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Stoichiometry-dependent oxidation of tris(2-methoxyphenyl)antimony with diiodine

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Experimental

The IR spectra were recorded on an IR-Fourier spectrometer Shimadzu IR Affinity-1S in the KBr pellets in the range of 4000–400 cm^{-1}. Elemental analyses for C and H were performed on a Carlo Erba CHNS-O EA 1108 elemental analyzer. Melting points were measured on a SMP 30 instrument. NMR spectra were measured on a Bruker Avance III 500 FT-spectrometer with working frequencies 500.03 and 125.73 MHz for ^{1}H and ^{13}C nuclei, respectively.

Tris(2-methoxyphenyl)stibine 1, solvate with benzene **1**×0.125 C_6H_6**.** *o*-Bromoanisole (60 g, 321 mmol) was added at room temperature to PhLi solution prepared from bromobenzene (63 g, 401 mmol) and lithium metal (7 g, 1 mol) in diethyl ether (250 ml). After 15 min stirring, a solution of $SbCl_3$ (18 g, 78.8 mmol) in Et_2O (100 ml) was added, and this was stirred at room temperature for 30 min. Excess of 2-methoxyphenyllithium was decomposed by addition of water (2 ml). The solvent was removed, benzene was added to the solid residue, and inorganic salts (LiBr and LiCl) were filtered off. The target compound was recrystallized from benzene. Yield 57%, m.p. 179 °C. IR (KBr, cm^{-1}): 3053, 2993, 2956, 2933, 2899, 2831, 1791, 1710, 1571, 1462, 1429, 1290, 1269, 1234, 1174, 1157, 1116, 1053, 1018, 935, 852, 785, 754, 717, 686, 567, 534, 478, 441, 418. Anal. Calcd for $C_{174}H_{174}O_{24}Sb_8$ [8 $C_{21}H_{21}O_3Sb$•C_6H_6]: C, 57.63; H, 4.80. Found: C, 57.58; H, 4.88.

Diiodo[tris(2-methoxyphenyl)]stiborane 2. Compound **1**×0.125 C_6H_6 (0.226 g, 0.5 mmol) was dissolved in benzene (20 ml), followed by addition of molecular iodine (0.127 g, 0.5 mmol). After that, *n*-octane (2 ml) was added, and the solvent was evaporated to ca. 3 ml volume, which resulted in formation of pale yellow crystals of product **2**. Yield 88%, m.p. 175 °C. IR (KBr, cm^{-1}): 3082, 3053, 2993, 2956, 2933, 2899, 2831, 1795, 1710, 1571, 1462, 1429, 1290, 1269, 1234, 1176, 1157, 1116, 1053, 1018, 941, 852, 786, 754, 719, 686, 567, 534, 480, 441, 418. Anal. Calcd for $C_{21}H_{21}O_3I_2Sb$: C, 36.15; H, 3.01. Found: C, 36.07; H, 3.08.

Iodo[tris(2-methoxyphenyl)]stibonium triiodide 3. The procedure was similar to that for **2**, using compound **1**×0.125 C_6H_6 (0.226 g, 0.5 mmol) and molecular iodine (0.254 g, 1.0 mmol) in benzene (50 ml). The mixture was then heated at 80°C for 1 h, cooled and concentrated *in vacuo*. The residue was recrystallized from chloroform to afford product **3** as dark-brown crystals. Yield 91%, m.p. 140 °C. IR (KBr, cm^{-1}): 3055, 3005, 2972, 2937, 2837, 1573, 1471, 1456, 1433, 1298, 1274, 1244, 1176, 1161, 1122, 1043, 1004, 983, 854, 848, 785, 754, 707, 567, 482, 457, 432, 424. Anal. Calcd for $C_{21}H_{21}O_3I_4Sb$: C, 26.51; H, 2.21. Found: C, 26.46; H, 2.25.

