Electronic Supporting Information for

Tuning the emission properties of luminescent 1,2,3-diazaborinates

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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 (DCM) 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; δ_{ref}(C_6D_6) = 128.06 ppm; δ_{ref}(THF-d_8) = 67.21 ppm, 25.31 ppm, δ_{ref}(CD_2Cl_2) = 53.84 ppm) or residual protons (^1H: δ_{ref}(DMSO-d_6) = 2.50 ppm; δ_{ref}(C_6D_6) = 7.16 ppm; δ_{ref}(THF-d_8) = 3.58 ppm, 1.72 ppm, δ_{ref}(CD_2Cl_2) = 5.32 ppm) of the solvent.[1] $SiMe_4$ was used as an external standard for ^1H and ^{13}C NMR spectra. Heteronuclei NMR spectra are referenced to external standards (^7Li: LiCl; ^{11}B: $BF_3 \cdot OEt_2$; ^{19}F: $CFCl_3$). All NMR spectroscopy measurements were carried out at room temperature (296 K). Resonances are given as singlet (s), doublet (d), sextet (sext), doublet of doublet of doublets (ddd), doublet of triplet (dt), triplet (t), triplet of doublets (td), quartet (q), quintet (quint), multiplet (m) or broad singlet (br s). The spectra were plotted using the MestReNova program.

Mass spectra. High-resolution mass spectrometry was performed on a *THERMO SCIENTIFIC* mass spectrometer (Exactive Plus Spectrometer) using a *LIFDI 700* unit from LINDEN CMS source 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.

Single crystal structure analyses. Single crystals suitable for X-ray diffraction analysis were coated with 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*),[2] expanded Fourier expansion, and refined using the *SHELXL* software package.[3] All non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were included in the structure factor calculation at idealized positions. The images of the solid-state structures were created using the *Pov-Ray™* and *Mercury 2023.1.0* software. Important data and parameters of the compounds can be found in the synthesis and characterization of compounds section.

UV-vis and fluorescence spectra. All photophysical measurements were performed in standard quartz cuvettes (1 cm × 1 cm cross-section) under inert atmosphere. UV-visible absorption spectra were recorded using an *AGILENT 8453* diode array UV-visible spectrophotometer and a *METTLER TOLEDO UV7* 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. Thin PMMA-films were prepared from a solution of 60 mg poly(methyl methacrylate) (PMMA) and 0.25 mg of the compounds in 1.0 mL THF by slow evaporation on the side of the cuvettes under inert conditions.

Photostability tests. The photostability of selected DABates was tested by irradiating THF solutions and powder samples of the respective DABate with a UV lamp (254 nm and 365 nm) for a time period of 3 h and measuring UV-vis spectra at t = 0 h and t = 3 h.

Table S1. Origin and purification of solvents and reactants.

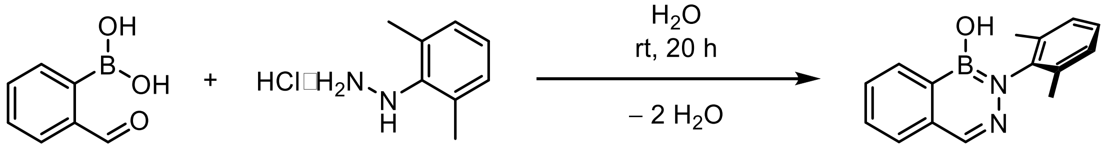
Substance	**Origin**	**Purity / Purification**
2-Formylphenylboronic acid [40138-16-7]	BLD Pharmatech®	99.97% / none stored under Ar
Phenylhydrazine [100-63-1]	Sigma Aldrich®	≥97% / none stored under Ar
N,O-Bis(trimethylsilyl)acetamide [10416-59-8]	Sigma Aldrich®	≥95% / none stored under Ar
n-Butyllithium (1.6 M, *n*-hexane) [109-72-8]	Sigma Aldrich®	- / none stored under Ar
Methyllithium (1.6 M, Et_2O) [917-54-4]	Sigma Aldrich®	- / none dried *in vacuo*, stored under Ar and used as solid
(2-Formylthiophen-3-yl)boronic acid [4347-31-3]	BLD Pharmatech®	97% / none stored under Ar
2-Thienyllithium [2786-07-4]	synthesized[4]	-
9-(4-Bromophenyl)-9*H*-carbazole [57102-42-8]	BLD Pharmatech®	99.83% / none
2,2’-Dibromobiphenyl [13029-09-9]	Activate Scientific®	98% / none
18-Crown-6 [17455-13-9]	Sigma Aldrich®	≥99.0% / none dried in C_6H_6 over MS, then *in vacuo*, stored under Ar
4-Bromobenzotrifluoride [402-43-7]	Abcr GmbH®	99% / none
4-Bromoanisole [104-92-7]	ACROS Organics®	98% / none
Tetra-*n*-butylammonium fluoride (1.0 M, THF) [429-41-4]	Sigma Aldrich®	≥95.0% / none stored under Ar
Tetra-*n*-butylammonium chloride [1112-67-0]	Sigma Aldrich®	dried at 85 °C (high vacuum, hours), stored under Ar
Methyl trifluoromethanesulfonate [333-27-7]	Sigma Aldrich®	≥98% / none stored under Ar
Bromobenzene [108-86-1]	Sigma Aldrich®	≥99.5% / dried over MS, stored under Ar
Phenylmagnesium bromide (3.0 M, Et_2O) [100-58-3]	Sigma Aldrich®	- / none stored under Ar

(2,6-Dimethylphenyl)hydrazine hydrochloride [2538-61-6]	BLD Pharmatech®	97% / none
2-Acetylphenylboronic acid [308103-40-4]	fluorochem®	97% / none
Acetonitrile [75-05-8]	local trade	Purified and dried over local solvent purification system (SPS), stored under Ar over molecular sieves (3 Å).
Dichloromethane [71-43-2]	local trade	Purified and dried over local solvent purification system (SPS), stored under Ar over molecular sieves (3 Å).
Benzene [71-43-2]	local trade	dried over Na, freshly distilled prior to use, stored under Ar over molecular sieves (4 Å).
Toluene [108-88-3]	local trade	
n-Pentane [109-66-0]	local trade	
Diethyl ether (Et_2O) [60-29-7]	local trade	
Tetrahydrofuran (THF) [109-99-9]	local trade	
Benzene-d_6 (C_6D_6) [1076-43-3]	Sigma Aldrich®	99.6 atom % D / none stored under Ar over molecular sieves.
Dimethylsulfoxide-d_6 (DMSO-d_6) [2206-27-1]	Sigma Aldrich®	99.5 atom % D / none
Tetrahydrofurane-d_8 (THF-d_8) [1693-74-9]	Sigma Aldrich®	≥99.5 atom % D / none stored under Ar over molecular sieves.
Dichlormethane-d_2 (CD_2Cl_2) [1665-00-5]	Sigma Aldrich®	99.5 atom % D / none

2 Syntheses and characterization of compounds

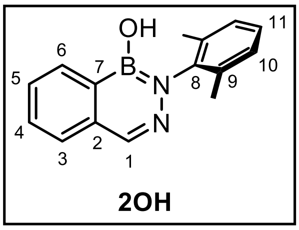
Compounds **1OH**, **1OTMS, [Li]5Ph** and **[TBA]5Ph** were prepared following a procedure previously described by Gois and coworkers or our groups.[5, 6]

3-(2,6-Dimethylphenyl)-4-hydroxy-4,3-borazaroisoquinoline (2OH)



2OH (79%)

Open to the atmosphere, 2-formylphenylboronic acid (3.00 g, 20.0 mmol, 1.00 eq.) was suspended in distilled water (250 mL) in a 500 mL round bottom flask with a dumbbell stirring bar and stirred until total dissolution (approx. 10 min). (2,6-Dimethylphenyl)hydrazine hydrochloride (3.45 g, 20.0 mmol, 1.00 eq.) was added under rapid stirring at ambient temperature, which resulted in the immediate formation of an off-white precipitate. Optionally, a few milliliters (~5 mL) of $NaHCO_3$ solution can be added to ensure complete precipitation of the product. After stirring for 20 h, the solid was filtered off and washed with distilled water (2 × 50 mL). The filter cake was dried in suction vacuum, and the obtained off-white powder was additionally dried in a vacuum desiccator (orange gel) until a consistent weight was achieved. **Yield of 2OH**: 3.97 g (15.9 mmol, 79%) of an off-white powder. The compound is air- and moisture-stable.



2OH

^{1}H NMR (500 MHz, 298 K, DMSO-d_6): δ = 8.47 (s, 1H, B–O*H*), 8.38 (d, $^3J_{HH}$ = 7.64 Hz, 1H, *H*-3), 8.18 (s, 1H, *H*-1), 7.82 (d, $^3J_{HH}$ = 7.68 Hz, *H*-6), 7.77 (dt, $^3J_{HH}$ = 7.15 Hz, $^4J_{HH}$ = 1.29 Hz, 1H, *H*-5), 7.66 (dt, $^3J_{HH}$ = 7.27 Hz, $^4J_{HH}$ = 1.28 Hz, 1H, *H*-4), 7.14-7.15 (m, 3H, *H*-10 + *H*-11), 2.02 (s, 6H, $-CH_3$) ppm. **^{11}B NMR** (160 MHz, 298 K, DMSO-d_6) δ = 27.4 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, DMSO-d_6): δ = 143.7 (C_q^N-8), 139.0 (*C*-1), 135.5 (C_q-2), 134.8 (C_q-9), 131.5 (*C*-3), 131.2 (*C*-5), 129.9 (C_q^B-7), 128.8 (*C*-4), 127.9 (*C*-10), 127.0 (*C*-6), 126.7 (*C*-11) ppm. **HRMS** (ASAP$_{pos}$, toluene): expected: m/z 250.1387, 251.1350, 252.1384 $[C_{15}H_{15}BN_2O+H]^+$; found: m/z 250.1383, 251.1345, 252.1378 $[C_{15}H_{15}BN_2O+H]^+$. Crystalline material of **2OH** as colorless plates for single-crystal XRD was obtained by storing a saturated diethyl ether solution at –20 °C for several days.

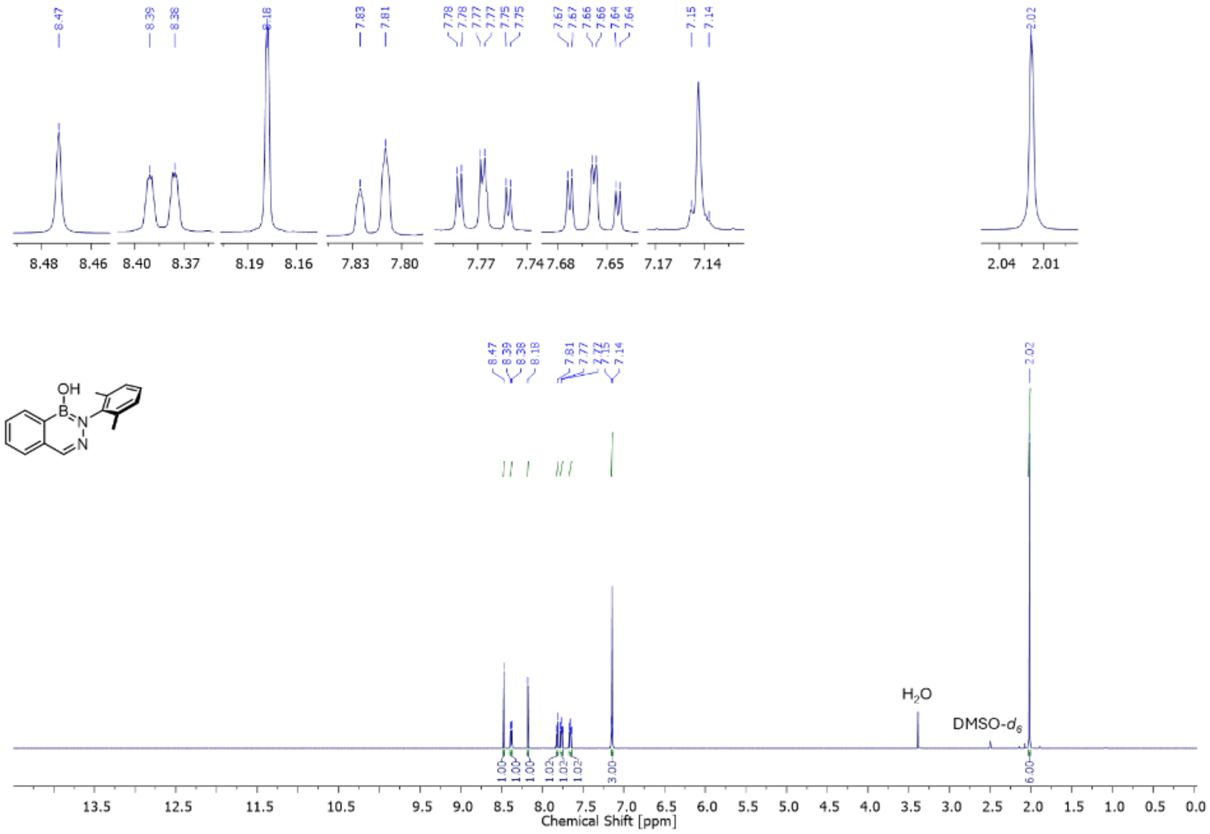


Fig. S1 ^{1}H NMR spectrum of compound **2OH** in DMSO-*d*$_6$.

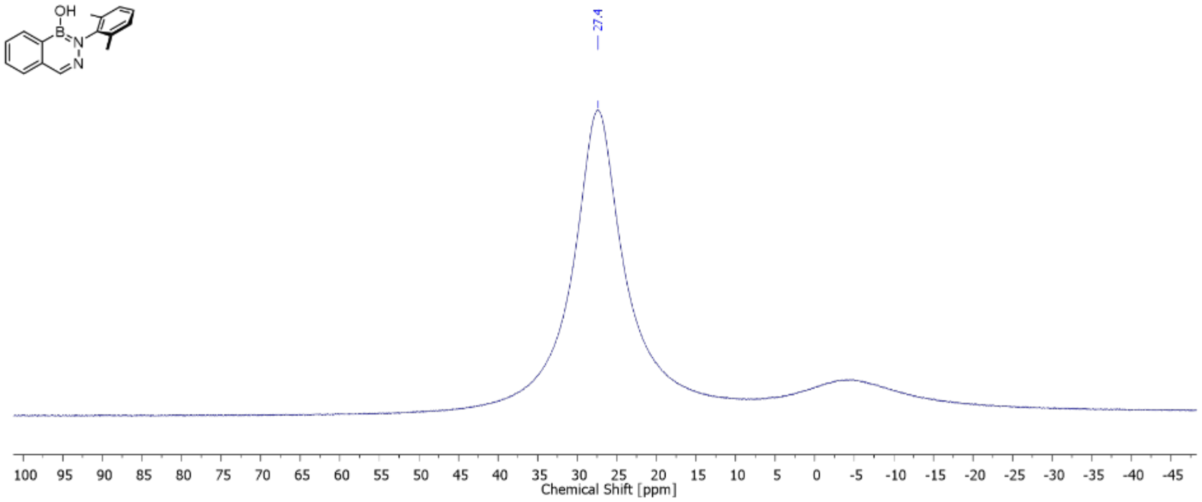


Fig. S2 Background-reduced ^{11}B NMR spectrum of compound **2OH** in in DMSO-*d*$_6$.

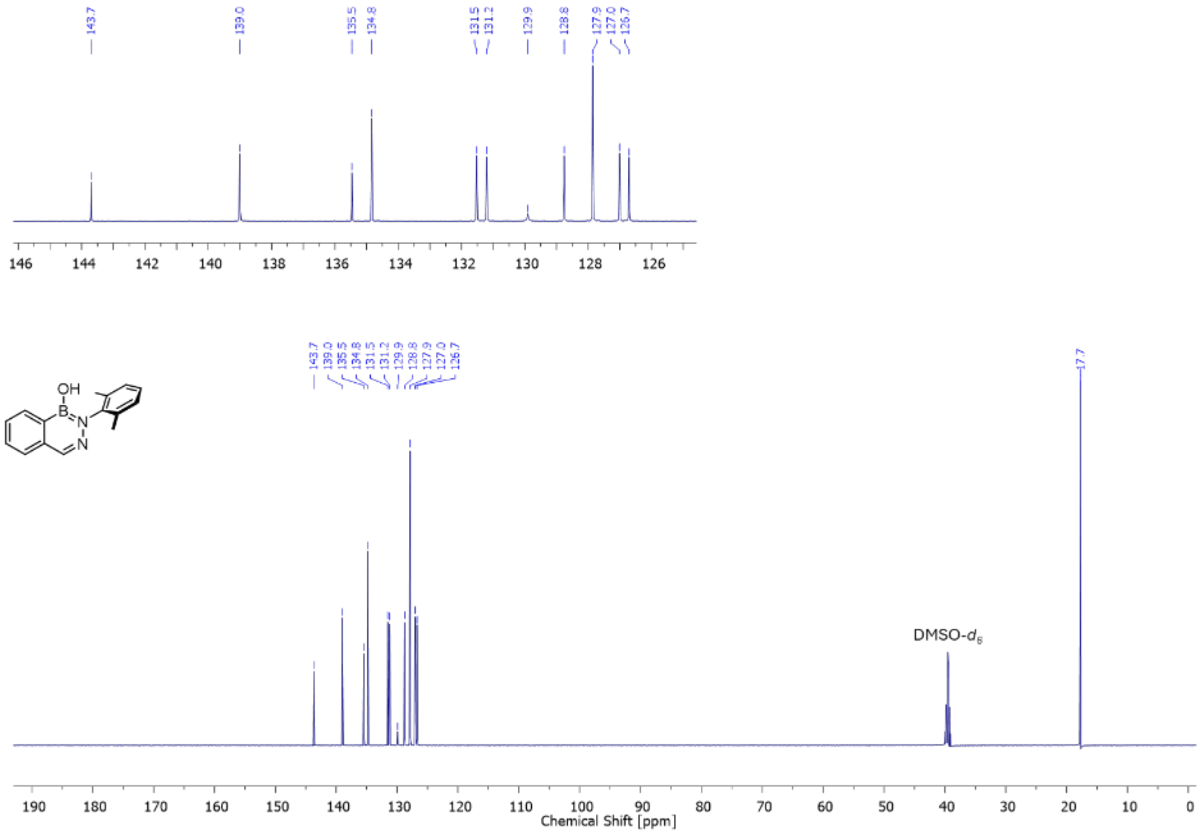


Fig. S3 $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **2OH** in in DMSO-d_6 (^{11}B decoupled at 28 ppm).

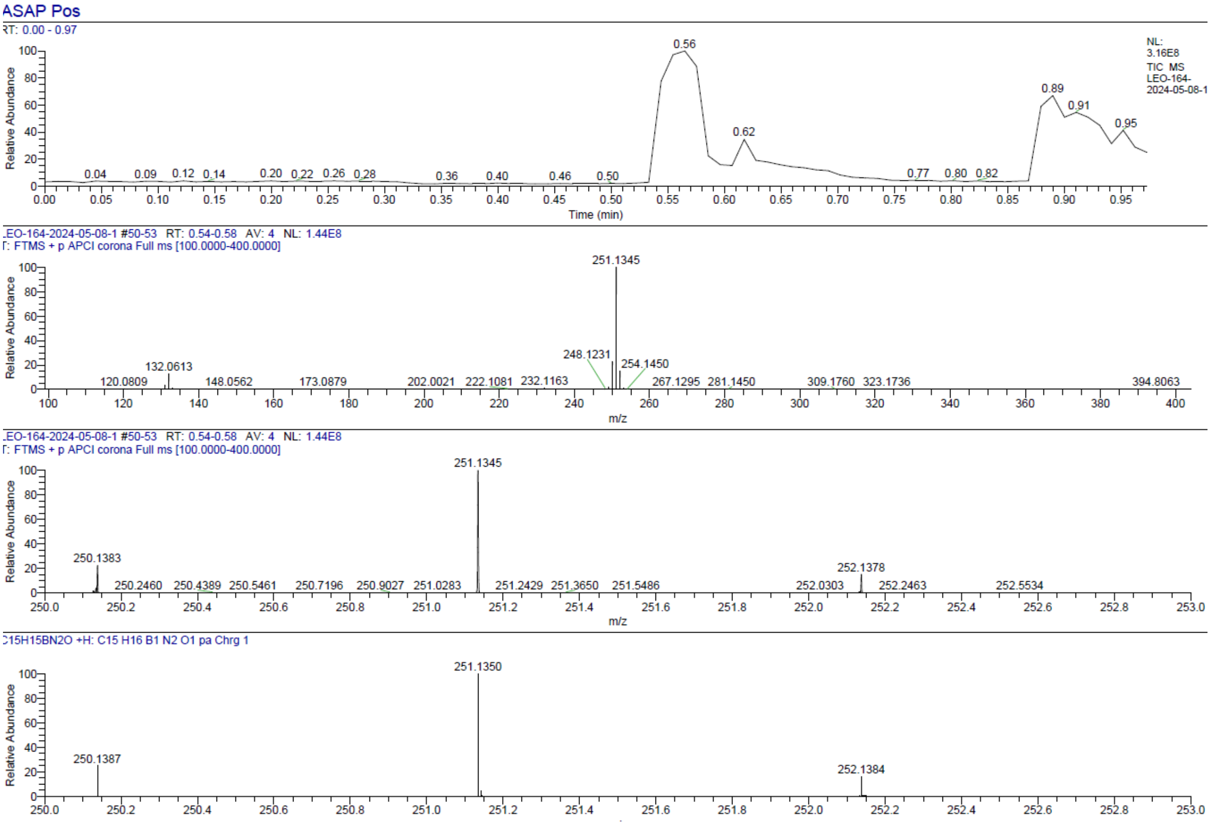


Fig. S4 ASAP$_{pos}$ mass spectrum of compound **2OH** (toluene).

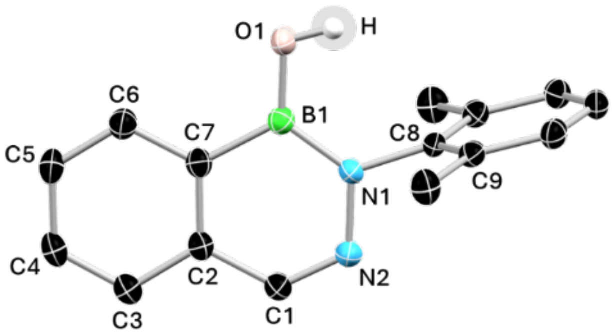
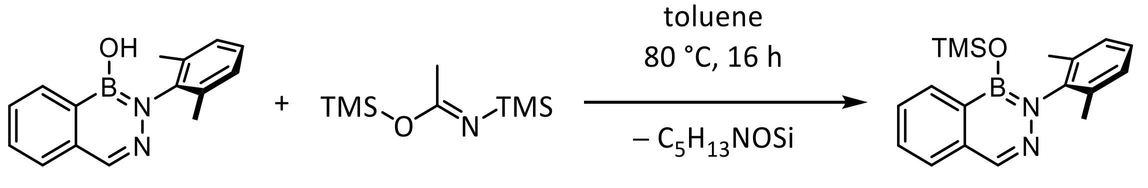


Fig. S5 Molecular structure of compound **2OH**. Ellipsoids drawn at 50% probability (100 K). All H-atoms except for the borinic acid omitted. Selected bond lengths (Å) and angles (°) of **2OH**: B1–N1 1.4285(19), N1–N2 1.3941(16), N2–C1 1.2955(17), C1–C2 1.4450(19), C2–C3 1.4077(19), C3–C4 1.377(2), C4–C5 1.400(2), C5–C6 1.386(2), C6–C7 1.406(2), C2–C7 1.402(2), C7–B1 1.5476(19), B1–O1 1.3532(19), N1–C8 1.4425(16), B1–N1–N2–C1 0.8(2), N2–N1–C8–C9 90.97(14).

Crystal data: $C_{15}H_{15}BN_2O$, $M_r = 250.10$, clear colorless plate, 0.240×0.090×0.050 mm^3, monoclinic space group $P2_1/n$, $a = 11.0957(2)$ Å, $b = 10.40610(10)$ Å, $c = 12.2828(2)$ Å, $b = 107.670(2)°$, $V = 1351.30(4)$ Å^3, $Z = 4$, $r_{calcd} = 1.229$ g·cm^{-3}, $m = 0.607$ mm^{-1}, $F(000) = 528$, $T = 100(2)$ K, $R_1 = 0.0533$, $wR_2 = 0.1139$, 2702 independent reflections [$2q \leq 147.662°$] and 176 parameters.

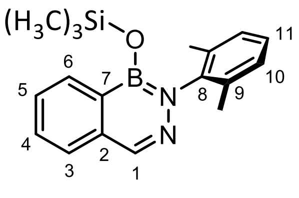
CCDC number: 2453532

3-(2,6-Dimethylphenyl)-4-(trimethylsilyloxy)-4,3-borazaroisoquinoline (2OTMS)



2OH **2OTMS** (82%)

DAB **2OH** (3.00 g, 12.0 mmol, 1.00 eq.) was dissolved in toluene (100 mL) in a 200 mL Schlenk tube. Under rapid stirring, *N,O*-bis(trimethylsilyl)acetamide (24.3 mL, 98.4 mmol, xs., ρ = 0.83 g/mL) was added at ambient temperature. After stirring for 1 min, a clear, orange solution was obtained. The reaction suspension was heated to 80 °C for 16 h. All volatile components were removed *in vacuo* with an external cooling trap. For the removal of the byproduct *N*-(trimethylsilyl)acetamide *via* sublimation, the obtained yellow oil was heated to 80 °C at $1.2 \cdot 10^{-2}$ mbar. The remaining orange oil was extracted with *n*-pentane (3 × 25 mL) via filter cannulation. The remaining solid, consisting of the **2-O-2** anhydride was discarded and all volatile components of the filtrate were removed *in vacuo*. Compound **2OTMS** was obtained as an orange oil. After storing the pure oil at −30 °C in a glovebox for several weeks, the oil started crystalizing. **Yield of 2OTMS:** 3.18 g, 9.87 mmol, 82%, orange oil.



2OTMS

^{1}H NMR (600 MHz, 298 K, C_6D_6): δ = 8.17-8.21 (m, 2H, *H*-1+*H*-3), 7.35-7.40 (m, 2H, *H*-4+*H*-5), 7.31-7.34 (m, 1H, *H*-6), 7.04-7.06 (m, 1H, *H*-11), 7.00-7.03 (m, 2H, *H*-10), 2.13 (s, 6H, xyl-CH_3), 0.04 (s, 9H, –Si(CH_3)$_3$) ppm. **^{11}B{^{1}H} NMR** (128 MHz, 298 K, C_6D_6) δ = 26.0 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6): δ = 144.6 (C_q^N-8), 140.5 (*C*-1), 137.0 (C_q-2), 135.9 (C_q-9), 132.5 (C_q-7), 131.8 (*C*-3), 131.4 (*C*-4), 128.9 (*C*-5), 128.5 (*C*-10), 127.5 (*C*-11), 127.2 (*C*-6), 18.4 (xyl-CH_3), 1.4 (–Si(CH_3)$_3$) ppm. **HRMS** (ASAP$_{pos}$, toluene): expected: m/z 321.1704, 322.1667, 323.1701 [$C_{18}H_{23}BN_2OSi$]$^+$; found: m/z 321.1703, 322.1670, 323.1730 [$C_{18}H_{23}BN_2OSi$]$^+$. Crystalline material of **2OTMS** as colorless plates for single-crystal XRD was obtained by storing the obtained oil at –30 °C for several weeks.

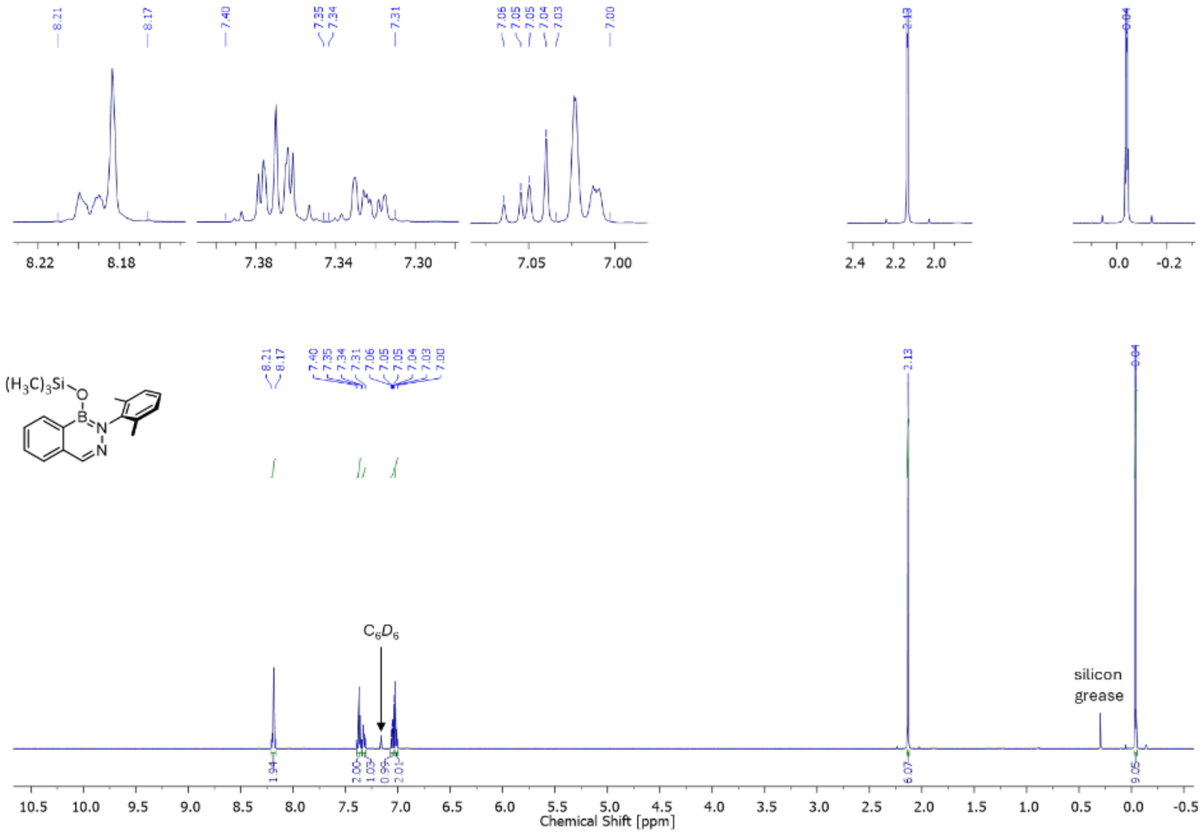


Fig. S6 ^{1}H NMR spectrum of compound **2OTMS** in C_6D_6.

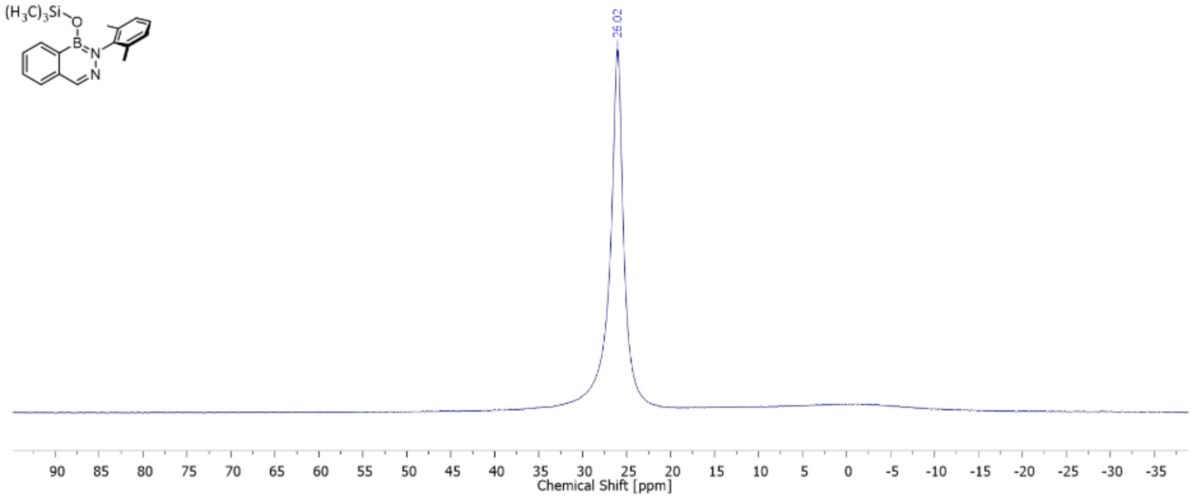


Fig. S7 Background-reduced $^{11}B\{^1H\}$ NMR spectrum of compound **2OTMS** in C_6D_6.

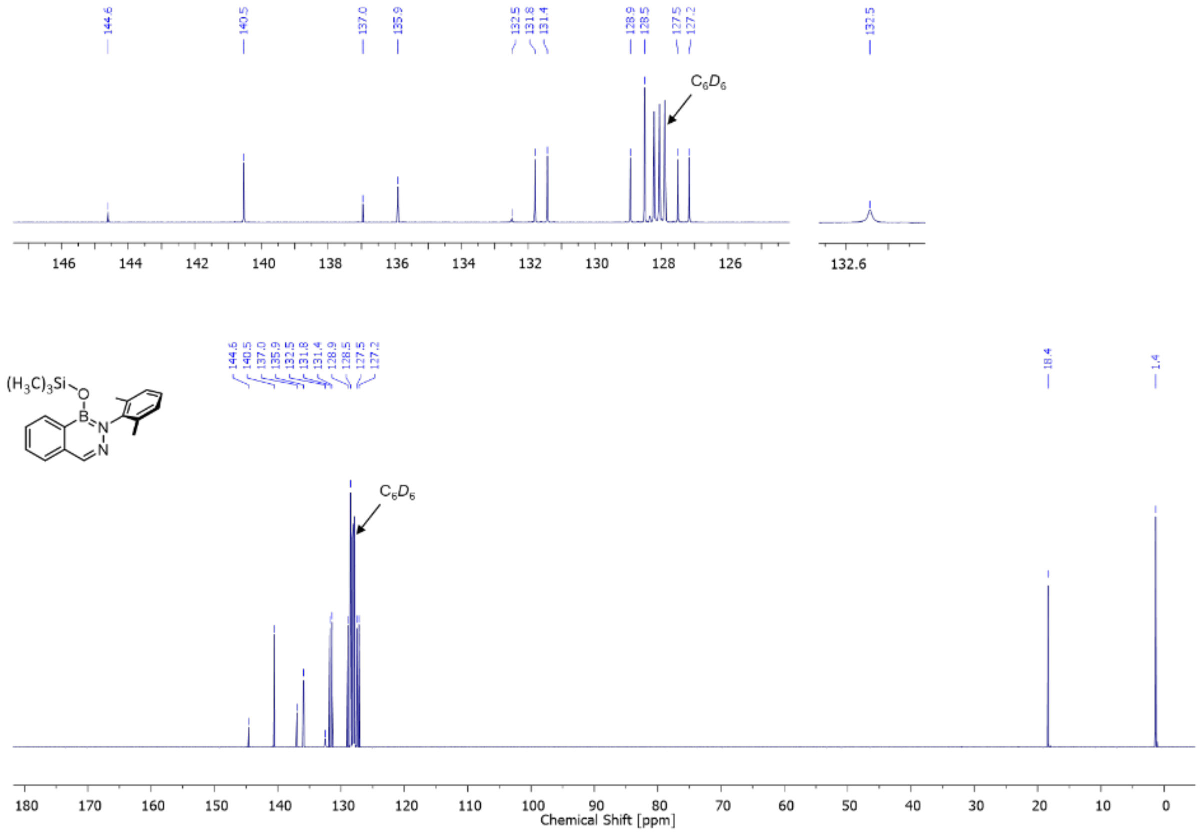


Fig. S8 $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **2OTMS** in C_6D_6 (^{11}B decoupled at 26 ppm).

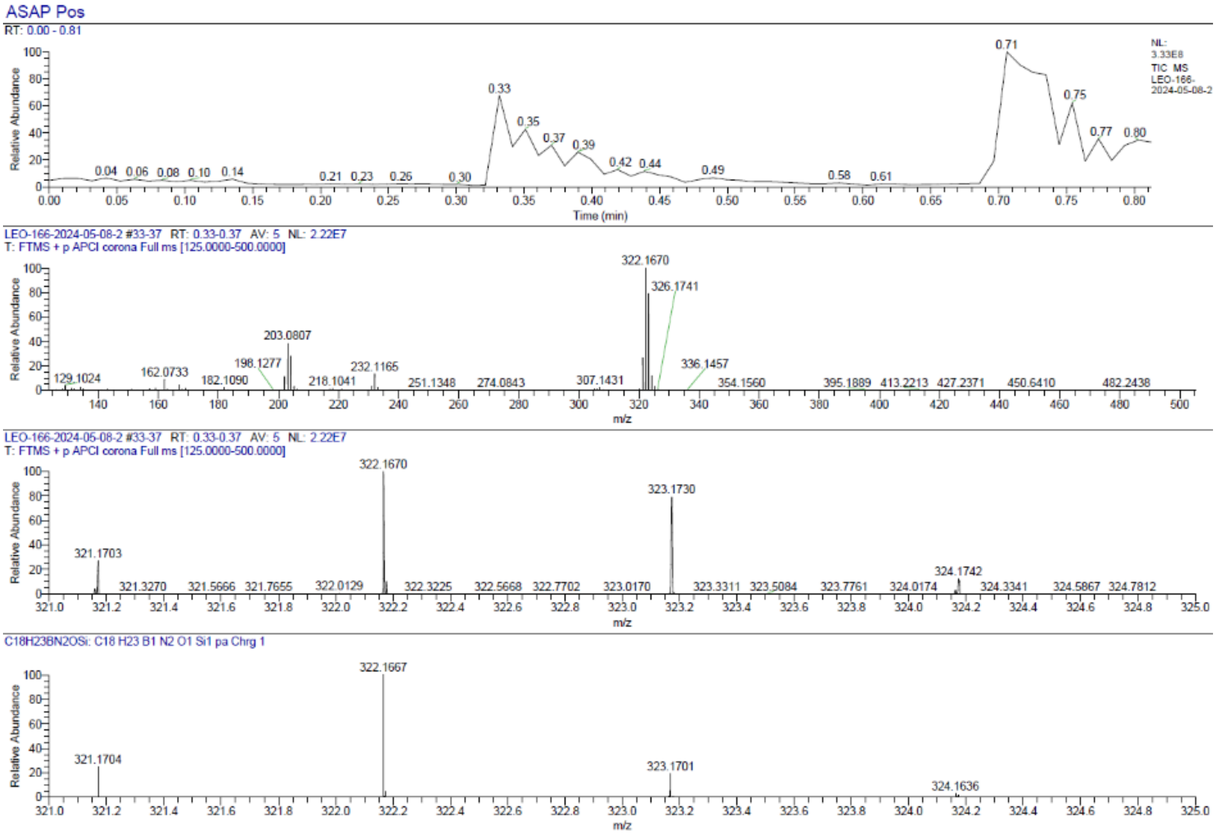


Fig. S9 ASAP$_{pos}$ mass spectrum of compound **2OTMS** (toluene).

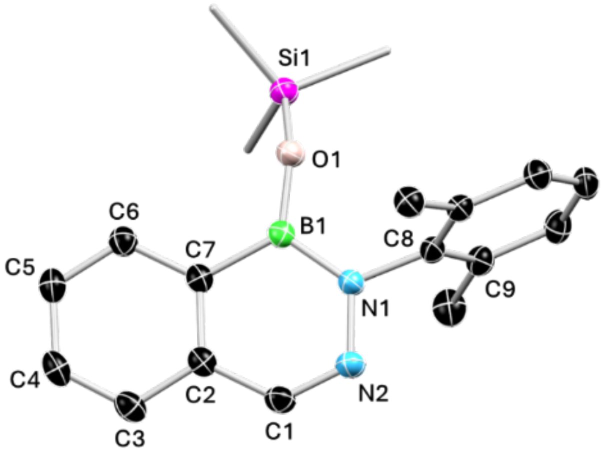


Fig. S10 Molecular structure of compound **2OTMS**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted and methyl groups of the TMS ether shown as wireframe. Selected bond lengths (Å) and angles (°) of **2OTMS**: B1–N1 1.4287(15), N1–N2 1.3891(13), N2–C1 1.2968(15), C1–C2 1.4450(16), C2–C3 1.4065(15), C3–C4 1.3787(17), C4–C5 1.3956(17), C5–C6 1.3861(16), C6–C7 1.4057(16), C2–C7 1.4080(16), C7–B1 1.5414(16), B1–O1 1.3671(14), N1–C8 1.4453(13), B1–N1–N2–C1 0.39(15), N2–N1–C8–C9 80.58(12).

Crystal data: $C_{18}H_{23}BN_2OSi$, $M_r = 322.28$, colorless plate, 0.300×0.260×0.100 mm^3, orthorhombic space group *Pbca*, $a = 13.59130(10)$ Å, $b = 12.40900(10)$ Å, $c = 21.75130(10)$ Å, $V = 3668.45(4)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.167$ g·cm^{-3}, $\mu = 1.155$ mm^{-1}, $F(000) = 1376$, $T = 100(2)$ K, $R_1 = 0.0343$, $wR_2 = 0.0915$, 3713 independent reflections [$2\theta \leq 150.442°$] and 213 parameters.

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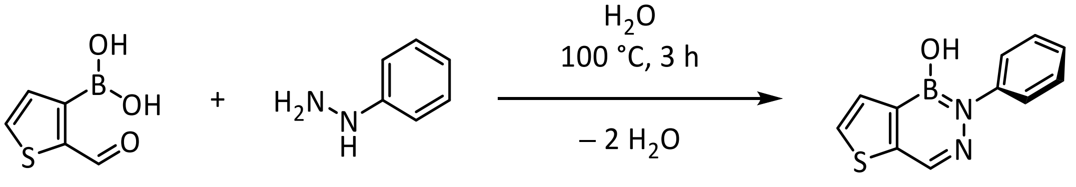
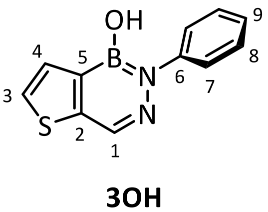
3-Hydroxy-4-phenyl-3,4-borazarothieno[3,2-*d*]pyridine (**3OH**)



3OH (89%)

Open to the atmosphere, 2-formyl-3-thiopheneboronic acid (2.05 g, 13.2 mmol, 1.00 eq.) was suspended in distilled water (240 mL) in a 500 mL round bottom flask with a dumbbell stirring bar. The solution was stirred until total dissolution. Phenylhydrazine (1.50 g, 1.36 mL, 13.6 mmol, 1.10 eq). was added dropwise under rapid stirring at ambient temperature, which resulted in the formation of a yellow precipitate. The round bottom flask was equipped with a reflux condenser and heated at 100 °C for 3 h. The mixture was cooled to ambient temperature and the solid was filtered off and washed with water (2 × 30 mL) and *n*-hexane (2 × 30 mL). The filter cake was dried in suction vacuum and the obtained yellow powder was additionally dissolved in ethyl acetate (20 mL), dried over Na_2SO_4 and filtered. All volatile components were removed *in vacuo* and compound **3OH** was obtained as a yellow solid. **Yield of 3OH:** 2.66 g (11.7 mmol, 89%), yellow powder. The compound is air- and moisture-stable.



3OH

^{1}H NMR (600 MHz, 298 K, DMSO-*d*$_6$): δ = 8.97 (s, 1H, B-O*H*), 8.37 (s, 1H, *H*-1), 7.86 (d, 1H, $^{3}J_{HH}$ = 4.97 Hz, *H*-3), 7.83 (d, 1H, $^{3}J_{HH}$ = 4.97 Hz, *H*-4), 7.56 (d, 2H, $^{3}J_{HH}$ = 7.47 Hz, *H*-7), 7.40 (t, 2H, $^{3}J_{HH}$ = 8.12 Hz, *H*-8), 7.23 (t, 1H, $^{3}J_{HH}$ = 7.47 Hz, *H*-9) ppm. **^{11}B NMR** (161 MHz, 298 K, DMSO-*d*$_6$): δ = 27.4 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, DMSO-*d*$_6$, 298 K): δ = 146.2 (C_q^{N}-6), 145.1 (C_q-2), 138.3 (C_q^{B}-5), 132.7 (*C*-1), 130.0 (*C*-4), 129.6 (*C*-3), 128.2 (*C*-7), 125.3 (*C*-8), 125.1 (*C*-9) ppm. **HRMS** (ASAP$_{pos}$, toluene): expected: m/z 228.0638, 229.0601, 230.0635 $[C_{11}H_9BN_2OS+H]^+$; found: m/z 228.0634, 229.0598, 230.0631 $[C_{11}H_9BN_2OS+H]^+$. Crystalline material of **3OH** as yellow plates for single-crystal XRD was obtained by slow evaporation of a saturated acetone solution at ambient temperature.

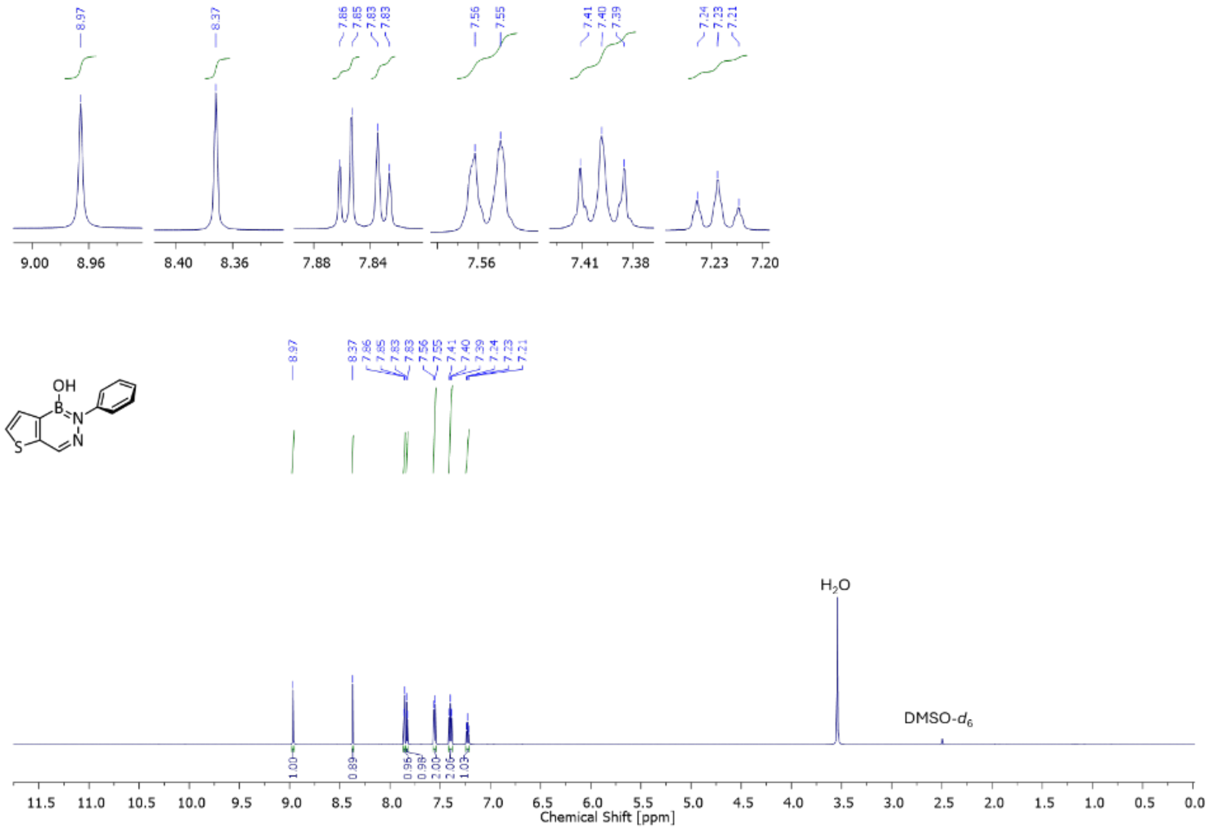


Fig. S11 ^{1}H NMR spectrum of compound **3OH** in DMSO-*d*6.

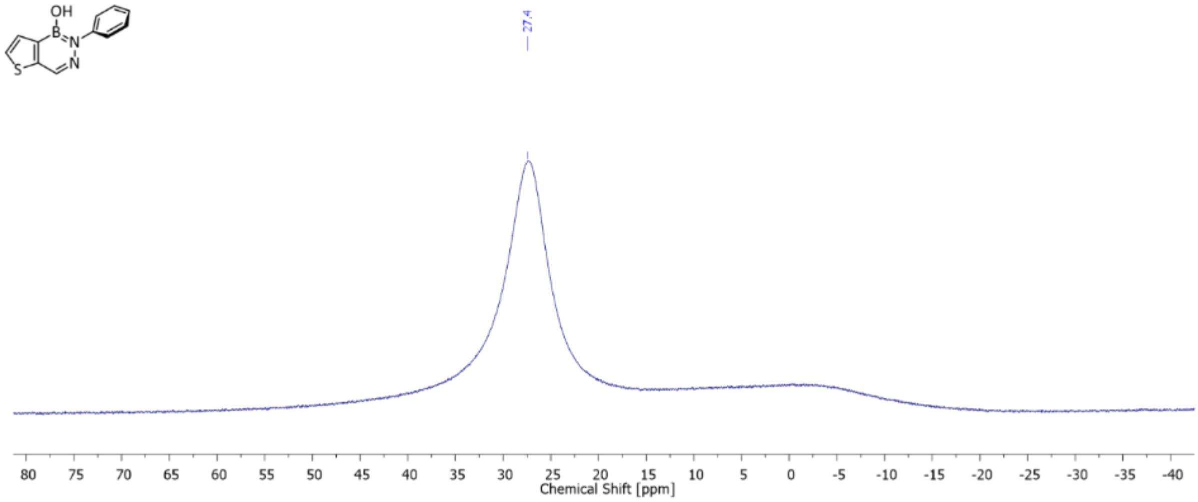


Fig. S12 Background-reduced ^{11}B NMR spectrum of compound **3OH** in DMSO-*d*6.

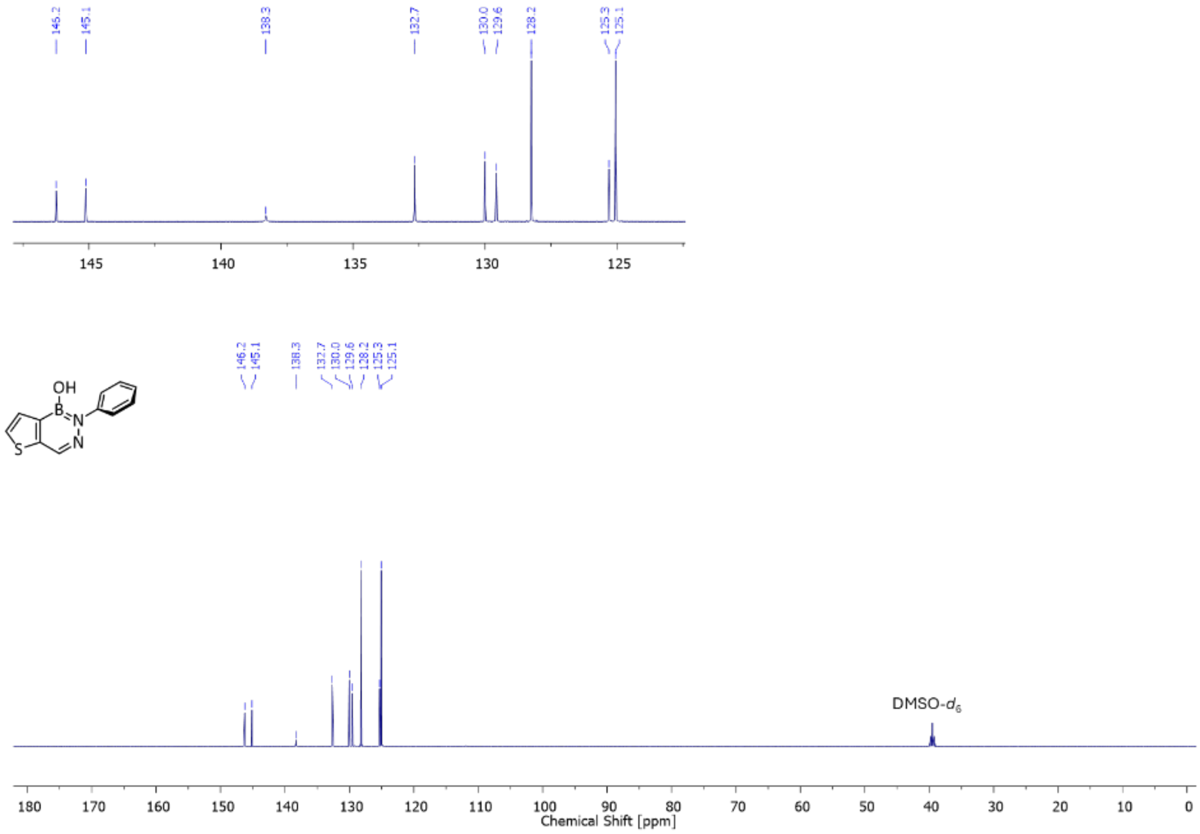


Fig. S13 $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **3OH** in DMSO-d_6 (^{11}B decoupled at 27 ppm).

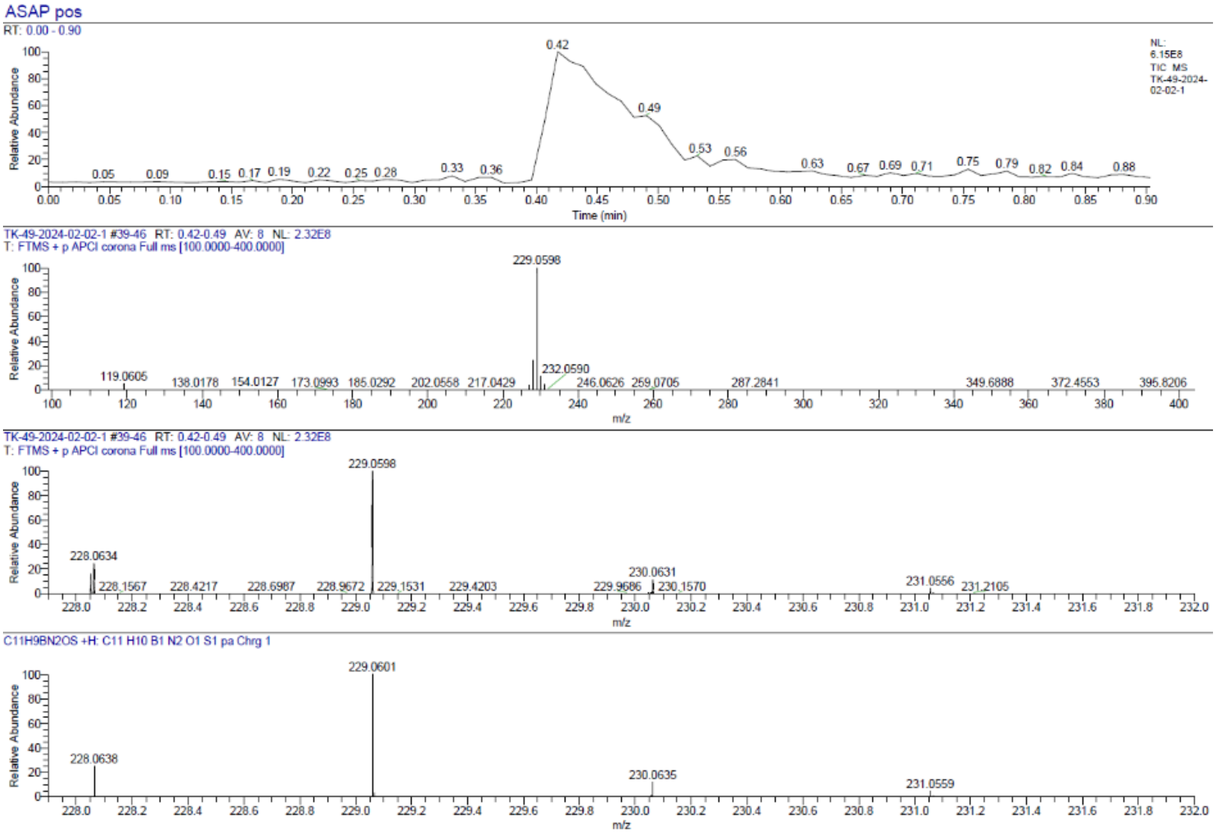


Fig. S14 ASAP$_{pos}$ mass spectrum of compound **3OH** (toluene).

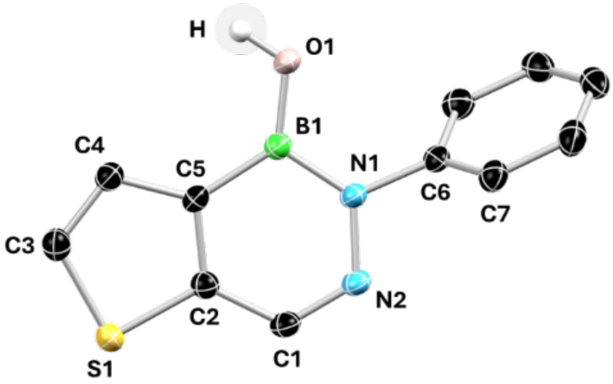
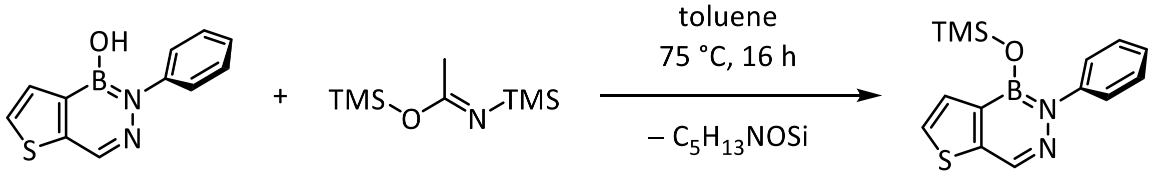


Fig. S15 Molecular structure of compound **3OH**. Ellipsoids drawn at 50% probability (100 K). All H-atoms except for the borinic acid omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.448(3), N1–N2 1.379(2), N2–C1 1.303(2), C1–C2 1.423(3), C2–S1 1.7272(19), S1–C3 1.714(2), C3–C4 1.363(3), C4–C5 1.428(3), C5–C2 1.383(3), C5–B1 1.541(3), B1–O1 1.356(2), N1–C6 1.443(2), B1–N1–N2–C1 6.3(3), N2–N1–C6–C7 118.74(19).

Crystal data: $C_{11}H_9BN_2OS$, M_r = 228.07, clear light yellow plate, 0.270×0.190×0.030 mm^3, orthorhombic space group *Pbcn*, a = 10.1843(3) Å, b = 12.2526(4) Å, c = 17.1356(5) Å, V = 2138.25(11) Å^3, Z = 8, ρ_{calcd} = 1.417 g·cm^{-3}, μ = 2.490 mm^{-1}, F(000) = 944, T = 100(2) K, R_1 = 0.0507, wR_2 = 0.1316, 2135 independent reflections [$2\theta \leq 147.51°$] and 149 parameters.
Some reflections were removed from refinement as outliers.

CCDC number: 2453546

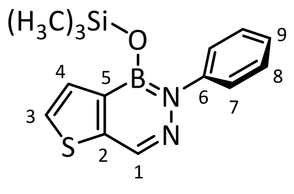
3-Phenyl-4-(trimethylsiloxy)-3,4-borazarothieno[3,2-*d*]pyridine (**3OTMS**)



3OTMS

3OTMS (79%)

Compound **3OTMS** (2.00 g, 8.77 mmol, 1.00 eq.) was suspended in toluene (200 mL) in a 500 mL Schlenk flask. Under rapid stirring, *N,O*-bis(trimethylsilyl)acetamide (6.43 mL, 26.3 mmol, 3.00 eq., ρ = 0.83 g/mL) was added. The yellow reaction solution was stirred for 15 min at ambient temperature and then heated to 75 °C for 16 h. All volatile components were removed *in vacuo* with an external cooling trap. For the removal of the byproduct *N*-(trimethylsilyl)acetamide *via* sublimation, the obtained yellow oil was carefully heated with a heat gun at $1.2 \cdot 10^{-2}$ mbar. Then, the remaining oil was extracted with *n*-pentane (3 × 2 mL) via filter cannulation and the *n*-pentane solution was stored at −20 °C for 1 d until crystallization of **3OTMS**. The excess solution was removed using a glass pipet and the remaining solid was washed with cold (−20 °C) *n*-pentane (0.5 mL) and dried *in vacuo*. **Yield of 3OTMS:** 2.09 g (6.95 mmol, 79%), off-white, crystalline solid.



3OTMS

^{1}H NMR (600 MHz, 298 K, C_6D_6): δ = 8.11 (s, 1H, *H*-1), 7.57 (d, 1H, $^3J_{HH}$ = 8.37 Hz, *H*-7), 7.38 (d, 1H, $^3J_{HH}$ = 4.87 Hz, *H*-4), 7.20 (t, 2H, $^3J_{HH}$ = 7.87 Hz, $^4J_{HH}$ = 1.77 Hz, *H*-8), 7.05 (t, 1H, $^3J_{HH}$ = 7.47 Hz, $^4J_{HH}$ = 7.17 Hz, *H*-9), 6.97 (d, 1H, $^3J_{HH}$ = 4.97 Hz, *H*-3), 0.04 (s, 9H, –Si(C*H*$_3$)$_3$) ppm. **^{11}B{^{1}H} NMR** (193 MHz, 298 K, C_6D_6): δ = 25.4 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6): δ = 147.0 (C_q^N-6), 147.0 (C_q-2), 140.0 (C_q-5), 133.3 (*C*-1), 129.5 (*C*-4), 128.5 (*C*-3), 128.4 (*C*-8), 126.4 (*C*-7), 126.1 (*C*-9), 1.5 (–Si(CH$_3$)$_3$) ppm. **HRMS** (LIFDI, toluene): expected: m/z 299.0955, 300.0918, 301.0952 $[C_{14}H_{17}BN_2OSSi]^+$; found: m/z 299.0947, 300.0911, 301.0945 $[C_{14}H_{17}BN_2OSSi]^+$. Crystalline material of **3OTMS** as colorless blocks for single-crystal XRD was obtained by storing a saturated *n*-pentane solution at –20 °C for one day.

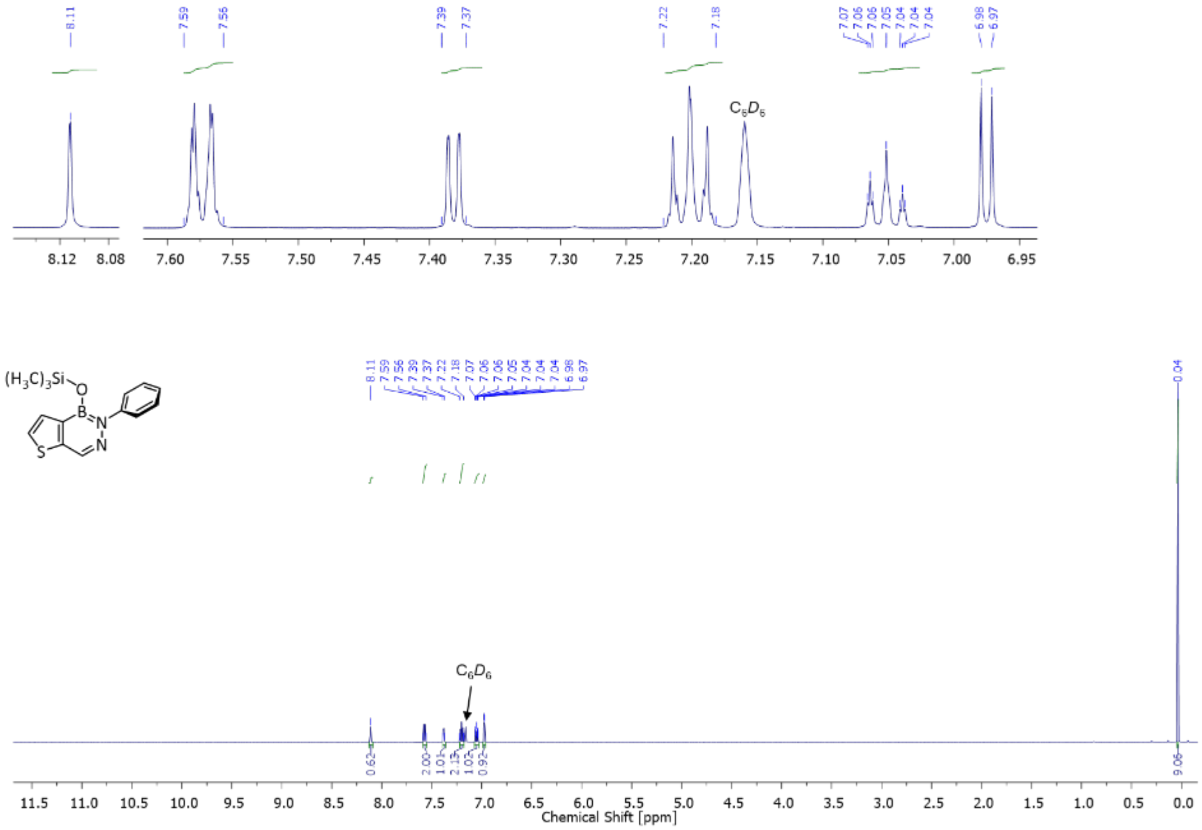


Fig. S16 ^{1}H NMR spectrum of compound **3OH** in C_6D_6.

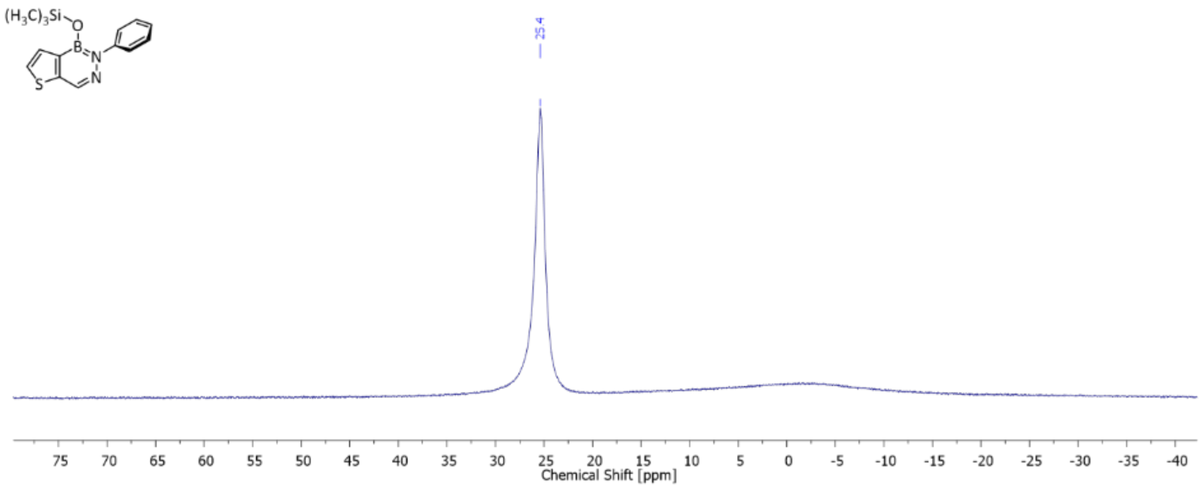


Fig. S17 Background-reduced $^{11}B\{^1H\}$ NMR spectrum of compound **3OH** in C_6D_6.

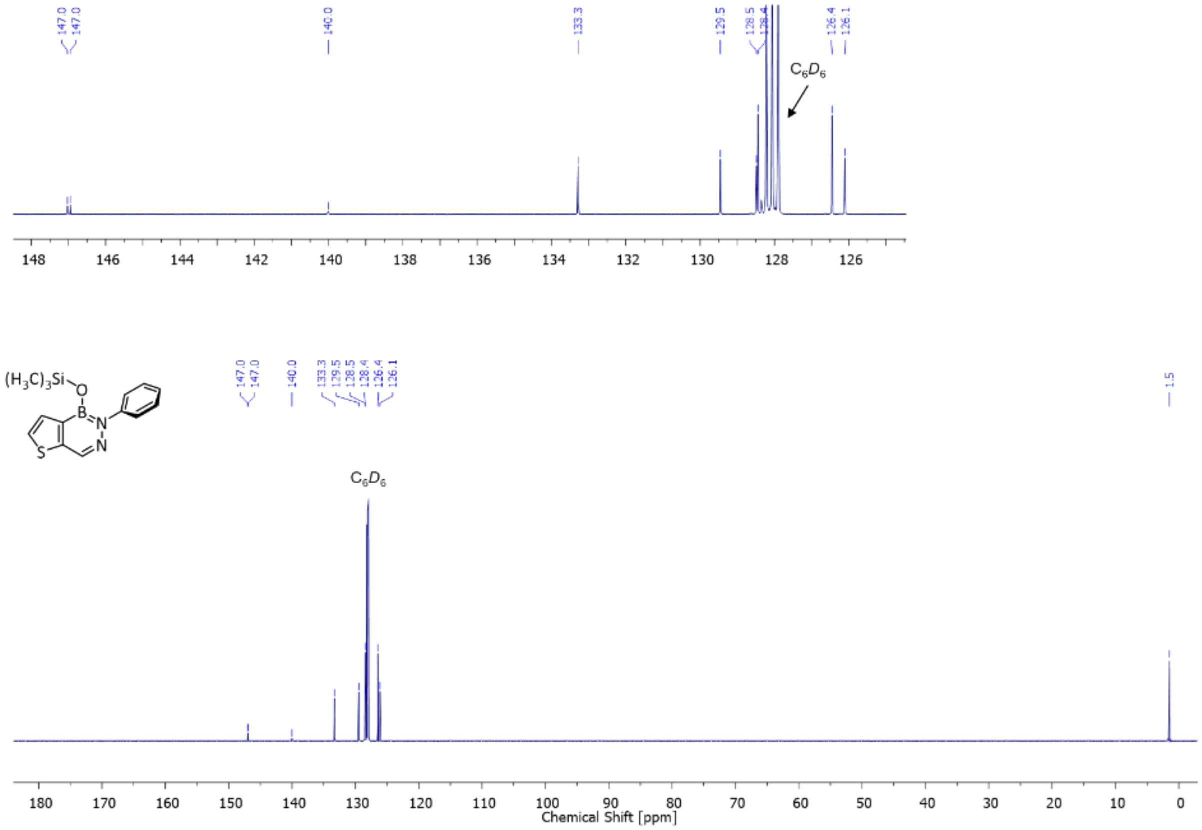


Fig. S18 $^{13}C\{^1H^{11}B\}$ NMR spectrum of compound **3OH** in C_6D_6 (^{11}B decoupled at 25 ppm).

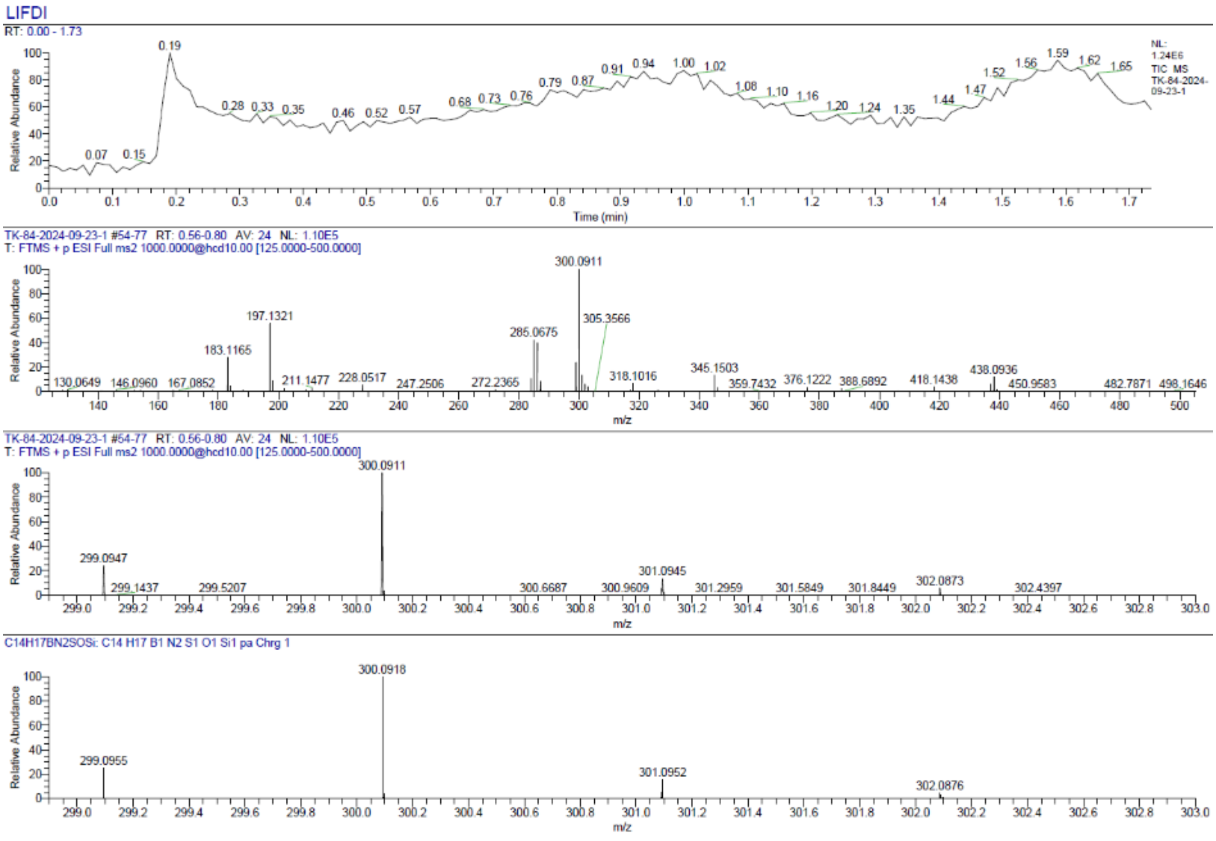


Fig. S19 LIFDI mass spectrum of compound **3OH** (toluene).

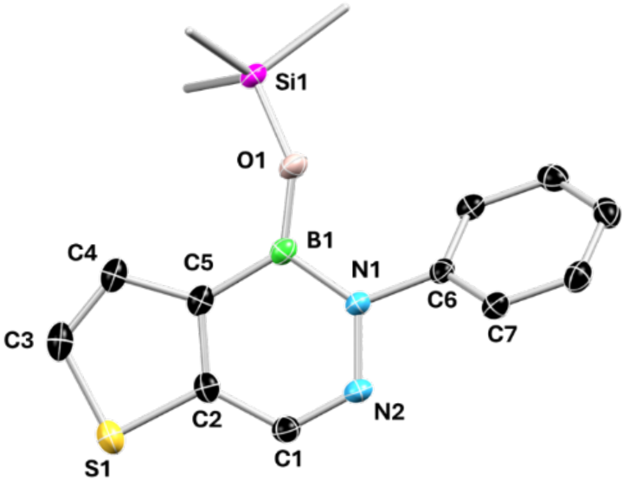
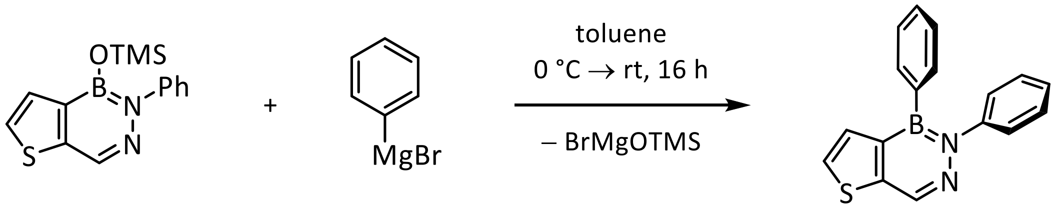


Fig. S20 Molecular structure of compound **3OTMS**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.4544(18), N1–N2 1.3844(15), N2–C1 1.2976(18), C1–C2 1.4271(19), C2–S1 1.7273(14), S1–C3 1.7175(16), C3–C4 1.358(2), C4–C5 1.4315(18), C5–C2 1.385(2), C5–B1 1.532(2), B1–O1 1.3566(18), N1–C6 1.4378(17), B1–N1–N2–C1 2.0(2), N2–N1–C6–C7 135.87(12).

Crystal data: $C_{14}H_{17}BN_2OSSi$, M_r = 300.25, clear colorless block, 0.150×0.110×0.070 mm^3, triclinic space group $P\overline{1}$, a = 8.77130(10) Å, b = 9.38310(10) Å, c = 10.18550(10) Å, α = 84.2310(10)°, β = 69.7730(10)°, γ = 75.2450(10)°, V = 760.580(15) Å^3, Z = 2, ρ_{calcd} = 1.311 g·cm^{-3}, μ = 2.604 mm^{-1}, F(000) = 316, T = 100(2) K, R_1 = 0.0310, wR_2 = 0.0872, 2974 independent reflections [$2\theta \leq 149.512°$] and 184 parameters.

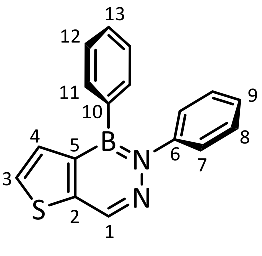
CCDC number: 2453528

3,4-Bis(phenyl)-3,4-borazarothieno[3,2-*d*]pyridine (3Ph)



3OTMS **3Ph** (49%)

Compound **3OTMS** (500 mg, 1.67 mmol, 1.00 eq.) was suspended in toluene (175 mL) in a 250 mL Schlenk flask. Phenylmagnesium bromide (3.0 M solution in diethyl ether, 0.53 mL, 1.58 mmol, 0.95 eq.) was added in small portions at 0 °C (ice bath). Upon addition of the Grignard reagent a color change from colorless to yellow was observed. The cooling bath was removed, and the reaction was stirred for 16 h at ambient temperature. On air, celite was added to the solution and all volatile components were removed *in vacuo* without further aqueous workup or quenching. The obtained powder was purified by column chromatography (aluminum oxide (Act. I), *n*-hexane → *n*-hexane / ethyl acetate 10:1, TLC controls were performed with *n*-hexane / ethyl acetate 4:1, R_f(**3OH**) = 0.16, R_f(**3Ph**) = 0.41). Yield of **3Ph**: 93.0 mg (323 μmol, 49%) of a colorless, crystalline solid. The compound is air- and moisture-stable.



