Electronic Supporting Information for

Planarity-induced emission of neutral 1,2,3-diazaborines mediated by C–H borylation

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1 Experimental details

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

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

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

Single crystal structure analyses. Single crystals suitable for X-ray diffraction analysis were coated with polyisobutylene or perfluorinated polyether oil in a glovebox, transferred to a nylon loop, and then to the goniometer of a diffractometer. The crystal data were collected on a *RIGAKU XtalLAB SYNERGY-R* diffractometer with HPA area detector and multilayer mirror 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. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center. For the CCDC number of all compounds see synthesis and characterization section.

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.

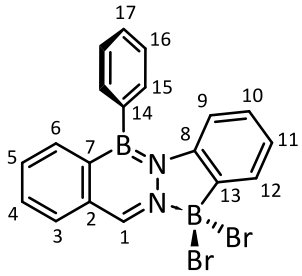
Table S1. Origin and purification of solvents and reactants.

Substance	**Origin**	**Purity / Purification**
(2-Formylphenyl)boronic acid [40138-16-7]	BLD Pharmatech®	99.97% / none stored under Ar
(2-Formylthiophen-3-yl)boronic acid [100-63-1]	BLD Pharmatech®	97% / none stored under Ar
Phenylhydrazine [100-63-1]	Sigma Aldrich®	≥97% / none stored under Ar
1,4-Diazabicyclo[2.2.2]octane (DABCO) [280-57-9]	Sigma Aldrich®	≥99% (crystals) / none
Boron tribromide (BBr_3) [10294-33-4]	Sigma Aldrich®	- / copper wire stored under Ar
Sodium sulfate (anhydrous) [7757-82-6]	sourced in house	- / none
Ethyl acetate [141-78-6]	sourced in house	Distilled prior to use
Dichloromethane [71-43-2]	sourced in house	Purified and dried over local solvent purification system (SPS), stored over MS (3 Å) under Ar
Benzene-d_6 (C_6D_6) [1076-43-3]	Sigma Aldrich®	99.6 atom % D / none stored under Ar over molecular sieves (4 Å)
Dimethylsulfoxide-d_6 (DMSO-d_6) [2206-27-1]	Sigma Aldrich®	99.5 atom % D / none

2 Syntheses and characterization

Compounds **1**$^{\text{Benz}}$, **3**$^{\text{Benz}}$ and **3**$^{\text{Thio}}$ were prepared following previously described procedures.[4]

Compound 2$^{\text{Benz}}$



2$^{\text{Benz}}$ (44%)

DAB **1**$^{\text{Benz}}$ (400 mg, 1.24 mmol, 1.00 eq.) and DABCO (79.5 mg, 708 μmol, 0.50 eq.) were dissolved in CH_2Cl_2 (20 mL) in a 100 mL Schlenk tube and cooled to 0 °C (ice bath). BBr_3 (neat, 0.65 mL, 6.85 mmol, xs., ρ = 2.64 g/mL) was added in small portions and a momentary deep red coloration of the reaction solution was observed upon addition, which quickly faded again. After 5 min, the cooling bath was removed, and the reaction was stirred for 2 d at ambient temperature. All volatile components were removed *in vacuo*, the remaining solid was washed with a cold (−20 °C) mixture of CH_2Cl_2 / *n*-pentane (2:1, 3 × 2 mL) and dried *in vacuo*.

Yield: 280 mg (621 μmol, 44%), colorless powder. The compound is air- and moisture-sensitive.

^{1}H NMR (600 MHz, 298 K, C_6D_6): δ = 9.41 (s, 1H, *H*-1), 8.02 (d*[1], $^3J_{HH}$ = 7.26 Hz, 1H, *H*-12), 7.44-7.49 (m, 1H, *H*-3), 7.21-7.28 (m, 3H, *H*-16 + *H*-17), 7.04-7.09 (m, 2H, *H*-15), 6.96-7.00 (m, 2H, *H*-4 + *H*-5), 6.94 (ddd, $^3J_{HH}$ = 7.39 Hz; 7.39 Hz, $^4J_{HH}$ = 0.90 Hz, 1H, *H*-11), 6.80-6.84 (m, 1H, *H*-6), 6.65-6.69 (m, 1H, *H*-10), 6.62 (d*[2], $^3J_{HH}$ = 8.34 Hz, 1H, *H*-9) ppm.*[3] **^{11}B{^{1}H} NMR** (160 MHz, 298 K, C_6D_6) δ = 36.7 (br s, B^{endo}), −0.7 (br s, $-BBr_2$) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, C_6D_6): δ = 147.5 (*C*-1), 145.1 (C_q^N-8), 138.3 (br, C_q^B-7), 137.4 (br, C_q^B-13), 135.9 (*C*-3), 135.6 (C_q^B-14), 133.9 (*C*-4), 132.7 (*C*-5), 132.1 (*C*-15), 131.7 (*C*-12), 130.9 (*C*-6), 130.6 (C_q-2), 129.4 (*C*-17), 128.8 (*C*-16 + *C*-10), 127.7 (*C*-11), 116.0 (*C*-9) ppm. **HRMS** (LIFDI, toluene): expected: *m/z* 370.0557, 371.0521, 372.0537, 373.0501, 374.0534 $[C_{19}H_{14}B_2Br_2N_2-Br]^+$; found: *m/z* 370.0548, 371.0512, 372.0530, 373.0491, 374.0524 $[C_{19}H_{14}B_2Br_2N_2-Br]^+$. Crystalline material of **2**$^{\text{Benz}}$ as colorless blocks was

*[1] The resonance shows a more complicated fine structure, but no additional coupling constants could be identified. Parent splitting pattern is a doublet.

*[2] The resonance shows a more complicated fine structure, but no additional coupling constants could be identified. Parent splitting pattern is a doublet.

*[3] The sample contains ca. 3% $[DABCO]H_2[BBr_4]_2$ salt as inseparable impurity.

obtained by slow diffusion of *n*-pentane into a saturated dichloromethane solution at ambient temperature in a glovebox.

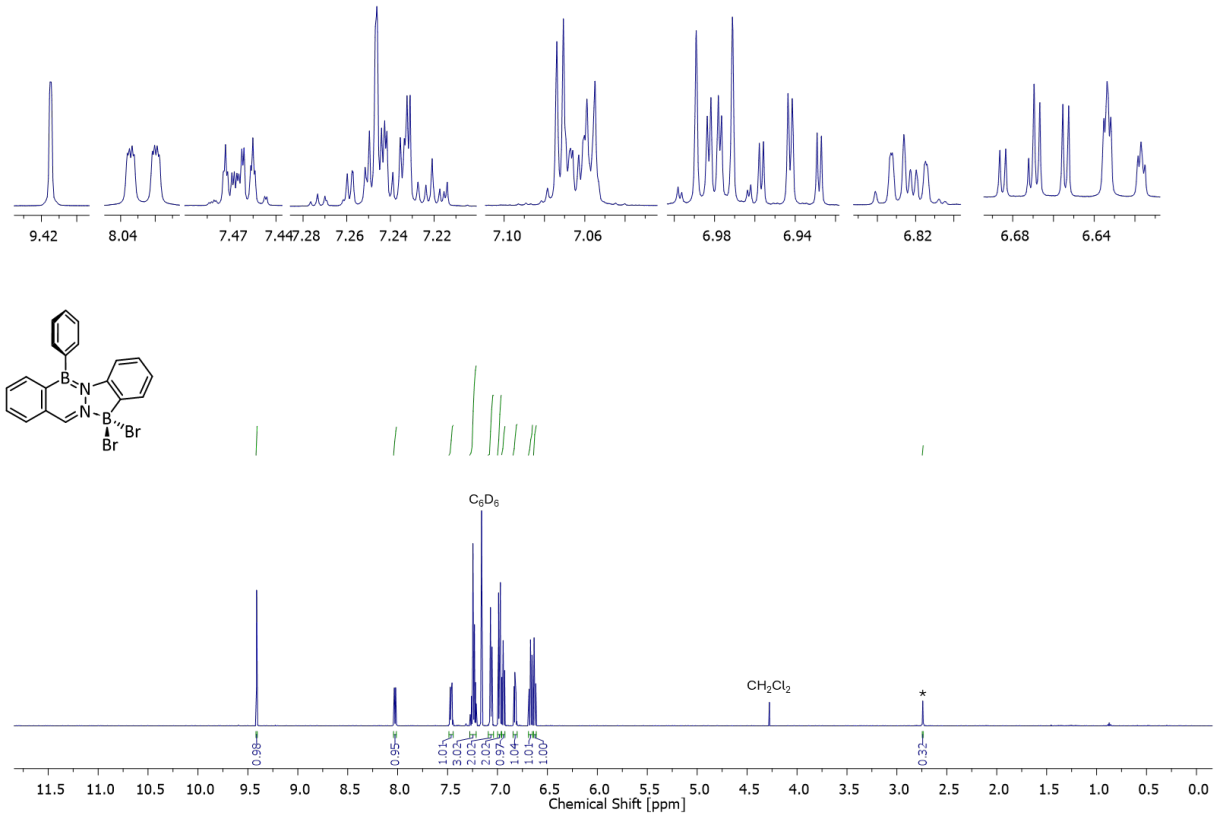


Figure S1. ^{1}H NMR spectrum of compound **2^{Benz}** in C_6D_6. The sample contains ca. 3% $[DABCO]H_2[BBr_4]_2$ salt as inseparable impurity (resonance marked with * corresponds to 12H of DABCO).

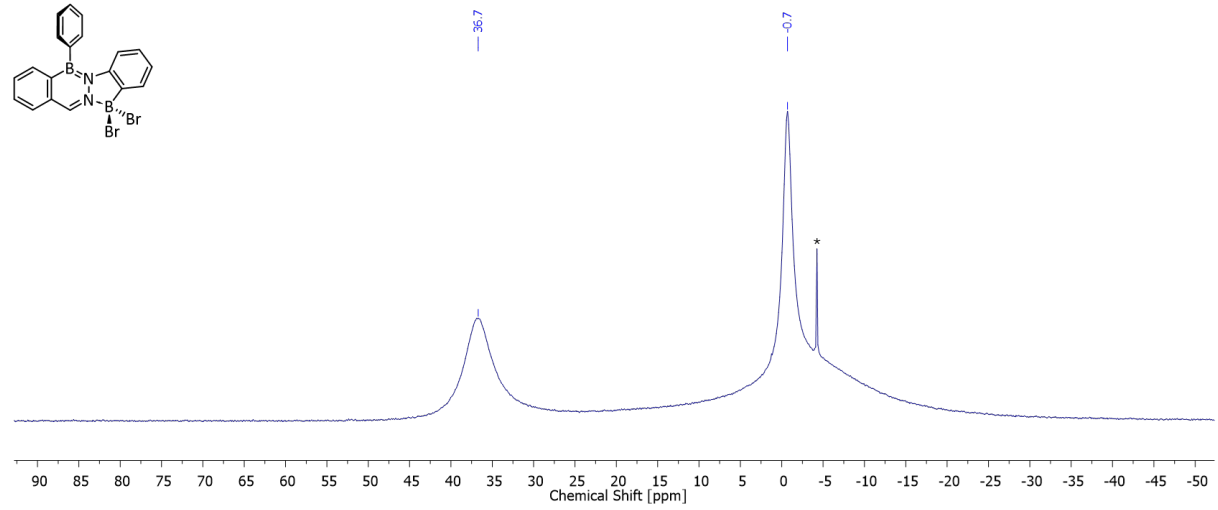


Figure S2. Background-reduced $^{11}B\{^1H\}$ NMR spectrum of compound **2**^{Benz} in C_6D_6. The sample contains ca. 3% $[DABCO]H_2[BBr_4]_2$ salt as inseparable impurity (marked with *).

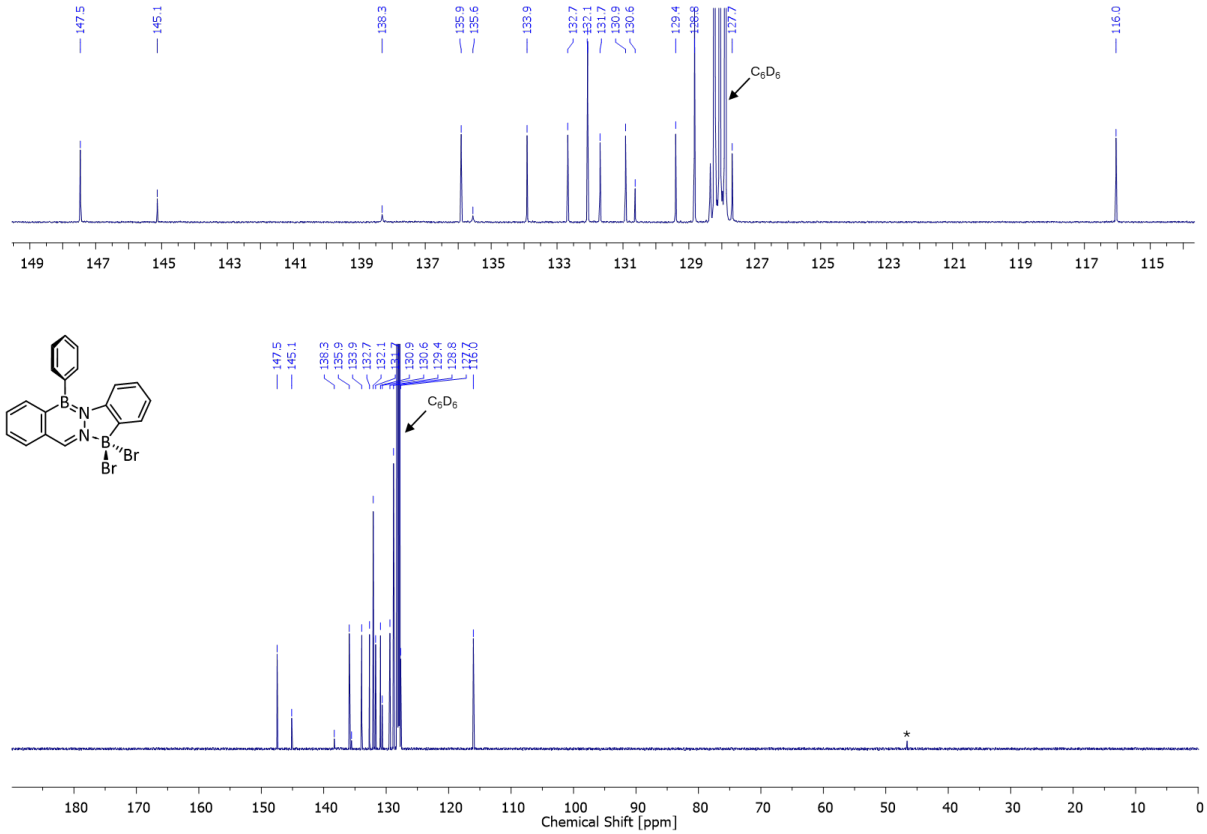


Figure S3. $^{13}C\{^1H^{11}B\}$ NMR spectrum of compound **2**^{Benz} in C_6D_6 (^{11}B decoupled at 36 ppm). The sample contains ca. 3% $[DABCO]H_2[BBr_4]$ salt as inseparable impurity (marked with *).

