Electronic Supporting Information for

Attempted halogenation of ambiphilic 1,2,3-benzodiazaborines: Balancing Lewis acidity and Lewis basicity

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1 Experimental details

General Information. Unless stated otherwise, all manipulations were performed under oxygen- and moisture free conditions under an inert atmosphere of argon using standard Schlenk techniques or an inert atmosphere glovebox (*VIGOR SG1200/750TS-F*). All glassware was heated three times in vacuo using a heat gun and cooled under argon atmosphere. Solvents were transferred using syringes, steel or PE cannulas, which were purged with argon prior to use. Solvents and reactants were either obtained from commercial sources or synthesized as detailed in ***Table S1***. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å or 3 Å (for CH_2Cl_2) molecular sieves.

Liquid-phase NMR spectra. NMR spectra were acquired on a *BRUKER AVANCE 400*, *BRUKER AVANCE* 500 or *BRUKER AVANCE NEO* I 600 spectrometer and analyzed using the associated *TOPSPIN 4.1.1™*. Chemical shifts (δ) are reported in ppm and internally referenced to the carbon nuclei ($^{13}C\{^1H\}$: δ_{ref}(DMSO-d_6) = 39.52 ppm; $\delta_{ref}(C_6D_6)$ = 128.06 ppm; $\delta_{ref}(CD_2Cl_2)$ = 53.84 ppm) or residual protons (^1H: δ_{ref}(DMSO-d_6) = 2.50 ppm; $\delta_{ref}(C_6D_6)$ = 7.16 ppm; $\delta_{ref}(CD_2Cl_2)$ = 5.32 ppm) of the solvent.[1] $SiMe_4$ was used as an external standard for ^1H and ^{13}C NMR spectra. Heteronuclei NMR spectra are referenced to external standards (^{11}B: $BF_3 \cdot OEt_2$). Unless stated otherwise, all NMR spectroscopy measurements were carried out at room temperature (296 K). Resonances are given as singlet (s), doublet (d), sextet (sext), doublet of doublet of doublets (ddd), doublet of triplet (dt), triplet (t), triplet of doublets (td), quartet (q), quintet (quint), multiplet (m) or broad singlet (br s).

Mass spectra. High-resolution mass spectrometry was performed on a *THERMO SCIENTIFIC* mass spectrometer (Exactive Plus Spectrometer) using a *LIFDI 700* unit from LINDEN CMS source. Spectra were processed using the Qual Browser of the XCalibur software. The figures show the total spectrum in the upper part, the product peak with isotope distribution in the middle and a corresponding simulation in the lower part.

Single crystal structure analyses. Single crystals suitable for X-ray diffraction analysis were coated with polyisobutylene or perfluorinated polyether oil in a glovebox, transferred to a nylon loop, and then to the goniometer of a diffractometer. The crystal data were collected on a *RIGAKU XtalLAB SYNERGY-R* diffractometer with HPA area detector and multilayer mirror monochro-

mator using CuK_α radiation (λ = 1.54178 Å). The structures were solved using the intrinsic phasing method (*ShelXT*),[2] expanded Fourier expansion, and refined using the *SHELXL* software package.[3] All non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were included in the structure factor calculation at idealized positions. The images of the solid-state structures were created using the *Pov-Ray™* and *Mercury 2023.1.0* software. Important data and parameters of the compounds can be found in the synthesis and characterization of compounds section. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. For the CCDC number of all compounds see synthesis and characterization section.

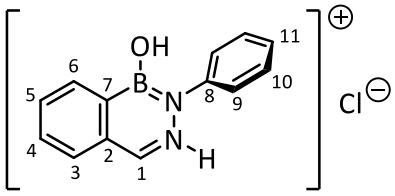
Table S1. Origin and purification of solvents and reactants.

Substance	**Origin**	**Purity / Purification**
2-Formylphenylboronic acid [40138-16-7]	BLD Pharmatech®	99.97% / none stored under Ar
Phenylhydrazine [100-63-1]	Sigma Aldrich®	≥97% / none stored under Ar
Hydrogen chloride solution ($HCl \cdot OEt_2$, 3.85 M in Et_2O) [7647-01-0]	synthesized	- / none stored under Ar
Boron trichloride (BCl_3, 4.00 M in CH_2Cl_2) [10294-34-5]	synthesized	- / none stored under Ar
Boron tribromide (BBr_3) [10294-33-4]	Sigma Aldrich®	- / copper wire stored under Ar
Potassium bis(trimethylsilyl)amide (K[HMDS]) [4039-32-1]	Sigma Aldrich®	95% / none stored under Ar
Lithium 2,2,6,6-tetramethylpiperidide ([LiTMP]) [38277-87-1]	Sigma Aldrich®	95% / none stored under Ar
Pyridine (anhydr.) [110-86-1]	Sigma Aldrich®	≥99.8% / none stored over MS under Ar
2,2'-bipyridine [366-18-7]	Sigma Aldrich®	99% / none stored under Ar
4,4'-dipyridyl [553-26-4]	Sigma Aldrich®	99% / none stored under Ar
Dichloromethane [71-43-2]	local trade	purified and dried over local solvent purification system (SPS), stored over MS (3 Å) under Ar
Benzene [71-43-2]	local trade	dried over Na, freshly distilled prior to use, stored under Ar over molecular sieves (4 Å)
n-Pentane [109-66-0]	local trade	
Diethyl ether (Et_2O) [60-29-7]	local trade	
Benzene-d_6 (C_6D_6) [1076-43-3]	Sigma Aldrich®	99.6 atom% D / none stored under Ar over molecular sieves.
Dimethylsulfoxide-d_6 (DMSO-d_6) [2206-27-1]	Sigma Aldrich®	99.5 atom% D / none
Dichlormethane-d_2 (CD_2Cl_2) [1665-00-5]	Sigma Aldrich®	99.5 atom% D / none

2 Syntheses and characterization

Compound **1OH** was prepared following previously described procedures.[4-5]

Compound [1OH]·HCl



[1OH] HCl (81%)

Compound **1OH** (1.00 g, 4.50 mmol, 1.00 equiv.) was partially dissolved in Et_2O (25 mL) in a 250 mL Schlenk tube. $HCl \cdot OEt_2$ (3.85 M solution in Et_2O, 2.40 mL, 6.75 mmol, 1.50 equiv.) was added in portions at 0 °C (ice bath). After 5 min, the cooling bath was removed, and the colorless suspension was stirred at ambient temperature for 24 h. The supernatant was removed using a PE filter cannula, the solid was washed with Et_2O (2 × 15 mL) and very briefly dried *in vacuo*.*[1]

Yield: 945 mg (3.67 mmol, 81%), colorless solid. The compound is air- and moisture stable.

^{1}H NMR (500 MHz, 298 K, DMSO-d_6): δ = 8.42 (d, $^3J_{HH}$ = 7.65 Hz, 1H, *H*-3), 8.20 (s, 1H, *H*-1), 7.81 (d, $^3J_{HH}$ = 7.51 Hz, 1H, *H*-6), 7.77 (ddd, $^3J_{HH}$ = 7.94 Hz + 6.91 Hz, $^4J_{HH}$ = 1.16 Hz, 1H, *H*-5), 7.66 (ddd, $^3J_{HH}$ = 7.62 Hz + 7.04 Hz, $^4J_{HH}$ = 1.39 Hz, 1H, *H*-4), 7.56-7.59 (m, 2H, *H*-9), 7.38-7.43 (m, 2H, *H*-10), 7.20-7.24 (m, 1H, *H*-11), 5.12 (br s, 2H, B-O*H* + N-*H*) ppm. **^{11}B{^{1}H} NMR** (160 MHz, 298 K, DMSO-d_6) δ = 28.1 (br s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, 298 K, DMSO-d_6) δ = 146.3 (C_q^N-8), 139.2 (*C*-1), 135.0 (C_q-2), 131.7 (*C*-3), 131.5 (*C*-5), 129.8 (br, C_q^B-7), 129.0 (*C*-4), 128.2 (*C*-10), 127.0 (*C*-6), 124.9 (*C*-11), 124.6 (*C*-9) ppm.

*[1] Longer periods of drying *in vacuo* or a vacuum desiccator (orange gel) can lead to the removal of gaseous HCl and recovery of **1OH**.

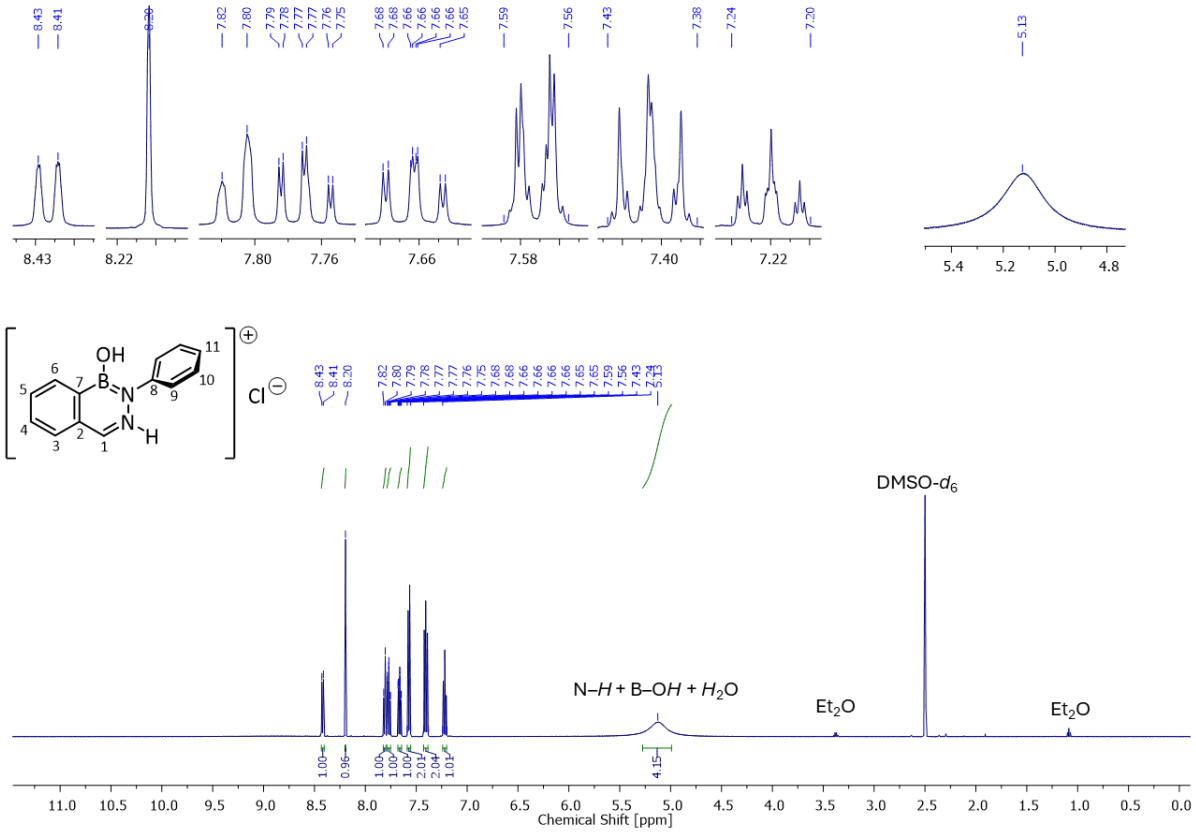


Figure S1. ^{1}H NMR spectrum of compound **[1OH]·HCl** in DMSO-d_6. The N–*H* and B–O*H* resonances are shifted to 5.13 ppm due to a dynamic exchange with water from the deuterated solvent and detected as one broad singlet.

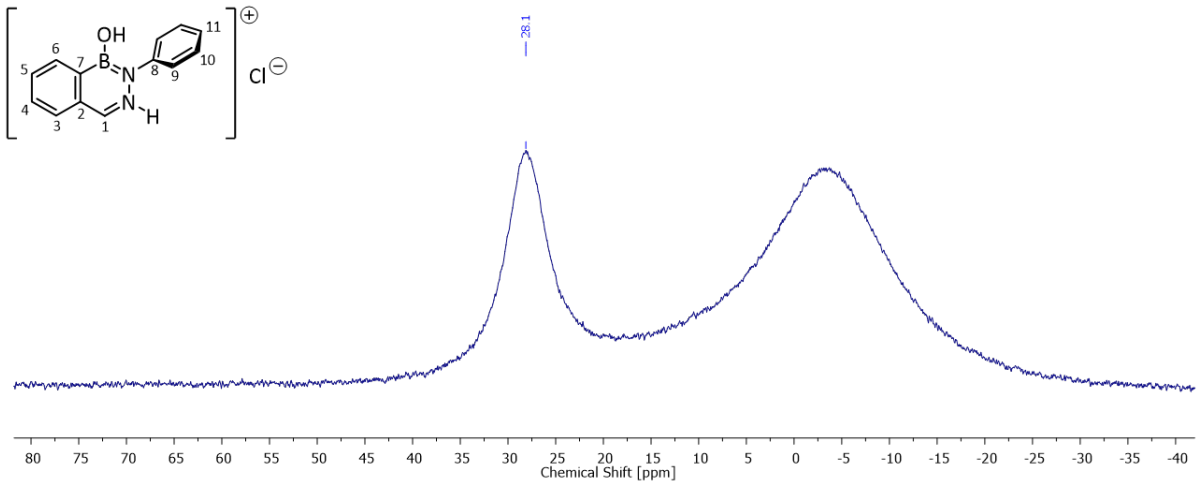


Figure S2. Background-reduced ^{11}B{^{1}H} NMR spectrum of compound **[1OH]·HCl** in DMSO-d_6.