3Ph

^{1}H NMR (600 MHz, 298 K, CD_2Cl_2) δ = 8.68 (s, 1H, *H*-1), 7.71 (d, 1H, $^3J_{HH}$ = 4.95 Hz, *H*-3), 7.60 (d, 1H, $^3J_{HH}$ = 4.95 Hz, *H*-4), 7.37 (dd, 2H, $^3J_{HH}$ = 7.69 Hz, $^4J_{HH}$ = 1.61 Hz, *H*-11), 7.23-7.30 (m, 8H, *H*-7 + *H*-8 + *H*-9 + *H*-12 + *H*-13) ppm. **^{11}B NMR** (193 MHz, 298 K, CD_2Cl_2): δ = 34.0 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, CD_2Cl_2) δ = 148.5 (C_q^N-6), 145.7 (C_q-5), 144.6 (C_q-2), 138.7 (*C*-10), 136.7 (*C*-1), 134.1 (*C*-11), 131.6 (*C*-4), 130.1 (*C*-3), 128.7 (*C*-13), 128.3 (*C*-12), 127.9 (*C*-7/*C*-8), 127.6 (*C*-7/*C*-8), 126.9 (*C*-9) ppm. **HRMS** ($ASAP_{pos}$, toluene): expected: m/z 288.1002, 289.0965, 290.0999 $[C_{17}H_{13}BN_2S+H]^+$; found: m/z 288.0994, 289.0955, 290.0989 $[C_{17}H_{13}BN_2S+H]^+$. Crystalline material of **3Ph** as colorless blocks for single-crystal XRD was obtained by storing a saturated *n*-pentane solution at –20 °C for one day.

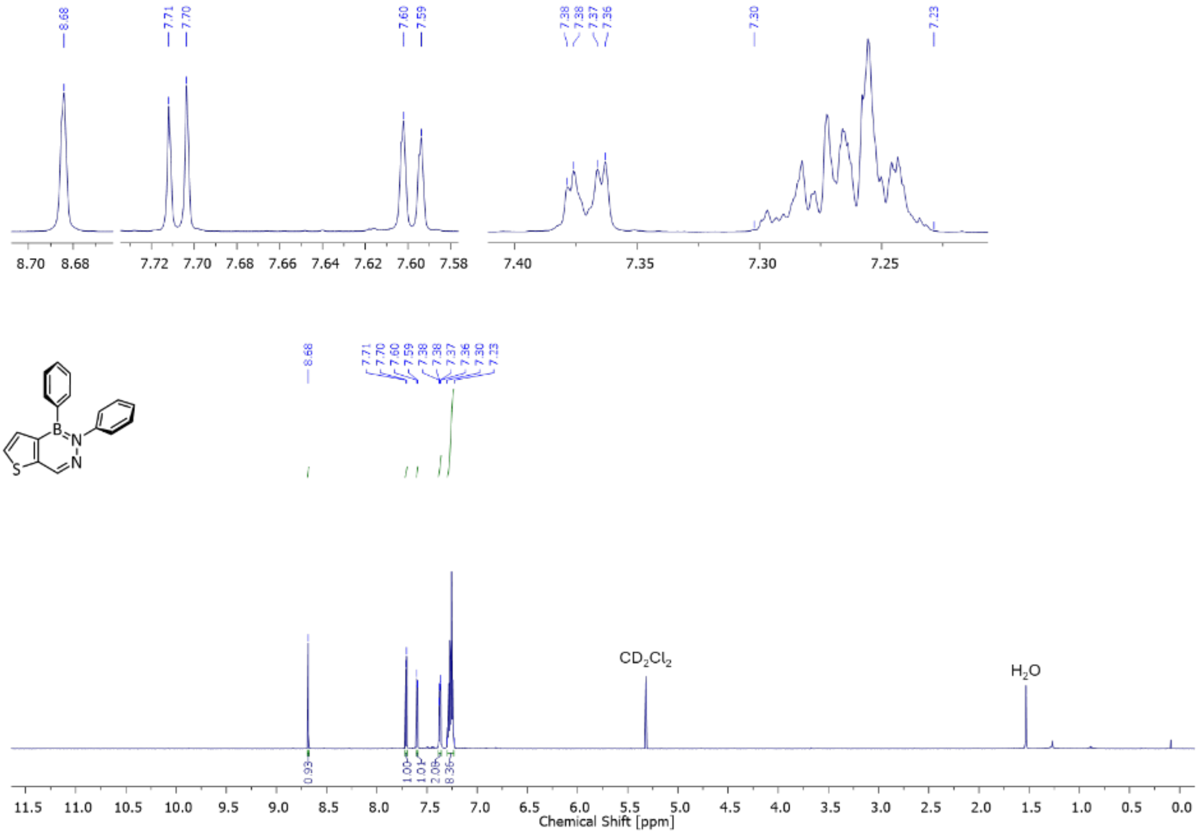


Fig. S21 ^{1}H NMR spectrum of compound **3Ph** in C*D*$_2$Cl$_2$.

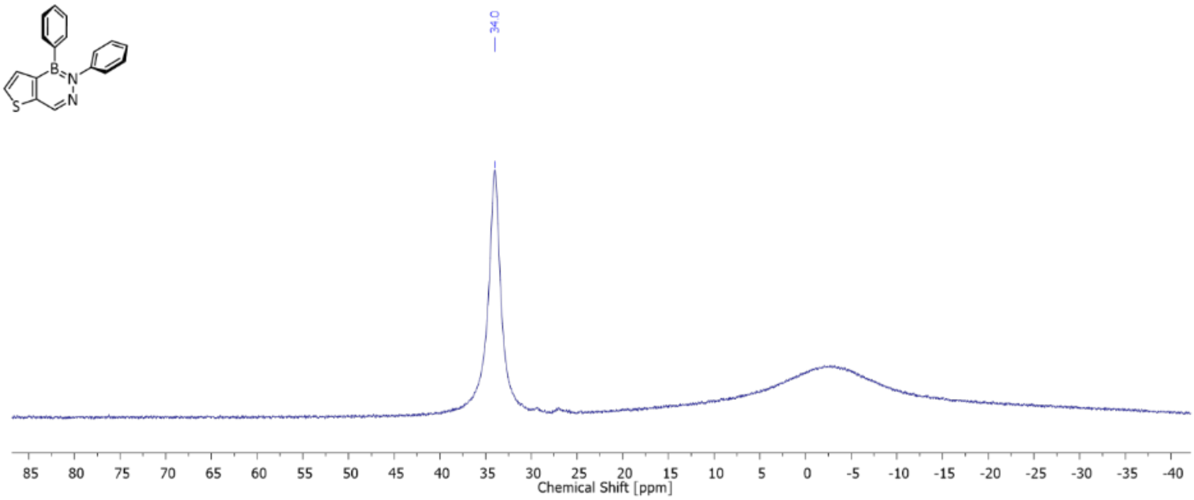


Fig. S22 Background-reduced ^{11}B NMR spectrum of compound **3Ph** in C*D*$_2$Cl$_2$.

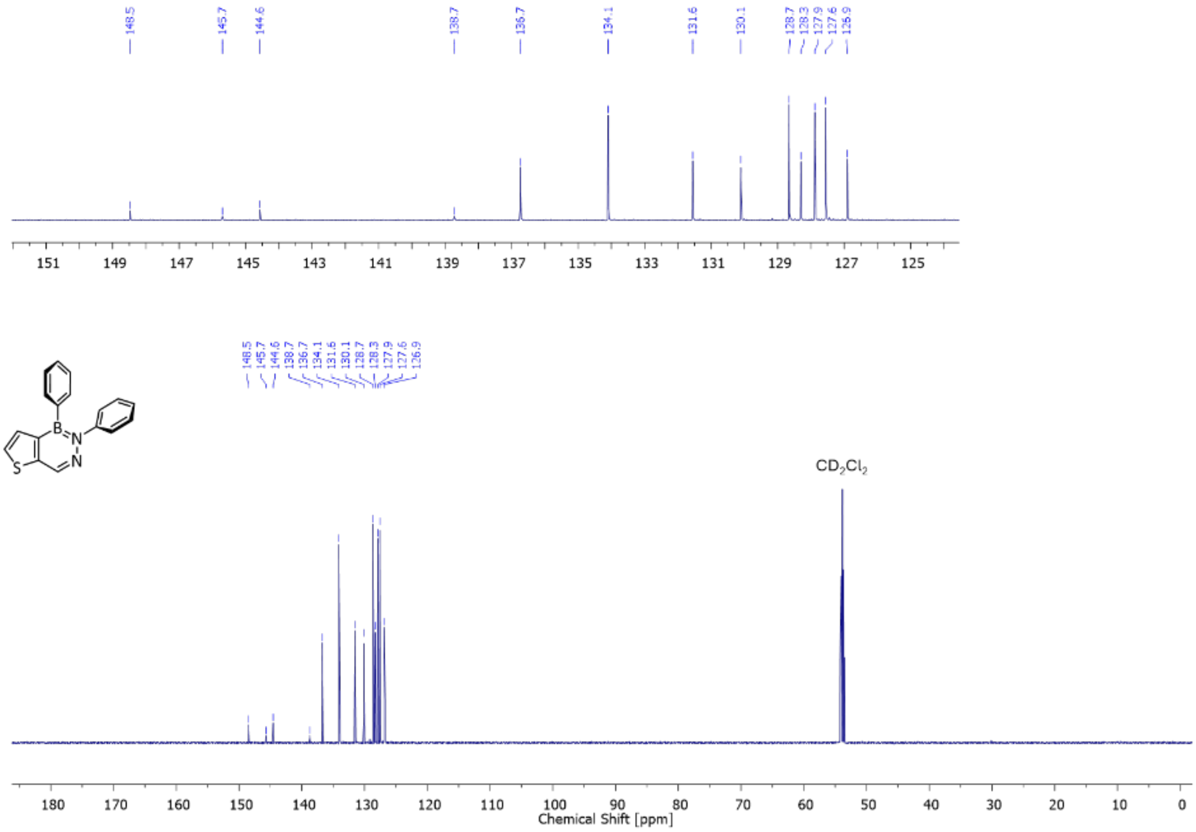


Fig. S23 ^{13}C{^{1}H^{11}B} NMR spectrum of compound **3Ph** in CD_2Cl_2 (^{11}B decoupled at 34 ppm).

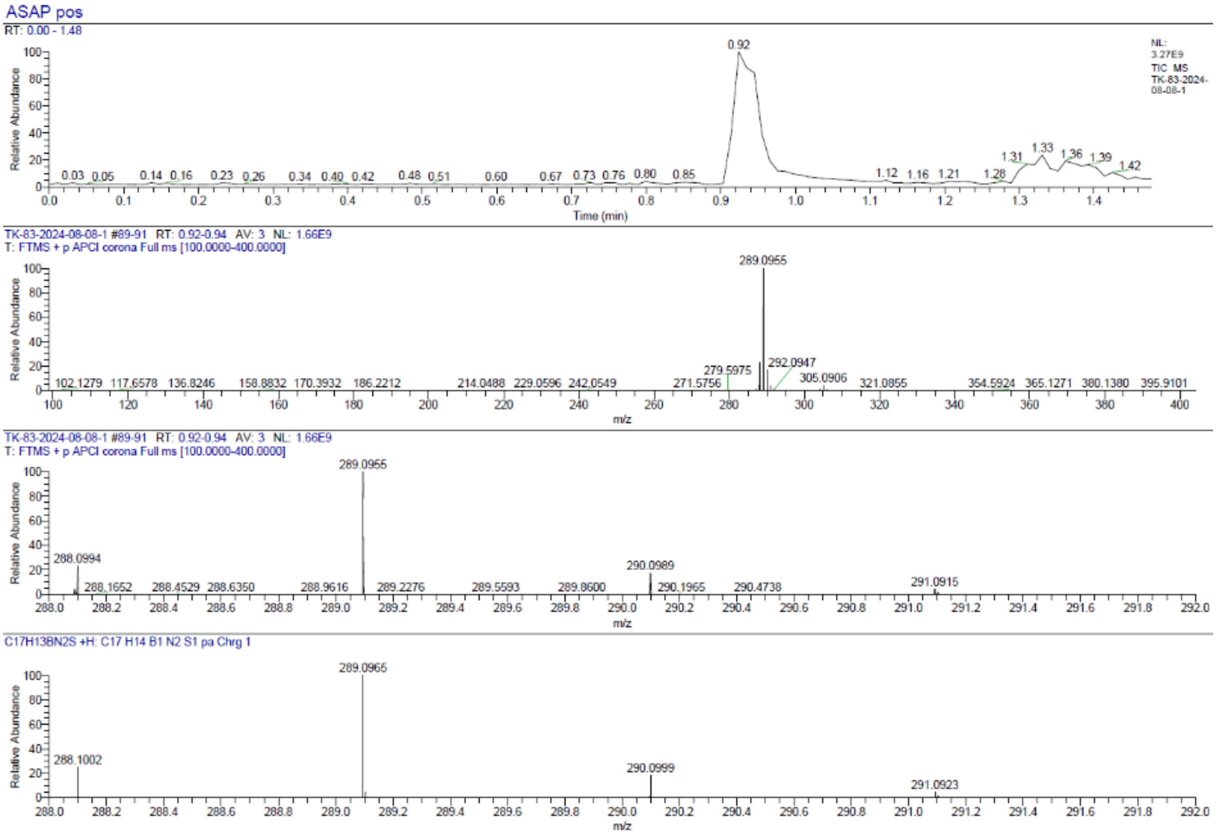


Fig. S24 ASAP$_{pos}$ mass spectrum of compound **3Ph** (toluene).

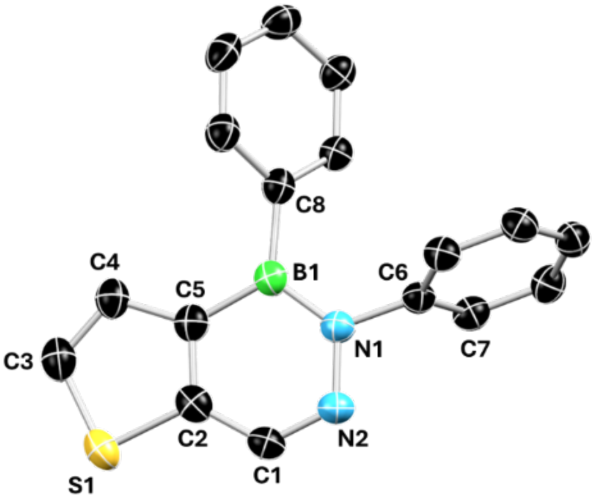
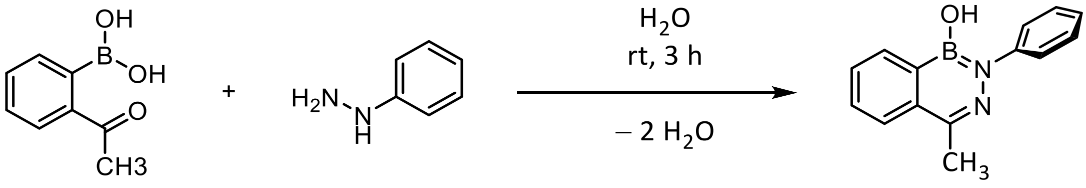


Fig. S25 Molecular structure of compound **3Ph**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.423(3), N1–N2 1.386(2), N2–C1 1.307(3), C1–C2 1.423(3), C2–S1 1.729(2), S1–C3 1.728(3), C3–C4 1.360(3), C4–C5 1.431(3), C5–C2 1.382(3), C5–B1 1.531(3), B1–C8 1.577(3), N1–C6 1.441(2), B1–N1–N2–C1 0.8(3), N2–N1–C6–C7 76.4(2).

Crystal data: $C_{17}H_{13}BN_2S$, $M_r = 288.16$, colorless block, $0.280 \times 0.090 \times 0.060$ mm^3, monoclinic space group $P2_1/n$, $a = 11.1933(2)$ Å, $b = 9.5312(2)$ Å, $c = 13.9740(3)$ Å, $\beta = 101.575(2)°$, $V = 1460.51(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.311$ g·cm^{-3}, $\mu = 1.888$ mm^{-1}, $F(000) = 600$, $T = 100(2)$ K, $R_1 = 0.0519$, $wR_2 = 0.1324$, 2851 independent reflections [$2\theta \leq 149.43°$] and 190 parameters.

CCDC number: 2453529

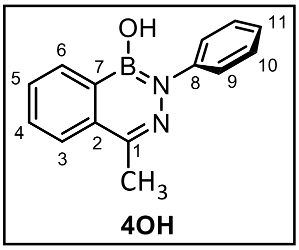
1-Methyl-3-phenyl-4-hydroxy-4,3-borazaroisoquinoline (4OH)



4OH (76%)

Open to the atmosphere, 2-acetylphenylboronic acid (4.93 g, 30.1 mmol, 1.00 eq.) was suspended in distilled water (600 mL) in a 1 L round bottom flask with a dumbbell stirring bar and stirred until total dissolution (approx. 10 min). Phenylhydrazine (2.96 mL, 30.1 mmol, 1.00 eq., ρ = 1.10 g/mL) was added under rapid stirring at ambient temperature, which resulted in the immediate formation of a colorless precipitate. After stirring for 3 h, the solid was filtered off and washed with distilled water (2 × 50 mL). The filter cake was dried in suction vacuum, and the obtained off-white powder was additionally dried in a vacuum desiccator (orange gel) until a consistent weight was achieved. **Yield of 4OH:** 5.41 g, 22.9 mmol, 76%, colorless powder. The compound is air- and moisture-stable.

^{1}H NMR (600 MHz, 298 K, DMSO-d_6): δ = 8.77 (s, 1H, B-O*H*), 8.42 (d, $^3J_{HH}$ = 7.58 Hz, 1H, *H*-6), 7.89 (d, $^3J_{HH}$ = 8.03 Hz, 1H, *H*-3), 7.78 (dd, $^3J_{HH}$ = 7.6 Hz, 7.6 Hz; 1H, *H*-4), 7.67 (dd, $^3J_{HH}$ = 7.57 Hz, 7.57 Hz; 1H, *H*-5), 7.58 (d, $^3J_{HH}$ = 7.85 Hz, 2H, *H*-9), 7.39 (d, $^3J_{HH}$ = 7.25 Hz, 2H, *H*-10), 7.20 (d, $^3J_{HH}$ = 7.27 Hz, 1H, *H*-11), 2.55 (s, 3H, –C*H*$_3$) ppm. **^{11}B NMR** (193 MHz, 298 K, DMSO-d_6) δ = 28.2 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, DMSO-d_6): δ = 146.4 (C_q^N-8), 142.7 (C_q-1), 134.8 (C_q-2), 131.9 (*C*-6), 131.4 (*C*-4), 130.2 (C_q^B-7), 128.7 (*C*-5), 128.1 (*C*-10), 125.3 (*C*-3), 124.6 (*C*-11), 124.4 (*C*-9), 20.0 (–*C*H$_3$) ppm. **HRMS** (ASAP$_{pos}$, acetone): expected: m/z 236.1230, 237.1194, 238.1227 [$C_{14}H_{13}BN_2O$+H]; found: m/z 236.1220, 237.1182, 238.1214 [$C_{14}H_{13}BN_2O$+H]. Crystalline material of **4OH** as colorless plates for single-crystal XRD was obtained by slow evaporation of a saturated acetone/H_2O mixture at ambient temperature open to the atmosphere.



4OH

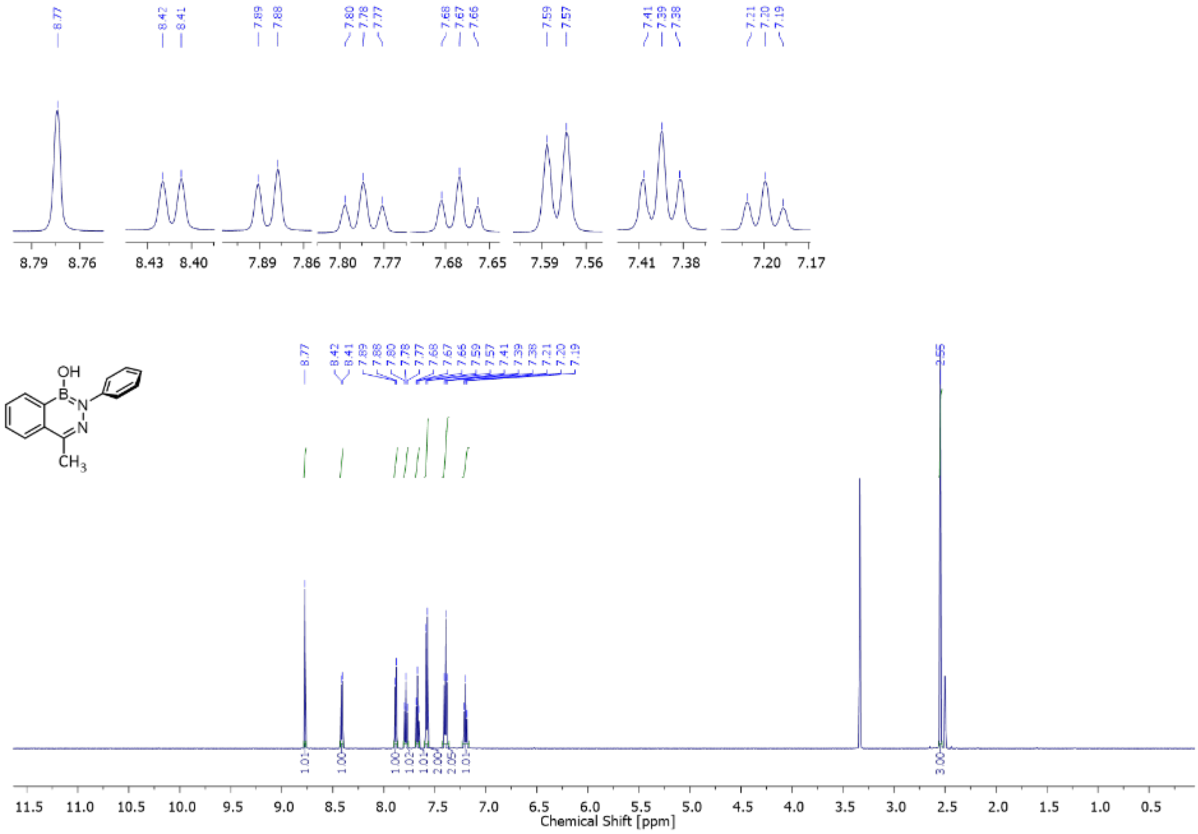


Fig. S26 ^{1}H NMR spectrum of compound **4OH** in DMSO-d_6.

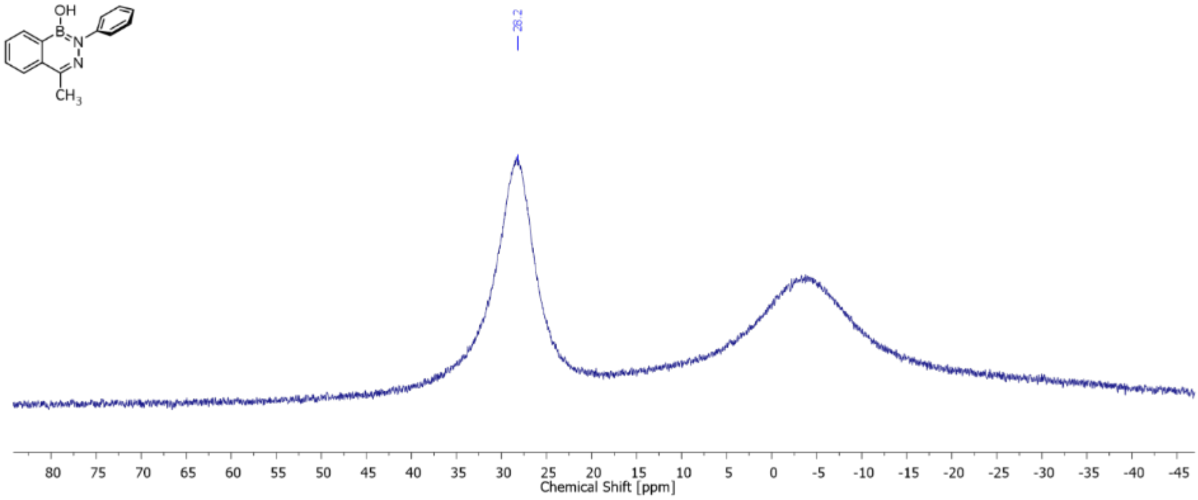


Fig. S27 Background-reduced ^{11}B NMR spectrum of compound **4OH** in DMSO-d_6.

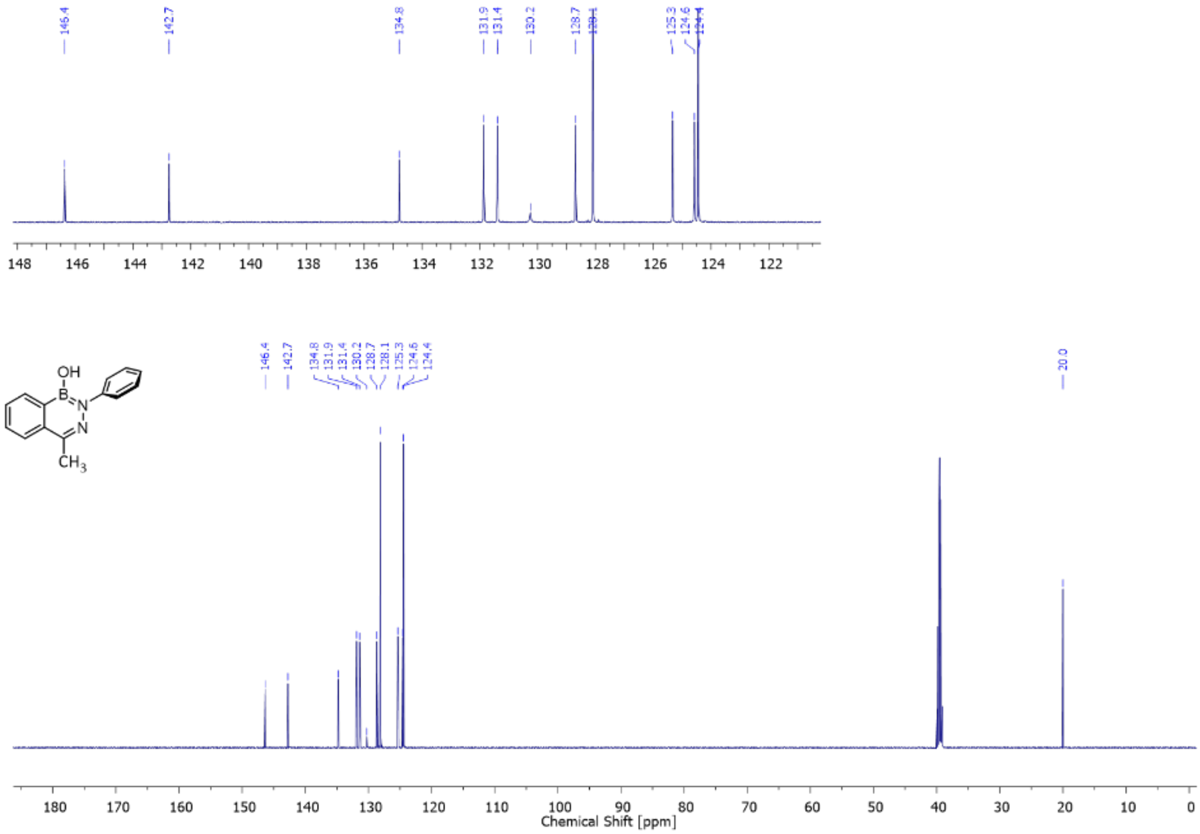


Fig. S28 $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **4OH** in DMSO-*d*₆ (decoupled at 28 ppm).

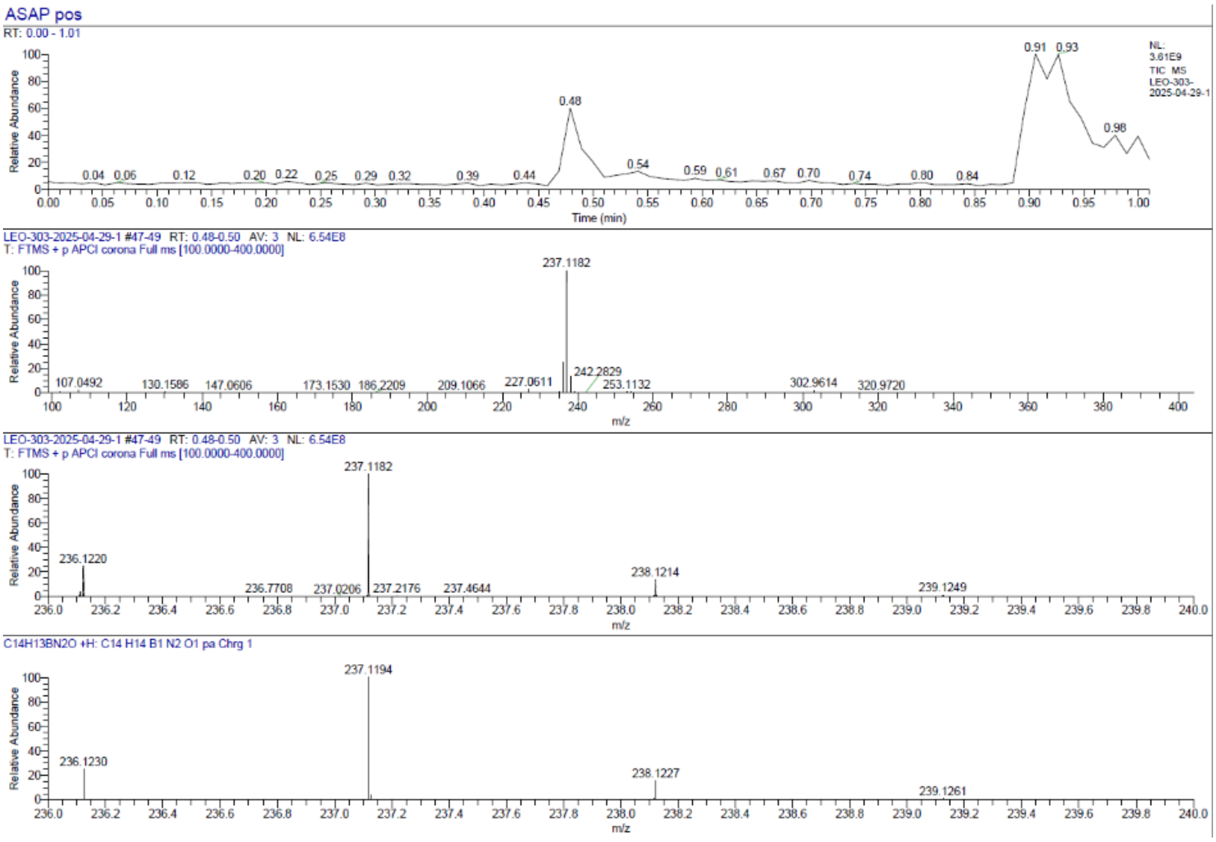


Fig. S29 ASAP$_{pos}$ mass spectrum of compound **4OH** (acetone).

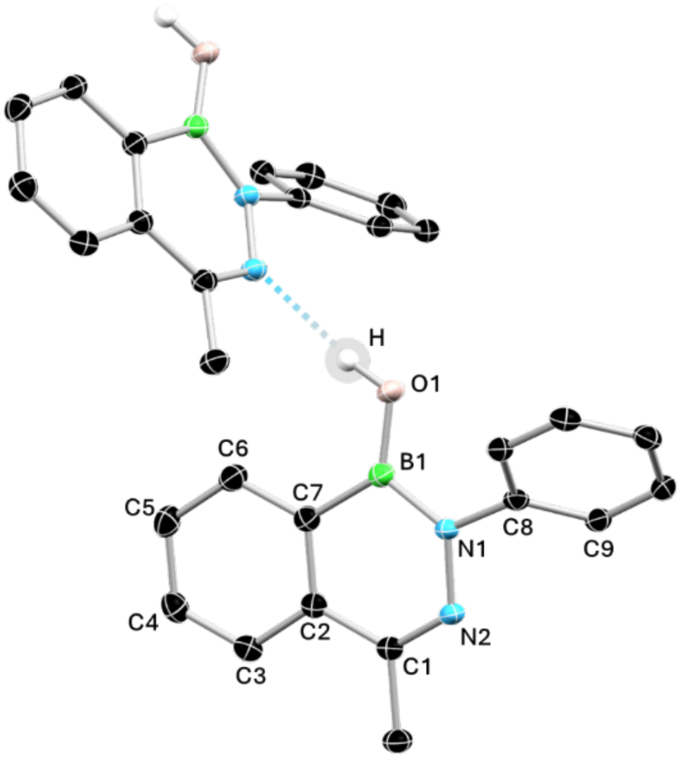
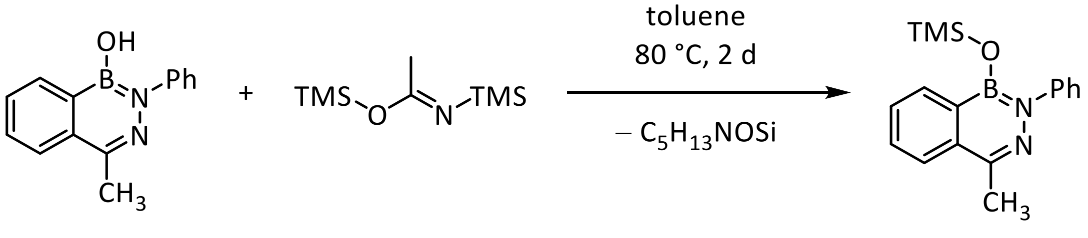


Fig. S30 Molecular structure of compound **4OH**. Ellipsoids drawn at 50% probability (100 K). All H-atoms except for the borinic acid omitted. Selected bond lengths (Å) and angles (°) of **4OH**: B1–N1 1.4393(15), N1–N2 1.3920(12), N2–C1 1.3028(14), C1–C2 1.4620(15), C2–C3 1.4056(16), C3–C4 1.3818(16), C4–C5 1.3965(17), C5–C6 1.3844(16), C6–C7 1.4068(15), C2–C7 1.4081(15), C7–B1 1.5452(16), B1–O1 1.3648(15), N1–C8 1.4354(14), B1–N1–N2–C1 7.76(15), N2–N1–C8–C9 45.32(13).

Crystal data: $C_{14}H_{13}BN_2O$, $M_r = 236.07$, clear colorless plate, 0.490×0.320×0.050 mm^3, triclinic space group $P\bar{1}$, $a = 10.7572(2)$ Å, $b = 10.8505(2)$ Å, $c = 11.0433(3)$ Å, $\alpha = 76.604(2)°$, $\beta = 70.642(2)°$, $\gamma = 74.681(2)°$, $V = 1158.10(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.354$ g·cm^{-3}, $\mu = 0.676$ mm^{-1}, $F(000) = 496$, $T = 100(2)$ K, $R_1 = 0.0393$, $wR_2 = 0.1001$, 4562 independent reflections [$2\theta \leq 148.032°$] and 333 parameters.

CCDC number: 2453530

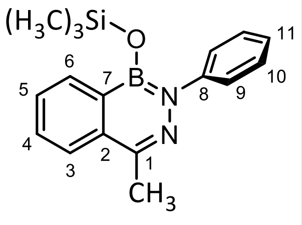
1-Methyl-3-phenyl-4-(trimethylsilyloxy)-4,3-borazaroisoquinoline (**4OTMS**)



4OH **4OTMS** (81%)

DAB **4OH** (3.00 g, 12.7 mmol, 1.00 eq.) was suspended in toluene (150 mL) in a 250 mL Schlenk tube. Under rapid stirring, *N,O*-bis(trimethylsilyl)acetamide (20.0 mL, 82.6 mmol, xs., *ρ* = 0.83 g/mL) was added at ambient temperature. After stirring the suspension for 10 min, a clear, light yellow solution was obtained. The reaction was then 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* sublimation, the obtained yellow oil was heated to 80 °C at $1.2 \cdot 10^{-2}$ mbar. The remaining yellow oil was extracted with *n*-pentane (3 × 4 mL) via filter cannulation and all volatile components were removed *in vacuo*. Compound **4OTMS** was obtained as yellow oil. After storing the pure oil at −30 °C in a glovebox for several weeks, the oil started crystalizing. **Yield of 4OTMS:** 3.16 g, 10.2 mmol, 81%, yellow oil.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 8.22-8.26 (m, 1H, *H*-3), 7.60-7.62 (m, 2H, *H*-9), 7.49-7.53 (m, 1H, *H*-6), 7.38-7.42 (m, 2H, *H*-4 + *H*-5), 7.20-7.24 (m, 2H, *H*-10), 7.03-7.07 (m, 1H, *H*-11), 2.50 (s, 3H, $-CH_3$), 0.04 (s, 9H, $-Si(CH_3)_3$) ppm. **^{11}B NMR** (160 MHz, 298 K, C_6D_6) δ = 26.8 (br s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, 298 K, C_6D_6): δ = 147.4 (C_q^N-8), 144.1 (C_q-1), 136.5 (C_q-2), 133.0 (C_q^B-7), 132.3 (*C*-3), 131.3 (*C*-5), 128.7 (*C*-6), 128.6 (*C*-10), 126.5 (*C*-9), 125.8 (*C*-11), 125.5 (*C*-6), 20.3 ($-CH_3$), 1.6 ($-Si(CH_3)_3$) ppm. **HRMS** (LIFDI, toluene): expected: m/z 307.1547, 08.1511, 309.1544 [$C_{17}H_{21}BN_2OSi$]; found: m/z 307.1539, 308.1502, 309.1536 [$C_{17}H_{21}BN_2OSi$]. Crystalline material of **4OTMS** as colorless plates for single-crystal XRD was obtained by storing the obtained oil at –30 °C for several weeks.



4OTMS

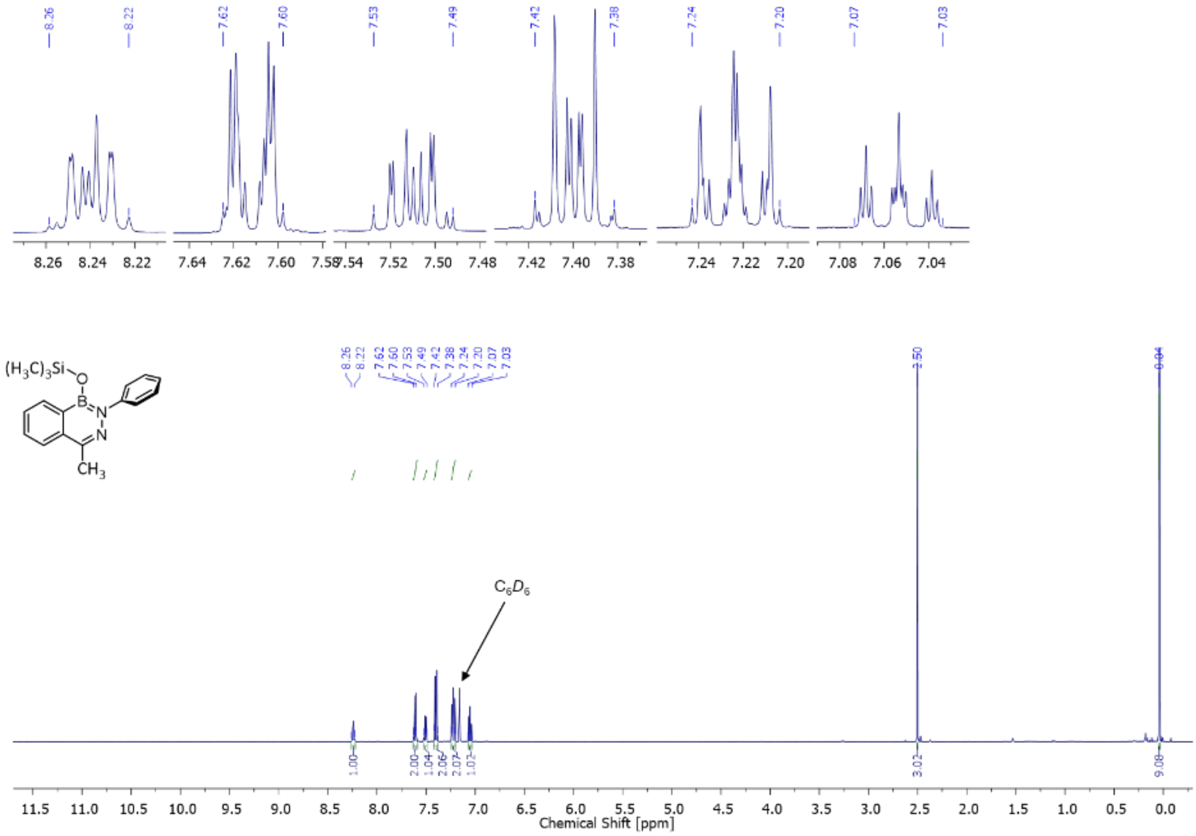


Fig. S31 ^{1}H NMR spectrum of compound **4OTMS** in C$_6$*D*$_6$.

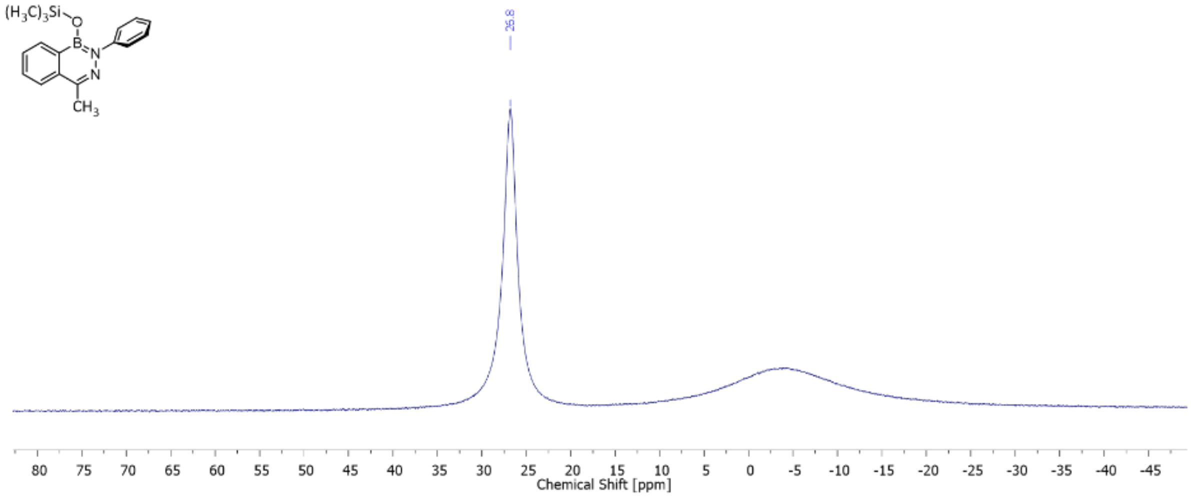


Fig. S32 Background-reduced ^{11}B NMR spectrum of compound **4OTMS** in C$_6$*D*$_6$.

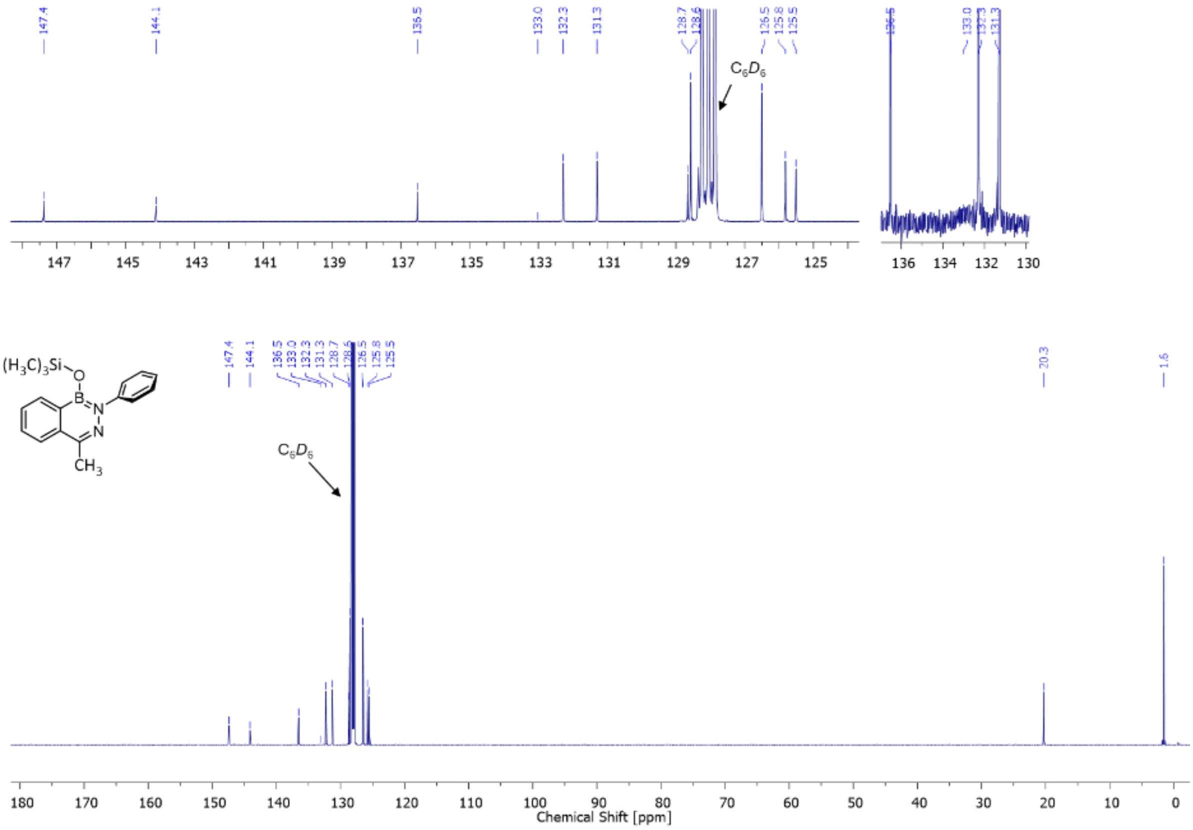


Fig. S33 $^{13}C\{^1H\}$ NMR spectrum of compound **4OTMS** in C_6D_6.

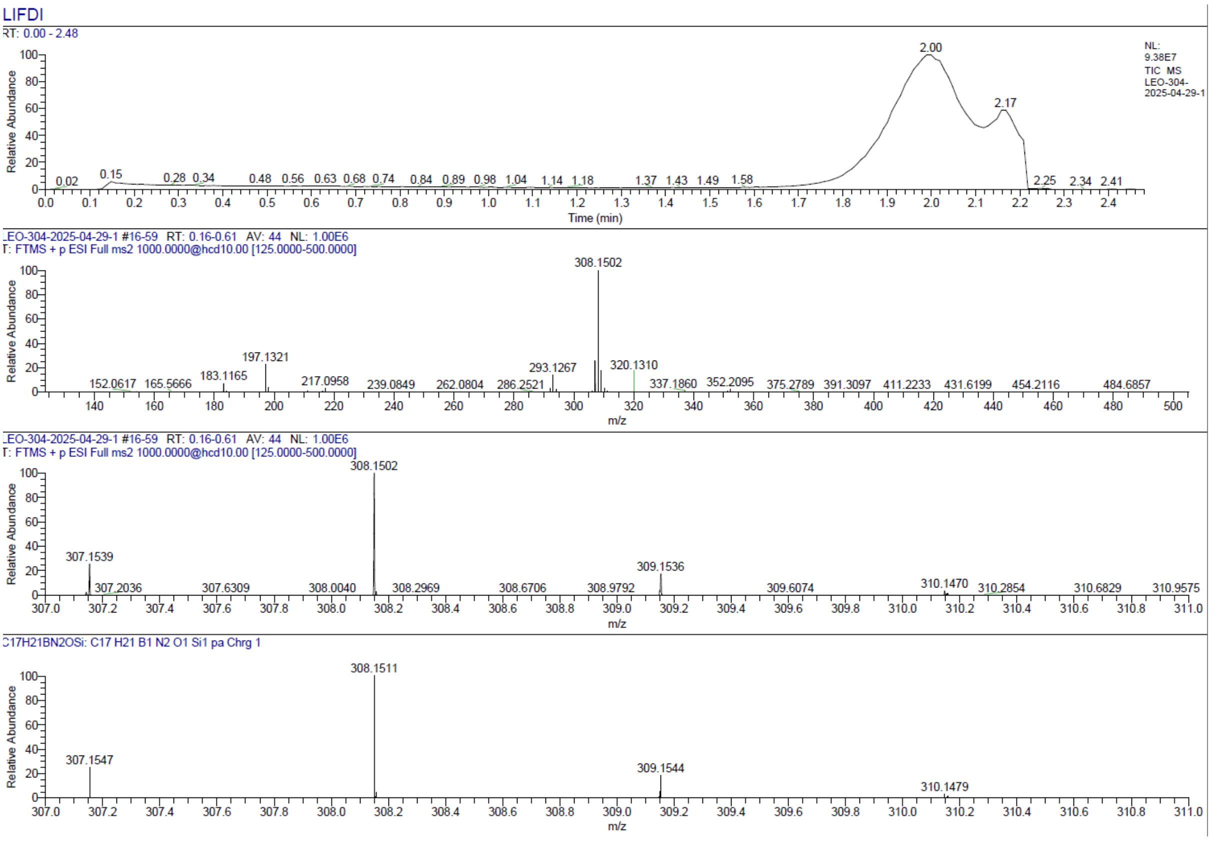


Fig. S34 LIFDI mass spectrum of compound **4OTMS** (toluene).

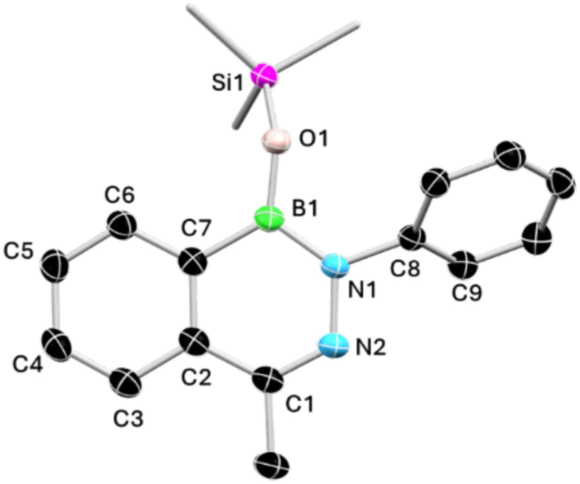
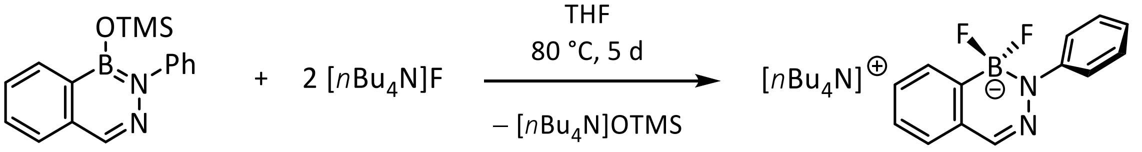


Fig. S35 Molecular structure of compound **4OTMS**. Ellipsoids drawn at 50% probability (100 K). All H-atoms except for the borinic acid omitted and methyl groups of the TMS-group shown as wireframe. Selected bond lengths (Å) and angles (°) of **4OTMS**: B1–N1 1.4279(19), N1–N2 1.3950(15), N2–C1 1.3025(18), C1–C2 1.455(2), C2–C3 1.411(2), C3–C4 1.375(2), C4–C5 1.399(2), C5–C6 1.381(2), C6–C7 1.406(2), C2–C7 1.4084(19), C7–B1 1.540(2), B1–O1 1.3662(18), N1–C8 1.4381(17), B1–N1–N2–C1 3.47(19), N2–N1–C8–C9 54.67(15).

Crystal data: $C_{17}H_{21}BN_2OSi$, M_r = 308.26, translucent colorless plate, 0.410×0.370×0.060 mm^3, monoclinic space group $P2_1/c$, a = 10.4615(2) Å, b = 14.0366(3) Å, c = 12.1057(3) Å, β = 105.153(2)°, V = 1715.84(7) Å^3, Z = 4, ρ_{calcd} = 1.193 g·cm^{-3}, μ = 1.213 mm^{-1}, $F(000)$ = 656, T = 100(2) K, R_1 = 0.0408, wR_2 = 0.1014, 3443 independent reflections [$2\theta \leq 149.402°$] and 203 parameters.

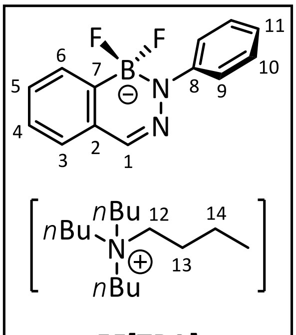
CCDC number: 2453531

Tetra(n-butyl)ammonium 3-(phenyl)-4-bis(fluoro)-4,3-borazaroisoquinolinate (5F[TBA])



1OTMS **5F[TBA]** (65%)

Compound **1OTMS** (118 mg, 400 μmol, 1.00 eq.) was dissolved in THF (4 mL) in a Schlenk tube equipped with a stirring bar. Tetra-*n*-butylammonium fluoride (1.0 M solution in THF, 1.60 mL, 1.60 mmol, 4.00 eq.) was added dropwise at ambient temperature. Upon addition, the colorless reaction mixture turned yellow. The reaction mixture was then stirred for 5 d at 80 °C. The solvent was removed under reduced pressure and the obtained yellow, sticky solid was recrystallized from MeCN (1.0 mL) at −30 °C, washed with cold (−30 °C) MeCN (3 × 1.0 mL) and dried *in vacuo*. **Yield of 5F[TBA]**: 127 mg, 260 μmol, 65%, pale-yellow powder.



5F[TBA]

^{1}H NMR (500 MHz, 298 K, THF-d_8): δ = 7.75 (d, $^3J_{HH}$ = 8.07 Hz, 2H, *H*-9), 7.58-7.61 (m, 1H, *H*-3), 7.14 (s, 1H, *H*-1), 7.03-7.09 (m, 2H, *H*-4 + *H*-5), 6.96-7.01 (m, 3H, *H*-10 + *H*-6), 6.54 (tt, $^3J_{HH}$ = 7.12 Hz; $^4J_{HH}$ = 1.15 Hz, 1H, *H*-11), 2.67-2.75 (m, 8H, *H*-12), 1.16-1.25 (m, 8H, *H*-13), 1.06 (sext, $^3J_{HH}$ = 7.66 Hz, 8H, *H*-14), 0.77 (t, $^3J_{HH}$ = 7.30 Hz, 12H, ^{n}Bu-CH_3) ppm. **^{11}B{^{19}F} NMR** (160 MHz, 298 K, THF-d_8) δ = 3.4 (br s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, 298 K, THF-d_8) δ = 151.8 (t, $^3J_{CF}$ = 3.07 Hz, C_q^N-8), 145.0 (br, C_q^B-7), 134.1 (t, $^3J_{CF}$ = 3.41 Hz, C_q-2), 132.3 (*C*-1), 131.6 (*C*-3), 128.0 (*C*-10), 126.5 (C-4), 126.1 (C-5), 123.4 (C-9), 117.8 (t, $^4J_{CF}$ = 3.27 Hz, *C*-6), 117.7 (*C*-11), 58.4 (*C*-12), 24.1 (*C*-13), 20.0 (*C*-14), 13.7 (^{n}Bu-CH_3) ppm. **^{19}F{^{11}B} NMR** (471 MHz, 298 K, THF-d_8) δ = −131.5 (s) ppm. **HRMS** (ESI$_{neg}$, THF): expected: m/z 242.0947, 243.0911, 244.0944 $[C_{13}H_{10}BF_2N_2]^-$; found: m/z 242.0947, 243.0908, 244.0939 $[C_{13}H_{10}BF_2N_2]^-$. Crystalline material of **5F[TBA]** as colorless blocks for single-crystal XRD was obtained by slow evaporation of a saturated THF solution at −30 °C.

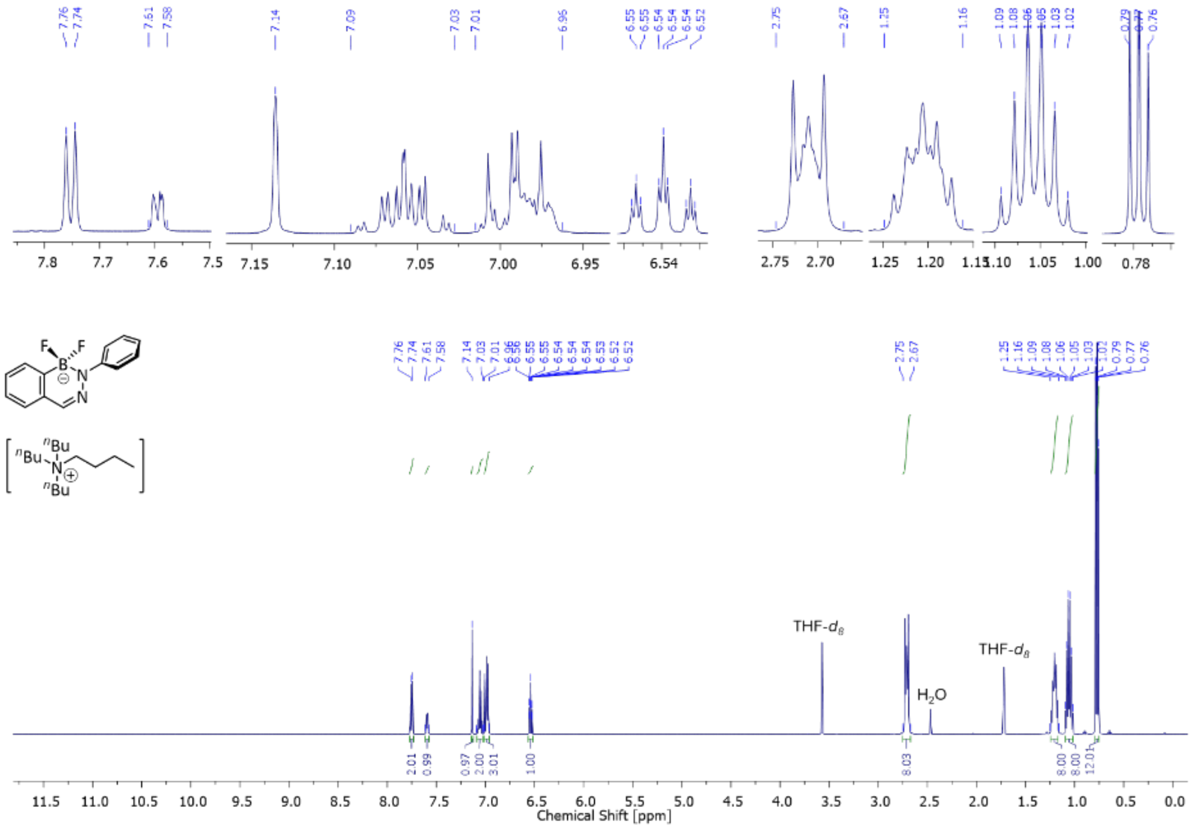


Fig. S36 ^1H NMR spectrum of compound **5F[TBA]** in THF-d_8.

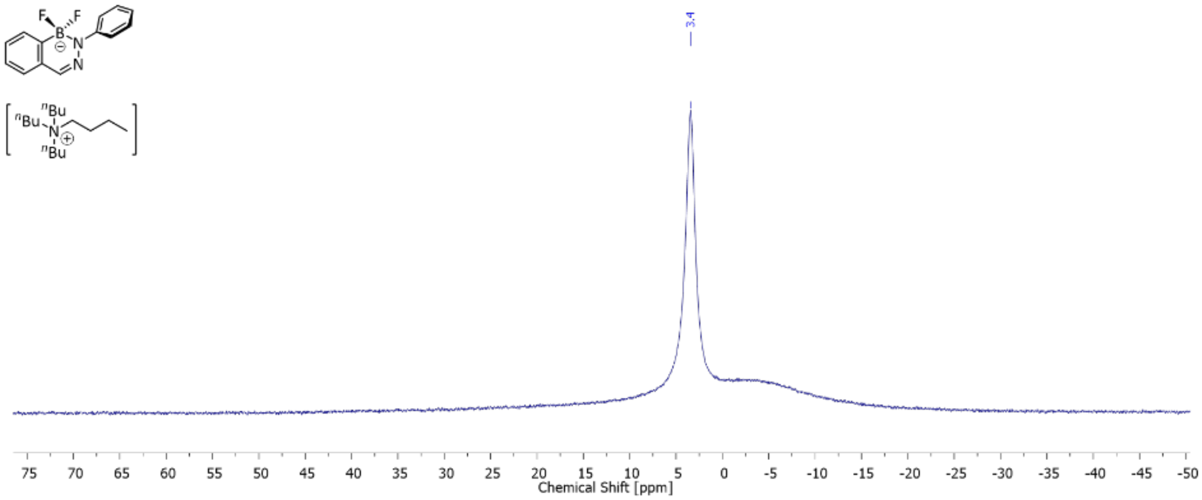


Fig. S37 $^{11}B\{^{19}F\}$ NMR spectrum of compound **5F[TBA]** in THF-d_8 (^{19}F decoupled at −131 ppm).

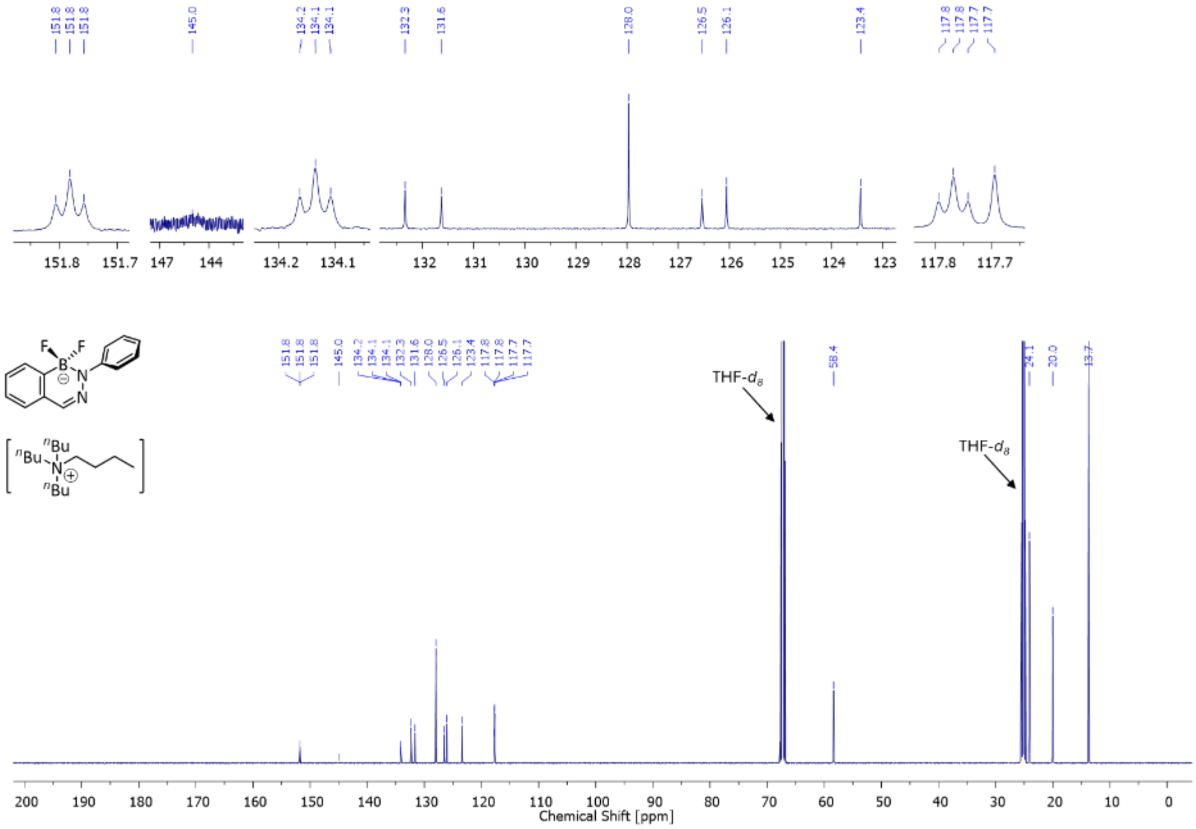


Fig. S38 ^{13}C{^{1}H} NMR spectrum of compound **5F[TBA]** in THF-d_8.

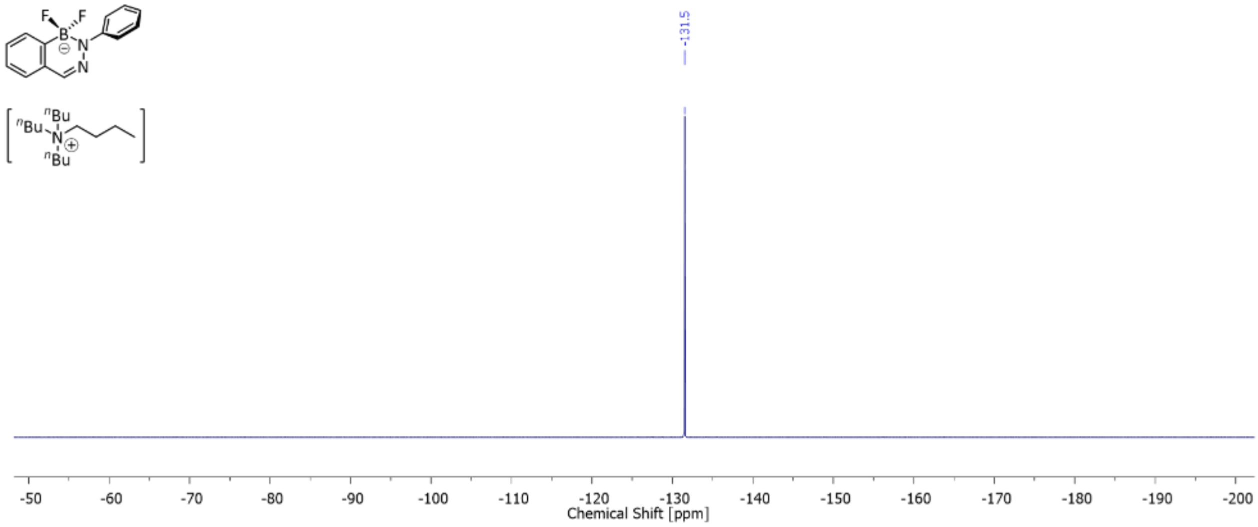


Fig. S39 ^{19}F{^{11}B} NMR spectrum of compound **5F[TBA]** in THF-d_8 (^{11}B decoupled at 3 ppm).

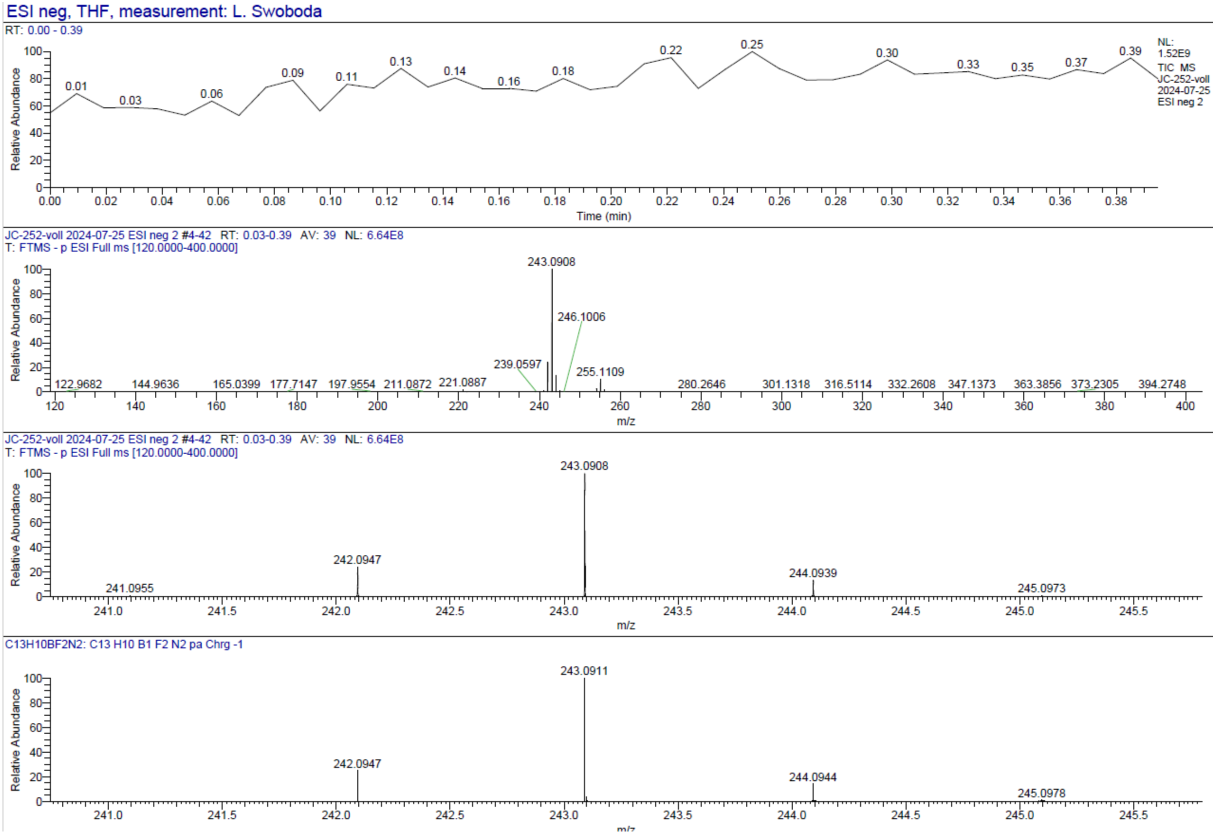


Fig. S40 ESI$_{neg}$ mass spectrum of compound **5F[TBA]** (THF).

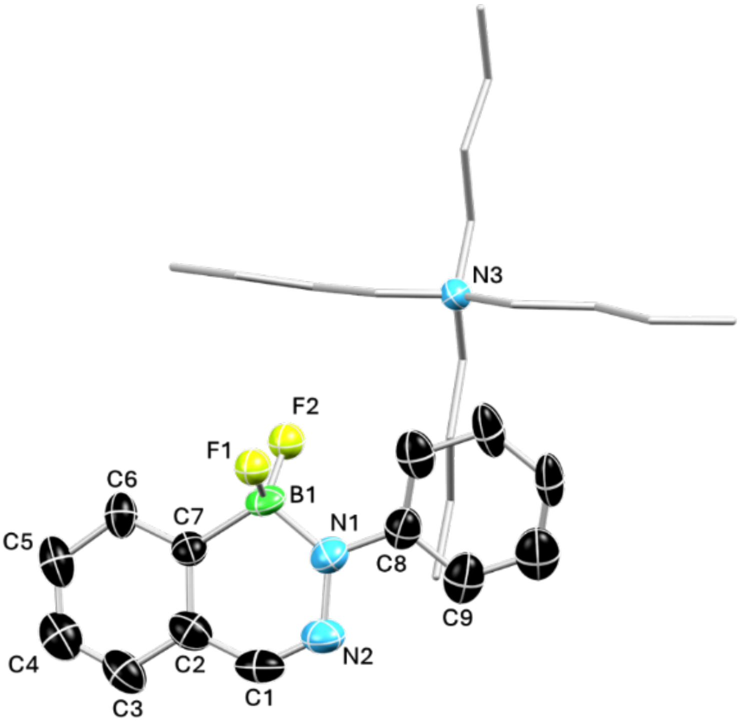


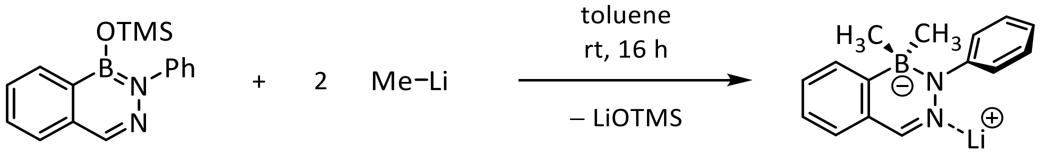
Fig. S41 Molecular structure of compound **5F[TBA]**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. *n*-Butyl substituents of the cation rendered as wireframe for clarity. Due to the presence of a whole molecule disorder of the borate anion (see appendix), no discussion of bond length is possible.

Crystal data: $C_{29}H_{45}BF_2N_3$, M_r = 490.49, colorless block, 0.250×0.100×0.080 mm^3, monoclinic space group *Pn*, a = 9.7015(2) Å, b = 9.6925(2) Å, c = 14.9167(3) Å, β = 92.447(2)°, V = 1401.36(5) Å^3, Z = 2, ρ_{calcd} = 1.162 g·cm^{-3}, μ = 0.605 mm^{-1}, F(000) = 532, T = 100(2) K, R_1 = 0.0668, wR_2 = 0.1892, Flack parameter = 0.02(6), 4942 independent reflections [$2\theta \leq$ 147.978°] and 473 parameters.

The main molecule has a whole molecule disorder. The atomic displacement parameters of the diazaborinate and phenyl atoms B1_1 to C6_21 were restraint with RIGU keyword in ShelXL input with esd = 0.016 ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of the diazaborinate and phenyl atoms B1_1 to C6_21 were restrained to the same value with similarity restraint SIMU with esd = 0.016. The Uii displacement parameters of the diazaborinate and phenyl atoms B1_1 to C6_21 were restrained with ISOR keyword to approximate isotropic behavior. Idealized geometry for the phenyl groups were constrained using AFIX 66. A third whole molecule disorder was refined isotropically and is constrained using AFIX 6. A constant U_{ii} value of 0.05576 was obtained by free refinement of U_{ii} with a free variable using SIMU for the whole diazaborinate molecule.

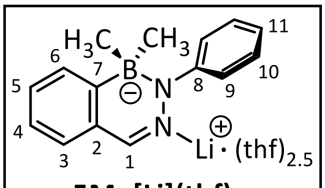
CCDC number: 2453536

Lithium 3-phenyl-4-bis(methyl)-4,3-borazaroisoquinolinate (**5Me[Li]**)



1OTMS **5Me[Li]** (64%)

In a glovebox, compound **1OTMS** (134 mg, 455 µmol, 1.00 eq.) was dissolved in toluene (2 mL) and a few drops of diethyl ether in a glass vial equipped with a stirring bar. Solid methyllithium $MeLi(OEt_2)_{0.25}$ (36.1 mg, 910 µmol, 2.00 eq.) was added in portions at ambient temperature. Upon addition, no immediate solid formation was observed. After approx. 1 h, the precipitation of a solid was observed. The reaction suspension was stirred for 2 d in the glovebox at ambient temperature. The solid was separated via pipet filtration and the filter cake was washed with cold toluene (2 × 1 mL), *n*-pentane (1 × 1 mL) and briefly dried *in vacuo*. **Yield of 5Me[Li](OEt$_2$)$_2$:** 113 mg (290 µmol, 64%), yellow solid. To obtain the adduct **5Me[Li](thf)$_{2.5}$**, some of the solid was re-dissolved in tetrahydrofuran (1 mL) and the solvent was removed under reduced pressure.



5Me[Li](thf)$_{2.5}$

^{1}H NMR (600 MHz, 298 K, C_6D_6): δ = 7.94 (d, $^3J_{HH}$ = 7.25 Hz, 1H, *H*-3), 7.49-7.52 (m, 2H, *H*-9), 7.37 (td, $^3J_{HH}$ = 7.34 Hz, $^4J_{HH}$ = 1.25 Hz, 1H, *H*-4), 7.19-7.24 (m, 2H, *H*-10), 7.18 (td, $^3J_{HH}$ = 7.35 Hz, $^4J_{HH}$ = 1.34 Hz, 2H, *H*-5)*[1], 7.09 (d, $^3J_{HH}$ = 7.45 Hz, 1H, *H*-6), 6.92 (s, 1H, *H*-1), 6.83 (tt, $^3J_{HH}$ = 7.27 Hz, $^4J_{HH}$ = 1.07 Hz, 1H, *H*-11), 3.15-3.21 (m, 10H, 2.5 × C*H*$_2$-thf), 1.24-1.30 (m, 10H, 2.5 × C*H*$_2$-thf), 0.74 (s, 6H, 2 × C*H*$_3$) ppm. **^{7}Li NMR** (233 MHz, 298 K, C_6D_6) δ = −0.36 (s) ppm. **^{11}B NMR** (128 MHz, 298 K, C_6D_6) δ = −7.1 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6) δ = 158.9 (C_q^B-7), 154.3 (C_q^N-8), 140.0 (*C*-1), 131.4 (*C*-3), 131.2 (*C*-2), 129.4 (*C*-4), 129.3 (*C*-10), 123.9 (*C*-5), 123.8 (*C*-6), 120.2 (*C*-9), 119.5 (*C*-11), 68.2 (*C*H$_2$-thf), 25.4 (*C*H$_2$-thf), 12.2 (*C*H$_3$) ppm. **HRMS** (LIFDI, toluene): expected: m/z 235.1516, 236.1479, 237.1513 $[C_{15}H_{16}BN_2+H]^+$; found: m/z 235.1513, 236.1476, 237.1513 $[C_{15}H_{16}BN_2+H]^+$. Crystalline material of **5Me[Li](OEt$_2$)$_2$** as yellow blocks for single-crystal XRD was obtained by storing a saturated diethyl ether solution at −30 °C for 2 d in a glovebox whilst passive diffusion of *n*-pentane.

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*[1] Superimposed with C_6D_6 solvent signal. Assigned with $^1H/^1H$ COSY NMR and $^1H/^{13}C$ HSQC NMR spectra.

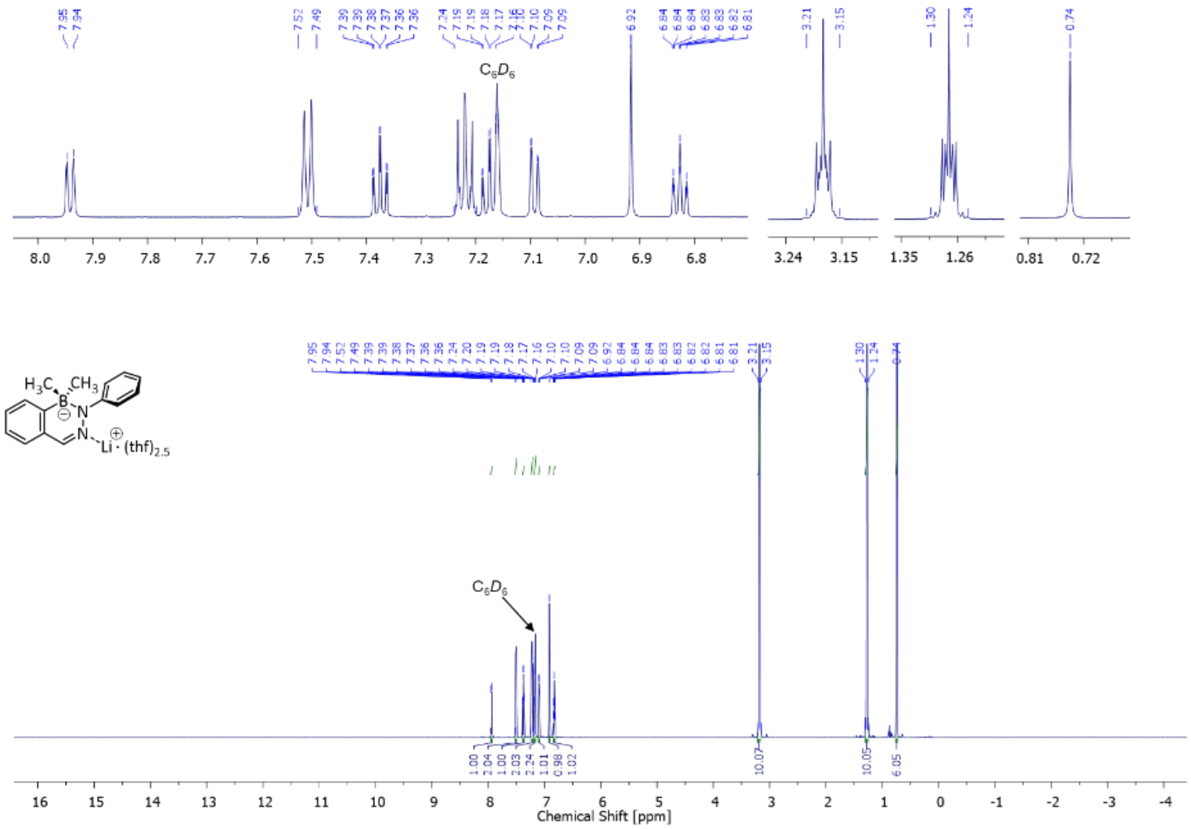


Fig. S42 ^{1}H NMR spectrum of compound **5Me[Li](thf)$_{2.5}$** in C_6D_6.

