Supporting Information for

Direct Detection, Dimerization and Chemical Trapping of Dimethyl- and Diphenylstannylene from Photolysis of Stannacyclopent-3-enes in Solution.

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surface scans of the Sn-Sn bond distances ($d_{Sn\text{-}Sn}$) in **17b** and **20** at the ωB97XD/6-31+G(d,p)^{C,H,O}-LANL2DZdp^{Sn} level of theory. The calculated structures at various $d_{Sn\text{-}Sn}$ values in the calculations are also shown.

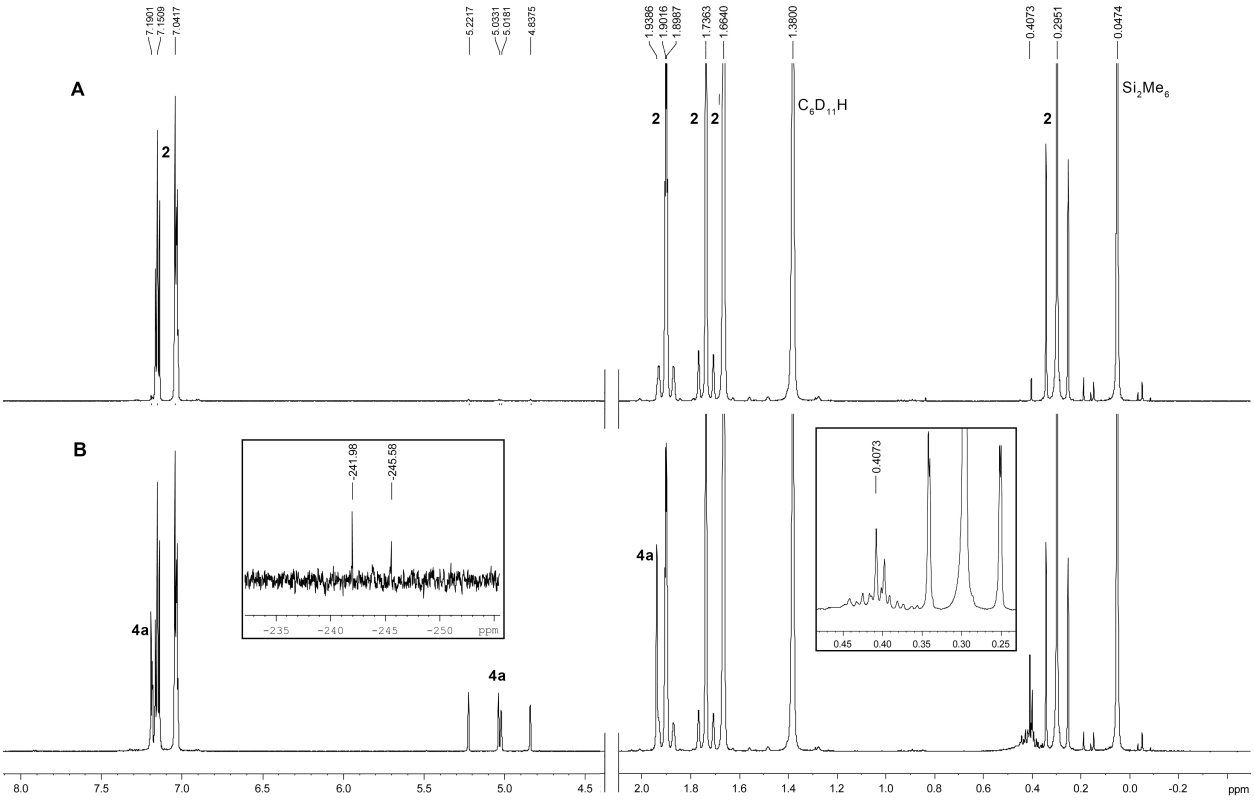


Figure S1. ^{1}H NMR spectra of a deaerated 0.04 M solution of **2** in C_6D_{12} (a) before and (b) after 10 minutes photolysis with 254 nm light. The insets in B show an expansion of the δ 0.23-0.48 region of the spectrum and the portion of the ^{119}Sn[^{1}H] spectrum containing product peaks.

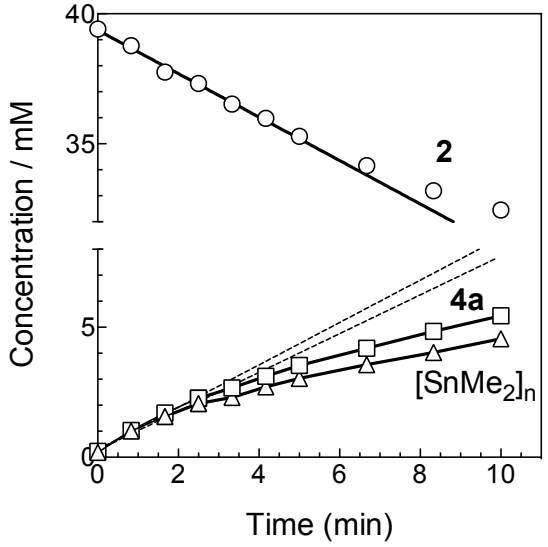


Figure S2. Concentration vs. time plots for the photolysis of the solution of Fig. S1. The initial slopes of the three plots are **2**, -0.84 ± 0.04; **4a**, 0.82 ± 0.05; $[SnMe_2]_n$ (δ 0.407) 0.75 ± 0.07 (units, mM min^{-1}).

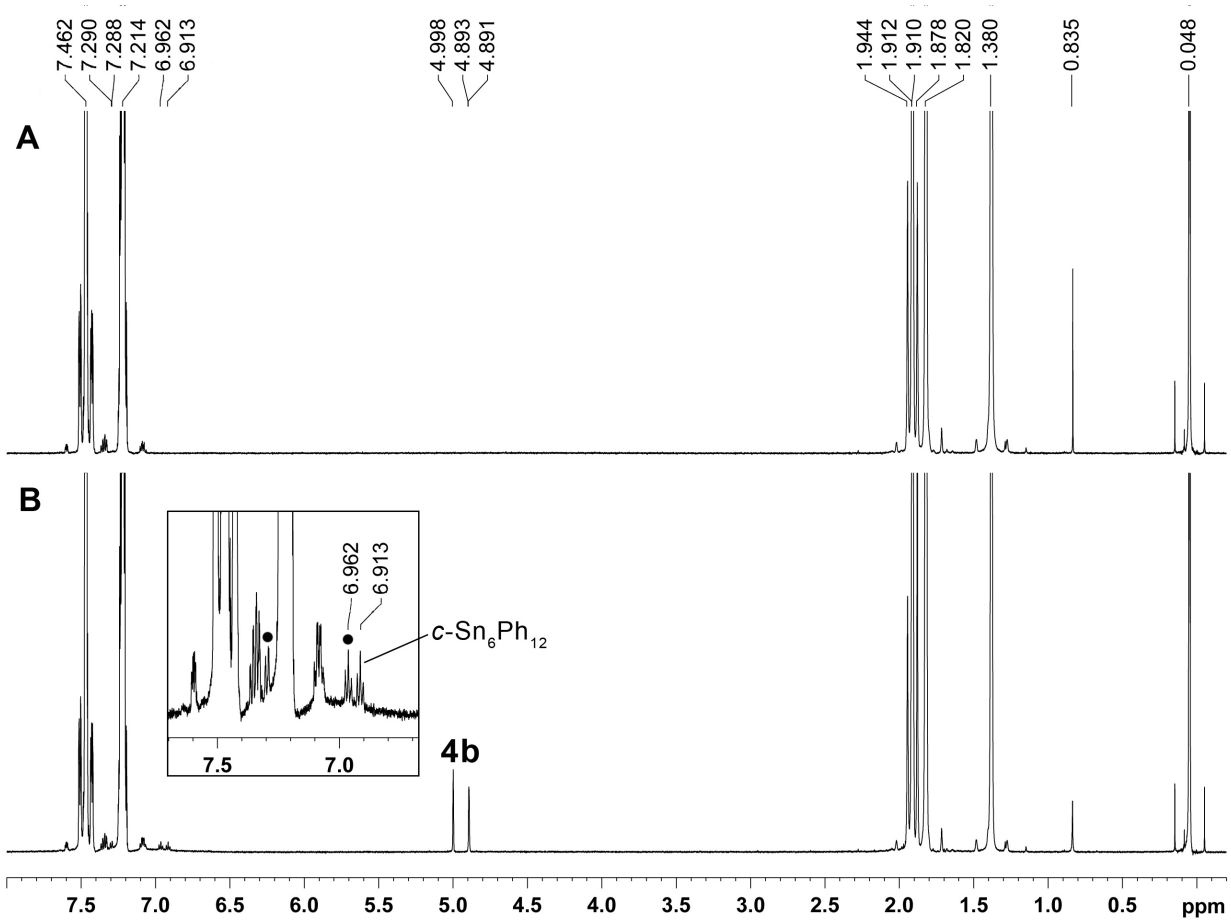


Figure S3. ^{1}H NMR spectra of a deaerated 0.04 M solution of **3** in C_6D_{12} (a) before and (b) after 8.3 minutes photolysis with 254 nm light. The resonances marked with ● disappeared after allowing the photolysed solution to stand for 18 hours in the dark.

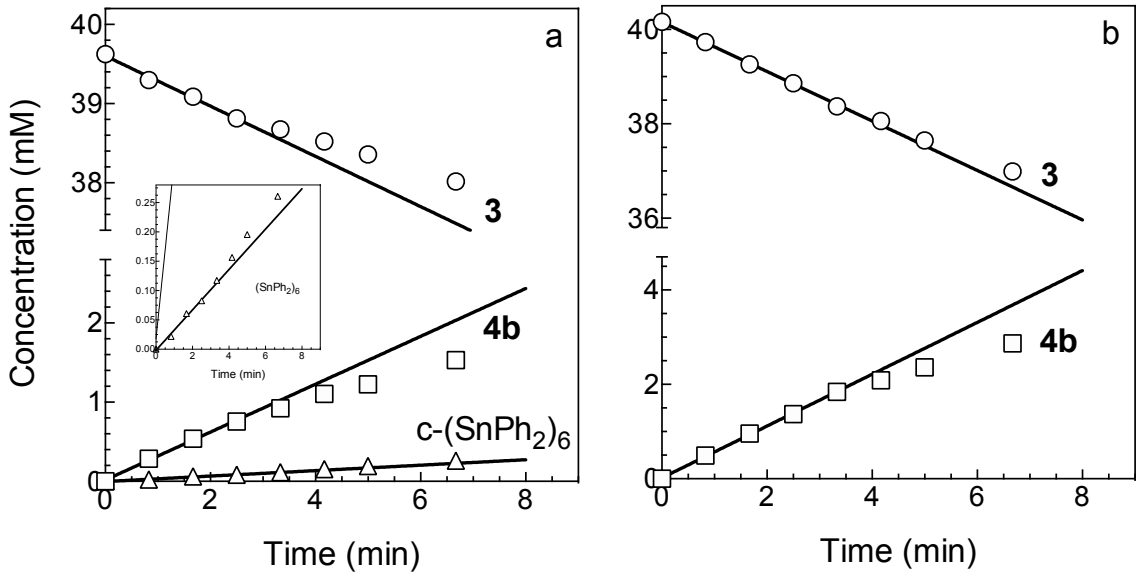


Figure S4. Concentration vs. time plots for photolysis of ca. 0.04 M solutions of **3** in C_6D_{12}, (a) deaerated (slopes (in units of mM min^{-1}): **3**, -0.32 ± 0.02; **4b**, 0.30 ± 0.01; c-$(SnPh_2)_6$, 0.0057 ± 0.0005); (b) air-saturated (slopes: **3**, -0.52 ± 0.01; **4b**, 0.55 ± 0.02).

