ELECTRONIC SUPPORTING INFORMATION

Bis-borylated Arylisoquinoline-Derived Dyes with a Central Aromatic Core: Towards Efficient Fluorescent Singlet-Oxygen Photosensitizers

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1. Materials and methods

General information and materials

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 MHz or 100 MHz, respectively, using the residual solvent signal as reference. ^{11}B NMR spectra were recorded with complete proton decoupling at 160 MHz, using $BF_3 \times Et_2O$ (0.00 ppm for ^{11}B NMR) as standard. For the variable temperature NMR spectroscopy a Young´s tap NMR tube was used. All chemical reactions were carried out in oven-dried Schlenk tubes under argon atmosphere, employing standard techniques. Anhydrous 1,4-dioxane was obtained by distillation, using an Na/benzophenone drying system. Other solvents such as toluene, methanol, isopropanol, and cyclohexane were used as received. Bis(pinacolate)diboron (B_2pin_2), pinacolborane (HBpin), and $(Mes)_2BF$ were purchased from Frontier Scientific, Aldrich, and TCI, respectively, and used without further purification. $[Ir(\mu\text{-}OMe)(cod)]_2$, $[Pd(PPh_3)_4]$, and $CuBr_2$ were purchased from Aldrich. The starting diboronic esters **1A**–**3A** were synthesized according to procedures described in the literature.[1, 2]

Photophysical measurements

All measurements were done at room temperature (25 ºC) with dye solutions in spectroscopic-grade organic solvents (tetrahydrofuran, toluene). Quartz cuvettes with 1 cm optical pathlength were used. For the photochemical stability experiments a 150 W xenon lamp (Oriel GmbH & Co. KG) with a 395-nm optical long-pass filter was used. UV/vis absorption measurements were done with a CARY 5000 UV/Vis spectrophotometer (Agilent). The fluorescence spectra were recorded with a Varian Eclipse fluorimeter and corrected for the response of the

photomultiplier. The fluorescence quantum yields were determined with 4-amino-*N*-propyl-1,8-naphthalimide (Φ_f = 0.48 in acetonitrile) as reference.[3] This reference was calibrated against quinine sulfate in 0.05 M sulfuric acid (Φ_f = 0.55).[4, 5] Where indicated, the solutions were de-aerated by careful bubbling with inert gas during 10 minutes.

Time-correlated single-photon-counting (TCSPC) measurements were performed with an Edinburgh Instruments FLS 920 fluorimeter. As excitation light source a picosecond pulsed diode laser EPL-445 (output 442.2 nm, pulse width at FWHM: 78 ps) was employed. Fluorescence lifetimes were obtained by deconvolution analysis of the decay curves, taking into account the instrument response function.

The two-photon absorption (2PA) cross sections were determined by observation of the two-photon-excited (2PE) fluorescence on femtosecond pulsed excitation (MaiTai Ti:Sapphire HP laser; Spectra-Physics, Inc.) and with the aid of an inverted Leica SP5 AOBS MP confocal microscope. Dye solutions in toluene (15–17 μM), contained in Suprasil quartz cells (2 mm optical pathlength), were excited at wavelengths between 730 nm and 1040 nm (10 nm steps) and the 2PE fluorescence was detected. Rhodamine 6G (in methanol) was used as reference.[6] The 2PA cross sections were measured for laser excitation powers where two-photon absorption applied.

Nanosecond laser-flash photolysis experiments were done with a pulsed Nd:YAG laser (output at 355 nm, 10 ns pulse duration, 1–10 mJ/pulse). Beside the pulsed laser, the system included a pulsed xenon lamp as detecting light source, a monochromator, and a photomultiplier. The output signal from the oscilloscope was transferred to a personal computer. The measurements were done with toluene or acetonitrile solutions, contained in 10 × 10 mm^2 quartz cells. When indicated, the

solutions were de-aerated by bubbling with nitrogen gas during 10 minutes. The experiments were carried out at room temperature (25 ºC) and each measurement was done using freshly prepared solutions of the dyes. The bimolecular rate constant for the quenching of excited triplet state by oxygen was estimated with the Stern-Volmer equation ($\tau_0/\tau = 1 + k_q\tau_0[O_2]$) by comparing the lifetimes in the presence of oxygen in air-equilibrated solution ($[O_2] = 2 \times 10^{-3}$ M)[7] and in the absence of oxygen.

The $^1O_2$ phosphorescence decay traces were registered at 1276 nm, employing a Peltier-cooled (–62.8 ºC) Hamamatsu NIR detector. A pulsed Nd:YAG laser was used (output at 355 nm, 10 ns pulse duration, 5 mJ/pulse). All measurements were made with air-equilibrated toluene solutions of the dyes ($OD_{355\ nm} = 0.3$) at room temperature (25 ºC). The quantum yield for $^1O_2$ formation (Φ_Δ) was calculated using perinaphthenone as reference ($\Phi_\Delta = 0.97$ in toluene).[8]

Quantum-mechanical calculations

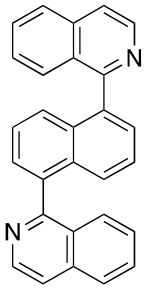
All calculations were done with the Gaussian 16 package.[9] The geometrical parameters for the ground (S_0) and the excited (S_1) states have been determined with the density functional level of theory (DFT), employing the PBE0 functional[10, 11] and the 6-31G(d,p) basis set. The absolute nature of the energetic minima was established by the absence of a negative frequency in the vibrational analysis. The linear-response (LR) approach was employed for computing the absorption and emission energies using the time-dependent density functional response theory (TD-DFT) with the same functional and basis set as used for the optimization of the S_0 and S_1 geometries and using the first ten excited states. The solvent effect was taken

into account by employing the polarizable-continuum model (PCM)[12] and toluene as solvent. The TPA cross sections were estimated at the TD-DFT/B3LYP/6-31G(d,p) level for the minimum ground-state geometries, using the software package Dalton 2018 with default parameters.[13, 14]

2. Synthesis

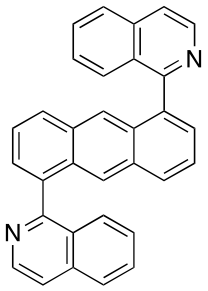
General procedure for Suzuki coupling

Following a described procedure, a Schlenk tube was charged with the corresponding diboronic ester **1A**–**3A**, [$Pd(PPh_3)_4$] (6 mol%), and 1-chloroisoquinoline (2.6 equiv.). After three cycles of vacuum/nitrogen flushing, a deoxygenated toluene/methanol (2:1) mixture and Na_2CO_3 (2.6 equiv.) in water were added. The resulting reaction mixture was stirred at 90 °C for 18 hours, cooled to room temperature, diluted with CH_2Cl_2 (70 mL), and washed with H_2O (3 × 15 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered, concentrated to dryness, and the crude product was purified by column chromatography, yielding **1B**–**3B**.

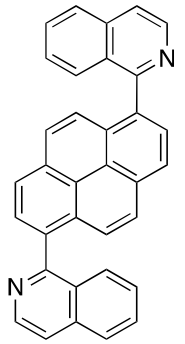


Synthesis of 1,5-di(isoquinolin-1-yl)naphthalene (1B). Following the general procedure starting from **1A** (1.00 mmol, 380 mg) and using [$Pd(PPh_3)_4$] (6 mol%), 1-chloroisoquinoline (2.60 mmol, 425 mg), 9.5 mL of deoxygenated toluene/methanol (2:1) mixture and Na_2CO_3 (2.60 mmol, 276 mg) in 3.0 mL of H_2O. Flash chromatography on silica gel (cyclohexane/EtOAc 1:1 → 1:2) gave 267 mg (70%) of **1B** as an amorphous pale brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ 8.75 (d, 2H, *J* = 5.7 Hz), 7.94 (d, 2H, *J* = 8.2 Hz), 7.77 (d, 2H, *J* = 5.7 Hz), 7.70 (t, 2H, *J* = 8.2 Hz), 7.65 (d, 2H, *J* = 8.5 Hz), 7.59–7.53 (m, 4H), 7.47–7.41 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 333 K): δ 160.8, 142.5, 137.6, 136.6, 132.7, 130.3, 128.6, 128.0,

127.7, 127.3, 127.0, 126.8, 125.6, 120.2 ppm. HRMS (ESI) calcd. for $C_{28}H_{19}N_2$ (M + H^+) 383.1543. Found 383.1539.



Synthesis of 1,5-di(isoquinolin-1-yl)anthracene (2B). Following the general procedure starting from **2A** (0.84 mmol, 360 mg) and using [$Pd(PPh_3)_4$] (6 mol%), 1-chloroisoquinoline (2.18 mmol, 356 mg), 8 mL of deoxygenated toluene/methanol (2:1) mixture and Na_2CO_3 (2.18 mmol, 231 mg) in 2.5 mL of H_2O. Flash chromatography on silica gel (toluene/EtOAc 2:1 $\rightarrow$ 1:1) gave 220 mg (61%) of **2B** as a pale yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$, 333 K): δ 8.78 (d, 2H, *J* = 5.7 Hz), 8.08 (s, 2H), 7.97 (d, 2H, *J* = 8.2 Hz), 7.83 (d, 2H, *J* = 9.5 Hz), 7.81 (d, 2H, *J* = 5.7 Hz), 7.72–7.65 (m, 4H), 7.53 (d, 2H, *J* = 5.7 Hz), 7.48 (m, 2H), 7.40 (t, 2H, *J* = 7.4 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 333 K): δ 160.5, 142.5, 137.0, 136.7, 132.1, 130.8, 130.1, 129.5, 128.5, 127.8, 127.4, 127.1, 126.8, 125.4, 124.5, 120.2 ppm. HRMS (ESI) calcd. for $C_{32}H_{21}N_2$ (M + H^+) 433.1699. Found 433.1694.



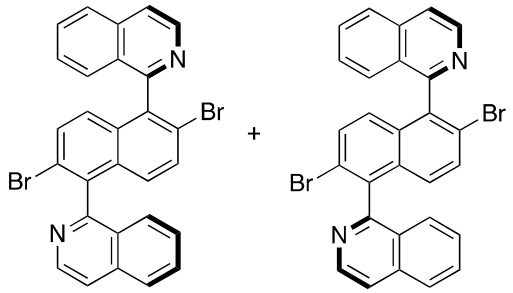
Synthesis of 1,6-di(isoquinolin-1-yl)pyrene (3B). Following the general procedure starting from **3A** (1.26 mmol, 570 mg) and using [$Pd(PPh_3)_4$] (6 mol%), 1-chloroisoquinoline (3.28 mmol, 535 mg), 10 mL of deoxygenated toluene/methanol

(2:1) mixture and Na_2CO_3 (3.28 mmol, 348 mg) in 3.8 mL of H_2O. Flash chromatography on silica gel (toluene/EtOAc 3:1 → 1:1) gave 460 mg (78%) of **3B** as a pale yellow amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$, 333 K) showed a ~1.1:0.9 mixture of rotamers: δ 8.80 (d, 2H, *J* = 5.6 Hz), 8.30 (d, 0.9H, *J* = 7.8 Hz), 8.29 (d, 1.1H, *J* = 7.8 Hz), 8.14 (d, 1.1H, *J* = 7.8 Hz), 8.13 (d, 0.9H, *J* = 7.8 Hz), 8.04–7.98 (m, 4H), 7.84 (d, 2H, *J* = 5.6 Hz), 7.76 (d, 1.1H, *J* = 9.2 Hz), 7.75 (d, 0.9H, *J* = 9.2 Hz), 7.72 (t, 2H, *J* = 7.8 Hz), 7.63 (d, 0.9H, *J* = 8.4 Hz), 7.62 (d, 1.1H, *J* = 8.4 Hz), 7.43 (t, 1.1H, *J* = 8.3 Hz), 7.41 (t, 0.9 H, *J* = 8.3 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 333 K): δ 160.7, 160.7, 142.5, 142.4, 136.5 (2×), 134.7, 134.6, 131.2, 130.3, 130.2, 129.9, 128.5, 128.0, 127.9 (2×), 127.4, 127.3, 127.0, 126.9, 125.6, 124.8 (2×), 120.3 ppm. HRMS (ESI) calcd. for $C_{34}H_{21}N_2$ ($M + H^+$) 457.1699. Found 457.1692.

General procedure for C–H borylation/bromination

A dried Schlenk tube was charged with $[Ir(\mu\text{-OMe})(cod)]_2$ (4 mol%, 13.3 mg), ligand (2-pyridinecarboxaldehyde *N*,*N*-dibenzylhydrazone, 8 mol%, 12 mg), B_2pin_2 (1.40 mmol, 356 mg), and **1B**–**3B** (0.500 mmol). After three cycles of vacuum/argon flushing, anhydrous 1,4-dioxane (5 mL) and HBpin (10 mol%, 8 μL) were added and the reaction mixture was stirred at 90–100 °C for 2–3 days (monitoring of the consumption of the starting materials by TLC analysis). Then the reaction mixture was cooled to room temperature and concentrated to dryness. The resulting crude was dissolved in an ^{i}PrOH/MeOH 2:3 mixture (9 mL) and treated with a solution of $CuBr_2$ (3.00 mmol, 676 mg in 3 mL H_2O). The mixture was stirred overnight at 90 °C, subsequently cooled to room temperature, diluted with CH_2Cl_2 (40 mL), and finally washed with aqueous NH_3 solution (30%) to remove the copper salts. The organic phase was dried over anhydrous

$MgSO_4$, filtered, concentrated to dryness, and the crude product was purified by column chromatography, yielding **1C**–**3C**. Both *meso* and *rac* diastereomers could be separated by column chromatography, but they could not be differentiated by NMR spectroscopy due to the fact that both are symmetric. Herein the isomers are referred to **D1** (higher R_f) and **D2** (lower R_f).



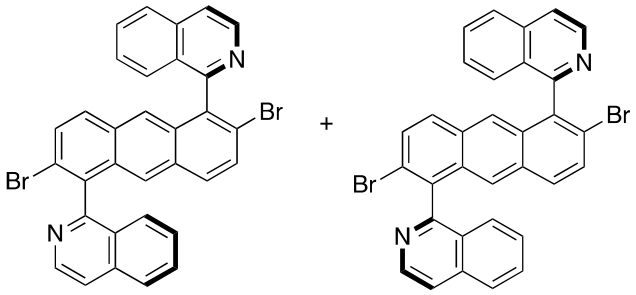
meso *rac*

Synthesis of 1,1'-(2,6-dibromonaphthalene-1,5-diyl)diisoquinoline (1C). Following the general procedure starting from **1B** (0.500 mmol, 191 mg), flash chromatography on silica gel (*n*-hexane/EtOAc 1:1 → 1:2) gave 65 mg of impure **1C.D1** and 83 mg **1C.D2**, contaminated with a ~30% of the monobrominated product. Considering these impurities (the impurity for **1C.D1** isomer is unknown), we can estimate ~15% yield for **1C.D1** and ~22% yield for **1C.D2**.

NMR data for **1C.D1** (low solubility in $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.79 (d, 2H, *J* = 5.6 Hz), 7.99 (d, 2H, *J* = 8.2 Hz), 7.85 (d, 2H, *J* = 5.6 Hz), 7.76–7.72 (m, 4H), 7.59 (d, 2H, *J* = 8.9 Hz), 7.51–7.41 (m, 2H), 7.07 (d, 2H, *J* = 8.9 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 158.9, 142.6, 137.1, 136.4, 132.9, 131.3, 130.7, 128.2, 128.0, 127.1, 126.7, 122.3, 121.0, ppm. Some carbons are missing. HRMS (ESI) calcd. for $C_{28}H_{17}Br_2N_2$ ($M + H^+$) 538.9753 (^{79}Br), 540.9733 (^{81}Br). Found 538.9745, 540.9723.

NMR data for **1C.D2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.79 (d, 2H, *J* = 5.7 Hz), 7.99 (d, 2H, *J* = 8.2 Hz), 7.84 (d, 2H, *J* = 5.7 Hz), 7.76–7.72 (m, 2H), 7.58 (d, 2H, *J* =

9.0 Hz), 7.51–7.41 (m, 4H), 7.09 (d, 2H, J = 9.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 158.7, 142.8, 137.2, 136.4, 132.8, 131.2, 130.5, 130.3, 128.0, 127.8, 127.2, 127.0, 126.9, 126.6, 122.2, 120.9 ppm. HRMS (ESI) calcd. for $C_{28}H_{17}Br_2N_2$ ($M + H^+$) 538.9753 (^{79}Br), 540.9733 (^{81}Br). Found 538.9749, 540.9728.



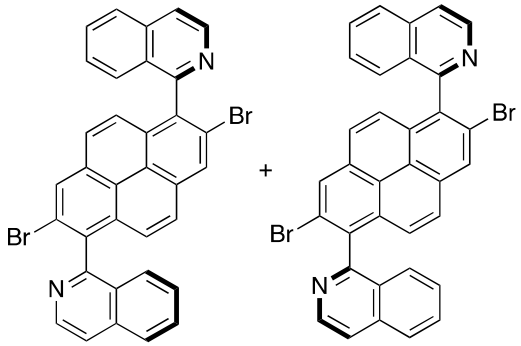
meso *rac*

Synthesis of 1,1'-(2,6-dibromoanthracene-1,5-diyl)diisoquinoline (2C). Following the general procedure starting from **2B** (0.500 mmol, 216 mg), flash chromatography on silica gel (toluene/EtOAc 4:1 → 1:1) gave 68 mg (23%) of the first isomer **2C.D1** and 83 mg (28%) of the second isomer **2C.D2**.

NMR data for **2C.D1** (low solubility in $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.81 (d, 2H, J = 5.7 Hz), 8.01 (d, 2H, J = 8.3 Hz), 7.89 (d, 2H, J = 5.7 Hz), 7.74 (ddd, J = 8.1, 6.3 and 1.6 Hz, 2H), 7.67 (s, 2H), 7.66 (d, 2H, J = 9.1 Hz), 7.62 (d, 2H, J = 9.1 Hz), 7.48–7.41 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 159.1, 142.7, 136.5, 136.4, 131.9, 130.9, 130.6 (2x), 130.0, 127.9, 127.8, 127.1, 126.8, 125.6, 122.0, 121.0 ppm. HRMS (ESI) calcd. for $C_{32}H_{19}Br_2N_2$ ($M + H^+$) 588.9910 (^{79}Br), 590.9889 (^{81}Br). Found 588.9902, 590.9884.

NMR data for **2C.D2**: ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.83 (d, 2H, J = 5.8 Hz), 8.01 (d, 2H, J = 8.3 Hz), 7.89 (d, 2H, J = 5.8 Hz), 7.74–7.70 (m, 4H), 7.68 (d, 2H, J = 9.1 Hz), 7.62 (d, 2H, J = 9.1 Hz), 7.46–7.40 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 159.0, 142.8, 136.5, 136.3, 131.9, 130.8, 130.6, 130.5, 130.0, 127.8, 127.7,

127.2, 126.7, 125.5, 122.1, 120.9 ppm. HRMS (ESI) calcd. for $C_{32}H_{19}Br_2N_2$ ($M + H^+$) 588.9910 (^{79}Br), 590.9889 (^{81}Br). Found 588.9904, 590.9884.



meso *rac*

Synthesis of 1,1'-(2,7-dibromopyrene-1,6-diyl)diisoquinoline (3C). Following the general procedure starting from **3B** (0.500 mmol, 241 mg), flash chromatography on silica gel (*n*-hexane/EtOAc 2:1) gave 115 mg (37%) of the first isomer **3C.D1** and 130 mg (42%) of the second isomer **3C.D2**.

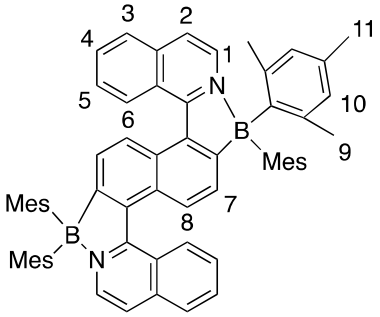
NMR data for **1C.D1**: ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.83 (d, 2H, J = 5.7 Hz), 8.51 (s, 2H), 8.02 (d, 2H, J = 8.3 Hz), 7.91 (d, 2H, J = 8.9 Hz), 7.89 (d, 2H, J = 5.7 Hz), 7.74 (t, 2H, J = 8.0 Hz), 7.48–7.38 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 159.4, 142.6, 136.4, 135.1, 132.0, 131.7, 130.6, 128.9, 128.3, 127.9, 127.8, 127.1, 127.0, 126.6, 123.4, 122.1, 121.0 ppm. HRMS (ESI) calcd. for $C_{34}H_{19}Br_2N_2$ ($M + H^+$) 612.9910 (^{79}Br), 614.9989 (^{81}Br). Found 612.9904, 614.9883.

NMR data for **1C.D2**: ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.83 (d, 2H, J = 5.7 Hz), 8.52 (s, 2H), 8.02 (d, 2H, J = 8.3 Hz), 7.91 (d, 2H, J = 9.6 Hz), 7.90 (d, 2H, J = 5.7 Hz), 7.74 (t, 2H, J = 8.3 Hz), 7.44–7.40 (m, 4H), 7.36 (d, 2H, J = 8.3Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 159.4, 142.6, 136.4, 135.0, 131.9, 131.7, 130.5, 129.0, 128.3, 127.9, 127.7, 127.2, 126.8, 126.6, 123.4, 122.1, 120.9 ppm. HRMS (ESI) calcd.

for $C_{34}H_{19}Br_2N_2$ (M + H^+) 612.9910 (^{79}Br), 614.9889 (^{81}Br). Found 612.9901, 614.9881.

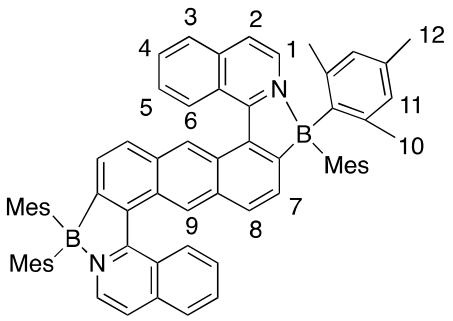
General procedure for lithiation/borylation

A dried Schlenk tube was charged with the second isomer **1C**–**3C.D2** (1 eq.) and after three cycles of vacuum/argon flushing, dry THF (4 mL/0.1 mmol substrate) was added. The reaction mixture was cooled to –78 °C, then *n*-BuLi (1.6 M in hexane, 2.4 eq.) was added dropwise, and the resulting solution was stirred at this temperature for one hour. Then, Mes_2BF (3 eq.) was added at –78 °C under Schlenk conditions and the resulting mixture was stirred at this temperature for 15 minutes and then at room temperature overnight. The reaction was quenched with water and the mixture was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous $MgSO_4$, filtered, concentrated to dryness, and the crude product was purified by column chromatography (*n*-hexane/CH_2Cl_2 or cyclohexane/toluene as eluent mixtures), yielding the target dyes **1**–**3**.



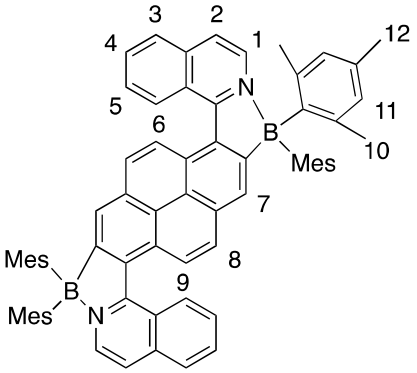
Synthesis of 13,13,29,29-Tetrakis(mesityl)-12,28-diaza-13,29-diboraoctacyclo[15.15.0.0^{2,14}.0^{3,12}.0^{4,9}.0^{18,30}.0^{19,28}.0^{20,25}]dotriaconta-1,3,5,7,9,11,14,18(30),19,21,23,25,27,31-tetradecaene-12,28-diium-13,29-diuide (1). Following the general procedure starting from **1C.D2** (0.05 mmol, 27 mg), flash chromatography on silica gel (*n*-hexane/CH_2Cl_2 10:1→ CH_2Cl_2) gave **1** (20 mg, 46%)

as an amorphous light yellow solid. M.p. > 250 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.88 (d, 2H, J = 8.6 Hz, H_6), 8.54 (d, 2H, J = 6.5 Hz, H_1), 8.10 (d, 2H, J = 8.3 Hz, H_8), 7.92–7.83 (m, 4H, H_4 and H_3), 7.80 (d, 2H, J = 8.4 Hz, H_7), 7.68 (t, 2H, J = 7.8 Hz, H_5), 7.54 (d, 2H, J = 6.5 Hz, H_2), 6.83 (br s, 2H, H_{10}), 6.72 (br s, 2H, H_{10}), 6.59 (br s, 2H, H_{10}), 6.39 (br s, 2H, H_{10}), 2.25–2.21 (br s, 18H, H_{11} and H_9), 2.10 (br s, 6H, H_9), 1.78 (br s, 6H, H_9), 1.52 (br s, 6H, H_9) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 171.3, 160.5, 145.0, 143.6, 142.4, 142.1, 141.9, 137.8, 137.5 (C_1), 134.5, 133.4, 132.6 (C_4), 131.4, 130.1 (br), 130.1, 129.7 (C_6), 129.0, 128.9 (C_8), 128.2 (C_7), 127.5 (C_5), 127.1 (C_3), 124.3, 119.5 (C_2), 26.9 (br, C_9), 25.5 (br, C_9), 23.5 (br, C_9), 20.8 (C_{11}), 20.7 (C_{11}), (*C*–B and some C_{quat} were not observed) ppm. ^{11}B NMR (128 MHz, $CDCl_3$, 298 K): δ 6.2 (br s) ppm. HRMS (ESI) calcd. for $C_{64}H_{61}B_2N_2$ ($M + H^+$) 879.5015. Found 879.5016.



Synthesis of 15,15,33,33-Tetrakis(mesityl)-14,32-diaza-15,33-diboranonacyclo[19.15.0.0^{3,19}.0^{4,16}.0^{5,14}.0^{6,11}.0^{22,34}.0^{23,32}.0^{24,29}]hexatriaconta-1,3,5,7,9,11,13,16,18,20,22(34),23,25,27,29,31,35-heptadecaene-14,32-diium-15,33-diuide (2). Following the general procedure starting from **2C.D2** (0.1 mmol, 59 mg), flash chromatography on silica gel (cyclohexane/toluene 2:1→1:1) gave **2** (34 mg, 37%) as an amorphous orange solid. M.p. > 250 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 343 K): δ 8.95 (d, 2H, J = 8.6 Hz, H_6), 8.68 (s, 2H, H_9), 8.51 (d, 2H, J = 6.6 Hz, H_1), 7.96 (d, 2H,

J = 7.8 Hz, H_8), 7.88 (d, 2H, J = 8.0 Hz, H_3), 7.85 (t, 2H, J = 7.9 Hz, H_4), 7.68–7.61 (m, 4H, H_5 and H_7), 7.46 (d, 2H, J = 6.6 Hz, H_2), 6.62 (br s, 8H, H_{11}), 2.16 (s, 12H, H_{12}), 1.97 (br s, 24H, H_{10}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 343 K): δ 175.6, 161.0, 143.9 (br), 141.1 (br), 140.9 (br), 138.0, 137.3 (C_1), 134.1, 132.6 (C_4), 132.0 (C_7), 131.4, 129.8 (C_{11}), 129.5 (C_6), 129.4 (C_8), 128.4, 127.2, 127.1 (C_3), 126.9 (C_5), 124.4, 123.9 (C_9), 118.9 (C_2), 24.9 (br, C_{10}), 20.5 (C_{12}), (*C*–B and some C_{quat} were not observed) ppm. ^{11}B NMR (128 MHz, $CDCl_3$, 343 K): δ 6.1 (br) ppm. HRMS (ESI) calcd. for $C_{68}H_{63}B_2N_2$ ($M + H^+$) 929.5172. Found 929.5173.



Synthesis of 13,13,31,31-Tetrakis(mesityl)-12,30-diaza-13,31-diboradecacyclo[17.17.2.0^{2,14}.0^{3,12}.0^{4,9}.0^{16,37}.0^{20,32}.0^{21,30}.0^{22,27}.0^{34,38}]octatriaconta-1(37),2(14),3,5,7,9,11,15,17,19,21,23,25,27,29,32,34(38),35-octadecaene-12,30-diium-13,31-diuide (3). Following the general procedure starting from **3C.D2** (0.1 mmol, 61 mg), flash chromatography on silica gel (cyclohexane/toluene 3:2) gave **3** (28 mg, 30%) as an amorphous orange solid. M.p. > 250 ºC. ^{1}H NMR (400 MHz, $CDCl_3$, 343 K): δ 8.78 (d, 2H, J = 8.6 Hz, H_6), 8.62 (d, 2H, J = 6.5 Hz, H_1), 8.60 (s, 2H, H_7), 8.42 (d, 2H, J = 9.2 Hz, H_8), 7.97 (d, 2H, J = 9.2 Hz, H_9), 7.89–7.82 (m, 4H, H_4 and H_3), 7.66 (t, 2H, J = 7.9 Hz, H_5), 7.55 (d, 2H, J = 6.5 Hz, H_2), 6.62 (br s, 8H, H_{11}), 2.15 (br s, 12H, H_{12}), 1.98 (br s, 24H, H_{10}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 343 K): δ 167.7, 160.7, 145.2, 140.9, 137.9, 137.6 (C_1), 133.9, 132.6 (C_4), 131.1, 129.9 (C_6), 129.8 (C_{11}),

127.9 (C_7), 127.9 (C_9), 127.5 (C_5), 127.3, 126.9 (C_3), 126.2 (C_8), 124.8, 124.5, 119.9 (C_2), 25.1 (br, C_{10}), 20.5 (C_{12}), (*C*–B and some C_{quat} were not observed) ppm. ^{11}B NMR (128 MHz, $CDCl_3$, 343 K): δ 6.0 (br s) ppm. HRMS (ESI) calcd. for $C_{70}H_{63}B_2N_2$ ($M + H^+$) 953.5172. Found 953.5175.

