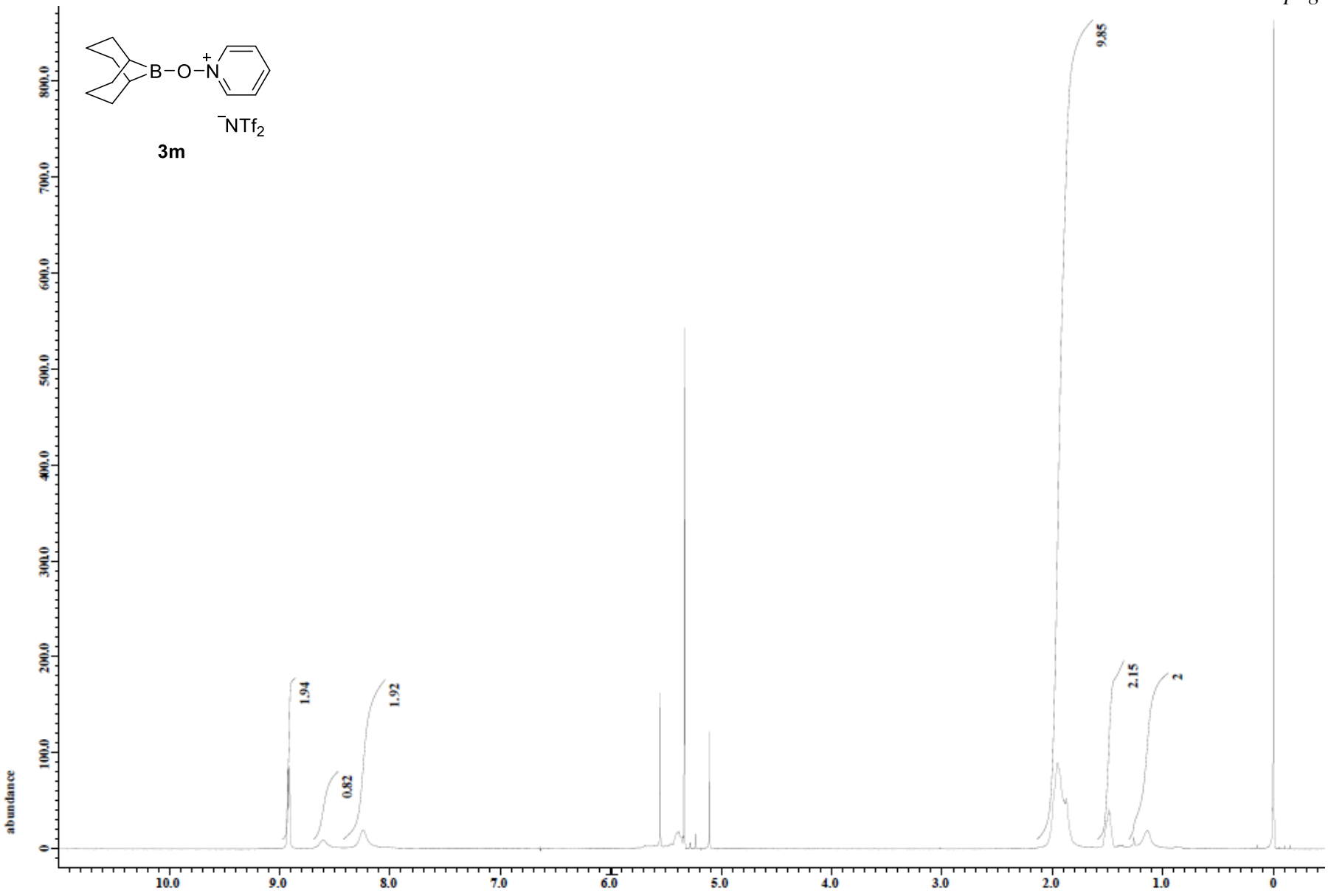

B−S=P(NMe2)3
+
−NTf2
3l
4l
1
3l
(Thousands)
X : parts per Million : 11B

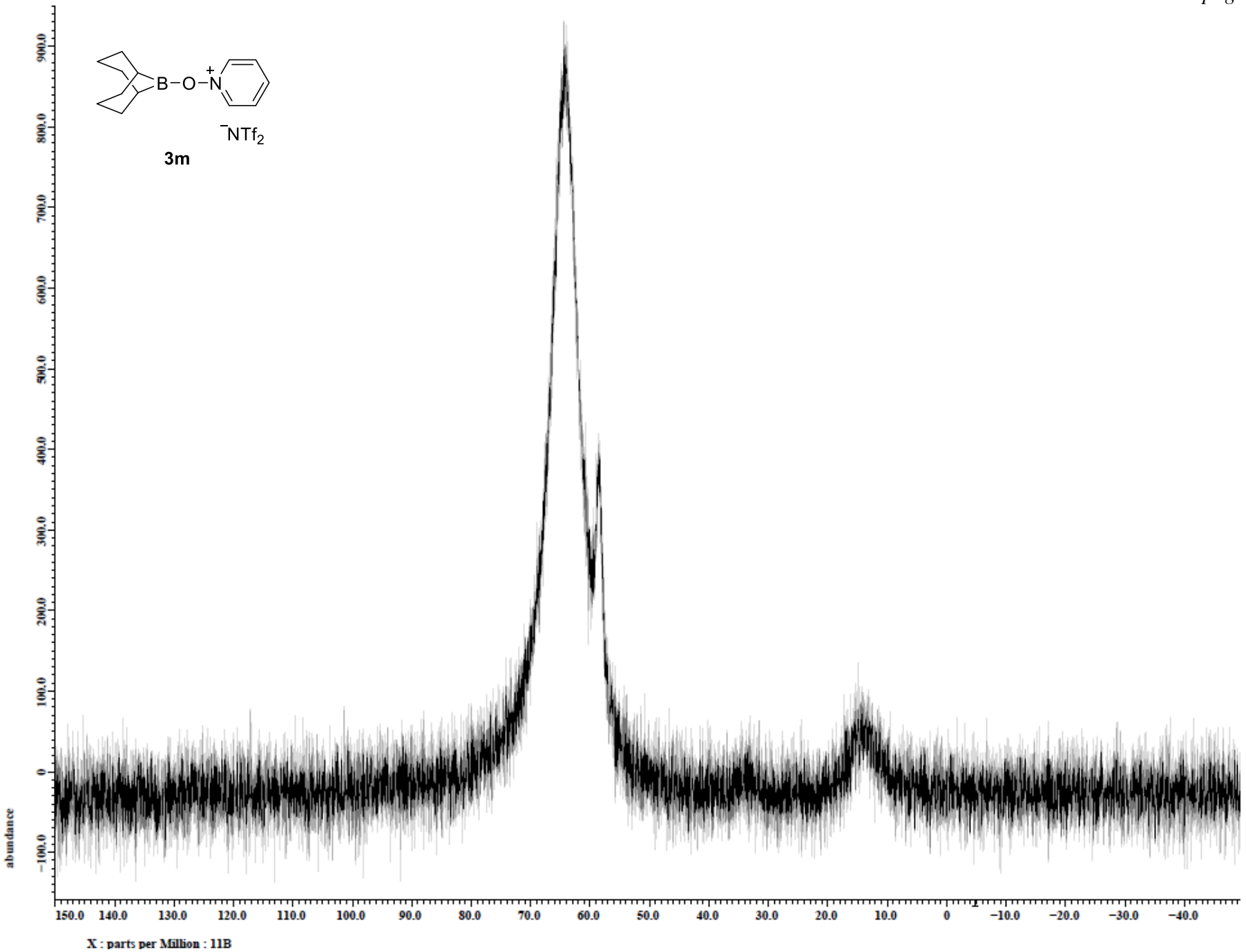

S=P(NMe2)3
S=P(NMe2)3
B
+
−NTf2
4l
36
10.75
2.22
2.29
abundance
300.0
200.0
100.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

