**Supplementary Information**

# The interplay of thermally activated delayed fluorescence (TADF) and room temperature organic phosphorescence in sterically-constrained donor–acceptor charge-transfer molecules

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Contents Page



## S1 - General experimental details

All reactions were carried out under an argon atmosphere unless otherwise stated. Starting materials were purchased commercially and were used as received. Solvents were dried using an Innovative Technology solvent purification system and were stored in ampoules under argon.

TLC analysis was carried out using Merck Silica gel 60 $F_{254}$ TLC plates and spots were visualised using a TLC lamp emitting at 365, 312 or 254 nm. Silica gel column chromatography was performed using silica gel 60 purchased from Sigma Aldrich.

$^{1}$H and $^{13}$C NMR spectra were recorded on Bruker AV400, Varian VNMRS 500 and 700, and Varian Inova 500 NMR spectrometers. Residual solvent peaks were referenced as described in the literature[1], and all NMR data was processed in MestReNova V10.

Melting points were carried out on a Stuart SMP40 machine with a ramping rate of 4 °C $min^{-1}$. Videos were replayed manually to determine the melting point.

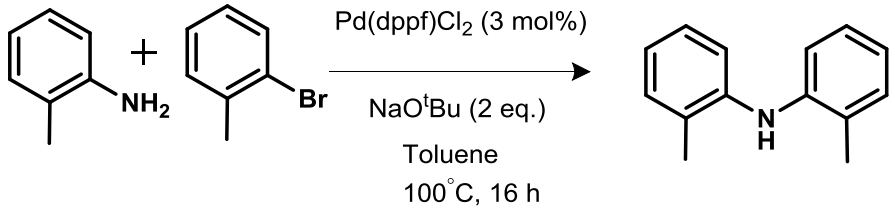
High resolution mass spectroscopy was carried out on a Waters LCT Premier XE using ASAP ionisation. Samples were analysed directly as solids.

Elemental analysis was performed on an Exeter Analytical E-440 machine.

Any stated use of hexane refers to a mixed isomers grade.

## S2 - Synthesis and characterisation

**Synthesis of di(*o*-tolyl)amine : General procedure 1**

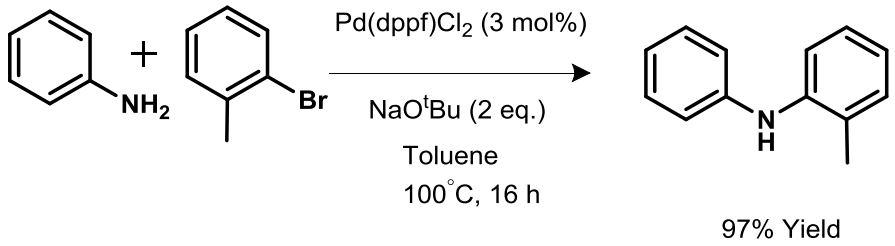



This synthesis was based on a modified literature procedure.[2]

To a 250 mL round-bottomed flask equipped with a stirrer bar was added $NaO^tBu$ (9.62 g, 100 mmol, 2 eq.), $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (1.22 g, 1.5 mmol, 0.03 eq.) and the flask was flushed with argon. Dry toluene (120 mL) was then added *via* syringe, followed by *o*-toluidine (6.05 g/6.0 mL, 56.5 mmol, 1.1 eq.) and 1-bromo-2-methylbenzene (6.75 mL, 50 mmol, 1 eq.). The solution was bubbled with argon for 15 minutes, and the mixture was heated to 100 °C with stirring for 16 h. On cooling the reaction mixture to ambient temperature the entire reaction mixture solidified, and so the toluene was removed on a rotary evaporator at 50 °C. The crude residue was diluted with 500 mL of $CH_2Cl_2$ and was washed with 1 M $HCl_{(aq)}$ (500 mL). The organic layer was washed with water (200 mL) and brine (200 mL) and the solvent was removed to give a crude brown oil. The crude oil was purified by silica gel column chromatography eluting with 1:2 *v/v* $CH_2Cl_2$:hexane. The crude oil was loaded on to the column neat. Removal of solvent yielded the title product as a yellow solid (8.97 g, 90% yield)

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 8.0, 1.3 Hz, 2H), 6.96 (td, *J* = 7.0, 1.3 Hz, 2H), 5.20 (s, 1H), 2.32 (s, 6H); $^{13}$C NMR (101 MHz, CDCl3) δ 142.1, 130.9, 127.6, 126.9, 121.5, 118.4, 17.9; HRMS-ASAP$^+$ *m/z* calculated for $C_{14}H_{15}N$ $[M]^+$ 197.1204, found: 197.1201

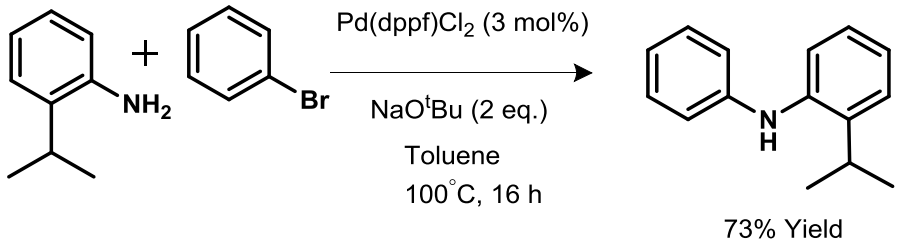
**Synthesis of *N*-(2-methylphenyl)aniline**



Using general procedure **1**, 2-bromotoluene (8.53 g/6 mL, 50 mmol, 1 eq.) and aniline (5.26 g/ 5.15 mL, 56.5 mmol, 1.1 eq.) were used to make the title compound. The solvent was removed from the reaction mixture and the crude oil was directly purified using silica gel column chromatography eluting with 40% *v/v* $CH_2Cl_2$:hexane. Removal of solvent under reduced pressure gave the title compound as a yellow solid (8.93 g, 97% yield).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 4H), 7.21 – 7.15 (m, 1H), 7.03 – 6.90 (m, 4H), 5.41 (s, 1H), 2.29 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 144.1, 141.3, 131.1, 129.4, 128.4, 126.9, 122.1, 120.6, 118.9, 117.6, 18.0; HRMS-ASAP$^+$ *m/z* calculated for $C_{13}H_{13}N$ $[M]^+$ 183.1048, found: 183.1045.

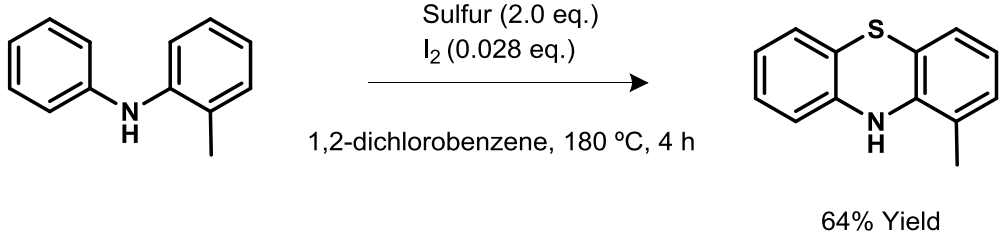
**Synthesis of *N*-(2-isopropylphenyl)aniline**




Using general procedure **1**, bromobenzene (5.00 g/3.35 mL, 31.8 mmol, 1 eq.) and 2-isopropylaniline (4.73 g/4.9 mL, 35.0 mmol, 1.1 eq.) and toluene (80 mL) were used to make the title compound. The solvent was removed from the reaction mixture and the crude mixture was loaded onto silica with $CH_2Cl_2$ which was subsequently removed under reduced pressure. The silica/product mixture was purified using silica gel column chromatography eluting with 20% *v/v* $CH_2Cl_2$:hexane increasing to 30%. Removal of solvent under reduced pressure gave the title compound as a clear green oil (4.90 g, 73% yield).

$^1$H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.19 – 7.10 (m, 1H), 7.08 (td, *J* = 7.4, 1.3 Hz, 1H), 6.92 – 6.83 (m, 3H), 5.41 (s, 1H), 3.16 (hept, *J* = 6.9 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 6H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 145.4, 140.8, 139.7, 129.4, 126.6, 126.2, 123.6, 122.1, 119.9, 116.6, 27.8, 23.2; HRMS-ASAP$^+$ *m/z* calculated for $C_{15}H_{17}NS$ $[M]^+$ 211.1363, found: 211.1361.

**Synthesis of 1-methylphenothiazine: General procedure 2**



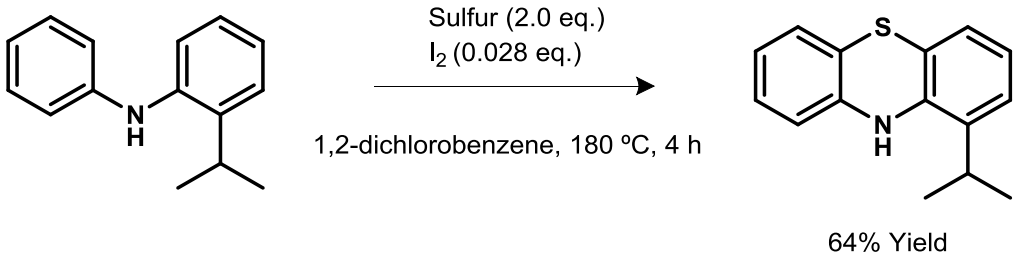

This synthesis was based on a modified literature procedure.[3]

To a 50 mL two-neck round-bottomed flask equipped with a stirrer bar was added *N*-(2-methylphenyl)aniline (4.58 g, 25 mmol, 1 eq.), sulfur (1.60 g, 50 mmol, 2 eq.) and $I_2$ (178 mg, 0.7 mmol, 0.028 eq.). Under a flow of argon was added 1,2-dichlorobenzene (9 mL). The reaction mixture was then deoxygenated by bubbling with argon for 30 minutes, and was then heated to 180

°C for 4 hours. After cooling the reaction mixture to room temperature, the mixture was purified by loading neat on to a silica column packed with hexane. After eluting 1,2-dichlorobenzene with hexane, the product was eluted with 5 – 15% *v/v* EtOAc/hexane increasing EtOAc in 5% increments. Removal of solvent under reduced pressure gave a bright yellow solid (3.4 g, 64% yield).

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.11 (s, 1H), 7.02 – 6.96 (m, 1H), 6.96 – 6.91 (m, 2H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.85 – 6.77 (m, 2H), 6.71 (t, *J* = 7.6 Hz, 1H), 2.24 (s, 3H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 142.2, 140.1, 129.2, 127.3, 126.0, 124.2, 122.4, 122.0, 121.5, 117.2, 116.5, 115.6, 17.6; HRMS-ASAP$^+$ *m/z* calculated for $C_{13}H_{11}NS$ $[M+H]^+$ 213.0612, found: 213.0629.

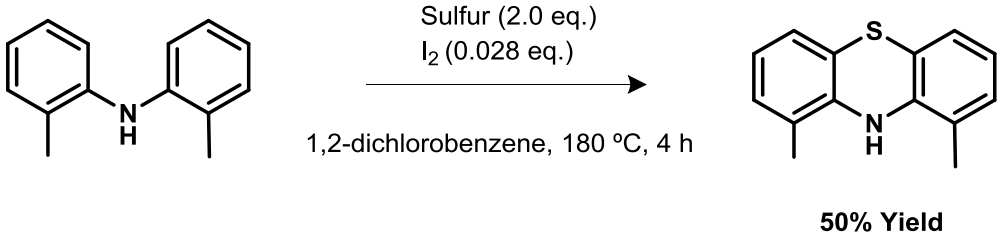
**Synthesis of 1-isopropylphenothiazine**




Using general procedure **2**, *N*-(2-isopropylphenyl)aniline (4.9 g, 23.18 mmol, 1 eq.), sulfur (1.49 g, 46.4 mmol, 2 eq.), $I_2$ (165 mg, 0.649 mmol, 0.028 eq.) and 1,2-dichlorobenzene (9 mL) were used to make the title compound. Column chromatography was carried out as in general procedure 2, but with 20 – 40% *v/v* $CH_2Cl_2$/hexane in 10% increments after the initial hexane wash.

$^1$H NMR (400 MHz, acetone-$d_6$) δ 7.29 (s, 1H), 7.08 – 6.97 (m, 4H), 6.89 – 6.80 (m, 3H), 3.24 (hept, *J* = 6.7 Hz, 1H), 1.23 (d, *J* = 6.7 Hz, 6H); $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 143.9 , 140.4, 133.8, 128.1, 127.0, 125.2, 124.8, 123.2, 123.0, 119.8, 119.2, 116.3, 27.4, 23.0; HRMS-ASAP$^+$ *m/z* calculated for $C_{15}H_{14}NS$ $[M-H]^+$ 240.0847, found: 240.0861.

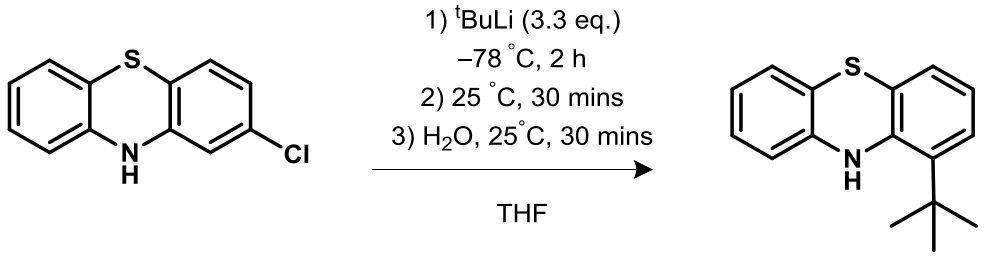
**Synthesis of 1,9-dimethylphenothiazine.**




Using general procedure **2**, di(*o*-tolyl)amine (5.00 g, 25 mmol, 1 eq.), sulfur (1.61 g, 50 mmol, 2 eq.), $I_2$ (177 mg, 0.7 mmol, 0.028 eq.) and 1,2-dichlorobenzene (9 mL) were used to make the title compound. Column chromatography was carried out as in procedure **2**, but with 38:62 $CH_2Cl_2$/hexane after the initial hexane elution. The product was isolated as a green-yellow solid (2.85 g, 50% yield).

$^1$H NMR (400 MHz, acetone-$d_6$) δ 6.93 (d, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.76 (t, *J* = 7.5 Hz, 2H), 6.21 (s, 1H), 2.29 (s, 6H); $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 141.2, 129.9, 125.2, 123.4, 122.9, 119.1, 16.9; HRMS-ASAP$^+$ *m/z* calculated for $C_{14}H_{13}NS$ $[M]^+$ 227.0769, found: 227.0767.

**Synthesis of 1-tertbutylphenothiazine.**



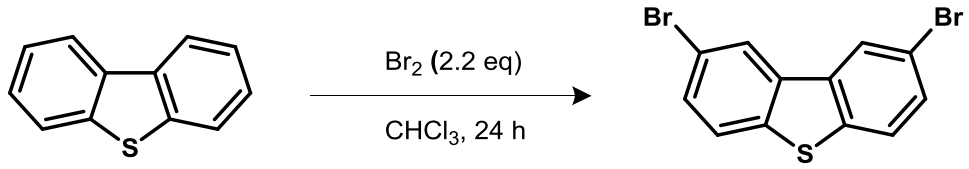

62% Yield

This synthesis was performed based on a modified literature procedure.[4]

To a stirred deoxygenated solution of 2-chlorophenothiazine (2.00 g, 8.56 mmol, 1 eq.) in dry THF under argon at −78 °C was slowly added $^t$BuLi (0.9 M solution in heptane, 31 mL, 28.2 mmol, 3.3 eq.). The reaction mixture was stirred at −78 °C for 2 h and was allowed to warm to 25 °C for 30 minutes. Water (10 mL) was added slowly *via* syringe, and stirring was continued for a further 30 minutes. The organic layer was separated and the aqueous layer was extracted with $Et_2O$ (2 × 50 mL). The combined organic layers were dried with $MgSO_4$, filtered and solvent was removed to give crude product which was purified by silica gel column chromatography eluting with 30:70 *v/v* $CH_2Cl_2$:hexane. Removal of solvent under reduced pressure yielded the product as clear oil, which solidified after drying under high vacuum. (1.34 g, 62% yield).

