Supporting Information

O,S-Heterocyclic Stannylenes: Synthesis and Reactivity

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Experimental Section

All the air and moisture sensitive manipulations were done under a dry N_2 atmosphere using either standard Schlenk or glovebox [Jacomex (GP Concept)-T2 workstation] techniques. Tetrahydrofuran was dried over sodium wire and benzophenone. Dichloromethane and $CDCl_3$ were dried over P_2O_5 and 4 Å molecular sieves, respectively. $SnCl_2$ and InCl were purchased from Alfa Aesar and used as received. Sodium 2-mercaptopyridine-*N*-oxide, $GeCl_2$·dioxane, and $SbCl_3$ were purchased from Aldrich and used as received. Melting points were recorded on a Unitech Sales digital melting point apparatus by sealing the compounds in glass capillaries. Elemental analyses were performed using a PerkinElmer CHN analyzer. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded in $CDCl_3$/DMSO-d_6 on a 300 MHz Bruker DPX-300/400 MHz JEOL NMR spectrometers. The chemical shifts δ are reported in ppm and internally referenced with respect to residual solvent (^{1}H NMR) and solvent (^{13}C NMR) resonances.[S1] $(CH_3)_4Sn$ was used as external reference for ^{119}Sn NMR spectroscopic studies.

Synthesis of (2-mpno)$_2$Sn (2). To a stirred solution of $SnCl_2$ (500 mg, 2.64 mmol) in tetrahydrofuran (150 mL) was added sodium 2-mpno (787 mg, 5.27 mmol) in portions at room temperature and the reaction mixture was further stirred for 24 h. Then, the reaction mixture was filtered through a sintered funnel with celite. All the volatiles were removed from the filtrate under reduced pressure to give compound **2** as a white solid. The diffusion of hexane in the tetrahydrofuran solution of compound **2** afforded single-crystals suitable for X-ray diffraction studies. Yield: 950 mg (2.56 mmol, 97%). Mp: 148 °C (decomp). Anal. Calcd for $C_{10}H_8N_2O_2S_2Sn$ (M = 371.02): C, 32.37; H, 2.17; N, 7.55. Found: C, 32.43; H, 2.19; N, 7.51. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.86 (t, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*), 7.15 (t, $^3J_{HH}$ = 7.5 Hz, 8.1 Hz, 1H, C*H*), 7.55 (d, $^3J_{HH}$ = 8.1 Hz, 1H, C*H*), 8.14 (d, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*). ^{13}C{^{1}H} NMR (75 MHz,

$CDCl_3$): δ 117.90 (*C*H), 129.60 (*C*H), 129.94 (*C*H), 138.29 (*C*H), 159.08 (*C*). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −261.0.

Synthesis of (2-mpno)SnCl (3). To a stirred solution of $SnCl_2$ (200 mg, 1.05 mmol) in tetrahydrofuran (100 mL) was added sodium salt of 2-mpno (157 mg, 1.05 mmol) in portions and the reaction mixture was stirred for 24 h. Then, the reaction mixture was filtered through a sintered funnel with celite. All the volatiles were removed from the filtrate under reduced pressure to give compound **3** as a white solid. The suitable single-crystals of compound **3** were obtained from its tetrahydrofuran solution by slow evaporation method. Yield: 283 mg (1.01 mmol, 96%). Mp: 202 °C. Anal. Calcd for $C_5H_4ClNOSSn$ (M = 280.32): C, 21.42; H, 1.44; N, 5.00. Found: C, 21.45; H, 1.43; N, 4.98. ^1H NMR (400.13 MHz, DMSO-D_6): δ 7.12 (t, $^3J_{HH}$ = 6.0 Hz, 1H, C*H*), 7.42 (t, $^3J_{HH}$ = 6.0 Hz, 1H, C*H*), 7.69 (d, $^3J_{HH}$ = 6.0 Hz, 1H, C*H*), 8.45 (d, $^3J_{HH}$ = 6.0 Hz, 1H, C*H*). $^{13}C\{^1H\}$ NMR (100.63 MHz, DMSO-D_6): δ 119.65 (*C*H), 129.52 (*C*H), 131.62 (*C*H), 139.20 (*C*H). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, DMSO-D_6): δ −288.6.

