Reactions of an Isolable Dialkylstannylene with Carbon Disulfide and Related Heterocumulenes

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Supporting Information

Contents

1. X-ray analysis of 8, 9 and 11.

Molecular structure determination. Single crystals of **8**, **9** and **11** suitable for X-ray analysis were obtained by the recrystallization from hexane. The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω-2θ scan mode. The structures were solved by direct methods and refined on *F2* by full-matrix least-squares methods using SHELX-2000.[S1] Crystal and refinement data for **8**, **9**, and **11** are deposited with CCDC; CCDC Nos. are 1432785, 1432786 and 1432787, respectively.

Table S1. Crystal and Refinement Data for **8**, **9** and **11**

Parameters	8	9	11
Empirical formula	$C_{34}H_{80}S_4Si_8Sn_2$	$C_{34}H_{80}S_4Si_8Sn_2$	$C_{29}H_{59}NO_2Si_4Sn$
Formula weight	1079.32	1079.32	684.82
Crystal system, Space group	Monoclinic,P2(1)/c	Triclinic, P-1	Triclinic, P1
a [Å]	11.6252(10)	11.5533(12)	11.545(2)
b [Å]	28.719(3)	15.0410(15)	11.929(3)
c [Å]	17.7048(16)	17.1546(18)	15.061(4)
α [deg]	90	88.192(2)	75.183(6)
β [deg]	108.850(2)	71.330(2)	67.479(3)
γ [deg]	90	76.698(2)	76.791(4)
V [Å^{-3}]	5594.0(9)	2745.5(5)	1832.4(7)
Z, D_{calcd} [Mg /m^{-3}]	4, 1.282	2, 1.306	2, 1.241
μ [mm^{-1}]	1.235	1.258	0.852
F (000)	2240	1120	724
Reflections collected	30544	32975	18570
Independent Reflections	9733	12389	6375
R(int)	0.0404	0.0251	0.0238
Data/restraints /parameters	9733 / 26 / 453	12389 / 0 / 457	6375 / 2 / 350
final R indices [$I>2\sigma(I)$] R_1 ,wR2	0.0486 , 0.1228	0.0333, 0.0922	0.0252, 0.0791
R indices (all data) wR_2	0.0735 , 0.1372	0.0440, 0.1042	0.0327, 0.1160

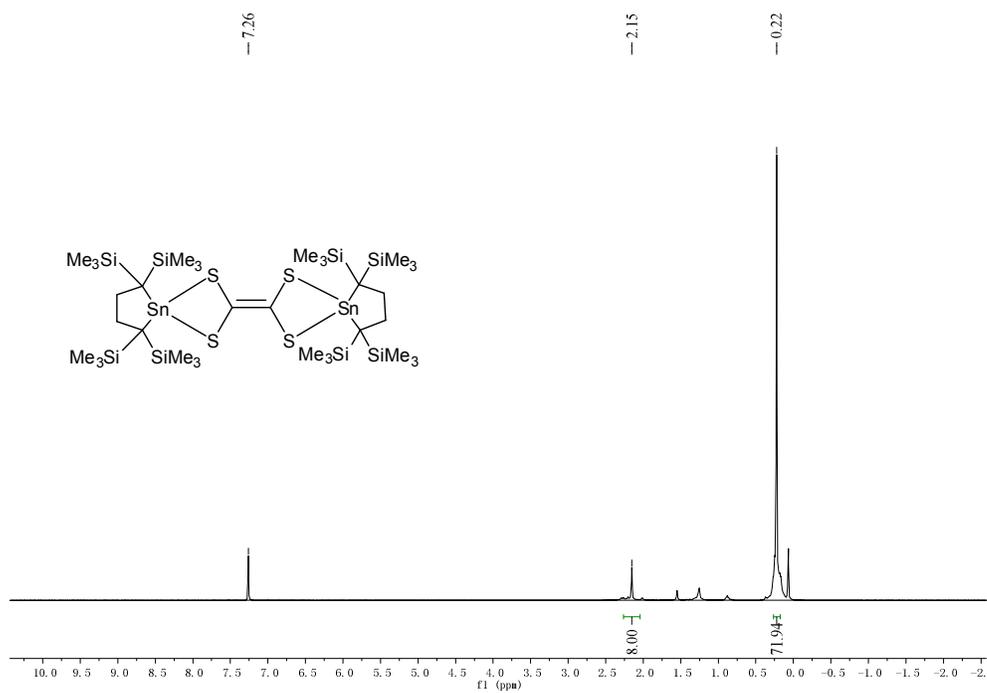## 2. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra of 8, 9 and 11.

