Electronic Supporting Information for

Alkali metal salts of 1,2,3-benzodiazaborines: Platforms for late-stage N-functionalization and metal complexation

Leonie Wüst,[ab] Lea Scheuring,[ab] Tim Wellnitz,[ab] Krzysztof Radacki,[ab] Holger Braunschweig[ab]*

[a] Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[b] Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

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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 (CH_2Cl_2, MeCN) 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; δ_{ref}(THF-d_8) = 67.21 ppm or 25.31 ppm; δ_{ref}(tol-d_8) = 20.43 ppm; $\delta_{ref}(CD_2Cl_2)$ = 53.84 ppm, $\delta_{ref}(CDCl_3)$ = 77.16 ppm) or residual protons (^1H: δ_{ref}(DMSO-d_6) = 2.50 ppm; $\delta_{ref}(C_6D_6)$ = 7.16 ppm; δ_{ref}(THF-d_8) = 3.58 ppm, 1.72 ppm; δ_{ref}(tol-d_8) = 2.08 ppm; $\delta_{ref}(CD_2Cl_2)$ = 5.32 ppm, $\delta_{ref}(CDCl_3)$ = 7.26 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 (^7Li: LiCl; ^{11}B: $BF_3 \cdot OEt_2$). All NMR spectroscopy measurements were carried out at room temperature (298 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).

^{1}H DOSY NMR spectra. The ^1H DOSY NMR experiments were performed on a *BRUKER AVANCE NEO 600* NMR spectrometer with an LED pulse sequence with bipolar gradients and two spoiler gradients (ledbpgp2s) using a standard 5 mm ATM BBO sample with z-gradients at 25 °C. The ^1H NMR frequency was 600.20 MHz. The temperature was calibrated using a sample of 4% MeOH in MeOD-d_4 according to literature.[2] The gradient strength of the sample was calibrated using a sample of "doped water" provided by Bruker (Z10906 · D_2O with 0.1 mg/mL $GdCl_2$, 1% H_2O and 0.1% $^{13}CH_3OH$ at a filling height of 40 mm). For the NMR sample of the compounds in toluene-d_8 and THF-d_8, the 90° ^1H pulse length was accurately determined and the diffusion time Δ(d20) and the gradient length δ(p30) were subsequently

optimized (see Section 3: ^{1}H DOSY NMR spectra for respective values of the samples). The pseudo-2D experiments were performed with eight scans in direct dimension and 24 linear gradient slopes in indirect dimension. Data evaluation was carried out both as a 2D DOSY NMR spectrum and using the T1/T2 relaxation component to fit the diffusion decay using the SimFit algorithm of the *TOPSPIN™ 4.4.0 pl7* software package provided by *BRUKER*.

Mass spectra. High-resolution mass spectrometry was performed on a *THERMO SCIENTIFIC* mass spectrometer (Exactive Plus Spectrometer with an orbitrap detector) using a *LIFDI 700* unit from LINDEN CMS source or with an atmospheric pressure chemical ionization (APCI) / atmospheric solids analysis probe (ASAP) / electron spray ionization (ESI) 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.

IR spectra. Infrared spectra of powder samples were recorded on a *JASCO FT-IR-6100* spectrometer equipped with an ATR unit at ambient temperature (32 scans) and the transmission was normalized. Relative intensities are reported according to the following intervals: weak (w, 0-33%), medium (m, 33-66%), strong (s, 66-100%). **Raman spectra.** Raman spectra were recorded with a *MULTIRAM FT-RAMAN* spectrometer using the 1064 nm excitation line of a Nd/YAG laser on powder samples in melting point capillaries in the range of 3500-100 cm^{-1} with a resolution of 4 cm^{-1} at ambient temperature.

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 monochromator using CuK_α radiation (λ = 1.54178 Å). The structures were solved using the intrinsic phasing method (*ShelXT*),[3] expanded Fourier expansion and refined using the *SHELXL* program.[4] 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.

UV-vis and fluorescence spectra. All photophysical measurements were performed in standard quartz Schlenk cuvette (1 cm × 1 cm cross-section) under inert atmosphere. UV-visible absorption spectra were recorded using a *METTLER TOLEDO UV7* UV-visible spectrophotometer. The emission spectra were recorded using an *EDINBURGH INSTRUMENTS FLSP920* spectrometer equipped with a double

monochromator for both excitation and emission, operating in right-angle geometry mode, and all spectra were fully corrected for the spectral response of the instrument. The fluorescence quantum yields of solutions were measured using a calibrated integrating sphere (inner diameter: 150 mm) from Edinburgh Instruments combined with the *FLSP920* spectrometer described above.

Table S1. Origin and purification of solvents and reactants.

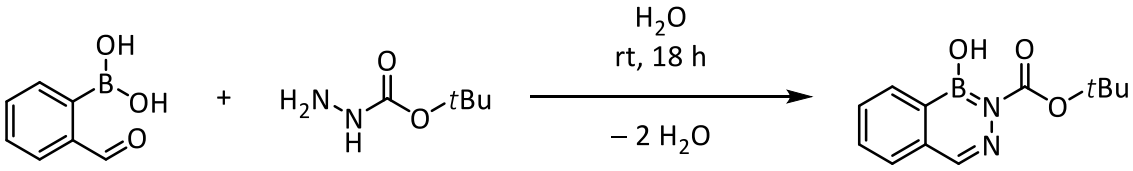
Substance	**Origin**	**Purity / Purification**
2-Formylphenylboronic acid [40138-16-7]	BLD Pharmatech®	99.97% / none stored under Ar
tert-Butylcarbazate [870-46-2]	Sigma Aldrich®	98% / none
N,O-Bis(trimethylsilyl)acetamide [10416-59-8]	Sigma Aldrich®	≥95% / none stored under Ar
Trifluoroacetic acid (TFA) [76-05-1]	Sigma Aldrich®	≥99% / none
Trimethylsilyl chloride (TMSCl) [75-77-4]	Sigma Aldrich®	≥99% / none
Methyl iodide (MeI) [74-88-4]	Sigma Aldrich®	≥99% / none
1-Bromo-2,3,5,6-tetramethylbenzene [1646-53-3]	synthesized[5]	- / none
Magnesium (Turnings acc. to Grignard for synthesis) [7439-95-4]	Sigma Aldrich®	99.9% / none
Lithium diethylamide (LEA) [816-43-3]	Sigma Aldrich®	≥95% / none stored under Ar
1,2-Dibromoethane [106-93-4]	Sigma Aldrich®	98% / none
Lithium bis(trimethylsilyl)amide (Li[HMDS]) [4039-32-1]	Sigma Aldrich®	97% / none stored under Ar
Sodium bis(trimethylsilyl)amide (Na[HMDS]) [1070-89-9]	Sigma Aldrich®	95% / none stored under Ar
Potassium bis(trimethylsilyl)amide (K[HMDS]) [4039-32-1]	Sigma Aldrich®	95% / none stored under Ar
Methyllithium (1.6 M solution in Et_2O) [917-54-4]	Sigma Aldrich®	- / dried *in vacuo*, used as solid stored under Ar
Lithium 2,2,6,6-tetramethylpiperidide (LiTMP) [38277-87-1]	Sigma Aldrich®	95% / none stored under Ar

2-Bromo-1,3,2-benzodioxaborole (CatBBr) [51901-85-0]	Sigma Aldrich®	97% / none stored under Ar
Silver trifluoromethanesulfonate (AgOTf) [2923-28-6]	Sigma Aldrich®	≥99.95% / none stored under Ar
Chloro(dimethylsulfid)copper (CuCl(DMS)) [54678-22-7]	synthesized adapted to [6]	- / none
Chloro(tetrahydrothiophene)gold (AuCl(THT)) [39929-21-0]	synthesized[6]	- / none
Sodium carbonate [497-19-8]	sourced in house	- / none
Sodium sulfate (anhydrous) [7757-82-6]	sourced in house	- / none
Dichloromethane [71-43-2]	sourced in house	Purified and dried over local solvent purification system (SPS), stored under Ar over molecular sieves.
Benzene [71-43-2]	sourced in house	dried over Na, freshly distilled prior to use, stored under Ar over molecular sieves.
Toluene [108-88-3]	sourced in house	
n-Pentane [109-66-0]	sourced in house	
Tetrahydrofuran (THF) [109-99-9]	sourced in house	
n-Hexane (column chromatography) [110-54-3]	sourced in house	- / none
Ethyl acetate (column chromatography) [141-78-6]	sourced in house	- / none
Dichloromethane [71-43-2]	sourced in house	distilled prior to use
Aluminum oxide 90, neutral (Act. I) [1344-28-1]	Macherey-Nagel®	- / none
Benzene-d_6 (C_6D_6) [1076-43-3]	Sigma Aldrich®	99.6 atom % D / none stored under Ar over molecular sieves.
Tetrahydrofuran-d_8 (THF-d_8) [1693-74-9]	Sigma Aldrich®	≥99.5 atom % D / none stored under Ar over molecular sieves.

Chloroform-*d* ($CDCl_3$) [865-49-6]	Sigma Aldrich®	99.8 atom % D / none
Dimethylsulfoxide-d_6 (DMSO-d_6) [2206-27-1]	Sigma Aldrich®	99.5 atom % D / none
Toluene-d_8 (tol-d_8) [2037-26-5]	Sigma Aldrich®	99 atom % D / none
Dichloromethane-d_2 (CD_2Cl_2) [1665-00-5]	Sigma Aldrich®	99.5 atom % D / none

2 Syntheses and characterization of compounds

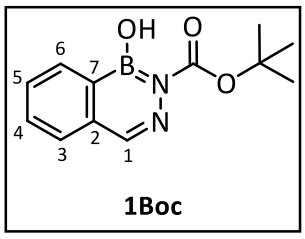
3-*Tert*-butoxycarbonyl-4-hydroxy-4,3-borazaroisoquinoline (1Boc)



1Boc (90%)

Open to the atmosphere, 2-formylphenylboronic acid (5.00 g, 33.4 mmol, 1.00 eq.) was suspended in distilled water (500 mL) in a 1 L round bottom flask with a dumbbell stirring bar and stirred until total dissolution (approx. 10 min). *tert*-Butylcarbazate (4.41 g, 33.4 mmol, 1.00 eq.) was added under rapid stirring at ambient temperature, which resulted in the immediate formation of a colorless precipitate. After stirring for 18 h, the solid was filtered off and washed with distilled water (3 × 30 mL). The filter cake was dried in suction vacuum and the obtained off-white powder was additionally dissolved in dichloromethane (150 mL), dried over Na_2SO_4 and filtered.*[1] All volatile components were removed *in vacuo* and compound **1Boc** was obtained as a colorless solid. **Yield of 1Boc:** 7.40 g (30.1 mmol, 90%) of a colorless powder. The compound is air- and moisture-stable.

Crystalline material of **1Boc** as colorless blocks for single-crystal XRD was obtained by slow evaporation of a saturated acetone solution at ambient temperature. **^{1}H NMR** (500 MHz, 298 K, CD_2Cl_2): δ = 8.57 (s, 1H, B-O*H*), 8.18 (d, $^3J_{HH}$ = 7.55 Hz, 1H, *H*-3), 8.03 (s, 1H, *H*-1), 7.72-7.77 (m, 1H, *H*-5), 7.62-7.67 (m, 2H, *H*-4 + *H*-6), 1.65 (s, 9H, −C*H*$_3$) ppm.*[2] **^{11}B{^{1}H} NMR** (160 MHz, 298 K, CD_2Cl_2): δ = 30.0 (s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2) δ = 158.8 (*C*$_q$=O), 142.9 (*C*-1), 135.0 (*C*$_q$-2), 132.9 (*C*-5), 132.2 (*C*-3), 130.6 (*C*-4), 127.7 (*C*-6), 84.9 (−*C*$_q$(CH$_3$)$_3$), 28.3 (−*C*H$_3$) ppm.*[3] **HRMS** (APCI$_{pos,}$ toluene): expected: m/z 246.1176 [$C_{12}H_{15}BN_2O_3$]$^+$; found: m/z 147.0721 [$C_7H_8BN_2O$, **1Boc**−Boc+H]$^+$, 191.0619 [$C_8H_8BN_2O_3$, **1Boc**−C_4H_8+2H]$^+$, 275.1263 [$C_{14}H_{13}B_2N_4O$, **1-O-1**+H]$^+$. **IR** (ATR, 24 scans, powder) $\tilde{\nu}$ **=** 3454 (w), 3327 (w), 2975 (w), 1695 (m), 1616 (w), 1555 (w), 1487 (w), 1446 (w), 1426 (w), 1395 (s, *C*=*O*), 1369 (m), 1328 (s), 1291 (s), 1240 (s), 1024 (s), 969 (w), 938 (w), 894 (s), 845 (m), 810 (w), 785 (m), 765 (m), 732 (m), 692 (s), 618 (m), 592 (s), 571 (m), 473 (w), 430 (w) cm^{-1}.



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*[1] Compound **1Boc** tends to complex H_2O, even after storage in a dessicator for several days. This step proved to be more effective to obtain the anhydrous compound **1Boc**.

*[2] In DMSO-d_6, compound **1Boc** forms donor-acceptor interactions with the deuterated solvent, as well as water traces from the solvent, resulting in overall very complicated spectra of the analytically pure substance.

*[3] The quaternary carbon atom C_q^B-7 adjacent to the boron atom was not detected in the ^{13}C NMR spectrum due to quadrupolar broadening caused by the boron nucleus.

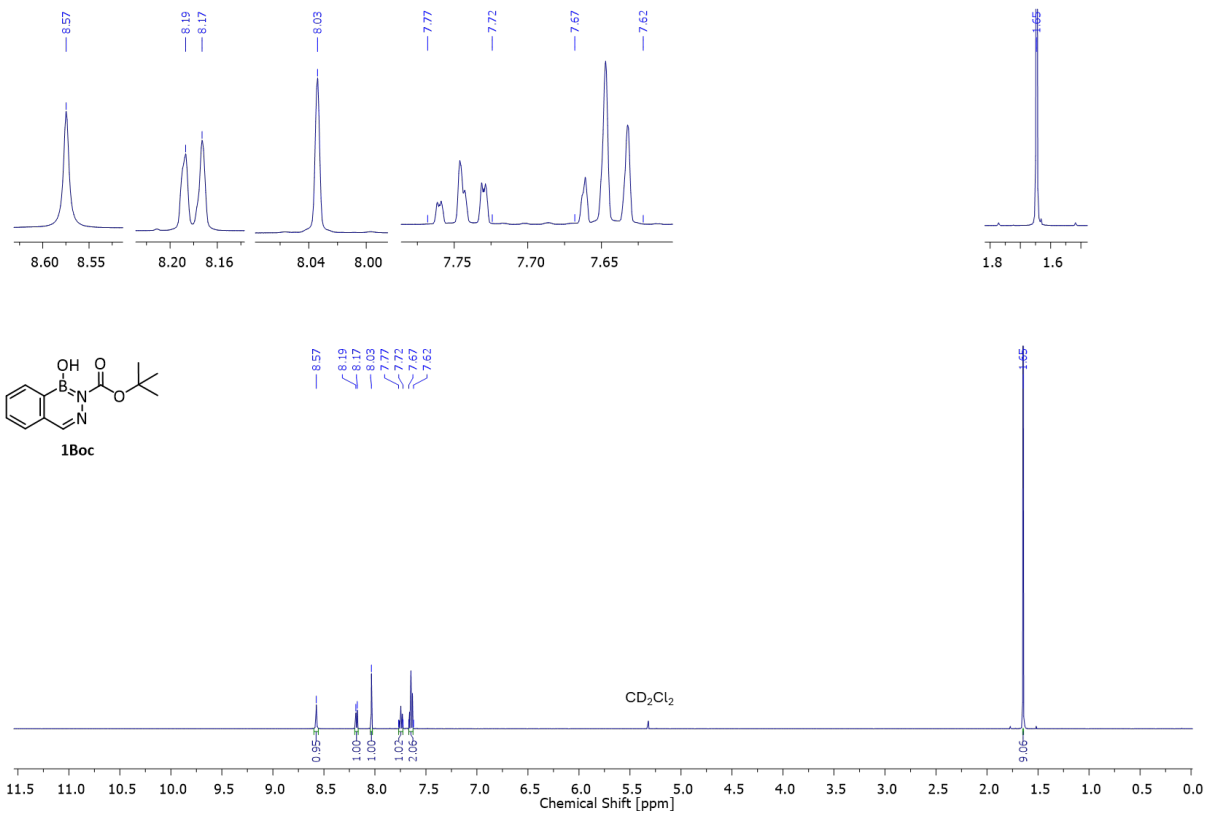


Figure S1. ^{1}H NMR spectrum of compound **1Boc** in C*D*$_2$Cl$_2$.

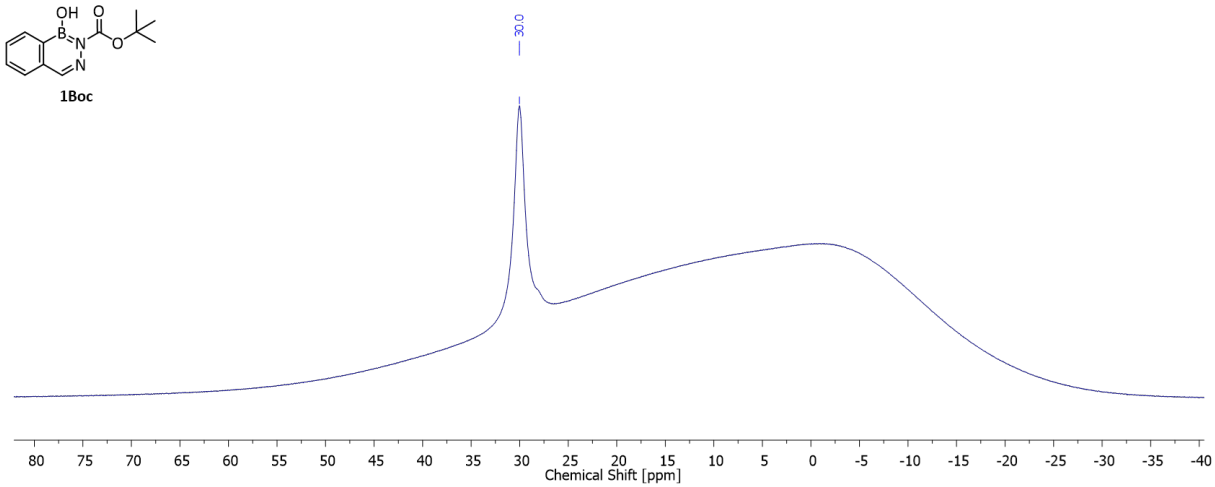


Figure S2. ^{11}B{^{1}H} NMR spectrum of compound **1Boc** in C*D*$_2$Cl$_2$.

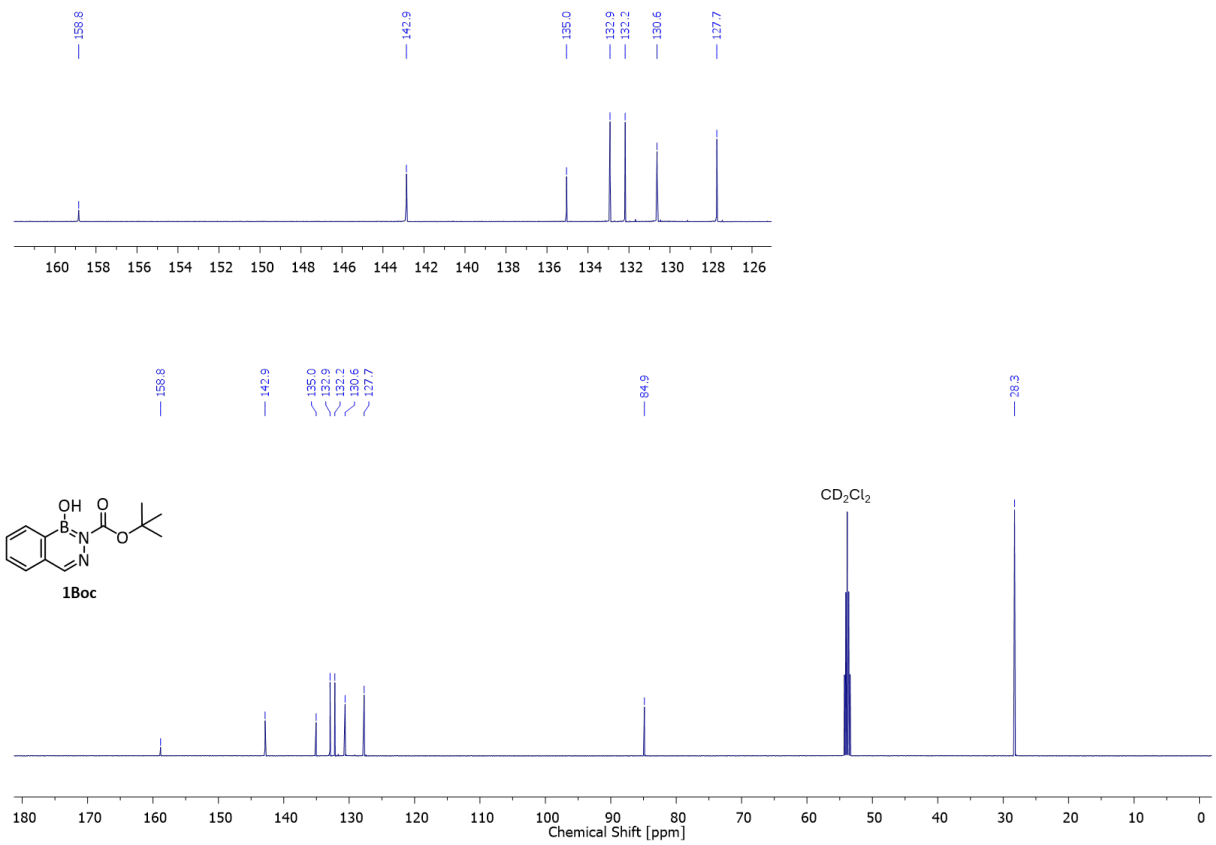


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1Boc** in CD_2Cl_2.

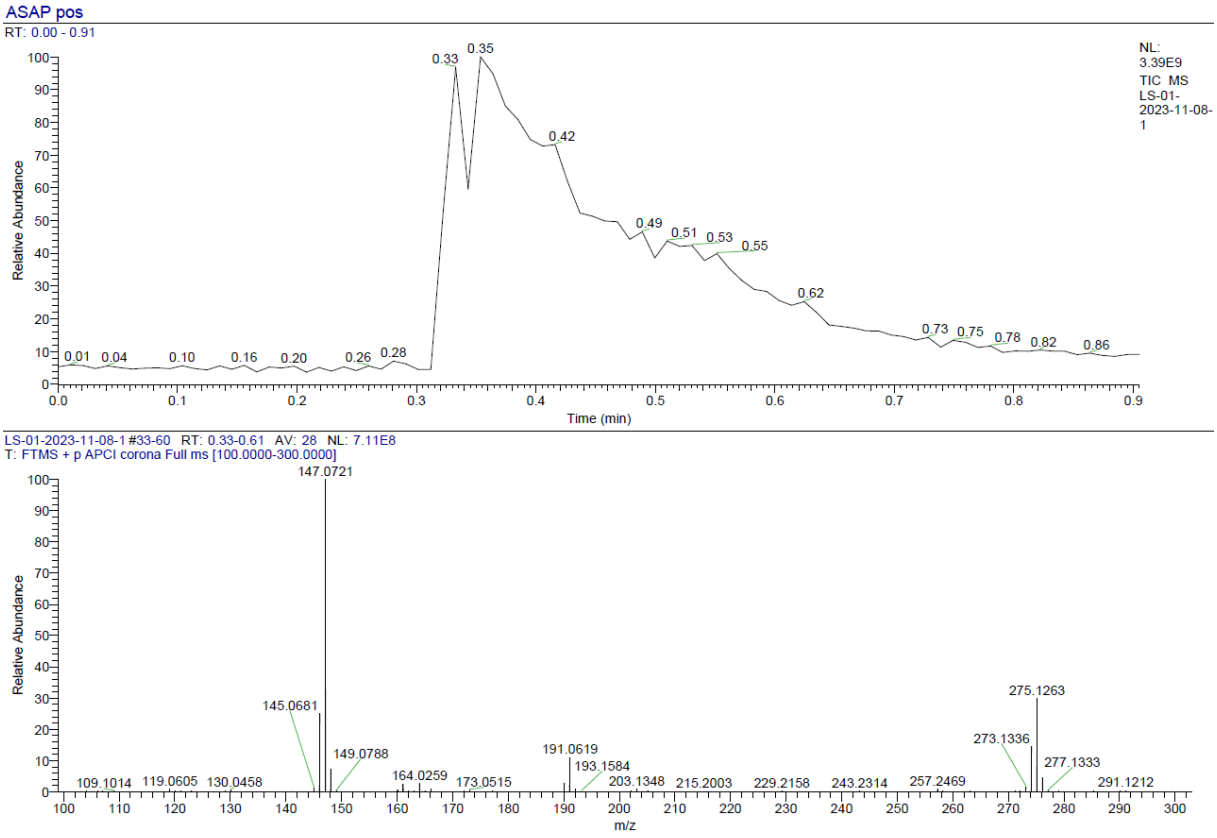


Figure S4. $ASAP_{pos}$ high resolution mass spectrum of compound **1Boc** (toluene). Major fragmentation due to partial or complete loss of the Boc-group.

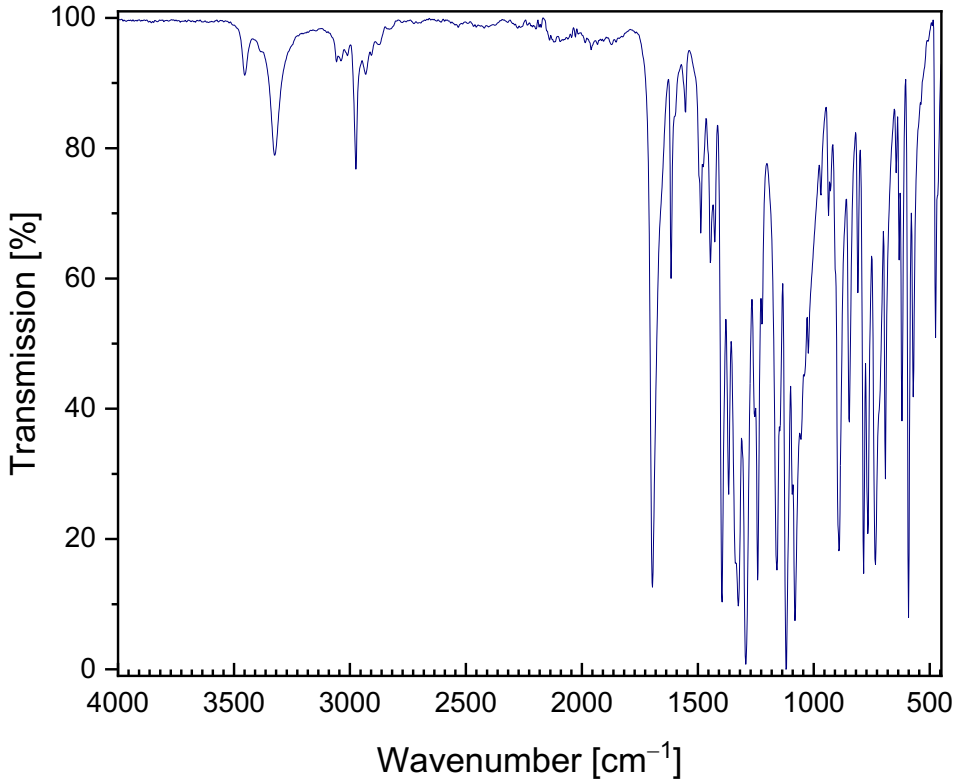


Figure S5. Normalized infrared spectrum of compound **1Boc** (powder).

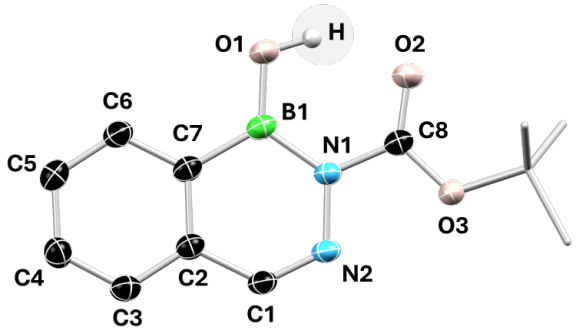
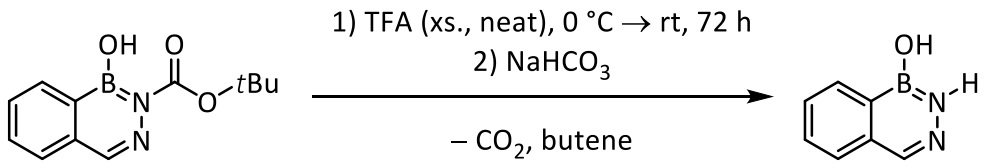


Figure S6. Molecular structure of compound **1Boc**. Ellipsoids drawn at 50% probability. All H-atoms except for the borinic acid omitted. *tert*-Butyl group rendered as wireframe. Selected bond lengths (Å) and angles (°) of **1Boc**: B1–N1 1.4656(19), N1–N2 1.3983(14), N2–C1 1.2825(18), C1–C2 1.4537(18), C2–C3 1.4059(17), C3–B1 1.534(2), C3–C4 1.4038(19), C4–C5 1.377(2), C5–C6 1.3988(19), C6–C7 1.383(2), C7–C2 1.400(2), B1–O1 1.3534(17), C3–B1–O1 122.05(13), C3–B1–N1 115.34(11), O1–B1–N1 122.56(14), B1–N1–C8 121.29(11), C8–N1–N2 114.74(10), N2–N1–B1 123.78(11), B1–N1–N2–C1 2.45(19).

Crystal data:
$C_{12}H_{15}BN_2O_3$, M_r = 246.07, clear colorless block, 0.300×0.140×0.120 mm^3, monoclinic space group $P2_1/n$, a = 12.7968(3) Å, b = 5.9025(2) Å, c = 17.2316(4) Å, β = 103.002(2)°, V = 1268.19(6) Å^3, Z = 4, ρ_{calcd} = 1.289 g·cm^{-3}, μ = 0.753 mm^{-1}, F(000) = 520, T = 100(2) K, R_1 = 0.0490, wR_2 = 0.1102, 2470 independent reflections [$2\theta \leq 147.882°$] and 170 parameters.

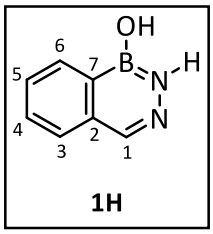
CCDC number: 2425627

4-Hydroxy-4,3-borazaroisoquinoline (1H)



1Boc **1H** (99%)

Open to the atmosphere, compound **1H** (7.00 g, 28.4 mmol, 1.00 eq.) was added portionwise under moderate stirring to pure trifluoroacetic acid (100 mL, xs.) at 0 °C (ice bath) in a 500 mL round bottom Schlenk flask. After 5 min, the cooling bath was removed, and the clear brown reaction mixture was stirred at ambient temperature for 72 h. During this time, gas evolution was observed. All volatile components were removed *in vacuo* on a Schlenk line using an external cooling trap.*[1] The obtained light yellow solid ([**1H**]H^+[TFA^-]) was carefully neutralized with a saturated $NaHCO_3$ solution (ca. 200 mL). Ethyl acetate (100 mL) was added, and the two phases were transferred into a separating funnel. The aqueous layer was extracted with ethyl acetate (2 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and all volatile components were removed *in vacuo*. The obtained pale yellow solid was dried in a dessicator (orange gel) until constant weight was achieved. **Yield:** 4.41 g (28.5 mmol, 99%) of a pale yellow powder. The compound is air- and moisture-stable.



Crystalline material of **1H** as colorless blocks for single-crystal XRD was obtained by slow evaporation of a saturated acetone solution at ambient temperature. **^{1}H NMR** (500 MHz, 298 K, DMSO-d_6): δ = 9.93 (s, 1H, N-*H*), 8.17-8.20 (m, 2H, B-O*H* + *H*-3), 7.99 (s, 1H, *H*-1), 7.68-7.72 (m, 2H, *H*-5 + *H*-6), 7.55-7.59 (m, 1H, *H*-4) ppm. **^{11}B NMR** (160 MHz, 298 K, DMSO-d_6): δ = 27.8 (s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, 298 K, DMSO-d_6): δ = 138.5 (*C*-1), 135.8 (C_q-2), 130.9 (*C*-3 + *C*-5), 130.3 (br s, C_q^B-7), 128.3 (*C*-4), 126.7 (*C*-6) ppm. **HRMS** ($APCI_{pos}$, ethyl acetate): expected: m/z 147.0724 $[C_7H_7BN_2O+H]^+$; found: m/z 147.0720 $[C_7H_7BN_2O+H]^+$. **IR** (ATR, 24 scans, powder) $\tilde{\nu}$ = 3325 (m, *N–H*), 3160 (w), 3064 (w), 3013 (w), 2962 (w), 1601 (w), 1557 (m), 1495 (s), 1459 (w), 1438 (m), 1375 (s), 1340 (s), 1304 (m), 1259 (w), 1222 (w), 1151 (s), 1118 (s), 1091 (s), 1034 (m), 1008 (s), 961 (w), 902 (m), 802 (s), 783 (s), 761 (s), 749 (s), 696 (s), 645 (m), 630 (s), 586 (s), 500 (w), 465 (w), 451 (w), 433 (w), 406 (w) cm^{-1}.

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*[1] The re-distilled TFA can be re-used for the next batch of **1H**.

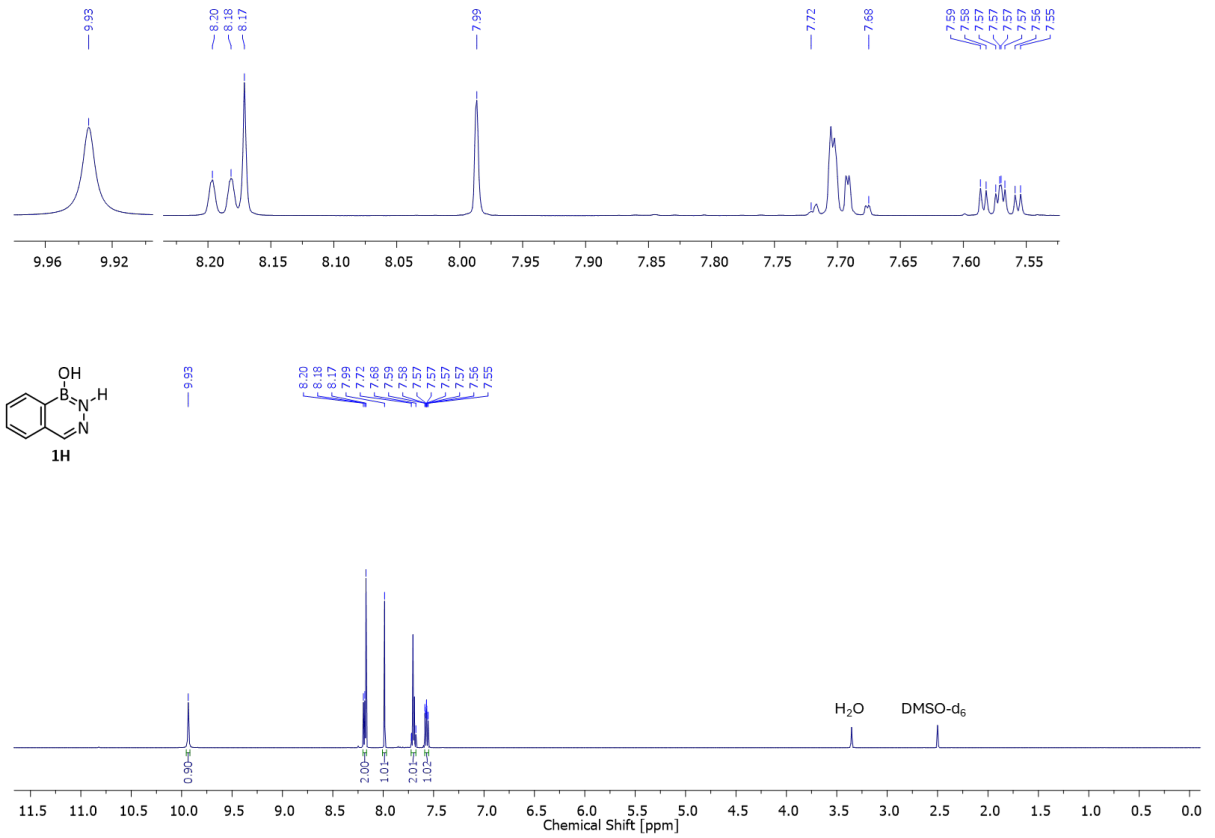


Figure S7. ^{1}H NMR spectrum of compound **1H** in DMSO-d_6.

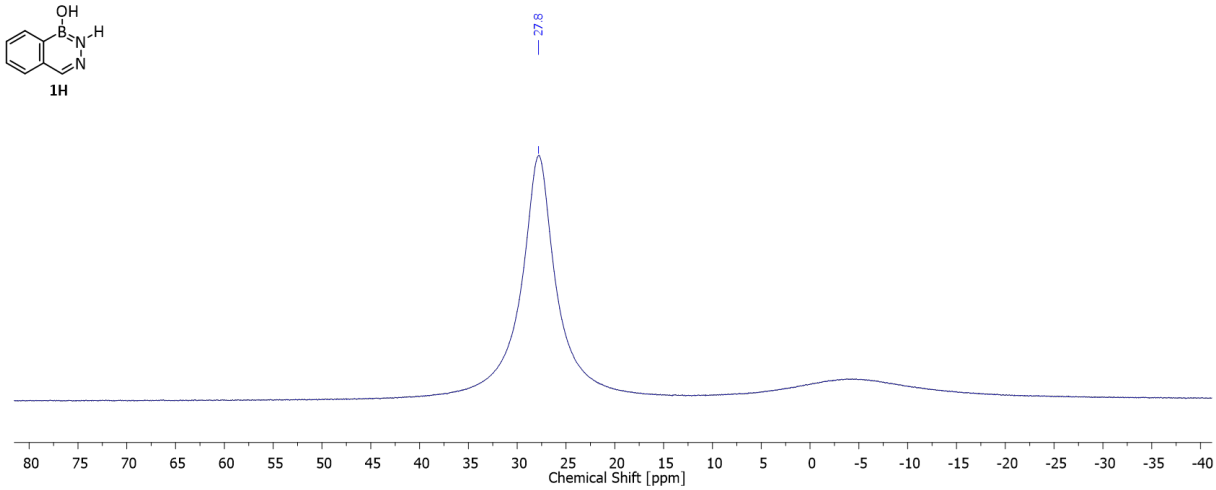


Figure S8. Background reduced ^{11}B NMR spectrum of compound **1H** in DMSO-d_6.

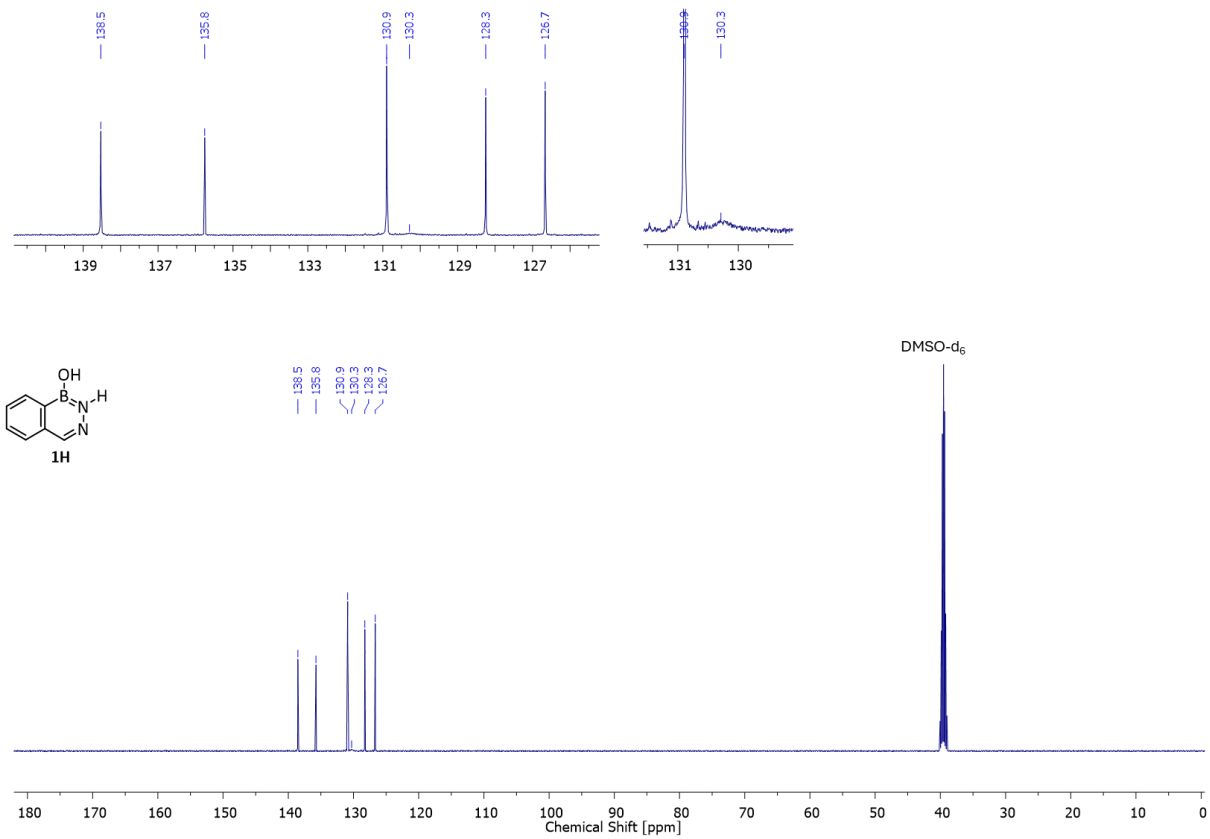


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of compound **1H** in DMSO-d_6.

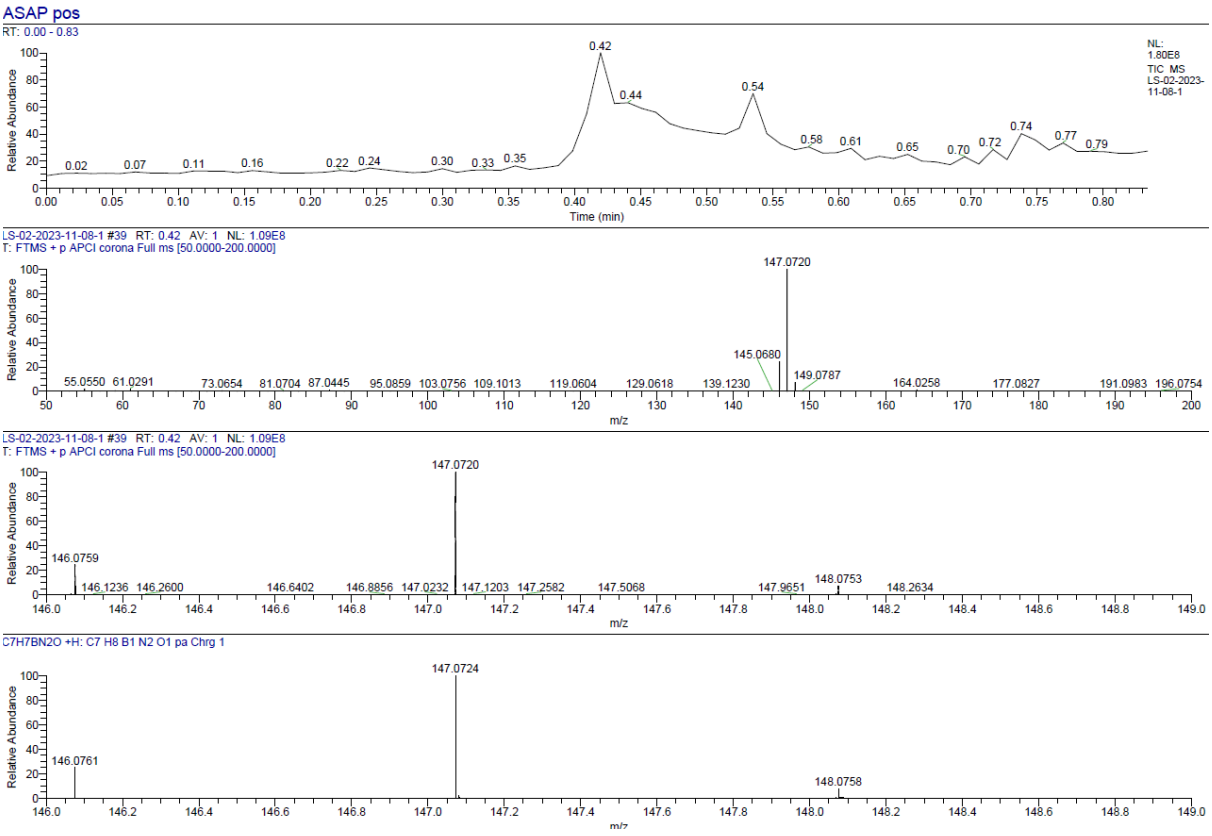


Figure S10. $ASAP_{pos}$ high resolution mass spectrum of compound **1H** (ethyl acetate).

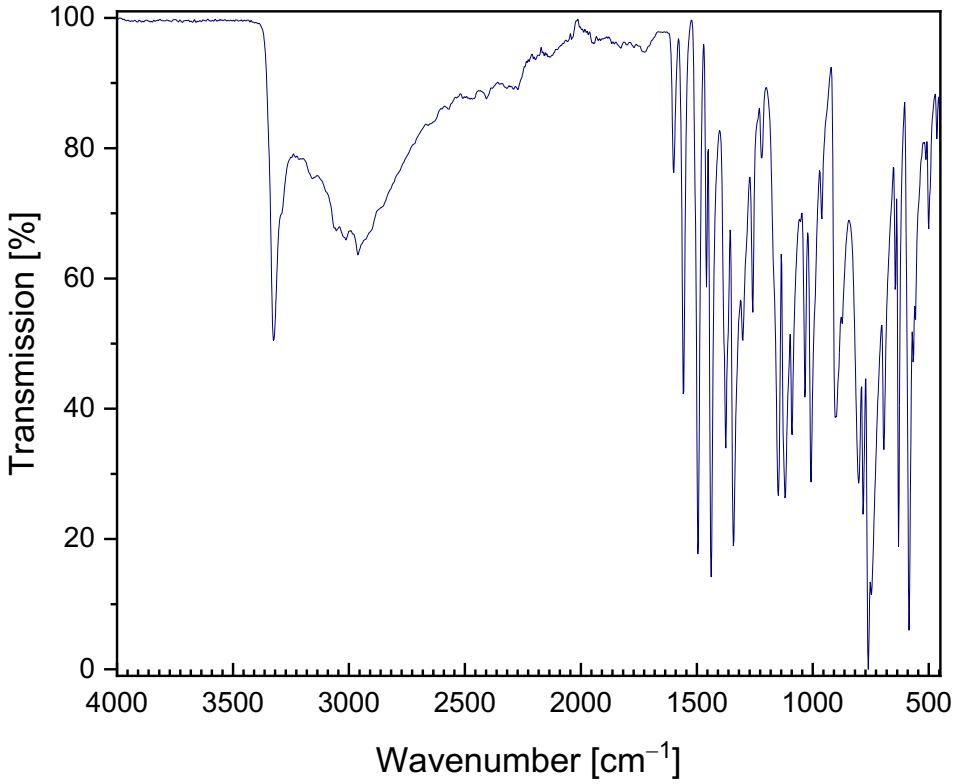


Figure S11. Normalized infrared spectrum of compound **1H** (powder).

The molecular structure of compound **1H** has been reported by Groziak and coworkers.[7]

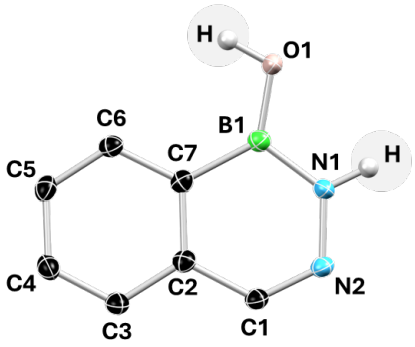
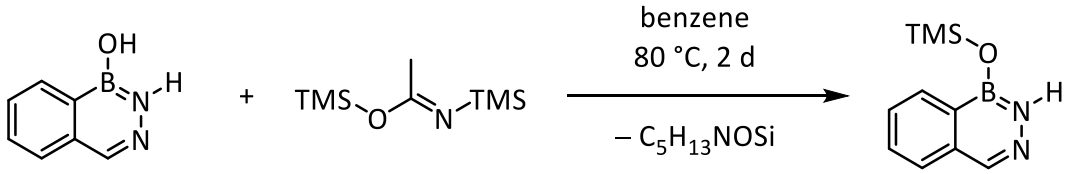


Figure S12. Molecular structure of compound **1H**. Ellipsoids drawn at 50% probability. All H atoms except for the borinic acid and secondary amine function omitted. Selected bond lengths (Å) and angles (°) of **1H**: B1–N1 1.4288(16), N1–N2 1.3752(14), N2–C1 1.2943(17), C1–C2 1.4465(17), C2–C3 1.4114(17), C3–B1 1.5445(19), C3–C4 1.4061(17), C4–C5 1.3782(18), C5–C6 1.4027(18), C6–C7 1.3776(18), C7–C2 1.4056(18), B1–O1 1.3706(16), C3–B1–O1 127.29(12), C3–B1–N1 115.35(11), O1–B1–N1 117.36(12), B1–N1–N2–C1 1.63(17).

