Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Antimony Diiminopyridine Complexes

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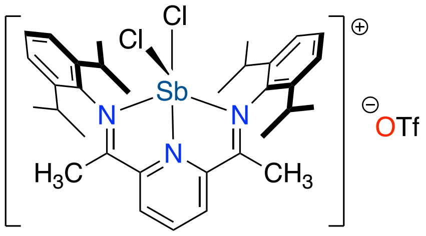
EXPERIMENTAL DETAILS

General Considerations: All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun Unilab glove box or using standard Schlenk techniques. CD_3CN for NMR spectroscopy was purchased from Cambridge Isotope Laboratories, Inc., dried by stirring for 5 days over CaH_2, distilled, and stored over 3 Å molecular sieves. *m*-Xylene for crystallizations was purchased from Alfa Aesar, dried by stirring for 5 days over CaH_2, distilled, and stored over 3 Å molecular sieves. All other solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 3 or 4 Å molecular sieves. Ligands **1H**, **1CH$_3$**, and **1Ph** were prepared by the literature procedures.[1] Antimony(III) trichloride was purchased from Alfa Aesar (>99%) and was ground into a fine powder with a mortar and pestle. Trimethylsilyl trifluoromethanesulfonate was purchased from Alfa Aesar (99%) and used as received. Multinuclear NMR spectra (^1H, $^{13}C\{^1H\}$, ^{19}F) were recorded on a Bruker Avance III HD 400 MHz or 600MHz instrument. ^{19}F NMR spectra were referenced to an internal standard, fluorobenzene, which was purchased from Aldrich Chemical (99%) and dried over 3 Å molecular sieves. High Resolution mass spectra (HRMS) were obtained in the Baylor University Mass Spectrometry Center on a Thermo Scientific LTQ Orbitrap Discovery spectrometer using +ESI. Melting points were measured with a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. Single crystal X-ray diffraction data were collected on a Bruker Apex III-CCD detector using Mo-Kα radiation ($\lambda = 0.71073$ Å). Crystals were selected under paratone oil, mounted on MiTeGen micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL and figures produced using OLEX2.[2]

General procedure for the synthesis of **2Ph**, **2H**, and **2CH$_3$** (quantities and characterization details follow): Antimony(III) trichloride was dissolved in acetonitrile (3 mL) and neat trimethylsilyl trifluoromethanesulfonate was added. The mixture was then added dropwise to an acetonitrile solution of ligand (1 mL) at room temperature and stirred. After 1 h, the volatiles were removed in vacuo giving a solid that was clean by NMR spectroscopy.



$2CH_3$: $SbCl_3$ (130.4 mg, 0.5716 mmol), TMSOTf (0.1030 mL, 0.5691 mmol), **$1CH_3$** (275.1 mg, 0.5711 mmol), yellow powder, Yield: quantitative (514.9 mg). Single crystals for X-ray diffraction studies were grown *via* vapor diffusion of a benzene solution of **$2CH_3$** into toluene.; d.p. 100-105 ˚C.

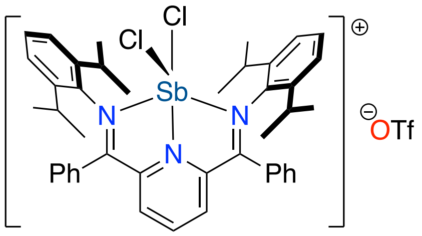
^{1}H NMR (600 MHz, CD_3CN): δ (ppm) 9.07 (t, *J* = 7.8 Hz, 1H), 8.97 (d, *J* = 7.8 Hz, 2H), 7.50-7.44 (m, 6H), 3.12 (br, 4H), 2.77 (s, 6H), 1.24 (d, *J* = 6.6 Hz, 12H), 1.16 (d, *J* = 6.6 Hz, 12H)

$^{13}C\{^1H\}$ NMR (151 MHz, CD_3CN): δ (ppm) 173.86, 148.40, 147.80, 142.90, 136.18, 134.54, 130.76, 126.58, 124.92, 122.80, 120.68, 29.43, 25.48, 24.85, 20.86

^{19}F NMR (565 MHz, CD_3CN): δ (ppm) -79.2

FT-IR [cm^{-1} (ranked intensity)]: 2962 (9), 1632 (13), 1589 (15), 1459 (10), 1366 (8), 1275 (2), 1222 (12), 1159 (7), 1030 (3), 803 (5), 770 (11), 688 (4), 636 (1), 573 (12), 517 (6), 434 (14)

High-resolution mass spectrometry electrospray ionization (HRMS-ESI) for $C_{33}H_{43}N_3SbCl_2^+$ $[M]^+$ calc. 672.1872 *m/z*; found: 672.1858 *m/z.*



2Ph: $SbCl_3$ (21.2 mg, 0.09293 mmol), TMSOTf (0.0160 mL, 0.08847 mmol), **1Ph** (53.6 mg, 0.08847 mmol), red powder, Yield: quantitative (83.8 mg). Single crystals for X-ray diffraction studies were grown *via* vapor diffusion of a dichloromethane solution of **2Ph** into toluene. d.p. 135-140 ˚C.

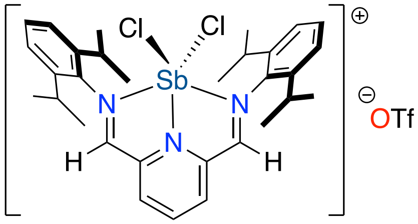
^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.81 (t, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 4H), 7.53 (d, *J* = 7.6 Hz, 4H), 7.40 (t, *J* = 7.6f Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 4H), 3.29 (sept, *J* = 6.6 Hz, 4H), 1.28 (d, *J* = 6.4 Hz, 12H), 0.82 (d, *J* = 6.8 Hz, 12H)

^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ (ppm) 170.05, 149.31, 148.39, 142.94, 137.32, 136.52, 134.60, 131.81, 130.88, 130.44, 129.53, 126.64, 123.20, 120.01, 29.56, 27.08, 24.09

^{19}F NMR (376 MHz, CD_3CN): δ (ppm) -79.1

FT-IR [cm^{-1} (ranked intensity)]: 2966 (9), 1572 (5), 1464 (15), 1445 (8), 1274 (11), 1204 (3), 1056 (14), 1017 (2), 805 (10), 783 (6), 769 (13), 696 (4), 633 (1), 575 (12), 514 (7)

High-resolution mass spectrometry electrospray ionization (HRMS-ESI) for $C_{43}H_{47}N_3SbCl_2^+$ $[M]^+$ calc. 796.2185 *m/z*; found: 796.2205 *m/z.*



2H: $SbCl_3$ (61.8 mg, 0.2709 mmol), TMSOTf (0.0470 mL, 0.2599 mmol), **1H** (117.9 mg, 0.2599 mmol), orange powder, Yield: quantitative (206.7 mg). Single crystals for X-ray diffraction studies were grown *via* vapor diffusion of a benzene solution of **2H** into meta-xylene. d.p. 88-90 ˚C.

^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.22 (s, 2H), 8.87 (t, J = 7.6 Hz, 1H), 8.72 (d, J = 7.6 Hz, 2H), 7.40 (s, 6H), 3.18 (sept, J = 6.6 Hz, 4H), 1.23 (d, J = 6.8 Hz, 24H)

^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ (ppm) 164.86, 148.23, 146.77, 142.37, 135.64, 129.92, 126.62, 125.52, 123.43, 120.24, 117.06, 29.66, 24.86

^{19}F NMR (376 MHz, CD_3CN): δ (ppm) -79.2

FT-IR [cm^{-1} (ranked intensity)]: 2963 (7), 1588 (12), 1463 (8), 1364 (15), 1282 (9), 1222 (2), 1162 (6), 1099 (14), 1055 (10), 1017 (3), 802 (4), 759 (11), 635 (1), 573 (13), 518 (5)

High-resolution mass spectrometry electrospray ionization (HRMS-ESI) for $C_{31}H_{39}N_3SbCl_2^+$ $[M]^+$ calc. 644.1559 *m/z*; found: 644.1556 *m/z.*

Figure S-1: ^{1}H NMR spectrum of **2CH$_3$** in CD$_3$CN.

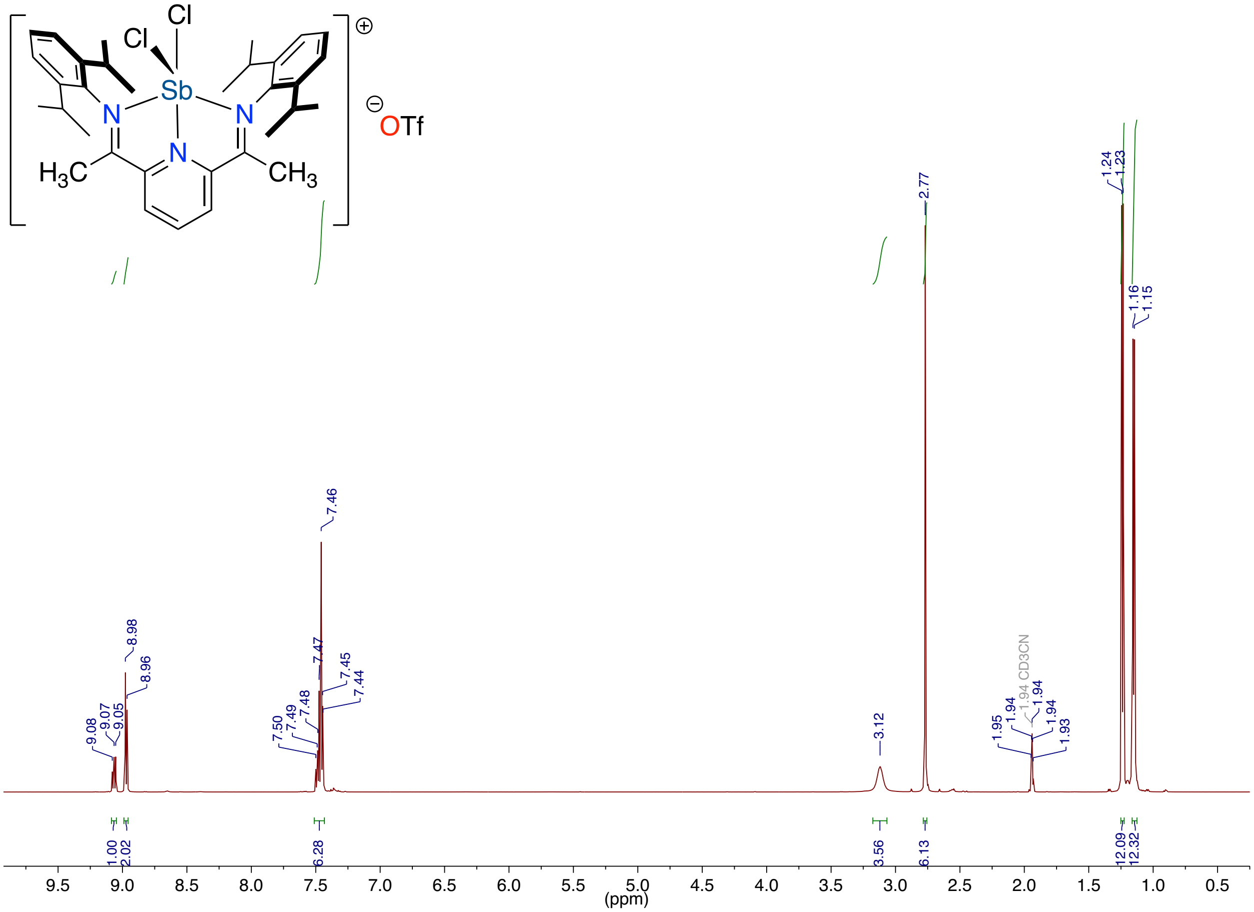


Figure S-2: Expansion of ^{1}H NMR spectrum of **$2CH_3$** in CD_3CN (aryl region).

