# Electronic Supplementary Information: Synthesis of chelating diamidotin(IV) compounds from oxidation of Sn(II) stannylenes and directly from Sn(IV) starting materials

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Table ESI 1. Additional crystallographic information

| Compound | **1** | **2** | **3** | **4** | **5 monoclinic** | **5 triclinic** |
|---|---|---|---|---|---|---|
| Colour, habit | Colourless block | Colourless plate | Colourless prism | Yellow block | Pale yellow block | Pale yellow plate |
| Size/mm | 0.30×0.20×0.05 | 0.30×0.20×0.05 | 0.25×0.25×0.05 | 0.50×0.50×0.40 | 0.25×0.20×0.05 | 0.18×0.11×0.04 |
| Empirical Formula | $C_{28}H_{44}N_2Sn$ | $C_{29}H_{46}N_2Sn$ | $C_{38}H_{50}N_2SiSn$ | $C_{27}H_{40}Cl_2N_2Sn$ | $C_{26}H_{39}Cl_3N_2Sn$ | $C_{26}H_{39}Cl_3N_2Sn$ |
| M | 527.34 | 541.37 | 681.58 | 582.22 | 604.63 | 604.63 |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic | Orthorhombic | Monoclinic | Triclinic |
| Space group | *Pna*2$_1$ | *P*2$_1$ | *P*2$_1$/*c* | *Pnma* | *P*2$_1$/*c* | *P***Error!** |
| *a*/Å | 9.480(6) | 10.0169(5) | 10.542(3) | 12.053(2) | 17.2286(11) | 10.2328(9) |
| *b*/Å | 18.791(12) | 10.7935(6) | 24.047(6) | 22.006(4) | 10.6563(7) | 15.1239(14) |
| *c*/Å | 15.689(10) | 13.1689(7) | 14.835(4) | 10.470(2) | 15.6640(10) | 20.634(3) |
| $\alpha$/° | 90 | 90 | 90 | 90 | 90 | 102.086(4) |
| $\beta$/° | 90 | 99.6880(10) | 110.70(5) | 90 | 95.1990(10) | 100.379(4) |
| $\gamma$/° | 90 | 90 | 90 | 90 | 90 | 109.057(3) |
| V/Å$^3$ | 2795(3) | 1403.48(13) | 3518(2) | 2777.2(10) | 2864.0(3) | 2842.8(5) |
| Z | 4 | 2 | 4 | 4 | 4 | 4 |
| $\mu$/mm$^{-1}$ | 0.930 | 0.928 | 0.788 | 1.129 | 1.188 | 1.197 |
| T/K | 100 | 173 | 100 | 100 | 173 | 100 |
| $\theta_{min,max}$ | 1.69,27.56 | 1.57,27.51 | 1.69,27.48 | 2.58,27.48 | 1.19,27.50 | 2.05,28.35 |
| Completeness to $\theta_{max}$ | 0.999 | 0.995 | 1.000 | 0.999 | 1.000 | 0.967 |
| Reflections: total/independent | 26833/6345 | 9323/5917 | 40293/8086 | 18836/3274 | 29975/6582 | 42869/13760 |
| $R_{int}$ | 0.1192 | 0.0302 | 0.0643 | 0.0265 | 0.0657 | 0.0591 |
| Final *R*1 (I>2σ) and *wR*2 (all data) | 0.0503, 0.0863 | 0.0379, 0.0827 | 0.0545, 0.1191 | 0.0235, 0.0607 | 0.0379, 0.0939 | 0.0490, 0.1260 |
| Largest peak, hole/eÅ$^{-3}$ | 0.685, -0.593 | 0.629, -0.708 | 1.758, -1.358 | 0.761, -0.457 | 0.562, -0.435 | 1.393, -1.716 |
| $\rho_{calc}$/g cm$^{-3}$ | 1.253 | 1.281 | 1.287 | 1.392 | 1.402 | 1.413 |
| Flack parameter | -0.05(3) | -0.01(3) | n/a | n/a | n/a | n/a |

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Table ESI 1 continued.

