Electronic Supplementary Material (ESI) for Chemical Science.


# Silicon Clusters with Six and Seven Unsubstituted Vertices *via* a Two-step Reaction from Elemental Silicon

## Supporting Information

## 1. PXRD of the Zintl phase precursor $K_{12}Si_{17}$

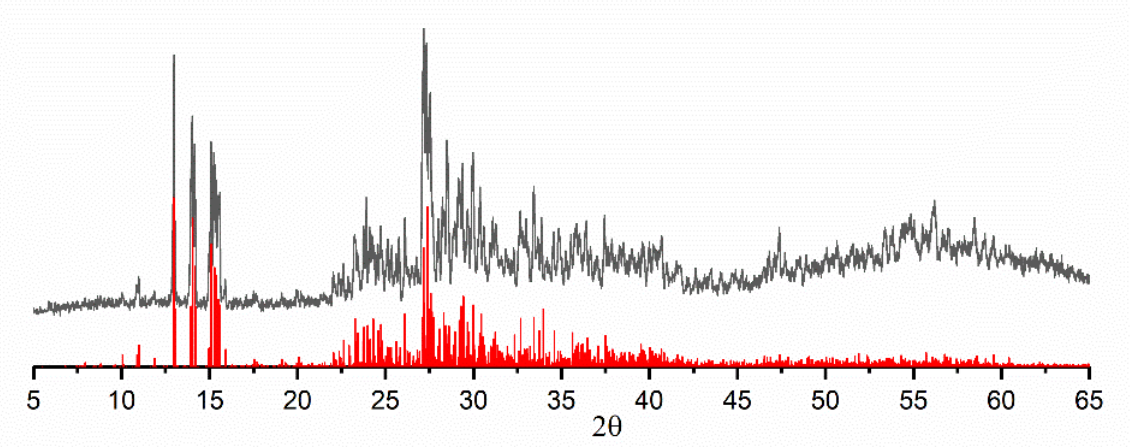



**Figure SI 1.** Powder X-ray diffractogram of the Zintl phase precursor $K_{12}Si_{17}$ (gray: *measd*.; red: *calcd*. from single crystal data).[1]

## 2. ESI-MS spectra

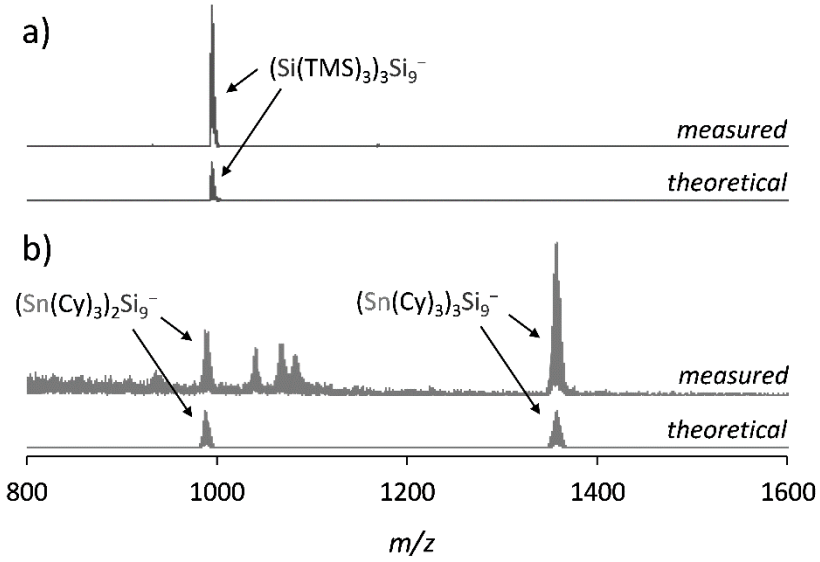



**Figure SI 2.** a) ESI-MS spectrum of the bulk material containing **1a** in thf (*m/z* = 996, **1a**); b) ESI-MS spectrum of the bulk material containing **2a** in pyridine (*m/z* = 1357, **2a**; *m/z* = 989, **2b**).

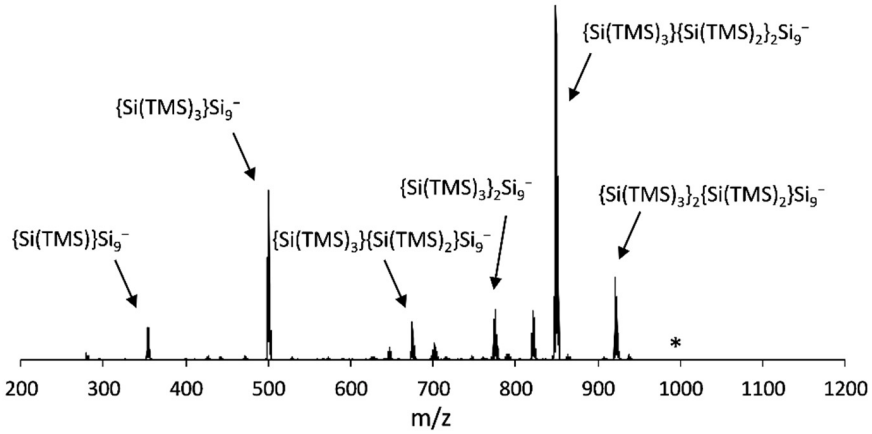



**Figure SI 3.** ESI-MS fragmentation spectrum of the $\{Si(TMS)_3\}_3Si_9^-$ (**1a**) mass peak (fragmented mass at *m/z* = 996: *) in thf; negative mode, 4000 V, 300 °C.

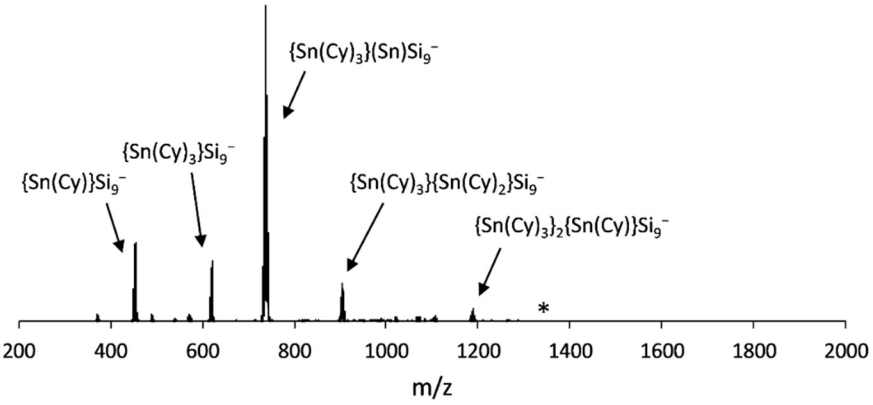



**Figure SI 4.** ESI-MS fragmentation spectrum of the $(SnCy_3)_3Si_9^-$ (**2a**) mass peak (fragmented mass at *m/z* = 1357: *) in pyridine; negative mode, 4500 V, 300 °C.

