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Electronic Supplementary Information (ESI)

Antiaromatic Bisindeno-[*n*]thienoacenes With Small Singlet Biradical Characters: Syntheses, Structures and Chain Length Dependent Physical Properties

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1. Experimental Section

1.1. General

All reagents were purchased from commercial sources and used without further purification. Anhydrous dichloromethane (DCM) and *N*,*N*-dimethylformamide (DMF) were distilled from CaH_2. Anhydrous toluene and THF were distilled from sodium benzophenone immediately prior to use. The ^1H NMR and ^{13}C NMR spectra were recorded in solution of $CDCl_3$ or DMSO-d_6 on Bruker DRX 500 NMR spectrometer with tetramethylsilane (TMS) as the internal standard. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. MALDI-TOF mass spectra were recorded on a Bruker Autoflex instrument. High resolution (HR) EI mass spectra were recorded on Agilent 5975C DIP/MS mass spectrometer. HR ACPI mass spectra were recorded on a MicrOTOF-QII instrument. UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-1700 and UV-3600 spectrometer. The electrochemical measurements were carried out in anhydrous DCM with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte at a scan rate of 0.05 V/s at room temperature under the protection of nitrogen. A gold disk was used as working electrode, platinum wire was used as counting electrode, and Ag/AgCl (3M KCl solution) was used as reference electrode. The potential was calibrated against the ferrocene/ferrocenium couple. Continuous wave X-band ESR spectra were obtained with a Bruker ELEXSYS E500 spectrometer using a variable temperature Bruker liquid nitrogen cryostat.

1064 nm FT–Raman spectra were obtained in an FT–Raman accessory kit (FRA/106–S) of a Bruker Equinox 55 FT–IR interferometer. A continuous–wave Nd–YAG laser working at 1064 nm was employed for excitation. A germanium detector operating at liquid nitrogen temperature was used. Raman scattering radiation was collected in a back–scattering configuration with a standard spectral resolution of 4 cm^{-1}. 1000–3000 scans were averaged for each spectrum. Raman spectra with the excitation lasers at 532, 633 and 785 nm were collected by using the 1×1 camera of a Bruker Senterra Raman microscope by averaging spectra during 50 minutes with a resolution of 3–5 cm^{-1}. A CCD camera operating at -50 ºC was used for the Raman detection.

In situ UV-Vis-NIR spectroelectrochemical studies were conducted on a Cary 5000 spectrophotometer from Varian operating in a maximal 175-3300 nm range. A C3 epsilon potentiostat from BASi was used for the electrolysis using a thin layer cell

from a demountable omni cell from Specac. In this cell a three electrodes system was coupled to conduct *in situ* spectroelectrochemistry. A Pt gauze was used as the working electrode, a Pt wire as the counter electrode and a Ag wire as the pseudo-reference electrode. The spectra were collected a constant potential electrolysis and the potentials were changed in interval of 100 mV. The electrochemical medium used was 0.1 M $(n\text{-}C_4H_9)_4NPF_6$ in fresh distilled CH_2Cl_2, at room temperature with sample concentrations of 10^{-3} M.

The femtosecond time-resolved transient absorption spectrometer used for this study consisted of a femtosecond optical parametric amplifier (Quantronix, Palitra-FS) pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an accompanying optical detection system. The generated OPA pulses had a pulse width of ~100 fs and an average power of 1 mW in the range 450 to 800 nm, which were used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (3 mm thick) by focusing of small portion of the fundamental 800 nm pulses, which were picked off by a quartz plate before entering into the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses were monitored by miniature spectrograph (OceanOptics, USB2000+). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 4000 pulses were used to excite samples and to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7^o) using a Glan-laser polarizer with a half-wave retarder to prevent polarization-dependent signals. The cross-correlation fwhm in the pump-probe experiments was less than 200 fs, and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm regions. To minimize chirp, all reflection optics were used in the probe beam path, and a quartz cell of 2 mm path length was employed. After completing each set of fluorescence and TA experiments, the absorption spectra of all compounds were carefully checked to rule out the presence of artifacts or spurious signals arising from, for example, degradation or photo-oxidation of the samples in question.

