

Synthesis of an N-heterocyclic Carbene-Stabilized Siladiimide

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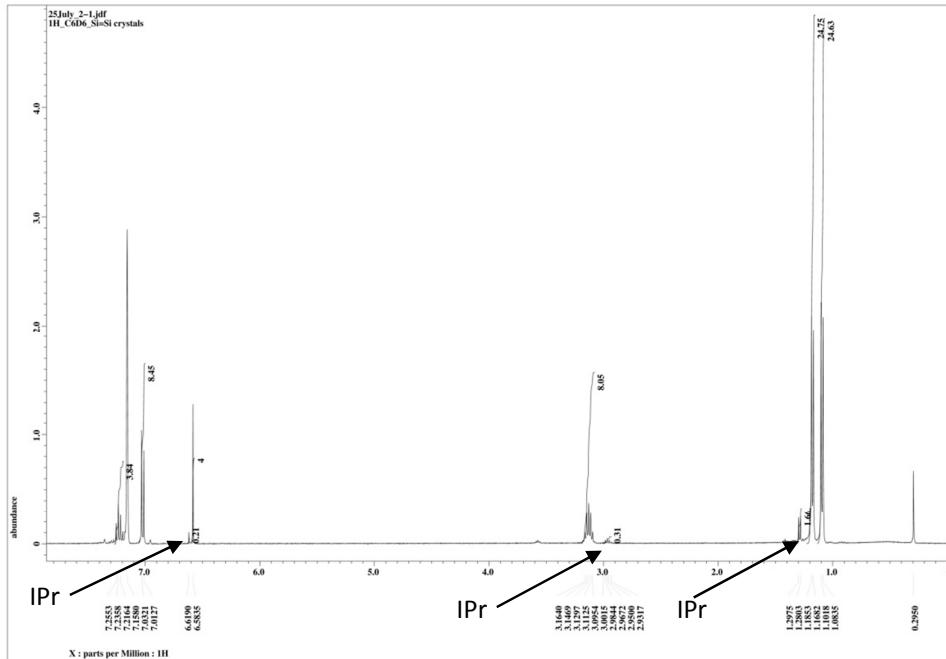
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1. Experimental procedures

General Procedure. All manipulations were carried out under an inert atmosphere of argon gas using standard Schlenk techniques. THF and toluene were dried and distilled over K prior to use. **1** was prepared as described in the literature.¹ It contained around 5% of IPr, which was illustrated by the following ¹H NMR spectrum of **1**.



The ¹H, ¹³C and ²⁹Si spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts (δ) are relative to SiMe₄ for ¹H, ¹³C and ²⁹Si. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

Synthesis of **2**.IPr (IPr = :C{N(Ar)CH}₂, Ar = 2,6-iPr₂C₆H₃). A solution of 2,6-diisopropylphenyl azide (0.061 g, 0.30 mmol) in THF (10 mL) was added dropwise to a solution of compound **1** (0.125 g, 0.15 mmol) in THF (8 mL). The red solution changed to blue-green upon addition and the resulting solution was stirred at room temperature for 3 hours to afford an orange solution. The solution was filtered and the filtrate was concentrated to afford pale yellow crystals of **2**.IPr (0.06 g). Yield: 34.6 %. M.p.: 215 °C (decomposed). Elemental analysis calculated (%) for C₇₈H₁₀₆N₆Si: C, 81.06; H, 9.25; N, 7.27. Found: C, 80.92; H, 9.08; N, 7.16. With reference to the ¹H and ¹³C NMR spectra of IPr, the NMR resonances of **2** can be identified. ¹H NMR: (395.9 MHz, C₆D₆, 25 °C): δ 0.89 (d, $^3J_{\text{H-H}} = 6.80$ Hz, 12H, CH(CH₃)₂), 1.11 (d, $^3J_{\text{H-H}} = 6.77$ Hz, 12H, CH(CH₃)₂), 1.18 (d, $^3J_{\text{H-H}} = 6.77$ Hz, 12H, CH(CH₃)₂), 1.27 (d, $^3J_{\text{H-H}} = 6.80$ Hz, 12H, CH(CH₃)₂), 2.97 (sept, $^3J_{\text{H-H}} = 6.80$ Hz, 4H, CH(CH₃)₂), 3.15 (sept, $^3J_{\text{H-H}} = 6.80$ Hz, 4H, CH(CH₃)₂), 6.19 (s, 2H, NCH), 6.88 (t, $^3J_{\text{H-H}} = 7.46$ Hz, 2H, Ar-H), 7.05 (t, $^3J_{\text{H-H}} = 6.79$ Hz, 2H, Ar-H), 7.17 (d, $^3J_{\text{H-H}} = 7.68$ Hz, 4H, Ar-H), 7.29 ppm (d, $^3J_{\text{H-H}} = 7.24$ Hz, 4H, Ar-H). ¹³C{¹H} NMR (99.5 MHz, C₆D₆,

25 °C): δ 22.69 ($\text{CH}(\text{CH}_3)_2$), 23.10 ($\text{CH}(\text{CH}_3)_2$), 24.54 ($\text{CH}(\text{CH}_3)_2$), 25.66 ($\text{CH}(\text{CH}_3)_2$), 28.04 ($\text{CH}(\text{CH}_3)_2$), 29.38 ($\text{CH}(\text{CH}_3)_2$), 117.25, 121.44, 122.28, 124.79, 125.40, 128.87, 131.77, 134.45 (C_{Ar}), 138.42 (CHN), 145.73 ppm (NCN). ^{29}Si NMR (78.65 MHz, C_6D_6): δ -65.0 ppm.

