

## Supporting Information

### Photochromic Dithienylethene-Containing Four-Coordinate Boron(III) Compounds with a Spirocyclic Scaffold

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## Experimental Details

### Materials and Reagents

*n*-Butyllithium, lithium diisopropylamide, tetramethylethylenediamine and 1,2-dibromotetrachloroethane were purchased from *J&K Chemical Ltd.* 2-Bromophenylboronic acid and other derivatives were purchased from *AK Scientific, Inc.* Tetrakis(triphenylphosphine)palladium(0) catalyst<sup>1</sup> for Suzuki coupling and 2,2',5,5'-tetramethyl-3,2':3',3''-terthiophene (Th-DTE)<sup>2</sup> were synthesised according to reported procedures. (2-Phenylpyridinato-C<sup>2</sup>,*N*)boron dibromide (ppyBBr<sub>2</sub>), (2-benzo[*b*]thienylpyridinato-C<sup>2</sup>,*N*)boron dibromide (bzthpyBBr<sub>2</sub>) and (2-phenylquinolinato-C<sup>2</sup>,*N*)boron dibromide (phquinBBr<sub>2</sub>) were prepared according to the literature procedures with slight modifications.<sup>3</sup> All solvents were purified and distilled using standard procedures before use. All other reagents were of analytical grade and were used as received.

### Physical Measurements and Instrumentation

<sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) or Bruker DRX 500 (500 MHz) fourier transform NMR spectrometer with chemical shifts ( $\delta$ , ppm) relative to tetramethylsilane (Me<sub>4</sub>Si) at 353 K. <sup>19</sup>F{<sup>1</sup>H} NMR spectra were recorded on a Bruker AVANCE 400 (376 MHz) or Bruker DRX 500 (470 MHz) fourier transform NMR spectrometer with chemical shifts ( $\delta$ , ppm) relative to trichlorofluoromethane (CFC<sub>3</sub>) at 353 K. <sup>11</sup>B{<sup>1</sup>H} NMR spectra were recorded on a Bruker DRX 500 (160 MHz) NMR fourier transform NMR spectrometer with chemical shifts ( $\delta$ , ppm) relative to BF<sub>3</sub>•OEt<sub>2</sub> at 353 K. Electron impact (EI) and electrospray-ionization (ESI) high-resolution mass spectra (HRMS) were obtained on a Thermo Scientific DFS High Resolution Magnetic Sector mass spectrometer and a Bruker maXis II Ultrahigh-

Resolution Time-of-Flight mass spectrometer, respectively. Elemental analyses were performed with a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing, P. R. China. Cyclic voltammetric measurements were performed on a CH Instrument, Inc. model CHI620 electrochemical analyzer. A glassy carbon (CH Instrument) electrode and a Ag/AgNO<sub>3</sub> (0.1 M in acetonitrile) electrode were used as the working electrode and reference electrode, respectively. The counter electrode was a platinum wire that was separated from the glassy carbon (CH Instrument) electrode by a sintered-glass frit in the electrolytic cell. The internal reference was the ferrocenium/ferrocene couple (Fc<sup>+</sup>/Fc).<sup>4,5</sup> Electronic absorption spectra of the open form isomers were recorded on a Varian Cary 50 spectrophotometer equipped with Xenon flash lamp. The other UV–visible absorption spectra for photochromic studies were obtained on an Agilent Technologies Cary 8454 UV–visible spectrophotometer with a 300 W Oriel Corporation Model 66011 Xe (ozone free) lamp as the light source and with an Applied Photophysics F 3.4 monochromator to control the wavelength of the monochromatic light. All the measurements were performed at room temperature unless specified otherwise. Prior to the measurements, the sample solutions were degassed with no fewer than four freeze-pump-thaw cycles on a high vacuum line in a degassing cell with a 10-cm<sup>3</sup> Pyrex round bottom flask connected by a side-arm to a 1-cm quartz fluorescence cuvette and was sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Steady-state emission spectra were recorded using an Edinburgh Instruments FS5 spectrofluorometer. Toluene solutions of the compounds (10<sup>-5</sup> M) were prepared to investigate their absorption and photoluminescence characteristics in the solution state. The sample solutions were degassed with at least four freeze-pump-thaw cycles on a high-vacuum line prior to the measurements. Relative luminescence quantum yields

were determined by the optical dilute method developed by Demas and Crosby.<sup>6</sup> The sample solutions with  $A < 0.1$  at the excitation wavelength were prepared to minimize inner filter effect. A degassed aqueous solution of quinine sulfate in 0.5 M sulfuric acid at 298 K ( $\phi_{\text{lum}} = 0.546$ ,  $\lambda_{\text{ex}} = 365$  nm) was used as the standard.<sup>7</sup> Excited-state lifetimes were measured on a Quantaaurus-Tau C11367-34 fluorescence lifetime spectrometer with the 335 nm excitation source. Photochromic quantum yields were determined with calibration of the incident photon flux by chemical actinometry. Ferrioxalate actinometer<sup>8</sup> was employed for the measurement of photocyclization quantum yields, while Reinecke's salt actinometer<sup>9</sup> was employed for the measurement of photocycloreversion quantum yields. Sample solutions with absorbance at the excitation wavelength slightly higher than 2 were prepared. The photochromic quantum yields were determined from the initial rate of change of absorbance,  $(\Delta A/\Delta t)$ , by monitoring the absorption band of the closed form at a specified wavelength.

## Synthesis and Characterisation

5'-Bromo-2,2",5,5"-tetramethyl-3,2':3',3"-terthiophene (BrTh-DTE). To a solution of Th-DTE (2 g, 6.6 mmol) and tetramethylethylenediamine (1.5 mL, 10.1 mmol) in THF (50 mL) was added *n*-butyllithium in hexane (2.4 M, 4.2 mL, 10.1 mmol) dropwise at  $-78$  °C and the mixture was stirred for 1.5 hr. To the resulting solution was then added 1,2-dibromotetrachloroethane (3.5 g, 10.7 mmol) dissolved in minimal amount of THF in a dropwise manner, and the mixture was allowed to stir at room temperature for 12 hr. The resulting mixture was extracted with diethyl ether, washed with brine, and was dried over anhydrous magnesium sulfate. After solvent removal, the crude product was purified by column chromatography on silica gel (70–230 mesh) using hexane as the eluent to afford colourless oil. Further purification was achieved by recrystallisation in

minimal amount of hexane and stored at  $-18\text{ }^{\circ}\text{C}$  to afford the product as a white solid. Yield: 2.0 g, 5.7 mmol; 86 %.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta/\text{ppm}$ ):  $\delta$  2.00 (s, 3H,  $-\text{CH}_3$ ), 2.01 (s, 3H,  $-\text{CH}_3$ ), 2.36 (s, 6H,  $-\text{CH}_3$ ), 6.37 (s, 1H, thienyl), 6.43 (s, 1H, thienyl), 6.98 (s, 1H, thienyl). HRMS (positive EI) calcd for  $[\text{C}_{16}\text{H}_{16}\text{BrS}_3]^+$ :  $m/z = 381.9514$ ; found: 381.9525  $[\text{M}+\text{H}]^+$ .

4',5'-Dibromo-2,2'',5,5''-tetramethyl-3,2':3',3''-terthiophene ( $\text{Br}_2\text{ThDTE}$ ). To a solution of  $\text{BrTh-DTE}$  (2 g, 5.2 mmol) in THF (50 mL) was added lithium diisopropylamide in THF (2.0 M, 7.9 mL, 15.8 mmol) dropwise at  $-78\text{ }^{\circ}\text{C}$  and the mixture was stirred for 4 hr at  $0\text{ }^{\circ}\text{C}$ . To the resulting solution was then added 1,2-dibromotetrachloroethane (5.34 g, 16.4 mmol) dissolved in minimal amount of THF in a dropwise manner, and the mixture was allowed to stir at room temperature for 12 hr. The resulting mixture was quenched with water, extracted with diethyl ether, washed with brine, and was dried over anhydrous magnesium sulfate. After solvent removal, the crude product was purified by column chromatography on silica gel (70–230 mesh) using hexane as the eluent to afford a colourless oil. Further purification was achieved by recrystallisation in minimal amount of hexane and stored at  $-18\text{ }^{\circ}\text{C}$  to afford the product as a white solid. Yield: 1.9 g, 4.2 mmol; 81 %.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta/\text{ppm}$ ):  $\delta$  1.96 (s, 3H,  $-\text{CH}_3$ ), 2.09 (s, 3H,  $-\text{CH}_3$ ), 2.32 (s, 3H,  $-\text{CH}_3$ ), 2.40 (s, 3H,  $-\text{CH}_3$ ), 6.30 (s, 1H, thienyl), 6.46 (s, 1H, thienyl). HRMS (positive EI) calcd for  $[\text{C}_{16}\text{H}_{15}\text{Br}_2\text{S}_3]^+$ :  $m/z = 459.8619$ ; found: 459.8602  $[\text{M}+\text{H}]^+$ .

4'-Bromo-5'-(2-bromophenyl)-2,2'',5,5''-tetramethyl-3,2':3',3''-terthiophene ( $\text{BrPh}^{\wedge}\text{Br}_2\text{Th-DTE}$ ). The product was synthesised by Suzuki coupling reaction under standard Schlenk techniques. To a solution of  $\text{Br}_2\text{Th-DTE}$  (1 g, 2.2 mmol) in THF (30

mL) was added 2-bromophenylboronic acid (575 mg, 2.9 mmol), aqueous caesium carbonate (2 M, 3.3 mL, 6.6 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.25 g, 0.22 mmol). The solution was allowed to reflux for 12 hr. The resulting mixture was extracted with diethyl ether, washed with brine, and was dried over anhydrous magnesium sulfate. After removal of solvent, the crude product was purified by column chromatography on silica gel (70–230 mesh) using hexane as the eluent to afford the product as a colourless oil. Further purification was achieved by recrystallisation from slow evaporation of solvent from a concentrated hexane solution of the crude product to afford the product as a white solid. Yield: 790 mg, 1.5 mmol; 68 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K,  $\delta$ /ppm):  $\delta$  2.04 (s, 3H, –CH<sub>3</sub>), 2.16 (s, 3H, –CH<sub>3</sub>), 2.34 (s, 3H, –CH<sub>3</sub>), 2.41 (s, 3H, –CH<sub>3</sub>), 6.39 (s, 1H, dimethylthienyl), 6.54 (s, 1H, dimethylthienyl), 7.29 (t,  $J = 7.9$  Hz, 1H, phenyl), 7.38 (t,  $J = 7.9$  Hz, 1H, phenyl), 7.48 (d,  $J = 7.9$  Hz, 1H, phenyl), 7.71 (d,  $J = 7.9$  Hz, 1H, phenyl). HRMS (positive EI) calcd for [C<sub>22</sub>H<sub>19</sub>Br<sub>2</sub>S<sub>3</sub>]<sup>+</sup>:  $m/z = 535.8932$ ; found: 535.8926 [M+H]<sup>+</sup>.

4'-Bromo-5'-(2-bromo-4-methylphenyl)-2,2'',5,5''-tetramethyl-3,2':3',3''-terthiophene (BrMePh<sup>^</sup>Br<sub>2</sub>Th-DTE). The synthetic procedure is similar to that of BrPh<sup>^</sup>Br<sub>2</sub>Th-DTE except (2-bromo-4-methylphenyl)boronic acid was used instead of 2-bromophenylboronic acid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K,  $\delta$ /ppm):  $\delta$  2.03 (s, 3H, –CH<sub>3</sub>), 2.15 (s, 3H, –CH<sub>3</sub>), 2.34 (s, 3H, –CH<sub>3</sub>), 2.40 (s, 3H, –CH<sub>3</sub>), 2.41 (s, 3H, –CH<sub>3</sub>), 6.39 (s, 1H, thienyl), 6.53 (s, 1H, thienyl), 7.20 (d,  $J = 7.8$  Hz, 1H, phenyl), 7.36 (d,  $J = 7.8$  Hz, 1H, phenyl), 7.53 (s, 1H, phenyl). HRMS (positive EI) calcd for [C<sub>23</sub>H<sub>21</sub>Br<sub>2</sub>S<sub>3</sub>]<sup>+</sup>:  $m/z = 549.9088$ ; found: 549.9096 [M+H]<sup>+</sup>.

4'-Bromo-5'-(2-bromo-4-methoxyphenyl)-2,2'',5,5''-tetramethyl-3,2':3',3''-terthiophene (BrOMePh<sup>^</sup>Br<sub>2</sub>Th-DTE). The synthetic procedure is similar to that of BrPh<sup>^</sup>Br<sub>2</sub>Th-DTE except (2-bromo-4-methoxyphenyl)boronic acid was used instead of 2-bromophenylboronic acid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, δ/ppm): δ 2.03 (s, 3H, –CH<sub>3</sub>), 2.15 (s, 3H, –CH<sub>3</sub>), 2.34 (s, 3H, –CH<sub>3</sub>), 2.41 (s, 3H, –CH<sub>3</sub>), 3.85 (s, 3H, –OCH<sub>3</sub>), 6.39 (s, 1H, thienyl), 6.54 (s, 1H, thienyl), 6.93 (d, *J* = 8.4 Hz, 1H, phenyl), 7.25 (s, 1H, phenyl), 7.38 (d, *J* = 8.4 Hz, 1H, phenyl). HRMS (positive EI) calcd for [C<sub>23</sub>H<sub>21</sub>Br<sub>2</sub>OS<sub>3</sub>]<sup>+</sup>: *m/z* = 565.9038; found: 549.9029 [M+H]<sup>+</sup>.

4'-Bromo-5'-(2-bromo-4-(trifluoromethyl)phenyl)-2,2'',5,5''-tetramethyl-3,2':3',3''-terthiophene (BrCF<sub>3</sub>Ph<sup>^</sup>Br<sub>2</sub>Th-DTE). The synthetic procedure is similar to that of BrPh<sup>^</sup>Br<sub>2</sub>Th-DTE except (2-bromo-4-trifluoromethylphenyl)boronic acid was used instead of 2-bromophenylboronic acid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, δ/ppm): δ 2.04 (s, 3H, –CH<sub>3</sub>), 2.15 (s, 3H, –CH<sub>3</sub>), 2.35 (s, 3H, –CH<sub>3</sub>), 2.41 (s, 3H, –CH<sub>3</sub>), 6.39 (s, 1H, thienyl), 6.53 (s, 1H, thienyl), 7.61 (d, *J* = 8.0 Hz, 1H, phenyl), 7.65 (d, *J* = 8.0 Hz, 1H, phenyl), 7.97 (s, 1H, phenyl). <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, CDCl<sub>3</sub>, 298 K, δ/ppm): δ –62.8. HRMS (positive EI) calcd for [C<sub>23</sub>H<sub>18</sub>Br<sub>2</sub>F<sub>3</sub>S<sub>3</sub>]<sup>+</sup>: *m/z* = 603.8805; found: 603.8792 [M+H]<sup>+</sup>.

ppyBzBTh-DTE (**1**). To a solution of BrPh<sup>^</sup>Br<sub>2</sub>Th-DTE in toluene was added *n*-butyllithium dropwise at –78 °C and the mixture was stirred for 1 hr. The resulting solution was added ppyBBr<sub>2</sub> at once, and was allowed to stir at room temperature for 12 hr. The resulting mixture was quenched with water, extracted with diethyl ether, washed with brine, and was dried over anhydrous magnesium sulfate. After solvent removal, the crude product was purified by column chromatography on silica gel (30–

70 mesh) using hexane-ethyl acetate (3:1 v/v) as the eluent to afford the product as a pale yellow solid. Further purification was achieved by recrystallisation from layering of methanol onto a concentrated dichloromethane solution of the compound to afford pale yellow crystals.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ , 353 K,  $\delta/\text{ppm}$ ):  $\delta$  1.36 (s, 3H,  $-\text{CH}_3$ ), 1.88 (s, 3H,  $-\text{CH}_3$ ), 2.05 (s, 3H,  $-\text{CH}_3$ ), 2.23 (s, 3H,  $-\text{CH}_3$ ), 5.17 (s, 1H, thienyl), 6.38 (s, 1H, thienyl), 6.65 (d,  $J = 7.1$  Hz, 1H, phenyl), 6.84 (t,  $J = 7.1$  Hz, 1H, phenyl), 7.11–7.14 (m, 2H, phenyl), 7.25–7.31 (m, 3H, phenyl), 7.36 (t,  $J = 6.0$  Hz, 1H, pyridine), 7.91 (d,  $J = 6.0$  Hz, 1H, pyridine), 7.96 (d,  $J = 6.0$  Hz, 1H, phenyl), 8.14–8.20 (m, 2H, pyridine).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{DMSO-}d_6$ , 353 K,  $\delta/\text{ppm}$ ):  $\delta$  0.14.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta/\text{ppm}$ ):  $\delta$  12.92, 13.82, 14.01, 14.43, 14.86, 15.12, 15.23, 117.38, 118.05, 118.17, 121.03, 121.12, 121.93, 122.49, 124.75, 125.98, 126.74, 126.89, 127.02, 127.07, 127.30, 127.55, 127.85, 129.72, 129.97, 130.32, 130.47, 130.74, 131.21, 131.89, 131.95, 132.58, 132.69, 134.12, 134.40, 134.69, 134.75, 135.63, 136.34, 137.87, 140.20, 141.55, 142.52, 143.74, 147.50, 150.47, 159.17. HRMS (positive ESI) calcd for  $[\text{C}_{33}\text{H}_{26}\text{BNS}_3]^+$ :  $m/z = 543.1320$ ; found: 543.1319  $[\text{M}]^+$ . Elemental analyses, found (%): C 72.52, H 4.80, N 2.82; calcd (%) for  $\text{C}_{33}\text{H}_{26}\text{BNS}_3$ : C 72.78, H 4.78, N 2.57.

ppyMeBzBTh-DTE (**2**). The synthetic procedure is similar to that of **1** except  $\text{BrMePh}^{\wedge}\text{Br}_2\text{Th-DTE}$  was used instead of  $\text{BrPh}^{\wedge}\text{Br}_2\text{Th-DTE}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ , 353 K,  $\delta/\text{ppm}$ ):  $\delta$  1.35 (s, 3H,  $-\text{CH}_3$ ), 1.88 (s, 3H,  $-\text{CH}_3$ ), 2.04 (s, 3H,  $-\text{CH}_3$ ), 2.10 (s, 3H,  $-\text{CH}_3$ ), 2.22 (s, 3H,  $-\text{CH}_3$ ), 5.16 (s, 1H, thienyl), 6.37 (s, 1H, phenyl), 6.47 (s, 1H, thienyl), 6.93 (d,  $J = 7.8$  Hz, 1H, phenyl), 7.14 (d,  $J = 5.8$  Hz, 1H, phenyl), 7.19 (d,  $J = 7.8$  Hz, 1H, phenyl), 7.25–7.31 (m, 2H, phenyl), 7.36 (t,  $J = 5.5$  Hz, 1H, pyridine), 7.90 (d,  $J = 5.5$  Hz, 1H, pyridine), 7.96 (d,  $J = 5.8$  Hz, 1H, phenyl), 8.13–8.21 (m, 2H,



pyridine).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, DMSO- $d_6$ , 353 K,  $\delta$ /ppm):  $\delta$  0.15.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ /ppm):  $\delta$  12.93, 13.82, 14.00, 14.43, 14.86, 15.13, 15.23, 21.43, 21.66, 117.35, 117.87, 118.03, 121.01, 121.14, 121.92, 122.49, 125.96, 126.77, 127.01, 127.11, 127.66, 127.71, 127.90, 128.54, 129.98, 130.37, 130.55, 130.72, 130.87, 131.23, 131.74, 131.88, 132.05, 132.43, 132.64, 132.90, 133.44, 134.05, 134.12, 134.24, 134.34, 134.66, 135.36, 135.46, 135.62, 137.05, 140.15, 141.53, 142.32, 142.60, 143.77, 144.79, 150.63, 157.93, 159.11. HRMS (positive ESI) calcd for  $[\text{C}_{34}\text{H}_{28}\text{BNS}_3]^+$ :  $m/z = 557.1477$ ; found: 557.1472  $[\text{M}]^+$ . Elemental analyses, found (%): C 72.66, H 4.98, N 2.55; calcd (%) for  $\text{C}_{34}\text{H}_{28}\text{BNS}_3 \cdot 0.5\text{CH}_3\text{OH}$ : C 72.24, H 5.27, N 2.44.

ppyOMeBzBTh-DTE (**3**). The synthetic procedure is similar to that of **1** except BrOMePh<sup>^</sup>Br<sub>2</sub>Th-DTE was used instead of BrPh<sup>^</sup>Br<sub>2</sub>Th-DTE.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , 353 K,  $\delta$ /ppm):  $\delta$  1.37 (s, 3H, -CH<sub>3</sub>), 1.91 (s, 3H, -CH<sub>3</sub>), 2.06 (s, 3H, -CH<sub>3</sub>), 2.25 (s, 3H, -CH<sub>3</sub>), 3.61 (s, 3H, -OCH<sub>3</sub>), 5.18 (s, 1H, thienyl), 6.26 (d,  $J = 2.5$  Hz, 1H, phenyl), 6.39 (s, 1H, thienyl), 6.93 (d,  $J = 8.0, 2.5$  Hz, 1H, phenyl), 7.15–7.19 (m, 1H, phenyl), 6.39 (s, 1H, thienyl), 6.93 (d,  $J = 8.0, 2.5$  Hz, 1H, phenyl), 7.15–7.19 (m, 1H, phenyl), 7.24 (d,  $J = 8.0$  Hz, 1H, phenyl), 7.29–7.33 (m, 2H, phenyl), 7.40 (td,  $J = 6.2, 2.0$  Hz, 1H, pyridine), 7.94 (d,  $J = 6.2$  Hz, 1H, pyridine), 7.96–7.99 (m, 1H, phenyl), 8.16–8.22 (m, 2H, pyridine).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, DMSO- $d_6$ , 353 K,  $\delta$ /ppm):  $\delta$  0.07.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ /ppm):  $\delta$  12.92, 13.81, 14.01, 14.42, 14.85, 15.12, 15.22, 55.20, 111.13, 112.45, 116.75, 117.36, 118.03, 118.44, 120.98, 121.15, 121.34, 121.92, 122.51, 125.98, 126.77, 127.04, 127.09, 127.88, 128.68, 129.92, 129.95, 130.40, 130.56, 130.73, 131.70, 131.89, 132.04, 132.33, 132.38, 132.51, 132.62, 132.85, 133.27, 133.40, 133.51, 134.22, 134.31, 134.65, 135.34, 135.49, 135.66, 137.80, 140.21, 140.51, 141.57, 142.06, 142.58, 143.73, 150.37,

157.70, 157.97, 158.99. HRMS (positive ESI) calcd for  $[\text{C}_{34}\text{H}_{28}\text{BNOS}_3]^+$ :  $m/z = 573.1426$ ; found: 573.1428  $[\text{M}]^+$ . Elemental analyses, found (%): C 70.63, H 4.85, N 2.47; calcd (%) for  $\text{C}_{34}\text{H}_{28}\text{BNOS}_3 \cdot 0.5\text{CH}_3\text{OH}$ : C 70.28, H 5.13, N 2.38.