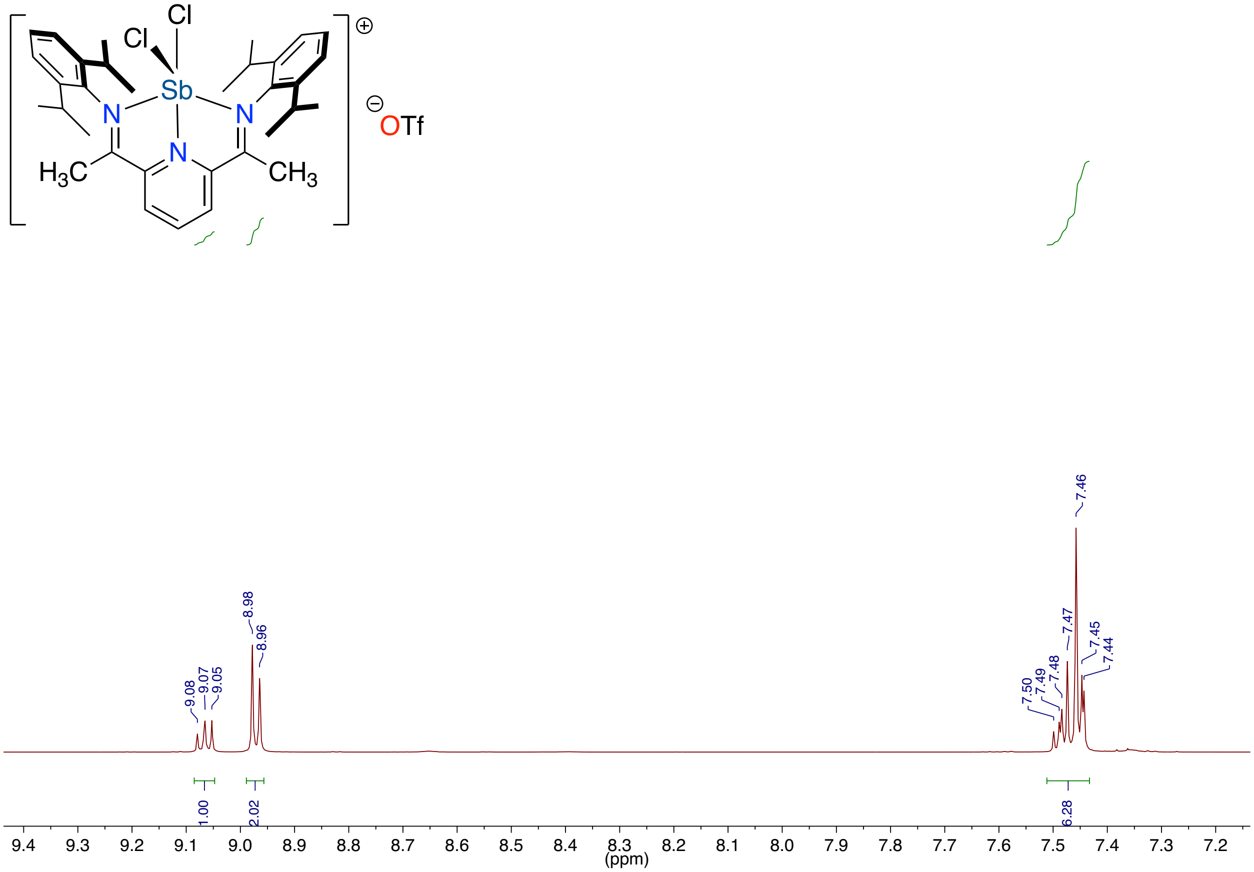


Figure S-3: Expansion of ^{1}H NMR spectrum of **$2CH_3$** in CD_3CN (aliphatic region).

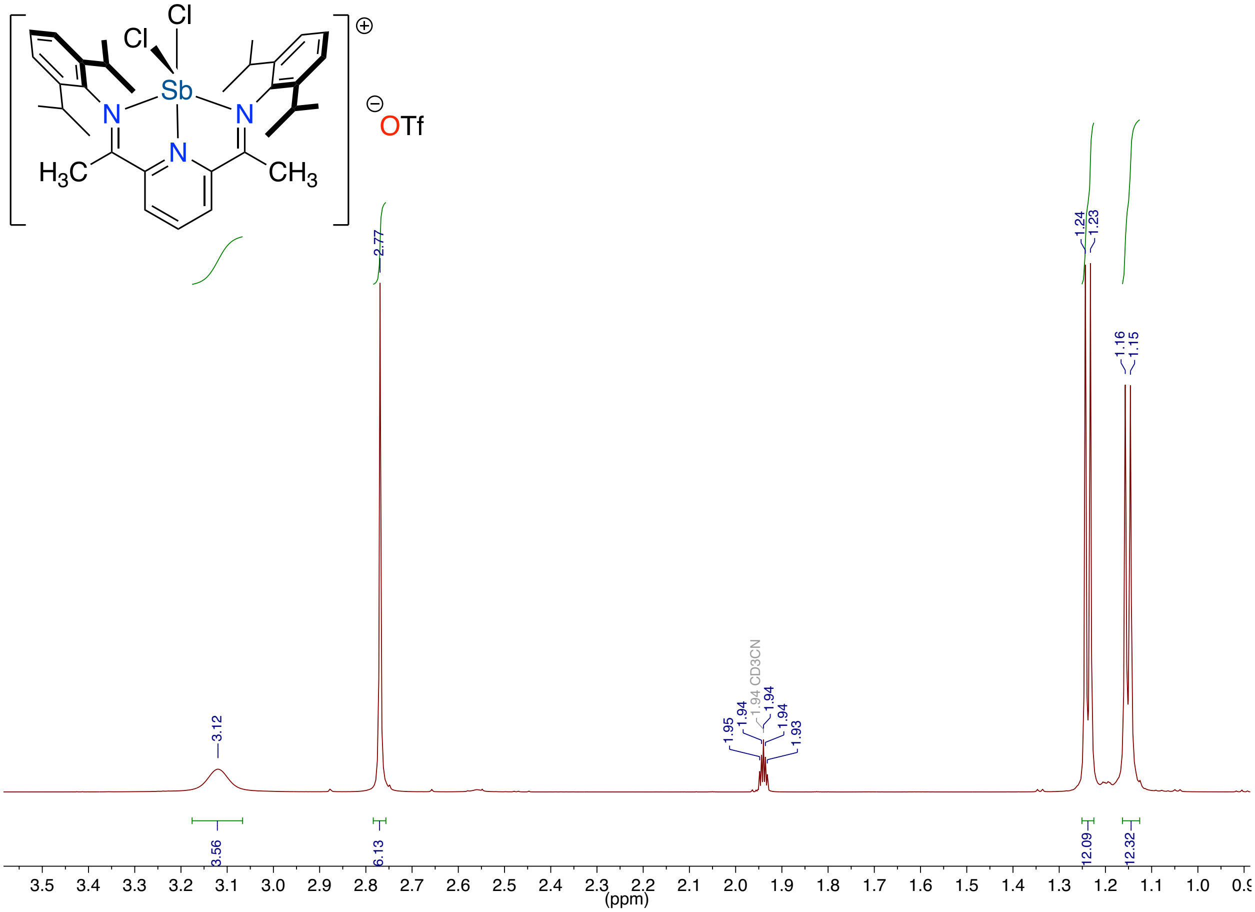


Figure S-4: $^{13}C\{^{1}H\}$ NMR spectrum of **$2CH_3$** in CD_3CN.

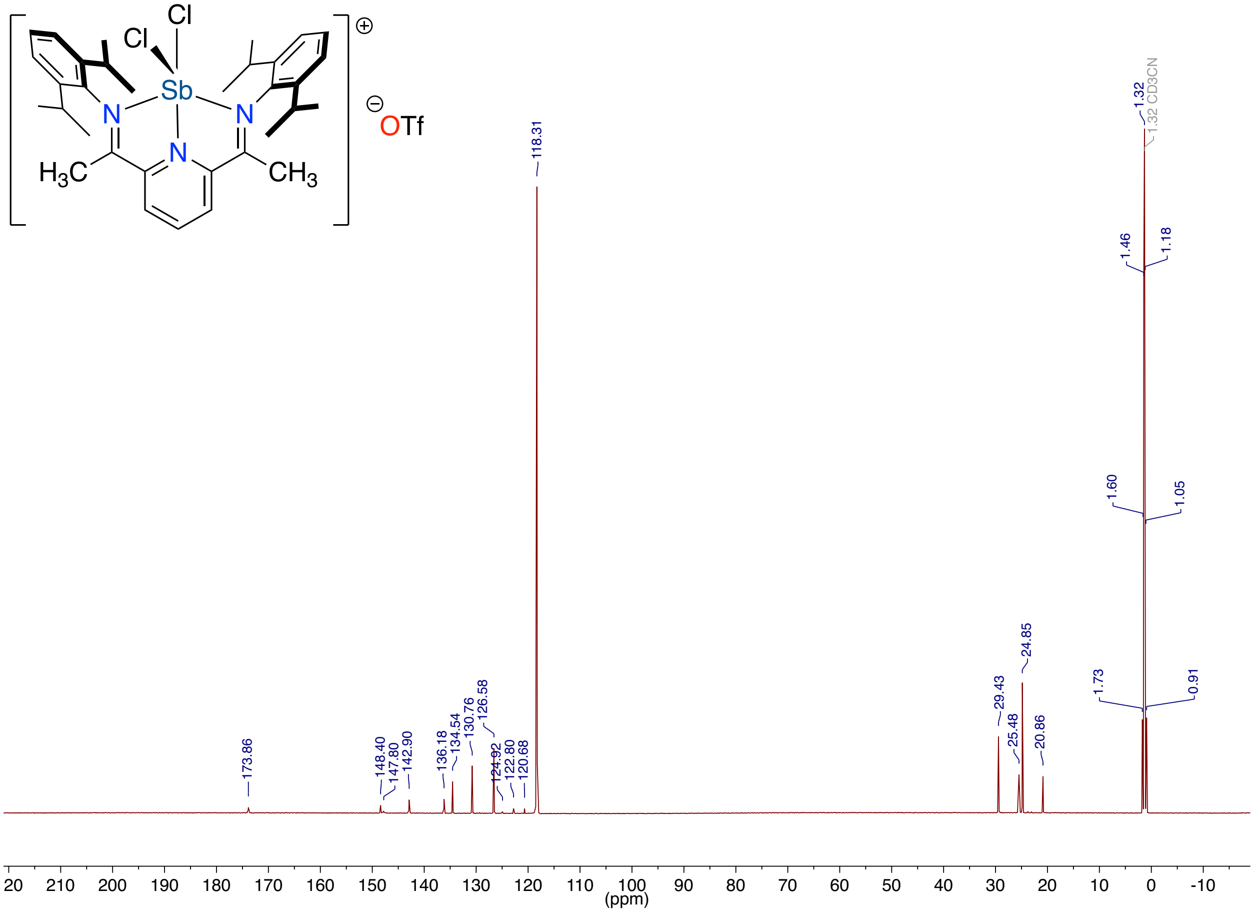


Figure S-5: Expansion of ^{13}C{^{1}H} NMR spectrum of **2CH$_3$** in CD$_3$CN (aryl region).