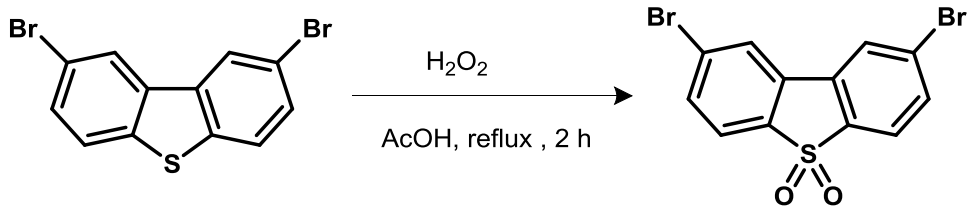
$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.18 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.14 – 7.02 (m, 3H), 6.99 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.85 (t, *J* = 7.8 Hz, 1H), 1.48 (s, 9H); HRMS-ASAP$^+$ *m/z* calculated for $C_{16}H_{17}NS$ $[M]^+$ 255.1082, found: 255.1071;

**Synthesis of 2,8-dibromodibenzothiophene-*S*,*S*-dioxide**




This compound was prepared exactly as according to the literature and NMR data was in agreement.[5] Recrystallization can be performed from toluene if required.

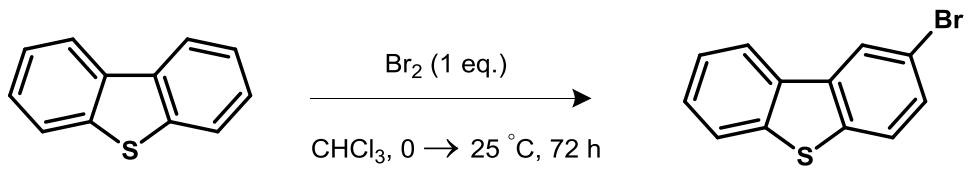
**Synthesis of 2,8-dibromodibenzothiophene-*S*,*S*-dioxide**




90% Yield

The compound was prepared using the literature procedure for dibenzothiophene-*S*,*S*-dioxide[6], but 2,8-dibromodibenzothiophene (2.50 g, 7.31 mmol, 1 eq.), AcOH (134 mL), and aqueous $H_2O_2$ (35% wt. in $H_2O$, 40 mL + 13 mL) were used to make the title compound (2.45 g, 90% yield). $^1$H NMR data was in agreement with literature values[7].

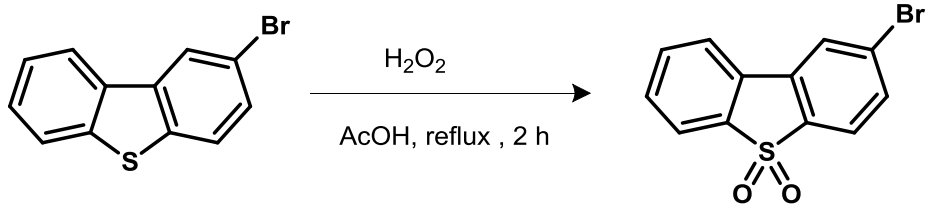
**Synthesis of 2-bromodibenzothiophene**




44% Yield

To a stirred solution of dibenzothiophene (5.5 g, 29.84 mmol, 1 eq.) in $CHCl_3$ (50 mL) at 0 °C was slowly added bromine (4.84 g/ 1.55 mL, 30.3 mmol, 1.02 eq.) in $CHCl_3$. The reaction was allowed to warm to ambient temperature and was stirred for a further 72 h. The reaction mixture was washed with sodium thiosulfate$_{(aq)}$ (30 mL) and $H_2O$ (30 mL). The organic layer was dried with $MgSO_4$ and filtered and the solvent was removed under reduced pressure to give crude material. The crude material was dissolved in $CHCl_3$ (30 mL) and cold methanol was added to precipitate the product, which was collected by filtration and washed with cold methanol (2 × 20 mL). This gave the product as a white solid containing 10% wt. 2,8-dibromodibenzothiophene (3.85 g, 44% yield).$^1$H NMR data was in agreement with the literature.[8] This material was used directly in the next step.

**Synthesis of 2-bromodibenzothiophene-*S*,*S*-dioxide**



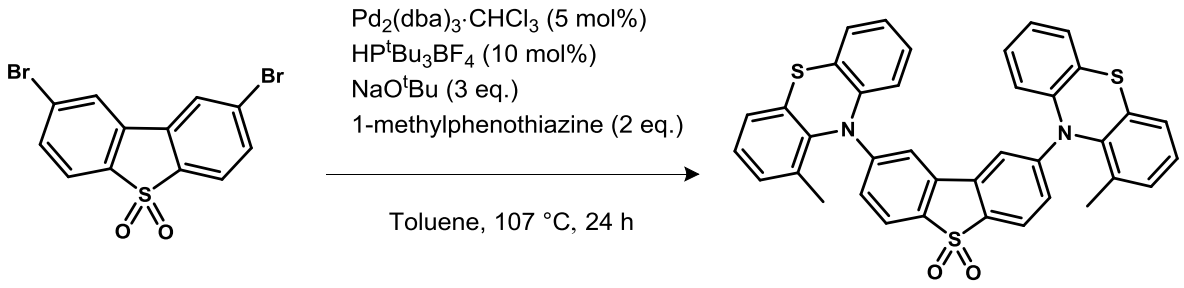

77% Yield

This compound was synthesised using a slightly modified literature procedure.[6, 9, 10]

2-bromodibenzothiophene (4.15 g, 15.8 mmol, 1 eq.) was heated to 80 °C for 30 minutes in AcOH (250 mL) and $H_2O_{2\ (aq)}$ (100 mL) was slowly added *via* a reflux condenser. The mixture was refluxed for 2 h and the reaction mixture was cooled to ambient temperature. The precipitate that formed was filtered and washed with water and dried overnight at 70 °C to obtain the product as a white solid containing 10 wt.% 2,8-dibromodibenzothiophene-*S*,*S*-dioxide (4.02 g, 77% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.55 (d, *J* = 1.7 Hz, 1H), 8.28 (dt, *J* = 7.8, 1.0 Hz, 1H), 8.01 (m, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.86 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.83 (td, *J* = 7.7, 1.0 Hz, 1H), 7.70 (td, *J* = 7.7, 1.0 Hz, 1H).

**Synthesis of 2,8-Bis(1-methylphenothiazin-10-yl)dibenzothiophene-*S,S*-dioxide (2): General Procedure 3**



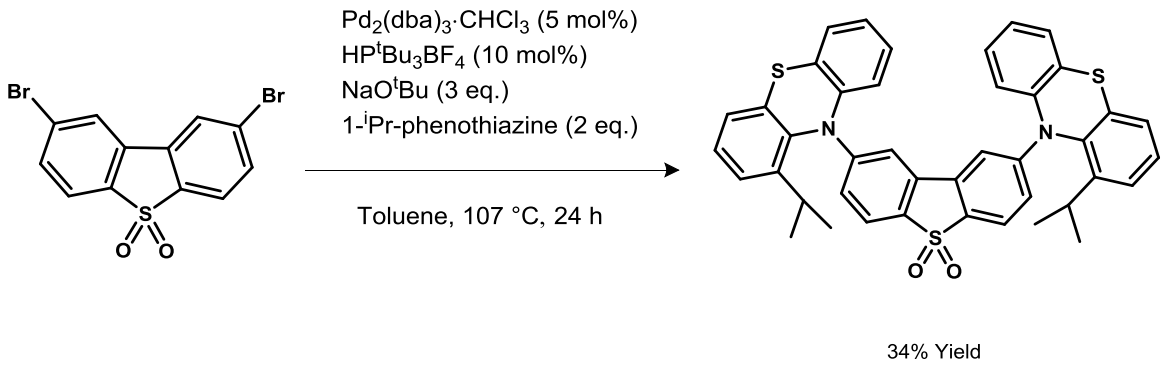

27% Yield

This compound was synthesised using a modified literature procedure for 2,8-Bis[*N*,*N*-di(4-butylphenyl)amino]dibenzothiophene-*S*,*S*-dioxide.[11]

2,8-dibromodibenzothiophene-*S*,*S*-dioxide (412 mg ,1.10 mmol, 1 eq.) and 1-methylphenothiazine (470 mg, 2.20 mmol, 2 eq.) were dried under vacuum for 30 minutes in a two-neck 100 mL round-bottomed flask fitted with a reflux condenser. The flask was back-filled with argon and dry toluene (25 mL) was added. The reaction mixture was bubbled with argon for 30 minutes, then $Pd_2(dba)_3{\cdot}CHCl_3$ (56 mg, 55 μmol, 0.05 eq.) and $HP^tBu_3BF_4$ (32 mg, 110 μmol, 0.1 eq.) was added and the reaction mixture was bubbled with argon for a further 30 minutes. $NaO^tBu$ (318 mg, 3.30 mmol, 3 eq.) was added under a high flow of argon and the reaction was then heated to 107 °C with stirring for 24 h. At the end of the reaction the solvent was removed under reduced pressure and the crude mixture was purified by silica gel column chromatography eluting with 60% *v/v* $CH_2Cl_2$/hexane switching to 70% $CH_2Cl_2$. Removal of solvent under reduced pressure gave product as a yellow solid. Recrystallisation of the residue from boiling toluene with slow addition of acetone followed by cooling to −18 °C gave pure product as a slightly off-white solid (192 mg, 27% yield). Toluene was removed by heating (>350 °C) under high vacuum ($9 \times 10^{-2}$ mbar). This compound would not sublime under the attempted conditions. Crystals suitable for X-ray diffraction were obtained by layering in THF:cyclohexane and allowing complete solvent evaporation.

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.76 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.66 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.60 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.55 (d, *J* = 8.6, 2H), 7.52 – 7.43 (m, 6H), 7.39 (t, *J* = 7.5 Hz, 2H), 6.71 (dd, *J* = 8.6, 2.3 Hz, 2H), 6.65 (d, *J* = 2.3 Hz, 2H), 2.40 (s, 6H); $^{13}$C NMR (101 MHz, $CD_2Cl_2$) δ 150.6, 141.2, 139.5, 137.5, 137.1 , 136.7, 133.4, 129.9, 129.7, 129.6, 129.4, 127.6, 127.5, 127.4, 127.1, 122.9, 114.5, 105.2, 18.0; HRMS-ASAP$^+$ *m/z* calculated for $C_{38}H_{27}N_2O_2S_3$ $[M+H]^+$ 639.1235, found: 639.1241; Anal. Calc. for $C_{38}H_{26}N_2O_2S_3$ C, 71.45; H, 4.10; N, 4.39. Found: C, 71.19; H, 4.05; N, 4.32; m.p. decomp. > 350 °C.

**Synthesis of 2,8-Bis(1-isopropylphenothiazin-10-yl)dibenzothiophene-*S*,*S*-dioxide (3)**

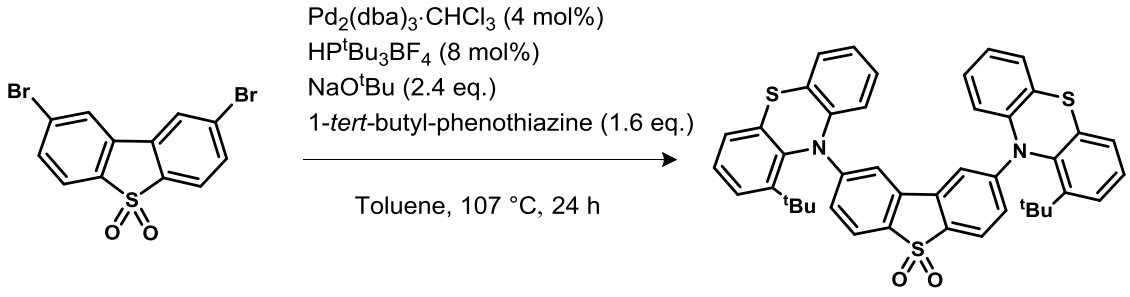



34% Yield

Using general procedure **3**, 2,8-dibromodibenzothiophene-*S*,*S*-dioxide (400 mg, 1.07 mmol, 1 eq.), 1-isopropylphenothiazine (516 mg, 2.14 mmol, 2 eq.), $Pd_2(dba)_3{\cdot}CHCl_3$ (55 mg, 53 μmol, 0.05 eq.), $HP^tBu_3BF_4$ (31 mg, 107 μmol, 0.1 eq.), $NaO^tBu$ (308 mg, 3.2 mmol, 3 eq.) and toluene (25 mL) were used to make the title compound. The crude mixture was purified by silica gel column chromatography eluting with $CH_2Cl_2$. Removal of solvent under reduced pressure gave the title compound as a green solid (248 mg, 34% yield). The title compound can be sublimed under vacuum ($9 \times 10^{-2}$ mbar, > 350 °C). Crystals suitable for X-ray diffraction were obtained by layering with $CH_2Cl_2$:hexane.

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.77 – 7.71 (m, 2H), 7.68 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.60 (td, *J* = 7.6, 1.5 Hz, 2H), 7.57 – 7.45 (m, 10H), 6.77 – 6.66 (m, 2H), 6.61 – 6.49 (m, 2H), 3.38 (hept, *J* = 6.9 Hz, 2H), 1.28 – 1.06 (m, 12H); $^{13}$C NMR (101 MHz, $CD_2Cl_2$) δ 151.7, 151.6, 148.1, 141.6, 141.5, 138.1, 137.5, 136.9, 133.3, 129.9, 129.6, 129.4, 129.3, 128.0, 127.6, 127.1, 125.2, 122.8, 114.6, 114.4, 105.4, 105.2, 29.1, 25.6, 21.4; HRMS-ASAP$^+$ *m/z* calculated for $C_{42}H_{34}N_2O_2S_3$ $[M]^+$ 694.1782, found: 694.1780; Anal. Calc. for $C_{42}H_{34}N_2O_2S_3$ C, 72.59; H, 4.93; N, 4.03. Found: C, 72.45; H, 4.86; N, 4.03; m.p. decomp. > 350 °C.

**Synthesis of 2,8-Bis(1-*tert*-butylphenothiazin-10-yl)dibenzothiophene-*S*,*S*-dioxide (4)**



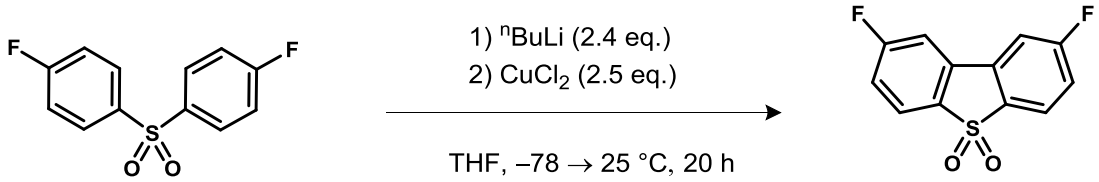

33% Yield

Using general procedure **3**, 2,8-dibromodibenzothiophene-*S*,*S*-dioxide (500 mg, 1.33 mmol, 1 eq.), 1-*tert*-butylphenothiazine (546 mg, 2.12 mmol, 1.6 eq.), $Pd_2(dba)_3{\cdot}CHCl_3$ (55 mg, 53 μmol, 0.04 eq.), $HP^tBu_3BF_4$ (31 mg, 107 μmol, 0.08 eq.), $NaO^tBu$ (305 mg, 3.17 mmol, 2.4 eq.) and toluene (20 mL) were used to make the title compound. The crude mixture was purified by silica gel column chromatography eluting with 70:30 *v/v* $CH_2Cl_2$:hexane increasing to 80:20. Removal of solvent under reduced pressure gave a white residue. The residue was recrystallized from boiling $CH_2Cl_2$ with slow addition of hexane followed by cooling to −18 °C. The product was filtered and washed with *n*-

pentane to give the title product as an off-white solid (320 mg, 33% yield). The title compound can be sublimed under vacuum ($7 \times 10^{-2}$ mbar, > 350 °C).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.90 – 7.75 (m, 2H), 7.74 – 7.34 (m, 14H), 6.54 (s, br., 2H), 5.86 (s, br. 2H), 1.36 (s, 18H); $^{13}$C NMR (176 MHz, DMSO-$d_6$) δ 153.4, 148.9, 148.8, 142.1, 141.9, 137.9, 137.2(4), 137.1(9), 135.8, 131.0, 129.3, 129.2, 129.0, 128.9, 128.8, 128.11 – 127.60 (m), 127.6 – 127.1 (m), 122.7, 116.4 – 115.4 (m), 105.8, 35.9(4), 35.8(6), 31.4, 31.3; HRMS-ASAP$^+$ *m/z* calculated for $C_{44}H_{38}N_2O_2S_3$ $[M]^+$ 722.2095, found: 722.2117; Anal. Calc. for $C_{44}H_{38}N_2O_2S_3$ C, 73.10; H, 5.30; N, 3.87. Found: C, 71.33; H, 5.59; N, 3.63; m.p. decomp. > 350 °C.