Synthesis of [(2-mpno)SbCl]$_2$O (4). To a stirred solution of compound **2** (200 mg, 0.54 mmol) in tetrahydrofuran (80 mL) was added a solution of $SbCl_3$ (123 mg, 0.54 mmol) in tetrahydrofuran (15 ml) and the reaction mixture was further stirred for 5 h. Then, the solvent was removed under reduced pressure to give a white residue. The residue was dissolved in dichloromethane and filtered through a sintered funnel with celite. All the volatiles were removed from the filtrate under reduced pressure to get an analytically pure sample of compound **4** as a white solid. Hexane diffusion in the tetrahydrofuran solution of compound **4** gave its suitable single-crystals. Yield: 140 mg (0.24 mmol, 89%). Mp: 207 °C. Anal. Calcd for $C_{10}H_8Cl_2N_2O_3S_2Sb_2$ (M = 582.74): C, 20.61; H, 1.38; N, 4.81. Found: C, 20.68; H, 1.39; N, 4.79. ^1H NMR (300 MHz, $CDCl_3$): δ 7.07 (broad, 1H, C*H*), 7.41 (t, $^3J_{HH}$ = 7.5 Hz, 7.2 Hz, 1H, C*H*),

7.69 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C*H*), 8.24 (d, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 132.45 (*C*H), 138.38 (*C*H).

Synthesis of (2-mpno)GeCl (5). To a stirred solution of compound **2** (100 mg, 0.27 mmol) in tetrahydrofuran (50 mL) was added a solution of $GeCl_2$.(1,4-dioxane) (124mg, 0.54 mmol) in tetrahydrofuran (10 ml) and the reaction mixture was further stirred for 2 h. Then, the solvent was removed under reduced pressure to give a white residue. The residue was dissolved in dichloromethane and filtered through a sintered funnel with celite. All the volatiles were removed from the filtrate under reduced pressure to afford an analytically pure sample of compound **5** as a white solid. Tetrahydrofuran solution of compound **5** yielded its single-crystal through slow evaporation of the solvent. Yield: 61 mg (0.26 mmol, 96%). Mp: 134 °C (decomp). Anal. Calcd for $C_5H_4ClGeNOS$ (*M* = 234.25): C, 25.64; H, 1.72; N, 5.98. Found: C, 25.68; H, 1.72; N, 5.97. ^1H NMR (300 MHz, $CDCl_3$): δ 7.17 (t, $^3J_{HH}$ = 6.9 Hz, 6.2 Hz, 1H, C*H*), 7.58 (t, $^3J_{HH}$ = 7.2 Hz, 8.4 Hz, 1H, C*H*), 7.82 (d, $^3J_{HH}$ = 8.4 Hz, 1H, C*H*), 8.34 (d, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 119.27 (*C*H), 128.39 (*C*H), 134.19 (*C*H), 137.31 (*C*H), 156.63 (*C*).

Synthesis of (2-mpno)InCl·2thf (6). To a stirred solution of compound **5** (100 mg, 0.36 mmol) in tetrahydrofuran (40 mL) was added InCl (54 mg, 0.36 mmol) in portions and the reaction mixture was stirred for 3 h. Then, the reaction mixture was filtered through a sintered funnel with celite. All the volatiles were removed from the filtrate under reduced pressure to give compound **6** as a white solid. Suitable single-crystals of compound **6** were obtained in a similar manner as in case of compound **5**. Yield: 155 mg (0.34 mmol, 95%). Mp: 217 °C (decomp). Anal. Calcd for $C_{13}H_{20}Cl_2InNO_3S$ (*M* = 456.09): C, 34.23; H, 4.42; N, 3.07. Found: C, 34.28; H, 4.45; N, 3.08. ^1H NMR (300 MHz, $CDCl_3$): δ 1.89-1.93 (m, 8H, $O(CH_2CH_2)_2$), 3.90 (t, $^3J_{HH}$ = 6.3 Hz, 8H,

O(CH_2CH_2)$_2$), 7.05-7.10 (m, 1H, C*H*), 7.39 (t, $^3J_{HH}$ = 7.5 Hz, 8.1 Hz, 1H, C*H*), 7.69-7.72 (m, 1H, C*H*), 8.51 (d, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 25.58 (O(CH$_2$*C*H$_2$)$_2$), 69.02 (O(*C*H$_2$CH$_2$)$_2$), 119.45 (*C*H), 130.13 (*C*H), 132.15 (*C*H), 139.17 (*C*H), 157.01 (*C*).