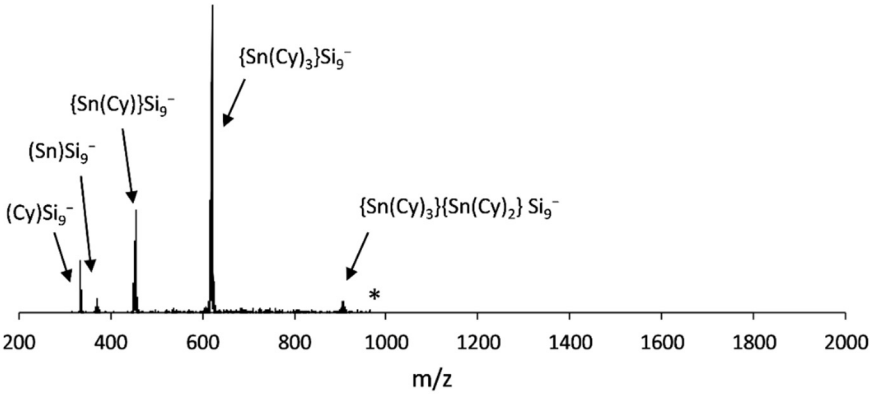



**Figure SI 5.** ESI-MS fragmentation spectrum of the $(SnCy_3)_2Si_9^-$ mass peak (fragmented mass at *m/z* = 989: *) in pyridine; negative mode, 3500 V, 300 °C.