Crystal data:
$C_7H_7BN_2O$, M_r = 145.96, clear colorless block, 0.140×0.070×0.060 mm^3, monoclinic space group $P2_1/c$, a = 7.6003(2) Å, b = 7.2677(2) Å, c = 12.3523(3) Å, β = 96.378(2)°, V = 678.08(3) Å^3, Z = 4, ρ_{calcd} = 1.430 g·cm^{-3}, μ = 0.782 mm^{-1}, $F(000)$ = 304, T = 100(2) K, R_1 = 0.0418, wR_2 = 0.0968, 1328 independent reflections [$2\theta \leq 149.188°$] and 102 parameters.

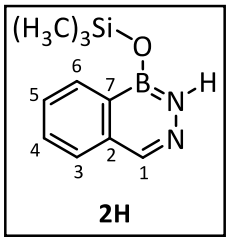
CCDC number: 2425635

4-(Trimethylsiloxy)-4,3-borazaroisoquinoline (2H)



1H **2H** (79%)

Compound **1H** (2.00 g, 13.7 mmol, 1.00 eq.) was suspended in benzene (200 mL) in a 500 mL Schlenk flask. Under rapid stirring, *N,O*-bis(trimethylsilyl)-acetamide (9.98 mL, 41.1 mmol, xs., ρ = 0.83 g/mL) was added at ambient temperature. After stirring the suspension for 10 min, a clear yellow solution was obtained. The reaction mixture was heated to 80 °C for 2 d. All volatile components were removed *in vacuo* with an external cooling trap. For the removal of the byproduct *N*-(trimethylsilyl)acetamide *via* fractional sublimation, the obtained yellow oil was heated to 50 °C at $2.0 \cdot 10^{-2}$ mbar using a sublimation finger. The initial sublimation fraction of the byproduct was discarded. Subsequently, the light brown residue was heated again to 80 °C at $2.0 \cdot 10^{-2}$ mbar, resulting in the sublimation of **2H**. **Yield:** 2.32 g (10.8 mmol, 79%) of a colorless, crystalline solid.



2H

Crystalline material of **2H** as colorless rhombohedrons for single-crystal XRD was obtained by storing a saturated *n*-pentane solution at −30 °C. **^{1}H NMR** (500 MHz, 298 K, C_6D_6): δ = 8.50 (s, 1H, N-*H*), 8.13-8.18 (m, 1H, *H*-3), 8.10 (s, 1H, *H*-1), 7.28-7.34 (m, 2H, *H*-4 + *H*-5), 7.24-7.26 (m, 1H, *H*-6), 0.14 (s, 9H, −Si(CH_3)$_3$) ppm. **^{11}B NMR** (160 MHz, 298 K, C_6D_6): δ = 26.5 (s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, 298 K, C_6D_6): δ = 140.9 (*C*-1), 137.0 (C_q-2), 132.6 (br, C_q^B-7), 131.5 (*C*-3), 131.3 (*C*-5), 128.8 (*C*-4), 127.1 (*C*-6), 1.4 (−Si(CH_3)$_3$) ppm. **HRMS** ($ASAP_{pos}$, toluene): expected: m/z 219.1119, 220.2253 $[C_{10}H_{15}BN_2OSi+H]^+$; found: m/z 219.1114, 220.1147 $[C_{10}H_{15}BN_2OSi+H]^+$. **IR** (ATR, 24 scans, powder) $\tilde{\nu}$ = 3295 (m, *N–H*), 3213 (w), 3166 (w), 3109 (w), 3074 (w), 3023 (w), 2958 (w), 2899 (w), 1601 (w), 1557 (w), 1493 (m), 1464 (w), 1438 (m), 1379 (m), 1363 (s), 1334 (s), 1293 (s); 1253 (s), 1216 (m), 1134 (w), 1098 (w), 1040 (m), 1008 (m), 969 (w), 922 (s), 834 (s), 804 (s), 767 (s), 753 (s), 671 (m), 637 (m), 592 (s), 537 (w), 504 (m), 455 (m) cm^{-1}. Sublimation point of **2H**: 70-75 °C ($2.0 \cdot 10^{-2}$ mbar).

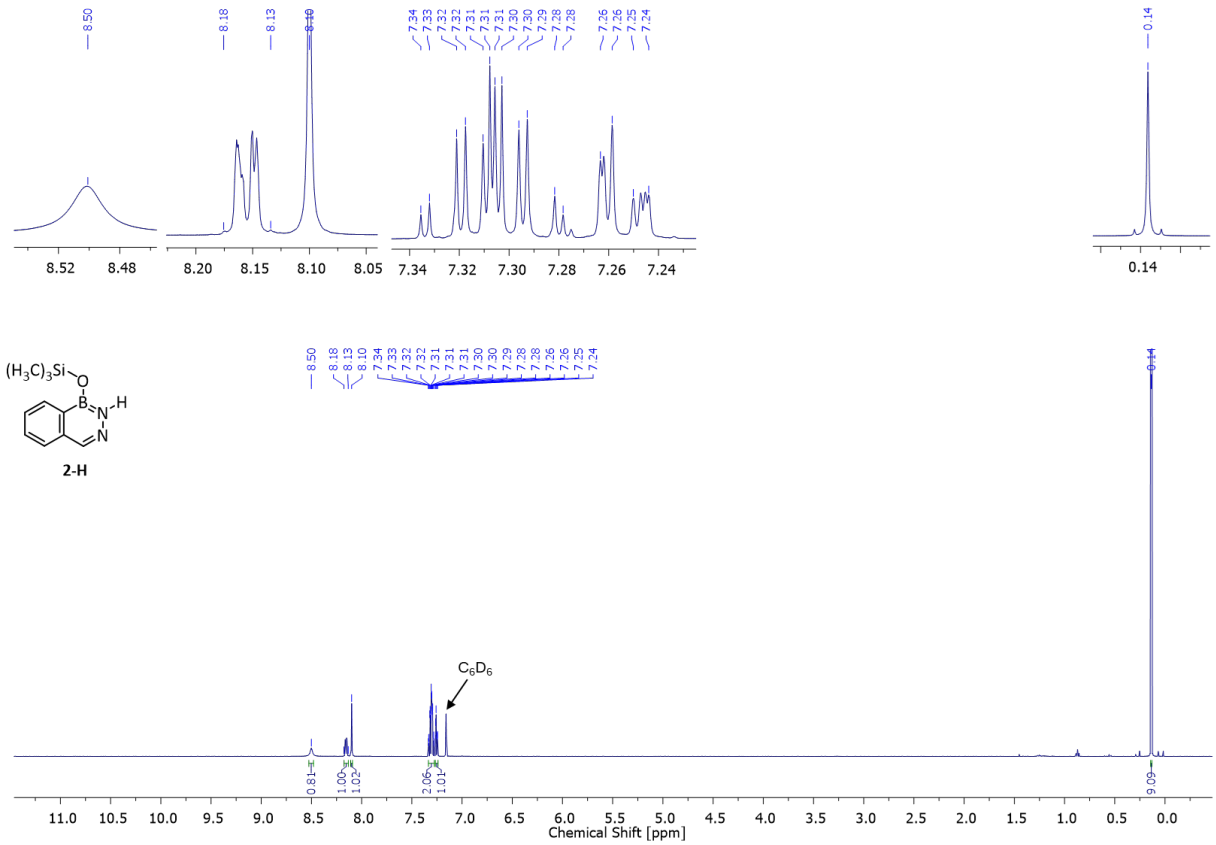


Figure S13. ^{1}H NMR spectrum of compound **2H** in C_6D_6.

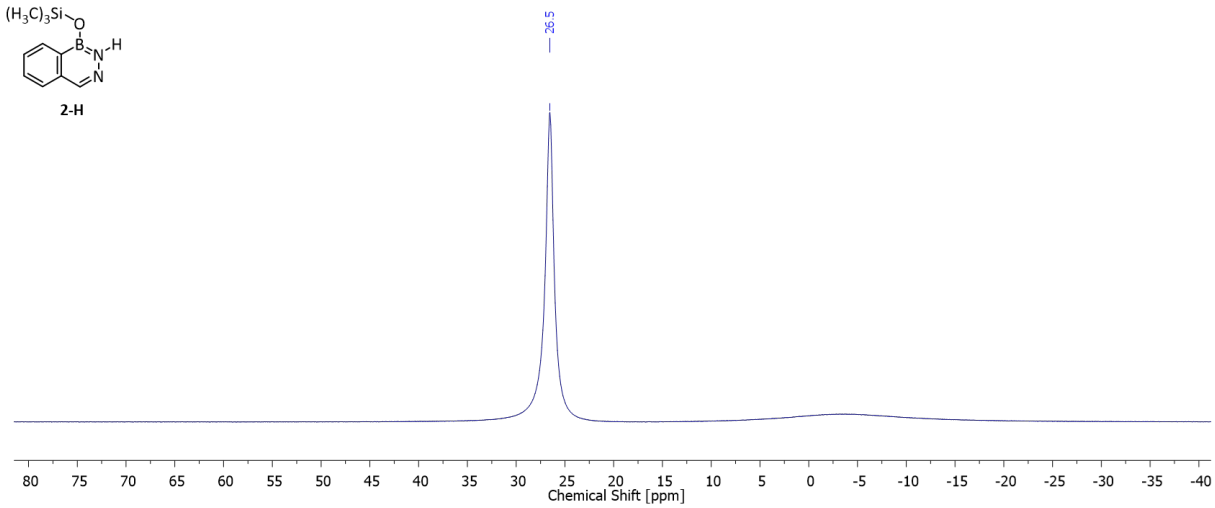


Figure S14. Background reduced ^{11}B NMR spectrum of compound **2H** in C_6D_6.

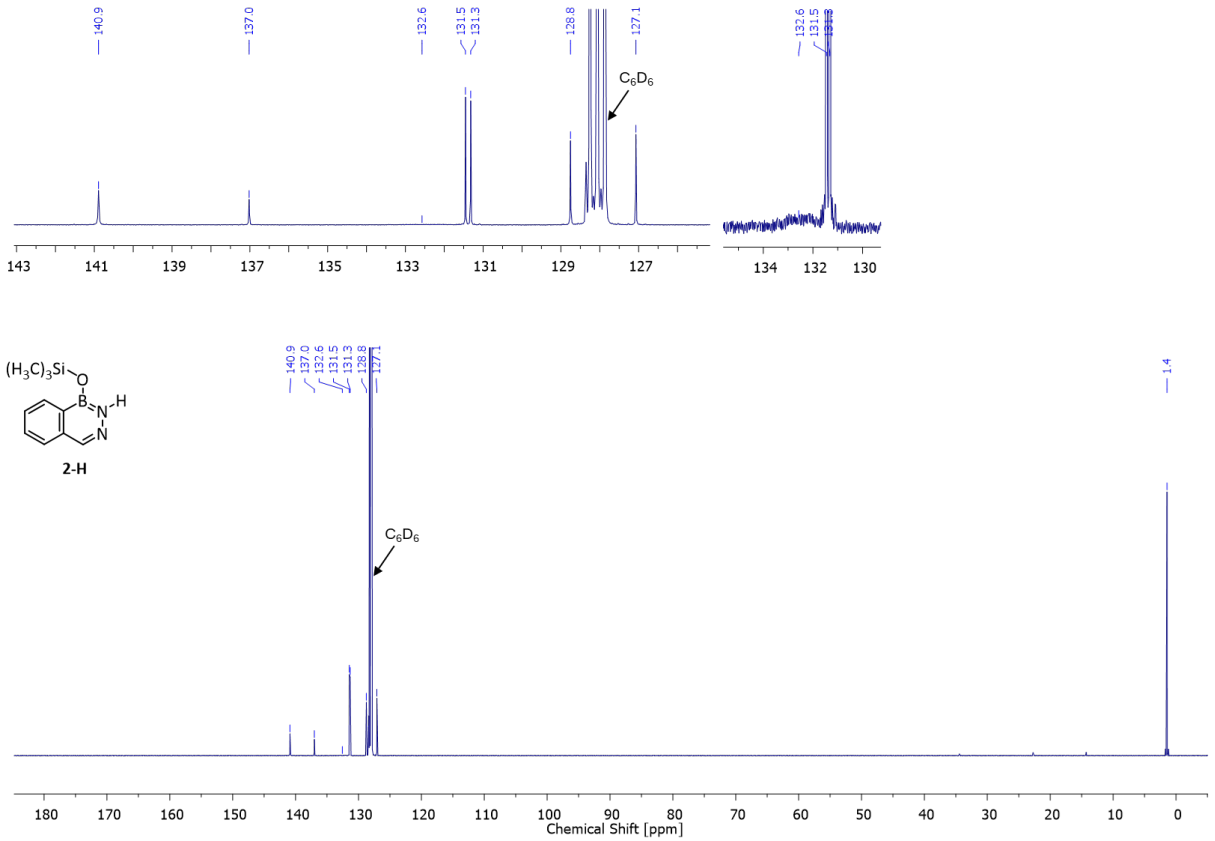


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2H** in C_6D_6.

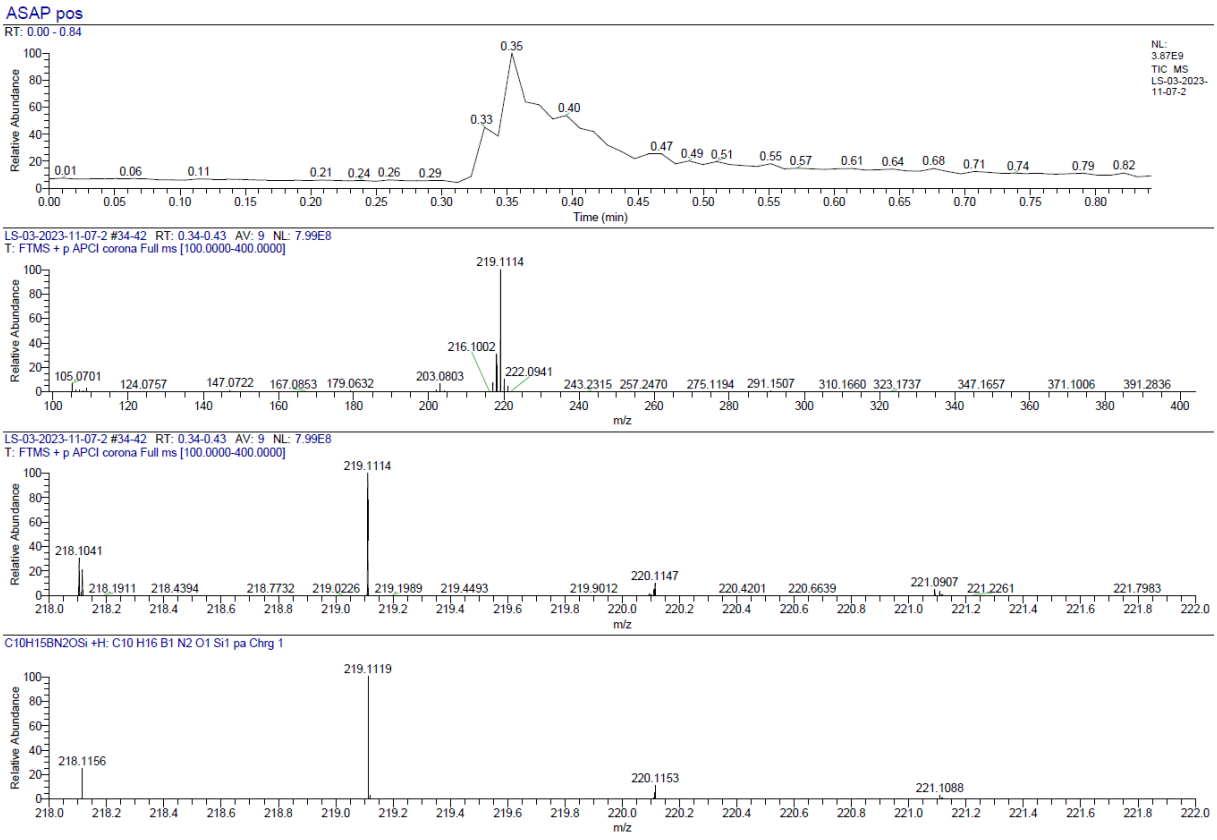


Figure S16. $ASAP_{pos}$ high resolution mass spectrum of compound **2H** (toluene).

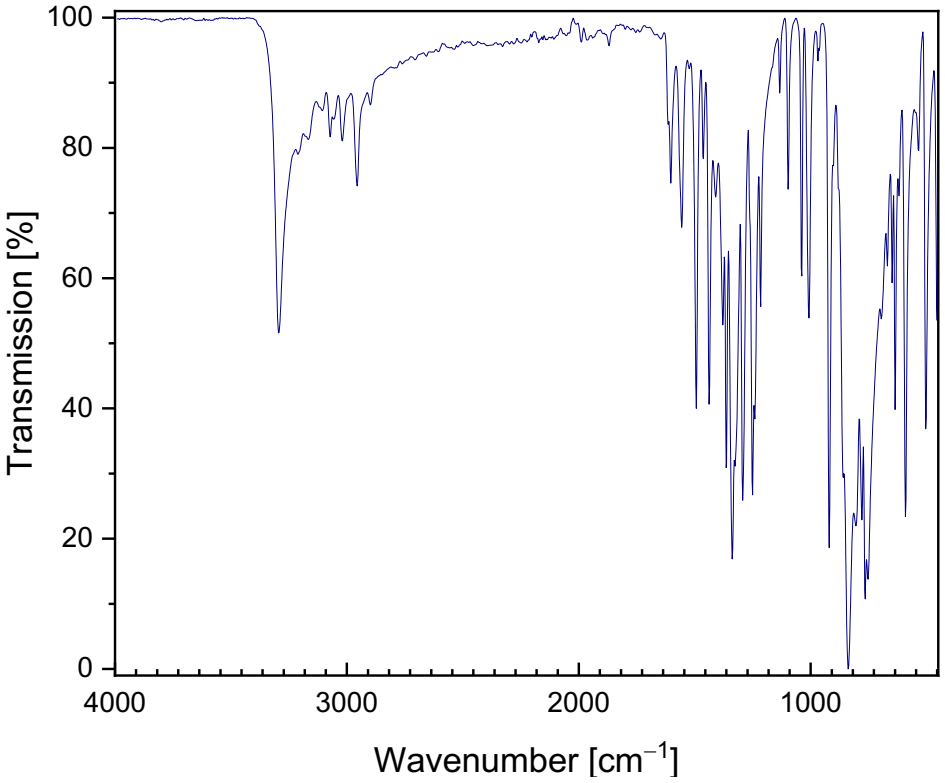


Figure S17. Normalized infrared spectrum of compound **2H** (powder).

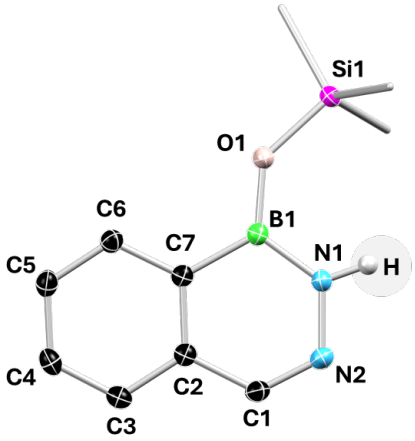
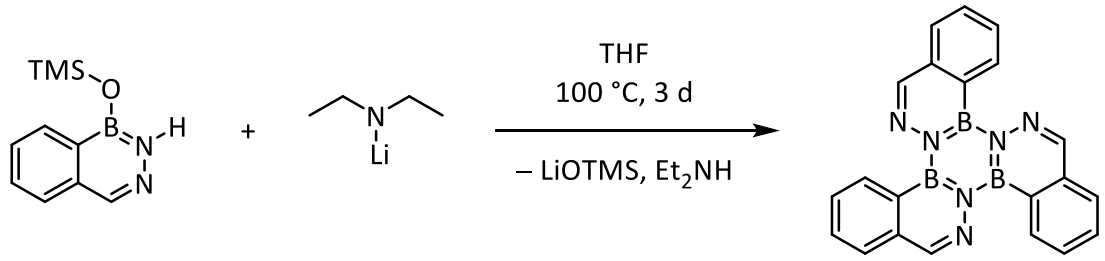


Figure S18. Molecular structure of compound **2H**. Ellipsoids drawn at 50% probability. All H-atoms omitted and methyl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **2H**: B1–N1 1.4253(15), N1–N2 1.3808(13), N2–C1 1.2945(15), C1–C2 1.4489(15), C2–C3 1.4109(15), C3–B1 1.5416(15), C3–C4 1.4074(14), C4–C5 1.3830(16), C5–C6 1.4001(16), C6–C7 1.3808(16), C7–C2 1.4059(15), B1–O1 1.3641(14), C3–B1–O1 123.25(10), C3–B1–N1 114.79(10), O1–B1–N1 121.96(10), N2–N1–B1 126.13(9), B1–N1–N2–C1 1.46(16).

Crystal data:
$C_{10}H_{15}BN_2OSi$, M_r = 218.14, clear colorless plate, 0.240×0.170×0.100 mm^3, orthorhombic space group *Pbca*, a = 8.23510(10) Å, b = 12.22030(10) Å, c = 24.1907(2) Å, V = 2434.44(4) Å^3, Z = 8, ρ_{calcd} = 1.190 g·cm^{-3}, μ = 1.502 mm^{-1}, $F(000)$ = 928, T = 100(2) K, R_1 = 0.0297, wR_2 = 0.0807, 2489 independent reflections [$2\theta \leq 149.916°$] and 143 parameters.

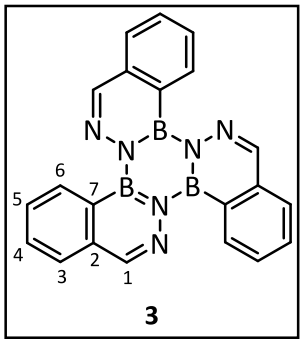
CCDC number: 2425624

Tris(borazaroisoquinoline)borazine (3)



2H **3** (72%)

Compound **2H** (20.0 mg, 91.7 μmol, 1.00 eq.) was dissolved in tetrahydrofuran (0.5 mL) in a J.-Young-style NMR tube and lithium diethylamide (7.25 mg, 91.7 μmol, 1.00 eq.) was added at ambient temperature in a glovebox. A slow color change from colorless to yellow was observed and after a few minutes, the reaction mixture turned cloudy. The suspension was then heated to 100 °C for 3 d, during which a voluminous, colorless solid formed and the reaction mixture turned colorless again. In a glovebox, the supernatant was removed via glass pipette and the obtained colorless voluminous solid was washed with cold tetrahydrofuran (1 × 1 mL), *n*-pentane (2 × 1 mL) and dried *in vacuo*. **Yield:** 8.40 mg (21.9 μmol, 72%) of a colorless, voluminous solid.



3

Crystalline material of **3** could not be obtained, despite attempts in various solvents (CH_2Cl_2, $CHCl_3$, CH_3CN, bromobenzene) due to the compounds' poor solubility as result of extensive π-π stacking. **^{1}H NMR** (500 MHz, 298 K, C*D*Cl_3): δ = 9.85 (d, $^3J_{HH}$ = 7.99 Hz, 3H, *H*-3), 8.72 (s, 3H, *H*-1), 7.79-7.86 (m, 9H, *H*-4 + *H*-5 + *H*-6) ppm. **^{11}B{^{1}H} NMR** (160 MHz, 298 K, C*D*Cl_3): δ = 30.5 (br s, $\Delta\nu_{½}$ = 575 Hz) ppm.**^{13}C{^{1}H} NMR** (126 MHz, 298 K, C*D*Cl_3): δ = 146.2 (*C*-1), 138.0 (*C*-3), 134.8 (C_q-2), 131.9 (*C*-5), 130.1 (*C*-6), 127.7 (*C*-4) ppm.*[1] **HRMS** (LIFDI, CH_2Cl_2): expected: m/z 383.1668, 384.1632, 385.1665 $[C_{21}H_{15}B_3N_6]^+$; found: m/z 383.1670, 384.1634, 385.1665 $[C_{21}H_{15}B_3N_6]^+$. **IR** (ATR, 24 scans, powder) $\tilde{\nu}$ = 1477 (w), 1444 (w), 1410 (w), 1395 (w), 1308 (w), 987 (br, s), 792 (w), 775 (w), 751 (w), 675 (w), 579 (w), 440 (br, s) cm^{-1}. **Raman** (Nd/YAG, resolution 4 cm^{-1}, powder) $\tilde{\nu}$ = 3031 (w, br), 1615 (m), 1593 (m), 1544 (s), 1469 (w), 1440 (w), 1305 (w), 1228 (s), 1120 (w), 1043 (w), 981 (w), 925 (w), 785 (w), 652 (w), 569 (w), 493 (w), 303 (w), 268 (w), 241 (w), 125 (s) cm^{-1}.

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*[1] The carbon atoms C_q^B-7 adjacent to the boron atom were not detected in the ^{13}C{^{1}H} NMR spectra due to quadrupole broadening by the boron nucleus.

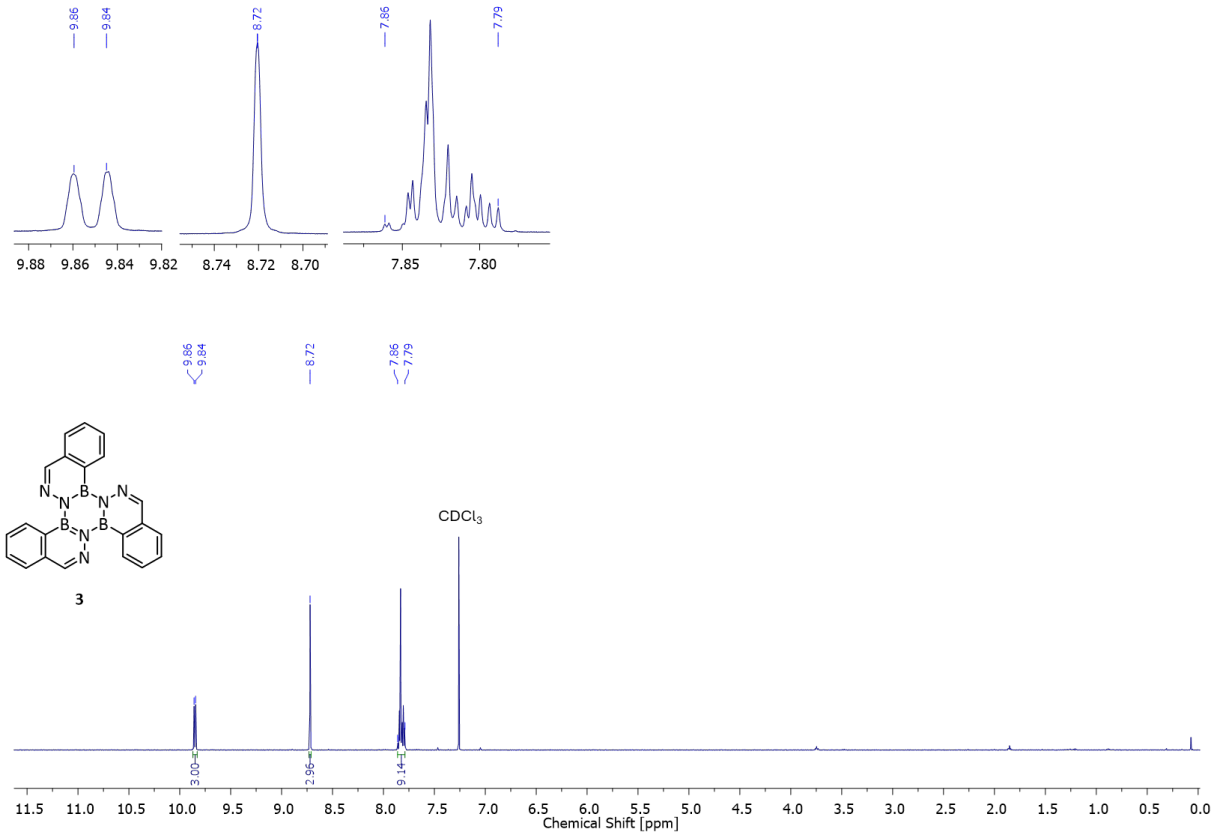


Figure S19. ^{1}H NMR spectrum of compound **3** in C*D*Cl$_3$.

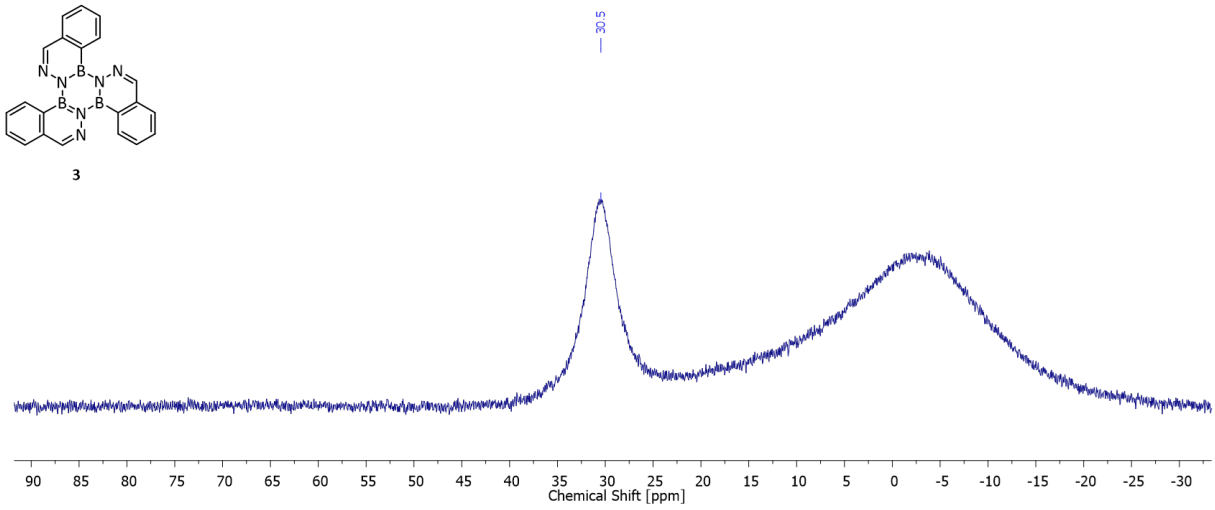


Figure S20. Background reduced ^{11}B{^{1}H} NMR spectrum of compound **3** in C*D*Cl$_3$.

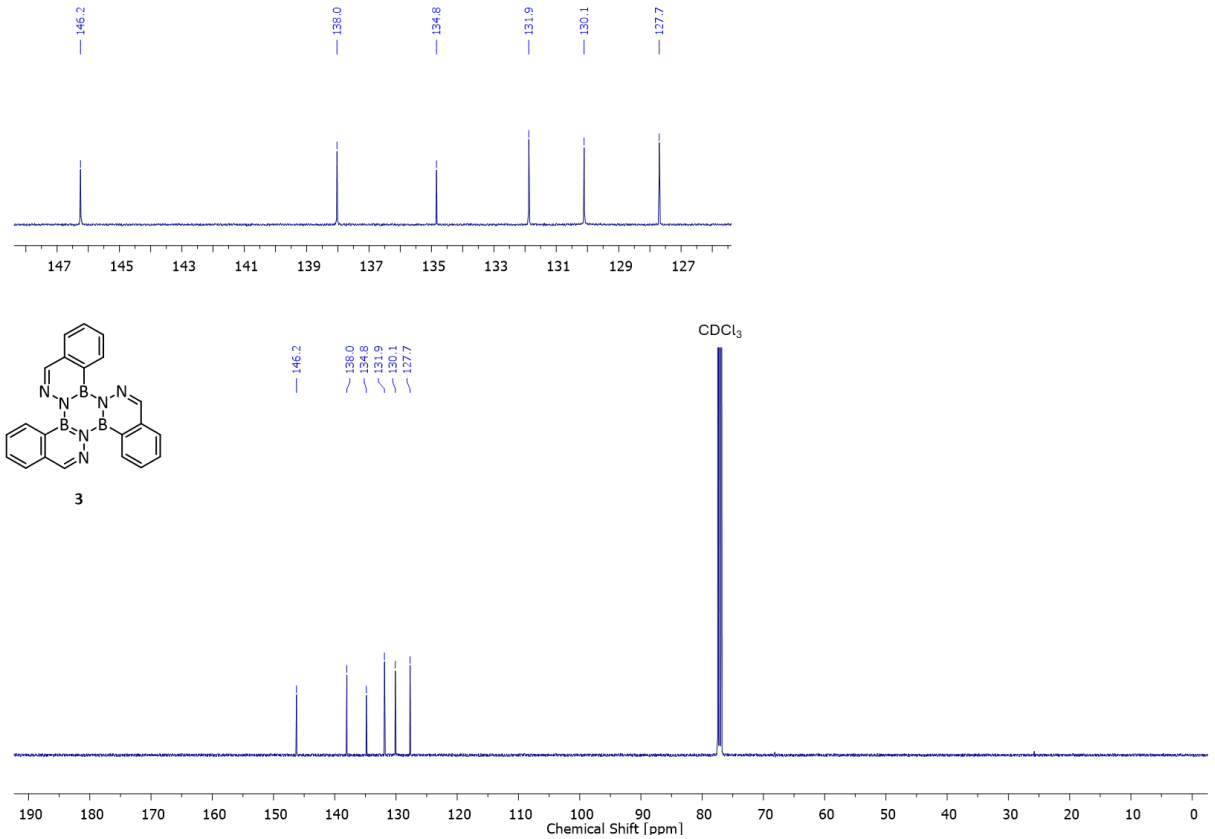


Figure S21. ^{13}C NMR spectrum of compound **3** in C*D*Cl$_3$.

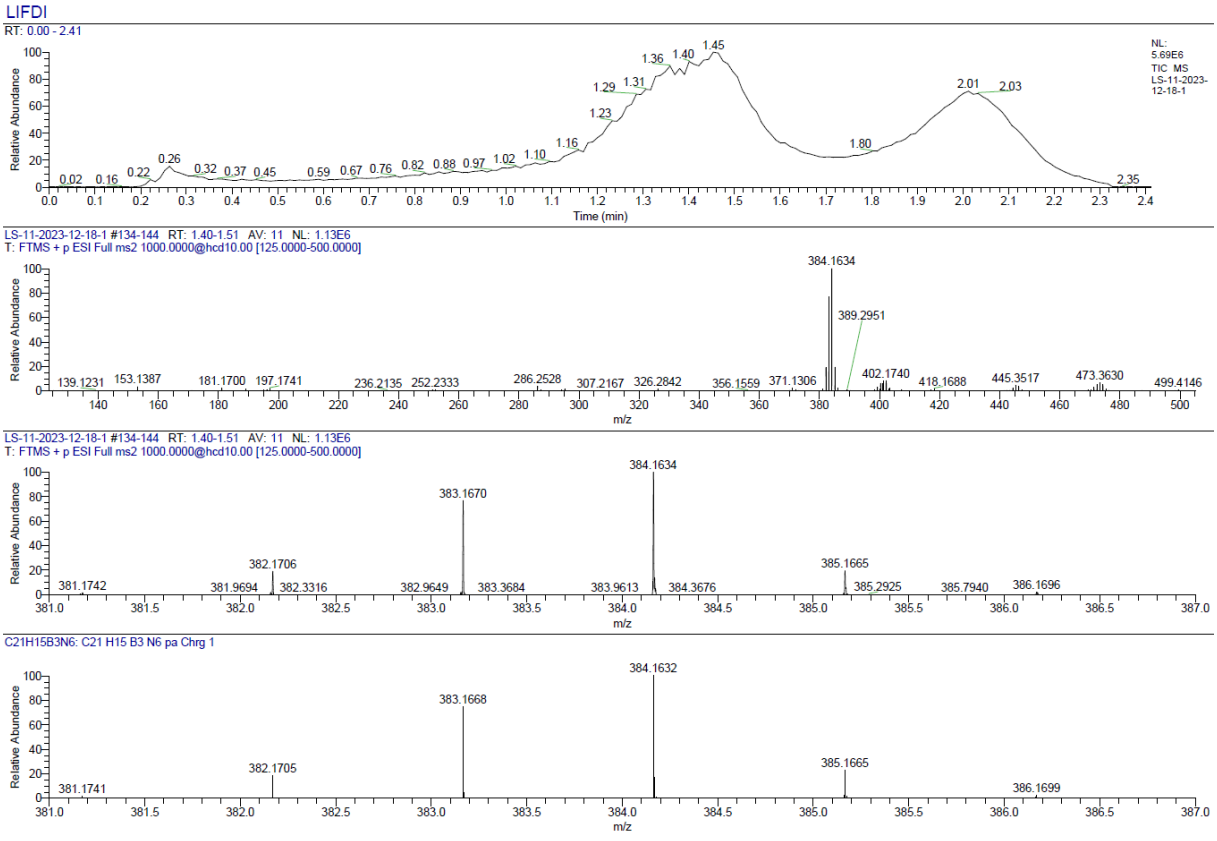


Figure S22. LIFDI high resolution mass spectrum of compound **3** (CH_2Cl_2).

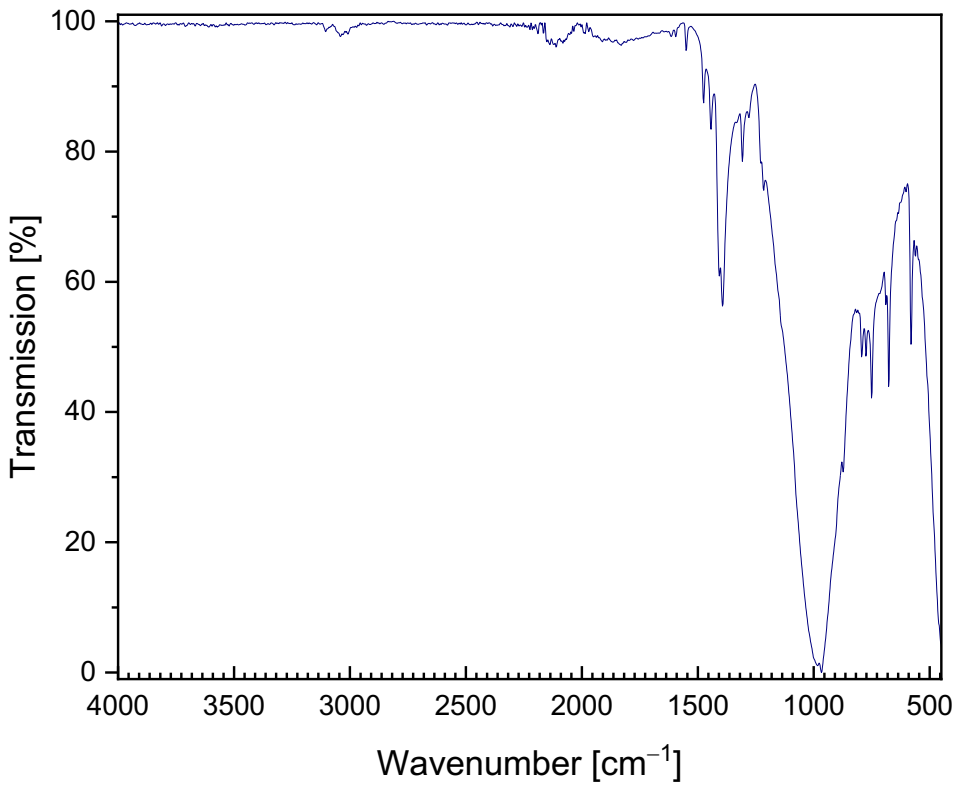


Figure S23. Standardized infrared spectrum of compound **3** (powder).

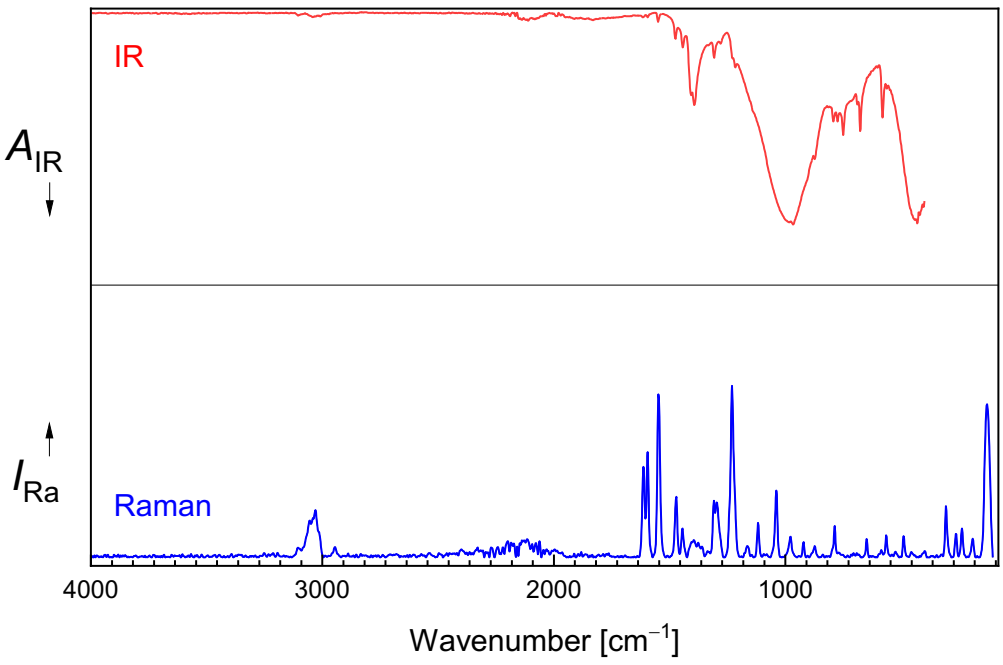
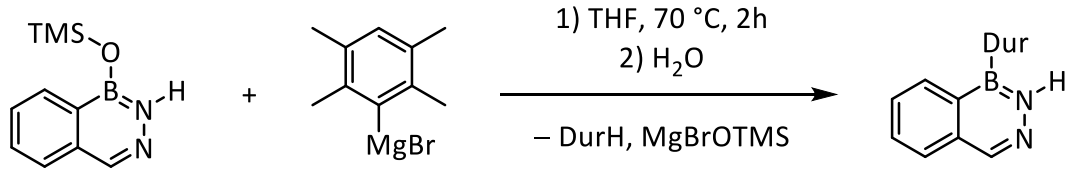


Figure S24. Infrared spectrum (red) and Raman spectrum (blue) of compound **3** (powder).

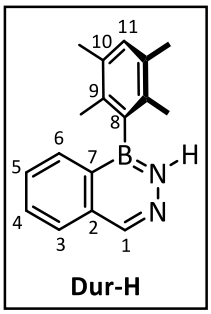
4-(2,3,5,6-Tetramethylphenyl)-4,3-borazaroisoquinoline (6H)



2H **6H** (97%)

Magnesium turnings (457 mg, 18.8 mmol, 4.10 eq.) were placed in a 500 mL three-neck flask equipped with a reflux condenser and bubbler under Ar atmosphere and heated *in vacuo* for several minutes. The magnesium turnings were layered with dry tetrahydrofuran (5 mL). Three drops of 1,2-dibromoethane were added without stirring and the suspension was carefully heated with a heat gun until the activation of the magnesium turnings was observed. 1-Bromo-2,3,5,6-tetramethylbenzene (3.91 g, 18.3 mmol, 4.00 eq.) was dissolved in dry tetrahydrofuran (150 mL) in a 200 mL Schlenk tube and added dropwise to the suspension of activated magnesium turnings under slow stirring. The dropping speed was adapted accordingly, and the reaction mixture carefully heated with a heat gun for a few seconds to ensure an ongoing reaction. After complete addition, the slightly brown suspension was refluxed for 2 h, until most of the magnesium turnings were consumed. The solution was filtered into a 500 mL Schlenk tube. In another 200 mL Schlenk tube, compound **2H** (1.00 g, 4.58 mmol, 1.00 eq.) was dissolved in tetrahydrofuran (20 mL), and the Grignard solution was added at 0 °C (ice bath) dropwise. An immediate color change from colorless to orange was observed. After 10 min, the cooling bath was removed, and the reaction mixture was refluxed for 2 h at 70 °C. After 2 h, the reaction was quenched with ice under continuous Ar flow. A color change from orange to yellow and the precipitation of a colorless solid was observed. Ethyl acetate (200 mL) and brine (40 mL) were added, and the two phases were transferred into a separating funnel. The aqueous layer was extracted with ethyl acetate (2 × 100 mL). The combined organic layers were washed with distilled water (3 × 100 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. The obtained colorless solid was purified via sublimation at 55 °C at $1.1 \cdot 10^{-2}$ mbar using a sublimation finger for the separation of 1,2,4,5-tetramethylbenzene. While this procedure yields **6H** in sufficient purity (94% ^{1}H NMR purity), better results for the subsequent deprotonation reaction were obtained, when **6H** was additionally was purified via column chromatography (aluminum oxide (Act. I), *n*-hexane : ethyl acetate 4:1; R_f(**6H**) = 0.50). **Yield:** 1.17 g (4.46 mmol, 97%) of a colorless solid. The compound is air- and moisture-stable.

Crystalline material of **6H** as colorless blocks for single-crystal XRD was obtained by slow evaporation of a saturated diethyl ether solution at ambient temperature. **^{1}H NMR** (600 MHz, 298 K, CD_2Cl_2): δ = 9.42 (s, 1H, N-*H*), 8.43 (s, 1H, *H*-1), 7.84 (d, $^{3}J_{HH}$ = 7.86 Hz, 1H, *H*-6), 7.79 (ddd, $^{3}J_{HH}$ = 7.42 Hz, $^{4}J_{HH}$ = 1.34 Hz, 1H, *H*-5), 7.73 (d, $^{3}J_{HH}$ = 6.84 Hz, 1H, *H*-3), 7.58 (ddd, $^{3}J_{HH}$ = 7.22 Hz, $^{4}J_{HH}$ = 1.16 Hz, 1H, *H*-4), 7.00 (s, 1H, *H*-11), 2.24 (s, 6H, *m*-CH_3), 1.98 (s, 6H, *o*-CH_3) ppm. **^{11}B NMR** (193 MHz, 298 K, CD_2Cl_2): δ = 36.9 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, CD_2Cl_2): δ = 143.9 (*C*-1), 138.0 (br s, C_q^B-8), 136.6 (C_q-9), 135.6 (br s, C_q^B-7), 134.6 (*C*-3), 133.7 (C_q-2), 133.5 (C_q-10), 132.1 (*C*-5), 131.9 (*C*-11), 129.7 (*C*-4), 127.9 (*C*-6), 20.1 (*o*-CH_3), 19.8 (*m*-CH_3) ppm. **HRMS** ($ASAP_{pos}$, toluene): expected: m/z 263.1714, 264.1748 $[C_{17}H_{19}BN_2+H]^+$; found: m/z 263.1709, 264.1743 $[C_{17}H_{19}BN_2+H]^+$. **IR** (ATR, 32 scans, powder): $\tilde{\nu}$= 3248 (m, *N–H*), 3195 (w), 3150 (m), 3095 (w), 3068 (m), 3009 (m), 2985 (m), 2958 (m), 2919 (m), 2856 (w), 1975 (w), 1946 (w), 1814 (w), 1781 (w), 1722 (w), 1618 (w), 1597 (m), 1563 (m), 1497 (w), 1459 (m), 1424 (s), 1397 (w), 1367 (m), 1334 (m), 1310 (s), 1261 (w), 1236 (m), 1218 (w), 1189 (m), 1159 (w), 1126 (w), 1093 (w), 1061 (w), 1012 (w), 957 (m), 885 (m), 823 (m), 789 (s), 759 (s), 643 (m), 598 (m), 563 (w), 523 (m), 504 (m), 484 (w), 443 (w) cm^{-1}.



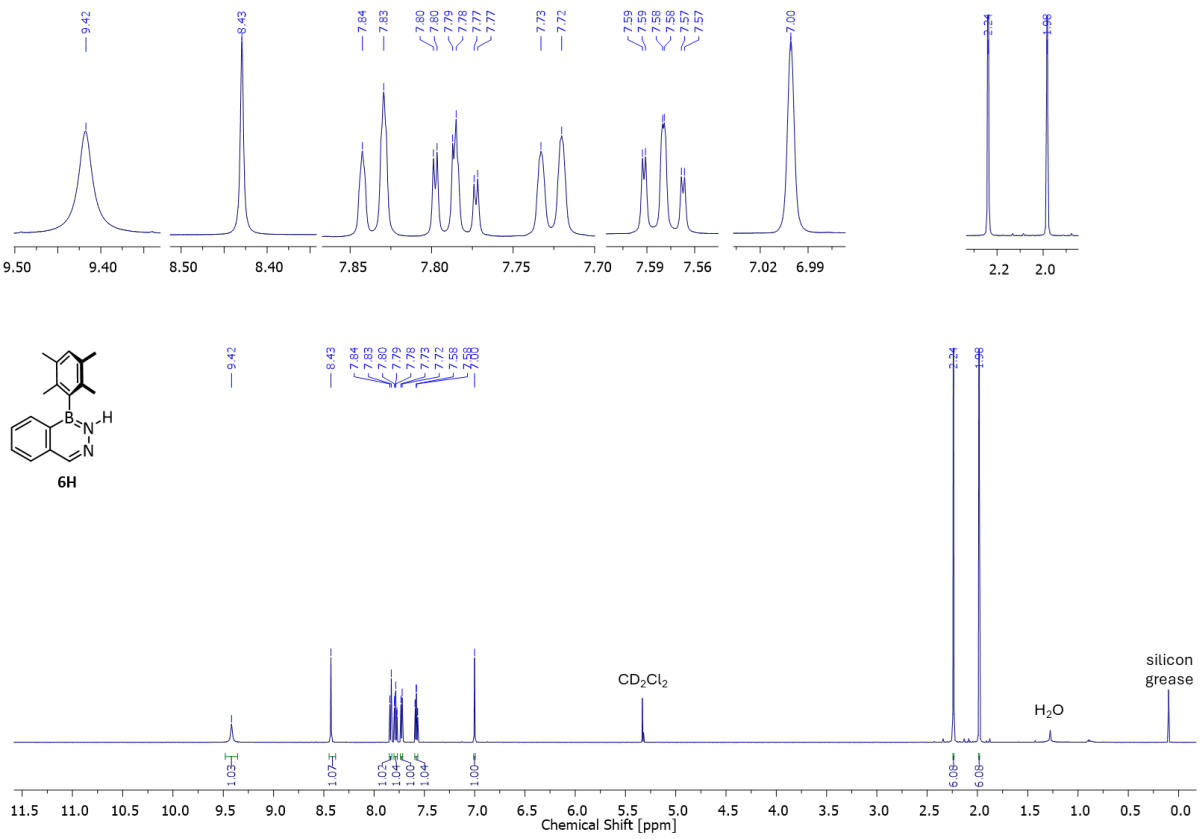


Figure S25. ^{1}H NMR spectrum of compound **6H** in CD_2Cl_2.

