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Electronic Supplementary Information

Unsupported monomeric stibine oxides (R_3SbO) remain undiscovered

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CONTENTS

Experimental methods

General methods. Reagents and solvents were purchased from commercial vendors and used as received unless otherwise specified. All solvents were dried over 4-Å molecular sieves. The syntheses of trimesitylstibine, hydroxytrimesitylstibonium benzenesulfonate, and hydroxytrimesitylstibonium trifluoromethanesulfonate (triflate) were performed using flame-dried glassware under a nitrogen atmosphere. Other manipulations were performed under ambient conditions. NMR spectra were collected using a Bruker Avance III HD 500 spectrometer equipped with a multinuclear Smart Probe. Signals in the ^{1}H and ^{13}C NMR spectra are reported in ppm as chemical shifts from tetramethylsilane and were referenced using the $CHCl_3$ (^{1}H, 7.26 ppm) and $CDCl_3$ (^{13}C, 77.16 ppm) solvent signals. The frequencies of ^{11}B NMR signals are reported in ppm as chemical shifts from $BF_3{\cdot}Et_2O$ and those of ^{19}F NMR spectra as shifts from $CFCl_3$ (referenced to $BF_3{\cdot}Et_2O$ at –152.8 ppm). IR spectra were collected using a PerkinElmer Spectrum One FT-IR spectrometer. Mass spectrometry measurements were collected using an LTQ-Orbitrap Velos Pro MS instrument. Elemental analysis was performed by Midwest Microlabs (Indianapolis, IN) using an Exeter CE440 analyzer. Melting point data were collected with an electrothermal Mel-Temp apparatus and a partial-immersion thermometer; temperatures are uncorrected.

Synthesis of trimesitylstibine (Mes_3Sb). A dry 250 mL two-necked round bottom flask with a water jacket condenser was charged with a stir bar and magnesium turnings (1.451 g, 59.69 mmol). The magnesium turnings were suspended in 45 mL of dry tetrahydrofuran (THF) and activated with 1,2-dibromoethane (5.606 g, 29.84 mmol) at 0 °C for 3 h. 2-Bromomesitylene (5.942 g, 29.84 mmol) was then added dropwise and the reaction was refluxed for 6 h. A solution of trichlorostibine (2.269 g, 9.947 mmol) in dry THF (5 mL) was then added dropwise into the yellow solution of mesitylmagnesium bromide, which became dark brown. The reaction mixture was refluxed for 14 h. The resulting mixture was cooled to room temperature, diluted with diethyl ether (200 mL), and washed with water (200 mL). The aqueous wash was back-extracted with diethyl ether (2 × 50 mL), and the organic phases were combined, washed with water (3 × 100 mL), and washed with brine (1 × 100 mL). The organic phase was dried over anhydrous sodium sulfate for 30 min and stripped of solvent under reduced pressure to yield a crude yellow oil. Cold ethanol was added dropwise with sonication to precipitate a white powder that was collected via vacuum filtration and dried in vacuo. Yield: 3.288 g, 69%. Analytical data match those previously reported for this compound.[1] M.p. 129 °C **IR (KBr, cm^{-1})** ν 1438 (s), 844 (s), 546 (s). **δ^1H(500 MHz; $CDCl_3$)** 6.83 (1 H, s, *m*-H), 2.29 (18 H, s, *o*-Me), 2.27 (9 H, s, *p*-Me). **δ^{13}C{^{1}H}(125 MHz; $CDCl_3$)** 144.90, 137.93, 136.80, 128.98, 25.46, (*o*-Me), 21.02 (*p*-Me).

Synthesis of *trans*-dihydroxytrimesitylstiborane (*trans*-$Sb(OH)_2Mes_3$). Trimesitylstibine (1.061 g, 2.213 mmol) was suspended in acetone (25 mL) and cooled to 0 °C. A solution of 50% hydrogen peroxide (0.828 mL, 12.17 mmol H_2O_2) in acetone (4 mL) was added dropwise to the suspension of trimesitylstibine. The white suspension was warmed to room temperature and stirred for 2 h. The volume of solvent was reduced by approximately 90% under reduced pressure and hexanes (30 mL) were added to precipitate a white powder that was collected via vacuum filtration and dried in vacuo. Yield: 856 mg, 75%. Analytical data match those previously reported for this compound.[2] M.p. 109 °C. **IR (KBr, cm^{-1})** ν_{OH} 3642 (s), ν_{SbO} 517 (s). **δ^1H(500 MHz; $CDCl_3$)** 6.97 (6 H, s, *m*-H), 2.57 (18 H, s, *o*-Me), 2.31 (9 H, s, *p*-Me). **δ^{13}C{^{1}H}(125 MHz; $CDCl_3$)** 142.33, 142.19, 139.79, 130.18, 24.79 (*o*-Me), 21.08 (*p*-Me).

Synthesis of hydroxytrimesitylstibonium benzenesulfonate ([Mes$_3$Sb(OH)][PhSO$_3$], 1). *trans*-Dihydroxytrimesitylstiborane (94 mg, 0.18 mmol) was suspended in dichloromethane (DCM, 2 mL) and a solution of benzenesulfonic acid (29 mg, 0.184 mmol) in DCM (3 mL) was added dropwise into the reaction mixture. The reaction mixture clarified over the course of the addition and was stirred at room temperature for 30 min. Hexanes (30 mL) were added and the reaction mixture was cooled to –20 °C to yield a crop of colorless crystals. Yield: 70 mg, 58%. Diffraction-quality crystals of **1** were grown by layering hexanes over a CDCl$_3$ solution of the compound. M.p. 218 °C (decomp). **Found:** C, 60.32; H, 5.93. **Calc. for C$_{33}$H$_{39}$O$_4$SSb:** C, 60.65; H, 6.02 %. **ESI-MS (*m/z*)** M$^+$ 495.34 (calc 495.16). **IR (KBr, cm^{-1}) ν_{SbO}** 612 (s). **δ^{1}H(500 MHz; CDCl$_3$)** 9.08 (1 H, s br, OH), 7.605 (2 H, d, *J* = 7.5 Hz, *o*-H), 7.24 (1 H, t, *J* = 7.5 Hz, *p*-H), 7.17 (2H, t, *J* = 7.5 Hz, *m*-H), 6.97 (6 H, s, *m*-H), 2.41 (18 H, s, *o*-Me), 2.31 (9 H, s, *p*-Me). **δ^{13}C{^{1}H}(125 MHz; CDCl$_3$)** 146.09, 143.87, 143.47, 131.76, 131.34, 129.04, 127.64, 126.21, 24.04 (*o*-Me), 21.32 (*p*-Me).

Synthesis of hydroxytrimesitylstibonium triflate ([Mes$_3$Sb(OH)][CF$_3$SO$_3$], 2). Dihydroxytrimesitylstiborane (366 mg, 0.714 mmol) was suspended in DCM (2 mL) and a solution of triflic acid (63 μL, 0.714 mmol) in DCM (3 mL) was added dropwise into the cloudy mixture. The reaction mixture clarified over the course of the addition and was stirred at room temperature for 30 min. Hexanes (30 mL) were added and the reaction mixture was cooled to –20 °C to yield a crop of colorless crystals. Yield: 361 mg, 79%. Diffraction-quality crystals of **2** were grown by layering hexanes over a CDCl$_3$ solution of the compound. M.p. 252 °C (decomp). **Found:** C, 52.04; H, 5.20**. Calc. for C$_{28}$H$_{34}$F$_3$O$_4$SSb:** C, 52.11; H, 5.31 %. **ESI-MS (*m/z*)** M$^+$ 495.32 (calc 495.16). **IR (KBr, cm^{-1}) ν_{SbO}** 637 (s). **δ^{1}H(500 MHz; CDCl$_3$)** 7.51 (1 H, s, OH),7.05 (6 H, s, *m*-H), 2.41 (18 H, s, *o*-Me), 2.35 (9 H, s, *p*-Me). **δ^{13}C{^{1}H}(125 MHz; CDCl$_3$)** 144.59, 143.25, 131.54, 130.80, 120.46 (q, J_{FC} = 319 Hz), 23.98 (*o*-Me), 21.30 (*p*-Me). **δ^{19}F{^{1}H}(470 MHz; CDCl$_3$)** –78.28 (s).

Synthesis of potassium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (KBAr^F). A dry 250 mL two-necked round bottom flask with a water jacket condenser was charged with a stir bar, magnesium turnings (2.015 g, 82.9 mmol), and sodium tetrafluoroborate (1.821 g, 16.6 mmol). The reagents were suspended in diethyl ether (100 mL). The magnesium turnings were activated with 1,2-dibromoethane (1.44 mL, 16.6 mmol), and the reaction mixture was brought to a reflux. 1,3-Bis(trifluoromethyl)-5-bromobenzene (11.44 mL, 66.3 mmol) was added dropwise to the suspension. The reaction mixture was refluxed for 18 h to produce a cloudy brown suspension. The contents were poured into a 2 L beaker and diluted with diethyl ether (90 mL). A solution of potassium carbonate (24 g, 0.17 mol) in water (240 mL) was added to the reaction mixture, and the contents were stirred vigorously for 1 h. The suspension was filtered to remove undissolved salts, and the filtrate was transferred to a separation funnel. The aqueous layer was extracted with diethyl ether (3 × 30 mL), and the combined organic layers were dried over Na$_2$SO$_4$. The organic layer was stripped of solvent to yield a yellow-brown oil. A mixture of DCM and hexanes was added to precipitate the product as a white powder. Yield: 2.290 g, 15.3%. Analytical data match those previously reported for this compound.[3] **IR (KBr, cm^{-1}) ν** 1360 (s), 1285 (s), 1146 (s), 887 (w). **δ^{1}H(500 MHz; CD$_3$N)** 7.72 (8H, br m, *o*-H), 7.69 (4H, s, *p*-H) . **δ^{13}C{^{1}H}(125 MHz; CD$_3$N)** 162.59 (q, J_{BC} = 50 Hz, *ipso*-C), 135.64, 129.91 (qq, $J_{FC,1}$ = 32.5 Hz, $J_{\text{FC},2}$ = 3.75 Hz), 125.45 (q, J_{FC} = 271.25 Hz) **δ^{19}F{^{1}H}(470 MHz; CDCl$_3$)** -81.85 (s). **δ^{11}B{^{1}H}(160 MHz; CD$_3$N)** –6.59 (s).

Synthesis of hydroxytrimesitylstibonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ([Mes$_3$Sb(OH)][BAr^F], 3). A solution of **2** (201 mg, 0.311 mmol) in DCM (4 mL) was added dropwise to a cloudy suspension of potassium tetrakis(bis(3,5-trifluoromethyl)phenyl)borate (295 mg, 0.327 mmol) in DCM (20 mL). The cloudy suspension briefly became clear before potassium triflate precipitated from solution as a colorless solid. The suspension was vacuum filtered and the filtrate was stripped of solvent to yield a yellowish oil. The oil was taken up in $CHCl_3$ (3 mL) and passed through a pad of Celite to remove any excess $KBAr^F$. The solvent volume was reduced and pentane was added to precipitate the product as a white powder. The white powder was dried under vacuum for 72 h. Yield: 264 mg, 63% Diffraction quality crystals of **3** were grown from a mixture of $CHCl_3$ and pentane at –20 °C. **Found:** C, 52.28; H, 3.38**. Calc. for $C_{28}H_{34}F_3O_4SSb$:** C, 52.12; H, 3.41 %. **ESI-MS (*m/z*)** M^+ 495.54 (calc 495.16). **IR (KBr, cm^{-1}) ν_{SbO}** 683 (s). **δ^{1}H(500 MHz; $CDCl_3$)** 7.70 (8 H, s, *o*-H), 7.50 (4 H, s, *p*-H) 7.08 (6 H, s, *m*-H), 2.86 (1 H, s br, OH), 2.35 (18 H, s, *o*-Me), 2.32 (9 H, s, *p*-Me). **δ^{13}C{^{1}H}(125 MHz; $CDCl_3$)** 161.81 (q, J_{BC} = 50 Hz, *ipso*-C), 146.20, 142.70, 134.95, 132.18, 130.14, 129.04 (qq, $J_{FC,1}$ = 31.25 Hz, $J_{FC,2}$ = 2.50 Hz) 120.46 (q, J_{FC} = 271.25 Hz), 117.58, 23.86 (*o*-Me), 21.25 (*p*-Me). **δ^{19}F{^{1}H}(470 MHz; $CDCl_3$)** –62.30 (s). **δ^{11}B{^{1}H}(160 MHz; $CDCl_3$)** –6.72 (s).

Computational experiments. All density functional theory (DFT) calculations were carried out using ORCA 4.2.1.[4, 5] Geometry optimizations and frequency calculations were performed at the PBE0/def2-TZVPP level of theory with the RIJCOSX approximation and def2/J auxiliary basis set.[6-10] A relaxed surface scan of a H atom across the Sb–O···O–S interatomic vector of **1** was carried out at BP86/def2-TZVP level of theory with the RI approximation and def2/J auxiliary basis set. Proton affinities were estimated by calculating the Gibbs free energy for the reaction of $PhSO_3^-$ or Mes_3SbO with H^+ with implicit DCM solvation provided by a conductor-like polarizable continuum model (CPCM).

X-ray crystallography. Crystals of **1**, **2**, and **3** were grown as described above, selected under a microscope, loaded onto a nylon fiber loop using Paratone-N, and mounted onto a Rigaku XtaLAB Synergy-S single crystal diffractometer. Each crystal was cooled to 100 K under a stream of nitrogen. Diffraction of Mo Kα radiation from a PhotonJet-S microfocus source was detected using a HyPix-6000HE hybrid photon counting detector. Screening, indexing, data collection, and data processing were performed with CrysAlis^{Pro}.[11] The structures were solved using SHELXT and refined using SHELXL following established strategies.[12-14] All non-H atoms were refined anisotropically. Carbon-bound H atoms were placed at calculated positions and refined with a riding model and coupled isotropic displacement parameters (1.2 × U_{eq} for aryl groups and 1.5 × U_{eq} for methyl groups). The oxygen-bound H atoms were located in the difference Fourier synthesis; their positional parameters were refined semi-freely and their isotropic displacement parameters were set equal to 1.5 × U_{eq} of the oxygen atom. In the case of **2**, the triflate counterion was disordered across two positions and was refined with similarity restrains on bond lengths, bond angles, and displacement parameters. In the case of **3**, the two pentane molecules in the unit cell were each disordered across a distinct crystallographic inversion center and were modeled with similarity restrains on bond lengths, bond angles, and displacement parameters.

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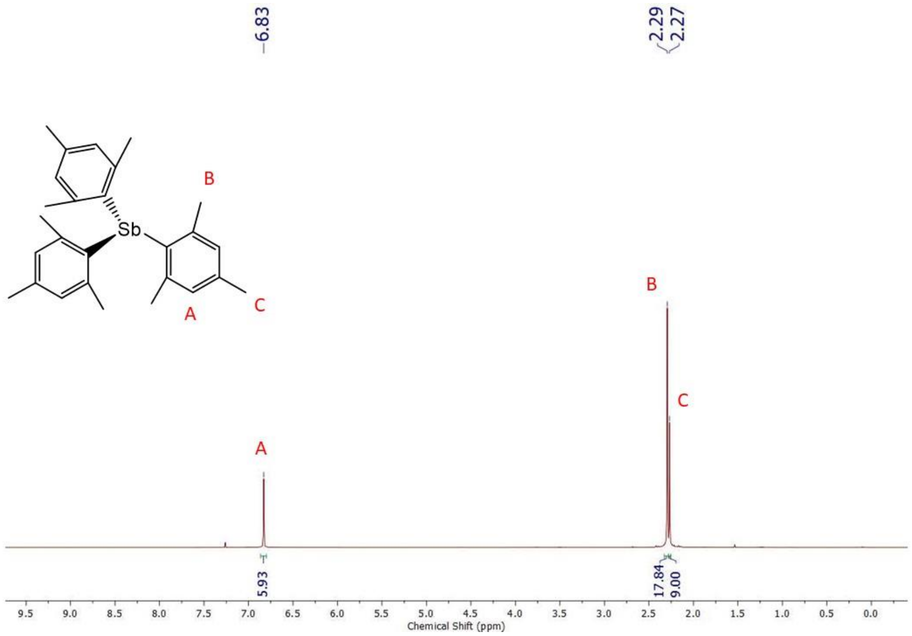

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of trimesitylstibine at room temperature.

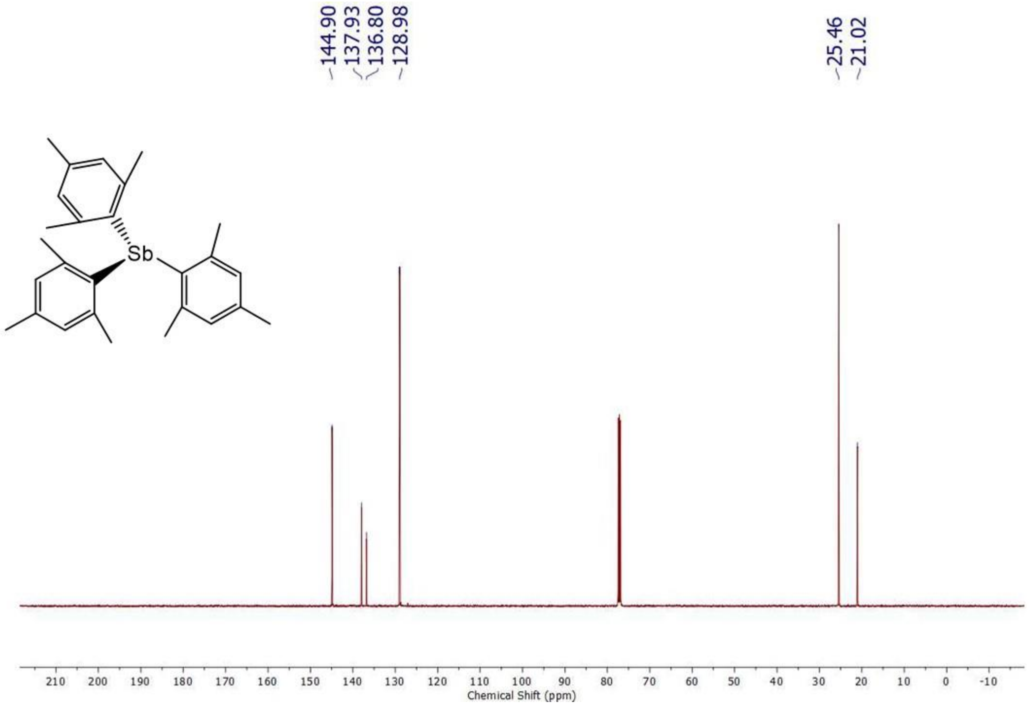

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of trimesitylstibine at room temperature.