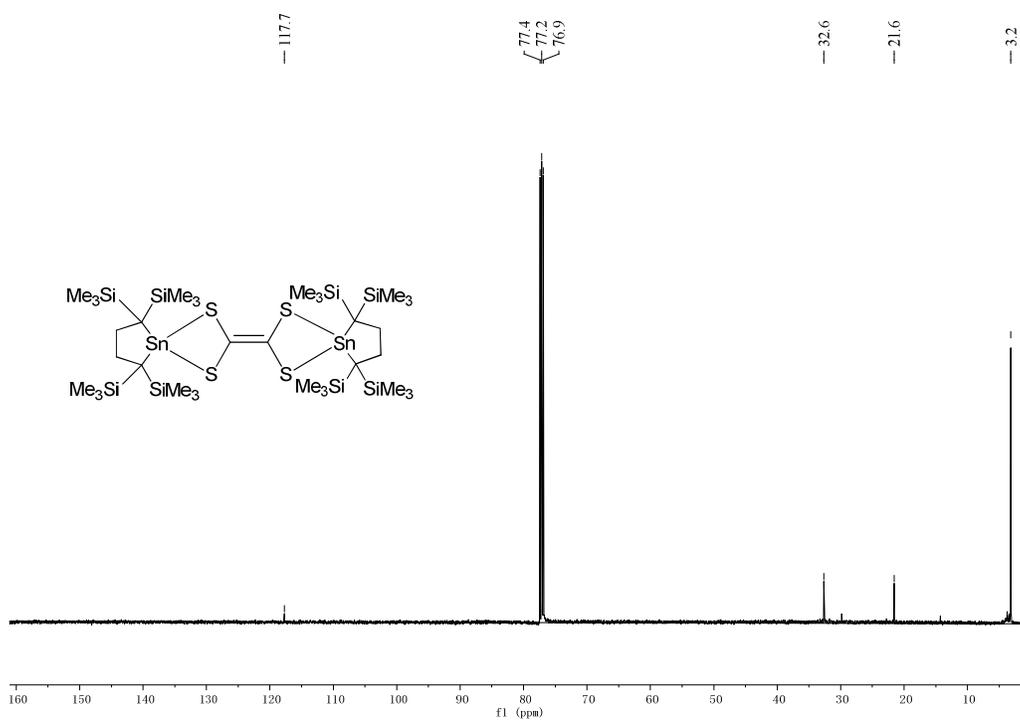**Figure S1**. ^{1}H NMR spectrum of compound **8** in CDCl$_3$.

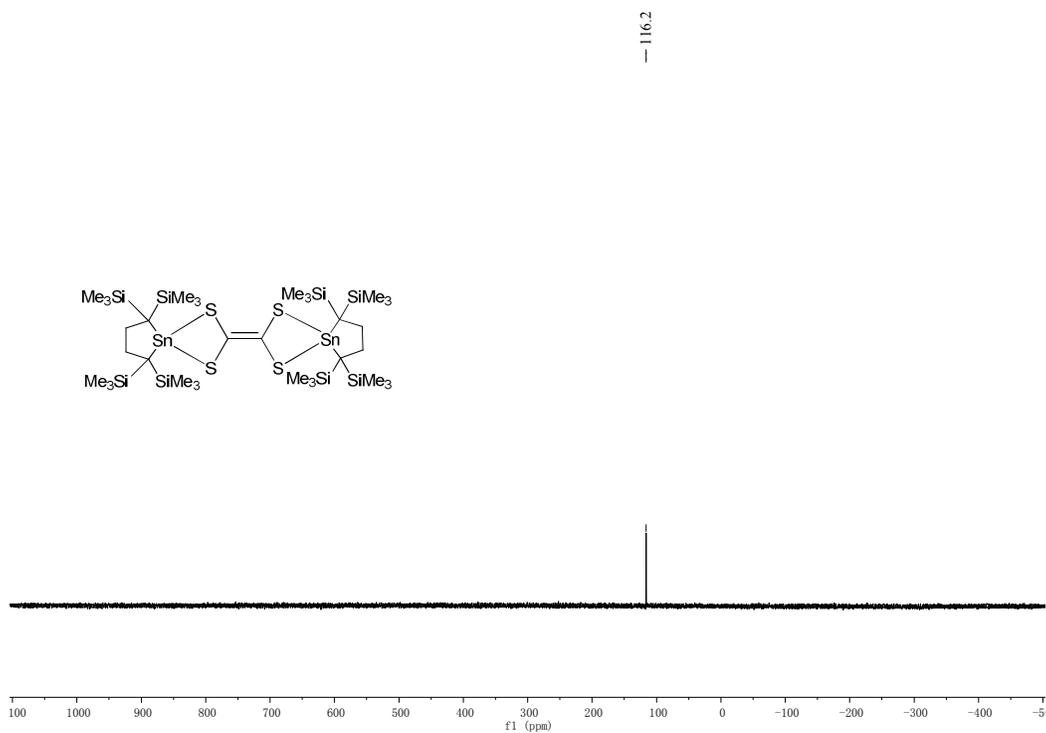**Figure S2**. ^{13}C NMR spectrum of compound **8** in CDCl$_3$.

— 116.2

Figure S3. ^{119}Sn NMR spectrum of compound **8** in CDCl$_3$.

