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**SUPPORTING INFORMATION**

# Aluminum containing molecular bowls and pyridinophanes: Use of pyridine modules to access different molecular topologies

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## 1. Experimental Procedures

### General considerations

All manipulations were performed under nitrogen/argon atmosphere using Schlenk line or glove box techniques. All glassware were dried at 150 °C in an oven for at least 12 h and assembled hot and cooled in vacuo prior to use. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Sigma-Aldrich and used without further purification. The starting material bis(trimethylsilyl)-N,N'-2,6-diaminopyridine (bap)[1] was prepared using reported procedures. The $^{1}H$, $^{13}C$, $^{29}Si$, $^{11}B$ and $^{19}F$ NMR spectra were recorded with a Bruker 400 MHz spectrometer with TMS, $BF_3{\cdot}OEt_2$ and $CFCl_3$ respectively, as external references. Chemical shifts were reported in ppm. High resolution mass spectra were recorded on a Waters SYNAPT G2-S instrument. IR spectra of the complexes were recorded in the range 4000-400 $cm^{-1}$ using a Perkin Elmer Lambda 35-spectrophotometer. The absorptions of the characteristic functional groups were only assigned and other absorptions (moderate to very strong) were only listed. Melting points were obtained in sealed capillaries on a Büchi B–540 melting point instrument.

## 2. Heteronuclear NMR Spectra of Compounds 1, 2, 4, 5 and 6.

### Heteronuclear NMR spectra of [2–(Me$_3$SiN)–6–(Me$_3$SiNH)C$_5$H$_3$N](AlMe$_2$) (1)

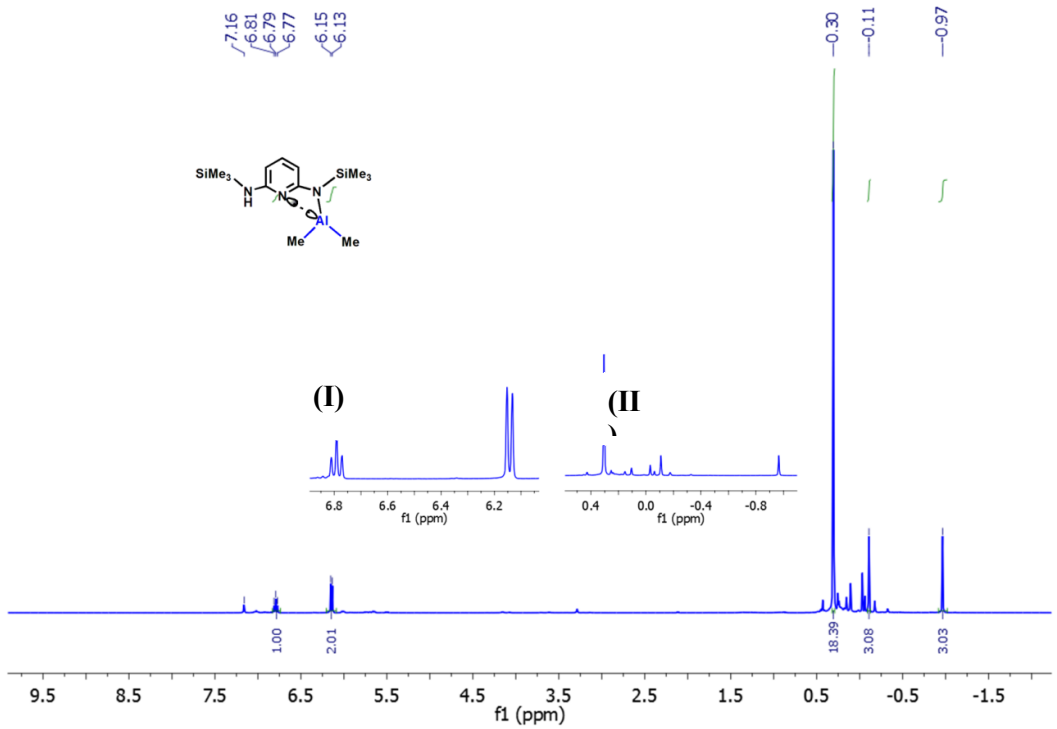



**Figure S1.** $^1$H NMR spectrum (400 MHz, $C_6D_6$) of [2–(Me$_3$SiN)–6–(Me$_3$SiNH)C$_5$H$_3$N](AlMe$_2$) **(1).** Inset **(I)** and **(II)** show expanded aromatic and aliphatic spectral region respectively.

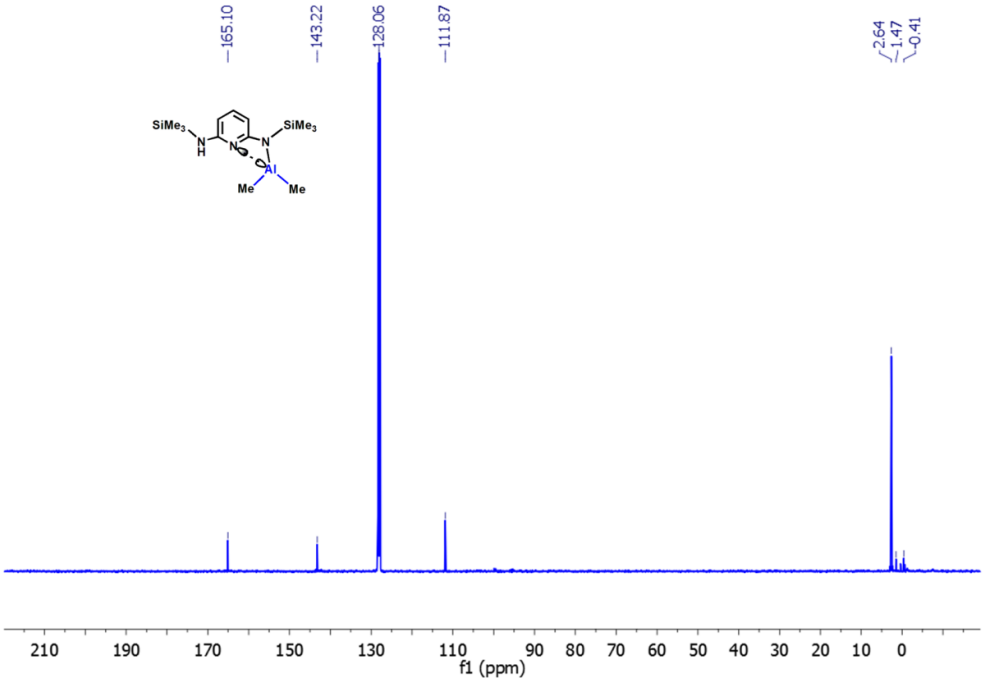



**Figure S2.** $^{13}$C NMR spectrum (100 MHz, $C_6D_6$) of [2–(Me$_3$SiN)–6–(Me$_3$SiNH)C$_5$H$_3$N](AlMe$_2$) **(1).**

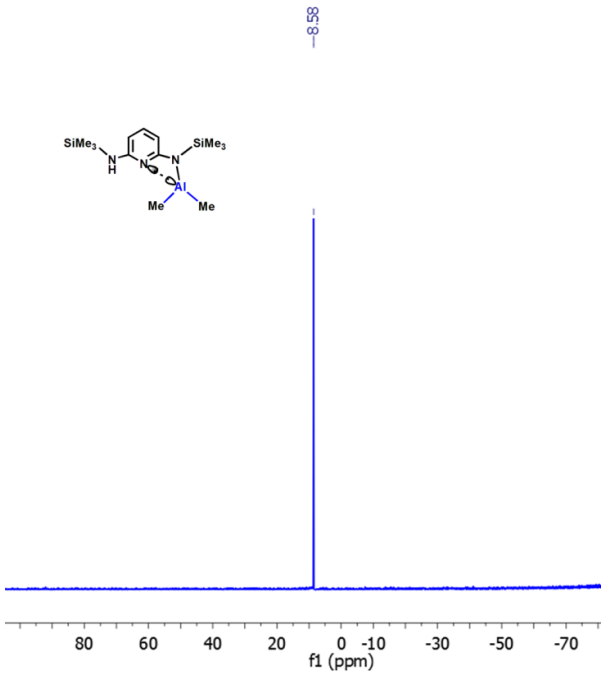



**Figure S3.** $^{29}$Si NMR spectrum (79.5 MHz, $C_6D_6$) of [2–($Me_3SiN$)–6–($Me_3SiNH$)$C_5H_3N$]($AlMe_2$) **(1).**

**Heteronuclear NMR spectra of [2–($Me_3SiN$)–6–($Me_3SiNH$)$C_5H_3N$]$_2$AlMe (2)**

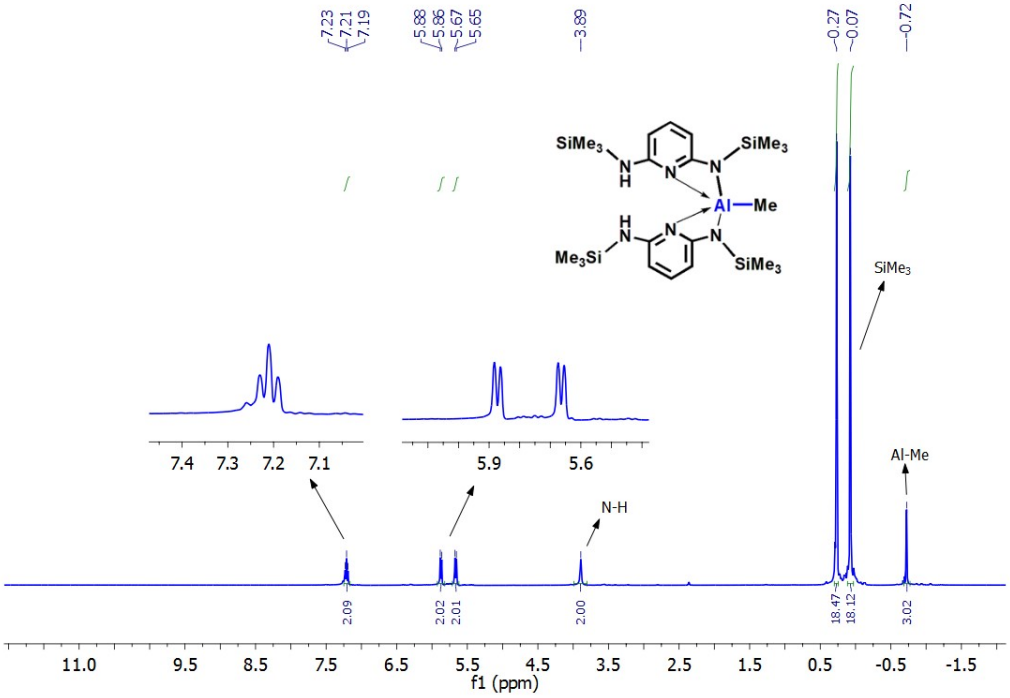



**Figure S4.** $^1$H NMR spectrum (400 MHz, $CDCl_3$) of [2–($Me_3SiN$)–6–($Me_3SiNH$)$C_5H_3N$]$_2$AlMe **(2).**

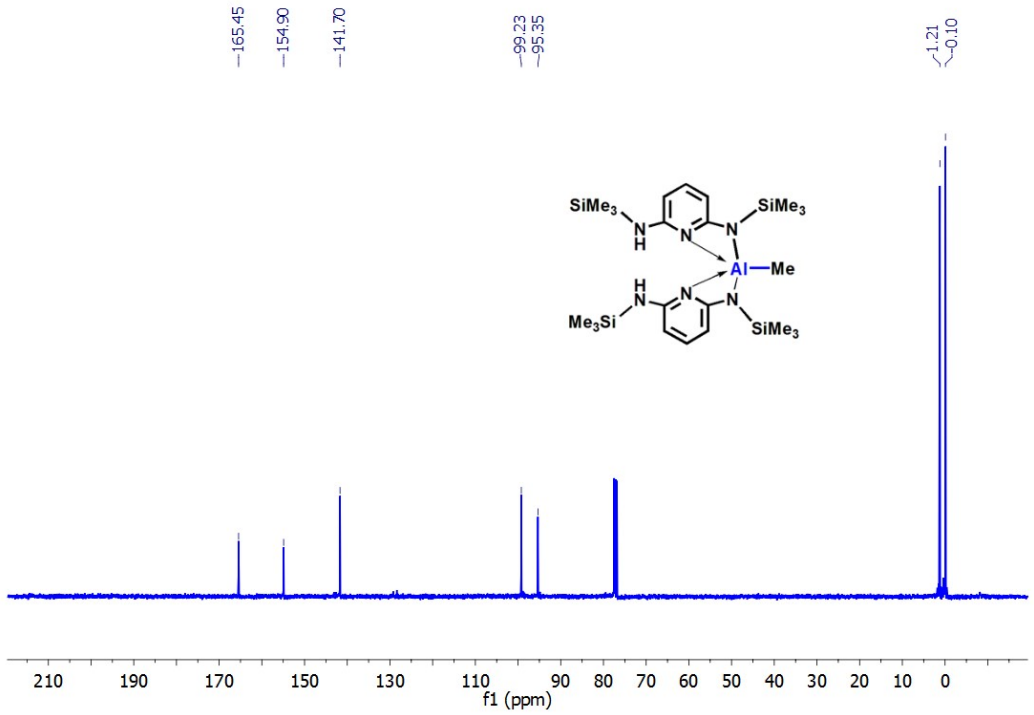



**Figure S5.** $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$) of $[2–(Me_3SiN)–6–(Me_3SiNH)C_5H_3N]_2AlMe$ **(2).**