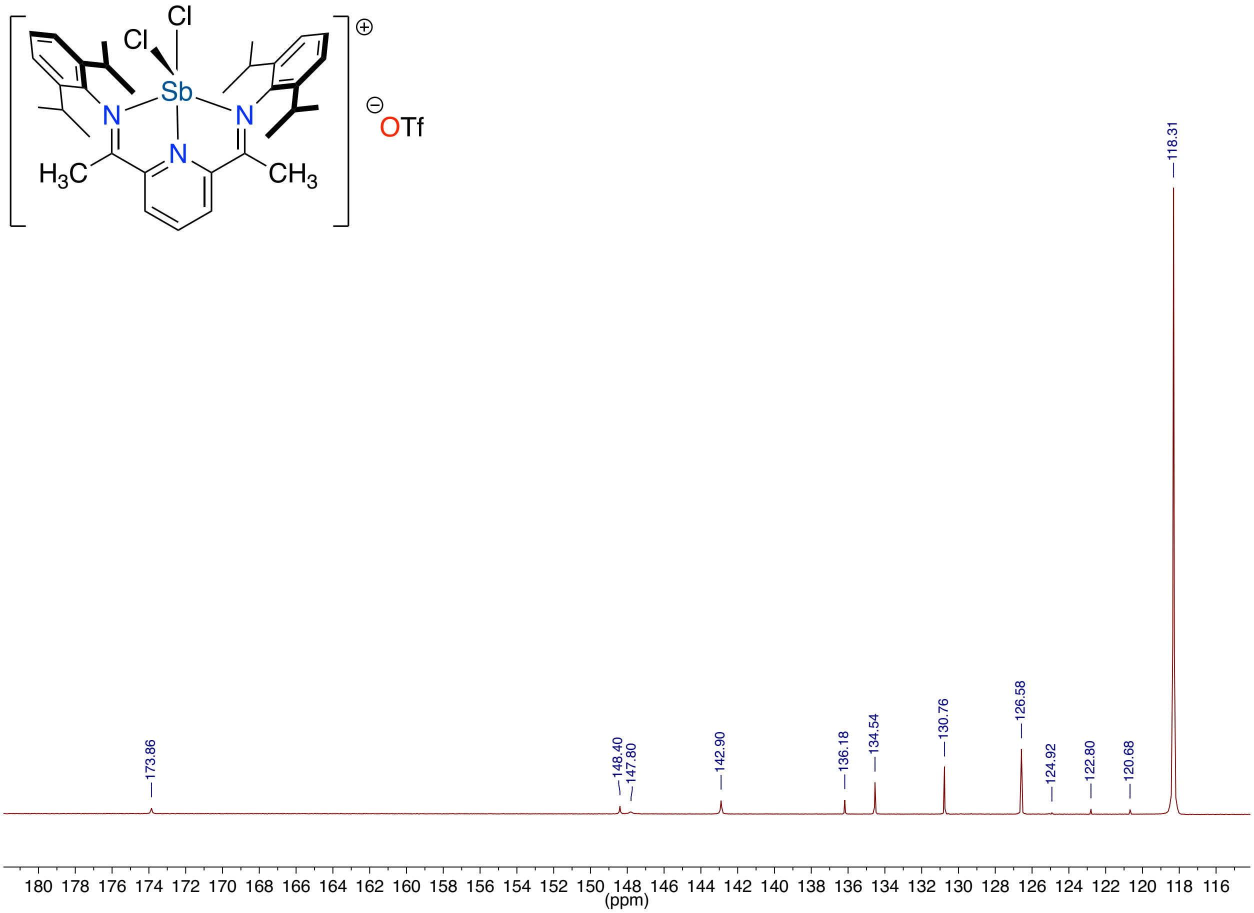


Figure S-6: ^{19}F NMR spectrum of **2CH$_3$** in CD$_3$CN with internal standard C$_6$H$_5$F.

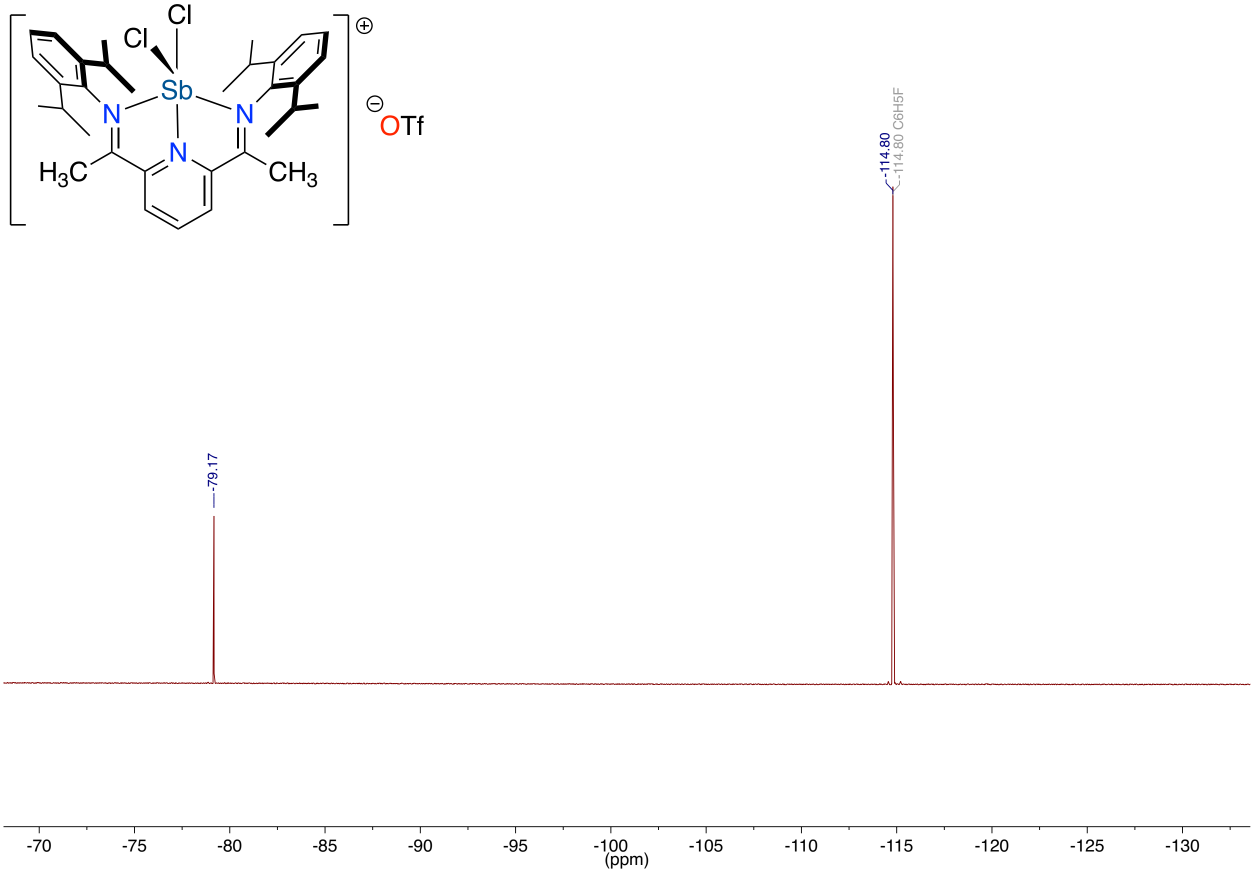


Figure S-7: ^{19}F NMR spectrum of tristrimethylsilyl trifluoromethanesulfonate in CD_3CN with internal standard C_6H_5F.

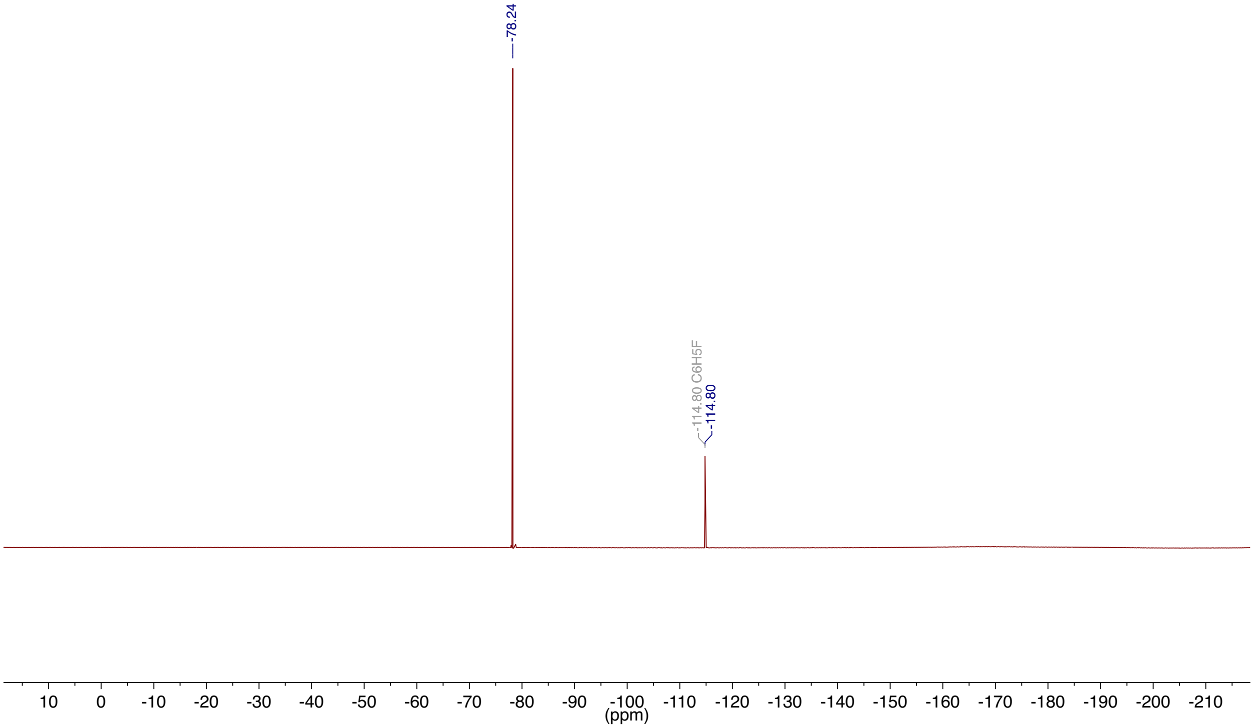


Figure S-8: FT-IR spectrum of **2CH$_3$**.

