Electronic Supplementary Information ESI

Reactivity of an NHC-stabilized Pyramidal Hydrosilylene with Electrophilic Boron Sources

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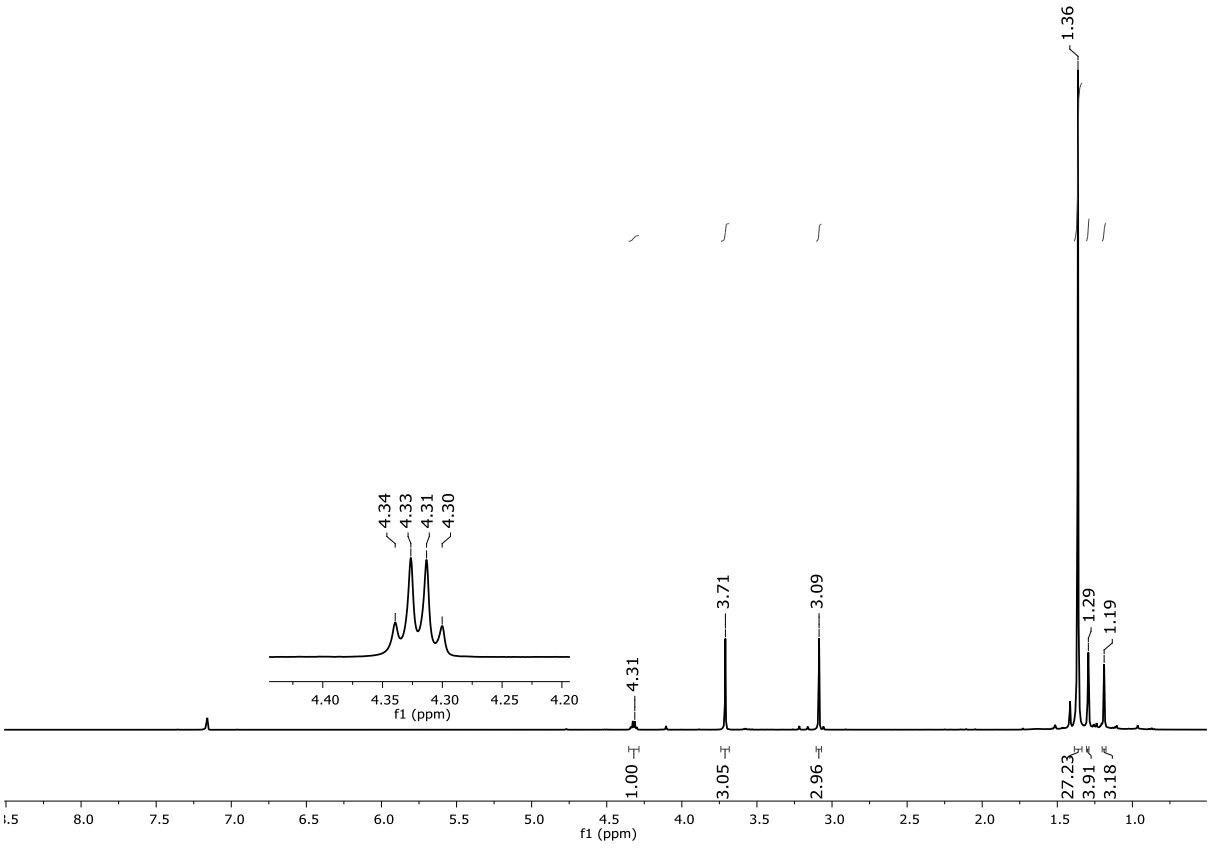

Figure S1. ^{1}H NMR of compound **1**→BH_3 in C_6D_6 at 25 °C.

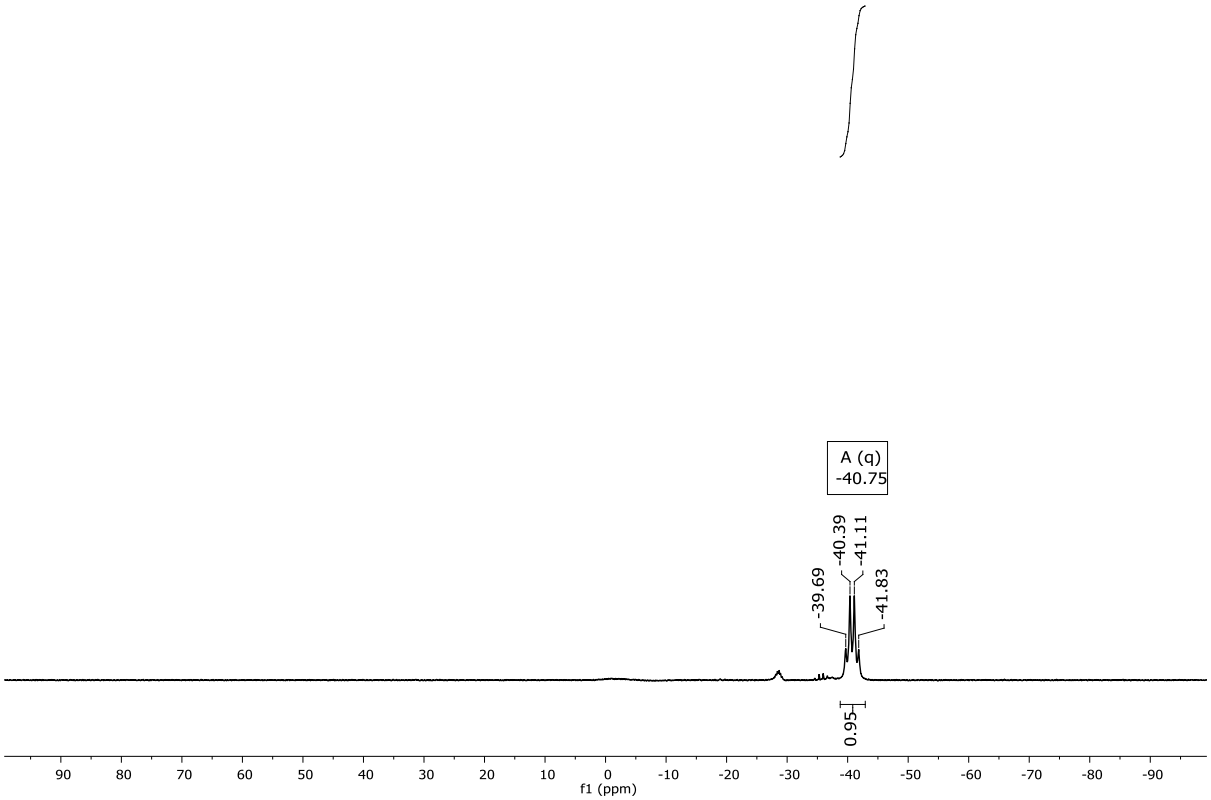

Figure S2. ^{11}B NMR spectrum of compound **1**→BH_3 in C_6D_6 at 25 °C.

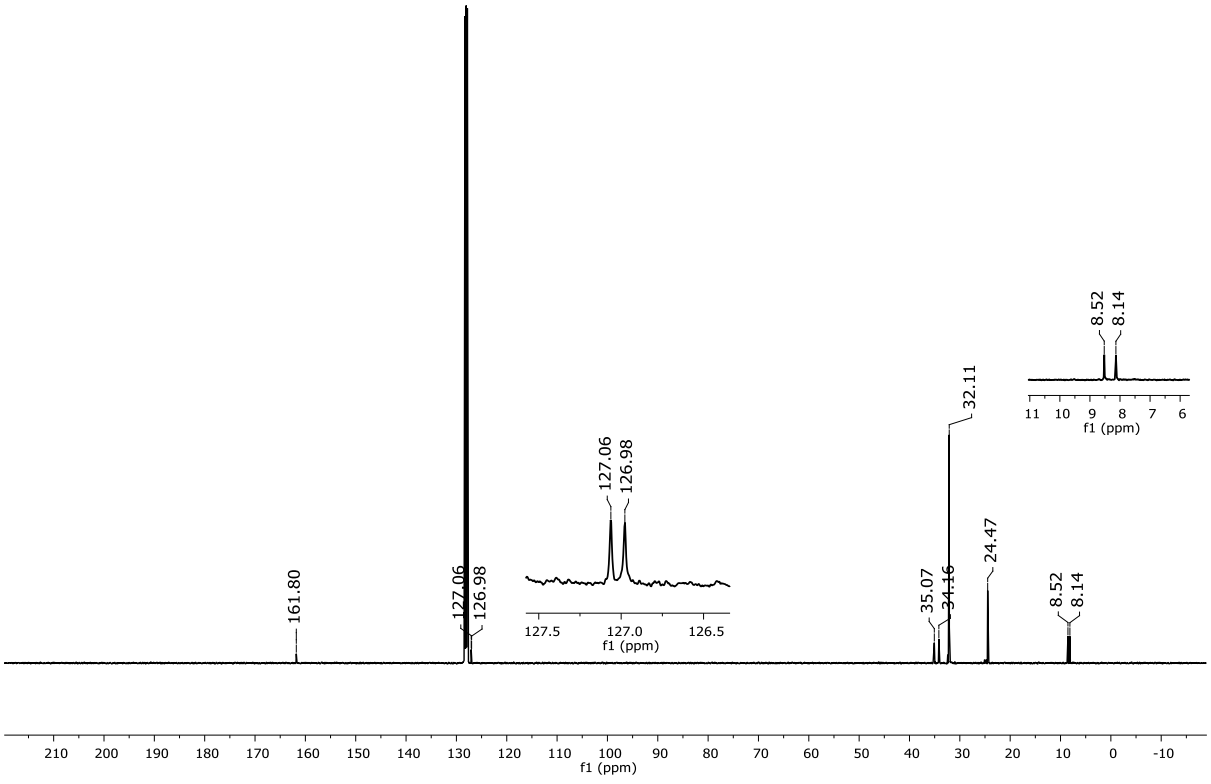

Figure S3. ^{13}C NMR spectrum of compound **1**→BH_3 in C_6D_6 at 25 °C.

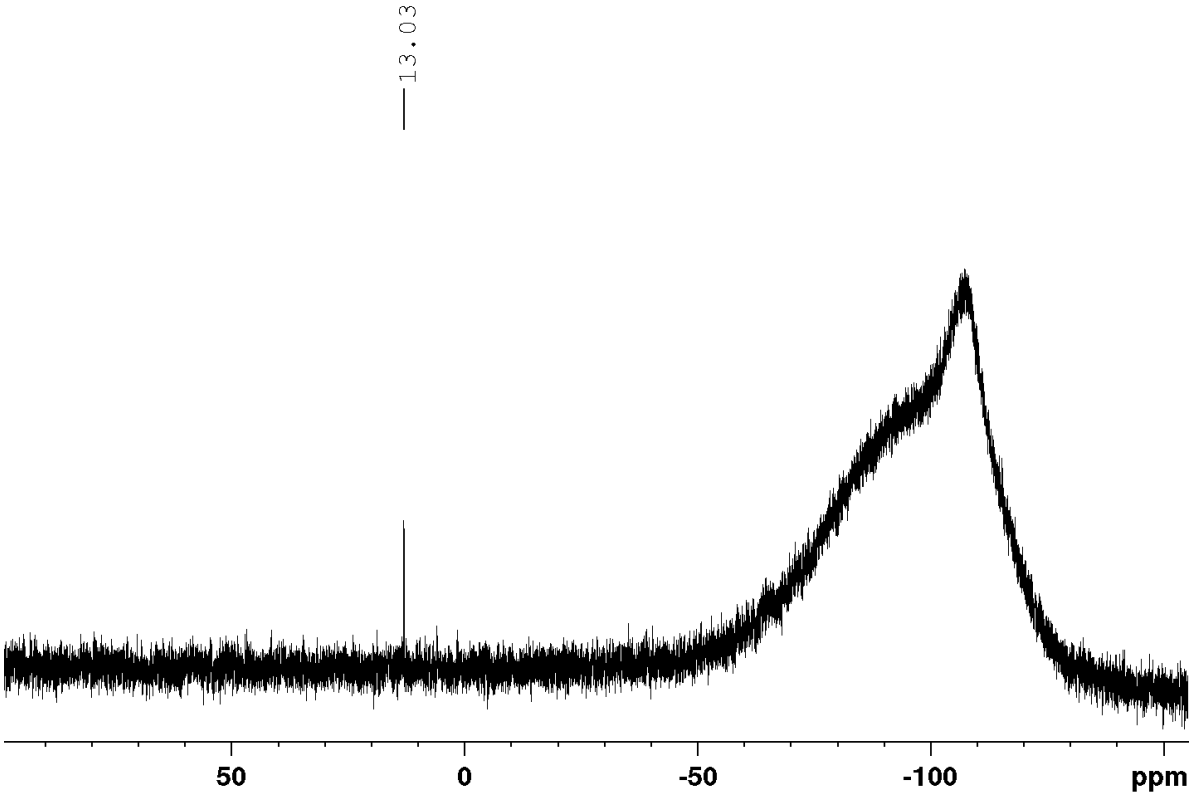

Figure S4. $^{29}Si\{^{1}H\}$ NMR spectrum of compound **1**→BH_3 in C_6D_6 at 25 °C.

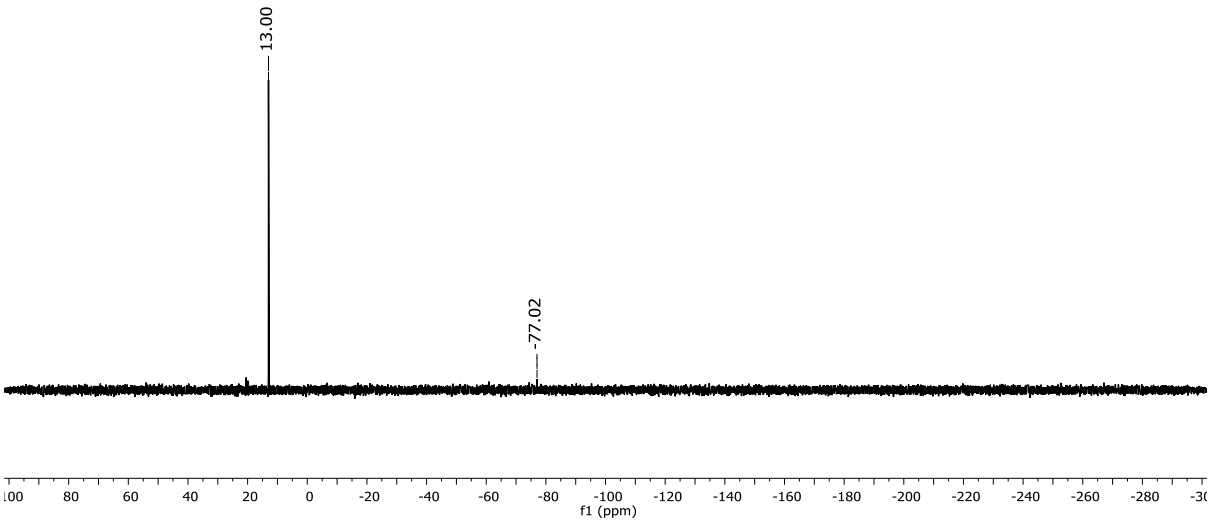

Figure S5. $^{29}Si\{^{1}H\}$ INEPT NMR spectrum of compound **1**→BH_3 in C_6D_6 at 25 °C.

