

Supporting information for:

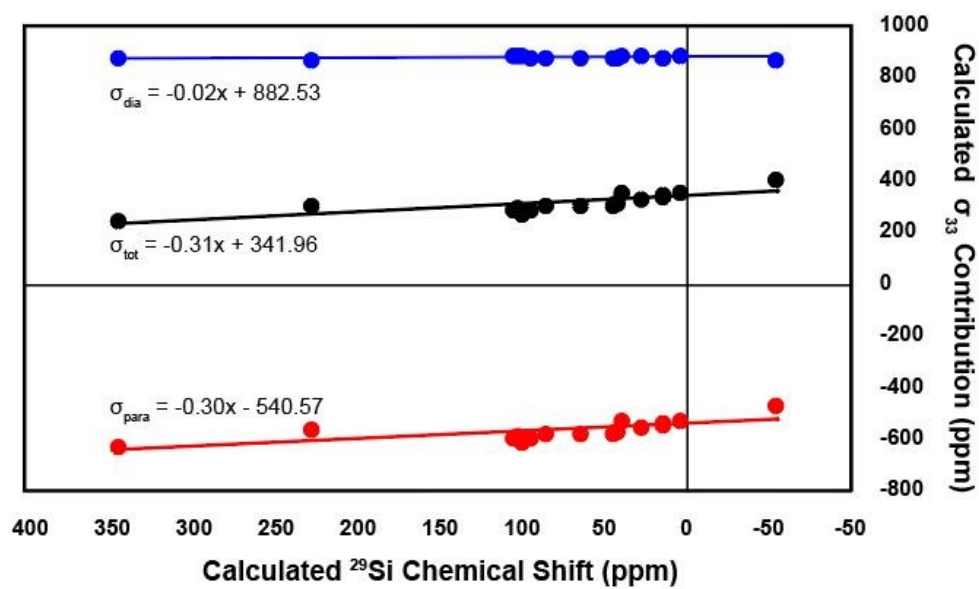
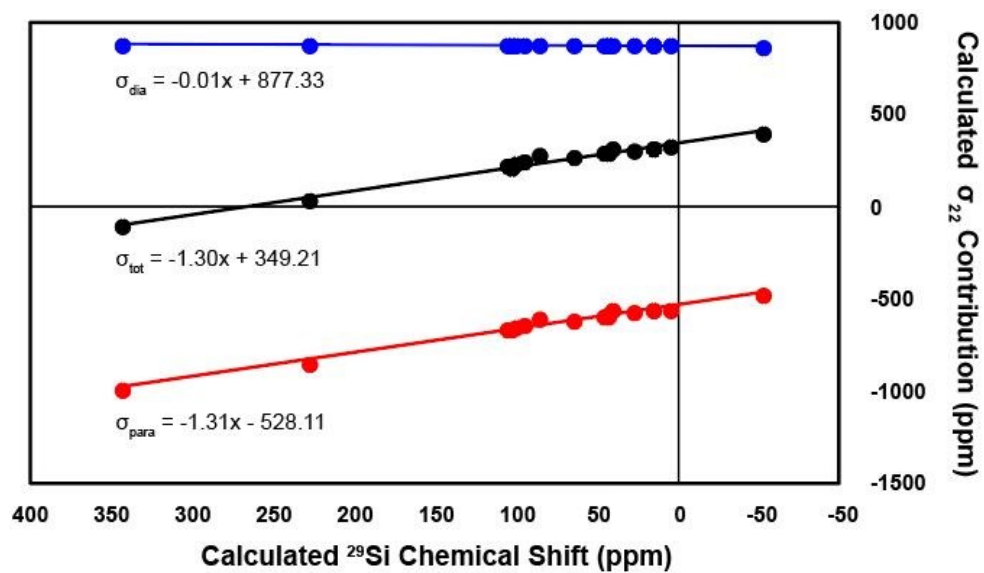
## Origin of the $^{29}\text{Si}$ NMR Chemical Shift in $\text{R}_3\text{Si-X}$ and Relationship to the formation of Silylium ( $\text{R}_3\text{Si}^+$ ) Ions

Winn Huynh and Matthew P. Conley\*

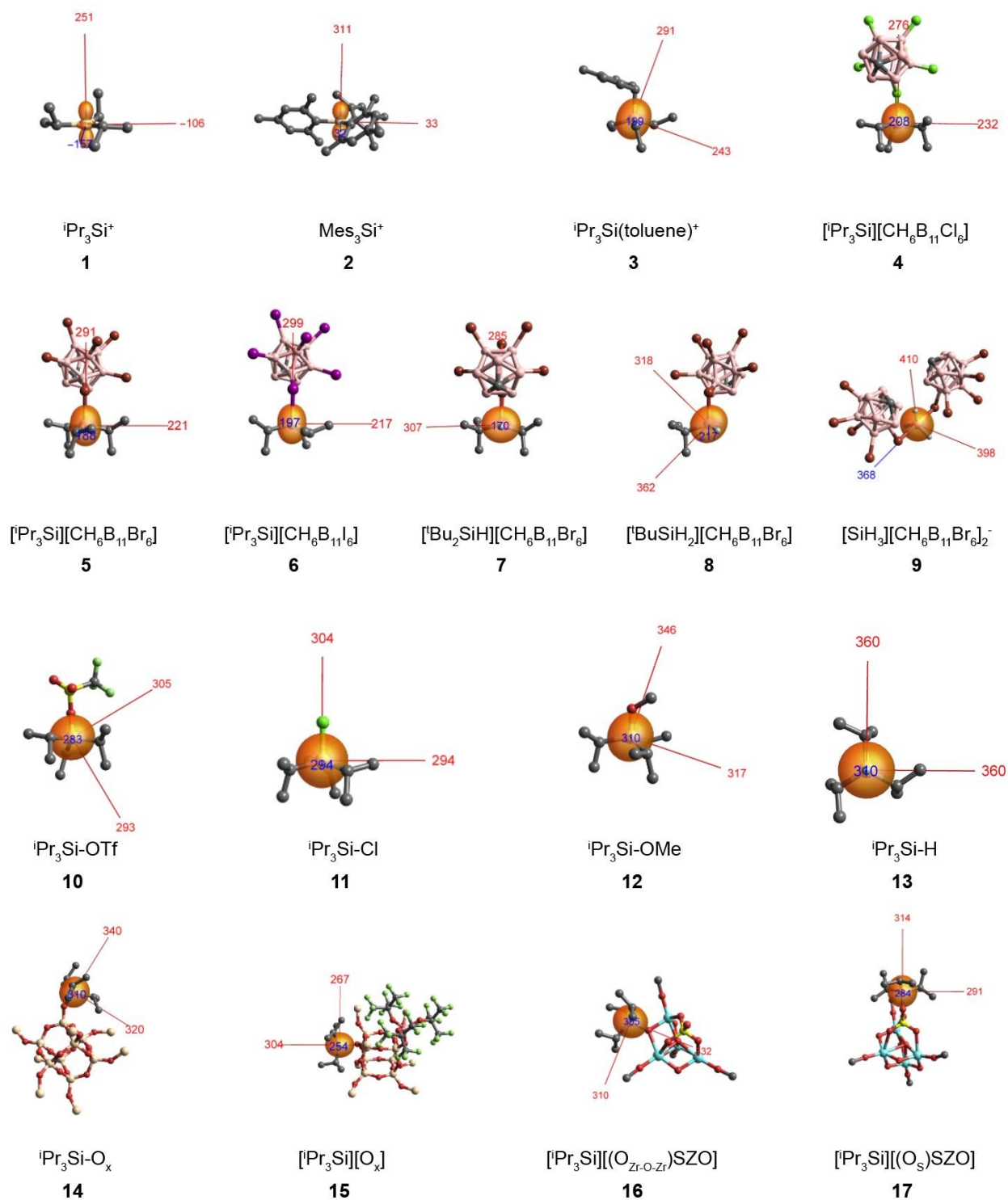
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Basis Set			DZ			TZ2P(Si) / DZ		
Entry		Expt.	BP86	PBE	B3LYP	BP86	PBE	B3LYP
<b>3</b>	$[\text{iPr}_3\text{Si}][\text{CH}_6\text{B}_{11}\text{Br}_6]$	110 (solid)	127	93	94	107	105	107
<b>5</b>	$\text{iPr}_3\text{Si-OTf}$	42 (neat)	58	24	23	45	42	45
<b>8</b>	$\text{iPr}_3\text{Si-H}$	12 (tol-d8)	0	1	2	3	4	6

Table S1. Calculated  $\delta(^{29}\text{Si})$  for **3**, **5**, and **8** using referenced to  $\text{Me}_4\text{Si}$  at the appropriate levels of theory.