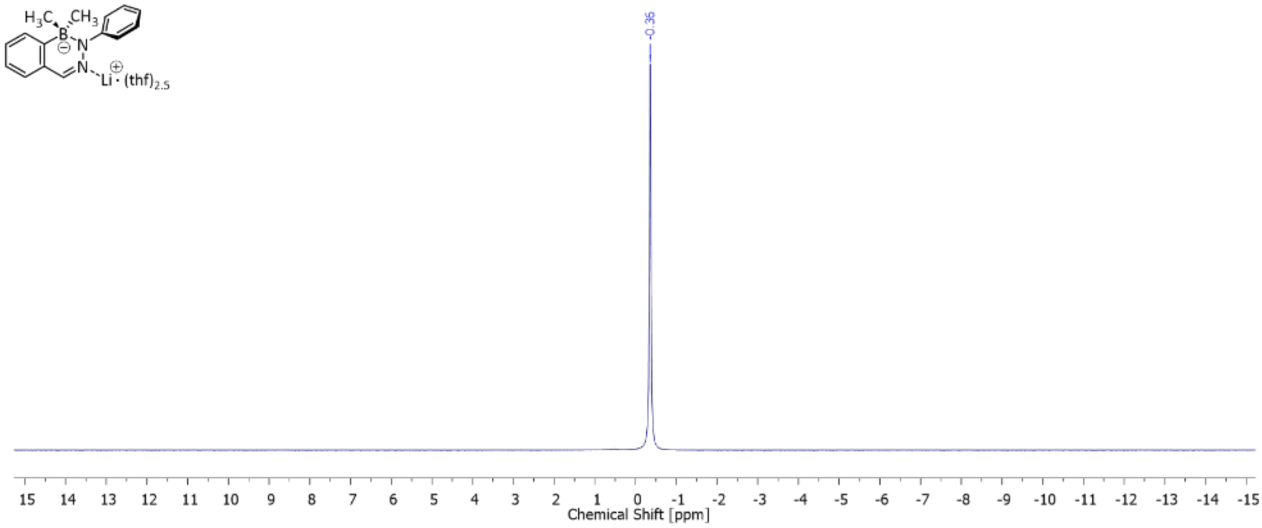


Fig. S43 ^{7}Li NMR spectrum of compound **5Me[Li](thf)$_{2.5}$** in C_6D_6.

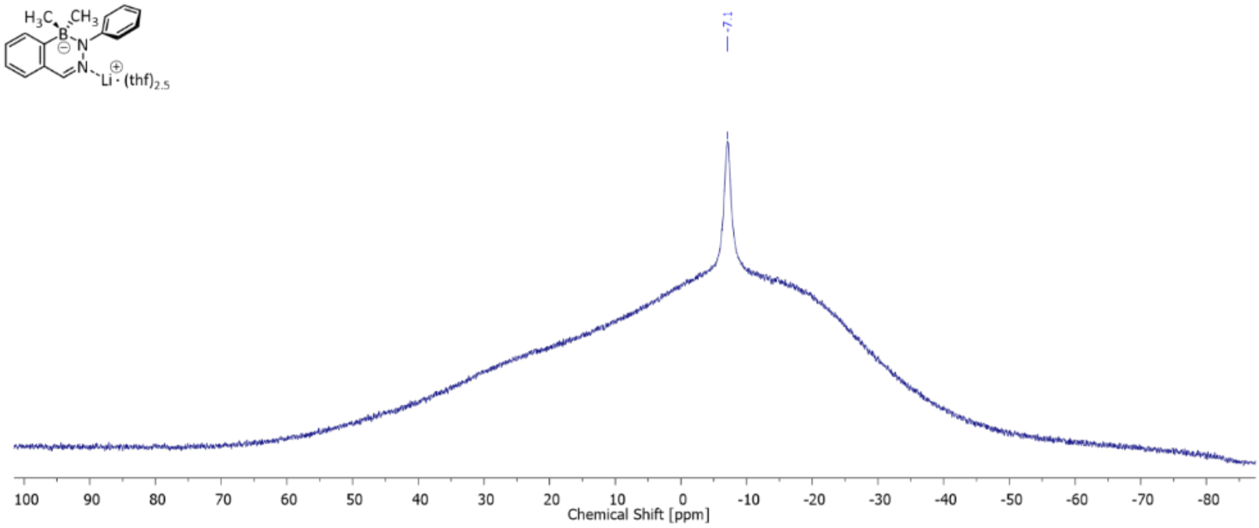


Fig. S44 ^{11}B NMR spectrum of compound **5Me[Li](thf)$_{2.5}$** in C_6D_6.

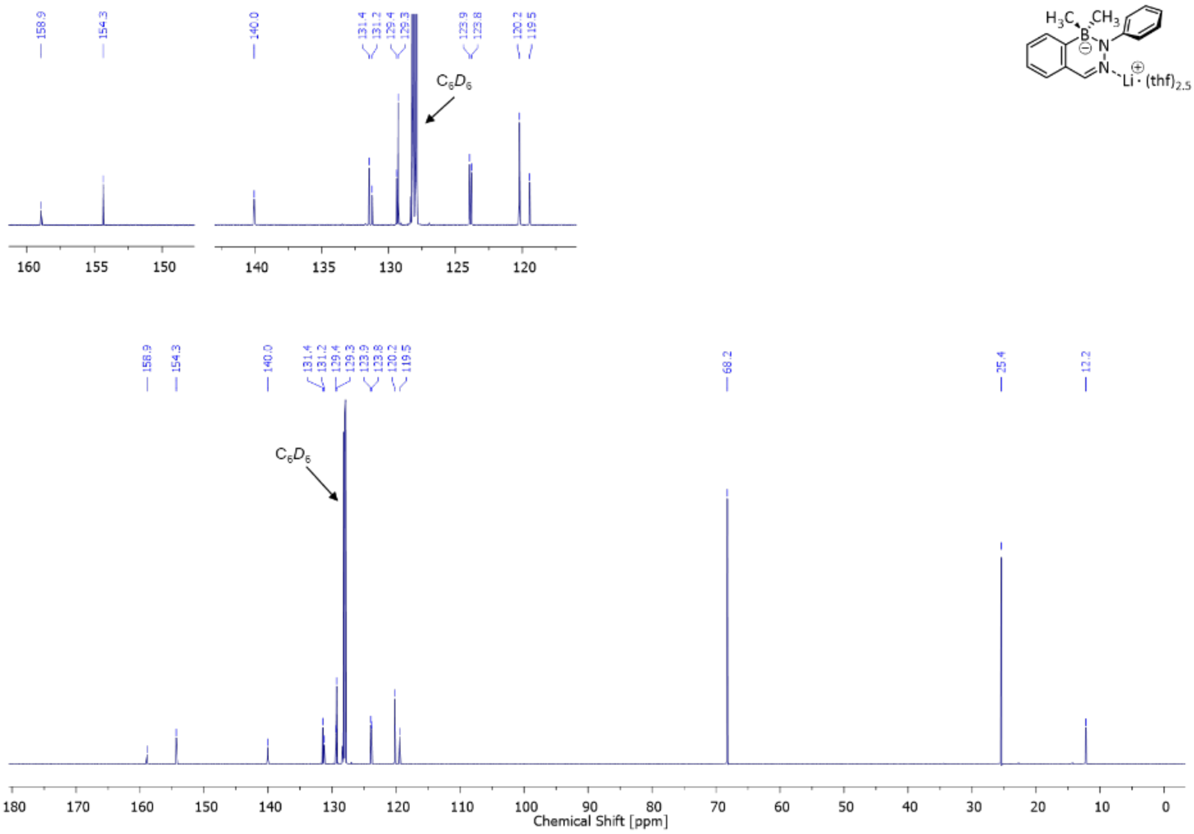


Fig. S45 ^{13}C{^{1}H^{11}B} NMR spectrum of compound **5Me[Li](thf)$_{2.5}$** in C_6D_6 (decoupled at −7 ppm).

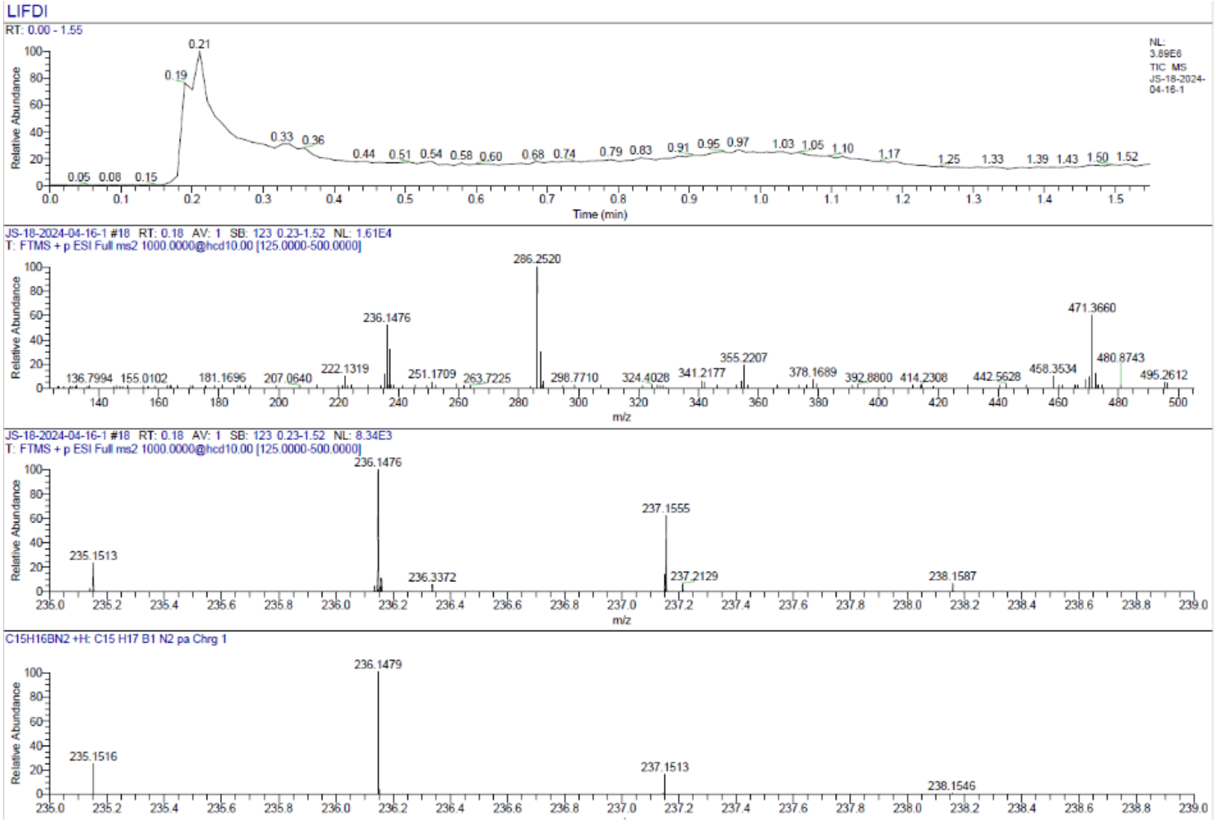


Fig. S46 LIFDI mass spectrum of compound **5Me[Li](thf)$_{2.5}$** (toluene).

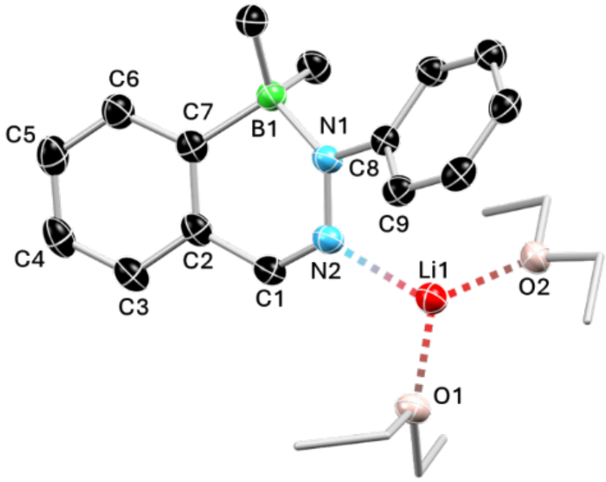
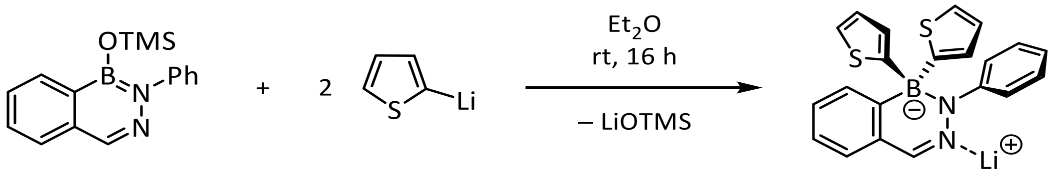


Fig. S47 Molecular structure of compound **5Me[Li](OEt$_2$)$_2$**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Complexing ether rendered as wireframe for clarity. Selected bond lengths (Å) and angles (°) of **5Me[Li](OEt$_2$)$_2$**: N2–Li1 2.017(2), B1–N1 1.6073(15), N1–N2 1.3735(13), N2–C1 1.3010(15), C1–C2 1.4500(16), C2–C3 1.4038(15), C3–C4 1.3829(18), C4–C5 1.3855(19), C5–C6 1.3930(17), C6–C7 1.3967(16), C2–C7 1.4092(16), C7–B1 1.6237(16), N1–C8 1.4012(14), B1–N1–N2–C1 17.32(15), B1–C7–C2–C1 10.21(15), N2–N1–C8–C9 41.00(13).

Crystal data: $C_{23}H_{36}BLiN_2O_2$, M_r = 390.29, yellow block, 0.780×0.330×0.110 mm^3, orthorhombic space group *Pbca*, a = 14.84100(10) Å, b = 17.19650(10) Å, c = 18.57070(10) Å, V = 4739.49(5) Å^3, Z = 8, ρ_{calcd} = 1.094 g·cm^{-3}, μ = 0.522 mm^{-1}, F(000) = 1696, T = 100(2) K, R_1 = 0.0451, wR_2 = 0.1118, 4810 independent reflections [$2q$ ≤150.478°] and 268 parameters.

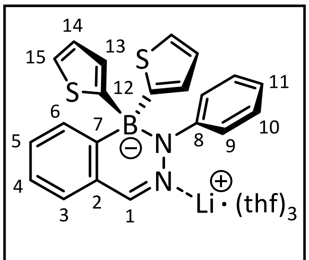
CCDC number: 2453540

Lithium 3-phenyl-4-bis(thienyl)-4,3-borazaroisoquinolinate (5Thio[Li])



1OTMS **5Thio[Li]** (77%)

In a glovebox, compound **1OTMS** (100 mg, 340 μmol, 1.00 eq.) was dissolved in diethyl ether (2 mL) in a glass vial equipped with a stirring bar. 2-Thienyllithium (61.2 mg, 680 μmol, 2.00 eq.) was added in portions at ambient temperature. Upon addition, the immediate formation of a pale-yellow solid was observed. The reaction suspension was stirred for 16 h in the glovebox at ambient temperature. The solid was separated via pipet filtration and the filter cake was washed with cold toluene (2 × 1 mL), *n*-pentane (1 × 1 mL) and briefly dried *in vacuo*. To obtain the adduct **5Thio[Li](thf)$_3$**, the solid was re-dissolved in tetrahydrofurane (1 mL) and the solvent was removed under reduced pressure. **Yield of 5Thio[Li](thf)$_3$:** 157 mg (264 μmol, 77%), pale-yellow, crystalline solid.



5Thio[Li](thf)$_3$

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 7.70 (d, $^3J_{HH}$ = 7.23 Hz, 1H, *H*-3), 7.49 (dd, $^3J_{HH}$ = 3.26 Hz, $^4J_{HH}$ = 1.03 Hz, 2H, *H*-13), 7.45-7.48 (m, 2H, *H*-9), 7.30 (dd, $^3J_{HH}$ = 4.72 Hz, $^4J_{HH}$ = 0.95 Hz, 2H, *H*-15), 7.27 (ddd, $^3J_{HH}$ = 7.36 Hz, 6.39 Hz, $^4J_{HH}$ = 2.14 Hz, 1H, *H*-4), 7.22 (s, 1H, *H*-1), 7.17-7.21 (m, 2H, *H*-5 + *H*-6), 7.14-7.17 (m, 5H, *H*-14)*[1], 6.99-7.04 (m, 2H, *H*-10), 6.66 (tt, $^3J_{HH}$ = 7.19 Hz, $^4J_{HH}$ = 1.20 Hz, 1H, *H*-11), 3.12-3.16 (m, 12H, 3 × C*H*$_2$-thf), 1.21-1.26 (m, 12H, 3 × C*H*$_2$-thf) ppm. **^{7}Li NMR** (194 MHz, 298 K, C_6D_6) δ = −0.36 (s) ppm. **^{11}B NMR** (160 MHz, 298 K, C_6D_6) δ = −6.6 (s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6) δ = 160.9 (C_q^B-12), 152.8 (C_q^N-8), 152.6 (C_q^B-7), 140.6 (*C*-1), 134.2 (*C*-3), 130.3 (C_q-2), 130.2 (*C*-13), 129.8 (*C*-4), 128.6 (*C*-10), 126.9 (*C*-14), 125.2 (*C*-15), 125.0 (*C*-5), 123.5 (*C*-6), 120.0 (*C*-9), 119.2 (*C*-11), 68.2 (*C*H$_2$-thf), 25.4 (*C*H$_2$-thf) ppm. **HRMS** (LIFDI, toluene): expected: m/z 371.0957, 372.0921, 373.0954 $[C_{21}H_{16}BN_2S_2+H]^+$; found: m/z 371.0952, 372.0915, 373.0950 $[C_{21}H_{16}BN_2S_2+H]^+$. Crystalline material of **5Thio[Li](OEt$_2$)$_2$** as colorless blocks for single-crystal XRD was obtained by storing the supernatant reaction solution, combined with the toluene wash solution at −30 °C for 2 d in a glovebox.

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*[1] Superimposed with C_6D_6 solvent signal. Assigned with ^{1}H/^{1}H COSY NMR and ^{1}H/^{13}C HSQC NMR spectra

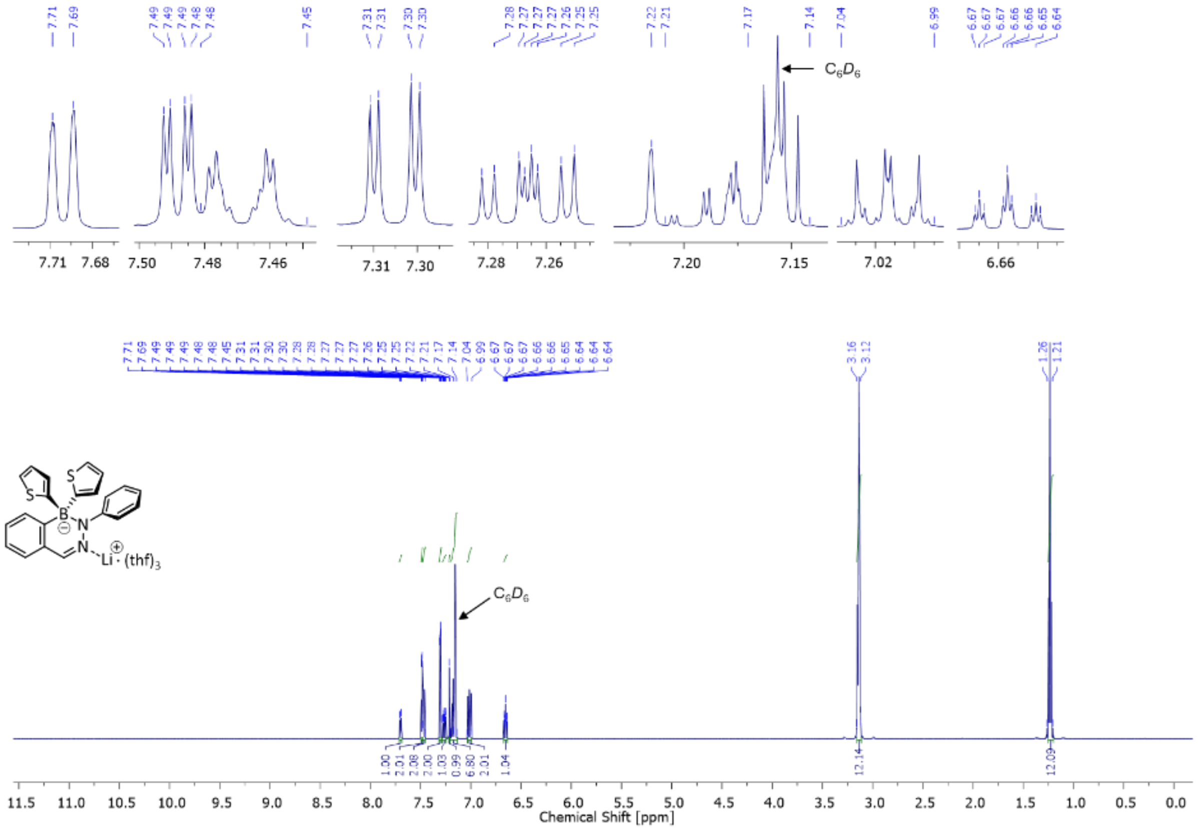


Fig. S48 ^{1}H NMR spectrum of compound **5Thio[Li](thf)$_3$** in C_6D_6.

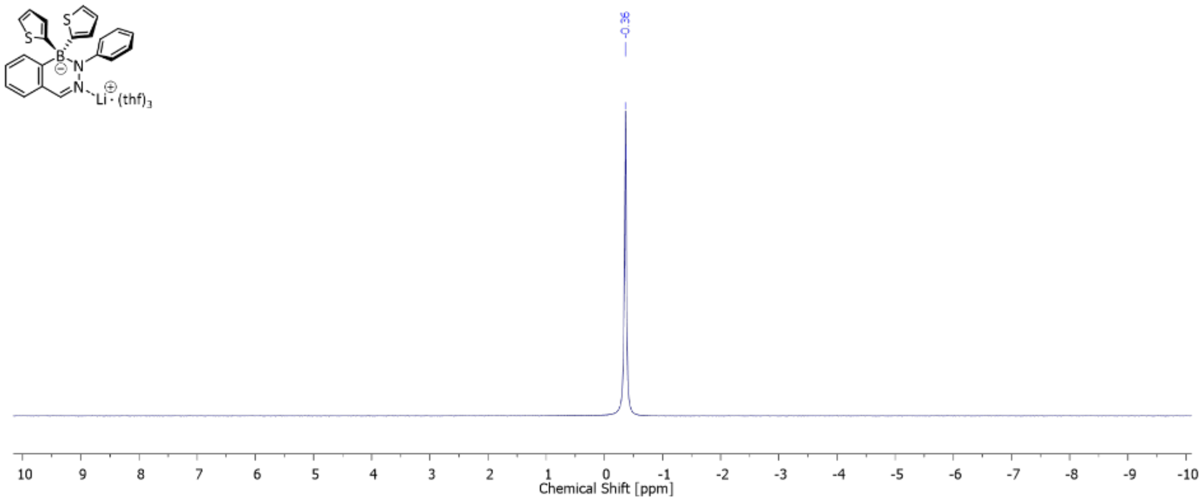


Fig. S49 ^{7}Li NMR spectrum of compound **5Thio[Li](thf)$_3$** in C_6D_6.

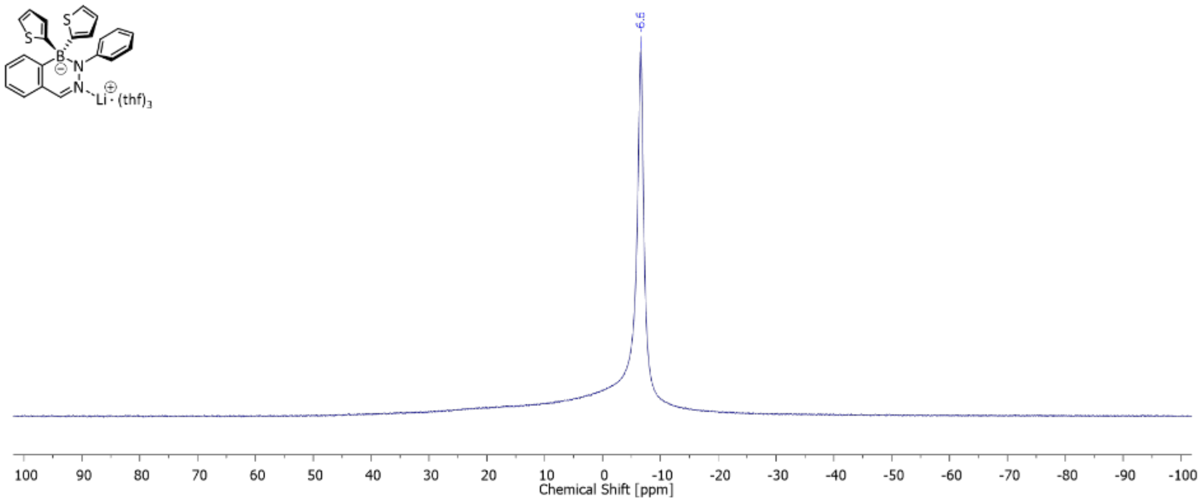


Fig. S50 Background-reduced ^{11}B NMR spectrum of compound **5Thio[Li](thf)$_3$** in C_6D_6.

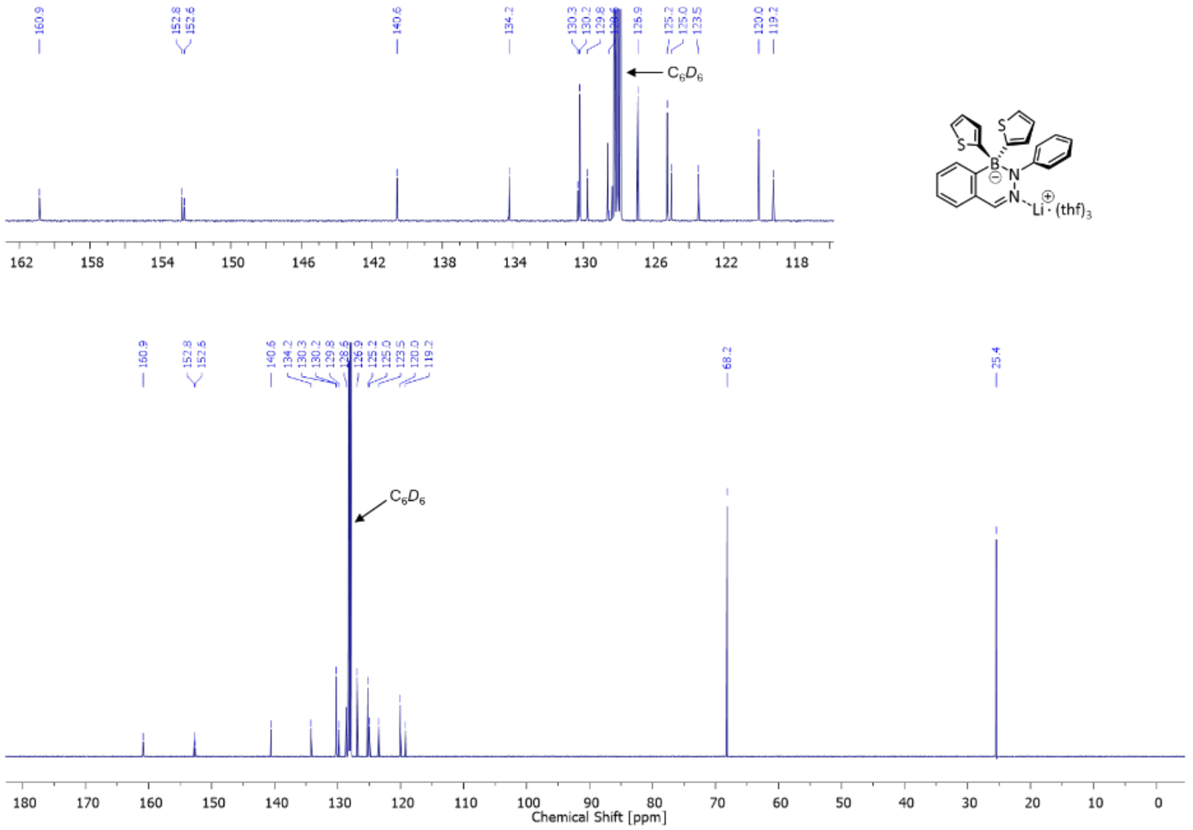


Fig. S51 ^{13}C{^{1}H^{11}B} NMR spectrum of compound **5Thio[Li](thf)$_3$** in C_6D_6 (decoupled at −7 ppm).

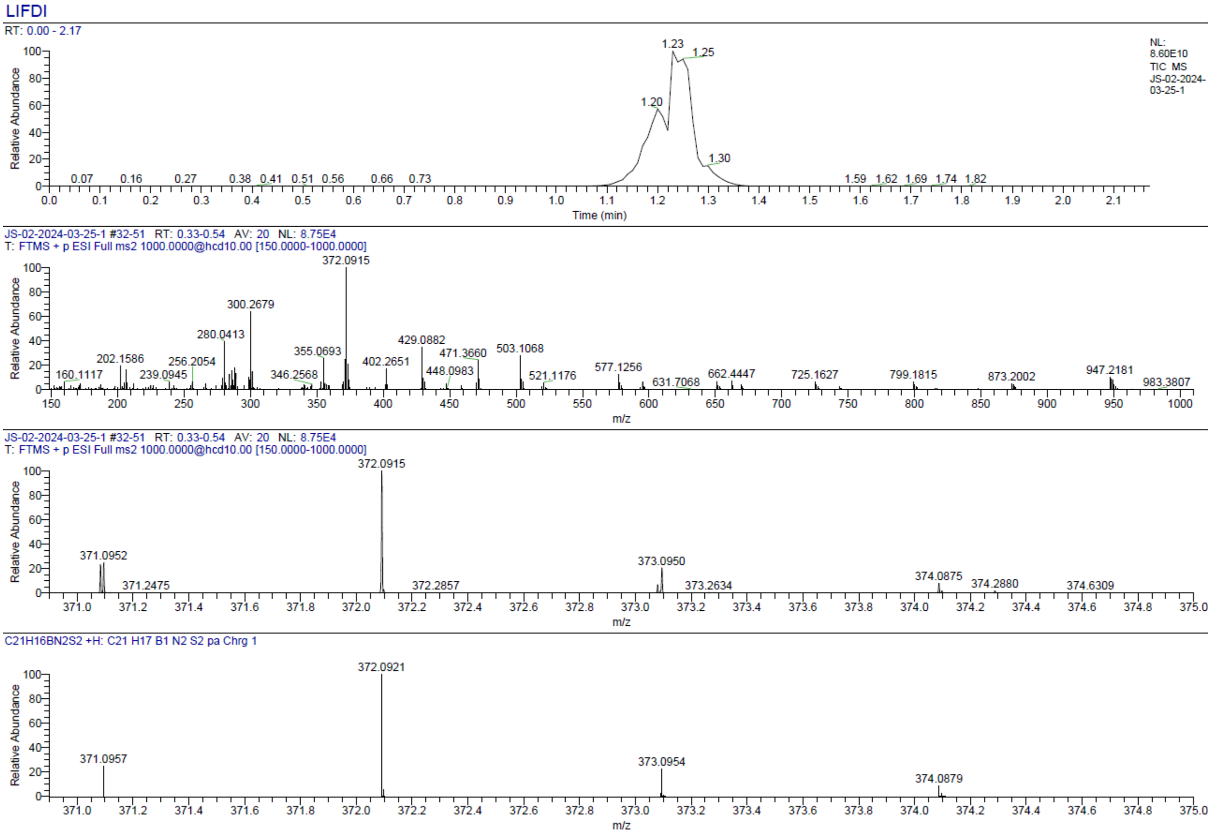


Fig. S52 LIFDI mass spectrum of compound **5Thio[Li]** (toluene).

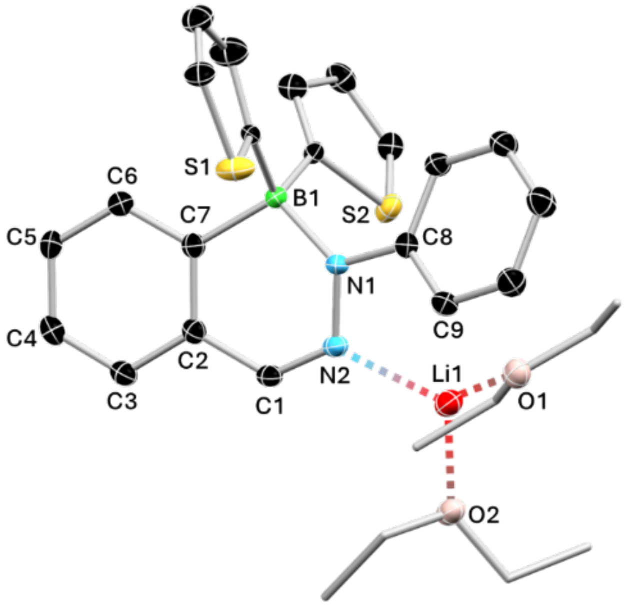


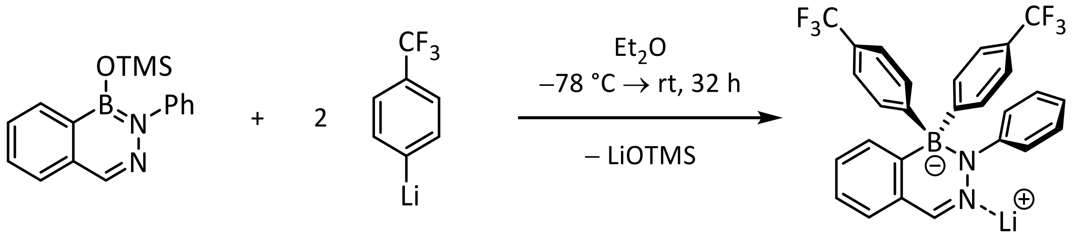
Fig. S53 Molecular structure of compound **5Thio[Li](OEt$_2$)$_2$**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Complexing ether rendered as wireframe for clarity. Selected bond lengths (Å) and angles (°) of **5Thio[Li](OEt$_2$)$_2$**: N2–Li1 2.072(3), B1–N1 1.581(2), N1–N2 1.3759(18), N2–C1 1.293(2), C1–C2 1.453(2), C2–C3 1.407(2), C3–C4 1.385(2), C4–C5 1.395(2), C5–C6 1.388(2), C6–C7 1.399(2), C2–C7 1.402(2), C7–B1 1.624(2), N1–C8 1.404(2), B1–N1–N2–C1 18.7(2), B1–C7–C2–C1 1.7(2), N2–N1–C8–C9 28.8(2).

Crystal data: $C_{29}H_{36}BLiN_2O_2S_2$, M_r = 526.47, colorless block, 0.210×0.130×0.070 mm^3, orthorhombic space group *Pna*2$_1$, a = 16.02590(10) Å, b = 17.59330(10) Å, c = 10.05670(10) Å, V = 2835.47(4) Å^3, Z = 4, ρ_{calcd} = 1.233 g·cm^{-3}, μ = 1.915 mm^{-1}, F(000) = 1120, T = 100(2) K, R_1 = 0.0222, wR_2 = 0.0588, Flack parameter = 0.002(3), 5666 independent reflections [$2\theta \leq 149.79°$] and 430 parameters.

Both thiophene molecules are disordered. The atomic displacement parameters of all thiophene atoms S1_3 to C4_41 were restraint with RIGU keyword in ShelXL input with esd = 0.008 ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of all thiophene atoms S1_3 to C4_41 were restrained to the same value with similarity restraint SIMU (esd = 0.008). The U_{ii} displacement parameters of all thiophene atoms S1_3 to C4_41 were restrained with ISOR keyword with esd = 0.008 to approximate isotropic behavior. The distances between atoms B1_1 and C1_3 and B1_1 and C1_31 were restrained during refinement to the same value using SADI. The distances between atoms B1_1 and C1_4 and B1_1 and C1_41 were restrained during refinement to the same value using SADI.

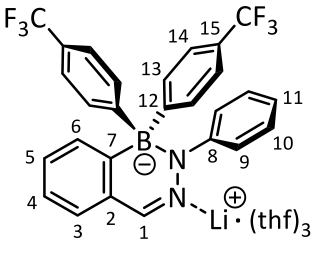
CCDC number: 2453538

Lithium 3-phenyl-4-bis(4-(trifluoromethyl)phenyl)-4,3-borazaroisoquinolinate (**5CF$_3$[Li]**)



1OTMS **5CF$_3$[Li]** (68%)

4-Bromobenzotrifluoride (238 µL, 1.70 mmol, 2.00 eq., ρ = 1.61 g/mL) was dissolved in diethyl ether (10 mL) in a 50 mL Schlenk tube and cooled to −78 °C (*i*PrOH/dry ice). Slowly, *n*-butyllithium (1.6 M solution in *n*-hexane, 1.06 mL, 1.70 mmol, 2.00 eq.) was added under moderate stirring and the colorless reaction mixture was stirred for 2 h at −78 °C. A gradual color change to light brown was observed over the course of the lithiation. Compound **1OTMS** (250 mg, 850 µmol, 1.00 eq.) was dissolved in diethyl ether (4 mL) in a 100 mL Schlenk flask and cooled to −78 °C (*i*PrOH/dry ice). Then, the freshly prepared 4-(trifluoromethyl)phenyl lithium solution was added dropwise to compound **1OTMS**. Upon addition, a color change from colorless to orange and no initial solid formation was observed. The reaction was stirred for 5 min at −78 °C. After 5 min, the cooling bath was removed, half of the solvent was evaporated under reduced pressure until the sudden formation of a pale orange solid was observed. The suspension was stirred for 32 h at ambient temperature. After 32 h, the suspension was filtrated via a filter pipet in a glovebox and the filter cake was washed with cold diethyl ether (1 × 1 mL), cold toluene (2 × 2 mL), *n*-pentane (1 × 1 mL) and briefly dried *in vacuo*. **Yield of 5CF$_3$[Li](OEt$_2$)$_2$:** 376 mg (578 µmol, 68%), pale gray-green powder. To obtain the adduct **5CF$_3$[Li](thf)$_3$**, some of the solid was re-dissolved in tetrahydrofuran (1 mL) and the solvent was removed under reduced pressure.



5CF$_3$[Li](thf)$_3$

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 7.84 (d, $^3J_{HH}$ = 7.80 Hz, 4H, *H*-13), 7.51-7.55 (m, 4H, *H*-14), 7.28-7.31 (m, 1H, *H*-3), 7.26 (td, $^3J_{HH}$ = 7.11 Hz, $^4J_{HH}$ = 1.31 Hz, 1H, *H*-4), 7.17 (td, $^3J_{HH}$ = 7.29 Hz, $^4J_{HH}$ = 1.47 Hz, 5H, *H*-5)^{*1}, 7.09-7.12 (m, 2H, *H*-1 + *H*-6), 7.04-7.08 (m, 2H, *H*-9), 6.85-6.89 (m, 2H, *H*-10), 6.55 (tt, $^3J_{HH}$ = 7.23 Hz, $^4J_{HH}$ = 1.11 Hz, 1H, *H*-11), 3.03-3.08 (m, 11H, 2.75 × C*H*$_2$-thf)^{*2}, 1.16-1.23 (m, 11H, 2.75 × C*H*$_2$-thf)^{*2} ppm. **^{7}Li NMR** (194 MHz, 298 K, C_6D_6) δ = −0.26 (s) ppm. **^{11}B NMR** (160 MHz, 298 K, C_6D_6) δ = −3.6 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6) δ = 162.5 (C_q^B-12), 152.6 (C_q^N-8), 152.4 (C_q^B-7), 141.2 (*C*-1), 135.2 (*C*-13), 133.8 (*C*-3), 130.8 (*C*-2), 130.1 (*C*-4), 128.8 (*C*-10), 126.4 (q, $^1J_{CF}$ = 271.3 Hz, *C*F$_3$), 126.3 (q, $^2J_{CF}$ = 31.1 Hz, C_q-15), 125.0 (*C*-5), 123.6 (*C*-6), 123.4 (q, $^3J_{CF}$ = 4.13 Hz, *C*-14), 119.7 (*C*-9), 119.4 (*C*-11), 68.2 (*C*H$_2$-thf), 25.3 (*C*H$_2$-thf) ppm. **^{19}F{^{1}H^{11}B} NMR** (471 MHz, 298 K, C_6D_6) δ = −61.2 (s) ppm.

HRMS (LIFDI, toluene): expected: m/z 494.1498, 495.1462, 496.1495 $[C_{27}H_{18}BF_6N_2]^+$; found: m/z 494.1492, 495.1455, 496.1498 $[C_{27}H_{18}BF_6N_2]^+$. Crystalline material of **5CF$_3$[Li](OEt$_2$)$_2$** as yellow blocks for single-crystal XRD was obtained by storing the combined washing solutions at −30 °C in a glovebox.

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*[1] Superimposed with C_6D_6 solvent signal. Assigned with $^1H/^1H$ COSY NMR and $^1H/^{13}C$ HSQC NMR spectra.

*[2] The thf equivalents are rounded to three in the compounds name and formula.

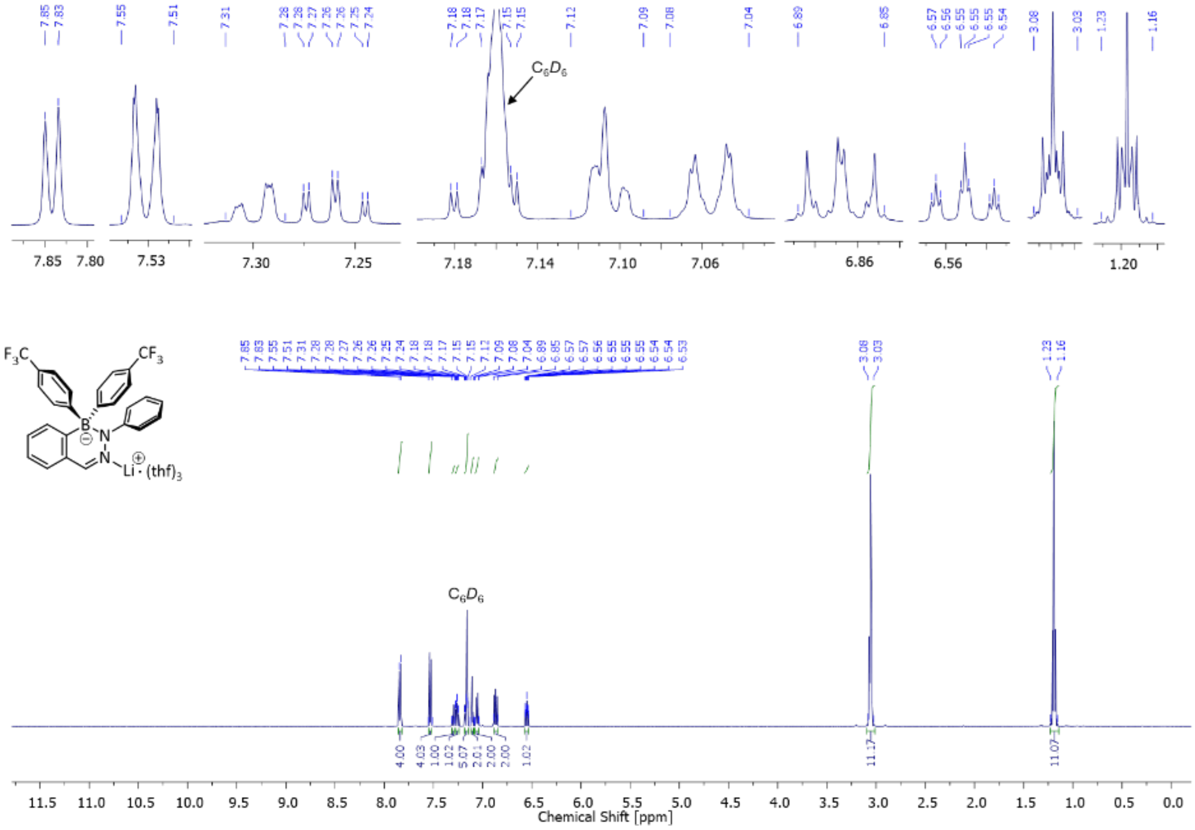


Fig. S54 ^1H NMR spectrum of compound **5CF$_3$[Li](thf)$_3$** in C_6D_6.

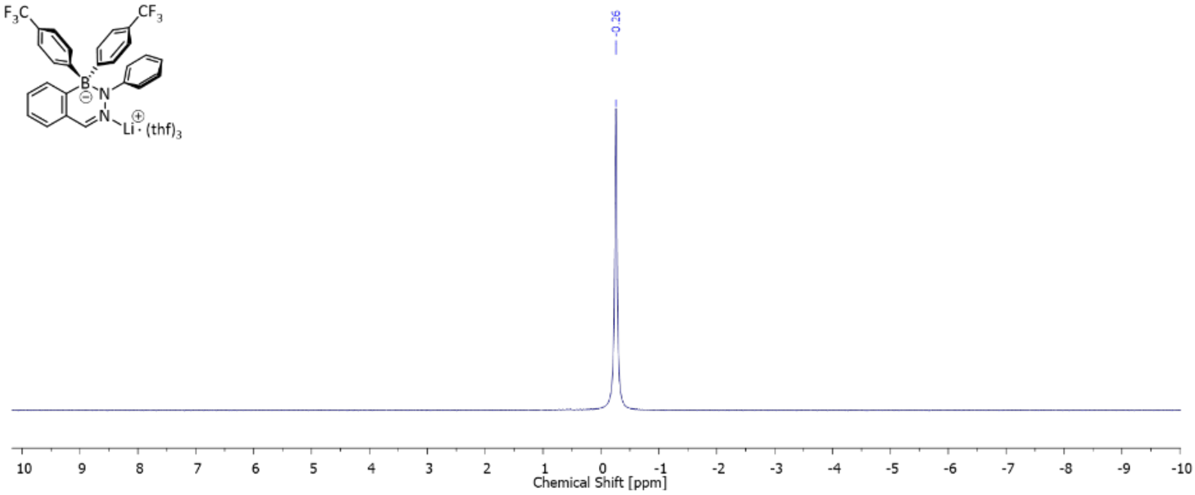


Fig. S55 ^7Li NMR spectrum of compound **5CF$_3$[Li](thf)$_3$** in C_6D_6.

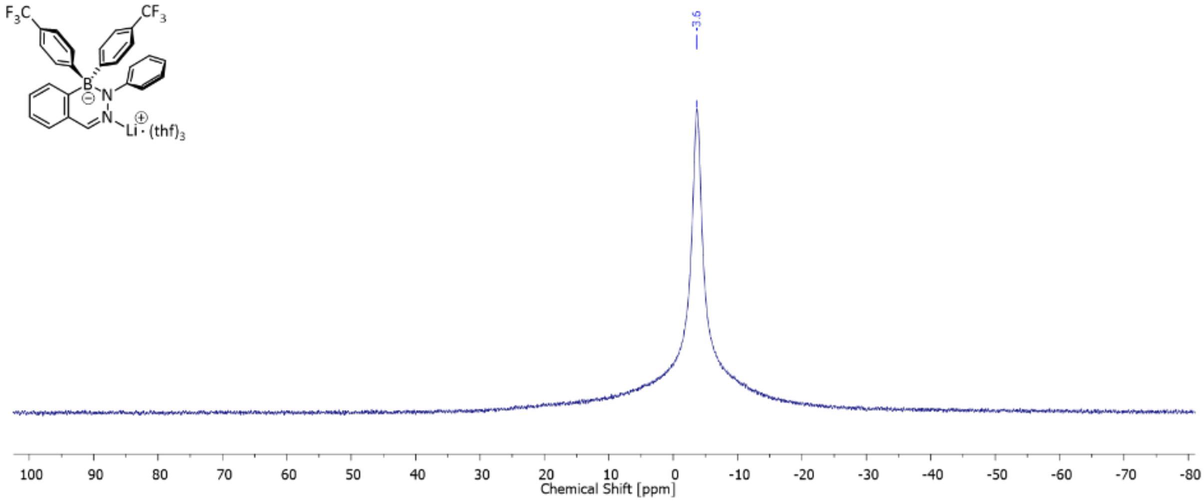


Fig. S56 Background-reduced ^{11}B NMR spectrum of compound **5CF$_3$[Li](thf)$_3$** in C$_6$*D*$_6$.

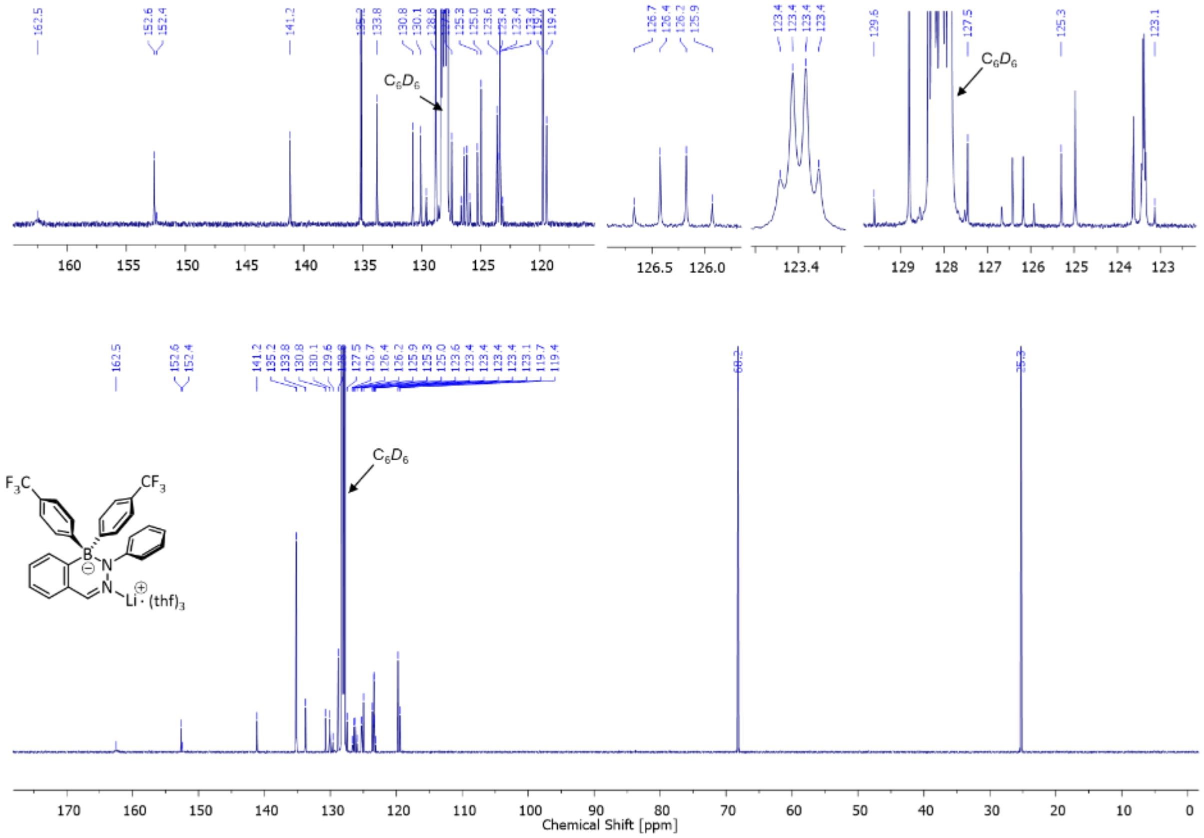


Fig. S57 ^{13}C{^{1}H^{11}B} NMR spectrum of compound **5CF$_3$[Li](thf)$_3$** in C$_6$*D*$_6$ (decoupled at −3 ppm).

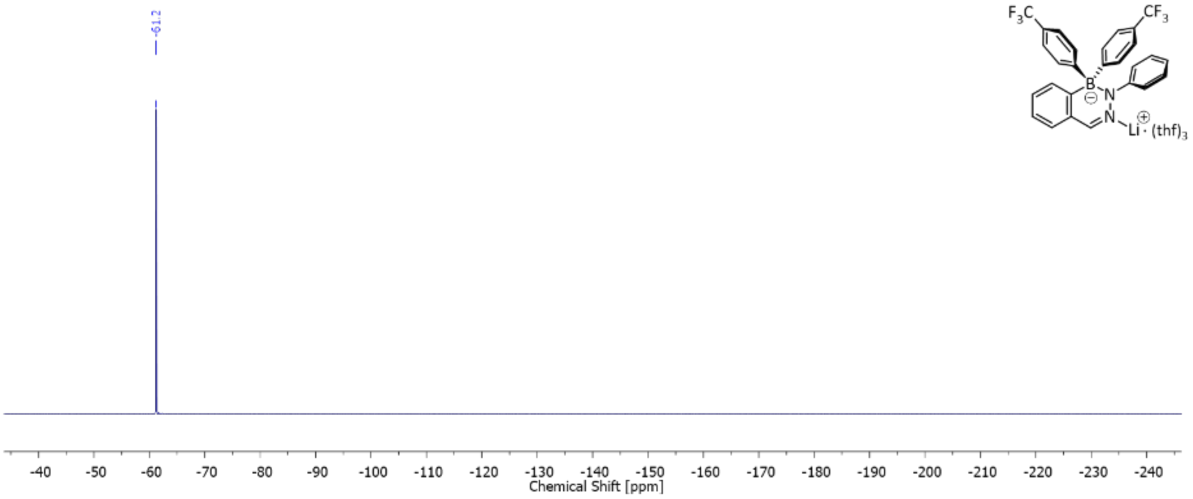


Fig. S58 ^{19}F{^{1}H^{11}B} NMR spectrum of compound **5CF$_3$[Li](thf)$_3$** in C$_6$*D*$_6$.

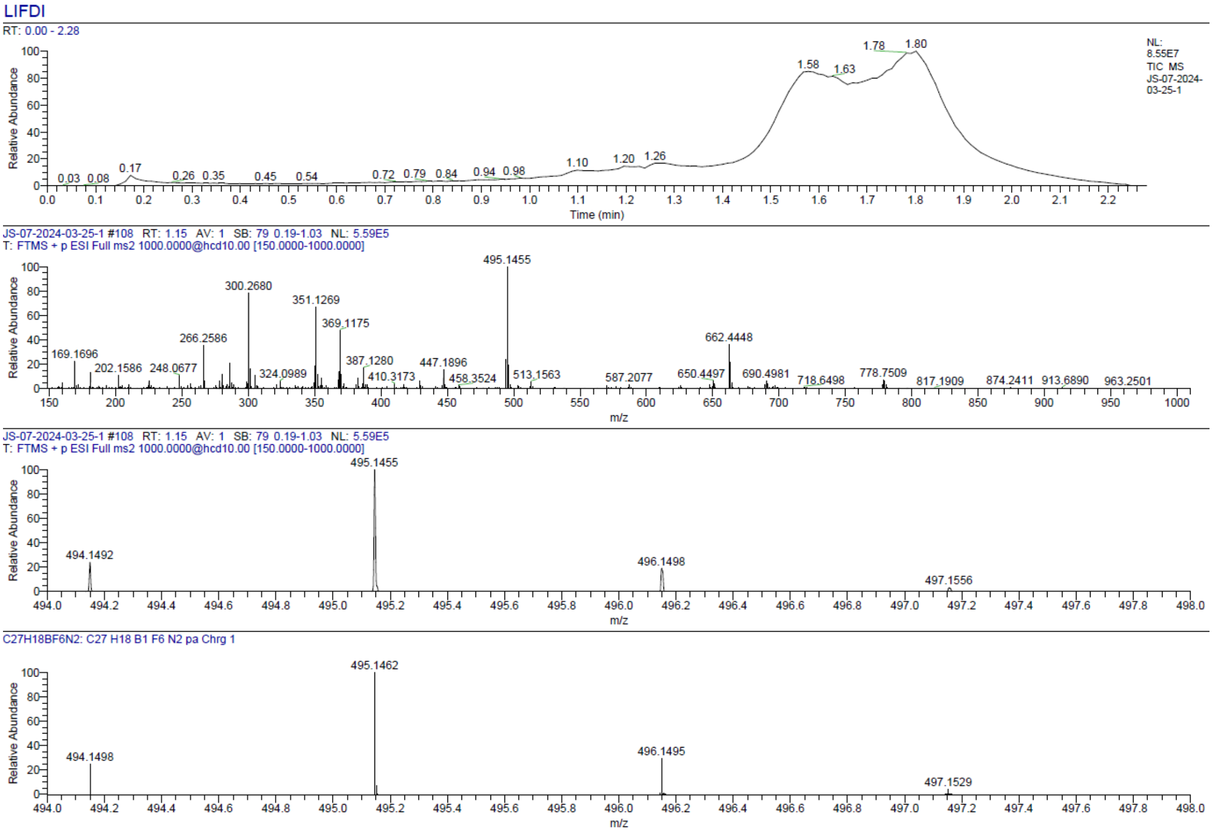


Fig. S59 LIFDI mass spectrum of compound **5CF$_3$[Li]** (toluene).

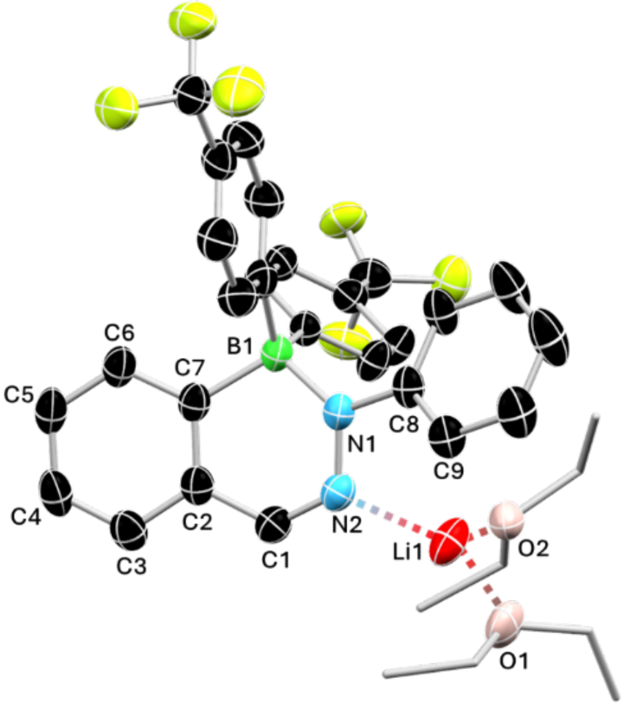


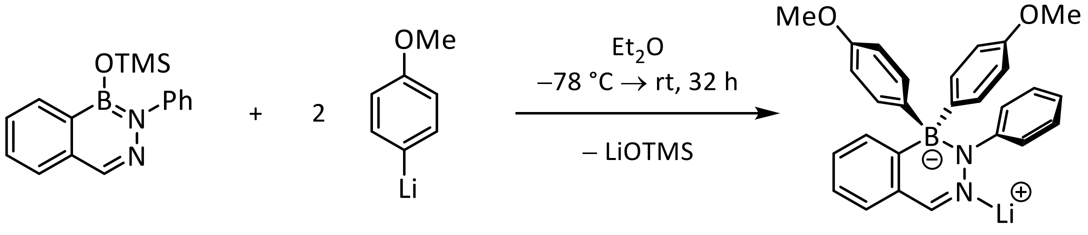
Fig. S60 Molecular structure of compound **5CF$_3$[Li](OEt$_2$)$_2$**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Complexing ether rendered as wireframe for clarity. Selected bond lengths (Å) and angles (°) of **5CF$_3$[Li](OEt$_2$)$_2$**: N2–Li1 2.047(3), B1–N1 1.5716(17), N1–N2 1.3767(15), N2–C1 1.2933(18), C1–C2 1.4532(18), C2–C3 1.3989(19), C3–C4 1.386(2), C4–C5 1.384(2), C5–C6 1.387(2), C6–C7 1.3998(18), C2–C7 1.4027(19), C7–B1 1.6205(19), N1–C8 1.4049(16), B1–N1–N2–C1 19.64(17), B1–C7–C2–C1 7.93(18), N2–N1–C8–C9 33.39(16).

Crystal data: $C_{35}H_{38}BF_6LiN_2O_2$, $M_r = 650.42$, yellow block, 0.370×0.150×0.080 mm^3, monoclinic space group $P2_1/n$, $a = 13.06060(10)$ Å, $b = 14.89200(10)$ Å, $c = 17.83520(10)$ Å, $\beta = 99.73°$, $V = 3419.02(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.264$ g·cm^{-3}, $\mu = 0.838$ mm^{-1}, $F(000) = 1360$, $T = 100(2)$ K, $R_1 = 0.0447$, $wR_2 = 0.1163$, 6871 independent reflections [$2\theta \leq 150.288°$] and 590 parameters.

Both diethyl ether molecules are disordered. The atomic displacement parameters of all Et2O atoms O1_7 to C4_81 were restraint with RIGU (esd = 0.008) keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of all Et$_2$O atoms O1_7 to C4_81 were restrained to the same value with similarity restraint SIMU (esd = 0.008). The U_{ii} displacement parameters of all Et$_2$O atoms O1_7 to C4_81 were restrained with ISOR keyword (esd = 0.008) to approximate isotropic behavior. The distances between atoms Li1_6 and O1_7 and Li1_6 and O1_71 were restrained during refinement to the same value using SADI (esd = 0.002).The distances between atoms Li1_6 and O1_8 and Li1_6 and O1_81 were restrained during refinement to the same value using SADI (esd = 0.002). Both CF$_3$ groups are disordered. The atomic displacement parameters of all CF3 groups atoms C1_4 to F3_51 were restraint with RIGU (esd = 0.008) keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of all CF$_3$ groups atoms C1_4 to F3_51 were restrained to the same value with similarity restraint SIMU (esd = 0.008). The U_{ii} displacement parameters of all CF$_3$ groups atoms C1_4 to F3_51 were restrained with ISOR keyword (esd = 0.008) to approximate isotropic behavior. The distances between atoms C4_2 and C1_4 and C4_2 and C1_41 were restrained during refinement to the same value using SADI (esd = 0.002).The distances between atoms C4_3 and C1_5 and C4_3 and C1_51 were restrained during refinement to the same value using SADI (esd = 0.002).

CCDC number: 2453544

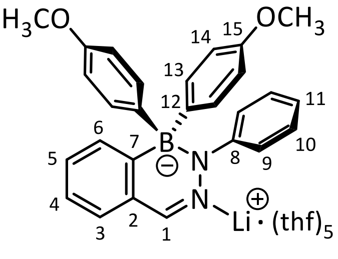
Lithium 3-phenyl-4-bis(4-(methoxy)phenyl)-4,3-borazaroisoquinolinate (5OMe[Li])



1OTMS

5OMe[Li] (37%)

4-Bromoanisole (213 *µ*L, 1.70 mmol, 2.00 eq., *ρ* = 1.49 g/mL) was dissolved in diethyl ether (7 mL) in a 50 mL Schlenk tube and cooled to −78 °C (*i*PrOH/dry ice). Slowly, *n*-butyllithium (1.6 M solution in *n*-hexane, 1.06 mL, 1.70 mmol, 2.00 eq.) was added under moderate stirring. The colorless reaction mixture was stirred for 1 h at −78 °C and then 30 min at ambient temperature. A slightly cloudy, colorless suspension was obtained over the course of the lithiation. Compound **1OTMS** (250 mg, 850 *µ*mol, 1.00 eq.) was dissolved in diethyl ether (4 mL) in a 50 mL Schlenk flask and cooled to −78 °C (*i*PrOH/dry ice). Then, the freshly prepared 4-(methoxy)phenyl lithium solution was added dropwise to compound **1OTMS**. Upon addition, a color change from colorless to deep yellow and the formation of a solid was observed. The reaction was stirred for 5 min at −78 °C. After 5 min, the cooling bath was removed. Upon warm up to ambient temperature, the solid completely dissolved again and the precipitation of an orange oil was observed. After 32 h, the orange oil was separated from the solution via cannulation. In a glovebox, the oil was redissolved in tetrahydrofurane (3 mL). After pipet filtration, the solution was layered with toluene (2 mL) and the layered solution was stored at −30 °C until crystallization of **5OMe[Li]**. This procedure was repeated two times to obtain **5OMe[Li](thf)$_4$** in sufficient purity. The supernatant was removed, and the crystals were briefly dried *in vacuo*. **Yield of 5OMe[Li](thf)$_4$:** 226 mg (316 *µ*mol, 37%) pale yellow, crystalline solid.



5OMe[Li](thf)$_5$

^{1}H NMR (600 MHz, 298 K, C$_6$*D*$_6$): *δ* = 7.85-7.89 (m, 4H, *H*-13), 7.58 (d, $^{3}J_{HH}$ = 7.30 Hz, 1H, *H*-3), 7.34-7.37 (m, 2H, *H*-9), 7.30 (td, $^{3}J_{HH}$ = 7.25 Hz, $^{4}J_{HH}$ = 1.28 Hz, 1H, *H*-4), 7.14-7.17 (m, 5H, *H*-5)^{*1}, 7.09-7.12 (m, 2H, *H*-1 + *H*-6), 6.96-6.99 (m, 2H, *H*-10), 6.86-6.89 (m, 4H, *H*-14), 6.62 (tt, $^{3}J_{HH}$ = 7.21 Hz, $^{4}J_{HH}$ = 1.07 Hz, 1H, *H*-11), 3.38 (s, 6H, OC*H*$_3$), 3.33-3.36 (m, 20H, 5 × C*H*$_2$-thf), 1.30-1.34 (m, 20H, 5 × C*H*$_2$-thf) ppm. **^{7}Li NMR** (233 MHz, 298 K, C$_6$*D*$_6$) *δ* = −0.18 (s) ppm. **^{11}B NMR** (193 MHz, 298 K, C$_6$*D*$_6$) *δ* = −3.2 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C$_6$*D*$_6$) *δ* = 156.8 (C_q-15), 155.0 (C_q^{B}-7), 153.5 (C_q^{N}-8), 150.3 (C_q^{B}-12), 140.8 (*C*-1), 136.2 (*C*-14), 134.0 (*C*-3), 131.4 (C_q-2), 129.2 (*C*-4), 128.5 (*C*-10), 124.2 (*C*-5), 123.3 (*C*-6), 120.3 (*C*-9), 118.6 (*C*-11), 113.4 (*C*-13), 68.0 (*C*H$_2$-thf), 55.9 (−O*C*H$_3$), 25.6 (*C*H$_2$-thf) ppm. **HRMS** (LIFDI, toluene): expected: m/z 418.1962, 419.1925, 420.1959

$[C_{27}H_{24}BN_2O_2]^+$; found: m/z 418.1956, 419.1920, 420.2002 $[C_{27}H_{24}BN_2O_2+H]^+$. Crystalline material of **5OMe[Li](thf)₄** as neon yellow blocks for single-crystal XRD was obtained by storing a saturated tetrahydrofurane solution layered with toluene at −30 °C for several days in a glovebox.

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*[1] Superimposed with C_6D_6 solvent signal. Assigned with ^{1}H/^{1}H COSY NMR and ^{1}H/^{13}C HSQC NMR spectra.

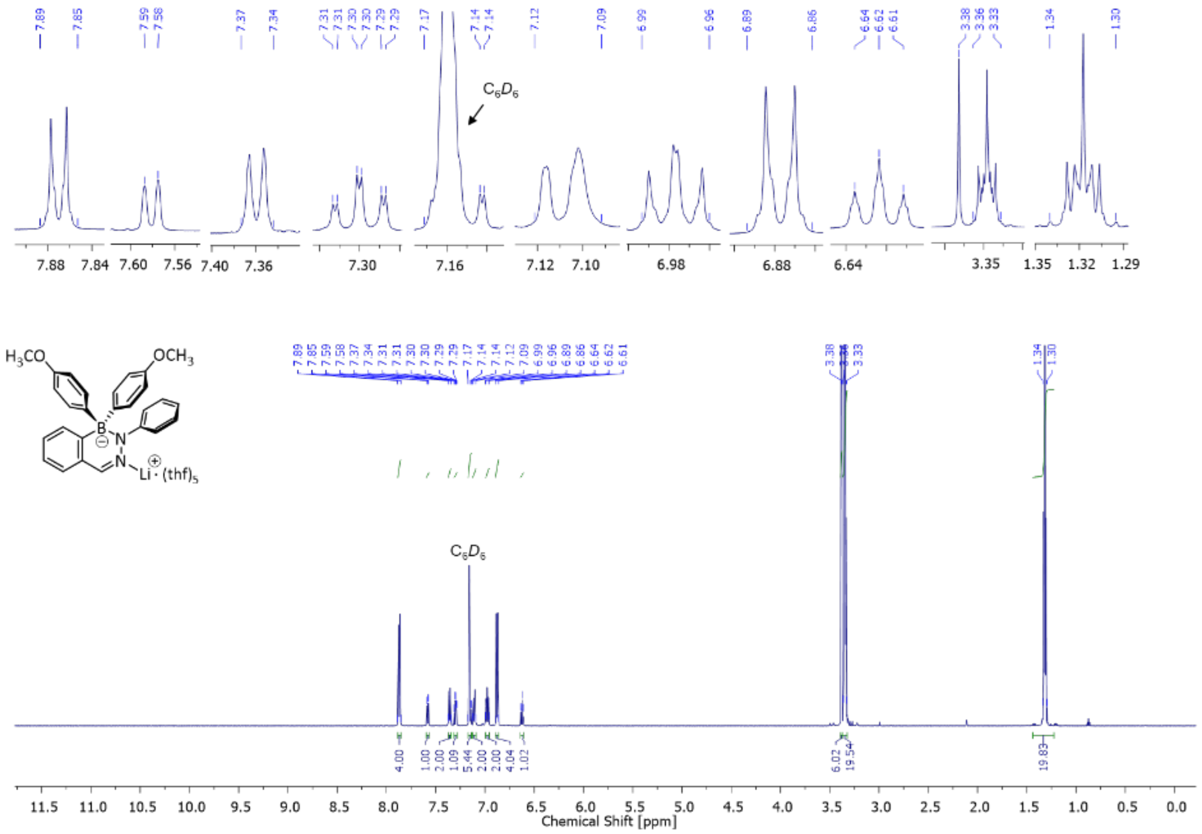


Fig. S61 ^{1}H NMR spectrum of compound **5OMe[Li](thf)₅** in C_6D_6.

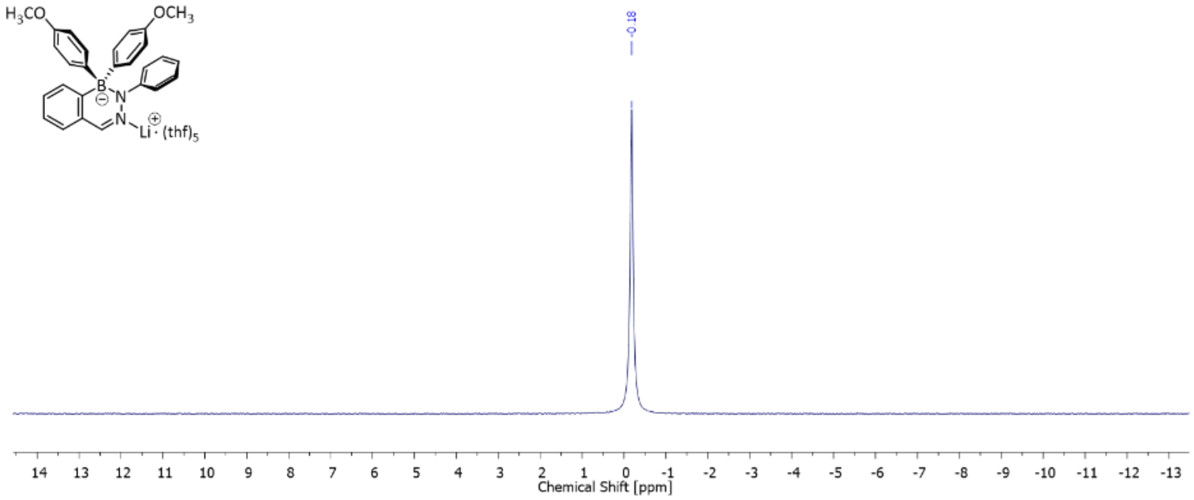


Fig. S62 ^{7}Li NMR spectrum of compound **5OMe[Li](thf)₅** in C_6D_6.

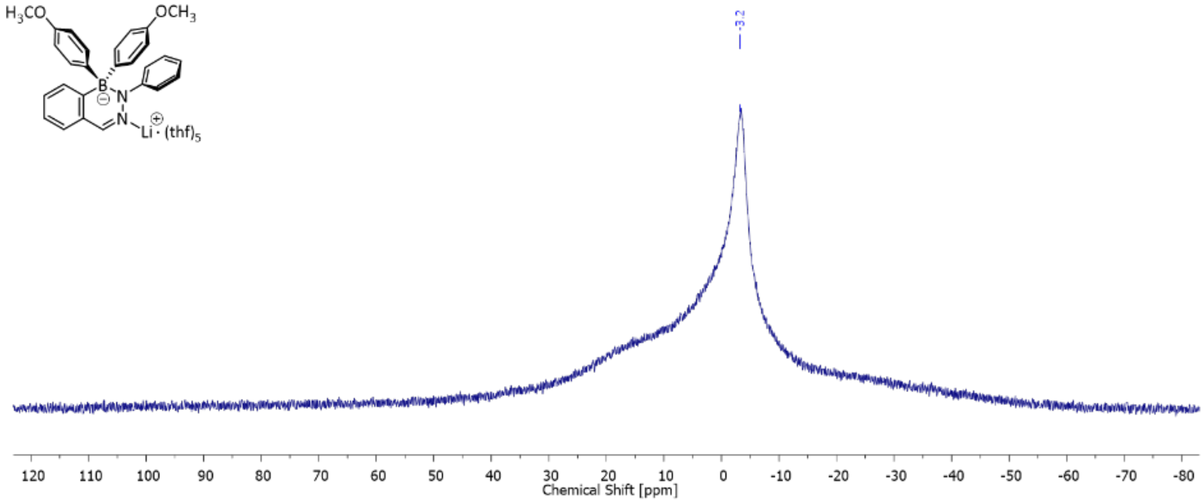


Fig. S63 Background-reduced ^{11}B NMR spectrum of compound **5OMe[Li](thf)₅** in C_6D_6.

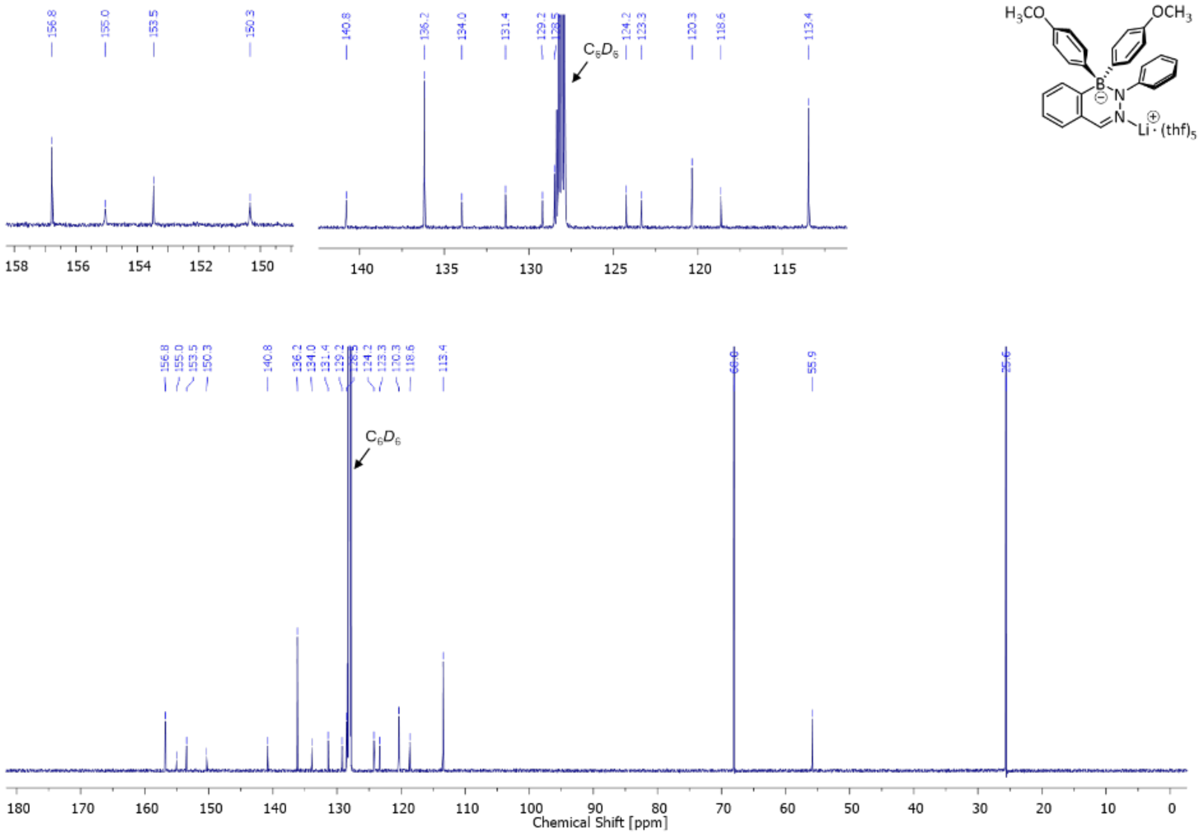


Fig. S64 $^{13}C\{^1H^{11}B\}$ NMR spectrum of compound **5OMe[Li](thf)₅** in C_6D_6 (selectively decoupled at −3 ppm).