— 7.26 — 2.18 — 0.19

8.00 72.06
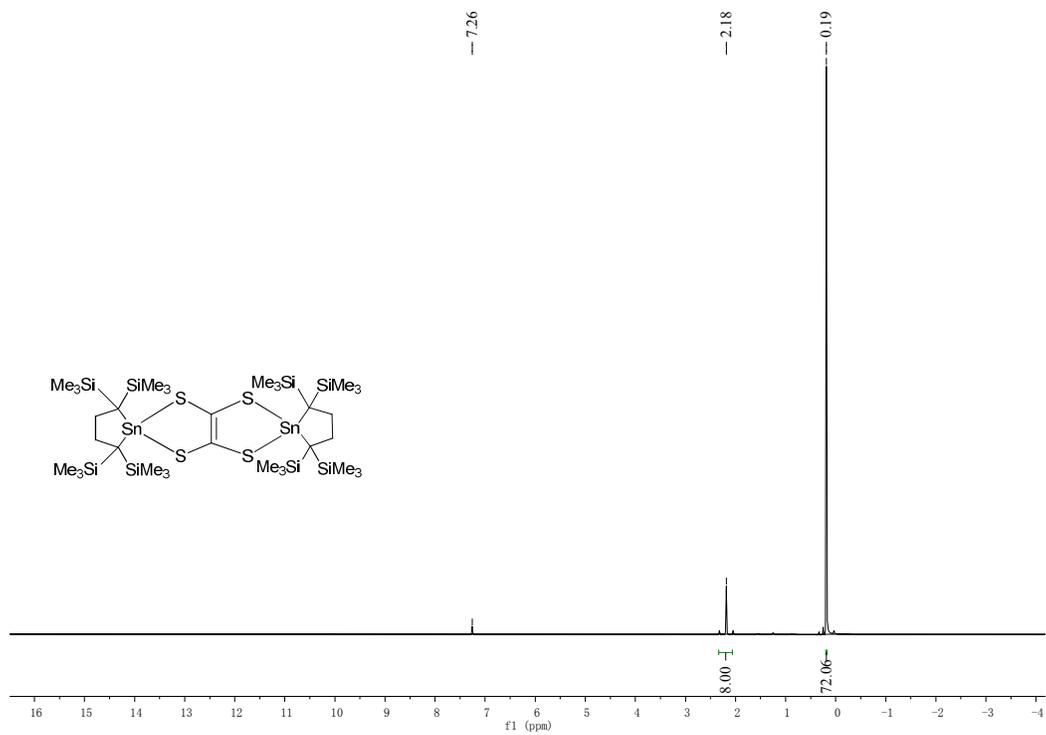
Figure S4. ^{1}H NMR spectrum of compound **9** in CDCl$_3$.