3. NMR spectra

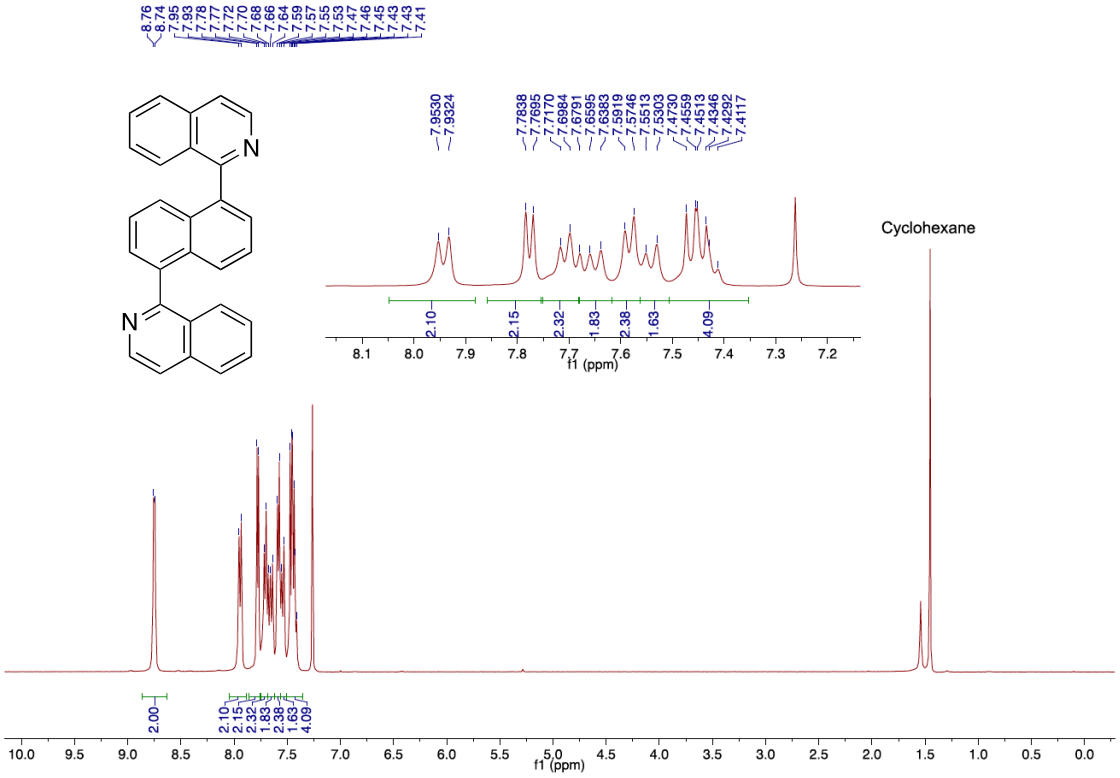


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 333 K) of **1B**.

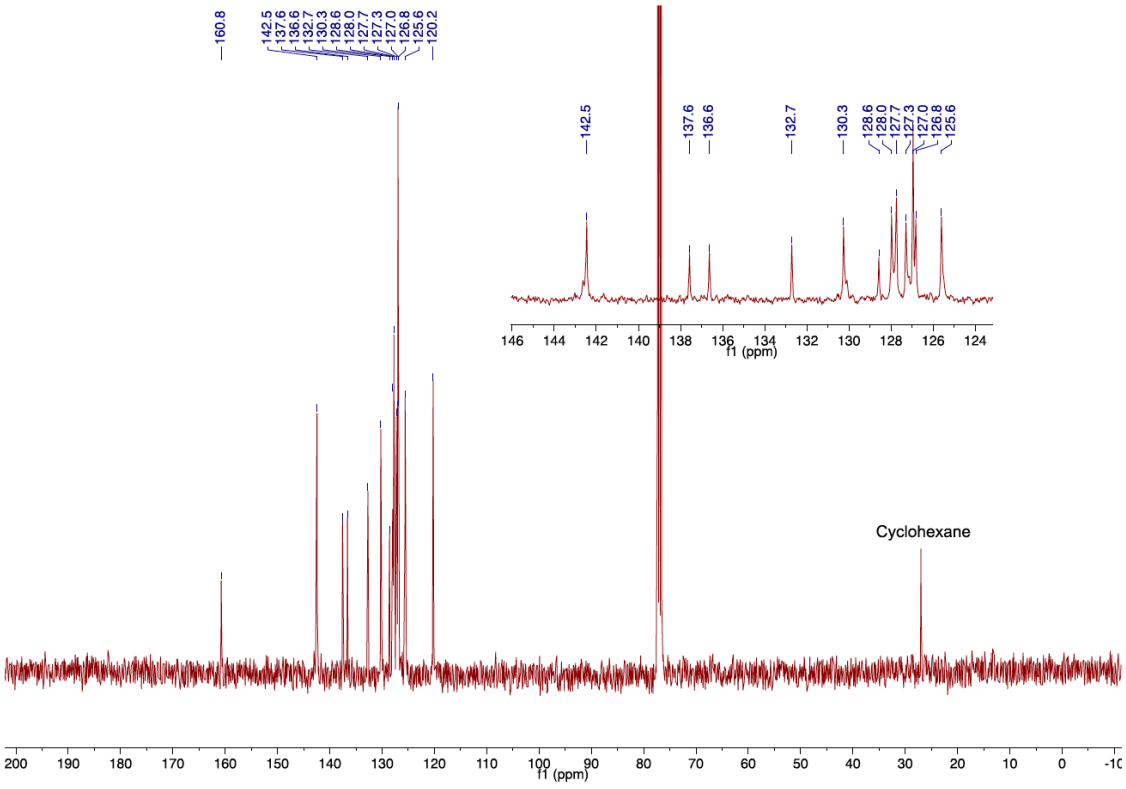


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 333 K) of **1B**.

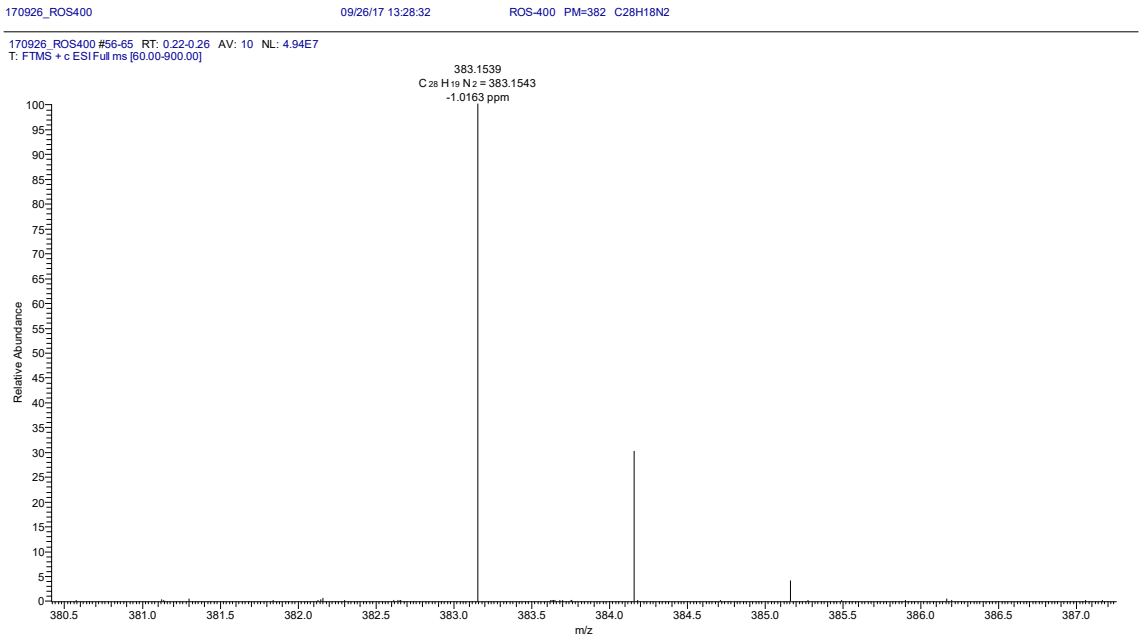


Figure S3. HRMS of **1B**.

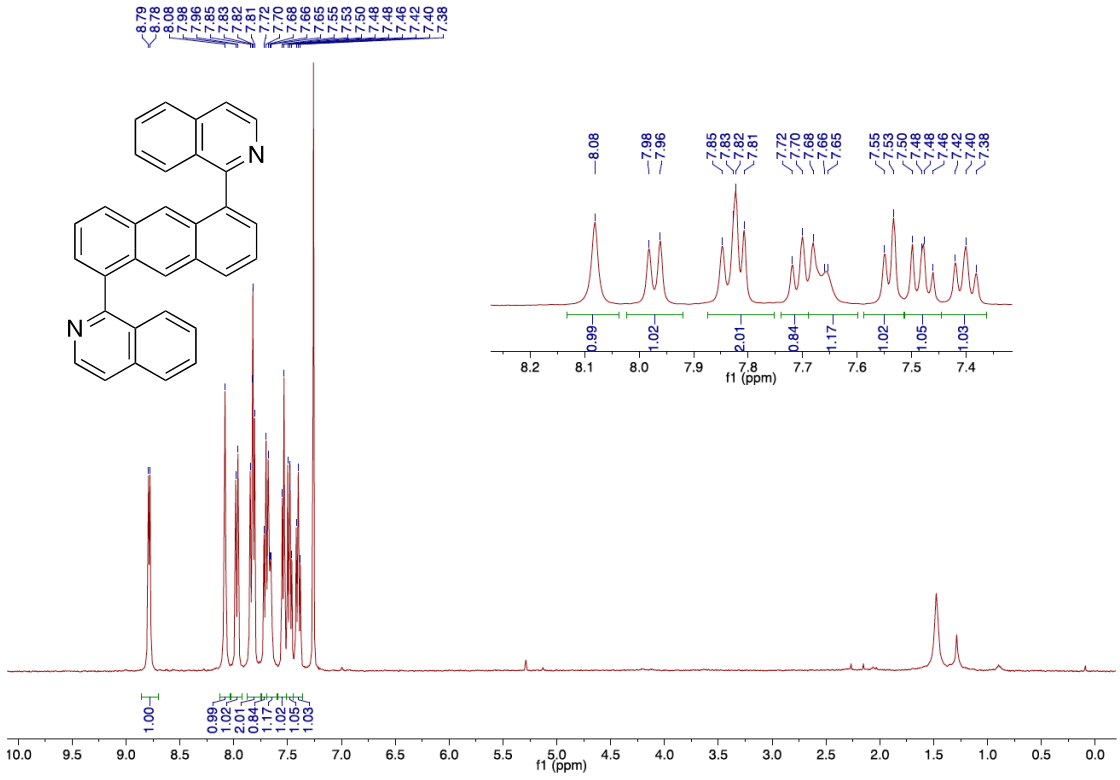


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 333 K) of **2B**.

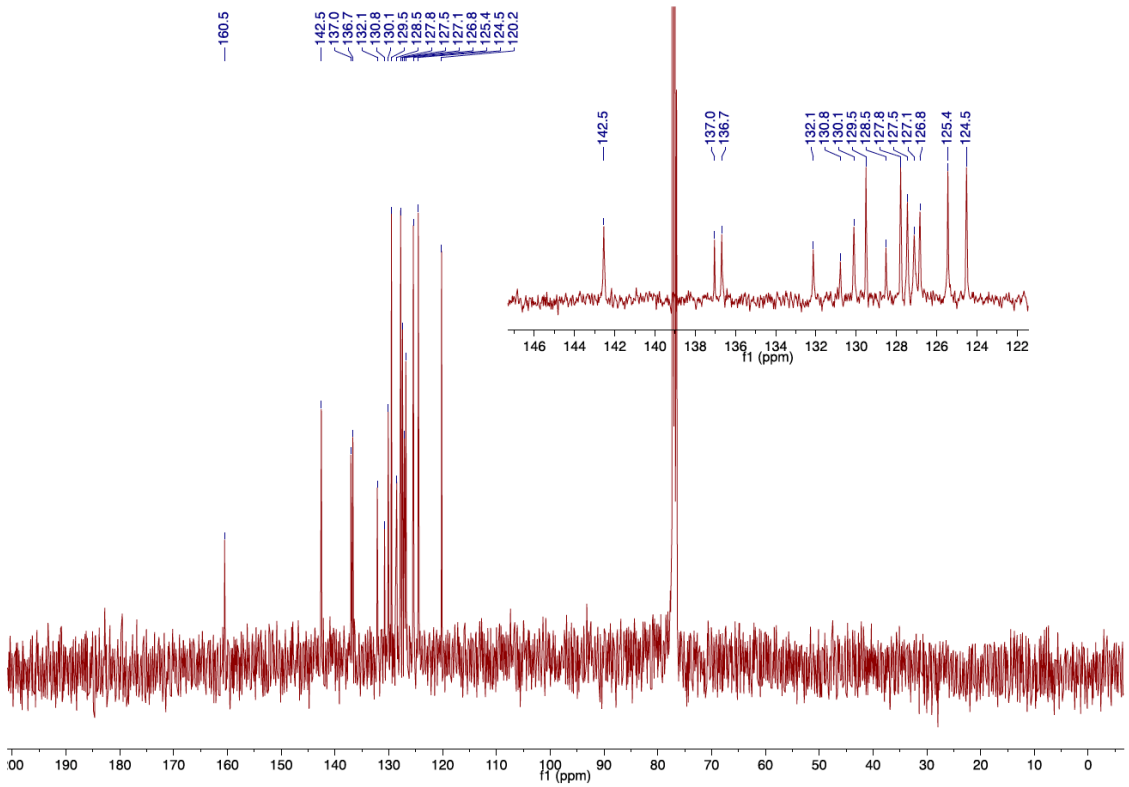


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 333 K) of **2B**.

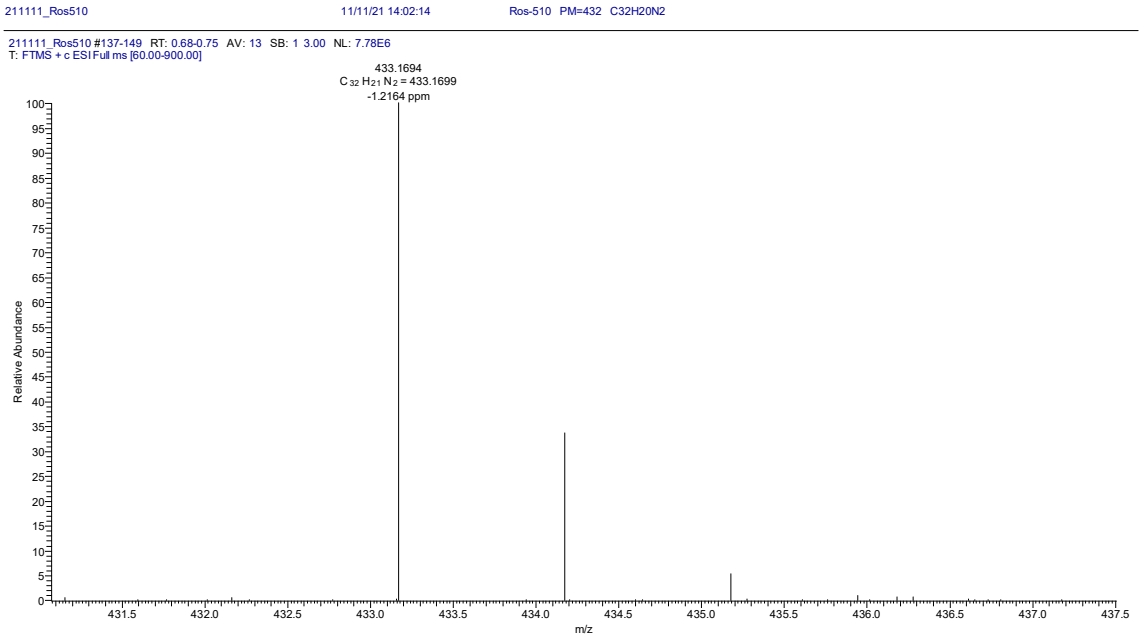


Figure S6. HRMS of **2B**.

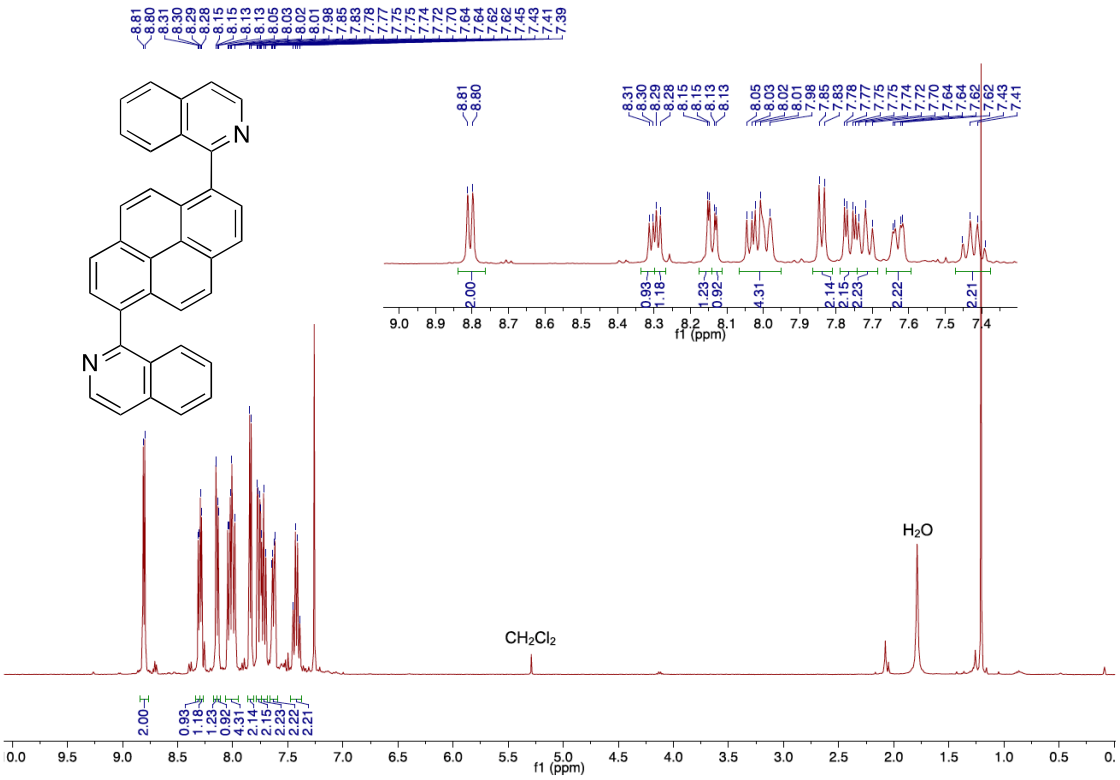


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 333 K) of **3B**.

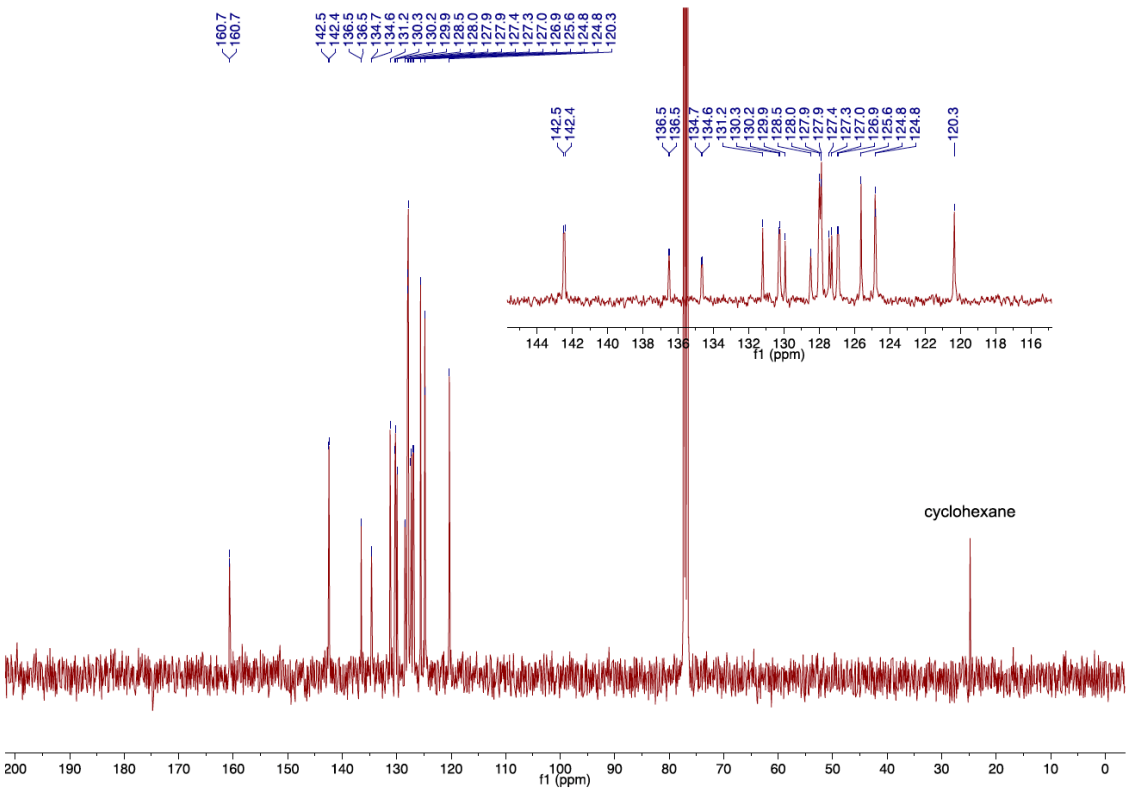


Figure S8. ^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$, 333 K) of **3B**.

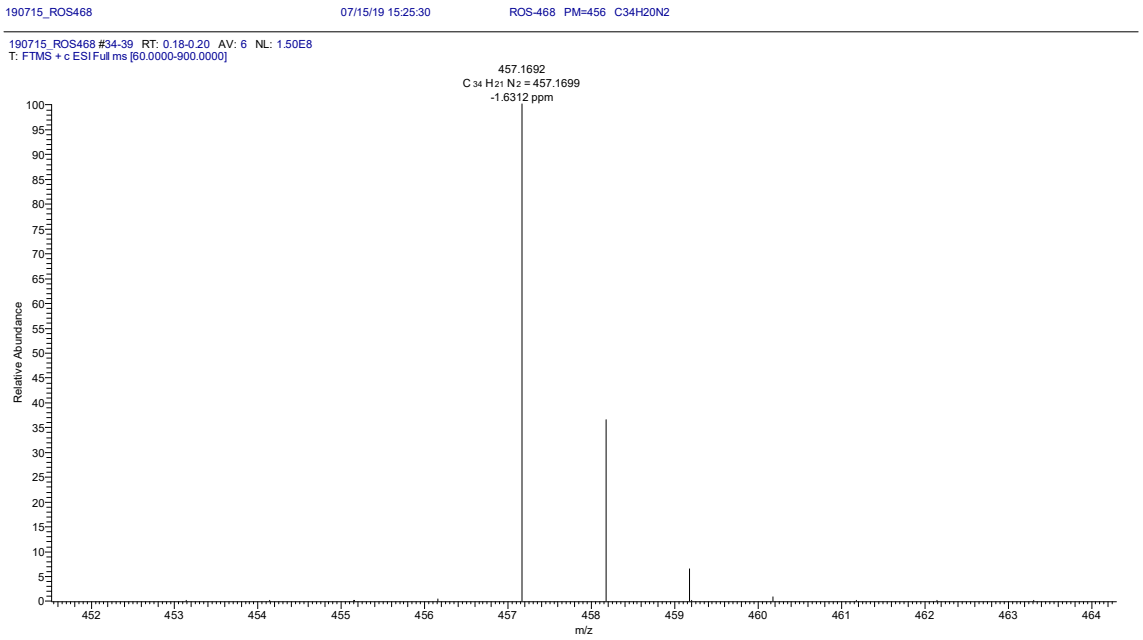


Figure S9. HRMS of **3B**.

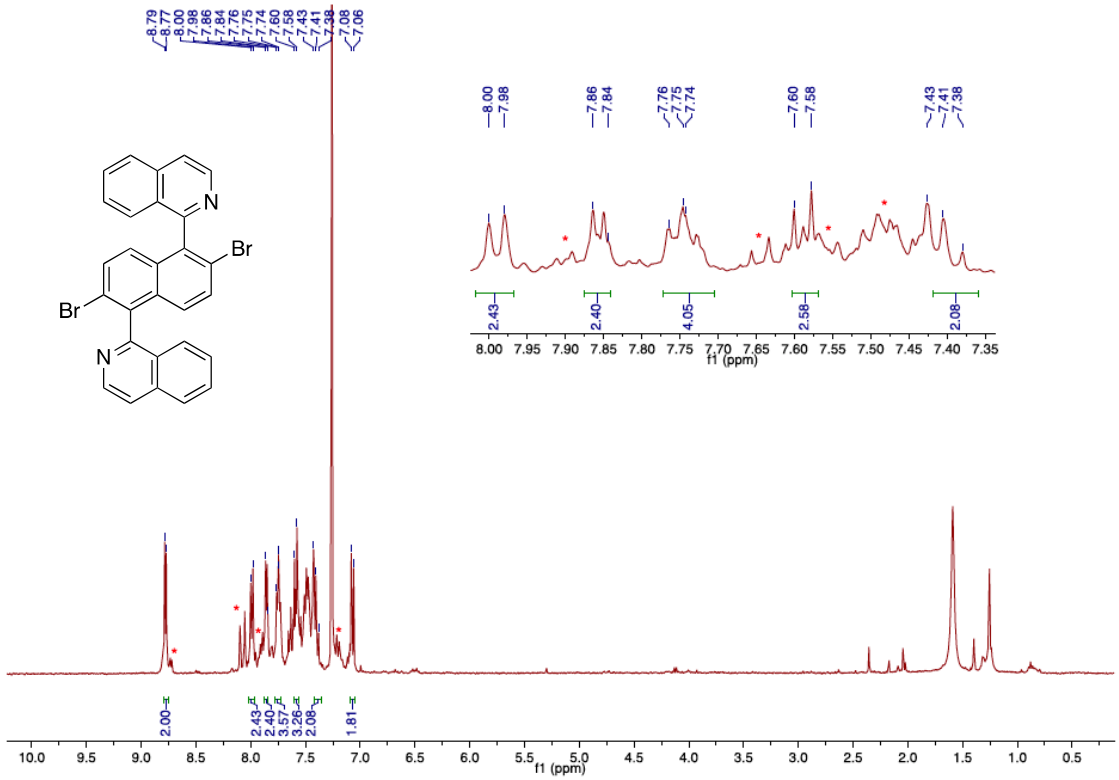


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1C.D1**. (* denotes traces of unknown impurities).

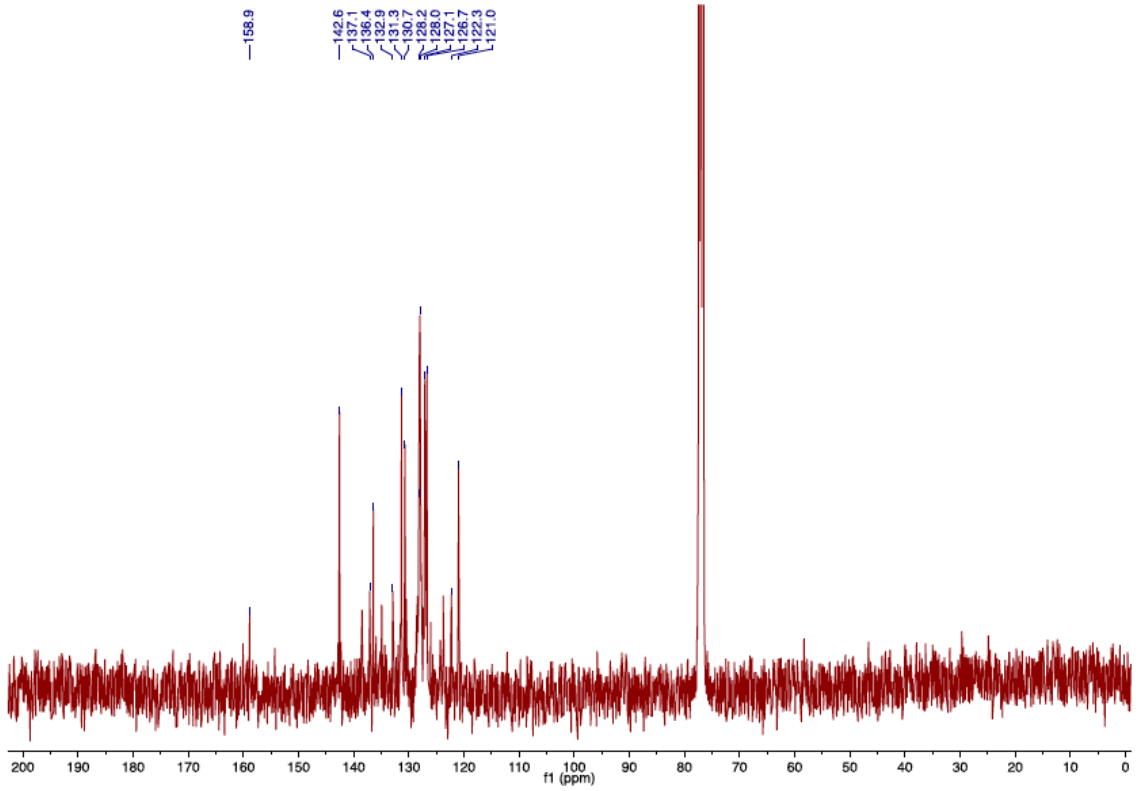


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **1C.D1**.

