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SUPPORTING INFORMATION

Group 13 element containing conformationally rigid "N-E-N" heteroatomic bridged [3.3](2,6)pyridinophanes (E = B, Al)

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Experimental section.

General considerations

All manipulations were performed under nitrogen/argon atmosphere using Schlenk line or glove box techniques. All chemicals were purchased from Sigma-Aldrich and used without further purification. The starting materials bis(trimethylsilyl)-N,N'-2,6-diaminopyridine[1] lithium bis(trimethylsilyl)-N,N'-2,6-diamidopyridine[2] were prepared by following the reported procedures. IR spectra of the complexes were recorded in the range 4000–400 cm^{-1} with a Perkin–Elmer Lambda 35-spectrophotometer. The ^{1}H, ^{13}C and ^{29}Si spectra were recorded with a Bruker 400 MHz spectrometer with TMS as external reference; chemical shift values are reported in ppm. High-resolution mass spectrometry was performed with a Waters SYNAPT G2-S.

Synthesis of tetraazadibora[3.3](2,6)pyridinophane (1): A solution of lithium bis(trimethylsilyl)-N,N'-2,6-diamidopyridine (19.76 mmol, 5.24 g) in hexane (150 mL) was added slowly to a solution of BCl_3 (19.8 mL, 19.76 mmol, 1 M in toluene) in hexane (150 mL) at −78 °C. The reaction mixture allowed to warm to room temperature and stirred for further 12 hours. The mixture was then filtered to remove LiCl and the volume of the filtrate was reduced to (250 mL) and stored at 4 °C to afford colorless crystals of **1**. Yield: 2.2 g (37 %). Mp. 247–251 °C. IR (Nujol) ν: 3085, 2923, 2852, 1601, 1456), 1401, 1342, 1287, 1250, 1096, 1029, 956, 912, 846, 794, 728, 682, 599, 510, 420 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (t, 2H, *p*–ArH, $^{3}J_{H\text{-}H}$ = 8 Hz), 6.21 (broad, 4H, *m*–ArH), 0.33 (s, 18H, $Si(CH_3)_3$), 0.08 (s, 18H, $Si(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0, 155.9, 143.9, 112.5, 101.8, 1.9 $Si(CH_3)_3$, 0.2 $Si(CH_3)_3$ ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 8.1 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 6.29, 4.18 ppm. HRMS (AP^{+}): *m/z* calcd for $C_{22}H_{43}B_2Cl_2N_6Si_4$: (595.2201) [M+H]$^{+}$; found: (595.2179).

Synthesis of tetraazadibora[3.3](2,6)pyridinophane (2): A solution of lithium bis(trimethylsilyl)-N,N'-2,6-diamidopyridine (19.76 mmol, 5.24 g) in hexane (70 mL) was added slowly to a solution of $BHCl_2{\cdot}SMe_2$ (2.3 mL, 19.76 mmol, 8.7 M in SMe_2) in hexane (100 mL) at −78 °C. The reaction mixture allowed to come at room temperature and stirred for further 12 hours to afford orange solution. The mixture was then filtered to remove LiCl and the volume of the filtrate was reduced to (10 mL) and stored at –20 °C to afford orange transparent crystals of **2**. Yield: 1.1 g (21 %). Mp. 116–120 °C. IR (in Nujol) ν: 3051, 2955, 2855, 2444, 1938, 1581, 1453, 1355, 1258, 1017, 842 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.02 (t, 2H, *p*–Ar*H*, $^{3}J_{\text{H-H}}$ = 7.6 Hz), 6.17 (d, 4H, *m*–Ar*H*, $^{3}J_{\text{H-H}}$ = 7.6 Hz), 0.05 (s, 36H, $Si(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 137.7, 119.4, 1.2 $Si(CH_3)_3$ ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = 27.0 ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 11 ppm. HRMS (AP^{+}): *m/z* calcd for $C_{22}H_{45}B_2N_6Si_4$: (527.2979) [M+H]$^{+}$; found: (527.2992).

Synthesis of trihydridoborane adduct with bis(trimethylsilyl)-N,N'-2,6-diaminopyridine (2a): A solution of $BH_3{\cdot}SMe_2$ (0.4 mL, 3.9 mmol, 10 M in SMe_2) was added slowly to a stirred solution of bis(trimethylsilyl)-N,N'-2,6-diaminopyridine (1.0 g, 3.9 mmol) in pentane (30 mL) at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 12 hours. This was followed by removal of all volatiles under vacuum to afford a white solid (99.0 % conversion). This solid was crystallized by hexane solution at 4 °C. Yield: 0.9 g (84 %). Mp. 97-100 °C. IR (Nujol) ν: 3302 (N–H), 2958, 2924, 2856, 2324 (B–H), 1623, 1582, 1466, 1381, 1313, 1255, 1221, 1176, 1108, 1057, 935, 846, 778, 730, 699, 625, 567, 455 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25 (t, 1H, *p*–ArH, Ar, $^{3}J_{\text{H-H}}$ = 8.0 Hz), 6.38 (s, 2H, *m*–ArH, NH), 5.96 (d, 2H, Ar, $^{3}J_{\text{H-H}}$ = 8 Hz), 0.32 (s, 18H, $Si(CH_3)_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 138.2, 98.4, 0.3 $Si(CH_3)_3$ ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 5.5 ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ = –24.5 (broad) ppm. HRMS (AP^{+}): *m/z* calcd for $C_{11}H_{25}BN_3Si_2$: (266.1683) [M–H]$^{+}$; found: (266.1671).

Alternative synthesis of tetraazadibora[3.3](2,6)pyridinophane **(2):** The freshly made adduct **2a** (using the above method) (5.3 g, 19.76 mmol) was dissolved in toluene (70 mL) and refluxed for 28 hours. Alternatively, $BH_3{\cdot}SMe_2$ (2 mL, 19.76 mmol, 10 M in SMe_2) was added slowly to a stirred solution of bis(trimethylsilyl)-N,N'-2,6-diaminopyridine (5.0 g, 19.76 mmol) in toluene (80 mL) at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 2 hours at room temperature, followed by reflux for next 28 hours. In both the approaches, on reflux after half an hour there was a change in color of the reaction mixture from transparent to orange colour. After 28 hours, all the volatiles were removed under vacuum to afford an orange solid. Yield: 4.2 g (88 %). The spectroscopic characterization of this product was identical to that mentioned above.

Estimation of Lewis acidity of 2 by Gutmann–Beckett method

Quantitative estimation of Lewis acidity of compound **2** was made by using the Gutmann–Beckett method.[3] The Gutmann–Beckett method provides acceptor number (AN) as a measure of relative Lewis acidity based on the perturbation of the ^{31}P NMR signal of Et_3PO upon coordination with Lewis acids.[3] This scale assigns an acceptor number (AN) of 0 for n-hexane and an AN of 100 for the powerful Lewis acid SbF_5. According to the method of Beckett on addition of compound **2** to a solution of Et_3PO in C_6D_6 no change was observed in the ^{31}P{^{1}H} NMR resonance as compared to free Et_3PO (45.72 ppm). This shows that the boron centres of **2** do not show Lewis acidic character as the coordination of Et_3PO to boron atoms on **2** could not occur.

Synthesis of tetraazadialumino[3.3](2,6)pyridinophane (3):

$AlMe_3$ (10.0 mL, 19.76 mmol, 2.0 M in toluene) was added slowly to a stirred solution of bis(trimethylsilyl)-N,N'-2,6-diaminopyridine (5.0 g, 19.76 mmol) in toluene (80 mL) at 0 °C. The reaction mixture was allowed to come to room temperature and stirred for 1 hour followed by 36 hours of reflux. All volatiles were removed under vacuum to give an oily material, which was crystallized with dry pentane (40 mL) at – 20 °C. Yield: 3.8 g (65 %). Mp. 268–272 °C. IR (nujol) v: 3084, 2956, 2928, 2857, 1593, 1547, 1454, 1394, 1351, 1256, 1192, 1159, 1064, 904, 844, 734, 687, 634, 531, 474 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, 2H, *p*–ArH, Ar, $^3J_{H\text{-}H}$ = 8.0 Hz), 5.79 (broad singlet, 4H, *m*–ArH, Ar), 0.13 (s, 36H, $Si(CH_3)_3$), −0.49 (s, 6H, $AlCH_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 154.9, 143.2, 109.5, 102.1, 2.3 ($Si(CH_3)_3$), 0.5 ($Si(CH_3)_3$), −10.5 ($AlCH_3$) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = 3.76 ($Si(CH_3)_3$), −2.38 ($Si(CH_3)_3$) ppm. HRMS (AP$^+$): *m/z* calcd for $C_{24}H_{49}Al_2N_6Si_4$: (587.2726) $[M+H]^+$; found: (587.2708).

2. Heteronuclear NMR spectra of tetraazadibora[3.3](2,6)pyridinophane (1).

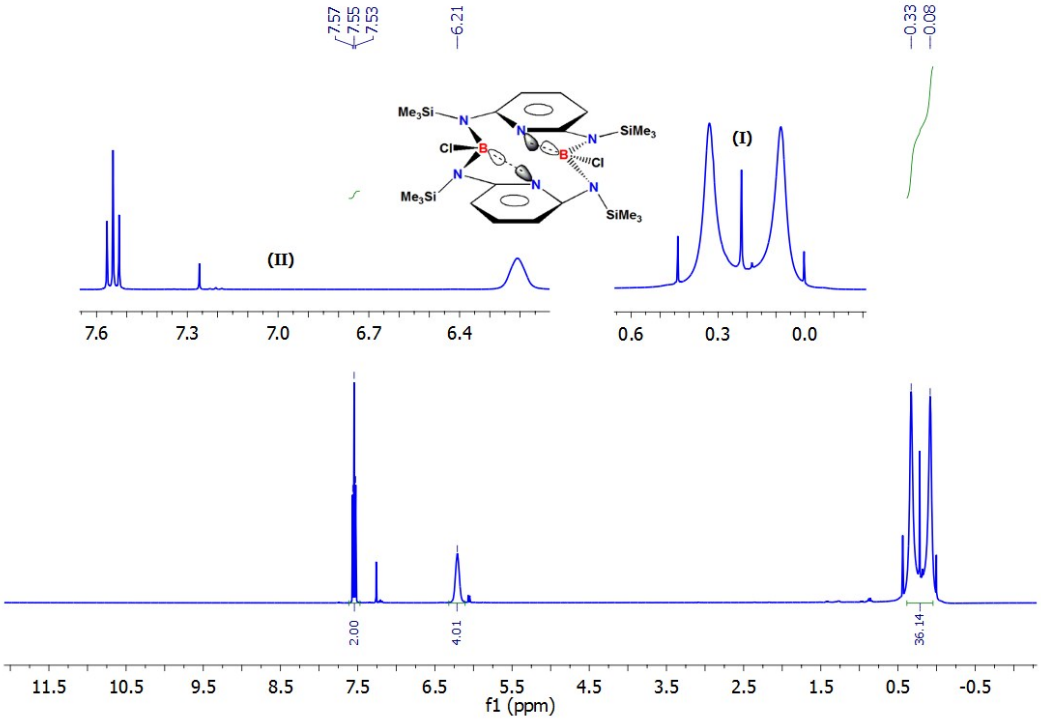

Fig S1. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of tetraazadibora[3.3](2,6)pyridinophane **(1)**. Insets **(I)** and **(II)** show expanded aliphatic and aromatic spectral regions, respectively.