Figure S5. ^{13}C NMR spectrum of compound **9** in CDCl$_3$.
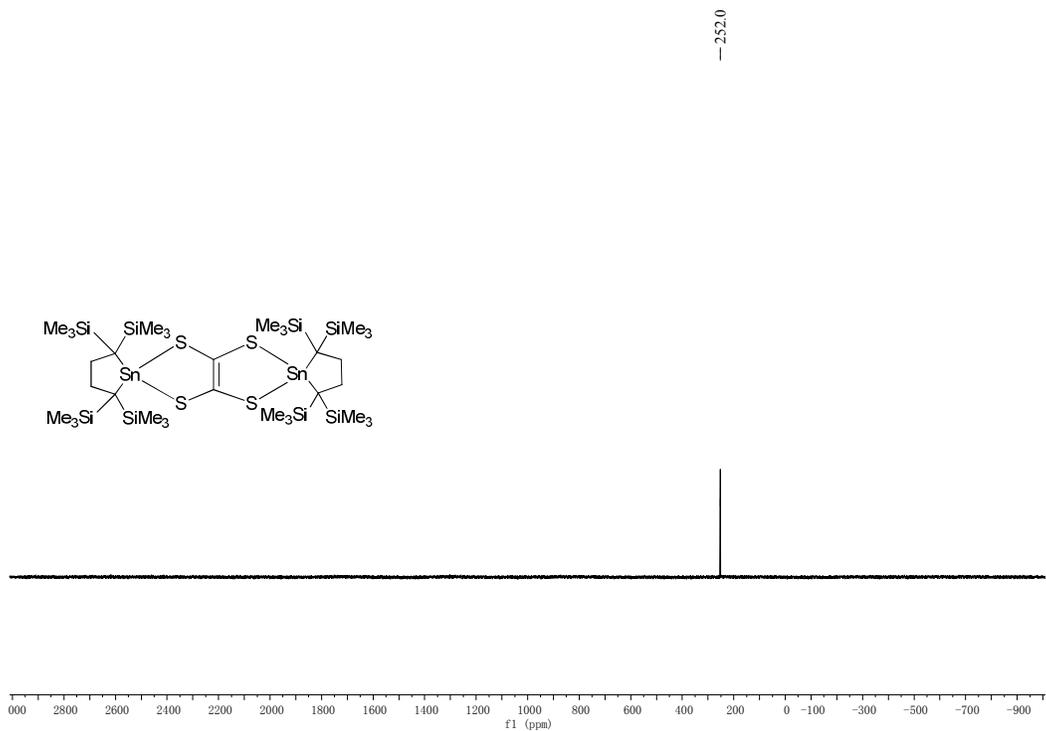
Figure S6. ^{119}Sn NMR spectrum of compound **9** in CDCl$_3$.
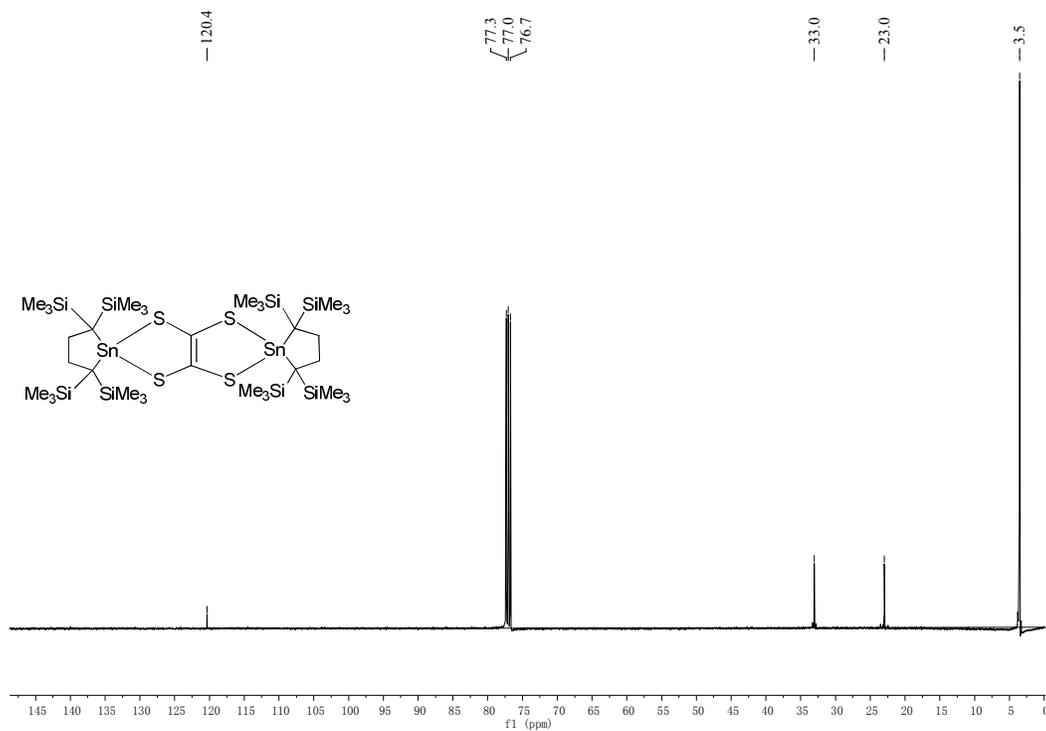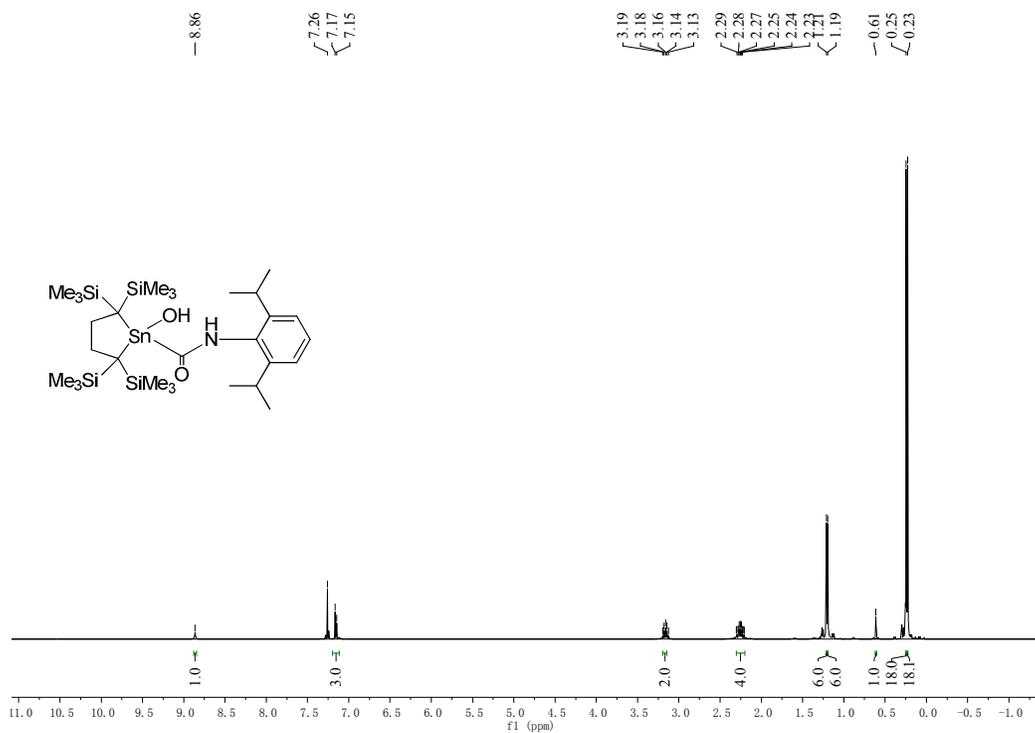
Figure S7. ^{1}H NMR spectrum of compound **11** in CDCl$_3$.
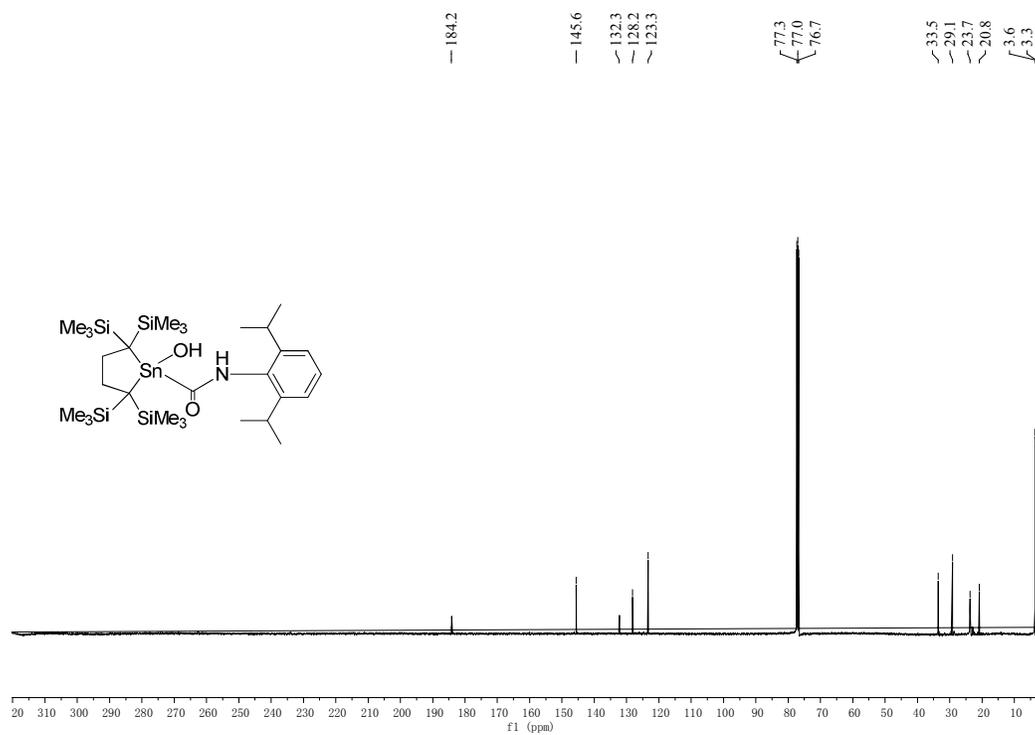