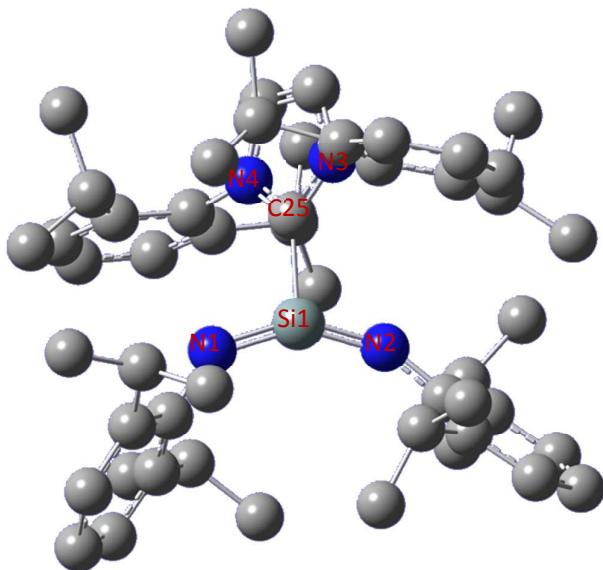
Synthesis of **2 and **3**.** A solution of 2,6-diisopropylphenyl azide (0.122 g, 0.60 mmol) in THF (10 mL) was added dropwise to a solution of **1** (0.125 g, 0.15 mmol) in THF (8 mL). The resulting solution was stirred at room temperature for 1 hour. Volatiles were removed under vacuo and the residue was extracted with toluene. The solution was filtered and the filtrate was concentrated to afford pale yellow crystals of compound **3** (0.107 g, 30 % yield). The residue was extracted with THF and the filtrate was concentrated to afford a few pieces (ca. 3 – 7 pieces) of yellow crystals of **2**.

2: IR (Nujol) ν = 721 (w), 747 (w), 756 (w), 800 (w), 937 (w), 1061 (w), 1103 (w), 1261 (w), 1377 (m, C-H bending at *iPr* substituents), 1461 (m, unsymmetric N-Si-N stretch and C-H bending at *NAr* substituents), 2854 (s, unsymmetric C-H stretch of *iPr* of *NAr* substituents), 2924 cm^{-1} (s, unsymmetric C-H stretch of *iPr* at IPr).

3: M.p.: 241 °C. Elemental analysis calculated (%) for $\text{C}_{78}\text{H}_{106}\text{N}_{10}$: C, 79.10; H, 9.03; N, 11.80. Found: C, 78.86; H, 9.01; N, 11.72. ^1H NMR (395.9 MHz, C_6D_6 , 25 °C): δ 1.08 (d, $^3J_{\text{H-H}} = 6.77$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, $^3J_{\text{H-H}} = 6.80$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.22 (d, $^3J_{\text{H-H}} = 6.77$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 2.68 (sept, $^3J_{\text{H-H}} = 6.80$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 3.00 (sept, $^3J_{\text{H-H}} = 6.79$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 5.90 (s, 2H, NCH), 6.99 - 7.06 ppm (m, 9H, Ar-H). $^{13}\text{C}\{\text{H}\}$ NMR (99.5 MHz, C_6D_6 , 25 °C): δ 23.00 ($\text{CH}(\text{CH}_3)_2$), 23.38 ($\text{CH}(\text{CH}_3)_2$), 24.22 ($\text{CH}(\text{CH}_3)_2$), 27.02 ($\text{CH}(\text{CH}_3)_2$), 29.28 ($\text{CH}(\text{CH}_3)_2$), 117.58, 122.32, 124.02, 124.97, 129.97, 134.44, 139.75, 146.68 (C_{Ar}), 150.12 (CHN), 155.61 ppm (NCN).

X-ray Data Collection and Structural Refinement. Intensity data for compounds **2** and **2**.*iPr* were collected using a Bruker APEX II diffractometer. Their crystals were measured at 103(2) K. The structures were solved by a direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on F^2 .² All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride on their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations.

Theoretical studies. Compound **2** was investigated using DFT³ B3PW91⁴ method with the 6-31G* level. All calculations were carried out using the Gaussian 09 packages.⁵ There is no imaginary frequency in the structure. The absolute energy is -2493.25253 Hartree. The NBO analyses were performed using the NBO 3.1 program at the same level. The optimized geometry is in good agreement with the X-ray crystallographic data of **2**.



Calculated molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles (deg): C25-Si1 1.920, N1-Si1 1.610, N2-Si1 1.602, N1-Si1-C25 105.86, N2-Si1-C25 105.63, N1-Si1-N2 148.36.