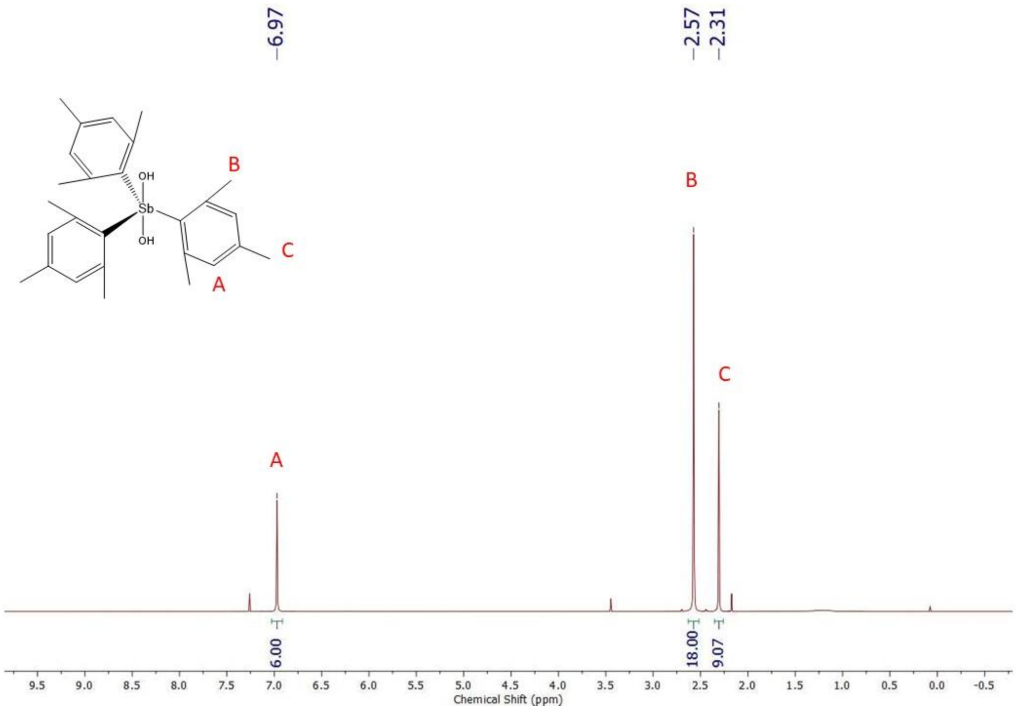

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of dihydroxytrimesitylstiborane at room temperature.

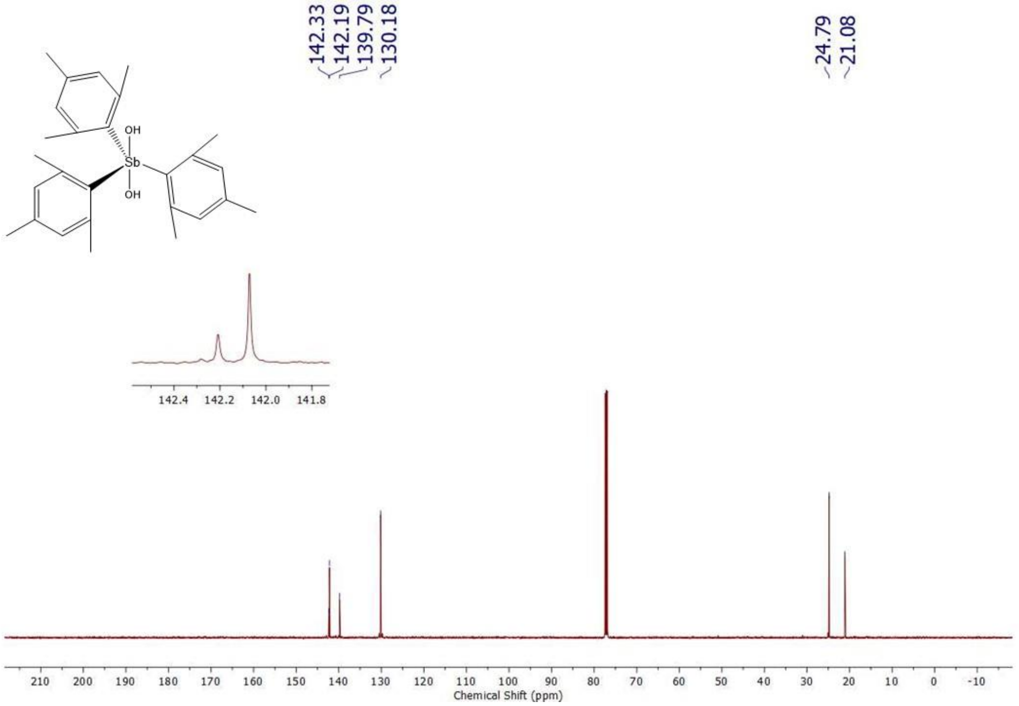

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of dihydroxytrimesitylstiborane at room temperature.

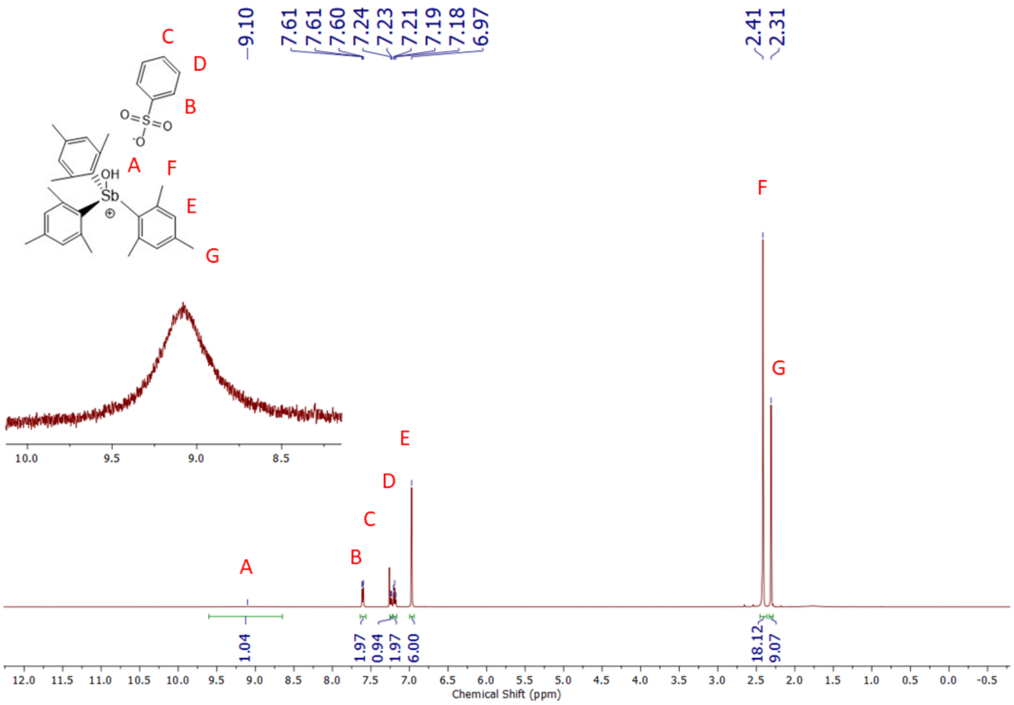

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of hydroxytrimesitylstibonium benzenesulfonate (**1**) at room temperature.

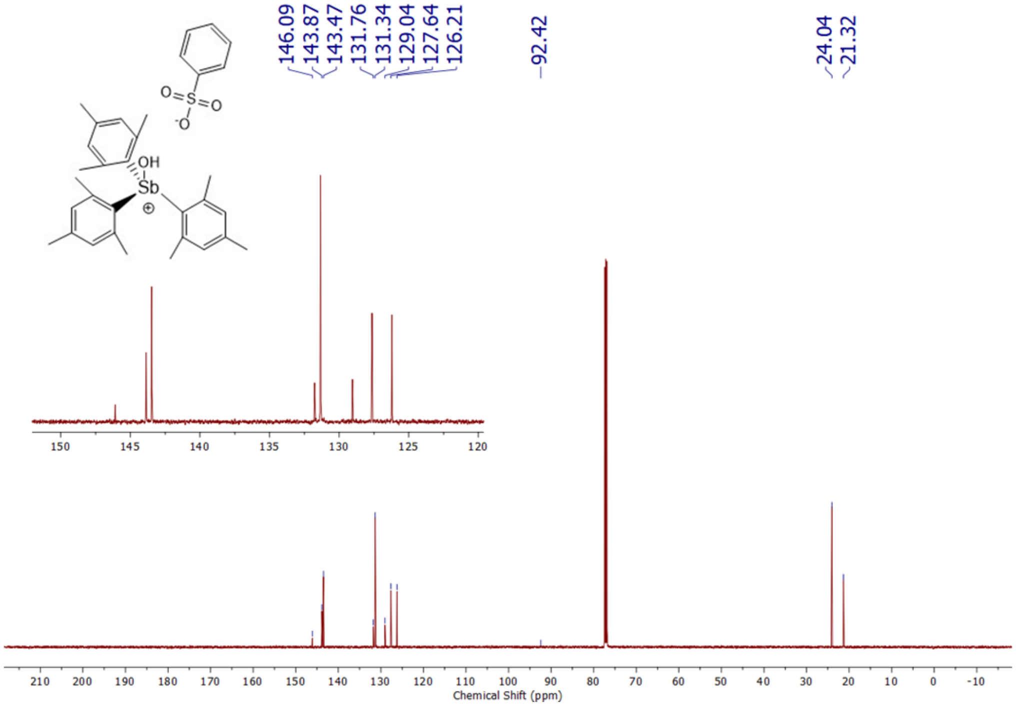

Figure S6. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of hydroxytrimesitylstibonium benzenesulfonate (**1**) at room temperature.