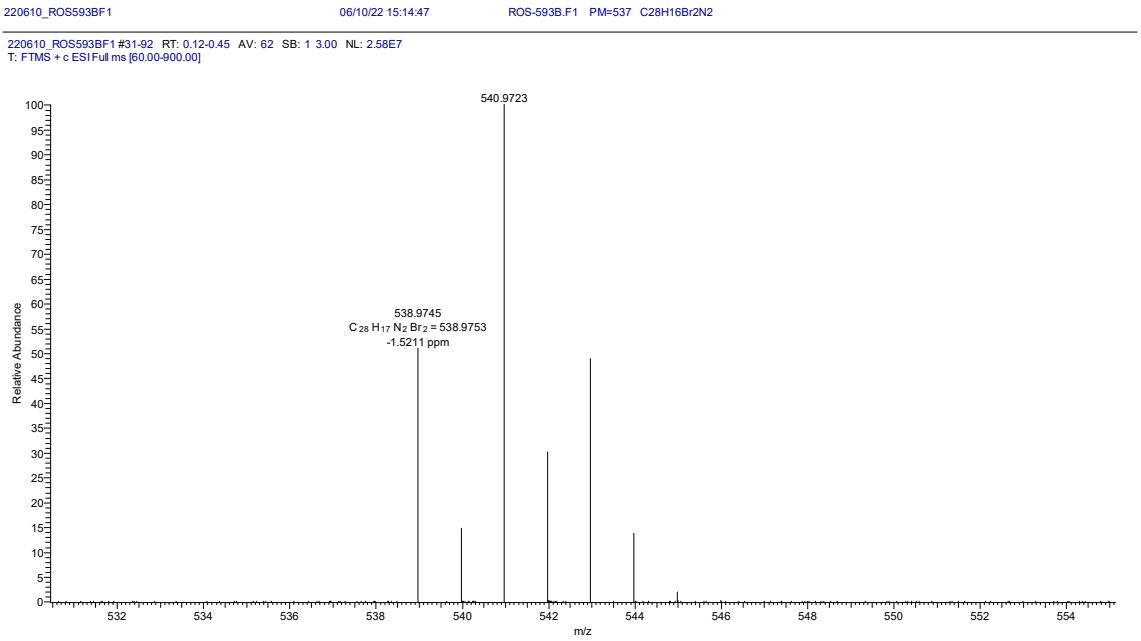


Figure S12. HRMS of **1C.D1**.

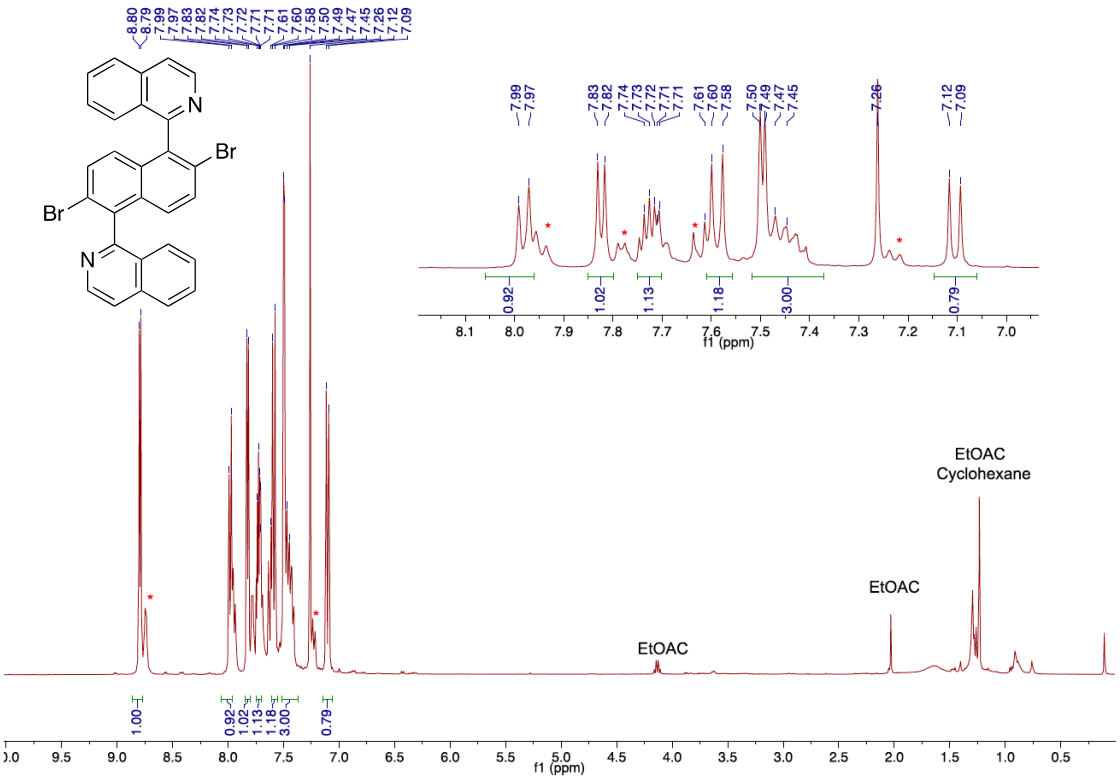


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1C.D2**. (* denotes traces of monobrominated compound.)

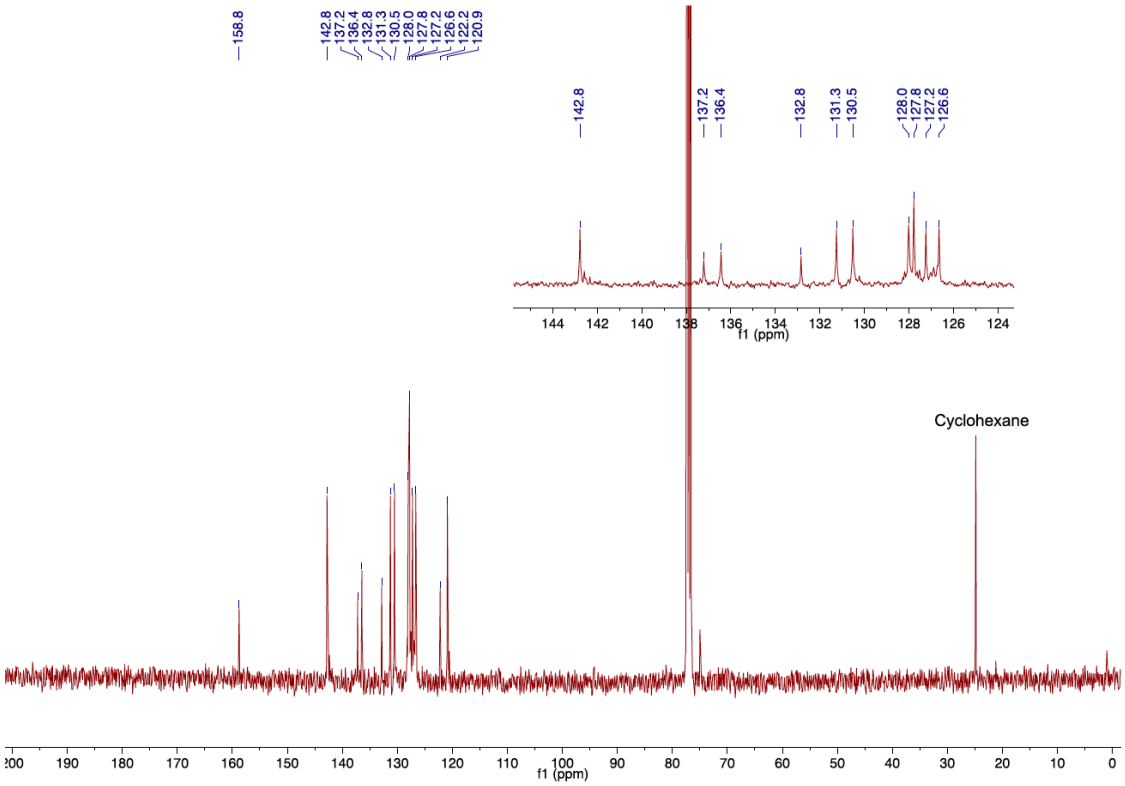


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **1C.D2**.

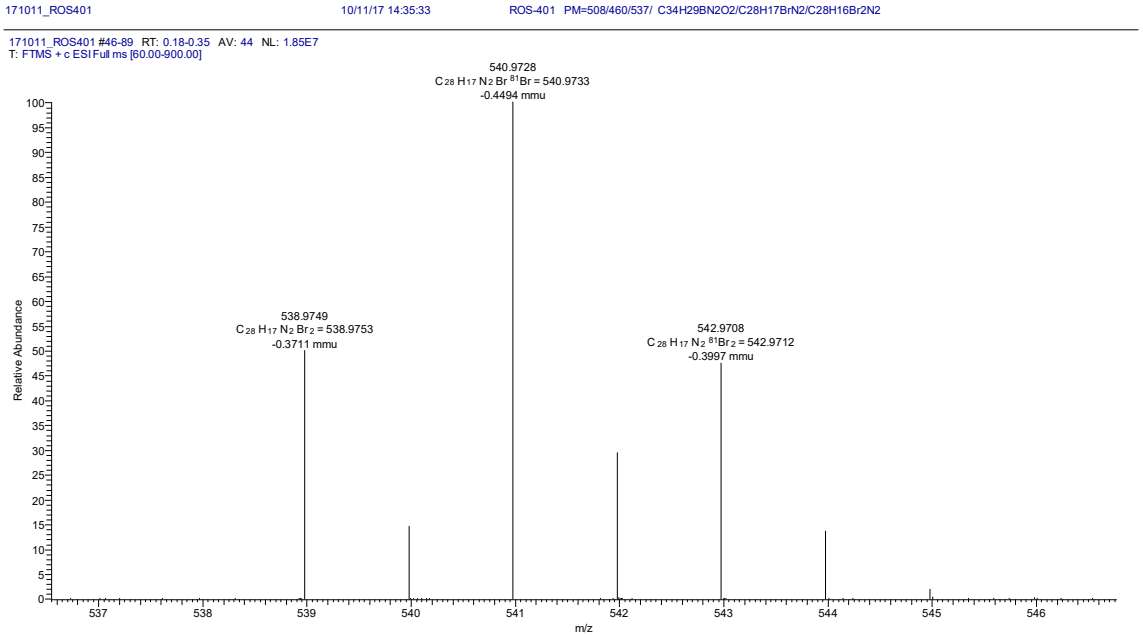


Figure S15. HRMS of **1C.D2**.

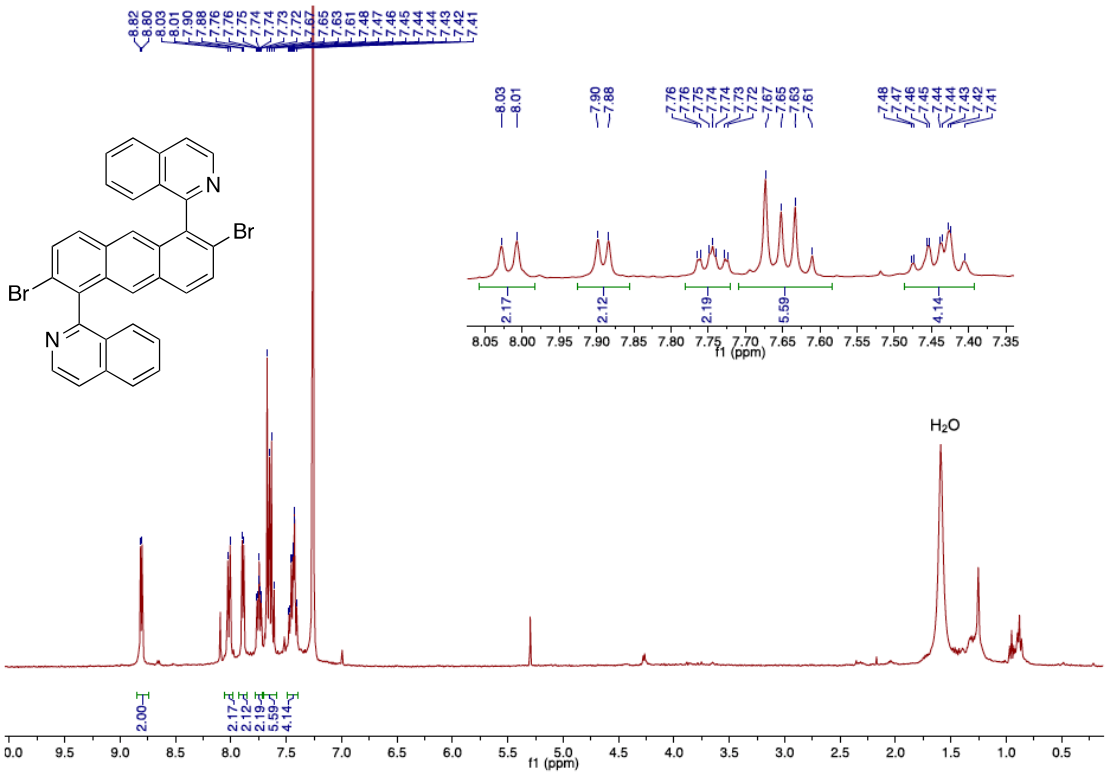


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2C.D1**.

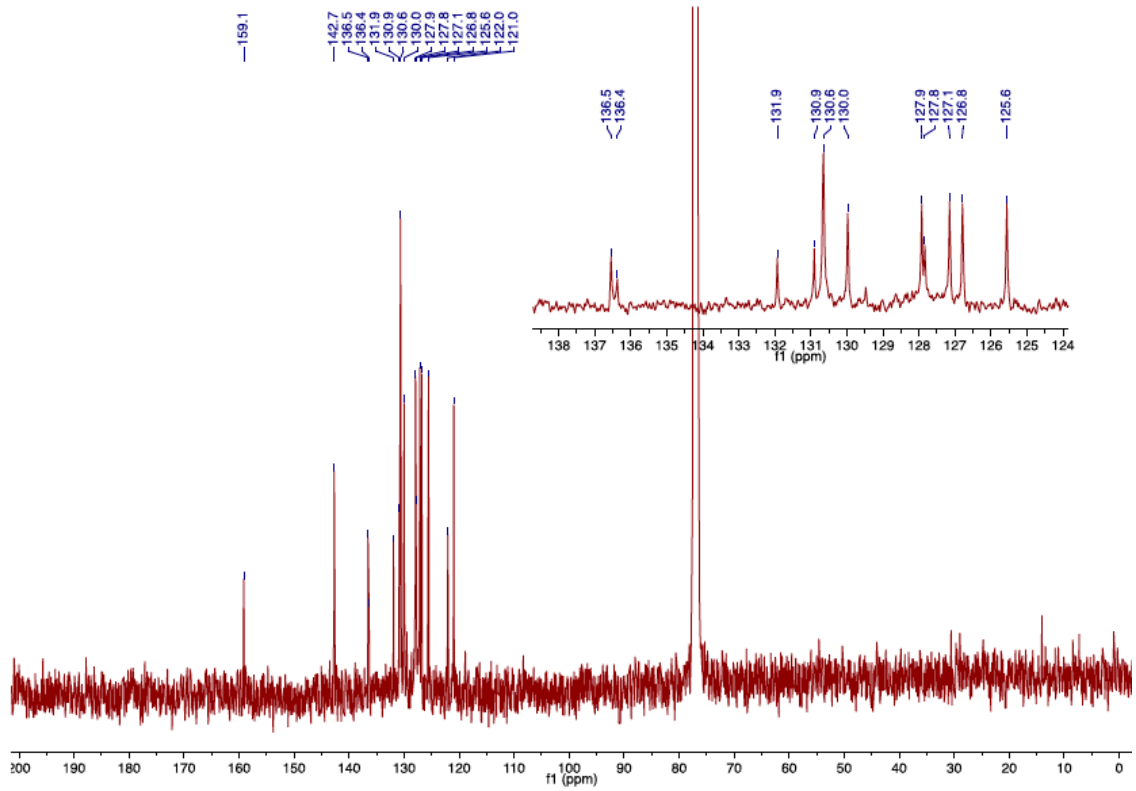


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **2C.D1**.

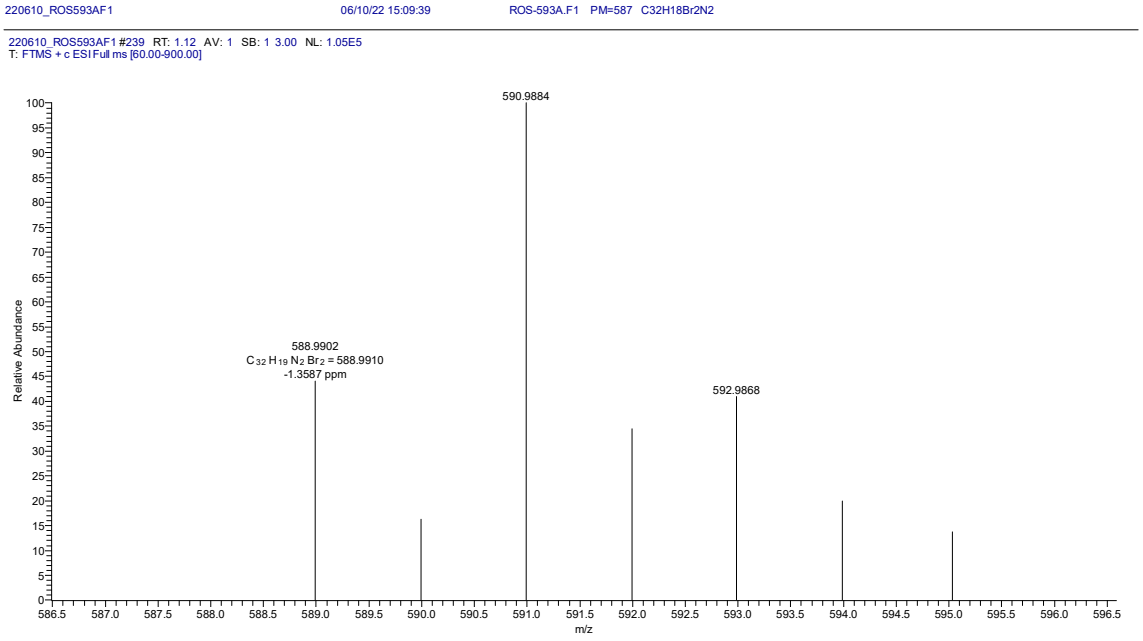


Figure S18. HRMS of **2C.D1**.

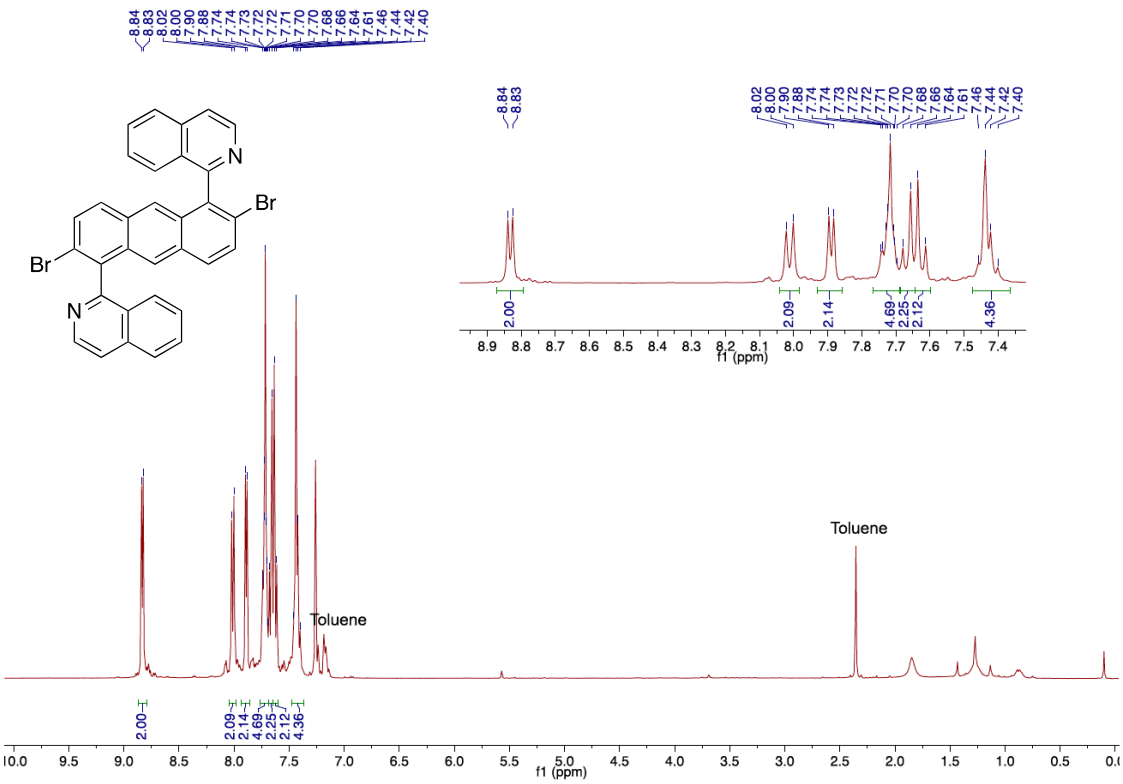


Figure S19. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **2C.D2**.

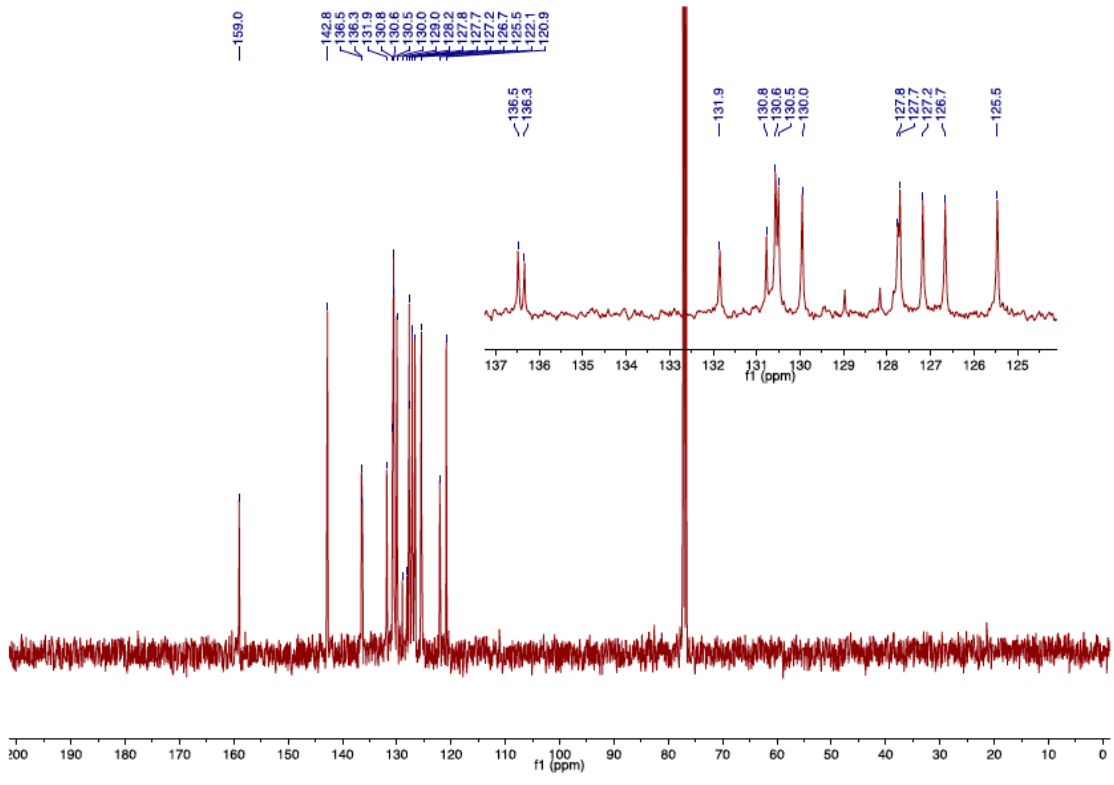


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **2C.D2**.

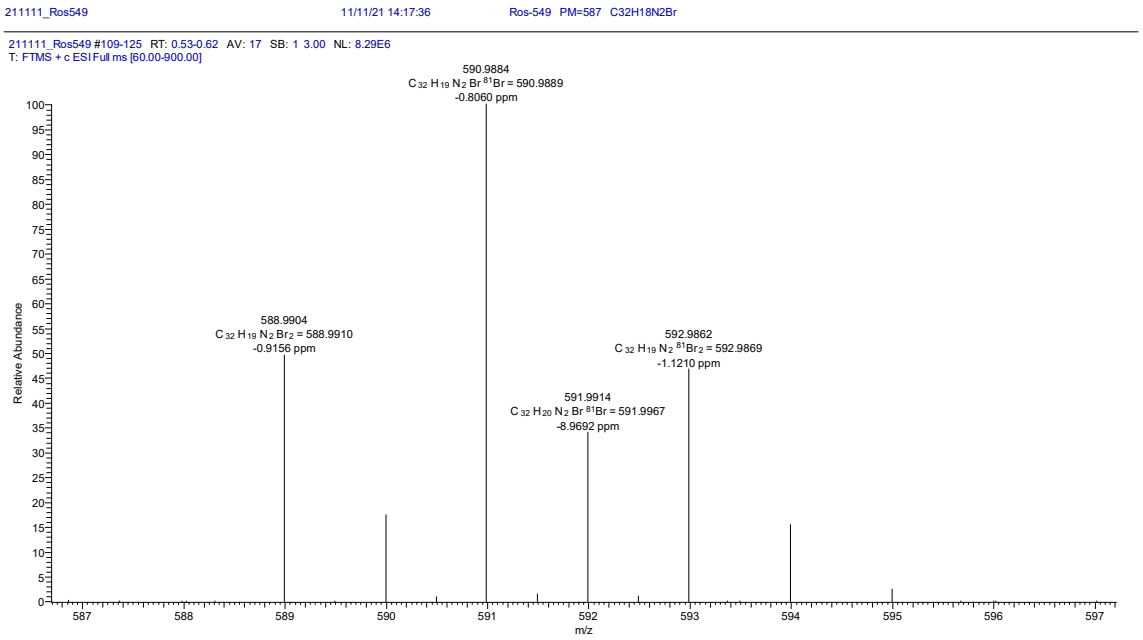


Figure S21. HRMS of **2C.D2**.

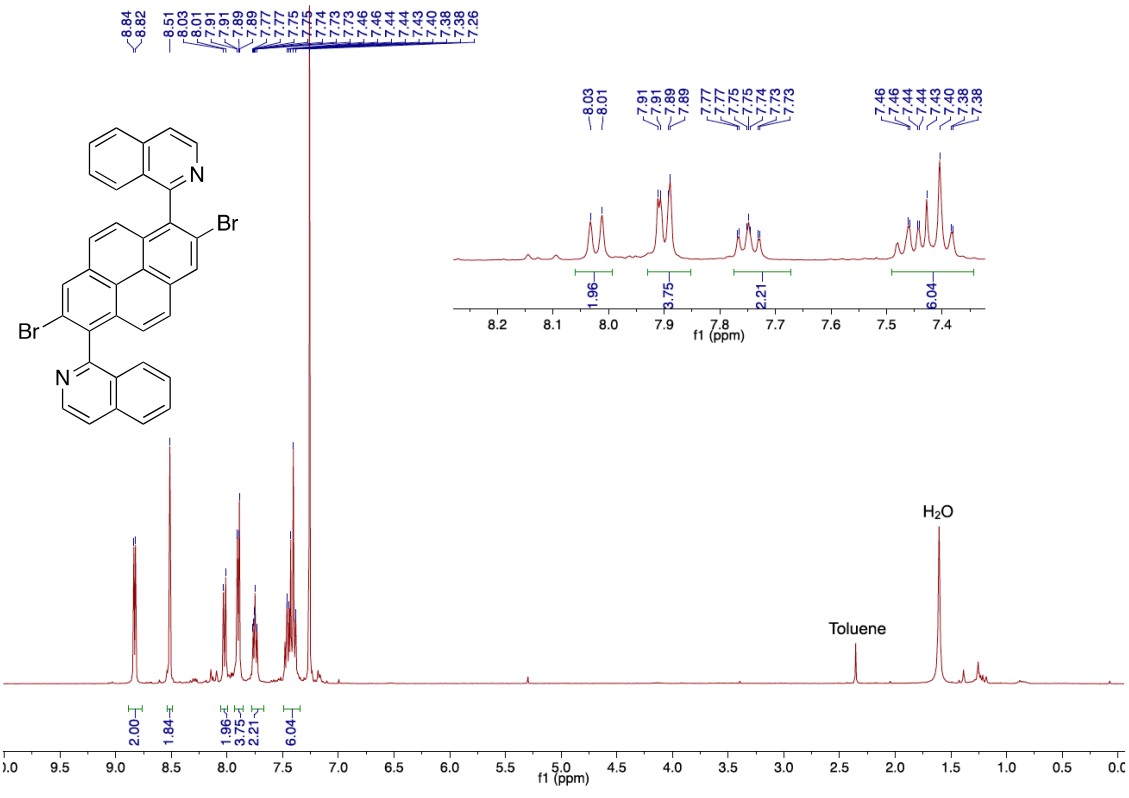


Figure S22. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **3C.D1**.