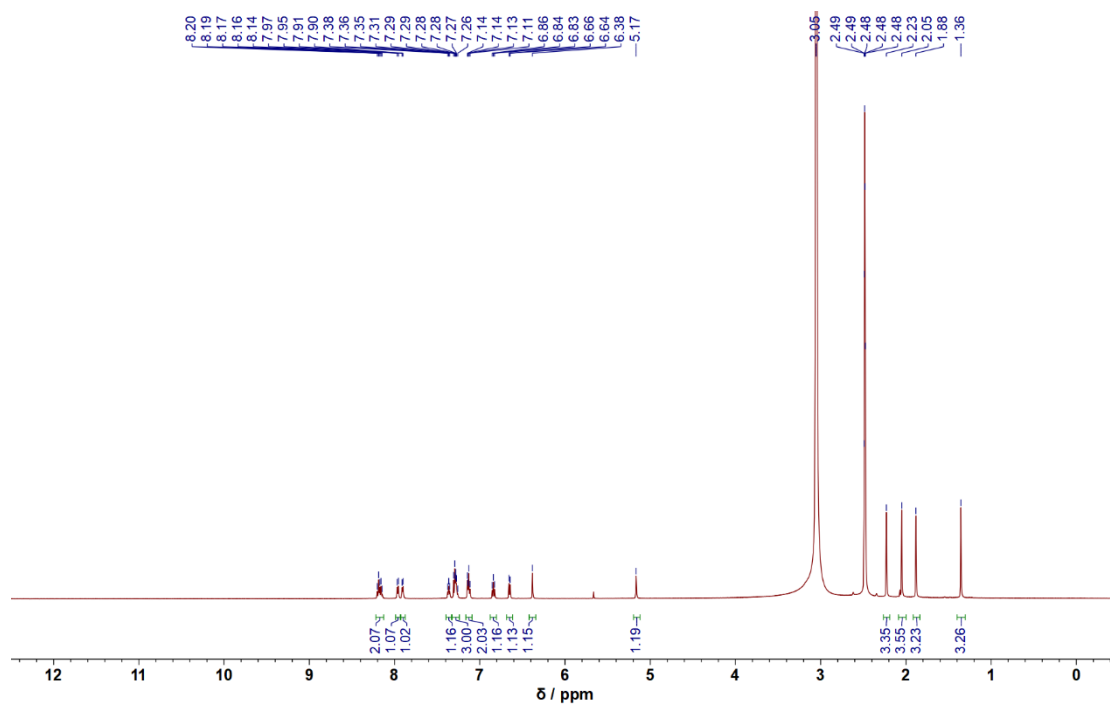
ppyCF<sub>3</sub>BzBTh-DTE (**4**). The synthetic procedure is similar to that of **1** except BrCF<sub>3</sub>Ph<sup>^</sup>Br<sub>2</sub>Th-DTE was used instead of BrPh<sup>^</sup>Br<sub>2</sub>Th-DTE. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 353 K,  $\delta/\text{ppm}$ ):  $\delta$  1.38 (s, 3H, -CH<sub>3</sub>), 1.92 (s, 3H, -CH<sub>3</sub>), 2.08 (s, 3H, -CH<sub>3</sub>), 2.26 (s, 3H, -CH<sub>3</sub>), 5.19 (s, 1H, thienyl), 6.42 (s, 1H, thienyl), 6.90 (s, 1H, phenyl), 7.15 (d,  $J = 6.5$  Hz, 1H, phenyl), 7.30–7.37 (m, 2H, phenyl), 7.41 (t,  $J = 6.0$  Hz, 1H, pyridine), 7.48–7.52 (m, 2H, phenyl), 7.97 (d,  $J = 6.0$  Hz, 1H, phenyl), 7.90 (d,  $J = 6.0$  Hz, 1H, pyridine), 8.01 (d,  $J = 7.5$  Hz, 1H, phenyl), 8.20–8.26 (m, 2H, pyridine). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, DMSO-*d*<sub>6</sub>, 353 K,  $\delta/\text{ppm}$ ):  $\delta$  0.15. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CDCl<sub>3</sub>, 298 K,  $\delta/\text{ppm}$ ):  $\delta$  12.91, 13.80, 13.99, 14.42, 14.86, 15.11, 15.22, 117.55, 117.59, 118.19, 121.19, 121.36, 122.02, 122.66, 124.34, 124.90, 124.93, 124.95, 124.98, 125.80, 125.98, 126.01, 126.04, 126.06, 126.14, 126.21, 126.30, 126.42, 126.59, 126.92, 127.25, 127.70, 128.84, 129.95, 130.11, 130.29, 130.94, 131.50, 131.58, 131.96, 132.07, 132.88, 132.95, 132.98, 133.07, 133.67, 133.70, 133.77, 134.66, 134.93, 135.62, 135.76, 136.54, 137.94, 140.53, 140.58, 141.81, 142.42, 143.62, 148.87, 150.85, 158.05, 159.33. <sup>19</sup>F{<sup>1</sup>H} NMR (470 MHz, DMSO-*d*<sub>6</sub>, 353 K,  $\delta/\text{ppm}$ ):  $\delta$  -61.46. HRMS (positive ESI) calcd for  $[\text{C}_{34}\text{H}_{25}\text{BF}_3\text{NS}_3]^+$ :  $m/z = 611.1195$ ; found: 611.1196  $[\text{M}]^+$ . Elemental analyses, found (%): C 66.66, H 4.13, N 2.31; calcd (%) for  $\text{C}_{34}\text{H}_{25}\text{BF}_3\text{NS}_3$ : C 66.77, H 4.13, N 2.29.

bzthpyBzBTh-DTE (**5**). The synthetic procedure is similar to that of **1** except bzthpyBBr<sub>2</sub> was used instead of ppyBBr<sub>2</sub>. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 353 K,

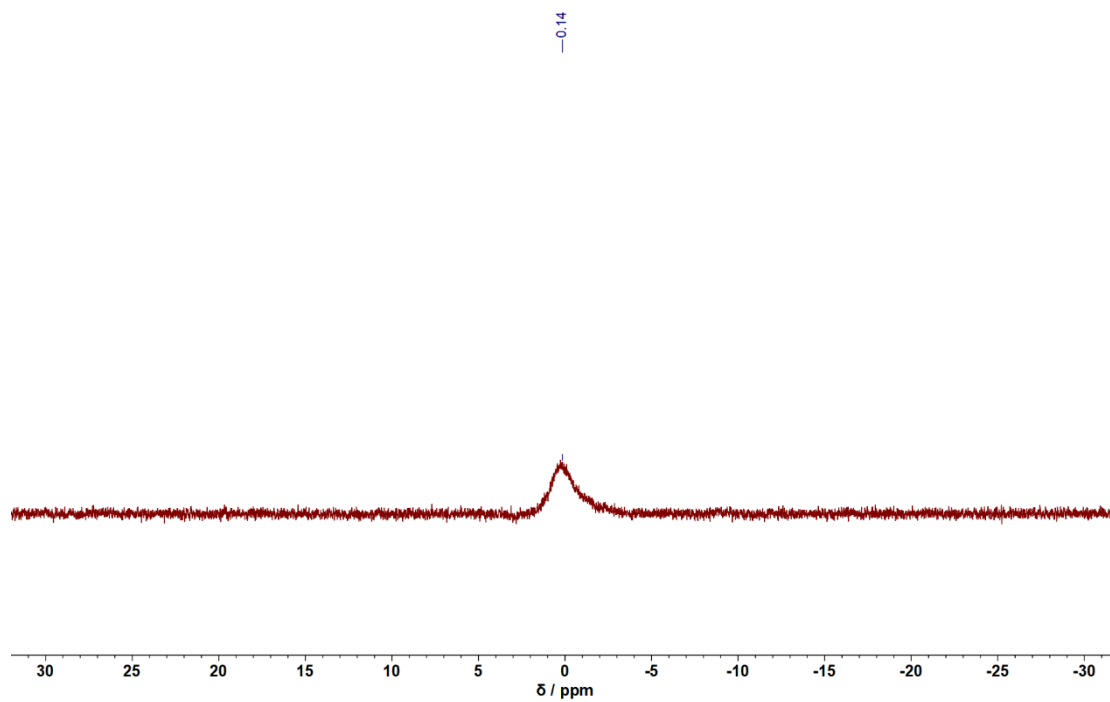
$\delta$ /ppm):  $\delta$  1.16 (s, 3H,  $-\text{CH}_3$ ), 1.91 (s, 3H,  $-\text{CH}_3$ ), 2.03 (s, 3H,  $-\text{CH}_3$ ), 2.21 (s, 3H,  $-\text{CH}_3$ ), 5.13 (s, 1H, thienyl), 6.36 (s, 1H, thienyl), 6.74 (d,  $J = 7.2$  Hz, 1H, phenyl), 6.86 (t,  $J = 7.2$  Hz, 1H, phenyl), 7.12 (d,  $J = 7.2$  Hz, 1H, phenyl), 7.17 (t,  $J = 7.5$  Hz, 2H, phenyl), 7.28–7.34 (m, 2H, phenyl & pyridine), 7.38 (d,  $J = 7.5$  Hz, 1H, phenyl), 7.82 (d,  $J = 8.0$  Hz, 1H, pyridyl), 7.96–8.00 (m, 2H, phenyl & pyridine), 8.16 (t,  $J = 8.0$  Hz, 1H, pyridine).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, DMSO- $d_6$ , 353 K,  $\delta$ /ppm):  $\delta$   $-0.86$ .  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ /ppm):  $\delta$  12.67, 13.85, 14.02, 14.45, 14.96, 15.11, 15.21, 15.25, 117.37, 118.33, 119.43, 122.92, 124.53, 124.88, 125.86, 126.21, 126.52, 127.01, 127.03, 127.49, 127.80, 129.80, 131.80, 132.64, 133.07, 133.85, 134.43, 134.83, 135.70, 139.84, 140.62, 142.07, 143.09, 144.08, 145.82, 147.35, 150.82, 155.79. HRMS (positive ESI) calcd for  $[\text{C}_{35}\text{H}_{26}\text{BNS}_4]^+$ :  $m/z = 599.1042$ ; found: 599.1039  $[\text{M}]^+$ . Elemental analyses, found (%): C 69.54, H 4.34, N 2.28; calcd (%) for  $\text{C}_{35}\text{H}_{26}\text{BNS}_4 \cdot 0.5\text{CH}_3\text{OH}$ : C 69.29, H 4.58, N 2.28.

phquinBzBTh-DTE (**6**). The synthetic procedure is similar to that of **1** except phquinBB $\text{r}_2$  was used instead of ppyBB $\text{r}_2$ .  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , 353 K,  $\delta$ /ppm):  $\delta$  0.96 (s, 3H,  $-\text{CH}_3$ ), 1.85 (s, 3H,  $-\text{CH}_3$ ), 2.02 (s, 3H,  $-\text{CH}_3$ ), 2.22 (s, 3H,  $-\text{CH}_3$ ), 4.86 (s, 1H, thienyl), 6.35 (s, 1H, thienyl), 6.71 (d,  $J = 7.0$  Hz, 1H, phenyl), 6.85 (t,  $J = 7.3$  Hz, 1H, phenyl), 7.12 (d,  $J = 7.0$  Hz, 1H, phenyl), 7.20 (t,  $J = 7.3$  Hz, 1H, phenyl), 7.33–7.42 (m, 3H, phenyl), 7.47 (d,  $J = 7.5$  Hz, 1H, quinoline), 7.53–7.57 (m, 2H, quinoline), 8.11–8.09 (m, 1H, quinoline), 8.18 (d,  $J = 7.5$  Hz, 1H, phenyl), 8.36 (d,  $J = 8.5$  Hz, 1H, quinoline), 8.77 (d,  $J = 8.5$  Hz, 1H, quinoline).  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz, DMSO- $d_6$ , 353 K,  $\delta$ /ppm):  $\delta$  0.11.  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CDCl}_3$ , 298 K,  $\delta$ /ppm):  $\delta$  12.00, 13.81, 14.07, 14.45, 14.81, 15.07, 15.26, 114.90, 118.87, 121.90, 122.86, 122.92, 124.63, 125.86, 126.54, 126.87, 126.92, 127.03, 127.07, 127.14,

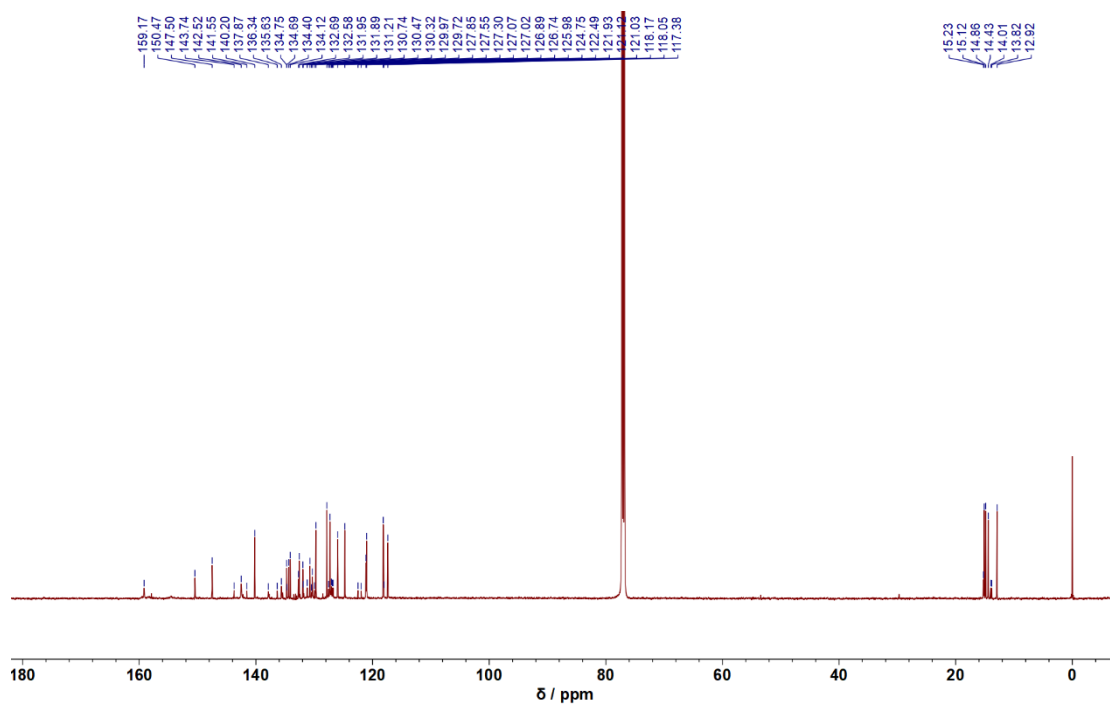
127.81, 128.15, 129.74, 129.96, 131.26, 131.84, 132.34, 132.39, 132.49, 133.97, 134.27, 134.67, 141.28, 141.44, 146.48, 149.07, 160.62. HRMS (positive ESI) calcd for  $[\text{C}_{37}\text{H}_{28}\text{BNS}_3]^+$ :  $m/z = 593.1477$ ; found: 593.1476  $[\text{M}]^+$ . Elemental analyses, found (%): C 74.54, H 4.72, N 2.36; calcd (%) for  $\text{C}_{37}\text{H}_{28}\text{BNS}_3$ : C 74.86, H 4.76, N 2.36.



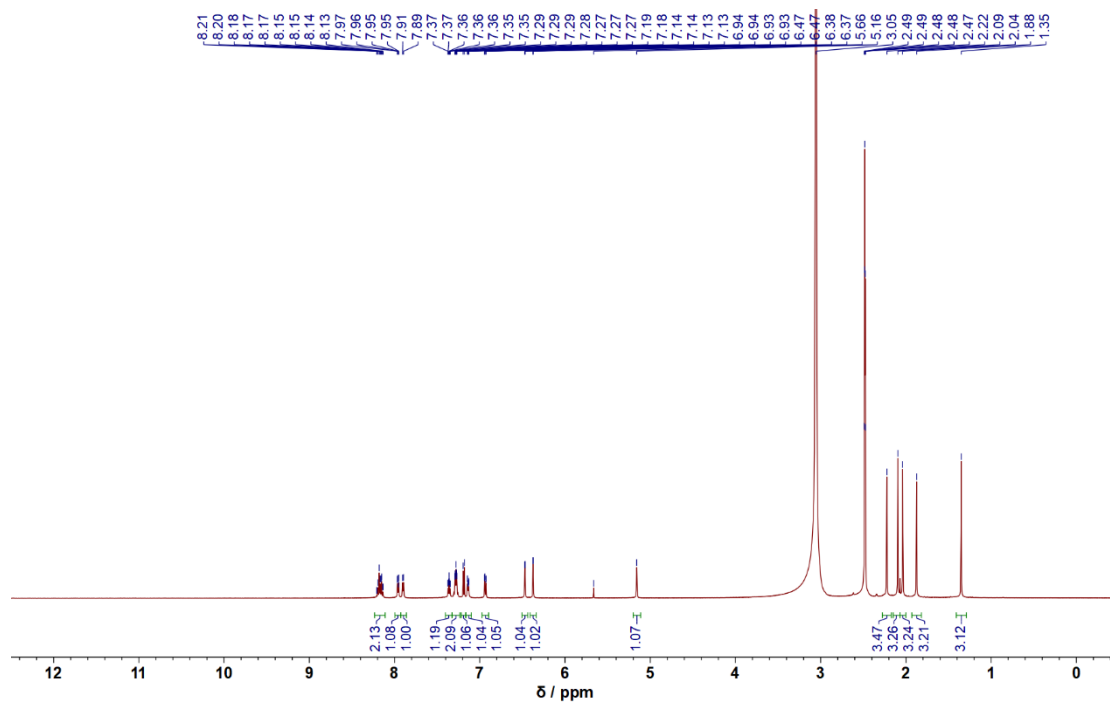
**Figure S1**  $^1\text{H}$  NMR spectrum of compound **1** at 353 K in  $\text{DMSO-}d_6$ .



