Supporting Information

Reactions of an Isolable Dialkylstannylene with Propynoates and Benzyne

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Contents

1. X-ray analysis of 2-4

Single crystals of **2-4** suitable for X-ray analysis were obtained by the recrystallization from *n*-pentane and hexane, respectively. 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 **2-4** are shown in Table S1. Crystal and refinement data for **2**, **3**, and **4** are deposited with CCDC; CCDC Nos. 1817474, 1817475 and 1817473, respectively.

Table S1. Crystal and Refinement Data for **2-4**.

Parameters	**2**	**3**	**4**
Empirical formula	$C_{24}H_{48}O_4Si_4Sn$	$C_{26}H_{52}O_4Si_4Sn$	$C_{22}H_{44}Si_4Sn$
Formula weight	631.67	659.72	539.62
Crystal system, Space group	Monoclinic, Pn	Monoclinic, C2/c	Triclinic, P-1
a [Å]	21.645(3)	26.625 (15)	9.7303(8)
b [Å]	9.4247(15)	9.400(5)	12.2848(10)
c [Å]	33.426(5)	28.376(14)	12.3194(10)
α [deg]	90	90	85.9670(10)
β [deg]	106.772(2)	102.642(16)	84.2360(10)
γ [deg]	90	90	85.4800(10)
V [Å^{-3}]	6528.8(18)	6930(6)	1457.7(2)
Z, D_{calcd}[Mg/m^{-3}]	8, 1.285	8, 1.265	2, 1.229
μ [mm^{-1}]	0.954	0.902	1.047
F (000)	2640	2768	564
Reflections collected	41561	26807	17732
Independent Reflections	20827	7722	6638
R(int)	0.0260	0.0705	0.0259
Data/restraints /parameters	20827/2/1245	7722/0/ 329	6638/0/ 255
final R indices [$I>2\sigma(I)$] R_1 ,$wR2$	0.0299, 0.0689	0.0643, 0.1431	0.0338, 0.0933
R indices (all data) wR_2	0.0348, 0.0710	0.0905, 0.1541	0.0460, 0.1033

2. ^{1}H, ^{13}C, ^{29}Si , and ^{119}Sn NMR spectra of 2-4.

