

Supporting Information for:

Synthesis of Phenanthrylboroles and Formal Nitrene Insertion to Access Azaborapyrenes

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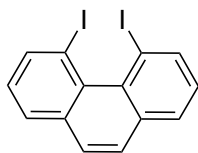
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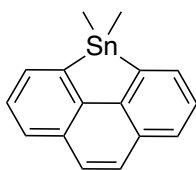
Experimental details

General Considerations: All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun Unilab glove box or using standard Schlenk techniques. Solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 4 Å molecular sieves. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories and dried by stirring for 5 days over CaH₂, distilled, and stored over 4 Å molecular sieves. Solutions of *n*BuLi in hexanes were purchased from Acros Organics and titrated to determine the precise molarity before use. Boron trichloride solution (1 M in methylene chloride) and PhBCl₂ were purchased from Acros Organics and used as received. Multinuclear NMR spectra (¹H, ¹³C{¹H}, ³¹P{¹H}, ¹¹B) were recorded on a Bruker Ascend 400 MHz instrument. High Resolution mass spectra (HRMS) were obtained at the Baylor University Mass Spectrometry Center on a Thermo Scientific LTQ Orbitrap Discovery spectrometer using +ESI. Melting points were measured with a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. The photophysical experiments were conducted utilizing standard quartz cuvettes with dimensions of 1 cm × 1 cm. UV-visible absorption spectra were acquired employing an Agilent 8453 diode array UV-visible spectrophotometer. Extinction coefficients were derived from five independently prepared samples dissolved in dichloromethane (DCM). Fluorescence quantum yields were determined employing a calibrated integrating sphere with an inner diameter of 150 mm, in conjunction with the FLSP920 spectrometer. Fluorescence lifetimes were recorded using the time-correlated single-photon counting (TCSPC) method employing the FLSP920 spectrometer. Samples were excited using a picosecond pulsed diode laser emitting at a wavelength of 273.8 nm. Single crystal X-ray diffraction data were collected on a Bruker Apex III-CCD detector using Mo-Kα radiation ($\lambda = 0.71073 \text{ \AA}$). Crystals were selected under paratone oil, mounted on MiTeGen micromounts, and immediately placed in a cold stream of N₂. Structures were solved and refined using SHELXTL and figures produced using OLEX2.^{1,2}



4,5-Diiodophenanthrene: 4,5-Diiodophenanthrene was prepared by the procedure reported by Bock and Havlas with modifications to the work up detailed below.³ A solution of *n*BuLi in hexane (2.5 M, 7.12 mL, 17.8 mmol)

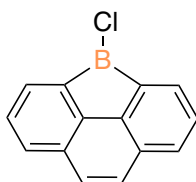
was added to a suspension of phenanthrene (1.51 g, 8.45 mmol) in tetramethylethylenediamine (3.00 mL, 18.9 mmol) at 0 °C. The resulting mixture was stirred at 23 °C for 30 min, then was refluxed at 70 °C for 2 h. After the reaction cooled to 23 °C, the volatiles were removed under vacuum. The residue was dissolved in tetrahydrofuran (10 mL) and cooled to -78 °C. A solution of iodine in tetrahydrofuran (4.73 g, 18.6 mmol, 20 mL) was slowly added over a 15 min period. The resulting dark purple solution was stirred for 1 h at -78 °C, then the bath was removed to allow the solution to warm to 23 °C and stirring was continued for 17 h. The reaction mixture was quenched with 10 % aqueous NaHSO₃ (50 mL) and extracted with diethyl ether (3 × 50 mL). The organic phase was washed twice with brine, dried over MgSO₄, filtered, and the volatiles removed under reduced pressure. Acetone (5 mL) was added to the residue to generate a solid. The solid was recrystallized by dissolving in warm chloroform and storing at -78 °C to afford pale-yellow crystals (0.763 g, 21% yield). The multinuclear NMR spectra match the literature data.



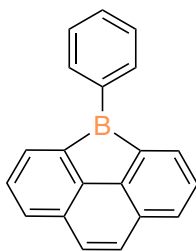
1: A hexanes solution of *n*BuLi (2.37 M in hexanes, 1.30 mL, 2.93 mmol) was added dropwise to a diethyl ether solution of 4,5-diiodophenanthrene (0.600 g, 1.40 mmol, 5.0 mL) at -78 °C. The reaction was stirred for 2 h at 23 °C and a

diethyl ether solution of SnCl₂(CH₃)₂ (0.43 g, 2.0 mmol, 5 mL) was added dropwise over a 10 min period to the reaction mixture which was then stirred for 17 h. The reaction mixture was filtered to obtain a yellow solution. The volatiles were removed from the supernatant under reduced pressure and the product extracted with 3 mL *n*-pentane at -78 °C. The solvent was removed under reduced pressure to obtain the product as a pale-yellow oil (0.380 g, 84% yield). ¹H NMR (400

MHz, CDCl₃): δ 7.91 (dd, $J = 7$, 1 Hz, 2H), 7.87 (dd, $J = 8$, 1 Hz, 2H), 7.74 – 7.71 (m, 2H), 7.62 (dd, $J = 8$, 7 Hz, 2H), 0.64 (s, $^2J_{\text{H-Sn}} = 32$ Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl₃): δ 142.51, 140.60, 134.08, 131.27, 127.99, 126.94, 126.85, –8.07. High-resolution mass spectrometry (HRMS) electrospray ionization: +ESI-HRMS for [C₁₆H₁₅Sn₁]⁺ calcd. m/z 327.0196, found: 327.0189.

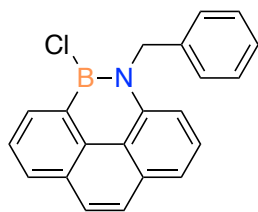


2Cl: A hexanes solution of **1** (0.0925 g, 0.285 mmol, 5.0 mL) was prepared in a pressure tube charged with a magnetic stir bar. A solution of 1 M boron trichloride in CH₂Cl₂ (315 μL , 0.315 mmol) was added dropwise and the pressure tube was closed and heated at 70 °C for 48 h while stirring. The reaction mixture was filtered and the supernatant stripped of volatiles under vacuum. The product was extracted in *n*-pentane (5 mL) at –78 °C. Removing the *n*-pentane at reduced pressure afforded the product as pale-yellow crystals (0.027 g, 43% yield). Crystals for X-ray crystallography were obtained at 23 °C by dissolving the product in a 1:1 mixture of benzene and hexanes. ^1H NMR (400 MHz, CDCl₃): δ 7.78 – 7.73 (m, 4H), 7.62 (s, 2H), 7.44 (t, $J = 8$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl₃): δ 130.63, 130.56, 128.56, 128.26, 127.85, 125.19. ^{11}B NMR (128 MHz, CDCl₃): δ 63.3.

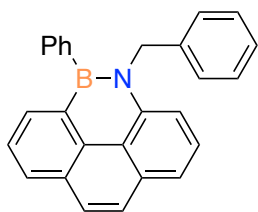


2Ph: A hexanes solution of **1** (0.296 g, 1.00 mmol, 10 mL) was prepared in a pressure tube charged with a magnetic stir bar. Dichlorophenylborane (0.159 g, 1.00 mmol) was added dropwise and the mixture was heated at 75 °C for 48 h while stirring. The reaction mixture was filtered, the volatiles were removed under vacuum from the supernatant, and the product was extracted with *n*-pentane at –78 °C. Removing the *n*-pentane at reduced pressure gave the product as a yellow oil (0.084 g, 32% yield). ^1H NMR (400 MHz, CDCl₃): δ 8.52 - 8.46 (m, 2H), 8.08 (dd, $J = 7$, 1 Hz, 2H), 7.77 (dd, $J = 8$, 0.5 Hz, 2H), 7.70 - 7.58 (m, 5H), 7.46 (dd, $J = 8$, 7 Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl₃): δ

147.99, 137.30, 137.23, 133.37, 133.18, 133.11, 130.99, 128.46, 128.19, 128.03, 125.18. ^{11}B NMR (128 MHz, CDCl_3): δ 63.1.



3Cl: To a hexanes solution of **2Cl** (0.019 g, 0.10 mmol, 5.0 mL), benzyl azide (10.7 μL , 0.100 mmol) was added dropwise and the reaction was stirred for 15 min at 23 $^\circ\text{C}$. The addition of *n*-pentane (5 mL) gave a white precipitate. Filtering and drying the precipitate at reduced pressure gave the product (0.025 g, 76% yield). Single crystals for X-ray diffraction were grown by vapor diffusion from a chloroform solution of **3Cl** into toluene. ^1H NMR (400 MHz, C_6D_6): δ 8.84 (d, $J = 8$, 1H), 7.98 (d, $J = 8$ Hz, 1H), 7.72 - 7.66 (m, 3H), 7.54 (d, $J = 8$ Hz, 1H), 7.41 - 7.31 (m, 2H), 7.06 - 6.95 (m, 5H), 5.43 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6) δ 138.50, 136.75, 134.59, 132.70, 131.94, 131.18, 129.95, 129.67, 127.87, 127.68, 126.16, 126.04, 125.83, 125.04, 124.97, 120.87, 119.62, 112.99, 50.36. ^{11}B NMR (128 MHz, C_6D_6): δ 37.2.



3Ph: To a hexanes solution of **2Ph** (0.237 g, 0.100 mmol, 5.0 mL), benzyl azide (10.7 μL , 0.100 mmol) was added dropwise and the reaction was stirred for 15 min at 23 $^\circ\text{C}$. The addition of *n*-pentane (5 mL) generated a precipitate, the supernatant was decanted, and drying the precipitate in vacuo gave a yellow residue. The residue was loaded onto a silica column and **3Ph** was isolated by chromatography using 9:1 hexanes/ CH_2Cl_2 as the eluent, giving **3Ph** as a pale-yellow oil (0.025 g, 67% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.27 (dd, $J = 8$, 1 Hz, 1H), 8.06 (dd, $J = 7$, 1 Hz, 1H), 8.04 - 7.96 (m, 2H), 7.86 - 7.77 (m, 2H), 7.70 (t, $J = 8$ Hz, 1H), 7.64 - 7.51 (m, 3H), 7.47 - 7.35 (m, 3H), 7.26 - 7.10 (m, 5H), 5.52 (s, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ 139.74, 137.96, 137.54, 133.93, 133.46, 133.31, 133.16, 132.42, 131.18, 131.09, 130.90, 129.34, 129.08, 127.38, 127.25, 127.05, 126.27, 126.18, 125.33, 122.09, 120.86, 114.23 ^{11}B NMR (128 MHz, CDCl_3): δ 29.6.

Figure S1: ^1H NMR spectrum of **1** in CDCl_3 (400 MHz)

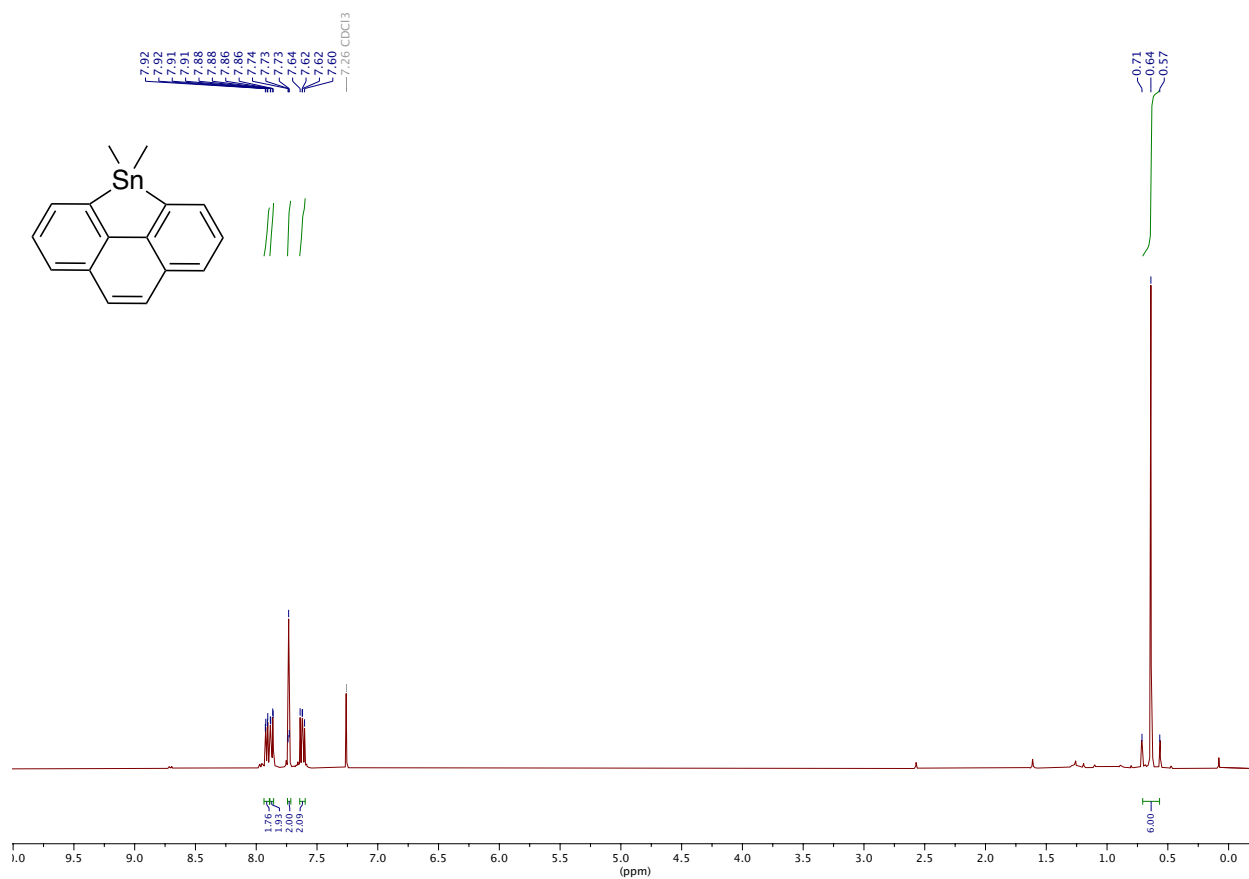


Figure S2: ^1H NMR spectrum of **1** in CDCl_3 (400 MHz, expanded view of the aryl region)

