Electronic Supplementary Information

Diverse Reactions of a Fluorostannylenoid towards Ethynes

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Contents

1. X-ray analysis of 7

Molecular structure determination. Single crystals of **7** 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 (λ = 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 **7** is deposited with CCDC; CCDC No. 1474964.

Table S1. Crystal and Refinement Data for 7.

Parameters	**7**
Empirical formula	$C_{38}H_{86}Si_8Sn_2$
Formula weight	1005.17
Crystal system, Space group	Triclinic, P-1
a [Å]	11.7540(6)
b [Å]	15.3810(8)
c [Å]	16.6332(9)
α [deg]	65.5380(10)
β [deg]	77.7190(10)
γ [deg]	85.8960(10)
V [Å^{-3}]	2674.1(2)
Z,D_{calcd}[Mg/m^{-3}]	2, 1.248
μ [mm^{-1}]	1.136
F (000)	1052
Reflections collected	33375
Independent Reflections	12199
R(int)	0.0227
Data/restraints/parameters	12199/0/457
final R indices [$I>2\sigma(I)$] R_1 ,$wR2$	0.0284, 0.0931
R indices (all data) wR_2	0.0421, 0.1307

2. ^{1}H, ^{13}C and ^{119}Sn spectra of 6- 8 (Figures S1-S9)

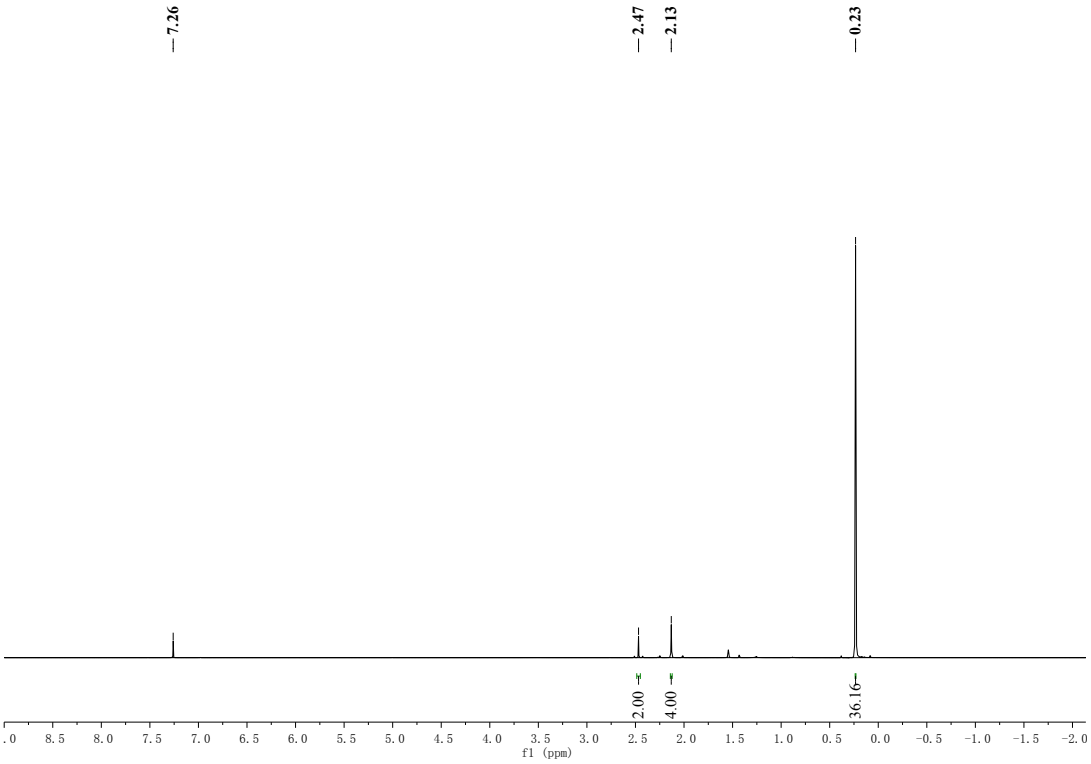


Figure S1.^{1}H NMR spectrum of compound **6** in $CDCl_3$.