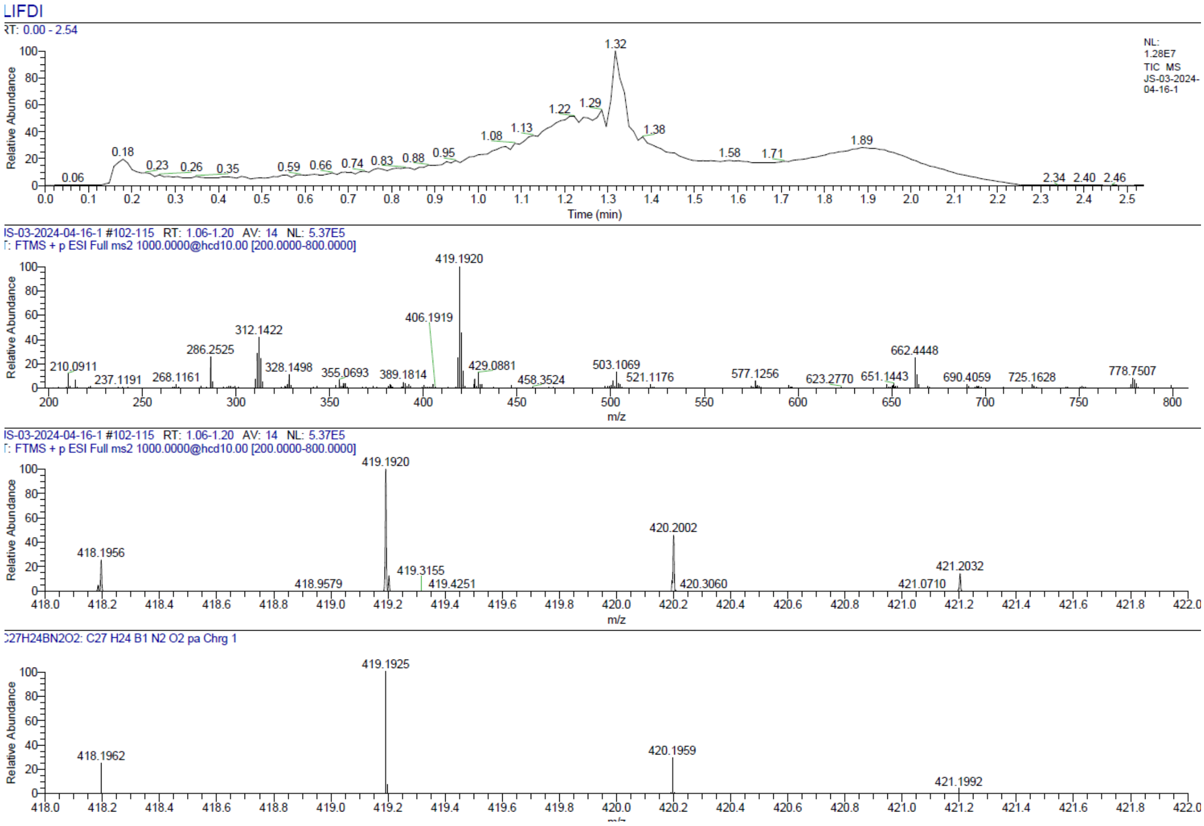


Fig. S65 LIFDI mass spectrum of compound **5OMe[Li]** (toluene).

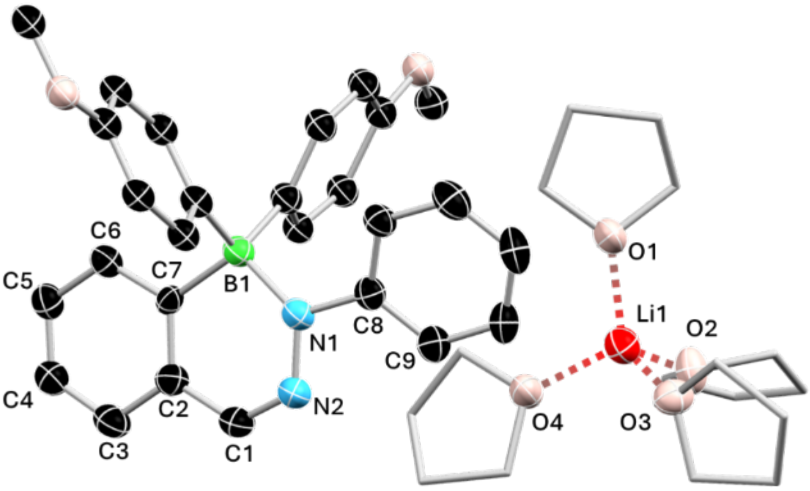


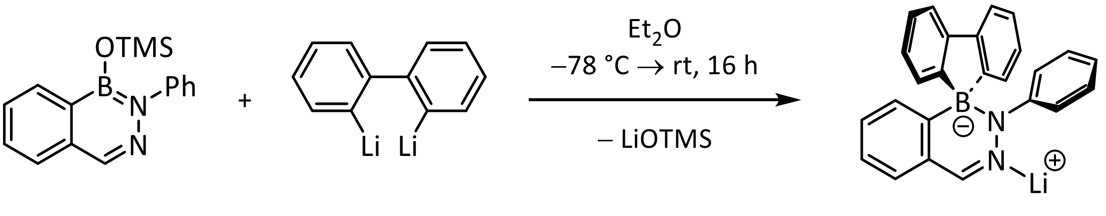
Fig. S66 Molecular structure of compound **5OMe[Li](thf)$_4$**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Complexing THF and methoxy substituents rendered as wireframe for clarity. Due to the presence of a whole molecule disorder of the borate anion, no discussion of bond lengths is possible.

Crystal data: $C_{43}H_{56}BLiN_2O_6$, M_r = 714.64, fluorescent yellow block, 0.730×0.440×0.250 mm^3, monoclinic space group $P2_1/n$, a = 18.5827(2) Å, b = 10.59080(10) Å, c = 21.2108(2) Å, β = 110.6840(10)°, V = 3905.33(7) Å^3, Z = 4, ρ_{calcd} = 1.215 g·cm^{-3}, μ = 0.627 mm^{-1}, F(000) = 1536, T = 100(2) K, R_1 = 0.0661, wR_2 = 0.1685, 7834 independent reflections [2θ≤150.584°] and 767 parameters.

The diazaborinate unit was disordered by a whole molecule disorder, which is freely refined with a ratio of 0.61423. The atomic displacement parameters of atoms B1_1 to C7_11 were restraint with RIGU (ESD = 0.03) keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of atoms B1_1 to C7_11 of the residue 1 were restrained to the same value with similarity restraint SIMU (ESD = 0.03). The Uii displacement parameters of atoms B1_1 to C7_11 were restrained with ISOR (ESD = 0.008) keyword to approximate isotropic behavior. The atomic displacement parameters of atoms O1_3 to C7_41 were restraint with RIGU (ESD = 0.002) keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of atoms O1_3 to C7_41 of the residues 3 and 4 were restrained to the same value with similarity restraint SIMU (ESD = 0.002). The Uii displacement parameters of atoms O1_3 to C7_41 were restrained with ISOR (ESD = 0.008) keyword to approximate isotropic behavior. The phenyl substituent residue 2 with the atoms C1 > C6 was corrected with FLAT (ESD = 0.008) keyword.

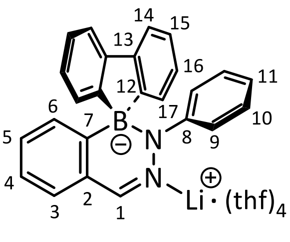
CCDC number: 2453533

Lithium 3-phenyl-4-(2,2'-biphenyl)-4,3-borazaroisoquinolinate (5Biph[Li])



1OTMS **5Biph[Li]** (54%)

2,2'-Dibromobiphenyl (265 mg, 850 μmol, 1.00 eq.) was dissolved in diethyl ether (7 mL) in a 50 mL Schlenk tube and cooled to −78 °C (*i*PrOH/dry ice). Slowly, *n*-butyllithium (1.6 M solution in *n*-hexane, 1.06 mL, 1.70 mmol, 2.00 eq.) was added under moderate stirring and the colorless reaction mixture was stirred for 30 min at −78 °C. The cooling bath was removed, and the reaction mixture was then stirred for 60 min at ambient temperature. Compound **1OTMS** (250 mg, 850 μmol, 1.00 eq.) was dissolved in diethyl ether (10 mL) in a 100 mL Schlenk flask and cooled to −78 °C (*i*PrOH/dry ice). Then, the freshly prepared 2,2'-dilithiobiphenyl solution was added dropwise to compound **1OTMS**. Upon addition, a color change from colorless to yellow and the formation of a neon yellow solid was observed. The reaction was stirred for 5 min at −78 °C. After 5 min, the cooling bath was removed, and the suspension was stirred for 16 h at ambient temperature. Half of the solvent was removed under reduced pressure and the suspension was filtrated via filter cannulation at 0 °C. The remaining solid was washed with cold diethyl ether (1 × 2 mL), cold toluene (1 × 4 mL) and briefly dried *in vacuo*. **Yield of 5Biph[Li](OEt$_2$)$_2$:** 235 mg (459 μmol, 54%), neon yellow powder. To obtain the adduct **5Biph[Li](thf)$_4$**, some of the solid was re-dissolved in tetrahydrofuran (1 mL) and the solvent was removed under reduced pressure.



5Biph[Li](thf)$_4$

^{1}H NMR (600 MHz, 298 K, C_6D_6): δ = 8.08 (d, $^{3}J_{HH}$ = 7.49 Hz, 2H, *H*-14), 7.77 (d, $^{3}J_{HH}$ = 6.63 Hz, 2H, *H*-17), 7.39 (dt, $^{3}J_{HH}$ = 7.32 Hz, $^{4}J_{HH}$ = 1.09 Hz, 2H, *H*-15), 7.19-7.24 (m, 4H, *H*-16 + *H*-1 + *H*-6), 7.06-7.11 (m, 2H, *H*-3 + *H*-5), 6.99 (d, $^{3}J_{HH}$ = 7.82 Hz, 2H, *H*-9), 6.94 (dt, $^{3}J_{HH}$ = 7.32 Hz, $^{4}J_{HH}$ = 0.93 Hz, 1H, *H*-4), 6.80-6.84 (m, 2H, *H*-10), 6.48-6.52 (m, 1H, *H*-11), 3.26-3.30 (m, 16H, 4 × C*H*$_2$-thf), 1.24-1.28 (m, 16H, 4 × C*H*$_2$-thf) ppm. **^{7}Li NMR** (233 MHz, 298 K, C_6D_6) δ = −0.24 (s) ppm. **^{11}B NMR** (193 MHz, 298 K, C_6D_6) δ = −3.6 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6) δ = 165.2 (C_q^{B}-12), 153.3 (C_q^{N}-8), 152.5 (C_q^{B}-7), 148.1 (C_q-13), 139.6 (*C*-1), 132.9 (*C*-3), 131.8 (*C*-17), 131.2 (C_q-2), 129.6 (*C*-4), 129.0 (*C*-10), 126.2 (*C*-16), 125.7 (*C*-15), 124.6 (*C*-5), 124.3 (*C*-6), 119.6 (*C*-14), 119.1 (*C*-11), 118.4 (*C*-9), 68.1 (*C*H$_2$-thf), 25.5 (*C*H$_2$-thf) ppm. **HRMS** (LIFDI, toluene): expected: m/z 357.1672, 358.1636, 359.1669 [$C_{25}H_{18}BN_2$+H]$^+$; found: m/z 357.1553, 358.1630, 359.1663 [$C_{25}H_{18}BN_2$+H]$^+$. Crystalline material of **5Biph[Li](OEt$_2$)$_2$** as neon yellow blocks for single-crystal XRD was obtained by storing the combined wash solutions at −30 °C for several days in a glovebox.

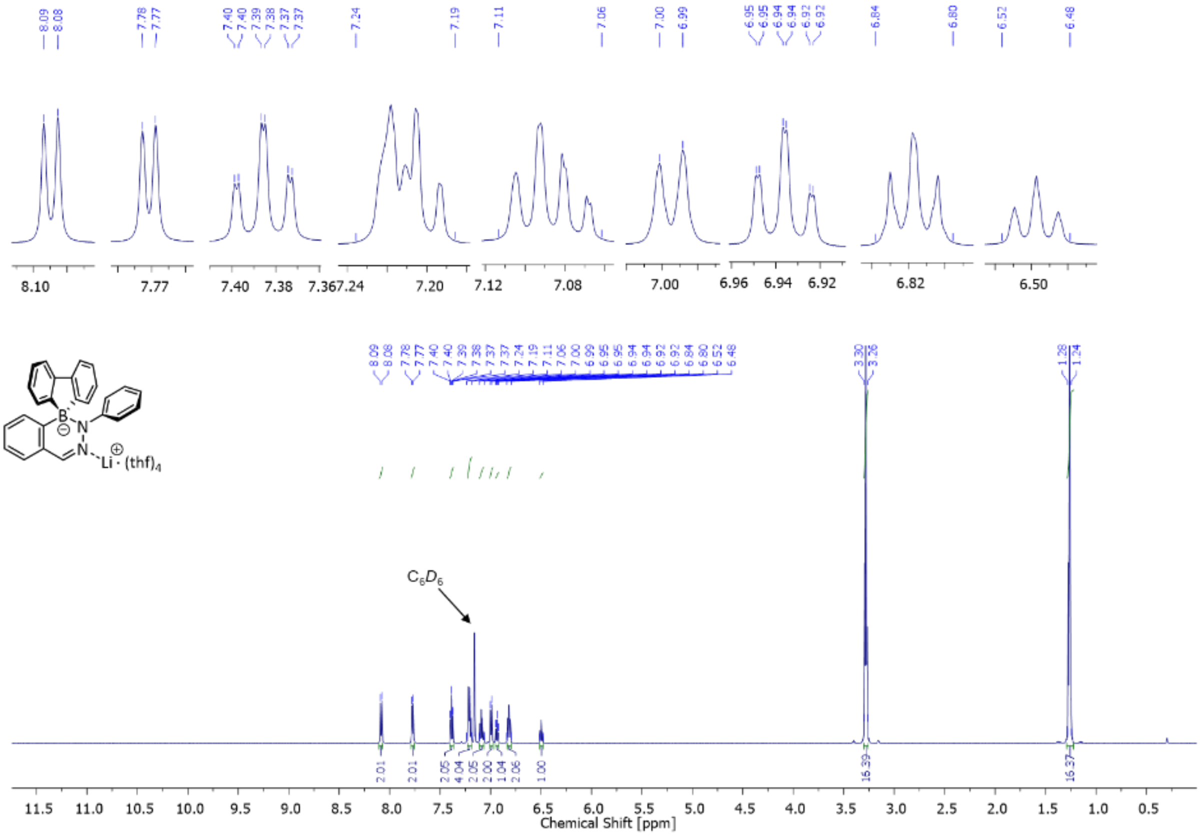


Fig. S67 ^{1}H NMR spectrum of compound **5Biph[Li](thf)₄** in C_6D_6.

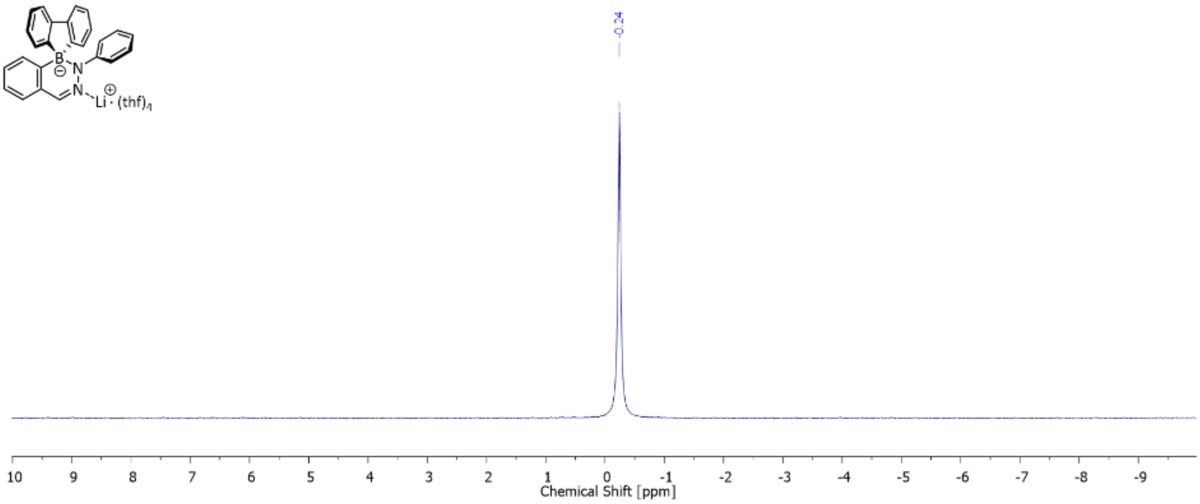


Fig. S68 ^{7}Li NMR spectrum of compound **5Biph[Li](thf)₄** in C_6D_6.

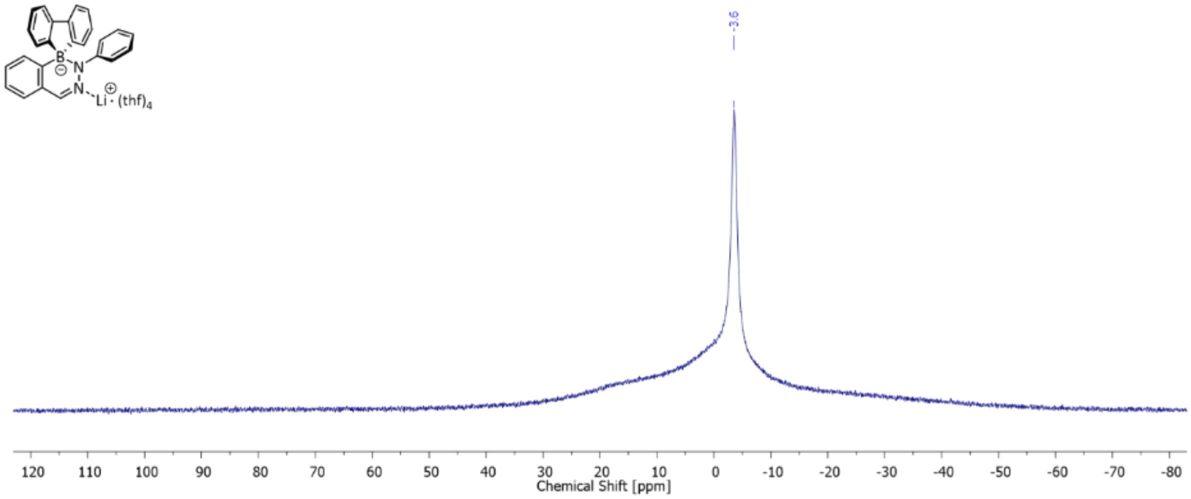


Fig. S69 Background-reduced ^{11}B NMR spectrum of compound **5Biph[Li](thf)$_4$** in C_6D_6.

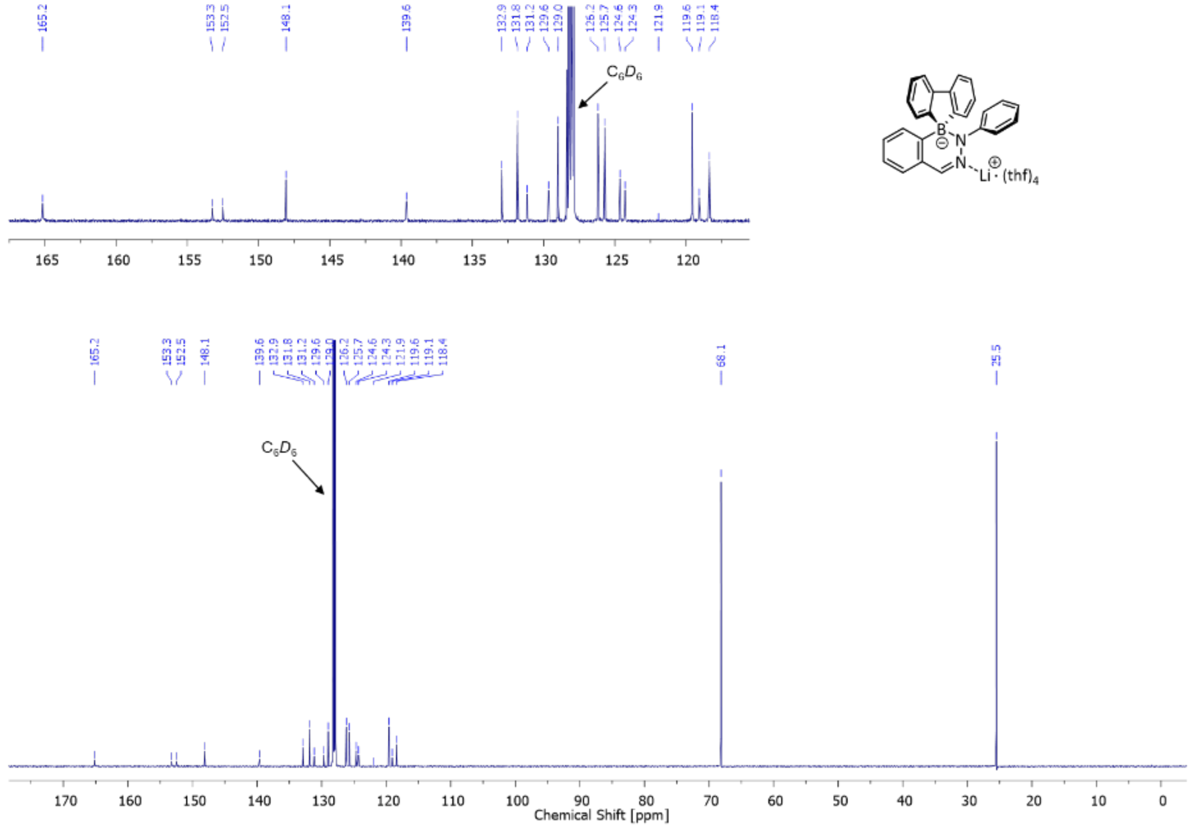


Fig. S70 ^{13}C{^{1}H^{11}B} NMR spectrum of compound **5Biph[Li](thf)$_4$** in C_6D_6 (selectively decoupled at −3 ppm).

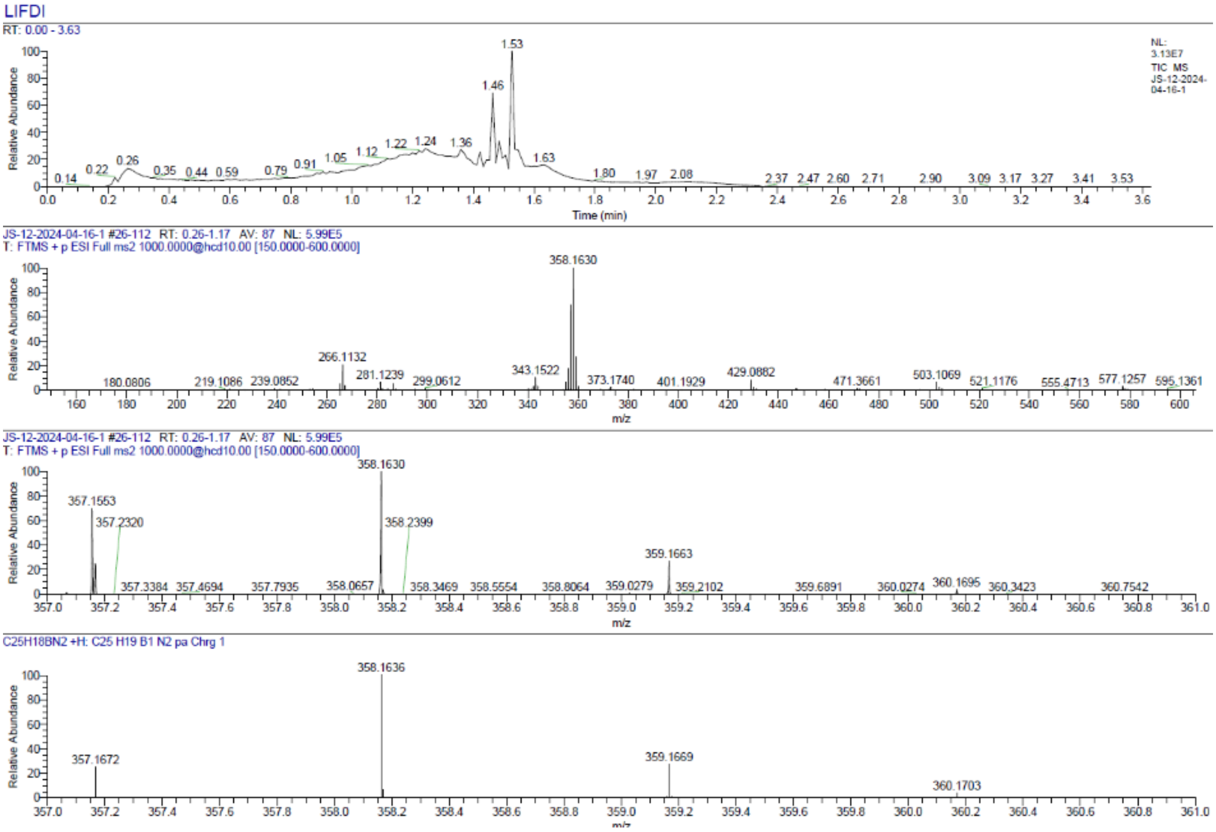


Fig. S71 LIFDI mass spectrum of compound **5Biph[Li]** (toluene).

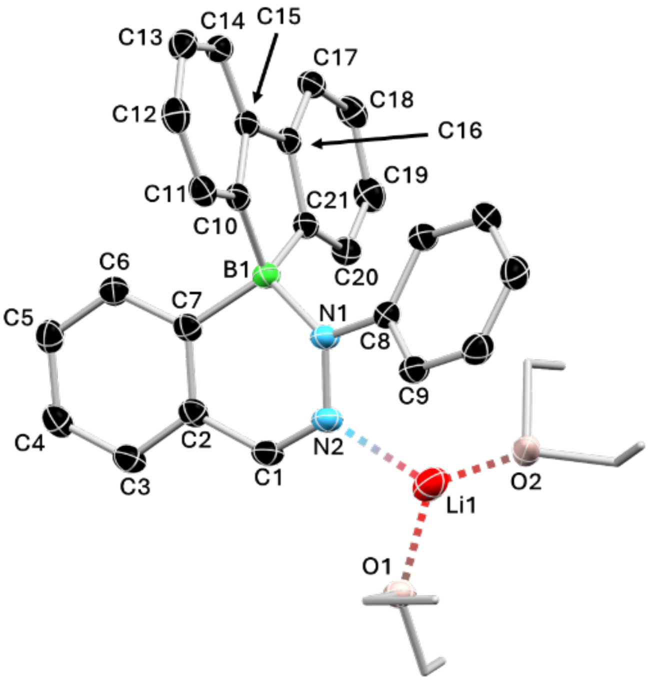


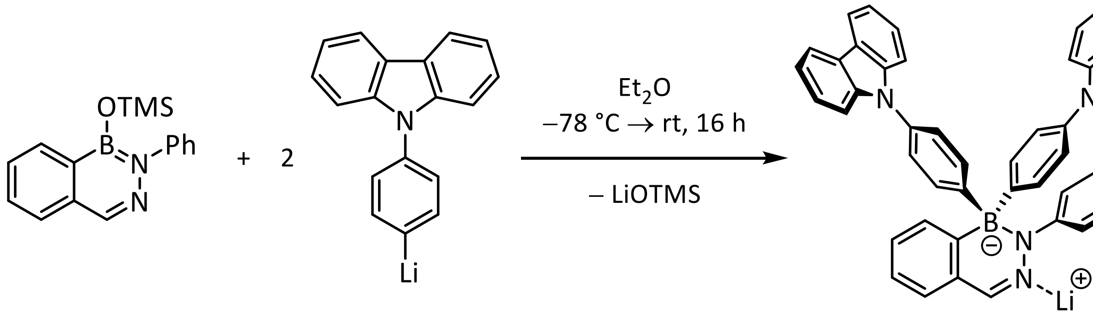
Fig. S72 Molecular structure of compound **5Biph[Li](OEt₂)₂**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Complexing ether rendered as wireframe for clarity. Selected bond lengths (Å) and angles (°) of **5Biph[Li](OEt₂)₂**: N2–Li1 1.996(2), B1–N1 1.5708(13), N1–N2 1.3753(11), N2–C1 1.2963(13), C1–C2 1.4498(14), C2–C3 1.4046(14), C3–C4 1.3839(15), C4–C5 1.3924(16), C5–C6 1.3917(15), C6–C7 1.3996(14), C2–C7 1.4041(14), C7–B1 1.6241(14), N1–C8 1.4023(13), B1–C10 1.6313(14), C10–C11 1.3921(14), C11–C12 1.3948(15), C12–C13 1.3903(16), C13–C14 1.3929(15), C14–C15 1.3927(14), C15–C10 1.4146(14), C15–C16 1.4770(13), C16–C17 1.3923(14), C17–C18 1.3894(15), C18–C19 1.3900(16), C19–C20 1.3962(15), C20–C21 1.3927(14), C16–C21 1.4107(13), C21–B1 1.6399(14), B1–N1–N2–C1 15.80(14), B1–C7–C2–C1 6.16(14), N2–N1–C8–C9 32.11(13), C10–C15–C16–C21 1.57(11).

Crystal data: $C_{33}H_{38}BLiN_2O_2$, $M_r = 512.40$, yellow block, 0.390×0.150×0.090 mm^3, monoclinic space group $P2_1/c$, $a = 14.82620(10)$ Å, $b = 10.01210(10)$ Å, $c = 19.99020(10)$ Å, $\beta = 99.70°$, $V = 2924.94(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.164$ g·cm^{-3}, $\mu = 0.546$ mm^{-1}, $F(000) = 1096$, $T = 100(2)$ K, $R_1 = 0.0383$, $wR_2 = 0.0966$, 5864 independent reflections [$2\theta \leq 150.202°$] and 444 parameters.

Both Et_2O molecules are disordered. The atomic displacement parameters of all Et_2O atoms O1_4 to C4_61 were restrained with RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list) with esd = 0.016 . The displacement parameters of all Et_2O atoms O1_4 to C4_61 were restrained to the same value with similarity restraint SIMU (esd = 0.032). The U_{ii} displacement parameters of all Et2O atoms O1_4 to C4_61 were restrained with ISOR keyword with esd = 0.016 to approximate isotropic behavior.

CCDC number: 2453534

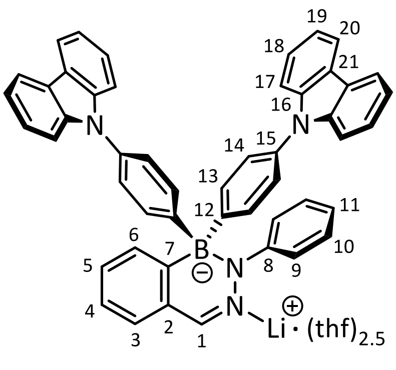
Lithium 3-phenyl-4-bis(4-(9H-carbazol-9-yl)phenyl)-4,3-borazaroisoquinolinate (5Cbz[Li])



1OTMS

5Cbz[Li] (61%)

9-(4-Bromophenyl)-9*H*-carbazol (438 mg, 1.36 mmol, 2.00 eq.) was dissolved in diethyl ether (8 mL) in a 100 mL Schlenk tube and cooled to −78 °C (*i*PrOH/dry ice). Slowly, *n*-butyllithium (1.6 M solution in *n*-hexane, 0.85 mL, 1.36 mmol, 2.00 eq.) was added under moderate stirring and the colorless reaction mixture was stirred for 45 min at −78 °C. A gradual color change to light yellow was observed over the course of the lithiation. Compound **1OTMS** (200 mg, 680 μmol, 1.00 eq.) was dissolved in diethyl ether (2 mL) in a 100 mL Schlenk flask and cooled to −78 °C (*i*PrOH/dry ice). Then, the freshly prepared 4-(9*H*-carbazol-9-yl)phenyl) lithium solution was added dropwise to compound **1OTMS**. Upon addition, a color change from colorless to yellow and the formation of a yellow solid was observed. The reaction was stirred for 5 min at −78 °C. After 5 min, the cooling bath was removed, and the suspension was stirred for 16 h at ambient temperature. The suspension was filtrated via filter cannulation. The remaining solid was washed with cold diethyl ether (1 × 6 mL), cold toluene (1 × 4 mL) and briefly dried *in vacuo*. **Yield of 5Cbz[Li](OEt_2)$_2$:** 350 mg (414 μmol, 61%) of a pale yellow powder. To obtain the adduct **5Cbz[Li](thf)$_3$**, some of the solid was re-dissolved in tetrahydrofurane (1 mL) and the solvent was removed under reduced pressure.



5Cbz[Li](thf)$_{2.5}$

^{1}H NMR (600 MHz, 298 K, C_6D_6): δ = 8.08-8.11 (m, 4H, *H*-13), 8.05-8.08 (m, 4H, *H*-20), 7.73 (d, $^3J_{HH}$ = 7.31 Hz, 1H, *H*-3), 7.51 (d, $^3J_{HH}$ = 8.19 Hz, 4H, *H*-17), 7.40 (pseudo td, $^3J_{HH}$ = 7.18 Hz, $^4J_{HH}$ = 1.27 Hz, *H*-4), 7.36-7.39 (m, 4H, *H*-14), 7.26-7.32 (m, 6H, *H*-9 + H-18), 7.24 (s, 1H, *H*-1), 7.18-7.24 (m, 6H, *H*-5 + *H*-6 + *H*-19), 6.99-7.03 (m, 2H, *H*-10), 6.67 (t, $^3J_{HH}$ = 7.31 Hz, 1H, *H*-11), 3.11-3.15 (m, 12H, 3 × C*H*$_2$-thf), 1.17-1.22 (m, 12H, 3 × C*H*$_2$-thf) ppm. **^{7}Li NMR** (223 MHz, 298 K, C_6D_6) δ = −0.25 (s) ppm. **^{11}B NMR** (193 MHz, 298 K, C_6D_6) δ = −3.1 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6) δ = 157.6 (C_q^B-12), 153.6 (C_q^B-7), 153.0 (C_q^N-8), 142.1 (C_q^N-16), 141.5 (*C*-1), 136.3 (*C*-13), 134.1 (*C*-3), 133.9 (C_q^N-15), 131.2 (C_q-2), 130.0 (*C*-4), 128.5 (*C*-10), 126.0 (*C*-18), 125.5 (*C*-14), 124.9 (*C*-5), 123.7 (C_q-21), 123.6 (*C*-6), 120.5 (*C*-9), 120.3 (*C*-20), 119.7 (C-19), 119.1 (*C*-11), 110.8 (*C*-17), 68.1

(CH$_2$-thf), 25.4 (CH$_2$-thf) ppm. **HRMS** (LIFDI, powder): expected: m/z 689.2986, 690.2949, 691.2983, 692.3016 [$C_{49}H_{34}BN_4$+H]$^+$; found: m/z 689.2849, 690.2930, 691.2969, 692.3002 [$C_{49}H_{34}BN_4$+H]$^+$. Crystalline material of **5Cbz[Li](18-crown-6)** as neon yellow plates for single-crystal XRD was obtained by adding a few milligrams of 18-crown-6 to a saturated solution of **5Cbz[Li](thf)$_3$** in benzene and storing the mixture in a closed vial at ambient temperature in a glovebox for several weeks.

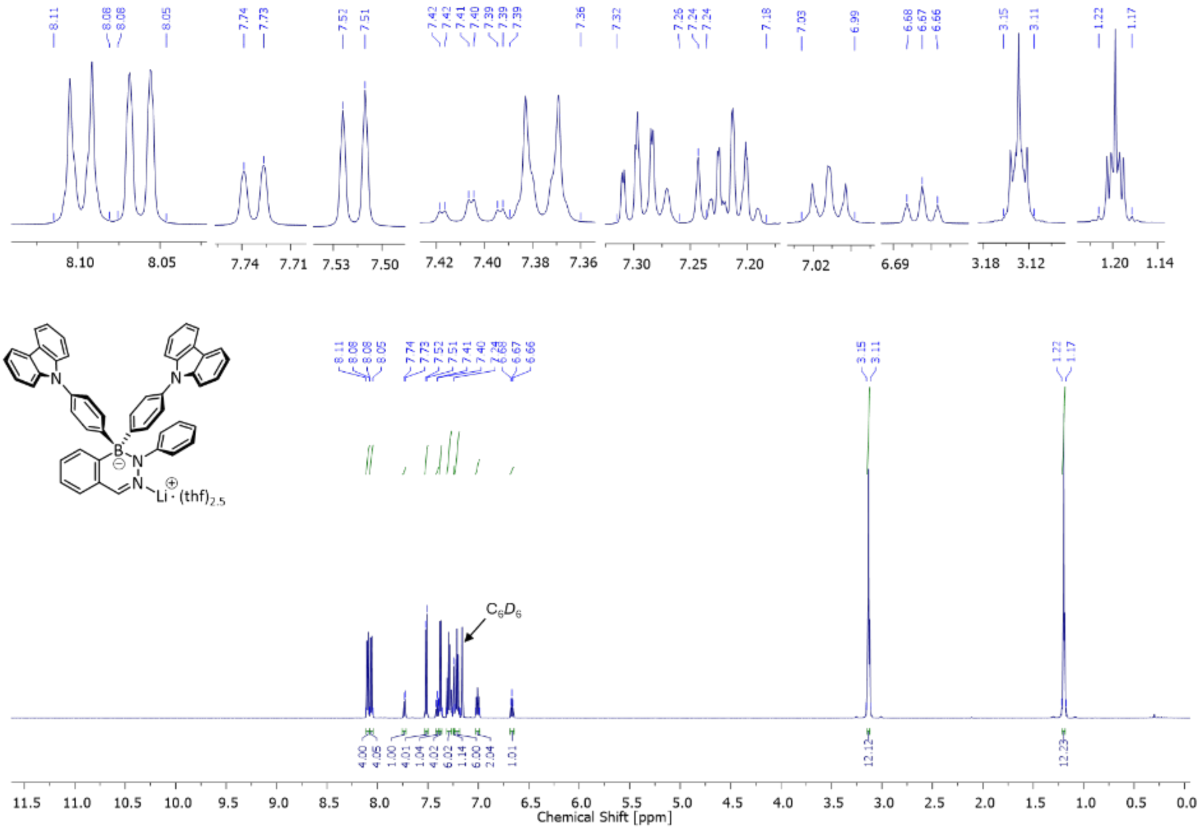


Fig. S73 ^{1}H NMR spectrum of compound **5Cbz[Li]Cbz(thf)$_{2.5}$** in C_6D_6.

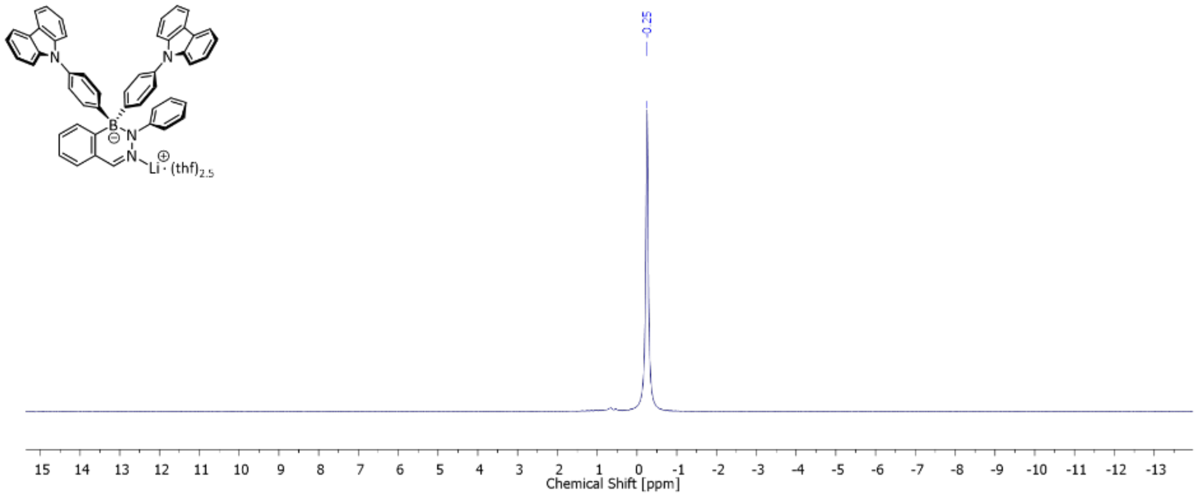


Fig. S74 ^{7}Li NMR spectrum of compound **5Cbz[Li]Cbz(thf)$_{2.5}$** in C_6D_6.

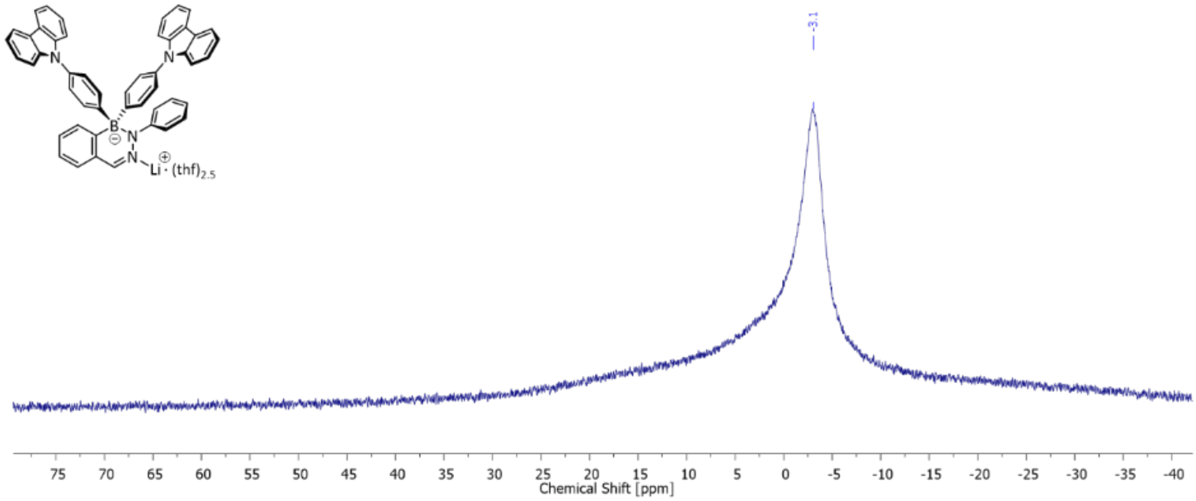


Fig. S75 Background-reduced ^{11}B NMR spectrum of compound **5Cbz[Li]Cbz(thf)$_{2.5}$** in C_6D_6.

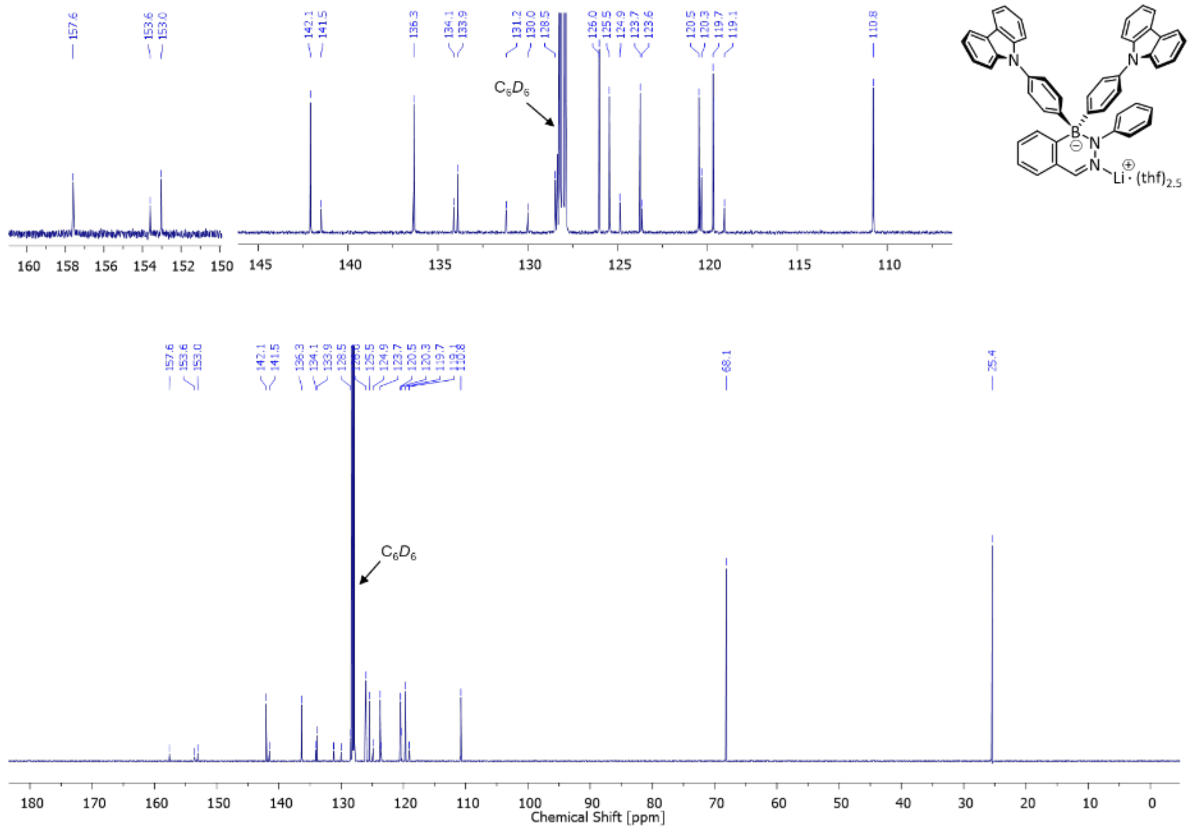


Fig. S76 $^{13}C\{^1H^{11}B\}$ NMR spectrum of compound **5Cbz[Li](thf)$_{2.5}$** in C_6D_6 (^{11}B decoupled at −3 ppm).

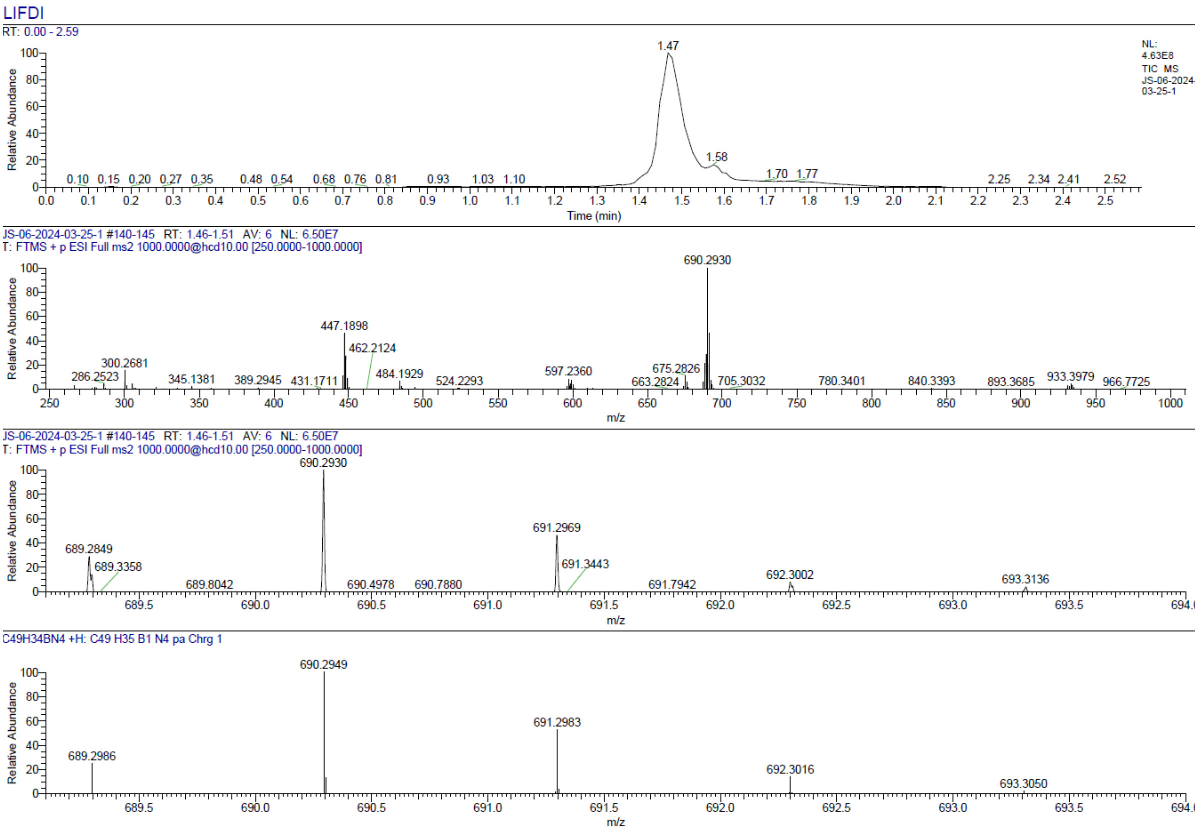


Fig. S77 LIFDI mass spectrum of compound **5Cbz[Li]** (powder).

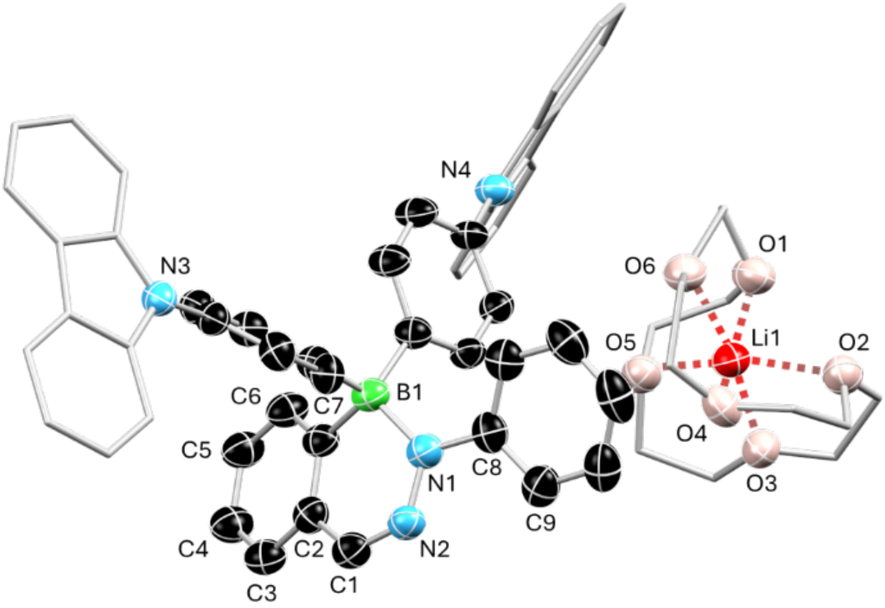


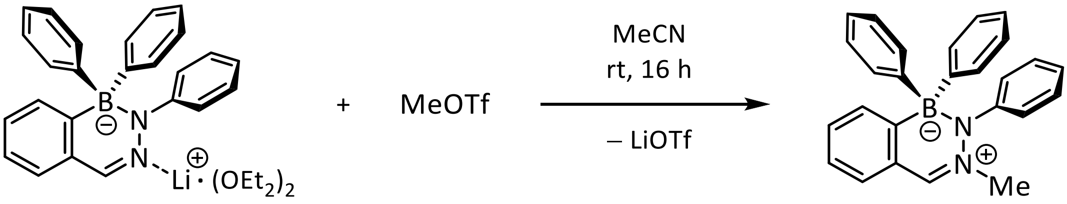
Fig. S78 Molecular structure of compound **5Cbz[Li](18-crown-6)**. Ellipsoids drawn at 50% probability (100 K). All H atoms and two co-crystallized, free crown ether molecules omitted for clarity. Complexing crown ether and 9*H*-carbazole substituents rendered as wireframe for clarity. Due to poor crystal quality and heavily disordered crown ethers, the wR$_2$ value is high. Since no disorders are present in the main diazaborinate molecule, the discussion of bond length is warranted, despite the wR$_2$ value. Selected bond lengths (Å) and angles (°) of **5Cbz[Li](18-crown-6)**: B1–N1 1.563(6), N1–N2 1.373(5), N2–C1 1.299(6), C1–C2 1.442(6), C2–C3 1.413(6), C3–C4 1.369(7), C4–C5 1.404(7), C5–C6 1.379(6), C6–C7 1.377(6), C2–C7 1.399(6), C7–B1 1.640(7), N1–C8 1.407(6), B1–N1–N2–C1 19.7(5), B1–C7–C2–C1 8.0(6), N2–N1–C8–C9 23.2(5).

Crystal data: $C_{73}H_{82}BLiN_4O_{12}$, M_r = 1225.17, yellow plate, 0.100×0.080×0.030 mm^3, monoclinic space group $P2_1/c$, a = 19.8918(3) Å, b = 14.6116(2) Å, c = 23.1516(4) Å, β = 102.0619(18)°, V = 6580.5(2) Å^3, Z = 4, ρ_{calcd} = 1.237 g·cm^{-3}, μ = 0.669 mm^{-1}, F(000) = 2608, T = 100(2) K, R_1 = 0.1282, wR_2 = 0.3151, 13205 independent reflections [$2\theta \leq 150.388°$] and 1201 parameters.

Some reflections were removed from refinement as outliers. Crown-ether showed disorder. Equivalent distances in this moiety were restrained using SADI command. The atomic displacement parameters of disordered atoms were restrained with RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list), similarity restraint SIMU and additionally U$_{ii}$ displacement parameters were restrained with ISOR keyword to approximate isotropic behavior.

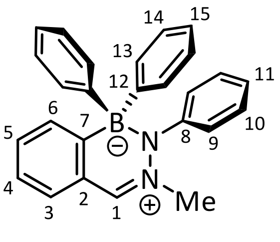
CCDC number: 2453535

2-Methyl-3-phenyl-4-bis(phenyl)-4,3-borazaroisoquinoline (**5Ph[Me]**)



5Ph[Li](OEt$_2$)$_2$ **5Ph[Me]** (86%)

In a glovebox compound **5Ph[Li](OEt$_2$)$_2$** (100 mg, 194 μmol, 1.00 eq.) was dissolved in acetonitrile (2 mL) in a glass vial equipped with a stirring bar. Methyl triflate (10 drops, xs.) was added in portions at ambient temperature. Upon addition, an immediate color change from pale-yellow to deep orange and the formation of an orange solid was observed. The reaction suspension was stirred for 16 h at ambient temperature in the glovebox. The solid was separated via pipet filtration and the filter cake was washed with cold acetonitrile (2 × 0.5 mL), *n*-pentane (1 × 1 mL) and dried *in vacuo*. **Yield of 5Ph[Me]:** 63.0 mg (167 μmol, 86%) of an intense orange powder.



5Ph[Me]

^{1}H NMR (500 MHz, 298 K, THF-d_8): δ = 8.15 (s, 1H, *H*-1), 7.40 (ddd, $^3J_{HH}$ = 7.36 Hz; 7.36 Hz, $^4J_{HH}$ = 1.28 Hz, 1H, *H*-4), 7.32 (d, $^3J_{HH}$ = 7.59 Hz, 1H, *H*-6), 7.18 (ddd, $^3J_{HH}$ = 7.45 Hz; 7.45 Hz, $^4J_{HH}$ = 1.31 Hz, 1H, *H*-5), 7.09 (d, $^3J_{HH}$ = 7.43 Hz, 1H, *H*-3), 6.98-7.02 (m, 4H, *H*-13), 6.90-6.95 (m, 6H, *H*-14 + *H*-10), 6.85-6.89 (m, 2H, *H*-15), 6.82 (tt, $^3J_{HH}$ = 7.25 Hz, $^4J_{HH}$ = 1.20 Hz, 1H, *H*-11) 6.72-6.76 (m, 2H, *H*-9), 3.77 (d, $^4J_{HH}$ = 0.48 Hz, $-CH_3$) ppm. **^{11}B{^{1}H} NMR** (160 MHz, 298 K, THF-d_8) δ = −1.3 (br s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, 298 K, THF-d_8) δ = 156.7 (br, C_q^B-7), 153.8 (br, C_q^B-12), 150.4 (*C*-1), 145.3 (C_q^N-8), 135.3 (*C*-13), 134.0 (*C*-3), 133.9 (*C*-4), 129.9 (C_q-2), 128.1 (*C*-10), 127.5 (*C*-6), 126.7 (*C*-14), 126.5 (*C*-11), 125.4 (*C*-5), 124.7 (*C*-15), 124.0 (*C*-11), 47.8 ($-CH_3$) ppm. **HRMS** (LIFDI, THF): expected: m/z 373.1985, 374.1949, 375.1982 $[C_{26}H_{23}BN_2]^+$; found: m/z 373.1866, 374.1946, 375.1980 $[C_{26}H_{23}BN_2]^+$. Crystalline material of **5Ph[Me]** as orange plates for single-crystal XRD was obtained by slow evaporation of a saturated benzene solution at ambient temperature in a glovebox.

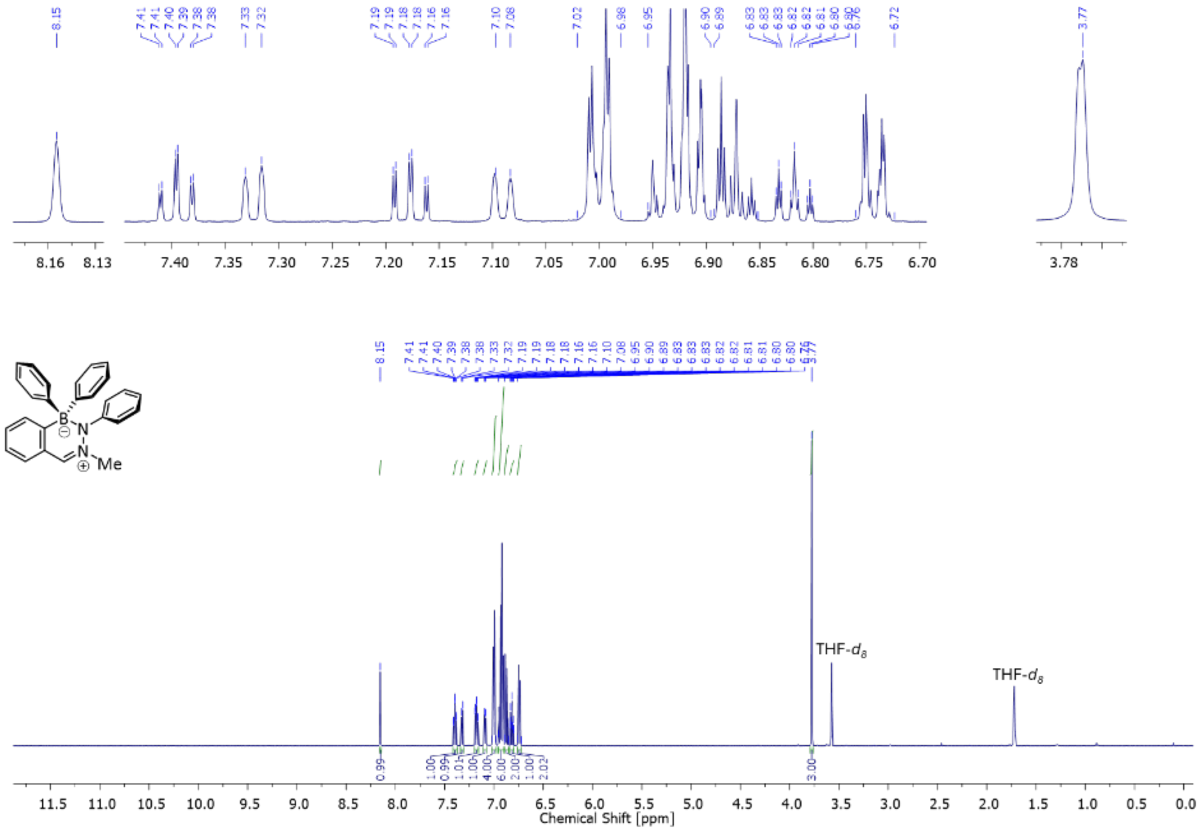


Fig. S79 ^{1}H NMR spectrum of compound **5Ph[Me]** in THF-d_8.

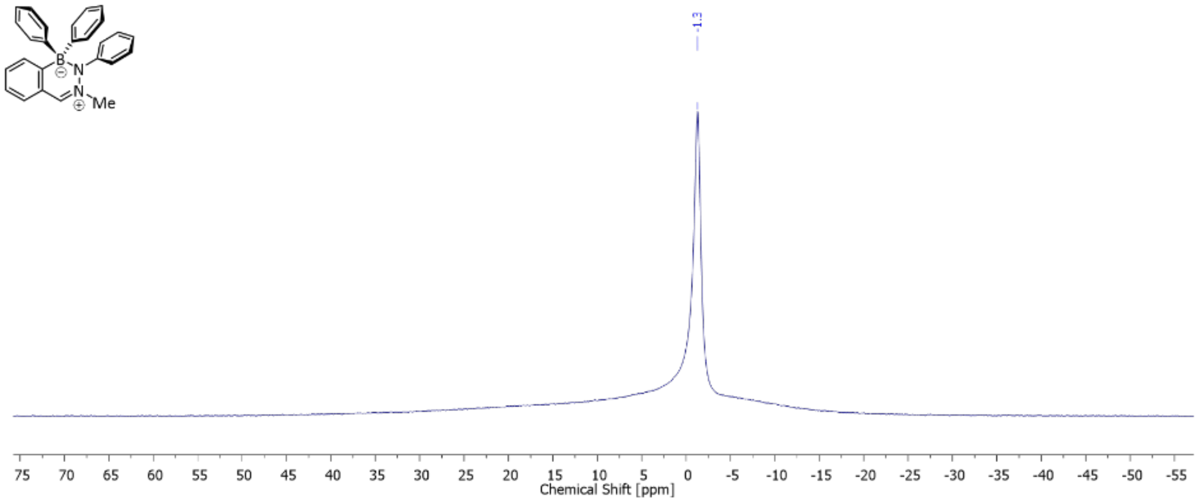


Fig. S80 Background-reduced ^{11}B{^{1}H} NMR spectrum of compound **5Ph[Me]** in THF-d_8.

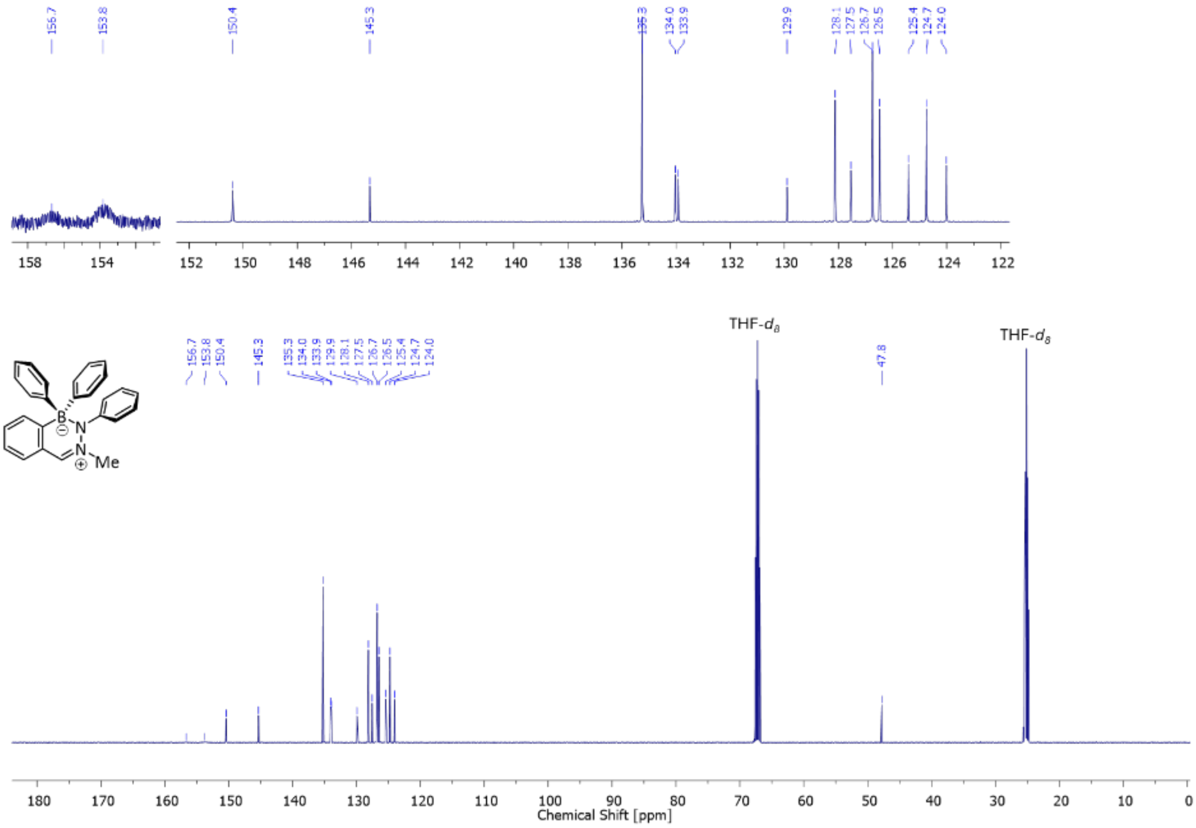


Fig. S81 $^{13}C\{^1H\}$ NMR spectrum of compound **5Ph[Me]** in THF-d_8.

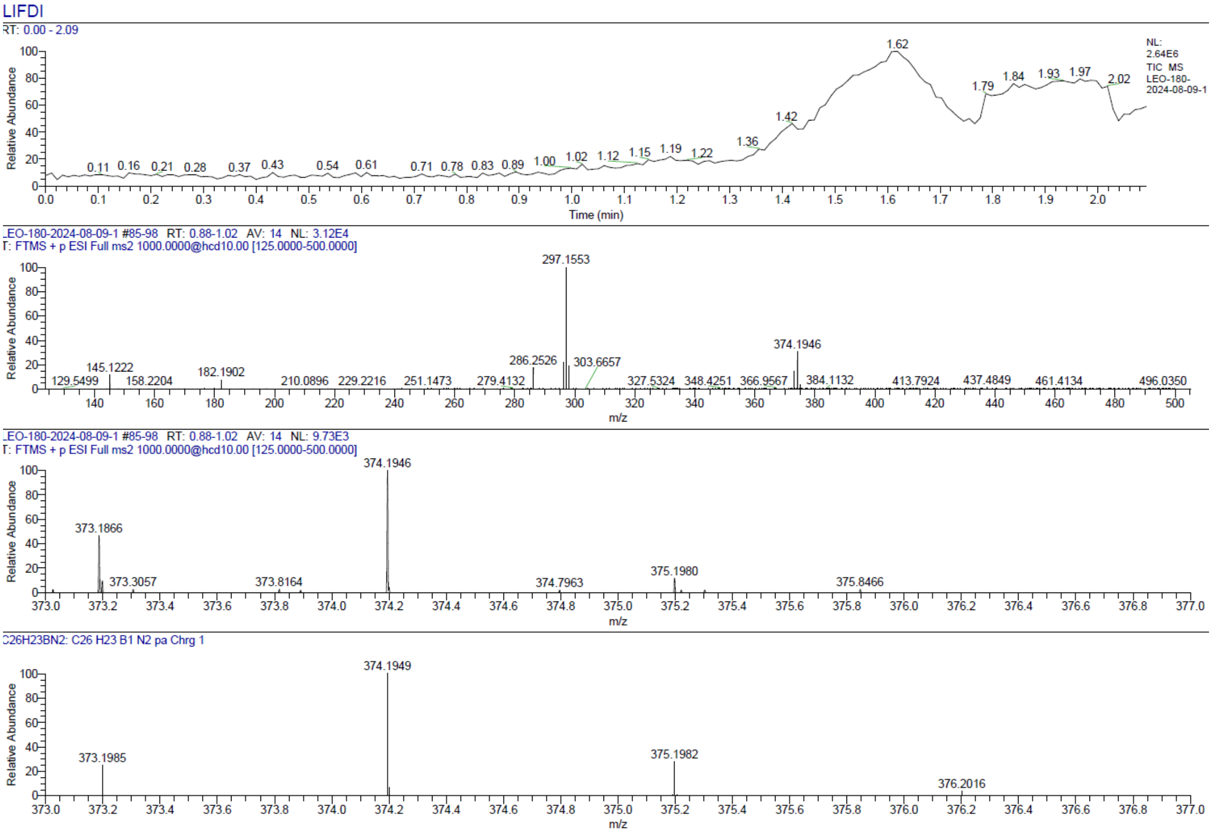
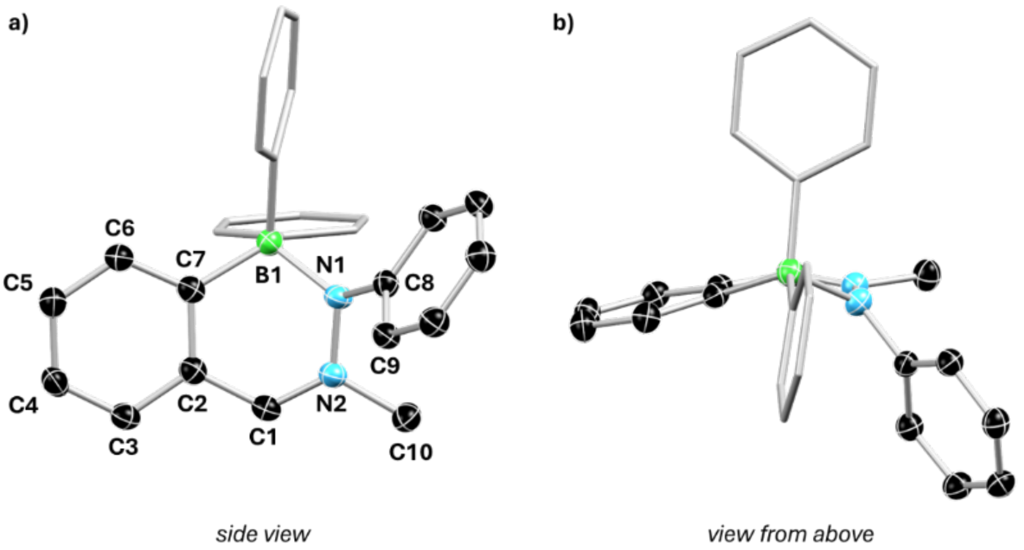


Fig. S82 LIFDI mass spectrum of compound **5Ph[Me]** (THF).



side view

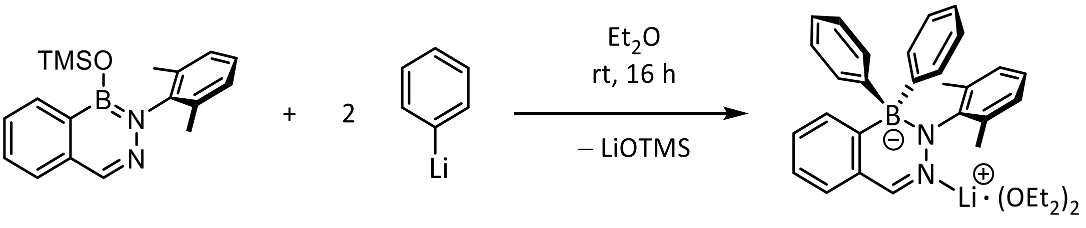
view from above

Fig. S83 Molecular structure of compound **5Ph[Me]**. a) side view; b) view from above. Ellipsoids drawn at 50% (100 K) probability. All H-atoms omitted. Selected bond lengths (Å) and angles (°) of **5Ph[Me]**: B1–N1 1.603(2), N1–N2 1.3844(17), N2–C1 1.4208(19), C1–C2 1.438(2), C2–C3 1.406(2), C3–C4 1.380(2), C4–C5 1.392(2), C5–C6 1.386(2), C6–C7 1.397(2), C2–C7 1.411(2), C7–B1 1.618(2), N1–C8 1.4208(19), N2–C10 1.4777(19), B1–N1–N2–C1 24.96(19), B1–C7–C2–C1 12.3(2), N2–N1–C8–C9 37.51(19).

Crystal data: $C_{26}H_{23}BN_2$, M_r = 374.27, orange plate, 0.210×0.150×0.030 mm^3, monoclinic space group $P2_1/n$, a = 14.1594(4) Å, b = 9.8690(2) Å, c = 15.6500(5) Å, β = 111.203(3)°, V = 2038.87(10) Å^3, Z = 4, ρ_{calcd} = 1.219 g·cm^{-3}, μ = 0.538 mm^{-1}, $F(000)$ = 792, T = 100(2) K, R_1 = 0.0580, wR_2 = 0.1195, 3972 independent reflections [$2\theta \leq 147.404°$] and 263 parameters.

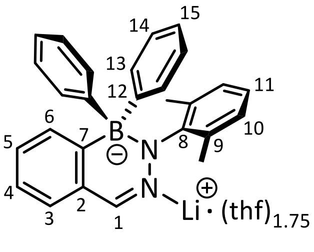
CCDC number: 2453541

Lithium 3-(2,6-dimethylphenyl)-4-bis(phenyl)-4,3-borazaroisoquinolinate (6Ph[Li])



2OTMS **6Ph[Li]** (73%)

In a glovebox, compound **2OTMS** (105 mg, 326 μmol, 1.00 eq.) was dissolved in diethyl ether (2 mL) and in a glass vial equipped with a stirring bar. Phenyllithium (54.8 mg, 652 μmol, 2.00 eq.) was added in portions at ambient temperature. Upon addition, the immediate formation of a neon yellow solid was observed. The reaction suspension was stirred for 16 h in the glovebox at ambient temperature. The solid was separated via a PE-syringe equipped with a *Whatman* filter and the filter cake was washed with cold diethyl ether (1 × 1 mL), *n*-pentane (1 × 1 mL) and briefly dried *in vacuo*. **Yield of 6Ph[Li](OEt_2)$_2$:** 129 mg (238 μmol, 73%), neon yellow solid. To obtain the adduct **6Ph[Li](thf)$_{2.5}$**, some of the solid was re-dissolved in tetrahydrofuran (1 mL) and the solvent was removed under reduced pressure.



6Ph[Li](thf)$_{1.75}$

^{1}H NMR (500 MHz, 298 K, THF-d_8): δ = 7.27-7.31 (m, 4H, *H*-13), 7.26 (s, 1H, *H*-1), 6.99 (d, $^{3}J_{HH}$ = 7.31 Hz, *H*-3), 6.90 (ddd, $^{3}J_{HH}$ = 7.30 Hz; 7.12 Hz, $^{4}J_{HH}$ = 1.40 Hz, 1H, *H*-4), 6.75-6.80 (m, 5H, *H*-14 + *H*-5), 6.72 (d, $^{3}J_{HH}$ = 7.03 Hz, 1H, *H*-6), 6.67 (tt, $^{3}J_{HH}$ = 7.18 Hz, $^{4}J_{HH}$ = 1.41 Hz, 2H, *H*-10), 6.55-6.58 (m, 2H, *H*-11), 6.50-6.53 (m, 1H, *H*-11), 3.59-3.63 (m, 7H, 1.75 × C*H*$_2$-thf), 1.93 (s, 6H, –C*H*$_3$), 1.75-1.78 (m, 7H, 1.75 × C*H*$_2$-thf) ppm. **^{7}Li NMR** (194 MHz, 298 K, THF-d_8) δ = −0.45 (s) ppm. **^{11}B{^{1}H} NMR** (160 MHz, 298 K, THF-d_8) δ = −3.8 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, THF-d_8) δ = 157.3 (C_q^B-12), 152.1 (C_q^B-7), 151.8 (C_q^N-8), 138.6 (*C*-1), 138.5 (C_q-9), 135.6 (*C*-13), 132.6 (C_q-2), 132.1 (*C*-3), 127.9 (*C*-10), 127.8 (*C*-4), 125.5 (*C*-15), 123.6 (*C*-11), 123.1 (*C*-5), 123.0 (*C*-11), 122.2 (*C*-6), 68.0 (*C*H$_2$-thf), 26.2 (*C*H$_2$-thf), 21.2 (–*C*H$_3$) ppm. **HRMS** (LIFDI, toluene): expected: m/z 386.2063, 387.2027, 388.2061, 389.2094 $[C_{27}H_{24}BN_2]^+$; found: m/z 386.2058, 387.2021, 388.2105, 389.2134 $[C_{27}H_{24}BN_2]^+$. Crystalline material of **6Ph[Li](OEt_2)$_2$** as neon yellow plates for single-crystal XRD was obtained by storing slow evaporation of a saturated THF solution at ambient temperature in a glovebox.

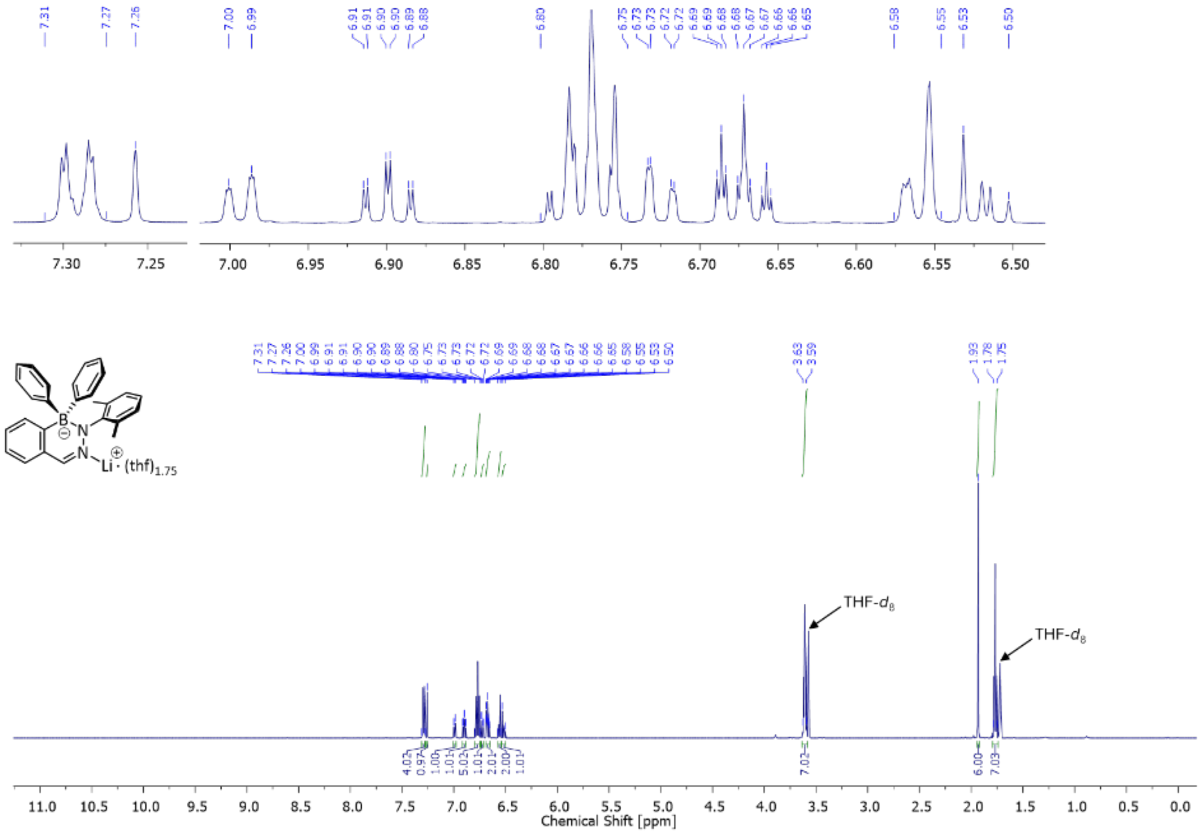


Fig. S84 ^{1}H NMR spectrum of compound **6Ph[Li](thf)$_3$** in THF-d_8.