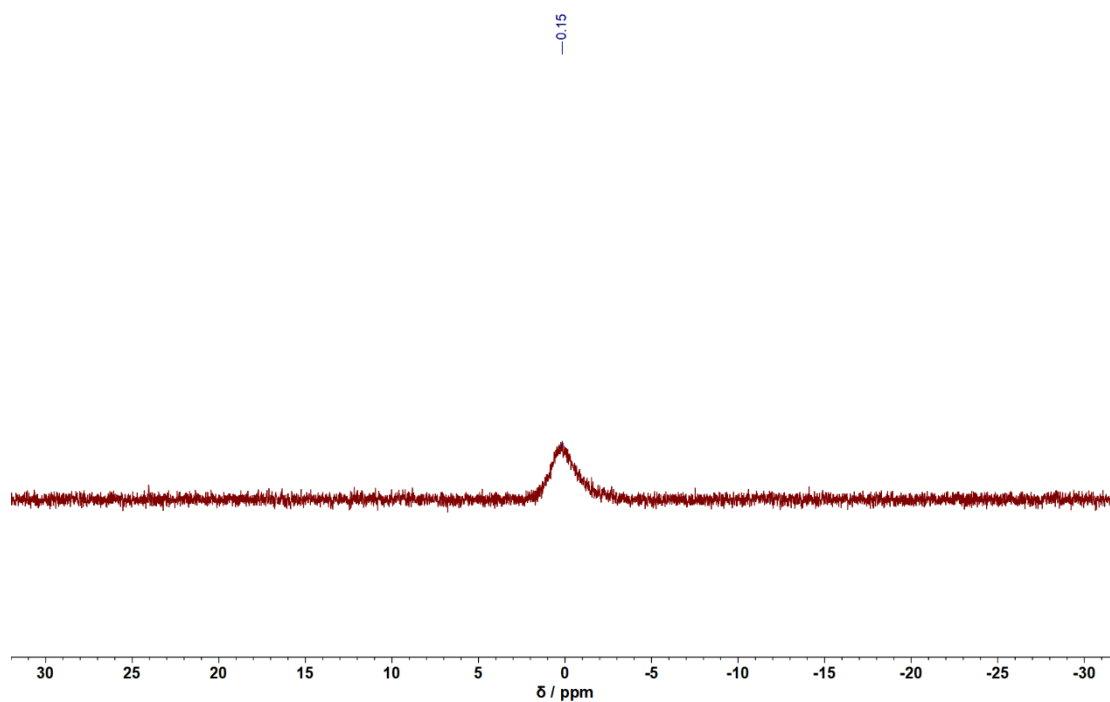
**Figure S2**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **1** at 353 K in  $\text{DMSO-}d_6$ .



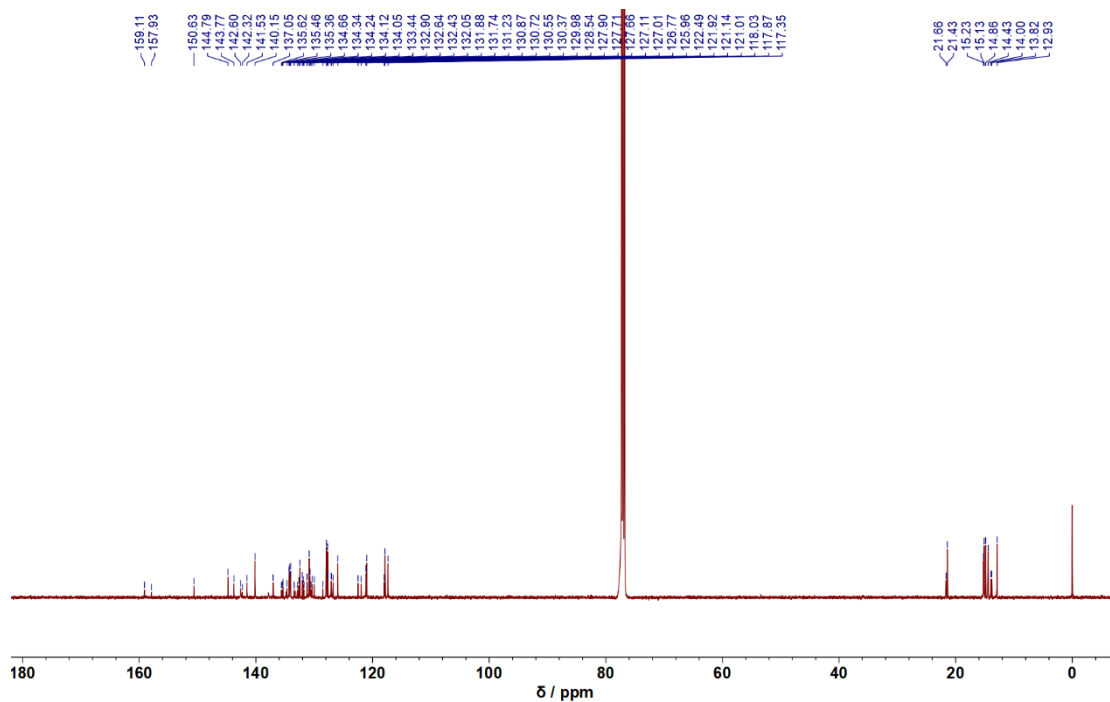
**Figure S3**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **1** at 298 K in  $\text{CDCl}_3$ .



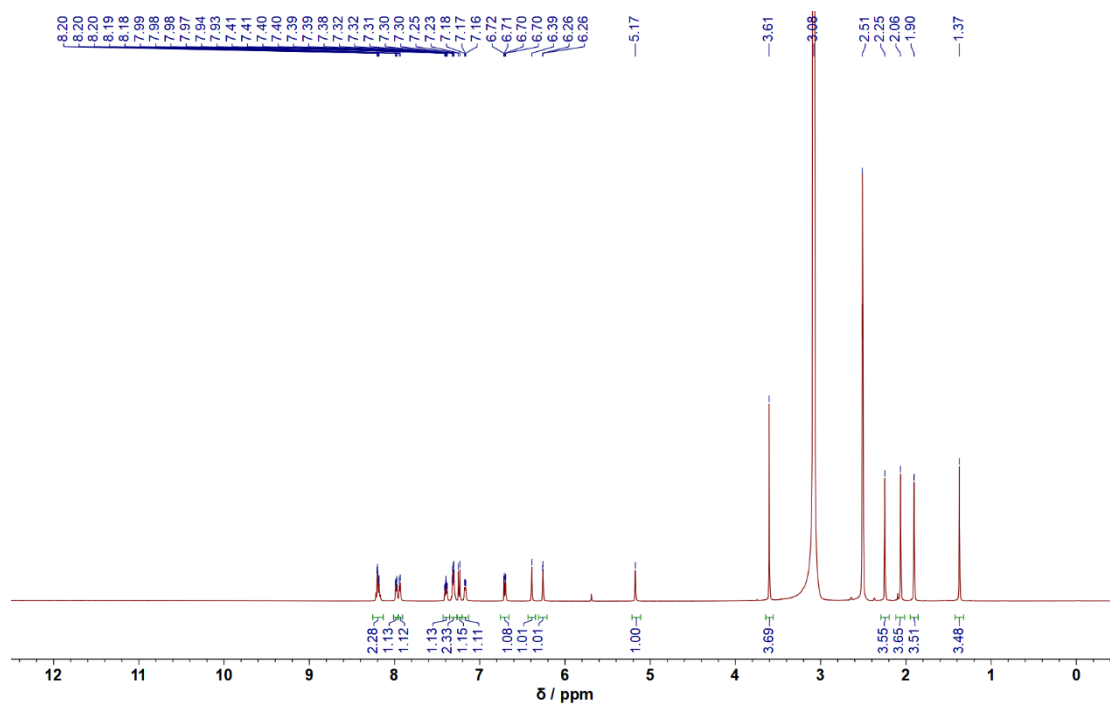
**Figure S4**  $^1\text{H}$  NMR spectrum of compound **2** at 353 K in  $\text{DMSO-}d_6$ .



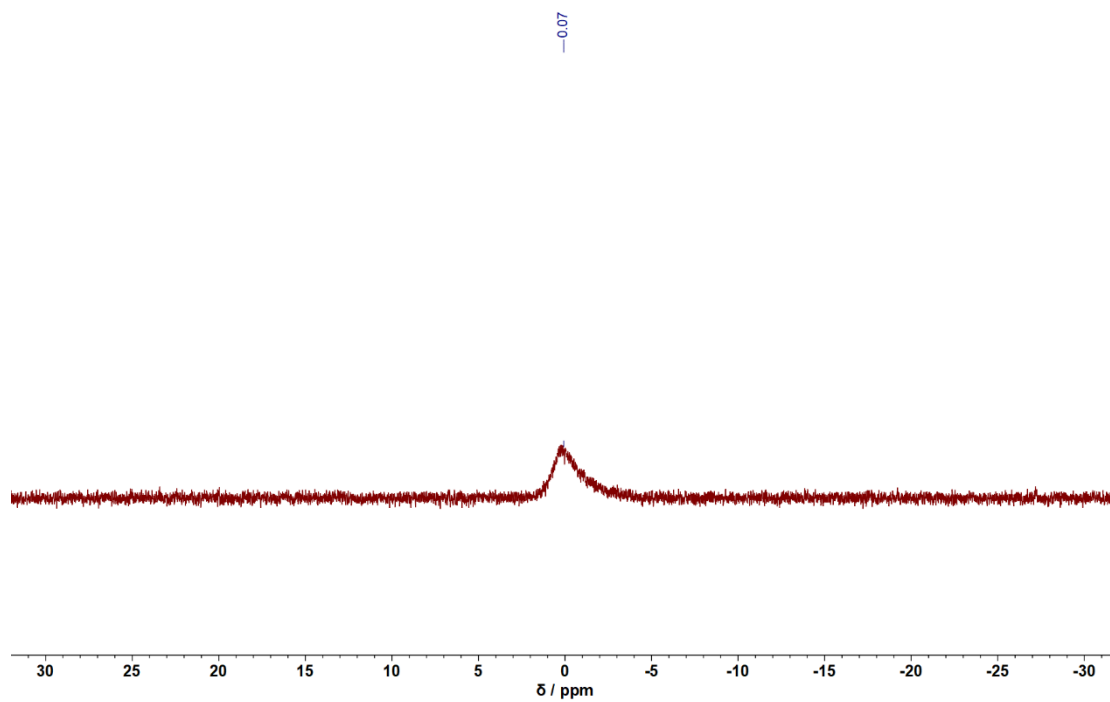
**Figure S5**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **2** at 353 K in  $\text{DMSO-}d_6$ .



**Figure S6**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **2** at 298 K in  $\text{CDCl}_3$ .

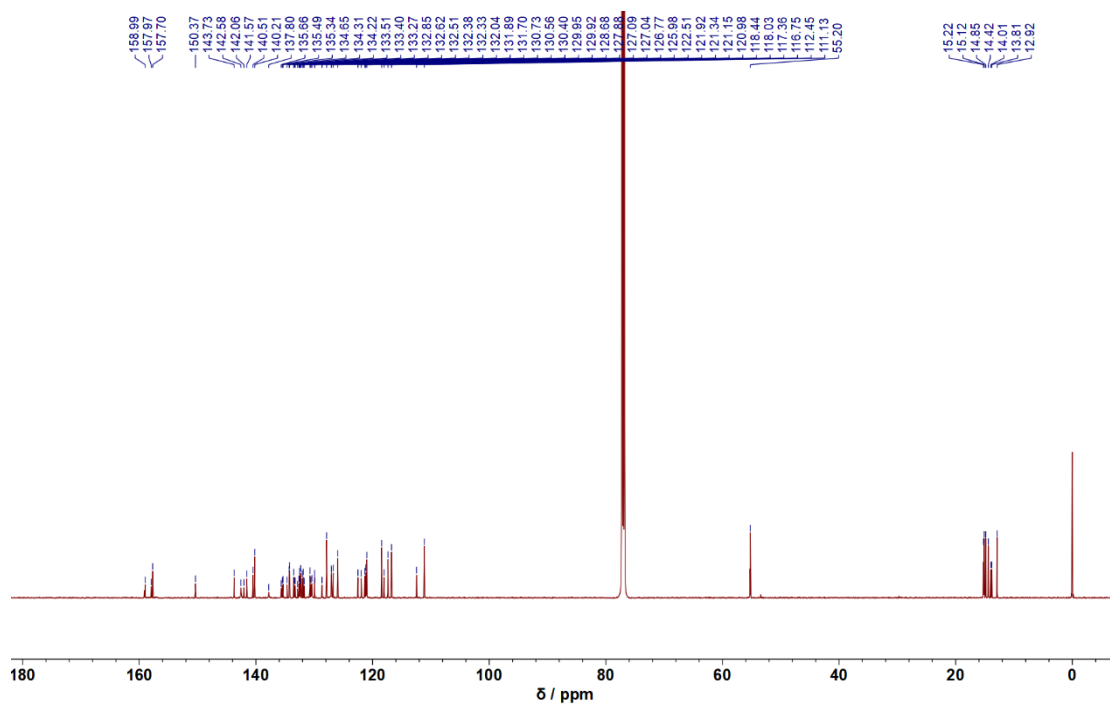


**Figure S7**  $^1\text{H}$  NMR spectrum of compound **3** at 353 K in  $\text{DMSO-}d_6$ .

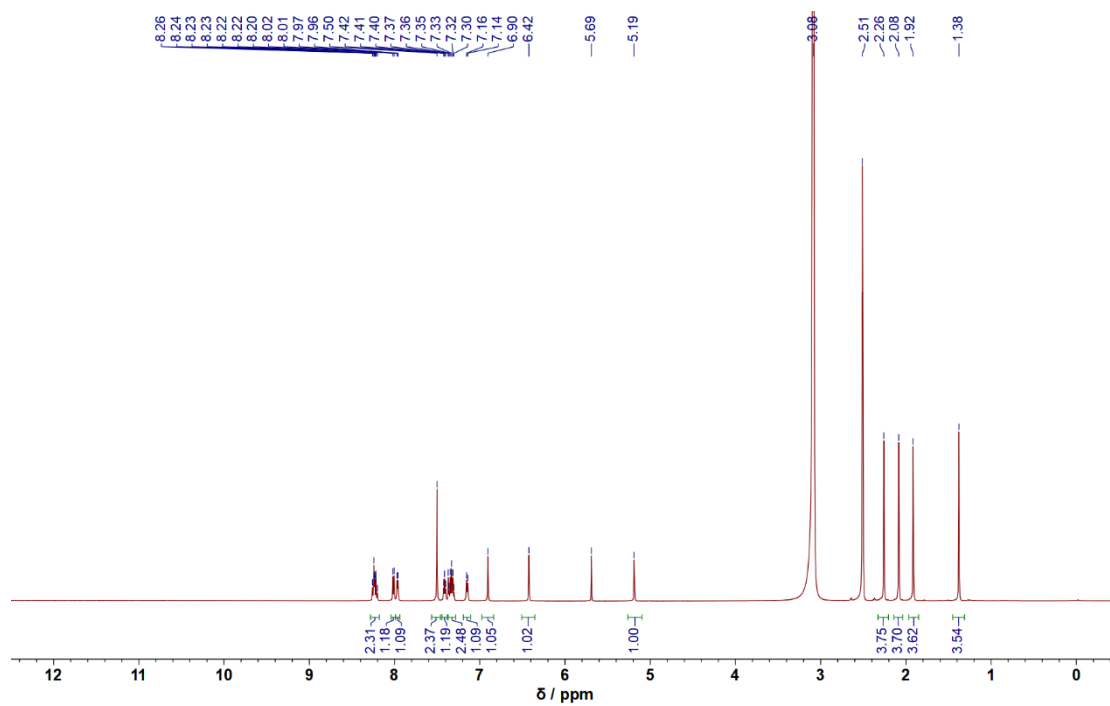


**Figure S8**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **3** at 353 K in  $\text{DMSO-}d_6$ .

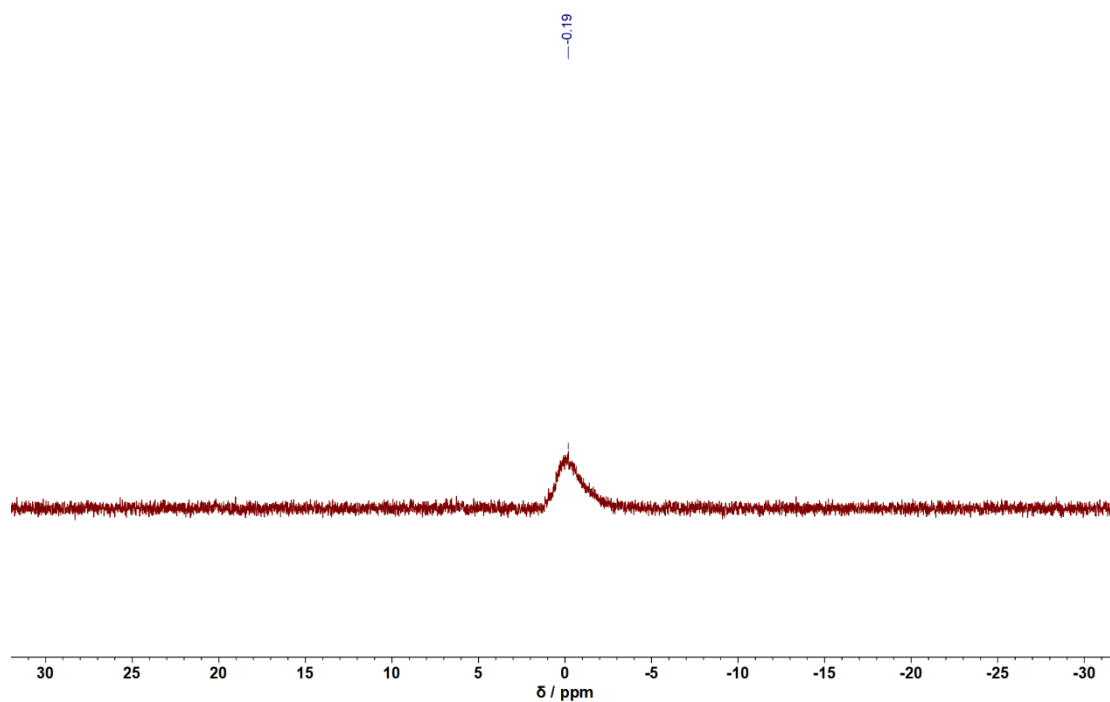




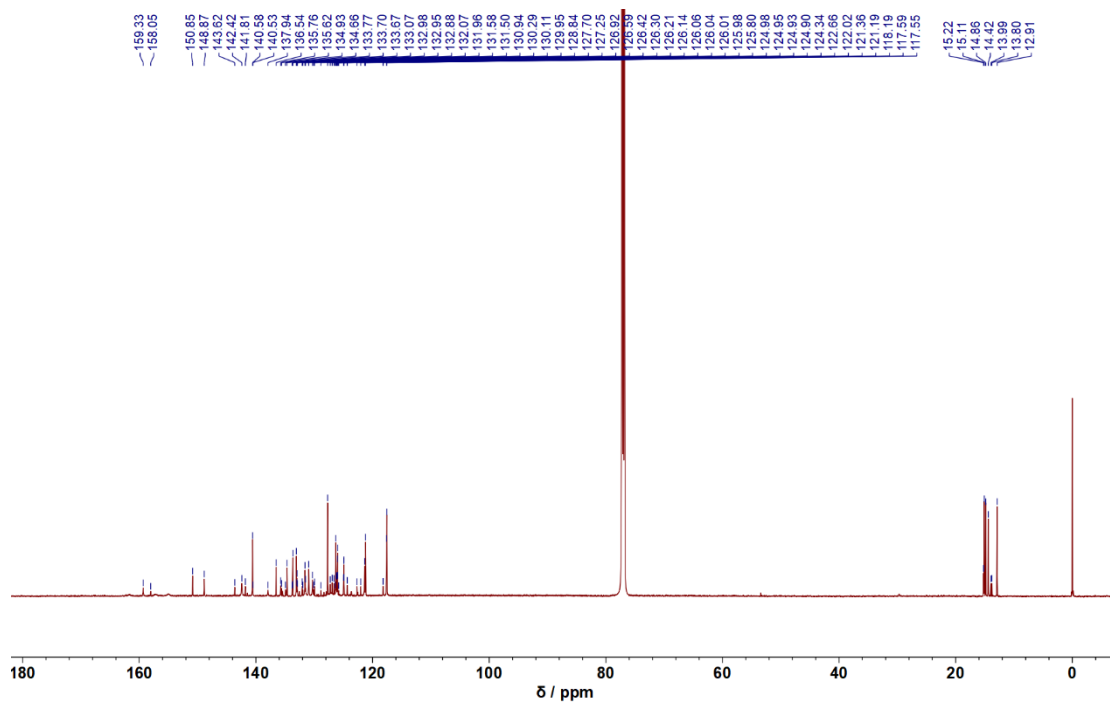
**Figure S9**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **3** at 298 K in  $\text{CDCl}_3$ .