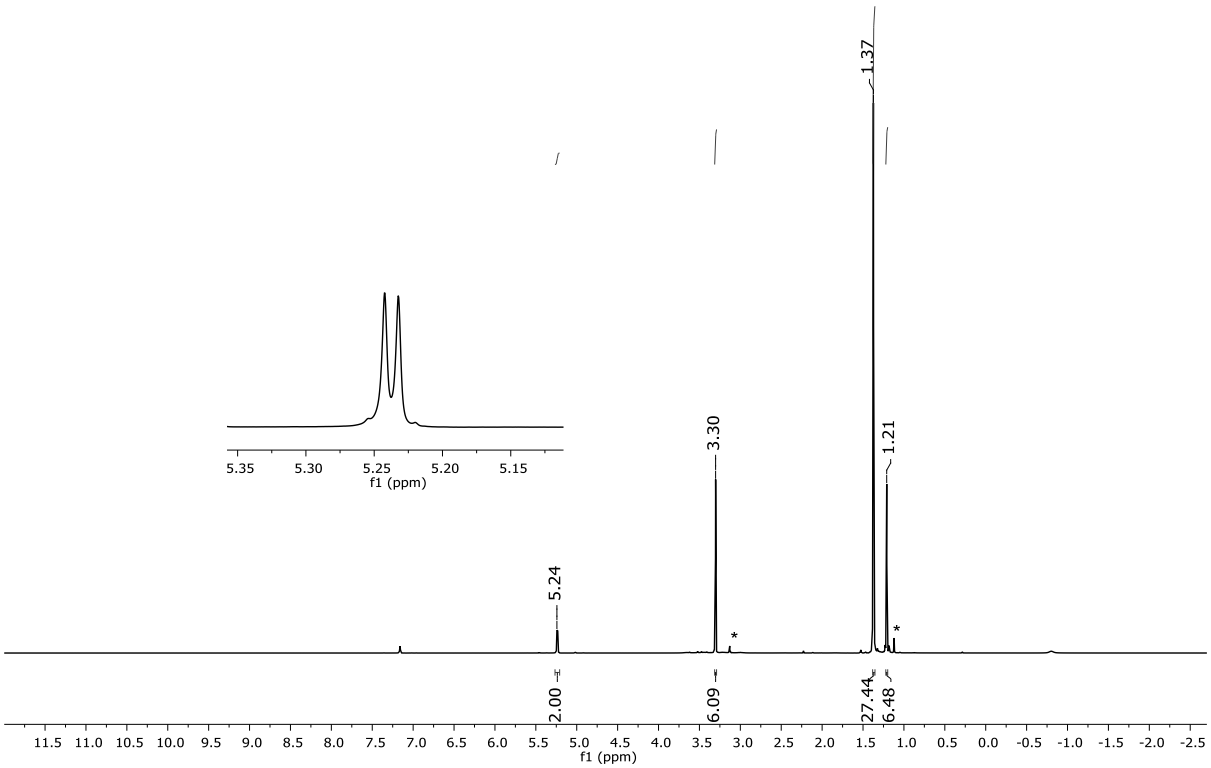

Figure S6. ^{1}H NMR spectrum of compound **2** in C_6D_6 at 25 °C. (*: tBu_3SiSiH_3, 2%)

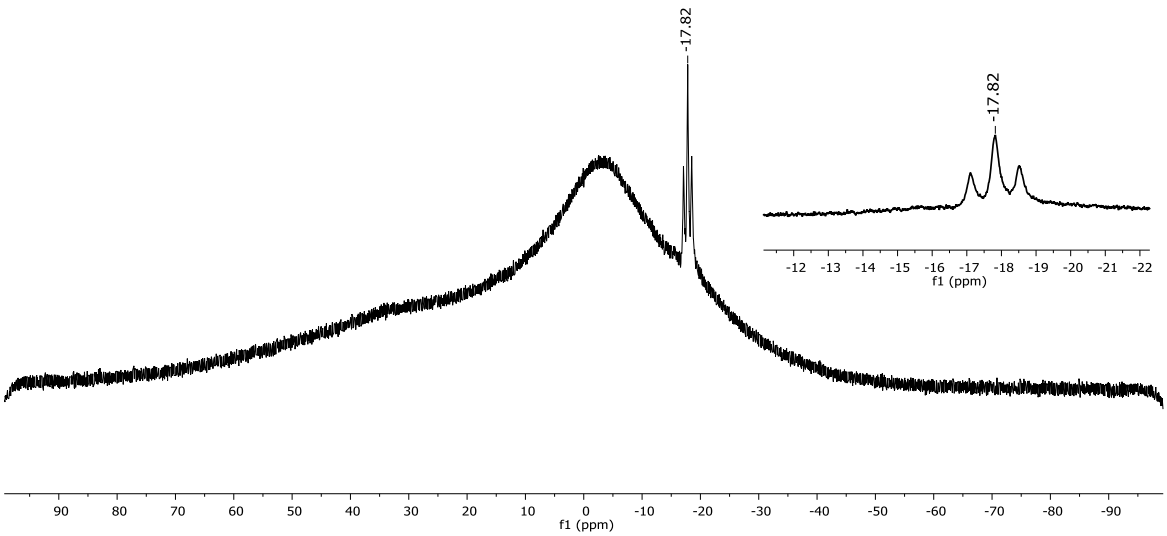

Figure S7. ^{11}B NMR spectrum of compound **2** in C_6D_6 at 25 °C.

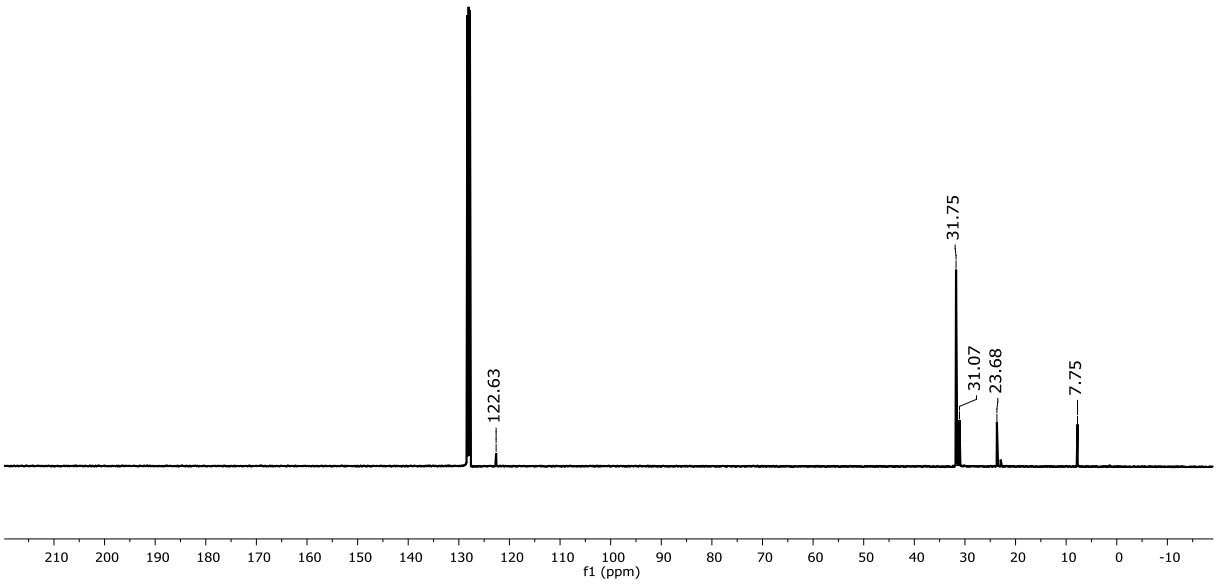

Figure S8. $^{13}C\{^{1}H\}$NMR spectrum of compound **2** in C_6D_6 at 25 °C.

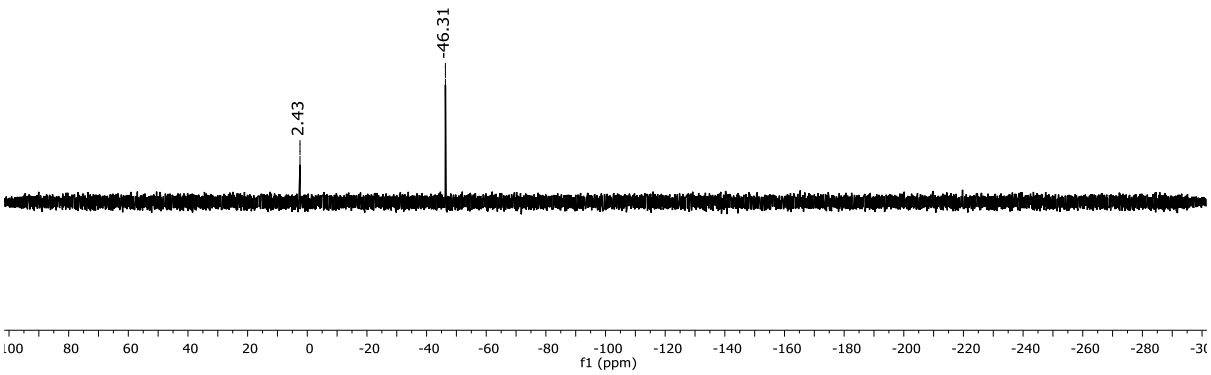

Figure S9. $^{29}Si\{^{1}H\}$ NMR spectrum of compound **2** in C_6D_6 at 25 °C.

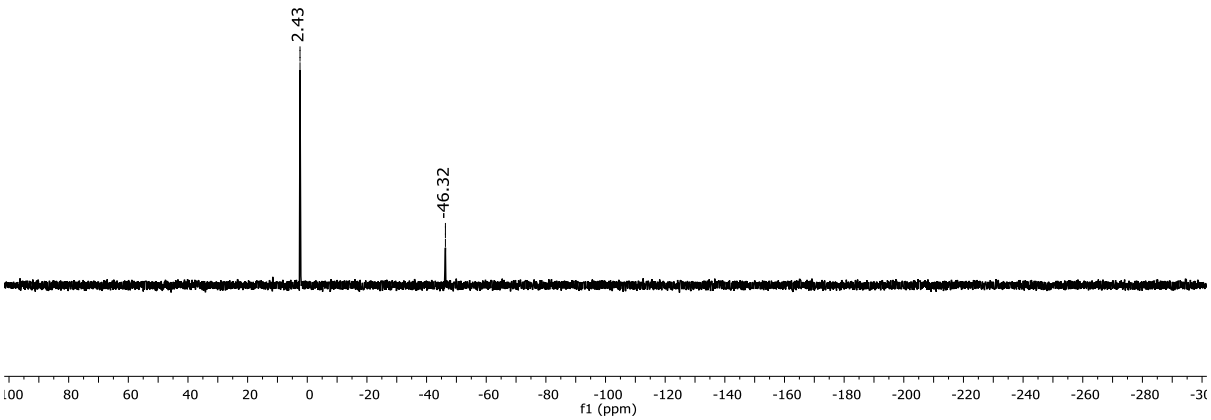

Figure S10. $^{29}Si\{^{1}H\}$ INEPT NMR spectrum of compound **2** in C_6D_6 at 25 °C.

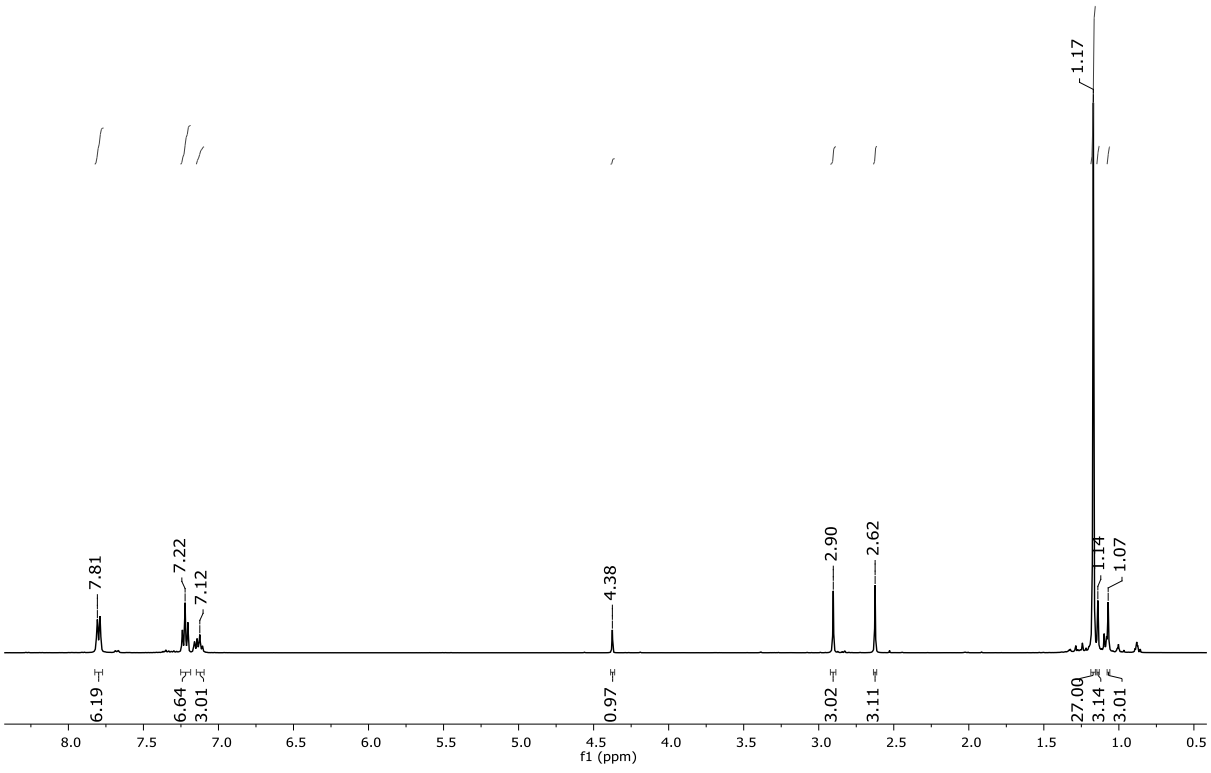

Figure S11. ^{1}H NMR spectrum of compound **1**→BPh_3 in C_6D_6 at 25 °C.

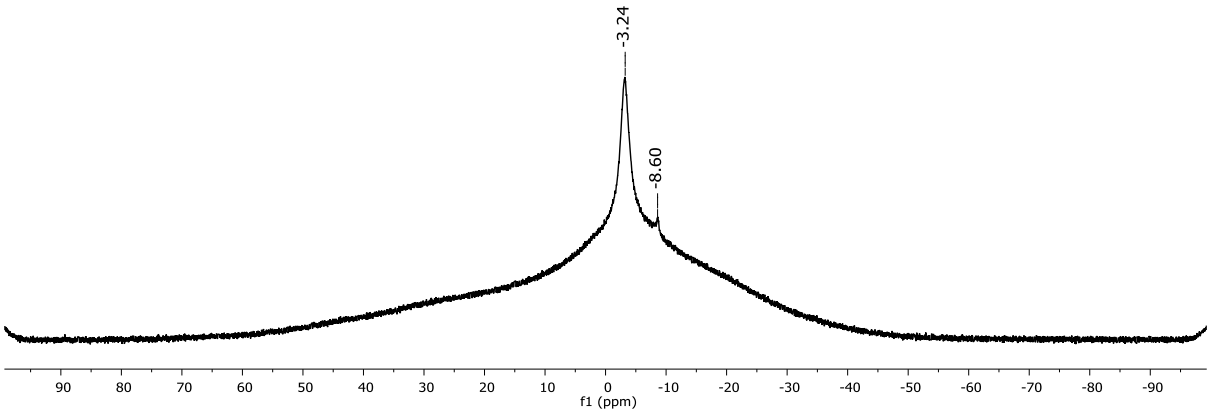

Figure S12. ^{11}B NMR spectrum of compound **1**→BPh_3 in C_6D_6 at 25 °C.

