Electronic Supplementary Information

Synthesis of a Helical Boron-Doped PAH by Post-Functionalization of 3,9-Diboraperylene

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1. Materials and Methods

General considerations. Where indicated, glovebox synthetic manipulations were carried out under an atmosphere of dry, O_2-free N_2 in a glovebox (M. Braun Inertgas-Systeme GmbH) using oven-dried glassware. 1,3-Diisopropylimidazol-2-ylidene borane,[1] anthracene-9,10-dicarboxaldehyde,[2] and 1-bromo-2-(prop-1-en-2-yl)naphthalene[3] were prepared according to a literature procedure. Bis(trifluoromethylsulfonyl)imide and 2,2,6,6-tetramethylpiperidine-1-oxyl free radical (TEMPO radical), scandium (III) triflate, 2-mesitylmagnesium bromide, 1-bromo-2-methylnaphthalene, magnesium turnings, 1,2-dibromoethane, methyltriphenylphosphonium bromide, *n*-butyllithium, 9,10-dibromoanthracene, tri-*o*-tolylphosphine, triethylamine, palladium(II)acetate, 4-*tert*-butylstyrene, and boron tribromide were purchased from common commercial sources and used without further purification. Anhydrous chlorobenzene and tetrachloroethane were purchased from Sigma Aldrich and dried over 4 Å molecular sieves before use. THF and dichloromethane were purified with a Grubbs-type column system manufactured by Innovative Technology. Deuterated solvents were purchased from commercial sources and used without further purification. Anhydrous hexane was purchased from Sigma Aldrich and used without further purification. All other solvents for spectroscopic measurements were

spectroscopic grade and used without further purification. Column chromatography was performed with commercial glass columns using silica-gel 60M (particle size 0.04–0.063 mm). All other reagents and solvents were purchased from commercial sources and used without further purification.

UV/Vis absorption spectra were recorded on a Jasco V-670 or Jasco V-770 spectrophotometer for solution phase measurements.

Fluorescence spectra were recorded on an Edinburgh Instruments FLS980 fluorescence spectrometer. Relative fluorescence quantum yields were determined using the comparative method at four excitation wavelengths with respect to standards: N,N'-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenebis(dicarboximide) in $CHCl_3$ (**2** and **3**),[4] N,N'-bis(2,6- diisopropylphenyl)-1,6,7,12-tetraphenoxy-3,4:9,10-perylenebis(dicarboximide) in $CHCl_3$ (**4** and **5**),[4] [7-(diethylamino)phenoxazin-3-ylidene]-diethylazanium ("oxazine 1") in EtOH (**tBuPh-4** and **(B-Dbf)₂**).[5] Time-resolved measurements were performed with Edinburgh S3 Instruments picosecond pulsed laser diodes and a TCSPC detection unit.

NMR spectra were recorded on Bruker Avance III HD 400 or Bruker Avance III HD 600 spectrometers. Chemical shifts are listed in parts per million and are given relative to $SiMe_4$ and referenced to a residual solvent signal (^1H, ^{13}C). Coupling constants (J) are quoted in Hertz (Hz). In some cases ^{11}B and ^{13}C signals for boron-containing compounds could not be observed due to broadening and/or poor solubility. ^{13}C NMR spectra are broad band proton decoupled.

High resolution mass spectrometry was carried out on a Bruker Daltonics micrOTOF focus or on a Bruker Daltonics ultrafleXtreme instrument.

Cyclic voltammetry was carried out using a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three-electrode single-compartment cell. The supporting electrolyte tetrabutylammonium hexafluorophosphate ((n-Bu)₄NPF₆) was prepared according to the literature,[6] and recrystallized from ethanol/water. The measurements were carried out using ferrocene (Fc) as an internal standard for the calibration of the potential. Potentials of irreversible redox events were determined by square wave voltammetry experiments. An Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively.

Single crystal X-ray diffraction data were collected on a Bruker D8 Quest diffractometer with a PhotonII detector using Cu Kα radiation at 100 K for **3** and **(B-Dbf)₂**. The data for **4** were collected at the P11 beamline at DESY by a single 360° scan ϕ sweep at 100 K and were indexed, integrated, and scaled using the XDS program package.[7] The structures were solved using SHELXT,[8] expanded with Fourier techniques and refined using the SHELX software package.[9] Hydrogen atoms were

assigned at idealized positions and were included in the calculation of structure factors. All non-hydrogen atoms were refined anisotropically. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2149816 (**3**), CCDC 2149815 (**4**), CCDC 2149817 (**(B-Dbf)₂**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data.request/cif.

Computational details. Geometry optimizations were performed by the density functional theory (DFT) calculations employing B3LYP as functional[10-12] and 6-311G** as basis set[13-15] as implemented in the Gaussian 09 program package.[16] The optimized geometries were confirmed to have no negative frequency by frequency calculations. The electron affinities of compounds **2**, **3**, **4**, **Ph-3**, **tBuPh-4**, and **(B-Dbf)₂** were calculated from the energy difference between the geometry-optimized structure of the neutral molecule and the geometry-optimized structure of the anion.[17] Time-dependent density functional theory (TDDFT) calculations were performed on the geometry-optimized structures employing the same basis set and functional as for the geometry optimizations. The absorption spectra were simulated by the GaussView 5 visualization software package.[18]

2. Synthetic Procedures
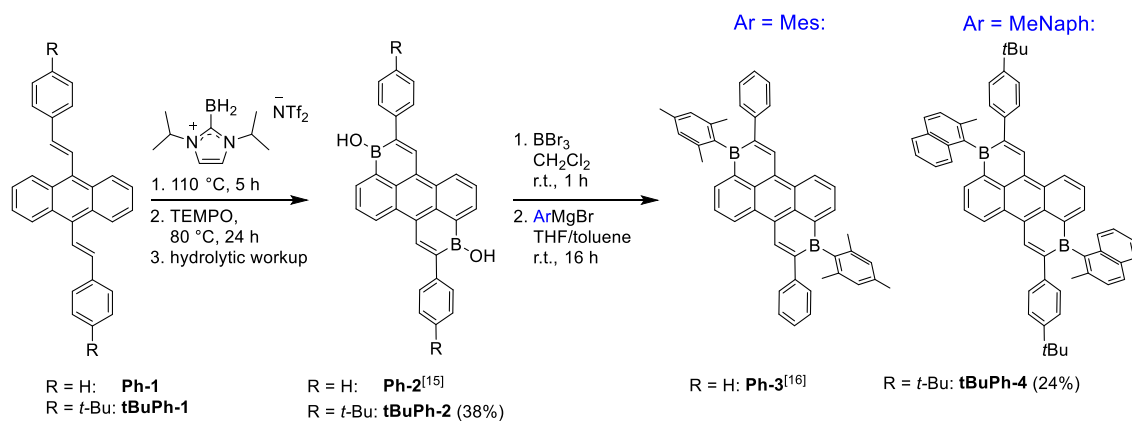
Scheme S1. Synthesis of diborinic acid **tBuPh-2** and tetraaryl-substituted boron-doped PAH **tBuPh-4** and structures of previously reported **Ph-2**[19] and **Ph-3**[20]. TEMPO: 2,2,6,6-tetramethylpiperidinyloxyl, Tf: trifluoromethanesulfonyl.

Borinic acid **2** was prepared according to the procedure used for our previous study.[21]

**Synthesis of 9,10-bis((*E*)-4-(*tert*-butyl)styryl)anthracene (tBuPh-1)**

tBuPh-1
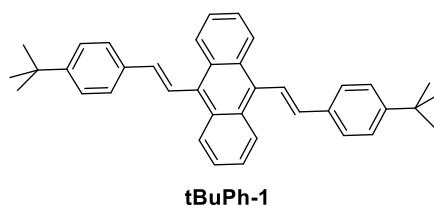
9,10-Dibromoanthracene (5.00 g, 14.9 mmol) and tri-*o*-tolylphosphine (913 mg, 3.00 mmol) were dissolved in dry DMF (25 mL) and triethylamine (10 mL) in a round bottom flask and the mixture was degassed by bubbling nitrogen through the solution for 10 min. Palladium(II)acetate (135 mg, 600 µmol) and 4-*tert*-butylstyrene (6.5 mL, 5.69 g, 35.5 mmol) were added and the reaction mixture was stirred under nitrogen for 16 h at 90 °C. The reaction was cooled to room temperature and 2 M aq. HCl (200 mL) was added. The precipitate was collected by filtration and washed with 2 M aq. HCl (100 mL) and water (300 mL). The crude product was purified by recrystallization from chloroform and dried under reduced pressure to furnish 9,10-bis((*E*)-4-(*tert*-butyl)styryl)anthracene as a yellow solid (5.58 g, 11.3 mmol, 76%). **^{1}H NMR** (400.1 MHz, CD$_3$Cl, 298 K): δ [ppm] = 8.40 (m, 4H, Ar-*H*), 7.91 (d, 2H, $^3J_{HH}$ = 16.4 Hz, Vinyl-*H*), 7.65 (d, 4H, $^3J_{HH}$ = 8.2 Hz, Ar-*H*), 7.50 (d, 4H, $^3J_{HH}$ = 8.4 Hz, Ar-*H*), 7.46 (m, 4H, Ar-*H*), 6.92 (d, 2H, $^3J_{HH}$ = 16.5 Hz, Vinyl-*H*), 1.39 (s, 18H, -C(C*H*$_3$)$_3$). The ^{1}H NMR spectrum is in accordance with the reported data, where **tBuPh-1** was synthesized via Horner-Wadsworth-Emmons reaction.[24]

**General procedure for the preparation of Grignard Reagents**

Under nitrogen atmosphere Mg turnings (20 equiv.) were overlayed with dry THF (2 mL) and dibromoethane (3.34 equiv.) was added. The aryl bromides (2 equiv.) were dissolved in dry THF (1.0 mL) and added via syringe. The mixtures were refluxed for 3–6 h. Subsequently, all volatiles were removed under reduced pressure and the residue was again dissolved in dry THF (10 mL). The Grignard reagents were each time freshly prepared and used without further purification.

Synthesis of 2,8-bis((4-*tert*-butyl)phenyl)-3,9-dihydroxy-3,9-diboraperylene (tBuPh-2)


tBuPh-2
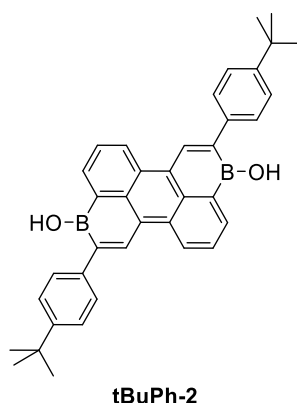
In a nitrogen-filled glovebox 1,3-diisopropylimidazol-2-ylidene borane (399 mg, 2.40 mmol) and bis(trifluoromethylsulfonyl)imide (686 mg, 2.44 mmol) were dissolved in chlorobenzene (10 mL) and the mixture was stirred at room temperature for 90 min. 9,10-Bis((*E*)-4-(*tert*-butyl)styryl)anthracene (495 mg, 1.00 mmol) was added and the flask was sealed with a dropping funnel filled with 2,2,6,6-tetramethylpiperidine-1-oxyl free radical (TEMPO) (719 mg, 4.60 mmol) dissolved in chlorobenzene (10 mL). The apparatus was brought out of the glovebox and heated at 110 °C for 6 h. After cooling to 80 °C, the TEMPO solution was added and the mixture was stirred at 80 °C for another 38 h. The reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. Purification with column chromatography (eluent: toluene/dichloromethane 3/1) yielded **tBuPh-2** as a black solid (166 mg, 0.38 mmol, 38%). **M.P.:** > 300 °C. **^{1}H NMR** (400.1 MHz, CD$_2$Cl$_2$, 298 K): δ [ppm] = 9.86 (s, 2H, Ar-O*H*), 9.30 (d, 2H, $^3J_{HH}$ = 9.3 Hz, Ar-*H*), 9.04 (s, 2H, Ar-*H*), 8.83 (d, 2H, $^3J_{HH}$ = 6.4 Hz, Ar-*H*), 7.93 (dd, 2H, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.6 Hz, Ar-*H*), 7.81 (d, 4H, $^3J_{HH}$ = 8.6 Hz, Ar-*H*), 7.50 (d, 4H, $^3J_{HH}$ = 8.5 Hz, Ar-*H*), 1.37 (s, 18H, *t*Bu-*H*). **^{11}B** and **^{13}C** signals for **tBuPh-2** could not be observed due to poor solubility. **HRMS** (MALDI-TOF, positive mode): m/z: 546.30752, [M]$^+$ calculated for C$_{38}$H$_{36}$B$_2$O$_2$: 546.28959.

Synthesis of 2,8-bis((4-*tert*-butyl)phenyl)-3,9-bis(2-methylnaphthyl)-3,9-diboraperylene (tBuPh-4)
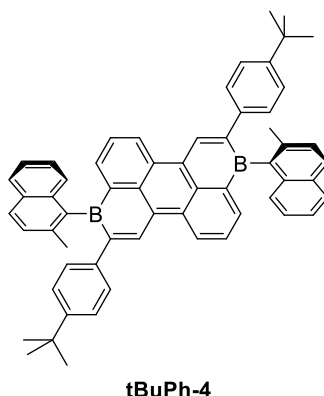

tBuPh-4

The borinic acid **tBuPh-2** (20.0 mg, 36.6 µmol) was dissolved in dry dichloromethane (4 mL) under nitrogen atmosphere. BBr$_3$ (17.4 µL, 183 µmol) was added and the mixture was stirred at room temperature for 5 h. All volatiles were removed under reduced pressure. The remaining solid was dissolved in toluene (4 mL) and and the Grignard reagent, which was freshly prepared according to the abovementioned general procedure from 1-bromo-2-methylnaphthalene (80.9 mg, 366 µmol), was added under nitrogen atmosphere. The mixture was stirred at room temperature for 13 h. Solvent evaporation and column chromatography (eluent: cyclohexane) yielded **tBuPh-4** as a blue solid (6.98 mg, 8.79 µmol, 24%). **M.P.:** >300 °C. **^{1}H NMR** (400.1 MHz, CD$_2$Cl$_2$, 298 K): δ [ppm] = 9.49 (d, 2H, $^3J_{HH}$ = 8.2 Hz, Ar-*H*), 9.42 (s, 2H, Ar-*H*), 8.21 (dd, 2H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.1 Hz, Ar-*H*), 7.90–7.84 (m, 6H, Ar-*H*), 7.42–7.36 (m, 10H, Ar-*H*), 7.23–7.20 (m, 6H, Ar-*H*), 2.22 (s, 6H, Me-*H*), 1.25 (s, 18H, ^{t}Bu-*H*). **^{11}B** and **^{13}C** signals for **tBuPh-4** could not be observed due to poor solubility. **HRMS** (MALDI-TOF, negative mode): m/z: 794.42594, [M]$^-$ calculated for C$_{60}$H$_{52}$B$_2$: 794.42606. **CV** (7 × 10^{-4} M, 0.1 M (*n*-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$, vs. Fc$^{+/0}$, 298 K): E_{red1} (M/M$^-$) = −1.04 V, E_{red2} (M$^-$/M^{2-}) = −1.38 V. **UV/Vis** (1.01 × 10^{-5} M in CH$_2$Cl$_2$, 298 K): λ_{max} (ε_{max}) =632 nm (23400), 423 nm (8000). **Fluorescence** (1.01 × 10^{-6} M in CH$_2$Cl$_2$, 298 K): λ_{max} = 704 nm (Φ_F = 0.35).

Synthesis of 3,9-dimesityl-3,9-diboraperylene (3)
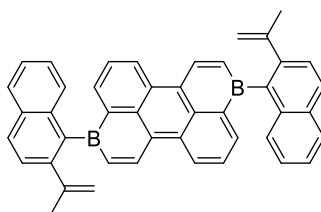

3
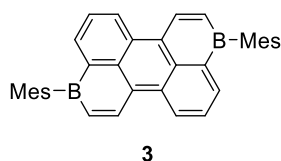
The borinic acid **2** (250 mg, 887 µmol) was dissolved in dichloromethane (3 mL) in a nitrogen-filled glovebox. The vessel was sealed, removed from the glovebox and BBr$_3$ (0.42 mL, 1.11 g, 4.43 mmol) was added to the solution under nitrogen atmosphere. The mixture was stirred at room temperature for 1 h and then all volatiles were removed under reduced pressure. The remaining solid was dissolved in dry dichloromethane (10 mL) and 2-mesitylmagnesium bromide (6.21 mL, 1.39 g, 6.21 mmol) was added under nitrogen atmosphere. The solution was stirred at room temperature for 16 h. The solvent was evaporated and the crude product was purified with column chromatography (eluent: hexane/CH$_2$Cl$_2$ 2/1). The product was then washed with MeOH to yield **3** as a red solid (80 mg, 165 µmol, 19%). **M.P.:** >275 °C (decomp.). **^{1}H NMR** (400.1 MHz, CD$_2$Cl$_2$, 298 K): δ [ppm] = 9.40 (d, 2H, $^3J_{HH}$ = 12.4 Hz, Ar-*H*), 9.33 (dd, 2H, $^3J_{HH}$ = 9.36 Hz, $^4J_{HH}$ = 1.2 Hz, Ar-*H*), 8.36 (dd, 2H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.2 Hz, Ar-*H*), 7.94 (dd, 2H, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.6 Hz, *Ar-H*), 7.53 (dd, 2H, $^3J_{HH}$ = 11.9 Hz, Ar-*H*), 6.94 (d, 4H, $^5J_{HH}$ = 0.6 Hz, Ar-*H*), 2.37 (s, 6H, *p*-Me-*H$_3$*), 2.09 (s, 12H, *o*-Me-*H$_3$*). **^{13}C NMR** (100 MHz, CD$_2$Cl$_2$, 298 K): δ [ppm] = 146.0, 144.3, 142.0 (br.), 139.4 (br.), 139.0, 137.3, 137.1 (br.), 132.2, 131.8, 131.7, 128.6, 128.4, 127.4, 23.7, 21.3. **HRMS** (MALDI-TOF, negative mode): m/z: 486.26738, [M]$^-$ calculated for C$_{36}$H$_{32}$B$_2$: 486.26956. **CV** (7 × 10^{-4} M, 0.1 M (*n*-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$, vs. Fc$^{+/0}$, 298 K): E_{red1} (M/M$^-$) = −1.13 V, E_{red2} (M$^-$/M^{2-}) = −1.51 V. **UV/Vis** (1.84 × 10^{-5} M in CH$_2$Cl$_2$, 298 K): λ_{max} (ε_{max}) = 555 nm (24200), 517 nm (17400), 424 nm (7500). **Fluorescence** Solution: (4.07 × 10^{-6} M in CH$_2$Cl$_2$, 298 K): λ_{max} = 580 nm (Φ_F = 0.78). Solid state: (Φ_F = 0.08).

Synthesis of 3,9-bis(2-methylnaphthyl)-3,9-diboraperylene (4)
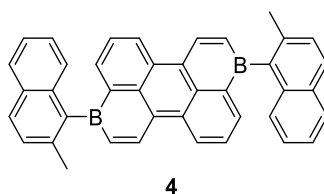
4

The borinic acid **2** (50.0 mg, 177 µmol) was dissolved in dichloromethane (3 mL) in a nitrogen-filled glovebox. The vessel was sealed, removed from the glovebox and BBr$_3$ (0.08 mL, 0.22 g, 0.89 mmol) was added to the solution under nitrogen atmosphere. The mixture was stirred at room temperature for 1 h and then all volatiles were removed under reduced pressure. The remaining solid was dissolved in dry toluene (10 mL) and the Grignard reagent, which was freshly prepared according to the abovementioned general procedure from 1-bromo-2-methylnaphthalene (391 mg, 1.77 mmol), was added under nitrogen atmosphere. The solution was stirred at room temperature for 16 h. The solvent was evaporated and the crude product was purified by column chromatography (eluent: hexane/CH$_2$Cl$_2$ 4/1). The product was then washed with MeOH to yield **4** as a red-brown solid (14.0 mg, 26.4 µmol, 15%). **M.P.:** >280°C (decomp.). **^{1}H NMR** (400.1 MHz, CD$_2$Cl$_2$, 298 K): δ [ppm] = 9.51 (d, 2H, $^3J_{HH}$ = 12.4 Hz, Ar-*H*), 9.41 (d, 2H, $^3J_{HH}$ = 8.3 Hz, Ar-*H*), 8.33 (dd, 2H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.2 Hz, Ar-*H*), 7.92 (dd, 2H, $^3J_{HH}$ = 8.8 Hz, $^3J_{HH}$ = 6.6 Hz, Ar-*H*), 7.89 (d, 2H, $^3J_{HH}$ = 8.3 Hz, Ar-*H*), 7.87 (d, 2H, $^3J_{HH}$ = 8.5 Hz, Ar-*H*), 7.66 (d, 2H, $^3J_{HH}$ = 11.8 Hz, Ar-*H*), 7.47 (d, 2H, $^3J_{HH}$ = 8.1 Hz, Ar-*H*), 7.45–7.37 (m, 4H, Ar-*H*), 7.25–7.20 (m, 2H, Ar-*H*), 2.36 (s, 6H, Me-*H*$_3$). **^{11}B** and **^{13}C** signals for **4** could not be observed due to poor solubility. **HRMS** (MALDI-TOF, positive mode): m/z: 530.23775, [M]$^+$ calculated for C$_{40}$H$_{28}$B$_2$: 530.23716. **CV** (7 × 10^{-4} M, 0.1 M (*n*-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$, vs. Fc$^{+/0}$, 298 K): E_{red1} (M/M$^-$) = −1.10 V, E_{red2} (M$^-$/M^{2-}) = −1.47 V. **UV/Vis** (1.19 × 10^{-5} M in CH$_2$Cl$_2$, 298 K): λ_{max} (ε_{max}) = 562 nm (30300), 526 nm (22500), 439 nm (10000), 424 nm (10200), 396 nm (8800). **Fluorescence** (1.19 × 10^{-5} M in CH$_2$Cl$_2$, 298 K): λ_{max} = 623 nm (Φ_F < 0.01).

Synthesis of 3,9-bis(2-isopropenylnaphthyl)-3,9-diboraperylene (5)

5

The borinic acid **2** (50.0 mg, 177 µmol) was dissolved in dichloromethane (6 mL) in a nitrogen-filled glovebox. The vessel was sealed, removed from the glovebox and BBr_3 (84.2 µL, 222 mg, 887 µmol) was added to the solution under nitrogen atmosphere. The mixture was stirred at room temperature for 15 min and then all volatiles were removed under reduced pressure. The remaining solid was dissolved in dry toluene (8 mL) and the Grignard reagent, which was freshly prepared according to the abovementioned general procedure from 1-bromo-2-(prop-1-en-2-yl)naphthalene[3] (340 mg, 1.38 mmol), was added under nitrogen atmosphere. The solution was stirred at room temperature for 18 h. The solvent was evaporated and the crude product was purified with column chromatography (eluent: hexane/CH_2Cl_2 4/1). The product was then washed with MeOH to yield **5** as a black solid (59.3 mg, 102 µmol, 57%). **M.P.:** 271 °C (decomp). **^{1}H NMR** (400.1 MHz, CD_2Cl_2, 298 K): δ [ppm] = 9.28 (d, 2H, $^3J_{HH}$ = 12.0 Hz, Ar-H), 9.24 (d, 2H, $^3J_{HH}$ = 8.2 Hz, Ar-H), 8.19 (dt, 2H, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.3 Hz, Ar-H), 7.85 (d, 2H, $^3J_{HH}$ = 8.6 Hz, Ar-H), 7.92 (d, 2H, $^3J_{HH}$ = 8.2 Hz, Ar-H), 7.77 (dd, 2H, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 6.6 Hz, Ar-H), 7.56–7.52 (m, 6H, Ar-H), 7.37–7.33 (m, 2H, Ar-H), 7.18–7.14 (m, 2H, Ar-H), 4.79 (dt, 4H, $^3J_{HH}$ = 10.4 Hz, $^4J_{HH}$ = 1.5 Hz, Ar-H), 4.75 (bd, 2H, $^3J_{HH}$ = 7.8 Hz, Ar-H), 2.02 (dt, 6H, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 1.0 Hz, Me-H_3). **^{13}C NMR** (100 MHz, CD_2Cl_2, 298 K): δ [ppm] = 148.7, 145.0, 144.9, 142.7, 142.2 (br.), 140.3 (br.), 137.8 (br.), 136.5, 132.7, 132.2, 131.7, 131.3, 130.5, 128.8, 128.5, 128.2, 127.9, 125.6, 125.5, 125.3, 118.9 (2x), 24.6. **^{11}B NMR**: δ [ppm] = 56.83. **HRMS** (MALDI-TOF, positive mode): m/z: 582.26835, $[M]^+$ calculated for $C_{44}H_{32}B_2$: 582.26846. **CV** (7×10^{-4} M, 0.1 M (n-Bu)$_4$NPF$_6$ in CH_2Cl_2, vs. Fc$^{+/0}$, 298 K): E_{red1} (M/M^-) = −1.20 V, E_{red2} (M^-/M^{2-}) = −1.57 V. **UV/Vis** (1.10×10^{-5} M in CH_2Cl_2, 298 K): λ_{max} (ε_{max}) = 570 nm (23200), 532 nm (16200), 422 nm (6500), 388 nm (5500), 364 nm (4500). **Fluorescence** (2.15×10^{-6} M in CH_2Cl_2, 298 K): λ_{max} = 610 nm (Φ_F = 0.11).