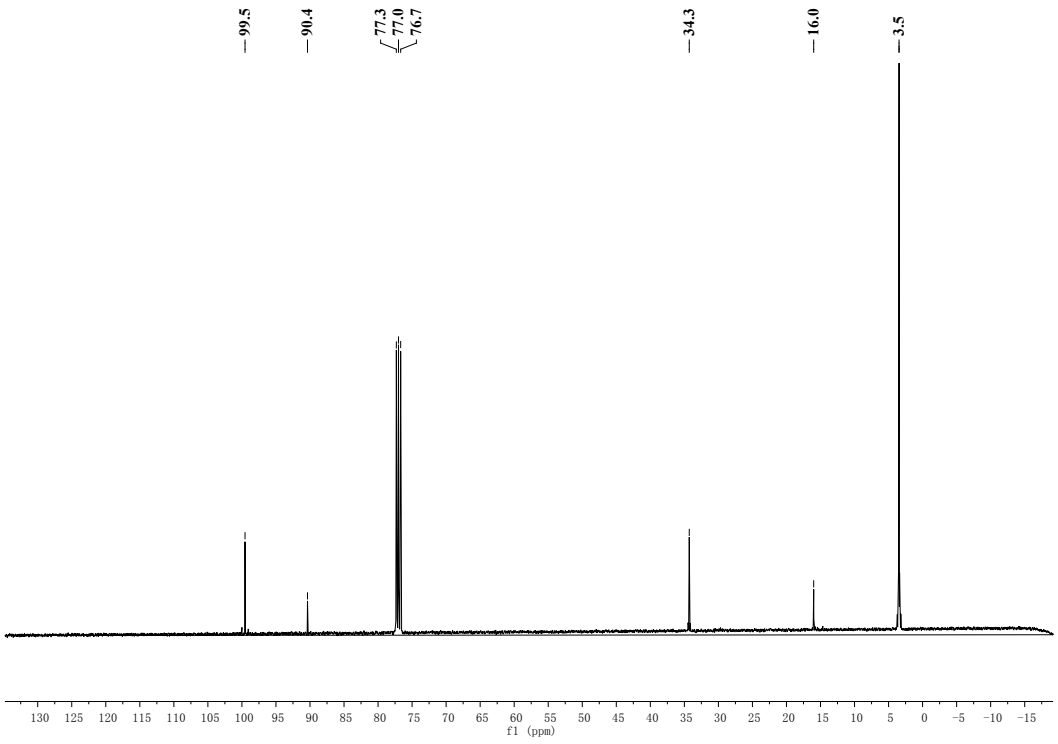


Figure S2.^{13}C NMR spectrum of compound **6** in $CDCl_3$.