| Compound | **10** | **11** | **12** | **13** | **14** | **15** |
|---|---|---|---|---|---|---|
| Colour, habit | Pale yellow prism | Yellow prism | Colourless shard | Colourless shard | Colourless needle | Colourless shard |
| Size/mm | 0.30×0.20×0.20 | 0.50×0.25×0.10 | 0.40×0.20×0.10 | 0.30×0.20 by 0.10 | 0.15×0.05×0.05 | 0.30×0.10×0.05 |
| Empirical Formula | $C_{52}H_{76}N_4S_2Sn_2$ | $C_{52}H_{76}N_4Se_2Sn_2$ | $C_{27}H_{41}IN_2Sn$ | $C_{28}H_{43}IN_2Sn$ | $C_{37}H_{47}IN_2SiSn$ | $C_{29}H_{45}IN_2OSn$ |
| M | 1058.699 | 1152.51 | 639.23 | 653.23 | 793.45 | 683.26 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | *P***Error!** | *P***Error!** | $P2_1/n$ | $Cc$ | $P2_1/n$ | $C2/c$ |
| $a$/Å | 12.343(3) | 12.4204(19) | 9.5611(3) | 24.111(5) | 10.405(2) | 22.270(3) |
| $b$/Å | 13.215(3) | 13.1557(15) | 15.7041(5) | 11.350(2) | 18.412(4) | 8.4192(13) |
| $c$/Å | 34.597(7) | 34.524(4) | 19.0768(6) | 21.180(4) | 19.168(4) | 32.306(7) |
| $\alpha$/° | 79.946(6) | 79.399(12) | 90 | 90 | 90 | 90 |
| $\beta$/° | 88.904(8) | 87.652(11) | 95.7590(10) | 91.02(3) | 102.47(3) | 99.877(13) |
| $\gamma$/° | 72.595(6) | 71.981(9) | 90 | 90 | 90 | 90 |
| V/Å$^3$ | 5299(2) | 5272.2(12) | 2849.90(16) | 5795(2) | 3585.5(12) | 5967.5(18) |
| Z | 4 | 4 | 4 | 8 | 4 | 8 |
| $\mu$/mm$^{-1}$ | 1.057 | 2.364 | 1.995 | 1.964 | 1.634 | 1.913 |
| T/K | 173 | 100 | 173 | 100 | 100 | 173 |
| $\theta_{min,max}$ | 1.20, 27.48 | 1.20, 27.48 | 2.15, 27.51 | 2.20, 27.48 | 1.55, 27.48 | 1.28, 27.51 |
| Completeness to $\theta_{max}$ | 0.990 | 0.996 | 0.997 | 0.999 | 0.999 | 0.998 |
| Reflections: total/independent | 56751/24042 | 60677/24071 | 29761/6543 | 32343/13109 | 25079/8220 | 30740/6833 |
| $R_{int}$ | 0.0360 | 0.0605 | 0.0250 | 0.0175 | 0.1626 | 0.0688 |
| Final $R1$ (I>2σ) and $wR2$ (all data) | 0.0348, 0.0945 | 0.0562, 0.1361 | 0.0235, 0.0588 | 0.0190, 0.0443 | 0.0899, 0.2239 | 0.0528, 0.1245 |
| Largest peak, hole/eÅ$^{-3}$ | 0.615, -0.708 | 1.077, -1.732 | 0.874, -0.732 | 0.992, -0.364 | 1.937, -2.094 | 2.124, -1.548 |
| $\rho_{calc}$/g cm$^{-3}$ | 1.327 | 1.452 | 1.49 | 1.497 | 1.47 | 1.521 |
| Flack parameter | n/a | n/a | n/a | -0.002(9) | n/a | n/a |

Table ESI 1 continued.

