

Supplementary Information

Generation and aromaticity of 2-silaimidazolium ion, a new p-conjugated silylium ion

Shintaro Ishida, Tohru Nishinaga, Robert West, and Koichi Komatsu

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Organosilicon Research Center, University of Wisconsin-Madison, 1101 University Ave, Madison, Wisconsin 53706

Contents

1. Details of experiments

- Synthesis of chlorosilane **4** (S2)
- Generation of 2-silaimidazolium cation **5** (S2)
- Reaction of 2-silaimidazolium cation **5** with *n*-Bu₄NBr (S3)

2. NMR spectra

- VT-¹H NMR spectra of chlorosilane **4** in CD₂Cl₂ (S4)
- ¹³C NMR spectrum of **4** in CD₂Cl₂ at 25 °C (S6)
- VT-¹H NMR spectra of 2-silaimidazolium cation **5** in CD₂Cl₂ (S7)
- ¹³C NMR spectra of **4** and **5** in CD₂Cl₂ at -60 °C (S9)
- ¹³C DEPT spectra of **5** in CD₂Cl₂ (S10)
- C-H COSY spectrum of **5** in CD₂Cl₂ (S11)
- ²⁹Si NMR spectrum of chlorotriethylsilane and [Et₃Si(benzene)]⁺•TPFPB⁻ in CD₂Cl₂ (S11)
- ¹H NMR spectra of cation **5** in C₇D₈ at -60 °C (S12)
- ¹³C NMR spectra of cation **5** in C₇D₈ at -60 °C (S12)

3. Theoretical studies

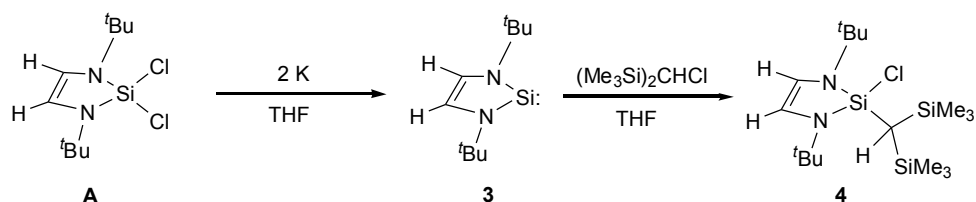
- Methods (S13)
- Results of NICS and total energy calculations (S13)
- Cartesian coordinates from the optimized structures (S14)

4. References (S19)

1. Details of experiments

General Procedures. All experiments were performed under argon using a standard vacuum system. THF was dried and distilled over sodiumbenzophenone ketyl. Toluene-*d*₈ was dried in a glass tube with potassium mirror. Dichloromethane was dried in a glass tube over calcium hydride. Sampling of air-sensitive materials was carried out in a glove box. ¹H (400 MHz), ¹³C (99.5 MHz), and ²⁹Si (78.5 MHz) NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-700 mass spectrometer. Melting point was determined on a Yanaco MP-500D apparatus and uncorrected. Elemental analysis was carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University.

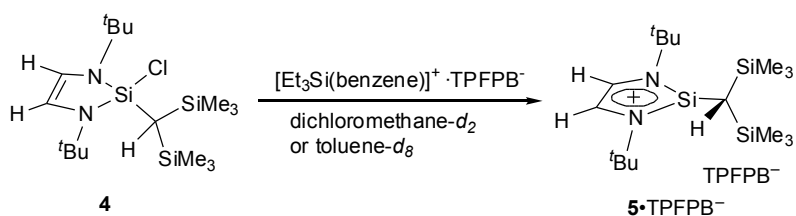
Synthesis of chlorosilane 4. In a two-necked flask equipped with a magnetic stirring bar, a rubber septum, and a reflux condenser, diaminosilylene **3** was prepared from dichlorosilane **A** (9.20 g, 34.6 mmol) and potassium (2.74 g, 70.3 mmol) in THF (100 ml) according to the published procedure.¹ Into the flask containing freshly prepared **3**, bis(trimethylsilyl)methyl chloride (6.8 g, 35.0 mmol) was introduced using a syringe and the solution was refluxed for 24 h. After completion of the reaction, the solvent was evaporated under reduced pressure, and hexane (100 ml) was added. Precipitated insoluble materials were removed by filtration. The filtrate was evaporated under reduced pressure to give crude product as a pale yellow solid, which was then chromatographed over SiO₂ eluted with hexane to afford chlorosilane **4** (10.0 g, 25.6 mmol) in 74% yield as colorless crystals. The physical data are given in reference 7 of the main text.



Generation and NMR measurement of 2-silaimidazolium cation 5. In a 5 mm NMR tube connectable to a vacuum line, chlorosilane **4** (46 mg, 0.118 mmol) and [Et₃Si(benzene)]⁺•TPFPB⁻² (104 mg, 0.119 mmol) were placed, and the tube was connected to a vacuum line. Into this was added dry dichloromethane-*d*₂ (0.7 ml) by vacuum transfer. After being sealed, the tube was gently shaken so that the reactants were mixed well in a cold methanol bath at the temperature below -70 °C. The color of the solution turned to intense yellow, and then NMR spectra were recorded at low temperatures (-60 ~ -10 °C). A similar method was applied to the reaction in toluene-*d*₈ as a solvent. The resulting toluene-*d*₈ solution in a sealed NMR tube separated into two layers. The NMR tube was adjusted so that the lower layer part was positioned in the center of the probe, and the NMR measurement was conducted. Due to the high viscosity of the lower layer at lower temperatures, ¹H and ¹³C NMR signals were too much broadened to give reliable information. The ²⁹Si NMR spectrum was also slightly broadened, but afforded reliable signals as shown in

(S2)

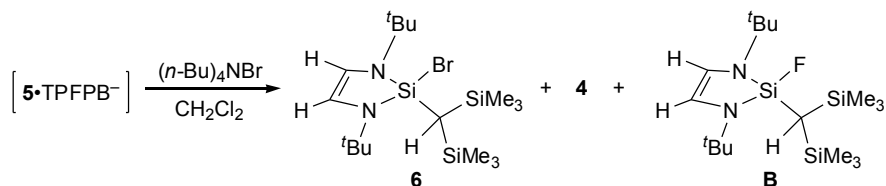
Figure 2 of the main text. The assignment of the NMR signals of **5** was made on the basis of the spectra obtained by C–H COSY and ^{13}C DEPT techniques.



Reaction of 2-silaimidazolium cation 5 with $n\text{-Bu}_4\text{NBr}$: In a Schlenk tube equipped with a magnetic stirring bar and a rubber septum, chlorosilane **4** (151 mg, 0.387 mmol) and $[\text{Et}_3\text{Si}(\text{benzene})]^+\cdot\text{TPFPB}^-$ (342 mg, 0.390 mmol) were placed, and dry dichloromethane (5 ml) was added with cooling at $-50\text{ }^\circ\text{C}$. During 2 h when the mixture was stirred at $-50\text{ }^\circ\text{C}$, the solution turned to intense yellow in color, indicating the formation of cation **5**. Then, a solution of $n\text{-Bu}_4\text{NBr}$ (189 mg, 0.586 mmol) in dichloromethane (5 ml), which had been cooled at $-50\text{ }^\circ\text{C}$, was added using a cannula and the reaction mixture was stirred overnight. After the solvent was exchanged to hexane as described above and insoluble materials were removed by filtration, the filtrate was evaporated under reduced pressure to give a mixture containing bromosilane **6** as pale orange-red semisolid. Since isolation of **6** was not possible by any means including flash chromatography, preparative HPLC, and recrystallization, yield of **6** was determined by ^1H NMR spectroscopy on the crude product mixture using a known quantity of hexamethylbenzene as an internal standard. Fluorosilane **B** is only detected by MS spectroscopy.

6: ^1H NMR (313 K, CD_2Cl_2) δ 0.25 (brs, 18 H), 0.65 (s, 1 H), 1.41 (s, 18 H), 5.83 (s, 2 H); ^{13}C NMR (313 K, CD_2Cl_2) δ 3.1 (SiMe_3), 15.4 ($>\text{CH}-$), 31.1 (CH_3), 52.8 ($>\text{C}<$), 112.4 ($=\text{CH}-$); ^{29}Si NMR (313 K, CD_2Cl_2) δ -24.2 (SiBr) 0.4 (SiMe_3); MS (EI, 70 eV) m/z (%) 434 (M^+ , 90), 322 (100), 73 (98); HRMS m/z calcd for $\text{C}_{17}\text{H}_{39}\text{N}_2^{79}\text{BrSi}_3$ 434.1604, found 434.1599, calcd for $\text{C}_{17}\text{H}_{39}\text{N}_2^{81}\text{BrSi}_3$ 436.1584, found 436.1598.