## 3. NMR spectra

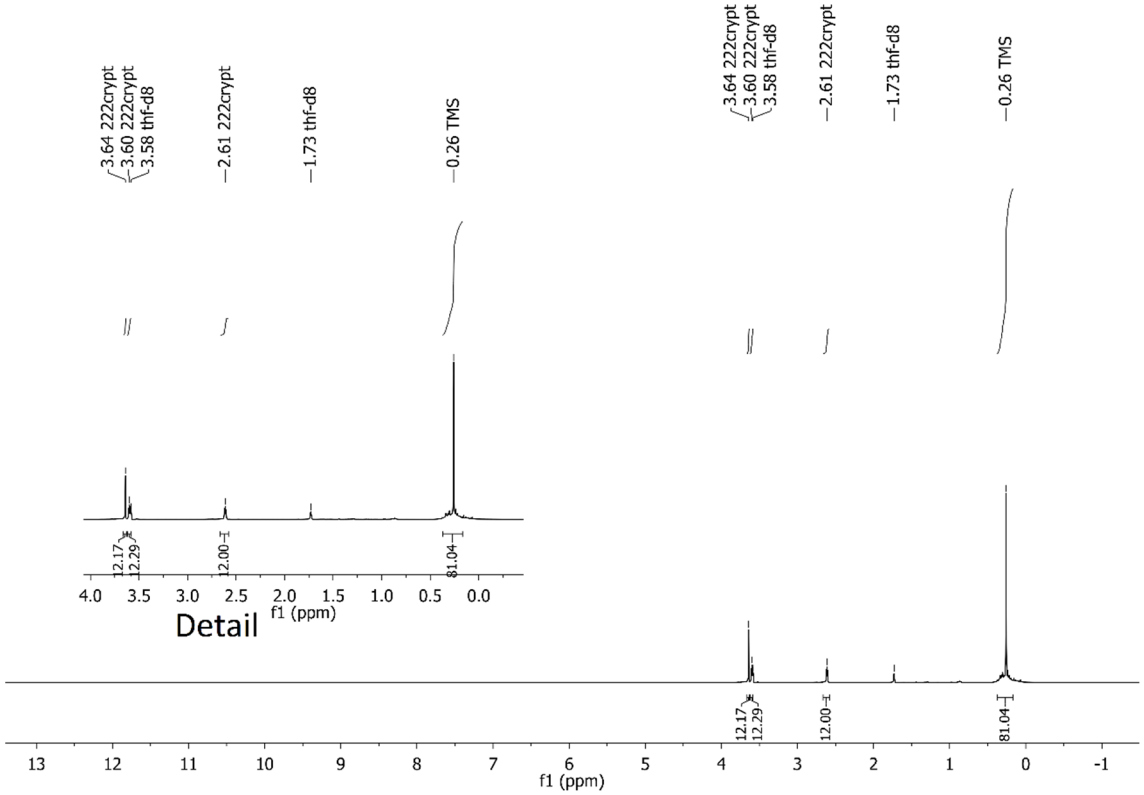



**Figure SI 6.** $^{1}$H NMR (thf-*d8*) spectrum of the bulk material containing **1a**.

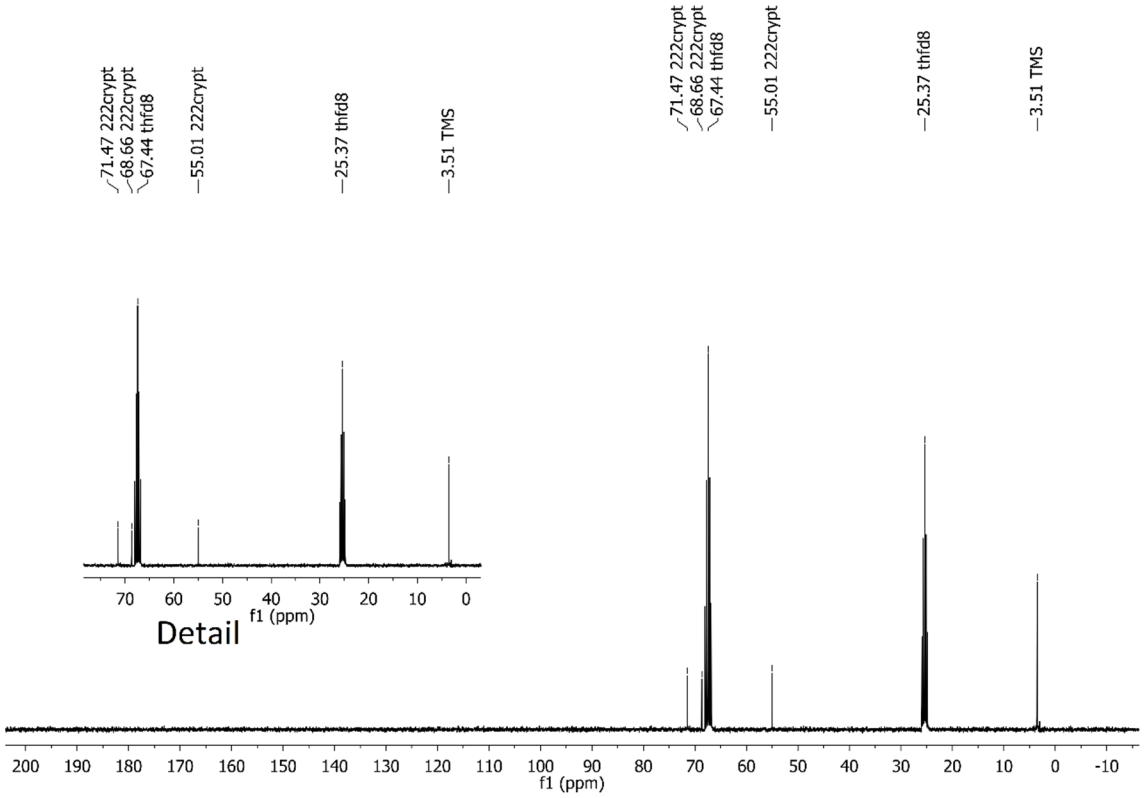



**Figure SI 7.** $^{13}$C{$^{1}$H} NMR (thf-*d8*) spectrum of the bulk material containing **1a**.

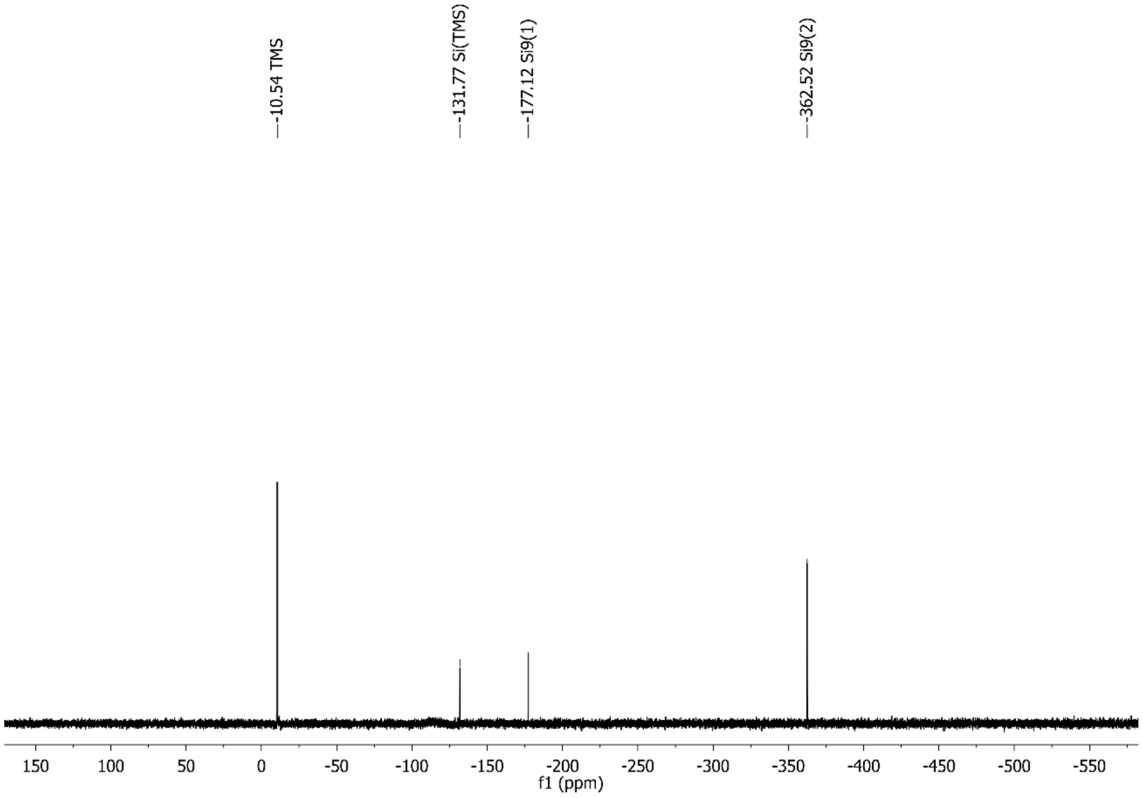



**Figure SI 8.** $^{29}Si\{^{1}H\}$ NMR (thf-*d8*) spectrum of the bulk material containing **1a**.

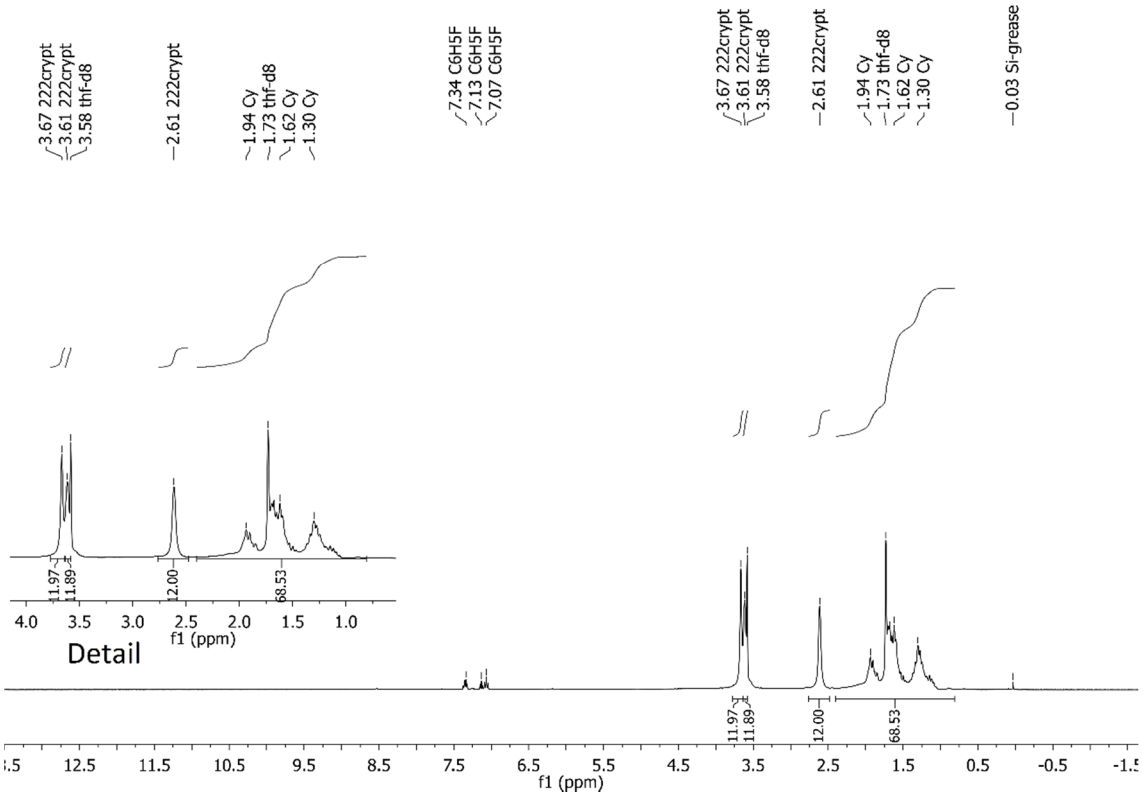



**Figure SI 9.** $^{1}H$ NMR (thf-*d8*) spectrum of the bulk material containing **2a**.

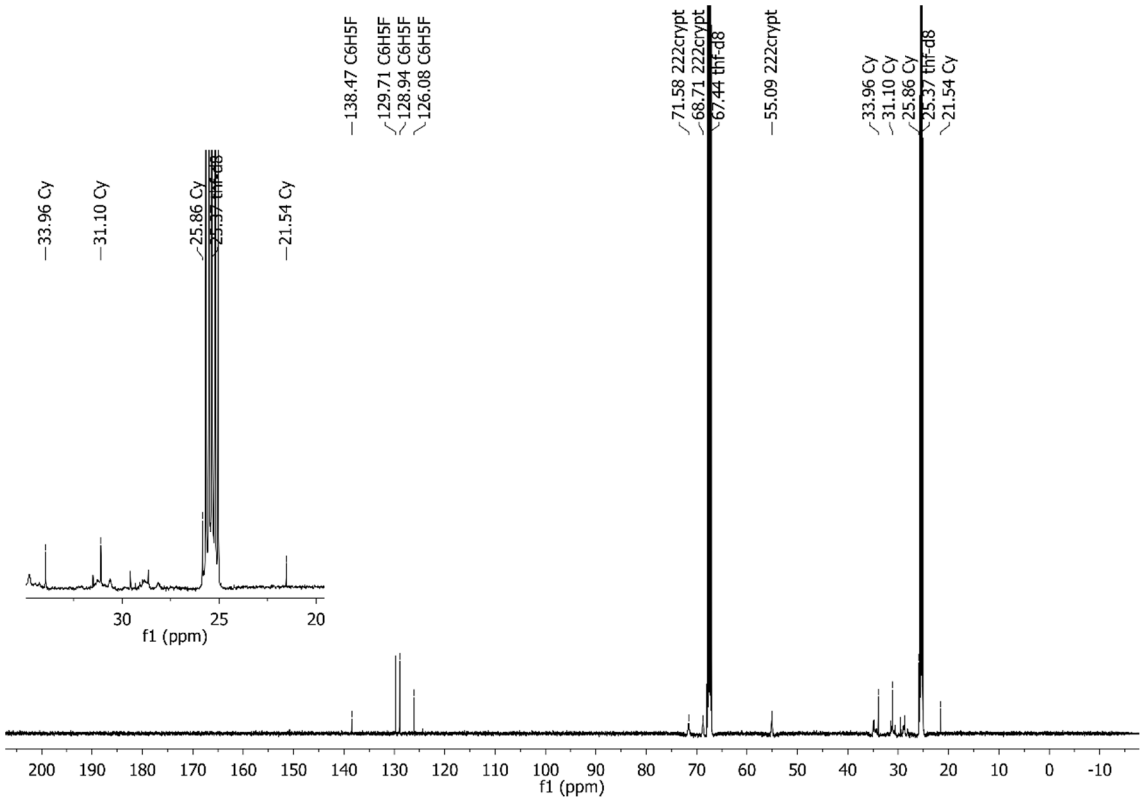



**Figure SI 10.** $^{13}C\{^{1}H\}$ NMR (thf-*d8*) spectrum of the bulk material containing **2a**.

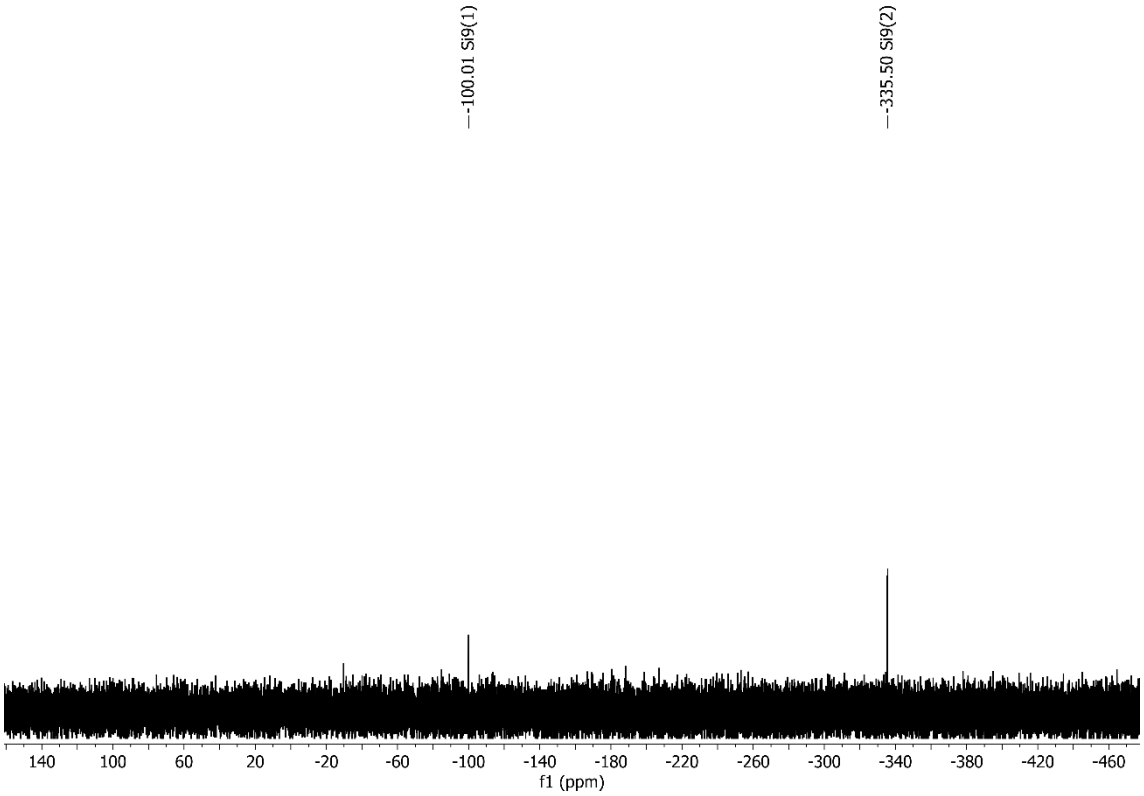



**Figure SI 11.** $^{29}Si\{^{1}H\}$ NMR (thf-*d8*) spectrum of the bulk material containing **2a**.

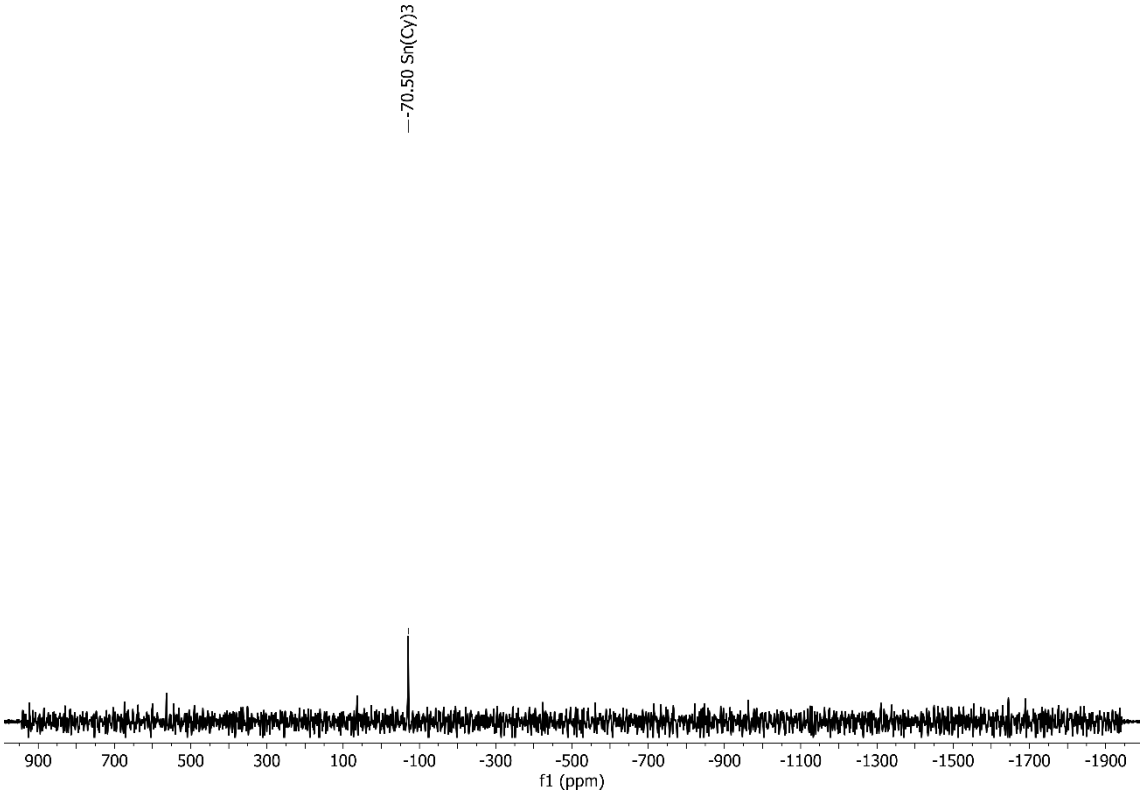