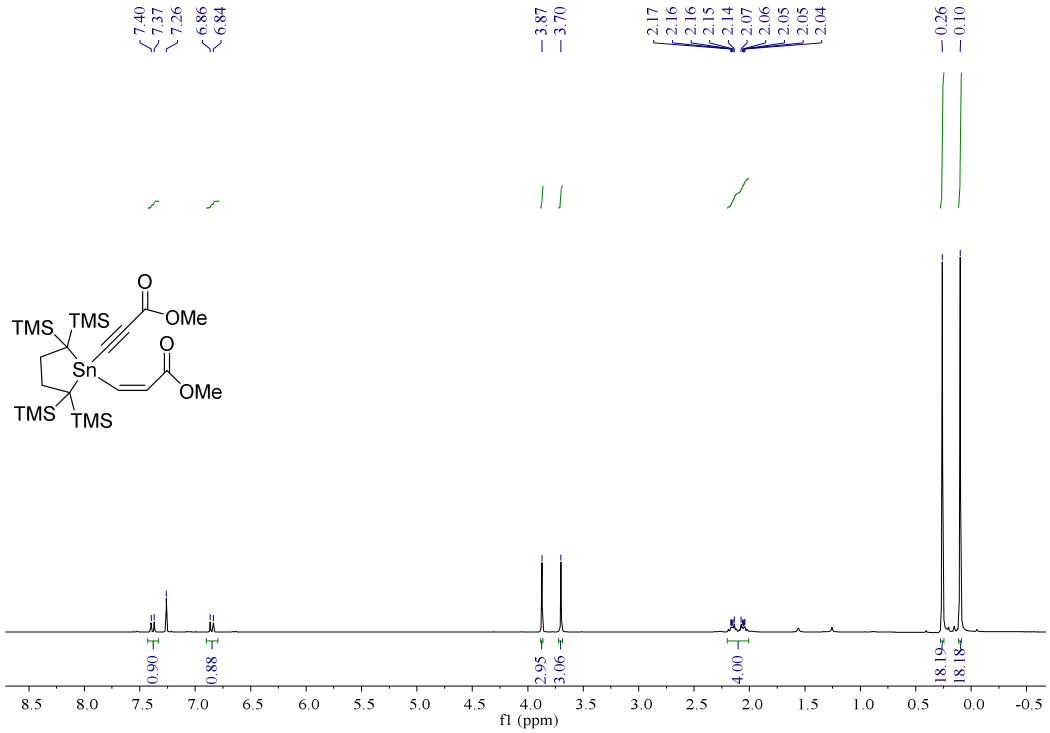


Figure S1. ^{1}H NMR spectrum of **2** in $CDCl_3$

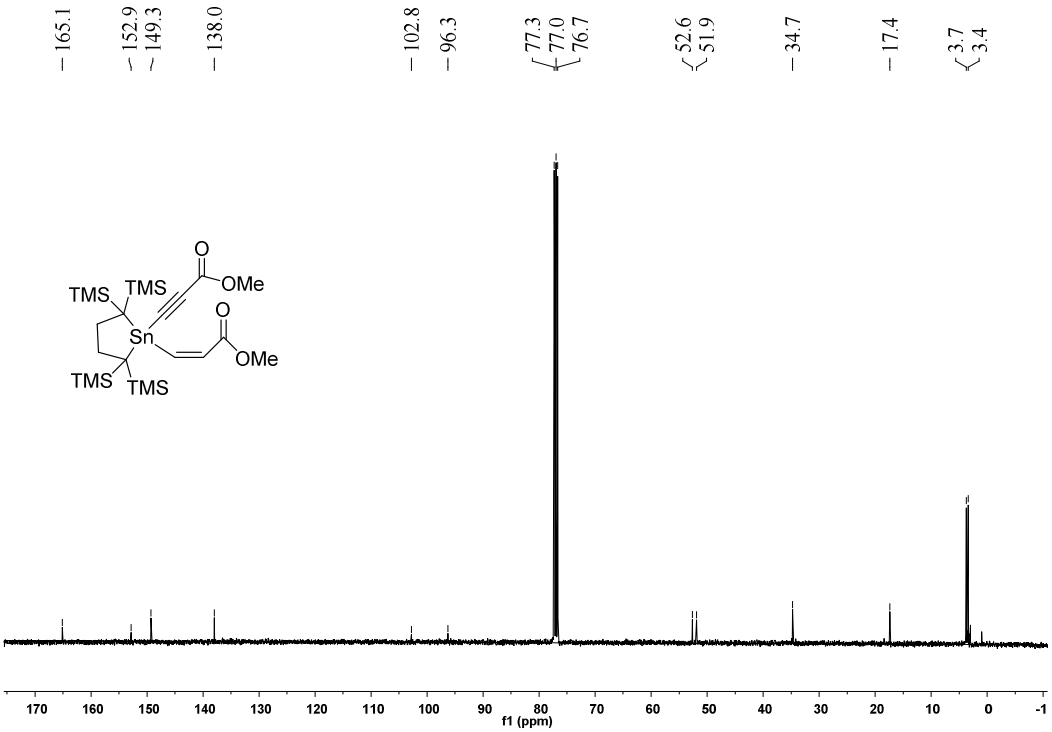


Figure S2. ^{13}C NMR spectrum of **2** in $CDCl_3$

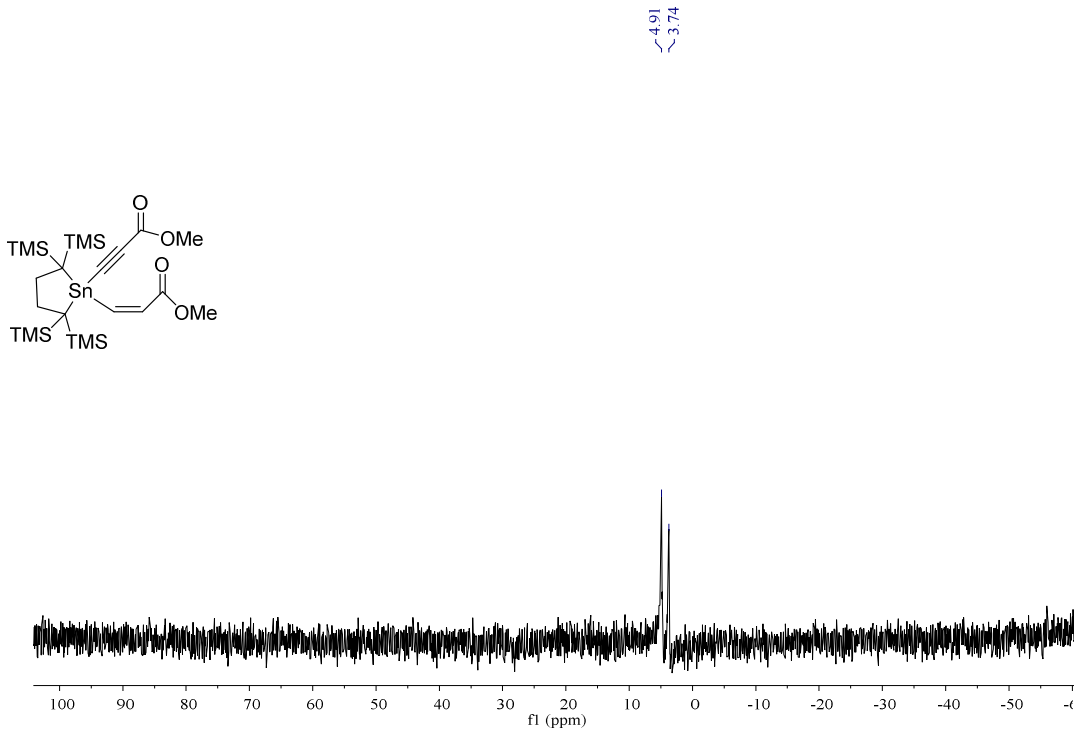


Figure S3. ^{29}Si NMR spectrum of **2** in $CDCl_3$

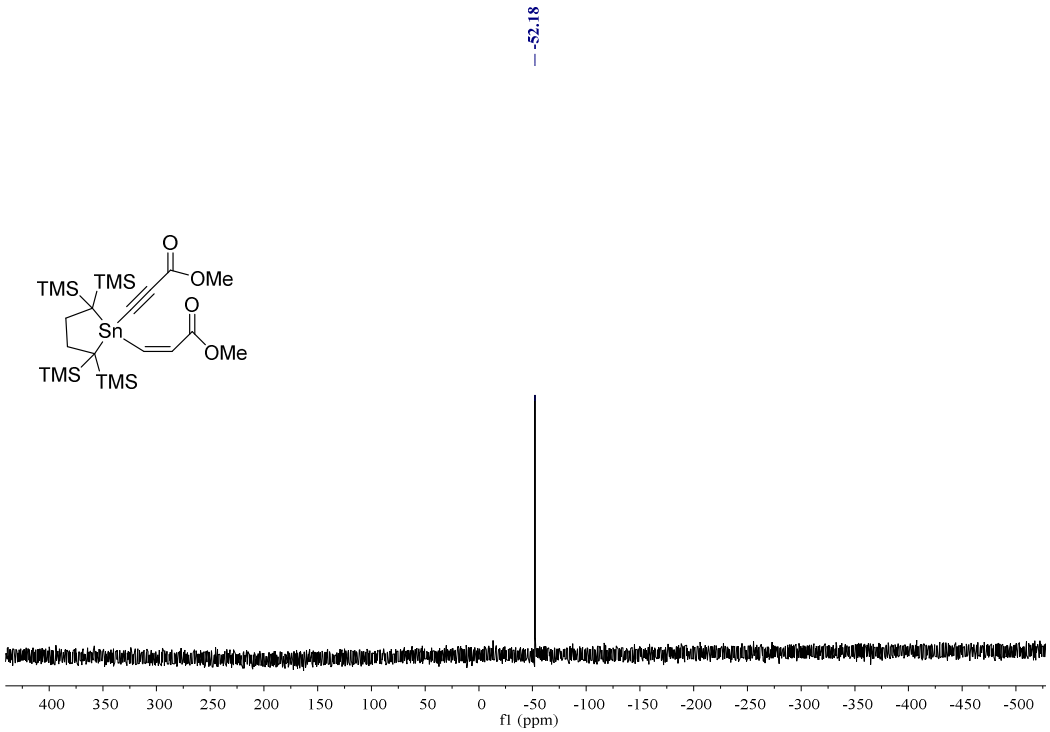