B: MS (EI, 70 eV) m/z (%) 374 (M^+ , 100), 262 (85), 73 (45); HRMS calcd for $\text{C}_{17}\text{H}_{39}\text{N}_2\text{FSi}_3$ 374.2405, found 374.2399.



(S3)

2. NMR spectra

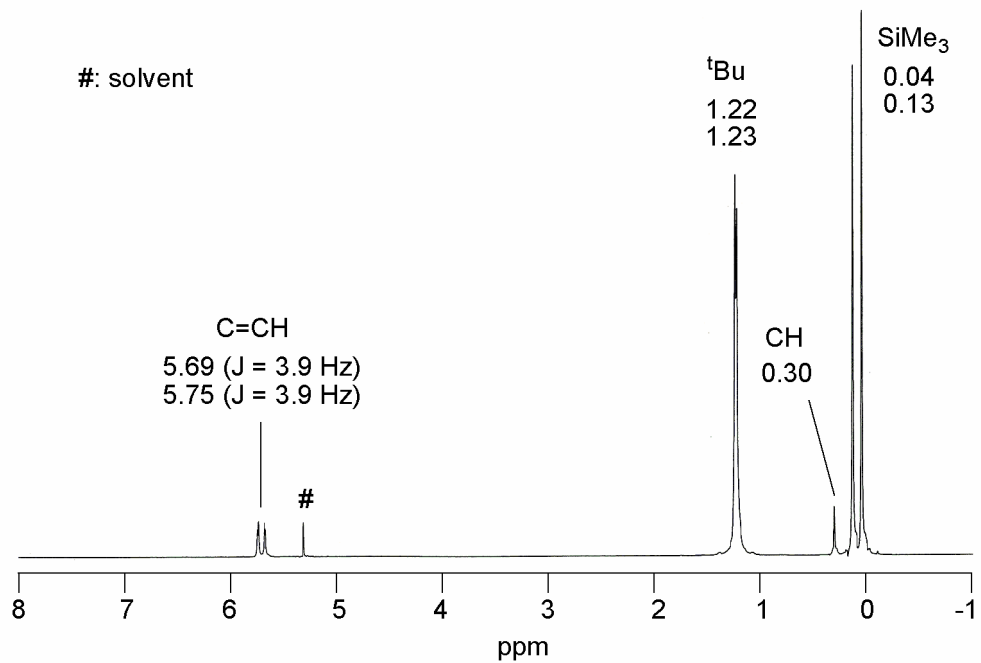


Figure S1. ¹H NMR spectrum of **4** in CD₂Cl₂ at -90 °C (# = CH₂Cl₂ in solvent).

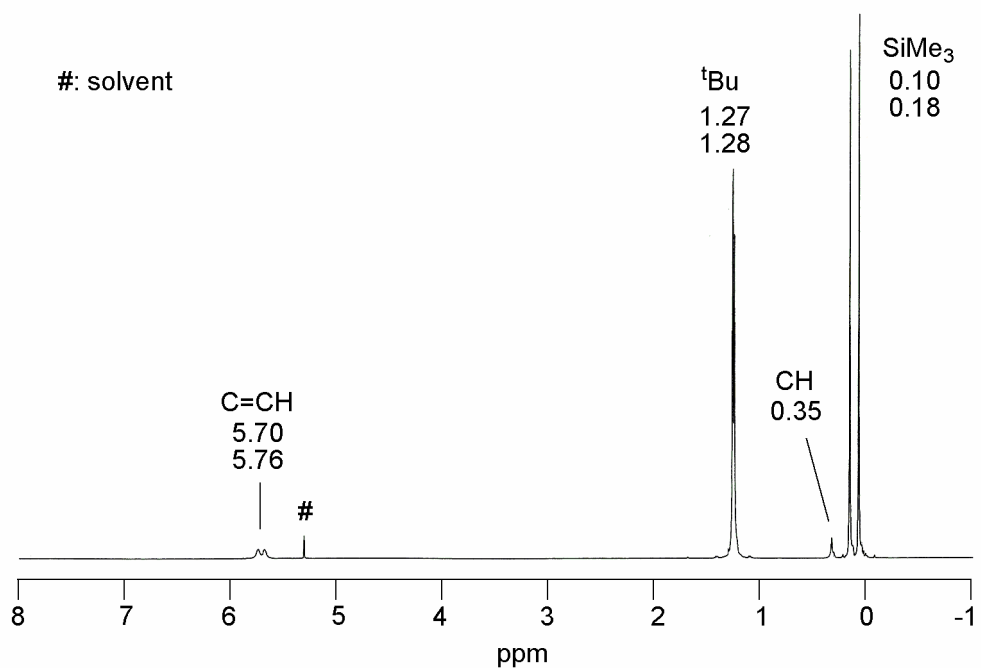


Figure S2. ¹H NMR spectrum of **4** in CD₂Cl₂ at -60 °C.

(S4)

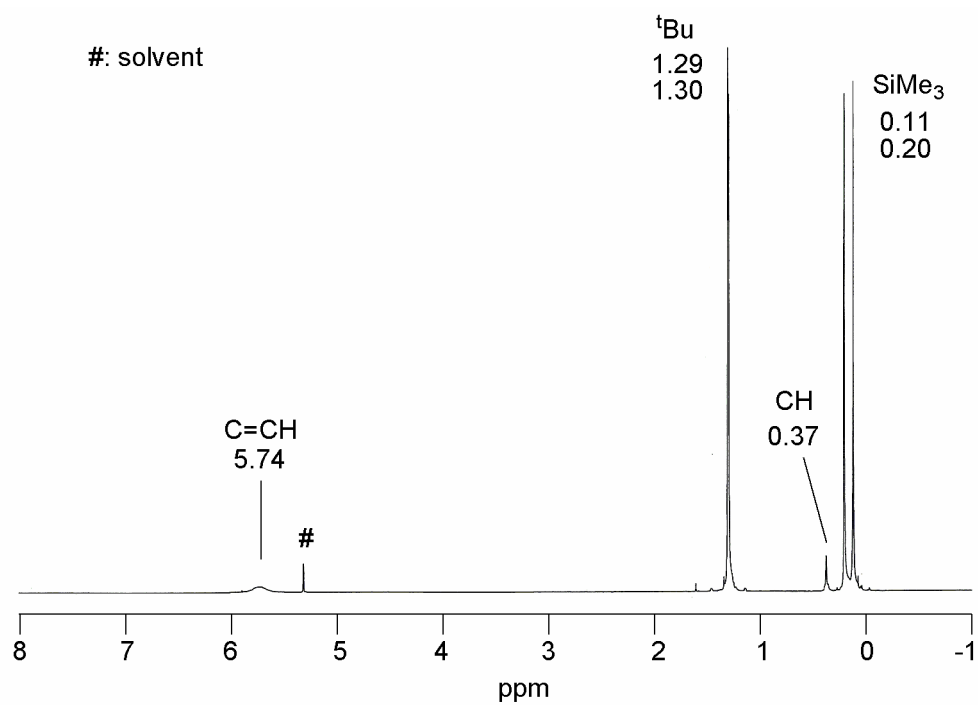


Figure S3. ¹H NMR spectrum of **4** in CD₂Cl₂ at -20 °C.

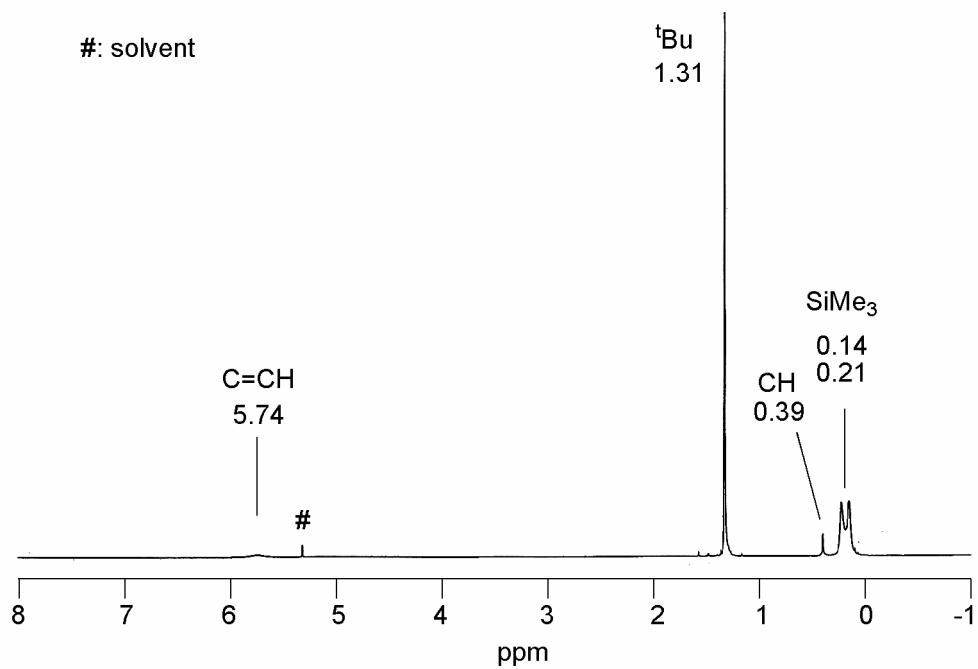


Figure S4. ¹H NMR spectrum of **4** in CD₂Cl₂ at 0 °C.