The two-photon absorption spectrum was measured in the NIR region using the open-aperture Z-scan method with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a repetition rate of 1 kHz generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). After passing through a 10 cm focal length lens, the laser beam was focused and passed through a 1 mm quartz cell. Since the position of the sample cell could be controlled along the laser beam direction (z axis) using the motorcontrolled delay stage, the local power density within the sample cell could be simply controlled under constant laser intensity. The transmitted laser beam from the sample cell was then detected by the same photodiode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point, I_0, ranged from 40 to 60 GW cm^{-2}. For a Gaussian beam profile, the nonlinear absorption coefficient can be obtained by curve fitting of the observed open-aperture traces $T(z)$ with the following equation:

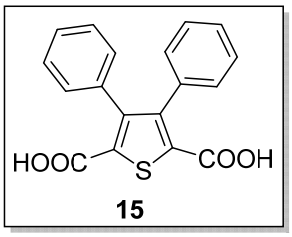
$$T(z)=1-\frac{\beta I_0(1-e^{-\alpha_0 l})}{2\alpha_0[1+(z/z_0)^2]}$$

where α_0 is the linear absorption coefficient, l is the sample length, and z_0 is the diffraction length of the incident beam. After the nonlinear absorption coefficient has been obtained, the TPA cross section $\sigma^{(2)}$ of one solute molecule (in units of GM, where 1 GM = $10^{-50}cm^4$ s $photon^{-1}$ $molecule^{-1}$) can be determined by using the following relationship:

$$\beta=\frac{10^{-3}\sigma^{(2)}N_A d}{h\nu}$$

where N_A is the Avogadro constant, d is the concentration of the compound in solution, h is the Planck constant, and ν is the frequency of the incident laser beam.

1.2. Detailed synthetic procedures and characterization data



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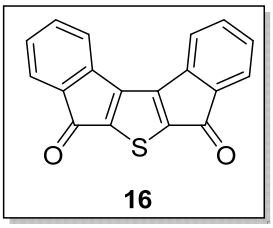
This compound was synthesized according to a published procedure with minor modification (*Macromolecules,* 2005, **38**, 19.). To a mixture of diethyl thiodiacetate (**13**, 2 g, 9.70 mmol) and benzil (**14**, 2.04 g, 9.70 mmol) in ethanol (30 mL), NaOMe (1.57 g, 29.10 mmol) was added as a solid. The mixture was stirred at room temperature for 4 h and then stirred at 60 ^{o}C for 12 h. After cooling down to room temperature NaOH (1.60 g, 40.00 mmol) and additional ethanol (20 mL) were added to the above reaction mixture. The mixture was heated to reflux for additional 12 h. The alcohol was evaporated and 10% HCl was slowly added. During this period diacid **15** was precipitated. After filtration, a pale yellow solid was obtained. The crude product was purified by washing with hexane (30 mL) and DCM (30 mL) to give a white solid (1.89 g, 60% yield). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ = 13.26 (br, 1H), 7.15-7.14 (m, 3H), 7.01-6.99 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ = 162.28, 147.76, 134.87, 132.90, 129.79, 127.15, 127.12. HR MS (EI): calcd for $C_{18}H_{12}O_4S$ (M^+), 324.0456; found, 324.0447 (error: -2.78 ppm).



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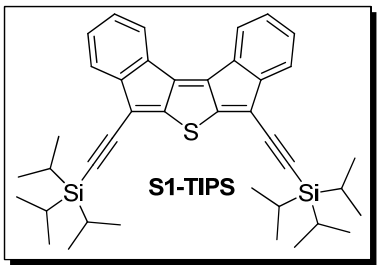
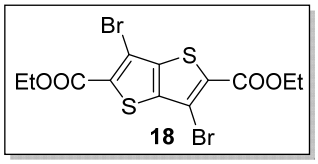
Compound **15** (973 mg, 3.00 mmol) was dissolved in anhydrous DCM (30 mL), followed by the addition of excess of thionyl chloride (2 ml). To this mixture anhydrous DMF (1-2 drops) was added at room temperature. The resultant mixture was heated at reflux overnight. During this period the insoluble diacid **15** became soluble in DCM. After cooling down the solvent was removed under reduced pressure to afford crude acid chloride. This intermediate compound was dissolved in anhydrous DCM (30 mL) then anhydrous $AlCl_3$ (1.60 g, 12.00 mmol) was added carefully at 0 °C. The resultant mixture was allowed to warm up to room temperature and stirred overnight, then slowly quenched by 10% HCl solution, extracted with large amount of DCM. The combined organic phase was washed with 10% HCl and brine. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM) to afford compound **16** as an orange solid (735 mg,

85% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.62 (d, *J* = 7.0 Hz, 1H), 7.51 (dd, *J* = 7.1 Hz, 1H), 7.44 (d, *J* = 6.8 Hz, 1H), 7.32 (dd, *J* = 7.1 Hz, 1H). ^{13}C NMR spectrum was not obtained due to its poor solubility. HR MS (EI): calcd for $C_{18}H_8O_2S$ (M^+), 288.0245; found, 288.0236 (error: -3.12 ppm). Anal. Calcd for $C_{18}H_8O_2S$: C, 74.98; H, 2.80; S, 11.12; found: C, 74.95; H, 2.72; S, 11.08.

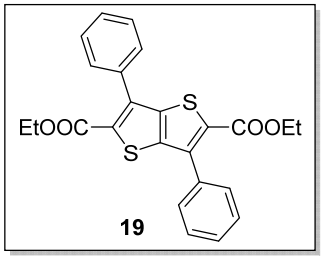


S1-TIPS

To a solution of triisopropylsilylacetylene (1.10 g, 6.00 mmol) in anhydrous THF (30 mL) at 0 ^{o}C was added dropwise *n*-BuLi (1.6 M in hexanes, 3.75 mL, 6.00 mmol). The solution was stirred for 30 min at 0 ^{o}C. Then diketone **16** (288 mg, 1.00 mmol) was added as solid in one portion. The mixture was slowly warmed to room temperature and stirred overnight. During this period the insoluble diketone disappeared and the solution became clear. The reaction was quenched with 10% HCl solution (10 mL) and extracted in $CHCl_3$. The organic layer was dried (Na_2SO4), filtered, and evaporated to dryness under vacuum. After that the crude diol was dissolved in dry toluene (20 mL) and degassed by bubbling through argon. $SnCl_2$ (758.5 mg, 4.00 mmol) was added to the mixture and stirred overnight. During this period the color of the reaction mixture became green-to-blue. The resulting solution was then filtered and the filtrate was subsequently evaporated to dryness. The residue was purified by column chromatography (silica gel, hexane: DCM = 5: 1). Compound **S1-TIPS** was further purified by recrystallization from CH_3CN/CH_2Cl_2 as a dark green solid (430 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.51 (d, *J* = 7.2 Hz, 1H), 7.19 (dd, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.06 (dd, *J* = 7.6 Hz, 1H), 1.17-1.15 (br, 21H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 153.75, 148.86, 144.01, 130.75, 130.16, 125.76, 124.34, 120.66, 116.29, 105.87, 99.68, 18.70, 11.25. HR MS (EI): calcd for $C_{40}H_{50}SSi_2$ (M^+), 618.3172; found, 618.3167 (error: -0.81 ppm).

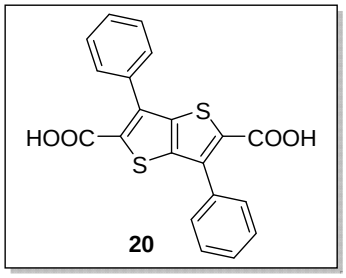


Under argon and anhydrous condition at -78 ^{o}C, *n*-BuLi (1.6 M in hexane, 6.25 mL, 10.00 mmol) was slowly added to a solution of 2,3,5,6-tetrabromothieno[3,2-b]thiophene (**17**, 2.28 g, 5.00 mmol) in THF (40 mL) and the mixture was stirred for 1 h. Ethyl cyanoformate (1 mL, 10.00 mmol) was added by syringe at -78 ^{o}C. The reaction was slowly warmed to room temperature and stirred overnight. The reaction was quenched by water at 0 ^{o}C. All of the organic solvents were removed and the organic precipitate was collected by filtration. The crude product was washed by hexane and methanol to give pure compound **18** as a white solid (1.55 g, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 4.43 (q, *J* = 7.1 Hz, 4H), 1.42 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 160.48, 142.46, 132.04, 109.55, 62.13, 14.19. HR MS (EI): calcd for $C_{12}H_{10}Br_2O_4S_2$ (M^+), 441.8367; found, 441.8365 (error: -0.45 ppm).