Figure S4. ^{119}Sn NMR spectrum of **2** in $CDCl_3$

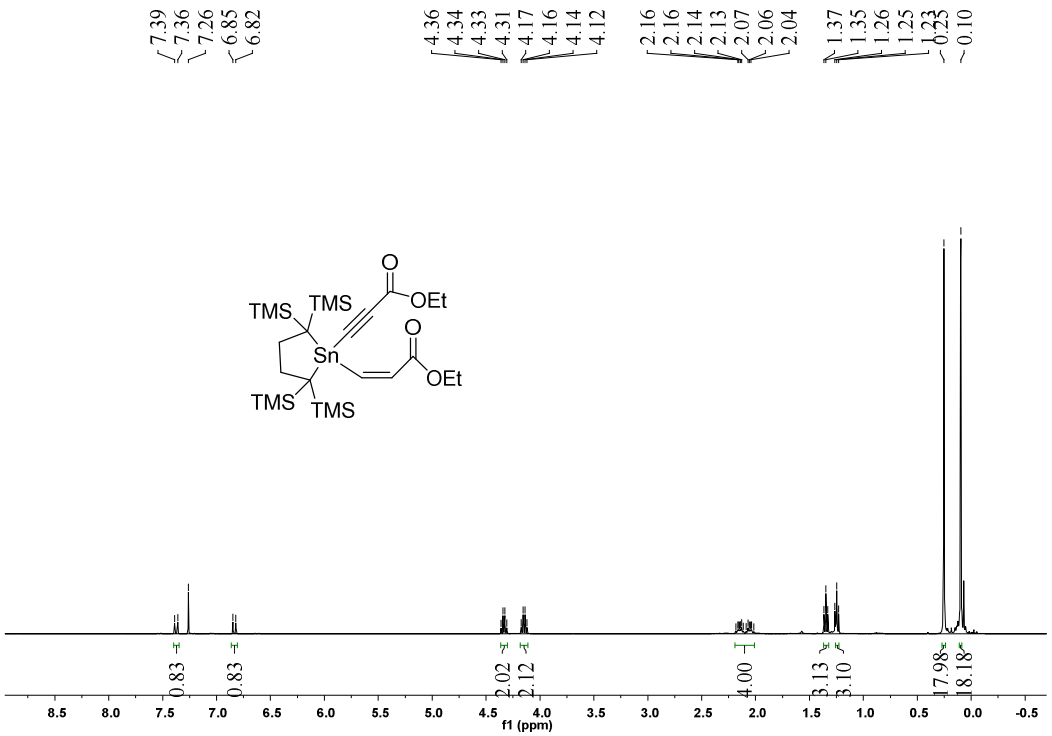


Figure S5. ^{1}H NMR spectrum of **3** in $CDCl_3$

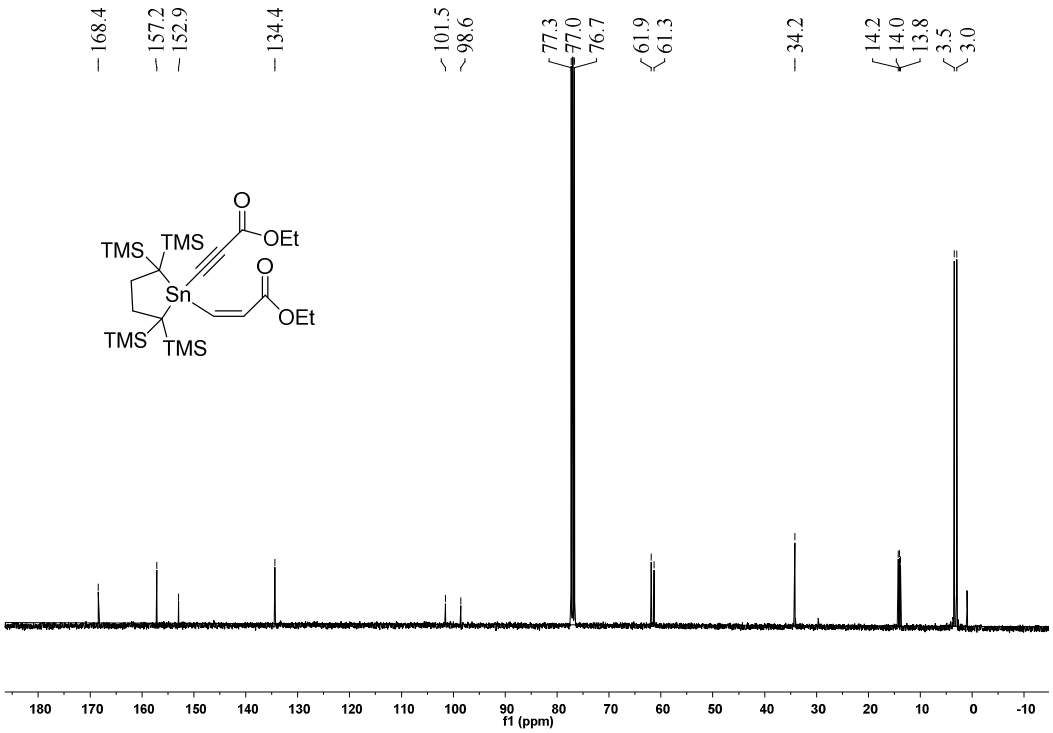


Figure S6. ^{13}C NMR spectrum of **3** in $CDCl_3$

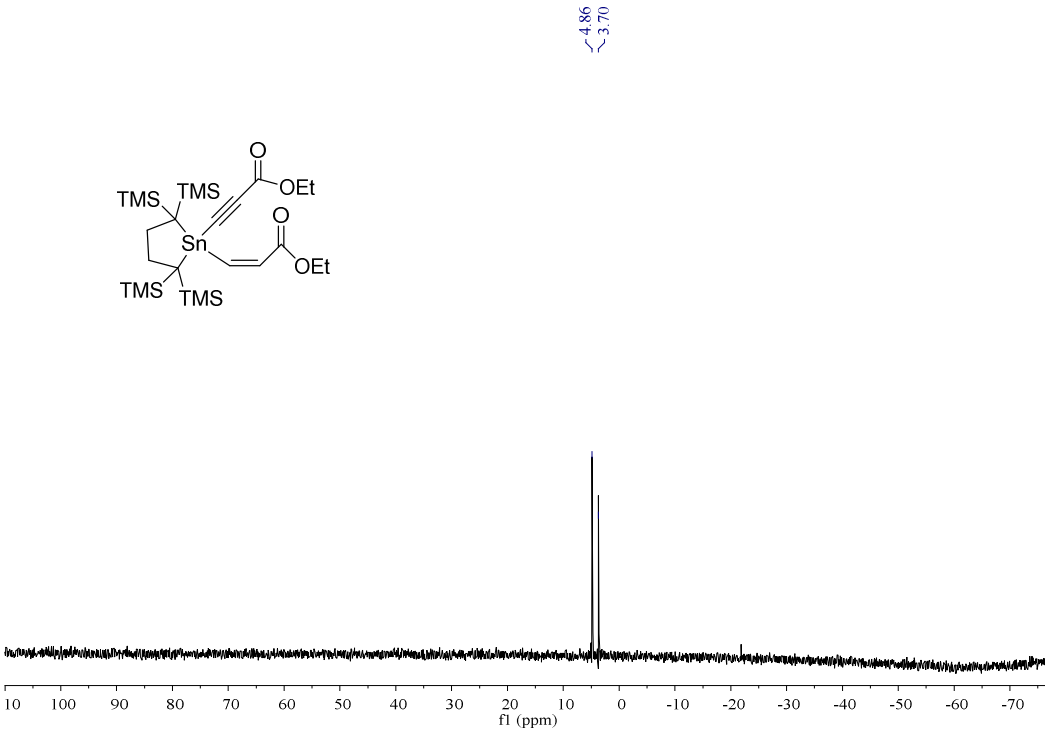


Figure S7. ^{29}Si NMR spectrum of **3** in $CDCl_3$

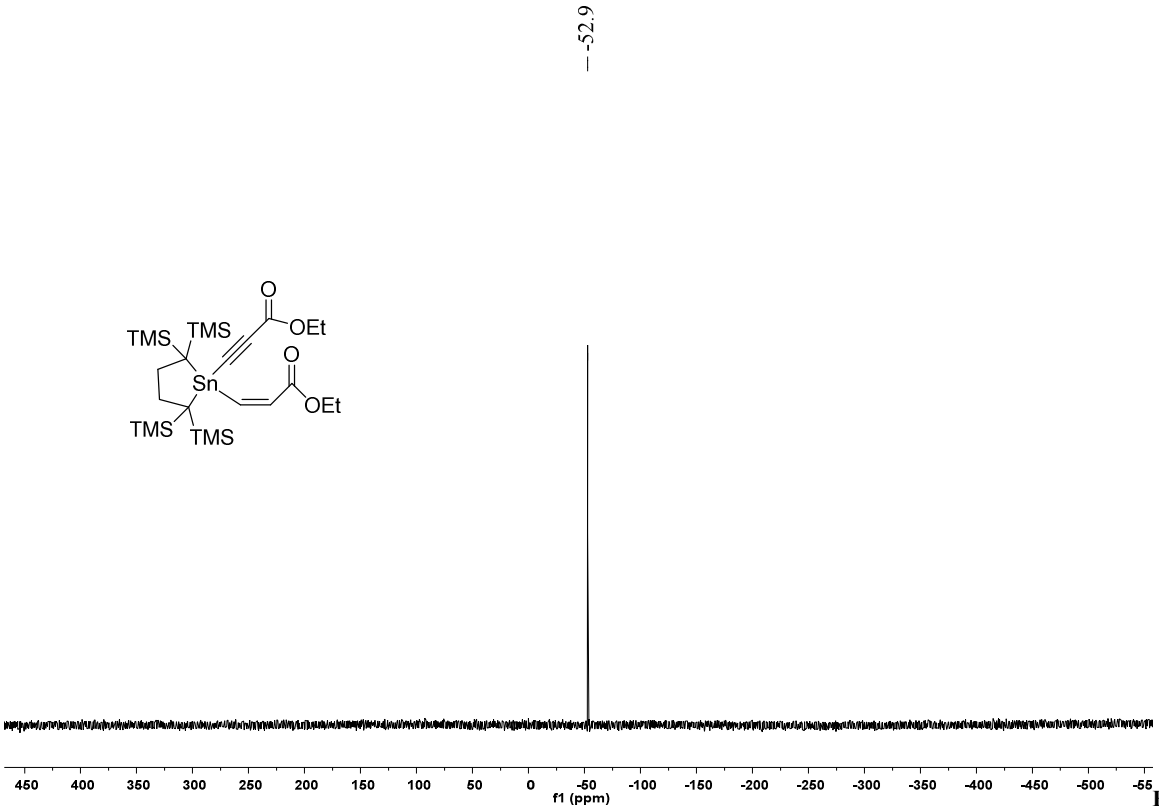