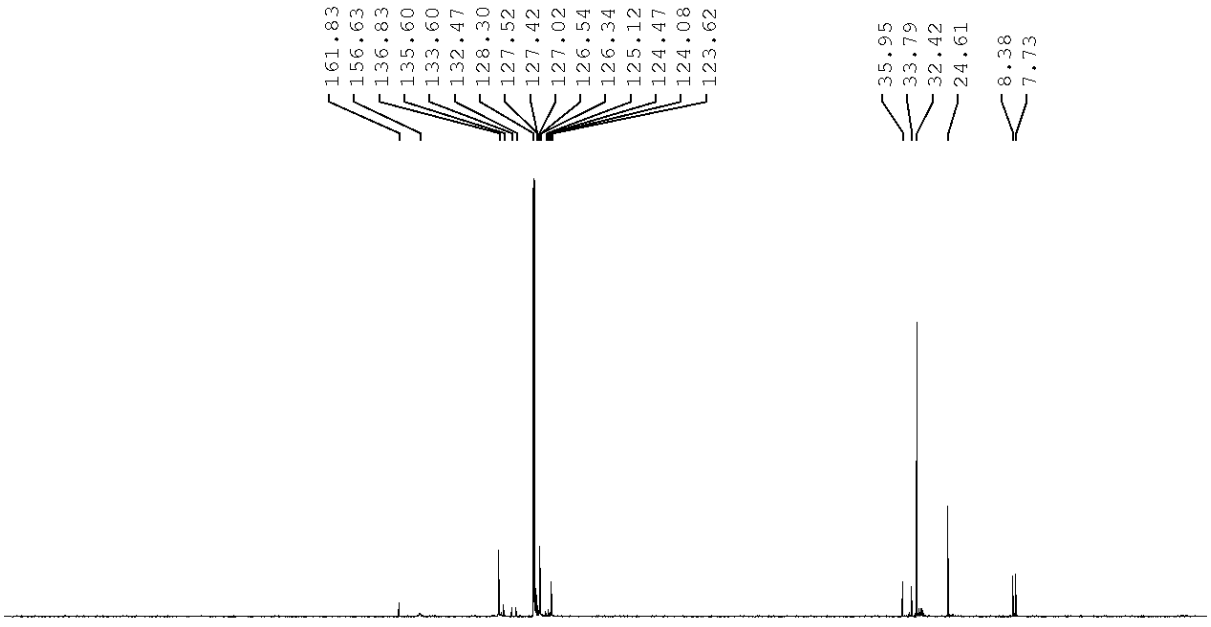

Figure S13. $^{13}C\{^1H\}$ NMR spectrum of compound **1**→BPh_3 in C_6D_6 at 25 °C.

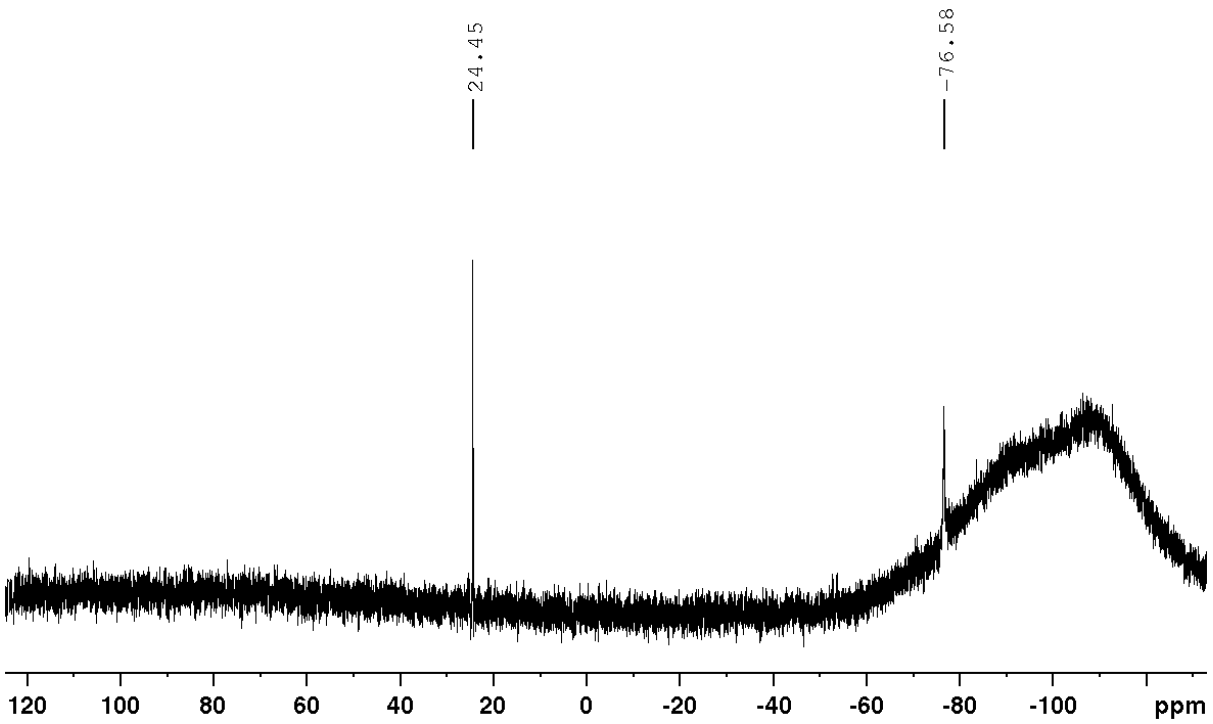

Figure S14. $^{29}Si\{^{1}H\}$ NMR spectrum of compound **1**→BPh_3 in C_6D_6 at 25 °C.

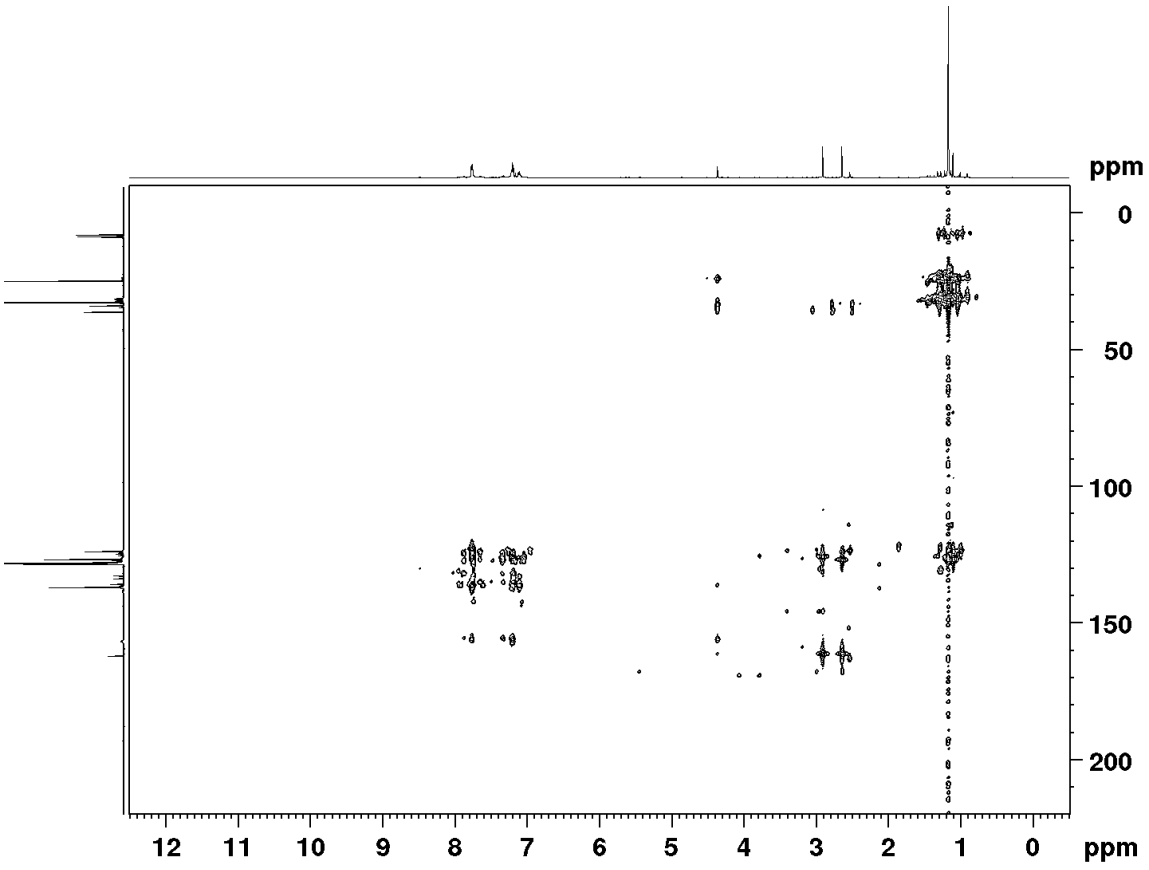

Figure S15. ^{1}H-^{13}C-HMBC NMR spectrum of compound **1**→BPh_3 in C_6D_6 at 25 °C.

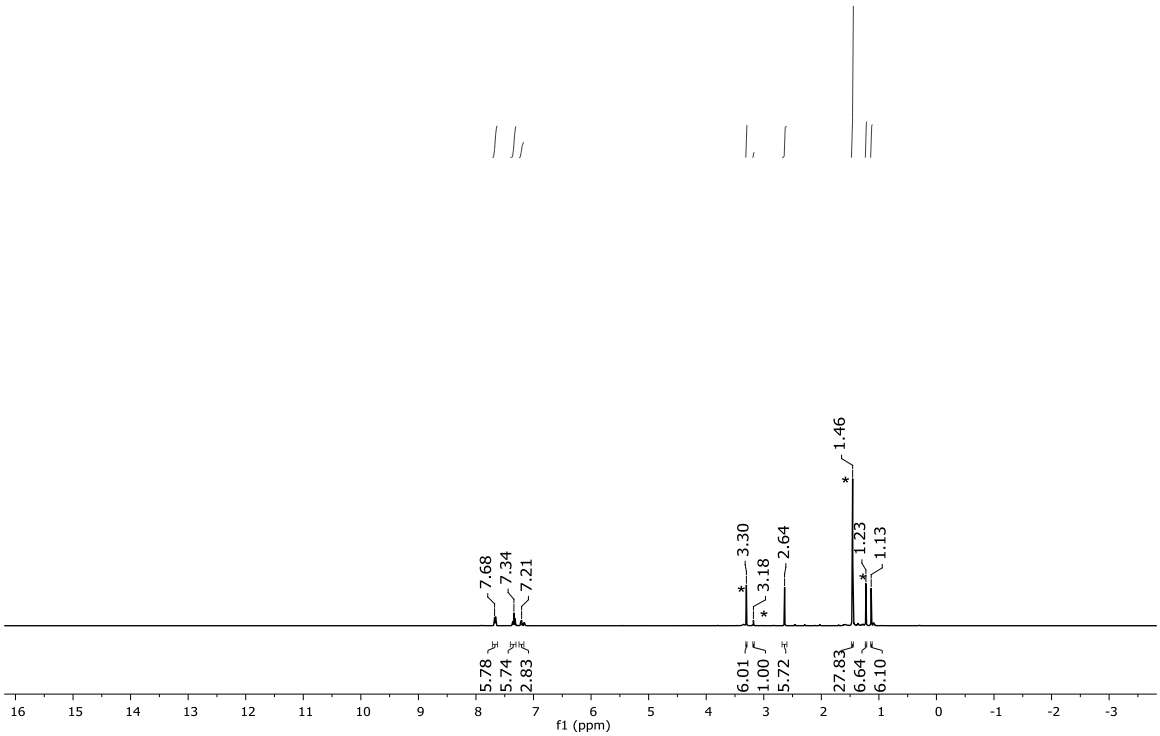

Figure S16. ^{1}H NMR spectrum of the reaction of compound **1**→BPh_3 with 1 equivalent of L^{Me4} in C_6D_6 at 25˚C. (*: *t*$Bu_3SiSi(H)L^{Me4}$, **1**)

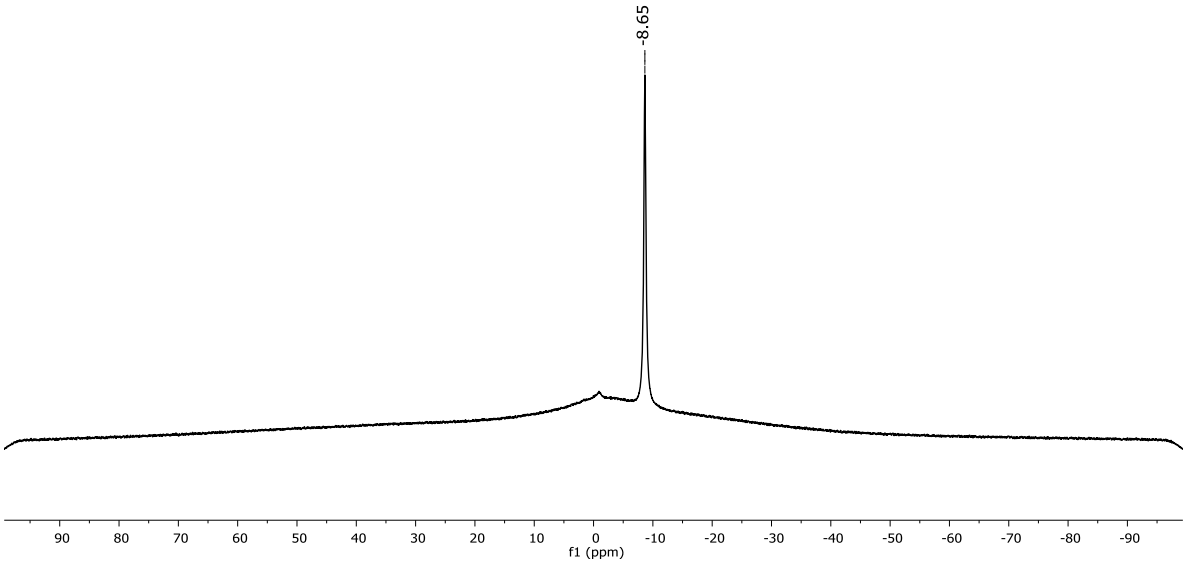

Figure S17. ^{11}B NMR spectrum of the reaction of compound **1**→BPh_3 with 1 equivalent of L^{Me4} in C_6D_6 at 25˚C.