Table S1. Crystallographic, experimental and refinement data for structures **1, 2, 3**

Data	Compound **1** ($24\ \mathbf{1} \times 3\ C_6H_6$)	Compound **2**	Compound **3**
Formula	$C_{522}H_{522}O_{72}Sb_{24}$	$C_{21}H_{21}O_3I_2Sb$	$C_{21}H_{21}I_4O_3Sb$
M	10869.37	696.93	970.73
Crystal system	trigonal	triclinic	triclinic
Space group	*R-3*	*P-1*	*P-1*
a, Å	23.266(7)	9.192(8)	11.192(9)
b, Å	23.480(9)	9.415(7)	11.665(13)
c, Å	25.480(9)	15.254(11)	12.320(15)
α, °	90	81.42(4)	63.87(5)
β, °	90	80.42(4)	77.39(5)
γ, °	120	63.30(4)	72.58(4)
V, Å^3	11944(8)	1158.7(16)	1371(3)
Z	1	2	2
$D_{calc,}$ g/cm^3	1.511	1.998	2.304
μ, mm^{-1}	1.404	3.872	5.529
F(000)	5454.0	656.0	868.0
Crystal size, mm^3	0.37 × 0.35 × 0.21	0.3 × 0.23 × 0.14	0.4 × 0.17 × 0.08
2Θ range, °	6.232 – 56.974	5.94 – 65.42	5.592 to 56.994
Index ranges	–31 ≤ *h* ≤ 30, –31 ≤ *k* ≤ 31, –34 ≤ *l* ≤ 34	–13 ≤ *h* ≤ 13, –14 ≤ *k* ≤ 14, –23 ≤ *l* ≤ 23	–15 ≤ *h* ≤ 15, –15 ≤ *k* ≤ 15, –16 ≤ *l* ≤ 16
Reflections collected	77674	73387	63334
Independent reflections (R_{int})	6699 (R_{int} = 0.0434)	8464 (R_{int} = 0.0360)	6918 (R_{int} = 0.0385)
No. of parameters	346	247	269
Goodness-of-fit on F^2	1.127	1.026	1.031
Final R indexes (I > 2σ(I))	R_1 = 0.0315, *w*R_2 = 0.0667	R_1 = 0.0404, *w*R_2 = 0.0972	R_1 = 0.0322, *w*R_2 = 0.0743
Final R indexes [all data]	R_1 = 0.0442, *w*R_2 = 0.0708	R_1 = 0.0650, *w*R_2 = 0.1100	R_1 = 0.0402, *w*R_2 = 0.0784
Largest diff. peak/hole, e/Å^{-3}	0.59/–0.77	1.27/–1.87	1.71/–1.40