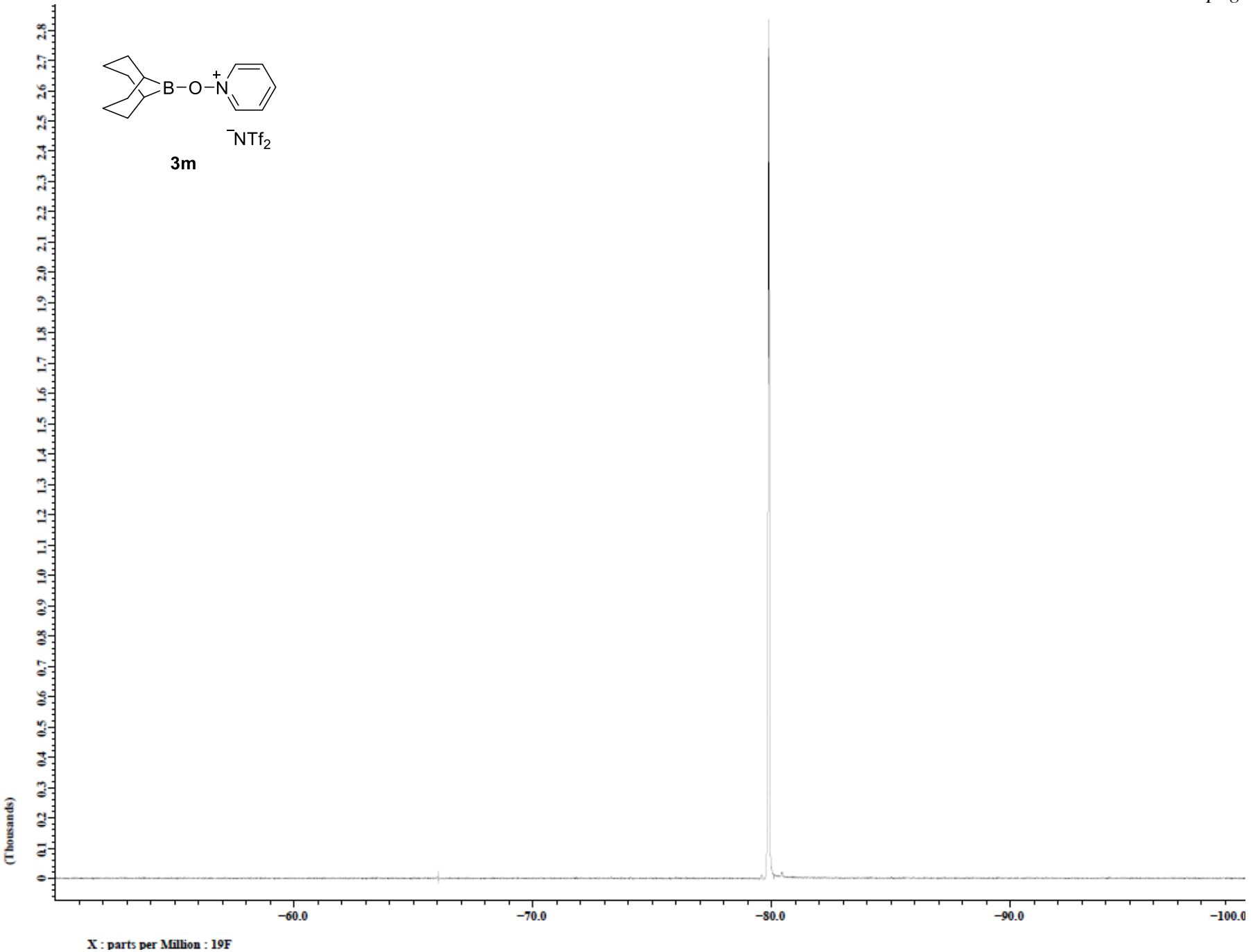

S=P(NMe2)3
S=P(NMe2)3
B
+
−NTf2
4l
(Thousands)
X : parts per Million : 11B

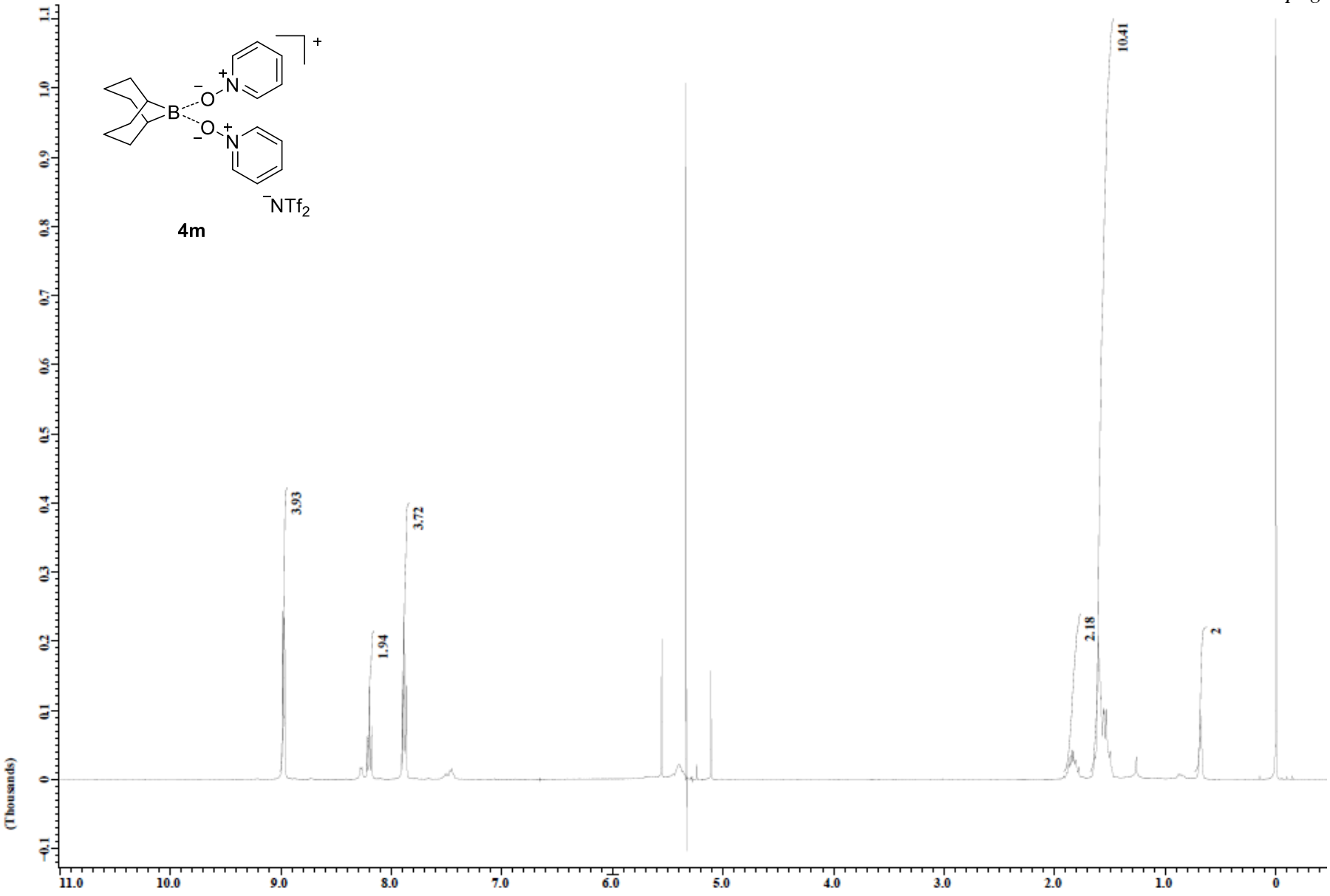

S=P(NMe2)3
S=P(NMe2)3
B
+
−NTf2
4l
(Thousands)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F


S=P(NMe2)3
S=P(NMe2)3
B
+
−NTf2
4l
(Thousands)
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
−60.0
−70.0
−80.0
−90.0
X : parts per Million : 31P


B–O–N
$^{-}NTf_2$
3m
abundance
0
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0
1.94
0.82
1.92
9.85
2.15
2
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

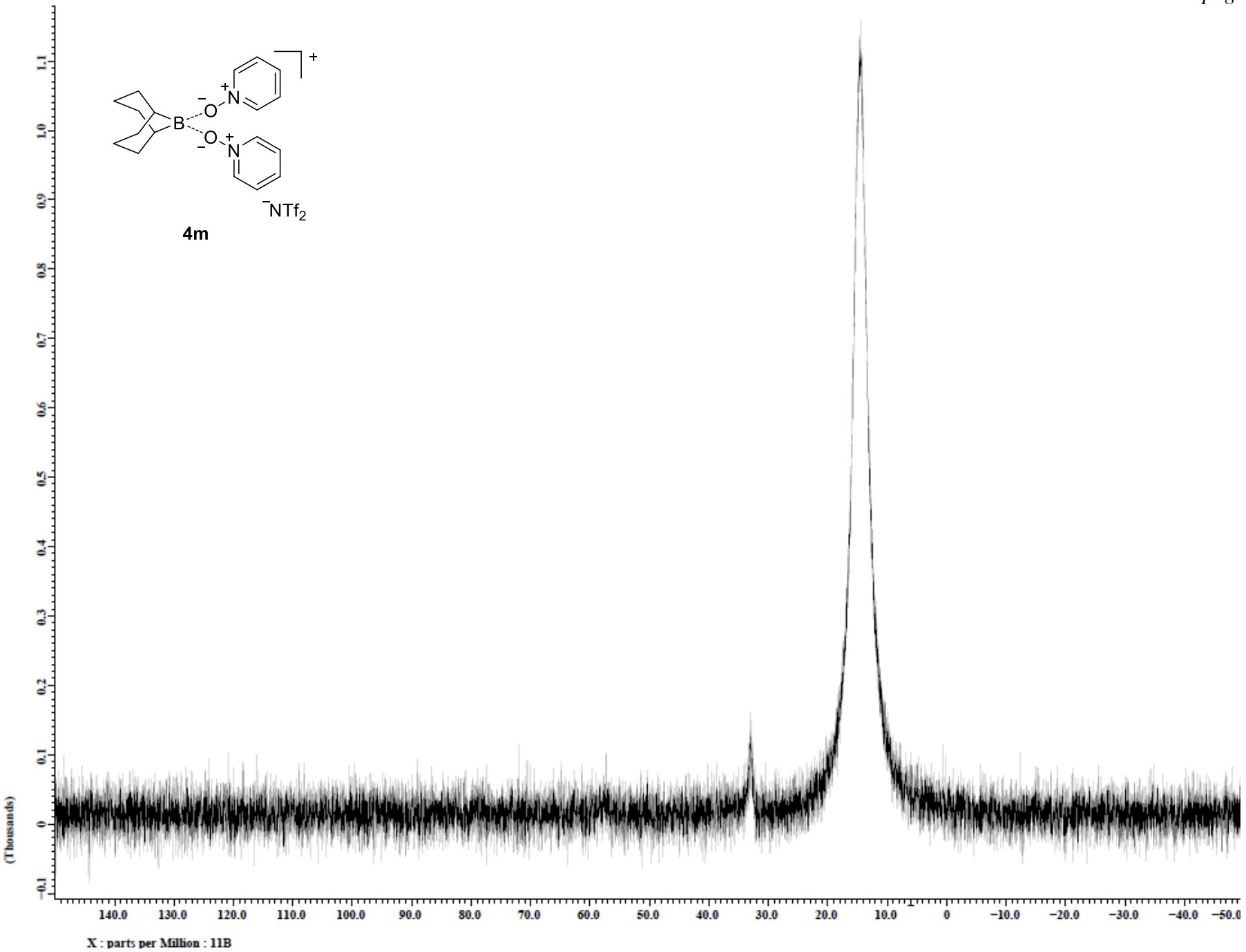

B–O–N
+
$^{-}NTf_2$
3m
abundance
900.0
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
−100.0
150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0
X : parts per Million : 11B

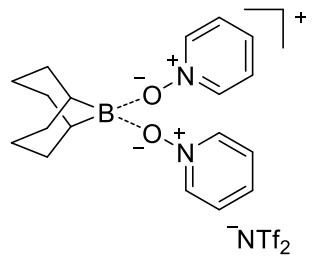

B–O–N
$^{-}NTf_2$
3m
(Thousands)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F


3.93
1.94
3.72
10.41
2.18
2
(Thousands)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