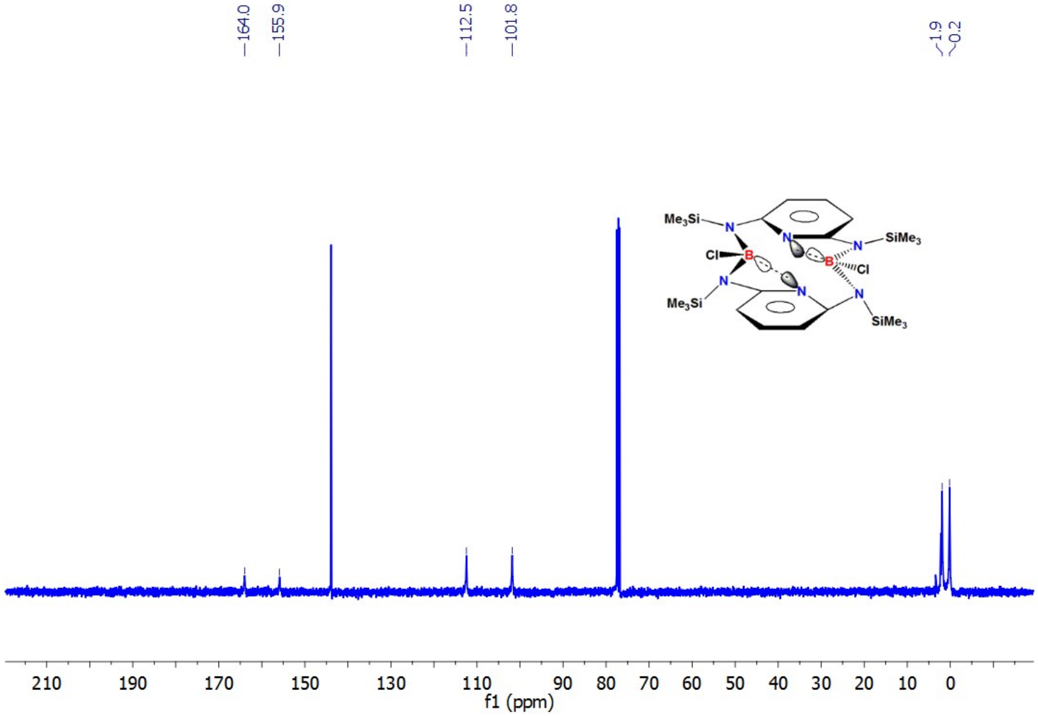

Fig S2. ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of tetraazadibora[3.3](2,6)pyridinophane **(1)**.

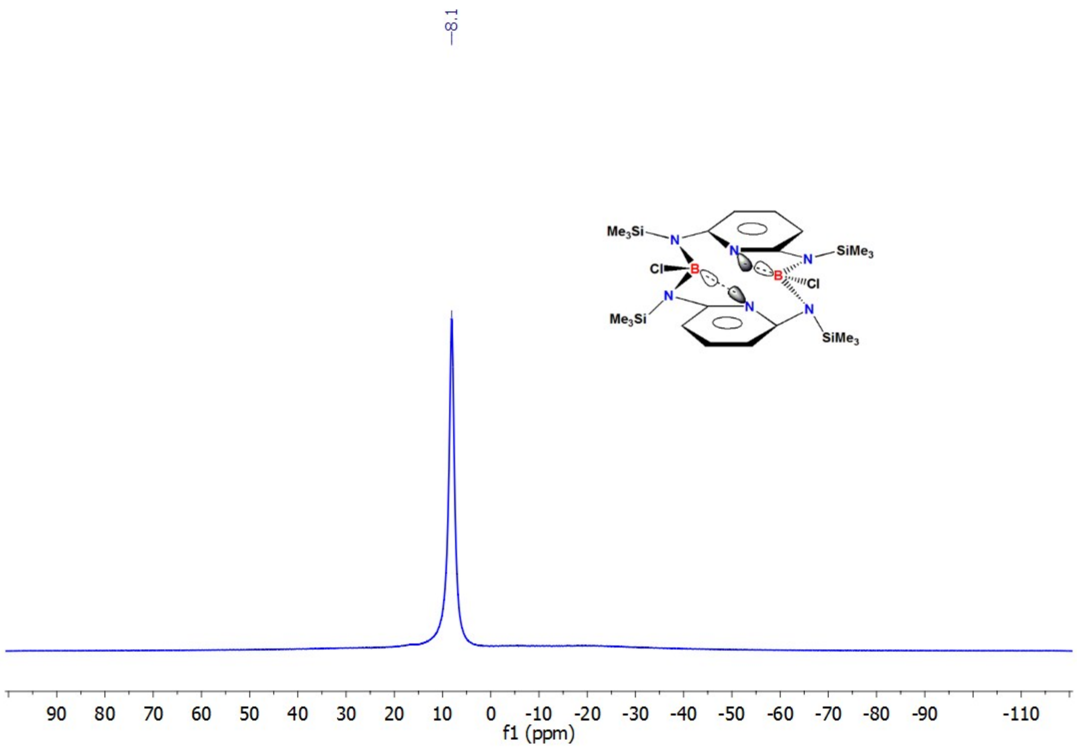

Fig S3. ^{11}B NMR spectrum (162 MHz, $CDCl_3$) of tetraazadibora[3.3](2,6)pyridinophane **(1)**.

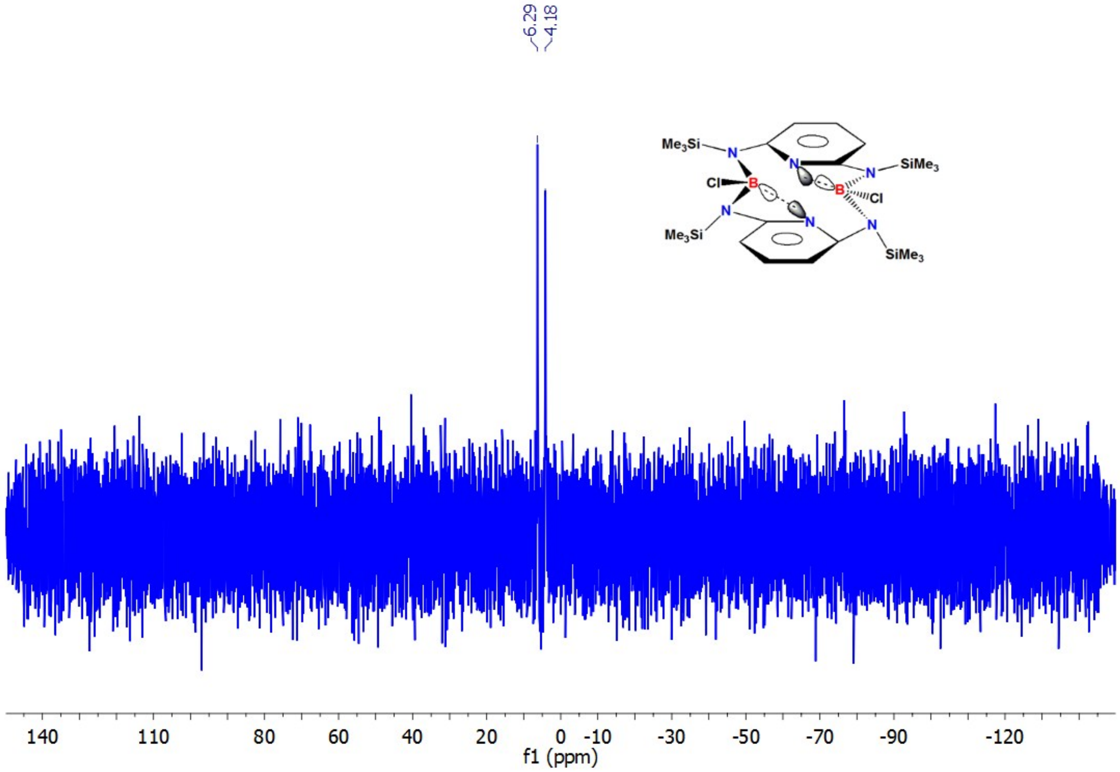

Fig S4. ^{29}Si NMR spectrum (79.5 MHz, $CDCl_3$) of tetraazadibora[3.3](2,6)pyridinophane **(1)**.

3. Variable temperature heteronuclear NMR spectra of pyridinophane 1.

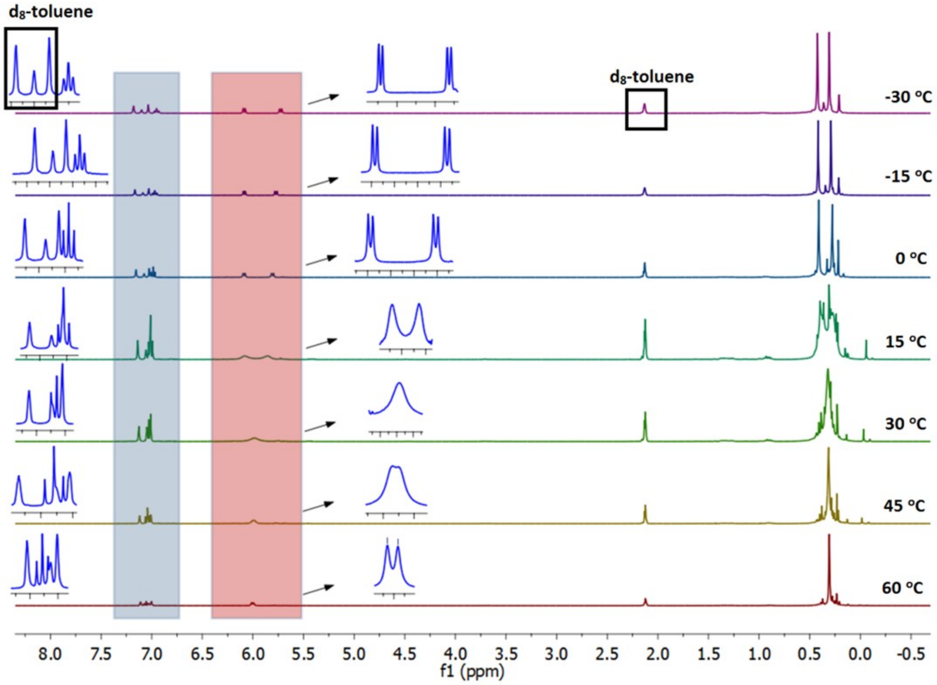

Fig S5. Variable temperature ^1H NMR spectra (400 MHz, d_8-toluene) of pyridinophane **1**.