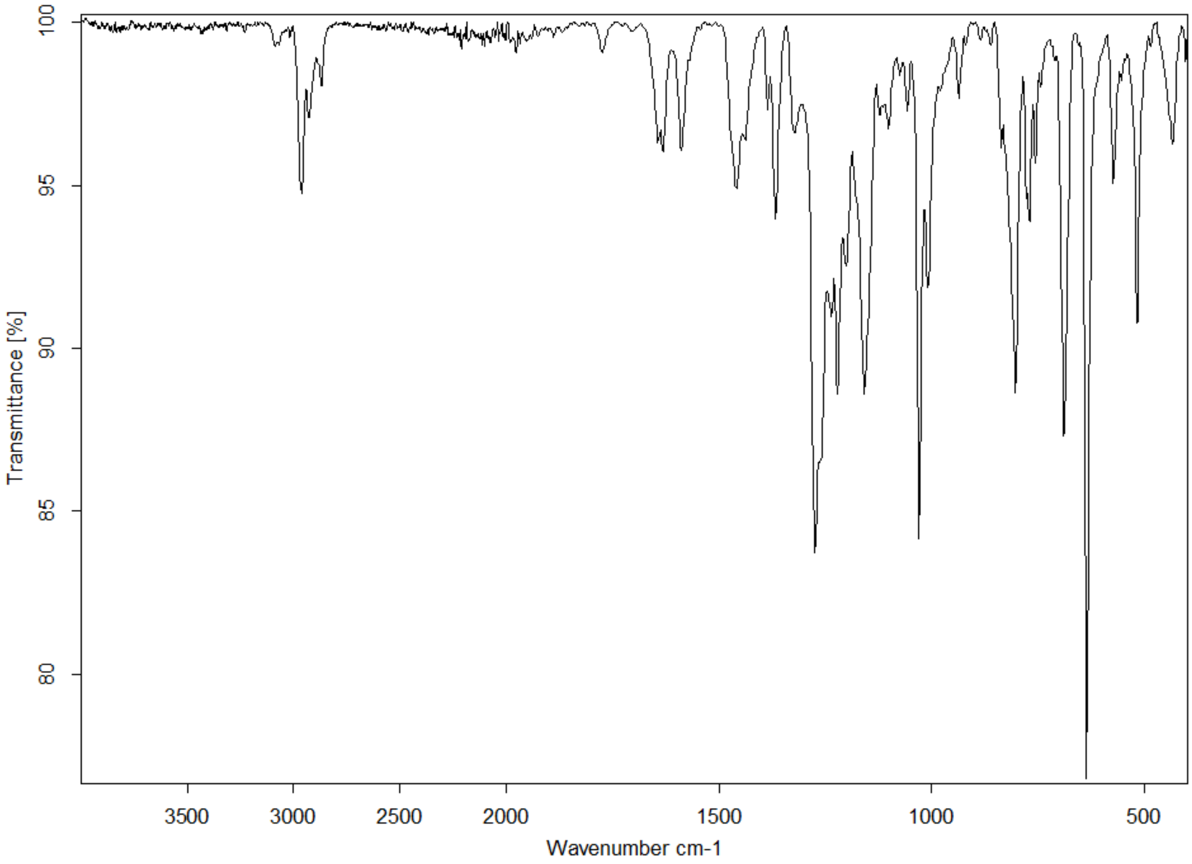


Figure S-9: ^{1}H NMR spectrum of **2Ph** in CD_3CN.

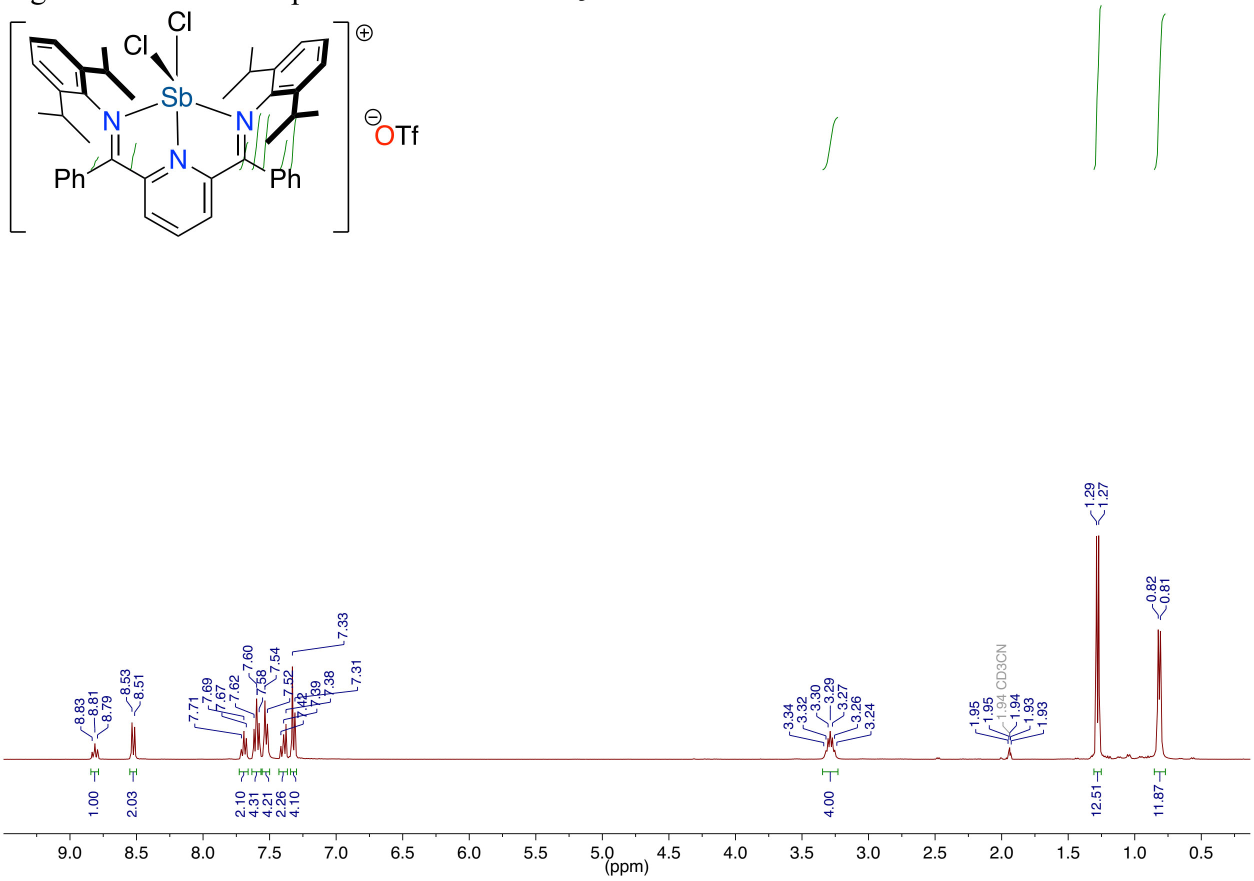


Figure S-10: Expansion of ^{1}H NMR spectrum of **2Ph** in CD_3CN (aryl region).

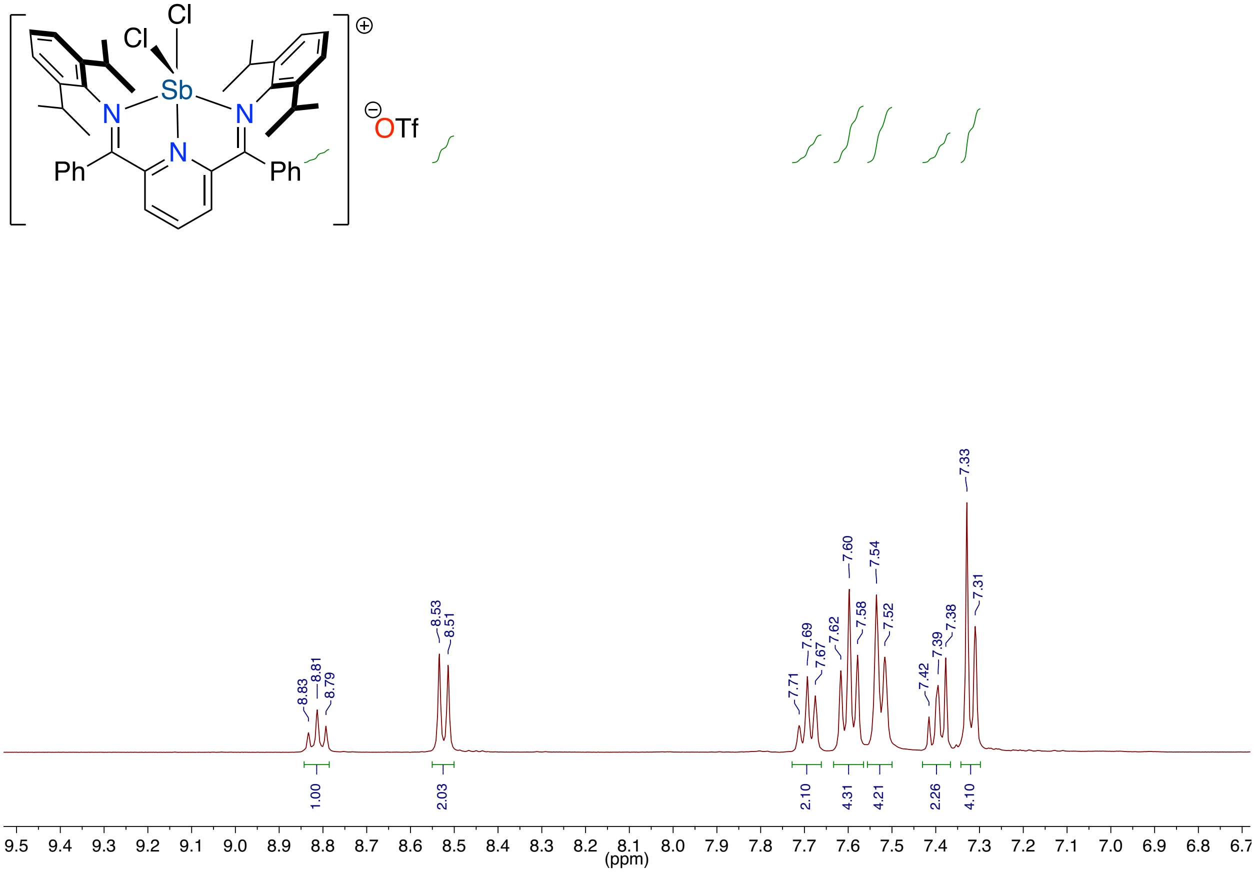


Figure S-11: Expansion of ^{1}H NMR spectrum of **2Ph** in CD_3CN (aliphatic region).

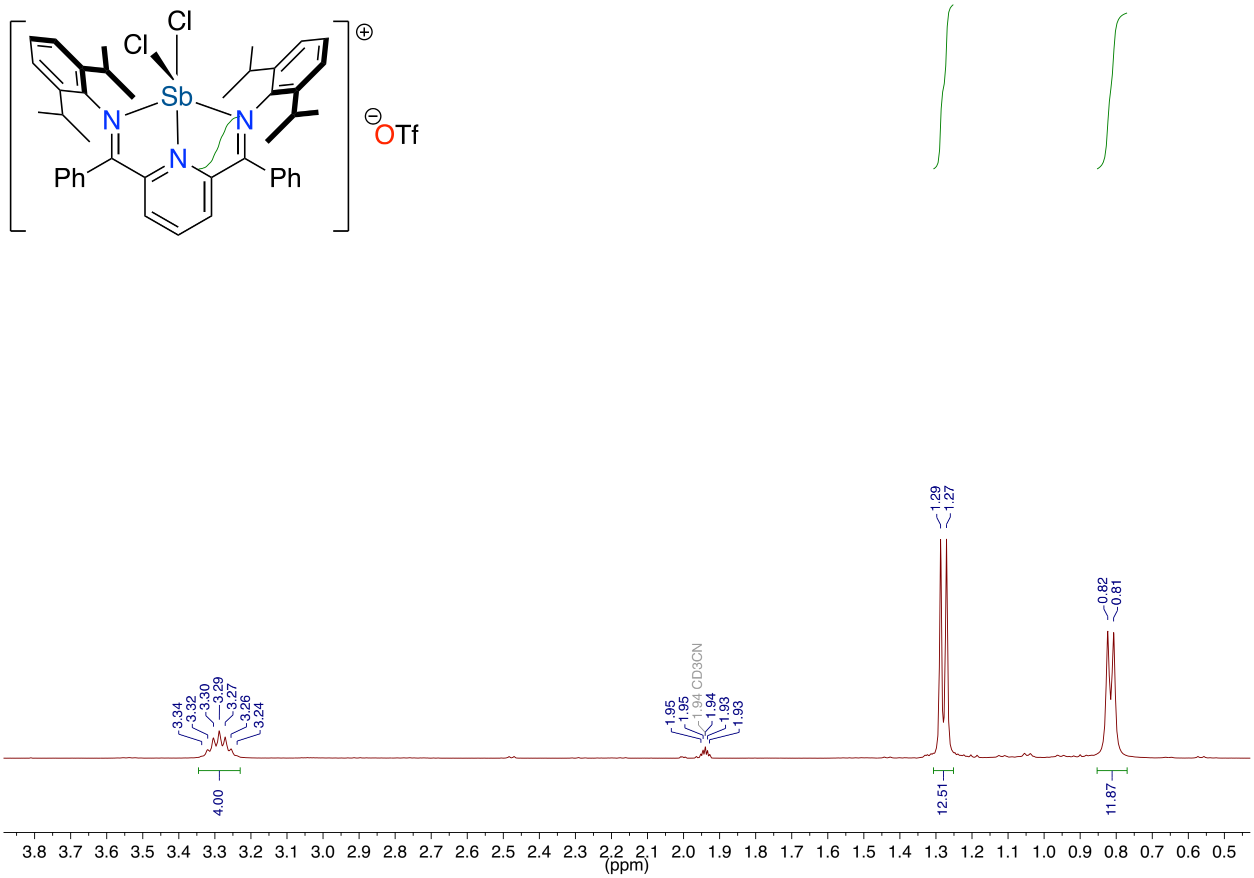


Figure S-12: $^{13}C\{^{1}H\}$ NMR spectrum of **2Ph** in CD_3CN.