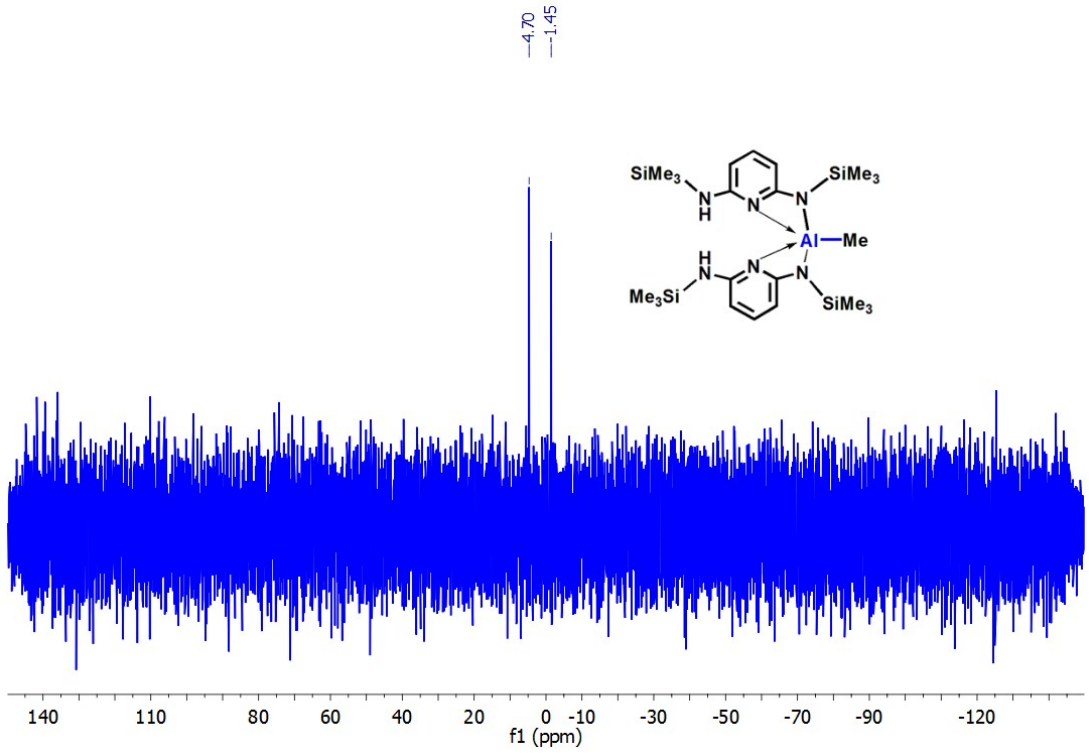



**Figure S6.** $^{29}Si$ NMR spectrum (79.5 MHz, $CDCl_3$) of $[2–(Me_3SiN)–6–(Me_3SiNH)C_5H_3N]_2AlMe$ **(2).**

**Heteronuclear NMR spectra of aluminum bowl [2,6–$(Me_3SiN)_2C_5H_3N(AlMe_2)]_2[AlMe]$ (4)**

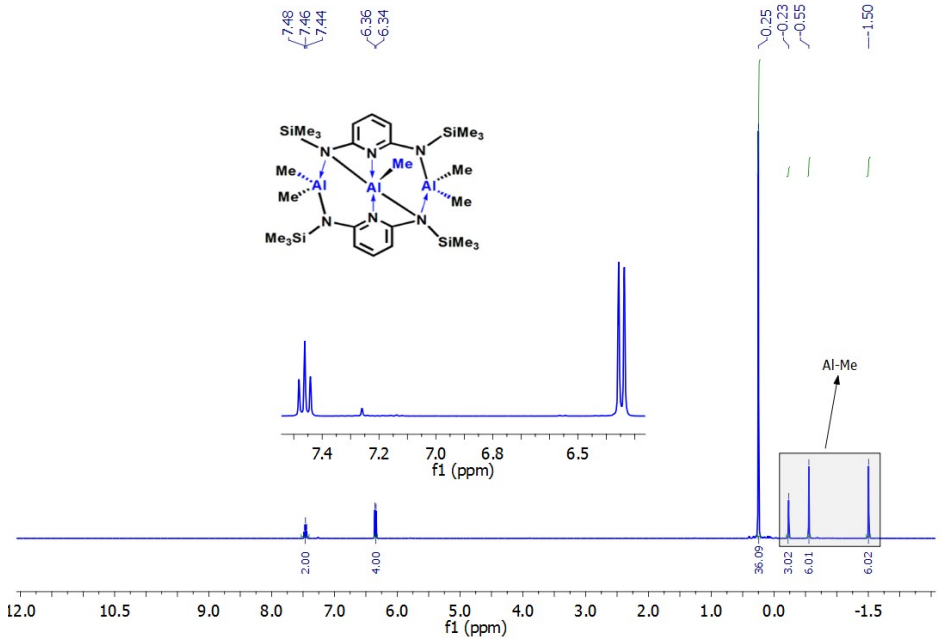



**Figure S7.** $^1H$ NMR spectrum (400 MHz, $CDCl_3$) of aluminum bowl [2,6–$(Me_3SiN)_2C_5H_3N(AlMe_2)]_2[AlMe]$ **(4)**. Inset shows expanded aromatic spectral region.

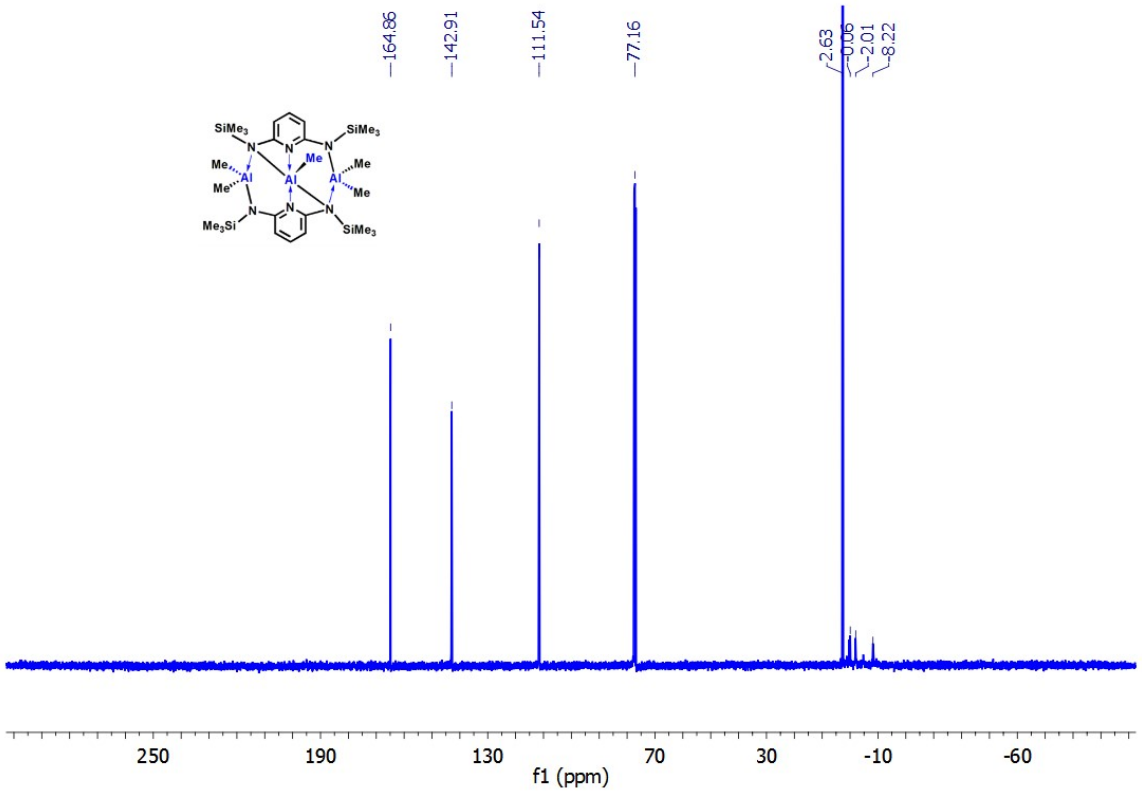



**Figure S8.** $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$) of aluminum bowl [2,6–$(Me_3SiN)_2C_5H_3N(AlMe_2)]_2[AlMe]$ **(4)**.

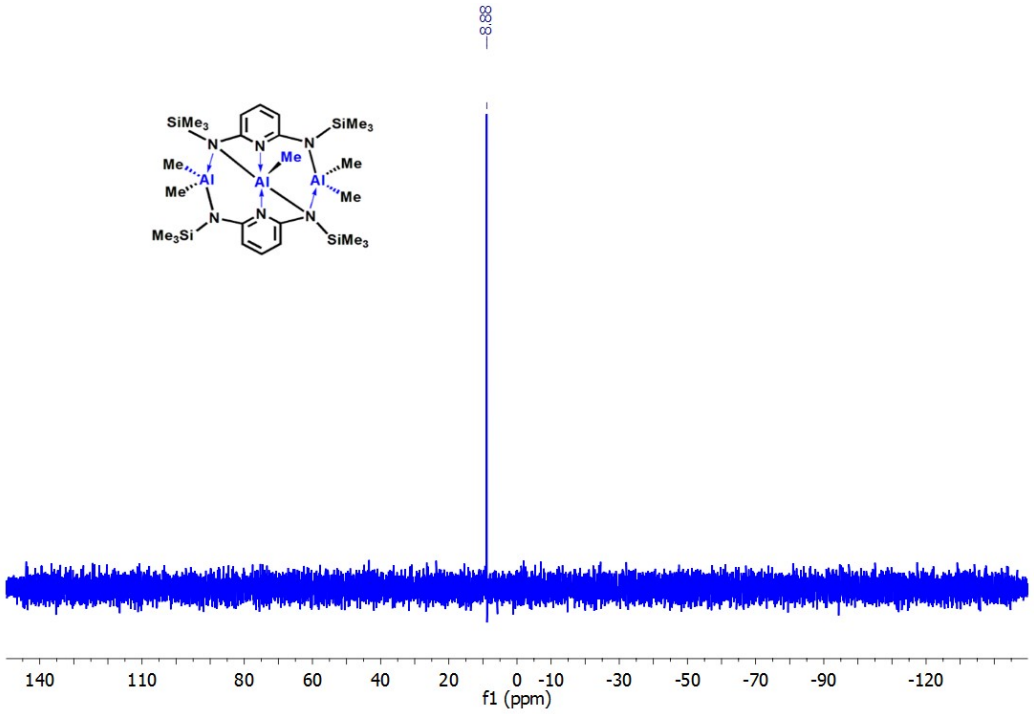



**Figure S9.** $^{29}Si$ NMR spectrum (79.5 MHz, $CDCl_3$) of aluminum bowl [2,6–$(Me_3SiN)_2C_5H_3N(AlMe_2)]_2[AlMe]$ **(4)**.

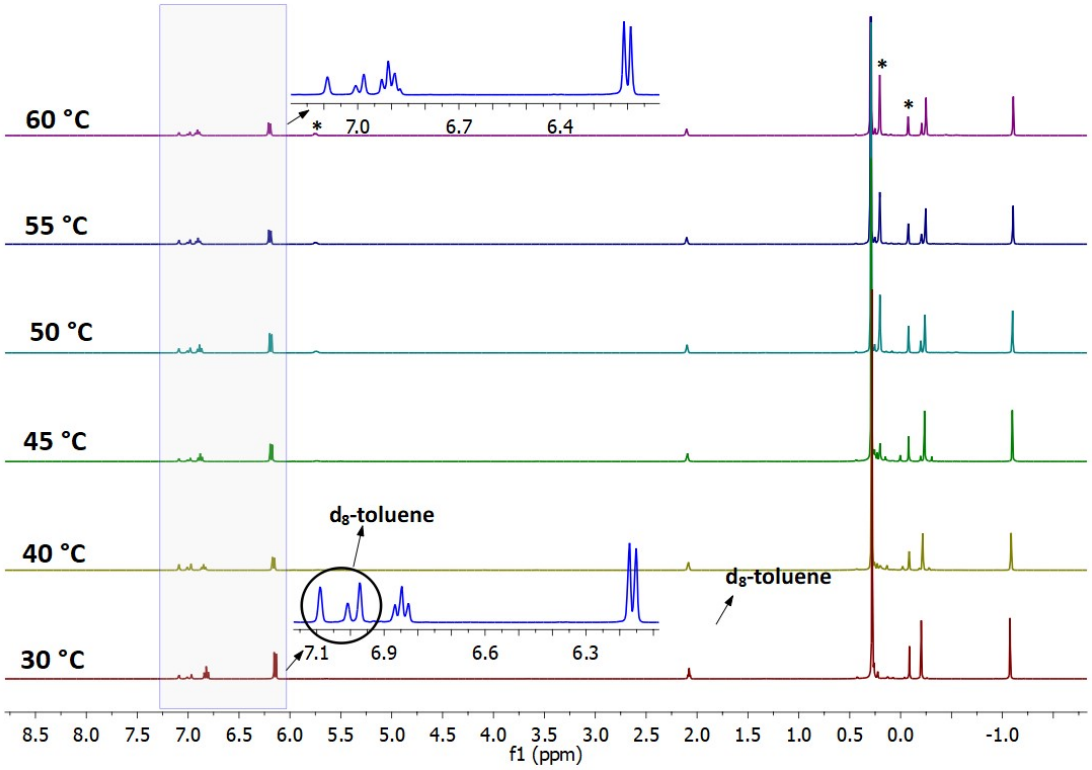



**Figure S10.** Variable temperature $^1H$ NMR spectra (400 MHz, $d_8$-toluene) of bowl shaped pyridinophane **4**. The * corresponds to slight decomposition during above RT measurements.