(S5)

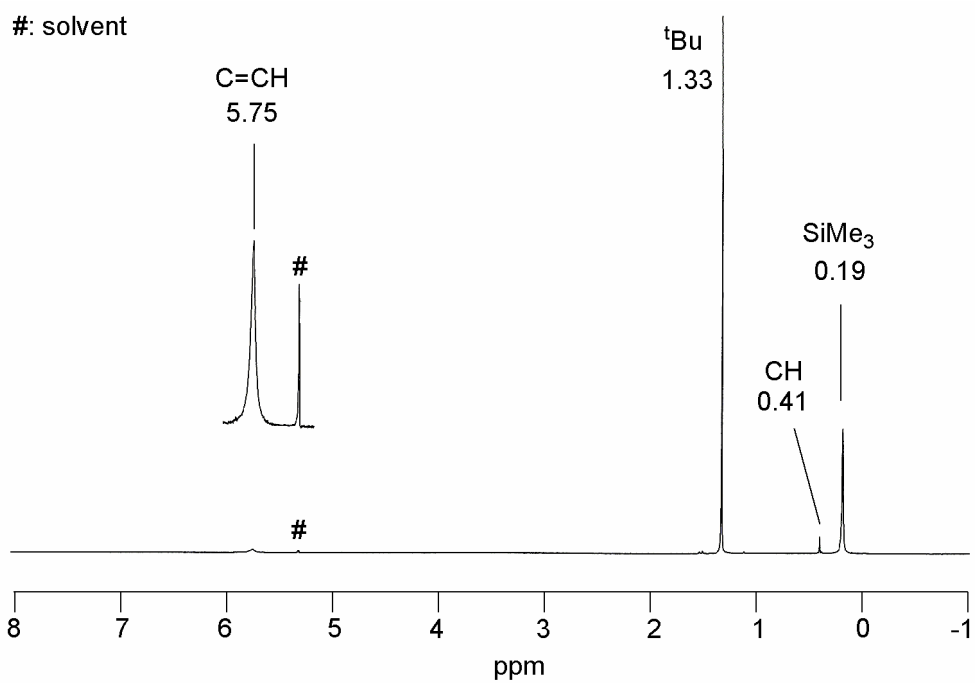


Figure S5. ¹H NMR spectrum of **4** in CD₂Cl₂ at 25 °C.

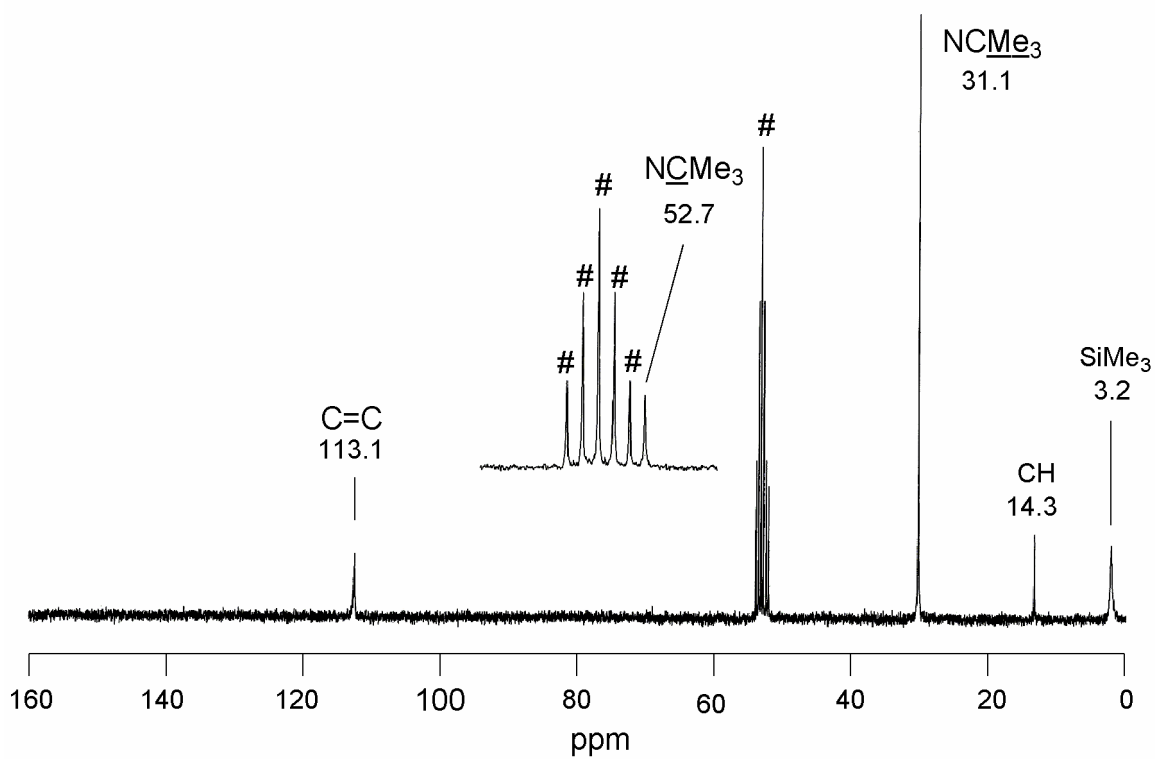


Figure S6. ¹³C NMR spectrum of **4** in CD₂Cl₂ at 25 °C.

(S6)

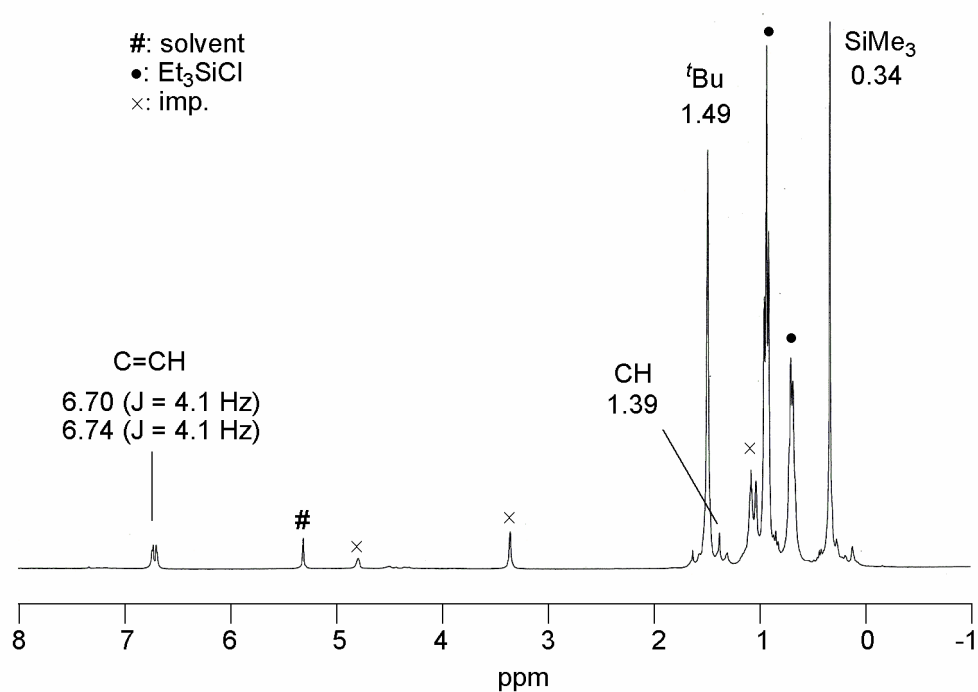


Figure S7. ¹H NMR spectrum of cation **5** in CD₂Cl₂ at -60 °C.

