Facile preparation of metallic triflates and triflimidates by oxidative dissolution of metal powders.

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Supporting information

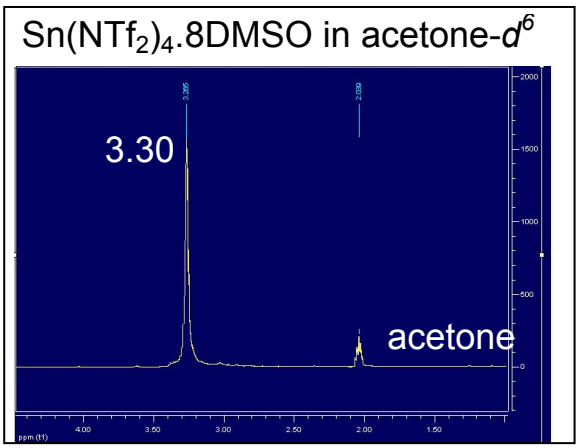
We have used elemental analysis to determine the formulas of the salts obtained (see below, formulas in bold). NMR spectroscopy of ^{1}H- and ^{19}F nuclei was also used to check the purity (only one signal observed in ^{1}H and ^{19}F-NMR) and the absence of water. FT-IR was also used to check the absence of water, however, absorption spectra in nujol suspensions were not giving satisfactory results, and the preparation of KBr pellets under air sometimes led to contamination of the product by moisture. However, some IR spectra are presented below.

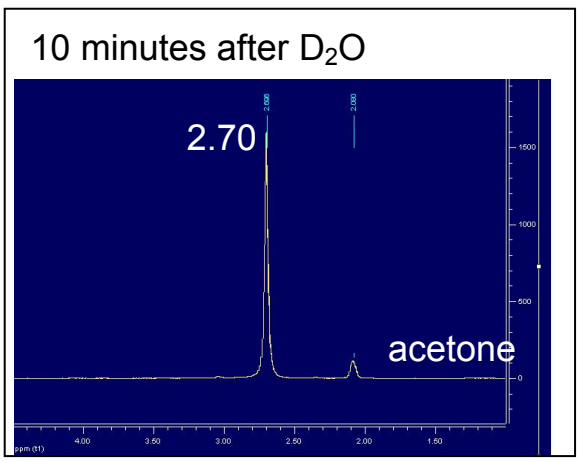
It is possible, by adding pentafluorobenzene as internal standard to the analytical solutions containing the metal salts, to roughly evaluate the F/H ratio, and therefore to extrapolate value of x in the formulas $M(OTf)_n.xDMSO$ or $M(NTf_2)_n.xDMSO$. A good correlation was somtimes observed between the NMR method and elemental analysis method to determine this x value, making the NMR method a cheap and fast method for routine analysis. In some cases, the phase correction did not allow to have a good correction for the triflate or triflimidate moiety (-70 to -80 ppm) and the pentafluorobenzene (-141.0; -156.9; -164.8 ppm) and the method could not be used (noted N.D. below).

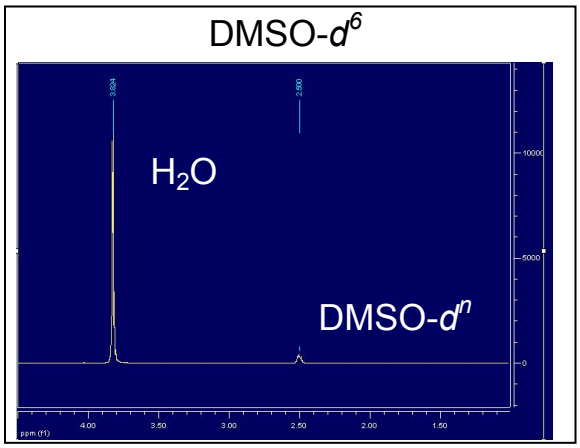
^{1}H- and ^{19}F-NMR spectra were recorded on a Bruker AC 200 FT spectrometer at 20 °C, in [D6]-acetone, unless stated otherwise. Elemental analyses were carried out at the Service Central d'Analyse of CNRS, at Vernaison (France). Chemicals were purchased from Sigma-Aldrich, and used as received. DMSO was dried over calcium hydride overnight and distilled under reduced pressure prior to use.

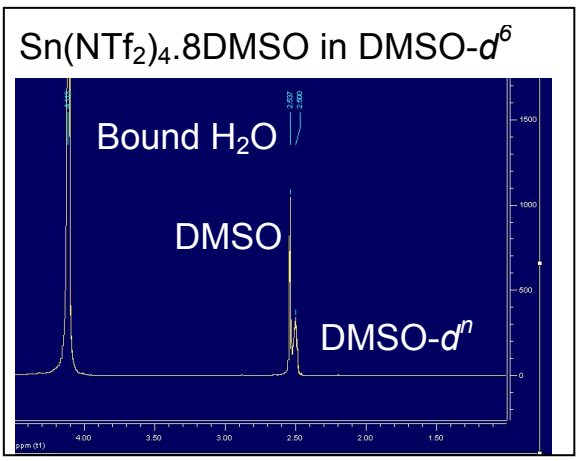
! The use of HOTf and $HNTf_2$ requires appropriate protection !

General procedure for the preparation of metallic triflates or triflimidates: The metallic powder (10 mmol), is placed into a Schlenck flask containing a magnetic stirrer. The system is purged and placed under an O_2 atmosphere. Freshly distilled DMSO (10 mL) is introduced, followed by the superacid (30 mmol) in three portions. The mixture is heated at 100 °C until disappearance of the powder. Removal of the solvent by rectification under 1-10 mbar at 80 °C followed by quick washing with cold dichloromethane or cold diethyl ether under a nitrogen atmosphere affords the salt as a solid.