B
O
N
O
N
+
NTf2

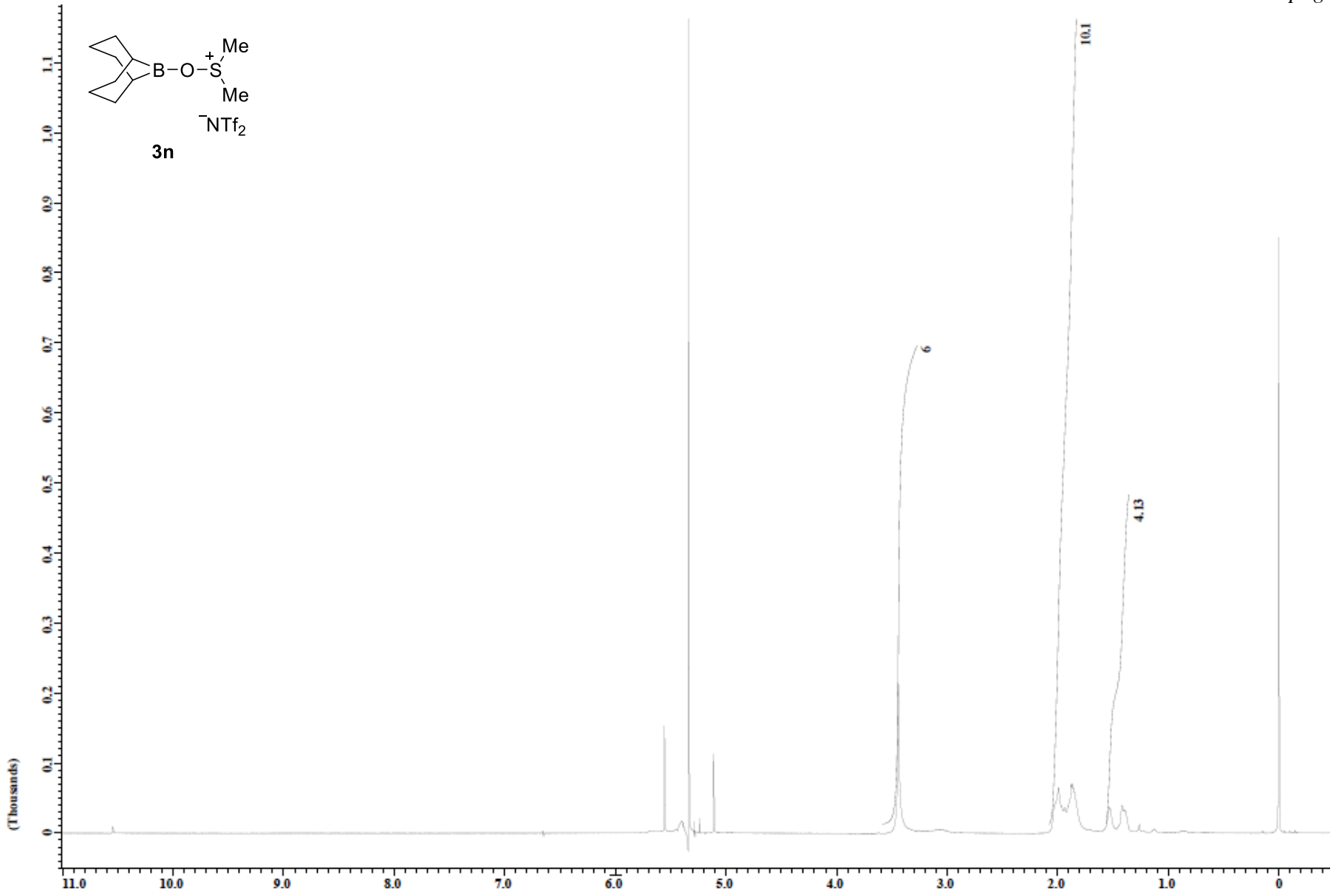
4m

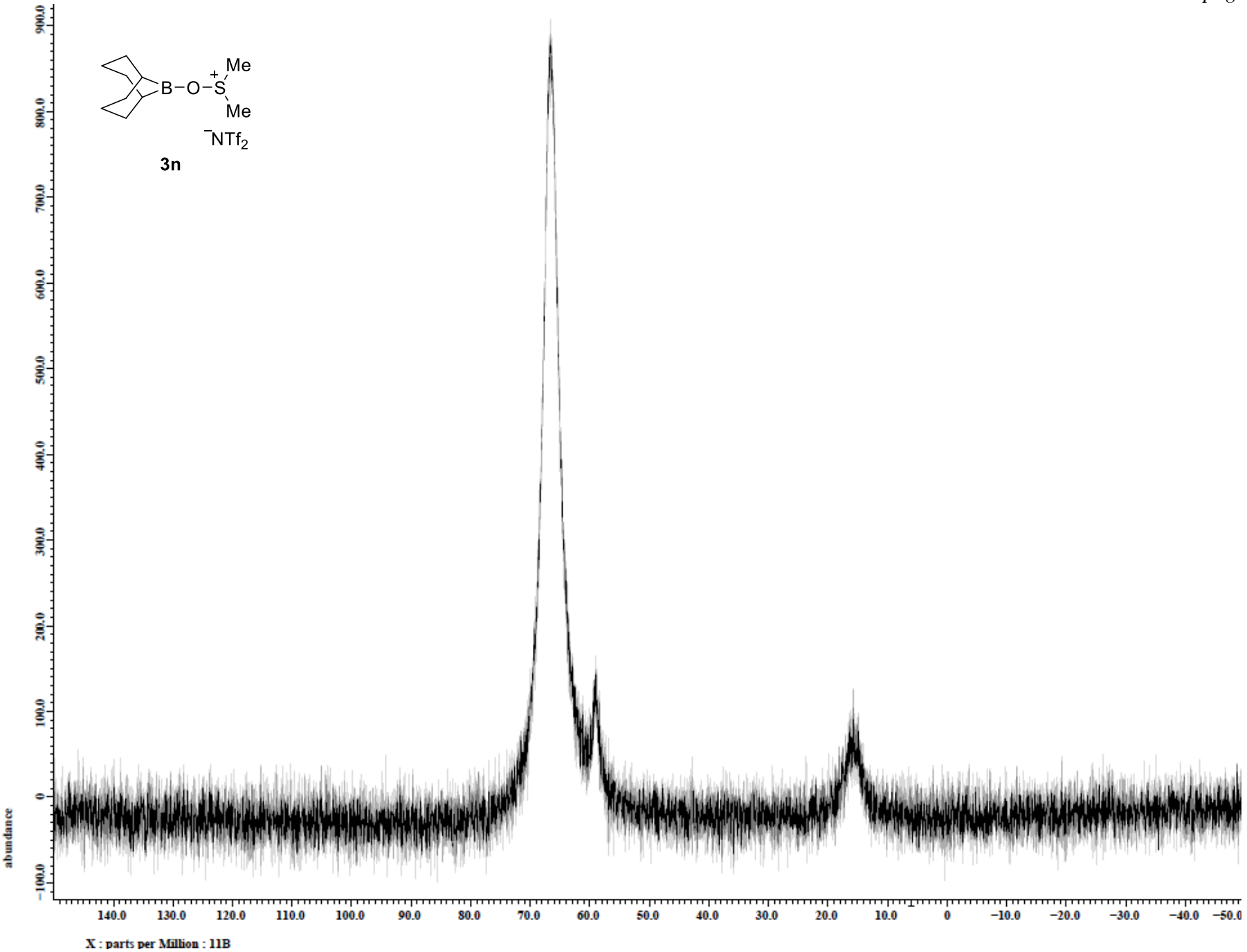

B
O
N
O
N
+
−
$^{-}NTf_2$
4m
(Thousands)
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
X : parts per Million : 11B

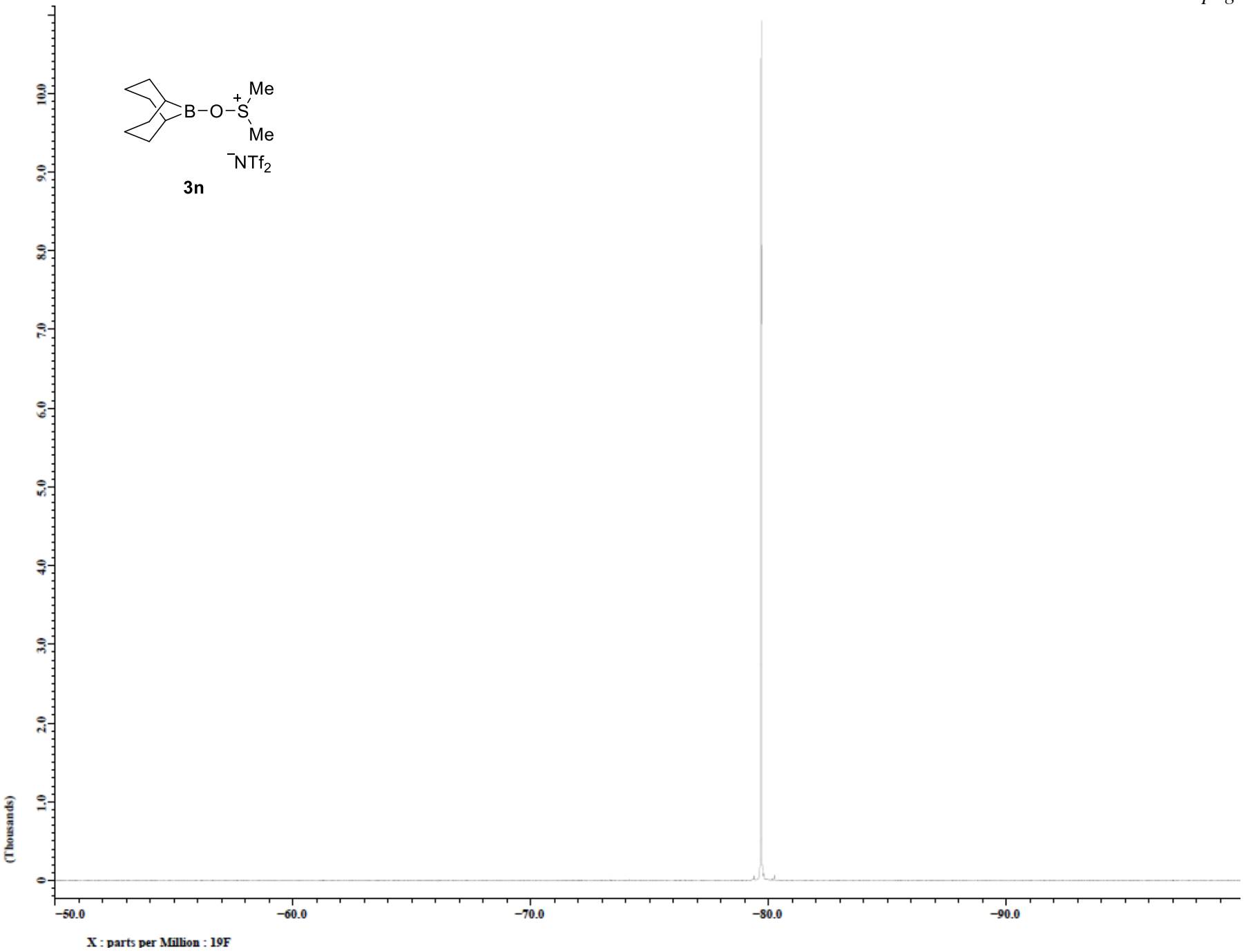


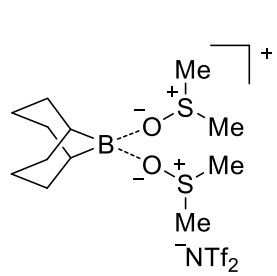
4m

30.0
20.0
10.0
0
(Thousands)
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F