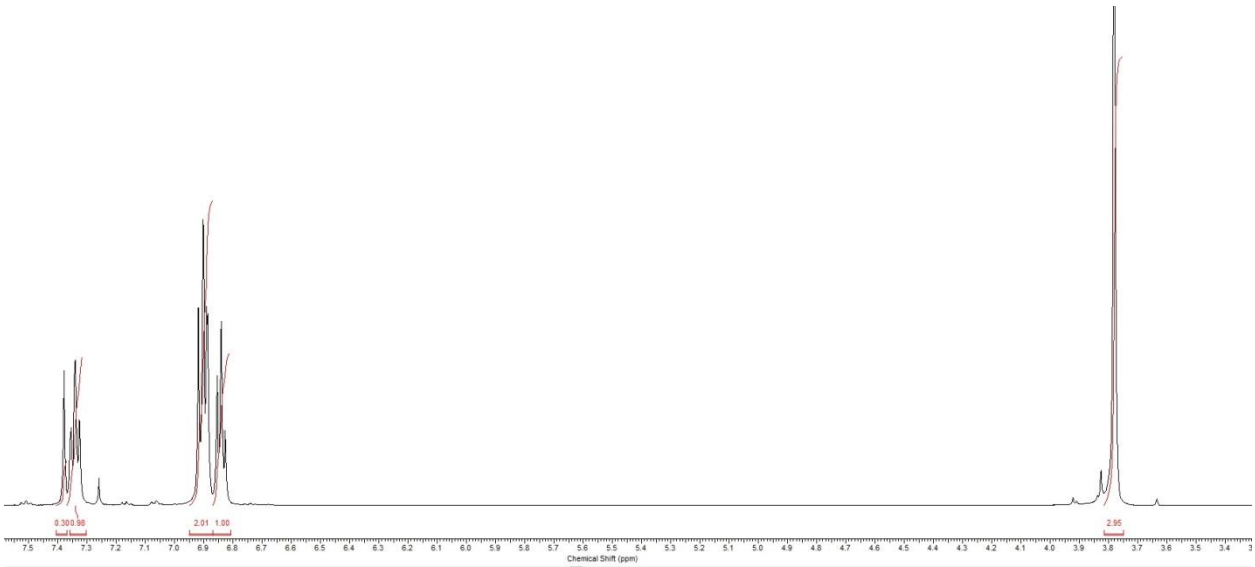

Figure S1. ^{1}H NMR spectrum of compound **1**

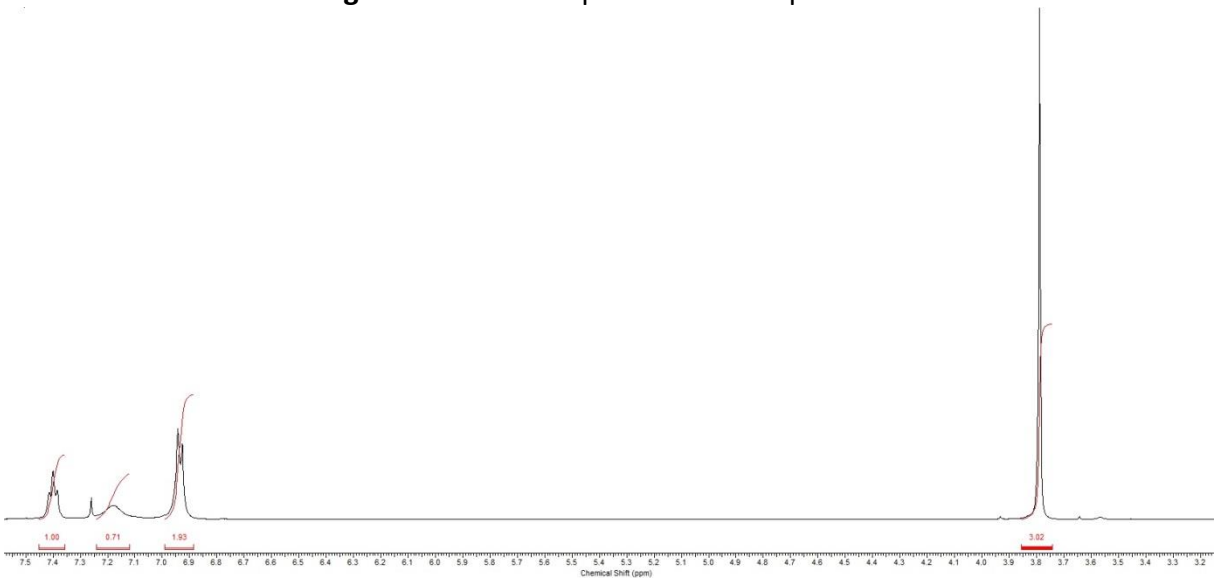

Figure S2. ^{1}H NMR spectrum of compound **2**