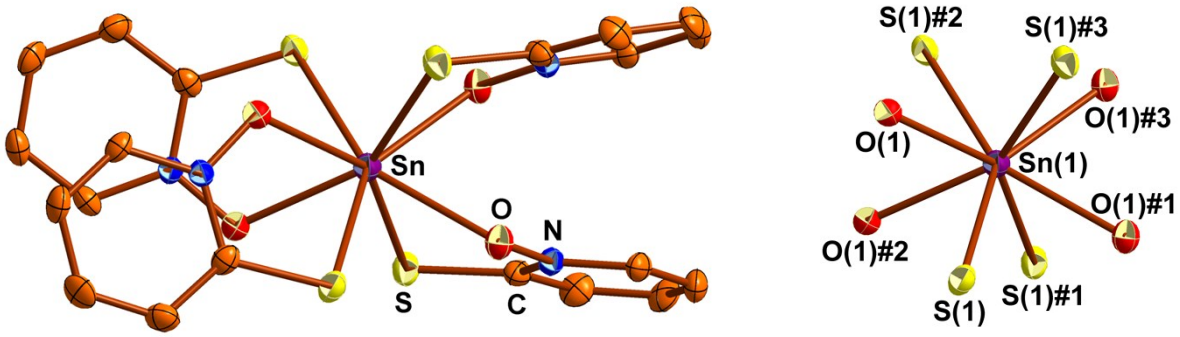

Figure S1. Molecular structure of compound **7** (left) and coordination environment around tin atom in compound **7** (right). Selected bond lengths (Å) and angles (°): Sn(1)-O(1) 2.383(5), Sn(1)-S(1) 2.540(2); O(1)-Sn(1)-S(1) 71.6(1), O(1)#2-Sn(1)-O(1) 76.1(2), O(1)#1-Sn(1)-O(1) 128.3(2), S(1)#1-Sn(1)-O(1) 147.0(1), S(1)#2-Sn(1)- O(1) 78.2(1), S(1)#3-Sn(1)-O(1) 71.4(1), S(1)#1-Sn(1)-S(1) 96.2(1), S(1)#2-Sn(1)-S(1) 141.5(1). Equivalent atoms (#) are symmetry (y,1/2-x,1/2-z) generated.