2. X-ray crystal structure of compound **2**

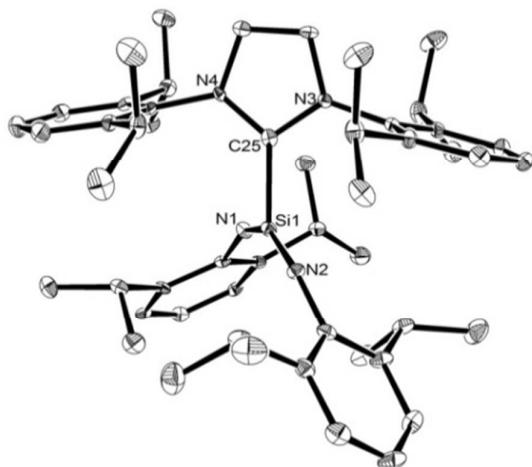
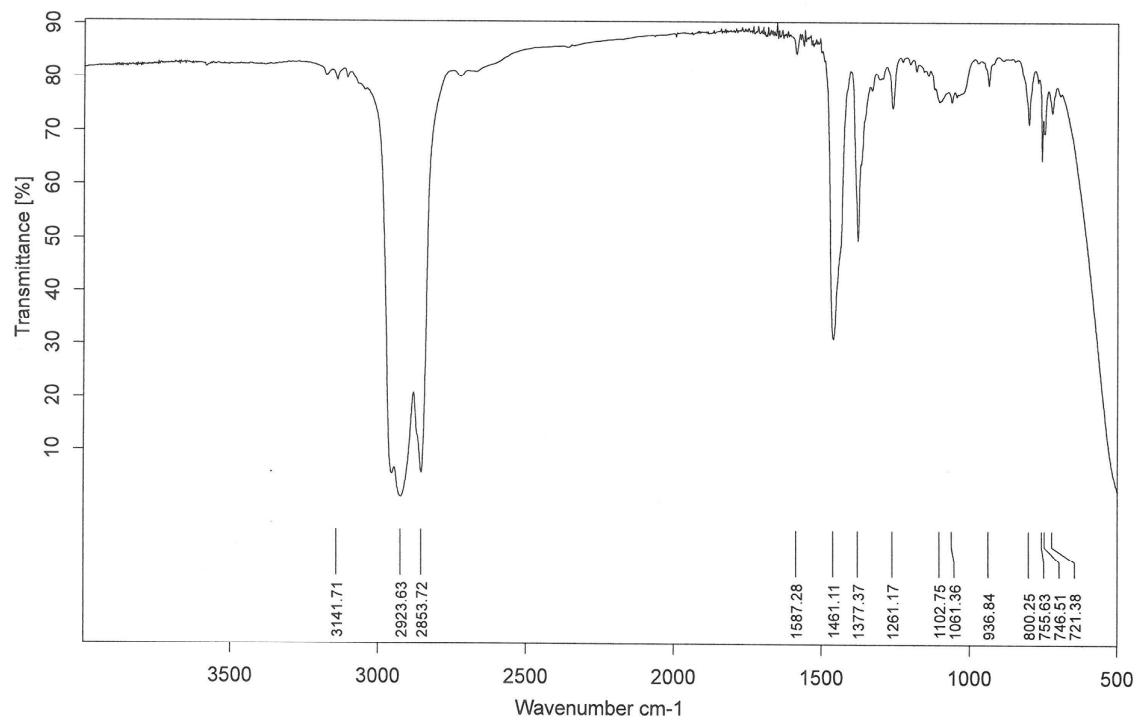


Figure S1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (\AA) and angles (deg): C25-Si1 1.889(5), N1-Si1 1.591(5), N2-Si1 1.593(5), N1-Si1-C25 102.7(3), N2-Si1-C25 109.5(2), N1-Si1-N2 147.7(2).