Me
B–O–S
Me
$^{-}NTf_2$
3n
10.1
6
4.13
(Thousands)
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

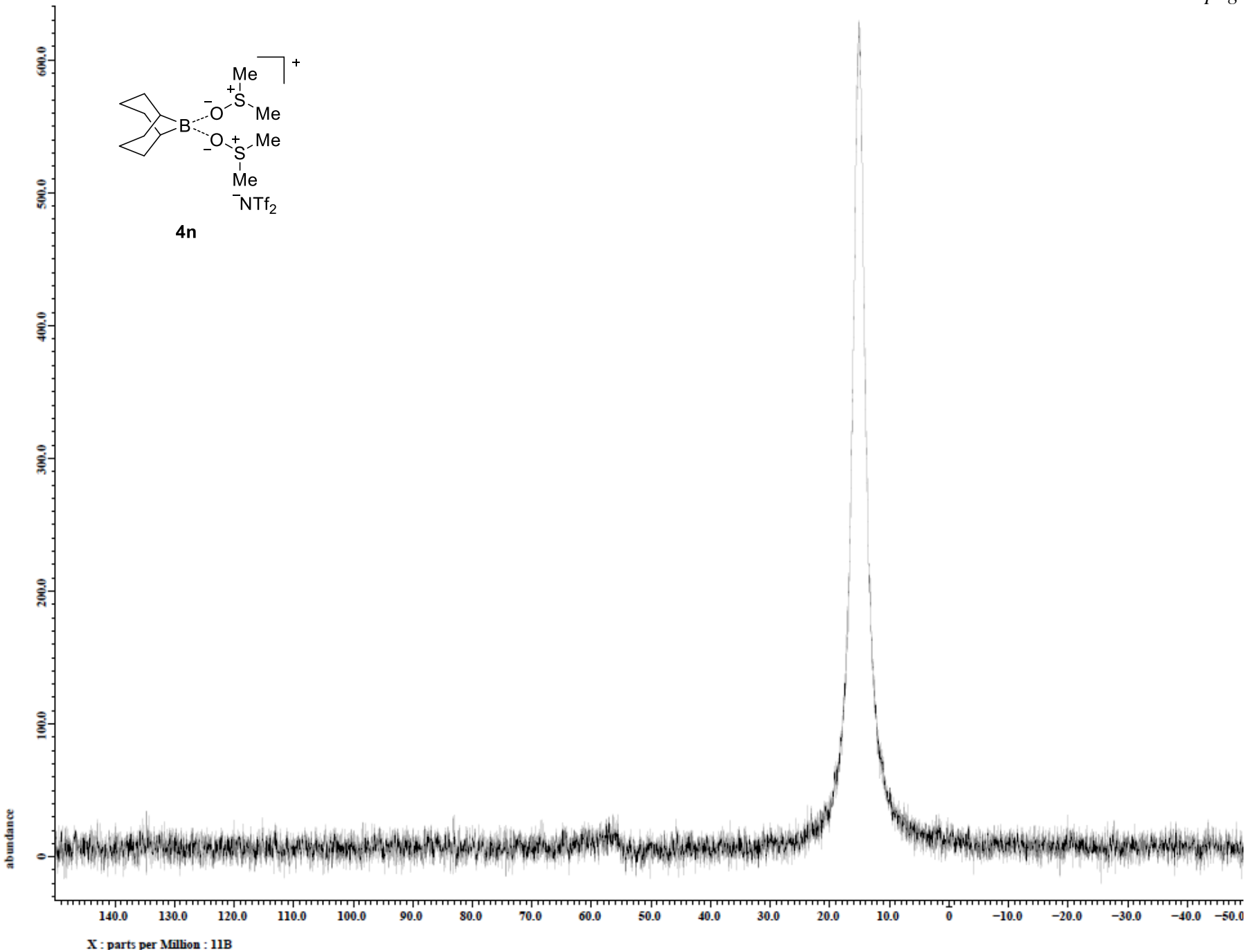

Me
B–O–S
Me
NTf2
3n
abundance
X : parts per Million : 11B

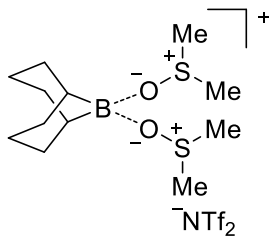

Me
B–O–S
Me
NTf2
3n
(Thousands)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−50.0
−60.0
−70.0
−80.0
−90.0
X : parts per Million : 19F


Me
S
Me
B
O
O
S
Me
Me
NTf2

4n

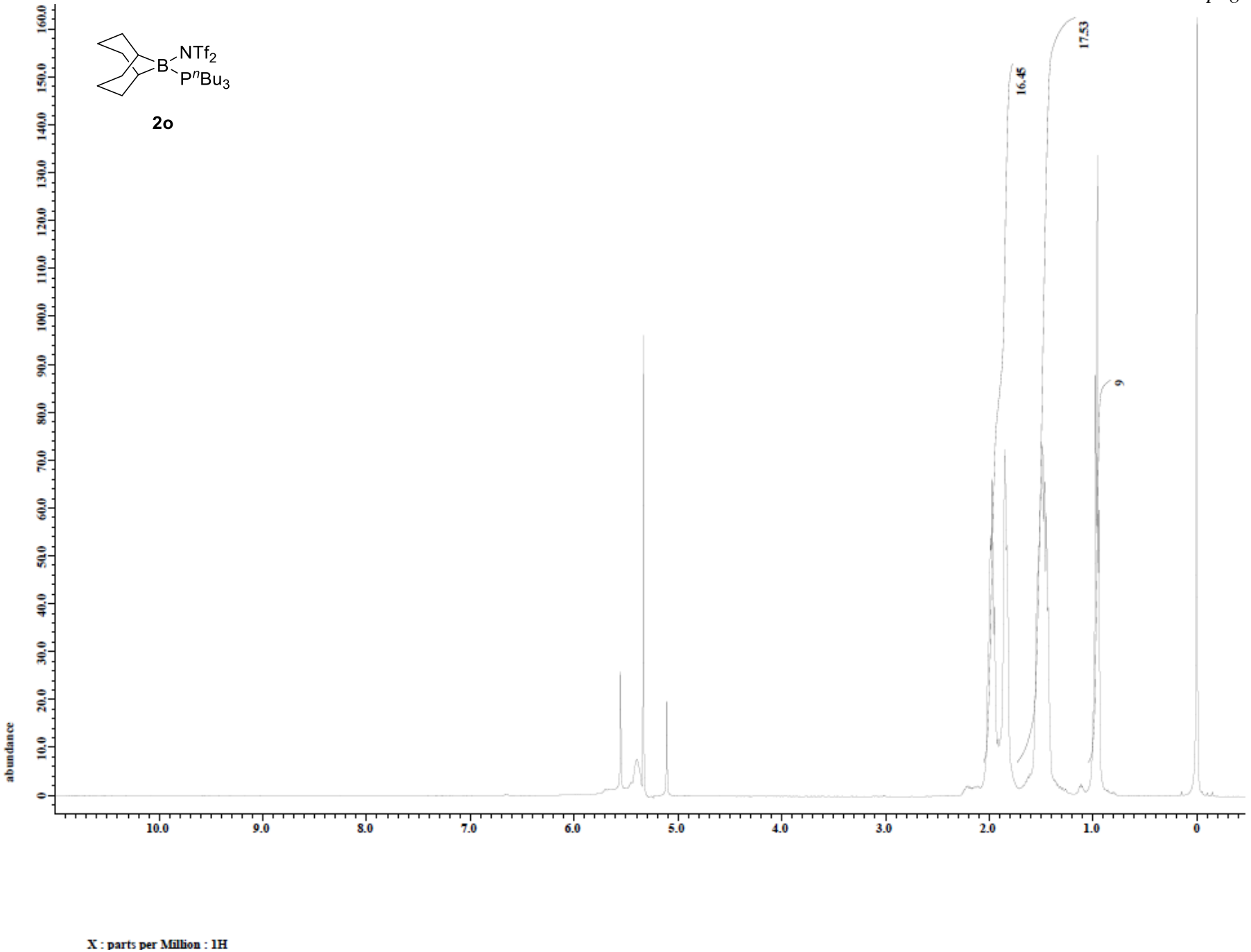
12
5.93
3.57
1.89
1.82
abundance
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
-100.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