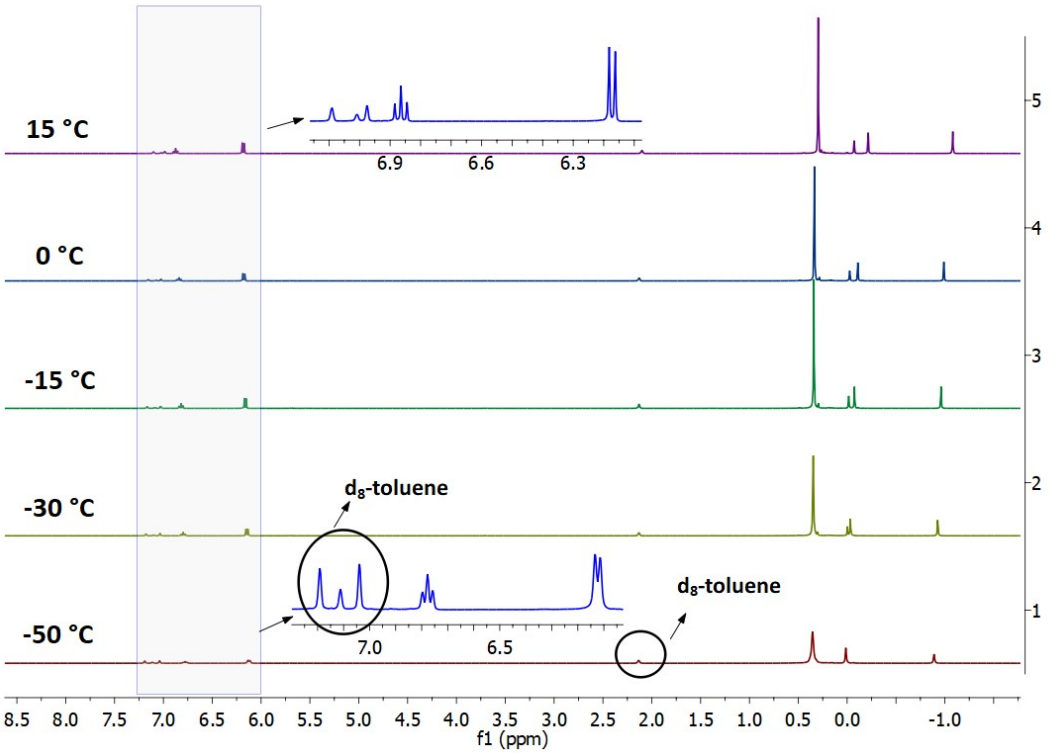



**Figure S11.** Variable temperature $^{1}$H NMR spectra (400 MHz, $d_8$-toluene) of bowl shaped pyridinophane **4**.

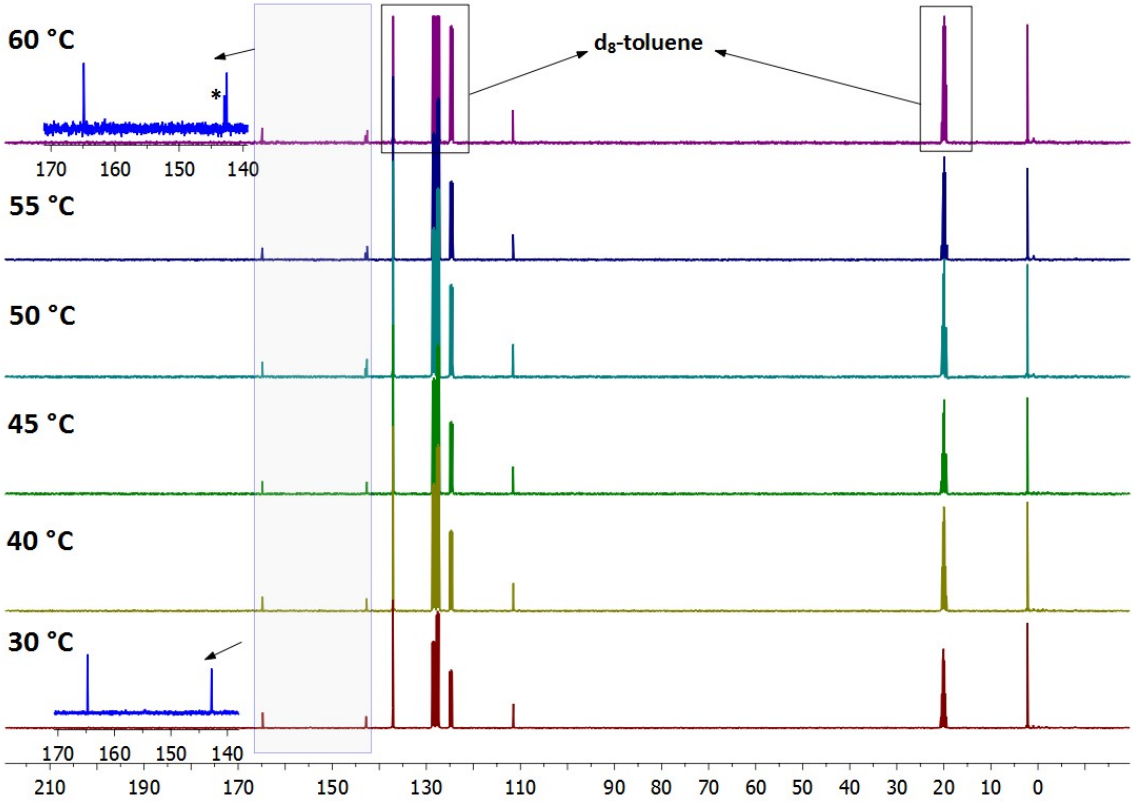



**Figure S12.** Variable temperature $^{13}$C NMR spectra (100 MHz, $d_8$-toluene) of bowl shaped pyridinophane **4**. The * corresponds to slight decomposition during above RT measurements.

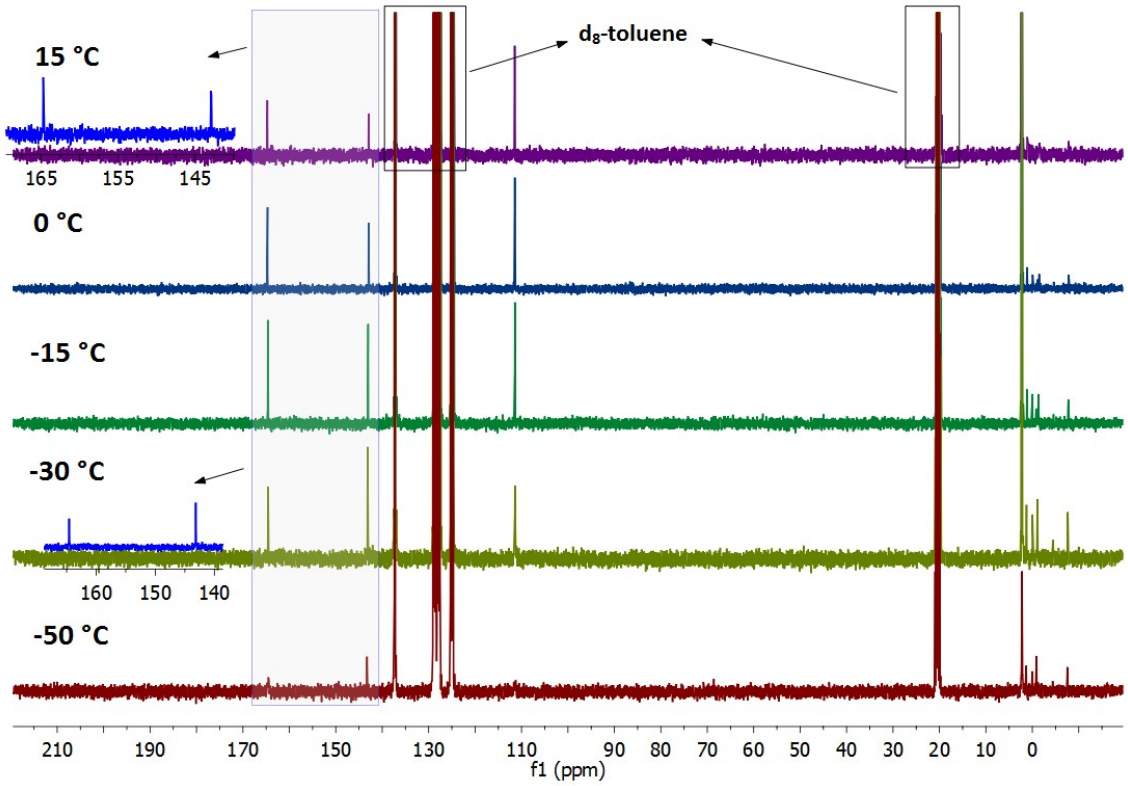



**Figure S13.** Variable temperature $^{13}C$ NMR spectra (100 MHz, $d_8$-toluene) of bowl shaped pyridinophane **4**.

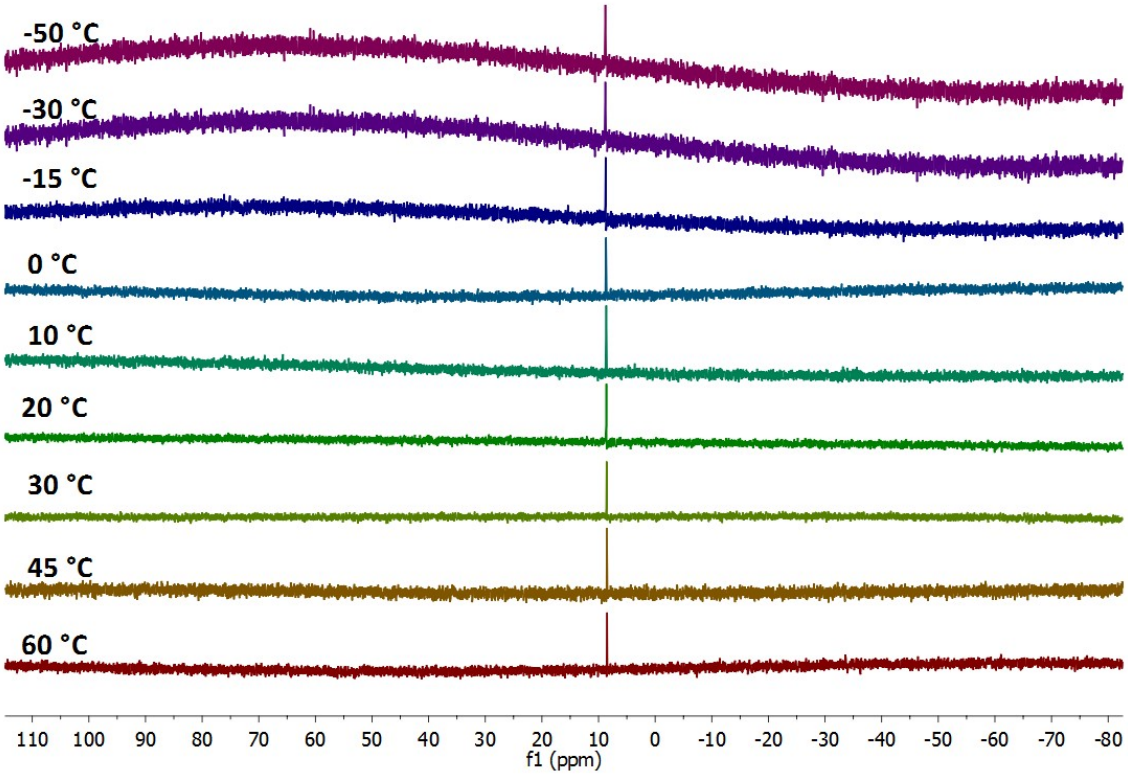



**Figure S14.** Variable temperature $^{29}Si$ NMR spectra (79.5 MHz, $d_8$-toluene) of bowl shaped pyridinophane **4**.

**Heteronuclear NMR spectra of monocationic aluminum bowl [{2,6–$(Me_3SiN)_2C_5H_3N\}_2(AlMe_2)(AlMe)(AlMe)]^+[MeB(C_6F_5)_3]^-$ (5)**

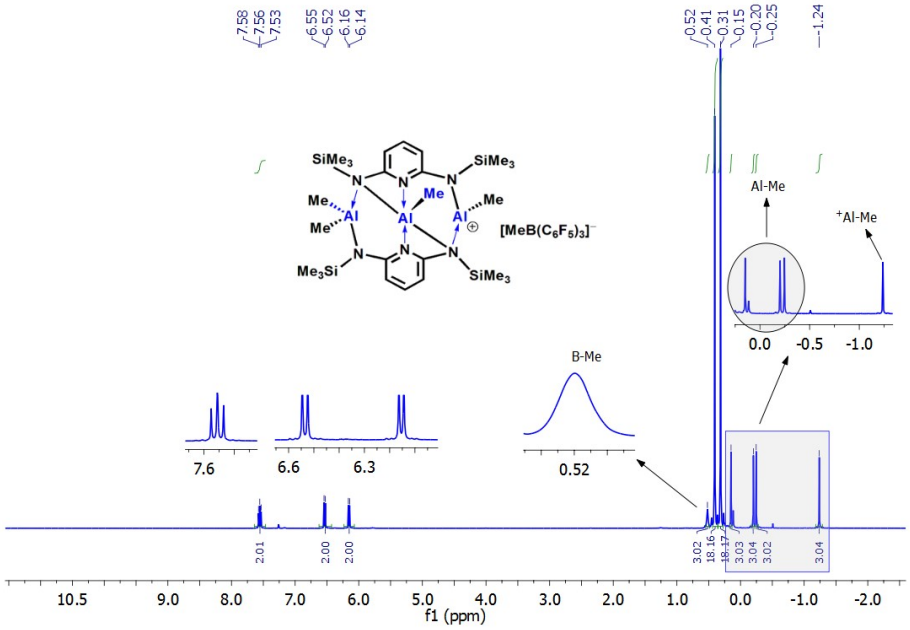



**Figure S15.** $^1H$ NMR spectrum (400 MHz, $CDCl_3$) of monocationic aluminum bowl [{2,6–$(Me_3SiN)_2C_5H_3N\}_2(AlMe_2)(AlMe)(AlMe)]^+[MeB(C_6F_5)_3]^-$ **(5)**.