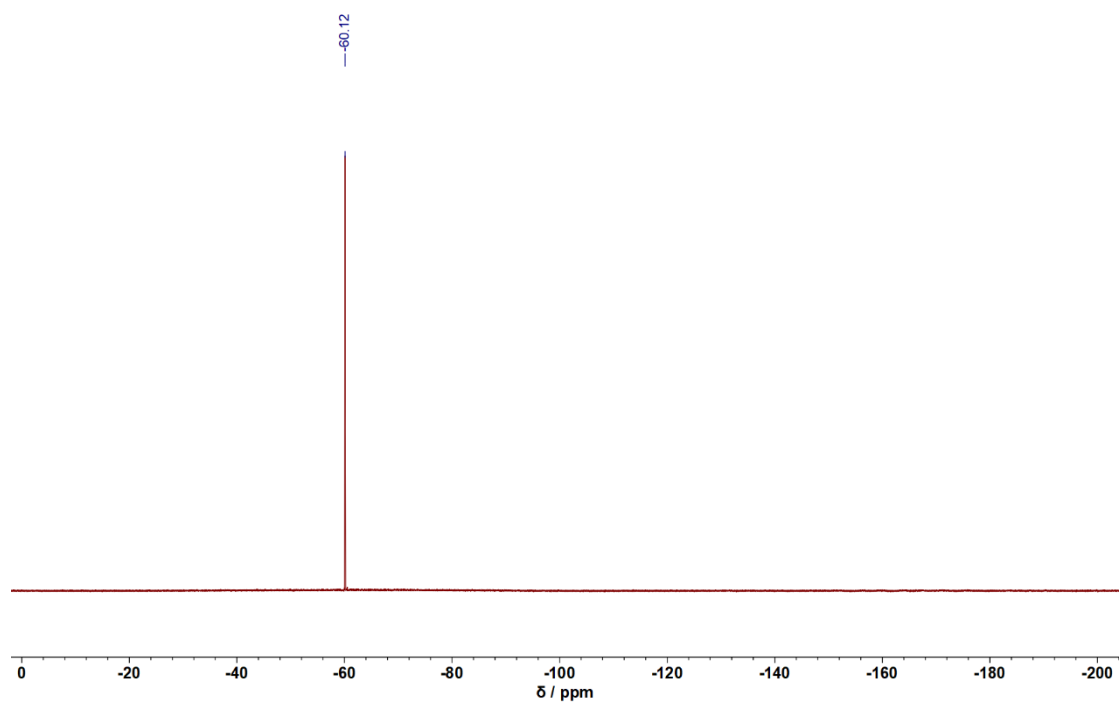
**Figure S10**  $^1\text{H}$  NMR spectrum of compound **4** at 353 K in  $\text{DMSO-}d_6$ .



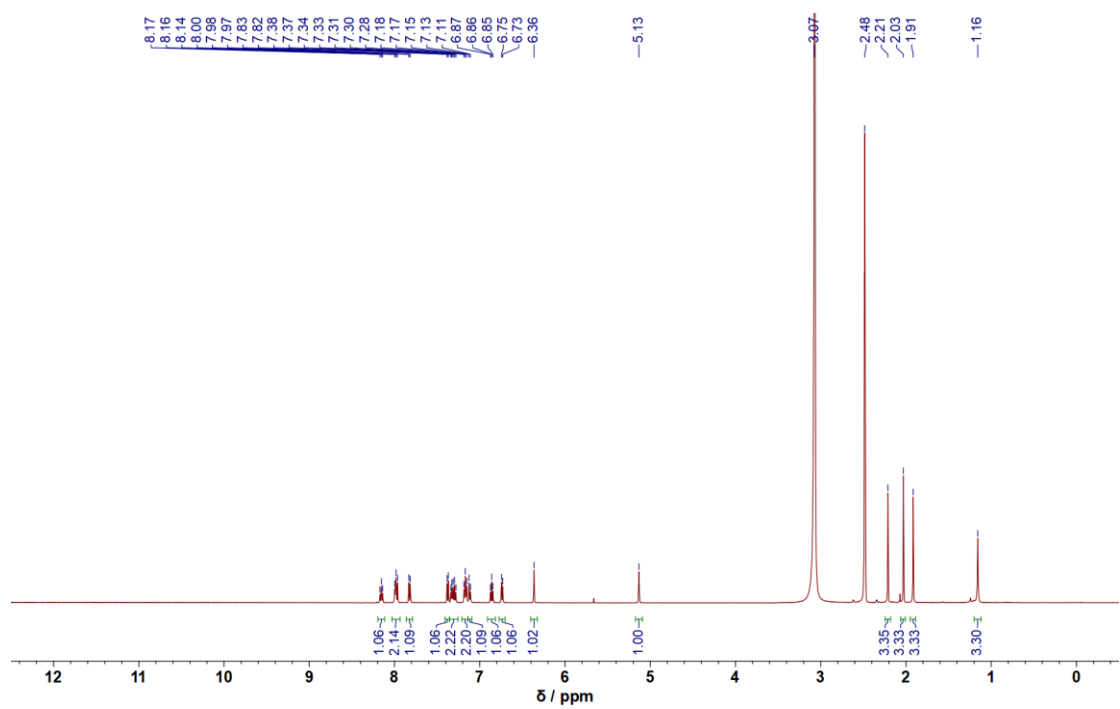
**Figure S11**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **4** at 353 K in  $\text{DMSO-}d_6$ .



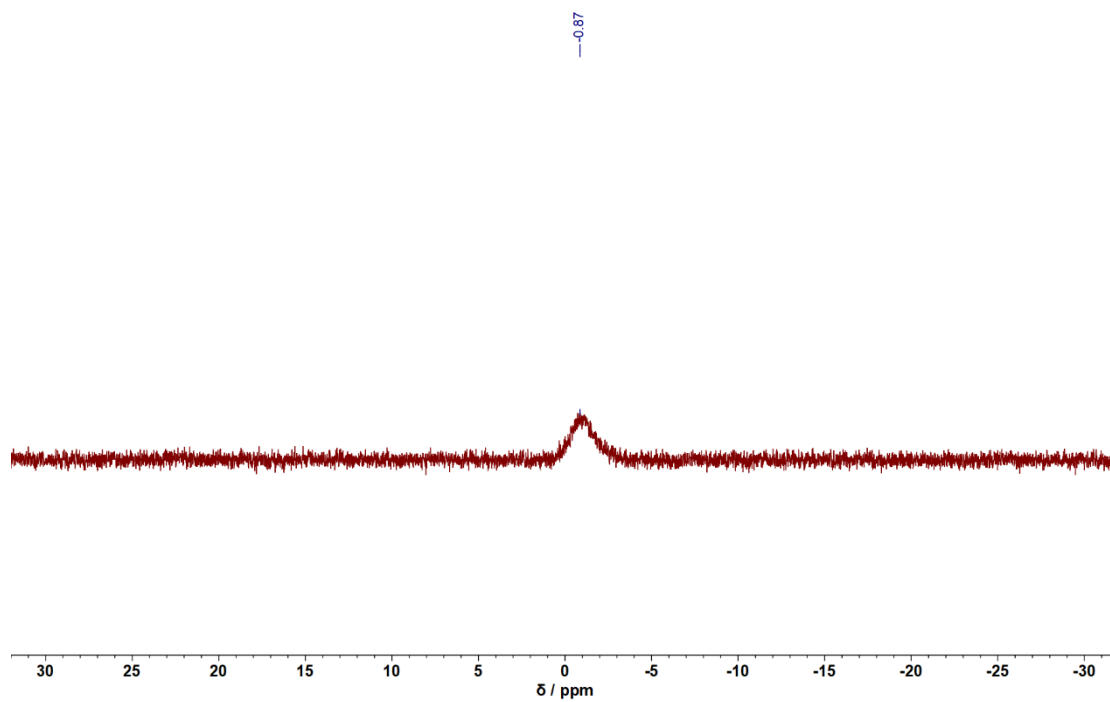
**Figure S12**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **4** at 298 K in  $\text{CDCl}_3$ .



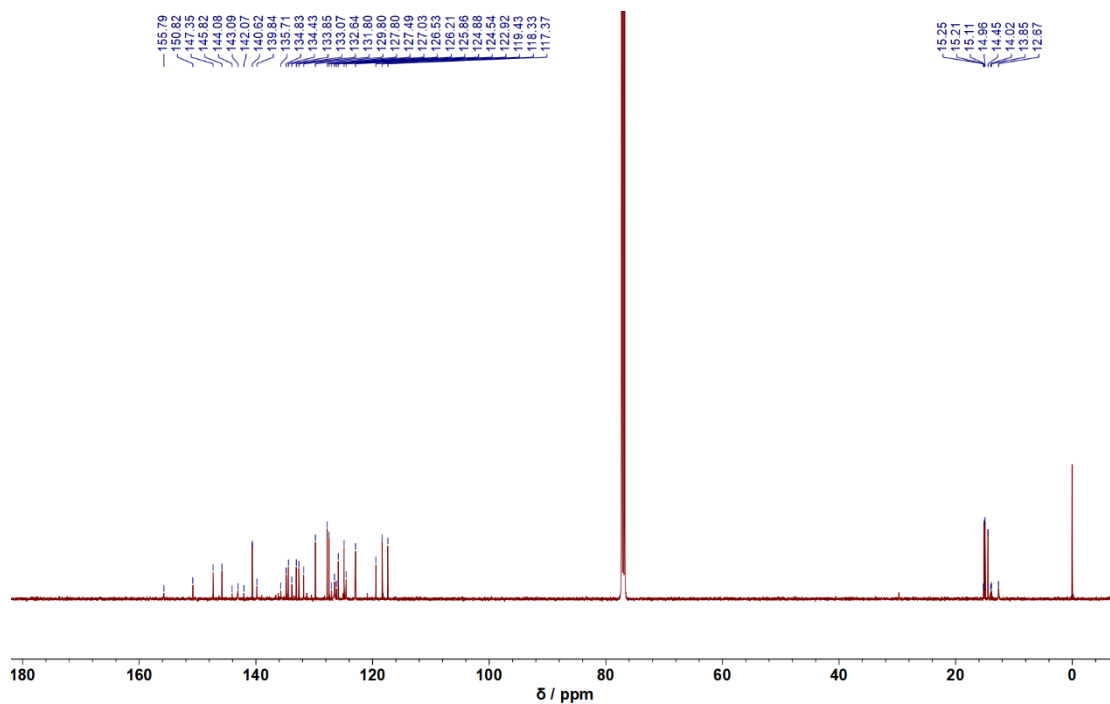
**Figure S13**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of compound **4** at 353 K in  $\text{DMSO-}d_6$ .



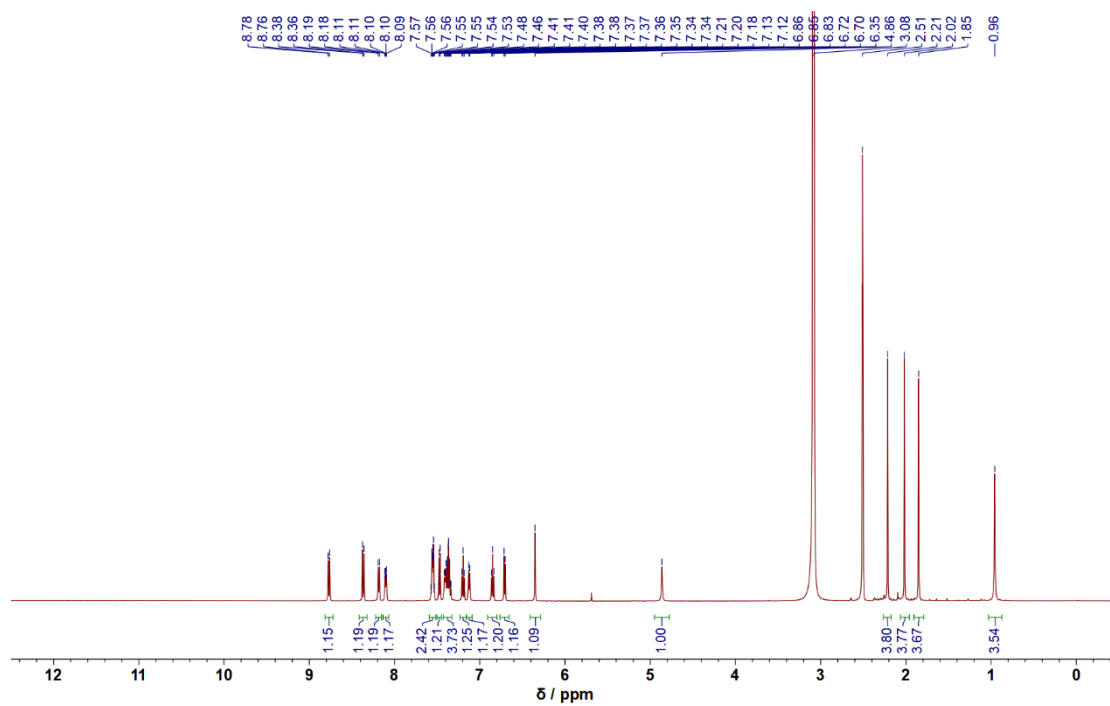
**Figure S14**  $^1\text{H}$  NMR spectrum of compound **5** at 353 K in  $\text{DMSO-}d_6$ .



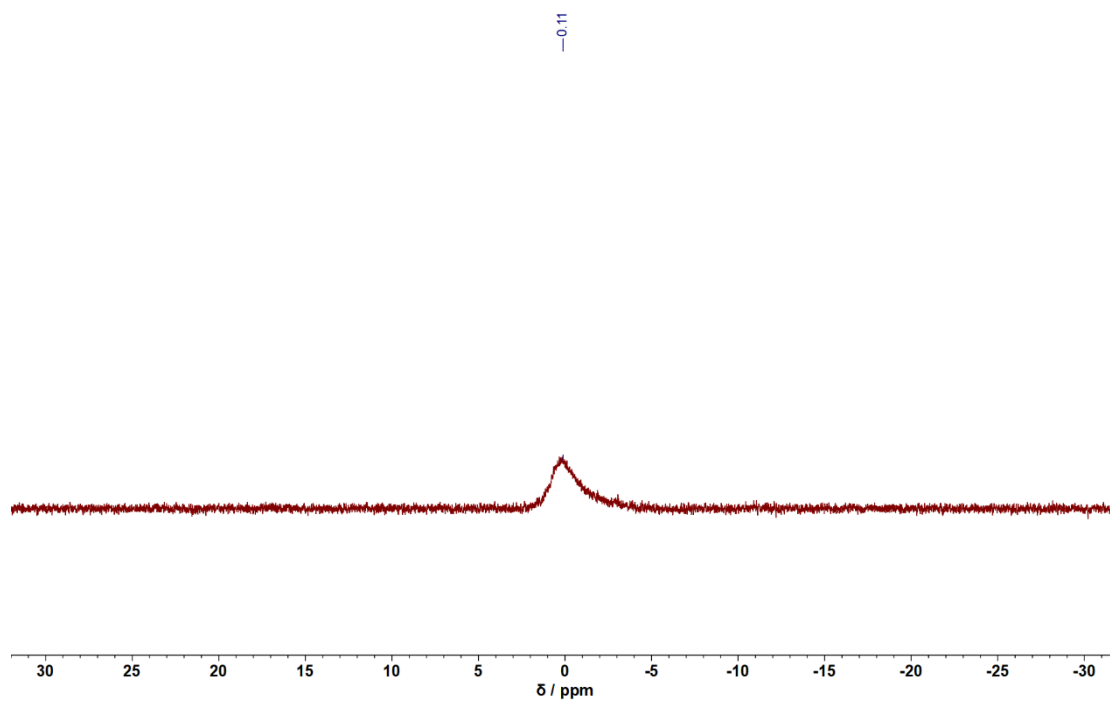
**Figure S15**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **5** at 353 K in  $\text{DMSO-}d_6$ .



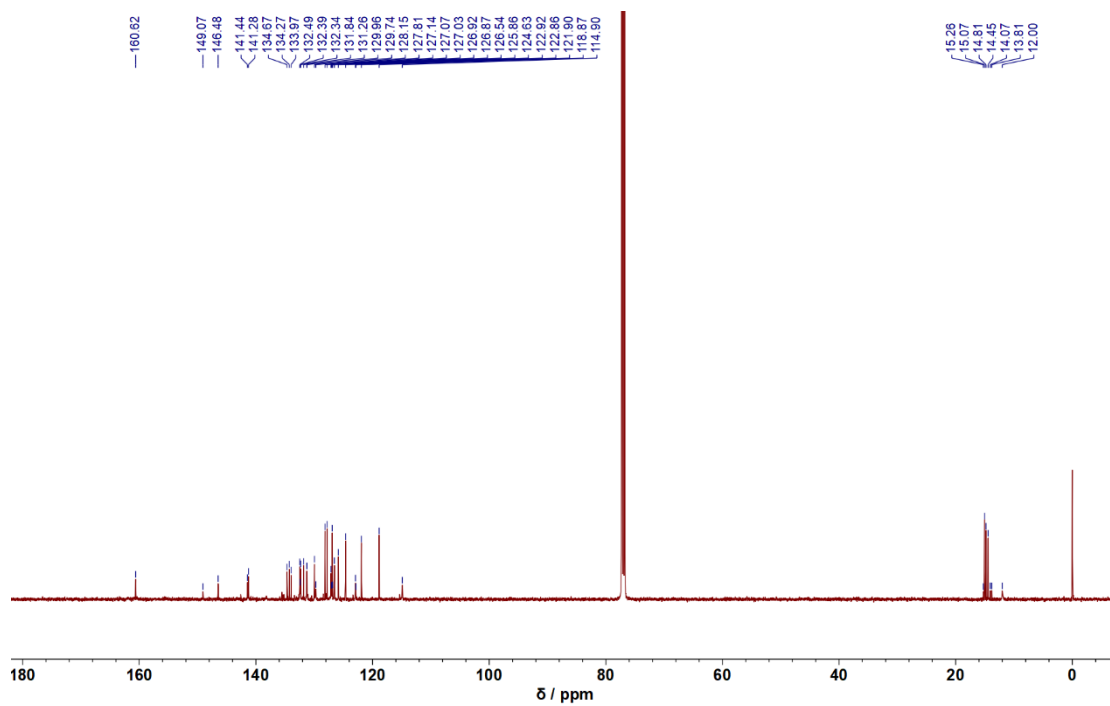
**Figure S16**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **5** at 298 K in  $\text{CDCl}_3$ .