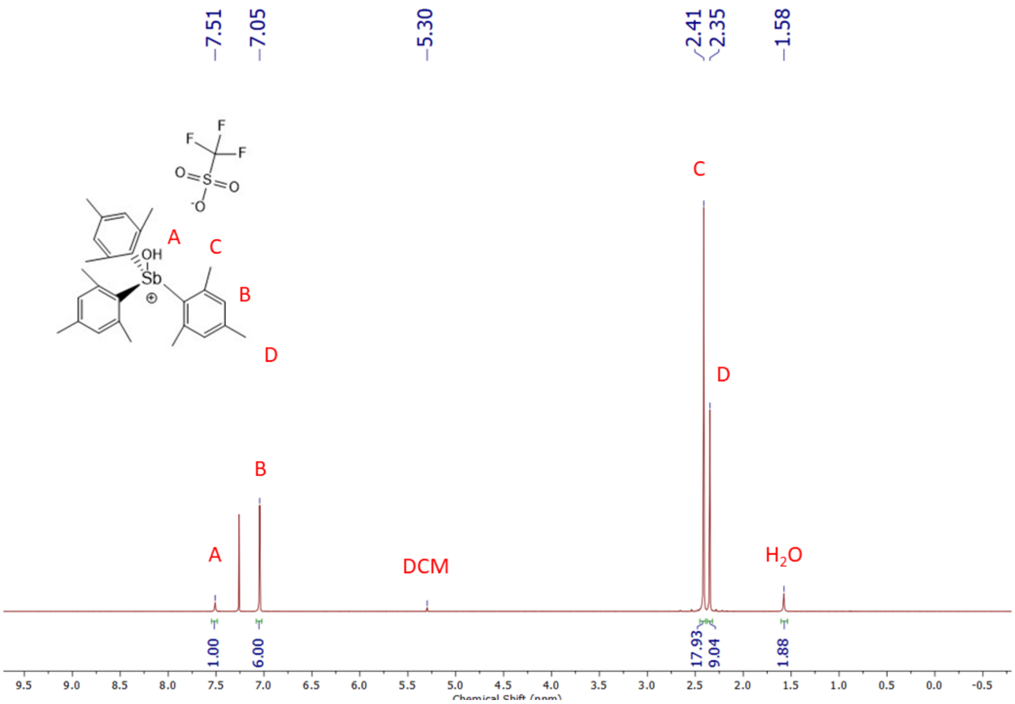

Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of hydroxytrimesitylstibonium triflate (**2**) at room temperature.

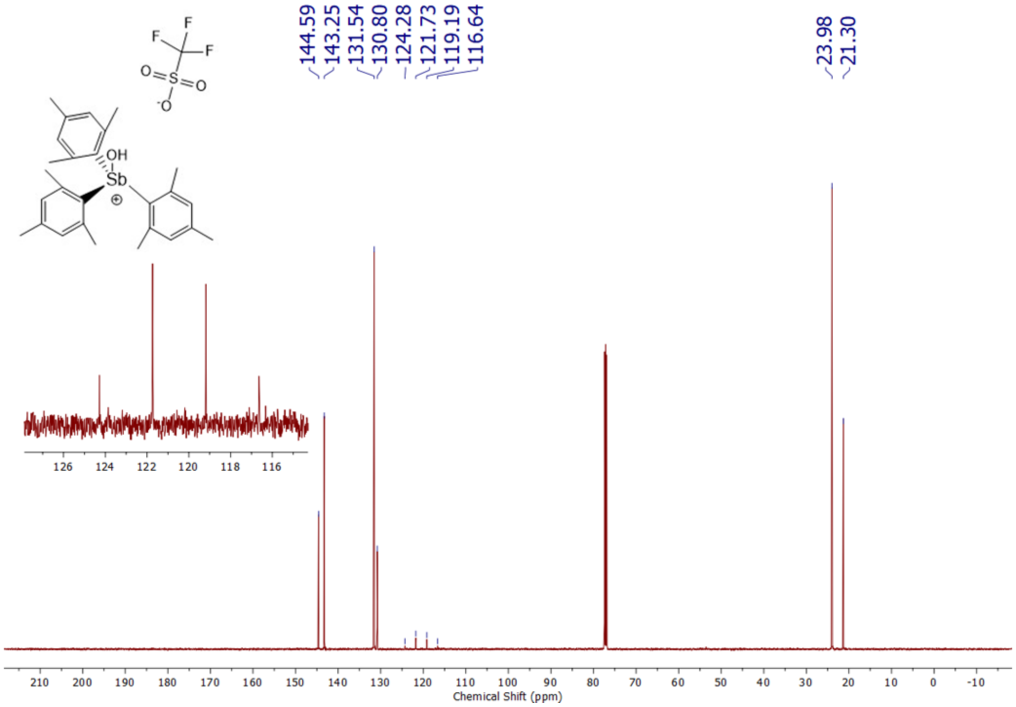

Figure S8. $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of hydroxytrimesitylstibonium triflate (**2**) at room temperature.

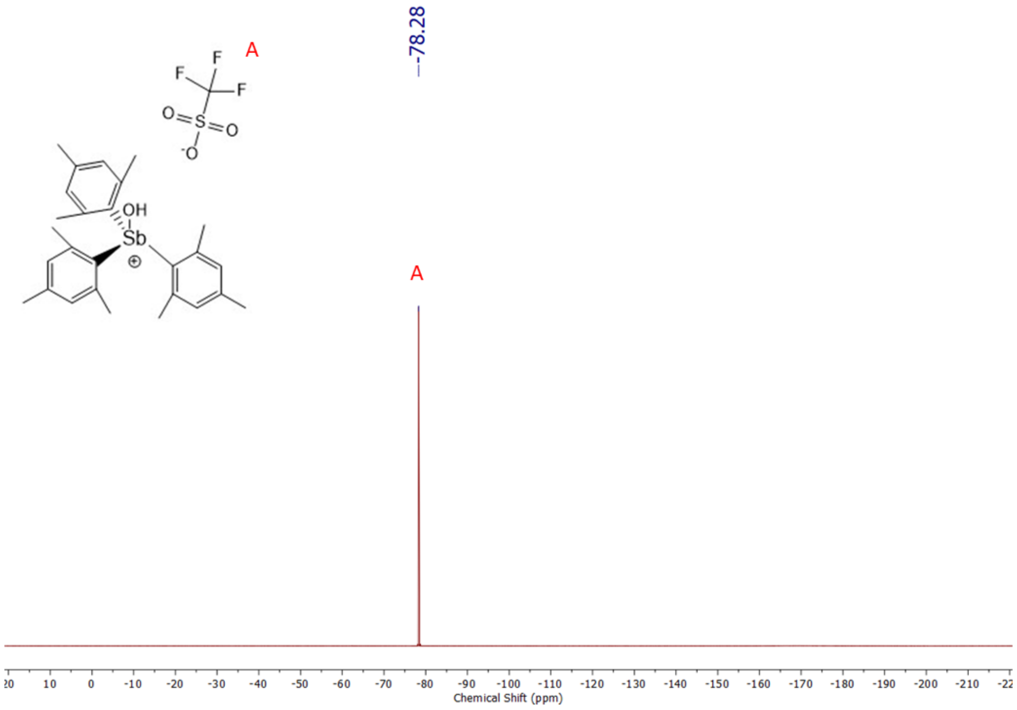

Figure S9. ^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of hydroxytrimesitylstibonium triflate (**2**) at room temperature.

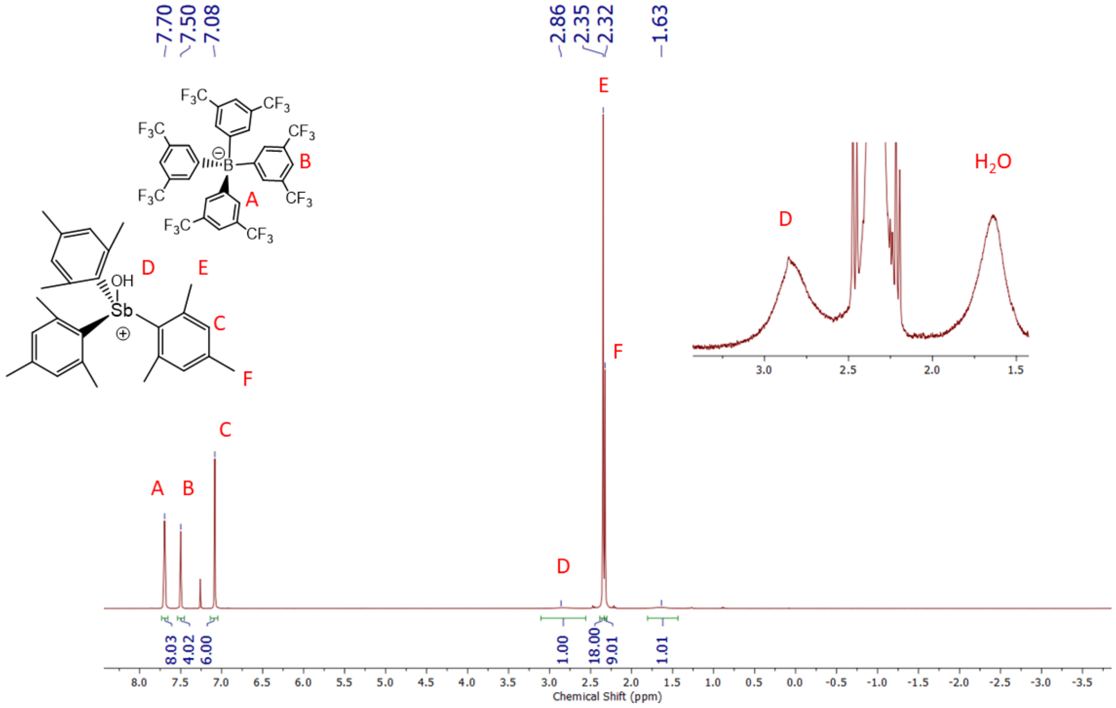

Figure S10. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of hydroxytrimesitylstibonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**3**) at room temperature.