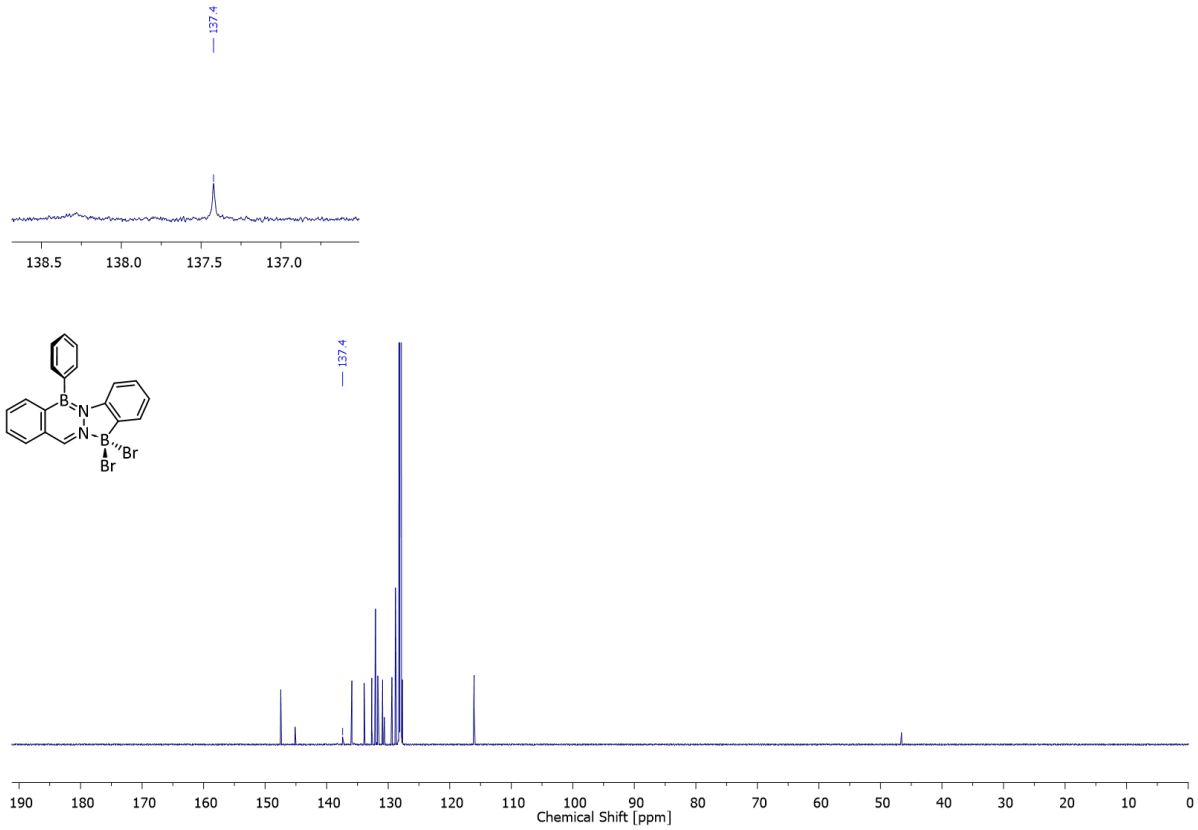


Figure S4. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **2**^{Benz} in C_6D_6 (^{11}B decoupled at 0.2 ppm). The sample contains ca. 3% $[DABCO]H_2[BBr_4]$ salt as inseparable impurity (marked with *).

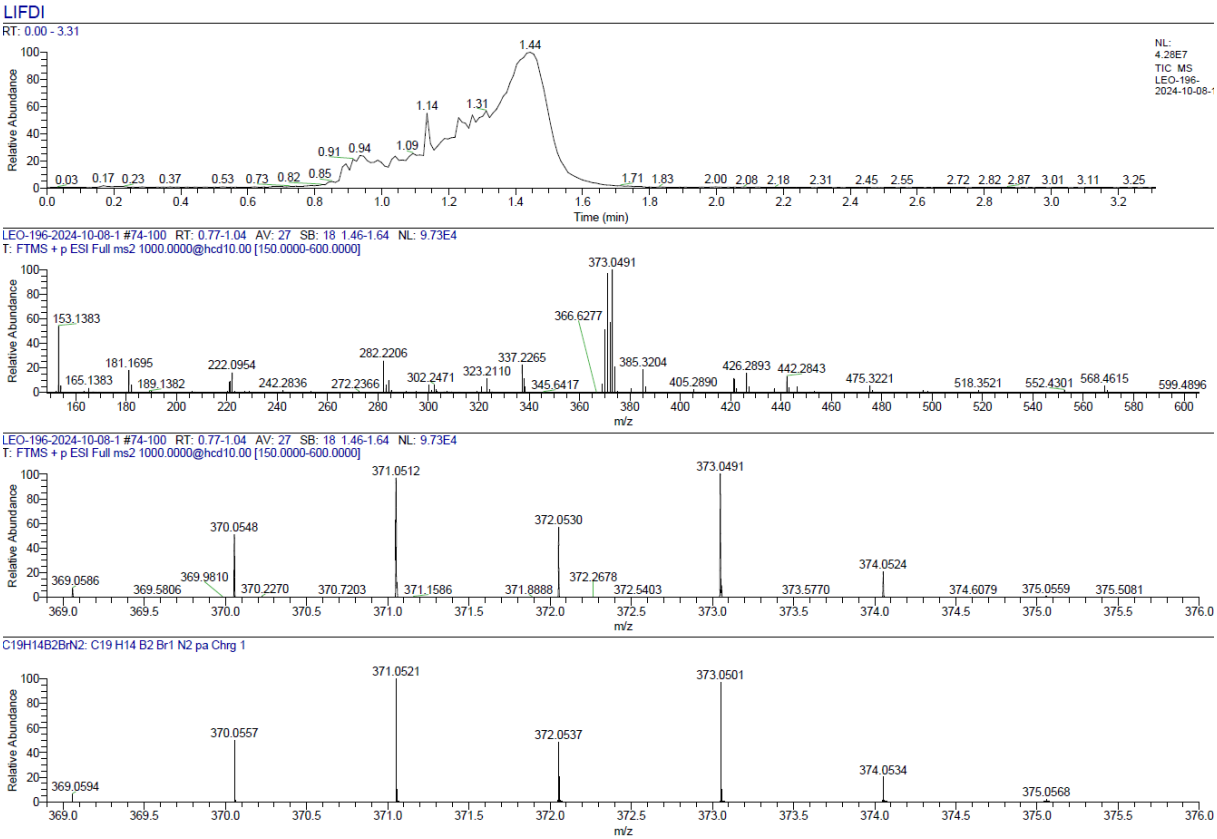


Figure S5. LIFDI mass spectrum of compound **2**^{Benz} (toluene).

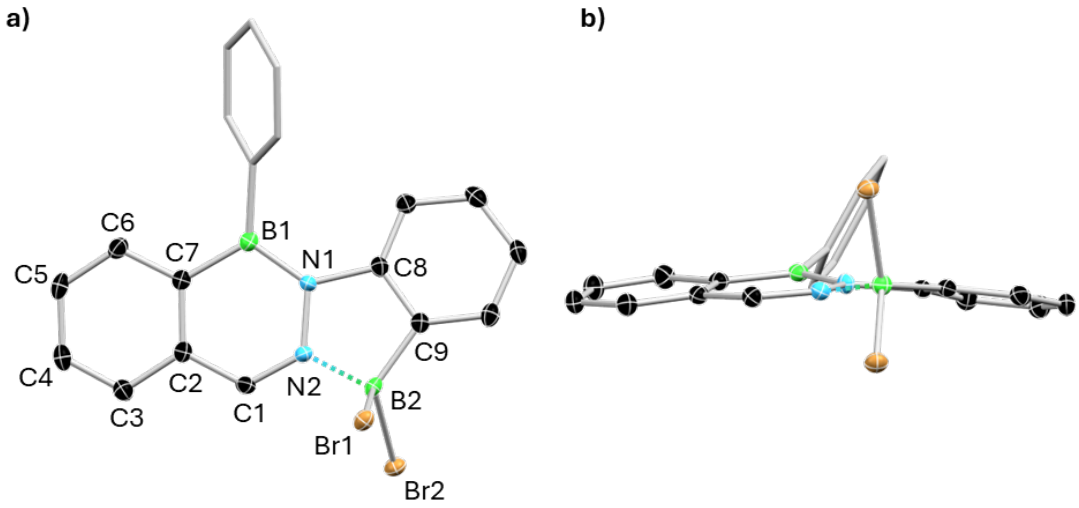
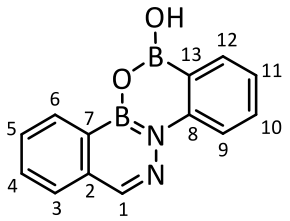


Figure S6. Molecular structure of compound **2**^{Benz}. Ellipsoids drawn at 50% probability. All H-atoms omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.434(3), N1–N2 1.397(3), N2–C1 1.299(3), C1–C2 1.418(4), C2–C3 1.409(3), C3–C4 1.375(4), C4–C5 1.399(4), C5–C6 1.382(4), C6–C7 1.407(3), C7–C2 1.413(3), B1–C7 1.543(3), N1–C8 1.445(3), N2–B2 1.580(3), B2–C9 1.570(4), N2–N1–C8–C9 9.2(2), B1–N1–N2–C1 8.7(3).

Crystal data: $C_{19}H_{14}B_2Br_2N_2$, M_r = 451.76, clear colorless block, 0.310×0.090×0.070 mm^3, orthorhombic space group $P2_12_12_1$, a = 10.1408(17) Å, b = 10.5705(17) Å, c = 16.4231(18) Å, V = 1760.4(5) Å^3, Z = 4, ρ_{calcd} = 1.704 g·cm^{-3}, μ = 5.850 mm^{-1}, $F(000)$ = 888, T = 100(2) K, R_1 = 0.0141, wR_2 = 0.0385, Flack parameter = –0.021(3), 3453 independent reflections [$2\theta \leq 146.696°$] and 226 parameters.

CCDC number: 2541881

Compound 6^{Benz}



6^{Benz} (76%)

DAB **3^{Benz}** (500 mg, 2.25 mmol, 1.00 eq.) and DABCO (126 mg, 1.13 mmol, 0.50 eq.) were dissolved in CH_2Cl_2 (50 mL) in a 150 mL Schlenk tube and cooled to 0 °C (ice bath). BBr_3 (neat, 0.65 mL, 6.76 mmol, xs., ρ = 2.64 g/mL) was added in small portions and a momentary deep red coloration of the reaction solution was observed upon addition, which quickly faded again. After 5 min, the cooling bath was removed, and the reaction was stirred for 2 d at ambient temperature. All volatile components were removed *in vacuo* and the remaining solid was carefully quenched with ice. Upon addition, a color change from pale yellow to deep yellow was observed. The quenching suspension was stirred for 3 h at ambient temperature. Ethyl acetate (100 mL) was added, and the suspension was transferred to a separating funnel. The organic layer was washed with water (3 × 50 mL) and dried over Na_2SO_4. All volatile components were removed under reduced pressure and the obtained solid was washed with cold (−20 °C, 3 mL) CH_2Cl_2 to remove remaining DABCO salts.

Yield: 423 mg (1.71 mmol, 76%), colorless powder. The compound is air- and moisture-stable.

^{1}H NMR (600 MHz, 298 K, DMSO-d_6): δ = 9.41 (s, 1H, B-O*H*), 8.54 (s, 1H, *H*-1), 8.26 (d, $^3J_{HH}$ = 8.58 Hz, 2H, *H*-12 + *H*-3), 7.99 (dd, $^3J_{HH}$ = 7.41 Hz, $^4J_{HH}$ = 1.69 Hz, 1H, *H*-9), 7.96 (d, $^3J_{HH}$ = 7.79 Hz, 1H, *H*-6), 7.87 (ddd, $^3J_{HH}$ = 7.78 Hz; 7.33 Hz, $^4J_{HH}$ = 1.47 Hz, 1H, *H*-5), 7.77 (ddd, $^3J_{HH}$ = 7.40 Hz; 7.40 Hz, $^4J_{HH}$ = 1.14 Hz, 1H, *H*-4), 7.68 (ddd, $^3J_{HH}$ = 8.42 Hz; 7.11 Hz, $^4J_{HH}$ = 1.87 Hz, *H*-10), 7.26 (ddd, $^3J_{HH}$ = 7.25 Hz, 7.25 Hz, $^4J_{HH}$ = 1.17 Hz, *H*-11) ppm. **^{11}B{^{1}H} NMR** (160 MHz, 298 K, DMSO-d_6) δ = 27.7 (vbr s, $\Delta\nu_{½}$ = 1165 Hz) ppm. **^{13}C{^{1}H^{11}B} NMR** (151 MHz, 298 K, DMSO-d_6): δ = 150.3 (C_q^N-8), 141.4 (*C*-1), 135.0 (C_q-2), 134.0 (*C*-9), 133.0 (*C*-10), 132.2 (*C*-5), 130.9 (*C*-3), 130.0 (*C*-4), 129.6 (C_q^B-7), 127.7 (*C*-6), 123.2 (*C*-11), 118.1 (C_q^B-13), 114.3 (*C*-12) ppm. **HRMS** ($ASAP_{pos}$, acetone): expected: *m/z* 248.1037, 249.1001, 250.1035 $[C_{13}H_{10}B_2N_2O_2]^+$; found: *m/z* 248.1030, 249.0993, 250.1027 $[C_{13}H_{10}B_2N_2O_2]^+$. Crystalline material of **6^{Benz}** as colorless needles was obtained by slow evaporation of a saturated ethyl acetate solution at ambient temperature.