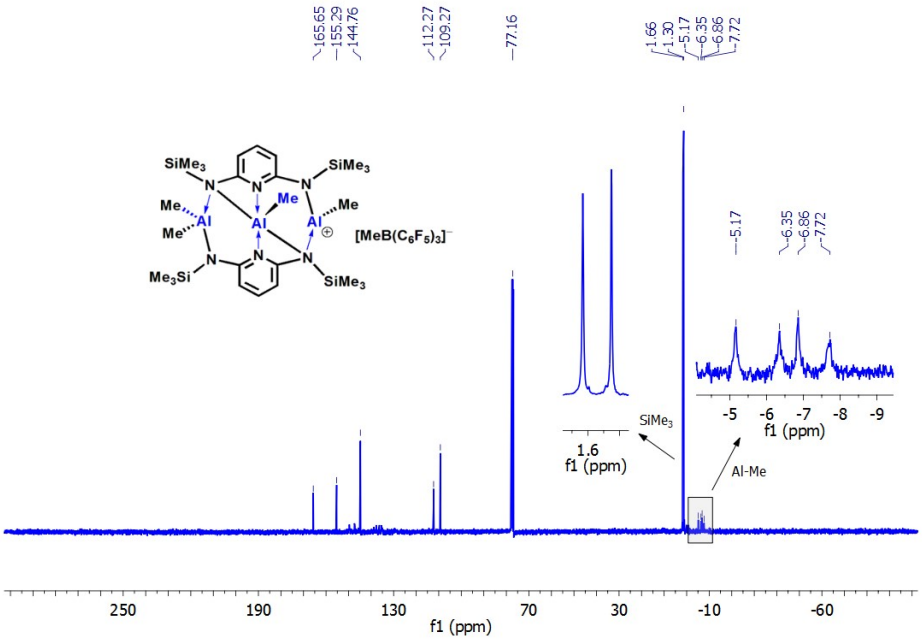



**Figure S16.** $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$) of monocationic aluminum bowl [{2,6–$(Me_3SiN)_2C_5H_3N\}_2(AlMe_2)(AlMe)(AlMe)]^+[MeB(C_6F_5)_3]^-$ **(5).**

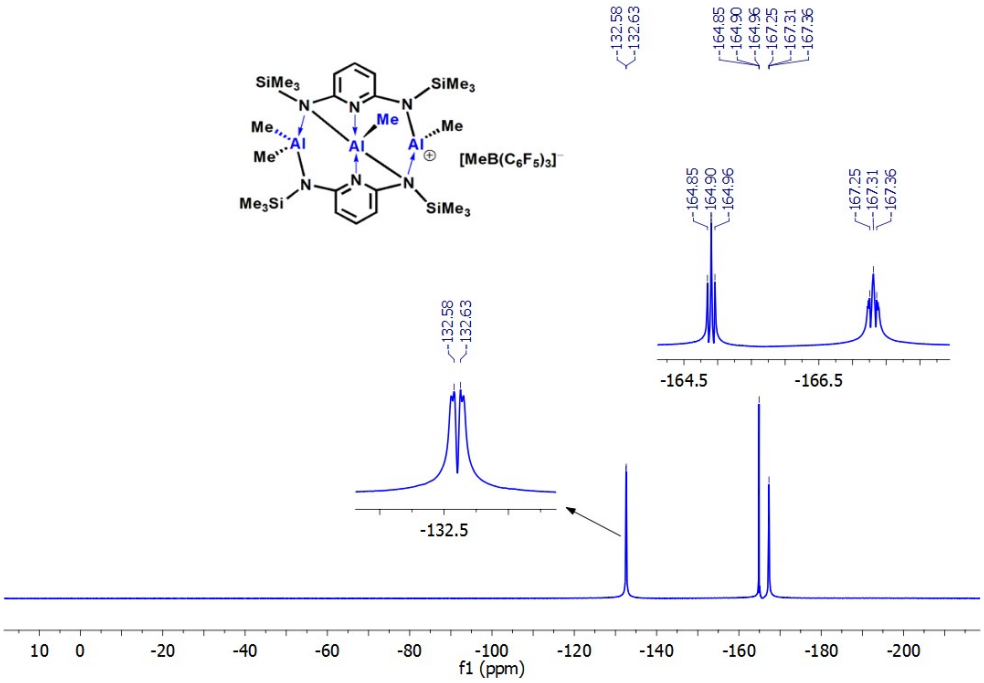



**Figure S17.** $^{19}F$ NMR spectrum (376 MHz, $CDCl_3$) of monocationic aluminum bowl [{2,6–$(Me_3SiN)_2C_5H_3N\}_2(AlMe_2)(AlMe)(AlMe)]^+[MeB(C_6F_5)_3]^-$ **(5)**.

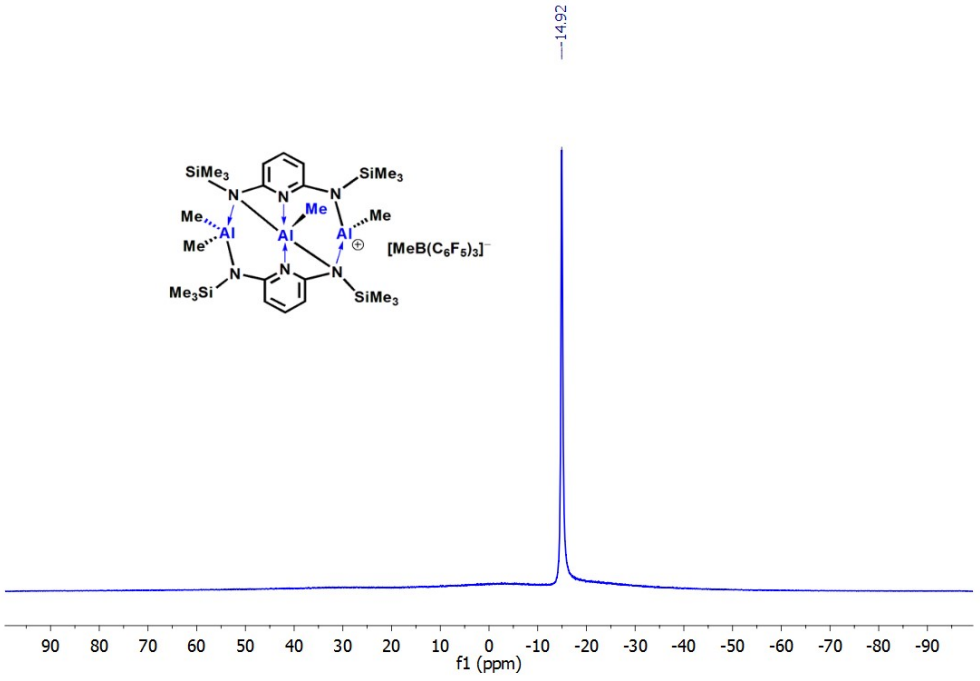



**Figure S18.** $^{11}B$ NMR spectrum (128 MHz, $CDCl_3$) of monocationic aluminum bowl [{2,6–$(Me_3SiN)_2C_5H_3N\}_2(AlMe_2)(AlMe)(AlMe)]^+[MeB(C_6F_5)_3]^-$ **(5)**.

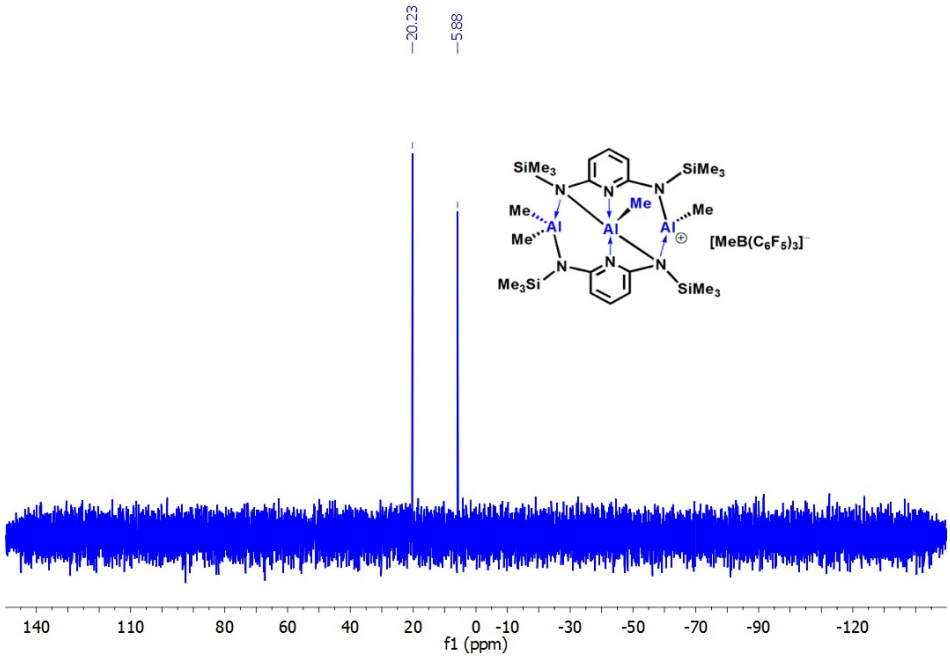



**Figure S19.** $^{29}$Si NMR spectrum (128 MHz, $CDCl_3$) of monocationic aluminum bowl [{2,6–$(Me_3SiN)_2C_5H_3N$}$_2$$(AlMe_2)(AlMe)(AlMe)]^+[MeB(C_6F_5)_3]^-$ **(5)**.

**Heteronuclear NMR spectra of aluminum based bicyclic pyridinophane, [2,6–$(Me_3SiN)_2C_5H_3N]_3Al_2$ (6)**

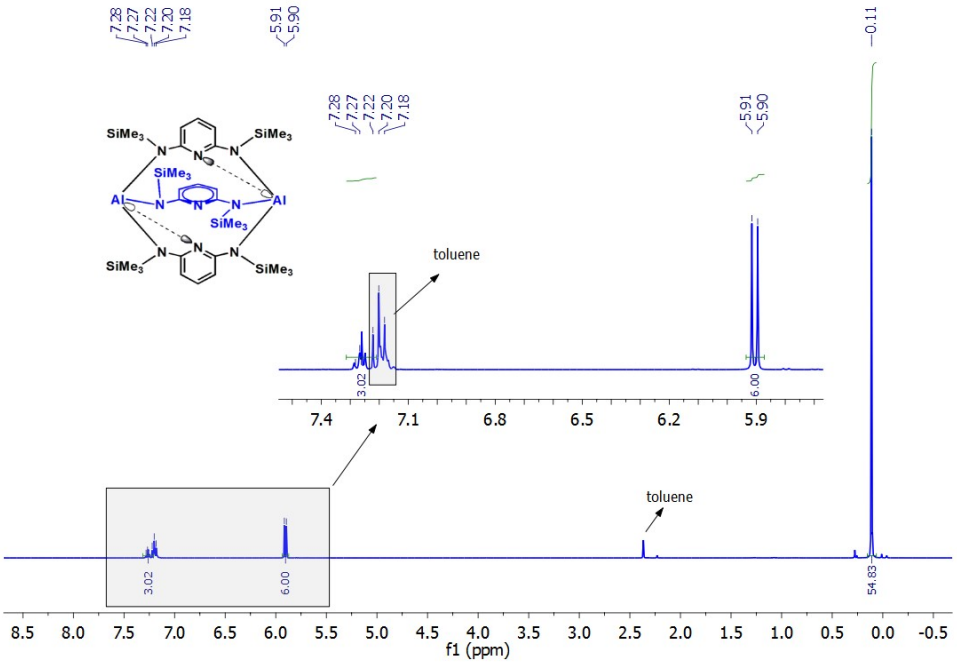



**Figure S20.** $^1$H NMR spectrum (400 MHz, $CDCl_3$) aluminum based bicyclic pyridinophane, [2,6–$(Me_3SiN)_2C_5H_3N]_3Al_2$ **(6)**.

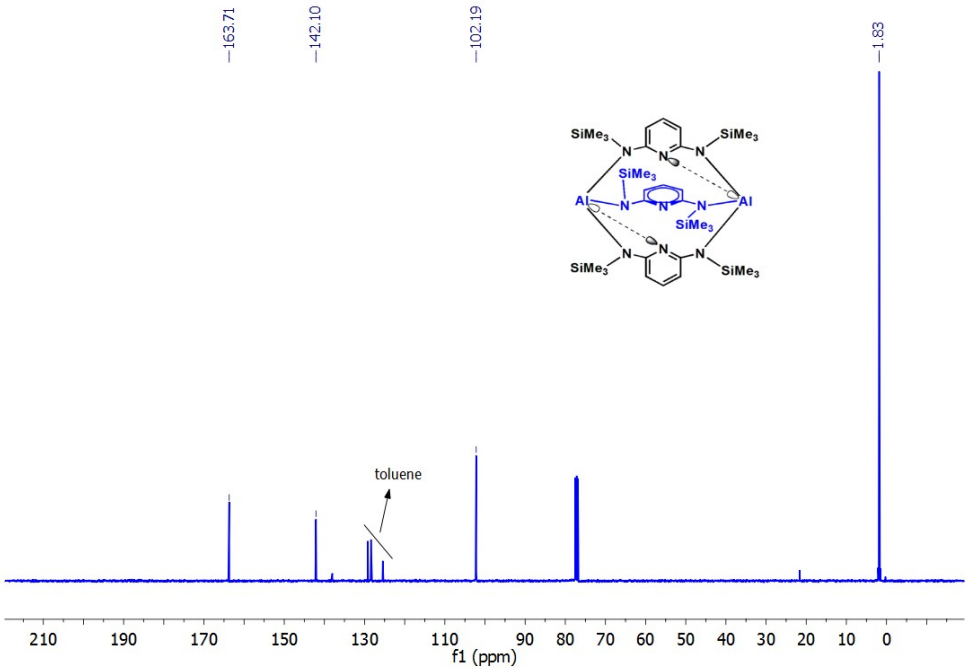



**Figure S21.** $^{13}C$ NMR spectrum (100 MHz, $CDCl_3$) of aluminum based bicyclic pyridinophane, [2,6–$(Me_3SiN)_2C_5H_3N]_3Al_2$ **(6)**.