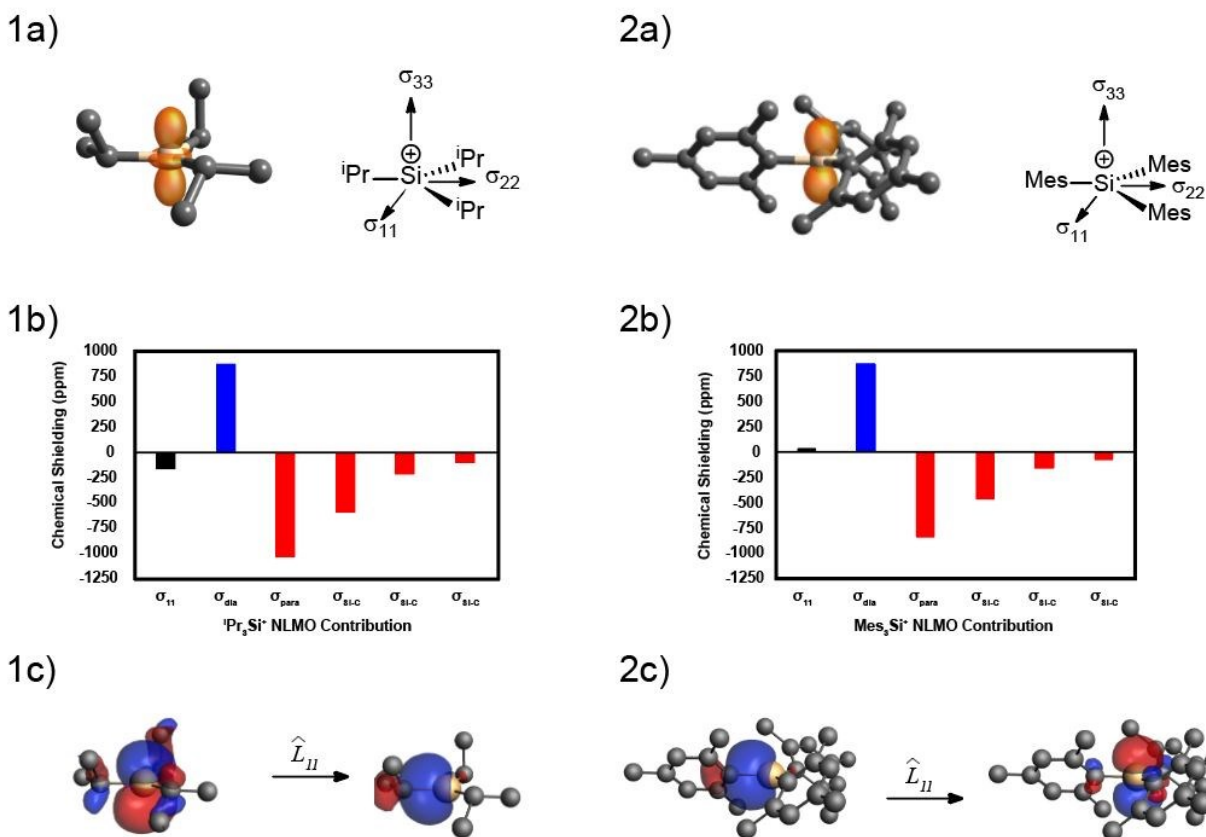


**Figure S1.** Comparison of calculated  $\sigma$ ,  $\sigma^{\text{d}}$  and  $\sigma^{\text{p}}$  versus calculated isotropic  $^{29}\text{Si}$  NMR chemical shift for  $\sigma_{22}$   $\sigma_{33}$  in **1** – **17**.

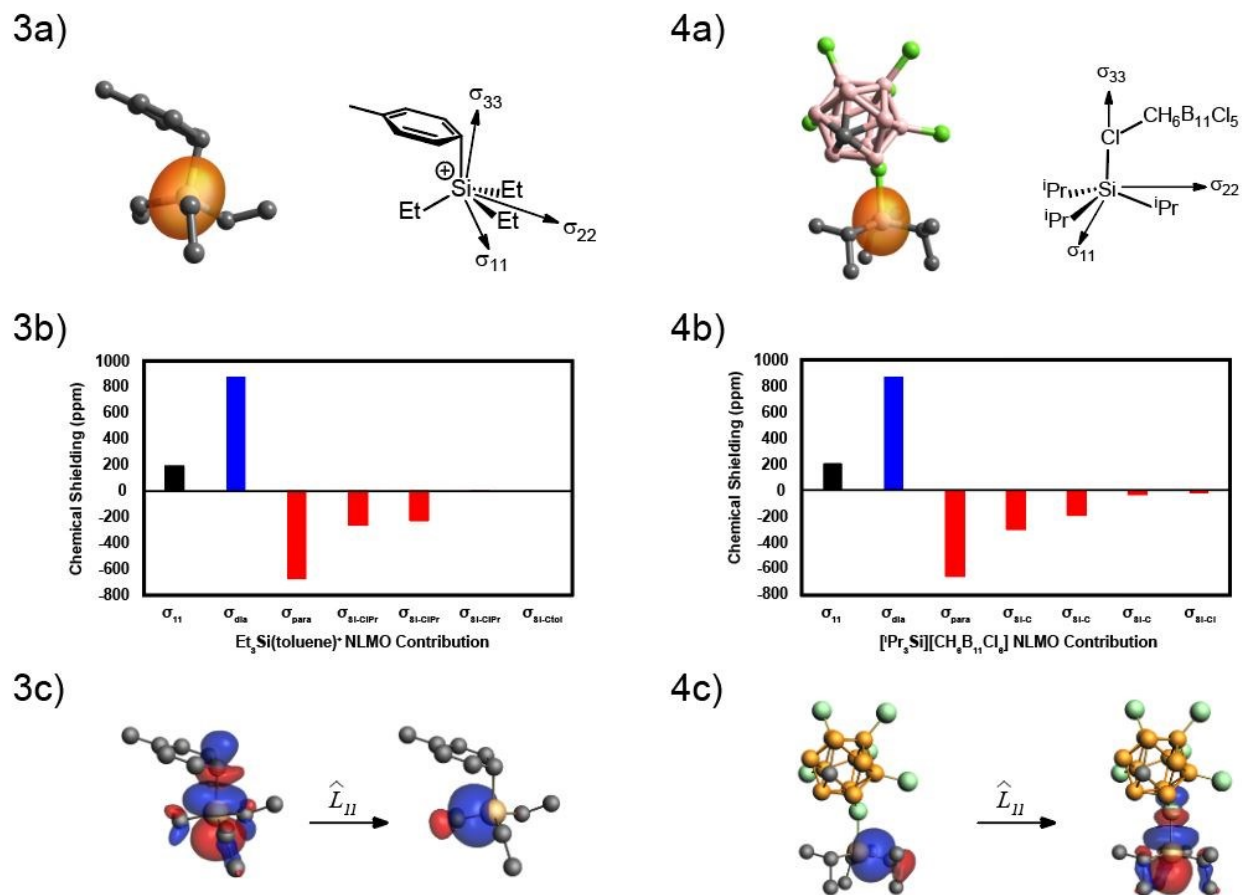


**Figure S2.** Chemical Shielding Tensors for 1-17 with axes shown. When possible,  $\sigma_{11}$ , colored blue, is pointing towards the reader. Selected hydrogens are omitted for clarity.