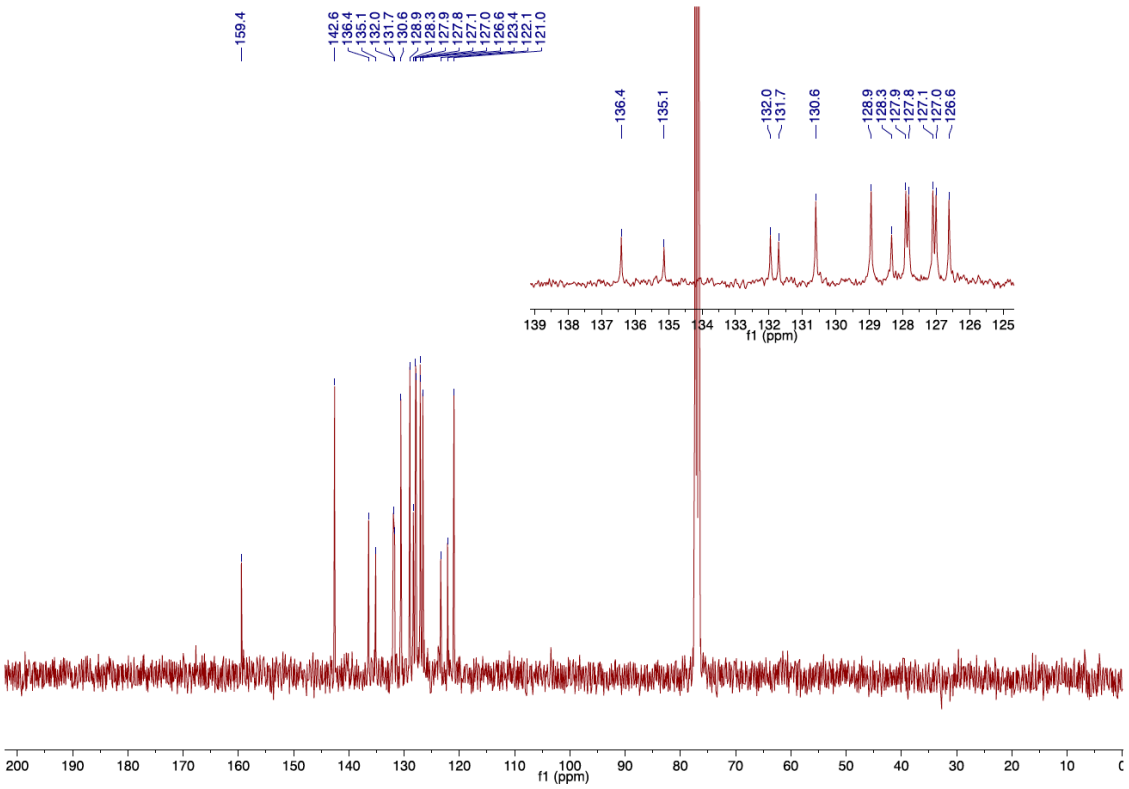


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3C.D1**.

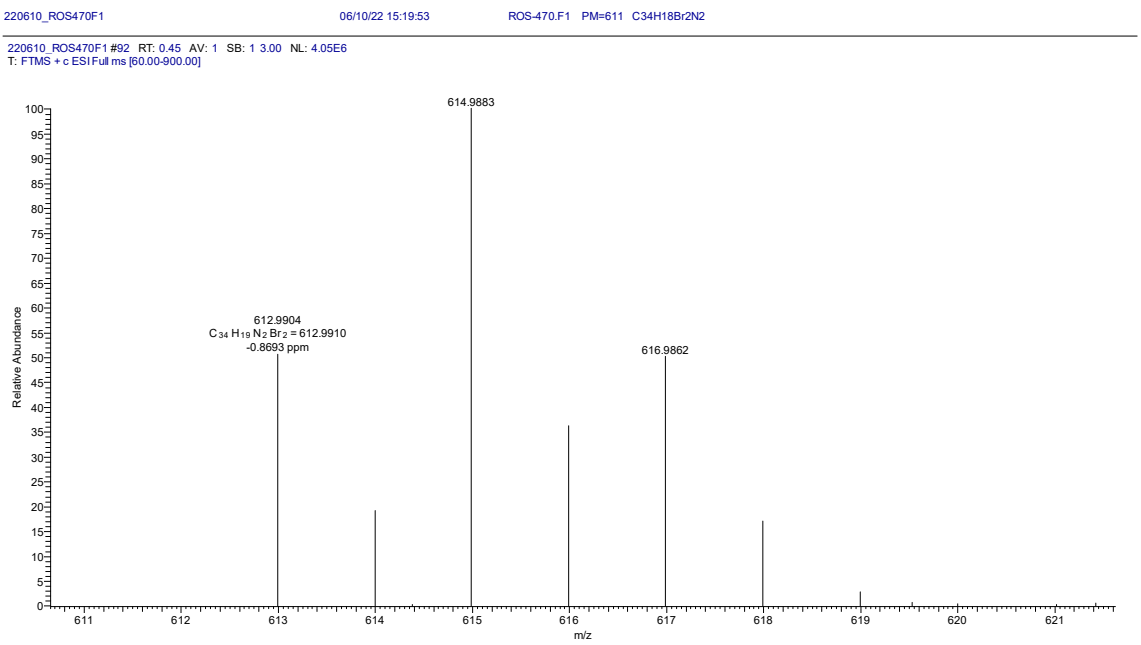


Figure S24. HRMS of **3C.D1**.

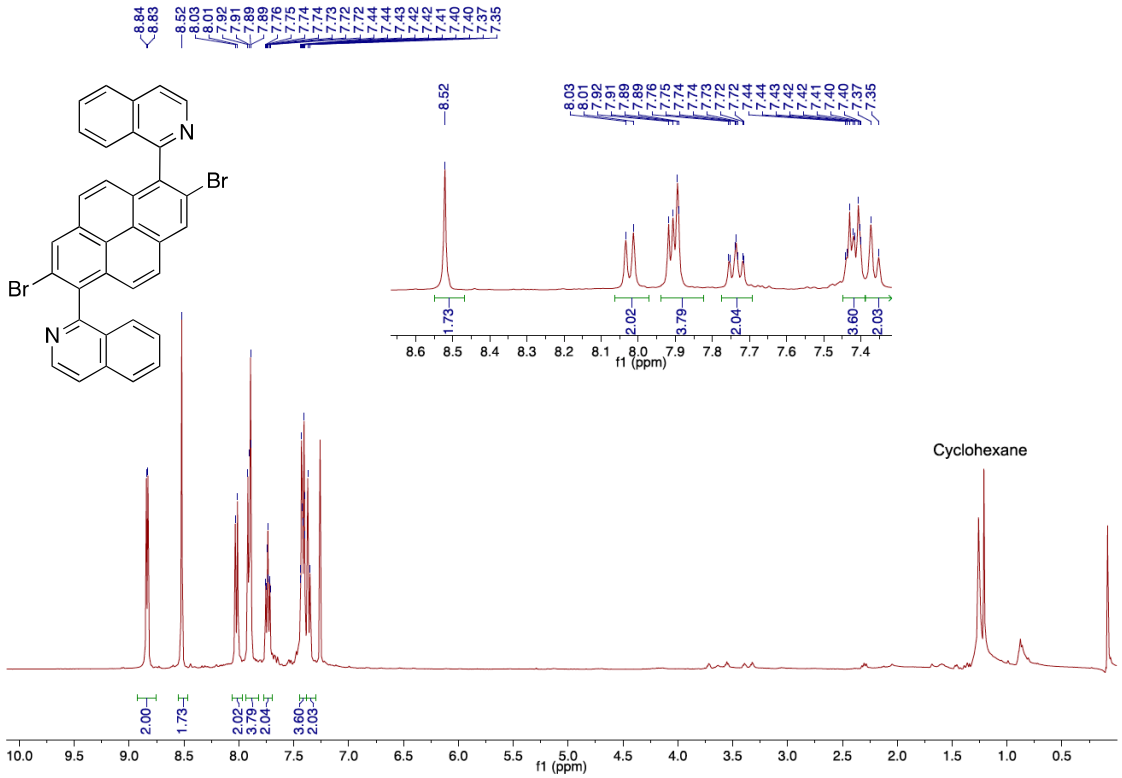


Figure S25. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **3C.D2**.

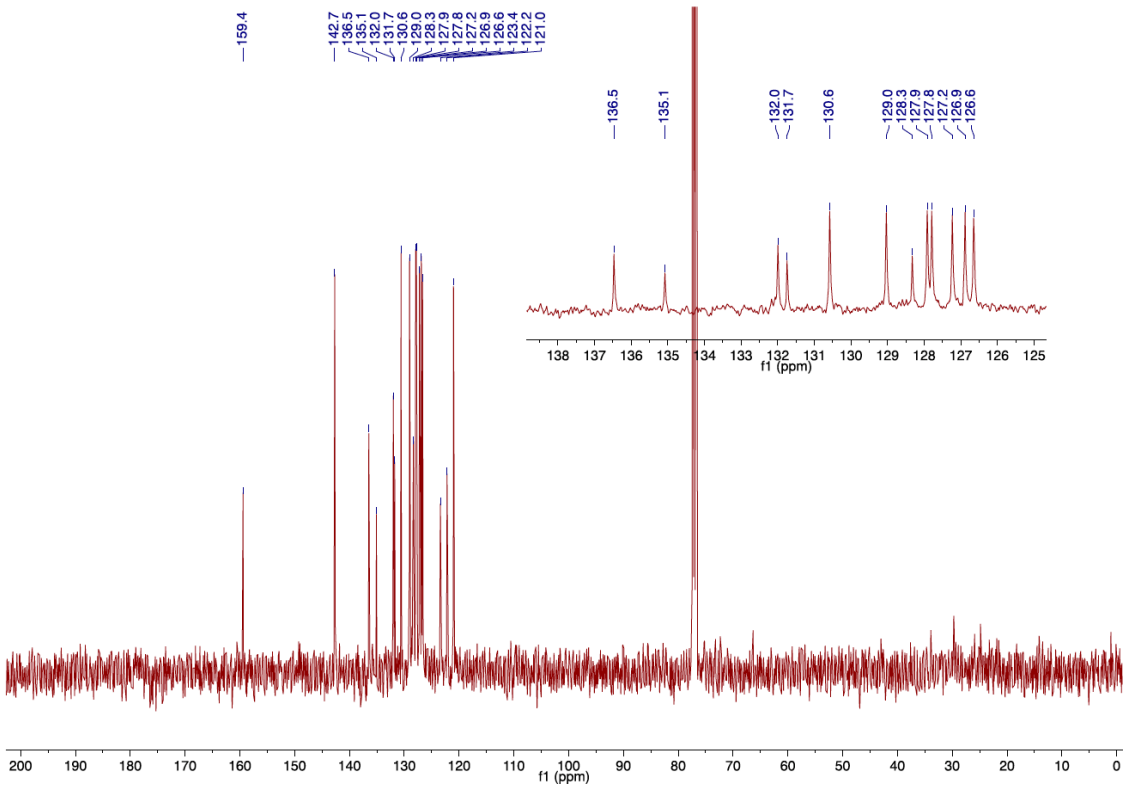


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3C.D2**.

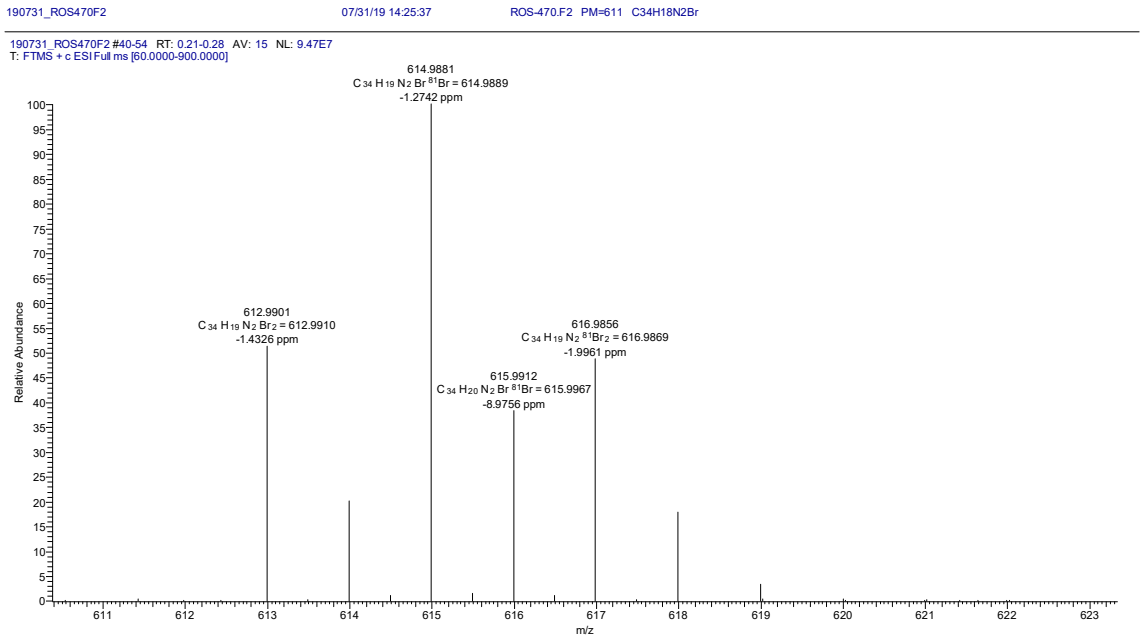


Figure S27. HRMS of **3C.D2**.

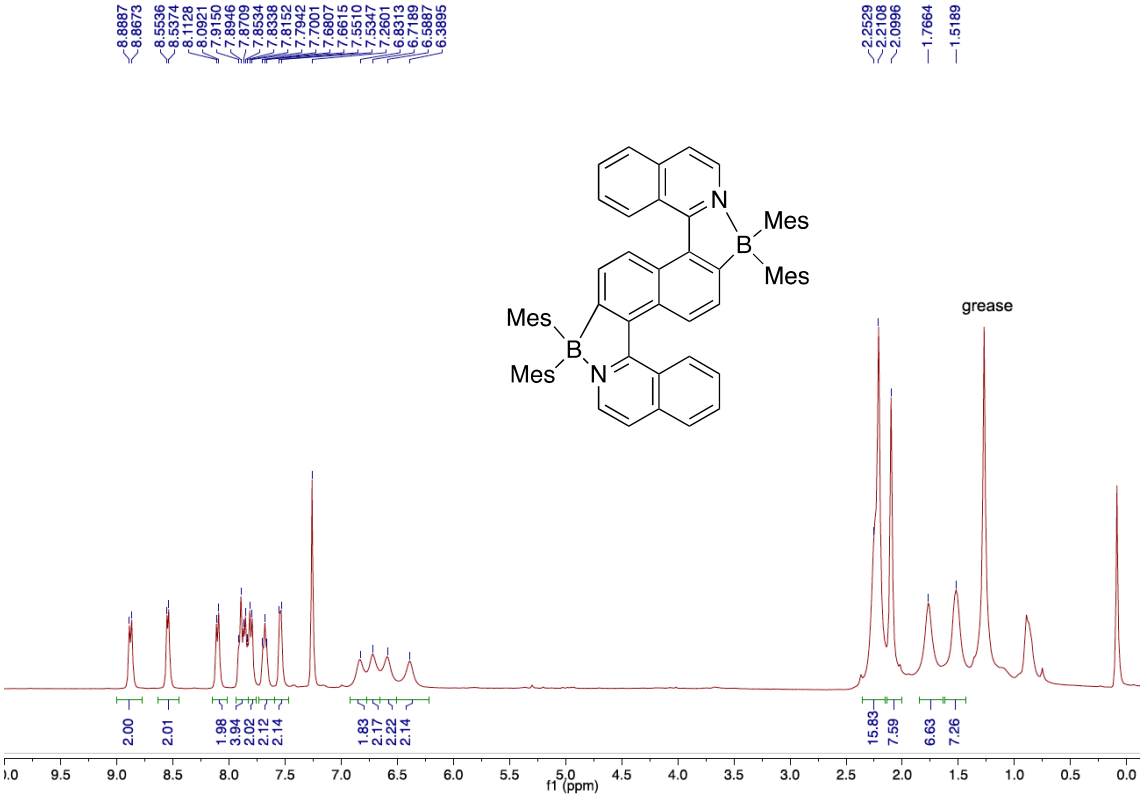


Figure S28. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **1**.

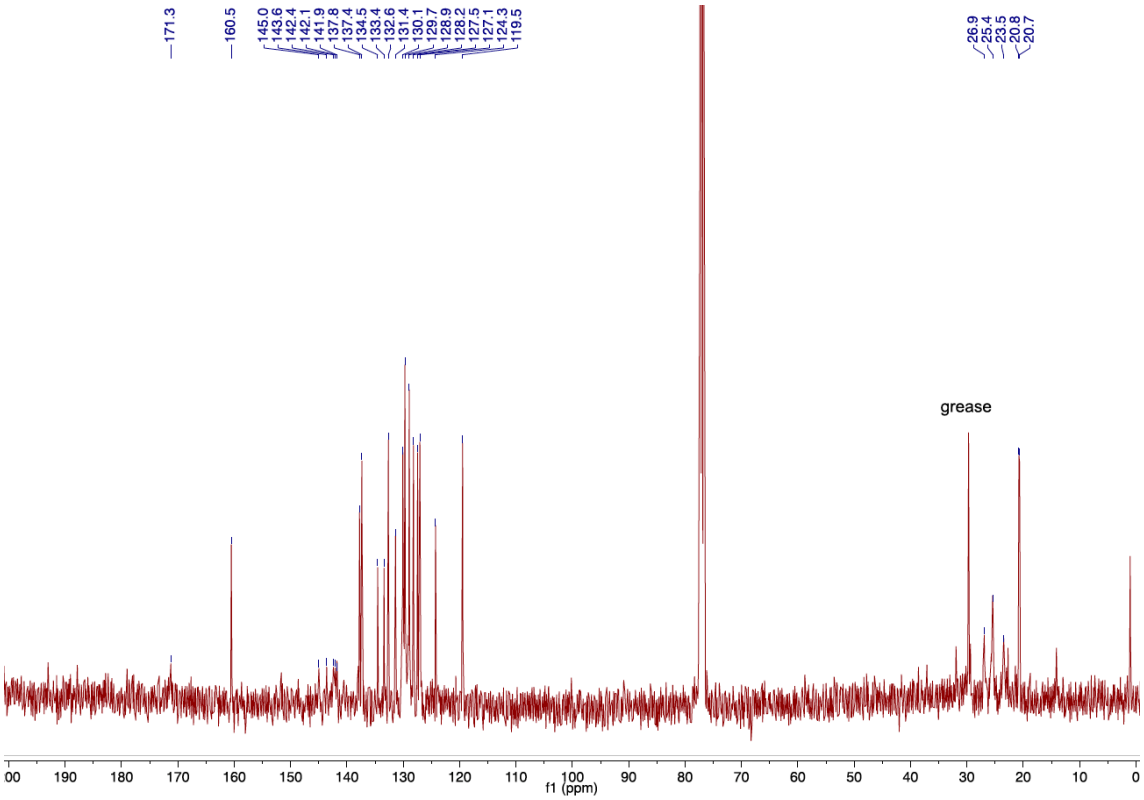


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **1**.

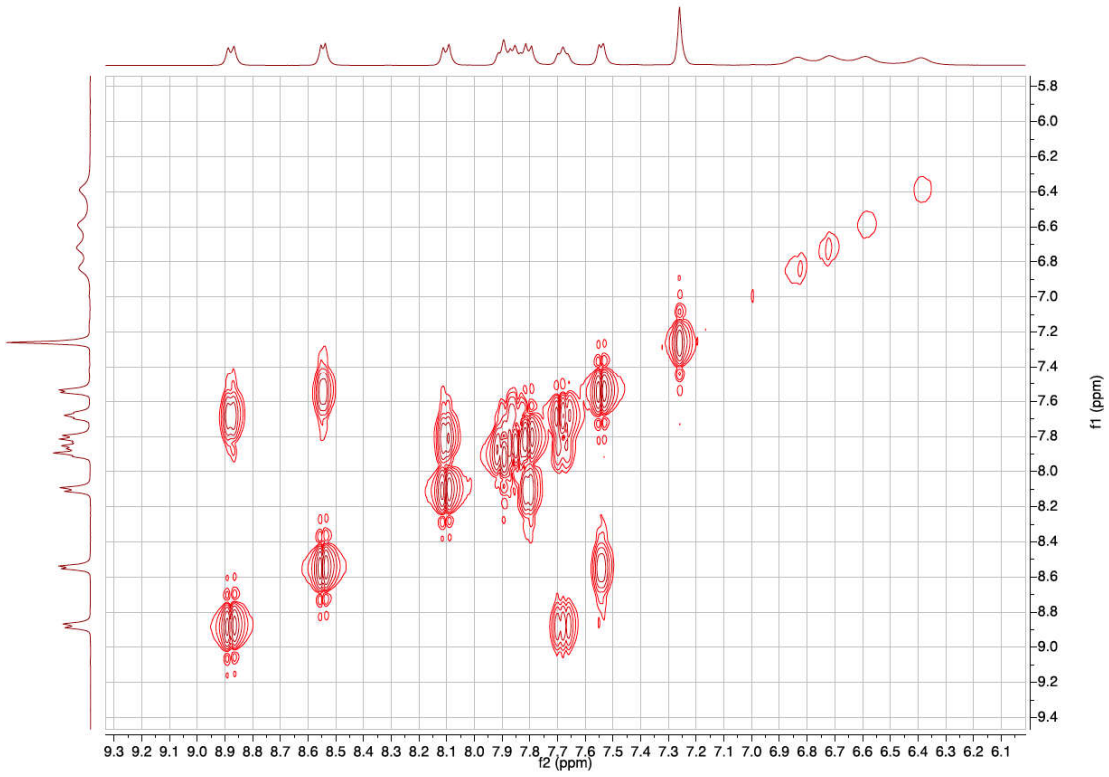


Figure S30. COSY spectrum (100 MHz, $CDCl_3$, 298 K) of **1**.

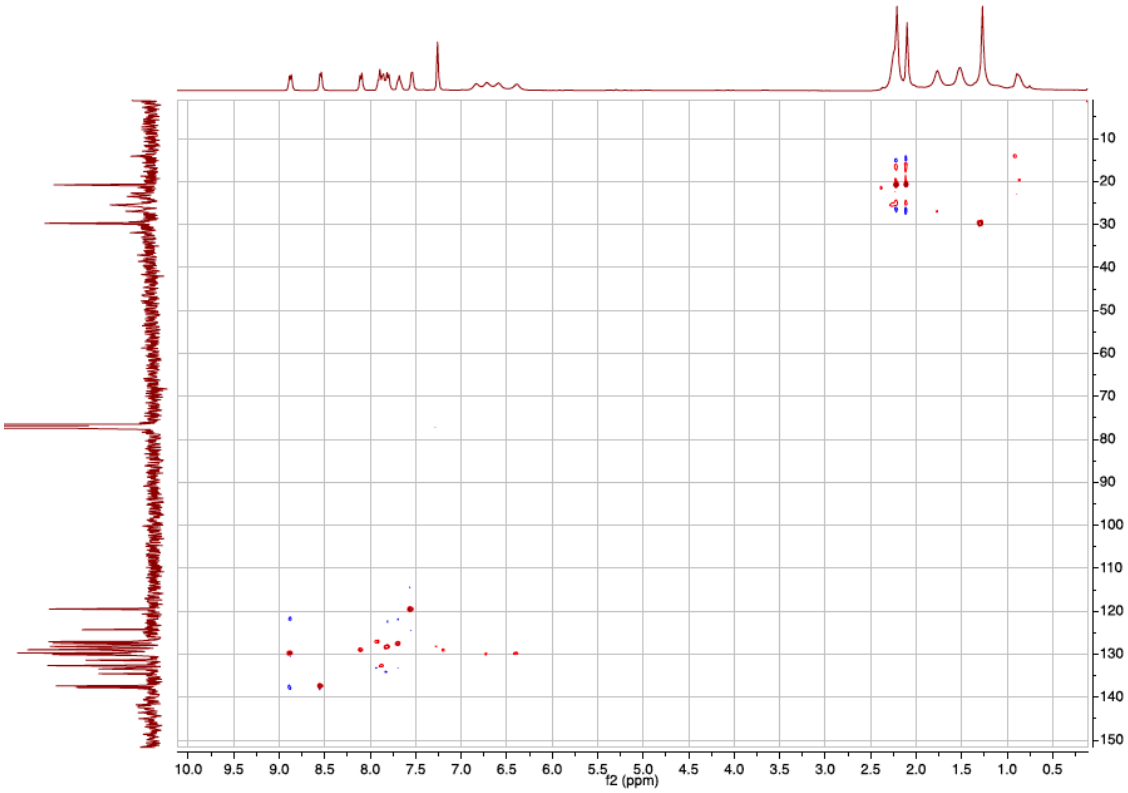


Figure S31. HSQC-edited spectrum (100 MHz, $CDCl_3$, 273 K) of **1**.

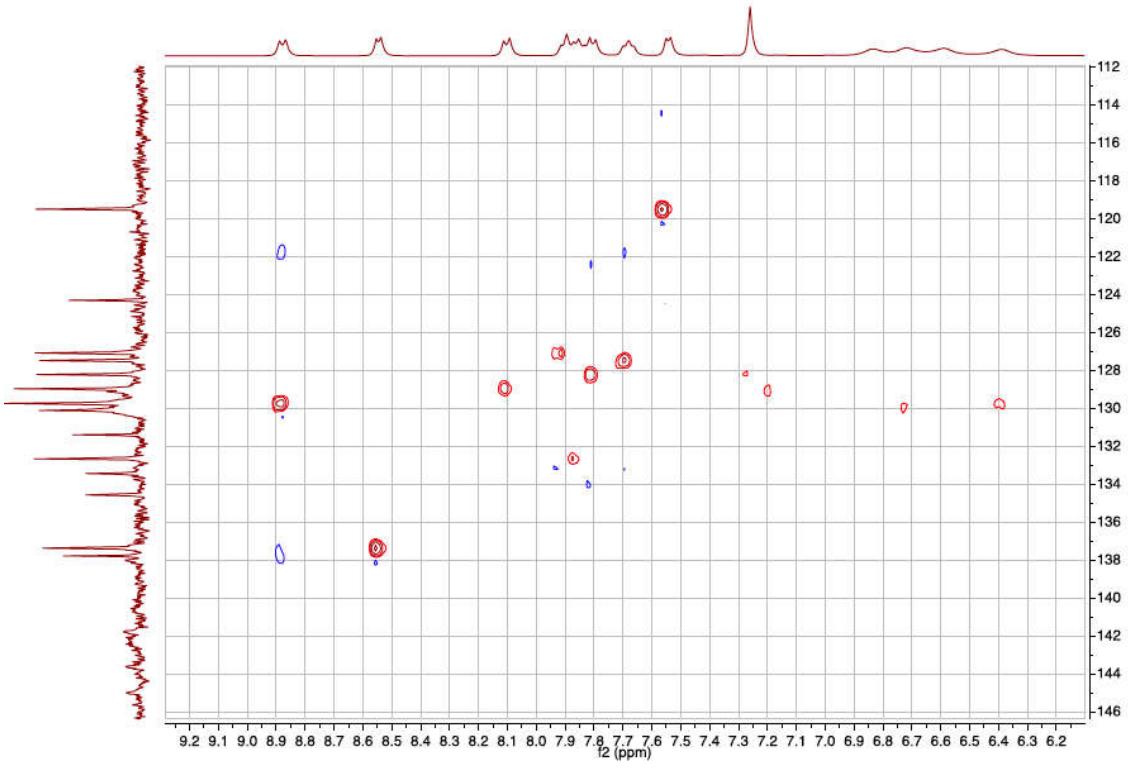


Figure S32. HSQC-edited spectrum (100 MHz, $CDCl_3$, 273 K) of **1**.

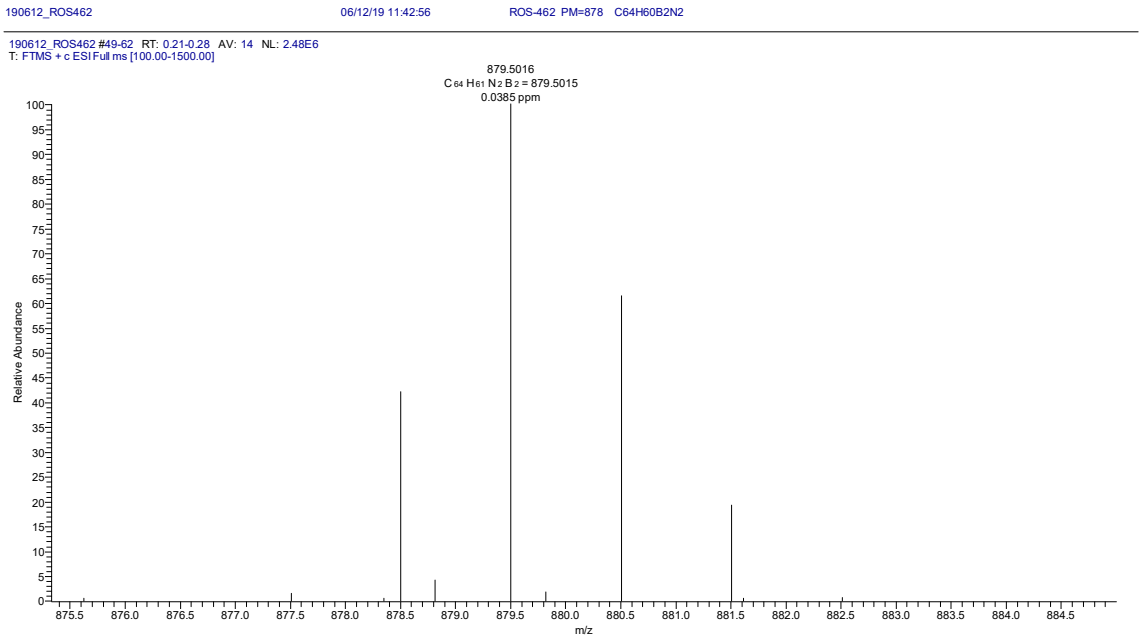


Figure S33. HRMS of **1**.