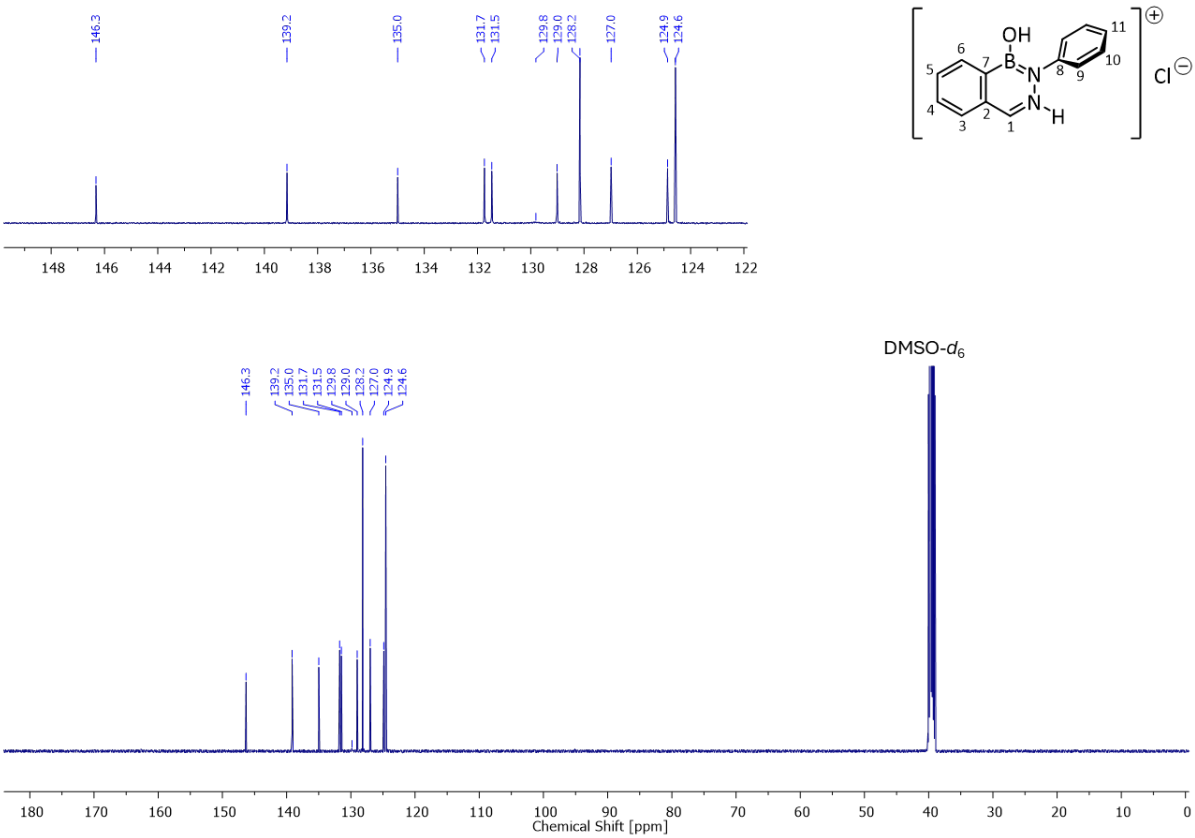
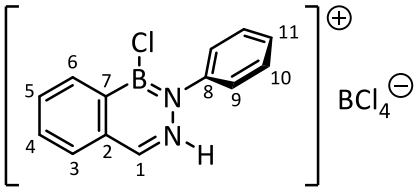


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of compound **[1OH]·HCl** in DMSO-d_6.

Compound [1Cl]·H[BCl_4]



[1Cl] H[BCl_4] (59%)

Compound [**1OH]·HCl** (2.00 g, 9.01 mmol, 1.00 equiv.) was partially dissolved in CH_2Cl_2 (50 mL) in a 250 mL Schlenk tube. BCl3 (4.00 M solution in CH_2Cl_2, 4.50 mL, 18.0 mmol, 2.00 equiv.) was added slowly at 0 °C (ice bath). After 5 min, the cooling bath was removed, and the beige suspension was stirred at ambient temperature for 2 d. After 1 h, a slight clearing of the suspension was observed. After 2 d, the supernatant was removed using a PE filter cannula, the solid was washed with CH_2Cl_2 (2 × 10 mL) and discarded. All volatile components of the filtrate were removed *in vacuo*.

Yield: 1.81 mg (4.59 mmol, 59%), colorless solid. The compound is air- and moisture sensitive.

^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 15.0 (br s, 1H, N–*H*)*[2], 8.44 (s, 1H, *H*-1), 8.40 (d, $^3J_{HH}$ = 7.75 Hz, 1H, *H*-3), 7.96-8.00 (m, 2H, *H*-5 + *H*-6), 7.91-7.96 (m, 1H, *H*-4), 7.53-7.57 (m, 2H, *H*-9), 7.47-7.51 (m, 3H, *H*-10 + *H*-11) ppm. **^{11}B-NMR** (160 MHz, 298 K, CD_2Cl_2) δ = 34.3 (br s, endo-*B*), 6.9 (s, *B*Cl_4^-) ppm. **^{13}C{^{1}H} NMR** (151 MHz, 298 K, CD_2Cl_2) δ = 143.6 (C_q^N-8), 143.5 (*C*-1), 133.6 (*C*-5), 133.3 (*C*-3), 132.6 (*C*-4), 131.9 (C_q-2), 129.3 (*C*-6 + *C*-9), 128.6 (*C*-11), 127.2 (*C*-10) ppm.*[3]

*[2] Integrates to only 0.3 H due to dynamic solvent effects and signal broadness.
*[3] Atom C_q^B-7 was not detected due to the quadrupolar broadening of the boron nucleus.

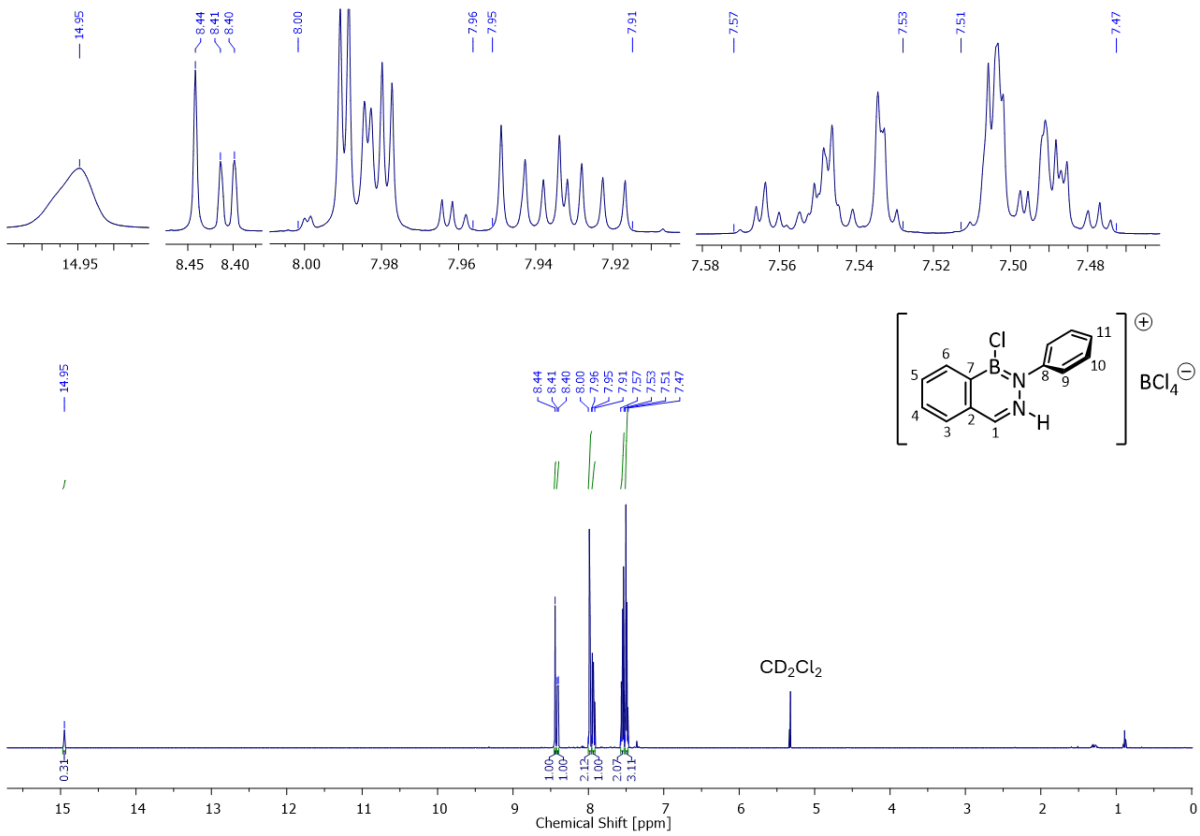


Figure S4. ^{1}H NMR spectrum of compound **[1Cl]·H[BCl$_4$]** in CD_2Cl_2.

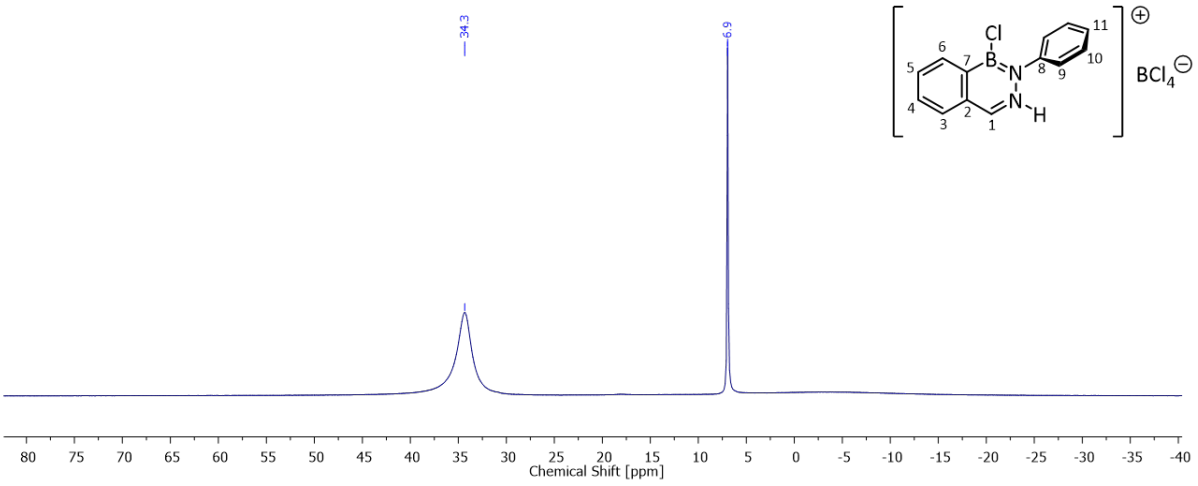


Figure S5. Background-reduced ^{11}B{^{1}H} NMR spectrum of compound **[1Cl]·H[BCl$_4$]** in CD_2Cl_2.

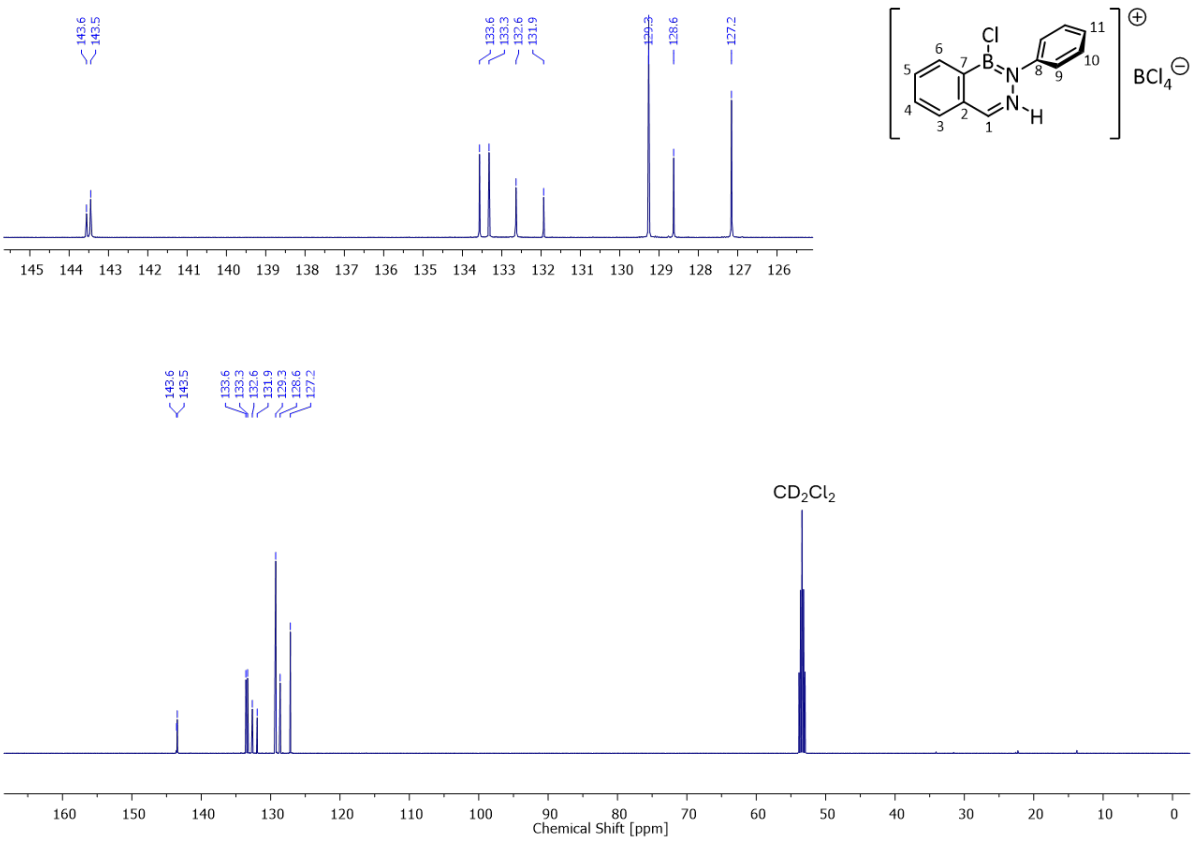
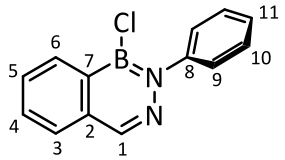


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound **[1Cl]·H[BCl₄]** in CD_2Cl_2.