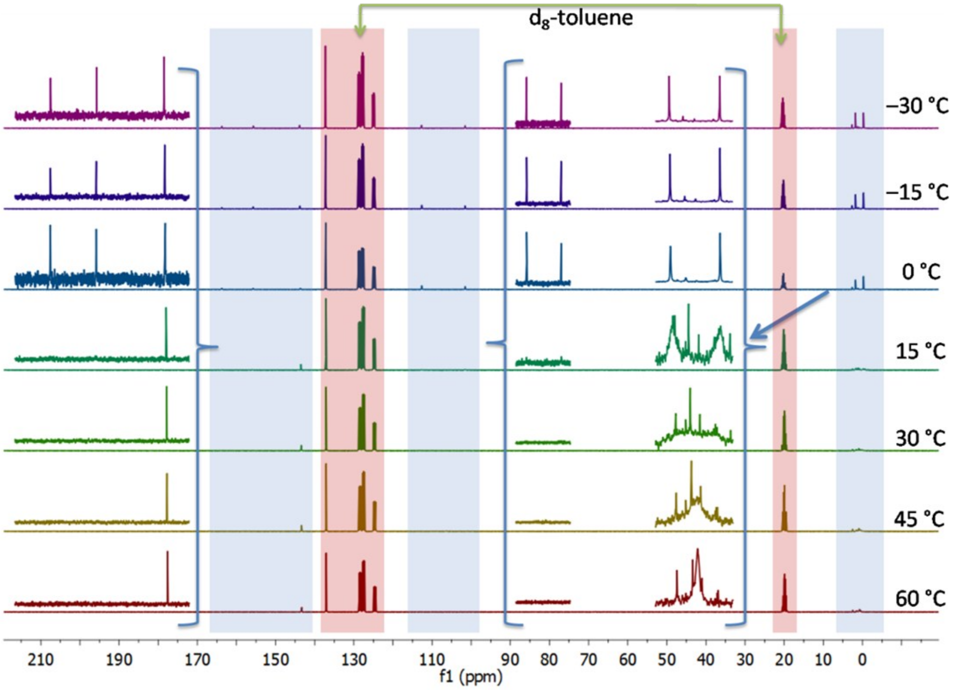

Fig S6. Variable temperature ^{13}C NMR spectra (100 MHz, d_8-toluene) of pyridinophane **1**.

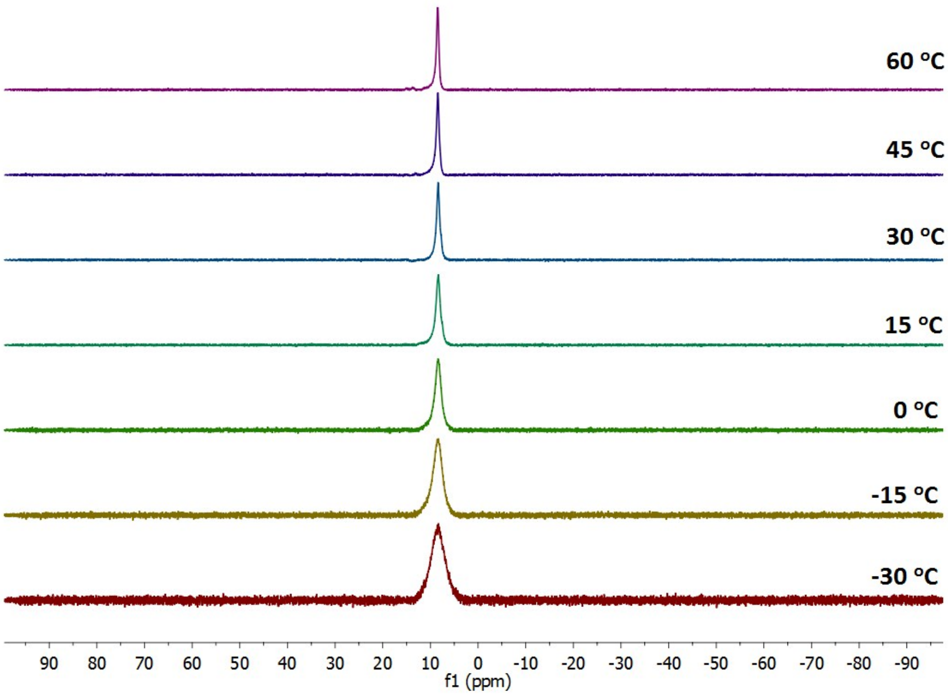

Fig S7. Variable temperature ^{11}B NMR spectra (128 MHz, d_8-toluene) of pyridinophane **1**.

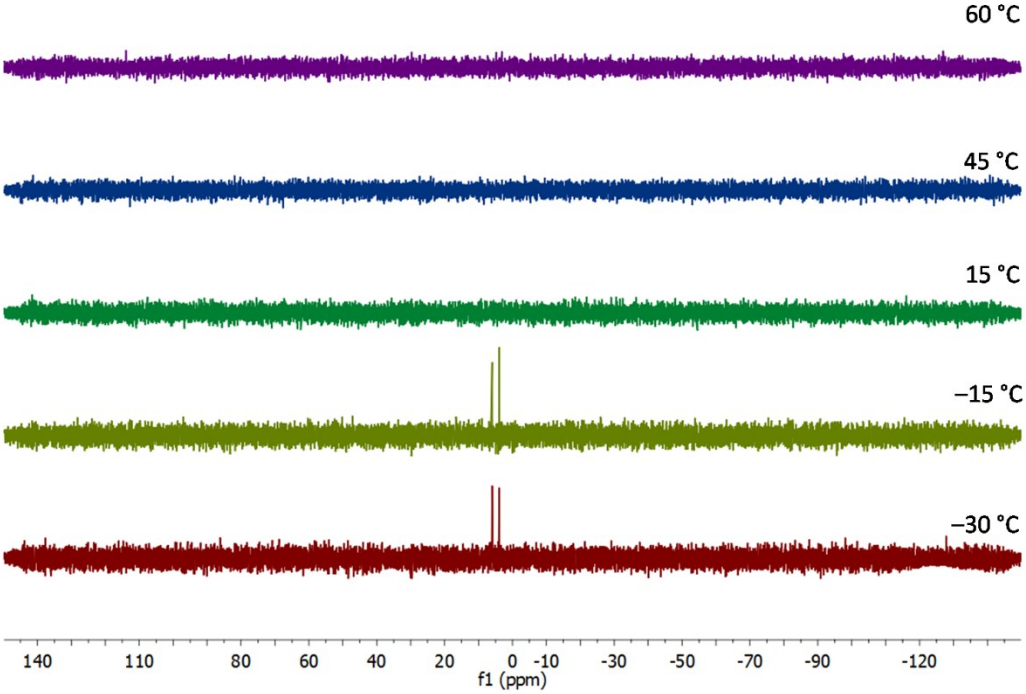

Fig S8. Variable temperature ^{29}Si NMR spectra (79.5 MHz, d_8-toluene) of pyridinophane **1**.

4. Heteronuclear NMR spectra of trihydridoborane adduct with bis(trimethylsilyl)-N,N'-2,6-diaminopyridine (2a).

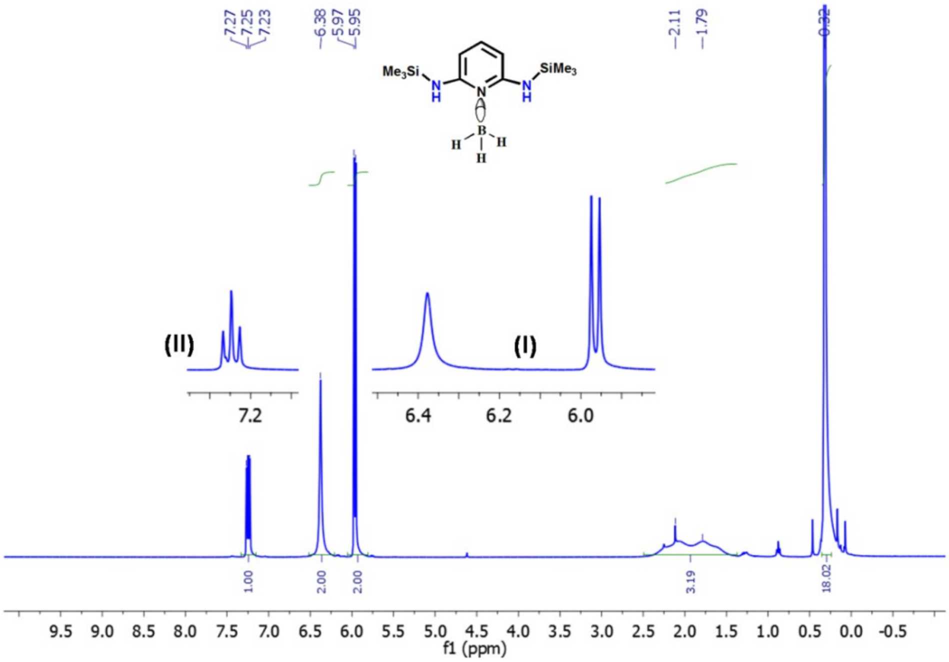

Fig S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of trihydridoborane adduct with bis(trimethylsilyl)-N,N'-2,6-diaminopyridine **(2a)**. Insets (I) and (II) show expanded aromatic spectral region.

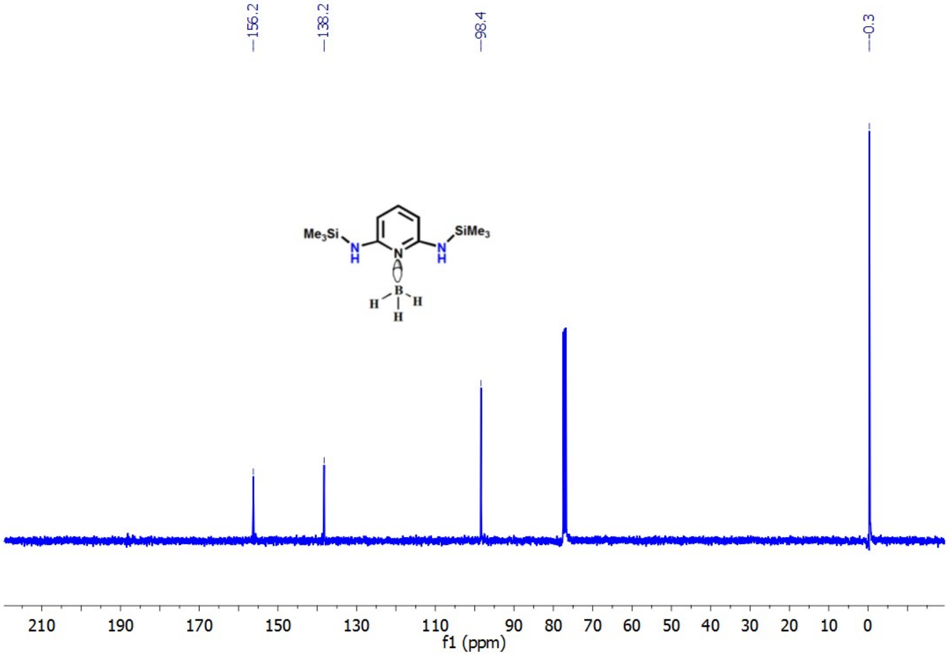

Fig S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of trihydridoborane adduct with bis(trimethylsilyl)-N,N'-2,6-diaminopyridine **(2a)**.