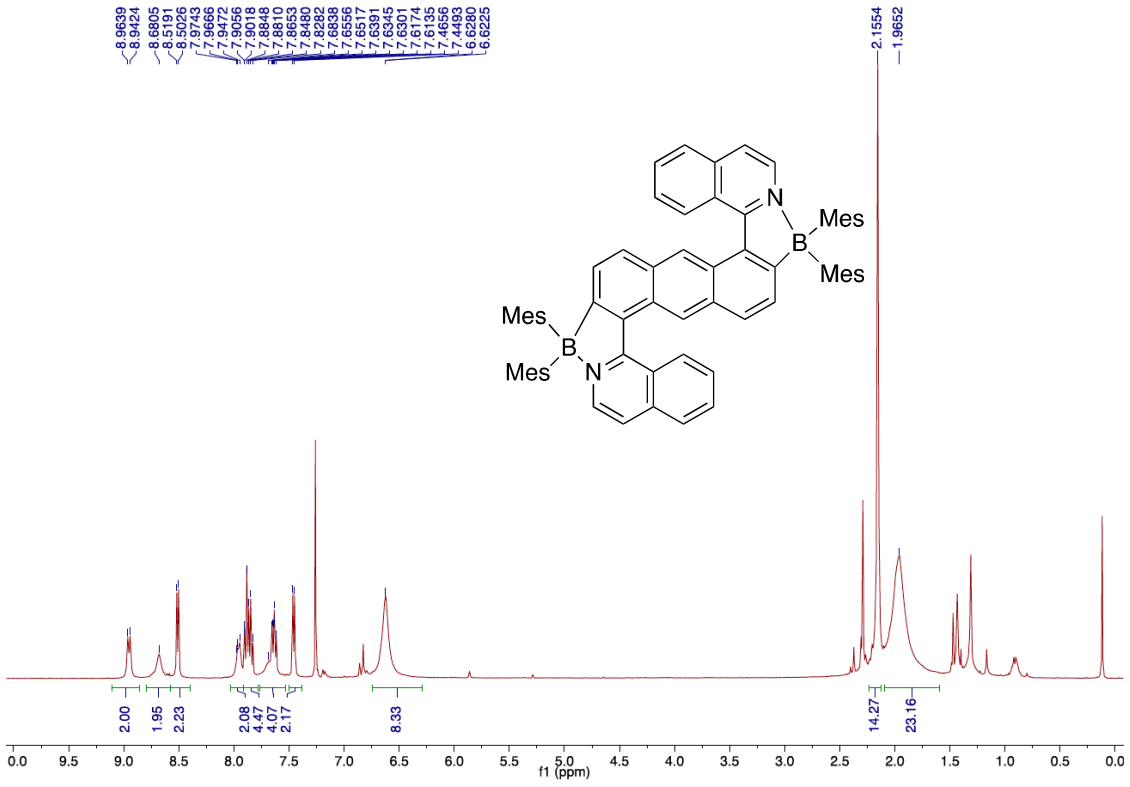


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 343 K) of **2**.

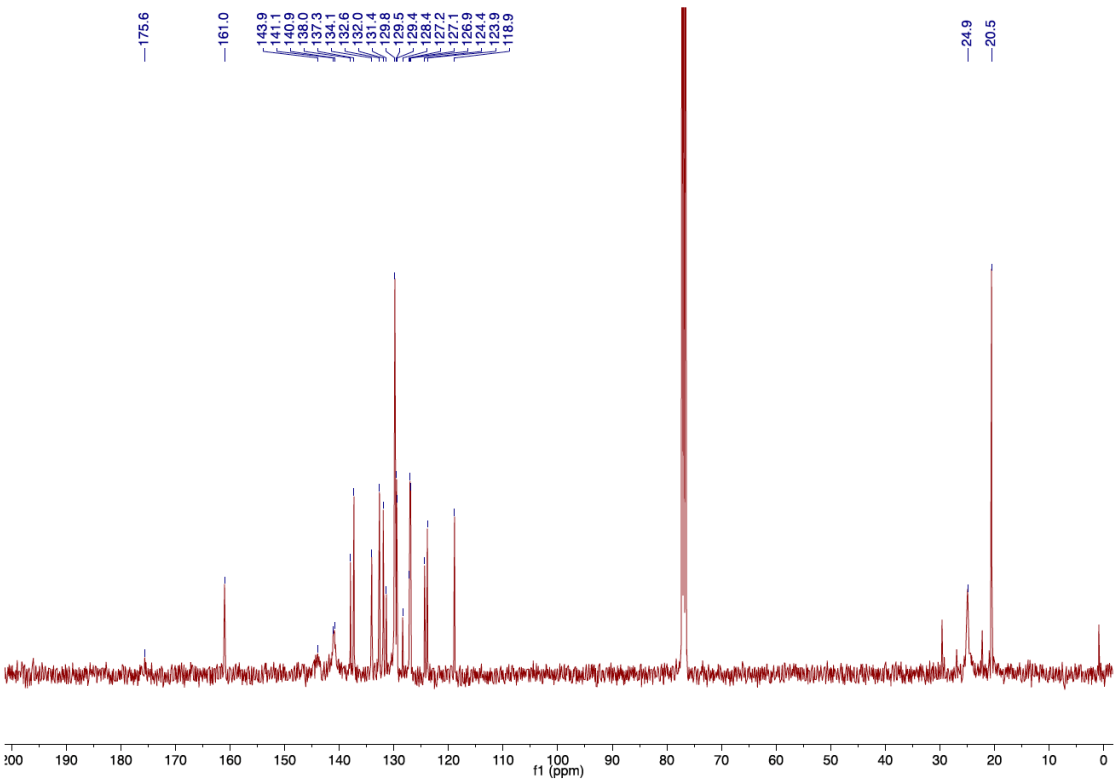


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 343 K) of **2**.

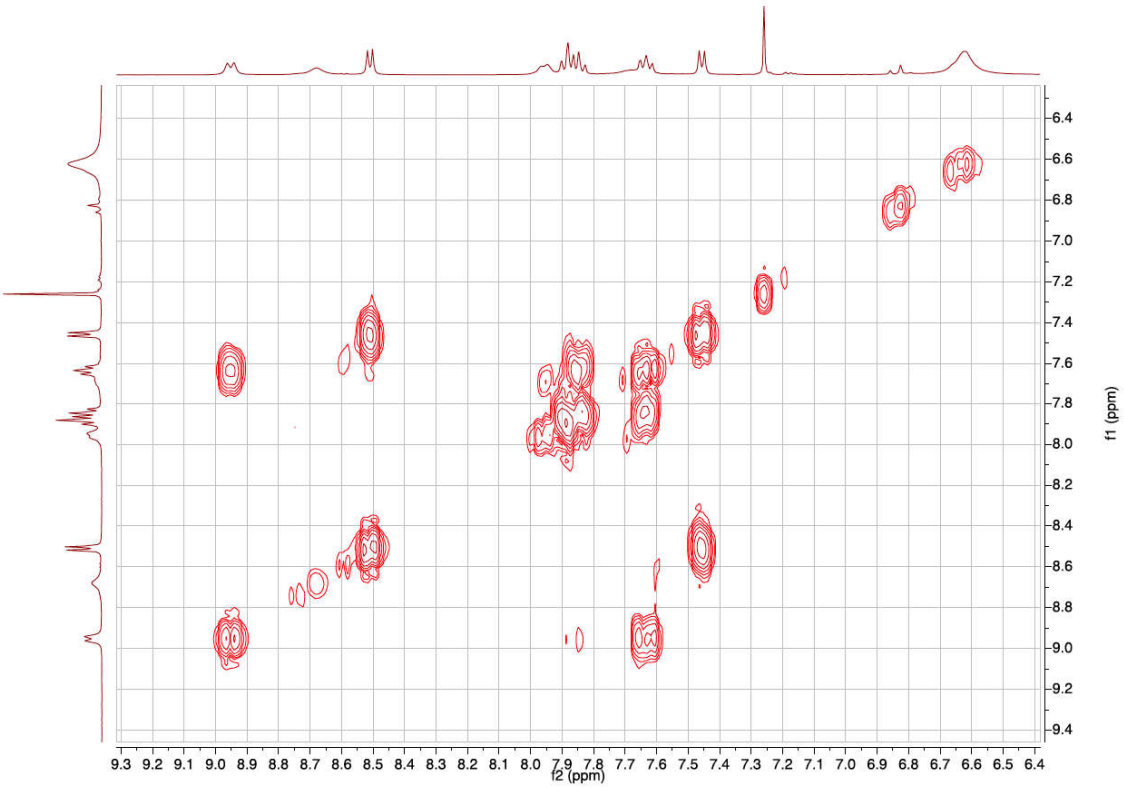


Figure S36. COSY spectrum (100 MHz, $CDCl_3$, 343 K) of **2**.

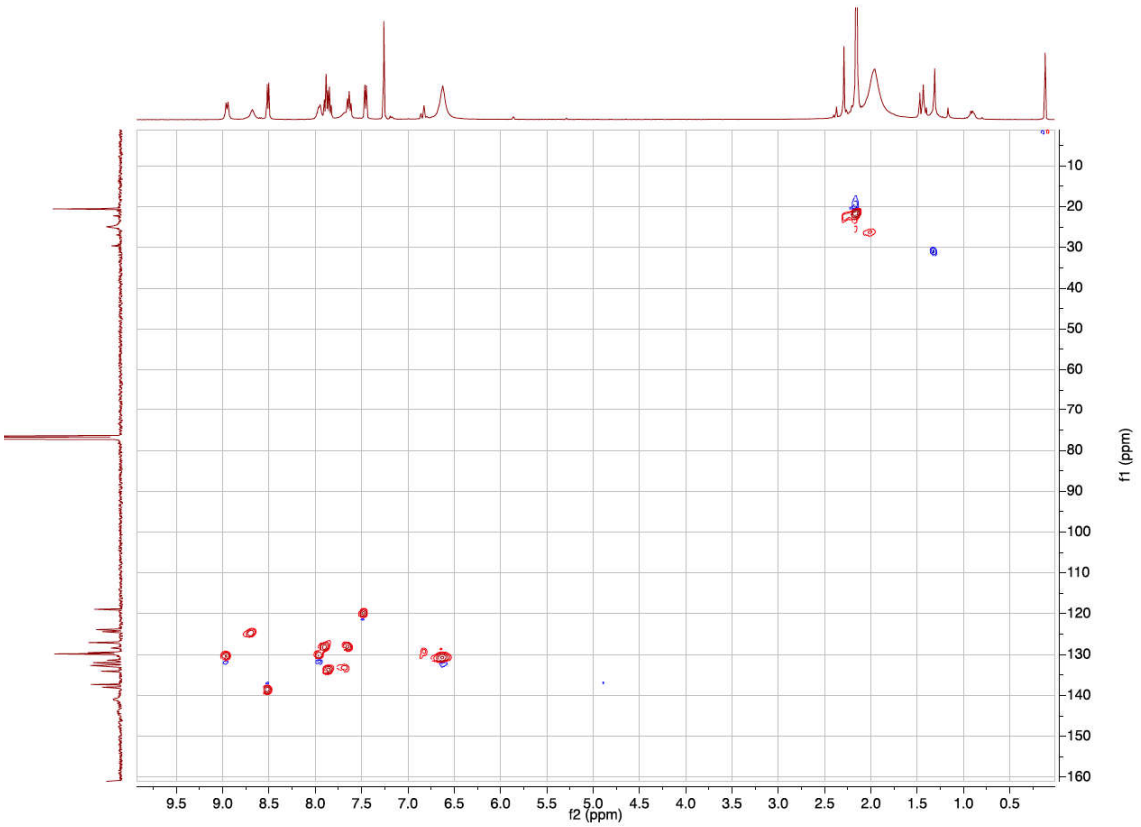


Figure S37. HSQC-edited spectrum (100 MHz, $CDCl_3$, 343 K) of **2**.

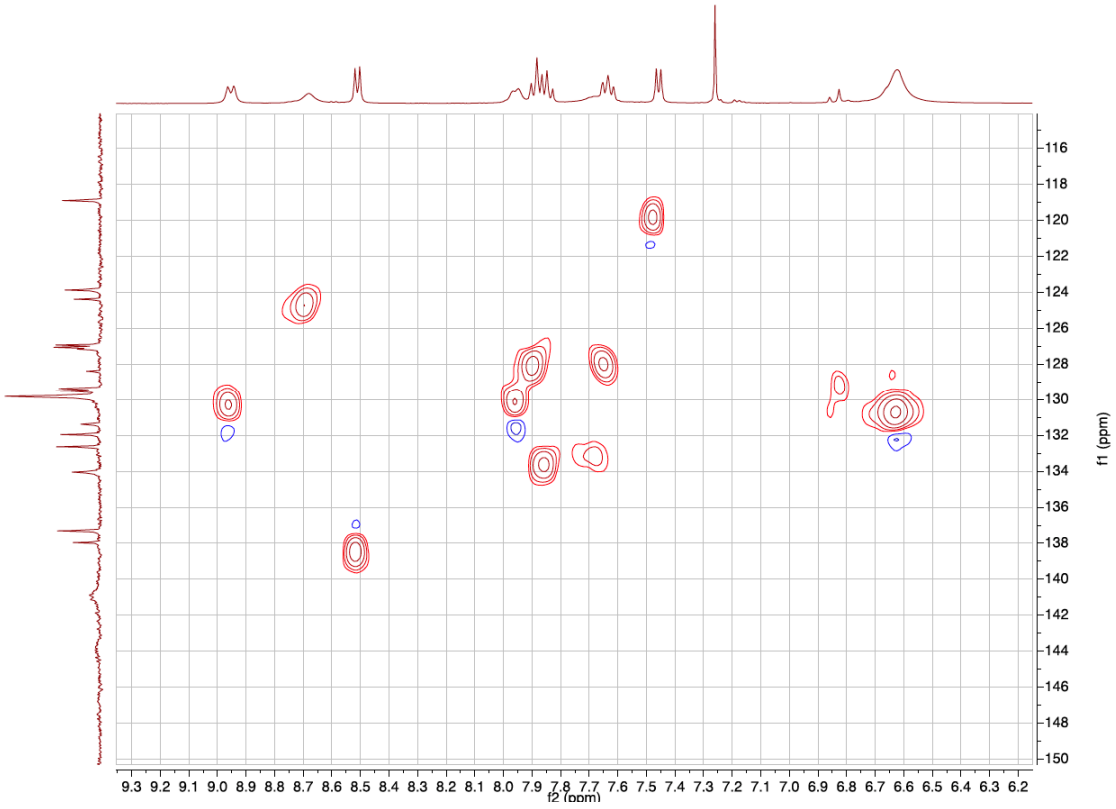


Figure S38. HSQC-edited spectrum (100 MHz, $CDCl_3$, 343 K) of **2**.

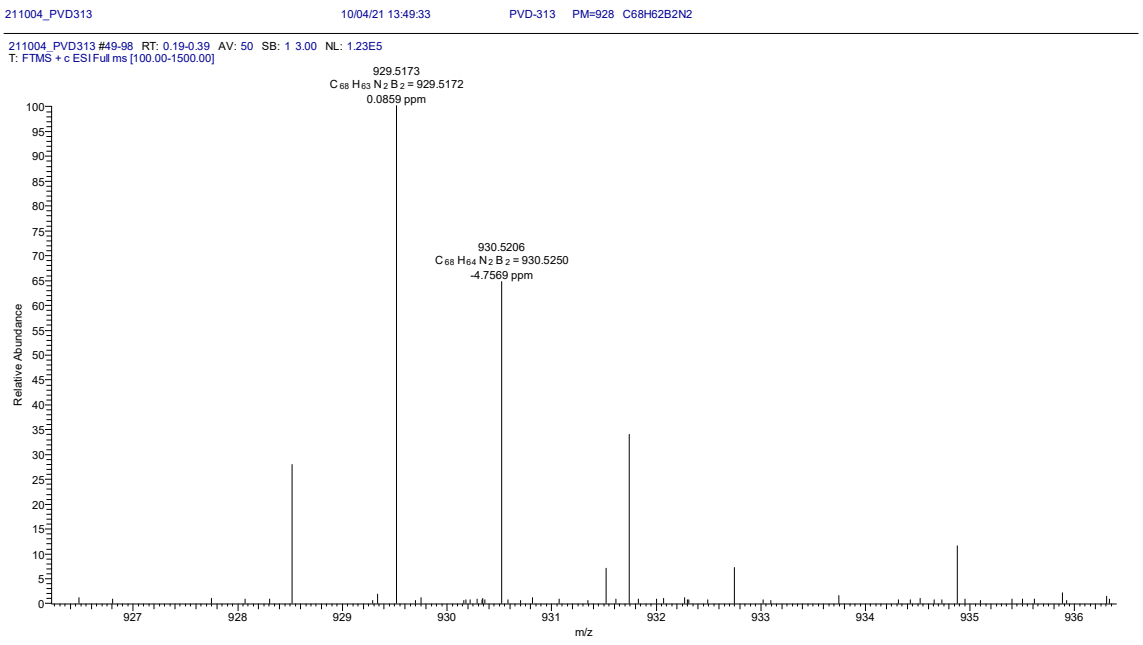


Figure S39. HRMS of **2**.

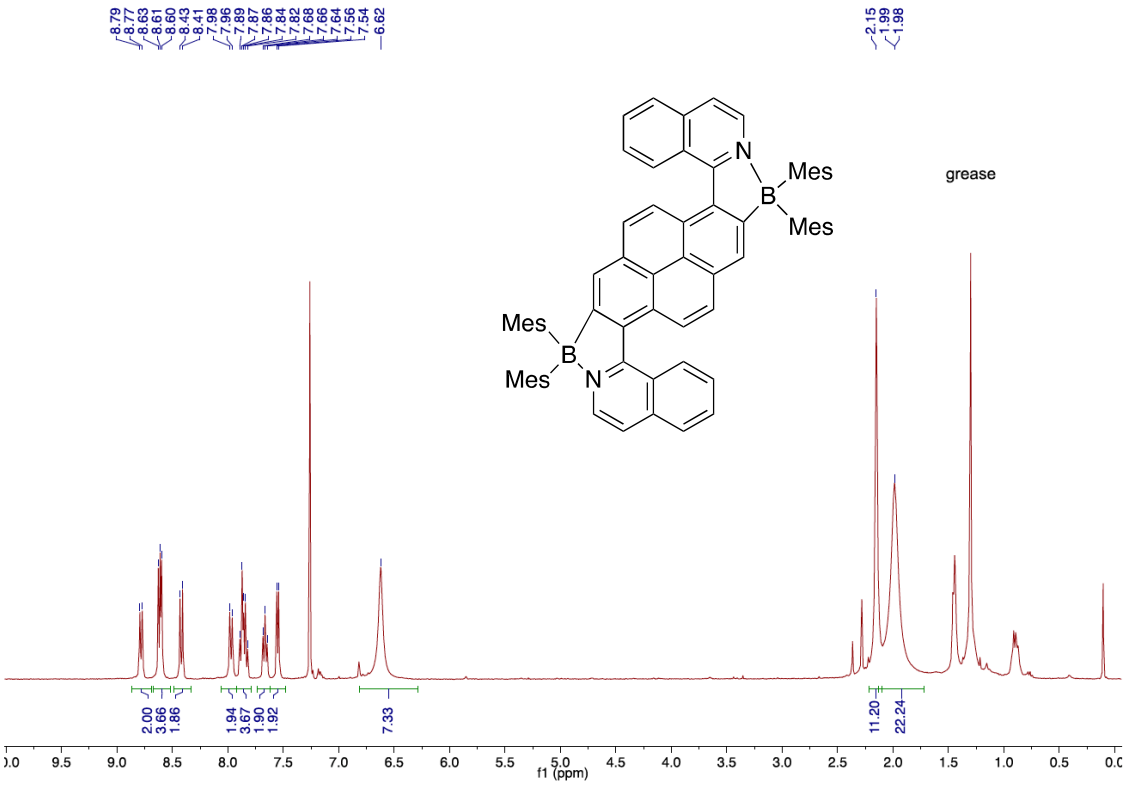


Figure S40. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 343 K) of **3**.

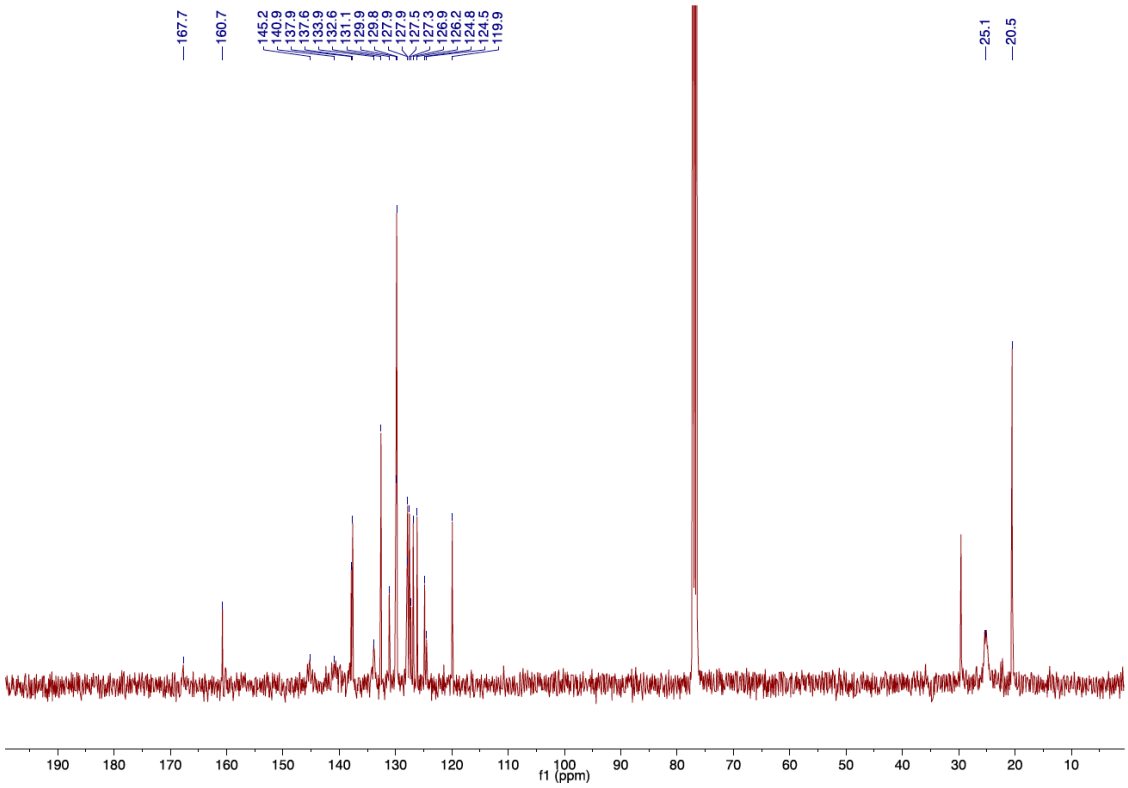


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$, 343 K) of **3**.

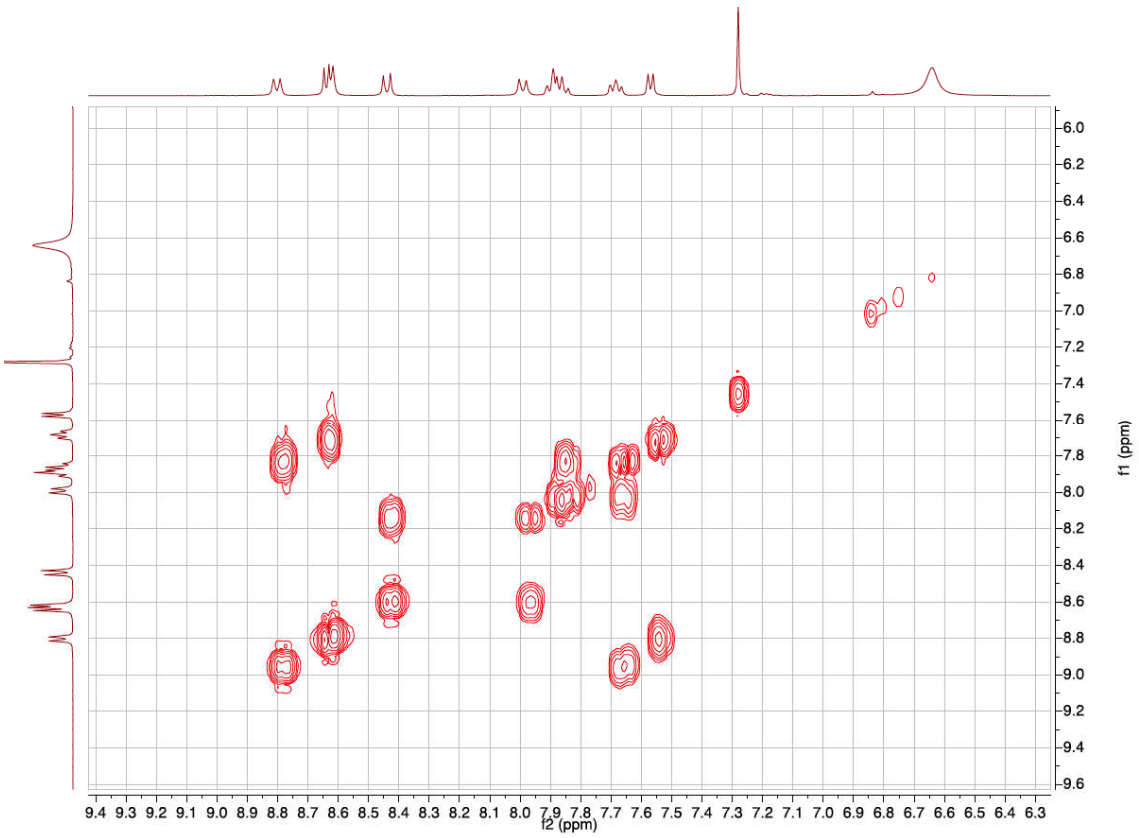


Figure S42. COSY spectrum (400 MHz, $CDCl_3$, 343 K) of **3**.

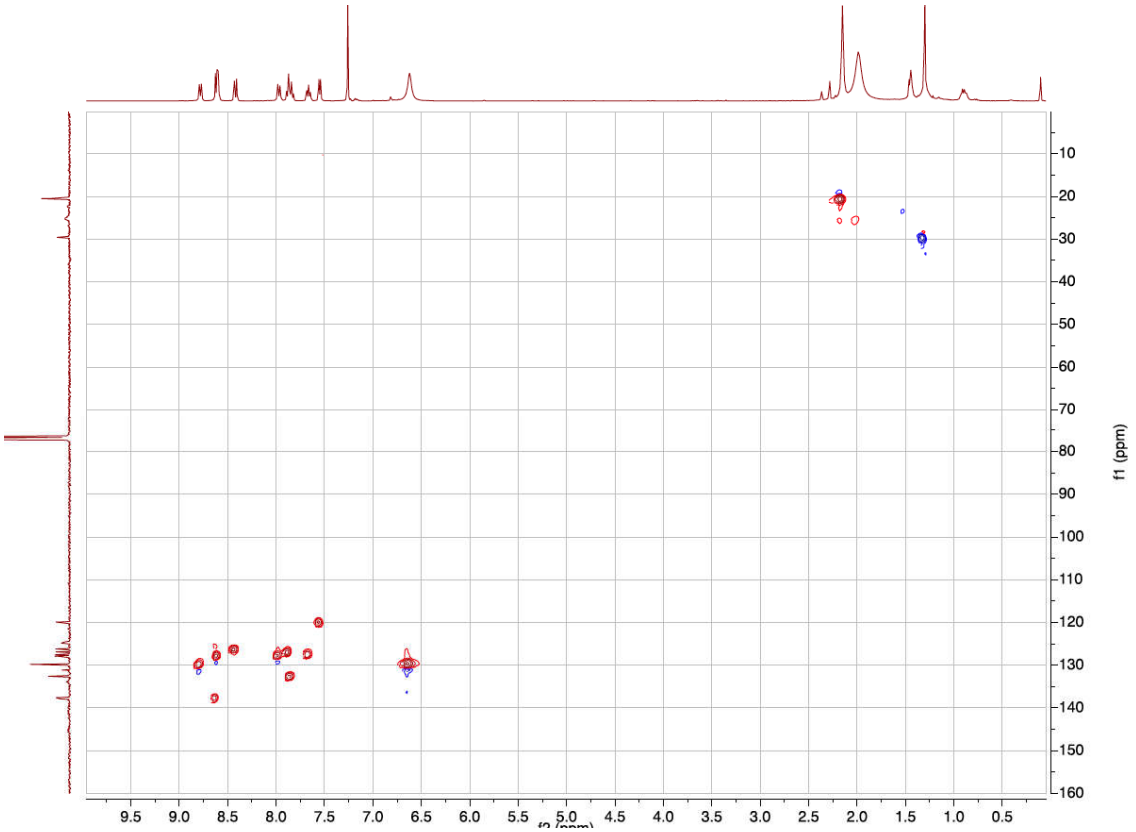


Figure S43. HSQC-edited spectrum (100 MHz, $CDCl_3$, 343 K) of **3**.