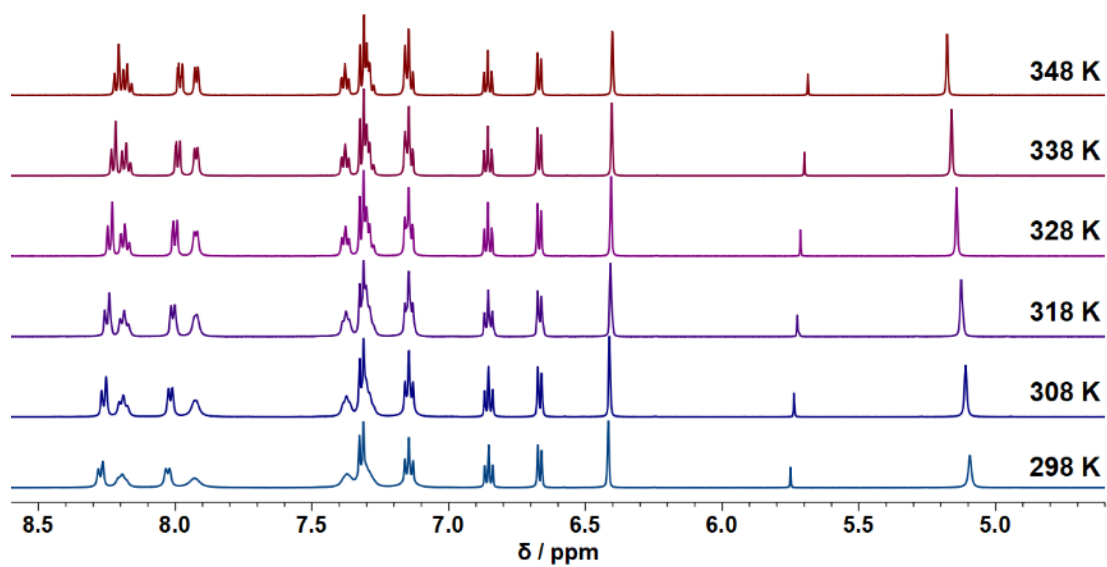
**Figure S17**  $^1\text{H}$  NMR spectrum of compound **6** at 353 K in  $\text{DMSO-}d_6$ .



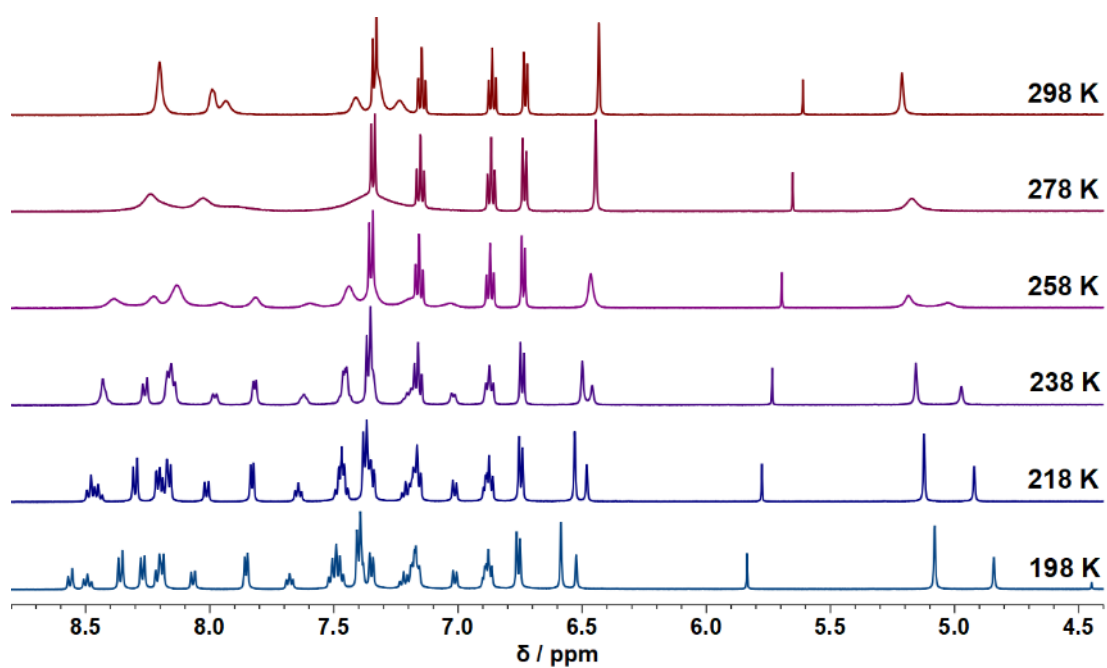
**Figure S18**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of compound **6** at 353 K in  $\text{DMSO-}d_6$ .



**Figure S19**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of compound **6** at 298 K in  $\text{CDCl}_3$ .



**Figure S20**  $^1\text{H}$  NMR spectra of compound **1** at various temperatures in  $\text{DMSO-}d_6$ .



**Figure S21**  $^1\text{H}$  NMR spectra of compound **1** at various temperatures in  $\text{acetone-}d_6$ .

## X-ray Crystallography

**Table S1** Crystal and structure determination data of **1** and **6**.

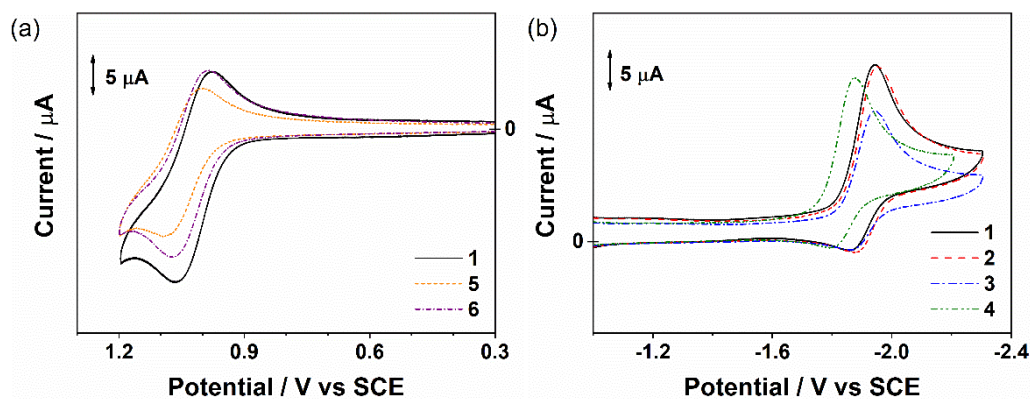
| Compound                                            | <b>1</b>                                                            | <b>6</b>                                                            |
|-----------------------------------------------------|---------------------------------------------------------------------|---------------------------------------------------------------------|
| Empirical formula                                   | C <sub>33</sub> H <sub>26</sub> BNS <sub>3</sub>                    | C <sub>37</sub> H <sub>28</sub> BNS <sub>3</sub>                    |
| Formula weight                                      | 543.54                                                              | 593.59                                                              |
| Temp, K                                             | 150                                                                 | 173                                                                 |
| Wavelength, Å                                       | 0.71073                                                             | 1.54178                                                             |
| Crystal system                                      | monoclinic                                                          | monoclinic                                                          |
| Space group                                         | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                  | <i>P</i> 2 <sub>1</sub> / <i>n</i>                                  |
| <i>a</i> , Å                                        | 12.534 (12)                                                         | 13.4218 (8)                                                         |
| <i>b</i> , Å                                        | 17.556 (18)                                                         | 13.8031 (8)                                                         |
| <i>c</i> , Å                                        | 12.832 (11)                                                         | 17.3437 (10)                                                        |
| $\alpha$ , deg                                      | 90                                                                  | 90                                                                  |
| $\beta$ , deg                                       | 102.25 (2)                                                          | 108.866 (4)                                                         |
| $\gamma$ , deg                                      | 90                                                                  | 90                                                                  |
| Volume, Å <sup>3</sup>                              | 2759 (5)                                                            | 3040.5 (3)                                                          |
| <i>Z</i>                                            | 4                                                                   | 4                                                                   |
| Density (calcd), g cm <sup>-3</sup>                 | 1.308                                                               | 1.297                                                               |
| Crystal size                                        | 0.25 mm × 0.10 mm<br>× 0.03 mm                                      | 0.21 mm × 0.14 mm<br>× 0.11 mm                                      |
| Index ranges                                        | -14 ≤ <i>h</i> ≤ 14,<br>-20 ≤ <i>k</i> ≤ 20,<br>-15 ≤ <i>l</i> ≤ 15 | -16 ≤ <i>h</i> ≤ 16,<br>-16 ≤ <i>k</i> ≤ 16,<br>-20 ≤ <i>l</i> ≤ 20 |
| Reflections collected                               | 26416                                                               | 33180                                                               |
| Independent reflections                             | 4904 [ <i>R</i> (int) = 0.082]                                      | 5547 [ <i>R</i> (int) = 0.123]                                      |
| GOF on <i>F</i> <sup>2</sup>                        | 1.06                                                                | 1.05                                                                |
| Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] | <i>R</i> <sub>1</sub> = 0.057,<br><i>wR</i> <sub>2</sub> = 0.115    | <i>R</i> <sub>1</sub> = 0.068,<br><i>wR</i> <sub>2</sub> = 0.193    |
| Largest diff. Peak and hole, e Å <sup>-3</sup>      | 0.31 and -0.37                                                      | 0.65 and -0.44                                                      |



**Table S2** Selected bond lengths and angles for **1** and **6** with estimated standard deviations (esds) given in parentheses.

| <b>Compound</b> | <b>Bond lengths / Å</b> |          | <b>Bond angles / deg</b> |          |
|-----------------|-------------------------|----------|--------------------------|----------|
| <b>1</b>        | B(1)—N(1)               | 1.611(6) | N(1)—B(1)—C(2)           | 111.3(3) |
|                 | B(1)—C(2)               | 1.607(5) | N(1)—B(1)—C(10)          | 114.9(3) |
|                 | B(1)—C(10)              | 1.617(4) | N(1)—B(1)—C(21)          | 96.8(2)  |
|                 | B(1)—C(21)              | 1.565(7) | C(2)—B(1)—C(10)          | 99.3(2)  |
|                 | N(1)—C(15)              | 1.364(5) | C(2)—B(1)—C(21)          | 117.2(4) |
|                 | C(15)—C(16)             | 1.451(4) | C(10)—B(1)—C(21)         | 118.2(3) |
|                 | C(16)—C(21)             | 1.368(6) |                          |          |
|                 | C(1)—C(2)               | 1.358(4) |                          |          |
|                 | C(1)—C(5)               | 1.454(4) |                          |          |
|                 | C(5)—C(10)              | 1.412(4) |                          |          |
| <b>6</b>        | B(1)—N(1)               | 1.601(5) | N(1)—B(1)—C(3)           | 110.2(3) |
|                 | B(1)—C(3)               | 1.616(5) | N(1)—B(1)—C(6)           | 115.7(3) |
|                 | B(1)—C(6)               | 1.631(6) | N(1)—B(1)—C(11)          | 97.0(3)  |
|                 | B(1)—C(11)              | 1.624(6) | C(3)—B(1)—C(6)           | 98.2(3)  |
|                 | N(1)—C(17)              | 1.329(5) | C(3)—B(1)—C(11)          | 117.1(3) |
|                 | C(16)—C(17)             | 1.493(6) | C(6)—B(1)—C(11)          | 119.5(3) |
|                 | C(11)—C(16)             | 1.376(6) |                          |          |
|                 | C(3)—C(4)               | 1.364(5) |                          |          |
|                 | C(4)—C(5)               | 1.470(5) |                          |          |
|                 | C(5)—C(6)               | 1.420(5) |                          |          |

## Electrochemical Studies



**Figure S22** Cyclic voltammograms for (a) the oxidative scans of compounds **1**, **5** and **6** and (b) reductive scans of **1–4** in tetrahydrofuran ( $0.1 \text{ mol dm}^{-3}$   ${}^n\text{Bu}_4\text{NPF}_6$ ). Scan rate:  $100 \text{ mV s}^{-1}$ .

**Table S3** Electrochemical data of **1–6**.<sup>a</sup>

| Compound | Oxidation <sup>b</sup>                                          | Reduction <sup>b</sup>                                          |
|----------|-----------------------------------------------------------------|-----------------------------------------------------------------|
|          | $E_{1/2}^c / \text{V vs SCE}$<br>( $\Delta E_p^d / \text{mV}$ ) | $E_{1/2}^c / \text{V vs SCE}$<br>( $\Delta E_p^d / \text{mV}$ ) |
| <b>1</b> | +1.02 (79)                                                      | -1.90 (82)                                                      |
| <b>2</b> | +0.95 (71)                                                      | -1.91 (67)                                                      |
| <b>3</b> | +0.84 (68)                                                      | -1.90 (77)                                                      |
| <b>4</b> | +1.16 (83)                                                      | -1.83 (81)                                                      |
| <b>5</b> | +1.05 (83)                                                      | -1.76 (77)                                                      |
| <b>6</b> | +1.03 (75)                                                      | -1.46 (69)                                                      |

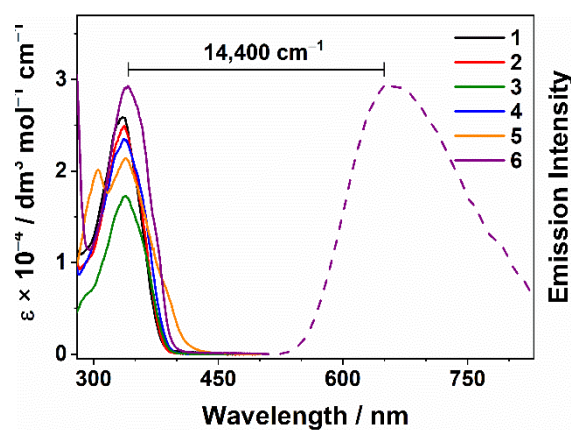
<sup>a</sup> In tetrahydrofuran with  $0.1 \text{ mol dm}^{-3}$   ${}^n\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte.

<sup>b</sup> Working electrode, glassy carbon; scan rate,  $100 \text{ mV s}^{-1}$ .

<sup>c</sup>  $E_{1/2} = (E_{pa} + E_{pc})/2$ ;  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials, respectively.

<sup>d</sup>  $\Delta E_p = |E_{pa} - E_{pc}|$ .

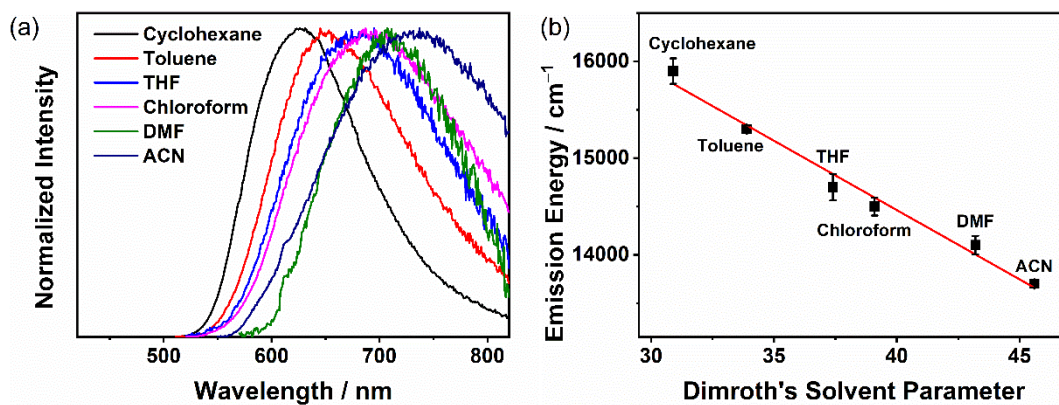
## Photophysical Studies



**Figure S23** Electronic absorption spectra (solid line) of **1–6** in their open form and emission spectra of **6** (dashed line) in degassed benzene solution at 298 K.

**Table S4** Electronic absorption data of **1–6** in degassed benzene at 298 K.

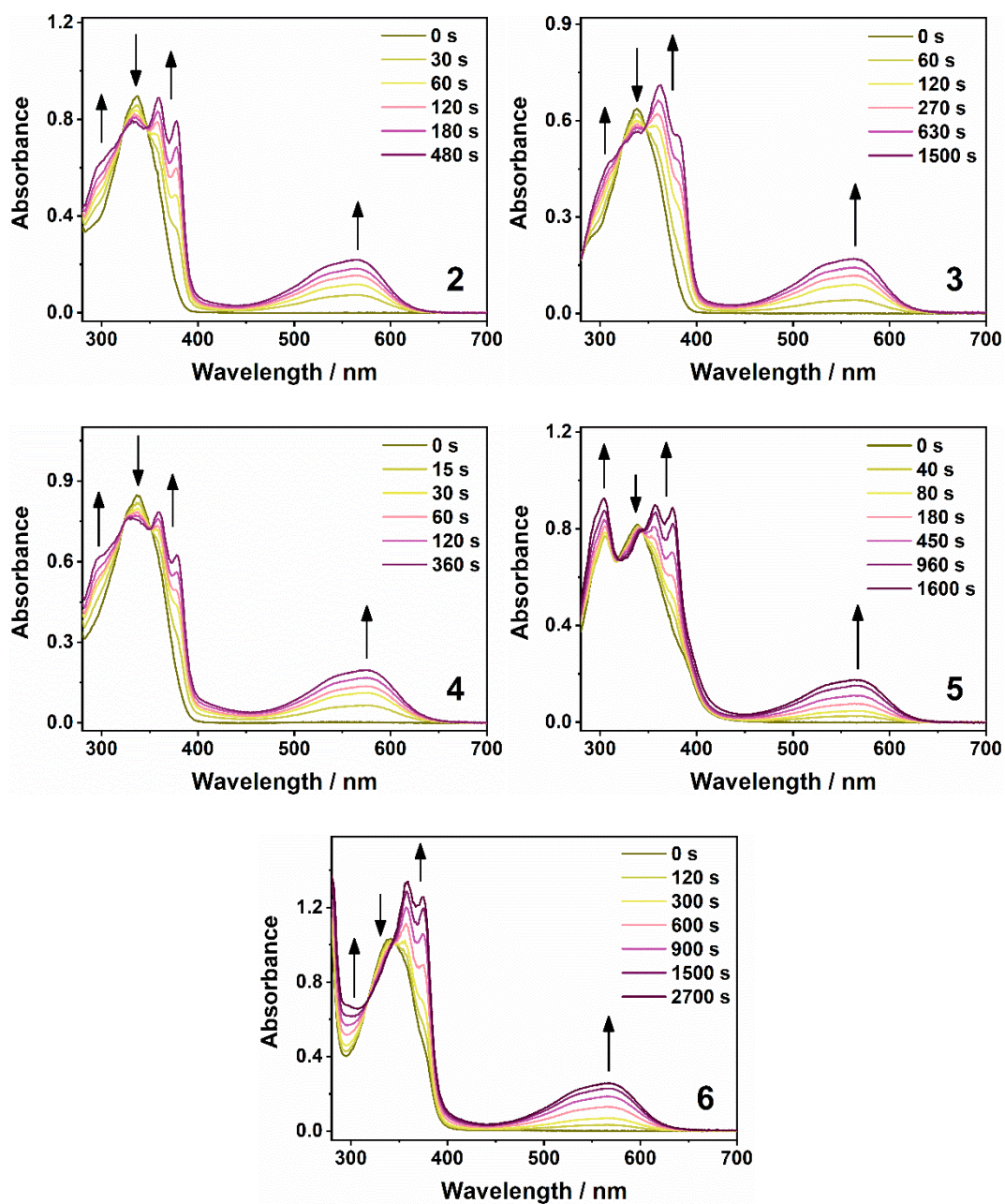
| Compound | Configuration | Absorption                         |                                                           |
|----------|---------------|------------------------------------|-----------------------------------------------------------|
|          |               | $\lambda_{\text{abs}} / \text{nm}$ | $(\epsilon / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$ |
| <b>1</b> | open          | 335                                | (25900)                                                   |
|          | closed        | 332, 357, 375, 566                 | (23800), (25100), (23100), (6980)                         |
| <b>2</b> | open          | 337                                | (24900)                                                   |
|          | closed        | 332, 359, 378, 566                 | (21500), (26100), (24500), (6910)                         |
| <b>3</b> | open          | 339                                | (17257)                                                   |
|          | closed        | 363, 382, 563                      | (22600), (20000), (6450)                                  |
| <b>4</b> | open          | 337                                | (23500)                                                   |
|          | closed        | 329, 360, 379, 577                 | (19800), (21500), (18600), (6130)                         |
| <b>5</b> | open          | 306, 339                           | (20100), (21400)                                          |
|          | closed        | 304, 358, 375, 564                 | (25000), (24700), (25500), (5420)                         |
| <b>6</b> | open          | 341                                | (29300)                                                   |
|          | closed        | 359, 374, 568                      | (38900), (37000), (7580)                                  |



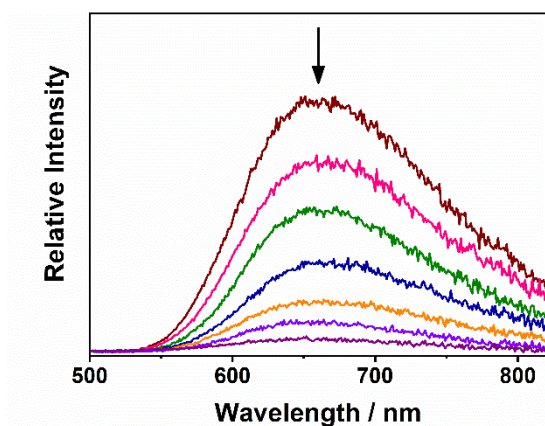
**Figure S24** (a) Normalized emission spectra of complex **6** in various solvents at 298 K.  
(b) A plot of emission energy of the open form of **6** in different solvents versus the Dimroth's solvent parameter and its linear least-squares fit.