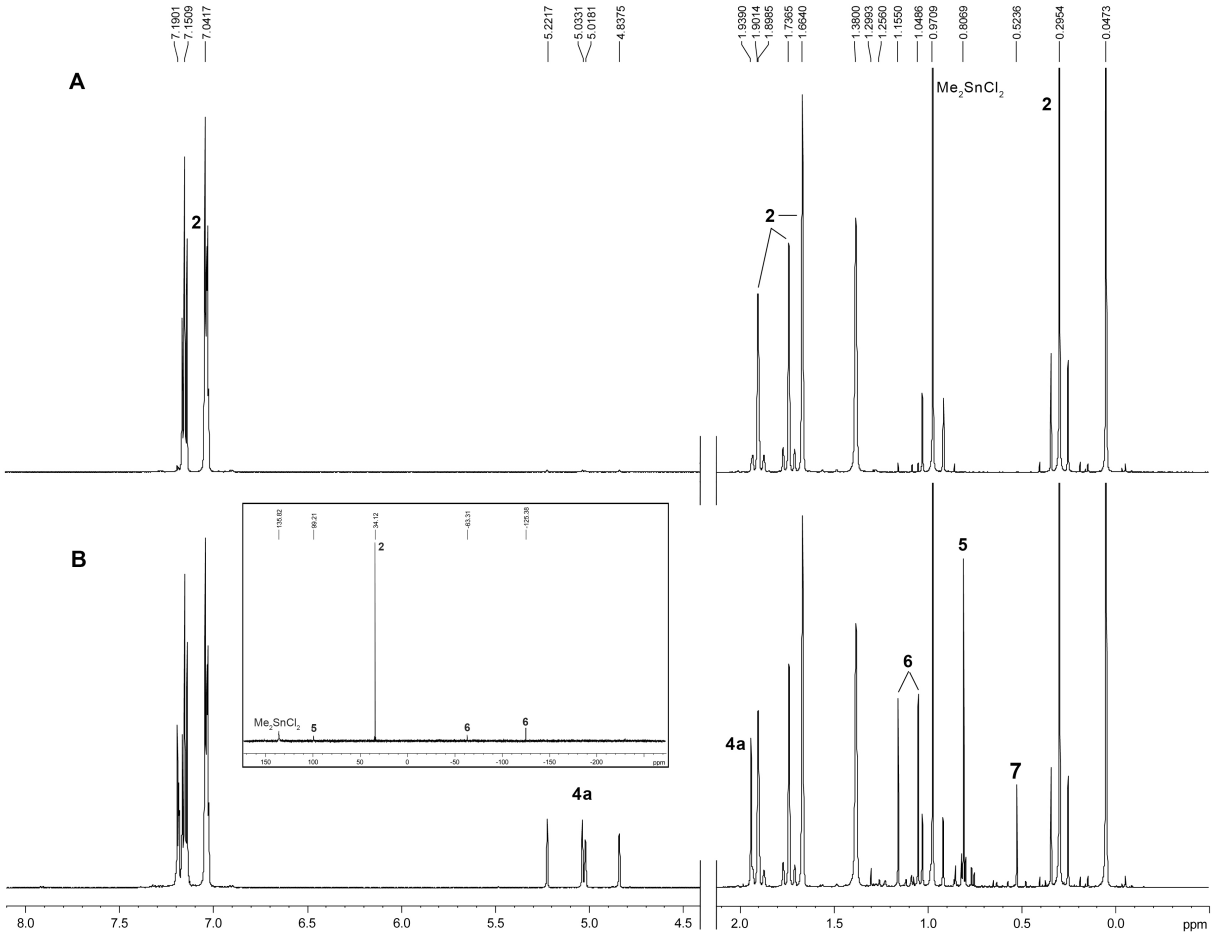


Figure S5. ^{1}H NMR spectra of a deaerated 0.04 M solution of **2** in C_6D_{12} containing Me_2SnCl_2 (0.031 M) (a) before and (b) after 10 minutes photolysis with 254 nm light. The inset in B shows the ^{119}Sn[^{1}H] NMR spectrum of the photolyzed mixture.

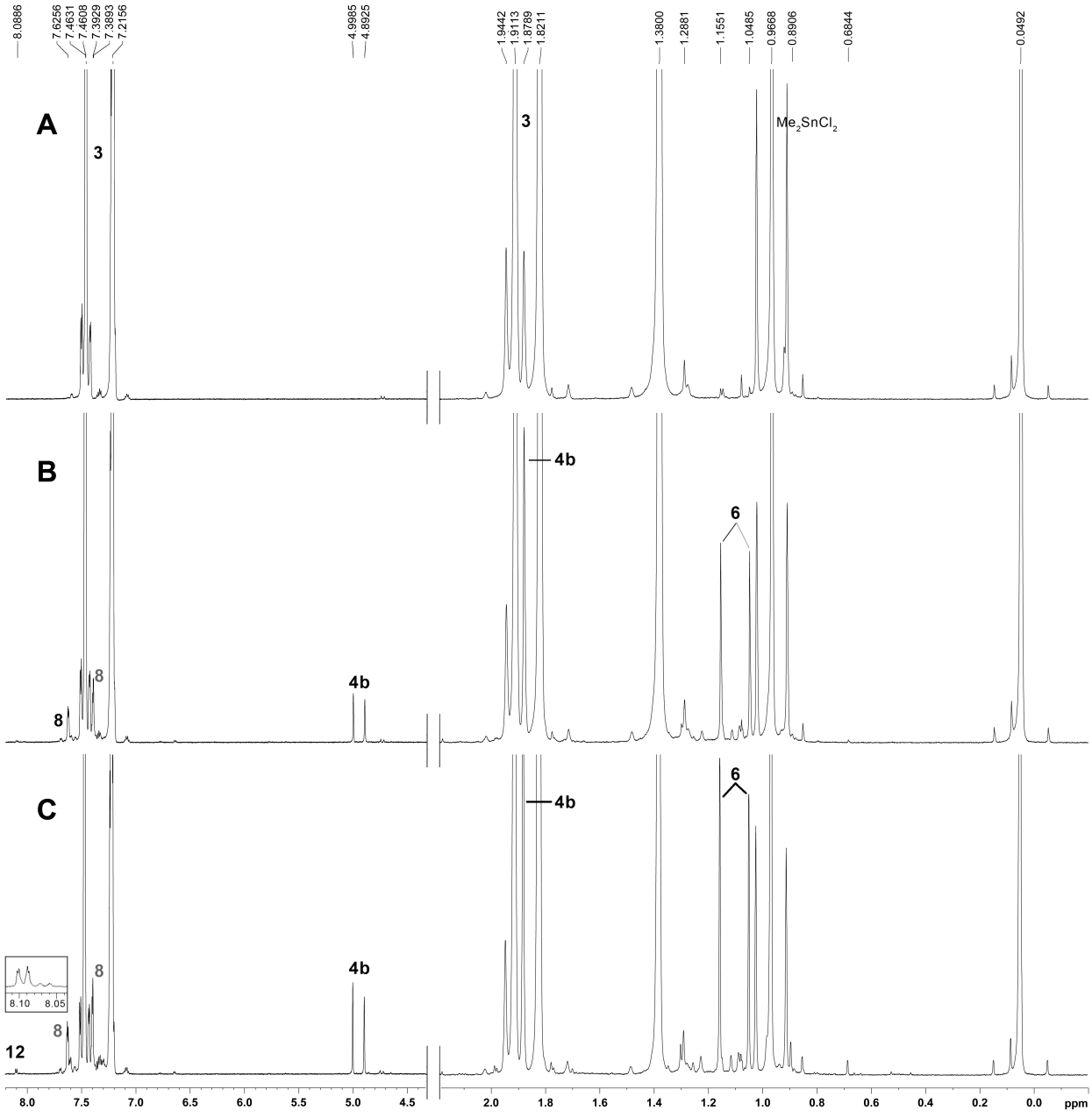


Figure S6. ^{1}H NMR spectra of an undeaerated 0.04 M solution of **3** in C_6D_{12} containing Me_2SnCl_2 (0.037 M) (a) before, (b) after 2.5 minutes, and (c) after 6.7 minutes photolysis with 254 nm light. No attempt was made to replenish the air in the photolyzate as the experiment proceeded.

Equilibrium Constants for Interconversion of Cyclodistannoxanes **6**, **12**, and **11** ($CDCl_3$, 22 °C).

A mixture of **6** (13.7 mg, 11.9 mM) and hexamethyldisilane (4.00 µL, 13.0 mM) in $CDCl_3$ (1.50 mL) was ultrasonicated in a 5 mL screw cap glass vial at 22 °C, and then the ^{1}H-NMR spectrum of the resulting opaque solution was recorded. The NMR sample was recombined with the bulk of the solution, **8** (24.2 mg, 46.9 mM) was added, the solution was shaken briefly, and the ^{1}H-NMR spectrum of the resulting clear colourless solution (solution 'a') was recorded. The procedure was repeated with an additional amount of **8** (26.7 mg, 51.8 mM; solution 'b'), and again with two successive additions of Me_2SnCl_2 (31.8 mg, 96.5 mM (solution 'c') and 31.5 mg, 95.6 mM (solution 'd')).

The relative concentrations of the five components of each of the mixtures (see Table below) were calculated from the NMR integrals, using the signals at δ 1.19 (s, 12H), δ 8.06 (d, 4H), δ 8.03 (d, 8H), δ 1.21 (s, 6H), and δ 7.71 (d, 4H) for **6**, **12**, **11**, Me_2SnCl_2, and Ph_2SnCl_2 (**8**), respectively. The equilibrium constants $K_{\mathbf{11}\text{<>}\mathbf{12}}$ and $K_{\mathbf{12}\text{<>}\mathbf{6}}$ were then calculated by least squares analysis of plots of the concentration ratios of the cyclodistannoxanes vs. those of the dichlorostannanes (Fig. S7).