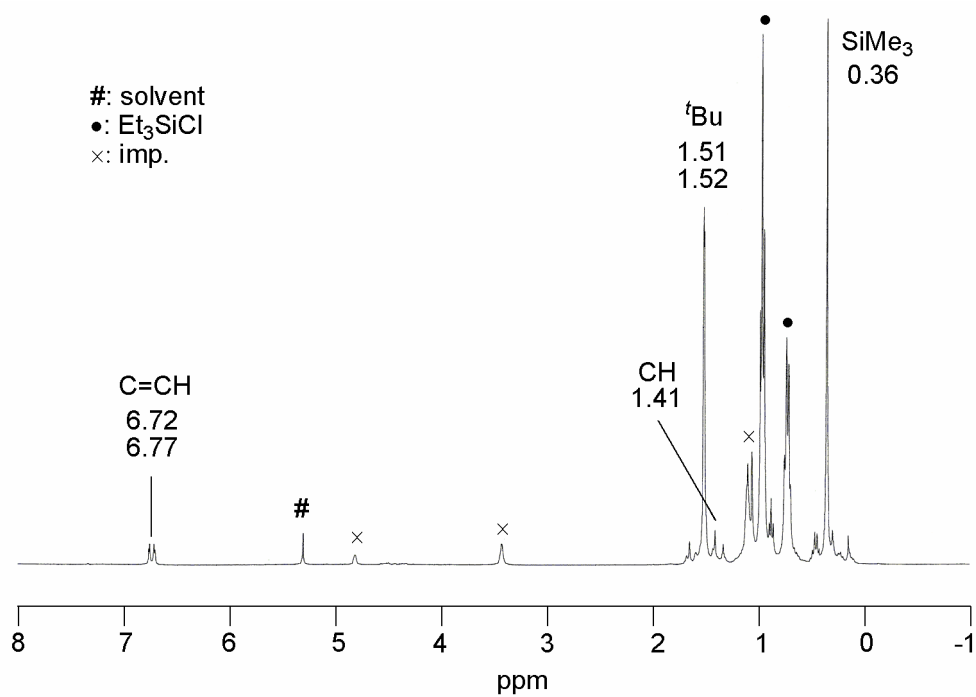


Figure S8. ¹H NMR spectrum of cation **5** in CD₂Cl₂ at -30 °C.

(S7)

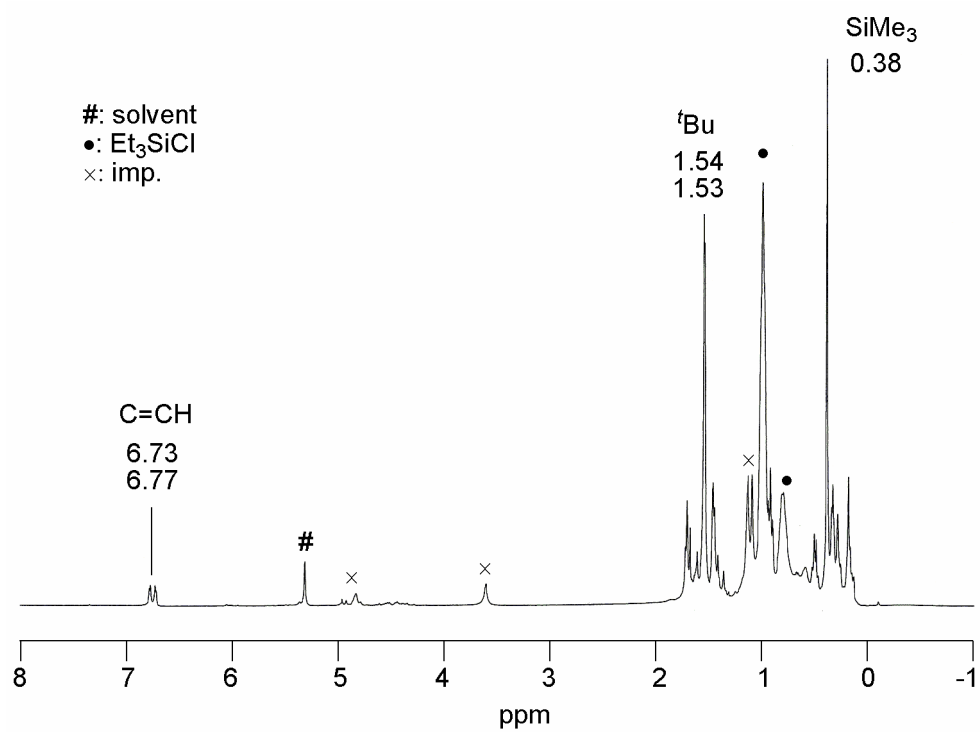


Figure S9. ¹H NMR spectrum of cation **5** in CD₂Cl₂ at -10 °C.

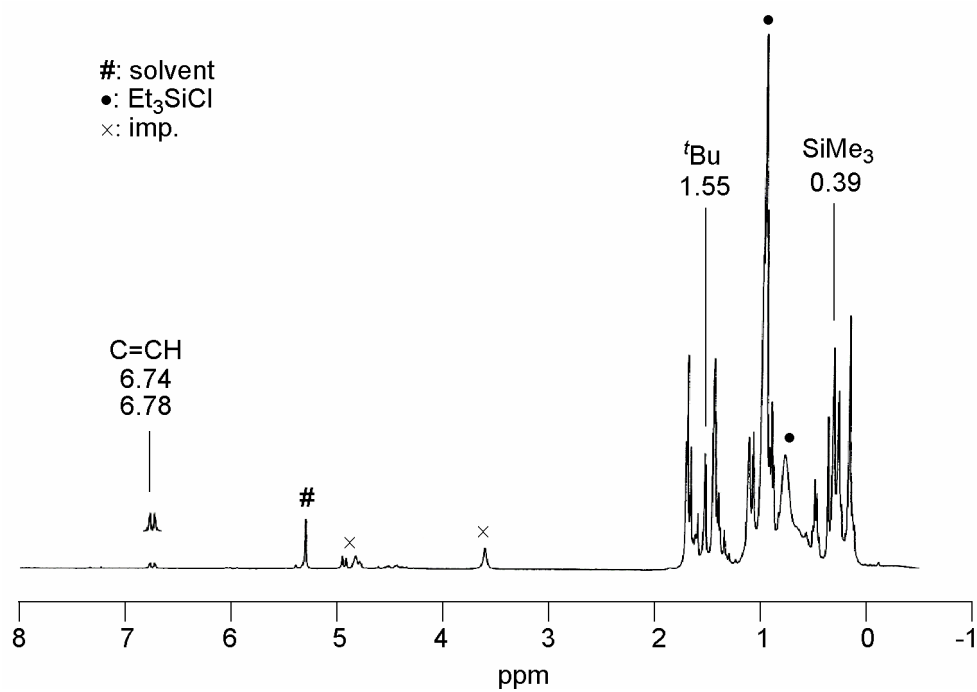
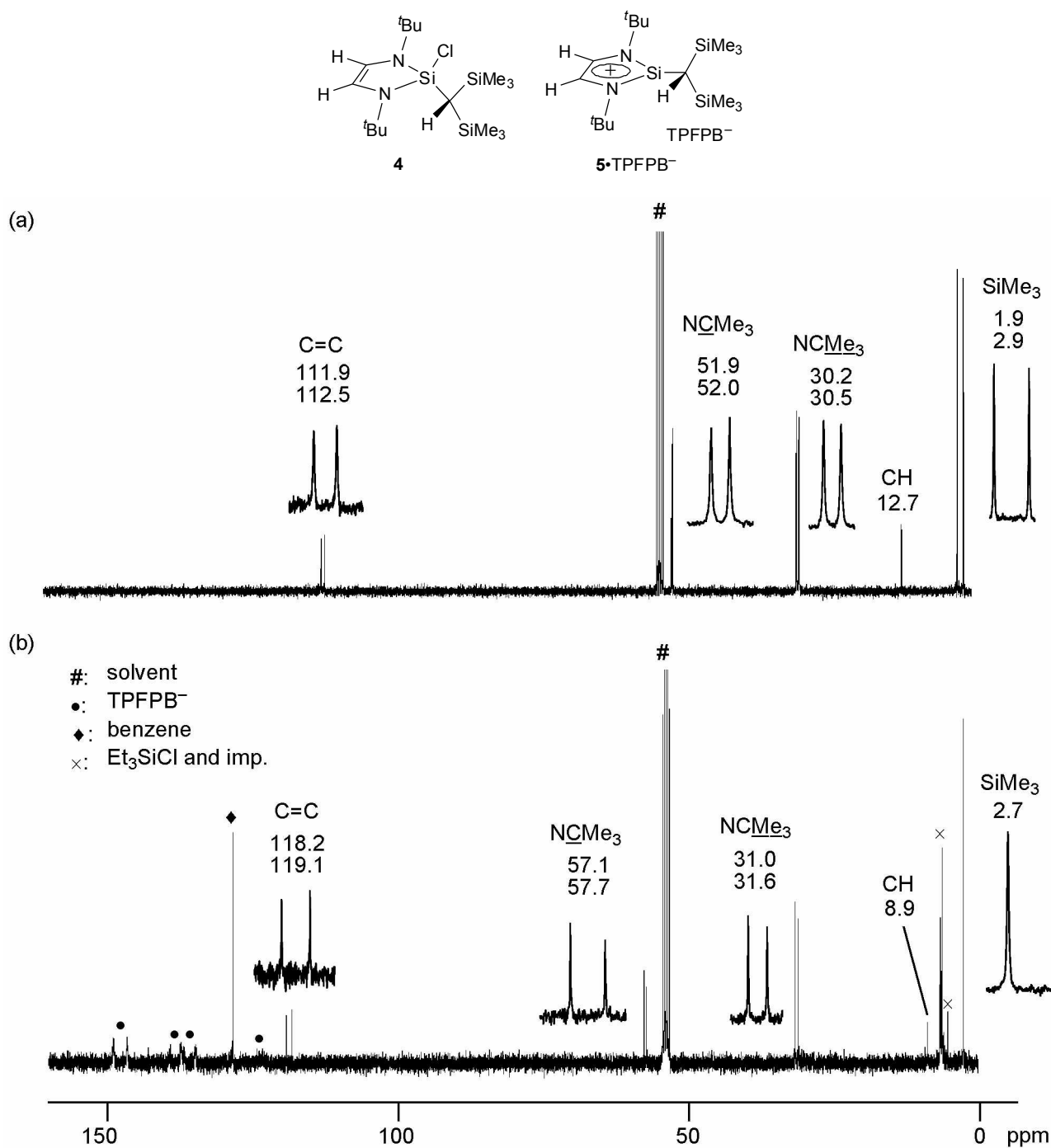