Figure S8. ^{119}Sn NMR spectrum of **3** in $CDCl_3$

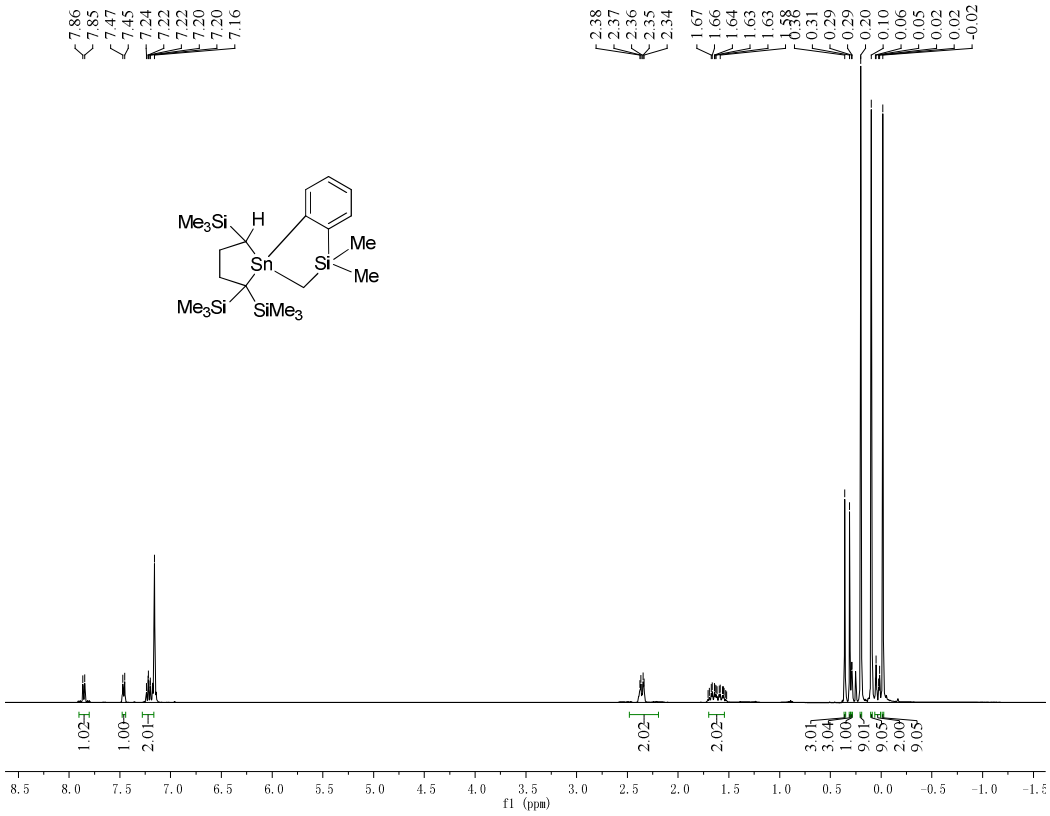


Figure S9. ^{1}H NMR spectrum of **4** in C_6D_6

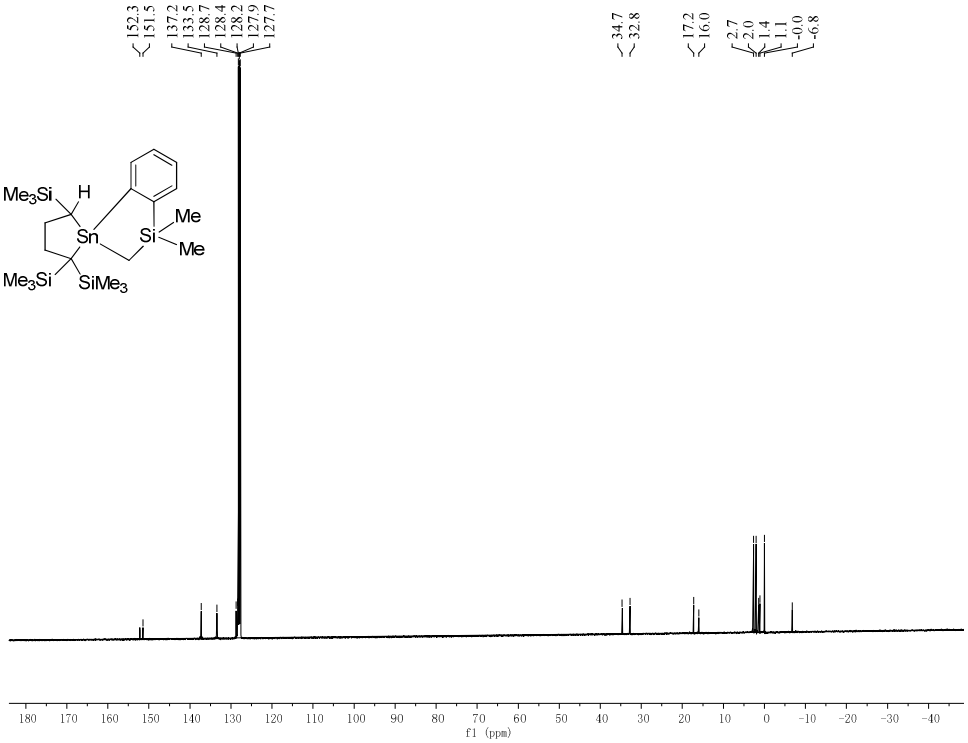


Figure S10. ^{13}C NMR spectrum of **4** in C_6D_6

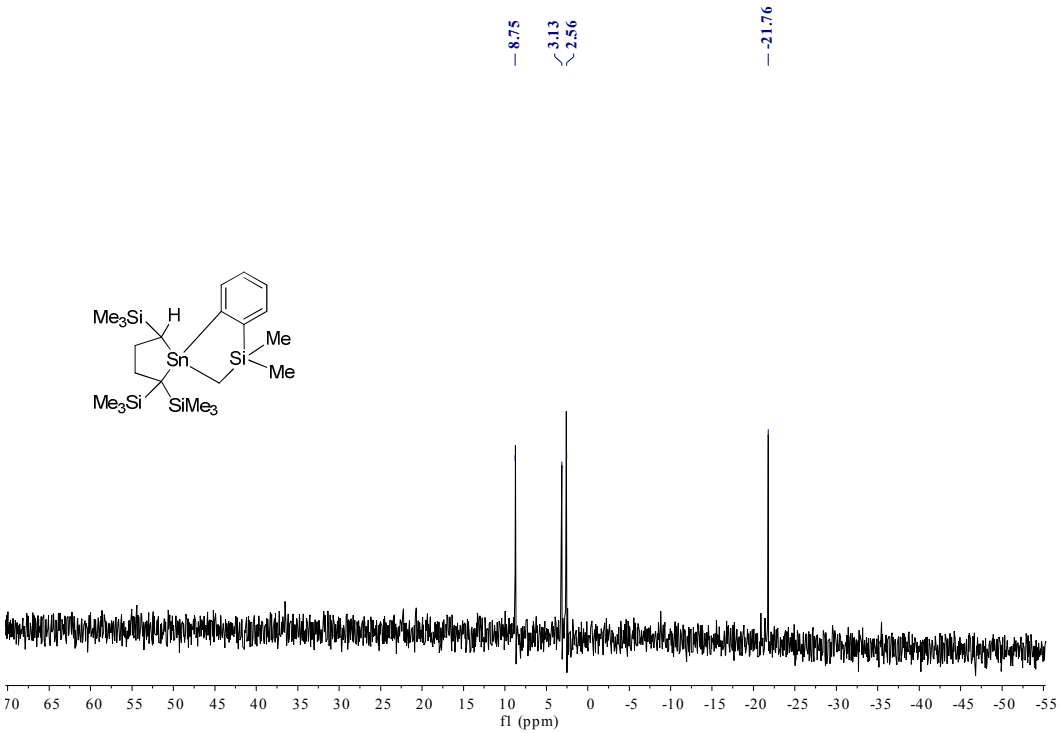


Figure S11. ^{29}Si NMR spectrum of **4** in C_6D_6