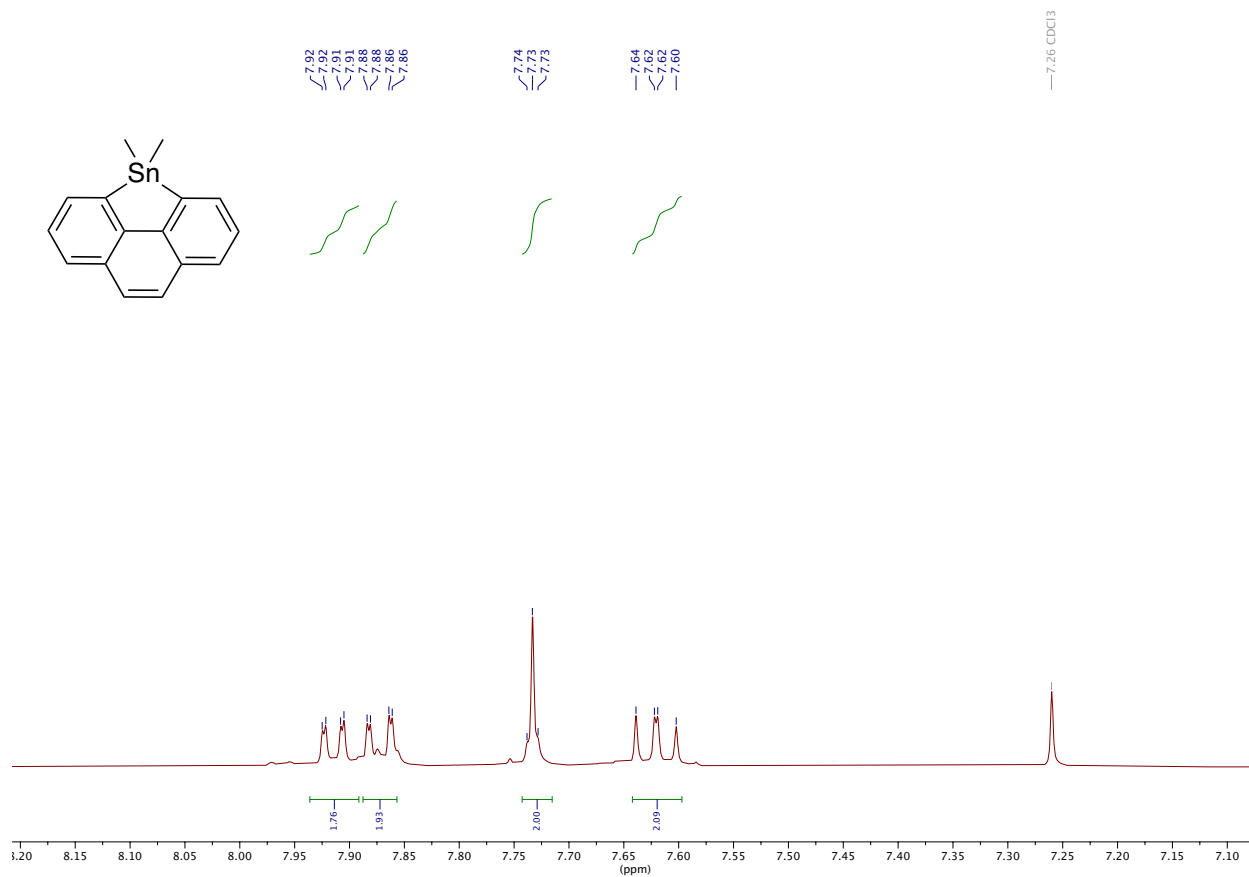


Figure S3: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in CDCl_3 (101 MHz)

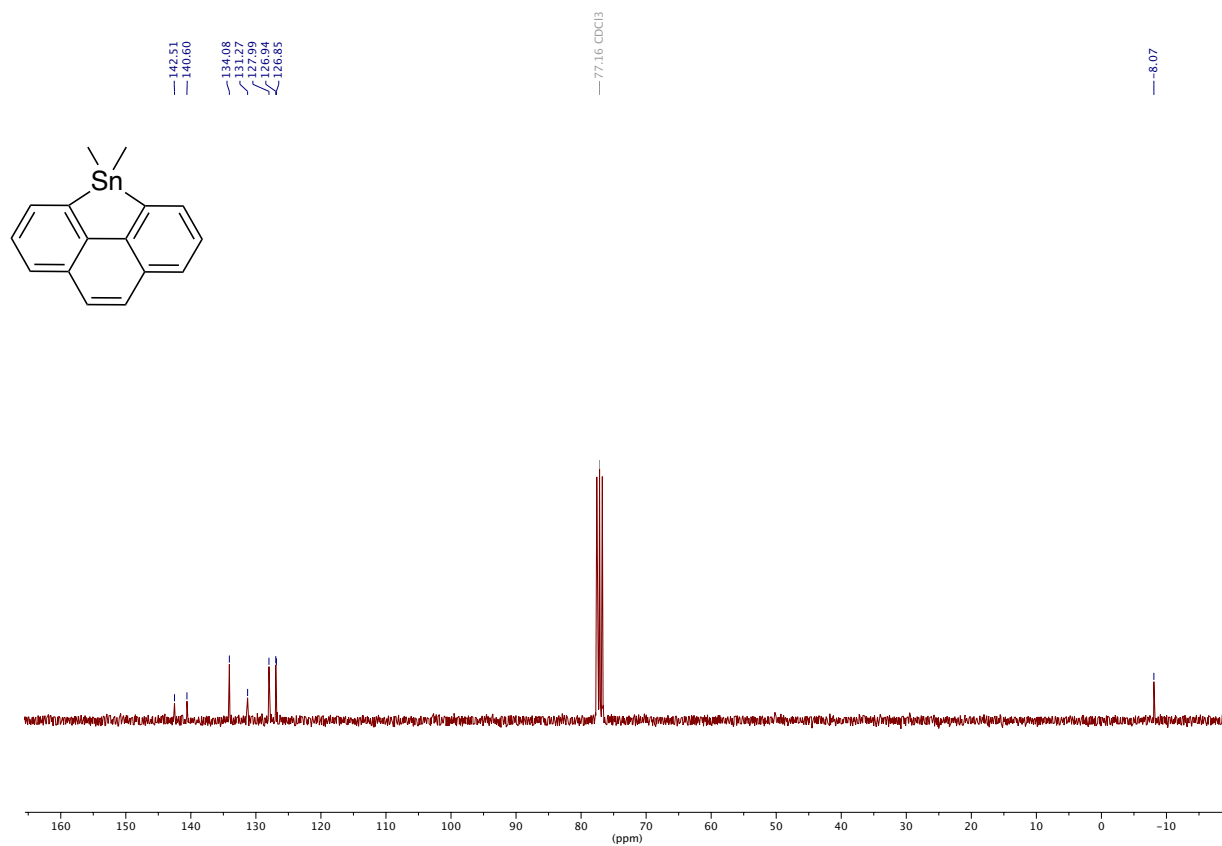


Figure S4: ^1H NMR spectrum of **2Cl** in CDCl_3 (400 MHz)

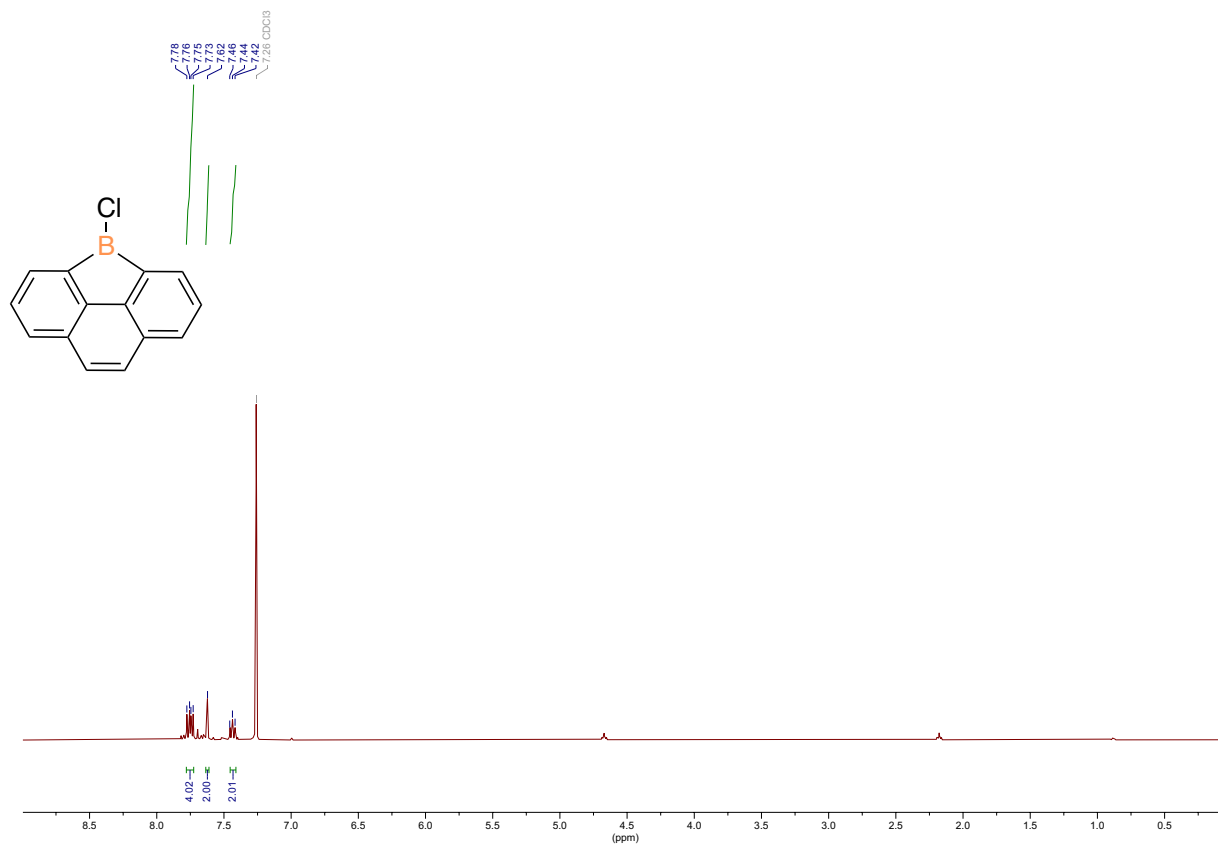


Figure S5: ^1H NMR spectrum of **2Cl** in CDCl_3 (400 MHz, expanded view of the aryl region)