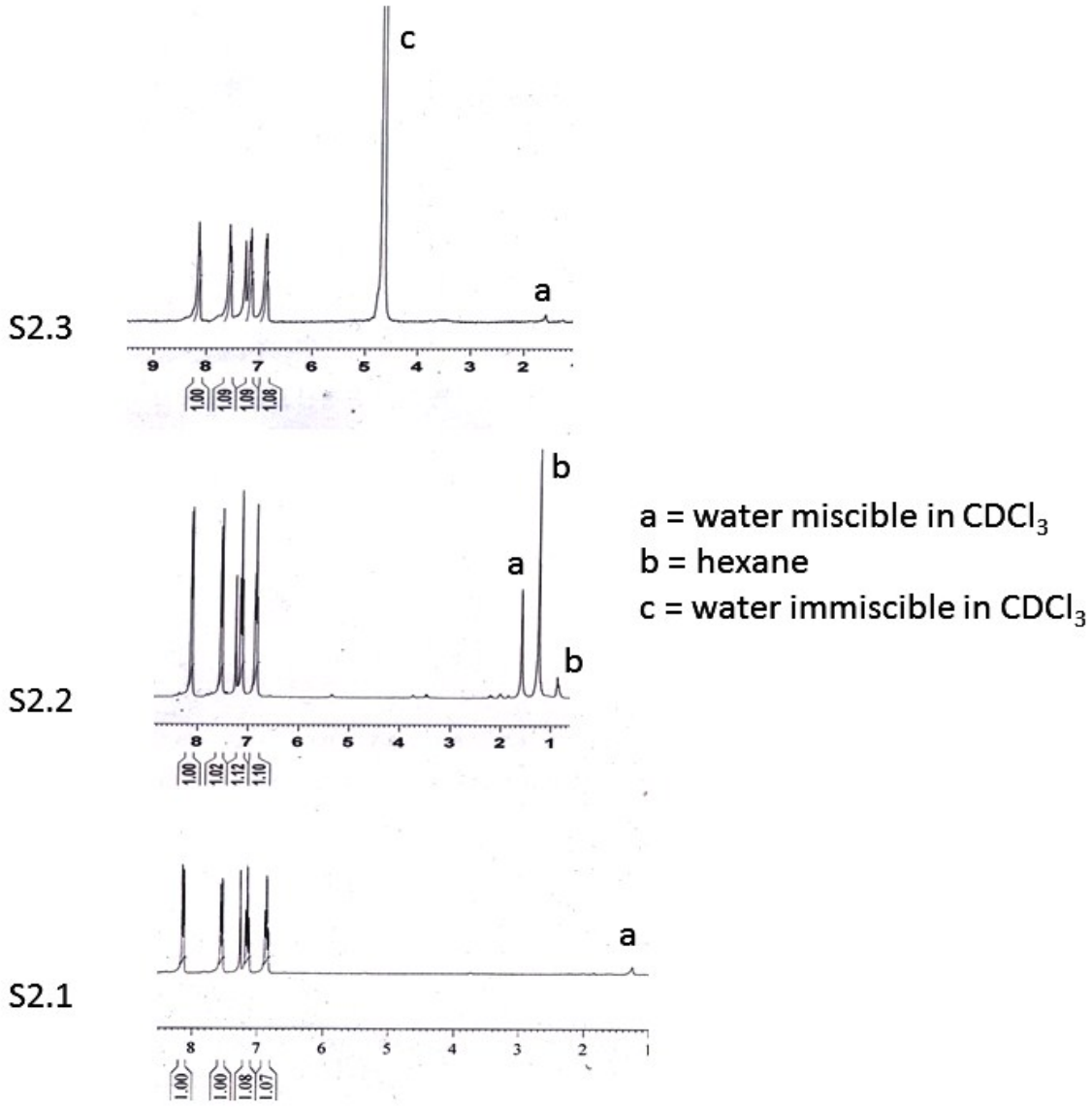

Figure S2. ^{1}H NMR spectrum of compound **2** in: (1) Dry $CDCl_3$, (2) Normal $CDCl_3$ after 24 h, and (3) Normal $CDCl_3$ and D_2O.

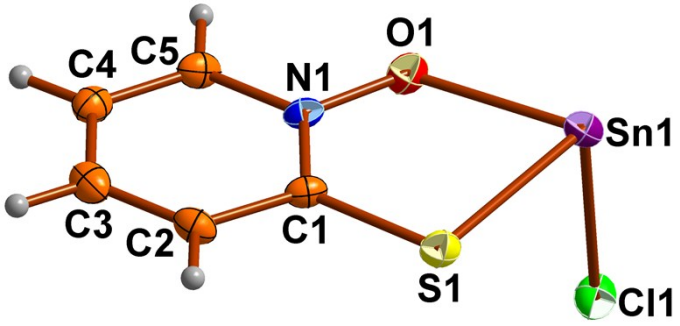

Figure S3. Molecular structure of compound **3**. Selected bond lengths (Å) and angles (°): Sn(1)-O(1) 2.181(4), Sn(1)-S(1) 2.547(2), Sn(1)-Cl(1) 2.567(2); O(1)-Sn(1)-S(1) 77.3(1), O(1)-Sn(1)-Cl(1) 91.2(1), S(1)-Sn(1)-Cl(1) 93.0(1).