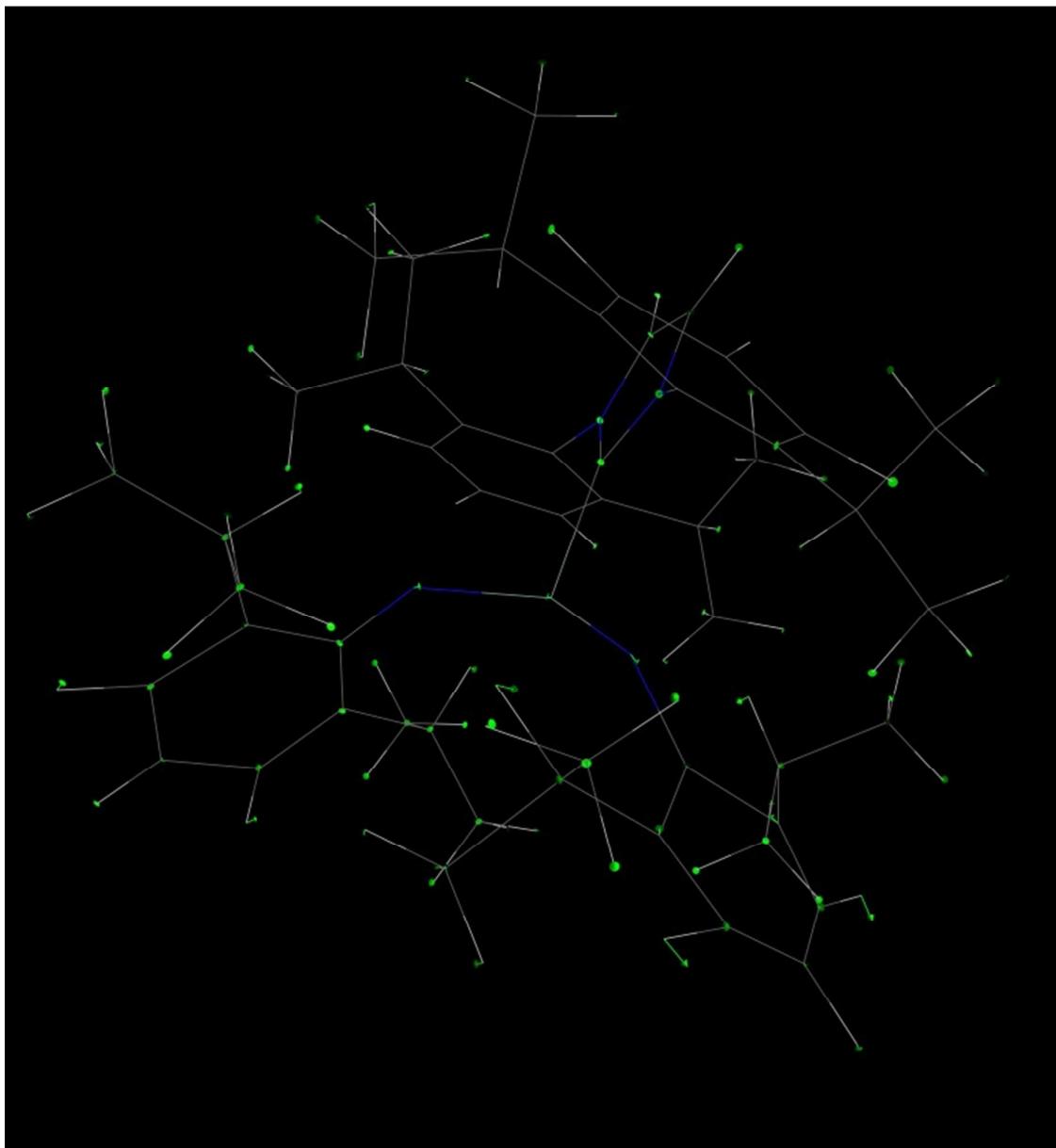
3. Comparison of experimental and calculated bond lengths and angles

	Experimental bond lengths (\AA) and angles ($^{\circ}$)	Calculated bond lengths (\AA) and angles ($^{\circ}$)
C25-Si1	1.889(5)	1.920
N1-Si1	1.591(5)	1.610
N2-Si1	1.593(5)	1.602
N1-Si1-C25	102.7(3)	105.86
N2-Si1-C25	109.5(2)	105.63
N1-Si1-N2	147.7(2)	148.36

4. **Figure S2.** IR spectrum of compound 2



5. **Figure S3.** The Si-N unsymmetric stretch and C-H bending at the theoretical value of 1447 cm⁻¹



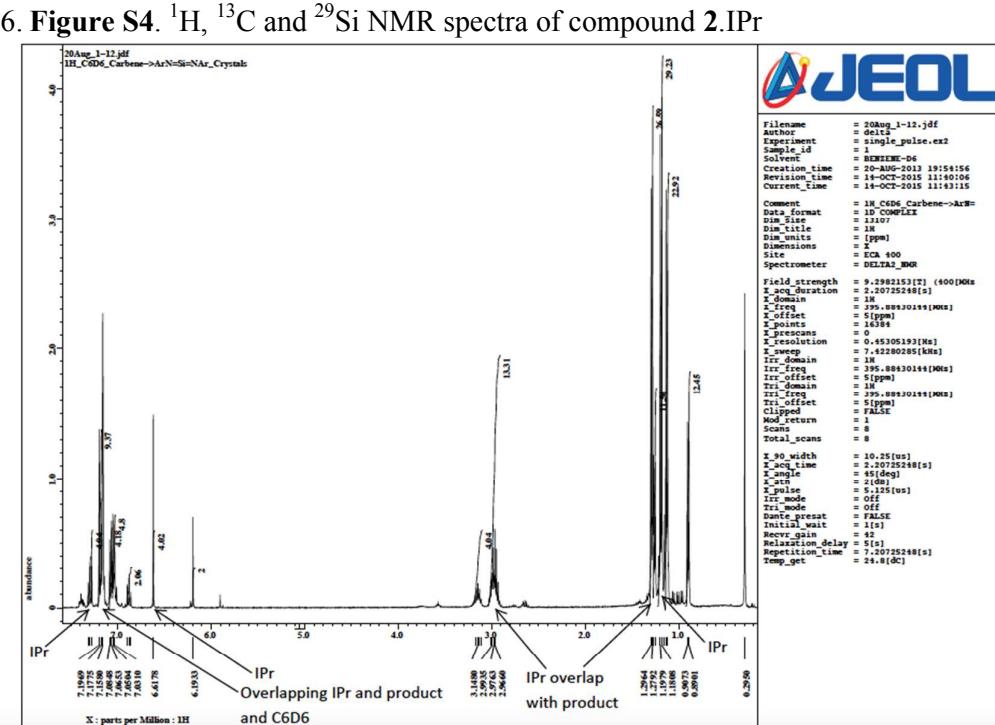
Green arrow represents vibrational direction