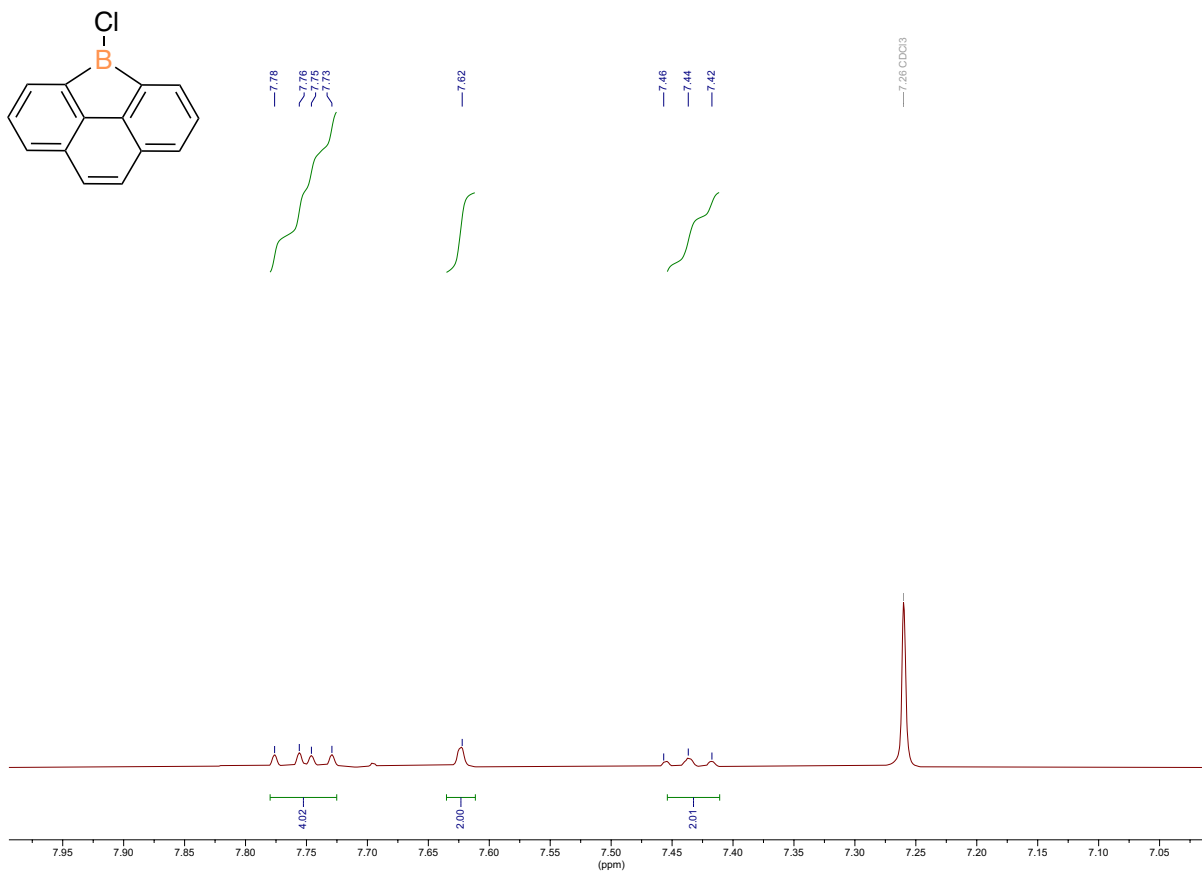


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2Cl** in CDCl_3 (101 MHz)

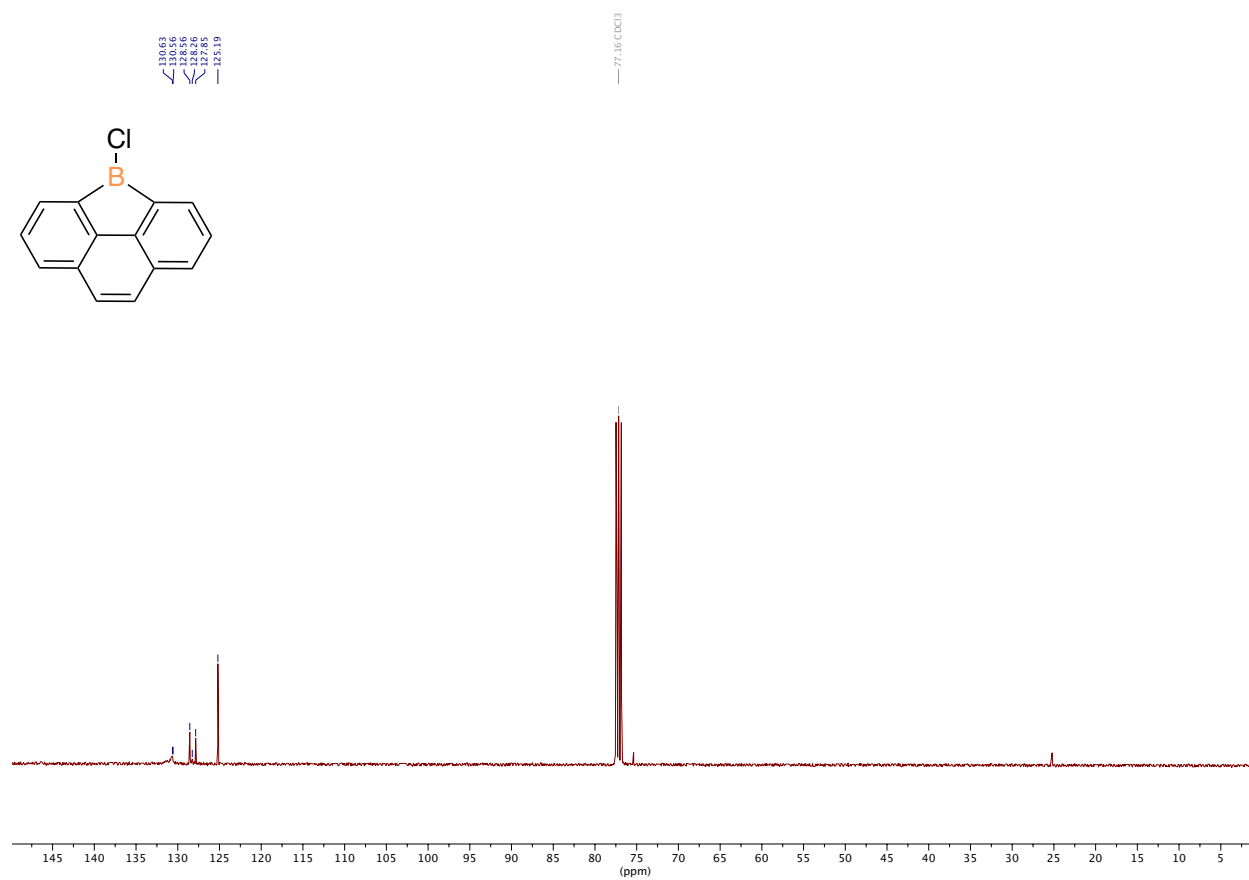


Figure S7: ^{11}B NMR spectrum of **2Cl** in CDCl_3 (128 MHz)

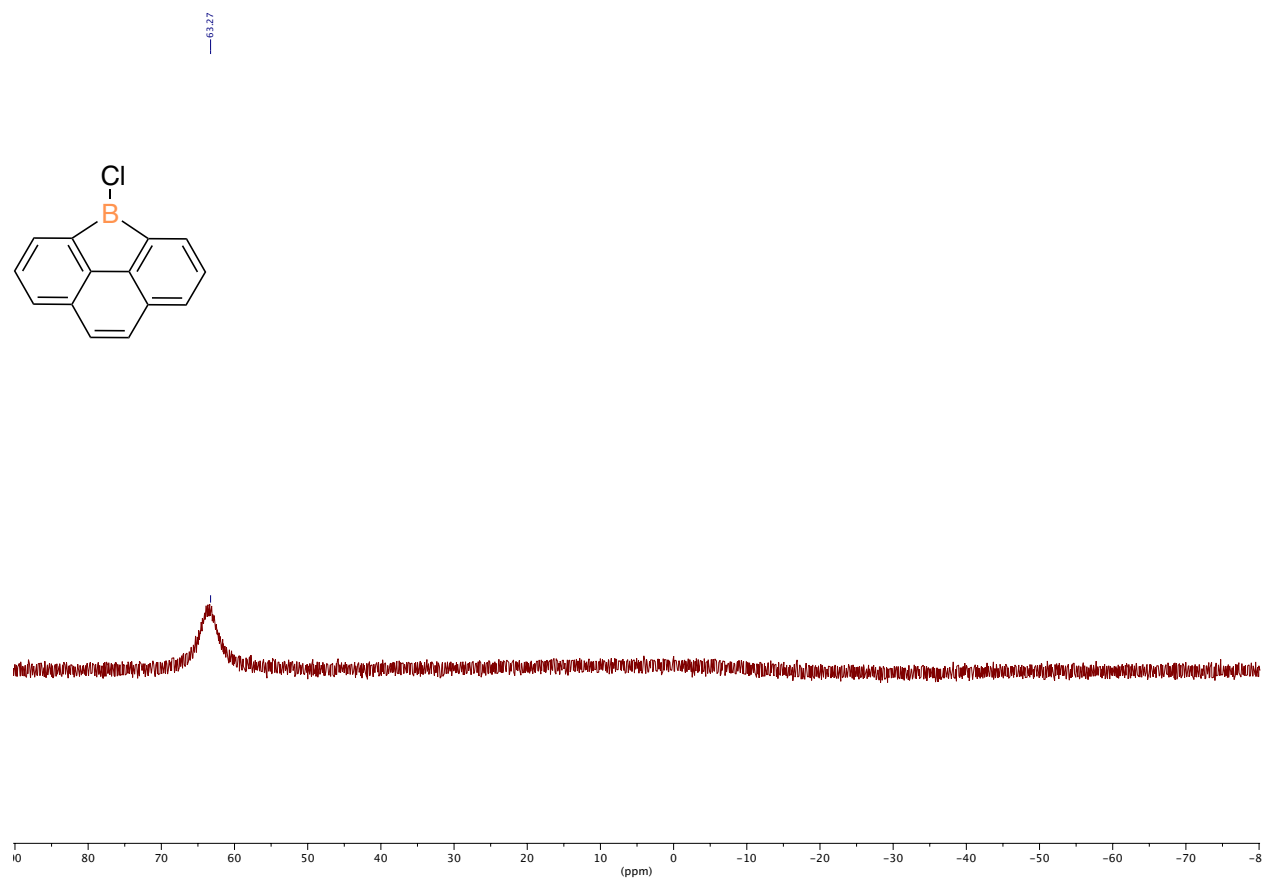


Figure S8: ^1H NMR spectrum of **2Ph** in CDCl_3 (400 MHz)

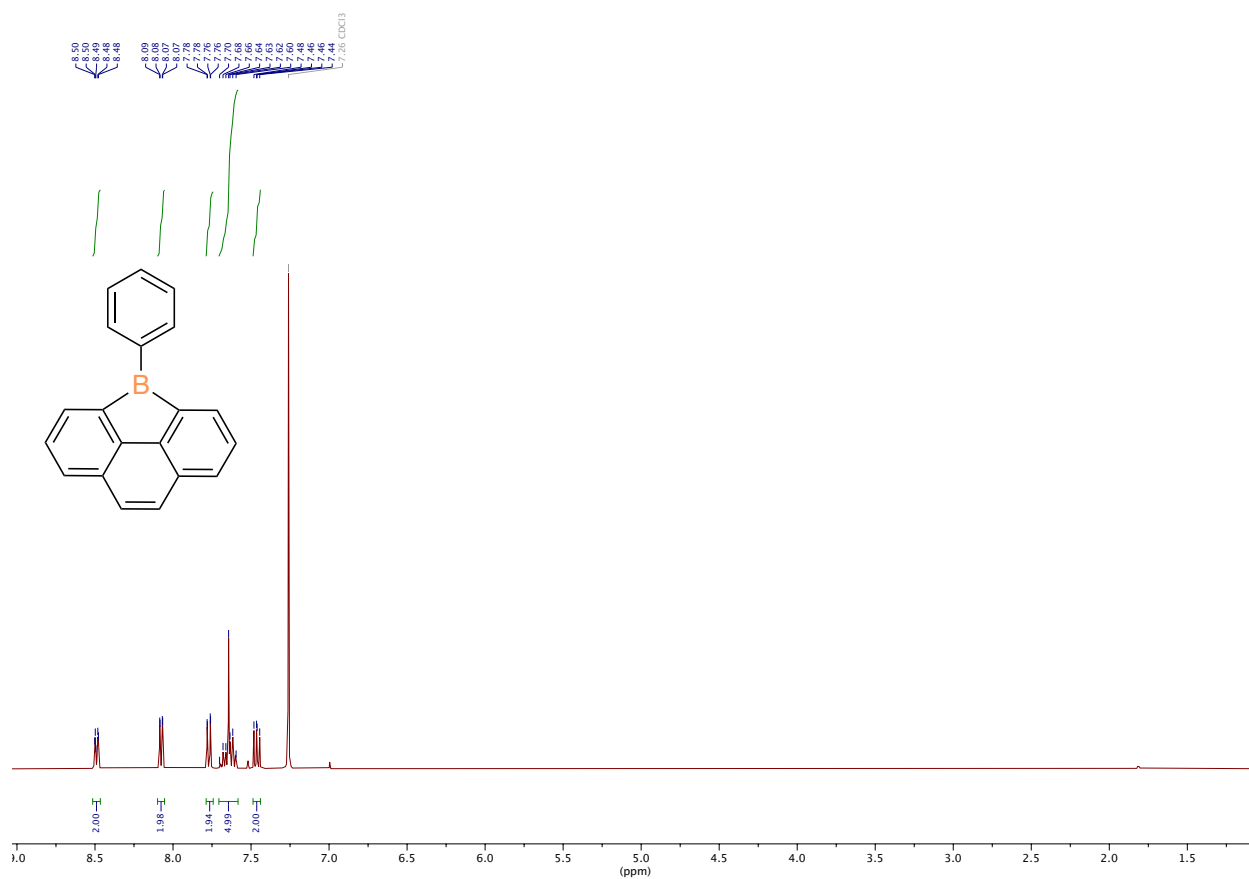


Figure S9: ^1H NMR spectrum of **2Ph** in CDCl_3 (400 MHz, expanded view of the aryl region)