Figure S8. ^{13}C NMR spectrum of compound **11** in CDCl$_3$.
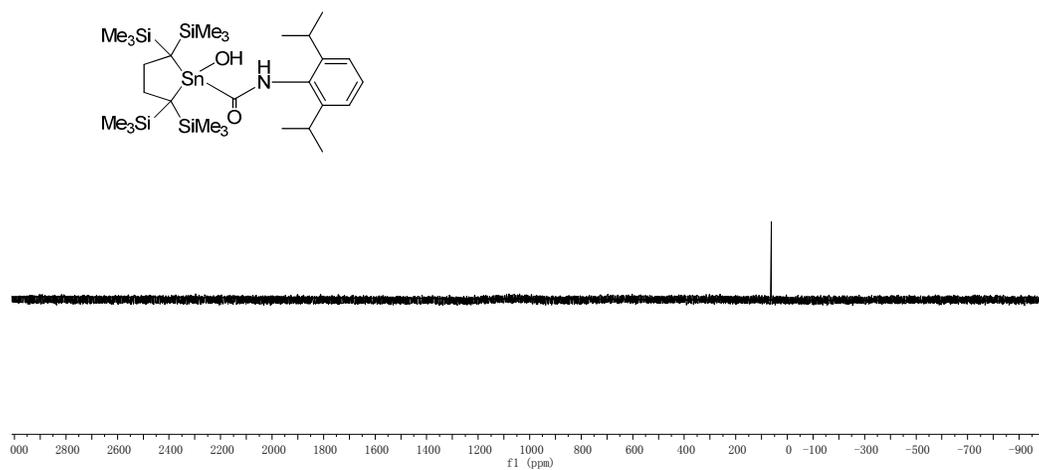
Figure S9. ^{119}Sn NMR spectrum of compound **11** in CDCl3.
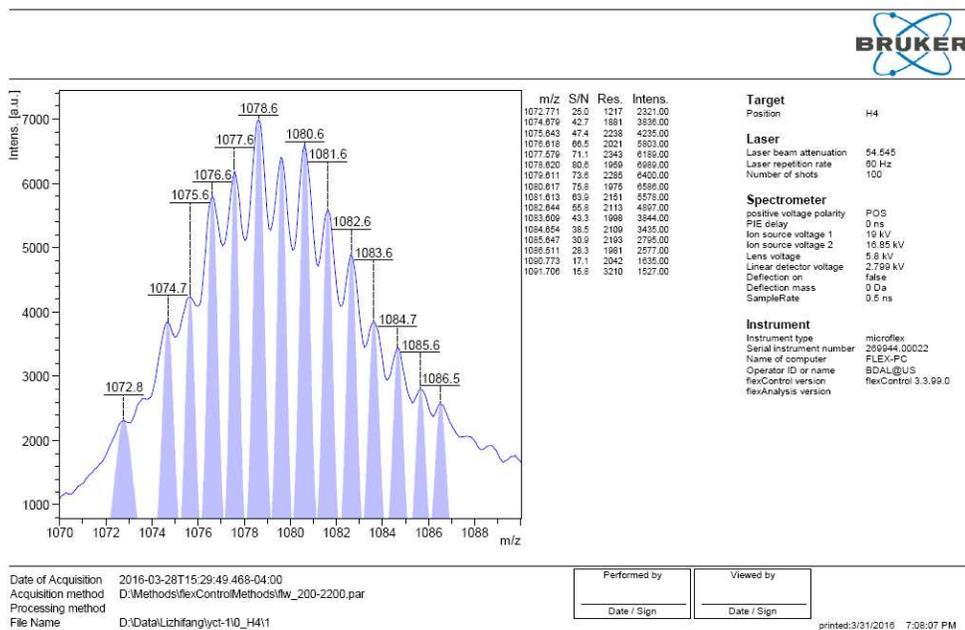
3. MALDI-TOFMS spectra of 8 and 9.
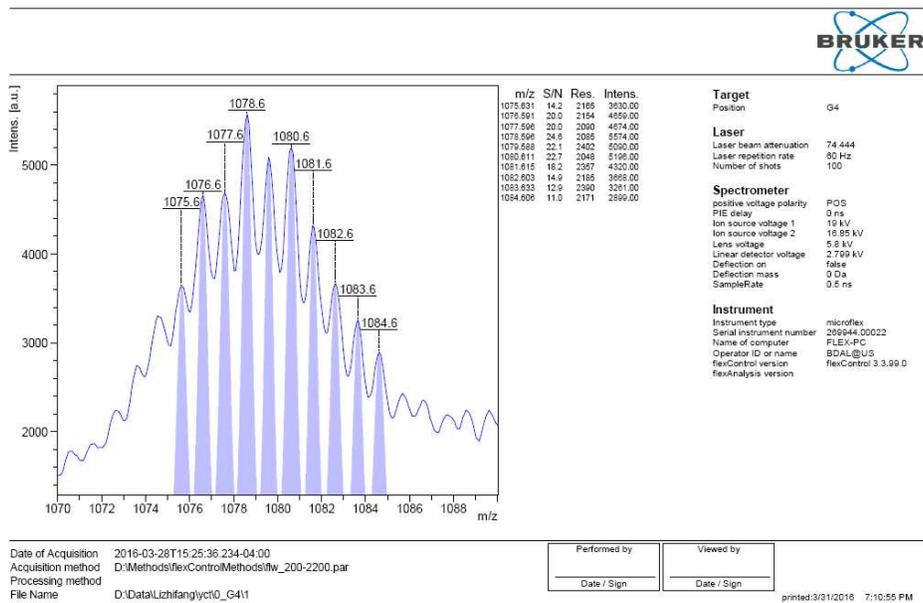