**Figure SI 12.** $^{119}Sn\{^{1}H\}$ NMR (thf-*d8*) spectrum of the bulk material containing **2a**.

## 4. Crystallographic details

**Table SI 1.** Crystallographic data and details of the structure determinations of (K-222crypt)$_2$**1b** and (K-222crypt)$_2$**2b**.

| **Compound** | **(K-222crypt)$_2$1b ·C$_6$H$_5$F** | **(K-222crypt)$_2$2b** |
|---|---|---|
| formula | $C_{60}H_{131}FK_2N_4O_{12}Si_{17}$ | $C_{72}H_{138}K_2N_4O_{12}Si_9Sn_2$ |
| crystal shape | yellow block | yellow block |
| crystal size [mm] | 0.4 x 0.2 x 0.3 | 0.4 x 0.2 x 0.1 |
| fw (g·mol$^{-1}$) | 1675.41 | 1820.25 |
| space group (no) | $P_n$ (7) | $C2/c$ (15) |
| $a$ (Å) | 16.4939(9) | 31.6324(14) |
| $b$ (Å) | 25.3561(17) | 11.8423(7) |
| $c$ (Å) | 22.6197(12) | 25.7817(12) |
| $\alpha$ (deg) | 90 | 90 |
| $\beta$ (deg) | 90.756(4) | 108.231(3) |
| $\gamma$ (deg) | 90 | 90 |
| $V$ (Å$^3$) | 9459.2(10) | 9173.0(8) |
| $Z$ | 4 | 4 |
| $T$ (K) | 120(2) | 150(2) |
| $\rho_{calc}$ (g·cm$^{-3}$) | 1.176 | 1.318 |
| $\mu$ (mm$^{-1}$) | 0.366 | 0.806 |
| measured reflections | 60136 | 97474 |