Synthesis of 7,7,18,18-tetramethyl-11b,22b-dibora-7,18-dihydro[bis(benzo[6,7]-indeno)[2,1-*b*:2,1-*k*]perylene] ((B-Dbf)₂)

(B-Dbf)₂
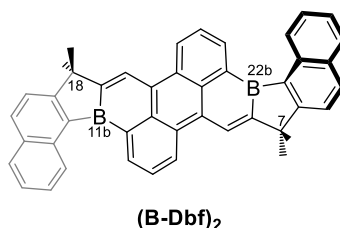
5 (5.0 mg, 8.59 µmol) and Sc(OTf)$_3$ (8.9 mg, 18.0 µmol) were weighted into a pressure tube in a nitrogen-filled glovebox. Dry tetrachloroethane (2 mL) was added and the tube was tightly sealed and brought out of the glovebox. The suspension was stirred for 1.5 days at 130 °C upon a colour change to purple was observed. After cooling to room temperature, the mixture was directly purified by column chromatography (hexane/CH$_2$Cl$_2$: 4/1). The crude product was washed with hexanes to yield **(B-Dbf)₂** as a black solid (3.0 mg, 5.15 µmol, 60%). **M.P.:** >300 °C. **¹H NMR** (400.1 MHz, CD$_2$Cl$_2$, 298 K): δ [ppm] = 9.63 (d, 2H, $^3J_{HH}$ = 6.6 Hz, Ar-*H*), 9.51 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ar-*H*), 9.11 (d, 2H, $^3J_{HH}$ = 7.9 Hz, Ar-*H*), 9.08 (s, 2H, Ar-*H*), 8.16 (d, 2H, $^3J_{HH}$ = 8.9 Hz, Ar-*H*), 8.15 (dd, 2H, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 6.8 Hz, Ar-*H*), 8.01 (d, 2H, $^3J_{HH}$ = 7.0 Hz, Ar-*H*), 7.81 (d, 2H, $^3J_{HH}$ = 8.7 Hz, Ar-*H*), 7.78–7.74 (m, 2H, Ar-*H*), 7.62–7.58 (m, 2H, Ar-*H*), 1.77 (s, 12H, Me-*H₃*). **¹³C** and **¹¹B** signals could not be observed due to low solubility. **HRMS** (MALDI-TOF, negative mode): m/z: 582.26730, [M]⁻ calculated for C$_{44}$H$_{32}$B$_2$: 582.26956. **CV** (7 × 10⁻⁴ M, 0.1 M (*n*-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$, vs. Fc$^{+/0}$, 298 K): E_{red1} (M/M⁻) = −1.17 V, E_{red2} (M⁻/M^{2-}) = −1.51 V. **UV/Vis** (7.42 × 10⁻⁶ M in CH$_2$Cl$_2$, 298 K): λ_{max} (ε_{max}) = 630 nm (61700), 581 nm (38900), 542 nm (14400), 426 nm (8600), 399 nm (9100), 354 nm (21300), 339 nm (19000). **Fluorescence** (1.73 × 10⁻⁶ M in CH$_2$Cl$_2$, 298 K): λ_{max} = 659 nm (Φ_F = 0.73).
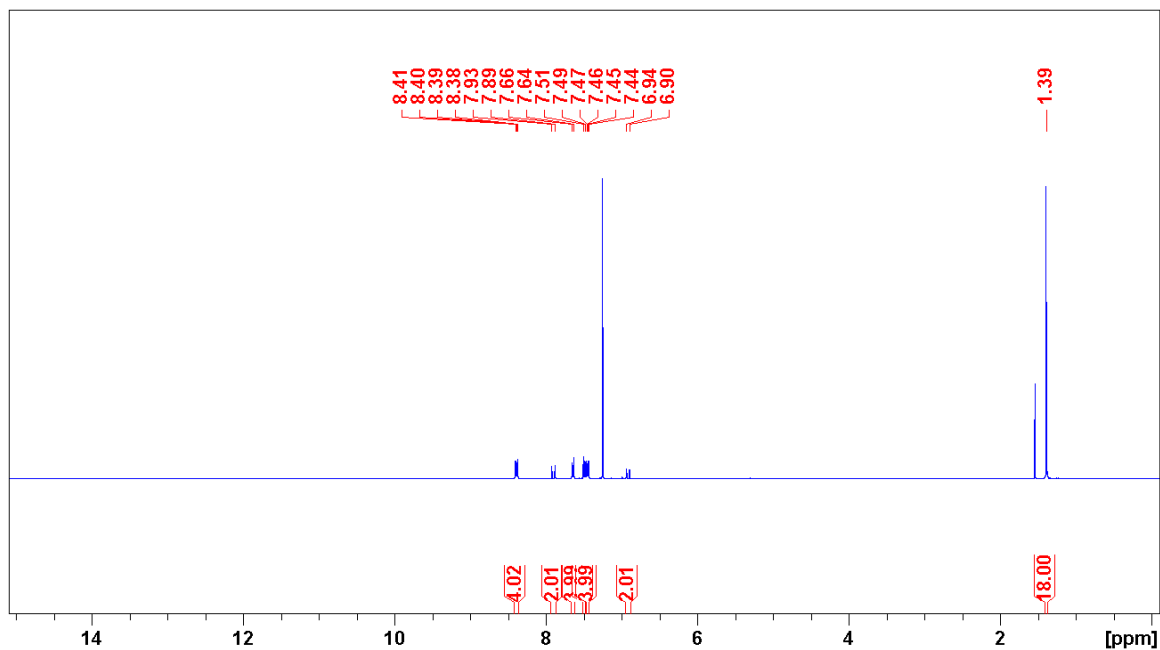
3. NMR Spectra

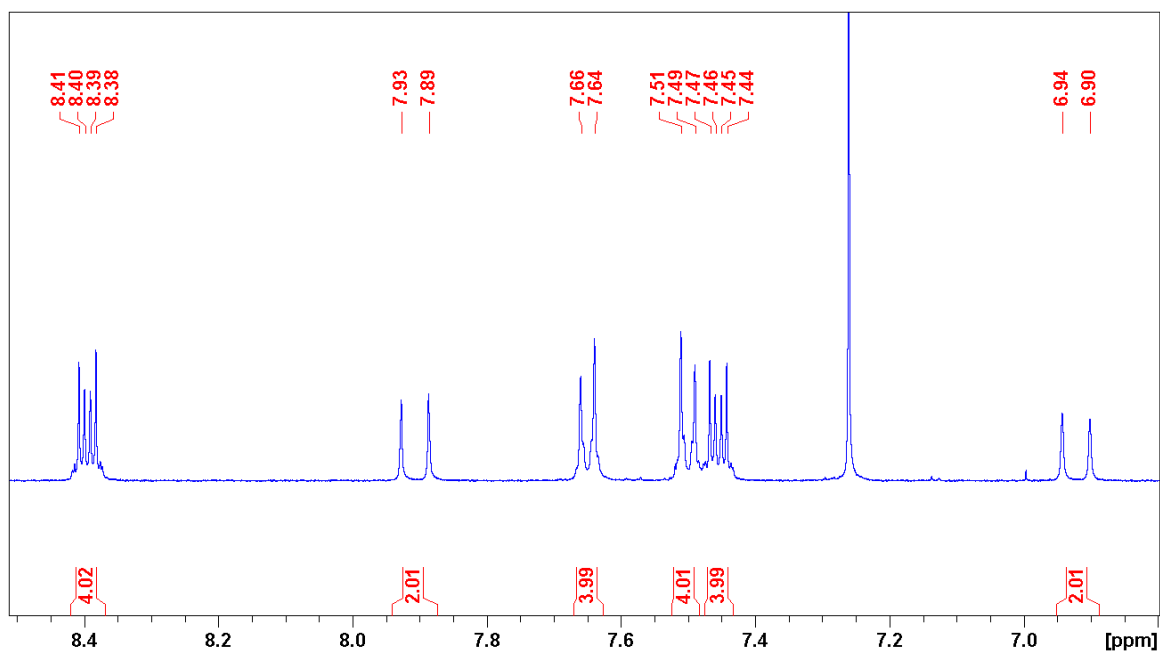**Figure S1.** ^{1}H NMR spectrum of **tBuPh-1** (400 MHz, CDCl$_3$, 298 K).

Figure S2. Magnified aromatic region of the ^{1}H NMR spectrum of **tBuPh-1** (400 MHz, CDCl$_3$, 298 K).
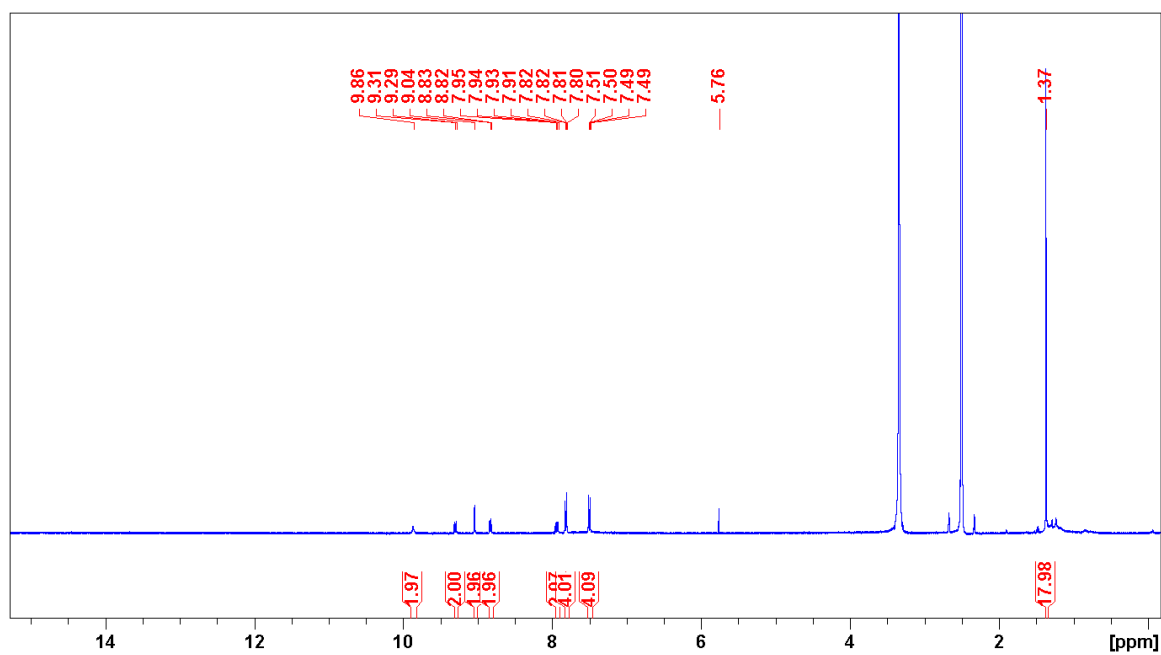
Figure S3. ^{1}H NMR spectrum of **tBuPh-2** (400 MHz, DMSO-d_6, 298 K). Signal at 5.76 ppm corresponds to CH_2Cl_2.
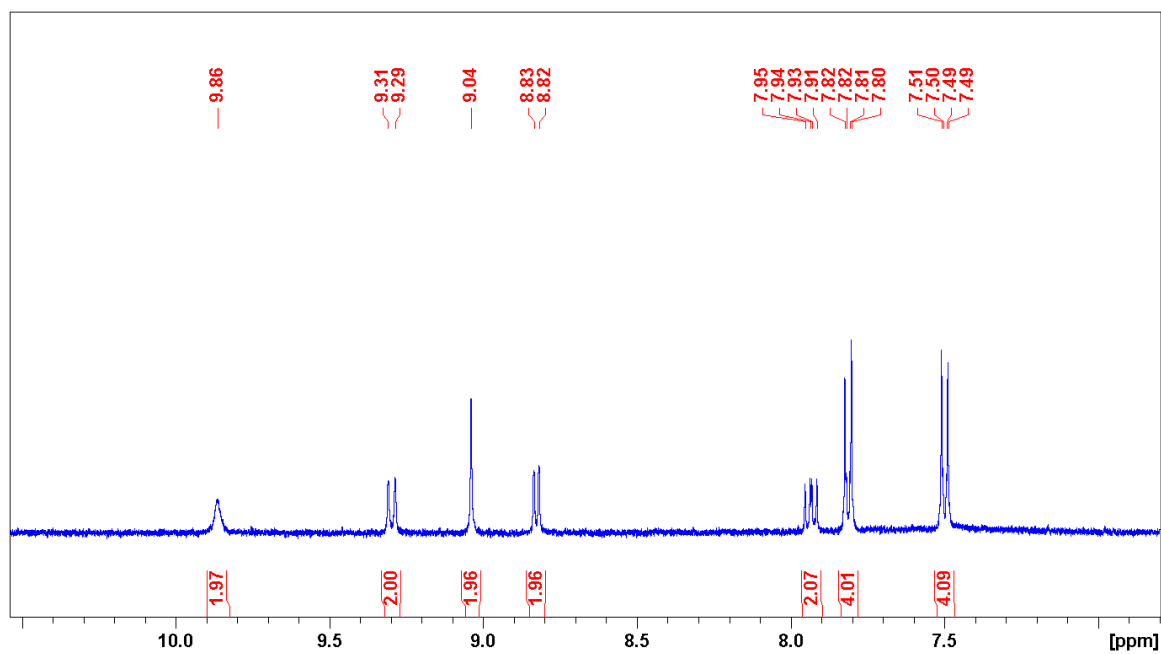

Figure S4. Magnified aromatic region of the ^{1}H NMR spectrum of **tBuPh-2** (400 MHz, DMSO-d_6, 298 K).
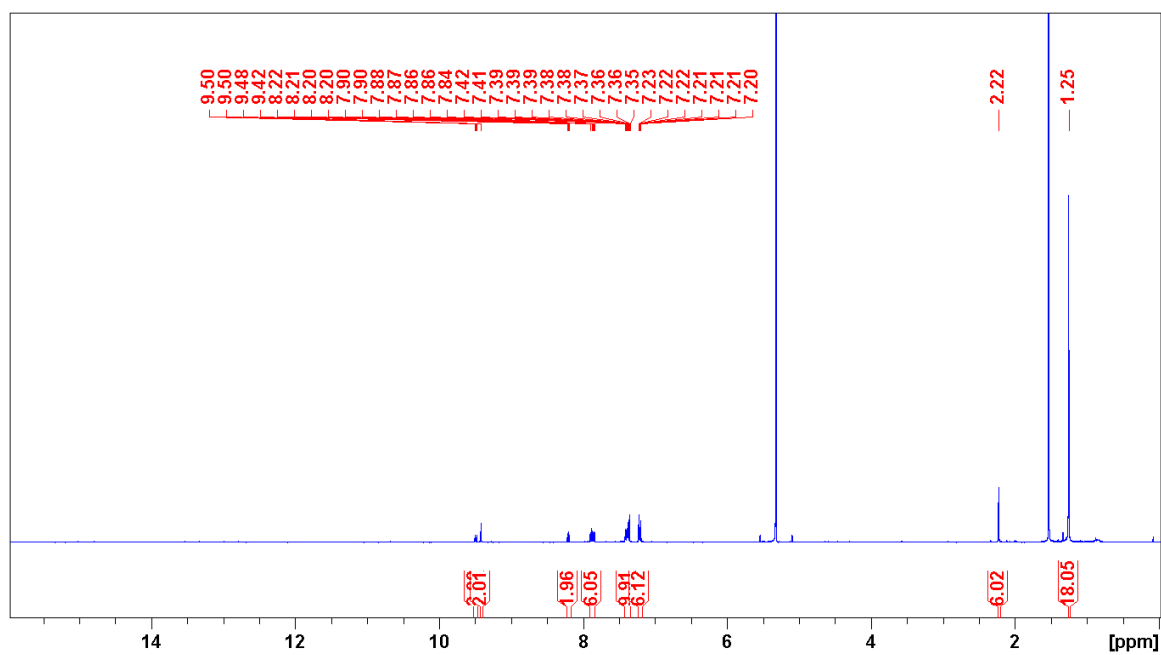
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Figure S5. ^{1}H NMR spectrum of **tBuPh-4** (400 MHz, CD$_2$Cl$_2$, 298 K).
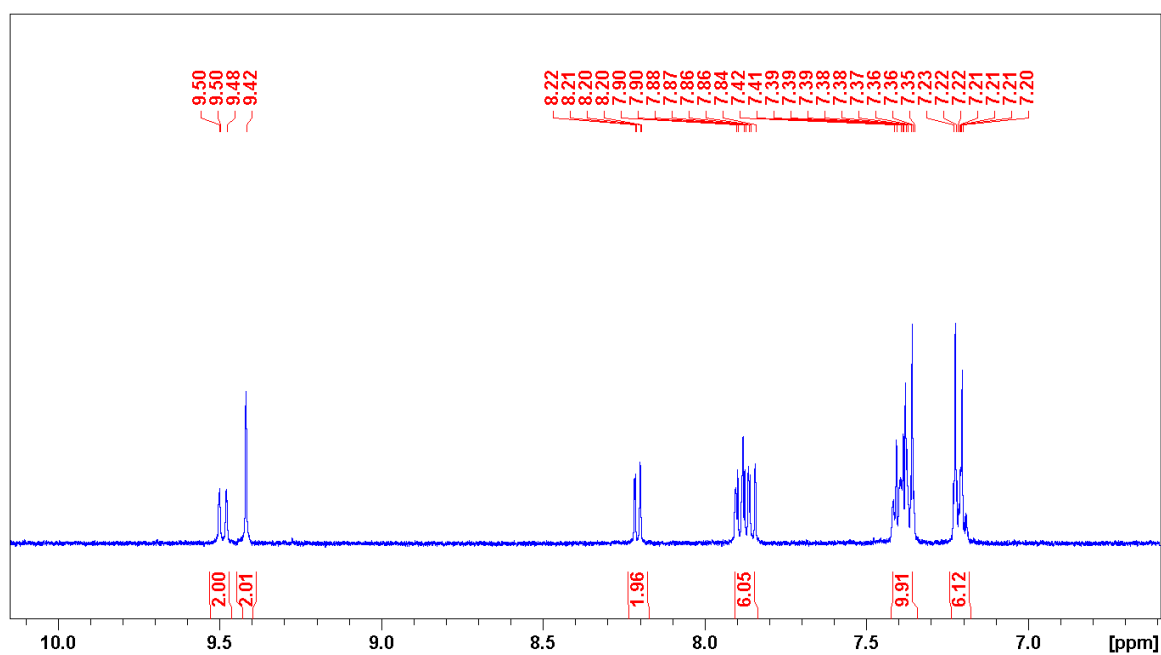

Figure S6. Magnified aromatic region of the ^{1}H NMR spectrum of **tBuPh-4** (400 MHz, CD$_2$Cl$_2$, 298 K).

Figure S7. ^{1}H NMR spectrum of **3** (400 MHz, CD_2Cl_2, 298 K).

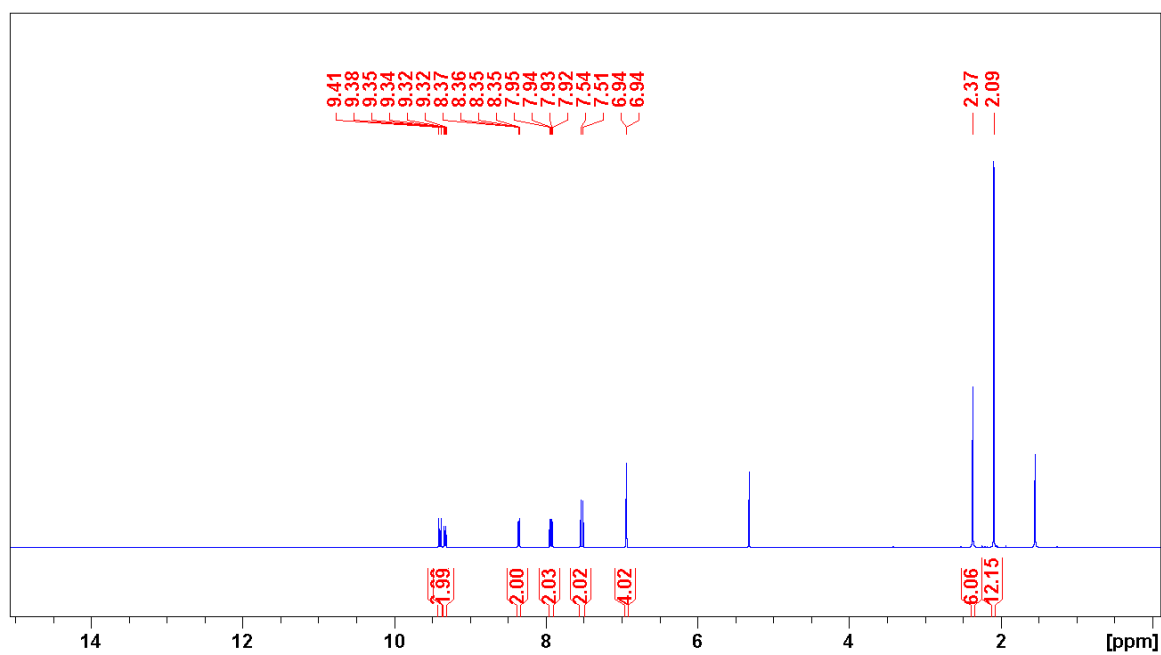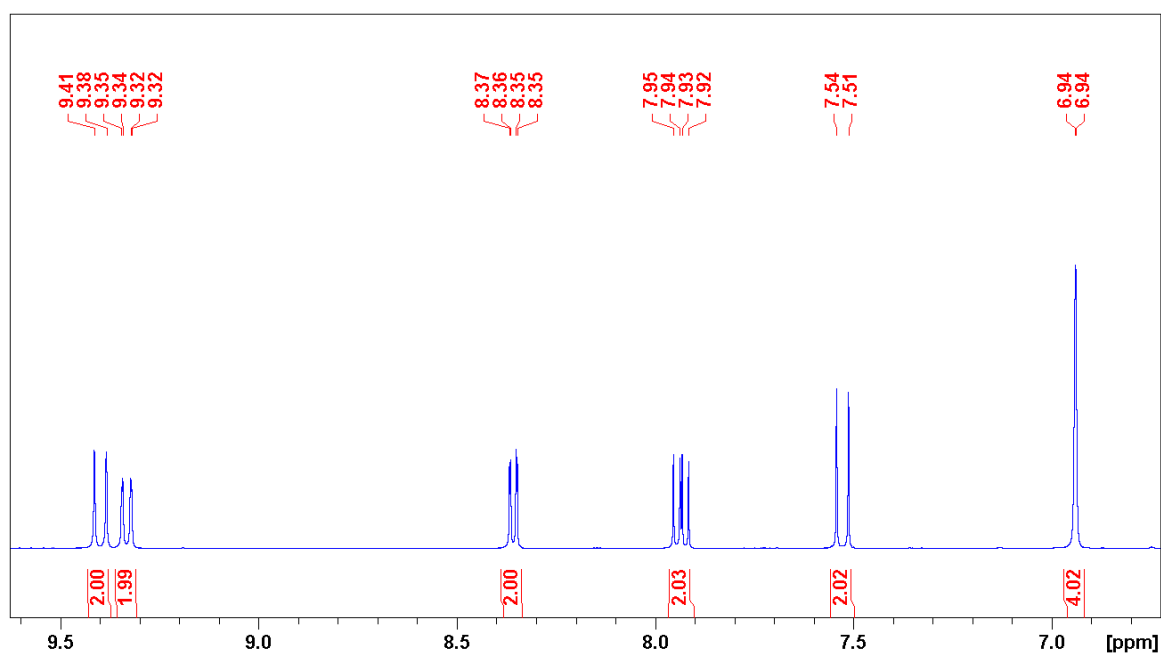**Figure S8.** Magnified aromatic region of the ^{1}H NMR spectrum of **3** (400 MHz, CD_2Cl_2, 298 K).

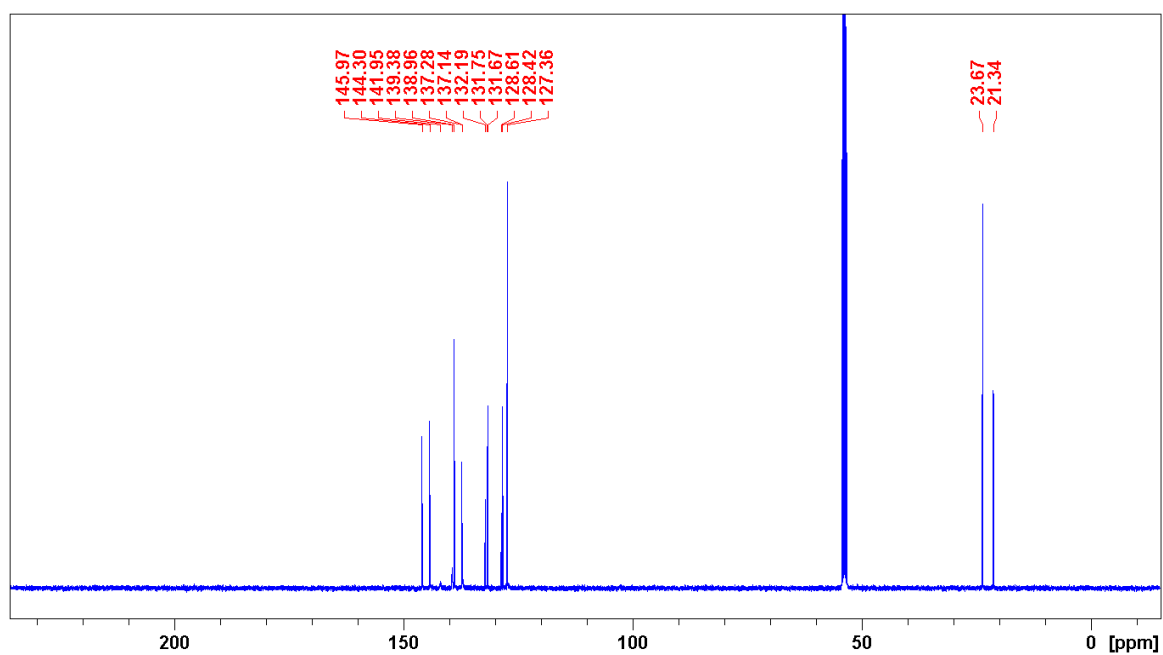**Figure S9.** ^{13}C NMR spectrum of **3** (100 MHz, CD_2Cl_2, 298 K).
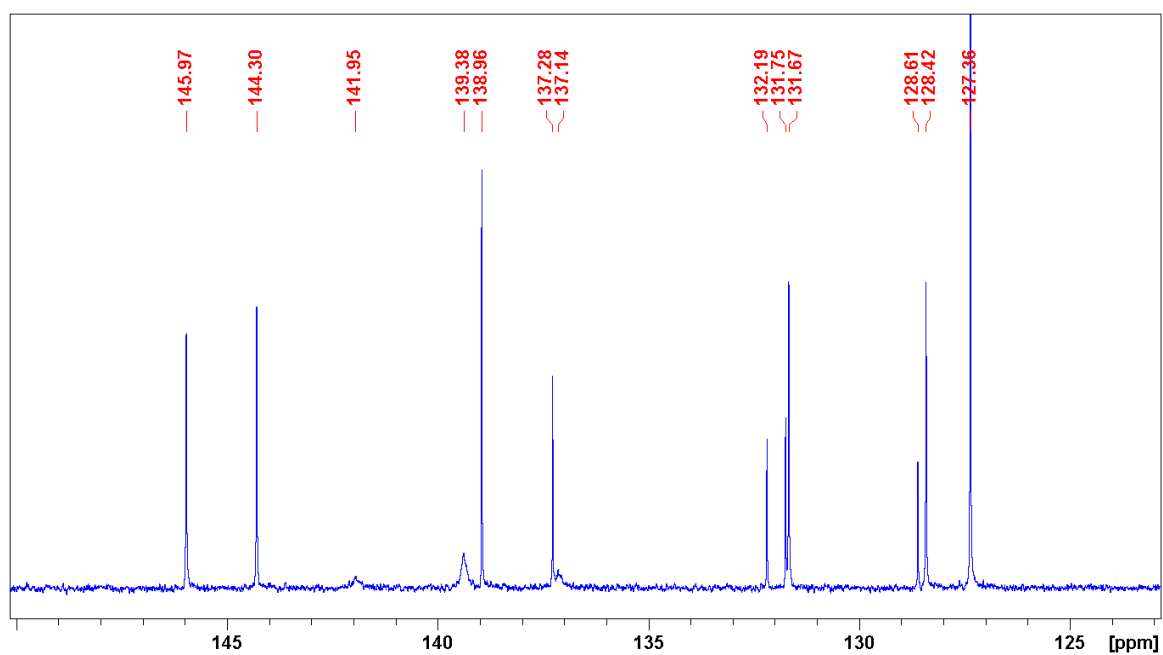
Figure S10. Magnified aromatic region of the ^{13}C NMR spectrum of **3** (100 MHz, CD_2Cl_2, 298 K).