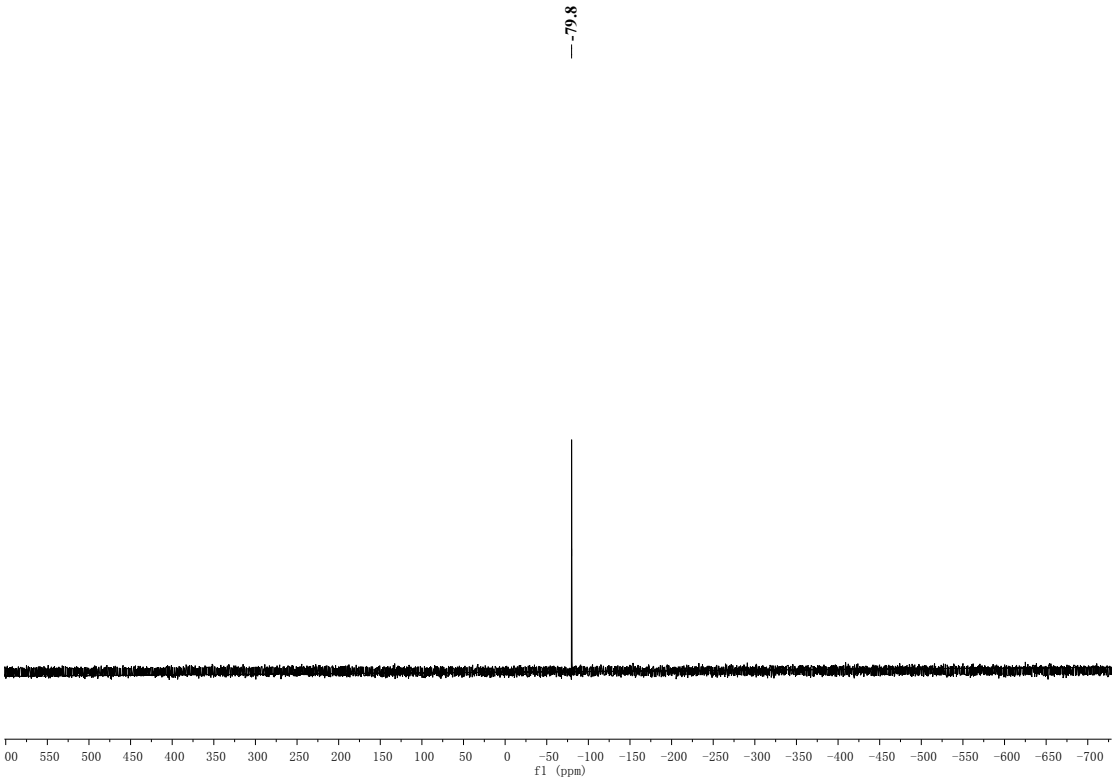


Figure S3. ^{119}Sn NMR spectrum of compound **6** in $CDCl_3$.

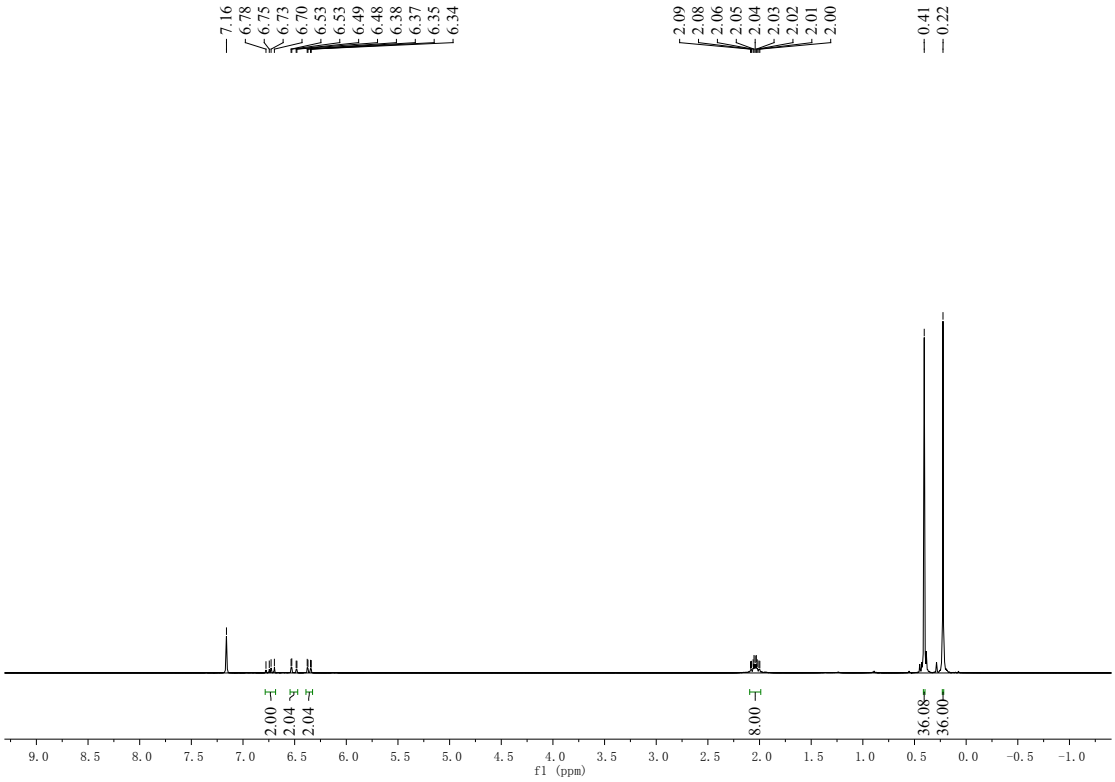


Figure S4. ^{1}H NMR spectrum of compound **7** in C_6D_6.