Compound 1Cl



1Cl (*in situ*)

Compound **[1Cl]·H[BCl$_4$]** (30.0 mg, 76.1 μmol, 1.00 equiv.) was suspended in C_6H_6 (0.5 mL) in a Young NMR tube and K[HMDS] (15.9 mg, 79.9 μmol, 1.05 equiv.) was added at ambient temperature in a glovebox. The reaction suspension was sonicated for 20 min and then filtered in a glove box, using a glass pipet equipped with a glass fibre filter. The filter cake was extracted with C_6H_6 (2 × 0.5 mL) and then discarded. All volatile components of the filtrate were removed *in vacuo* at 50 °C on a Schlenk line for 30 min. The remaining solid was redissolved in benzene-d_6 for analysis via ^{1}H, ^{11}B and ^{13}C{^{1}H} NMR spectroscopy and HRMS.

^{1}H NMR (400 MHz, 298 K, C_6D_6): δ = 8.26-8.31 (m, 1H, *H*-3), 8.13 (s, 1H, *H*-1), 7.43-7.48 (m, 2H, *H*-9), 7.21-7.29 (m, 2H, *H*-4 + *H*-5), 7.12-7.19 (m, *H*-10 + *H*-6)*[4], 7.04 (tt, $^3J_{HH}$ = 7.44 Hz, $^4J_{HH}$ = 1.22 Hz, 1H, *H*-11) ppm. **^{11}B NMR** (129 MHz, 298 K, C_6D_6): δ = 34.1 (br s) ppm. **^{13}C{^{1}H} NMR** (101 MHz, 298 K, C_6D_6) δ = 146.8 (C_q^N-8), 143.1 (*C*-1), 133.7 (C_q-2), 133.3 (*C*-3), 132.5 (*C*-5), 130.1 (*C*-4), 128.8 (*C*-10), 127.3 (*C*-11 + *C*-6), 127.2 (*C*-9) ppm.*[5] **HRMS** (LIFDI, CH_2Cl_2): expected: *m/z* 239.0656, 240.0620, 242.0591 $[C_{13}H_{10}BClN_2]^+$, found: *m/z* 239.0652, 240.0615, 242.0585 $[C_{13}H_{10}BClN_2]^+$. Crystalline material of **1Cl** as colorless blocks for XRD analysis were obtained by slow evaporation of a saturated *n*-pentane solution at −30 °C in a glove box.

*[4] No integral due to overlap with the C_6D_6 solvent resonance.
*[5] Atom C_q^B-7 was not detected in the ^{13}C{^{1}H} NMR spectrum due to the quadrupolar broadening caused by the boron nucleus.

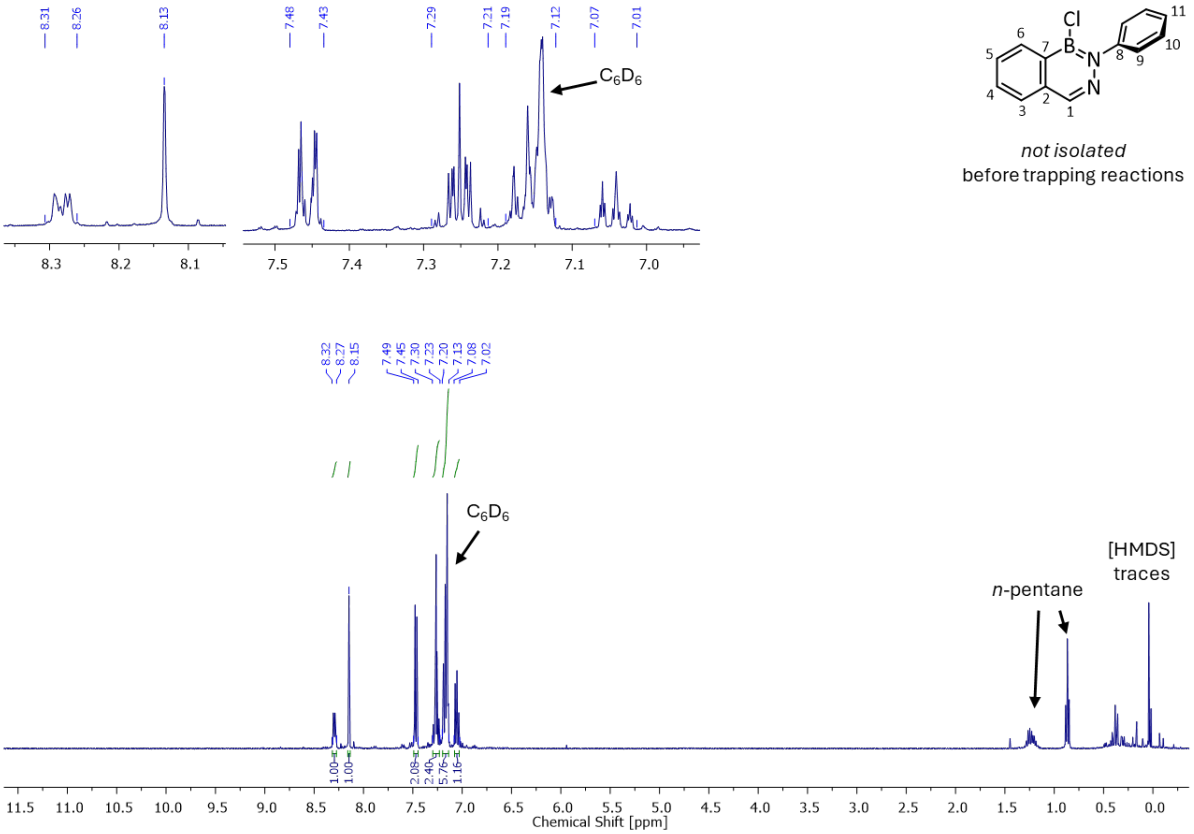


Figure S7. ^{1}H NMR spectrum of compound **1Cl** in benzene-d_6.

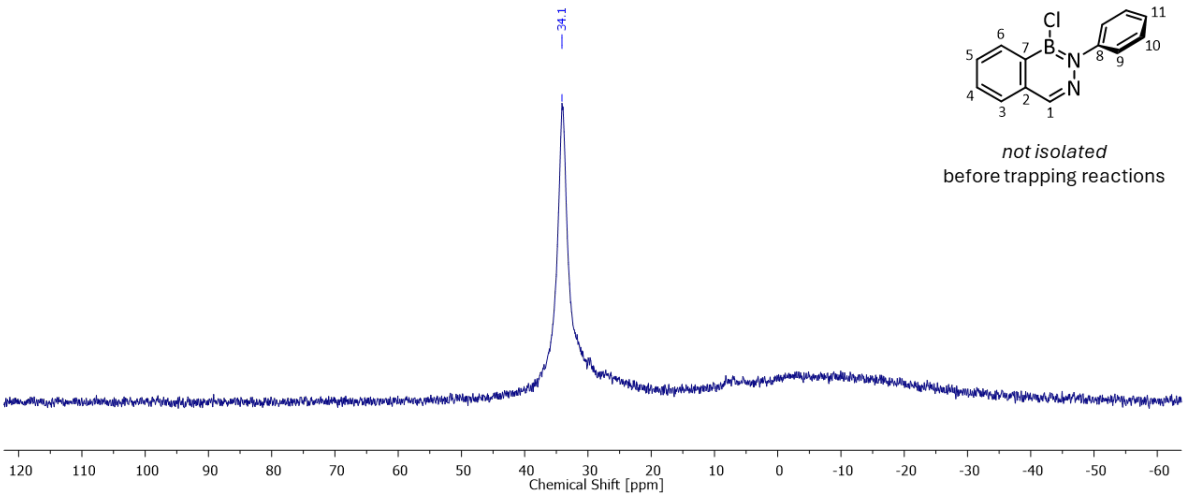


Figure S8. Background-reduced ^{11}B{^{1}H} NMR spectrum of compound **1Cl** in benzene-d_6.

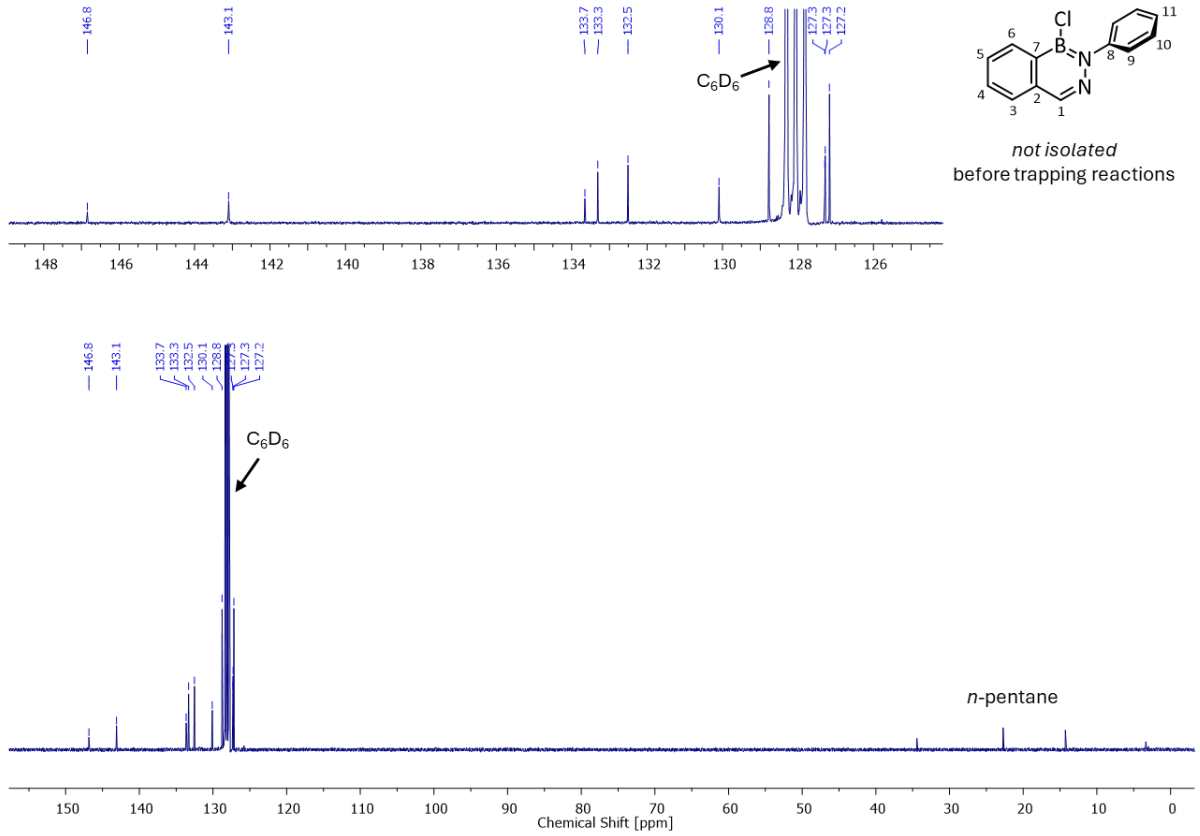


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1Cl** in benzene-d_6.