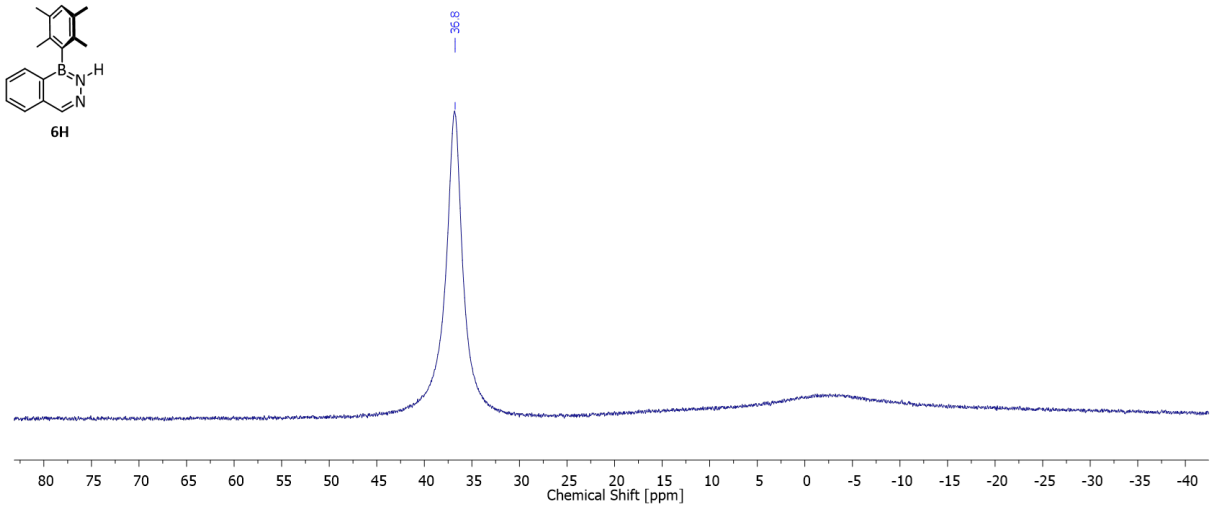


Figure S26. Background reduced ^{11}B NMR spectrum of compound **6H** in CD_2Cl_2.

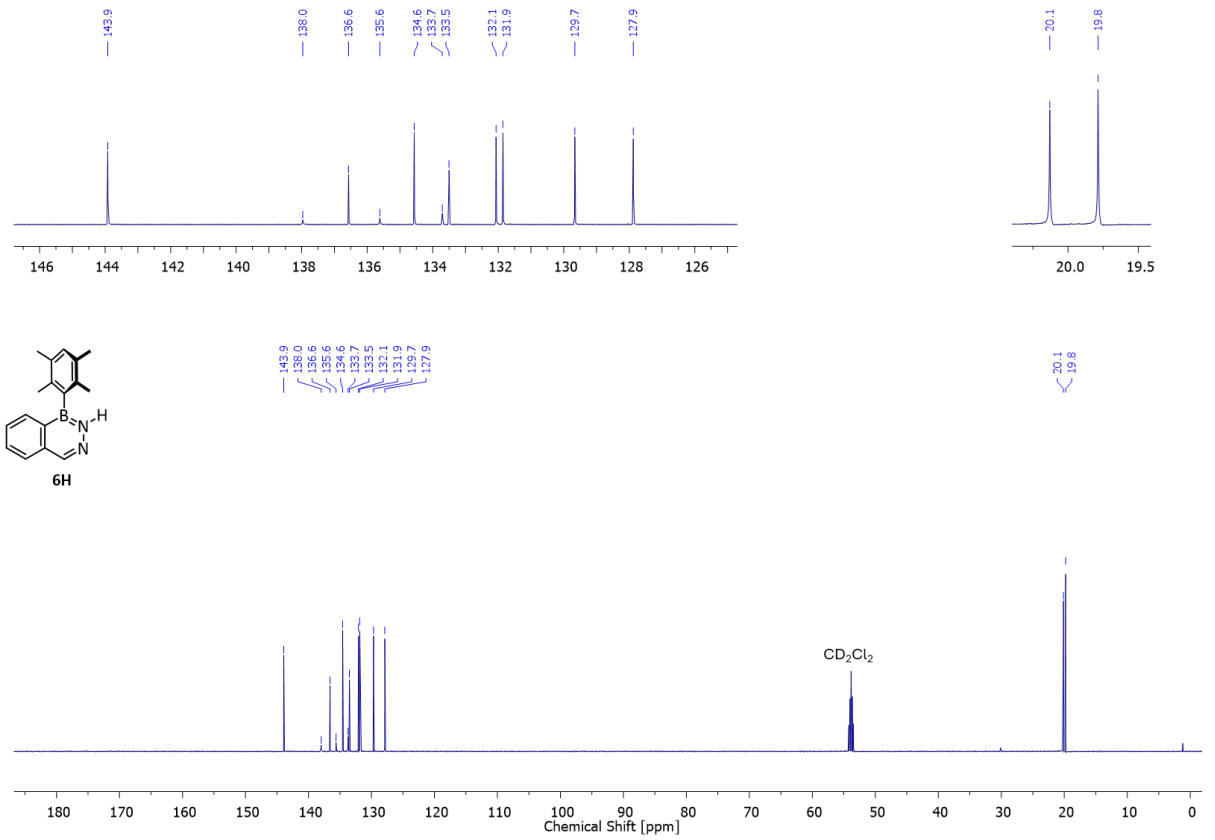


Figure S27. $^{13}C\{^1H^{11}B\}$ NMR spectrum of compound **6H** in CD_2Cl_2 (selectively ^{11}B-decoupled at +38 ppm).

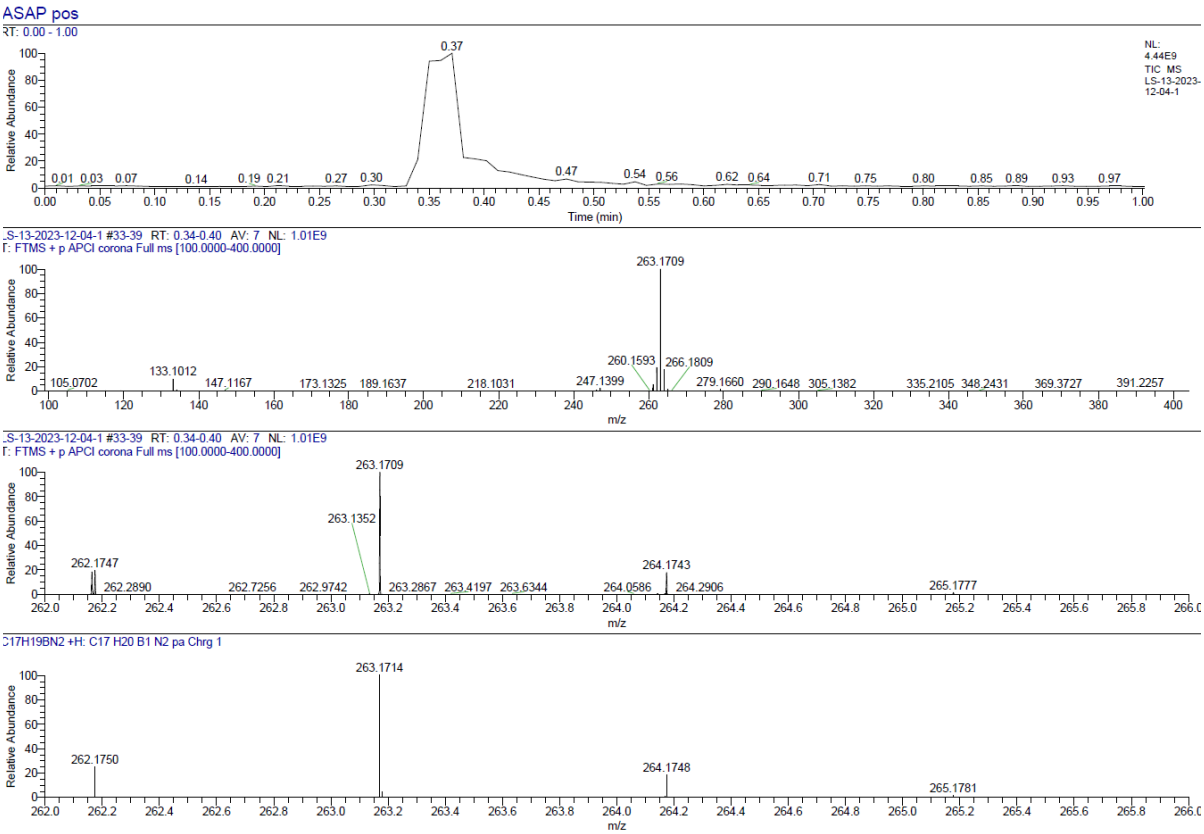


Figure S28. ASAP$_{pos}$ high resolution mass spectrum of compound **6H** (toluene).

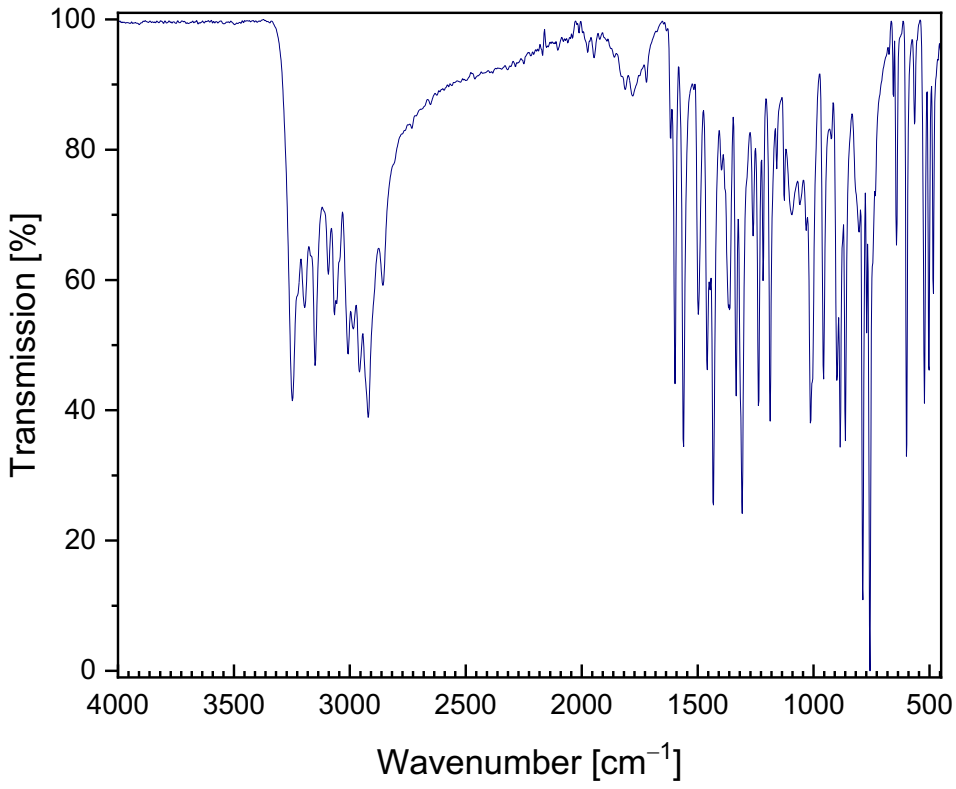


Figure S29. Normalized infrared spectrum of compound **6H** (powder).

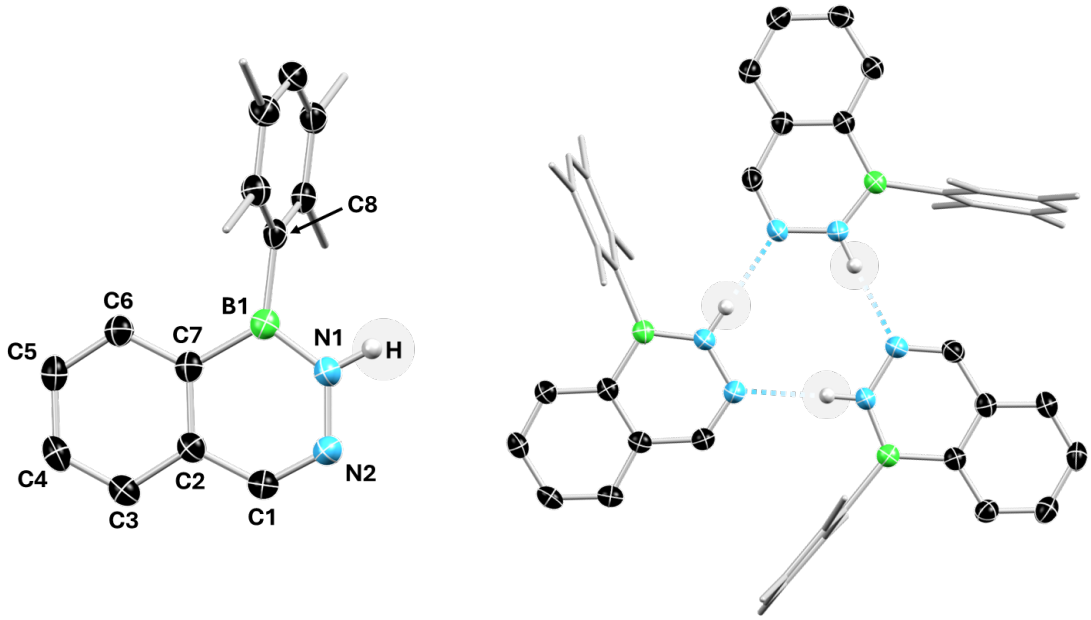


Figure S30. Molecular structure of compound **6H** (left). Trimerization of compound **6H** in via intermolecular hydrogen bridges (right). Ellipsoids drawn at 50% probability. All H-atoms omitted, duryl and methyl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6H**: B1–N1 1.400(3), N1–N2 1.375(2), N2–C1 1.296(3), C1–C2 1.441(3), C2–C3 1.416(3), C3–B1 1.534(3), C3–C4 1.407(3), C4–C5 1.374(3), C5–C6 1.402(3), C6–C7 1.373(3), C7–C2 1.405(3), B1–C8 1.580(3), C3–B1–C8 126.09(18), C3–B1–N1 114.77(18), C8–B1–N1 119.13(7), C1–N2–N1–B1 0.5(3).

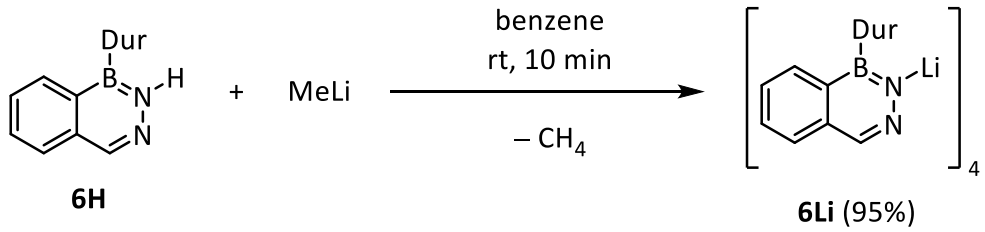
Crystal data:
$C_{17}H_{19}BN_2$, M_r = 262.15, colorless needle, 0.340×0.070×0.050 mm^3, triclinic space group $P\bar{1}$, a = 12.2579(1) Å, b = 14.7917(2) Å, c = 14.9932(3) Å, α = 119.224(2)°, β = 97.468(1)°, γ = 92.874(1)°, V = 2331.99(7) Å^3, Z = 6, ρ_{calcd} = 1.120 g·cm^{-3}, μ = 0.496 mm^{-1}, $F(000)$ = 840, T = 100(2) K, R_1 = 0.0716, wR_2 = 0.1973, 9136 independent reflections [$2\theta \leq 150.364°$] and 553 parameters.

The reflections [5 -5 3], [0 4 3] and [0 -4 8] were removed from refinement as outliers.

CCDC number: 2425628

3-Lithium-4-(2,3,5,6-tetramethylphenyl)-borazaroisoquinoline (6Li)

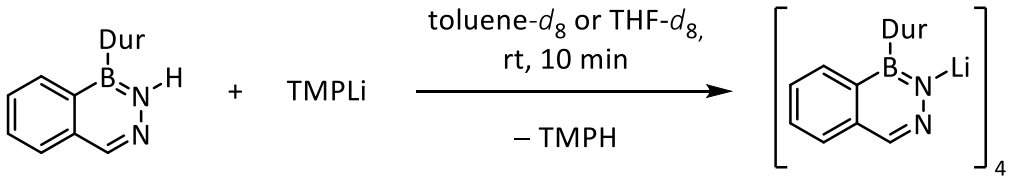
Isolation method:



6H **6Li** (95%)

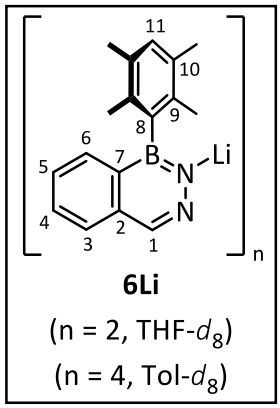
Compound **6H** (15.0 mg, 57.2 *µ*mol, 1.00 eq.) was suspended in benzene-d_6 (0.5 mL) in a J.-Young-style NMR tube and $MeLi(OEt_2)_{0.8}$ powder (4.65 mg, 57.2 µmol, 1.00 eq.) was added at ambient temperature in a glovebox. After 10 min, the suspension was filtrated using a glass pipette equipped with a glass fibre filter and subsequently, all volatile components were removed *in vacuo*. **Yield:** 14.5 mg (54.1 *µ*mol, 95%) of a colorless solid. The compound is air and moisture sensitive.

In-situ method:



6H **6Li** (*in situ*)

Compound **6H** (10.0 mg, 38.1 *µ*mol, 1.00 eq.) was suspended in THF-d_8 or toluene-d_8 (0.5 mL) in a J.-Young-style NMR tube and LiTMP (7.30 mg, 49.6 µmol, 1.30 eq.) was added at ambient temperature in a glovebox. Full conversion to **6Li** was confirmed by ^{1}H and ^{7}Li NMR spectroscopy after 10 min at ambient temperature and the sample was subsequently used for the ^{1}H DOSY NMR experiments.



6Li
(n = 2, THF-d_8)
(n = 4, Tol-d_8)

Crystalline material of **[6Li]$_4$** as colorless blocks for single-crystal XRD was obtained by was obtained by storing a saturated benzene solution, layered with *n*-pentane at ambient temperature. Crystalline material of **[6Li]$_2$(thf)$_2$** as colorless blocks for single-crystal XRD was obtained by storing a saturated tetrahydrofuran solution at ambient temperature for several weeks. **^{1}H NMR** (600 MHz, 298 K, THF-d_8): δ = 8.64 (s, 1H, *H*-1), 7.54 (d, $^3J_{HH}$ = 8.15 Hz, 1H, *H*-6), 7.43 (app. t, $^3J_{HH}$ = 7.29 Hz, 1H, *H*-5), 7.39 (d, $^3J_{HH}$ = 7.56 Hz, 1H, *H*-3), 7.23 (t, $^3J_{HH}$ = 7.16 Hz, 1H, *H*-4), 6.81 (s, 1H, *H*-11), 2.19 (s, 6H, *m*-CH_3), 1.96 (s, 6H, *o*-CH_3) ppm. **^{7}Li NMR** (233 MHz, 298 K, THF-d_8): δ = 1.3 ppm. **^{11}B NMR** (192 MHz, 298 K, THF-d_8): δ = 37.9 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, THF-d_8): δ = 147.6 (br s, C_q^B-8), 143.7 (*C*-1),

136.6 (C_q-9), 134.8 (br s, C_q^B-7), 133.8 (C_q-2), 133.6 (*C*-3), 132.1 (C_q-10), 129.8 (*C*-11), 128.7 (*C*-4), 126.8 (*C*-5), 126.2 (*C*-6), 20.3 (*o*-CH_3), 20.0 (*m*-CH_3) ppm. **HRMS** ($ASAP_{neg}$, solid): expected: m/z 260.1605, 261.1569, 262.1602 $[C_{17}H_{18}BN_2]^-$ (monomer); found: m/z 260.1606, 261.1568, 262.1597 $[C_{17}H_{18}BN_2]^-$. **IR** (ATR, 32 scans, powder): $\tilde{\nu}$= 2973 (w), 2924 (w), 2865 (w), 2242(w), 2106 (w), 1463 (m), 1428 (w), 1385 (w), 1371 (w), 1301 (m), 1268 (w), 1235 (s), 1180 (m), 1097 (m), 1034 (s), 968 (s), 956 (s), 888 (w), 861 (w), 836 (m), 754 (s), 647 (s), 606 (s), 587 (s), 524 (s) cm^{-1}.

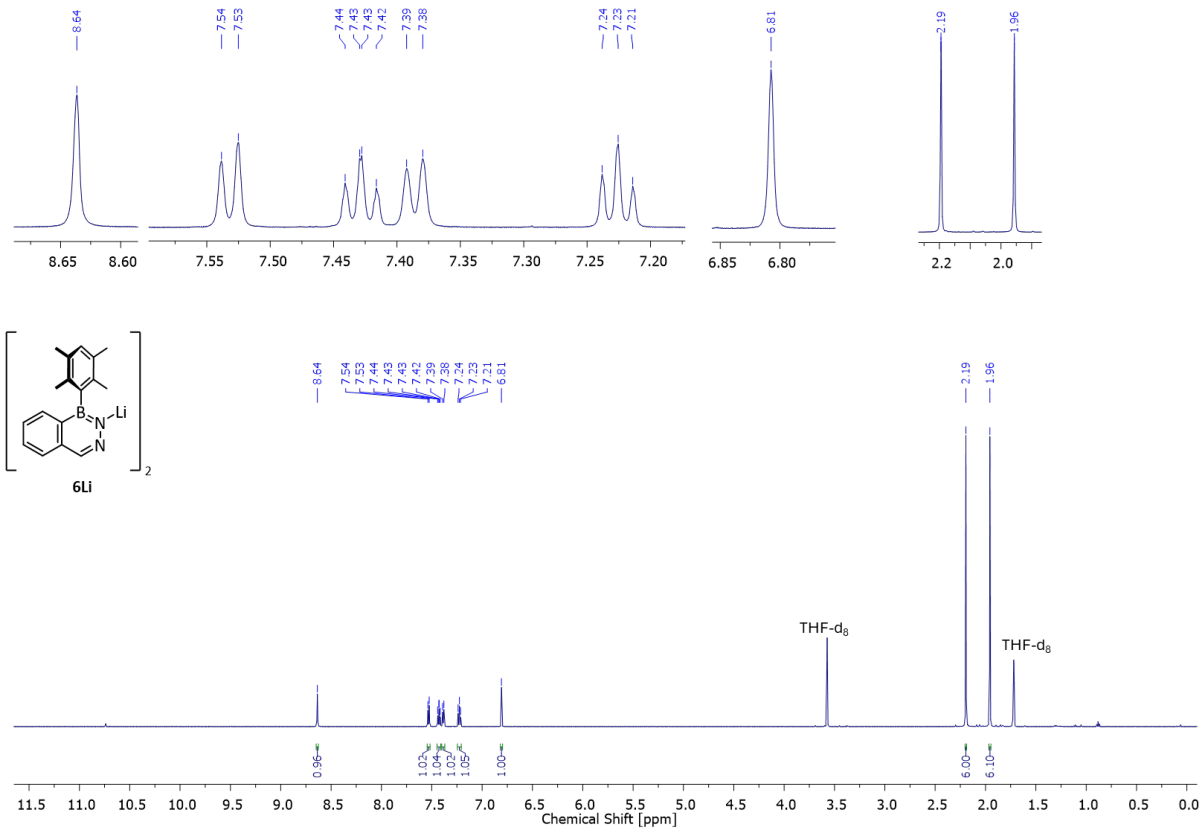


Figure S31. ^{1}H NMR spectrum of isolated compound **6Li** in THF-d_8.

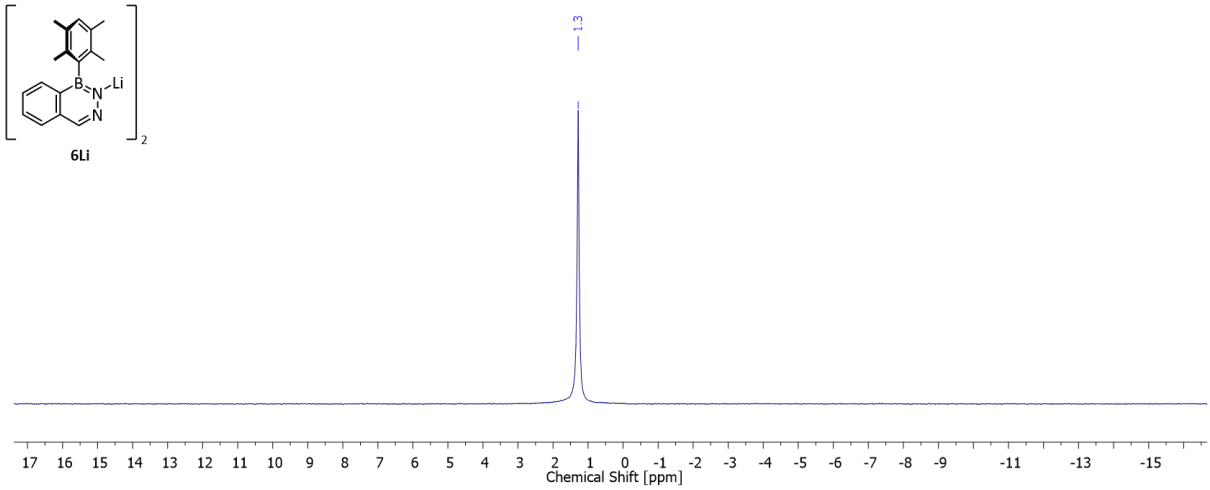


Figure S32. ^{7}Li NMR spectrum of isolated compound **6Li** in THF-d_8.

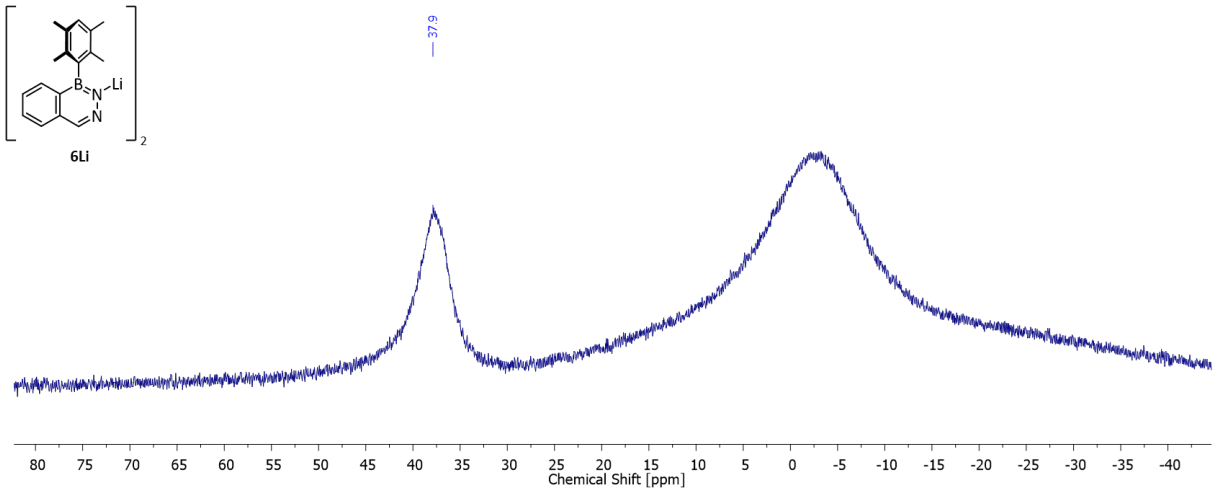


Figure S33. Background-reduced ^{11}B NMR spectrum of isolated compound **6Li** in THF-d_8.

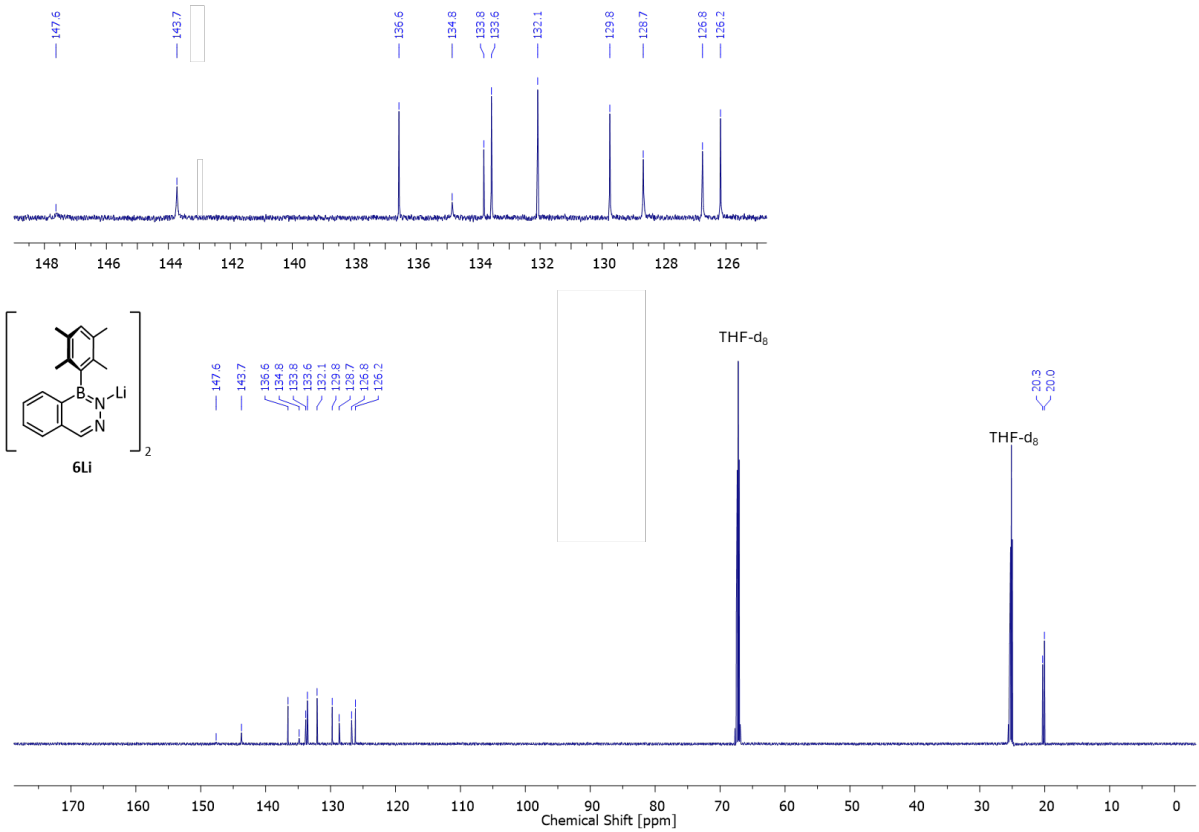


Figure S34. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of isolated compound **6Li** in THF-d_8 (selectively ^{11}B-decoupled at +38 ppm).

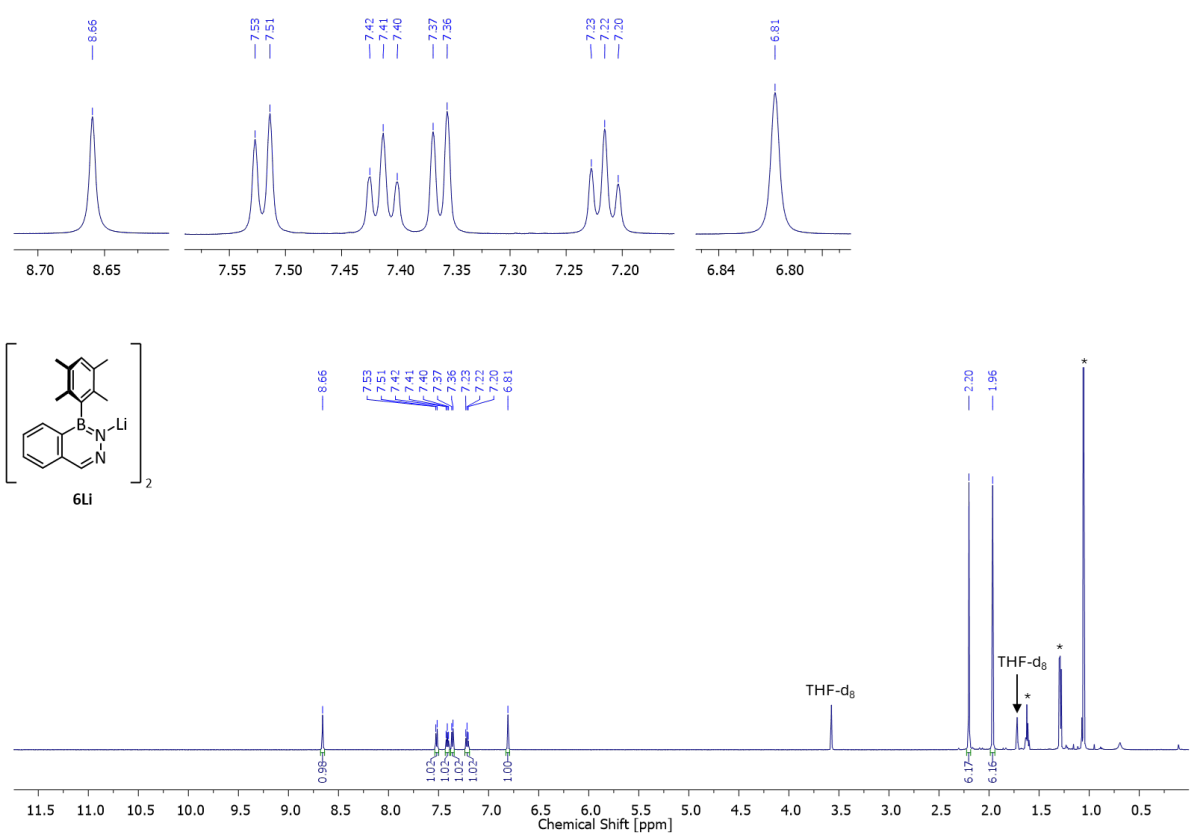


Figure S35. *In-situ* ^{1}H NMR spectrum of compound **6Li** in THF-d_8 used for ^{1}H DOSY NMR. Marked resonances correspond to TMPH.

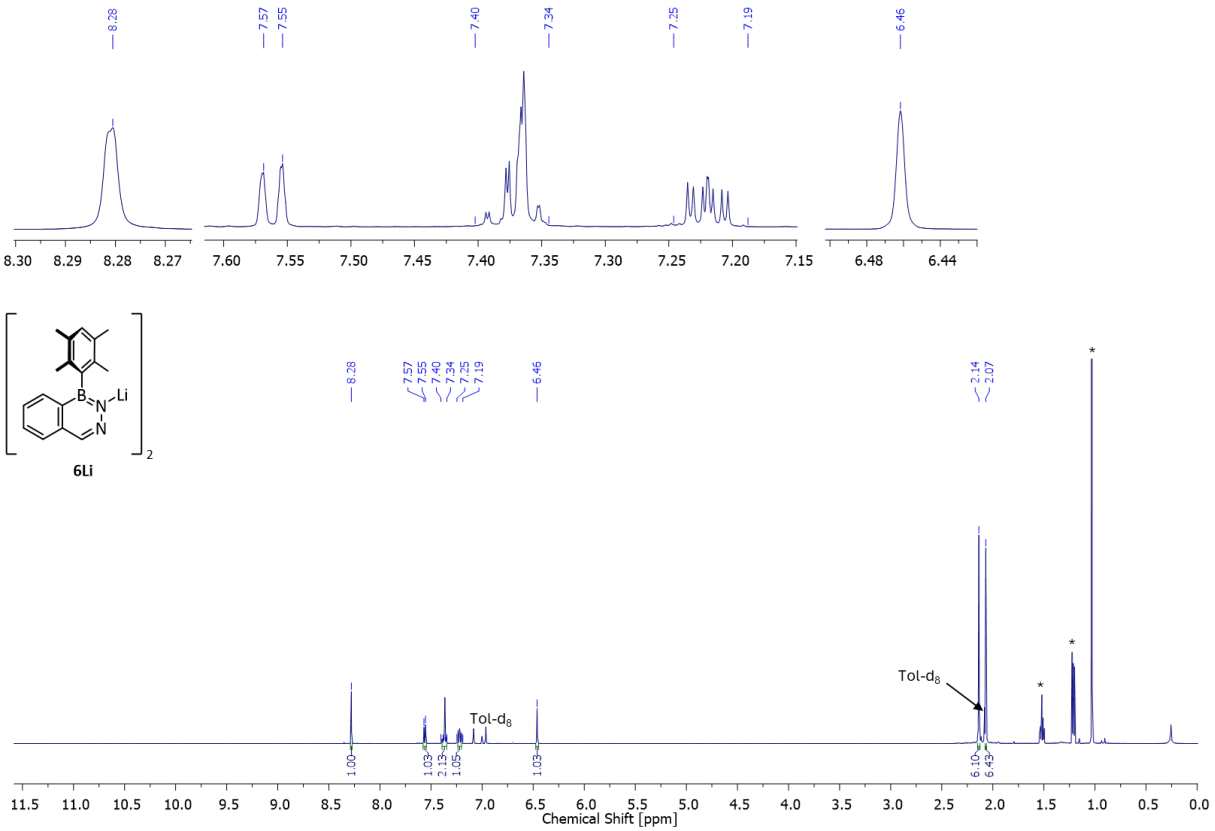


Figure S36. *In-situ* ^{1}H NMR spectrum of compound **6Li** in toluene-d_8. Marked resonances correspond to TMPH.

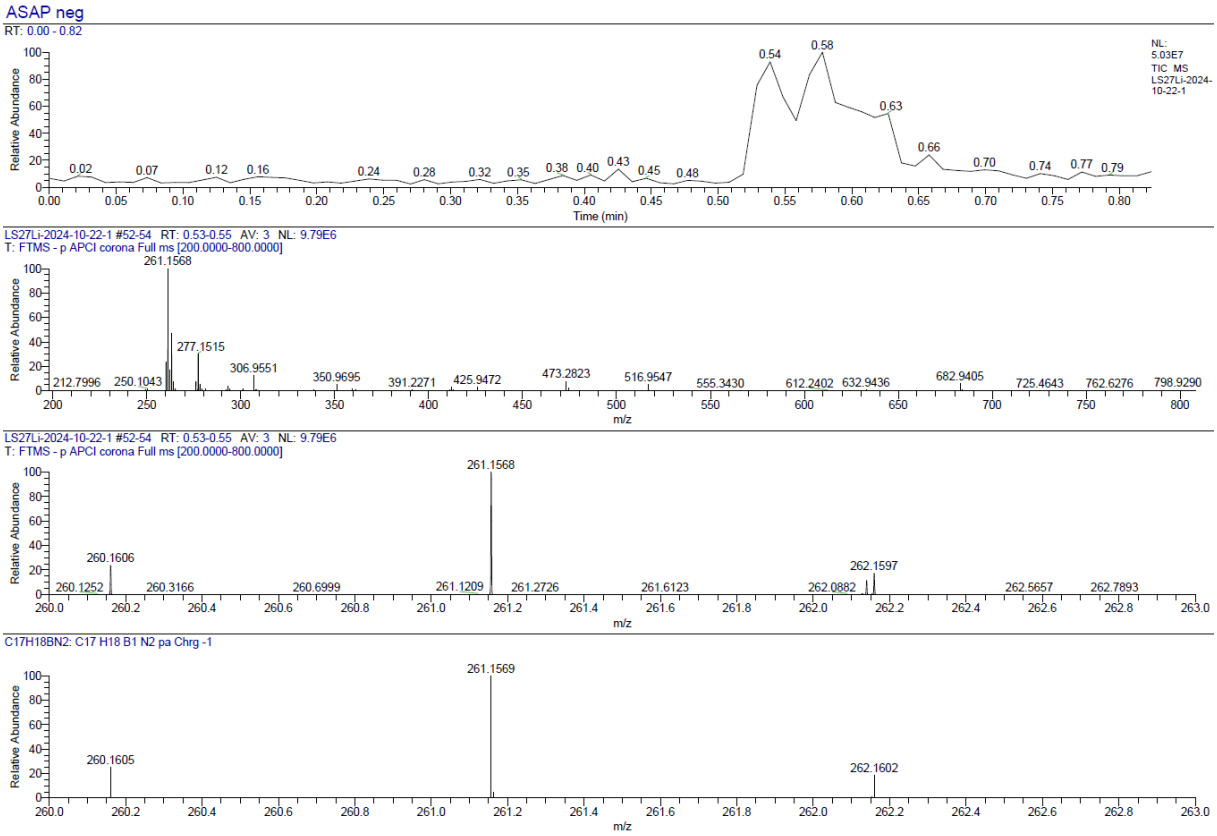


Figure S37. ASAP$_{neg}$ high resolution mass spectrum of compound **6Li** (solid).

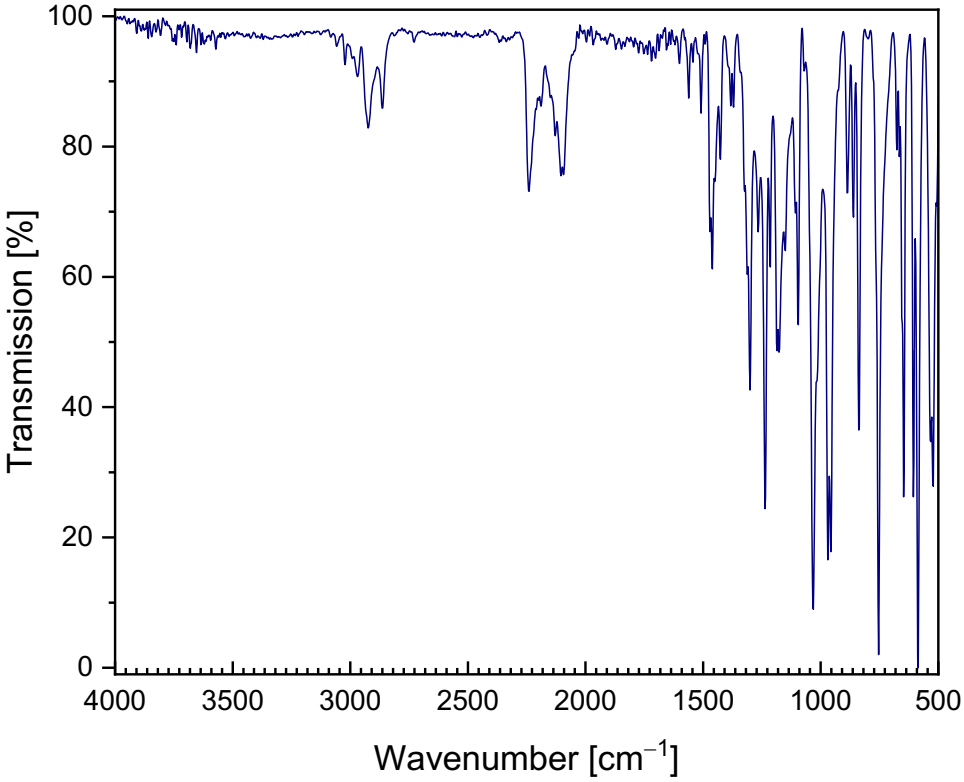


Figure S38. Normalized infrared spectrum of compound **6Li** (powder).

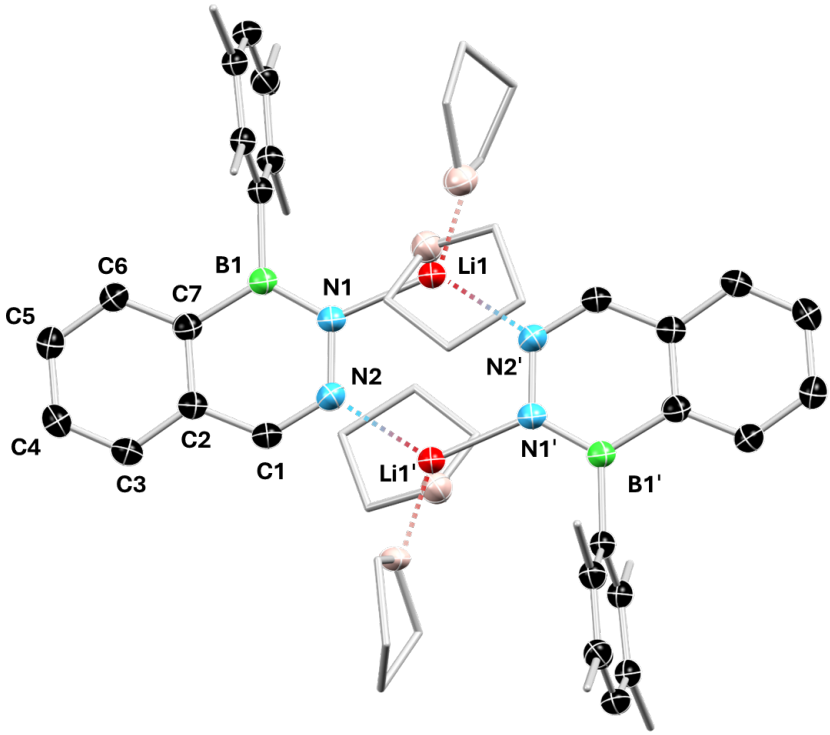


Figure S39. Molecular structure of compound **6Li** (dimer) in THF. Ellipsoids drawn at 50% probability. All H-atoms omitted, complexing THF and methyl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6Li**: B1–N1 1.422(3), N1···Li1 2.000(3), N2···Li1' 2.077(4), N1–N2 1.380(2), N2–C1 1.315(3), B1–N1–N2–C1 1.6(3), Li1···N1···N2···Li1' 42.8(2).

Crystal data:
$C_{50}H_{68}B_2Li_2N_4O_4$, M_r = 824.58, clear colorless block, 0.280×0.100×0.060 mm^3, triclinic space group *P*1, *a* = 12.1298(1) Å, *b* = 14.7250(2) Å, *c* = 19.7956(2) Å, α = 89.493(1)°, β = 81.215(1)°, γ = 81.463(1)°, *V* = 3455.18(7) Å^3, *Z* = 3, ρ_{calcd} = 1.189 g·cm^{-3}, μ = 0.568 mm^{-1}, *F*(000) = 1332, *T* = 100(2) K, R_1 = 0.0870, wR_2 = 0.2279, 13797 independent reflections [2θ≤150.754°] and 1075 parameters.

Five of the thf molecules were disordered. The atomic displacement parameters of the disordered thf molecule atoms (O1 to C4) were restrained to the same value with similarity restraint SIMU (esd = 0.016) and with 'enhanced rigid bond' restraint RIGU (0.008).Additionally the U_{ii} parameters were restrained with ISOR (esd = 0.004) keyword to approximate isotropic behavior. The 1–2 and 1–3 distances of the disordered thf molecule atoms (O1 to C4) were restrained to the similar values with SAME.