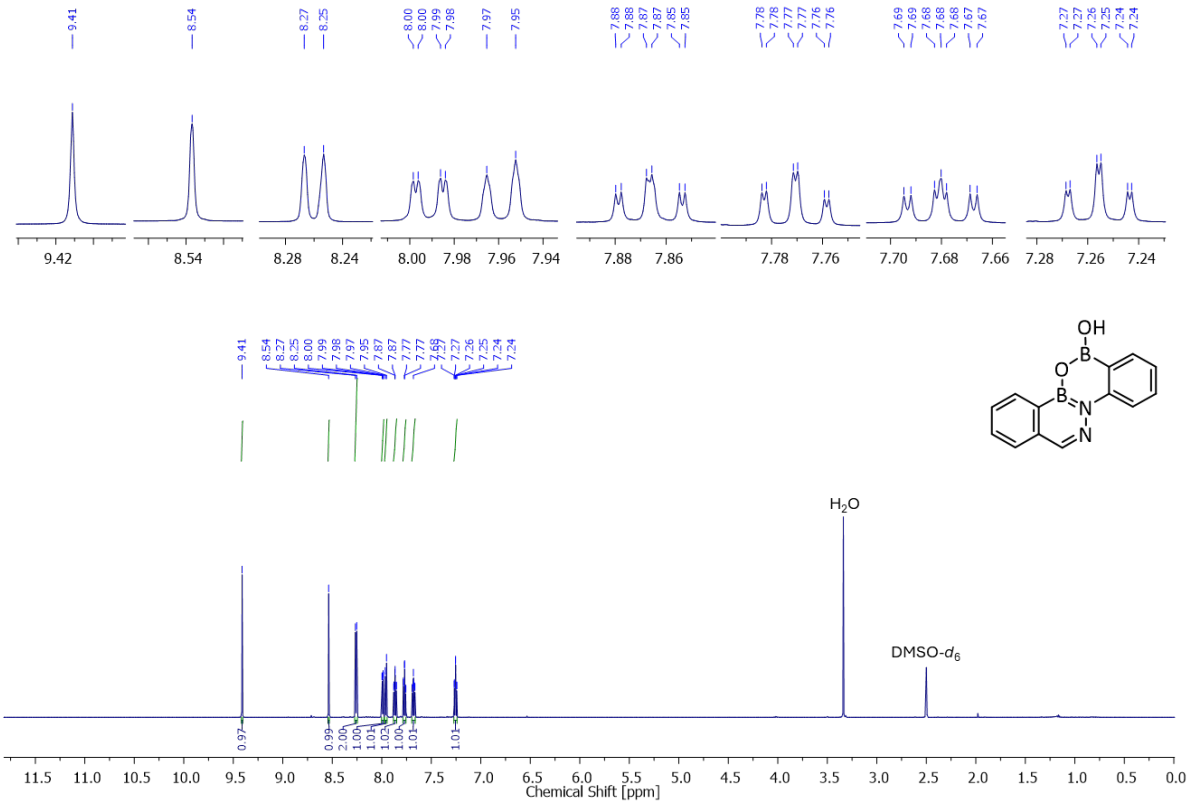


Figure S7. ^{1}H NMR spectrum of compound **6^{Benz}** in DMSO-d_6.

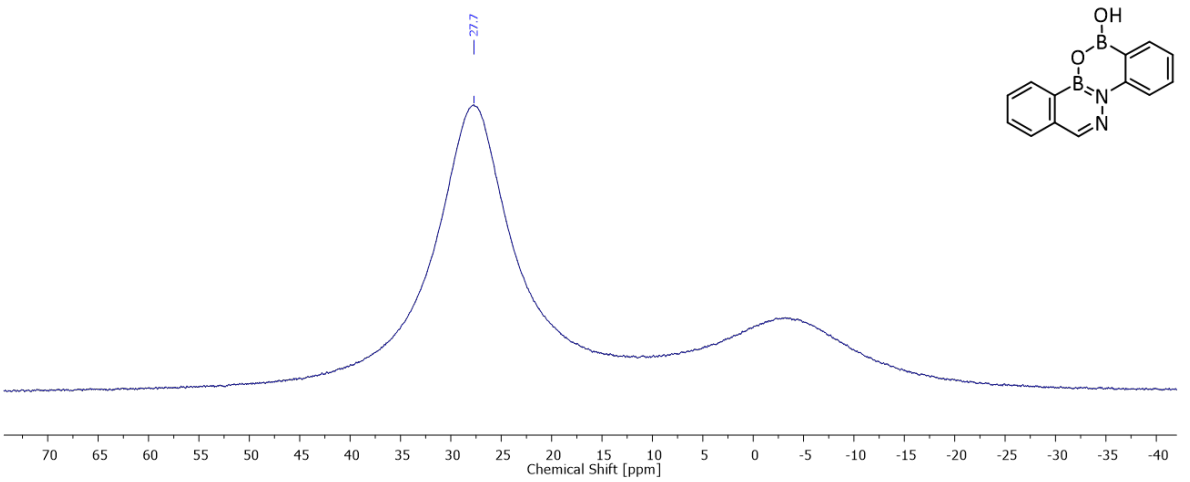


Figure S8. Background-reduced ^{11}B{^{1}H} NMR spectrum of compound **6^{Benz}** in DMSO-d_6.

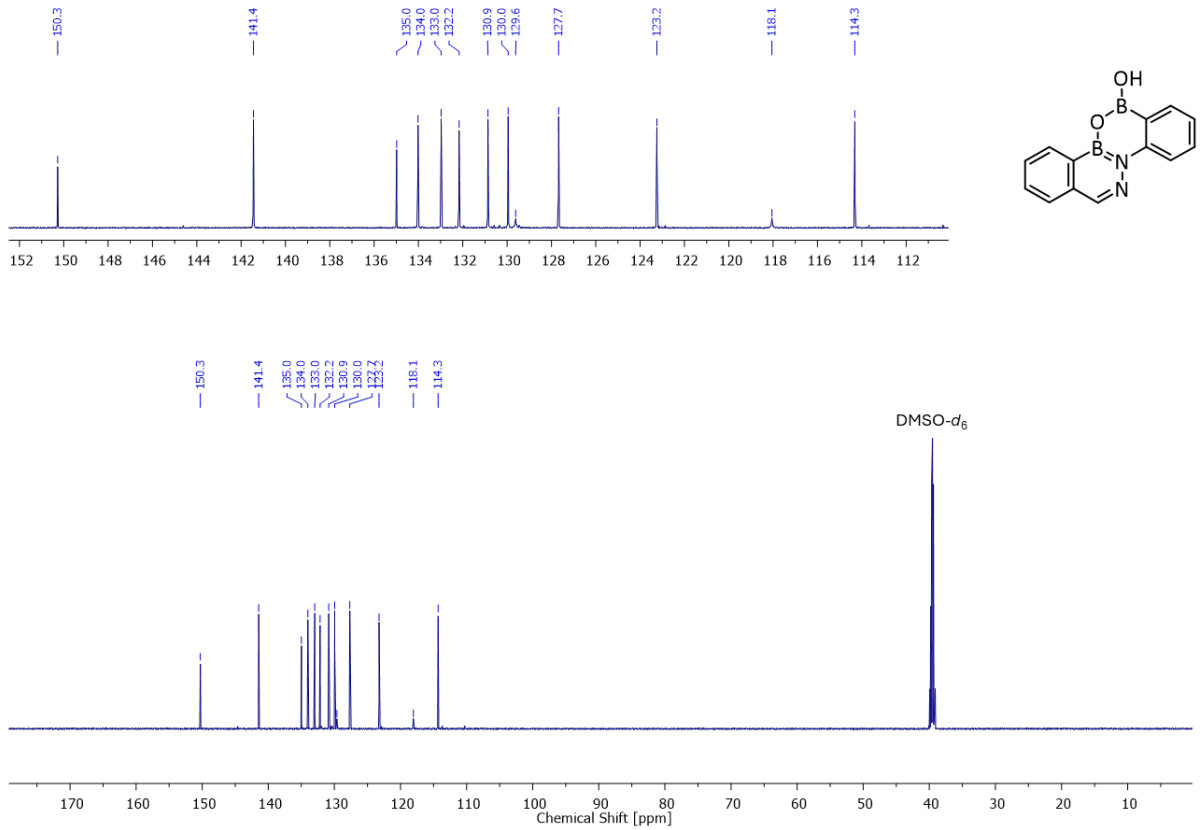


Figure S9. $^{13}C\{^{1}H^{11}B\}$ NMR spectrum of compound **6^{Benz}** in DMSO-d_6 (^{11}B decoupled at 29 ppm).

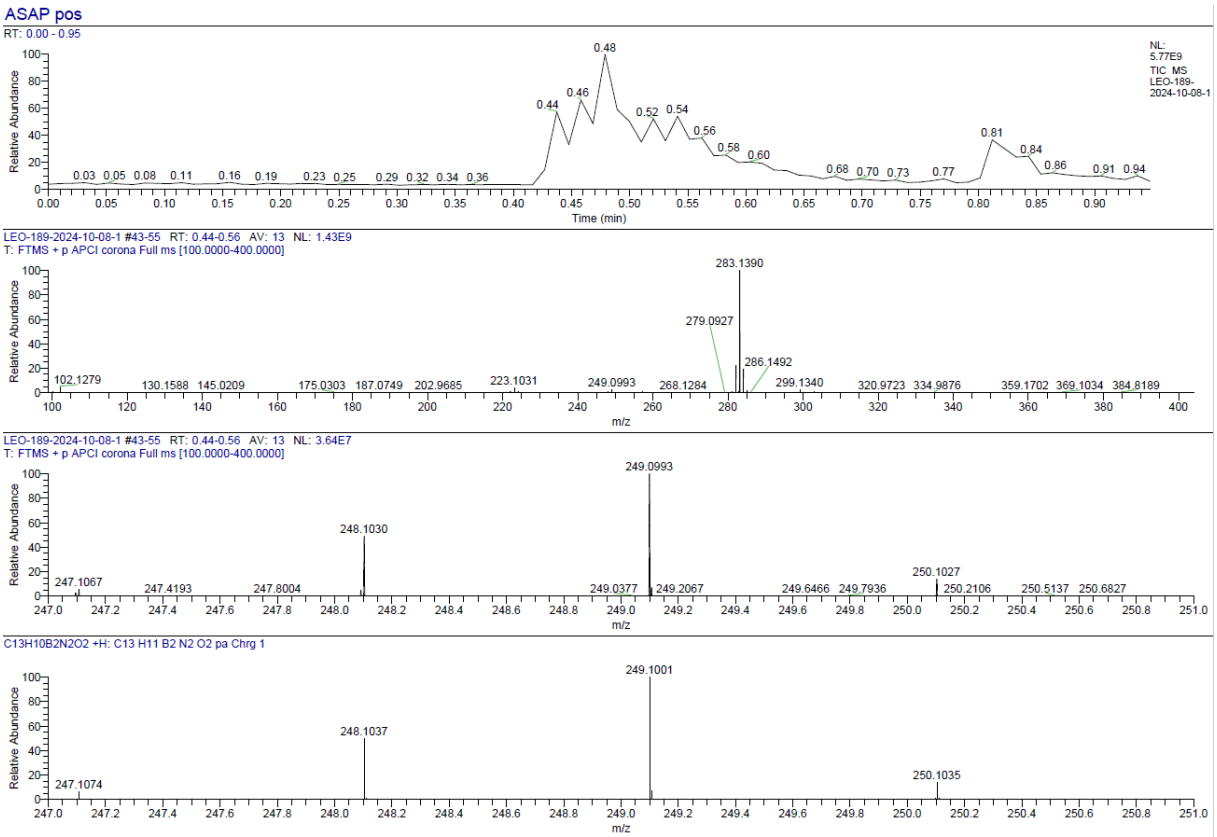


Figure S10. $ASAP_{pos}$ mass spectrum of compound **6^{Benz}** (acetone).

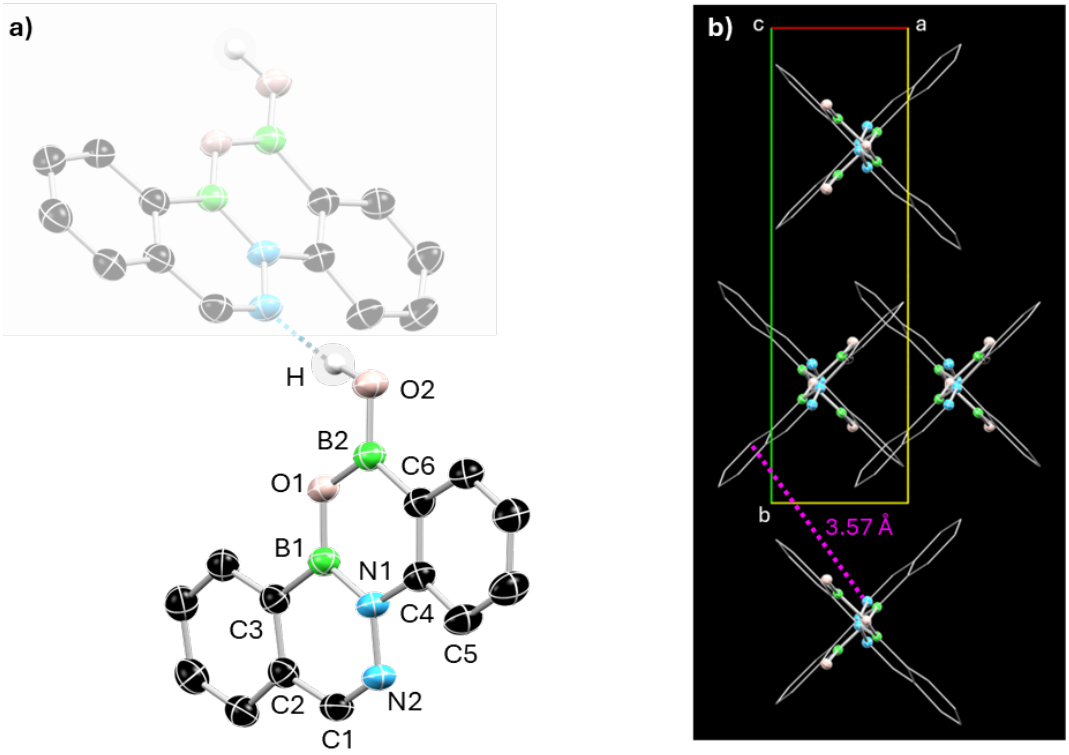
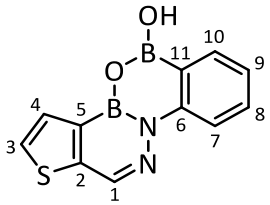


Figure S11. Molecular structure of compound **6**^{Benz}. Ellipsoids drawn at 50% probability. All H-atoms omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.436(2), N1–N2 1.3805(19), N2–C1 1.298(2), C1–C2 1.442(3), C2–C3 1.404(2), C3–B1 1.535(3), N1–C4 1.432(2), C4–C5 1.396(3), C4–C6 1.400(2), B2–C6 1.551(3), B1–O1 1.373(2), B2–O1 1.381(2), B2–O2 1.353(2), N2–N1–C4–C5 4.8(2), B1–N1–N2–C1 1.8(2), N1–C4–C6–B2 1.0(2), N1–B1–O1–B2 0.5(3).

