Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Silylene induced cooperative B–H bond activation and unprecedented aldehyde C–H bond splitting with amidinate ring expansion

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Table of Contents

General Experimental Information. All manipulations were carried out in an inert atmosphere of argon using standard Schlenk techniques and in argon filled glove box. Solvents especially toluene and hexane were purified by MBRAUN solvent purification system MB SPS-800.The starting material, [PhC(NtBu)2SiN(Si(CH3)3)2] was prepared by using literature procedures.S1 Other chemical purchased from Sigma Aldrich and TCI Chemicals were used without further purification. ^{1}H, ^{13}C, ^{29}Si, ^{11}B and ^{19}F NMR spectra were recorded in C_6D_6 using a Bruker Avance DPX 200, Bruker Avance DPX 400 or a Bruker Avance DPX 500 spectrometer referenced to external $SiMe_4$, in the case of ^{1}H, ^{13}C and ^{29}Si NMR and $CFCl_3$ for the ^{19}F NMR spectra, respectively. Elemental analysis was performed by CSIR-National Chemical Laboratory, Pune. Furthermore, Melting points were measured in a sealed glass tube on a Stuart SMP-30 melting point apparatus.

Synthesis and characterization of compound 2. A toluene solution of **1** (0.2 g, 0.47 mmol in toluene 10 mL) was added drop by drop to a toluene solution (10 mL) of pinacolborane (0.06 g, 0.47 mmol) at ambient conditions and the reaction was stirred for 3 hours. Then the solvent was removed under reduced pressure and extracted with toluene (15 mL). The solvent was again reduced *in vacuo* to 5 mL and stored at -30 °C in a freezer for 2 days to obtain colorless crystals of **2**. Yield: 0.237g (90.7%). Mp: 133.6 °C. ^{1}H NMR (400.31 MHz, $CDCl_3$, 25 ^{o}C) δ 0.42 (s, 18H, $SiMe_3$), 0.99 (s, 18H, *t*Bu), 1.31 (s, 12H, pinCH_3), 7.17-7.24 (m, 5H, Ph) ppm; ^{13}C NMR (100.67 MHz, $CDCl_3$, 25 ^{o}C); δ 6.44 ($SiMe_3$), 25.92 (PinCH_3), 30.83 (*t*Bu), 50.74 (C*t*Bu), 73.46 (CH), 83.41($OC(CH_3)_2$), 127.26, 128.39, 129.97, 141.73, 147.65 (Ph) ppm; $^{29}Si\{^{1}H\}$ NMR (79.53 MHz, $CDCl_3$, 25 °C); δ -52.41 ($SiN(SiMe_3)_2$), 3.13 ($N(SiMe_3)_2$) ppm; ^{11}B NMR (128.44 MHz, $CDCl_3$, 25 ^{o}C); δ 37.84 ppm. HRMS (m/z): calcd: 547.36, found: 547.3611. Elemental

analysis (%) calcd for $C_{27}H_{54}BN_3O_2Si_3$ (547.81): C, 59.20; H, 9.94; N, 7.67; found: C, 58.98; H, 9.63; N, 7.88.

Synthesis and characterization of compound 3. A toluene solution of **1** (0.2 g, 0.47 mmol, 10 mL) was added drop by drop to a solution of benzaldehyde (0.05 g, 0.47 mmol in 5 mL toluene) at ambient conditions. The reaction was monitored by NMR spectroscopy which indicates after 12 hours the formation of a product. The solvent was then removed under reduced pressure and extracted with freshly distilled toluene (15 mL). The solvent was again reduced to 5 mL and stored at -30 °C in a freezer for 3 days to obtain colorless crystals of **3**. Yield: 0.180 g (72 %). ^{1}H NMR (400.31 MHz, C_6D_6, 25 ^{o}C): δ 0.32 (s, 9H, $SiMe_3$), 0.43 (s, 9H, $SiMe_3$), 1.27 (s, 9H, *t*Bu), 1.46 (s, 9H, *t*Bu), 4.93 (brs, 1H, NH), 6.96-7.04 (m, 5H, Ph), 7.12-7.14 (m, 5H, Ph) ppm; ^{13}C NMR (100.67 MHz, C_6D_6, 25 ^{o}C): δ 2.51 ($SiMe_3$), 8.00 ($SiMe_3$), 33.19 (*t*Bu), 33.82(*t*Bu), 53.54 (C*t*Bu), 55.56 (C*t*Bu), 124.69, 142.46 (C ═ C), 128.53, 130.62, 131.07, 133.40, 133.61, 133.71, 134.07, 135.92, 137.61, 140.93 (Ph) ppm; ^{29}Si{^{1}H}NMR (79.53 MHz, C_6D_6, 25 °C): δ -39.48 ($SiN(SiMe_3)_2$), 1.47, 2.18 ($N(SiMe_3)_2$) ppm. HRMS (ESI, m/z): calcd: 525.95, found: 526.3100 $[M+H]^+$. Elemental analysis (%) calcd. for $C_{28}H_{47}N_3OSi_3$ (525.96): C, 63.94; H, 9.01; N, 7.99; found: C, 63.61; H, 8.82; N, 8.12.

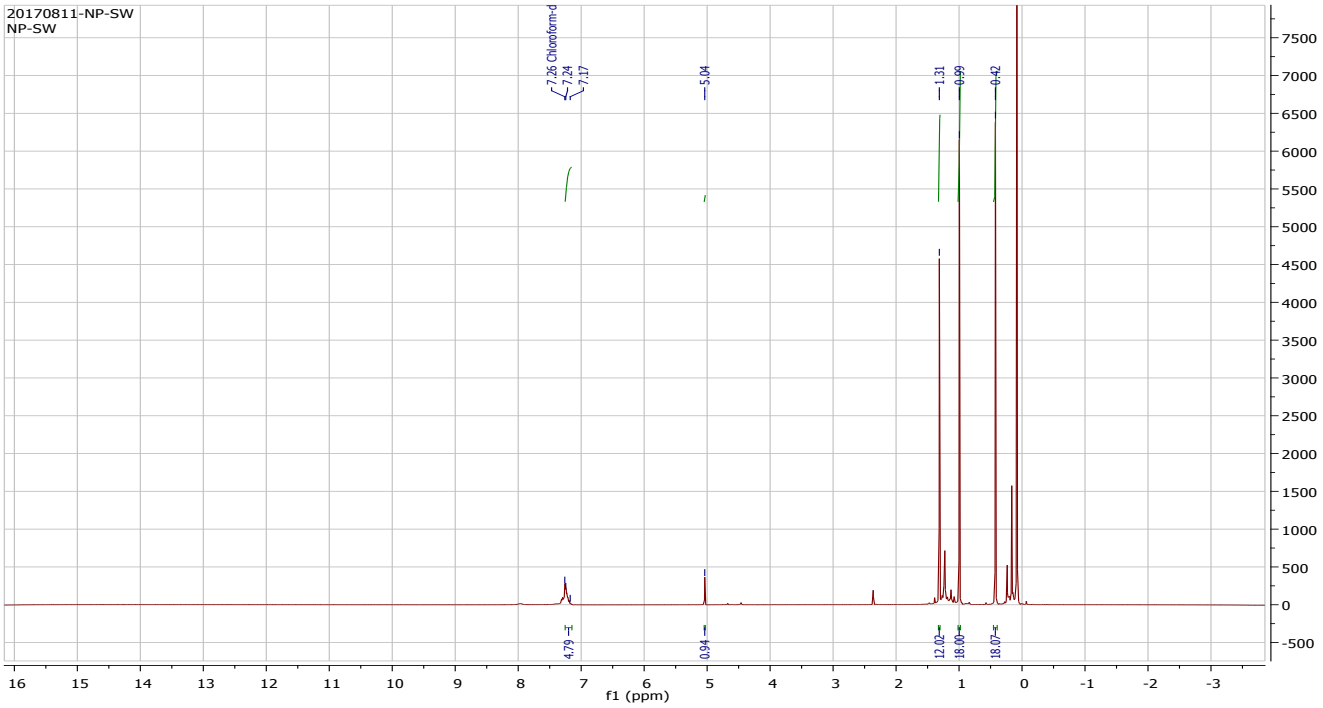
Synthesis and characterization of compounds 4 and 5. A toluene solution of 4-fluorobenzaldehyde (0.059 g, 0.47 mmol, 10 mL) was added drop by drop to a toluene solution (10 mL) of **1** (0.2 g, 0.47 mmol) at room temperature. The reaction mixture was slowly turned from yellow to colorless. After six hours, the ^{1}H NMR spectrum was recorded and indicated the formation of two products. The solution was removed under reduced pressure and extracted with toluene (10 mL) which was reduced *in vacuo* to 5 mL and kept at room temperature for 7 days to obtain colorless crystals of **4** in major fraction along with the formation of minor product **5**.

Spectroscopic data for 4. Yield: 0.200 g (63.1%). Mp: 154.3 °C. ^{1}H NMR (400.31 MHz, C_6D_6, 25 °C); δ 0.33 (s, 9H, $SiMe_3$), δ 0.44 (s, 9H, $SiMe_3$), 1.28 (s, 9H, *t*Bu), 1.47 (s, 9H, *t*Bu), 6.61-6.66 (m, 2H, CHCH), 7.01-7.04 (dd, 4H, Ph), 7.10-7.14 (m, 5H, Ph), 7.30-7.33 (d, 2H, Ph), 7.52-7.55 (d, 2H, Ph) ppm; ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C); δ 2.48 ($SiMe_3$), 7.97 ($SiMe_3$), 33.15 (*t*Bu), 33.81 (*t*Bu), 53.53 (C*t*Bu), 55.55 (C*t*Bu), 114.68 (CHCH), 114.89 (CHCH), 126.09, 126.17, 128.48, 128.59, 128.65, 130.09, 130.11, 130.35, 137.43, 140.94, 153.02, 159.49 (Ph), 161.91 (NCN) ppm; ^{19}F NMR (376.63 MHz, C_6D_6, 25 °C); δ -118.93 (s, 1F, Ar F), -118.99 (s, 1F, Ar F) ppm; ^{29}Si{^{1}H}NMR (79.53 MHz, C_6D_6, 25 °C); δ -38.17 ($SiN(SiMe_3)_2$), 2.88, 3.49 ($N(SiMe_3)_2$) ppm. HRMS (ESI, m/z): calcd: 668.05, found: 668.3330 $[M+H]^+$. Elemental analysis (%) calcd. for $C_{35}H_{52}F_2N_3O_2Si_3$ (668.05) C, 62.83; H, 7.83; N, 6.28; found: C, 56.75; H, 7.11; N, 5.46.

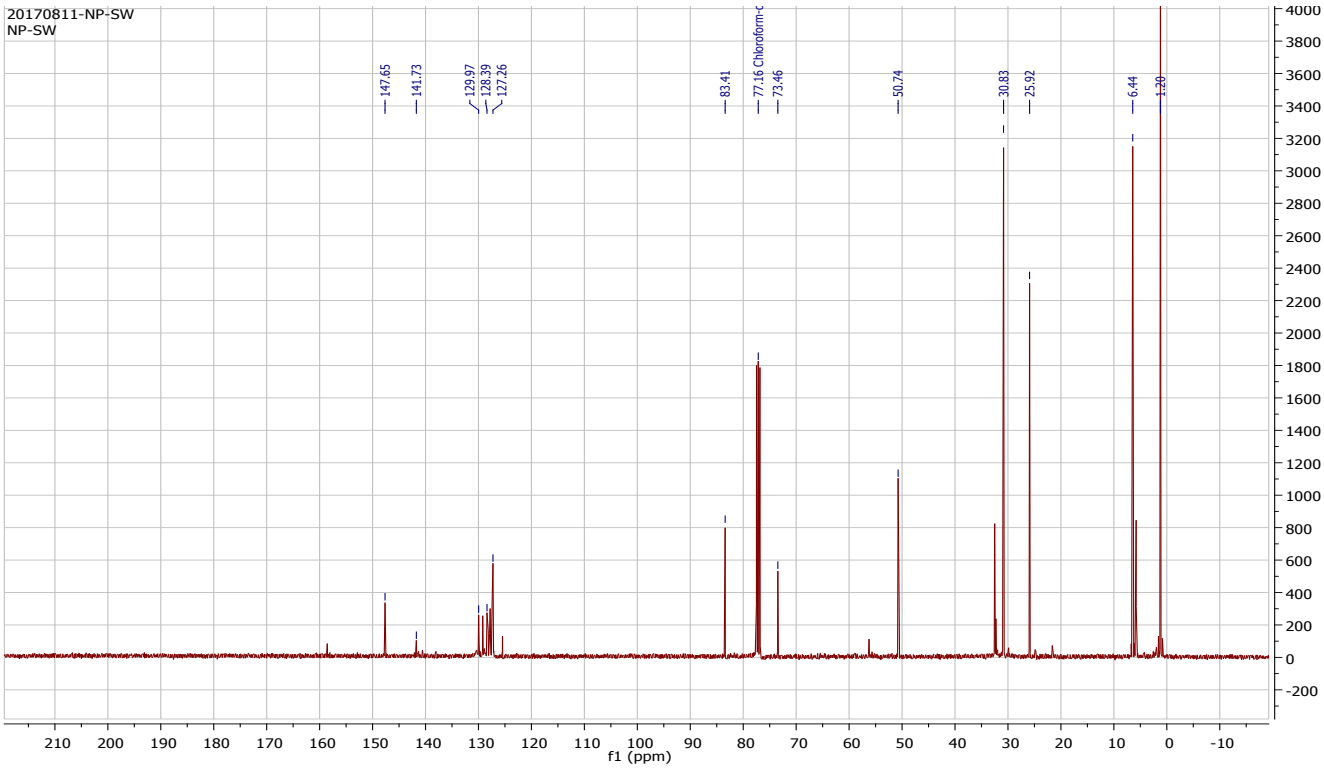
Spectroscopic data for 5. Yield: 0.020 g (8%) ^{1}H NMR (400.31 MHz, C_6D_6, 25 °C); δ 0.32 (s, 9H, $SiMe_3$), δ 0.44 (s, 9H, $SiMe_3$), 1.28 (s, 9H, *t*Bu), 1.47 (s, 9H, *t*Bu), 4.90 (brs, 1H, NH), 6.61-6.65 (m, 2H, Ph), 7.00-7.13 (m, 5H, Ph), 7.13 (d, 1H, Ph), 7.53 (d, 1H, Ph) ppm; ^{19}F NMR (376.63 MHz, C_6D_6, 25 °C); δ -118.96 (s, 1F, Ar F) ppm; HRMS (ESI, m/z): calcd: 543.95, found: 544.3005 $[M+H]^+$. As the formation of **5** is always accompanied by formation of **4** as major product, we were not able fully resolve the ^{13}C NMR of **5**. Similarly, in the ^{29}Si NMR, we have always obtained the resonances corresponding to **4**.