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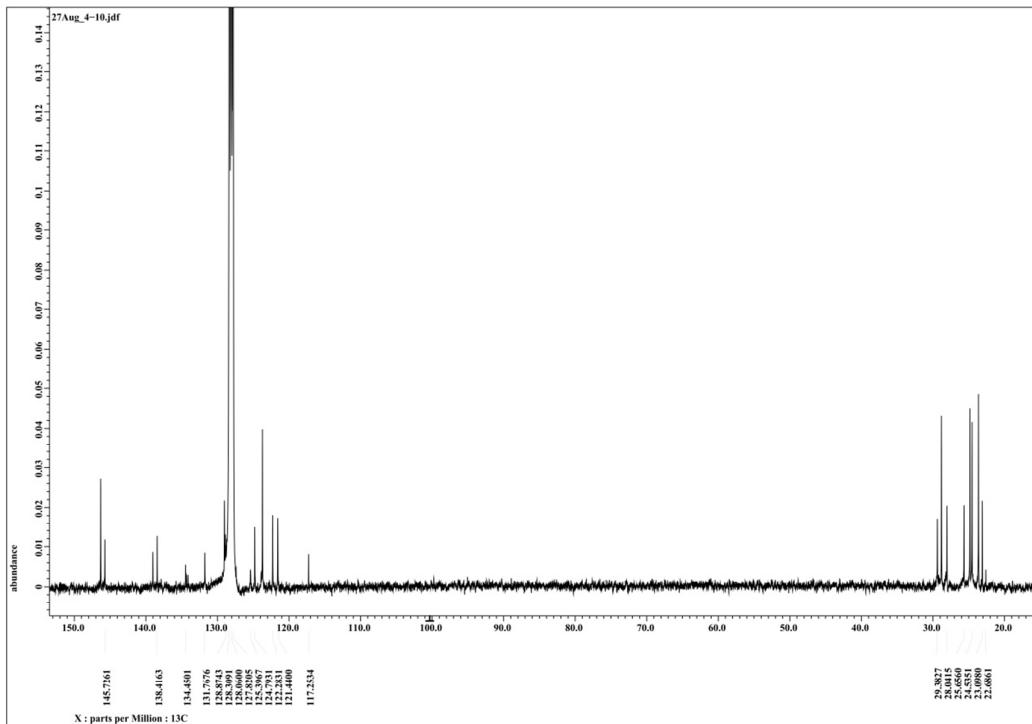
    252
      A
Frequencies -- 1447.0320
Red. masses -- 2.4735
Frc consts -- 3.0515
IR Inten -- 103.1622
Atom AN   X       Y       Z
  1   6   -0.01   0.00  -0.02
  2   6   -0.08  -0.04  -0.11
  3   6    0.00   0.05   0.05
  4   6   -0.01  -0.04   0.00
  5   6    0.01  -0.01  -0.02
  6   6   -0.01   0.06   0.04
  7   6    0.04  -0.03   0.01
  8   6    0.00  -0.05  -0.04
  9   6   -0.10   0.12   0.01
 10   6    0.01  -0.06  -0.04
    