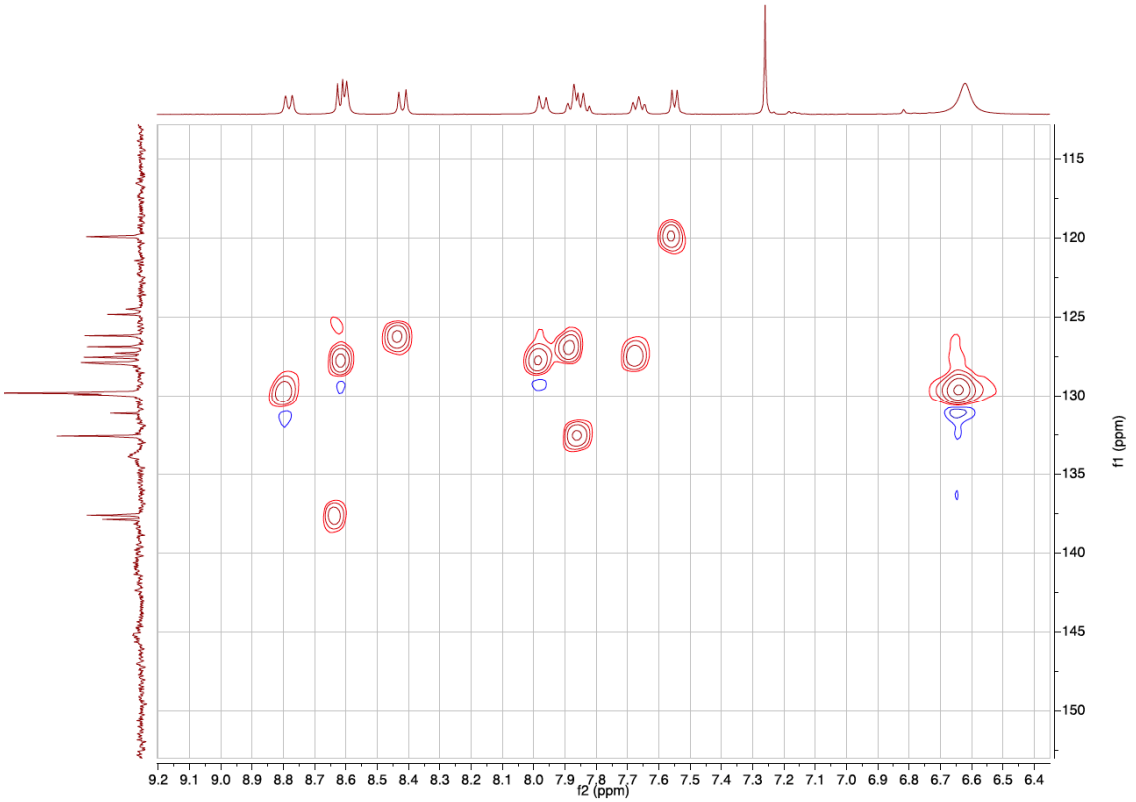


Figure S44. HSQC-edited spectrum (100 MHz, $CDCl_3$, 343 K) of **3**.

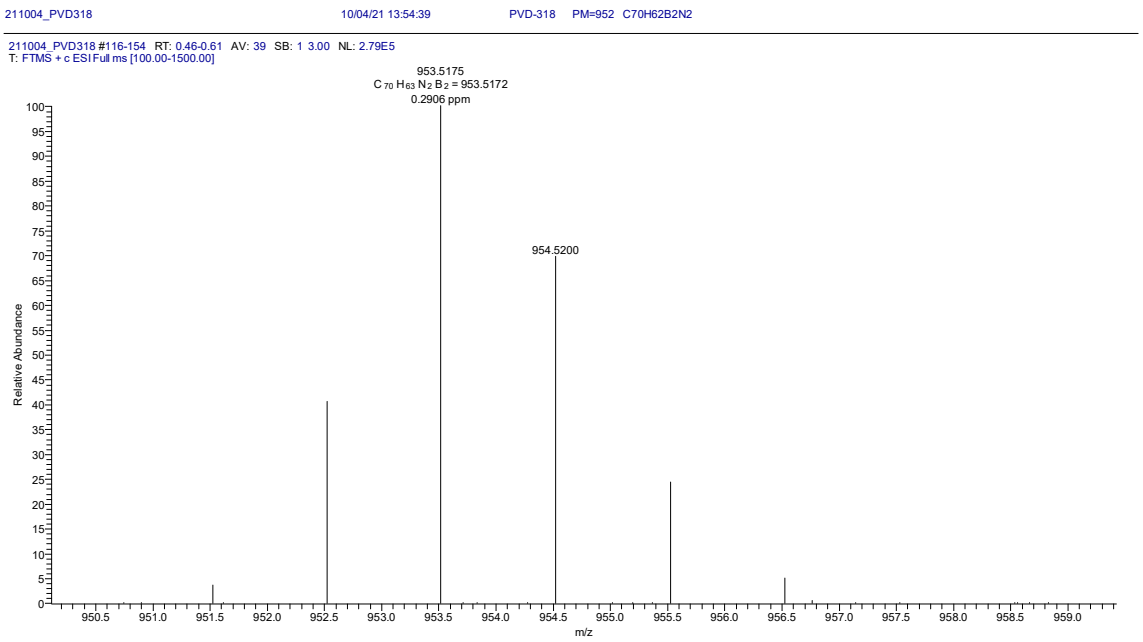
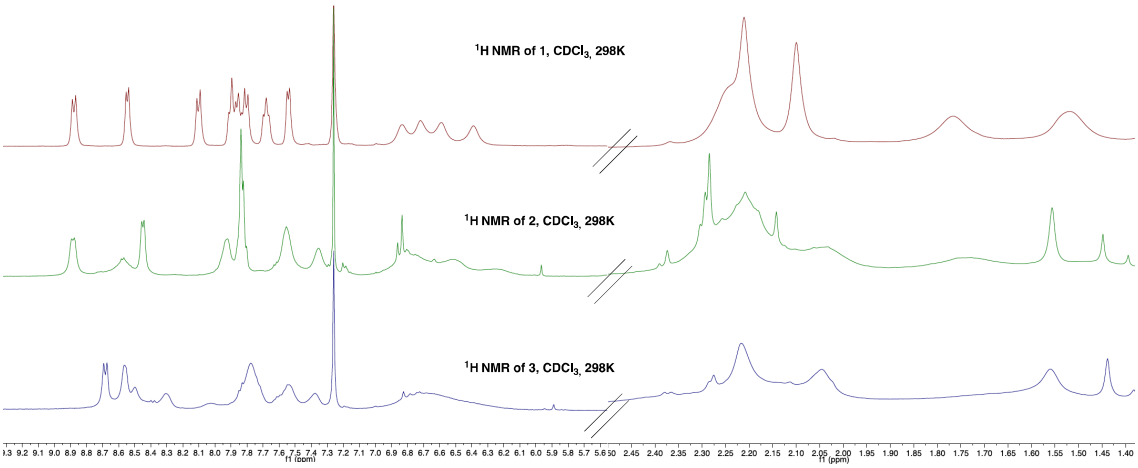


Figure S45. HRMS of **3**.

a)



b)

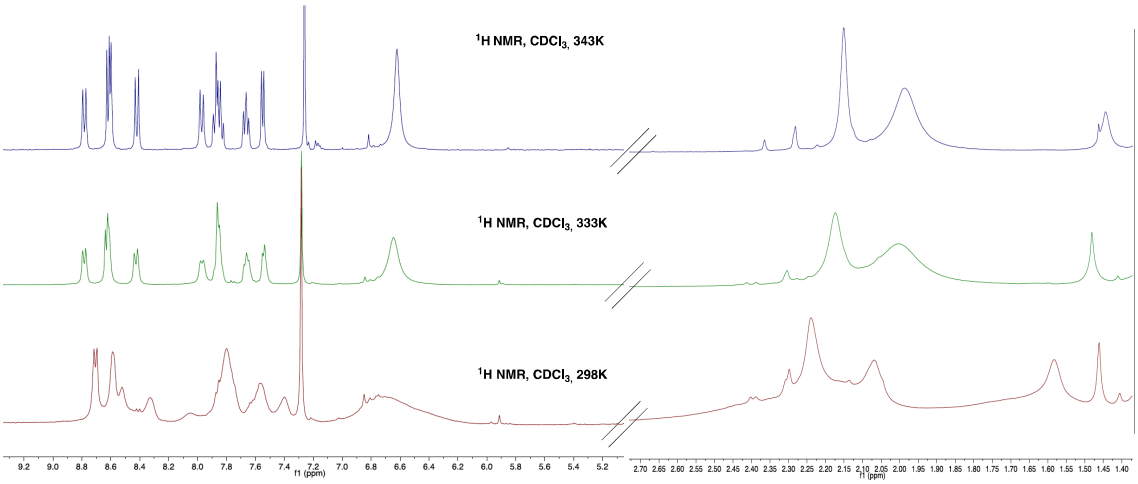


Figure S46. a) Comparison of the ^{1}H NMR spectra of the diboranes **1**–**3** at 298 K. b) ^{1}H NMR spectra at variable temperature for dye **3**. All in $CDCl_3$ as solvent.

4. Calculation of intersystem crossing quantum yields

The molar absorption coefficients of the dyes' triplet states were estimated by the energy-transfer method, using benzophenone (BP) as triplet energy donor [optical density - OD; $OD_{355\ nm}(BP) > 3$ and [dye] *ca*. 20–40 μM in N_2-saturated acetonitrile]. Toluene could not be used for this experiment, due to the interception of photoinduced hydrogen transfer.[15] The molar absorption coefficient of the excited triplet state of each dye was determined with equation (1).[16]

$$\varepsilon(^3\text{dye}^*)_\lambda = \Delta A(^3\text{dye}^*)_\lambda \times \varepsilon(^3\text{BP}^*)_{525\ nm}/(\Delta A(^3\text{BP}^*)_{525\ nm} \times (k_2 - k_1/k_2)) \quad (1)$$

$\Delta A(^3\text{BP}^*)_{525\ nm}$ is the absorbance change of ^{3}BP* at 525 nm, immediately after the laser flash, and k_1 is the decay rate constant of ^{3}BP* in the absence of dye. $\Delta A(^3\text{dye}^*)_\lambda$ corresponds to the absorbance change of ^{3}dye* at the observation wavelength λ and k_2 is the decay rate constant of ^{3}BP* in the presence of dye. The molar absorption coefficient $\varepsilon(^3\text{BP}^*)_{525\ nm}$ in acetonitrile was taken as 6500 $M^{-1}cm^{-1}$.[17]

The intersystem crossing (ISC) quantum yields (Φ_{ISC}) of the dyes in toluene were obtained by a comparative method (see equation 2),[16] assuming that the molar absorption coefficient of their excited triplet states has comparable values in acetonitrile and in toluene. Toluene solutions of each dye and acetonitrile solutions of BP, as reference, were used ($OD_{355\ nm} = 0.3$).

$$\Phi_{ISC}(\text{dye}) = \Phi_{ISC}(\text{BP}) \times \Delta A(^3\text{dye}^*)_\lambda \times \varepsilon(^3\text{BP}^*)_{525\ nm}/(\Delta A(^3\text{BP}^*)_{525\ nm} \times \varepsilon(^3\text{dye}^*)_\lambda) \quad (2)$$

5. Atomic coordinates for the optimized geometries of dyes 1–3

Atomic coordinates for the optimized ground state (S_0) of compound 1 at PCM(toluene)/PBE0/6-31G(d,p) level.

Energy (Hartrees) –2631.275730
Imaginary freq. 0
Point group Ci

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	2.534924	–0.218877	0.409755
C	1.723590	0.686366	–0.283126
C	0.305053	0.513271	–0.392978
C	–0.305053	–0.513271	0.392978
C	0.520767	–1.258954	1.274141
C	1.890618	–1.169979	1.229291
H	–0.060725	1.939323	–1.981837
C	–0.520767	1.258954	–1.274141
C	–1.723590	–0.686366	0.283126
H	0.060725	–1.939323	1.981837
H	2.475962	–1.832624	1.858617
C	–2.534924	0.218877	–0.409755
C	–1.890618	1.169979	–1.229291
H	–2.475962	1.832624	–1.858617
C	–2.578480	–1.708887	0.882736
C	–2.298761	–3.072440	1.227190
C	–1.126497	–3.753349	0.816851
C	–3.307431	–3.809881	1.914364
C	–4.818475	–1.981039	1.568301
C	–0.921291	–5.067584	1.165215
H	–0.398394	–3.242159	0.199151
C	–3.051800	–5.146851	2.296004
C	–4.574244	–3.205326	2.112063
H	–5.801018	–1.529393	1.575535
C	–1.874837	–5.759775	1.939031
H	–0.022549	–5.577148	0.832604
H	–3.816337	–5.689108	2.844810
H	–5.367567	–3.746407	2.615843
H	–1.691060	–6.791467	2.223700
C	2.578480	1.708887	–0.882736
C	2.298761	3.072440	–1.227190
C	1.126497	3.753349	–0.816851
C	3.307431	3.809881	–1.914364
C	4.818475	1.981039	–1.568301
C	0.921291	5.067584	–1.165215
H	0.398394	3.242159	–0.199151
C	3.051800	5.146851	–2.296004
C	4.574244	3.205326	–2.112063
H	5.801018	1.529393	–1.575535

C	1.874837	5.759775	–1.939031
H	0.022549	5.577148	–0.832604
H	3.816337	5.689108	–2.844810
H	5.367567	3.746407	–2.615843
H	1.691060	6.791467	–2.223700
N	3.838647	1.250830	–0.976686
N	–3.838647	–1.250830	0.976686
B	4.077102	–0.086617	–0.075379
B	–4.077102	0.086617	0.075379
C	5.316553	0.371628	0.904022
C	6.669678	0.130476	0.552484
C	5.092412	1.098712	2.102703
C	7.710346	0.545369	1.392681
C	6.157747	1.484327	2.919149
C	7.482186	1.206273	2.593091
H	8.736736	0.341720	1.089710
H	5.943285	2.034297	3.834354
C	–5.316553	–0.371628	–0.904022
C	–6.669678	–0.130476	–0.552484
C	–5.092412	–1.098712	–2.102703
C	–7.710346	–0.545369	–1.392681
C	–6.157747	–1.484327	–2.919149
C	–7.482186	–1.206273	–2.593091
H	–8.736736	–0.341720	–1.089710
H	–5.943285	–2.034297	–3.834354
C	4.277615	–1.516280	–0.873079
C	4.682445	–2.647993	–0.119436
C	3.956348	–1.743870	–2.235662
C	4.807226	–3.903374	–0.722608
C	4.104960	–3.012801	–2.802920
C	4.541307	–4.112380	–2.070813
H	5.124229	–4.746098	–0.108873
H	3.855366	–3.145252	–3.854772
C	–4.277615	1.516280	0.873079
C	–4.682445	2.647993	0.119436
C	–3.956348	1.743870	2.235662
C	–4.807226	3.903374	0.722608
C	–4.104960	3.012801	2.802920
C	–4.541307	4.112380	2.070813
H	–5.124229	4.746098	0.108873
H	–3.855366	3.145252	3.854772
C	3.717888	1.513912	2.563204
H	3.186449	2.095241	1.803596
H	3.081104	0.656939	2.801235
H	3.789912	2.134906	3.460723
C	–3.717888	–1.513912	–2.563204
H	–3.081104	–0.656939	–2.801235
H	–3.186449	–2.095241	–1.803596
H	–3.789912	–2.134906	–3.460723
C	7.115066	–0.583859	–0.705626

H	7.166714	–1.668111	–0.556162
H	6.449347	–0.438852	–1.557486
H	8.116397	–0.245434	–0.990822
C	–7.115066	0.583859	0.705626
H	–6.449347	0.438852	1.557486
H	–7.166714	1.668111	0.556162
H	–8.116397	0.245434	0.990822
C	8.611987	1.604249	3.500608
H	8.760799	0.863592	4.295804
H	9.555059	1.687326	2.952694
H	8.415347	2.564165	3.988136
C	–8.611987	–1.604249	–3.500608
H	–9.555059	–1.687326	–2.952694
H	–8.760799	–0.863592	–4.295804
H	–8.415347	–2.564165	–3.988136
C	5.039940	–2.603231	1.349664
H	4.783182	–3.554563	1.827293
H	6.116171	–2.448685	1.491819
H	4.549664	–1.799513	1.897228
C	–5.039940	2.603231	–1.349664
H	–6.116171	2.448685	–1.491819
H	–4.783182	3.554563	–1.827293
H	–4.549664	1.799513	–1.897228
C	3.426233	–0.671314	–3.155060
H	2.505811	–0.222030	–2.769166
H	4.141704	0.140957	–3.316095
H	3.194142	–1.096956	–4.135203
C	–3.426233	0.671314	3.155060
H	–4.141704	–0.140957	3.316095
H	–2.505811	0.222030	2.769166
H	–3.194142	1.096956	4.135203
C	4.721749	–5.460343	–2.710517
H	3.995904	–5.623652	–3.513040
H	5.720437	–5.559951	–3.153309
H	4.609534	–6.267754	–1.980765
C	–4.721749	5.460343	2.710517
H	–5.720437	5.559951	3.153309
H	–3.995904	5.623652	3.513040
H	–4.609534	6.267754	1.980765

Atomic coordinates for the optimized excited state (S_1) of compound 1 at PCM(toluene)/PBE0/6-31G(d,p) level.

Energy (Hartrees) –2631.178572
Imaginary freq. 0
Point group C1

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	2.465397	–0.153863	0.410633
C	1.647117	0.713433	–0.333467
C	0.228228	0.515680	–0.452328
C	–0.368127	–0.500637	0.372940
C	0.461576	–1.191678	1.288543
C	1.832236	–1.076741	1.265828
H	–0.166823	1.873287	–2.091743
C	–0.603526	1.210982	–1.354033
C	–1.780883	–0.729831	0.280403
H	–0.001136	–1.858464	2.007711
H	2.420352	–1.699930	1.931427
C	–2.605994	0.166141	–0.445577
C	–1.984823	1.088401	–1.288721
H	–2.577927	1.716939	–1.946840
C	–2.581195	–1.788435	0.855953
C	–2.264851	–3.146870	1.198087
C	–1.045116	–3.786714	0.876627
C	–3.280357	–3.944377	1.820961
C	–4.876697	–2.195021	1.359075
C	–0.791823	–5.092586	1.263162
H	–0.298259	–3.254576	0.300530
C	–2.989294	–5.256430	2.222248
C	–4.602697	–3.403137	1.924670
H	–5.891464	–1.822743	1.279545
C	–1.750033	–5.827024	1.968257
H	0.159968	–5.546907	1.003154
H	–3.769406	–5.833131	2.712730
H	–5.404810	–4.004459	2.337984
H	–1.539863	–6.844298	2.284305
C	2.495864	1.716765	–0.962523
C	2.209508	3.062590	–1.379983
C	1.024244	3.748788	–1.023397
C	3.222539	3.781417	–2.079401
C	4.749019	1.993764	–1.618836
C	0.812006	5.045649	–1.430092
H	0.285228	3.247938	–0.410264
C	2.960786	5.098135	–2.522577
C	4.501680	3.186602	–2.226876
H	5.737433	1.555844	–1.585318
C	1.772502	5.715609	–2.213496
H	–0.099926	5.558278	–1.139842

H	3.730370	5.623635	–3.080757
H	5.297868	3.714868	–2.739463
H	1.584666	6.732068	–2.546587
N	3.769581	1.278939	–1.011033
N	–3.916455	–1.397148	0.845596
B	4.011034	–0.014150	–0.056413
B	–4.160875	–0.062121	0.044176
C	5.227160	0.498822	0.928185
C	6.590714	0.261733	0.615827
C	4.969883	1.274872	2.089011
C	7.608242	0.725837	1.458878
C	6.012697	1.710553	2.909445
C	7.347023	1.434945	2.624387
H	8.643270	0.522955	1.185986
H	5.771985	2.297325	3.794929
C	–5.420387	–0.347896	–0.968261
C	–6.751747	–0.036621	–0.601841
C	–5.233751	–1.028759	–2.197900
C	–7.817860	–0.335600	–1.458480
C	–6.321243	–1.301643	–3.030007
C	–7.625616	–0.948301	–2.691738
H	–8.830644	–0.087855	–1.143639
H	–6.141752	–1.823735	–3.968743
C	4.249167	–1.468186	–0.799763
C	4.663175	–2.566177	–0.002024
C	3.953430	–1.748782	–2.158498
C	4.823754	–3.837996	–0.560043
C	4.136994	–3.032920	–2.679633
C	4.584215	–4.097811	–1.904372
H	5.145510	–4.653286	0.087402
H	3.904726	–3.206480	–3.729489
C	–4.301063	1.304983	0.940383
C	–4.483620	2.563903	0.224667
C	–4.007619	1.410201	2.358271
C	–4.172389	3.762759	0.832953
C	–3.718244	2.639293	2.916082
C	–3.765469	3.833844	2.174905
H	–4.259252	4.684816	0.263998
H	–3.447588	2.692088	3.967397
C	3.581069	1.694345	2.500649
H	3.062373	2.235791	1.703558
H	2.947674	0.841132	2.759637
H	3.627114	2.354445	3.371891
C	–3.884338	–1.524732	–2.649021
H	–3.205348	–0.707215	–2.908151
H	–3.386618	–2.104754	–1.866621
H	–3.989356	–2.167058	–3.528085
C	7.072695	–0.495751	–0.603014
H	7.140161	–1.571900	–0.408299
H	6.420671	–0.397677	–1.471836

H	8.073460	–0.151139	–0.883123
C	–7.125851	0.612363	0.711763
H	–6.518606	0.259384	1.550439
H	–7.027788	1.704473	0.686182
H	–8.169815	0.396976	0.959177
C	8.452534	1.884812	3.537697
H	8.601965	1.173523	4.359230
H	9.403561	1.968820	3.003683
H	8.228838	2.856044	3.989981
C	–8.774694	–1.226069	–3.619527
H	–9.730439	–1.212129	–3.088015
H	–8.831424	–0.474581	–4.416388
H	–8.669762	–2.201188	–4.105290
C	4.991974	–2.466480	1.471043
H	4.729639	–3.401235	1.977478
H	6.064721	–2.301754	1.628265
H	4.486584	–1.646592	1.978964
C	–4.989873	2.631062	–1.185673
H	–6.082326	2.545650	–1.205208
H	–4.721068	3.587681	–1.640570
H	–4.626577	1.814820	–1.808334
C	3.411132	–0.722021	–3.122404
H	2.478288	–0.278282	–2.761155
H	4.111285	0.098216	–3.308671
H	3.196488	–1.189835	–4.087269
C	–3.968548	0.223233	3.274639
H	–4.890507	–0.362682	3.231663
H	–3.153535	–0.455945	3.014625
H	–3.823942	0.552384	4.306151
C	4.800493	–5.462995	–2.494419
H	4.100124	–5.661682	–3.311420
H	5.813007	–5.563820	–2.904642
H	4.676496	–6.247864	–1.742283
C	–3.402998	5.134643	2.803432
H	–3.699812	5.169255	3.855184
H	–2.312549	5.264355	2.776657
H	–3.847112	5.980613	2.274178

Atomic coordinates for the optimized ground state (S_0) of compound 2 at PCM(toluene)/PBE0/6-31G(d,p) level.

Energy (Hartrees) –2784.743949
Imaginary freq. 0
Point group Ci

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	–0.304815	–0.601674	–3.702142
C	0.563093	0.044787	–2.822144
C	0.336394	0.048553	–1.396867
C	–0.655539	–0.860120	–0.892653
C	–1.420343	–1.637479	–1.812316
C	–1.305025	–1.456551	–3.161042
C	0.935499	0.911825	–0.477240
C	–0.935499	–0.911825	0.477240
C	–0.336394	–0.048553	1.396867
C	0.655539	0.860120	0.892653
C	1.420343	1.637479	1.812316
H	2.159248	2.326803	1.410145
C	1.305025	1.456551	3.161042
C	0.304815	0.601674	3.702142
C	–0.563093	–0.044787	2.822144
H	1.655393	1.650583	–0.812253
H	–2.159248	–2.326803	–1.410145
H	–1.979931	–1.984734	–3.825939
H	–1.655393	–1.650583	0.812253
H	1.979931	1.984734	3.825939
C	–1.585993	–0.739786	3.594218
C	–2.916654	–1.133394	3.230871
C	–3.560636	–0.694946	2.048609
C	–3.664243	–1.910418	4.163409
C	–1.922094	–1.571784	5.775748
C	–4.844081	–1.095342	1.758907
H	–3.046294	–0.014701	1.381110
C	–4.966921	–2.340509	3.822219
C	–3.108959	–2.151617	5.445416
H	–1.513104	–1.619933	6.775479
C	–5.541025	–1.950804	2.635965
H	–5.326532	–0.741027	0.853439
H	–5.516229	–2.955430	4.529283
H	–3.660623	–2.723425	6.183314
H	–6.547076	–2.274629	2.386608
C	1.585993	0.739786	–3.594218
C	2.916654	1.133394	–3.230871
C	3.560636	0.694946	–2.048609
C	3.664243	1.910418	–4.163409
C	1.922094	1.571784	–5.775748
C	4.844081	1.095342	–1.758907

H	3.046294	0.014701	–1.381110
C	4.966921	2.340509	–3.822219
C	3.108959	2.151617	–5.445416
H	1.513104	1.619933	–6.775479
C	5.541025	1.950804	–2.635965
H	5.326532	0.741027	–0.853439
H	5.516229	2.955430	–4.529283
H	3.660623	2.723425	–6.183314
H	6.547076	2.274629	–2.386608
N	–1.176287	–0.894470	4.865689
N	1.176287	0.894470	–4.865689
B	0.121708	0.026448	5.207344
B	–0.121708	–0.026448	–5.207344
C	–0.415370	0.924465	6.476966
C	–0.241292	0.491792	7.816489
C	–1.150200	2.124203	6.287605
C	–0.735317	1.253884	8.882567
C	–1.614452	2.862148	7.378400
C	–1.409395	2.453567	8.693369
H	–0.582717	0.889214	9.897691
H	–2.168458	3.780838	7.191000
C	0.415370	–0.924465	–6.476966
C	0.241292	–0.491792	–7.816489
C	1.150200	–2.124203	–6.287605
C	0.735317	–1.253884	–8.882567
C	1.614452	–2.862148	–7.378400
C	1.409395	–2.453567	–8.693369
H	0.582717	–0.889214	–9.897691
H	2.168458	–3.780838	–7.191000
C	1.564102	–0.742679	5.426551
C	2.651647	0.009266	5.942272
C	1.846994	–2.072488	5.022383
C	3.915229	–0.570512	6.091896
C	3.121746	–2.617629	5.200687
C	4.175575	–1.891327	5.745738
H	4.723161	0.039975	6.493990
H	3.297124	–3.645297	4.885548
C	–1.564102	0.742679	–5.426551
C	–2.651647	–0.009266	–5.942272
C	–1.846994	2.072488	–5.022383
C	–3.915229	0.570512	–6.091896
C	–3.121746	2.617629	–5.200687
C	–4.175575	1.891327	–5.745738
H	–4.723161	–0.039975	–6.493990
H	–3.297124	3.645297	–4.885548
C	0.831476	–2.976023	4.367534
H	–0.011171	–3.214054	5.023930
H	0.418691	–2.530999	3.456750
H	1.298505	–3.923221	4.084009
C	–0.831476	2.976023	–4.367534

H	–0.418691	2.530999	–3.456750
H	0.011171	3.214054	–5.023930
H	–1.298505	3.923221	–4.084009
C	2.548443	1.448637	6.396741
H	2.311262	1.512724	7.465241
H	3.505733	1.958111	6.245301
H	1.771861	2.017203	5.886243
C	–2.548443	–1.448637	–6.396741
H	–3.505733	–1.958111	–6.245301
H	–2.311262	–1.512724	–7.465241
H	–1.771861	–2.017203	–5.886243
C	5.530016	–2.508186	5.954299
H	5.597115	–2.998298	6.933423
H	5.744732	–3.268816	5.197515
H	6.322855	–1.755278	5.914573
C	–5.530016	2.508186	–5.954299
H	–5.744732	3.268816	–5.197515
H	–5.597115	2.998298	–6.933423
H	–6.322855	1.755278	–5.914573
C	–1.489654	2.668421	4.923003
H	–0.598487	2.940566	4.349576
H	–2.041852	1.944246	4.316307
H	–2.112227	3.563038	5.014818
C	1.489654	–2.668421	–4.923003
H	2.041852	–1.944246	–4.316307
H	0.598487	–2.940566	–4.349576
H	2.112227	–3.563038	–5.014818
C	0.484085	–0.773148	8.223477
H	0.415238	–1.580725	7.493742
H	1.556463	–0.593467	8.359740
H	0.090975	–1.137333	9.178175
C	–0.484085	0.773148	–8.223477
H	–1.556463	0.593467	–8.359740
H	–0.415238	1.580725	–7.493742
H	–0.090975	1.137333	–9.178175
C	–1.894032	3.276865	9.853421
H	–2.010292	2.668399	10.754907
H	–1.186905	4.080883	10.091124
H	–2.856609	3.749685	9.634967
C	1.894032	–3.276865	–9.853421
H	1.186905	–4.080883	–10.091124
H	2.010292	–2.668399	–10.754907
H	2.856609	–3.749685	–9.634967

Atomic coordinates for the optimized excited state (S_1) of compound 2 at PCM(toluene)/PBE0/6-31G(d,p) level.