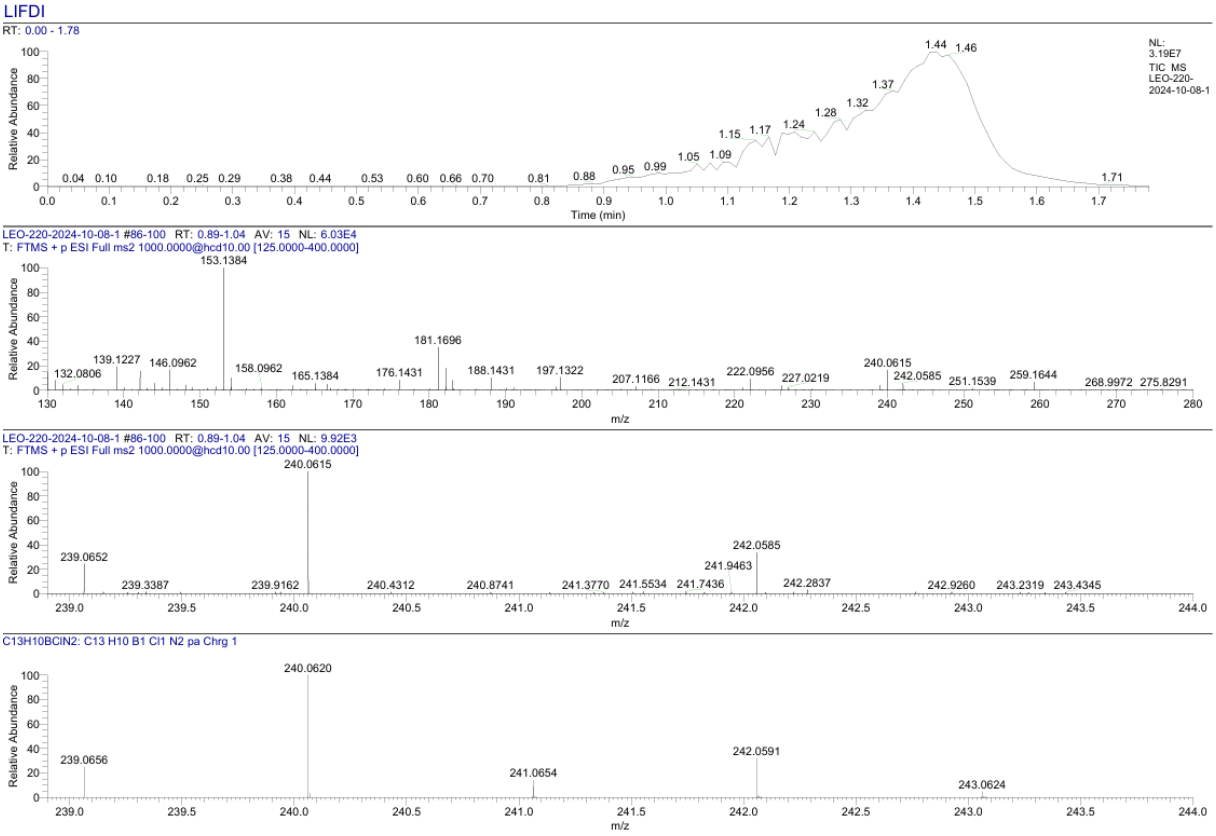


Figure S10. LIFDI mass spectrum of compound **1Cl** (CH_2Cl_2).

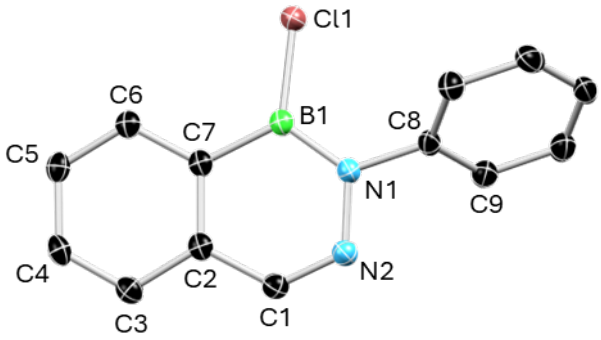
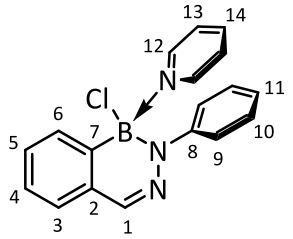


Figure S11. Molecular structure of compound **1Cl**. Ellipsoids drawn at 50% probability. All hydrogen atoms omitted. Selected bond lengths (Å) and angles (°) of **1Cl**: B1–Cl1 1.7822(13), B1–N1 1.4146(16), N1–N2 1.3928(14), N2–C1 1.2945(15), C1–C2 1.4416(16), C2–C3 1.4043(16), C3–C4 1.3799(17), C4–C5 1.3988(17), C5–C6 1.3844(16), C6–C7 1.4038(16), C2–C7 1.4060(16), C7–B1 1.5268(16), N1–C8 1.4381(14), C7–B1–Cl1 121.95(9), Cl1–B1–N1 120.26(9), N1–B1–C7 117.73(10), B1–N1–N2–C1 1.89(15), B1–C7–C2–C1 0.34(14), N2–N1–C8–C9 61.42(15).

Crystal data: $C_{13}H_{10}BClN_2$, M_r = 240.49, clear colorless plate, 0.320×0.200×0.050 mm^3, monoclinic space group $P2_1/c$, a = 9.60800(10) Å, b = 6.84400(10) Å, c = 17.5242(2) Å, β = 95.1530(10)°, V = 1147.68(2) Å^3, Z = 4, ρ_{calcd} = 1.392 g·cm^{-3}, μ = 2.719 mm^{-1}, $F(000)$ = 496, T = 100(2) K, R_1 = 0.0267, wR_2 = 0.0816, 2287 independent reflections [$2\theta \leq 147.83°$] and 154 parameters.

CCDC number: 2531213

Compound 1Cl←py



1Cl **py** (70%)

Compound **[1Cl]·H[BCl$_4$]** (25.0 mg, 63.4 μmol, 1.00 equiv.) was suspended in C_6H_6 (0.5 mL) in a Young NMR tube and LiTMP (4.67 mg, 31.7 μmol, 0.50 equiv.) was added at ambient temperature in a glovebox. The reaction suspension was sonicated for 20 min and then filtered in a glove box, using a glass pipet equipped with a glass fibre filter. The filter cake was extracted with C_6H_6 (2 × 0.5 mL) and then discarded. All volatile components of the filtrate were removed *in vacuo* at 50 °C on a Schlenk line for 30 min. The remaining solid was redissolved in *n*-pentane (0.5 mL) and pyridine (3 drops, xs.) was added at ambient temperature in a glovebox, which resulted in the immediate formation of a deep yellow solid. The suspension was filtered and the solid was washed with *n*-pentane (3 × 0.5 mL) and dried by slow evaporation of *n*-pentane traces at ambient temperature in a glovebox.

Yield: 14.2 mg (44.4 μmol, 70%), deep red solid. The compound is air- and moisture sensitive.

^{1}H-NMR (600 MHz, 233 K, CD_2Cl_2): δ = 8.99 (br s, 2H, *H*-12), 8.10 (br t, $^3J_{HH}$ = 9.29 Hz, 1H, *H*-14), 7.73 (s, 1H, *H*-1), 7.68 (br t, $^3J_{HH}$ = 6.27 Hz, 2H, *H*-13), 7.29-7.38 (m, 6H, *H*-9 + *H*-3 + *H*-4 + *H*-5 + *H*-6), 7.13-7.17 (m, 2H, *H*-10), 6.88 (t, $^3J_{HH}$ = 7.24 Hz, 1H, *H*-11) ppm. **^{11}B{^{1}H} NMR** (160 MHz, 222 K, CD_2Cl_2): δ = 7.9 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 233 K, CD_2Cl_2) δ = 147.4 (C_q-8), 145.3 (*C*-12), 141.9 (*C*-14), 137.1 (C_q^B-7), 136.7 (*C*-1), 130.7 (*C*-3 or *C*-4 or *C*-5), 129.6 (C_q-2), 128.4 (*C*-3 or *C*-4 or *C*-5), 128.2 (*C*-9), 126.2 (*C*-13), 125.2 (*C*-3), 121.3 (*C*-3 or *C*-4 or *C*-5), 119.5 (*C*-11) ppm. *Note: NMR spectra were recorded at 233 K, where the equilibrium is completely shifted to the adduct. The temperature of 233 K for 2D NMR data collection was chosen, as spectra at lower temperatures showed the formation of a second species in trace amounts, which is presumed to be the adduct of compound **1Cl** with itself via the Nβ position.* Attempts to characterize **1Cl←py** using HRMS method only resulted in the detection of **1Cl** or its hydrolysis products due to the labile nature of the adduct during ionization. Crystalline material of **1Cl←py** as yellow blocks for XRD analysis were obtained by slow evaporation of a saturated benzene solution at ambient temperature in a glovebox.

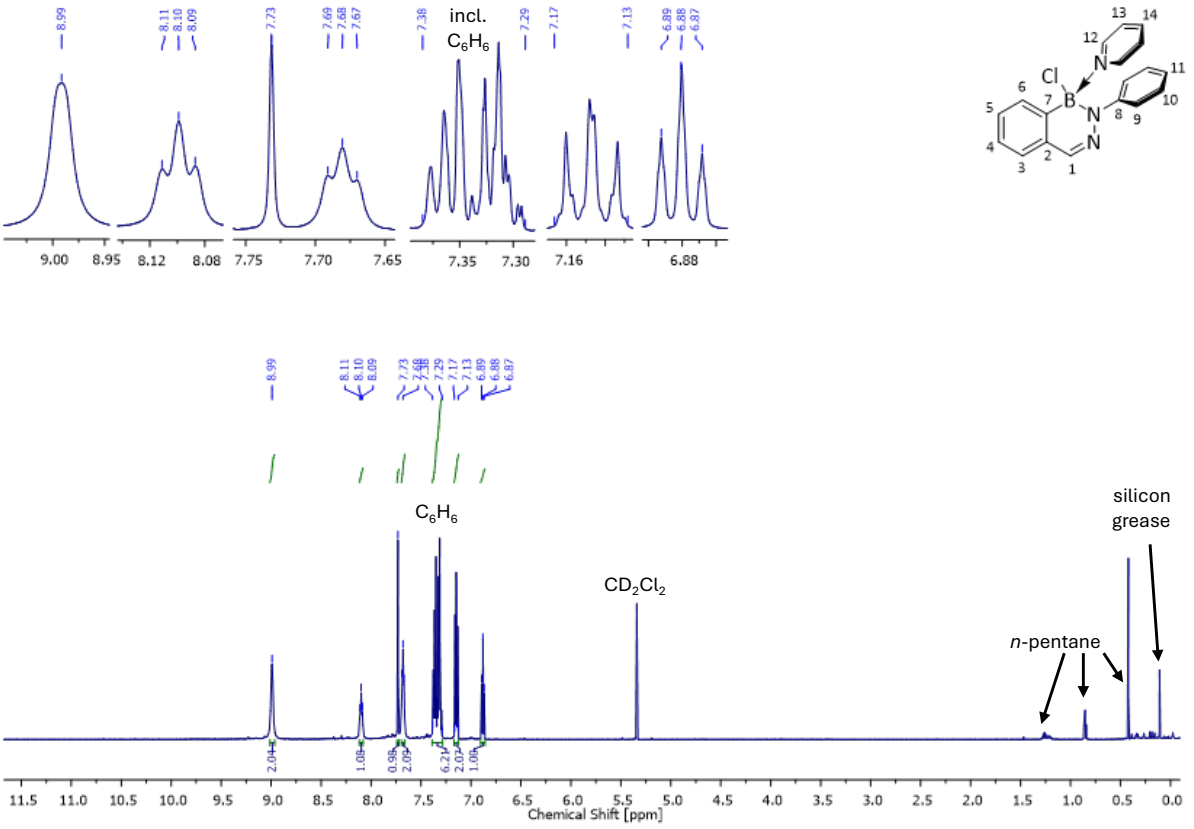


Figure S12. ^{1}H NMR spectrum of compound **1Cl←py** in CD_2Cl_2 (at 233 K).

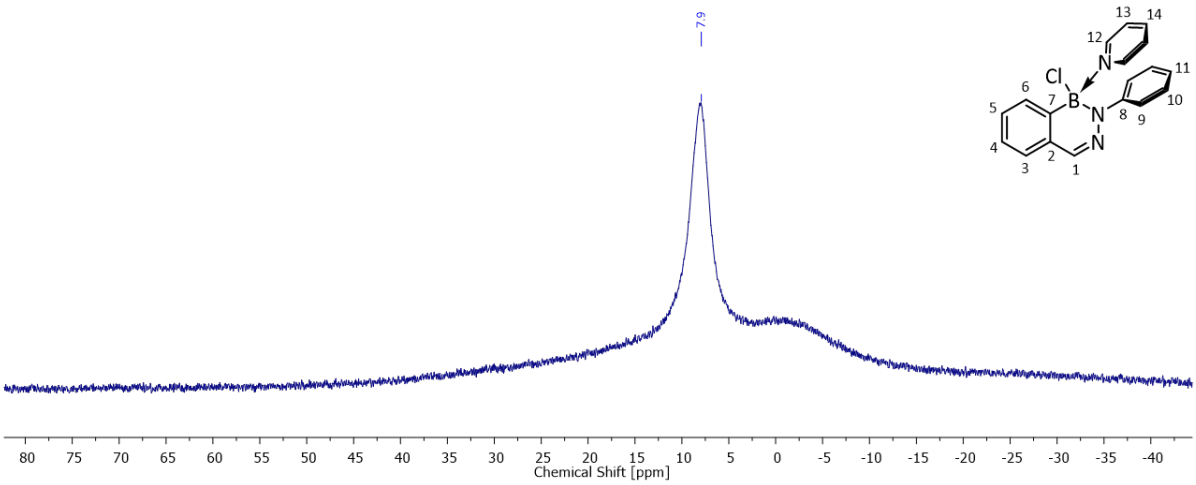


Figure S13. Background-reduced ^{11}B{^{1}H} NMR spectrum of compound **1Cl←py** in CD_2Cl_2 (at 233 K).