```

11	6	0.00	0.01	0.02
12	6	0.01	0.02	0.00
13	6	-0.01	-0.01	0.01
14	6	-0.03	0.03	0.05
15	6	0.00	-0.03	-0.01
16	6	-0.01	0.02	0.00
17	6	0.00	0.01	0.00
18	6	0.00	-0.03	0.00
19	6	0.01	0.00	-0.02
20	6	0.00	0.03	0.01
21	6	-0.02	-0.05	0.03
22	6	0.00	0.03	0.00
23	6	-0.01	-0.01	-0.01
24	6	0.00	-0.01	0.00
25	6	0.01	0.01	0.00
26	6	0.01	0.00	0.02
27	6	0.01	0.01	-0.01
28	6	0.00	0.00	0.00
29	6	0.00	0.00	0.00
30	6	0.00	0.00	0.00
31	6	0.00	0.00	0.00
32	6	0.00	0.00	0.00
33	6	0.00	0.00	0.00
34	6	0.00	0.00	0.00
35	6	0.00	0.00	0.00
36	6	0.00	0.00	0.00
37	6	0.00	0.00	0.00
38	6	0.00	0.00	0.01
39	6	-0.01	0.01	-0.01
40	6	0.00	0.00	0.00
41	6	0.00	0.00	0.00
42	6	0.00	0.00	0.00
43	6	0.01	-0.01	-0.01
44	6	0.00	-0.01	0.01
45	6	0.00	0.00	0.00
46	6	0.00	0.00	0.00
47	6	0.00	0.00	0.00
48	6	0.01	0.00	0.00
49	6	0.00	0.00	0.00
50	6	0.00	0.00	0.00
51	6	0.00	0.00	0.00
52	1	0.07	-0.30	-0.19
53	1	0.01	0.14	0.06
54	1	0.10	0.06	-0.04
55	1	0.03	0.14	0.01
56	1	0.02	-0.03	0.06
57	1	-0.05	0.03	0.05
58	1	-0.04	0.07	0.08
59	1	0.31	-0.21	0.08
60	1	0.05	0.00	0.05
61	1	0.31	0.00	0.26
62	1	0.04	0.25	0.30
63	1	0.00	-0.07	-0.06
64	1	0.03	0.02	-0.02
65	1	-0.04	-0.03	-0.07
66	1	-0.03	-0.07	-0.02
67	1	0.02	-0.04	0.04
68	1	-0.04	-0.08	-0.03
69	1	0.02	0.14	0.00
70	1	0.06	-0.01	-0.01
71	1	0.03	-0.08	-0.02
72	1	0.05	-0.05	0.02
73	1	-0.03	-0.03	0.01
74	1	-0.01	0.00	-0.03
75	1	-0.01	-0.05	0.00
76	1	0.08	0.09	-0.12
77	1	0.01	0.01	-0.02
78	1	0.08	-0.02	-0.14
79	1	0.02	-0.11	-0.05
80	1	0.01	0.04	0.02
81	1	0.03	0.01	0.00
82	1	0.02	0.03	0.02
83	1	0.00	0.01	-0.02
84	1	-0.01	0.01	0.02
85	1	0.00	0.04	0.01
86	1	-0.04	-0.02	-0.04
87	1	-0.03	-0.04	0.02
88	1	0.01	-0.02	0.00
89	1	0.00	0.00	0.01
90	1	-0.01	0.00	0.00
91	1	-0.01	0.00	0.00
92	1	0.00	0.01	0.00
93	1	0.00	0.00	-0.01
94	1	0.00	0.01	0.00
95	1	-0.01	-0.01	0.00
96	1	0.00	0.00	0.00

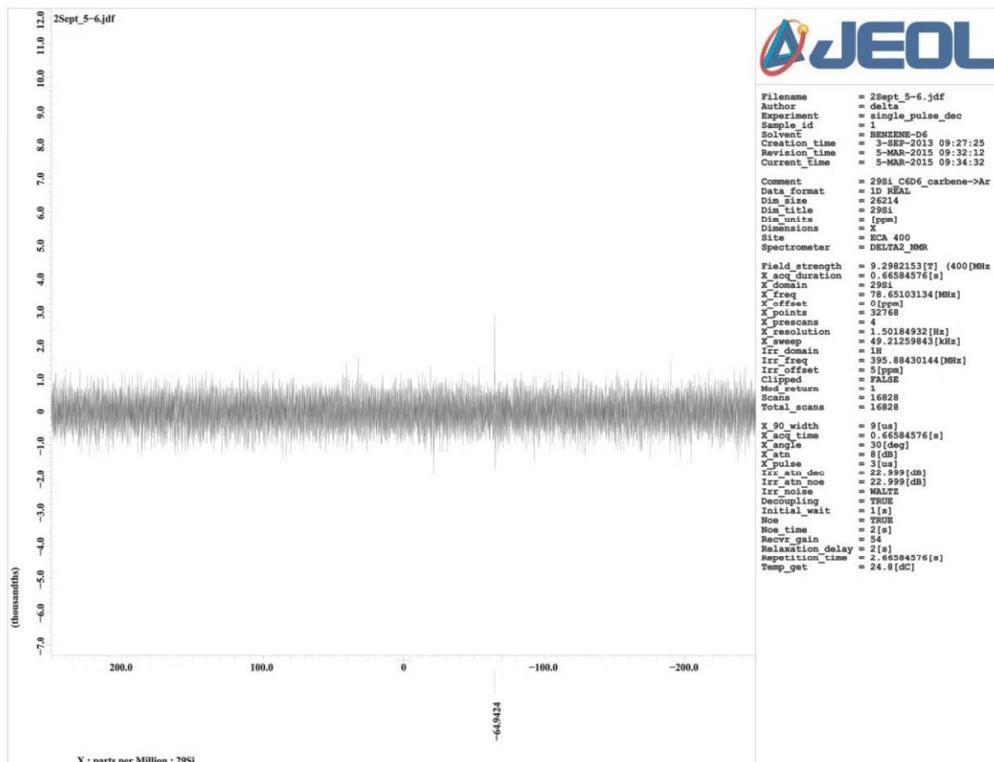
97	1	-0.02	0.00	0.00
98	1	-0.01	0.00	0.00
99	1	-0.01	-0.01	-0.02
100	1	-0.01	-0.01	-0.02
101	1	0.01	0.01	-0.02
102	1	0.01	0.00	0.00
103	1	0.00	-0.03	0.07
104	1	0.07	-0.04	0.00
105	1	0.00	0.00	0.00
106	1	0.00	0.03	0.04
107	1	-0.02	0.05	0.04
108	1	-0.04	0.00	0.06
109	1	-0.01	0.03	-0.02
110	1	0.01	0.02	-0.03
111	1	-0.02	0.01	-0.03
112	1	-0.01	0.00	0.00
113	1	0.00	0.00	0.00
114	1	-0.01	-0.02	-0.01
115	1	0.01	-0.01	-0.02
116	1	-0.01	0.01	0.01
117	1	0.00	0.00	0.01
118	1	0.00	0.01	0.01
119	1	-0.01	0.01	0.00
120	1	0.00	-0.01	0.00
121	1	-0.01	-0.01	0.01
122	7	0.13	-0.06	0.05
123	7	0.07	0.00	-0.06
124	7	-0.01	-0.01	0.00
125	7	-0.01	-0.01	-0.01
126	14	-0.06	0.02	0.01



(a) ^1H NMR spectrum



(b) ^{13}C NMR spectrum



(c) ^{29}Si NMR spectrum

7. The bond dissociation energy of the C-Si bond in **2**

	2	IPr	ArNSiNAr
B3PW91/6-31G*	-2493.252532	-1159.608814	-1333.575395
Zero point correction (ZPVE)	1.109313	0.572946	0.531521
B3PW91/6-311+G(2d,p)//B3PW91/6-31G*	-2493.853079	-1159.910154	-1333.877715
B3PW91/6-311+G(2d,p)//B3PW91/6-31G* + scaled ZPVE ^{[a], 6}	-2492.768836	-1159.350157	-1333.358206

Remark: [a] scaling factor = 0.9774

Bond dissociation energy with zero point correction