Crystal data: $C_{13}H_{10}B_2N_2O_2$, M_r = 247.85, clear colorless block, 0.440×0.090×0.040 mm^3, monoclinic space group $P2_1/c$, a = 4.8451(7) Å, b = 16.779(3) Å, c = 14.398(2) Å, β = 92.093(8)°, V = 1169.7(3) Å^3, Z = 4, ρ_{calcd} = 1.407 g·cm^{-3}, μ = 0.757 mm^{-1}, $F(000)$ = 512, T = 100(2) K, R_1 = 0.0588, wR_2 = 0.1615, 2284 independent reflections [$2\theta \leq 144.89°$] and 174 parameters.

CCDC number: 2541880

Compound 6^{Thio}



6^{Thio} (58%)

DAB **3^{Thio}** (514 mg, 2.25 mmol, 1.00 eq.) and DABCO (126 mg, 1.13 mmol, 0.50 eq.) were dissolved in CH_2Cl_2 (25 mL) in a 100 mL Schlenk flask and cooled to 0 °C (ice bath). BBr_3 (neat, 0.64 mL, 6.76 mmol, xs., ρ = 2.64 g/mL) was added dropwise. After 10 min, the cooling bath was removed, the reaction was stirred for 2 d at ambient temperature and the slow formation of a solid was observed. The reaction suspension was carefully quenched with ice. Then, CH_2Cl_2 was added until complete dissolution of the solid. The mixture was transferred into a separating funnel, and the organic layer was separated, washed with water (3 × 50 mL) and dried over Na_2SO_4. All volatile components were removed under reduced pressure and the obtained solid was first washed with small amounts of CH_2Cl_2 (2 mL) and then extracted with CH_2Cl_2 (3 × 10 mL) to obtain the product from DABCO salts.

Yield: 331 mg (1.30 mmol, 58%), colorless powder. The compound is air- and moisture-stable.

^{1}H NMR (500 MHz, 298 K, CD_2Cl_2): δ = 9.41 (s, 1H, B–O*H*), 8.73 (s, 1H, *H*-1), 8.30 (d, $^3J_{HH}$ = 8.20 Hz, 1H, *H*-10), 8.04 (d, $^3J_{HH}$ = 4.95 Hz, 1H, *H*-10), 7.97 (dd, $^3J_{HH}$ = 7.42 Hz, $^4J_{HH}$ = 1.38, 1H, *H*-7), 7.70-7.68 (m, 1H, *H*-8), 7.68-7.66 (m, 1H, *H*-4), 7.27 (ddd, $^3J_{HH}$ = 7.37 Hz, $^3J_{HH}$ = 7.37 Hz, $^4J_{HH}$ = 0.92 Hz, 1H, *H*-9) ppm. **^{11}B{^{1}H} NMR** (161 MHz, 298 K, CD_2Cl_2): δ = 27.0 (br s) ppm. **^{13}C{^{1}H} NMR** (126 MHz, 298 K, CD_2Cl_2) δ = 150.3 (C_q^N-6), 145.7 (C_q-2), 138.5 (br, C_q^B-5), 134.7 (*C*-1), 134.0 (*C*-7), 133.0 (*C*-8), 131.7 (*C*-3), 128.6 (*C*-4), 123.6 (*C*-9), 118.4 (br, C_q^B-11), 114.9 (*C*-10) ppm. **HRMS** ($ASAP_{pos}$, solid): expected *m/z* 153.0638, 254.062, 255.0565, 256.0599 $[C_{11}H_9B_2N_2O_2S+H]^+$; found: *m/z* 253.0630, 254.0593, 255.0556 $[C_{11}H_9B_2N_2O_2S+H]^+$. Crystalline material of **6^{Thio}** as colorless needles for XRD analysis was obtained by slow evaporation of a saturated dichloromethane solution at ambient temperature.

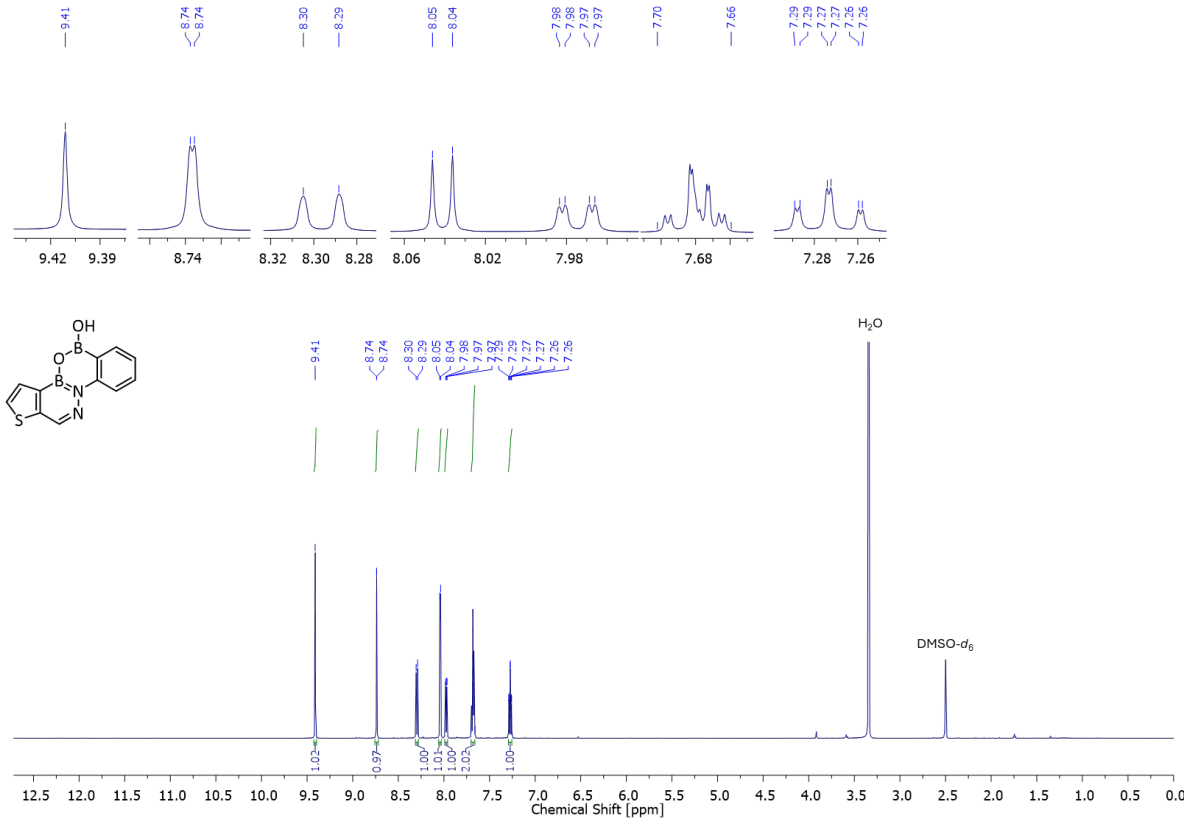


Figure S12. ^{1}H NMR spectrum of compound **6^{Thio}** in DMSO-d_6.

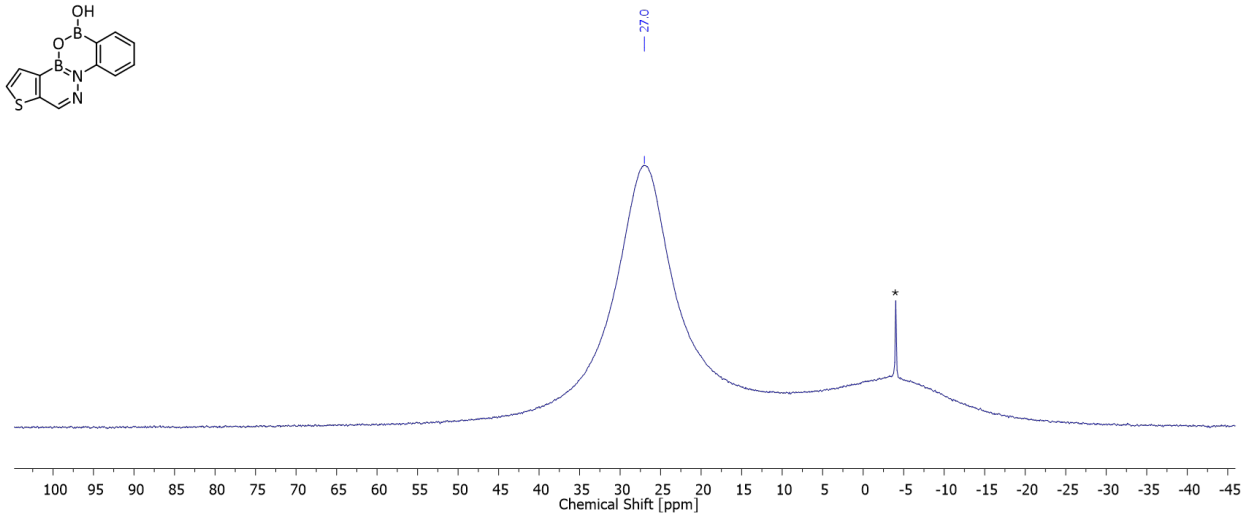


Figure S13. Background-reduced ^{11}B{^{1}H} NMR spectrum of compound **6^{Thio}** in DMSO-d_6. The sample contains very minor amounts of a BBr_4 salt as inseparable impurity (marked with *).

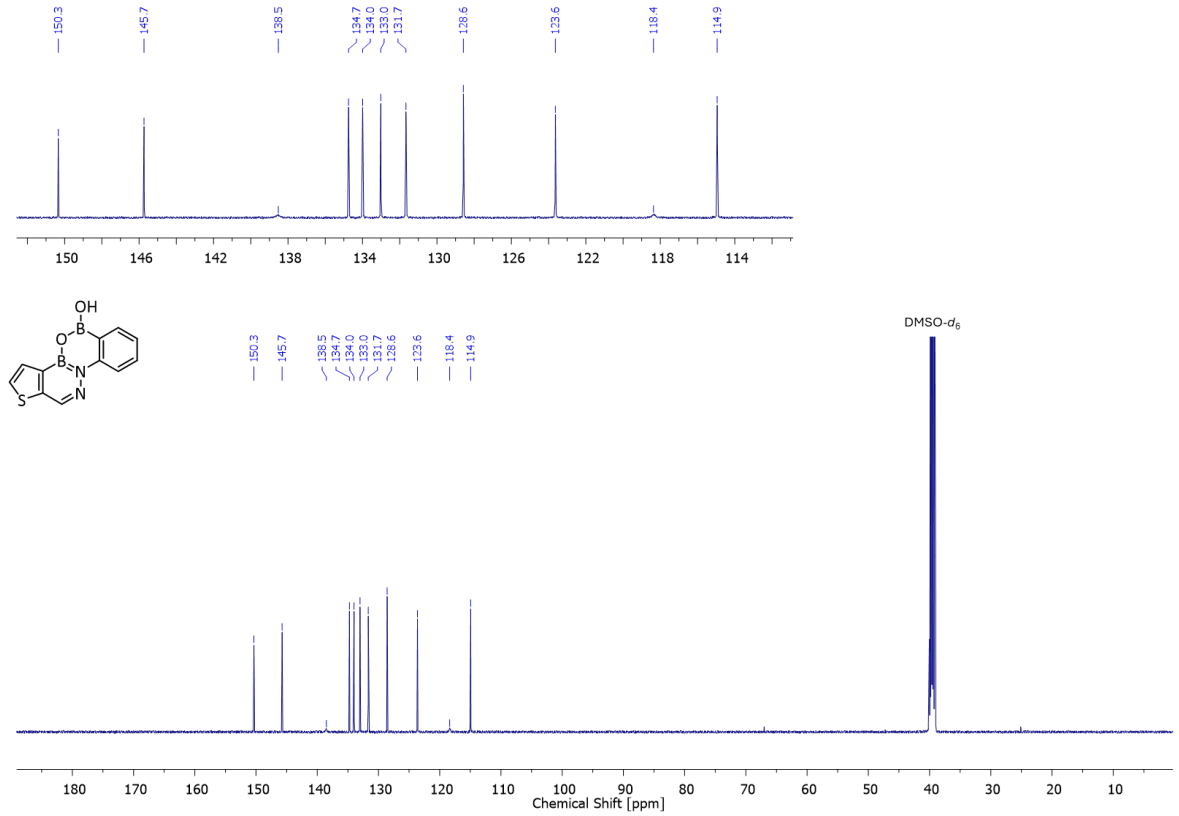


Figure S14. $^{13}C\{^1H\}$ NMR spectrum of compound **6^{Thio}** in DMSO-d_6.