CCDC number: 2425625

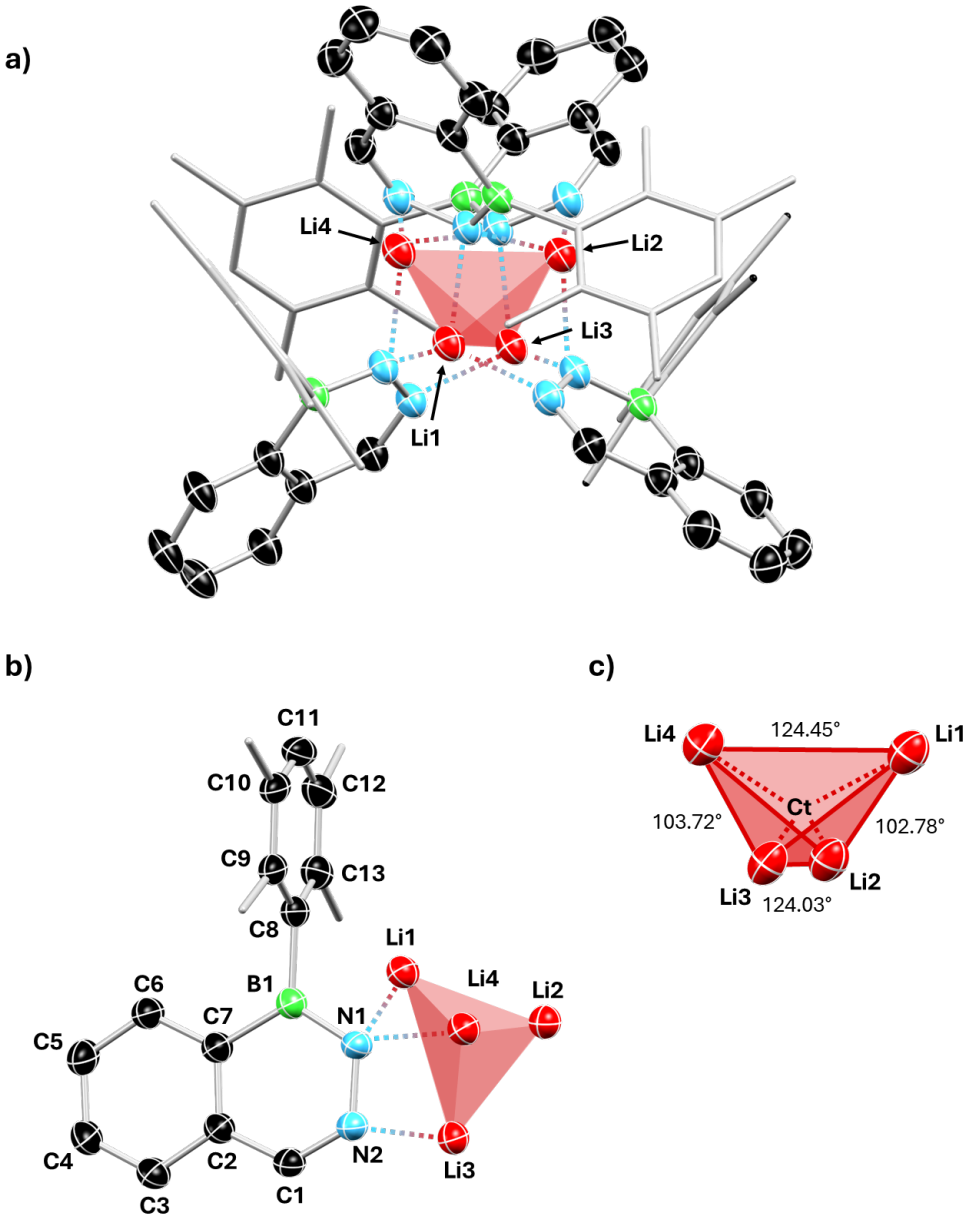


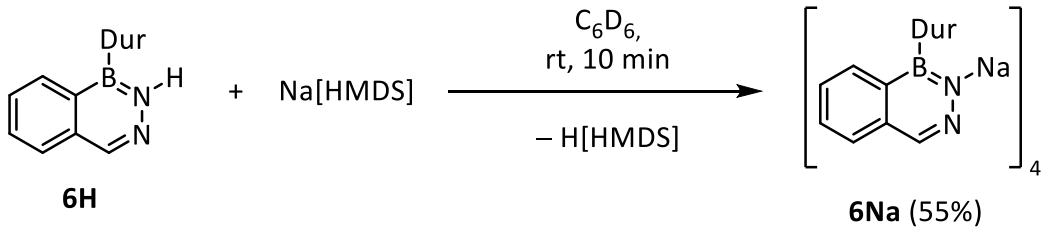
Figure S40. Molecular structure of compound **6Li** (tetramer) in benzene. Ellipsoids drawn at 50% probability. All H atoms omitted, and duryl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6Li**: B1–N1 1.414(2), N1–N2 1.4076(19), N2–C1 1.300(2), N1–Li1 2.068(3), N1–Li4 2.061(3), N1–Li3 2.542(3), N2–Li3 1.985(3), B1–N1–N2–C1 2.3(2), Li1···Li2 3.045(4), Li2···Li3 2.667(4), Li3···Li4 3.020(4), Li4···Li1 2.712(4).

Crystal data:

$C_{79}H_{90}B_4Li_4N_8$, M_r = 1222.58, colorless block, 0.320×0.130×0.080 mm^3, triclinic space group $P\bar{1}$, a = 13.5030(2) Å, b = 14.2330(2) Å, c = 21.0535(2) Å, α = 83.073(1)°, β = 73.678 (1)°, γ = 66.260(1)°, V = 3554.45(9) Å^3, Z = 2, ρ_{calcd} = 1.142 g·cm^{-3}, μ = 0.491 mm^{-1}, $F(000)$ = 1304, T = 100(2) K, R_1 = 0.0671, wR_2 = 0.1604, 13958 independent reflections [$2\theta \leq 150.538°$] and 874 parameters.

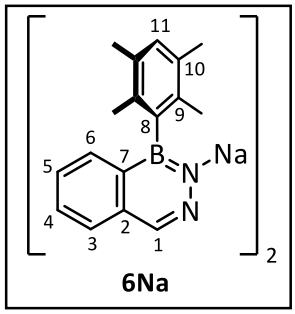
CCDC number: 2425637

3-Sodium-4-(2,3,5,6-tetramethylphenyl)-borazaroisoquinoline (6Na)



6H **6Na** (55%)

Compound **6H** (20.0 mg, 176 μmol, 1.00 eq.) was dissolved in benzene-d_6 (0.5 mL) in a J.-Young-style NMR tube and sodium bis(trimethylsilyl)amide (Na[HMDS], 18.2 mg, 99.2 μmol, 1.30 eq.) was added at ambient temperature in a glovebox. An immediate color change from colorless to yellow and a slight clouding of the reaction solution was observed. After 10 min, the suspension was filtered in a glovebox using a glass pipette equipped with a glass fibre filter. Vapor diffusion of *n*-pentane (0.3 mL) into a saturated benzene solution at ambient temperature resulted in crystallization of compound **6Na**. The supernatant was removed with a glass pipette, and the obtained crystalline solid was dried *in vacuo*. **Yield:** 15.0 mg (42.2 μmol, 55%) of a colorless, crystalline solid.



Crystalline material of **[6Na]$_4$** as colorless blocks for single-crystal XRD was obtained by was obtained by slow vapor diffusion of *n*-pentane into a saturated benzene solution at ambient temperature.*[1] **^{1}H NMR** (600 MHz, 298 K, THF-d_8): δ = 8.69 (s, 2H, *H*-1), 7.50 (d, $^3J_{HH}$ = 7.91 Hz, 2H, *H*-6), 7.40 (dt, $^3J_{HH}$ = 7.40 Hz, $^4J_{HH}$ = 1.33 Hz, 2H, *H*-5), 7.37 (d, $^3J_{HH}$ = 7.15 Hz, 2H, *H*-3), 7.20 (dt, $^3J_{HH}$ = 7.25 Hz, $^4J_{HH}$ = 1.14 Hz, 2H, *H*-4), 6.79 (s, 2H, *H*-11), 2.19 (s, 12H, *m*-C*H*$_3$), 1.96 (s, 12H, *o*-C*H*$_3$) ppm. **^{11}B NMR** (192 MHz, 298 K, THF-d_8): δ = 37.4 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, THF-d_8): δ = 148.2 (br s, C_q^B-8), 144.6 (*C*-1), 136.8 (C_q-9), 134.4 (br s, C_q^B-7), 133.8 (C_q-2), 133.6 (*C*-3), 132.3 (C_q-10), 129.9 (*C*-11), 128.5 (*C*-5), 126.5 (*C*-4), 126.1 (*C*-6), 20.5 (*o*-*C*H$_3$), 20.3 (*m*-*C*H$_3$) ppm. **HRMS** (LIFDI, THF): expected: m/z 284.1461 [$C_{17}H_{18}BNaN_2$]$^+$ (monomer); found: m/z 261.1672, 262.1636, 263.1669 [$C_{17}H_{18}BNaN_2$–Na+H]$^+$. **IR** (ATR, 32 scans, powder): $\tilde{\nu}$= 2963 (w), 2918 (w), 2860 (w), 2117 (w), 1603 (w), 1564 (w), 1504 (w), 1461 (m), 1375 (w), 1301 (m), 1270 (w), 1235 (s), 1214 (w), 1184 (m), 1097 (w), 1027 (s), 951 (s), 884 (m), 861 (m), 836 (m), 773 (s), 643 (m), 606 (s), 577 (s), 524 (s) cm^{-1}.

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*[1] This crystallization method can only be performed with a freshly prepared and filtered solution of **6Na**, as the compound slowly precipitates from benzene.

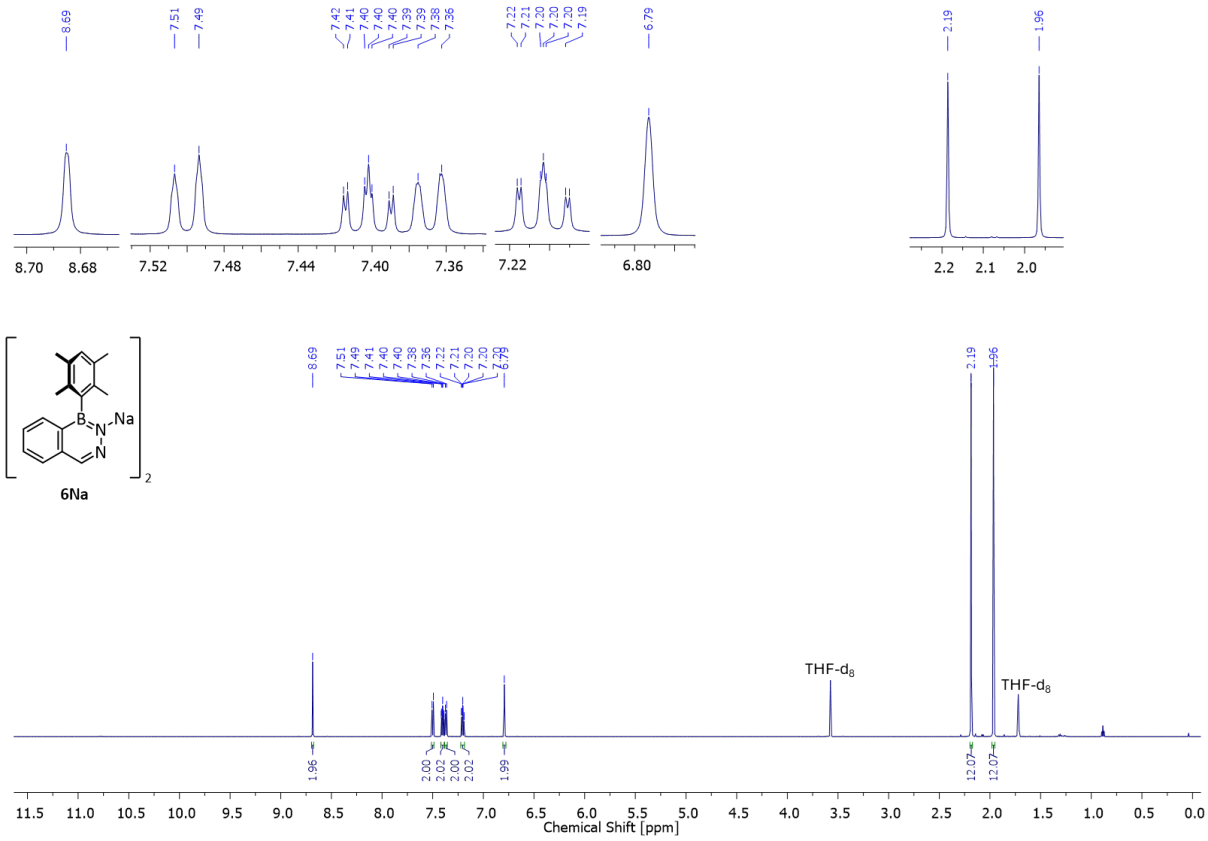


Figure S41. ^{1}H NMR spectrum of compound **6Na** in THF-d_8.

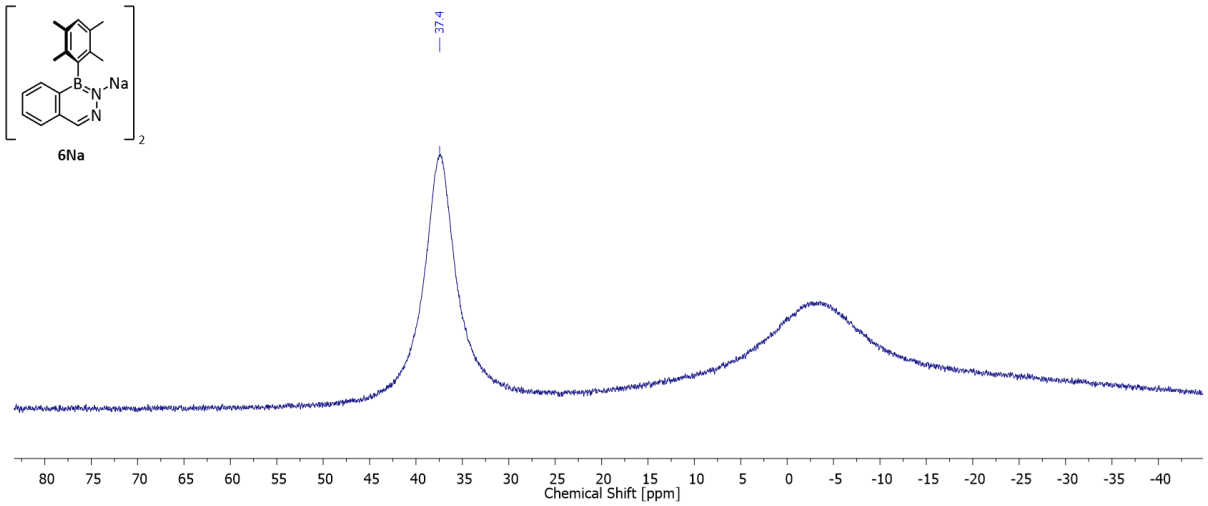


Figure S42. Background reduced ^{11}B NMR spectrum of compound **6Na** in THF-d_8.

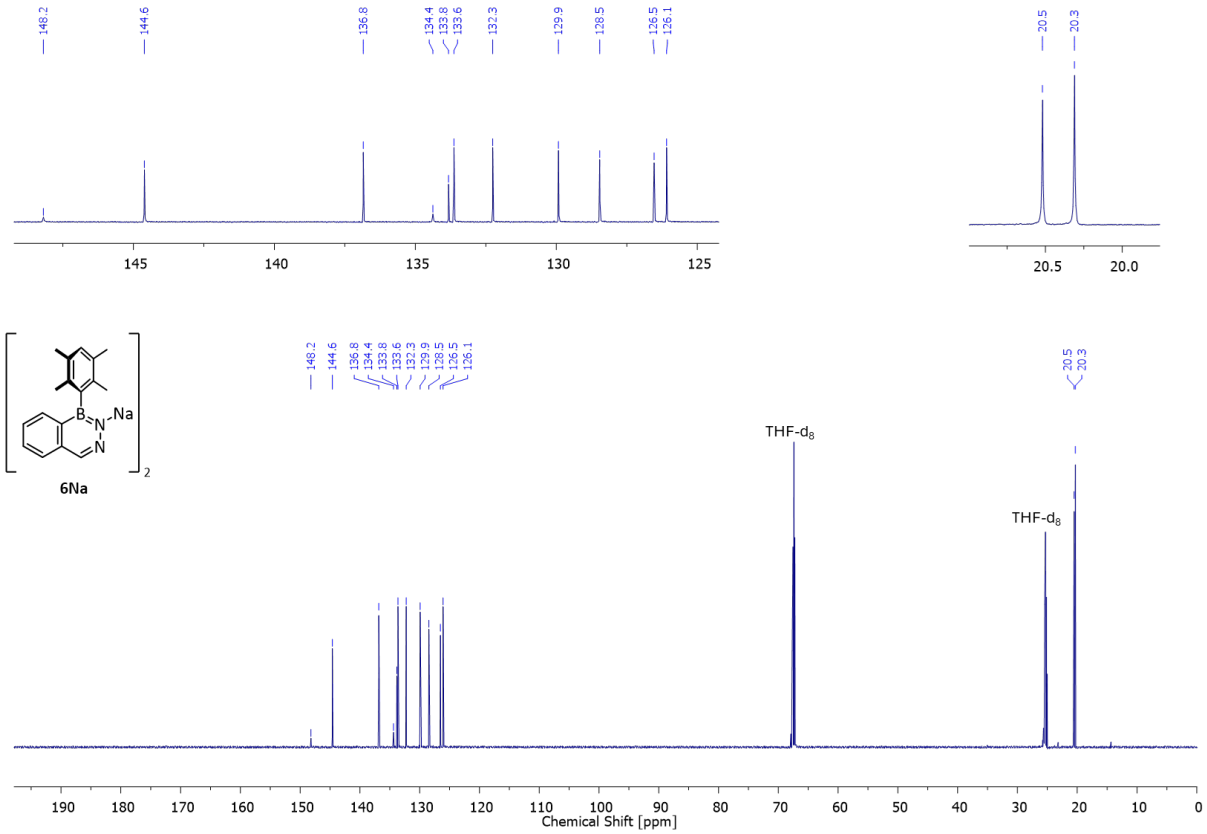


Figure S43. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6Na** in THF-d_8 (selectively ^{11}B-decoupled at +37 ppm).

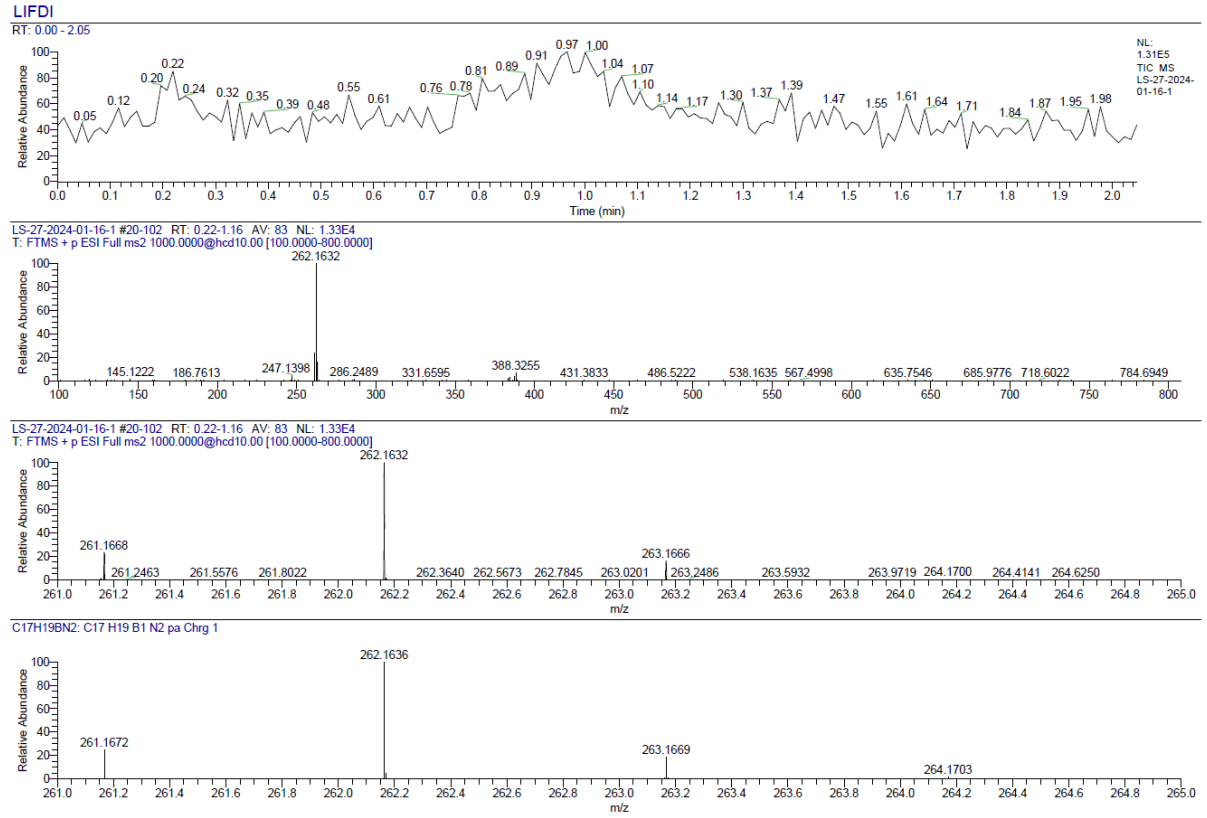


Figure S44. LIFDI high resolution mass spectrum of compound **6Na** (THF), detected as the re-protonated species **6H**.

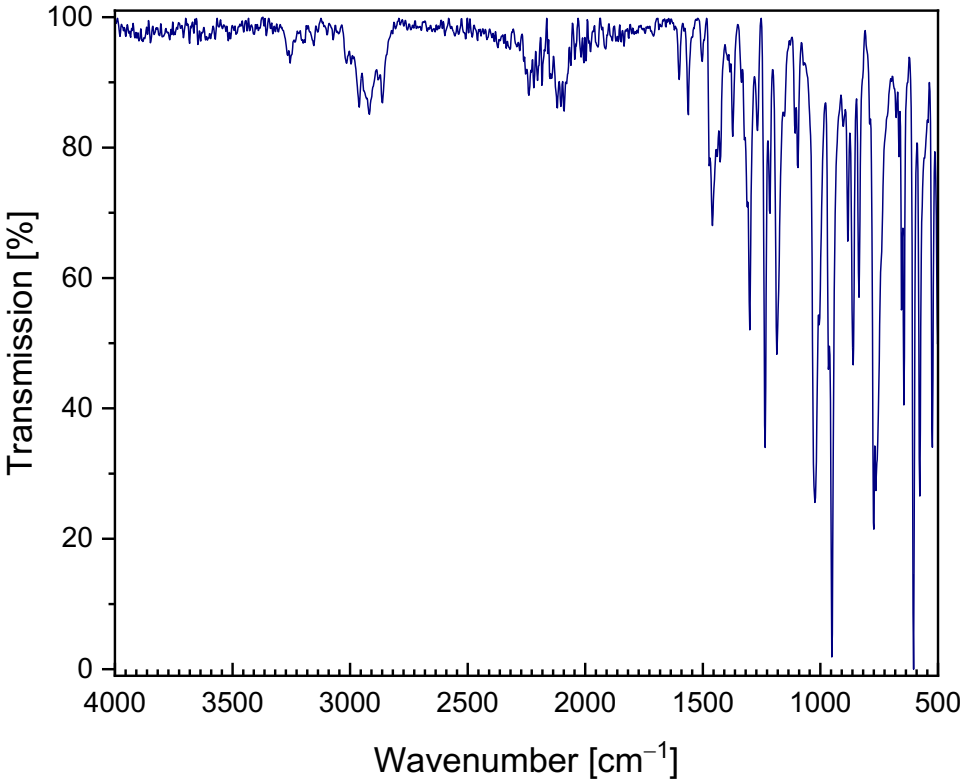


Figure S45. Normalized infrared spectrum of compound **6Na** (powder).

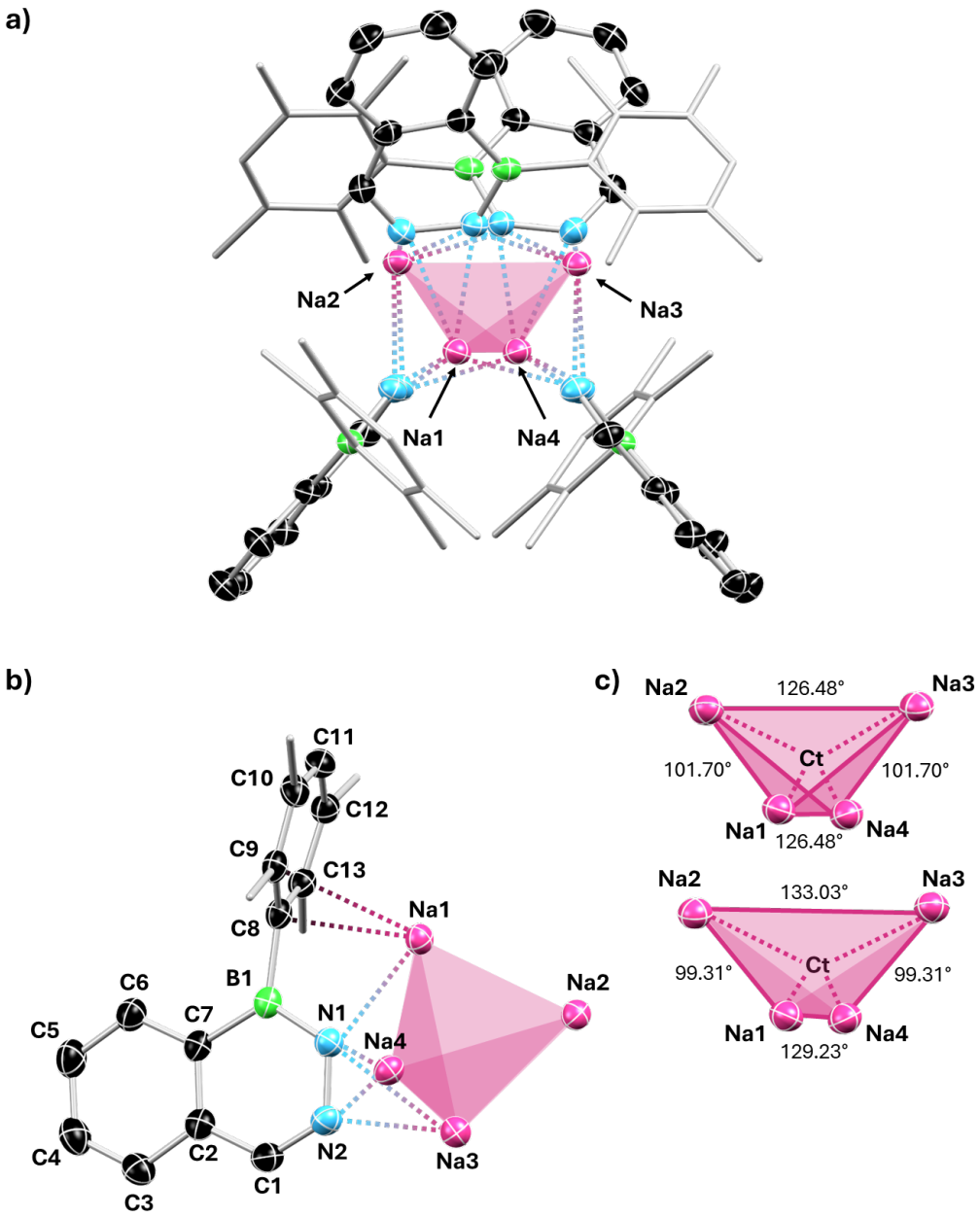


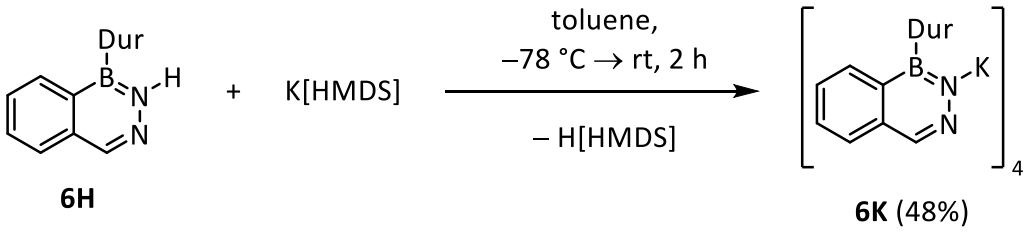
Figure S46. Molecular structure of compound **6Na** (tetramer) in benzene. Ellipsoids drawn at 50% probability. All H atoms omitted, and duryl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6Na**: (A) B1–N1 1.410(3), N1–N2 1.396(3), N2–C1 1.304(3), N1–Na1 2.504(2), N1–Na4 2.483(2), N1–Na3 2.768(2), N2–Na3 2.366(2), N2–Na4 2.666(2), B1–N1–N2–C1 2.8(3), Na···Na 3.1068(15); (B) B1–N1 1.418(3), N1–N2 1.396(3), N2–C1 1.303(3), N1–Na1 2.476(2), N1–Na4 2.943(2), N1–Na3 2.450(2), N2–Na3 2.403(2), N2–Na4 2.539(2), B1–N1–N2–C1 1.6(3), Na···Na 3.1328(14).

Crystal data:
$C_{68}H_{72}B_4N_8Na_4$, M_r = 1136.53, translucent colorless plate, 0.110×0.050×0.040 mm^3, tetragonal space group $P\bar{4}2_1c$, a = 22.5318(1) Å, b = 22.5318(1) Å, c = 24.2167(1) Å, V = 12294.38(12) Å^3, Z = 8, ρ_{calcd} = 1.228 g·cm^{-3}, μ = 0.798 mm^{-1}, F(000) = 4800, T = 100(2) K, R_1 = 0.0379, wR_2 = 0.0972, Flack parameter = 0.50(5), 12558 independent reflections [$2\theta \leq 152.122°$] and 774 parameters.

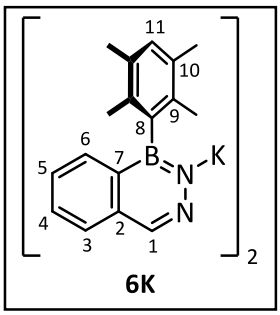
Refined as a two-component inversion twin. The BASF parameter was refined to 49.7%. Some reflections were removed from refinement as outliers.

CCDC number: 2425630

3-Potassium-4-(2,3,5,6-tetramethylphenyl)-borazaroisoquinoline (6K)



Compound **6H** (400 mg, 1.53 mmol, 1.00 eq.) was suspended in toluene (5 mL) in a 50 mL Schlenk tube. In a separate 50 mL Schlenk tube, potassium bis(trimethylsilyl)amide (K[HMDS], 396 mg, 1.98 mmol, 1.30 eq.) was dissolved in toluene (2 mL) and slowly added dropwise at −78 °C (*i*PrOH/CO_2) to the suspension of **6H**. The suspension was stirred for 5 min at −78 °C, during which a brief clearing, followed by subsequent re-clouding was observed. After 5 min, the cooling bath was removed, and the suspension was stirred at room temperature for 16 h. Subsequently, the supernatant was removed via filter cannulation and the remaining solid was washed with toluene (1 × 3 mL), *n*-pentane (2 × 3 mL) and dried *in vacuo*. **Yield:** 220 mg (734 μmol, 48%) of a colorless solid.



Crystalline material of **[6K]$_4$** as colorless blocks for single-crystal XRD was obtained by was obtained by slow vapor diffusion of *n*-pentane into a saturated benzene solution at ambient temperature.*[1] **^{1}H NMR** (600 MHz, 298 K, THF-d_8): δ = 8.72 (s, 2H, *H*-1), 7.47 (d, $^3J_{HH}$ = 7.63 Hz, 2H, *H*-6), 7.34-7.38 (m, 4H, *H*-5 + *H*-3), 7.16 (t, $^3J_{HH}$ = 7.16 Hz, 2H, *H*-4), 6.78 (s, 2H, *H*-11), 2.18 (s, 12H, *m*-CH_3), 1.96 (s, 12H, *o*-CH_3) ppm. **^{11}B NMR** (193 MHz, 298 K, THF-d_8): δ = 37.3 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, THF-d_8): δ = 149.3 (br s, C_q^B-8), 144.1 (*C*-1), 136.7 (C_q-9), 134.0 (br s, C_q^B-7), 133.8 (C_q-2), 133.5 (*C*-3), 132.2 (C_q-10), 129.8 (*C*-11), 128.1 (*C*-5), 126.1 (*C*-4), 125.9 (*C*-6), 20.5 (*o*-CH_3), 20.3 (*m*-CH_3) ppm. **HRMS** (LIFDI, THF): expected: m/z 300.1200 $[C_{17}H_{18}BKN_2]^+$ (monomer); found: m/z 261.1672, 262.1636, 263.1669 $[C_{17}H_{18}BKN_2–K+H]^+$. **IR** (ATR, 32 scans, powder): $\tilde{\nu}$= 2961 (w), 2923 (w), 2865 (w), 1689 (w), 1601 (w), 1562 (w), 1469 (w), 1453 (w), 1424 (w), 1383 (w), 1319 (m), 1299 (m), 1268 (w), 1235 (m), 1214 (w), 1184 (m), 1003 (w), 951 (s), 879 (w), 861 (w), 758 (s), 643 (m), 602 (s), 575 (m), 524 (m) cm^{-1}.

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*[1] This crystallization method can only be performed with a freshly prepared and filtered solution of **6K**, as the compound slowly precipitates from benzene.

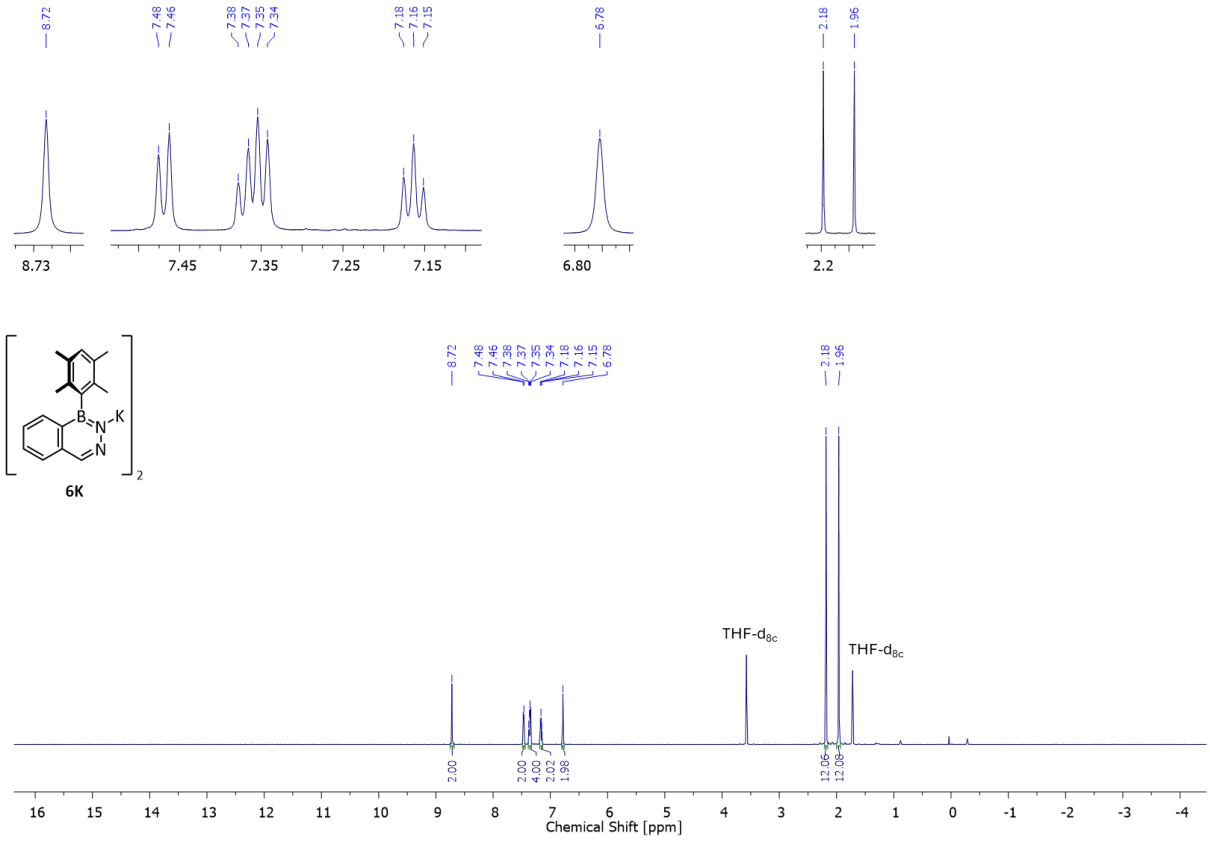


Figure S47. ^{1}H NMR spectrum of compound **6K** in THF-d_8.

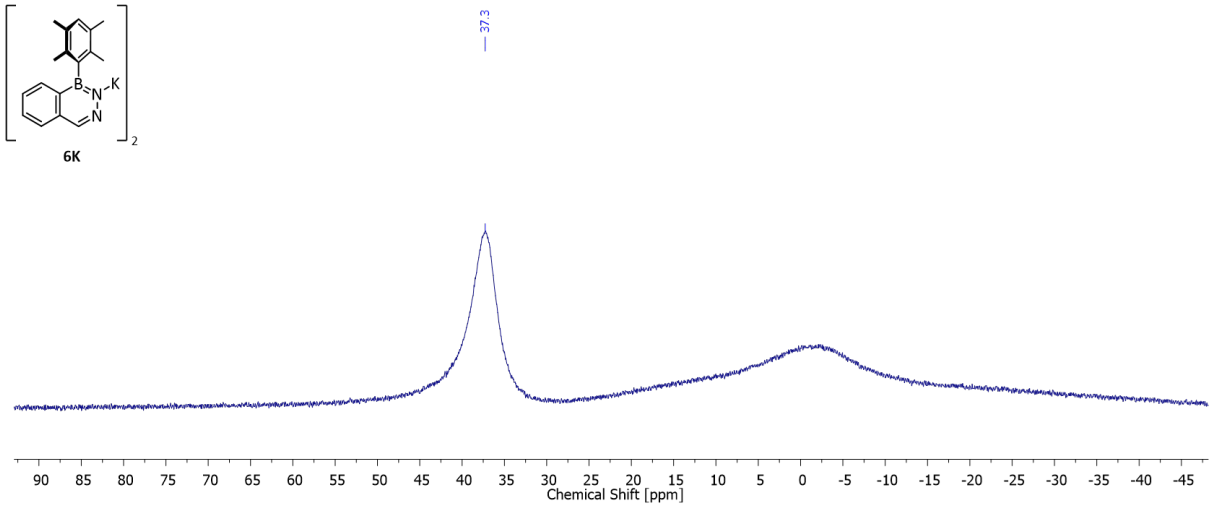


Figure S48. Background-reduced ^{11}B NMR spectrum of compound **6K** in THF-d_8.

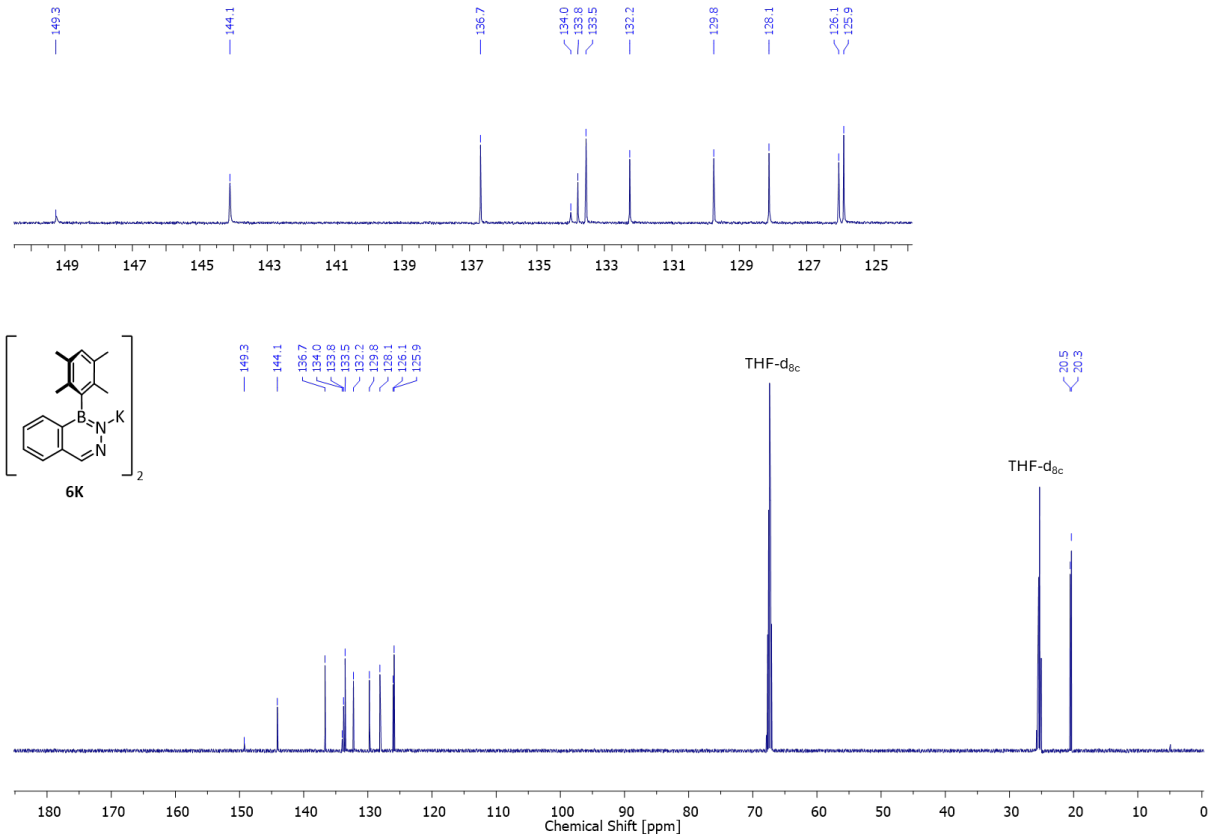


Figure S49. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6K** in THF-d_8 (selectively ^{11}B-decoupled at +37 ppm).

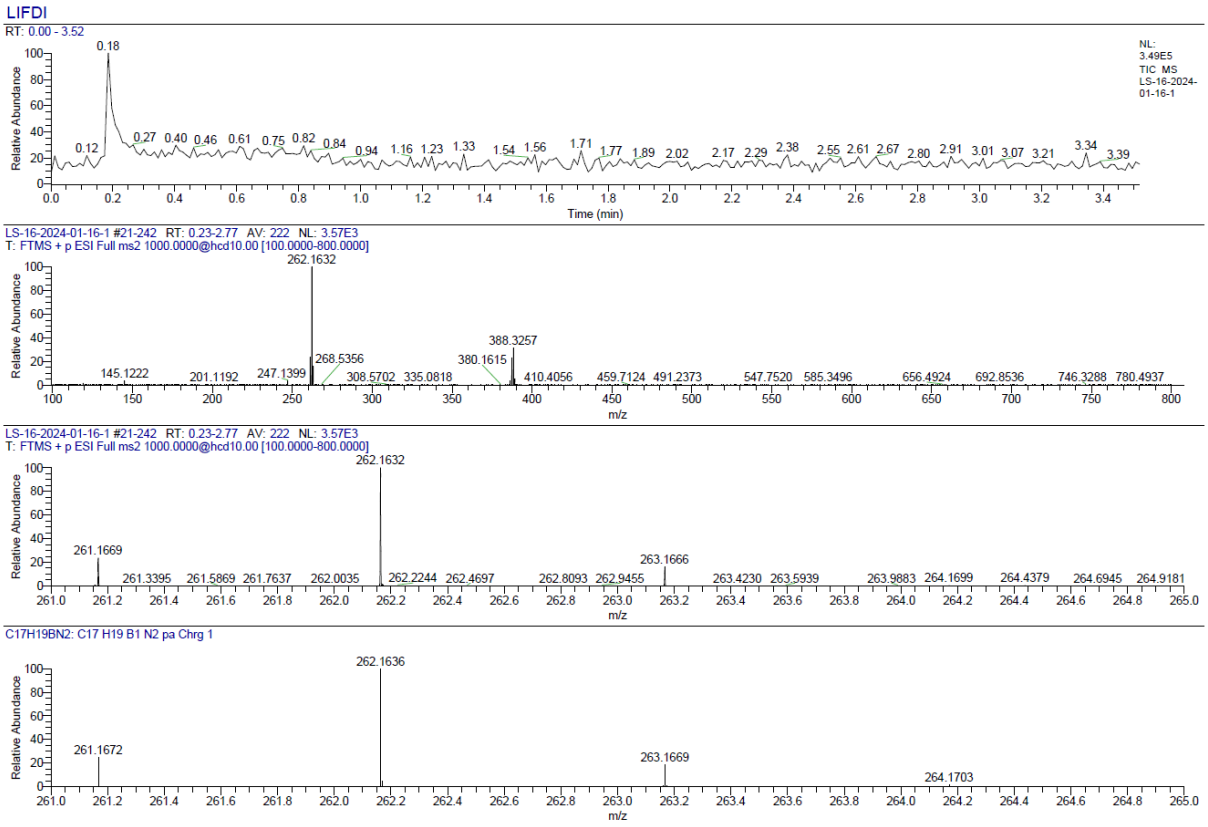


Figure S50. LIFDI high resolution mass spectrum of compound **6K** (THF), detected as the re-protonated species **6H**.

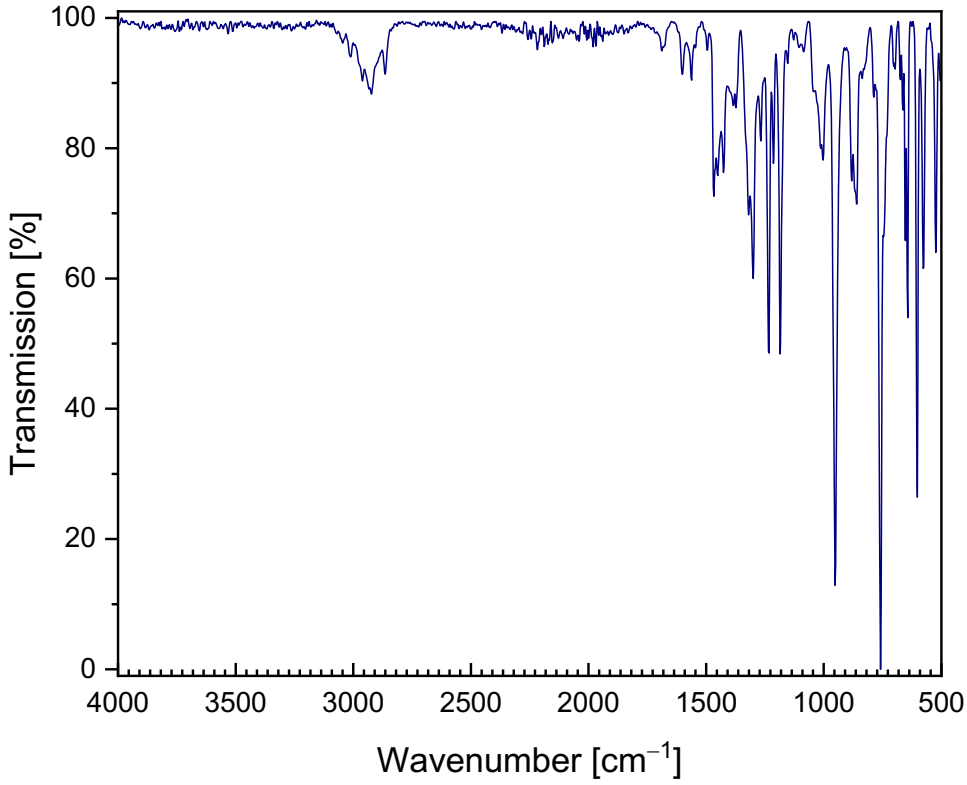


Figure S51. Normalized infrared spectrum of compound **6K** (powder).

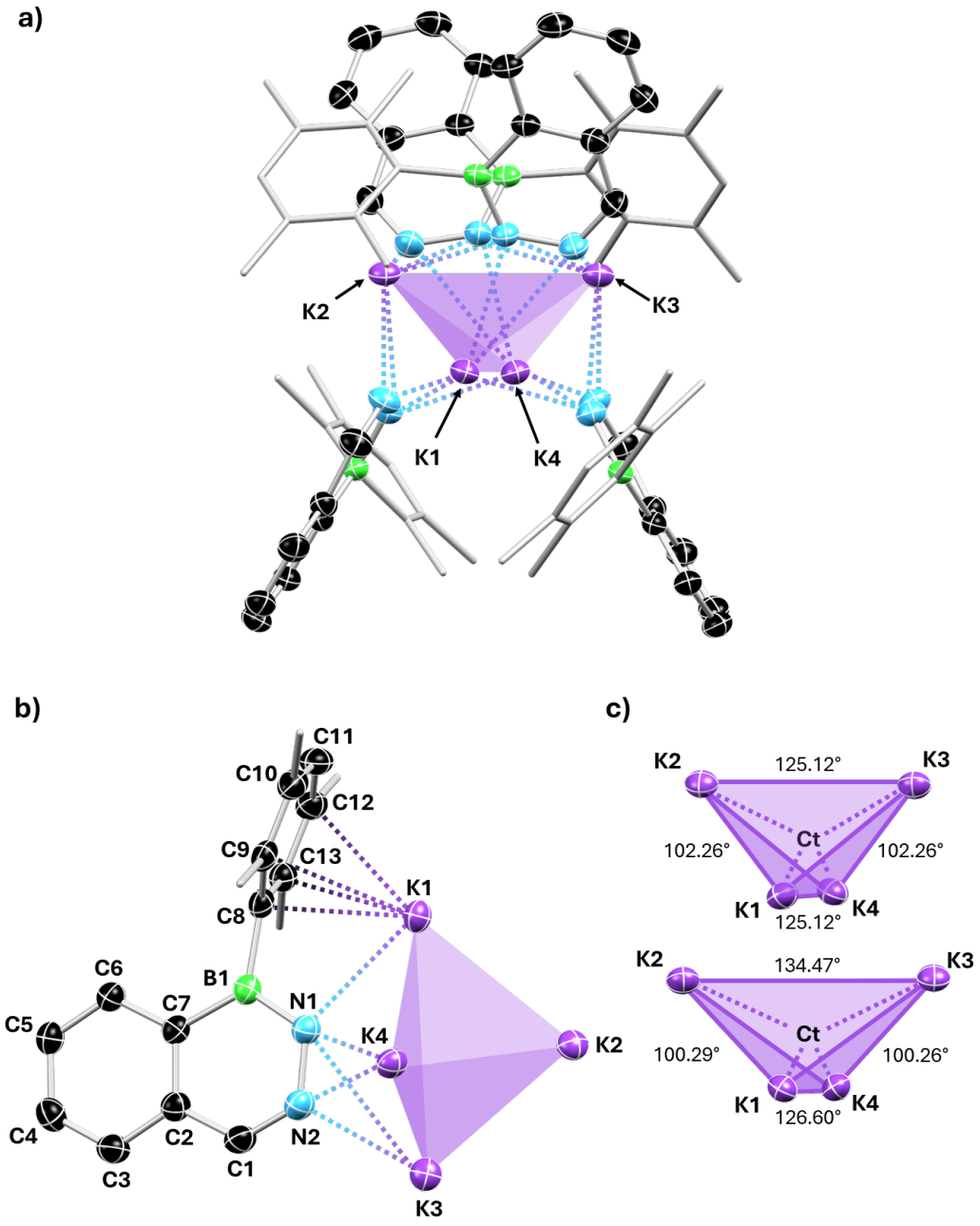


Figure S52. Molecular structure of compound **6K** (tetramer) in benzene. Ellipsoids drawn at 50% probability. All H-atoms omitted, and duryl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6K**: (A) B1–N1 1.415(3), N1–N2 1.394(2), N2–C1 1.306(3), N1–K1 2.9761(18), N1–K4 3.0373(18), N1–K3 2.8027(18), N2–K3 2.8650(19), N2–K4 2.6861(19), B1–N1–N2–C1 1.0(3), K1···K2 3.5821(7), K2···K3 4.0834(6), K3···K4 3.5821(7), K4···K1 4.0834(6); (B) B1–N1 1.415(3), N1–N2 1.382(3), N2–C1 1.305(3), N1–K1 2.8921(18), N1–K4 2.8009(18), N2–K4 2.7827(19), N2–K3 2.767(2), B1–N1–N2–C1 1.0(3), K1···K2 3.6675(7), K2···K3 3.6529(7), K3···K4 3.6675(7), K4···K1 3.6529(7).