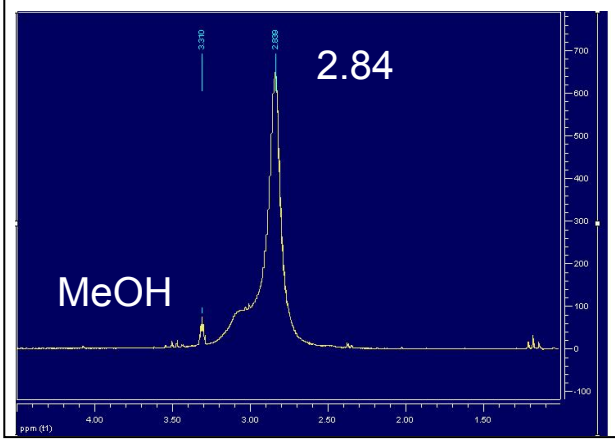

Sn(NTf2)4.8DMSO in acetone-d6
3.30
acetone


10 minutes after D2O
2.70
acetone

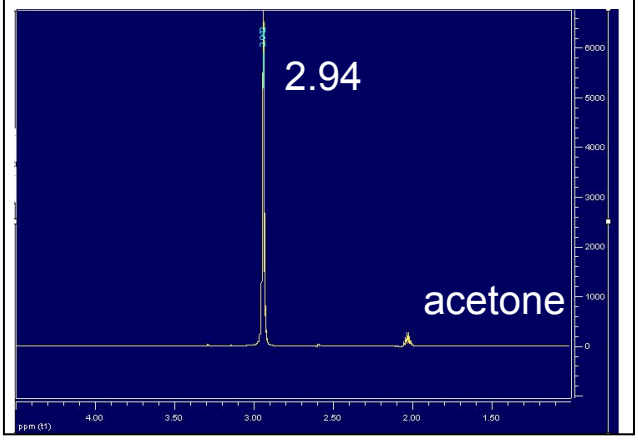

DMSO-d^6
H_2O
DMSO-d^n


$Sn(NTf_2)_4$.8DMSO in DMSO-d^6
Bound H_2O
DMSO
DMSO-d^n

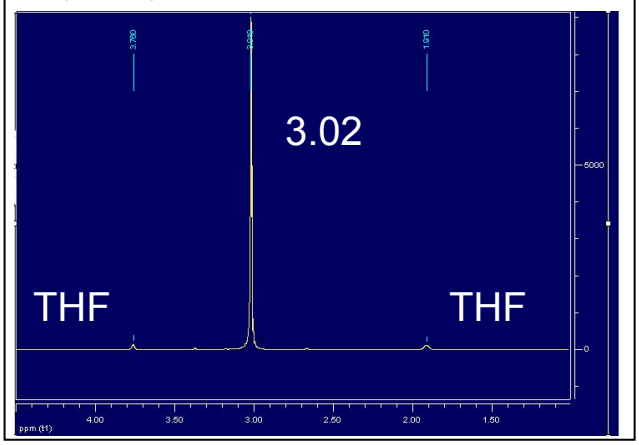
$Sn(NTf_2)_4.8DMSO$ in MeOH-d^4



$Bi(NTf_2)_3.7DMSO$ in acetone-d^6



$Bi(NTf_2)_3.7DMSO$ in THF-d^8



$Bi(OTf)_3.7.8DMSO$ (NMR method=6.6DMSO)

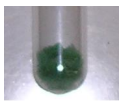
White solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -79.38 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 2.98 ppm, s.

Elemental analysis: calculated %C=17.8, %H=3.8, %F=13.4, %S=27.5, and %Bi=16.3 and experimental %C=17.5, %H=3.7, %F=13.2, %S=27.7, and %Bi=16.2.

$Cu(OTf)_2.5.0DMSO$ (NMR method=N.D.)



Green solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -78.34 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 2.98 ppm, s.

Elemental analysis: calculated %C=19.2, %H=4.0, %F=15.1, %S=29.8, and %Cu=8.4 and experimental %C=19.1, %H=4.2, %F=14.2, %S=28.5, and %Cu=8.4.

$Sn(OTf)_4.6.1DMSO$ (NMR method=N.D.)

White-grey solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -78.90 ppm, s.

Elemental analysis: calculated %C=16.2, %H=3.1, %F=19.5, and %Sn=9.7 and experimental %C=16.2, %H=3.1, %F=19.5, and %Sn=9.7.

$Fe(OTf)_3.6.2DMSO$ (NMR method=N.D.)

Yellow solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -77.8 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 2.97 ppm, s.

Elemental analysis: calculated %C=18.7, %H=3.8, %F=17.3, %S=29.8, and %Fe=5.7 and experimental %C=18.4, %H=3.9, %F=15.8, %S=30.2, and %Fe=5.7.

$Sm(OTf)_3.9.7DMSO$ (NMR method=4.3DMSO)

White grey solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -79.32 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 2.96 ppm, s.

Elemental analysis: calculated %C=18.6, %F=11.9, %S=28.0, and %Sm=10.4 and experimental %C=19.8, %F=12.6, %S=30.0, and %Sm=11.1.

$Mg(OTf)_2.3.9DMSO$ (NMR method=2.1DMSO)

White solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -79.39 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 2.77 ppm, s.

Elemental analysis: calculated %C=18.7, %H=3.7, %F=18.3, %S=30.0, and %Mg=3.9 and experimental %C=18.4, %H=4.1, %F=14.9, %S=29.6, and %Mg=3.9.

$Ca(OTf)_2.6.4DMSO$ (NMR method=5.0DMSO)

White solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -79.20 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 2.72 ppm, s.

Elemental analysis: calculated %C=21.2, %H=4.6, %F=13.6, %S=32.1, and %Ca=4.7 and experimental %C=20.6, %H=4.6, %F=10.1, %S=31.3, and %Ca=4.7.

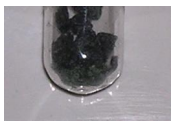
$In(OTf)_3.xDMSO$ (NMR method=9.5DMSO)

White solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -79.39 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 2.97 ppm, s.

$Cu(NTf_2)_2.4.4DMSO$ (NMR method=N.D.)



Dark green solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -80.27 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 3.15 ppm, s.

Elemental analysis: calculated %C=15.9, %H=2.8, %F=23.6, %S=27.8, and %Cu=6.6 and experimental %C=15.5, %H=2.9, %F=22.4, %S=27.2, and %Cu=6.5.

$Sn(NTf_2)_4.7.9DMSO$ (NMR method=7.2DMSO)

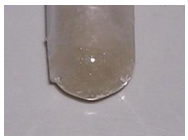
White grey solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -80.34 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 3.33 ppm, s.

Elemental analysis: calculated %C=15.4, %H=2.6, %F=24.5, %S=27.4, and %Sn=6.4 and experimental %C=14.7, %H=2.3, %F=24.2, %S=26.7, and %Sn=6.1.

$Bi(NTf_2)_3$.10.8DMSO (NMR method=3.4DMSO)



White grey solid.

^{19}F-NMR, [D_6]-acetone, 20 °C: -80.31 ppm, s.

^{1}H-NMR, [D_6]-acetone, 20 °C: 2.94 ppm, s.