Analytical data for compounds 2-5.

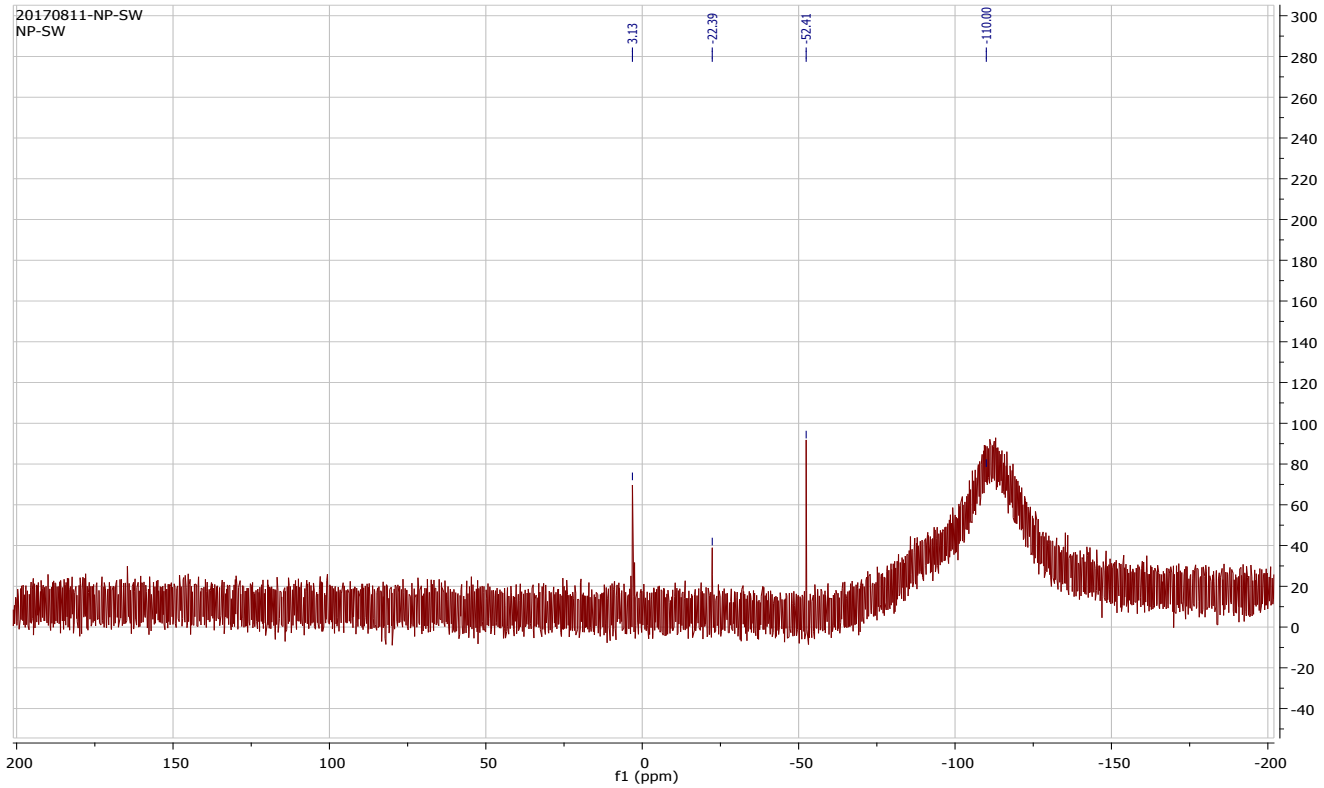
^{1}H NMR of 2:



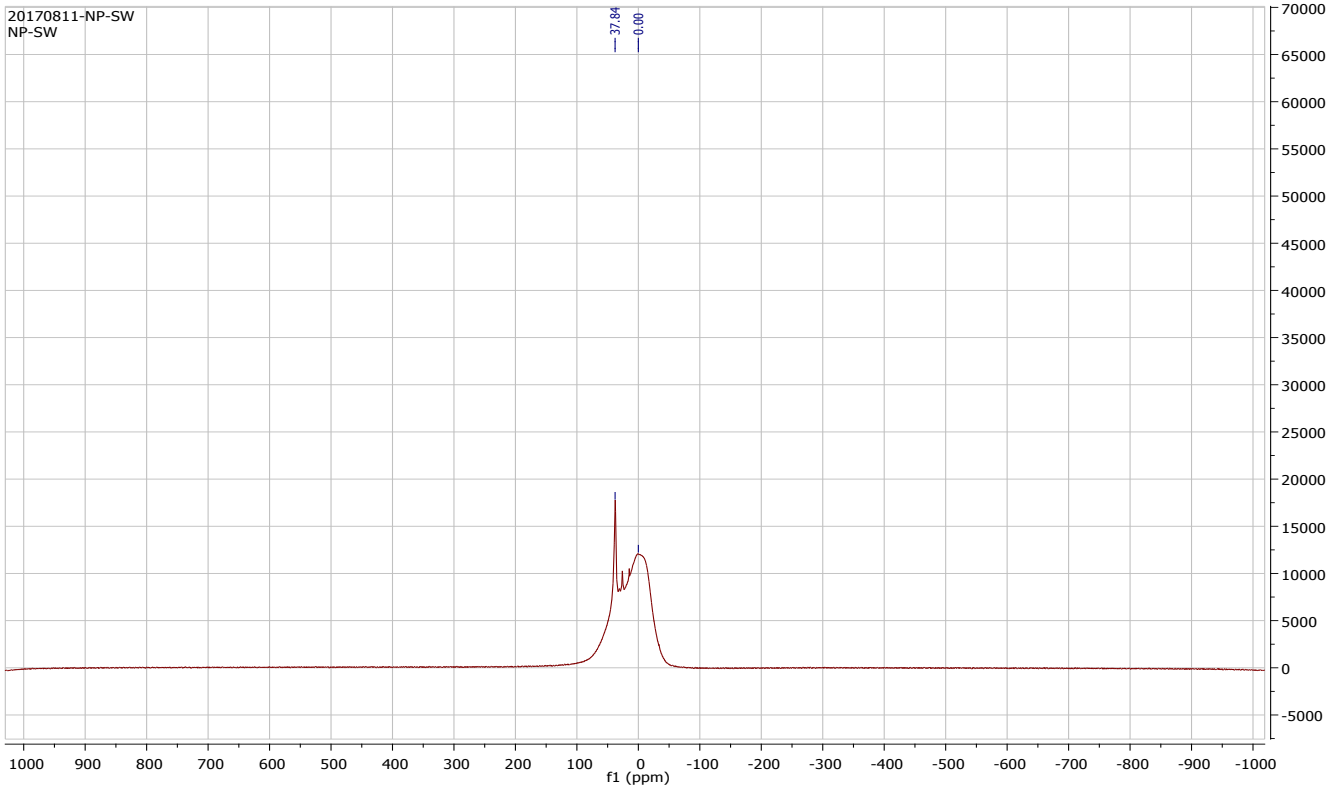
^{13}C NMR of 2:



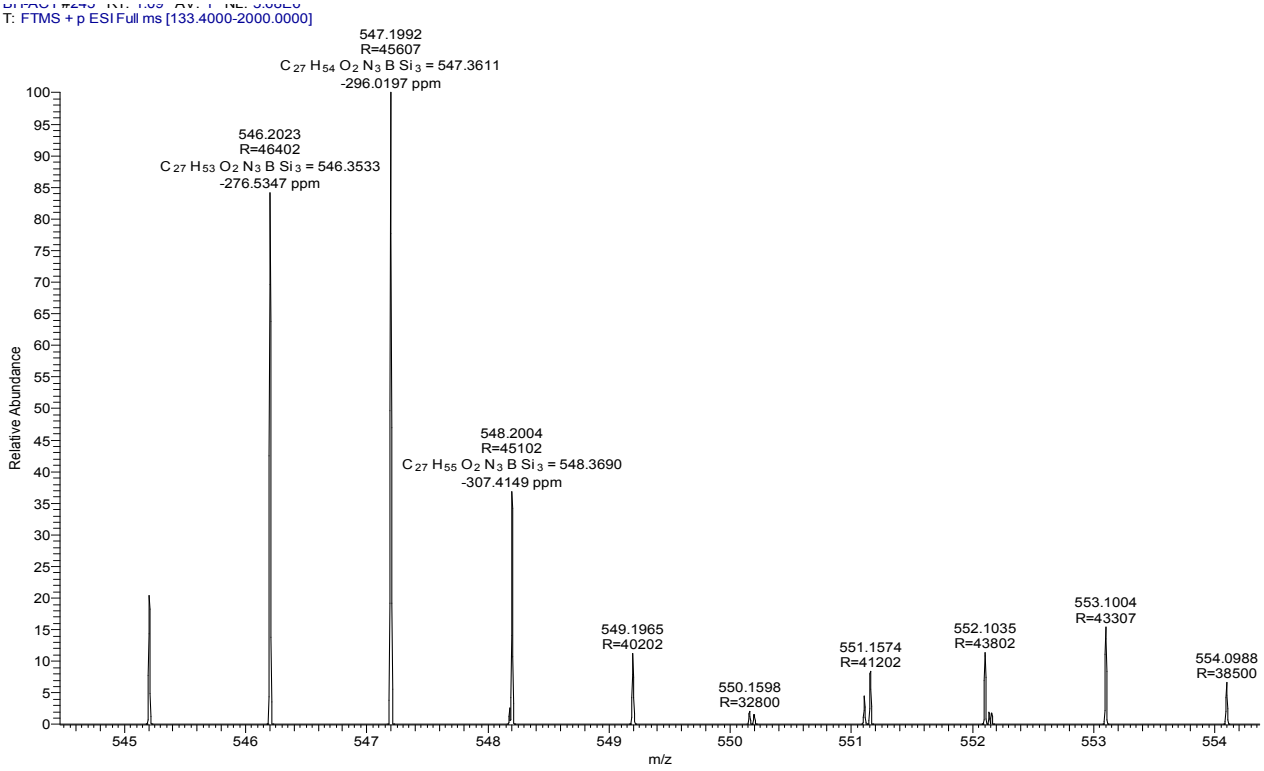
^{29} Si NMR of 2:



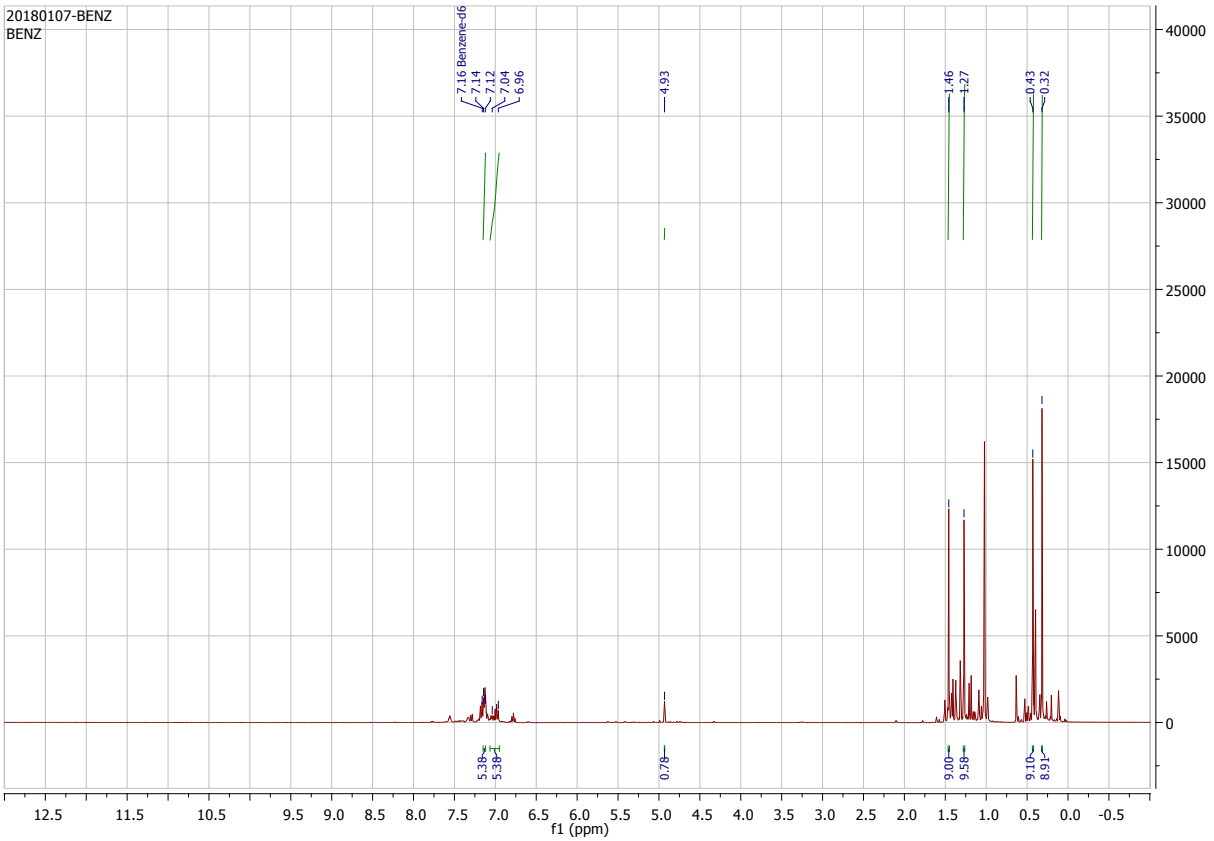
^{11}B NMR of 2:



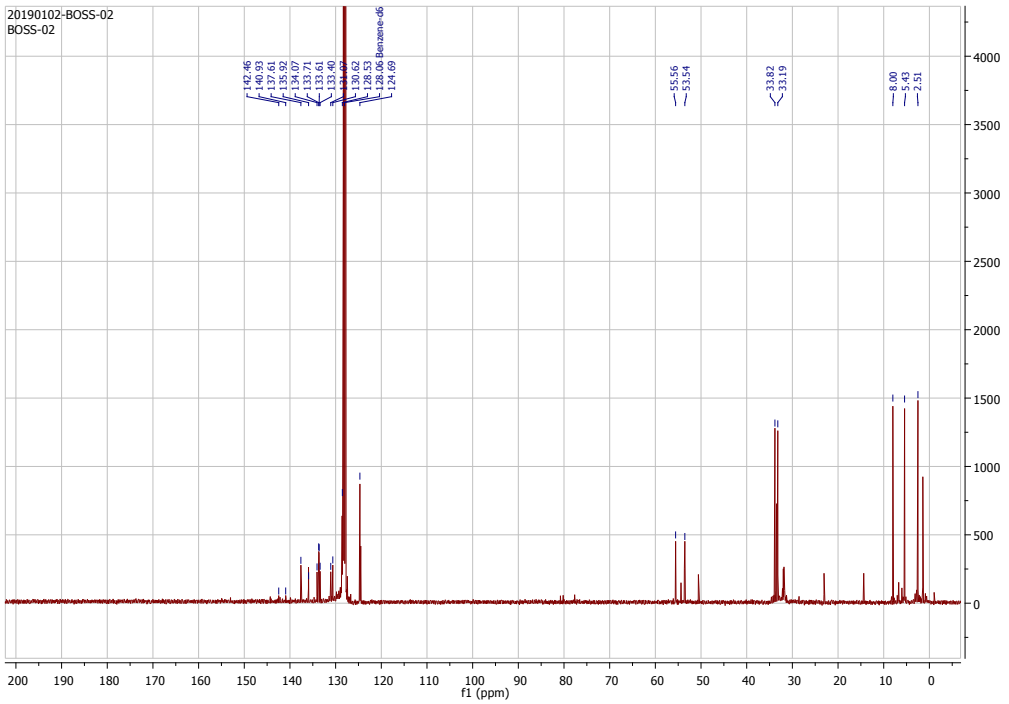
HRMS of 2:


T: FTMS + p ESI Full ms [133.4000-2000.0000]
547.1992
R=45607
C 27 H 54 O 2 N 3 B Si 3 = 547.3611
-296.0197 ppm
546.2023
R=46402
C 27 H 53 O 2 N 3 B Si 3 = 546.3533
-276.5347 ppm
548.2004
R=45102
C 27 H 55 O 2 N 3 B Si 3 = 548.3690
-307.4149 ppm
549.1965
R=40202
550.1598
R=32800
551.1574
R=41202
552.1035
R=43802
553.1004
R=43307
554.0988
R=38500
Relative Abundance
m/z

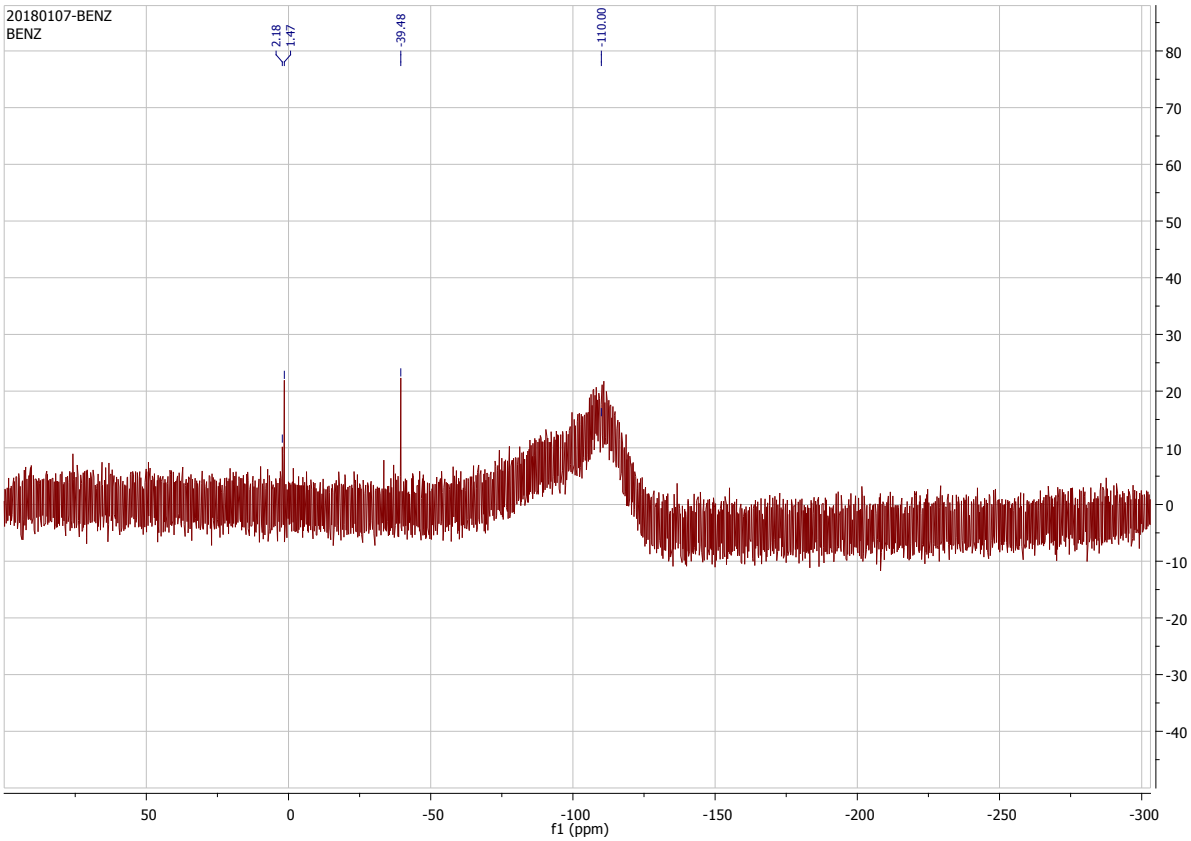
^{1}H NMR of 3:



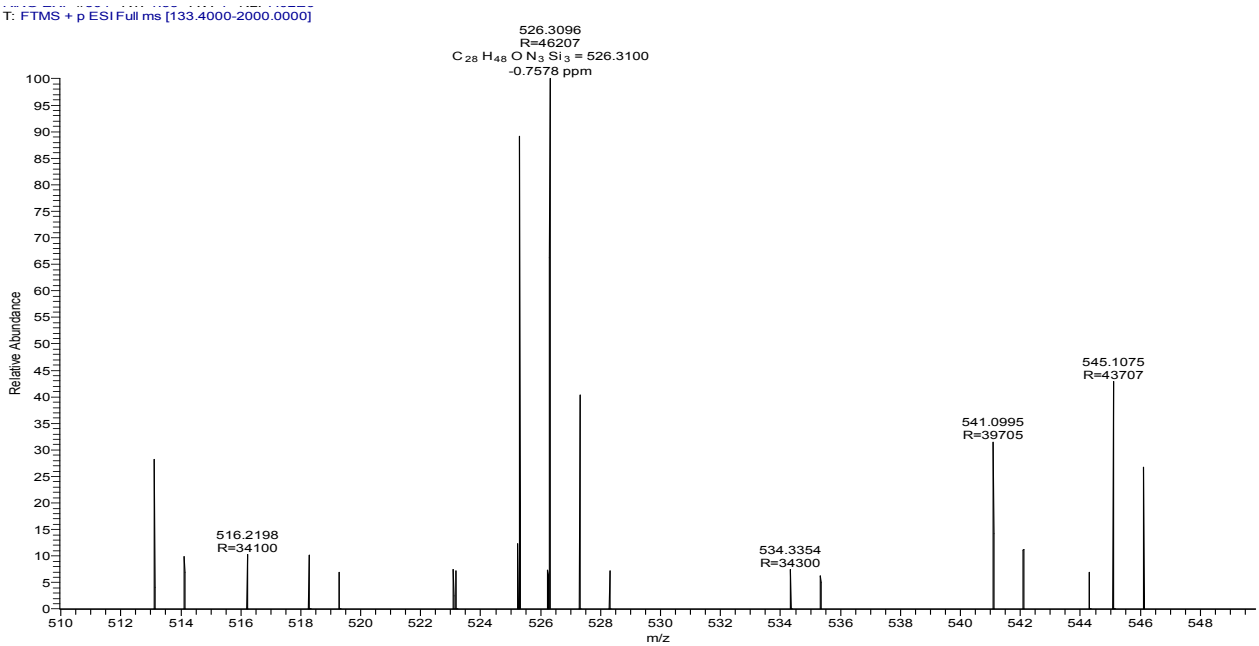
^{13}C NMR of 3:



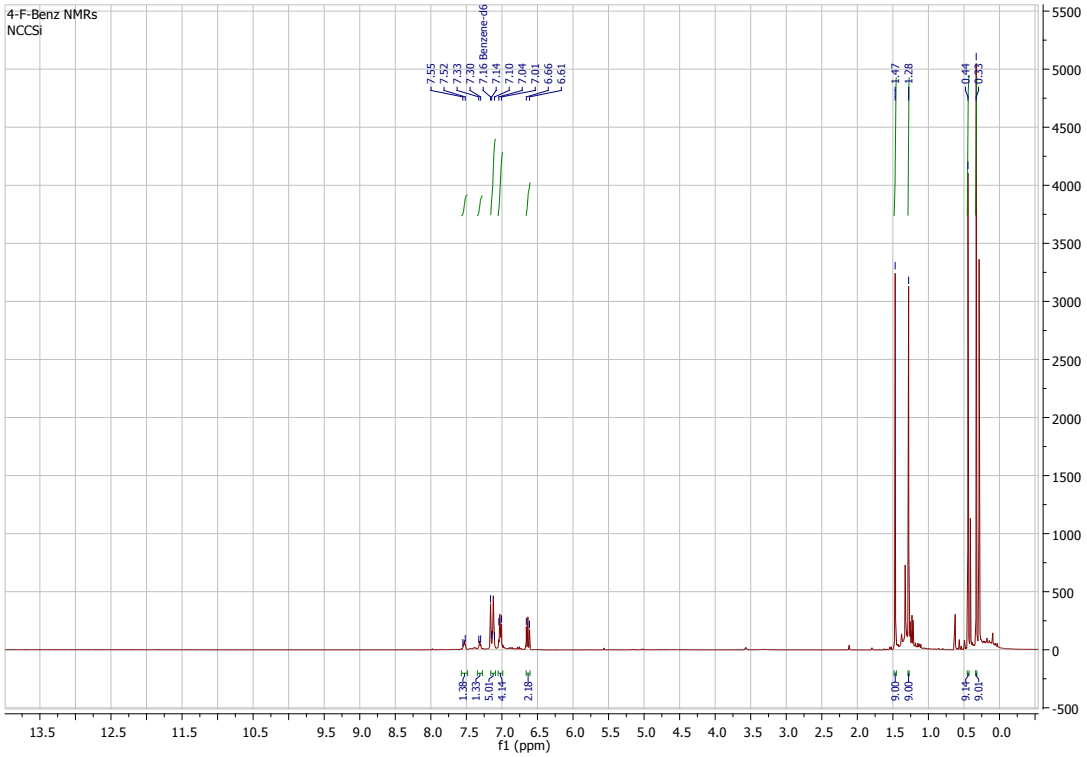
^{29}Si NMR of 3:



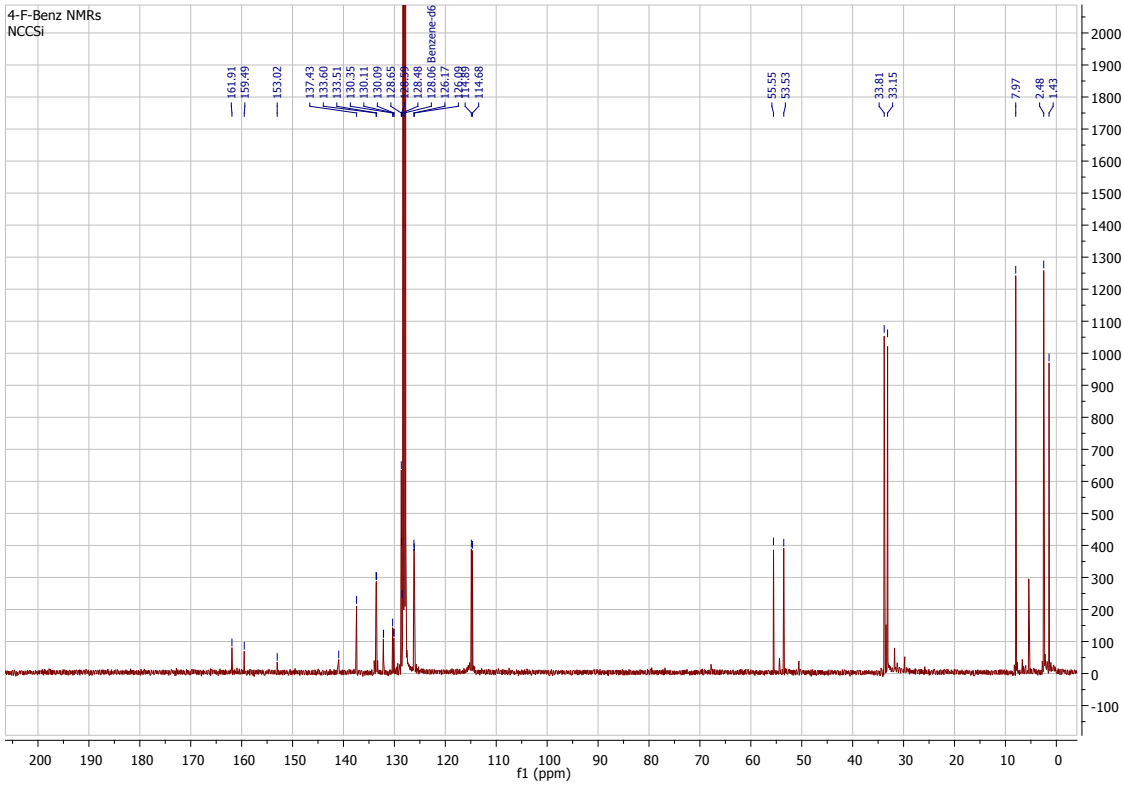
HRMS of 3:



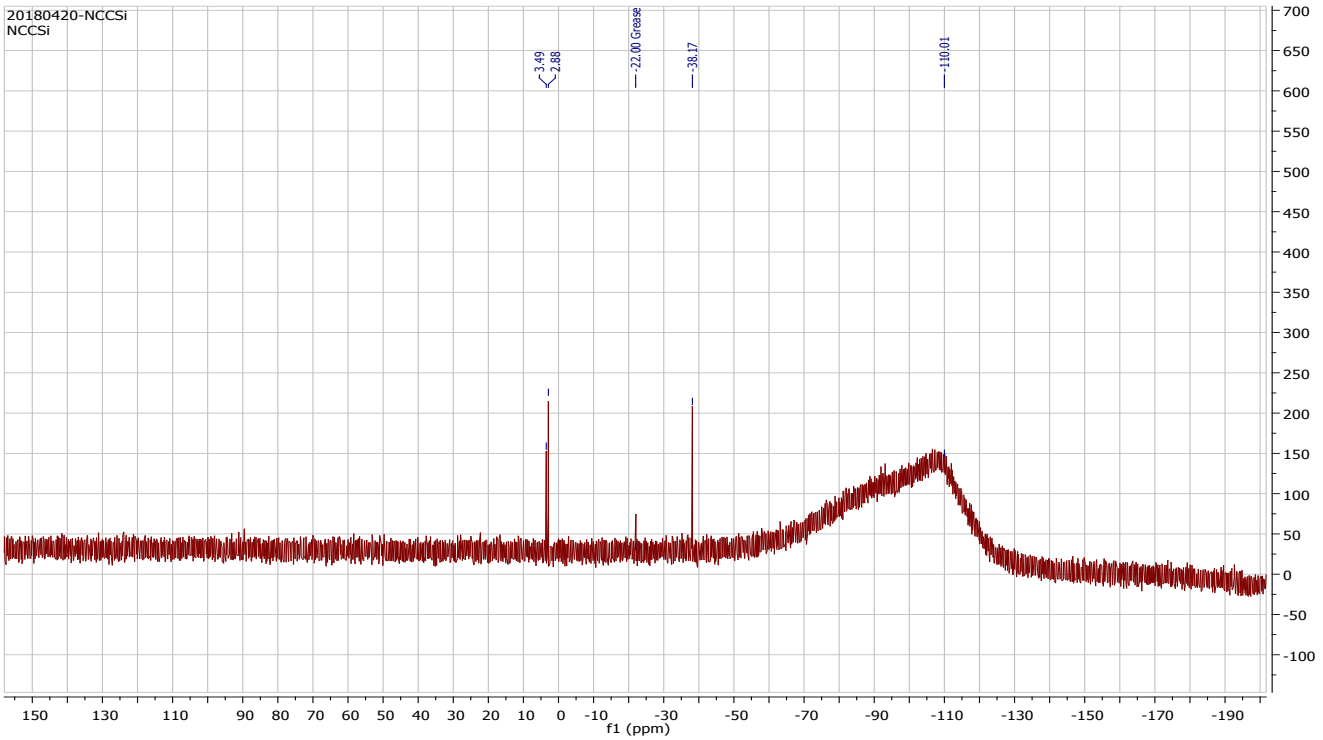
^{1}H NMR of 4:



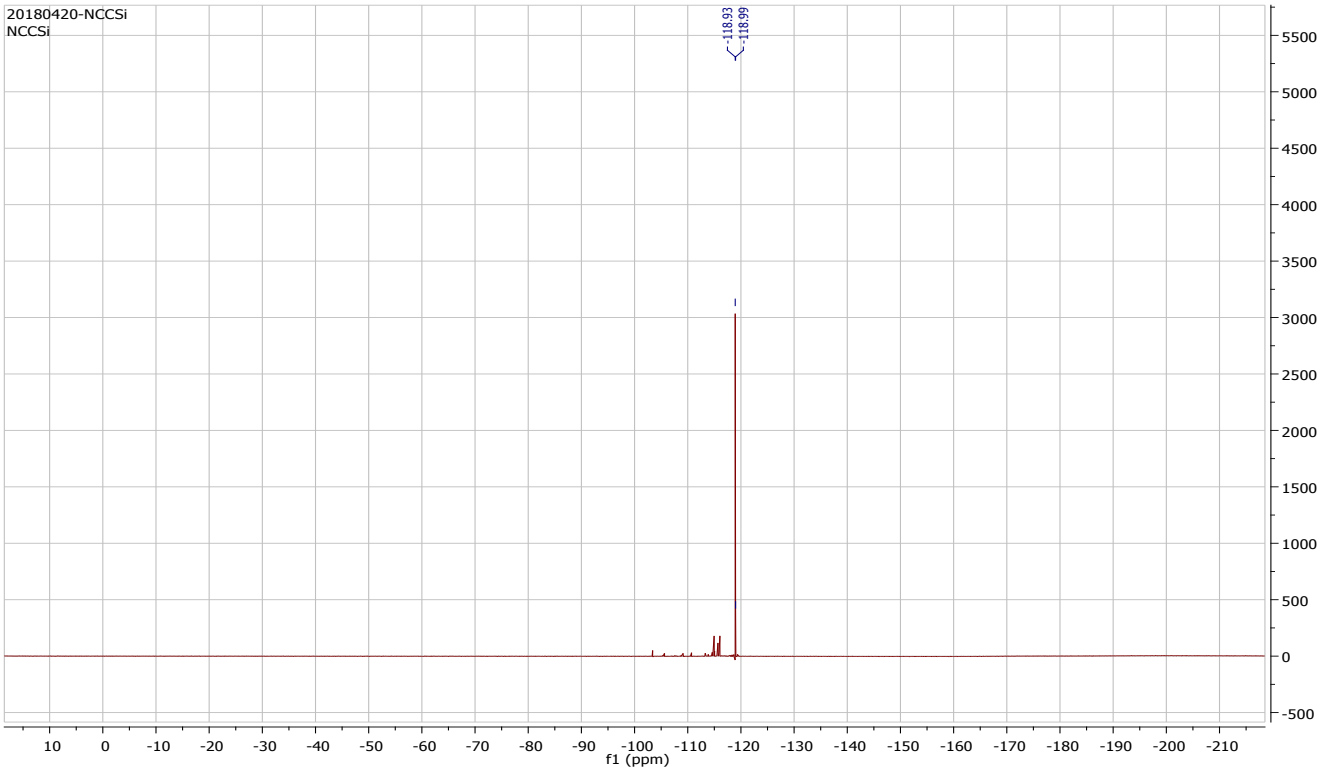
^{13}C NMR of 4:



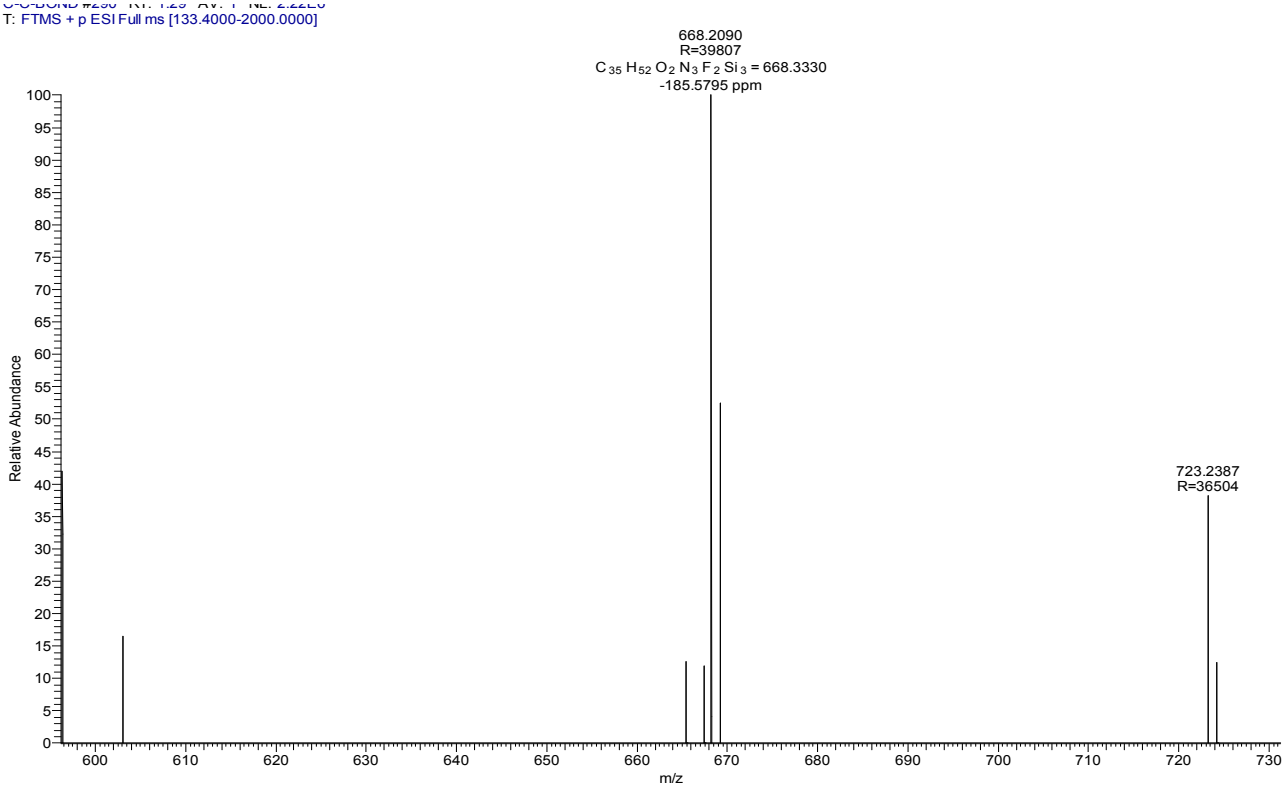
^{29}Si NMR of 4:



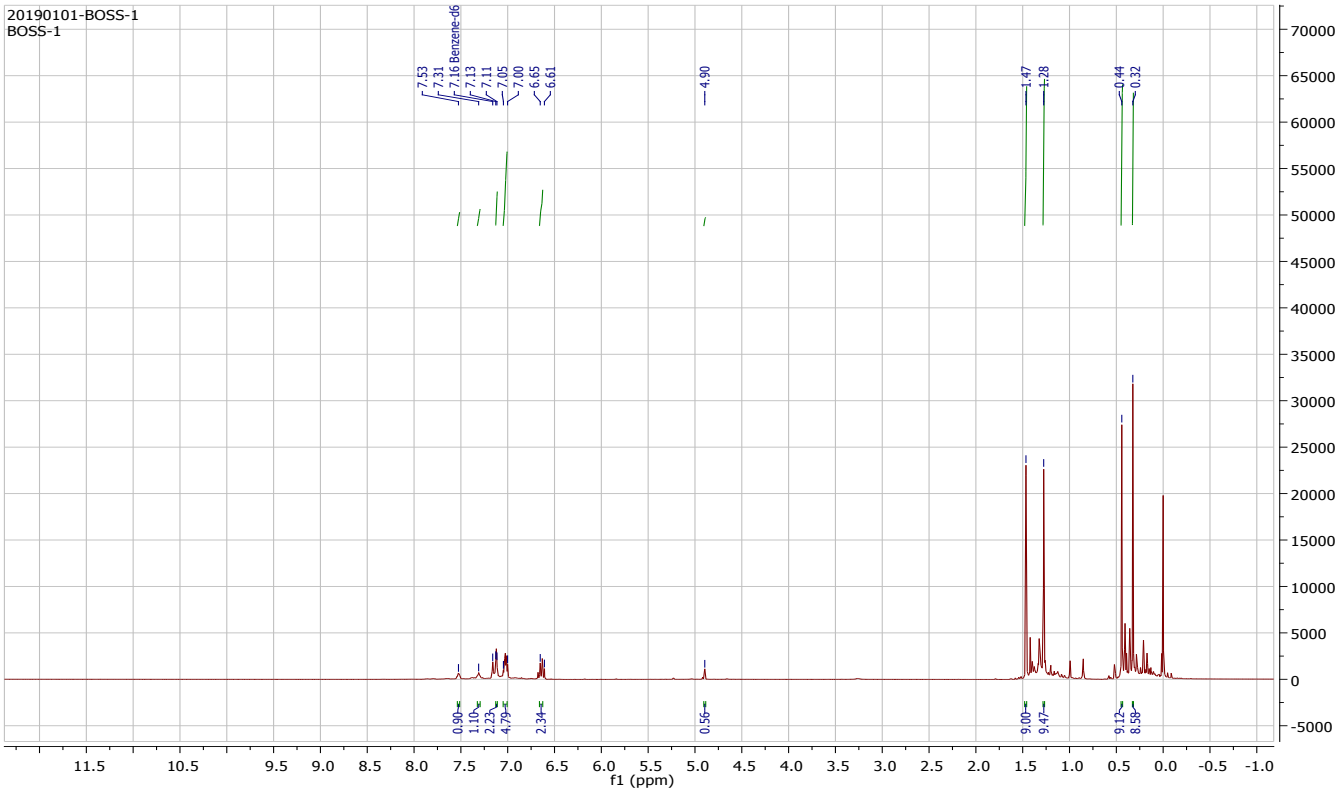
^{19}F NMR of 4:



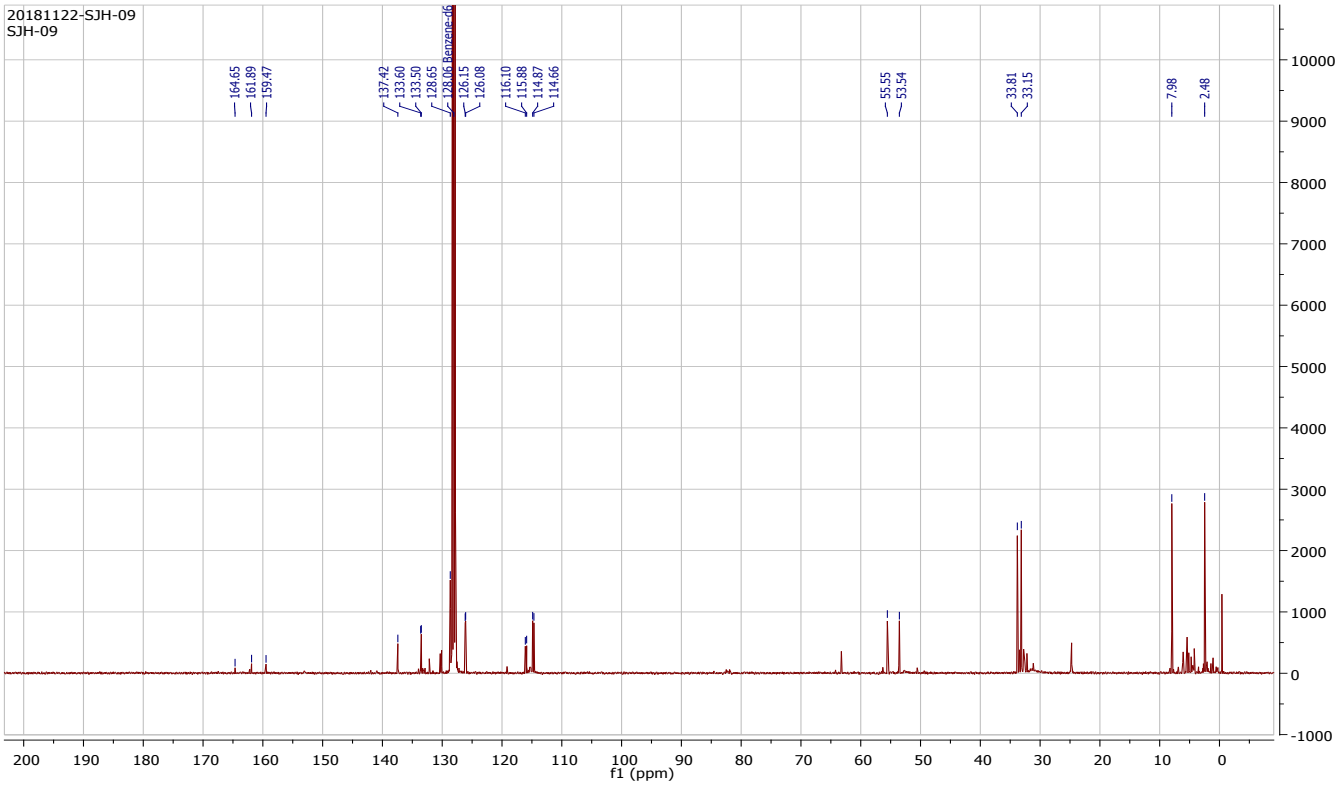
HRMS of 4:


T: FTMS + p ESI Full ms [133.4000-2000.0000]
668.2090
R=39807
C35 H52 O2 N3 F2 Si3 = 668.3330
-185.5795 ppm
723.2387
R=36504
Relative Abundance
m/z

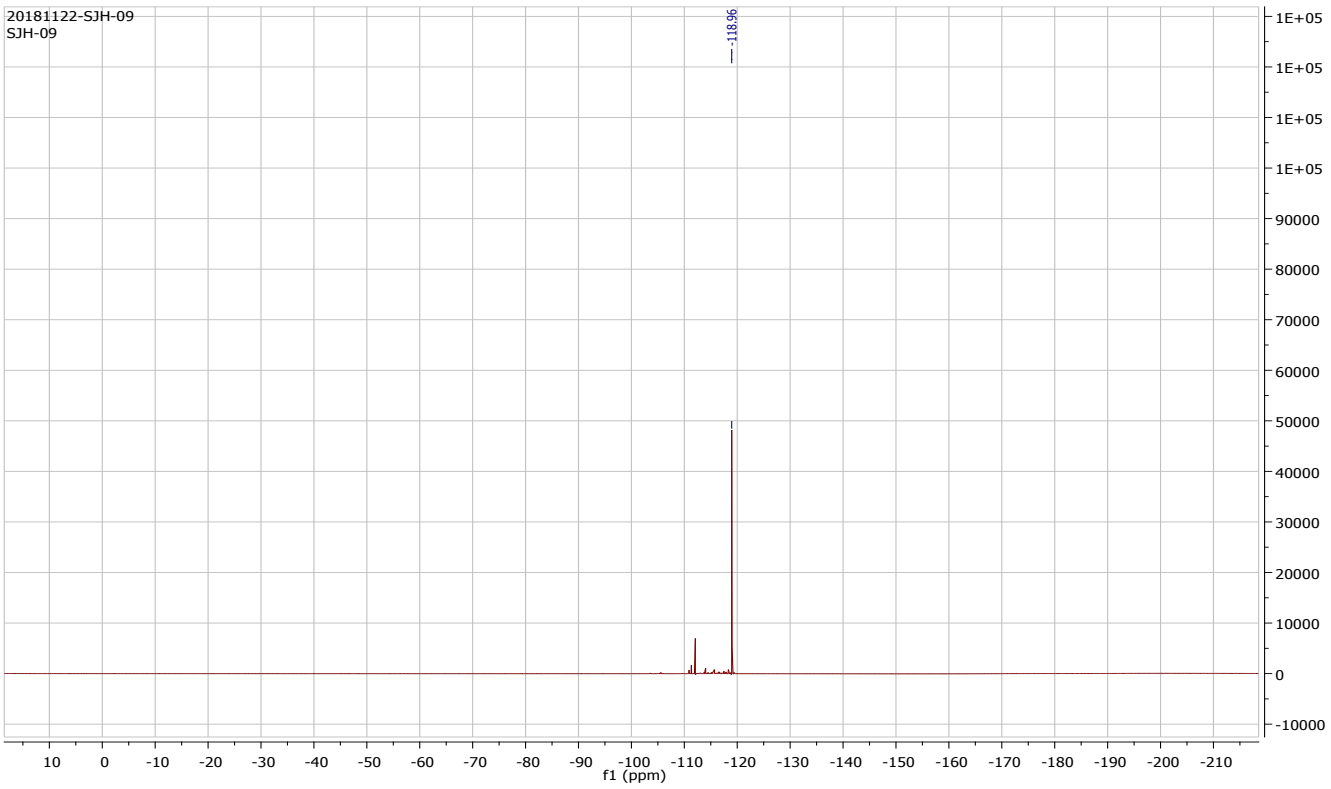
^{1}H NMR of 5:



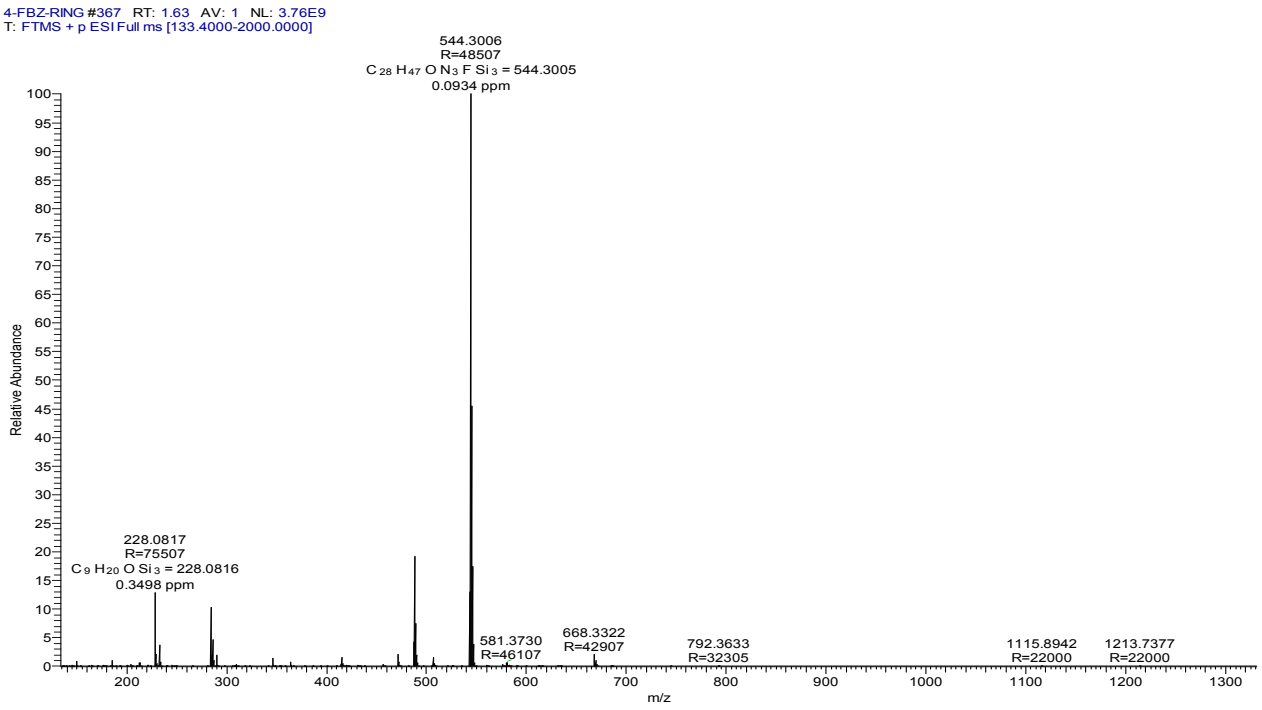
^{13}C NMR of 5:



^{19}F NMR of 5:



HRMS of 5:



Crystallographic data for the structural analysis of compounds 2, 3, 4 and 5. X-ray intensity data measurements of **2** and **3-5** were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (CuKα= 1.54178 Å) and (MoKα= 0.71073 Å) radiation, respectively. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).S2 All the data were corrected for Lorentzian, polarization, and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on *F*2.S3 All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An *ORTEP III*S4 view of compounds **2**, **3, 4** and **5** were drawn with 50% probability displacement ellipsoids and H atoms omitted for clarity.