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Figure S11. ^{1}H NMR spectrum of **4** (400 MHz, CD$_2$Cl$_2$, 298 K).

Figure S12. Magnified aromatic region of the ^{1}H NMR spectrum of **4** (400 MHz, CD$_2$Cl$_2$, 298 K).

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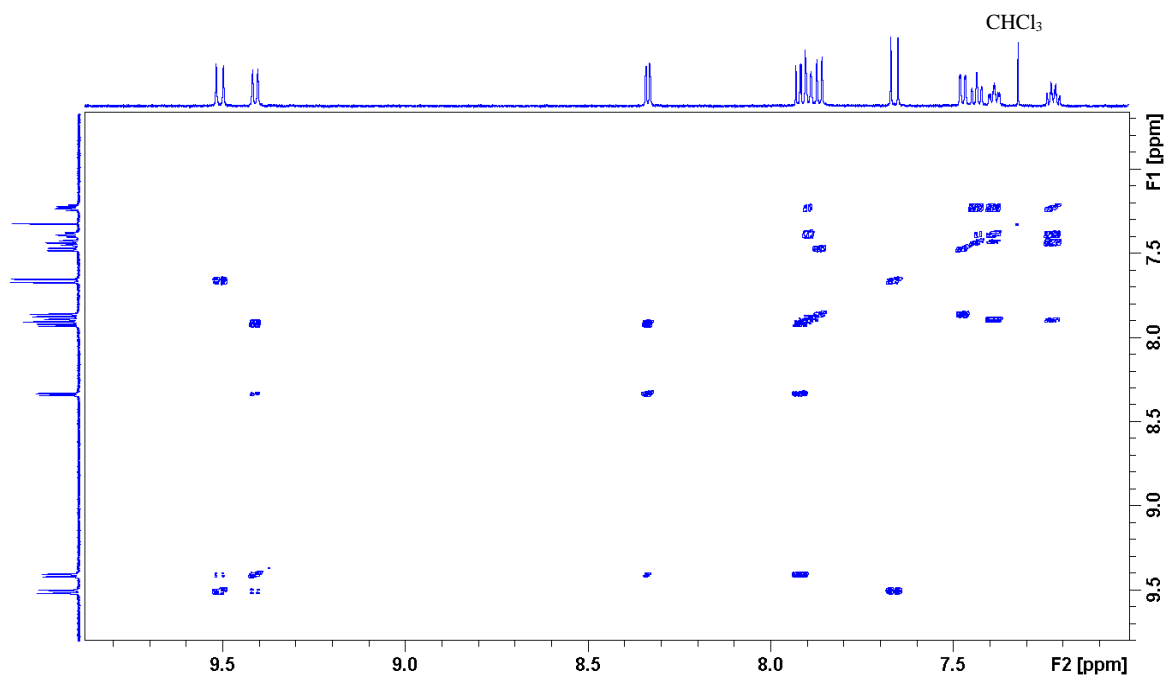
Figure S13. ^1H–^1H COSY NMR spectrum of **4** (400 MHz, CD$_2$Cl$_2$, 298 K) showing the aromatic region.
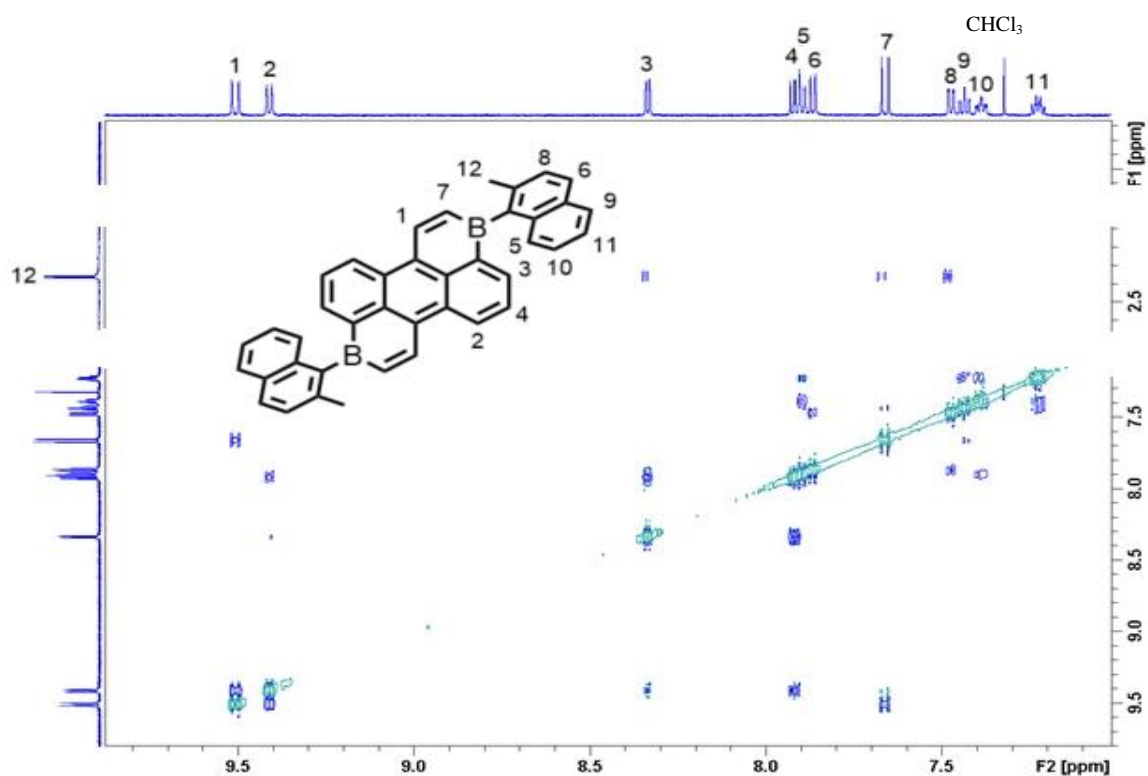
Figure S14. ^1H–^1H ROESY NMR spectrum of **4** (400 MHz, CD$_2$Cl$_2$, 298 K).
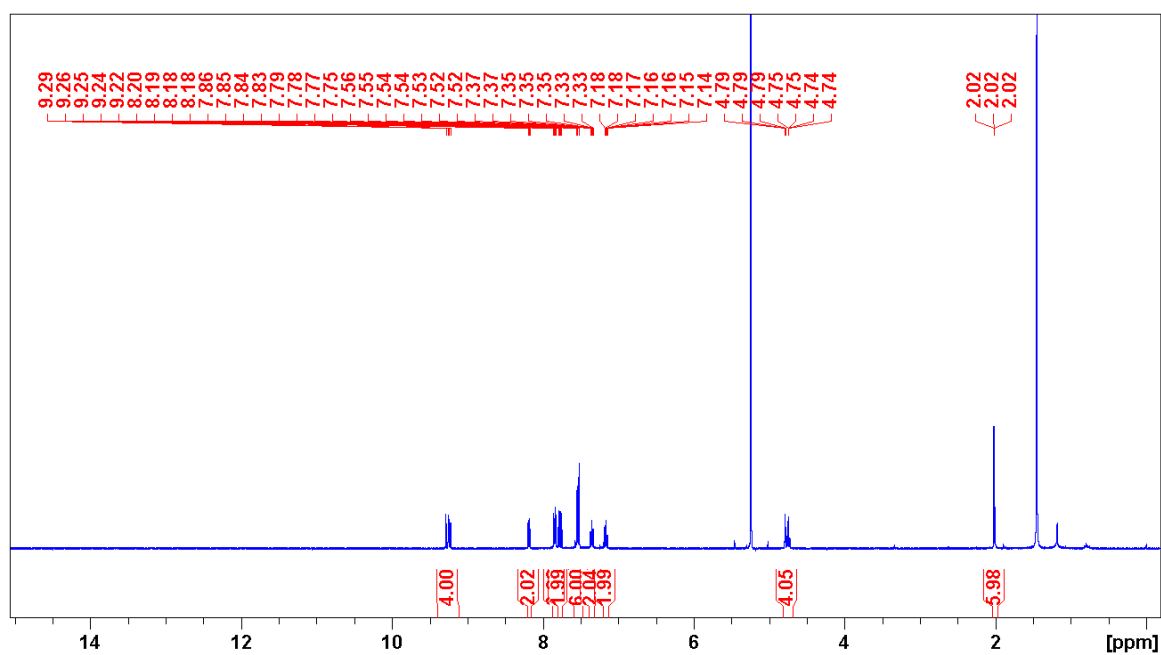
Figure S15. ^{1}H NMR spectrum of **5** (400 MHz, CD$_2$Cl$_2$, 298 K).
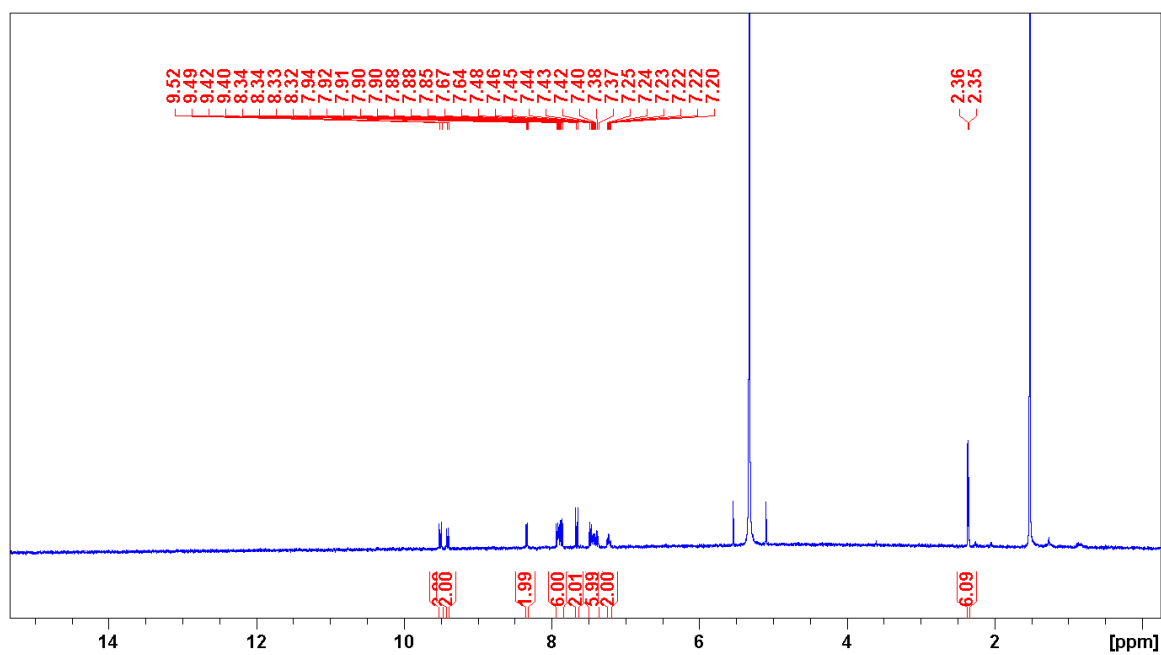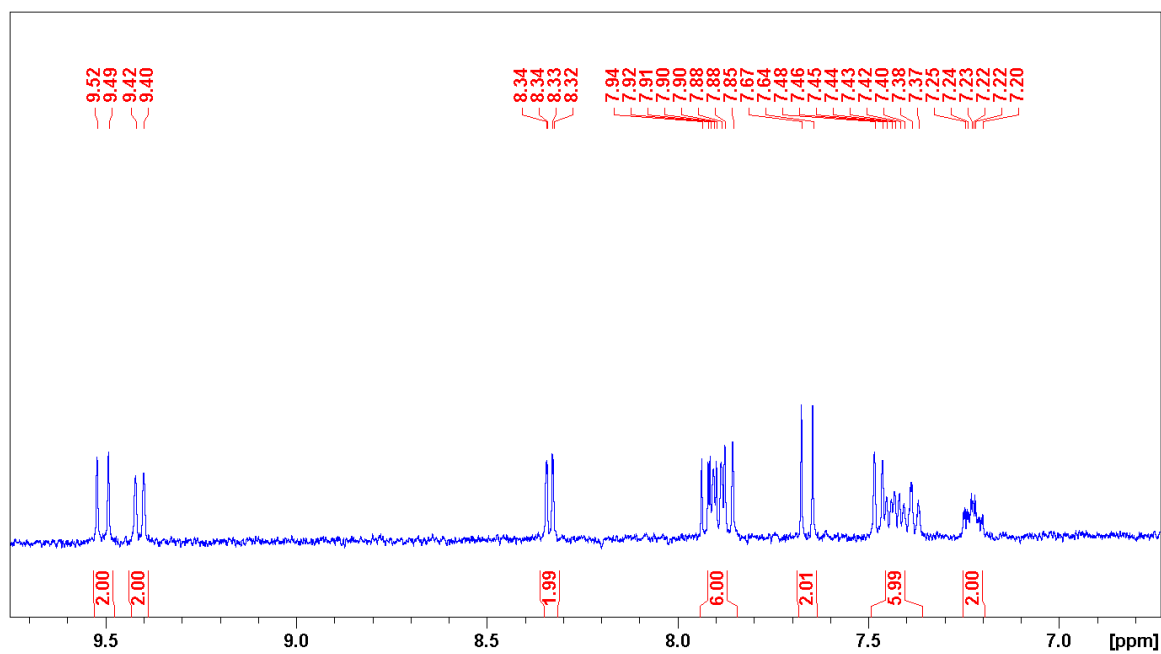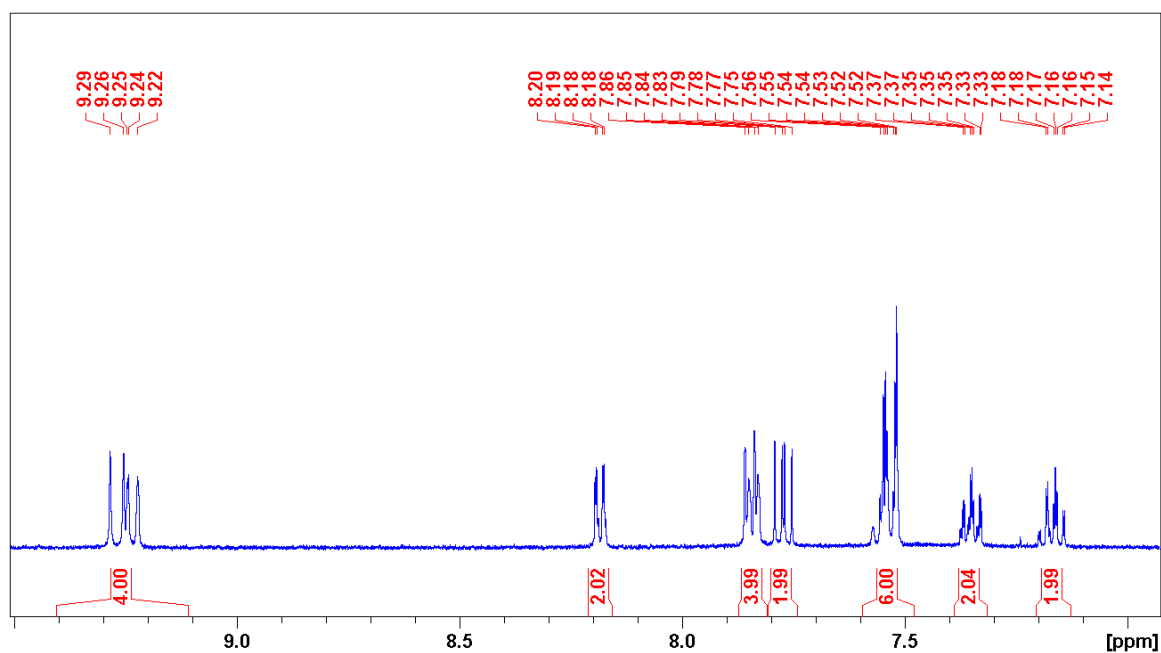

Figure S16. Magnified aromatic region of the ^{1}H NMR spectrum of **5** (400 MHz, CD$_2$Cl$_2$, 298 K).
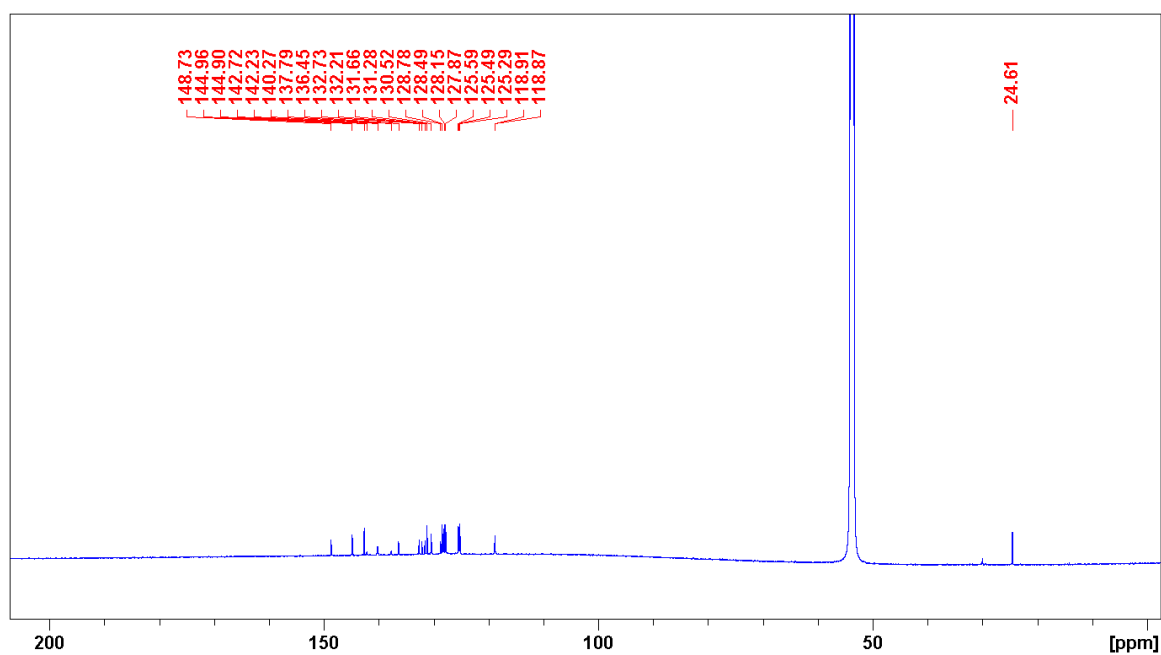
Figure S17. ^{13}C NMR spectrum of **5** (151 MHz, CD$_2$Cl$_2$, 298 K).
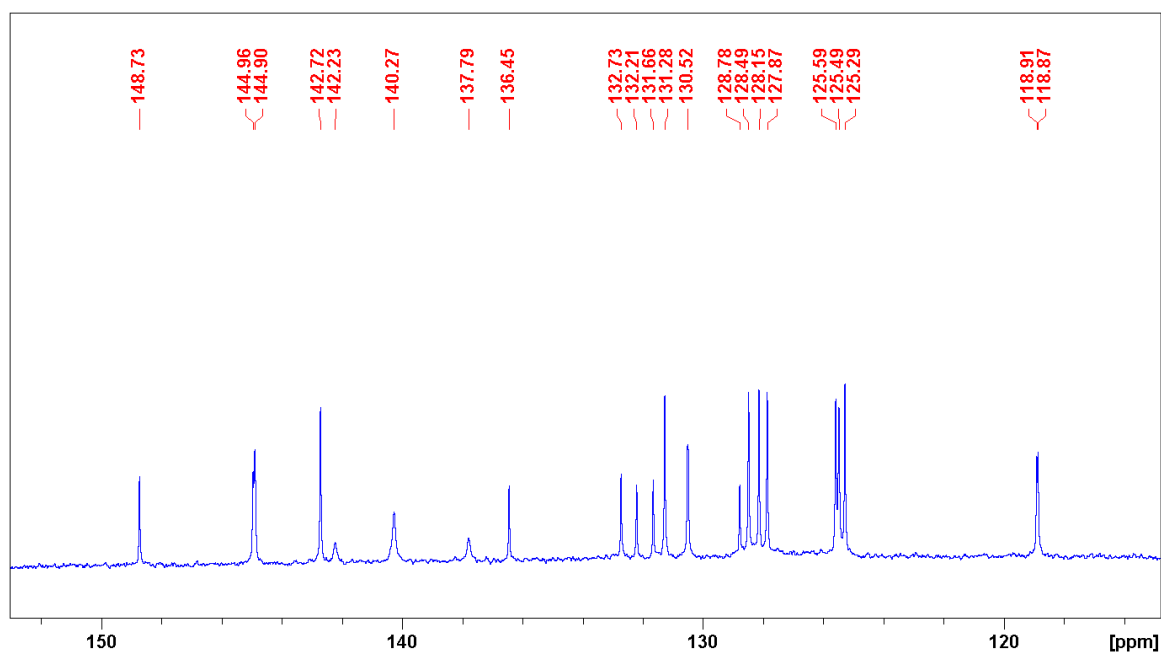
Figure S18. Magnified aromatic region of the ^{13}C NMR spectrum of **5** (151 MHz, CD$_2$Cl$_2$, 298 K).
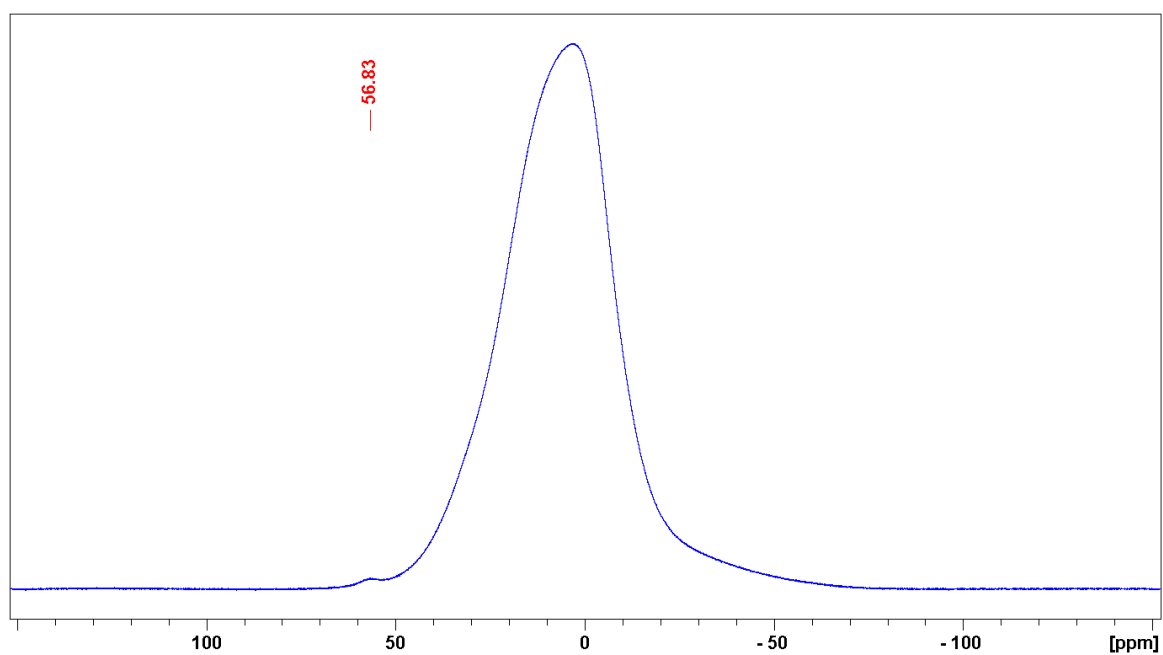
Figure S19. ^{11}B NMR spectrum of **5** (128 MHz, CD_2Cl_2, 298 K).
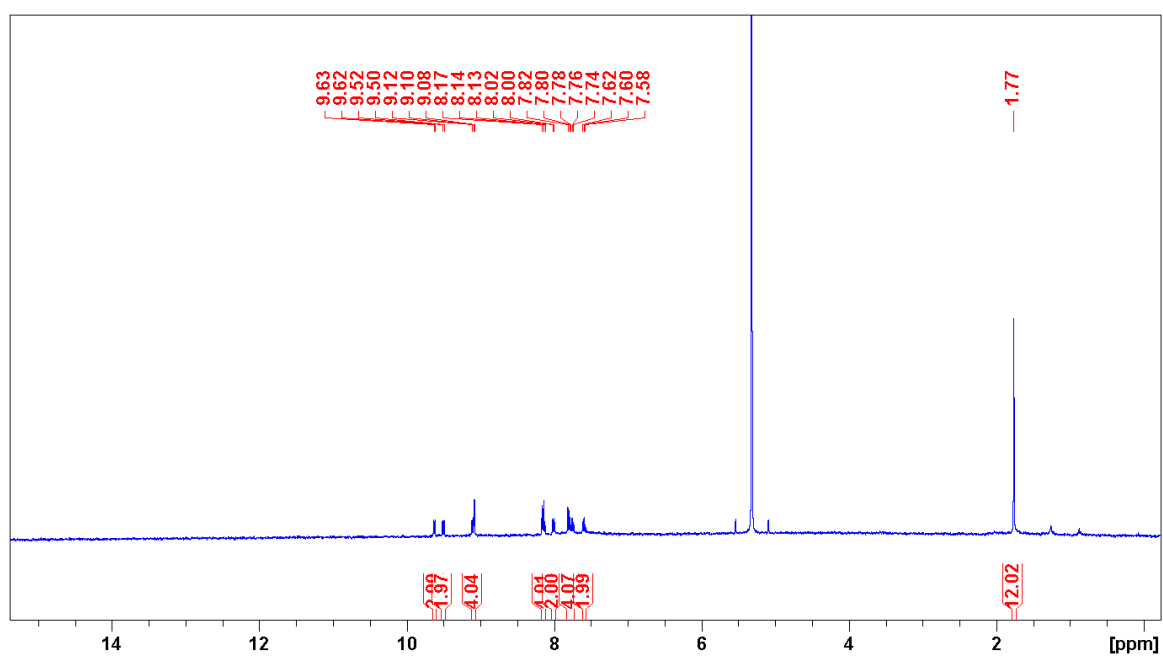
Figure S20. ^1H NMR spectrum of **(B-Dbf)₂** (400 MHz, CD_2Cl_2, 298 K).
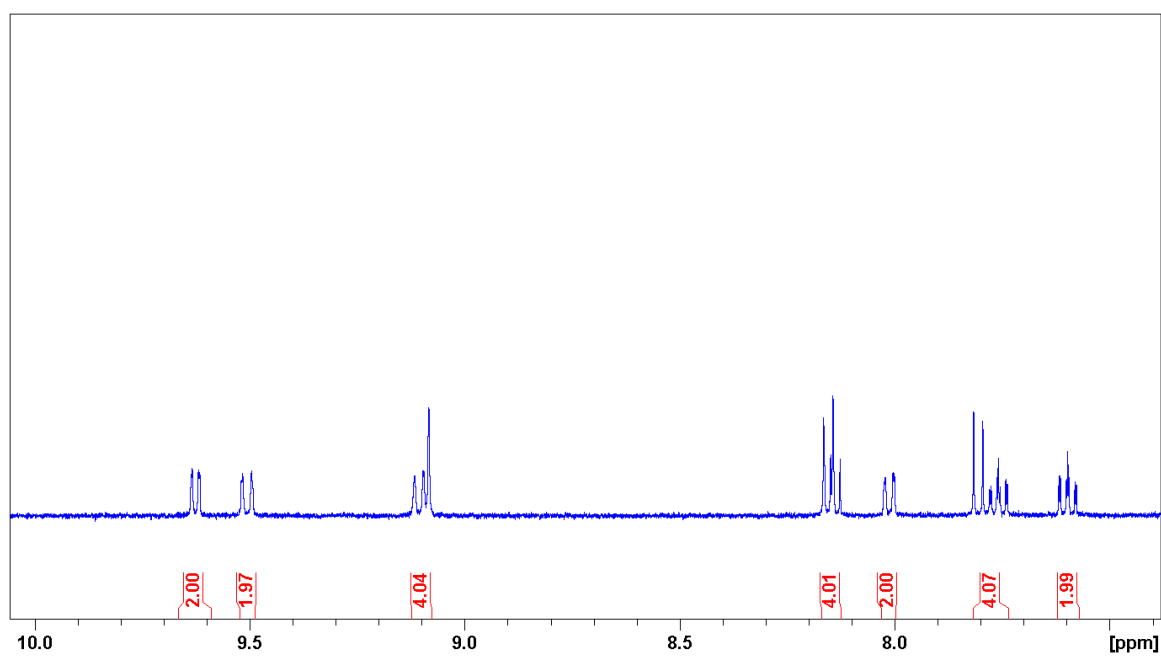
Figure S21. Magnified aromatic region of the ^{1}H NMR spectrum of **(B-Dbf)$_2$** (400 MHz, CD$_2$Cl$_2$, 298 K).
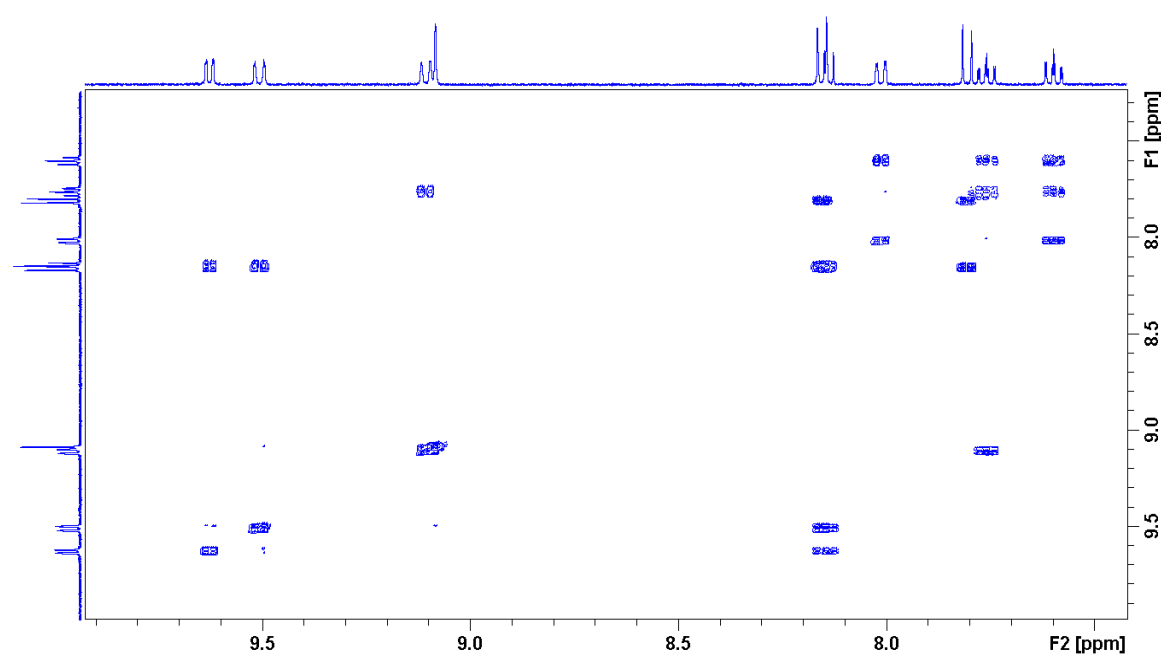
Figure S22. ^{1}H–^{1}H COSY NMR spectrum of **(B-Dbf)$_2$** (400 MHz, CD$_2$Cl$_2$, 298 K) showing the aromatic region.
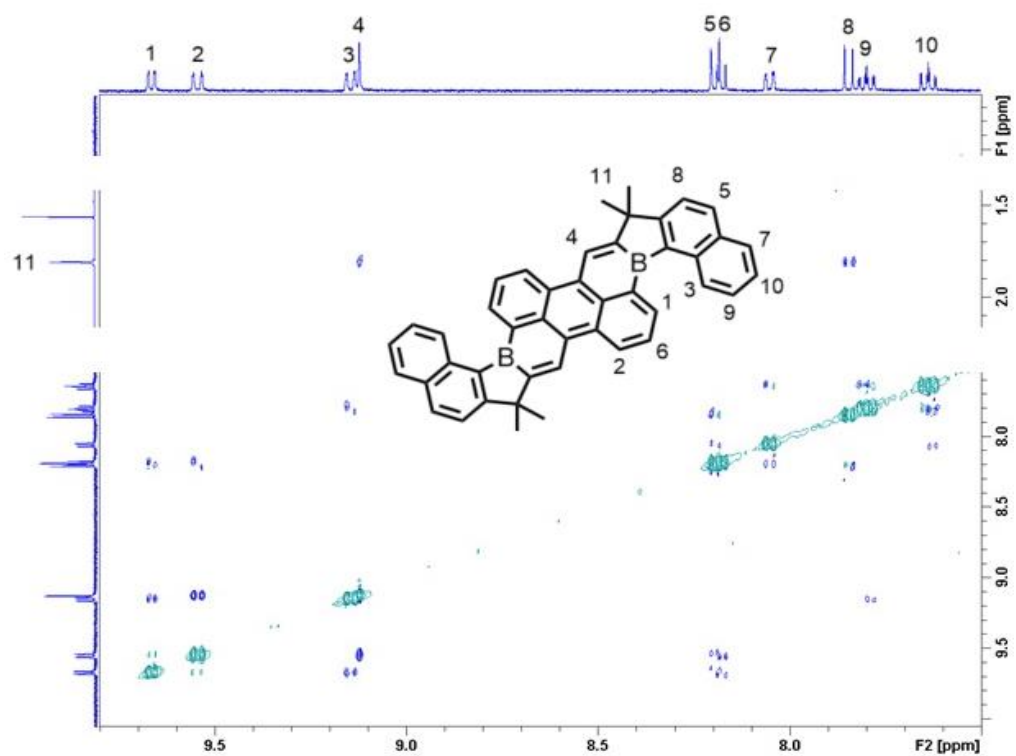
Figure S23. ^{1}H–^{1}H ROESY NMR spectrum of **(B-Dbf)$_2$** (400 MHz, CD$_2$Cl$_2$, 298 K) showing the aromatic region.