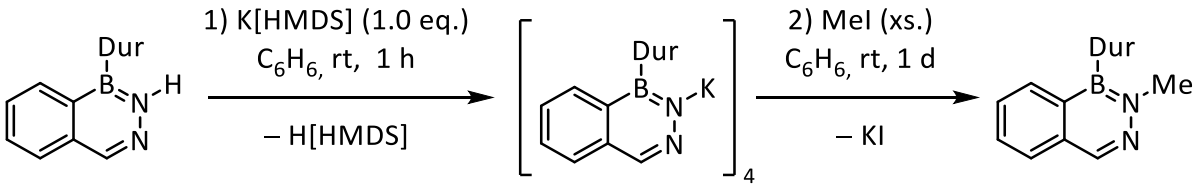
Crystal data:

$C_{68}H_{72}B_4K_4N_8$, M_r = 1200.97, colorless block, 0.430×0.320×0.270 mm^3, tetragonal space group $P\bar{4}2_1c$, a = 22.279 Å, b = 22.279 Å, c = 25.81660(10) Å, V = 12814.28(5) Å^3, Z = 8, ρ_{calcd} = 1.245 g·cm^{-3}, μ = 2.829 mm^{-1}, F(000) = 5056, T = 100(2) K, R_1 = 0.0264, wR_2 = 0.0703, Flack parameter = 0.447(5), 13124 independent reflections [$2\theta \leq 150.614°$] and 774 parameters.

Refined as a two-component inversion twin. The BASF parameter was refined to 44.7%.

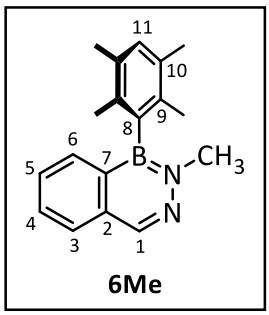
CCDC number: 2425632

3-Methyl-4-(2,3,5,6-tetramethylphenyl)-borazaroisoquinoline (6Me)



6H **6K** *in situ* **6Me** (95%)

Compound **6H** (70.0 mg, 267 μmol, 1.00 eq.) was dissolved in benzene (3.0 mL) in 50 mL Schlenk tube and KHMDS (53.3 mg, 267 μmol, 1.00 eq.) was added at ambient temperature in portions. A slight color change from colorless to light yellow and slow clouding of the reaction mixture was observed. After 1 h, methyl iodide (250 μL, 4.01 mmol, xs., ρ = 2.28 g/mL) was added and the reaction mixture was stirred overnight at ambient temperature and monitored via TLC. All volatile components were removed *in vacuo* and the remaining solid was quenched with ice. Ethyl acetate was added, and the two phases were transferred into a separating funnel. The aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure. The obtained colorless solid redissolved in *n*-hexane and the solution was filtered for the separation of insoluble **6H**. The solvent was removed under reduced pressure and compound **6Me** was purified via column chromatography (aluminum oxide (Act. I), *n*-hexane : ethyl acetate 8:1; R_f(**6Me**) = 0.55). **Yield:** 70.1 mg (254 μmol, 95%) of a colorless, crystalline solid. The compound is air- and moisture-stable.



6Me

Crystalline material of **6Me** as colorless blocks for single-crystal XRD was obtained by was obtained by slow evaporation of a saturated *n*-hexane solution at ambient temperature. . **^{1}H NMR** (600 MHz, 298 K, CD_2Cl_2): δ = 8.45 (s, 1H, *H*-1), 7.81 (d, $^3J_{HH}$ = 7.87 Hz, 1H, *H*-6), 7.73 (ddd, $^3J_{HH}$ = 8.15 Hz, 8.15; $^4J_{HH}$ = 0.20 Hz, 1H, *H*-5), 7.59 (d, $^3J_{HH}$ = 8.01 Hz, 1H, *H*-3), 7.52 (ddd, $^3J_{HH}$ = 7.70 Hz, 6.89 Hz; $^4J_{HH}$ = 1.13, 1H, *H*-4), 7.02 (s, 1H, *H*-11), 3.58 (s, 3H, N−CH_3), 2.26 (s, 6H, *m*-CH_3), 1.93 (s, 6H, *o*-CH_3) ppm. **^{11}B NMR** (193 MHz, 298 K, CD_2Cl_2): δ = 36.8 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, CD_2Cl_2): δ = 143.1 (*C*-1), 139.3 (C_q^B-8), 136.1 (C_q^B-7), 135.6 (C_q-9), 134.4 (*C*-3), 133.5 (C_q-10), 132.8 (C_q-2), 131.5 (*C*-11+*C*-5), 129.5 (*C*-4), 127.5 (*C*-6), 43.8 (N−CH_3), 19.8 (*m*-CH_3), 19.5 (*o*-CH_3) ppm. **HRMS** ($ASAP_{pos}$, toluene): expected: m/z 276.1907, 277.1871, 278.1904 $[C_{18}H_{21}BN_2]^+$; found: m/z 276.1788, 277.1863, 278.1897 $[C_{18}H_{21}BN_2]^+$. **IR** (ATR, 32 scans, powder): $\tilde{\nu}$= 3392 (w), 3254 (w), 3152 (w), 3092 (w), 3011 (w), 2962 (m), 2931 (m), 2860 (w), 1599 (w), 1563 (w), 1536 (w), 1477 (w), 1456 (m), 1442 (m), 1397 (w), 1373 (w), 1348 (m), 1334 (m), 1314 (m), 1303 (m), 1261 (m), 1244 (m), 1228 (w), 1212 (w), 1167 (w), 1144 (w), 1126 (m),

1083 (s), 1014 (s), 951 (m), 898 (m), 883 (m), 867 (m), 780 (s), 761 (s), 747 (s), 704 (w), 659 (w), 647 (m), 560 (s), 563 (w), 522 (s), 506 (m) cm^{-1}.

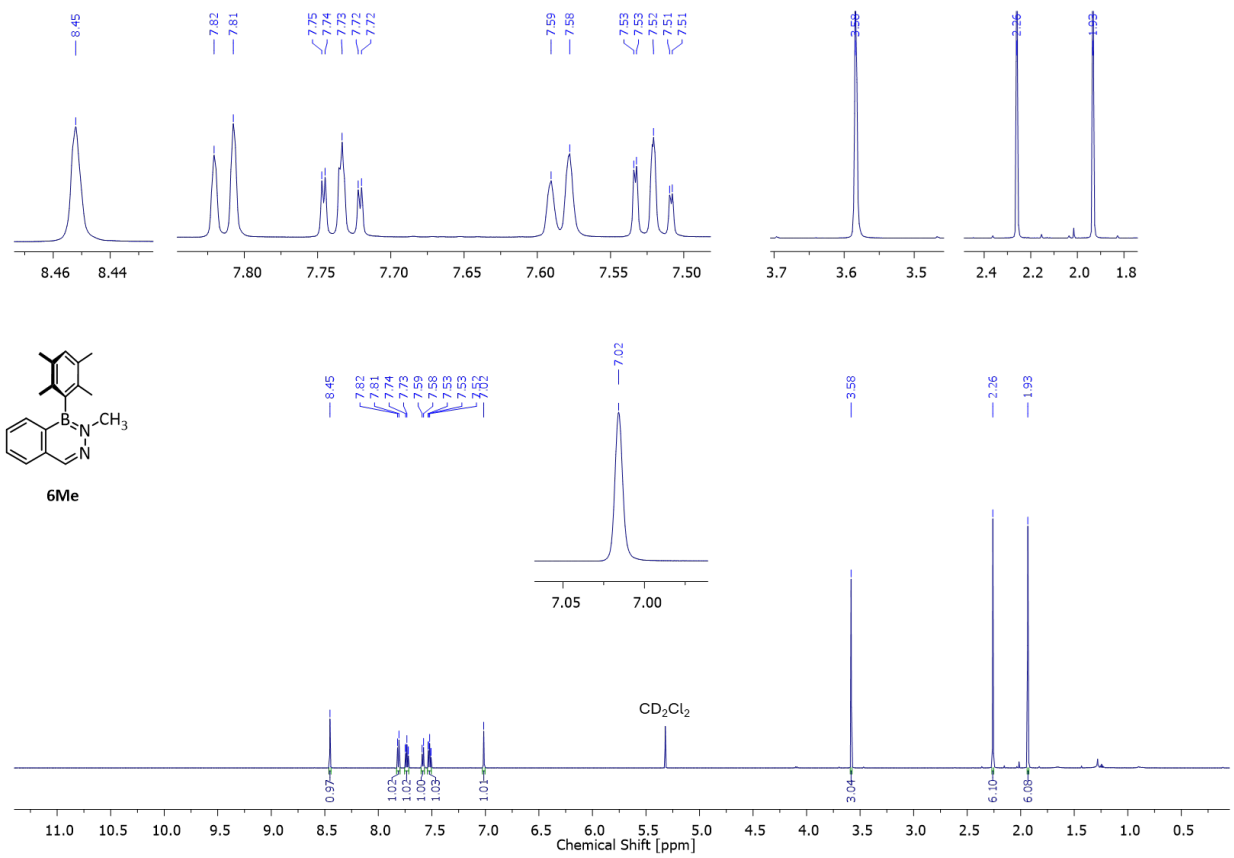


Figure S53. ^{1}H NMR spectrum of compound **6Me** in CD_2Cl_2.

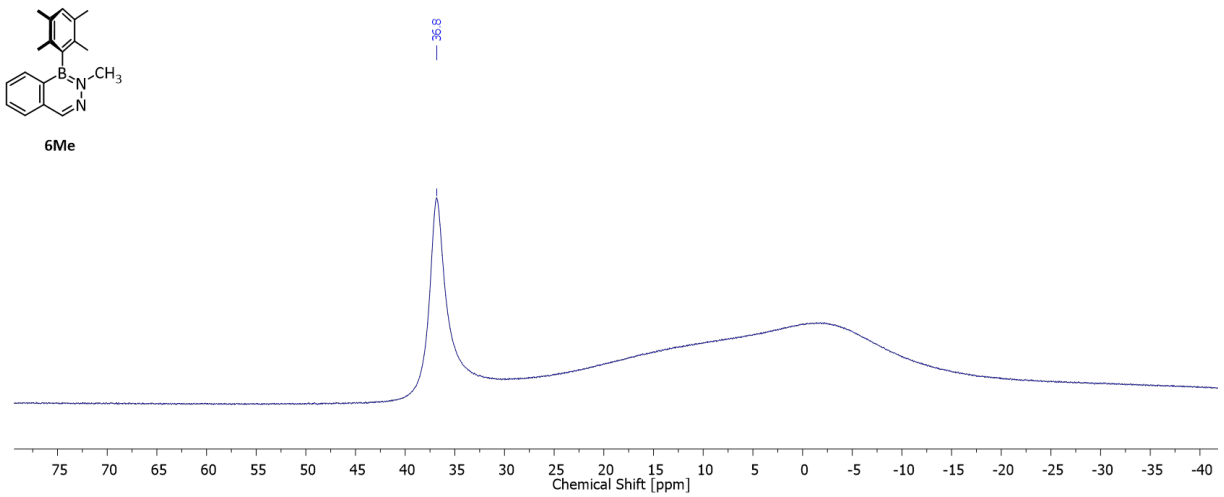


Figure S54. Background-reduced $^{11}B\{^{1}H\}$ NMR spectrum of compound **6Me** in CD_2Cl_2.

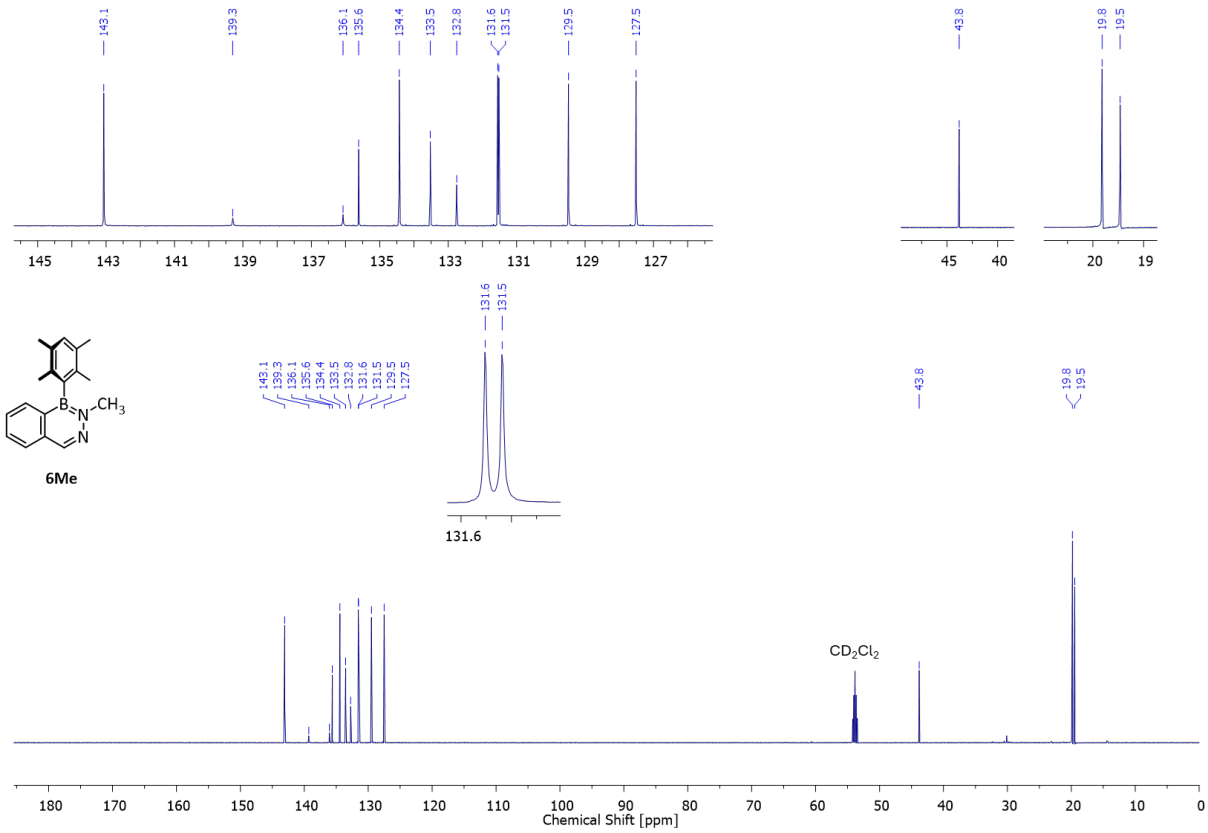


Figure S55. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6Me** in CD_2Cl_2 (selectively ^{11}B-decoupled at +37 ppm).

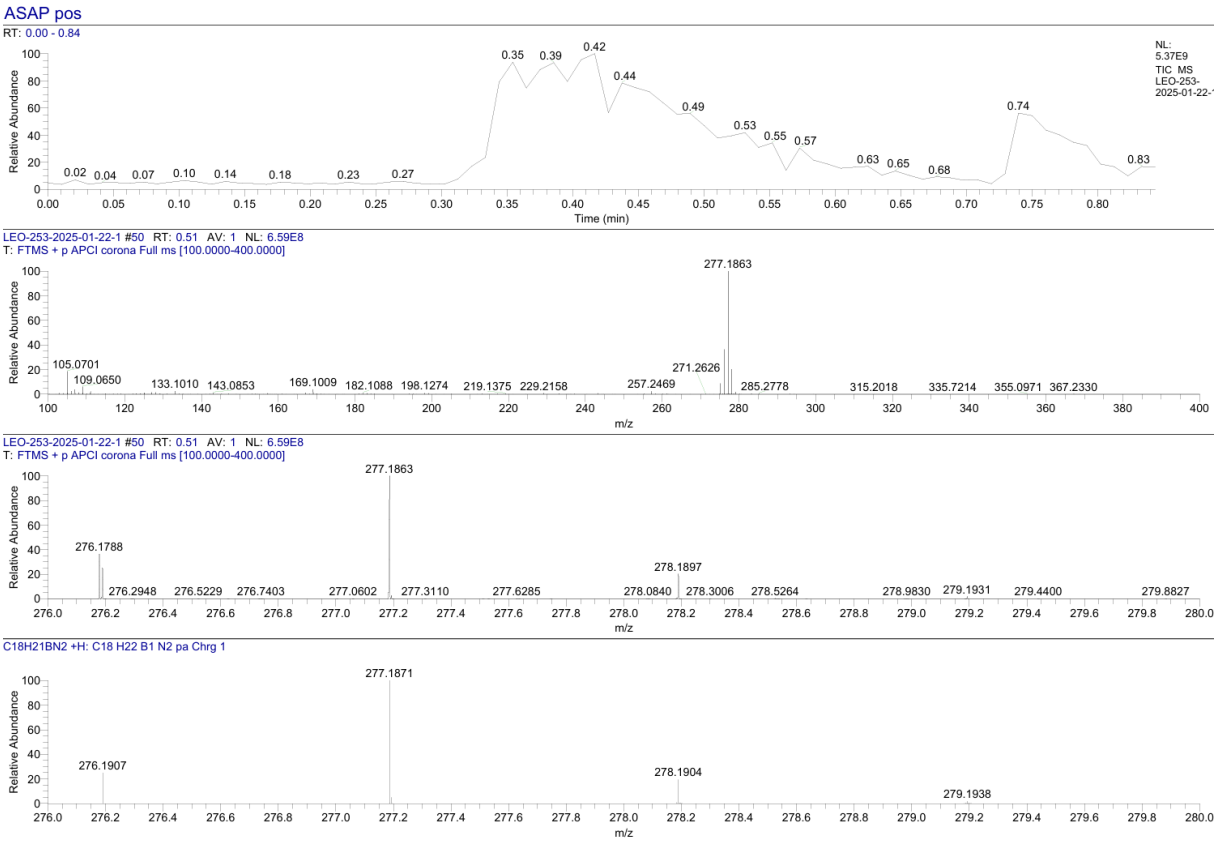


Figure S56. ASAP$_{pos}$ high resolution mass spectrum of compound **6Me** (toluene).

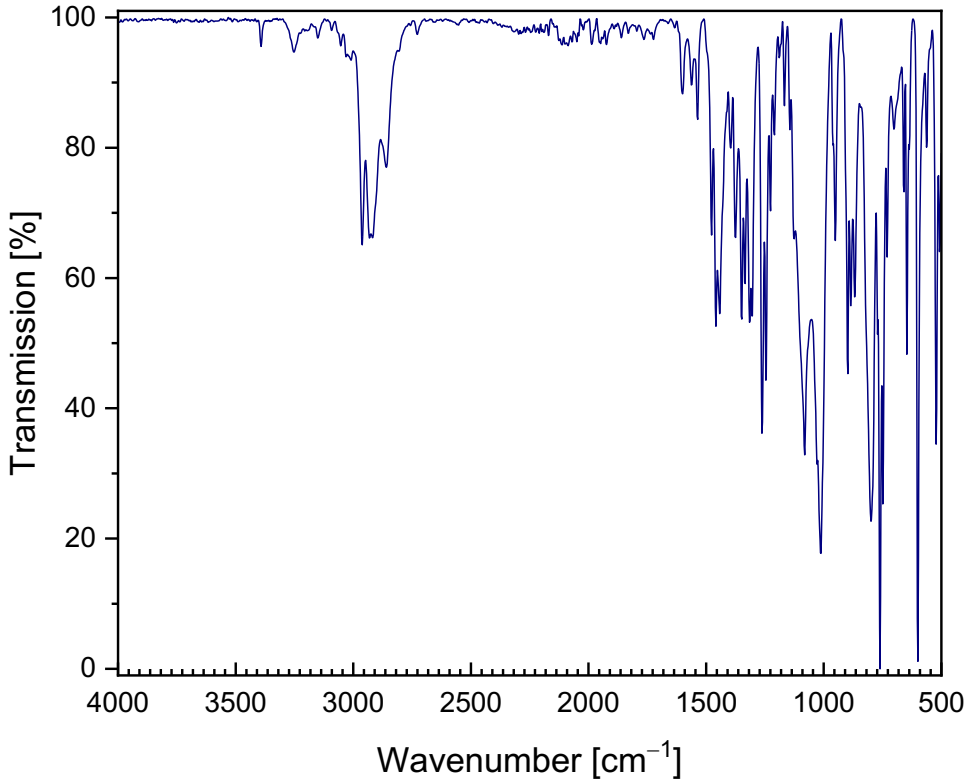


Figure S57. Normalized infrared spectrum of compound **6Me** (powder).

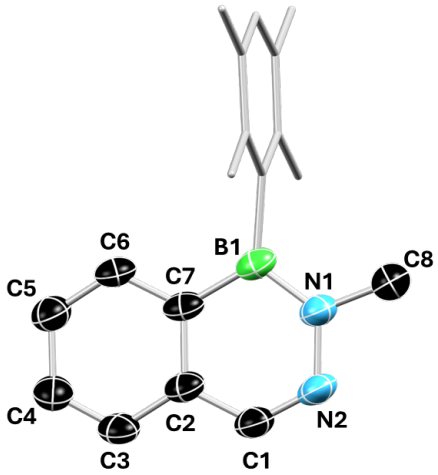
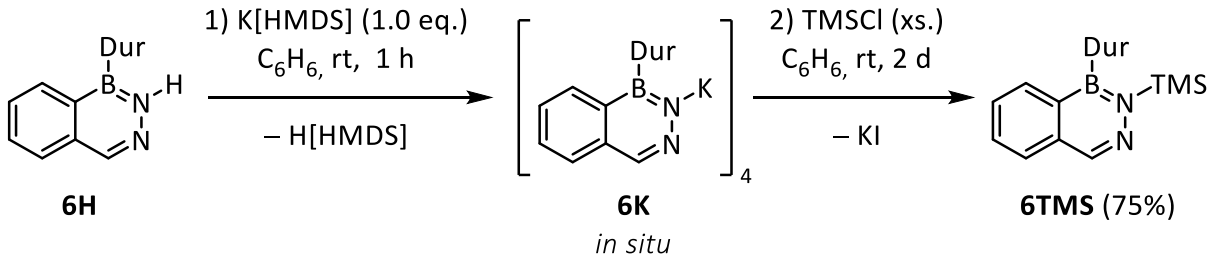


Figure S58. Molecular structure of compound **6Me**. Ellipsoids drawn at 50% probability. All H atoms omitted, and duryl substituent rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6Me**: B1–N1 1.417(3), N1–N2 1.394(2), N2–C1 1.287(3), C1–C2 1.430(3), C2–C3 1.400(3), C3–C4 1.365(3), C4–C5 1.404(3), C5–C6 1.374(3), C6–C7 1.398(3), C7–C2 1.424(2), B1–C8 1.443(3), C1–N2–N1–B1 0.5(3).

Crystal data:
$C_{18}H_{21}BN_2$, M_r = 276.18, colorless plate, 0.170×0.160×0.040 mm^3, monoclinic space group $P2_1/n$, a = 8.3573(2) Å, b = 10.3560(3) Å, c = 17.9111(5) Å, β = 94.531(2)°, V = 1545.33(7) Å^3, Z = 4, ρ_{calcd} = 1.187 g·cm^{-3}, μ = 0.523 mm^{-1}, F(000) = 592, T = 100(2) K, R_1 = 0.0689, wR_2 = 0.1731, 3056 independent reflections [$2\theta \leq 150.544°$] and 195 parameters.

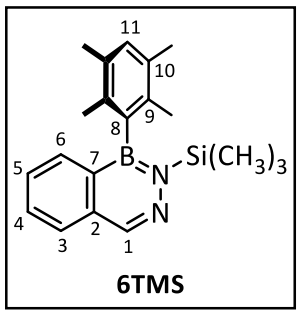
CCDC number: 2425634

3-Trimethylsilyl-4-(2,3,5,6-tetramethylphenyl)-borazaroisoquinoline (6TMS)



6H **6K** *in situ* **6TMS** (75%)

Compound **6H** (70.0 mg, 267 μmol, 1.00 eq.) was dissolved in benzene (3.0 mL) in 50 mL Schlenk tube and KHMDS (53.3 mg, 267 μmol, 1.00 eq.) was added at ambient temperature in portions. A slight color change from colorless to light yellow and slow clouding of the reaction mixture was observed. After 1 h, trimethylsilyl chloride (400 μL, 3.17 mmol, xs., ρ = 0.86 g/mL) was added and the reaction mixture was stirred for 2 d at ambient temperature. Attempts to monitor the reaction via TLC or later purify **6TMS** via column chromatography were not successful, as **6TMS** was not stable on silica or alumina plates. All volatile components were removed *in vacuo* and the remaining solid was extracted with *n*-pentane (2 mL) on air. The *n*-pentane solution was filtrated for the separation of **6H**. The solvent was removed under reduced pressure and the extraction process was repeated two more times to obtain the analytically pure compound **6TMS**. **Yield:** 67.1 mg (200 μmol, 75%) of a colorless, crystalline solid. The compound is air- and moisture-stable.



6TMS

Crystalline material of **6TMS** as colorless blocks for single-crystal XRD was obtained by was obtained by slow evaporation of a saturated dichloromethane solution at ambient temperature. **^{1}H NMR** (500 MHz, 298 K, CD_2Cl_2): δ = 8.66 (s, 1H, *H*-1), 7.75-7.80 (m, 2H, *H*-4+*H*-5), 7.52-7.56 (m, 2H, *H*-3+*H*-6), 7.01 (s, 1H, *H*-11), 2.26 (s, 6H, *m*-CH_3), 1.94 (s, 6H, *o*-CH_3), 0.12 (s, 9H, –Si(CH_3)$_3$) ppm. **^{11}B{^{1}H} NMR** (160 MHz, 298 K, CD_2Cl_2): δ = 40.0 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, CD_2Cl_2): δ = 145.4 (*C*-1), 140.9 (C_q^B-8), 135.6 (C_q-9), 341.9 (C_q^B-7), 134.5 (*C*-3/*C*-6), 133.2 (C_q-10), 132.3 (C_q-2), 132.1 (*C*-4/*C*-5), 131.2 (*C*-11), 129.8 (*C*-3/*C*-6), 127.3 (*C*-4/*C*-5), 20.2 (*o*-CH_3), 19.7 *(m*-CH_3), 0.6 (–Si(CH_3)$_3$) ppm. **HRMS** (ASAP$_{pos}$, toluene): expected: m/z 333.2067, 334.2032, 335.2065 [$C_{20}H_{27}BN_2Si$]$^+$; found: m/z 333.2061, 334.2024, 335.2099 [$C_{20}H_{27}BN_2Si$]$^+$. **IR** (ATR, 32 scans, powder): $\tilde{\nu}$= 2958 (w), 2921 (w), 2851 (w), 1474 (w), 1458 (w), 1371 (w), 1333 (w), 1311 (m), 1287 (m), 1244 (m), 1222 (m), 1189 (w), 1160 (w), 1130 (w), 983 (m), 935 (w), 903 (w), 838 (s), 817 (s), 758 (s), 683 (w) cm^{-1}.

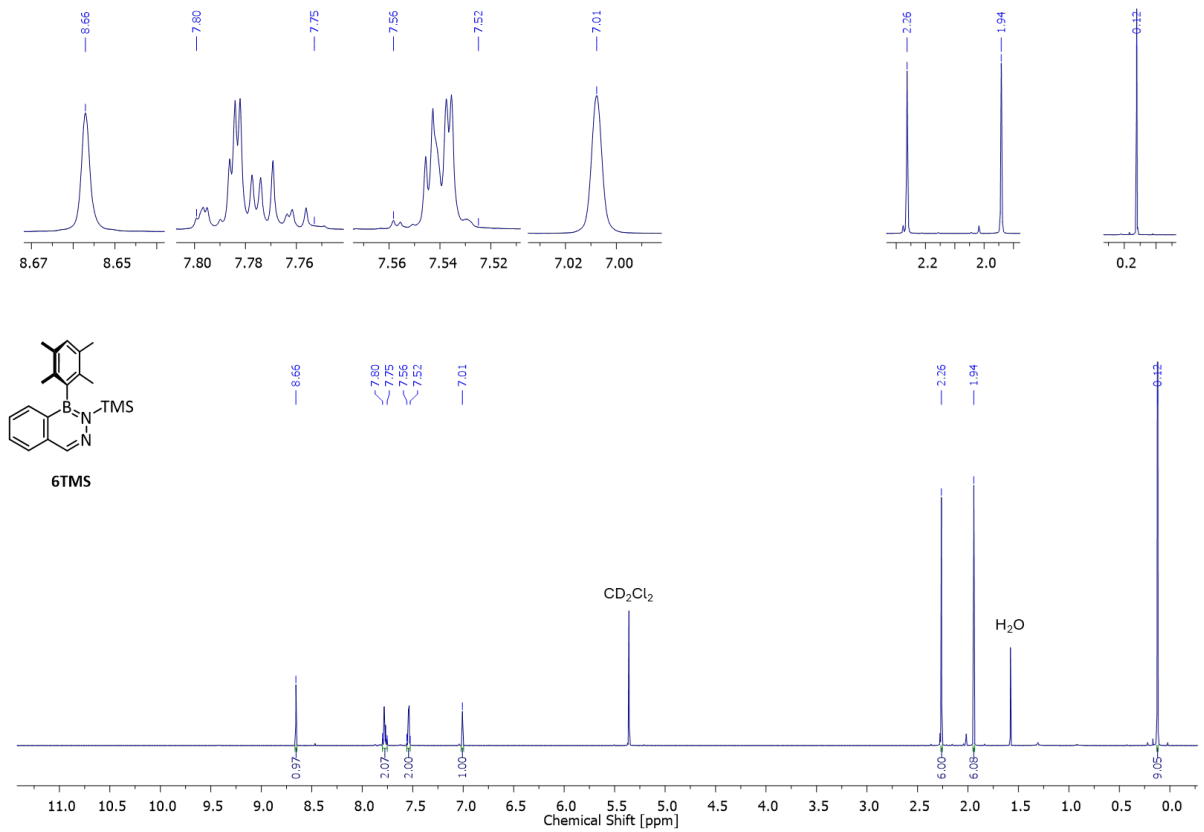


Figure S59. ^{1}H NMR spectrum of compound **6TMS** in CD_2Cl_2.

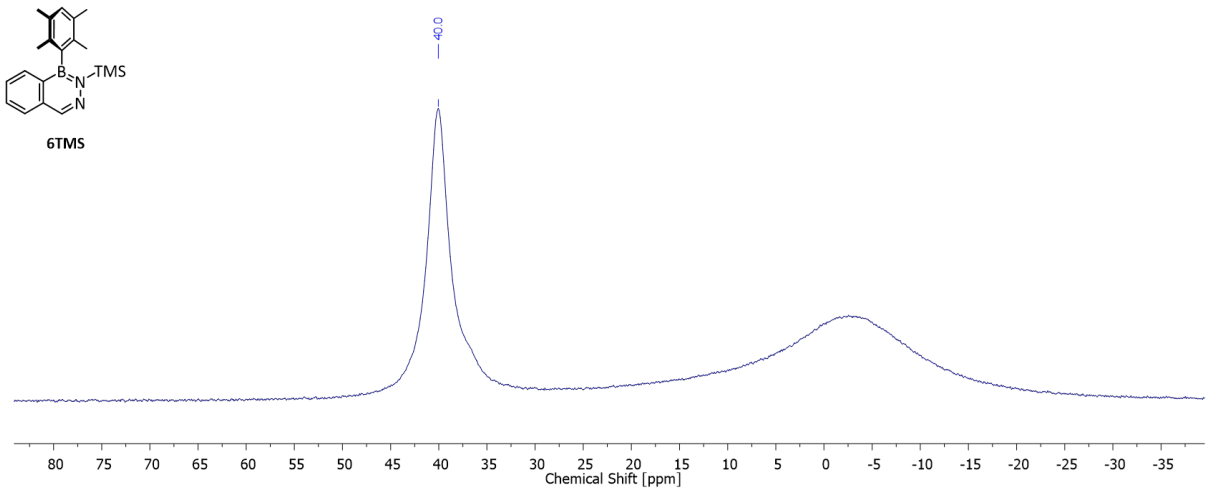


Figure S60. Background-reduced $^{11}B\{^{1}H\}$ NMR spectrum of compound **6TMS** in CD_2Cl_2.

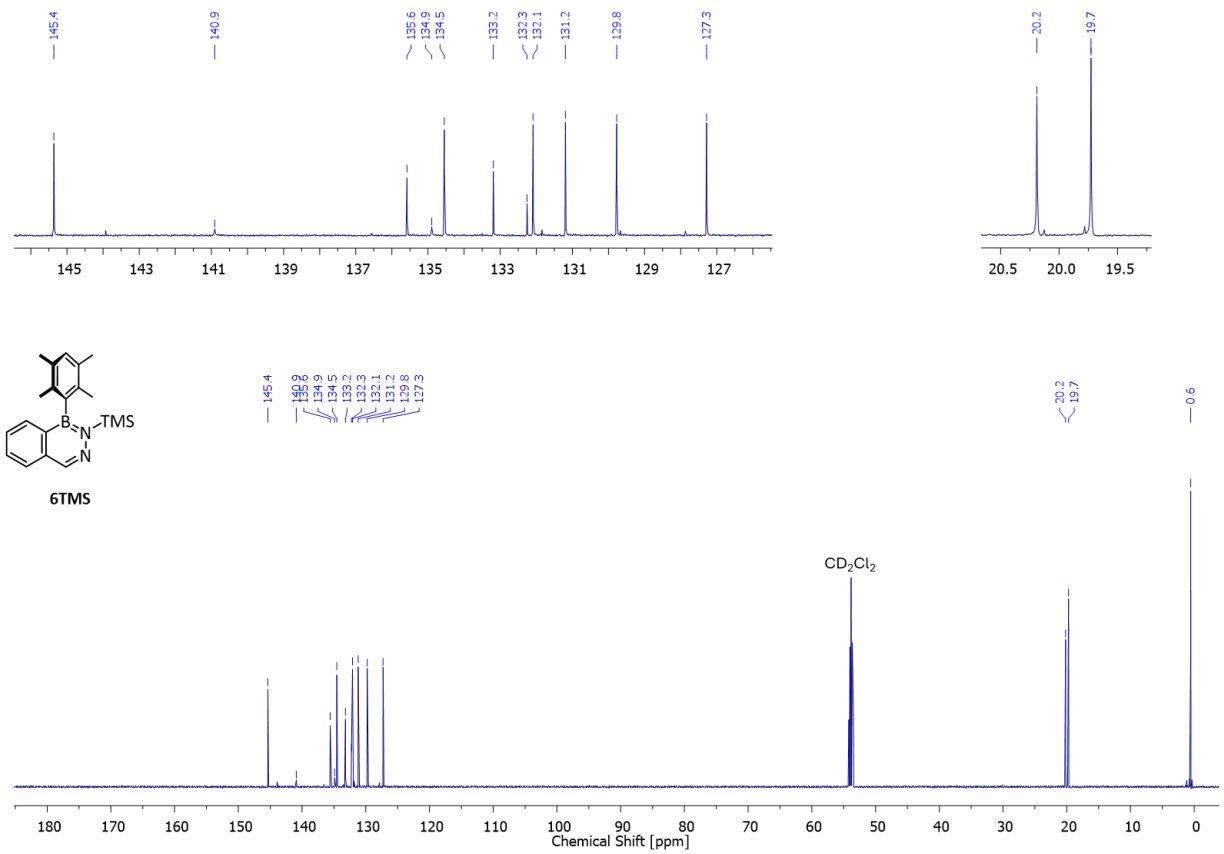


Figure S61. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6TMS** in CD_2Cl_2 (selectively ^{11}B-decoupled at +40 ppm).

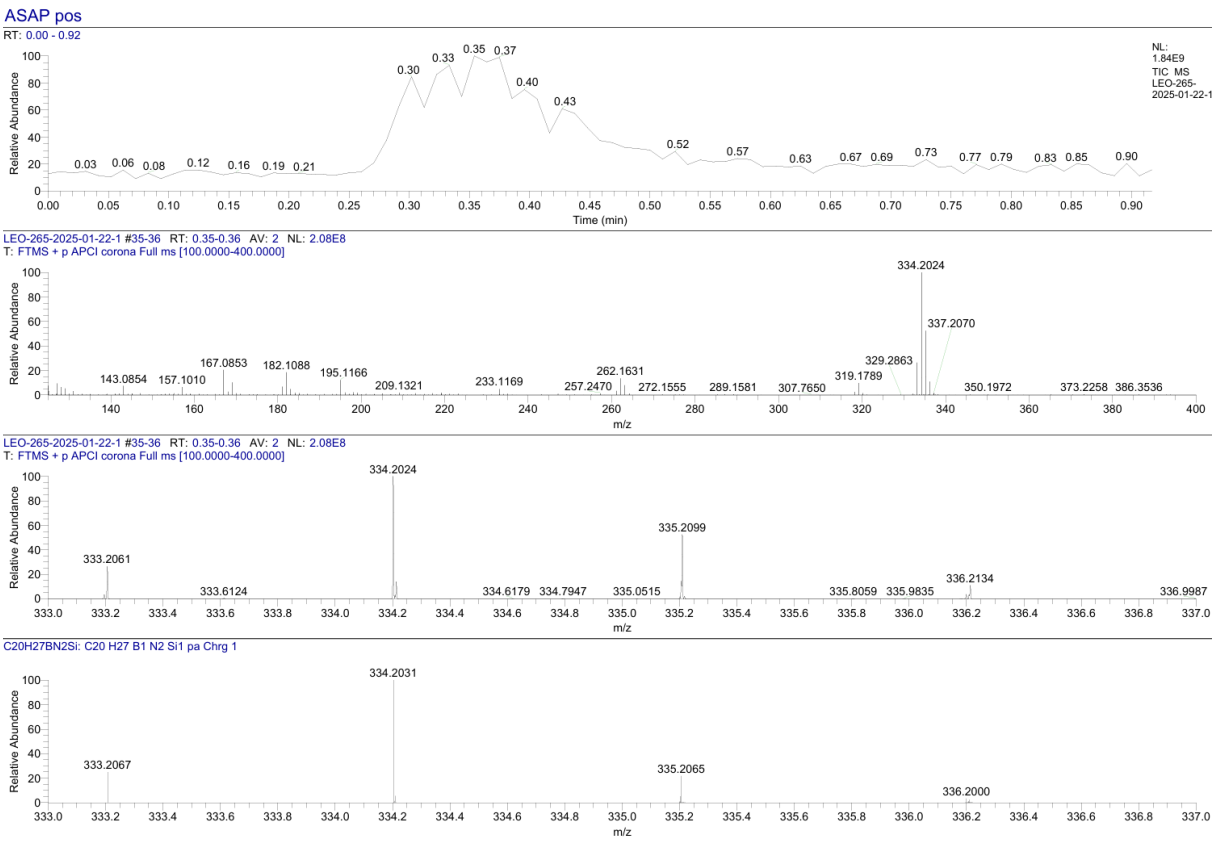


Figure S62. $ASAP_{pos}$ high resolution mass spectrum of compound **6TMS** (toluene).

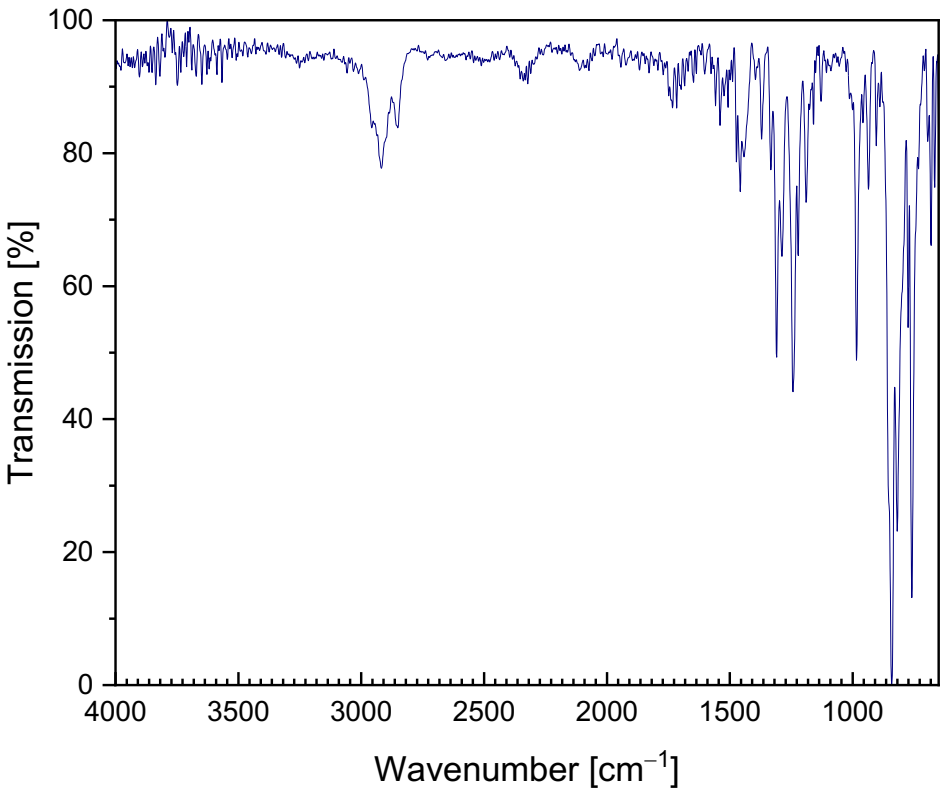


Figure S63. Normalized infrared spectrum of compound **6TMS** (powder).

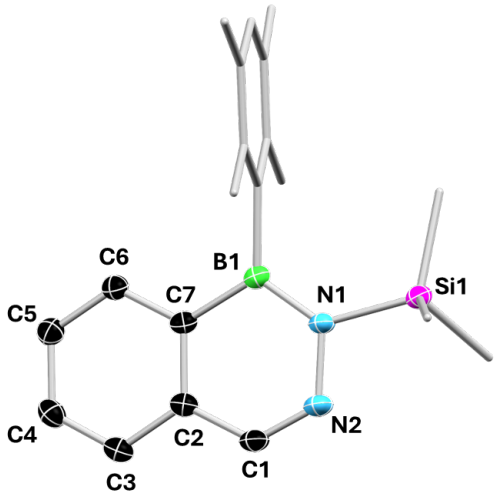


Figure S64. Molecular structure of compound **6TMS**. Ellipsoids drawn at 50% probability. All H atoms omitted, duryl and methyl substituents rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6TMS**: B1–N1 1.419(4), N1–N2 1.413(3), N2–C1 1.290(4), C1–C2 1.443(4), C2–C3 1.407(4), C3–C4 1.377(3), C4–C5 1.395(4), C5–C6 1.382(4), C6–C7 1.406(4), C7–C2 1.405(4), B1–Si1 1.787(2), C1–N2–N1–B1 3.6(4).

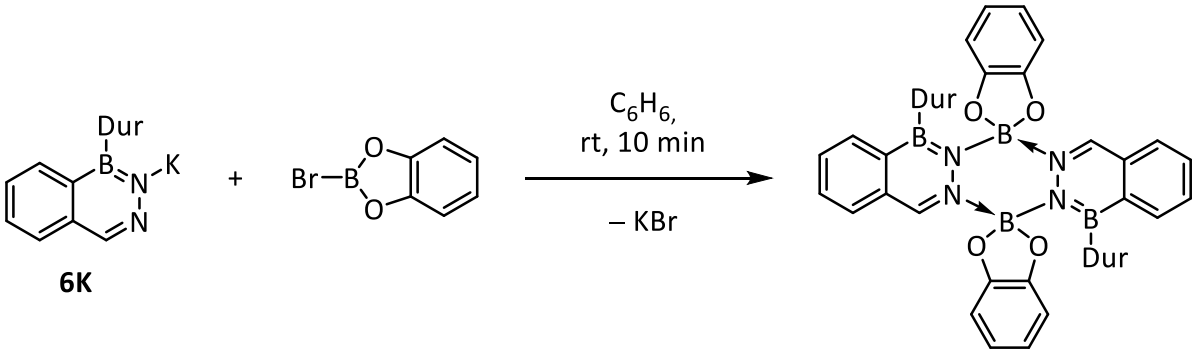
Crystal data:

$C_{20}H_{27}BN_2Si$, M_r = 334.33, clear colorless block, 0.170×0.052×0.025 mm^3, triclinic space group $P\bar{1}$, a = 6.7806(2) Å, b = 19.1991(7) Å, c = 22.5503(6) Å, α = 83.564(3)°, β = 85.956(2)°, γ = 83.743(2)°, V = 2894.70(16) Å^3, Z = 6, ρ_{calcd} = 1.151 g·cm^{-3}, μ = 1.072 mm^{-1}, $F(000)$ = 1080, T = 100(2) K, R_1 = 0.0817, wR_2 = 0.1775, 20540 independent reflections [$2\theta \leq 150.332°$] and 671 parameters.

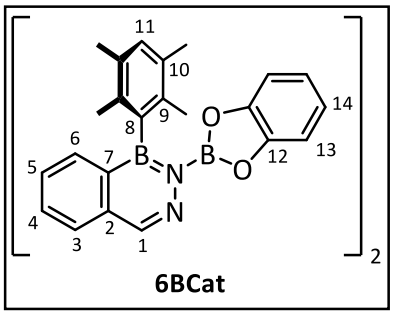
Refined as a two-component twin. Component 2 rotated by –180° around [–0.00 0.71 –0.71] (reciprocal) or [–0.11 0.80 –0.59] (direct) axis. The BASF parameter was refined to 52.1%.

CCDC number: 2425638

3-(1,3,2-Benzodioxaborol)-4-(2,3,5,6-tetramethylphenyl)-borazaroisoquinoline (6BCat)



Isolated compound **6K** (16.0 mg, 53.3 μmol, 1.00 eq.) was suspended in benzene-d_6 (0.5 mL) in a J.-Young-style NMR tube and 2-bromo-1,2,3-benzodioxaborole (10.6 mg, 53.3 μmol, 1.00 eq.) was added at ambient temperature. Upon addition, a color change from colorless to light yellow and momentary clearing with subsequent re-clouding of the suspension was observed. After 10 min, the suspension was filtrated in a glovebox using a glass pipette equipped with a glass fibre filter. Vapor diffusion of *n*-pentane (0.3 mL) into a saturated benzene solution at ambient temperature resulted in crystallization of compound **6BCat**. The supernatant was removed with a glass pipette, and the obtained crystalline solid was dried *in vacuo*. **Yield:** 10.3 mg (27.1 μmol, 51%) of a pale yellow, crystalline solid.