| $R_{int}$ | 0.0524 | 0.1068 |
| | $-20 < h < 20$ | $-38 < h < 38$ |
| $hkl$ range | $-27 < k < 29$ | $-14 < k < 14$ |
| | $-26 < l < 27$ | $-31 < l < 31$ |
| 2 θ range | 5.416 – 52.000 | 5.188 – 51.994 |
| independent reflections | 24142 | 9014 |
| reflections [$I > 2\,\sigma(I)$] | 12835 | 5313 |
| parameters / restraints | 1892 / 422 | 511 / 0 |
| $R_1$ [$I > 2\,\sigma(I)$ / all data] | 0.0729 / 0.1411 | 0.0444 / 0.0978 |
| w$R_2$ [$I > 2\,\sigma(I)$ / all data] | 0.1606 / 0.1880 | 0.0836 / 0.0997 |
| goodness of fit | 0.932 | 0.928 |
| largest difference peak/hole [e Å$^{-3}$] | 0.925 / −0.448 | 1.074 / −0.365 |
| CCDC number | 1896557 | 1896556 |

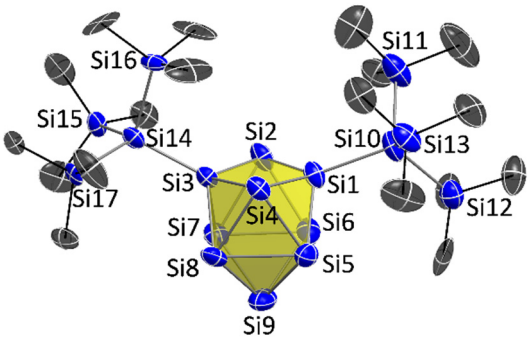



**Figure SI 13.** Molecular structure of $\{Si(TMS)_3\}_2Si_9^{2-}$ (**1b**) from the single crystal structure determination: Si and C atoms (in blue and black, respectively) are shown as ellipsoids at 50% probability level, H atoms are omitted, minor occupations of the disordered silyl groups are not shown.