4. Mass Spectrometry
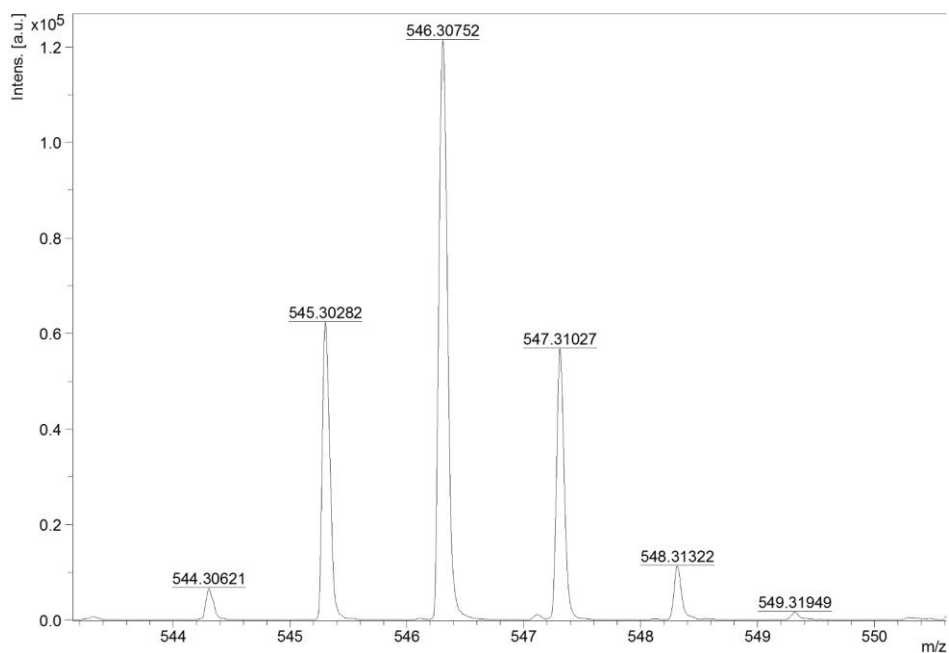
Figure S24. Found isotope pattern of the high-resolution mass spectrum of **tBuPh-2** (MALDI-TOF, positive mode).
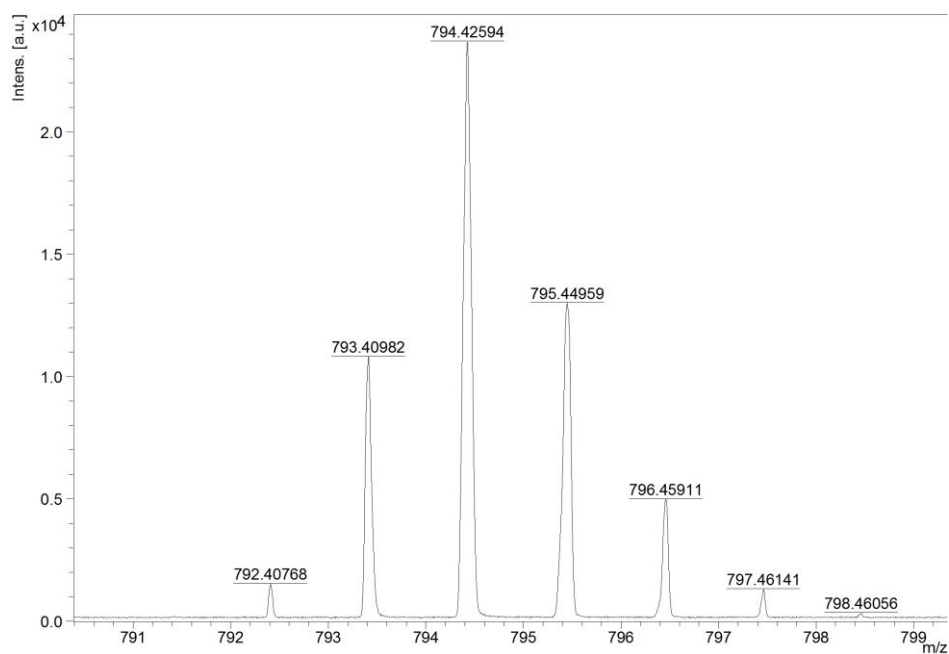
Figure S25. Found isotope pattern of the high-resolution mass spectrum of **tBuPh-4** (MALDI-TOF, negative mode).
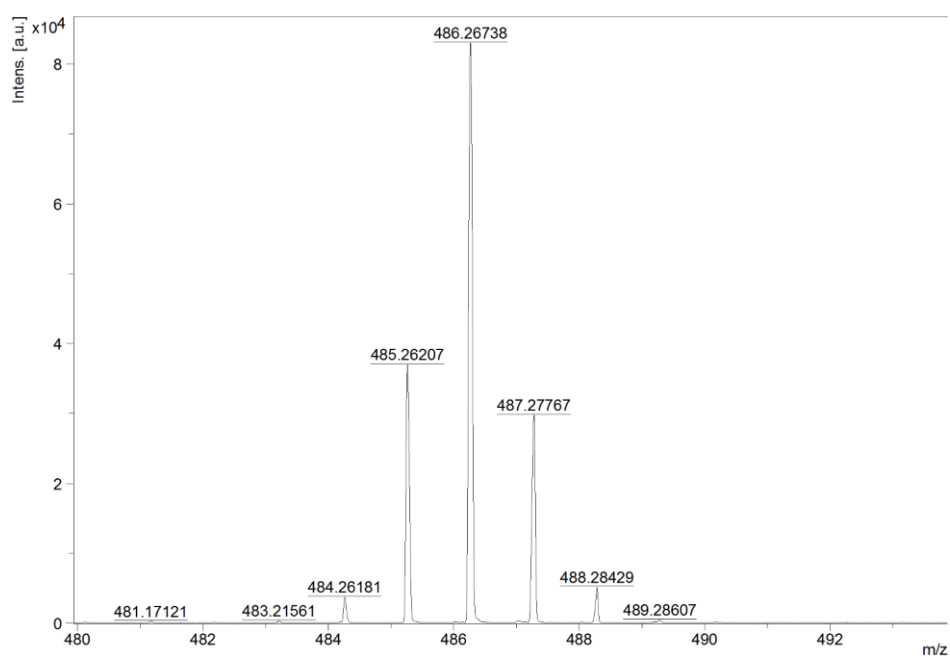
Figure S26. Found isotope pattern of the high-resolution mass spectrum of **3** (MALDI-TOF, negative mode).
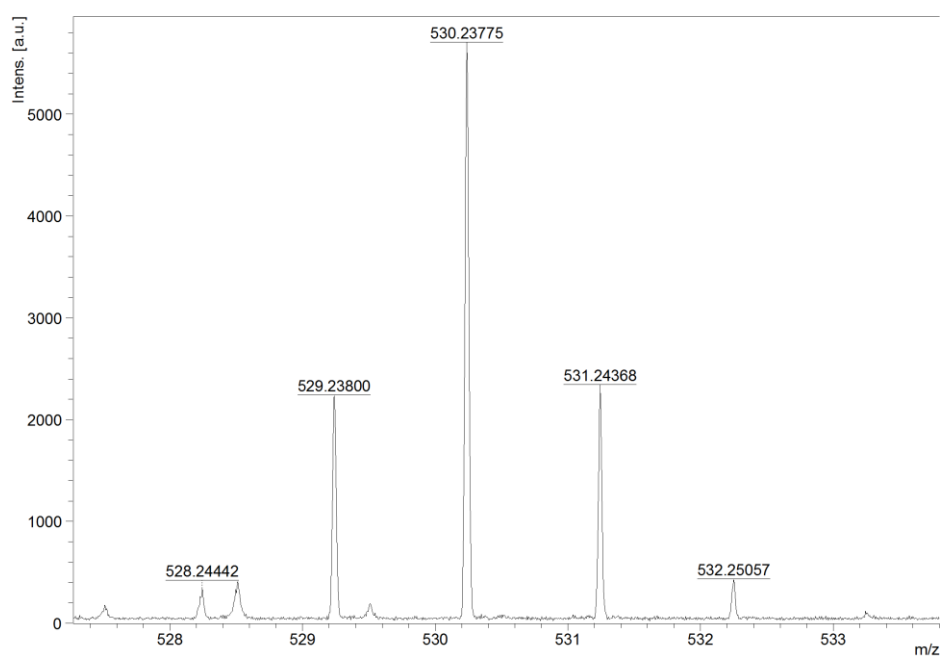
Figure S27. Found isotope pattern of the high-resolution mass spectrum of **4** (MALDI-TOF, positive mode).
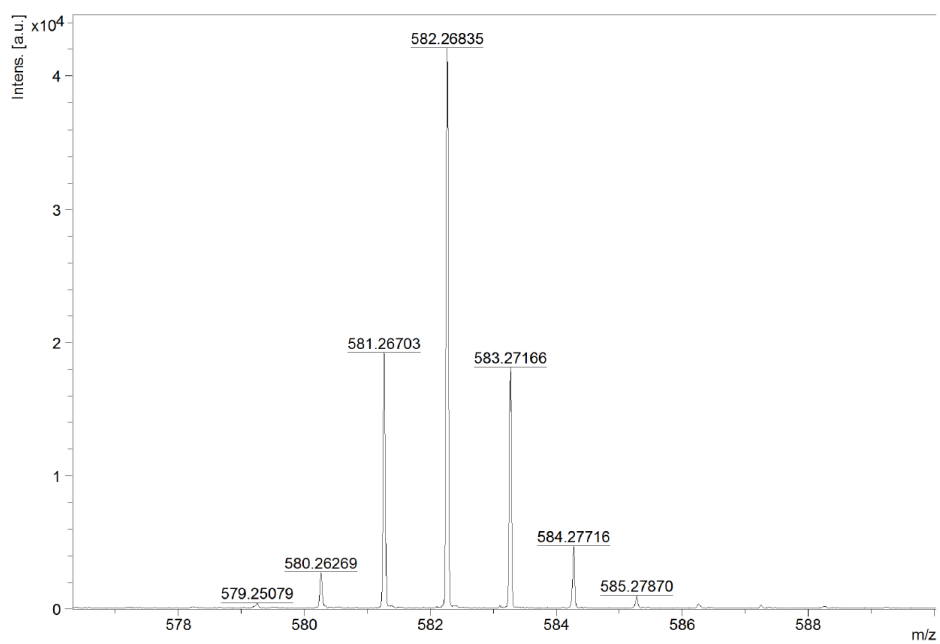
Figure S28. Found isotope pattern of the high-resolution mass spectrum of **5** (MALDI-TOF, positive mode).
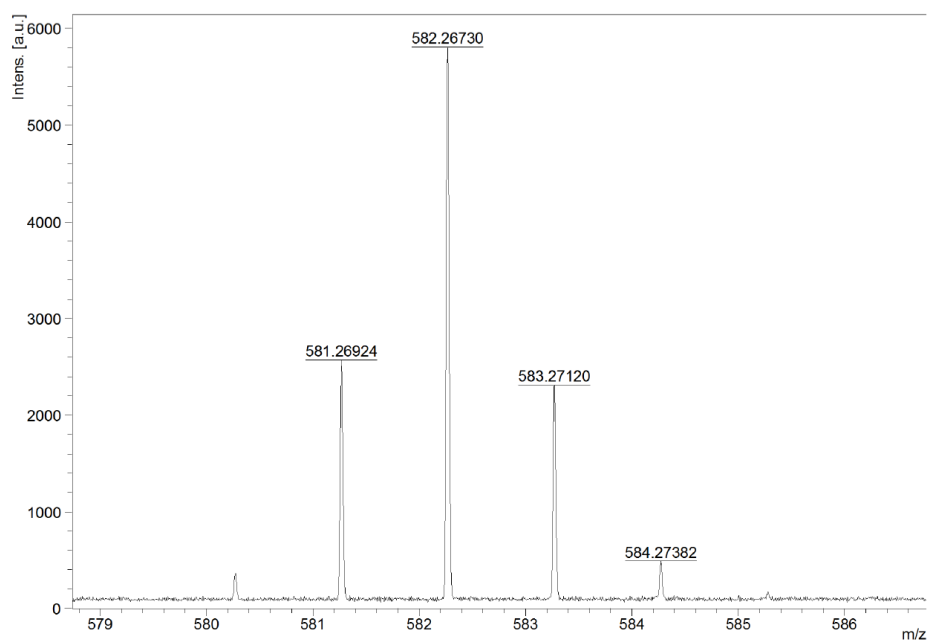
Figure S29. Found isotope pattern of the high-resolution mass spectrum of **(B-Dbf)₂** (MALDI-TOF, negative mode).

5. UV/Vis and Fluorescence Spectra
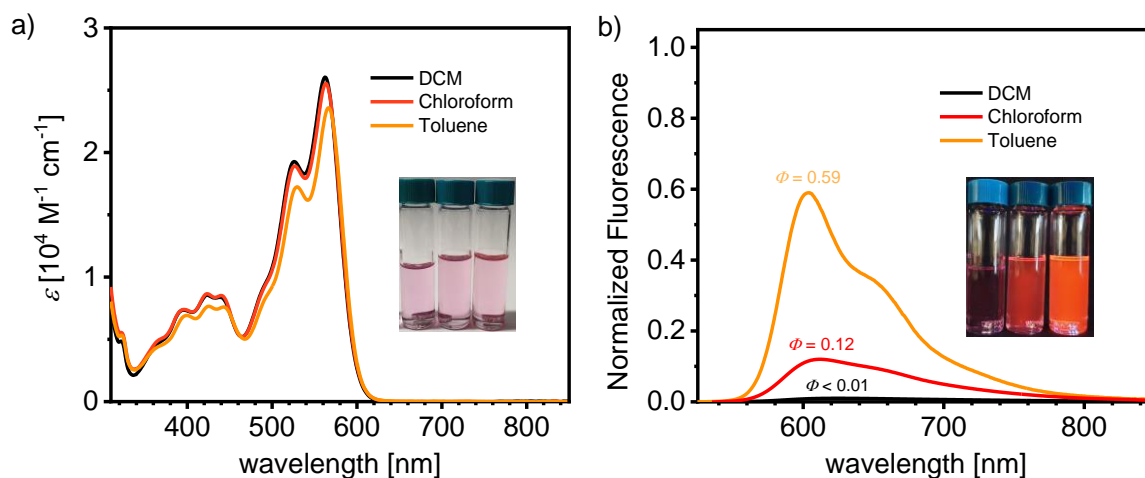
Figure S30. a) UV/Vis absorption (~10^{-5} M) and b) emission spectra (~ 10^{-5} M) of **4** in toluene (orange), CHCl$_3$ (red), and CH$_2$Cl$_2$ (black) at 298 K.

Table S1. Solvent dependent optical properties of **tBuPh-4**, **3**, and **4**.

Compound	Solvent	λ_{abs} [nm][a] (ε [M^{-1} cm^{-1}])	λ_{em} [nm][a]	Φ_F[b]	τ_1 [ns]	τ_2 [ns]	Stokes Shift [cm^{-1}]
tBuPh-4	Toluene	638 (n.d.)	706[d]	0.37	5.0	–	1500
	CHCl$_3$	638 (n.d.)	709[d]	0.32	5.2	–	1600
	CH$_2$Cl$_2$	632 (n.d.)	704[e]	0.35	4.1	–	1600
3	Toluene	557 (n.d.)	583[f]	0.74	11.1	–	800
	CHCl$_3$	555 (n.d.)	580[f]	0.75	11.3	–	800
	CH$_2$Cl$_2$	555 (24160)	580[g]	0.78[c]	8.8	–	600
4	Toluene	566 (23600)	604[h]	0.59	7.6	–	1100
	CHCl$_3$	563 (25500)	612[i]	0.12	–	–	1400
	CH$_2$Cl$_2$	562 (30300)	623[j]	0.01	0.7 (24%)	7.3 (76%)	1700
	DMSO	563 (n.d.)	642[f]	< 0.01	–	–	2200

[a] Optical measurements were carried out at 298 K with OD of 0.5–1.0. [b] Fluorescence quantum yield determined via absolute method. [c] Fluorescence quantum yield determined via relative method. All measurements for fluorescence quantum yield were carried out with O$_2$ containing and free solvents, showing no difference. Excitation wavelengths are [d] 580, [e] 590 nm, [f] 518 nm, [g] 520 nm, [h] 505 nm, [i] 525 nm, [j] 495 nm. n.d.: not determined.
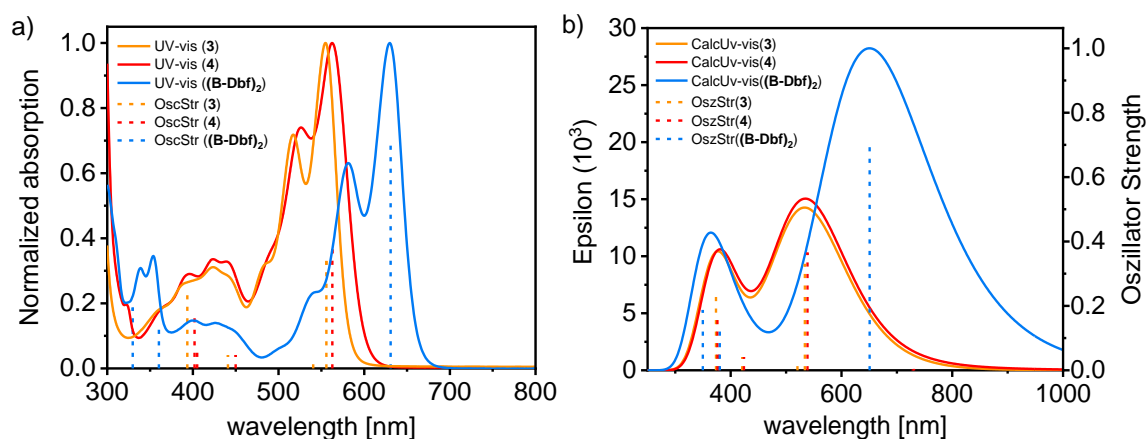
Figure S31. a) UV/Vis absorption spectra (~1 × 10^{-5} M) and b) time-dependent DFT calculated UV-vis spectrum of **3** (orange), **4** (red) and **(B-Dbf)₂** (blue) with corresponding oscillator strengths as obtained from TD-DFT calculations (B3LYP/6–311G**).