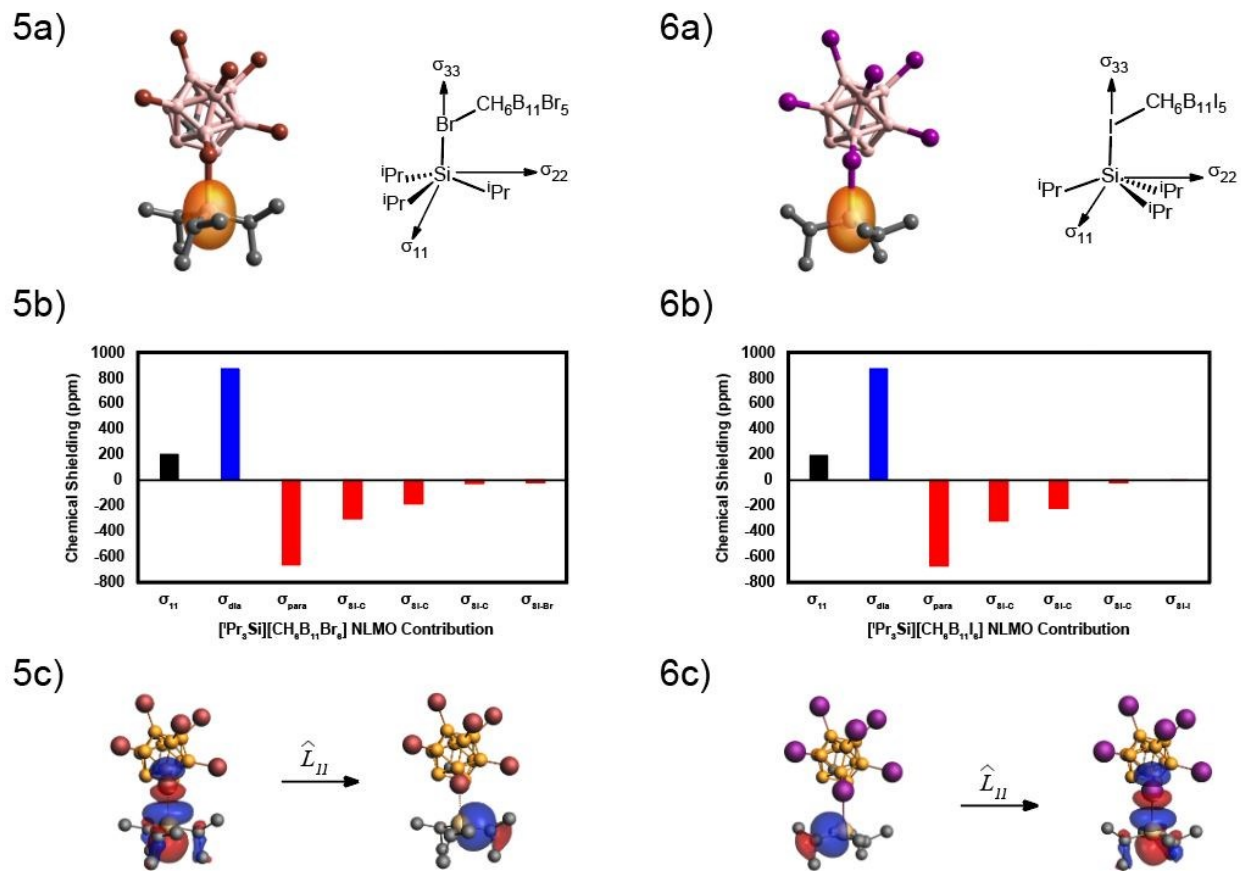
Tensor plot, tensor orientation, and NLMO contributions to  $\sigma_{11}$  for **1** – **18**.



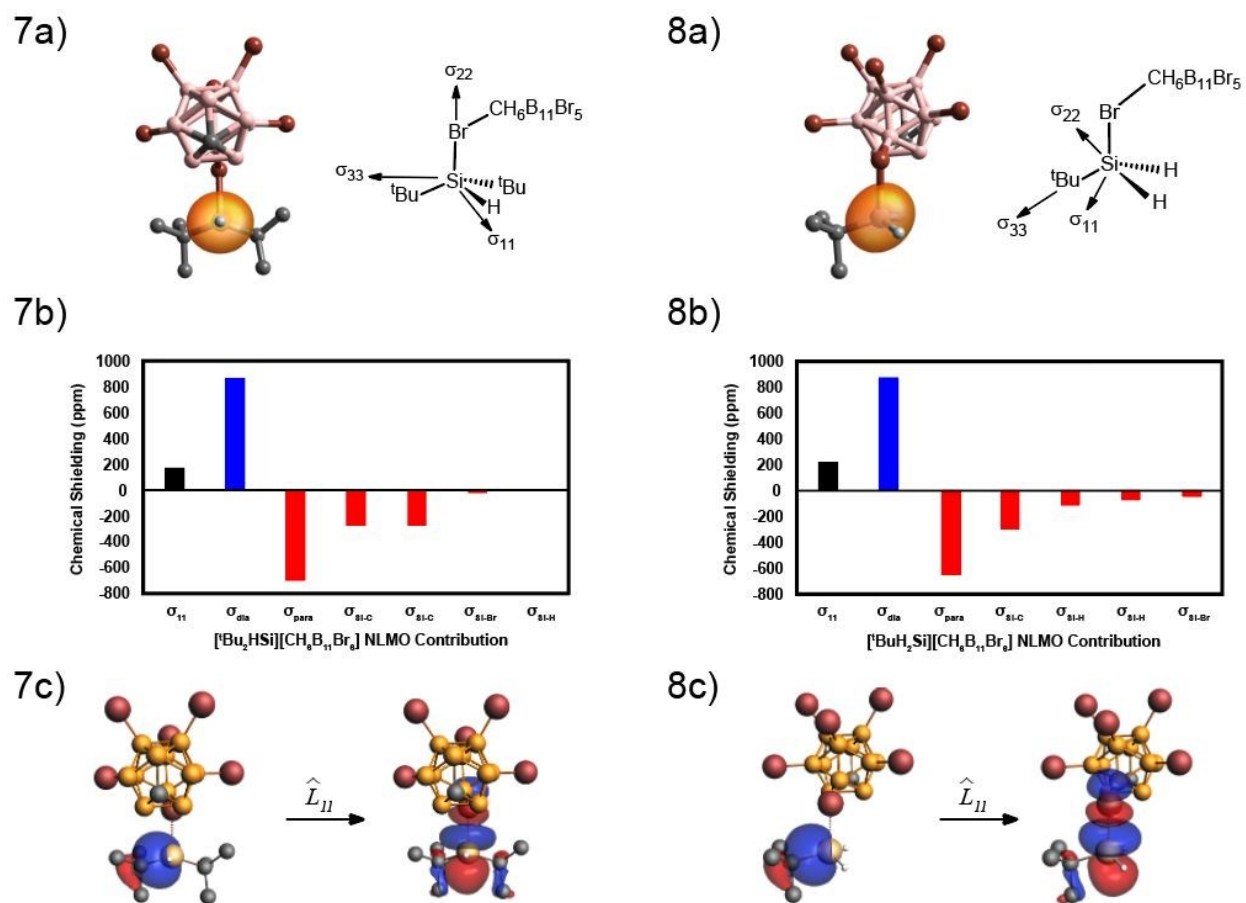
**Figure S3.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **1** and **2**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.