Crystaline material of **6BCat** as yellow blocks for single-crystal XRD was obtained by was obtained by slow vapor diffusion of *n*-pentane into a saturated benzene solution at ambient temperature. **^{1}H NMR** (600 MHz, 298 K, C_6D_6): δ = 9.05 (s, 2H, *H*-1), 7.76 (d, $^3J_{HH}$ = 7.75 Hz, 2H, *H*-3), 7.07 (dt, $^3J_{HH}$ = 7.49 Hz, $^4J_{HH}$ = 1.12 Hz, 2H, *H*-4), 6.94 (dt, $^3J_{HH}$ = 7.64 Hz, $^4J_{HH}$ = 1.30 Hz, 2H, *H*-5), 6.85 (s, 2H, *H*-11), 6.68-6.71 (m, 6H, *H*-6 + *H*-13), 6.62-6.65 (m, 4H, *H*-14), 2.20 (s, 12H, *o*-CH_3), 2.18 (s, 12H, *m*-CH_3) ppm. **^{11}B NMR** (193 MHz, 298 K, C_6D_6): δ = 9.8 (s), 43.3 (br s, $\Delta\nu_{½}$ = 2295 Hz) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6): δ =150.8 (C_q^O-12), 144.4 (*C*-1), 139.6 (br s, C_q^B-8), 138.1 (br s, C_q^B-7), 135.2 (*C*-3), 135.1 (C_q-9), 133.2 (*C*-4), 132.7 (C_q-10), 132.2 (*C*-5), 131.1 (C_q-2), 131.1 (*C*-11), 130.6 (*C*-6), 120.0 (*C*-14), 110.1 (*C*-13), 20.7 (*o*-CH_3), 19.8 (*m*-CH_3) ppm. **HRMS** (ASAP$_{neg}$, solid): expected: m/z 757.3740, 758.3710, 759.3689, 760.3710, 761.3736 $[C_{46}H_{43}B_4N_4O_4]^-$ (dimer); found: m/z 757.3757, 758.3726, 759.3699, 760.3726, 761.3765 $[C_{46}H_{43}B_4N_4O_4]^-$ (dimer). **IR** (ATR, 32 scans, powder): $\tilde{\nu}$= 3064 (w), 2281 (w), 1613 (w), 1547 (w), 1512 (w), 1486 (s), 1442 (m), 1369 (w), 1334 (w), 1315 (m), 1286 (w), 1241 (s), 1196 (w), 1149 (m), 1089 (s), 1046 (m), 1007 (m), 978 (s), 900 (s), 859 (m), 808 (m), 766 (m), 732 (s), 619 (m) cm^{-1}.

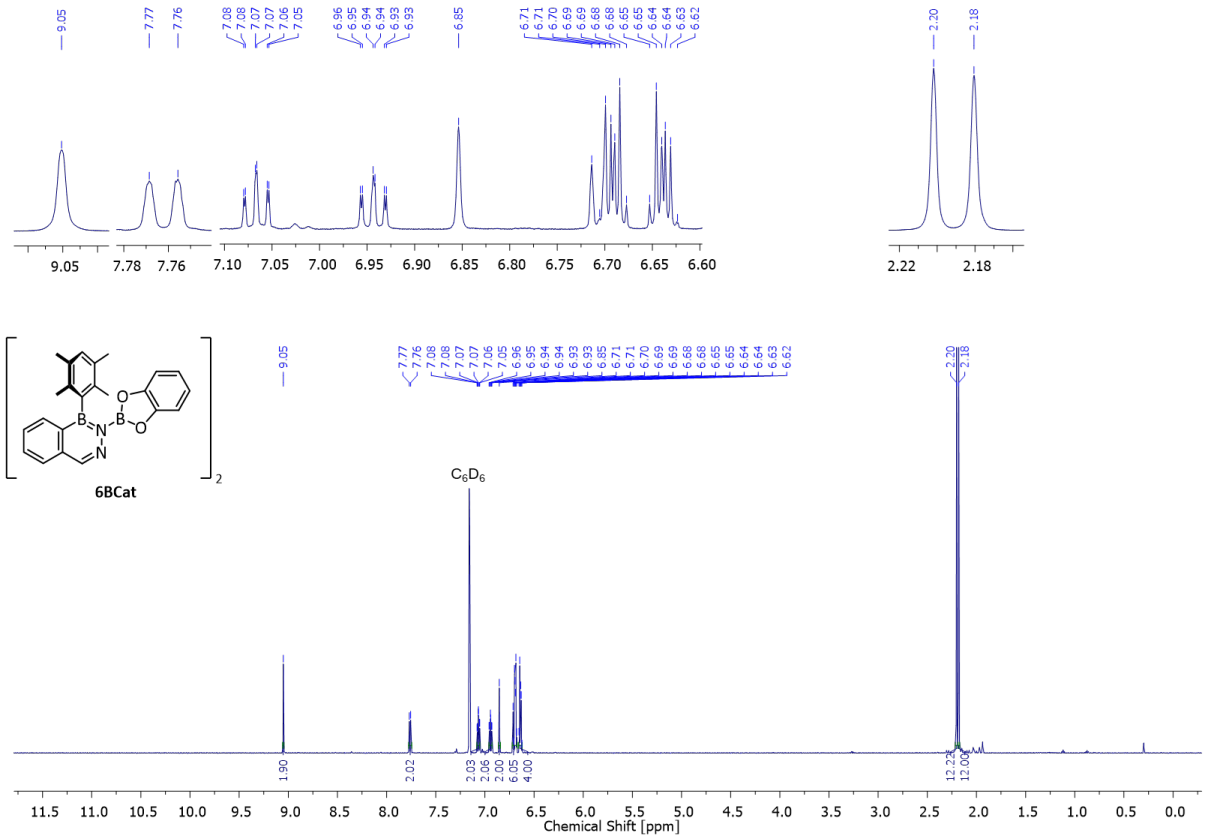


Figure S65. ^{1}H NMR spectrum of compound **6BCat** in C_6D_6.

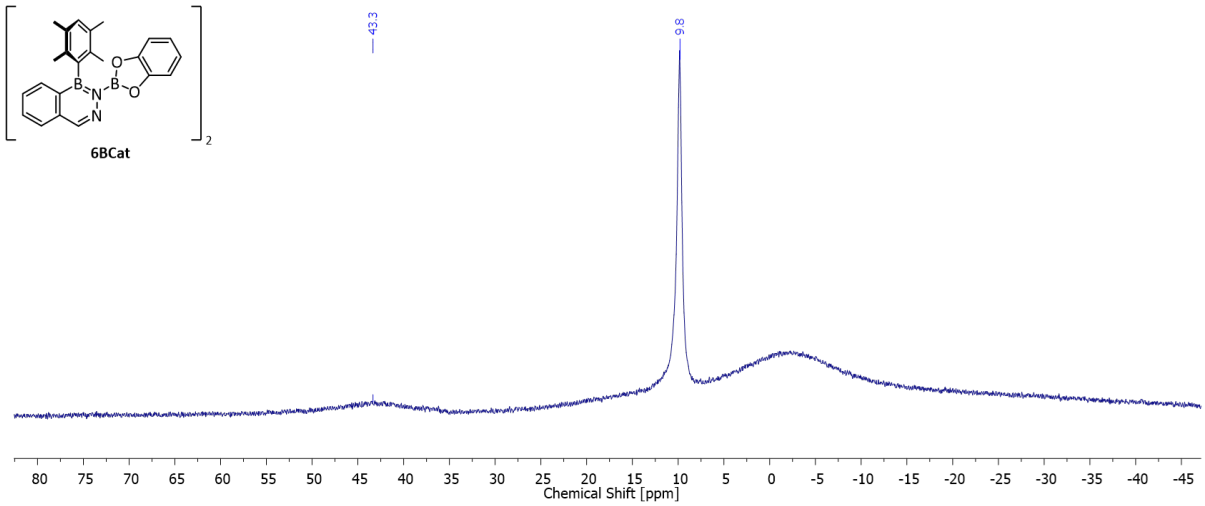


Figure S66. Background-reduced ^{11}B NMR spectrum of compound **6BCat** in C_6D_6.

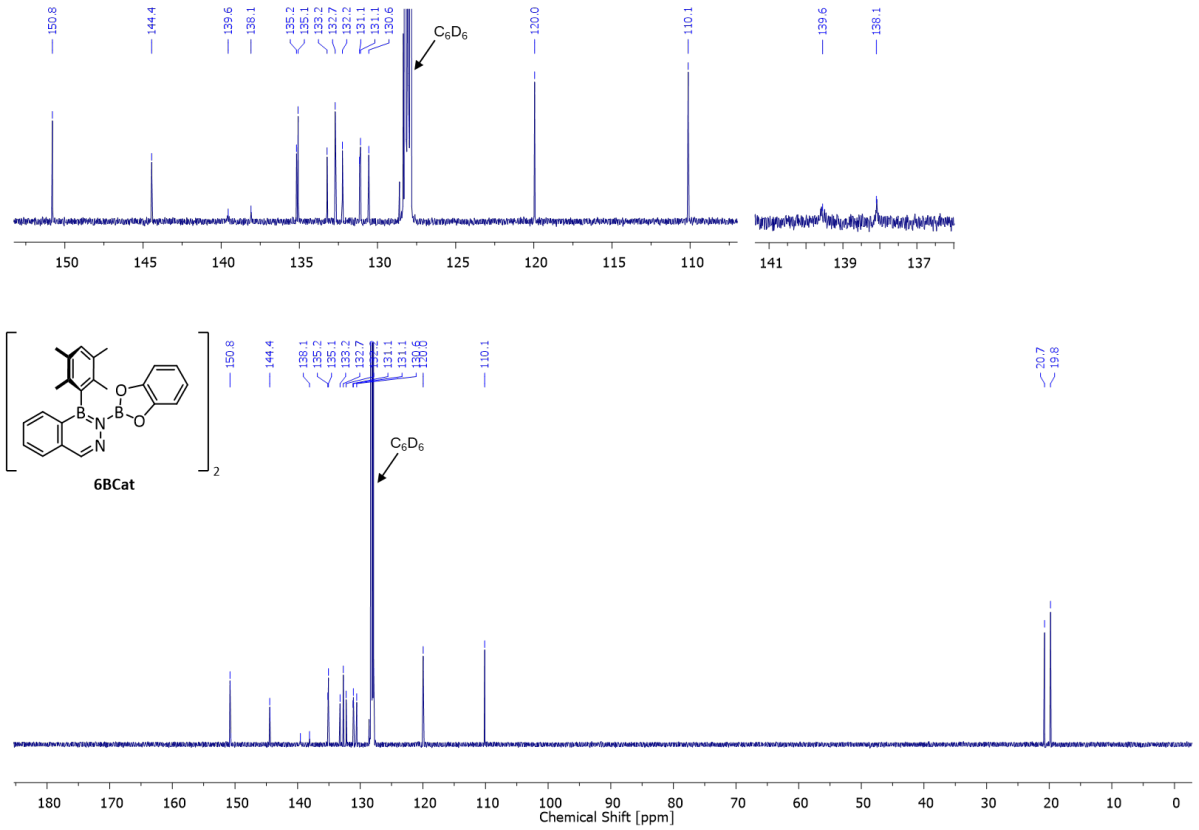


Figure S67. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6BCat** in C_6D_6 (selectively ^{11}B-decoupled at +10 ppm).

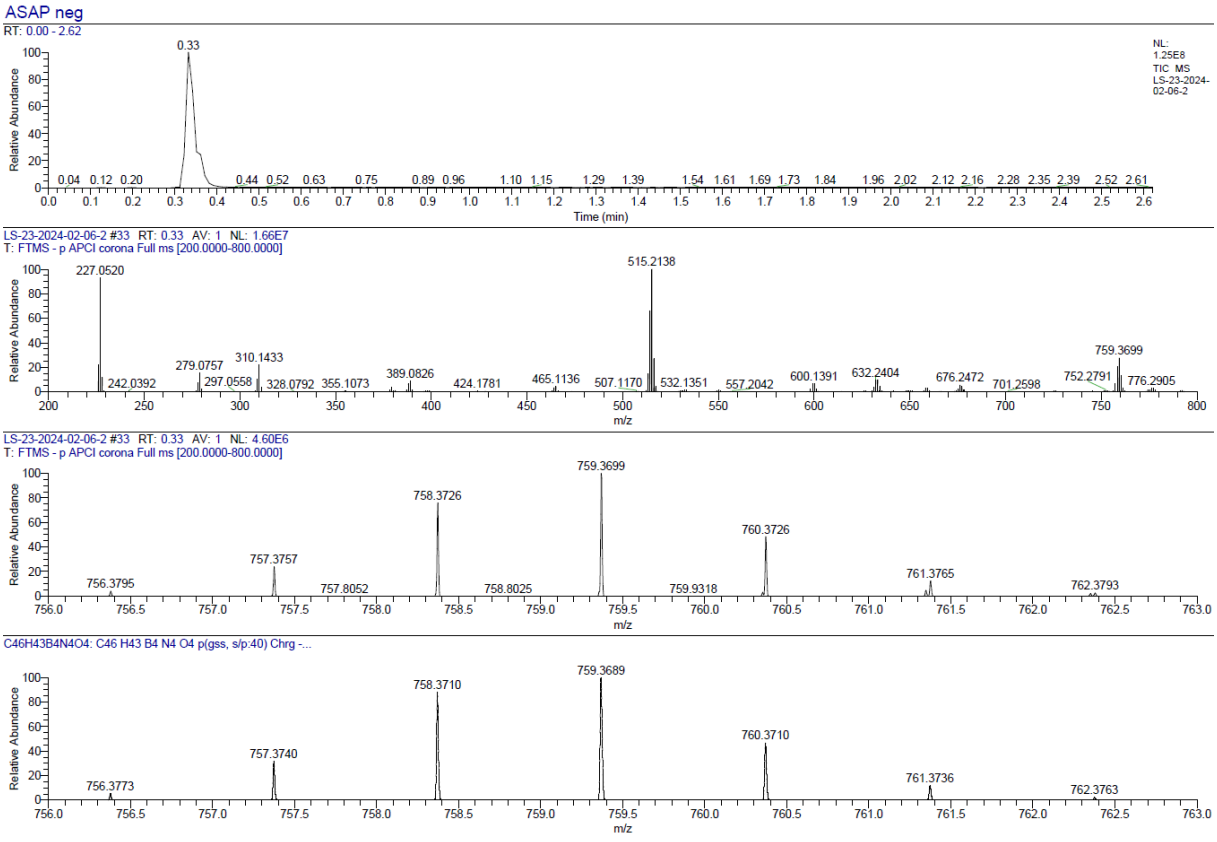


Figure S68. $ASAP_{neg}$ high resolution mass spectrum of compound **6BCat** (solid).

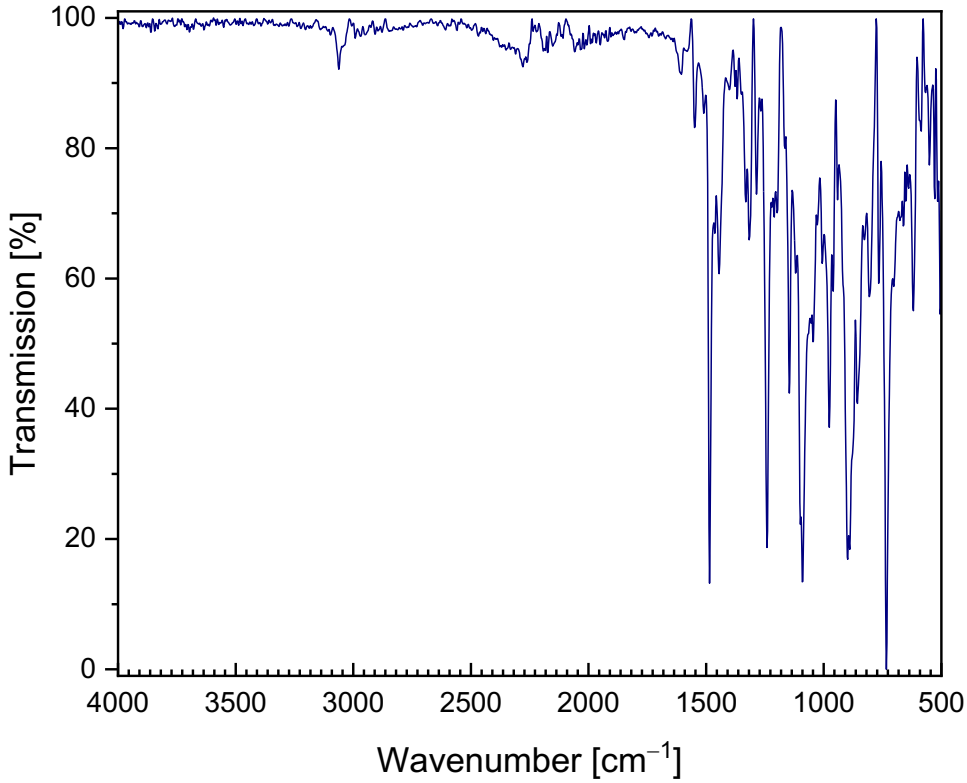


Figure S69. Normalized infrared spectrum of compound **6BCat** (powder).

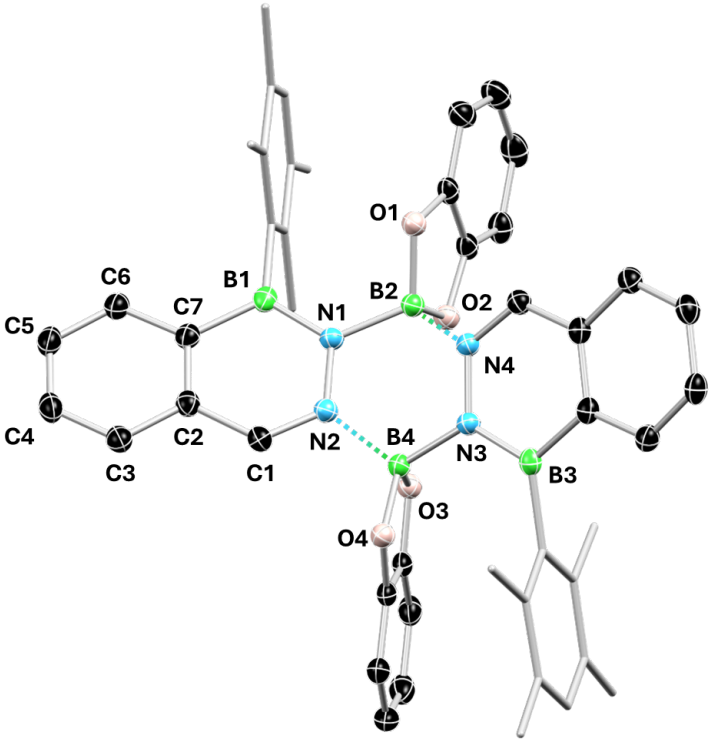


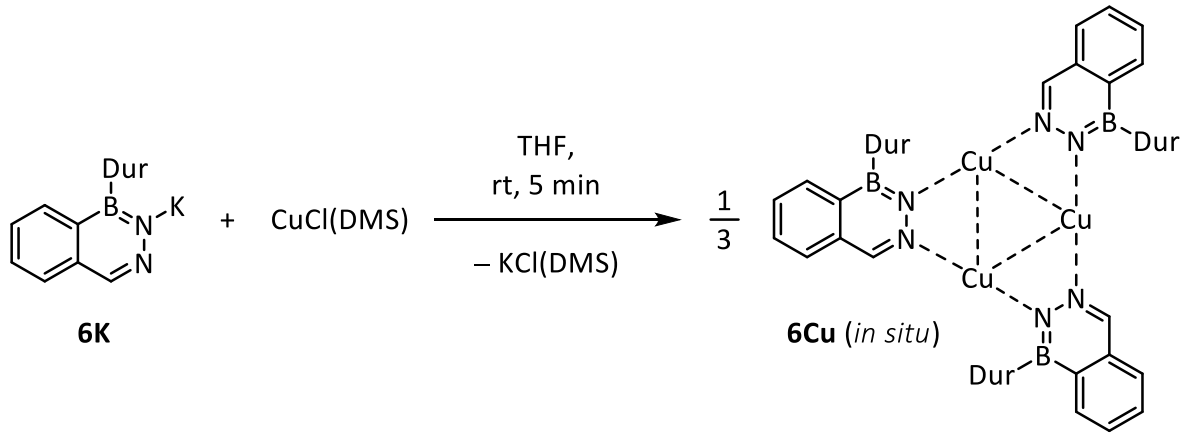
Figure S70. Molecular structure of compound **6BCat** (dimer). Ellipsoids drawn at 50% probability. All H atoms omitted, and duryl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6BCat**: B1–N1 1.4306(16), N1–N2 1.3864(13), N2–C1 1.3052(15), C1–C2 1.4308(16), C2–C3 1.4058(17), C3–B1 1.5425(17), C3–C4 1.4053(16), C4–C5 1.3828(18), C5–C6 1.3985(19), C6–C7 1.3817(17), C7–C2 1.4067(16), B1–C8 1.5721(18), N1–B2 1.5466(15), N2→B4 1.6137(15), C1–N2–N1–B1 10.99(16), B2–N1–N2–B4 24.68(13).

Crystal data:

$C_{64}H_{62}B_4N_4O_4$, M_r = 994.41, yellow irregular block, 0.210×0.110×0.070 mm^3, monoclinic space group $P2_1/n$, a = 14.9410(1) Å, b = 18.7016(1) Å, c = 20.4482(1) Å, β = 110.607(1)°, V = 5348.07(6) Å^3, Z = 4, ρ_{calcd} = 1.235 g·cm^{-3}, μ = 0.588 mm^{-1}, F(000) = 2104, T = 100(2) K, R_1 = 0.0450, wR_2 = 0.0996, 10749 independent reflections [$2\theta \leq 151.402°$] and 693 parameters.

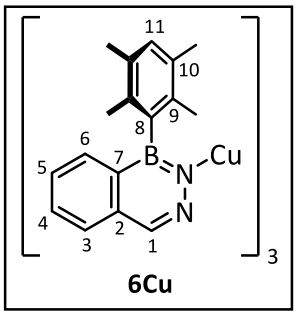
CCDC number: 2425629

Cu(I)-diazaboramide complex [Cu_3(μ-DAB)$_3$] (6Cu)



6K **6Cu** (*in situ*)

Isolated compound **6K** (8.00 mg, 26.6 μmol, 1.00 eq.) was dissolved in pre-cooled (−30 °C) THF-d_8 (0.5 mL) in a brown glass J.-Young-style NMR tube and chloro(dimethylsulfide)copper(I) (4.30 mg, 26.6 μmol, 1.00 eq.) was added. Upon addition, a color change from colorless to light yellow was observed. The 1D, 2D and ^{1}H DOSY NMR spectra and HRMS were measured directly afterwards due to quick decomposition of **6Cu** in solution to **6H** and Cu(0). Yield not determined. The compound is not stable in solution.



6Cu

Crystaline material of **6Cu** in form of colorless needles was obtained by storing a saturated THF solution, which was layered with equal amounts of *n*-pentane at −30 °C in a glovebox. However, despite careful coating of the crystals in perfluorinated oil and quick transfer to a pre-cooled microscope slide, the crystals turned immediately black upon air exposure which prevented further XRD analysis. **^{1}H NMR** (600 MHz, 298 K, THF-d_8): δ = 7.70-7.75 (m, 6H, *H*-3+*H*-4), 7.58-7.62 (m, 6H, *H*-5+*H*-6), 7.27 (s, 3H, *H*-1), 7.24 (s, 3H, *H*-11), 2.39 (s, 18H, *m*-CH_3), 2.12 (s, 18H, *o*-CH_3) ppm. **^{11}B NMR** (193 MHz, 298 K, THF-d_8): δ = 39.6 (br s, $\Delta\nu_{½}$ = 1837 Hz). **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, THF-d_8): δ = 147.4 (*C*-1), 143.3 (C_q^B-8), 137.2 (C_q-9), 136.4 (C_q^B-7), 134.3 (C_q-2+*C*-3), 133.9 (C_q-10), 131.7 (*C*-11), 131.3 (*C*-4), 130.6 (*C*-5), 128.3 (*C*-6), 20.8 (*o*-*C*H$_3$), 20.1 (*m*-*C*H$_3$) ppm. **HRMS** (LIFDI, THF): expected: m/z 972.2577 [$C_{51}H_{54}Cu_3B_3N_6$]$^+$ (trimer); found: 262.1635 [$C_{51}H_{54}Cu_3B_3N_6$–dimer–Cu+H]$^+$ (**6H**).*[2]

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*[1] Due to spectral overlap and general signal broadness, only one coupling constant could be determined.
*[2] No M+ peak detected due to the compound's low stability despite using the mildest ionization source available.

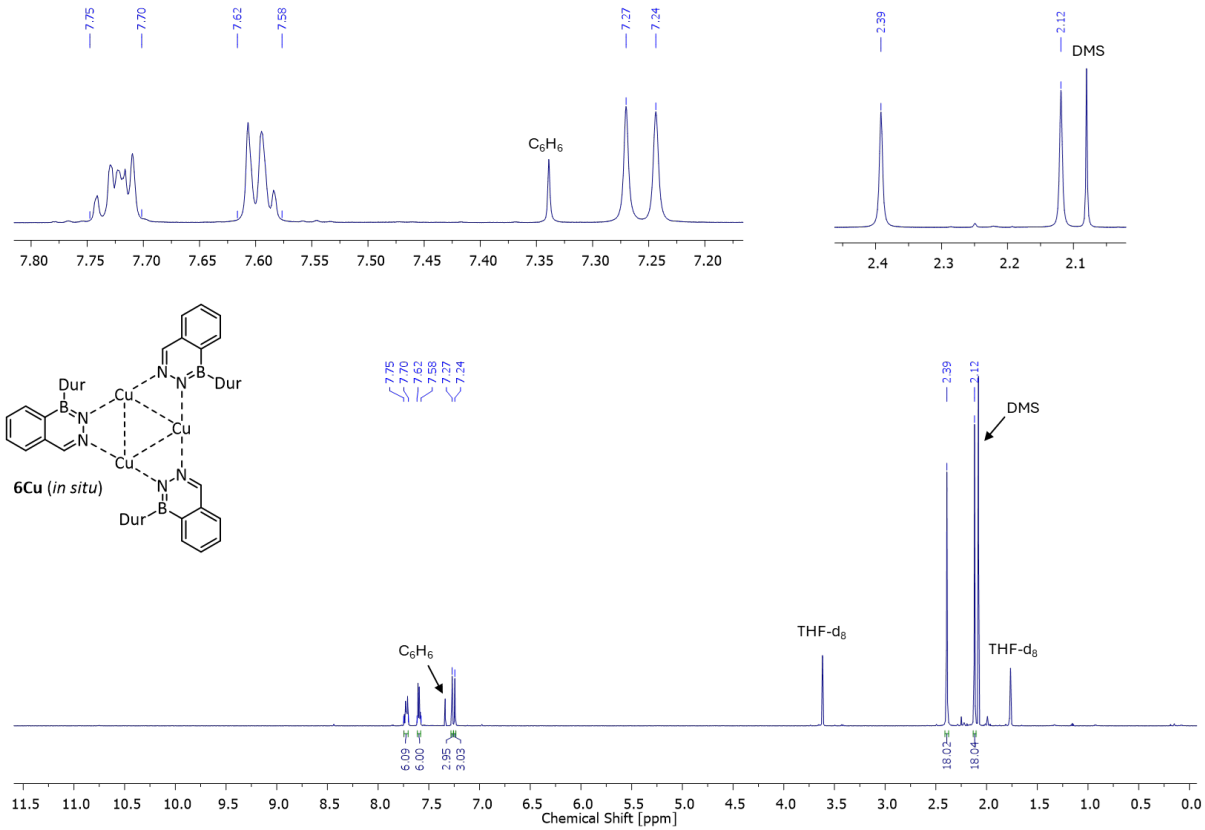


Figure S71. *In-situ* ^{1}H NMR spectrum of compound **6Cu** in THF-d_8.

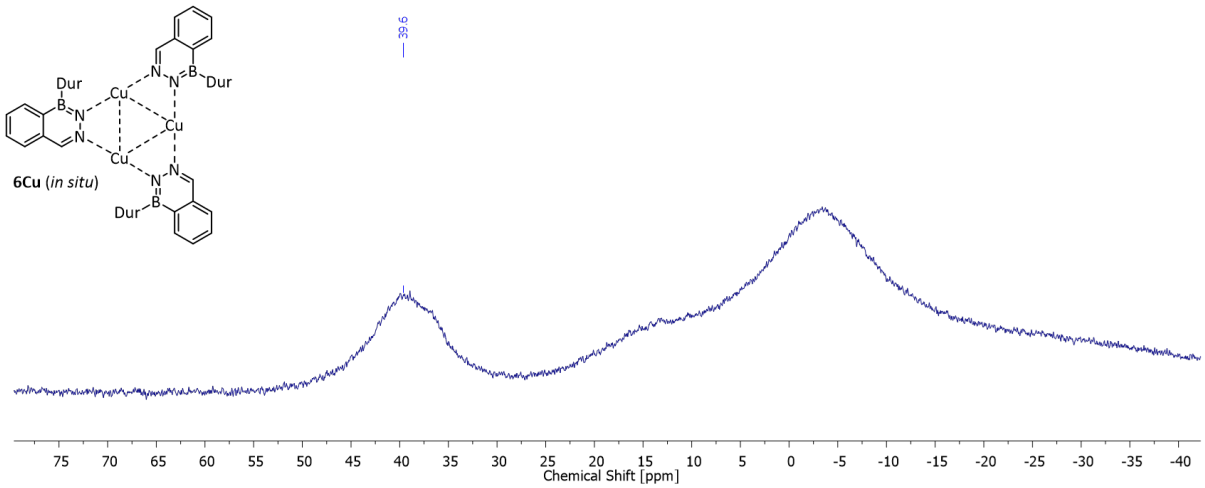


Figure S72. *In-situ* background-reduced ^{11}B NMR spectrum of compound **6Cu** in THF-d_8.

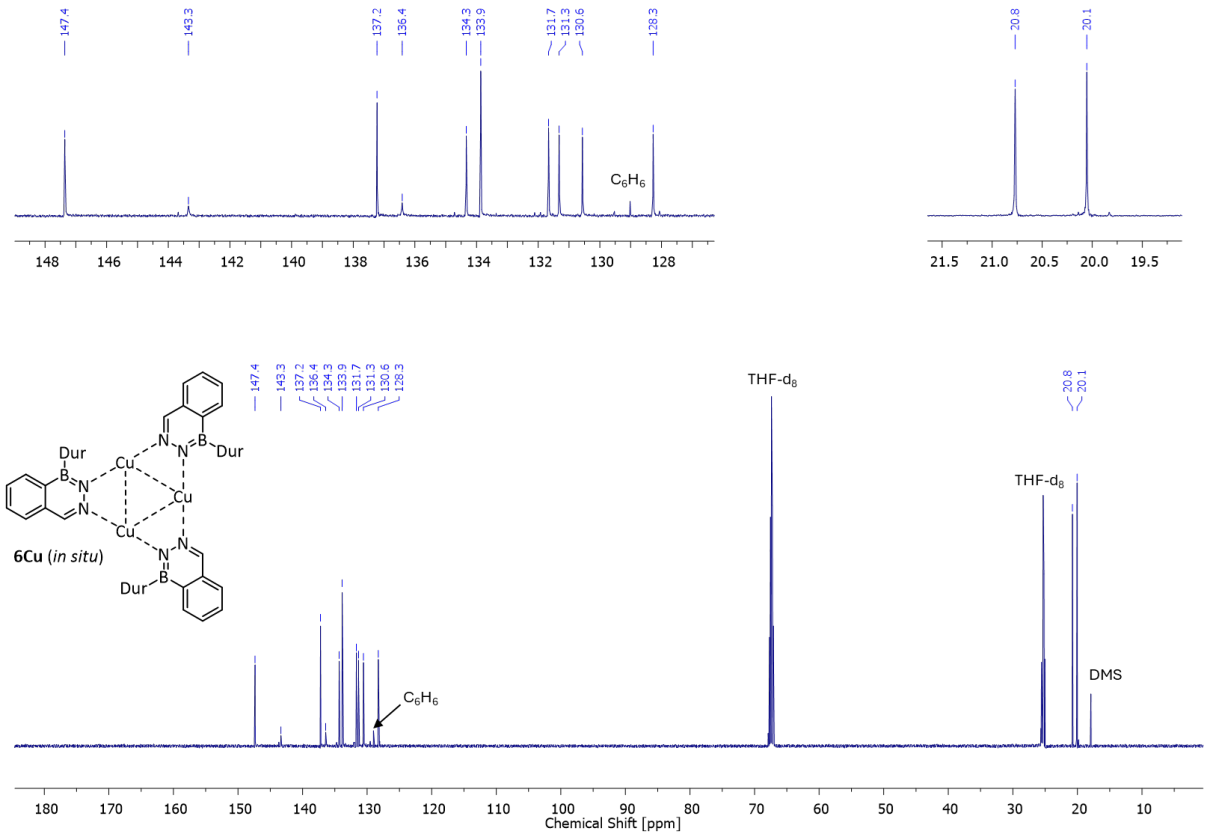


Figure S73. *In-situ* $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6Cu** in THF-d_8 (selectively ^{11}B-decoupled at +42 ppm).

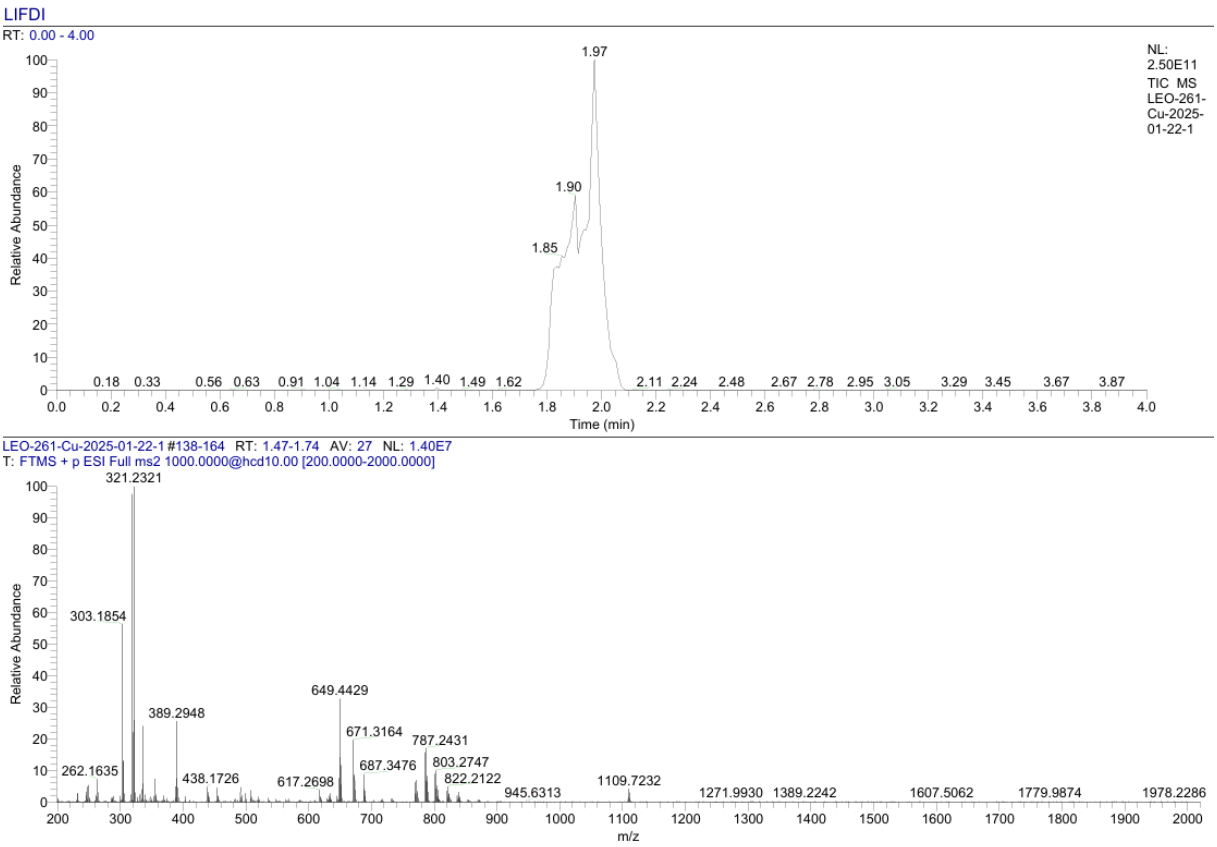
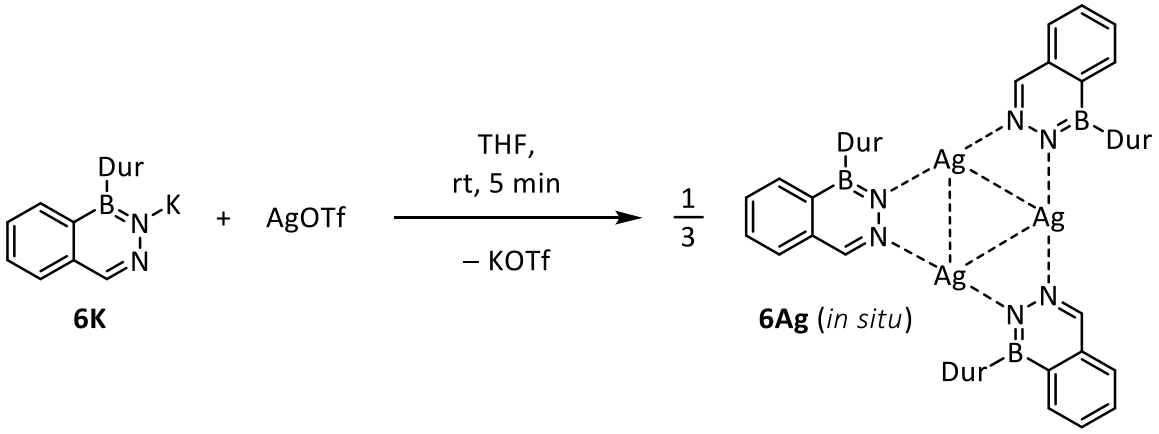
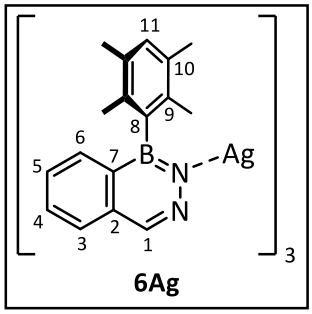


Figure S74. *In-situ* LIFDI high resolution mass spectrum of compound **6Cu** (THF). No M^+ peak detected due to the compound's low stability.

Ag(I)-diazaboramide complex [$Ag_3(\mu$-DAB)$_3$] (6Ag)



Isolated compound **6K** (8.00 mg, 26.6 μmol, 1.00 eq.) was dissolved in in pre-cooled (–30 °C) THF-d_8 (0.5 mL) in a brown glass J.-Young-style NMR tube and silver trifluoromethanesulfonate (6.85 mg, 26.6 μmol, 1.00 eq.) was added. A color change from colorless to light brown was observed. The 1D, 2D and ^{1}H DOSY NMR spectra and HRMS were measured directly afterwards due to rapid decomposition of **6Ag** in solution to **6H** and Ag(0), visually indicated by gradual precipitation of a grey solid. Yield not determined. The compound is not stable in solution.



Crystaline material of **6Ag** in form of colorless blocks was obtained by storing a saturated THF solution, which was layered with equal amounts of *n*-pentane at –30 °C in a glovebox. **^{1}H NMR** (600 MHz, 298 K, THF-d_8): δ = 7.65-7.70 (m, 2H, *H*-3+*H*-4), 7.61-7.62 (d, $^3J_{HH}$ = 7.77 Hz, 1H, *H*-6), 7.52-7.55 (ddd+s, $^3J_{HH}$ = 7.77 Hz,*[1] 1H, *H*-5+*H*-1), 7.14 (s, 1H, *H*-11), 2.33 (s, 6H, *m*-CH_3), 2.06 (s, 6H, *o*-CH_3) ppm. **^{11}B NMR** (193 MHz, 298 K, THF-d_8): δ = 40.7 (br s, $\Delta\nu_{½}$ = 2041 Hz) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, THF-d_8): δ = 149.5 (*C*-1), 144.4 (C_q^B-8), 136.9 (C_q-9), 135.9 (C_q^B-7), 134.2 (*C*-3), 133.5 (C_q-2), 133.4 (C_q-10), 131.3 (*C*-11), 130.9 (*C*-4), 130.2 (*C*-5), 127.8 (*C*-6), 20.5 (*o*-CH_3), 19.9 (*m*-CH_3) ppm. **HRMS** (LIFDI, THF): expected: m/z 1104.1842 [$C_{51}H_{54}Ag_3B_3N_6$]$^+$ (trimer); found: 262.1635 [$C_{51}H_{54}Ag_3B_3N_6$–dimer–Ag+H]$^+$ (**6H**).*[2]

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*[1] Due to spectral overlap and general signal broadness, only one coupling constant could be determined.
*[2] No M+ peak detected due to the compound's low stability despite using the mildest ionization source available.

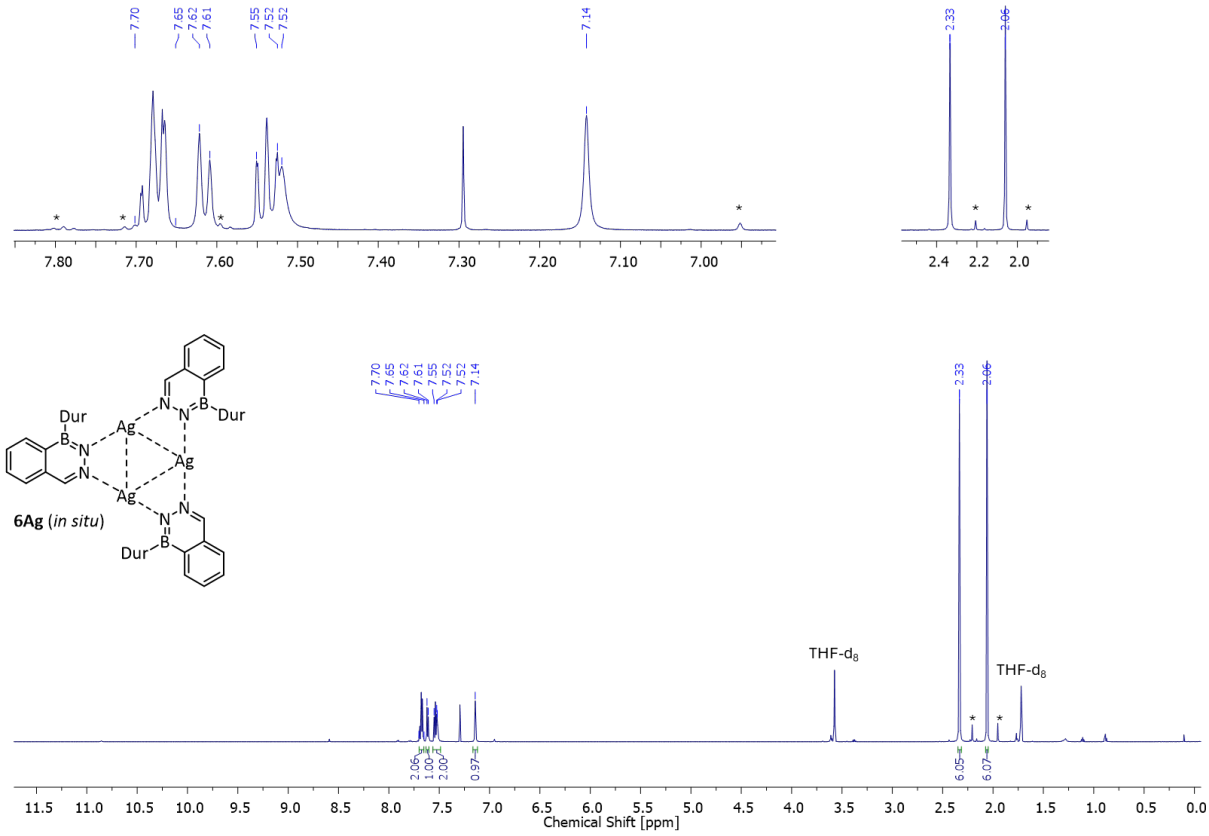


Figure S75. *In-situ* ^{1}H NMR spectrum of compound **6Ag** in THF-d_8. Marked resonances correspond to decomposition product **6H**.

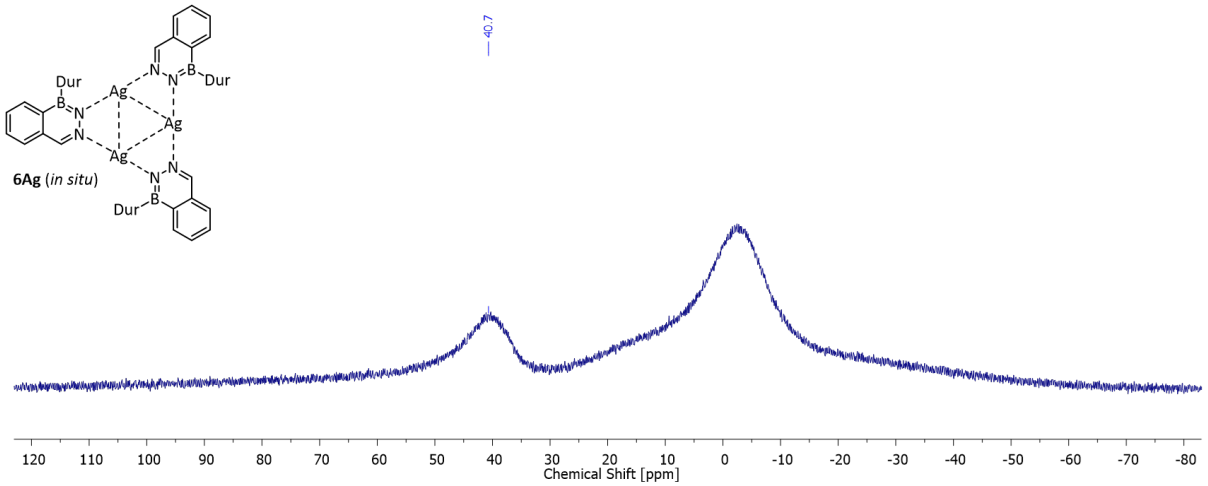


Figure S76. *In-situ* background-reduced ^{11}B NMR spectrum of compound **6Ag** in THF-d_8.

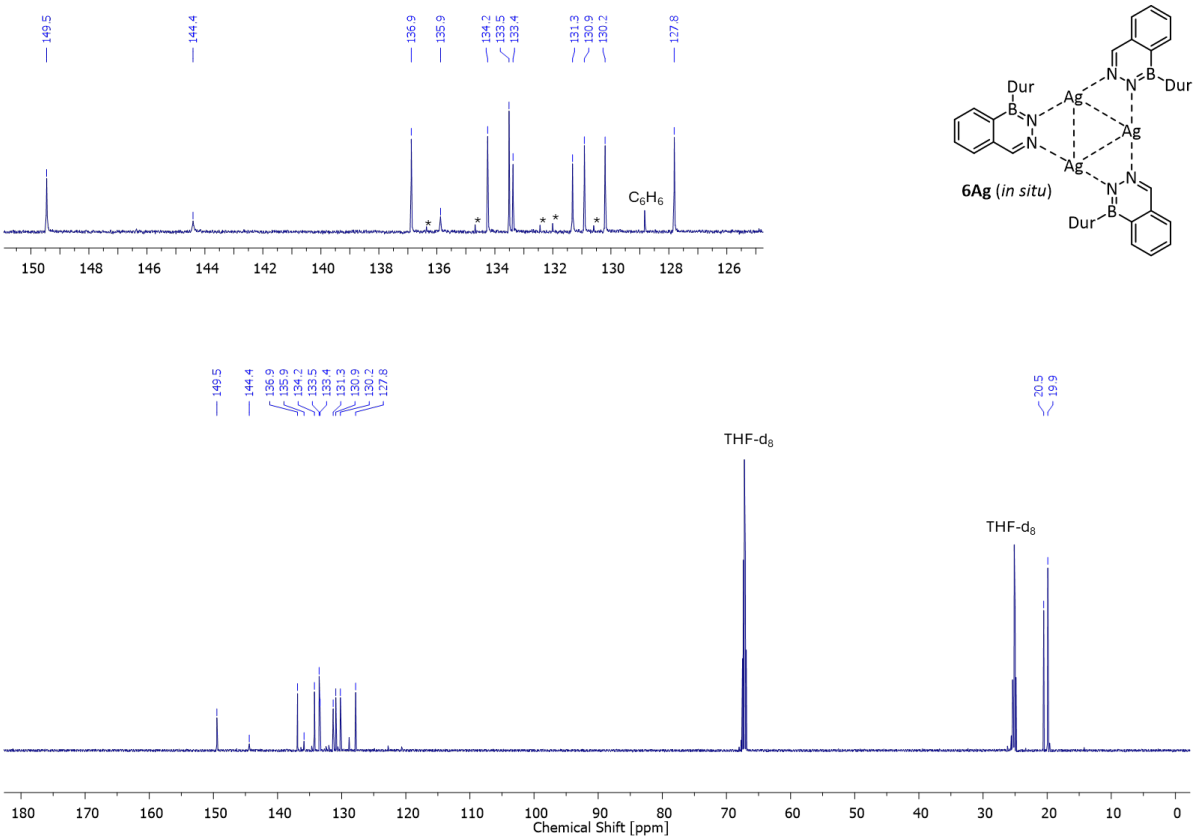


Figure S77. *In-situ* $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6Ag** in THF-d_8 (selectively ^{11}B-decoupled at +39 ppm). Marked resonances correspond to decomposition product **6H**.