Figure S10. ¹H NMR spectrum of cation **5** in CD₂Cl₂ at 0 °C.

(S8)



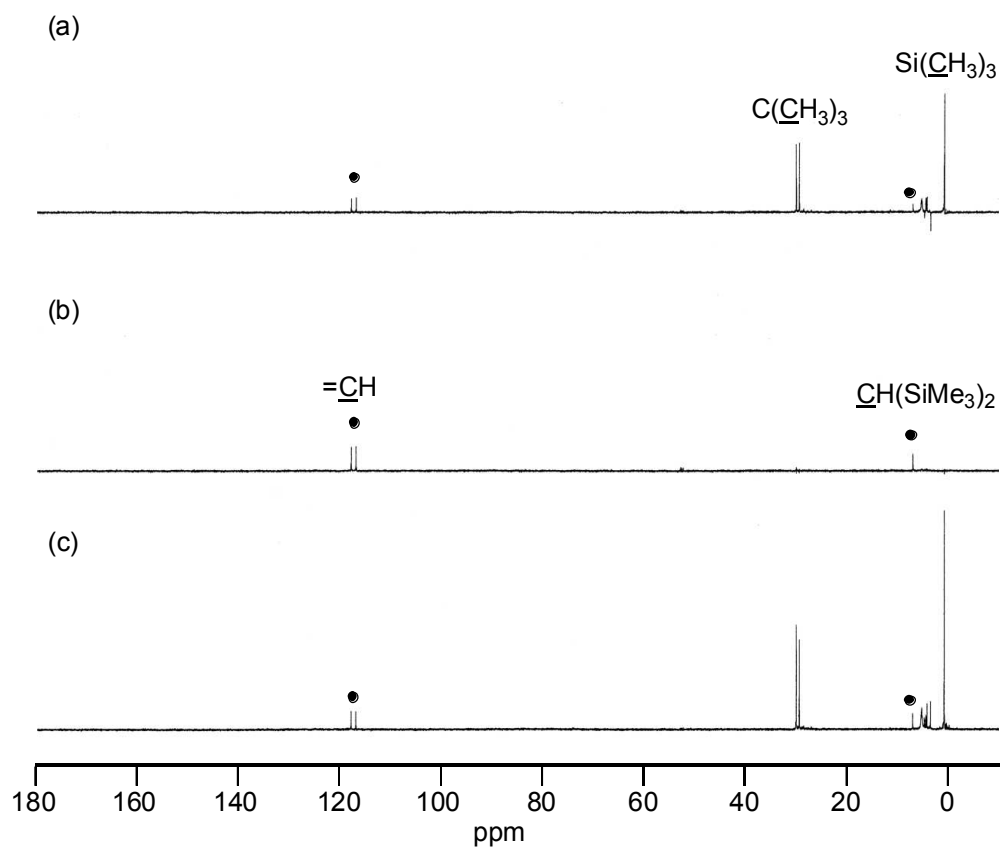


Figure S12. ^{13}C NMR DEPT spectra of **5** in CD_2Cl_2 at $-60\text{ }^\circ\text{C}$. (a) DEPT135, (b) DEPT90, and (c) DEPT45.

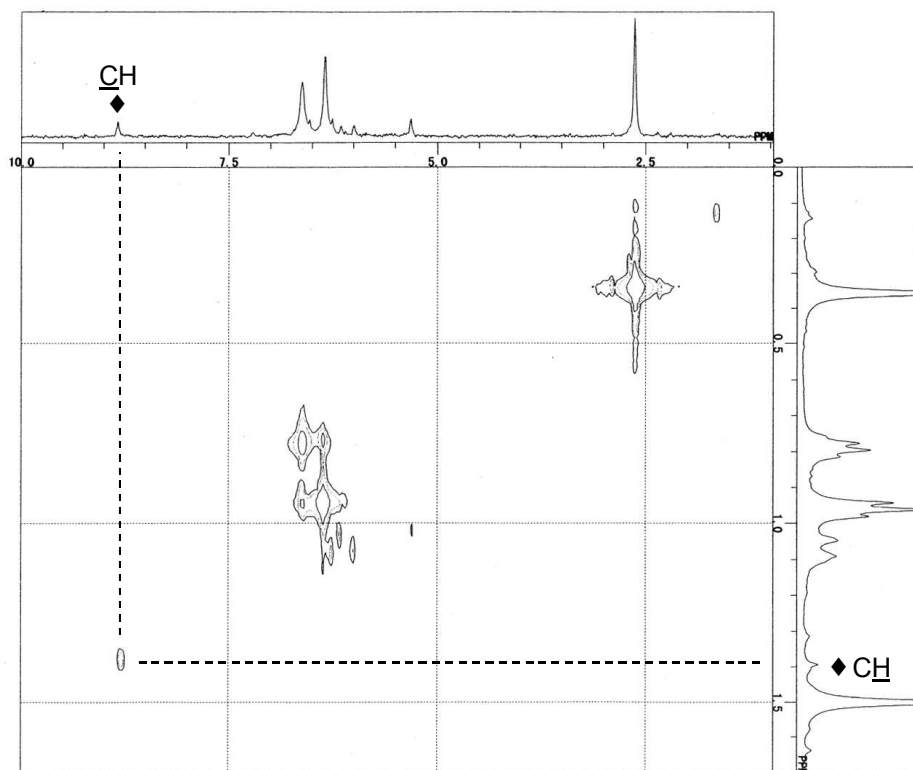


Figure S13. ^{13}C - ^1H COSY spectrum of **5** in CD_2Cl_2 at $-60\text{ }^\circ\text{C}$.

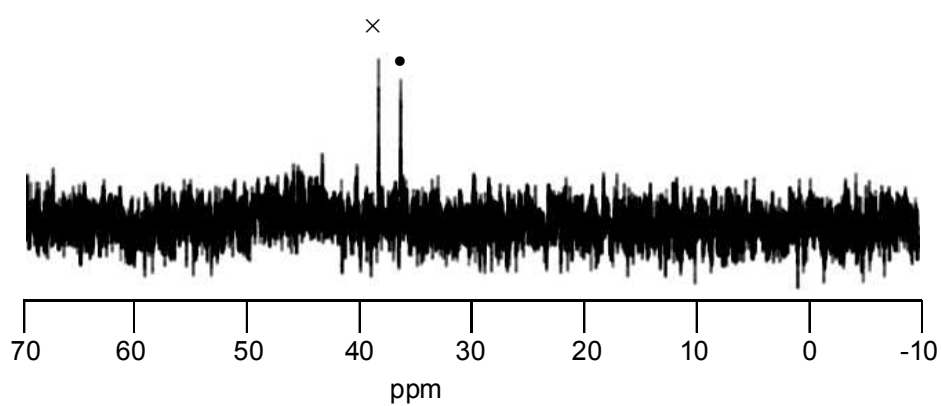


Figure S14. ^{29}Si NMR spectrum of chlorotriethylsilane and $[\text{Et}_3\text{Si}(\text{benzene})]^+\cdot\text{TPFPB}^-$ in CD_2Cl_2 at $-60\text{ }^\circ\text{C}$. \times = chlorotriethylsilane, \bullet = unidentified compound.