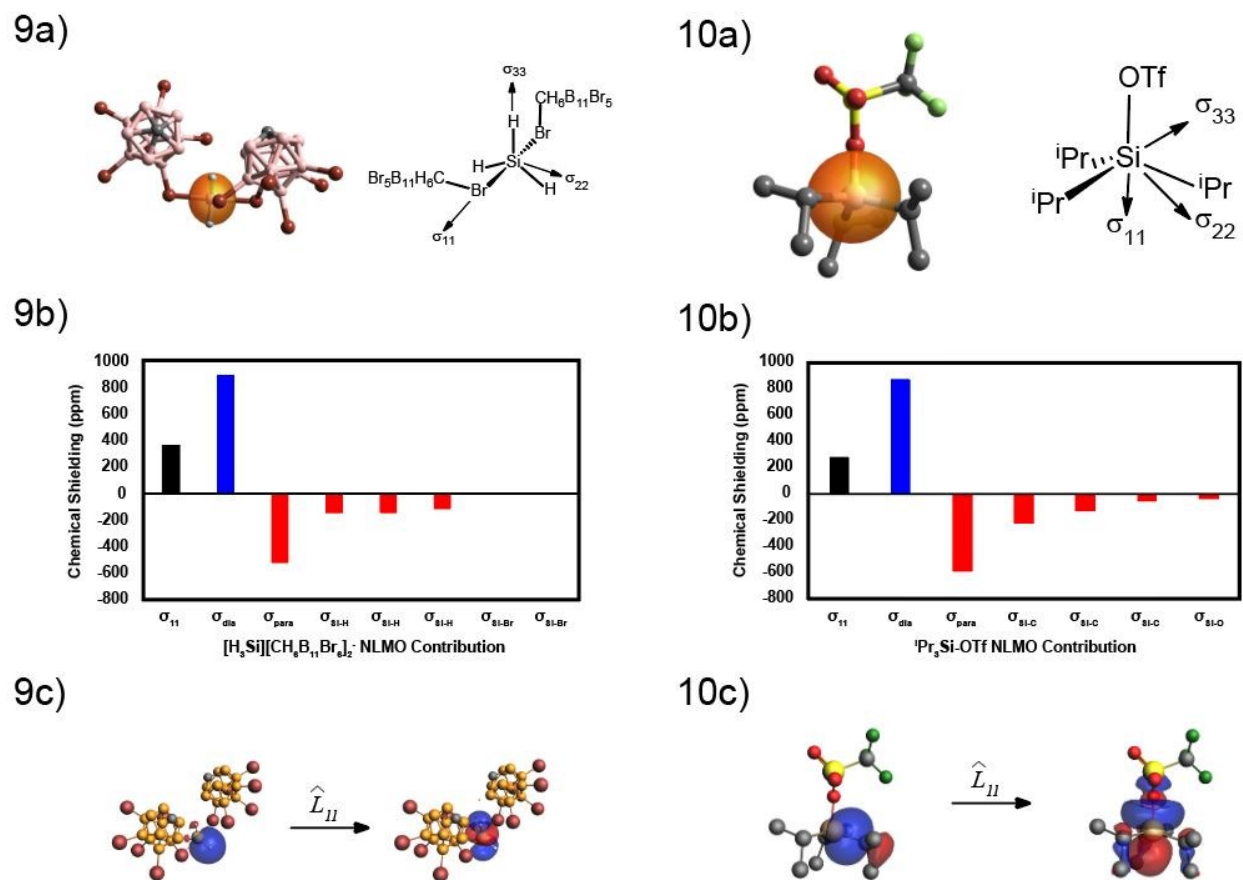
**Figure S4.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **3** and **4**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.



**Figure S5.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **5** and **6**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.

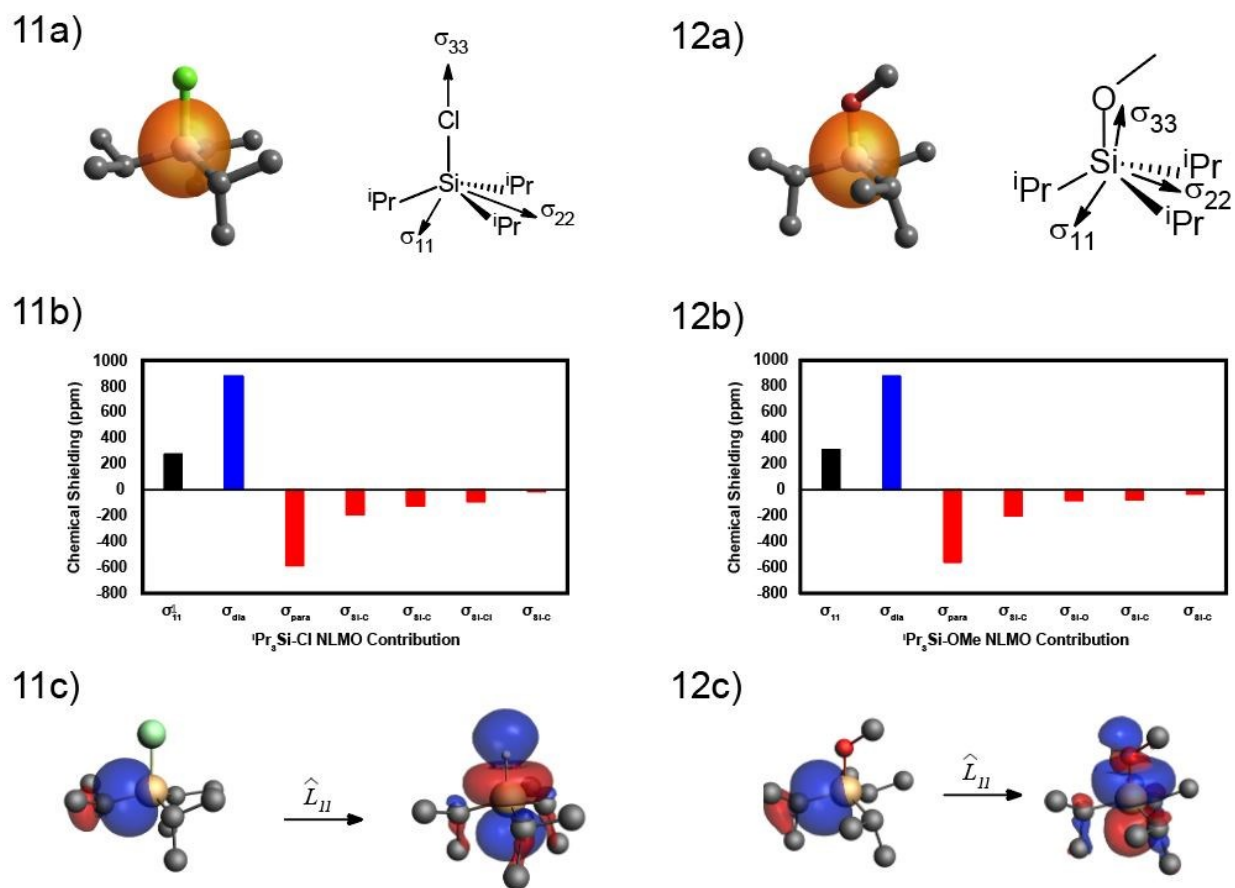


**Figure S6.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **7** and **8**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.



**Figure S7.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **9** and **10**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.



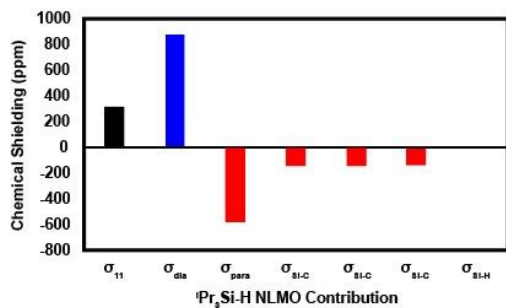


**Figure S8.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **11** and **12**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.