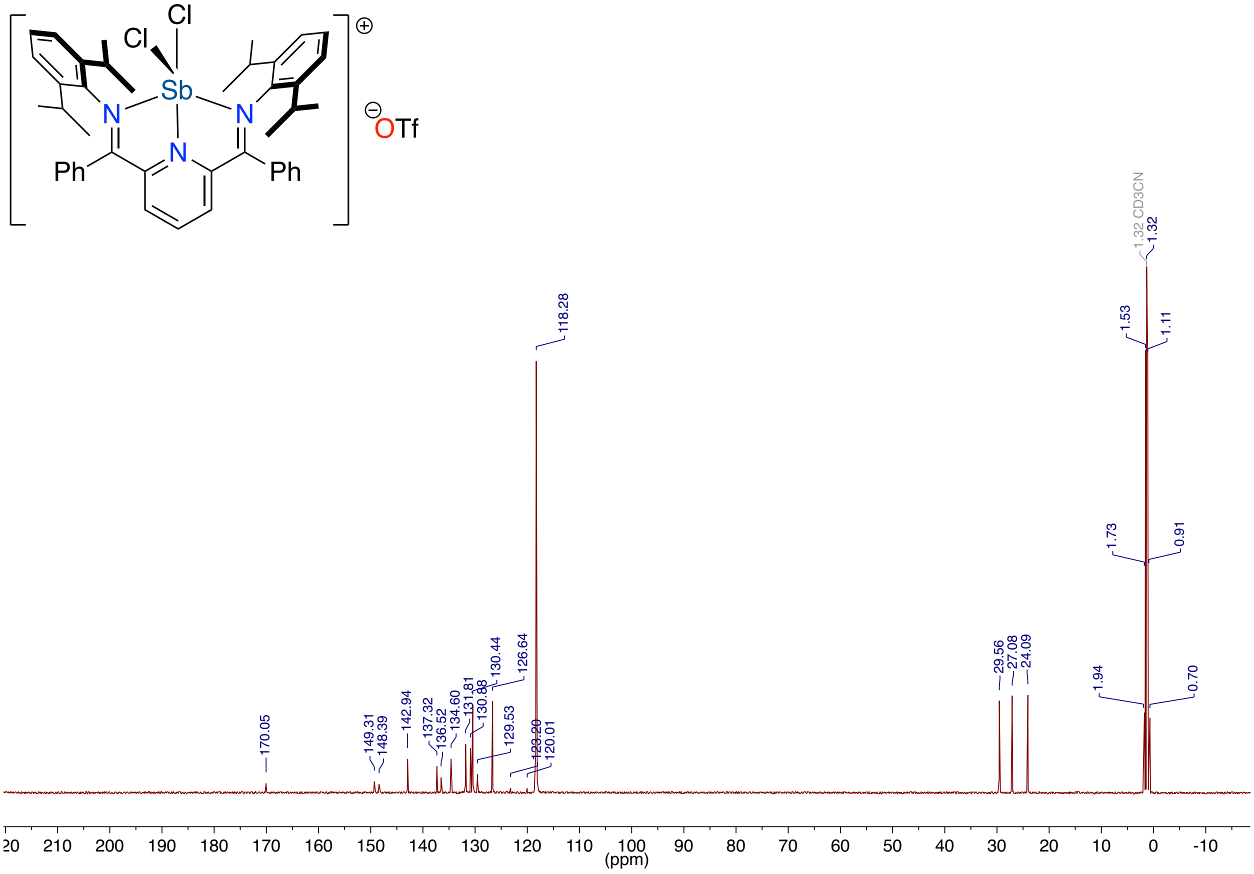


Figure S-13: Expansion of $^{13}C\{^1H\}$ NMR spectrum of **2Ph** in CD_3CN (aryl region).

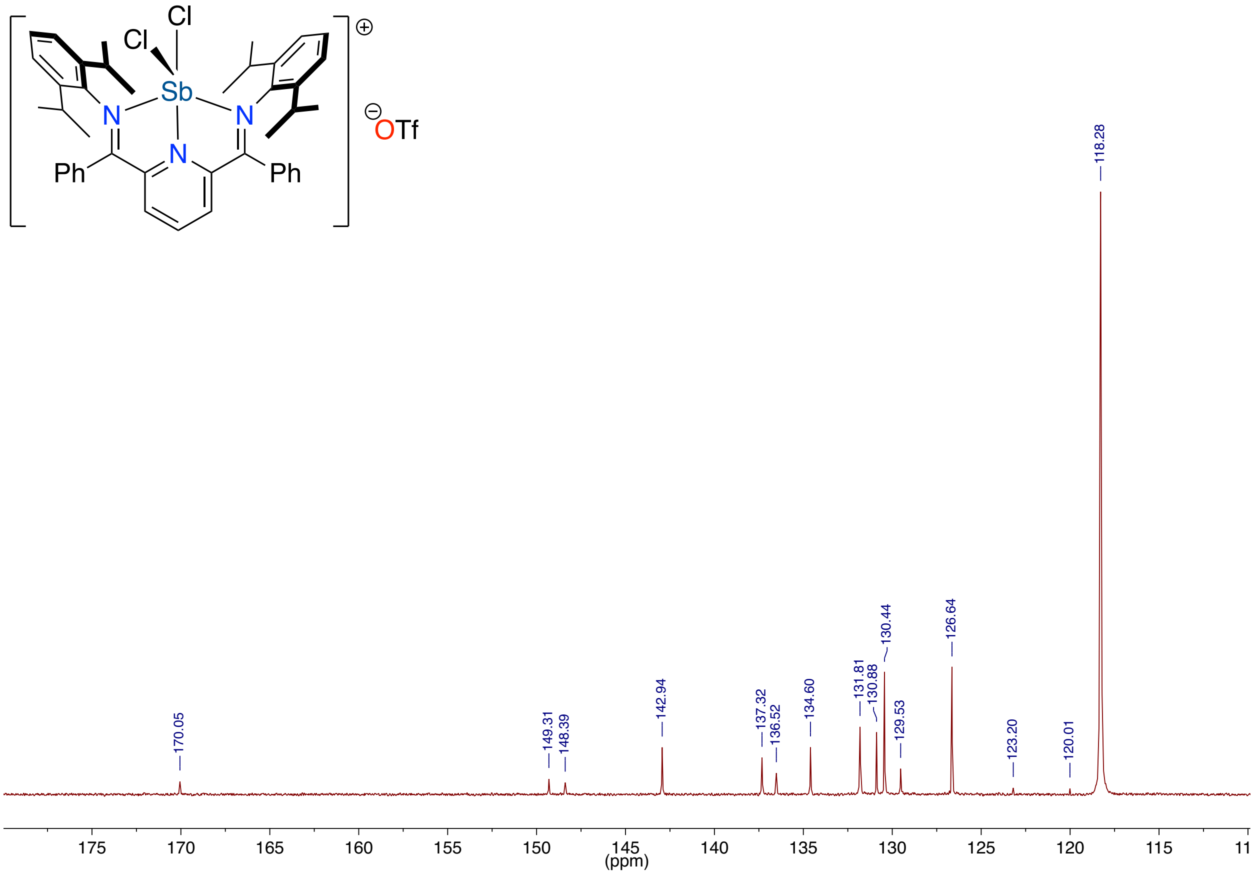


Figure S-14: ^{19}F NMR spectrum of **2Ph** in CD_3CN with internal standard C_6H_5F.

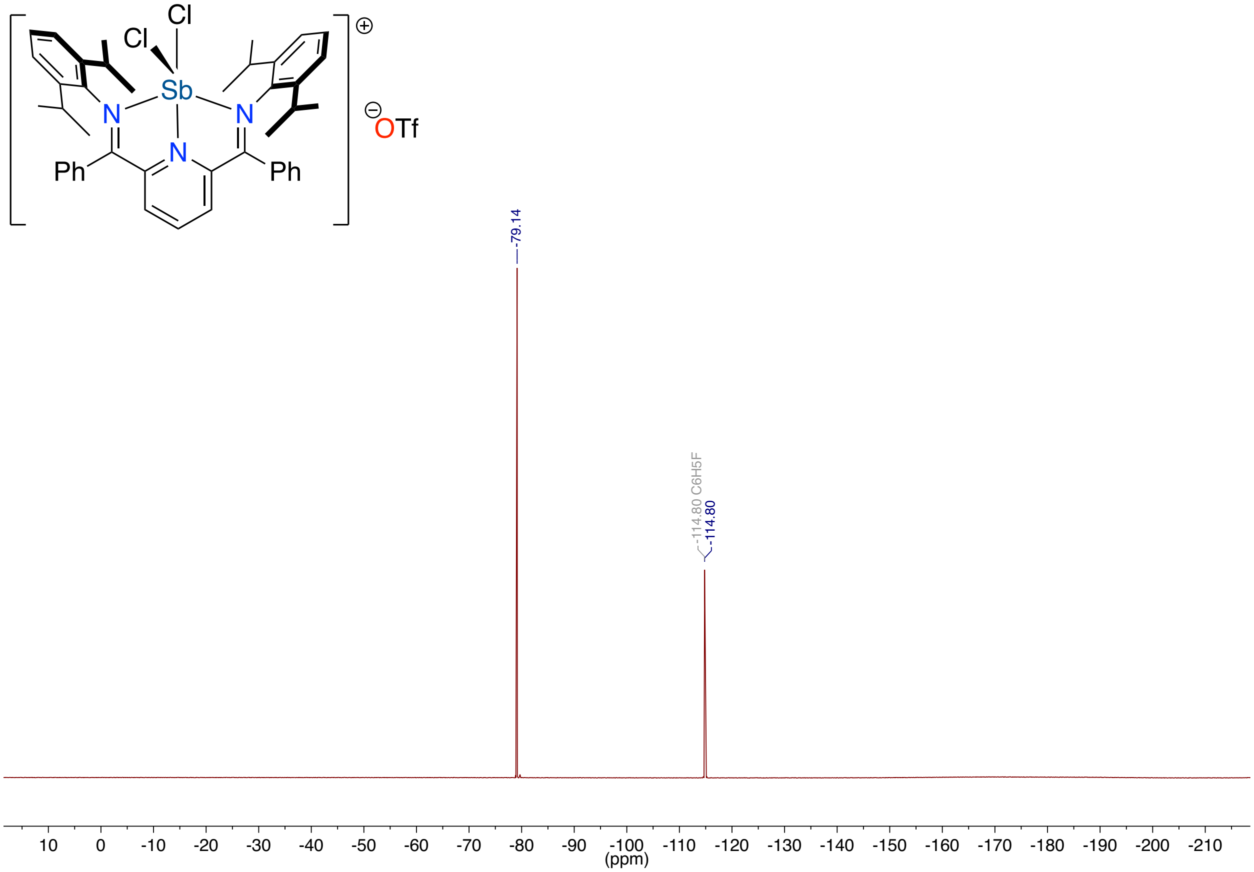


Figure S-15: FT-IR spectrum of **2Ph**.