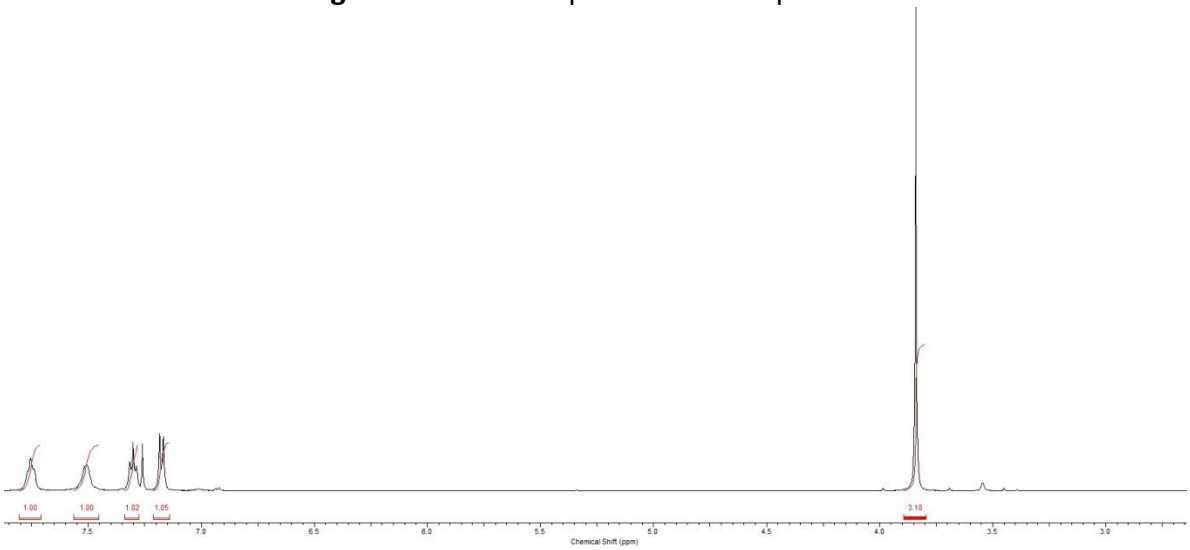

Figure S3. ^{1}H NMR spectrum of compound **3**

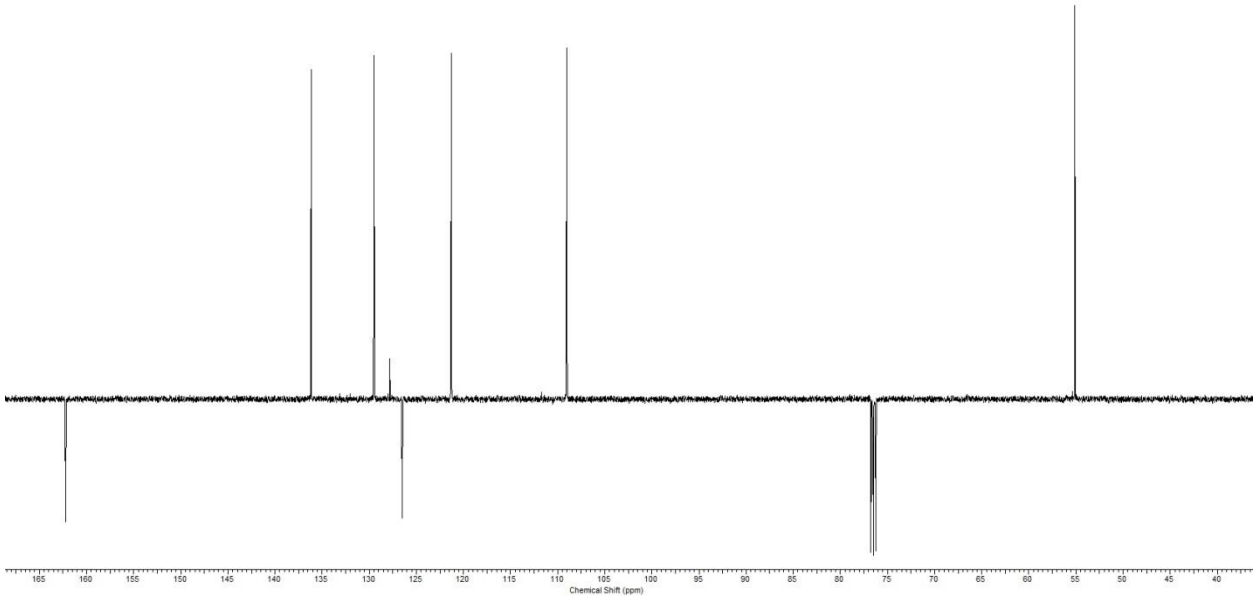

Figure S4. ^{13}C NMR spectrum of compound **1**