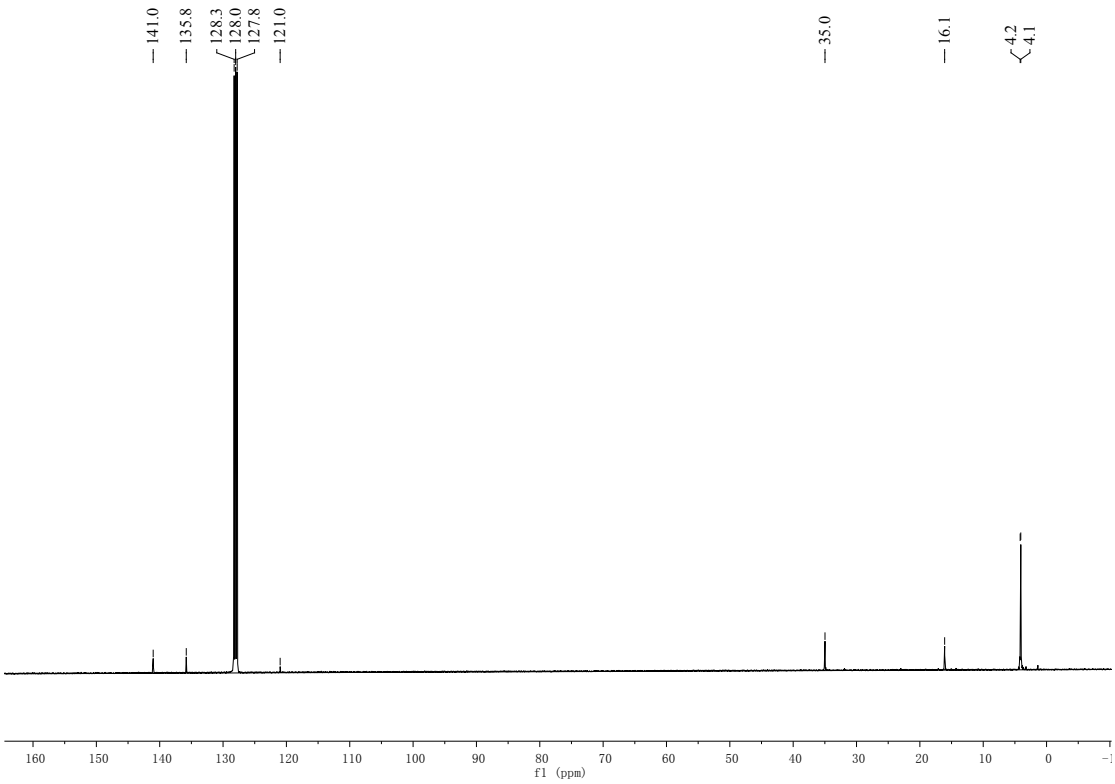


Figure S5. ^{13}C NMR spectrum of compound **7** in C_6D_6.