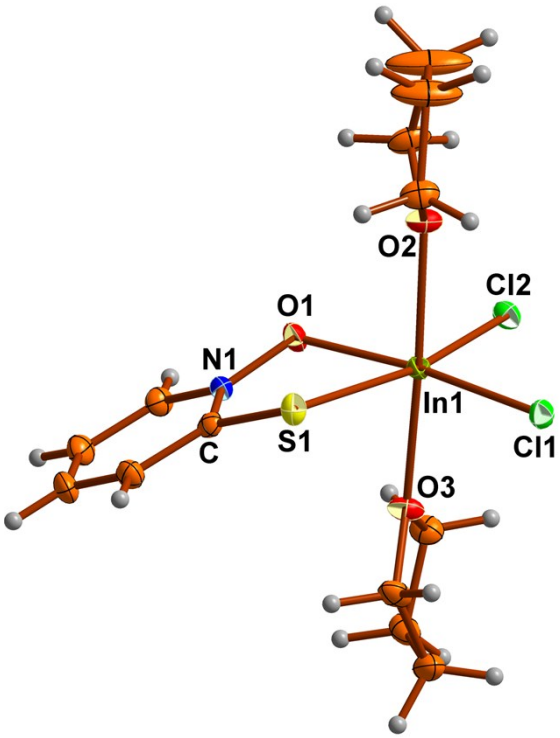

Figure S4. Molecular structure of compound **6**. Selected bond lengths (Å) and angles (°): In(1)-O(1) 2.174(2), In(1)-O(2) 2.277(2), In(1)-O(3) 2.262(2), In(1)-S(1) 2.530(1), In(1)-Cl(1) 2.428(1), In(1)-Cl(2) 2.417(1); O(1)-In(1)-S(1) 77.9(1), Cl(1)-In(1)-Cl(2) 99.9(1), O(1)-In(1)-Cl(2) 88.3(1), Cl(1)-In(1)-S(1) 94.0(1), O(3)-In(1)-O(2) 174.8(1).

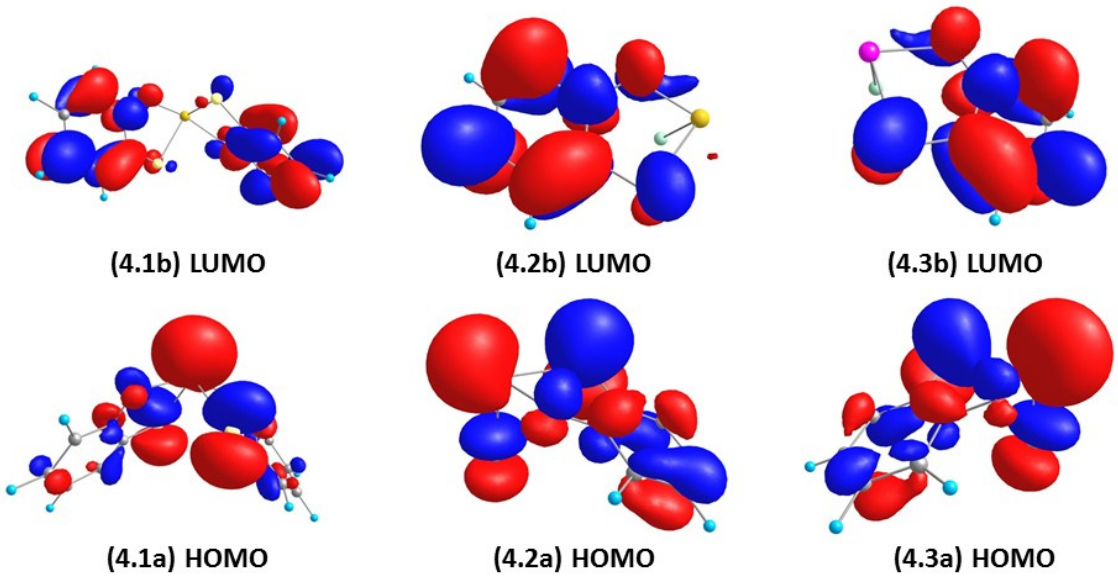

Figure S5. Molecular orbitals of compounds **2** (4.1a-b), **3** (4.2a-b), and **5** (4.3a-b).

X-ray data collection for compounds 2-7

Single crystals of compounds **2-7** were coated with a cryprotectant and mounted on a glass fiber. The data were collected at low temperature on a Bruker SMART APEX CCD diffractometer with a 3-axis goniometer.[S2] SAINT and SADABS software were used for data integration and empirical absorption correction, respectively.[S3] The structures of these compounds were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL.[S4] All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated using a riding model and refined isotropically. Detailed crystallographic data for these compounds are given in Table S1.