Crystal Data for compound 2. $C_{27}H_{54}B_1N_3O_2Si_3$, M =547.81, colorless, 0.33 x 0.25 x 0.16 mm^3, orthorhombic, space group '*P* b c a', a = 11.4586 (16) Å, b = 19.143 (3) Å, c = 30.168 (4) Å, $\alpha=\beta=\gamma=90°$, V = 6617.4 (16) $Å^3$, Z = 8, T = 296(2) K, $2\theta_{max}$=124.998°, D_{calc} (g cm^{-3}) = 1.100, $F(000)$ = 2400, μ (mm^{-1}) = 1.516, 124812 reflections collected, 5261 unique reflections (R_{int}= 0.1669), 4011 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.666, T_{max} = 0.785, 346 refined parameters, S = 1.198, $R1$ = 0.0742, $wR2$ = 0.2282 (all data R = 0.1006, $wR2$ =0.2282), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.544, $\Delta\rho_{min}$= -0.830 ($eÅ^{-3}$).

Crystal Data for compound 3. $C_{28}H_{47}N_3O_1Si_3$, M =525.95, colorless, 0.38 x 0.28 x 0.18 mm^3, triclinic, space group *P* -1, a = 10.8132 (14) Å, b = 10.9099 (13) Å, c = 13.5038 (17) Å, α =

80.743 (3) °, β = 78.036 (3) °, γ = 79.717 (3) °, V = 5120.7 (3) Å^3, Z = 2, T = 296 (2) K, $2\theta_{max}$=49.994°, D_{calc} (g cm^{-3}) = 1.149, $F(000)$ = 572.0, μ (mm^{-1}) = 0.181, 54149 reflections collected, 5343 unique reflections (R_{int}= 0.1319), 3489 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.941, T_{max} = 0.968, 329 refined parameters, S = 1.026, $R1$ = 0.0535, $wR2$ = 0.1049 (all data R = 0.1084, $wR2$ =0.1049), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.301, $\Delta\rho_{min}$= -0.403 (eÅ^{-3}).

Crystal Data for compound 4. $C_{35}H_{51}F_2N_3O_2Si_3$, M =668.05, colorless, 0.38 x 0.28 x 0.17 mm^3, monoclinic, space group 'P 21/c', a = 11.174 (4) Å, b = 16.174 (6) Å, c = 20.535 (8) Å, α= γ = 90°, β =101°.522 (9), V = 3636 (2) Å^3, Z = 4, T = 296(2) K, $2\theta_{max}$=50.00°, D_{calc} (g cm^{-3}) = 1.220, $F(000)$ = 1432, μ (mm^{-1}) = 0.175, 123259 reflections collected, 6408 unique reflections (R_{int}= 0.2604), 3736 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.943, T_{max} = 0.971, 419 refined parameters, S = 1.046, $R1$ = 0.0693, $wR2$ = 0.1185 (all data R = 0.1479, $wR2$ =0.1185), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.353, $\Delta\rho_{min}$= -0.285 (eÅ^{-3}).

Crystal Data for compound 5. $C_{28}H_{46}F_1N_3O_1Si_3$, M =543.95, colorless, 0.38 x 0.28 x 0.17 mm^3, orthorhombic, space group P 21/c, a = 11.5454 (3) Å, b = 16.4615 (4) Å, c = 17.4112 (4) Å, α =γ 90 °, β = 106.504 (10) °, V = 3172.5 (14) Å^3, Z = 4, T = 217 (2) K, $2\theta_{max}$=49.99°, D_{calc} (g cm^{-3}) = 1.139, $F(000)$ = 1176.0, μ (mm^{-1}) = 0.179, 28441 reflections collected, 5477 unique reflections (R_{int}= 0.0294), 4667 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, T_{min} = 0.924, T_{max} = 0.965, 341 refined parameters, S = 1.020, $R1$ = 0.0377, $wR2$ = 0.0923 (all data R = 0.0469, $wR2$ =0.0923), maximum and minimum residual electron densities; $\Delta\rho_{max}$ = 0.368, $\Delta\rho_{min}$= -0.329 (eÅ^{-3}).

Tentative mechanisms for the formation of 3-5.

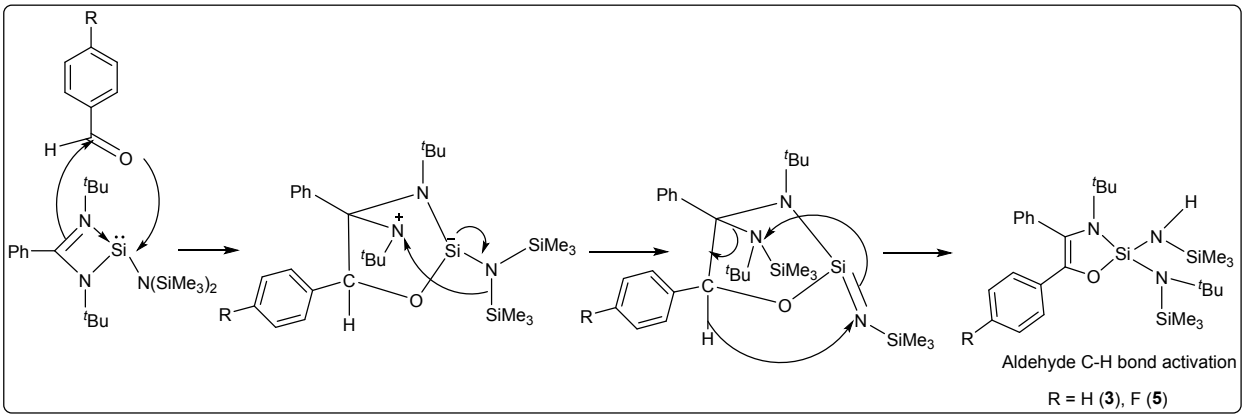


Fig. S1. Tentative mechanism for the formation of **3** and **5**.

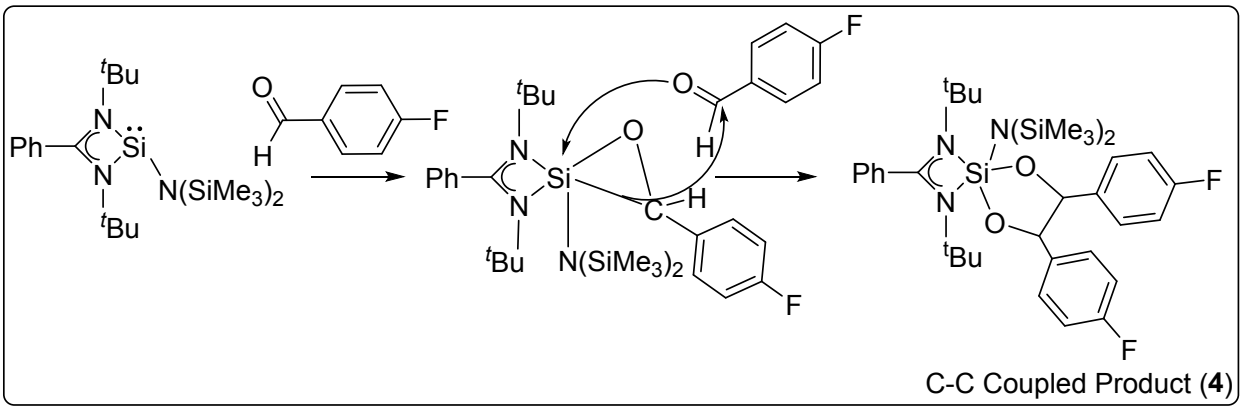


Fig. S2. Tentative mechanism for the formation of **4**.

Details of the theoretical computational for compound 2. All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.1 suite of programs,[S5] using the PBE functional.[S6] The TZVP3 basis set has been employed. The resolution of identity (RI),[S7] along with the multipole accelerated resolution of identity (marij)[S8] approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent correction were incorporated with optimization calculations using the COSMO model,[S9] with toluene (ε = 2.374) as the solvent. The values reported are ΔG values, with

zero point energy corrections, internal energy and entropic contributions were included through frequency calculations on the optimized minima, with the temperature taken to be 298.15 K. The translational entropy term in the calculated structures was corrected through a free volume correction introduced by Mammen *et al.*[S10] This volume correction is to account for the unreasonable enhancement in translational entropy that is generally observed in computational softwares. Harmonic frequency calculations were performed for all stationary points to confirm them as a local minima or transition state structures.

PBE/TZVP optimized geometries for all the compounds and transition state.

(i) **1**

68

Si	-0.671973	1.049147	0.433024
Si	-2.168870	-1.468587	-0.950269
C	-3.383888	-2.583618	0.004940
C	-2.690198	-1.371082	-2.778260
C	-0.516214	-2.400224	-0.949884
H	-0.680284	-3.363112	-1.458947
H	-0.150770	-2.601564	0.064198
H	0.260748	-1.849819	-1.495537
H	-3.052492	-2.694418	1.048650
H	-3.405171	-3.585303	-0.452367
H	-4.412783	-2.198954	0.019094
H	-2.694088	-2.380391	-3.219312
H	-3.688524	-0.935973	-2.914999
N	-2.096226	0.155094	-0.211599
H	-1.972005	-0.759419	-3.345388
C	-4.166563	0.699749	1.930739
Si	-3.612879	1.046568	0.146428
C	-5.034547	0.575336	-1.028929
H	-5.289291	-0.492395	-1.034349
H	-4.812201	0.884100	-2.060822
H	-5.929062	1.128793	-0.701285
C	-3.402301	2.922047	-0.082135
H	-4.387070	3.405094	0.026837
H	-3.021811	3.149943	-1.089489
H	-2.712572	3.361344	0.649878
H	-0.461993	2.743969	-1.975372
C	-0.002825	2.005781	-2.650458
H	0.263957	2.513160	-3.588228
H	-0.751391	1.231567	-2.867417
C	1.252650	1.391609	-2.008945
C	2.257853	2.519222	-1.703987
H	2.477707	3.085958	-2.621468
H	1.836605	3.211466	-0.960139
H	3.204244	2.120618	-1.316654
N	0.792928	0.717908	-0.778053
C	1.871499	0.377320	-2.986866
H	2.127589	0.878979	-3.932004
H	1.158970	-0.430452	-3.208266
H	2.789219	-0.066272	-2.579240
H	-1.284890	-0.277961	2.988246
C	2.944644	-0.213419	0.197238
C	1.479434	0.056533	0.174904
C	3.445781	-1.390686	-0.379532
C	4.815257	-1.662379	-0.348165
C	5.695840	-0.760797	0.258435
C	5.201916	0.415066	0.832756
C	3.832656	0.689483	0.801900
C	1.689338	-2.011369	2.527743
H	1.678660	-2.448249	3.537025
H	2.729772	-1.774767	2.272719
H	1.322958	-2.770245	1.821318
H	2.754445	-2.098102	-0.841942
H	5.195124	-2.581996	-0.797330
H	6.766167	-0.974050	0.283755
H	5.885163	1.123655	1.304936

H	3.448412	1.610790	1.243212
C	1.381061	0.320770	3.436012
H	1.424116	-0.045526	4.473078
H	2.400689	0.588809	3.127119
H	0.756905	1.225180	3.406960
N	0.594738	-0.231765	1.146388
C	0.791152	-0.762192	2.510575
C	-0.610431	-1.146750	3.014372
H	-0.555861	-1.510607	4.050093
H	-1.048449	-1.936154	2.387349
H	-5.115706	1.209454	2.158787
H	-3.406343	1.059617	2.640577
H	-4.303855	-0.378717	2.099022

(ii) **HBpin**

22

B	-0.002005	-0.022616	1.380222
O	-1.254551	-0.098141	1.944349
O	0.000362	0.005214	0.004735
C	-1.382250	-0.284107	-0.425799
C	-2.224289	0.103729	0.849174
C	-1.683850	0.542580	-1.667695
C	-1.430924	-1.778569	-0.750735
H	-1.208715	-2.388501	0.136374
H	-0.676532	-2.001290	-1.517596
H	-2.416899	-2.070016	-1.138748
H	-1.041988	0.210983	-2.495671
H	-1.500709	1.610325	-1.497962
H	-2.732087	0.408532	-1.972873
C	-3.436558	-0.778994	1.108817
H	-3.947794	-0.444136	2.022158
H	-3.153155	-1.830382	1.240179
H	-4.148781	-0.707981	0.273545
H	-3.392058	1.806547	0.138877
H	-1.753914	2.233317	0.706415
C	-2.619919	1.581423	0.887667
H	-3.022704	1.816128	1.882474
H	1.001125	0.015821	2.031255

(iii) **RC"**

90

Si	-0.720730	0.156726	0.182872
B	2.390556	2.123208	0.856674
O	2.912102	2.461094	-0.373782
O	1.817765	3.173462	1.536390
C	2.122636	4.393831	0.768808
C	2.443233	3.828415	-0.667864
C	0.916100	5.320056	0.832779
C	3.331809	5.041047	1.448475
H	4.209424	4.380295	1.415035
H	3.086117	5.231495	2.502259
H	3.593625	5.997992	0.975185
H	0.759241	5.648918	1.869581
H	0.003763	4.818353	0.489373
H	1.082730	6.213293	0.212632
C	3.546250	4.565690	-1.414675
H	3.711686	4.087683	-2.390478
H	4.492624	4.551712	-0.860374
H	3.256984	5.612108	-1.592087
H	0.790861	4.656423	-1.833478
H	0.425310	3.097481	-1.030991
C	1.202599	3.678503	-1.547919
H	1.480529	3.138692	-2.463675
Si	-3.341866	-1.589089	-0.568563
C	-4.907382	-1.844965	0.489787
C	-3.843996	-1.548301	-2.403868
C	-2.331065	-3.177192	-0.340098
H	-2.961752	-4.017072	-0.672222
H	-2.055723	-3.347366	0.707774
H	-1.416120	-3.170357	-0.944351
H	-4.641644	-1.938620	1.553621
H	-5.398028	-2.781681	0.180739
H	-5.645180	-1.036458	0.394899
H	-4.432202	-2.446226	-2.650851
H	-4.446418	-0.665071	-2.654078
N	-2.486675	-0.090868	-0.101460
H	-2.951419	-1.545020	-3.047084
C	-4.120188	1.376449	2.002603
Si	-3.446905	1.386612	0.224964
C	-4.902576	1.568791	-0.989293
H	-5.618038	0.735897	-0.961573
H	-4.534619	1.670015	-2.021096
H	-5.452658	2.488874	-0.735578
C	-2.422641	2.973023	0.014021
H	-3.094170	3.836456	0.152533
H	-1.988070	3.034432	-0.994368
H	-1.603191	3.041234	0.741080
H	-0.052106	1.137069	-2.532442
C	-0.155277	0.174997	-3.055209