## Photochromic Studies

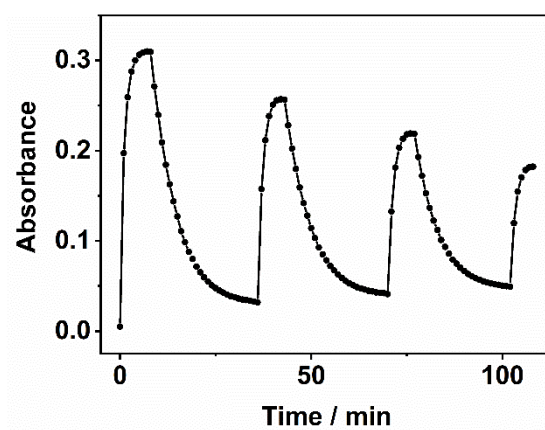
Regarding the absorption profile of the closed forms, neither the variation in substituent on the C<sup>^</sup>C ligand nor the nature of the N<sup>^</sup>C ligand imposes significant differences in the lowest-energy absorption maxima, which is probably due to its predominant  $\Pi$  [ $\pi \rightarrow \pi^*$ ] (C<sup>^</sup>C) character localized on the ring-closed moiety. In addition, for compound **6**, luminescence quenching is also observed during the photocyclization owing to the gradual conversion of an emissive open form to a non-emissive closed form (Figure S26). Upon photoexcitation at *ca.* 565 nm, the photochromic changes are reversed, suggestive of the occurrence of photocycloreversion to regenerate the open forms.



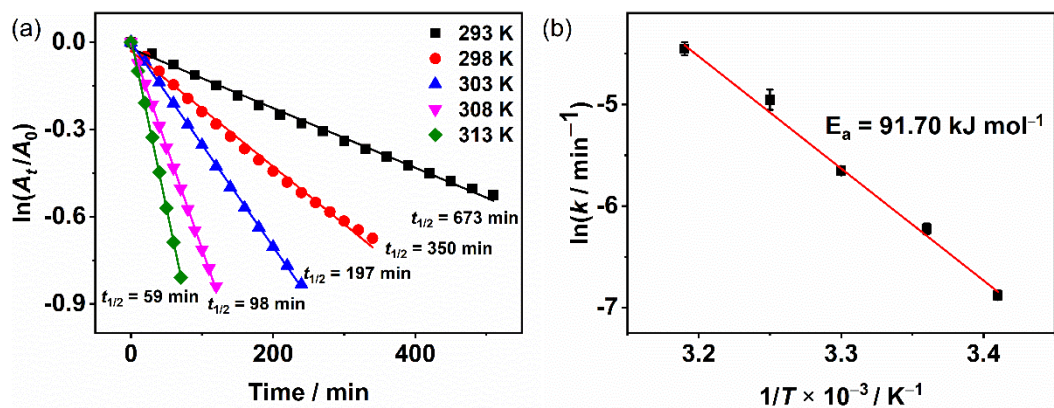
**Figure S25** UV-Visible absorption spectral changes of **2–5** in degassed benzene solution upon photoexcitation at 335 nm at 298 K.



**Figure S26** Emission spectral changes of **6** in degassed benzene solution upon photoexcitation at 335 nm at 298 K.



**Figure S27** Absorbance changes of **1** at 565 nm upon alternate excitation at 335 and 565 nm over three cycles in degassed benzene solution at 298 K.



**Figure S28** (a) Plot of  $\ln(A_t/A_0)$  versus time for the absorbance decay of **1** at 565 nm in nitrogen-flushed toluene solution at various temperatures. (b) Arrhenius plot for the thermal backward reaction of **1** in closed form in nitrogen-flushed toluene solution and its linear least-squares fit.



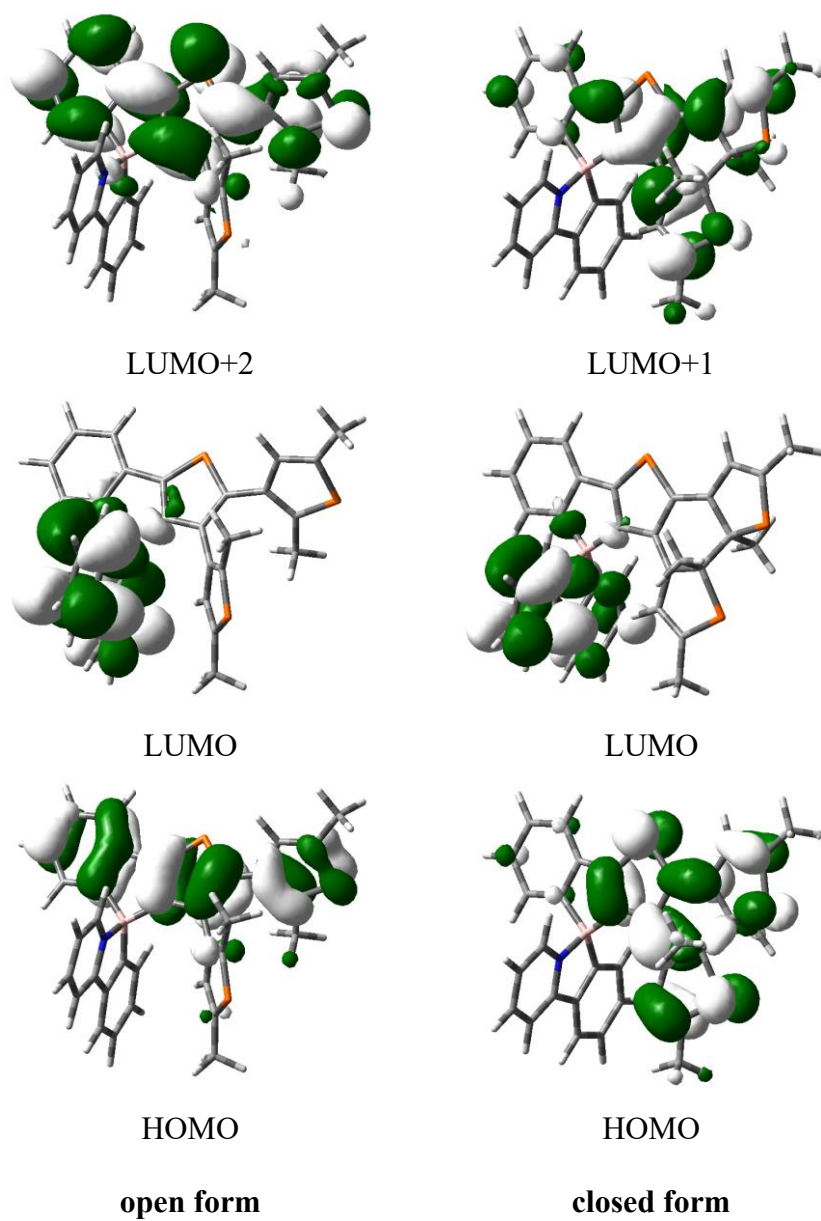
## Computational Details

All calculations were carried out with the Gaussian 16 suite of program.<sup>10</sup> Geometrical optimizations of compounds **1** and **6** were calculated in the framework of density functional theory (DFT) at hybrid Perdew, Burke, and Ernzerhof (PBE0)<sup>11–13</sup> level of theory. Pople 6-311+G(3df) basis set was used to describe S atoms, while Pople 6-311++G(d,p) basis set is employed to describe all other atoms. All geometries were optimized in an implicit solvent environment (benzene) described by the conductor-like polarizable continuum model (CPCM).<sup>14,15</sup> Time-dependent density functional theory<sup>16–18</sup> (TDDFT) calculations at the same level associated with CPCM were carried out on the optimized S<sub>0</sub> geometries of the complexes in benzene to compute the singlet-singlet transitions in the electronic absorption spectra of **1** and **6** (Table S5 & Figure S31). Harmonic frequency analyses were performed for all optimized geometries to evaluate the thermal corrections to enthalpies at 298 K, no imaginary frequencies observed (NIMAG = 0), verifying all stationary points to be minima on the potential energy surface. In order to gain further insights into the excited states involved in photocycloreversion, the geometries the lowest (S<sub>1</sub>) and second lowest singlet (S<sub>2</sub>) excited state of the closed form of **1** and **6** were optimized using TDDFT at the same level associated with CPCM. All DFT and TDDFT calculations were performed with a pruned (175,974) grid for numerical integration. The Cartesian coordinates of the optimized geometries of the compounds are given in Tables S6–S13).

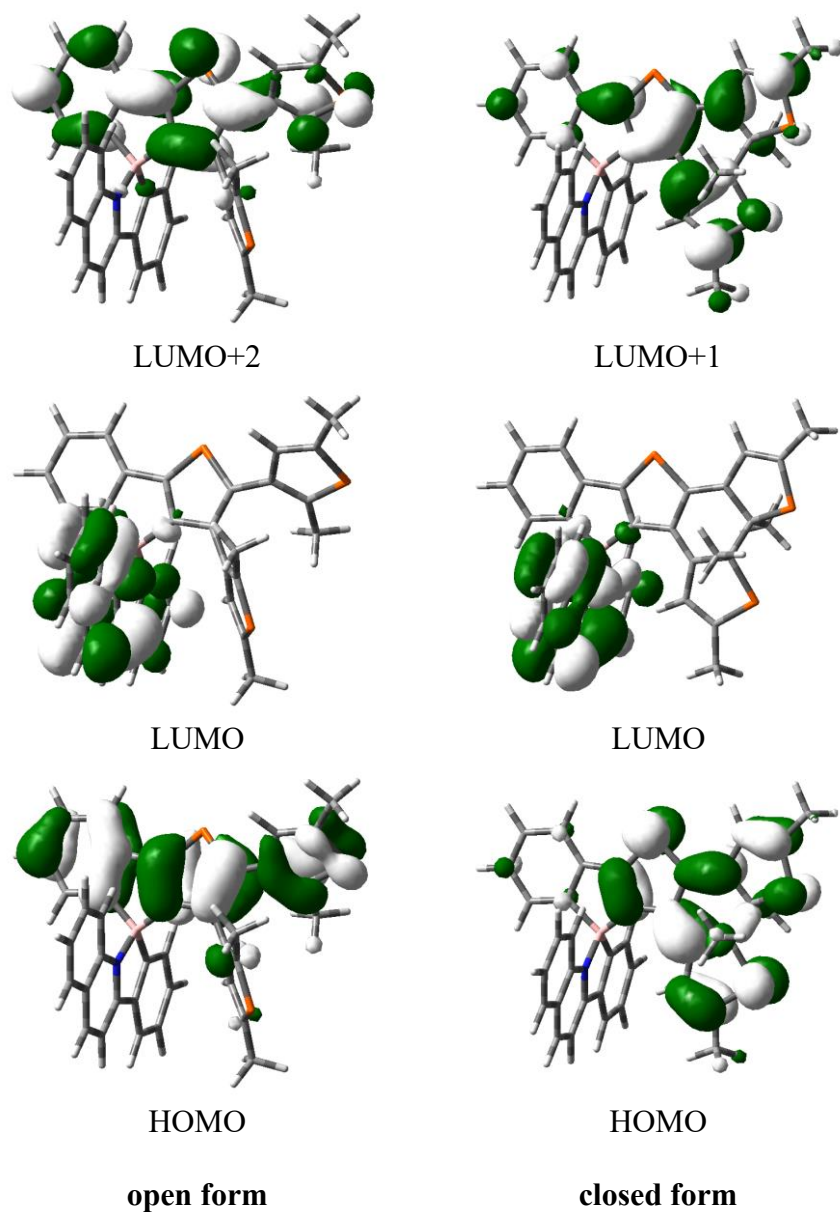
In order to gain deeper insights and a better understanding of the electronic structures and the origins of electronic transitions of the open and closed forms of the photochromic compounds, density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations have been carried out for compounds **1** and **6**.

The HOMOs of the open forms of **1** and **6** are found to localize on the  $\pi$  orbital of the C<sup>^</sup>C ligand, while the LUMOs and LUMO+2s correspond to the  $\pi^*$  orbitals of the N<sup>^</sup>C and C<sup>^</sup>C ligands, respectively (Figure S29 & S30). For the closed forms, the HOMOs of **1** and **6** are the  $\pi$  orbitals of the dithienylethene moiety, whereas the LUMO+1s are the  $\pi^*$  orbitals of the dithienylethene-containing C<sup>^</sup>C ligand (Figure S29 & S30). From the results of TDDFT calculations (Table S5 & Figure S31), the low-lying absorption band of **1** and **6** are dominated by the  $S_0 \rightarrow S_4$  transitions in the open forms and the  $S_0 \rightarrow S_2$  transitions in the closed forms respectively. The  $S_0 \rightarrow S_4$  transition corresponds to the HOMO  $\rightarrow$  LUMO+2 excitation in the open forms of **1** and **6**, whereas the  $S_0 \rightarrow S_2$  is dominated by the HOMO  $\rightarrow$  LUMO+1 excitation in their closed forms. Therefore, the low-lying absorption band in the open form of **1** and **6** is attributed to intraligand (IL) [ $\pi \rightarrow \pi^*$ ] transition of the C<sup>^</sup>C ligand, and that of the closed forms can be assigned as the IL [ $\pi \rightarrow \pi^*$ ] transition of the dithienylethene moiety of the C<sup>^</sup>C ligand, without any significant charge transfer character. Besides, the  $S_0 \rightarrow S_1$  transitions of **1** and **6** correspond to the HOMO  $\rightarrow$  LUMO transitions, which are from the  $\pi$  orbital localized on the C<sup>^</sup>C ligand to the  $\pi^*$  orbital localized on the N<sup>^</sup>C ligand. This is in good agreement with the emission observed in **6** that is originated from the LLCT [ $\pi(\text{C}^{\wedge}\text{C}) \rightarrow \pi^*(\text{N}^{\wedge}\text{C})$ ] excited state.

The HOMO energies of the open forms of **1** and **6** are almost the same (-5.40 eV), while the LUMO energy of **1** (-2.02 eV) is higher than that of **6** (-2.48 eV), in line with the trend observed in the electrochemical and photophysical measurements. The energies of frontier orbitals of the open and closed forms of **1** and **6** are summarized in Figure S32.



**Figure S29** Spatial plots (isovalue = 0.03) of selected molecular orbitals of compound **1** at the optimized ground-state geometry.



**Figure S30** Spatial plots (isovalue = 0.03) of selected molecular orbitals of compound **6** at the optimized ground-state geometry.

**Table S5** The first ten singlet excited states ( $S_n$ ) of **1** and **6** computed by TDDFT/CPCM using benzene as the solvent.

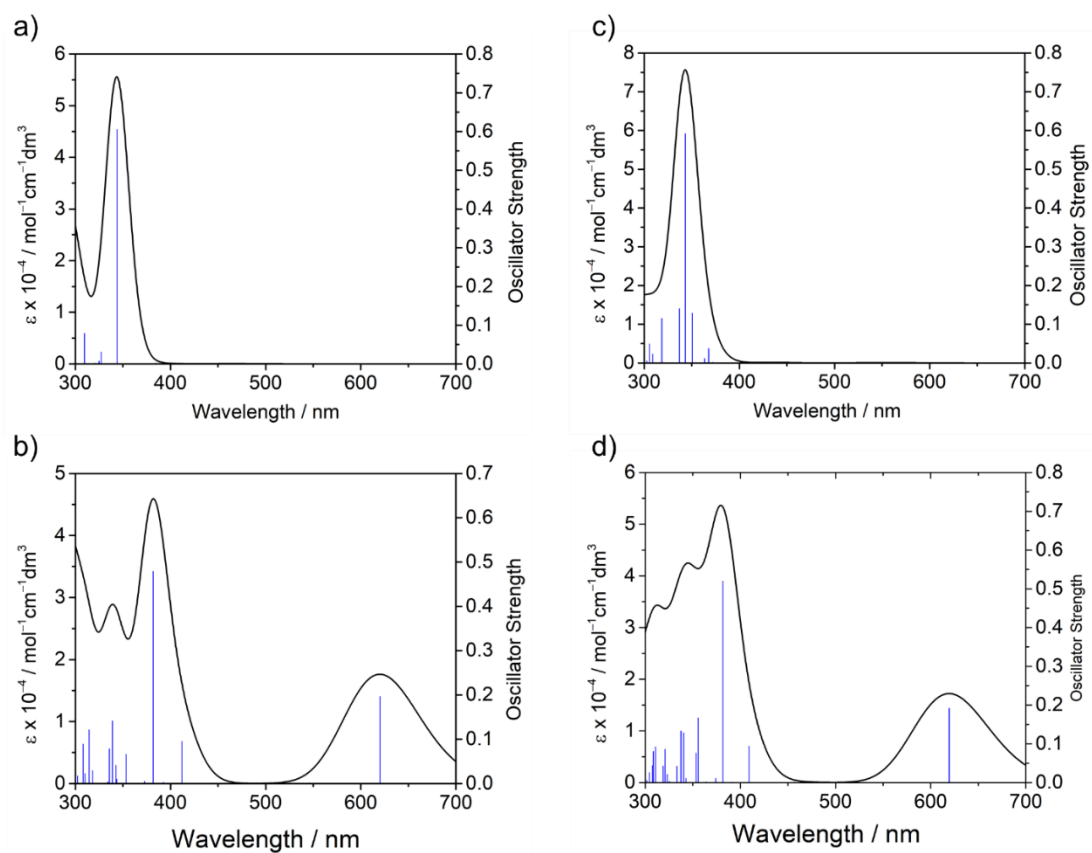
| Compound | Configuration | $S_n$    | Excitation <sup>a</sup><br>(Coefficient) <sup>b</sup> | Vertical excitation<br>wavelength / nm | $f^c$ |
|----------|---------------|----------|-------------------------------------------------------|----------------------------------------|-------|
| <b>1</b> | open          | $S_1$    | H→L (0.70)                                            | 464                                    | 0.001 |
|          |               | $S_2$    | H→L+1 (0.70)                                          | 385                                    | 0.002 |
|          |               | $S_3$    | H-1→L (0.70)                                          | 378                                    | 0.000 |
|          |               | $S_4$    | H→L+2 (0.70)                                          | 344                                    | 0.605 |
|          |               | $S_5$    | H-3→L (0.65)                                          | 327                                    | 0.030 |
|          |               | $S_6$    | H-1→L+1 (0.66)                                        | 325                                    | 0.007 |
|          |               | $S_7$    | H-2→L (0.69)                                          | 321                                    | 0.002 |
|          |               | $S_8$    | H-4→L (0.68)                                          | 310                                    | 0.078 |
|          |               | $S_9$    | H-1→L+2 (0.36)                                        | 299                                    | 0.002 |
|          |               | $S_{10}$ | H→L+3 (0.51)<br>H-5→L (0.59)                          | 298                                    | 0.088 |
|          | closed        | $S_1$    | H→L (0.70)                                            | 718                                    | 0.000 |
|          |               | $S_2$    | H→L+1 (0.71)                                          | 620                                    | 0.196 |
|          |               | $S_3$    | H→L+2 (0.70)                                          | 546                                    | 0.001 |
|          |               | $S_4$    | H→L+3 (0.69)                                          | 412                                    | 0.095 |
|          |               | $S_5$    | H-1→L (0.69)                                          | 393                                    | 0.003 |
|          |               | $S_6$    | H-1→L+1 (0.67)                                        | 382                                    | 0.479 |
|          |               | $S_7$    | H→L+7 (0.56)<br>H→L+4 (-0.32)                         | 373                                    | 0.004 |
|          |               | $S_8$    | H→L+4 (0.62)                                          | 353                                    | 0.066 |
|          |               | $S_9$    | H-2→L (0.57)<br>H-2→L+1 (0.32)                        | 343                                    | 0.010 |
|          |               | $S_{10}$ | H-2→L+1 (0.43)<br>H-2→L (-0.40)                       | 343                                    | 0.041 |
| <b>6</b> | open          | $S_1$    | H→L (0.70)                                            | 553                                    | 0.001 |
|          |               | $S_2$    | H-1→L (0.70)                                          | 437                                    | 0.001 |
|          |               | $S_3$    | H→L+1 (0.70)                                          | 372                                    | 0.002 |
|          |               | $S_4$    | H-3→L (0.66)                                          | 368                                    | 0.036 |
|          |               | $S_5$    | H-2→L (0.65)                                          | 364                                    | 0.011 |
|          |               | $S_6$    | H-4→L (0.67)                                          | 351                                    | 0.128 |
|          |               | $S_7$    | H→L+2 (0.68)                                          | 343                                    | 0.591 |
|          |               | $S_8$    | H-5→L (0.67)                                          | 337                                    | 0.140 |
|          |               | $S_9$    | H-7→L (0.57)<br>H-6→L (0.38)                          | 319                                    | 0.115 |
|          |               | $S_{10}$ | H-1→L+1 (0.70)                                        | 317                                    | 0.001 |
|          | closed        | $S_1$    | H→L (0.71)                                            | 961                                    | 0.001 |
|          |               | $S_2$    | H→L+1 (0.71)                                          | 619                                    | 0.192 |
|          |               | $S_3$    | H→L+2 (0.71)                                          | 522                                    | 0.000 |
|          |               | $S_4$    | H-1→L (0.70)                                          | 456                                    | 0.001 |
|          |               | $S_5$    | H→L+3 (0.68)                                          | 409                                    | 0.094 |
|          |               | $S_6$    | H-2→L (0.70)                                          | 391                                    | 0.001 |

