Dalton Transactions

Supporting information

Small molecule activation: SbF_3 auto-ionization supported by transfer and mesoionic NHC rearrangement

B. Alič,[a, b] A. Štefančič[a, b] and G. Tavčar[a, b, *]

[a.] *Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*
[b.] *Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia*

Contents

$[(L^{Dipp})H]^+[SbF_4]^-$ (1)

Reaction "$[SbF_3(tmen)]$ + (L^{Dipp}) –> $[(L^{Dipp})H]^+[SbF_4]^-$":

^{1}H NMR spectrum CD_3CN

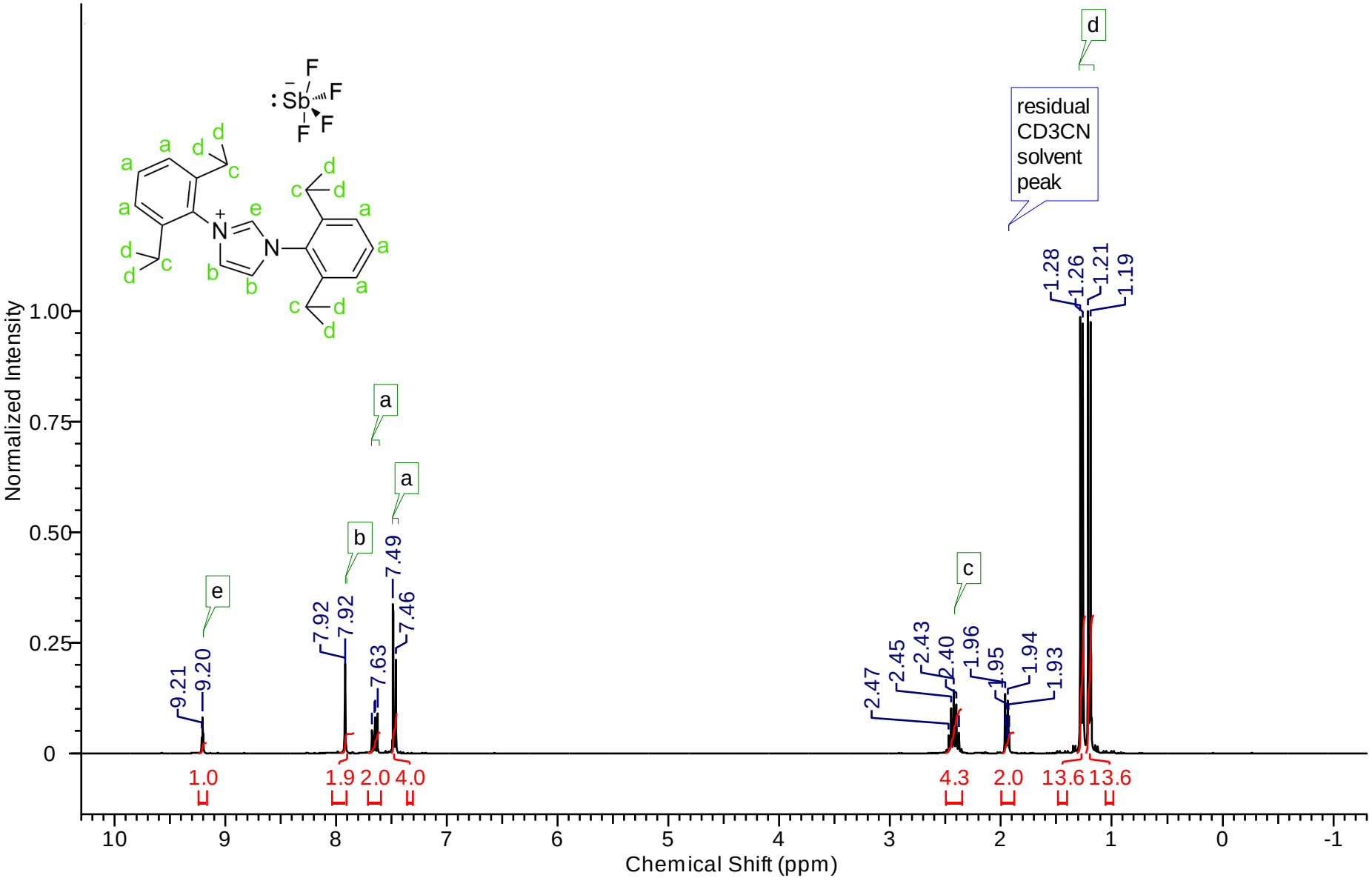
^{19}F spectrum NMR CD_3CN

^{13}C spectrum NMR CD_3CN

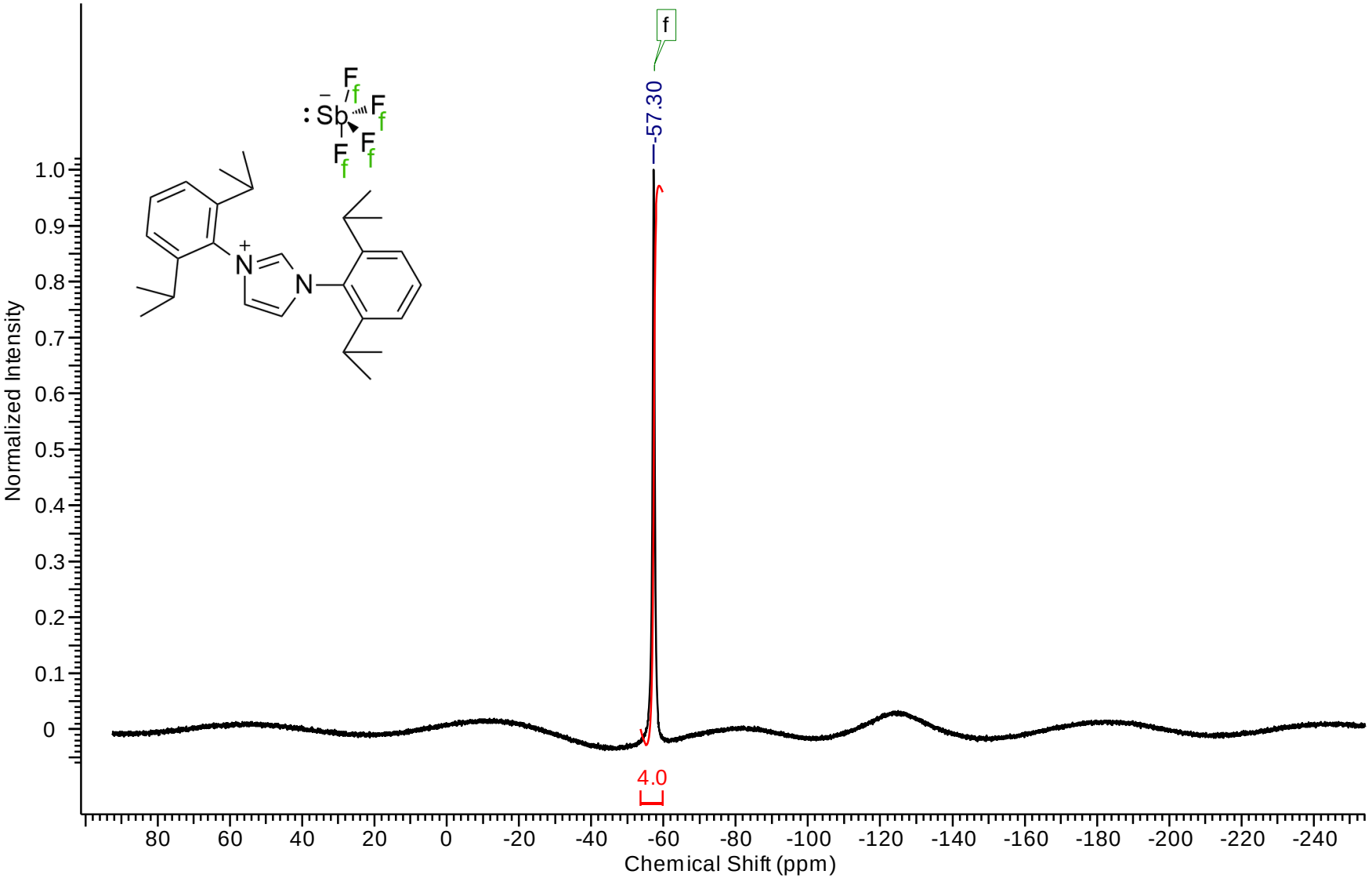
Raman spectrum

Superimposed spectra of reaction (L^{Dipp}) + SbF_3 -> $[(L^{Dipp})H]^+[SbF_4]^-$ (**1**) performed in CH_3CN *vs.* CD_3CN

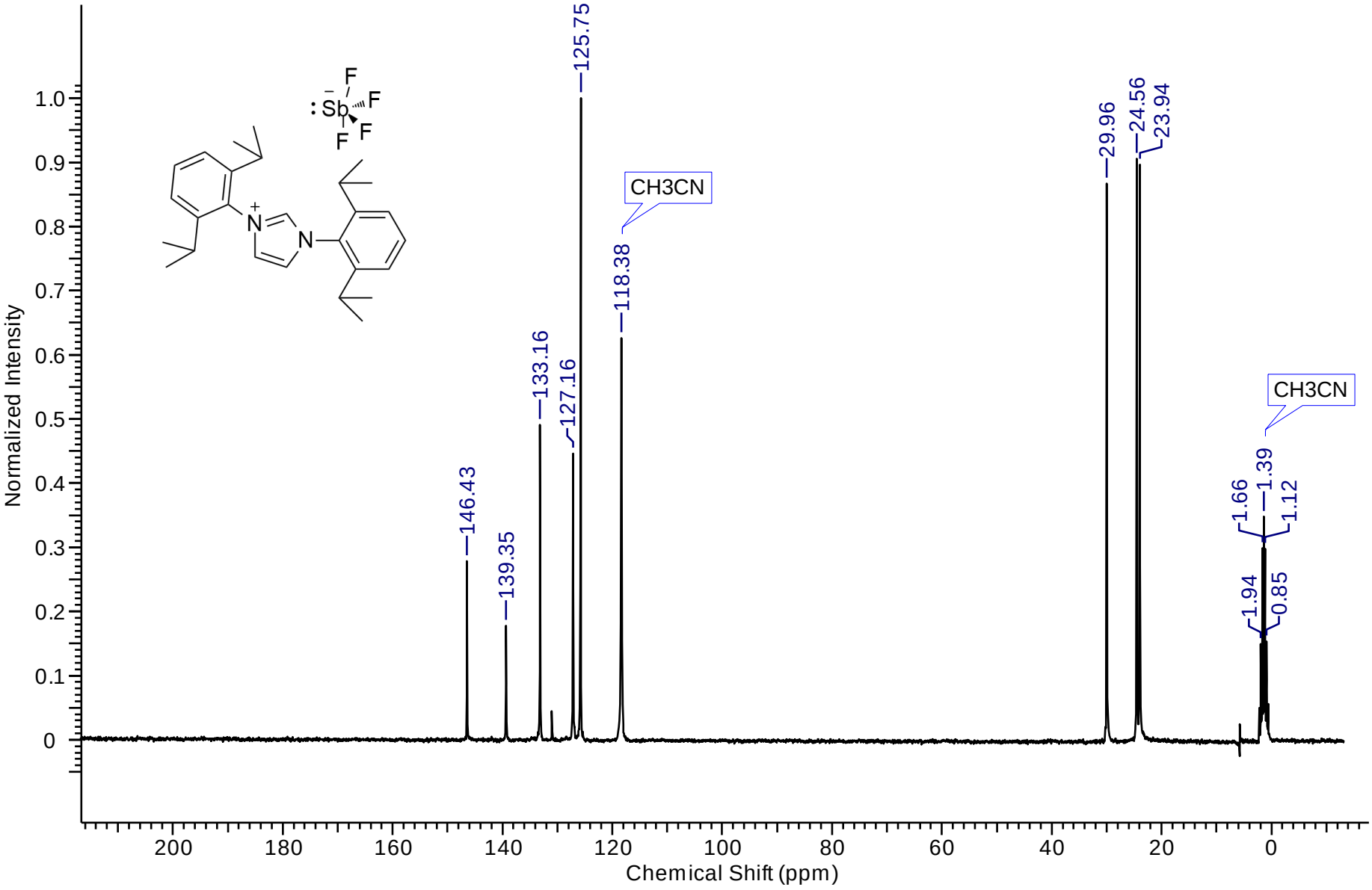
^{1}H NMR spectrum of $[(L^{Dipp})H]^{+}[SbF_4]^{-}$ in CD_3CN, Frequency (MHz) 302.97:



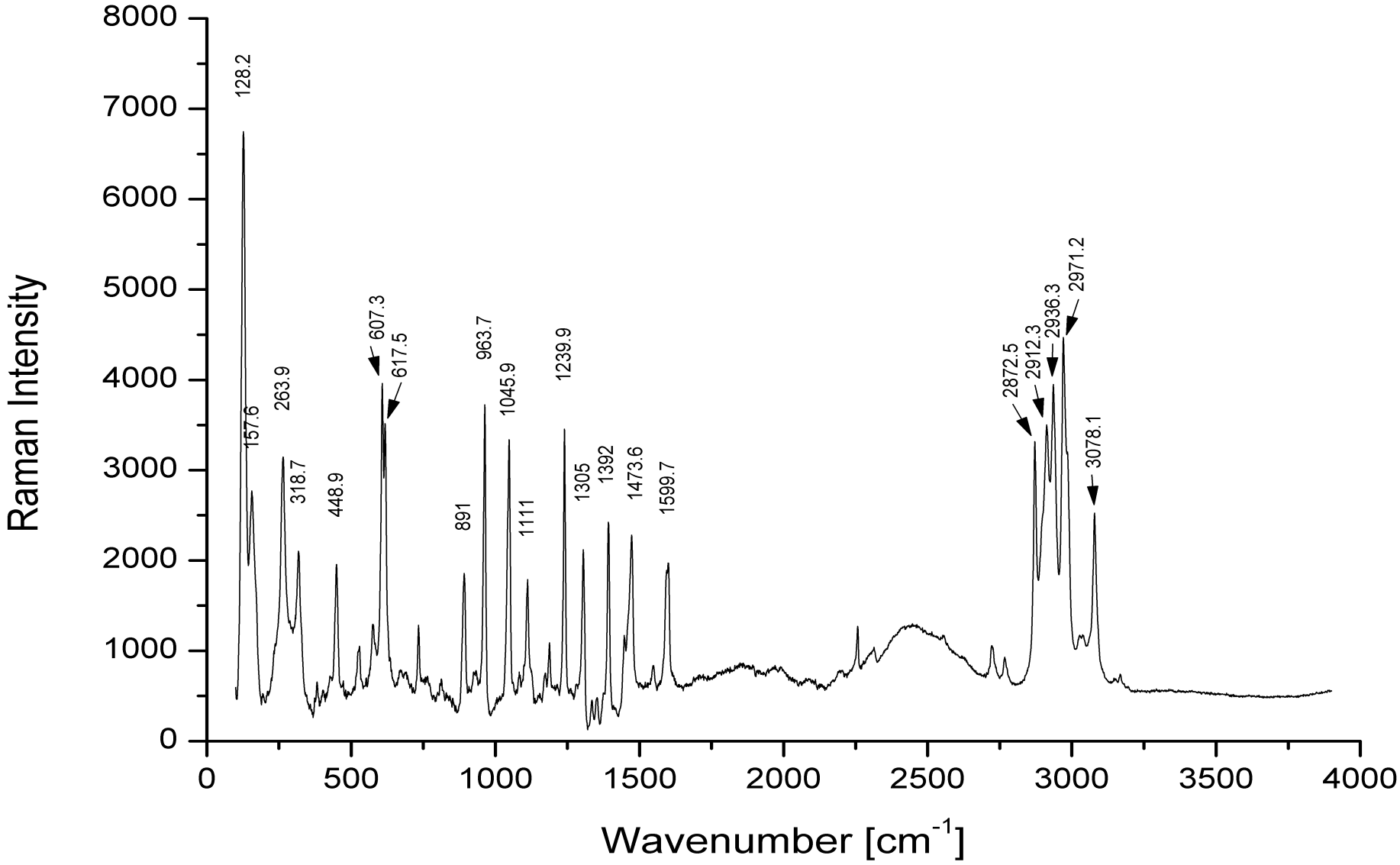
^{19}F NMR spectrum of $[(L^{Dipp})H]^+[SbF_4]^-$ in CD_3CN, Frequency (MHz) 285.05:



^{13}C NMR spectrum of $[(L^{Dipp})H]^+[SbF_4]^-$ in CD_3CN, Frequency (MHz) 76.19:



Raman spetra of $[(L^{Dipp})H]^{+}[SbF_4]^{-}$ (1)



Superimposed spectra of reaction (L^{Dipp}) + SbF_3 -> $[(L^{Dipp})H]^+[SbF_4]^-$ (1) performed in CH_3CN *vs.* CD_3CN

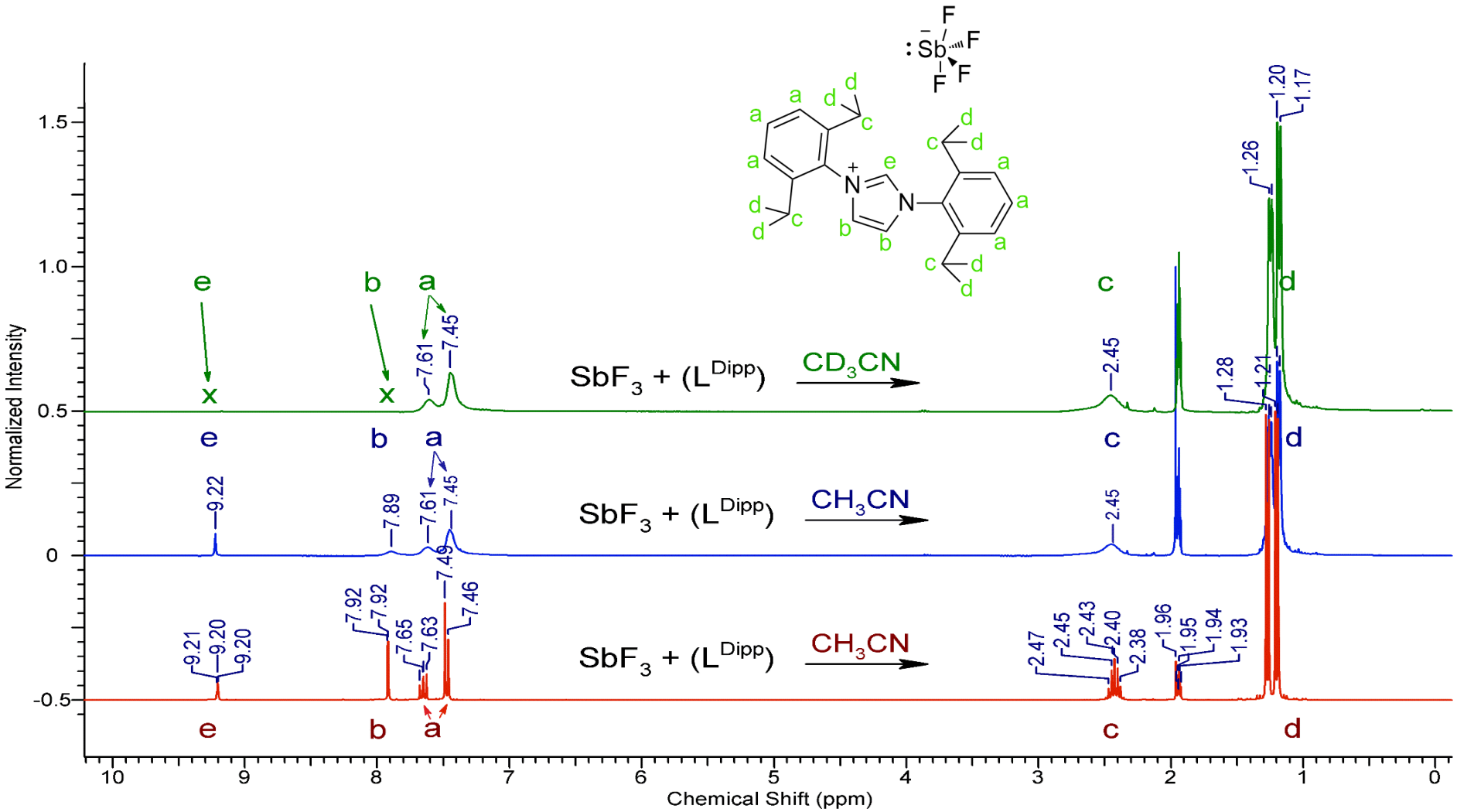


*Figure 1: Superimposed spectra of reaction "SbF_3 + (L^{Dipp})" performed in CH_3CN vs. CD_3CN. Reaction in CH_3CN (**blue**) shows all imidazolium peaks for protons (e) and (b) while reaction in CD_3CN (**green**) shows no imidazolium peaks, showing: **a)** proton (e) arrises from solvent molecule and **b)** all three imidazolium protons (e) and (b) undergo H/D exchange with deuterated solvent. **Red** spectra, for comparison, represents isolated product of $[(L^{Dipp})H]^+[SbF_4]^-$ (**1**)*

$[SbF_3(tmen)]$ (2)

Reaction "SbF_3 + 3tmen + –> $[SbF_3(tmen)]$":