Phenylboronic acid (488 mg, 4 mmol), **18** (442 mg, 1.00 mmol), and Na_2CO_3 (424 mg, 4.00 mmol) were dissolved in water (3 mL) and toluene (15 mL). $Pd(PPh_3)_4$ (70 mg) was added as a catalyst and the mixture was refluxed for 12 h. After cooling down cold methanol was added and a white precipitate was formed. The crude product was collected by filtration and further purified by column chromatography (silica, hexane: DCM = 1: 1) to give a white solid (410 mg, 94% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.60-7.59 (m, 2H), 7.51-7.46 (m, 3H), 4.25 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ =161.92, 142.53, 140.70, 133.64,

131.32, 129.03, 128.83, 128.32, 61.41, 14.00. HR MS (EI): calcd for $C_{24}H_{20}O_4S_2$ (M^+), 436.0803; found, 436.0805 (error: 0.46 ppm).



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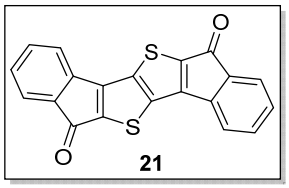
Compound **19** (436 mg, 1.00 mmol) was dissolved in methanol and THF (20 mL, 1:1 v/v), followed by the addition of sodium hydroxide (240 mg, 6.00 mmol). This mixture was heated at reflux overnight. The solvent was removed under reduced pressure after the reaction was completed. To the residue then concentrated hydrochloric acid was added. The precipitate formed was collected by filtration and washed with water and a little amount of DCM, then dried in vacuum to afford product **20** as a white solid (365 mg, 96% yield). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ = 13.40 (br, 1H), 7.62-7.61 (m, 2H), 7.53-7.48 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ =162.56, 141.41, 139.39, 133.28, 132.23, 128.98, 128.80, 128.38. HR MS (EI): calcd for $C_{20}H_{12}O_4S_2$ (M^+), 380.0177; found, 380.0159 (error: -4.74 ppm).



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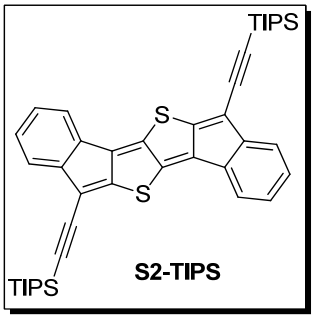
Compound **20** (380 mg, 1.00 mmol) was added in anhydrous DCM (20 mL), followed by the addition of excess of thionyl chloride (1 mL). To this mixture anhydrous DMF (1-2 drops) was added at room temperature. The resultant mixture was heated at reflux overnight. During this period the insoluble diacid **20** became soluble in DCM. After cooling down the solvent was removed under reduced pressure to afford crude acid chloride. This intermediate compound was dissolved in anhydrous DCM (20 mL)

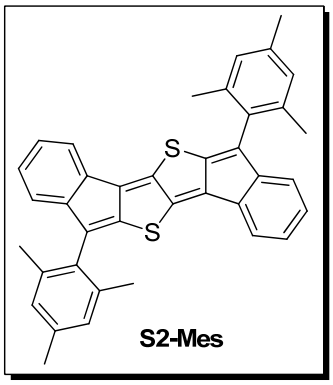
then anhydrous $AlCl_3$ (533 mg, 4.00 mmol) was added carefully at 0 °C. The resultant mixture was allowed to warm up to room temperature and stirred overnight, then slowly quenched by 10% HCl solution to form a red precipitate. The crude precipitate was rinsed with 10% NaOH, MeOH, DCM and THF until the washings were colorless, giving **21** as an insoluble red solid (286 mg, 83% yield). Both ^{1}H NMR and ^{13}C NMR data were not obtained due to its poor solubility. HR MS (EI): calcd for $C_{20}H_8O_8S_2$ (M^+), 343.9966; found, 343.9962 (error: -1.16 ppm). Anal. Calcd for $C_{20}H_8O_2S_2$: C, 69.75; H, 2.34; S, 18.62; found: C, 69.55; H, 2.08; S, 18.97.