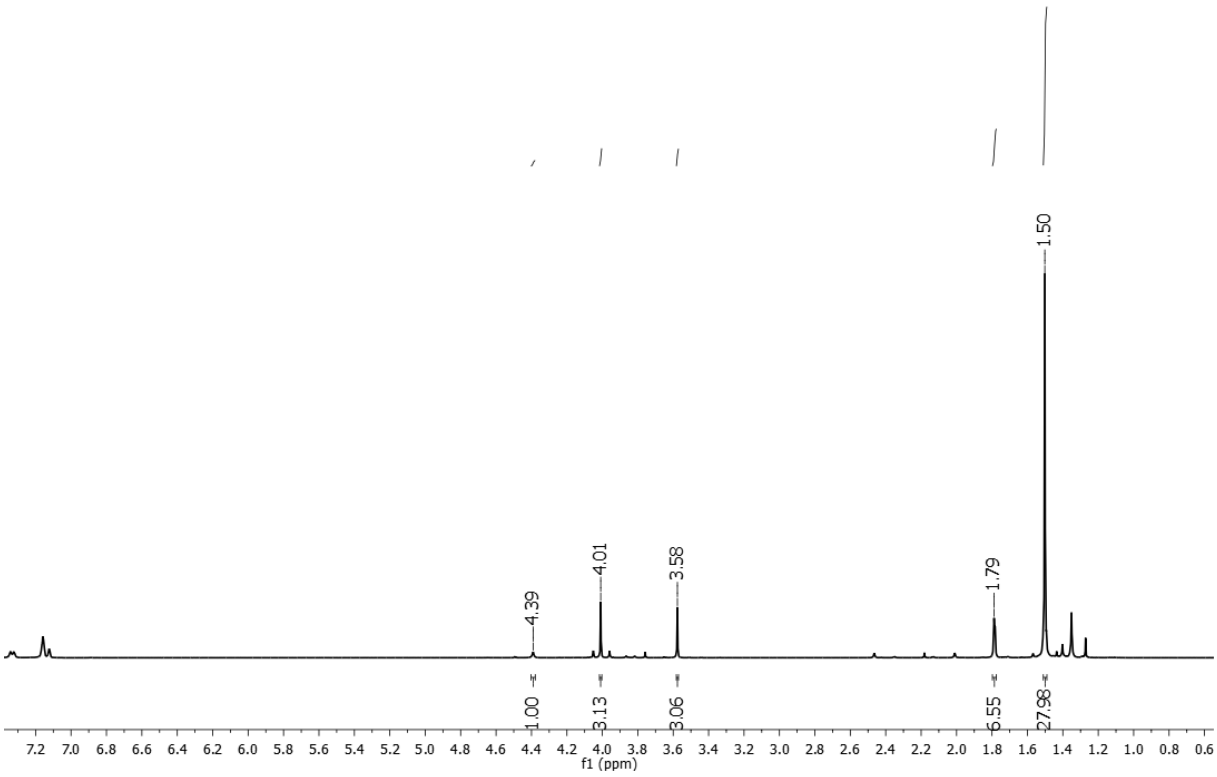

Figure S18. ^{1}H NMR spectrum of the compound **1**·BF_3 in C_6D_5F at 25 °C.

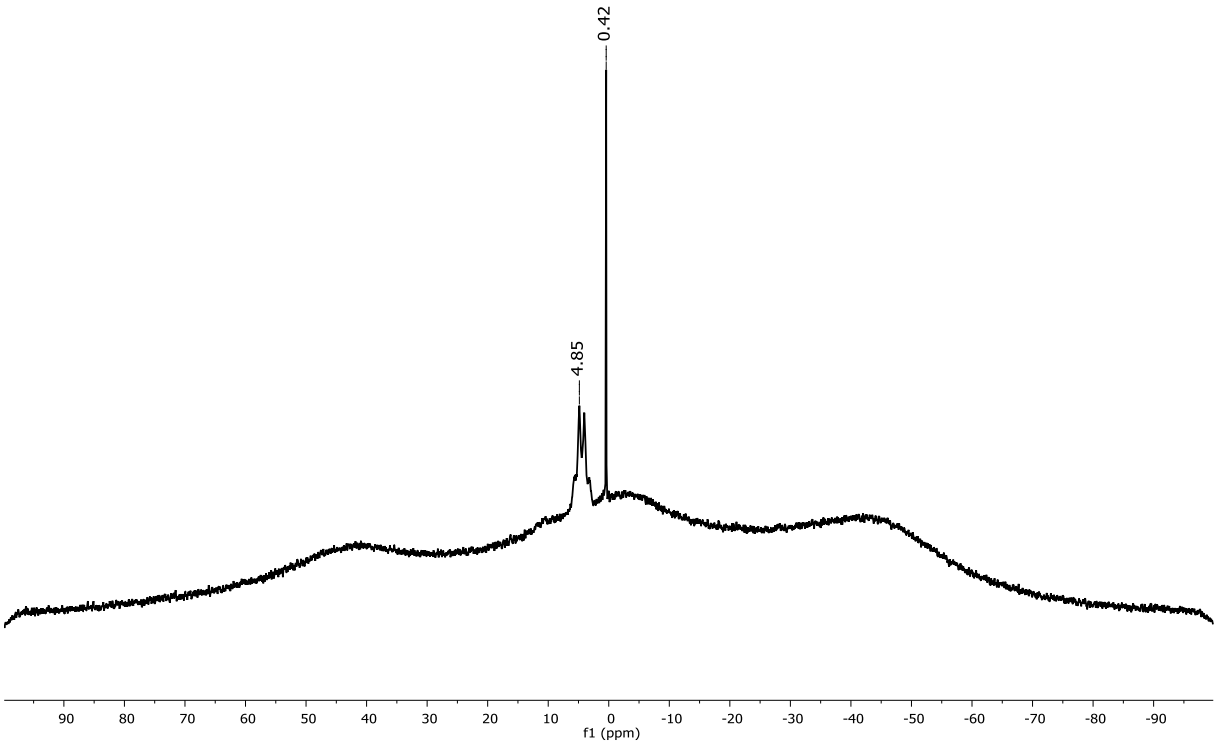

Figure S19. ^{11}B NMR spectrum of the compound **1**·BF_3 in C_6D_5F at 25 °C.

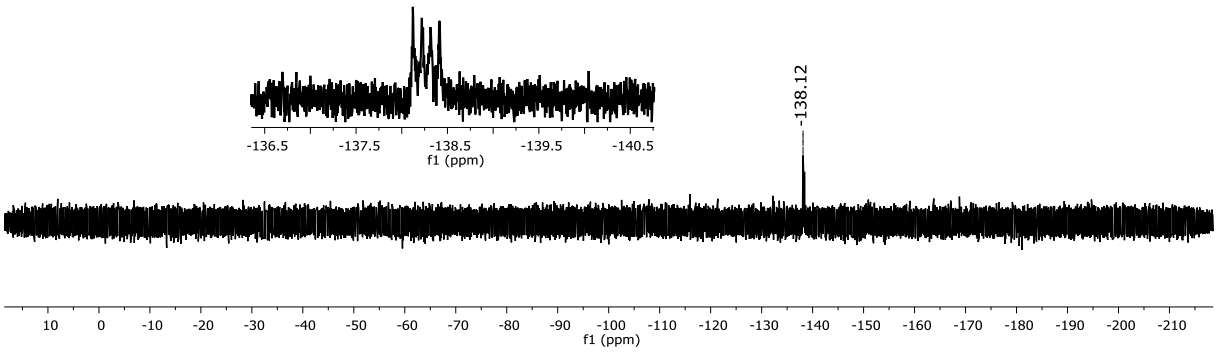

Figure S20. ^{19}F NMR spectrum of the compound **1**·BF_3 in C_6D_6 at 25 °C. (RT 1 h)

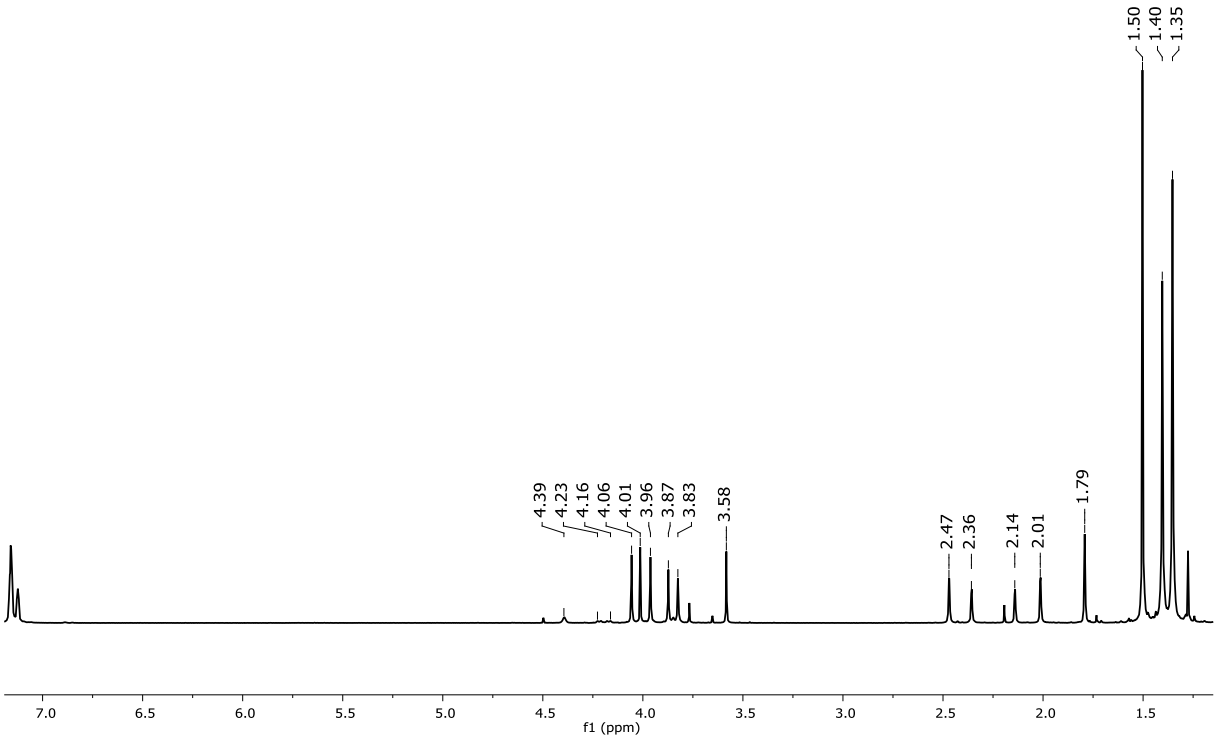

Figure S21. ^{1}H NMR spectrum of the compound **1**·BF_3 in C_6D_5F at 25 °C after 20 hrs.

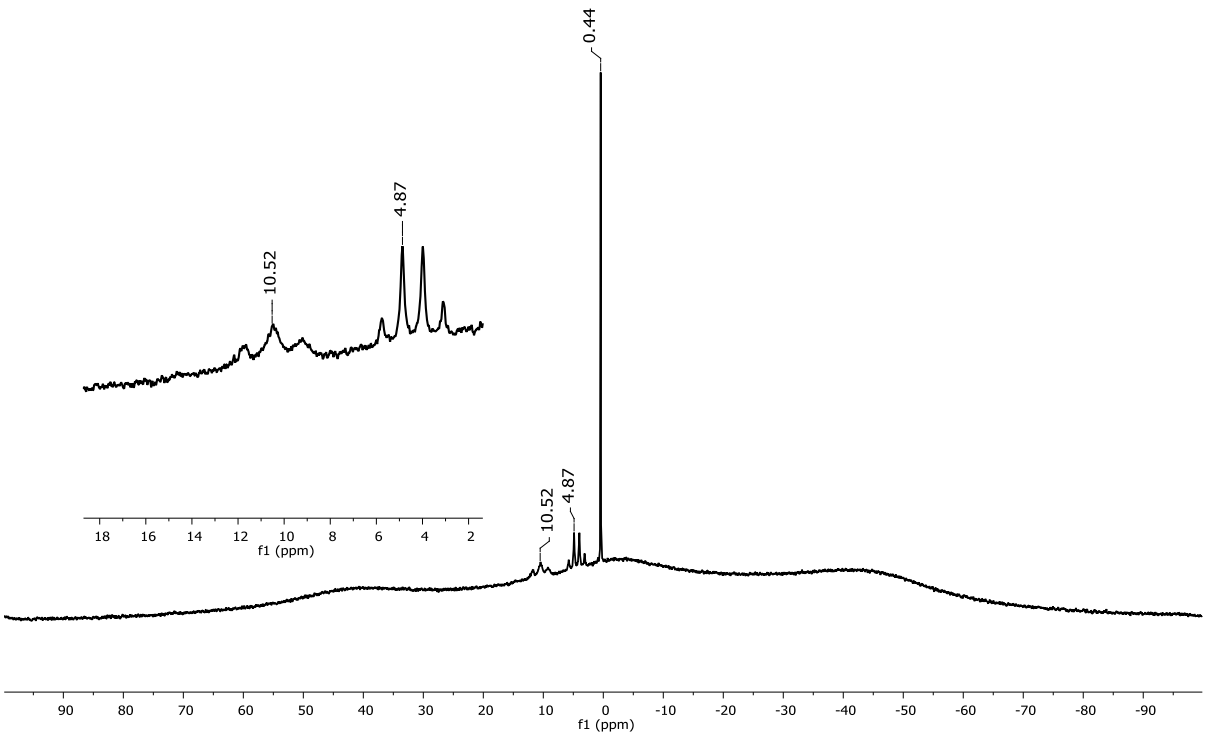

Figure S22. ^{11}B NMR spectrum of the compound **1**·BF_3 in C_6D_5F at 25 °C after 20 hrs.

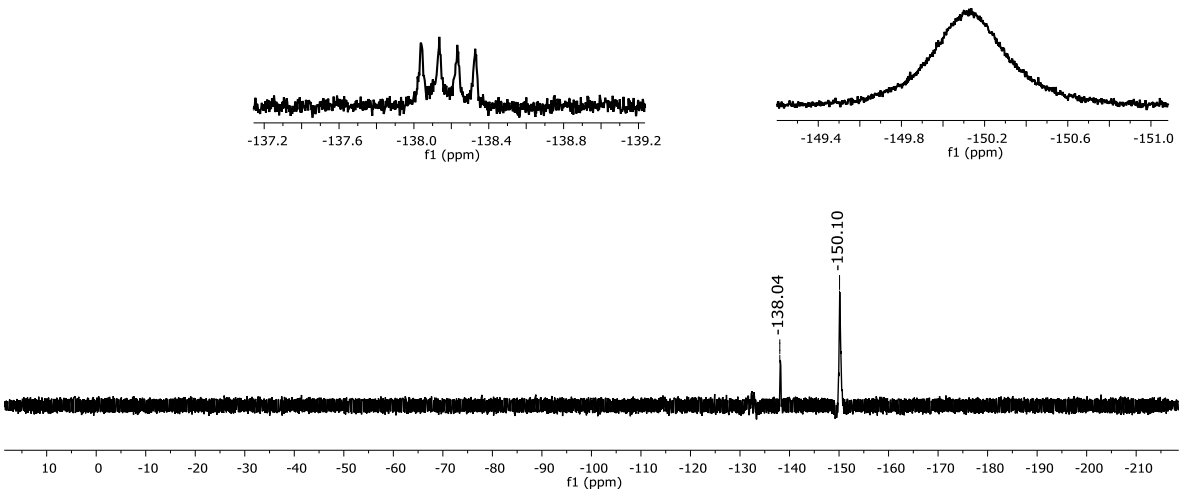

Figure S23. ^{19}F NMR spectrum of the compound **1**·BF_3 in C_6D_6 at 25 °C after heating 70 °C 1h.