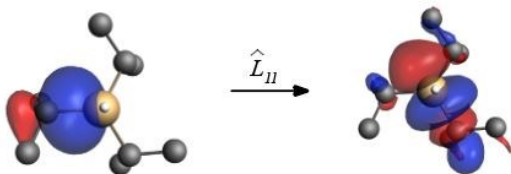
13a)



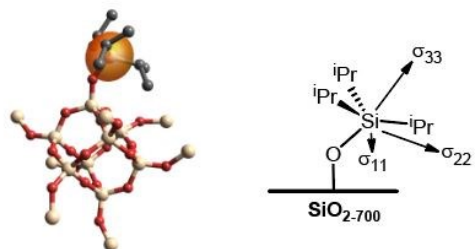
13b)



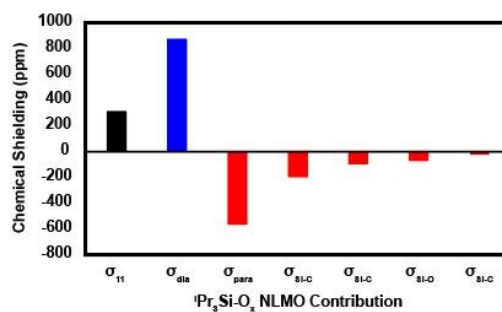
13c)



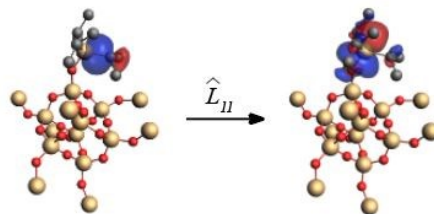
14a)



14b)

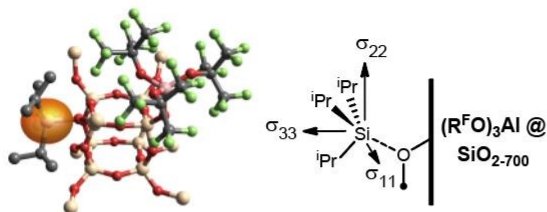


14c)

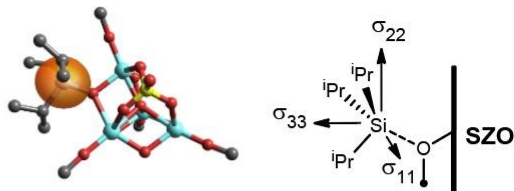


**Figure S9.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **13** and **14**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.

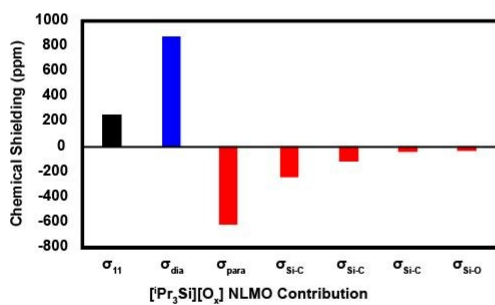
15a)



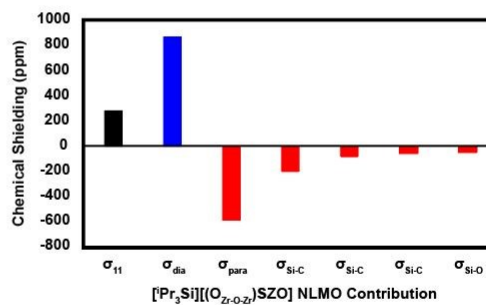
16a)



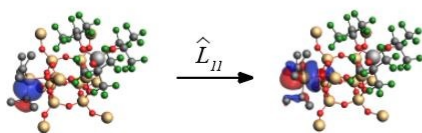
15b)



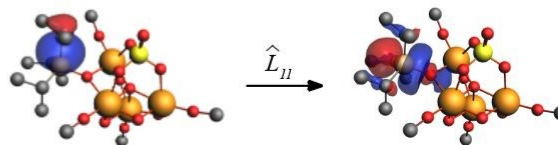
16b)



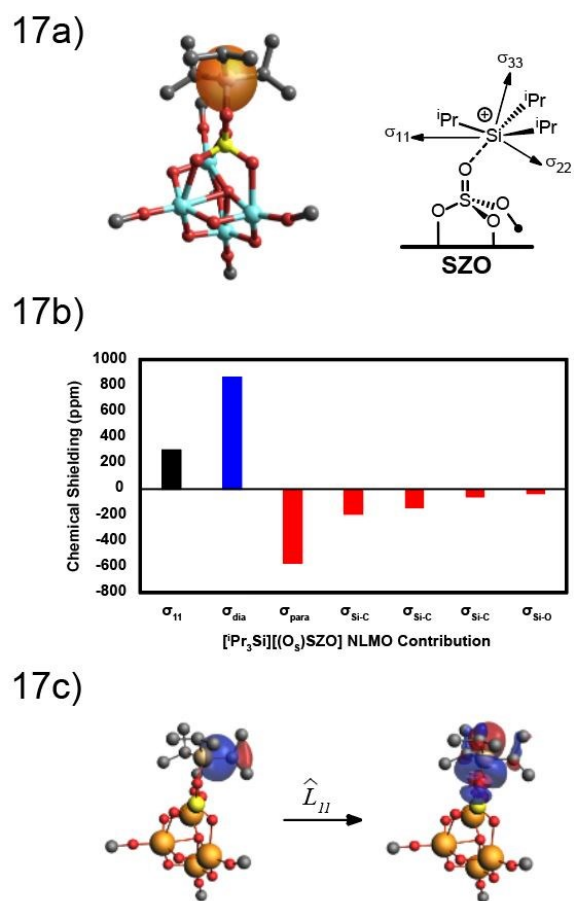
15c)



16c)



**Figure S10.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **15** and **16**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.



**Figure S11.** Chemical shielding tensor plot and schematic with axes (a), NLMO contributions to  $\sigma_{11}$  (b), and major NLMO contributor to  $\sigma_{11}$  deshielding (c) for **17**.  $\sigma_{11}$  is pointing towards the reader. Selected hydrogens are omitted for clarity.