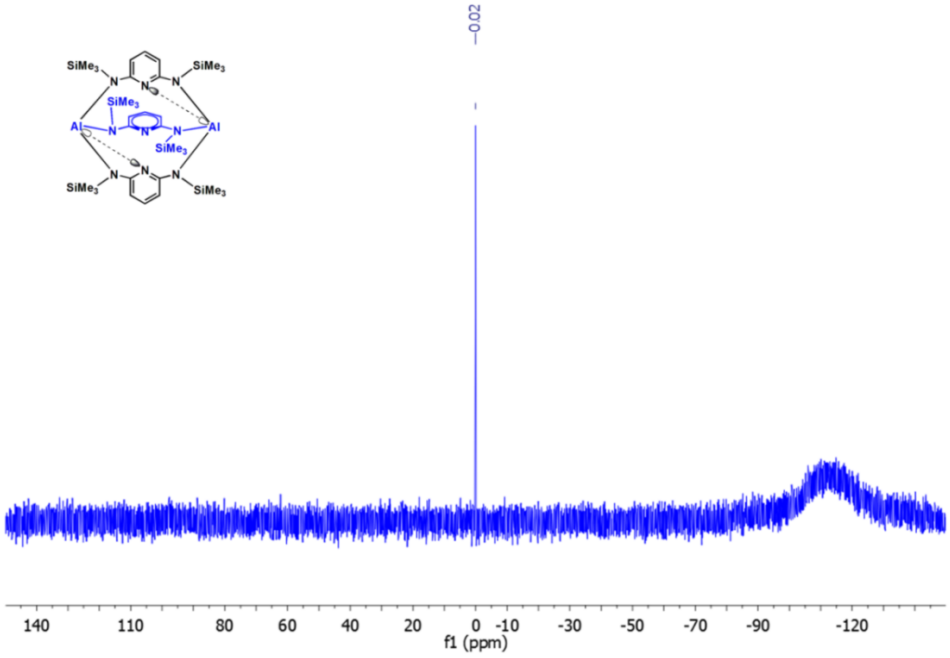



**Figure S22.** $^{29}Si$ NMR spectrum (79.5 MHz, $CDCl_3$) of aluminum based bicyclic pyridinophane, [2,6–$(Me_3SiN)_2C_5H_3N]_3Al_2$ **(6)**.

### 3. Crystal Data and Refinement Details for Compounds 1, 2, 4 and 6

Single crystal X-ray diffraction data were collected using a Rigaku XtaLAB mini diffractometer equipped with Mercury375M CCD detector. The data were collected with graphite monochromatic

MoKα radiation (λ = 0.71073 Å) at 100.0(2) K using scans. During the data collection, the detector distance was maintained at 50 mm and the detector was placed at 2θ = 29.85° (fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite.[2] The crystal structures were solved by using OLEX2[3] and the structure were refined using XL.[4] All non hydrogen atoms were refined anisotropically. A disordered toluene molecule found in the asymmetric unit of **6** that could not be treated using standard commands available in SHELXL. The mask method was used to remove the contribution of these disordered molecules from the original hkl file.

**Table S1: Crystal Data and Refinement Details for Compounds 1, 2, 4 and 6**

| **Compound**[a] | **1** | **2** | **4** | **6** |
|---|---|---|---|---|
| Chemical formula | $C_{13}H_{28}AlN_3Si_2$ | $C_{23}H_{54}AlN_6Si_4$ | $C_{27}H_{57}Al_3N_6Si_4$ | $C_{16.5}H_{31.5}AlN_{4.5}Si_3$ |
| Molar mass | 309.54 | 590.09 | 659.08 | 404.21 |
| Crystal system | monoclinic | monoclinic | orthorhombic | orthorhombic |
| Space group | $P2_1/c$ | $P2_1/c$ | *Pbcn* | $C222_1$ |
| *T* [K] | 100(2) | 100(2) | 100(2) | 100(2) |
| *a* [Å] | 6.379(2) | 12.1076(8) | 18.013(7) | 17.001(3) |
| *b* [Å] | 13.613(3) | 11.8845(8) | 14.239(6) | 20.578(4) |
| *c* [Å] | 22.304(7) | 24.8155(18) | 15.420(6) | 14.373(2) |
| *α* [°] | 90 | 90 | 90 | 90 |
| *β* [°] | 94.760(13) | 94.202(4) | 90 | 90 |
| *γ* [°] | 90 | 90 | 90 | 90 |
| *V* [Å$^3$] | 1930.1(10) | 3561.2(4) | 3955(3) | 5028.3(16) |
| *Z* | 4 | 4 | 4 | 8 |
| *D*(calcd.) [g·cm$^{-3}$] | 1.065 | 1.101 | 1.107 | 1.068 |
| $\mu$(Mo-$K_\alpha$) [mm$^{-1}$] | 0.223 | 0.216 | 0.242 | 0.232 |
| Reflections collected | 10902 | 37445 | 11008 | 6914 |
| Independent reflections | 3410 | 8103 | 3455 | 5335 |
| Data/restraints/parameters | 3410/0/184 | 8103/0/356 | 3455/0/191 | 5335/0/236 |
| *R*1,*wR*2[$I>2\sigma(I)$][a] | 0.0651, 0.1657 | 0.0554, 0.1370 | 0.0669, 0.1791 | 0.0711, 0.1331 |
| R1, wR2 (all data)[a] | 0.0801, 0.1857 | 0.0687, 0.1491 | 0.910, 0.2081 | 0.1139, 0.1635 |
| GOF | 1.149 | 1.098 | 1.069 | 0.987 |
| CCDC | 1829446 | 1829448 | 1829450 | 1829451 |

[a] $R1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. $wR2 = [\Sigma w(|Fo^2| - |Fc^2|)^2/\Sigma w|Fo^2|^2]^{1/2}$

**4. Computational Details:**

DFT calculations at the B3LYP/6-311G(d) level of theory with Gaussian 09 package[5] were performed to optimize the geometry of boron pyridinophane ($\mathbf{B^{Py}}$) and the analogous aluminum pyridinophane ($\mathbf{Al^{Py}}$); similarly, for the boron containing bicyclic pyridinophane ($\mathbf{B^{biPy}}$) and the analogous aluminum containing bicyclic pyridinophane ($\mathbf{Al^{biPy}}$). We represent the zero point corrected Gibbs free energy of formation ($\Delta G_f$), electronic energy, zero point energy (ZPE), thermal correction in Gibbs energy and Cartesian co-ordinates of the optimized geometry. NBO charge analysis for $\mathbf{B^{Py}}$ has been done at DFT optimized geometry.[6] The molecular orbitals of $\mathbf{B^{Py}}$ have been visualized by Chemcraft-graphical software.[7]

**Cartesian coordinates of the optimized structures:**

**Borane ($BH_3$)**

| | | | |
|---|---|---|---|
| B | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 0.000000000 | 1.191654000 | 0.000000000 |
| H | 1.032003000 | -0.595827000 | 0.000000000 |
| H | -1.032003000 | -0.595827000 | 0.000000000 |

| | |
|---|---|
| Zero-point correction = | 0.026054 (Hartree/Particle) |
| Thermal correction to Energy = | 0.028941 |
| Thermal correction to Enthalpy = | 0.029886 |
| Thermal correction to Gibbs Free Energy = | 0.008504 |
| Sum of electronic and zero-point Energies = | -26.591324 |
| Sum of electronic and thermal Energies = | -26.588437 |
| Sum of electronic and thermal Enthalpies = | -26.587493 |
| Sum of electronic and thermal Free Energies = | -26.608875 |

**Alane ($AlH_3$)**

| | | | |
|---|---|---|---|
| H | 0.000000000 | 1.583850000 | 0.000000000 |
| H | 1.371654000 | -0.791925000 | 0.000000000 |
| H | -1.371654000 | -0.791925000 | 0.000000000 |
| Al | 0.000000000 | 0.000000000 | 0.000000000 |

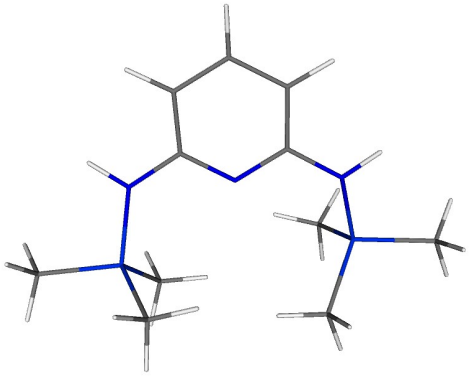
| | |
|---|---|
| Zero-point correction = | 0.018614 (Hartree/Particle) |
| Thermal correction to Energy = | 0.021716 |
| Thermal correction to Enthalpy = | 0.022660 |
| Thermal correction to Gibbs Free Energy = | -0.000881 |
| Sum of electronic and zero-point Energies = | -244.207372 |
| Sum of electronic and thermal Energies = | -244.204271 |
| Sum of electronic and thermal Enthalpies = | -244.203326 |
| Sum of electronic and thermal Free Energies = | -244.226867 |

**Dihydrogen ($H_2$)**

| | | | |
|---|---|---|---|
| H | 0.000000000 | 0.000000000 | 0.370950000 |
| H | 0.000000000 | 0.000000000 | -0.370950000 |

| | |
|---|---|
| Zero-point correction = | 0.010010 (Hartree/Particle) |
| Thermal correction to Energy = | 0.012371 |
| Thermal correction to Enthalpy = | 0.013315 |
| Thermal correction to Gibbs Free Energy = | -0.001475 |
| Sum of electronic and zero-point Energies = | -1.166622 |
| Sum of electronic and thermal Energies = | -1.164261 |
| Sum of electronic and thermal Enthalpies = | -1.163317 |
| Sum of electronic and thermal Free Energies = | -1.178107 |

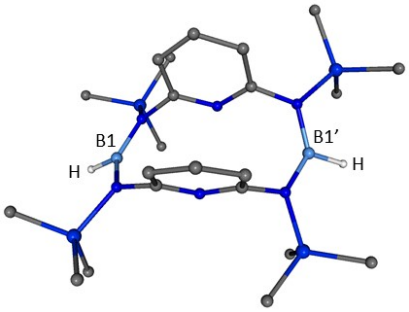
**Bis(trimethylsilyl)–N,N'–2,6–diaminopyridine (bap)**



| | | | |
|---|---|---|---|
| C | -1.143255000 | 1.532975000 | -0.164803000 |
| C | 1.143253000 | 1.532976000 | 0.164798000 |
| N | 2.309917000 | 0.802106000 | 0.313288000 |
| Si | 2.637993000 | -0.903370000 | -0.028682000 |
| N | 0.000000000 | 0.847116000 | -0.000004000 |
| N | -2.309917000 | 0.802103000 | -0.313296000 |
| Si | -2.637992000 | -0.903372000 | 0.028682000 |
| C | -4.504485000 | -1.036009000 | -0.226421000 |
| H | -4.850218000 | -2.056868000 | -0.036509000 |
| H | -5.061679000 | -0.380084000 | 0.450154000 |
| H | -4.797892000 | -0.785335000 | -1.250772000 |
| C | -2.210565000 | -1.318613000 | 1.813984000 |
| H | -2.329931000 | -2.387218000 | 2.020193000 |
| H | -1.180004000 | -1.047041000 | 2.050592000 |
| H | -2.860558000 | -0.774265000 | 2.505740000 |
| C | -1.772994000 | -2.062594000 | -1.171298000 |
| H | -2.087659000 | -3.098554000 | -1.005795000 |
| H | -2.013671000 | -1.806292000 | -2.207248000 |
| H | -0.688313000 | -2.023834000 | -1.065467000 |
| C | 2.210563000 | -1.318623000 | -1.813980000 |
| H | 2.860555000 | -0.774278000 | -2.505741000 |
| H | 2.329930000 | -2.387228000 | -2.020182000 |
| H | 1.180001000 | -1.047053000 | -2.050588000 |
| C | 1.772999000 | -2.062586000 | 1.171306000 |
| H | 2.013683000 | -1.806283000 | 2.207254000 |
| H | 0.688317000 | -2.023824000 | 1.065482000 |
| H | 2.087660000 | -3.098548000 | 1.005804000 |
| C | 4.504487000 | -1.036004000 | 0.226419000 |
| H | 4.850221000 | -2.056863000 | 0.036512000 |
| H | 5.061679000 | -0.380082000 | -0.450161000 |
| H | 4.797896000 | -0.785324000 | 1.250768000 |
| H | -3.117960000 | 1.383135000 | -0.487076000 |
| H | 3.117959000 | 1.383140000 | 0.487068000 |
| C | -1.187892000 | 2.939372000 | -0.179402000 |
| H | -2.129820000 | 3.460940000 | -0.311076000 |
| C | 1.187888000 | 2.939373000 | 0.179402000 |
| H | 2.129815000 | 3.460943000 | 0.311078000 |
| C | -0.000003000 | 3.631181000 | 0.000001000 |
| H | -0.000004000 | 4.717240000 | 0.000003000 |

| | |
|---|---|
| Zero-point correction = | 0.325360 (Hartree/Particle) |
| Thermal correction to Energy = | 0.347640 |
| Thermal correction to Enthalpy = | 0.348584 |
| Thermal correction to Gibbs Free Energy = | 0.274946 |
| Sum of electronic and zero-point Energies = | -1176.272375 |
| Sum of electronic and thermal Energies = | -1176.250095 |
| Sum of electronic and thermal Enthalpies = | -1176.249151 |
| Sum of electronic and thermal Free Energies = | -1176.322789 |