Table S2. Absorption properties of boron-doped PAHs presented herein as obtained from TD-DFT calculations (B3LYP/6–311G**). The relevant transitions are listed with the respective wavelengths and oscillator strengths as well as the orbitals that are mainly involved in the transitions.

Compound	Wavelength [nm]	Oscillator strength	Transitions	Character
tBuPh-4	712	0.1314	HOMO → LUMO (57%)	LE
	649	0.4301	HOMO−2→ LUMO (57%)	LE
3	536	0.3305	HOMO → LUMO (68%) HOMO−4 → LUMO (11%)	LE
	520	0.0165	HOMO−4 → LUMO (62%)	CT
	421	0.0409	HOMO−5 → LUMO (66%)	LE
	373	0.2385	HOMO−6 → LUMO (64%) HOMO−5 → LUMO (19%)	LE
4	731	0.0041	HOMO → LUMO (70%)	CT
	729	0.0041	HOMO−1 → LUMO (70%)	CT
	537	0.3656	HOMO−2 → LUMO (70%)	LE
	376	0.1727	HOMO−6 → LUMO (52%)	LE
(B-Dbf)₂	651	0.6963	HOMO → LUMO (70%)	LE
	380	0.1339	HOMO−6 → LUMO (64%) HOMO → LUMO+4 (21%)	LE
	350	0.1873	HOMO → LUMO+2 (66%)	LE
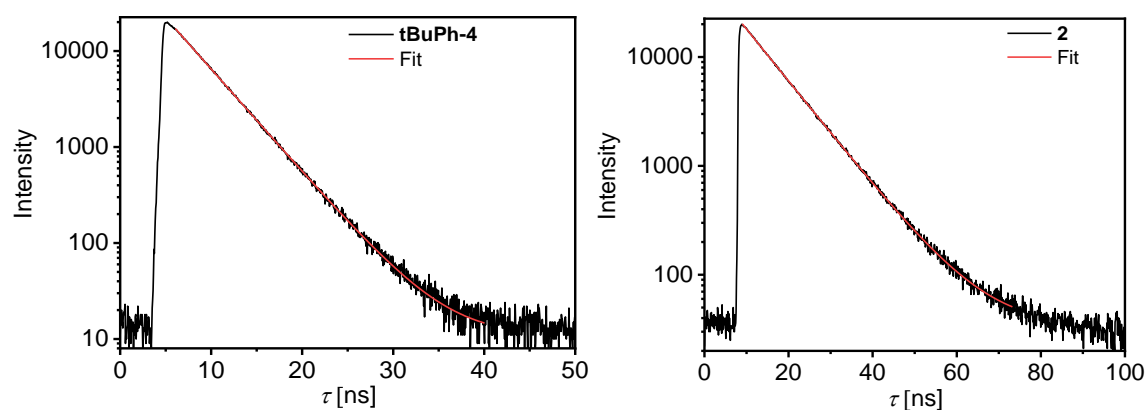
Figure S32. Fluorescence decay of **tBuPh-4** (left) and **2** (right) in CH_2Cl_2 at 298 K in air.
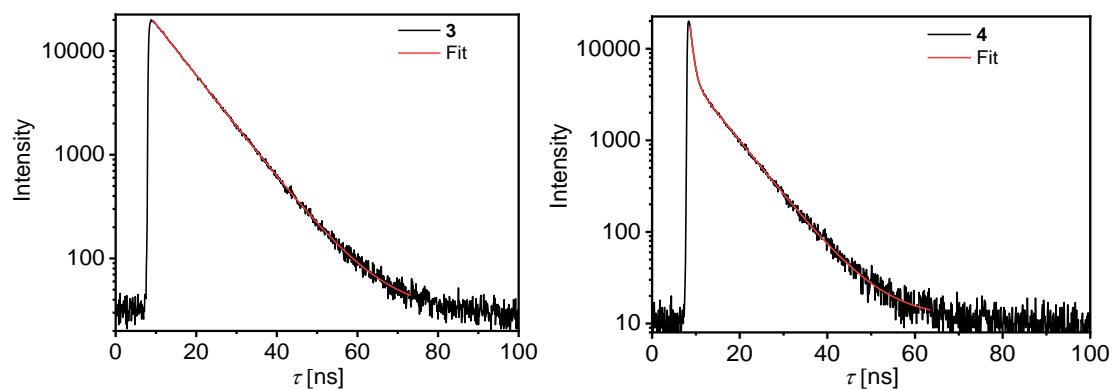
Figure S33. Fluorescence decay of **3** (left) and **4** (right) in CH_2Cl_2 at 298 K in air.
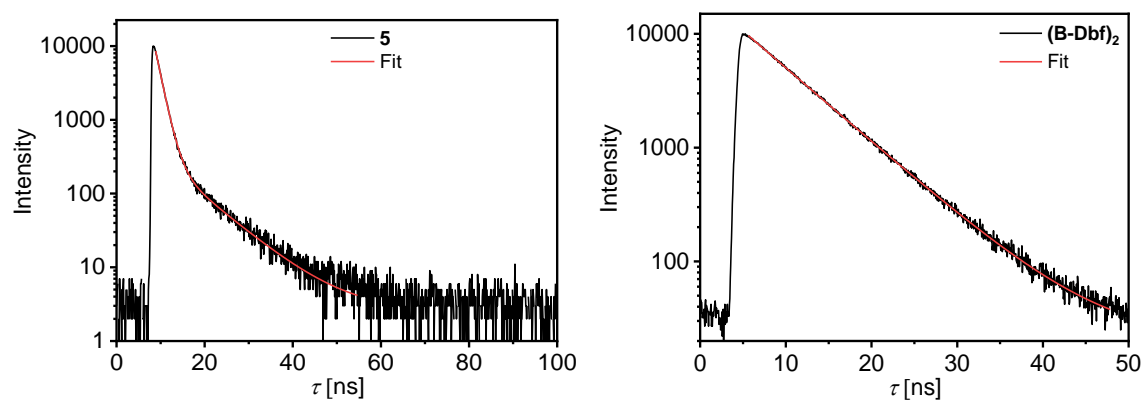
Figure S34. Fluorescence decay of **5** (left) and **(B-Dbf)₂** in CH_2Cl_2 at 298 K in air.

6. Differential Pulse, Square Wave and Cyclic Voltammetry
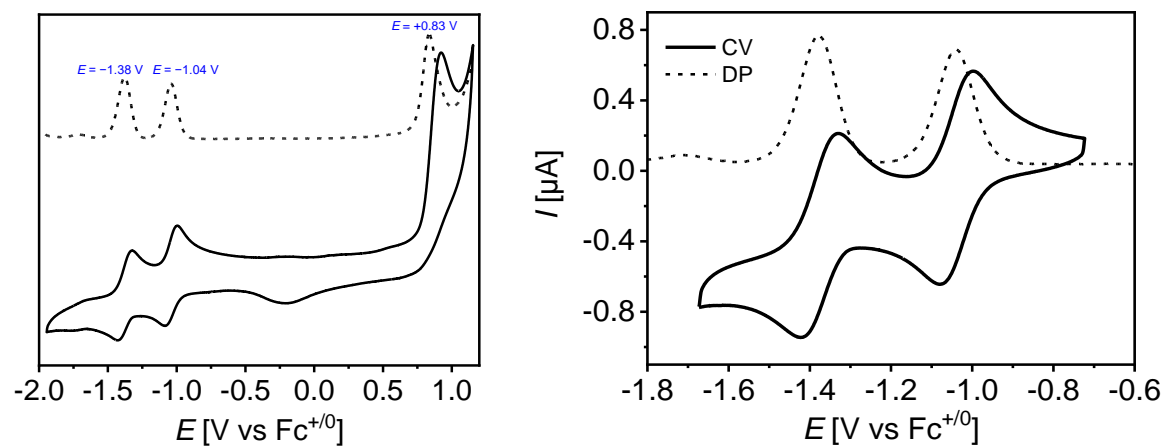
Figure S35. Full (left) cyclic (solid line) and differential pulse (dashed line) voltammetry and magnified reduction waves (right) of **tBuPh-4** (7×10^{-4} M, 0.1 M (n-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$, vs. Fc$^{+/0}$, 298 K) referenced versus ferrocene/ferrocenium redox couple.
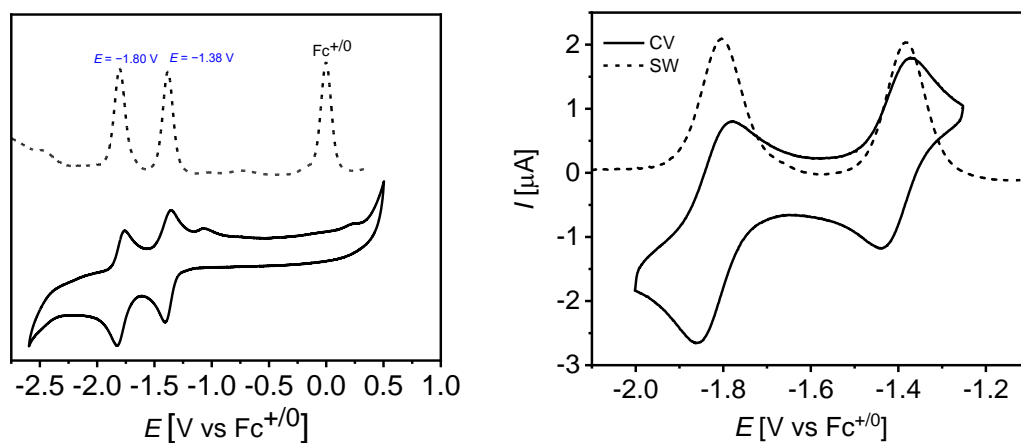
Figure S36. Full (left) cyclic (solid line) and differential pulse (dashed line) voltammetry and magnified reduction waves (right) of **2** (7×10^{-4} M, 0.1 M (n-Bu)$_4$NPF$_6$ in DMSO, vs. Fc$^{+/0}$, 298 K) referenced versus ferrocene/ferrocenium redox couple.
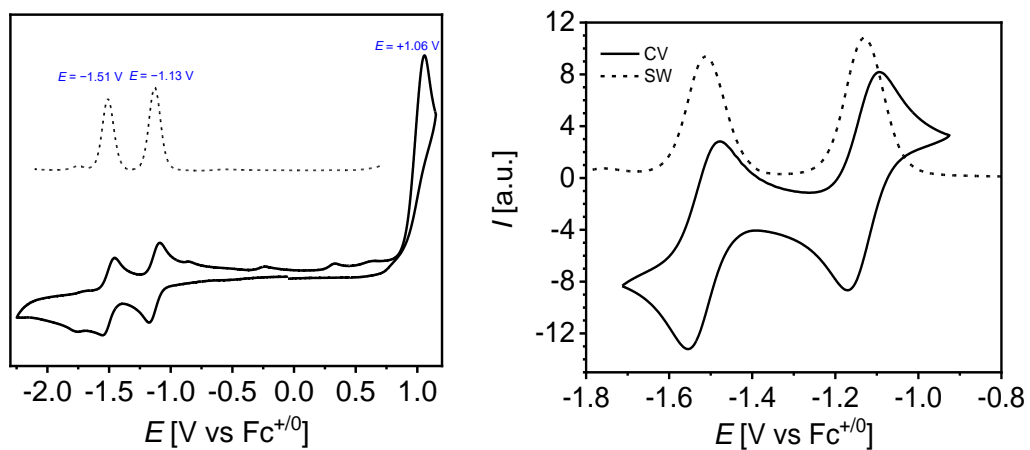
Figure S37. Full (left) cyclic (solid line) and differential pulse (dashed line) voltammetry and magnified reduction waves (right) of **3** (7 × 10^{-4} M, 0.1 M (*n*-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$, 298 K) referenced versus ferrocene/ferrocenium redox couple.
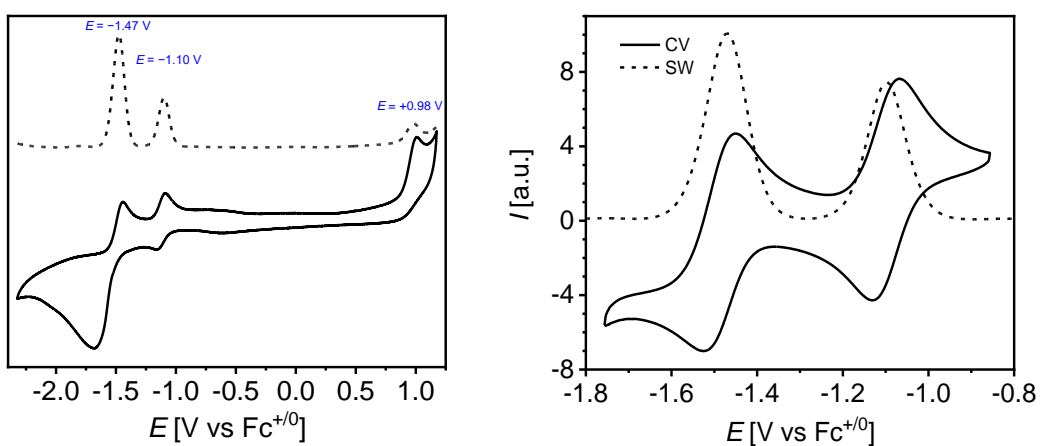
Figure S38. Full (left) cyclic (solid line) and differential pulse (dashed line) voltammetry and magnified reduction waves (right) of **4** (7 × 10^{-4} M, 0.1 M (*n*-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$, vs. Fc$^{+/0}$, 298 K) referenced versus ferrocene/ferrocenium redox couple.
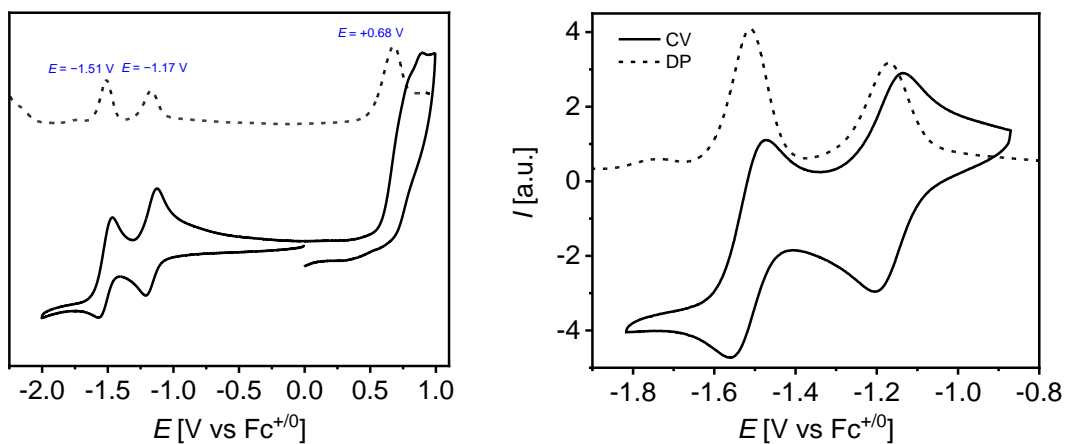
Figure S39. Full (left) cyclic (solid line) and differential pulse (dashed line) voltammetry and magnified reduction waves (right) of **(B-Dbf)$_2$** (7×10^{-4} M, 0.1 M (n-Bu)$_4$NPF$_6$ in CH$_2$Cl$_2$, vs. Fc$^{+/0}$, 298 K) referenced versus ferrocene/ferrocenium redox couple.

7. X-ray Crystallography
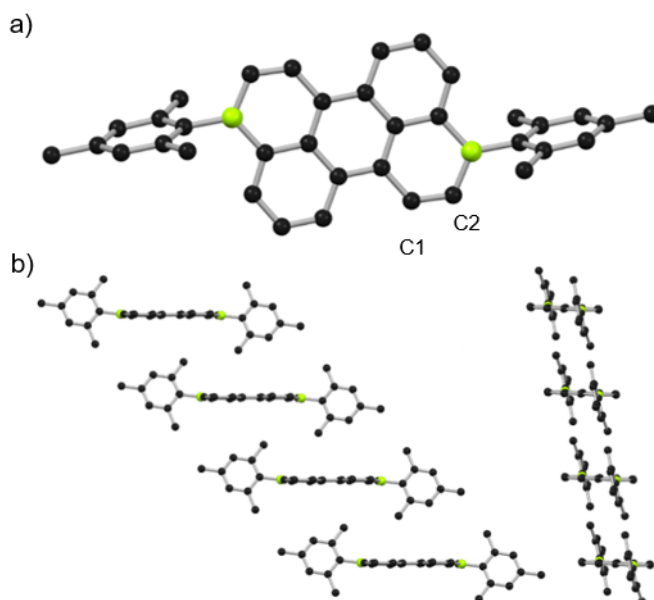
Figure S40. Solid-state structures (a) and packing (b) of **3**. C: black, B: yellow-green. H atoms omitted for clarity.

Table A1. Crystallographic information for compounds **3**, **4** and **(B-Dbf)₂**.

	3	4	(B-Dbf)₂
CCDC number	2149816	2149815	2149817
Emperical formula	$C_{36}H_{32}B_2$	$C_{40}H_{28}B_2$	$C_{44}H_{32}B_2$
Mr	486.23	530.24	582.32
Temperature [K]	100(2)	100(2)	100(2)
Wavelength [Å]	1.54178	0.61992	1.54178
Crystal size [mm]	0.177 × 0.144 × 0.109	0.100 × 0.040 × 0.040	0.797 × 0.030 × 0.026
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group, Z	$P2_1/c$, 2	$P\bar{1}$, 1	$Pbcn$, 4
a [Å], α [°]	8.6564(4), 90	6.788(3), 81.222(4)	19.3031(6), 90
b [Å], β [°]	23.1604(10), 106.488(2)	8.682(2), 80.922(9)	16.0030(5), 90
c [Å], γ [°]	6.9901(3), 90	12.145(3), 72.872(4)	9.77381(3), 90
V [Å³]	1343.79(10)	671.1(3)	3008.17(16)
ρ(calcd) [g · cm⁻¹]	1.202	1.312	1.286
μ [mm⁻¹]	0.497	0.057	0.540
$F_{(000)}$	516	278	1224
GooF(F^2)	1.127	1.038	1.200
R_1, wR_2 ($I > 2\sigma(I)$)	0.05832, 0.1193	0.0714, 0.2171	0.0669, 0.1424
R_1, wR_2 (all data)	0.0733, 0.1307	0.0984, 0.2389	0.0796, 0.1467
Reflections collected / unique	22572 / 2655 [R(int) = 0.0581]	3028 / 3028 [R(int) = 0.074]	35755 / 3289 [R(int) = 0.0880]
θ range [°]	3.817 to 72.046	1.490 to 23.735	3.588 to 80.782
Completeness [%]	100	99.2	100
Restraints / Parameters/	0 / 175	0 / 191	0 / 210

8. Computations
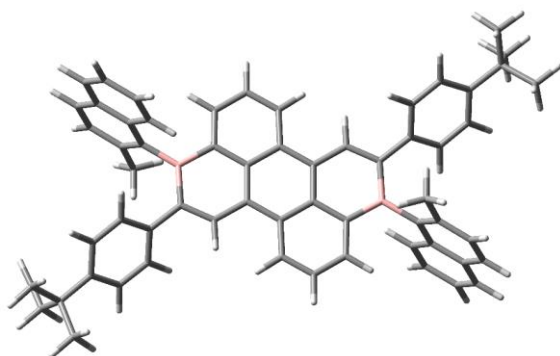
Figure S41. Geometry-optimized structure of **tBuPh-4** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).

HOMO	LUMO
−5.70 eV	−3.53 eV
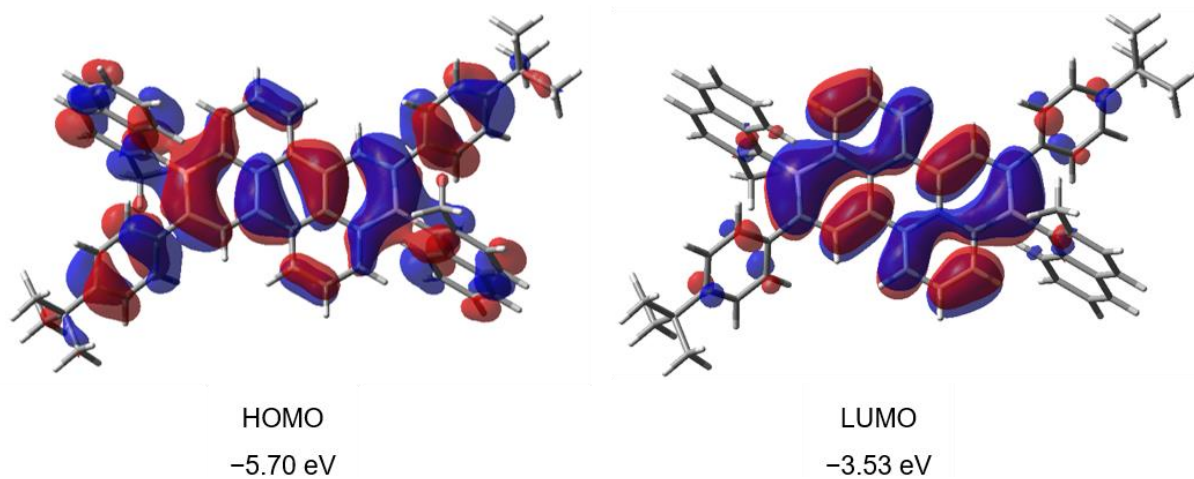
Figure S42. Frontier molecular orbitals (isovalue = 0.015) of **tBuPh-4** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).
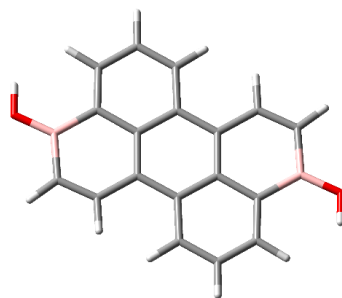
Figure S43. Geometry-optimized structure of **2** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).
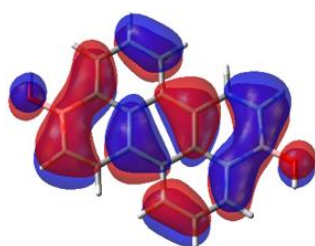
HOMO

−5.74 eV
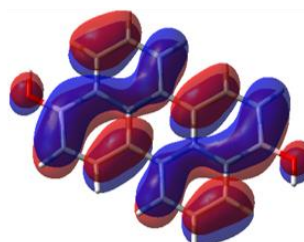
LUMO

−3.17 eV

Figure S44. Frontier molecular orbitals (isovalue = 0.015) of **2** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).
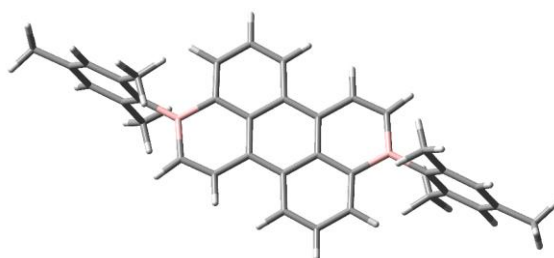
Figure S45. Geometry-optimized structure of **3** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).

HOMO
−6.02 eV

LUMO
−3.48 eV
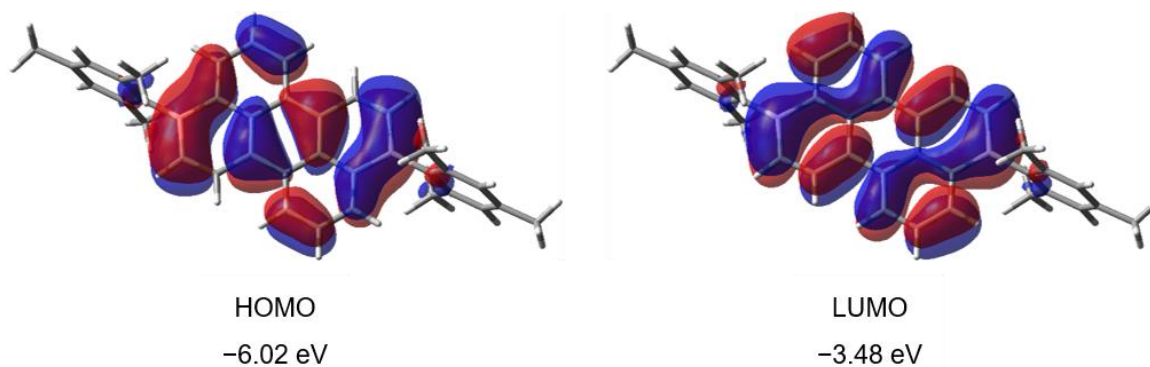
Figure S46. Frontier molecular orbitals (isovalue = 0.015) of **3** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).
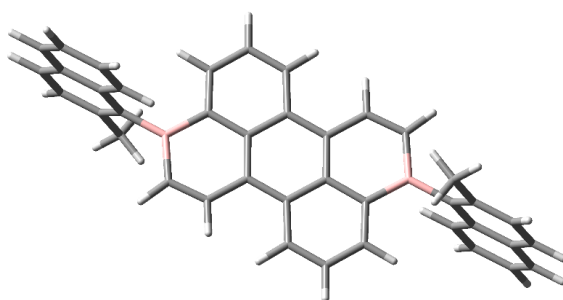
Figure S47. Geometry-optimized structure of **4** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).

HOMO
−5.89 eV
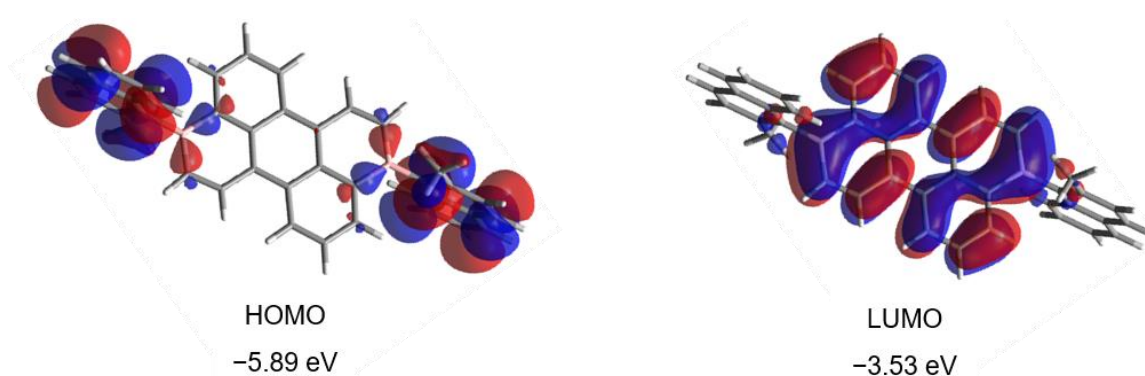
LUMO
−3.53 eV

Figure S48. Frontier molecular orbitals (isovalue = 0.015) of **4** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).