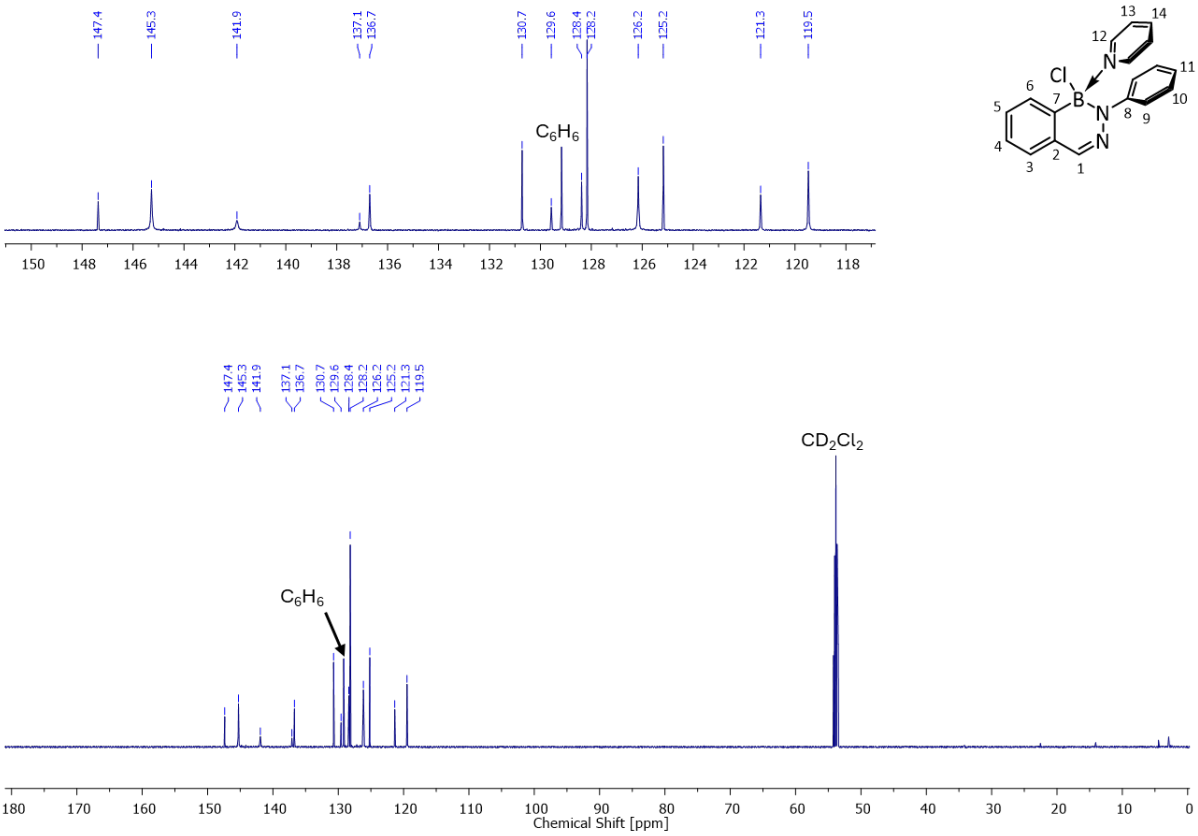


Figure S14. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **1Cl←py** in CD_2Cl_2 (at 233 K, ^{11}B decoupled at 8 ppm).

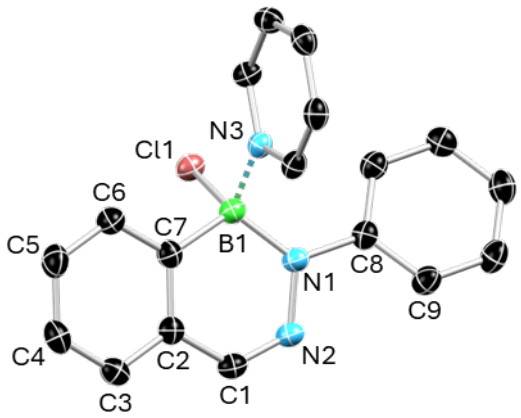


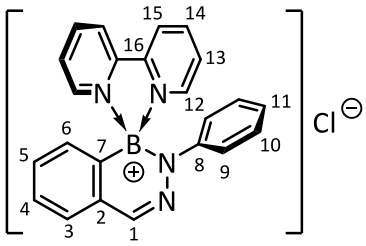
Figure S15. Molecular structure of compound **1Cl←py**. Ellipsoids drawn at 50% probability. All hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): B1–Cl1 1.9442(14), B1–N1, 1.5035(16), B1–N3 1.6163(16), N1–N2 1.3830(14), N2–C1 1.2916(16), C1–C2 1.4494(17), C2–C3 1.4081(17), C3–C4 1.3788(18), C4–C5 1.394(2), C5–C6 1.3867(18), C6–C7 1.3975(17), C2–C7 1.3993(17), C7–B1 1.5830(17), N1–C8 1.4204(15), B1–N1–N2–C1 12.12(17), N2–N1–C8–C9 27.01(15).

Crystal data: $C_{18}H_{15}BClN_3$, M_r = 319.59, yellow block, 0.350×0.180×0.150 mm^3, monoclinic space group $P2_1/n$, a = 11.6844(9) Å, b = 11.7017(17) Å, c = 11.9578(9) Å, β = 105.719(6)°, V = 1573.8(3) Å^3, Z = 4, ρ_{calcd} = 1.349 g·cm^{-3}, μ = 2.142 mm^{-1}, $F(000)$ = 664, T = 100(2) K, R_1 = 0.0293, wR_2 = 0.0761, 3194 independent reflections [$2\theta \leq 151.24°$] and 227 parameters.

Whole-molecule disorder was present (2% only). The geometry of residue 4 (a minor component of the disorder) was constrained during refinement using the AFIX 6 command. Rotation of the aromatic groups was permitted, while the distance between the rings was restrained using the DFIX command and 1–3 distances with SADI. U_{iso} parameters were constrained to the same value and their value was estimated using similarity restraint SIMU with small esd value.

CCDC number: 2531215

Compound [1bpy]Cl



[1bpy]Cl (57%)

Compound **[1Cl]·H[BCl$_4$]** (30.0 mg, 76.1 μmol, 1.00 equiv.) was suspended in C_6H_6 (0.5 mL) in a Young NMR tube and K[HMDS] (15.9 mg, 79.9 μmol, 1.05 equiv.) was added at ambient temperature in a glovebox. The reaction suspension was sonicated for 10 min and then filtered in a glove box, using a glass pipet equipped with a glass fibre filter. The filter cake was extracted with C_6H_6 (2 × 0.5 mL) and then discarded. All volatile components of the filtrate were removed *in vacuo* at 50 °C on a Schlenk line for 30 min. The remaining oil was redissolved in C_6H_6 (0.5 mL) and 2,2'-bipyridine (11.9 mg, 76.1 μmol, 1.00 equiv.) was added at ambient temperature in a glovebox, which resulted in the immediate formation of an orange solid. The suspension was filtered and the solid was washed with C_6H_6 (2 × 1.0 mL) and *n*-pentane (1 × 1.0 mL) and dried briefly *in vacuo*.

Yield: 17.3 mg (43.6 μmol, 57%), orange solid. The compound is air- and moisture sensitive.

^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 10.73 (ddd, $^3J_{HH}$ = 8.11 Hz, $^4J_{HH}$ = 0.95 Hz; 0.95 Hz, 2H, *H*-12), 8.70 (ddd, $^3J_{HH}$ = 7.90 Hz + 7.90 Hz, $^4J_{HH}$ = 1.43 Hz, 2H, *H*-13), 8.33 (ddd, $^3J_{HH}$ = 5.63 Hz, $^4J_{HH}$ = 1.33 Hz + 0.88 Hz, 2H, *H*-15), 7.90 (d, $^4J_{HH}$ = 0.62 Hz, 1H, *H*-1), 7.89 (ddd, $^3J_{HH}$ = 7.67 Hz + 5.63 Hz, $^4J_{HH}$ = 1.09 Hz, 2H, *H*-14), 7.56 (d, $^3J_{HH}$ = 7.75 Hz, 1H, *H*-6), 7.49 (ddd, $^3J_{HH}$ = 7.70 Hz + 7.32 Hz, $^4J_{HH}$ = 1.15 Hz, 1H, *H*-5), 7.20 (ddd, $^3J_{HH}$ = 7.41 Hz + 7.41 Hz, $^4J_{HH}$ = 1.23 Hz, 1H, *H*-4), 6.99-7.03 (m, 2H, *H*-10), 6.86 (tt, $^3J_{HH}$ = 7.33 Hz, $^4J_{HH}$ = 1.17 Hz, 1H, *H*-11), 6.55-6.58 (m, 2H, *H*-9), 6.51 (d, $^3J_{HH}$ = 7.52 Hz, 1H, *H*-3) ppm. **^{11}B{^{1}H} NMR** (160 MHz, 298 K, CD_2Cl_2): δ = 6.8 (br s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, 298 K, CD_2Cl_2) δ = 147.9 (C_q^N-8), 146.9 (*C*-13), 145.1 (C_q^N-16), 143.8 (*C*-15), 137.1 (*C*-1), 131.5 (br, C_q^B-7)*[6], 131.1 (C_q-2), 130.5 (*C*-5), 130.3 (*C*-4), 129.8 (*C*-3), 129.5 (*C*-10), 129.5 (*C*-14), 127.7 (*C*-12), 127.0 (*C*-6), 123.9 (*C*-11), 120.6 (*C*-9) ppm. **HRMS** (LIFDI, CH_2Cl_2): expected: *m/z* 360.1655, 361.1619, 362.1653, 363.1686 $[C_{23}H_{18}BClN_4]^+$, found: *m/z* 360.1642, 361.1605, 362.1638, 363.1670 $[C_{23}H_{18}BClN_4]^+$. Crystalline material of **[1bpy]Cl** as

*[6] Not detected in the ^{13}C{^{1}H} NMR spectrum due to the quadrupolar broadening caused by the boron nucleus. Assigned *via* ^{1}H^{13}C HMBC NMR spectrum.

orange plates for XRD analysis was obtained by slow evaporation (silicon grease absorption) of a saturated dichloromethane solution at ambient temperature in a glovebox.

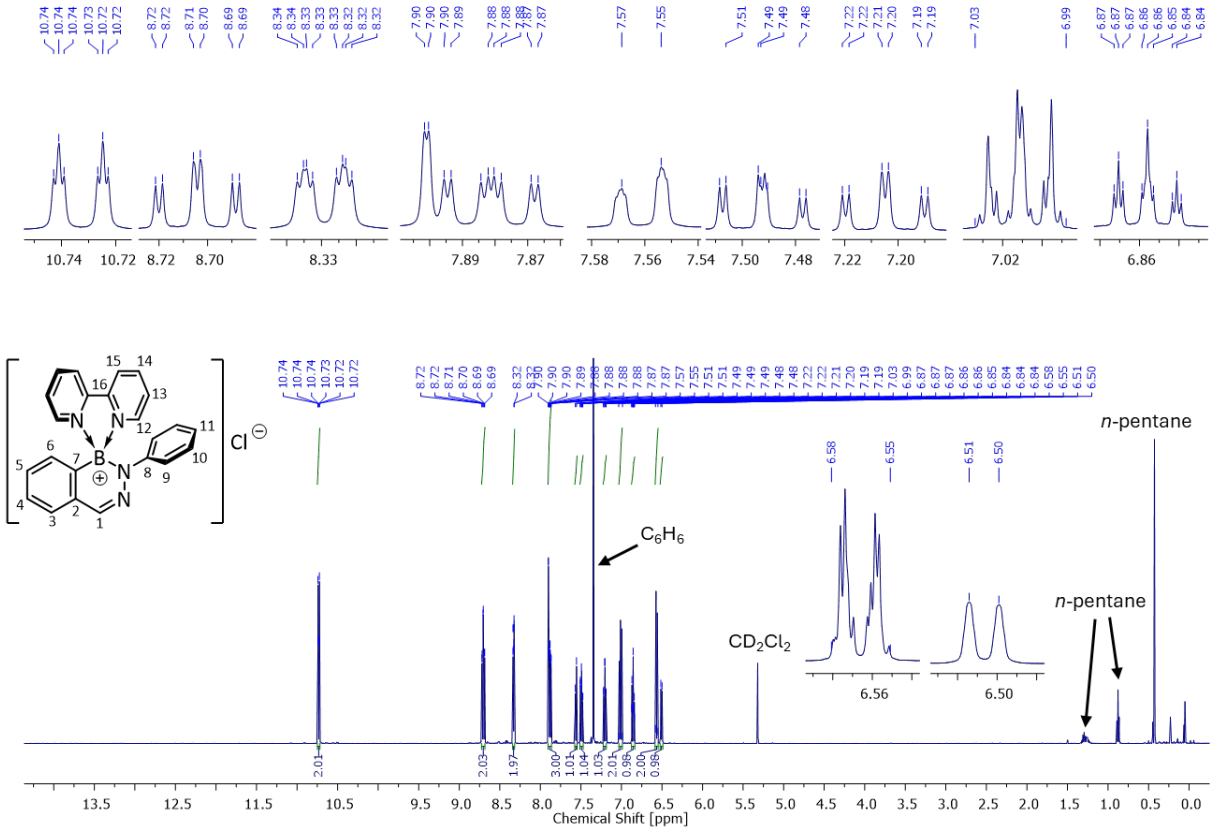


Figure S16. ^{1}H NMR spectrum of compound **[1bpy]Cl** in CD_2Cl_2.

