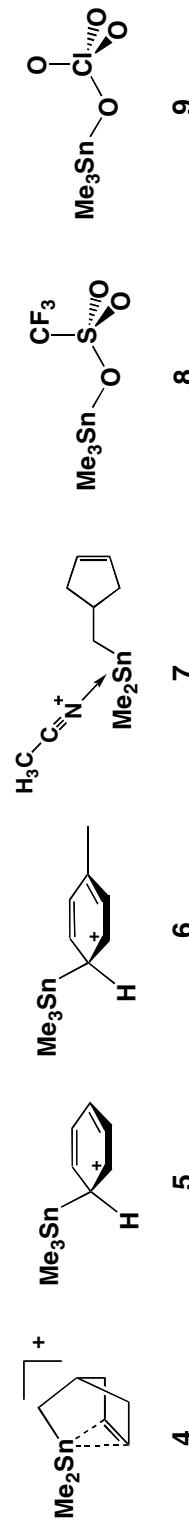


Table S3. Absolute energies and calculated and experimental chemical shifts of stannylium ions and related compounds.

entry	cpd.	B3LYP/A ^{a,b}	MPW1PW91/A ^{a,b}	GIAO/B3LYP/A ^{a,c}	δ	δ	δ (exp)
1	Tips ₃ Sn ⁺ , 1	-7781.57978	-7781.57824	799	763	714 ^e	
2	Mes ₃ Sn ⁺ , 2	-7073.94505 ^f	-7074.09606 ^f	904	856	806 ^g	
3	Me ₃ Sn ⁺ , 3	-6144.89048	-6145.24204	1573	1466	-	
4	4	-6339.07064 ^h	-6339.36808 ^h	426	406	334 ^{i,k}	
5	5	-6377.17317	-6377.47113	502	482	360 ^{l,m}	
6	6	-6416.49509	-6416.78453	456	438	434 ^{l,n}	
7	7	-6471.83969	-6472.11881	175	170	54 ^{i,k}	
8	8	-7106.59903	-7106.82895	229	229	172 ^{l,o}	
9	9	-6905.89656	-6906.18635	228	228	234 ^m	

a) Basis A is: 6-31G(d), (C,H,N,O,S,F) and tzv (19s,15p,9o)[8s,7p,5q] (Sn). b) Geometry was optimized at B3LYP/6-31G(d) (C,H,N,O,S,F), SDD (Sn). c) Calculated vs. Me₄Sn; σ (Sn) = 2641. d) Calculated vs. Me₄Sn; σ (Sn) = 2685. e) This work. f) A HF/6-31G(d) (C,H) Sn (SDD) optimized geometry is used. g) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001. h) A MP2/6-311G(d,p) (C,H) SDD (Sn) optimized geometry is used.. i) Comparison is made with the dibutyl compound. k) Müller, T. Bauch, C. Ostermaier, M. Bolte, M. Auher, N. *J. Am. Chem. Soc.* **2003**, *125*, 2158. l.) Comparison is made with the tributyl compound. m) Lambert, J. B.; Kuhlmann, B. *J. Chem. Soc., Chem. Commun.* **1992**, 931. n) Blackwell, J. M. Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1295. o) Arshadi, M.; Johnels, D.; Edlund, U. *J. Chem. Soc., Chem. Commun.* **1996**, 1279.



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- 5.

Figure S1. Linear Correlation between theoretical $\delta^{119}\text{Sn}(\text{calc})$ and experimental $\delta^{119}\text{Sn}(\text{exp})$, at GIAO/MPW1PW91/A, see also Table S1. $\delta^{119}\text{Sn}(\text{calc}) = (0.957 \pm 0.07) \delta^{119}\text{Sn}(\text{exp}) + (74.7 \pm 32.1)$; $R = 0.98$.

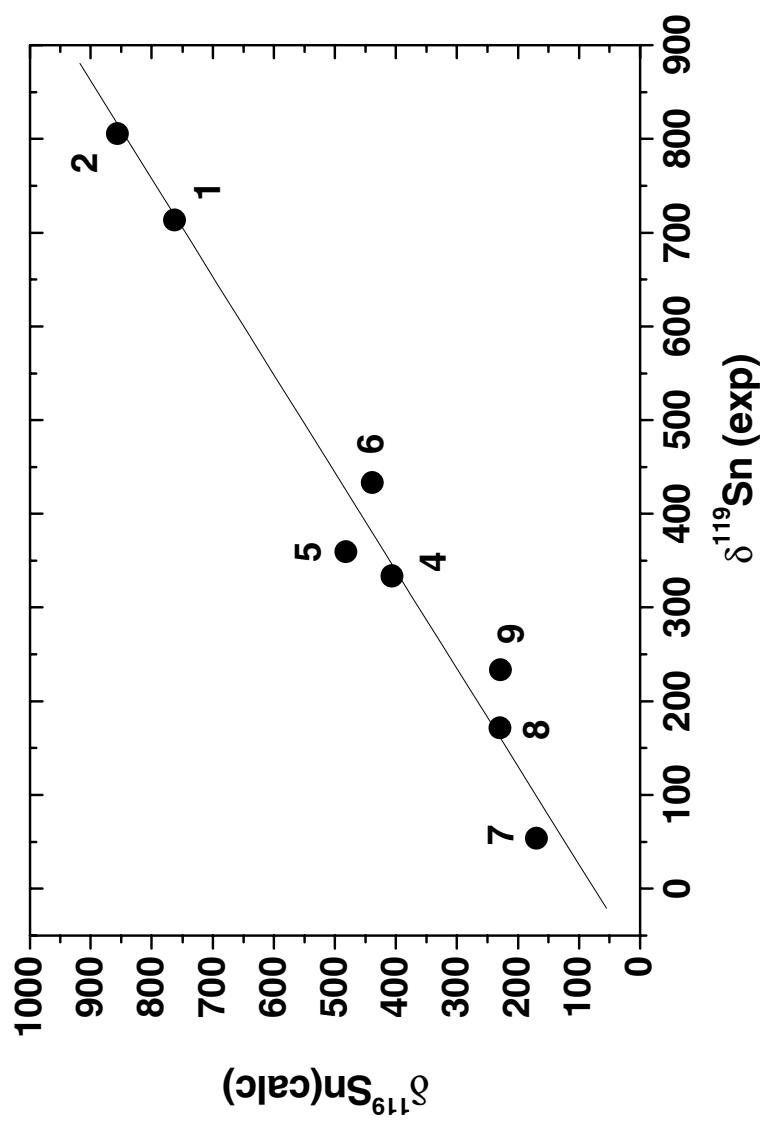


Figure S2. Linear Correlation between theoretical $\delta^{119}\text{Sn}(\text{calc})$ and experimental $\delta^{119}\text{Sn}(\text{exp})$, at GIAO/B3LYP/A, see also Table S1.
 $\delta^{119}\text{Sn}(\text{calc}) = (1.019 \pm 0.08) \delta^{119}\text{Sn}(\text{exp}) + (68.9 \pm 35.7)$; $R = 0.98$.