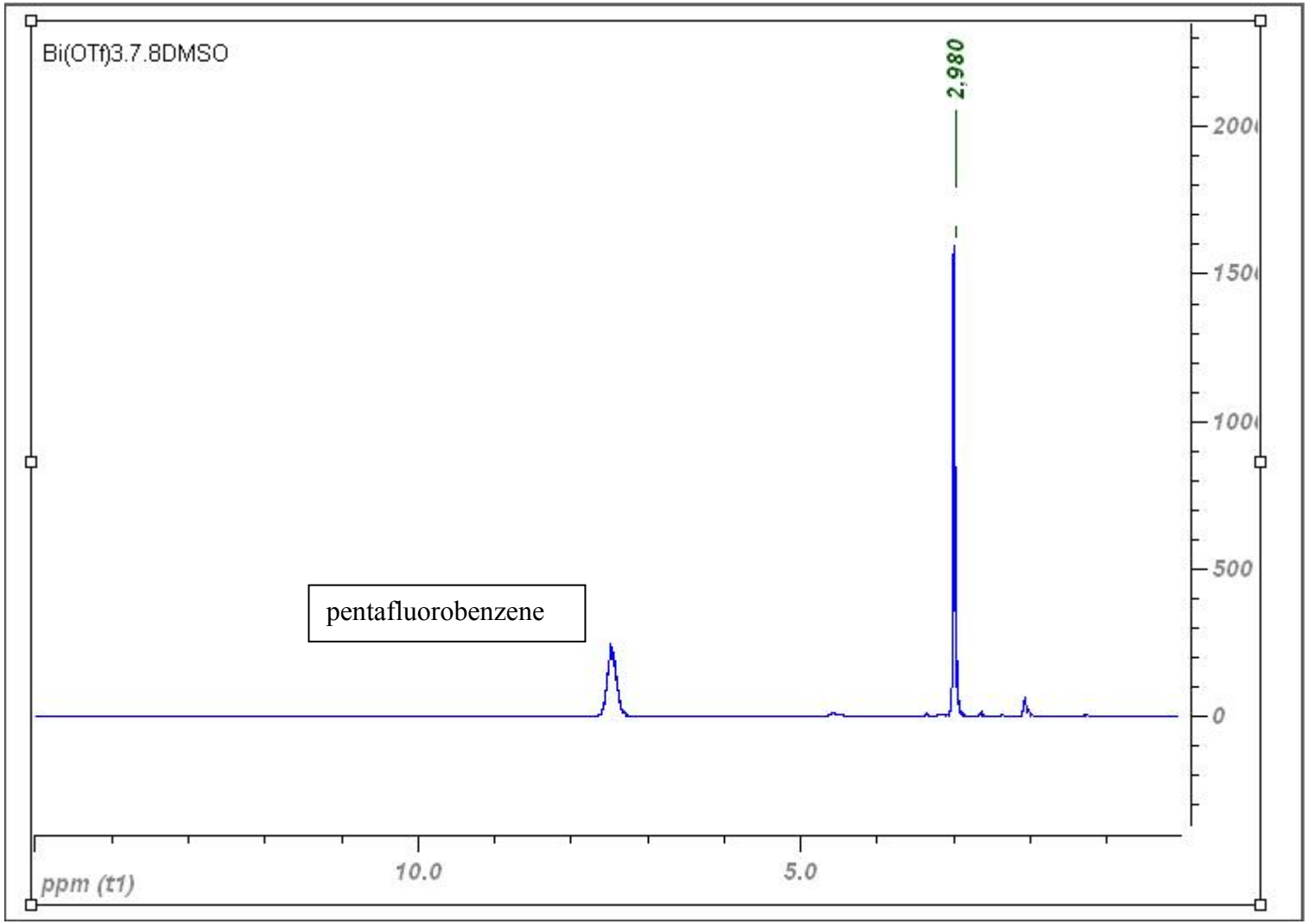
Elemental analysis: calculated %C=17.5, %H=3.5, %F=18.1, %S=28.4, and %Bi=11.0 and experimental %C=15.9, %H=2.9, %F=20.0, %S=26.9, and %Bi=10.0.

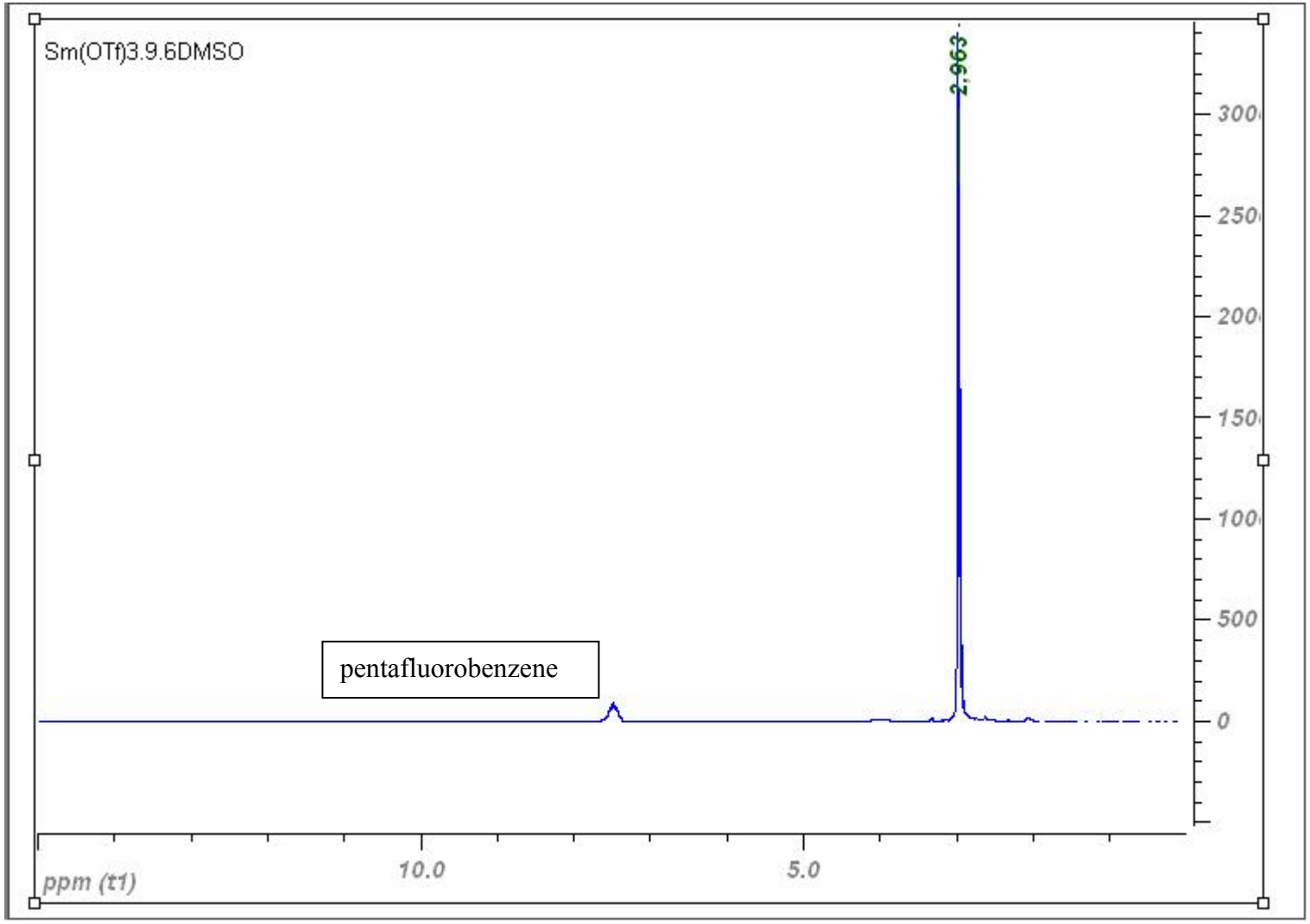
$Mg(NTf_2)_2$.5.0DMSO (NMR method=3.8DMSO)