(S11)

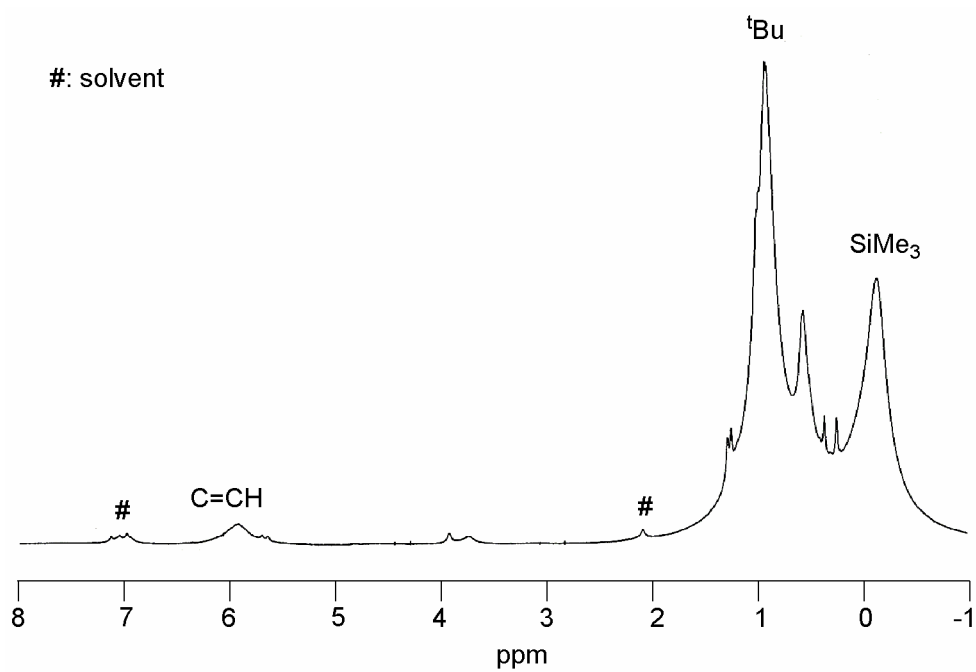


Figure S15. ^1H NMR spectrum of cation **5** in toluene- d_8 (C_7D_8) at -60°C .

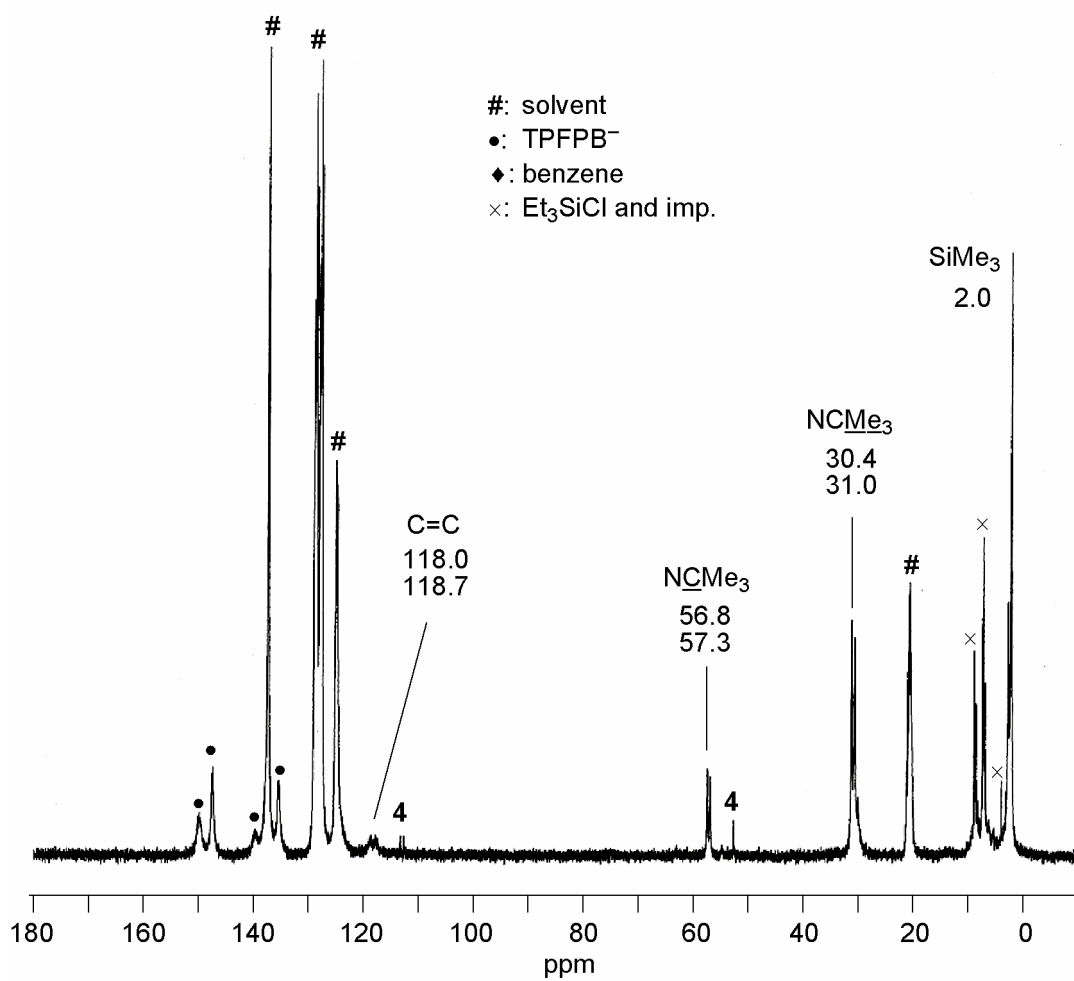


Figure S16. ^{13}C NMR spectrum of cation **5** in C_7D_8 at -60°C .

(S12)

3. Theoretical studies

All calculations were conducted using Gaussian 98 programs² and the representations of the molecular structures were generated with the MOLEKEL program³. The geometries were optimized at the B3LYP/6-31G(d) level for **5** and at the B3LYP/6-31+G(d,p) level for **7–14** and no imaginary frequency numbers were found in all the optimized structures. The GIAO calculation of **5** was carried at the B3LYP/6-311+G(2df,p) level and a tetramethylsilane (C_s symmetry) calculated at the same level was used as a reference. The NICS values were obtained at the GIAO/B3LYP/6-311+G(2df,p) level and the cartesian coordinates of ghost atoms were given in tables. The ghost atoms for NICS calculations of **7** and **8** were positioned at the center of the five-membered ring for NICS(0) and at 1 Å above the center of the five-membered ring for NICS(1). Total energies of **7–14** for homodesmotic reaction were estimated by the MP2/6-31G+(d,p) method with zero-point energy correction.