**Pyridinophane containing boron ($B^{Py}$)**




| | | | |
|---|---|---|---|
| Si | -4.390015000 | 1.004783000 | -0.094768000 |
| Si | 4.390035000 | -1.004771000 | -0.094128000 |
| Si | -1.425899000 | -3.322120000 | 1.324121000 |
| Si | 1.425681000 | 3.322049000 | 1.324533000 |
| N | -2.813631000 | 0.207457000 | -0.404849000 |
| N | -1.504404000 | -1.985061000 | 0.126906000 |
| N | 0.713624000 | -1.238217000 | -0.206037000 |
| N | 2.813691000 | -0.207442000 | -0.404406000 |
| N | 1.504377000 | 1.985044000 | 0.127271000 |
| N | -0.713597000 | 1.238222000 | -0.206078000 |
| C | -1.741365000 | 0.933103000 | -1.001885000 |
| C | -1.755540000 | 1.269300000 | -2.360485000 |
| H | -2.600919000 | 0.997721000 | -2.980883000 |
| C | -0.644880000 | 1.911207000 | -2.892392000 |
| H | -0.622280000 | 2.185145000 | -3.942661000 |
| C | 0.454352000 | 2.163933000 | -2.077769000 |
| H | 1.354536000 | 2.627657000 | -2.462830000 |
| C | 0.382929000 | 1.785057000 | -0.735351000 |
| C | 1.741524000 | -0.933058000 | -1.001658000 |
| C | 1.755923000 | -1.269183000 | -2.360273000 |
| H | 2.601403000 | -0.997572000 | -2.980519000 |

| | | | |
|---|---|---|---|
| C | 0.645352000 | -1.911065000 | -2.892397000 |
| H | 0.622925000 | -2.184948000 | -3.942684000 |
| C | -0.454015000 | -2.163833000 | -2.077968000 |
| H | -1.354135000 | -2.627538000 | -2.463201000 |
| C | -0.382815000 | -1.785024000 | -0.735520000 |
| C | -4.451321000 | 2.661052000 | -0.992676000 |
| H | -3.626771000 | 3.322105000 | -0.713311000 |
| H | -5.381650000 | 3.173530000 | -0.725351000 |
| H | -4.439021000 | 2.563268000 | -2.080823000 |
| C | -4.594700000 | 1.325386000 | 1.751074000 |
| H | -4.601053000 | 0.399602000 | 2.331507000 |
| H | -5.534294000 | 1.849073000 | 1.956861000 |
| H | -3.779697000 | 1.946203000 | 2.134415000 |
| C | -5.787838000 | -0.091958000 | -0.722564000 |
| H | -5.694492000 | -0.280717000 | -1.796400000 |
| H | -6.761010000 | 0.381813000 | -0.555870000 |
| H | -5.806830000 | -1.062209000 | -0.219723000 |
| C | 0.066368000 | -4.396122000 | 0.916331000 |
| H | 0.020714000 | -4.802110000 | -0.098296000 |
| H | 0.110904000 | -5.245496000 | 1.605778000 |
| H | 1.004390000 | -3.844660000 | 1.010842000 |
| C | -2.984206000 | -4.376682000 | 1.192938000 |
| H | -3.890519000 | -3.818920000 | 1.439258000 |
| H | -2.926882000 | -5.227002000 | 1.880924000 |
| H | -3.108454000 | -4.779815000 | 0.183444000 |
| C | -1.256123000 | -2.627934000 | 3.064926000 |
| H | -0.371535000 | -1.989578000 | 3.139258000 |
| H | -1.158566000 | -3.426793000 | 3.807706000 |
| H | -2.122011000 | -2.021644000 | 3.346070000 |
| C | 4.451520000 | -2.660962000 | -0.992168000 |
| H | 3.626932000 | -3.322053000 | -0.713002000 |
| H | 5.381811000 | -3.173450000 | -0.724730000 |
| H | 4.439404000 | -2.563082000 | -2.080308000 |
| C | 4.594418000 | -1.325523000 | 1.751721000 |
| H | 4.600676000 | -0.399784000 | 2.332228000 |
| H | 5.533981000 | -1.849224000 | 1.957619000 |
| H | 3.779355000 | -1.946373000 | 2.134882000 |
| C | 5.787944000 | 0.092046000 | -0.721600000 |
| H | 5.694796000 | 0.280855000 | -1.795444000 |
| H | 6.761100000 | -0.381701000 | -0.554744000 |
| H | 5.806808000 | 1.062273000 | -0.218707000 |
| C | 2.984044000 | 4.376570000 | 1.193693000 |
| H | 3.890292000 | 3.818777000 | 1.440180000 |
| H | 2.926607000 | 5.226876000 | 1.881687000 |
| H | 3.108504000 | 4.779723000 | 0.184232000 |
| C | -0.066475000 | 4.396113000 | 0.916500000 |
| H | -0.020608000 | 4.802146000 | -0.098099000 |
| H | -0.111125000 | 5.245457000 | 1.605977000 |
| H | -1.004533000 | 3.844674000 | 1.010799000 |
| C | 1.255544000 | 2.627788000 | 3.065273000 |
| H | 0.370917000 | 1.989462000 | 3.139401000 |
| H | 1.157874000 | 3.426613000 | 3.808073000 |

| | | | |
|---|---|---|---|
| H | 2.121354000 | 2.021449000 | 3.346554000 |
| B | -2.602210000 | -1.071561000 | 0.223651000 |
| H | -3.505265000 | -1.446678000 | 0.918746000 |
| B | 2.602165000 | 1.071537000 | 0.224141000 |
| H | 3.505106000 | 1.446611000 | 0.919408000 |

Zero-point correction = 0.637228 (Hartree/Particle)

Thermal correction to Energy = 0.682532

Thermal correction to Enthalpy = 0.683476

Thermal correction to Gibbs Free Energy = 0.556460

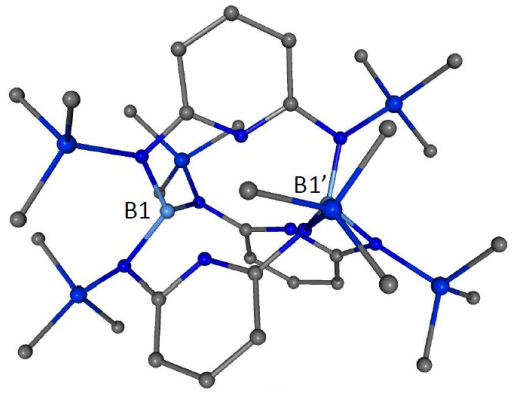
Sum of electronic and zero-point Energies = -2401.158536

Sum of electronic and thermal Energies = -2401.113233

Sum of electronic and thermal Enthalpies = -2401.112289

Sum of electronic and thermal Free Energies = -2401.239304

**Boron containing bicyclic pyridinophane ($B^{biPy}$)**




| | | | |
|---|---|---|---|
| Si | -2.003285000 | 0.556982000 | -2.945148000 |
| Si | 4.328678000 | -2.097595000 | 0.185837000 |
| Si | -3.529522000 | 1.897208000 | 1.535958000 |
| N | 0.900579000 | -0.939139000 | -1.053816000 |
| N | 2.922530000 | -1.223798000 | -0.434682000 |
| N | -1.375720000 | -0.259246000 | -1.473762000 |
| N | -0.000014000 | 1.604923000 | -0.000078000 |
| N | -2.224386000 | 1.338535000 | 0.441188000 |
| C | 1.982095000 | -1.743230000 | -1.269667000 |
| C | -0.284134000 | -1.094538000 | -1.704228000 |
| C | -1.204789000 | 3.630626000 | 0.174849000 |

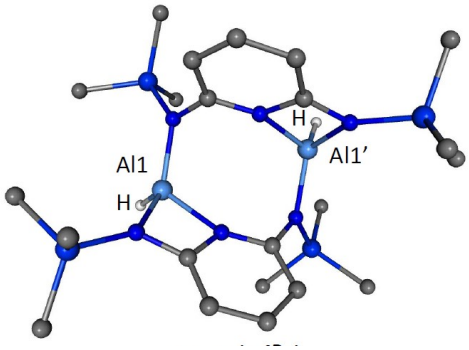
| | | | |
|---|---|---|---|
| H | -2.131693000 | 4.180180000 | 0.272718000 |
| C | 1.954205000 | -2.787248000 | -2.200019000 |
| H | 2.817090000 | -3.410334000 | -2.383795000 |
| C | -1.152212000 | 2.224124000 | 0.215344000 |
| C | -0.347018000 | -2.147401000 | -2.636209000 |
| H | -1.284958000 | -2.349159000 | -3.128346000 |
| C | 0.000001000 | 4.308497000 | -0.000099000 |
| H | 0.000006000 | 5.394787000 | -0.000104000 |
| C | 5.283165000 | -2.944302000 | -1.214216000 |
| H | 4.838406000 | -3.901328000 | -1.500970000 |
| H | 6.300329000 | -3.165181000 | -0.872620000 |
| H | 5.369985000 | -2.332182000 | -2.114045000 |
| C | 0.754881000 | -2.964873000 | -2.874927000 |
| H | 0.663275000 | -3.772687000 | -3.595280000 |
| C | -2.975077000 | -0.573195000 | -4.124157000 |
| H | -2.332580000 | -1.238591000 | -4.705836000 |
| H | -3.506897000 | 0.056346000 | -4.846514000 |
| H | -3.728627000 | -1.188093000 | -3.627304000 |
| C | -0.545234000 | 1.238241000 | -3.924905000 |
| H | -0.011194000 | 1.997727000 | -3.350295000 |
| H | -0.898278000 | 1.709772000 | -4.848249000 |
| H | 0.173682000 | 0.465843000 | -4.210412000 |
| C | -3.146267000 | 1.994630000 | -2.547341000 |
| H | -4.027105000 | 1.717086000 | -1.969993000 |
| H | -3.496897000 | 2.406344000 | -3.500582000 |
| H | -2.635895000 | 2.795417000 | -2.012617000 |
| C | -4.839413000 | 2.901323000 | 0.608056000 |
| H | -4.431180000 | 3.757627000 | 0.065440000 |
| H | -5.576441000 | 3.288841000 | 1.319939000 |
| H | -5.383152000 | 2.292589000 | -0.119216000 |
| C | 3.817099000 | -3.468463000 | 1.379620000 |
| H | 3.385016000 | -3.083210000 | 2.304680000 |
| H | 4.680866000 | -4.085625000 | 1.649785000 |
| H | 3.073567000 | -4.130611000 | 0.925382000 |
| C | 5.490000000 | -0.894751000 | 1.049675000 |
| H | 5.930853000 | -0.173758000 | 0.357302000 |
| H | 6.316547000 | -1.451593000 | 1.503614000 |
| H | 5.008489000 | -0.331357000 | 1.849795000 |
| C | -2.840151000 | 2.974677000 | 2.931796000 |
| H | -2.259295000 | 2.372912000 | 3.635724000 |
| H | -3.683591000 | 3.393659000 | 3.492094000 |
| H | -2.212059000 | 3.808347000 | 2.619139000 |
| C | -4.450600000 | 0.533956000 | 2.456596000 |
| H | -5.147310000 | -0.025517000 | 1.835394000 |
| H | -5.040895000 | 1.022485000 | 3.240775000 |
| H | -3.785270000 | -0.178695000 | 2.946986000 |
| Si | 3.529494000 | 1.897071000 | -1.536120000 |
| N | 2.224362000 | 1.338505000 | -0.441298000 |
| C | 1.204785000 | 3.630613000 | -0.175029000 |
| H | 2.131699000 | 4.180152000 | -0.272892000 |
| C | 1.152191000 | 2.224111000 | -0.215501000 |
| C | 4.839527000 | 2.901045000 | -0.608272000 |

| | | | |
|---|---|---|---|
| H | 4.431389000 | 3.757380000 | -0.065633000 |
| H | 5.576558000 | 3.288505000 | -1.320185000 |
| H | 5.383245000 | 2.292255000 | 0.118967000 |
| C | 2.840178000 | 2.974647000 | -2.931905000 |
| H | 2.259119000 | 2.372990000 | -3.635757000 |
| H | 3.683648000 | 3.393432000 | -3.492306000 |
| H | 2.212299000 | 3.808461000 | -2.619206000 |
| C | 4.450369000 | 0.533734000 | -2.456845000 |
| H | 5.147125000 | -0.025770000 | -1.835723000 |
| H | 5.040588000 | 1.022207000 | -3.241115000 |
| H | 3.784931000 | -0.178894000 | -2.947124000 |
| Si | 2.003319000 | 0.557188000 | 2.945116000 |
| Si | -4.328667000 | -2.097646000 | -0.185701000 |
| N | -0.900601000 | -0.939042000 | 1.053905000 |
| N | -2.922545000 | -1.223775000 | 0.434778000 |
| N | 1.375699000 | -0.259113000 | 1.473789000 |
| C | -1.982114000 | -1.743122000 | 1.269821000 |
| C | 0.284112000 | -1.094380000 | 1.704332000 |
| C | -1.954224000 | -2.787050000 | 2.200275000 |
| H | -2.817104000 | -3.410125000 | 2.384111000 |
| C | 0.346997000 | -2.147158000 | 2.636412000 |
| H | 1.284936000 | -2.348874000 | 3.128567000 |
| C | -5.283153000 | -2.944244000 | 1.214416000 |
| H | -4.838379000 | -3.901240000 | 1.501246000 |
| H | -6.300316000 | -3.165163000 | 0.872844000 |
| H | -5.369971000 | -2.332044000 | 2.114190000 |
| C | -0.754901000 | -2.964607000 | 2.875203000 |
| H | -0.663296000 | -3.772356000 | 3.595629000 |
| C | 2.975213000 | -0.572917000 | 4.124110000 |
| H | 2.332759000 | -1.238256000 | 4.705902000 |
| H | 3.507122000 | 0.056663000 | 4.846368000 |
| H | 3.728697000 | -1.187873000 | 3.627230000 |
| C | 0.545297000 | 1.238439000 | 3.924921000 |
| H | 0.011095000 | 1.997753000 | 3.350234000 |
| H | 0.898392000 | 1.710184000 | 4.848136000 |
| H | -0.173495000 | 0.466012000 | 4.210663000 |
| C | 3.146225000 | 1.994861000 | 2.547178000 |
| H | 4.026983000 | 1.717338000 | 1.969701000 |
| H | 3.496980000 | 2.406568000 | 3.500375000 |
| H | 2.635765000 | 2.795649000 | 2.012535000 |
| C | -3.817061000 | -3.468595000 | -1.379380000 |
| H | -3.385042000 | -3.083394000 | -2.304492000 |
| H | -4.680815000 | -4.085816000 | -1.649451000 |
| H | -3.073479000 | -4.130676000 | -0.925125000 |
| C | -5.489974000 | -0.894903000 | -1.049697000 |
| H | -5.930956000 | -0.173899000 | -0.357416000 |
| H | -6.316437000 | -1.451810000 | -1.503711000 |
| H | -5.008395000 | -0.331524000 | -1.849786000 |
| B | -1.872759000 | -0.075108000 | -0.026453000 |
| B | 1.872737000 | -0.075098000 | 0.026460000 |

Zero-point correction = 0.926070 (Hartree/Particle)

| | |
|---|---|
| Thermal correction to Energy = | 0.990321 |
| Thermal correction to Enthalpy = | 0.991265 |
| Thermal correction to Gibbs Free Energy = | 0.833777 |
| Sum of electronic and zero-point Energies = | -3575.033370 |
| Sum of electronic and thermal Energies = | -3574.969119 |
| Sum of electronic and thermal Enthalpies = | -3574.968175 |
| Sum of electronic and thermal Free Energies = | -3575.125663 |