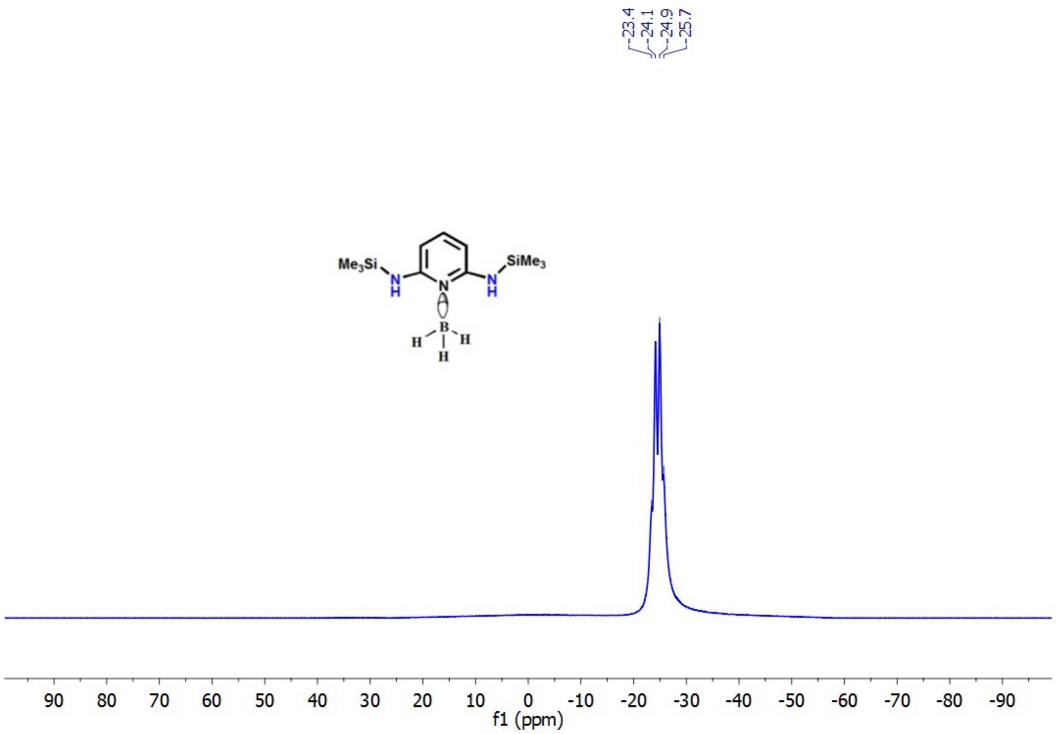

Fig S11. ^{11}B NMR spectrum (162 MHz, CDCl$_3$) of trihydridoborane adduct with bis(trimethylsilyl)-N,N’-2,6-diaminopyridine **(2a)**.

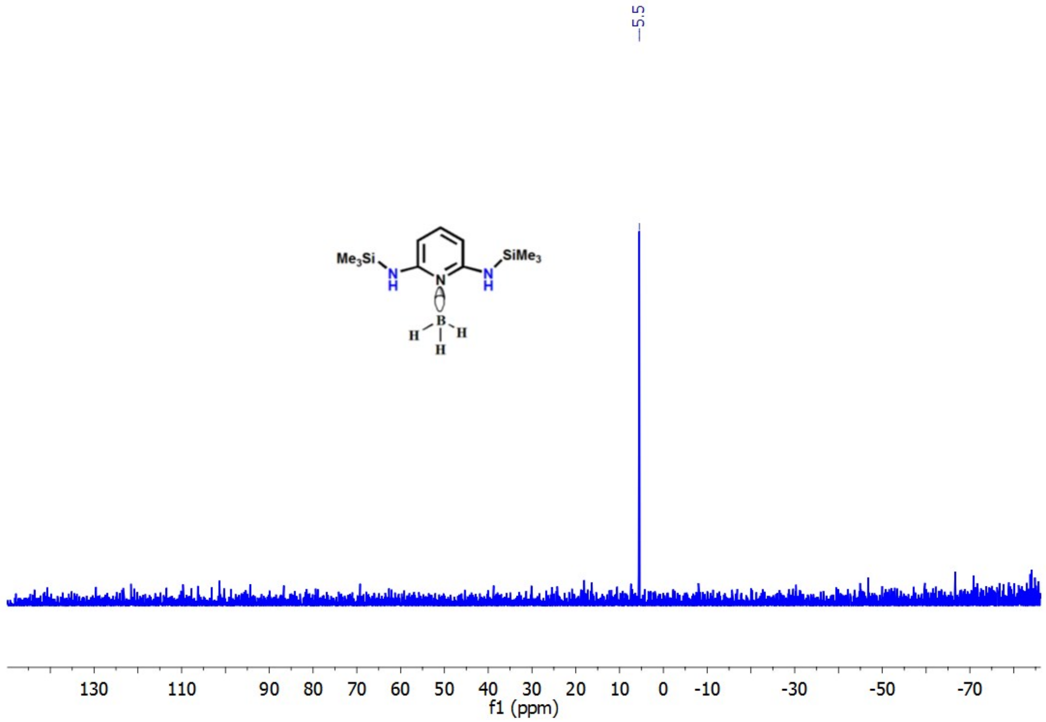

Fig S12. ^{29}Si NMR spectrum (79.5 MHz, CDCl$_3$) of trihydridoborane adduct with bis(trimethylsilyl)-N,N’-2,6-diaminopyridine **(2a)**.

5. Heteronuclear NMR spectra of tetraazadibora[3.3](2,6)pyridinophane (2)

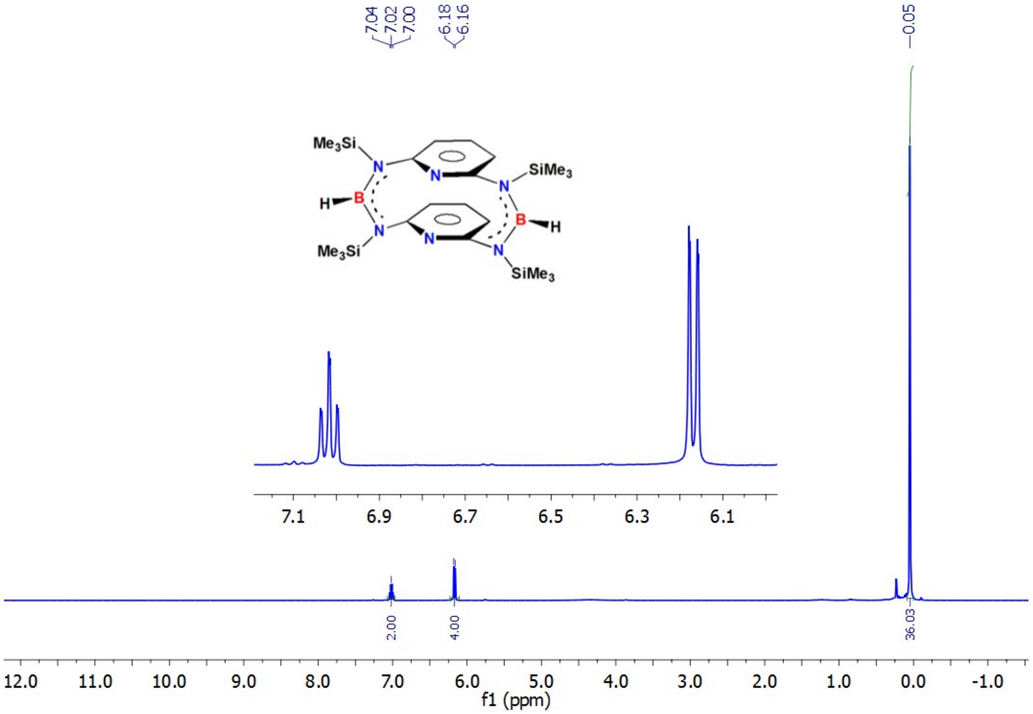

Fig S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of tetraazadibora[3.3](2,6)pyridinophane **(2)**. Inset shows the expansion for the aromatic spectral region.

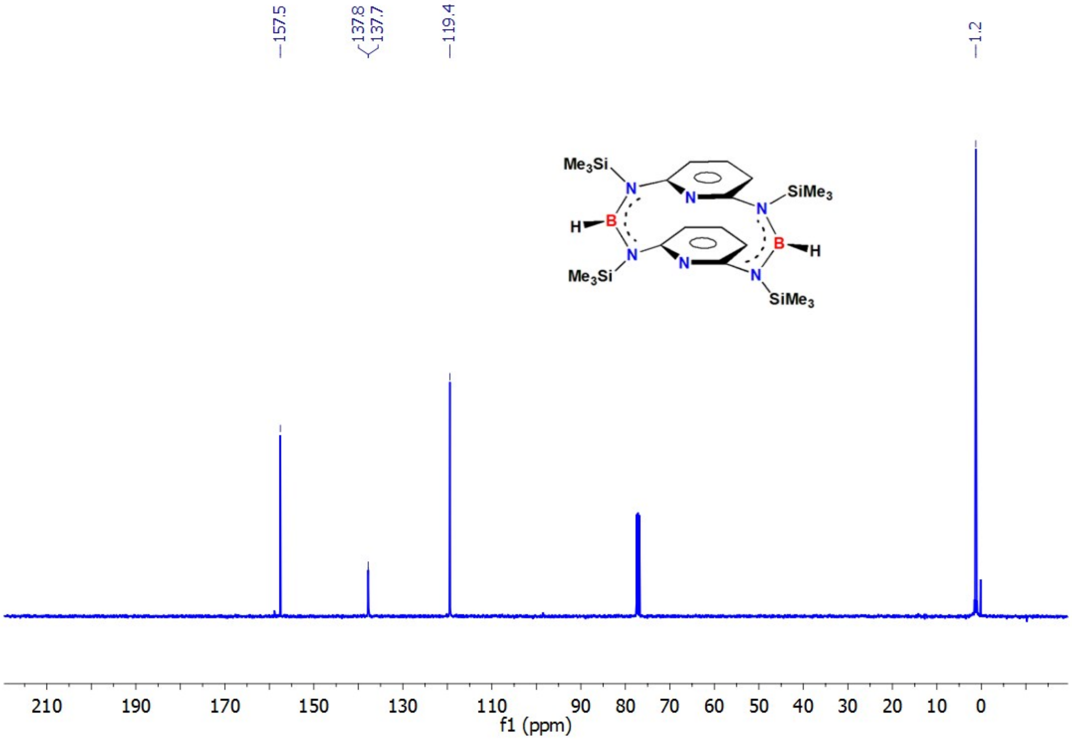

Fig S14. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of tetraazadibora[3.3](2,6)pyridinophane **(2)**.

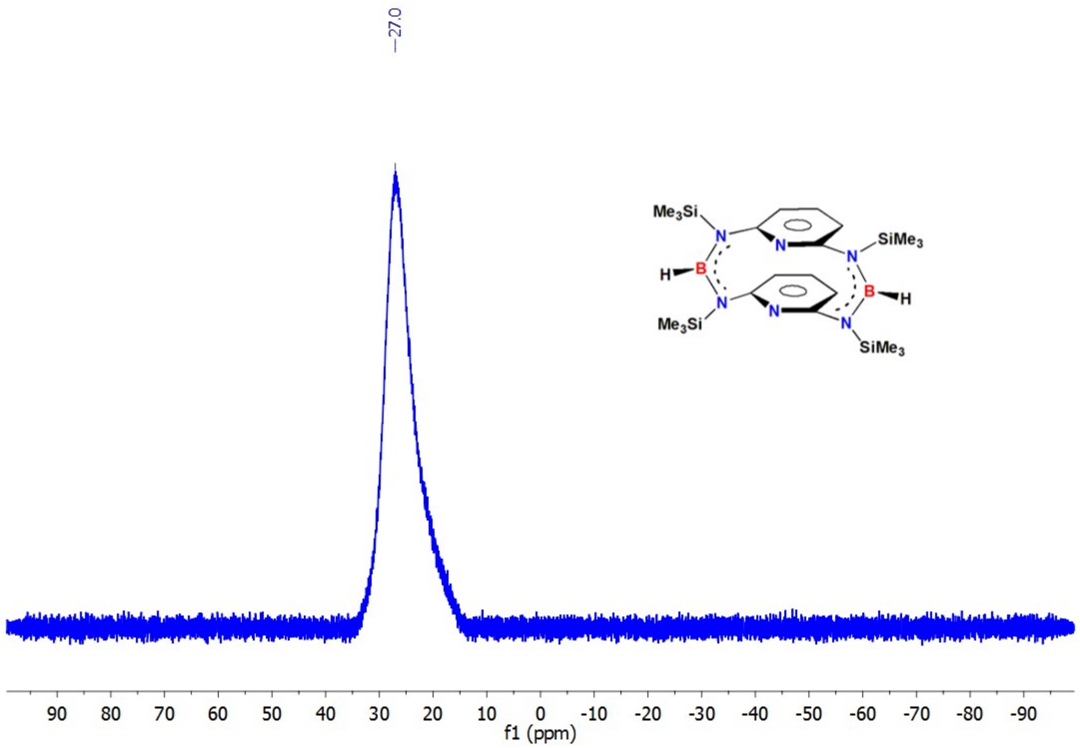

Fig S15. ^{11}B NMR spectrum (128 MHz, $CDCl_3$) of tetraazadibora[3.3](2,6)pyridinophane **(2)**.