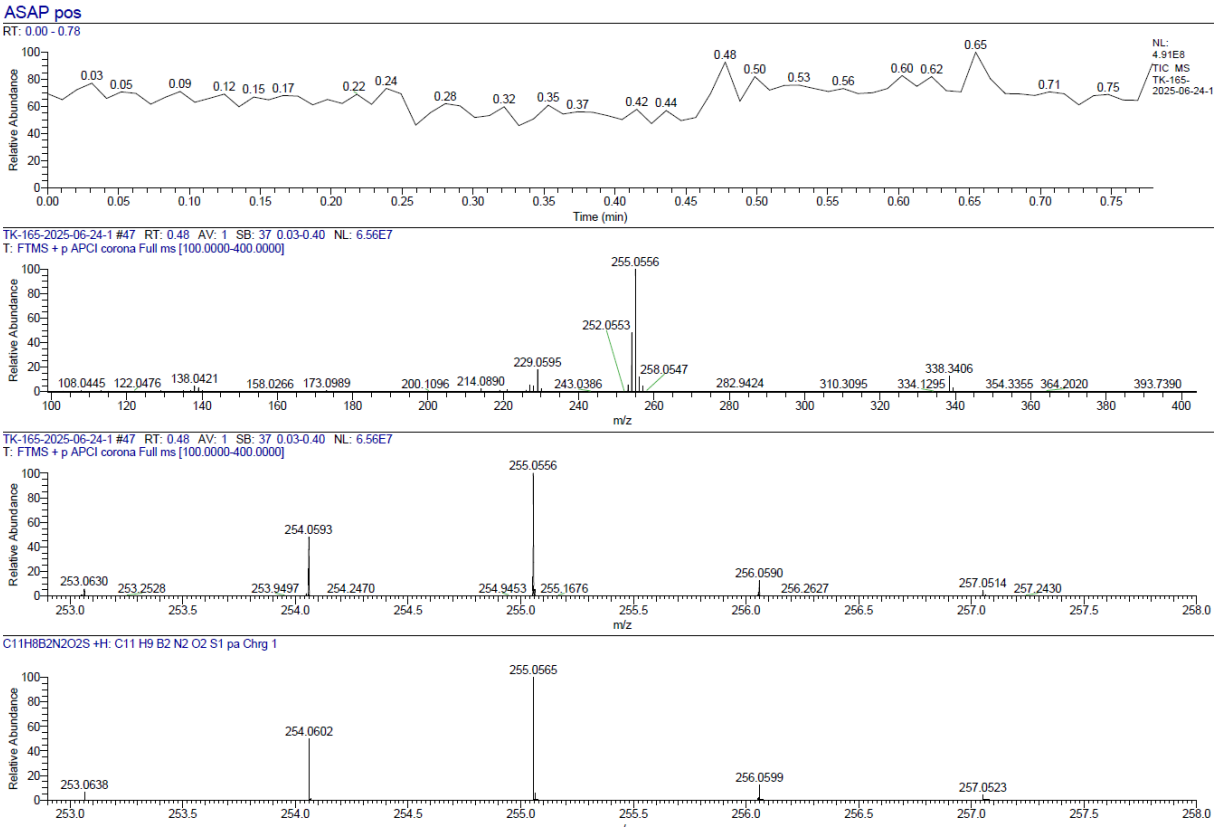


Figure S15. ASAP$_{pos}$ mass spectrum of compound **6^{Thio}** (solid).

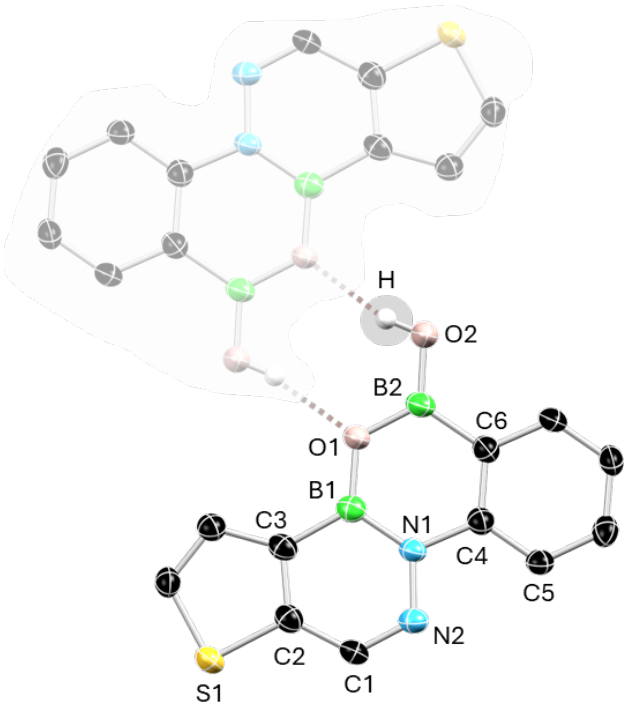


Figure S16. Molecular structure of compound **6**^{Thio} with hydrogen bonds to a second molecule (faded), forming a dimer in the solid state. Ellipsoids drawn at 50% probability. All H-atoms except for the borinic acid function omitted. Selected bond lengths (Å) and angles (°): B1–N1 1.431(5), N1–N2 1.376(4), N2–C1 1.304(4), C1–C2 1.420(5), C2–C3 1.394(5), C3–B1 1.523(5), N1–C4 1.430(4), C4–C5 1.395(5), C4–C6 1.403(5), B2–C6 1.535(6), B1–O1 1.391(5), B2–O1 1.391(5), B2–O2 1.356(5), N2–N1–C4–C5 0.9(5), B1–N1–N2–C1 2.0(5), N1–C4–C6–B2 0.2(5), N1–B1–O1–B2 0.8(5).

Crystal data: $C_{11}H_8B_2N_2O_2S$, M_r = 253.87, clear pale yellow needle, 0.360×0.060×0.050 mm^3, monoclinic space group *I*2/*a*, *a* = 16.396(4) Å, *b* = 5.0103(8) Å, *c* = 27.778(6) Å, β = 93.702(8)°, *V* = 2277.1(8) Å^3, *Z* = 8, ρ_{calcd} = 1.481 g·cm^{-3}, μ = 2.460 mm^{-1}, *F*(000) = 1040, *T* = 100(2) K, R_1 = 0.0967, wR_2 = 0.2138, 2266 independent reflections [$2\theta \leq 150.492°$] and 165 parameters.

CCDC number: 2541879

3 Spectroscopic details

Table S2 Photophysical data of the compounds **6**^{Benz} and **6**^{Thio} in THF, DMSO and as PMMA film.

	$\lambda_{abs,\,max}$ [nm]			ε [10^4 L mol^{-1} cm^{-1}]	$\lambda_{em,\,max}$ [nm]			Φ_{fl} [%]		
	THF	**DMSO**	**PMMA**	**THF**	**THF**	**DMSO**	**PMMA**	**THF**	**DMSO**	**PMMA**
6^{Benz}	313, 326	315, 327	313, 326	1.60	368, 525	412	375	4	5	10
6^{Thio}	316	317	315	2.70	376	406	369	8	6	5

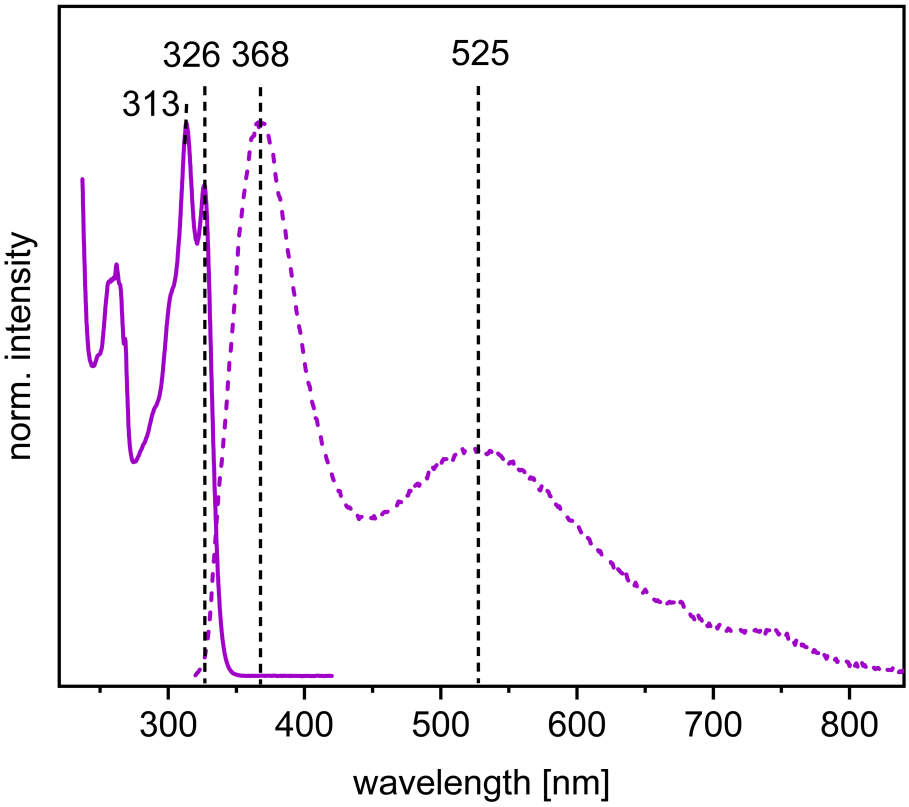


Fig. S17 Normalized absorption (solid line) and emission (dashed line) spectra of **6**^{Benz} in THF.

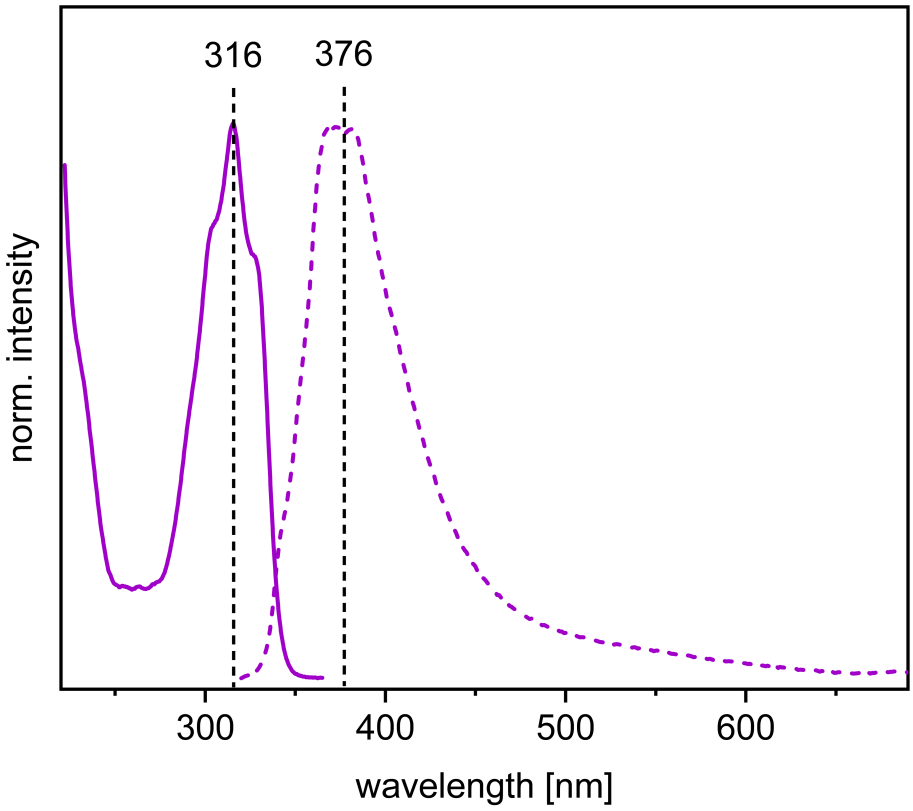


Fig. S18 Normalized absorption (solid line) and emission (dashed line) spectra of $\mathbf{6}^{\mathbf{Thio}}$ in THF.

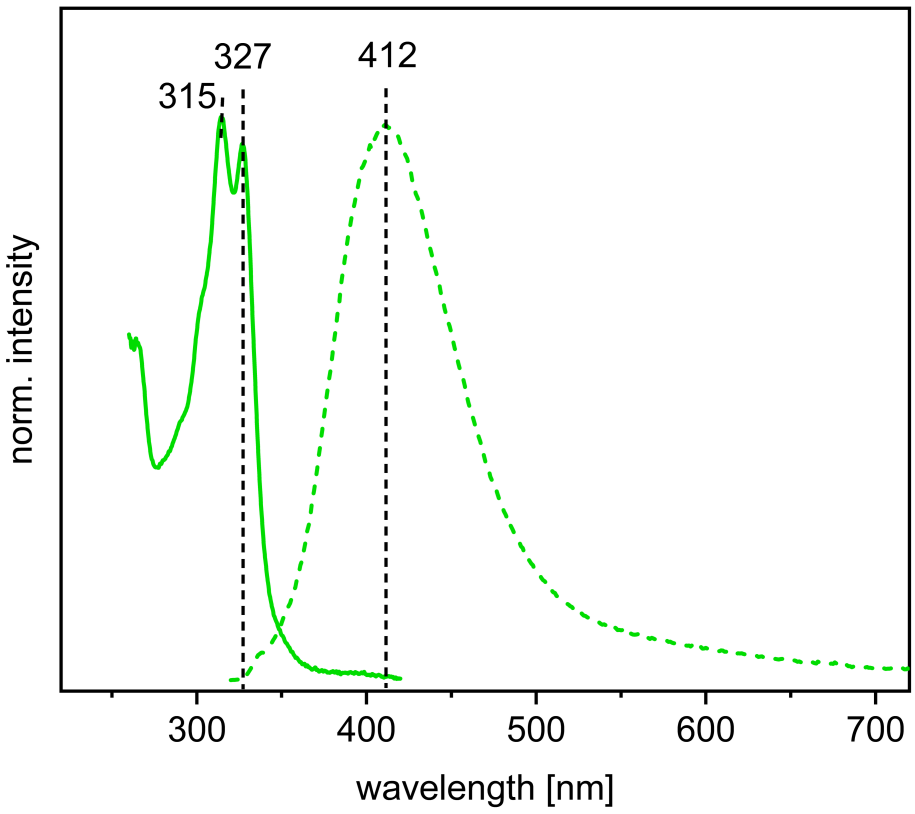


Fig. S19 Normalized absorption (solid line) and emission (dashed line) spectra of $\mathbf{6}^{\mathbf{Benz}}$ in DMSO.