Quantities Mixed / mM						
Solution	**6**	Me_2SnCl_2	**8**	$([\mathbf{6}]/[\mathbf{12}])_e$	$([\mathbf{12}]/[\mathbf{11}])_e$	$([Me_2SnCl_2]/[\mathbf{8}])_e$
(a)	11.9	0	46.9	0.266	0.758	0.383
(b)	11.9	0	98.7	0.205	0.560	0.191
(c)	11.9	96.5	98.7	0.780	1.90	1.32
(d)	11.9	192	98.7	1.23	2.43	2.45

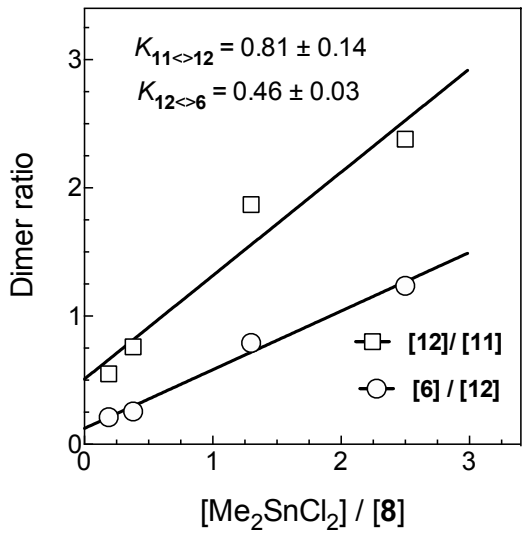


Figure S7. Plots of the concentration ratios of cyclodistannoxanes **6**, **11**, and **12** (i.e. [**6**]/[**12**] and [**12**]/[**11**]) vs. the dichlorostannane concentration ratio $[Me_2SnCl_2]/[\mathbf{8}]$, measured from the ^{1}H NMR spectra of a ca. 0.012 M solution of **6** in $CDCl_3$ to which sequential portions of Ph_2SnCl_2 (**8**) and Me_2SnCl_2 were added at ca. 22 °C. The solid lines are the linear least squares fits of the data to $[\mathbf{6}]/[\mathbf{12}] = K_{\mathbf{12}\Leftrightarrow\mathbf{6}}[Me_2SnCl_2]/[\mathbf{8}]$ (○) and $[\mathbf{12}]/[\mathbf{11}] = K_{\mathbf{11}\Leftrightarrow\mathbf{12}}[Me_2SnCl_2]/[\mathbf{8}]$ (□); errors are quoted as the standard errors from the least squares analysis.

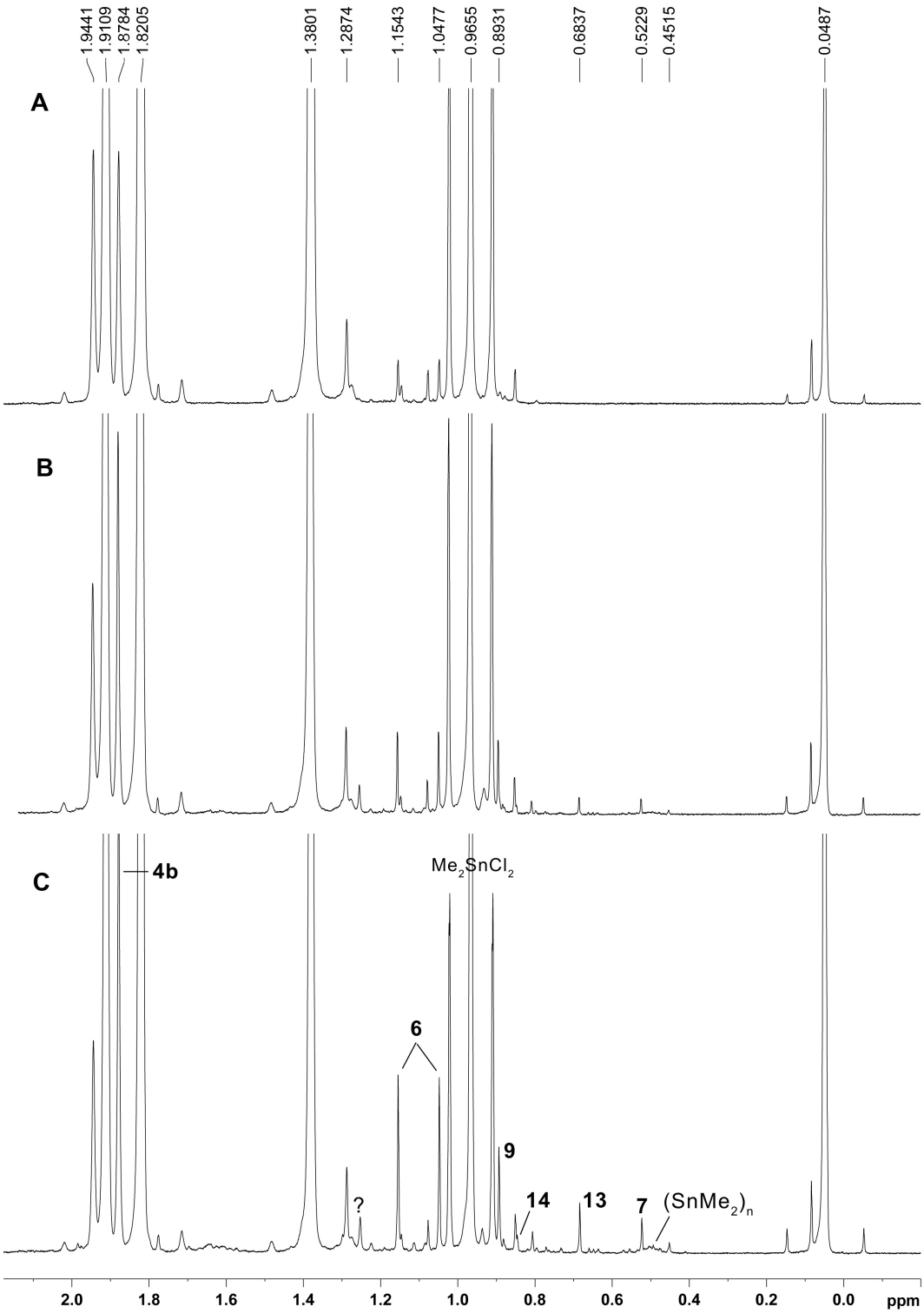


Figure S8. Partial ^{1}H NMR spectra of a deaerated 0.038 M solution of **3** in C_6D_{12} containing Me_2SnCl_2 (0.034 M) (a) before, (b) after 2.5 minutes, and (c) after 6.7 minutes photolysis.

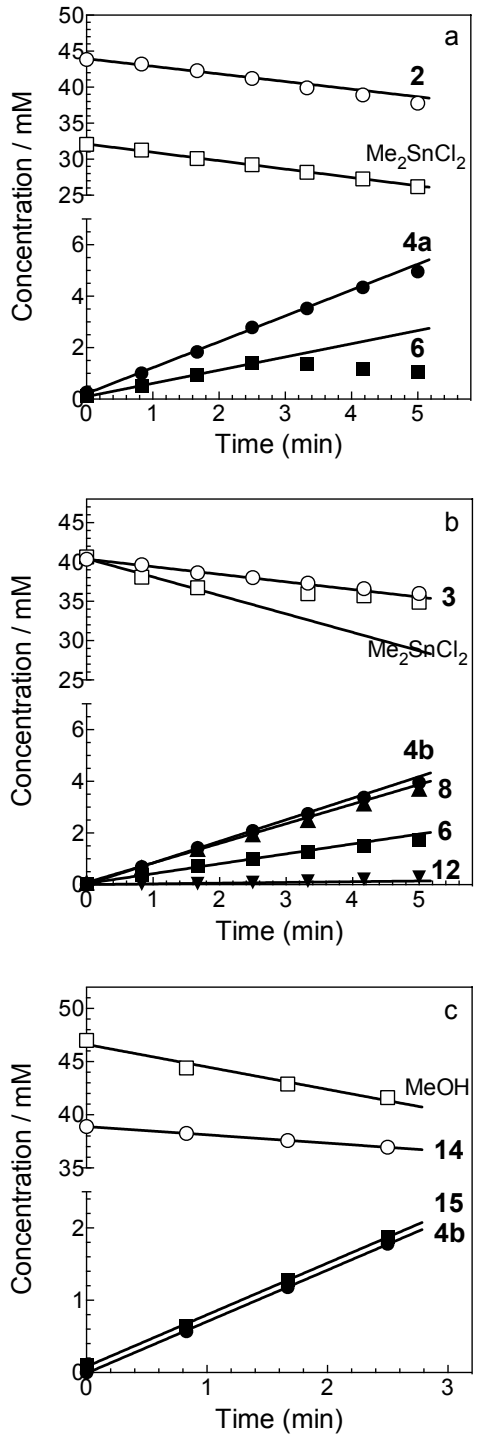


Figure S9. Concentration vs. time plots for the photolysis of air-saturated C_6D_{12} solutions of (a) **2** and (b) **3** containing ca. 0.04 M Me_2SnCl_2, and of (c) a deoxygenated C_6D_{12} solution of **15** containing 0.05 M MeOH; all three solutions also contained Si_2Me_6 (ca. 0.01 M) as internal integration standard. The initial slopes of the plots for the various compounds are (in mM min^{-1}): (a) **2**, -1.06 ± 0.09; Me_2SnCl_2, -1.16 ± 0.05; **4a**, 1.01 ± 0.04; **6**, 0.51 ± 0.01 (A solid, presumed to be **6**, began to precipitate halfway through the experiment, so only the first 4 points were used to evaluate the yield of this product); (b) **3**, -0.97 ± 0.07; Me_2SnCl_2, -1.74 ± 0.40; **4b**, 0.83 ± 0.01; **6**, 0.38 ± 0.02; **8**, 0.76 ± 0.03; **12**, 0.03 ± 0.01; (c) **14**, -0.781 ± 0.002; **4b**, 0.713 ± 0.006; **15**, 0.716 ± 0.012.