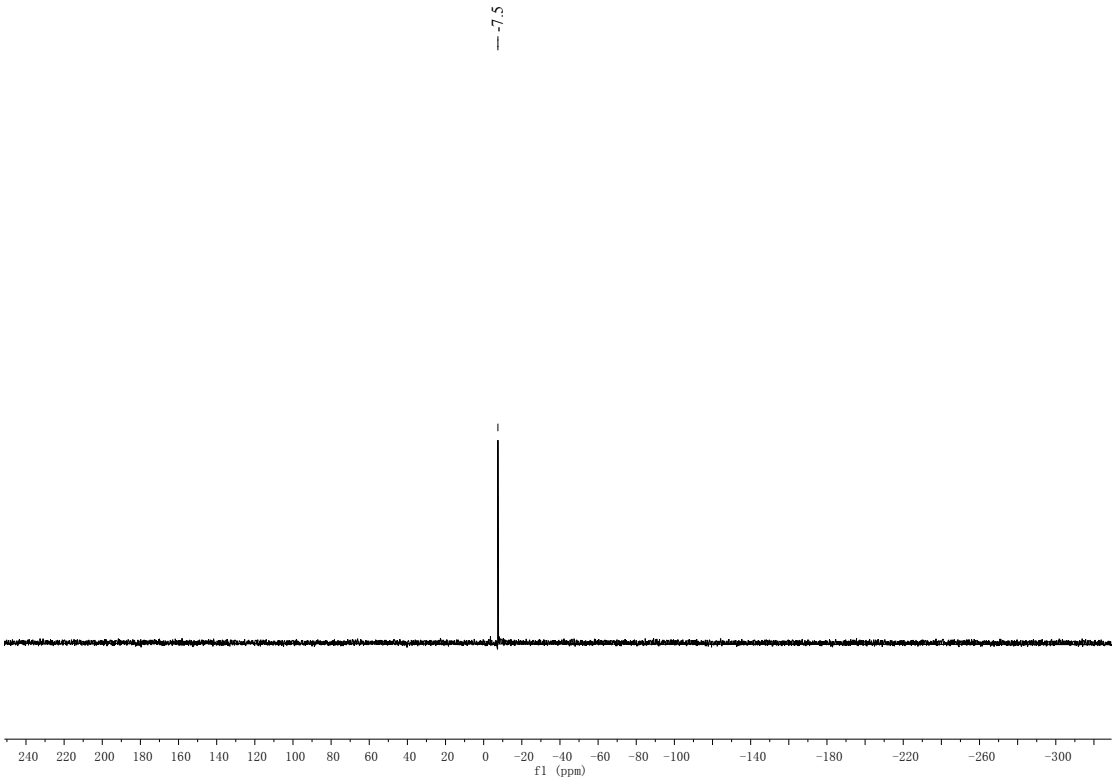


Figure S6. ^{119}Sn NMR spectrum of compound **7** in C_6D_6.

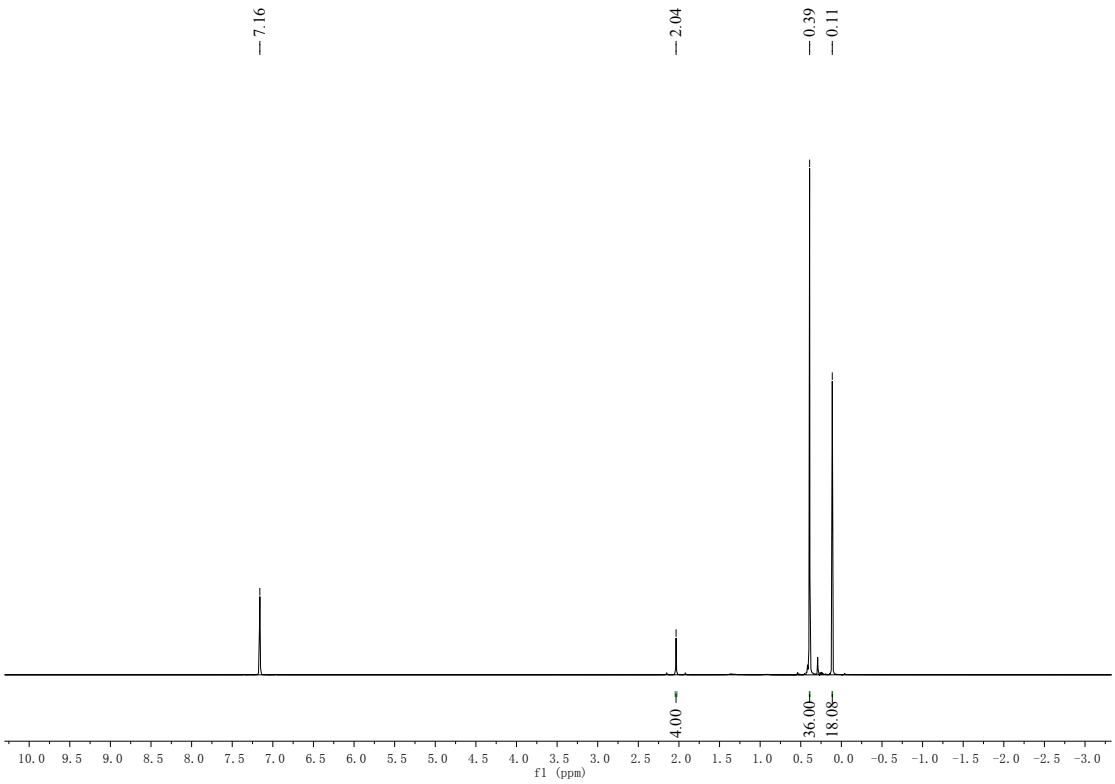


Figure S7.[1]H NMR spectrum of compound **8** in C_6D_6.