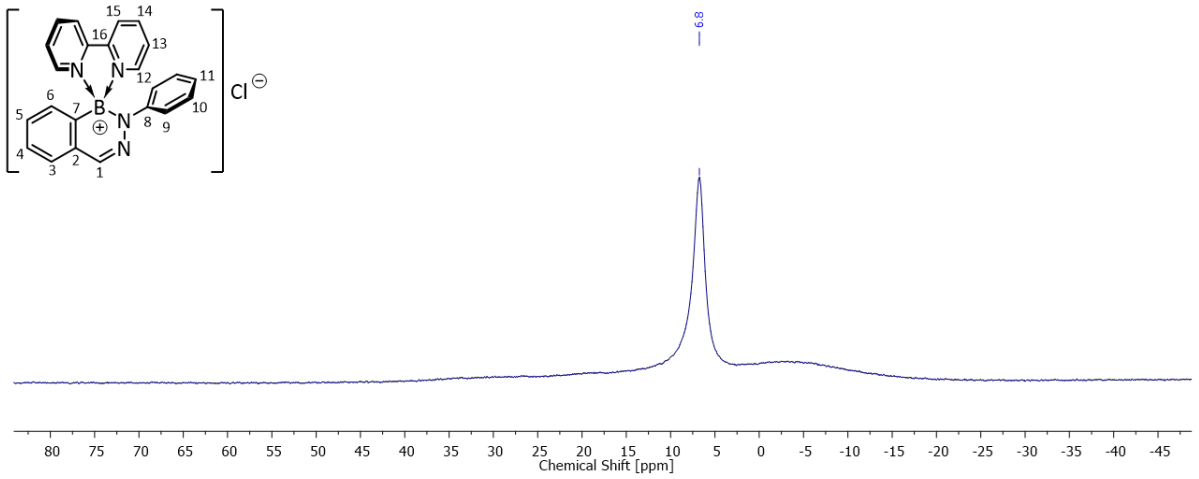


Figure S17. Background-reduced $^{11}B\{^{1}H\}$ NMR spectrum of compound **[1bpy]Cl** in CD_2Cl_2.

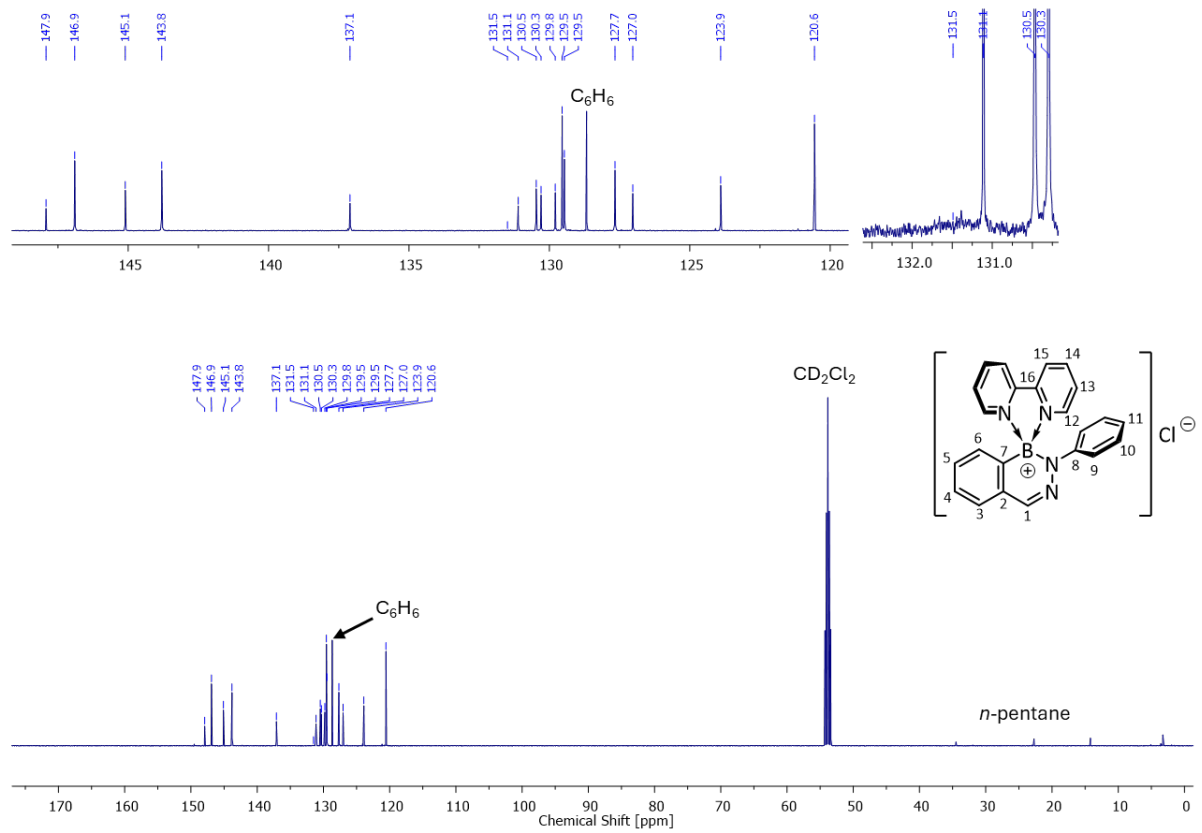


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of compound **[1bpy]Cl** in CD_2Cl_2.

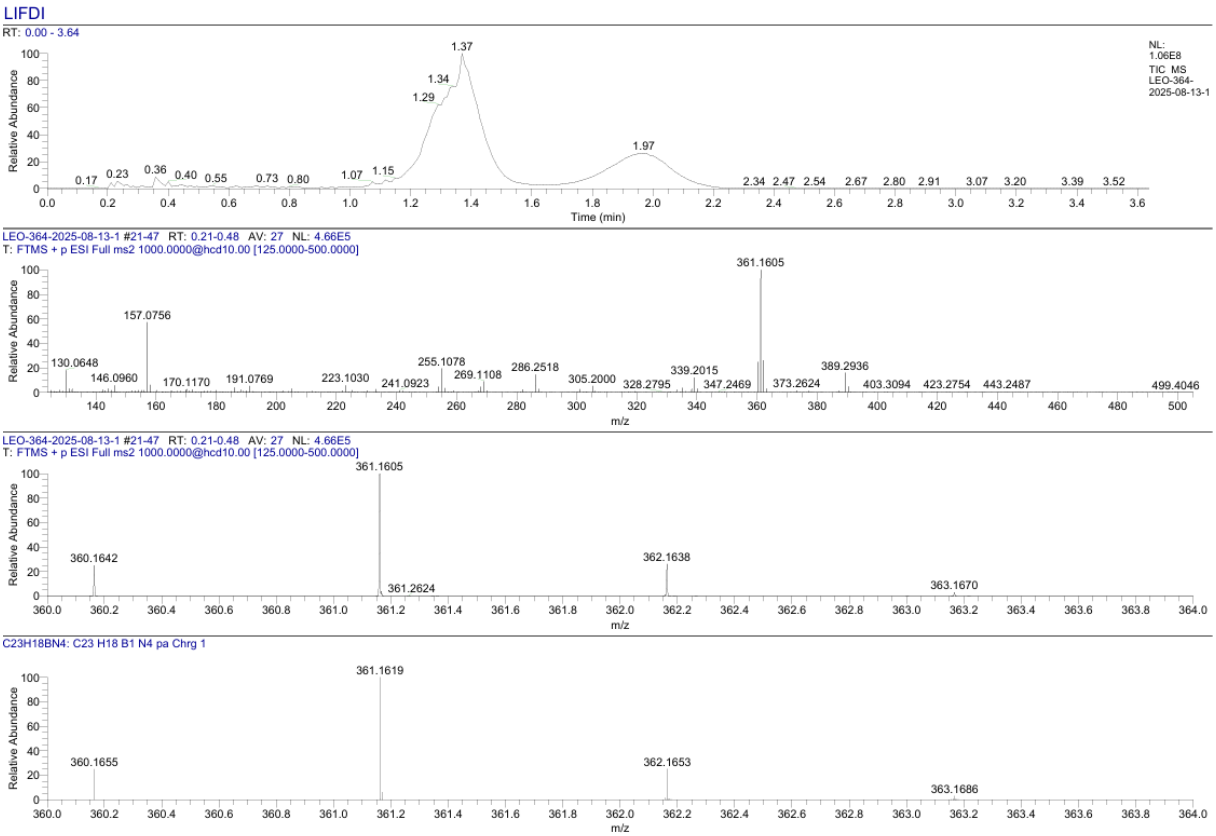


Figure S19. LIFDI mass spectrum of compound **[1bpy]Cl** (dichloromethane).

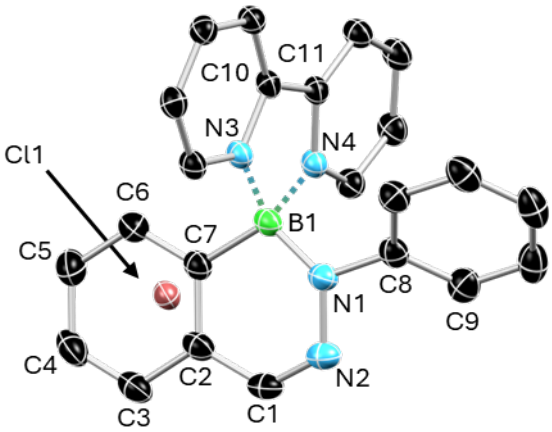


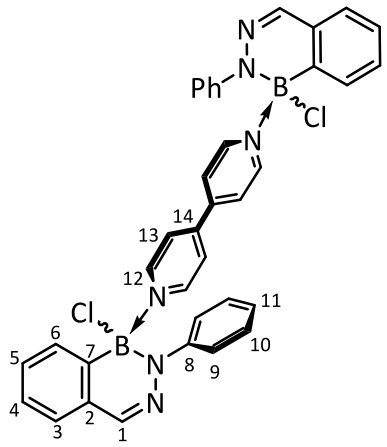
Figure S20. Molecular structure of compound **[1bpy]Cl**. Ellipsoids drawn at 50% probability. All hydrogen atoms except for the borinic acid omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.501(3), B1–N3 1.600(3), B1–N4 1.620(3), N1–N2 1.382(3), N2–C1 1.293(3), C1–C2 1.447(3), C2–C3 1.405(3), C3–C4 1.371(4), C4–C5 1.398(4), C5–C6 1.390(3), C6–C7 1.394(3), C2–C7 1.403(3), N1–C8 1.432(3), B1–C7 1.580(3), B1–N1–N2–C1 13.4(3), N2–N1–C8–C9 140.9(2).

Crystal data: $C_{26}H_{21}BClN_4$, M_r = 435.73, intense orange plate, 0.210×0.150×0.040 mm^3, monoclinic space group *C*2/*c*, *a* = 19.169(3) Å, *b* = 17.046(2) Å, *c* = 13.646(2) Å, β = 95.110(10)°, *V* = 4440.9(11) Å^3, *Z* = 8, ρ_{calcd} = 1.303 g·cm^{-3}, μ = 1.680 mm^{-1}, *F*(000) = 1816, *T* = 100(2) K, R_1 = 0.0587, wR_2 = 0.1587, 4473 independent reflections [2$\theta \leq$150.62°] and 269 parameters.

Some reflections were removed from refinement as outliers. Benzene molecule was placed on inversion center. Its geometry was constrained to the idealized one. EADP constraint was applied to all atoms in this residue.

CCDC number: 2531216

Compound 1Cl←bpy→1Cl



1Cl bpy 1Cl (76%)

Compound **[1Cl]·H[BCl$_4$]** (25.0 mg, 63.4 μmol, 1.00 equiv.) was suspended in C_6H_6 (0.5 mL) in a Young NMR tube and LiTMP (4.67 mg, 31.7 μmol, 0.50 equiv.) was added at ambient temperature in a glovebox. The reaction suspension was sonicated for 20 min and then filtered in a glovebox, using a glass pipet equipped with a glass fibre filter. The filter cake was extracted with C_6H_6 (2 × 0.5 mL) and then discarded. All volatile components of the filtrate were removed *in vacuo* at

50 °C on a Schlenk line for 30 min. The remaining solid was redissolved in *n*-pentane (0.5 mL) and 4,4'-bipyridine (4.95 mg, 31.7 μmol, 0.50 equiv.) was added at ambient temperature in a glovebox, which resulted in the immediate formation of a deep red solid. The suspension was filtered and the solid was washed with *n*-pentane (2 × 0.5 mL) and dried briefly *in vacuo*.

Yield: 15.3 mg (24.0 μmol, 76%), deep red solid. The compound is air- and moisture sensitive.