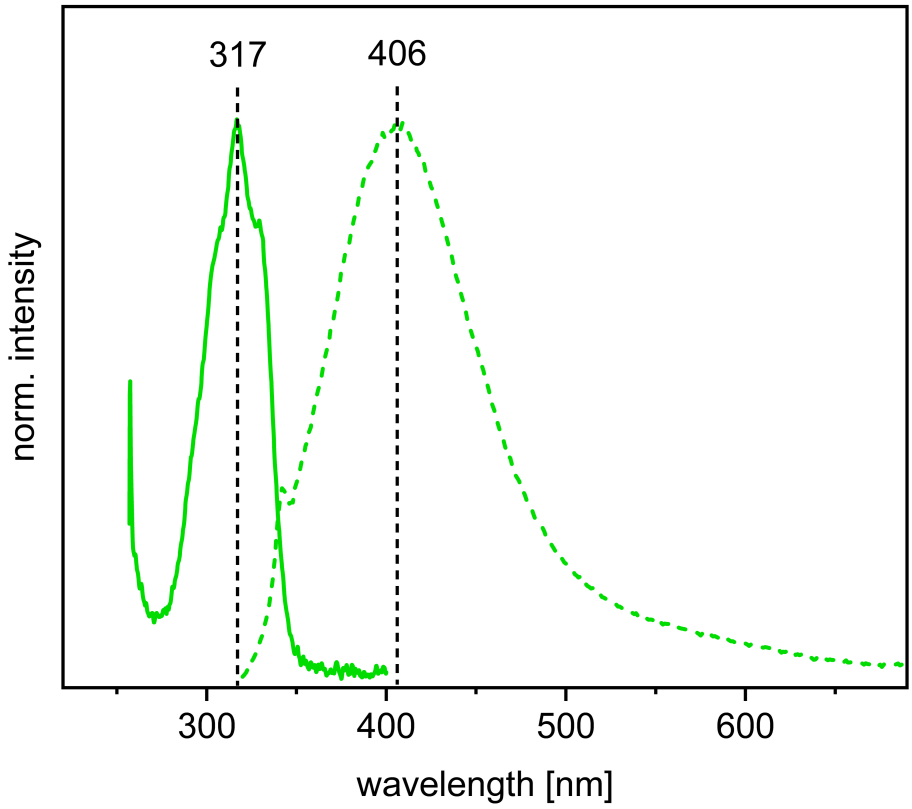


Fig. S20 Normalized absorption (solid line) and emission (dashed line) spectra of $\mathbf{6}^{\mathbf{Thio}}$ in DMSO.

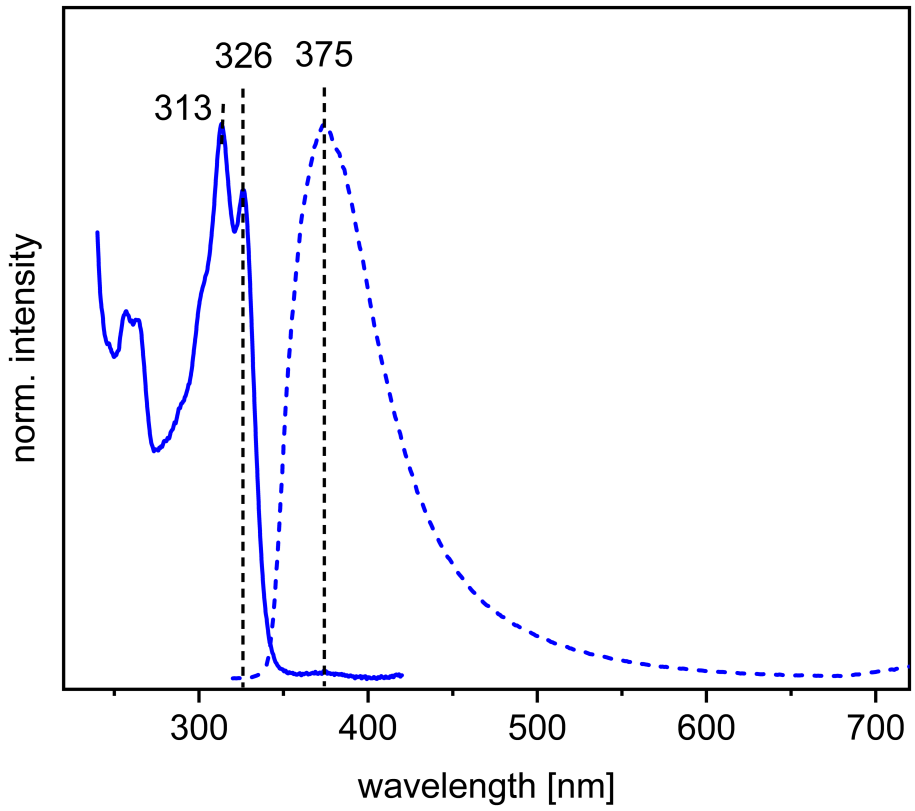


Fig. S21 Normalized absorption (solid line) and emission (dashed line) spectra of $\mathbf{6}^{\mathbf{Benz}}$ as PMMA film.

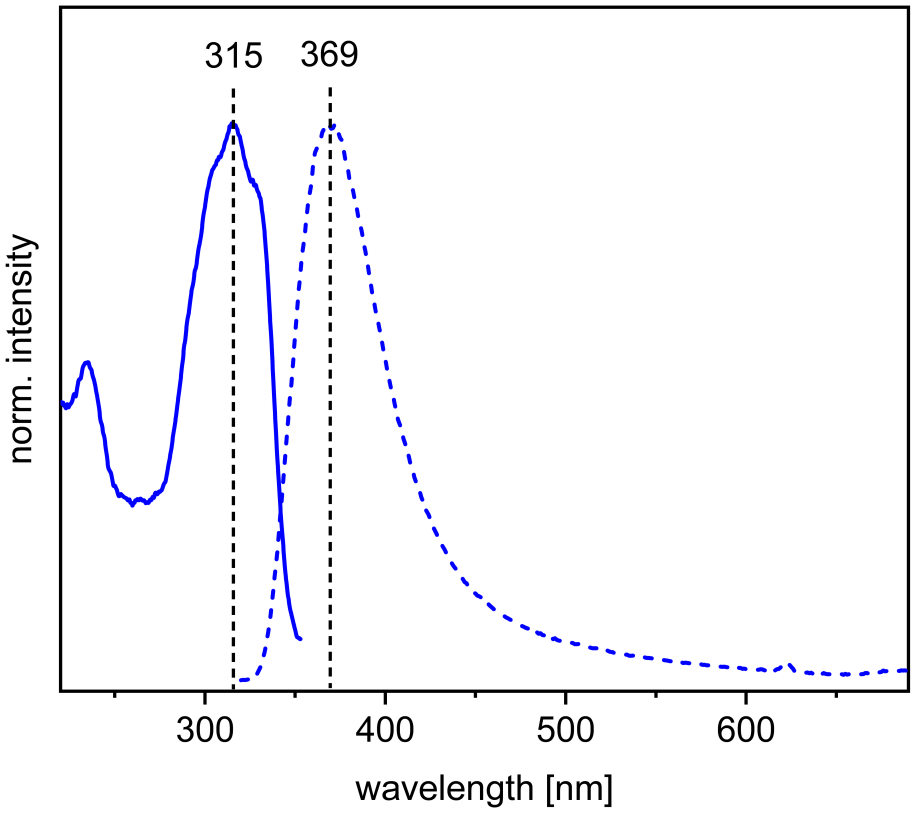


Fig. S22 Normalized absorption (solid line) and emission (dashed line) spectra of $\mathbf{6}^{\mathbf{Thio}}$ as PMMA film.

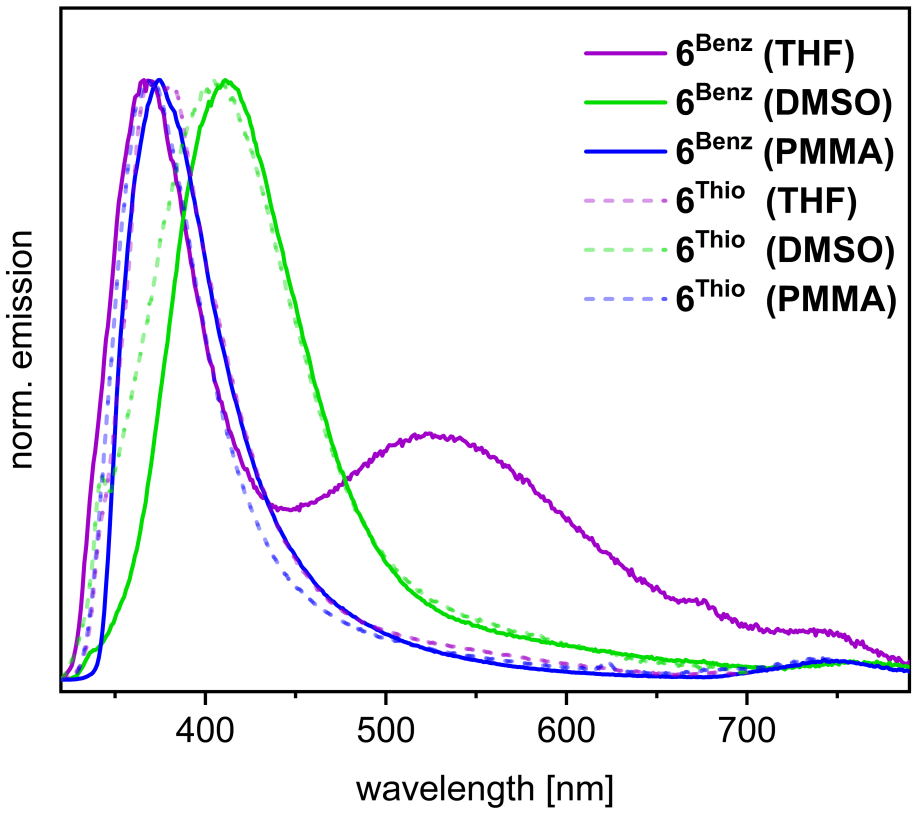


Fig. S23 Normalized emission spectra of $\mathbf{6}^{\mathbf{Benz}}$ and $\mathbf{6}^{\mathbf{Thio}}$ in THF, DMSO and as PMMA film.

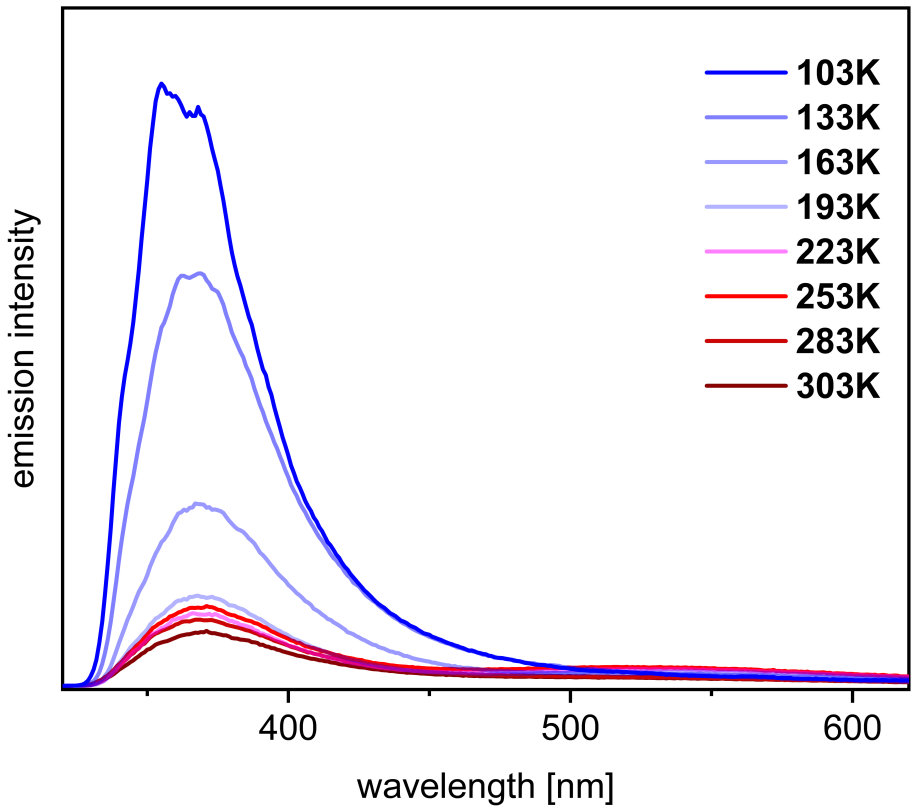


Fig. S24 Emission spectra of $\mathbf{6}^{\mathbf{Benz}}$ in 2-MeTHF at different temperatures.

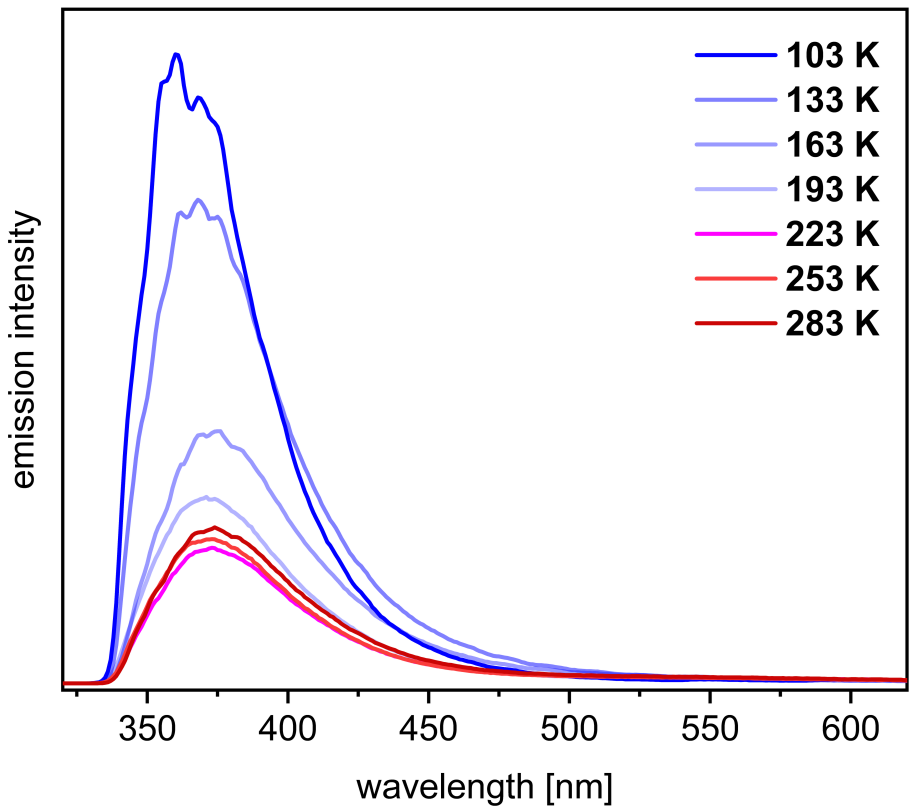


Fig. S25 Emission spectra of $\mathbf{6}^{\mathbf{Thio}}$ in 2-MeTHF at different temperatures.