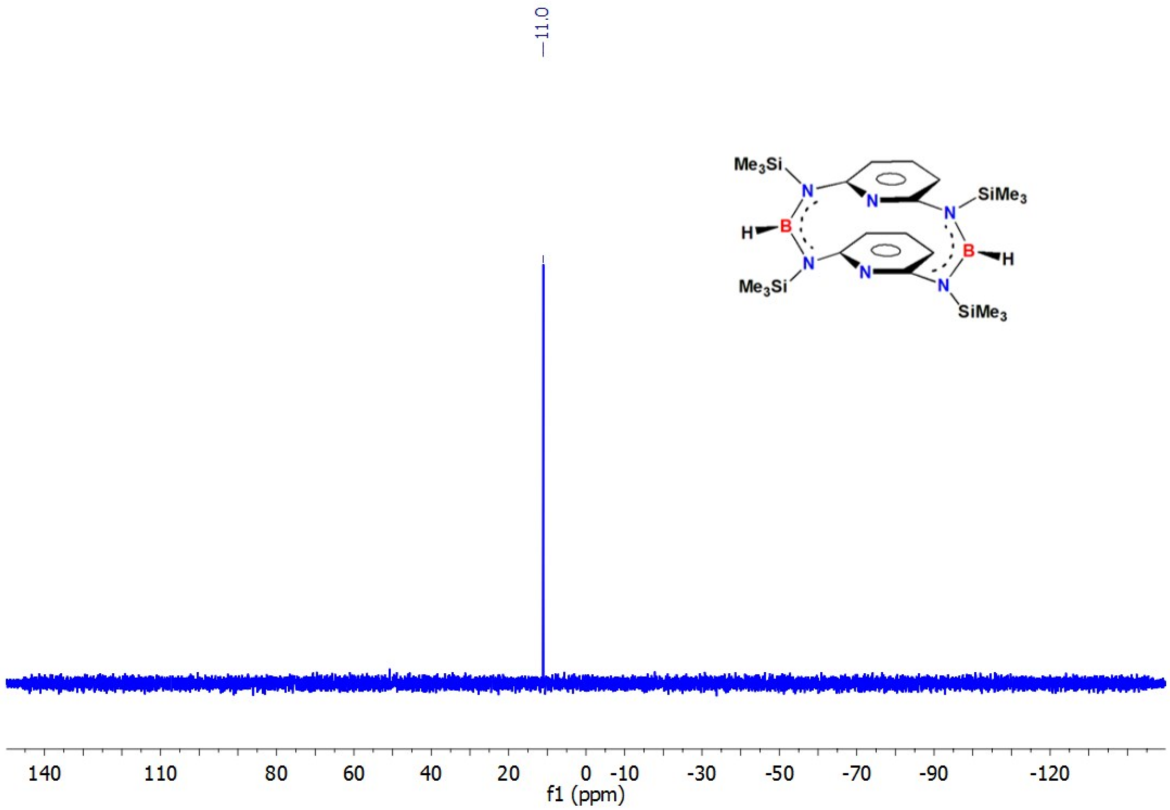

Fig S16. ^{29}Si NMR spectrum (79.5 MHz, $CDCl_3$) of tetraazadibora[3.3](2,6)pyridinophane **(2)**.

6. Variable temperature heteronuclear NMR spectra of pyridinophane 2.

Investigation of dynamic behavior of 2 in solution: The ^1H NMR spectra (in d_8-toluene) of the pyridinophane **2** in the temperature range +50 to –60 °C are shown in Fig S17 below. The spectra show that the NMR spectral feature (a doublet (6.07 ppm, *J* = 8 Hz) and a triplet (6.72 ppm, *J* = 8 Hz) due to pyridyl hydrogens and a singlet due to $SiMe_3$ group (0.19 ppm)) of **2** remain unchanged in this temperature range indicating its conformational rigidity in solution. The signal for **2** at 29.6 ppm (in d_8-toluene) in ^{11}B NMR spectra (Fig S19) did not show any change in the coordination number of boron in the temperature range +50 to –60 °C.

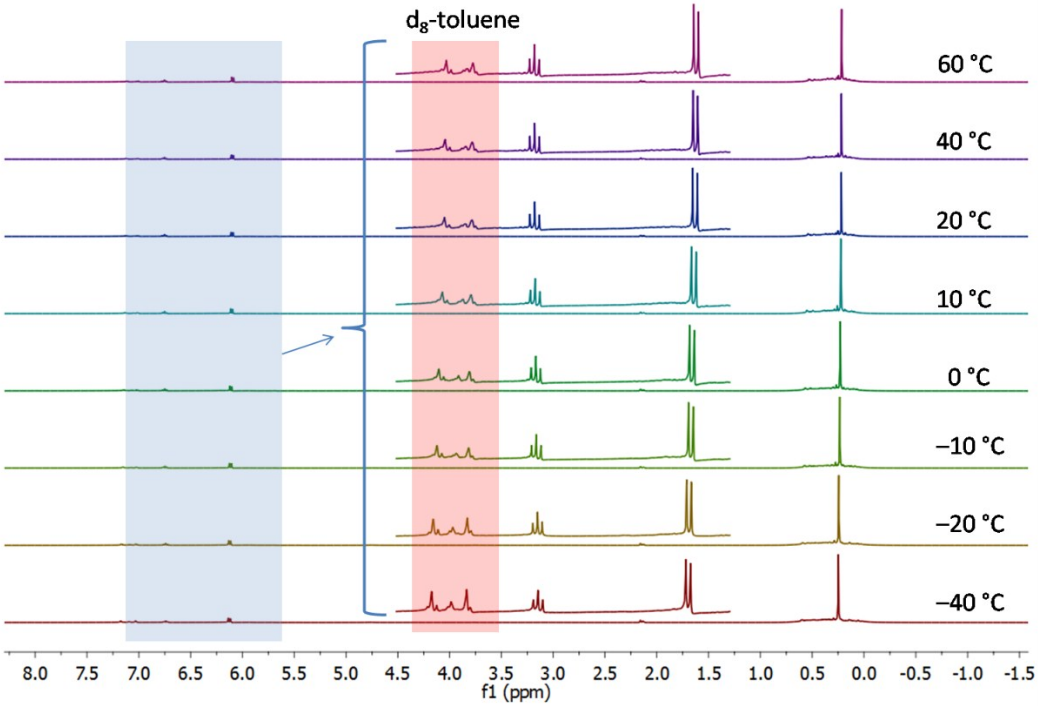

Fig S17. Variable temperature ^1H NMR spectra (400 MHz, d_8-toluene) of pyridinophane **2**.

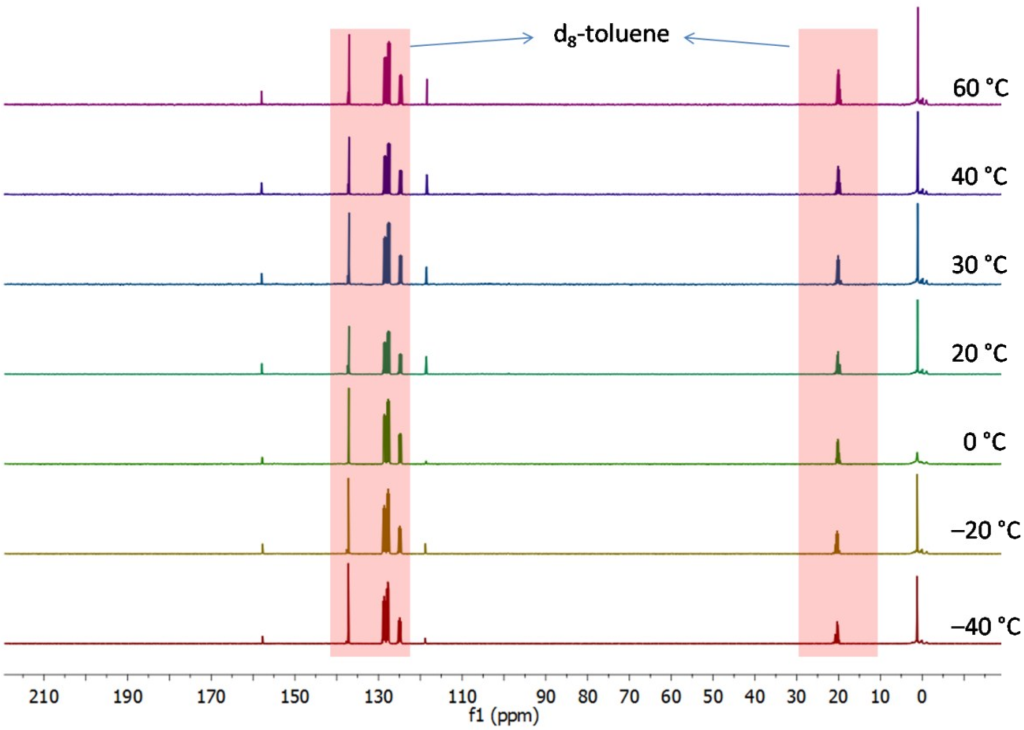

Fig S18. Variable temperature ^{13}C NMR spectra (100 MHz, d_8-toluene) of pyridinophane **2**.