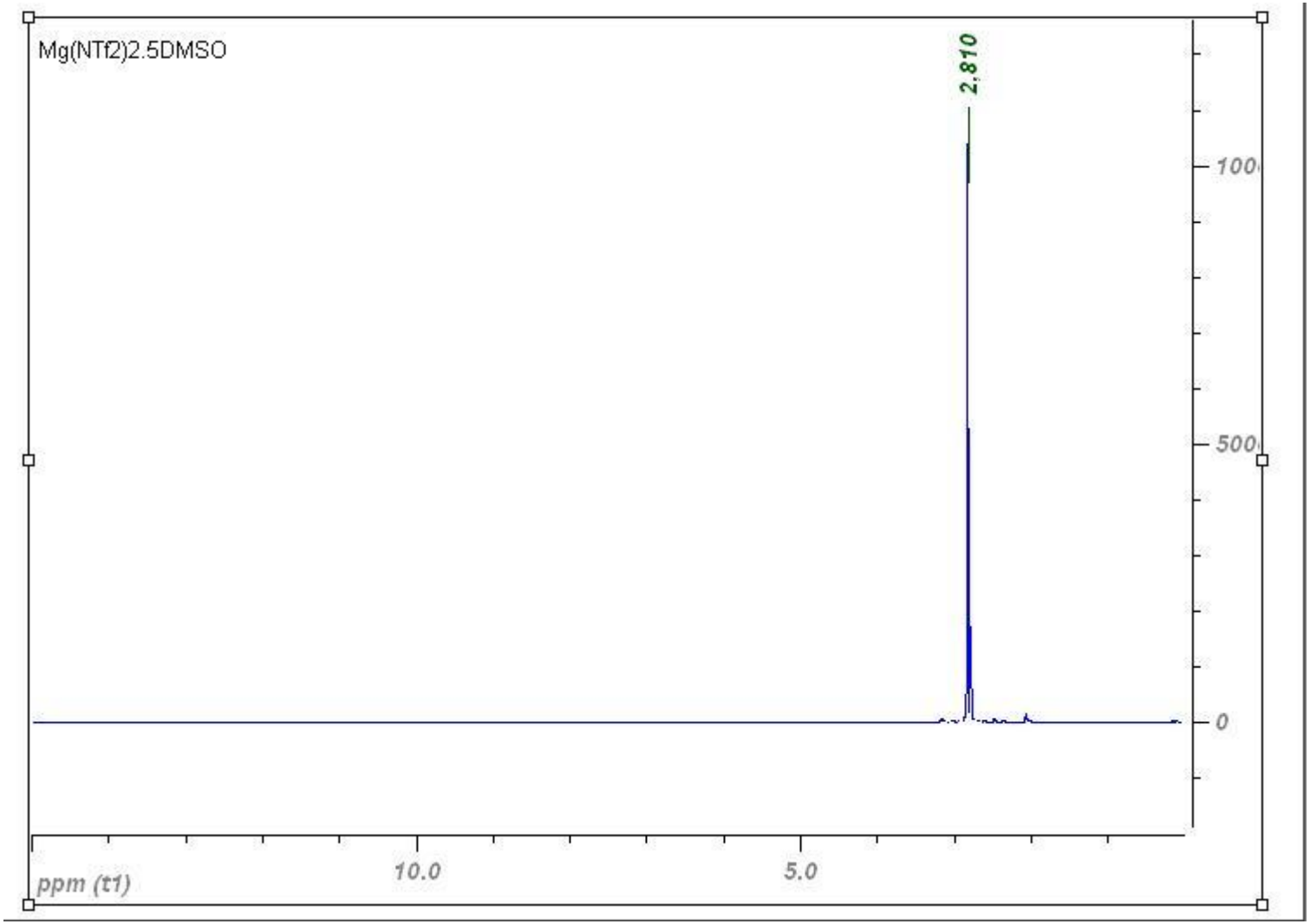
White solid.

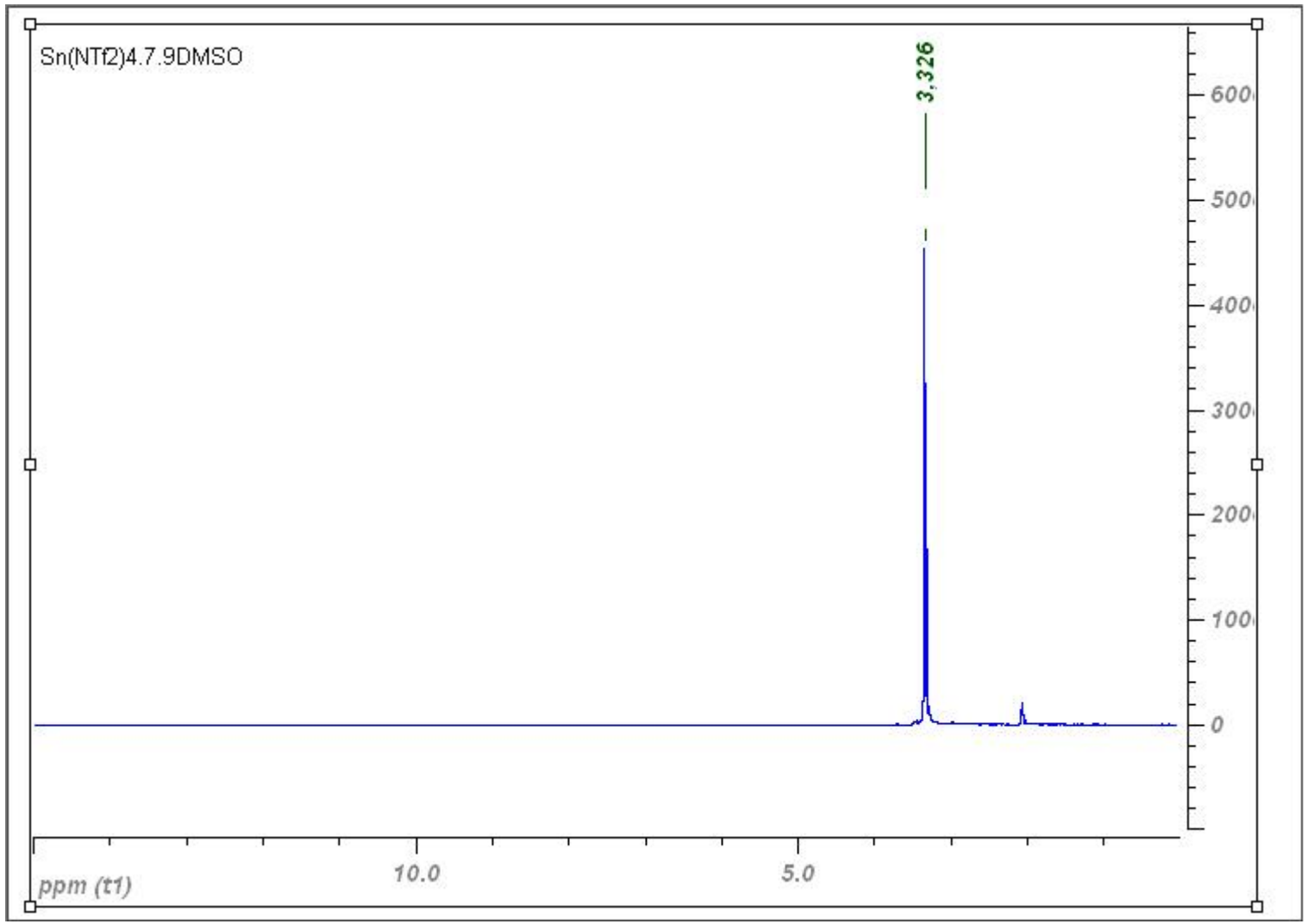
^{19}F-NMR, [D_6]-acetone, 20 °C: -80.32 ppm, s.