**Table SI 2.** Selected interatomic distances from the single crystal structure determination of $(K\text{-}222crypt)_2$**1b**.

| Atom 1 | Atom 2 | Distance [Å] | Atom 1 | Atom 2 | Distance [Å] |
|---|---|---|---|---|---|
| Si1 | Si2 | 2.396(5) | Si4 | Si8 | 2.488(5) |
| Si2 | Si3 | 2.395(4) | Si4 | Si5 | 2.485(6) |
| Si3 | Si4 | 2.398(5) | Si5 | Si6 | 2.772(6) |
| Si4 | Si1 | 2.427(5) | Si6 | Si7 | 2.569(6) |
| Si1 | Si3 | 2.992(6) | Si7 | Si8 | 2.738(5) |
| Si2 | Si4 | 3.759(6) | Si8 | Si5 | 2.585(6) |
| Si1 | Si5 | 2.415(6) | Si5 | Si9 | 2.468(6) |
| Si1 | Si6 | 2.425(5) | Si6 | Si9 | 2.470(6) |
| Si2 | Si6 | 2.446(6) | Si7 | Si9 | 2.427(6) |
| Si2 | Si7 | 2.521(5) | Si8 | Si9 | 2.475(7) |
| Si3 | Si7 | 2.418(5) | Si1 | Si10 | 2.357(5) |
| Si3 | Si8 | 2.401(5) | Si3 | Si14 | 2.339(5) |

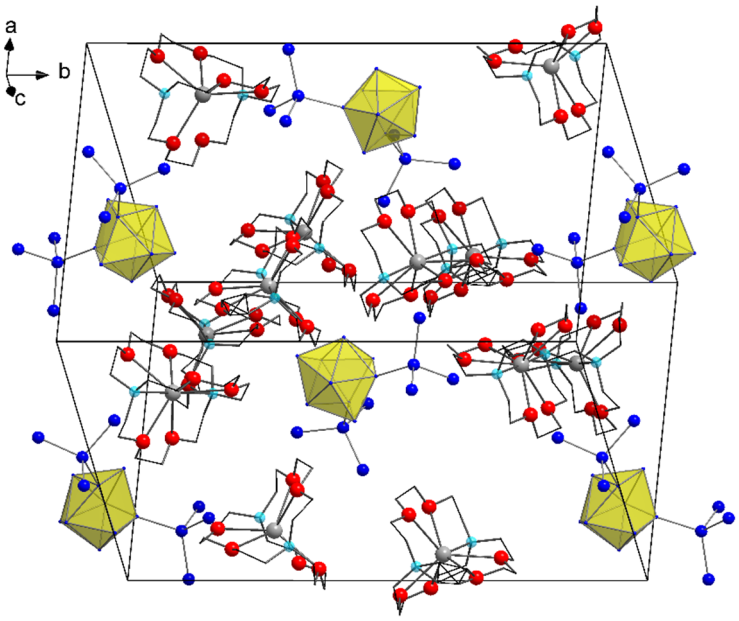



**Figure SI 14.** Extended unit cell of (K-222crypt)$_2$**1b** [$Si_9$ clusters are shown as yellow polyhedra, the Si atoms of the $Si(TMS)_3$ substituents (blue), K atoms (gray), O atoms (red), and N atoms (turquoise) are shown as balls, C atoms of 222crypt are shown as wire-sticks, TMS groups and H atoms of 222crypt are omitted].

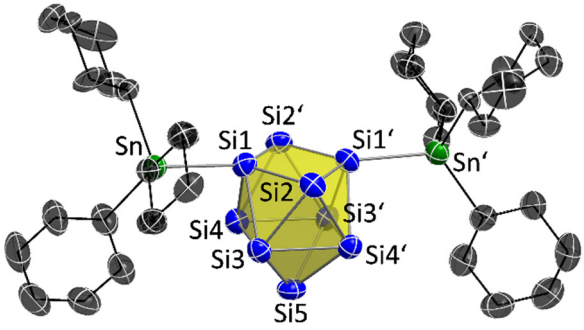



**Figure SI 15.** Molecular structure of $(SnCy_3)_2Si_9^{2-}$ (**2b**) from the single crystal structure determination: Si, Sn and C atoms (blue, green and black, respectively) are shown as ellipsoids at 50% probability level, H atoms are omitted, minor occupation of the disordered Cy group is not shown, symmetry operation (') −x, y, 0.5−z.

**Table SI 3.** Selected interatomic distances from the single crystal structure determination of (K-222crypt)$_2$**2b**.

| Atom 1 | Atom 2 | Distance [Å] | Atom 1 | Atom 2 | Distance [Å] |
|---|---|---|---|---|---|
| Si1 | Si2 | 2.430(2) | Si2' | Si4 | 2.466(2) |
| Si2 | Si1' | 2.433(2) | Si3 | Si4 | 2.664(2) |
| Si1' | Si2' | 2.430(2) | Si3' | Si4 | 2.565(2) |
| Si2' | Si1 | 2.433(2) | Si3' | Si4' | 2.664(2) |
| Si1 | Si4 | 2.457(2) | Si3 | Si4' | 2.565(2) |
| Si1 | Si3 | 2.456(2) | Si4 | Si5 | 2.436(2) |
| Si2 | Si3 | 2.478(2) | Si3 | Si5 | 2.432(2) |
| Si2 | Si4' | 2.466(2) | Si4' | Si5 | 2.436(2) |
| Si1' | Si4' | 2.457(2) | Si3' | Si5 | 2.432(2) |
| Si1' | Si3' | 2.456(2) | Si1 | Sn | 2.578(1) |
| Si2' | Si3' | 2.478(2) | Si1' | Sn' | 2.578(1) |