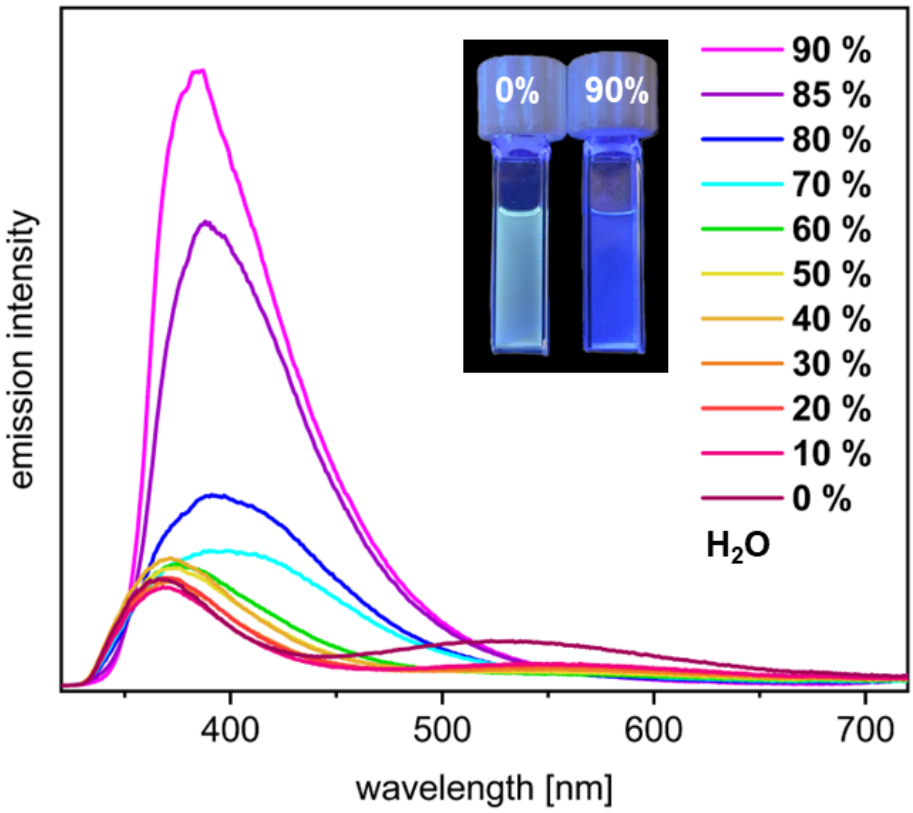


Fig. S26 Emission spectra of **6**^{Benz} in THF/ water mixtures (conc. 5 · 10^{-5} M) with different water fractions (0 – 90 %).

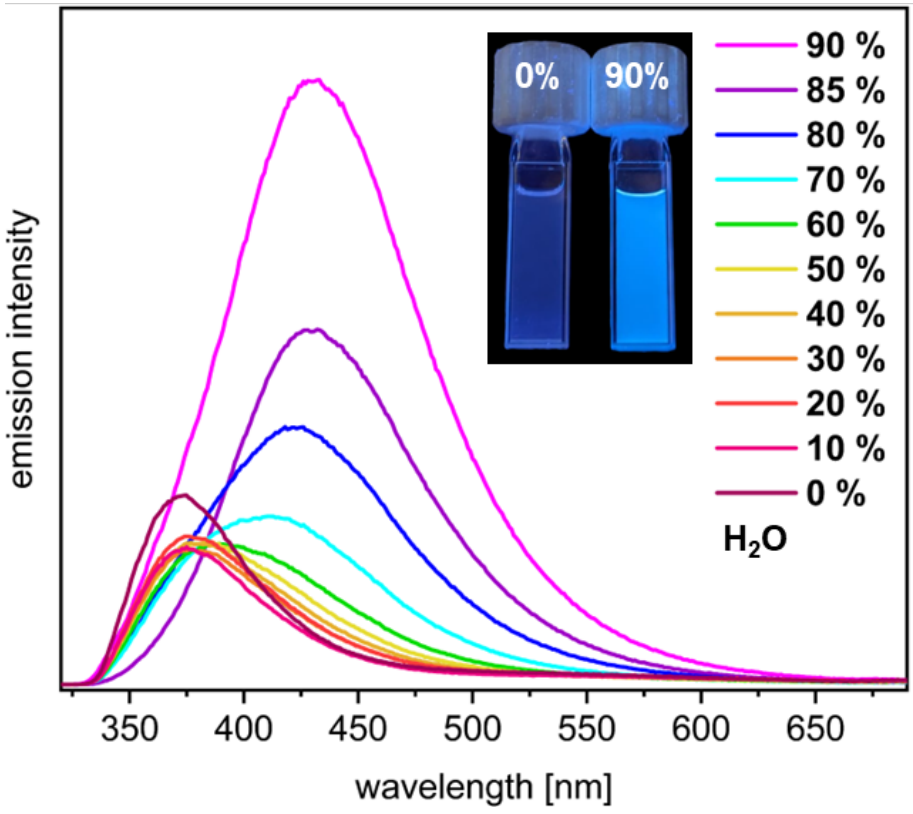


Fig. S27 Emission spectra of **6**^{Thio} in THF/ water mixtures (conc. 5 · 10^{-5} M) with different water fractions (0 – 90 %).

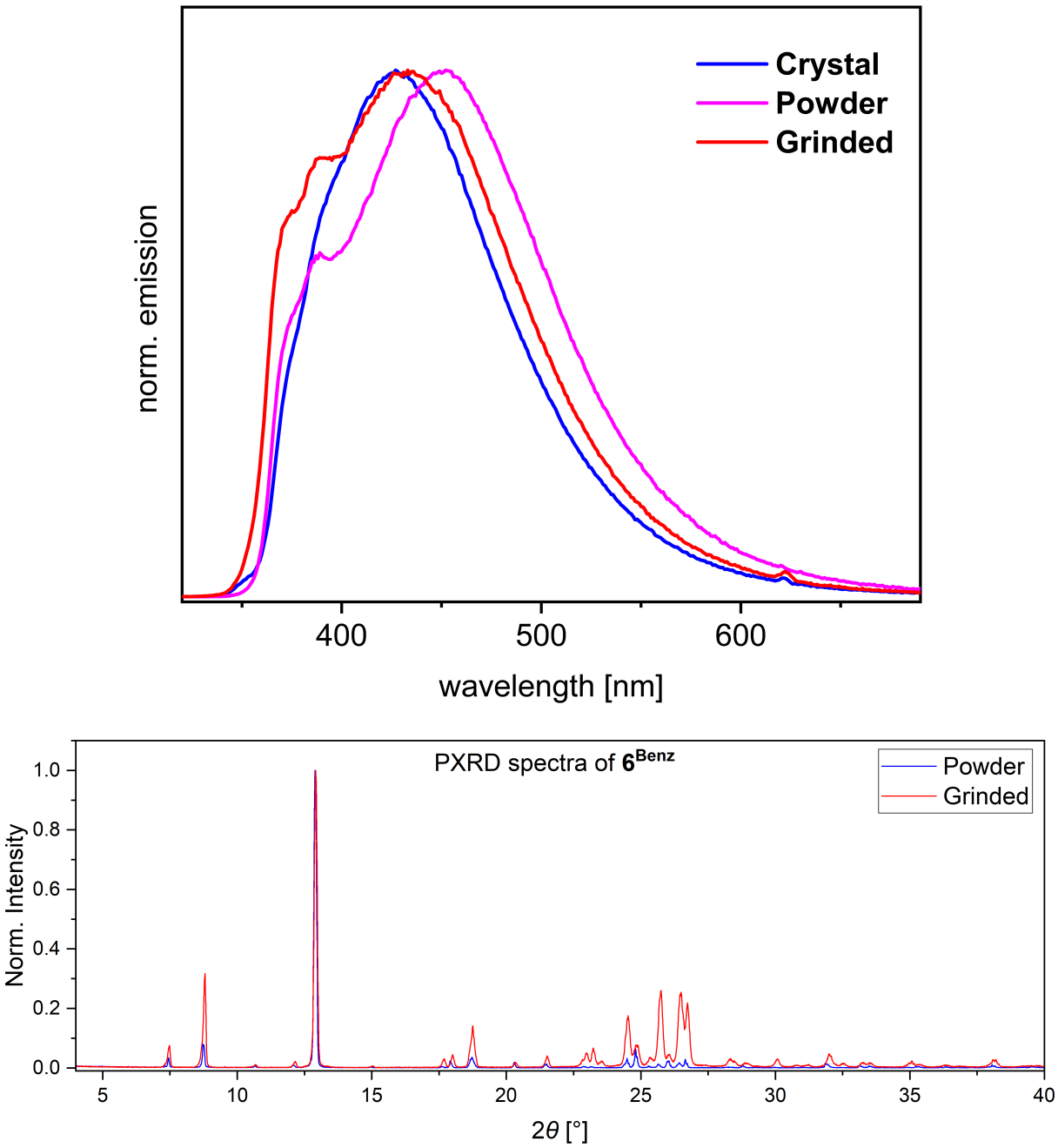


Fig. S28 Solid state emission spectra of $\mathbf{6}^{\mathbf{Benz}}$ under different conditions (top) and the corresponding PXRD patterns (bottom).

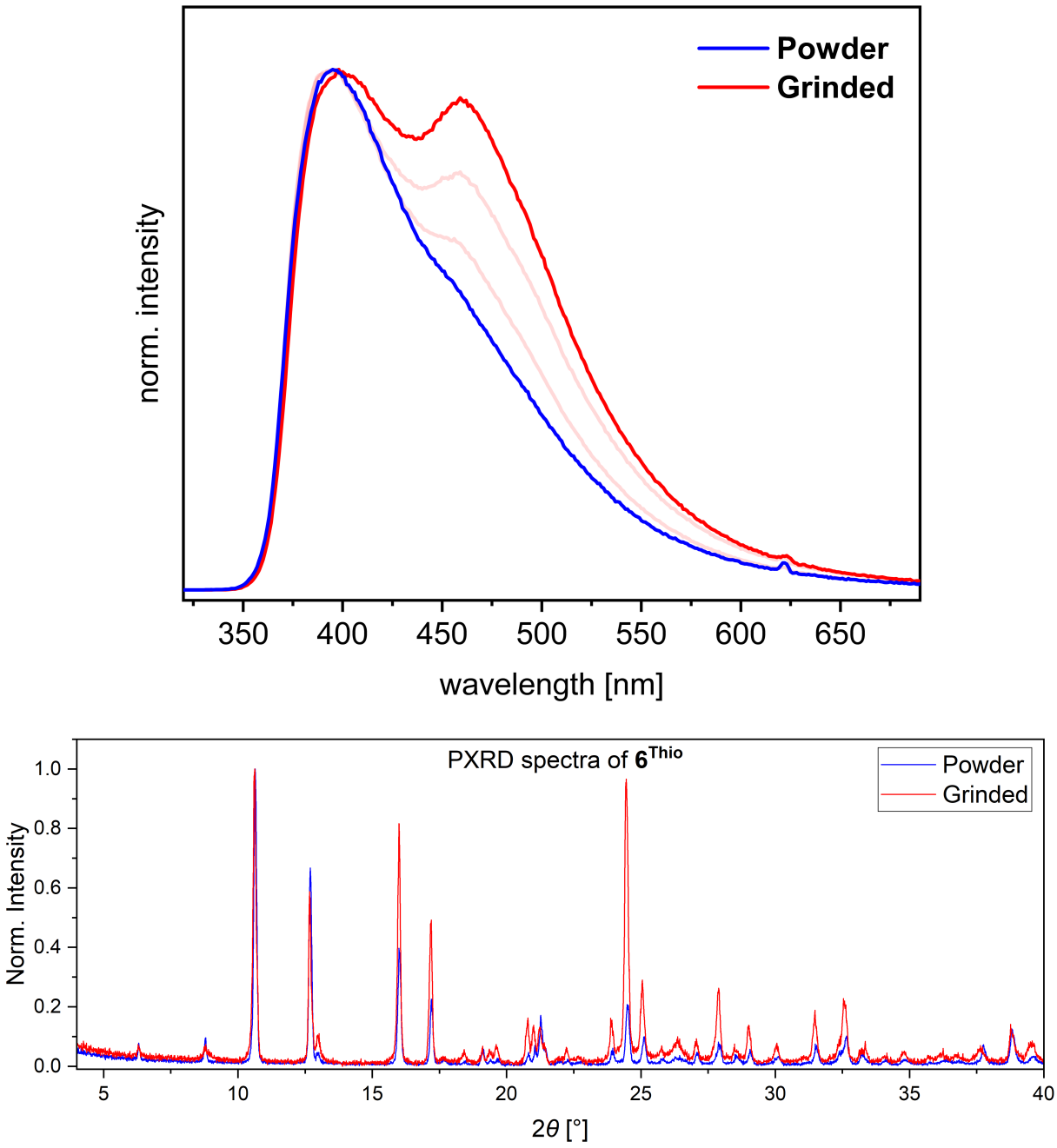


Fig. S29 Solid state emission spectra of $\mathbf{6}^{\mathbf{Thio}}$ under different conditions(top) and the corresponding PXRD patterns (bottom).