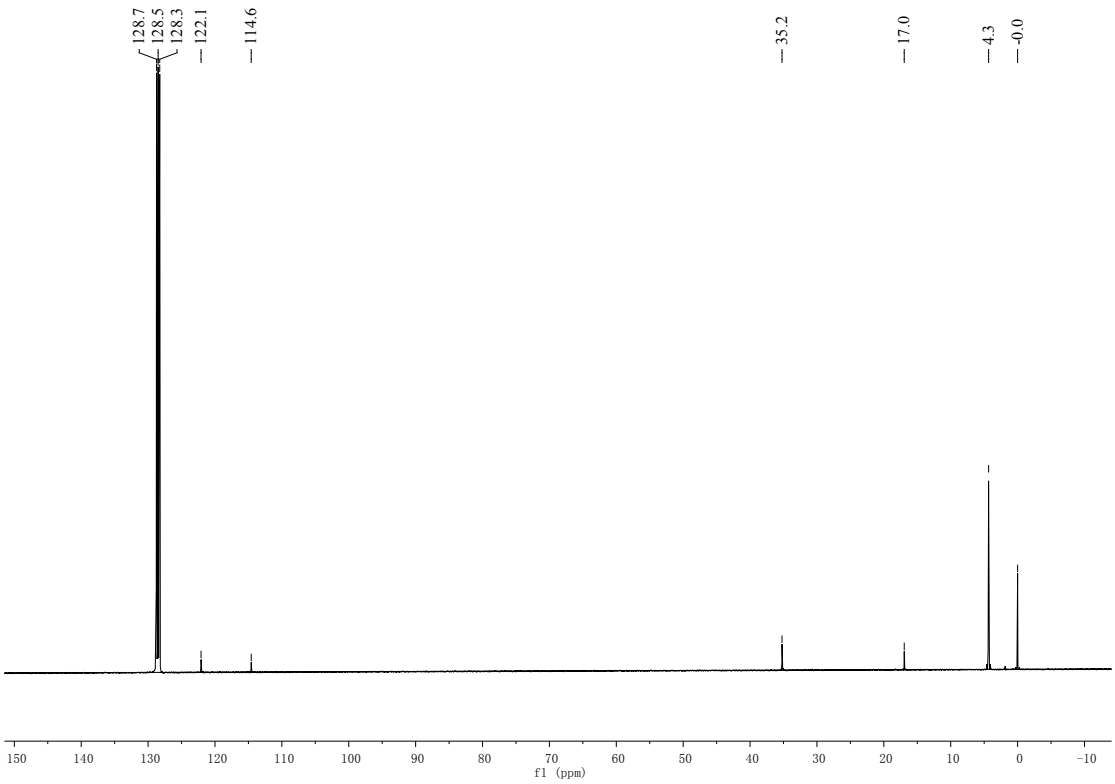


Figure S8.[13]C NMR spectrum of compound **8** in C_6D_6.