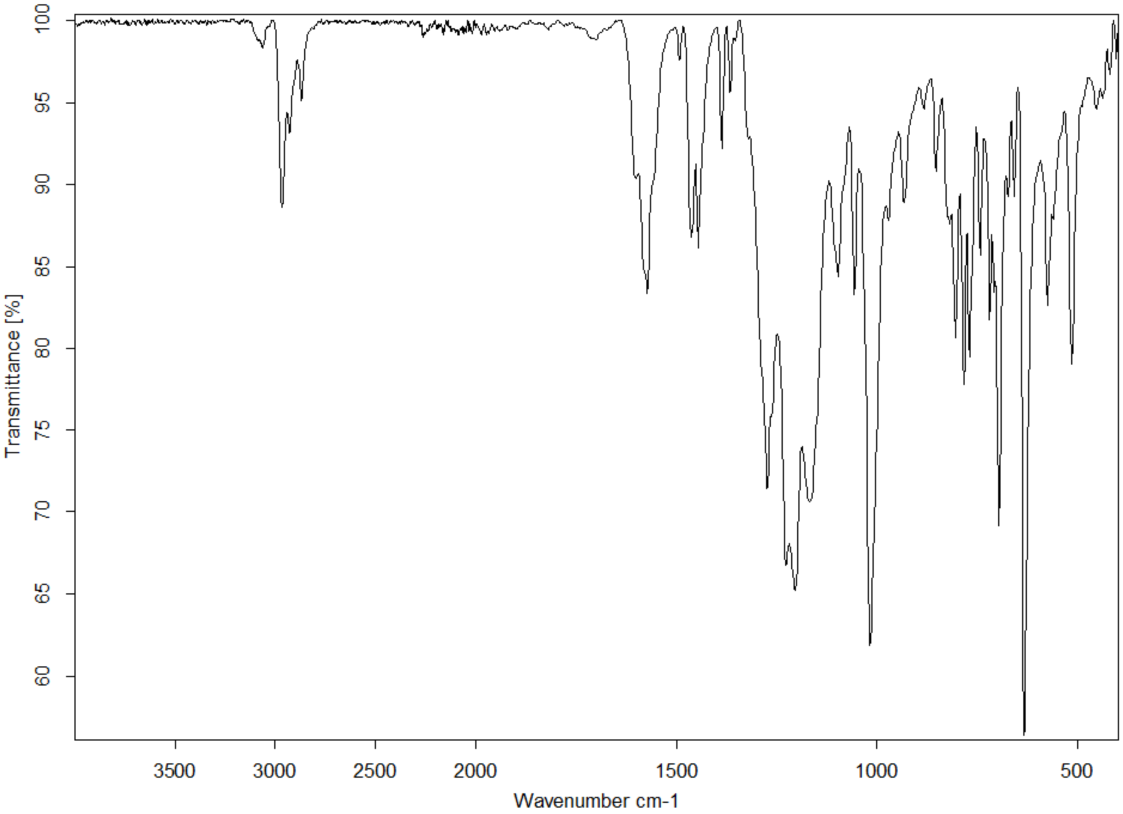


Figure S-16: ^{1}H NMR spectrum of **2H** in CD_3CN.

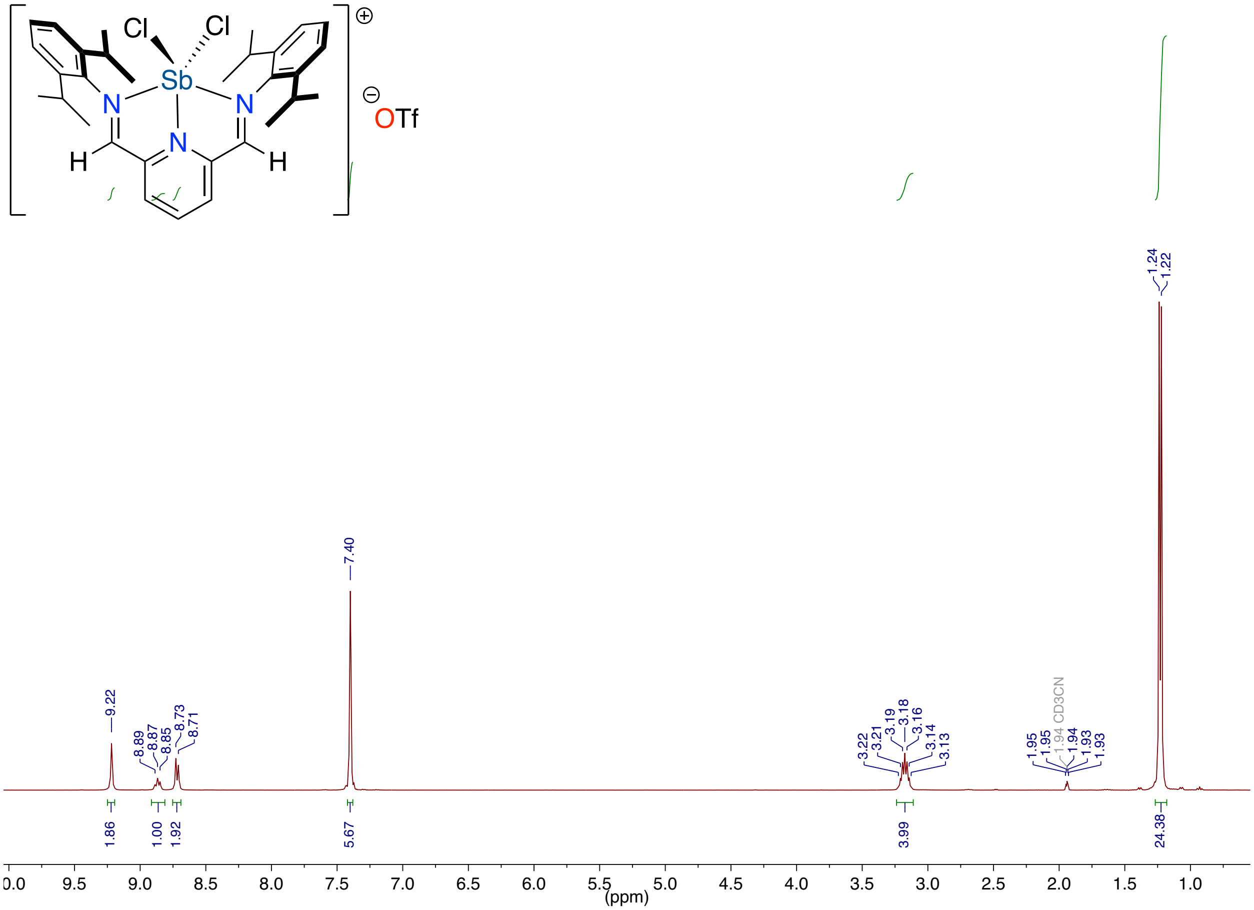


Figure S-17: Expansion of ^{1}H NMR spectrum of **2H** in CD_3CN (aryl region).

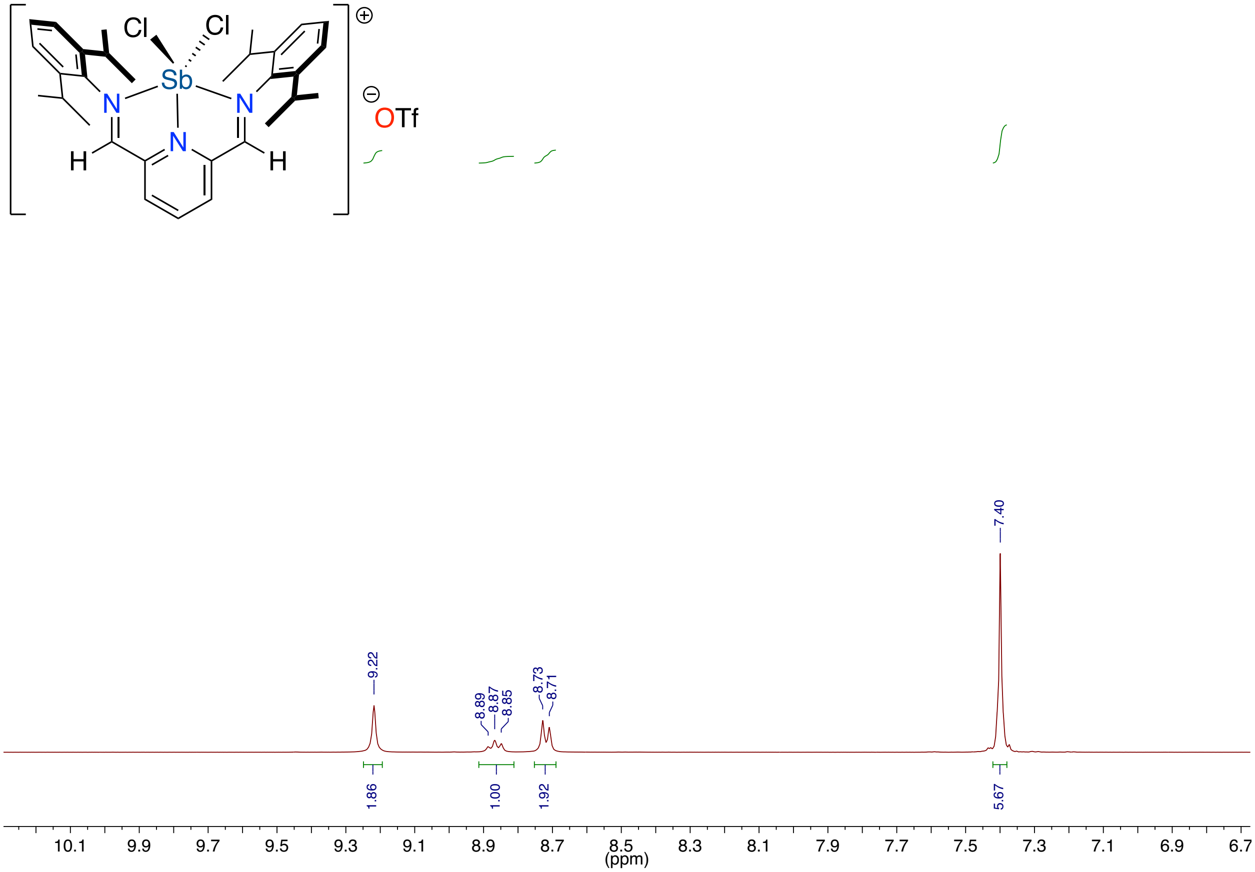


Figure S-18: Expansion of ^{1}H NMR spectrum of **2H** in CD$_3$CN (aliphatic region).