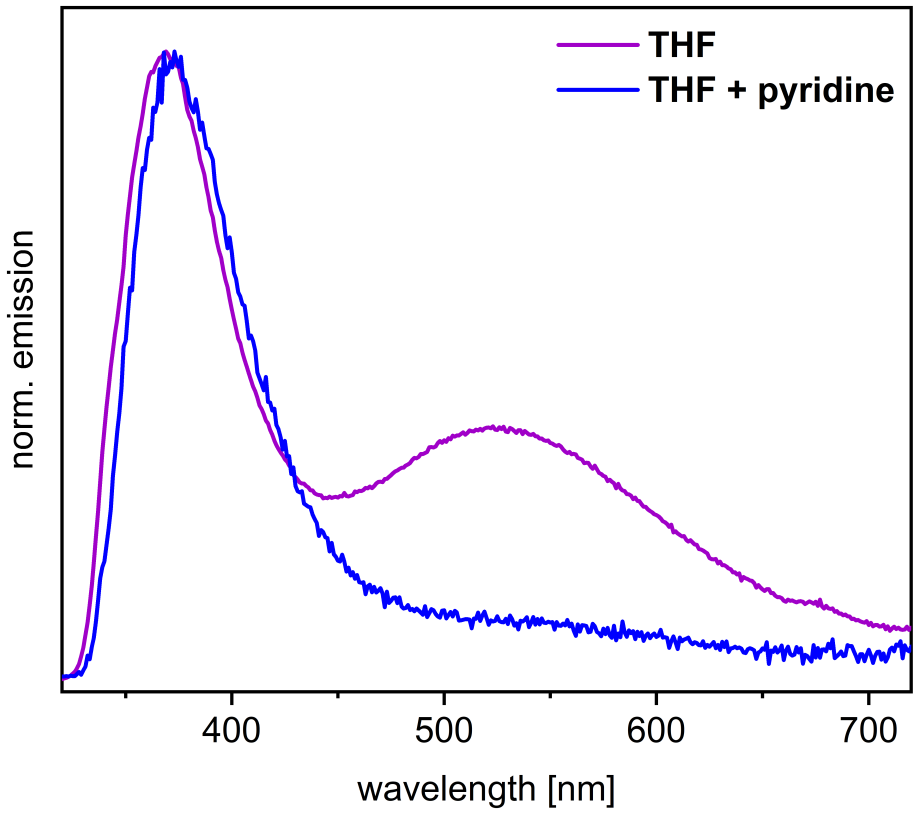


Fig. S30 Emission spectra of **6**^{Benz} in THF before and after adding pyridine.

5 Computational details

DFT geometry optimizations of **6**^{Benz} and **6**^{Thio} were carried out with the Gaussian 16, Revision C.01 program package[5] using the ωB97X-D functional[6] in combination with the def2-SVP basis set[7]. The structures were fully optimized and confirmed as minima on the corresponding potential energy surface by vibrational frequency computation, which revealed that all eigenvalues of the Hessian matrix are positive. NBO analysis was carried out with the NBO 7.0 extension[8] (see **Table S4**). The frontier molecular orbitals were visualized with the open-source program IQmol 2.8.0 molecular viewer.[9]

Vertical singlet excitations (10 states) were calculated with the geometry from the DFT-calculations (ωB97X-D / def2-SVP) by means of time dependent (TD) DFT with Gaussian 16, using the tHCTHhyb functional[10] and the def2-TZVPP basis set[7, 11] in a solvation model mimicking THF (see **Table S3**).

The electron excitation analysis were performed using the Multiwfn program package[12] and the TD-DFT-calculation results, selecting the $S_0 \rightarrow S_1$ excitation. The hole-electron and transition density analysis was visualized from the post-processing menu as isosurface plot (isovalue 0.002).

Calculated UV-Vis spectra

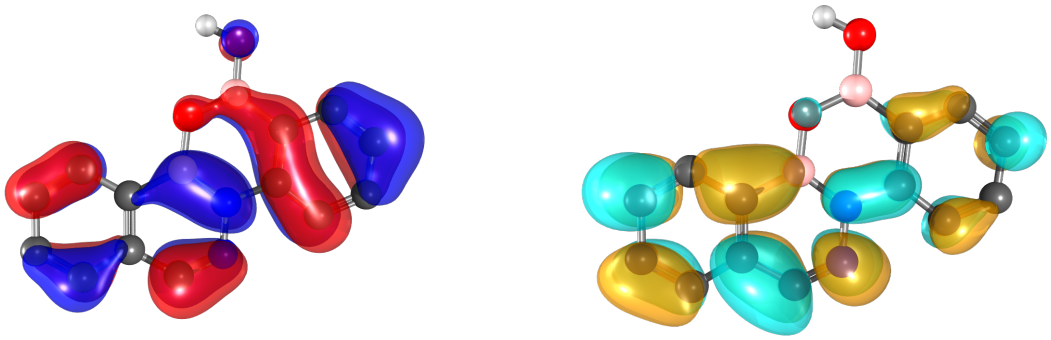
Table S3. Calculated electronic excitations with the largest oscillator strength (tHCTHhyb / def2-TZVPP / solvent=tetrahydrofuran / td(nstates=10)) and experimental absorption maxima of **6**^{Benz} and **6**^{Thio}.

6	State	Symmetry	λ_{exp} [nm]	λ_{calc} [nm]	Oscillator strength	Main excitation
6^{Benz}	S_1	^{1}A	313 326	319	0.4871	HOMO→LUMO
6^{Thio}	S_1	^{1}A	316	324	0.5307	HOMO→LUMO

Frontier molecular orbitals

Table S4. Calculated HOMO and LUMO energy of compound **6**^{Benz} and **6**^{Thio} (ωB97X-D / def2-SVP).

Compound	HOMO energy (eV)	LUMO energy (eV)	HOMO-LUMO gap (eV)
6^{Benz}	−7.946217007222	0.22961153930494	8.17582854652694
6^{Thio}	−8.00027366697	0.07504140074782	8.07531506771782



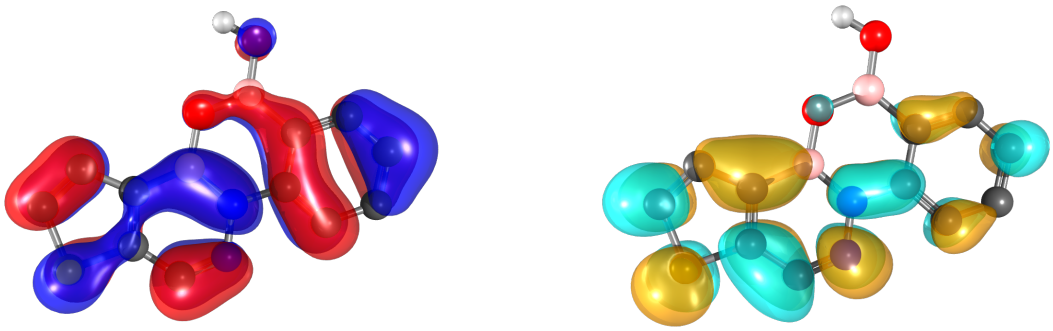
HOMO

−7.95 eV

LUMO

0.23 eV

Figure S31. Calculated frontier molecular orbitals (isovalue 0.06 eÅ^{-3}) of **6**^{Benz} (ωB97X-D / def2-SVP).



HOMO

−8.00 eV

LUMO

0.08 eV

Figure S32. Calculated frontier molecular orbitals (isovalue 0.06 eÅ^{-3}) of **6**^{Thio} (ωB97X-D / def2-SVP).

Electron excitation analysis

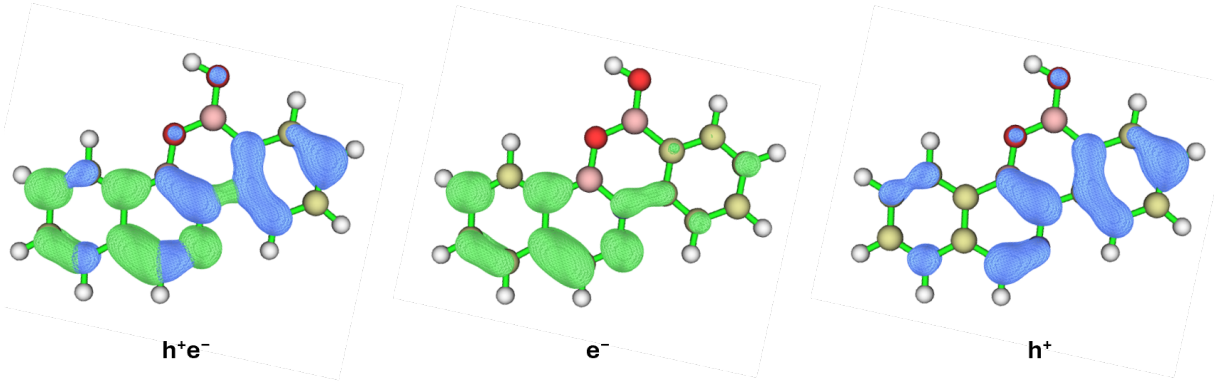


Figure S33. Visualized hole-electron and transition density analysis of $\mathbf{6}^{\mathbf{Benz}}$. Simultaneous isosurface of hole (h^+) and electron (e^-) distribution (left), isosurface of electron distribution (middle, green) and isosurface of hole distribution (right, blue), isovalue 0.002.

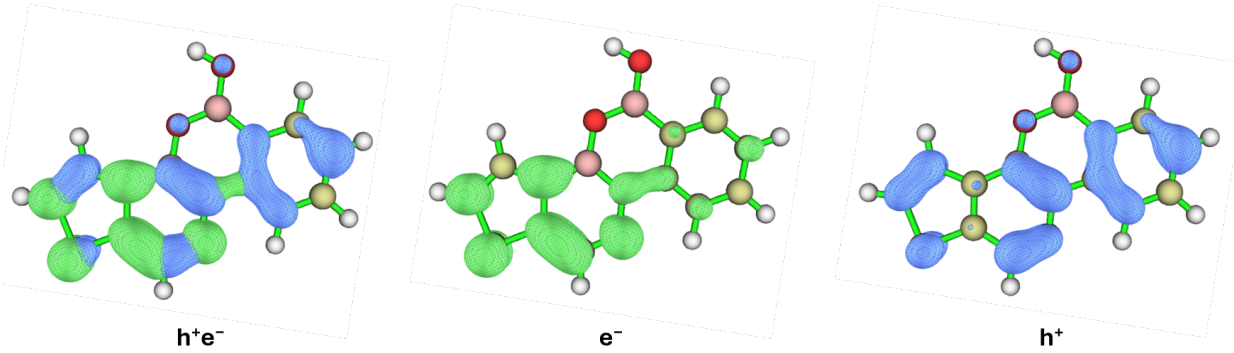
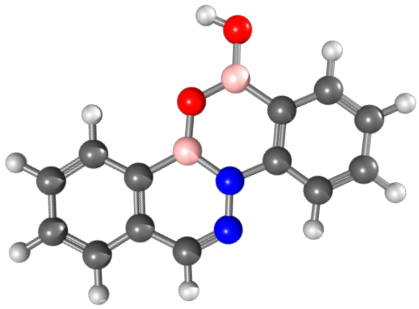


Figure S34. Visualized hole-electron and transition density analysis of $\mathbf{6}^{\mathbf{Thio}}$. Simultaneous isosurface of hole (h^+) and electron (e^-) distribution (left), isosurface of electron distribution (middle, green) and isosurface of hole distribution (right, blue), isovalue 0.002.

Optimized structures (.xyz-files)

Compound **6**^{Benz}

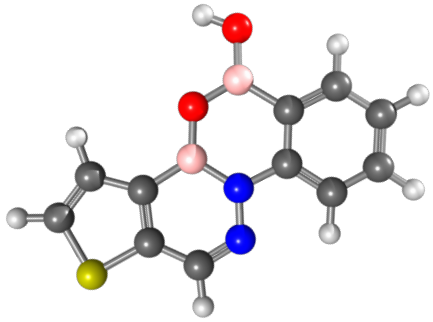


0 1

C	1.54496400	-2.05457800	-0.00056800
H	1.90900900	-3.08755600	-0.00078200
N	-0.28670900	-0.69001800	-0.00041900
O	-0.12014900	1.74767700	-0.00067800
B	0.49508700	0.52156900	-0.00042100
O	-2.04698700	3.11581900	0.00001200
H	-1.38308000	3.81209000	-0.00045200
N	0.26501700	-1.93038600	-0.00064800
C	2.50967200	-0.96996000	-0.00021800
B	-1.49112700	1.87936300	-0.00027800
C	3.89495500	-1.21945400	0.00033900
H	4.26203000	-2.24903000	0.00040500
C	4.78363200	-0.15755200	0.00077900
H	5.85928400	-0.34760700	0.00131000
C	4.30958700	1.16482800	0.00059000
H	5.02053600	1.99404200	0.00081400
C	2.94629300	1.41539900	0.00008600
H	2.57441900	2.44272000	0.00000500
C	2.02507500	0.35263100	-0.00027500
C	-1.70711400	-0.66377600	-0.00017400
C	-2.35355800	0.58805200	-0.00005500
C	-3.75664100	0.61723700	0.00037000
H	-4.25739200	1.58849100	0.00036000
C	-4.50274300	-0.55362500	0.00071100

H	-5.59383400	-0.51615400	0.00112500
C	-3.83902200	-1.78408900	0.00053900
H	-4.41467300	-2.71283800	0.00084000
C	-2.45145100	-1.85001300	0.00003400
H	-1.92905500	-2.80455900	-0.00027200

Compound **6**^{Thio}



0 1

C	1.61037300	-1.89107000	0.00001700
H	2.03250100	-2.89981600	0.00003700
N	-0.29098100	-0.62219300	-0.00000200
O	-0.28030400	1.82957100	-0.00002100
B	0.41329800	0.64600800	-0.00001400
O	-2.28920900	3.07349600	0.00003300
H	-1.67110900	3.81077500	0.00003000
N	0.32049200	-1.82717500	0.00001600
C	2.45898700	-0.73577700	0.00000100
B	-1.65537800	1.87520300	0.00000600
C	4.22547300	0.98486900	-0.00005700
H	5.18413900	1.50221600	-0.00025100
C	2.97725200	1.53670900	0.00002300
H	2.79565600	2.61137300	0.00001800
C	1.93910600	0.55086300	-0.00000900
C	-1.71425900	-0.67797900	-0.00000500
C	-2.43498000	0.53199500	0.00000500
C	-3.83734800	0.47639200	0.00000400

H	-4.39533000	1.41585200	0.00001300
C	-4.51165000	-0.73709300	-0.00000800
H	-5.60299400	-0.76533700	-0.00001000
C	-3.77507500	-1.92513600	-0.00001900
H	-4.29319200	-2.88709300	-0.00002900
C	-2.38608300	-1.90667900	-0.00001700
H	-1.80821200	-2.82852900	-0.00002300
S	4.18798100	-0.74293900	0.00002800

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