**Synthesis of 2,8-difluorodibenzothiophene-*S*,*S*-dioxide**



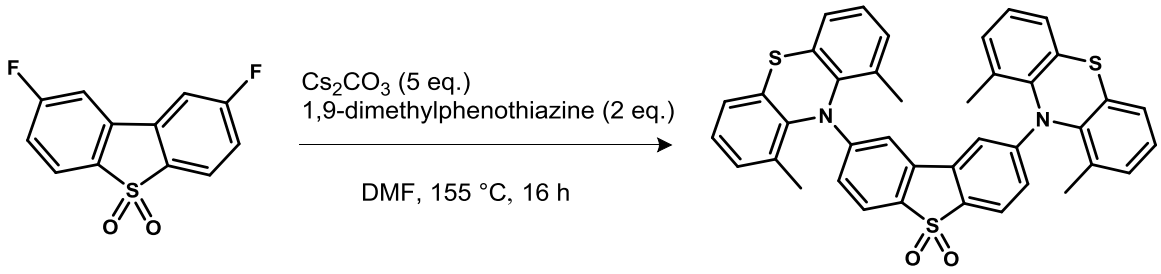

26% Yield

The synthesis proceeded as previously reported with additional experimental details/data.[12]

To a solution of bis(4-fluorophenyl)sulfone, (5.00 g, 19.67 mmol, 1 eq.) in dry THF (100 mL) at −78 °C was added $^n$BuLi (2.5 M in hexanes, 19 mL, 47.5 mmol, 2.4 eq.) The mixture was stirred for 10 minutes and dry $CuCl_2$ (6.61 g, 49.1 mmol, 2.5 eq.) was added at −78 °C in portions under a high argon flow, and was stirred for 30 minutes. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. Saturated $NH_4Cl_{(aq)}$ (100 mL) was added and the organic layer was extracted with $CH_2Cl_2$ (4 × 100 mL). The organic layer was washed with brine (200 mL) and was dried with $MgSO_4$ and filtered. Removal of solvent under reduced pressure gave crude product as a yellow/brown solid. The crude product was recrystallized from ethanol to give an off-yellow solid (1.30 g, 26% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.20 (dd, *J* = 9.0, 2.4 Hz, 2H), 8.12 (dd, *J* = 8.7, 4.9 Hz, 2H), 7.55 (td, *J* = 8.7, 2.3 Hz, 2H); $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ − 103.63 (td, J = 9.0, 4.9 Hz); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 166.2 (d, *J* = 252.0 Hz), 134.4 (d, *J* = 2.9 Hz), 133.60 (dd, *J* = 10.8, 2.4 Hz), 125.32 (d, *J* = 10.2 Hz), 119.1 (d, *J* = 24.1 Hz), 111.52 (d, *J* = 25.7 Hz); HRMS-ASAP$^+$ *m/z* calculated for $C_{12}H_6F_2O_2S$ $[M]^+$ 252.0057, found: 252.0060.

**Synthesis of 2,8-Bis(1,9-dimethyl-phenothiazin-10-yl)dibenzothiophene-*S,S*-dioxide(5)**



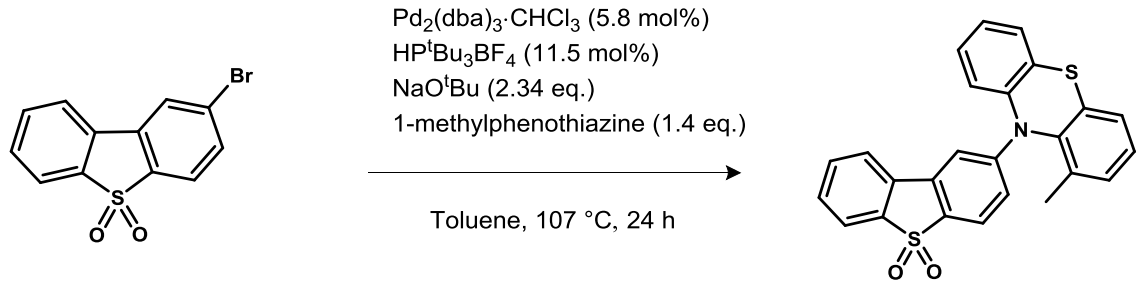

23% Yield

This procedure was based on a modified literature procedure for the synthesis of 1,8-dimethyl-9-(4-nitrophenyl)carbazole.[13]

To a stirred solution of 1,9-dimethylphenothiazine (590 mg, 2.6 mmol, 2 eq.) in dry DMF (17 mL) under argon was added $Cs_2CO_3$ (2.11 g, 6.5 mmol, 5 eq.). The reaction mixture was stirred at ambient temperature for 30 minutes after which 2,8-difluorodibenzothiophene-*S,S*-dioxide (327 mg, 1.3 mmol, 1 eq.) was added in one portion. The reaction mixture was then heated with vigorous stirring at 155 °C for 16 h. The reaction mixture was allowed to cool to ambient temperature and then water (50 mL) was added. The aqueous mixture was then extracted with $CH_2Cl_2$ (4 × 75 mL). The combined organic extracts were dried with $MgSO_4$ and were filtered. The solvent was removed under reduced pressure to give a crude residue. The residue was purified by silica gel column chromatography eluting with $CH_2Cl_2$. The solvent was removed under reduced pressure to give the title compound as an off-white solid (200 mg, 23% yield). The title compound can be sublimed as described for compound **4**. Crystals suitable for X-ray diffraction were obtained by layering with $CH_2Cl_2$:hexane.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.66 (d, *J* = 8.7 Hz, 2H), 7.52 (m, 4H), 7.48 (m, 4H), 7.39 (t, *J* = 7.7 Hz, 4H), 6.39 (dd, *J* = 8.7, 2.3 Hz, 2H), 6.17 (d, *J* = 2.3 Hz, 2H), 2.39 (s, 12H); $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 148.9, 138.8, 136.8, 135.5, 132.0, 129.6, 128.7, 127.6, 126.7, 123.6, 114.0, 103.5, 17.5; HRMS-ASAP$^+$ *m/z* calculated for $C_{40}H_{31}N_2O_2S_3$ $[M+H]^+$ 667.1548, found: 667.1565; Anal. Calc. for $C_{40}H_{30}N_2O_2S_3$ C, 72.04; H, 4.53; N. 4.20. Found: C, 71.84; H, 4.40; N, 4.21; m.p. decomp > 350 °C.

**Synthesis of 2(1-methylphenothiazin-10-yl)dibenzothiophene-*S,S*-dioxide (7)**



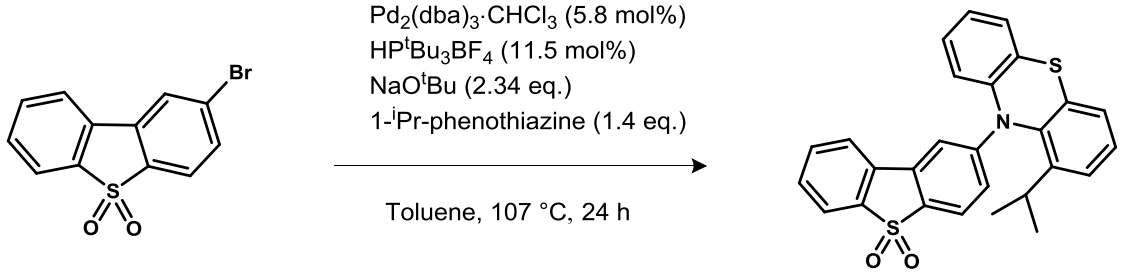

38% Yield

Using general procedure **3**, 2-bromodibenzothiophene-*S,S*-dioxide (400 mg, 1.22 mmol, 1 eq.), 1-methylphenothiazine (366 mg, 1.718 mmol, 1.4 eq.), $Pd_2(dba)_3{\cdot}CHCl_3$ (74 mg, 71 μmol, 0.058 eq.), $HP^tBu_3BF_4$ (41 mg, 141 μmol, 0.115 eq.), $NaO^tBu$ (275 mg, 2.86 mmol, 2.34 eq.) and toluene (25 mL) were used to make the title compound. The crude mixture was purified using silica gel column

chromatography eluting with $CH_2Cl_2$. Solvent was removed under reduced pressure to give a yellow residue. The residue was recrystallized by slow layer diffusion with $CH_2Cl_2$/hexane. Solvent was pipetted from the formed off-yellow crystals to give pure product (198 mg, 38% yield). The crystals obtained were used for X-ray diffraction analysis.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.92 – 7.85 (m, 2H), 7.79 – 7.67 (m, 4H), 7.64 – 7.52 (m, 3H), 7.48 – 7.39 (m, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 6.65 (dd, *J* = 8.7, 2.3 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 150.8, 141.1, 139.3, 139.1, 137.2, 137.1, 136.8, 133.6, 133.4, 131.8, 130.4, 129.6, 129.6, 129.1, 128.2, 127.6, 127.2(6), 127.3(4), 127.1, 123.4 , 122.0, 121.4, 114.4, 105.1, 18.1; HRMS-ASAP$^+$ *m/z* calculated for $C_{25}H_{17}NO_2S_2$ $[M]^+$ 427.0701, found: 427.0705; Anal. Calc. for $C_{25}H_{17}NO_2S_2$ C, 70.23; H, 4.01; N, 3.28. Found: C, 69.92; H, 3.97; N, 3.21; m.p. 290 – 292 °C.

**Synthesis of 2-(1-isopropylphenothiazin-10-yl)dibenzothiophene-*S*,*S*-dioxide (8)**

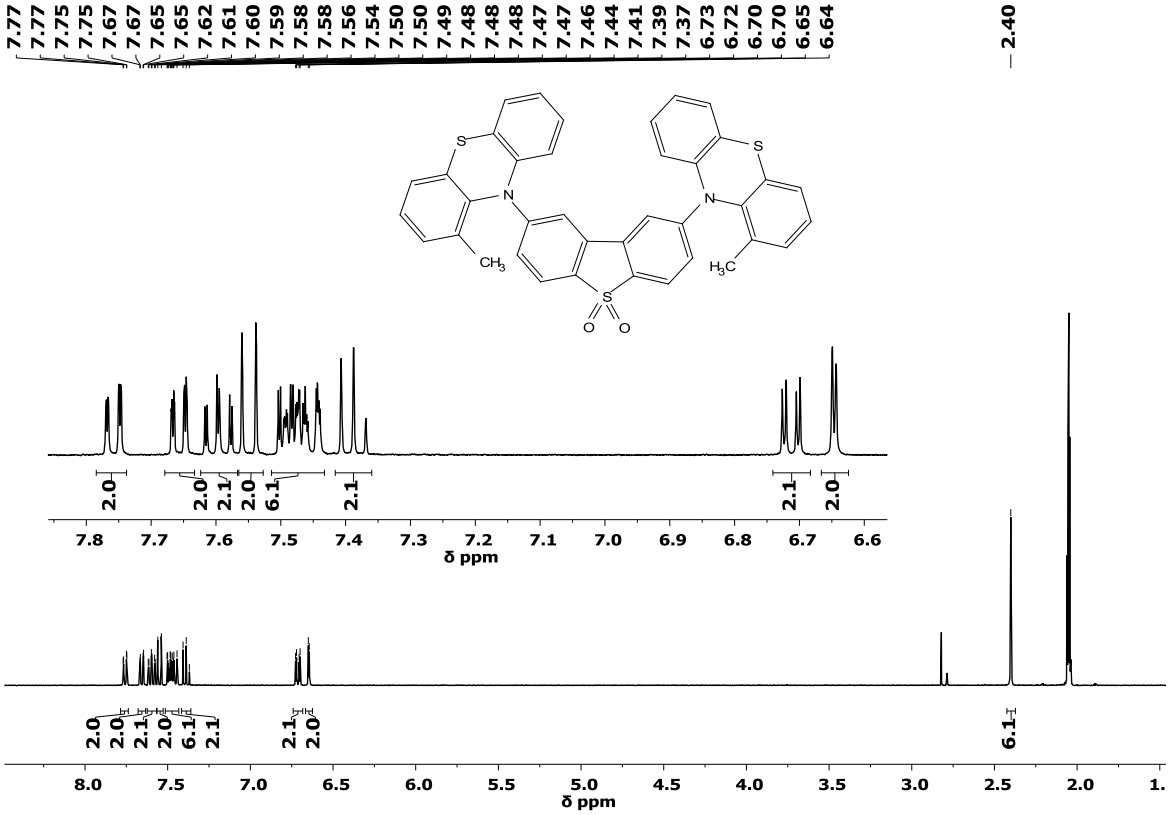


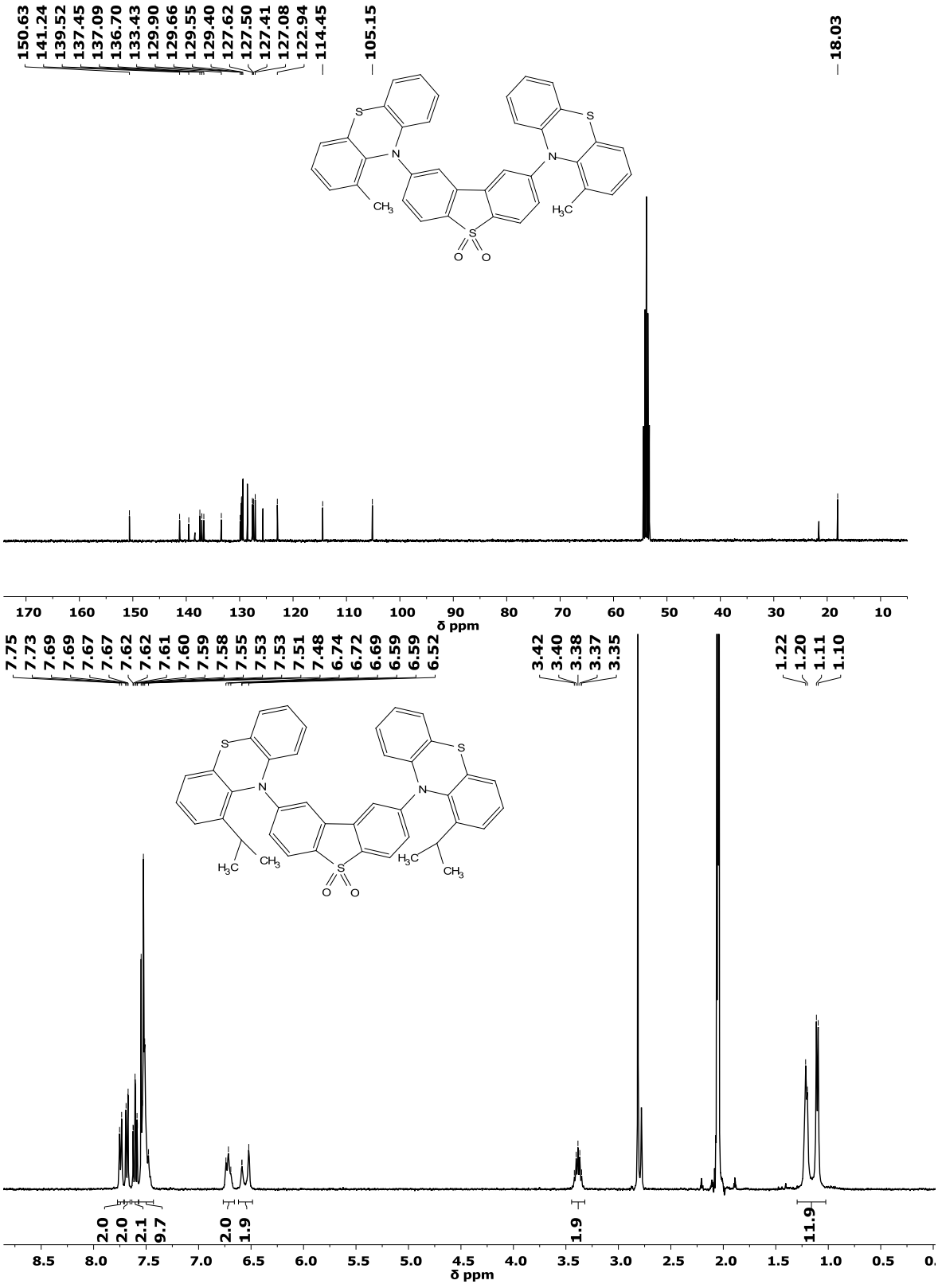

31% Yield

Using general procedure **3**, 2,8-dibromodibenzothiophene-*S*,*S*-dioxide (400 mg, 1.22 mmol, 1 eq.), 1-isopropylphenothiazine (516 mg, 1.72 mmol, 1.4 eq.), $Pd_2(dba)_3{\cdot}CHCl_3$ (74 mg, 71 μmol, 0.058 eq.), $HP^tBu_3BF_4$ (41 mg, 141 μmol, 0.115 eq.), $NaO^tBu$ (275 mg, 2.86 mmol, 2.34 eq.) and toluene (20 mL) were used to make the title compound. The crude mixture was purified by silica gel column chromatography eluting with $CH_2Cl_2$. Removal of solvent under reduced pressure gave a yellow residue. The residue was recrystallized by stirring in boiling hexane (10 mL) for 10 minutes and slowly adding $CHCl_3$ until dissolution was achieved. Gradual cooling down to −18 °C resulted in product crystallisation. The product was filtered and washed with hexane to give the title product as an off-white solid (170 mg, 31% yield). The title compound can be sublimed as described for compound **3**.