^1H NMR spectrum in THF-d^8

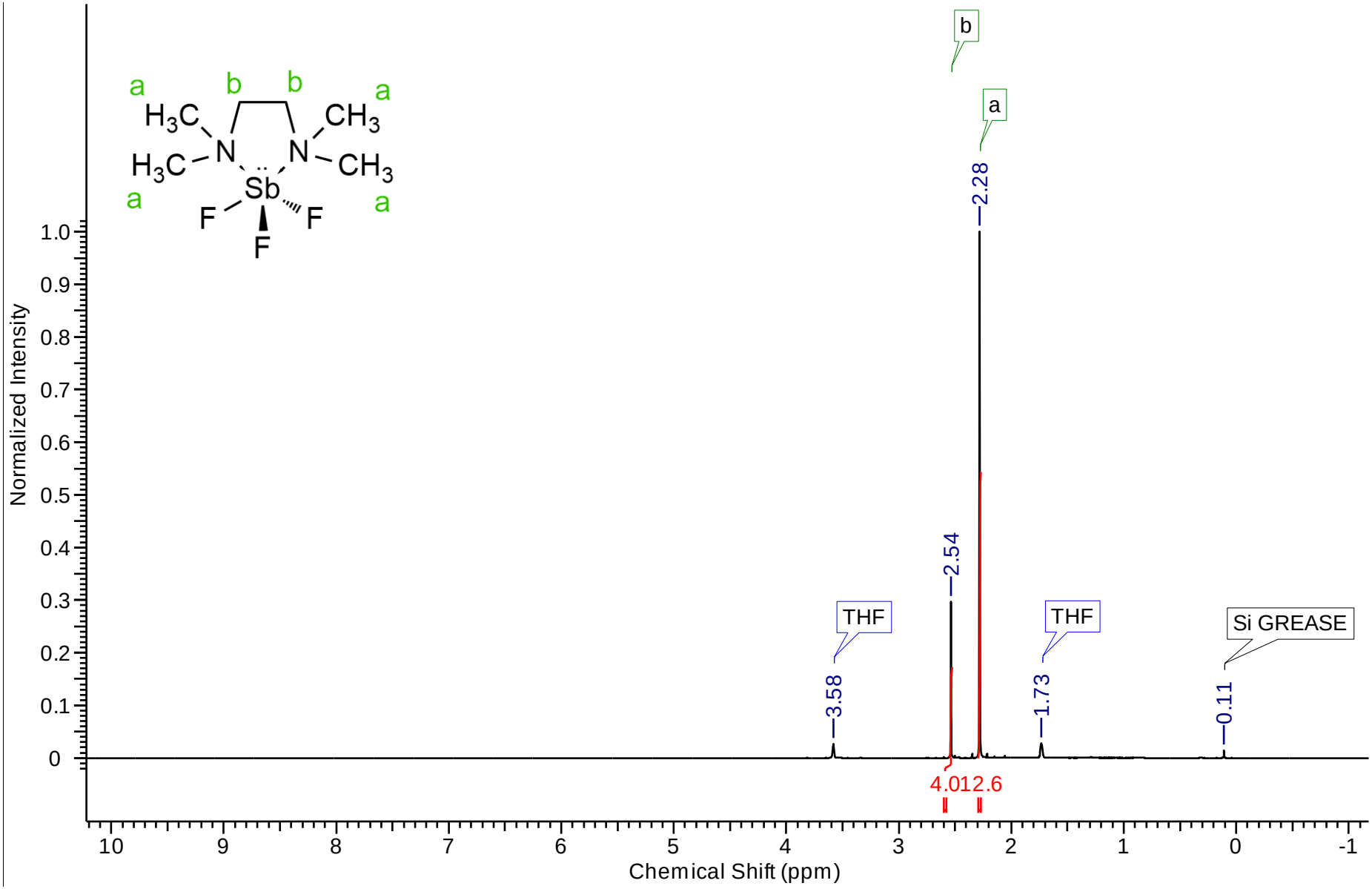
^{19}F NMR spectrum in THF-d^8

^1H NMR spectrum in C_6D_6

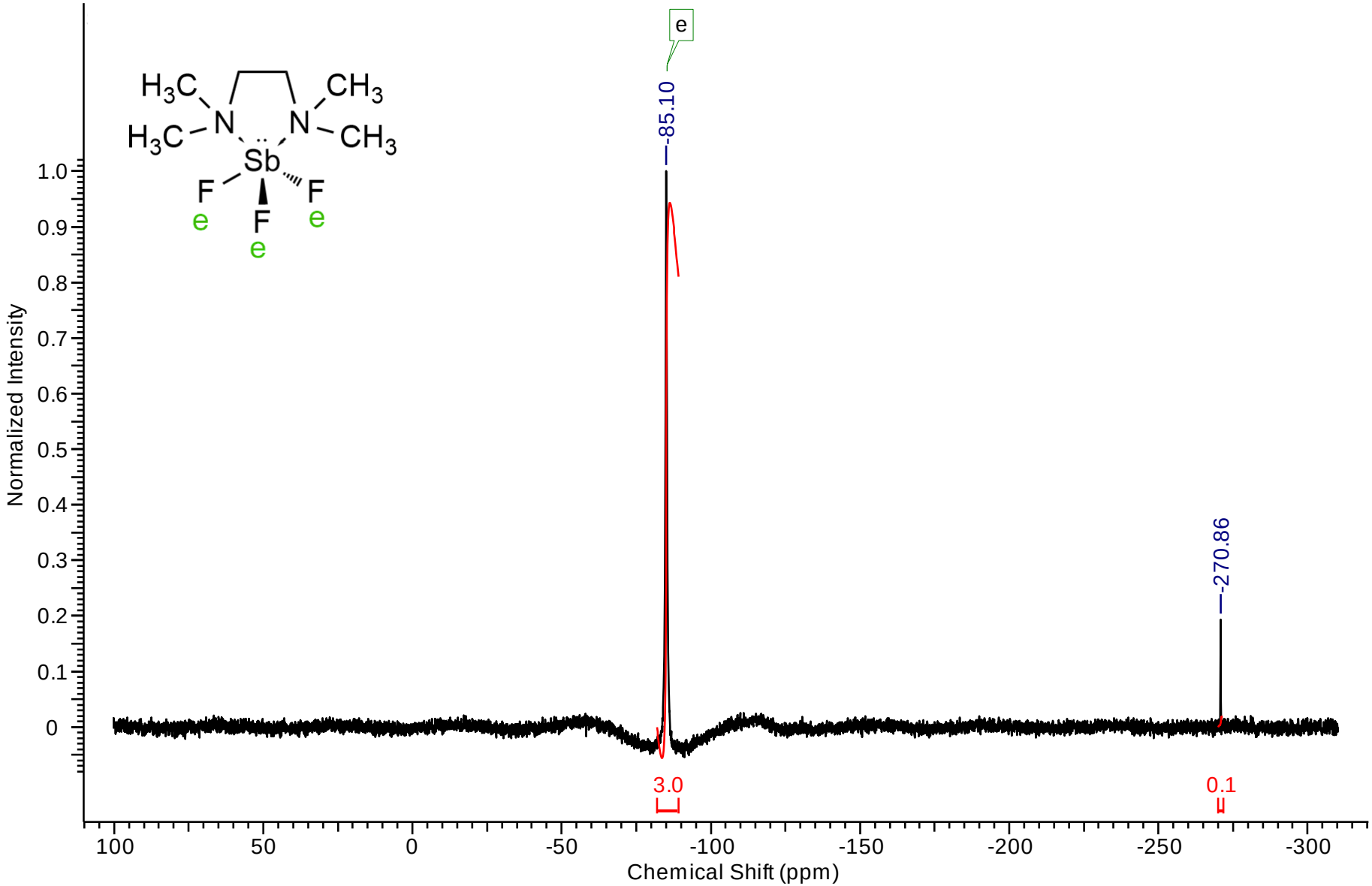
^{19}F NMR spectrum in C_6D_6

Raman spectrum

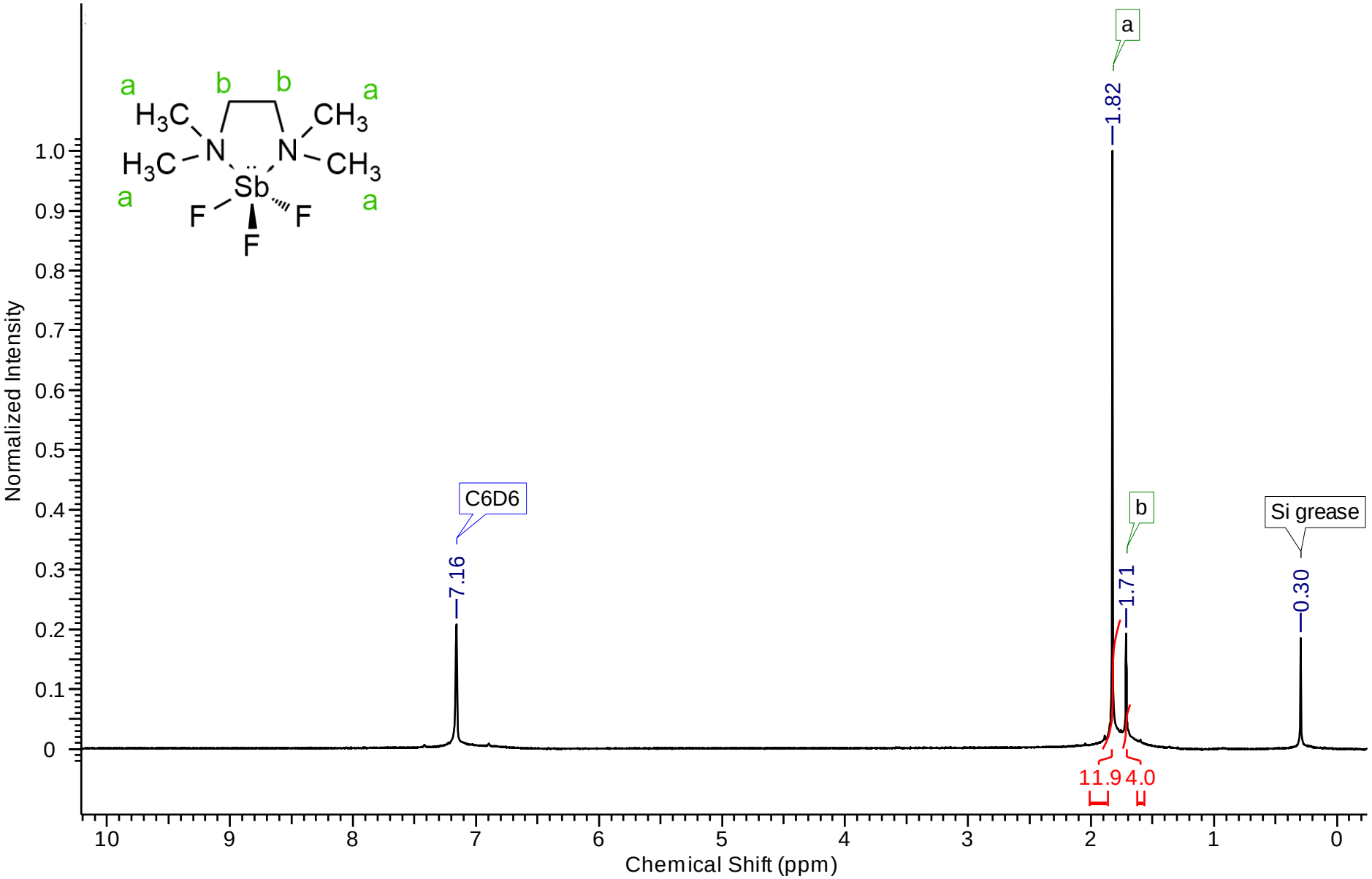
^{1}H NMR spectrum of [SbF_3(tmen)] complex in THF-d^8, Frequency (MHz) 302.97:



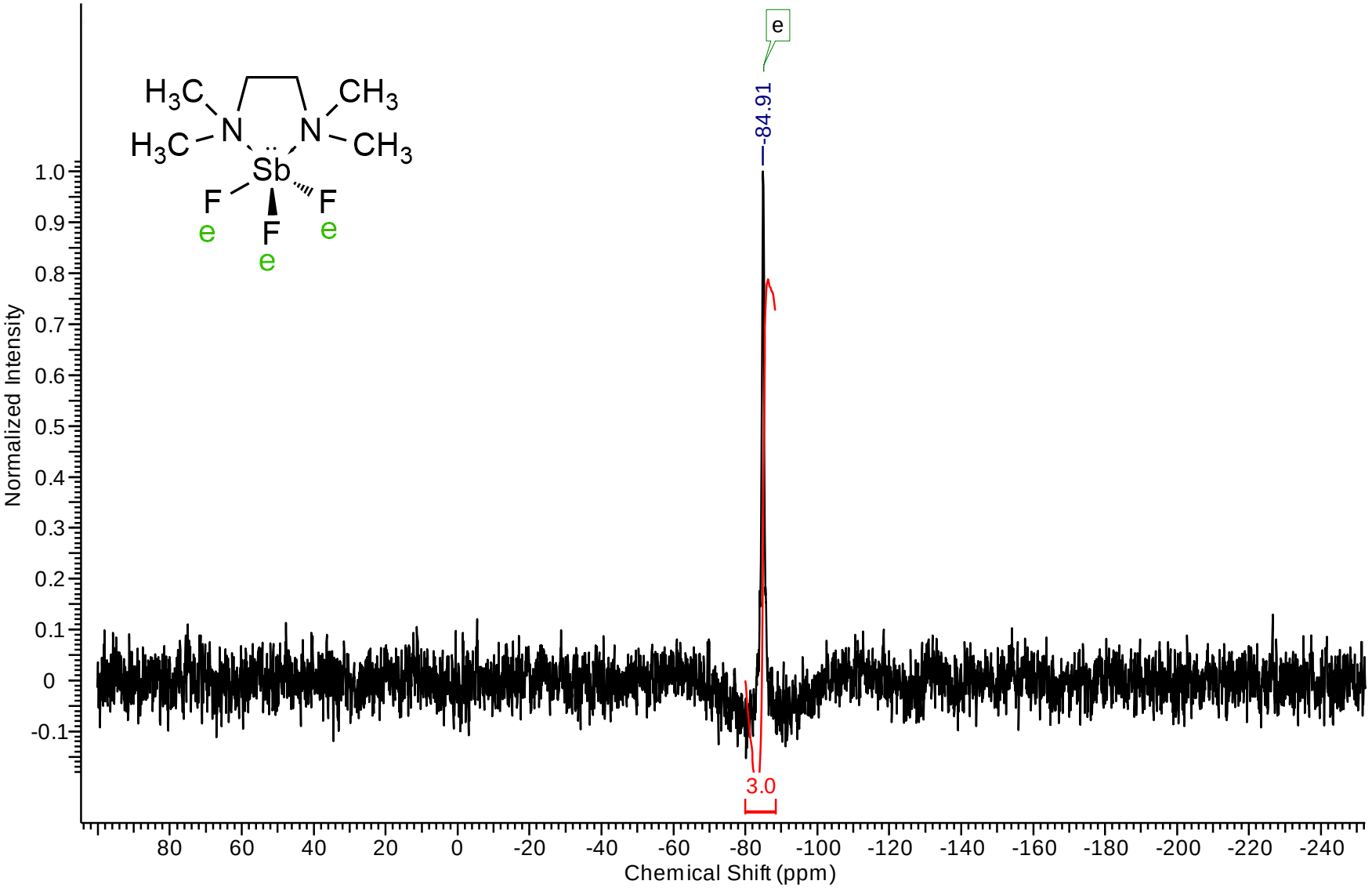
^{19}F NMR spectrum of $[SbF_3(tmen)]$ complex in THF-d^8, Frequency (MHz) 285.05:



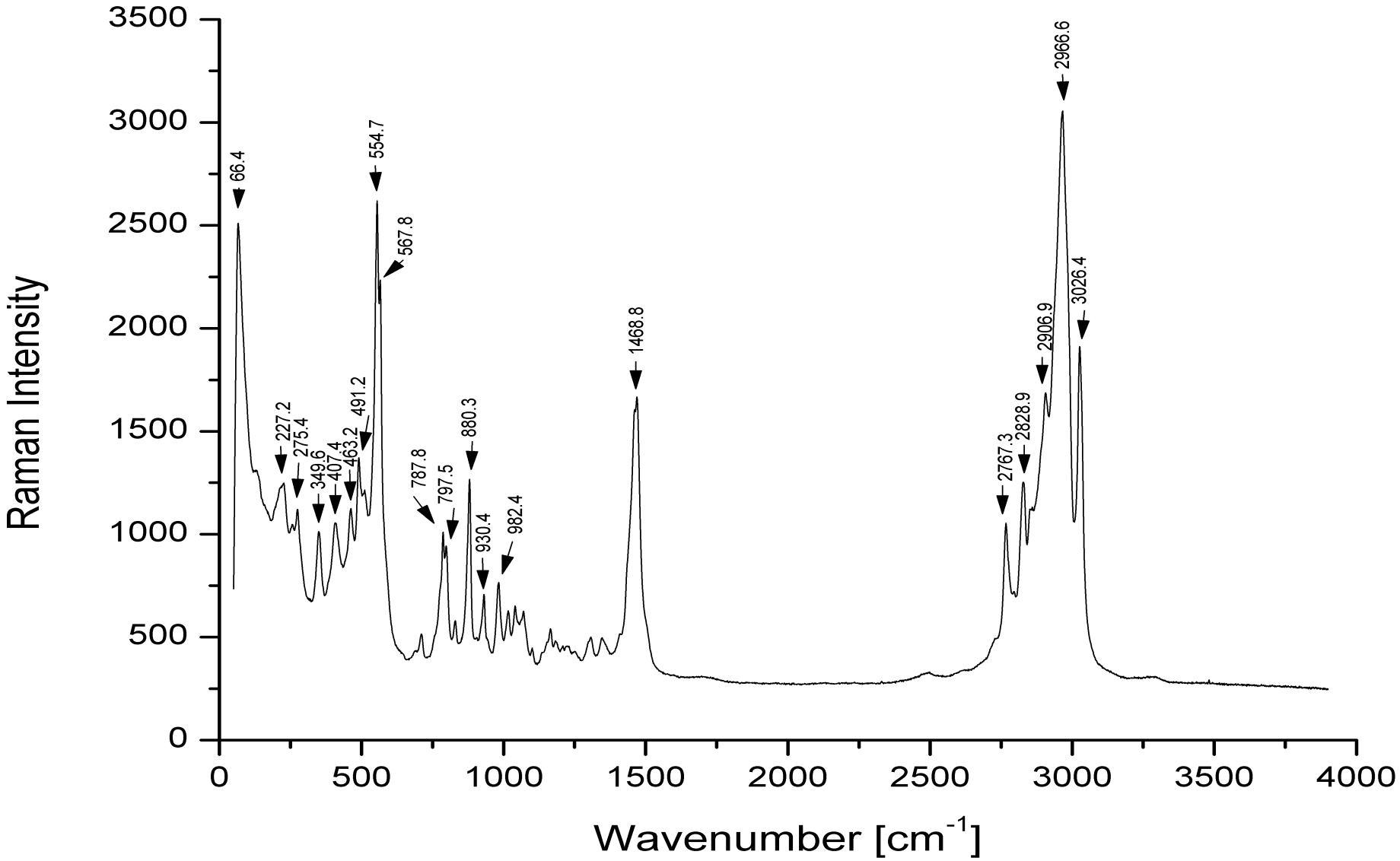
^{1}H NMR spectrum of [SbF_3(tmen)] complex in C_6D_6, Frequency (MHz) 302.97:



^{19}F NMR spectrum of $[SbF_3(tmen)]$ complex in C_6D_6, Frequency (MHz) 285.05:



Raman spectra of $[SbF_3(tmen)]$ (2)



$[(L^{Dipp})SbF_3]$ (3)

Reaction "$[SbF_3(tmen)]$ + (L^{Dipp}) –> $[(L^{Dipp})SbF_3]$":

^{1}H NMR spectrum in C_6D_6

^{19}F NMR spectrum in C_6D_6

^{13}C NMR spectrum in C_6D_6

Reaction "$[SbF_3(tmen)]$ + (L^{Dipp}) +2tmen –> $[(L^{Dipp})SbF_3]$":

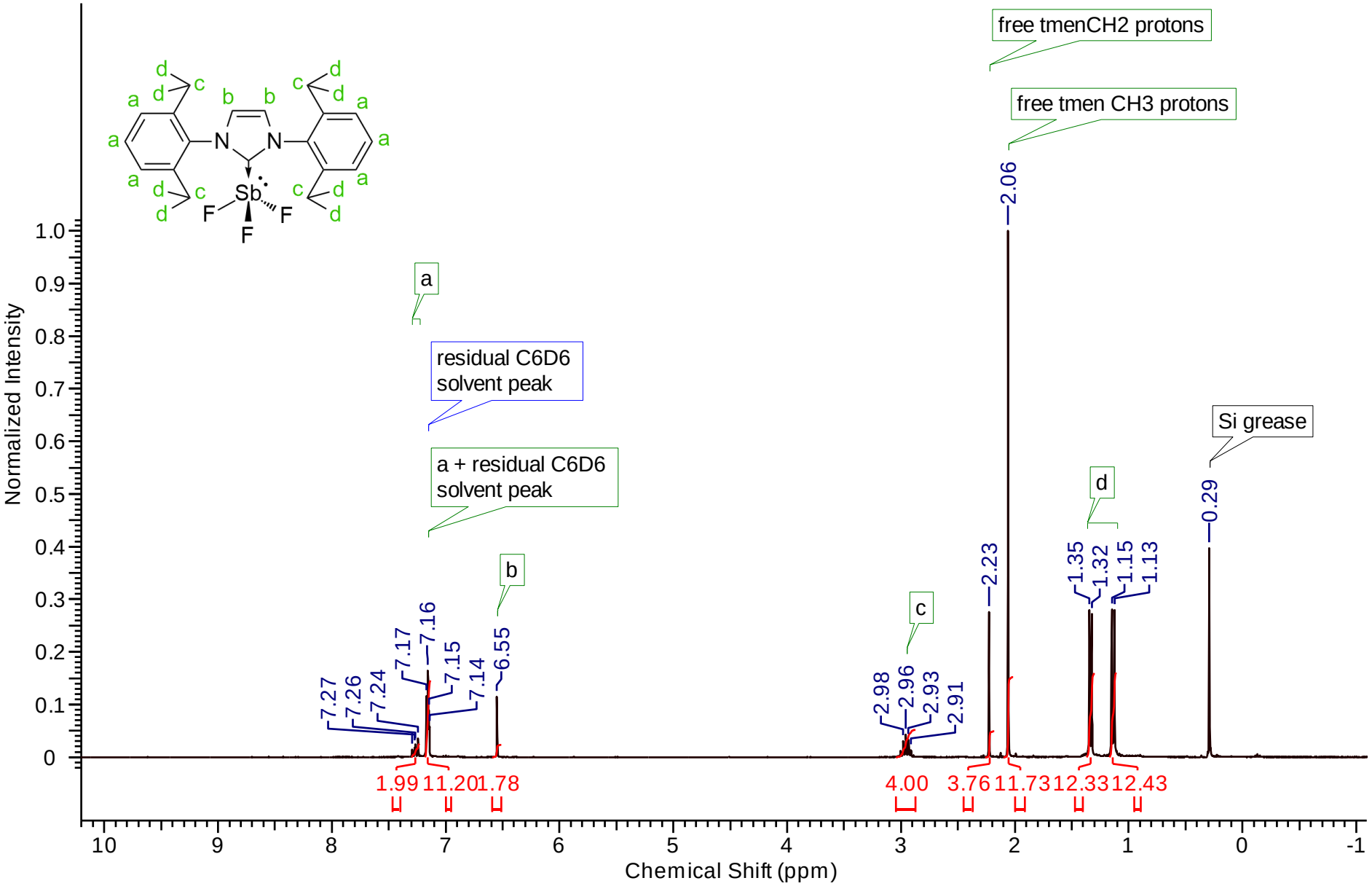
^{1}H NMR spectrum in C_6D_6

Reaction "SbF_3 + (L^{Dipp}) + 2dme –> $[(L^{Dipp})SbF_3]$":