HOMO−2
−6.07 eV
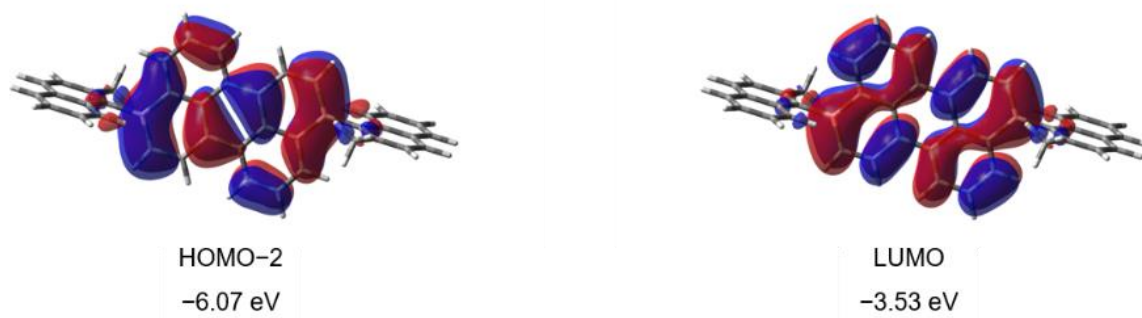
LUMO
−3.53 eV

Figure S49. HOMO−2 and LUMO (isovalue = 0.015) of **4** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).
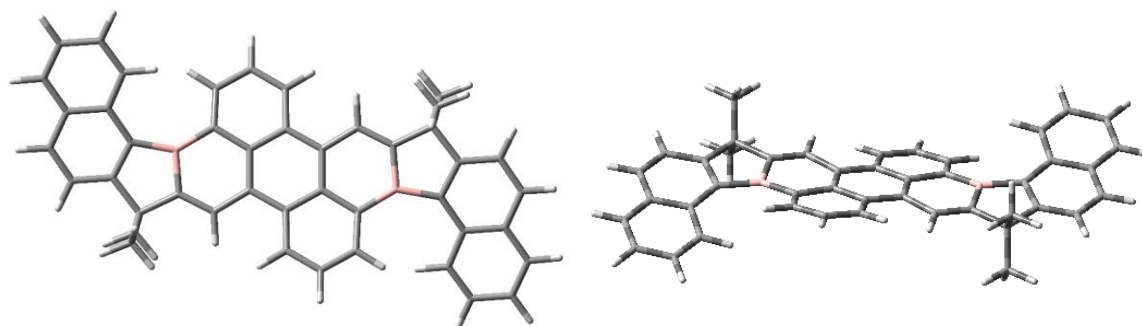
Figure S50. Top view (left) and side view (right) Geometry-optimized structure of **(B-Dbf)$_2$** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).

HOMO
−5.47 eV

LUMO
−3.31 eV
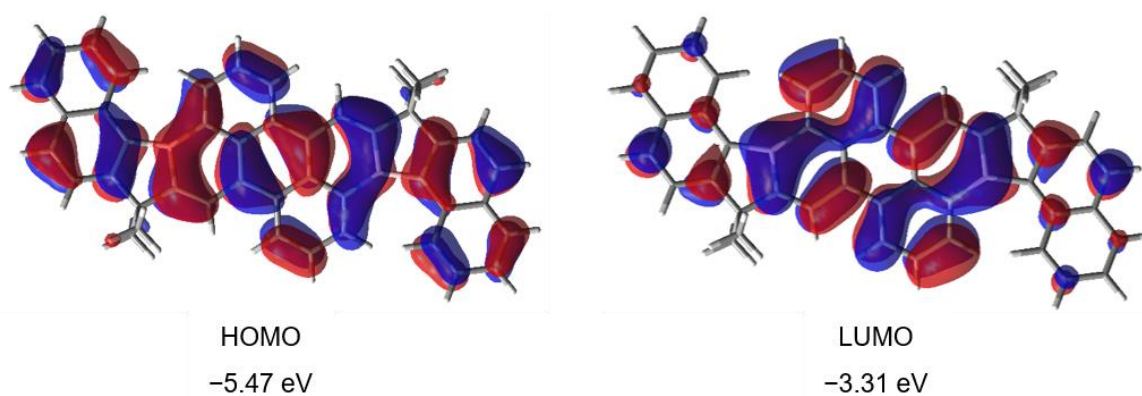
Figure S51. Frontier molecular orbitals (isovalue = 0.015) of **(B-Dbf)$_2$** by DFT calculations at the B3LYP/6-311G** level of theory with PCM (CH$_2$Cl$_2$).
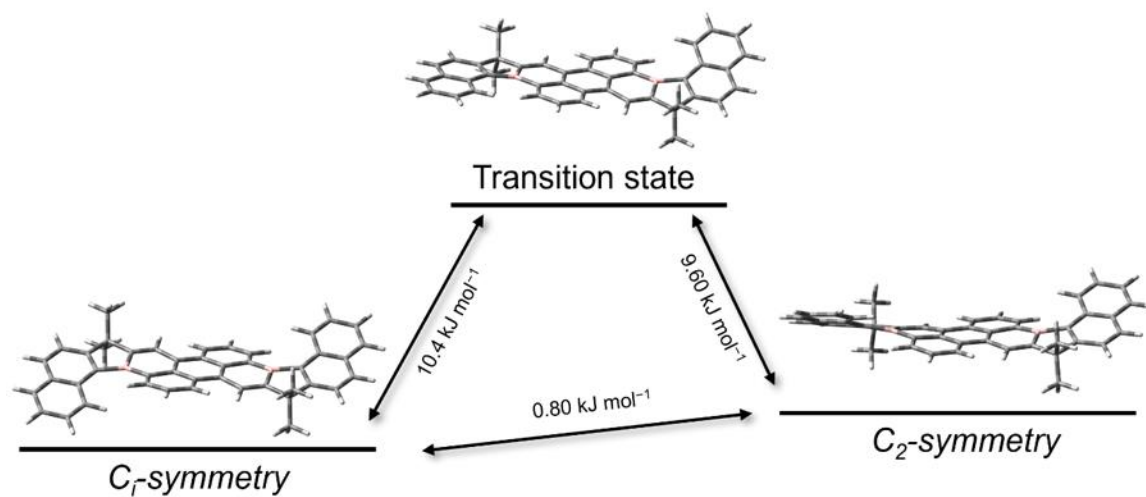
Figure S52. Calculated energy diagram for the interconversion of the two isomers of **(B-Dbf)₂** (B3LYP/6-311G**).

Cartesian coordinates and absolute energy of the geometry-optimized structure

Level of theory: B3LYP/6-311G**, PCM=CH$_2$Cl$_2$

Table S3. Compound **tBuPh-4**.

|	x	y	z
C	0.71368315	−3.55470100	0.89903055
C	2.01679848	−3.03007082	0.81241378
C	2.25137388	−1.70327771	0.47947840
C	1.12070822	−0.84904822	0.22741227
C	−0.21462358	−1.37175706	0.30655052
C	−0.36709899	−2.74828548	0.64982350
C	1.33548256	0.51575086	−0.09903171
C	0.20919270	1.35786741	−0.36802010
C	−1.12630331	0.83686671	−0.28278904
C	−1.34165978	−0.52647458	0.04983098
C	0.36300498	2.72951509	−0.72965876
C	−0.71712302	3.53465969	−0.98543700
C	−2.02079613	3.01419800	−0.88425933
C	−2.25635814	1.69174259	−0.53502395
B	−3.71012626	1.15814631	−0.43069071
C	−3.84344483	−0.34490951	−0.08882345
C	−2.68706636	−1.04892077	0.12221087
B	3.70449411	−1.16348328	0.39605893
C	3.83545340	0.34491474	0.07890721
C	2.67931742	1.04460198	−0.14718095
C	−4.94111072	2.11461342	−0.71022838
C	−5.13393192	−1.07664566	−0.00294491
C	4.93678926	−2.11925009	0.67199978
C	−5.29725789	−2.33983537	−0.59864026
C	−6.49436356	−3.03818988	−0.49939274
C	−7.59429906	−2.52184103	0.20397719
C	−7.43030973	−1.26286267	0.79285622
C	−6.23569093	−0.55270325	0.68528825
C	5.42387535	−3.00669982	−0.34520151
C	6.53013266	−3.87735588	−0.07816130
C	7.12469309	−3.84608614	1.20732733
C	6.64656123	−2.99477668	2.17084961
C	5.55500917	−2.12281477	1.91986466
C	4.84843598	−3.04907463	−1.64789044
C	5.32820920	−3.89664908	−2.61861808
C	6.41692101	−4.75666757	−2.34338671
C	7.00170447	−4.74379355	−1.10030100
C	−8.90185741	−3.32732453	0.29349417
C	−9.46550262	−3.54963288	−1.12979013
C	−8.61866064	−4.69869653	0.95027589
C	−9.97591260	−2.60799609	1.12939805
C	−5.41421125	3.02278788	0.29517020
C	−6.51840403	3.89432137	0.02249262
C	−7.12457435	3.84353343	−1.25692608
C	−6.65973039	2.97250837	−2.20926797
C	−5.57065028	2.09924065	−1.95233157
C	−4.82699873	3.08519459	1.59179137
C	−5.29405441	3.95204728	2.55163182
C	−6.38089203	4.81264263	2.27083420
C	−6.97656326	4.78104029	1.03328208
C	5.12111457	1.08872329	0.03680820
C	5.25736818	2.33688421	0.66085243
C	6.45192153	3.05383364	0.60848774
C	7.57011481	2.56304349	−0.07424615
C	7.43224461	1.31075812	−0.69465318
C	6.24780707	0.58714507	−0.63572628
C	8.90270547	3.32690289	−0.16195365
C	8.85636188	4.67135644	0.58674743
C	10.03158628	2.46918071	0.45616793
C	9.23289414	3.61317214	−1.64566801
C	5.08418230	−1.20956182	3.03163866
C	−5.11488084	1.16308957	−3.05124370
H	0.56309598	−4.59540582	1.16114037
H	2.85991308	−3.68170341	1.01136157
H	−1.35227397	−3.18428680	0.72241901
H	1.34890749	3.16146953	−0.81503459
H	−0.56564783	4.57112099	−1.26335631
H	−2.86362864	3.66551148	−1.08527698
H	−2.78846080	−2.09484618	0.38301870
H	2.78001620	2.09427345	−0.39281371
H	−4.48028633	−2.77018832	−1.16796046
H	−6.56893712	−4.00316917	−0.98830746
H	−8.24090720	−0.81223521	1.35049570
H	−6.15686606	0.41451405	1.16549793
H	7.96126803	−4.50423125	1.41854805
H	7.10804729	−2.98210315	3.15323853
H	4.01201357	−2.39752881	−1.87698543
H	4.87067220	−3.90774538	−3.60165283

H	6.78686634	−5.42173091	−3.11560756
H	7.83951609	−5.39790841	−0.88055211
H	−10.39301508	−4.12861300	−1.08389034
H	−9.68533349	−2.59436249	−1.61481052
H	−8.76167439	−4.09450725	−1.76315343
H	−9.54205737	−5.28170824	1.02092521
H	−8.21925395	−4.57147464	1.96043352
H	−7.89807411	−5.28385360	0.37445905
H	−10.24752531	−1.64118682	0.69725678
H	−10.88105557	−3.22006984	1.16558572
H	−9.64592836	−2.44253574	2.15862151
H	−7.95953270	4.50234694	−1.47241364
H	−7.13021490	2.94464484	−3.18706881
H	−3.99179651	2.43352532	1.82498096
H	−4.82781166	3.97806751	3.53028703
H	−6.74073325	5.49299616	3.03446217
H	−7.81297145	5.43554667	0.80939146
H	4.42250399	2.74728898	1.21883942
H	6.49791212	4.00702151	1.11881465
H	8.26677587	0.88497705	−1.24039501
H	6.18991662	−0.37055434	−1.13753676
H	9.82224339	5.17481056	0.49274102
H	8.09391372	5.33904093	0.17641065
H	8.65590758	4.53646048	1.65312525
H	10.98617161	3.00080090	0.39553656
H	10.14686167	1.51481643	−0.06267204
H	9.82721459	2.25699317	1.50939055
H	8.45253174	4.22518024	−2.10680209
H	10.18045691	4.15503459	−1.72368213
H	9.32532452	2.69232588	−2.22612510
H	5.61380997	−1.41694382	3.96350065
H	5.25417963	−0.15789786	2.77965239
H	4.01331478	−1.32612209	3.22408409
H	−5.65606631	1.35204786	−3.98037109
H	−4.04637469	1.27439386	−3.25953554
H	−5.28266437	0.11698723	−2.77564127

E = −2368.09346310 a.u.

Table S4. Compound **2**.

	x	y	z
C	2.40890381	−2.85875946	−0.00007171
C	1.05665804	−2.64513297	0.00008591
C	0.49936862	−1.32944159	0.00004884
C	1.41336704	−0.21592621	−0.00002369
C	2.83728028	−0.45740773	−0.00012778
C	3.29265821	−1.76084309	−0.00020194
C	0.91211190	1.11294538	0.00003244
C	1.83328273	2.24577380	0.00008878
C	3.18249941	2.14350603	0.00015001
B	3.82456126	0.75139659	0.00002361
C	−0.91211023	−1.11293975	0.00002480
C	−0.49936873	1.32944755	0.00004917
C	−1.41336645	0.21593097	−0.00002779
C	−2.83728061	0.45740740	−0.00013355
C	−3.29266253	1.76084113	−0.00021272
C	−2.40891108	2.85875960	−0.00008536
C	−1.05666467	2.64513687	0.00007860
C	−1.83327491	−2.24577246	0.00006859
C	−3.18249198	−2.14350952	0.00013352
B	−3.82455841	−0.75140109	0.00001385
O	5.19102159	0.64148046	0.00002294
O	−5.19102199	−0.64148837	0.00005150
H	2.79834183	−3.87008142	−0.00008335
H	0.40873389	−3.50838213	0.00024840
H	4.35911310	−1.96896688	−0.00035052
H	1.39523541	3.23521007	0.00005340
H	3.76420497	3.06206541	0.00022365
H	−4.35911794	1.96896185	−0.00036693
H	−2.79835214	3.87008045	−0.00010462
H	−0.40874646	3.50838914	0.00023765
H	−1.39522038	−3.23520676	0.00001894
H	−3.76419396	−3.06207109	0.00019856
H	5.52252817	−0.26225399	−0.00009777
H	−5.52253071	0.26224539	−0.00001705

E = −893.66721304 a.u.

Table S5. Compound **3**.

	x	y	z
C	2.29964829	−2.94440208	0.15792409
C	3.22440173	−1.88334054	0.10126045
C	2.81717475	−0.56033020	0.02971984
C	1.40397008	−0.27143326	0.01456538
C	0.44974475	−1.34560897	0.07216792
C	0.95509497	−2.67975874	0.14367261
C	0.95337836	1.07353023	−0.05767494
C	−0.44973664	1.34568077	−0.07188878
C	−1.40396168	0.27150425	−0.01431405
C	−0.95337116	−1.07345374	0.05804056

C	−0.95508539	2.67982537	−0.14350226
C	−2.29963822	2.94446032	−0.15795132
C	−3.22439213	1.88339629	−0.10134889
C	−2.81716552	0.56039479	−0.02963550
B	−3.86587506	−0.58315400	0.03220497
C	−3.26855725	−1.99165105	0.10774839
C	−1.91981320	−2.15794258	0.11692561
B	3.86588275	0.58322394	−0.03209021
C	3.26856192	1.99173312	−0.10735899
C	1.91981744	2.15802861	−0.11638686
C	−5.42464689	−0.32345872	0.01877093
C	−6.13506083	−0.12610904	1.22227551
C	−7.51884590	0.07279595	1.19423334
C	−8.23651164	0.08182636	−0.00264124
C	−7.52700846	−0.11253255	−1.18947270
C	−6.14435626	−0.31556195	−1.19629164
C	5.42464964	0.32348796	−0.01883260
C	6.14445833	0.31523886	1.19618957
C	7.52708360	0.11214616	1.18921309
C	8.23649820	−0.08193751	0.00226348
C	7.51875149	−0.07255194	−1.19454019
C	6.13495479	0.12641733	−1.22242433
C	5.41059305	0.12266028	−2.55237423
C	−5.41079763	−0.12213578	2.55227798
C	−5.42931031	−0.52038631	−2.51536702
C	−9.73598411	0.26477454	−0.01339872
C	9.73596321	−0.26495024	0.01290303
C	5.42950600	0.51974172	2.51536398
H	2.64898929	−3.96888388	0.21280265
H	4.28601025	−2.10572246	0.11345209
H	0.27322159	−3.51551454	0.18844939
H	−0.27321025	3.51558231	−0.18822674
H	−2.64897803	3.96893732	−0.21292344
H	−4.28600105	2.10576613	−0.11373049
H	−3.87993221	−2.88975302	0.15726887
H	−1.52874298	−3.16588077	0.17200746
H	3.87993306	2.88984514	−0.15674069
H	1.52874654	3.16598272	−0.17116803
H	−8.04810073	0.22367009	2.13128578
H	−8.06291684	−0.10694780	−2.13497434
H	8.06307464	0.10631058	2.13466687
H	8.04792425	−0.22316689	−2.13168080
H	6.11266769	0.05093406	−3.38548418
H	4.71607461	−0.72044474	−2.62833071
H	4.81955993	1.03385750	−2.69004086
H	−4.82084019	−1.03392591	2.69067841
H	−4.71529519	0.72020285	2.62763953
H	−6.11285328	−0.04897622	3.38527766
H	−6.13505766	−0.55058073	−3.34794779

H	−4.71403600	0.28455609	−2.71377354
H	−4.86259001	−1.45709986	−2.52280739
H	−10.07657592	0.81627635	0.86596689
H	−10.06538435	0.80569311	−0.90403713
H	−10.25149726	−0.70220441	−0.01234437
H	10.06530545	−0.80673925	0.90303647
H	10.07656449	−0.81562832	−0.86697313
H	10.25151785	0.70200620	0.01280712
H	4.71457386	−0.28549143	2.71383288
H	6.13534881	0.55017513	3.34785530
H	4.86241667	1.45622862	2.52291333

E = −1441.23690832 a.u.

Table S6. Compound **4**.

	x	y	z
C	2.27515052	−0.22440974	−2.95966921
C	3.19453987	−0.36623173	−1.90233518
C	2.79253053	−0.34545865	−0.57566677
C	1.39175147	−0.17213125	−0.27912412
C	0.44306660	−0.02828428	−1.34974419
C	0.94177177	−0.06150794	−2.68788315
C	0.94820666	−0.14304242	1.06997843
C	−0.44309688	0.02770734	1.34961726
C	−1.39176720	0.17166831	0.27899697
C	−0.94822639	0.14253198	−1.07010495
C	−0.94182223	0.06078729	2.68775189
C	−2.27518541	0.22381401	2.95953967
C	−3.19453636	0.36591219	1.90221174
C	−2.79252284	0.34516575	0.57554392
B	−3.83211764	0.50652066	−0.56373421
C	−3.24760694	0.45490795	−1.97692997
C	−1.91003855	0.28516574	−2.15059543
B	3.83215844	−0.50655114	0.56361977
C	3.24764587	−0.45496938	1.97681398
C	1.91003285	−0.28557080	2.15047016
C	−5.37692790	0.71260212	−0.28975812
C	−6.25213611	−0.42203494	−0.19438746
C	−7.65431877	−0.23843623	0.03309157
C	−8.15503067	1.08227403	0.15903603
C	−7.30834792	2.15589961	0.06216475
C	−5.91499083	1.98855101	−0.16256740
C	5.37699236	−0.71243374	0.28963348
C	6.25209828	0.42230938	0.19459130
C	7.65430924	0.23890211	−0.03286653

C	8.15515408	−1.08173433	−0.15909659
C	7.30856854	−2.15546160	−0.06253122
C	5.91517557	−1.98829891	0.16215495
C	5.77029933	1.75585624	0.32314353
C	−5.04736443	3.22726734	−0.23089561
C	−5.77048009	−1.75566377	−0.32267207
C	5.04766981	−3.22711886	0.23018550
C	−6.61570893	−2.83680133	−0.23182085
C	−7.99835791	−2.64599122	−0.00511723
C	−8.50234690	−1.37380734	0.12330309
C	6.61542635	2.83710234	0.23258716
C	7.99810247	2.64648170	0.00591649
C	8.50222625	1.37437468	−0.12277081
H	2.61955149	−0.24371183	−3.98704771
H	4.24680677	−0.49496853	−2.13109761
H	0.26396404	0.04396566	−3.52142866
H	−0.26404349	−0.04490861	3.52129279
H	−2.61960355	0.24299629	3.98691449
H	−4.24677844	0.49484476	2.13097675
H	−3.85740929	0.54877605	−2.87222156
H	−1.52609023	0.25229137	−3.16218808
H	3.85746077	−0.54870981	2.87211002
H	1.52605843	−0.25289825	3.16205971
H	−9.21679175	1.23044909	0.32764032
H	−7.70440137	3.16266485	0.15432157
H	9.21693849	−1.22976813	−0.32767874
H	7.70472406	−3.16216799	−0.15489110
H	4.71195749	1.92038137	0.49609969
H	−4.70056085	3.52211819	0.76614048
H	−4.16029574	3.07315239	−0.84961045
H	−5.60141336	4.07377016	−0.64405277
H	−4.71216584	−1.92033267	−0.49565441
H	5.60182845	−4.07368035	0.64307194
H	4.16062931	−3.07326484	0.84900499
H	4.70082271	−3.52172603	−0.76690711
H	−6.22210234	−3.84204088	−0.33386369
H	−8.65633658	−3.50478559	0.06620221
H	−9.56243212	−1.21793359	0.29657375
H	6.22170906	3.84227761	0.33483479
H	8.65600373	3.50535494	−0.06516915
H	9.56233539	1.21865092	−0.29603030

E = −1591.28248272 a.u.

Table S7. *Ci*-structure of compound **(B-Dbf)₂**.

	x	y	z
C	1.88407135	3.08158865	−0.95257418
C	2.94633695	2.18271951	−0.74154374
C	2.73709267	0.87368399	−0.33546411
C	1.36790783	0.41626850	−0.17409384
C	0.28315659	1.35211114	−0.30437482
C	0.59568175	2.68352210	−0.71146824
C	1.07435911	−0.95289446	0.08591401
C	−0.28311248	−1.35160430	0.30553120
C	−1.36788402	−0.41583386	0.17504351
C	−1.07438067	0.95329583	−0.08523065
C	−0.59547611	−2.68282944	0.71334883
C	−1.88381442	−3.08085491	0.95478886
C	−2.94615456	−2.18219047	0.74323745
C	−2.73703786	−0.87333330	0.33650802
B	−3.87738170	0.15569023	0.13514354
C	−3.43657013	1.61802055	0.08048354
C	−2.13307181	1.95055940	−0.05868557
B	3.87734058	−0.15558775	−0.13480987
C	3.43638040	−1.61790565	−0.08084893
C	2.13288058	−1.95032510	0.05857324
C	−5.43739117	0.20857842	0.03634486
C	5.43736762	−0.20870661	−0.03653541
C	4.63367805	−2.55102431	−0.17539389
C	−4.63400513	2.55106939	0.17404778
C	−6.47963132	−0.77049879	−0.12851569
C	−7.85014345	−0.35828409	−0.03307639
C	−8.15112333	1.01596387	0.16881198
C	−7.15483175	1.95807660	0.23240003
C	−5.80250744	1.55971621	0.15247367
C	−6.22820127	−2.13072496	−0.44268803
C	−7.25353188	−3.03849210	−0.59484145
C	−8.59720070	−2.63543132	−0.44086895
C	−8.88566750	−1.31787807	−0.17402290
C	6.47976642	0.77015291	0.12859556
C	7.85019971	0.35786115	0.03235504
C	8.15095876	−1.01627987	−0.17059279
C	7.15454753	−1.95825160	−0.23440406
C	5.80229688	−1.55980857	−0.15366996
C	6.22858969	2.13018380	0.44381499
C	7.25407302	3.03773438	0.59623388
C	8.59764230	2.63464317	0.44147478
C	8.88587483	1.31725025	0.17358528
C	−4.60502294	3.35699946	1.49381958
C	−4.72368123	3.52293072	−1.02390894
C	4.60411003	−3.35618897	−1.49561951
C	4.72369467	−3.52359713	1.02196109

	x	y	z
H	2.08592848	4.08958906	−1.29601583
H	3.95420110	2.52896172	−0.92924081
H	−0.19789095	3.39706974	−0.87537361
H	0.19822380	−3.39615148	0.87765346
H	−2.08558491	−4.08865322	1.29887230
H	−3.95399060	−2.52843659	0.93108433
H	−1.84315433	2.99311066	−0.12348020
H	1.84274407	−2.99285765	0.12282973
H	−9.19211124	1.31342862	0.24485364
H	−7.41057930	3.00566414	0.34837563
H	−5.20890389	−2.45185127	−0.60352548
H	−7.02759505	−4.06914512	−0.84491914
H	−9.39591666	−3.35970772	−0.55287277
H	−9.91560904	−0.98864930	−0.08273841
H	9.19188581	−1.31379826	−0.24725339
H	7.41014247	−3.00578735	−0.35117681
H	5.20938320	2.45130607	0.60525127
H	7.02833812	4.06823331	0.84712788
H	9.39647500	3.35875640	0.55370046
H	9.91574896	0.98798377	0.08168222
H	−5.50805422	3.96464515	1.60223405
H	−4.53451760	2.69224991	2.35827062
H	−3.74369339	4.03026631	1.50965580
H	−5.62895809	4.13418396	−0.96881504
H	−3.86560129	4.20070419	−1.03086580
H	−4.73640084	2.97736035	−1.97062109
H	5.50702851	−3.96388180	−1.60471884
H	3.74269461	−4.02934437	−1.51152060
H	4.53336351	−2.69093755	−2.35966461
H	5.62888798	−4.13491096	0.96617188
H	4.73682336	−2.97858447	1.96898848
H	3.86554425	−4.20128155	1.02883150

E = −1746.16103462 a.u.