| Compound | **16** | **17** | **18** | **19** |
|---|---|---|---|---|
| Colour, habit | Colourless prism | Colourless block | Colourless prism | Colourless block |
| Size/mm | 0.25×0.20×0.20 | 0.20×0.15×0.15 | 0.14×0.11×0.02 | 0.40×0.25×0.10 |
| Empirical Formula | $C_{28}H_{41}F_3N_2O_3SSn$ | $C_{29}H_{43}F_3N_2O_3SSn$ | $C_{38}H_{47}F_3N_2O_3SSiSn$ | $C_{30}H_{45}F_3N_2O_4SSn$ |
| M | 661.41 | 675.4 | 815.62 | 705.43 |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | *P***Error!** | $P2_1/n$ | $P2_1/n$ |
| $a$/Å | 11.855(4) | 12.227(2) | 10.7144(1) | 10.1512(16) |
| $b$/Å | 21.038(7) | 14.922(3) | 18.7210(2) | 19.839(3) |
| $c$/Å | 12.201(7) | 19.768(4) | 19.6338(2) | 16.025(3) |
| $\alpha$/° | 90 | 104.833(3) | 90 | 90 |
| $\beta$/° | 90.80(3) | 102.680(3) | 103.5506(11) | 92.500(4) |
| $\gamma$/° | 90 | 105.209(3) | 90 | 90 |
| V/Å$^3$ | 3043(2) | 3201.8(10) | 3828.60(7) | 3224.3(9) |
| Z | 4 | 4 | 4 | 4 |
| $\mu$/mm$^{-1}$ | 0.957 | 0.911 | 6.555 | 0.91 |
| T/K | 100 | 173 | 100 | 100 |
| $\theta_{min,max}$ | 1.93, 27.48 | 1.50, 27.53 | 3.31, 66.78 | 1.63, 27.48 |
| Completeness to $\theta_{max}$ | 1.000 | 0.985 | 0.983 | 1.000 |
| Reflections: total/independent | 34683/6973 | 33754/14529 | 21340/6679 | 36751/7384 |
| $R_{int}$ | 0.0386 | 0.1202 | 0.0304 | 0.0587 |
| Final $R1$ (I>2σ) and $wR2$ (all data) | 0.0440, 0.1120 | 0.0704, 0.1946 | 0.0272, 0.0679 | 0.0422, 0.0835 |
| Largest peak, hole/eÅ$^{-3}$ | 1.909, -1.159 | 2.072, -1.750 | 0.521, -0.635 | 0.570, -0.927 |
| $\rho_{calc}$/g cm$^{-3}$ | 1.444 | 1.401 | 1.415 | 1.453 |
| Flack parameter | n/a | n/a | n/a | n/a |

# Electronic Supplementary Information: Chelating diamidotin(IV) compounds from oxidation of Sn(II) stannylenes and directly from Sn(IV) starting materials

Diagrams depicting the molecular structures of compounds **1** – **5** and **10** – **19** with all of the thermal ellipsoids at the 50% probability level.

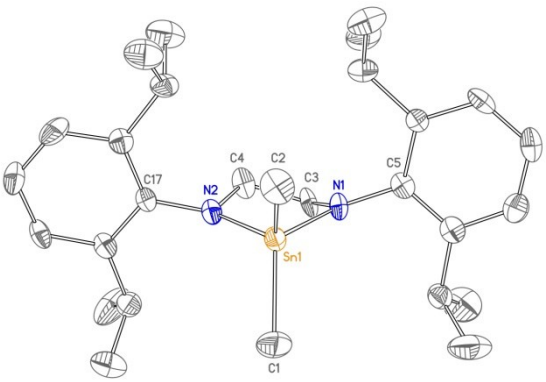


Figure ESI 1. Thermal ellipsoid plot of **1**. All hydrogens have been removed for clarity.

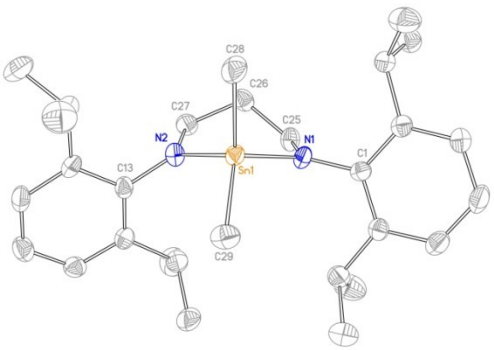


Figure ESI 2. Thermal ellipsoid plot of **2**. All hydrogens have been removed for clarity.

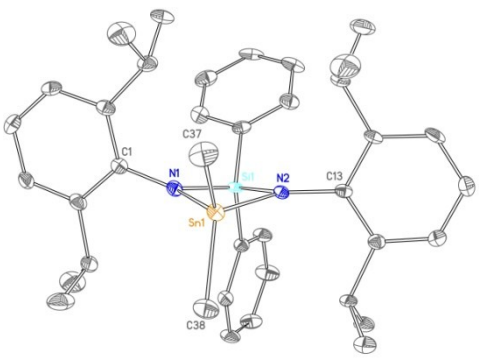


Figure ESI 3. Thermal ellipsoid plot of **3**. All hydrogens have been removed for clarity.