**Aluminum containing pyridinophane ($Al^{Py}$)**




| | | | |
|---|---|---|---|
| Si | -4.156858000 | 1.219306000 | -1.654678000 |
| Si | 4.179001000 | -1.248935000 | -1.634862000 |
| Si | -2.201545000 | -2.494776000 | 2.192896000 |
| Si | 2.152176000 | 2.504573000 | 2.239316000 |
| N | -2.633941000 | 1.154043000 | -0.786578000 |
| N | -1.540801000 | -1.366098000 | 0.989950000 |
| N | 0.576899000 | -1.431189000 | -0.025599000 |
| N | 2.665665000 | -1.144432000 | -0.750146000 |
| N | 1.573181000 | 1.455604000 | 0.927364000 |
| N | -0.545096000 | 1.478439000 | -0.082940000 |
| C | -1.466908000 | 1.803853000 | -1.051962000 |
| C | -1.101202000 | 2.697443000 | -2.073510000 |
| H | -1.806181000 | 2.981752000 | -2.843293000 |
| C | 0.195215000 | 3.191280000 | -2.061475000 |
| H | 0.506245000 | 3.873588000 | -2.847461000 |
| C | 1.118855000 | 2.822350000 | -1.081166000 |
| H | 2.138756000 | 3.181577000 | -1.107323000 |
| C | 0.727302000 | 1.937473000 | -0.070492000 |
| C | 1.495382000 | -1.800640000 | -0.982328000 |
| C | 1.127467000 | -2.736587000 | -1.964844000 |

| | | | |
|---|---|---|---|
| H | 1.832269000 | -3.056894000 | -2.720305000 |
| C | -0.170656000 | -3.222122000 | -1.934316000 |
| H | -0.485357000 | -3.934552000 | -2.691570000 |
| C | -1.093741000 | -2.805463000 | -0.972253000 |
| H | -2.117454000 | -3.151448000 | -0.993835000 |
| C | -0.698758000 | -1.880421000 | 0.001280000 |
| C | -3.949943000 | 0.583656000 | -3.420577000 |
| H | -3.240000000 | 1.181813000 | -3.999416000 |
| H | -4.901364000 | 0.596603000 | -3.962423000 |
| H | -3.581492000 | -0.446427000 | -3.425929000 |
| C | -4.854704000 | 2.973981000 | -1.690139000 |
| H | -5.005316000 | 3.356126000 | -0.676050000 |
| H | -5.823913000 | 3.003349000 | -2.199079000 |
| H | -4.198031000 | 3.680071000 | -2.206692000 |
| C | -5.340818000 | 0.099507000 | -0.711151000 |
| H | -4.984808000 | -0.934454000 | -0.679003000 |
| H | -6.328821000 | 0.087112000 | -1.181783000 |
| H | -5.480272000 | 0.436057000 | 0.320889000 |
| C | -0.815027000 | -3.625236000 | 2.790197000 |
| H | -0.385304000 | -4.217944000 | 1.977359000 |
| H | -1.187072000 | -4.329531000 | 3.541486000 |
| H | -0.000158000 | -3.055916000 | 3.246553000 |
| C | -3.598442000 | -3.570548000 | 1.503863000 |
| H | -4.400194000 | -2.967419000 | 1.066465000 |
| H | -4.045283000 | -4.168585000 | 2.305577000 |
| H | -3.254091000 | -4.271755000 | 0.738865000 |
| C | -2.890957000 | -1.521622000 | 3.649441000 |
| H | -2.146670000 | -0.859962000 | 4.098579000 |
| H | -3.216138000 | -2.225823000 | 4.423096000 |
| H | -3.755253000 | -0.906748000 | 3.387623000 |
| C | 4.872814000 | -3.005049000 | -1.597743000 |
| H | 5.040647000 | -3.337700000 | -0.569034000 |
| H | 5.832997000 | -3.061726000 | -2.121266000 |
| H | 4.206071000 | -3.733867000 | -2.067687000 |
| C | 5.377104000 | -0.087246000 | -0.765376000 |
| H | 5.018317000 | 0.946025000 | -0.769114000 |
| H | 6.354012000 | -0.093462000 | -1.258877000 |
| H | 5.540706000 | -0.376267000 | 0.277102000 |
| C | 3.945232000 | -0.695617000 | -3.424952000 |
| H | 3.236160000 | -1.325278000 | -3.970169000 |
| H | 4.891551000 | -0.723196000 | -3.975153000 |
| H | 3.566570000 | 0.329688000 | -3.471563000 |
| C | 4.024284000 | 2.347482000 | 2.409146000 |
| H | 4.331421000 | 1.321030000 | 2.629769000 |
| H | 4.394164000 | 2.975579000 | 3.226492000 |
| H | 4.542140000 | 2.658134000 | 1.496797000 |
| C | 1.699556000 | 4.302626000 | 1.894051000 |
| H | 2.206760000 | 4.713319000 | 1.017703000 |
| H | 1.985822000 | 4.917987000 | 2.753573000 |
| H | 0.624831000 | 4.438412000 | 1.744082000 |
| C | 1.344675000 | 1.982861000 | 3.862448000 |
| H | 0.254556000 | 2.061526000 | 3.807168000 |

| | | | |
|---|---|---|---|
| H | 1.679271000 | 2.610736000 | 4.695229000 |
| H | 1.586825000 | 0.946954000 | 4.116039000 |
| H | -2.501721000 | 1.111791000 | 2.187454000 |
| Al | 1.966869000 | -0.364164000 | 0.872648000 |
| H | 2.569334000 | -0.909233000 | 2.229757000 |
| Al | -1.925722000 | 0.454955000 | 0.873409000 |

Zero-point correction = 0.624273 (Hartree/Particle)

Thermal correction to Energy = 0.671441

Thermal correction to Enthalpy = 0.672385

Thermal correction to Gibbs Free Energy = 0.542586

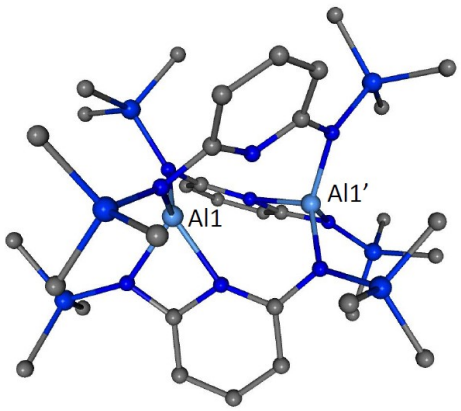
Sum of electronic and zero-point Energies = -2836.450529

Sum of electronic and thermal Energies = -2836.403361

Sum of electronic and thermal Enthalpies = -2836.402417

Sum of electronic and thermal Free Energies = -2836.532217

**Aluminum containing bicyclic pyridinophane ($Al^{biPy}$)**




| | | | |
|---|---|---|---|
| Al | 1.700431000 | -0.017769000 | 0.066270000 |
| Si | 1.961200000 | 0.207586000 | 3.339617000 |
| Si | -4.317358000 | -2.399861000 | -0.248074000 |
| Si | 3.746985000 | 2.306950000 | -1.267177000 |
| N | -0.857585000 | -1.205906000 | 1.173969000 |
| N | -2.908209000 | -1.530288000 | 0.346535000 |
| N | 1.276235000 | -0.488704000 | 1.854574000 |
| N | 0.104626000 | 1.829042000 | 0.152930000 |
| N | 2.324601000 | 1.695247000 | -0.400386000 |
| C | -1.967573000 | -2.021206000 | 1.205703000 |
| C | 0.227737000 | -1.382026000 | 1.973093000 |

| | | | |
|---|---|---|---|
| C | 1.273655000 | 3.917937000 | -0.015992000 |
| H | 2.188649000 | 4.470344000 | -0.172226000 |
| C | -1.994977000 | -3.125363000 | 2.069500000 |
| H | -2.854963000 | -3.778409000 | 2.115337000 |
| C | 1.248453000 | 2.514743000 | -0.105444000 |
| C | 0.217126000 | -2.482832000 | 2.850271000 |
| H | 1.086824000 | -2.693128000 | 3.453442000 |
| C | 0.094461000 | 4.576900000 | 0.299139000 |
| H | 0.086892000 | 5.661684000 | 0.356191000 |
| C | -5.483064000 | -2.951019000 | 1.136615000 |
| H | -5.083292000 | -3.773418000 | 1.735955000 |
| H | -6.428557000 | -3.302862000 | 0.709618000 |
| H | -5.718508000 | -2.132446000 | 1.821217000 |
| C | -0.884591000 | -3.331569000 | 2.877585000 |
| H | -0.871384000 | -4.186252000 | 3.548215000 |
| C | 2.797501000 | -1.044422000 | 4.497146000 |
| H | 2.080867000 | -1.590747000 | 5.115796000 |
| H | 3.460152000 | -0.507486000 | 5.184888000 |
| H | 3.412576000 | -1.780582000 | 3.972607000 |
| C | 0.588104000 | 1.047052000 | 4.321456000 |
| H | 0.156204000 | 1.882084000 | 3.764354000 |
| H | 0.967299000 | 1.440360000 | 5.270536000 |
| H | -0.223257000 | 0.352682000 | 4.559525000 |
| C | 3.263981000 | 1.486470000 | 2.882888000 |
| H | 4.114502000 | 1.058257000 | 2.346998000 |
| H | 3.657779000 | 1.923049000 | 3.807169000 |
| H | 2.867565000 | 2.304070000 | 2.279681000 |
| C | 4.873631000 | 3.347194000 | -0.157335000 |
| H | 4.388054000 | 4.237299000 | 0.251068000 |
| H | 5.748125000 | 3.688656000 | -0.721938000 |
| H | 5.242905000 | 2.767523000 | 0.693388000 |
| C | -3.778489000 | -3.924451000 | -1.222766000 |
| H | -3.161637000 | -3.648720000 | -2.082823000 |
| H | -4.642029000 | -4.484175000 | -1.597129000 |
| H | -3.187023000 | -4.611787000 | -0.610388000 |
| C | -5.267980000 | -1.234373000 | -1.382083000 |
| H | -5.635357000 | -0.345843000 | -0.860437000 |
| H | -6.142833000 | -1.744487000 | -1.797784000 |
| H | -4.661457000 | -0.898519000 | -2.225829000 |
| C | 3.219881000 | 3.334553000 | -2.764146000 |
| H | 2.648651000 | 2.726507000 | -3.471726000 |
| H | 4.105894000 | 3.702336000 | -3.292874000 |
| H | 2.606035000 | 4.202040000 | -2.514787000 |
| C | 4.776425000 | 0.880716000 | -1.928953000 |
| H | 5.235499000 | 0.285015000 | -1.139745000 |
| H | 5.588411000 | 1.290650000 | -2.539550000 |
| H | 4.196525000 | 0.204464000 | -2.559634000 |
| Si | -3.502774000 | 2.179735000 | 1.714211000 |
| N | -2.150754000 | 1.649115000 | 0.689364000 |
| C | -1.076935000 | 3.873385000 | 0.538208000 |
| H | -1.998060000 | 4.398804000 | 0.744450000 |
| C | -1.047590000 | 2.467036000 | 0.478460000 |

| | | | |
|---|---|---|---|
| C | -4.673958000 | 3.379336000 | 0.833318000 |
| H | -4.205102000 | 4.318599000 | 0.529429000 |
| H | -5.506382000 | 3.636523000 | 1.497442000 |
| H | -5.103922000 | 2.931150000 | -0.066657000 |
| C | -2.869334000 | 2.982450000 | 3.302382000 |
| H | -2.324904000 | 2.258404000 | 3.914743000 |
| H | -3.716232000 | 3.339895000 | 3.898080000 |
| H | -2.205200000 | 3.832718000 | 3.136937000 |
| C | -4.543600000 | 0.699381000 | 2.229627000 |
| H | -5.065361000 | 0.233932000 | 1.392957000 |
| H | -5.308064000 | 1.045019000 | 2.934371000 |
| H | -3.962008000 | -0.076855000 | 2.731080000 |
| Al | -1.784095000 | -0.013705000 | -0.086093000 |
| Si | -1.979734000 | 0.945893000 | -3.226249000 |
| Si | 4.130833000 | -2.550374000 | -0.180204000 |
| N | 0.775034000 | -0.944716000 | -1.402401000 |
| N | 2.794397000 | -1.497934000 | -0.628222000 |
| N | -1.343022000 | -0.070657000 | -1.915217000 |
| C | 1.855113000 | -1.783555000 | -1.568939000 |
| C | -0.314356000 | -0.952174000 | -2.212204000 |
| C | 1.847555000 | -2.717014000 | -2.620269000 |
| H | 2.683216000 | -3.383115000 | -2.780193000 |
| C | -0.338553000 | -1.873505000 | -3.271892000 |
| H | -1.213359000 | -1.946653000 | -3.899680000 |
| C | 5.299422000 | -2.935272000 | -1.619332000 |
| H | 4.856404000 | -3.587612000 | -2.376428000 |
| H | 6.189599000 | -3.450452000 | -1.241864000 |
| H | 5.638500000 | -2.028876000 | -2.126930000 |
| C | 0.739808000 | -2.736785000 | -3.453655000 |
| H | 0.704616000 | -3.455716000 | -4.267534000 |
| C | -2.831740000 | -0.014705000 | -4.623370000 |
| H | -2.122031000 | -0.472920000 | -5.316726000 |
| H | -3.445254000 | 0.677353000 | -5.210662000 |
| H | -3.497928000 | -0.801413000 | -4.258699000 |
| C | -0.564987000 | 1.925280000 | -3.997622000 |
| H | -0.102003000 | 2.602216000 | -3.275053000 |
| H | -0.919863000 | 2.528966000 | -4.839593000 |
| H | 0.219221000 | 1.265383000 | -4.380809000 |
| C | -3.261017000 | 2.132904000 | -2.526628000 |
| H | -4.127892000 | 1.620065000 | -2.101890000 |
| H | -3.633663000 | 2.760956000 | -3.343040000 |
| H | -2.854728000 | 2.796069000 | -1.762593000 |
| C | 3.468644000 | -4.184514000 | 0.498476000 |
| H | 2.854129000 | -4.025531000 | 1.389232000 |
| H | 4.284351000 | -4.861936000 | 0.772486000 |
| H | 2.844320000 | -4.707364000 | -0.232378000 |
| C | 5.135308000 | -1.688698000 | 1.160389000 |
| H | 5.620027000 | -0.775095000 | 0.805803000 |
| H | 5.928918000 | -2.352863000 | 1.517910000 |
| H | 4.523450000 | -1.425195000 | 2.024901000 |

Zero-point correction = 0.915839 (Hartree/Particle)

| | |
|---|---|
| Thermal correction to Energy = | 0.983795 |
| Thermal correction to Enthalpy = | 0.984739 |
| Thermal correction to Gibbs Free Energy = | 0.813627 |
| Sum of electronic and zero-point Energies = | -4010.4203440 |
| Sum of electronic and thermal Energies = | -4010.3523890 |
| Sum of electronic and thermal Enthalpies = | -4010.3514450 |
| Sum of electronic and thermal Free Energies = | -4010.5225570 |

**Calculation of Gibbs free energy of the reaction for the formation of $B^{Py}$, $B^{biPy}$, $Al^{Py}$ and $Al^{biPy}$**

The Gibbs free energy of a reaction is calculated by

$$\Delta G_r = \Sigma \Delta G_f \text{(products)} - \Sigma \Delta G_f \text{ (reactant)}$$

where $\Delta G_f$ is the Gibbs free energy of formation calculated using Gaussian 09 package[5], see above for the calculations to obtain $\Delta G_f$ (for bap, $BH_3$, $AlH_3$, $H_2$, $B^{Py}$, $B^{biPy}$, $Al^{Py}$ and $Al^{biPy}$).