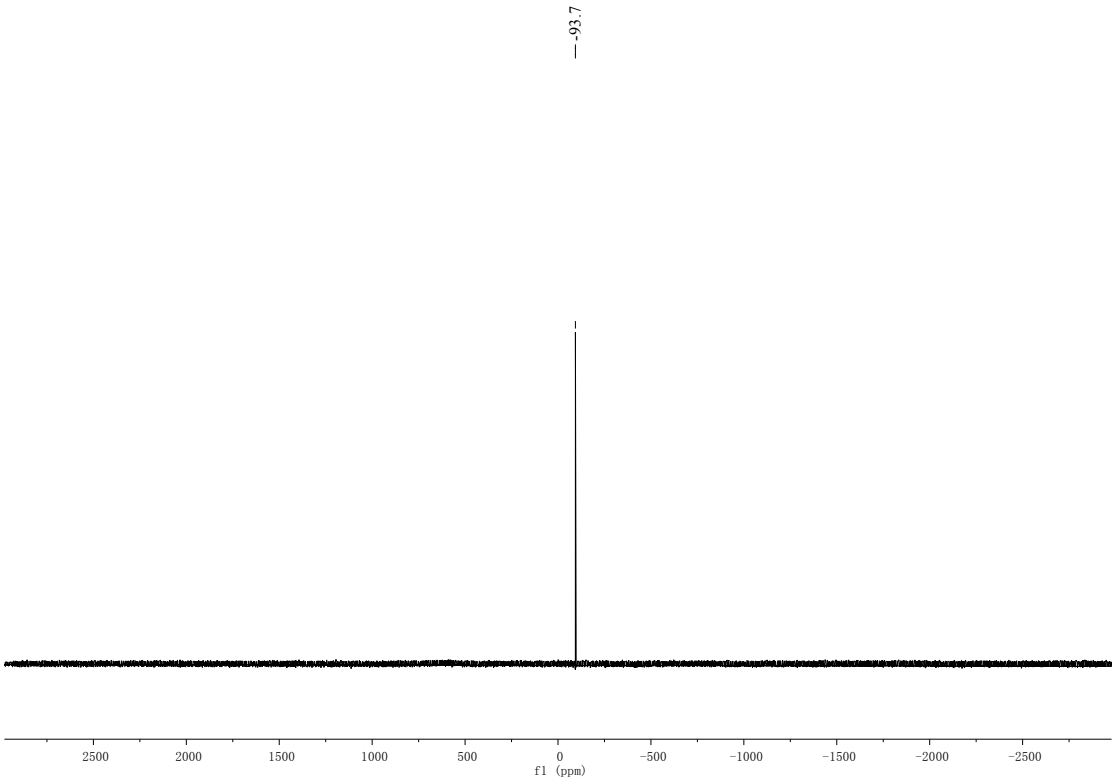


Figure S9. ^{119}Sn NMR spectrum of compound **8** in C_6D_6.

3. H_2 mass spectrum observed in the reaction of stannylenoid 2 with PhC≡CH

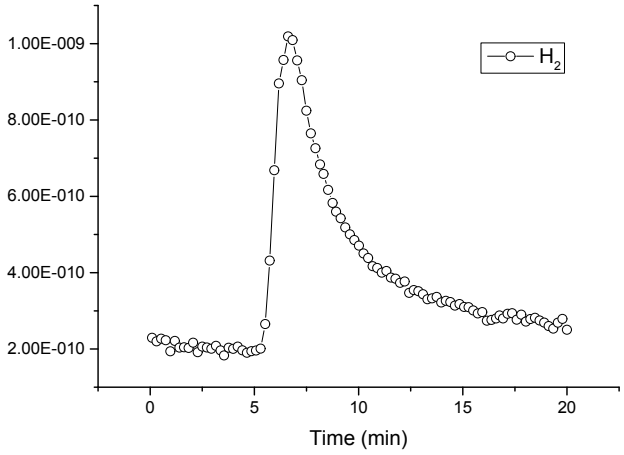
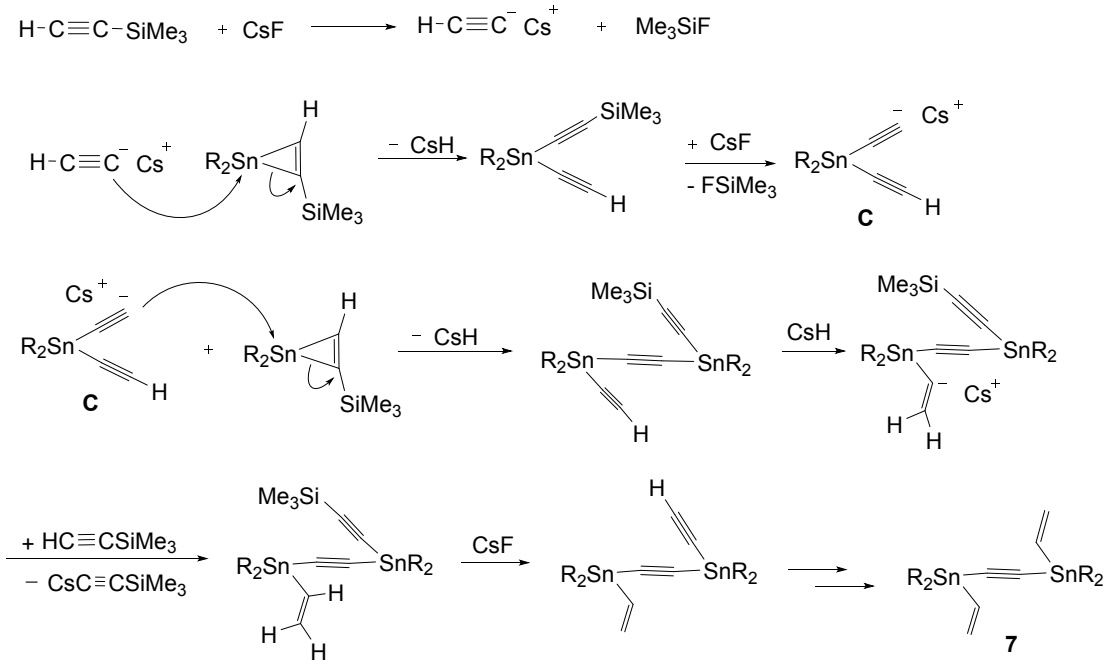


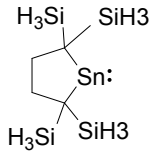
Figure S10. Mass spectrum of H_2 detected during the reaction of phenylacetylene with **2**.