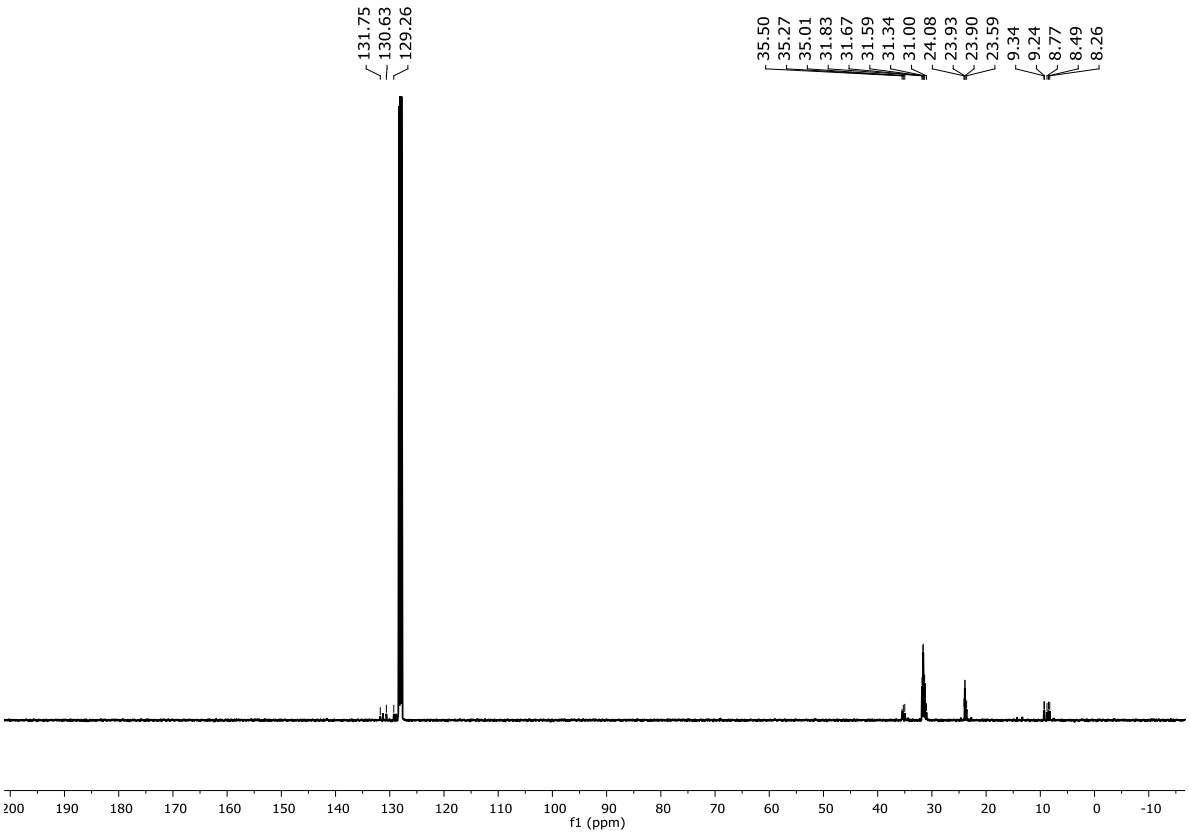

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of the compound **1**·BF_3 in C_6D_6 at 25 °C after heating 70 °C 1h.

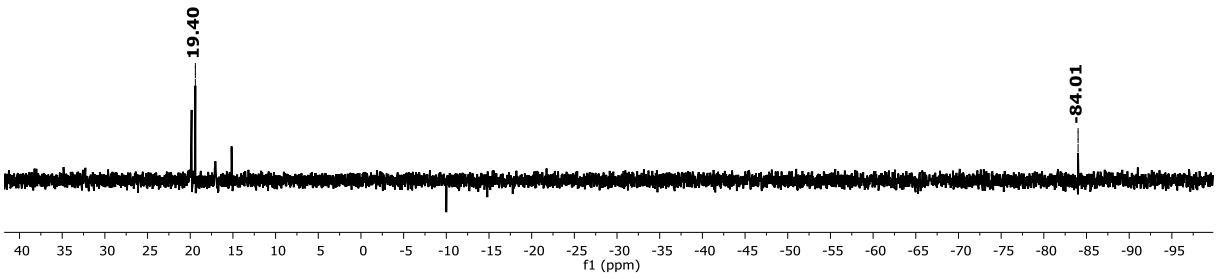

Figure S25. $^{29}Si\{^{1}H\}$ spectrum of the compound **1**·BF_3 in C_6D_5F at 25 °C after 20 hours.

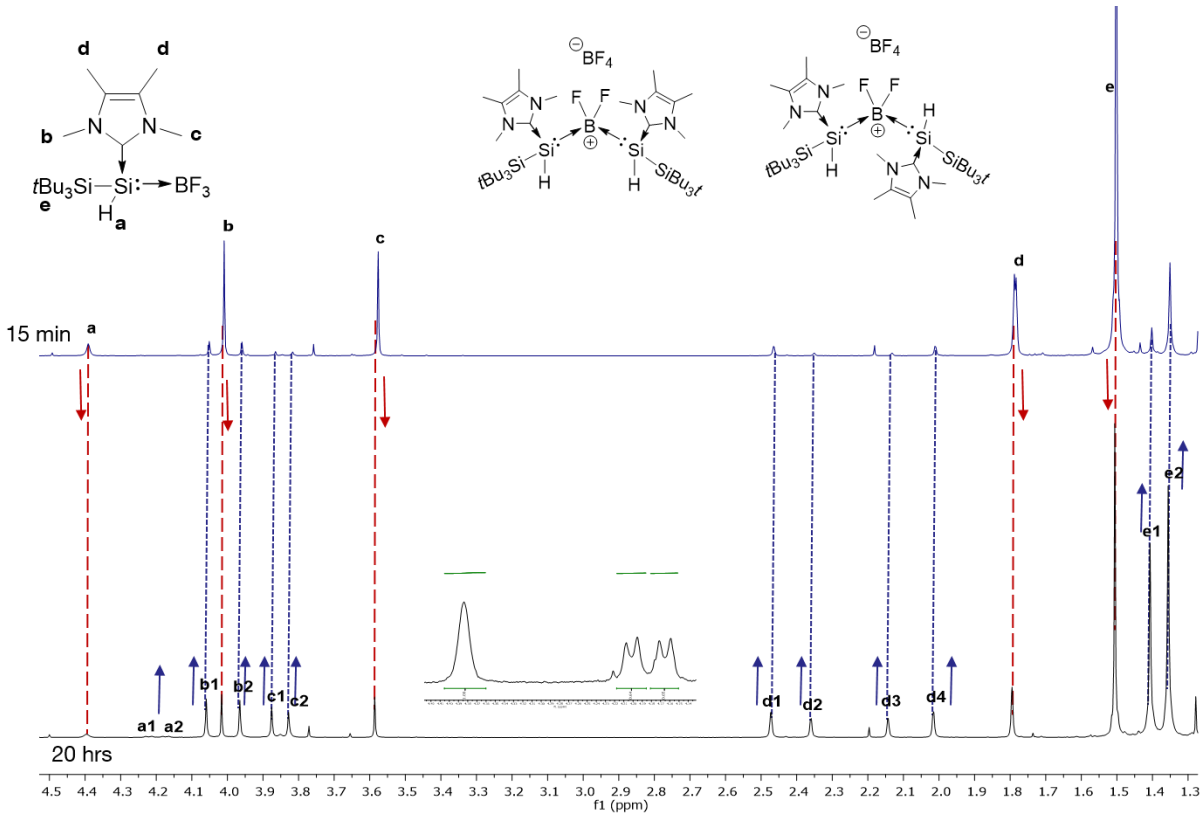

Figure S26. Comparison of ^{1}H NMR spectrum for **1**·BF_3 in C_6D_5F at 25 ˚C after 15 min and 20 hours.

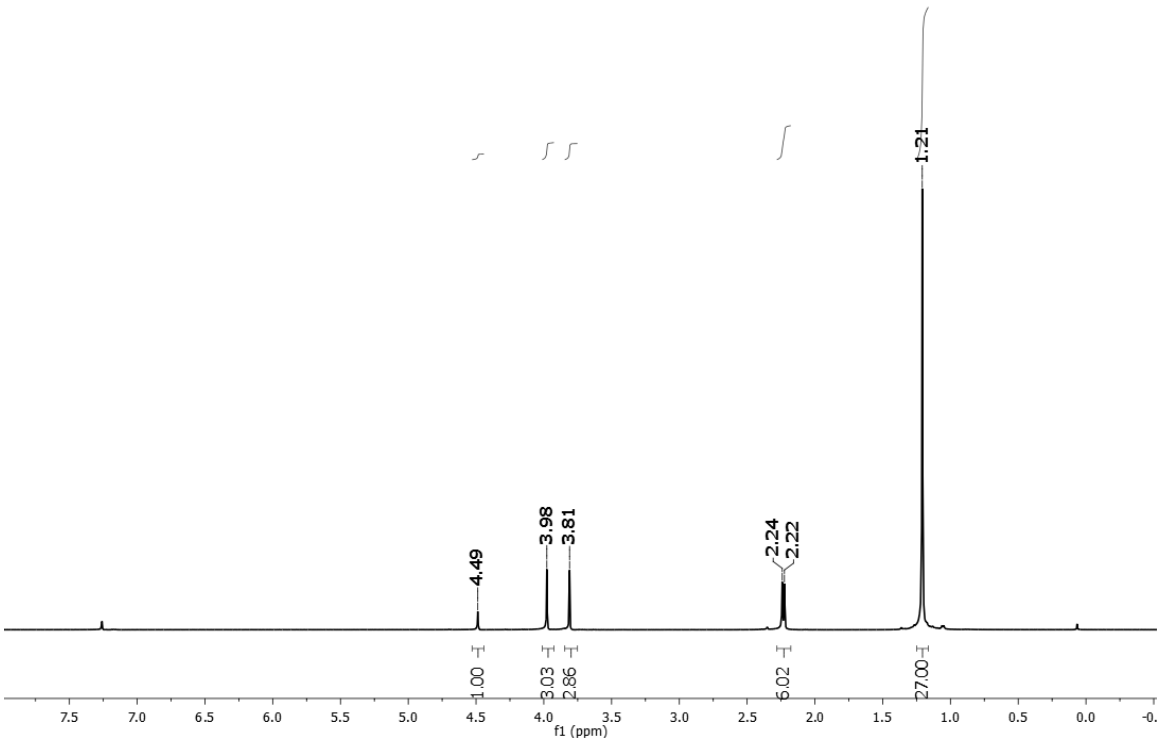

Figure S27. ^{1}H NMR spectrum of compound **1**·BCl_3 in CD_3Cl at 25 °C.

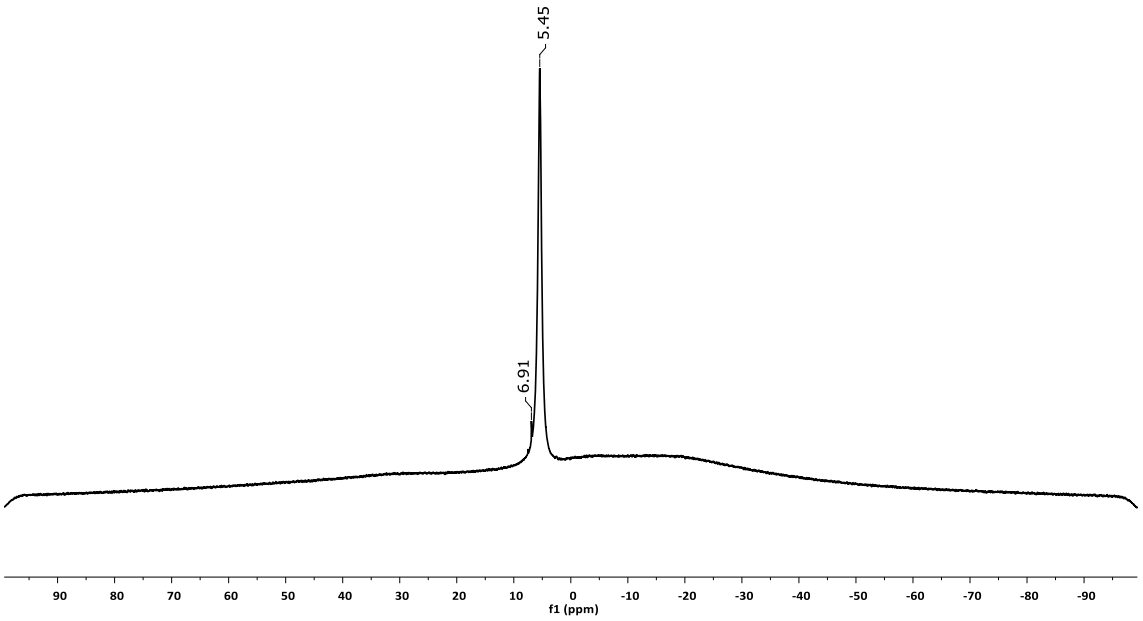

Figure S28. ^{11}B NMR spectrum of compound **1**·BCl_3 in CD_2Cl_2 at 25 °C.

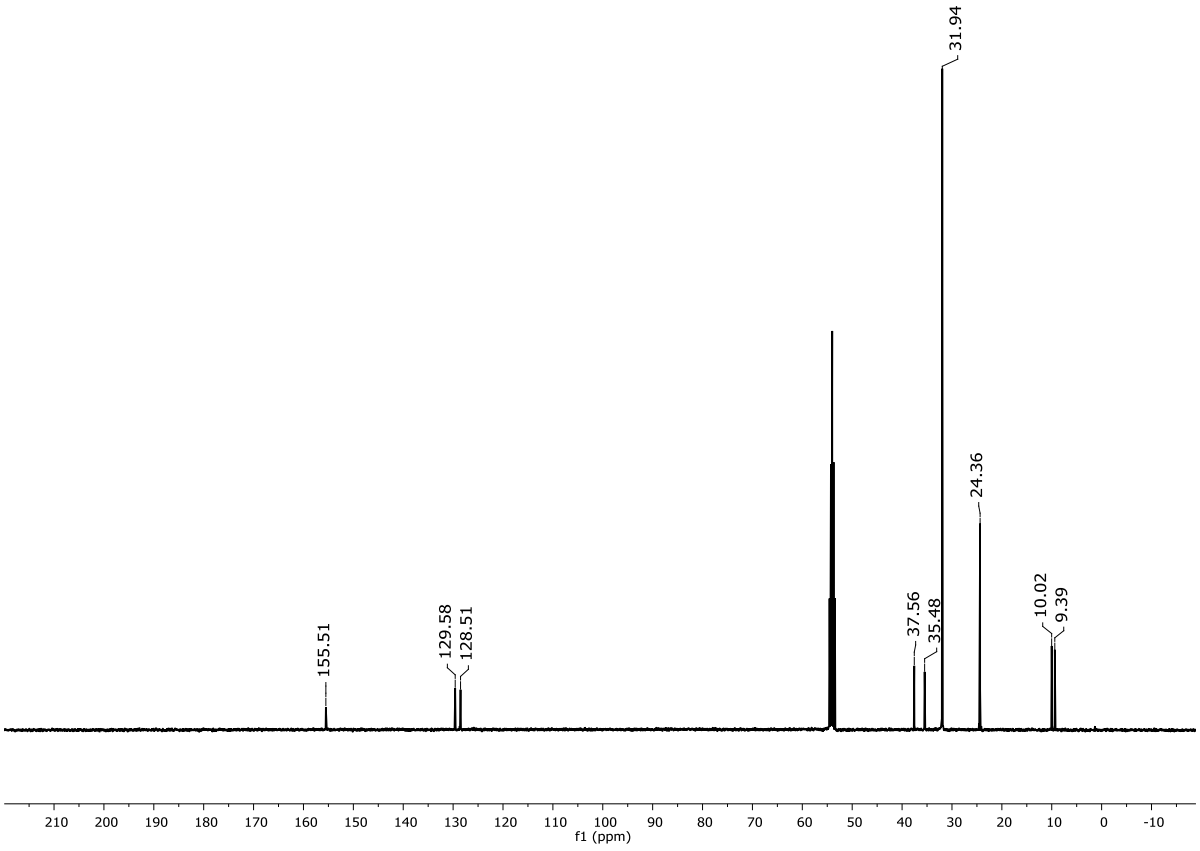

Figure S29. $^{13}C\{^1H\}$ NMR spectrum of compound **1**·BCl_3 in CD_2Cl_2 at 25 °C.