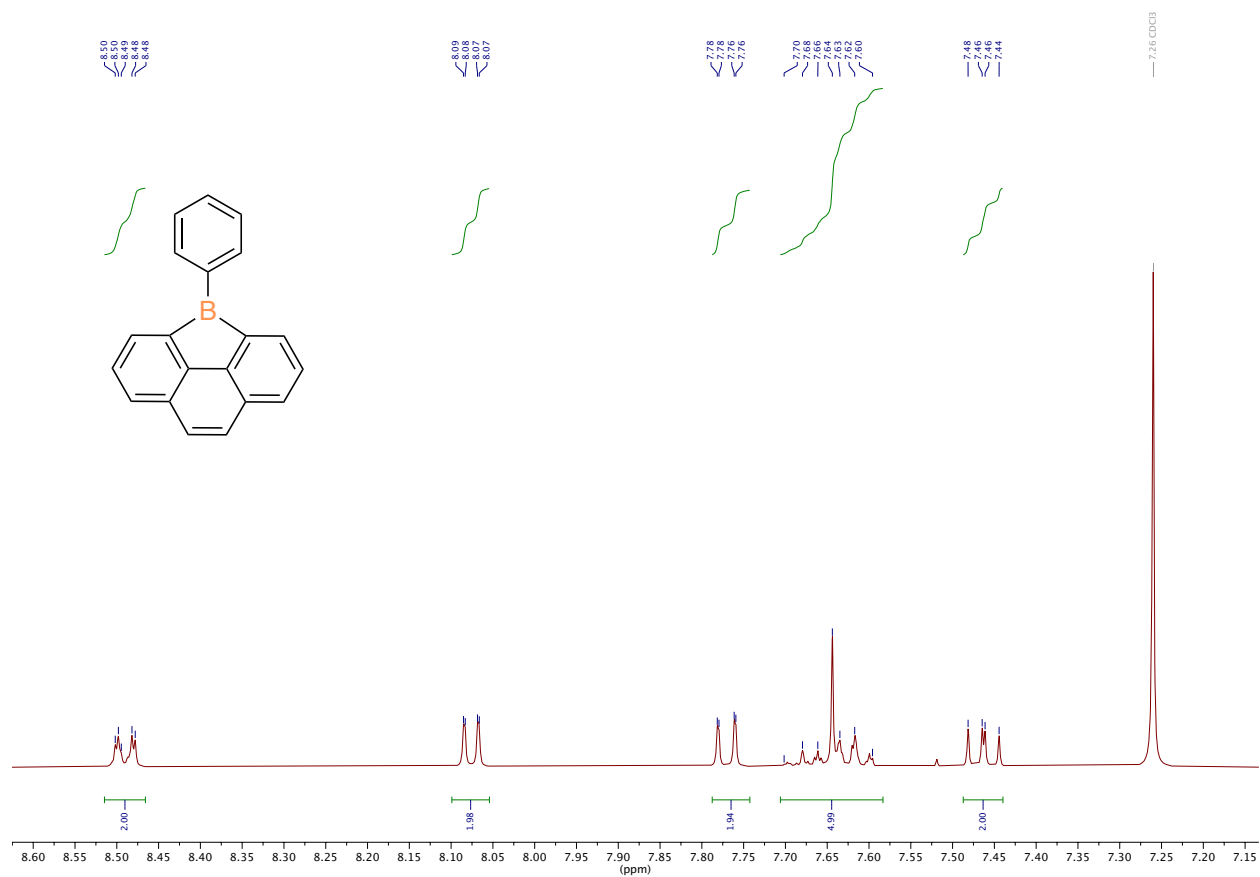


Figure S10: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2Ph** in CDCl_3 (101 MHz)

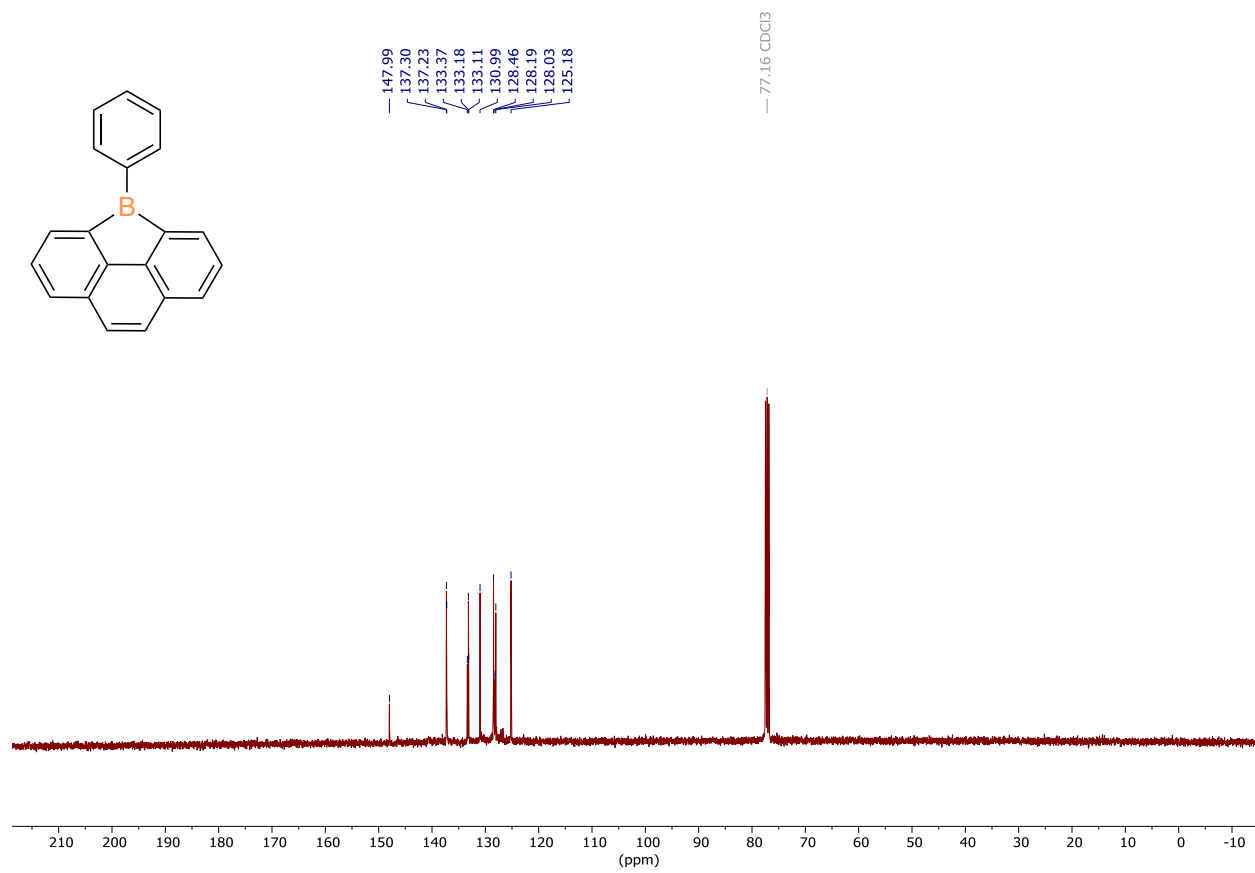
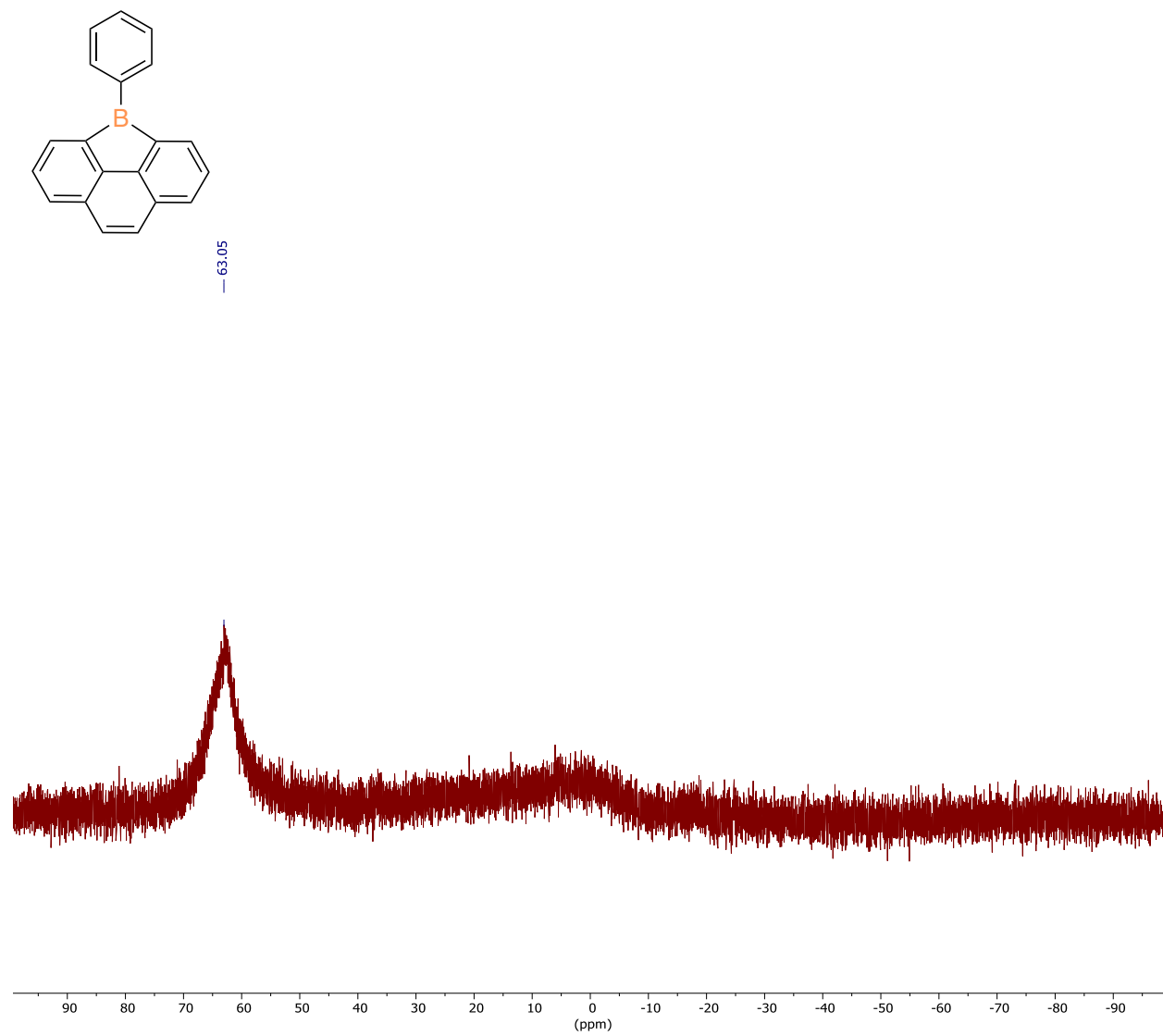


Figure S11: ^{11}B NMR spectrum of **2Ph** in CDCl_3 (128 MHz)



Determination of the Lewis acidity using Gutmann–Beckett method:

In a small vial, a solution of Et₃PO (0.02 mmol in 1.0 mL of C₆D₆) was added to a solution of the corresponding phenanthrylboroles (0.02 mmol **2Cl** or **2Ph** in 1.0 mL of C₆D₆). The reaction mixture was stirred and the ³¹P{¹H} spectrum recorded. The ³¹P{¹H} chemical shifts of Et₃PO·**2Cl** and Et₃PO·**2Ph** are shown in Figures S12 and S13, respectively.