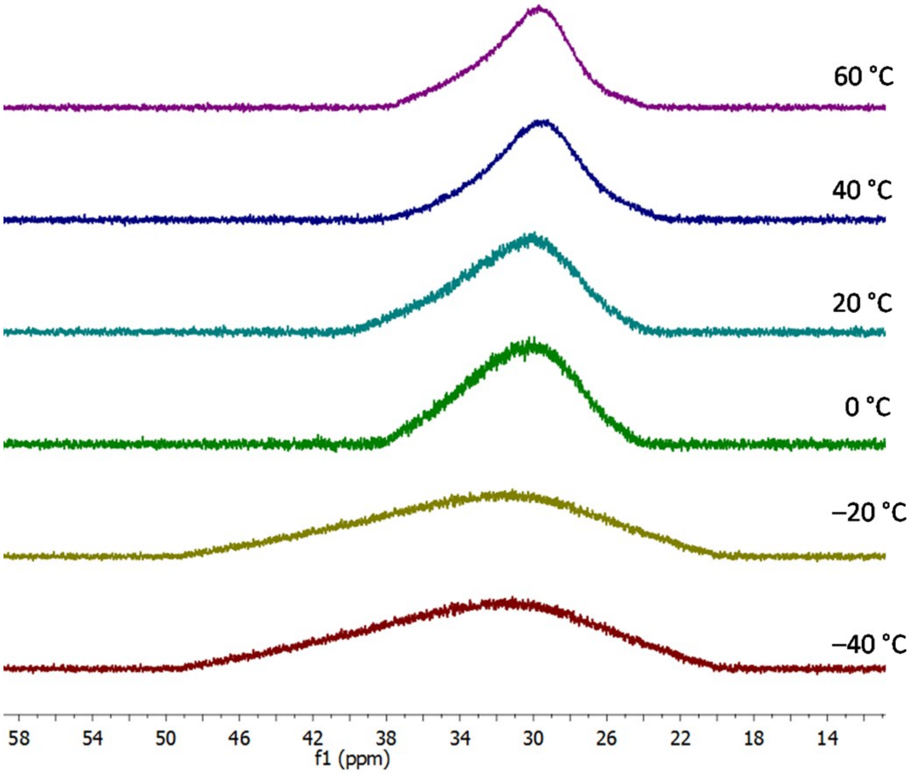

Fig S19. Variable temperature ^{11}B NMR spectra (128 MHz, d_8-toluene) of pyridinophane **2**.

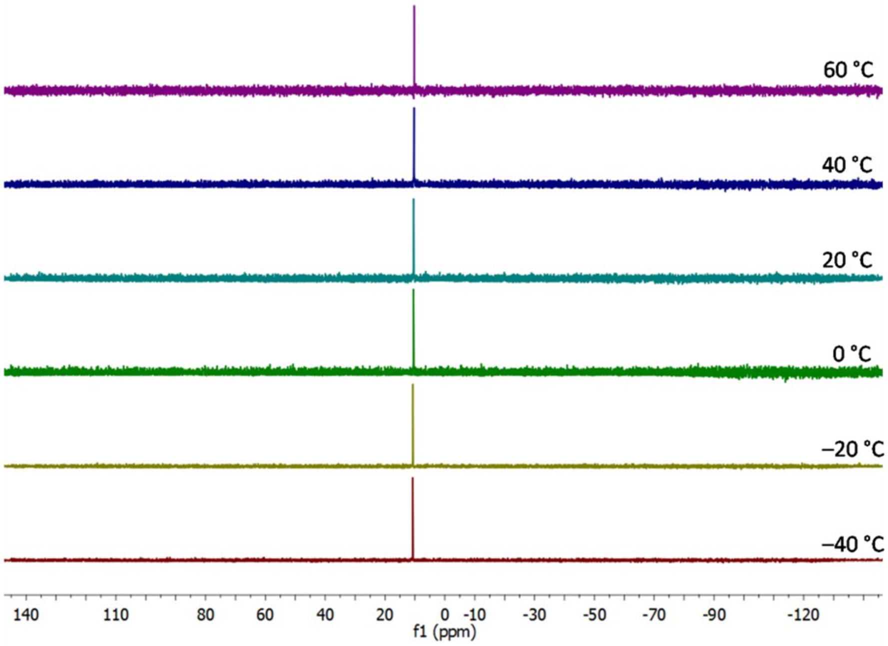

Fig S20. Variable temperature ^{29}Si NMR spectra (79.5 MHz, d_8-toluene) of pyridinophane **2**.

7. Heteronuclear NMR spectral investigation of reaction between 2 and $Et_3P{=}O$ in C_6D_6.

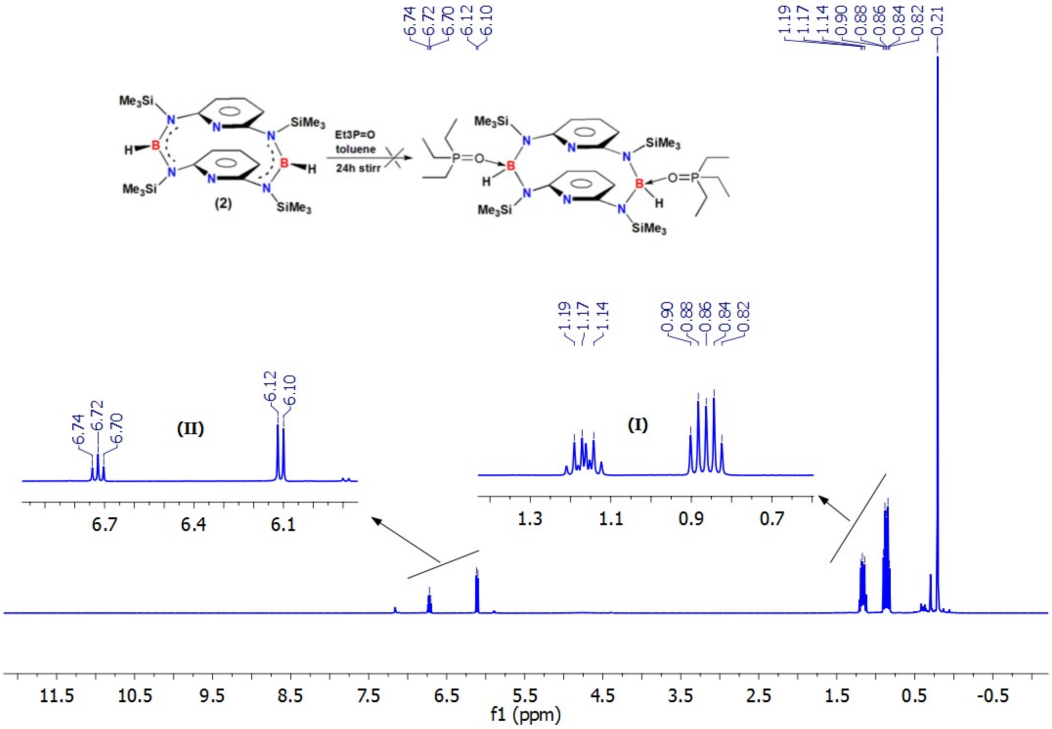

Fig S21. ^{1}H NMR spectrum (400 MHz, C_6D_6) showing no interaction between **2** and $Et_3P{=}O$. Insets **(I)** and **(II)** show expanded aliphatic and aromatic spectral regions, respectively.

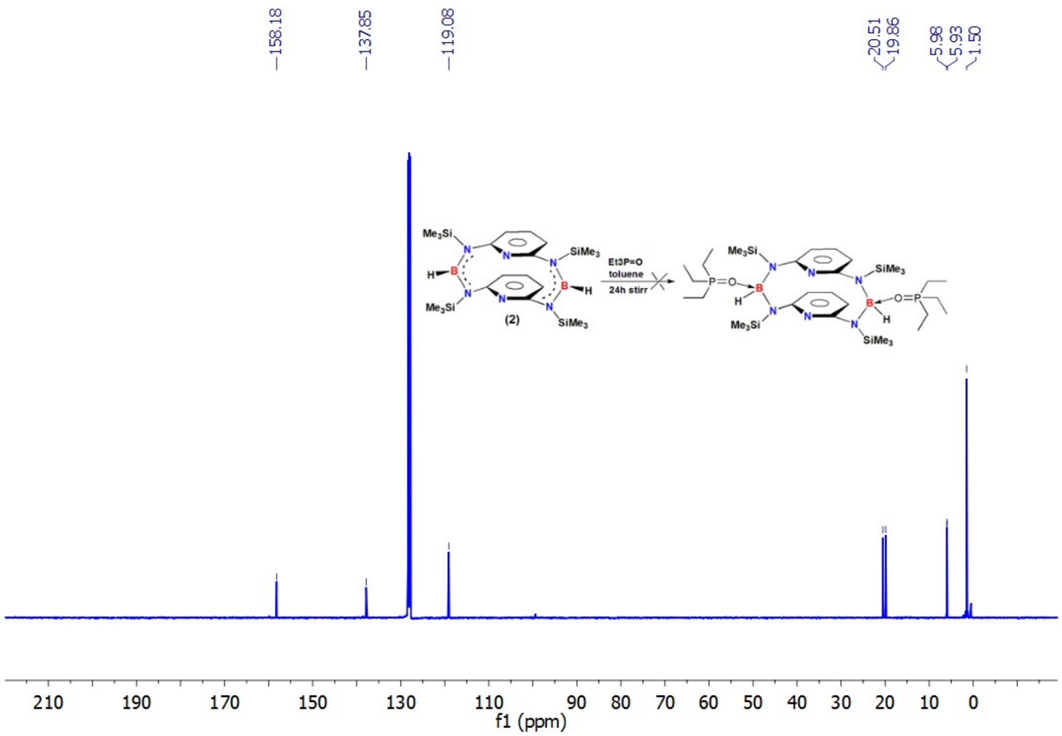

Fig S22. ^{13}C NMR spectrum (100 MHz, C_6D_6) showing no interaction between **2** and Et_3P=O.

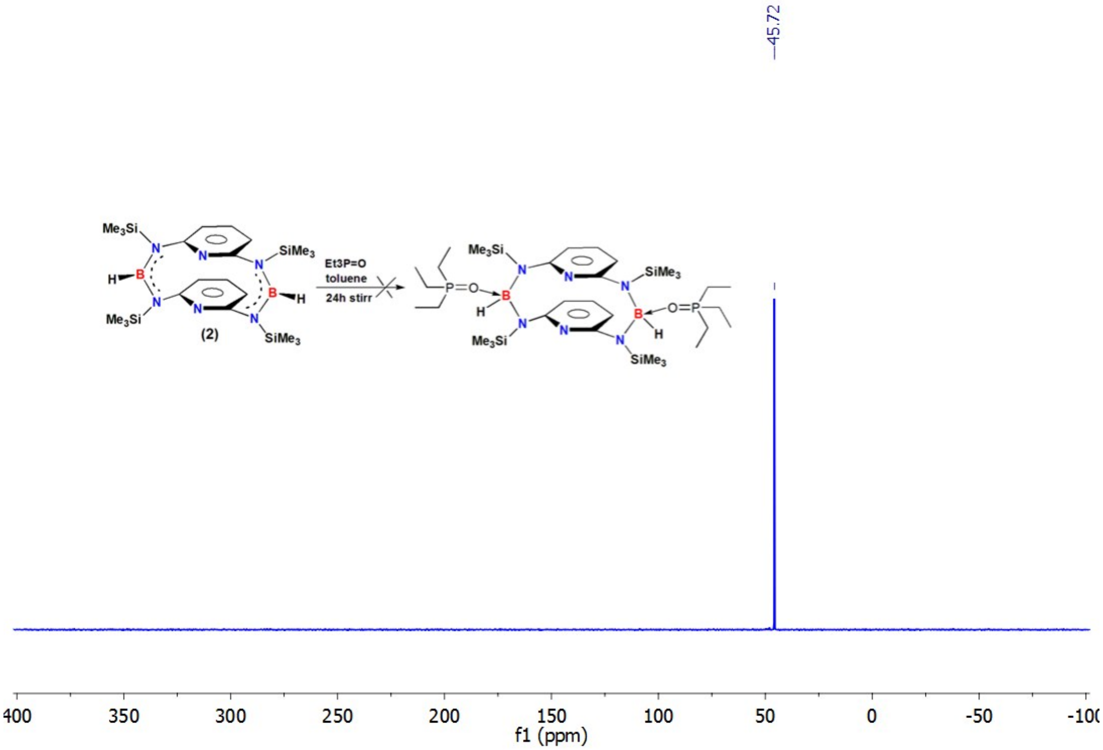

Fig S23. ^{31}P NMR spectrum (162 MHz, C_6D_6 showing no interaction between **2** and Et_3P=O.