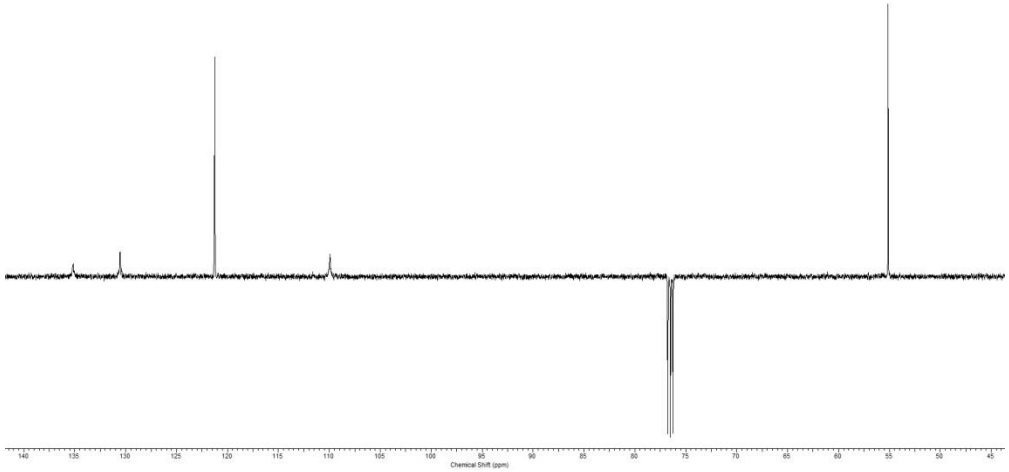

Figure S5. ^{13}C NMR spectrum of compound **2**

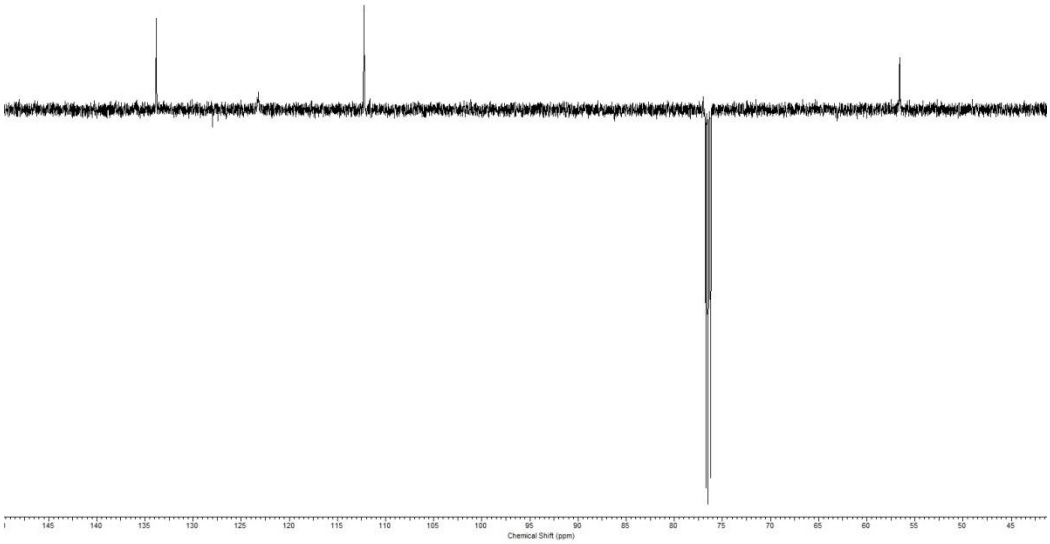

Figure S6. ^{13}C NMR spectrum of compound **3**