Figure S10. MALDI-TOFMS spectrum of **8**.

Figure S11. MALDI-TOFMS spectrum of **9**.

4. The rearrangement of 8 into 9

Thermal rearrangement of 8 to 9. In an NMR tube was added compound **8** (13 mg, 0.012 mmol), and C_6D_6 (0.6 mL) and then the mixture was stirred for 48 h at 100 °C. The ^{119}Sn NMR spectrum showed the formation of **9** in 9% yields as shown in Figure S12.

Rearrangement of 8 to 9 catalyzed by dialkylstannylene 1. A mixture of **8** (52 mg, 0.048 mmol), dialkylstannylene **1** (20 mol%), and hexane (10 mL) was stirred for 24h at room temperature in a 20 mL flask. The solvent was removed under vacuo. The ^{119}Sn NMR spectrum of the residue in $CDCl_3$ showed quantitative formation of **9** (Figure S13).

Rearrangement of 8 to 9 catalyzed with BF₃. A mixture of **8** (13 mg, 0.012 mmol), $CDCl_3$ (0.6 mL), and a catalytic amount of BF_3 (10 mol%) in an NMR tube was stirred for 30 min at room temperature and then the ^{119}Sn NMR spectrum was measured. Compound **9** was found to form in 92% (Figure S14).
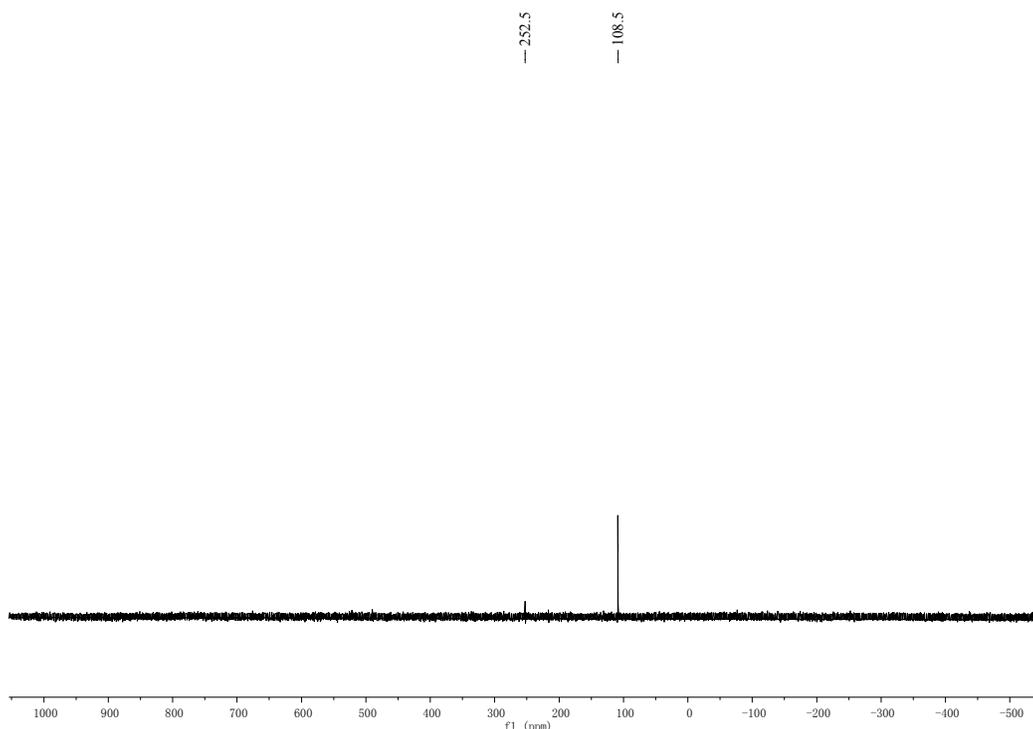
Figure S12. ^{119}Sn NMR spectrum obtained after the thermal reaction of **8** in C_6D_6.