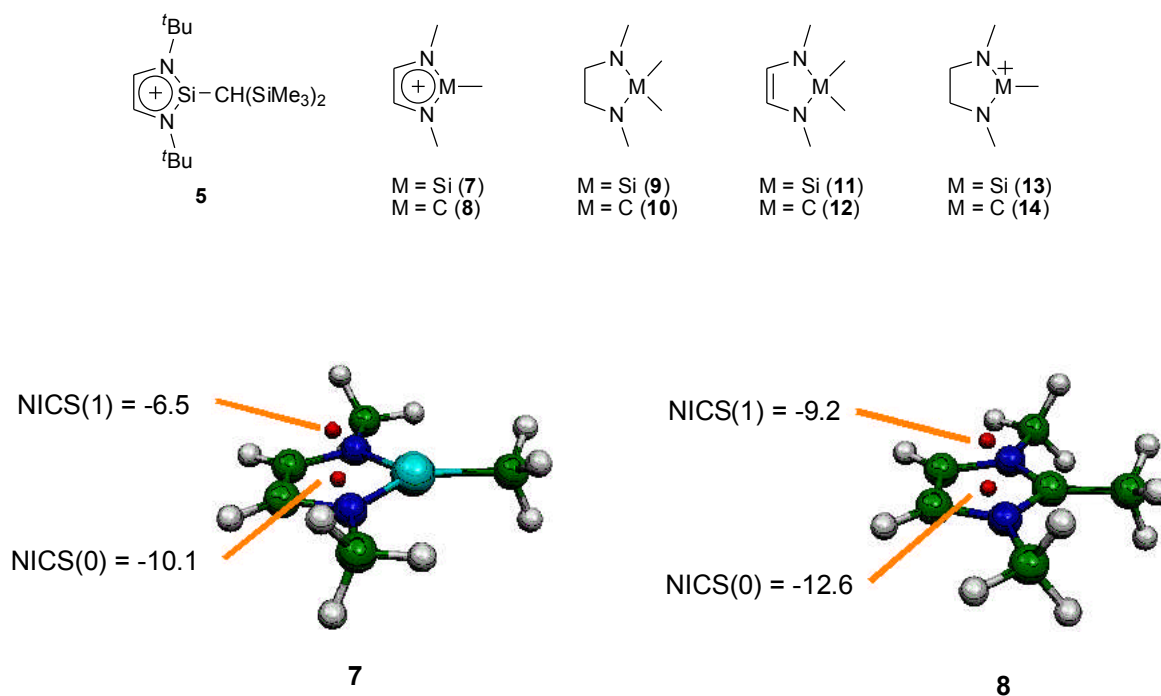


Figure S17. Optimized structures of **7** and **8** with NICS(0) and NICS(1) values (ppm).

Table S1. Total Energies of benzene, **5**, and **7–14** calculated at the B3LYP/6-31+G(d,p)+ZPE level

Compound	Energy (hartree)	Compound	Energy (hartree)
benzene	-232.167969	5	-1648.661478
7	-595.806835	8	-344.409933
9	-637.138497	10	-385.664251
11	-635.942092	12	-384.462434
13	-596.998372	14	-345.593767

(S13)

Table S1 . Total Energies of **7–14** for Homodesmic Reaction calculated at the MP2/6-31+G(d,p)+ZPE level

Compound	Energy (hartree)	Compound	Energy (hartree)
7	−594.345605	8	−343.336646
9	−635.505207	10	−384.23260
11	−634.325598	12	−383.239306
13	−595.516284	14	−344.493063

Table S2. Cartesian Coordinates for the Optimized Structure of **5**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.665100	1.644999	0.100002
2	6	0	3.171544	0.395282	0.069758
3	7	0	1.266470	1.724958	0.011965
4	7	0	2.219905	-0.630834	-0.035569
5	6	0	2.721269	-2.052716	-0.136018
6	14	0	0.669302	0.115696	-0.082491
7	6	0	1.549787	-3.031162	-0.277326
8	6	0	0.621901	3.088749	0.024910
9	6	0	1.304208	3.989710	-1.022380
10	6	0	0.769342	3.682791	1.436901
11	6	0	-0.981582	-0.672768	-0.031665
12	6	0	-0.856969	2.951269	-0.342073
13	6	0	3.504460	-2.390273	1.146587
14	6	0	3.618932	-2.171730	-1.382311
15	14	0	-1.838510	-0.694401	1.729957
16	14	0	-2.092738	-0.521053	-1.640200
17	6	0	-2.686594	-2.271731	-2.024507
18	6	0	-1.030757	0.066877	-3.093529
19	6	0	-3.576766	0.615942	-1.392160
20	6	0	-3.163517	-2.036652	1.671266
21	6	0	-2.614584	0.945061	2.248258
22	6	0	-0.516447	-1.167808	2.999007
23	1	0	3.252706	2.547246	0.171660
24	1	0	4.223463	0.156629	0.108704
25	1	0	1.946093	-4.045867	-0.374208
26	1	0	0.955366	-2.831948	-1.176265
27	1	0	0.899936	-3.024279	0.603989
28	1	0	0.759838	4.936745	-1.088924
29	1	0	1.293303	3.519474	-2.011114
30	1	0	2.339223	4.231545	-0.765747
31	1	0	0.330289	4.684946	1.468191
32	1	0	1.820453	3.768862	1.729675
33	1	0	0.259038	3.061947	2.181044
34	1	0	-0.677674	-1.727928	-0.101329
35	1	0	-1.344104	3.927844	-0.264456
36	1	0	-1.385186	2.272649	0.331099
37	1	0	-0.979423	2.604541	-1.372537
38	1	0	3.860601	-3.424073	1.098603
39	1	0	2.867702	-2.287059	2.031312
40	1	0	4.379261	-1.747363	1.278114
41	1	0	3.974201	-3.202100	-1.481498
42	1	0	4.499262	-1.525438	-1.324350
43	1	0	3.063378	-1.911988	-2.289631
44	1	0	-3.288889	-2.262607	-2.941123
45	1	0	-3.310542	-2.692031	-1.229180
46	1	0	-1.850752	-2.961310	-2.194931
47	1	0	-1.642437	0.081520	-4.004276
48	1	0	-0.191818	-0.613492	-3.288363
49	1	0	-0.621509	1.075868	-2.970361
50	1	0	-4.161284	0.641893	-2.320207
51	1	0	-3.303430	1.647992	-1.152048
52	1	0	-4.244346	0.250805	-0.603808
53	1	0	-3.585050	-2.171305	2.675000
54	1	0	-2.762382	-3.006233	1.354720
55	1	0	-3.994095	-1.781155	1.004429
56	1	0	-3.180795	0.771242	3.172219
57	1	0	-3.316914	1.346868	1.511158
58	1	0	-1.873710	1.719342	2.475208
59	1	0	-0.975668	-1.255272	3.991447
60	1	0	0.281377	-0.419008	3.084898
61	1	0	-0.048834	-2.134791	2.778070

Table S3. Cartesian Coordinates for the Optimized Structure of **7**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-0.064546	0.770154	-0.047384
2	7	0	-1.223606	-0.469101	0.011143
3	6	0	-0.542251	-1.694476	0.038987
4	6	0	0.811332	-1.583036	0.026672
5	7	0	1.282490	-0.262732	-0.011657
6	6	0	-0.215214	2.611975	-0.024882
7	6	0	-2.695928	-0.433246	0.019632
8	6	0	2.729090	0.013050	-0.029962
9	1	0	-0.281295	2.987810	1.000532
10	1	0	0.657229	3.057794	-0.512035
11	1	0	-1.109714	2.917544	-0.575867
12	1	0	-3.087196	-0.958839	-0.854923
13	1	0	-3.072998	-0.904932	0.930433
14	1	0	-3.043312	0.600530	-0.007745
15	1	0	3.184913	-0.443163	-0.912153
16	1	0	3.194598	-0.389109	0.873253
17	1	0	2.902529	1.089594	-0.062394
18	1	0	-1.105289	-2.617780	0.059277
19	1	0	1.518084	-2.401775	0.035399
20	0	0	0.084624	-0.660722	-0.004249
21	0	0	0.101046	-0.628883	0.995110

Table S4. Cartesian Coordinates for the Optimized Structure of **8**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.336746	0.511348	0.004955
2	7	0	-1.004585	0.372974	-0.019322
3	7	0	-1.323232	-0.974163	-0.034786
4	6	0	-0.149595	-1.662786	-0.016675
5	6	0	0.870481	-0.727206	0.009582
6	6	0	1.088954	1.794594	0.052098
7	6	0	-1.978716	1.474649	-0.032276
8	6	0	2.307248	-1.040104	0.033793
9	1	0	1.259652	2.112723	1.087838
10	1	0	2.061065	1.693320	-0.434575
11	1	0	0.537777	2.587095	-0.458049
12	1	0	-1.898868	2.037731	-0.964562
13	1	0	-2.977424	1.046401	0.040826
14	1	0	-1.811202	2.133826	0.821054
15	1	0	2.781151	-0.708240	-0.892425
16	1	0	2.418708	-2.119723	0.124019
17	1	0	2.781337	-0.560801	0.891843
18	1	0	-2.344000	-1.321262	-0.057319
19	1	0	0.045630	-2.723363	-0.020167
20	0	0	-0.266579	-0.537068	-0.013240
21	0	0	-0.283914	-0.544443	0.986583