Figure S12: ³¹P{¹H} NMR spectrum of **2Cl** in C₆D₆ (162 MHz)

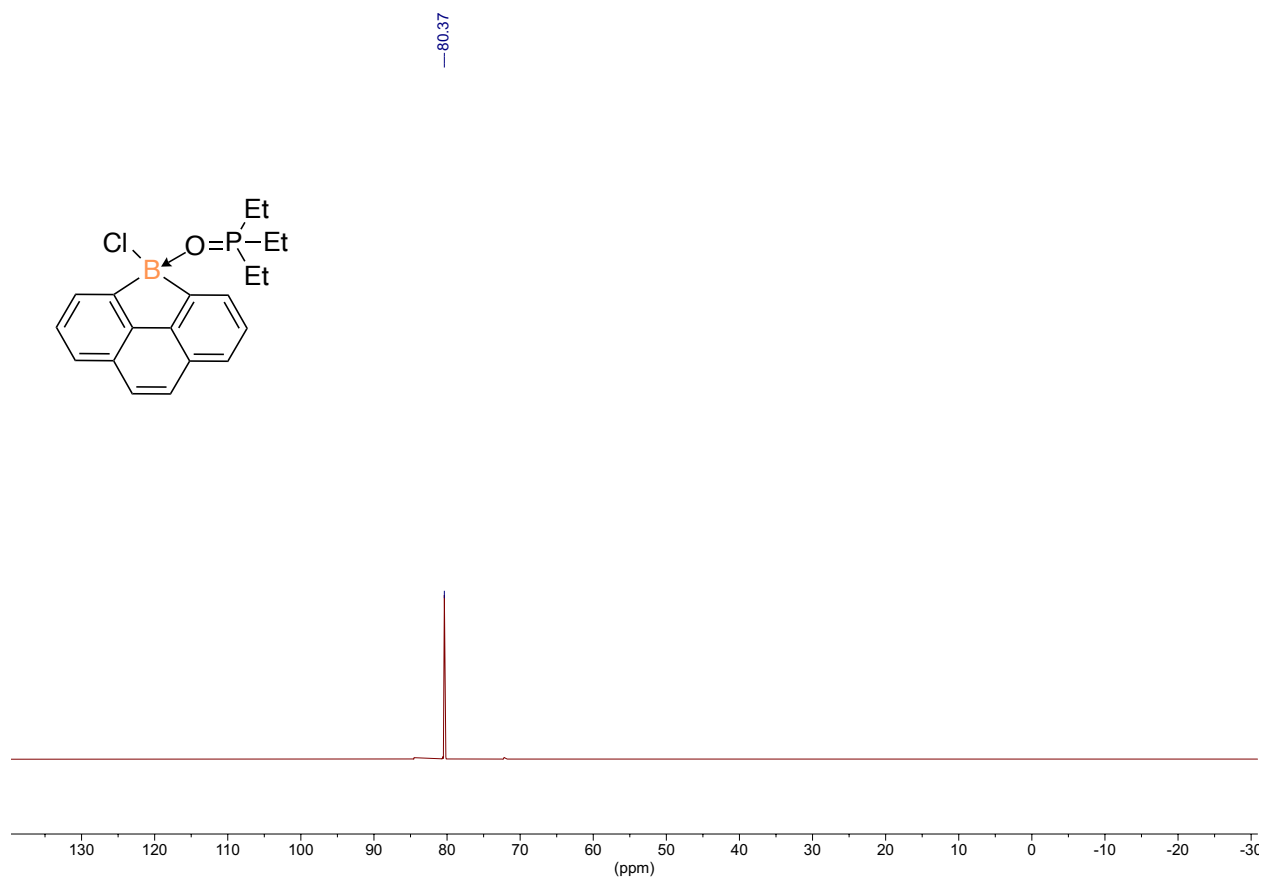


Figure S13: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2Ph** in C_6D_6 (162 MHz)

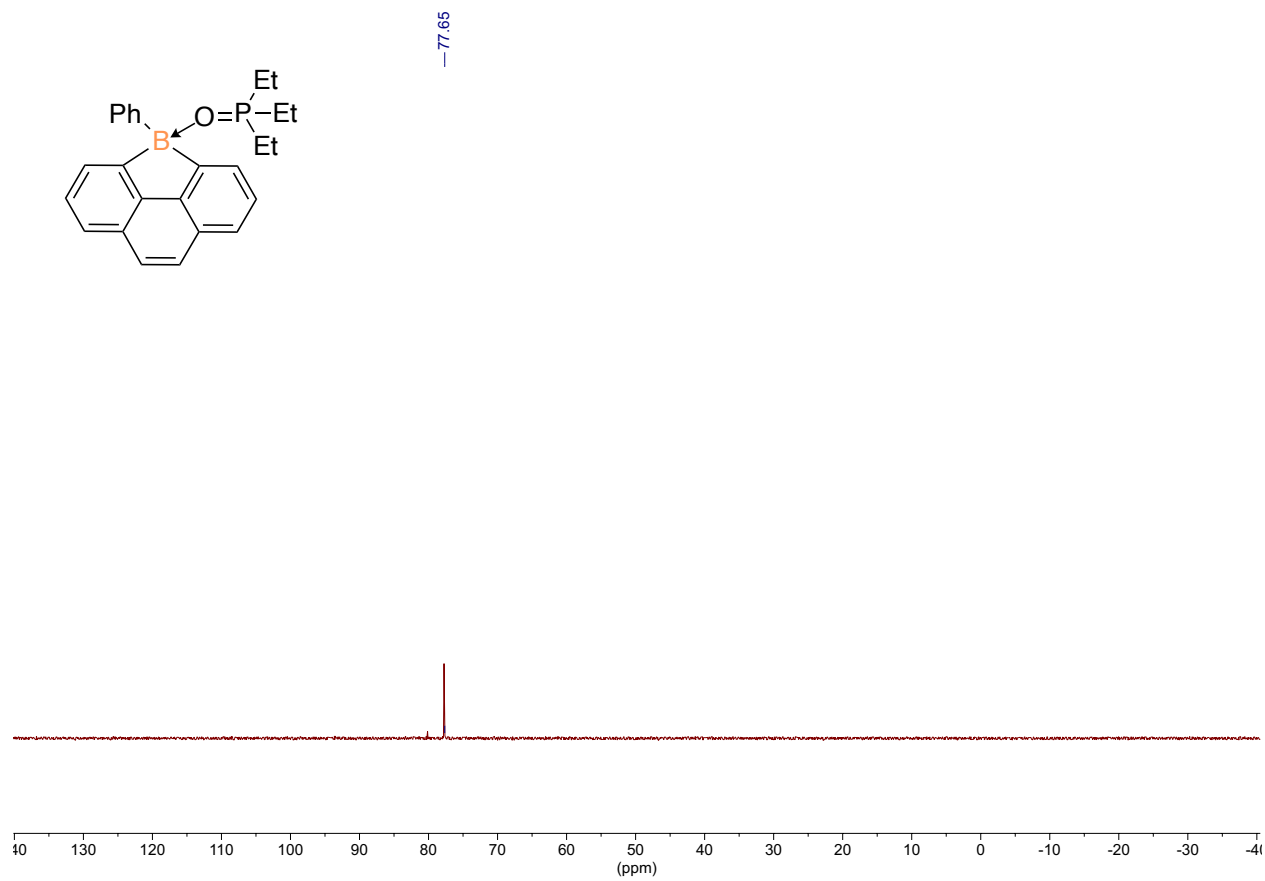


Figure S14: ^1H NMR spectrum of **3Cl** in C_6D_6 (400 MHz)

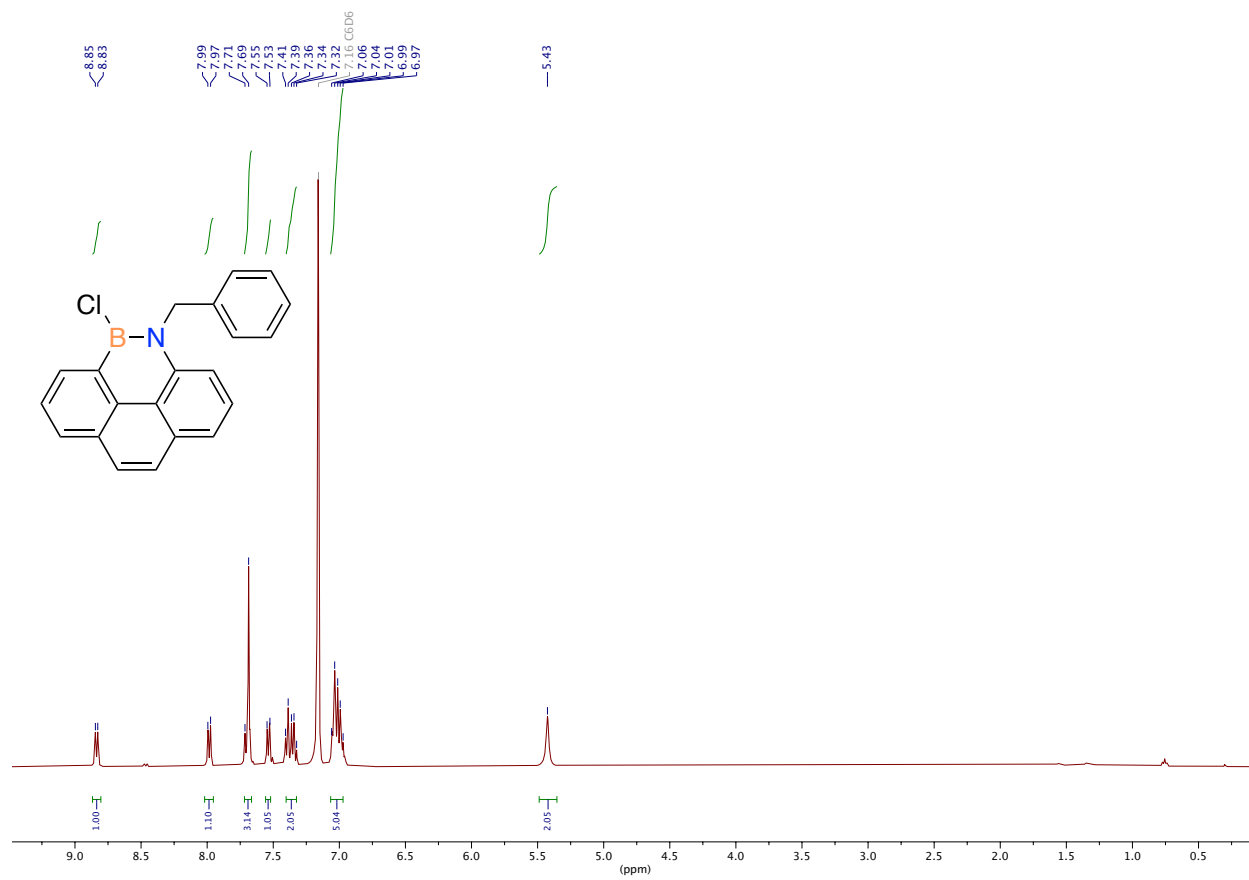


Figure S15: ^1H NMR spectrum of **3Cl** in C_6D_6 (400 MHz, expanded view of the aryl region)

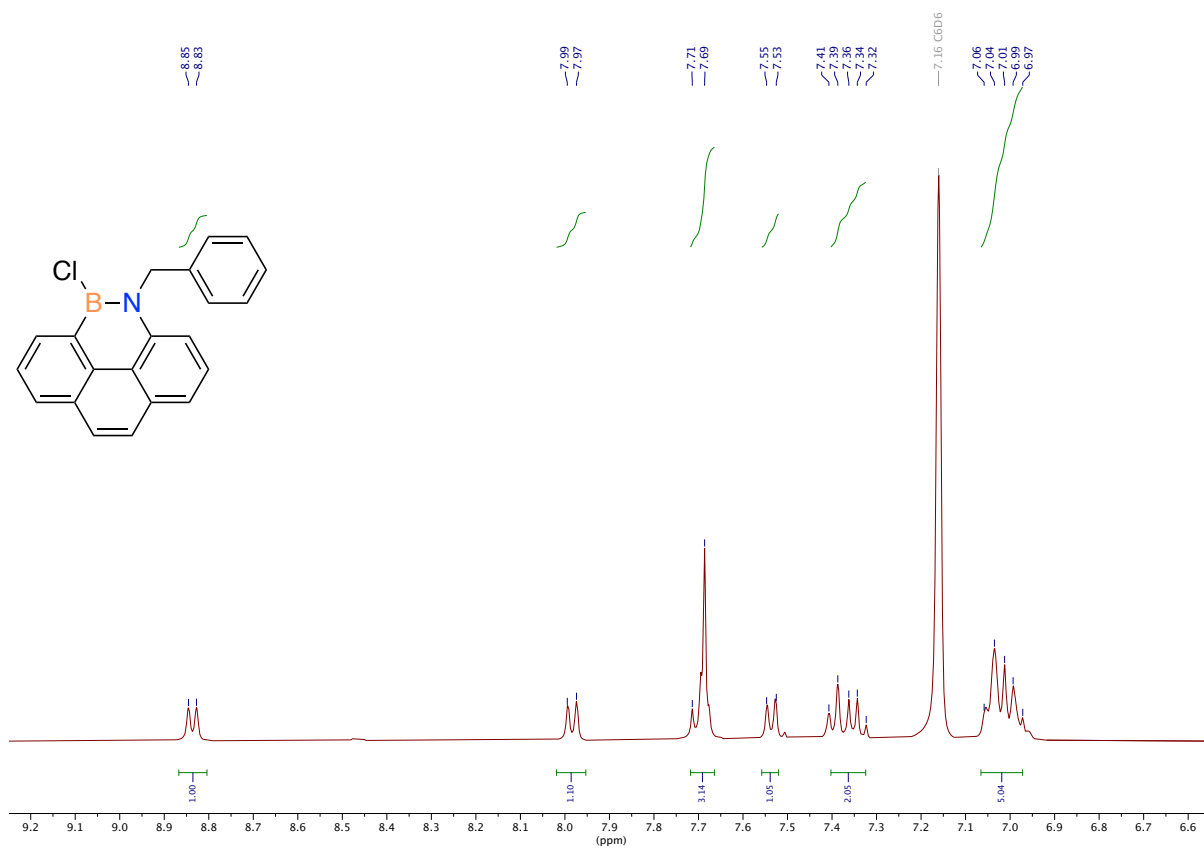


Figure S16: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3Cl** in C_6D_6 (101 MHz)