—— 252.0

Figure S13. ^{119}Sn NMR spectrum obtained after **8** was treated in the presence of stannylene **1** (20 mol%) in hexane at rt showing the quantitative formation of **9**.   The NMR spectrum was measured in CDCl$_3$.

—— 251.9

—— 115.7

Figure S14. ^{119}Sn NMR spectrum obtained after compound **8** was treated with BF$_3$ (10 mol%) for 30 min in CDCl$_3$.

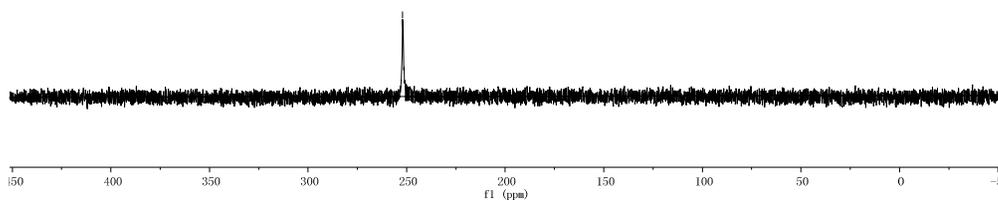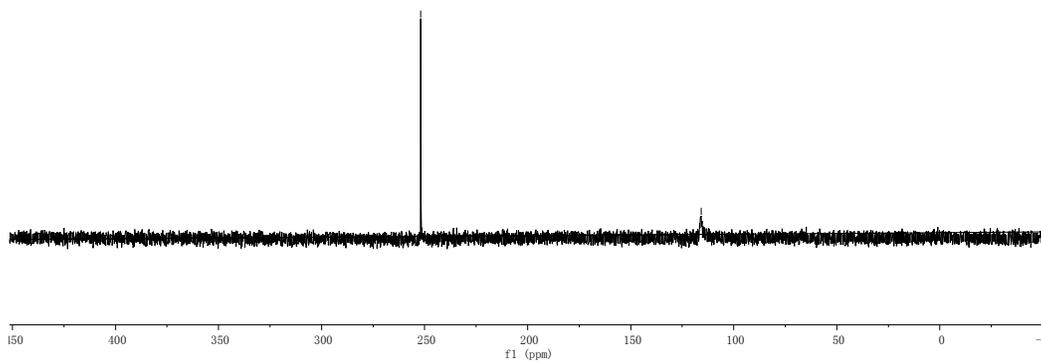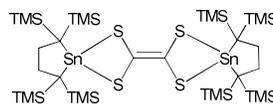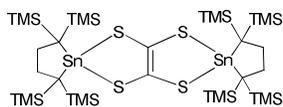**5. Kinetic study of the rearrangement of 8 to 9.** For a kinetic study, a C_6D_6 (1 mL) solution of **8** (50 mg, 0.046 mmol) containing stannylene **1** (1.1 mg, 5 mol%) in an NMR tube was kept at 10 °C and monitored the time course of the relative ^{119}Sn NMR signal intensities of **8** and **9**. The molar ratio of **8**/(**8**+**9**) was determined using the relative NMR signal intensities of **8** (I_8) and **9** (I_9) by assuming the same relaxation times for the ^{119}Sn nuclei in **8** and **9**. As the slope of a linear plot of $\ln(I_8/(I_8+I_9))$ against reaction time (t/h) (Figure S13) , the first-order rate constant (k') was determined as $5.2 \times 10^{-3}\ h^{-1}$ or $1.4 \times 10^{-6}\ s^{-1}$. Assuming that the rearrangement is bimolecular with the unimolecular contribution of **1**, the 2nd-order rate constant (k) is estimated to be $6.3 \times 10^{-4}\ M^{-1}\ s^{-1}$ at 10 °C. The assumption for the relaxation times, the significant temperature turbulence, and other minor ambiguities during the experiment make the rate constant rather inaccurate but the results support the proposed mechanism for the rearrangement (eq 8).
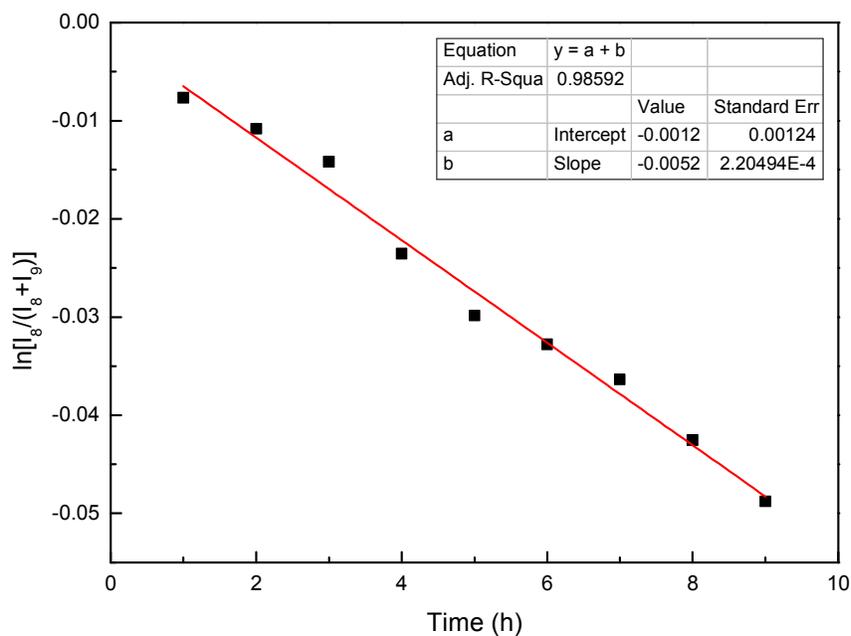