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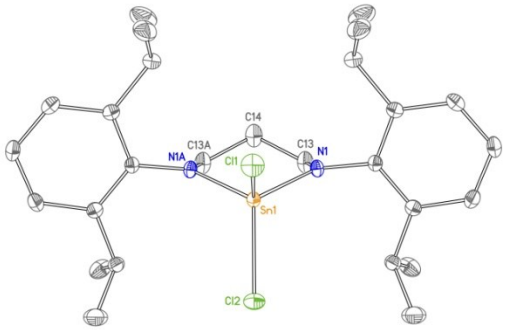


Figure ESI 4. Thermal ellipsoid plot of **4**. All hydrogens have been removed for clarity. Symmetry operator for symmetry generated atoms: x, -y + 3/2, z

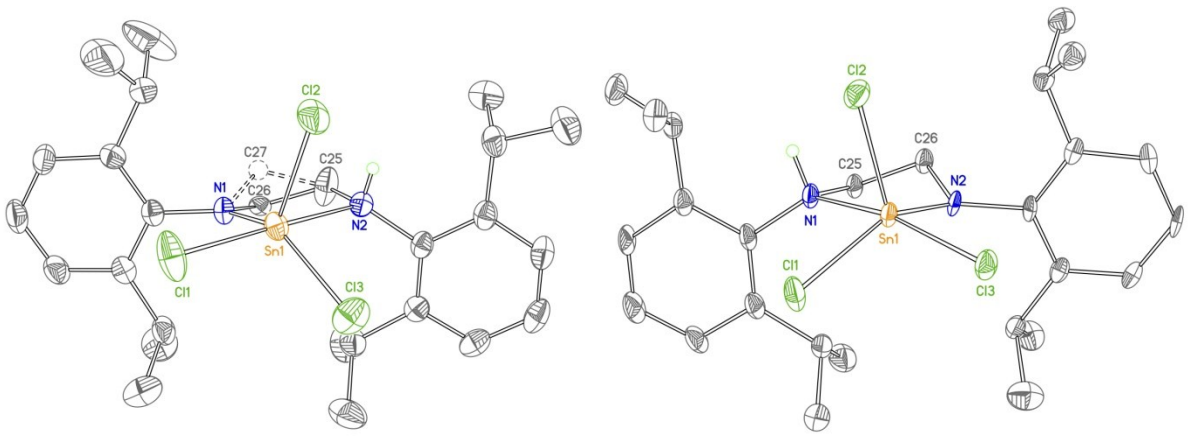


Figure ESI 5. Thermal ellipsoid plot of **5 monoclinic** (left) and one of the two molecules in the asymmetric unit of **5 triclinic** (right). All hydrogens have been removed for clarity and both positions of the disordered $CH_2$ group are shown and refined with final site occupancy of 0.52/0.48 major/minor (minor component shown with dotted circles).

Table ESI 2. Selected bond lengths (Å) and angles (°) for both of the polymorphs of the trichloro tin compound **5**

| | Sn-N | Sn←N | Sn-Cl | N-Sn-N | Σ (angles at N) |
|---|---|---|---|---|---|
| **5** triclinic molecule A | N(2): 2.023(4) | N(1): 2.349(3) | Cl(1): 2.3281(12) | 77.84(13) | N(2): 354.5 |
| | | | Cl(2): 2.3408(12) | | N(1): 345.1 |
| | | | Cl(3): 2.3810(11) | | |
| **5** triclinic molecule B | N(3): 2.000(3) | N(4): 2.368(3) | Cl(6): 2.3248(11) | 77.74(13) | N(3): 353.7 |
| | | | Cl(5): 2.3501(11) | | N(4): 346.3 |
| | | | Cl(4): 2.3769(11) | | |
| **5** monoclinic | N(1): 2.013(2) | N(2): 2.340(3) | Cl(1): 2.3665(9) | 78.19(10) | N(1): 359.5 |
| | | | Cl(2): 2.3529(9) | | N(2): 347.1 |
| | | | Cl(3): 2.3206(10) | | |