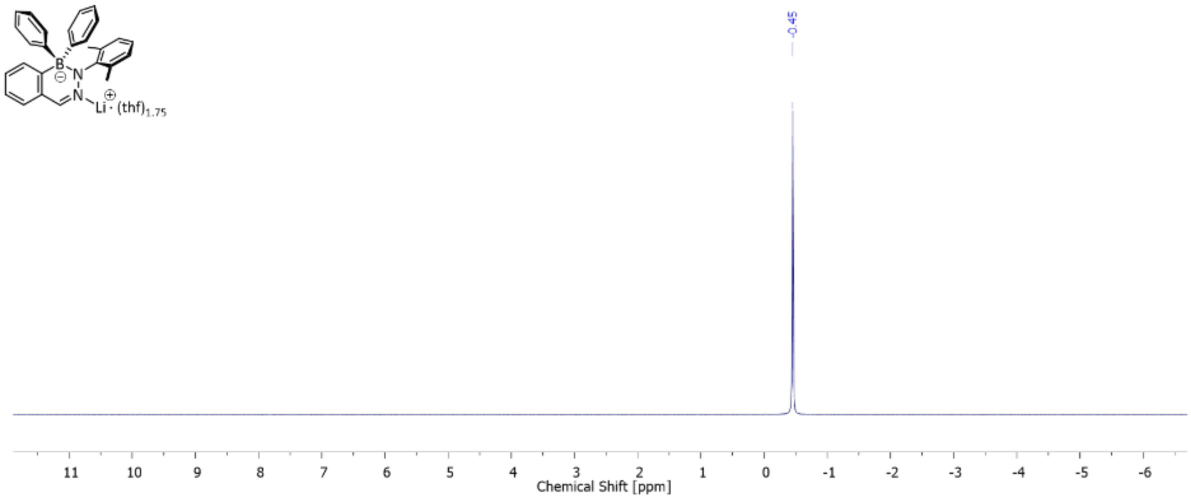


Fig. S85 ^{7}Li NMR spectrum of compound **6Ph[Li](thf)$_3$** in THF-d_8.

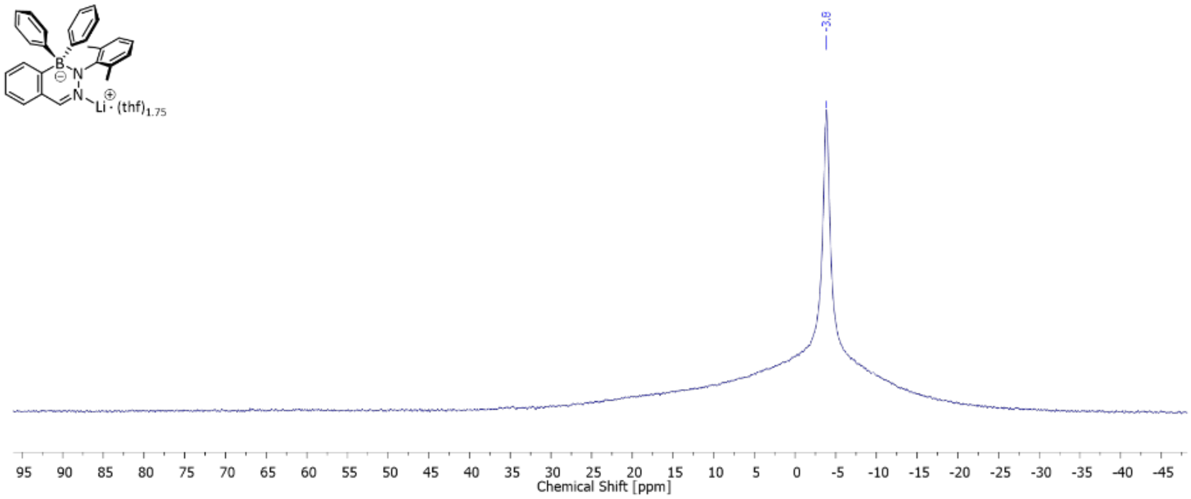


Fig. S86 Background-reduced ^{11}B{^{1}H} NMR spectrum of compound **6Ph[Li](thf)$_3$** in THF-d_8.

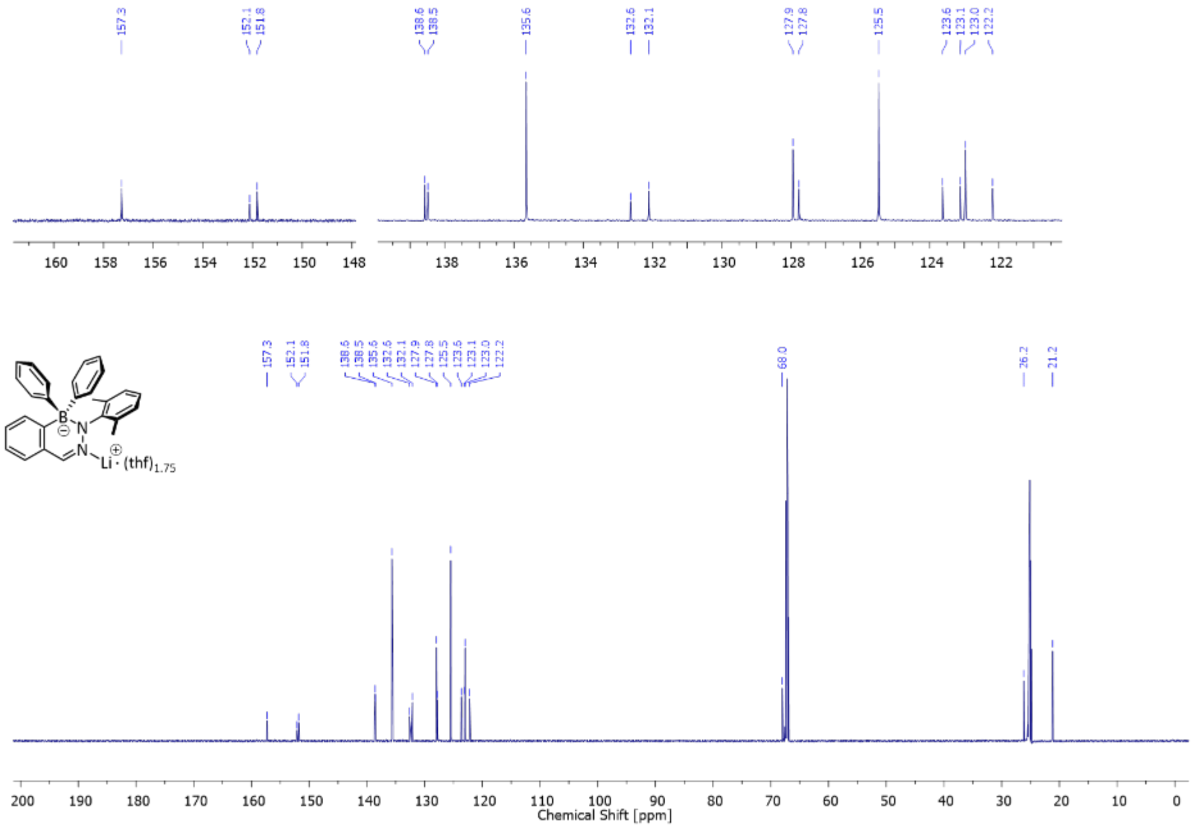


Fig. S87 ^{13}C{^{1}H^{11}B} NMR spectrum of compound **6Ph[Li](thf)$_3$** in THF-d_8 (decoupled at −4 ppm).

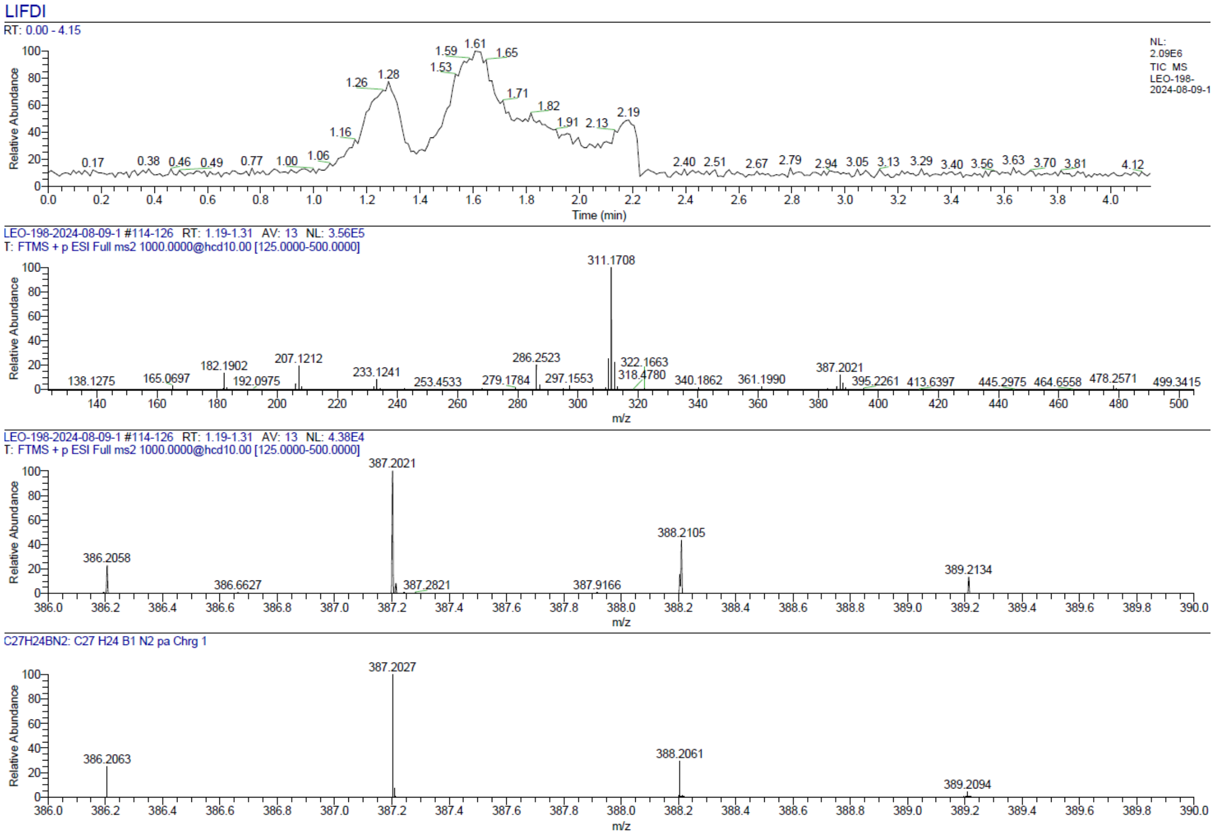
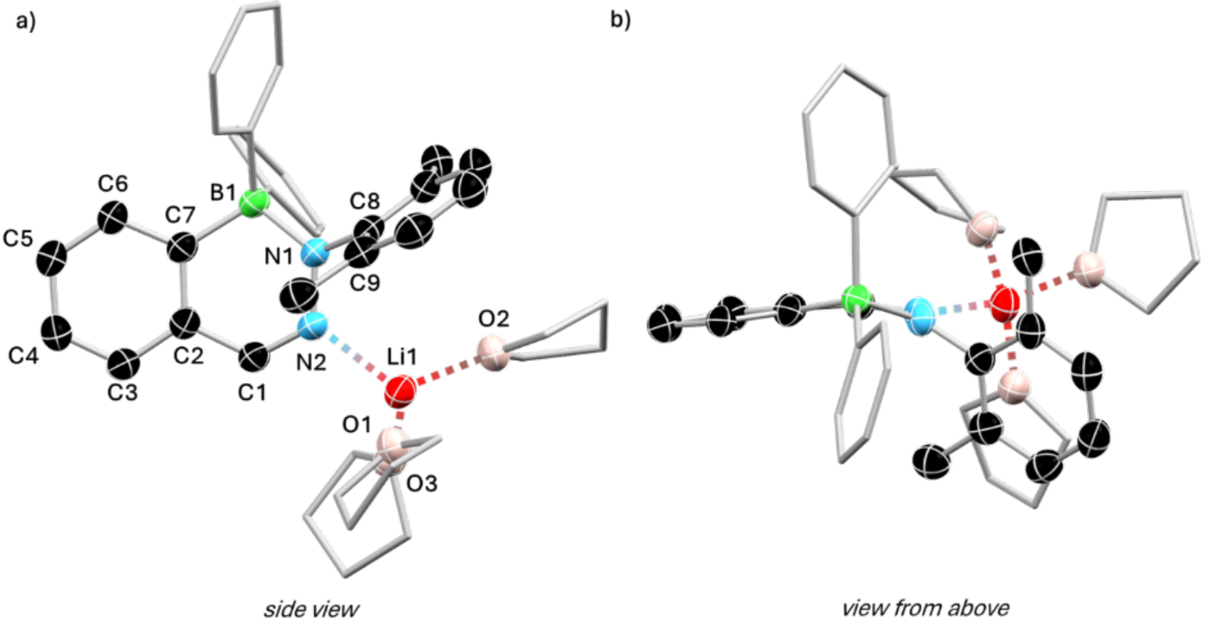


Fig. S88 LIFDI mass spectrum of compound **6Ph[Li]** (toluene).



side view *view from above*

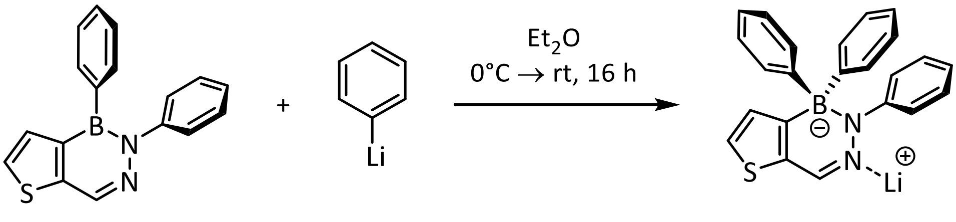
Fig. S89 Molecular structure of compound **6Ph[Li](thf)₃**. a) side view; b) view from above. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Selected bond lengths (Å) and angles (°) of **6Ph[Li](thf)₃**. Due to the presence of a whole molecule disorder of the borate anion (see appendix), no discussion of bond length is possible.

Crystal data: $C_{39}H_{47}BLiN_2O_3$, $M_r = 609.53$, clear yellow plate, 0.130×0.100×0.050 mm³, triclinic space group $P\overline{1}$, $a = 10.9272(2)$ Å, $b = 17.6925(3)$ Å, $c = 18.5888(4)$ Å, $\alpha = 77.105(2)°$, $\beta = 80.910(2)°$, $\gamma = 88.455(2)°$, $V = 3459.01(12)$ Å³, $Z = 4$, $\rho_{calcd} = 1.170$ g·cm⁻³, $\mu = 0.560$ mm⁻¹, $F(000) = 1308$, $T = 100(2)$ K, $R_1 = 0.0792$, $wR_2 = 0.1856$, 13516 independent reflections [$2\theta \leq 148.268°$] and 1420 parameters.

Reflections [3 −1 2]. [3 3 3] and [6 2 0] were removed from refinement as outliers. All THF molecules are disordered. The atomic displacement parameters of all thf atoms O1_1 to C5_61 were restrained with RIGU keyword with esd = 0.008 in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of all thf atoms O1_1 to C5_61 were restrained to the same value with similarity restraint SIMU with esd = 0.008. The U_{ii} displacement parameters of all thf atoms O1_1 to C5_61 were restrained with ISOR keyword with esd 0 0.008 to approximate isotropic behavior. Both diazaborinin molecules with substituents had a whole molecule disorder. The atomic displacement parameters of the atoms B1_7 to C6_141 and the atoms of a xylyl substituent C1_11 to C8_119 were restrained with RIGU keyword with esd = 0.008 in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of the atoms B1_7 to C6_141 and the atoms of a xylyl substituent C1_11 to C8_119 were restrained to the same value with similarity restraint SIMU with esd = 0.008. The U_{ii} displacement parameters of the atoms B1_7 to C6_141 and the atoms of a xylyl substituent C1_11 to C8_119 were restrained with ISOR keyword with esd 0 0.008 to approximate isotropic behavior.

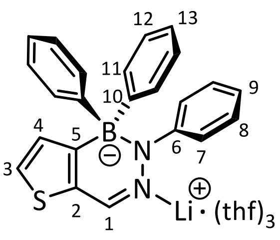
CCDC number: 2453542

Lithium 3-phenyl-4-bis(phenyl)-4,3-borazarothieno[3,2-*c*]pyridinate (7Ph[Li])



3Ph **7Ph[Li]** (72%)

Compound **3Ph** (98.0 mg, 340 μmol, 1.00 eq.) was dissolved in diethyl ether (5 mL) and cooled to 0 °C with a cooling bath (ice). Phenyllithium (1.9 M solution in diethyl ether, 0.18 mL, 340 μmol, 1.00 eq.) was added in dropwise under rapid stirring. Upon addition, a color change to yellow was observed. The cooling bath was removed, and the solution was stirred for 16 h at ambient temperature. All volatile components were removed *in vacuo*. The remaining oil was re-dissolved in tetrahydrofurane, all volatile components were removed *in vacuo* again to exchange the coordinating solvent from diethyl ether to tetrahydrofurane and the remaining oil was lyophilized to obtain a powderous substance. **Yield of 7Ph[Li](thf)$_3$**: 91.0 mg, 245 μmol, 72% of a yellow solid. The compound is air- and moisture-sensitive.



7Ph[Li](thf)$_3$

^{1}H NMR (600 MHz, C_6D_6, 298 K) δ = 8.00 (d, 4H, $^3J_{HH}$ = 6.84 Hz, *H*-11), 7.34 (t, 4H, $^3J_{HH}$ = 7.55 Hz, *H*-12), 7.25 (d, 2H, $^3J_{HH}$ = 7.82 Hz, *H*-7), 7.18 (tt, 1H, $^3J_{HH}$ = 7.28 Hz, $^4J_{HH}$ = 1.22 Hz, *H*-13),*[1] 7.12 (d, 1H, $^3J_{HH}$ = 4.58 Hz, *H*-3), 7.05 (d, 1H, $^3J_{HH}$ = 4.85 Hz, *H*-4), 6.88 (t, 2H, $^3J_{HH}$ = 7.82 Hz, *H*-8), 6.54 (t, 1H, $^3J_{HH}$ = 7.11 Hz, *H*-9), 3.17 (m, 7H, 3 × CH_2-thf), 1.22 (m, 7H, 3 × CH_2-thf) ppm. ppm. **^{7}Li NMR** (223 MHz, 298 K, C_6D_6) δ = –0.51 (s) ppm. **^{11}B NMR** (193 MHz, 298 K, C_6D_6) δ = –2.3 (s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, C_6D_6, 298 K) δ = 160.5 (C_q^B-5), 157.1 (C_q^B-10), 153.5 (C_q^N-6), 135.0 (*C*-11), 134.6 (*C*-3), 133.4 (*C*-1), 129.1 (*C*-2), 128.8 (*C*-8), 127.0 (*C*-12), 125.8 (*C*-4), 124.2 (*C*-13), 119.4 (*C*-7), 118.7 (*C*-9) ppm. **HRMS** (LIFDI, toluene): expected: m/z 364.1315, 365.1278, 366.1312 [$C_{23}H_{18}BN_2S$]; found: m/z 364.1311, 365.1274, 366.1306 [$C_{23}H_{18}BN_2S$]. Crystalline material of **7Ph[Li](OEt$_2$)$_2$** as yellow blocks for single-crystal XRD was obtained from a different batch by skipping the tetrahydrofurane work-up step and slow evaporation of a saturated benzene solution at ambient temperature in a glovebox.

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*[1] Partially superimposed with C_6D_6 solvent signal.

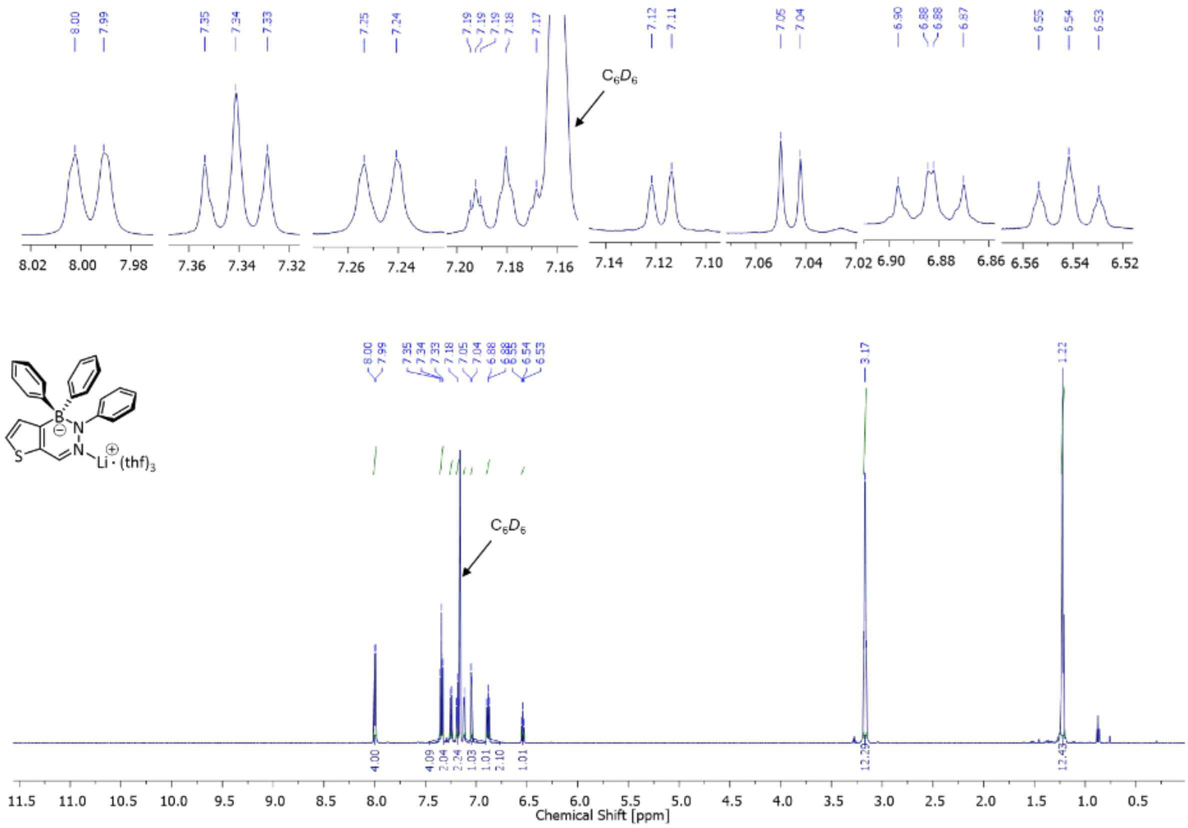


Fig. S90 ^{1}H NMR spectrum of compound **7Ph[Li](thf)$_3$** in C_6D_6.

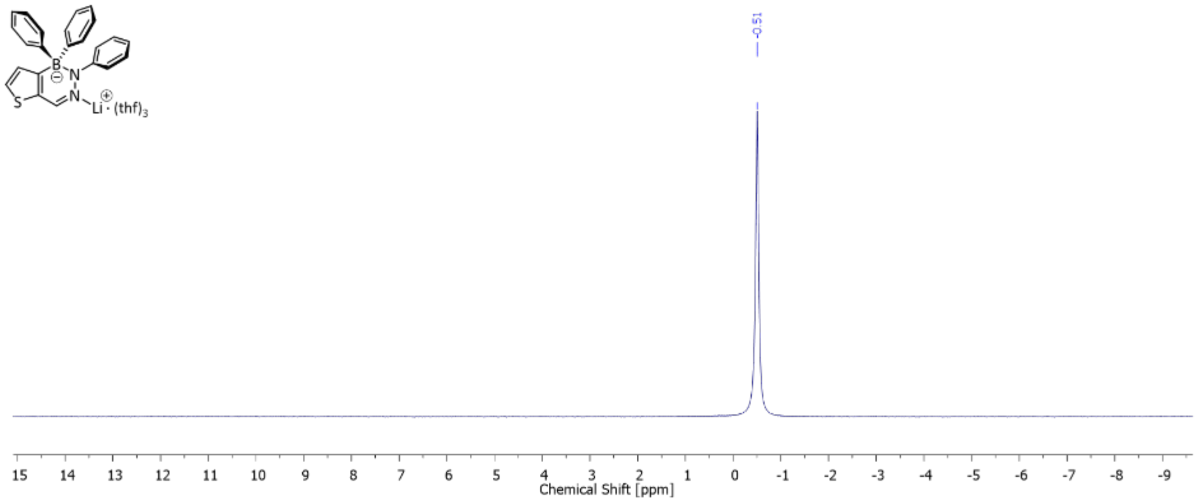


Fig. S91 ^{7}Li NMR spectrum of compound **7Ph[Li](thf)$_3$** in C_6D_6.

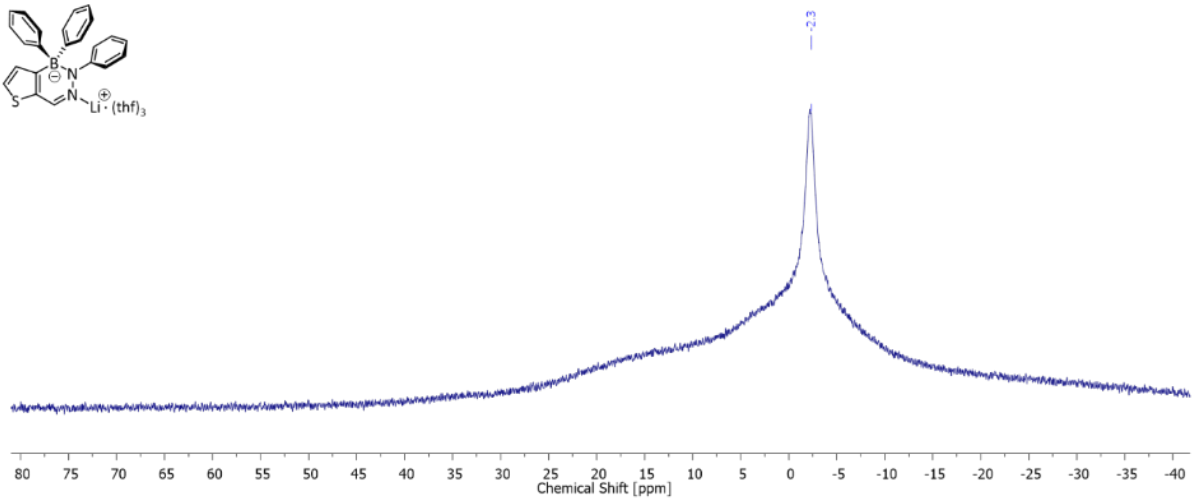


Fig. S92 Background-reduced ^{11}B NMR spectrum of compound **7Ph[Li](thf)$_3$** in C_6D_6.

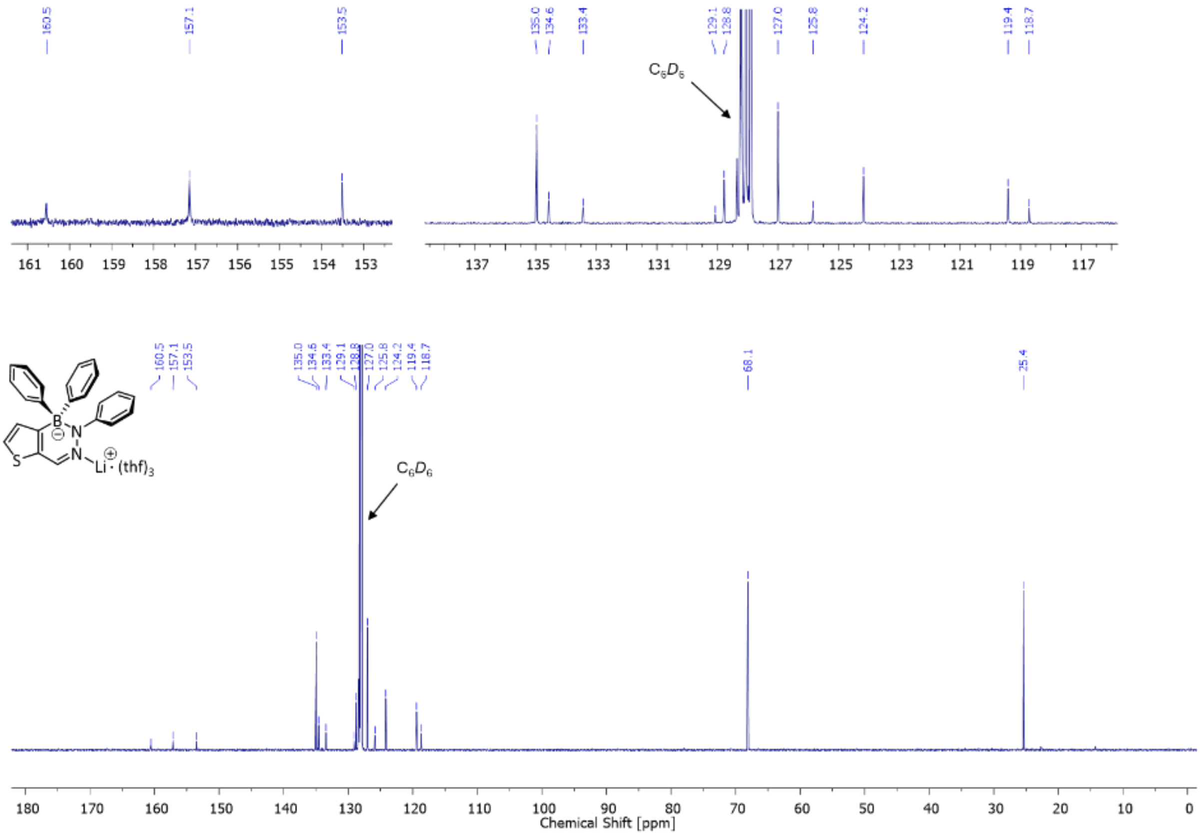


Fig. S93 ^{13}C{^{1}H^{11}B} NMR spectrum of compound **7Ph[Li](thf)$_3$** in C_6D_6 (^{11}B decoupled at −2.8 ppm).

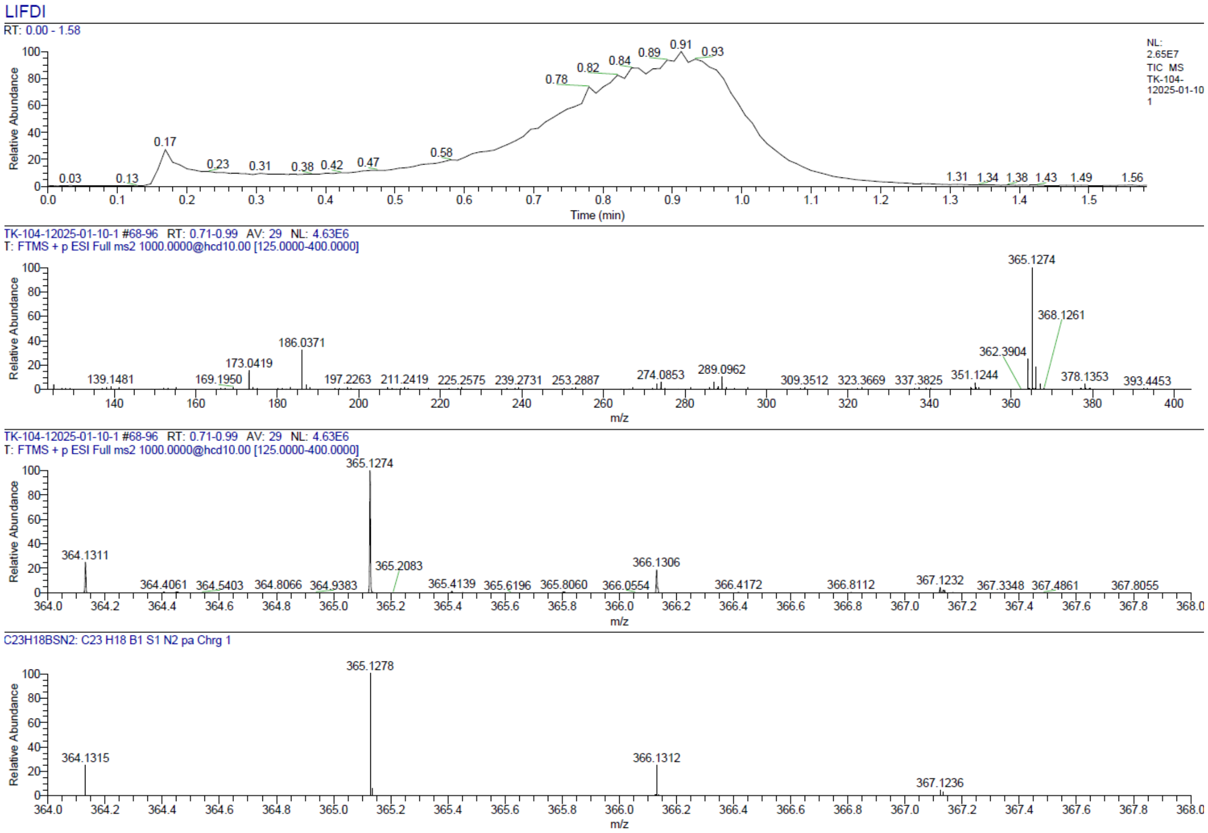
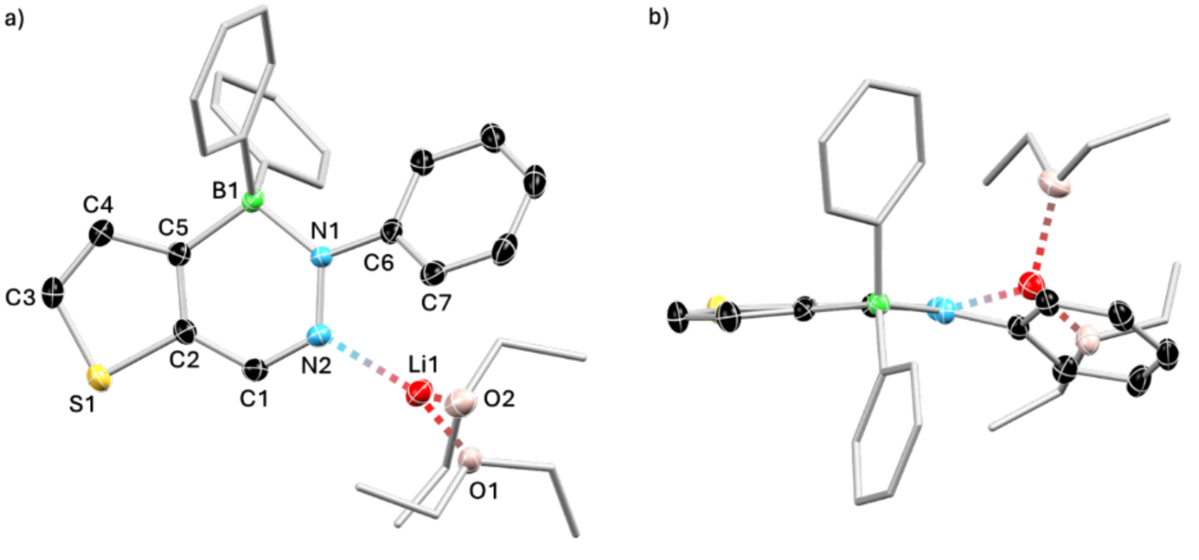


Fig. S94 LIFDI mass spectrum of compound **7Ph[Li]** (toluene).



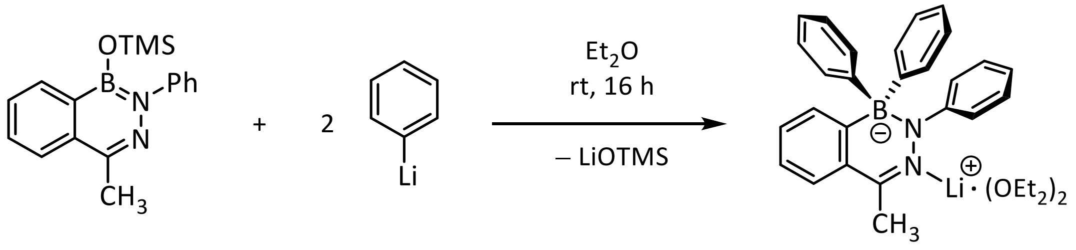
side view *view from above*

Fig. S95 Molecular structure of compound **7Ph[Li](OEt₂)₂**. a) side view; b) view from above. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Selected bond lengths (Å) and angles (°) of **7Ph[Li](OEt₂)₂**: N2–Li1 2.042(4), B1–N1 1.619(2), N1–N2 1.384(3), N2–C1 1.297(2), C1–C2 1.428(3), C2–S1 1.7376(19), S1–C3 1.714(2), C3–C4 1.359(3), C4–C5 1.428(3), C2–C5 1.372(3), C5–B1 1.615(3), N1–C6 1.402(2), B1–N1–N2–C1 5.0(3), B1–C5–C2–C1 6.0(3), N2–N1–C6–C7 28.1(2).

Crystal data: $C_{31}H_{38}BLiN_2O_2S$, $M_r = 520.44$, clear light yellow plate, 0.170×0.120×0.050 mm³, orthorhombic space group $P2_12_12_1$, $a = 9.01030(10)$ Å, $b = 15.58450(10)$ Å, $c = 20.4878(2)$ Å, $V = 2876.92(5)$ Å³, $Z = 4$, $\rho_{calcd} = 1.202$ g·cm⁻³, $\mu = 1.221$ mm⁻¹, $F(000) = 1112$, $T = 100(2)$ K, $R_1 = 0.0305$, $wR_2 = 0.0709$, Flack parameter = 0.017(7), 5811 independent reflections [$2\theta \leq 150.002°$] and 348 parameters.

CCDC number: 2453543

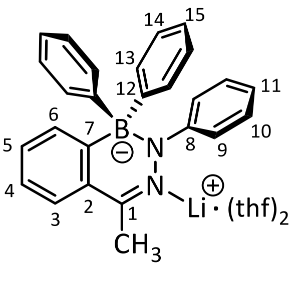
Lithium 1-Methyl-3-phenyl-4-bis(phenyl)-4,3-borazaroisoquinolinate (8Ph[Li])



4OTMS

8Ph[Li] (62%)

In a glovebox, compound **4OTMS** (167 mg, 542 *µ*mol, 1.00 eq.) was dissolved in diethyl ether (2 mL) and in a glass vial equipped with a stirring bar. Phenyllithium (91.0 mg, 1.08 mmol, 2.00 eq.) was added in portions at ambient temperature. Upon addition, the immediate formation of a neon yellow solid was observed. The reaction suspension was stirred for 16 h in the glovebox at ambient temperature. The solid was separated via a PE-syringe equipped with a *Whatman* filter and the filter cake was washed with cold diethyl ether (1 × 1 mL), *n*-pentane (1 × 1 mL) and briefly dried *in vacuo*. **Yield of 8Ph[Li](OEt$_2$)$_2$:** 177 mg (335 *µ*mol, 62%), neon yellow solid. To obtain the adduct **8Ph[Li](thf)$_{2.5}$**, some of the solid was re-dissolved in tetrahydrofuran (1 mL) and the solvent was removed under reduced pressure.



8Ph[Li](thf)$_2$

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ = 7.91 (d, $^3J_{HH}$ = 6.47 Hz, 4H, *H*-13), 7.61 (d, $^3J_{HH}$ = 7.31 Hz, 1H, *H*-6), 7.30-7.35 (m, 6H, *H*-14 + *H*-3 + *H*-5), 7.17-7.24 (m, 3H, *H*-15 + *H*-4), 7.13 (d, $^3J_{HH}$ = 7.59 Hz, 2H, *H*-9), 6.85-6.90 (m, 2H, *H*-10), 6.53 (tt, $^3J_{HH}$ = 7.19 Hz, $^4J_{HH}$ = 1.23 Hz, 1H, *H*-11), 2.99-3.03 (m, 8H, 2 × CH_2-thf), 2.00 (s, 3H, −CH_3), 1.15-1.20 (m, 8H, 2 × CH_2-thf) ppm. **^{7}Li NMR** (194 MHz, 298 K, C_6D_6) δ = −0.02 (s) ppm. **^{11}B NMR** (160 MHz, 298 K, C_6D_6) δ = −3.3 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6) δ = 157.6 (C_q^B-12), 156.0 (C_q^B-7), 153.4 (C_q^N-8), 145.3 (*C*-1), 135.3 (*C*-13), 134.6 (*C*-6), 131.5 (C_q-2), 129.9 (C-5), 129.2 (*C*-10), 127.0 (*C*-14), 124.2 (*C*-4), 124.2 (*C*-15), 121.8 (*C*-3), 118.7 (*C*-9), 118.2 (C-11), 68.2 (CH_2-thf), 25.3 (CH_2-thf), 20.4 (−CH_3) ppm. **HRMS** (LIFDI, THF): expected: m/z 372.1907, 373.1871, 374.1904 $[C_{26}H_{22}BN_2]^+$; found: m/z 372.1897, 373.1861, 374.1892 $[C_{26}H_{22}BN_2]^+$. Crystalline material of **8Ph[Li](OEt$_2$)$_2$** as neon yellow blocks for single-crystal XRD was obtained by slow evaporation of a saturated diethyl ether solution at ambient temperature in a glovebox.

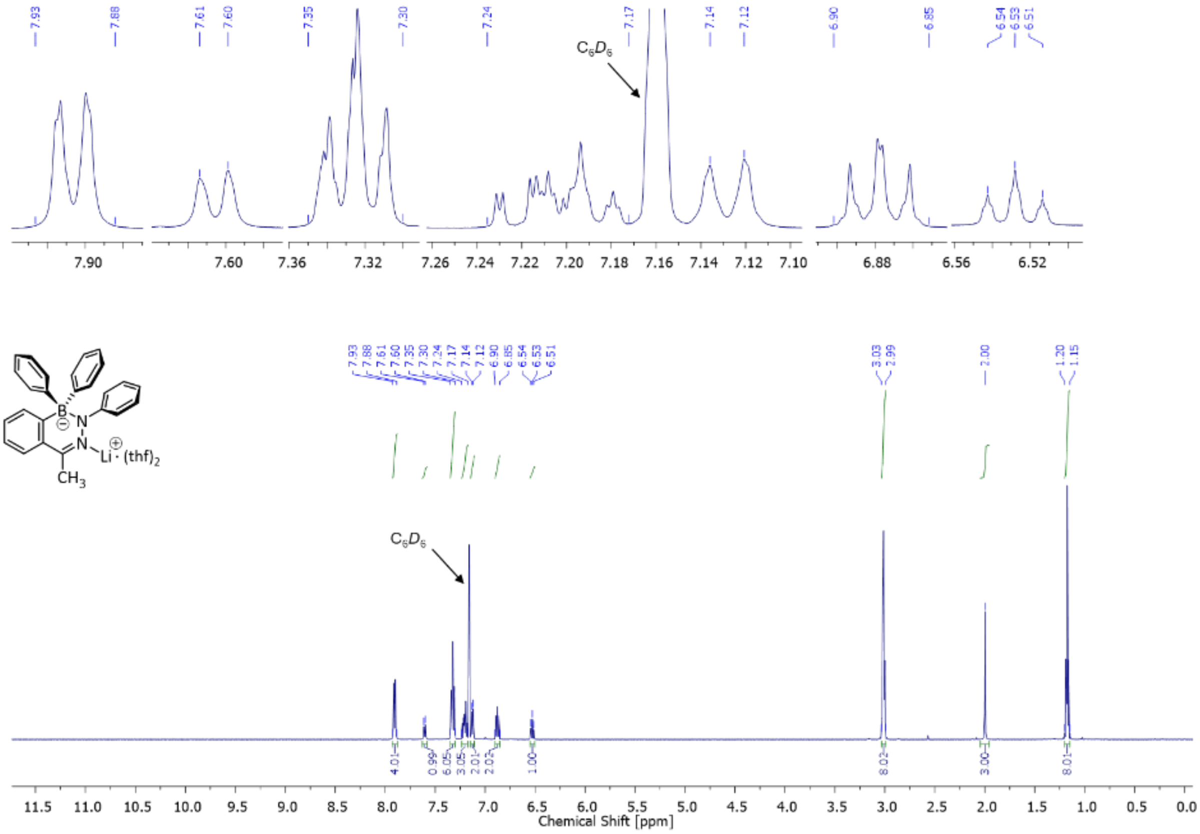


Fig. S96 ^{1}H NMR spectrum of compound **8Ph[Li](thf)₂** in C_6D_6.

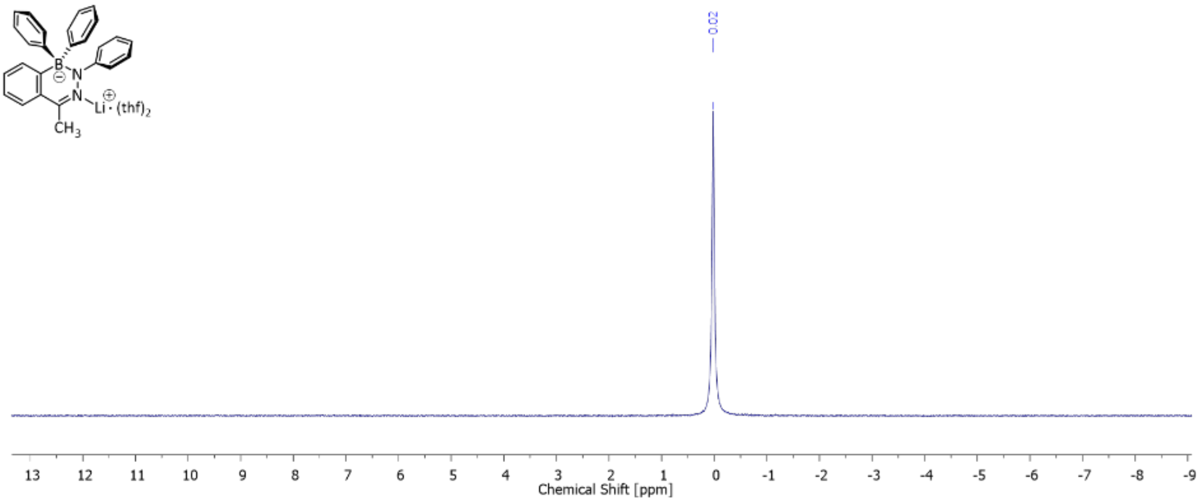


Fig. S97 ^{7}Li NMR spectrum of compound **8Ph[Li](thf)₂** in C_6D_6.

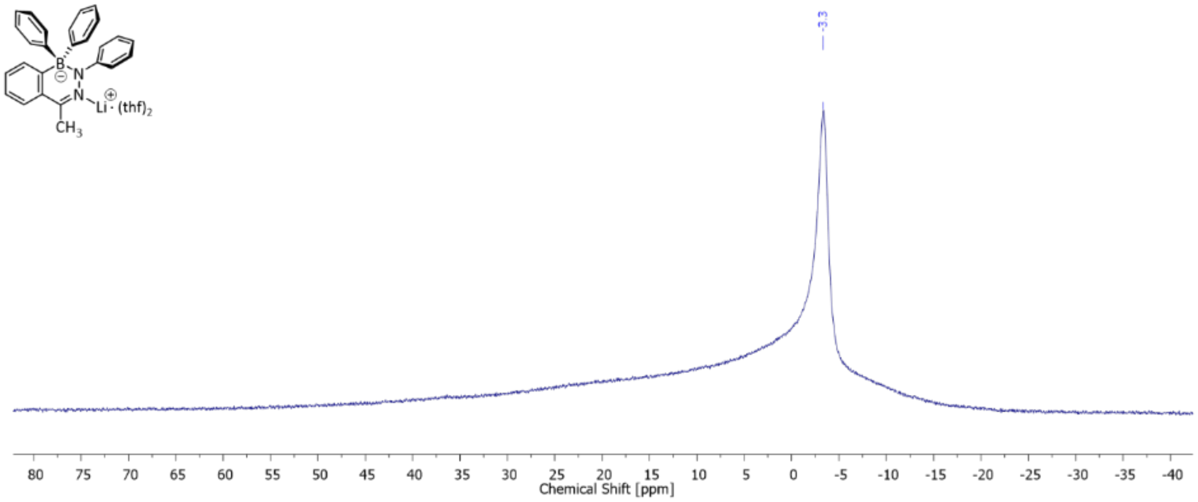


Fig. S98 Background-reduced ^{11}B NMR spectrum of compound **8Ph[Li](thf)$_2$** in C_6D_6.

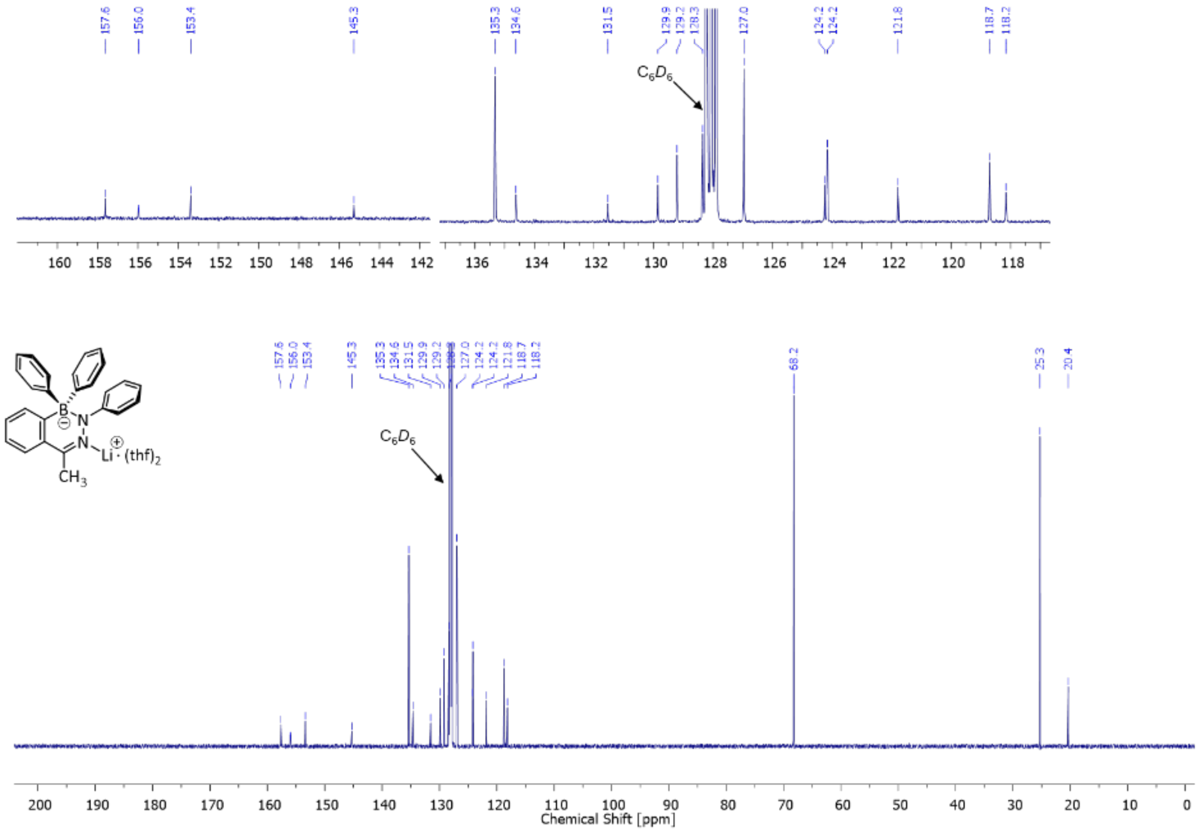


Fig. S99 $^{13}C\{^1H^{11}B\}$ NMR spectrum of compound **8Ph[Li](thf)$_2$** in C_6D_6 (decoupled at −3 ppm).

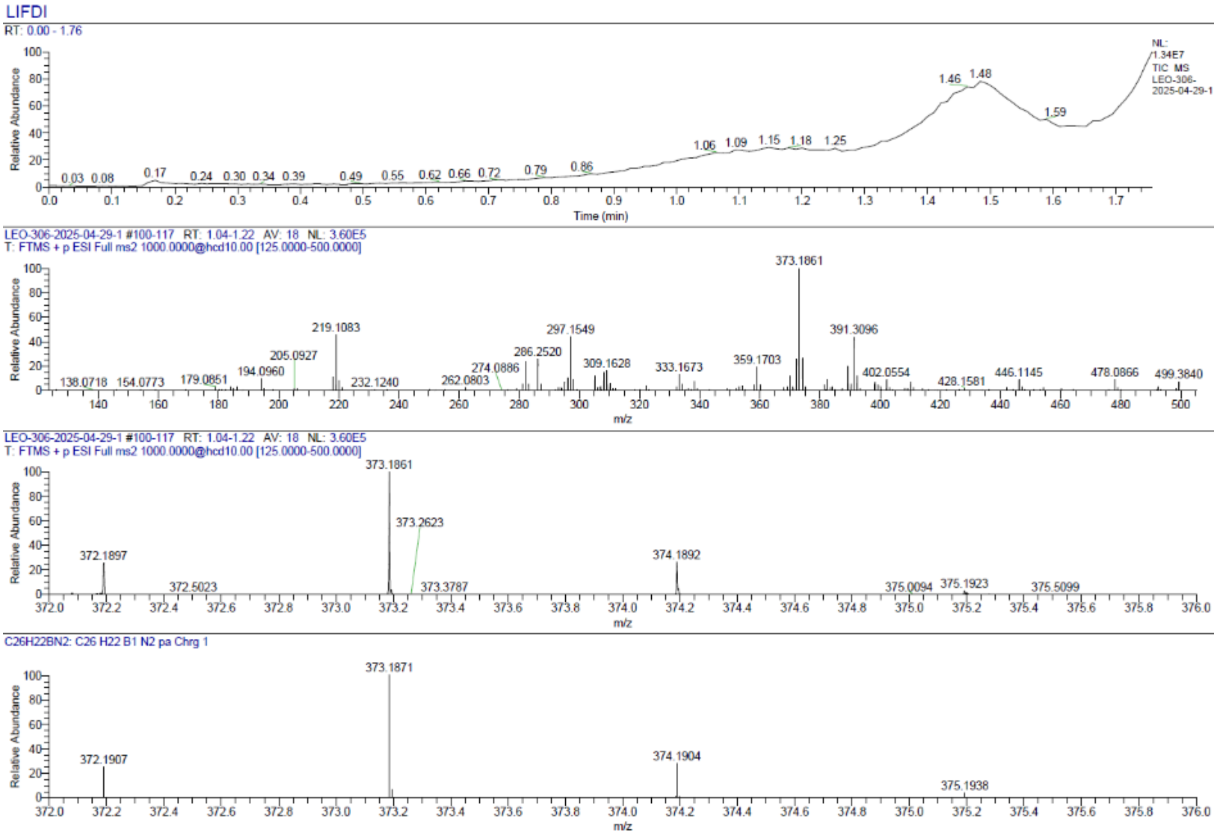


Fig. S100 LIFDI mass spectrum of compound **8Ph[Li]** (THF).

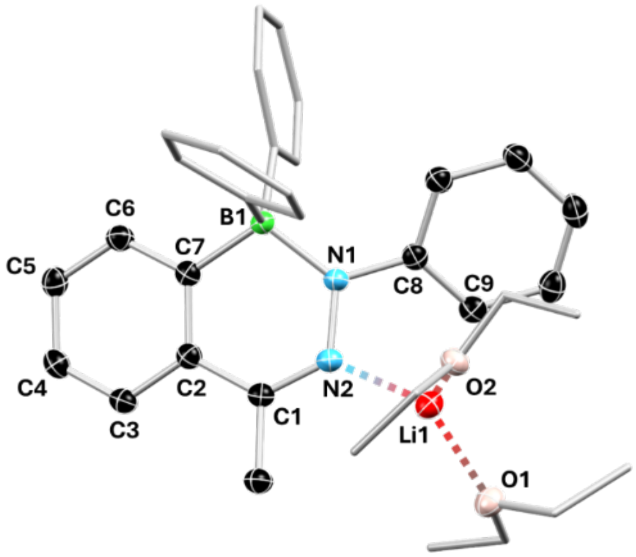
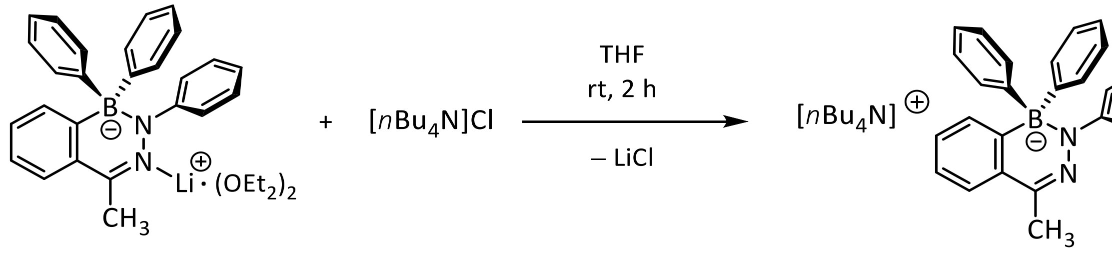


Fig. S101 Molecular structure of compound **8Ph[Li](OEt$_2$)$_2$**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Complexing ether rendered as wireframe for clarity. Selected bond lengths (Å) and angles (°) of **8Ph[Li](OEt$_2$)$_2$**: N2−Li1 2.056(2), B1−N1 1.5813(15), N1−N2 1.3891(12), N2−C1 1.3015(14), C1−C2 1.4667(15), C2−C3 1.4070(15), C3−C4 1.3864(16), C4−C5 1.3920(16), C5−C6 1.3896(16), C6−C7 1.4002(15), C2−C7 1.4063(15), C7−B1 1.6225(16), N1−C8 1.3949(14), B1−N1−N2−C1 23.31(14), B1−C7−C2−C1 5.24(15), N2−N1−C8−C9 29.04(14).

Crystal data: $C_{34}H_{42}BLiN_2O_2$, M_r = 528.44, yellow block, 0.513×0.203×0.154 mm^3, monoclinic space group $P2_1/n$, a = 13.14620(10) Å, b = 13.84270(10) Å, c = 16.70950(10) Å, β = 101.4410(10)°, V = 2980.35(4) Å^3, Z = 4, ρ_{calcd} = 1.178 g·cm^{-3}, μ = 0.548 mm^{-1}, F(000) = 1136, T = 100(2) K, R_1 = 0.0391, wR_2 = 0.0984, 6006 independent reflections [2θ≤150.828°] and 366 parameters.

CCDC number: 2453539

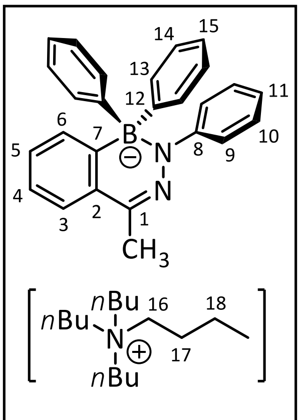
Tetra(*n*-butyl)ammonium 1-Methyl-3-phenyl-4-bis(phenyl)-4,3-borazaroisoquinolinate (8Ph[TBA])



$8Ph[Li](OEt_2)_2$ **8Ph[TBA]** (quant.)

Compound **$8Ph[Li](OEt_2)_2$** (50.0 mg, 94.5 *μ*mol, 1.00 eq.) was dissolved in tetrahydrofurane (3 mL) and tetra(*n*-butyl)ammonium chloride (26.3 mg, 94.5 *μ*mol, 1.00 eq.) was added at ambient temperature. The reaction was stirred for 2 h at ambient temperature. All volatile components were removed *in vacuo*. A separation from the byproduct lithium chloride was not possible due to the similar solubility of both salts in all common solvents. **Yield of 8Ph[TBA]:** quantitative recovery of **8Ph[TBA]** · LiCl, intense neon yellow solid. The compound is air- and moisture-stable.

^{1}H NMR (600 MHz, 298 K, THF-d_8): δ = 7.44 (d, $^3J_{HH}$ = 6.81 Hz, 4H, *H*-13), 7.20 (d, $^3J_{HH}$ = 7.91 Hz, 2H, *H*-9), 6.94-6.96 (m, 1H, *H*-3), 6.87 (t+m, $^3J_{HH}$ = 7.61 Hz, 5H, *H*-14 + *H*-6), 6.71-6.76 (m, 4H, *H*-15 + *H*-4 + *H*-5), 6.64 (t, $^3J_{HH}$ = 7.93 Hz, 2H, *H*-10), 6.19 (t, $^3J_{HH}$ = 7.06 Hz, 1H, *H*-11), 2.85-2.90 (m, 8H, *H*-16), 2.27 (s, 3H, –CH_3), 1.41-1.47 (m, 8H, *H*-17), 1.26 (sext, $^3J_{HH}$ = 7.41 Hz, 8H, *H*-18), 0.93 (t, $^3J_{HH}$ = 7.34 Hz, 12H, ^{n}Bu-CH_3) ppm. **^{11}B NMR** (193 MHz, 298 K, THF-d_8) δ = −4.9 (br s) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, THF-d_8) δ = 160.1 (C_q^B-12), 156.7 (C_q^B-7), 153.9 (C_q^N-8), 136.0 (C_q-1), 135.3 (*C*-13), 134.1 (*C*-6), 132.2 (C_q-2), 126.7 (*C*-10), 126.4 (*C*-4), 126.0 (*C*-14), 123.1 (*C*-5), 122.7 (*C*-15), 120.4 (*C*-3), 118.8 (*C*-9), 114.7 (*C*-11), 58.9 (*C*-16), 24.4 (C-17), 21.3 (–CH_3), 20.3 (C-18), 13.8 (^{n}Bu-CH_3) ppm. Crystalline material of **8Ph[TBA]** as fluorescent neon yellow plates for single-crystal XRD was obtained by storing a saturated H_2O/THF mixture at ambient temperature in a vial open to the atmosphere.



8Ph[TBA]

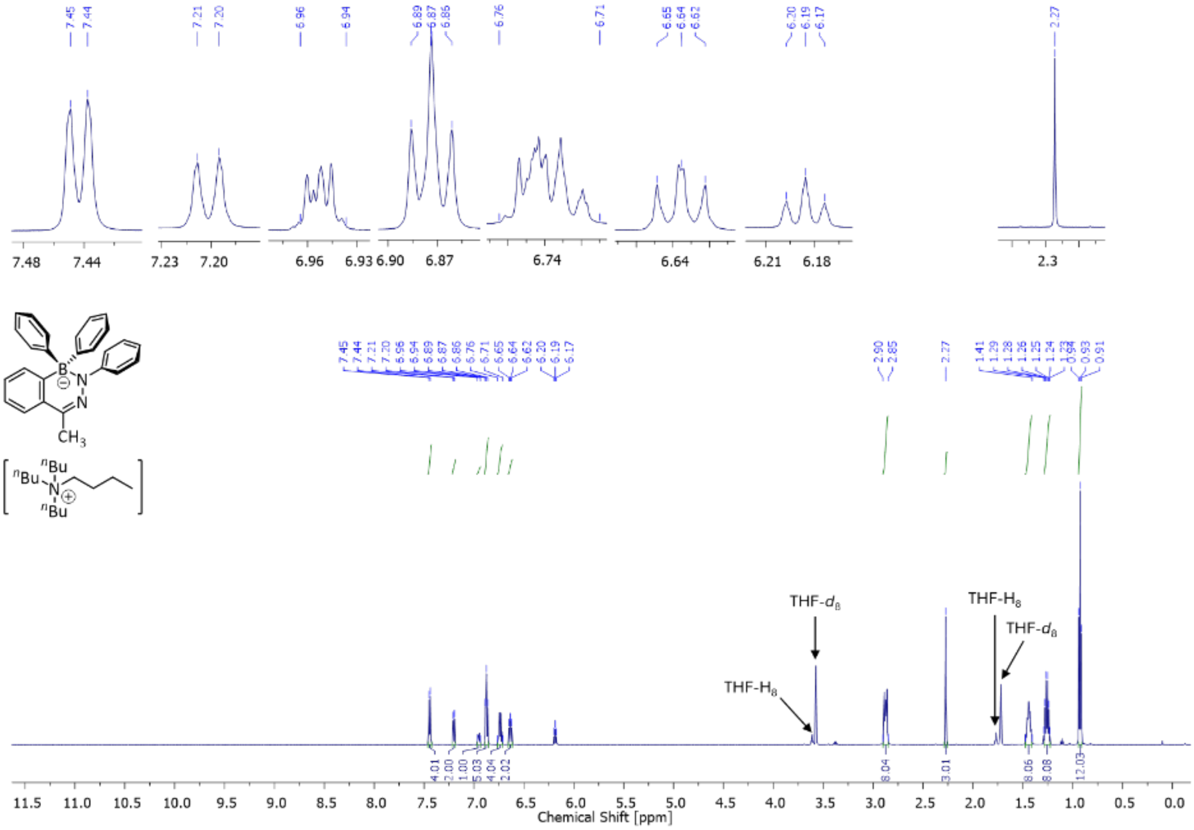


Fig. S102 ^{1}H NMR spectrum of compound **8Ph[TBA]** in THF-d_8.

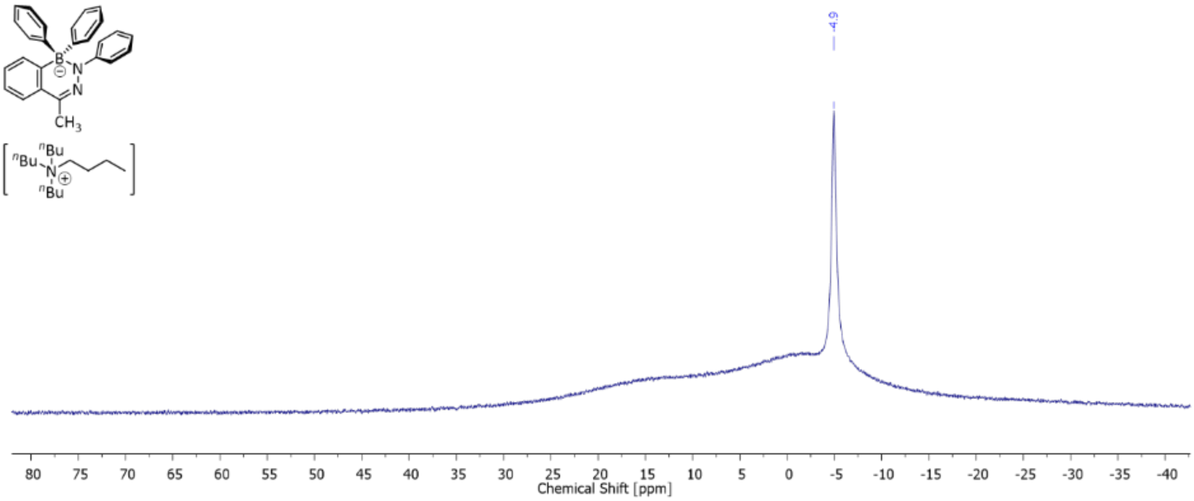


Fig. S103 Background-reduced ^{11}B NMR spectrum of compound **8Ph[TBA]** in THF-d_8.

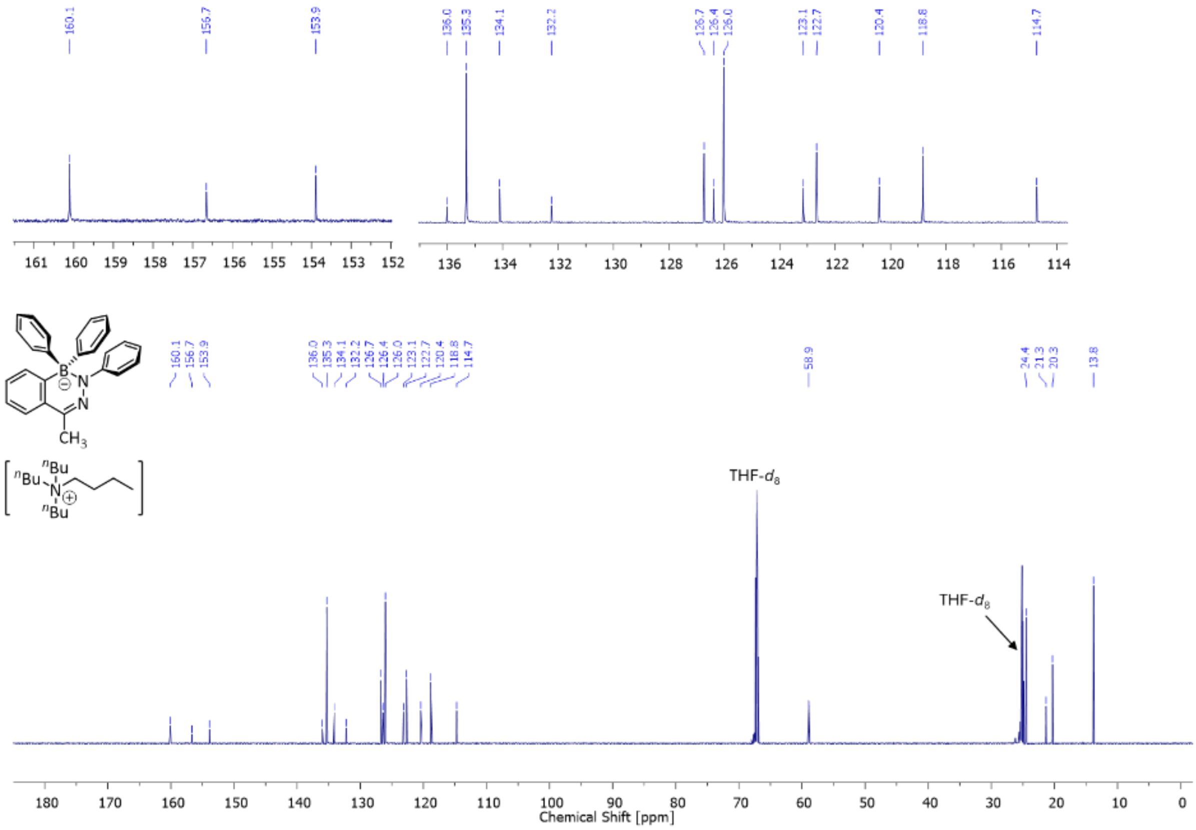


Fig. S104 ^{13}C{^{1}H^{11}B} NMR spectrum of compound **8Ph[TBA]** in THF-d_8 (decoupled at –6 ppm).

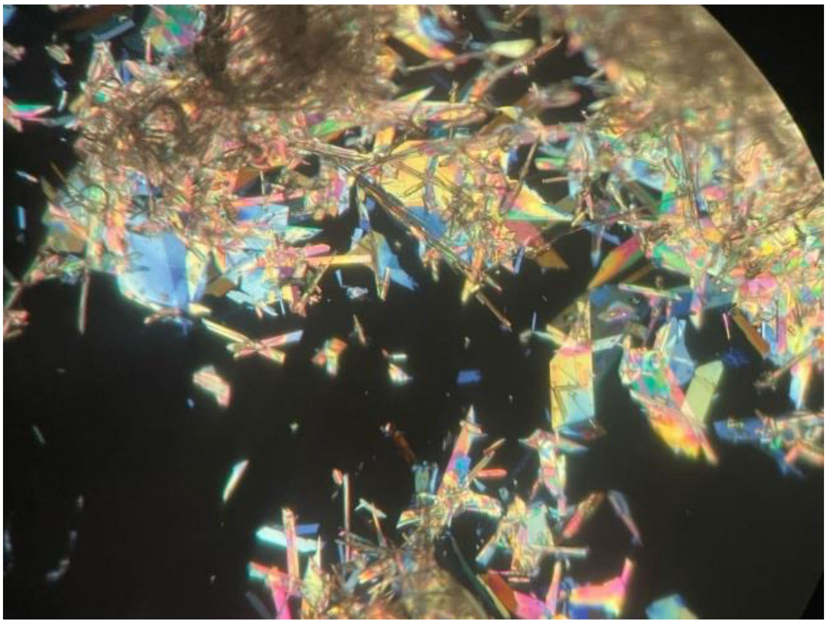
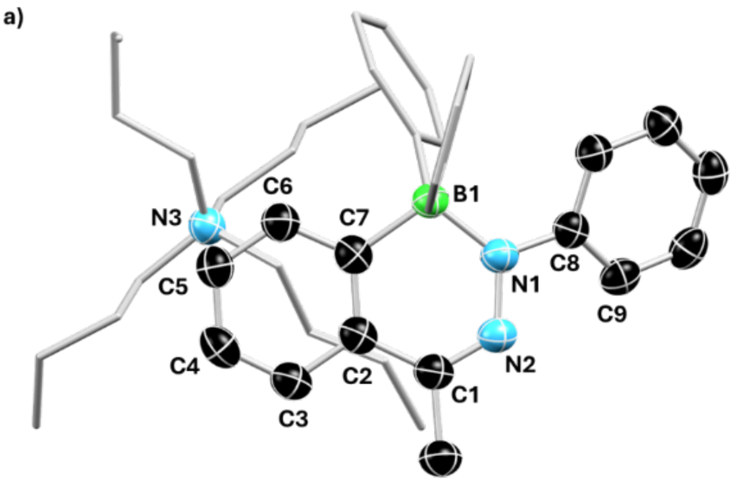
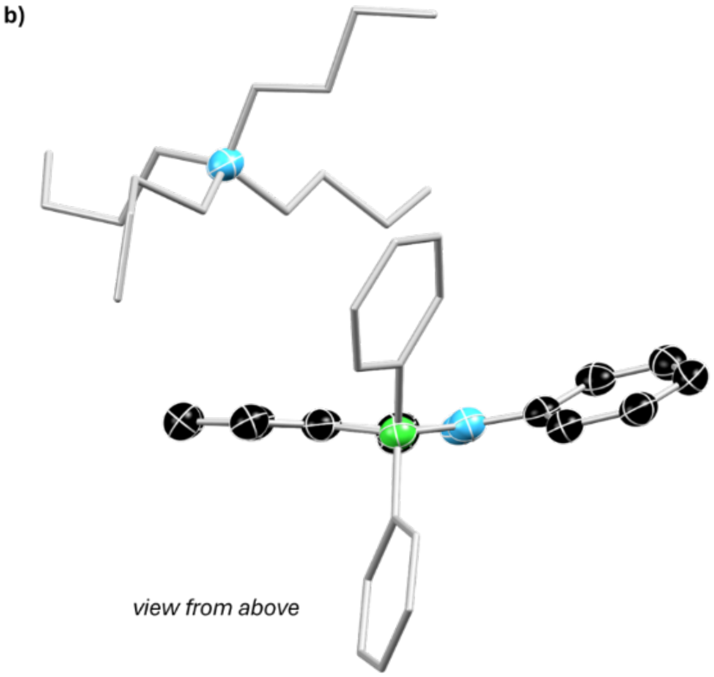


Fig. S106 Crystals of compound **8Ph[TBA]**, grown from a THF/H_2O mixture on air.



side view



view from above

Fig. S105 Molecular structure of compound **8Ph[TBA]**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted, B–Ph substituents and *n*-butyl groups rendered as wireframe. Due to the presence of a whole molecule disorder of the borate anion, no discussion of bond lengths is possible.

Crystal data: $C_{42}H_{58}BN_3$, $M_r = 615.72$, yellow plate, 0.170×0.120×0.090 mm^3, monoclinic space group $P2_1/n$, $a = 9.6431(2)$ Å, $b = 18.5866(4)$ Å, $c = 20.3530(4)$ Å, $\beta = 95.344(2)°$, $V = 3632.06(13)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.126$ g·cm^{-3}, $\mu = 0.482$ mm^{-1}, $F(000) = 1344$, $T = 100(2)$ K, $R_1 = 0.0918$, $wR_2 = 0.2596$, 7309 independent reflections [$2\theta \leq 151.558°$] and 426 parameters.

The reflections [1 1 5], [−1 1 4], [0 6 3], [2 3 5] and [2 4 4] were removed from the refinement as outliers. The structure shows a whole molecule disorder with an occupancy factor of 95.7% regarding to the second free variable. The geometry of the disordered diazaborinate part (residues 11, 21, 31, and 41) were constrained using AFIX 6 during refinement. The atoms of the disordered diazaborinate part (residues 11, 21, 31, and 41) were refined isotropic with constrained U_{iso}. The value of this tensor was computed using a free variable and SIMU command.

CCDC number: 2453537

Appendix

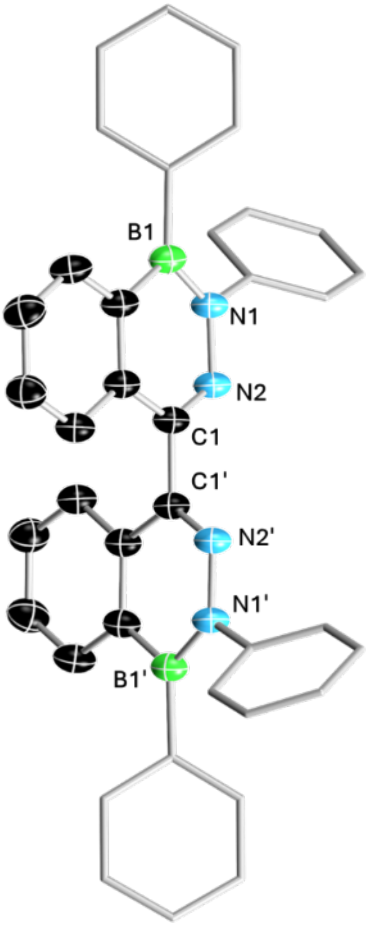


Fig. S107 Molecular structure of decomposition product **9**. Ellipsoids drawn at 50% probability (100 K). All H-atoms omitted. Selected bond lengths (Å) and angles (°) of **9**: B1–N1 1.424(2), N1–N2 1.394(1), N2–C1 1.295(2), C1–C1' 1.505(1), B1–N1–N2–C1 2.5(2), N2–C1–C1'–N2' 79.5(1).

Crystal data: $C_{38}H_{28}B_2N_4$, M_r = 562.26, red plate, 0.060×0.060×0.030 mm^3, monoclinic space group $C2/c$, a = 16.5211(3) Å, b = 12.6459(2) Å, c = 15.0585(3) Å, β = 112.305(2)°, V = 2910.68(10) Å^3, Z = 4, ρ_{calcd} = 1.283 g·cm^{-3}, μ = 0.578 mm^{-1}, F(000) = 1176, T = 100(2) K, R_1 = 0.0465, wR_2 = 0.1043, 2925 independent reflections [$2\theta \leq 147.416°$] and 199 parameters.