Energy (Hartrees) –2784.655690
Imaginary freq. 0
Point group Ci

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	–0.302256	–0.629881	–3.707684
C	0.578053	0.044011	–2.811381
C	0.330390	0.046627	–1.400923
C	–0.634233	–0.894575	–0.896665
C	–1.366311	–1.690637	–1.796215
C	–1.252993	–1.502594	–3.168731
C	0.890442	0.945835	–0.486954
C	–0.890442	–0.945835	0.486954
C	–0.330390	–0.046627	1.400923
C	0.634233	0.894575	0.896665
C	1.366311	1.690637	1.796215
H	2.088662	2.398654	1.398105
C	1.252993	1.502594	3.168731
C	0.302256	0.629881	3.707684
C	–0.578053	–0.044011	2.811381
H	1.561912	1.720964	–0.841387
H	–2.088662	–2.398654	–1.398105
H	–1.922117	–2.049221	–3.824457
H	–1.561912	–1.720964	0.841387
H	1.922117	2.049221	3.824457
C	–1.597814	–0.737286	3.565830
C	–2.914756	–1.165316	3.188874
C	–3.556381	–0.779881	1.988538
C	–3.658820	–1.945197	4.127993
C	–1.938583	–1.535886	5.761436
C	–4.824717	–1.230328	1.686027
H	–3.058919	–0.097133	1.310155
C	–4.940086	–2.419506	3.778490
C	–3.111418	–2.148434	5.422660
H	–1.548851	–1.562069	6.770495
C	–5.510530	–2.080994	2.569547
H	–5.298382	–0.914390	0.761607
H	–5.481616	–3.031920	4.493908
H	–3.661050	–2.716304	6.165152
H	–6.501212	–2.444012	2.313370
C	1.597814	0.737286	–3.565830
C	2.914756	1.165316	–3.188874
C	3.556381	0.779881	–1.988538
C	3.658820	1.945197	–4.127993
C	1.938583	1.535886	–5.761436
C	4.824717	1.230328	–1.686027

H	3.058919	0.097133	–1.310155
C	4.940086	2.419506	–3.778490
C	3.111418	2.148434	–5.422660
H	1.548851	1.562069	–6.770495
C	5.510530	2.080994	–2.569547
H	5.298382	0.914390	–0.761607
H	5.481616	3.031920	–4.493908
H	3.661050	2.716304	–6.165152
H	6.501212	2.444012	–2.313370
N	–1.195235	–0.857080	4.861924
N	1.195235	0.857080	–4.861924
B	0.107182	0.041417	5.210417
B	–0.107182	–0.041417	–5.210417
C	–0.403071	0.951088	6.480931
C	–0.216691	0.528663	7.822964
C	–1.144696	2.147216	6.290157
C	–0.701622	1.298370	8.887071
C	–1.600915	2.892717	7.379090
C	–1.379487	2.496256	8.694957
H	–0.542136	0.940776	9.903612
H	–2.161571	3.807033	7.189842
C	0.403071	–0.951088	–6.480931
C	0.216691	–0.528663	–7.822964
C	1.144696	–2.147216	–6.290157
C	0.701622	–1.298370	–8.887071
C	1.600915	–2.892717	–7.379090
C	1.379487	–2.496256	–8.694957
H	0.542136	–0.940776	–9.903612
H	2.161571	–3.807033	–7.189842
C	1.538899	–0.757413	5.418601
C	2.647631	–0.017259	5.907042
C	1.794282	–2.098283	5.030701
C	3.905141	–0.612691	6.041304
C	3.064751	–2.658966	5.192649
C	4.140057	–1.941298	5.706210
H	4.728689	–0.009534	6.422369
H	3.219012	–3.693959	4.890626
C	–1.538899	0.757413	–5.418601
C	–2.647631	0.017259	–5.907042
C	–1.794282	2.098283	–5.030701
C	–3.905141	0.612691	–6.041304
C	–3.064751	2.658966	–5.192649
C	–4.140057	1.941298	–5.706210
H	–4.728689	0.009534	–6.422369
H	–3.219012	3.693959	–4.890626
C	0.755052	–3.005138	4.416418
H	–0.072490	–3.226164	5.097498
H	0.319800	–2.576442	3.508766
H	1.209285	–3.960300	4.138690
C	–0.755052	3.005138	–4.416418

H	–0.319800	2.576442	–3.508766
H	0.072490	3.226164	–5.097498
H	–1.209285	3.960300	–4.138690
C	2.573037	1.426708	6.352244
H	2.384020	1.498905	7.429982
H	3.525697	1.929798	6.156200
H	1.777113	1.995760	5.874088
C	–2.573037	–1.426708	–6.352244
H	–3.525697	–1.929798	–6.156200
H	–2.384020	–1.498905	–7.429982
H	–1.777113	–1.995760	–5.874088
C	5.489409	–2.575023	5.895409
H	5.570281	–3.050887	6.880521
H	5.676628	–3.350421	5.146375
H	6.292193	–1.834808	5.827113
C	–5.489409	2.575023	–5.895409
H	–5.676628	3.350421	–5.146375
H	–5.570281	3.050887	–6.880521
H	–6.292193	1.834808	–5.827113
C	–1.500068	2.679220	4.924699
H	–0.623370	3.039878	4.377874
H	–1.971467	1.918729	4.294708
H	–2.201463	3.513930	5.013276
C	1.500068	–2.679220	–4.924699
H	1.971467	–1.918729	–4.294708
H	0.623370	–3.039878	–4.377874
H	2.201463	–3.513930	–5.013276
C	0.503722	–0.738951	8.229452
H	0.388381	–1.560122	7.520661
H	1.583937	–0.578609	8.318800
H	0.141667	–1.075869	9.206038
C	–0.503722	0.738951	–8.229452
H	–1.583937	0.578609	–8.318800
H	–0.388381	1.560122	–7.520661
H	–0.141667	1.075869	–9.206038
C	–1.853885	3.327306	9.853457
H	–1.964516	2.724558	10.759478
H	–1.143286	4.131254	10.081105
H	–2.817029	3.800857	9.639215
C	1.853885	–3.327306	–9.853457
H	1.143286	–4.131254	–10.081105
H	1.964516	–2.724558	–10.759478
H	2.817029	–3.800857	–9.639215

Atomic coordinates for the optimized ground state (S_0) of compound 3 at PCM(toluene)/PBE0/6-31G(d,p) level.

Energy (Hartrees) –2860.900057
Imaginary freq. 0
Point group Ci

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	–0.229713	–0.309336	–3.533336
C	0.888136	0.317268	–2.930962
C	0.960618	0.549214	–1.533559
C	–0.015205	–0.080711	–0.708472
C	–1.042501	–0.865348	–1.306690
C	–1.168935	–0.905156	–2.700554
C	1.883735	1.447016	–0.903146
C	0.015205	0.080711	0.708472
C	1.042501	0.865348	1.306690
C	1.934921	1.579308	0.449346
C	1.168935	0.905156	2.700554
H	2.030690	1.417748	3.118094
C	0.229713	0.309336	3.533336
C	–0.888136	–0.317268	2.930962
C	–0.960618	–0.549214	1.533559
C	–1.883735	–1.447016	0.903146
C	–1.934921	–1.579308	–0.449346
H	–2.656411	–2.253601	–0.903283
H	–2.546141	–2.044212	1.518950
H	2.546141	2.044212	–1.518950
H	–2.030690	–1.417748	–3.118094
H	2.656411	2.253601	0.903283
C	–1.817763	–0.723550	3.980128
C	–3.235410	–0.931229	3.930780
C	–4.039087	–0.550538	2.828744
C	–3.878196	–1.442322	5.096467
C	–1.813578	–1.188596	6.290019
C	–5.397016	–0.765598	2.844773
H	–3.582382	–0.059598	1.978233
C	–5.269773	–1.690330	5.070294
C	–3.111467	–1.601908	6.277469
H	–1.220679	–1.171271	7.194063
C	–6.012775	–1.370050	3.959713
H	–6.000330	–0.457033	1.996911
H	–5.743718	–2.105994	5.954744
H	–3.573841	–1.972448	7.185720
H	–7.083474	–1.550643	3.951226
C	1.817763	0.723550	–3.980128
C	3.235410	0.931229	–3.930780
C	4.039087	0.550538	–2.828744
C	3.878196	1.442322	–5.096467

C	1.813578	1.188596	–6.290019
C	5.397016	0.765598	–2.844773
H	3.582382	0.059598	–1.978233
C	5.269773	1.690330	–5.070294
C	3.111467	1.601908	–6.277469
H	1.220679	1.171271	–7.194063
C	6.012775	1.370050	–3.959713
H	6.000330	0.457033	–1.996911
H	5.743718	2.105994	–5.954744
H	3.573841	1.972448	–7.185720
H	7.083474	1.550643	–3.951226
N	1.183202	0.769014	–5.163627
N	–1.183202	–0.769014	5.163627
B	–0.271869	0.026196	–5.124524
B	0.271869	–0.026196	5.124524
C	–0.098983	–1.112811	–6.301588
C	–0.480588	–0.857555	–7.644733
C	0.516845	–2.367002	–6.046701
C	–0.302081	–1.830829	–8.635695
C	0.665785	–3.315055	–7.061491
C	0.250086	–3.077049	–8.368233
H	–0.607725	–1.597694	–9.655006
H	1.137054	–4.267328	–6.822431
C	0.098983	1.112811	6.301588
C	0.480588	0.857555	7.644733
C	–0.516845	2.367002	6.046701
C	0.302081	1.830829	8.635695
C	–0.665785	3.315055	7.061491
C	–0.250086	3.077049	8.368233
H	0.607725	1.597694	9.655006
H	–1.137054	4.267328	6.822431
C	–1.610853	0.978655	–5.238530
C	–2.865103	0.342983	–5.425889
C	–1.634769	2.383373	–5.047493
C	–4.046465	1.089259	–5.475769
C	–2.836451	3.094314	–5.116827
C	–4.061001	2.472163	–5.336835
H	–4.988135	0.563187	–5.630378
H	–2.811132	4.174531	–4.979556
C	1.610853	–0.978655	5.238530
C	2.865103	–0.342983	5.425889
C	1.634769	–2.383373	5.047493
C	4.046465	–1.089259	5.475769
C	2.836451	–3.094314	5.116827
C	4.061001	–2.472163	5.336835
H	4.988135	–0.563187	5.630378
H	2.811132	–4.174531	4.979556
C	1.060268	–2.755241	–4.694577
H	1.781970	–2.025992	–4.313979
H	0.274857	–2.838208	–3.938047

H	1.570801	–3.720693	–4.754531
C	–1.060268	2.755241	4.694577
H	–0.274857	2.838208	3.938047
H	–1.781970	2.025992	4.313979
H	–1.570801	3.720693	4.754531
C	–1.108869	0.430904	–8.132165
H	–2.200423	0.405953	–8.040606
H	–0.792041	1.317374	–7.581545
H	–0.873581	0.581380	–9.190738
C	1.108869	–0.430904	8.132165
H	0.792041	–1.317374	7.581545
H	2.200423	–0.405953	8.040606
H	0.873581	–0.581380	9.190738
C	0.392385	–4.122140	–9.438639
H	–0.450363	–4.823944	–9.421161
H	0.420478	–3.672665	–10.435512
H	1.304628	–4.711666	–9.304581
C	–0.392385	4.122140	9.438639
H	–0.420478	3.672665	10.435512
H	0.450363	4.823944	9.421161
H	–1.304628	4.711666	9.304581
C	–3.038086	–1.147383	–5.620720
H	–4.001059	–1.469202	–5.210541
H	–3.032592	–1.413951	–6.684314
H	–2.251600	–1.744511	–5.160491
C	3.038086	1.147383	5.620720
H	3.032592	1.413951	6.684314
H	4.001059	1.469202	5.210541
H	2.251600	1.744511	5.160491
C	–0.403546	3.203002	–4.746637
H	0.120519	2.838640	–3.857628
H	0.317248	3.208248	–5.570341
H	–0.682092	4.243002	–4.555343
C	0.403546	–3.203002	4.746637
H	–0.317248	–3.208248	5.570341
H	–0.120519	–2.838640	3.857628
H	0.682092	–4.243002	4.555343
C	–5.344217	3.254243	–5.371807
H	–5.763164	3.377842	–4.365505
H	–5.190564	4.256827	–5.782453
H	–6.102561	2.751242	–5.979185
C	5.344217	–3.254243	5.371807
H	5.190564	–4.256827	5.782453
H	5.763164	–3.377842	4.365505
H	6.102561	–2.751242	5.979185

Atomic coordinates for the optimized excited state (S_1) of compound 3 at PCM(toluene)/PBE0/6-31G(d,p) level.

Energy (Hartrees) –2860.815761
Imaginary freq. 0
Point group Ci

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	–0.199173	–0.280004	–3.545852
C	0.919906	0.350711	–2.945377
C	0.962771	0.585913	–1.525266
C	–0.007396	–0.076771	–0.706139
C	–1.016318	–0.873392	–1.312727
C	–1.140673	–0.880072	–2.724303
C	1.853674	1.479502	–0.891605
C	0.007396	0.076771	0.706139
C	1.016318	0.873392	1.312727
C	1.898278	1.597016	0.481905
C	1.140673	0.880072	2.724303
H	2.007735	1.378015	3.148195
C	0.199173	0.280004	3.545852
C	–0.919906	–0.350711	2.945377
C	–0.962771	–0.585913	1.525266
C	–1.853674	–1.479502	0.891605
C	–1.898278	–1.597016	–0.481905
H	–2.622709	–2.263398	–0.942720
H	–2.522174	–2.084013	1.493260
H	2.522174	2.084013	–1.493260
H	–2.007735	–1.378015	–3.148195
H	2.622709	2.263398	0.942720
C	–1.851458	–0.745075	3.972129
C	–3.269022	–0.988906	3.917379
C	–4.077505	–0.649979	2.809457
C	–3.909749	–1.498948	5.086709
C	–1.861153	–1.169209	6.301428
C	–5.433582	–0.904703	2.814455
H	–3.630773	–0.161847	1.951753
C	–5.290871	–1.782755	5.053207
C	–3.148541	–1.619954	6.281978
H	–1.285117	–1.121143	7.216199
C	–6.040840	–1.504014	3.930308
H	–6.033951	–0.630881	1.952329
H	–5.759264	–2.196102	5.942066
H	–3.612993	–1.980937	7.192754
H	–7.105320	–1.718333	3.918982
C	1.851458	0.745075	–3.972129
C	3.269022	0.988906	–3.917379
C	4.077505	0.649979	–2.809457
C	3.909749	1.498948	–5.086709

C	1.861153	1.169209	–6.301428
C	5.433582	0.904703	–2.814455
H	3.630773	0.161847	–1.951753
C	5.290871	1.782755	–5.053207
C	3.148541	1.619954	–6.281978
H	1.285117	1.121143	–7.216199
C	6.040840	1.504014	–3.930308
H	6.033951	0.630881	–1.952329
H	5.759264	2.196102	–5.942066
H	3.612993	1.980937	–7.192754
H	7.105320	1.718333	–3.918982
N	1.223244	0.755059	–5.184270
N	–1.223244	–0.755059	5.184270
B	–0.216318	0.029900	–5.145406
B	0.216318	–0.029900	5.145406
C	–0.091986	–1.123870	–6.305778
C	–0.494009	–0.877431	–7.643218
C	0.509728	–2.383637	–6.045827
C	–0.351752	–1.864999	–8.625376
C	0.621812	–3.347477	–7.050178
C	0.183882	–3.118027	–8.351522
H	–0.670855	–1.638911	–9.642188
H	1.083028	–4.304062	–6.808690
C	0.091986	1.123870	6.305778
C	0.494009	0.877431	7.643218
C	–0.509728	2.383637	6.045827
C	0.351752	1.864999	8.625376
C	–0.621812	3.347477	7.050178
C	–0.183882	3.118027	8.351522
H	0.670855	1.638911	9.642188
H	–1.083028	4.304062	6.808690
C	–1.560978	0.980845	–5.218282
C	–2.826532	0.346066	–5.386680
C	–1.580038	2.387494	–4.995402
C	–4.003484	1.096399	–5.408557
C	–2.778521	3.098191	–5.039203
C	–4.009345	2.479235	–5.256218
H	–4.950440	0.576863	–5.549038
H	–2.752536	4.175138	–4.881009
C	1.560978	–0.980845	5.218282
C	2.826532	–0.346066	5.386680
C	1.580038	–2.387494	4.995402
C	4.003484	–1.096399	5.408557
C	2.778521	–3.098191	5.039203
C	4.009345	–2.479235	5.256218
H	4.950440	–0.576863	5.549038
H	2.752536	–4.175138	4.881009
C	1.071470	–2.754805	–4.697296
H	1.773360	–2.003949	–4.322639
H	0.290619	–2.856564	–3.936745

H	1.605285	–3.707644	–4.756523
C	–1.071470	2.754805	4.697296
H	–0.290619	2.856564	3.936745
H	–1.773360	2.003949	4.322639
H	–1.605285	3.707644	4.756523
C	–1.103778	0.420923	–8.126794
H	–2.195325	0.417050	–8.028025
H	–0.760463	1.300451	–7.580213
H	–0.874824	0.567923	–9.187236
C	1.103778	–0.420923	8.126794
H	0.760463	–1.300451	7.580213
H	2.195325	–0.417050	8.028025
H	0.874824	–0.567923	9.187236
C	0.287517	–4.178306	–9.411276
H	–0.569441	–4.861947	–9.372643
H	0.309681	–3.741285	–10.413816
H	1.189148	–4.785309	–9.283961
C	–0.287517	4.178306	9.411276
H	–0.309681	3.741285	10.413816
H	0.569441	4.861947	9.372643
H	–1.189148	4.785309	9.283961
C	–3.009003	–1.140197	–5.592720
H	–3.963640	–1.461671	–5.163587
H	–3.031174	–1.391190	–6.659769
H	–2.212201	–1.746419	–5.163700
C	3.009003	1.140197	5.592720
H	3.031174	1.391190	6.659769
H	3.963640	1.461671	5.163587
H	2.212201	1.746419	5.163700
C	–0.343491	3.192275	–4.687621
H	0.173661	2.813954	–3.800323
H	0.379942	3.187967	–5.508032
H	–0.612076	4.233908	–4.492005
C	0.343491	–3.192275	4.687621
H	–0.379942	–3.187967	5.508032
H	–0.173661	–2.813954	3.800323
H	0.612076	–4.233908	4.492005
C	–5.281038	3.273225	–5.322153
H	–5.266993	4.111580	–4.618900
H	–5.429604	3.696176	–6.323593
H	–6.153045	2.652254	–5.098451
C	5.281038	–3.273225	5.322153
H	5.429604	–3.696176	6.323593
H	5.266993	–4.111580	4.618900
H	6.153045	–2.652254	5.098451

Atomic coordinates for the optimized ground state (S_0) of compound 1 at PCM(toluene)/B3LYP/6-31G(d,p) level.

Energy (Hartrees) –2634.3820904
Imaginary freq. 0
Point group Ci

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	2.544406	–0.228176	0.401222
C	1.732885	0.685572	–0.288713
C	0.307723	0.515827	–0.393755
C	–0.307723	–0.515827	0.393755
C	0.522894	–1.267944	1.270203
C	1.895991	–1.179697	1.221984
H	–0.066712	1.950251	–1.976409
C	–0.522894	1.267944	–1.270203
C	–1.732885	–0.685572	0.288713
H	0.066712	–1.950251	1.976409
H	2.479981	–1.844730	1.848785
C	–2.544406	0.228176	–0.401222
C	–1.895991	1.179697	–1.221984
H	–2.479981	1.844730	–1.848785
C	–2.592442	–1.712310	0.890072
C	–2.317238	–3.084925	1.225400
C	–1.148598	–3.775443	0.806180
C	–3.328574	–3.824490	1.918677
C	–4.835779	–1.979615	1.597757
C	–0.948628	–5.095869	1.147723
H	–0.419583	–3.268193	0.189029
C	–3.077171	–5.168404	2.292797
C	–4.592453	–3.211579	2.131645
H	–5.814761	–1.524637	1.624085
C	–1.903983	–5.789008	1.924637
H	–0.054207	–5.608462	0.808756
H	–3.841215	–5.708316	2.844088
H	–5.383405	–3.750032	2.641499
H	–1.724572	–6.823004	2.202898
C	2.592442	1.712310	–0.890072
C	2.317238	3.084925	–1.225400
C	1.148598	3.775443	–0.806180
C	3.328574	3.824490	–1.918677
C	4.835779	1.979615	–1.597757
C	0.948628	5.095869	–1.147723
H	0.419583	3.268193	–0.189029
C	3.077171	5.168404	–2.292797
C	4.592453	3.211579	–2.131645
H	5.814761	1.524637	–1.624085
C	1.903983	5.789008	–1.924637

H	0.054207	5.608462	–0.808756
H	3.841215	5.708316	–2.844088
H	5.383405	3.750032	–2.641499
H	1.724572	6.823004	–2.202898
N	3.856536	1.246733	–0.995656
N	–3.856536	–1.246733	0.995656
B	4.095922	–0.107067	–0.078836
B	–4.095922	0.107067	0.078836
C	5.333545	0.364755	0.913474
C	6.696448	0.142207	0.563439
C	5.102783	1.084683	2.122366
C	7.734101	0.567854	1.407966
C	6.167478	1.480325	2.941556
C	7.498340	1.222059	2.613763
H	8.762422	0.377985	1.104664
H	5.946802	2.021584	3.859802
C	–5.333545	–0.364755	–0.913474
C	–6.696448	–0.142207	–0.563439
C	–5.102783	–1.084683	–2.122366
C	–7.734101	–0.567854	–1.407966
C	–6.167478	–1.480325	–2.941556
C	–7.498340	–1.222059	–2.613763
H	–8.762422	–0.377985	–1.104664
H	–5.946802	–2.021584	–3.859802
C	4.309901	–1.545029	–0.879124
C	4.715476	–2.682655	–0.124466
C	4.001900	–1.775014	–2.250628
C	4.847643	–3.940077	–0.730976
C	4.158237	–3.046551	–2.818906
C	4.585546	–4.150524	–2.082321
H	5.169577	–4.781133	–0.118525
H	3.926142	–3.176464	–3.874533
C	–4.309901	1.545029	0.879124
C	–4.715476	2.682655	0.124466
C	–4.001900	1.775014	2.250628
C	–4.847643	3.940077	0.730976
C	–4.158237	3.046551	2.818906
C	–4.585546	4.150524	2.082321
H	–5.169577	4.781133	0.118525
H	–3.926142	3.176464	3.874533
C	3.721032	1.487249	2.600919
H	3.177819	2.074354	1.854903
H	3.091513	0.625480	2.838696
H	3.798171	2.099352	3.504197
C	–3.721032	–1.487249	–2.600919
H	–3.091513	–0.625480	–2.838696
H	–3.177819	–2.074354	–1.854903
H	–3.798171	–2.099352	–3.504197
C	7.163315	–0.566837	–0.700381
H	7.229310	–1.650460	–0.554429

H	6.507013	–0.425333	–1.558646
H	8.162965	–0.214988	–0.975409
C	–7.163315	0.566837	0.700381
H	–6.507013	0.425333	1.558646
H	–7.229310	1.650460	0.554429
H	–8.162965	0.214988	0.975409
C	8.628687	1.632485	3.527221
H	8.792107	0.889406	4.318210
H	9.569957	1.734411	2.978631
H	8.418762	2.586274	4.022161
C	–8.628687	–1.632485	–3.527221
H	–9.569957	–1.734411	–2.978631
H	–8.792107	–0.889406	–4.318210
H	–8.418762	–2.586274	–4.022161
C	5.073250	–2.646886	1.353763
H	4.835761	–3.609219	1.819334
H	6.145548	–2.472725	1.501120
H	4.563440	–1.864351	1.912084
C	–5.073250	2.646886	–1.353763
H	–6.145548	2.472725	–1.501120
H	–4.835761	3.609219	–1.819334
H	–4.563440	1.864351	–1.912084
C	3.484250	–0.700878	–3.189188
H	2.562363	–0.242129	–2.820047
H	4.205008	0.106063	–3.351672
H	3.260549	–1.134168	–4.168034
C	–3.484250	0.700878	3.189188
H	–4.205008	–0.106063	3.351672
H	–2.562363	0.242129	2.820047
H	–3.260549	1.134168	4.168034
C	4.713920	–5.517371	–2.712319
H	3.747227	–6.036241	–2.747405
H	5.078946	–5.451205	–3.742418
H	5.403424	–6.153887	–2.149407
C	–4.713920	5.517371	2.712319
H	–5.078946	5.451205	3.742418
H	–3.747227	6.036241	2.747405
H	–5.403424	6.153887	2.149407

Atomic coordinates for the optimized ground state (S_0) of compound 2 at PCM(toluene)/B3LYP/6-31G(d,p) level.

Energy (Hartrees) –2788.0278477
Imaginary freq. 0
Point group Ci

	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	–0.318472	–0.586161	–3.716578
C	0.557331	0.057547	–2.835749

C	0.334430	0.054710	–1.403792
C	–0.663650	–0.855476	–0.897388
C	–1.432477	–1.630373	–1.820606
C	–1.316935	–1.446283	–3.172158
C	0.940019	0.911697	–0.477114
C	–0.940019	–0.911697	0.477114
C	–0.334430	–0.054710	1.403792
C	0.663650	0.855476	0.897388
C	1.432477	1.630373	1.820606
H	2.171114	2.320831	1.420812
C	1.316935	1.446283	3.172158
C	0.318472	0.586161	3.716578
C	–0.557331	–0.057547	2.835749
H	1.662000	1.647946	–0.808510
H	–2.171114	–2.320831	–1.420812
H	–1.990813	–1.975648	–3.835849
H	–1.662000	–1.647946	0.808510
H	1.990813	1.975648	3.835849
C	–1.583552	–0.756672	3.611339
C	–2.924161	–1.140663	3.252719
C	–3.578941	–0.690109	2.075878
C	–3.673220	–1.925867	4.186281
C	–1.911485	–1.616894	5.792949
C	–4.870123	–1.081690	1.792174
H	–3.068282	–0.009601	1.408231
C	–4.984318	–2.346502	3.849809
C	–3.106930	–2.186248	5.463285
H	–1.496753	–1.687275	6.787343
C	–5.567851	–1.941879	2.669444
H	–5.356824	–0.718134	0.892881
H	–5.531131	–2.965185	4.555136
H	–3.654504	–2.766349	6.197452
H	–6.577524	–2.257525	2.425147
C	1.583552	0.756672	–3.611339
C	2.924161	1.140663	–3.252719
C	3.578941	0.690109	–2.075878
C	3.673220	1.925867	–4.186281
C	1.911485	1.616894	–5.792949
C	4.870123	1.081690	–1.792174
H	3.068282	0.009601	–1.408231
C	4.984318	2.346502	–3.849809
C	3.106930	2.186248	–5.463285
H	1.496753	1.687275	–6.787343
C	5.567851	1.941879	–2.669444
H	5.356824	0.718134	–0.892881
H	5.531131	2.965185	–4.555136
H	3.654504	2.766349	–6.197452
H	6.577524	2.257525	–2.425147
N	–1.164980	–0.925483	4.885712
N	1.164980	0.925483	–4.885712

B	0.146438	0.013596	5.231159
B	–0.146438	–0.013596	–5.231159
C	–0.408431	0.923340	6.498671
C	–0.252120	0.493607	7.847692
C	–1.140548	2.130829	6.302333
C	–0.758367	1.260350	8.909373
C	–1.617001	2.871464	7.391135
C	–1.429404	2.463606	8.711724
H	–0.618070	0.896978	9.926126
H	–2.165462	3.791413	7.197032
C	0.408431	–0.923340	–6.498671
C	0.252120	–0.493607	–7.847692
C	1.140548	–2.130829	–6.302333
C	0.758367	–1.260350	–8.909373
C	1.617001	–2.871464	–7.391135
C	1.429404	–2.463606	–8.711724
H	0.618070	–0.896978	–9.926126
H	2.165462	–3.791413	–7.197032
C	1.596987	–0.756684	5.467263
C	2.688502	–0.002548	5.987142
C	1.885888	–2.093693	5.070597
C	3.954257	–0.584162	6.145621
C	3.163507	–2.638751	5.258513
C	4.217440	–1.909150	5.806196
H	4.760249	0.027338	6.548574
H	3.340581	–3.667484	4.949846
C	–1.596987	0.756684	–5.467263
C	–2.688502	0.002548	–5.987142
C	–1.885888	2.093693	–5.070597
C	–3.954257	0.584162	–6.145621
C	–3.163507	2.638751	–5.258513
C	–4.217440	1.909150	–5.806196
H	–4.760249	–0.027338	–6.548574
H	–3.340581	3.667484	–4.949846
C	0.874769	–3.013854	4.412256
H	0.035279	–3.262929	5.068227
H	0.455616	–2.577980	3.500768
H	1.353221	–3.955985	4.130482
C	–0.874769	3.013854	–4.412256
H	–0.455616	2.577980	–3.500768
H	–0.035279	3.262929	–5.068227
H	–1.353221	3.955985	–4.130482
C	2.592501	1.447548	6.438090
H	2.340072	1.519787	7.502289
H	3.558108	1.945306	6.300610
H	1.835087	2.025088	5.911357
C	–2.592501	–1.447548	–6.438090
H	–3.558108	–1.945306	–6.300610
H	–2.340072	–1.519787	–7.502289
H	–1.835087	–2.025088	–5.911357

C	5.577425	–2.528081	6.025372
H	5.643992	–3.010277	7.009226
H	5.794382	–3.295804	5.275829
H	6.371529	–1.776180	5.980760
C	–5.577425	2.528081	–6.025372
H	–5.794382	3.295804	–5.275829
H	–5.643992	3.010277	–7.009226
H	–6.371529	1.776180	–5.980760
C	–1.470030	2.690941	4.932007
H	–0.575976	2.963028	4.364216
H	–2.027258	1.979307	4.315911
H	–2.085459	3.589975	5.029494
C	1.470030	–2.690941	–4.932007
H	2.027258	–1.979307	–4.315911
H	0.575976	–2.963028	–4.364216
H	2.085459	–3.589975	–5.029494
C	0.469595	–0.776334	8.277511
H	0.406649	–1.591595	7.557638
H	1.539927	–0.598362	8.428796
H	0.062462	–1.130721	9.230130
C	–0.469595	0.776334	–8.277511
H	–1.539927	0.598362	–8.428796
H	–0.406649	1.591595	–7.557638
H	–0.062462	1.130721	–9.230130
C	–1.927879	3.293207	9.870954
H	–2.070611	2.682957	10.767911
H	–1.215735	4.087710	10.128082
H	–2.879986	3.780097	9.636097
C	1.927879	–3.293207	–9.870954
H	1.215735	–4.087710	–10.128082
H	2.070611	–2.682957	–10.767911
H	2.879986	–3.780097	–9.636097

Atomic coordinates for the optimized ground state (S_0) of compound 3 at PCM(toluene)/B3LYP/6-31G(d,p) level.