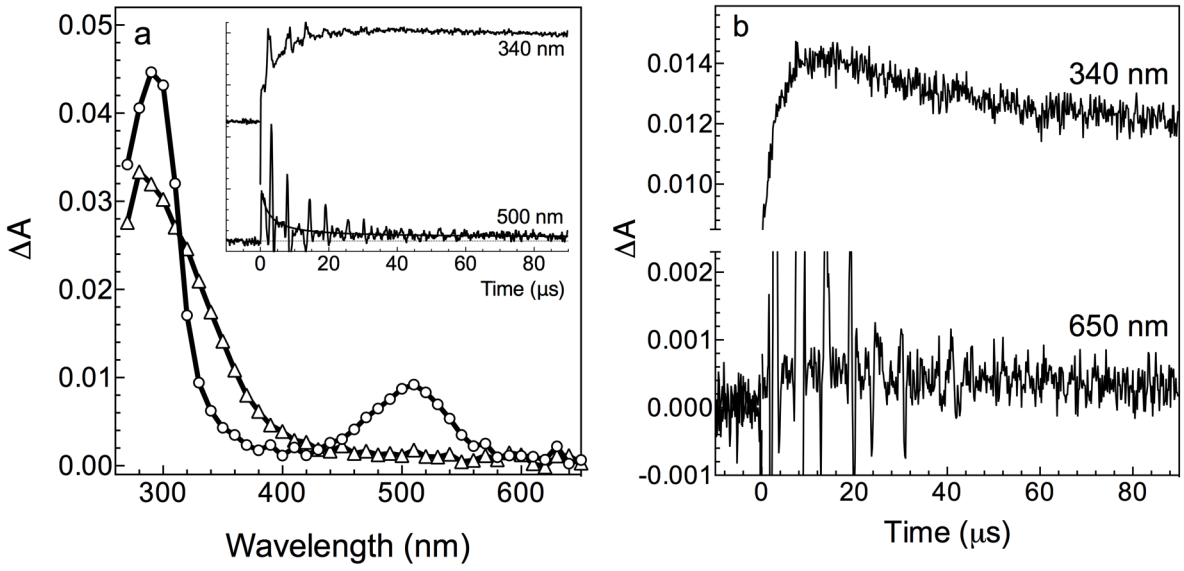


Figure S10. (a) Transient UV-vis absorption spectra from laser flash photolysis of a rapidly flowed, deoxygenated solution of **3** (7×10^{-4} M) in anhydrous hexanes at 25 °C, recorded over a longer timescale than that shown in Figure 5 of the paper. The spectra were recorded 0.64 – 0.96 μs (○) and 81.1 – 81.9 μs (Δ) after the pulse, using a Pyrex filter in the monitoring beam at wavelengths above 310 nm; the inset shows absorbance vs. time profiles recorded at 340 and 500 nm. (b) Transient absorbance-time profiles recorded for a flowed solution of **3** in deoxygenated hexanes, under similar conditions to those used for the experiment shown in (a) – the sample was different, however. The 340 nm ΔA-time profile was recorded as in (a) and is the average of 10 laser shots, while the 650 nm profile was recorded with a 520 nm cutoff filter (Corning 3-69) in the monitoring beam to filter out overtone absorptions, and is the average of 70 laser shots. The ΔA-time profile at 500 nm (recorded with a Pyrex filter) was quite similar to that obtained in the experiment of (a).

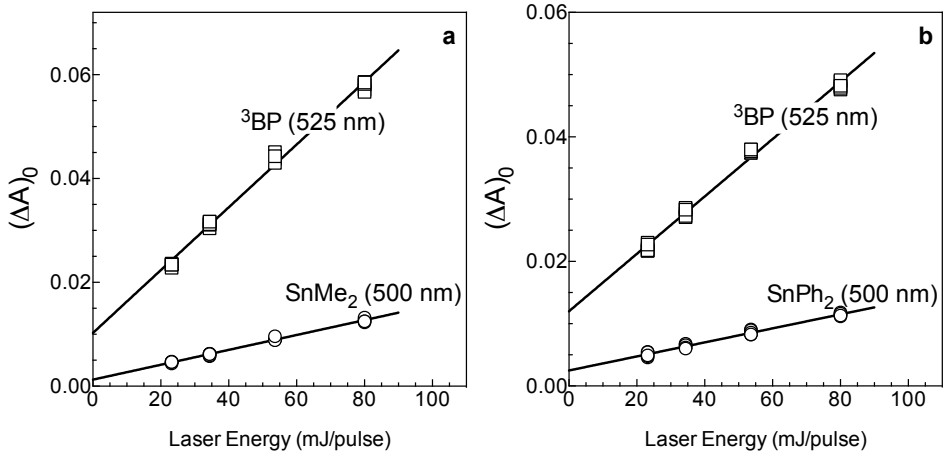


Figure S11. Plots of initial transient absorbance ($(\Delta A)_0$) vs. laser pulse energy from optically matched (at 248 nm), deoxygenated hexanes solutions of (a) benzophenone and **2**, and (b) benzophenone and **3**, for determination of the extinction coefficients of the $SnMe_2$ and $SnPh_2$ absorption bands at 500 nm. The benzophenone triplet (^{3}BP; $\Phi = 1.0$) was monitored at 525 nm ($\varepsilon = 6{,}250 \pm 1{,}250$ $M^{-1}cm^{-1}$).[1] The slopes of the plots are (a) ^{3}BP, $(6.0 \pm 0.1) \times 10^{-4}$, $SnMe_2$ $(1.43 \pm 0.02) \times 10^{-4}$; (b) ^{3}BP, $(4.61 \pm 0.08) \times 10^{-4}$, $SnPh_2$ $(1.13 \pm 0.03) \times 10^{-4}$.

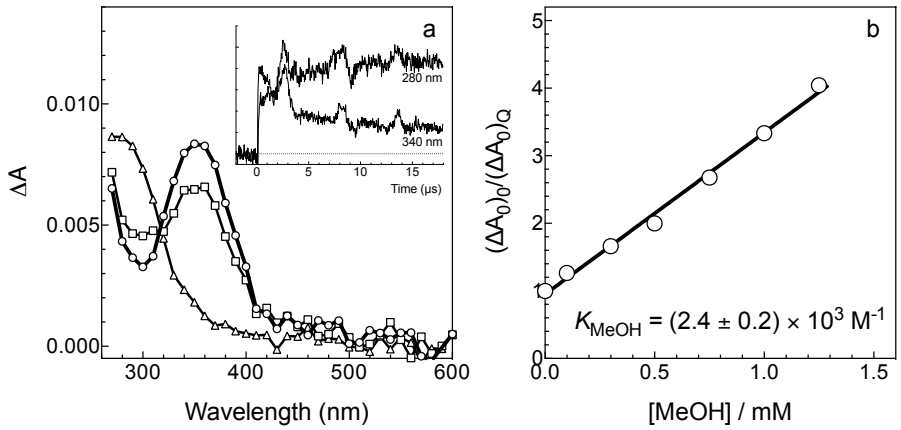


Figure S12. (a) Time-resolved UV-vis spectra recorded by laser photolysis of $SnMe_2$ precursor **2** in hexanes containing 7 mM MeOH, 0.22-0.29 μs (○), 1.25-1.31 μs (□) and 17.5-17.7 μs (Δ) after the laser pulse (25 °C), and absorbance-time profiles at selected wavelengths (inset). (b) Plot of $(\Delta A_0)_0 / (\Delta A_0)_Q$ for complexation of $SnMe_2$ with MeOH in hexanes at 25 °C; the solid line is the linear least squares fit of the data to equation 14.

Computational Studies

Theoretical calculations were carried out using the Gaussian09 (Rev. B.01) suite of programs.[2] Energies in the tables of calculated structures and energies are reported in units of Hartree/Particle.

Table S1. Calculated Electronic Energies, Standard Enthalpies (298.15 K), and Standard Free Energies (298.15 K) of Stationary Points in the Dimerization of $SnMe_2$ and $SnPh_2$, Calculated at the ωB97X/6-31+G(d,p)^{C,H,O}-LANL2DZdp^{Sn} Level of Theory Relative to the Isolated Reactants (in kcal mol^{-1}).

	ωB97X/6-31+G(d,p)^{C,H,O}-LANL2DZdp^{Sn}				
Species	ΔE_{elec}	$\Delta H°$	$\Delta G°$	$\Delta(\Delta H°)^a$	$\Delta(\Delta G°)^a$
$Me_2Sn=SnMe_2$ (**16a**)	-23.4	-20.7	-10.4	-1.4	-1.5
$MeSnSnMe_3$ (**17a**)	-32.2	-29.8	-20.3	-0.5	-0.8
$Ph_2Sn=SnPh_2$ (**16b**)	-19.5	-18.0	-8.3	-3.1	-3.1
$PhSnSnPh_3$ (**17b**)	-30.8	-29.3	-20.4	-3.7	-0.7
$PhSn(C_6H_5)SnPh_2$ (**23**)	-24.2	-22.9	-11.1	-5.4	-5.2
trans-$PhSn(C_6H_5)_2SnPh$ (**24**)	-14.0	-12.6	-0.2	-5.4	-5.6
Transition state **28**‡	+8.1	+8.6	+21.7	-7.6	-7.3
Transition state **29**‡	-24.2	-23.5	-10.3	-5.0	-5.4
Me_2Sn-O(H)Me (**19a**)^b	-14.0	-12.5	-2.6	+0.7	+0.7
Ph_2Sn-O(H)Me (**19b**)^b	-15.9	-14.4	-4.0	+0.1	+0.7

a. Defined as $\Delta(\Delta E) = \Delta E$(ωB97XD) - ΔE(ωB97X).

b. Corrected for Basis Set Superposition Error (BSSE).

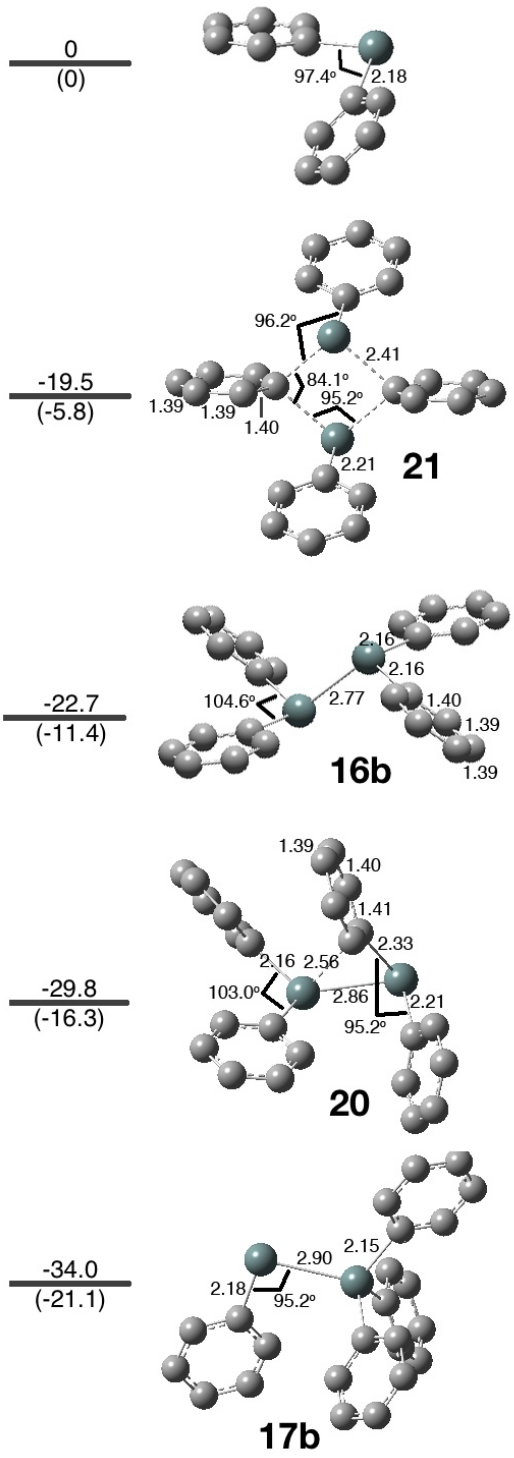


Figure S13. Selected geometric parameters, electronic energies and standard free energies (in parentheses) for $SnPh_2$ and the $SnPh_2$-dimers **16b, 17b, 20** and (*trans*-) **21**, calculated at the ωB97XD/6-31+G(d,p)^{C,H,O}-LANL2DZdp^{Sn} level (hydrogens omitted for clarity).