Level of theory: B3LYP/6-311G**

Table S8. Compound **Ph-3**.

	x	y	z
C	1.60397351	−3.31758729	0.60612743
C	2.73613715	−2.49621230	0.44558459
C	2.62262790	−1.13710318	0.19484957
C	1.30646284	−0.56375848	0.10438240
C	0.14238788	−1.39386623	0.23610152

C	0.34717844	−2.78097111	0.49777110
C	1.16814633	0.83126652	−0.11536376
C	−0.14239706	1.39385586	−0.23620493
C	−1.30647099	0.56375140	−0.10448571
C	−1.16816295	−0.83125294	0.11538834
C	−0.34717859	2.78093474	−0.49803878
C	−1.60397167	3.31751693	−0.60656802
C	−2.73613812	2.49614588	−0.44600854
C	−2.62263295	1.13707260	−0.19507757
B	−3.90023264	0.26403976	−0.03744025
C	−3.64485313	−1.25868022	0.09338884
C	−2.34195886	−1.67116427	0.18377216
B	3.90022736	−0.26404924	0.03735225
C	3.64481203	1.25869139	−0.09319272
C	2.34194070	1.67121990	−0.18348151
C	4.70748970	2.29821673	−0.10704149
C	−4.70749583	−2.29821432	0.10754328
C	−4.55731611	−3.48459631	−0.63274968
C	−5.53369423	−4.47590117	−0.61533451
C	−6.68893103	−4.30737225	0.14503330
C	−6.85894483	−3.13488710	0.87848929
C	−5.88615258	−2.14013856	0.85440713
C	4.55747018	3.48423195	0.63385016
C	5.53388124	4.47551805	0.61673321
C	6.68896050	4.30732071	−0.14393998
C	6.85880058	3.13518968	−0.87800891
C	5.88598546	2.14045902	−0.85421791
C	−5.33036232	0.93604696	−0.02947400
C	−5.82155639	1.57775406	1.12843955
C	−7.08570871	2.17251116	1.11464426
C	−7.88959637	2.16507485	−0.02498149
C	−7.39305131	1.53847330	−1.16843098
C	−6.13980062	0.92386826	−1.18660168
C	−5.65674196	0.25726784	−2.45618019
C	−4.99921937	1.62228543	2.40023894
C	−9.26476177	2.78898990	−0.01474614
C	5.33036904	−0.93600839	0.02927719
C	6.13974993	−0.92414346	1.18637778
C	7.39305078	−1.53875034	1.16806065
C	7.88961775	−2.16500520	0.02449564
C	7.08571289	−2.17218491	−1.11518156
C	5.82159856	−1.57745724	−1.12883812
C	4.99923816	−1.62164687	−2.40062653
C	5.65663999	−0.25802812	2.45619339
C	9.26485761	−2.78874827	0.01391066
H	1.72482026	−4.37483929	0.81375925
H	3.72503804	−2.93496466	0.52305127
H	−0.50064998	−3.43755675	0.62681815
H	0.50065790	3.43750521	−0.62710507

H	−1.72481958	4.37474385	−0.81432835
H	−3.72503483	2.93487581	−0.52364406
H	−2.17145651	−2.73167147	0.32206729
H	2.17144163	2.73177897	−0.32139269
H	−3.67590452	−3.61527539	−1.25111713
H	−5.39615873	−5.37628130	−1.20423166
H	−7.45191752	−5.07752755	0.15911026
H	−7.75485678	−2.99125478	1.47241002
H	−6.03777647	−1.23461860	1.42645509
H	3.67614624	3.61464419	1.25240105
H	5.39648799	5.37561692	1.20609292
H	7.45196996	5.07745757	−0.15779049
H	7.75459161	2.99183432	−1.47217844
H	6.03745928	1.23520472	−1.42672827
H	−7.44997491	2.65510230	2.01756435
H	−7.99819349	1.52447518	−2.07088507
H	−6.39151611	0.35523487	−3.25800059
H	−4.71766222	0.69533271	−2.80990383
H	−5.47610107	−0.81050250	−2.29811952
H	−4.65778538	0.62542193	2.69840565
H	−4.10302197	2.23870386	2.28012018
H	−5.57794239	2.03532442	3.22906871
H	−9.33925718	3.57829094	0.73706531
H	−9.51353758	3.22237968	−0.98675657
H	−10.03460714	2.04391896	0.21555484
H	7.99816820	−1.52498165	2.07052863
H	7.45000195	−2.65454417	−2.01822054
H	5.57771627	−2.03510859	−3.22941602
H	4.10267007	−2.23751092	−2.28044457
H	4.65839101	−0.62460784	−2.69889090
H	4.71800773	−0.69684462	2.81018816
H	6.39175683	−0.35555378	3.25775348
H	5.47515135	0.80962319	2.29833300
H	9.51663506	−3.21613677	0.98777639
H	9.33729673	−3.58259535	−0.73332292
H	10.03384401	−2.04495358	−0.22332145

E = −1903.44564587 a.u.

Table S9. Anion of compound **Ph-3**.

	x	y	z
C	1.64661914	−3.35392000	0.34804113
C	2.76546033	−2.53370175	0.24144607
C	2.64604004	−1.14550859	0.07465429
C	1.32598009	−0.57712483	0.01714881

C	0.16618760	−1.41846257	0.12279070
C	0.37576222	−2.80420404	0.28867398
C	1.17351457	0.83465789	−0.14136820
C	−0.15885878	1.40042125	−0.26664540
C	−1.31922692	0.56407161	−0.13272470
C	−1.16764688	−0.84339498	0.06331870
C	−0.36468193	2.77164859	−0.52841640
C	−1.63467028	3.31908786	−0.62110354
C	−2.75439914	2.51159551	−0.44763484
C	−2.63801023	1.13487239	−0.20046331
B	−3.89853646	0.25819081	−0.02454373
C	−3.64312364	−1.23724472	0.13964761
C	−2.32086671	−1.66195669	0.17446954
B	3.90543222	−0.25412112	−0.01896634
C	3.64606587	1.24844864	−0.08514256
C	2.32255444	1.66618735	−0.15244003
C	4.69203722	2.30279069	−0.03599151
C	−4.69645598	−2.28239524	0.21796376
C	−4.56881423	−3.49753263	−0.48359901
C	−5.54105503	−4.49104360	−0.40926260
C	−6.68268203	−4.30214596	0.36728223
C	−6.83519361	−3.10351612	1.06267385
C	−5.86175338	−2.11184906	0.98710841
C	4.51276015	3.46853288	0.73505185
C	5.47585071	4.47257257	0.77882426
C	6.66020305	4.34412681	0.05565117
C	6.86453797	3.19418754	−0.70549702
C	5.90019213	2.19167767	−0.74816738
C	−5.34757894	0.92367237	−0.05596070
C	−5.86681020	1.59736514	1.07242163
C	−7.13649264	2.18055397	1.02696459
C	−7.92727136	2.12972297	−0.12059490
C	−7.40814128	1.47602188	−1.23740120
C	−6.14574244	0.87647526	−1.21984365
C	−5.64337500	0.17812809	−2.46469120
C	−5.05729417	1.69761187	2.34854117
C	−9.31103573	2.73701478	−0.14346644
C	5.35423832	−0.92062360	−0.00355146
C	6.11898364	−0.98146253	1.18192156
C	7.37845089	−1.58725296	1.18111455
C	7.92616564	−2.14353359	0.02563035
C	7.16780654	−2.08844255	−1.14335333
C	5.90204853	−1.49569953	−1.17193354
C	5.12537936	−1.48239313	−2.47202797
C	5.58109322	−0.39530969	2.46890649
C	9.30640591	−2.75925269	0.03337374
H	1.76207491	−4.42552636	0.47963416
H	3.75723951	−2.97102058	0.29214194
H	−0.47004506	−3.47205420	0.37549490

H	0.48367185	3.42543334	−0.67740997
H	−1.74881156	4.37835606	−0.83062044
H	−3.74519467	2.94913965	−0.51432399
H	−2.15522792	−2.72306559	0.32328155
H	2.15115664	2.73426259	−0.22894066
H	−3.69993023	−3.64907098	−1.11469411
H	−5.41038302	−5.41202098	−0.96924651
H	−7.44378422	−5.07330732	0.42452244
H	−7.71834757	−2.93821910	1.67185118
H	−5.99969571	−1.18994061	1.53645083
H	3.60950896	3.57191617	1.32631175
H	5.30413592	5.35375063	1.38945967
H	7.41426058	5.12352166	0.09010855
H	7.78178349	3.07566612	−1.27386768
H	6.07980690	1.30807540	−1.34601572
H	−7.51502974	2.68976755	1.91048754
H	−8.00091717	1.42922990	−2.14806477
H	−6.33758750	0.31009593	−3.29906203
H	−4.66572384	0.56237971	−2.77014113
H	−5.52235412	−0.89557128	−2.29160706
H	−4.70991356	0.71483495	2.68253663
H	−4.16127637	2.30854089	2.20442494
H	−5.64560082	2.14252647	3.15563009
H	−9.37689348	3.60637860	0.51692346
H	−9.58883029	3.05811856	−1.15125781
H	−10.06953792	2.01806849	0.18905455
H	7.94560042	−1.62480628	2.10839213
H	7.56849326	−2.52098321	−2.05742578
H	5.73861632	−1.84235814	−3.30259359
H	4.23427547	−2.11422400	−2.40875648
H	4.77285109	−0.47638651	−2.71978574
H	4.60390909	−0.81824915	2.72044205
H	6.26038340	−0.58549107	3.30429512
H	5.44538630	0.68691545	2.38177688
H	9.54712726	−3.18611270	1.01105022
H	9.39277668	−3.55502908	−0.71191289
H	10.07860495	−2.01473655	−0.19503117

E = −1903.53621340 a.u.

Table S10. Compound **tBuPh-4**.

	x	y	z
C	0.71314698	−3.54329217	0.93495462
C	2.01683012	−3.02224619	0.83798452
C	2.25038709	−1.69927861	0.49248251

C	1.12021024	−0.84628659	0.23607435
C	−0.21534534	−1.36605643	0.32315301
C	−0.36713096	−2.73815767	0.68188289
C	1.33616977	0.51474912	−0.10344347
C	0.20980930	1.35464617	−0.37778297
C	−1.12588838	0.83639568	−0.28551565
C	−1.34236393	−0.52337917	0.05925618
C	0.36281307	2.72251968	−0.75180858
C	−0.71687972	3.52661256	−1.01039592
C	−2.02101231	3.00929362	−0.90109860
C	−2.25547331	1.69011543	−0.54183307
B	−3.71056137	1.15868640	−0.43230801
C	−3.84422339	−0.34325794	−0.08581288
C	−2.68799365	−1.04399325	0.13382818
B	3.70494425	−1.16217285	0.40148883
C	3.83640488	0.34452937	0.07652634
C	2.68039996	1.04113029	−0.15693105
C	−4.94045649	2.11616824	−0.70696178
C	−5.13411282	−1.07437676	−0.00148624
C	4.93585642	−2.11908894	0.67345487
C	−5.29276470	−2.34130566	−0.58918915
C	−6.48858876	−3.04039384	−0.49099378
C	−7.59168963	−2.52049189	0.20312271
C	−7.43278607	−1.25705740	0.78195083
C	−6.23988751	−0.54566292	0.67537541
C	5.40509146	−3.01966178	−0.34034534
C	6.51108022	−3.89122450	−0.07880464
C	7.12243245	−3.84729795	1.19756876
C	6.66220281	−2.98331313	2.15718653
C	5.57192168	−2.10955047	1.91149420
C	4.81254865	−3.07326789	−1.63423458
C	5.27623425	−3.93228057	−2.60176295
C	6.36411616	−4.79337828	−2.33186585
C	6.96458840	−4.76980532	−1.09730235
C	−8.89830970	−3.32745069	0.29232259
C	−9.45475773	−3.56229369	−1.13158587
C	−8.61716085	−4.69214358	0.96335028
C	−9.97826723	−2.60285397	1.11601557
C	−5.39623689	3.03572573	0.29589688
C	−6.50059166	3.90798616	0.02987540
C	−7.12357706	3.84606478	−1.24012851
C	−6.67639508	2.96378105	−2.18918587
C	−5.58825574	2.08875008	−1.93856861
C	−4.79213379	3.10758044	1.58353386
C	−5.24369579	3.98407935	2.54107749
C	−6.33000275	4.84572191	2.26667524
C	−6.94118485	4.80508530	1.03782910
C	5.12169096	1.08708405	0.03148783
C	5.25564656	2.34038400	0.64455681

C	6.44919056	3.05729081	0.58919890
C	7.56857533	2.56031327	−0.08553949
C	7.43319602	1.30240075	−0.69313949
C	6.25026457	0.57843723	−0.63131040
C	8.90151175	3.32292457	−0.17656992
C	8.85309733	4.67510091	0.55791945
C	10.02787294	2.47214870	0.45515663
C	9.23671141	3.59469736	−1.66166720
C	5.12761104	−1.17381206	3.01511749
C	−5.16018822	1.13069623	−3.02935412
H	0.56214394	−4.58143152	1.20841460
H	2.86199422	−3.67110768	1.03786081
H	−1.35392719	−3.16945564	0.76394182
H	1.35023216	3.15022711	−0.84446529
H	−0.56512203	4.56106732	−1.29706591
H	−2.86587837	3.65802576	−1.10249714
H	−2.79147521	−2.08749373	0.40461378
H	2.78330577	2.08798656	−0.41458145
H	−4.47293096	−2.77139385	−1.15494448
H	−6.56083431	−4.00850973	−0.97428084
H	−8.24730199	−0.80245675	1.33036585
H	−6.16575190	0.42643727	1.14587027
H	7.95890557	−4.50695438	1.40497532
H	7.13772329	−2.96092391	3.13279546
H	3.97530565	−2.42092366	−1.85799069
H	4.80564457	−3.95156281	−3.57856697
H	6.72147352	−5.46819383	−3.10165279
H	7.80257513	−5.42519755	−0.88159448
H	−10.38301099	−4.14060675	−1.08763649
H	−9.66971768	−2.61148954	−1.62689372
H	−8.74779010	−4.11215948	−1.75702644
H	−9.53924681	−5.27739142	1.03571918
H	−8.22114809	−4.55498668	1.97326869
H	−7.89237688	−5.28176618	0.39746220
H	−10.24889980	−1.64032187	0.67399621
H	−10.88357673	−3.21484700	1.15339297
H	−9.65430835	−2.42797022	2.14552399
H	−7.95856404	4.50650089	−1.45101660
H	−7.16089554	2.92736714	−3.15995526
H	−3.95592718	2.45503143	1.81056464
H	−4.76462091	4.01686284	3.51338903
H	−6.67771152	5.53441682	3.02854658
H	−7.77807179	5.46077424	0.81878462
H	4.41944644	2.75244561	1.19967880
H	6.49443336	4.01477944	1.09159220
H	8.27015244	0.87096243	−1.23067390
H	6.19500683	−0.38519645	−1.12144339
H	9.81870632	5.17911573	0.46280271
H	8.09203979	5.33848413	0.13810488

H	8.64934096	4.55126207	1.62499731
H	10.98390789	3.00151370	0.39380767
H	10.14466934	1.51187505	−0.05202389
H	9.81824503	2.26930246	1.50894566
H	8.45704927	4.20010737	−2.13204363
H	10.18451237	4.13587171	−1.74416708
H	9.32996207	2.66834064	−2.23286348
H	5.61616068	−1.41869211	3.96066319
H	5.37404272	−0.13472594	2.77359851
H	4.04682519	−1.22135130	3.17780104
H	−5.64795291	1.36820521	−3.97720497
H	−4.07934251	1.16006945	−3.19558596
H	−5.42088380	0.09898859	−2.77135373

E = −2368.08179644 a.u.

Table S11. Anion of compound **tBuPh-4**.

	x	y	z
C	0.74480326	−3.56570192	0.88903546
C	2.03412053	−3.05311752	0.79490938
C	2.26850720	−1.71028283	0.45977372
C	1.13378613	−0.85899040	0.21668655
C	−0.20038531	−1.38489741	0.30555895
C	−0.34644663	−2.74620280	0.64720786
C	1.33991998	0.51642258	−0.11149263
C	0.19394770	1.36692774	−0.38659314
C	−1.14052760	0.84402101	−0.28708563
C	−1.34751255	−0.52862551	0.05245119
C	0.34197080	2.71960927	−0.76005459
C	−0.74849138	3.53755120	−1.01044010
C	−2.03856170	3.03213735	−0.89171222
C	−2.27439684	1.69619399	−0.53078125
B	−3.71501353	1.15630123	−0.41496485
C	−3.84251792	−0.32307649	−0.07430443
C	−2.66949826	−1.03844223	0.12914351
B	3.70819706	−1.16148757	0.37423368
C	3.83287056	0.32479962	0.06448601
C	2.65967469	1.03539278	−0.15403554
C	−4.96091077	2.11194400	−0.70394702
C	−5.12344567	−1.06934661	0.01628150
C	4.95493105	−2.11559867	0.66471318
C	−5.27697556	−2.34094267	−0.56765159
C	−6.46649396	−3.05261613	−0.47155641
C	−7.57972367	−2.54142495	0.21191846
C	−7.43255921	−1.27451144	0.78651872

C	−6.24205174	−0.55694623	0.68871144	H	4.02602354	−2.43587592	−1.85741036
C	5.45493916	−3.01173168	−0.33981270	H	4.88943890	−3.95466221	−3.58243521
C	6.57077591	−3.87059944	−0.07050501	H	6.82818037	−5.44291059	−3.09404794
C	7.16813955	−3.82249404	1.21178492	H	7.89077231	−5.38596683	−0.86423288
C	6.67973980	−2.96752611	2.16645435	H	−10.34941527	−4.20237032	−1.08854842
C	5.57865038	−2.11022113	1.91047482	H	−9.64645722	−2.66690154	−1.63045847
C	4.87300277	−3.07584944	−1.63832194	H	−8.70672394	−4.15632890	−1.74423741
C	5.35560069	−3.92768846	−2.60318223	H	−9.51196401	−5.31525108	1.04704918
C	6.45492514	−4.77280640	−2.32646244	H	−8.20955069	−4.56886249	1.99182512
C	7.04514283	−4.74137551	−1.08691836	H	−7.85607442	−5.30166699	0.42590116
C	−8.87966737	−3.36068063	0.29663041	H	−10.24511210	−1.68248536	0.65646929
C	−9.42661011	−3.61289937	−1.12799113	H	−10.87562267	−3.26013084	1.14018892
C	−8.59537229	−4.71867337	0.97969308	H	−9.65777314	−2.45594154	2.13653004
C	−9.97378483	−2.64114611	1.10636488	H	−8.01354889	4.47299515	−1.46772041
C	−5.44128231	3.02938290	0.29079322	H	−7.17764601	2.90579678	−3.17270568
C	−6.55542797	3.89033597	0.02123952	H	−3.99503072	2.47182017	1.79876370
C	−7.17061880	3.82311987	−1.25172786	H	−4.82602025	4.02613528	3.50812410
C	−6.70108242	2.94754624	−2.19715426	H	−6.76235040	5.51740928	3.01956336
C	−5.60214754	2.08770126	−1.94050312	H	−7.85524515	5.42790768	0.80551901
C	−4.84113841	3.11305286	1.57985597	H	4.38880416	2.74742587	1.18041995
C	−5.30560788	3.98469246	2.53588443	H	6.44939731	4.03163393	1.08832052
C	−6.40352933	4.83159074	2.25900719	H	8.27798479	0.89739338	−1.20784483
C	−7.01060068	4.78203841	1.02823759	H	6.20789134	−0.36885868	−1.12421629
C	5.10864913	1.08390424	0.02386265	H	9.77749971	5.22625704	0.48945991
C	5.23459161	2.34083439	0.63613189	H	8.04939853	5.36537475	0.15061179
C	6.42134403	3.07101202	0.58874887	H	8.60135908	4.58719450	1.64229961
C	7.55331613	2.58449331	−0.07203549	H	10.96591158	3.05872561	0.43355679
C	7.43254995	1.32439812	−0.67798814	H	10.13720810	1.56057000	−0.01249147
C	6.25264444	0.59349365	−0.63033347	H	9.79367380	2.32117719	1.54167215
C	8.88085543	3.35861906	−0.15350857	H	8.44949299	4.23222488	−2.11135142
C	8.81540673	4.71227744	0.57738409	H	10.17685258	4.17935255	−1.71186044
C	10.01194597	2.52259612	0.48929101	H	9.32999806	2.70565385	−2.20338454
C	9.23023592	3.63295505	−1.63480293	H	5.58626503	−1.43783622	3.96677110
C	5.10568574	−1.19125109	3.01603059	H	5.33478624	−0.14624370	2.78415667
C	−5.15104610	1.14445652	−3.03467221	H	4.02322111	−1.25683453	3.15414498
H	0.58613281	−4.60715954	1.15146964	H	−5.64235914	1.37673548	−3.98353416
H	2.88200119	−3.70223007	0.98510123	H	−4.07000333	1.19861618	−3.18817193
H	−1.33344890	−3.17960219	0.73041931	H	−5.38514984	0.10588819	−2.77980477
H	1.33002833	3.14571034	−0.86560517				
H	−0.58868001	4.57210821	−1.29823493				
H	−2.88606403	3.68099168	−1.08439613				
H	−2.77817941	−2.08434707	0.39376322				
H	2.76684349	2.08704138	−0.39549790				
H	−4.44953083	−2.76669802	−1.12532090				
H	−6.52436024	−4.02518811	−0.95025971				
H	−8.25326735	−0.82224771	1.32926114				
H	−6.17595825	0.41484923	1.16122332				
H	8.01241793	−4.47068754	1.42755346				
H	7.14248451	−2.94077022	3.14914264				

E = −2368.17414513 a.u.

Table S12. Compound **2**.

	x	y	z
C	2.40693064	−2.85798508	0.01864448
C	1.05539689	−2.64351810	0.01423574

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	x	y	z
C	0.49778385	−1.32867112	0.00286360
C	1.41220187	−0.21593941	−0.00010625
C	2.83552629	−0.45750393	0.00171815
C	3.28962241	−1.75989518	0.01086073
C	0.91328281	1.11300284	−0.00417365
C	1.83585120	2.24476332	−0.01622333
C	3.18401509	2.14372180	−0.01785062
B	3.82460625	0.75184409	−0.00622317
C	−0.91328199	−1.11300341	−0.00417455
C	−0.49778275	1.32867061	0.00286379
C	−1.41220111	0.21593921	−0.00010880
C	−2.83552563	0.45750424	0.00171135
C	−3.28962112	1.75989572	0.01085580
C	−2.40692882	2.85798508	0.01864601
C	−1.05539523	2.64351757	0.01423952
C	−1.83585061	−2.24476398	−0.01622029
C	−3.18401478	−2.14372231	−0.01785140
B	−3.82460671	−0.75184361	−0.00623605
O	5.18877050	0.63648582	−0.00487491
O	−5.18877675	−0.63648441	−0.00486824
H	2.79585220	−3.86987104	0.02842054
H	0.40550090	−3.50535900	0.02257526
H	4.35732100	−1.96699527	0.01331693
H	1.39724003	3.23422680	−0.02740898
H	3.77002182	3.05881197	−0.02865988
H	−4.35731971	1.96699662	0.01330905
H	−2.79585001	3.86987106	0.02842555
H	−0.40549895	3.50535781	0.02258562
H	−1.39723944	−3.23422789	−0.02739742
H	−3.77002164	−3.05881274	−0.02865589
H	5.51052928	−0.26941856	0.00206255
H	−5.51053722	0.26941937	0.00208609

E = −893.65646804 a.u.

Table S13. Anion of compound **2**.

	x	y	z
C	2.46373116	−2.82946598	0.14503838
C	1.09384399	−2.62199065	0.11937242
C	0.52720375	−1.32961406	0.03033973
C	1.42863474	−0.20502908	0.00455052
C	2.85184880	−0.42644842	0.01305909
C	3.32786577	−1.73999876	0.08153772
C	0.90508354	1.12611857	−0.02977332
C	1.80468183	2.23878694	−0.11919709

	x	y	z
C	3.17245616	2.15148620	−0.13769942
B	3.81925167	0.78482894	−0.05581973
C	−0.90508240	−1.12611516	−0.02977759
C	−0.52720366	1.32961702	0.03033662
C	−1.42863363	0.20503078	0.00456001
C	−2.85184973	0.42644683	0.01308528
C	−3.32786810	1.73999654	0.08154900
C	−2.46373456	2.82946737	0.14501147
C	−1.09384774	2.62199469	0.11933684
C	−1.80467706	−2.23878437	−0.11923462
C	−3.17245174	−2.15148786	−0.13771162
B	−3.81925040	−0.78483434	−0.05577624
O	5.20922984	0.65571224	−0.05482906
O	−5.20923094	−0.65571617	−0.05486893
H	2.85426958	−3.84072469	0.21590828
H	0.44799740	−3.48705962	0.18283533
H	4.40070974	−1.93102345	0.09376595
H	1.35852871	3.22539008	−0.19404825
H	3.74010738	3.07760713	−0.21811888
H	−4.40071223	1.93102021	0.09378373
H	−2.85427446	3.84072741	0.21585460
H	−0.44800517	3.48706936	0.18275938
H	−1.35851780	−3.22538049	−0.19414494
H	−3.74010164	−3.07760650	−0.21816715
H	5.47614504	−0.26579792	−0.00574491
H	−5.47615070	0.26577310	−0.00541986

E = −893.72405968 a.u.