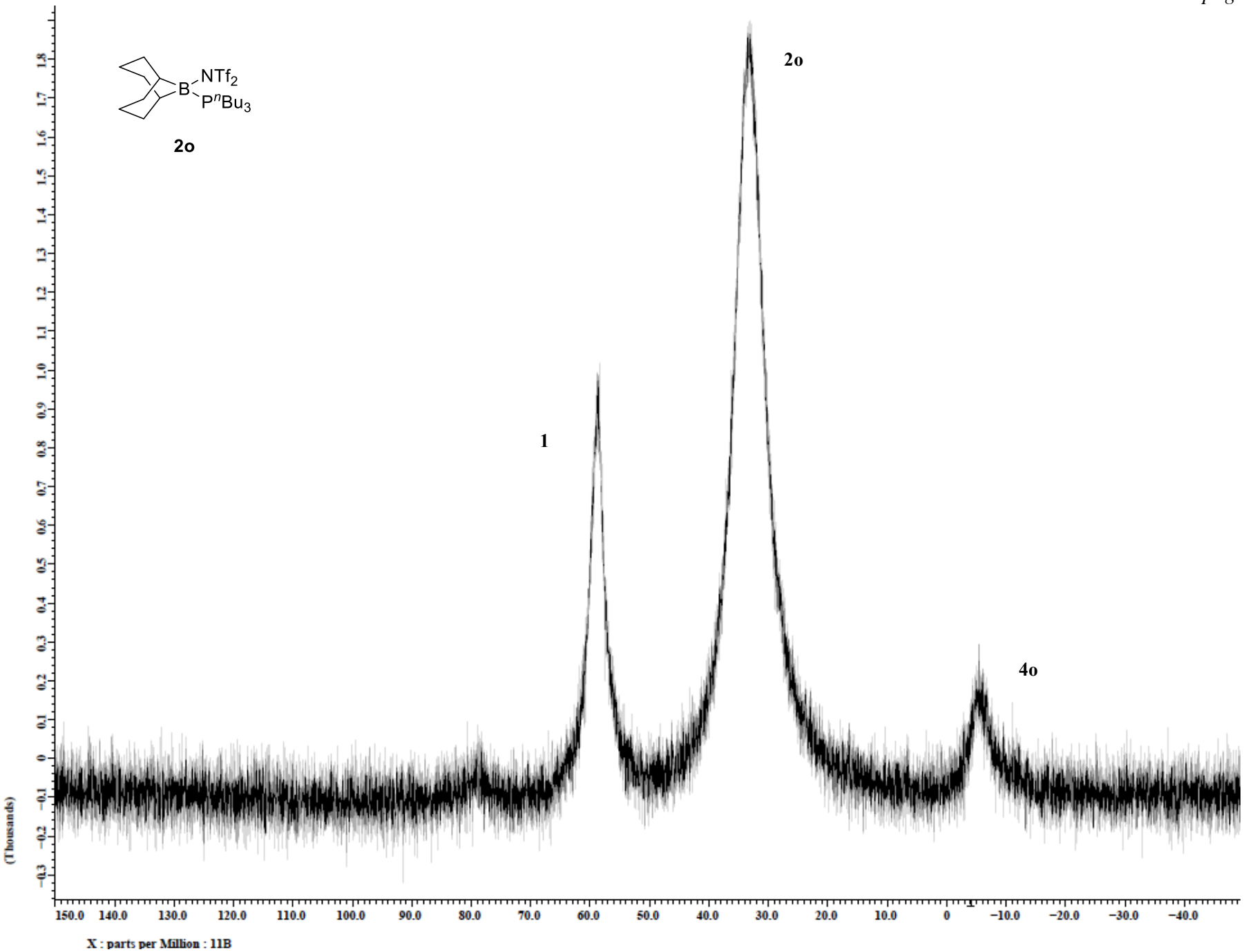

Me
S
Me
O
B
O
S
Me
Me
NTf2
4n
abundance
600.0
500.0
400.0
300.0
200.0
100.0
0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
X : parts per Million : 11B