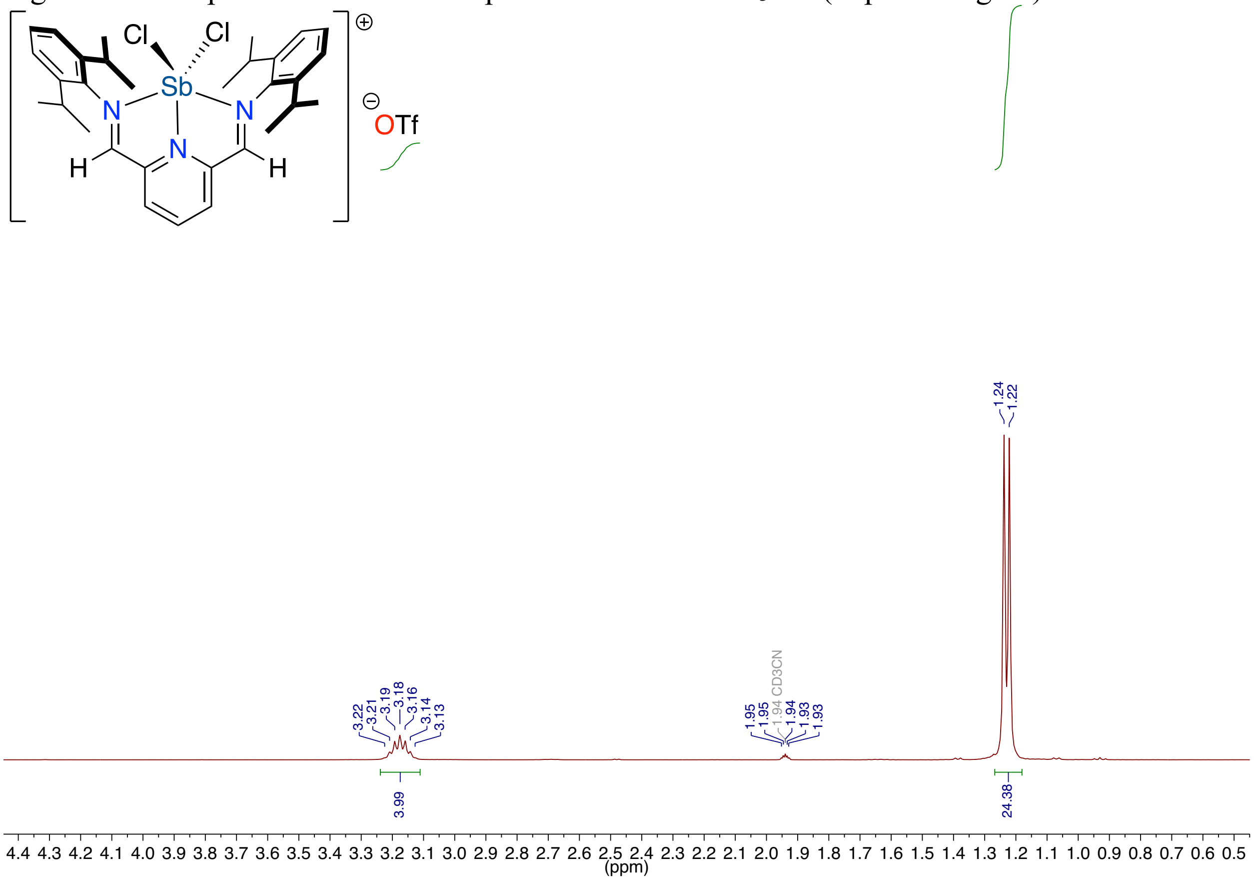


Figure S-19: $^{13}C\{^{1}H\}$ NMR spectrum of **2H** in CD_3CN.

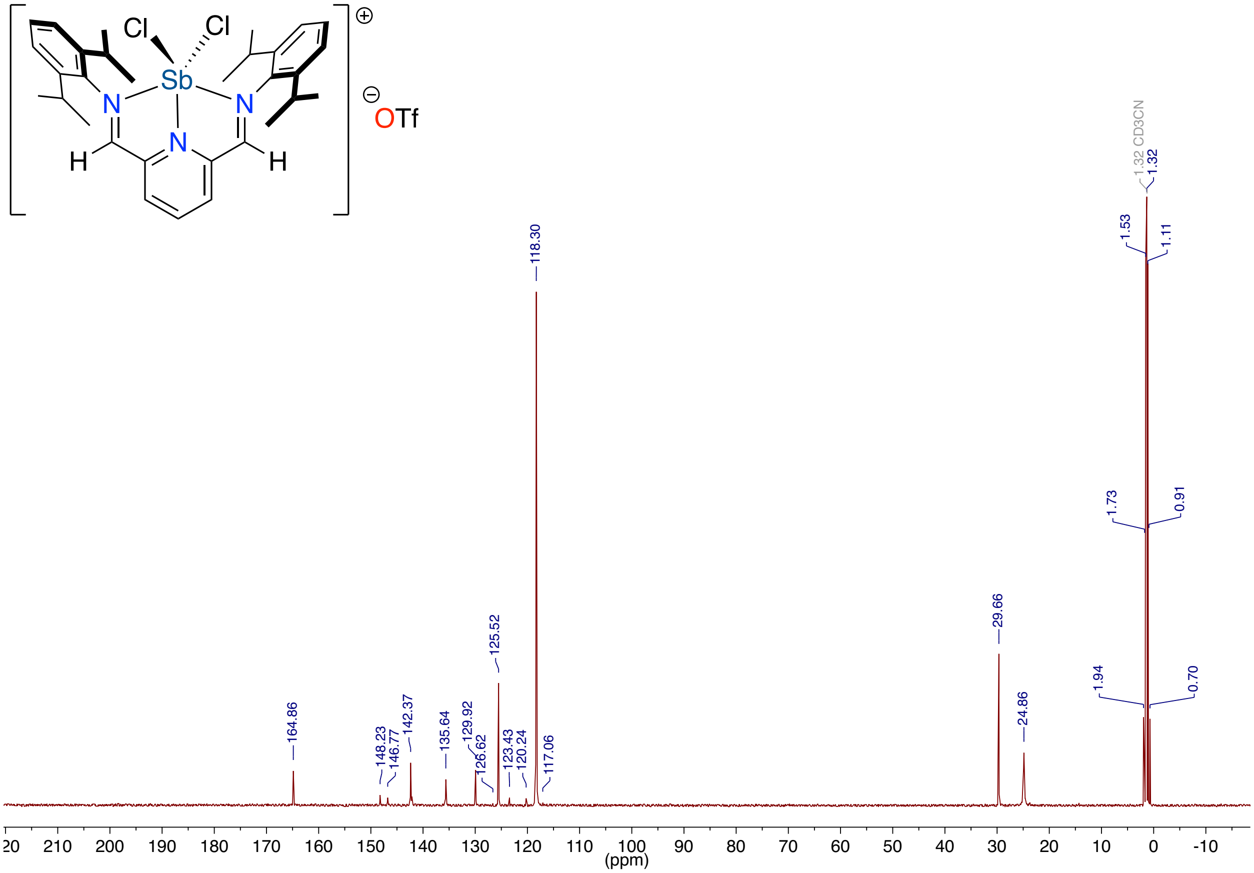


Figure S-20: Expansion of $^{13}C\{^1H\}$ NMR spectrum of **2H** in CD_3CN (aryl region).

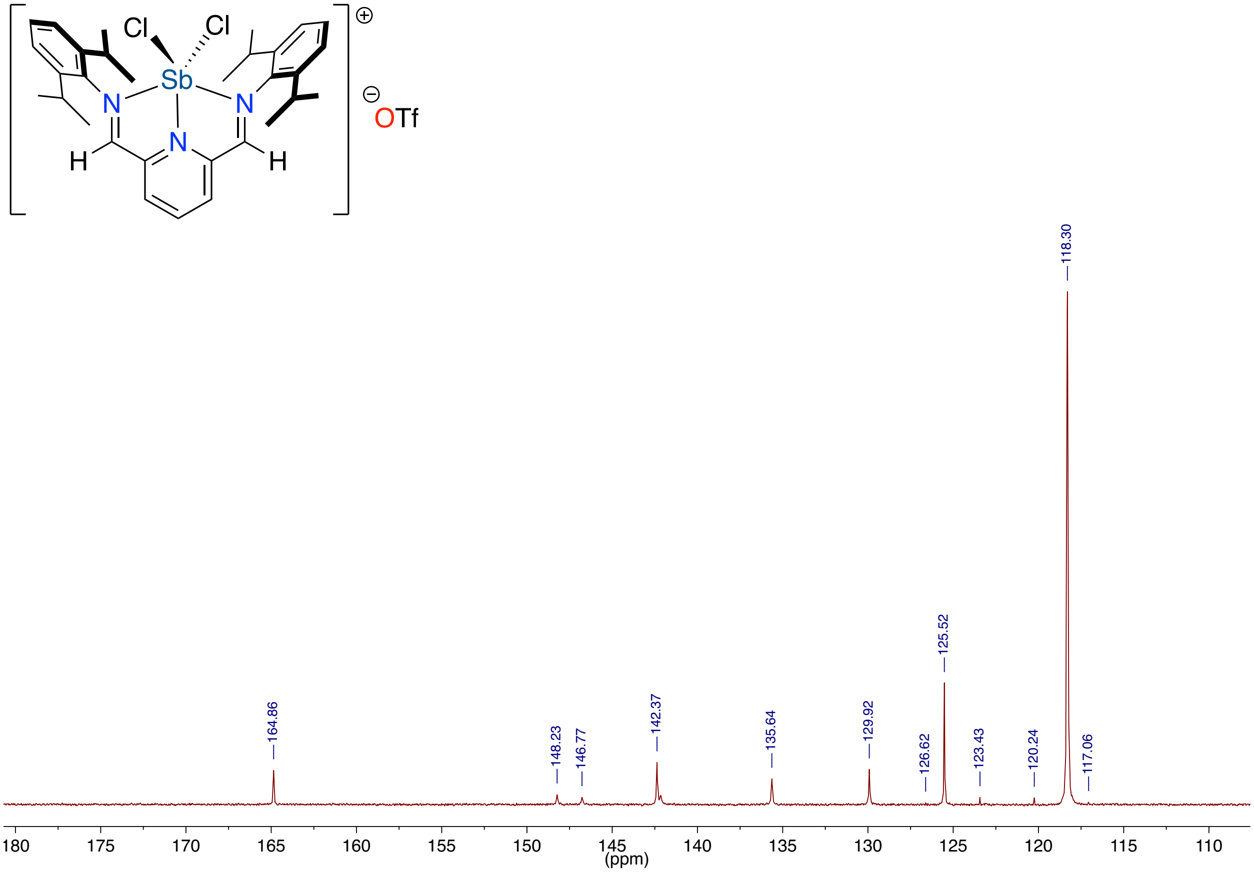


Figure S-21: ^{19}F NMR spectrum of **2H** in CD_3CN with internal standard C_6H_5F.