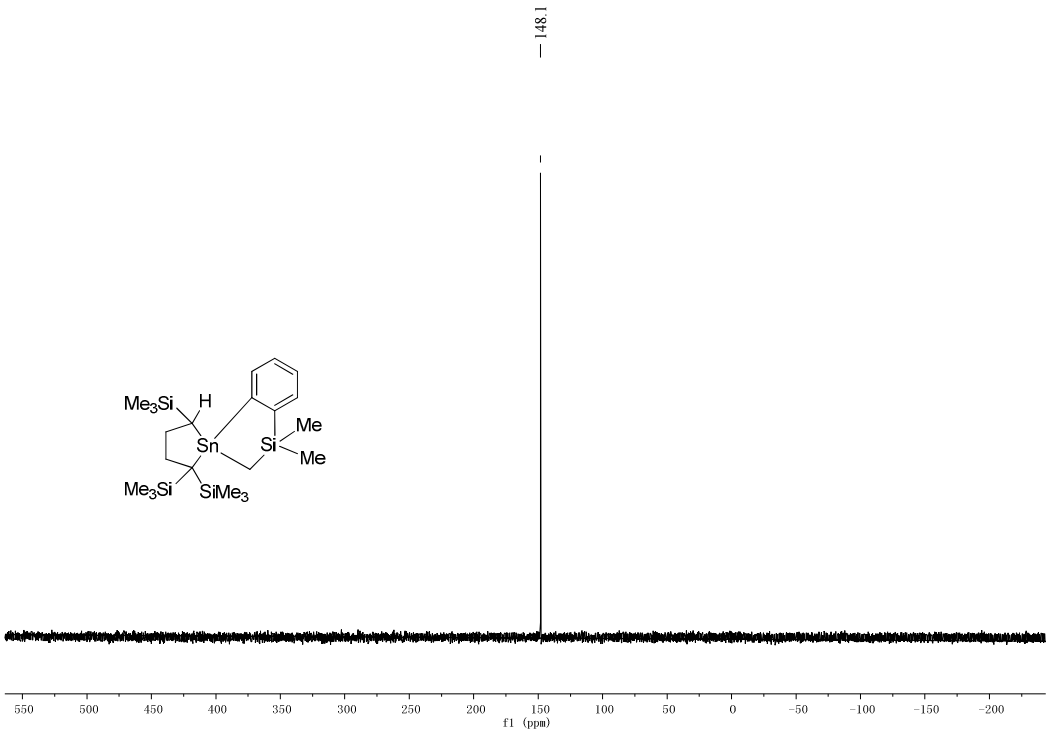


Figure S12. ^{119}Sn NMR spectrum of **4** in C_6D_6

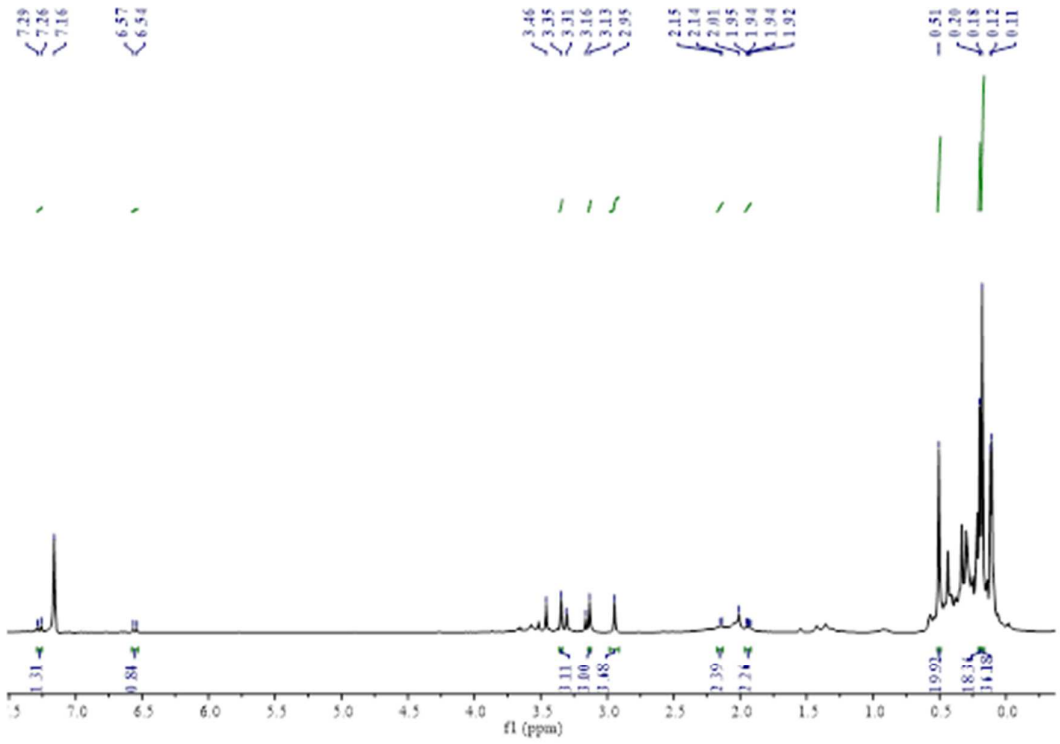


Figure S13. ^{1}H NMR spectrum of a product mixture of the reaction of **1** with one equivalent of methyl propynoate in C_6D_6.

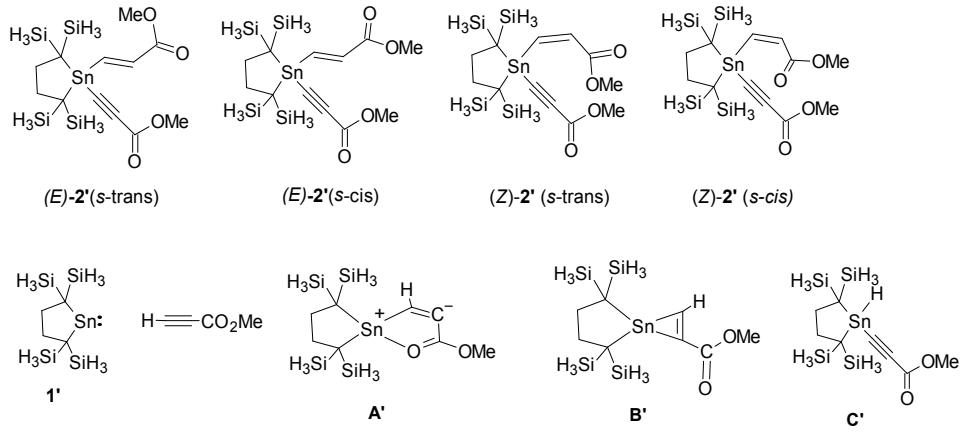
3. DFT-D Calculations

3.1 Calculation details

All calculations were performed using the Gaussian 09 package.[S2] Geometry optimizations of all stationary points were performed by using the dispersion-corrected DFT method at the B3PW91[S3]-GD3 level[S4] using the basis sets of 6-31+G(d,p) for C, H, O, and Si atoms + SDD for Sn. All of the structures obtained herein were verified by examination of their Hessian matrix as minima (all frequencies real). To evaluate the solvent effects on the relative stability of the compounds, the calculations were performed in heptane and THF as well as in gas phase using the polarizable continuum model (PCM) model.[S5]

3.2 Reaction of 1' + Methyl Propynoate

The DFT calculations were performed for the following compounds:



Scheme S1.