^{1}H NMR (600 MHz, 298 K, CD_2Cl_2): δ = 8.78-8.80 (m, 2H, *H*-12), 8.34 (s, 1H, *H*-1), 8.19 (d, $^{3}J_{HH}$ = 7.58 Hz, 1H, *H*-3), 7.76-7.81 (m, 2H, *H*-5 + *H*-6), 7.71 (ddd, $^{3}J_{HH}$ = 7.67 Hz + 6.64 Hz, $^{4}J_{HH}$ = 1.78 Hz, 1H, *H*-4), 7.60-7.62 (m, 2H, *H*-13), 7.42-7.48 (m, 4H, *H*-9 + *H*-10), 7.32 (tt, $^{3}J_{HH}$ = 7.13 Hz, $^{4}J_{HH}$ = 1.39 Hz, 1H, *H*-11) ppm. **^{11}B NMR** (193 MHz, 298 K, CD_2Cl_2): δ = 29.8 (br s) ppm. **^{13}C{^{1}H} NMR** (151 MHz, 298 K, CD_2Cl_2) δ = 150.3 (C-12), 146.9 (C_q^N-8), 146.3 (C_q-14), 142.4 (*C*-1), 133.6 (br, C_q^B-7), 133.1 (C_q-2), 132.9 (*C*-3), 132.4 (*C*-5), 130.5 (*C*-4), 128.7 (*C*-10), 127.4 (*C*-6), 126.7 (*C*-11), 126.0 (*C*-9), 122.2 (*C*-13) ppm. *Note: NMR spectra were recorded at 298 K, where almost complete dissociation to 0.5 equiv. 4,4'-dipyridyl and **1Cl** can be assumed. Cooling during VT NMR spectroscopic attempts resulted in the quantitative precipitation of **1Cl←bpy→1Cl** at 253 K. The spectra at 298 K only serve as proof of purity and correspond to the dissociated form.* Attempts to characterize **1Cl←bpy→1Cl** using HRMS method only resulted in the detection of free **1Cl** or its hydrolysis products due to the labile nature of the adduct during ionization. Crystalline material of **1Cl←bpy→1Cl** as deep red blocks for XRD analysis was obtained by slow evaporation (silicon grease absorption) of a saturated dichloromethane solution at ambient temperature in a glovebox.

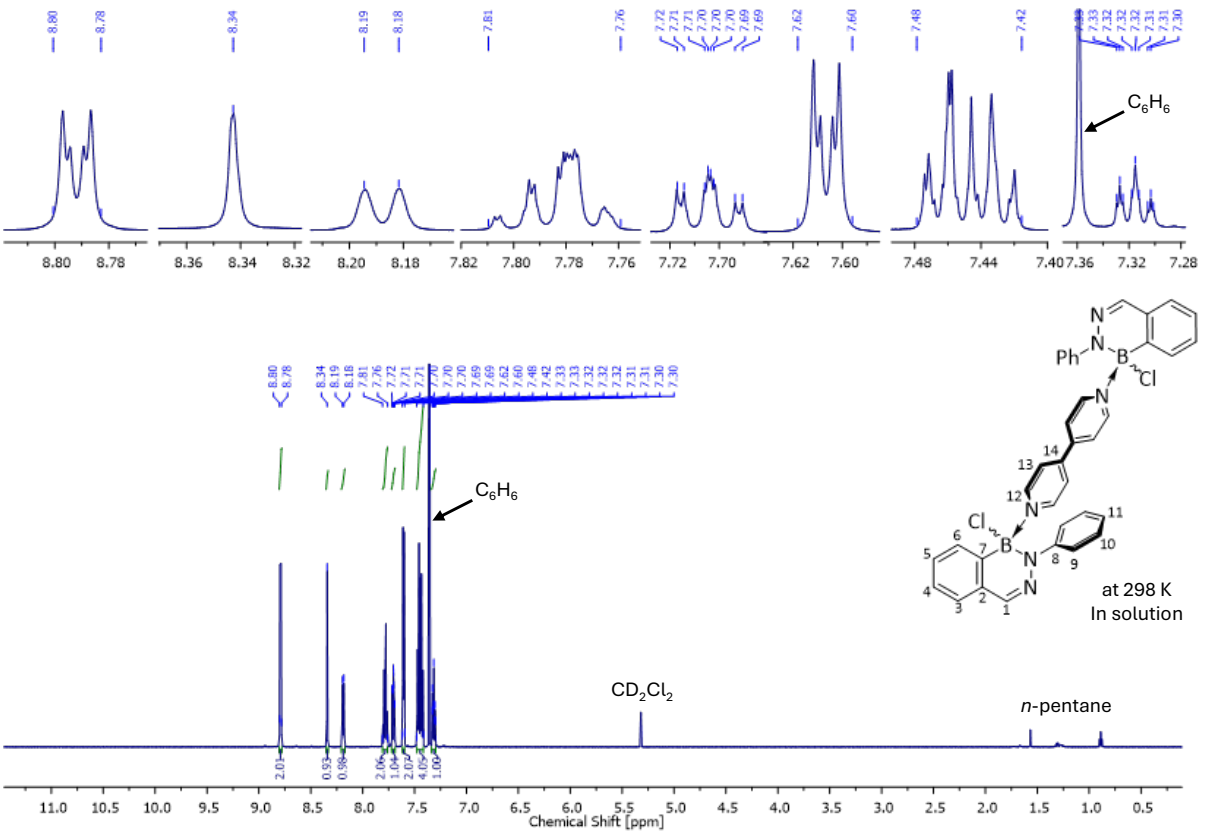


Figure S21. ^{1}H NMR spectrum of compound **1Cl←bpy→1Cl** in CD_2Cl_2.

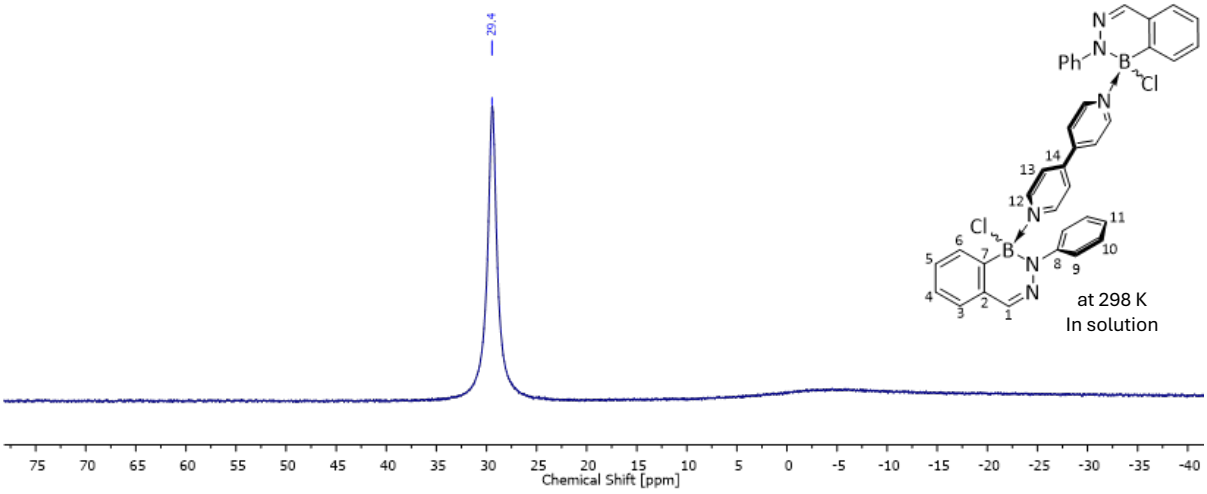


Figure S22. Background-reduced ^{11}B NMR spectrum of compound **1Cl←bpy→1Cl** in CD_2Cl_2.

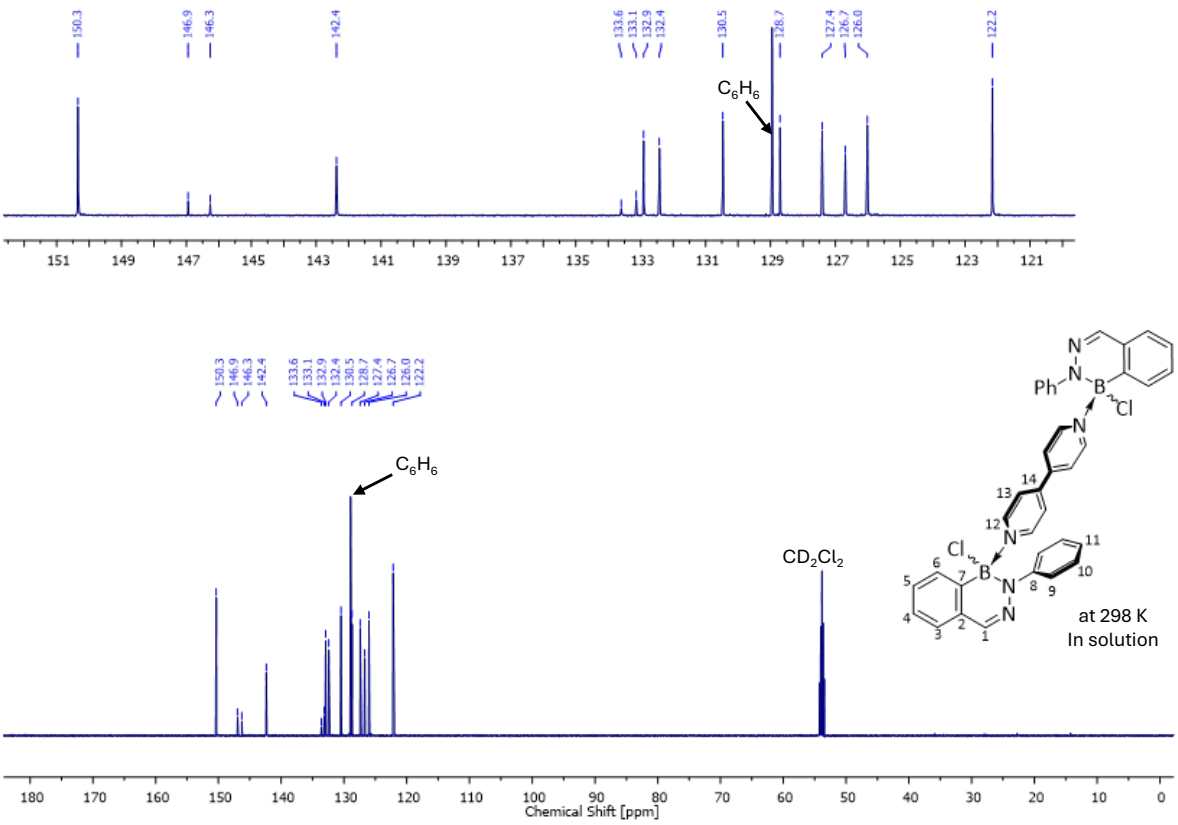


Figure S23. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **1Cl←bpy→1Cl** in CD_2Cl_2 (^{11}B decoupled at 30 ppm).

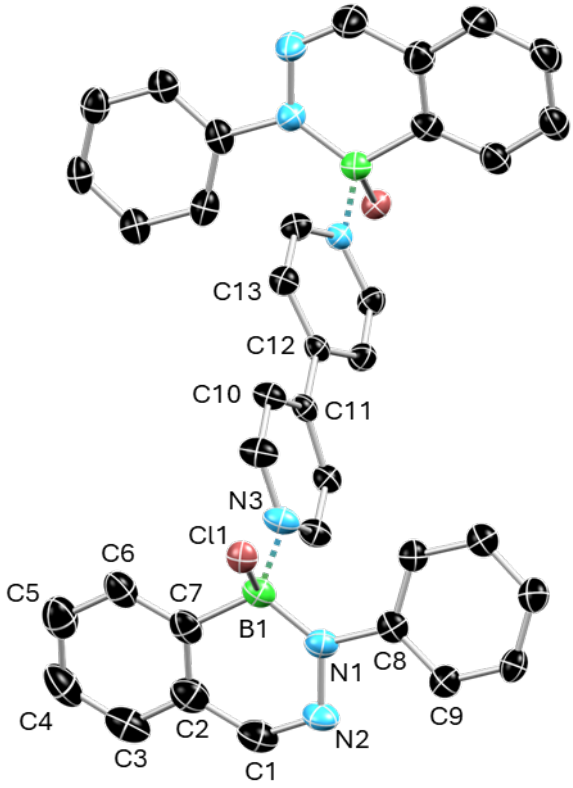


Figure S24. Molecular structure of compound **1Cl←bpy→1Cl**. Ellipsoids drawn at 50% probability. All hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): B1–Cl1 1.914(3), B1–N1 1.505(3), B1–N3 1.640(3), N1–N2 1.382(3), N2–C1 1.288(4), C1–C2 1.443(4), C2–C3 1.418(4), C3–C4 1.375(4), C4–C5 1.388(4), C5–C6 1.385(4), C6–C7 1.387(4), C2–C7 1.388(4), C7–B1 1.601(4), N1–C8 1.435(3), C11–C12 1.482(3), C7–B1–Cl1 109.73(17), Cl1–B1–N1 112.95(18), N1–B1–C7 112.3(2), B1–N1–N2–C1 2.3(4), N2–N1–C8–C9 4.8(3), C10–C11–C12–C13 10.6(3).

Crystal data: $C_{93}H_{80}B_4Cl_4N_{12}$, M_r = 1550.73, red block, 0.460×0.270×0.200 mm^3, monoclinic space group $P2_1/c$, a = 12.8021(8) Å, b = 13.9392(9) Å, c = 21.7034(12) Å, β = 90.015(4)°, V = 3873.0(4) Å^3, Z = 2, ρ_{calcd} = 1.330 g·cm^{-3}, μ = 1.839 mm^{-1}, $F(000)$ = 1620, T = 100(2) K, R_1 = 0.0618, wR_2 = 0.1457, 7838 independent reflections [$2\theta \leq 151.446°$] and 529 parameters.