4. A possible mechanism for the formation of 1,2-distannylethyne 7



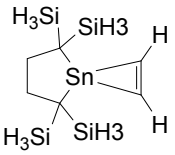
5. Preliminary theoretical calculations for the formation of a stannacyclopropene derivative

Theoretical calculations were performed for the following compounds (**L**, **M**, and **N**) at the B3PW91/6-31+G(d,p) for Si, C, and H and SDD for Sn level with the Gaussian 16 program package.[S2]



L

M



N

The total energies and cartesian coordinates of the optimized structures are shown as follows.

1) Compound **L** (Total energy = –1323.190908 au)

XYZ Coordinates

C	0.99279700	-1.11185900	-0.51851200
C	-0.99279700	1.11185900	-0.51851200
C	-0.70887300	0.29079300	-1.80133900
C	0.70887300	-0.29079300	-1.80133900
H	-1.43181700	-0.53688500	-1.88030300
H	-0.85513700	0.90084300	-2.70558700
H	0.85513700	-0.90084300	-2.70558700
H	1.43181700	0.53688500	-1.88030300
Si	-2.81588000	1.42986300	-0.23333400
H	-3.03838500	2.10349500	1.07698200
H	-3.41601800	2.28780000	-1.29976200
H	-3.55730200	0.13357500	-0.23324200
Si	0.00000000	2.71179600	-0.46174300
H	0.28132200	3.22557300	-1.83117300
H	-0.67873000	3.75584900	0.35261600
H	1.33810900	2.48173500	0.19422900
Si	0.00000000	-2.71179600	-0.46174300
H	-0.28132200	-3.22557300	-1.83117300
H	0.67873000	-3.75584900	0.35261600
H	-1.33810900	-2.48173500	0.19422900
Si	2.81588000	-1.42986300	-0.23333400
H	3.03838500	-2.10349500	1.07698200
H	3.41601800	-2.28780000	-1.29976200
H	3.55730200	-0.13357500	-0.23324200
Sn	0.00000000	0.00000000	1.19905700

2) Compound **M** (Total energy = –77.30063 au)

XYZ Coordinates

C	0.00000000	0.00000000	0.60414600
H	0.00000000	0.00000000	1.67155500
C	0.00000000	0.00000000	-0.60414600
H	0.00000000	0.00000000	-1.67155500

3) Compound **N** (Total energy = –1400.484197 au)

XYZ Coordinates

C	-1.55313500	0.73693700	-0.02189000
C	1.55322200	0.73738400	0.02236900
C	0.69392000	1.99115800	0.34595000
C	-0.69418200	1.99130800	-0.34420000
H	0.53898000	2.07067000	1.43184500
H	1.22829700	2.90460600	0.05010700
H	-1.22881900	2.90431200	-0.04746700
H	-0.53928200	2.07197200	-1.43001500
Si	2.82752900	0.37506900	1.35789000
H	3.50514800	-0.92365100	1.09592300
H	3.86547900	1.44660400	1.40918300
H	2.15346900	0.31899100	2.68640300
Si	2.37289100	0.81493400	-1.67471200
H	3.29694100	1.98520400	-1.74217900
H	3.14588600	-0.43160300	-1.92340300
H	1.36306700	0.96693100	-2.76101500
Si	-2.37479900	0.81338400	1.67426900
H	-3.30273800	1.98067100	1.73998300
H	-3.14398800	-0.43546800	1.92315600
H	-1.36650700	0.96953800	2.76140400
Si	-2.82630900	0.37531600	-1.35874600
H	-3.50532800	-0.92276800	-1.09725400
H	-3.86315900	1.44785500	-1.41103900
H	-2.15103400	0.31850000	-2.68659400
C	0.01404500	-2.83522200	-0.67196800
H	0.02994800	-3.62483000	-1.42418500
C	-0.01307200	-2.83636500	0.66910900
H	-0.02755700	-3.62708200	1.42016500
Sn	0.00012100	-0.82867000	0.00053900

6. 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 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.