Table S1. Crystal data and refinement parameters for compounds 2-7

	2	**4**	**5**	**3**	**6**	**7**
empirical formula	C_{10} H_8 N_2 O_2 S_2 Sn	C_{10} H_8 Cl_2 N_2 O_3 S_2 Sb_2	C_5 H_4 Cl Ge N O S	C_5 H_4 Cl N O S Sn	C_{13} H_{20} Cl_2 In N O_3 S	C_{20} H_{16} N_4 O_4 S_4 Sn
Fw	371.01	582.72	234.21	280.31	456.08	623.32
temperature, k	150(2)	175(2)	100(2)	150 (2)	100(2)	200(2)
wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	triclinic	monoclinic	triclinic	monoclinic	Tetragonal
space group	*P*-1	*P*-1	$P2_1/c$	*P*-1	$P2_1/c$	$P4_2/n$
unit cell dimens	a = 7.4019(10) Å	a = 9.4585(16) Å	a = 6.4885(19) Å	a = 5.9142(14) Å	a = 12.6099(16) Å	a = 9.2261(11) Å
	b = 7.5564(10) Å	b = 10.3141(18) Å	b = 13.237(4) Å	b = 7.4252(18) Å	b = 9.8845(13) Å	b = 9.2261(11) Å
	c = 11.4734(15) Å	c = 10.6648(18) Å	c = 9.119(3) Å	c = 9.479(2) Å	c = 14.1146(17) Å	c = 12.741(3) Å
	α = 88.006(2)°	α = 82.554(3)°		α = 79.270(4)°		
	β = 74.539(2)°	β = 64.039(3)°	β = 102.608(5)°	β = 72.376(4)°	β = 99.243(2)°	
	γ = 79.608(2)°	γ = 63.591(3)°		γ = 82.595(5)°		
volume, Å^3	608.30(14)	835.1(2)	764.3(4)	388.62(16)	1736.4(4)	1084.5(4)
Z	2	2	4	2	4	2
density (calcd), Mg/m^3	2.026	2.317	2.035	2.395	1.745	1.909
absorption coefficient, mm^{-1}	2.432	3.812	4.554	3.825	1.796	1.602
F(000)	360.0	548.0	456.0	264.0	912.0	620.0
cryst size, mm^3	0.438 x 0.355 x 0.299	0.420 x 0.306 x 0.255	0.476 x 0.402 x 0.353	0.449 x 0.357 x 0.275	0.513 x 0.391 x 0.322	0.488 x 0.415 x 0.367
θ range for data collection, deg	2.74 to 25.00	2.13 to 24.99	2.76 to 24.99	2.28 to 24.98	2.63 to 25.00	2.73 to 24.95
limiting indices	$-8 \le h \le 8$,	$-11 \le h \le 11$,	$-7 \le h \le 7$,	$-7 \le h \le 7$,	$-14 \le h \le 14$,	$-10 \le h \le 10$,
	$-8 \le k \le 8$,	$-12 \le k \le 12$,	$-15 \le k \le 15$,	$-8 \le k \le 8$,	$-9 \le k \le 11$,	$-10 \le k \le 10$,
	$-13 \le l \le 13$	$-12 \le l \le 12$	$-10 \le l \le 10$	$-11 \le l \le 11$	$-13 \le l \le 16$	$-14 \le l \le 15$
no. of reflns collected	3118	4294	3888	1936	8580	5581
no. of indep reflns	2139 (R_{int} = 0.0166)	2937 (R_{int} = 0.0215)	1347 (R_{int} = 0.0351)	1360 (R_{int} = 0.0207)	3058 (R_{int} = 0.0243)	953 (R_{int} = 0.0627)
abs corr	semiempirical	semiempirical	semiempirical	semiempirical	semiempirical	Semiempirical
refinement method	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix	full-matrix
	least-squares on F^2	least-squares on F^2	least-squares on F^2	least-squares on F^2	least-squares on F^2	least-squares on F^2
no. of data / restraints / params	2139 / 0 / 154	2937 / 0 / 190	1342 / 0 / 91	1360 / 0 / 91	3058 / 0 / 190	953 / 0 / 75
goodness-of-fit on F^2	1.058	1.049	1.140	1.069	1.026	1.282
final R indices [$I>2\sigma(I)$]	R_1 = 0.0244, wR_2 = 0.0569	R_1 = 0.0376, wR_2 = 0.0888	R_1 = 0.0513, wR_2 = 0.1327	R_1 = 0.0346, wR_2 = 0. 0.0814	R_1 = 0.0242, wR_2 = 0.0560	R_1 = 0.0665, wR_2 = 0.1297
R indices (all data)	R_1 = 0.0260, wR_2 = 0.0578	R_1 = 0.0478, wR_2 = 0.0934	R_1 = 0.0546, wR_2 = 0.1348	R_1 = 0.0398, wR_2 = 0.0833	R_1 = 0.0278, wR_2 = 0.0576	R_1 = 0.0777, wR_2 = 0.1345
largest diff peak and hole, e Å^{-3}	0.731 and −0.491	1.554 and −0.876	1.203 and −0.823	1.132 and −0.913	0.644 and −0.434	0.844 and −0.965