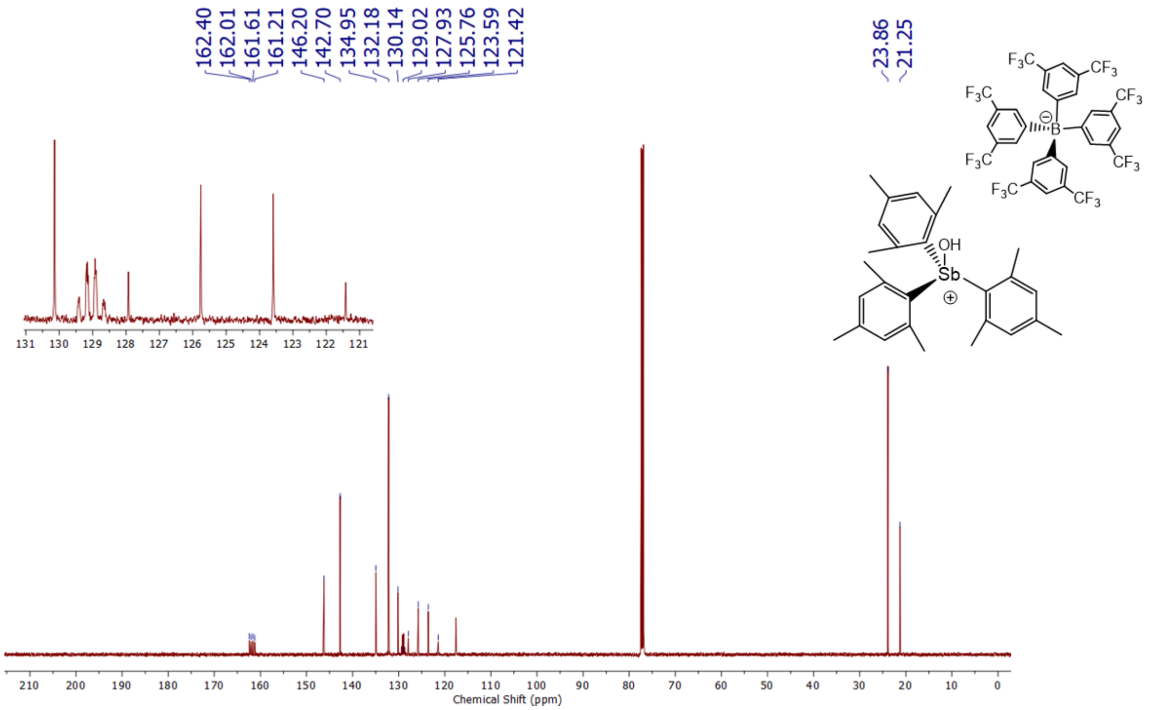

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 125 MHz) of hydroxytrimesitylstibonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**3**) at room temperature.

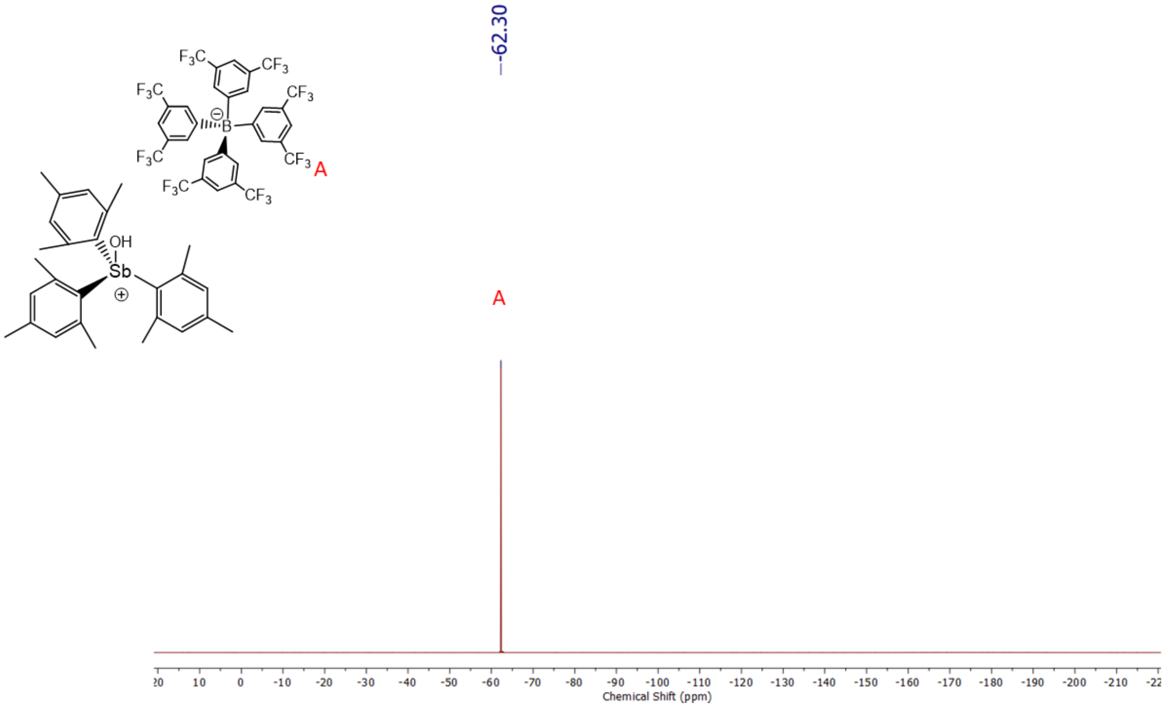

Figure S12. ^{19}F NMR spectrum ($CDCl_3$, 470 MHz) of hydroxytrimesitylstibonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**3**) at room temperature.

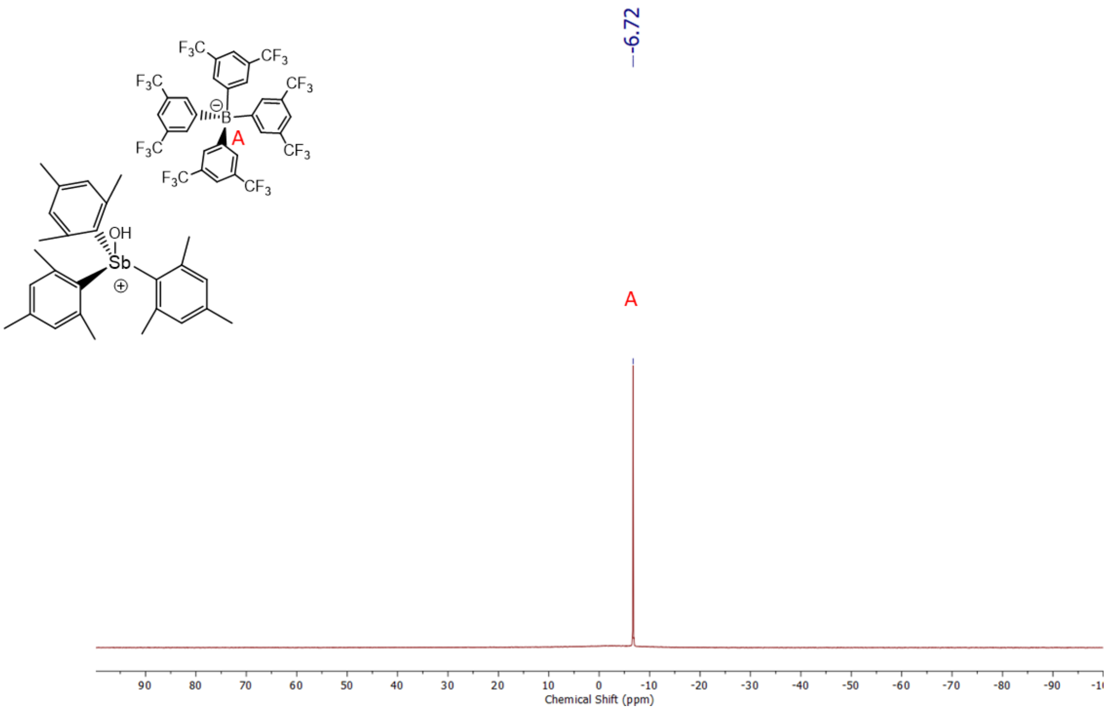

Figure S13. ^{11}B NMR spectrum (CDCl$_3$, 160 MHz) of hydroxytrimesitylstibonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**3**) at room temperature.