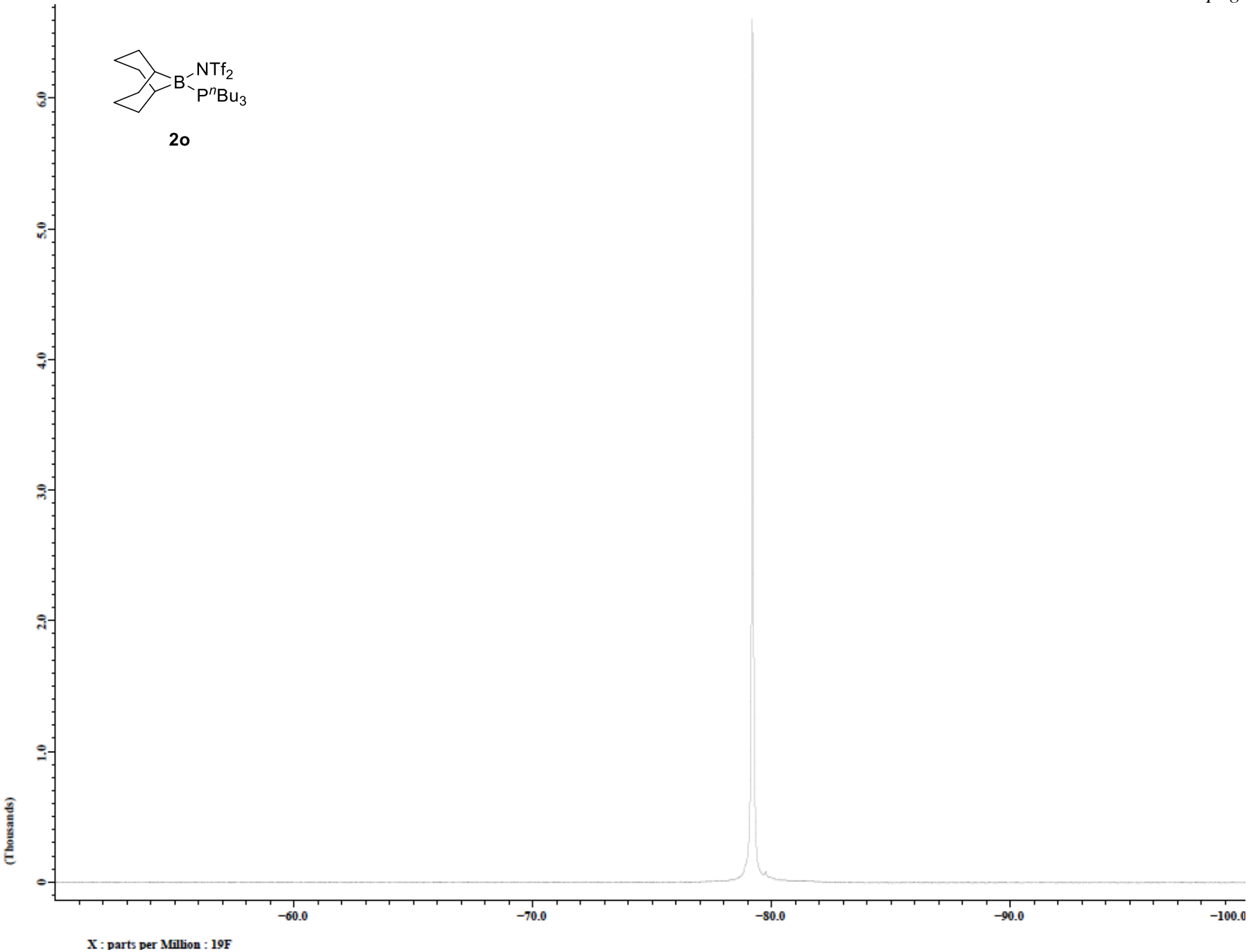

Me
S
Me
B
O
O
S
Me
Me
NTf2

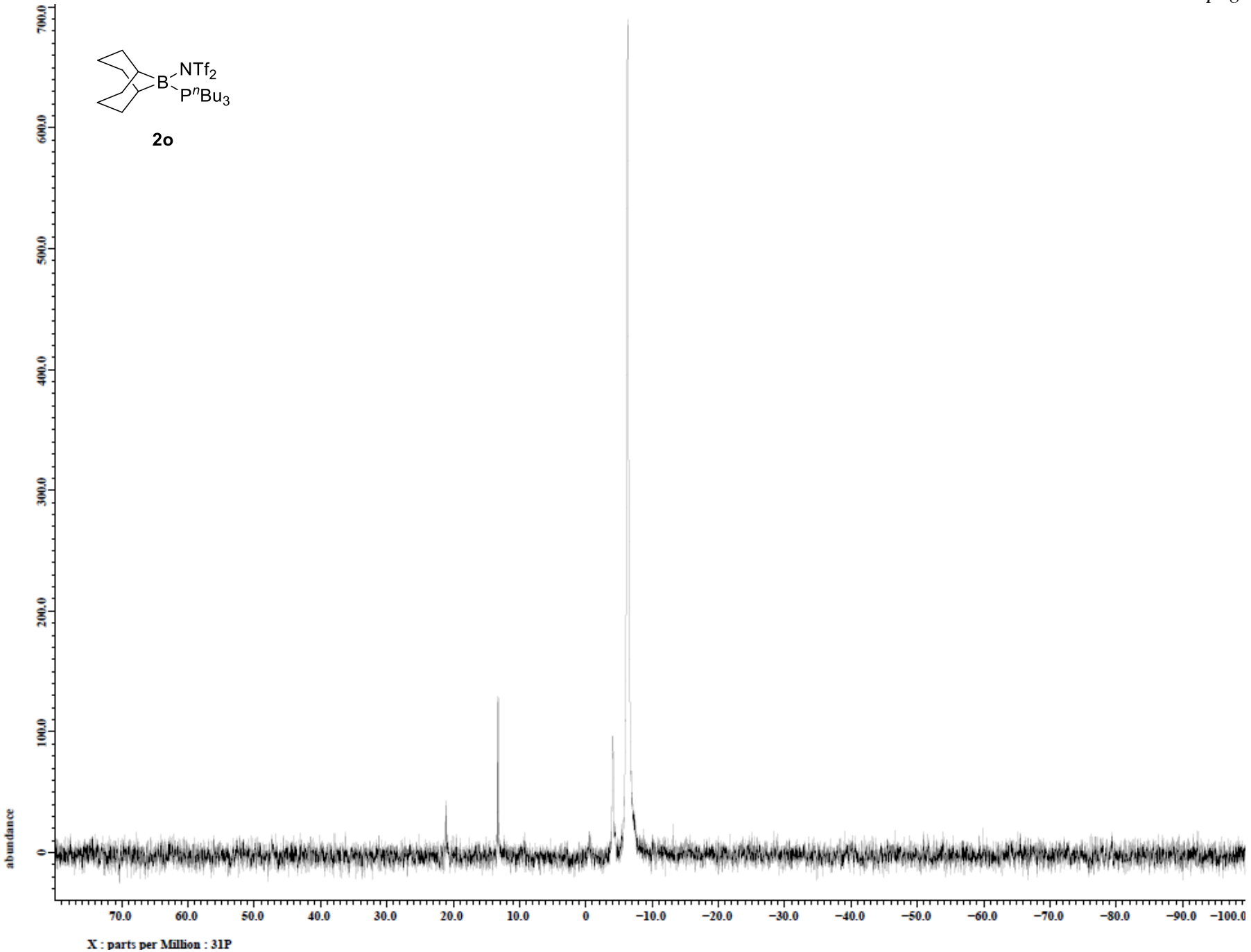
4n

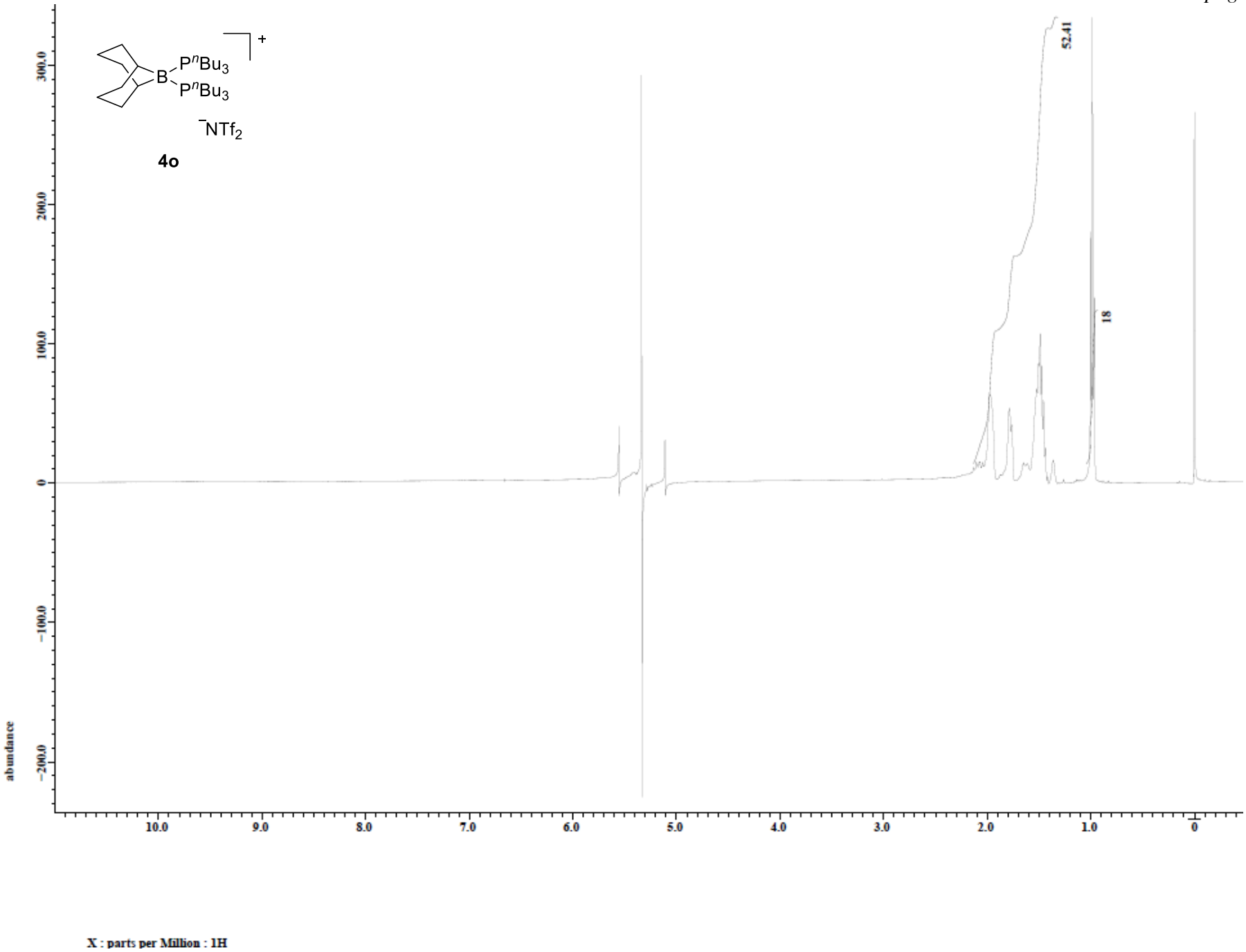
(Thousands)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−50.0
−60.0
−70.0
−80.0
−90.0
X : parts per Million : 19F