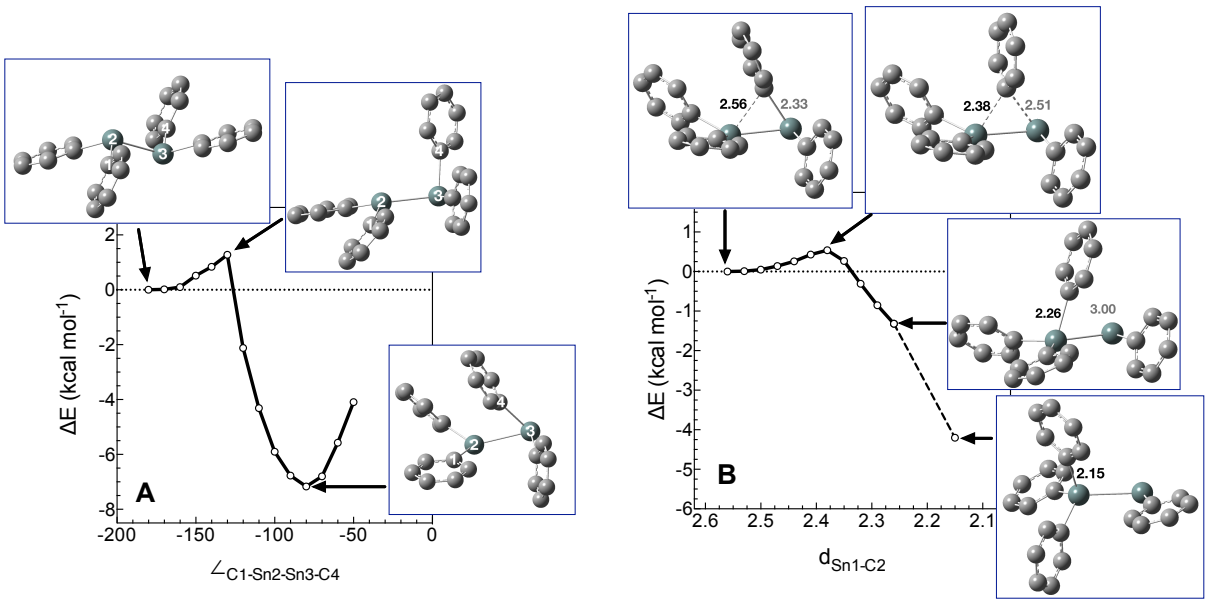


Figure S14. Plots of Δ*E* vs. geometry from relaxed PES scans of (A) the C1-Sn2-Sn3-C4 dihedral angle in **16b** and (B) the Sn-C bond distance involving the bridging phenyl group in stannylidenestannylene **20**, carried out at the ωB97XD/6-31+G(d,p)^{C,H,O}-LANL2DZdp^{Sn} level of theory.

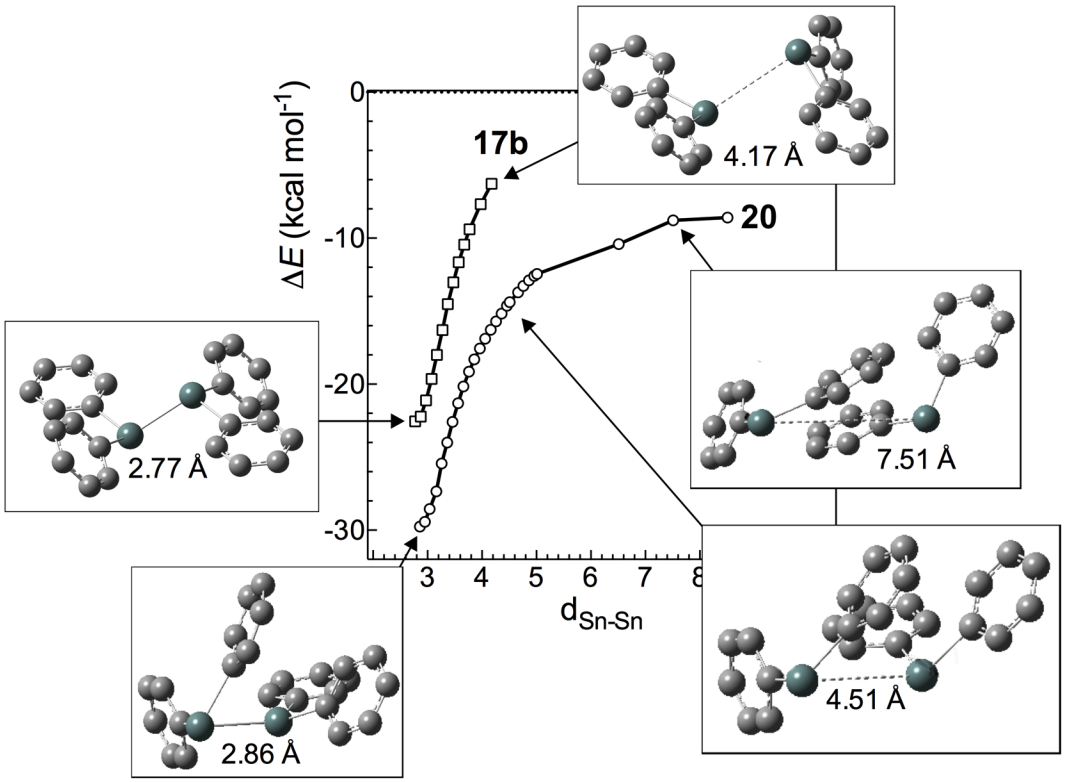
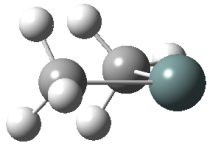


Figure S15. Plot of calculated relative electronic energies (ΔE; relative to two $SnPh_2$ moieties at infinite separation) vs. Sn-Sn bond distance, from relaxed potential energy surface scans of the Sn-Sn bond distances ($d_{Sn\text{-}Sn}$) in **17b** and **20** at the ωB97XD/6-31+G(d,p)^{C,H,O}-LANL2DZdp^{Sn} level of theory. The calculated structures at various $d_{Sn\text{-}Sn}$ values in the calculations are also shown.

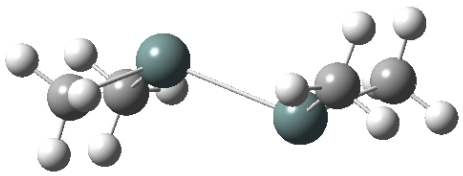
Calculated structures and energies (in Hartrees)

Dimethylstannylene [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

Zero-point correction= 0.070553 Thermal correction to Energy= 0.076414 Thermal correction to Enthalpy= 0.077358 Thermal correction to Gibbs Free Energy= 0.041357 Sum of electronic and zero-point Energies= -83.090800 Sum of electronic and thermal Energies= -83.084939 Sum of electronic and thermal Enthalpies= -83.083995 Sum of electronic and thermal Free Energies= -83.119996	

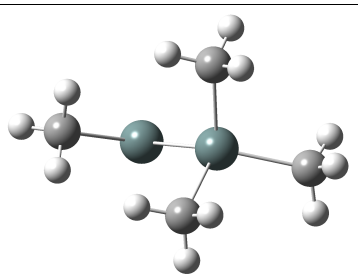
Sn	0.00000000	0.00000000	0.42625400
C	0.00000000	1.58572500	-1.08795300
C	0.00000000	-1.58572500	-1.08795300
H	0.78719500	-1.40335700	-1.83008100
H	-0.95629800	-1.55642000	-1.62796800
H	-0.12840600	2.58802300	-0.67058000
H	-0.78719500	1.40335700	-1.83008100
H	0.95629800	1.55642000	-1.62796800
H	0.12840600	-2.58802300	-0.67058000

Tetramethyldistannene (16a) [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

Zero-point correction= 0.145100 Thermal correction to Energy= 0.158137 Thermal correction to Enthalpy= 0.159081 Thermal correction to Gibbs Free Energy= 0.103332 Sum of electronic and zero-point Energies= -166.217246 Sum of electronic and thermal Energies= -166.204209 Sum of electronic and thermal Enthalpies= -166.203265 Sum of electronic and thermal Free Energies= -166.259014	

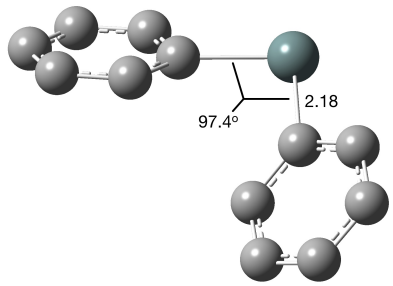
Sn	-0.26578200	-0.00348500	-1.34599500
C	0.61640400	-1.65746700	-2.44423400
C	0.48257600	1.72475300	-2.42881600
H	1.55748100	1.62122000	-2.60346700
H	-0.01648300	1.78750700	-3.40132000
H	0.49613700	-2.60419100	-1.91208300
H	0.12884200	-1.74541500	-3.42064300
H	1.68185100	-1.47361900	-2.61091200
H	0.29645300	2.65381900	-1.88463400
Sn	0.26578200	0.00348500	1.34599500
C	-0.61640400	1.65746700	2.44423400
C	-0.48257600	-1.72475300	2.42881600
H	-1.55748100	-1.62122000	2.60346700
H	0.01648300	-1.78750700	3.40132000
H	-0.49613700	2.60419100	1.91208300
H	-0.12884200	1.74541500	3.42064300
H	-1.68185100	1.47361900	2.61091200
H	-0.29645300	-2.65381900	1.88463400

Methyltrimethylstannylstannylene (17a) [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

Zero-point correction= 0.144310 Thermal correction to Energy= 0.157597 Thermal correction to Enthalpy= 0.158541 Thermal correction to Gibbs Free Energy= 0.101082 Sum of electronic and zero-point Energies= -166.230467 Sum of electronic and thermal Energies= -166.217180 Sum of electronic and thermal Enthalpies= -166.216236 Sum of electronic and thermal Free Energies= -166.273695	