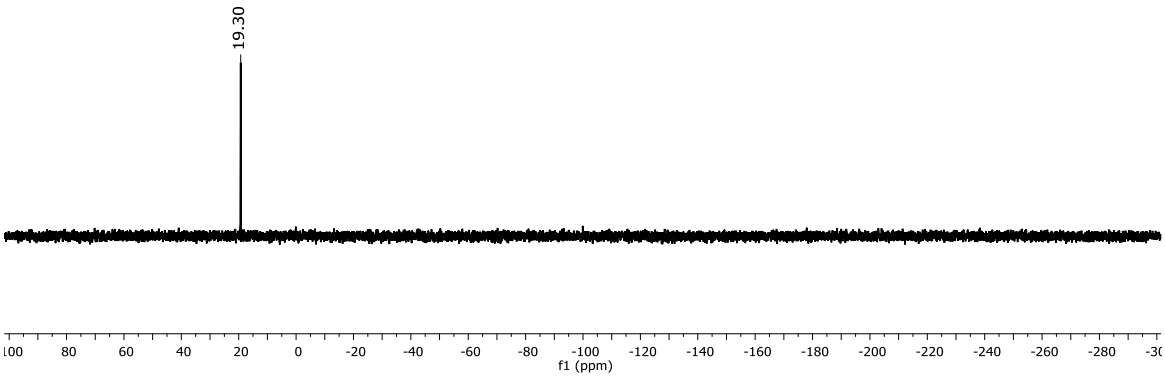

Figure S30. $^{29}Si\{^{1}H\}$ INEPT spectrum of compound **1**·BCl_3 in CD_2Cl_2 at 25 °C.

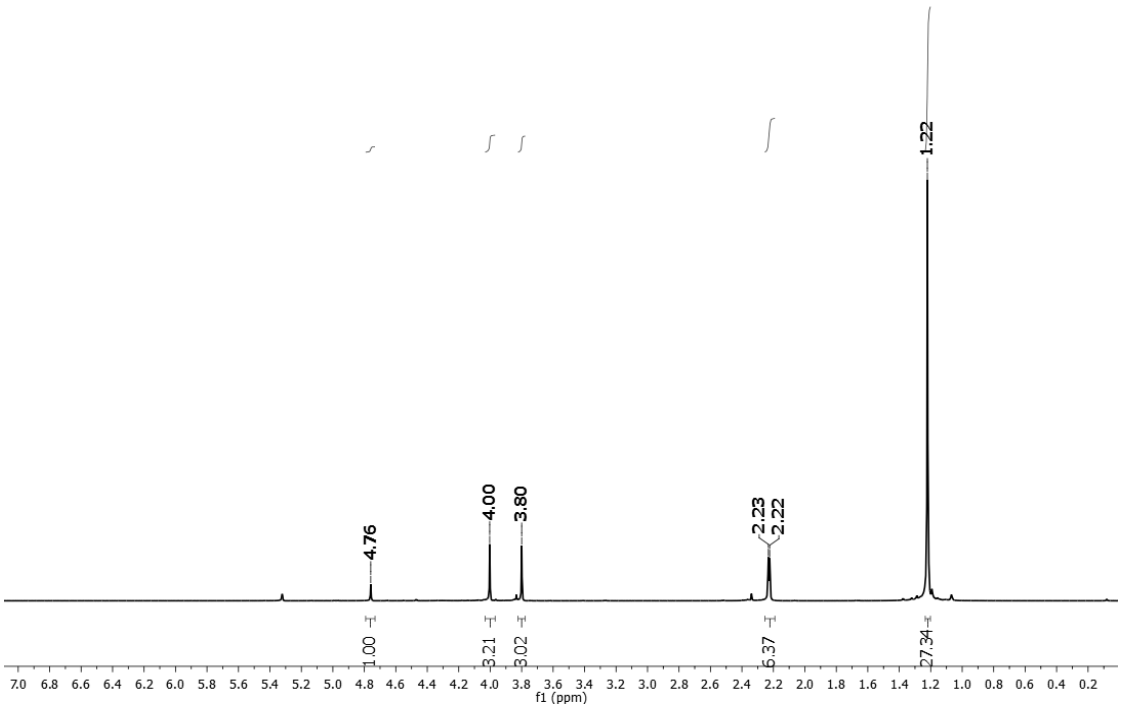

Figure S31. ^{1}H NMR spectrum of compound **1**→BBr_3 in CD_2Cl_2 at 25 °C.

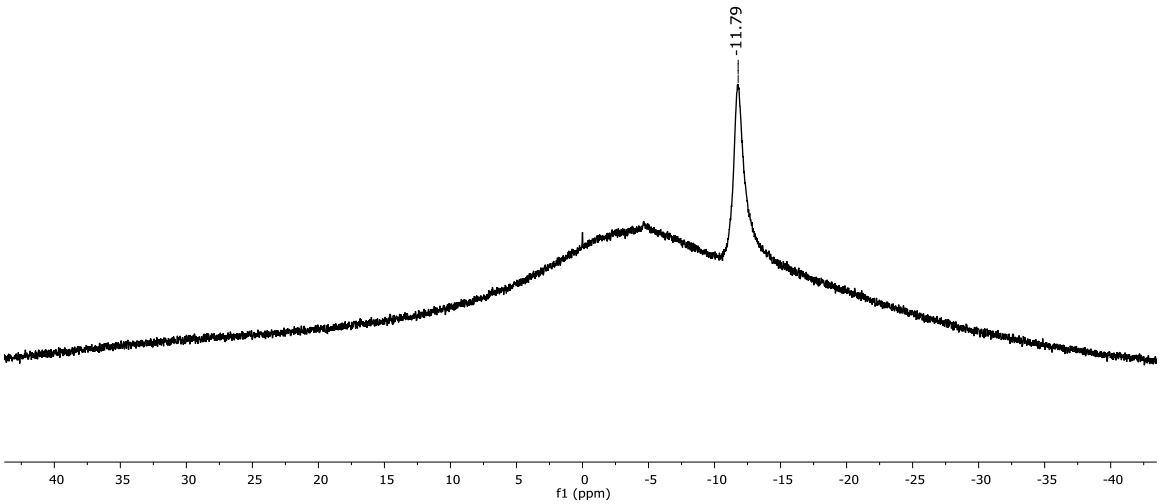

Figure S32. ^{11}B NMR spectrum of compound **1**→BBr_3 in CD_2Cl_2 at 25 °C.

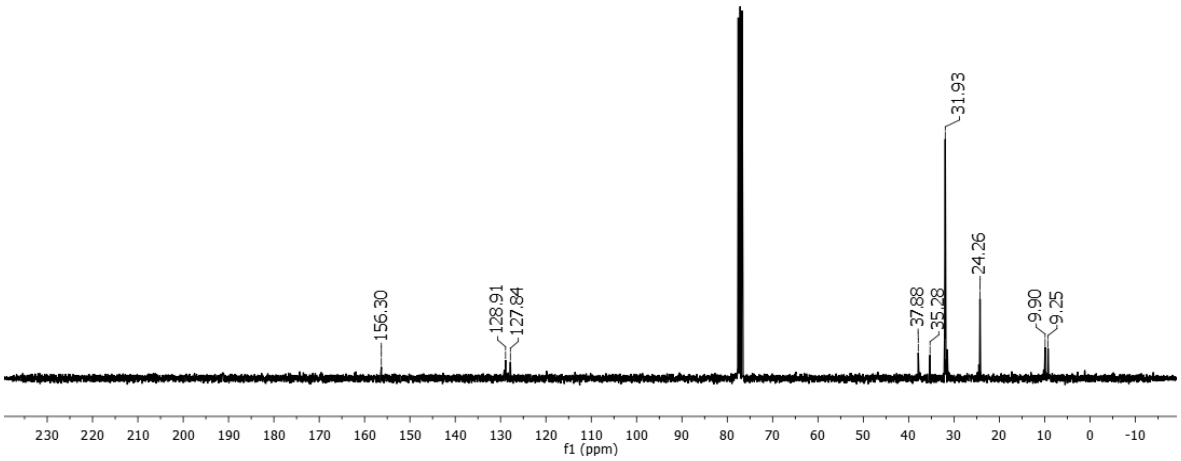

Figure S33. $^{13}C\{^1H\}$ NMR spectrum of **1**→BBr_3 in CD_3Cl at 25 °C.

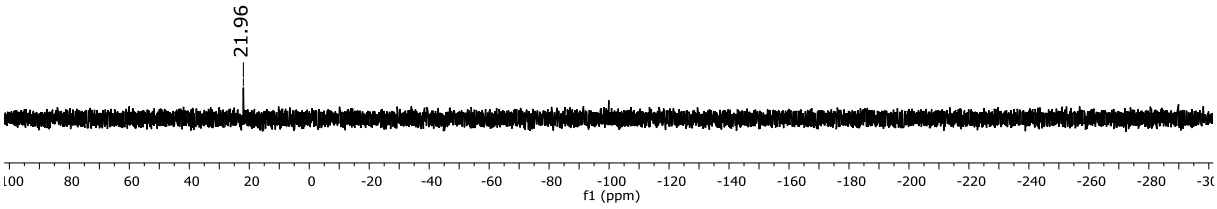

Figure S34. $^{29}Si\{^{1}H\}$ INEPT spectrum of compound 1→BBr_3 in CD_3Cl at 25 °C.

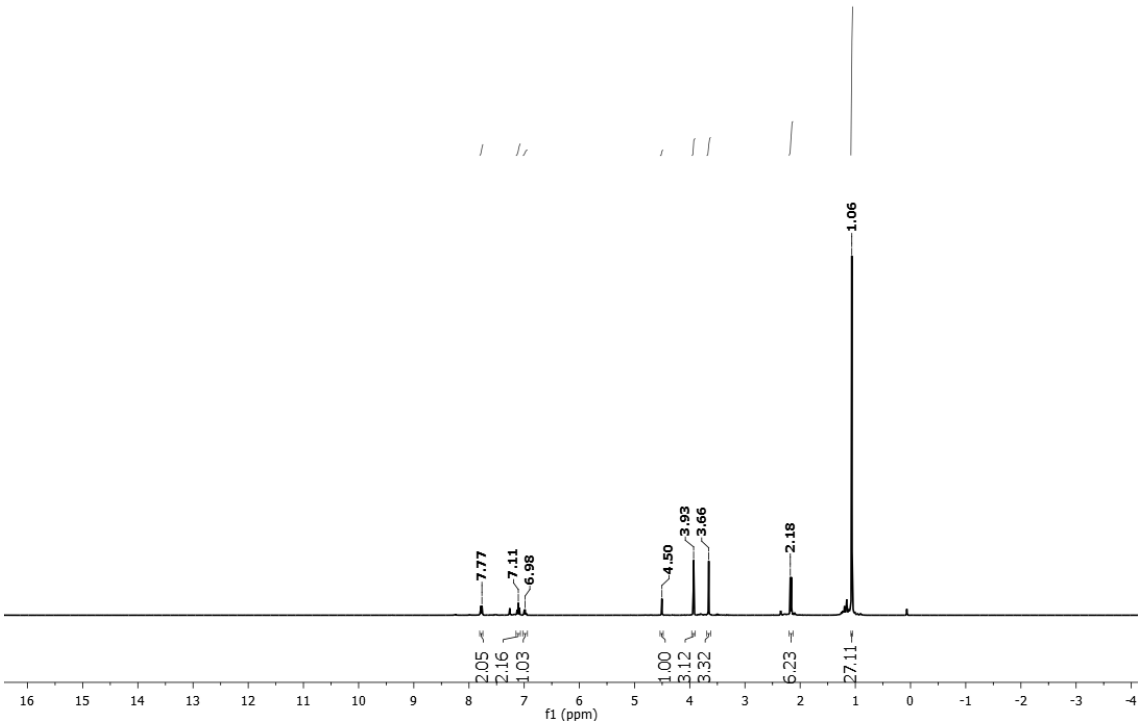

Figure S35. ^{1}H NMR spectrum of the compound **1**→$BPhBr_2$ in CD_3Cl at 25 °C.

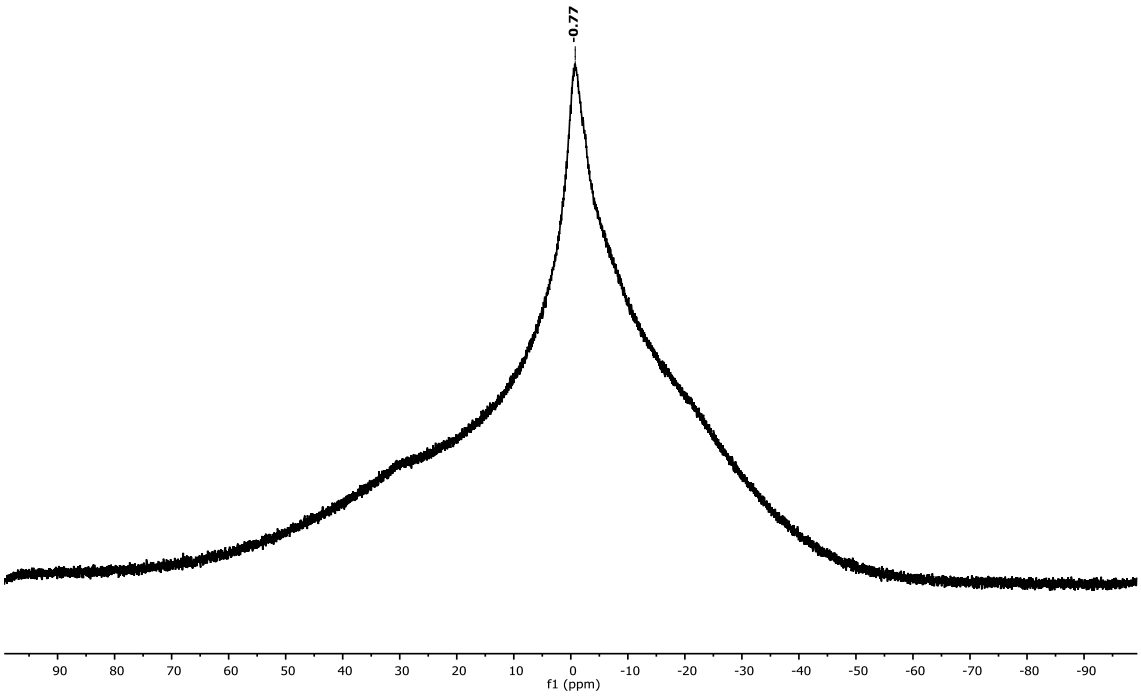

Figure S36. ^{11}B NMR spectrum of the compound **1**→$BPhBr_2$ in CD_3Cl at 25 °C.