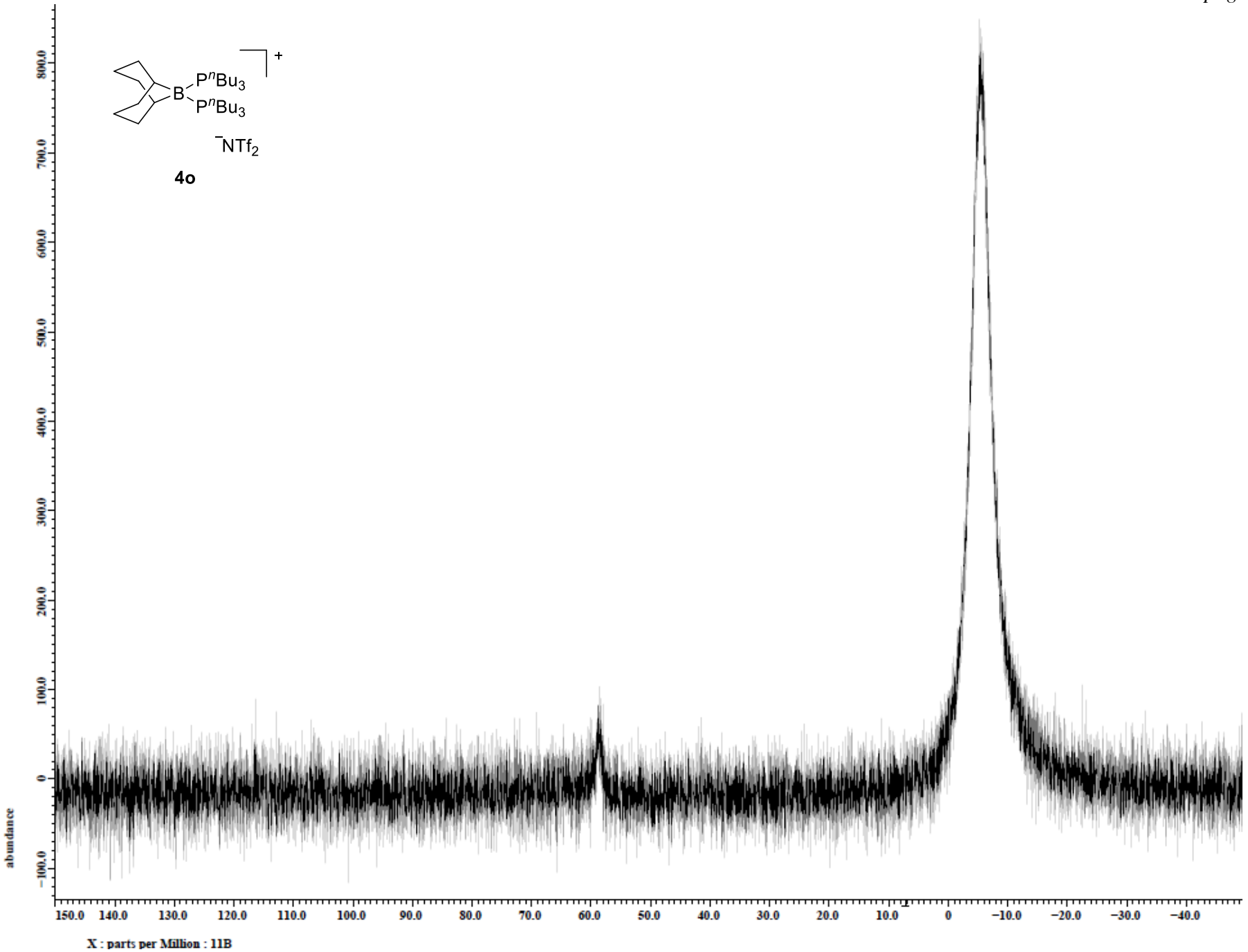

NTf2
B
P^nBu3
2o
16.45
17.53
9
abundance
X : parts per Million : 1H

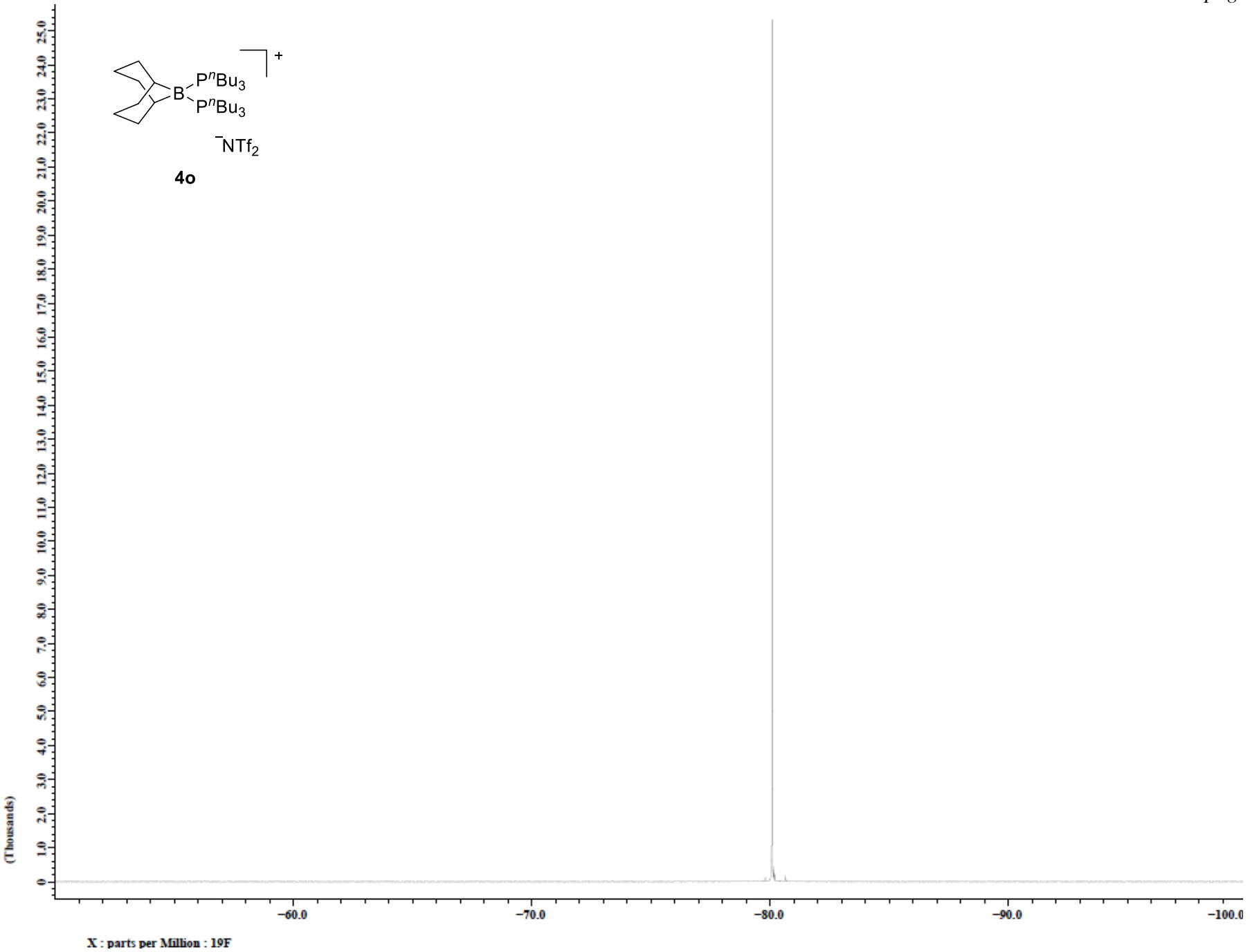

NTf2
B
P^nBu3
2o
2o
1
4o
(Thousands)
X : parts per Million : 11B

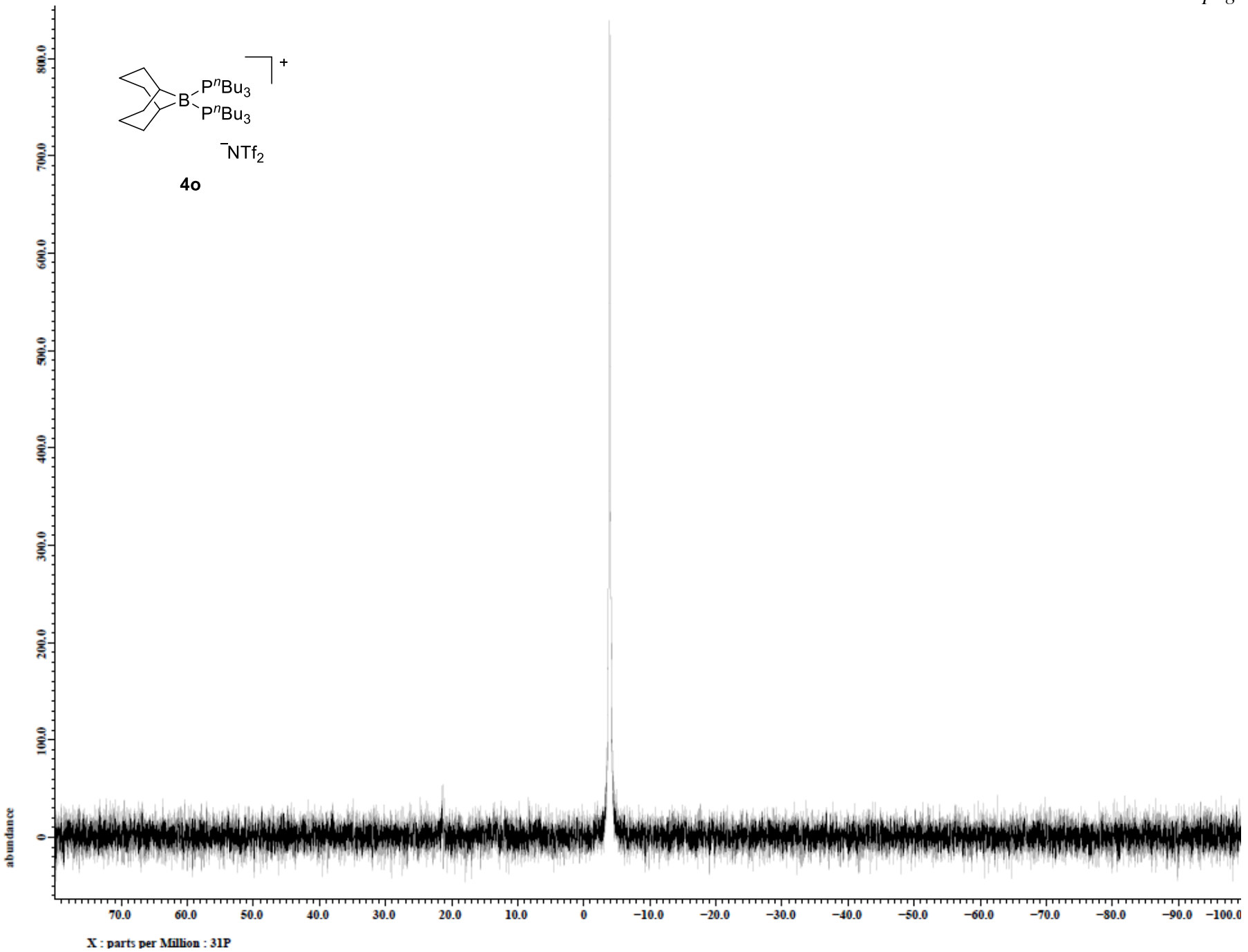

NTf2
B
P^nBu3
2o
6.0
5.0
4.0
3.0
2.0
1.0
0
(Thousands)
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F

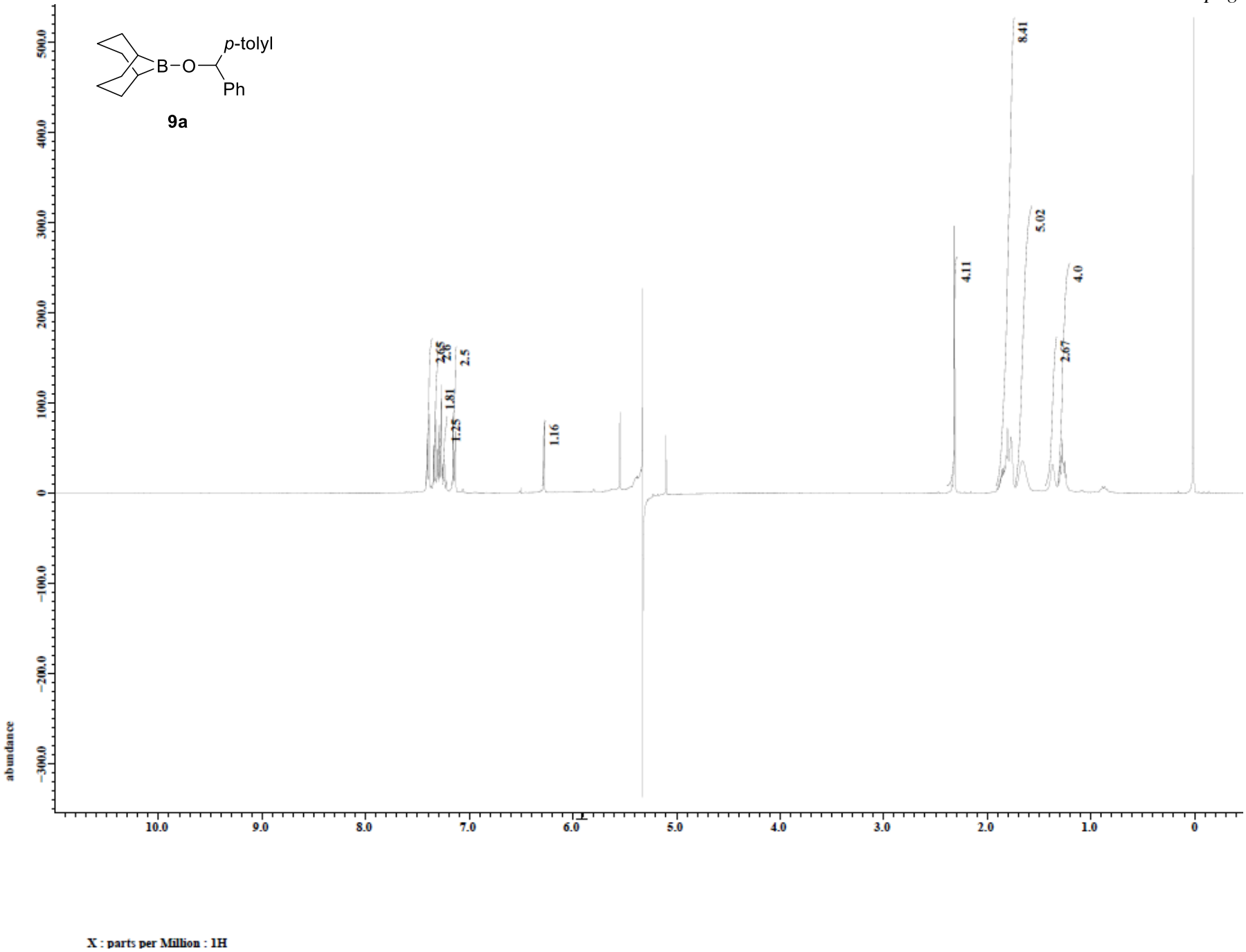

NTf2
B
P^nBu3
2o
abundance
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 31P