S2-TIPS

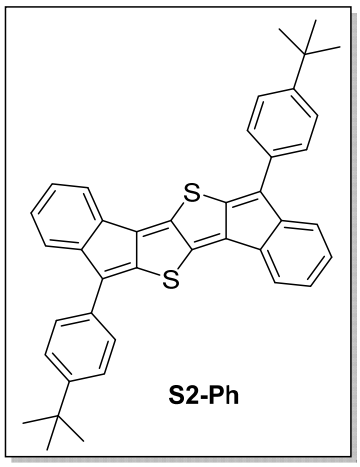
To a solution of triisopropylsilylacetylene (1.10 g, 6.00 mmol) in anhydrous THF (30 mL) at 0 ^{o}C was added dropwise *n*-BuLi (1.6 M in hexane, 3.75 mL, 6.00 mmol). The solution was stirred for 30 min at 0 ^{o}C. Then diketone **21** (344 mg, 1.00 mmol) was added as solid in one portion. The mixture was slowly warmed to room temperature and stirred overnight. During this period the insoluble diketone disappeared and the solution became clear with strong blue fluorescence. The reaction was quenched with 10% HCl solution (10 ml) and extracted in $CHCl_3$. The organic layer was dried (Na_2SO4), filtered, and evaporated to dryness under vacuum. After that the crude diol was dissolved in dry toluene (20 mL) and degassed by bubbling through Ar. $SnCl_2$ (758.5 mg, 4.00 mmol) was then added to the mixture and stirred overnight. During this period the color of the reaction mixture became deep blue. The resulting blue solution was then filtered and the filtrate was subsequently evaporated to dryness. The residue was purified by column chromatography (silica gel, hexane: DCM = 5: 1). Compound **S2-TIPS** was further purified by recrystallization from CH_3CN/CH_2Cl_2 as a dark blue solid (472 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.31 (d, *J* = 7.4 Hz, 1H), 7.21-7.16 (m, 2H), 7.09-7.05 (m, 1H), 1.19-1.17 (br, 21H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 150.11, 147.30, 146.96, 139.41, 129.60, 128.78, 125.50,

122.63, 120.71, 114.74, 105.40, 99.99, 18.76, 11.30. HR MS (EI): calcd for $C_{42}H_{50}S_2Si_2$ (M^+), 674.2892; found, 674.2893 (error: 0.15 ppm).



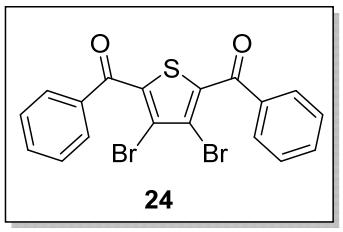
S2-Mes

To a solution of **21** (344 mg, 1.00 mmol) in anhydrous THF (30 mL) at 0 ^oC was added dropwise mesitylmagnesium bromide (1.0 M in ether, 6 mL, 6.00 mmol). The mixture was slowly warmed to room temperature and stirred overnight. During this period the insoluble diketone disappeared and the solution became clear. The reaction was quenched with 10% HCl solution (10 ml) and extracted in $CHCl_3$. The organic layer was dried (Na_2SO4), filtered, and evaporated to dryness under vacuum. After that the crude diol was dissolved in dry toluene (20 mL) and degassed with Ar. $SnCl_2$ (758.5 mg, 4.00 mmol) was then added to the mixture and stirred overnight. During this period the color of the reaction mixture became brown. The resulting brown solution was then filtered and the filtrate was subsequently evaporated to dryness. The residue was purified by column chromatography (silica gel, hexane: DCM = 5: 1). Compound **S2-Mes** was further purified by recrystallization from CH_3CN/CH_2Cl_2 as a dark solid (275 mg, 50% yield). ^1H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.33 (d, J = 7.0 Hz, 1H), 7.10-7.03 (m, 2H), 6.98 (s, 2H), 6.72 (d, J = 7.3 Hz. 1H), 2.36 (s, 3H), 2.22 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ =147.99, 147.12, 144.69, 138.55, 137.78, 137.09, 132.34, 130.33, 128.99, 128.33, 128.23, 124.56, 122.68, 120.53, 21.14, 20.23. HR MS (EI): calcd for $C_{38}H_{30}S_2$ (M^+), 550.1789; found, 550.1799 (error: 1.82 ppm).