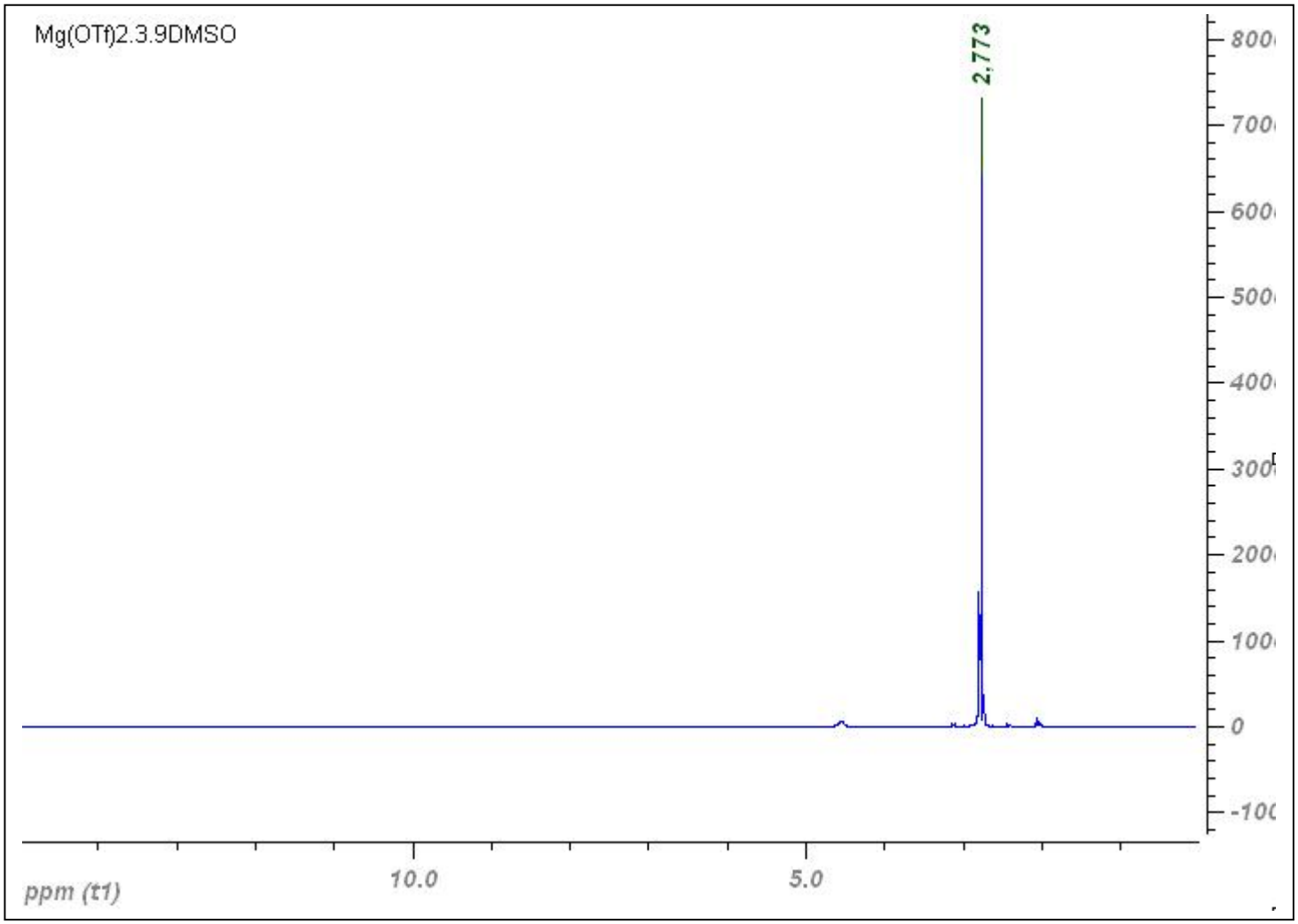
^{1}H-NMR, [D_6]-acetone, 20 °C: 2.81 ppm, s.