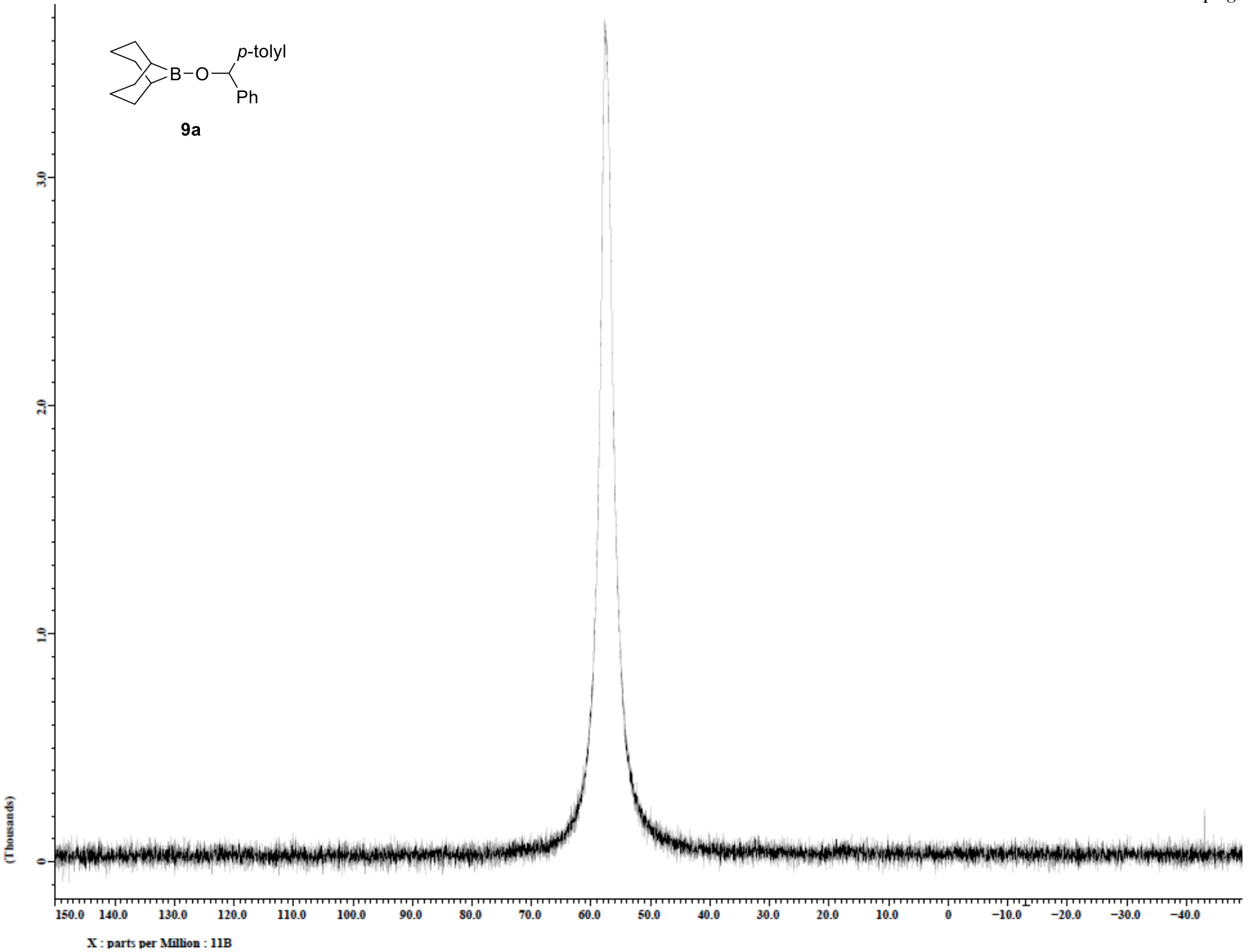

P^{n}Bu$_3$
B
P^{n}Bu$_3$
$^-$NTf$_2$
+
4o
52.41
18
abundance
300.0
200.0
100.0
0
−100.0
−200.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

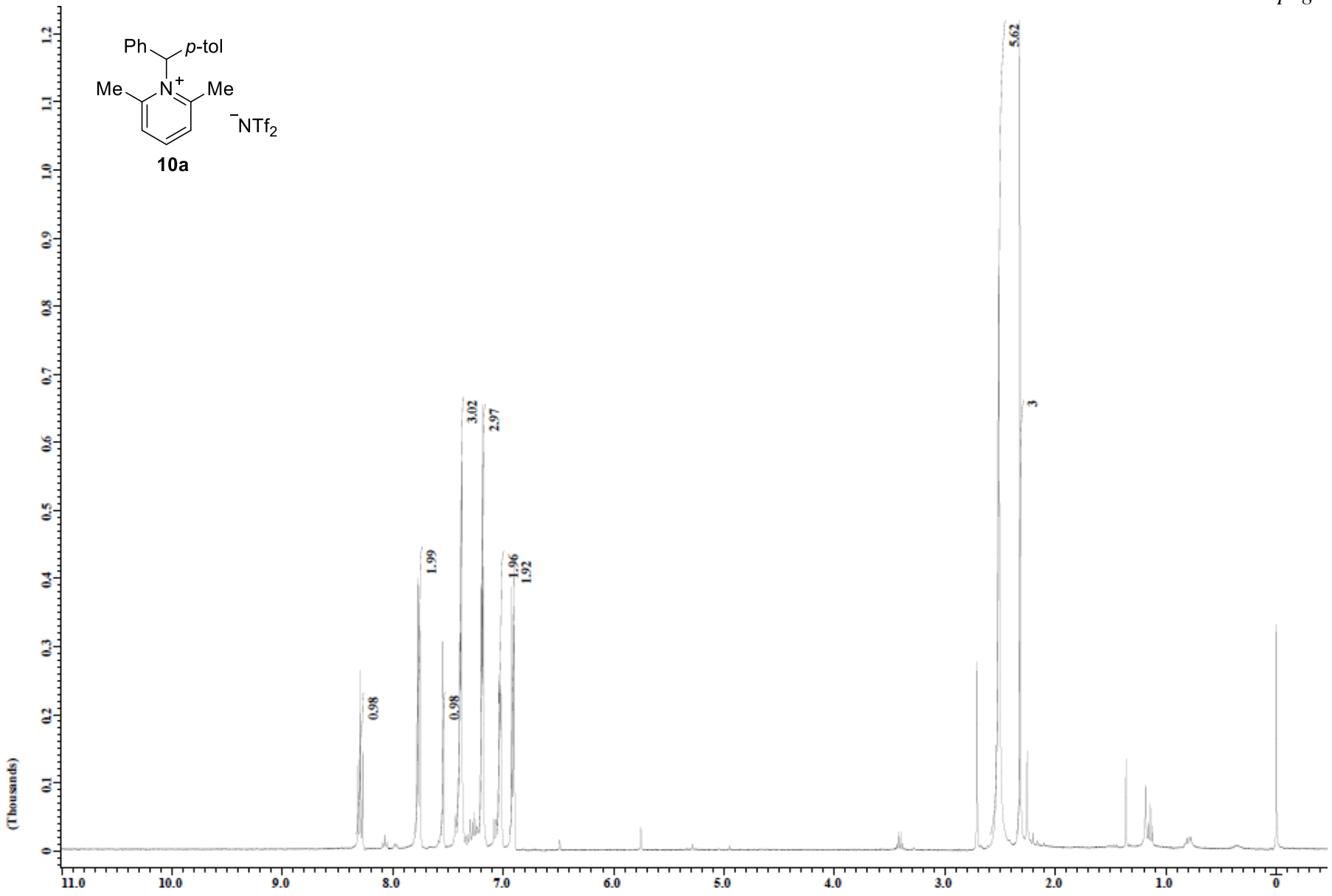

B
P^{n}Bu$_3$
P^{n}Bu$_3$
+
$^-$NTf$_2$
4o
abundance
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
−100.0
150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0
X : parts per Million : 11B


P^{n}Bu$_3$
P^{n}Bu$_3$
B
$^-$NTf$_2$
+
4o
(Thousands)
X : parts per Million : 19F
−60.0
−70.0
−80.0
−90.0
−100.0

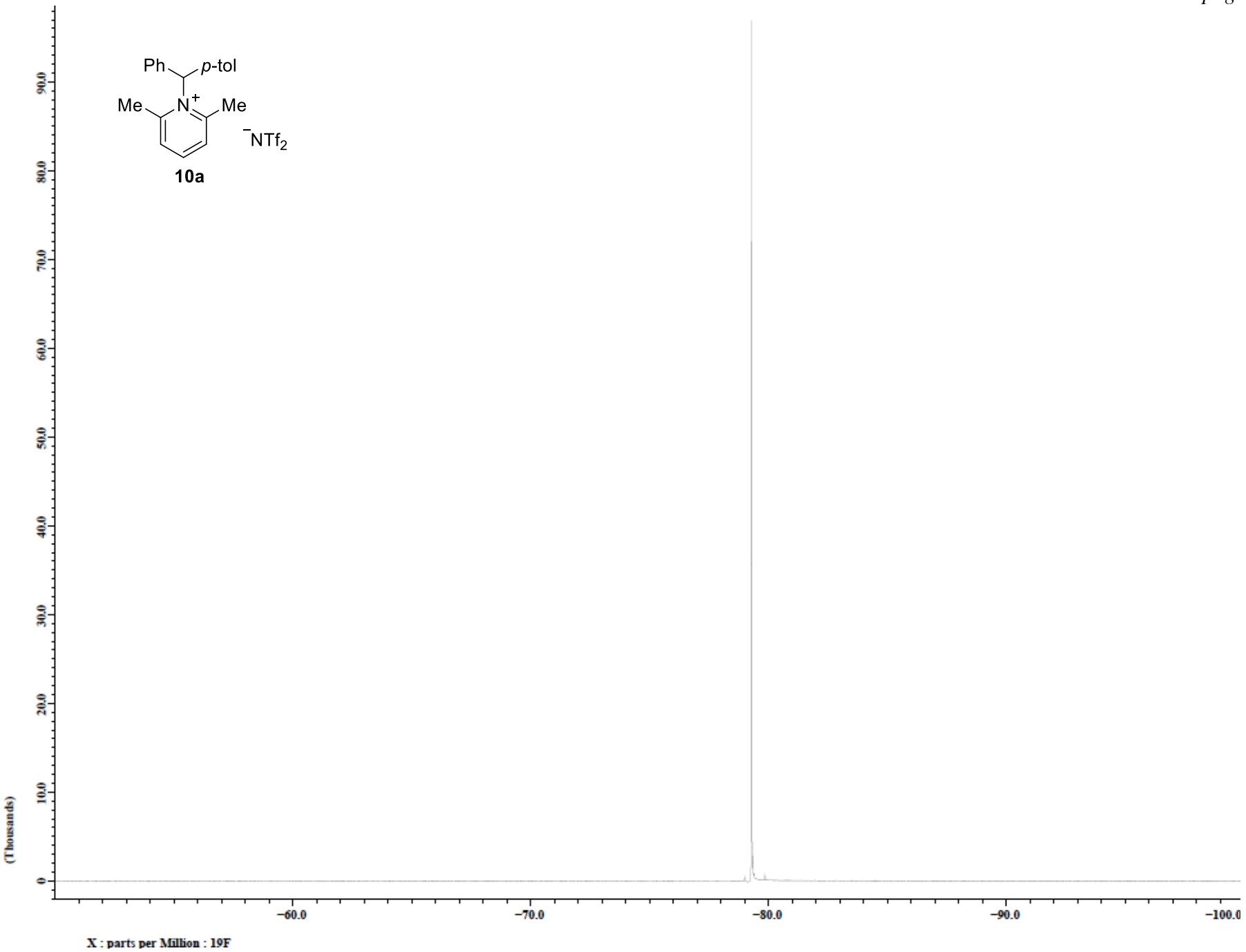

B
P^{n}Bu$_3$
P^{n}Bu$_3$
$^-$NTf$_2$
+
4o
abundance
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
−30.0
−40.0
−50.0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 31P


p-tolyl
B–O
Ph
9a
8.41
5.02
4.11
4.0
2.67
2.65
2.6
2.5
1.81
1.25
1.16
abundance
500.0
400.0
300.0
200.0
100.0
0
−100.0
−200.0
−300.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


p-tolyl
B–O
Ph
9a
3.0
2.0
1.0
0
(Thousands)
150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0 −30.0 −40.0
X : parts per Million : 11B



V X : parts per Million : 1H


Ph
p-tol
Me
N+
Me
−NTf2
10a
(Thousands)
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−60.0
−70.0
−80.0
−90.0
−100.0
X : parts per Million : 19F