Equation	y = a + b		
Adj. R-Squa	0.98592		
		Value	Standard Err
a	Intercept	-0.0012	0.00124
b	Slope	-0.0052	2.20494E-4

Figure S15. Plot of $\ln[I_8/(I_8+I_9)]$ vs time.

6. DFT Calculations

All calculations were performed on an SGI Altix 450 server using the Gaussian 03 package.[S2]   Geometry optimizations of all stationary points were performed by using the DFT method at the B3LYP level using the basis sets of 6-31G(d,p) for C, H, and S atoms + LanL2DZ for Sn.   GaussView was used for visual inspection of the final geometries and vibrational frequencies as well as for drawing pictures of the optimized structures. All of the structures obtained herein were verified by examination of their Hessian matrix as minima (all frequencies real) or transition states (one imaginary frequency). Zero-point vibrational energies (ZPE) were incorporated into the total energies without a scale factor.   At every transition state, the transition vector was animated with the GaussView program, and if necessary, the intrinsic reaction coordinate (IRC) was computed to connect the corresponding minima.

The DFT calculations were performed for the following compounds **8**, **9**, **8'**, **9'**, **8"**, and **9",** and stationary points appeared during the reaction of **1'** with CS_2.
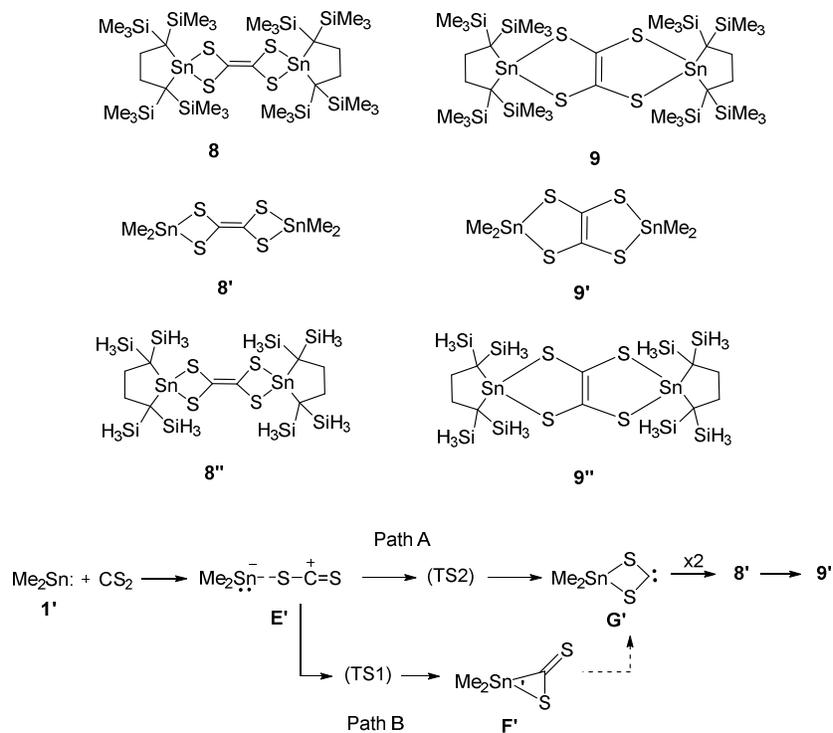
Table S2. Relative Energy Parameters for Species Shown in Chart S1 Calculated at the B3LYP/6-31G(d,p) for C, H, S atoms and LanL2DZ for Sn at 298.15K

	ΔE^a	ΔH^a	ΔG^a	ΔS^b
8	0.0	0.0	0.0	0.0
9	-12.8	-12.9	-13.0	-0.4
8'	0.0	0.0	0.0	0.0
9'	-15.4	-16.0	-13.5	-8.2
8"	0.0	0.0	0.0	0.0
9"	-15.1	-15.2	-15.3	0.3
1' + CS$_2$	0.0	0.0	0.0	0.0
E'	3.3	3.3	11.8	-28.5
F'	6.0	5.9	16.4	-35.1
G'	20.1	20.2	29.9	-32.6
TS1	10.1	9.8	20.4	-35.6
TS2	20.6	19.9	31.2	-37.7
(1/2) **8'**	-55.7	-56.2	-21.7	-115.9
(1/2) **9'**	-71.1	-72.2	-35.2	-124.1

a. in kcal.mol^{-1}; b. in cal.mol^{-1}.K^{-1}

7. References

(S1) (a) C. L. Picou, E. D. Stevens, M. Shah, J. H. Boyer, *Acta Crystallogr. Sect. C* **1990**, *46*, 1148.   (b) SMART, SAINT, SADABS and SHELXTL, Bruker AXS Inc., Madison, 2000.

(S2) Gaussian 03 (Revision D.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.