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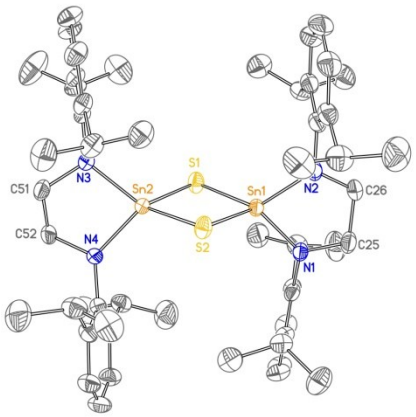


Figure ESI 6. Thermal ellipsoid plot of one of the two molecules in the asymmetric unit of the crystal structure of **10**. All hydrogens have been removed for clarity.

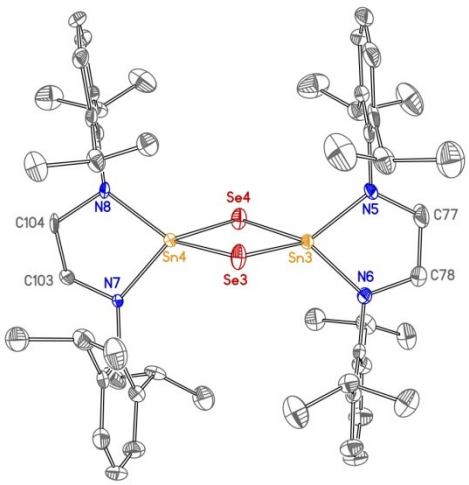


Figure ESI 7. Thermal ellipsoid plot of one of the two molecules in the asymmetric unit of the crystal structure of **11**. All hydrogens have been removed for clarity.

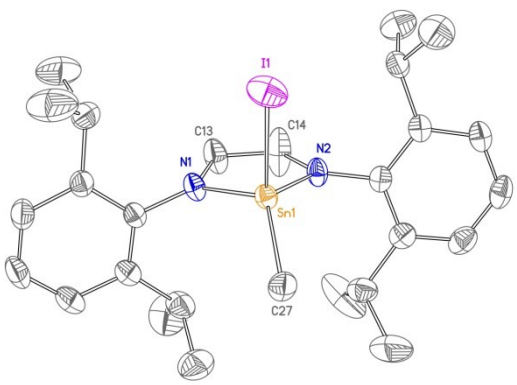


Figure ESI 8. Thermal ellipsoid plot of **12**. All hydrogens have been removed for clarity

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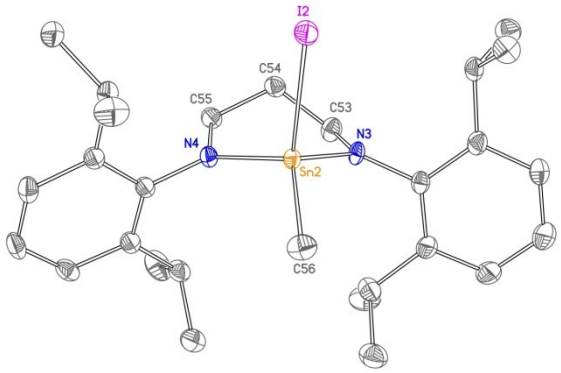


Figure ESI 9. Thermal ellipsoid plot of one of the two molecules in the asymmetric unit of the crystal structure of **13**. All hydrogens have been removed for clarity.

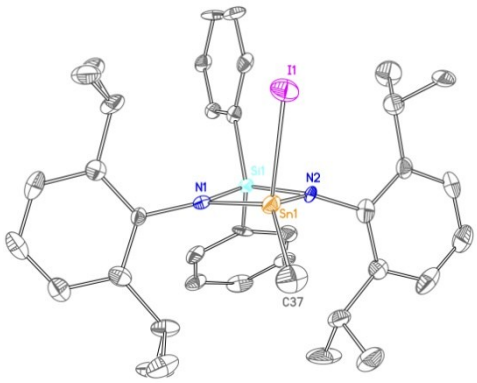


Figure ESI 10. Thermal ellipsoid plot of **14**. All hydrogens have been removed for clarity