The Gibbs free energies of the reactions ($\Delta G_r$) (eqn 1-eqn 6) are given in Table S2.

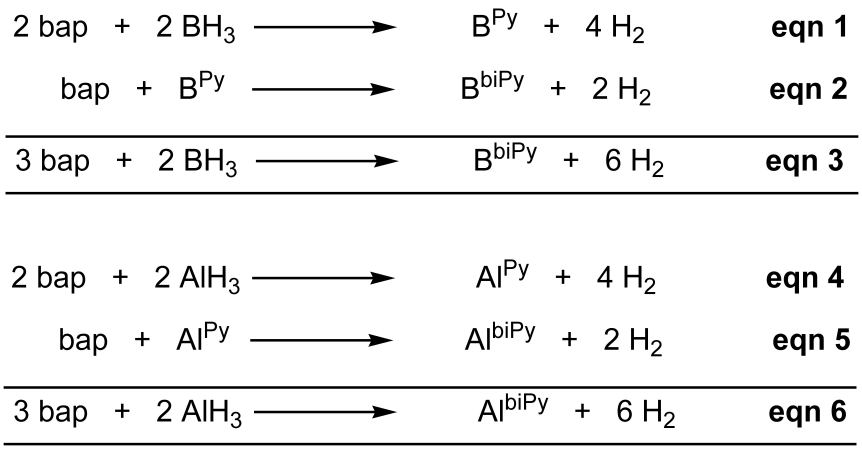



**Figure S23.** Reactions used for the calculation of free energy of the reaction for the formation of $B^{Py}$, $B^{biPy}$, $Al^{Py}$ and $Al^{biPy}$.

**Structures of compounds notations (bap, $B^{Py}$, $B^{biPy}$, $Al^{Py}$ and $Al^{biPy}$) in eqns 1-6 are shown below**

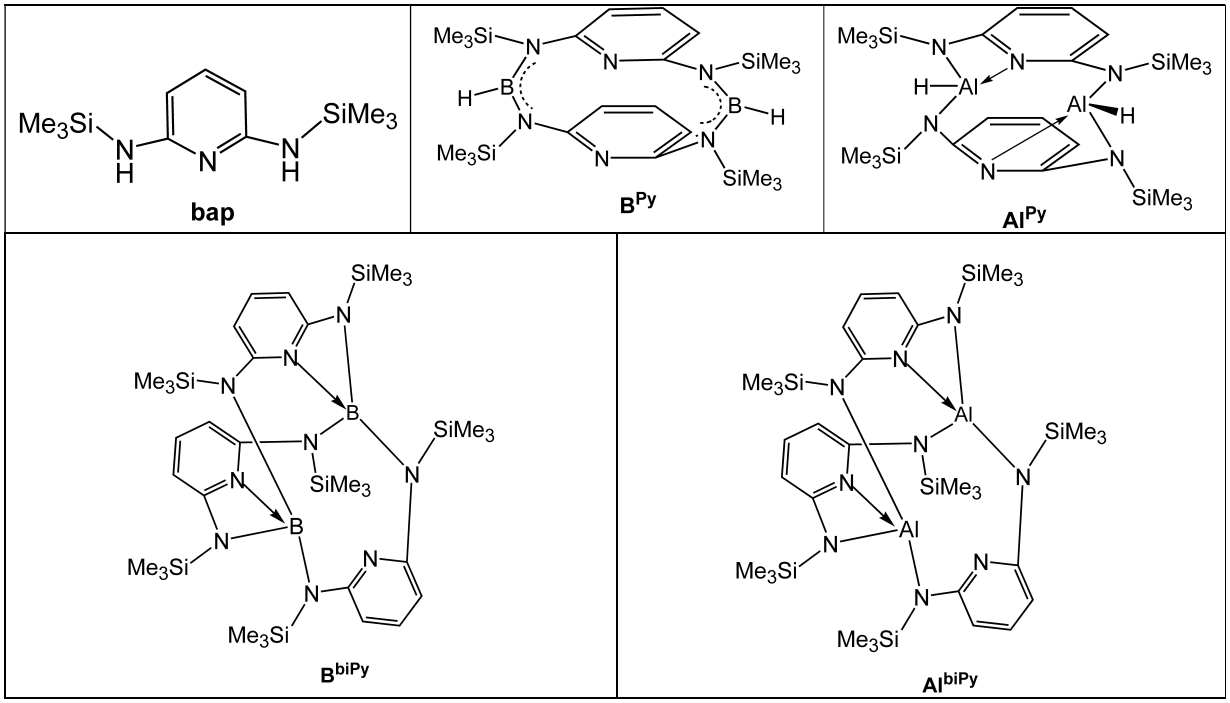



**Table S2.** Comupted values of bap, $H_2$, $BH_3$ and $AlH_3$ used for the calculation of Gibbs free energy

| **Values \ Molecules** | **bap** | **$H_2$** | **$BH_3$** | **$AlH_3$** |
|---|---|---|---|---|
| Electronic Energy (Hartree/Particle) | -1176.597735 | -1.176632 | -26.6173784 | -244.2259864 |
| Zero-point correction (Hartree/Particle) | 0.32536 | 0.01001 | 0.026054 | 0.018614 |
| Thermal correction to Energy (Hartree/Particle) | 0.34764 | 0.012371 | 0.028941 | 0.021716 |
| Thermal correction to Enthalpy (Hartree/Particle) | 0.348584 | 0.013315 | 0.029886 | 0.02266 |
| Thermal correction to Gibbs Free Energy (Hartree/Particle) | 0.274946 | -0.001475 | 0.008504 | -0.000881 |
| Sum of electronic and thermal Free Energies (Hartree/Particle)$G_f$ | -1176.322789 | -1.178107 | -26.608875 | -244.226867 |

**Table S3.** Comupted values of $B^{Py}$, $B^{biPy}$, $Al^{Py}$ and $Al^{biPy}$ used for the calculation of Gibbs free energy

| **Values \ Molecules** | **$B^{Py}$** | **$B^{bipy}$** | **$Al^{Py}$** | **$Al^{biPy}$** |
|---|---|---|---|---|
| Electronic Energy (Hartree/Particle) | -2401.795764 | -3575.95944 | -2837.074802 | -4011.336184 |
| Zero-point correction (Hartree/Particle) | 0.637228 | 0.92607 | 0.624273 | 0.915839 |
| Thermal correction to Energy (Hartree/Particle) | 0.682532 | 0.990321 | 0.671441 | 0.983795 |
| Thermal correction to Enthalpy (Hartree/Particle) | 0.683476 | 0.991265 | 0.672385 | 0.984739 |
| Thermal correction to Gibbs Free Energy (Hartree/Particle) | 0.55646 | 0.833777 | 0.542586 | 0.813627 |
| Sum of electronic and thermal Free Energies (Hartree/Particle) $G_f$ | -2401.239304 | -3575.125663 | -2836.532217 | -4010.522557 |

**Table S4.** Gibbs free energy of the reactions (eqn 1 - eqn 6)

| Values\eqns | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| **$\Delta G_r$ (kcal/mol)** | -55.5 | 50.4 | -5.1 | -91.2 | -14.9 | -106.1 |

**NBO charges for selected atoms in $B^{Py}$**

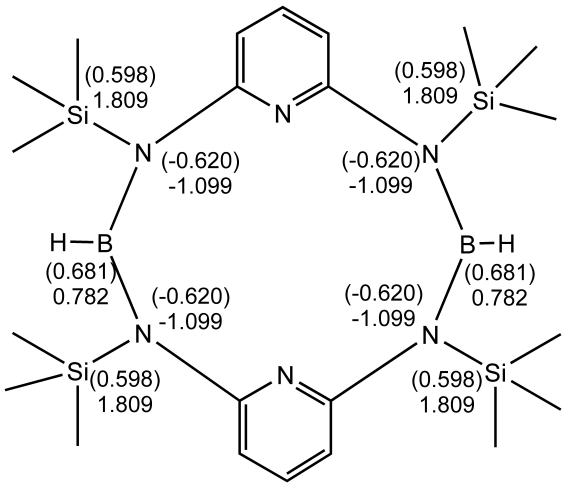



**Figure S24.** Calculated charges in the pyridinophane $\mathbf{B^{Py}}$. Numbers in the parentheses denote consolidated NBO charges whereas other numbers are bare NBO charges.

The NBO analysis for $\mathbf{B^{Py}}$ shows bare charges of +0.782e on B and −1.099e on N. Therefore, the B⋯N bond can be clearly considered a polar double-bond. The effective NBO charges at B and N are 0.681e and -0.620e respectively suggesting polar BN π bonds with small polarization towards N (Figure S24). The NBO calculation gives two π orbitals (occupations 1.922 and 1.920) localized on each of the NBN units. Hence, the shorter B-N distances, the π MOs and the NBO charges all support the view that $\mathbf{B^{Py}}$ does not have vacant orbital available on B to accommodate the third 2,6-$(Me_3SiN)_2C_5H_3N$ bridge, thus precluding the formation of $\mathbf{B^{biPy}}$.

**π-molecular orbitals of $B^{Py}$**

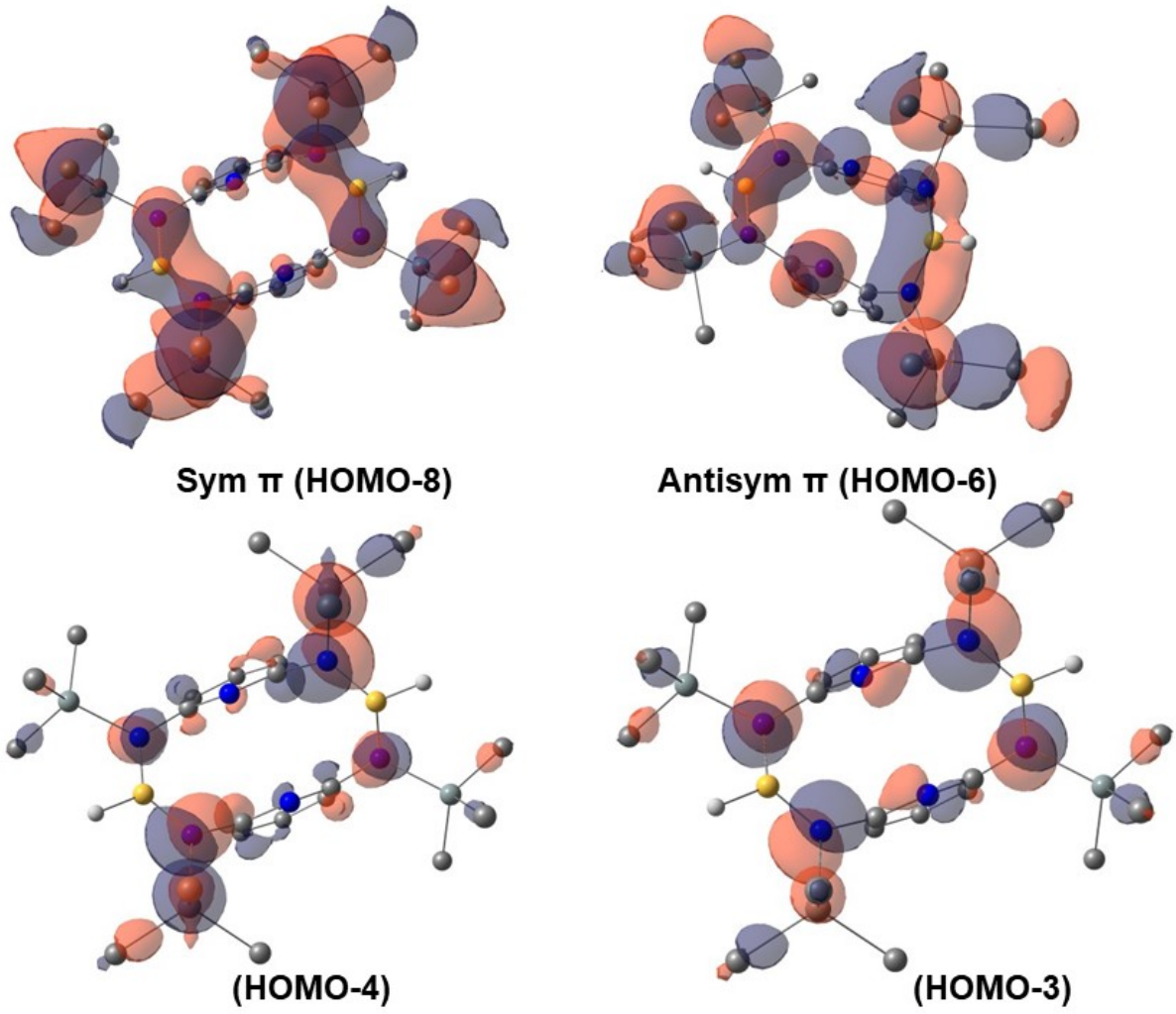



**Figure S25.** N⋯B⋯N based π-molecular orbitals of $\mathbf{B^{Py}}$.

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