See an attached file named as "optcoord.xyz" for the Cartesian coordinates of the optimized structures of these compounds,

Table S2. Total, Zero-point, and Gibbs Free Energies of Compounds Shown in Scheme S1.[a]

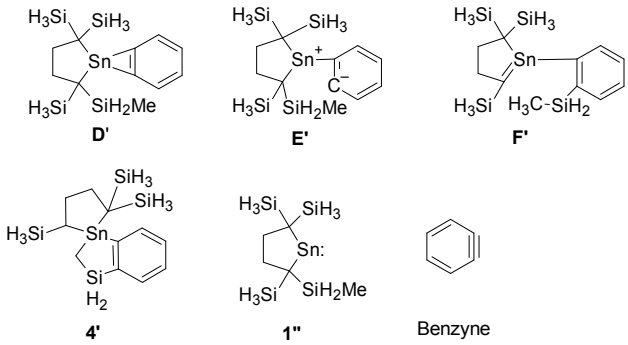
Compound	Solvent	Total Energy (au)	ZPE (au)	Sum of electronic and thermal Free Energies (au) at -298.15 K
(*E*)-**2'**(*s*-trans)	gas phase	-1933.485452	0.319799	-1933.233837
	heptane	-1933.490748	0.319636	-1933.238519
	THF	-1933.497617	0.319295	-1933.245453
(*E*)-**2'**(*s*-cis)	gas phase	-1933.486526	0.320085	-1933.233711
	heptane	-1933.491681	0.319786	-1933.238922
	THF	-1933.498375	0.319314	-1933.246304
(*Z*)-**2'**(*s*-trans)	gas phase	-1933.491466	0.320478	-1933.235729
	heptane	-1933.495923	0.320195	-1933.240648
	THF	-1933.501754	0.320019	-1933.246061
(*Z*)-**2'**(*s*-cis)	gas phase	-1933.481157	0.320389	-1933.225756
	heptane	-1933.487157	0.320179	-1933.231781
	THF	-1933.495212	0.319819	-1933.240196
A'	gas phase [b]	_____	_____	_____
	heptane	-1628.295585	0.244128	-1628.105457
	THF	-1628.301322	0.244058	-1628.112104
B'	gas phase	-1628.288639	0.244313	-1628.099695
	heptane	-1628.292056	0.244018	-1628.103178
	THF	-1628.296446	0.243527	-1628.108261
C'	gas phase	-1628.304565	0.241048	-1628.120088
	heptane	-1628.308074	0.240689	-1628.123763
	THF	-1628.312794	0.240232	-1628.128743
1'	gas phase	-1323.190941	0.170176	-1323.064515
	heptane	-1323.192193	0.170096	-1323.066265
	THF	-1323.194129	0.169896	-1323.068004
H—≡—CO_2Me	gas phase	-305.101201	0.07135	-305.059882
	heptane	-305.10406	0.071313	-305.062777
	THF	-305.107535	0.071243	-305.066343

a. Calculated at the B3PW91-GD3 level[S3,S4] using the basis sets of 6-31+G(d,p) for C, H, O, and Si atoms and SDD for Sn. Solvation effects in heptane and THF were considered using the polarizable continuum model (PCM) model.[S5]

b. No energy minimum geometry for the structure was located.

3.3 Reaction of Stannylene 1" with benzyne

The DFT calculations were performed for the following pathway:



Scheme S2.

Table S3. Total, Zero-point, and Gibbs Free Energies of Compounds Shown in Scheme S2.[a]

Compound	Solvent	Total Energy (au)	ZPE (au)	Sum of electronic and thermal Free Energies (au) at -298.15 K
D'	gas phase	-1593.413034	0.27861	-1593.188036
	heptane	-1593.41478	0.278345	-1593.189971
	THF	-1593.417239	0.277928	-1593.192908
F'	gas phase	-1593.417742	0.278295	-1593.193514
	heptane	-1593.420011	0.278002	-1593.195932
	THF	-1593.423201	0.277644	-1593.19911
4'	gas phase	-1593.489667	0.280616	-1593.26067
	heptane	-1593.491358	0.280279	-1593.263034
	THF	-1593.493889	0.279903	-1593.266116
1"	gas phase	-1362.512202	0.199313	-1362.359907
	heptane	-1362.513504	0.199203	-1362.36102
	THF	-1362.515492	0.19914	-1362.362535
benzyne	gas phase	-230.836809	0.075278	-230.788918
	heptane	-230.837986	0.075226	-230.790159
	THF	-230.839554	0.075143	-230.791829

a. Calculated at the B3PW91-GD3 level[S3,S4] using the basis sets of 6-31+G(d,p) for C, H, O, and Si atoms and SDD for Sn. Solvation effects in heptane and THF were considered using the polarizable continuum model (PCM) model.[S5]

b. No energy minimum geometry for the structure **E'** was located.

4. References

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(S2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö .; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision E.01;* Gaussian, Inc.: Wallingford, CT, 2009.

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(S5) Tomasi, J.; Persico, M. Molecular Interactions in Solution: An Overview of Methods Based on Continuous Distributions of the Solvent *Chem. Rev.* **1994**, *94*, 2027-2094.