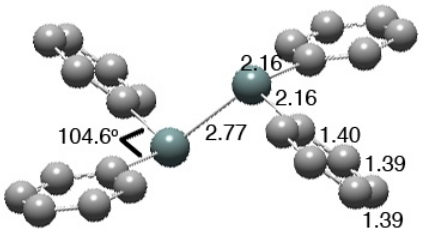
Sn	1.77332200	-0.43207300	-0.00348900
Sn	-1.10036500	-0.00612000	-0.00226000
C	2.09377800	1.74795300	-0.00127000
H	1.63502400	2.19703200	-0.89111100
H	1.60925000	2.20532900	0.87045400
H	3.15607200	2.00467700	0.01332200
C	-1.67517600	1.32619800	-1.61166100
H	-1.47950300	0.87678600	-2.58975600
H	-2.74587900	1.54408900	-1.54385200
H	-1.12783400	2.27144100	-1.54863300
C	-2.32072400	-1.78092400	-0.18957800
H	-3.37989800	-1.52182700	-0.09253400
H	-2.17176100	-2.25695100	-1.16339400
H	-2.07386500	-2.51049100	0.58733200
C	-1.70144900	0.97856100	1.83260900
H	-2.77971800	1.16660500	1.81031300
H	-1.47985000	0.36371200	2.70992200
H	-1.18845400	1.93847700	1.94476400

Diphenylstannylene [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

Zero-point correction= 0.181717 Thermal correction to Energy= 0.193336 Thermal correction to Enthalpy= 0.194280 Thermal correction to Gibbs Free Energy= 0.141738 Sum of electronic and zero-point Energies= -466.330374 Sum of electronic and thermal Energies= -466.318756 Sum of electronic and thermal Enthalpies= -466.317811 Sum of electronic and thermal Free Energies= -466.370353	

C	0.00000000	1.63830700	0.01432400
C	0.00000000	-1.63830700	0.01432400
C	-0.60552700	1.56949800	-1.25305800
C	-0.64048200	2.67516700	-2.10122900
C	-0.05641700	3.87766800	-1.70441600
C	0.54637600	3.97520800	-0.45181500
C	0.55786200	2.87012400	0.39899700
C	0.60552700	-1.56949800	-1.25305800
C	-0.55786200	-2.87012400	0.39899700
C	0.64048200	-2.67516700	-2.10122900
C	0.05641700	-3.87766800	-1.70441600
C	-0.54637600	-3.97520800	-0.45181500
H	-1.11919600	2.59770600	-3.07330500
H	0.99735100	4.91133200	-0.13537900
H	1.01458200	2.97862600	1.38221100
H	-1.01458200	-2.97862600	1.38221100
H	1.11919600	-2.59770600	-3.07330500
H	-1.05802800	0.63952800	-1.58933300
H	-0.07590400	4.73708800	-2.36829900
H	1.05802800	-0.63952800	-1.58933300
H	0.07590400	-4.73708800	-2.36829900
H	-0.99735100	-4.91133200	-0.13537900
Sn	0.00000000	0.00000000	1.45469200

Tetraphenyldistannene (16b) [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

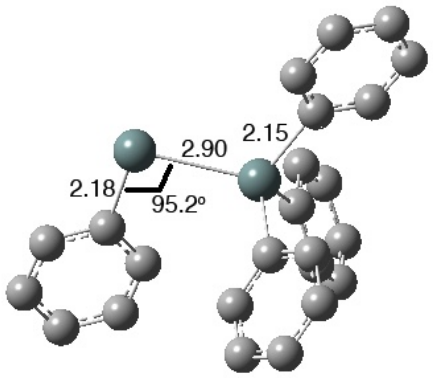
Zero-point correction= 0.365049 Thermal correction to Energy= 0.390241 Thermal correction to Enthalpy= 0.391186 Thermal correction to Gibbs Free Energy= 0.301573 Sum of electronic and zero-point Energies= -932.695367 Sum of electronic and thermal Energies= -932.670174 Sum of electronic and thermal Enthalpies= -932.669229 Sum of electronic and thermal Free Energies= -932.758842	

Sn	0.01178900	-0.76585000	-1.15671300
C	-1.71492600	-0.38127600	-2.38952100
C	1.70107600	-0.27954500	-2.41638000
C	-1.66179000	-0.42424200	-3.79020100
C	-2.80935600	-0.22956400	-4.55951500
C	-4.03306000	0.01062300	-3.93871900
C	-4.10800500	0.04603100	-2.54643000
C	-2.96075900	-0.15556900	-1.78207600
C	1.64471600	0.73216600	-3.38742200
C	2.92198200	-0.94460400	-2.22799900
C	2.76680700	1.06455800	-4.14497200
C	3.96956400	0.38803900	-3.94622700
C	4.04679700	-0.61847400	-2.98589800
H	-2.74587400	-0.26651900	-5.64329500
H	-5.06072500	0.22574400	-2.05679400
H	-3.04661500	-0.13368500	-0.69661900
H	3.00607700	-1.72923700	-1.47776000
H	2.70355000	1.85327900	-4.88905700
H	-0.71728600	-0.61059100	-4.29614200
H	-4.92703200	0.16500000	-4.53557600
H	0.71801400	1.27576000	-3.55458000
H	4.84410900	0.64635200	-4.53599600
H	4.98211100	-1.14693200	-2.82533100
Sn	-0.01178900	0.76585000	1.15671300
C	1.71492600	0.38127600	2.38952100
C	-1.70107600	0.27954500	2.41638000
C	1.66179000	0.42424200	3.79020100
C	2.80935600	0.22956400	4.55951500
C	4.03306000	-0.01062300	3.93871900
C	4.10800500	-0.04603100	2.54643000
C	2.96075900	0.15556900	1.78207600
C	-1.64471600	-0.73216600	3.38742200
C	-2.92198200	0.94460400	2.22799900
C	-2.76680700	-1.06455800	4.14497200
C	-3.96956400	-0.38803900	3.94622700
C	-4.04679700	0.61847400	2.98589800
H	2.74587400	0.26651900	5.64329500
H	5.06072500	-0.22574400	2.05679400
H	3.04661500	0.13368500	0.69661900
H	-3.00607700	1.72923700	1.47776000

H	-2.70355000	-1.85327900	4.88905700
H	0.71728600	0.61059100	4.29614200
H	4.92703200	-0.16500000	4.53557600
H	-0.71801400	-1.27576000	3.55458000
H	-4.84410900	-0.64635200	4.53599600
H	-4.98211100	1.14693200	2.82533100

Phenyl(triphenylstannyl)stannylene (17b) [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

Zero-point correction=	0.364756
Thermal correction to Energy=	0.389091
Thermal correction to Enthalpy=	0.390035
Thermal correction to Gibbs Free Energy=	0.304012
Sum of electronic and zero-point Energies=	-932.713531
Sum of electronic and thermal Energies=	-932.689196
Sum of electronic and thermal Enthalpies=	-932.688252
Sum of electronic and thermal Free Energies=	-932.774275

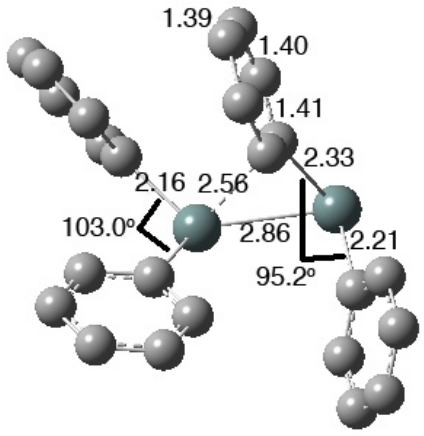


Sn	1.20589500	-1.71538200	-1.44602600
Sn	-0.71701600	-0.02183600	-0.08323900
C	2.95927600	-0.62050900	-0.75190200
C	4.18624600	-1.30755300	-0.82208100
C	5.37386600	-0.73116900	-0.37234400
H	6.30523800	-1.28687000	-0.43058500
C	5.36324600	0.56261900	0.14426500
H	6.28556200	1.01707300	0.49391900
C	4.16583300	1.27512100	0.20593000
H	4.15120200	2.28688800	0.60074100
C	2.98148700	0.68834500	-0.23328700
C	-2.76157500	-0.40992800	-0.61146900
C	-3.20594700	-1.71356000	-0.87508900
C	-4.54202400	-1.97464500	-1.17694500
H	-4.86459400	-2.99291100	-1.37435400
C	-5.46094800	-0.92779500	-1.22575200
H	-6.50266700	-1.12681300	-1.45940800
C	-5.03765200	0.37581000	-0.97313100
H	-5.74994200	1.19510200	-1.01025000
C	-3.69995800	0.63001600	-0.66936600
C	-0.45228700	2.10797900	-0.24916200
C	-0.60973500	2.76305400	-1.47880900
H	-0.89883000	2.20164500	-2.36579300
C	-0.41027600	4.13815100	-1.59521300
H	-0.54047200	4.62570900	-2.55708300
C	-0.04196100	4.88478500	-0.47699700
H	0.11780200	5.95521800	-0.56584900
C	0.11816200	4.25174500	0.75402400
H	0.40010300	4.82865200	1.63039100
C	-0.08653200	2.87599600	0.86500600
H	0.04018200	2.40009300	1.83531500
C	-0.53026300	-0.47634400	2.01339000

C	-1.65554900	-0.81007400	2.77996000
H	-2.63697100	-0.85511900	2.31249800
C	-1.54029000	-1.08387300	4.14298200
H	-2.42498400	-1.33804200	4.72001000
C	-0.29342500	-1.02910800	4.76343900
H	-0.20216300	-1.23900900	5.82508000
C	0.83735900	-0.70433300	4.01599600
H	1.81234900	-0.66166300	4.49292900
C	0.71821900	-0.43580300	2.65244800
H	1.61676500	-0.18839200	2.08945500
H	4.22297000	-2.31431800	-1.23561500
H	2.06764100	1.27277300	-0.17351200
H	-2.50593700	-2.54699800	-0.84528300
H	-3.38882500	1.65430000	-0.47472700

Singly-bridged $SnPh_2$-dimer (20) [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

Zero-point correction=	0.365021
Thermal correction to Energy=	0.389985
Thermal correction to Enthalpy=	0.390929
Thermal correction to Gibbs Free Energy=	0.304843
Sum of electronic and zero-point Energies=	-932.706577
Sum of electronic and thermal Energies=	-932.681613
Sum of electronic and thermal Enthalpies=	-932.680668
Sum of electronic and thermal Free Energies=	-932.766755