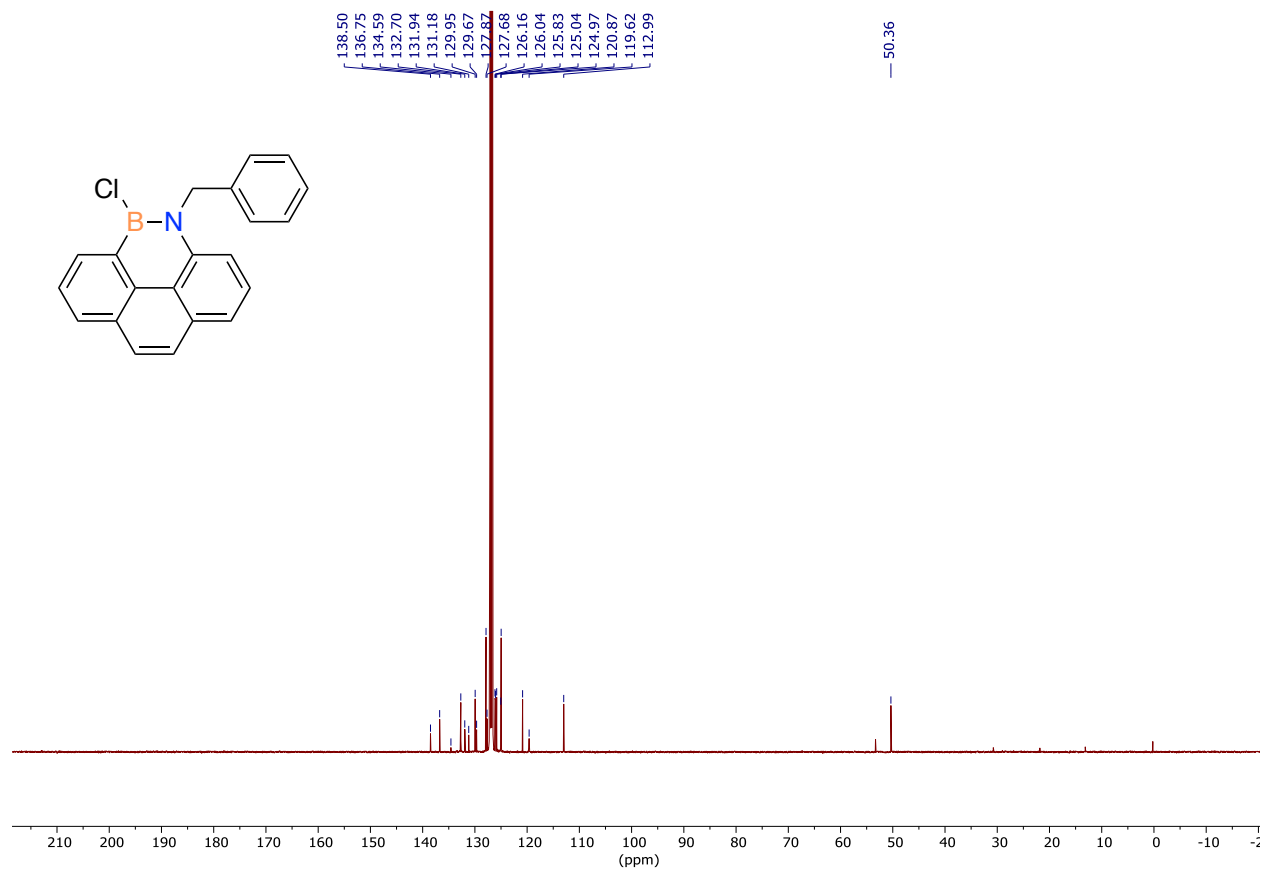


Figure S17: ^{11}B NMR spectrum of **3Cl** in CDCl_3 (128 MHz)

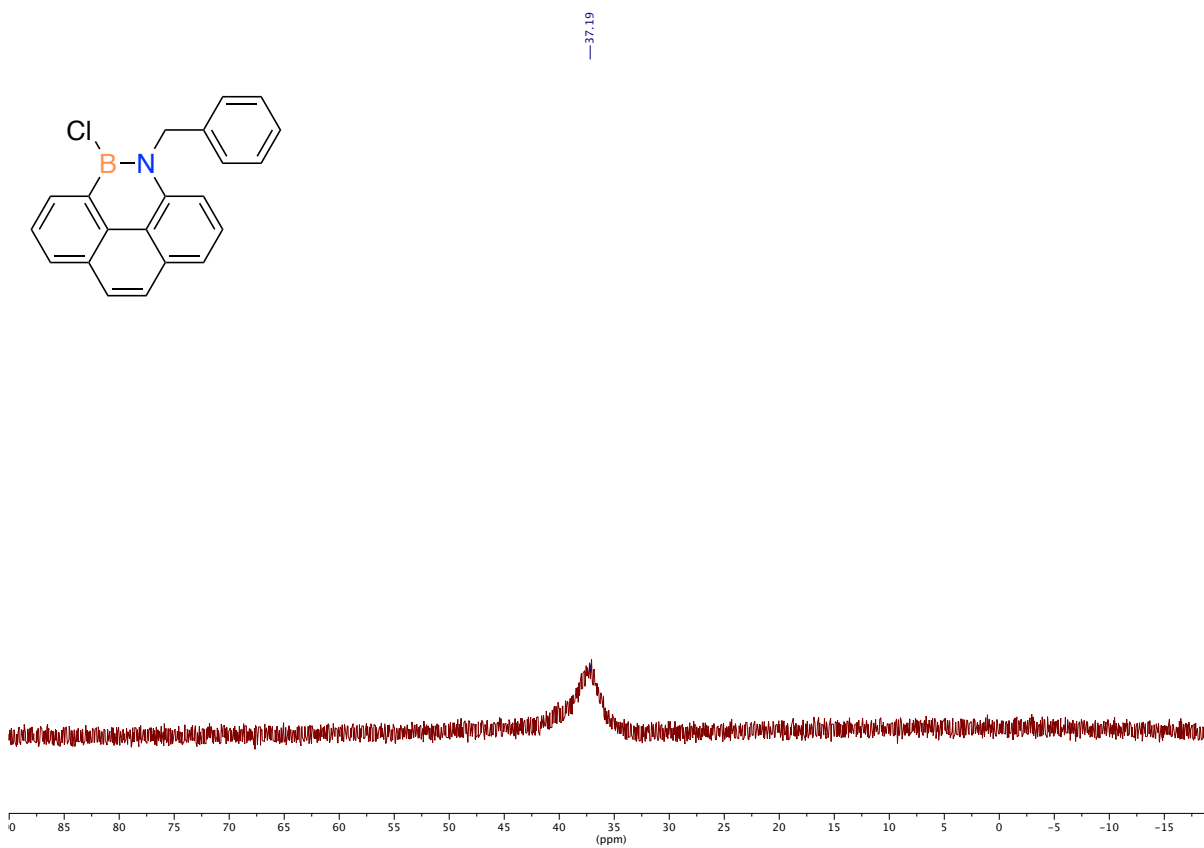


Figure S18: ^1H NMR spectrum of **3Ph** in CDCl_3 (400 MHz, * H_2O , # grease)

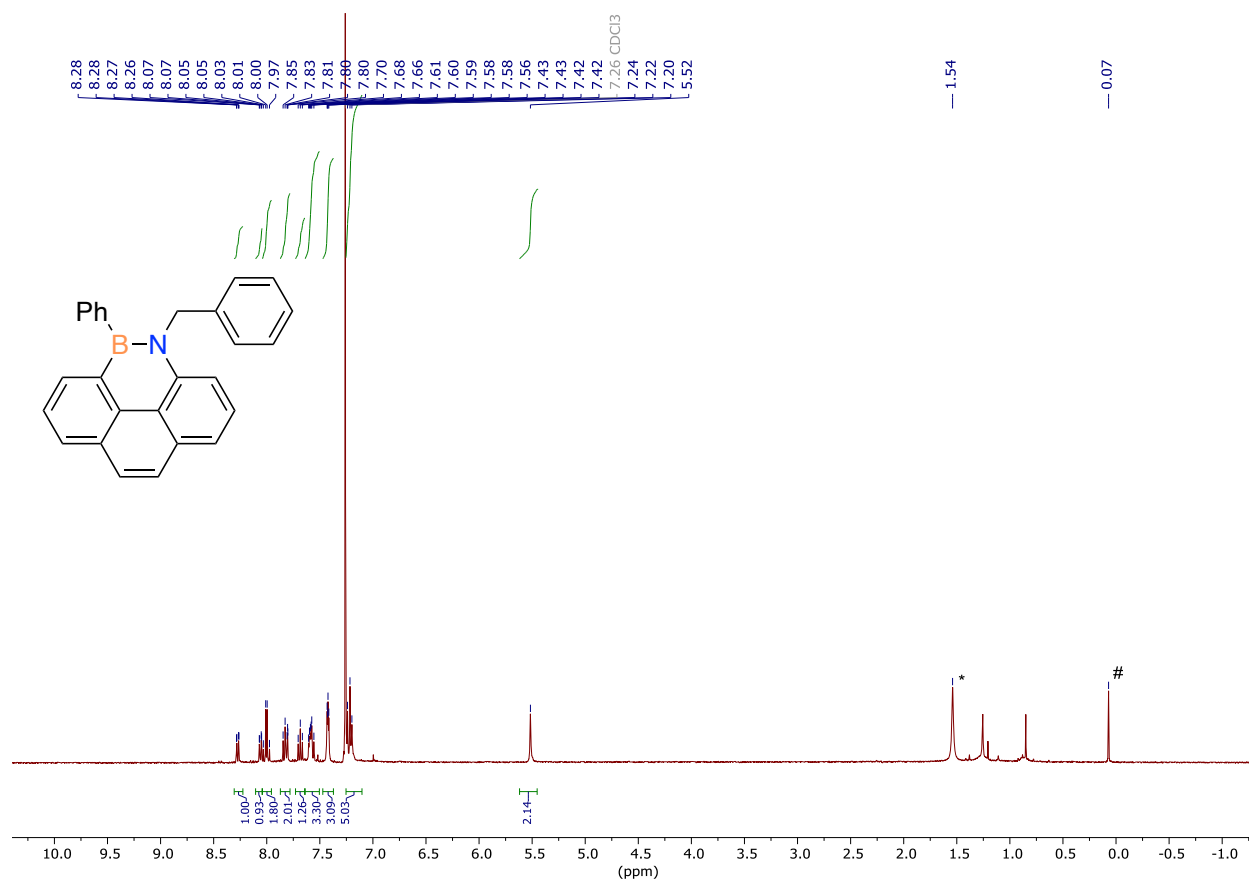


Figure S19: ^1H NMR spectrum of **3Ph** in CDCl_3 (400 MHz, expanded view of the aryl region)