Table S14. Compound **3**.

	x	y	z
C	2.30617491	−2.93797431	−0.14778062
C	3.22899920	−1.87521630	−0.09318466
C	2.81741986	−0.55434841	−0.02367983
C	1.40409567	−0.26867836	−0.00872805
C	0.45187729	−1.34430437	−0.06459144
C	0.96153675	−2.67644703	−0.13377522
C	0.95152185	1.07514507	0.06143752
C	−0.45188575	1.34389974	0.07424499
C	−1.40410482	0.26830747	0.01776151
C	−0.95153476	−1.07556909	−0.05139456
C	−0.96154343	2.67605920	0.14304356
C	−2.30618232	2.93765892	0.15567593
C	−3.22900911	1.87496994	0.09979910
C	−2.81742635	0.55406791	0.03089611

B	−3.86581238	−0.59117319	−0.02999074
C	−3.26527579	−1.99898531	−0.10070510
C	−1.91691018	−2.16104993	−0.10802131
B	3.86580147	0.59095822	0.03584271
C	3.26525780	1.99858089	0.11033481
C	1.91689634	2.16056656	0.11927125
C	−5.42256262	−0.32942684	−0.01999049
C	−6.14322519	−0.31473766	1.19355983
C	−7.52384329	−0.10579490	1.18368223
C	−8.22992396	0.08745191	−0.00409634
C	−7.51143387	0.07128026	−1.19920742
C	−6.12971027	−0.13379422	−1.22494175
C	5.42252838	0.32935789	0.01985561
C	6.13448329	0.13331596	1.22042278
C	7.51772087	−0.06914734	1.18827352
C	8.23038144	−0.08329511	−0.00890169
C	7.51867529	0.11315730	−1.19424691
C	6.13887499	0.31915215	−1.19777392
C	5.41965447	0.52961780	−2.51339289
C	−5.43029379	−0.52011007	2.51343743
C	−5.40296671	−0.14059699	−2.55333668
C	−9.72840280	0.27532579	0.00363449
C	9.72612109	−0.29168486	−0.03168973
C	5.41471238	0.13910070	2.55265113
H	2.65792224	−3.96215405	−0.20106050
H	4.29213999	−2.09136189	−0.10531000
H	0.28011902	−3.51294956	−0.17721817
H	−0.28013375	3.51254387	0.18694898
H	−2.65793464	3.96185477	0.20859433
H	−4.29214453	2.09122934	0.11042671
H	−3.87704253	−2.89679040	−0.14832895
H	−1.52283553	−3.16844958	−0.15977840
H	3.87702592	2.89633117	0.15898589
H	1.52282857	3.16784439	0.17338898
H	−8.06143181	−0.09559140	2.12820628
H	−8.03899867	0.22027801	−2.13752572
H	8.05009990	−0.21596323	2.12404029
H	8.05277982	0.10925080	−2.14098762
H	6.12205075	0.55528651	−3.34912974
H	4.69758709	−0.26973827	−2.71012832
H	4.86014291	1.47069168	−2.51848066
H	−4.87010409	−1.46073071	2.52437794
H	−4.70986436	0.28044306	2.71132210
H	−6.13677151	−0.54375530	3.34578697
H	−6.10281558	−0.06340182	−3.38800895
H	−4.69869223	0.69427164	−2.63135650
H	−4.82248437	−1.05897557	−2.68838589
H	−10.05835011	0.81660609	0.89400823
H	−10.06540176	0.83117888	−0.87457088

H	−10.24738947	−0.68984284	−0.00124602
H	10.11351281	−0.50420968	0.96696733
H	10.00235231	−1.12645412	−0.68327672
H	10.24488223	0.59624477	−0.40783947
H	4.71493237	−0.69907417	2.63584271
H	6.11931485	0.06646252	3.38373876
H	4.83057838	1.05487389	2.68947793

E = −1441.22945579 a.u.

Table S15. Anion of compound **3**.

	x	y	z
C	2.32767621	−2.94111005	−0.17089635
C	3.24563640	−1.89742603	−0.10912116
C	2.83254207	−0.55827144	−0.04165823
C	1.41874889	−0.27332315	−0.03579057
C	0.46656729	−1.35141480	−0.06612820
C	0.96859169	−2.66868986	−0.14860511
C	0.95853180	1.07976869	0.00139175
C	−0.46647051	1.35240237	−0.04697051
C	−1.41867555	0.27401854	−0.03215607
C	−0.95847389	−1.07948988	−0.01446348
C	−0.96839360	2.67072449	−0.11118063
C	−2.32745770	2.94350538	−0.12957601
C	−3.24548173	1.89910677	−0.08232795
C	−2.83246453	0.55909334	−0.03413852
B	−3.86413010	−0.58724337	0.01976388
C	−3.27547305	−1.97608692	0.07507312
C	−1.90775400	−2.14152749	0.05310651
B	3.86417446	0.58716802	0.02913209
C	3.27544912	1.97503442	0.10495336
C	1.90774765	2.14074803	0.08507942
C	−5.43723554	−0.32915409	0.02591439
C	−6.14427656	−0.15923788	1.23596884
C	−7.52888100	0.03676396	1.22754564
C	−8.25801507	0.07093502	0.03958634
C	−7.55837623	−0.09158825	−1.15609505
C	−6.17479152	−0.28988111	−1.17783880
C	5.43719077	0.32850581	0.03140446
C	6.14386793	0.13801288	1.23846854
C	7.52940907	−0.05186761	1.22744736
C	8.25904803	−0.06268193	0.03954806
C	7.56079579	0.12775353	−1.15290688
C	6.17645334	0.31986925	−1.17207692
C	5.47506473	0.52150419	−2.49839606

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C	−5.40785540	−0.17981330	2.55855051
C	−5.47147706	−0.45623958	−2.50803765
C	−9.75921415	0.24737966	0.04756982
C	9.75191732	−0.30033535	0.03968829
C	5.40763008	0.13916385	2.56131566
H	2.66805297	−3.97043317	−0.23627551
H	4.30944482	−2.11453823	−0.11784958
H	0.28234973	−3.50229739	−0.20647657
H	−0.28206924	3.50496694	−0.15766204
H	−2.66779668	3.97365281	−0.18055040
H	−4.30925909	2.11648300	−0.08765827
H	−3.88047928	−2.88052783	0.13517655
H	−1.51830859	−3.15313222	0.10317649
H	3.88036688	2.87851609	0.17888209
H	1.51820841	3.15145814	0.15024376
H	−8.04949818	0.16711673	2.17384254
H	−8.10255381	−0.06270605	−2.09777519
H	8.05095299	−0.19187307	2.17182286
H	8.10761438	0.12987114	−2.09352256
H	6.18726893	0.52107153	−3.32829874
H	4.73862639	−0.26724583	−2.68093921
H	4.92597487	1.46760611	−2.51675461
H	−4.84502785	−1.10953625	2.68417691
H	−4.67858166	0.63403657	2.61842671
H	−6.09947488	−0.08034562	3.39977173
H	−6.18258132	−0.43477563	−3.33860053
H	−4.73487653	0.33694343	−2.66931771
H	−4.92229735	−1.40157264	−2.54998933
H	−10.09140130	0.79554901	0.93366325
H	−10.10176921	0.79557331	−0.83493634
H	−10.27753882	−0.71933164	0.04981164
H	10.20205189	−0.00516884	0.99161450
H	9.99059319	−1.35903355	−0.11913971
H	10.24667196	0.26497308	−0.75565897
H	4.67784728	−0.67504167	2.60856096
H	6.09925040	0.02602684	3.40080256
H	4.84540961	1.06718285	2.70146549

E = −1441.31521950 a.u.

Table S16. Compound **4**.

	x	y	z
C	−2.30198604	−0.43955216	2.94537497
C	−3.22650270	−0.44099242	1.88305893
C	−2.81653135	−0.44334153	0.55962103
C	−1.40370107	−0.44427498	0.27113217
C	−0.45004467	−0.44367970	1.34664371
C	−0.95768947	−0.44115426	2.68127081
C	−0.95301770	−0.44531003	−1.07524775
C	0.45005175	−0.44376353	−1.34655786
C	1.40371014	−0.44430640	−0.27104770
C	0.95302581	−0.44522194	1.07533276
C	0.95769011	−0.44124509	−2.68118685
C	2.30198596	−0.43968390	−2.94529191
C	3.22650576	−0.44116296	−1.88297812
C	2.81654011	−0.44344102	−0.55953906
B	3.86375293	−0.44834908	0.58571615
C	3.26828526	−0.45058377	1.99610213
C	1.91986612	−0.44681647	2.16058033
B	−3.86373578	−0.44830408	−0.58563592
C	−3.26827354	−0.45078164	−1.99602419
C	−1.91985352	−0.44706482	−2.16049843
C	5.42200354	−0.45410032	0.32109227
C	6.13457357	0.78272839	0.16917320
C	7.54971450	0.78001372	−0.04777394
C	8.22477142	−0.46431342	−0.10894970
C	7.53218106	−1.63676786	0.04088064
C	6.12886390	−1.64953968	0.25854239
C	−5.42197877	−0.45405171	−0.32103588
C	−6.13464151	0.78269181	−0.16919111
C	−7.54980938	0.77985994	0.04765021
C	−8.22475052	−0.46450468	0.10880633
C	−7.53203993	−1.63692732	−0.04093838
C	−6.12873542	−1.64958992	−0.25849646
C	−5.47625781	2.04250479	−0.23392661
C	5.43490864	−2.98873775	0.39055427
C	5.47609165	2.04247448	0.23391545
C	−5.43439052	−2.98859895	−0.39049991
C	6.16763143	3.22178484	0.09230203
C	7.56421073	3.20964670	−0.12344803
C	8.23606845	2.01373110	−0.19074035
C	−6.16790814	3.22174945	−0.09241003
C	−7.56451654	3.20949834	0.12323247
C	−8.23627785	2.01353938	0.19051949
H	−2.65212590	−0.43601882	3.97140241
H	−4.28873717	−0.43806021	2.10254171
H	−0.27503256	−0.43953682	3.51789494
H	0.27502808	−0.43957064	−3.51780794
H	2.65212400	−0.43615182	−3.97132011
H	4.28873830	−0.43830779	−2.10246844
H	3.88259614	−0.44879438	2.89307578
H	1.52798467	−0.44344828	3.17008950
H	−3.88258108	−0.44910319	−2.89300153
H	−1.52796598	−0.44389575	−3.17000709

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H	9.29798019	−0.47455170	−0.27018709
H	8.06180044	−2.58373941	−0.00175999
H	−9.29797093	−0.47484315	0.26995752
H	−8.06159035	−2.58393276	0.00169582
H	−4.40445961	2.06915515	−0.39979733
H	4.55590528	−2.93247430	1.03717093
H	5.09618884	−3.35882025	−0.58408130
H	6.10813349	−3.74213932	0.80737521
H	4.40430448	2.06904653	0.39986498
H	−6.10902955	−3.74360193	−0.80204368
H	−4.55865113	−2.93318747	−1.04164480
H	−5.09039472	−3.35589522	0.58333663
H	5.64096534	4.16816792	0.14684212
H	8.10071412	4.14540613	−0.23403663
H	9.30897855	1.99507594	−0.35437516
H	−5.64132560	4.16817938	−0.14694619
H	−8.10110397	4.14521927	0.23373970
H	−9.30919954	1.99480048	0.35406910

E = −1591.27292838 a.u.

Table S17. Anion of compound **4**.

	x	y	z
C	−2.27881639	−0.51867227	2.98126750
C	−3.21389700	−0.47652007	1.95228939
C	−2.82297550	−0.43411982	0.60554298
C	−1.41412142	−0.42571202	0.29711079
C	−0.44444829	−0.44153862	1.35951754
C	−0.92450885	−0.50208658	2.68596356
C	−0.97623451	−0.39798829	−1.06369513
C	0.44444671	−0.44151913	−1.35958153
C	1.41411889	−0.42571441	−0.29717313
C	0.97623171	−0.39800223	1.06363262
C	0.92451108	−0.50203581	−2.68602847
C	2.27881889	−0.51862618	−2.98132983
C	3.21389757	−0.47650261	−1.95234921
C	2.82297309	−0.43412322	−0.60560276
B	3.87073808	−0.38727966	0.52407847
C	3.30801161	−0.30990211	1.92095445
C	1.94276455	−0.32517146	2.10916753
B	−3.87074085	−0.38726521	−0.52413670
C	−3.30801624	−0.30987727	−1.92101335
C	−1.94276921	−0.32515536	−2.10922843
C	5.44032286	−0.43085222	0.24444838
C	6.21743738	0.77556597	0.20674211

C	7.63467782	0.73320586	−0.00791720
C	8.25534241	−0.52668379	−0.18252368
C	7.50468972	−1.67447939	−0.14538658
C	6.10195265	−1.64446680	0.06569221
C	−5.44032366	−0.43084890	−0.24448651
C	−6.21744198	0.77556874	−0.20672950
C	−7.63466788	0.73320299	0.00801750
C	−8.25531828	−0.52669151	0.18266124
C	−7.50466654	−1.67448247	0.14546526
C	−6.10194011	−1.64446390	−0.06570563
C	−5.61409700	2.05407397	−0.37715023
C	5.34421528	−2.95536975	0.09202833
C	5.61407567	2.05407095	0.37711975
C	−5.34421131	−2.95537192	−0.09199095
C	6.35549163	3.21072466	0.34158136
C	7.75313976	3.15859588	0.13131793
C	8.37377583	1.94556605	−0.03891478
C	−6.35551629	3.21072580	−0.34157050
C	−7.75314982	3.15859144	−0.13122109
C	−8.37376974	1.94555809	0.03905374
H	−2.60210488	−0.56306602	4.01705280
H	−4.27347171	−0.47810281	2.18873968
H	−0.22498720	−0.54480687	3.50924955
H	0.22499246	−0.54472002	−3.50931836
H	2.60210931	−0.56299891	−4.01711536
H	4.27347328	−0.47809200	−2.18879486
H	3.92886917	−0.24512381	2.81369304
H	1.57128494	−0.26604295	3.12681151
H	−3.92887619	−0.24510345	−2.81375067
H	−1.57129324	−0.26603738	−3.12687393
H	9.32863828	−0.57115804	−0.34328728
H	7.99137927	−2.63722360	−0.27728158
H	−9.32860574	−0.57116893	0.34348013
H	−7.99134588	−2.63723144	0.27736753
H	−4.54353718	2.10010309	−0.54052176
H	4.70490862	−3.02667220	0.97615920
H	4.68571770	−3.05153825	−0.77706063
H	6.02859778	−3.80835491	0.09316864
H	4.54350556	2.10009574	0.54042306
H	−6.02862165	−3.80833398	−0.09457351
H	−4.70377128	−3.02608649	−0.97533666
H	−4.68684470	−3.05217016	0.77789592
H	5.86708807	4.17048679	0.47417532
H	8.33023020	4.07736793	0.10421118
H	9.44671233	1.89501591	−0.20226214
H	−5.86712490	4.17048930	−0.47419990
H	−8.33024316	4.07736060	−0.10408089
H	−9.44669593	1.89500374	0.20246711

E = −1591.36193769 a.u.

Table S18. C_i-structure of **(B-Dbf)$_2$**.

	x	y	z
C	1.88551735	3.07153571	−0.97472772
C	2.94752345	2.17468122	−0.75542499
C	2.73602177	0.86976833	−0.34021823
C	1.36748514	0.41416237	−0.17673420
C	0.28346194	1.34932179	−0.31165418
C	0.59741919	2.67608292	−0.73037650
C	1.07355695	−0.95309236	0.08888065
C	−0.28341015	−1.34876529	0.31279920
C	−1.36745548	−0.41368381	0.17766884
C	−1.07357746	0.95353589	−0.08823562
C	−0.59718515	−2.67532738	0.73228017
C	−1.88522630	−3.07073820	0.97699197
C	−2.94731451	−2.17410505	0.75715665
C	−2.73595536	−0.86938318	0.34126731
B	−3.87516490	0.15922135	0.13478869
C	−3.43473394	1.62138817	0.08002756
C	−2.13156484	1.95141076	−0.06063548
B	3.87512448	−0.15910683	−0.13447753
C	3.43452920	−1.62126009	−0.08048422
C	2.13135562	−1.95115044	0.06043336
C	−5.43385288	0.21051834	0.03498080
C	5.43382949	−0.21066011	−0.03516764
C	4.63306831	−2.55284363	−0.17808235
C	−4.63342360	2.55289565	0.17656985
C	−6.47244668	−0.77023702	−0.13222115
C	−7.84336824	−0.36344881	−0.03255464
C	−8.14697924	1.00857711	0.17423745
C	−7.15389981	1.95340314	0.23819439
C	−5.80108988	1.55980218	0.15497439
C	−6.21591219	−2.12700359	−0.45427208
C	−7.23745304	−3.03745688	−0.60854216
C	−8.58161109	−2.64073737	−0.44888268
C	−8.87436994	−1.32639792	−0.17543247
C	6.47258940	0.76985640	0.13238658
C	7.84342962	0.36297895	0.03196135
C	8.14680779	−1.00893141	−0.17593819
C	7.15359850	−1.95359969	−0.24021282
C	5.80086476	−1.55990471	−0.15622435
C	6.21631775	2.12641600	0.45551987
C	7.23801963	3.03663138	0.61013102
C	8.58207793	2.63987069	0.44973403
C	8.87459182	1.32570159	0.17520468
C	−4.60300615	3.35616829	1.49750589
C	−4.72560777	3.52484820	−1.02067078
C	4.60206404	−3.35519543	−1.49956777
C	4.72556485	−3.52564850	1.01843972
H	2.08754248	4.07626010	−1.32873948
H	3.95708486	2.51577311	−0.94516881
H	−0.19804534	3.38565262	−0.90351879
H	0.19842087	−3.38464621	0.90584012
H	−2.08715373	−4.07524405	1.33167701
H	−3.95684355	−2.51520208	0.94706714
H	−1.83884161	2.99386047	−0.12329982
H	1.83838216	−2.99357471	0.12250321
H	−9.18892697	1.30271878	0.25353273
H	−7.41244206	3.00016975	0.35728951
H	−5.19493542	−2.43972986	−0.62183909
H	−7.00851831	−4.06566146	−0.86650541
H	−9.37797903	−3.36747682	−0.56267942
H	−9.90573041	−1.00201909	−0.08075008
H	9.18869323	−1.30313417	−0.25581677
H	7.41197866	−3.00031025	−0.36014300
H	5.19543069	2.43914545	0.62364472
H	7.00929366	4.06467202	0.86893265
H	9.37856922	3.36643049	0.56381351
H	9.90588266	1.00127358	0.07993838
H	−5.50641848	3.96293079	1.61047166
H	−4.52993618	2.68962744	2.35988708
H	−3.74245136	4.03072555	1.51518406
H	−5.63133691	4.13588036	−0.96592961
H	−3.86852355	4.20437199	−1.02962940
H	−4.73878544	2.97917654	−1.96688228
H	5.50535398	−3.96200098	−1.61328549
H	3.74141129	−4.02962356	−1.51739707
H	4.52876829	−2.68804956	−2.36146188
H	5.63121054	−4.13673760	0.96295277
H	4.73913052	−2.98064783	1.96503267
H	3.86841214	−4.20508873	1.02721016

E = −1746.15147835 a.u.

Table S19. Anionic C_i-structure of **(B-Dbf)$_2$**.

	x	y	z
C	1.90621352	3.10226211	−0.89005434
C	2.96150970	2.21980200	−0.68164301
C	2.75254682	0.88828499	−0.29362522

C	1.38271976	0.42886548	−0.15141012		H	−1.84076688	2.97409117	−0.06831217
C	0.29600054	1.36305367	−0.28522290		H	1.84078069	−2.97414068	0.06786344
C	0.60413480	2.68411724	−0.67760997		H	−9.21869684	1.35550837	0.25524957
C	1.08027920	−0.95227662	0.07705661		H	−7.40572177	3.02482716	0.34377661
C	−0.29598851	−1.36310895	0.28487830		H	−5.26271048	−2.43963935	−0.57849818
C	−1.38270633	−0.42890307	0.15115662		H	−7.09140366	−4.05324780	−0.82089073
C	−1.08026994	0.95222674	−0.07737914		H	−9.45847848	−3.32482658	−0.52911666
C	−0.60410726	−2.68420044	0.67718307		H	−9.95963056	−0.95073688	−0.06418062
C	−1.90617017	−3.10232842	0.88974942		H	9.21873595	−1.35540637	−0.25482442
C	−2.96146891	−2.21982623	0.68152712		H	7.40580792	−3.02475652	−0.34368112
C	−2.75253101	−0.88830580	0.29351169		H	5.26256947	2.43961148	0.57867545
B	−3.88309175	0.14085392	0.11017856		H	7.09120136	4.05324946	0.82136139
C	−3.44697090	1.58470649	0.06198989		H	9.45832571	3.32489091	0.52984424
C	−2.12629177	1.92638886	−0.03870154		H	9.95958695	0.95083721	0.06484679
B	3.88309991	−0.14086813	−0.11022423		H	−5.48062791	3.98563569	1.57421139
C	3.44699361	−1.58473179	−0.06217729		H	−4.53352835	2.69284348	2.33547116
C	2.12630877	−1.92643331	0.03836911		H	−3.71289486	4.00490442	1.47896707
C	−5.46340907	0.20688937	0.04767781		H	−5.61365032	4.12703816	−0.99623709
C	5.46340568	−0.20688109	−0.04759161		H	−3.84653233	4.14704521	−1.07845215
C	4.63547002	−2.53120291	−0.15882928		H	−4.75675139	2.93036399	−1.98583101
C	−4.63542179	2.53120474	0.15867462		H	5.48083080	−3.98549584	−1.57441667
C	−6.52128365	−0.75325585	−0.11083766		H	3.71308736	−4.00479588	−1.47934397
C	−7.89135869	−0.32960420	−0.01685915		H	4.53378768	−2.69264762	−2.33565225
C	−8.18061930	1.04491908	0.17922745		H	5.61361767	−4.12712495	0.99602706
C	−7.16620118	1.97115570	0.23439102		H	4.75660442	−2.93055760	1.98564997
C	−5.82031102	1.55943539	0.15447976		H	3.84649343	−4.14717086	1.07807214
C	−6.28267419	−2.11786337	−0.42311155					
C	−7.31144080	−3.02001901	−0.57299494					
C	−8.65280332	−2.60615676	−0.41932890					
C	−8.93061968	−1.28699457	−0.15511398					
C	6.52123857	0.75327857	0.11108956					
C	7.89133276	0.32966169	0.01724330					
C	8.18064280	−1.04484279	−0.17890092					
C	7.16625028	−1.97109839	−0.23424243					
C	5.82034283	−1.55941302	−0.15444547					
C	6.28255947	2.11786638	0.42339855					
C	7.31128898	3.02003618	0.57344645					
C	8.65267928	2.60620921	0.41992238					
C	8.93055697	1.28706689	0.15567285					
C	−4.59192392	3.35347159	1.46730160					
C	−4.72252568	3.49183503	−1.04920229					
C	4.59210761	−3.35335340	−1.46753733					
C	4.72247726	−3.49194127	1.04896506					
H	2.09871555	4.11720316	−1.22466755					
H	3.97047244	2.56358048	−0.87090994					
H	−0.19525906	3.38830290	−0.86112887					
H	0.19529369	−3.38841883	0.86055507					
H	−2.09865856	−4.11729159	1.22430431					
H	−3.97041285	−2.56358162	0.87093690					

E = −1746.23346770 a.u.

Table S20. *C*₂-structure of **(B-Dbf)₂**.

	x	y	z
C	−1.89389435	3.22034188	0.40014232
C	−2.95090788	2.29804119	0.29425169
C	−2.73116393	0.93266277	0.21225365
C	−1.36600596	0.44821281	0.30409267
C	−0.27699996	1.38680544	0.36616528
C	−0.59897816	2.77597637	0.40877109
C	−1.08427619	−0.94533460	0.38491889
C	0.27699305	−1.38683798	0.36610368
C	1.36600128	−0.44824171	0.30407710
C	1.08427073	0.94530219	0.38492539
C	0.59896780	−2.77601764	0.40855736
C	1.89388199	−3.22038430	0.39993320
C	2.95090111	−2.29807170	0.29418625
C	2.73116532	−0.93269039	0.21225499

B	3.87263504	0.11041967	0.12977622
C	3.46948959	1.54692462	0.45637438
C	2.16836178	1.90495833	0.53018457
B	−3.87262824	−0.11044327	0.12971274
C	−3.46950150	−1.54693987	0.45637718
C	−2.16837747	−1.90497566	0.53024427
C	5.41452701	0.17669856	−0.11596451
C	−5.41452240	−0.17670280	−0.11599768
C	−4.69640707	−2.42915873	0.63058257
C	4.69638070	2.42917135	0.63053640
C	6.40465833	−0.74487758	−0.60483078
C	7.78957346	−0.37897590	−0.55263289
C	8.14954930	0.90872510	−0.07362145
C	7.19372654	1.81955933	0.30043345
C	5.82891269	1.46180693	0.26784286
C	6.08099040	−1.99102102	−1.19877455
C	7.05748293	−2.84892093	−1.65342890
C	8.42129547	−2.50722334	−1.54054945
C	8.77519228	−1.29050263	−1.00915004
C	−6.40463643	0.74488271	−0.60487664
C	−7.78955774	0.37900758	−0.55266540
C	−8.14955385	−0.90867452	−0.07361853
C	−7.19374697	−1.81951554	0.30046266
C	−5.82892603	−1.46179100	0.26785418
C	−6.08094426	1.99100974	−1.19884251
C	−7.05742228	2.84891853	−1.65351008
C	−8.42124117	2.50724641	−1.54062321
C	−8.77516068	1.29054305	−1.00919951
C	4.82134808	2.91909126	2.09184495
C	4.69254552	3.64366226	−0.32468473
C	−4.82138144	−2.91902219	2.09191000
C	−4.69259134	−3.64368546	−0.32459268
H	−2.10371364	4.28268564	0.45549288
H	−3.96538340	2.67498962	0.29109214
H	0.19054201	3.51126671	0.44411225
H	−0.19055734	−3.51130778	0.44375127
H	2.10370012	−4.28273482	0.45515890
H	3.96537709	−2.67501824	0.29108198
H	1.90361424	2.93884802	0.72015910
H	−1.90363506	−2.93884019	0.72035846
H	9.20200236	1.17197608	−0.03496929
H	7.49156184	2.81087242	0.62483977
H	5.04044857	−2.25130761	−1.33228743
H	6.77637127	−3.79021730	−2.11284971
H	9.18270776	−3.19431364	−1.89190622
H	9.81950971	−1.00195322	−0.94585900
H	−9.20201130	−1.17190657	−0.03495615
H	−7.49160243	−2.81081148	0.62490352
H	−5.04039671	2.25127500	−1.33235722

H	−6.77629592	3.79020302	−2.11294604
H	−9.18264077	3.19434409	−1.89199309
H	−9.81948368	1.00201556	−0.94590065
H	5.74468487	3.48726562	2.23922970
H	3.98262892	3.57181001	2.34953203
H	4.82352201	2.07789425	2.78876012
H	3.85293332	4.30659270	−0.09679284
H	5.61198854	4.22789922	−0.22531971
H	4.60212711	3.32314721	−1.36500718
H	−5.74472530	−3.48718019	2.23931403
H	−3.98267086	−3.57174181	2.34962361
H	−4.82354701	−2.07779856	2.78879317
H	−3.85298810	−4.30661876	−0.09667551
H	−5.61204384	−4.22790373	−0.22520497
H	−4.60216820	−3.32321090	−1.36492741

E = −1746.15151931 a.u.

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