Whole-molecule disorder was present (2% only). The geometry of residue 4 (a minor component of the disorder) was constrained during refinement using the AFIX 6 command. Rotation of the aromatic groups was permitted, while the distance between the rings was restrained using the DFIX command and 1–3 distances with SADI. U_{iso} parameters were constrained to the same value, and their value was estimated using similarity restraint SIMU with small esd value.

CCDC number: 2531217

3 VT NMR experiments

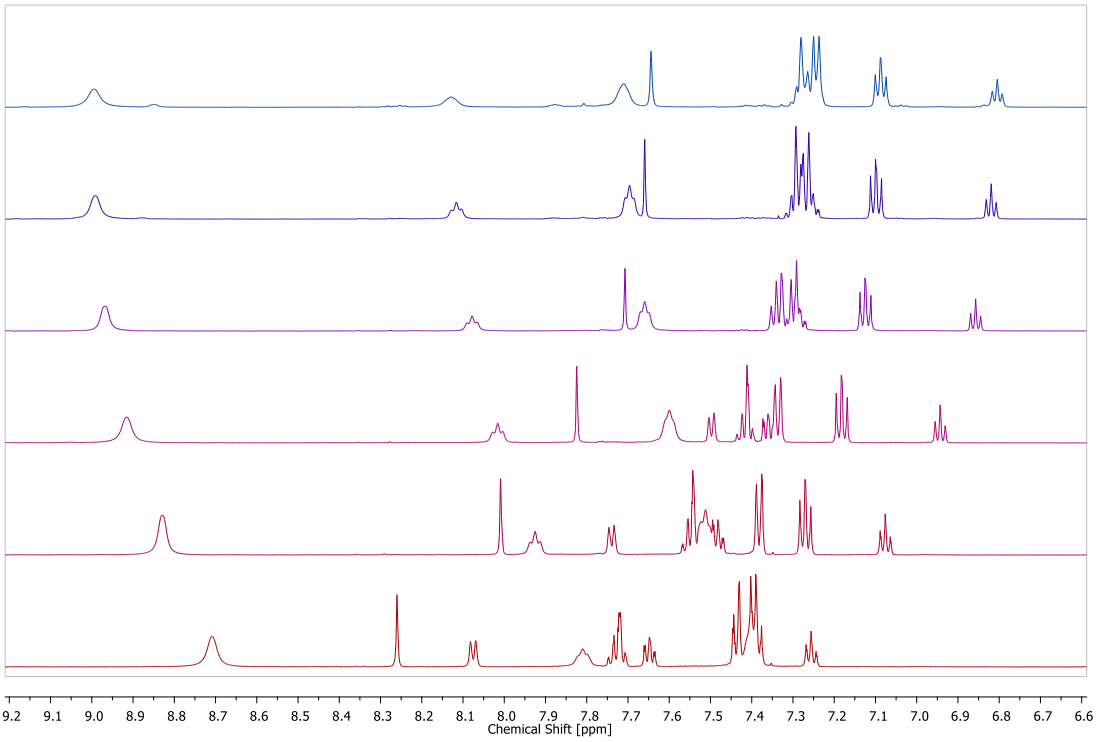


Figure S25. Stacked ^{1}H VT NMR spectra of compound **1Cl←py** (12 mg) in CD_2Cl_2 (0.5 mL) starting at +25 °C (298 K), progressively cooled to 0 °C (273 K), –20 °C (253 K), –40 °C (233 K), –60 °C (213 K) and –80 °C (193 K).

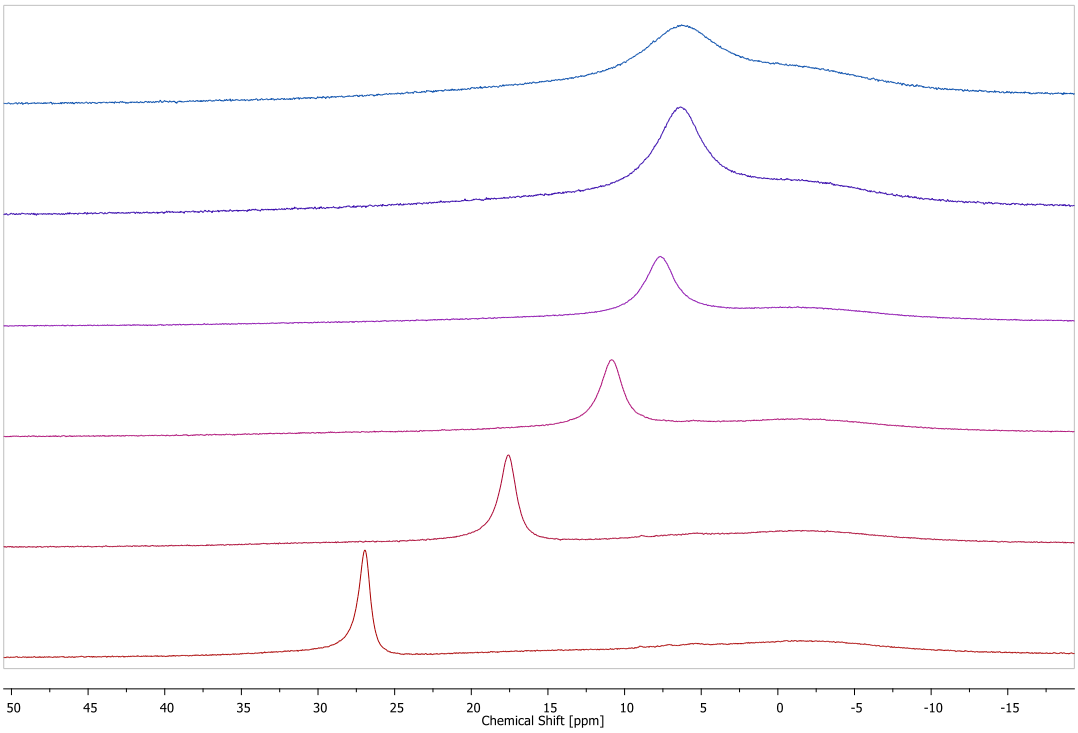


Figure S26. Stacked, background reduced ^{11}B VT NMR spectra of compound **1Cl←py** (12 mg) in CD_2Cl_2 (0.5 mL) starting at +25 °C (298 K), progressively cooled to 0 °C (273 K), –20 °C (253 K), –40 °C (233 K), –60 °C (213 K) and –80 °C (193 K).

4 Appendix

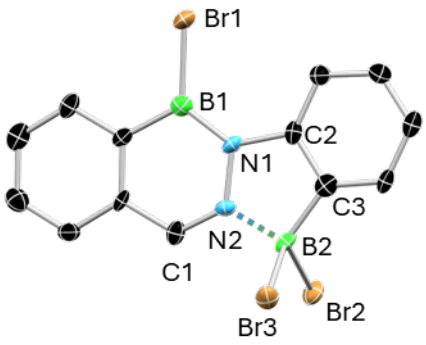


Figure S27. Molecular structure of compound **2**. Single crystals were obtained directly from the reaction mixture. Ellipsoids drawn at 50% probability. All hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.440(14), N1–N2 1.404(11), N2–C1 1.280(13), N2–B2 1.573(13), B1–N1–N2–C1 2.4(12), N2–N1–C2–C3 2.0(9), N1–C2–C3–B2 2.1(10).

Crystal data: $C_{27}H_{20}B_4Br_6Cl_2N_4$, M_r = 994.07, colorless plate, 0.102×0.045×0.007 mm^3, monoclinic space group *C*2/*c*, *a* = 25.1025(5) Å, *b* = 7.0534(2) Å, *c* = 35.7650(10) Å, *β* = 90.423(3)°, *V* = 6332.3(3) Å^3, *Z* = 8, ρ_{calcd} = 2.085 g·cm^{-3}, *μ* = 10.938 mm^{-1}, *F*(000) = 3792, *T* = 100(2) K, R_1 = 0.0780, wR_2 = 0.1883, 5489 independent reflections [2*θ*≤147.502°] and 389 parameters.

Refined as a two-component twin. Component 2 rotated by 0.42° around [0 0 1] (reciprocal) or [0 0 1] (direct) axis. The BASF parameter was refined to 10%.

CCDC number: 2531212

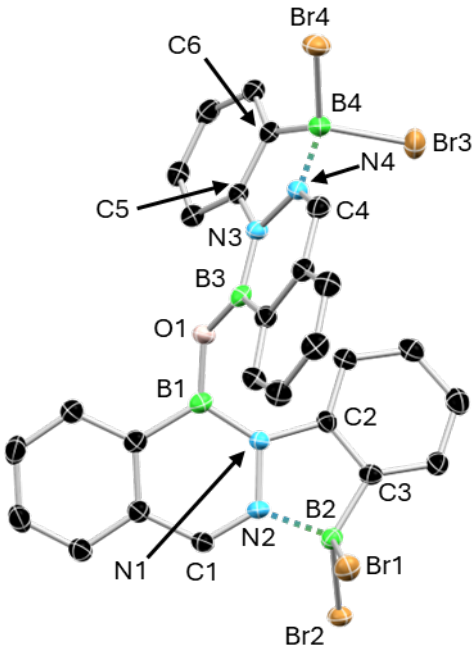


Figure S28. Molecular structure of a C–H borylated B–O–B species. Single crystals were obtained directly from the reaction mixture. Ellipsoids drawn at 50% probability. All hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.432(4), B1–O1 1.363(4), N1–N2 1.388(3), N2–C1 1.296(4), N2–B2 1.596(4), N1–C2 1.435(4), C2–C3 1.396(4), C3–B2 1.567(5), N2–N1–C2–C3 4.5(3), B1–N1–N2–C1 6.0(4).

Crystal data: $C_{33}H_{26}B_4Br_4N_4O$, M_r = 857.46, clear intense colorless block, 0.300×0.150×0.130 mm^3, monoclinic space group $P2_1/c$, a = 13.4361(7) Å, b = 15.706(10) Å, c = 16.2368(9) Å, β = 95.103(9)°, V = 3413(2) Å^3, Z = 4, ρ_{calcd} = 1.669 g·cm^{-3}, μ = 6.018 mm^{-1}, $F(000)$ = 1680, T = 100(2) K, R_1 = 0.0380, wR_2 = 0.0829, 6648 independent reflections [$2\theta \leq 146.916°$] and 366 parameters.

Geometry of toluene residues 1 and 2 was constrained during refinement to idealized toluene. The displacement parameters of atoms in these residues were constrained to the same value with EADP keyword.

CCDC number: 2531214

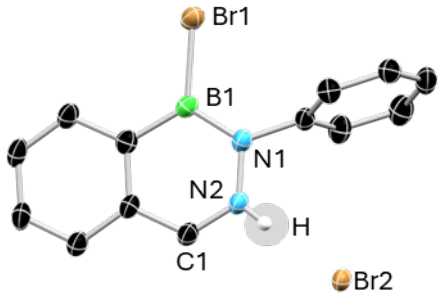


Figure S29. Molecular structure of compound **[1Br]·HBr**. Single crystals were obtained directly from the reaction mixture. Ellipsoids drawn at 30% probability. All hydrogen atoms omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.414(6), N1–N2 1.369(6), N2–C1 1.292(6), B1–Br1 1.926(6), N1–B1–Br1 118.7(4), B1–N1–N2–C1 5.5(7).

Crystal data: $C_{13}H_{11}BBr_2N_2$, M_r = 365.87, clear pale colorless block, 0.120×0.100×0.080 mm^3, monoclinic space group $P2_1/c$, a = 10.835(8) Å, b = 6.108(5) Å, c = 22.159(3) Å, β = 101.367(9)°, V = 1437.7(16) Å^3, Z = 4, ρ_{calcd} = 1.690 g·cm^{-3}, μ = 7.001 mm^{-1}, $F(000)$ = 712, T = 100(2) K, R_1 = 0.0515, wR_2 = 0.1120, 2796 independent reflections [$2\theta \leq 149.588°$] and 167 parameters.

Some reflections were omitted from the refinement as outliners.

CCDC number: 2531211

Attempted Gutmann-Beckett studies

Compound **[1Cl]·H[BCl$_4$]** (25.0 mg, 63.4 μmol, 1.00 equiv.) was suspended in C_6H_6 (0.5 mL) in a Young NMR tube and LiTMP (4.67 mg, 31.7 μmol, 0.50 equiv.) was added at ambient temperature in a glovebox. The reaction suspension was sonicated for 20 min and then filtered in a glove box, using a glass pipet equipped with a glass fibre filter. The filter cake was extracted with C_6H_6 (2 × 0.5 mL) and then discarded. All volatile components of the filtrate were removed *in vacuo* at 50 °C on a Schlenk line for 30 min. The remaining solid was redissolved in *n*-pentane (0.5 mL) and $OPEt_3$ (8.51 mg, 63.4 μmol, 1.00 equiv.) was added at ambient temperature in a glovebox, which resulted in the immediate formation of a colorless solid. The suspension was filtered and the solid was washed with *n*-pentane (3 × 0.5 mL) and dried by slow evaporation of *n*-pentane traces at ambient temperature in a glovebox. Upon dissolving the isolated solid in benzene-d_6, no significant shifting of the ^{11}B ($\Delta\delta$ = 0.2 ppm) or ^{31}P NMR ($\Delta\delta$ = 0.7 ppm) resonances was observed, which prevents an assessment of the Lewis acidity *via* this method, as the equilibrium is fully shifted to the dissociated form under these conditions.

5 References

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