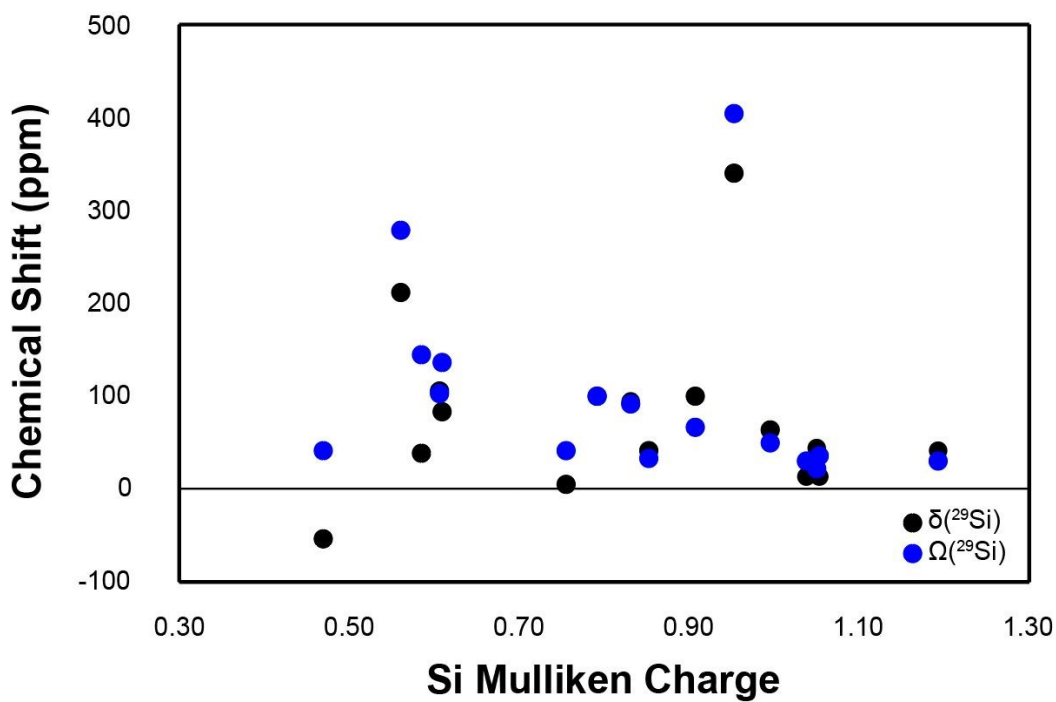
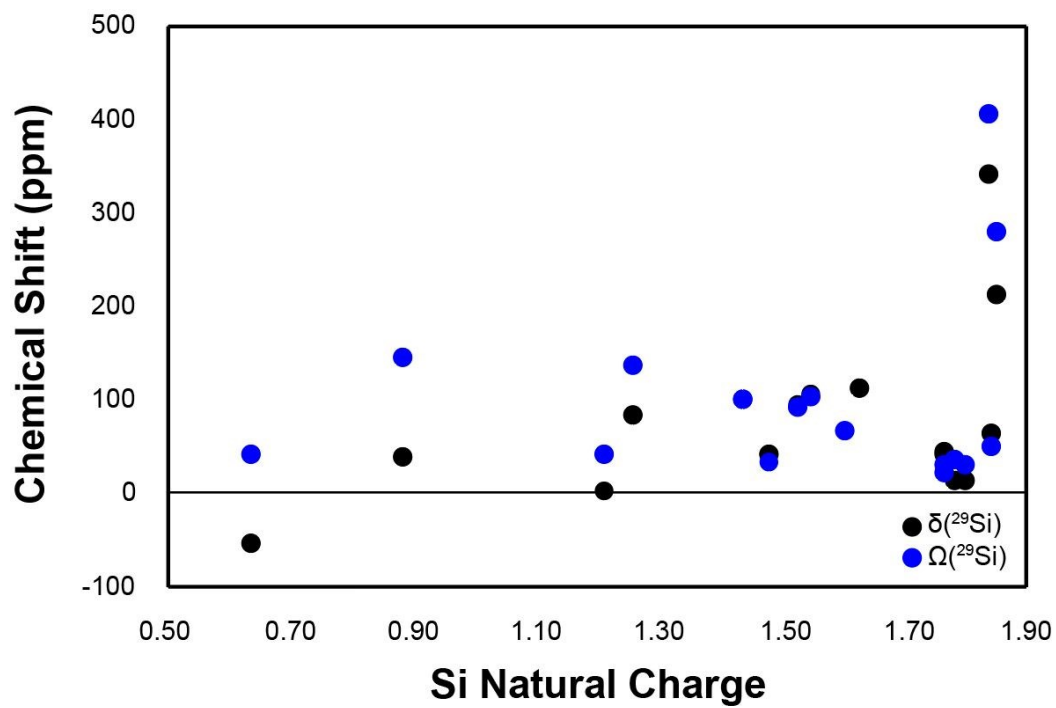


Figure S12. Plots of Chemical Shift and Span Versus Natural Charge and Mulliken Charge

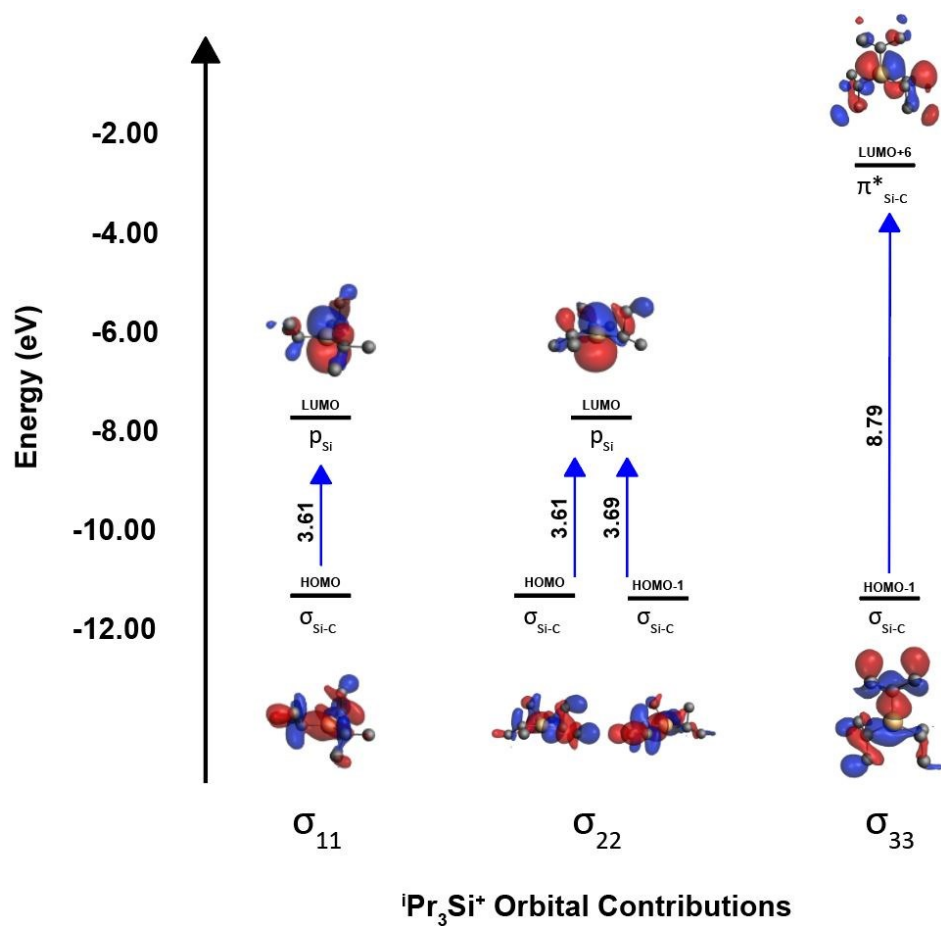


Figure S13. Energy differences in canonical orbital coupling in  ${}^1\text{Pr}_3\text{Si}^+$ . Hydrogens omitted for clarity. (ADF, PBE/Si(TZ2P),DZ)