Energy (Hartrees) –2864.2663573
Imaginary freq. 0
Point group Ci

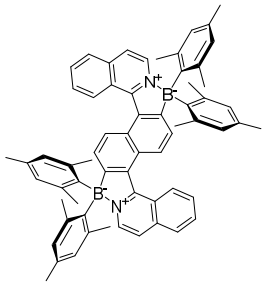
	Coordinates (Angstroms)		
Atom type	X	Y	Z
C	–0.234814	–0.295949	–3.546141
C	0.890371	0.327854	–2.943041
C	0.964492	0.554188	–1.539085
C	–0.015633	–0.078345	–0.711060
C	–1.047798	–0.861621	–1.312978
C	–1.173074	–0.896446	–2.711008
C	1.893127	1.447249	–0.901320
C	0.015633	0.078345	0.711060

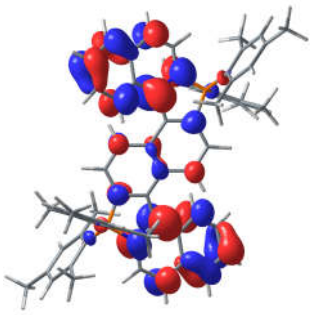
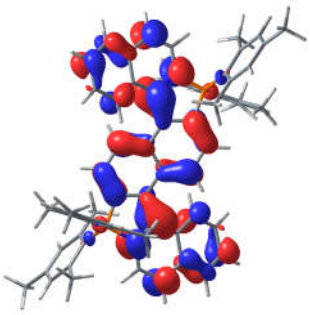
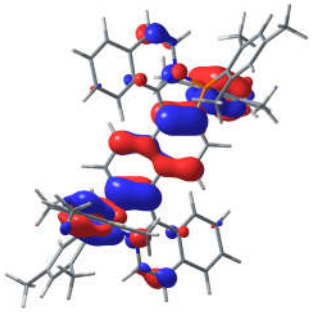
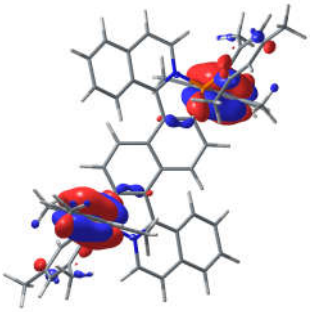
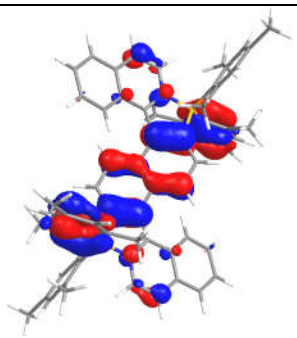
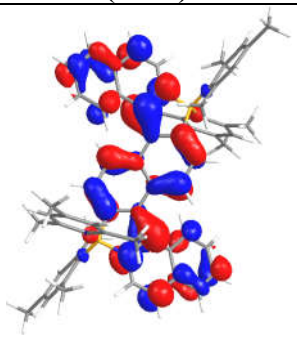
C	1.047798	0.861621	1.312978
C	1.944295	1.575984	0.454862
C	1.173074	0.896446	2.711008
H	2.033734	1.408690	3.128902
C	0.234814	0.295949	3.546141
C	–0.890371	–0.327854	2.943041
C	–0.964492	–0.554188	1.539085
C	–1.893127	–1.447249	0.901320
C	–1.944295	–1.575984	–0.454862
H	–2.669280	–2.245417	–0.909846
H	–2.559242	–2.042826	1.512398
H	2.559242	2.042826	–1.512398
H	–2.033734	–1.408690	–3.128902
H	2.669280	2.245417	0.909846
C	–1.823769	–0.736435	3.996000
C	–3.248701	–0.934050	3.950061
C	–4.059456	–0.541396	2.851970
C	–3.894573	–1.452414	5.118050
C	–1.818100	–1.227945	6.309850
C	–5.422146	–0.748072	2.872069
H	–3.606198	–0.049621	2.002015
C	–5.291705	–1.691061	5.095008
C	–3.122291	–1.630776	6.296673
H	–1.225072	–1.231904	7.212130
C	–6.039779	–1.356524	3.988059
H	–6.026278	–0.431021	2.028137
H	–5.764544	–2.110393	5.978014
H	–3.583603	–2.009681	7.201759
H	–7.111543	–1.529589	3.982710
C	1.823769	0.736435	–3.996000
C	3.248701	0.934050	–3.950061
C	4.059456	0.541396	–2.851970
C	3.894573	1.452414	–5.118050
C	1.818100	1.227945	–6.309850
C	5.422146	0.748072	–2.872069
H	3.606198	0.049621	–2.002015
C	5.291705	1.691061	–5.095008
C	3.122291	1.630776	–6.296673
H	1.225072	1.231904	–7.212130
C	6.039779	1.356524	–3.988059
H	6.026278	0.431021	–2.028137
H	5.764544	2.110393	–5.978014
H	3.583603	2.009681	–7.201759
H	7.111543	1.529589	–3.982710
N	1.183396	0.795614	–5.183971
N	–1.183396	–0.795614	5.183971
B	–0.288957	0.037367	–5.143928
B	0.288957	–0.037367	5.143928
C	–0.102540	–1.113510	–6.321617
C	–0.468541	–0.861662	–7.675975

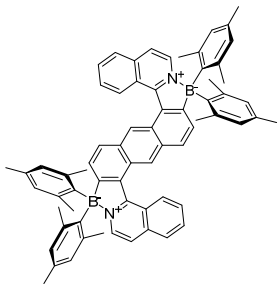
C	0.507794	–2.375901	–6.060259
C	–0.280052	–1.839070	–8.666024
C	0.666280	–3.326568	–7.076579
C	0.267242	–3.089001	–8.391452
H	–0.573466	–1.606547	–9.688461
H	1.130700	–4.280041	–6.831583
C	0.102540	1.113510	6.321617
C	0.468541	0.861662	7.675975
C	–0.507794	2.375901	6.060259
C	0.280052	1.839070	8.666024
C	–0.666280	3.326568	7.076579
C	–0.267242	3.089001	8.391452
H	0.573466	1.606547	9.688461
H	–1.130700	4.280041	6.831583
C	–1.638363	0.991306	–5.267191
C	–2.898807	0.354896	–5.455289
C	–1.667062	2.402092	–5.078084
C	–4.083611	1.102630	–5.504057
C	–2.873570	3.112644	–5.146813
C	–4.100531	2.488394	–5.364815
H	–5.024574	0.576184	–5.657820
H	–2.849733	4.192559	–5.011492
C	1.638363	–0.991306	5.267191
C	2.898807	–0.354896	5.455289
C	1.667062	–2.402092	5.078084
C	4.083611	–1.102630	5.504057
C	2.873570	–3.112644	5.146813
C	4.100531	–2.488394	5.364815
H	5.024574	–0.576184	5.657820
H	2.849733	–4.192559	5.011492
C	1.038810	–2.781007	–4.698336
H	1.764229	–2.063745	–4.303837
H	0.247628	–2.867309	–3.948872
H	1.541833	–3.750159	–4.763341
C	–1.038810	2.781007	4.698336
H	–0.247628	2.867309	3.948872
H	–1.764229	2.063745	4.303837
H	–1.541833	3.750159	4.763341
C	–1.094313	0.430471	–8.183687
H	–2.187074	0.404588	–8.112230
H	–0.785806	1.321104	–7.637469
H	–0.842090	0.574251	–9.239410
C	1.094313	–0.430471	8.183687
H	0.785806	–1.321104	7.637469
H	2.187074	–0.404588	8.112230
H	0.842090	–0.574251	9.239410
C	0.420283	–4.140477	–9.464451
H	–0.429942	–4.834514	–9.466735
H	0.474088	–3.691147	–10.460782
H	1.323433	–4.740402	–9.312775

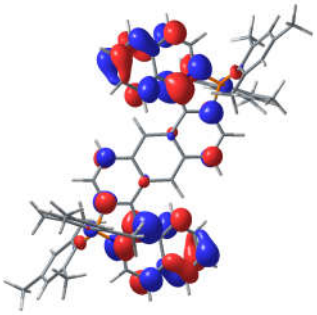
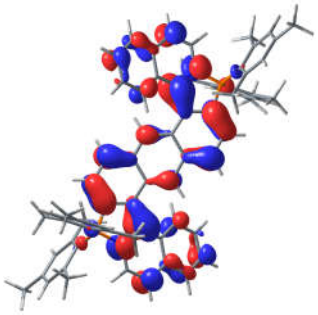
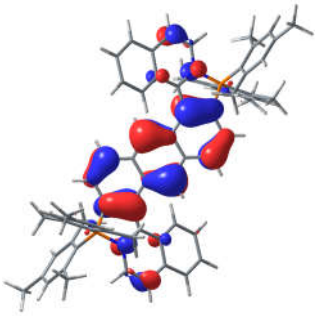
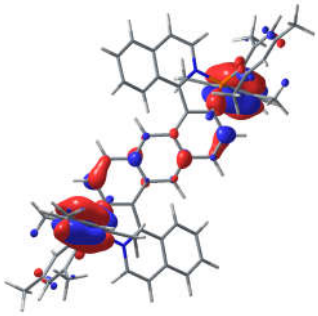
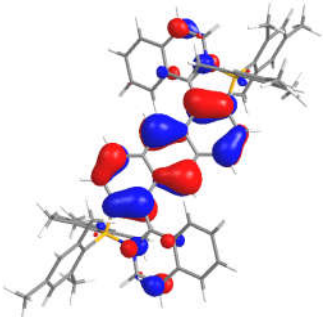
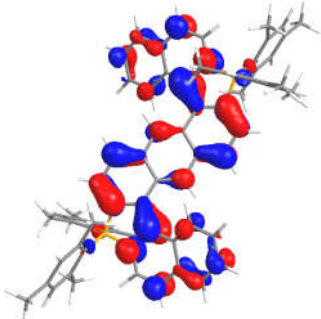
C	–0.420283	4.140477	9.464451
H	–0.474088	3.691147	10.460782
H	0.429942	4.834514	9.466735
H	–1.323433	4.740402	9.312775
C	–3.081024	–1.143055	–5.651308
H	–4.054801	–1.454911	–5.259164
H	–3.058616	–1.414140	–6.713279
H	–2.313094	–1.747087	–5.171570
C	3.081024	1.143055	5.651308
H	3.058616	1.414140	6.713279
H	4.054801	1.454911	5.259164
H	2.313094	1.747087	5.171570
C	–0.435471	3.237742	–4.779880
H	0.097370	2.881802	–3.893411
H	0.282105	3.251648	–5.605950
H	–0.724020	4.275068	–4.588362
C	0.435471	–3.237742	4.779880
H	–0.282105	–3.251648	5.605950
H	–0.097370	–2.881802	3.893411
H	0.724020	–4.275068	4.588362
C	–5.391137	3.272520	–5.398748
H	–5.817934	3.387008	–4.393892
H	–5.237480	4.279595	–5.799321
H	–6.146034	2.774519	–6.015243
C	5.391137	–3.272520	5.398748
H	5.237480	–4.279595	5.799321
H	5.817934	–3.387008	4.393892
H	6.146034	–2.774519	6.015243

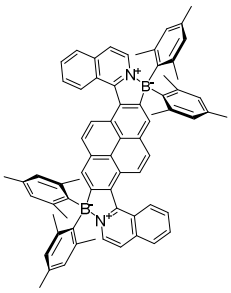
6. Additional theoretical calculation data

1	PCM(toluene)/PBE0/6-31G(d,p)	
Energy (Hartree)	–2631.2757300	
Energy (kcal/mol)	–1651151.83	
Dipole Moment (Debye)	0.00	
LUMO+1 (eV)	–2.01	
LUMO (eV)	–2.17	
HOMO (eV)	–5.65	
HOMO–1 (eV)	–5.87	
Gap LUMO-HOMO (eV)	3.48	

 LUMO+1 (–2.01 eV) (isosurface=0.03)	 LUMO (–2.17 eV) (isosurface=0.03)
 HOMO (–5.65 eV) (isosurface=0.03)	 HOMO–1 (–5.87 eV) (isosurface=0.03)
NTO Analysis	**Transition $S_1 \leftarrow S_0$ (0.311) NTO weight (95%)**
 Hole NTO	 Electron NTO

2	PCM(toluene)/ PBE0/6-31G(d,p)	
Energy (Hartree)	–2784.7439491	
Energy (kcal/mol)	–1747454.68	
Dipole Moment (Debye)	0.00	
LUMO+1 (eV)	–2.01	
LUMO (eV)	–2.25	
HOMO (eV)	–5.44	
HOMO–1 (eV)	–5.82	
Gap LUMO-HOMO (eV)	3.19	

 LUMO+1 (-2.01 eV) (isosurface=0.03)	 LUMO (-2.25 eV) (isosurface=0.03)
 HOMO (-5.44 eV) (isosurface=0.03)	 HOMO-1 (-5.82 eV) (isosurface=0.03)
NTO Analysis	**Transition $S_1 \leftarrow S_0$ (0.400) NTO weight (97%)**
 Hole NTO	 Electron NTO

3	PCM(toluene)/ PBE0/6-31G(d,p)	
Energy (Hartree)	–2860.9000569	
Energy (Kcal/mol)	–1795243.39	
Dipole Moment (Debye)	0.00	
LUMO+1 (eV)	–2.01	
LUMO (eV)	–2.50	
HOMO (eV)	–5.51	
HOMO–1 (eV)	–5.74	
Gap LUMO-HOMO (eV)	3.01	

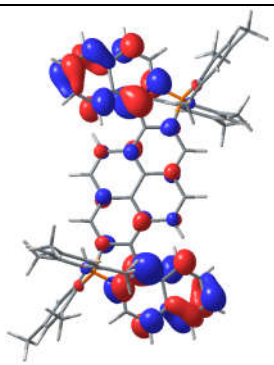
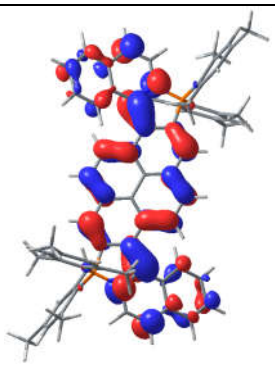
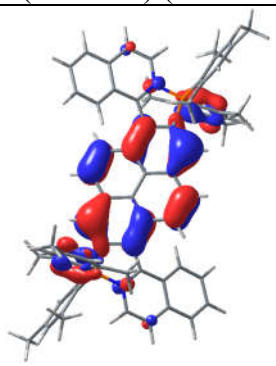
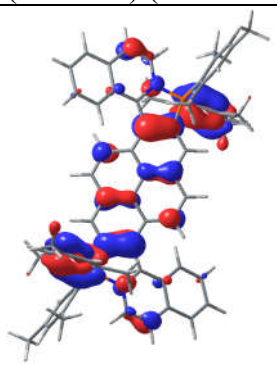
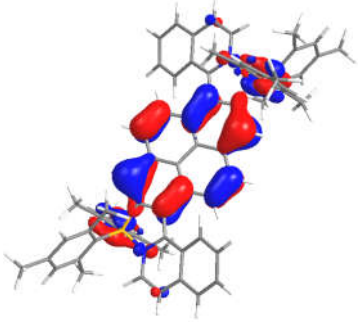
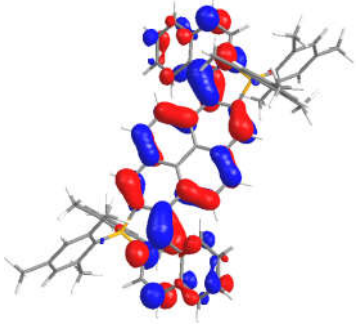
 LUMO+1 (-2.01 eV) (isosurface=0.03)	 LUMO (-2.50 eV) (isosurface=0.03)
 HOMO (-5.51 eV) (isosurface=0.03)	 HOMO-1 (-5.74 eV) (isosurface=0.03)
NTO Analysis	**Transition $S_1 \leftarrow S_0$ (0.701) NTO weight (98%)**
 Hole NTO	 Electron NTO

Table S1. Benchmark of TD-DFT calculated photophysical data for **1–3** at the PCM(toluene)/***functional***/6-31G(d,p) level.

	B3LYP		***CAM-B3LYP***		***M06-2X***		***PBE0***		
	E_{calc} (eV)	ΔE (eV)[a]	E_{calc} (eV)	ΔE (eV)[a]	E_{calc} (eV)	ΔE (eV)[a]	E_{calc} (eV)	ΔE (eV)[a]	E_{exp} (eV)
Absorption									
1	2.67	–0.10	3.28	+0.51	3.28	+0.51	2.81	+0.04	2.77
2	2.40	–0.13	3.00	+0.47	2.99	+0.46	2.54	+0.01	2.53
3	2.31	–0.20	2.92	+0.41	2.93	+0.42	2.44	–0.07	2.51
Emission									
1	2.42	–0.17					2.54	–0.05	2.59
2	2.16	–0.16					2.27	–0.05	2.32
3	2.05	–0.62					2.16	–0.51	2.67
	2.30	–0.09					2.43	+0.04	2.39

[a] $\Delta E = E_{calc} - E_{exp}$

7. UV/vis absorption and fluorescence spectra of 1-3 in THF

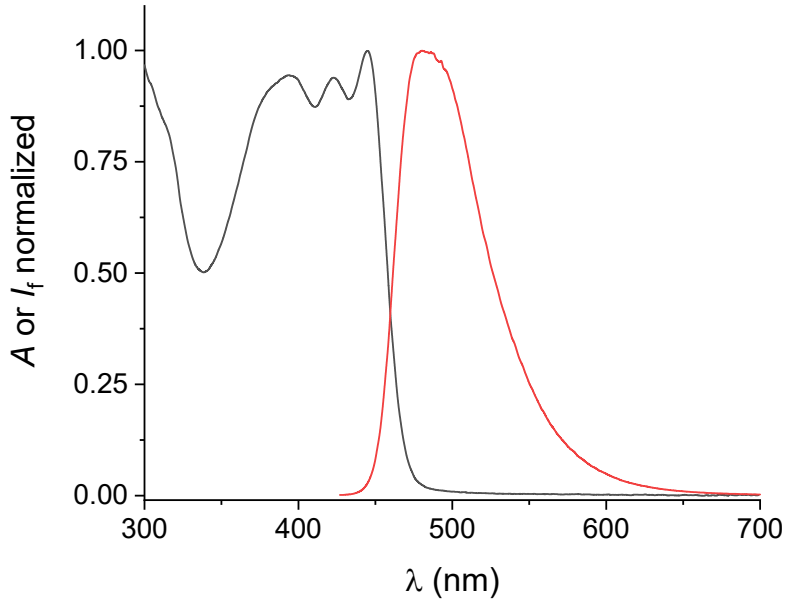


Figure S47. UV/vis absorption (black line) and fluorescence (λ_{exc} = 422 nm, red line) spectra of **1** (25 μM) in THF.

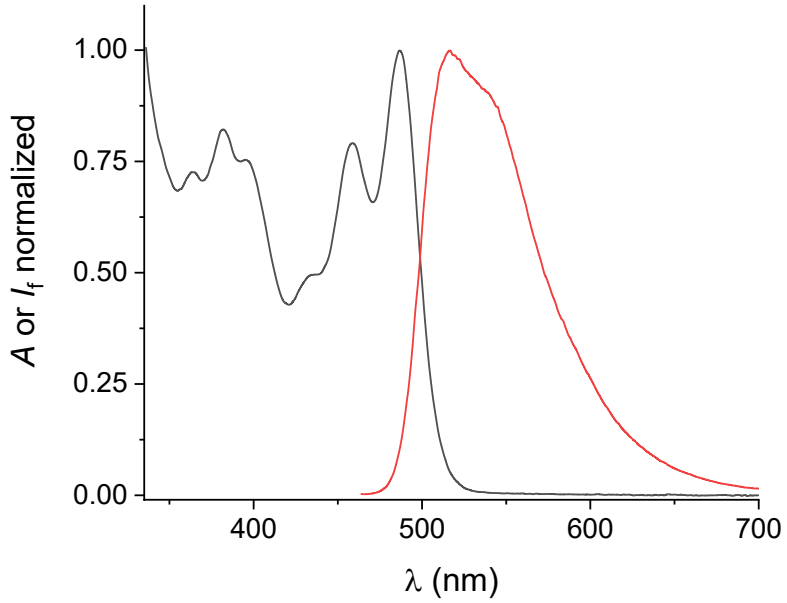


Figure S48. UV/vis absorption (black line) and fluorescence (λ_{exc} = 459 nm, red line) spectra of **2** (30 μM) in THF.

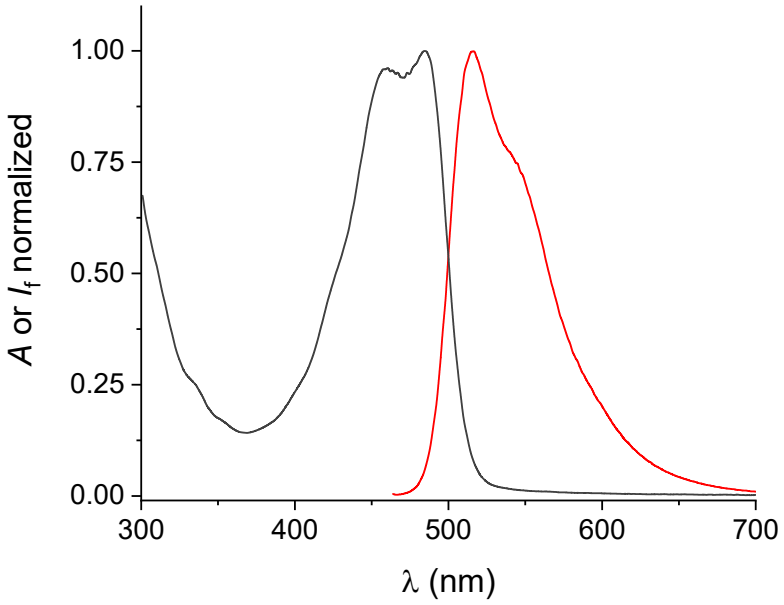


Figure S49. UV/vis absorption (black line) and fluorescence (λ_{exc} = 459 nm, red line) spectra of **3** (30 μM) in THF.

8. Photoreactivity of the dyes 1-3 in air-equilibrated toluene

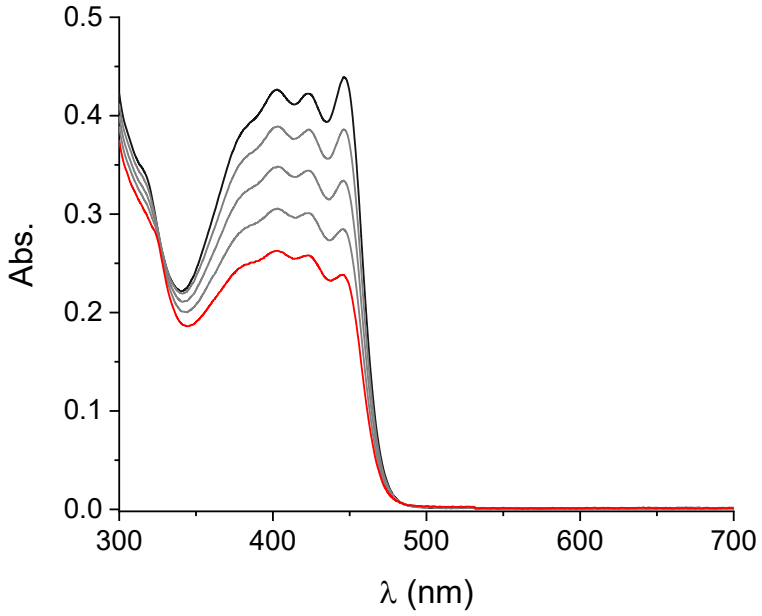


Figure S50. UV/vis absorption spectra for the continuous irradiation of **1** (150 W xenon lamp, λ_{irr} > 395 nm) in air-equilibrated toluene (black; t = 0 and red; t = 4 h).

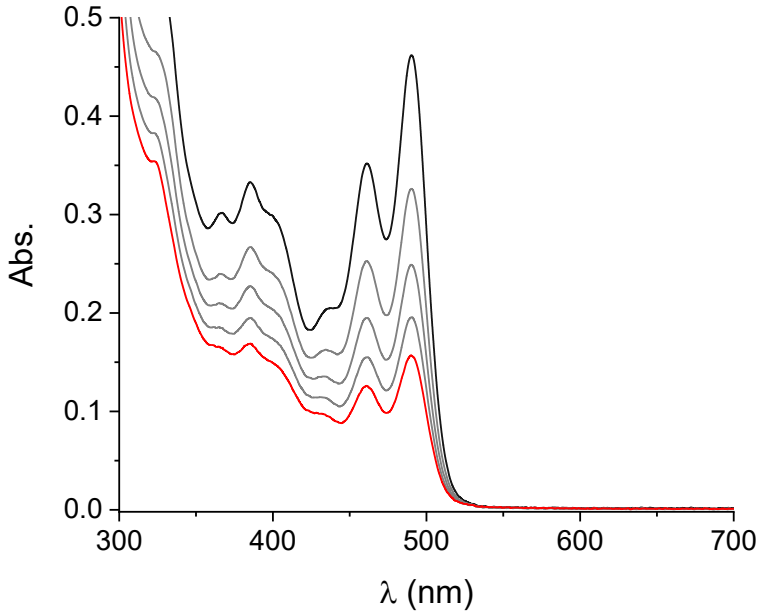


Figure S51. UV/vis absorption spectra for the continuous irradiation of **2** (150 W xenon lamp, $\lambda_{irr} > 395$ nm) in air-equilibrated toluene (black; $t = 0$ and red; $t = 4$ h).

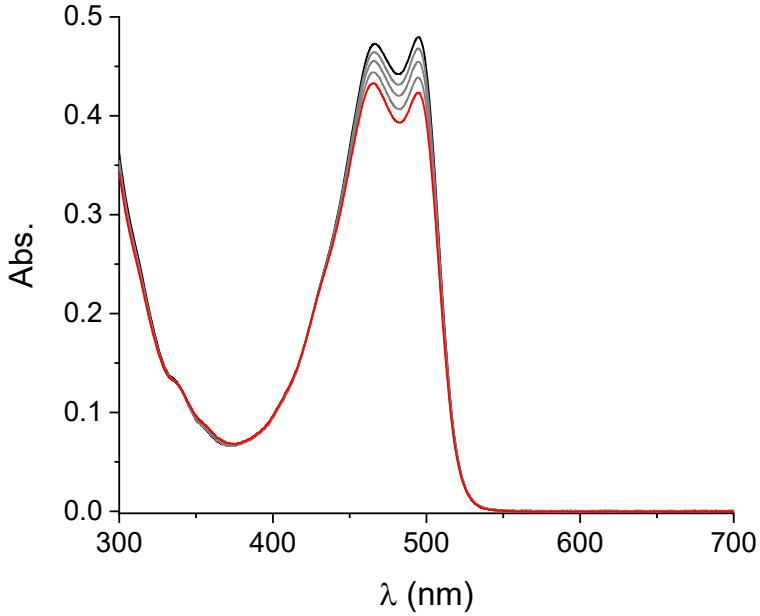


Figure S52. UV/vis absorption spectra for the continuous irradiation of **3** (150 W xenon lamp, $\lambda_{irr} > 395$ nm) in air-equilibrated toluene (black; $t = 0$ and red; $t = 4$ h).

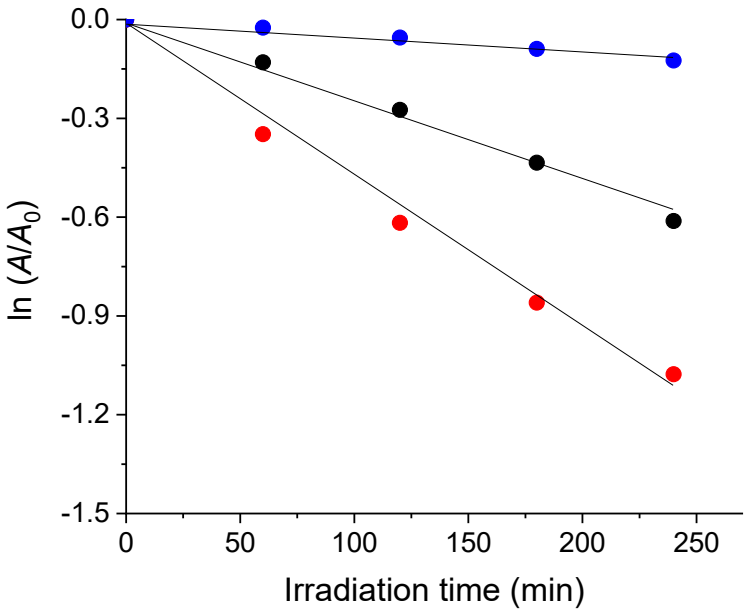


Figure S53. First-order plot of the photoreaction of the dyes **1** (black points) **2** (red points) and **3** (blue points) in air-equilibrated toluene under continuous irradiation (150 W xenon lamp, $\lambda_{irr} > 395$ nm).

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