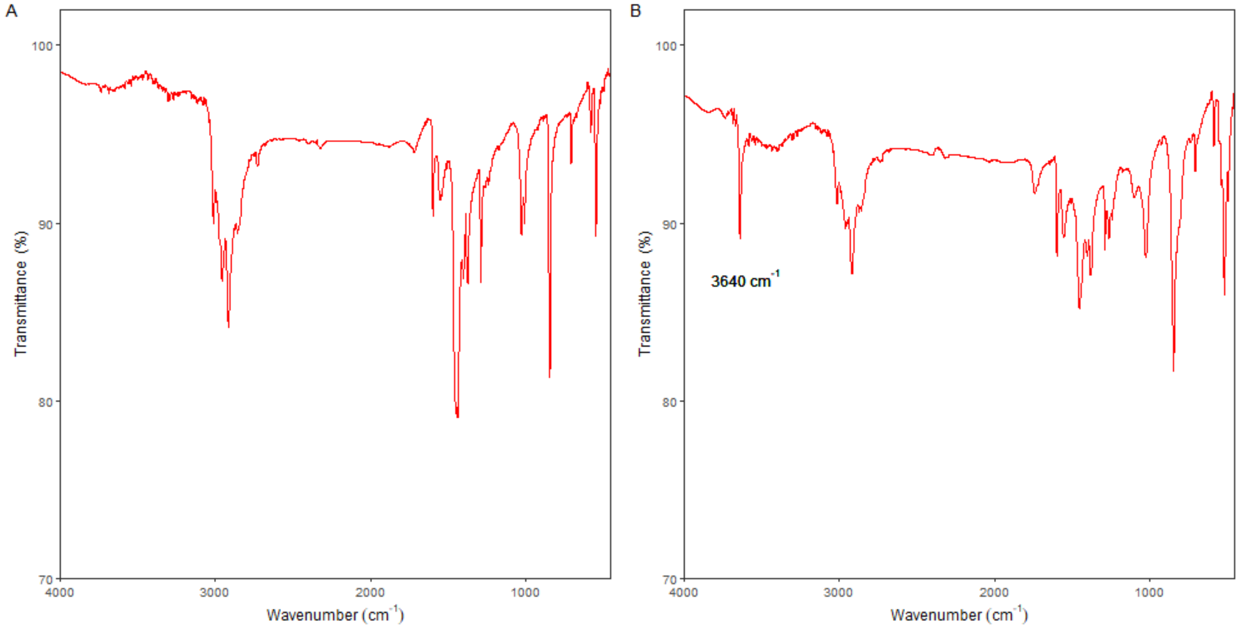

Figure S14. Experimental infrared spectra (KBr pellets) of (A) trimesitylstibine and (B) dihydroxytrimesitylstiborane (ν_{OH} 3642 cm^{-1} (s), ν_{SbO} 517 cm^{-1} (s)).

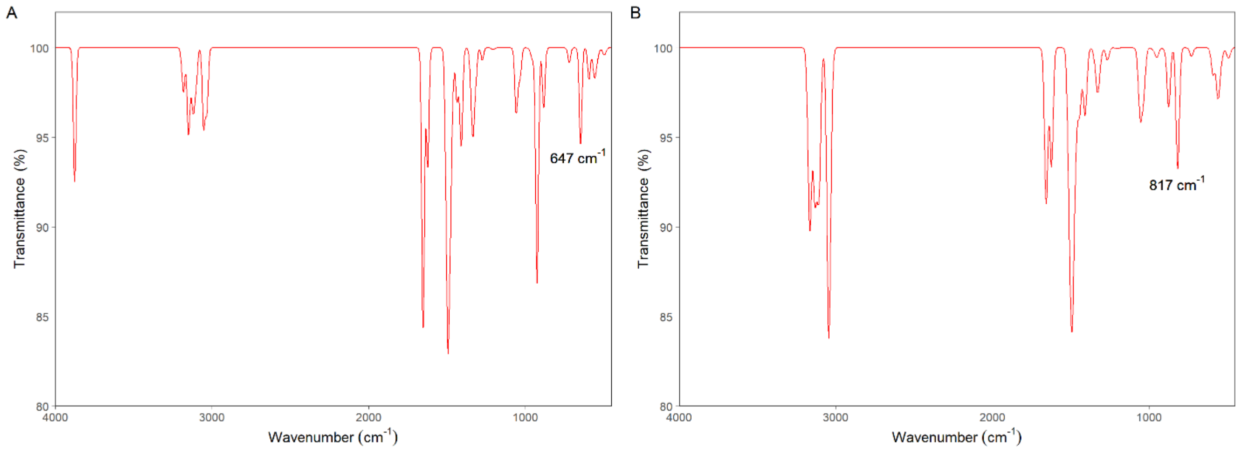

Figure S15. Calculated infrared spectra (PBE0/def2-TZVPP) of (A) the hydroxytrimesitylstibonium cation and (B) trimesitylstibine oxide.

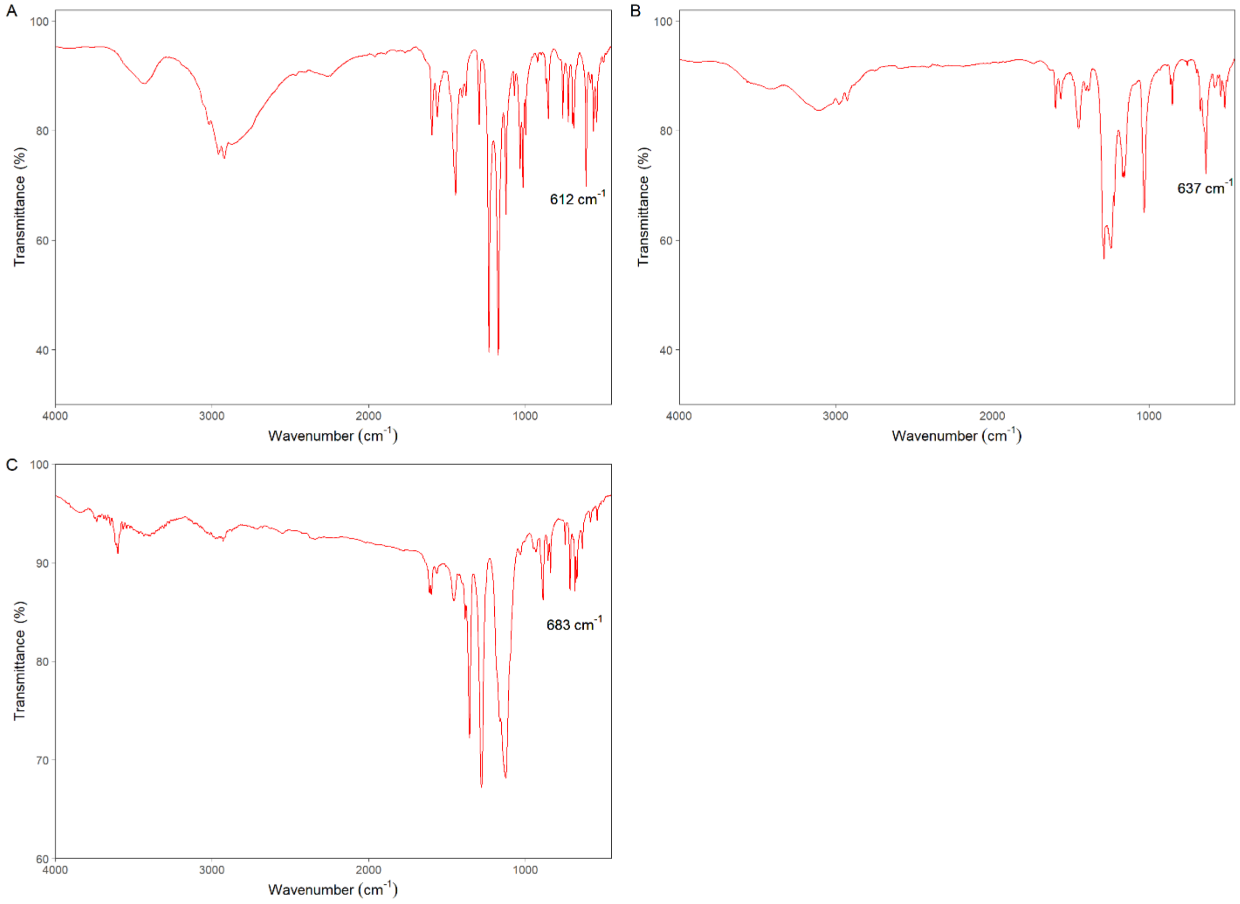

Figure S16. Experimental infrared spectra (KBr pellets) of (A) hydroxytrimesitylstibonium benzenesulfonate (**1**), (B) hydroxytrimesitylstibonium triflate (**2**), and (C) hydroxytrimesitylstibonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (**3**) (ν_{OH} 3601 cm^{-1} (s)).

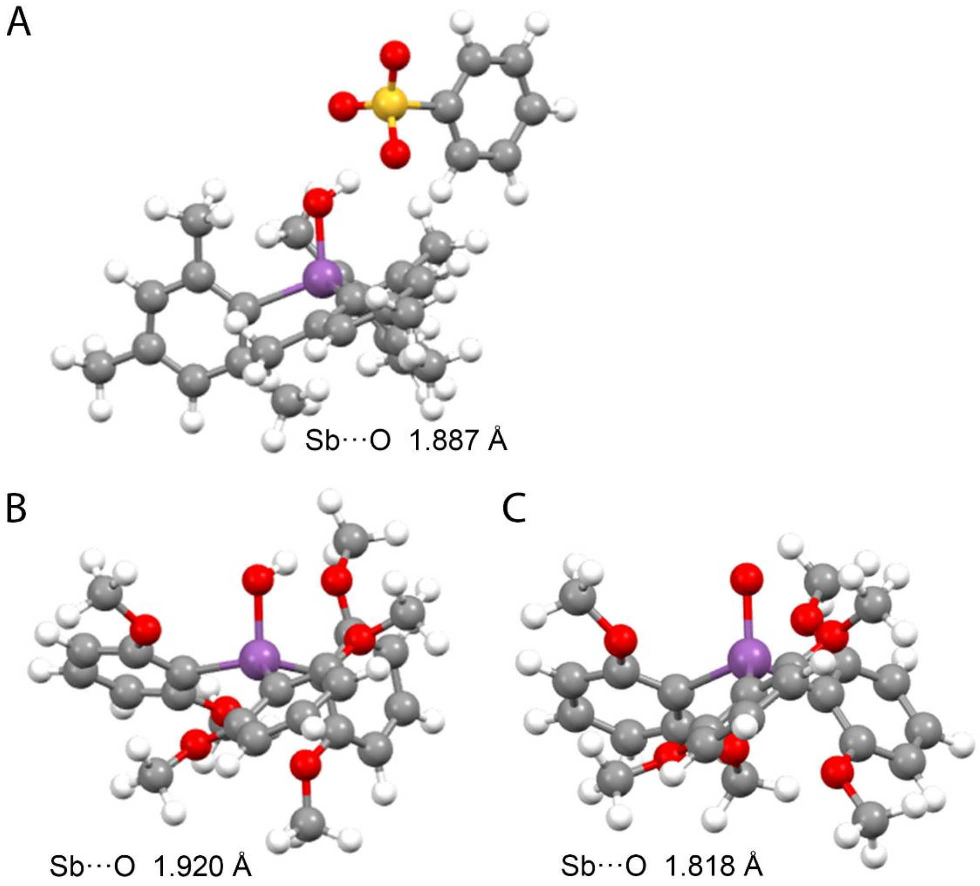

Figure S17. Ball-and-stick representation of the optimized structures (PBE0/def2-TZVPP) of (A) hydroxytrimesitylstibonium benzenesulfonate (**1),** (B) hydroxytris(2,6-dimethoxyphenyl)stibonium cation, and (C) tris(2,6-dimethoxyphenyl)stibine oxide. Color code: O red, Sb purple, C grey, H white, S yellow.