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 7.87 (dd, *J* = 7.8, 1.4, 1H), 7.82 – 7.79 (m, 1H), 7.72 – 7.66 (m, 3H), 7.66 – 7.58 (m, 3H), 7.57 – 7.51 (m, 2H), 7.49 – 7.39 (m, 2H), 7.12 (d, *J* = 2.3 Hz, 1H), 6.77 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.49 (hept, *J* = 7.0 Hz, 1H), 1.40 (d, *J* = 7.0 Hz, 3H), 1.14 (d, *J* = 7.0 Hz, 3H); $^{13}$C NMR (101 MHz, Acetone-$d_6$) δ 152.5, 148.6 , 142.2, 140.3, 138.7, 137.8, 137.4, 134.6, 133.8, 131.9, 131.6, 130.2, 130.1, 129.6, 129.0, 128.8, 128.4, 127.8, 126.2, 123.8, 122.4, 122.4, 115.4, 106.1, 29.5, 25.7, 21.4; HRMS-ASAP$^+$ *m/z* calculated for $C_{27}H_{21}NO_2S_2$ $[M]^+$ 455.1404, found: 455.1018; Anal. Calc. for $C_{27}H_{21}NO_2S_2$ C: 71.18 H: 4.65 N: 3.07, Found: C: 71.12 H: 4.60 N: 3.11; m.p. 254 – 256 °C.