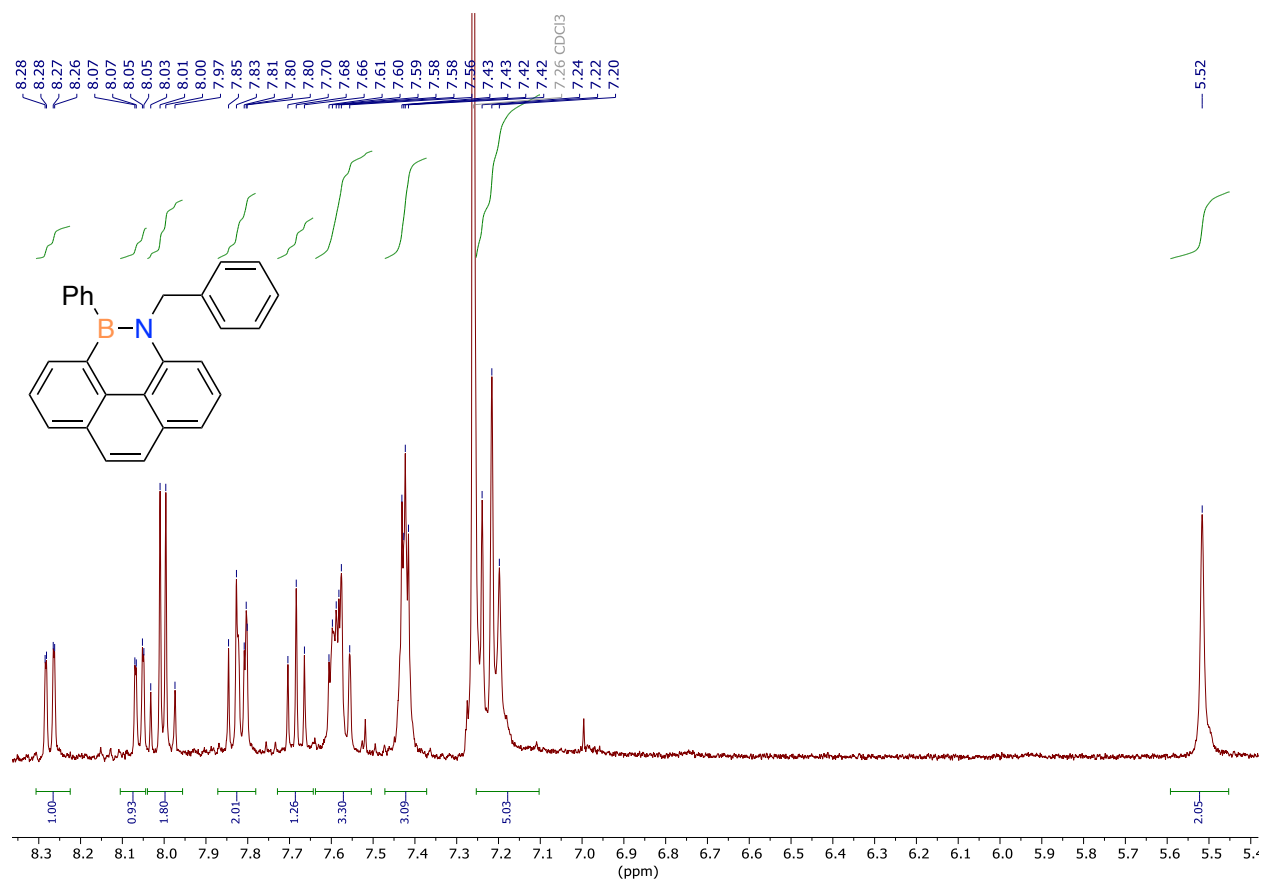


Figure S20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3Ph** in C_6D_6 (101 MHz, * grease)

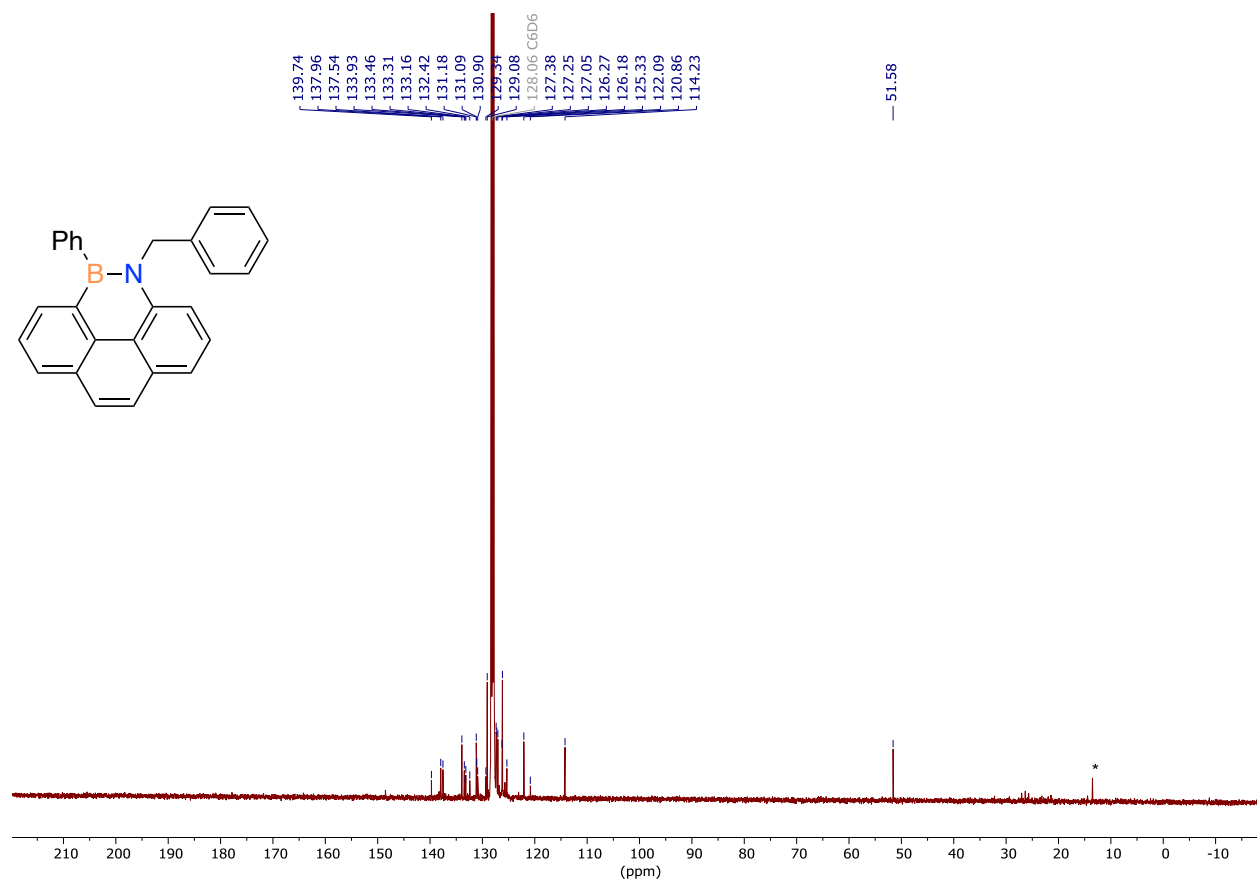


Figure S21: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3Ph** in CDCl_3 (128 MHz, expanded view of the aryl region)

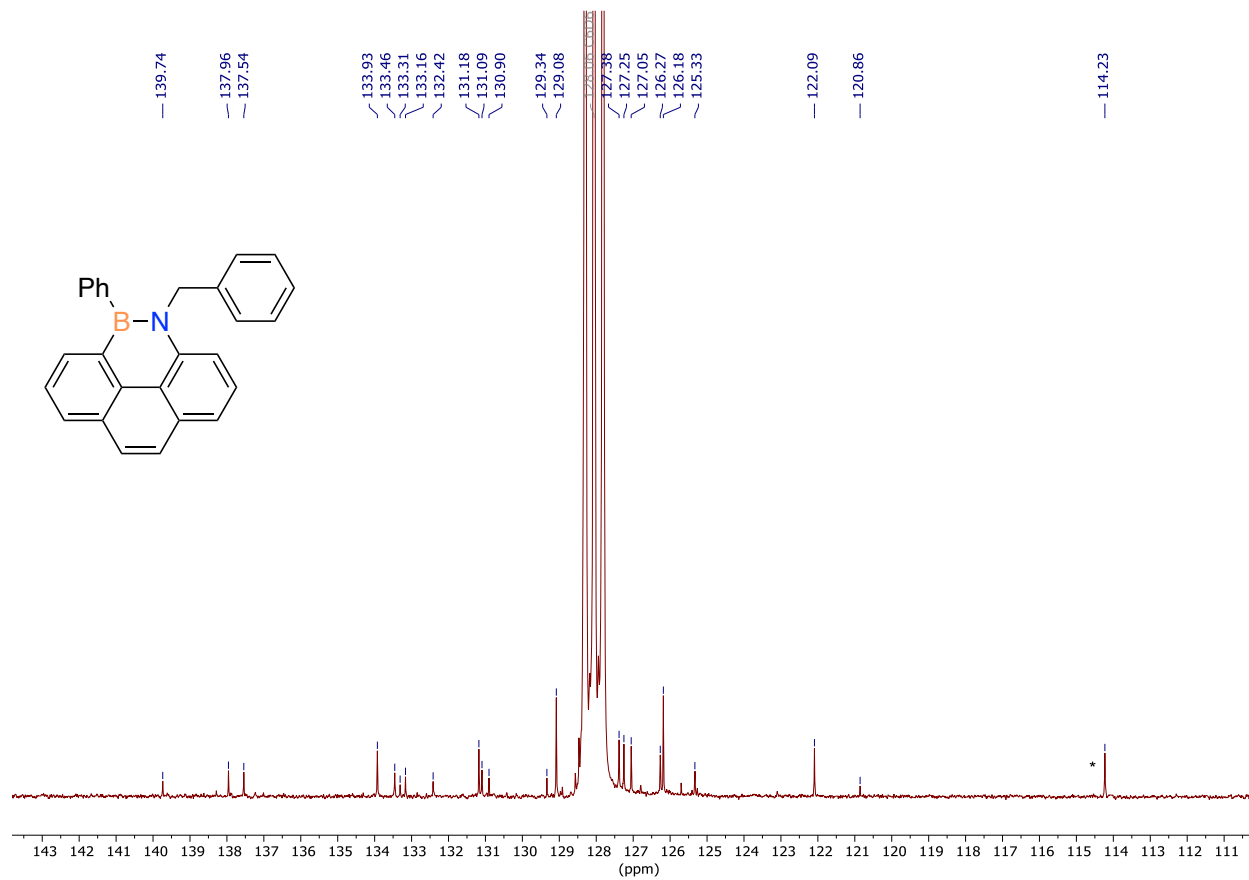


Figure S22: ^{11}B NMR spectrum of **3Ph** in CDCl_3 (128 MHz)

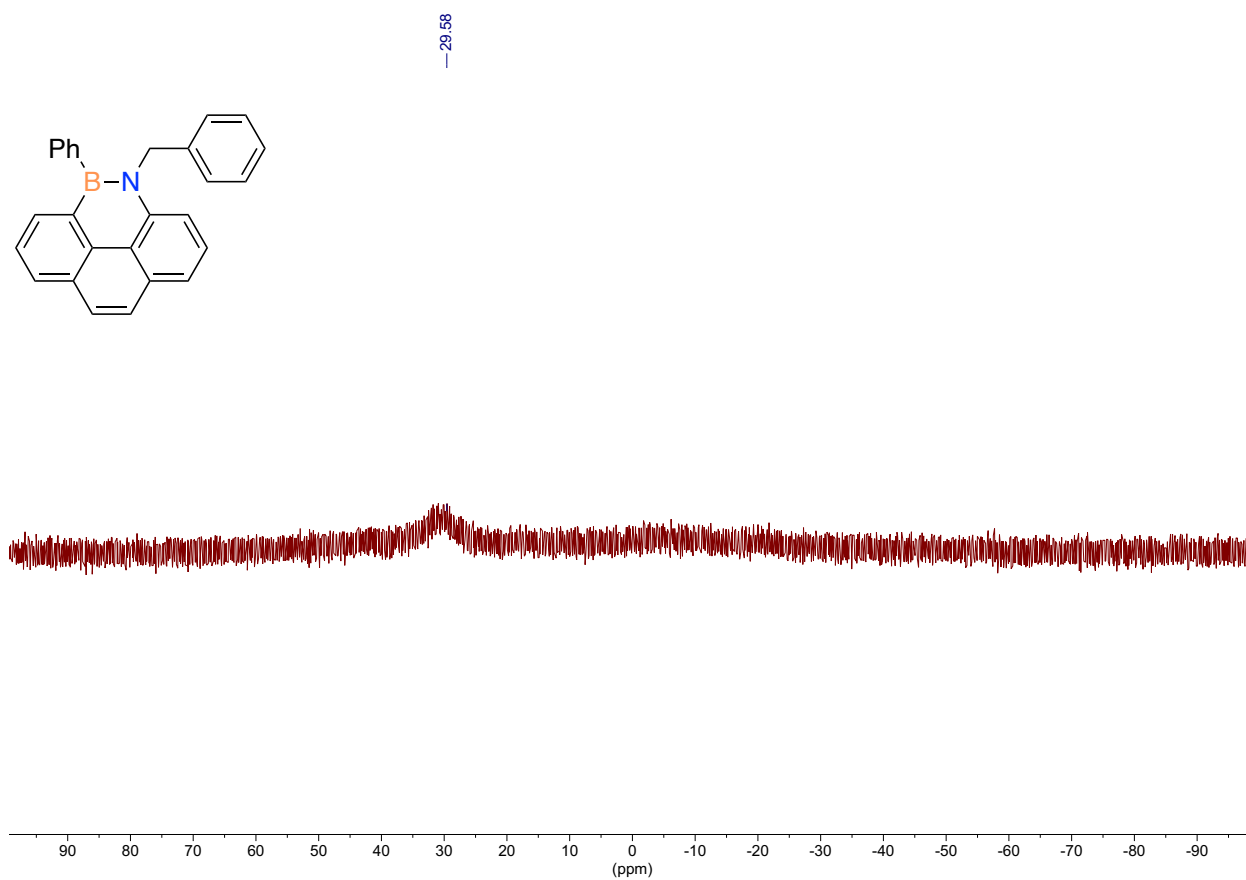


Figure S23: UV-Vis spectra of **2Ph** (a) **3Cl** (c) and **3Ph** (e) in DCM. Graphs showing their linear dependence of the absorbance on the concentration in (b, d, f, respectively)