 $= (-1333.358206) + (-1159.350157) - (-2492.768836)$
 $= 0.06047326 \text{ Hartree/mol} = 38.0 \text{ kcal/mol}$

8. **Table S1.** X-ray crystallographic data for compounds **2** and **2**.IPr

	2	2 .IPr
Formula	C ₅₅ H ₇₈ N ₄ OSi	C ₇₈ H ₁₀₆ N ₆ Si
Fw	839.30	1155.77
Color	Yellow	Orange
cryst syst	Orthorhomic	Monoclinic
space group	<i>P n a</i> 21	<i>P</i> 1 21/ <i>c</i> 1
<i>a</i> (Å)	19.024(4)	15.153(2)
<i>b</i> (Å)	18.708(4)	23.334(3)
<i>c</i> (Å)	14.086(3)	20.830(3)
α (deg)	90	90
β (deg)	90	110.043(4)
γ (deg)	90	90
<i>V</i> (Å ³)	5013.2(18)	6919.0(18)
<i>Z</i>	4	4
<i>d</i> _{calcd} (g cm ⁻³)	1.112	1.109
μ (mm ⁻¹)	0.088	0.080
<i>F</i> (000)	1832	2520
cryst size (mm)	0.010 x 0.300 x 0.400	0.140 x 0.180 x 0.220
2θ range (deg)	2.40 – 25.37	2.22 – 24.99
index range	-22 ≤ <i>h</i> ≤ 22 -18 ≤ <i>k</i> ≤ 22 -16 ≤ <i>l</i> ≤ 16	-17 ≤ <i>h</i> ≤ 17 -27 ≤ <i>k</i> ≤ 27 -24 ≤ <i>l</i> ≤ 24
no. of rflns collected	43439	86762
no. of indep rflns	9071	12115
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2(σ) <i>I</i>)	0.0516, 0.0803	0.0699, 0.1665
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1470, 0.0993	0.1515, 0.2093
goodness of fit, <i>F</i> ²	0.809	1.014
no. of data/restraints/params	9071/1/566	12115/569/ 903
largest diff peaks, eÅ ⁻³	0.392, -0.304	0.302, -0.392

9. The optimized geometry of compound 2

Standard orientation:

Atom	Coordinates (Angstroms)		
	X	Y	Z
C	2.553869	-1.256135	1.230237
C	3.088201	-0.552745	2.354136
C	2.400248	0.662738	2.949529
C	3.335410	1.866228	3.122533
C	1.733020	0.295241	4.284121
C	4.251368	-1.020546	2.969180
C	4.910820	-2.164049	2.535073
C	4.366530	-2.877604	1.474568
C	3.204681	-2.460570	0.824719
C	2.643023	-3.325775	-0.291212
C	3.550085	-3.337572	-1.529583
C	2.383038	-4.761919	0.186488
C	-2.139225	-0.212026	2.210694
C	-2.644847	0.844859	3.024607
C	-2.359282	2.290986	2.662668
C	-3.534998	3.237237	2.932363
C	-1.097965	2.793895	3.379092
C	-3.370864	0.545901	4.177643
C	-3.642446	-0.765675	4.550062
C	-3.193647	-1.796475	3.734037
C	-2.463099	-1.553854	2.568963
C	-2.021569	-2.735020	1.722953
C	-3.169215	-3.708658	1.423338
C	-0.841799	-3.473716	2.369864
C	-0.122910	0.520744	-1.401326
C	0.287908	1.594415	-3.334503
C	-0.727511	0.728102	-3.558332
C	-2.063293	-0.874167	-2.254822
C	-3.331467	-0.391538	-1.876699
C	-3.587163	1.062307	-1.516763
C	-4.575447	1.226433	-0.358158
C	-4.073761	1.842849	-2.749652
C	-4.391079	-1.301275	-1.904109
C	-4.202096	-2.619606	-2.300488
C	-2.940886	-3.060803	-2.676675
C	-1.838287	-2.200274	-2.665675
C	-0.481821	-2.706984	-3.130637
C	-0.390751	-2.709550	-4.665866
C	-0.167233	-4.105326	-2.586268
C	1.574626	2.405976	-1.402699
C	0.059691	3.673578	-1.064027
C	-0.390892	4.078301	-1.284765
C	-1.010066	4.744915	-0.051087
C	-0.511827	5.006053	-2.505447
C	1.958579	4.618946	-0.560559
C	3.305743	4.320918	-0.417377
C	3.786936	3.071132	-0.789415
C	2.941880	2.081964	-1.301590
C	3.511201	0.753839	-1.775703
C	3.756691	0.778874	-3.294743
C	4.806314	0.365986	-1.054060
H	1.612031	0.971541	2.253122
H	3.808818	2.141521	2.174127