CCDC number: 2453634

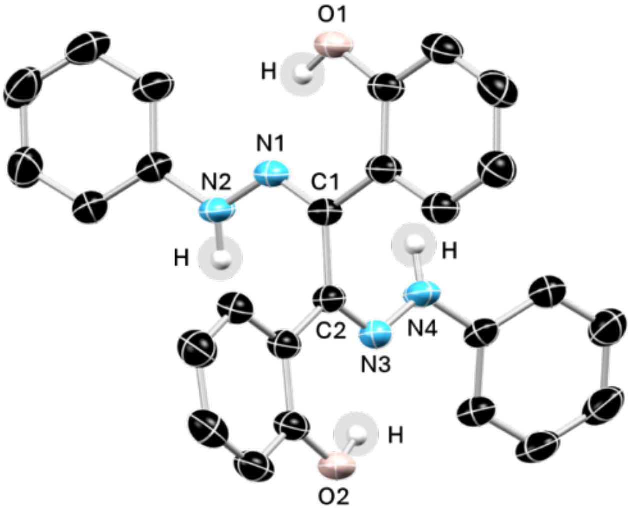


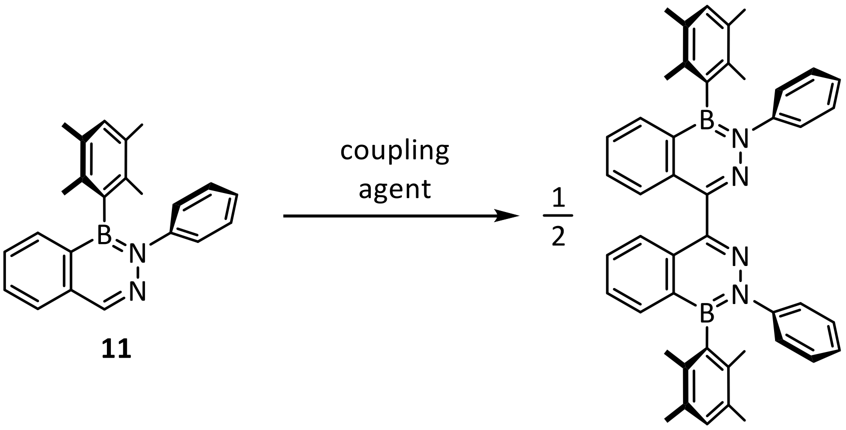
Fig. S108 Molecular structure of decomposition product **10**. Ellipsoids drawn at 50% probability (100 K). All H-atoms except for those bound to a heteroatom omitted. Selected bond lengths (Å) and angles (°) of **10**: C1–N1 1.297(2), N1–N2 1.347(2), C1–C2 1.505(3), C2–N3 1.293(3), N3–N4 1.353(3), N1–C1–C2–N3 97.9(2).

One of the co-crystallized benzene molecules was disordered. Geometry was idealized using AFIX66. One half of the molecule is symmetry generated due to its position on symmetry elements in the cell.

Crystal data: $C_{38}H_{34}N_4O_2$, M_r = 578.69, clear red needle, 0.230×0.030×0.030 mm^3, triclinic space group $P\bar{1}$, a = 10.1284(4) Å, b = 12.2505(5) Å, c = 13.3672(5) Å, α = 82.511(3)°, β = 89.613(3)°, γ = 70.539(4)°, V = 1549.29(11) Å^3, Z = 2, ρ_{calcd} = 1.240 g·cm^{-3}, μ = 0.612 mm^{-1}, $F(000)$ = 612, T = 100(2) K, R_1 = 0.0882, wR_2 = 0.1690, 6069 independent reflections [$2\theta \leq 149.226°$] and 428 parameters.

CCDC number: 2453635

Table S2 Attempted reaction conditions for a rational synthesis of a bis(diazaborinine) in analogy to the decomposition product **9**, by coupling of a neutral Duryl-congener **11** (to avoid hydrolysis / oxidation to **10**) via Scholl-reaction conditions or reductive coupling.



11

Starting Material	Coupling Agent	Reaction conditions	Observation	Possible Outcome
11	$FeCl_3$	2 eq., CD_2Cl_2	red solution ^{1}H: broad	**11**→$FeCl_3$ adduct
11	$FeCl_3$	cat., C_6D_6	red solution ^{1}H: broad	**11**→$FeCl_3$ adduct
11	$FeCl_3$	1 eq., $CDCl_3$	red solution ^{11}B: 57 ppm	**11**→$FeCl_3$ adduct
11	$AlCl_3$	1 eq., C_6D_6	Colorless	**11**→$AlCl_3$ adduct (observed via XRD)
11	$AlCl_3$	2.5 eq., CD_2Cl_2	red solution (fast)	new species but *H*-1 still observed as singlet
11	$AlCl_3$	2.5 eq., bromobenzene-*d*$_5$	red solution (slow)	
11	$AlCl_3$	xs., $CDCl_3$	violet oil	decomposition
11	$AlCl_3$, $CuCl_2$ (cat.)	1 eq., CD_2Cl_2	violet paramagnet.	-
11	DDQ + TFA	CD_2Cl_2	no reaction (several days at 50 °C)	[**11**]H$^+$[TFA]$^-$ recovered
11	Lithium naphthalene	1.00 eq., THF / DME	red solution	[**11**]$^{\cdot-}$ radical anion
11	Li-sand	xs., THF	red solution	[**11**]$^{\cdot-}$ radical anion
11	KC_8	xs., C_6D_6 / THF	no reaction	**11**
11	B_2pin_2[7]	0.5 eq., C_6D_6	no reaction	no B_2pin_2 adduct formation

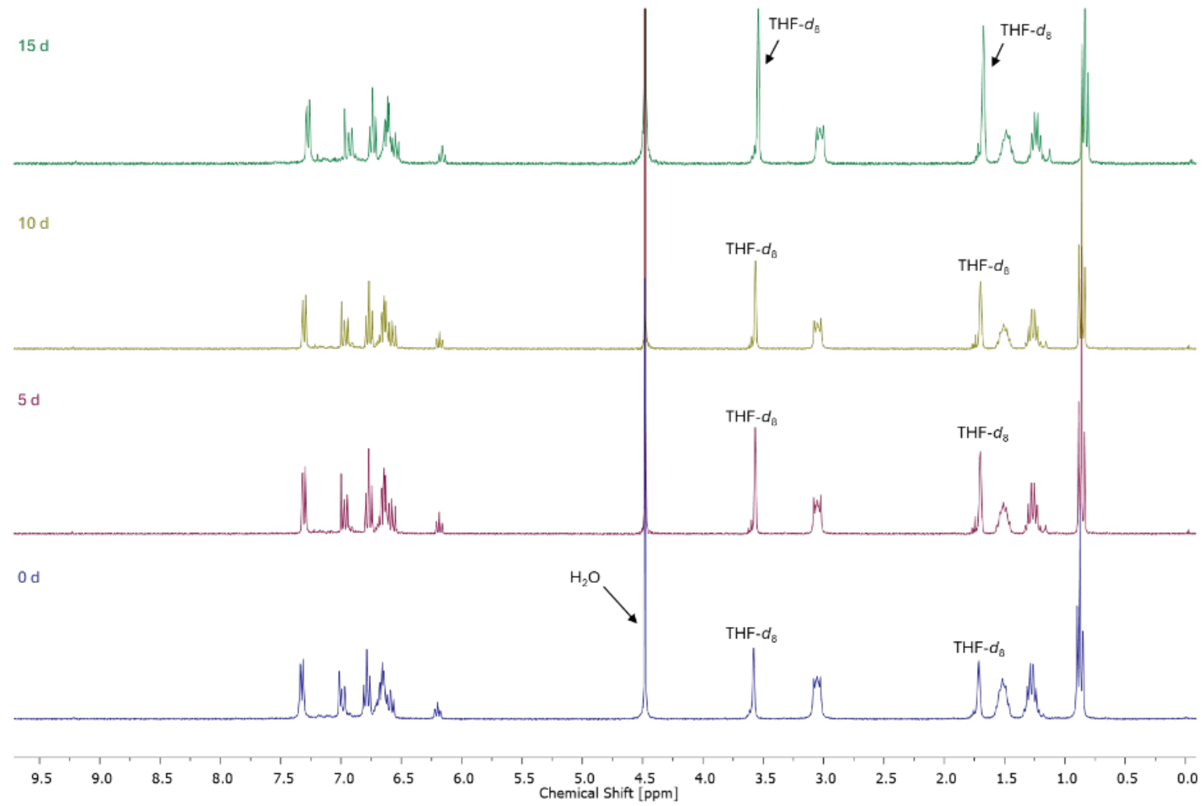


Fig. S109 Stacked hydrolysis study ^{1}H NMR spectra of compound **5Ph[TBA]** in a 1:1 mixture of THF-d_8 and H_2O after 10 min, 5 d, 10 d and 15 d under Ar-atmosphere at ambient temperature.

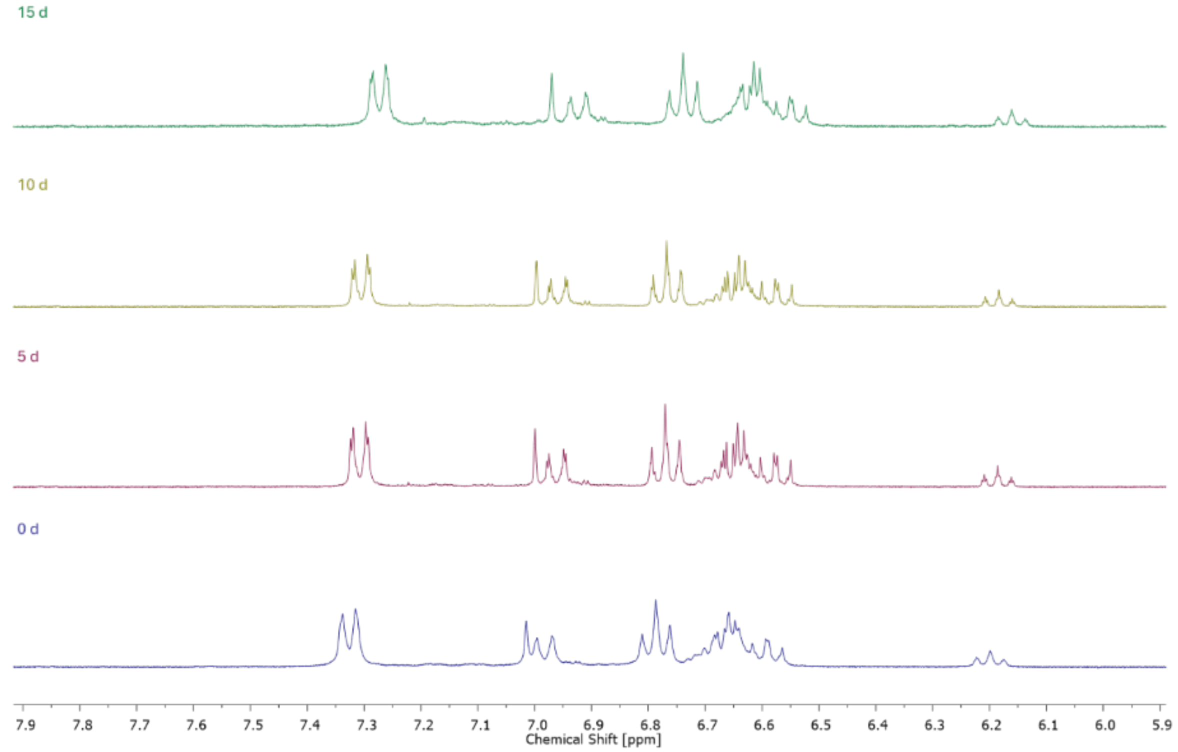


Fig. S110 Stacked hydrolysis study ^{1}H NMR spectra (aromatic region) of compound **5Ph[TBA]** in a 1:1 mixture of THF-d_8 and H_2O after 10 min, 5 d, 10 d and 15 d under Ar-atmosphere at ambient temperature.

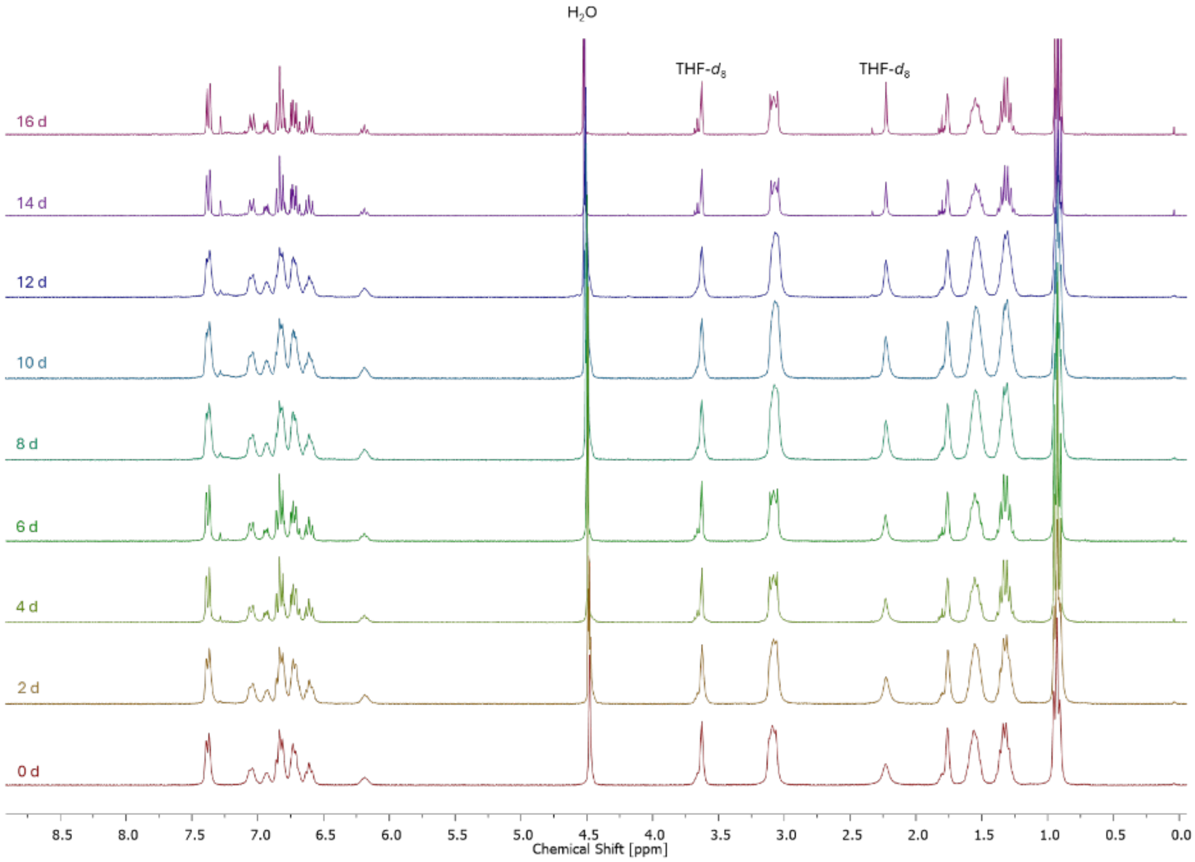


Fig. S111 Stacked hydrolysis study ^1H NMR spectra of compound **8Ph[TBA]** in a 1:1 mixture of THF-d_8 and H_2O open to the atmosphere after over a time period of 16 d at ambient temperature.

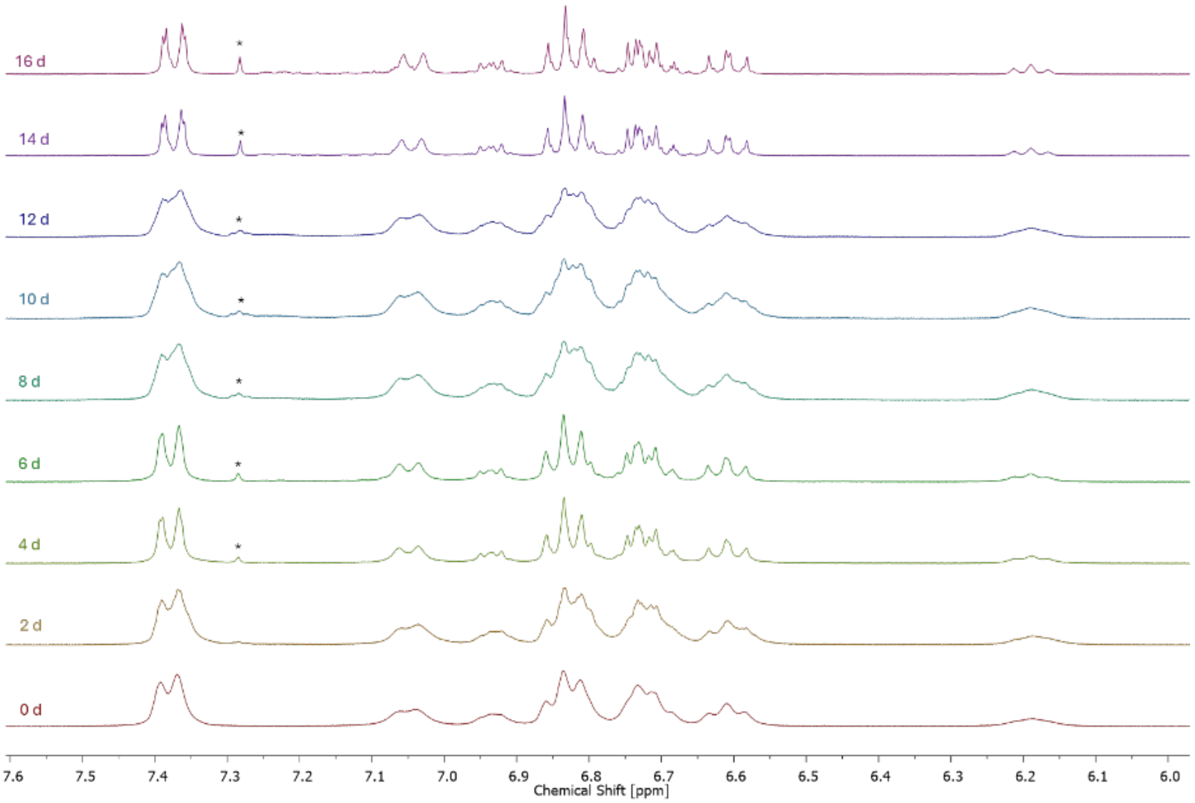


Fig. S112 Stacked hydrolysis study ^1H NMR spectra (aromatic region) of compound **8Ph[TBA]** in a 1:1 mixture of THF-d_8 and H_2O open to the atmosphere after over a time period of 16 d at ambient temperature. The marked impurity corresponds to a C_6H_6 impurity with increasing intensity as **8Ph[TBA]** slowly precipitates.

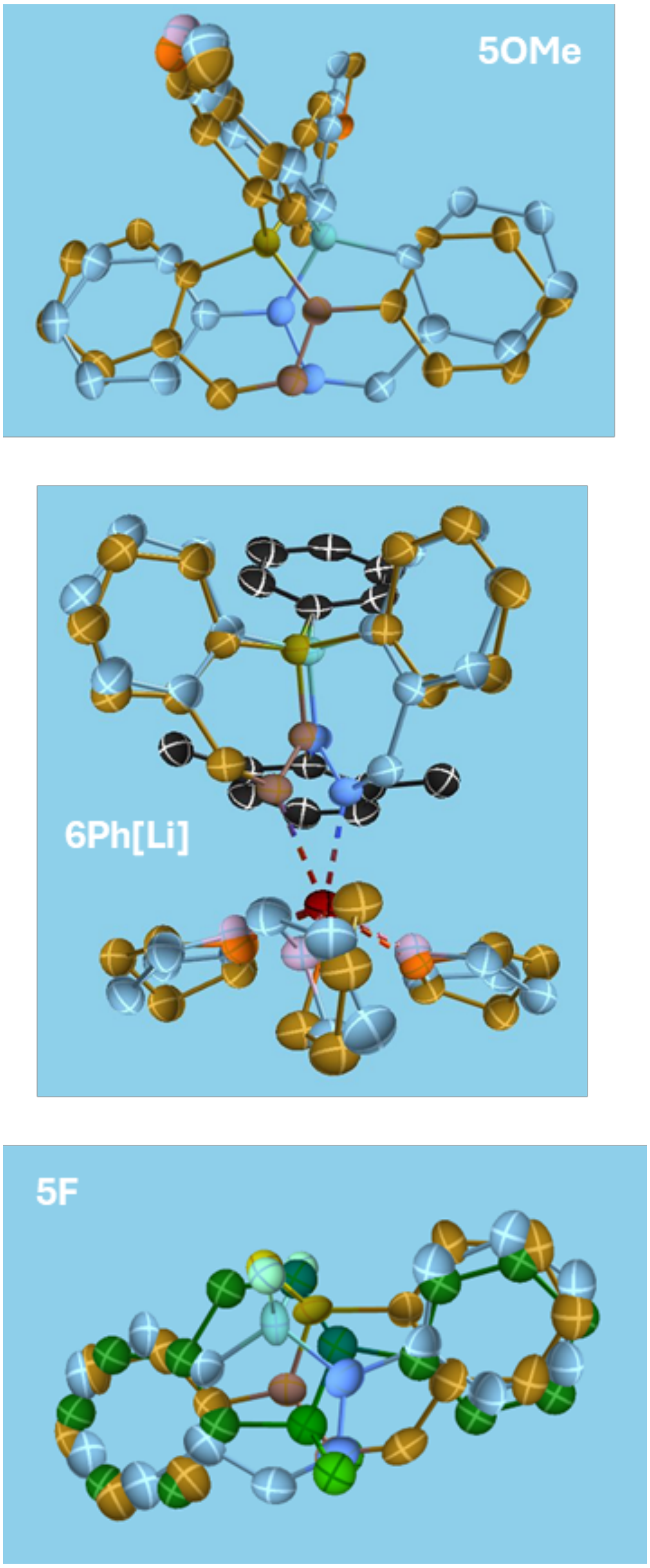


Fig. S113 Examples **5OMe[Li]** (counter cation omitted for clarity), **6Ph[Li]** and **5F[TBA]** (counter cation omitted for clarity) showcasing different kinds of 2- or 3-fold whole molecule disorders, that generally prevent in-depth XRD discussion for these and other derivatives (ShelXle screenshot).

3 Spectroscopic details

Table S3 Photophysical data of the compounds **1R-4R** in THF.

Compound	$\lambda_{abs,\ max}$ [nm]
1OH	307
1OTMS	304
2OH	304
2OTMS	305
3OH	306
3OTMS	301
3Ph	300
4OH	306
4OTMS	300

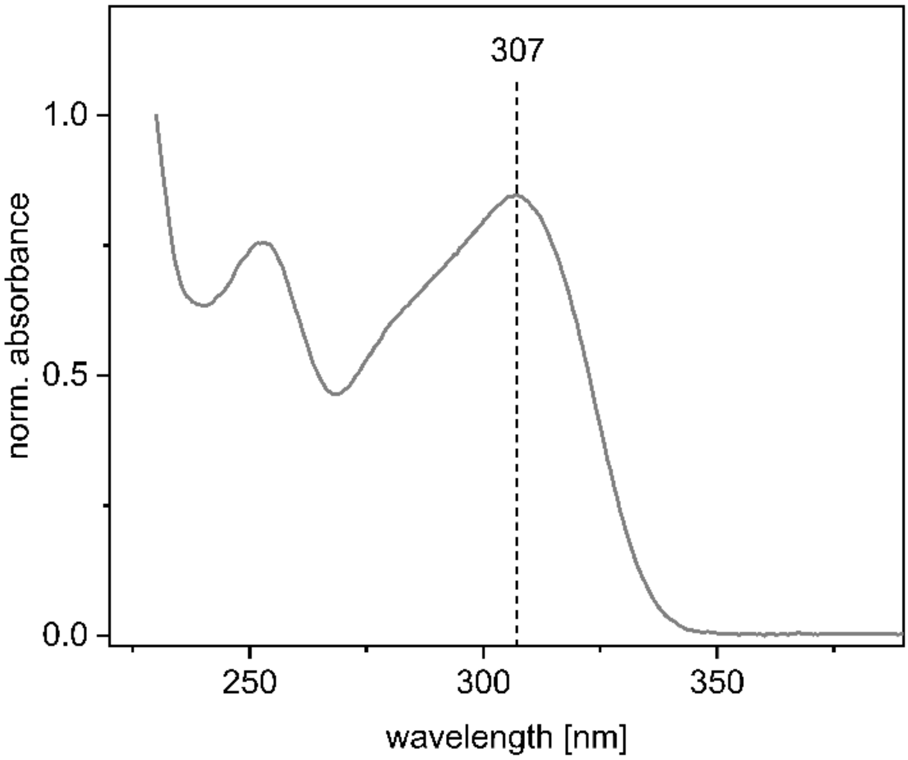


Fig. S114 Normalized absorption spectrum of **1OH** in THF.

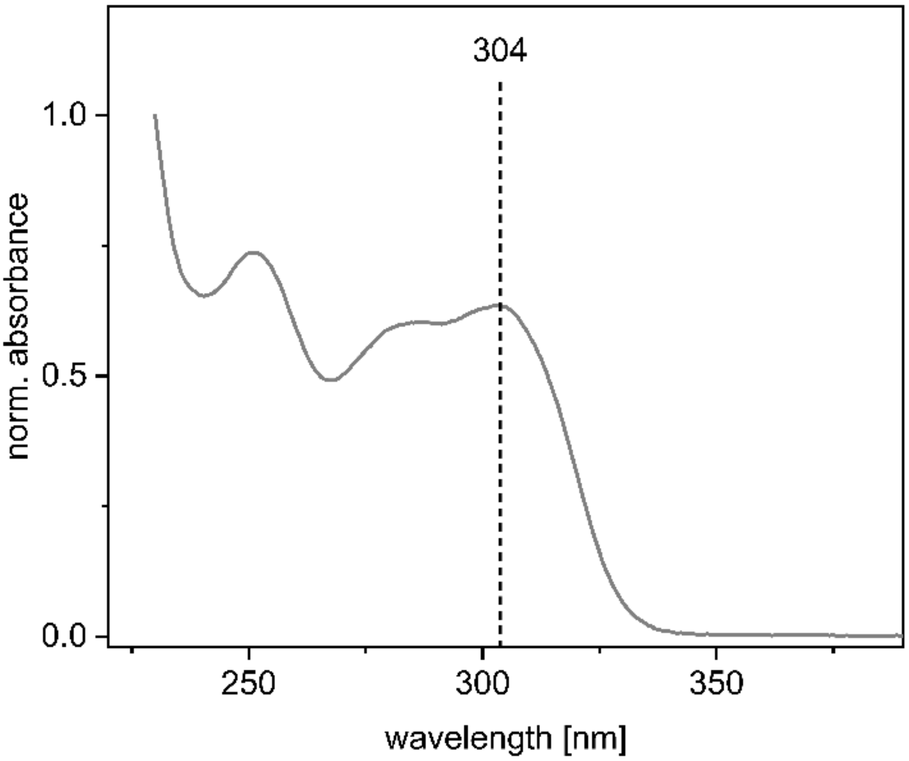


Fig. S115 Normalized absorption spectrum of **1OTMS** in THF.

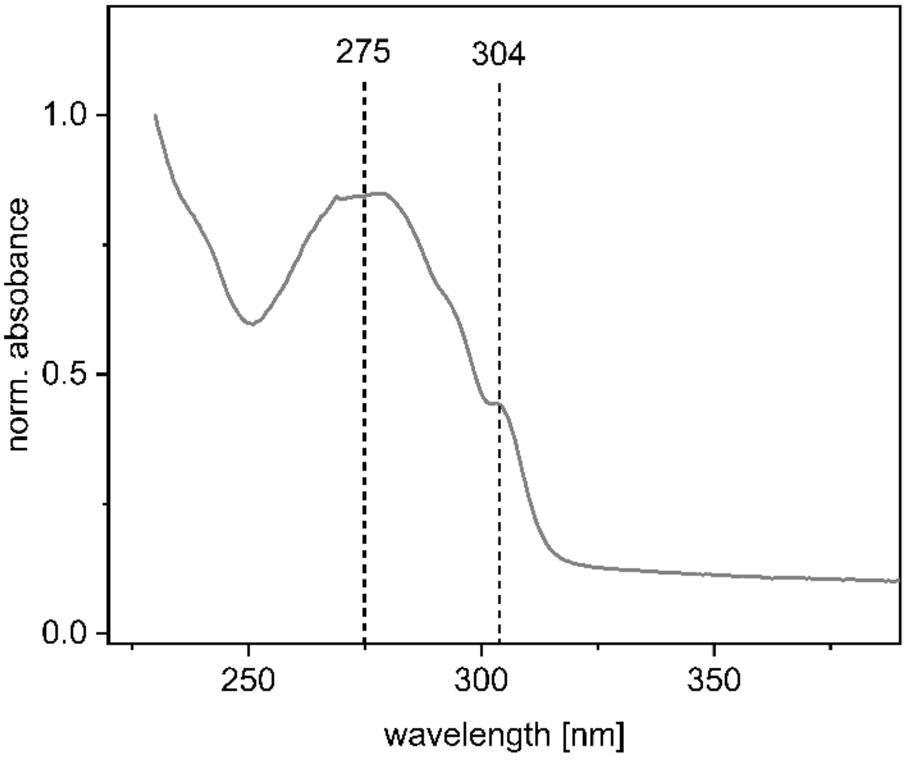


Fig. S116 Normalized absorption spectrum of **2OH** in THF.

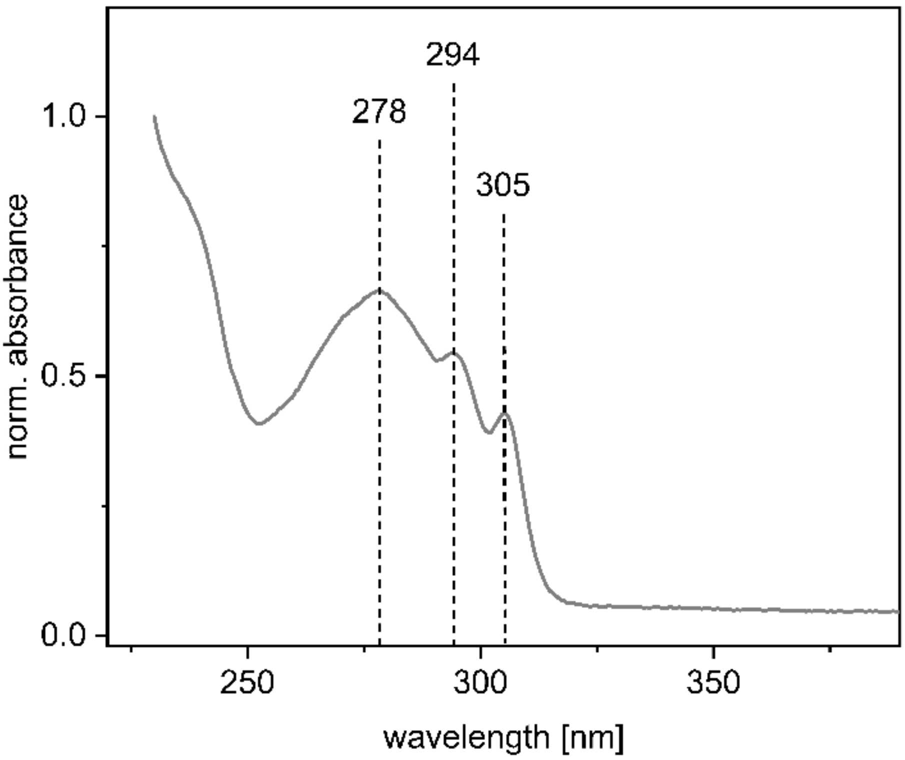


Fig. S117 Normalized absorption spectrum of **2OTMS** in THF.

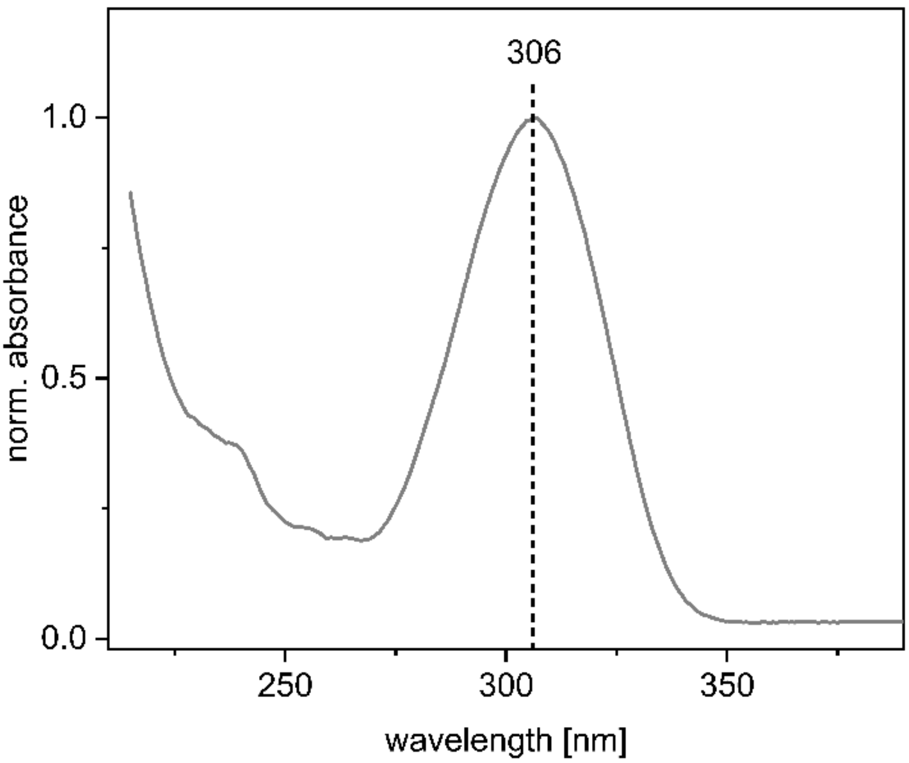


Fig. S118 Normalized absorption spectrum of **3OH** in THF.

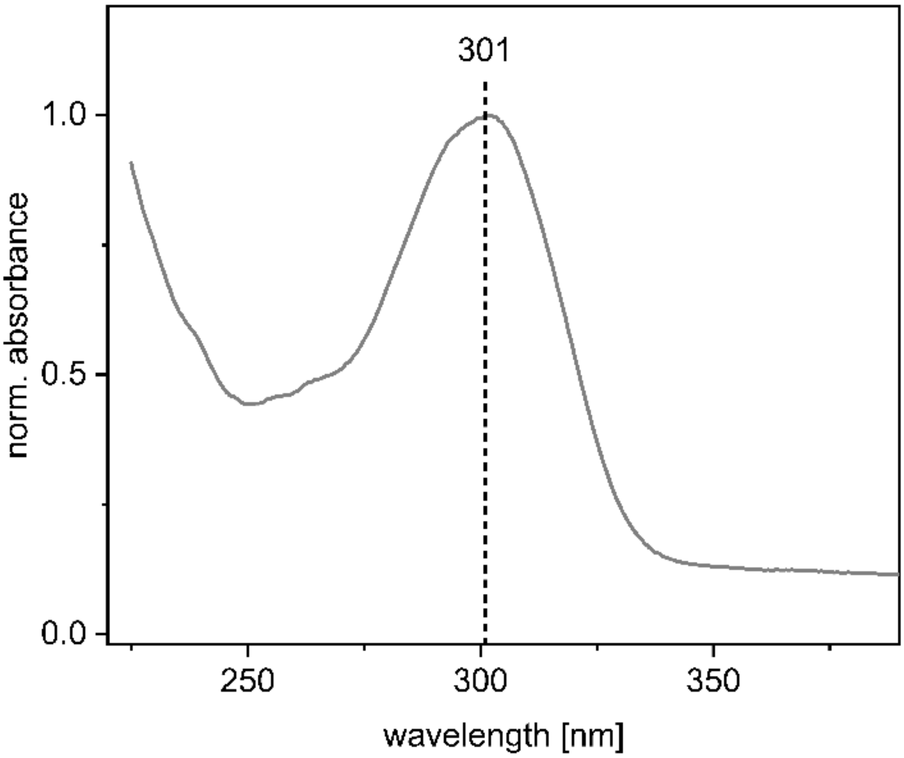


Fig. S119 Normalized absorption spectrum of **3OTMS** in THF.

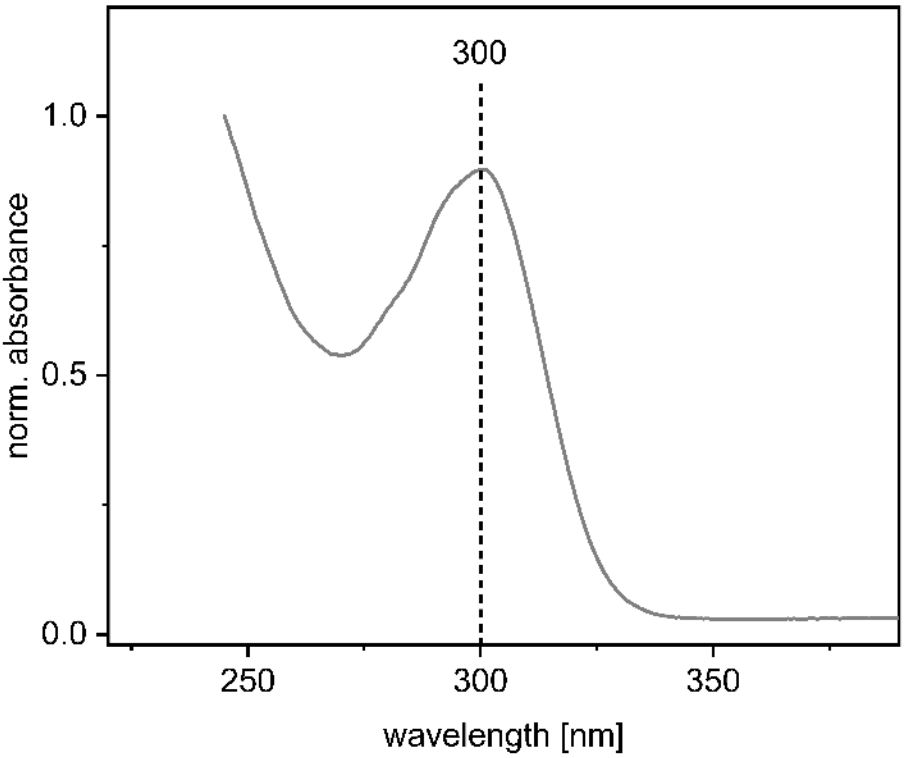


Fig. S120 Normalized absorption spectrum of **3Ph** in THF.

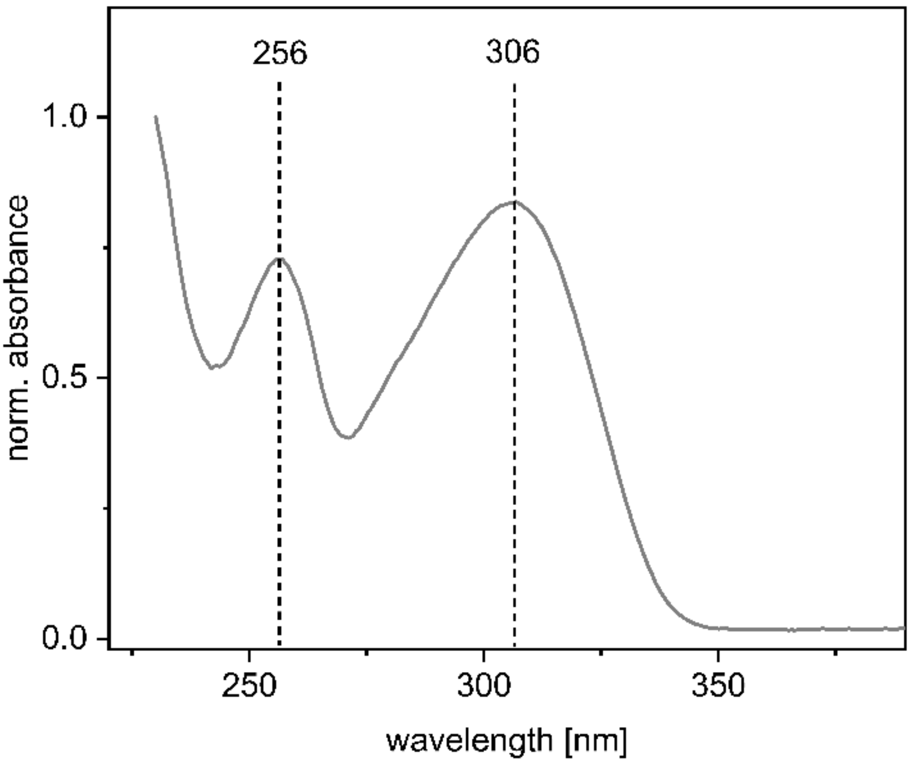


Fig. S121 Normalized absorption spectrum of **4OH** in THF.

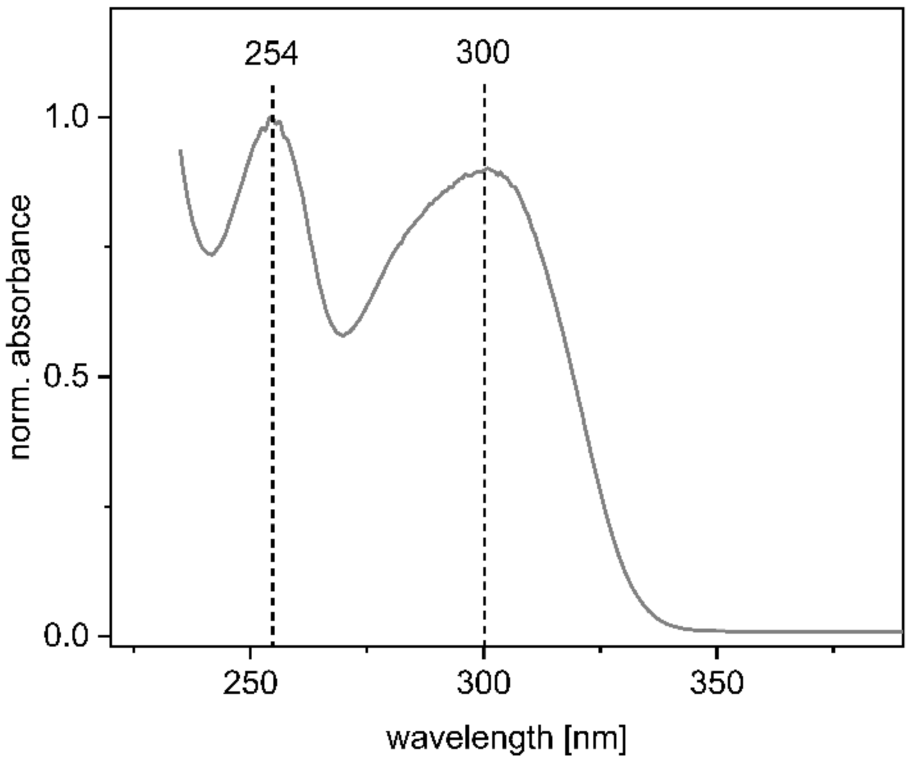


Fig. S122 Normalized absorption spectrum of **4OTMS** in THF.

Table S4 Photophysical data of the compounds **5R-8R** in THF and as PMMA film.

Compound	$\lambda_{\text{abs, max}}$ [nm]	$\lambda_{\text{abs, max}}^{[a]}$ [nm]	$\lambda_{\text{em, max}}$ [nm]	$\lambda_{\text{em, max}}^{[a]}$ [nm]	$\Phi_{\text{fl}}^{[b]}$ [%]	$\Phi_{\text{fl}}^{[a; b]}$ [%]	$\tau^{\text{fl [a]}}$ [ns]
5Ph[Li]	398	396	460	455	18	30	1.70; 2.57 (74%)
5Ph[TBA]	398	399	459	463	19	27	1.63; 2.57 (77%)
5F[TBA]	355	354	428	427	-	37	-
5Me[Li]	404	415	471	471	2	27	-
5Thio[Li]	388	384	450	448	19	38	1.03 (74%); 1.59
5CF$_3$[Li]	395	391	453	445	19	42	-
5OMe[Li]	398	403	457	457	18	25	1.88 (71%); 3.23
5Biph[Li]	404	406	467	457	18	32	1.62; 2.91 (89%)
5Cbz[Li]	397	395	456	451	12	34	1.65; 2.34 (57%)
5Ph[Me]	415	-	-	-	-	-	-
6Ph[Li]	390	387	501	483	7	3	2.16; 3.61 (72%)
7Ph[Li]	410	410	465	477	63	28	5.63
8Ph[Li]	403	402	463	463	26	5	2.96
8Ph[TBA]	403	404	464	474	26	9	2.92 (95%); 6.81

[a] PMMA film [b] Fluorescence quantum yields, determined using an integration sphere.

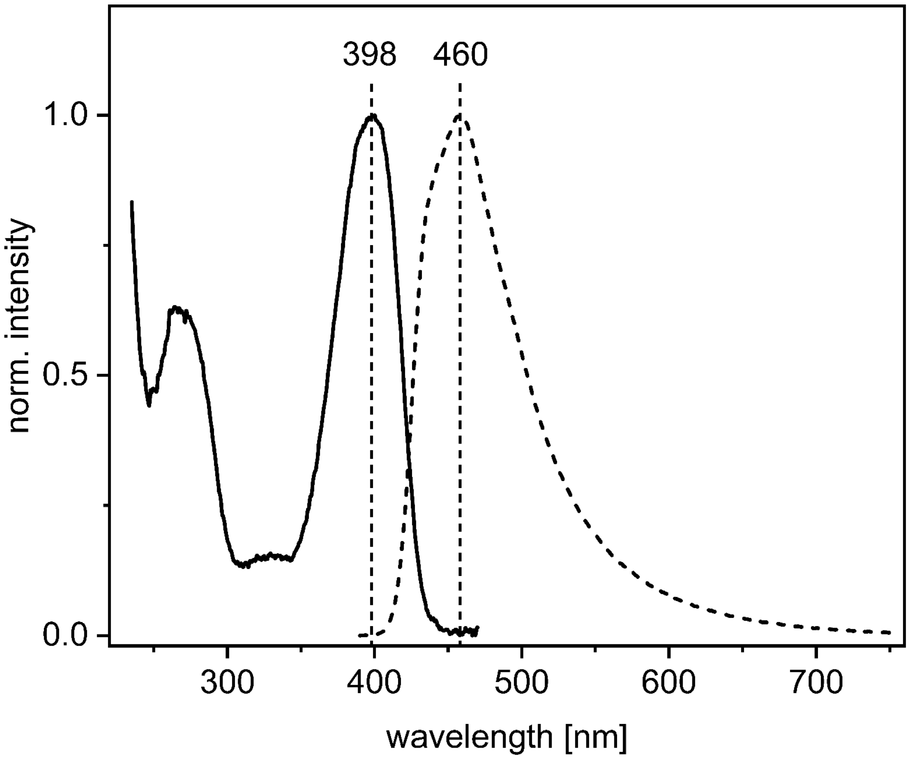


Fig. S123 Normalized absorption and emission spectra of **5Ph[Li]** in THF.

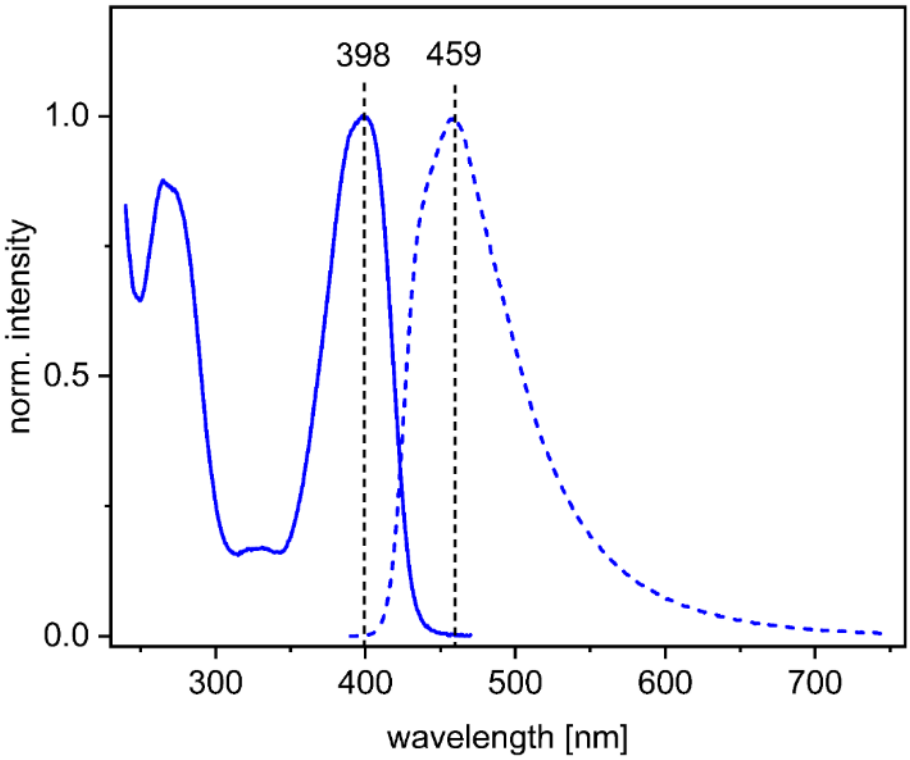


Fig. S124 Normalized absorption and emission spectra of **5Ph[TBA]** in THF.

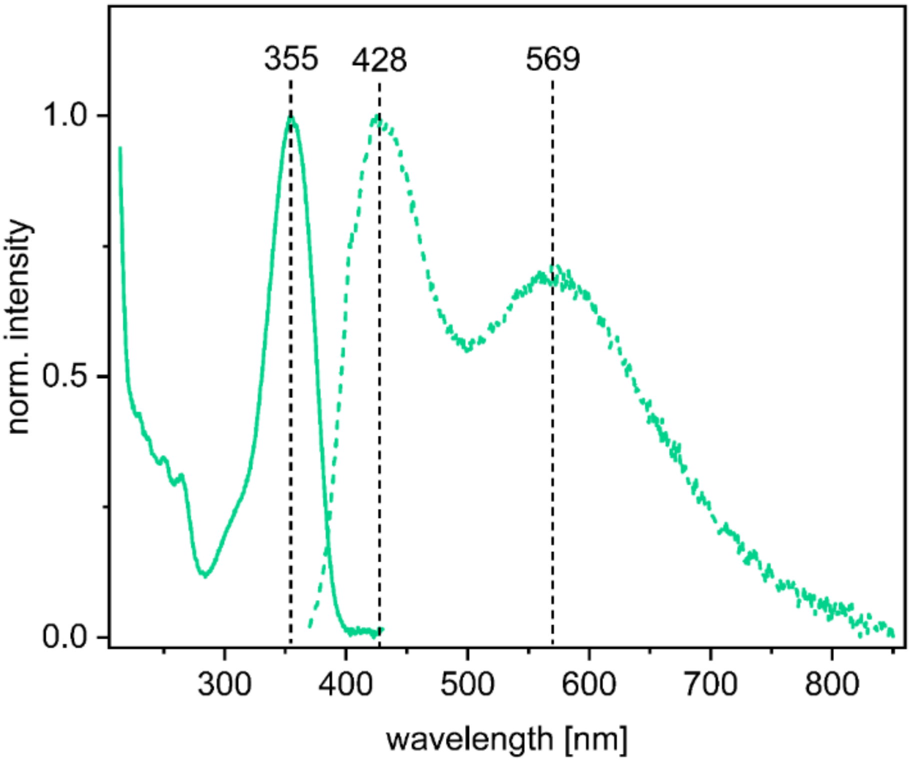


Fig. S125 Normalized absorption and emission spectra of **5F[TBA]** in THF.

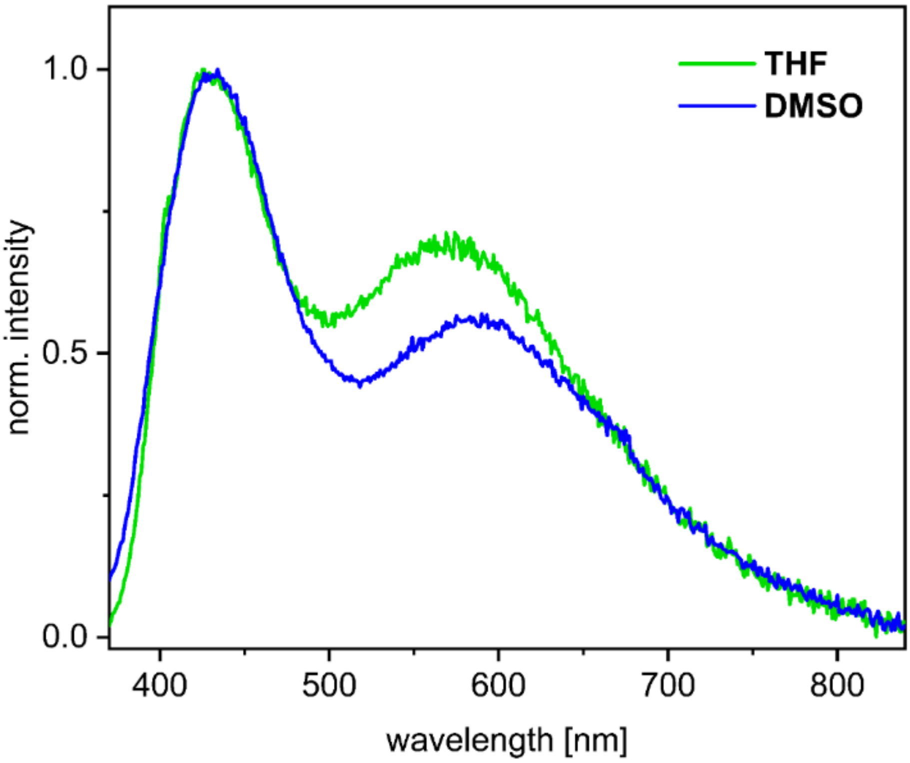


Fig. S126 Normalized emission spectra of **5F[TBA]** in THF and DMSO.

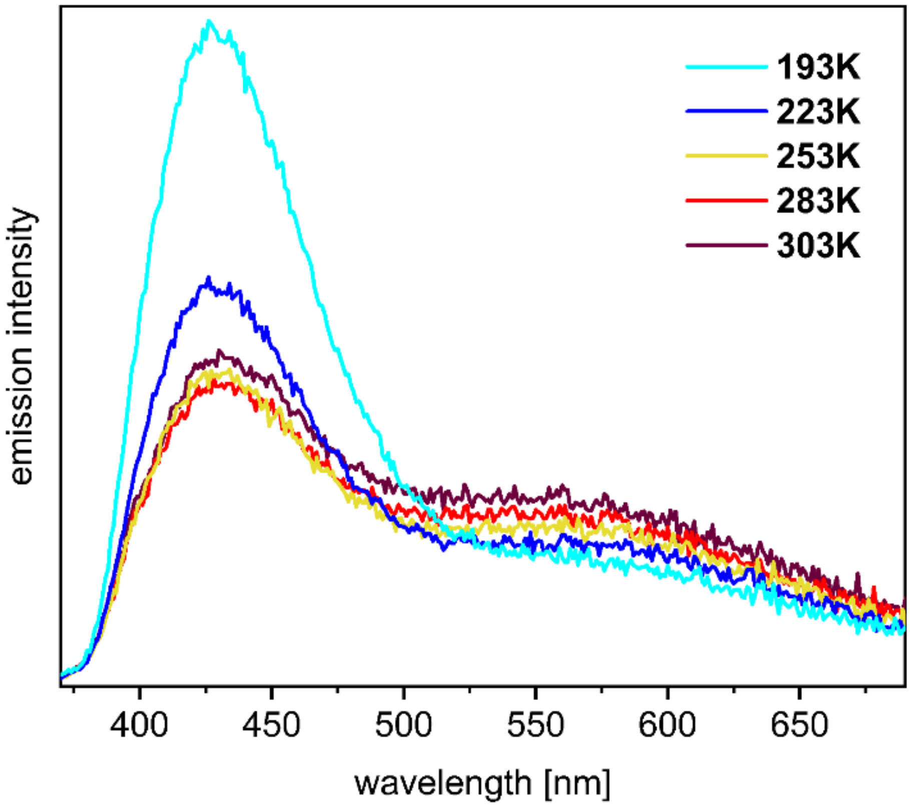


Fig. S127 Emission spectra of **5F[TBA]** in 2-MeTHF by variable-temperature.

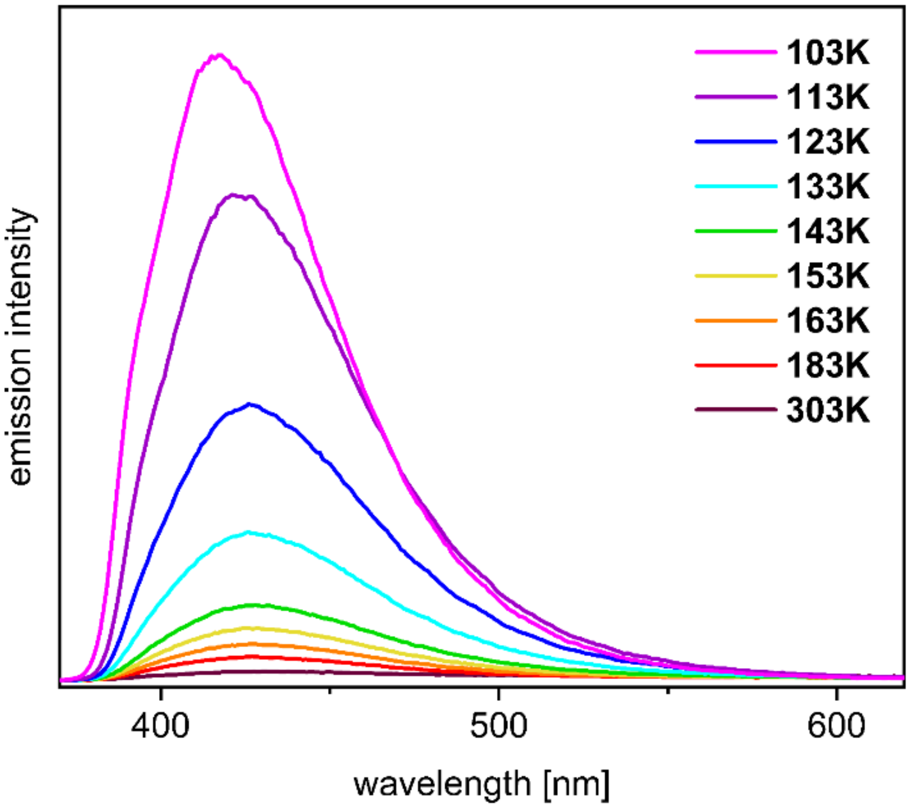


Fig. S128 Emission spectra of **5F[TBA]** in 2-MeTHF by variable-temperature.

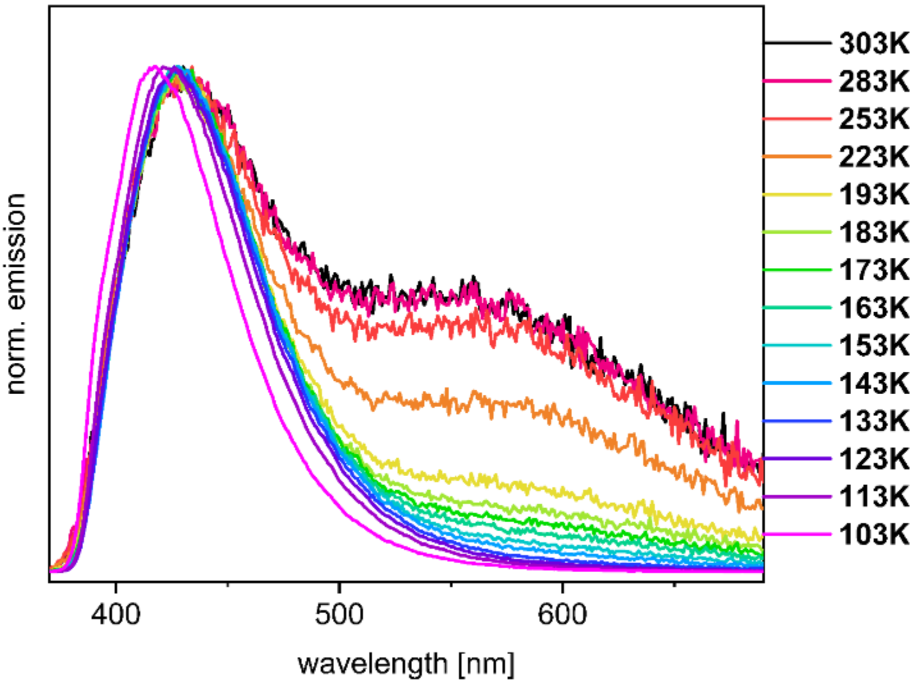


Fig. S129 Normalized emission spectra of **5F[TBA]** in 2-MeTHF by variable-temperature.

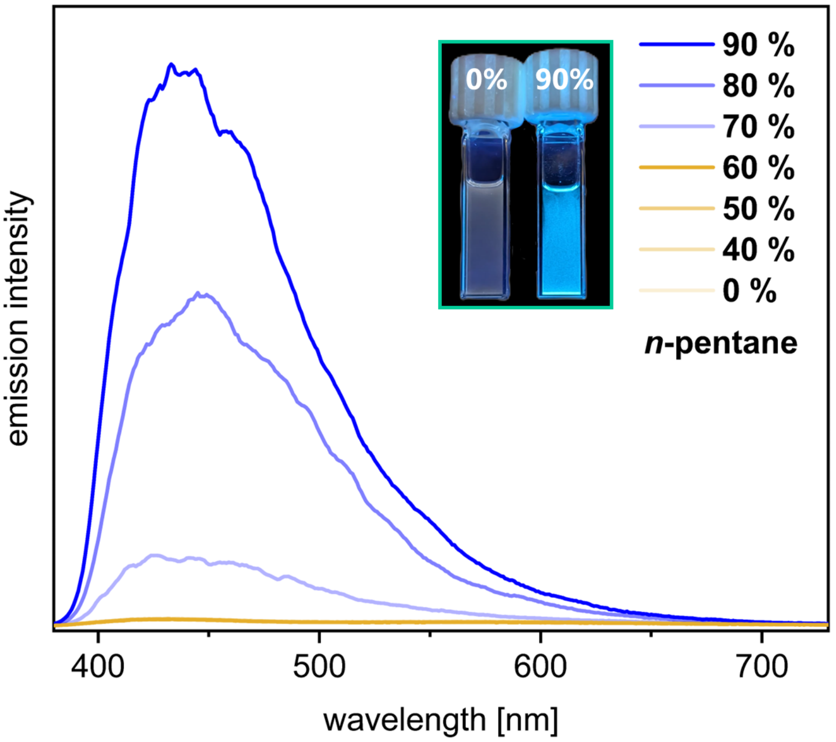


Fig. S130 Emission spectra of **5F[TBA]** in THF/*n*-pentane mixtures (conc. 5x10^{-5}M). Inset: Cuvettes of the sample with 0% (left) and 90% (right) *n*-pentane fraction under UV light.

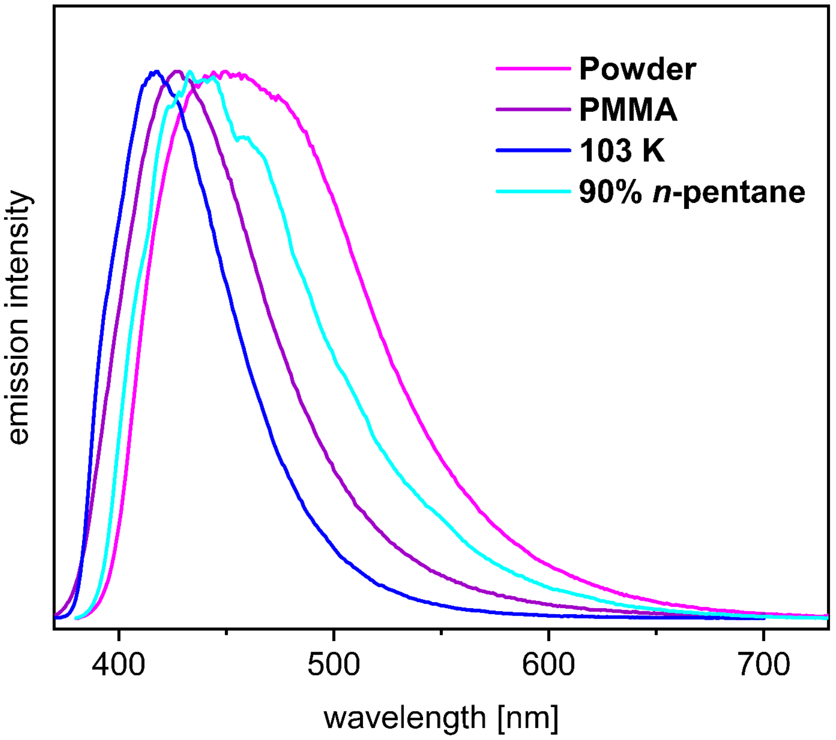


Fig. S131 Emission spectra of **5F[TBA]** in a rigid environment as powder, PMMA-film, at 103 K in Me-THF and in a 90% *n*-pentane/ 10% THF mixture (conc. 5x10^{-5}M).

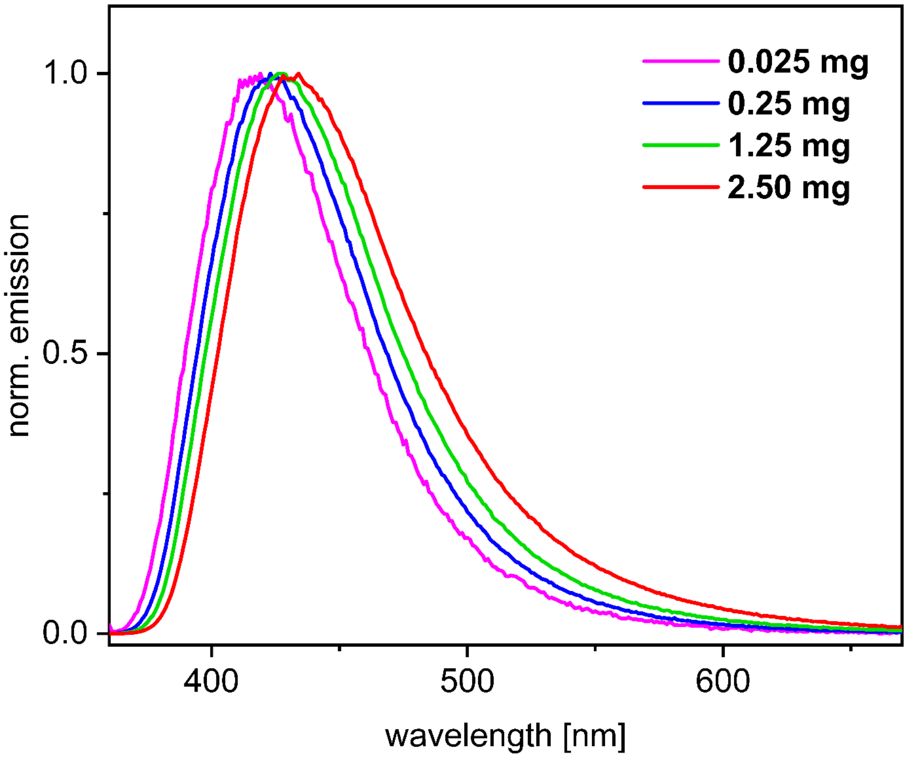


Fig. S132 Emission spectra of **5F[TBA]** as PMMA-film with different contents of DABate.

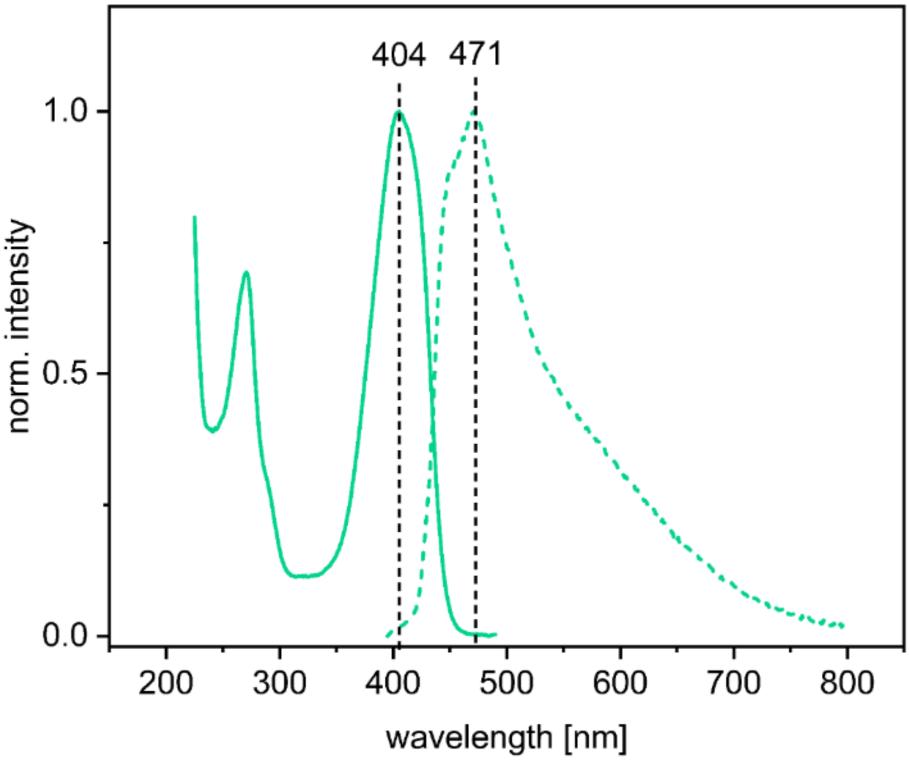


Fig. S133 Normalized absorption and emission spectra of **5Me[Li]** in THF.

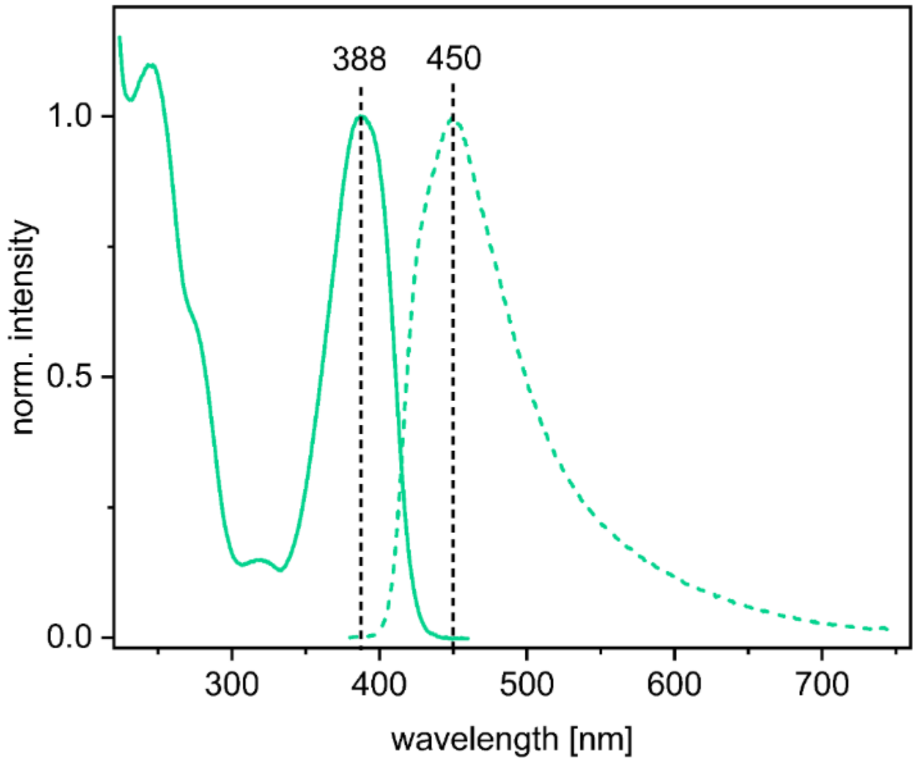


Fig. S134 Normalized absorption and emission spectra of **5Thio[Li]** in THF.

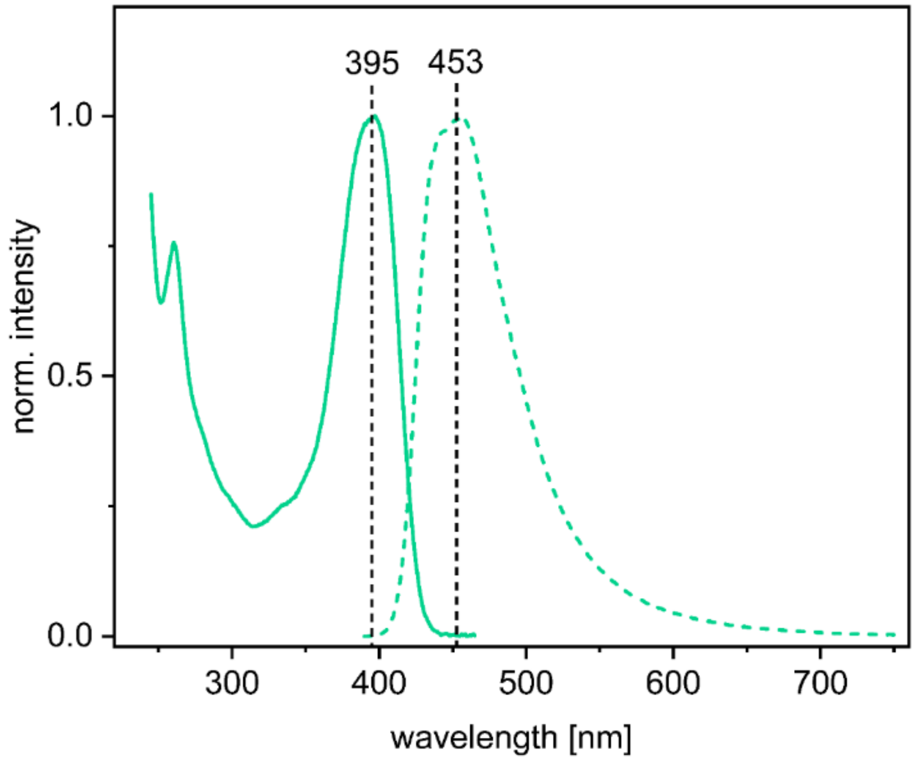


Fig. S135 Normalized absorption and emission spectra of **5CF$_3$[Li]** in THF.

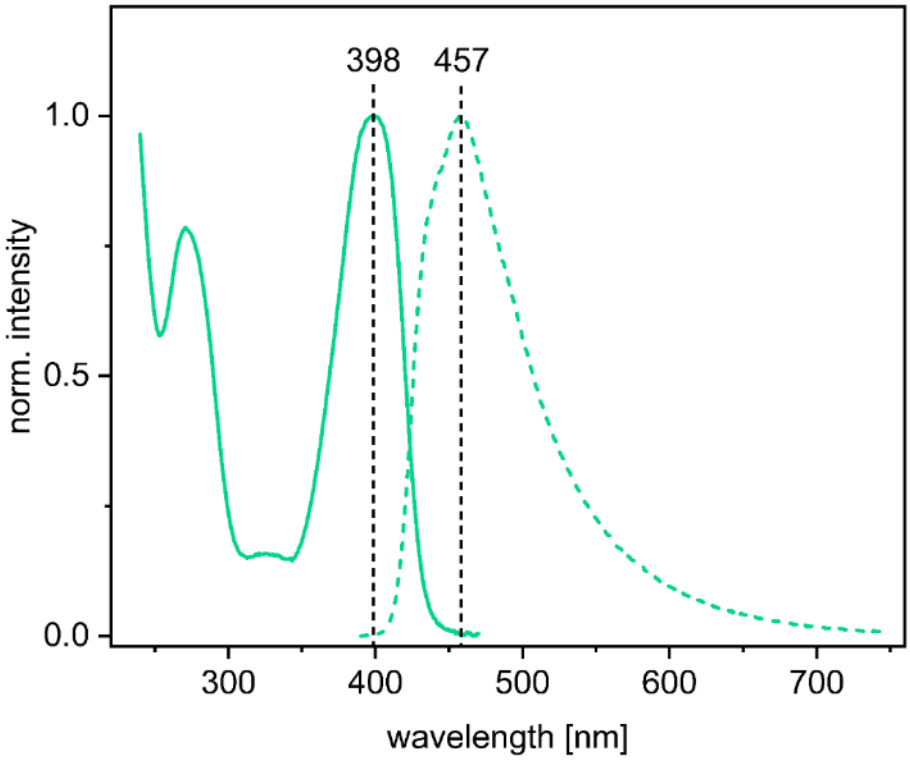


Fig. S136 Normalized absorption and emission spectra of **5OMe[Li]** in THF.

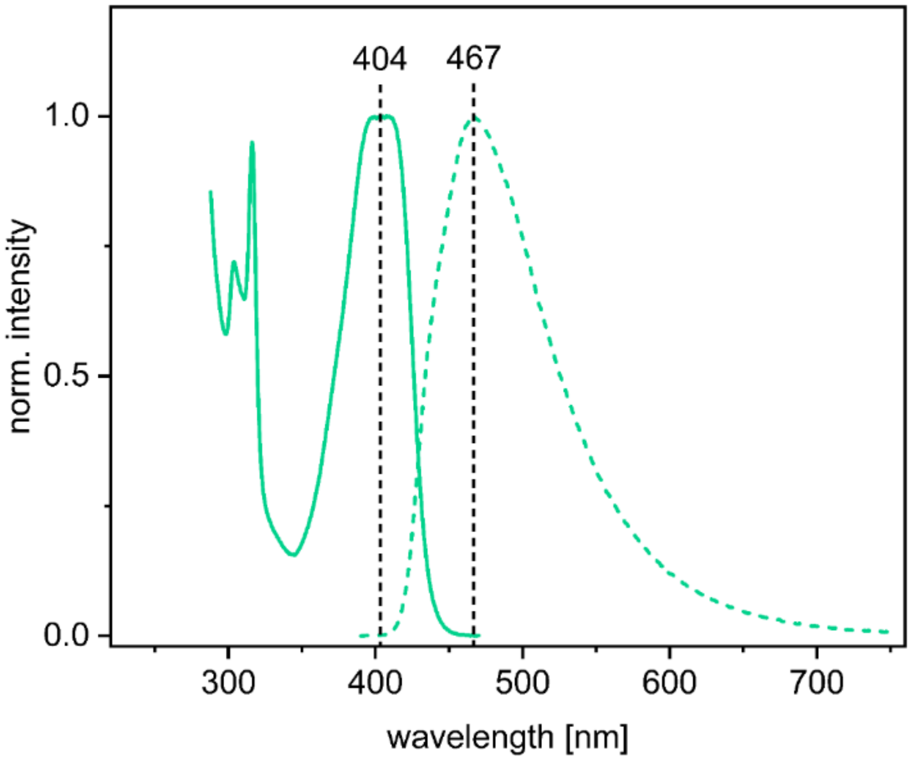


Fig. S137 Normalized absorption and emission spectra of **5Biph[Li]** in THF.