Table S1. Crystallographic details for **1**-**3**.

Compound	**1**	**2**	**3**·C_5H_{12}
Empirical formula	$C_{33}H_{39}O_4SSb$	$C_{28}H_{34}F_3O_4SSb$	$C_{64}H_{58}BF_{24}OSb$
Formula weight	653.45	645.36	1431.66
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbca*	$P2_1/n$	$P\bar{1}$
a (Å)	16.62251(11)	10.4609(2)	12.7443(4)
b (Å)	16.92326(15)	22.0134(4)	13.0965(4)
c (Å)	21.21101(15)	12.4071(2)	20.1296(7)
α (°)			76.697(3)
β (°)		95.2150(10)	79.142(3)
γ (°)			78.266(3)
Volume (Å^3)	5966.81(8)	2845.28(9)	3165.73(19)
Z	8	4	2
ρ_{calc} (Mg/m^3)	1.455	1.507	1.502
Crystal size (mm^3)	0.19 × 0.14 × 0.07	0.10 × 0.07 × 0.06	0.40 × 0.14 × 0.08
θ range (°)	1.967 to 38.084	2.163 to 31.113	2.385 to 25.027
Reflections collected	129747	67191	70027
Independent reflections	15556	7972	11179
Parameters	383	383	956
Completeness	100	100	99.9
R_{int}	0.0251	0.0429	0.0799
R_1 (I > 2σ)	0.0209	0.0291	0.0517
R_1 (all data)	0.0268	0.0377	0.0600
wR_2 (I > 2σ)	0.0563	0.0709	0.1342
wR_2 (all data)	0.0590	0.0734	0.1399
Goodness of fit, *S*	1.028	1.068	1.022

Table S2. Cartesian coordinates (Å) of the optimized (PBE0/def2-TZVPP) structure of hydroxytrimesitylstibonium benzenesulfonate (**1**).

Sb	3.142248	1.022823	3.285938
O	1.940629	2.353603	3.873714
C	2.112749	-0.8414	3.241118
C	2.735643	-1.87183	2.524078
C	1.999472	-3.01099	2.216246
C	0.671309	-3.14765	2.590548
C	0.110844	-2.14583	3.374666
C	0.800768	-0.98789	3.717777
C	4.169828	-1.8289	2.07734
C	-0.13859	-4.32964	2.154249
C	0.111853	0.036624	4.570065
C	4.653352	1.122958	4.785148
C	4.846585	0.101458	5.733854
C	5.687909	0.364751	6.804828
C	6.337659	1.579905	6.971231
C	6.136649	2.560676	6.013419
C	5.297546	2.362755	4.92015
C	4.222149	-1.26212	5.689552
C	7.225736	1.78876	8.15689
C	5.096733	3.485983	3.950541
C	3.52818	1.251832	1.2021
C	4.794987	1.163257	0.6146
C	4.874482	1.066362	-0.77399
C	3.746215	1.049036	-1.57788
C	2.506291	1.173759	-0.96609
C	2.360332	1.282822	0.41059
C	6.093564	1.160888	1.366608
C	3.839702	0.892292	-3.06332
C	0.971375	1.451904	0.944758
H	2.480161	-3.80763	1.65663
H	-0.90676	-2.26223	3.733499
H	4.62548	-2.81458	2.187294
H	4.26169	-1.53609	1.02923
H	4.781721	-1.13612	2.66118
H	-0.70872	-4.75563	2.982039
H	-0.85956	-4.03061	1.388958
H	0.488569	-5.11215	1.726688
H	-0.29892	0.854351	3.973675
H	-0.7082	-0.42657	5.11849
H	0.786392	0.501537	5.289563
H	5.834128	-0.41538	7.545128
H	6.628227	3.521563	6.119089
H	4.650023	-1.88167	6.476922
H	3.141247	-1.23177	5.844302
H	4.400877	-1.77112	4.743188
H	7.598626	2.811144	8.214404
H	6.685848	1.56576	9.080313
H	8.087231	1.117563	8.118239
H	4.120437	3.963405	4.071985
H	5.852866	4.258096	4.086677
H	5.163784	3.154352	2.911342
H	5.855272	0.97566	-1.23049
H	1.609897	1.173274	-1.57787
H	6.595863	2.12566	1.254026
H	5.985015	0.975507	2.435536
H	6.766558	0.402407	0.963289
H	3.11924	0.154601	-3.42021
H	3.605547	1.832693	-3.56909
H	4.835269	0.573111	-3.37313
H	0.786429	0.885137	1.856235
H	0.752135	2.501849	1.170829
H	0.247279	1.107416	0.206866
S	1.014239	5.380614	2.215957
O	2.164857	4.541768	2.659325
O	0.62271	6.368265	3.188275
O	-0.05558	4.561479	1.679553
C	1.678773	6.269582	0.817506
C	1.31884	7.594661	0.619625
C	1.764413	8.269714	-0.50955
C	2.580076	7.628105	-1.42964
C	2.94423	6.303841	-1.22336
C	2.493437	5.623478	-0.10315
H	0.69552	8.082703	1.358005
H	1.472385	9.300884	-0.67109
H	2.936357	8.157804	-2.30554
H	3.581852	5.798756	-1.93956
H	2.776327	4.592112	0.065765
H	1.97599	3.246033	3.350854

Table S3. Cartesian coordinates (Å) of the optimized (PBE0/def2-TZVPP) structure of the hydroxytrimesitylstibonium cation.

Sb	3.278115	0.832941	3.289304
O	2.120456	2.27066	3.860266
C	2.156932	-0.96325	3.266774
C	2.704367	-1.98792	2.485104
C	1.890274	-3.05735	2.134052
C	0.560635	-3.12496	2.52945
C	0.083317	-2.13818	3.385363
C	0.853121	-1.04973	3.775652
C	4.131151	-1.99311	2.020236
C	-0.33914	-4.2159	2.04412
C	0.248793	-0.04698	4.713095
C	4.726153	1.114401	4.791972
C	4.93148	0.131903	5.776806
C	5.705731	0.479221	6.872653
C	6.281644	1.735062	7.018488
C	6.085109	2.665615	6.008342
C	5.309875	2.38756	4.888153
C	4.383383	-1.26282	5.731647
C	7.09005	2.043823	8.236689
C	5.120996	3.460934	3.858803
C	3.588934	1.16853	1.216088
C	4.847512	1.081953	0.608894
C	4.908777	1.085134	-0.78455
C	3.774646	1.15184	-1.57691
C	2.541993	1.261219	-0.94263
C	2.417501	1.276005	0.437045
C	6.151113	0.97242	1.344579
C	3.846423	1.10328	-3.06829
C	1.029493	1.43239	0.991234
H	2.305543	-3.85442	1.526087
H	-0.92989	-2.21397	3.766577
H	4.573858	-2.97801	2.179403
H	4.217447	-1.7568	0.957364
H	4.765124	-1.28527	2.56361
H	-0.94389	-4.62938	2.852801
H	-1.03213	-3.81841	1.296987
H	0.22056	-5.02666	1.579441
H	-0.35215	0.695354	4.180003
H	-0.4213	-0.55296	5.408681
H	0.989408	0.49913	5.294798
H	5.866341	-0.26443	7.645565
H	6.538287	3.646982	6.091503
H	4.865358	-1.86802	6.497492
H	3.307256	-1.29347	5.921437
H	4.563565	-1.75119	4.774015
H	7.480448	3.060646	8.224144
H	6.480758	1.918717	9.134957
H	7.933919	1.356713	8.326082
H	4.135791	3.922739	3.952276
H	5.866048	4.245313	3.981129
H	5.217781	3.081074	2.838856
H	5.881992	1.005744	-1.25792
H	1.64177	1.325945	-1.54557
H	6.734505	1.887407	1.215036
H	6.046037	0.806223	2.417499
H	6.750569	0.156165	0.938053
H	3.113335	0.400578	-3.46667
H	3.612163	2.080741	-3.49797
H	4.833291	0.80134	-3.41737
H	0.844521	0.844102	1.891134
H	0.806379	2.483863	1.202843
H	0.295207	1.100988	0.257847
H	1.479116	2.524319	3.19183

Table S4. Cartesian coordinates (Å) of the optimized (PBE0/def2-TZVPP) structure of trimesitylstibine oxide.