Table S5. Cartesian Coordinates for the Optimized Structure of **9**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	0.000000	0.693265	0.000001
2	7	0	-1.249554	-0.508165	-0.251241
3	7	0	1.249556	-0.508163	0.251239
4	6	0	-0.235805	1.807043	1.507690
5	6	0	0.235801	1.807049	-1.507685
6	6	0	-2.677793	-0.305933	-0.102848
7	6	0	2.677794	-0.305929	0.102843
8	6	0	-0.757827	-1.835256	0.123856
9	6	0	0.757830	-1.835256	-0.123854
10	1	0	-0.418451	1.212822	2.409064
11	1	0	-1.077742	2.496998	1.372059
12	1	0	0.657191	2.419324	1.685491
13	1	0	-0.657200	2.419321	-1.685490
14	1	0	0.418458	1.212832	-2.409060
15	1	0	1.077730	2.497011	-1.372049
16	1	0	-3.026971	-0.439601	0.937204
17	1	0	-2.956394	0.704158	-0.421539
18	1	0	-3.239121	-1.011756	-0.731738
19	1	0	3.026969	-0.439596	-0.937210
20	1	0	2.956394	0.704163	0.421533
21	1	0	3.239125	-1.011751	0.731731
22	1	0	-0.967003	-2.057660	1.187163
23	1	0	-1.249660	-2.615164	-0.475237
24	1	0	0.967006	-2.057663	-1.187160
25	1	0	1.249664	-2.615161	0.475241

Table S6. Cartesian Coordinates for the Optimized Structure of **10**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000004	-0.594567	0.000016
2	7	0	-1.103827	0.338810	0.356210
3	7	0	1.103801	0.338824	-0.356239
4	6	0	-0.287181	-1.479115	-1.230440
5	6	0	0.287222	-1.479017	1.230536
6	6	0	-2.467945	-0.071607	0.085742
7	6	0	2.467938	-0.071582	-0.085845
8	6	0	-0.753770	1.677903	-0.100939
9	6	0	0.753748	1.677901	0.100958
10	1	0	-0.594761	-0.865571	-2.081732
11	1	0	-1.061925	-2.226571	-1.027066
12	1	0	0.623402	-2.014929	-1.517880
13	1	0	-0.623343	-2.014842	1.518014
14	1	0	0.594777	-0.865399	2.081785
15	1	0	1.061995	-2.226459	1.027220
16	1	0	-2.724054	-0.102201	-0.989486
17	1	0	-2.661269	-1.061102	0.511592
18	1	0	-3.152310	0.632290	0.571974
19	1	0	2.724107	-0.102165	0.989368
20	1	0	2.661242	-1.061080	-0.511697
21	1	0	3.152271	0.632314	-0.572124
22	1	0	-1.000568	1.850925	-1.166209
23	1	0	-1.271339	2.435478	0.498769
24	1	0	1.000549	1.850888	1.166233
25	1	0	1.271316	2.435496	-0.4987261

Table S7. Cartesian Coordinates for the Optimized Structure of **11**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	0.000000	0.665921	-0.003575
2	7	0	-1.257297	-0.562239	-0.011440
3	7	0	1.257297	-0.562238	-0.011464
4	6	0	0.000013	1.775569	1.526352
5	6	0	-0.000016	1.793740	-1.519296
6	6	0	-2.700455	-0.424079	0.011164
7	6	0	2.700456	-0.424076	0.011157
8	6	0	-0.675554	-1.849159	-0.006239
9	6	0	0.675556	-1.849158	-0.006249
10	1	0	0.000028	1.176572	2.442619
11	1	0	-0.882142	2.428156	1.543825
12	1	0	0.882160	2.428168	1.543802
13	1	0	-0.882164	2.446493	-1.528722
14	1	0	-0.000024	1.205519	-2.442412
15	1	0	0.882131	2.446495	-1.528739
16	1	0	-3.141159	-0.856430	0.922004
17	1	0	-2.978701	0.633985	-0.017547
18	1	0	-3.169854	-0.910542	-0.856528
19	1	0	3.169866	-0.910590	-0.856499
20	1	0	2.978702	0.633986	-0.017615
21	1	0	3.141148	-0.856373	0.922029
22	1	0	-1.309371	-2.727008	-0.008581
23	1	0	1.309374	-2.727007	-0.008599

Table S8. Cartesian Coordinates for the Optimized Structure of **12**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.000001	-0.557284	-0.089738
2	7	0	1.149504	0.366194	-0.329854
3	7	0	-1.149505	0.366192	-0.329854
4	6	0	0.000002	-1.118832	1.353848
5	6	0	0.000003	-1.697005	-1.114039
6	6	0	2.462553	0.014168	0.184517
7	6	0	-2.462554	0.014165	0.184517
8	6	0	0.671372	1.675993	-0.099266
9	6	0	-0.671376	1.675992	-0.099266
10	1	0	0.000005	-0.307495	2.088686
11	1	0	0.880414	-1.744626	1.525804
12	1	0	-0.880413	-1.744621	1.525808
13	1	0	0.883419	-2.333015	-0.989289
14	1	0	0.000004	-1.282624	-2.124234
15	1	0	-0.883413	-2.333016	-0.989292
16	1	0	2.540792	0.052824	1.284228
17	1	0	2.739399	-0.990146	-0.149334
18	1	0	3.197969	0.709839	-0.231694
19	1	0	-2.739394	-0.990154	-0.149326
20	1	0	-2.540795	0.052830	1.284227
21	1	0	-3.197973	0.709828	-0.231702
22	1	0	1.351966	2.515243	-0.074680
23	1	0	-1.351971	2.515241	-0.074680

Table S9. Cartesian Coordinates for the Optimized Structure of **13**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	14	0	-0.001719	0.758217	-0.000371
2	7	0	1.286210	-0.299863	0.040046
3	7	0	-1.283912	-0.306635	-0.041502
4	6	0	-0.008276	2.600698	0.001242
5	6	0	2.737698	-0.113389	0.022844
6	6	0	-2.736056	-0.124334	-0.023561
7	6	0	0.772196	-1.688501	-0.120994
8	6	0	-0.763684	-1.692216	0.122494
9	1	0	-0.552318	2.978137	-0.870845
10	1	0	1.016456	2.981284	-0.034129
11	1	0	-0.494485	2.981505	0.905261
12	1	0	3.161772	-0.494897	-0.912619
13	1	0	3.194536	-0.646536	0.862634
14	1	0	2.987018	0.945995	0.111064
15	1	0	-3.158419	-0.501644	0.914457
16	1	0	-3.192423	-0.663658	-0.859688
17	1	0	-2.988215	0.934003	-0.117369
18	1	0	1.013783	-2.036543	-1.132465
19	1	0	1.273421	-2.346405	0.595011
20	1	0	-1.003263	-2.040280	1.134461
21	1	0	-1.261147	-2.354076	-0.592538

Table S10. Cartesian Coordinates for the Optimized Structure of **14**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.010171	0.597074	0.000349
2	7	0	1.093221	-0.177296	0.061435
3	7	0	-1.109914	-0.121788	-0.059588
4	6	0	0.078805	2.088501	-0.000963
5	6	0	2.490316	0.241911	0.001639
6	6	0	-2.496882	0.332632	-0.001655
7	6	0	0.728644	-1.603614	-0.055694
8	6	0	-0.808582	-1.565598	0.054900
9	1	0	0.659358	2.438325	-0.859883
10	1	0	0.574273	2.440449	0.909158
11	1	0	-0.908643	2.542330	-0.046555
12	1	0	2.911712	0.028159	-0.986794
13	1	0	3.060332	-0.304658	0.757119
14	1	0	2.577838	1.308076	0.205807
15	1	0	-2.915874	0.150921	0.993854
16	1	0	-3.080156	-0.221764	-0.740848
17	1	0	-2.569202	1.393351	-0.233762
18	1	0	1.073188	-1.990392	-1.021357
19	1	0	1.201147	-2.182337	0.741406
20	1	0	-1.172065	-1.935509	1.020114
21	1	0	-1.309894	-2.118792	-0.742646

4. References

- (1) (a) M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.*, 1994, **116**, 2691; (b) M. Haaf, A. Schmiedl, T. A. Schmedake, D. A. Powell, A. J. Millevolte, M. Denk and R. West, *J. Am. Chem. Soc.*, 1998, **120**, 12714.
- (2) (a) J. B. Lambert and Y. Zhao, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 400; (b) T. Müller, Y. Zhao and J. B. Lambert, *Organometallics*, 1998, **17**, 278; (c) J. B. Lambert, Y. Zhao, H. Wu, W. C. Tse and B. Kuhimann, *J. Am. Chem. Soc.* 1999, **121**, 5001; (c) A. Sekiguchi, T. Matsuno and M. Ichinohe, *J. Am. Chem. Soc.* 2000, **122**, 11250.
- (3) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, Ö. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komáromi, R. Gomperts, 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, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98, Revision A.11*. Gaussian, Inc.: Pittsburgh, PA, 1998.
- (4) P. Flukiger, H. P. Luthi, S. Portmann and J. Weber, *MOLEKEL 4.3*; Swiss Center for Scientific Computing: Manno (Switzerland), 2000–2002.