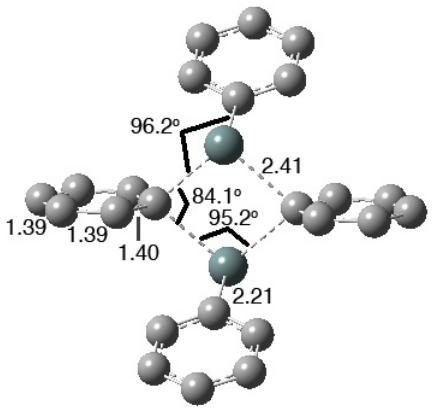
Sn	-1.09848800	-2.21172500	-0.52193400
Sn	0.52550100	0.11169400	-0.90763300
C	2.67798300	0.11192200	-0.78509800
C	3.45708800	-0.52849700	-1.75734500
C	3.33189000	0.68420300	0.31670700
C	4.84682200	-0.58942600	-1.64123200
H	2.98337500	-0.99644900	-2.61830500
C	4.71765300	0.61907100	0.44212900
H	2.75570200	1.17445000	1.09878600
C	5.47790800	-0.01609600	-0.53987700
H	5.43364300	-1.08824800	-2.40712000
H	5.20385200	1.06152700	1.30688300
H	6.55838200	-0.06768100	-0.44334000
C	0.16033600	-1.28417800	1.20788400
C	1.35441800	-1.97430400	1.51525500
C	-0.25648000	-0.29648900	2.12261300
C	2.07476000	-1.71384900	2.67399700
H	1.73238800	-2.72574200	0.82391900
C	0.46513100	-0.02279800	3.28508800
H	-1.15700300	0.27803300	1.92401200
C	1.62966400	-0.73300100	3.56271500
H	2.98987900	-2.26097500	2.87933900
H	0.12014700	0.74999300	3.96550100
H	2.19441400	-0.52046700	4.46574400

C	-2.83472200	-0.86346400	-0.25187700
C	-3.40257000	-0.19633800	-1.34856100
C	-3.45994700	-0.69805600	0.99335600
C	-4.51834000	0.62813800	-1.20748200
H	-2.95486400	-0.29793400	-2.33598600
C	-4.57436700	0.12811200	1.14735100
H	-3.06916900	-1.20802800	1.87221500
C	-5.10269800	0.80016700	0.04655500
H	-4.92614000	1.14216300	-2.07330000
H	-5.03005200	0.24713400	2.12659200
H	-5.96658800	1.44778000	0.16360700
C	0.00443200	2.11814700	-0.30584700
C	-1.31093400	2.45525400	0.05125600
C	0.96669700	3.13811000	-0.32566200
C	-1.64657800	3.76260100	0.39702200
H	-2.08953700	1.69802700	0.06278000
C	0.63210100	4.44932900	0.01442400
H	1.99423700	2.91747000	-0.60449700
C	-0.67515600	4.76249000	0.37997900
H	-2.67061300	3.99759900	0.67259900
H	1.39333200	5.22377100	-0.00602500
H	-0.93660100	5.78286600	0.64487800

Doubly-bridged $SnPh_2$-dimer (*trans*-21) [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

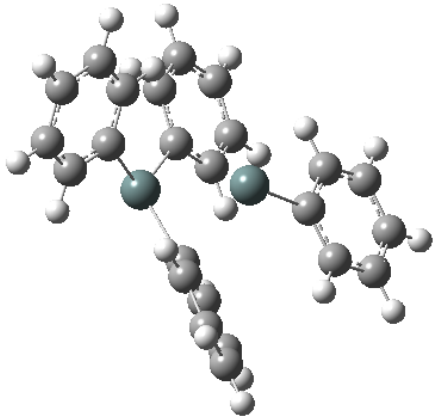
Zero-point correction=	0.365170
Thermal correction to Energy=	0.389986
Thermal correction to Enthalpy=	0.390930
Thermal correction to Gibbs Free Energy=	0.305331
Sum of electronic and zero-point Energies=	-932.690084
Sum of electronic and thermal Energies=	-932.665268
Sum of electronic and thermal Enthalpies=	-932.664324
Sum of electronic and thermal Free Energies=	-932.749923

Sn	-0.95482800	0.00010300	-1.30369500
Sn	0.95501300	-0.00003300	1.30380300
C	0.00008100	1.79220000	0.00020900
C	-0.82613300	2.53658900	0.87165500
C	0.82632000	2.53675900	-0.87107000
C	-0.83414200	3.92831100	0.87244900
H	-1.47541900	2.01031400	1.56717100
C	0.83431700	3.92848300	-0.87160400
H	1.47564800	2.01062100	-1.56665600
C	0.00008000	4.62692000	0.00048300
H	-1.48327900	4.46764200	1.55571200
H	1.48346400	4.46795100	-1.55475100
H	0.00007700	5.71297800	0.00059100
C	-0.00007500	-1.79212700	0.00007100
C	0.82614900	-2.53669400	-0.87121600
C	-0.82633200	-2.53650900	0.87148300



C	0.83410100	-3.92841900	-0.87177900
H	1.47549900	-2.01056200	-1.56678400
C	-0.83438300	-3.92823000	0.87225000
H	-1.47562600	-2.01022800	1.56698900
C	-0.00016700	-4.62684700	0.00028500
H	1.48323800	-4.46789300	-1.55493000
H	-1.48355100	-4.46755500	1.55549000
H	-0.00020100	-5.71290500	0.00037200
C	-2.92900700	0.00009600	-0.30199700
C	-3.63779200	1.19612500	-0.10522400
C	-3.63742800	-1.19606400	-0.10470400
C	-4.96950100	1.20232800	0.31069900
H	-3.15178900	2.15431600	-0.27781900
C	-4.96913200	-1.20249400	0.31122700
H	-3.15112400	-2.15418300	-0.27685700
C	-5.63824100	-0.00013700	0.52906500
H	-5.48398600	2.14752000	0.46115200
H	-5.48332600	-2.14777700	0.46210400
H	-6.67412900	-0.00022500	0.85540300
C	2.92897100	-0.00009500	0.30178600
C	3.63746900	-1.19621500	0.10455000
C	3.63747200	1.19599500	0.10438400
C	4.96906300	-1.20255800	-0.31173500
H	3.15132100	-2.15436000	0.27701900
C	4.96906700	1.20227500	-0.31190300
H	3.15133300	2.15416800	0.27672300
C	5.63793700	-0.00015800	-0.53007400
H	5.48334200	-2.14780800	-0.46252700
H	5.48334900	2.14750200	-0.46282900
H	6.67372600	-0.00018300	-0.85672800

Transition State 25‡ (17b ⇔ trans-21) [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

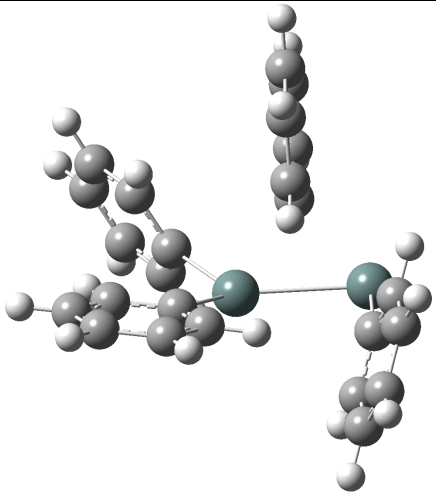
Zero-point correction= 0.364410 Thermal correction to Energy= 0.388593 Thermal correction to Enthalpy= 0.389537 Thermal correction to Gibbs Free Energy= 0.305896 Sum of electronic and zero-point Energies= -932.659204 Sum of electronic and thermal Energies= -932.635021 Sum of electronic and thermal Enthalpies= -932.634077 Sum of electronic and thermal Free Energies= -932.717718	

Sn	0.23355100	-0.82735800	1.41369800
C	0.01199900	-1.51582200	-1.12270700
C	1.21307500	-1.66831200	-1.86265100
C	1.81759300	-2.90169800	-2.00101800
C	1.25819700	-4.04943700	-1.41070600
C	0.09646400	-3.93447000	-0.67173200
C	-0.52026300	-2.67900400	-0.50953100
H	2.73771800	-2.98272500	-2.57200200
H	-0.35581900	-4.80869700	-0.21354400
H	-1.48357200	-2.63641700	-0.00441300
H	1.66750400	-0.80458600	-2.33779800
H	1.73622800	-5.01536300	-1.53754300
Sn	-1.06711900	0.34827300	-1.11528700
C	0.05040800	2.15917500	-0.85331000
C	-0.62473600	3.31517100	-0.43488400
C	0.04463200	4.53276000	-0.32839900
C	1.39834700	4.61998700	-0.65052900
C	2.07490400	3.48049400	-1.08012400
C	1.40757000	2.26169400	-1.18276000
H	-0.49457600	5.41516300	0.00386800
H	3.13123500	3.53301600	-1.32742500
H	1.96944400	1.38590000	-1.49363800
H	-1.68388000	3.27626800	-0.19089500
H	1.91927800	5.56906100	-0.56977400
C	-2.90885400	0.17703800	-0.01220300
C	-3.21872000	0.95889600	1.11037500
C	-3.86613900	-0.74273600	-0.46160900
C	-4.44452600	0.82626800	1.75911100
H	-2.49210400	1.66818800	1.49888700
C	-5.08472000	-0.89460400	0.20078900
H	-3.66920400	-1.34942000	-1.34280600
C	-5.37931500	-0.10608700	1.30984100
H	-4.66435700	1.44250800	2.62621800
H	-5.80742400	-1.62136500	-0.15871100
H	-6.33074200	-0.21586600	1.82119700
C	2.35707900	-0.39249000	1.09440200
C	2.81682500	0.90701600	1.35657500
C	3.30954100	-1.35785900	0.73369800
C	4.16716100	1.23862100	1.24111800
H	2.11520000	1.69402200	1.63109600

C	4.66007700	-1.03475100	0.61135500
H	3.00005900	-2.38189300	0.53596500
C	5.09174000	0.26799500	0.86219400
H	4.49268500	2.25652200	1.43712900
H	5.37716800	-1.79875400	0.32358100
H	6.14350700	0.52159400	0.76630300

Transition State 26‡ [ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output]

Zero-point correction=	0.364501
Thermal correction to Energy=	0.388796
Thermal correction to Enthalpy=	0.389740
Thermal correction to Gibbs Free Energy=	0.304982
Sum of electronic and zero-point Energies=	-932.706224
Sum of electronic and thermal Energies=	-932.681929
Sum of electronic and thermal Enthalpies=	-932.680985
Sum of electronic and thermal Free Energies=	-932.765743