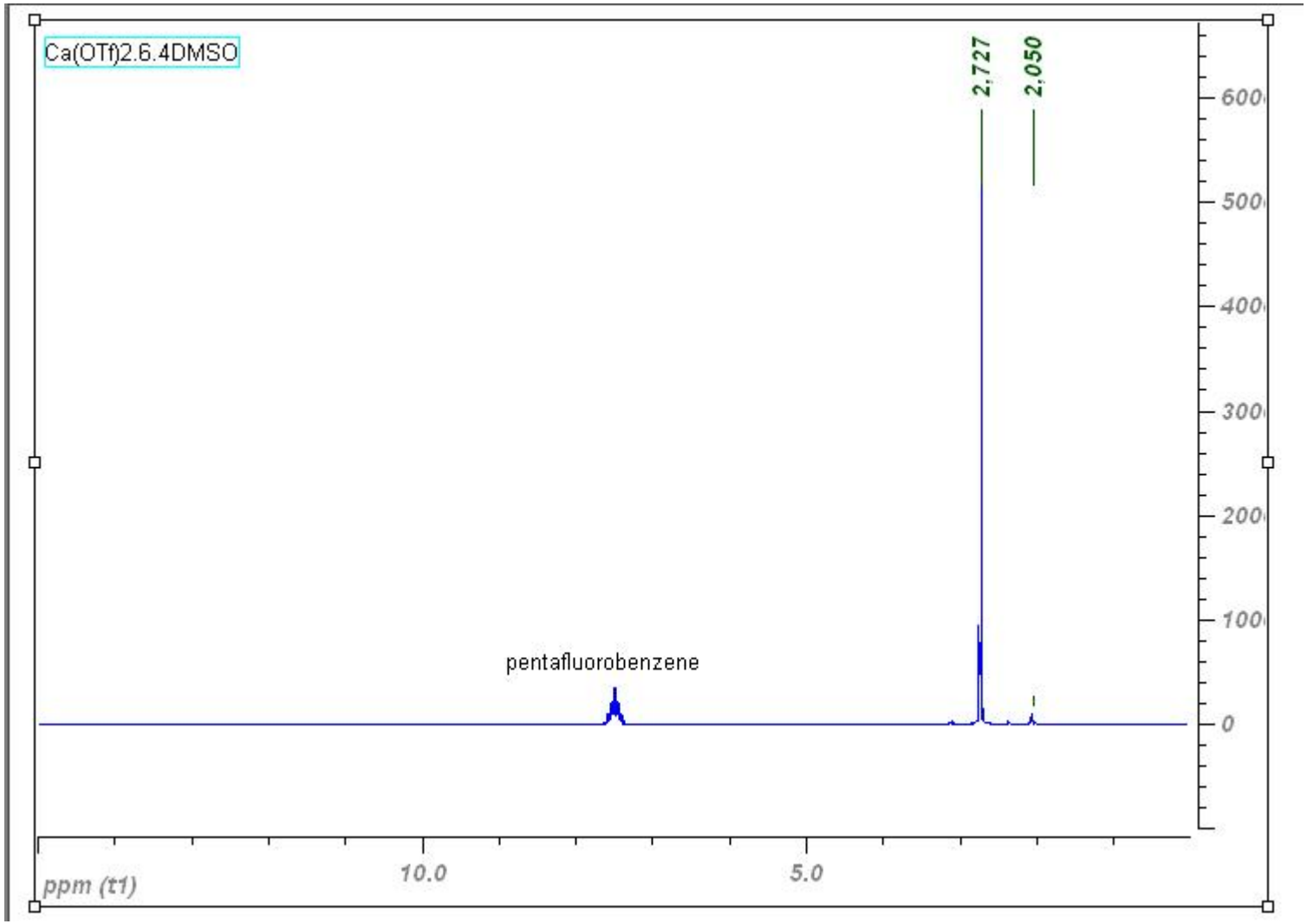

Bi(OTf)3.7.8DMSO
2,980
200
150
100
500
0
pentafluorobenzene
10.0
5.0
ppm (t1)

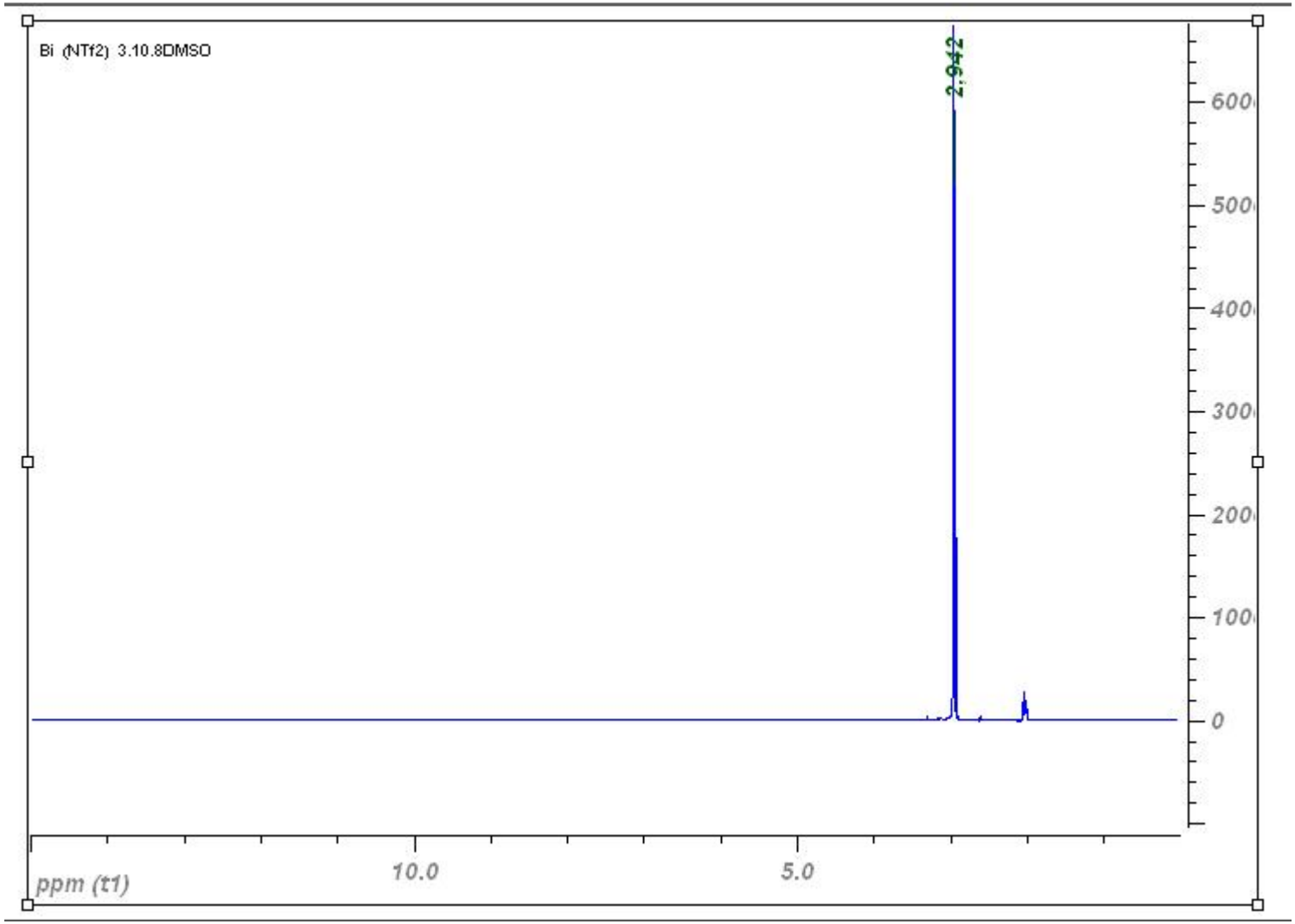

Sm(OTf)3.9.6DMSO
2.963
300
250
200
150
100
500
0
pentafluorobenzene
10.0
5.0
ppm (t1)