## S3 - $^{1}H$ and $^{13}C$ NMR spectra of new compounds

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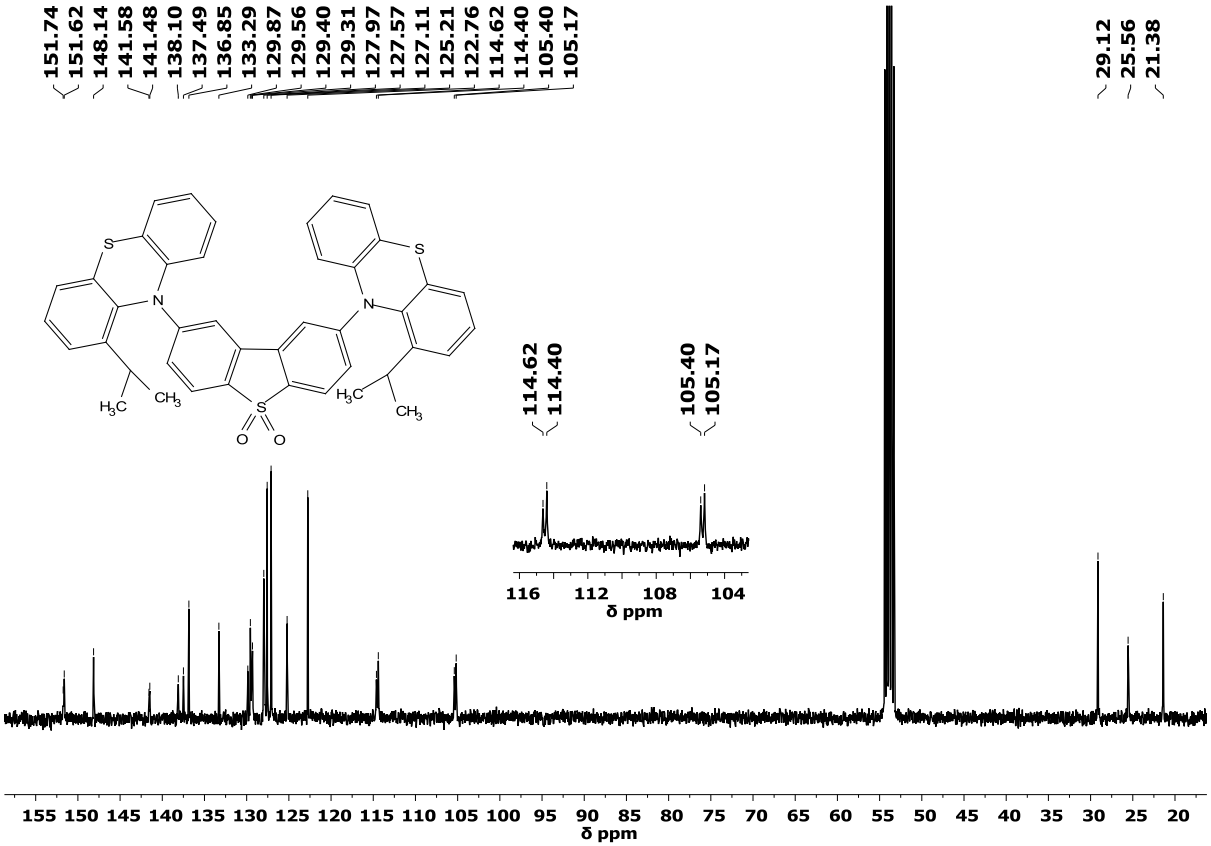
129.55
129.40
127.62
127.50
127.41
127.08
122.94
114.45
105.15
18.03
δ ppm
7.75
7.73
7.69
7.69
7.67
7.67
7.62
7.62
7.61
7.60
7.59
7.58
7.55
7.53
7.53
7.51
7.48
6.74
6.72
6.69
6.59
6.59
6.52
3.42
3.40
3.38
3.37
3.35
1.22
1.20
1.11
1.10
2.0
2.0
2.1
9.7
2.0
1.9
1.9
11.9
δ ppm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136.85
133.29
129.87
129.56
129.40
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127.97
127.57
127.11
125.21
122.76
114.62
114.40
105.40
105.17
29.12
25.56
21.38
S
N
S
N
H3C
CH3
S
O
O
H3C
CH3
114.62
114.40
105.40
105.17
116
112
108
104
δ ppm
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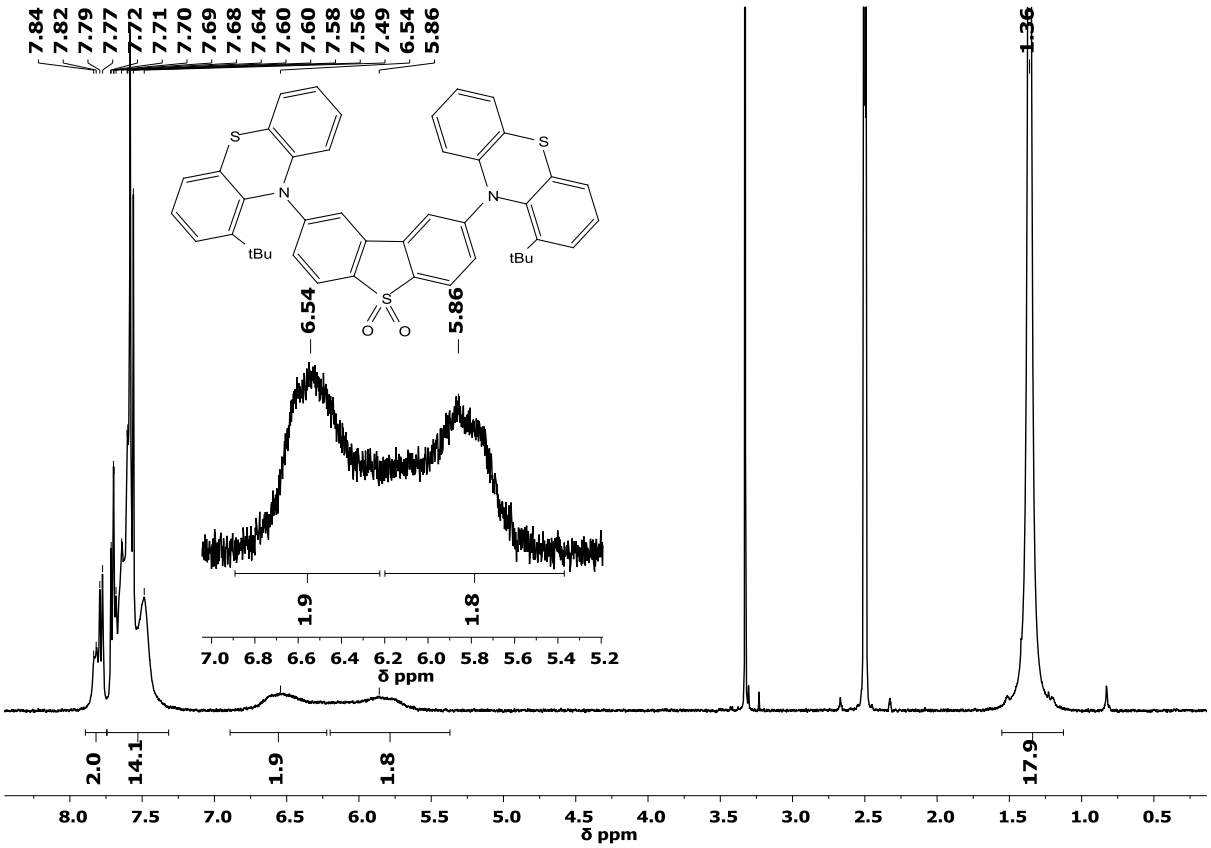
δ ppm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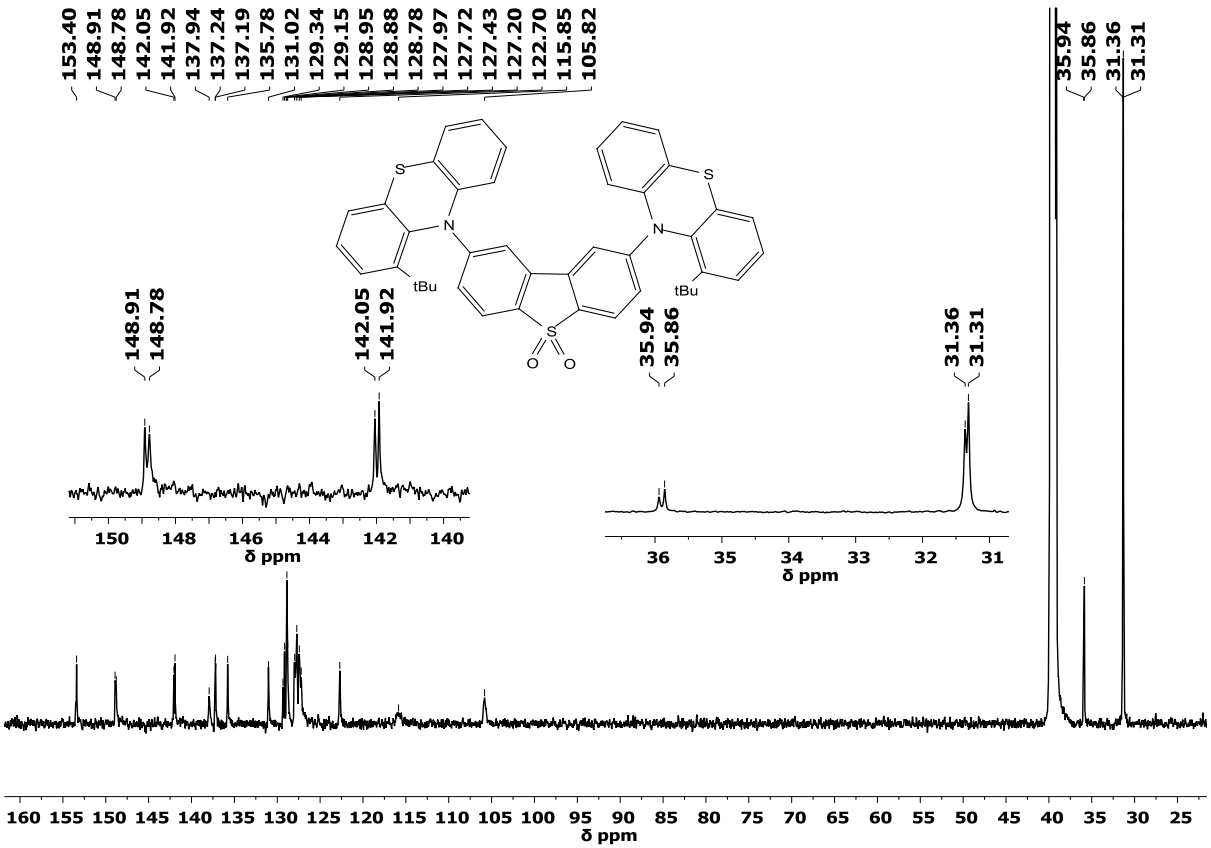
7.71
7.70
7.69
7.68
7.64
7.60
7.60
7.58
7.56
7.49
6.54
5.86
1.36
S
N
S
N
tBu
tBu
S
O
O
6.54
5.86
1.9
1.8
7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2
δ ppm
2.0
14.1
1.9
1.8
17.9
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
δ ppm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148.78
142.05
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137.24
137.19
135.78
131.02
129.34
129.15
128.95
128.88
128.78
127.97
127.72
127.43
127.20
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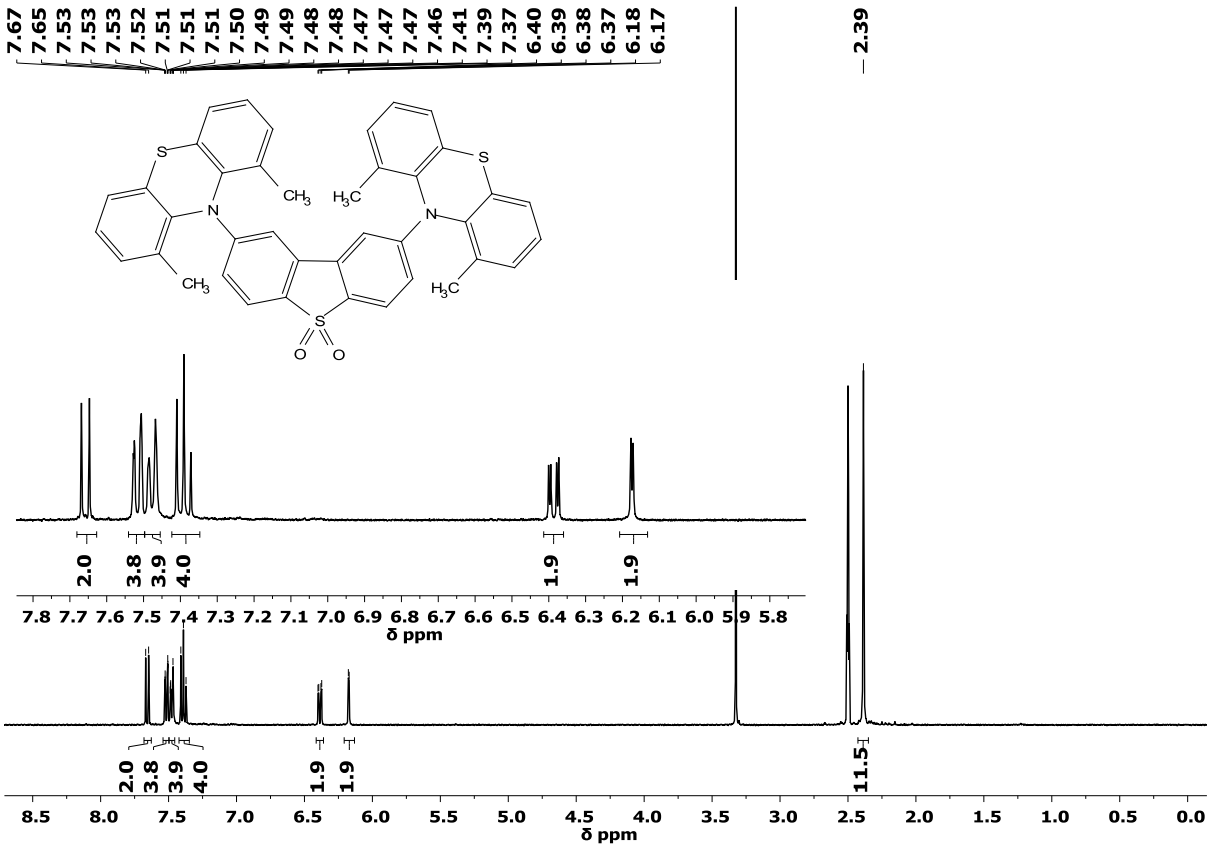
35.94
35.86
31.36
31.31
tBu
tBu
δ ppm
δ ppm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7.47
7.46
7.41
7.39
7.37
6.40
6.39
6.38
6.37
6.18
6.17
2.39
CH3
H3C
CH3
H3C
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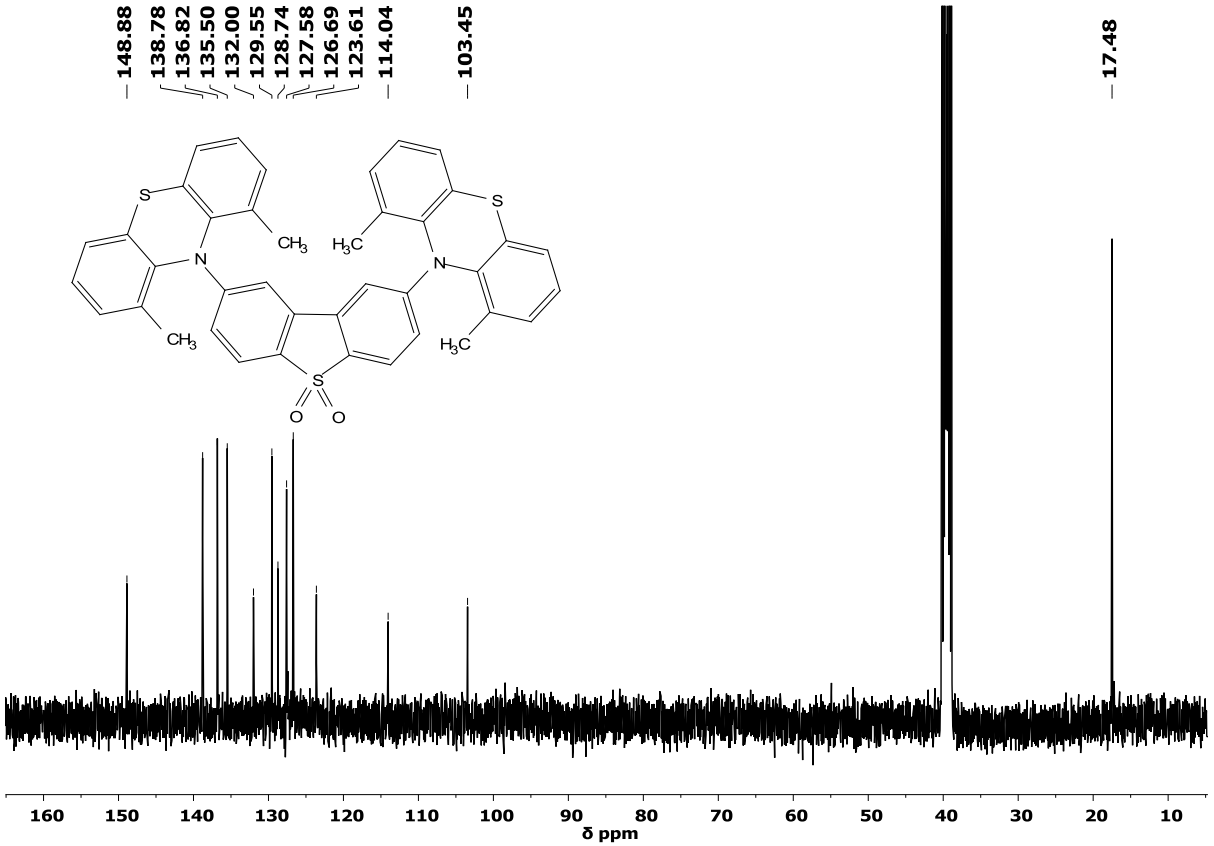
3.9
4.0
1.9
1.9
δ ppm
δ ppm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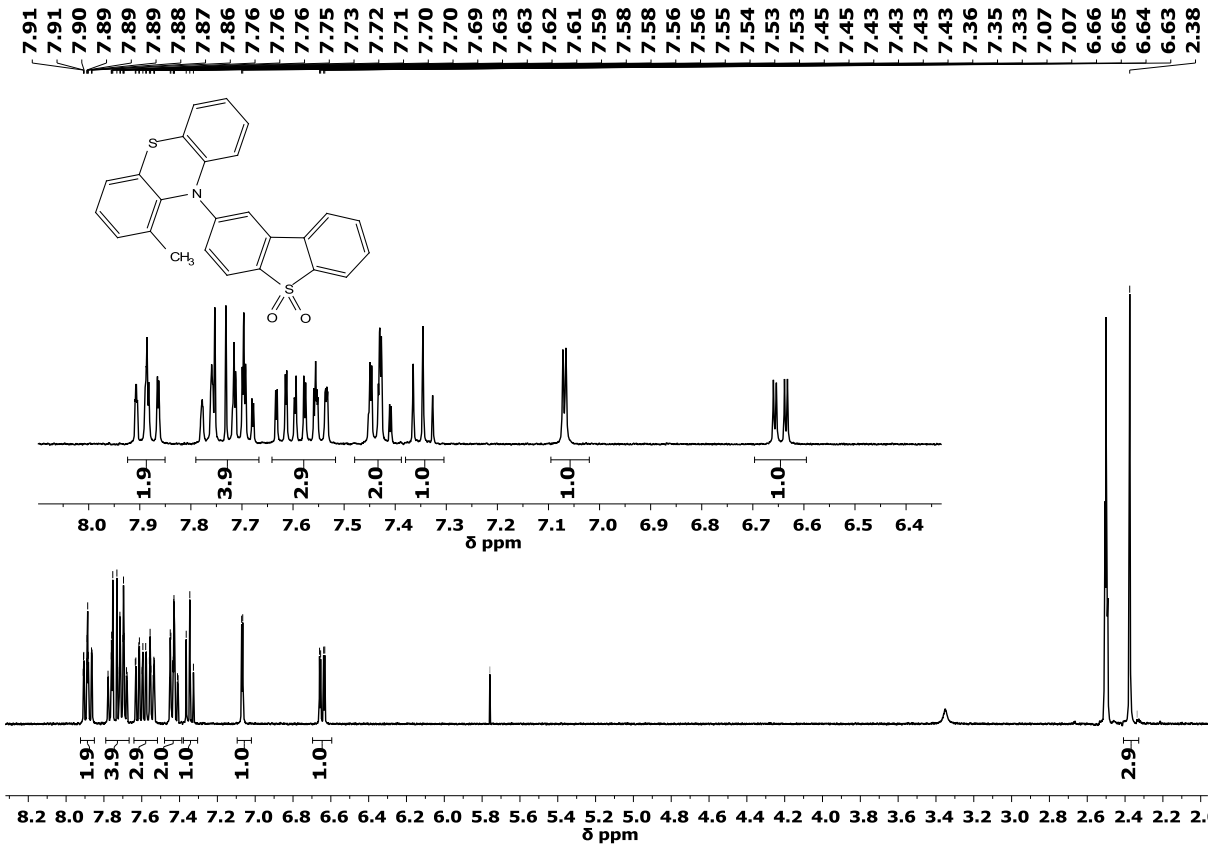
123.61
114.04
103.45
17.48
δ ppm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7.89
7.88
7.87
7.86
7.76
7.76
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7.73
7.72
7.71
7.70
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7.69
7.63
7.63
7.62
7.61
7.59
7.58
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7.55
7.54
7.53
7.53
7.45
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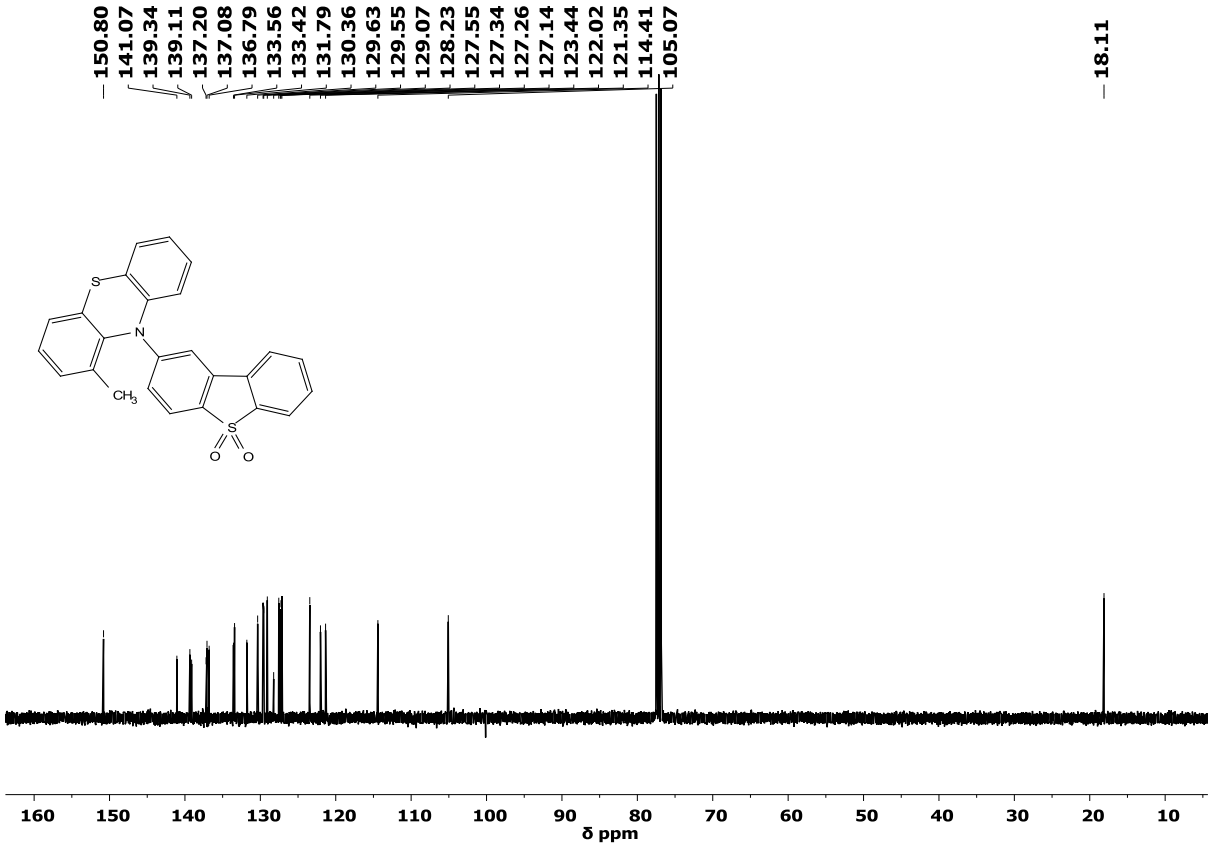
7.43
7.43
7.43
7.43
7.36
7.35
7.33
7.07
7.07
6.66
6.65
6.64
6.63
2.38
1.9
3.9
2.9
2.0
1.0
1.0
1.0
δ ppm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137.20
137.08
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133.56
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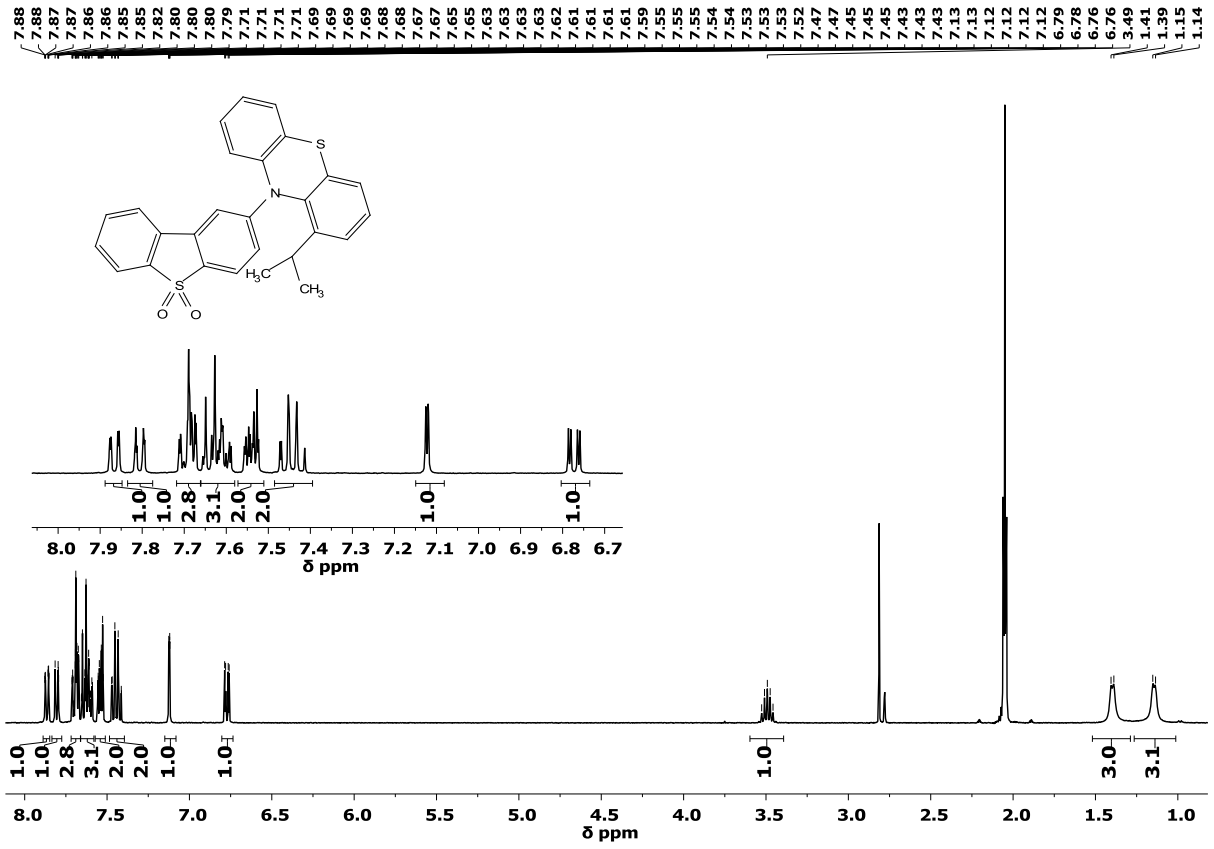
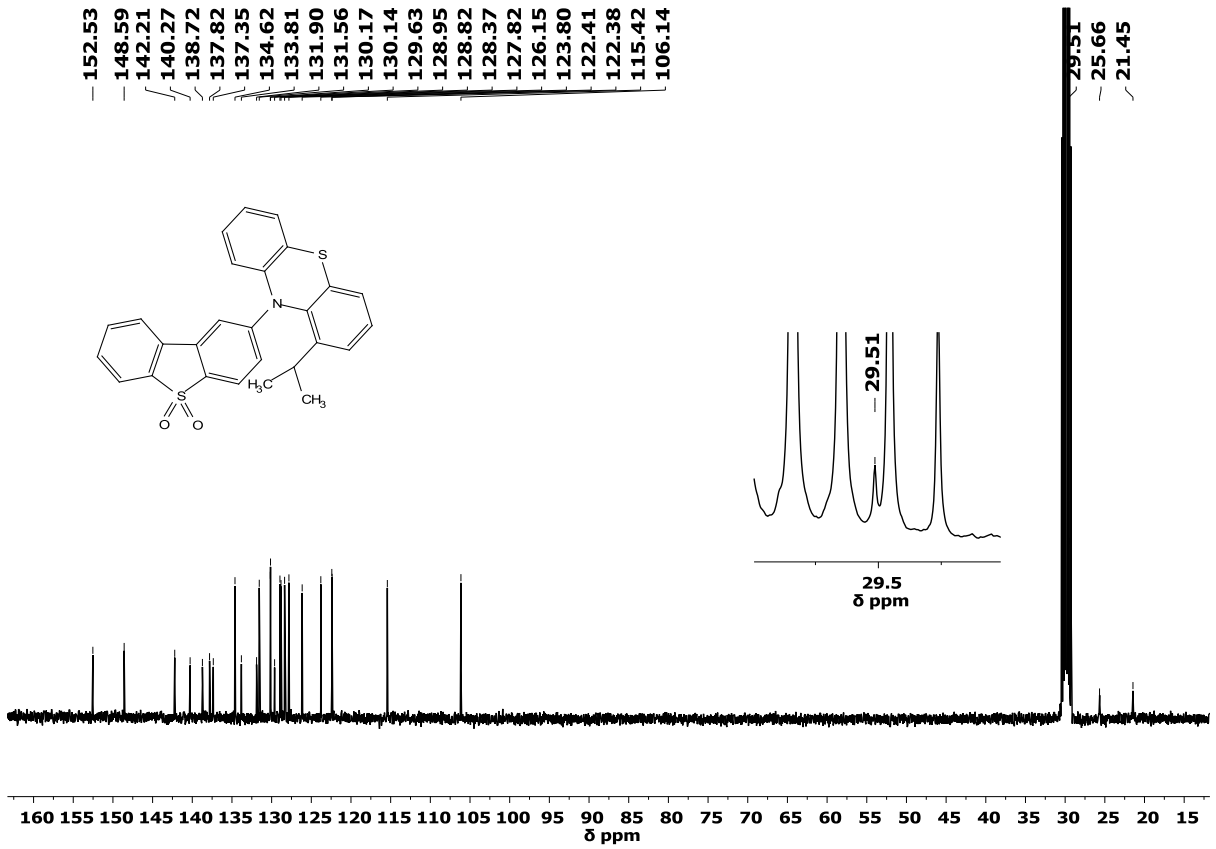
131.79
130.36
129.63
129.55
129.07
128.23
127.55
127.34
127.26
127.14
123.44
122.02
121.35
114.41
105.07
18.11
S
N
CH3
S
O
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
δ ppm