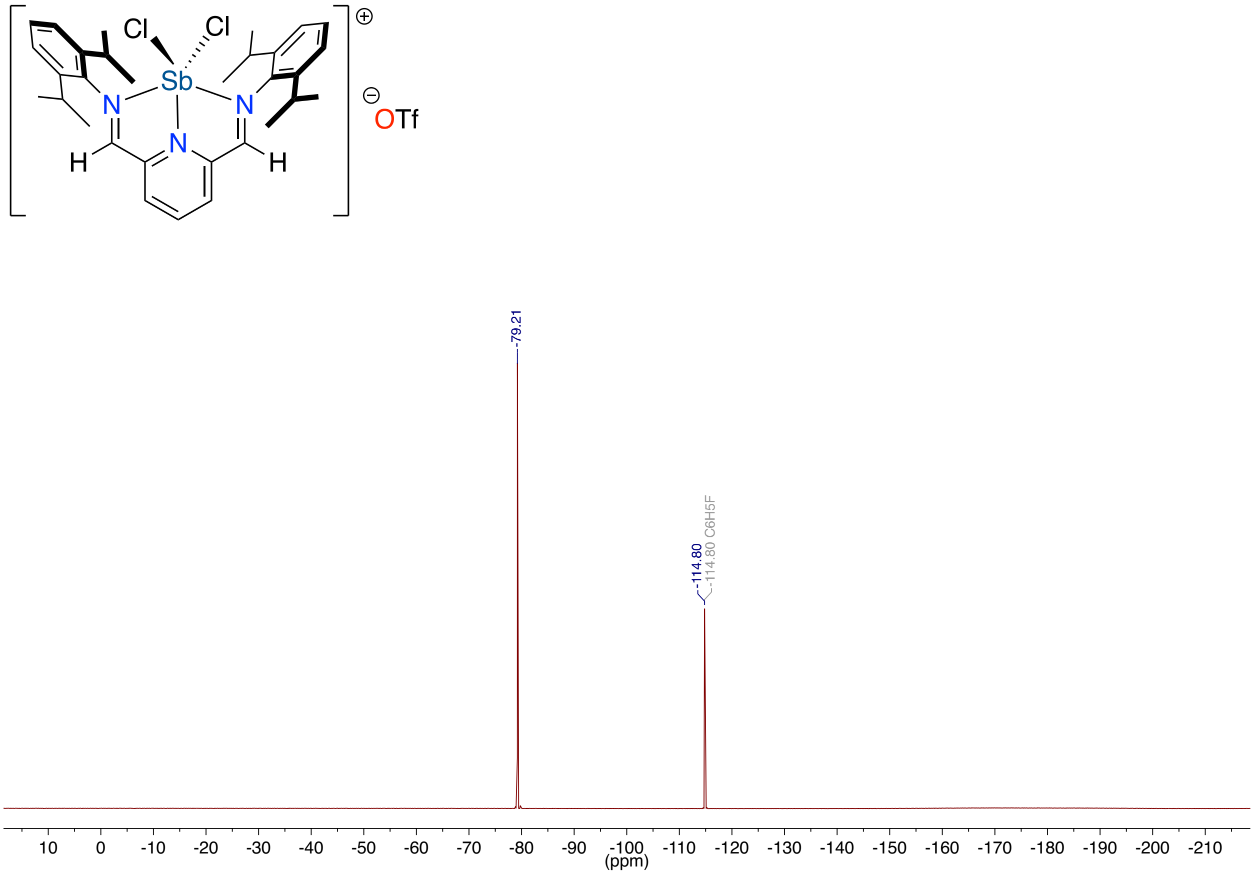


Figure S-22: FT-IR spectrum of **2H**.

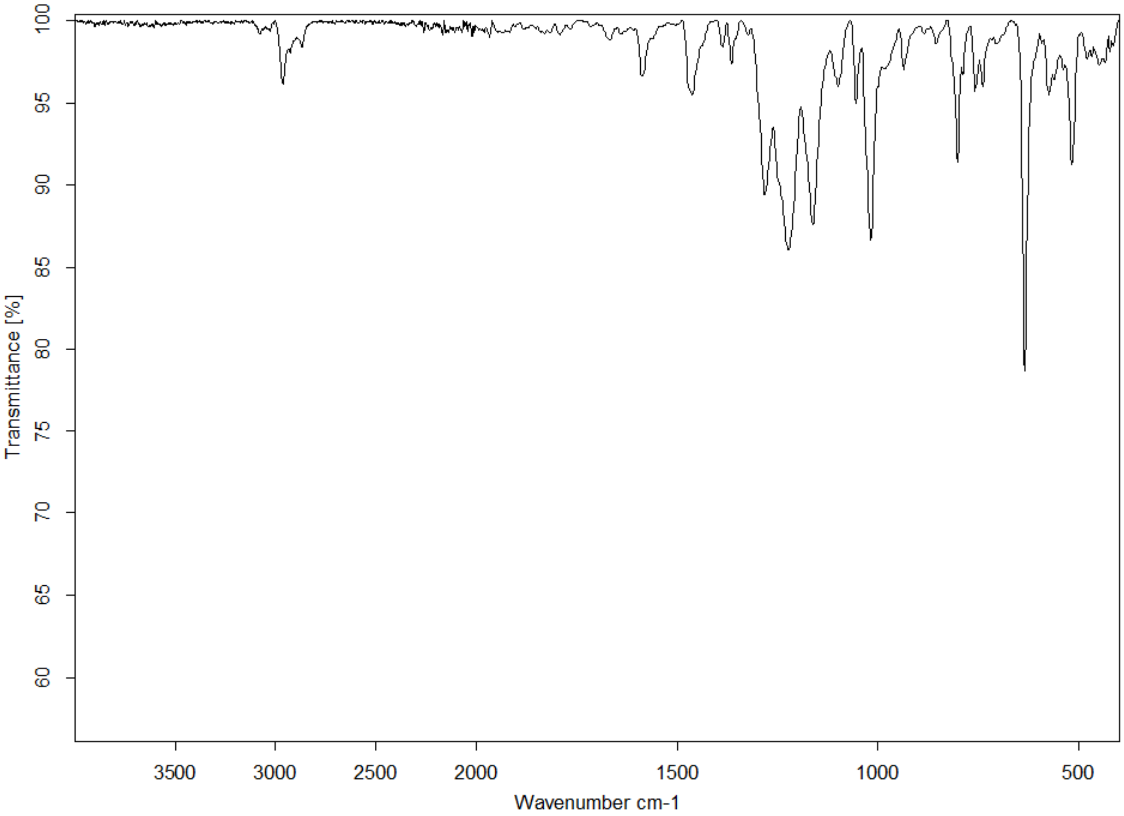


Figure S-23: ^{1}H NMR spectrum of **1H** in CD_3CN.

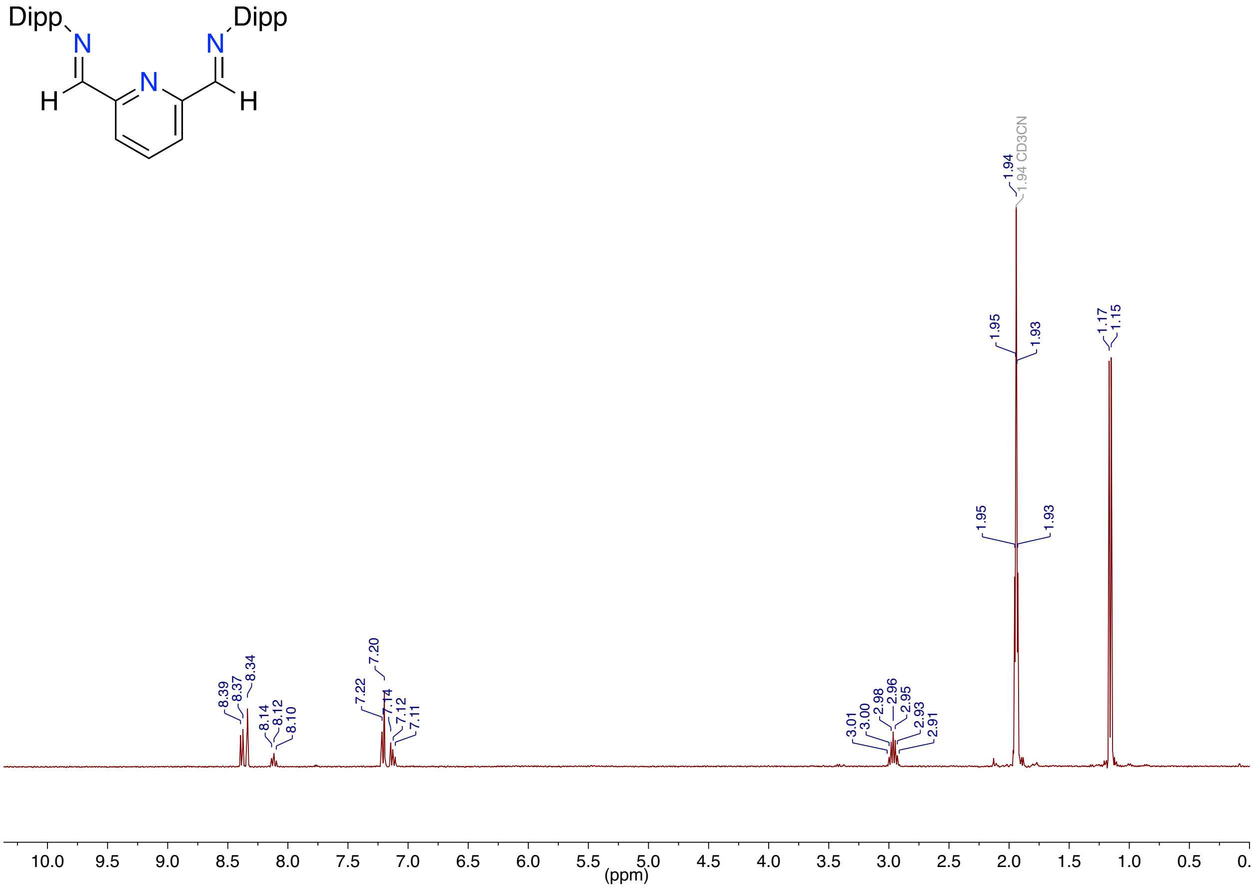


Table S-1: X-ray crystallographic details for **$2CH_3$**, **2Ph**, and **2H**.

	$2CH_3$	**2Ph**	**2H**
CCDC	2091549	2091550	2091551
Empirical Formula	$C_{40}H_{49}N_3Sb_1Cl_2O_3S_1F_3$	$C_{44}H_{47}N_3Sb_1Cl_2O_3S_1F_3$	$C_{72}H_{87}N_6Sb_2Cl_4O_6S_2F_6$
FW (g/mol)	901.53	947.55	1695.89
Crystal System	monoclinic	orthorhombic	orthorhombic
Space Group	$P2_1/c$	$P2_12_12_1$	$Pna2_1$
a (Å)	17.5725(7)	9.4978(2)	20.2985(8)
b (Å)	15.1574(7)	17.5189(4)	28.7063(12)
c (Å)	16.5994(7)	26.3589(8)	16.5024(7)
α (deg)	90	90	90
β (deg)	106.4215(15)	90	90
γ (deg)	90	90	90
V ($Å^3$)	4241.0(3)	4385.88(19)	9615.9(17)
Z	4	4	4
D_c (g cm^{-3})	1.412	1.435	1.171
Radiation λ (Å)	0.71073	0.71073	0.71073
Temp (K)	150	150	150
R1 [I>2(σ)I]^a	0.0310	0.0410	0.0451
wR2 (F^2)^a	0.0892	0.1166	0.1157
GOF (S)^a	1.065	1.156	1.063

[a] $R1(F[I > 2(I)]) = \sum\|F_o| - |F_c\|/ \sum |F_o|$; $wR2(F^2 [\text{all data}]) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2 (F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

References

1. (a) N. Kleigrewe, W. Steffen, T. Blömker, G. Kehr, R. Fröhlich, B. Wibbeling, G. Erker, J.-C. Wasilke, G. Wu and G. C. Bazan, *J. Am. Chem. Soc.*, 2005, **127**, 13955-13968; (b) M. D. Greenhalgh and S. P. Thomas, *J. Am. Chem. Soc.*, 2012, **134**, 11900-11903; (c) A.M.A. Bennett, Oligomerization of Propylene. EP1066229 (A1): 2001.
2. (a) G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112-122; (b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.