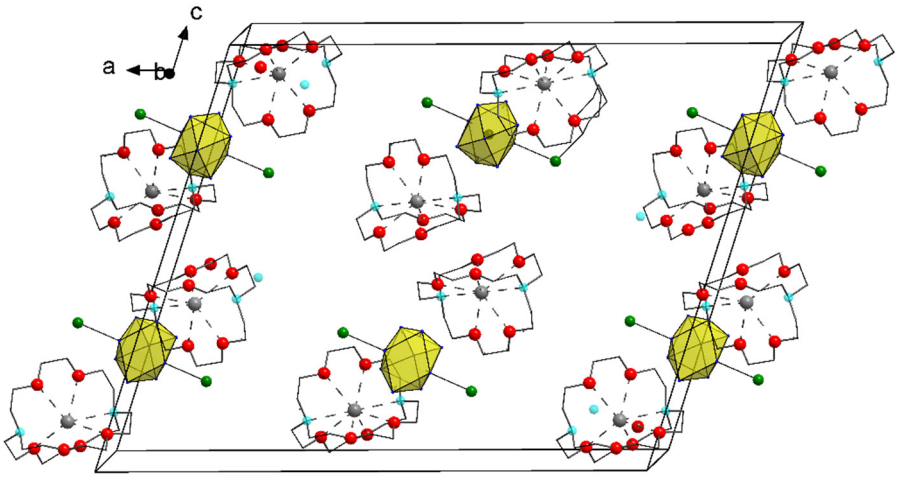
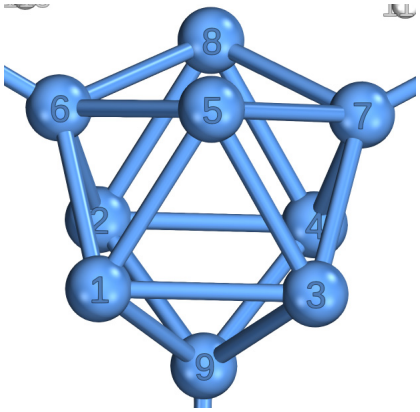



**Figure SI 16.** Extended unit cell of (K-222crypt)$_2$**2b** [$Si_9$ clusters are shown as yellow polyhedra, Sn atoms (green), K atoms (gray), O atoms (red), and N atoms (turquoise) are shown as balls, C atoms of 222crypt are shown as wire-sticks, Cy groups and H atoms of 222crypt are omitted].

## 5. Computational details

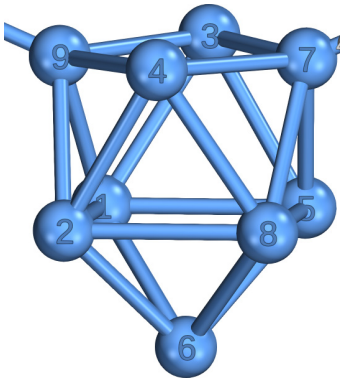
Quantum chemical calculations were carried out using the TURBOMOLE program package.[2, 3] We used the PBE0 hybrid density functional method[4, 5] and a triple-zeta-valence quality basis set with polarization functions (def2-TZVP for Si and Sn, def-TZVP for C and H).[6] Multipole-accelerated resolution-of-the-identity technique was used to speed up the calculations.[7-9] The COSMO continuum solvation model was used to counter the twofold negative charge of the dianions.[10] The molecular structures of the di- and tri-substituted clusters were fully optimized within $C_{2v}$ and $C_{3v}$ point group symmetry, respectively. In the 0 K calculations, the symmetry of the tri-substituted clusters is reduced from the ideal $D_{3h}$ to $C_{3v}$ because the ligands cannot rotate freely, but this does not affect the interpretation of the results. A hypothetical tetra-substituted cluster $\{Si(TMS)_3\}_4Si_9$ was optimized without any symmetry constraints. The optimized structures of the studied systems in XYZ format are reported below. Harmonic frequency calculations were carried out to confirm that the structures are true local minima (numerical frequency calculation with the COSMO solvent model). The structure **1b** had three imaginary vibrational modes corresponding to a rotation of methyl and TMS groups (140*i*, 63*i*, 55*i*). The rotational imaginary modes disappear by lowering the point group symmetry to $C_2$ (the ligands retain the same overall orientation as in the $C_{2v}$ point group). In the Raman spectrum calculations ($T$ = 298.15 K, experimental laser wavelength, unpolarized radiation, scattering angle of 90°),[11, 12] the COSMO solvent model was not used in the dynamic polarizability derivatives calculation. The Raman intensities are given relative to the most intensive peak. The harmonic frequencies of **2b** were scaled by a factor of 0.985 to facilitate comparisons with the experimental spectrum. The final Raman spectra were convoluted using Lorenzian peak profiles with FWHM of 10 $cm^{-1}$. The peak assignment was carried out by visual inspection of the normal modes (Jmol program package[13]). Intrinsic Atomic Orbitals (IAOs) and Intrinsic Bond Orbitals (IBO) were used to analyze the partial charges and bonding of the clusters, respectively.[14]

**Table SI 4.** Analysis of the Intrinsic Bond Orbitals (IBO) for **1a**. For each IBO, the atoms forming the IBO and their contributions in percentages are shown (in most cases, the contributions do not add up to 100%, because small contributions from other atoms are not listed separately). Each IBO contains two electrons. For the numbering scheme, see the figure below ([a] not a cluster atom).




| Atom 1 | % | Atom 2 | % | Atom 3 | % |
|---|---|---|---|---|---|
| Lone pairs (12 electrons in total) | | | | | |
| 1 | 91 | | | | |
| 2 | 91 | | | | |
| 4 | 91 | | | | |
| 5 | 91 | | | | |
| 8 | 91 | | | | |
| 9 | 91 | | | | |
| Exo-bonds (6 electrons in total) | | | | | |
| 9 | 51 | [a] | 46 | | |
| 7 | 51 | [a] | 46 | | |
| 6 | 51 | [a] | 46 | | |
| 3c–2e bonds in trigonal prism faces (4 electrons in total) | | | | | |
| 5 | 33 | 3 | 33 | 1 | 33 |
| 8 | 33 | 2 | 33 | 4 | 33 |
| 5c–6e system of the three trigonal prism faces and their capping atoms (18 electrons in total) | | | | | |
| 6 | 46 | 2 | 31 | 8 | 18 |
| 6 | 49 | 5 | 33 | 8 | 9 |
| 6 | 47 | 1 | 35 | 8 | 9 |

**Table SI 5.** Analysis of the Intrinsic Bond Orbitals (IBO) for **1b**. For each IBO, the atoms forming the IBO and their contributions in percentages are shown (in most cases, the contributions do not add up to 100%, because small contributions from other atoms are not listed separately). Each IBO contains two electrons. For the numbering scheme, see the figure below ([a] not a cluster atom).