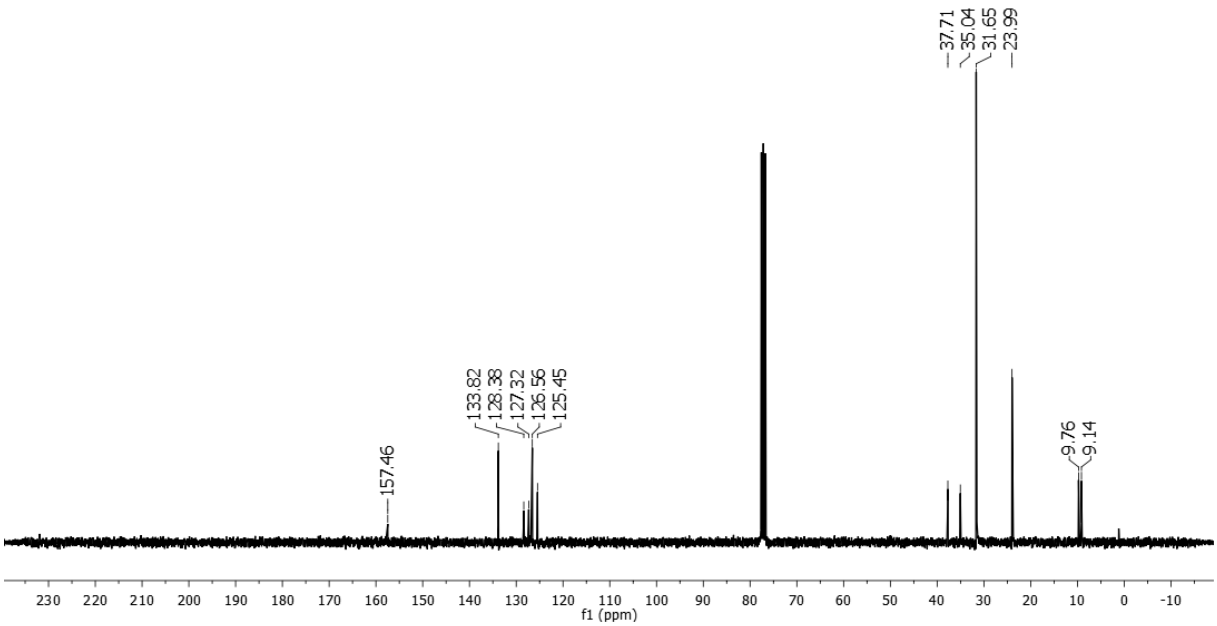

Figure S37. $^{13}C\{^1H\}$ NMR of spectrum of the compound **1**→$BPhBr_2$ in CD_3Cl at 25 °C.

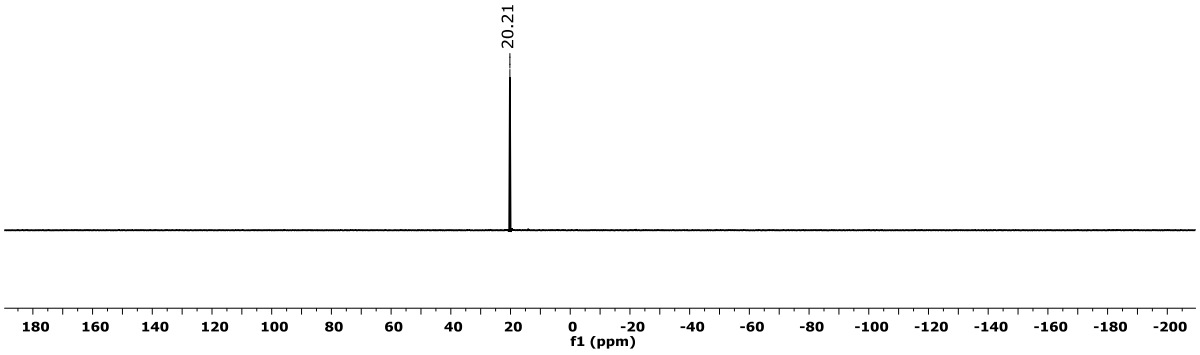

Figure S38. $^{29}Si\{^{1}H\}$ INEPT spectrum of the compound **1**→$BPhBr_2$ in CD_3Cl at 25 °C.

II. Mass Spectra

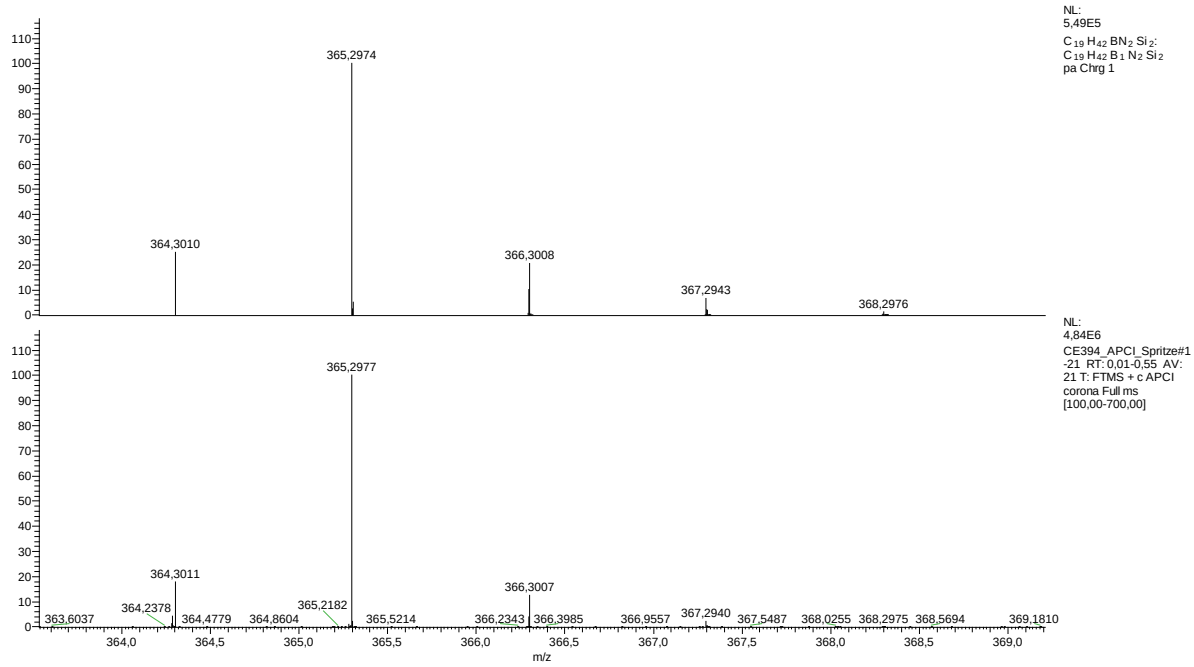

Figure S39. APCI-HRMS of $[M - H]^+$ signal of **1**→BH_3. Top (theor.) Bottom (expt.)

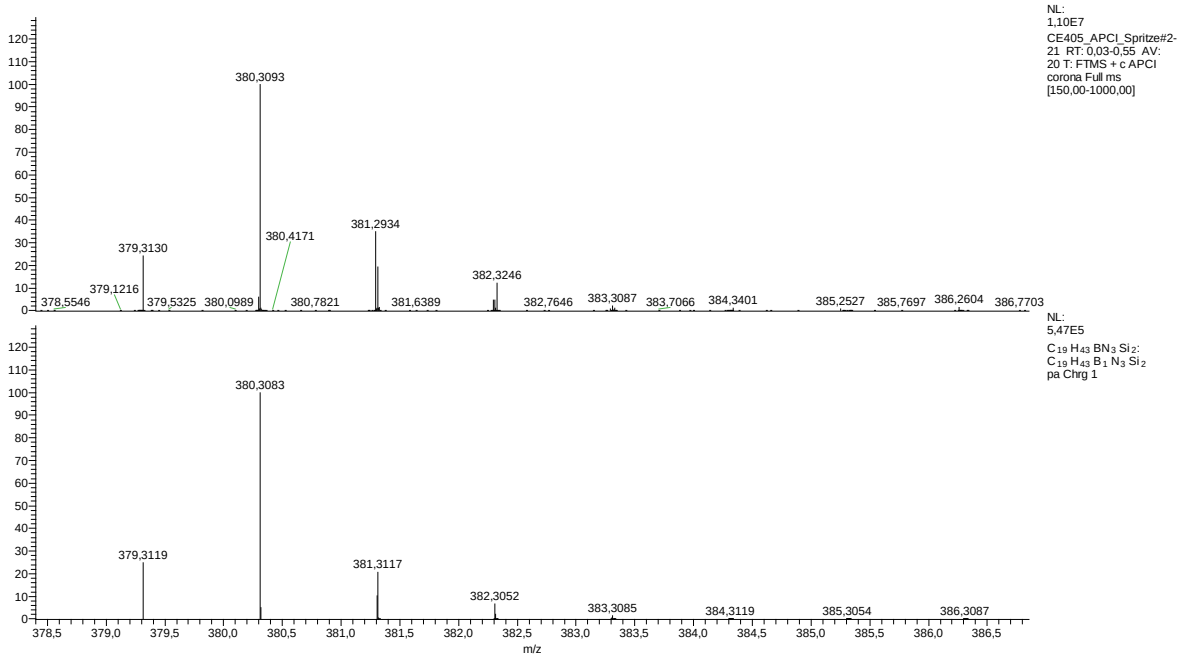

Figure S40. APCI-HRMS of $[M - H]^+$ Signal of **2**. Top (expt.) Bottom (theor.).

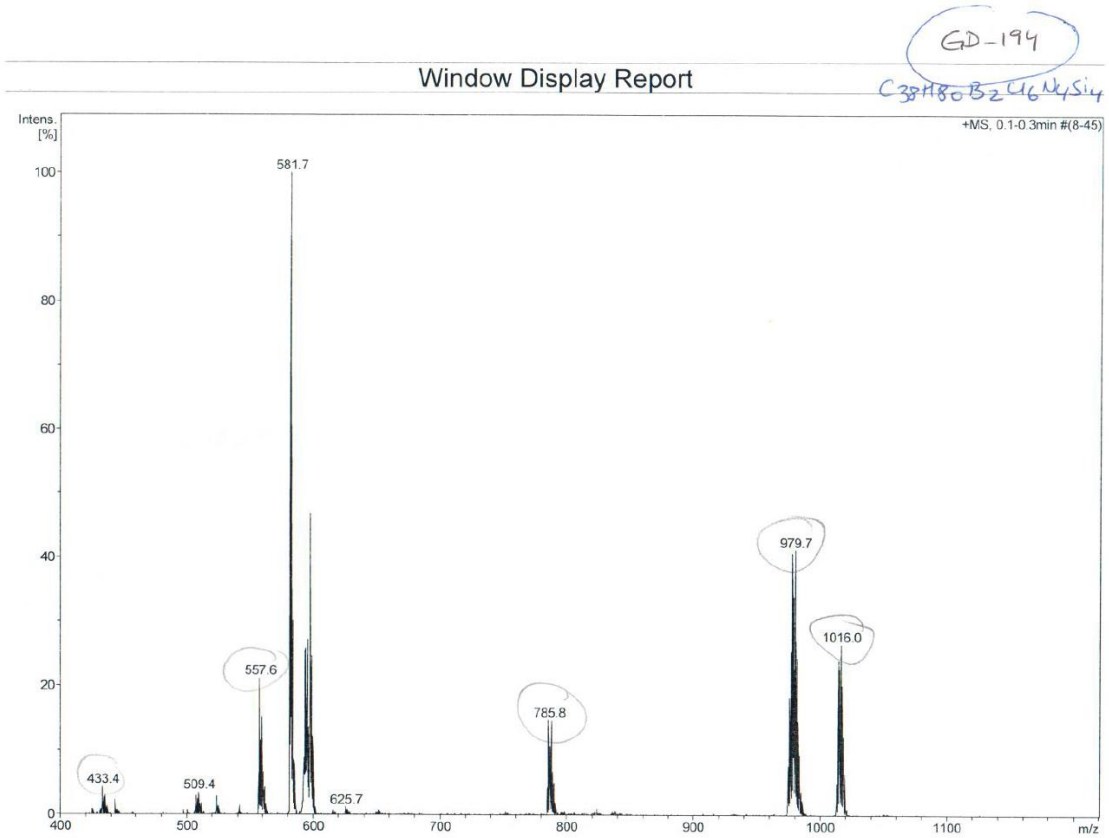

Figure S41. Scan of the original printout from the ESI measurement (positive mode) of **1**·BCl_3 (sample provided in CH_3CN solution). See Figure S42 for signal assignment.

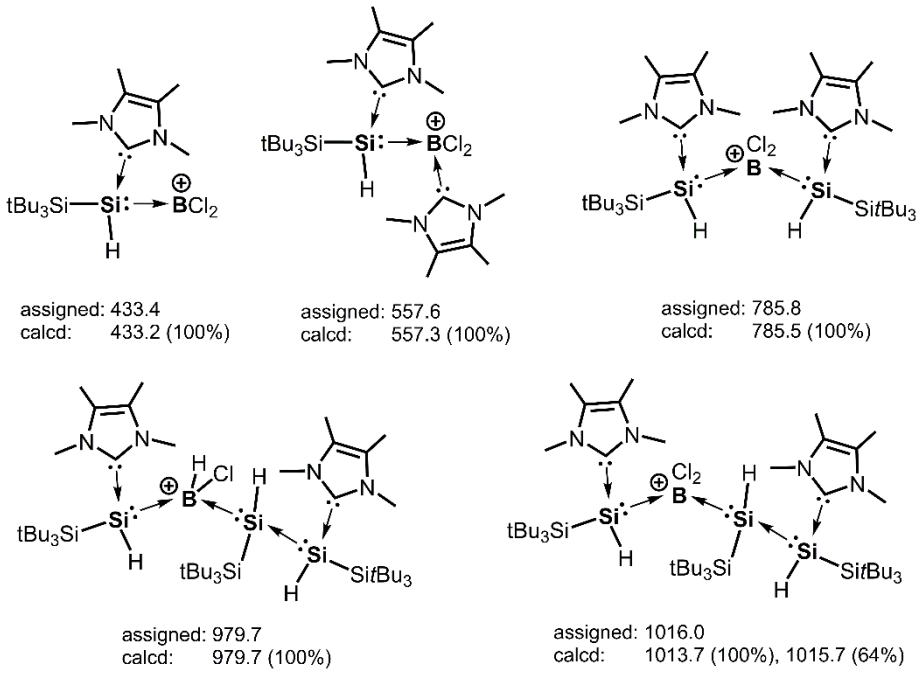

Figure S42. Suggested molecular structures derived from the stoichiometries assigned to the mass spectrum signals in Figure S41.