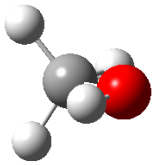


Sn	-1.03747300	-2.08198700	-0.78774200
Sn	0.60671900	0.17256600	-0.78677800
C	2.75964900	0.12427400	-0.72140200
C	3.50707100	-0.30589000	-1.82528700
C	3.45231400	0.49590300	0.44125900
C	4.90125400	-0.36130900	-1.77518900
H	3.00407000	-0.61018900	-2.74098000
C	4.84322400	0.43809400	0.49880600
H	2.90312500	0.82696400	1.32034500
C	5.57063200	0.01009300	-0.61199300
H	5.46159800	-0.69768000	-2.64275900
H	5.35961900	0.72533300	1.41028300
H	6.65478000	-0.03634200	-0.56806000
C	0.19588900	-1.12861100	1.16640200
C	1.25277800	-1.97757900	1.55157800
C	-0.51046400	-0.46921500	2.18850700
C	1.57730200	-2.17547100	2.88956100
H	1.83827100	-2.48933900	0.78994800
C	-0.19121800	-0.65955000	3.53107100
H	-1.31699700	0.21278100	1.93317300
C	0.85141900	-1.51557400	3.88168400
H	2.39381000	-2.83818900	3.15993600
H	-0.74877000	-0.13481800	4.30117200
H	1.10085400	-1.66644400	4.92790800
C	-2.79003800	-0.75685900	-0.51652200
C	-3.23845900	0.06404800	-1.56302400
C	-3.54818000	-0.76593000	0.66414500
C	-4.37430300	0.86243400	-1.43072800
H	-2.68055100	0.10943900	-2.49671400
C	-4.67790100	0.03962400	0.81206700
H	-3.25056100	-1.39952000	1.49799500
C	-5.09170300	0.86060200	-0.23576300

H	-4.68921500	1.49783700	-2.25365000
H	-5.23533600	0.02439400	1.74463300
H	-5.96960600	1.48987200	-0.12355300
C	0.09003800	2.14488500	-0.09453500
C	-1.23174300	2.48831300	0.22836700
C	1.07812100	3.13252700	0.01997800
C	-1.55126100	3.77216900	0.66618100
H	-2.02846900	1.75532200	0.13835700
C	0.76018100	4.42022200	0.45324100
H	2.11268200	2.90302100	-0.22506300
C	-0.55568400	4.74127000	0.77964300
H	-2.58150300	4.01361900	0.91174900
H	1.54082200	5.17105000	0.53553000
H	-0.80442600	5.74312700	1.11745900

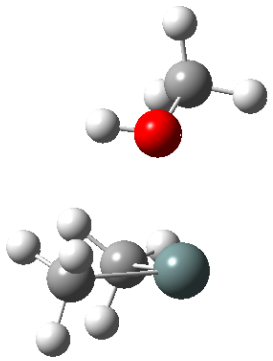
Methanol (ωB97XD/6-31+G(d,p) output)

Zero-point correction=	0.051874
Thermal correction to Energy=	0.055216
Thermal correction to Enthalpy=	0.056160
Thermal correction to Gibbs Free Energy=	0.029110
Sum of electronic and zero-point Energies=	-115.643298
Sum of electronic and thermal Energies=	-115.639957
Sum of electronic and thermal Enthalpies=	-115.639013
Sum of electronic and thermal Free Energies=	-115.666062



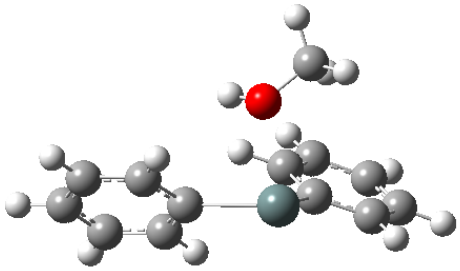
C	0.66276400	-0.02069000	0.00000300
H	1.08189800	0.98703500	-0.00054600
H	1.02462200	-0.54512500	0.89426900
O	-0.74485300	0.12210500	0.00000300
H	-1.14881200	-0.74858300	0.00000000
H	1.02453300	-0.54603100	-0.89376700

$SnMe_2$-MeOH Complex (18) (ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output)

Zero-point correction= 0.124995 Thermal correction to Energy= 0.135156 Thermal correction to Enthalpy= 0.136100 Thermal correction to Gibbs Free Energy= 0.088812 Sum of electronic and zero-point Energies= -198.754438 Sum of electronic and thermal Energies= -198.744276 Sum of electronic and thermal Enthalpies= -198.743332 Sum of electronic and thermal Free Energies= -198.790620	

Sn	-0.54634400	0.11873500	-0.44124500
C	2.76060200	-0.05030700	-0.02260000
H	2.75638200	0.36790500	-1.02976800
H	2.73696500	0.76392500	0.70774100
H	3.65796800	-0.65970700	0.11255900
O	1.58900600	-0.86417500	0.08044400
C	-1.28861000	-1.38119900	1.00117100
H	-1.18784100	-2.40282800	0.61793600
H	-0.78341900	-1.30965400	1.97346100
H	-2.35708000	-1.21010900	1.18414700
C	-0.08374900	1.60818200	1.12835900
H	0.53585000	2.43592400	0.76592600
H	-1.02396900	2.04152800	1.49455200
H	0.41185200	1.14480700	1.99147500
H	1.52898200	-1.25521900	0.95909000

$SnPh_2$-MeOH Complex (19) (ωB97XD/6-31+G(d,p)-LANL2DZdp(Sn) output)

Zero-point correction= 0.236251 Thermal correction to Energy= 0.252077 Thermal correction to Enthalpy= 0.253021 Thermal correction to Gibbs Free Energy= 0.190421 Sum of electronic and zero-point Energies= -581.998507 Sum of electronic and thermal Energies= -581.982681 Sum of electronic and thermal Enthalpies= -581.981737 Sum of electronic and thermal Free Energies= -582.044337	

C	1.56336900	0.28661900	-0.30611700
C	-1.71471000	0.15098100	-0.29330700
C	1.42900300	1.31775100	0.63923000
C	2.49754400	2.14652700	0.97917500
C	3.73865500	1.96885000	0.36704600
C	3.90061700	0.95920900	-0.57872800
C	2.82486100	0.12842200	-0.90059200
C	-1.71618600	1.52604500	-0.58048400
C	-2.88373800	-0.38584400	0.27257400
C	-2.82488700	2.32843300	-0.30951300
C	-3.96484900	1.77269100	0.26971000
C	-3.99299600	0.41066300	0.56285400
H	2.36283100	2.93413900	1.71590700
H	4.86356800	0.81506800	-1.06094700
H	2.98172600	-0.66262300	-1.63336500
H	-2.94178300	-1.45229400	0.48996900
H	-2.79680400	3.38907300	-0.54425100
H	0.46592100	1.49104000	1.11788700
H	4.57227000	2.61521100	0.62612300
H	-0.83315200	1.98810300	-1.01766700
H	-4.82724100	2.39625700	0.48690500
H	-4.88013300	-0.03267300	1.00686200
Sn	-0.02053400	-1.18294000	-0.76397300
C	1.06656700	-1.84364300	2.33414300
H	1.49506200	-2.73489700	1.87458100
H	1.78274700	-1.01952500	2.26688000
H	0.81788900	-2.05707500	3.37672900
O	-0.12549200	-1.54385600	1.59847500
H	-0.57179200	-0.77220200	1.96929100

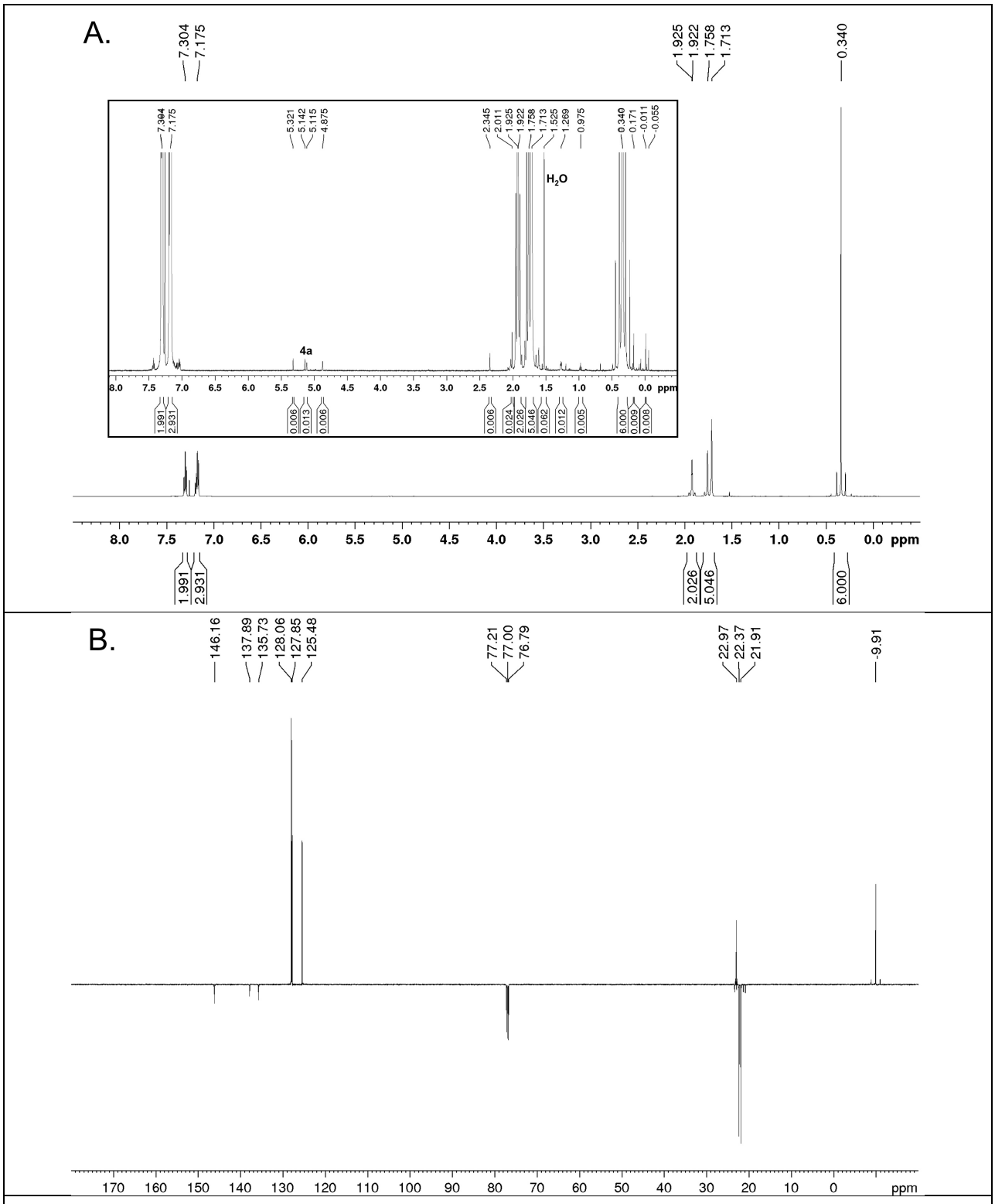


Figure S16. (a) ^{1}H and (b) DEPTq NMR spectra of **2** in $CDCl_3$. The inset in (a) contains an expansion of the spectrum to show contributions from impurities.

References

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