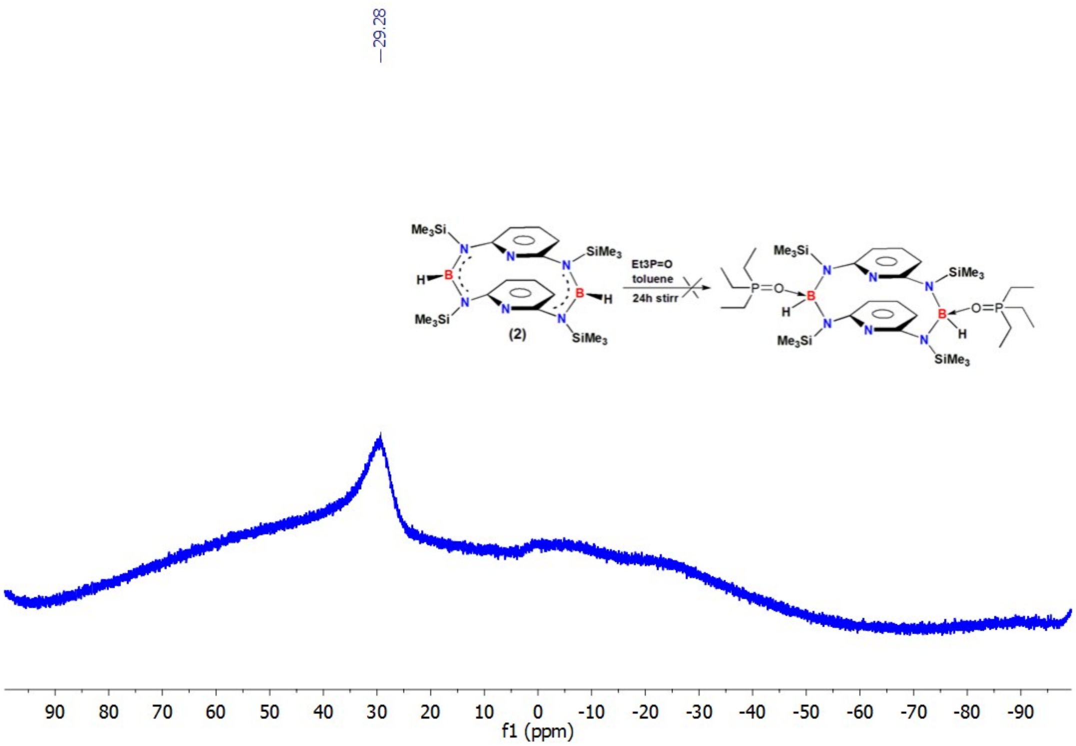

Fig S24. ^{11}B NMR spectrum (128 MHz, C_6D_6) showing no interaction between **2** and $Et_3P=O$.

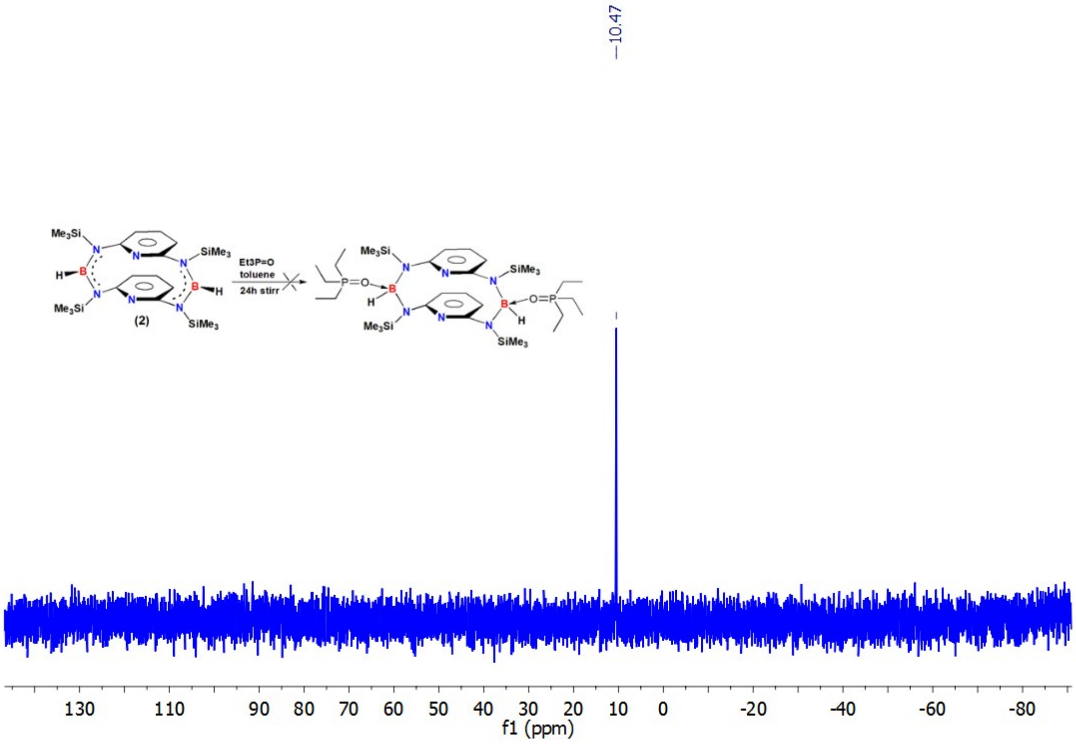

Fig S25. ^{29}Si NMR spectrum (79.5 MHz, C_6D_6) showing no interaction between **2** and $Et_3P=O$.

8. Heteronuclear NMR spectra of tetraazadialumino[3.3](2,6)pyridinophane (3)

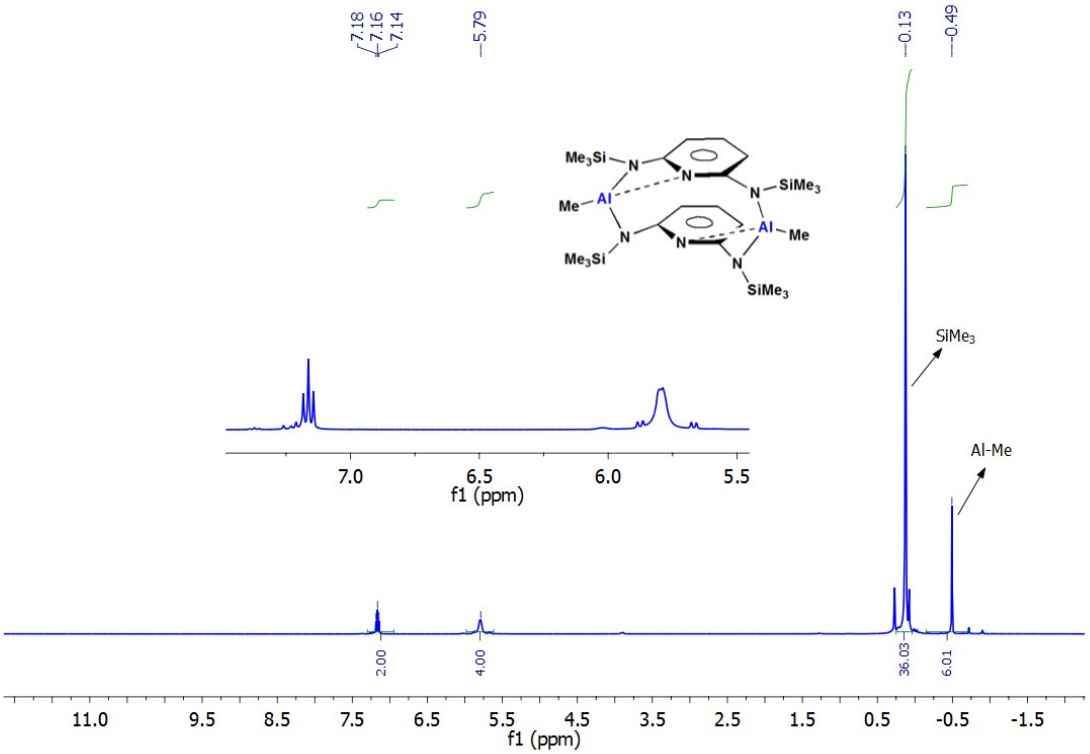

Fig S26. ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of tetraazadialumino[3.3](2,6)pyridinophane **(3).** Inset shows the expansion for the aromatic spectral region.

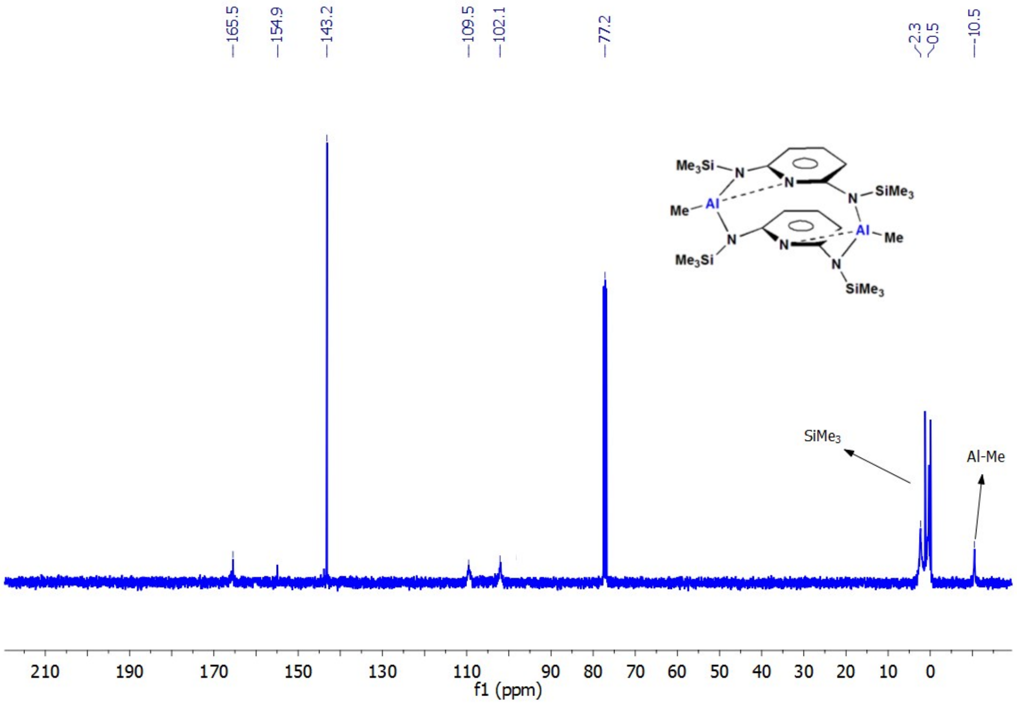

Fig S27. ^{13}C NMR spectrum (100 MHz, CDCl$_3$) of tetraazadialumino[3.3](2,6)pyridinophane **(3).**