7.88 7.88 7.87 7.87 7.86 7.86 7.85 7.85 7.82 7.80 7.80 7.80 7.79 7.71 7.71 7.71 7.69 7.69 7.69 7.69 7.68 7.68 7.67 7.67 7.65 7.65 7.63 7.63 7.63 7.62 7.61 7.61 7.61 7.59 7.55 7.55 7.55 7.54 7.54 7.53 7.53 7.53 7.52 7.47 7.47 7.45 7.45 7.43 7.43 7.43 7.13 7.12 7.12 7.12 7.12 6.79 6.78 6.76 6.76 3.49 1.41 1.39 1.15 1.14
S
N
S
O
O
H3C
CH3
1.0 1.0 2.8 3.1 2.0 2.0 1.0 1.0
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
δ ppm
1.0 1.0 2.8 3.1 2.0 2.0 1.0 1.0 1.0 3.0 3.1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
δ ppm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138.72
137.82
137.35
134.62
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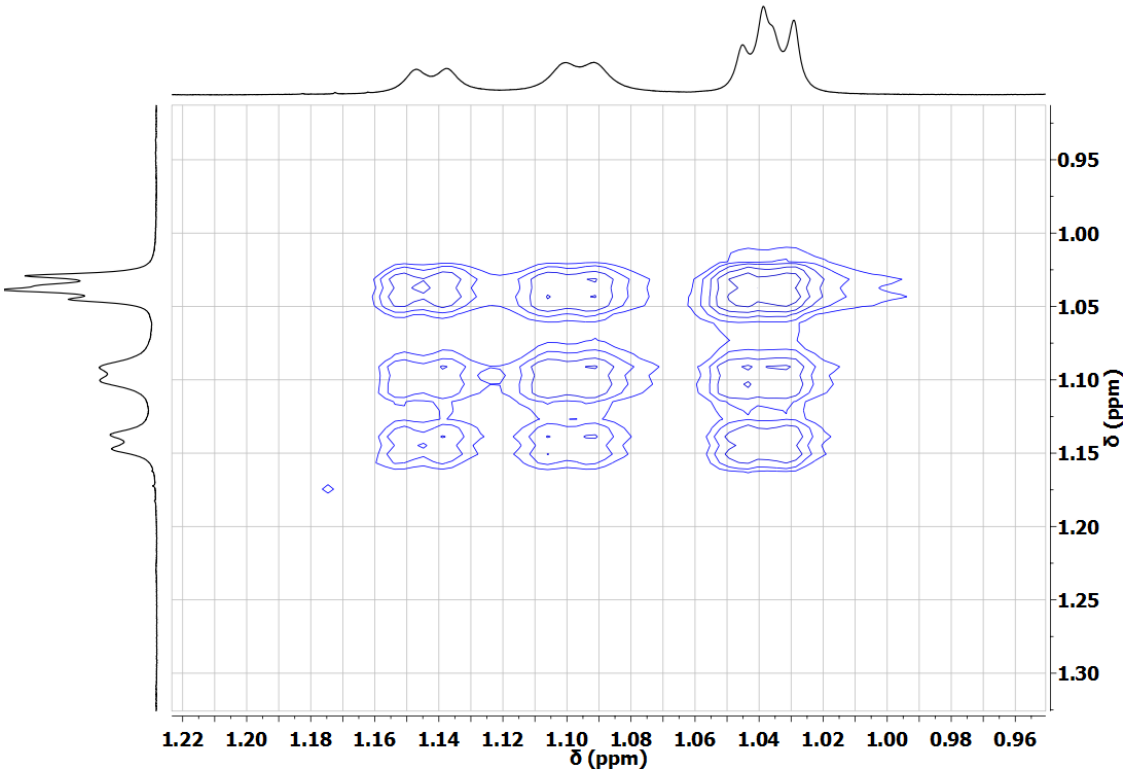
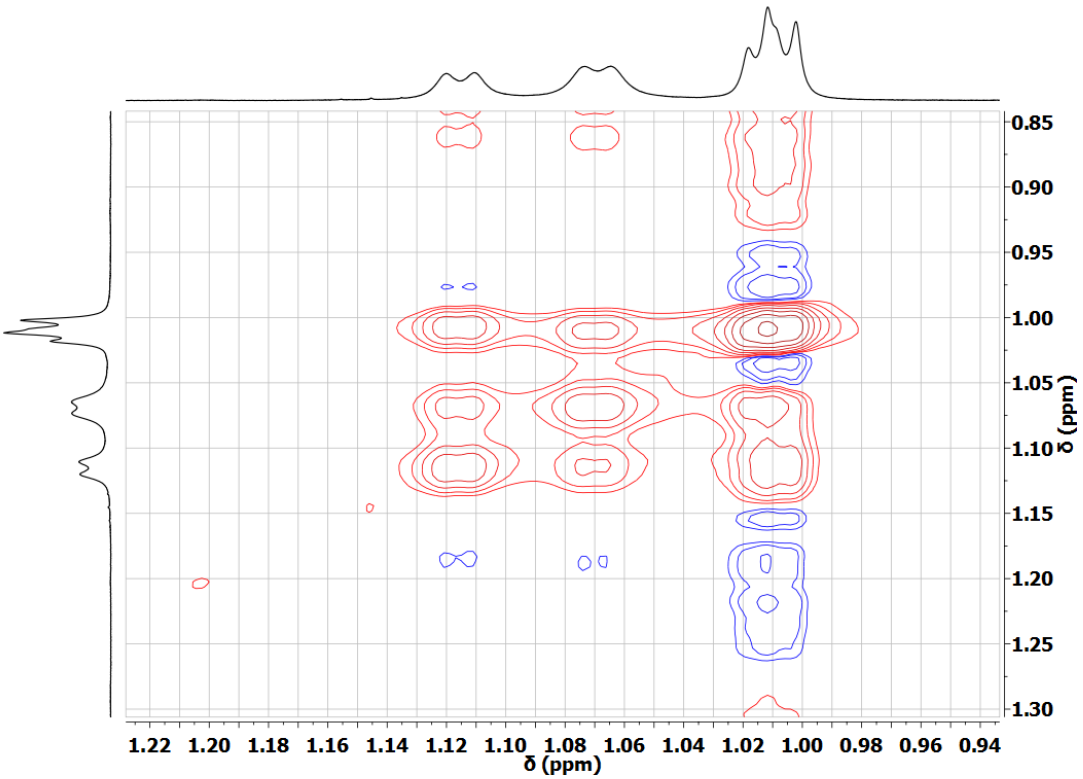
131.90
131.56
130.17
130.14
129.63
128.95
128.82
128.37
127.82
126.15
123.80
122.41
122.38
115.42
106.14
29.51
25.66
21.45
S
N
S
O
O
H3C
CH3
29.51
29.5
δ ppm
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
δ ppm

## S4 – Supplementary 2D NMR data

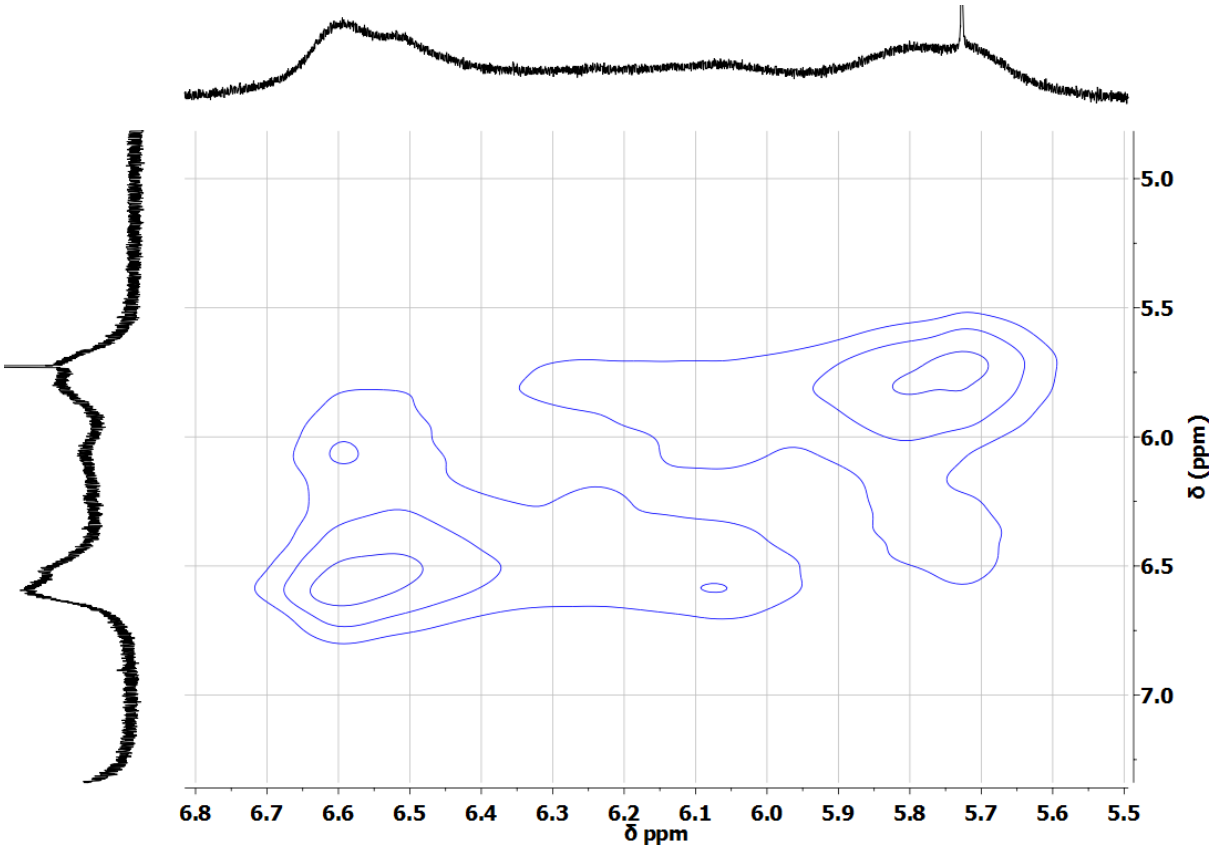
**$^{1}$H NOESY of compound 3 at 298 K**




**$^{1}$H ROESY of compound 3 at 298 K**



**$^{1}$H NOESY of 4 at 298 K**




## S5 – Photophysics: general experimental details

**Sample preparation**:

The solutions in toluene were degassed by freeze-pump-thaw techniques, in sequential cycles of freeze-pump-thaw in special cuvettes, repeated four times.

The thin films were fabricated by mixing a 1:2 *v/v* solution of the emissive compounds in toluene and zeonex in toluene (5 mg $mL^{-1}$ and 127 mg $mL^{-1}$, respectively). Films were then deposited on a sapphire substrate and dried under vacuum for 24 hours. A cryostat was used to carry out the experiments in solid state.

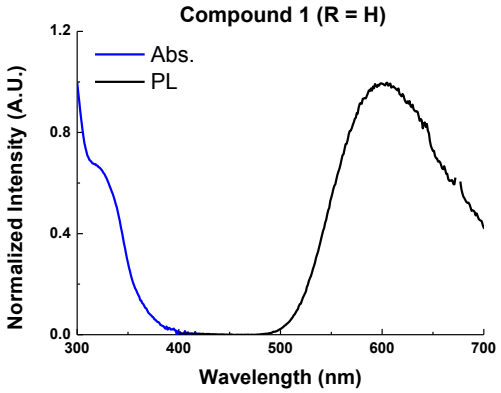
**Photophysics experiments**:

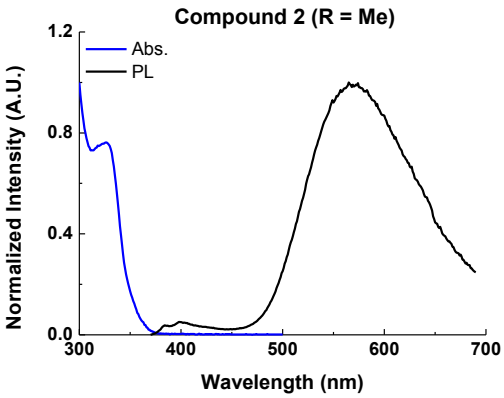
Steady-state fluorescence spectra were collected using a fluorometer (Flourolog - Horiba Jobin Yvon) excited at 355 nm. Steady-state absorption experiments were performed using a Shimadzu UV/VIS/NIR spectrometer.

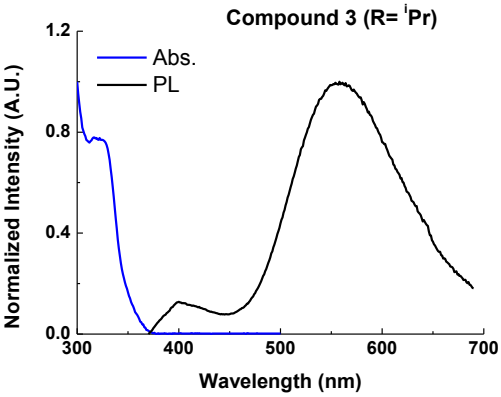
Time decay experiments were performed using a Nd:YAG pulsed laser, working at 10 Hz repetition rate, 150 ps pulse width and excitation wavelength of 355 nm. The luminescence was collected through a JY-190 spectrograph and detected with a single photon sensitive gated iCCD (intensified CCD) camera (Stanford Computer Optics 4 Picos) with 200 ps resolution.