S2-Ph

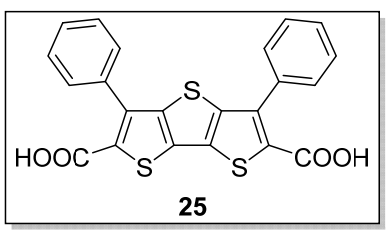
To a solution of 1-bromo-4-*tert*-butylbenzene (1.28 g, 6.00 mmol) in anhydrous THF (30 ml) at -78 ^{o}C was added dropwise *n*-BuLi (1.6 M in hexane, 3.75 mL, 6.00 mmol). The solution was stirred for 1 h at -78 ^{o}C. Then diketone **21** (344 mg, 1.00 mmol) was added as solid in one portion. The mixture was slowly warmed to room temperature and stirred overnight. During this period the insoluble diketone disappeared and the solution became clear. The reaction was quenched with 10% HCl solution (10 ml) and extracted in $CHCl_3$. The organic layer was dried (Na_2SO_4), filtered, and evaporated to dryness under vacuum. After that the crude diol was dissolved in dry toluene (20 mL) and degassed with Ar. $SnCl_2$ (758.5 mg, 4.00 mmol) was added to the mixture and stirred overnight. During this period the color of the reaction mixture became deep blue. The resulting blue solution was then filtered and the filtrate was subsequently evaporated to dryness. The residue was purified by column chromatography (silica gel, DCM). Compound **S2-Ph** was further purified by recrystallization from CH_3CN/CH_2Cl_2 as a dark blue solid (232 mg, 40% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.54-7.51 (m, 3H), 7.41 (d, *J* = 7.2 Hz. 1H), 7.20 (dd, *J* = 7.5 Hz, 1H), 7.11 (dd, *J* = 7.4 Hz, 1H), 1.39 (s, 9H). This compound has a poor solubility and the ^{13}C NMR was not obtained. HR MS (EI): calcd for $C_{40}H_{34}S_2$ (M^+), 578.2102; found, 578.2096 (error: -1.04 ppm). Anal. Calcd for $C_{40}H_{34}S_2$: C, 83.00; H, 5.92; S, 11.08; found: C, 82.65; H, 6.10; S, 10.98.



24

Under argon and anhydrous condition at -78 ^{o}C, *n*-BuLi (1.6 M in hexane, 6.25 mL, 10.00 mmol) was slowly added to a solution of tetrabromothiophene (**22**, 2.00 g, 5.00 mmol) in THF (40 mL) and the mixture was stirred for 1 h at this temperature. Benzaldehyde (1.06 g, 10.00 mmol) was added by syringe at -78 ^{o}C. The reaction was slowly warmed to room temperature and stirred overnight. The reaction was quenched by water at 0 ^{o}C. The organic solvent was removed and the organic precipitate was collected by filtration. The precipitate was washed by hexane to give the diol intermediate (**23**) which used for the next step reaction without further purification and characterization.

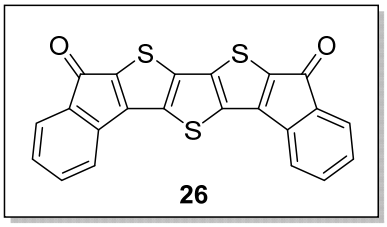
The above diol intermediate was dissolved in 40 mL of DCM. PCC (3.23 g, 15 mmol) was slowly added into the solution by portions. The reaction was stirred overnight at room temperature and the resulting mixture was poured into water and extracted with DCM. The combine extracts were dried (Na_2SO_4), the solvent removed under vacuum and the residue purified by column chromatography (silica gel, hexane: ethyl acetate (EA) = 5: 1). The title compound **24** was obtained as colorless oil (1.80 g, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.89-7.87 (m, 2H), 7.67-7.64 (m, 1H), 7.54-7.50 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 187.28, 139.14, 136.19, 134.00, 130.00, 128.73, 119.10. HR MS (EI): calcd for $C_{18}H_{10}Br_2O_2S$ (M^+), 447.8768; found, 447.8768 (error: -1.16 ppm).



25

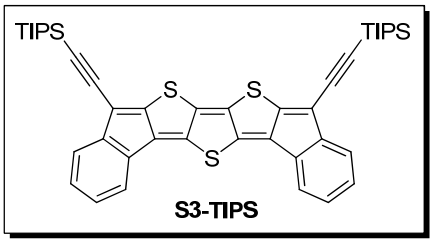
Ethyl mercaptoacetate (1.20 g, 10 mmol) and compound **24** (1.80 g, 4 mmol) were dissolved in 30 mL of ethanol. KOH (1.12 g, 20 mmol) was added to the above