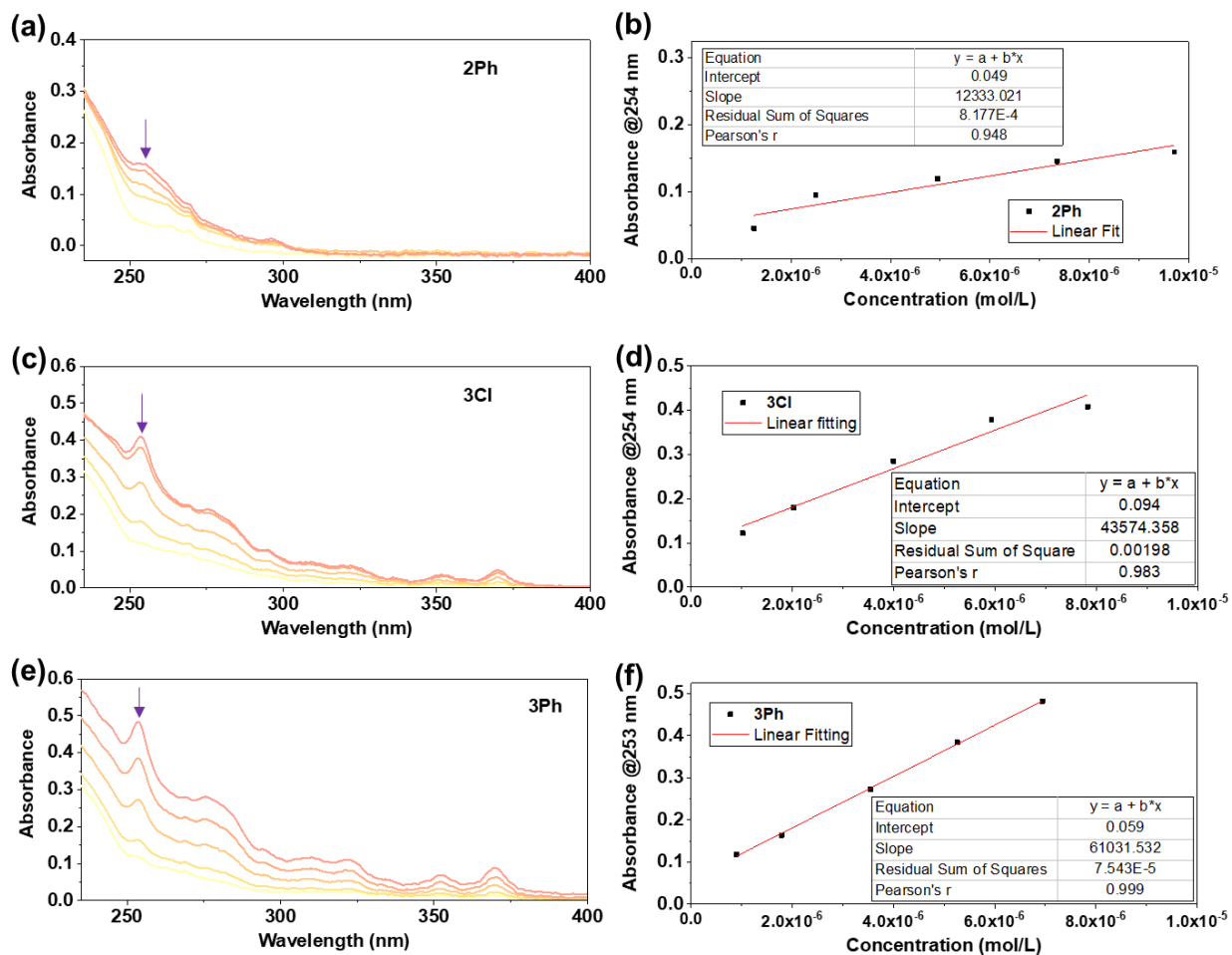


Figure S24: (a) Emission and excitation spectra of **2Ph**, **3Cl**, and **3Ph** in DCM. (b) Lifetime measurements of **2Ph**, **3Cl**, and **3Ph** in DCM using a 273.8 nm laser and monitoring PL peaks at 365 nm for **2Ph** and 375 nm for **3Cl** and **3Ph**.

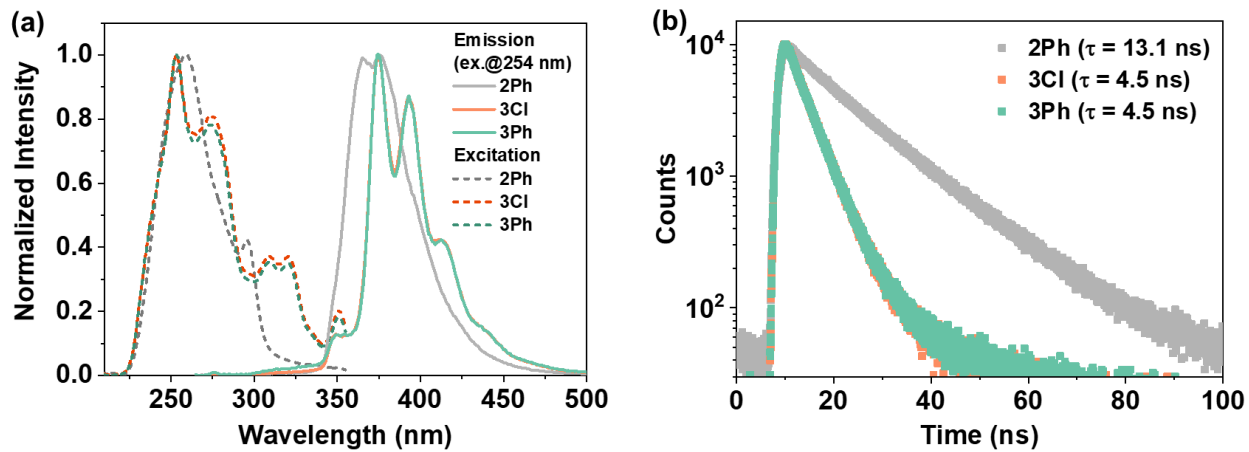


Table S1: X-ray crystallographic details for **2Cl** and **3Cl**.

Compound	2Cl	3Cl
CCDC	2357740	2357741
Empirical Formula	C ₁₄ H ₈ BCl	C ₂₁ H ₁₅ BCIN
FW (g/mol)	222.4780	327.6180
Crystal System	Monoclinic	Orthorhombic
Space Group	P2 ₁	P2 ₁ 2 ₁ 2 ₁
a (Å)	8.5508(5)	5.4556(3)
b (Å)	3.8729(3)	16.6414(13)
c (Å)	15.8451(10)	17.5759(13)
α (deg)	90°	90°
β (deg)	102.727(3)°	90°
γ (deg)	90°	90°
V (Å ³)	511.84(6)	1595.70(19)
Z	2	4
D _c (g cm ⁻³)	1.444	1.364
Radiation (Mo-K α) λ (Å)	0.71073	0.71073
Temp (K)	150	150
R1 [$I > 2(\sigma)I$] ^a	9.48%	3.52%
wR2 (F ²) ^a	22.73%	8.69%
GOF (S) ^a	1.228	1.122

^a $R_1(F[I > 2(I)]) = \sum ||F_o| - |F_c|| / \sum |F_o|$; $^b wR_2(F^2 [\text{all data}]) = \{[w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]\}^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$) where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

Figure S25: Solid-state structure of **2Cl**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

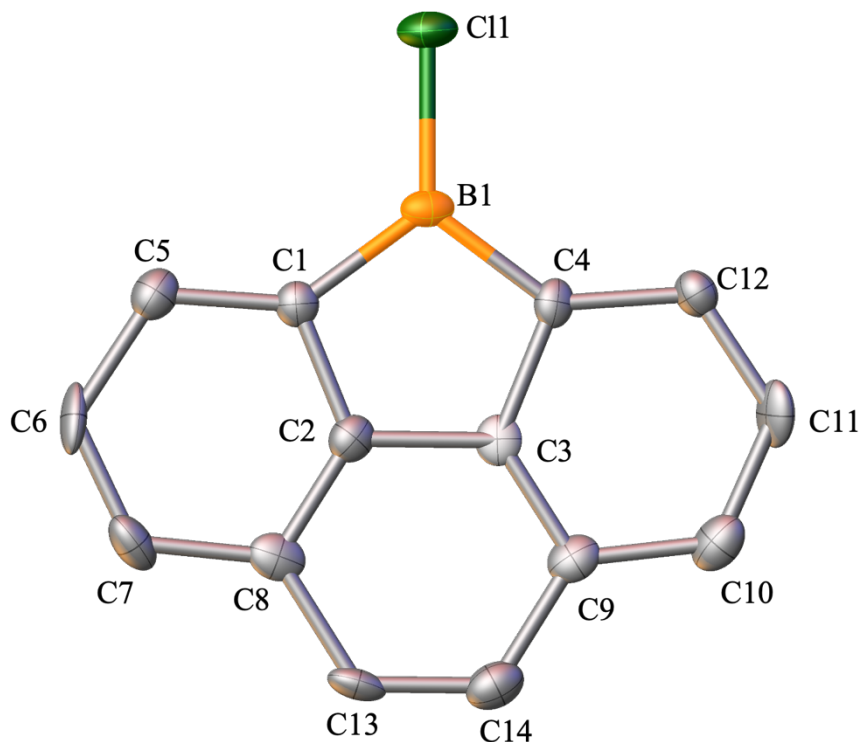


Table S2. Significant bond lengths and angles for **2Cl** and 9-Cl-9-borafluorene.⁴

Bond	2Cl	9-Cl-9-borafluorene ⁴
B1–C1	1.580(1) Å	1.536(4) Å
C1–C2	1.417(9) Å	1.416(3) Å
C2–C3	1.431(8) Å	1.481(3) Å
C3–C4	1.444(10) Å	1.409(3) Å
B1–C4	1.541(10) Å	1.547(4) Å
B1–Cl1	1.746(8) Å	1.752(3) Å
C4–B1–C1	106.6(6)°	105.9(2)°
B1–C1–C2	104.4(5)°	106.8(2)°
C1–C2–C3	112.5(6)°	110.2(2)°
C2–C3–C4	111.5(6)°	110.4(2)°
C3–C4–B1	104.9(5)°	106.6(2)°

Figure S26: Solid-state structure of **3Cl**. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity.

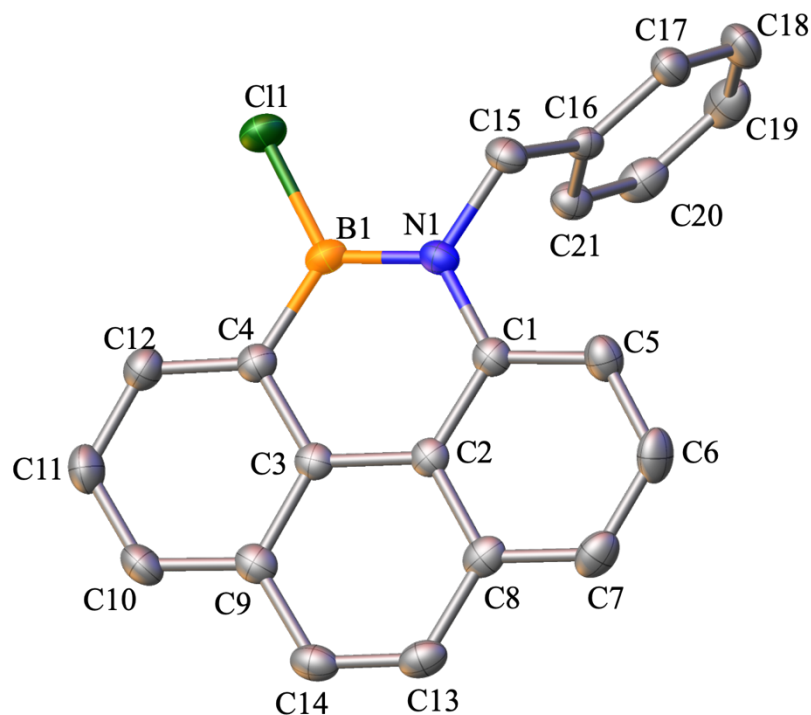


Table S3. Significant bond lengths and dihedral angles for **3Cl** and literature-known 9,10-B,N-phenanthrene.⁵

Bond	3Cl	8Cl ⁵	10Cl ⁵
B(1)–N(1)	1.406(3) Å	1.403(3) Å	1.416(2) Å
N(1)–C(1)	1.418(3) Å	1.420(2) Å	1.429(2) Å
C(1)–C(2)	1.424(3) Å	1.411(3) Å	1.431(2) Å
C(2)–C(3)	1.434(3) Å	1.473(3) Å	1.469(3) Å
C(3)–C(4)	1.422(3) Å	1.411(3) Å	1.408(3) Å
C(4)–B(1)	1.540(4) Å	1.523(3) Å	1.534(3) Å
B(1)–Cl(1)	1.789(3) Å	1.781(2) Å	1.797(2) Å

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