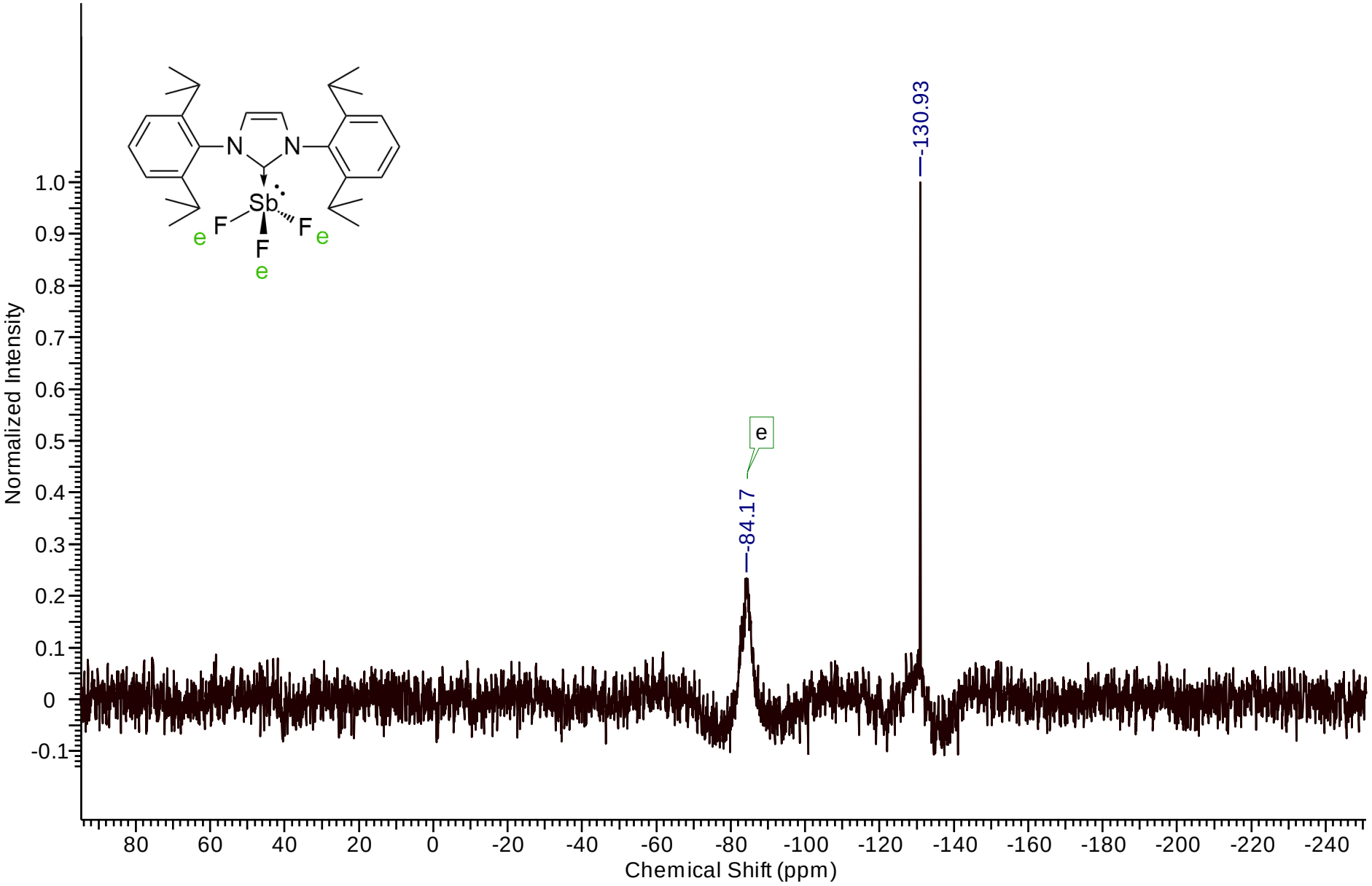
^{1}H NMR spectrum in C_6D_6

^{19}F NMR spectrum in C_6D_6

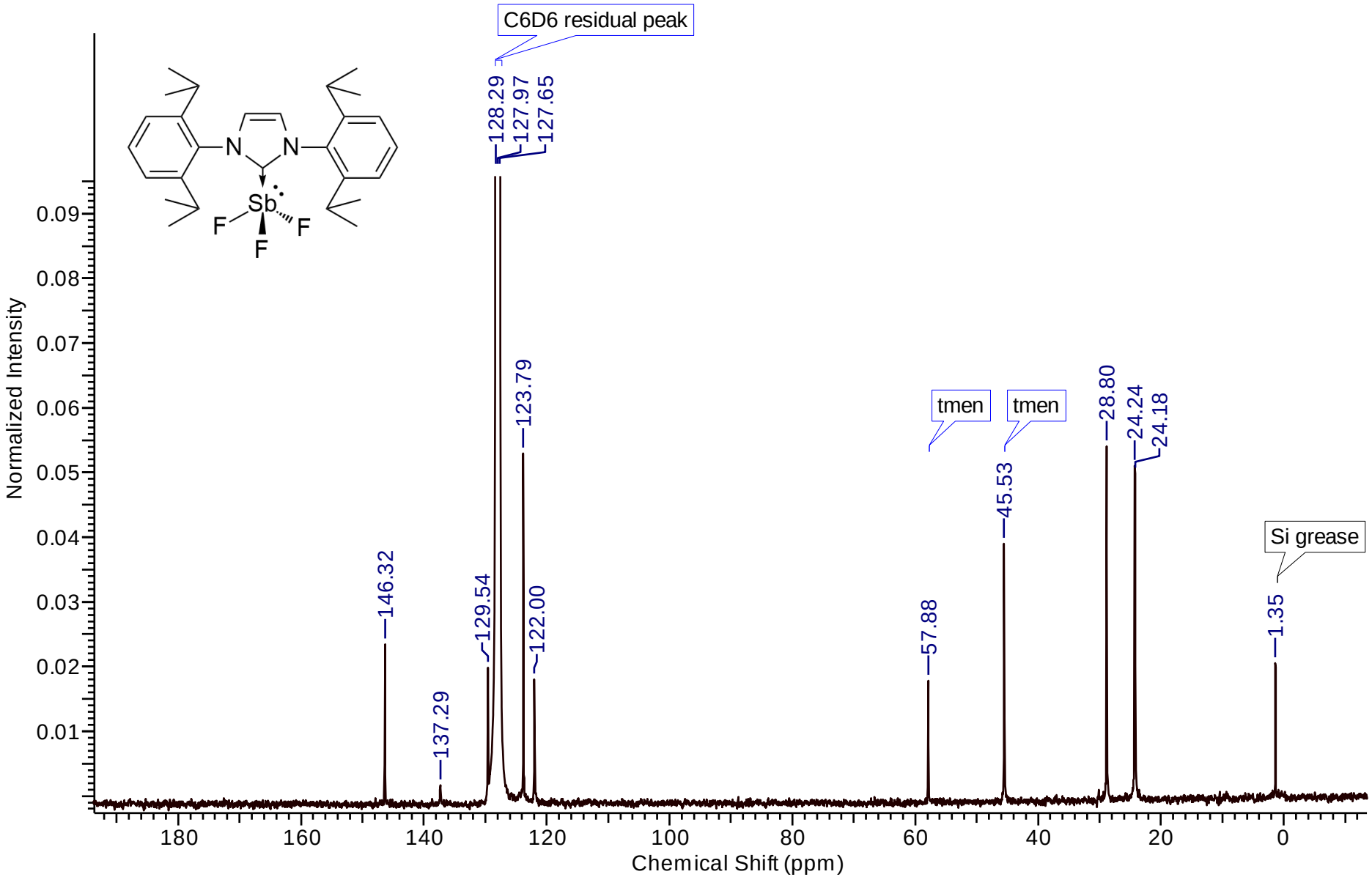
^{1}H NMR spectrum for reaction "[SbF_3(tmen)] + (L^{Dipp}) –> [(L^{Dipp})SbF_3]" in C_6D_6, Frequency (MHz) 302.97:



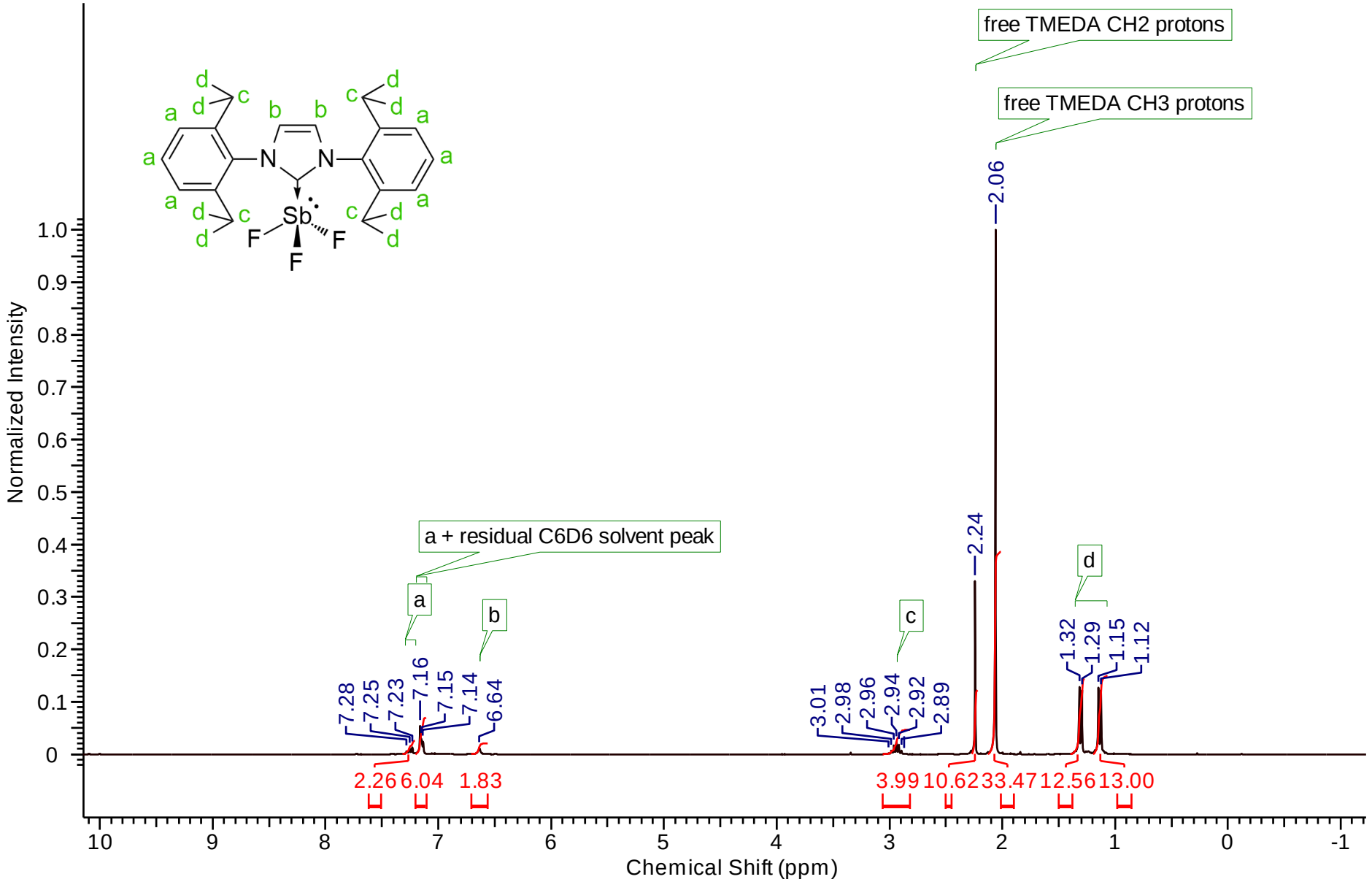
^{19}F NMR spectrum for reaction "[SbF_3(tmen)] + (L^{Dipp}) –> [(L^{Dipp})SbF_3]" in C_6D_6, Frequency (MHz) 285.05:



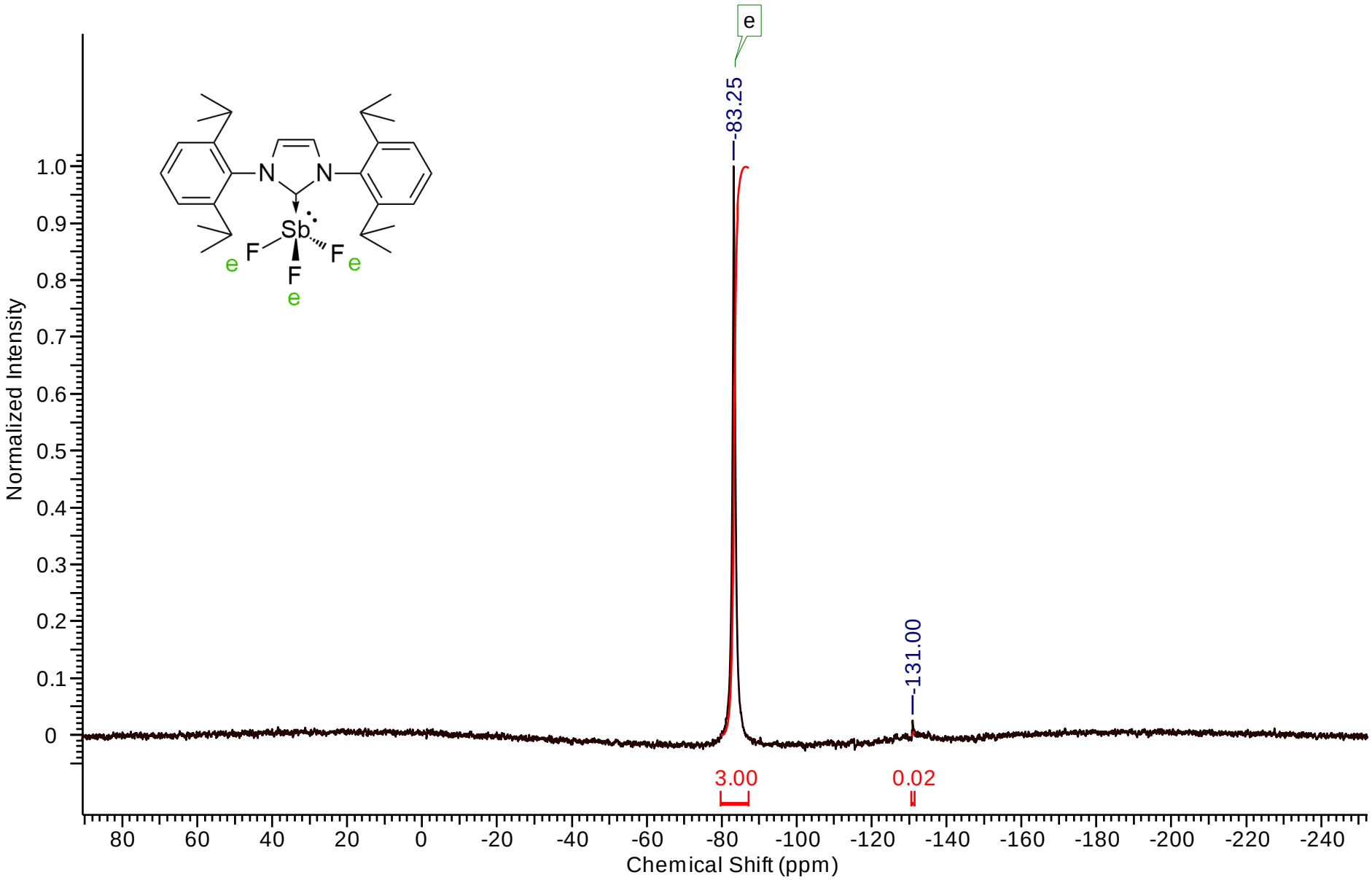
^{13}C NMR spectrum for reaction "[SbF_3(tmen)]+ (L^{Dipp}) –> [(L^{Dipp})SbF_3]" in C_6D_6, Frequency (MHz) 76.19:



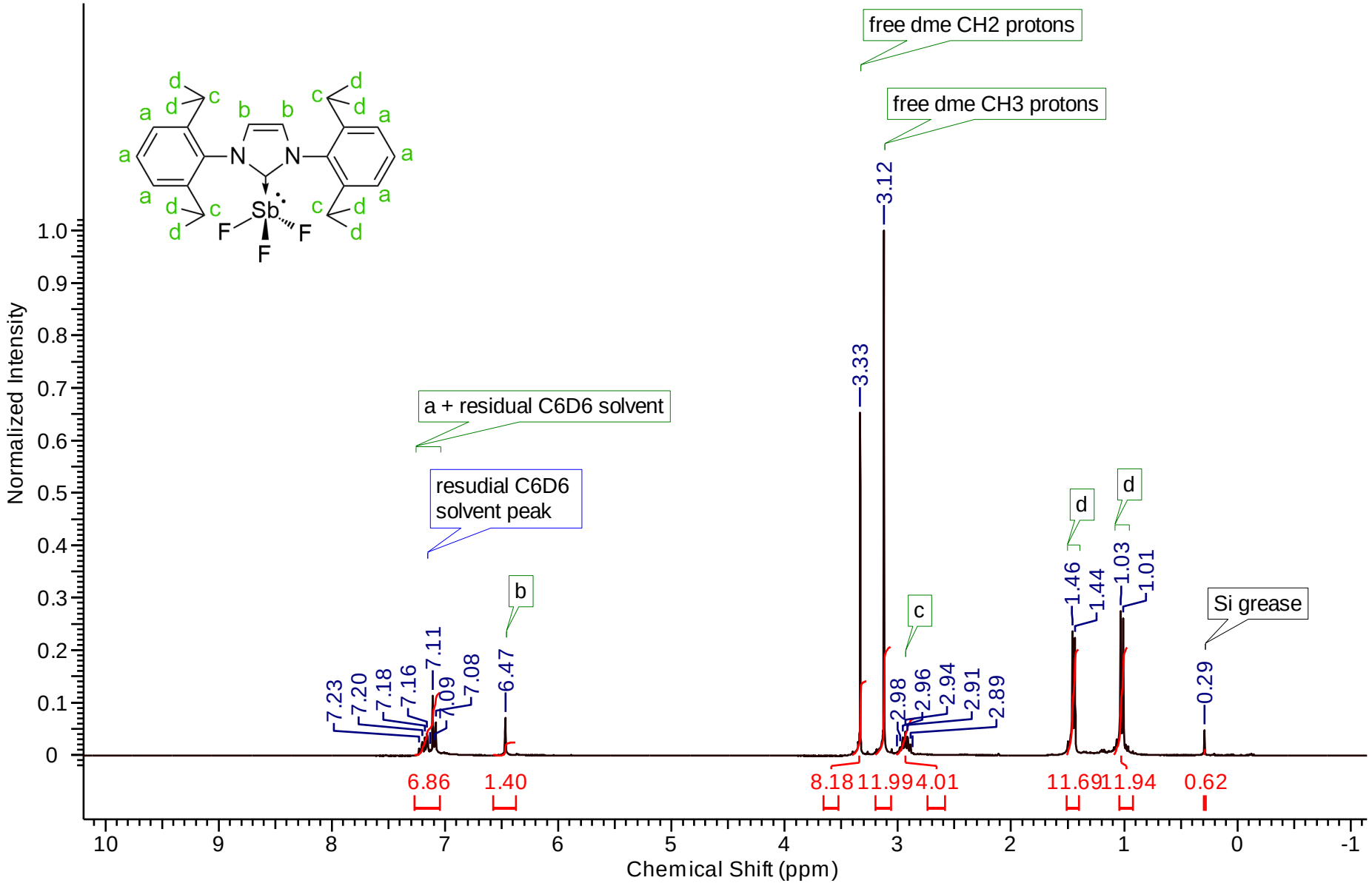
^{1}H NMR spectrum for reaction "[SbF_3(tmen)] + (L^{Dipp}) + 2tmen –> [(L^{Dipp})SbF_3]" in C_6D_6, Frequency (MHz) 302.97:



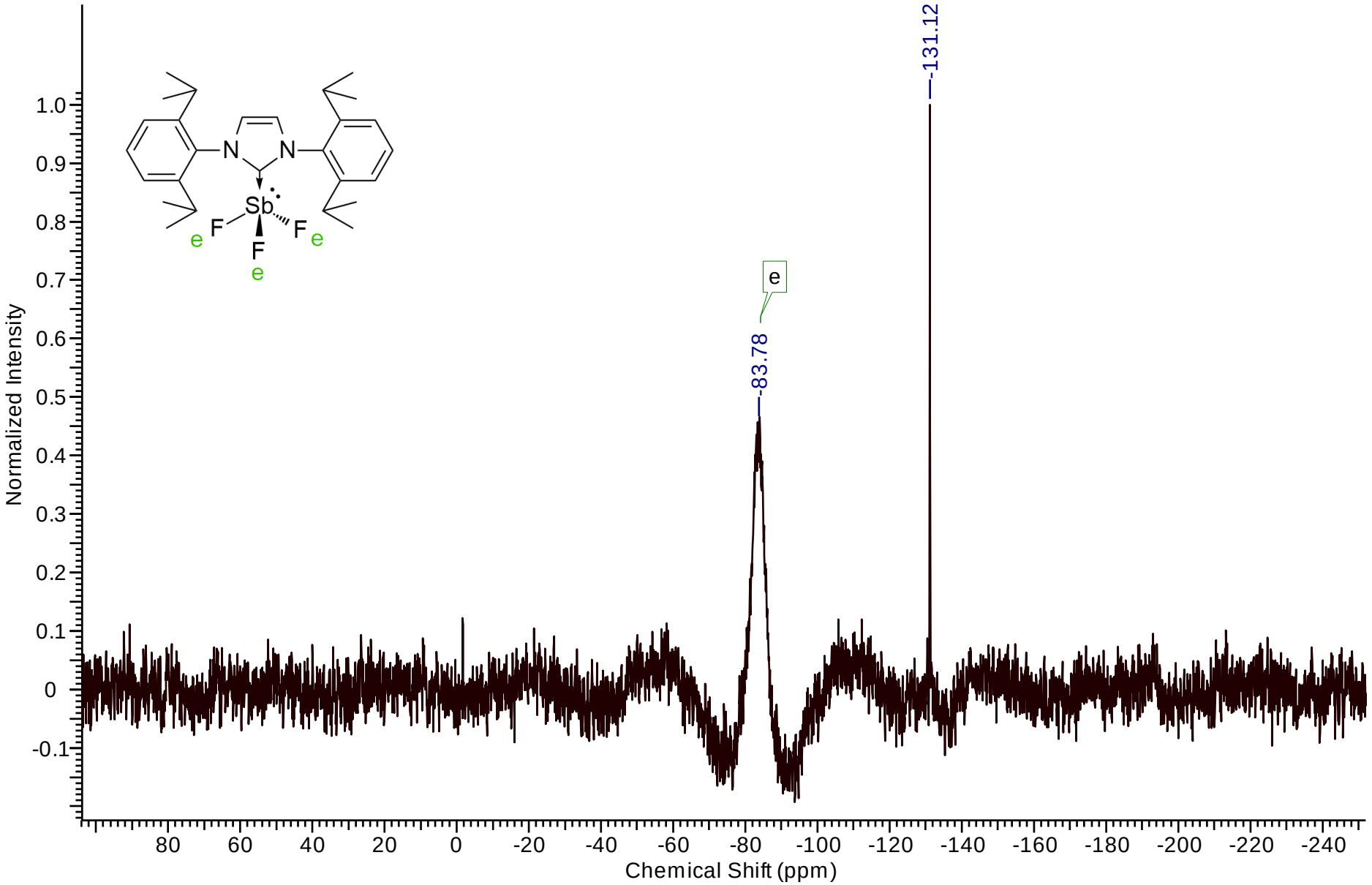
^{19}F NMR spectrum for reaction "$[SbF_3(tmen)]$ + (L^{Dipp}) + 2tmen –> $[(L^{Dipp})SbF_3]$" in C_6D_6, Frequency (MHz) 285.05:



^{1}H NMR spectrum for reaction "SbF_3 + (L^{Dipp}) + 2dme –> [(L^{Dipp})SbF_3]" in C_6D_6, Frequency (MHz) 302.97:



^{19}F NMR spectrum for reaction "SbF_3 + (L^{Dipp}) + 2dme –> [(L^{Dipp})SbF_3]" in C_6D_6, Frequency (MHz) 285.05:



$[(L^{Dipp})_2SbF_2]^+[SbF_4]^-$ (4)

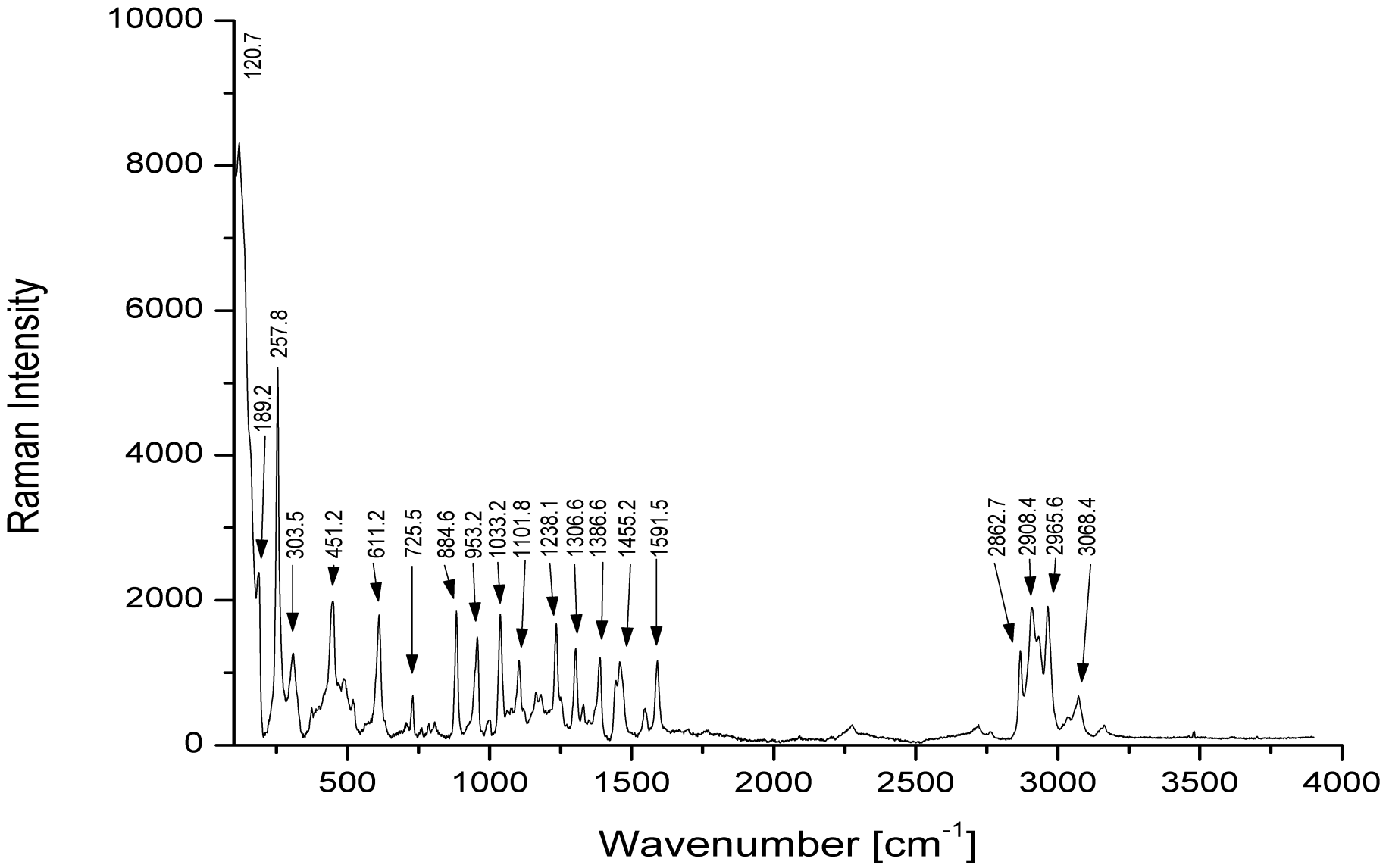
Reaction: "$[SbF_3(tmen)]$ + (L^{Dipp}) –> $[(L^{Dipp})_2SbF_2]^+[SbF_4]^-$"

or

"SbF_3 + 2dme + (L^{Dipp}) –> $[(L^{Dipp})_2SbF_2]^+[SbF_4]^-$"

Raman spectrum

Raman spectra of $[(L^{Dipp})_2SbF_2]^+[SbF_4]^-$ (4)



$[(Cl_2L^{Dipp})H]^+[SbF_4]^-$ (5)