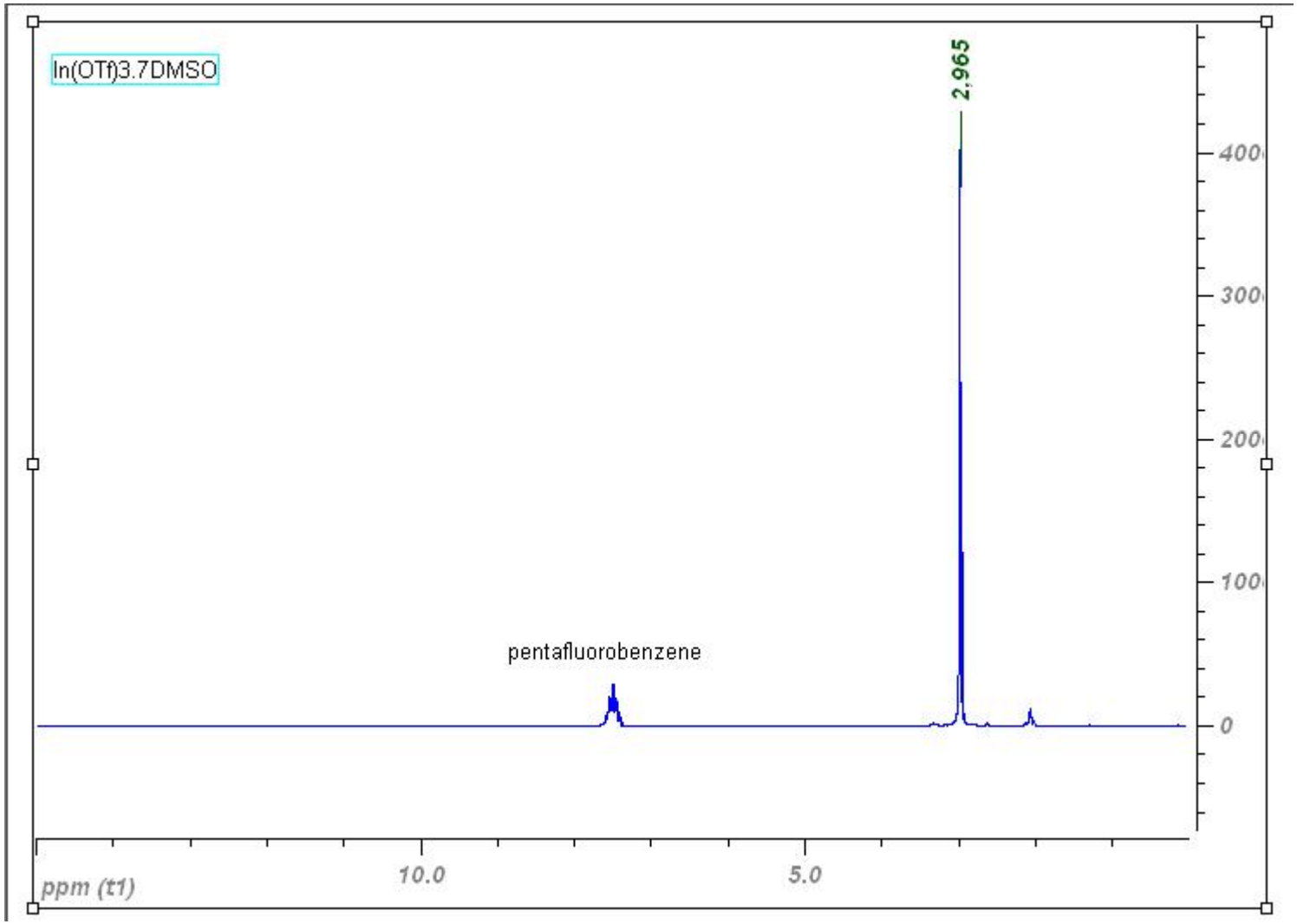

Mg(NTf2)2.5DMSO
2,810
100
500
0
10.0
5.0
ppm (t1)