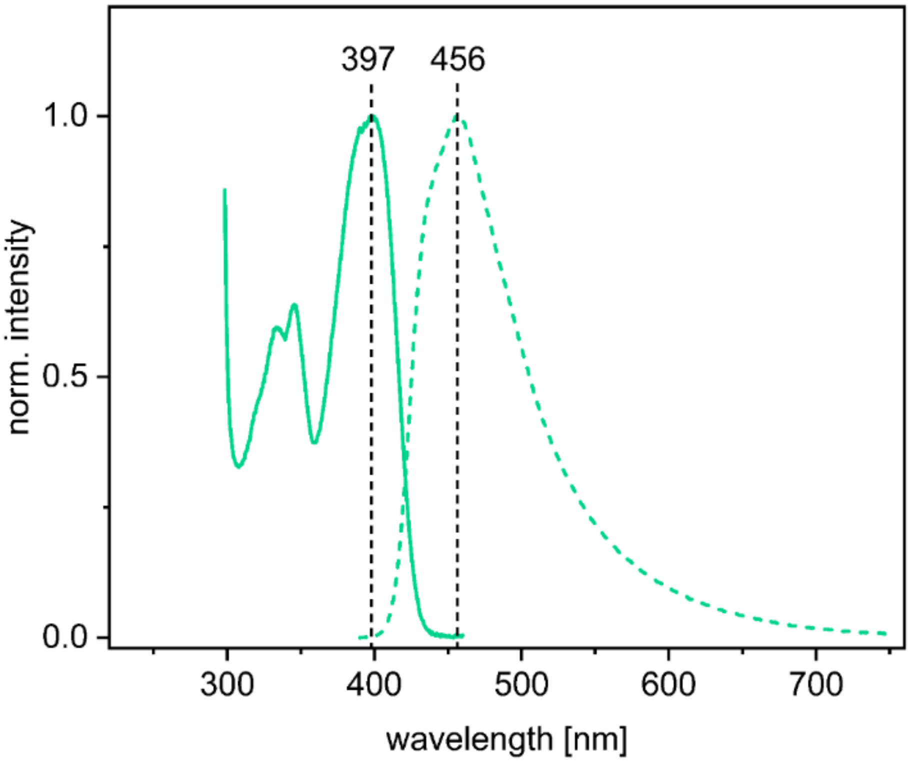


Fig. S138 Normalized absorption and emission spectra of **5Cbz[Li]** in THF.

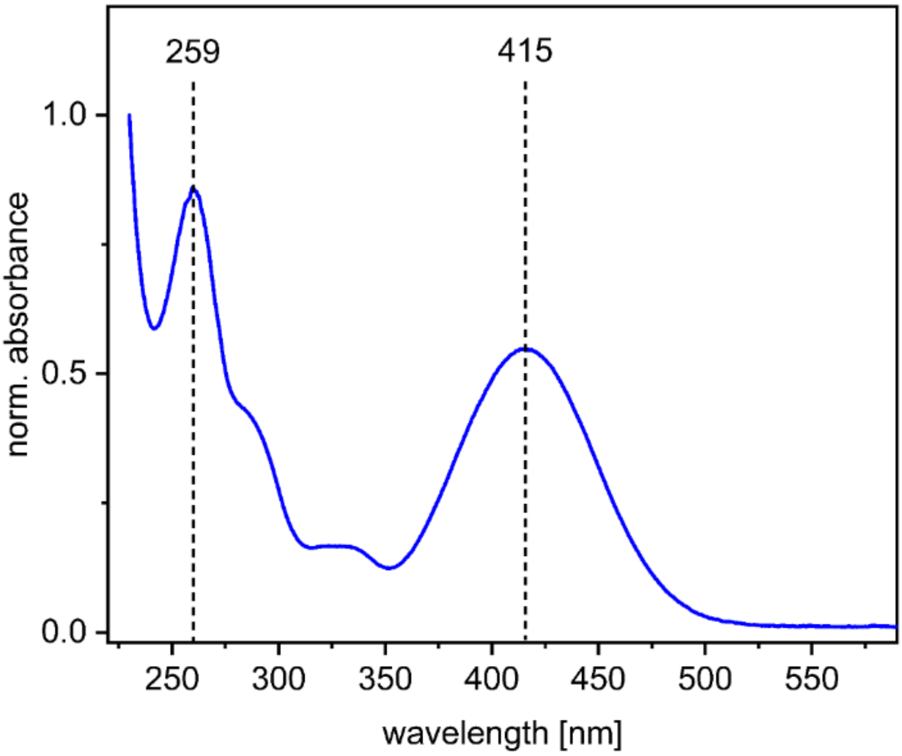


Fig. S139 Normalized absorption spectrum of **5Ph[Me]** in THF.

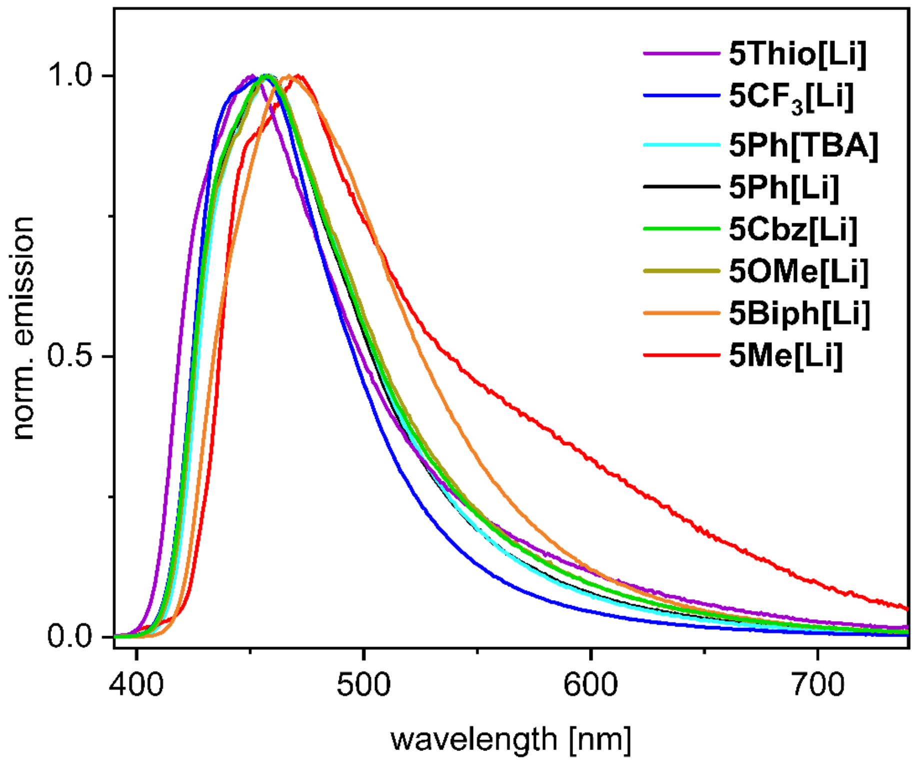


Fig. S140 Normalized emission spectra of the **5R** compounds in THF.

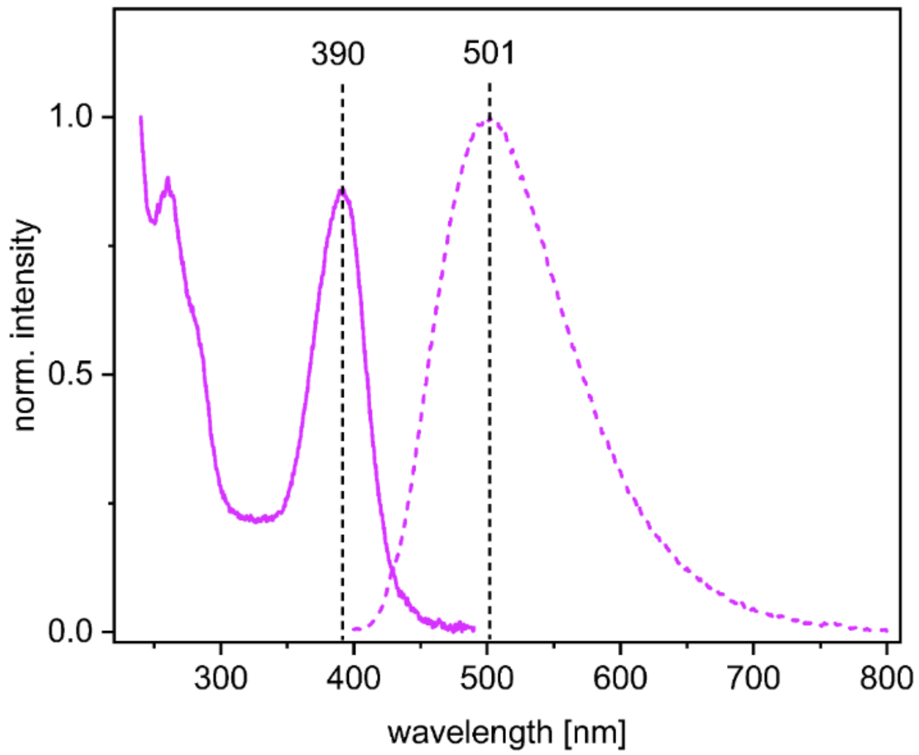


Fig. S141 Normalized absorption and emission spectra of **6Ph[Li]** in THF.

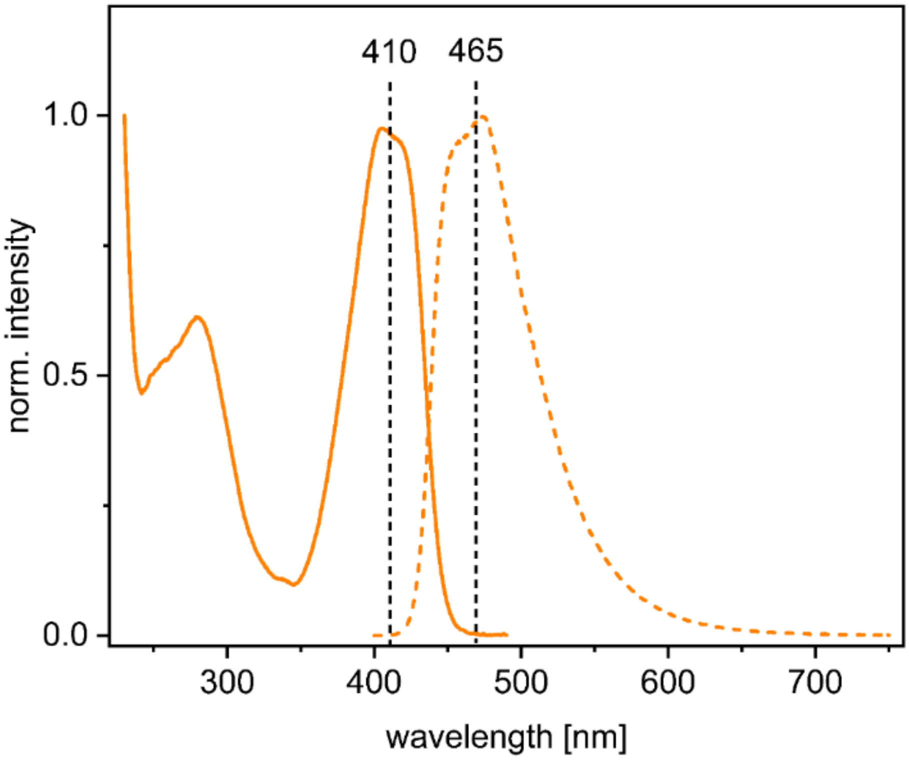


Fig. S142 Normalized absorption and emission spectra of **7Ph[Li]** in THF.

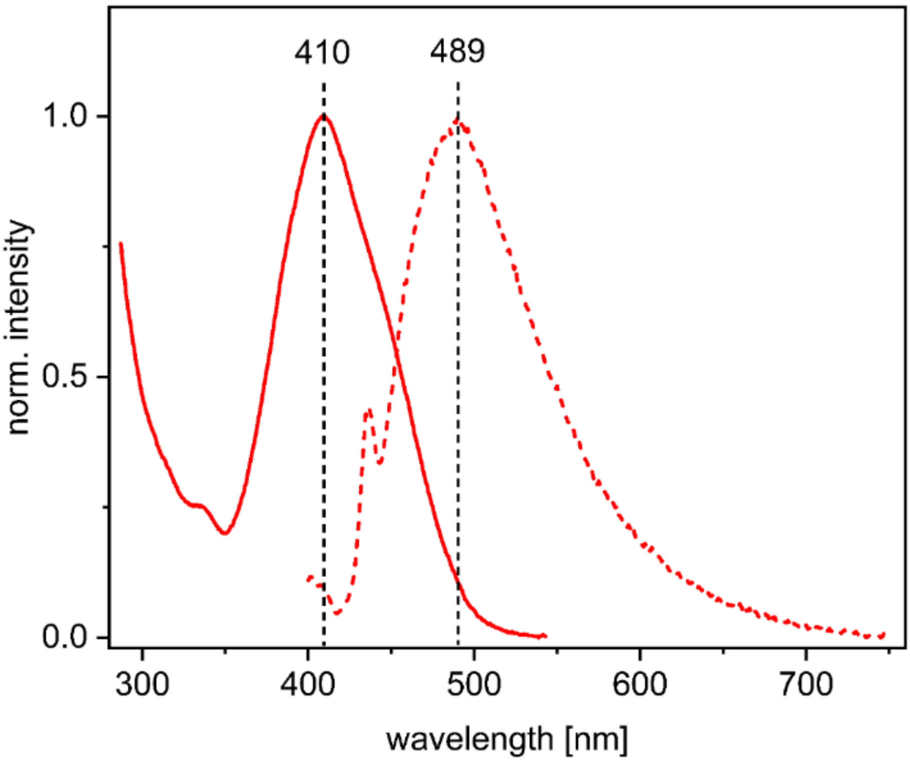


Fig. S143 Normalized absorption and emission spectra of **8Ph[Li]** in THF.

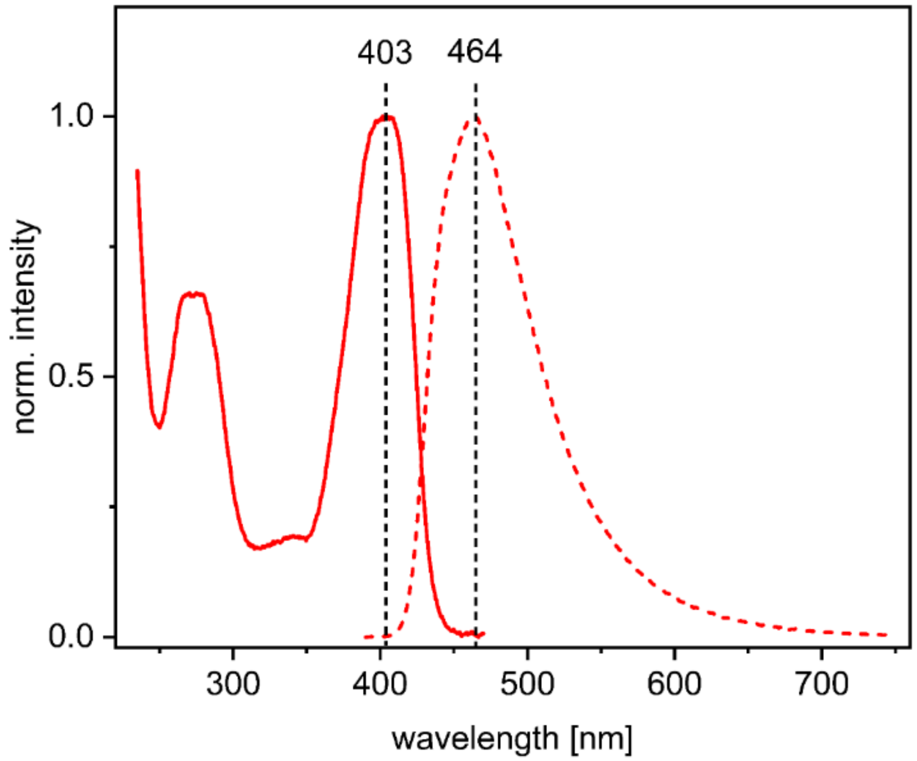


Fig. S144 Normalized absorption and emission spectra of **8Ph[TBA]** in THF.

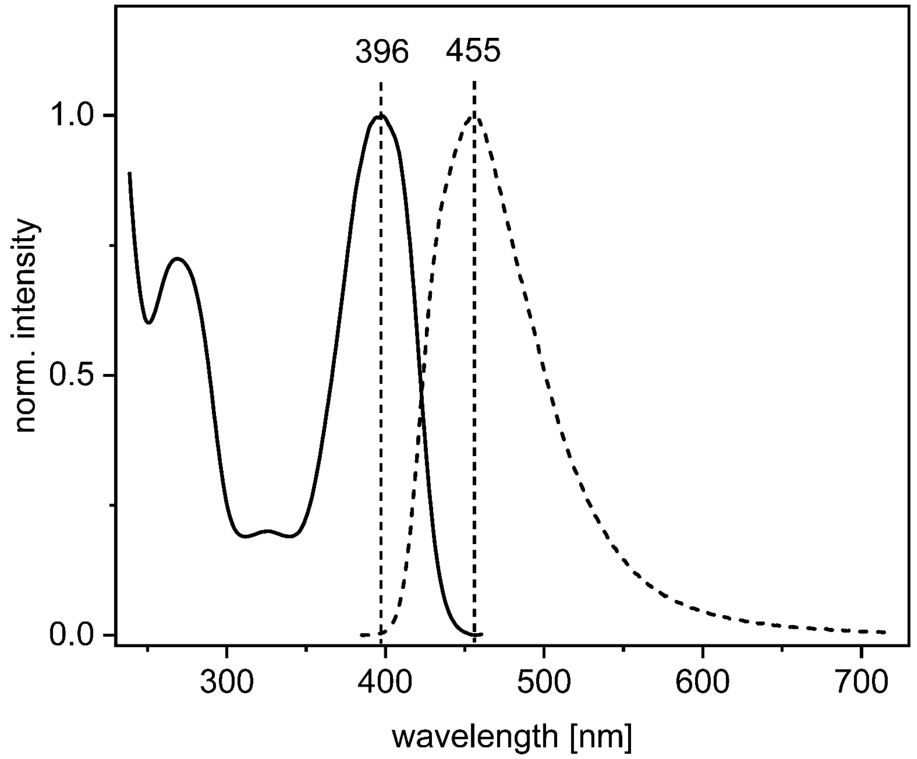


Fig. S145 Normalized absorption and emission spectra of **5Ph[Li]** as PMMA film.

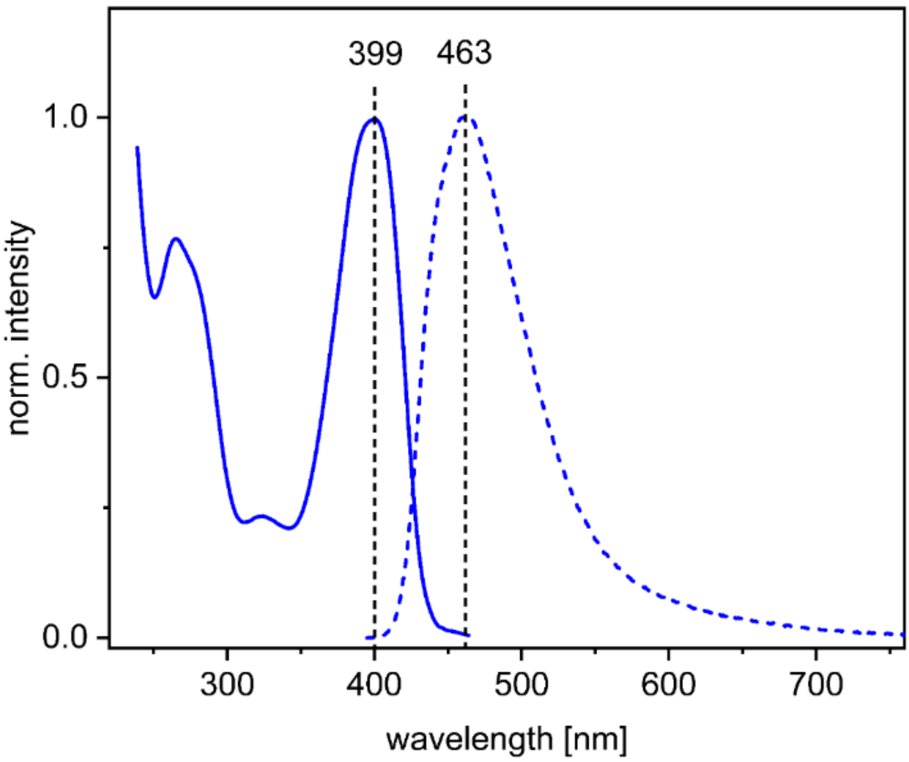


Fig. S146 Normalized absorption and emission spectra of **5Ph[TBA]** as PMMA film.

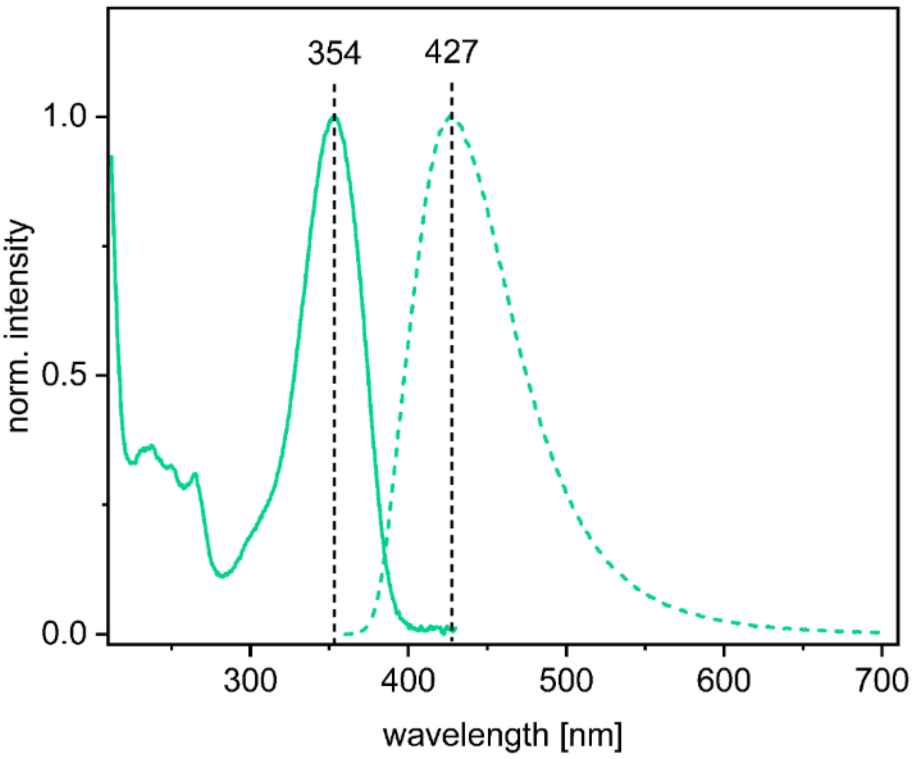


Fig. S147 Normalized absorption and emission spectra of **5F[TBA]** as PMMA film.

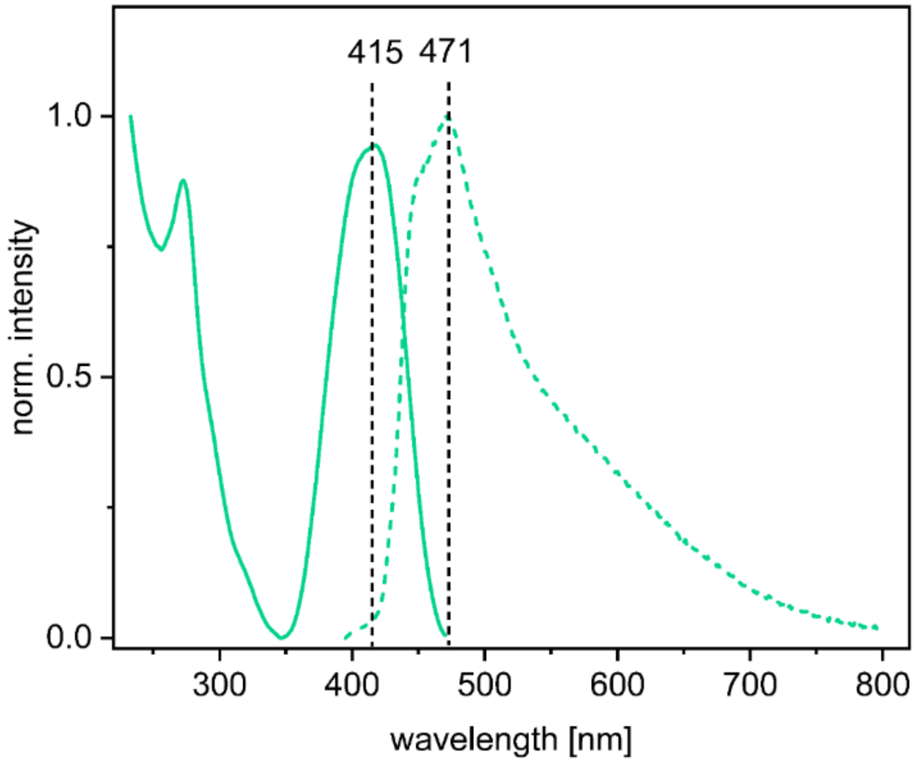


Fig. S148 Normalized absorption and emission spectra of **5Me[Li]** as PMMA film.

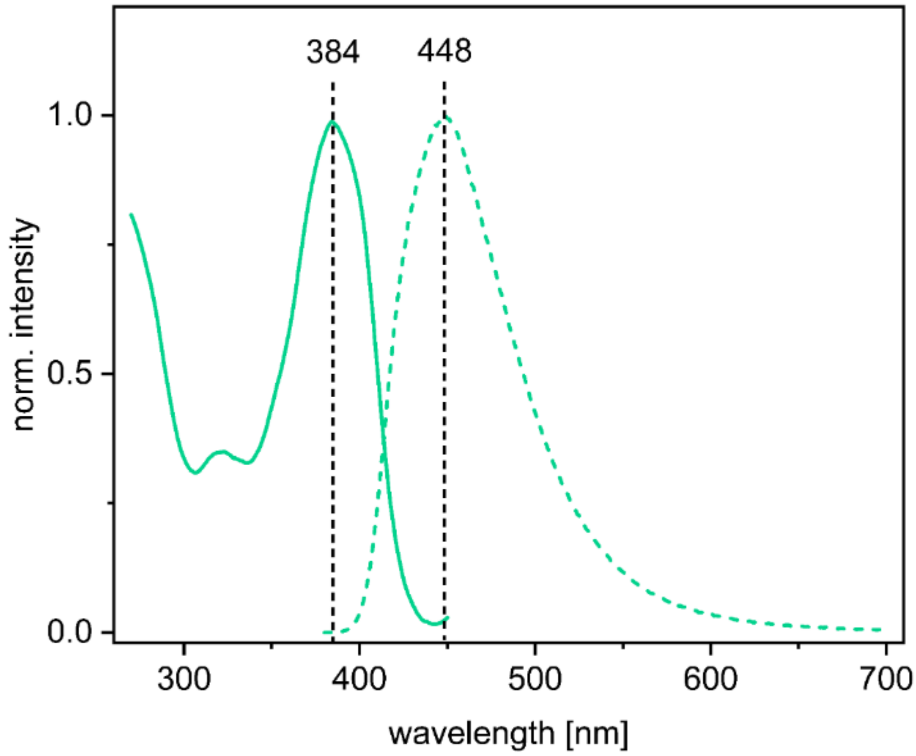


Fig. S149 Normalized absorption and emission spectra of **5Thio[Li]** as PMMA film.

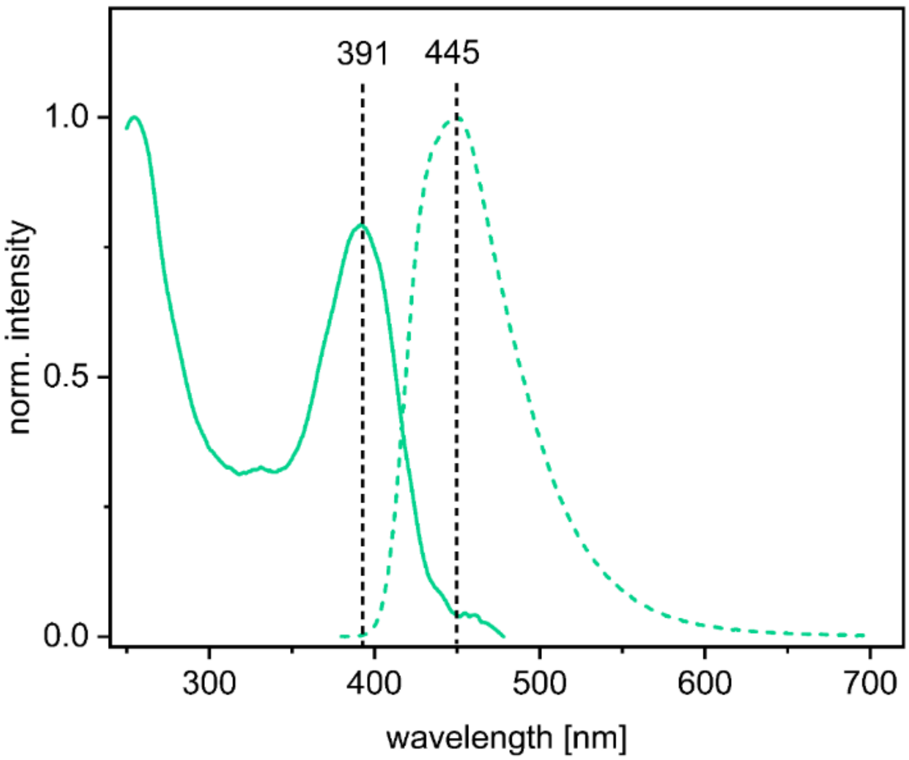


Fig. S150 Normalized absorption and emission spectra of **5CF$_3$[Li]** as PMMA film.

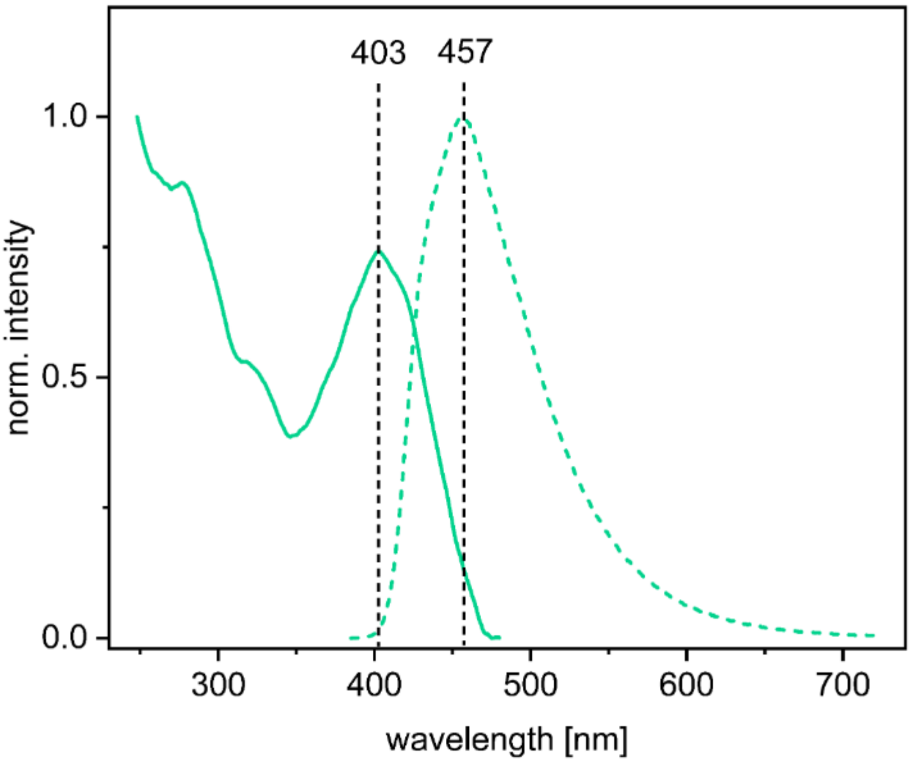


Fig. S151 Normalized absorption and emission spectra of **5OMe[Li]** as PMMA film.

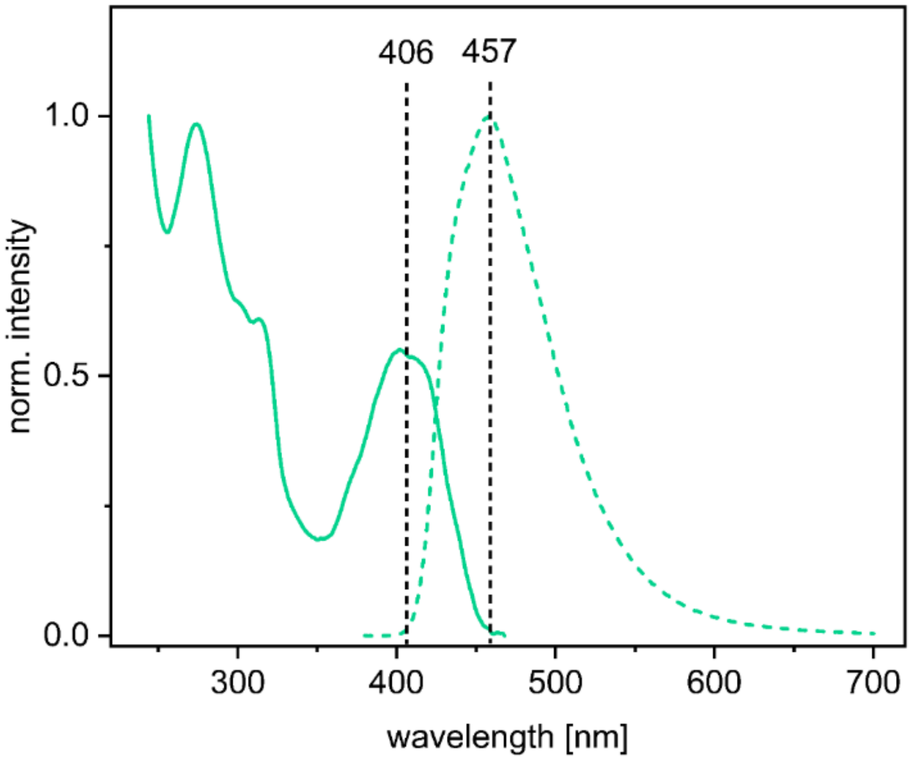


Fig. S152 Normalized absorption and emission spectra of **5Biph[Li]** as PMMA film.

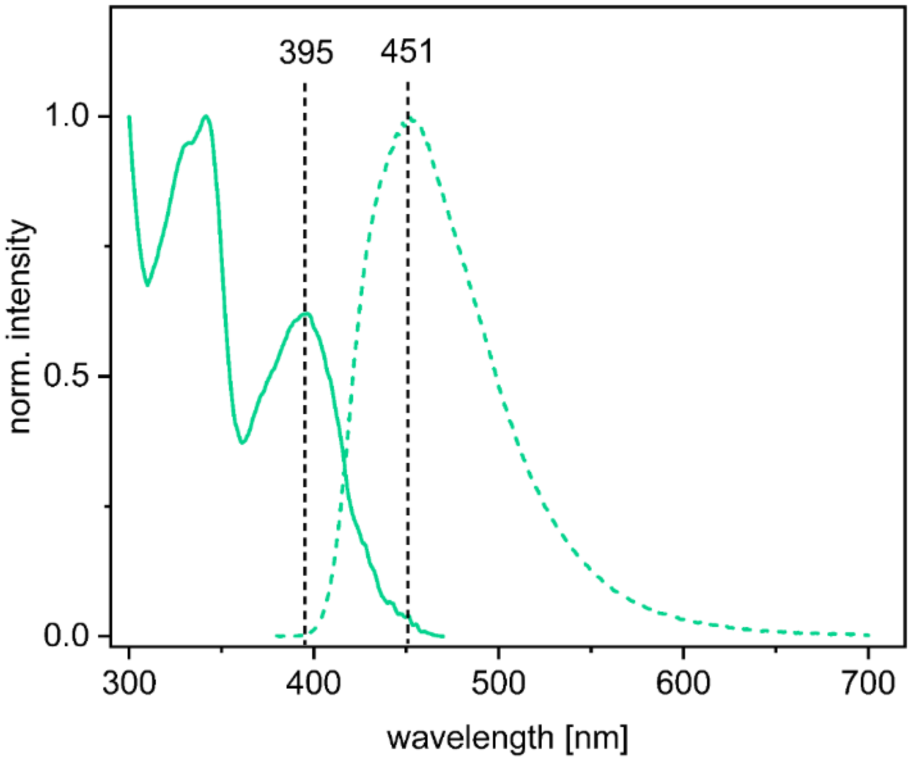


Fig. S153 Normalized absorption and emission spectra of **5Cbz[Li]** as PMMA film.

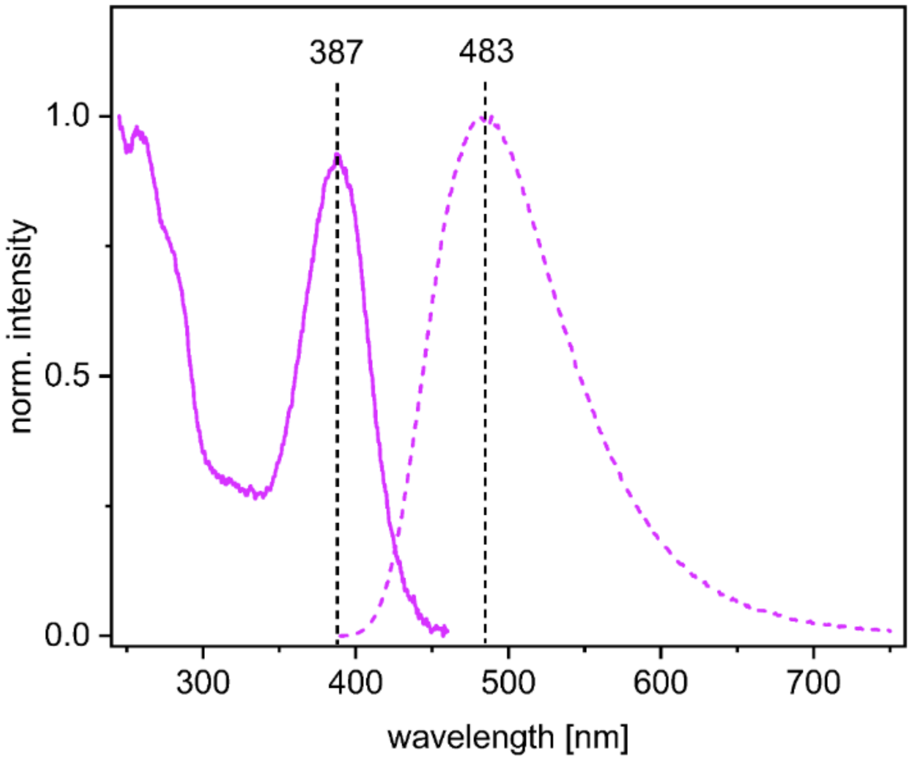


Fig. S154 Normalized absorption and emission spectra of **6Ph[Li]** as PMMA film.

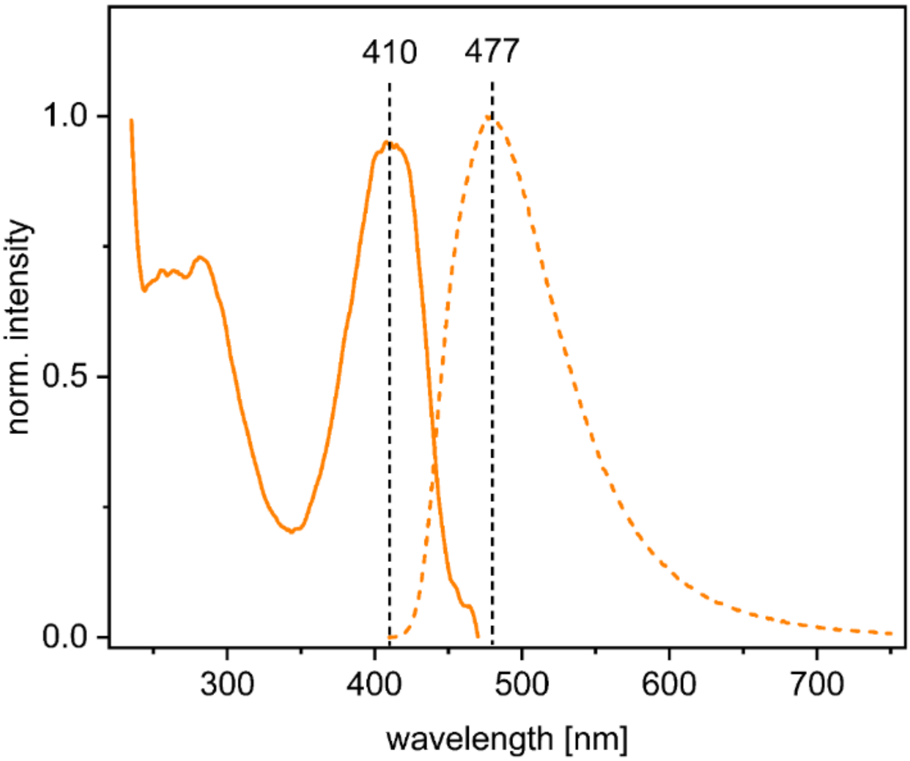


Fig. S155 Normalized absorption and emission spectra of **7Ph[Li]** as PMMA film.

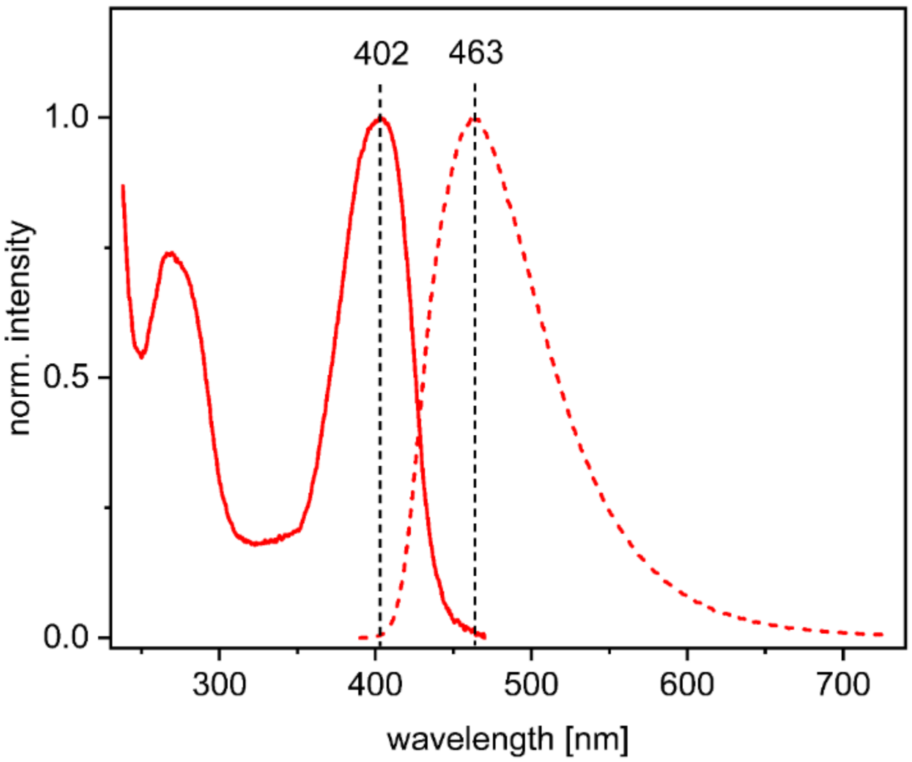


Fig. S156 Normalized absorption and emission spectra of **8Ph[Li]** as PMMA film.

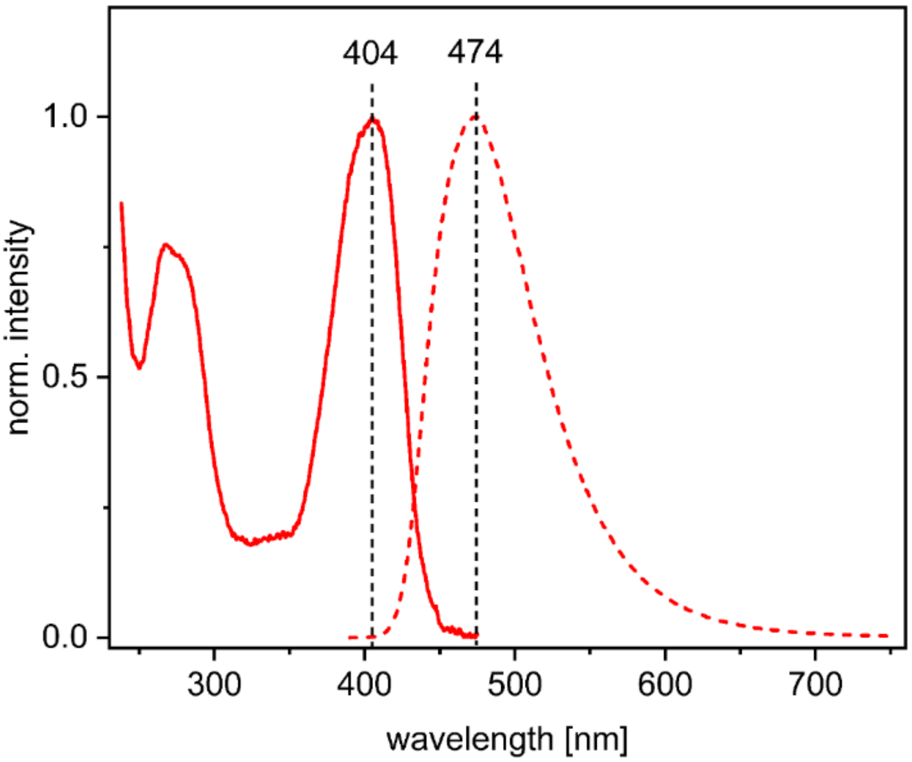


Fig. S157 Normalized absorption and emission spectra of **8Ph[TBA]** as PMMA film.

Table S5 Photophysical data of the compounds **5R-8R** in toluene.

Compound	$\lambda_{\text{abs, max}}$ [nm]	$\lambda_{\text{em, max}}$ [nm]	Φ_{fl}[a] [%]
5Ph[Li]	391	510	-
5Ph[TBA]	404	479	8
5F[TBA]	354	-	-
5Me[Li]	399	505	-
5Thio[Li]	384	543	-
5CF$_3$[Li]	388	529	-
5OMe[Li]	-	-	-
5Biph[Li]	397	516	-
5Cbz[Li]	390	510	-
5Ph[Me]	421	-	-
6Ph[Li]	393	504	-
7Ph[Li]	411	490	-
8Ph[Li]	410	489	-
8Ph[TBA]	-	485	-

[b] Fluorescence quantum yields, determined using an integration sphere.

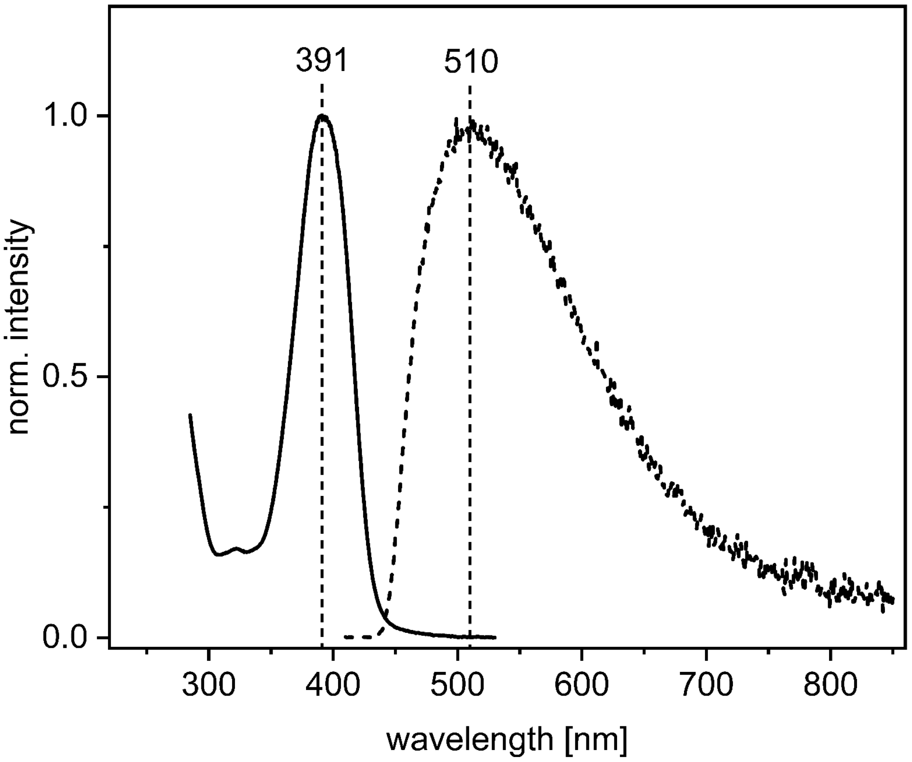


Fig. S158 Normalized absorption and emission spectra of **5Ph[Li]** in toluene.

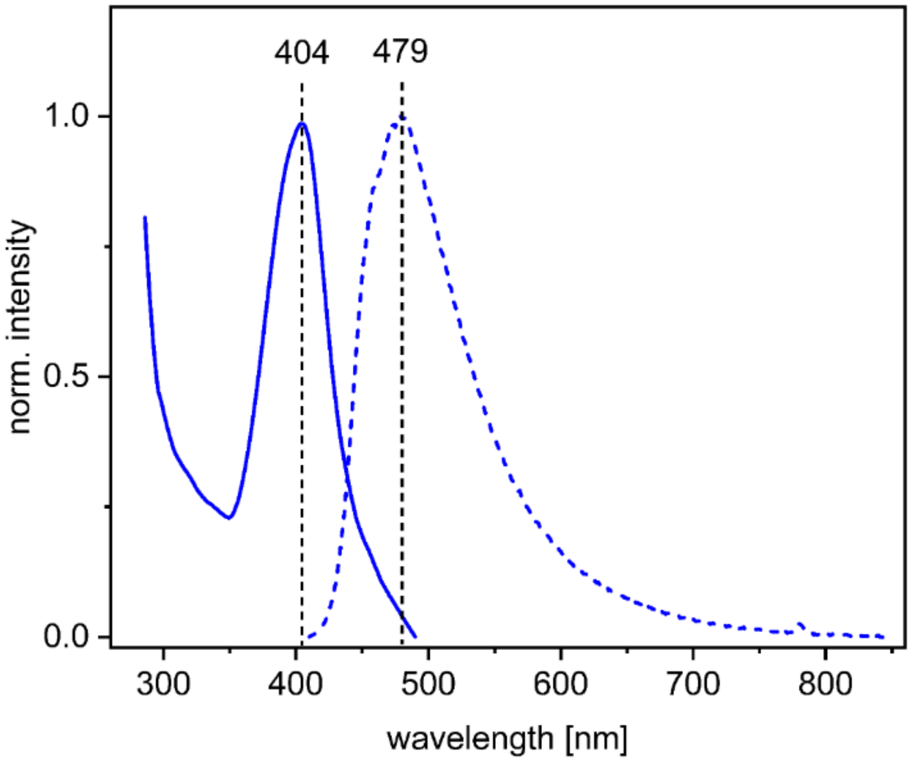


Fig. S159 Normalized absorption and emission spectra of **5Ph[TBA]** in toluene.

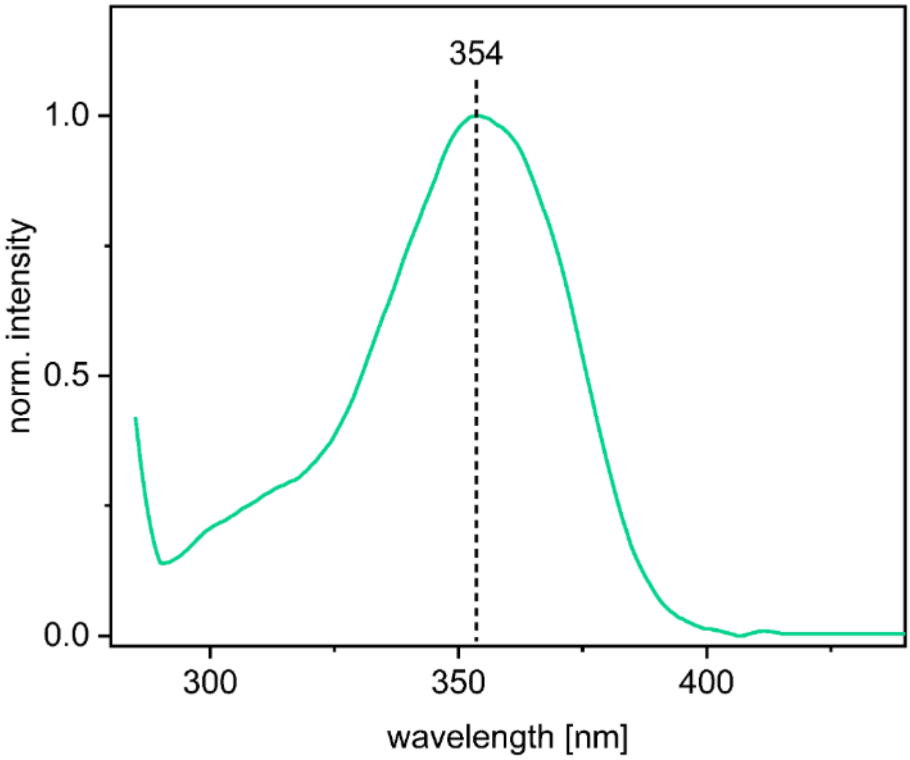


Fig. S160 Normalized absorption spectrum of **5F[TBA]** in toluene.

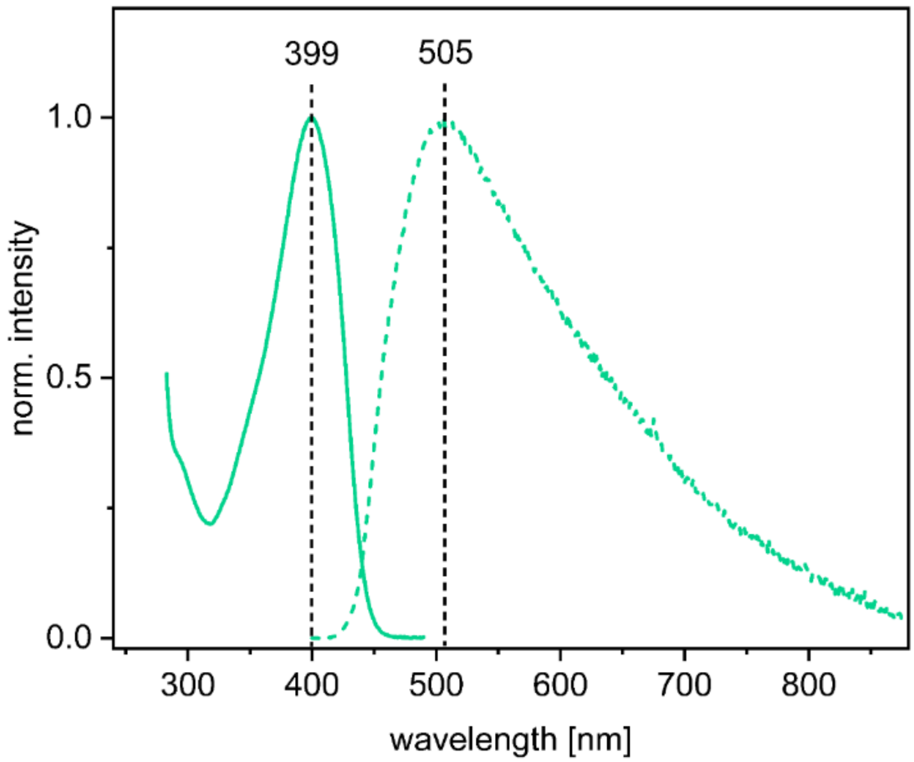


Fig. S161 Normalized absorption and emission spectra of **5Me[Li]** in toluene.

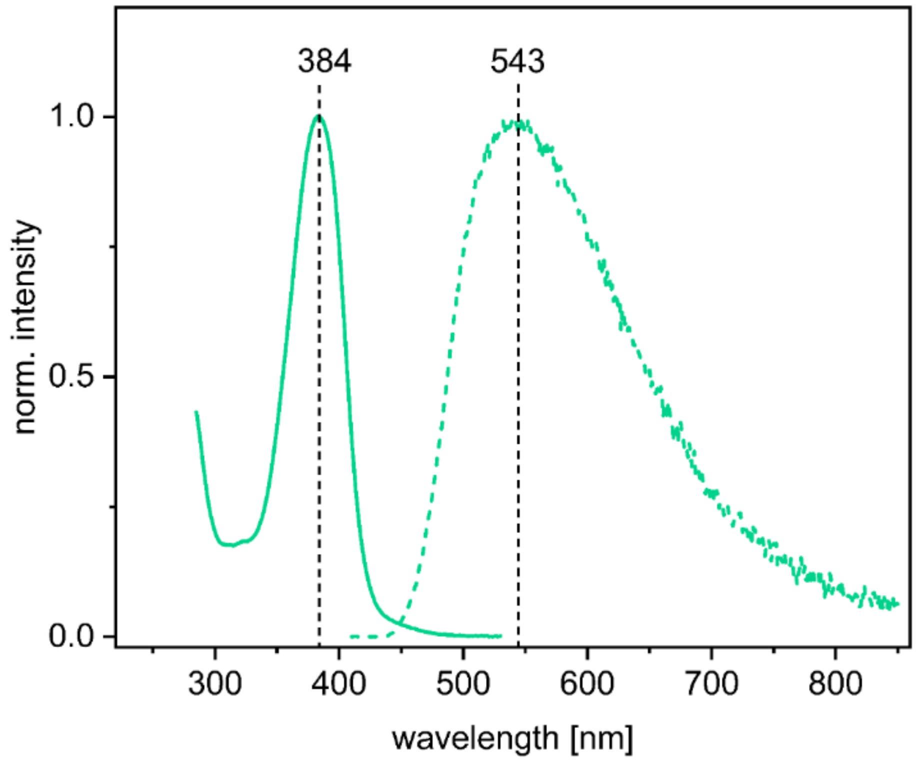


Fig. S162 Normalized absorption and emission spectra of **5Thio[Li]** in toluene.

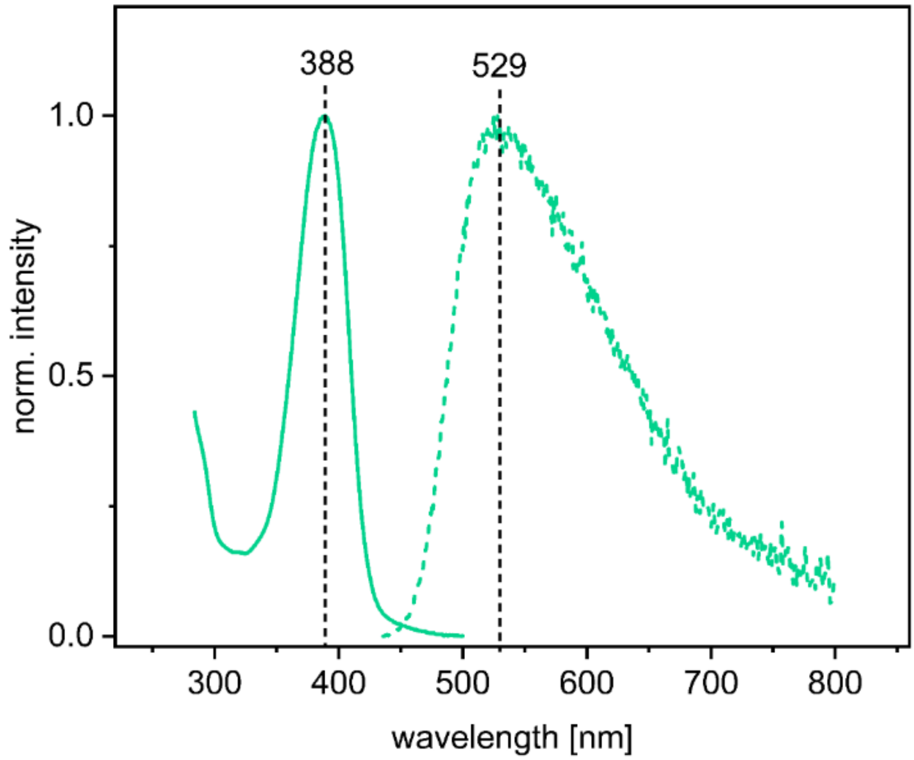


Fig. S163 Normalized absorption and emission spectra of **5CF$_3$[Li]** in toluene.

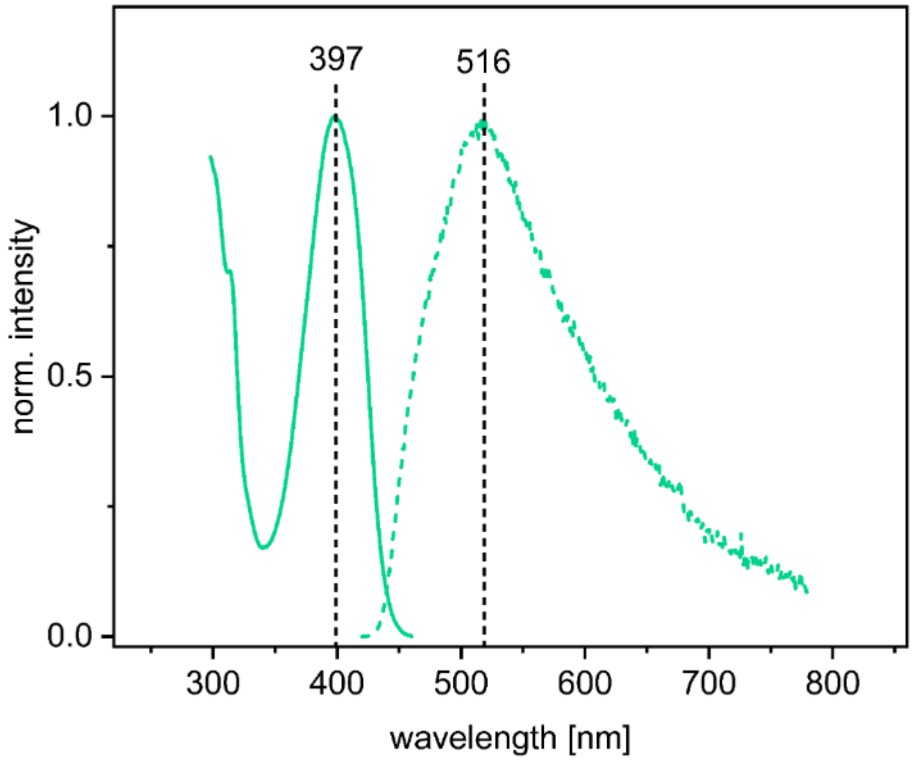


Fig. S164 Normalized absorption and emission spectra of **5Biph[Li]** in toluene.

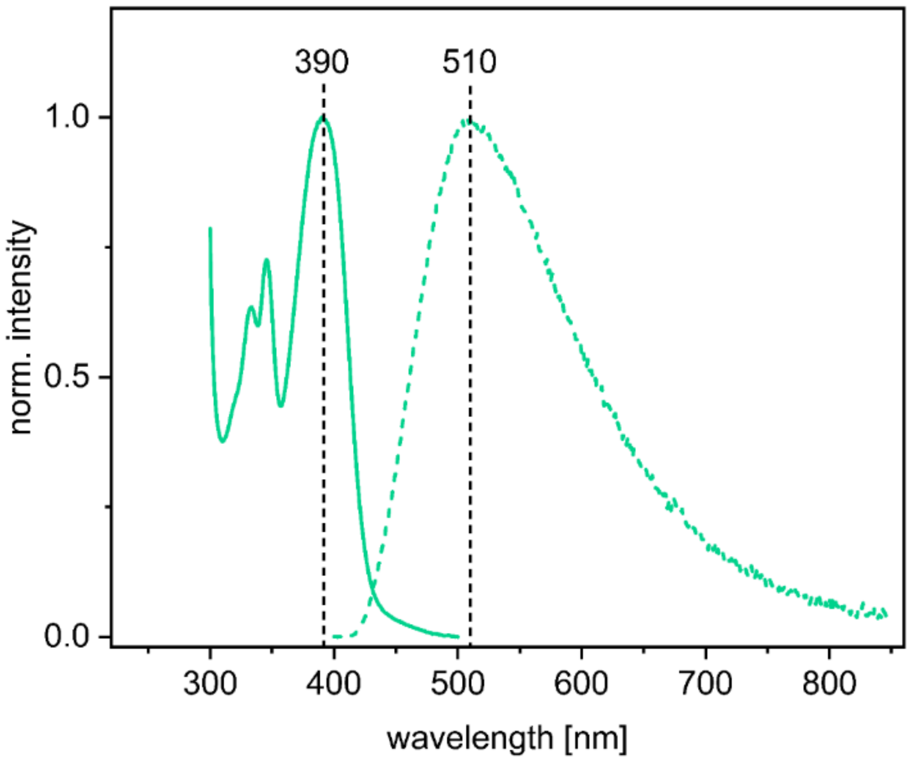


Fig. S165 Normalized absorption and emission spectra of **5Cbz[Li]** in toluene.

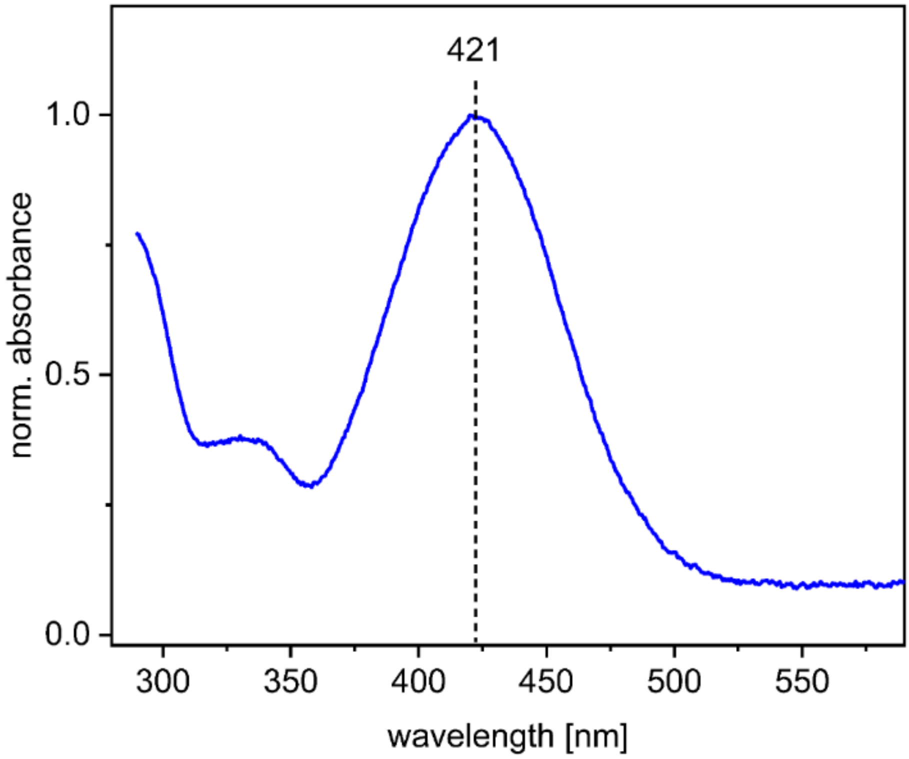


Fig. S166 Normalized absorption spectrum of **5Ph[Me]** in toluene.

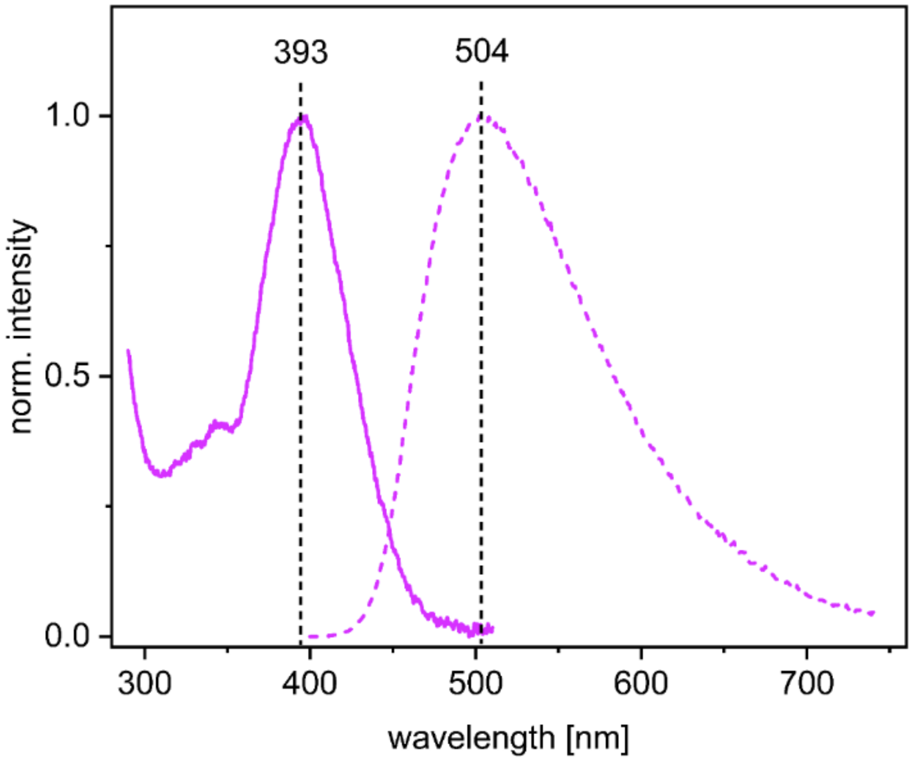


Fig. S167 Normalized absorption and emission spectra of **6Ph[Li]** in toluene.

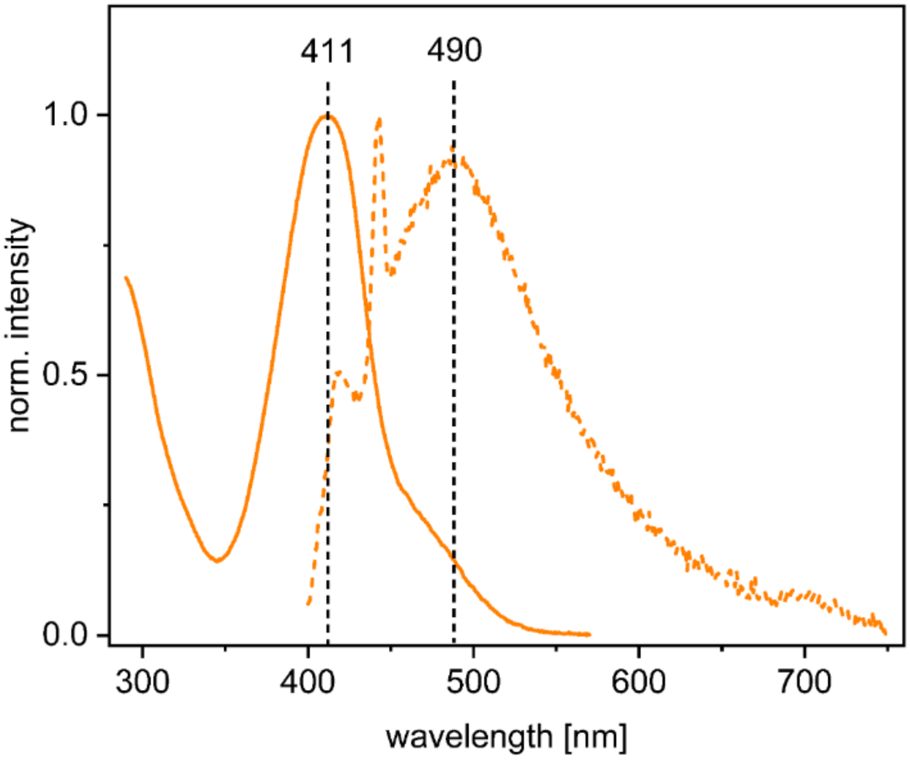


Fig. S168 Normalized absorption and emission spectra of **7Ph[Li]** in toluene.

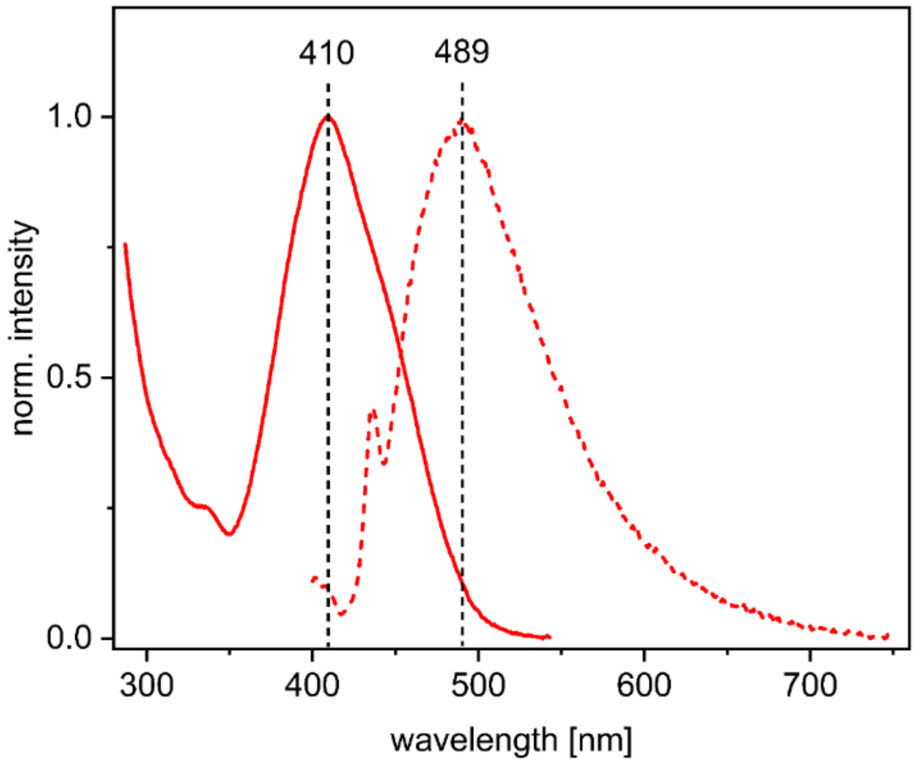


Fig. S169 Normalized absorption and emission spectra of **8Ph[Li]** in toluene.

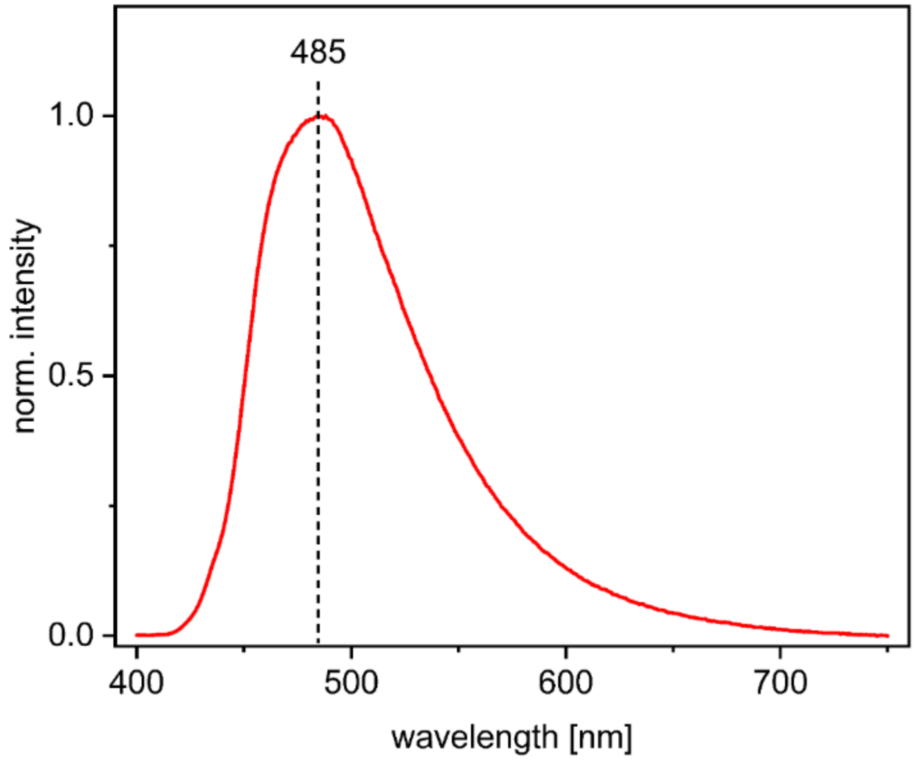


Fig. S170 Normalized emission spectrum of **8Ph[TBA]** in toluene.

4 Computational details

All calculations were carried out for the free borate anions without corresponding counter cation. DFT geometry optimizations of all compounds (ground state and excited states) were carried out with the Gaussian 16, Revision C.01 program package[8] using the ωB97X-D functional[9] in combination with the def2-SVP basis set.[10] 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[11] (see **Table S7**). The frontier molecular orbitals were visualized with the open-source program IQmol 2.8.0 molecular viewer.[12]

PES (Potential Energy Surface) scanning for the rotational barriers of the phenyl (**5Ph**$^-$) and xylyl (**6Ph**$^-$) substituents (see **Fig. S114** and **Fig. S115**) were performed by using opt=modredundant keyword at ωB97X-D[9] / def2-SVP[10] level of theory and scanning along the N_β–N_α–C_q^N–C^{Ph} dihedral angle α (360°, stepsize = 5.0).

Vertical singlet excitations (10 states) were calculated with the geometries from the DFT-calculations (ωB97X-D / def2-SVP) by means of time dependent (TD) DFT with Gaussian 16, using the tHCTHhyb functional[13] and the def2-TZVPP basis set[10, 14] in a solvatization model mimicking tetrahydrofuran (see **Table S6**). For **5Ph**$^-$, the first excited state was optimized and confirmed as minimum on the corresponding potential energy surface by vibrational frequency computation at ωB97X-D[9] / def2-SVP[10] level of theory.

The electron excitation analysis of **5Ph**$^-$, **5Ph[Me]**, **6Ph**$^-$ and **7Ph**$^-$ were performed using the Multiwfn program package[15] and the TD-DFT-calculation results, selecting the $S_0 \rightarrow S_1$ excitation. Mulliken-like partition was selected for the interfragment charge transfer (IFCT) analysis. The input atom indices of each fragment are given in **Table S9**. Only non-hydrogen-atoms were considered. As no significant contribution from the exocyclic boron substituents was found in preliminary computations, these atoms were not included in the calculation. The hole-electron and transition density analysis was visualized from the post-processing menu as isosurface plot (isovalue 0.002).