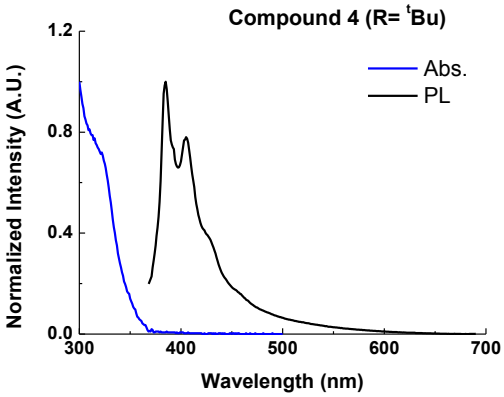
# S6 - Supplementary photophysical data

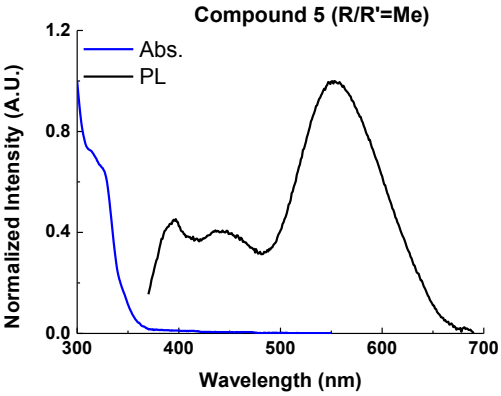
## S6.1 - Steady State Emission/Absorption in Toluene for 1–8, excited at 355 nm, without oxygen at 290 K

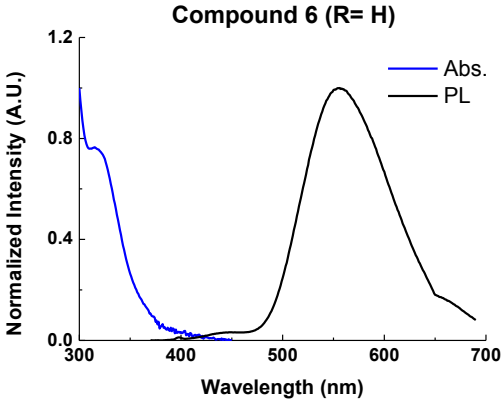


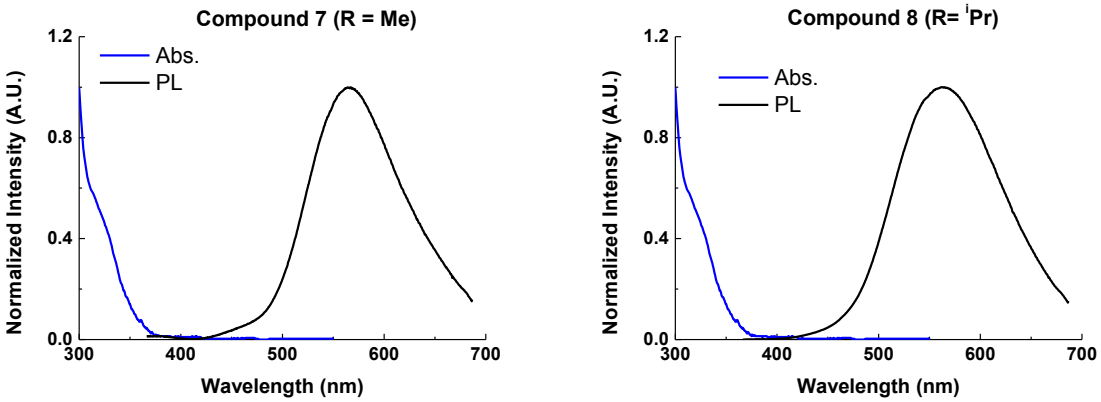



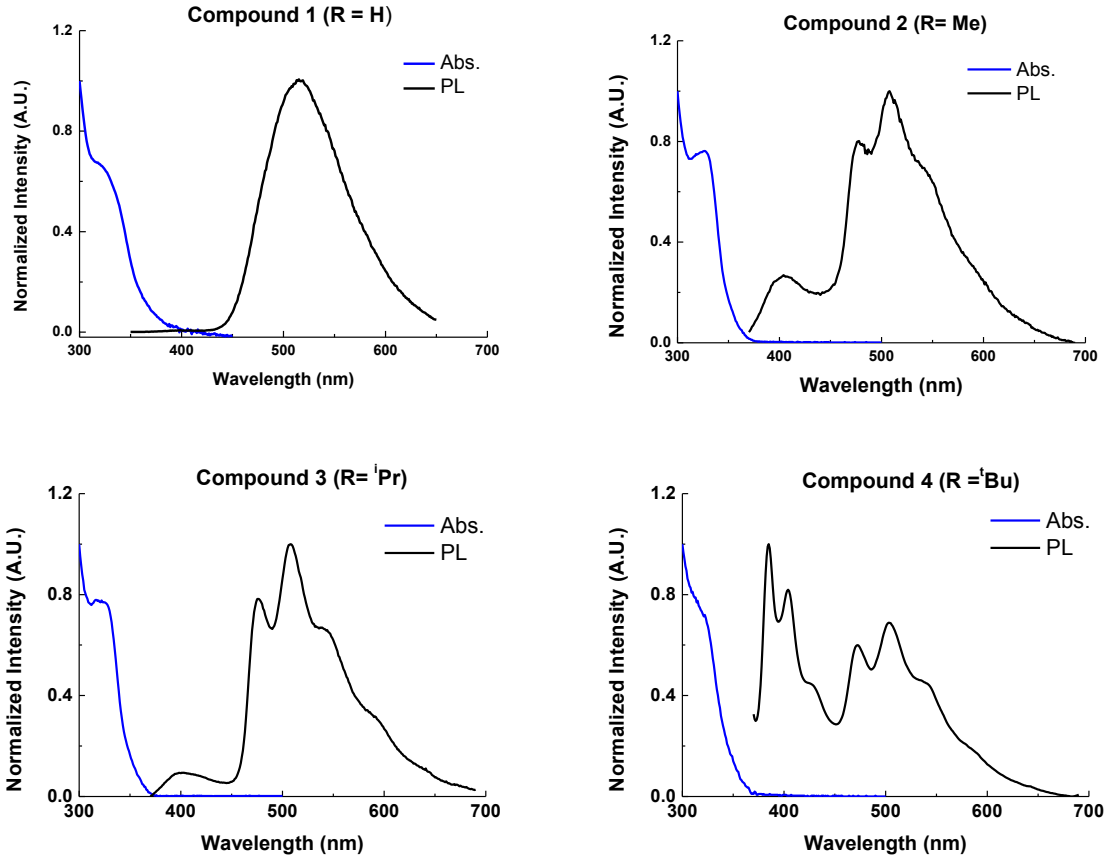



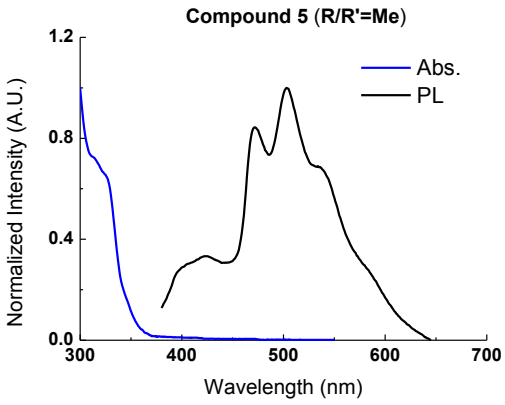



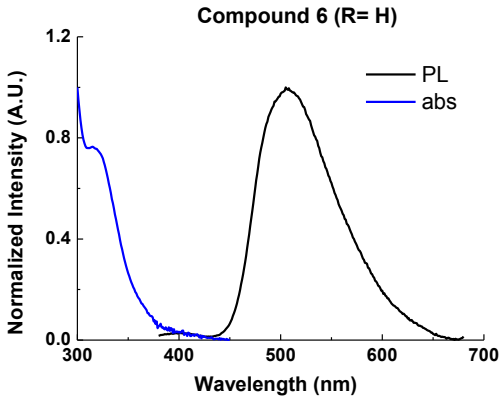



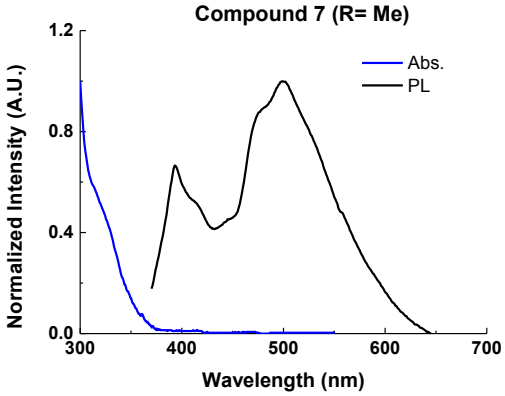


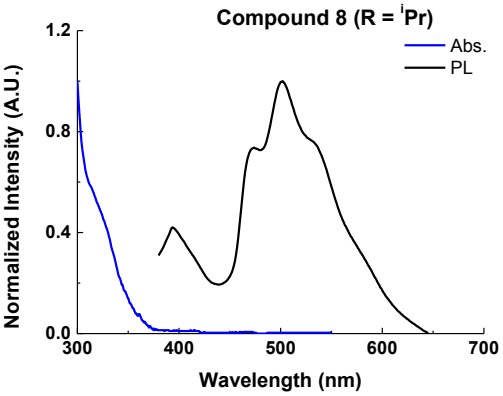

**S6.2 - Steady State Emission in zeonex thin film. Absorption in toluene for 1–8, excited at 355 nm, without oxygen at 290 K**



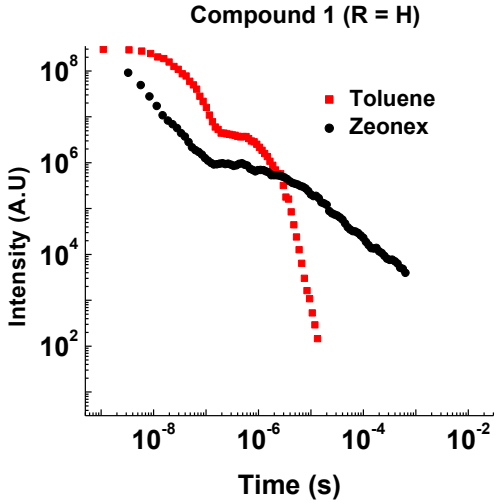


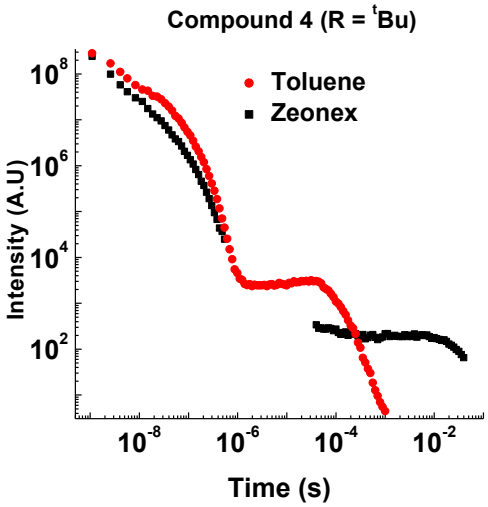



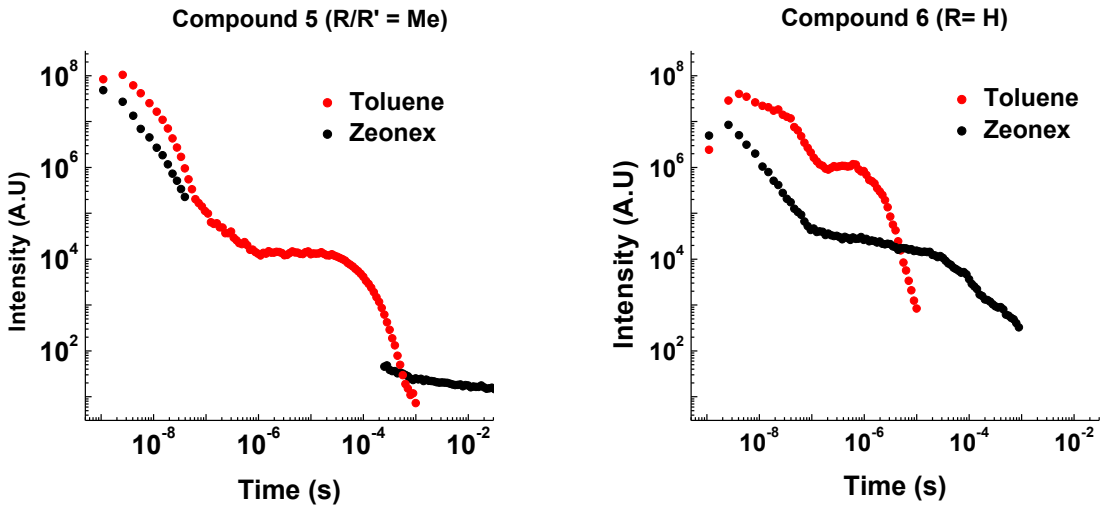



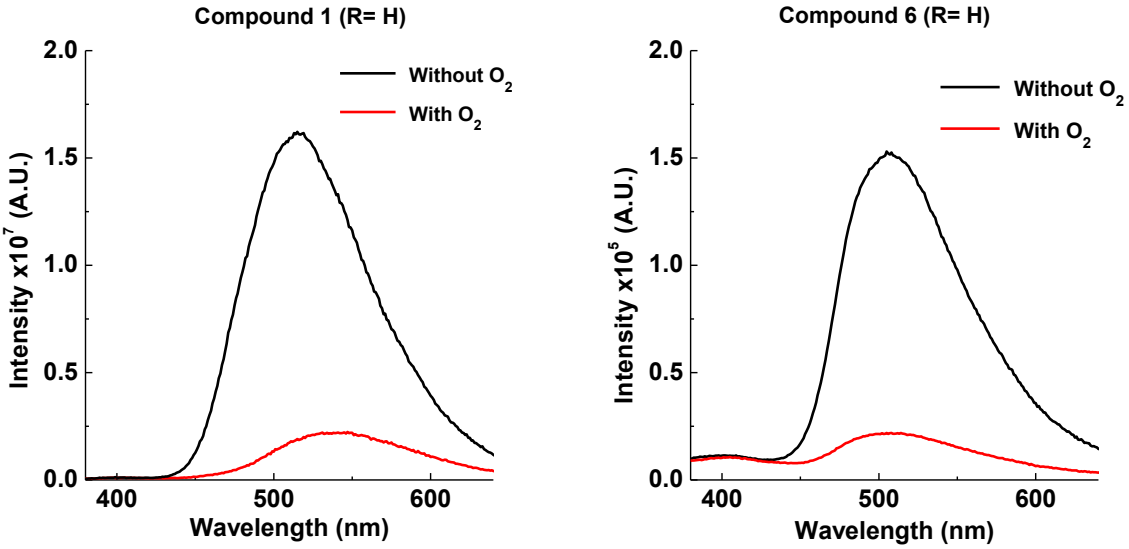

**S6.3 - Time resolved emission decay for compounds 1, 4, 5 and 6 in toluene and zeonex at 290 K**



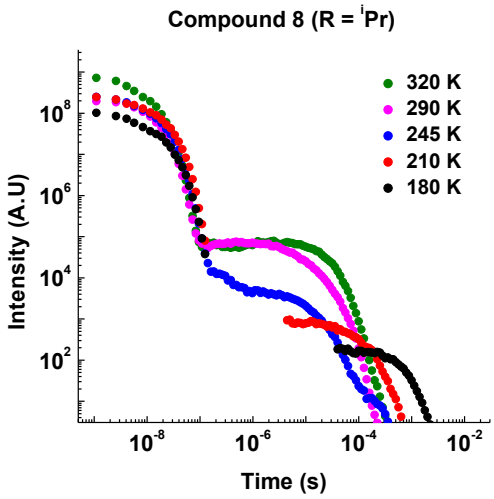





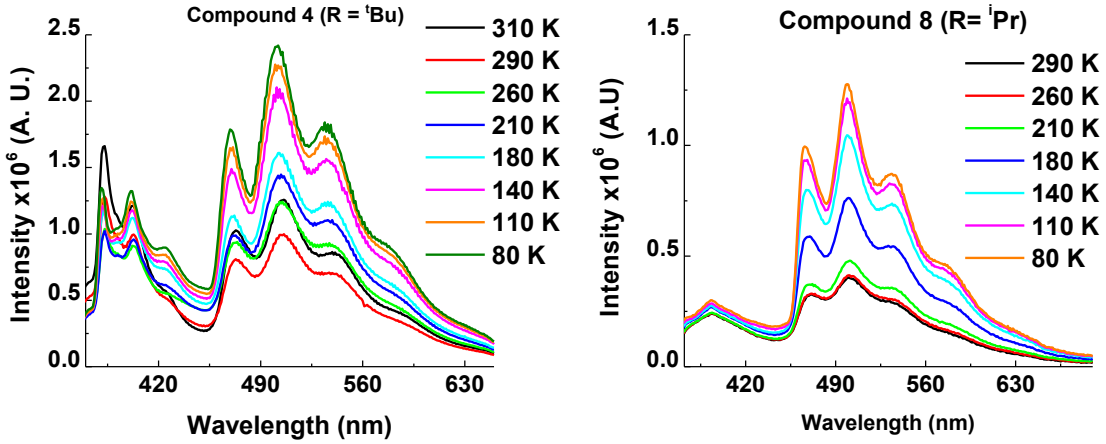

**S6.4 - Emission for 1 and 6 in zeonex film with and without oxygen at 290 K (excitation at 355 nm)**



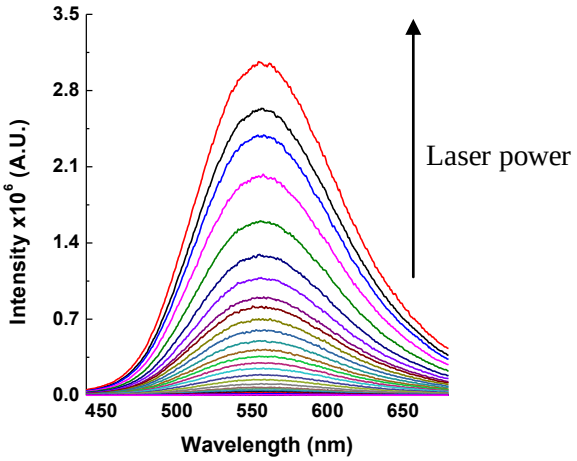
**S6.5 – Time resolved emission for 8 in toluene at varying temperature**