H	0.147284	0.314795	-4.102710
H	-1.214798	-0.113749	-3.030032
C	0.725427	-0.896518	-2.390703
C	2.193060	-0.432078	-2.436919
H	2.480911	-0.216251	-3.477355
H	2.330571	0.481423	-1.841603
H	2.872887	-1.205318	-2.055663
N	0.218977	-1.039298	-1.009361
C	0.563652	-2.223650	-3.154778
H	0.855201	-2.087051	-4.206668
H	-0.481862	-2.563587	-3.126701
H	1.198423	-3.010602	-2.726187
H	-1.463794	-0.296723	3.022481
C	1.885126	-2.654250	0.027219
C	0.700048	-1.751500	0.031300
C	1.737574	-4.003090	-0.331224
C	2.840089	-4.860700	-0.317025
C	4.099374	-4.378781	0.053944
C	4.252783	-3.034405	0.409149
C	3.152132	-2.174882	0.395928
C	0.302614	-3.273683	2.732353
H	0.226825	-3.505029	3.804907
H	1.295026	-3.588698	2.387700
H	-0.453483	-3.866123	2.198222
H	0.751047	-4.381755	-0.605141
H	2.713761	-5.909177	-0.593817
H	4.960539	-5.049556	0.066027
H	5.234389	-2.650728	0.693942
H	3.273551	-1.122603	0.658307
C	1.203215	-0.969050	3.203937
H	1.220030	-1.179264	4.284369
H	2.182510	-1.242006	2.788146
H	1.050919	0.109196	3.056977
H	2.498478	1.026756	1.316880
N	-0.043696	-1.410387	1.097793
C	0.072509	-1.766521	2.526073
C	-1.268791	-1.369644	3.167211
H	-1.247892	-1.573727	4.247118
H	-2.102298	-1.928629	2.718947
H	-4.726487	2.275831	2.192794
H	-3.286677	1.370623	2.721686
H	-4.742877	0.493012	2.199473

(iv) **TS_1”**

90

Si	-0.636974	-0.030565	0.024473
B	0.845045	2.127612	0.000865
O	1.093009	2.622768	-1.294311
O	0.241494	3.104802	0.817250
C	0.278809	4.365959	0.084157
C	0.407454	3.903070	-1.419846
C	-0.983546	5.161362	0.397507
C	1.514998	5.127138	0.579018
H	2.436110	4.569363	0.357400
H	1.441724	5.244847	1.669126
H	1.588307	6.126232	0.125696
H	-0.997045	5.425729	1.464658
H	-1.888808	4.583100	0.177846
H	-1.007943	6.094418	-0.185126
C	1.261325	4.817803	-2.292489
H	1.313770	4.407887	-3.311222
H	2.284279	4.905195	-1.906437
H	0.818675	5.823615	-2.351331
H	-1.520995	4.572155	-2.216419
H	-1.529807	2.924770	-1.522387
C	-0.939600	3.647042	-2.098897
H	-0.761136	3.224242	-3.097813
Si	-2.560096	-2.573638	-0.297577
C	-3.904391	-3.312690	0.833452
C	-3.143462	-2.757514	-2.097479
C	-1.073856	-3.723729	-0.049072
H	-1.410971	-4.749444	-0.266533
H	-0.709036	-3.694378	0.985544
H	-0.242658	-3.483675	-0.720985
H	-3.570974	-3.324190	1.881650
H	-4.065231	-4.357575	0.522766
H	-4.873768	-2.799504	0.785448
H	-3.383312	-3.810983	-2.311519
H	-4.042165	-2.155740	-2.292755
N	-2.234088	-0.850107	0.077230
H	-2.363838	-2.438965	-2.803750
C	-4.122669	-0.186662	2.394374
Si	-3.618731	0.168103	0.594960
C	-5.123883	-0.088231	-0.541399
H	-5.528035	-1.109553	-0.525053
H	-4.862716	0.160588	-1.580970
H	-5.927546	0.593732	-0.221768
C	-3.212710	2.015915	0.514643

H	-4.018339	2.561650	1.031815
H	-3.189241	2.364579	-0.527131
H	-2.253831	2.280608	0.982297
H	-0.214640	0.916944	-2.818353
C	-0.219823	-0.111717	-3.202807
H	-0.072889	-0.078947	-4.291608
H	-1.202778	-0.560576	-3.000301
C	0.907318	-0.924336	-2.545661
C	2.244406	-0.207150	-2.806516
H	2.370114	-0.066040	-3.890920
H	2.247820	0.780627	-2.327385
H	3.099709	-0.791742	-2.445311
N	0.559518	-1.009637	-1.106924
C	0.944774	-2.338601	-3.153664
H	1.127614	-2.273714	-4.236362
H	-0.008784	-2.862024	-2.996372
H	1.750725	-2.938676	-2.709453
H	-0.926466	-0.128899	3.004668
C	2.718370	-1.862785	-0.074343
C	1.321480	-1.349620	-0.043261
C	2.949764	-3.226451	-0.312054
C	4.253615	-3.727356	-0.326751
C	5.336485	-2.870873	-0.106809
C	5.110890	-1.510426	0.128283
C	3.809150	-1.006294	0.145063
C	1.536005	-2.571345	2.827255
H	1.619865	-2.669281	3.919417
H	2.542045	-2.665997	2.400613
H	0.921520	-3.403255	2.454401
H	2.103488	-3.898661	-0.465419
H	4.422554	-4.790652	-0.507849
H	6.355420	-3.262504	-0.119230
H	5.952939	-0.835823	0.294367
H	3.629856	0.057725	0.306170
C	1.811722	-0.070835	2.962536
H	1.948989	-0.131088	4.052827
H	2.801164	-0.135205	2.491286
H	1.372419	0.905763	2.718190
H	1.619196	1.306155	0.426609
N	0.581417	-1.100838	1.050279
C	0.894220	-1.214683	2.489849
C	-0.454359	-1.099607	3.219267
H	-0.304046	-1.172932	4.305276
H	-1.146237	-1.891585	2.901124
H	-5.001954	0.425178	2.651344
H	-3.308981	0.089669	3.080865
H	-4.376420	-1.238933	2.575294

(v) **Int_1"**

90

Si	-0.437958	-0.336573	0.083916
B	-0.957038	1.923378	0.402726
O	-1.129890	2.689658	-0.799846
O	-		
C	3.421116	1.994883	0.541491
C	2.876381	-1.096586	2.794214
H	3.011449	-1.265792	3.872370
H	3.670150	-0.418804	2.456913
H	2.998797	-2.059421	2.277607
H	4.192901	-1.146761	2.101081
	2.110318	1.248845	
C	-2.855691	3.230596	0.717381
C	-2.475788	3.222314	-0.814499
C	-4.338384	3.011295	1.003225
C	-2.365516	4.493883	1.438853
H	-1.299859	4.669868	1.237157
H	-2.488508	4.347676	2.521301
H	-2.935071	5.386593	1.142118
H	-4.510553	3.019668	2.089310
H	-4.683263	2.047185	0.610741
H	-4.944276	3.813501	0.555191
C	-2.432305	4.605886	-1.460366
H	-2.140557	4.507907	-2.515862
H	-1.701538	5.256182	-0.964551
H	-3.420174	5.089586	-1.421617
H	-4.395207	2.643318	-1.713494
H	-3.344583	1.275738	-1.247666
C	-3.354566	2.292336	-1.657857
H	-2.950952	2.252976	-2.679685
Si	-0.106990	-3.393354	-0.727128
C	-0.547233	-5.009513	0.180479
C	-0.426528	-3.649563	-2.582228
C	1.764751	-3.237236	-0.474320
H	2.220151	-4.175232	-0.827564
H	2.019646	-3.111097	0.585762
H	2.200076	-2.407990	-1.041832
H	-0.266855	-4.951917	1.242615
H	0.047500	-5.815454	-0.277780

H	-1.603500	-5.300969	0.118761
H	0.122784	-4.534721	-2.939112
H	-1.494673	-3.801045	-2.791083
N	-1.062752	-1.994013	-0.121076
H	-0.086830	-2.783581	-3.168258
C	-2.826661	-3.187605	2.079122
Si	-2.758301	-2.319252	0.389223
C	-3.663730	-3.376296	-0.907966
H	-3.238061	-4.378036	-1.054997
H	-3.670939	-2.860224	-1.879746
H	-4.709248	-3.501700	-0.585276
C	-3.767321	-0.732108	0.566706
H	-4.671801	-0.972311	1.148878
H	-4.095720	-0.372451	-0.418254
H	-3.238644	0.089869	1.071057
H	-0.825804	1.068918	-2.573999
C	-0.123172	0.384658	-3.068373
H	-0.045013	0.667871	-4.127278
H	-0.521233	-0.638520	-3.014331
C	1.257639	0.481414	-2.399626
C	1.719533	1.949109	-2.436552
H	1.701713	2.303842	-3.478417
H	1.038139	2.576330	-1.845966
H	2.744503	2.064595	-2.062280
N	1.076182	-0.035099	-1.019268
C	2.261525	-0.407477	-3.156173
H	2.344326	-0.067333	-4.198906
H	1.933424	-1.455930	-3.162232
H	3.260858	-0.354231	-2.702899
H	-0.589942	-1.042616	2.996774
C	3.229601	0.668339	0.124098
C	1.865960	0.077545	0.072450
C	4.338492	-0.109990	-0.240962
C	5.624572	0.432029	-0.187381
C	5.812092	1.753610	0.228448
C	4.708450	2.532704	0.591664
-0.548870			
H	6.481986	-0.181938	-0.469654
H	6.817486	2.176561	0.268668
H	4.849095	3.567031	0.910861
H	2.553715	2.603172	0.802664
C	1.356946	0.865626	3.232039
H	1.496975	0.750739	4.317280
H	2.121071	1.561962	2.861651
H	0.367951	1.307923	3.049033
H	0.174016	2.018914	0.861480
N	1.168489	-0.427957	1.103738
C	1.476452	-0.509450	2.547655
C	0.419908	-1.452942	3.144651
H	0.584174	-1.567846	4.225171
H	0.459537	-2.443842	2.672487
H	-3.874628	-3.434500	2.311369
H	-2.459887	-2.515531	2.868096
H	-2.239799	-4.113544	2.121055
(vi) **TS_2”**			
90			
Si	4.588603	9.768318	11.196998
Si	1.717995	9.393628	12.247319
Si	3.416508	11.865684	13.096688
O	6.567291	11.475367	9.502857
O	7.512018	10.752760	11.492575
N	5.137275	8.044824	11.425726
N	3.252798	10.341937	12.159292
N	4.235327	8.890410	9.634916
C	5.836196	6.922199	9.226614
C	5.330436	8.080983	10.028372
C	3.944550	9.391146	8.265331
C	7.818414	12.213830	9.636956
C	4.972835	5.832501	9.027994
H	3.972182	5.861564	9.462790
C	6.003155	7.386244	12.429686
C	5.159354	9.414388	7.319402
H	5.979507	10.003626	7.749081
H	4.858974	9.882273	6.369155
H	5.517821	8.402361	7.093298
C	2.846479	8.490908	7.665211
H	3.206418	7.457025	7.564418
H	2.551579	8.851336	6.667796
H	1.957671	8.484218	8.312756
C	4.850937	12.890455	12.419853
H	5.822787	12.405592	12.588920
H	4.857053	13.864060	12.934647
H	4.745302	13.073737	11.341216
C	8.589184	11.416668	10.765394
C	1.846961	12.921955	12.941496
H	1.671983	13.199106	11.891495
H	1.988095	13.849536	13.517985