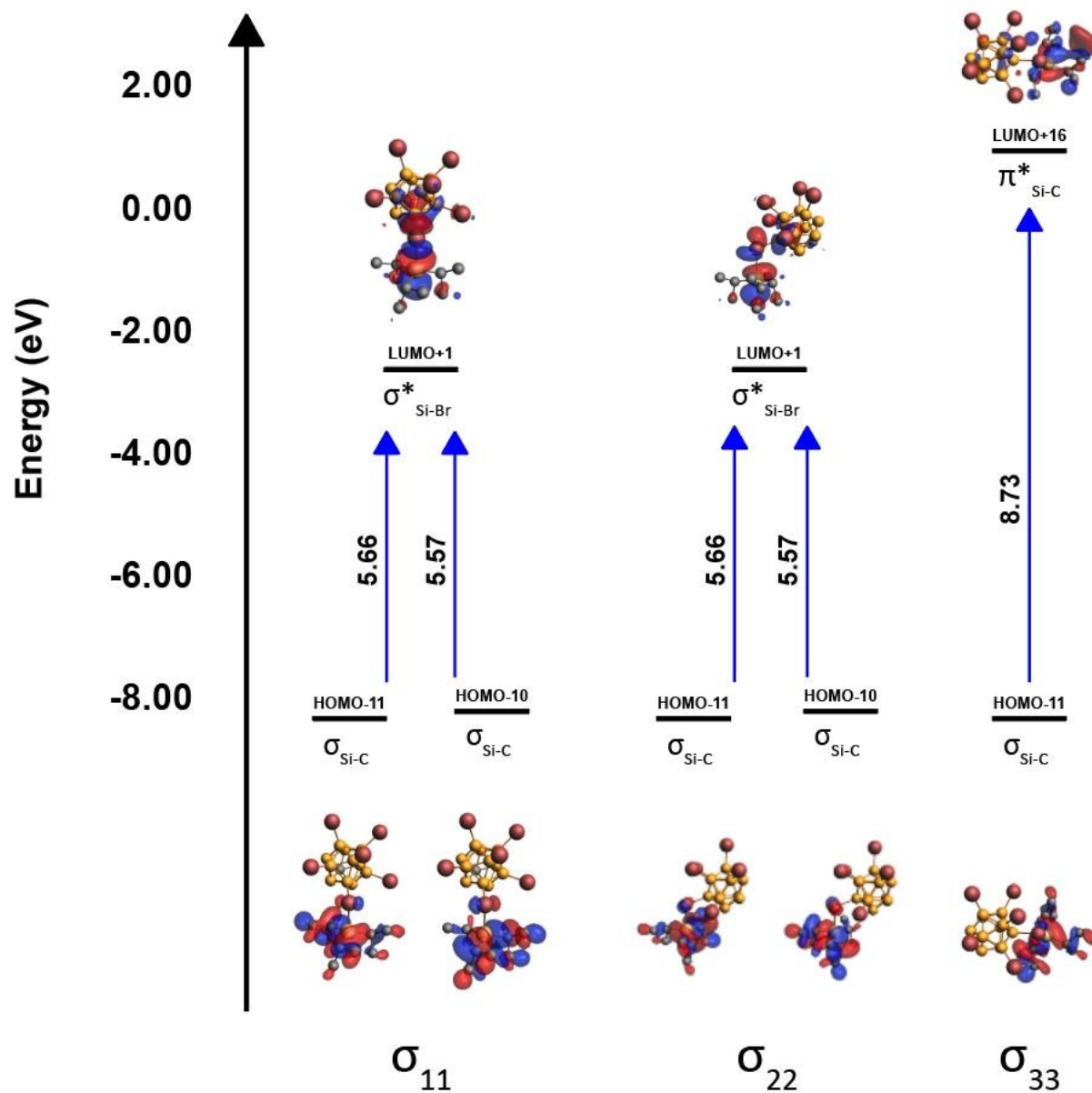


Figure S14. Energy differences in canonical orbital coupling in  $[{}^1\text{Pr}_3\text{Si}][\text{H}_6\text{B}_{11}\text{Br}_6]$ . Hydrogens are omitted for clarity. (ADF, PBE/Si(TZ2P),DZ)

Table S2. Calculated NLMO Contributions to  $\sigma_{11}$  for 1-14.

1 ${}^i\text{Pr}_3\text{Si}^+$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
15	1.93	bonding, Si - C2	-239.10	27.55	-211.55
16	1.93	bonding, Si - C3	-679.81	88.91	-590.91
17	1.93	bonding, Si - C4	-117.43	18.18	-99.26
45	0.16	Si, vacant p	0.00	0.00	0.00
				subtotal	-901.71
				total para	-1037.65
				total dia	881.12
				total	-156.53

2 ${}^i\text{Pr}_3\text{Si}[\text{C}_6\text{H}_6\text{B}_{11}\text{Cl}_6]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
97	1.94	bonding, Si - C8	-183.50	-7.64	-191.15
107	1.94	bonding, Si - C11	-307.39	4.54	-302.86
117	1.94	bonding, Si - C14	-36.44	5.80	-30.64
88	1.96	bonding, Si - C1	-19.97	-0.55	-20.52
				subtotal	-545.17
				total para	-669.34
				total dia	876.97
				total	207.63

3 ${}^i\text{Pr}_3\text{Si}[\text{C}_6\text{H}_6\text{B}_{11}\text{Br}_6]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
97	1.94	bonding, Si - C8	-183.50	-7.64	-191.15
107	1.94	bonding, Si - C11	-307.39	4.54	-302.86
117	1.94	bonding, Si - C14	-36.44	5.80	-30.64
88	1.96	bonding, Si - C1	-19.97	-0.55	-20.52
				subtotal	-545.17
				total para	-669.34
				total dia	876.97
				total	207.63

4 ${}^i\text{Pr}_3\text{Si}[\text{C}_6\text{H}_6\text{B}_{11}\text{I}_6]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
205	1.94	bonding, Si - C8	-217.31	-5.53	-222.84
215	1.94	bonding, Si - C11	-21.79	2.24	-19.55
225	1.94	bonding, Si - C14	-321.78	-4.65	-326.43
196	1.95	bonding, Si - I	-9.29	-0.07	-9.36
				subtotal	-578.17
				total para	-679.42
				total dia	876.56
				total	197.15

5 ${}^i\text{Pr}_3\text{Si-OTf}$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
47	1.93	bonding, Si - C1	-63.52	5.62	-57.90
51	1.94	bonding, Si - C2	-136.40	5.88	-130.52
55	1.94	bonding, Si - C3	-238.52	16.86	-221.66
78	1.97	bonding, Si - O	-41.18	1.33	-39.85
				subtotal	-449.93
				total para	-592.20
				total dia	875.40
				total	283.20

6 ${}^i\text{Pr}_3\text{Si-Cl}$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
23	1.94	bonding, Si - C2	-15.42	2.10	-13.32
24	1.94	bonding, Si - C3	-219.73	21.17	-198.56
25	1.94	bonding, Si - C4	-146.65	12.84	-133.80
26	1.98	bonding, Si - Cl	-105.56	3.70	-101.86
				subTotal	-402.76
				total para	-566.29
				total dia	875.84
				total	309.55

7 ${}^i\text{Pr}_3\text{Si-OMe}$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
19	1.94	bonding, Si - C2	-45.53	2.52	-43.01
20	1.94	bonding, Si - C3	-222.57	14.67	-207.90
21	1.94	bonding, Si - C4	-95.98	9.46	-86.52
22	1.97	bonding, Si - O	-98.89	6.17	-92.72
				subtotal	-430.16
				total para	-570.30
				total dia	879.96
				total	309.66

8 ${}^i\text{Pr}_3\text{Si-H}$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
15	1.92	bonding, Si - C2	-144.08	9.81	-134.27
16	1.92	bonding, Si - C3	-144.29	9.82	-134.46
17	1.92	bonding, Si - C4	-144.32	9.69	-134.62
18	1.97	bonding, Si - H32	0.22	0.38	0.597
				subtotal	-402.76
				total para	-566.29
				total dia	875.84
				total	309.55

9 $\text{Mes}_3\text{Si}^+$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
33	1.94	bonding, Si - C2	-528.95	59.18	-469.77
34	1.94	bonding, Si - C8	-84.08	8.66	-75.42
35	1.94	bonding, Si - C14	-191.59	22.56	-169.03
105	0.00	Si, vacant p	0.00	0.00	0.00
				subtotal	-714.21
				total para	-847.62
				total dia	879.85
				total	32.23

10 $\text{Et}_3\text{Si-(toluene)}^+$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
58	0.38	bonding, Si - C1	0.00	0.00	0.00
40	1.96	bonding, Si - C8	-257.72	23.09	-234.62
54	1.96	bonding, Si - C12	-300.98	35.66	-265.33
47	1.96	bonding, Si - C10	-6.56	-0.44	-7.00
				subtotal	-506.95
				total para	-679.74
				total dia	878.29
				total	198.54