| Atom 1 | % | Atom 2 | % | Atom 3 | % |
|---|---|---|---|---|---|
| Lone pairs (14 electrons in total) | | | | | |
| 1 | 94 | | | | |
| 2 | 93 | | | | |
| 3 | 93 | | | | |
| 4 | 92 | | | | |
| 5 | 92 | | | | |
| 6 | 92 | | | | |
| 8 | 92 | | | | |
| Exo-bonds (4 electrons in total) | | | | | |
| 9 | 51 | [a] | 46 | | |
| 7 | 51 | [a] | 46 | | |
| 3c–2e bonds with one open-square atom and two closed square atoms (8 electrons in total) | | | | | |
| 7 | 41 | 5 | 29 | 8 | 28 |
| 9 | 42 | 1 | 29 | 2 | 27 |
| 3 | 34 | 5 | 32 | 1 | 32 |
| 4 | 36 | 8 | 31 | 2 | 29 |
| 2c–2e bonds in open square, minor contribution from one closed square atom (8 electrons in total) | | | | | |
| 9 | 48 | 4 | 39 | 2 | 6 |
| 7 | 48 | 4 | 39 | 8 | 6 |
| 7 | 49 | 3 | 39 | 5 | 5 |
| 9 | 49 | 3 | 39 | 1 | 5 |
| 5c–6e system of cap atom and the closed square (6 electrons in total) | | | | | |
| 6 | 38 | 8 | 36 | 2 | 19 |
| 6 | 39 | 1 | 36 | 2 | 16 |
| 6 | 38 | 5 | 38 | 2 | 8 |

**Table SI 6**. Optimized XYZ coordinates of the studied systems [Å].

| $\{Si(TMS)_3\}_2Si_9^{2-}$ (**1b**) | | | | $(SnCy_3)_2Si_9^{2-}$ (**2b**) | | | | $\{Si(TMS)_3\}_4Si_9$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Si | -1.2743517 | 1.3358186 | -3.1399453 | Si | -1.2753634 | 1.344217 | -2.7316151 | Si | -0.3138832 | 0.7008659 | 1.0506022 |
| Si | -1.2743517 | -1.3358186 | -3.1399453 | Si | -1.2753634 | -1.344217 | -2.7316151 | Si | -0.5741312 | 0.7450059 | -2.5078788 |
| Si | 0 | 1.8459512 | -1.0760077 | Si | 0 | 1.8552706 | -0.6760474 | Si | -0.5750799 | -1.7152433 | 0.7111365 |
| Si | 0 | -1.8459512 | -1.0760077 | Si | 0 | -1.8552706 | -0.6760474 | Si | -0.756453 | -1.6634308 | -2.0380319 |
| Si | 1.2743517 | 1.3358186 | -3.1399453 | Si | 1.2753634 | 1.344217 | -2.7316151 | Si | 1.7971899 | -0.4427737 | 0.5577963 |
| Si | 0 | 0 | -4.7236547 | Si | 0 | 0 | -4.3102175 | Si | 1.0184658 | 1.4641647 | -0.812898 |
| Si | 1.5434157 | 0 | -1.1356343 | Si | 1.5380697 | 0 | -0.7249815 | Si | 1.1733504 | -2.3001762 | -0.7980015 |
| Si | 1.2743517 | -1.3358186 | -3.1399453 | Si | 1.2753634 | -1.344217 | -2.7316151 | Si | 1.5677971 | -0.4159911 | -2.1895272 |
| Si | -1.5434157 | 0 | -1.1356343 | Si | -1.5380697 | 0 | -0.7249815 | Si | -1.8768885 | -0.0947712 | -0.6231421 |
| Si | 3.7086121 | 0 | -0.1981656 | C | -5.0755216 | 0 | -2.2975266 | Si | 2.3407775 | -4.3215179 | -0.9723541 |
| Si | -3.7086121 | 0 | -0.1981656 | C | -5.8903127 | -1.2548252 | -2.6003642 | Si | -4.1983681 | -0.2052228 | -1.150224 |
| C | 2.4237878 | -1.9665689 | 2.416639 | C | -5.8903127 | 1.2548252 | -2.6003642 | Si | 2.3044001 | 3.3246248 | -1.5607163 |
| H | 2.4171276 | -2.9266684 | 2.9435383 | H | -4.2008555 | 0 | -2.9622829 | C | 4.7673778 | -3.1875098 | -3.2352091 |
| H | 2.5500531 | -1.1739079 | 3.1577716 | C | -6.378622 | -1.2601555 | -4.0487166 | H | 5.800384 | -2.8753199 | -3.4207675 |
| H | 1.4524988 | -1.8301103 | 1.9340826 | H | -6.7629604 | -1.3009855 | -1.9359048 | H | 4.5288542 | -3.9945282 | -3.9323332 |
| C | 2.4237878 | 1.9665689 | 2.416639 | H | -5.3010975 | -2.1574519 | -2.4046945 | H | 4.110819 | -2.3405517 | -3.4508895 |
| H | 2.5500531 | 1.1739079 | 3.1577716 | C | -6.378622 | 1.2601555 | -4.0487166 | C | 1.183006 | -4.431221 | -4.287625 |
| H | 2.4171276 | 2.9266684 | 2.9435383 | H | -6.7629604 | 1.3009855 | -1.9359048 | H | 2.1522569 | -4.0556817 | -4.6224229 |
| H | 1.4524988 | 1.8301103 | 1.9340826 | H | -5.3010975 | 2.1574519 | -2.4046945 | H | 0.7417891 | -5.0144234 | -5.1027541 |
| C | -2.4237878 | 1.9665689 | 2.416639 | C | -7.1736172 | 0 | -4.372602 | H | 0.5322742 | -3.5748091 | -4.0915075 |
| H | -2.4171276 | 2.9266684 | 2.9435383 | H | -6.9863387 | -2.1515343 | -4.2407083 | C | -3.397398 | -0.6809466 | -4.6540158 |
| H | -2.5500531 | 1.1739079 | 3.1577716 | H | -5.5086598 | -1.3209321 | -4.7153339 | H | -3.7576653 | -1.1194529 | -5.5914071 |
| H | -1.4524988 | 1.8301103 | 1.9340826 | H | -6.9863387 | 2.1515343 | -4.2407083 | H | -3.4042183 | 0.4059735 | -4.7585025 |
| C | -2.4237878 | -1.9665689 | 2.416639 | H | -5.5086598 | 1.3209321 | -4.7153339 | H | -2.3658564 | -0.9988614 | -4.4953278 |
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