|                 |                |     |       |
|-----------------|----------------|-----|-------|
| S <sub>7</sub>  | H-1→L+1 (0.67) | 382 | 0.520 |
| S <sub>8</sub>  | H→L+8 (0.48)   | 374 | 0.011 |
|                 | H→L+4 (-0.42)  |     |       |
| S <sub>9</sub>  | H→L+4 (0.56)   | 364 | 0.002 |
|                 | H→L+8 (0.36)   |     |       |
| S <sub>10</sub> | H-3→L (0.68)   | 356 | 0.166 |

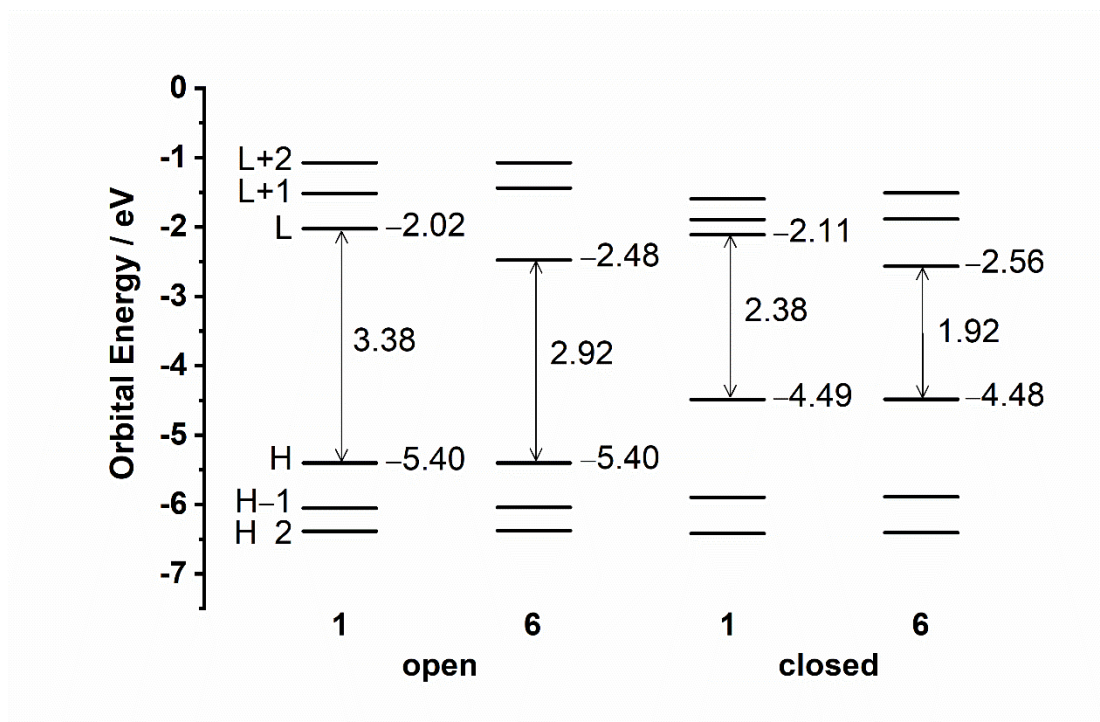
<sup>a</sup> Orbitals involved in the major excitation (H = HOMO and L = LUMO).

<sup>b</sup> The coefficients in the configuration interaction (CI) expansion that are less than or equal to 0.3 are not listed.

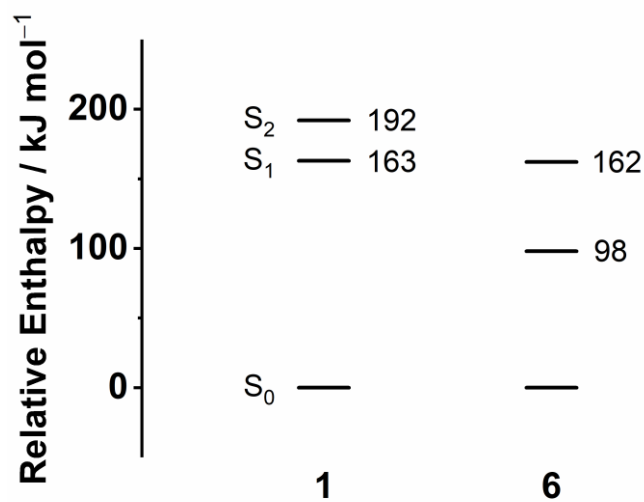
<sup>c</sup> Oscillator strengths.



**Figure S31** Simulated UV-vis spectra of **1** in (a) open and (b) closed form and **6** in (c) open and (d) closed form computed by TDDFT/CPCM in benzene.



**Figure S32** Orbital energy diagram of **1** and **6**.



**Figure S33** Enthalpies of  $S_1$  and  $S_2$  excited states relative to the ground state energy of compound **1** and **6** respectively.

**Table S6** Cartesian coordinates of compound **1** (open form) in benzene at the optimized ground-state geometry.

|   |          |          |          |   |          |          |          |
|---|----------|----------|----------|---|----------|----------|----------|
| S | 1.398661 | 2.779353 | -0.32999 | C | -3.54512 | -1.21013 | -3.20584 |
| S | 5.60079  | -0.16016 | -0.86987 | H | -3.61037 | -1.17779 | -4.2894  |
| S | 1.380393 | -3.52408 | 0.925065 | C | -2.84243 | -0.21936 | -2.52563 |
| N | -2.44432 | -0.08078 | 1.245369 | H | -2.36434 | 0.580635 | -3.08421 |
| C | -0.25433 | 2.353795 | -0.25027 | C | -2.75118 | -0.25523 | -1.13655 |
| C | -0.44788 | 0.992608 | -0.16917 | C | 1.583191 | -1.81627 | 1.035443 |
| C | 0.787577 | 0.276954 | -0.13645 | C | 0.864301 | -1.18372 | 0.048499 |
| C | 1.888663 | 1.117648 | -0.23017 | C | 0.14672  | -2.10996 | -0.77455 |
| C | -1.48103 | 3.141334 | -0.19448 | H | -0.48039 | -1.80077 | -1.60298 |
| C | -1.65961 | 4.519784 | -0.24454 | C | 0.325816 | -3.41753 | -0.43375 |
| H | -0.81105 | 5.1897   | -0.35213 | C | 2.431379 | -1.22953 | 2.113419 |
| C | -2.95329 | 5.033289 | -0.15392 | H | 2.343428 | -1.79714 | 3.044075 |
| H | -3.10899 | 6.107242 | -0.18909 | H | 2.126327 | -0.19843 | 2.307451 |
| C | -4.04369 | 4.179777 | -0.02207 | H | 3.489451 | -1.20691 | 1.830897 |
| H | -5.04579 | 4.59245  | 0.046338 | C | -0.25164 | -4.63318 | -1.07879 |
| C | -3.85354 | 2.793775 | 0.01645  | H | 0.524843 | -5.28118 | -1.49768 |
| H | -4.71875 | 2.140646 | 0.107895 | H | -0.91672 | -4.33457 | -1.8924  |
| C | -2.57738 | 2.25686  | -0.06326 | H | -0.8326  | -5.2335  | -0.3714  |
| C | -2.11437 | 0.246853 | 2.497027 | C | 3.89757  | -0.12136 | -1.11133 |
| H | -1.51671 | 1.144368 | 2.609958 | C | 3.319019 | 0.813955 | -0.28256 |
| C | -2.51918 | -0.52573 | 3.566449 | C | 4.289462 | 1.498296 | 0.520526 |
| H | -2.2406  | -0.24182 | 4.57329  | H | 4.02576  | 2.268504 | 1.237629 |
| C | -3.28304 | -1.66582 | 3.315315 | C | 5.572178 | 1.082599 | 0.322498 |
| H | -3.61183 | -2.29161 | 4.138132 | C | 3.261167 | -1.00225 | -2.13169 |
| C | -3.62003 | -1.99937 | 2.015082 | H | 3.923193 | -1.16055 | -2.98723 |
| H | -4.21069 | -2.88092 | 1.798095 | H | 2.335537 | -0.54584 | -2.49079 |
| C | -3.18451 | -1.18116 | 0.975347 | H | 3.000744 | -1.98204 | -1.71754 |
| C | -3.39297 | -1.30737 | -0.46078 | C | 6.818627 | 1.559111 | 0.990284 |
| C | -4.10256 | -2.30519 | -1.12877 | H | 6.574002 | 2.348453 | 1.704597 |
| H | -4.592   | -3.11041 | -0.58881 | H | 7.535175 | 1.966417 | 0.270259 |
| C | -4.17257 | -2.24936 | -2.51348 | H | 7.321879 | 0.754722 | 1.535644 |
| H | -4.71766 | -3.01181 | -3.06019 | B | -2.04022 | 0.720207 | -0.08224 |



**Table S7** Cartesian coordinates of compound **1** (closed form) in benzene at the optimized ground-state geometry.

|   |          |          |          |   |          |          |          |
|---|----------|----------|----------|---|----------|----------|----------|
| S | 1.398661 | 2.779353 | -0.32999 | C | -3.54512 | -1.21013 | -3.20584 |
| S | 5.60079  | -0.16016 | -0.86987 | H | -3.61037 | -1.17779 | -4.2894  |
| S | 1.380393 | -3.52408 | 0.925065 | C | -2.84243 | -0.21936 | -2.52563 |
| N | -2.44432 | -0.08078 | 1.245369 | H | -2.36434 | 0.580635 | -3.08421 |
| C | -0.25433 | 2.353795 | -0.25027 | C | -2.75118 | -0.25523 | -1.13655 |
| C | -0.44788 | 0.992608 | -0.16917 | C | 1.583191 | -1.81627 | 1.035443 |
| C | 0.787577 | 0.276954 | -0.13645 | C | 0.864301 | -1.18372 | 0.048499 |
| C | 1.888663 | 1.117648 | -0.23017 | C | 0.14672  | -2.10996 | -0.77455 |
| C | -1.48103 | 3.141334 | -0.19448 | H | -0.48039 | -1.80077 | -1.60298 |
| C | -1.65961 | 4.519784 | -0.24454 | C | 0.325816 | -3.41753 | -0.43375 |
| H | -0.81105 | 5.1897   | -0.35213 | C | 2.431379 | -1.22953 | 2.113419 |
| C | -2.95329 | 5.033289 | -0.15392 | H | 2.343428 | -1.79714 | 3.044075 |
| H | -3.10899 | 6.107242 | -0.18909 | H | 2.126327 | -0.19843 | 2.307451 |
| C | -4.04369 | 4.179777 | -0.02207 | H | 3.489451 | -1.20691 | 1.830897 |
| H | -5.04579 | 4.59245  | 0.046338 | C | -0.25164 | -4.63318 | -1.07879 |
| C | -3.85354 | 2.793775 | 0.01645  | H | 0.524843 | -5.28118 | -1.49768 |
| H | -4.71875 | 2.140646 | 0.107895 | H | -0.91672 | -4.33457 | -1.8924  |
| C | -2.57738 | 2.25686  | -0.06326 | H | -0.8326  | -5.2335  | -0.3714  |
| C | -2.11437 | 0.246853 | 2.497027 | C | 3.89757  | -0.12136 | -1.11133 |
| H | -1.51671 | 1.144368 | 2.609958 | C | 3.319019 | 0.813955 | -0.28256 |
| C | -2.51918 | -0.52573 | 3.566449 | C | 4.289462 | 1.498296 | 0.520526 |
| H | -2.2406  | -0.24182 | 4.57329  | H | 4.02576  | 2.268504 | 1.237629 |
| C | -3.28304 | -1.66582 | 3.315315 | C | 5.572178 | 1.082599 | 0.322498 |
| H | -3.61183 | -2.29161 | 4.138132 | C | 3.261167 | -1.00225 | -2.13169 |
| C | -3.62003 | -1.99937 | 2.015082 | H | 3.923193 | -1.16055 | -2.98723 |
| H | -4.21069 | -2.88092 | 1.798095 | H | 2.335537 | -0.54584 | -2.49079 |
| C | -3.18451 | -1.18116 | 0.975347 | H | 3.000744 | -1.98204 | -1.71754 |
| C | -3.39297 | -1.30737 | -0.46078 | C | 6.818627 | 1.559111 | 0.990284 |
| C | -4.10256 | -2.30519 | -1.12877 | H | 6.574002 | 2.348453 | 1.704597 |
| H | -4.592   | -3.11041 | -0.58881 | H | 7.535175 | 1.966417 | 0.270259 |
| C | -4.17257 | -2.24936 | -2.51348 | H | 7.321879 | 0.754722 | 1.535644 |
| H | -4.71766 | -3.01181 | -3.06019 | B | -2.04022 | 0.720207 | -0.08224 |

**Table S8** Cartesian coordinates of compound **6** (open form) in benzene at the optimized ground-state geometry.

|   |          |          |          |   |          |          |          |
|---|----------|----------|----------|---|----------|----------|----------|
| S | 1.580156 | 2.720319 | -0.68252 | C | 1.669717 | -1.78077 | 0.990804 |
| S | 5.825898 | -0.20794 | -0.69558 | C | 1.038079 | -1.21652 | -0.09196 |
| S | 1.486896 | -3.49423 | 0.966131 | C | 0.402032 | -2.19741 | -0.91853 |
| N | -2.42928 | -0.23109 | 0.634333 | H | -0.14793 | -1.94448 | -1.81802 |
| C | -0.07316 | 2.284571 | -0.6966  | C | 0.557232 | -3.48045 | -0.4849  |
| C | -0.26364 | 0.929702 | -0.53306 | C | 2.414799 | -1.11946 | 2.101264 |
| C | 0.969217 | 0.229599 | -0.37065 | H | 2.248406 | -1.63046 | 3.053666 |
| C | 2.069363 | 1.073632 | -0.43701 | H | 2.084748 | -0.08304 | 2.204351 |
| C | -1.30529 | 3.061184 | -0.76255 | H | 3.493515 | -1.10084 | 1.911694 |
| C | -1.48893 | 4.433752 | -0.90075 | C | 0.047765 | -4.73891 | -1.10476 |
| H | -0.63945 | 5.102971 | -1.00545 | H | 0.862788 | -5.40356 | -1.40852 |
| C | -2.78745 | 4.941288 | -0.90186 | H | -0.53881 | -4.49731 | -1.99423 |
| H | -2.94676 | 6.01035  | -1.00465 | H | -0.59448 | -5.30079 | -0.41902 |
| C | -3.87903 | 4.087788 | -0.77377 | C | 4.1478   | -0.19927 | -1.07524 |
| H | -4.8851  | 4.496467 | -0.77417 | C | 3.500717 | 0.780743 | -0.35608 |
| C | -3.68497 | 2.708087 | -0.64988 | C | 4.400321 | 1.522027 | 0.478302 |
| H | -4.55048 | 2.054784 | -0.5638  | H | 4.07617  | 2.332649 | 1.122326 |
| C | -2.40367 | 2.177035 | -0.63539 | C | 5.696331 | 1.105803 | 0.410814 |
| C | -2.29786 | 0.017764 | 1.973434 | C | 3.599272 | -1.14768 | -2.08607 |
| C | -2.86017 | -0.88573 | 2.91404  | H | 4.328345 | -1.35179 | -2.87479 |
| C | -3.5501  | -2.02147 | 2.42771  | H | 2.70296  | -0.72366 | -2.54524 |
| H | -3.98352 | -2.71886 | 3.138115 | H | 3.311616 | -2.10252 | -1.63348 |
| C | -3.66877 | -2.23352 | 1.084565 | C | 6.883233 | 1.632597 | 1.145968 |
| H | -4.19419 | -3.0952  | 0.692512 | H | 6.579896 | 2.464201 | 1.785949 |
| C | -3.0891  | -1.31021 | 0.191814 | H | 7.655536 | 1.998011 | 0.462012 |
| C | -3.09683 | -1.36503 | -1.25992 | H | 7.341482 | 0.868034 | 1.780954 |
| C | -3.68375 | -2.33668 | -2.07239 | B | -1.85558 | 0.64571  | -0.5809  |
| H | -4.22713 | -3.17738 | -1.65142 | C | -1.61615 | 1.16174  | 2.432148 |
| C | -3.55684 | -2.20581 | -3.44735 | C | -1.4982  | 1.387846 | 3.782667 |
| H | -4.00178 | -2.94424 | -4.10612 | H | -0.97272 | 2.271758 | 4.128625 |
| C | -2.85806 | -1.12174 | -3.98766 | H | -1.19098 | 1.849562 | 1.713261 |
| H | -2.76836 | -1.03283 | -5.06633 | C | -2.71833 | -0.62226 | 4.293738 |
| C | -2.27992 | -0.15936 | -3.16479 | C | -2.04783 | 0.495134 | 4.723037 |
| H | -1.74255 | 0.675475 | -3.60616 | H | -1.94112 | 0.695456 | 5.783512 |
| C | -2.39015 | -0.27044 | -1.78154 | H | -3.15061 | -1.31957 | 5.00446  |