Rotational barriers

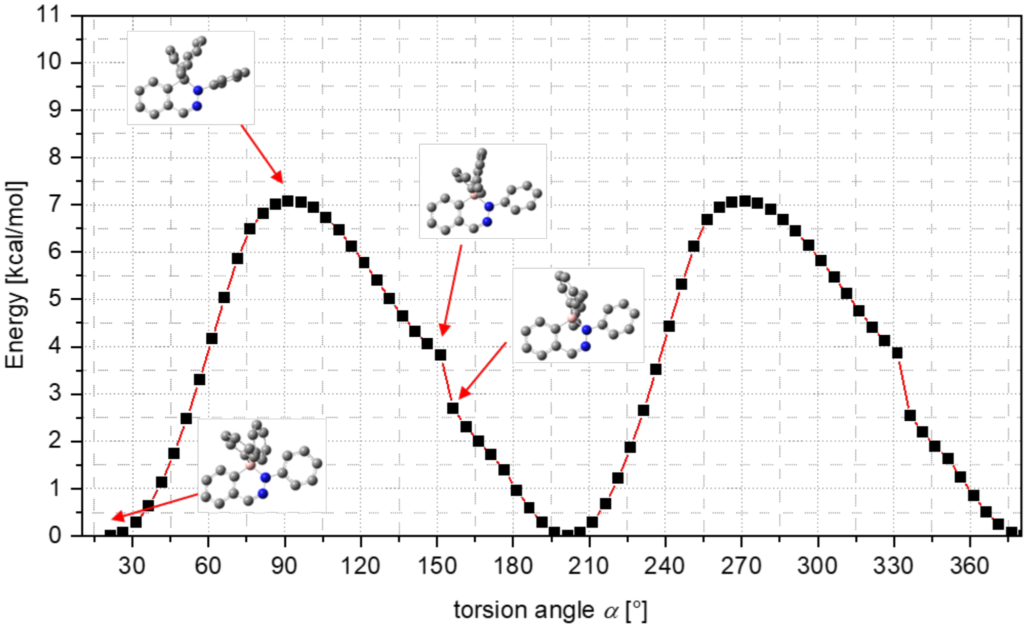


Fig. S114 PES scan of the rotation of the phenyl substituent of **5Ph**$^-$ by rotation around the N_β–N_α–$C_q{}^N$–C^{Ph} dihedral angle α, starting from optimized structure with α = 21.4° (ωB97X-D / def2-SVP, 360° scan, stepsize=5.0, dihedral scan).

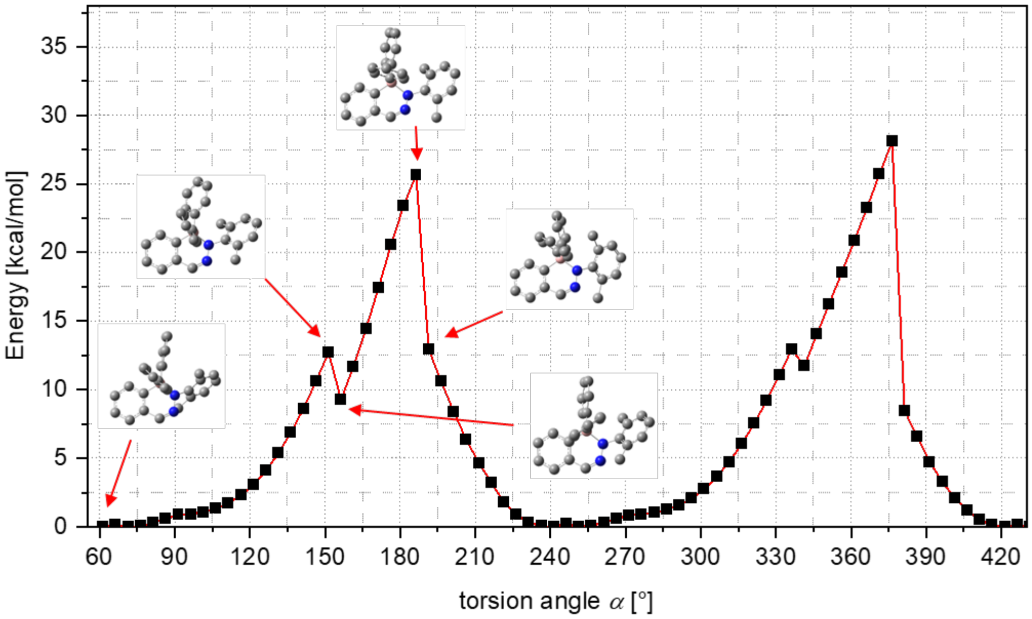


Fig. S115 PES scan of the rotation of the phenyl substituent of **6Ph**$^-$ by rotation around the N_β–N_α–$C_q{}^N$–C^{Ph} dihedral angle α, starting from optimized structure with α = 61.3° (ωB97X-D / def2-SVP, 360° scan, stepsize=5.0, dihedral scan).

Calculated UV-Vis spectra

Table S6 Calculated electronic excitations with the largest oscillator strength (tHCTHhyb / def2-TZVPP / solvent=tetrahydrofuran / td(nstates=10)) and experimental absorption maxima of **5R$^-$**, **6Ph$^-$**, **7Ph$^-$**, **8Ph$^-$**, and **5Ph[Me]**.

Compound	State	Symmetry	λ_{exp} [nm]	λ_{calc} [nm]	Oscillator strength	Main excitation
5F$^-$	1	^{1}A	355	362	0.6747	HOMO→LUMO
5Me$^-$	1	^{1}A	404	415	0.4337	HOMO→LUMO
5Thio$^-$	1	^{1}A	388	392	0.3821	HOMO→LUMO
5Ph$^-$	1	^{1}A	398	401	0.3687	HOMO→LUMO
5CF$_3$$^-$	1	^{1}A	395	404	0.2606	HOMO→LUMO[*1]
5OMe$^-$	1	^{1}A	398	401	0.3632	HOMO→LUMO
5Biph$^-$	2	^{1}A	404	409	0.3461	HOMO→LUMO
5Cbz$^-$	3	^{1}A	397	402	0.2999	HOMO→LUMO+2
6Ph$^-$	1	^{1}A	390	399	0.2452	HOMO→LUMO
7Ph$^-$	1	^{1}A	410	421	0.3152	HOMO→LUMO
5Ph[Me]	1	^{1}A	415	443	0.2043	HOMO→LUMO
8Ph$^-$	1	^{1}A	403	406	0.3507	HOMO→LUMO

[*1] With minor contribution from HOMO→LUMO+1.

Mulliken- and NBO-charges

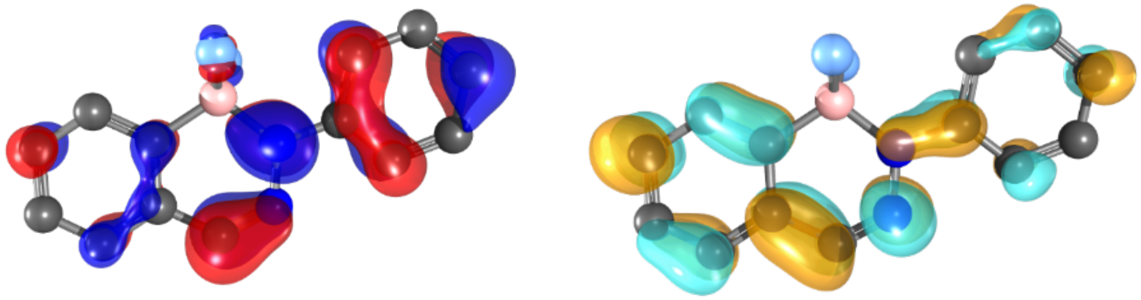
Table S7 Calculated Mulliken- and NBO charges for the neutral DAB **1Ph** and the parent DABate **5Ph$^-$** (ωB97X-D / def2-SVP).

Compound	Mulliken charges		NBO charges	
	B	N$_\alpha$	B	N$_\alpha$
1Ph (DAB)	−0.007	−0.137	+0.928	−0.495
5Ph$^-$ (DABate)	−0.027	−0.204	+0.686	−0.469

Frontier molecular orbitals

Table S8 Calculated HOMO and LUMO energies of **5R**$^{-}$, **6Ph**$^{-}$, **7Ph**$^{-}$, **8Ph**$^{-}$, and **5Ph[Me]** (ωB97X-D / def2-SVP).

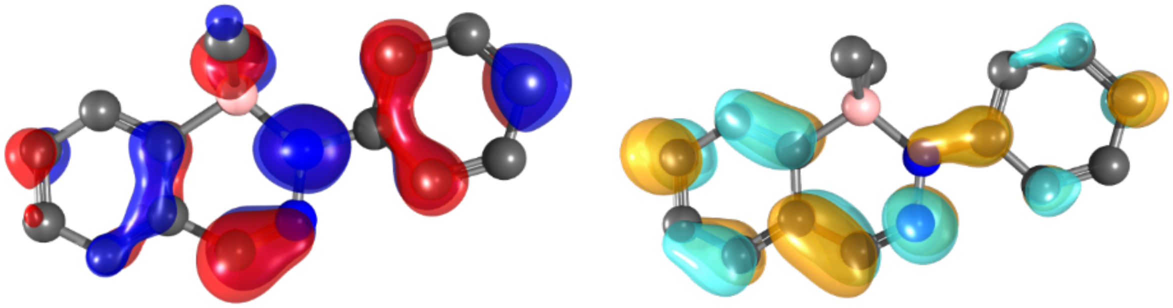
Compound	HOMO energy (eV)	LUMO energy (eV)	HOMO-LUMO gap (eV)
5F^{-}	−3.36698060368	4.179719420328	7.546700024011
5Me^{-}	−2.92066456656	4.279294583304	7.199959149864
5Thio^{-}	−3.48782846217	3.965969880496	7.453798342666
5Ph^{-}	−3.42583929448	3.947914548510	7.373753842993
5CF$_3^{-}$	−3.82552428210	3.556831827931	7.382356110043
5OMe^{-}	−3.49057256155	3.876534603240	7.367107164789
5Biph^{-}	−3.37364390818	3.944385802646	7.318029710820
5Cbz^{-}	−3.89641066338	2.664153355186	6.560564018568
6Ph^{-}	−3.43113450857	4.098930955512	7.530065464085
7Ph^{-}	−3.33287347540	3.883415029088	7.216288504485
5Ph[Me]	−7.60315103244	−0.617130491330	6.986020541114
8Ph^{-}	−3.36825416099	3.97087313870	7.339127299686



HOMO
−3.36698060368 eV

LUMO
4.179719420328 eV

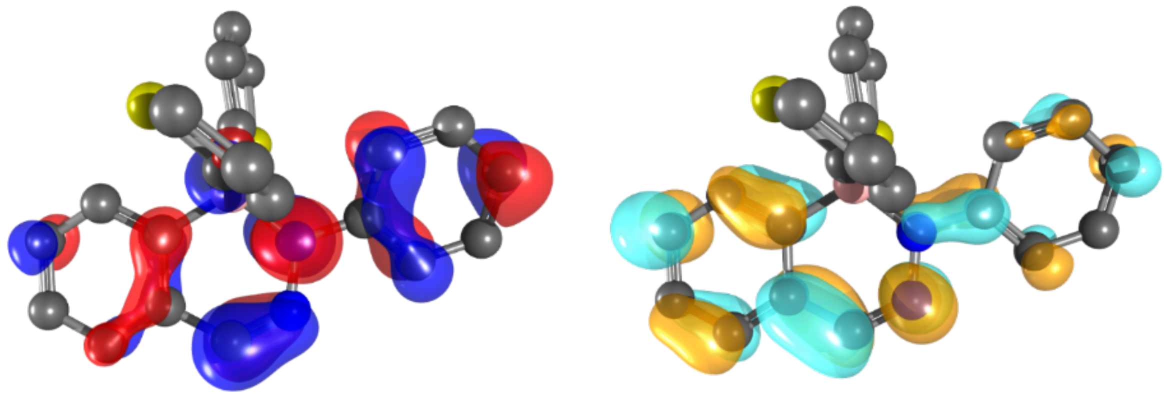
Fig. S116 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **5F**$^{-}$ (ωB97X-D / def2-SVP).



HOMO
−2.92066456656 eV

LUMO
4.279294583304 eV

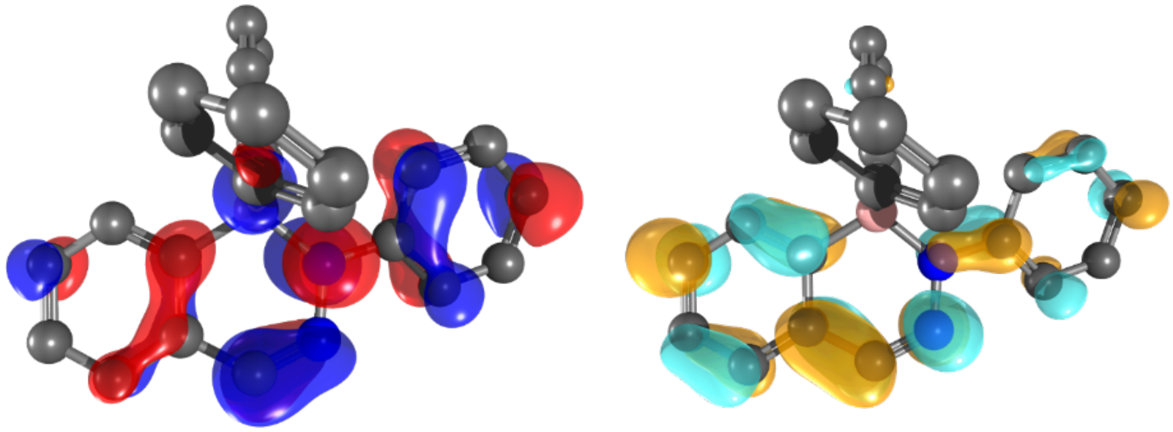
Fig. S117 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **5Me**$^{-}$ (ωB97X-D / def2-SVP).



HOMO
−3.48782846217 eV

LUMO
3.965969880496 eV

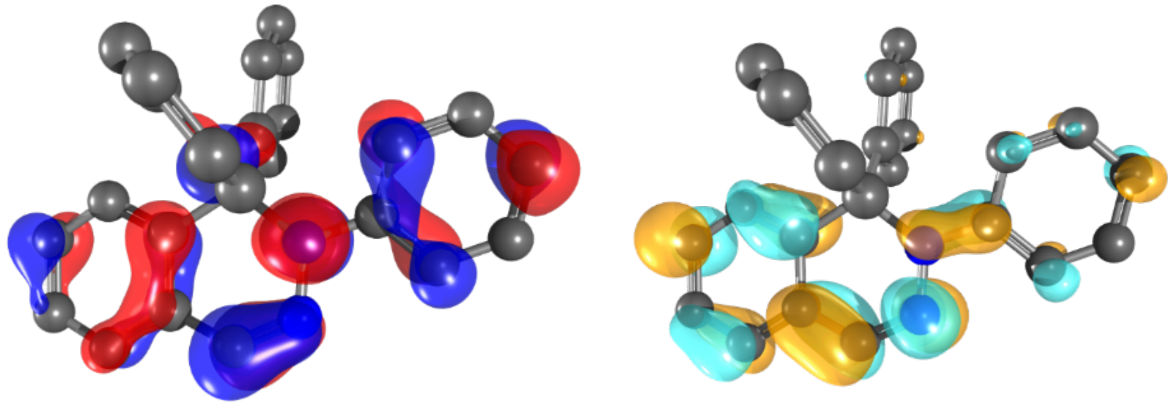
Fig. S118 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **5Thio**$^-$ (ωB97X-D / def2-SVP).



HOMO
−3.42583929448 eV

LUMO
3.947914548510 eV

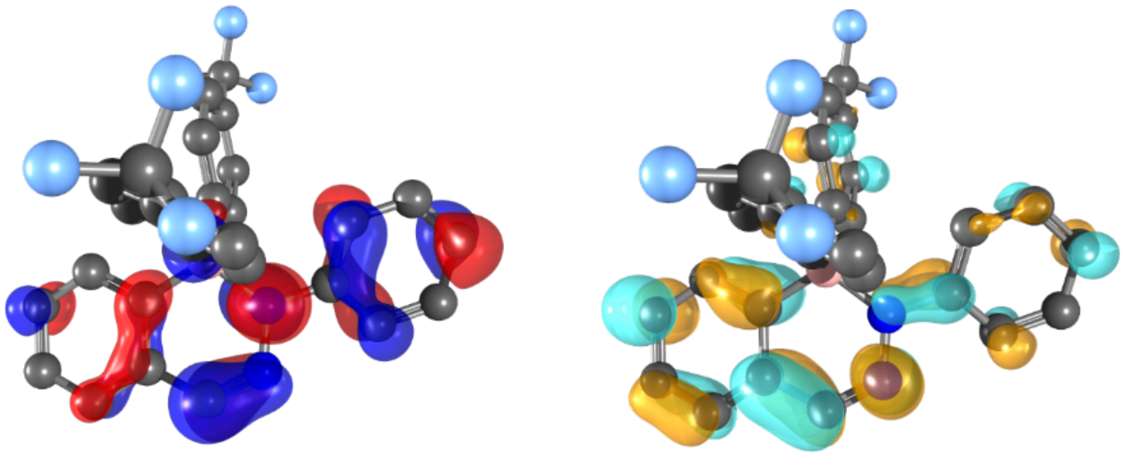
Fig. S119 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of the ground state S$_0$ of **5Ph**$^-$ (ωB97X-D / def2-SVP).



HOMO
−3.42583929448 eV

LUMO
3.947914548510 eV

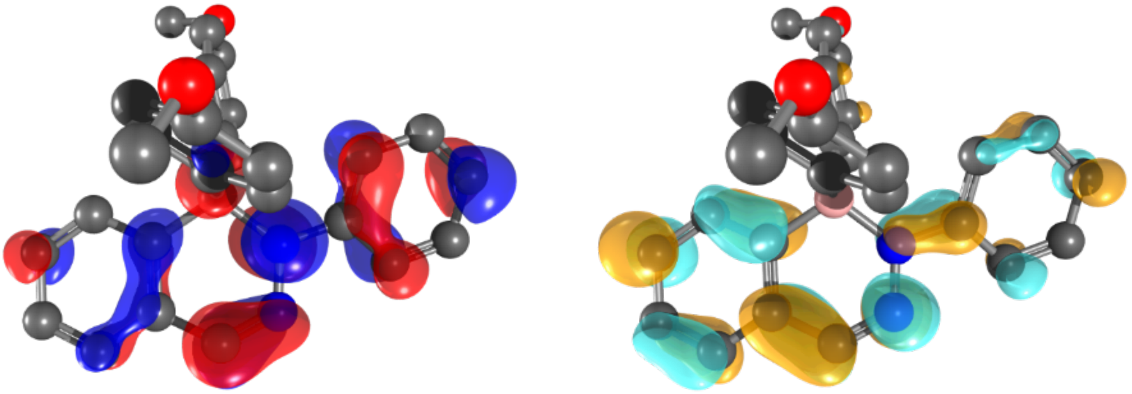
Fig. S120 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of the first excited state S$_1$ of **5Ph**$^-$ (ωB97X-D / def2-SVP).



HOMO
−3.82552428210 eV

LUMO
3.556831827931 eV

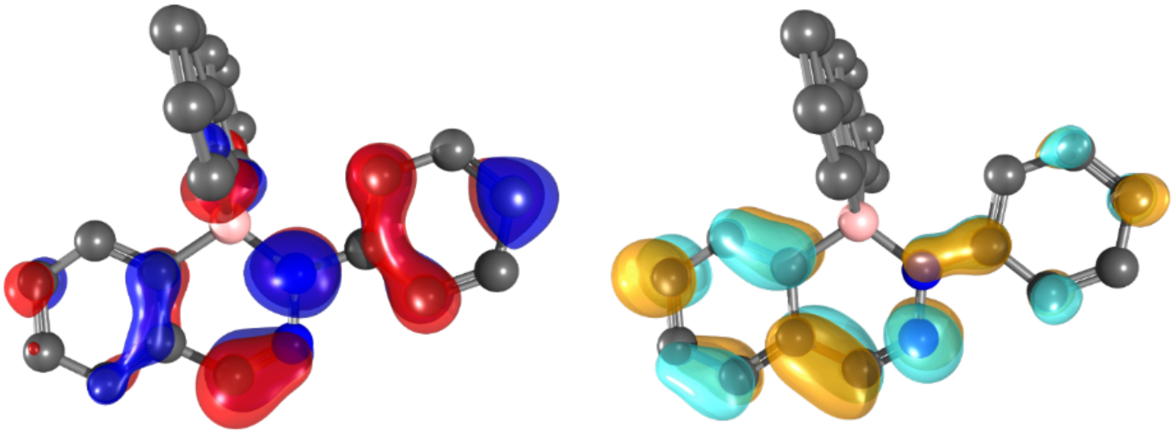
Fig. S121 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **5CF**$_3^-$ (ωB97X-D / def2-SVP).



HOMO
−3.49057256155 eV

LUMO
3.876534603240 eV

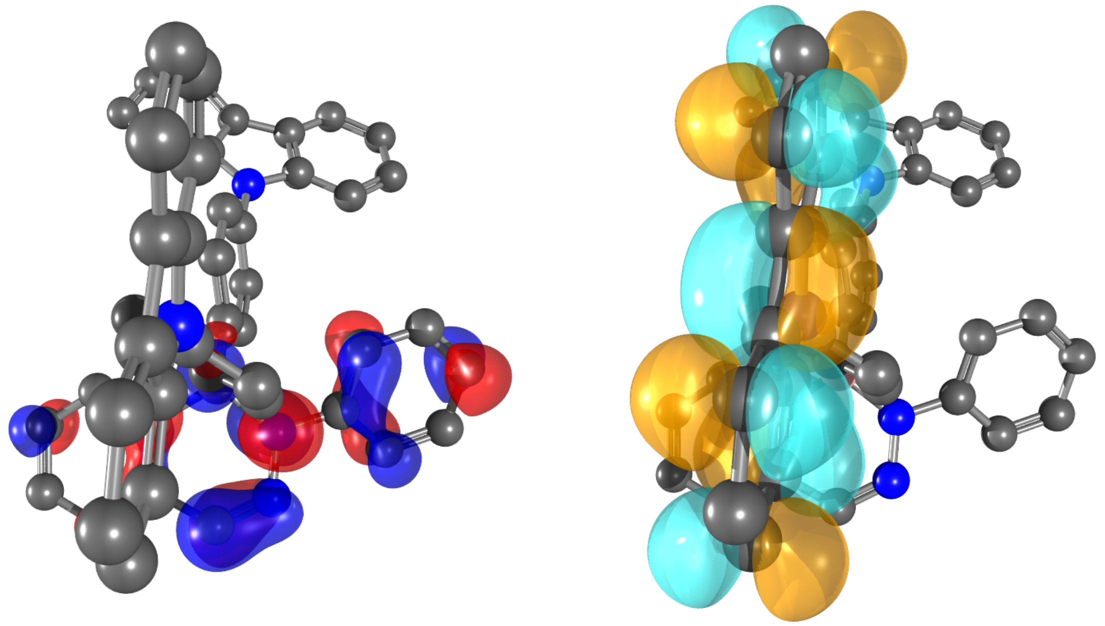
Fig. S122 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **5OMe**$^-$ (ωB97X-D / def2-SVP).



HOMO
−3.37364390818 eV

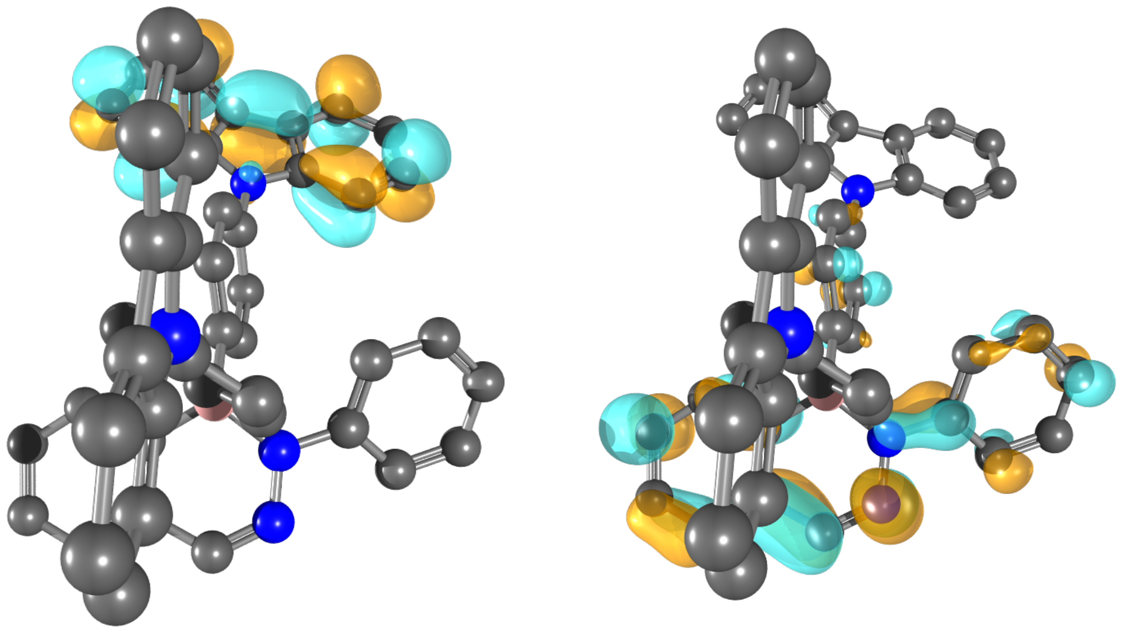
LUMO
3.944385802646 eV

Fig. S123 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **5Biph**$^-$ (ωB97X-D / def2-SVP).



HOMO
−3.89641066338 eV

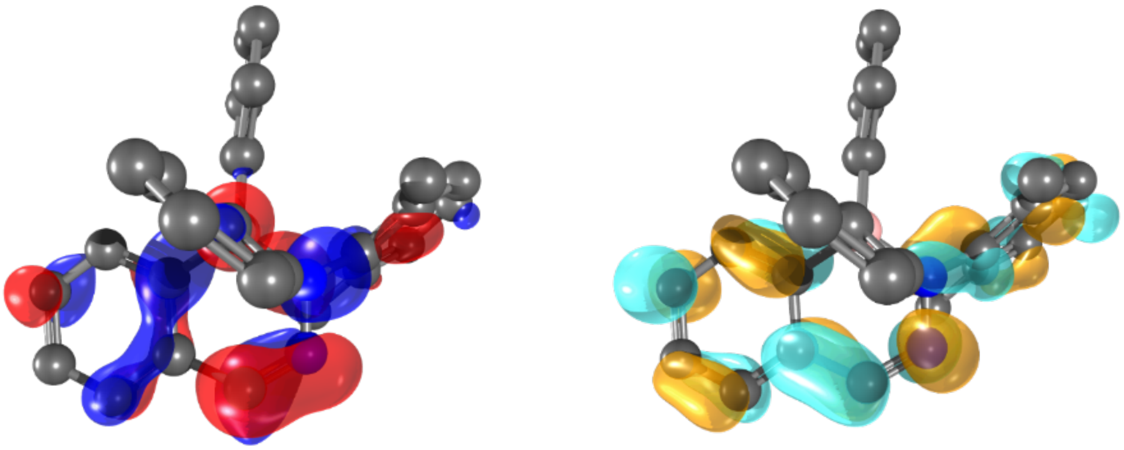
LUMO
2.664153355186 eV



LUMO+1
2.68418490241044 eV

LUMO+2
3.4872560389524 eV

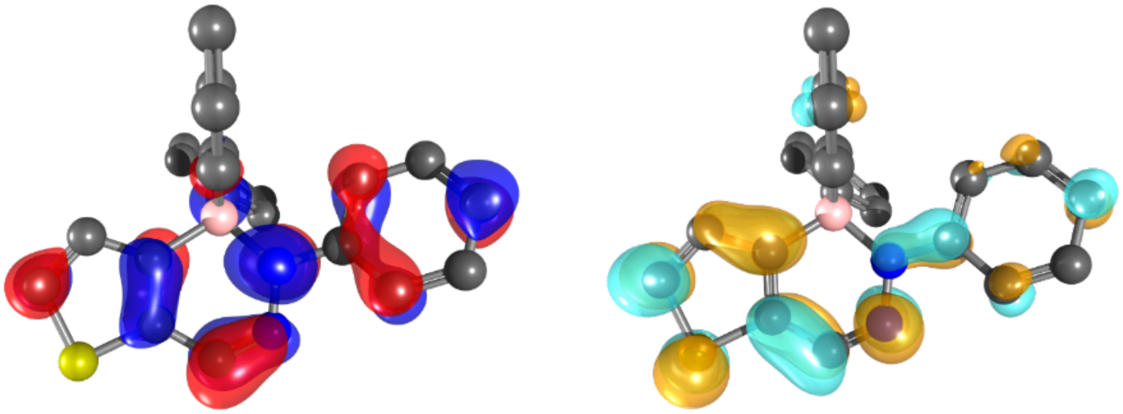
Fig. S124 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **5Cbz**$^{-}$ (ωB97X-D / def2-SVP).



HOMO
−3.43113450857 eV

LUMO
4.098930955512 eV

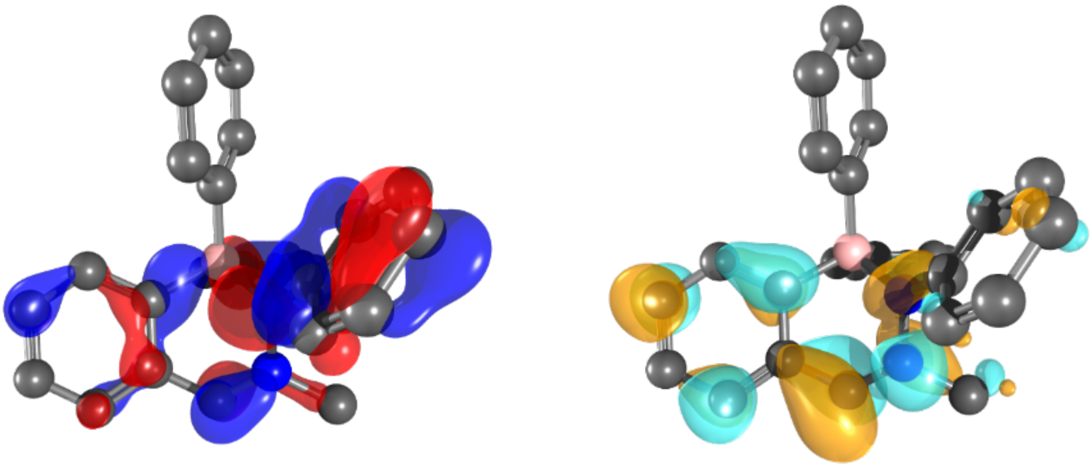
Fig. S125 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **6Ph**$^{-}$ (*ω*B97X-D / def2-SVP).



HOMO
−3.33287347540 eV

LUMO
3.883415029088 eV

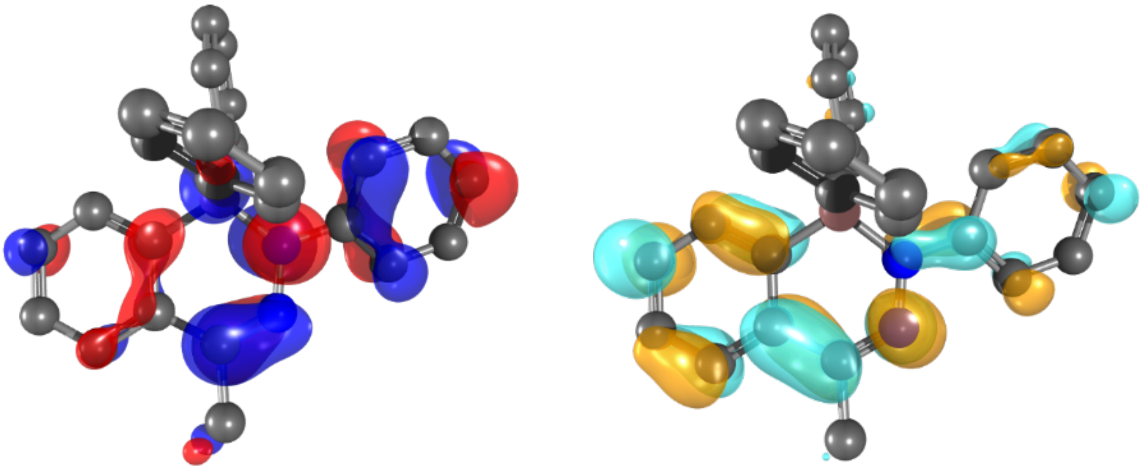
Fig. S126 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **7Ph**$^{-}$ (*ω*B97X-D / def2-SVP).



HOMO
−7.60315103244 eV

LUMO
−0.617130491330 eV

Fig. S127 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **5Ph[Me]** (*ω*B97X-D / def2-SVP).



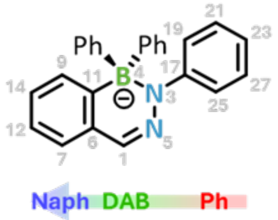
HOMO
−3.368254160986 eV

LUMO
3.9708731387 eV

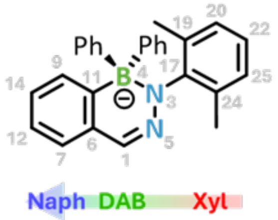
Fig. S128 Calculated frontier molecular orbitals (isovalue 0.10 eÅ^{-3}) of **8Ph**$^{-}$ (ωB97X-D / def2-SVP).

Electron excitation analysis

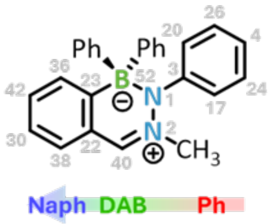
Table S9 Interfragment charge transfer (IFCT) analysis with Mulliken-like partition of **5Ph**$^-$, **6Ph**$^-$, **5Ph[Me]**, and **7Ph**$^-$ for the first excited state.



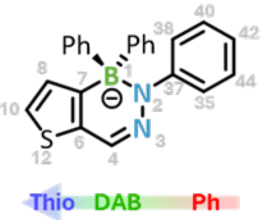
5Ph$^-$



6Ph$^-$



5Ph[Me]



7Ph$^-$

Fragment characterization					
	Fragment	Input atom indices	Hole (h$^+$)	Electron (e$^-$)	IF e$^-$ retribution
5Ph$^-$	Naph	6 7 9 11 12 14	15.09%	44.22%	0.06671
	DAB	1 3 4 5 6 11	56.03%	50.11%	0.28076
	Ph	17 19 21 23 25 27	27.36%	16.09%	0.04402
6Ph$^-$	Naph	6,7,9,11,12,14	19.28%	42.18%	0.08133
	DAB	1,3,4,5,6,11	70.86%	48.98%	0.34707
	Xyl	17,19,20,22,24,25	8.11%	18.08%	0.01466
5Ph[Me]	Naph	36,42,30,38,22,23	15.57%	35.40%	0.05511
	DAB	23,22,40,52,1,2	52.19%	64.66%	0.33746
	Ph	3,20,26,4,24,17	29.61%	6.38%	0.01890
7Ph$^-$	Thio	6,7,8,10,12	20.60%	46.89%	0.09660
	DAB	1,2,3,4,6,7	58.37%	50.61%	0.29541
	Ph	35,37,38,40,42,44	24.25%	14.14%	0.03429

Transferred electrons between fragments				
	Fragments	Electrons	Intrinsic CT	Intrinsic LE
5Ph$^-$	DAB→Naph	0.24776	69.59%	39.15%
	Ph→DAB	0.13711		
	Ph→Naph	0.12099		
6Ph$^-$	DAB→Naph	0.29885	63.02%	44.31%
	Xyl→DAB	0.03971		
	Xyl→Naph	0.03419		
5Ph[Me]	DAB→Naph	0.18474	62.49%	41.15%
	Ph→DAB	0.19145		
	Ph→Naph	0.10481		
7Ph$^-$	DAB→Thio	0.27371	72.61%	42.63%
	Ph→DAB	0.12272		
	Ph→Thio	0.11371		

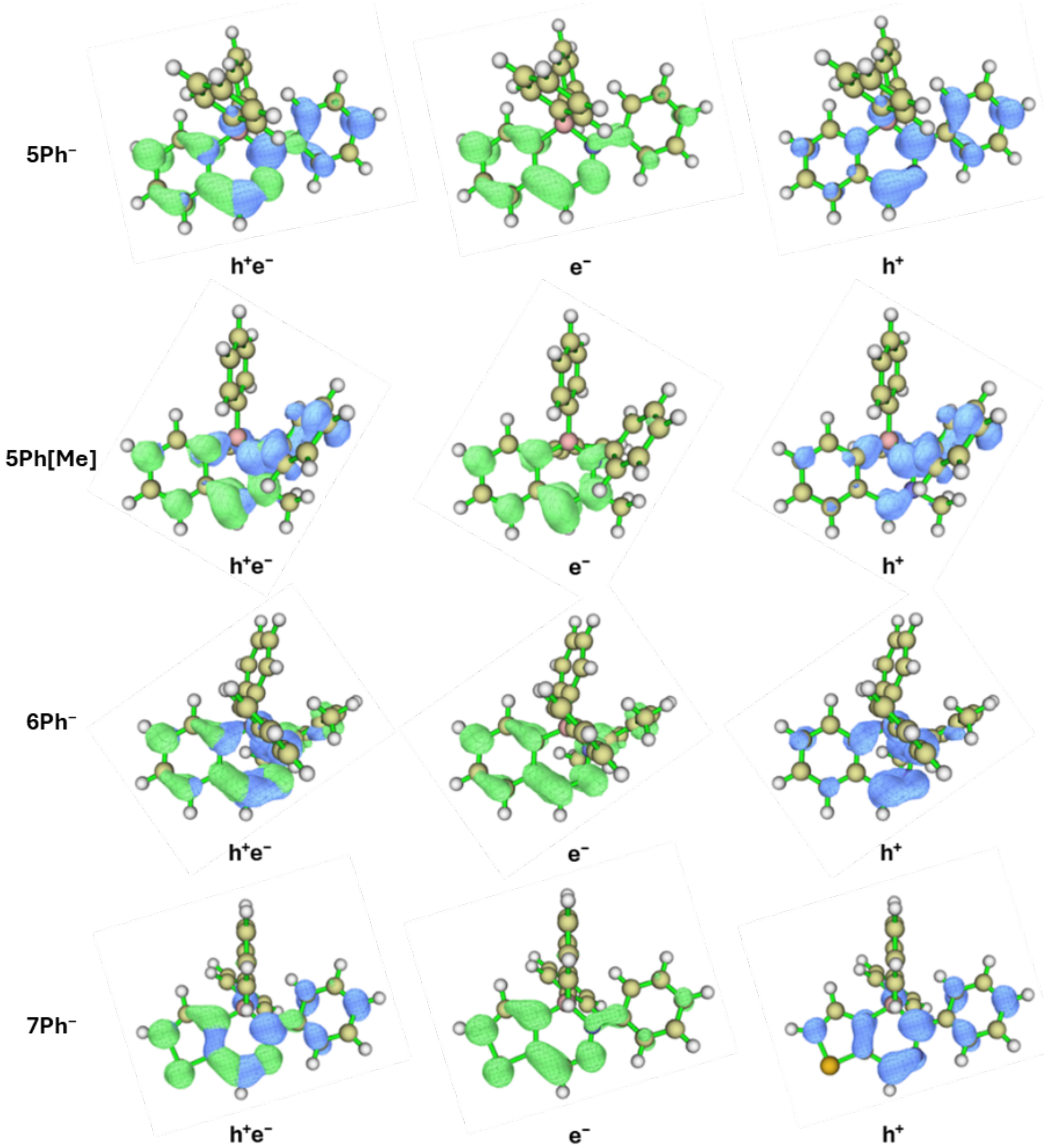
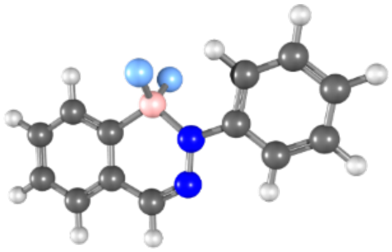


Fig. S129 Visualized hole-electron and transition density analysis of **5Ph$^-$**, **5Ph[Me]**, **6Ph$^-$**, and **7Ph$^-$**. Simultaneous isosurface of hole (h$^+$) and electron (e$^-$) distribution (top), isosurface of electron distribution (middle, green) and isosurface of hole distribution (bottom, blue), isovalue 0.002.

Optimized structures (.xyz-files)

Compound **5F⁻** @ ωB97XD / def2-SVP



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-1 1
 C          -1.11276600   1.93126900  -0.06838300
 H          -1.34428700   3.00389100  -0.09571100
 N           0.57198600   0.37315800  -0.06815000
 B          -0.36968500  -0.88069300   0.06651300
 N           0.14130700   1.64171000  -0.08502100
 C          -2.21669100   0.98008600  -0.03087500
 C          -3.55331300   1.41836500  -0.05663600
 H          -3.76861300   2.49141900  -0.09798000
 C          -2.97509300  -1.29867800   0.03981400
 H          -2.75255200  -2.36936300   0.07332800
 C          -1.90781100  -0.38953500   0.02220500
 C          -4.59225600   0.49705600  -0.03218000
 H          -5.63142300   0.83858700  -0.05173400
 C          -4.30074100  -0.87180500   0.01490100
 H          -5.11549100  -1.60207300   0.03127300
 C           1.96668100   0.25215900  -0.05088800
 C           2.57711000  -1.01221100  -0.18375900
 H           1.94784800  -1.88751500  -0.33086400
 C           3.96116500  -1.13840900  -0.14868500
 H           4.40098000  -2.13480900  -0.25315500
 C           4.78959000  -0.02521500   0.00678000
 H           5.87695000  -0.13407900   0.03123300
 C           2.80848600   1.37242100   0.10158600
 H           2.34386100   2.35210100   0.19899200
 C           4.19253800   1.22943400   0.12757900
 H           4.81510200   2.12133500   0.24989700
 F          -0.11855900  -1.79052000  -0.99771300
 F          -0.07459500  -1.54833900   1.27944700
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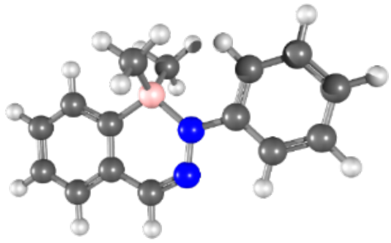
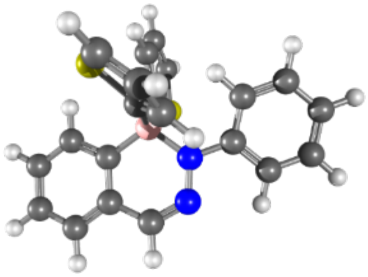
Compound **5Me**$^-$ @ ωB97XD / def2-SVP



-1 1

C	1.06473800	-1.93155000	-0.00004600
H	1.26797000	-3.01098500	-0.00003600
N	-0.59785600	-0.33562700	-0.00005300
B	0.39470800	0.94215800	0.00000800
N	-0.17823900	-1.61121400	-0.00002700
C	2.19845700	-1.01168500	-0.00004400
C	3.51317500	-1.50352900	-0.00008700
H	3.68097200	-2.58623900	-0.00016600
C	3.04021200	1.22391500	0.00012700
H	2.87358700	2.30644500	0.00022300
C	1.92789300	0.36859200	0.00003700
C	4.59438700	-0.62821500	-0.00002100
H	5.61874400	-1.01210800	-0.00006300
C	4.35172200	0.74745400	0.00009600
H	5.19033700	1.45077500	0.00017300
C	-1.98913900	-0.24488500	-0.00003200
C	-2.65369600	1.00191100	-0.00012700
H	-2.07156200	1.91765900	-0.00025200
C	-4.04251300	1.08546200	-0.00008900
H	-4.50672500	2.07648700	-0.00016500
C	-4.84111900	-0.05757900	0.00003600
H	-5.93158300	0.01514200	0.00005900
C	-2.81432800	-1.39701800	0.00008000
H	-2.32828900	-2.37001400	0.00013700
C	-4.20007500	-1.29794200	0.00011600
H	-4.79307200	-2.21823300	0.00020600
C	0.20507200	1.82684900	1.37982300
H	-0.76222500	2.34602600	1.48680300
H	0.32702100	1.19265400	2.27689200
H	0.98441300	2.60928300	1.43791400
C	0.20519000	1.82689400	-1.37980600
H	-0.76202600	2.34622400	-1.48681800
H	0.98463800	2.60922300	-1.43788000
H	0.32706500	1.19270600	-2.27689200

Compound **5Thio**$^{-}$ @ ωB97XD / def2-SVP



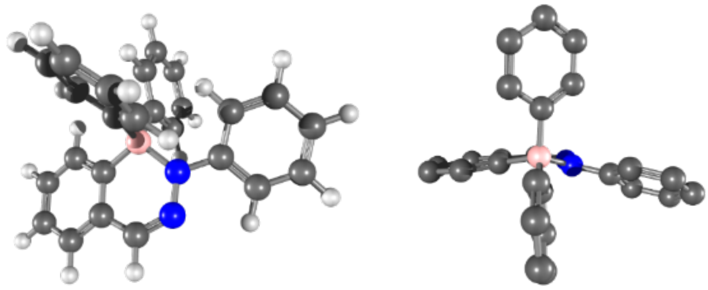
-1 1

C	0.91137700	-0.29767000	-2.82243300
H	1.09533300	-0.30437200	-3.90418400
N	-0.68500500	-0.08908100	-1.18372800
B	0.34816800	0.02225700	0.00633500
N	-0.31310900	-0.12265900	-2.47692100
C	2.02821700	-0.56526800	-1.92125800
C	3.28612700	-0.93045300	-2.42640800
H	3.43768000	-0.97670000	-3.51000200
C	2.85384500	-0.83698800	0.31385200
H	2.68881000	-0.81735700	1.39597600
C	1.79471400	-0.49913500	-0.53798500
C	4.32834700	-1.23878600	-1.55964800
H	5.30906400	-1.51974300	-1.95381700
C	4.10698300	-1.19520800	-0.18015000
H	4.91717700	-1.44392800	0.51141500
C	-2.07311400	0.01794400	-1.02208700
C	-2.64044000	0.43811700	0.19675700
H	-1.99411300	0.70717200	1.02847200
C	-4.02055500	0.52533200	0.34931100
H	-4.42211100	0.85451000	1.31179400
C	-4.88616900	0.21258300	-0.69830000
H	-5.96922300	0.28440900	-0.57106500
C	-2.95581100	-0.29195700	-2.07746600
H	-2.52898100	-0.60903800	-3.02726300
C	-4.33299900	-0.19274600	-1.91355100
H	-4.98611900	-0.44523000	-2.75444700
C	0.49224500	1.61017700	0.40777600
C	-0.06343000	2.68852500	-0.24079400
S	1.52828400	2.19990900	1.67240200
C	0.32663000	3.96181300	0.27623300
H	-0.74375700	2.55944600	-1.08470700
C	1.19477000	3.85584200	1.32783000
H	-0.02466400	4.91671100	-0.12041800
H	1.64870800	4.65649600	1.91085700
C	-0.10217200	-0.92697000	1.25918600
C	-0.14311900	-0.70883200	2.61683800
S	-0.54663900	-2.57381500	0.94246100
C	-0.52963700	-1.84855200	3.38840400

H	0.08812300	0.26370900	3.05546200
C	-0.78440000	-2.94266700	2.60780100
H	-0.61979600	-1.84935300	4.47679600
H	-1.10494700	-3.93395600	2.92674700

Compound **5Ph**$^-$ @ ωB97XD / def2-SVP

Ground state S$_0$

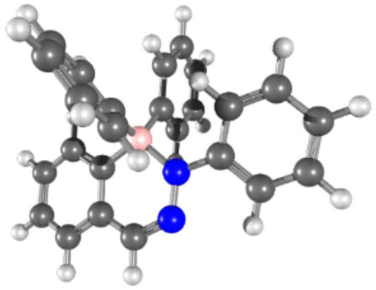


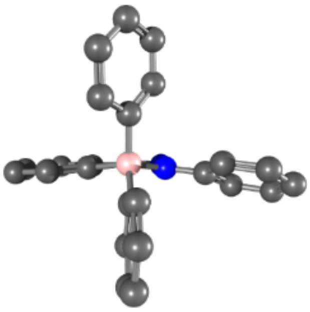
-1 1

C	1.08220700	0.62112900	-2.72617200
H	1.33298600	1.00588500	-3.72272700
N	-0.59644400	0.29645000	-1.19692300
B	0.38577600	-0.02241000	0.00557300
N	-0.15636200	0.72103500	-2.39608000
C	2.12129000	-0.05479700	-1.95416900
C	3.37145200	-0.33336300	-2.52751600
H	3.58689900	0.01472000	-3.54333100
C	2.76916100	-1.24589100	0.02262300
H	2.53337800	-1.63582600	1.01809500
C	1.80512500	-0.48616200	-0.65319300
C	4.32501700	-1.05650900	-1.81854800
H	5.30084000	-1.26871400	-2.26454500
C	4.01625200	-1.52261100	-0.53832300
H	4.75127100	-2.10709000	0.02285800
C	0.65770600	1.35112600	0.87759300
C	-1.98899800	0.35436300	-1.08106000
C	-0.18789400	-1.28272200	0.89052800
C	-2.62086700	0.39609500	0.17747900
H	-2.01900200	0.40925800	1.08316000
C	-4.00756400	0.43763500	0.28022700
H	-4.45994900	0.46800100	1.27535700
C	-4.81663600	0.45251500	-0.85571600
H	-5.90539400	0.48518600	-0.76749100
C	-2.81543500	0.37737500	-2.22402300
H	-2.33866000	0.35842300	-3.20278400
C	-4.20006100	0.42775700	-2.10754200
H	-4.80873800	0.44016100	-3.01681600
C	1.61546600	1.39501800	1.90735300

H	2.19044000	0.49289900	2.13794800
C	1.87556100	2.55317800	2.63890200
H	2.62830000	2.53898300	3.43316500
C	1.18465200	3.73161300	2.35312300
H	1.38481800	4.64488400	2.92088200
C	0.24373000	3.72712300	1.32513900
H	-0.29988000	4.64388200	1.07732100
C	-0.60450500	-2.44568400	0.21847600
H	-0.57708900	-2.45415400	-0.87581800
C	-0.24798800	-1.32009900	2.29087800
H	0.04758200	-0.43482700	2.86145500
C	-0.00775100	2.55710700	0.60513000
H	-0.74356500	2.58445900	-0.20325100
C	-1.05735100	-3.57493300	0.89559900
H	-1.37947800	-4.45624700	0.33281600
C	-0.69383100	-2.44812200	2.98616400
H	-0.72712800	-2.43448100	4.07995600
C	-1.10220000	-3.58410400	2.29153800
H	-1.45609900	-4.46796500	2.82996600

Excited state S_1



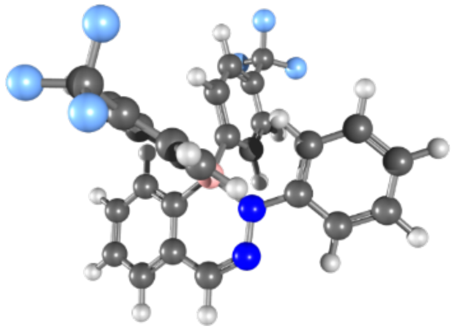


-1 1

C	1.22087000	0.13954900	-2.74585600
H	1.48922200	0.29987400	-3.79767400
N	-0.52929300	0.16185100	-1.24470900
B	0.39433300	-0.06351000	0.01193700
N	-0.08069700	0.34704500	-2.50996700
C	2.22565800	-0.25271000	-1.84591300
C	3.57446100	-0.49462600	-2.27326600
H	3.83696100	-0.33148800	-3.32415600
C	2.87483100	-0.89138400	0.40807200
H	2.61773200	-1.06753400	1.45810400
C	1.87848200	-0.43704500	-0.46094900
C	4.52145000	-0.92985800	-1.37886800
H	5.54648900	-1.11479200	-1.71534600
C	4.17686400	-1.14749400	-0.01883900
H	4.92735000	-1.51854500	0.68424300
C	0.54408300	1.39313100	0.78448000

C	-1.90570900	0.27069200	-1.13900100
C	-0.22230100	-1.30425700	0.89532500
C	-2.54062500	0.54380700	0.09793100
H	-1.94080900	0.71309000	0.98763100
C	-3.92183800	0.63864400	0.17536200
H	-4.38187100	0.85102600	1.14399900
C	-4.72253800	0.48295200	-0.96110800
H	-5.81023700	0.56086700	-0.88985100
C	-2.72371200	0.15339000	-2.29329300
H	-2.23124400	-0.02246700	-3.24735300
C	-4.10385400	0.24482800	-2.19229400
H	-4.71206300	0.13019700	-3.09434100
C	1.10446500	1.49075600	2.07124300
H	1.42889000	0.58248400	2.58464600
C	1.27519900	2.71632600	2.71232900
H	1.71081600	2.74635600	3.71552000
C	0.90377500	3.90190500	2.07591700
H	1.03938900	4.86603500	2.57367500
C	0.36338600	3.83517800	0.79304600
H	0.07166100	4.75281900	0.27365600
C	-0.26310500	-2.57010400	0.28279700
H	0.10982600	-2.66800200	-0.74167100
C	-0.69968900	-1.23195700	2.21030700
H	-0.70397700	-0.26937700	2.73033500
C	0.18563200	2.60241900	0.16379400
H	-0.24388100	2.58178100	-0.84174100
C	-0.75787900	-3.69494900	0.93663400
H	-0.77910200	-4.65992800	0.42173700
C	-1.18742200	-2.35607400	2.88596300
H	-1.54929100	-2.25695600	3.91380200
C	-1.22087000	-3.59397400	2.25189000
H	-1.60528600	-4.47502400	2.77360700

Compound **5CF$_3^-$** @ ωB97XD / def2-SVP

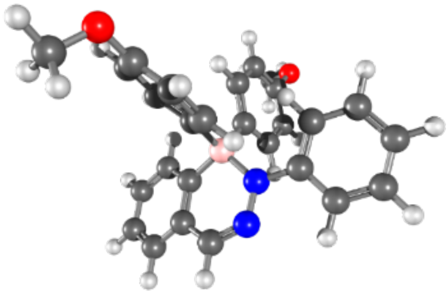


-1 1

C	0.87187300	3.67427500	-0.13175000
H	1.29938000	4.68037200	-0.04098500
N	0.00522100	1.88149700	1.00616700
B	0.08732400	0.89928800	-0.22664800
N	0.53323200	3.12036000	0.97771400
C	0.62437100	3.13510400	-1.46641800
C	0.79256100	3.93800000	-2.60474900
H	1.17147100	4.95900600	-2.49157000
C	-0.21533100	1.36396600	-2.84844300
H	-0.63926000	0.36035000	-2.95715100
C	0.13877200	1.81944400	-1.57180500
C	0.46870700	3.44756300	-3.86529000
H	0.60470800	4.07288700	-4.75187600
C	-0.04711700	2.15507100	-3.98507700
H	-0.32150500	1.76447400	-4.96905800
C	1.48787100	0.03160900	-0.15538200
C	-0.43797900	1.50923200	2.28104200
C	-1.26773100	-0.02424900	-0.31117700
C	-0.58441100	0.15613600	2.64229600
H	-0.32205800	-0.62595300	1.93323800
C	-1.04468100	-0.20065500	3.90613700
H	-1.14674000	-1.26177200	4.14893000
C	-1.36165900	0.76756100	4.85774200
H	-1.72282800	0.48090800	5.84822700
C	-0.75315900	2.48083900	3.25283200
H	-0.63091800	3.53019900	2.98890000
C	-1.20334600	2.11127400	4.51517600
H	-1.44269400	2.89233500	5.24280700
C	1.89924700	-0.79814500	-1.21483700
H	1.27320800	-0.87292400	-2.10836700
C	3.09015300	-1.51540800	-1.18399000
H	3.37494100	-2.14683700	-2.02884400
C	3.93367500	-1.41404300	-0.07438200
C	3.56878800	-0.58259400	0.98429500
H	4.22845900	-0.48096700	1.84870000
C	-2.51950600	0.60758500	-0.19813200

H	-2.54660300	1.68385900	-0.00510500
C	-1.28701100	-1.40569800	-0.54589400
H	-0.34246500	-1.95120600	-0.61915900
C	2.36853400	0.12392400	0.93361000
H	2.11128700	0.77900900	1.76959400
C	-3.71595600	-0.08803400	-0.30919700
H	-4.66917100	0.43508300	-0.20319700
C	-2.47732500	-2.12328700	-0.66769900
H	-2.45327800	-3.20077500	-0.84393000
C	-3.70034500	-1.46598500	-0.55014400
C	5.19029800	-2.22758000	-0.01086400
C	-4.98959000	-2.20848300	-0.72910800
F	5.76481600	-2.37687000	-1.21595800
F	6.11511500	-1.68613800	0.79634300
F	4.97088400	-3.47303000	0.45185700
F	-5.47230300	-2.10008000	-1.98165600
F	-5.95834900	-1.75347800	0.08135100
F	-4.86571000	-3.52285100	-0.48836000

Compound **5OMe**$^-$ @ ωB97XD / def2-SVP

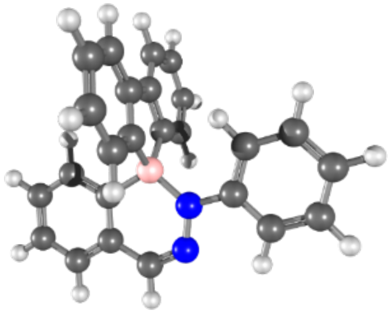


-1 1

C	-1.04493000	0.00025300	3.18735700
H	-1.52326000	0.13579800	4.16551900
N	-0.01086700	1.05336600	1.43123000
B	-0.10621300	-0.19503600	0.46040200
N	-0.60981100	1.07748000	2.63620500
C	-0.84484100	-1.35691600	2.68688600
C	-1.12609500	-2.46763000	3.49710000
H	-1.55649600	-2.31247700	4.49214100
C	0.01587100	-2.81840500	0.99285700
H	0.49194200	-2.96815300	0.01830600
C	-0.28939100	-1.51422600	1.40409500
C	-0.84894600	-3.75453800	3.04753600
H	-1.07335000	-4.61961800	3.67793900

C	-0.26585900	-3.92829800	1.79002700
H	-0.02782500	-4.93425400	1.43198300
C	-1.45237500	-0.05994900	-0.48313600
C	0.52320300	2.29457400	1.06796800
C	1.29266800	-0.37558900	-0.38108100
C	0.77585400	2.62017500	-0.27903200
H	0.53013600	1.90635000	-1.06188300
C	1.32229400	3.85156100	-0.62622000
H	1.50542900	4.06624700	-1.68262200
C	1.62488300	4.80695900	0.34360700
H	2.05428400	5.77204200	0.06371100
C	0.82549800	3.26998400	2.04077800
H	0.62228900	3.03445100	3.08433500
C	1.36306300	4.50042700	1.67973500
H	1.58873900	5.23109400	2.46235800
C	-1.87938100	-1.10924000	-1.31642300
H	-1.29637800	-2.03460900	-1.34971300
C	-3.03266400	-1.02988400	-2.09576600
H	-3.34171000	-1.85700600	-2.74072900
C	-3.81358400	0.12429100	-2.05552200
C	-3.43296900	1.18129400	-1.23295400
H	-4.05086500	2.08309200	-1.20521000
C	2.51298300	-0.33745600	0.31667000
H	2.49477700	-0.12919400	1.39101600
C	1.37539100	-0.62873000	-1.75672000
H	0.45891900	-0.64439800	-2.35356000
C	-2.27232100	1.07924400	-0.46354700
H	-1.99863700	1.91861000	0.18131600
C	3.73946900	-0.54001400	-0.30907500
H	4.67677000	-0.48850100	0.25189400
C	2.59470900	-0.84633100	-2.40550400
H	2.63972700	-1.03886600	-3.48074000
C	3.78042200	-0.80255800	-1.67960600
O	4.98637800	-1.00145300	-2.31819400
O	-4.95252100	0.21452000	-2.82849400
C	-6.12235400	-0.17923700	-2.16990100
H	-6.95911700	-0.06510200	-2.87483700
H	-6.07501400	-1.23520700	-1.84220600
H	-6.32367000	0.44234900	-1.27698300
C	5.48866200	-2.30170300	-2.20292700
H	4.80152500	-3.04811100	-2.64534300
H	6.44686600	-2.34022700	-2.74176900
H	5.66432300	-2.58792900	-1.14868500

Compound **5Biph**$^{-}$ @ ωB97XD / def2-SVP

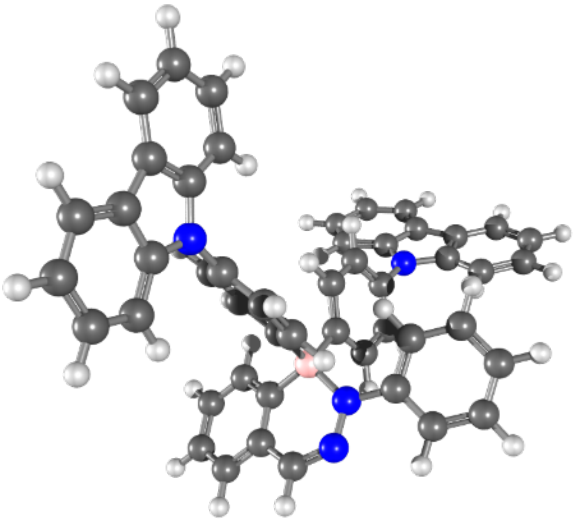


-1 1

C	0.98170200	-3.11519000	-0.00014900
H	1.17089600	-4.19631600	-0.00014200
N	-0.64662500	-1.49027200	-0.00017200
N	-0.25601200	-2.77634700	-0.00016100
C	2.12454400	-2.20659200	-0.00013100
C	3.43698200	-2.70795100	-0.00015500
H	3.59744400	-3.79139400	-0.00019500
C	2.98645000	0.02963900	-0.00005900
H	2.82212900	1.11177200	-0.00002200
C	1.87432300	-0.82494400	-0.00008400
C	4.52121800	-1.83929900	-0.00012800
H	5.54274700	-2.22987500	-0.00014700
C	4.29034100	-0.45976100	-0.00007400
H	5.13493100	0.23543300	-0.00004500
C	-2.03846700	-1.34537500	-0.00007900
C	-2.64032900	-0.07094400	-0.00008600
H	-2.02584800	0.82420200	-0.00017000
C	-4.02496100	0.06866800	-0.00000900
H	-4.44787500	1.07716900	-0.00003400
C	-4.86680400	-1.04231400	0.00009200
H	-5.95325200	-0.92444400	0.00013500
C	-2.90028800	-2.46490200	0.00004400
H	-2.45165800	-3.45597500	0.00007100
C	-4.28146900	-2.30935000	0.00013500
H	-4.91323300	-3.20303000	0.00022700
C	0.17520700	0.79262000	1.23854700
C	0.17525700	0.79280500	-1.23853800
C	0.13230600	0.60345500	2.61880500
C	0.15899500	2.11412800	0.74116400
C	0.13223000	0.60381400	-2.61881500
C	0.15895700	2.11423800	-0.74096100
C	0.07477700	1.69778800	3.48752300
H	0.14177300	-0.41313800	3.02543300
C	0.11463800	3.21332500	1.60127300
C	0.07450300	1.69826200	-3.48737500
H	0.14175300	-0.41272700	-3.02556800
C	0.11440000	3.21354700	-1.60092000

C	0.07137400	2.99964300	2.98039400
H	0.03340200	1.53820600	4.56926100
H	0.10606600	4.23379600	1.20578300
C	0.07102000	3.00004600	-2.98006500
H	0.03301100	1.53883700	-4.56913200
H	0.10577600	4.23396600	-1.20529600
H	0.03058600	3.85263500	3.66397100
H	0.03006900	3.85312400	-3.66352400
B	0.34366200	-0.26761200	-0.00007200

Compound **5Cbz**$^-$ @ ωB97XD / def2-SVP



-1 1

C	1.02500600	4.63512300	-0.57620600
H	1.49471700	5.62636300	-0.57242900
N	0.06983200	2.99350200	0.70794200
B	0.12549400	1.89881300	-0.43003300
N	0.64964600	4.20205900	0.57491400
C	0.76382100	3.98758800	-1.85937300
C	0.97358900	4.67571800	-3.06401400
H	1.39682700	5.68524200	-3.04045000
C	-0.14811500	2.13739400	-3.08367000
H	-0.61529500	1.14725800	-3.10396800
C	0.22011600	2.69040700	-1.85050500
C	0.63436300	4.08771500	-4.27805600
H	0.80295200	4.62347100	-5.21616100
C	0.06127900	2.81393800	-4.28566100
H	-0.22482900	2.34861100	-5.23315100
C	1.49192400	0.99223500	-0.26167700
C	-0.43052300	2.76805800	1.99573800

C	-1.25934400	1.01825700	-0.42164400
C	-0.62569500	1.46430600	2.49126300
H	-0.34625800	0.60676600	1.88320500
C	-1.15886800	1.25318400	3.75934300
H	-1.29775100	0.22627500	4.10829900
C	-1.49935900	2.32430500	4.58482700
H	-1.91737600	2.15261800	5.57952800
C	-0.76493300	3.84372400	2.84300900
H	-0.60368300	4.85636600	2.47597900
C	-1.28652400	3.62026100	4.11240100
H	-1.54051200	4.47901300	4.74063000
C	1.88056200	0.05344500	-1.23428400
H	1.26076900	-0.07960400	-2.12567800
C	3.04680100	-0.69886800	-1.12529900
H	3.33089400	-1.41290400	-1.90259800
C	3.87403700	-0.53302600	-0.01290500
C	3.52810700	0.39644700	0.96677700
H	4.17905000	0.52742600	1.83501200
C	-2.48639200	1.70142400	-0.35607800
H	-2.47574300	2.79415900	-0.30862900
C	-1.32668100	-0.38013000	-0.48543500
H	-0.40106500	-0.96079100	-0.52492600
C	2.36140300	1.14775600	0.82923200
H	2.11719400	1.88172600	1.60136800
C	-3.70681100	1.03761300	-0.32787000
H	-4.64766800	1.59018700	-0.26595900
C	-2.54006900	-1.06900100	-0.44896200
H	-2.56662700	-2.16158100	-0.46770200
C	-3.73513000	-0.35867500	-0.36249900
C	6.35806700	-0.80457700	0.07014900
C	5.13145600	-2.67114100	0.29451300
C	6.78709100	0.51490100	-0.11127800
C	7.27819100	-1.86896000	0.22725100
C	4.08528100	-3.59296600	0.41186800
C	6.48657500	-3.07384800	0.37138300
C	8.15601100	0.75047300	-0.12405300
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C	8.65185300	-1.60331700	0.21095400
C	4.42077400	-4.92786900	0.59950700
H	3.04594700	-3.26490500	0.35711100
C	6.79645200	-4.42505200	0.56056500
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H	9.37244600	-2.41591100	0.33198700
C	5.76179100	-5.34621900	0.67200000
H	3.62277200	-5.66820300	0.69438400
H	7.83842100	-4.74880800	0.62127800
H	10.15348900	-0.07126600	0.02296200

H	5.98846600	-6.40444400	0.81952800
C	-5.57066700	-1.79100500	-1.28363600
C	-5.79297900	-1.09312700	0.83865700
C	-5.12066300	-2.02307200	-2.58791000
C	-6.79455000	-2.32684700	-0.81391100
C	-5.59296300	-0.50668100	2.09348500
C	-6.93795700	-1.87558500	0.55580700
C	-5.91573900	-2.80809300	-3.41354400
H	-4.17698900	-1.59792500	-2.93398400
C	-7.57557700	-3.11419500	-1.66681900
C	-6.56968200	-0.71190100	3.05957400
H	-4.69991900	0.08732900	2.29747200
C	-7.90629400	-2.06527400	1.54812600
C	-7.13175500	-3.35234700	-2.96235800
H	-5.58766700	-3.00526000	-4.43701700
H	-8.52189400	-3.53427900	-1.31720100
C	-7.71792900	-1.48064100	2.79469900
H	-6.43969200	-0.26525600	4.04818300
H	-8.79583700	-2.66635900	1.34400300
H	-7.73095100	-3.96585000	-3.63882700
H	-8.46530400	-1.61931600	3.57910600
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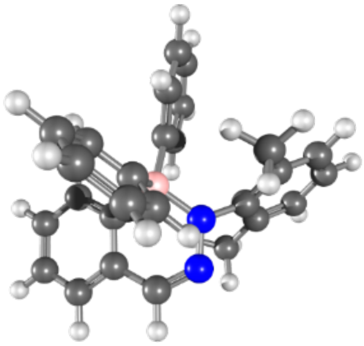
Compound **6Ph**$^-$ @ ωB97XD / def2-SVP



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B	-0.51730300	-0.07885500	0.12347600
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C	-1.91318800	1.95705300	-0.63830800
C	-2.87404200	2.96826100	-0.47559400
H	-3.18807400	3.55691600	-1.34416400

C	-2.01494400	1.50101000	1.72113500
H	-1.67737100	0.93165600	2.59344000
C	-1.48648400	1.18573800	0.46334500
C	-3.41203400	3.23456200	0.77932300
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C	-1.55339800	-1.27514800	-0.34128800
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C	0.43707200	-0.48379400	1.39381300
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H	4.29026000	-2.03321200	-1.33642100
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H	5.68406500	0.01310400	-1.10257900
C	2.58101100	1.44267400	-1.01935500
C	3.97396200	1.33041100	-1.01778000
H	4.57940700	2.23567300	-0.91061200
C	-2.41064200	-1.88188500	0.59458000
H	-2.34092400	-1.58304600	1.64590600
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H	-3.98994600	-3.29904500	0.99694800
C	-3.48134600	-3.22865300	-1.10317300
H	-4.21861400	-3.98197200	-1.39573300
C	-2.66404800	-2.62737200	-2.05886200
H	-2.76237600	-2.90380100	-3.11329700
C	1.20177000	0.50807300	2.03488300
H	1.12134100	1.54137500	1.68582500
C	0.57467800	-1.78521700	1.89998400
H	-0.00381700	-2.59608700	1.44744400
C	-1.72136500	-1.67001100	-1.67753900
H	-1.09515900	-1.20488900	-2.44346400
C	2.05923200	0.22498400	3.09535900
H	2.64096300	1.02908900	3.55553200
C	1.42711600	-2.08820400	2.96484800
H	1.50493500	-3.11944300	3.32239000
C	2.17874000	-1.08281800	3.56815000
H	2.85140400	-1.31378100	4.39915900
C	1.60813700	-2.23173400	-1.47277400
H	0.91700200	-2.41705700	-0.64099000
H	0.98690000	-2.14774000	-2.37606100
H	2.26450800	-3.10772400	-1.57908500
C	1.93903500	2.79534700	-0.85671400
H	1.55986800	3.17483600	-1.81750500
H	1.06813800	2.74211200	-0.18603200
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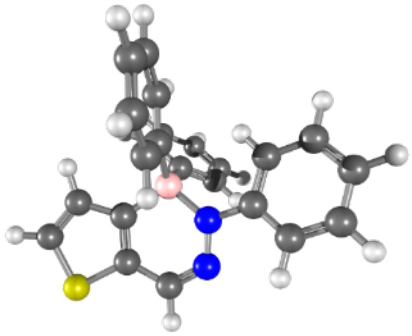
Compound **7Ph**$^-$ @ ωB97XD / def2-SVP



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C	-2.20435900	-0.68808300	-1.55814700
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C	-2.91825600	-0.87523900	0.62663100
H	-2.84351800	-0.84695300	1.71578300
C	-4.05633900	-1.26341500	-0.02734700
H	-5.00830700	-1.56988300	0.40477900
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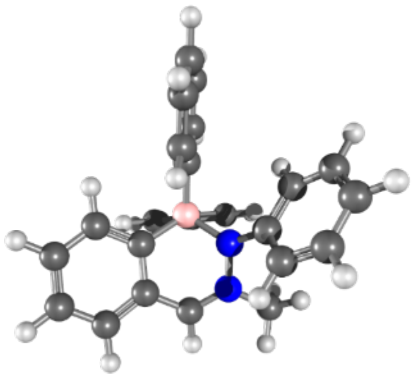
C	0.26144600	-0.92786300	1.29804300
C	0.46367000	-2.29083600	1.01810200
H	0.23853700	-2.65505700	0.01052400
C	0.94568800	-3.18394100	1.97197600
H	1.09473500	-4.23566100	1.70936000
C	1.23936700	-2.73921000	3.26268900
H	1.61727500	-3.43497900	4.01732800
C	1.04912600	-1.39428500	3.57167900
H	1.28130300	-1.02565900	4.57563200
C	0.57064300	-0.51024600	2.60061700
H	0.45196700	0.54461900	2.86570600
C	-0.48589600	1.62156600	0.50032700
C	-1.24862800	2.04857000	1.60293200
H	-1.73380300	1.29981500	2.23691800
C	-1.42256700	3.39637500	1.91579400
H	-2.02341000	3.68171700	2.78485100
C	-0.83695400	4.38083500	1.11879100
H	-0.96891200	5.44011300	1.35738500
C	-0.08856000	3.99136600	0.00912400
H	0.37035700	4.74864500	-0.63374700
C	0.07655600	2.63736300	-0.28906300
H	0.66035200	2.35705300	-1.17047400
C	2.64994700	-0.48909100	-2.36624100
H	2.10751100	-0.85940900	-3.23429500

C	1.90342700	-0.07634300	-1.24209000
C	2.62196300	0.41160600	-0.13246200
H	2.08669300	0.76502500	0.74518900
C	4.01191000	0.46578100	-0.14657400
H	4.53111600	0.85030300	0.73572700
C	4.74080500	0.05022500	-1.26042900
H	5.83269000	0.09514100	-1.26455100
C	4.03870800	-0.42277000	-2.36993900
H	4.58245200	-0.75584300	-3.25927400

Compound **5Ph[Me]** @ ωB97XD / def2-SVP



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C	4.60962500	-1.00028700	-1.01954800
H	5.69750300	-1.08224700	-1.06210600
C	0.54639400	1.18559600	1.06451600
C	0.51630100	2.58442900	0.97805500
H	-0.20219900	3.06282100	0.30680600
C	1.38448900	3.38657900	1.72293300
H	1.33475400	4.47464300	1.62949800
C	2.31148900	2.80325100	2.58340700
H	2.99428600	3.42712500	3.16560600
C	1.48141800	0.62583800	1.95351800
H	1.53650700	-0.46289500	2.05560000
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H	2.12639500	1.33485800	-1.15584100
C	-1.67899400	-2.01976900	0.46826600
C	-1.21103400	-0.85919200	1.12036700

C	3.82525100	-2.14046000	-0.85836900
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C	3.99320800	0.24792400	-1.12131800
H	4.59828000	1.14861700	-1.24383400
C	-1.15364500	1.58916000	-1.96413500
H	-0.13475400	1.42169400	-2.33064900
C	-2.80211100	-2.79503900	2.45678600
H	-3.42158200	-3.52692100	2.97871300
C	-2.83296000	1.31528900	-0.28713600
H	-3.16621600	0.92119200	0.67813200
C	-3.73119000	2.05442600	-1.05856500
H	-4.74576600	2.23292200	-0.69258800
C	-1.53543000	-0.72089100	2.47513400
H	-1.17977800	0.15981400	3.01614500
C	-2.48467400	-2.97355200	1.12023100
H	-2.84138000	-3.85532500	0.58046700
C	-1.31088100	-2.22280600	-0.90668300
H	-1.87133200	-2.90920200	-1.54428700
C	-2.32009500	-1.66603500	3.13211300
H	-2.57656500	-1.51987100	4.18444900
C	-0.00351600	-1.82364100	-2.88982500
H	1.07879900	-1.88525600	-3.04455900
H	-0.40475900	-0.95457700	-3.42976200
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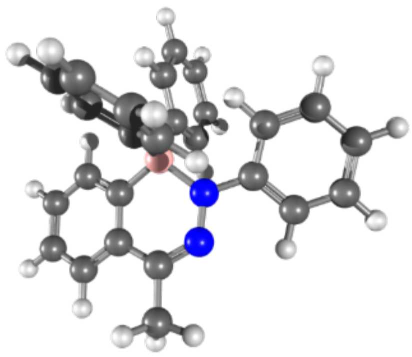
C	2.35510700	1.41289600	2.69922400
H	3.07536800	0.94195800	3.37320800
C	-3.33918500	2.56186100	-2.29657900
H	-4.04013200	3.13880900	-2.90480600
B	-0.43933500	0.23645900	0.19259000

Compound **8Ph**$^-$ @ ωB97XD / def2-SVP



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C	2.12129000	-0.05479700	-1.95416900
C	3.37145200	-0.33336300	-2.52751600
H	3.58689900	0.01472000	-3.54333100
C	2.76916100	-1.24589100	0.02262300
H	2.53337800	-1.63582600	1.01809500
C	1.80512500	-0.48616200	-0.65319300
C	4.32501700	-1.05650900	-1.81854800
H	5.30084000	-1.26871400	-2.26454500
C	4.01625200	-1.52261100	-0.53832300
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C	-1.98899800	0.35436300	-1.08106000
C	-0.18789400	-1.28272200	0.89052800
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H	2.62830000	2.53898300	3.43316500
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H	2.31300091	1.76823913	-4.06195531
H	1.61361145	0.34148902	-4.78880215
H	0.62042156	1.74880874	-4.49538836

5 References

1 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.

2 G. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3-8.

3 G. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

4 C. Pampillón, J. Claffey, M. Hogan and M. Tacke, *BioMetals*, 2008, **21**, 197-204.

5 L. Wüst, J. Chorbacher, T. Wellnitz, S. Nees, H. Helten and H. Braunschweig, *Chem. Sci.*, 2025, **16**, 7284-7293.

6 J. P. M. António, J. I. Carvalho, A. S. André, J. N. R. Dias, S. I. Aguiar, H. Faustino, R. M. R. M. Lopes, L. F. Veiros, G. J. L. Bernardes, F. A. da Silva and P. M. P. Gois, *Angew. Chem. Int. Ed.*, 2021, **60**, 25914-25921.

7 D. Chen, G. Xu, Q. Zhou, L. W. Chung and W. Tang, *J. Am. Chem. Soc.*, 2017, **139**, 9767-9770.

8 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian Inc. Wallingford CT, 2019.

9 J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615-6620.

10 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.

11 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis and F. Weinhold, *NBO 7.0*, University of Wisconsin, Madison, WI, 2018.

12 A. Gilber, *iQMol Molecular Viewer v2.13*, 2019.

13 A. D. Boese and N. C. Handy, *J. Chem. Phys.*, 2002, **116**, 9559-9569.

14 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.

15 T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.