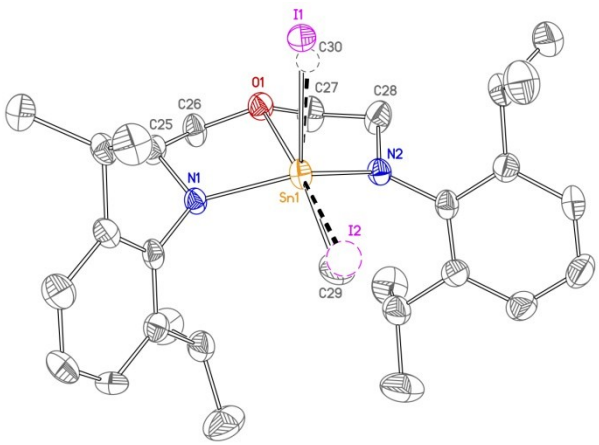


Figure ESI 11. Thermal ellipsoid plot of **15**. All hydrogens have been removed for clarity and both positions of the disordered Sn-Me group and iodine atom are shown and refined with final site occupancy of 0.847 / 0.153 major / minor (minor component shown with dotted circles).

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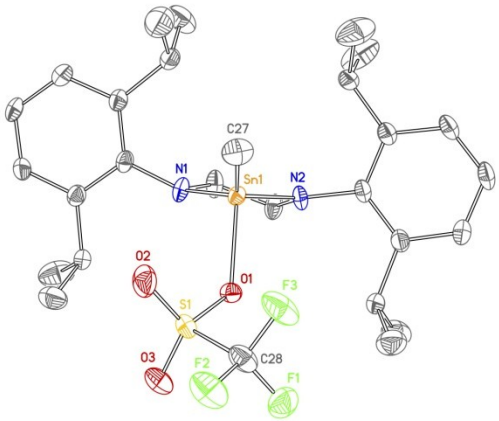


Figure ESI 12. Thermal ellipsoid plot of **16**. All hydrogens have been removed for clarity

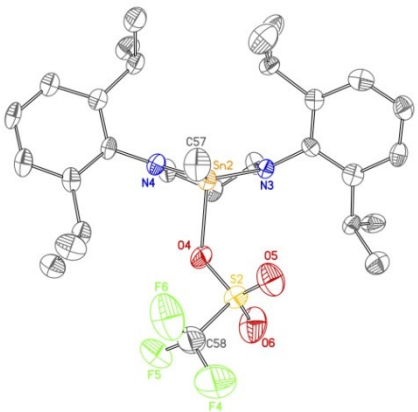


Figure ESI 13. Thermal ellipsoid plot of one of the two molecules in the asymmetric unit of the crystal structure of **17**. All hydrogens have been removed for clarity.

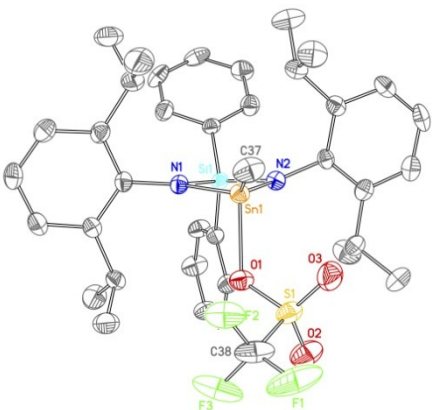


Figure ESI 14. Thermal ellipsoid plot of **18**. All hydrogens have been removed for clarity.

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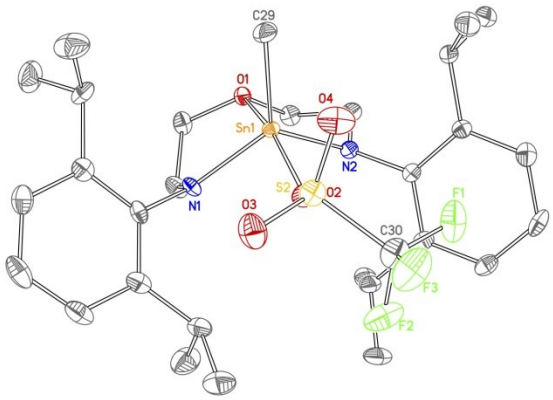


Figure ESI 15. Thermal ellipsoid plot of **19**. All hydrogens have been removed for clarity.