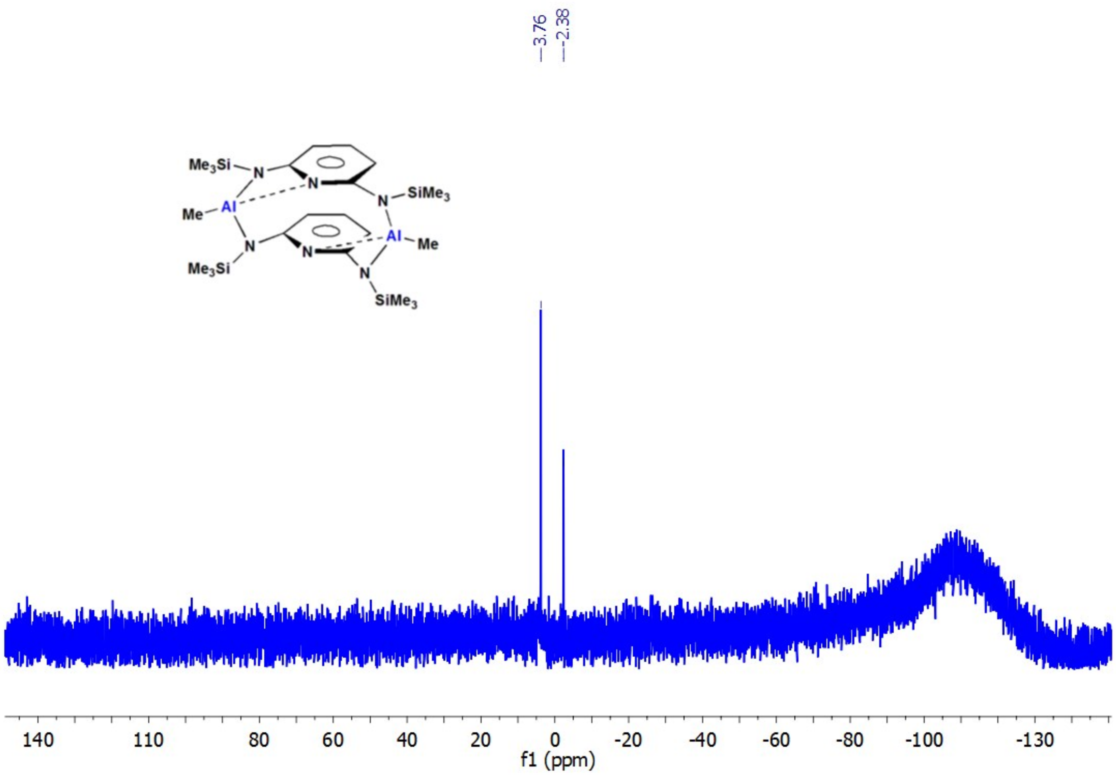

Fig S28. ^{29}Si NMR spectrum (79.5 MHz, $CDCl_3$) of tetraazadialumino[3.3](2,6)pyridinophane **(3)**.

9. X-ray crystallographic studies of 1, 2a, 2, 3-syn and 3-anti

Single crystal X-ray diffraction data of **1** was collected on a Bruker *AXS KAPPA APEX-II* CCD diffractometer with MoKα radiation using omega scans. Unit cell determination and refinement and data collection were done using the Bruker APPEX-II suite,[4] data reduction and integration were performed using SAINT v8.34A (Bruker, 2013)[5] and absorption corrections and scaling were done using SADABS-2014/5 (Bruker,2014/5).[6] Single crystal X-ray diffraction data of **2a**, **2** and **3** were collected using a Rigaku XtaLAB mini diffractometer equipped with Mercury375M CCD detector. The data were collected with MoK_{α} radiation (λ = 0.71073 Å) using omega scans. During the data collection, the detector distance was 49.9 mm (constant) and the detector was placed at $2\theta = 29.85°$ (fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite.[7] and all the crystal structures were solved through OLEX2[8] package using XT[9] and the structures were refined using XL.[9] All non-hydrogen atoms were refined anisotropically. All the figures were generated using Mercury 3.2. The geometric data reported here are taken from the CIF.

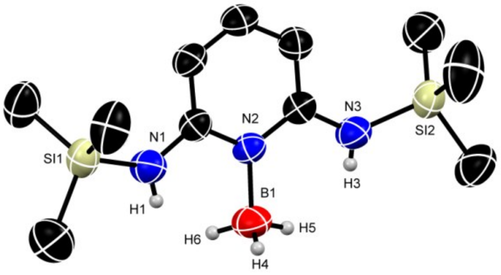

Fig S29. Solid state structure of trihydridoborane adduct with bis(trimethylsilyl)-N,N'-2,6-diaminopyridine **(2a).** All hydrogens except that on boron and nitrogen have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and angles (°): B1-H1 0.960(4), B1-H2 0.960(4), B1-H3 0.960(4), N1-H1 0.769(3), N3-H3 0.684(2), B1-N2 1.601(3); N2-B1-H4 109.47(2), N2-B1-H5 109.47(2), N2-B1-H6 109.47(2), H4-B1-H5 109.47(3), H5-B1-H6 109.47(3), H4-B1-H6 109.47(3).

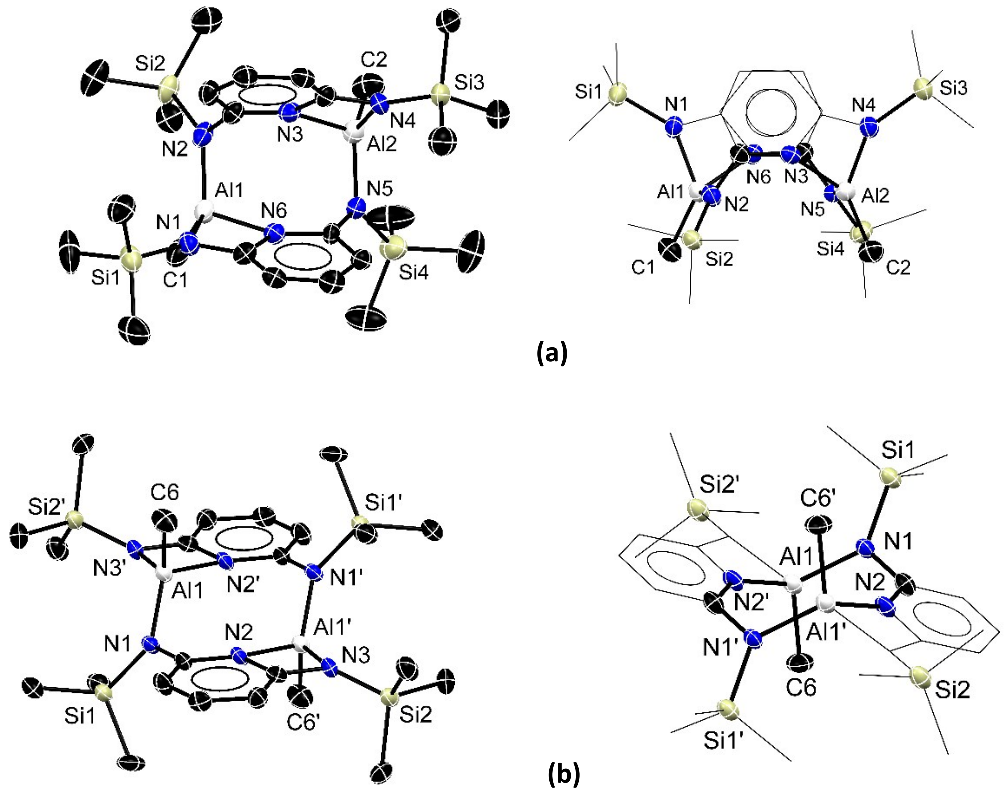

Fig S30. Single crystal X-ray structure of tetraazadialumino[3.3](2,6)pyridinophane; **(a)** syn(boat,boat) conformation **(3-syn)** and **(b)** the anti conformation (**3-anti)**. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: for **3-syn**: Al(1)–N(1) 1.914(2), Al(1)–N(2) 1.838(2), Al(1)–N(6) 1.941(2), Al(1)–C(1) 1.939(3), N(1)–Si(1) 1.735(2), N(2)–Si(2) 1.742(2); N(1)–Al(1)–N(2) 113.81(10), N(2)–Al(1)–N(6) 107.90(9), N(1)–Al(1)–N(6) 70.30(9), N(1)–Al(1)–C(1) 117.96(12), N(2)–Al(1)–C(1) 119.33(12), N(6)–Al(1)–C(1) 117.45(12), for **3-anti**: Al(1)–N(1) 1.851(2) Al(1)–N(2) 1.951(2), Al(1)–N(3) 1.900(2), Al(1)–C(6) 1.944(3), N(1)–Si(1) 1.752(2), N(3)–Si(2) 1.730(2); N(1)–Al(1)–C(6) 114.25(11) N(1)–Al(1)–N(3) 117.99(10).

Table S1: Crystallographic data for compounds 1-3.

Compound[a]	**1**	**2a**	**2**	**3-syn**	**3-anti**
Chemical formula	$C_{22}H_{42}$ $B_2Cl_2N_6Si_4$	$C_{11}H_{26}$ BN_3Si_2	$C_{22}H_{44}$ $B_2N_6Si_4$	$C_{24}H_{48}Al_2N_6Si_4$	$C_{24}H_{48}Al_2N_6Si_4$
Molar mass	595.50	267.34	526.61	587.00	587.00
Crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
T [K]	100(2)	280(2)	100(2)	100(2)	100(2)
a [Å]	11.3419(4)	7.1703(17)	6.5190(18)	17.2486(9)	11.6602(13)
b [Å]	14.9551(5)	18.860(4)	14.118(3)	12.6136(7)	12.6412(10)
c [Å]	16.2731(5)	12.843(3)	17.136(6)	16.1018(9)	12.9228(15)
α [°]	98.8330(10)	90	84.72(4	90	90
β [°]	110.2060(10)	98.818(12)	89.46(6)	91.704(5)	116.275(14)
γ [°]	102.878(2)	90	84.14(3)	90	90
V [Å^3]	2443.71(14)	1716.2(6)	1562.3(8)	3501.7(3)	1708.0(4)
Z	2	4	2	4	4
D(calcd.) [g·cm^{-3}]	1.214	1.035	1.120	1.113	1.141
μ(Mo-Kα) [mm^{-1}]	0.369	0.193	0.211	0.242	0.248
Index range	$-13 \leq l \leq 13$	$-24 \leq h \leq 24$	$-36 \leq h \leq 36$	$-25 \leq h \leq 24$	$-17 \leq h \leq 17$
	$-18 \leq l \leq 18$	$-24 \leq k \leq 24$	$-13 \leq k \leq 11$	$-18 \leq k \leq 14$	$-19 \leq k \leq 19$
	$-19 \leq l \leq 19$	$-13 \leq l \leq 13$	$-19 \leq l \leq 20$	$-24 \leq l \leq 24$	$-19 \leq l \leq 19$
Reflections collected	18442	12182	12117	48197	24025
Independent reflections	8893	3885	5321	12480	6131
Data/restraints/parameters	8893/0/505	3885/0/172	5321/0/327	12480/0/339	6131/0/170
R1,wR2[I>2σ(I)][a]	0.0269,0.0707	0.0516, 0.1407	0.0699, 0.1600	0.0715, 0.1627	0.814, 0.2115
R1, wR2 (all data)[a]	0.0310,0.0737	0.0623, 0.1542	0.1093, 0.2064	0.1322, 0.1912	0.1129, 0.2436
GOF	1.046	1.060	1.010	1.039	1. 081
CCDC reference	1813026	1813028	1813027	1813030	1813029

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

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