H	2.774460	2.735877	3.486527
H	4.131334	1.664944	3.849773
H	1.215899	1.157929	4.720364
H	0.999410	-0.507211	4.153808
H	2.481185	-0.049782	5.008376
H	4.646745	-0.473166	3.822721
H	5.819079	-2.502800	3.027093
H	4.855377	-3.791560	1.141551
H	1.683109	-2.882745	-0.577587
H	4.552486	-3.708191	-1.281907
H	3.144153	-3.990830	-2.313086
H	3.661486	-2.333806	-1.952462
H	1.747521	-4.773344	1.077475
H	1.889758	-5.352216	-0.595958
H	3.317458	-5.276622	0.440760
H	-2.155594	2.299674	1.584651
H	-3.328432	4.229228	2.511012
H	-4.464643	2.863485	2.489475
H	-3.711795	3.379239	4.005370
H	-0.228876	2.187714	3.107548
H	-0.880696	3.840405	3.126468
H	-1.223014	2.733981	4.467247
H	-3.732895	1.359658	4.802030
H	-4.203963	-0.980008	5.456050

H	-3.415265	-2.825446	4.010675
H	-1.683853	-2.334480	0.760032
H	-4.024655	-3.188363	0.979767
H	-2.838514	-4.483249	0.720312
H	-3.519006	-4.220171	2.328061
H	-0.529606	-4.327486	1.755060
H	0.023392	-2.814833	2.497160
H	-1.119963	-3.858162	3.359014
H	0.776762	2.303290	-3.983026
H	-1.303200	0.515315	-4.444506
H	-2.639355	1.492341	-1.177705
H	-5.593053	0.928353	-0.637397
H	-4.263816	0.645500	0.513688
H	-4.621088	2.280931	-0.065186
H	-5.024730	1.437750	-3.116188
H	-4.235512	2.896729	-2.494144
H	-3.355715	1.804552	-3.576267
H	-5.382126	-0.969376	-1.611796
H	-5.043768	-3.307133	-2.315659
H	-2.807356	-4.092574	-2.986135
H	0.288516	-2.027862	-2.746332
H	-0.540455	-1.711927	-5.091790
H	0.594116	-3.066485	-4.988177
H	-1.148868	-3.373208	-5.098377
H	-0.812195	-4.871466	-3.031307
H	0.865717	-4.374049	-2.828385
H	-0.284479	-4.150046	-1.499764
H	-0.978217	3.177016	-1.491578
H	-2.078266	4.922133	-0.218745
H	-0.903695	4.116481	0.836122
H	-0.549472	5.716200	0.162029
H	-0.123562	4.540637	-3.417783
H	-1.560925	5.270430	-2.681685
H	0.047092	5.935347	-2.345208
H	1.594280	5.604143	-0.284644
H	3.988704	5.067889	-0.021073
H	4.844526	2.857585	-0.681109
H	2.768283	-0.018521	-1.544076
H	4.474489	1.564899	-3.559656
H	4.173740	-0.179994	-3.623868
H	2.839606	0.953056	-3.867099
H	5.645039	1.011973	-1.343002
H	4.691159	0.397293	0.032908
H	5.084492	-0.657248	-1.321686
N	1.490510	-0.779888	0.500339
N	-1.418825	0.092883	1.069877
N	-0.974833	0.078086	-2.365297
N	0.651856	1.462270	-2.008881
Si	0.020210	-0.153392	0.390996

10. Reference

- Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer, III, P. v. R. Schleyer and G. H. Robinson, *Science*, 2008, **321**, 1069-1071.
- G. M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1997.
- a) D. Feller, *J. Chem. Phys.*, 1990, **93**, 579-589; b) P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864-B871.
- a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; b) J. P. Perdew, *Electronic Structure of Solids '91* (Eds: P. Ziesche, H. Eschig), Akademie Verlag, Berlin, 1991, pp. 11.
- Gaussian 09, 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, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E.

- Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
6. A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502 - 16513.