Sb	3.050493	1.022806	3.357373
O	1.916347	2.359928	3.871074
C	2.072296	-0.89038	3.256592
C	2.713545	-1.94243	2.585681
C	1.985096	-3.07959	2.253372
C	0.637487	-3.20146	2.561958
C	0.047505	-2.18099	3.293697
C	0.733142	-1.02298	3.654432
C	4.166251	-1.9107	2.205356
C	-0.15946	-4.38958	2.114244
C	-0.01332	0.004419	4.457467
C	4.659169	1.116676	4.778315
C	4.859598	0.142023	5.769083
C	5.751284	0.420816	6.79709
C	6.443573	1.619688	6.883428
C	6.219358	2.570621	5.900271
C	5.327343	2.348846	4.855327
C	4.155169	-1.18251	5.814672
C	7.392025	1.855015	8.017192
C	5.068129	3.457807	3.879907
C	3.523771	1.204205	1.257074
C	4.793375	1.11917	0.675644
C	4.898931	1.103082	-0.71646
C	3.788447	1.166238	-1.54032
C	2.541777	1.287621	-0.94118
C	2.380219	1.306431	0.437362
C	6.079277	1.035777	1.448072
C	3.904667	1.103355	-3.03144
C	0.97676	1.387386	0.96694
H	2.486026	-3.88725	1.727894
H	-0.99012	-2.27896	3.599638
H	4.602419	-2.90719	2.292887
H	4.30608	-1.57427	1.17525
H	4.754872	-1.24739	2.842682
H	-0.73312	-4.82165	2.937053
H	-0.87702	-4.09906	1.342595
H	0.478792	-5.16702	1.69366
H	-0.75087	0.519447	3.835563
H	-0.55682	-0.4876	5.266734
H	0.629473	0.782622	4.864788
H	5.896213	-0.32723	7.570562
H	6.729112	3.527184	5.953485
H	4.537808	-1.77848	6.643054
H	3.078003	-1.06794	5.957923
H	4.298916	-1.75722	4.900545
H	7.749036	2.885102	8.043032
H	6.909018	1.634478	8.972292
H	8.263953	1.201046	7.936755
H	4.03501	3.806481	3.974212
H	5.738622	4.298762	4.055103
H	5.209712	3.139806	2.844051
H	5.886707	1.020716	-1.1606
H	1.656372	1.354127	-1.56695
H	6.641322	1.968961	1.353209
H	5.936388	0.848667	2.511417
H	6.714177	0.242613	1.047988
H	3.19633	0.382748	-3.44408
H	3.67144	2.070568	-3.48501
H	4.906642	0.808542	-3.34539
H	0.588152	0.384509	1.164749
H	0.908982	1.96499	1.892564
H	0.325979	1.848348	0.223666

Table S5. Cartesian coordinates (Å) of the optimized (PBE0/def2-TZVPP) structure of tris(2,6-dimethoxyphenyl)stibine oxide. Sb-O bond length was calculated to be 1.818 Å.

Sb	-8.64281	-10.2795	-5.23386
O	-8.74433	-12.0119	-4.69099
O	-10.6962	-10.0509	-3.08071
O	-6.75149	-7.81661	-4.11012
O	-7.90985	-8.41434	-7.83712
O	-5.86133	-11.0308	-4.60913
O	-9.3588	-11.6114	-7.76538
O	-10.9925	-7.9838	-5.38784
C	-8.69826	-8.97048	-3.53913
C	-9.7347	-9.2094	-2.64139
C	-9.77926	-8.58611	-1.39676
H	-10.5835	-8.78816	-0.70301
C	-8.77534	-7.69251	-1.06805
H	-8.79582	-7.19976	-0.10322
C	-7.75	-7.40265	-1.95315
H	-6.9842	-6.69454	-1.67158
C	-7.71419	-8.04309	-3.19261
C	-11.4274	-10.7954	-2.13457
H	-11.983	-11.5377	-2.70361
H	-12.1288	-10.1641	-1.5784
H	-10.7559	-11.3019	-1.4365
C	-5.66717	-6.99237	-3.769
H	-4.99481	-7.0137	-4.62439
H	-5.13952	-7.37185	-2.8877
H	-5.98872	-5.96252	-3.58365
C	-6.8459	-9.78715	-6.27889
C	-6.75852	-8.96528	-7.39852
C	-5.52189	-8.72312	-8.00195
H	-5.44397	-8.1003	-8.88141
C	-4.3826	-9.28455	-7.45013
H	-3.42324	-9.0875	-7.91443
C	-4.43633	-10.0771	-6.3153
H	-3.53256	-10.4884	-5.88887
C	-5.6795	-10.3192	-5.73547
C	-7.88505	-7.65902	-9.02216
H	-8.90903	-7.33538	-9.19847
H	-7.54427	-8.26266	-9.86929
H	-7.24495	-6.77695	-8.92246
C	-4.79586	-11.7505	-4.04806
H	-5.23277	-12.3453	-3.24847
H	-4.03323	-11.0831	-3.63349
H	-4.33365	-12.4173	-4.78277
C	-10.2562	-9.85869	-6.55888
C	-10.3922	-10.7609	-7.61392
C	-11.5219	-10.7469	-8.4278
H	-11.6399	-11.4534	-9.23716
C	-12.5046	-9.80128	-8.17812
H	-13.3934	-9.78781	-8.79803
C	-12.3747	-8.86454	-7.16699
H	-13.1455	-8.12176	-7.01555
C	-11.2329	-8.88937	-6.36304
C	-9.44811	-12.6607	-8.69665
H	-8.57148	-13.2834	-8.53418
H	-9.43846	-12.2792	-9.72299
H	-10.3464	-13.2632	-8.53503
C	-12.0797	-7.30846	-4.80412
H	-11.6664	-6.74711	-3.96771
H	-12.8271	-8.01607	-4.43257
H	-12.5552	-6.6093	-5.49943

Table S6. Cartesian coordinates (Å) of the optimized (PBE0/def2-TZVPP) structure of hydroxytris(2,6-dimethoxyphenyl)stibonium cation. Sb-O bond length was calculated to be 1.920 Å.

Sb	-8.43841	-9.91846	-5.20058
O	-8.01304	-11.7622	-4.87398
O	-10.5597	-10.785	-3.3242
O	-7.19992	-7.57466	-3.38274
O	-8.10517	-8.65282	-8.14461
O	-5.57768	-10.066	-4.51269
O	-10.0111	-12.1869	-6.93494
O	-10.042	-7.68411	-5.88052
C	-8.83343	-9.23093	-3.27003
C	-9.86883	-9.88853	-2.59864
C	-10.1433	-9.58315	-1.27083
H	-10.9294	-10.0916	-0.73323
C	-9.38815	-8.60663	-0.64476
H	-9.60082	-8.36251	0.38878
C	-8.39032	-7.91063	-1.30659
H	-7.83981	-7.14134	-0.78707
C	-8.11536	-8.21551	-2.63774
C	-11.5056	-11.6021	-2.65743
H	-11.9315	-12.2537	-3.41644
H	-12.3021	-11.0006	-2.21369
H	-11.0164	-12.2036	-1.88751
C	-6.34567	-6.6551	-2.72762
H	-5.68094	-6.26045	-3.49186
H	-5.76125	-7.15952	-1.95345
H	-6.91312	-5.83292	-2.2851
C	-6.78584	-9.29585	-6.32451
C	-6.87353	-8.85465	-7.64968
C	-5.70753	-8.67426	-8.38845
H	-5.75239	-8.33038	-9.41096
C	-4.48113	-8.92786	-7.79827
H	-3.57902	-8.77127	-8.37687
C	-4.37388	-9.3762	-6.49312
H	-3.40411	-9.57553	-6.06162
C	-5.53945	-9.57641	-5.76223
C	-8.25727	-8.44059	-9.53444
H	-9.32117	-8.54281	-9.73715
H	-7.70732	-9.18767	-10.1092
H	-7.92088	-7.44145	-9.82301
C	-4.42391	-10.7216	-4.01175
H	-4.74041	-11.2463	-3.11416
H	-3.64362	-10.0001	-3.76101
H	-4.04229	-11.4405	-4.74033
C	-10.1438	-9.91153	-6.40862
C	-10.6271	-10.9962	-7.1288
C	-11.6838	-10.8049	-8.01752
H	-12.0902	-11.6292	-8.58482
C	-12.2128	-9.53379	-8.17376
H	-13.036	-9.39307	-8.86305
C	-11.7177	-8.433	-7.48667
H	-12.1377	-7.45055	-7.64977
C	-10.6732	-8.63948	-6.59731
C	-10.2329	-13.2148	-7.88807
H	-9.54889	-14.0199	-7.63226
H	-10.0115	-12.8571	-8.8965
H	-11.2587	-13.5858	-7.83878
C	-10.3741	-6.32447	-6.08525
H	-9.71793	-5.7569	-5.43174
H	-11.4132	-6.12938	-5.811
H	-10.1934	-6.0312	-7.12219
H	-8.61012	-12.3031	-5.40494

Table S7. Energies along the relaxed surface scan of SbO–H bond length of hydroxytrimesitylstibonium benzenesulfonate (**1**).

SbO–H Bond Length (Å)	Energy (E_h)
0.9	-2221.095869
0.952632	-2221.104861
1.005263	-2221.109199
1.057895	-2221.110664
1.110526	-2221.110588
1.163158	-2221.109817
1.215789	-2221.108928
1.268421	-2221.108183
1.321053	-2221.107578
1.373684	-2221.106854
1.426316	-2221.105519
1.478947	-2221.103297
1.531579	-2221.100973
1.584211	-2221.09983
1.636842	-2221.097751
1.689474	-2221.095581
1.742105	-2221.093497
1.794737	-2221.091467
1.847368	-2221.089824
1.9	-2221.088198

Table S8. Estimated proton affinities.

$PhSO_3^-$	270 kcal mol^{-1}
Mes_3SbO	286 kcal mol^{-1}