**Table S9** Cartesian coordinates of compound **6** (closed form) in benzene at the optimized ground-state geometry.

|   |          |          |          |   |          |          |          |
|---|----------|----------|----------|---|----------|----------|----------|
| S | 1.218689 | 3.042401 | -0.10312 | C | 2.753575 | -1.2053  | 0.40567  |
| S | 5.44928  | -0.31977 | 0.264833 | C | 1.318703 | -0.9139  | -0.03837 |
| S | 3.00876  | -2.98774 | 0.017983 | C | 0.561456 | -2.11507 | -0.17758 |
| N | -2.58187 | -0.52719 | 0.42838  | H | -0.50922 | -2.12338 | -0.33921 |
| C | -0.35688 | 2.324701 | -0.31695 | C | 1.288831 | -3.25834 | -0.1618  |
| C | -0.39075 | 0.959781 | -0.34419 | C | 2.81379  | -1.05    | 1.935707 |
| C | 0.924102 | 0.390246 | -0.17942 | H | 3.796417 | -1.32272 | 2.324698 |
| C | 1.946481 | 1.441756 | -0.10354 | H | 2.061674 | -1.70105 | 2.38662  |
| C | -1.65565 | 2.970986 | -0.42438 | H | 2.597589 | -0.01611 | 2.218868 |
| C | -1.97828 | 4.324609 | -0.40353 | C | 0.787785 | -4.65163 | -0.30293 |
| H | -1.20487 | 5.082567 | -0.31601 | H | 1.269068 | -5.16193 | -1.14445 |
| C | -3.31976 | 4.693347 | -0.49808 | H | -0.29151 | -4.65325 | -0.46962 |
| H | -3.59195 | 5.744131 | -0.48044 | H | 1.002421 | -5.24157 | 0.594913 |
| C | -4.31066 | 3.723662 | -0.61588 | C | 3.709314 | -0.26977 | -0.34198 |
| H | -5.35147 | 4.025028 | -0.68735 | C | 3.274348 | 1.174829 | -0.1028  |
| C | -3.97368 | 2.365481 | -0.64802 | C | 4.397813 | 2.05346  | 0.019747 |
| H | -4.76238 | 1.623691 | -0.75255 | H | 4.310644 | 3.135045 | 0.001115 |
| C | -2.64852 | 1.972307 | -0.54906 | C | 5.582536 | 1.427982 | 0.20914  |
| C | -2.64344 | -0.42283 | 1.791907 | C | 3.736897 | -0.50783 | -1.86127 |
| C | -3.31624 | -1.42356 | 2.542863 | H | 4.12933  | -1.49702 | -2.1019  |
| C | -3.91215 | -2.50173 | 1.846994 | H | 4.372643 | 0.248079 | -2.32753 |
| H | -4.43128 | -3.27044 | 2.41139  | H | 2.727422 | -0.41958 | -2.27303 |
| C | -3.83563 | -2.57123 | 0.485642 | C | 6.920468 | 2.053209 | 0.384928 |
| H | -4.28747 | -3.38659 | -0.06511 | H | 6.836793 | 3.141873 | 0.384828 |
| C | -3.15292 | -1.55661 | -0.21443 | H | 7.601701 | 1.755926 | -0.4195  |
| C | -2.95126 | -1.45943 | -1.6502  | H | 7.381351 | 1.740354 | 1.328043 |
| C | -3.37781 | -2.3554  | -2.63308 | B | -1.92531 | 0.515127 | -0.60494 |
| H | -3.94065 | -3.24953 | -2.38236 | C | -2.04995 | 0.665017 | 2.46052  |
| C | -3.06231 | -2.07717 | -3.95404 | C | -2.1246  | 0.744257 | 3.830575 |
| H | -3.3777  | -2.75396 | -4.74114 | H | -1.66424 | 1.58483  | 4.338946 |
| C | -2.33618 | -0.92592 | -4.27536 | H | -1.5347  | 1.423025 | 1.885418 |
| H | -2.095   | -0.72412 | -5.31478 | C | -3.37225 | -1.30998 | 3.948903 |
| C | -1.91975 | -0.04075 | -3.28589 | C | -2.78648 | -0.2443  | 4.584088 |
| H | -1.35794 | 0.848325 | -3.55808 | H | -2.8313  | -0.15922 | 5.66425  |
| C | -2.22358 | -0.2975  | -1.95206 | H | -3.8877  | -2.08032 | 4.51376  |

**Table S10** Cartesian coordinates of compound **1** (closed form) in benzene at the optimized  $S_1$  state geometry.

|   |          |          |          |   |          |          |          |
|---|----------|----------|----------|---|----------|----------|----------|
| S | 0.879371 | 3.062102 | -0.26748 | C | -3.38988 | -1.72522 | -3.18418 |
| S | 5.220301 | -0.204   | -0.09541 | H | -3.42667 | -1.73387 | -4.26943 |
| S | 2.846992 | -2.88581 | 0.189669 | C | -2.82549 | -0.63987 | -2.51938 |
| N | -2.52634 | -0.35009 | 1.251416 | H | -2.42862 | 0.193723 | -3.09221 |
| C | -0.69063 | 2.352175 | -0.22329 | C | -2.76797 | -0.6233  | -1.12841 |
| C | -0.67631 | 0.966195 | -0.16395 | C | 2.54377  | -1.09626 | 0.424486 |
| C | 0.645092 | 0.453802 | -0.13101 | C | 1.104671 | -0.88253 | 0.014036 |
| C | 1.628063 | 1.500074 | -0.21809 | C | 0.429917 | -2.07656 | -0.26675 |
| C | -2.00914 | 2.94581  | -0.20138 | H | -0.6129  | -2.10645 | -0.56432 |
| C | -2.38897 | 4.287063 | -0.25941 | C | 1.199384 | -3.21816 | -0.23327 |
| H | -1.64595 | 5.075064 | -0.34538 | C | 2.763203 | -0.76898 | 1.907098 |
| C | -3.74463 | 4.602522 | -0.20897 | H | 2.088738 | -1.36765 | 2.522668 |
| H | -4.05597 | 5.641915 | -0.25018 | H | 2.558131 | 0.290578 | 2.085022 |
| C | -4.70314 | 3.596861 | -0.11086 | H | 3.795115 | -0.98244 | 2.20008  |
| H | -5.75628 | 3.858363 | -0.07234 | C | 0.773861 | -4.60595 | -0.54863 |
| C | -4.31284 | 2.252728 | -0.0662  | H | 1.359572 | -5.02899 | -1.37438 |
| H | -5.07523 | 1.479306 | -0.00213 | H | -0.28011 | -4.61966 | -0.83535 |
| C | -2.97114 | 1.908372 | -0.10283 | H | 0.904457 | -5.27775 | 0.30884  |
| C | -2.24888 | 0.039246 | 2.500183 | C | 3.431418 | -0.1769  | -0.49898 |
| H | -1.76616 | 1.00506  | 2.599208 | C | 3.000422 | 1.252248 | -0.25873 |
| C | -2.56563 | -0.75406 | 3.58255  | C | 4.082493 | 2.125596 | -0.03466 |
| H | -2.33227 | -0.41657 | 4.584387 | H | 3.961806 | 3.196617 | 0.096052 |
| C | -3.18698 | -1.9852  | 3.353112 | C | 5.305948 | 1.520983 | 0.089416 |
| H | -3.44503 | -2.62856 | 4.187302 | C | 3.277779 | -0.55454 | -1.9763  |
| C | -3.47008 | -2.38263 | 2.057276 | H | 3.838767 | 0.145618 | -2.59893 |
| H | -3.94934 | -3.33308 | 1.855917 | H | 2.22205  | -0.51143 | -2.25896 |
| C | -3.12822 | -1.54166 | 1.001838 | H | 3.652233 | -1.56643 | -2.15453 |
| C | -3.29835 | -1.7256  | -0.43138 | C | 6.609611 | 2.168501 | 0.389209 |
| C | -3.87334 | -2.81687 | -1.08576 | H | 6.476562 | 3.244578 | 0.519564 |
| H | -4.28304 | -3.65672 | -0.53224 | H | 7.334855 | 2.00806  | -0.41694 |
| C | -3.91375 | -2.80829 | -2.47228 | H | 7.055686 | 1.762772 | 1.305023 |
| H | -4.35401 | -3.64392 | -3.0065  | B | -2.21607 | 0.465635 | -0.08914 |

**Table S11** Cartesian coordinates of compound **6** (closed form) in benzene at the optimized S<sub>1</sub> state geometry.

|   |          |          |          |   |          |          |          |
|---|----------|----------|----------|---|----------|----------|----------|
| S | 1.198005 | 3.077462 | 0.021464 | C | 2.690137 | -1.19116 | 0.301721 |
| S | 5.399461 | -0.35218 | 0.093859 | C | 1.268574 | -0.86855 | -0.1265  |
| S | 2.922242 | -2.95568 | -0.13401 | C | 0.513283 | -2.00947 | -0.41465 |
| N | -2.53581 | -0.59965 | 0.408649 | H | -0.54561 | -1.98356 | -0.63701 |
| C | -0.38424 | 2.400115 | -0.13785 | C | 1.241837 | -3.17425 | -0.46115 |
| C | -0.42952 | 1.022255 | -0.25006 | C | 2.77945  | -1.08254 | 1.835819 |
| C | 0.873279 | 0.473606 | -0.16877 | H | 3.770602 | -1.37503 | 2.187036 |
| C | 1.900185 | 1.490738 | -0.05996 | H | 2.033714 | -1.73492 | 2.293132 |
| C | -1.68266 | 3.043059 | -0.11947 | H | 2.581047 | -0.0555  | 2.151931 |
| C | -1.99292 | 4.396623 | 0.010654 | C | 0.7186   | -4.52963 | -0.76583 |
| H | -1.21168 | 5.147369 | 0.093662 | H | 1.247898 | -4.97376 | -1.61473 |
| C | -3.33143 | 4.76801  | 0.03829  | H | -0.34556 | -4.48112 | -0.9988  |
| H | -3.60223 | 5.813743 | 0.142545 | H | 0.860448 | -5.19845 | 0.089392 |
| C | -4.32936 | 3.797561 | -0.06395 | C | 3.643989 | -0.22915 | -0.42725 |
| H | -5.37169 | 4.101705 | -0.03608 | C | 3.239946 | 1.198958 | -0.08579 |
| C | -4.0044  | 2.447518 | -0.20349 | C | 4.358562 | 2.035996 | 0.139854 |
| H | -4.80065 | 1.7123   | -0.2872  | H | 4.285998 | 3.110346 | 0.266059 |
| C | -2.67583 | 2.041866 | -0.23418 | C | 5.540591 | 1.368116 | 0.267957 |
| C | -2.53192 | -0.70692 | 1.783006 | C | 3.603431 | -0.38944 | -1.95714 |
| C | -3.07308 | -1.87602 | 2.402916 | H | 3.961445 | -1.37722 | -2.25196 |
| C | -3.61681 | -2.90226 | 1.576972 | H | 4.237074 | 0.367915 | -2.4226  |
| H | -4.03716 | -3.78844 | 2.038708 | H | 2.580621 | -0.26003 | -2.32111 |
| C | -3.61086 | -2.74909 | 0.197081 | C | 6.873458 | 1.962769 | 0.546434 |
| H | -4.02549 | -3.51664 | -0.4473  | H | 6.790755 | 3.0417   | 0.684561 |
| C | -3.07531 | -1.6111  | -0.37498 | H | 7.563587 | 1.766701 | -0.28036 |
| C | -2.93966 | -1.27284 | -1.77813 | H | 7.316283 | 1.525844 | 1.446751 |
| C | -3.34883 | -2.01403 | -2.89142 | B | -1.98674 | 0.580296 | -0.46277 |
| H | -3.85549 | -2.96796 | -2.7732  | C | -2.00642 | 0.309287 | 2.588774 |
| C | -3.10271 | -1.51097 | -4.16267 | C | -2.00244 | 0.192    | 3.977132 |
| H | -3.41746 | -2.0756  | -5.03521 | H | -1.59343 | 0.997307 | 4.578544 |
| C | -2.45719 | -0.28356 | -4.3259  | H | -1.6098  | 1.201349 | 2.121486 |
| H | -2.27174 | 0.098911 | -5.32514 | C | -3.04971 | -1.96296 | 3.805641 |
| C | -2.05706 | 0.451254 | -3.2087  | C | -2.52214 | -0.94469 | 4.588624 |
| H | -1.56344 | 1.410411 | -3.34976 | H | -2.51957 | -1.03531 | 5.669966 |
| C | -2.292   | -0.03057 | -1.92696 | H | -3.46254 | -2.85285 | 4.2723   |

**Table S12** Cartesian coordinates of compound **1** (closed form) in benzene at the optimized S<sub>2</sub> state geometry.

|   |          |          |          |   |          |          |          |
|---|----------|----------|----------|---|----------|----------|----------|
| S | -0.94186 | 3.073363 | 0.043042 | C | 2.617189 | -0.24038 | 2.622528 |
| S | -5.2087  | -0.27706 | 0.043294 | H | 2.191342 | 0.677456 | 3.022938 |
| S | -2.77755 | -2.92645 | -0.14704 | C | 2.677021 | -0.4363  | 1.24835  |
| N | 2.61719  | -0.48192 | -1.15273 | C | -2.54479 | -1.13623 | -0.46001 |
| C | 0.632583 | 2.36042  | 0.01592  | C | -1.08598 | -0.87003 | -0.12933 |
| C | 0.657933 | 0.977787 | 0.001454 | C | -0.33406 | -2.04029 | 0.010494 |
| C | -0.65899 | 0.45874  | -0.01513 | H | 0.739357 | -2.04628 | 0.152519 |
| C | -1.67014 | 1.495978 | 0.049723 | C | -1.08128 | -3.19406 | 0.028223 |
| C | 1.940186 | 2.985257 | -0.02332 | C | -2.76074 | -0.90196 | -1.96709 |
| C | 2.266096 | 4.341125 | -0.03121 | H | -3.78389 | -1.15029 | -2.25475 |
| H | 1.494966 | 5.105916 | 0.007312 | H | -2.0706  | -1.52663 | -2.53676 |
| C | 3.607919 | 4.697583 | -0.09179 | H | -2.56815 | 0.144617 | -2.21583 |
| H | 3.891179 | 5.745208 | -0.1018  | C | -0.56369 | -4.57625 | 0.187209 |
| C | 4.592342 | 3.709689 | -0.141   | H | -1.05662 | -5.0885  | 1.019224 |
| H | 5.637258 | 4.002197 | -0.19098 | H | 0.511339 | -4.55876 | 0.369186 |
| C | 4.250243 | 2.356319 | -0.12357 | H | -0.75685 | -5.16544 | -0.71547 |
| H | 5.036747 | 1.606491 | -0.15592 | C | -3.41365 | -0.22278 | 0.422203 |
| C | 2.918173 | 1.96431  | -0.06511 | C | -3.00871 | 1.222655 | 0.164289 |
| C | 2.487571 | -0.29134 | -2.4978  | C | -4.12451 | 2.091667 | 0.101765 |
| C | 2.89795  | -1.22305 | -3.40494 | H | -4.03951 | 3.171593 | 0.057499 |
| C | 3.491681 | -2.44103 | -2.95356 | C | -5.32684 | 1.454008 | 0.020336 |
| H | 3.830253 | -3.18981 | -3.65795 | C | -3.24946 | -0.50853 | 1.925222 |
| C | 3.635692 | -2.62958 | -1.58032 | H | -3.60371 | -1.5114  | 2.169197 |
| H | 4.091657 | -3.5359  | -1.1939  | H | -3.82515 | 0.218001 | 2.501856 |
| C | 3.208594 | -1.66733 | -0.68516 | H | -2.19733 | -0.42517 | 2.210529 |
| C | 3.24424  | -1.63852 | 0.758315 | C | -6.66534 | 2.088707 | -0.09545 |
| C | 3.737627 | -2.611   | 1.638642 | H | -6.57131 | 3.174001 | -0.15331 |
| H | 4.179094 | -3.53015 | 1.262402 | H | -7.28813 | 1.836138 | 0.768673 |
| C | 3.663201 | -2.38708 | 3.006597 | H | -7.1911  | 1.733111 | -0.98693 |
| H | 4.046384 | -3.13497 | 3.694827 | B | 2.221273 | 0.48575  | 0.000855 |
| C | 3.104421 | -1.20688 | 3.505179 | H | 2.042358 | 0.649468 | -2.80162 |
| H | 3.055149 | -1.04297 | 4.577379 | H | 2.773288 | -1.02088 | -4.4622  |

**Table S13** Cartesian coordinates of compound **6** (closed form) in benzene at the optimized S<sub>2</sub> state geometry.

|   |          |          |          |   |          |          |          |
|---|----------|----------|----------|---|----------|----------|----------|
| S | 1.087291 | 3.009331 | -0.67333 | C | 2.69453  | -1.08654 | 0.425091 |
| S | 5.408079 | -0.20447 | 0.067318 | C | 1.300658 | -0.91033 | -0.12608 |
| S | 3.020585 | -2.8839  | 0.332197 | C | 0.669343 | -2.12179 | -0.42966 |
| N | -2.4797  | -0.50432 | 0.639988 | H | -0.33277 | -2.17448 | -0.84213 |
| C | -0.48175 | 2.295241 | -0.70206 | C | 1.434659 | -3.2546  | -0.26073 |
| C | -0.46558 | 0.915964 | -0.54268 | C | 2.794442 | -0.65824 | 1.893457 |
| C | 0.8495   | 0.415046 | -0.38288 | H | 3.799197 | -0.84781 | 2.282249 |
| C | 1.832259 | 1.459367 | -0.45697 | H | 2.07092  | -1.21418 | 2.493225 |
| C | -1.80157 | 2.878979 | -0.78058 | H | 2.578914 | 0.410526 | 1.980484 |
| C | -2.18565 | 4.214133 | -0.91691 | C | 1.057571 | -4.65876 | -0.56542 |
| H | -1.44292 | 5.002079 | -1.00584 | H | 1.73167  | -5.10578 | -1.30716 |
| C | -3.54321 | 4.523249 | -0.93763 | H | 0.040655 | -4.69643 | -0.96298 |
| H | -3.85649 | 5.557893 | -1.03973 | H | 1.099943 | -5.29743 | 0.325775 |
| C | -4.50176 | 3.518125 | -0.83052 | C | 3.659948 | -0.21679 | -0.48444 |
| H | -5.55652 | 3.775259 | -0.84696 | C | 3.206698 | 1.219111 | -0.37063 |
| C | -4.1086  | 2.180169 | -0.70638 | C | 4.259959 | 2.112749 | -0.09554 |
| H | -4.87028 | 1.406693 | -0.63452 | H | 4.121292 | 3.187795 | -0.03079 |
| C | -2.7653  | 1.842495 | -0.67336 | C | 5.470805 | 1.52888  | 0.170902 |
| C | -2.4019  | -0.20706 | 1.973702 | C | 3.628815 | -0.69795 | -1.9384  |
| C | -2.8954  | -1.13501 | 2.929466 | H | 4.020367 | -1.71648 | -2.01394 |
| C | -3.46313 | -2.34443 | 2.463719 | H | 4.236495 | -0.03801 | -2.56115 |
| H | -3.8443  | -3.0601  | 3.185809 | H | 2.599435 | -0.68435 | -2.3079  |
| C | -3.53139 | -2.60419 | 1.125246 | C | 6.737182 | 2.202401 | 0.560378 |
| H | -3.96462 | -3.52233 | 0.748892 | H | 6.587857 | 3.282762 | 0.619267 |
| C | -3.02363 | -1.65407 | 0.21721  | H | 7.538985 | 2.00706  | -0.16132 |
| C | -2.99248 | -1.75025 | -1.23262 | H | 7.093881 | 1.850681 | 1.536021 |
| C | -3.45544 | -2.80178 | -2.0267  | B | -2.00184 | 0.408077 | -0.59403 |
| H | -3.91816 | -3.6823  | -1.59112 | C | -1.84403 | 1.009593 | 2.411951 |
| C | -3.31021 | -2.69749 | -3.40167 | C | -1.77775 | 1.282108 | 3.757405 |
| H | -3.65881 | -3.49763 | -4.04616 | H | -1.34681 | 2.221456 | 4.087442 |
| C | -2.71502 | -1.56226 | -3.96098 | H | -1.46997 | 1.715811 | 1.682469 |
| H | -2.60717 | -1.49695 | -5.0396  | C | -2.80967 | -0.82197 | 4.303452 |
| C | -2.26132 | -0.52056 | -3.15761 | C | -2.25938 | 0.366298 | 4.712662 |
| H | -1.80381 | 0.352853 | -3.61372 | H | -2.19527 | 0.604657 | 5.768664 |
| C | -2.39413 | -0.60128 | -1.77415 | H | -3.18833 | -1.53827 | 5.025762 |

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