11 ${}^i\text{BuH}_2\text{Si}[\text{CH}_6\text{B}_{11}\text{Br}_6]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
143	1.97	bonding, Si - H8	-77.16	3.77	-73.38
144	1.98	bonding, Si - H9	-116.47	-1.19	-117.66
145	1.93	bonding, Si - C26	-283.51	-20.01	-303.52
136	1.97	bonding, Si - Br	-46.45	2.59	-43.86
				subtotal	-538.42
				total para	-655.88
				total dia	872.94
				total	217.06

12 ${}^i\text{H}_2\text{Si}[\text{CH}_6\text{B}_{11}\text{Br}_6]_2^-$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
143	1.97	bonding, Si - H8	-77.16	3.77	-73.38
144	1.98	bonding, Si - H9	-116.47	-1.19	-117.66
145	1.93	bonding, Si - C26	-283.51	-20.01	-303.52
136	1.97	bonding, Si - Br	-46.45	2.59	-43.86
				subtotal	-538.42
				total para	-655.88
				total dia	872.94
				total	217.06

13 ${}^i\text{H}_2\text{Si}[\text{CH}_6\text{B}_{11}\text{Br}_6]_2^-$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
276	1.98	bonding, Si - H15	-58.62	5.91	-52.71
277	1.98	bonding, Si - H16	-288.79	32.49	-256.30
278	1.98	bonding, Si - H17	-89.81	9.86	-79.95
269	1.97	bonding, Si - Br	-74.91	1.19	-73.71
205	1.83	lone pair, Br 1	-10.86	24.27	13.41
				subtotal	-449.26
				total para	-519.28
				total dia	871.77
				total	355.76

14 ${}^i\text{Pr}_3\text{Si-O}_2$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
211	1.94	bonding, Si - C79	-203.32	-1.49	-204.81
212	2.00	bonding, Si - C84	-117.66	17.41	-100.25
213	1.93	bonding, Si - C85	-28.88	3.40	-25.48
17	1.97	bonding, Si - O14	-68.50	-3.76	-72.26
				subtotal	-402.79
				total para	-567.15
				total dia	877.32
				total	310.16



Table S3. Calculated NLMO Contributions to  $\sigma_{11}$  for 15-17.

15						16					
$[\text{Pr}_3\text{Si}][\text{Ox}]$						$[\text{Pr}_3\text{Si}][(\mu\text{-O}_3)\text{SZO}_{300}]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total	NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
351	1.94	bonding, Si - C95	-102.66	-13.65	-116.31	181	1.93	bonding, Si - C19	-91.77	6.32	-85.44
352	1.93	bonding, Si - C96	-42.35	2.37	-39.99	185	1.93	bonding, Si - C20	-233.47	34.03	-199.44
353	1.93	bonding, Si - C97	-232.27	-12.03	-244.30	189	1.93	bonding, Si - C21	-65.34	4.08	-61.26
293	1.97	bonding, Si - O5	-37.44	1.89	-35.55	157	1.96	bonding, Si - O8	-54.20	2.97	-51.23
				subtotal	-436.15					subtotal	-397.37
				total para	-623.91					total para	-589.34
				total dia	877.45					total dia	873.71
				total	253.54					total	284.38

17					
$[\text{Pr}_3\text{Si}][(\mu\text{-O}_{22})\text{SZO}_{300}]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
181	1.94	bonding, Si - C19	-190.15	-6.79	-196.94
185	1.94	bonding, Si - C20	-136.27	-7.30	-143.57
189	1.93	bonding, Si - C21	-65.84	5.95	-59.88
163	1.96	bonding, Si - O13	-39.81	1.32	-38.49
				subtotal	-438.89
				total para	-570.10
				total dia	874.79
				total	304.69

Table S4. Calculated NLMO Contributions to  $\sigma_{22}$  and  $\sigma_{33}$  for 1, 2, 11 and 12.

1						1					
$\sigma_{22}$						$\sigma_{33}$					
$[\text{Pr}_3\text{Si}^+]$						$[\text{Pr}_3\text{Si}^+]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total	NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
15	1.93	bonding, Si - C2	-434.87	51.32	-383.55	15	1.93	bonding, Si - C2	-174.55	18.21	-156.34
16	1.93	bonding, Si - C3	-10.72	1.39	-9.34	16	1.93	bonding, Si - C3	-174.99	20.91	-154.08
17	1.93	bonding, Si - C4	-540.45	68.22	-472.23	17	1.93	bonding, Si - C4	-178.17	21.30	-156.87
45	0.16	Si, vacant P	0.00	0.00	0.00	45	0.16	Si, vacant P	0.00	0.00	0.00
				subtotal	-865.11					subtotal	-467.29
				total para	-986.00					total para	-626.42
				total dia	880.21					total dia	876.97
				total	-105.79					total	250.55

2						2					
$\sigma_{22}$						$\sigma_{33}$					
$[\text{Pr}_3\text{Si}][\text{CH}_6\text{B}_{11}\text{Br}_6]$						$[\text{Pr}_3\text{Si}][\text{CH}_6\text{B}_{11}\text{Br}_6]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total	NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
156	1.94	bonding, Si - C19	-321.10	1.96	-319.14	156	1.94	bonding, Si - C19	-178.01	16.05	-161.95
166	1.94	bonding, Si - C22	-33.62	4.15	-29.47	166	1.94	bonding, Si - C22	-163.40	19.86	-143.54
176	1.94	bonding, Si - C25	-188.06	-4.11	-192.17	176	1.94	bonding, Si - C25	-149.98	15.41	-134.57
142	1.96	bonding, Si - Br	-13.82	16.04	2.22	142	1.96	bonding, Si - Br	-0.25	0.53	0.28
				subtotal	-538.56					subtotal	-439.79
				total para	-655.99					total para	-592.95
				total dia	876.87					total dia	883.93
				total	220.88					total	290.98

11						11					
$\sigma_{22}$						$\sigma_{33}$					
$[\text{Bu}_2\text{HSi}][\text{CH}_6\text{B}_{11}\text{Br}_6]$						$[\text{Bu}_2\text{HSi}][\text{CH}_6\text{B}_{11}\text{Br}_6]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total	NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
147	1.97	bonding, Si - H8	-108.02	5.36	-102.66	147	1.97	bonding, Si - H8	-286.25	-11.90	-298.15
148	1.92	bonding, Si - C34	-217.89	25.77	-192.13	148	1.92	bonding, Si - C34	-71.47	-0.46	-71.93
149	1.92	bonding, Si - C38	-203.43	22.90	-180.53	149	1.92	bonding, Si - C38	-87.65	3.13	-84.52
111	1.94	bonding, Si-Br	-1.57	-0.04	-1.61	140	1.96	bonding, Si-Br	-60.48	12.36	-48.12
				subtotal	-476.93					subtotal	-502.72
				total para	-599.56					total para	-574.02
				total dia	885.02					total dia	880.56
				total	285.06					total	306.54

12						12					
$\sigma_{22}$						$\sigma_{33}$					
$[\text{BuH}_2\text{Si}][\text{CH}_6\text{B}_{11}\text{Br}_6]$						$[\text{BuH}_2\text{Si}][\text{CH}_6\text{B}_{11}\text{Br}_6]$					
NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total	NLMO	Occ.	Orbitals	Lewis	Non-Lewis	Total
145	1.93	bonding, Si - C26	-164.44	17.45	-147.00	145	1.93	bonding, Si - C26	-30.19	1.94	-28.25
144	1.98	bonding, Si - H9	-106.64	-1.53	-108.17	144	1.98	bonding, Si - H9	-169.01	-9.86	-178.87
143	1.97	bonding, Si - H8	-189.97	-1.02	-190.99	143	1.97	bonding, Si - H8	-223.66	0.46	-223.20
136	1.97	bonding, Si - Br	-22.79	2.21	-20.58	136	1.97	bonding, Si - Br	-21.97	1.44	-20.54
				subtotal	-466.74					subtotal	-450.85
				total para	-562.20					total para	-526.97
				total dia	880.39					total dia	888.58
				total	318.19					total	361.60