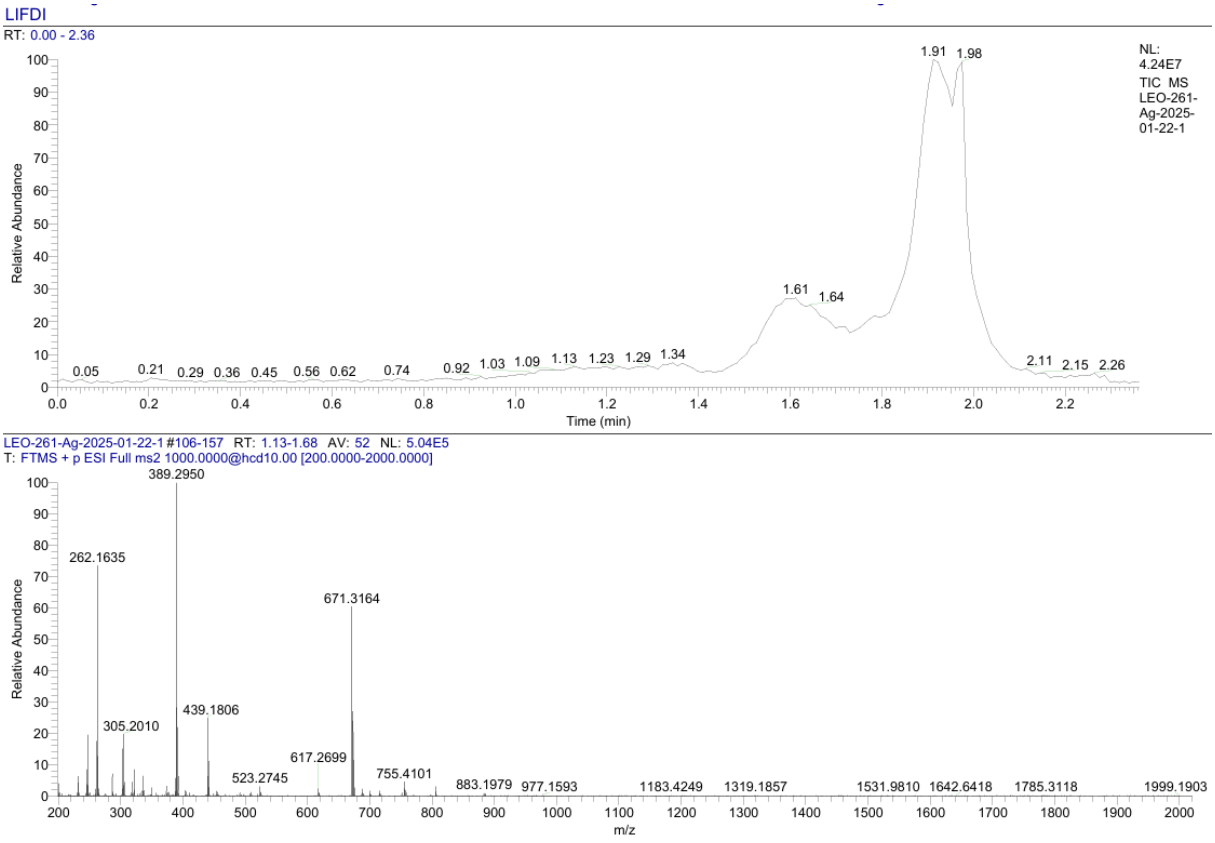


Figure S78. *In-situ* LIFDI high resolution mass spectrum of compound **6Ag** (THF). No M^+ peak detected due to the compound's low stability.

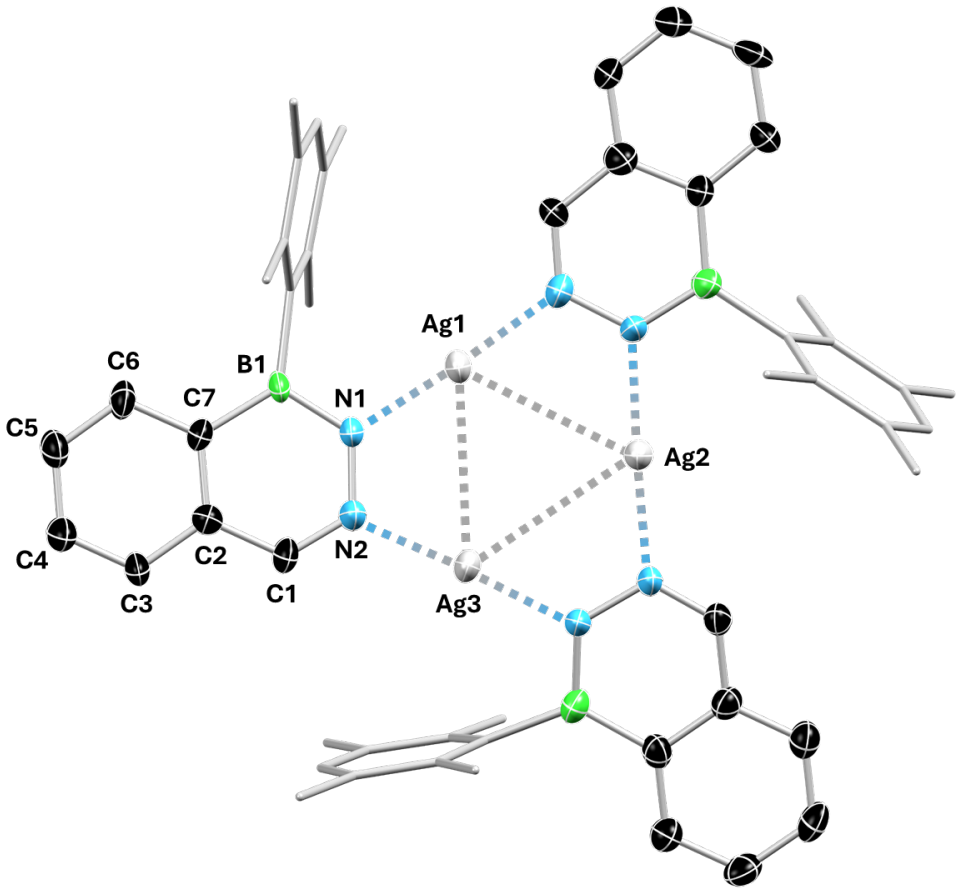


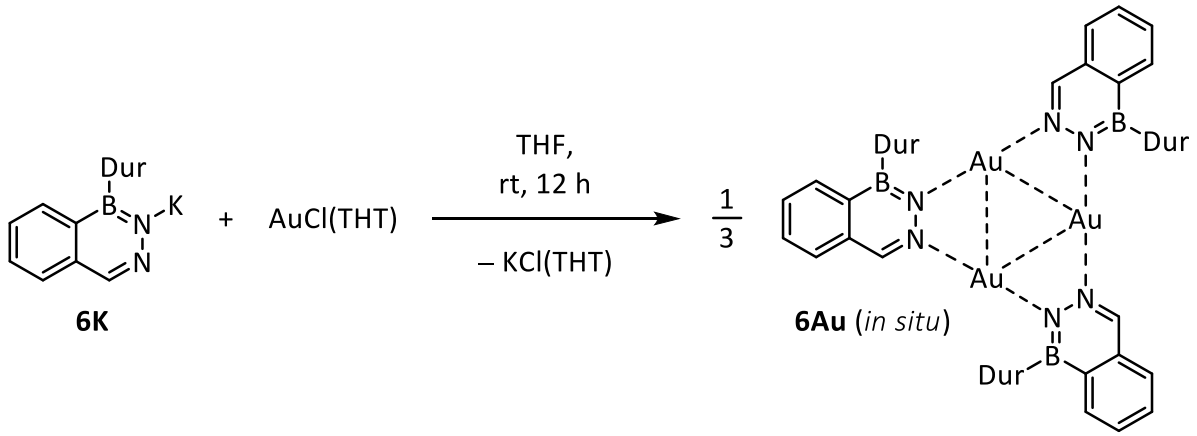
Figure S79. Molecular structure of compound **6Ag** (trimer). Ellipsoids drawn at 50% probability. All H atoms omitted, and duryl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6Ag**: B1–N1 1.410(9), N1–N2 1.367(8), N2–C1 1.289(9), N1–Ag1 2.074(7), N2–Ag3 2.071(8), Ag1···Ag2 3.3454(13), Ag2···Ag3 3.2805(13), Ag3···Ag1 3.2908(13), B1–N1–N2–C1 0.4(18), Ag3–N2–N1–Ag1 7.3(11).

Crystal data:
$C_{59}H_{70}Ag_3B_3N_6O_2$, M_r = 1251.25, clear colorless block, 0.078×0.049×0.041 mm^3, monoclinic space group $P2_1$, a = 11.843(2) Å, b = 19.898(4) Å, c = 12.410(3) Å, β = 107.45(2)°, V = 2789.9(10) Å^3, Z = 2, ρ_{calcd} = 1.489 g·cm^{-3}, μ = 8.726 mm^{-1}, F(000) = 1276, T = 100(2) K, R_1 = 0.0641, wR_2 = 0.1719, Flack parameter = 0.133(15), 10369 independent reflections [$2\theta \leq 152.718°$] and 599 parameters.

Crystal was a general (180° rotation around reciprocal 1 0 0 axis) and racemic twin (reflections for inverse domains were generated with Platon). The BASF parameters were refined to 19.2, 29.7 and 29.7%. One could also refine the structure in $P2_1/m$ instead of $P2_1$ space group, alas with much worse R_1 and wR_2 parameters. In the higher SG structure was mirrored by plain Ag1-X-C5_7 (X centroid of Ag2 and Ag3), which led to imperfect overlapping of atoms on opposite sides of molecule. Two poorly-defined solvent molecules (THF) were found in the asymmetric unit. The geometry of them was restrained with AFIX 9 (breathing and roto-translation), and U_{isor} parameters in each of THF were constrained to the same values with free variable.

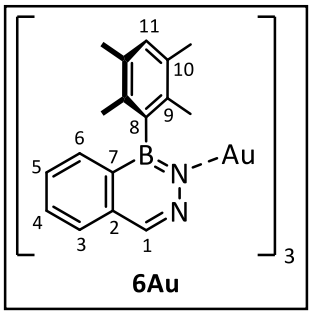
CCDC number: 2425639

Au(I)-diazaboramide complex [Au_3(μ-DAB)$_3$] (6Au)



6K **6Au** (*in situ*)

Isolated compound **6K** (8.00 mg, 26.6 μmol, 1.00 eq.) was dissolved in in pre-cooled (–30 °C) THF-d_8 (0.5 mL) in a brown glass J.-Young-style NMR tube and chloro(tetrahydrothiophene)gold(I) (8.54 mg, 26.6 μmol, 1.00 eq.) was added. A color change from colorless to light yellow was observed. The ^{1}H NMR spectra measured directly afterwards showed the conversion of an intermediate species (presumably the side-on η^2 isomer) to μ-bridging **6Au** over 20 h, visually accompanied by gradual violet coloration and precipitation of a dark solid. After 20 h 1D, 2D and ^{1}H DOSY NMR spectra and HRMS were measured *in-situ* due to slow decomposition of **6Au** in solution to **6H** and Au(0), Yield not determined. The compound is not stable in solution.



6Au

Crystaline material of **6Au** in form of colorless blocks was obtained by storing a saturated dichloromethane solution in a glovebox at ambient temperature. **^{1}H NMR** (600 MHz, 298 K, THF-d_8): δ = 7.69-7.73 (m, 2H, *H*-3+*H*-4), 7.58-7.63 (m, 2H, *H*-5+*H*-6), 7.46 (s, 1H, *H*-1), 7.14 (s, 1H, *H*-11), 2.32 (s, 6H, *m*-C*H*$_3$), 2.04 (s, 6H, *o*-C*H*$_3$) ppm. **^{11}B NMR** (193 MHz, 298 K, THF-d_8): δ = 42.0 (br s, $\Delta\nu_{½}$ = 2191 Hz) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, THF-d_8): δ = 149.4 (*C*-1), 142.5 (*C*$_q^B$-8), 136.9 (*C*$_q$-9), 136.4 (*C*$_q^B$-7), 134.6 (*C*-3), 133.8 (*C*$_q$-2), 133.3 (*C*$_q$-10), 131.8 (*C*-11), 131.4 (*C*-4), 131.2 (*C*-5), 128.3 (*C*-6), 20.2 (*o*-*C*H$_3$), 19.8 (*m*-*C*H$_3$) ppm. **HRMS** (LIFDI, THF): expected: m/z 1373.3717, 1374.3680, 1375.3714 [$C_{51}H_{54}Au_3B_3N_6$]$^+$ (trimer); found: m/z 1373.3714, 1374.3690, 1375.3707 [$C_{51}H_{54}Au_3B_3N_6$]$^+$ (trimer).

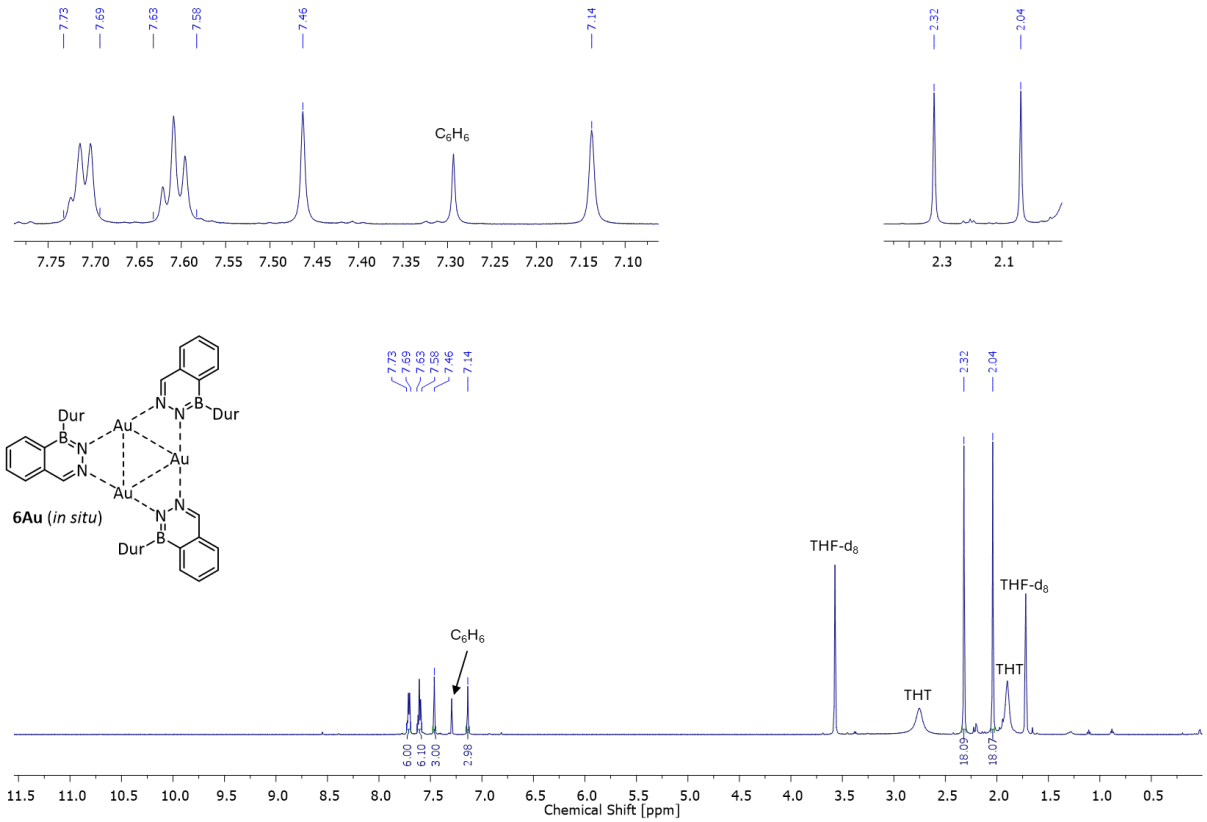


Figure S80. *In-situ* ^{1}H NMR spectrum of compound **6Au** in THF-d_8.

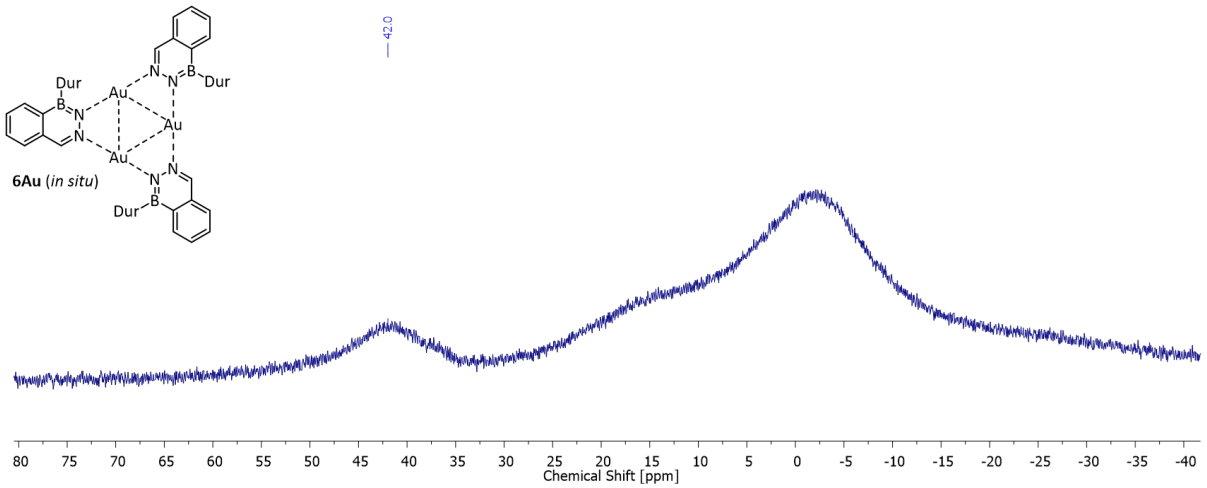


Figure S81. *In-situ* background-reduced ^{11}B NMR spectrum of compound **6Au** in THF-d_8.

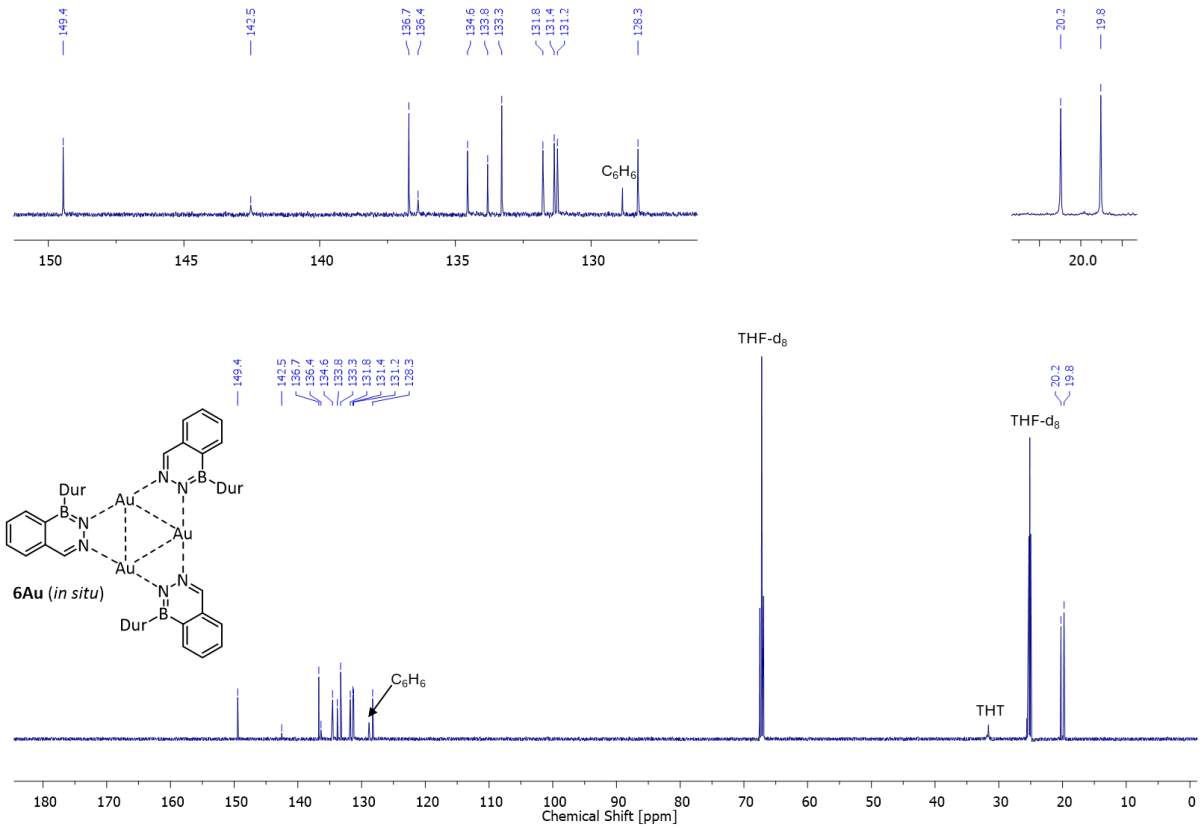


Figure S82. *In-situ* $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6Au** in THF-d_8 (selectively ^{11}B-decoupled at +43 ppm).

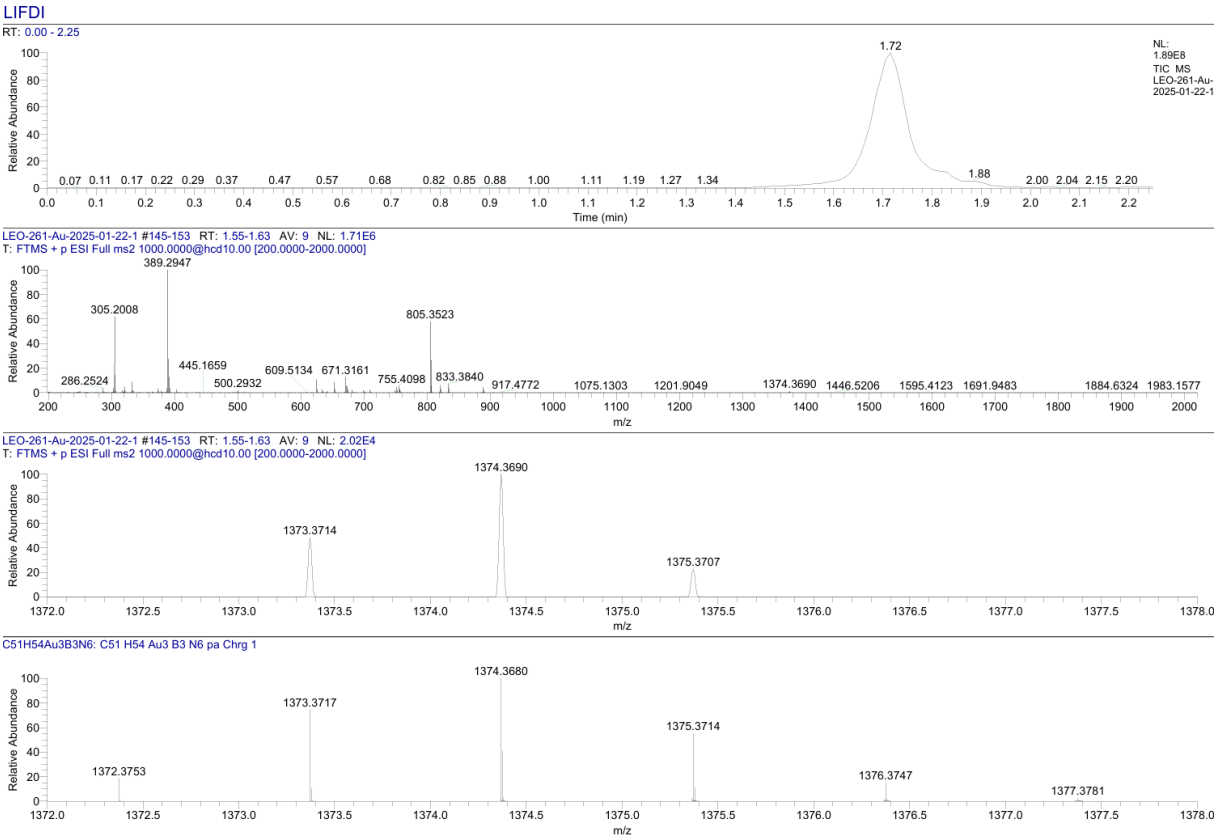


Figure S83. *In-situ* $ASAP_{neg}$ high resolution mass spectrum of compound **6Au** (THF).

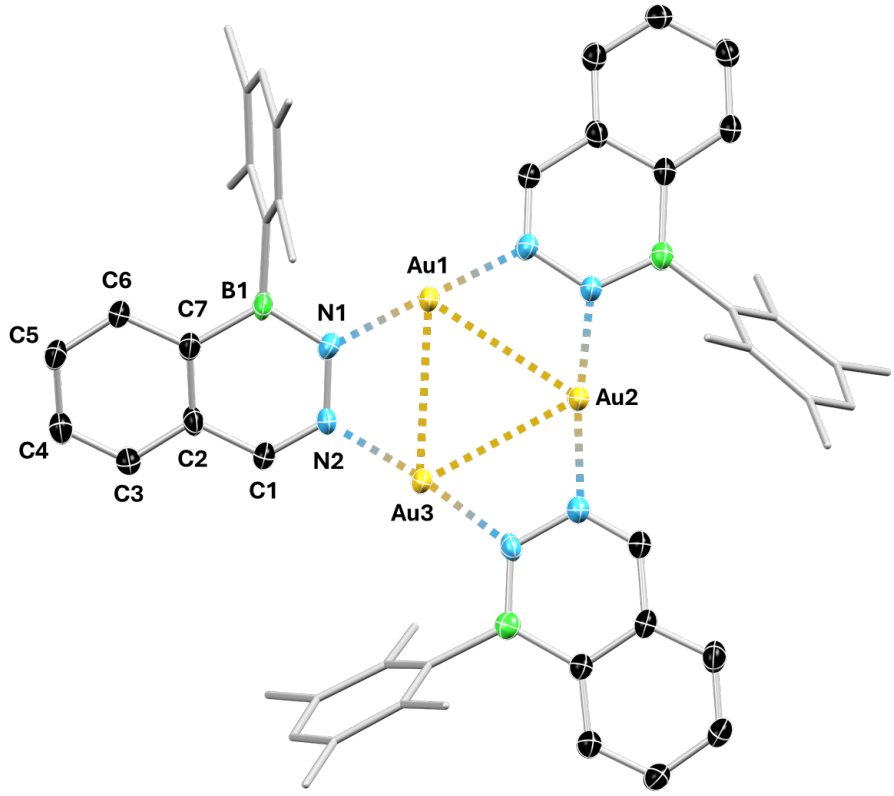


Figure S84. Molecular structure of compound **6Au** (trimer). Ellipsoids drawn at 50% probability. All H atoms omitted, and duryl groups rendered as wireframe. Selected bond lengths (Å) and angles (°) of **6Au**: B1–N1 1.414(7), N1–N2 1.390(5), N2–C1 1.298(6), N1–Au1 2.010(4), N2–Au3 2.016(4), Au1···Au2 3.2768(18), Au2···Au3 3.2475(16), Au3···Au1 3.1988(12), B1–N1–N2–C1 2.9(7), Au3–N2–N1–Au1 7.5(4).

Crystal data:
$C_{60}H_{63}Au_3B_3N_6$, M_r = 1491.49, clear colorless block, 0.090×0.070×0.030 mm^3, triclinic space group $P\bar{1}$, a = 12.050(5) Å, b = 14.853(7) Å, c = 15.153(7) Å, α = 82.33(4)°, β = 87.07(4)°, γ = 83.93(3)°, V = 2671(2) Å^3, Z = 2, ρ_{calcd} = 1.855 g·cm^{-3}, μ = 15.523 mm^{-1}, F(000) = 1434, T = 100(2) K, R_1 = 0.0328, wR_2 = 0.0755, 10472 independent reflections [$2\theta \leq 150.352°$] and 671 parameters.

Crystal showed whole-molecular disorder (96:4). The minor disorder component was modeled using the major component, and for the final refinement used as a constrained fragment. The ADPs of all atoms in minor components except gold atoms were refined using a common variable and SIMU restraint. After finding the U_{iso}, this variable was converted to constrained value and SIMU card was removed from input. ADPs of gold atoms in minor disorder component were were constrained to the nearest Au-atom in the major disorder component (EADP). A benzene molecule placed on the inversion center was refined using AFIX 66 and a set of ADP restraints (SIMU, RIGU, and ISOR).

CCDC number: 2425633

Appendix

Compound **3**

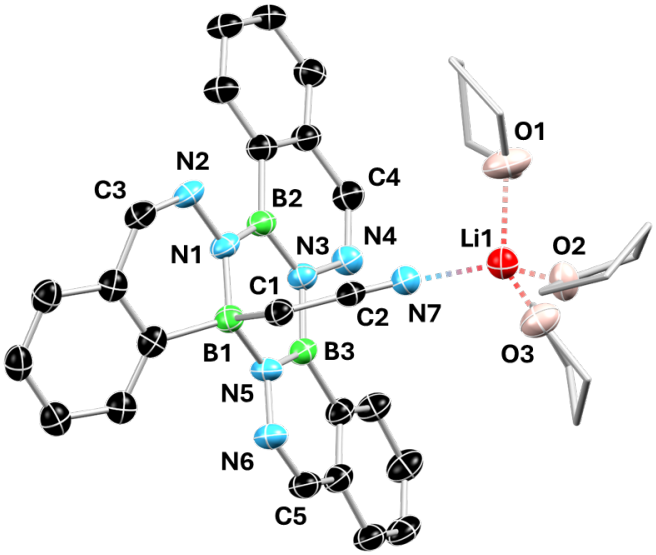


Figure S85. Molecular structure of the lithium borate salt of compound **3**, formed during workup of **3** by washing with MeCN in presence of residual base by attack of a deprotonated MeCN at one of the boron centers. Ellipsoids drawn at 50% probability. All H atoms omitted and complexing THF rendered as wireframe. Selected bond lengths (Å) and angles (°): B1–N1 1.546(2), B1–C1 1.685(3), N1–N2 1.4022(19), N1–B2 1.415(3), B2–N3 1.464(2), N3–N4 1.390(2), B3–N3 1.469(2), B3–N5 1.417(2), N5–N6 1.394(2), B1–N5 1.544(2), C1–C2 1.444(2), C2–N7 1.147(2), B1–N1–N2–C3 25.6(2), B2–N3–N4–C4 6.1(2), B3–N5–N6–C5 5.2(3).

Crystal data:

$C_{35}H_{41}B_3LiN_7O_3$, M_r = 647.12, yellow plate, 0.180×0.140×0.050 mm^3, monoclinic space group $P2_1/c$, a = 18.1164(2) Å, b = 12.66620(10) Å, c = 17.0662(2) Å, β = 118.098(1)°, V = 3454.57(7) Å^3, Z = 4, ρ_{calcd} = 1.244 g·cm^{-3}, μ = 0.628 mm^{-1}, $F(000)$ = 1368, T = 100(2) K, R_1 = 0.0699, wR_2 = 0.1682, 6922 independent reflections [$2\theta \leq 150.208°$] and 488 parameters.

The atomic displacement parameters of all THF atoms O1 to C4 were restrained to the same value with similarity restraint SIMU and an 'enhanced rigid bond' restraint RIGU. Their U_{ii} parameters were restrained with ISOR keyword to approximate isotropic behavior. Additionally, the displacement parameters of atoms C1_1 and N1_1 of residue_1 (borate center in **3**) were restrained to the same value with similarity restraint SIMU with esd = 0.005.

CCDC number: 2425626

Compounds **4M**

Despite our best efforts, it was not possible to isolate compounds **4Na** or **4K**. In these attempts, **2H** (25.0 mg, 115 μmol, 1.00 eq.) was dissolved in THF-d_8 (0.5 mL) in a J.-Young-style NMR tube and K[HMDS] (25.2 mg, 126 μmol, 1.10 eq.) or Na[HMDS] (23.1 mg, 126 μmol, 1.10 eq.) was added at ambient temperature. After 10 min, a color change from colorless to pale yellow was observed and the sample was analyzed via ^{1}H and ^{11}B NMR spectroscopy (**Figure S86** and **Figure S87**), indicating the formation of the borate **4M^{Int}**, before elimination of HMDSO as main product. Then, the reaction was heated to 80 °C for 3 d, which resulted in the formation of a pale-yellow solid. Extraction attempts with various solvents were not successful. Small amounts of crystalline material of **4K** in the form of colorless blocks were obtained by storing the MeCN washing solution at ambient temperature in a glovebox. No additional characterization was possible.

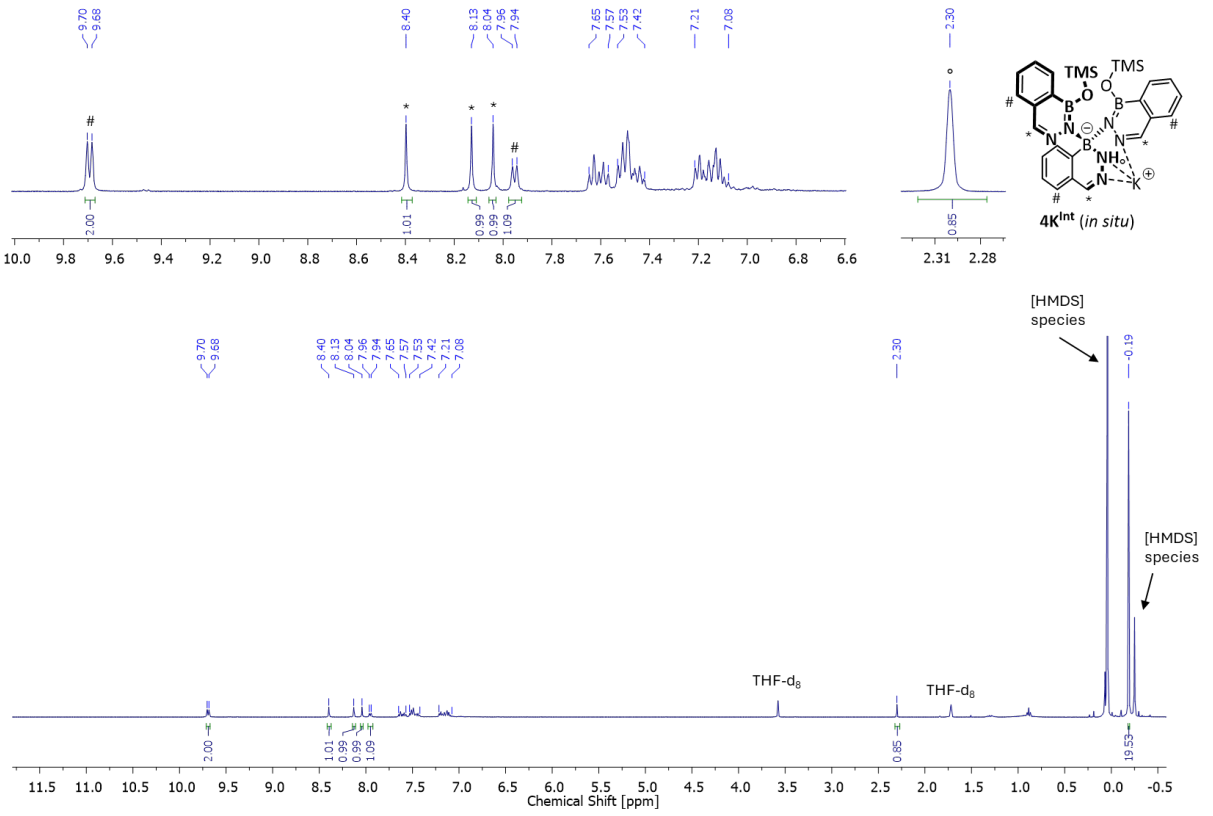


Figure S86. *In-situ* ^{1}H NMR spectrum of the intermediate **4K^{Int}** before elimination of HMDSO in THF-d_8. Characteristic resonances are marked in the spectrum and structure.

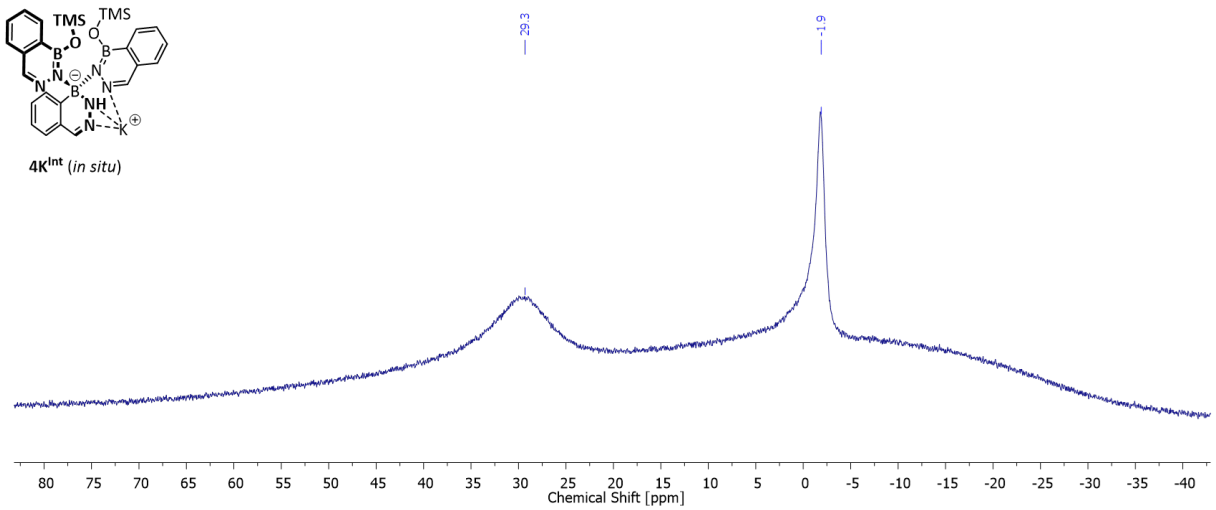


Figure S87. *In-situ* ^{11}B NMR spectrum of compound **4K** in THF-d_8.

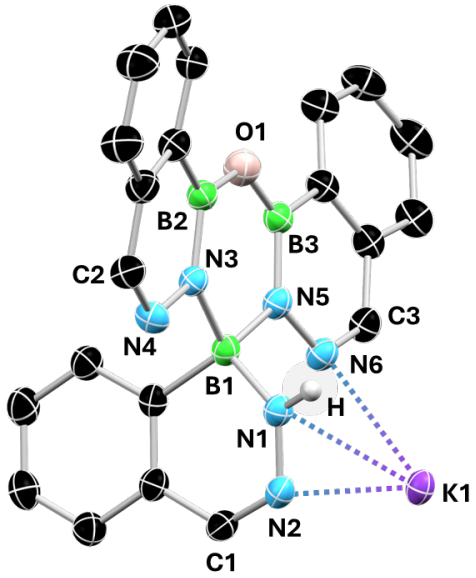


Figure S88. Molecular structure of **4K.** Ellipsoids drawn at 50% probability. All H atoms except that bound to the secondary amine omitted. Due to washing in the presence of residual base, the partial deprotonation and dimerization of MeCN was observed. These MeCN decomposition products form a coordination polymer with **4K** in the solid state and are omitted for clarity. Selected bond lengths (Å) and angles (°): B1–N1 1.534(3), B1–N3 1.643(17), B1–N5 1.563(3), B2–N3 1.43(3), B3–N5 1.432(3), B2–O1 1.46(3), B3–O1 1.410(3), N1–N2 1.359(3), N3–N4 1.40(3), N5–N6 1.378(3), B1–N1–N2–C1 14.9(3), B2–N3–N4–C2 6(3), B3–N5–N6–C3 1.3(3).

Crystal data:

$C_{52}H_{43}B_6K_4N_{17}O_2$, M_r = 1159.29, colorless block, 0.380×0.220×0.190 mm^3, monoclinic space group *P*2/*c*, *a* = 13.2068(2) Å, *b* = 15.3061(2) Å, *c* = 14.4664(2) Å, β = 106.609(1)°, *V* = 2802.29(7) Å^3, *Z* = 2, ρ_{calcd} = 1.374 g·cm^{-3}, μ = 3.290 mm^{-1}, *F*(000) = 1192, *T* = 100(2) K, R_1 = 0.0611, wR_2 = 0.1638, 5633 independent reflections [$2\theta \leq 149.314°$] and 457 parameters.

One diazaborinine (DAB) unit is disordered. The atomic displacement parameters of the atoms B1_2 to C7_21 were restrained to the same value with similarity restraint SIMU with esd = 0.016 and with the 'enhanced rigid bond' restraint RIGU. Additionally to approximate isotropic behavior their U_{ii} parameters were restrained with ISOR keyword with esd = 0.008. The acetonitrile molecule is on a special position and it was refined isotropically.

CCDC number: 2425636

Compound **5**

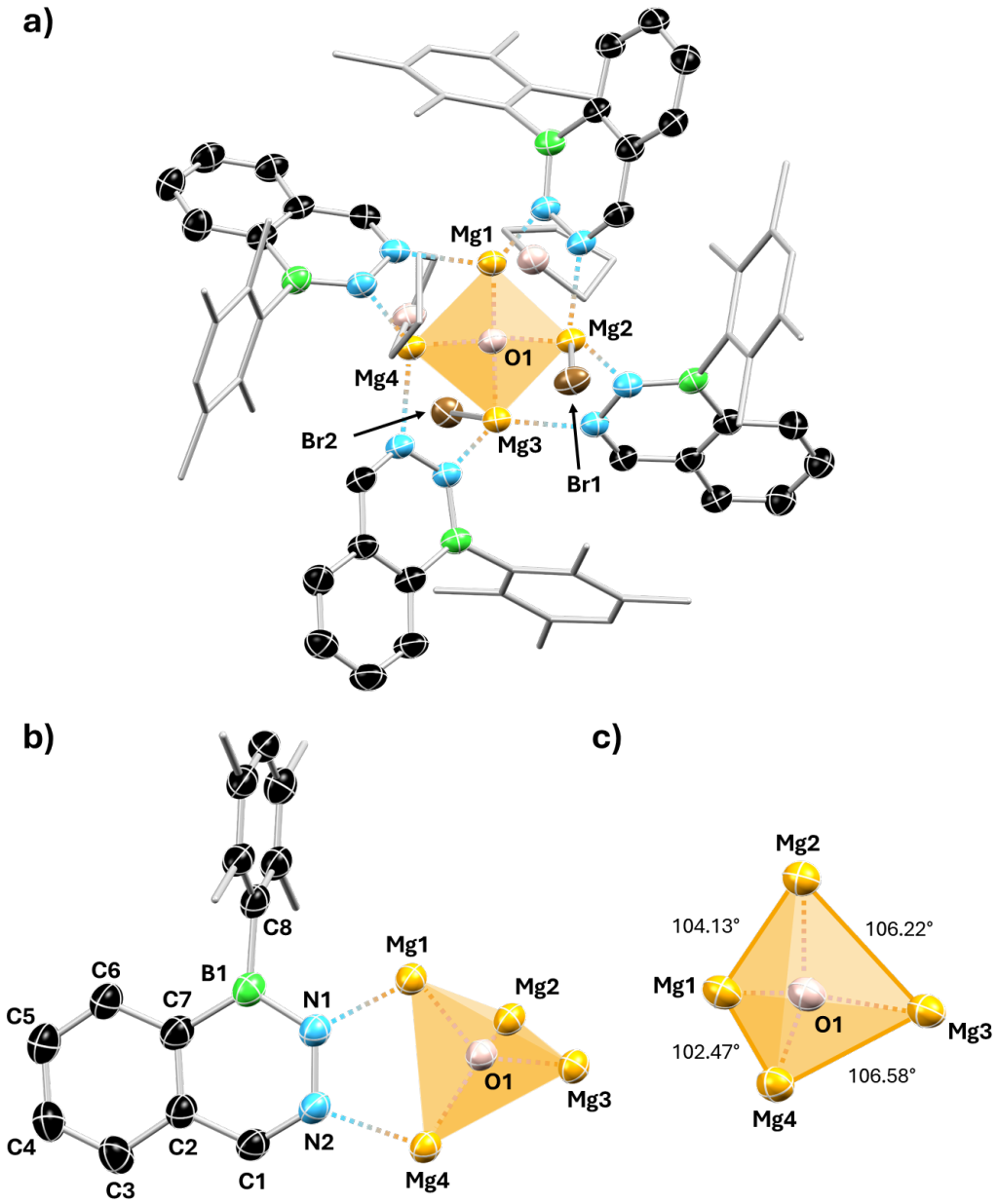


Figure S89. (a) Coordination tetramer with the μ_4-oxo[Mg_4O] core. (b) Molecular structure of the monomeric DAB unit of compound **5** with the μ_4-oxo[Mg_4O] core in the solid state. (c) μ_4-oxo[Mg_4O] coordination polyhedron. All H atoms omitted, duryl groups and complexing THF rendered as wireframe. Selected bond lengths (Å) and angles (°) of **5**: B1–N1 1.408(7), N1–N2 1.402(5), N2–C1 1.299(6), C1–C2 1.423(7), C2–C3 1.412(7), C3–B1 1.546(7), C3–C4 1.397(7), C4–C5 1.388(7), C5–C6 1.402(8), C6–C7 1.371(7), C7–C2 1.402(7), B1–C8 1.585(7), N1–Mg1 2.063(4), N2–Mg4 2.090(4), Mg1–O1 1.966(3), Mg2–O1 1.945(3), Mg3–O1 1.946(3), Mg4–O1 1.968(3), C8–B1–N1 118.5(4), Mg1–O1–Mg2 106.58(15), Mg2–O1–Mg3 106.22(16), Mg3–O1–Mg4 102.47(15), Mg4–O1–Mg1 104.13(15), C1–N2–N1–B1 0.2(6).

Crystal data:
$C_{86}H_{112}B_4Br_2Mg_4N_8O_3$, M_r = 1606.13, colorless plate, 0.240×0.160×0.060 mm^3, triclinic space group $P\ \bar{1}$, a = 15.0166(2) Å, b = 16.5087(3) Å, c = 19.7579(4) Å, α = 70.547(2)°, β = 74.162(2)°, γ = 76.507(2)°, V = 4388.02(15) Å^3, Z = 2, ρ_{calcd} = 1.216 g·cm^{-3}, μ = 1.837 mm^{-1}, $F(000)$ = 1692, T = 100(2) K, R_1 = 0.0977, wR_2 = 0.2354, 17296 independent reflections [$2\theta \leq 150.55°$] and 978 parameters.

Some reflections were removed from refinement as outliers. One pentane molecule is disordered. Both parts were refined isotropically. The displacement parameters of the disordered atoms C1 to C5 of residues 13 and 131 were restrained to the

same value with similarity restraint SIMU (esd = 0.008). The distances in the disordered pentane molecule between atoms C1 to C5 were restrained to the value of 1.55 and 2.65.

CCDC number: 2425631

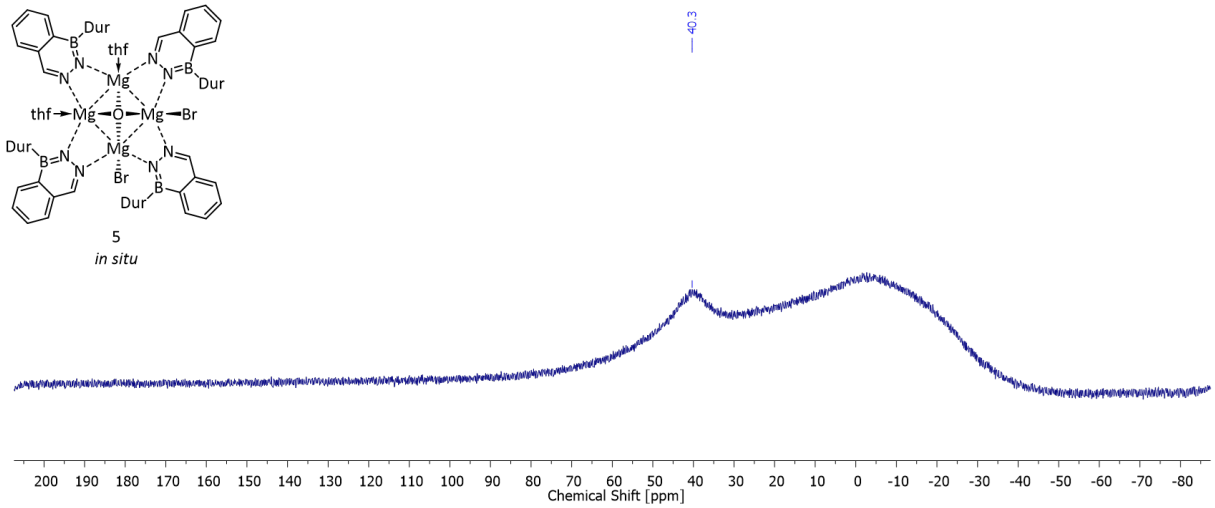
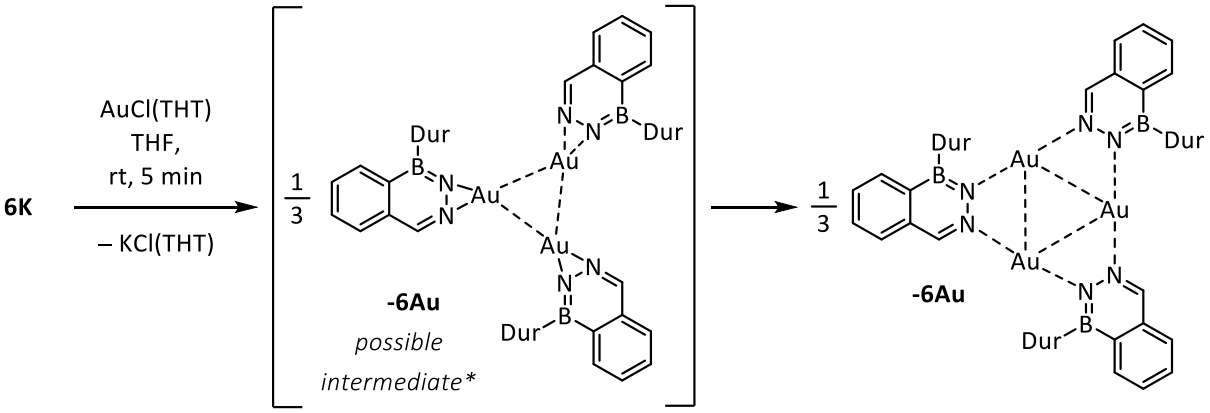


Figure S90. *In-situ* ^{11}B NMR spectrum (unlocked) of compound **5** in THF-H_8 after 2 h at 60 °C.