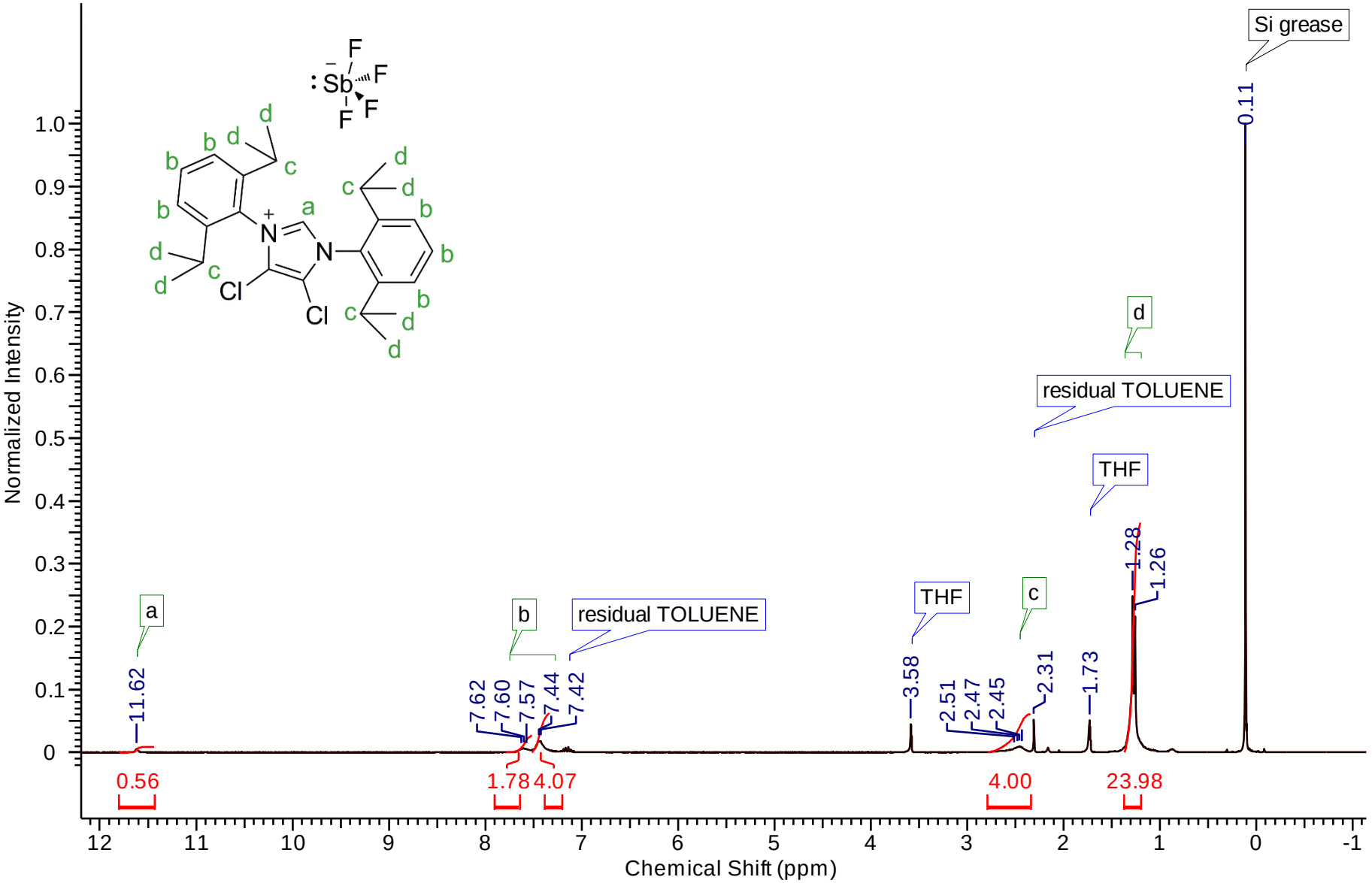
^{1}H NMR spectrum in THF-d^8

^{19}F NMR spectrum in THF-d^8

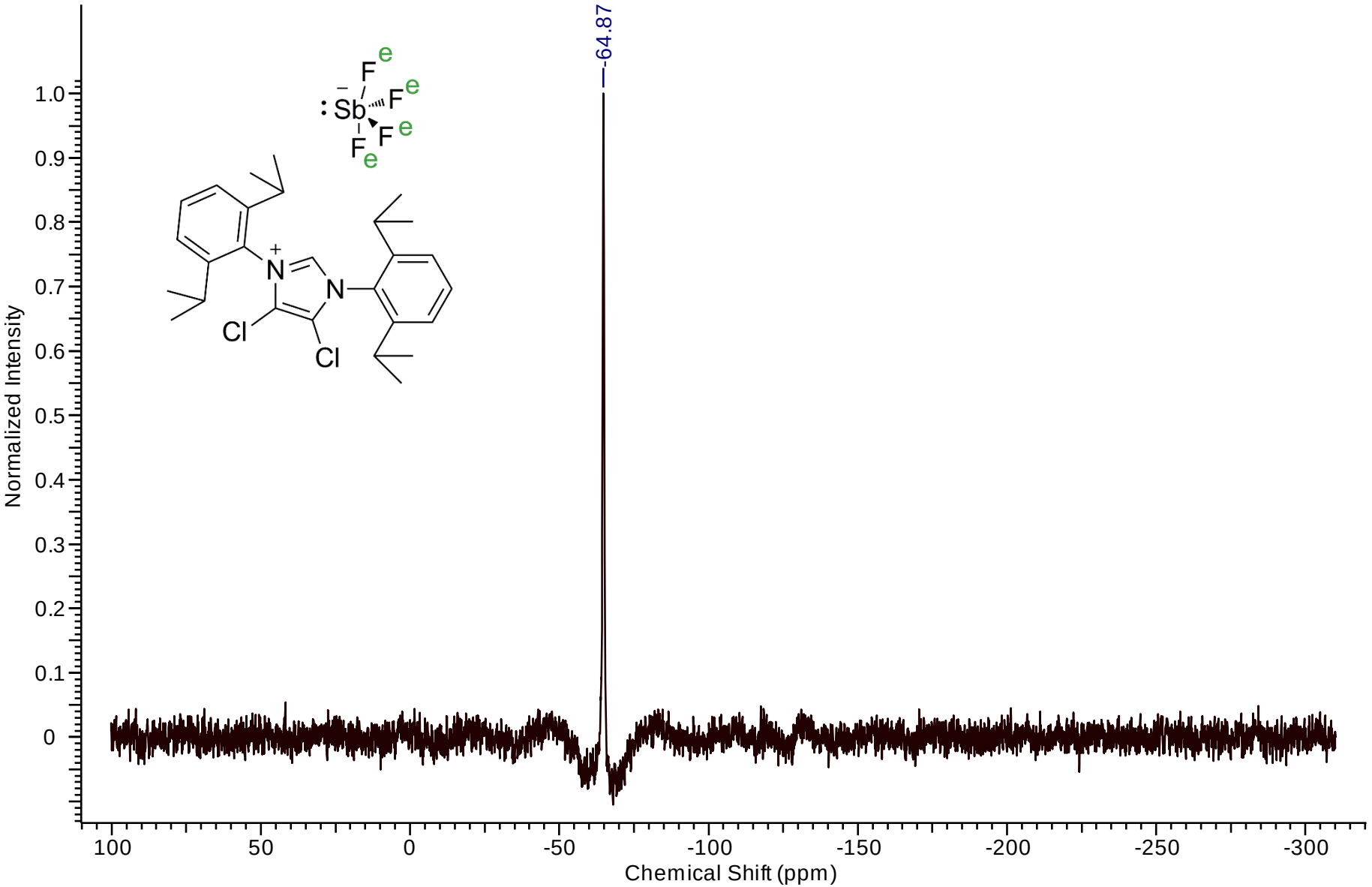
^{1}H NMR spectrum in C_6D_6 – empty, no other product could be obtained.

Raman spectra

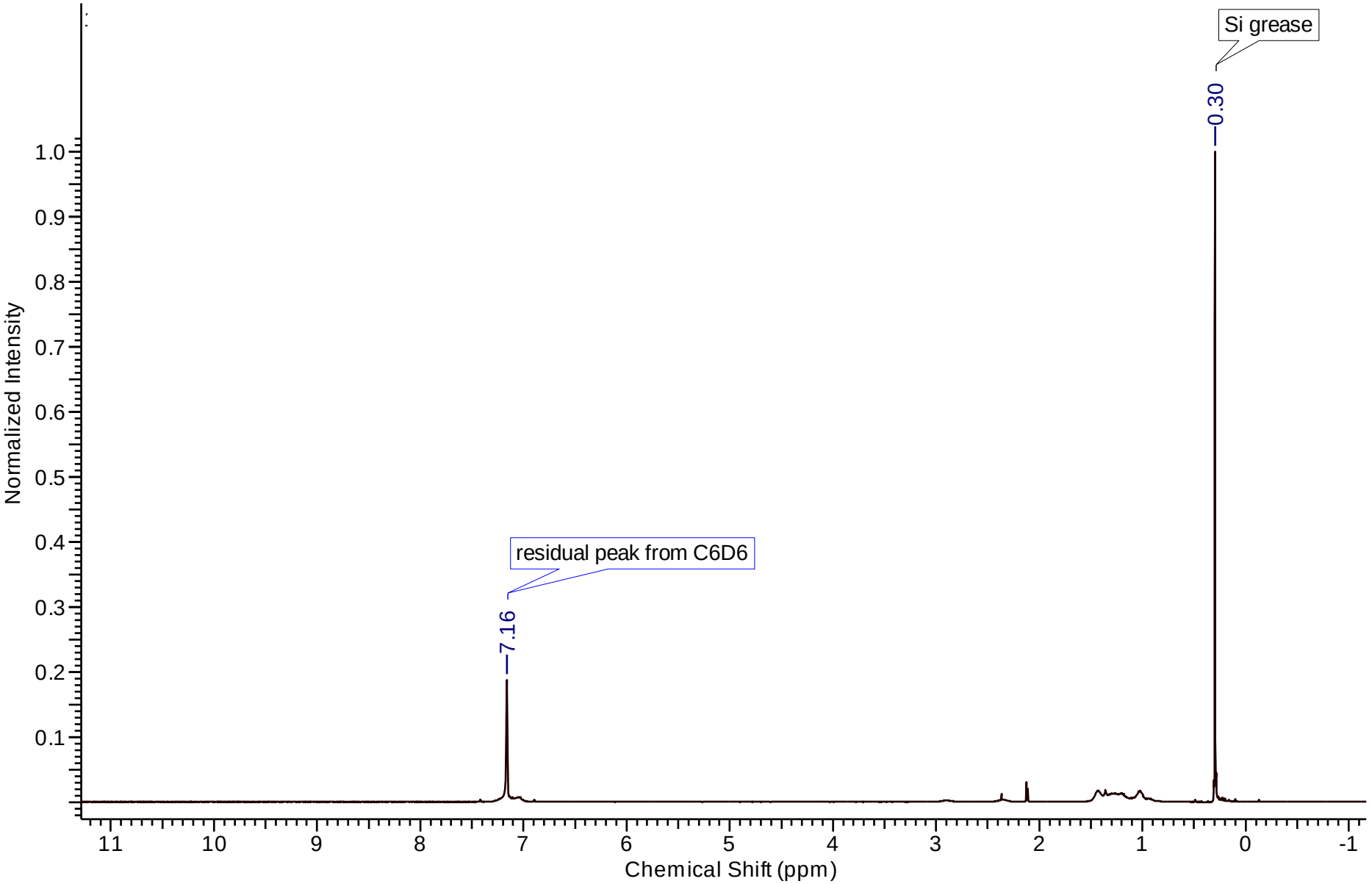
^{1}H NMR spectrum of $[(Cl_2L^{Dipp})H]^{+}[SbF_4]^{-}$ in THF-d^8, Frequency (MHz) 302.97:



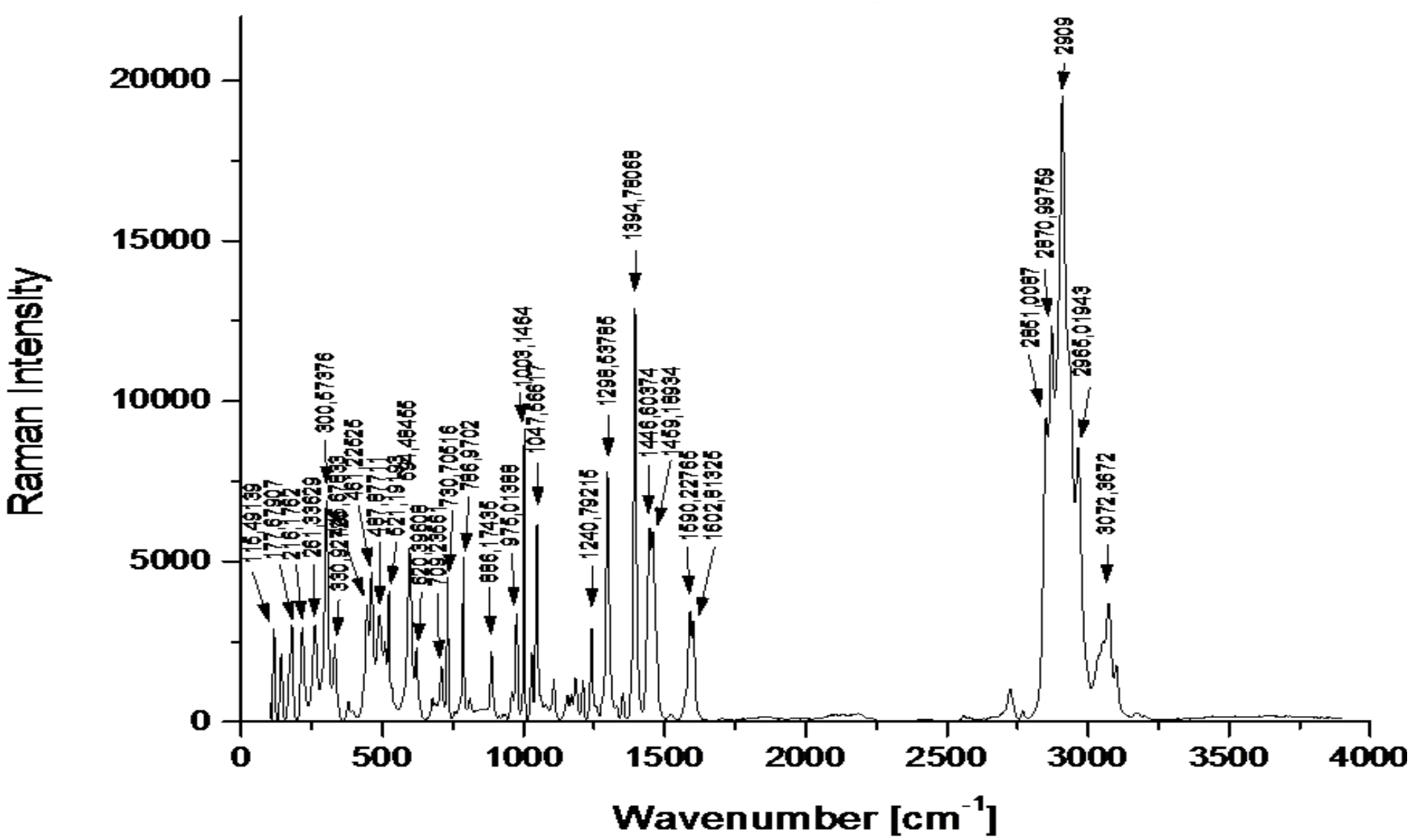
^{19}F NMR spectrum of $[(Cl_2L^{Dipp})H]^+[SbF_4]^-$ in THF-d^8, Frequency (MHz) 285.05:



^{1}H NMR spectrum of $[(Cl_2L^{Dipp})H]^{+}[SbF_4]^{-}$ in C_6D_6, Frequency (MHz) 302.97:

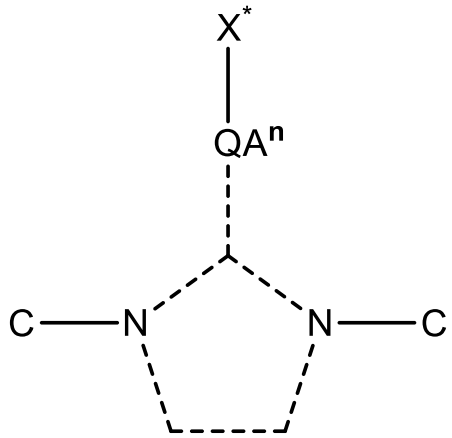


Raman spectra of $[(Cl_2L^{Dipp})H]^+[SbF_4]^-$ (5)



CSD search details

Cambridge Structural Database[1] was used for search of existing structures. Search was performed in the following way using CCDC ConQuest Version 1.18 (Built RC1).[2]



------ any bond

——— single bond

QA all elements of periodic table except: C, N, O, S

n number of bonded atoms

X any element of periodic table

∗ for MF compounds X = F

Table 1: Number of structures with different number of bonded atoms (n) for MF compounds

n	*number of crystal structures found*
2	9
3	1
4	29
5	12
6	44
7	0
SUM	**95**

1. C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallog. Sec. B*, 2016, **72**, 171.
2. I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson and R. Taylor, *Acta Crystallogr. Sec. B*, 2002, **58**, 389.