H	0.942676	12.428361	13.322119
C	3.407531	10.825937	8.409569
H	2.574982	10.865466	9.127067
H	3.037726	11.191050	7.440316
H	4.206535	11.500354	8.751805
C	5.394819	4.723275	8.291191
H	4.715753	3.881202	8.143195
C	5.600047	5.902409	12.533002
H	4.528549	5.806920	12.759203
H	6.173407	5.407784	13.331590
H	5.800247	5.374054	11.591084
C	7.123228	6.883809	8.677831
H	7.782738	7.740528	8.826472
C	5.711930	8.083700	13.767841
H	6.050076	9.131173	13.737499
H	6.245763	7.577910	14.585275
H	4.635913	8.070880	13.993998
C	0.428559	10.135877	11.067929
H	0.289394	11.214207	11.224813
H	-0.542271	9.638690	11.220079
H	0.725047	9.978122	10.020842
C	7.474335	13.653474	10.027599
H	6.776597	14.062733	9.283325
H	8.373476	14.286370	10.043948
H	6.991081	13.702778	11.010034
C	1.949779	7.577383	11.780877
H	2.403975	7.477741	10.786922
H	0.957107	7.099002	11.777648
H	2.589666	7.051564	12.501072
C	7.511535	7.485675	12.136176
H	7.778220	6.946771	11.217525
H	8.072002	7.027153	12.965658
H	7.824113	8.532297	12.036947
C	8.513173	12.212992	8.275692
H	8.648333	11.194215	7.892140
H	9.496840	12.702405	8.335378
H	7.898090	12.769114	7.554145
C	9.364246	12.287322	11.748394
H	8.704687	12.994081	12.266941
H	10.151621	12.854939	11.230636
H	9.843898	11.648384	12.503331
C	6.683321	4.691123	7.747020
H	7.013268	3.824371	7.170907
C	3.775178	11.499113	14.923055
H	2.952737	10.963480	15.415550
H	3.941356	12.442925	15.465613
H	4.685121	10.887920	15.016850
C	9.506178	10.320372	10.208002
H	9.879005	9.710271	11.042278
H	10.369126	10.743260	9.674393
H	8.958075	9.659016	9.523072
C	1.029745	9.414426	14.018725
H	1.745934	8.962707	14.720822
H	0.113049	8.804358	14.034693
H	0.769594	10.415791	14.386729
B	6.452394	10.555410	10.572526
C	7.546827	5.774421	7.942554
H	8.552775	5.756837	7.518496
H	6.438205	9.144520	9.983561

(vii) **Product"**

90

Si	4.461587	9.776114	11.243743
Si	1.769955	8.551856	12.140199
Si	2.190976	11.578242	12.386719
O	6.629901	11.748267	10.691316
O	5.977416	11.864598	12.896977
N	5.366874	8.235762	11.361383
N	2.895069	9.962454	12.024686
N	4.483147	9.172129	9.566885
C	5.350681	6.801097	9.261046
C	5.531032	8.176723	9.883281
C	4.370473	9.809165	8.245517
C	7.423787	12.848863	11.263688
C	4.139865	6.105319	9.373630
H	3.307989	6.579822	9.893756
C	6.421194	7.772637	12.281170
C	5.740101	10.255676	7.691401
H	6.255692	10.901327	8.416648
H	5.606080	10.812321	6.751007
H	6.383343	9.389950	7.472306
C	3.703674	8.850936	7.236874
H	4.308441	7.946738	7.087662
H	3.580545	9.347057	6.261514
H	2.713367	8.540045	7.599125
C	3.202361	13.066939	11.774681
H	4.056480	13.272922	12.429264
H	2.523647	13.934470	11.811914

H	3.558671	12.974540	10.739946
C	7.209354	12.672217	12.821668
C	0.521598	11.788865	11.493238
H	0.689249	11.807739	10.405360
H	0.091045	12.761229	11.780867
H	-0.225610	11.015339	11.707523
C	3.477680	11.045759	8.416284
H	2.519309	10.772774	8.882467
H	3.270002	11.509685	7.441420
H	3.977871	11.796342	9.046962
C	3.995053	4.835738	8.815388
H	3.045454	4.303827	8.909709
C	6.425946	6.231059	12.365227
H	5.455385	5.859968	12.721621
H	7.206759	5.890413	13.062797
H	6.623026	5.779657	11.383393
C	6.410938	6.204104	8.568772
H	7.356814	6.746059	8.471922
C	6.100432	8.341410	13.672976
H	6.147736	9.440330	13.682571
H	6.822080	7.964053	14.412319
H	5.092946	8.037528	13.989154
C	0.937955	8.265235	10.458645
H	0.287880	9.109617	10.186878
H	0.327746	7.349369	10.470219
H	1.706180	8.167540	9.678511
C	6.832896	14.142203	10.699017
H	6.880876	14.101826	9.602095
H	7.397893	15.021502	11.038844
H	5.781098	14.264565	10.988563
C	2.634845	6.968163	12.712433
H	3.505054	6.718058	12.097331
H	1.908881	6.140263	12.673796
H	2.971439	7.075380	13.754295
C	7.825301	8.246273	11.844903
H	8.154700	7.735859	10.927977
H	8.566216	8.030190	12.629364
H	7.827000	9.327744	11.646207
C	8.864304	12.682607	10.795177
H	9.265360	11.695917	11.056698
H	9.508628	13.454097	11.241585
H	8.907963	12.791477	9.702443
C	6.969677	13.971808	13.581723
H	6.100988	14.518639	13.195265
H	7.852061	14.624872	13.515866
H	6.789430	13.747130	14.642259
C	5.064162	4.241241	8.131218
H	4.950961	3.246797	7.694492
C	2.020598	11.820773	14.259574
H	1.343823	11.096290	14.729680
H	1.644874	12.833228	14.475290
H	3.013086	11.718889	14.724466
C	8.306737	11.862381	13.513529
H	7.992623	11.648448	14.544527
H	9.252180	12.421343	13.547961
H	8.484361	10.903816	13.009618
C	0.430346	8.809571	13.468442
H	0.880588	8.837113	14.471224
H	-0.222324	7.922476	13.424906
H	-0.206098	9.694419	13.348117
B	5.748530	11.299981	11.655400
C	6.273844	4.929764	8.006464
H	7.110627	4.475532	7.471035
H	6.535673	8.539518	9.581936

(viii) **TS_2'**

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Si	0.069077	1.167174	0.590990
Si	-2.786398	0.564911	1.726463
C	-3.277563	1.332913	3.396220
C	-4.327598	0.245532	0.656895
C	-2.148890	-1.180578	2.119950
H	-2.962427	-1.695680	2.654723
H	-1.260270	-1.193636	2.760518
H	-1.929227	-1.744597	1.204251
H	-2.397707	1.388043	4.054445
H	-4.037693	0.709404	3.892290
H	-3.682481	2.349060	3.299114
H	-4.898827	-0.584778	1.101069
H	-4.998846	1.108389	0.572941
N	-1.610346	1.619381	0.888094
H	-4.029859	-0.057913	-0.358448
C	-1.221834	4.572718	1.481834
Si	-2.101132	3.288919	0.402723
C	-3.971062	3.600911	0.588027
H	-4.393815	3.361817	1.571976

H	-4.552232	3.076864	-0.182618
H	-4.108617	4.682271	0.425131
C	-1.752912	3.584000	-1.435877
H	-2.126079	4.584037	-1.708851
H	-2.287136	2.843136	-2.048829
H	-0.680167	3.548475	-1.663008
H	-0.595746	0.976019	-2.311068
C	-1.063954	-0.018209	-2.329448
H	-1.255292	-0.294343	-3.376118
H	-2.025122	0.047758	-1.800905
C	-0.147944	-1.060767	-1.668971
C	1.205526	-1.074589	-2.405747
H	1.045811	-1.242781	-3.481336
H	1.719389	-0.111728	-2.271566
H	1.859471	-1.873235	-2.031361
N	0.010637	-0.622853	-0.263918
C	-0.821999	-2.441356	-1.750201
H	-1.031307	-2.690214	-2.801387
H	-1.774860	-2.437975	-1.200933
H	-0.181018	-3.229901	-1.336185
H	0.596804	1.766502	3.469498
C	1.594239	-2.349705	0.670647
C	0.833047	-1.074942	0.682419
C	0.965269	-3.569584	0.956272
C	1.705452	-4.753832	0.956609
C	3.072042	-4.728174	0.659315
C	3.699529	-3.512776	0.364069
C	2.966178	-2.324788	0.373850
C	1.671525	-1.520320	3.597610
H	2.003831	-1.412113	4.640218
H	2.390188	-2.168073	3.082613
H	0.692939	-2.021792	3.604627
H	-0.099010	-3.584826	1.197570
H	1.212733	-5.699675	1.189536
H	3.648384	-5.655290	0.658239
H	4.764942	-3.488933	0.127883
H	3.446131	-1.370749	0.146436
C	2.991734	0.489687	2.847397
H	3.458637	0.559130	3.841591
H	3.628409	-0.133803	2.205170
H	2.939820	1.488087	2.395843
N	0.923479	-0.117842	1.637819
C	1.582715	-0.117257	2.972905
C	0.728844	0.765523	3.902983
H	1.227941	0.861449	4.878120
H	-0.262200	0.320246	4.068862
H	-1.543305	5.587053	1.198437
H	-0.133665	4.501375	1.359791
H	-1.466102	4.413501	2.543148
B	1.446240	2.340484	-0.094138
O	1.339368	3.611381	-0.703127
O	2.799504	1.901966	-0.067985
C	3.595773	2.929470	-0.724105
C	3.816042	2.473855	-2.171723
H	2.858438	2.406153	-2.706979
H	4.275260	1.475097	-2.160187
H	5.497605	2.113452	-0.113959
H	4.481616	3.156187	-2.720408
C	4.931592	3.048623	0.002664
H	5.535184	3.868779	-0.415440
H	4.787055	3.227797	1.075224
H	3.848203	5.597131	-1.803950
C	2.823829	5.197103	-1.765756
C	2.675304	4.200048	-0.624095
H	2.588574	4.735019	-2.732687
H	2.133323	6.038659	-1.611776
C	2.797558	4.912673	0.727153
H	2.651306	4.205744	1.557333
H	2.015491	5.682192	0.794943
H	3.775320	5.401122	0.842418
H	0.915758	2.469023	1.493919

(ix) **Product'**

90

Si	-0.130617	1.225805	1.397478
Si	-2.435400	-0.116020	-0.337772
C	-3.943704	-0.658413	0.690376
C	-2.999292	0.335149	-2.099725
C	-1.363763	-1.668473	-0.526714

H	-1.973355	-2.426778	-1.043169	H	3.809214	1.317999	-2.553369	H	1.460573	-0.932302	4.963858
H	-1.043550	-2.083153	0.436866	H	3.385122	1.936569	-0.939290	H	2.589306	-0.323453	3.725955
H	-0.468836	-1.466984	-1.126193	H	4.062242	0.292919	-1.119322	H	1.139926	0.622149	4.143379
H	-3.632070	-0.884931	1.721423	N	1.282228	0.279185	-0.446119	N	0.774726	-0.348002	1.637744
H	-4.381683	-1.572278	0.259117	C	1.982074	-0.756704	-2.625193	C	0.736345	-1.141408	2.914267
H	-4.729198	0.107256	0.735516	H	2.339187	-0.490624	-3.631881	C	-0.738686	-1.289320	3.349117
H	-3.544049	-0.516413	-2.536909	H	0.972477	-1.180930	-2.725118	H	-0.781179	-1.830137	4.305607
H	-3.660430	1.211174	-2.139919	H	2.650105	-1.527996	-2.223401	H	-1.305987	-1.869151	2.606954
N	-1.621324	1.269617	0.427761	H	-1.229964	-0.318782	3.482309	H	-2.451293	4.892148	1.810561
H	-2.126262	0.541971	-2.736529	C	2.826371	-1.372736	0.599021	H	-0.909113	4.057609	2.084672
C	-1.983149	3.900838	1.919905	C	1.616145	-0.493572	0.546197	H	-2.395509	3.421206	2.818735
Si	-2.386821	2.886840	0.360184	C	2.855833	-2.628803	-0.023708	B	1.218446	2.737672	1.248383
C	-4.288324	2.817572	0.327897	C	4.010150	-3.413539	0.022514	O	1.471357	3.613852	0.209320
H	-4.684141	2.383717	1.257259	C	5.151454	-2.947620	0.683728	O	1.980819	3.014660	2.372533
H	-4.708360	2.262373	-0.521184	C	5.131279	-1.692194	1.301194	C	2.963522	4.050529	2.016999
H	-4.654402	3.854726	0.259311	C	3.974822	-0.909863	1.260681	C	4.288602	3.327585	1.766883
C	-1.787225	3.849143	-1.159803	C	1.282475	-2.575337	2.779632	H	4.205432	2.611620	0.938195
H	-2.263052	4.841682	-1.199705	H	1.010790	-3.126730	3.691634	H	4.561692	2.768815	2.673428
H	-2.025114	3.312481	-2.089592	H	2.372154	-2.614754	2.682807	H	3.522376	4.463842	4.057999
H	-0.697441	3.984126	-1.110709	H	0.832919	-3.097820	1.923590	H	5.097391	4.035737	1.539675
H	1.102156	2.504454	-1.866997	H	1.960286	-3.001689	-0.523627	C	3.101666	5.003479	3.198234
C	1.118755	1.578470	-2.454619	H	4.017371	-4.394127	-0.457590	H	3.780937	5.831938	2.949022
H	1.534178	1.792832	-3.451115	H	6.053773	-3.561207	0.718568	H	2.132593	5.421226	3.497814
H	0.083144	1.229533	-2.571281	H	6.019006	-1.321556	1.817533	H	4.029024	5.836231	-0.002234
C	1.960720	0.505622	-1.738657	H	3.956020	0.070100	1.741792	C	3.336505	5.061800	-0.363967
C	3.396473	1.039124	-1.571776	C	1.528561	-0.396071	4.004919	C	2.332616	4.693435	0.721834

H	3.921311	4.194253	-0.690802	H	0.870675	6.142272	0.092481
H	2.801953	5.462365	-1.236258	H	1.991188	6.762124	1.333726
C	1.414956	5.883371	1.011379	H	-0.627603	1.448048	2.813686
H	0.675519	5.645737	1.787119				

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