Computational details

The Gaussian-09 program was used to perform the DFT calculations on compounds **2**, **3**, and **5**.[S5] The geometry optimizations were performed on these compounds (**2**, **3**, and **5**) at B3LYP level of theory using LANL2DZ basis set for tin and germanium, and TZVP basis set for rest of the atoms (for coordinates of optimized geometries of these compounds, see the Appendix). The frequency calculations were carried out for on the optimized geometries of these compounds at the same level of theory to characterize the stationary points as minima. The input coordinates were taken from crystallographic information files (CIFs) of these compounds. The NBO analysis was performed on the optimized geometry of compound **2** at the same level of theory.[S6] The Chemcraft software was used for the graphical visualization of molecular orbitals (www.chemcraftprog.com).

Coordinates of the optimized geometries of:

Compound **2**

Sn	-0.000028000	1.696350000	-0.000066000
S	0.933706000	-0.084483000	1.742570000
S	-0.933563000	-0.084810000	-1.742465000
O	-2.020665000	1.028027000	0.780852000
O	2.020569000	1.027886000	-0.781089000
N	-2.644473000	-0.069919000	0.363007000
N	2.644433000	-0.069965000	-0.363064000
C	-3.666696000	-0.527658000	1.130518000
H	-3.830411000	0.050743000	2.026322000
C	-4.404686000	-1.620646000	0.756523000
H	-5.213076000	-1.955513000	1.390574000
C	-3.037319000	-1.804017000	-1.202217000

H	-2.759914000	-2.290282000	-2.126354000
C	4.083263000	-2.272324000	0.439314000
H	4.647576000	-3.136753000	0.763955000
C	-2.280039000	-0.684804000	-0.811233000
C	2.280088000	-0.684647000	0.811306000
C	3.037383000	-1.803803000	1.202414000
H	2.760053000	-2.289909000	2.126657000
C	3.666629000	-0.527802000	-1.130542000
H	3.830295000	0.050450000	-2.026452000
C	4.404642000	-1.620738000	-0.756428000
H	5.213030000	-1.955659000	-1.390453000
C	-4.083238000	-2.272418000	-0.439101000
H	-4.647573000	-3.136866000	-0.763656000

Compound **3**

Sn	1.670495000	0.114021000	-0.436443000
S	-0.146138000	1.850180000	0.332365000
Cl	1.559667000	-1.238127000	1.614003000
N	-1.314775000	-0.422966000	-0.574540000
O	-0.146148000	-0.709442000	-1.174698000
C	-1.477131000	0.740104000	0.132393000
C	-2.312143000	-1.324972000	-0.743587000
H	-2.025363000	-2.197113000	-1.309902000
C	-3.558212000	-1.099969000	-0.220611000
H	-4.334479000	-1.837036000	-0.366166000
C	-3.783445000	0.079726000	0.498079000
H	-4.755991000	0.283249000	0.926557000
C	-2.755068000	0.978531000	0.668097000
H	-2.896471000	1.890901000	1.228910000

Compound **5**

Ge	-1.807671000	0.074012000	-0.563144000
S	-0.199937000	1.841628000	0.090962000
Cl	-1.861452000	-1.012393000	1.483180000
O	-0.129900000	-0.800709000	-1.153428000
N	1.023973000	-0.469853000	-0.537265000
C	2.021404000	-1.383462000	-0.588773000
H	1.752061000	-2.307467000	-1.075921000
C	1.160315000	0.755366000	0.057231000
C	3.451881000	0.144674000	0.553637000
H	4.411432000	0.391931000	0.988298000
C	2.419423000	1.054040000	0.604813000
H	2.544013000	2.017168000	1.077770000
C	3.250428000	-1.101527000	-0.052077000
H	4.032333000	-1.845274000	-0.099706000

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