III. IR Spectrum

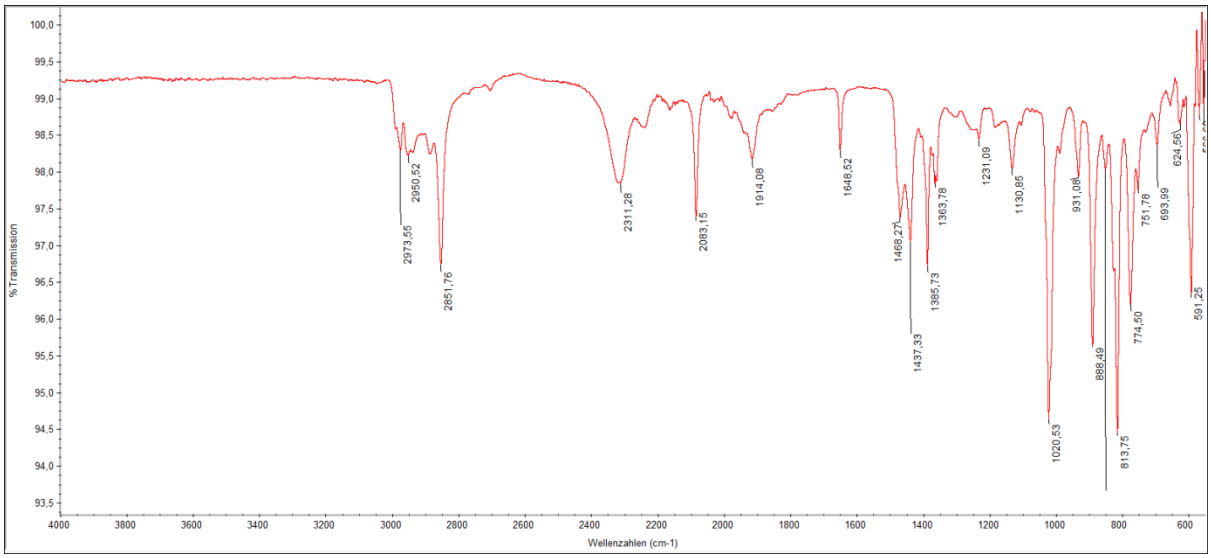

Figure S43. IR spectrum (no matrix) of compound **1**→BH_3

IV. Single-Crystal X-ray structure determination

Data for the Single Crystal XRD structure were collected on a Bruker D8 Venture Duo IMS system equipped with a Helios optic monochromator and a Mo IMS microsource (λ = 0.71073 Å). The individual crystals were mounted on a glass capillary or a MiTiGen MicroMount microsampling tool in per-fluoropolyether oil and measured in a cold N_2 flow. The data of the compound **1**·BH_3 were collected on an Oxford Diffraction SuperNova at 150 K (Cu-Kα radiation, λ = 1.5418 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[3] software package. The H atoms at the silicon and boron centers were found in the electron density map while all other hydrogen atoms were calculated and considered isotropically according to a riding model.

CCDC numbers: 1896328 (**1**→BH_3), 1896329 (**1**→BBr_3), 1896330 (**2**), 1896331 (**1**→$BPhBr_2$)

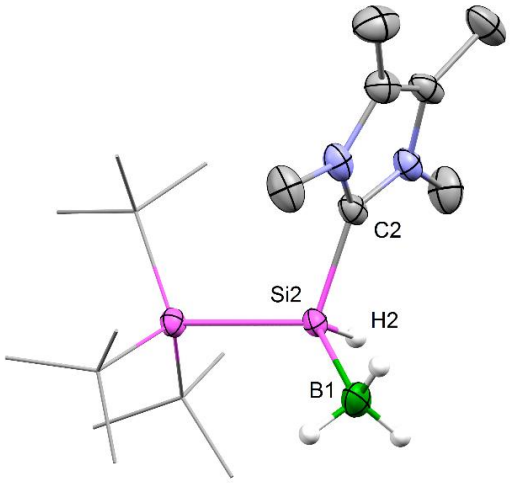

Figure S44. Molecular structure of compound **1**→BH_3. Thermal ellipsoids are drawn at the 30% probability level. H atoms except for the hydrogens at the silicon and at the boron have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1-Si2 2.401(1), Si2-C2 1.942(3), Si2-B1 2.009(5), Si1-Si2-B1 123.3(2), C2-Si2-B1 108.2(2), Si1-Si2-C2 111.3(2).

Table S1. Crystal data and structure refinement for compounds **1**→BH_3

Empirical formula	$C_{19}H_{43}BN_2Si_2$	
Formula weight	366.54	
Temperature	150.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 15.5684(6) Å	α = 90°.
	b = 8.9172(5) Å	β = 100.255(4)°
	c = 35.2491(17)	γ = 90°.
Volume	4815.3(4) $Å^3$	
Z	8	
Density (calculated)	1.011 Mg/m^3	
Absorption coefficient	1.340 mm^{-1}	
F(000)	1632	
Crystal size	0.40 x 0.28 x 0.06 mm^3	
Theta range for data collection	2.55 to 67.49°.	
Index ranges	-18<=h<=18,-9<=k<=10, -37<=l<=42	
Reflections collected	8677	
Independent reflections	4347[R(int) = 0.0413]	
Completeness to theta = 67.48°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9239 and 0.6136	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4347 / 0 / 243	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0714, wR2 = 0.1743	
R indices (all data)	R1 = 0.0844, wR2 = 0.1863	
Largest diff. peak and hole	0.712 and -0.332 e.$Å^{-3}$	

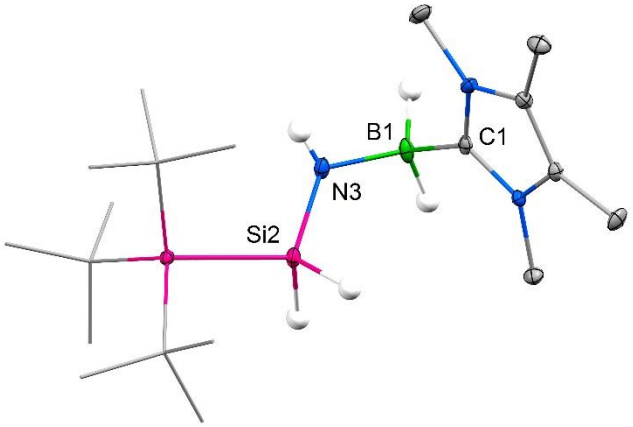

Figure S45. Molecular structure of compound **2**. Thermal ellipsoids are drawn at the 30% probability level. H atoms except for the hydrogens at the silicon, boron and nitrogen have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1-Si2 2.363(11), Si2-N3 1.703(3), B1-N3 1.542(4), B1-C1 1.635(4), Si1-Si2-N3 114.35(10), Si2-N3-B1 123.2(2), N3-B1-C1 110.2 (2).

Table S2. Crystal data and structure refinement for compound **2**.

Empirical formula	$C_{19}H_{44}BN_3Si_2$	
Formula weight	381.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.3084(7) Å	α = 81.990(3)°
	b = 8.5790(7) Å	β = 81.622(3)°
	c = 19.8196(16) Å	γ = 61.427(2)°
Volume	1223.45(18) Å3	
Z	2	
Density (calculated)	1.036 g/cm^3	
Absorption coefficient	0.152 mm^{-1}	
F(000)	424	
Crystal size	0.377 x 0.399 x 0.581 mm	
Theta range for data collection	2.71 to 25.03°	
Index ranges	-9<=h<=9, -10<=k<=10, -23<=l<=23	

Reflections collected	34475	
Independent reflections	4326 [R(int) = 0.0648]	
Completeness to theta	96.5%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9450 and 0.9170	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4326 / 0 / 255	
Goodness-of-fit on F^2	1.134	
Final R indices [I>2sigma(I)]	R1 = 0.0509, wR2 = 0.1179	
R indices (all data)	R1 = 0.0584, wR2 = 0.1258	
Largest diff. peak and hole	0.433 and -0.297 $eÅ^{-3}$	

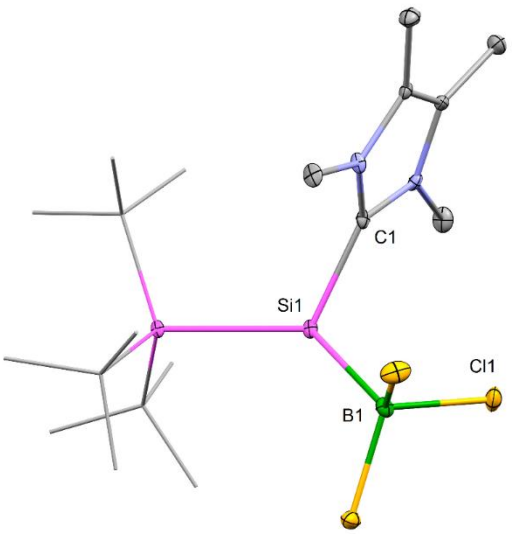

Figure S46. Molecular structure of compound **1**·BCl_3 in the solid state. Thermal ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Data quality is insufficent for parameter discussion. Space Group: monoclinic, $P2_1/n$. Cell Parameters: a = 8.97 Å, b = 19.71 Å, c = 13.57 Å; α = 90°, β = 91.9°, γ = 90.

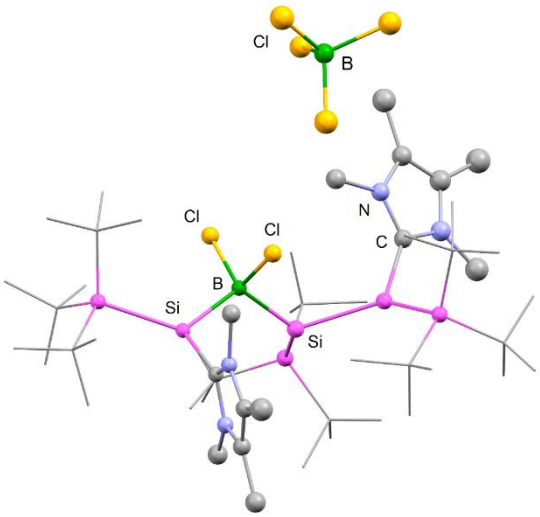

Figure S47. Molecular structure of compound [(**1**)BCl_2(SiH(SitBu_3)**1**)]$^+$[BCl_4]$^-$ in the solid state (Ball&Stick Model). H atoms have been omitted for clarity. Data quality is insufficient for parameter discussion. Space Group: monoclinic, $P2_1/n$. Cell Parameters: a = 14.85 Å, b = 21.26 Å, c = 21.75 Å; α = 90°, β = 104.6°, γ = 90.

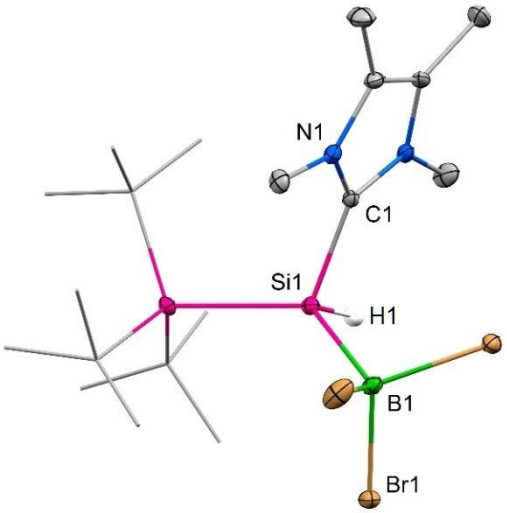

Figure S48. Molecular structure of compound **1**→BBr_3. Thermal ellipsoids are drawn at the 30% probability level. H atoms except for the hydrogens at the silicon have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1-Si2 2.428(2), Si1-C1 1.922(3), Si1-B1 2.045(3), Si2-Si1-B1 130.09(11), C1-Si1-B1 104.92(14), Si2-Si1-C1 113.56(10).

Table S3. Crystal data and structure refinement for compound **1**→BBr_3.

Empirical formula	$C_{19}H_{40}BBr_3N_2Si_2$	
Formula weight	603.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.131(5) Å	α = 90°
	b = 20.191(11) Å	β = 93.274(17)°
	c = 14.376(8) Å	γ = 90°
Volume	2646.(2) $Å^3$	
Z	4	
Density (calculated)	1.514 g/cm^3	
Absorption coefficient	4.672 mm^{-1}	
F(000)	1224	
Crystal size	0.263 x 0.286 x 0.344 mm	
Theta range for data collection	2.45 to 29.65°	
Index ranges	-12<=h<=12, -27<=k<=21, -17<=l<=19	
Reflections collected	23398	
Independent reflections	7373 [R(int) = 0.0396]	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.3730 and 0.2960	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7373 / 331 / 380	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0396, wR2 = 0.0784	
R indices (all data)	R1 = 0.0577, wR2 = 0.0837	
Largest diff. peak and hole	2.227 and -0.726 $eÅ^{-3}$	

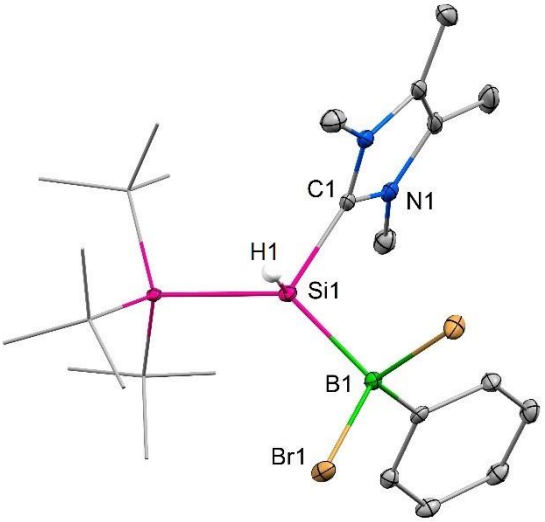

Figure S49. Molecular structure of compound **1**→$BPhBr_2$. Thermal ellipsoids are drawn at the 30% probability level. H atoms except for the hydrogen atom at the silicon atom have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Si1-Si2 2.421(1), Si1-C1 1.931(3), Si1-B1 2.074(3), Si2-Si1-B1 131.9(1), C1-Si1-B1 103.0(1), Si2-Si1-C1 113.1(1).

Table S4. Crystal data and structure refinement for compound **1**·$BPhBr_2$.

Empirical formula	$C_{25}H_{45}BBr_2N_2Si_2$	
Formula weight	600.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.6853(5) Å	α = 85.276(2)˚
	b = 9.0560(5) Å	β = 89.604(2)˚
	c = 20.7220(12) Å	γ = 63.638(2)˚
Volume	1454.61(15) $Å^3$	
Z	2	
Density (calculated)	1.371 g/cm^3	
Absorption coefficient	2.885 mm^{-1}	
F(000)	624.0	
Crystal size	0.263 x 0.286 x 0.344 mm	

Theta range for data collection	2.52 to 25.79˚	
Index ranges	-10<=h<=10, -11<=k<=11, -25<=l<=25	
Reflections collected	61899	
Independent reflections	5567 [R(int) = 0.0338]	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7453 and 0.5649	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5567 / 1 / 306	
Goodness-of-fit on F^2	1.169	
Final R indices [I>2sigma(I)]	R1 = 0.0378, wR2 = 0.0937	
R indices (all data)	R1 = 0.0395, wR2 = 0.0945	
Largest diff. peak and hole	2.222 and -0.745 $eÅ^{-3}$	