Compound **6Au**



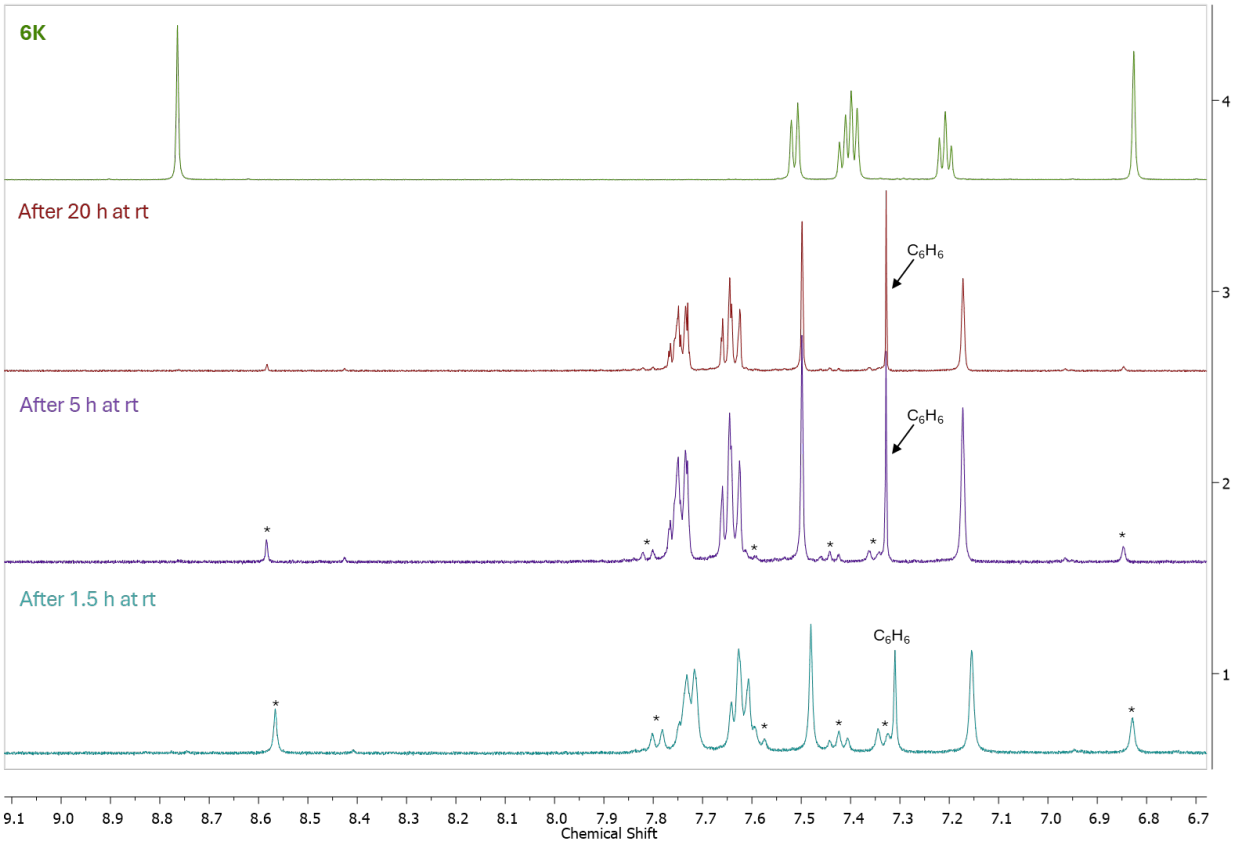


Figure S91. Stacked **6K** and *in-situ* ^{1}H NMR spectrum of compound **6Au** in THF-d_8 after 1.5 h, 5 h and 20 h at rt. Marked resonances correspond to an intermediate species.

To attempt photophysical characterization of our coinage metal complexes, we studied the properties of the most stable complex candidate, **6Au**, using a freshly prepared *in-situ* sample. Compound **6Au** was synthesized in THF-d_8 in a brown glass *J.-Young*-style NMR tube according to section 2 and a ^{1}H NMR spectrum was recorded after 15 h directly prior to the photophysical experiments, confirming the presence of **6Au** as the major species in solution (**Figure S92**, 70% ***μ*-6Au** and 30% ***η*²-6Au**). The time point of 15 h was chosen, as the full conversion of ***η*²-6Au** to ***μ*-6Au** requires a reaction time of approx. 20 h but the distinct formation of a violet solid (colloidal gold) was already observed after 15 h (see **Figure S92**, inset) and indicated progressing decomposition.

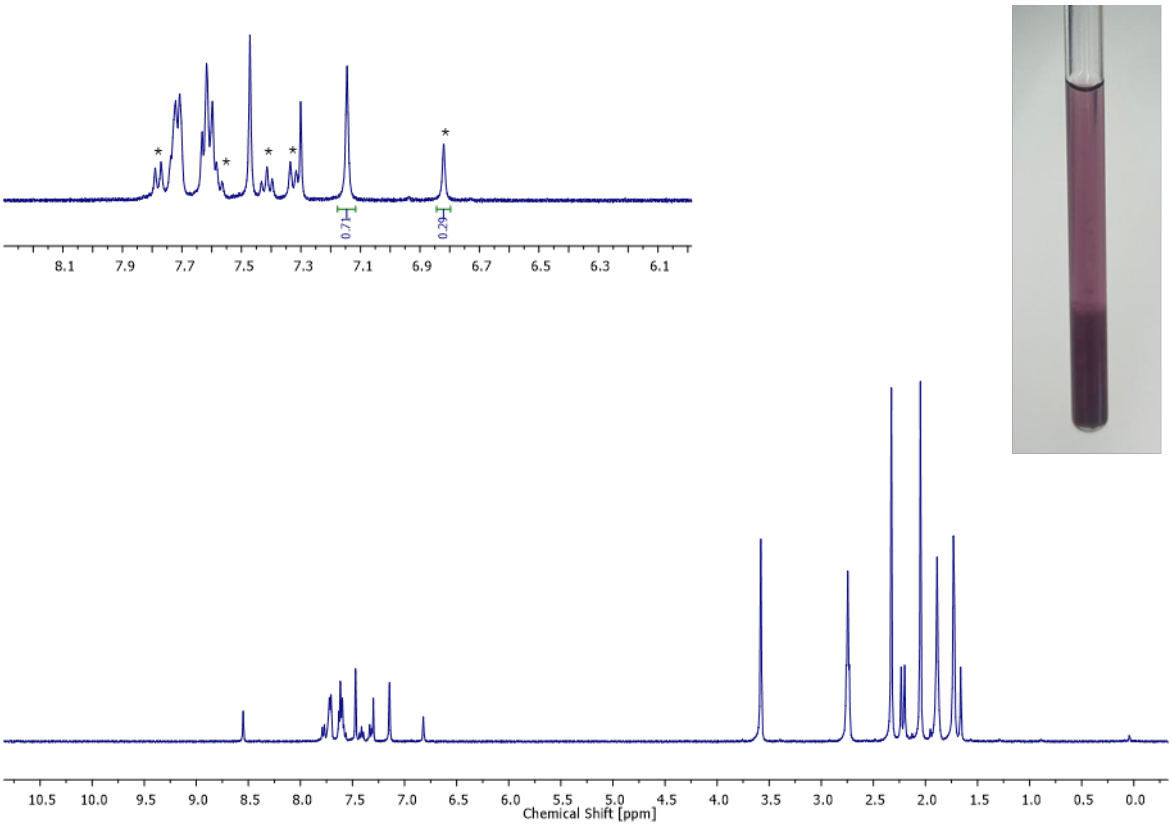


Figure S92. *In-situ* ^{1}H NMR spectrum of compound **6Au** in THF-d_8 after 15 h at ambient temperature and directly prior to the photophysical experiments. Marked resonances correspond to the intermediate species. Inset: NMR tube prior to the photophysical experiments, showing the formation of colloidal gold.

The photoabsorption and -emission spectra were recorded using an inert gas Schlenk cuvette as depicted in **Figure S93** and exhibit a complicated emission with several bands at λ_{em} = 483 nm, 520 nm, 563 nm and two additional broad shoulders at λ_{em} = 607 nm, 668 nm. These bands can be assigned to either multiple photoactive species (e.g. ***η*²-6Au** and ***μ*-6Au**), or correspond to a single one emission band, exhibiting a fine structure. Due to the limitation to an *in-situ* experiment, caused by the compound's low stability (*vide supra*), a more in-depth study was not possible or reasonable. A quantum yield of Φ_{THF}(**6Au**) of 14% was determined, using an integration sphere but is likewise to be interpreted with caution due to the nature of the measurement.

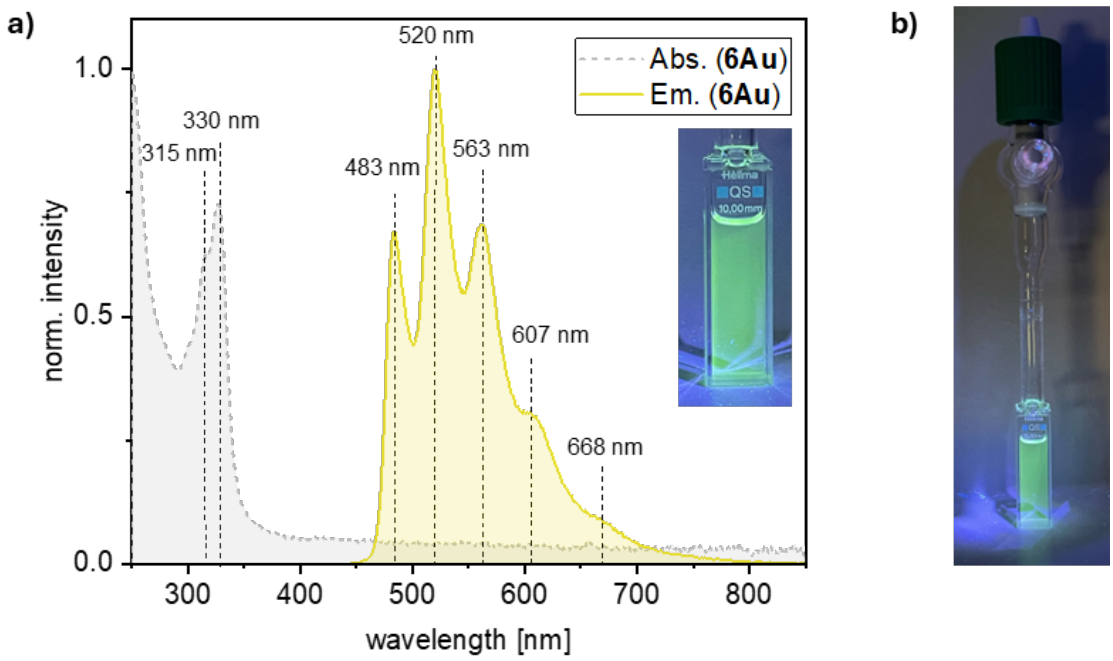


Figure S93. a) Normalized absorption and emission spectra of **6Au** in THF (*in situ*); b) Schlenk cuvette setup.

3 ^{1}H DOSY NMR spectra

The ^{1}H DOSY NMR experiments were performed at a temperature of 298.15 K with an *in-situ*-prepared solution of **6Li***[1] (c = 19 mM) in toluene-d_8 and THF-d_8 (c = 38 mM), **6Cu***[2] (c = 17 mM), **6Ag***[2] (c = 17 mM), **6Au***[2] (c = 17 mM) in THF-d_8 and with a solution of each isolated **6Na** (c = 8 mM) and **6K** (c = 19 mM) in THF-d_8.*[3]

The method published and made available in the form of an Excel file with external calibration curves and normalized diffusion coefficients by Neufeld and Stalke was used to calculate the molecular weight (MW) of the lower molecular weight compounds **6Li**, **6Na** and **6K** without heavy atoms.[8] Indene was used as an internal reference and the respective molecular form (**6Li**: "*expanded disc*" in THF-d_8, "*dissipated sphere*" in toluene-d_8) was estimated based on the solid-state structures or specified as "unknown" if no XRD data was available (**6Na**, **6K, 6Cu**: "*ECC merged/unknown*").[8] The obtained individual aryl diffusion coefficients, averaged aryl diffusion coefficients and calculated molecular weights for all compounds in toluene-d_8 or THF-d_8 are summarized in **Table S2.**

For the compounds containing the heavier transition metals **6Cu**, **6Ag** and **6Au**, the hydrodynamic radii r_H were determined instead, using the Stokes-Einstein equation (1):

$$r_H = \frac{k_B \cdot T}{6\pi \cdot \eta_{solv} \cdot \bar{x}(\mathrm{D})} = r_H = \frac{1.380649 \cdot 10^{-23}\,\frac{Nm}{K} \cdot 298.15\ K}{6\pi \cdot 0.000475\ \frac{N}{m^2} s \cdot \bar{x}(\mathrm{D})} \qquad (1)$$

where k_B is the Boltzmann constant, η the solvent viscosity ($\eta_{THF} = 0.000475\,\frac{N}{m^2}$) and $\bar{x}(\mathrm{D})$ the averaged aryl diffusion coefficient of the sample (summarized in **Table S3**).

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*[1] *In-situ* deprotonation was performed using lithium 2,2',6,6'-tetramethylpiperidide (LiTMP), see Section 2, *in-situ* method.
*[2] *In-situ* preparation as described in Section 2.
*[3] Due to their poor solubility, no ^{1}H DOSY NMR experiment was performed for **6Na** and **6K** in toluene-d_8.

Table S2. Chemical shift of respective aryl integrals, individual diffusion coefficients, averaged diffusion coefficients and calculated molecular weights of **6Li**, **6Na** and **6K** (toluene-d_8 and THF-d_8).

Compound	Solvent	$\delta(^1H)$ [ppm]	D [m^2/s]	$\bar{x}(D)$ [m^2/s]	MW_{calc} [g/mol]	MW_{found} [g/mol]	Error
6Li	THF-d_8	8.766-8.651	$7.34 \cdot 10^{-10}$	$7.304 \cdot 10^{-10}$	539 dimeric	549[a] dimeric	2%
		7.602-7.534	$7.29 \cdot 10^{-10}$				
		7.534-7.442	$7.25 \cdot 10^{-10}$				
		7.439-7.368	$7.35 \cdot 10^{-10}$				
		7.315-7.197	$7.31 \cdot 10^{-10}$				
		6.895-6.813	$7.29 \cdot 10^{-10}$				
	toluene-d_8	8.418-8.270	$5.42 \cdot 10^{-10}$	$5.415 \cdot 10^{-10}$	1072 tetrameric	910[b] tetrameric	8%
		7.644-7.545	$5.40 \cdot 10^{-10}$				
		7.463-7.380	$5.41 \cdot 10^{-10}$				
		7.324-7.234	$5.42 \cdot 10^{-10}$				
		6.541-6.485	$5.43 \cdot 10^{-10}$				
6Na	THF-d_8	9.004-8.286	$8.09 \cdot 10^{-10}$	$8.102 \cdot 10^{-10}$	568 dimeric	545[c] dimeric	4%
		7.652-7.505	$8.10 \cdot 10^{-10}$				
		7.470-7.430	$8.07 \cdot 10^{-10}$				
		7.429-7.388	$8.16 \cdot 10^{-10}$				
		7.271-7.212	$8.11 \cdot 10^{-10}$				
		6.925-6.773	$8.09 \cdot 10^{-10}$				
6K	THF-d_8	9.069-8.488	$8.03 \cdot 10^{-10}$	$8.015 \cdot 10^{-10}$	601 dimeric	555[c] dimeric	8%
		7.605-7.483	$7.96 \cdot 10^{-10}$				
		7.483-7.296	$8.02 \cdot 10^{-10}$				
		7.296-7.110	$8.04 \cdot 10^{-10}$				
		6.951-6.694	$8.03 \cdot 10^{-10}$				

Table S3. Chemical shift of respective aryl integrals, individual diffusion coefficients, averaged diffusion coefficients and calculated hydrodynamic radii of **6Cu**, **6Ag**, **6K** and **6Au** (THF-d_8).

Compound	Solvent	$\delta(^1H)$ [ppm]	D [m^2/s]	$\bar{x}(D)$ [m^2/s]	r_H^{calc} [Å]
6Cu	THF-d_8	7.762-7.688	$6.21 \cdot 10^{-10}$	$6.248 \cdot 10^{-10}$	7.358
		7.633-7.544	$6.29 \cdot 10^{-10}$		
		7.295-7.216	$6.25 \cdot 10^{-10}$		
6Ag	THF-d_8	7.734-7.696	$6.16 \cdot 10^{-10}$	$6.210 \cdot 10^{-10}$	7.403
		7.687-7.626	$6.28 \cdot 10^{-10}$		
		7.612-7.515	$6.22 \cdot 10^{-10}$		
		7.234-7.131	$6.19 \cdot 10^{-10}$		
6Au	THF-d_8	7.805-7.705	$6.19 \cdot 10^{-10}$	$6.200 \cdot 10^{-10}$	7.415
		7.707-7.578	$6.21 \cdot 10^{-10}$		
		7.546-7.474	$6.22 \cdot 10^{-10}$		
		7.260-7.128	$6.18 \cdot 10^{-10}$		

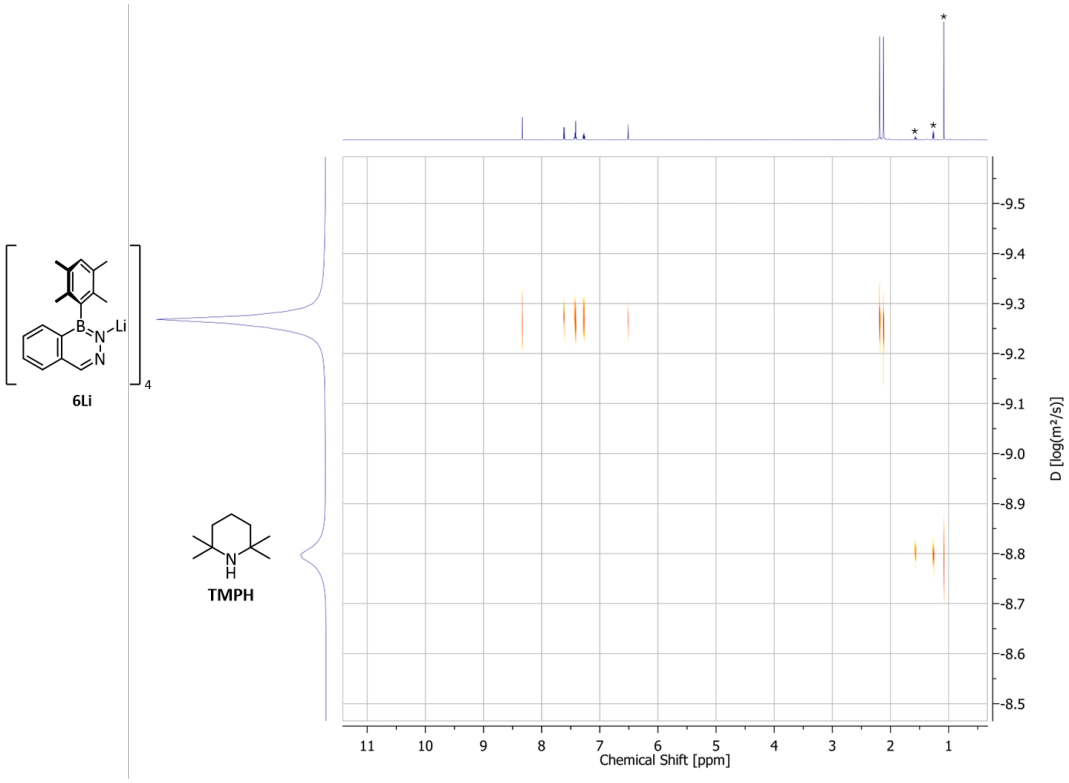


Figure S94. *In-situ* ^{1}H DOSY NMR spectrum of compound **6Li** in toluene-d_8. Marked resonances correspond to TMPH (2,2,6,6-tetramethylpiperdine). p1 = 13.8 μs, p30 = 1400 μs, d20 = 60 ms.

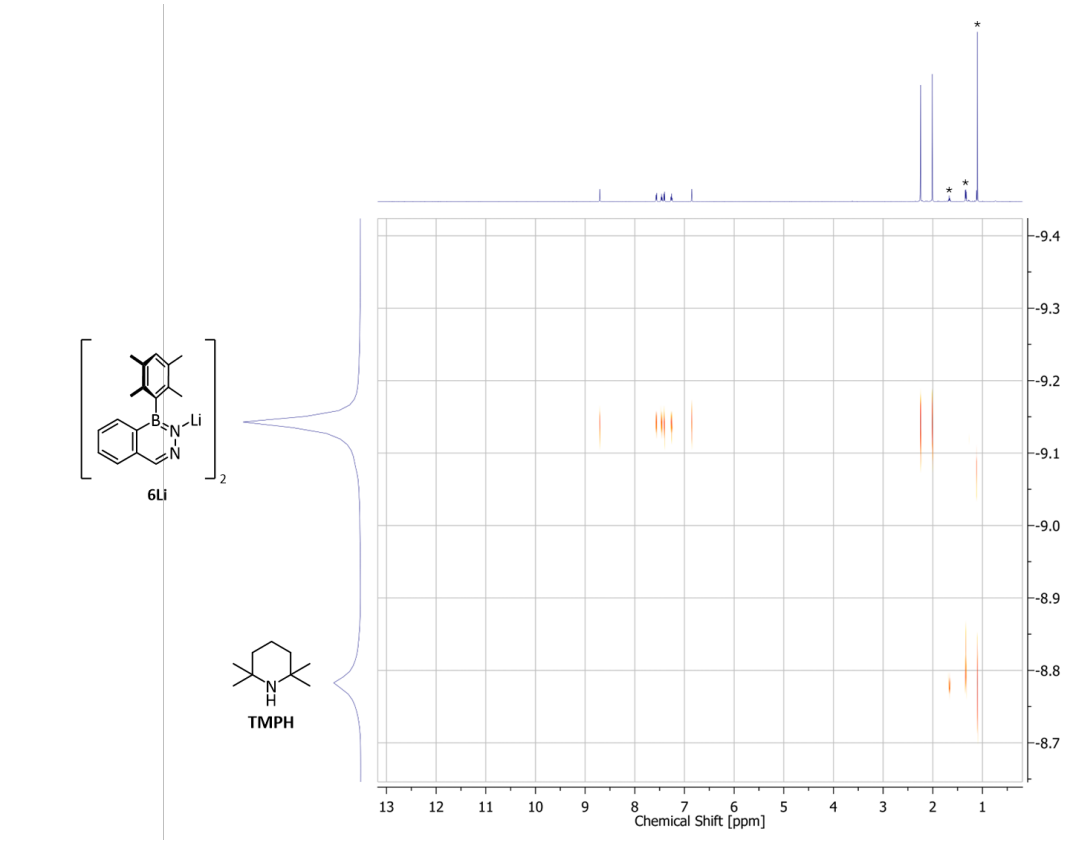


Figure S95. *In-situ* ^{1}H DOSY NMR spectrum of compound **6Li** in THF-d_8. Marked resonances correspond to TMPH (2,2,6,6-tetramethylpiperdine). p1 = 13.8 μs, p30 = 1200 μs, d20 = 60 ms.

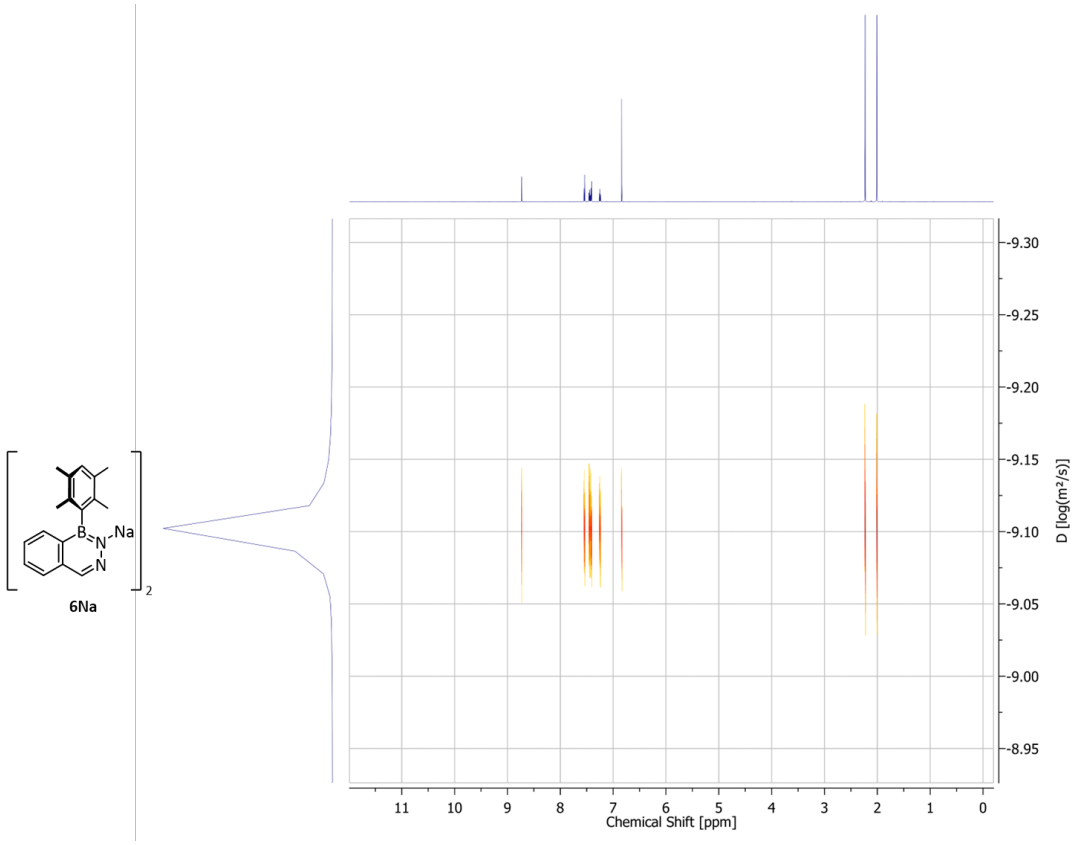


Figure S96. ^{1}H DOSY NMR spectrum of isolated compound **6Na** in THF-d_8. p1 = 13.8 μs, p30 = 1100 μs, d20 = 60 ms.

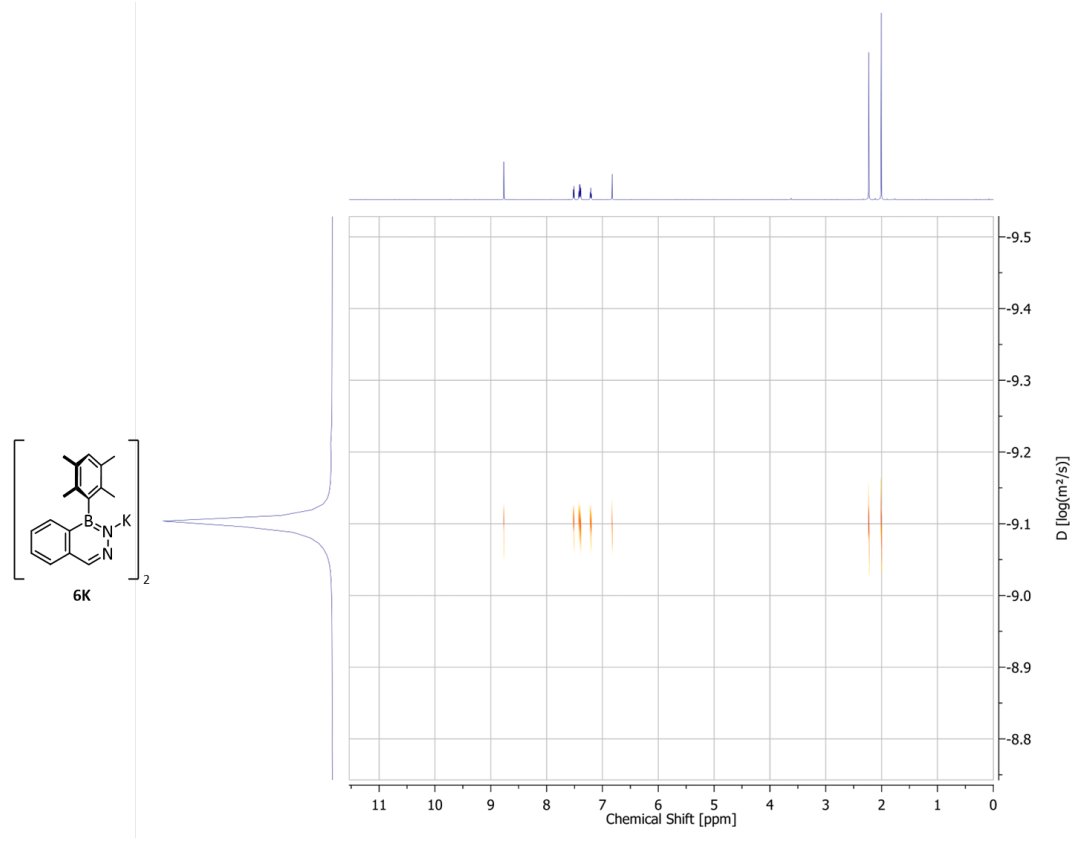


Figure S97. ^{1}H DOSY NMR spectrum of isolated compound **6K** in THF-d_8. p1 = 13.8 μs, p30 = 1200 μs, d20 = 60 ms.

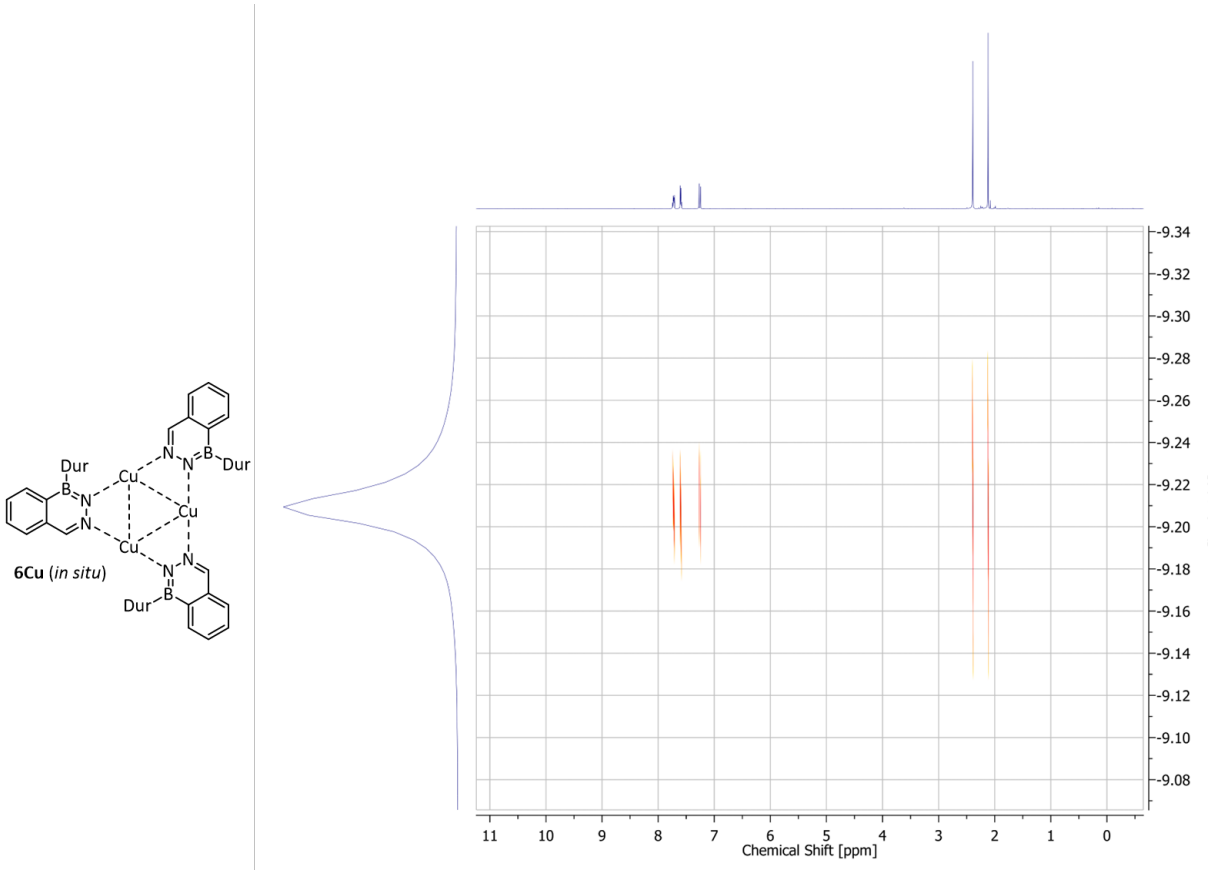


Figure S98. *In-situ* ^{1}H DOSY NMR spectrum of compound **6Cu** in THF-d_8. p1 = 14.3 μs, p30 = 1300 μs, d20 = 50 ms.

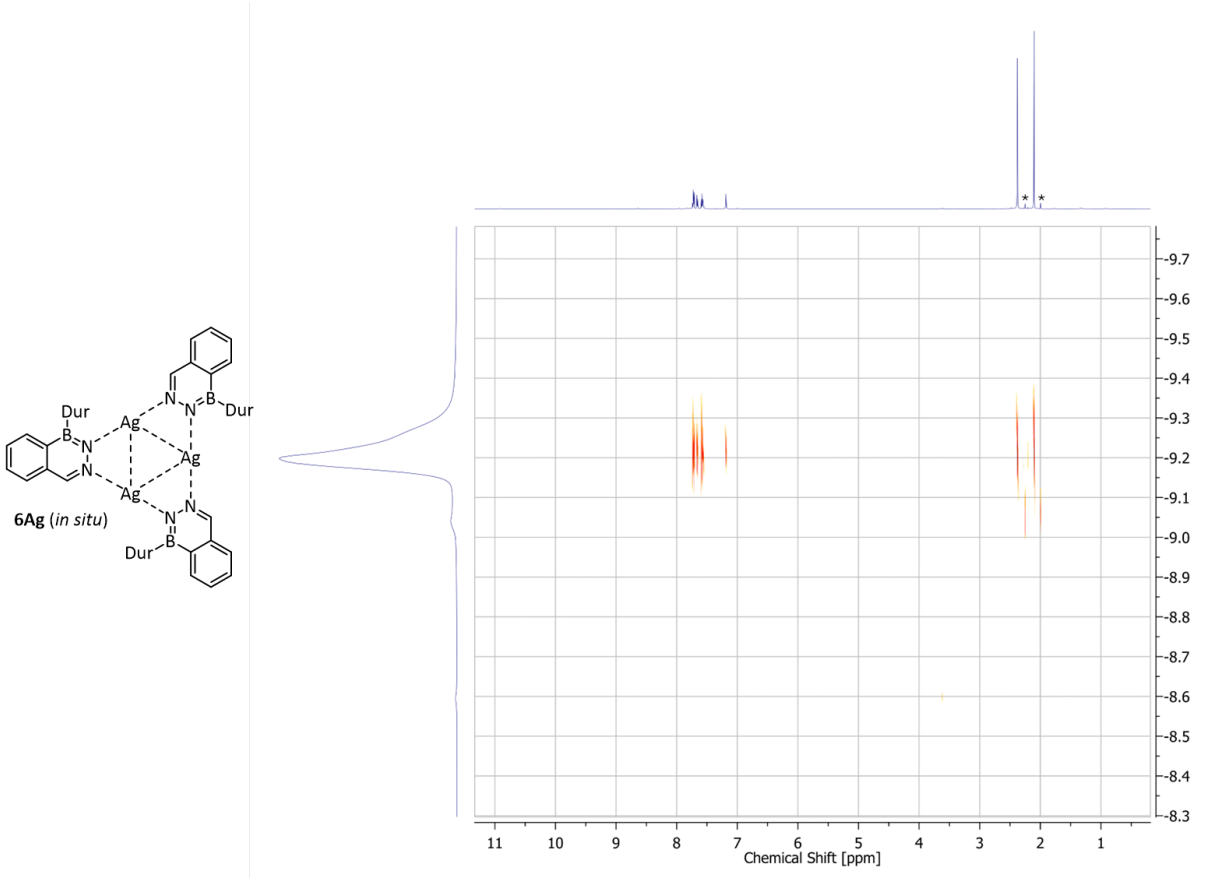


Figure S99. *In-situ* ^{1}H DOSY NMR spectrum of compound **6Ag** in THF-d_8. Marked resonances correspond to decomposition product **6H**. p1 = 15.0 μs, p30 = 1300 μs, d20 = 50 ms.

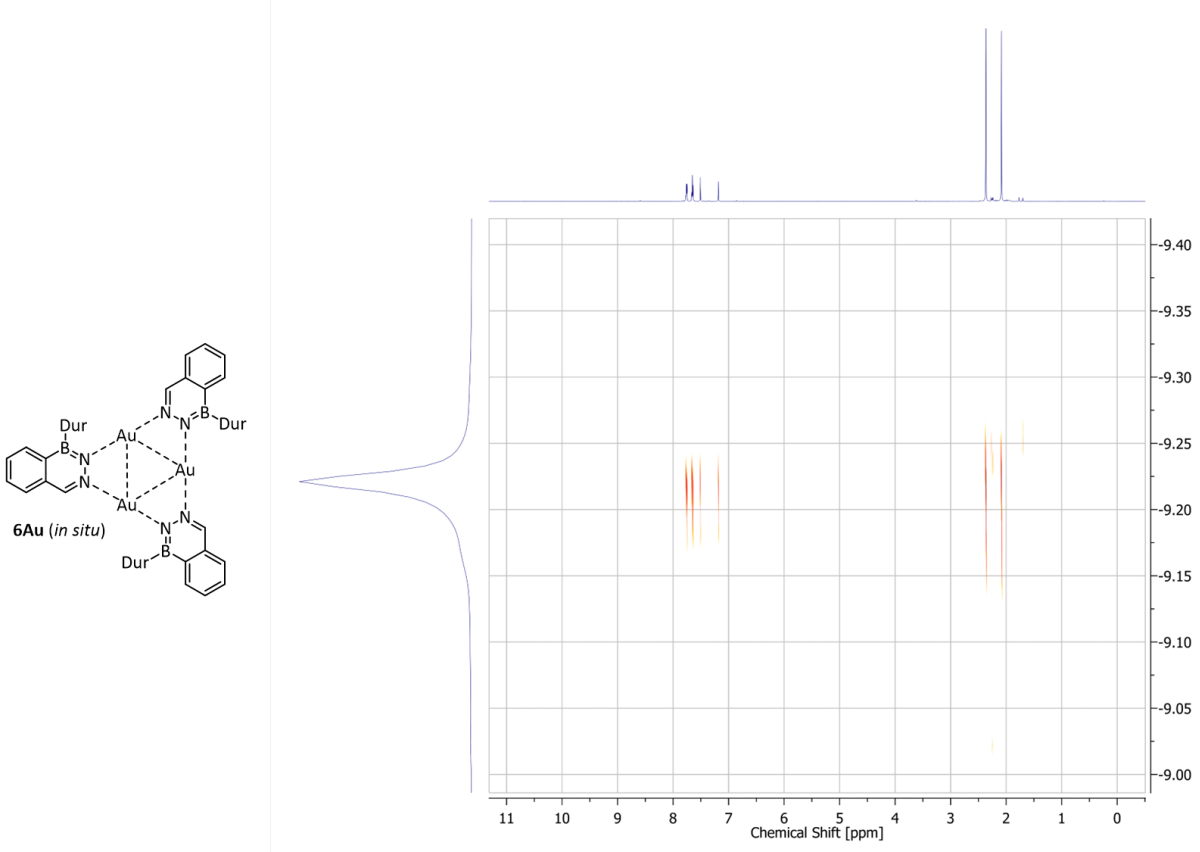
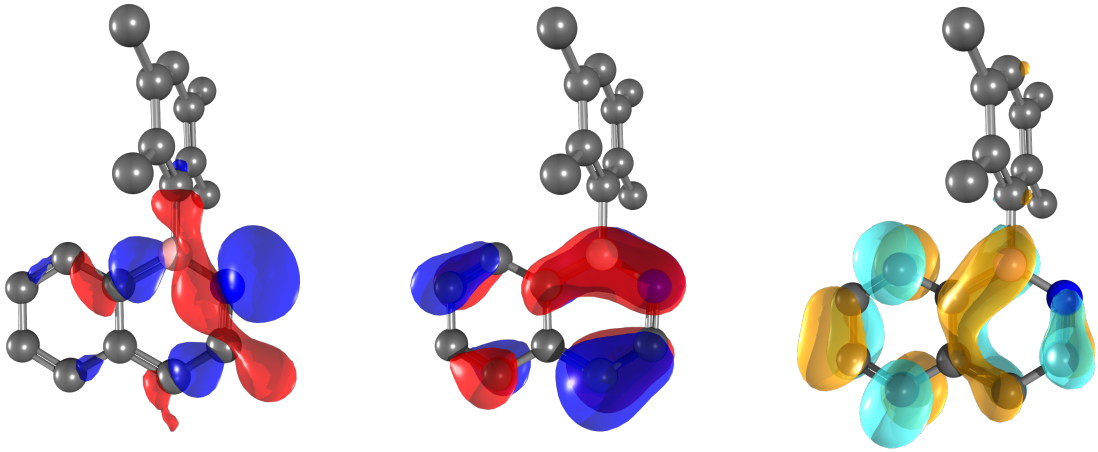


Figure S100. *In-situ* ^{1}H DOSY NMR spectrum of compound **6Au** in THF-d_8. p1 = 14.1 μs, p30 = 1300 μs, d20 = 50 ms.

4 Computational details

All calculations were carried out for the free, deprotonated azaborine monoanion **7**$^-$, the diazaborine monoanion **6**$^-$, or the pyrazolato (pz) ligand monoanion **8**$^-$ without a corresponding countercation. DFT geometry optimizations of both compounds were carried out with the Gaussian 16, Revision C.01 program package[9] using the ωB97X-D functional[10] in combination with the def2-SVP basis set.[11] All structures were fully optimized and confirmed as minima on the corresponding potential energy surface by vibrational frequency computations, which revealed that all eigenvalues of the Hessian matrices are positive. NBO analysis was carried out with the NBO 7.0 extension[12] at the same level of theory (see **Figure S101** and **Figure S102**). The frontier molecular orbitals were visualized with the open-source program IQmol 2.8.0 molecular viewer.[13]

Frontier molecular orbitals (FMOs)

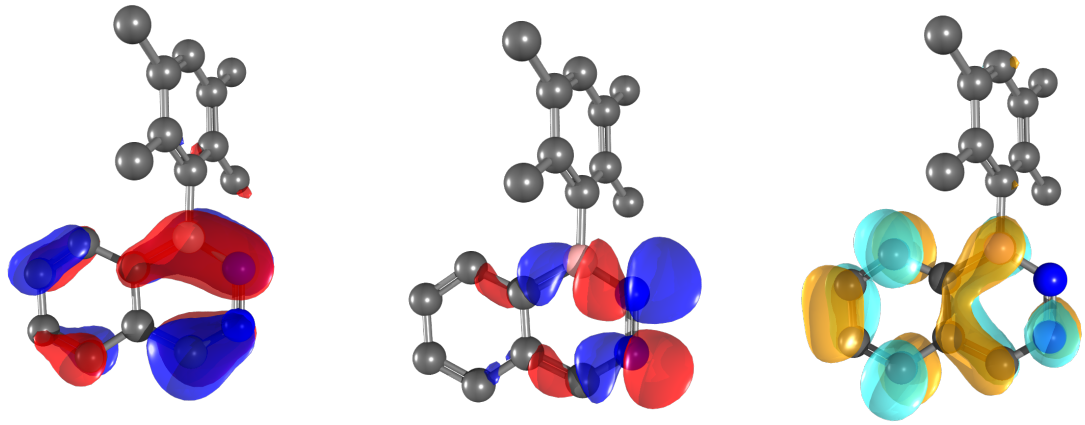


HOMO−1
(−3.64 eV)

HOMO
(−2.94 eV)

LUMO
(4.96 eV)

Figure S101. Frontier molecular orbitals (FMOs) and HOMO−1 with relative energetic level of azaborine monoanion **7**$^{-}$ (ωB97X-D/def2-SVP/isovalue 0.10 eÅ^{-3}).

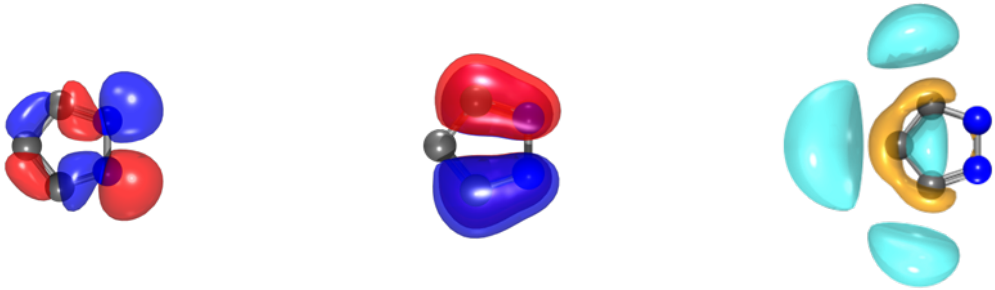


HOMO−1
(−3.35 eV)

HOMO
(−2.78 eV)

LUMO
(4.56 eV)

Figure S102. Frontier molecular orbitals (FMOs) and HOMO−1 with relative energetic level of diazaborine monoanion **6**$^{-}$ (ωB97X-D/def2-SVP/isovalue 0.10 eÅ^{-3}).



HOMO−1
(−2.53 eV)

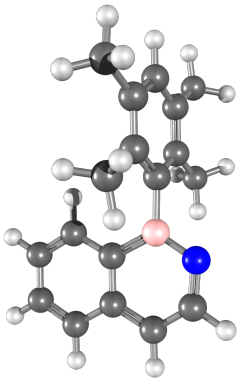
HOMO
(−2.52 eV)

LUMO
(9.22 eV)

Figure S103. Frontier molecular orbitals (FMOs) and HOMO−1 with relative energetic level of pyrazolato monoanion **8**$^{-}$ (ωB97X-D/def2-SVP/isovalue 0.10 eÅ^{-3}).

Optimized structures (.xyz files)

Compound **7**$^{-}$ @ ωB97XD / def2-SVP



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C	-1.67026800	-1.19186100	0.32402000
C	1.76300200	0.08643500	0.18871500
C	3.12029400	-0.20066100	-0.15908700
C	3.37559900	-1.03592300	-1.28611500
H	4.40804700	-1.26753300	-1.56842500
C	4.16641300	0.35610700	0.63037200
H	5.20567700	0.13540200	0.36308700
C	-2.81338500	1.27507500	-0.38842500
C	-3.55347300	0.31929700	0.30754300
H	-4.59245400	0.54123800	0.57795600
C	1.52413300	0.91530500	1.30959600
H	0.48457700	1.13523900	1.57857300
C	-1.47812800	0.98887400	-0.72733400
C	3.88855500	1.16137100	1.71505500
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C	-3.00460100	-0.91115800	0.67000100
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H	-0.08236800	-2.65691500	0.27269500
H	-0.96518800	-2.59664200	1.82239700
C	-3.83655100	-1.91617100	1.42689100
H	-3.96326900	-2.85203600	0.85670500
H	-3.36557500	-2.19604600	2.38399000
H	-4.83919000	-1.51985800	1.64791700
C	-3.44222400	2.59381700	-0.76302700
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C	2.31925100	-1.55386800	-2.01959900
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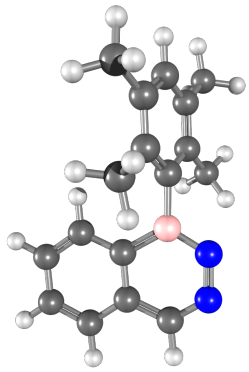
Compound **6**$^{-}$ @ ωB97XD / def2-SVP



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C	-1.72699000	-1.18116000	0.35162900
C	1.76235500	0.11427900	0.18394200
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C	3.25112700	-1.29911300	-1.14033400
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C	-2.77173800	1.31623400	-0.41586500
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C	3.98690000	1.29327500	1.46987500
H	4.84315600	1.75536100	1.97121700
C	-3.05639700	-0.85214700	0.66676300
C	2.67501000	1.69485700	1.80944400
H	2.52286500	2.46383000	2.57282200
C	-1.14252500	-2.51783500	0.74974800
H	-0.53594100	-2.91622400	-0.07625300
H	-0.46686300	-2.40566100	1.61543100

H	-1.90987800	-3.25701300	1.01940400
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H	-4.13215500	-2.73603800	0.85527300
H	-3.53030500	-2.09381500	2.39116000
H	-4.94045500	-1.34480300	1.60936300
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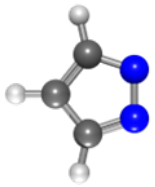
H	-4.38780700	2.75679000	-0.46821300
H	-2.76562000	3.48938900	-0.42376700
H	-3.36155900	2.76756300	-1.92178500
C	-0.59716800	1.98082100	-1.48507100
H	-0.40975600	2.89287400	-0.89178400
H	0.37758700	1.55734600	-1.75719200
H	-1.09787000	2.30015700	-2.41445200

Compound **8**$^{-}$ @ ωB97XD / def2-SVP



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C	-1.09164500	0.28715800	0.00006100
N	0.67514100	-0.98656200	0.00014000
H	2.15985400	0.53069200	0.00009400
H	-0.00446500	2.26529800	0.00001700
H	-2.16228700	0.52121100	0.00005700
N	-0.67099500	-0.98914200	-0.00026000

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