**S6.6 – Temperature dependence of emission of compounds 4 and 8 in zeonex**




**S6.7 – Power dependence spectra for 2 at 290 K**



**S6.8 – Key features of TADF and phosphorescence in the present context**

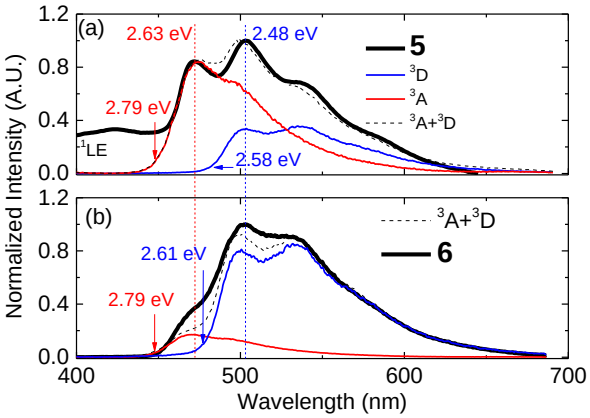
Both TADF and phosphorescence involve triplet harvesting. There are several standard ways to distinguish these two emissions, which we have used in this work.

1) TADF originates from a singlet state with charge transfer character and appears as a broad, structure-less Gaussian band and is strongly affected by the polarity of the solvent showing a shift to lower energies when the solvent polarity increases, concomitant with a large permanent dipole moment of the CT state. The phosphorescence is due to direct emission from a triplet excited state, normally a local triplet state, and so appears with a well-resolved spectrum, as is the case here, and without showing significant shifts with the solvent polarity concomitant with a local exciton having near zero dipole moment. This can be easily seen by comparing the emissions of compound **1** and **5** in zeonex (shown in SI S6.2). The restriction effect due to the presence of the two Me groups in **5**, enhances emission from $^1$LE at 400 nm, suppresses the CT state and activates $^3$LE phosphorescence.

2) TADF involves harvesting from a triplet state to a singlet state with CT character, and this process is thermally activated, i.e., by decreasing the temperature less TADF emission is observed. In contrast, the phosphorescence involves direct emission from the triplet state and so by decreasing the temperature the quenching effect of vibrations is reduced and the phosphorescence intensity increases, as observed in the present work (SI S6.6).

3) The lifetime of both TADF and phosphorescence follows the triplet state. However, TADF results from the interconversion of triplet states into singlet states by reverse intersystem crossing, and direct phosphorescence involves only the decay of the triplet state to the ground state. In the case of TADF the triplet lifetime is affected by an additional deactivation process and so TADF lifetimes are shorter than phosphorescence lifetimes. This effect can be observed by comparing the luminescence decays of compounds **6** (no phosphorescence) and **4** (phosphorescence) in zeonex. The relevant Figures are shown in SI S6.3.

4) Finally, phosphorescence is emission from a local triplet excited state and carries the clear signature of the phosphorescence emission of the phenothiazine donor ($^3$D) and dibenzothiophene-*S*,*S*-dioxide acceptor ($^3$A). This is seen in the figure below, where the phosphorescence of compound **6** at low temperature is compared with the phosphorescence of compound **5** at RT, and both are compared with the phosphorescence of the donor and acceptor isolated fragments. Clearly the phosphorescence of **5** and **6** are similar to the superposition of the phosphorescence of D and A which strongly indicates that the phosphorescence is from a local triplet state and not from a CT state.




## S7 – Cyclic voltammetric data [14-17]

### Materials and methods

The electrochemical cell comprised of platinum electrode with a 1 mm diameter of working area as a working electrode, an Ag/AgCl electrode as a reference electrode and a platinum coil as an auxiliary electrode. Cyclic voltammetry measurements were conducted at room temperature at a potential rate of 50 mV $s^{-1}$ and were calibrated against a ferrocene/ferrocenium redox couple.

CV measurements were conducted in 1.0 mM concentrations of all compounds in 0.1 M solutions of $Bu_4NBF_4$, 99% (Sigma Aldrich) in dichloromethane ($CH_2Cl_2$), CHROMASOLV®, 99.9% (Sigma Aldrich) at room temperature.

From the onset of the redox peaks it is possible to estimate the ionization potential (IP) and the electron affinity (EA) provided that these potentials are expressed on the absolute potential scale, i.e. with respect to the vacuum level. The absolute potential of $Fc/Fc^+$ in non-aqueous electrolytes is 5.1 V.This leads to the following equation:

$$IP(eV) = |e|(E_{ox(onset)} + 5.1) \quad (1)$$

$$EA(eV) = -|e|(E_{red(onset)} + 5.1) \quad (2)$$

The HOMO-LUMO levels were determined electrochemically, using cyclic voltammetry (CV) analysis by the estimation of the electron affinity and the ionization potentials which are similar to the HOMO and LUMO energies.

### Results

**Table S7.1 - HOMO-LUMO levels for compounds 2–5, 7–8**

| Compound | HOMO (eV) | LUMO (eV) |
|---|---|---|
| 2 (R = Me) | -5.78 | -2.70 |
| 3 (R = $^i$Pr) | -5.92 | -2.71 |
| 4 (R = $^t$Bu) | -6.11 | -2.68 |
| 5 (R/R' = Me) | -6.11 | -2.67 |
| 7 (R= Me) | -5.81 | -2.80 |

| | | |
|---|---|---|
| 8 (R = $^{i}$Pr) | -5.90 | -2.79 |

All of the investigated compounds showed both oxidation and reduction processes. The D–A derivatives of dibenzothiophene-*S*,*S*-dioxides (**7**, **8**) had slightly lower HOMO levels (ca. 0.03 eV) and much lower LUMO levels (ca. 0.1 eV) than their corresponding D–A–D analogues (**2**, **3**). With increasing of the size of alkyl side group a significant decrease in the HOMO was observed as a result of increased steric hindrance within the molecules. There is almost no difference in the energy of the HOMO-LUMO levels between *t*-butyl mono-substitution (compound **4**) and dimethyl substitution (compound **5**) suggesting that in both compounds there is an extensive twist between the planes of the D and A units.

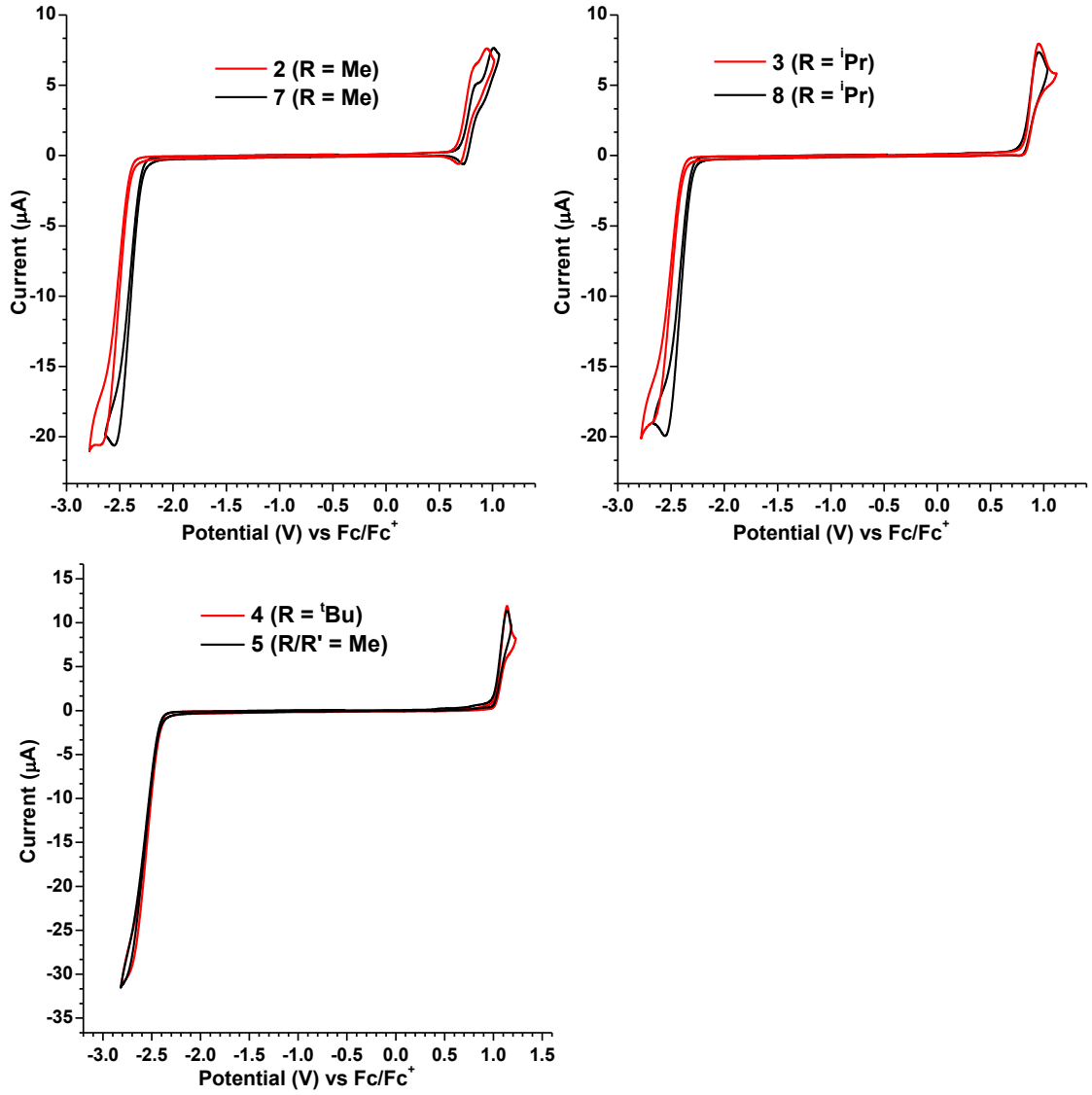
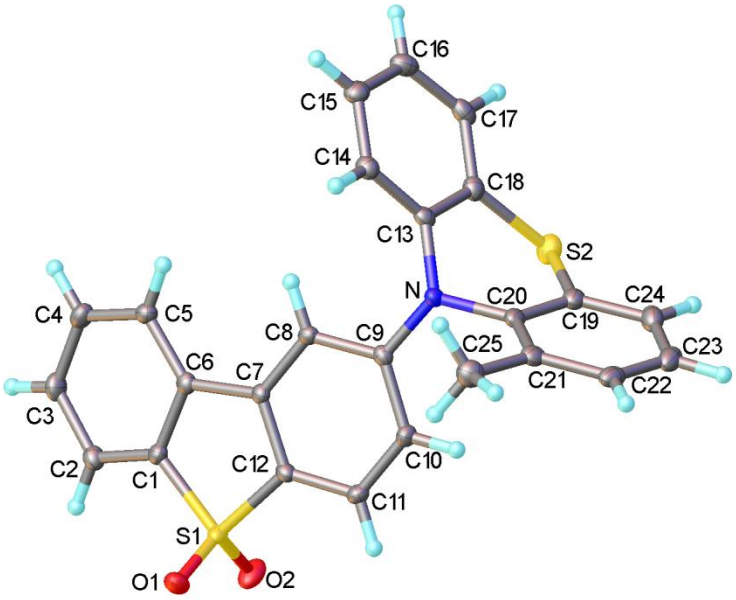


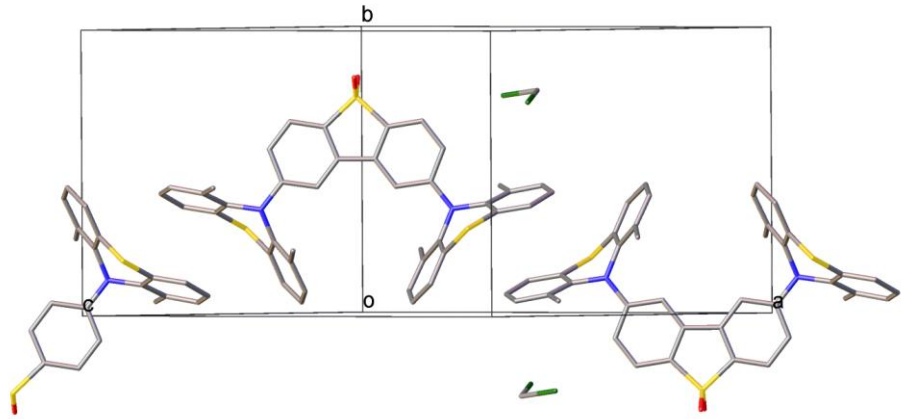

**Figure S7.2** Cyclic voltammetry of 1mM concentration of investigated compounds in 0.1 M $Bu_4NBF_4$/DCM. Measurement conditions: scan rate 50 mV/s, Ag/AgCl – quasi-reference electrode, calibrated against a ferrocene/ferrocenium redox couple.

# S8 – Additional X-ray crystallography data

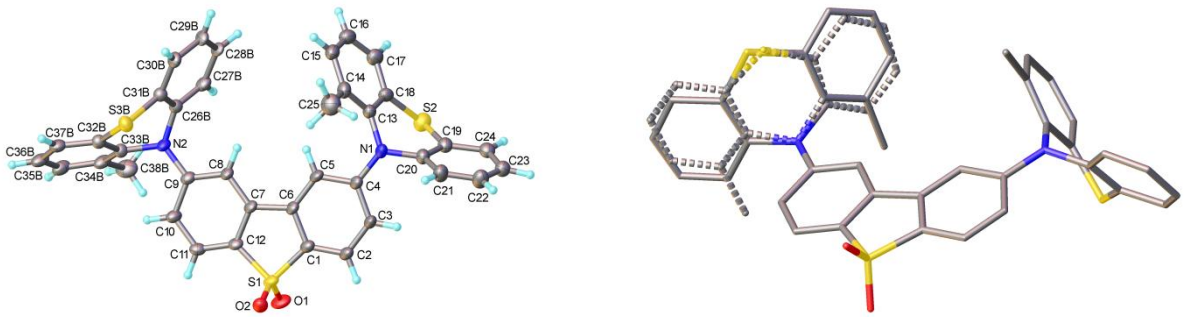
## S8.1 – X-ray molecular structure of 7 with thermal ellipsoids at 50% probability




## S8.2 – Packing of compound 5·2$CH_2Cl_2$ in the X-ray crystal structure.




## S8.3 – The minor conformer of compound 2 (left) and overlap of the two conformers of 2 (right).



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