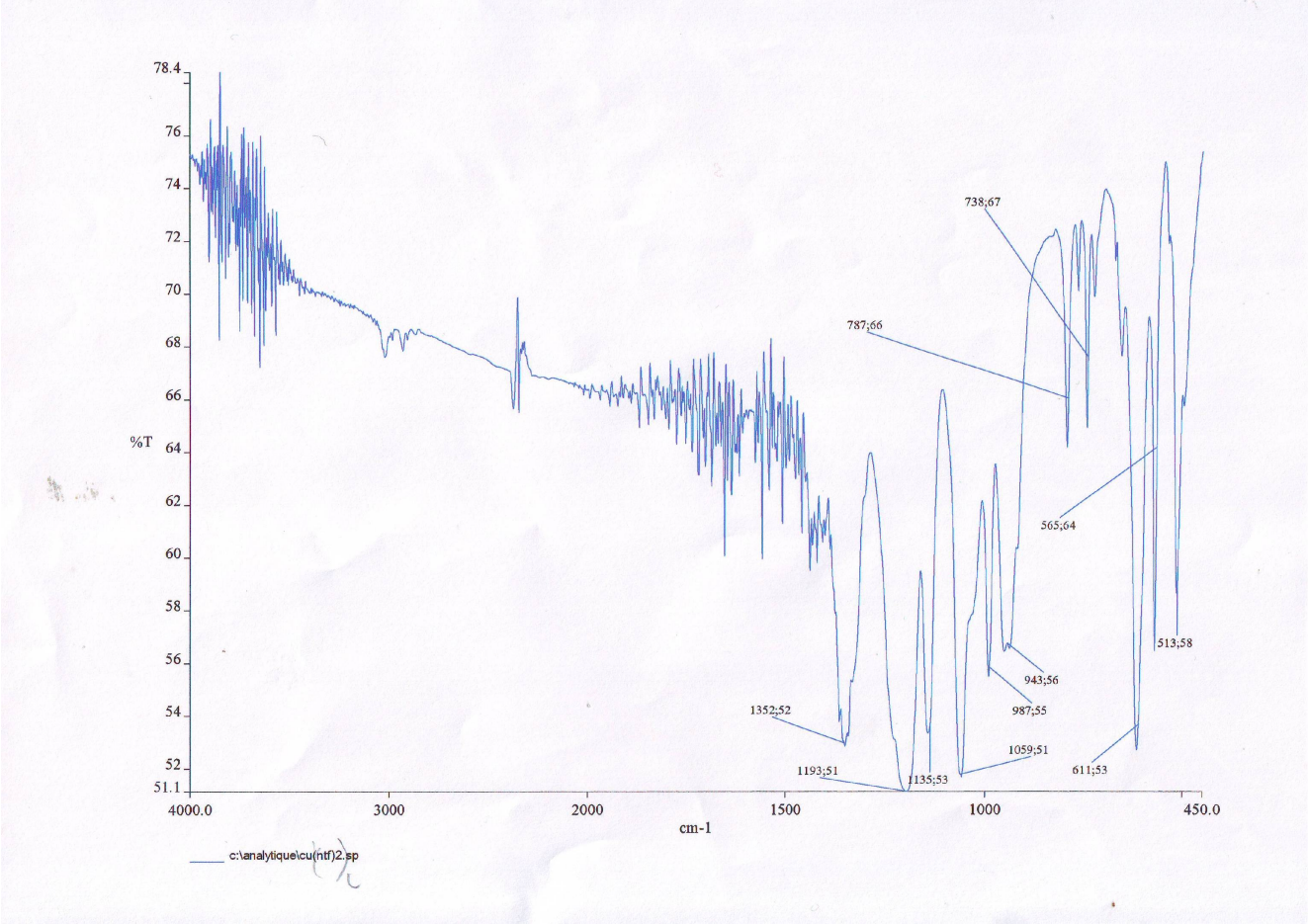

Sn(NTf2)4.7.9DMSO
3.326
600
500
400
300
200
100
0
ppm (t1)
10.0
5.0


Mg(OTf)2.3.9DMSO
2,773
800
700
600
500
400
300
200
100
0
-100
10.0
5.0
ppm (t1)

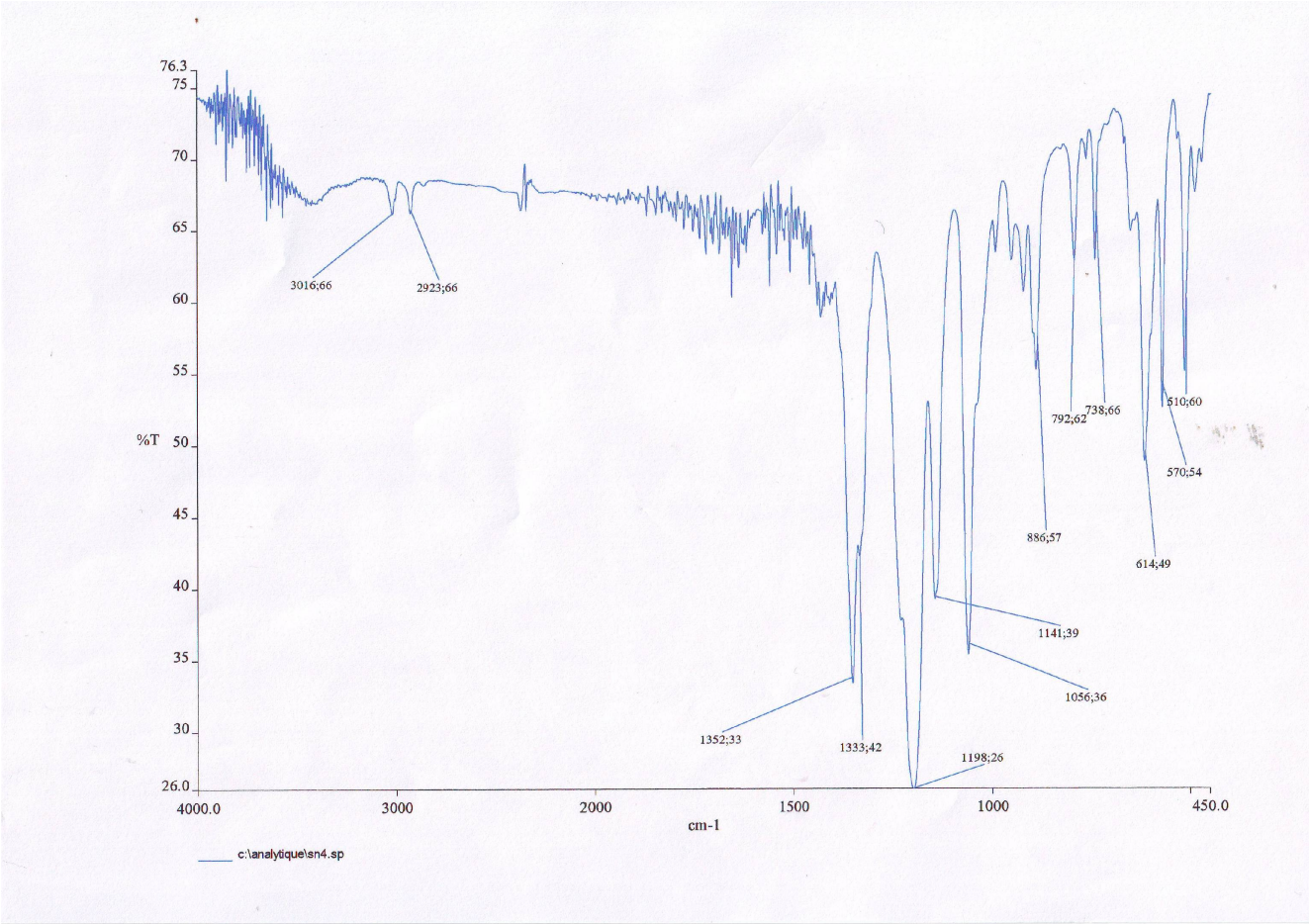

Ca(OTf)2.6.4DMSO
2,727
2,050
pentafluorobenzene
600
500
400
300
200
100
0
10.0
5.0
ppm (t1)


Bi (NTf2) 3.10.8DMSO
2.942
600
500
400
300
200
100
0
10.0
5.0
ppm (t1)


In(OTf)3.7DMSO
2,965
400
300
200
100
0
pentafluorobenzene
10.0
5.0
ppm (t1)



$Cu(NTf_2)_2$.4.4DMSO in KBr pellet. Selected peaks (cm^{-1}): 1353, 1194, 1136, 1060, 944, 788, 739, 612, 566, 514.



$Sn(NTf_2)_4.8DMSO$ in KBr pellet. Selected peaks (cm^{-1}): 1352, 1198, 1141, 1056, 887, 793, 739, 614, 571, 511.

(1) Picot, A.; Repichet, S.; Le Roux, C.; Dubac, J.; Roques, N. *J. Fluorine Chem.* **2002**, 116, 129-134.