reaction mixture. The reaction was stirred at room temperature for 2 h then stirred at 50-60 °C overnight. During this period the precipitate would be formed. Then excess of KOH (3g) was added and the reaction was heated to reflux for 24 h. After cooling down the alcohol was evaporated and 10% HCl was slowly added. During this period diacid **25** was precipitated. After filtration, a pale yellow solid was obtained. The crude product was purified by washing with hexane (30 mL) and DCM (30 mL) to give a pale yellow solid (1.66 g, 95% yield). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ = 13.35 (br, 1H), 7.56-7.54 (m, 2H), 7.49-7.43 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ =162.67, 144.73, 140.06, 133.39, 131.81, 130.64, 128.92, 128.68, 128.32. HR MS (EI): calcd for $C_{22}H_{12}O_4S_3$ (M^+), 435.9898; found, 435.9902 (error: -0.92 ppm).



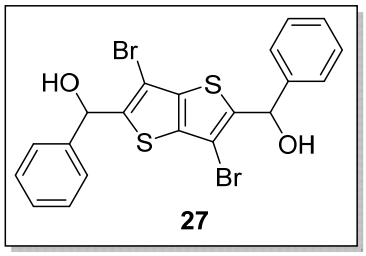
26

Compound **25** (873 mg, 2.00 mmol) was added in anhydrous DCM (20 mL), followed by the addition of excess of thionyl chloride (3 mL). To this mixture anhydrous DMF (1-2 drops) was added at room temperature. The resultant mixture was heated at reflux overnight. After cooling down the solvent was removed under reduced pressure to afford crude acid chloride. This intermediate compound was dissolved in anhydrous DCM (20 mL) then anhydrous $AlCl_3$ (1.07g, 8.00 mmol) was added carefully at 0 °C. The resultant mixture was allowed to warm up to room temperature and stirred overnight, then slowly quenched by 10% HCl solution to form a red precipitate. The crude precipitate was rinsed with 10% NaOH, MeOH, DCM and THF until the washings were colorless, giving **26** as an insoluble red solid (624 mg, 78% yield). Both ^{1}H NMR and ^{13}C NMR data were not obtained due to its poor solubility. HR MS (EI): calcd for $C_{22}H_8O_2S_3$ (M^+), 399.9686; found, 399.9690 (error: 1.00 ppm). Anal. Calcd for $C_{22}H_8O_2S_3$: C, 65.98; H, 2.01; S, 24.02; found: C, 65.68; H, 2.34; S, 23.98.



S3-TIPS

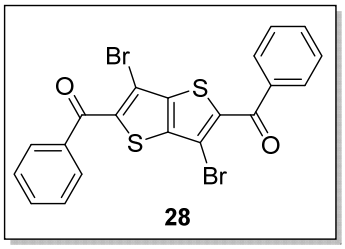
To a solution of triisopropylsilylacetylene (1.10 g, 6.00 mmol) in anhydrous THF (30 ml) at 0 ^{o}C was added dropwise *n*-BuLi (1.6 M in hexane, 3.75 mL, 6.00 mmol). The solution was stirred for 30 min at 0 ^{o}C. Then diketone **26** (400 mg, 1.00 mmol) was added as solid in one portion. The mixture was slowly warmed to room temperature and stirred overnight. During this period the insoluble diketone disappeared and the solution became clear with strong blue fluorescence. The reaction was quenched with 10% HCl solution (10 ml) and extracted in $CHCl_3$. The organic layer was dried (Na_2SO_4), filtered, and evaporated to dryness under vacuum. After that the crude diol was dissolved in dry toluene (20 mL) and degassed with Ar. $SnCl_2$ (758.5 mg, 4.00 mmol) was added to the mixture and stirred overnight. During this period the color of the reaction mixture became purple. The resulting purple solution was then filtered and the filtrate was subsequently evaporated to dryness. The residue was purified by column chromatography (silica gel, hexane: DCM = 5: 1). Compound **S3-TIPS** was further purified by recrystallization from CH_3CN/CH_2Cl_2 as a black solid (497 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.32 (d, *J* = 7.4 Hz. 1H), 7.25 (d, *J* = 6.1 Hz. 1H), 7.19 (dd, *J* = 7.5 Hz, 1H), 7.07 (dd, *J* = 7.5 Hz, 1H), 1.19-1.17 (br, 21H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 148.88, 146.62, 143.96, 142.99, 138.56, 129.26, 128.56, 125.11, 122.10, 120.76, 113.22, 105.48, 100.41, 18.74, 11.31. HR MS (EI): calcd for $C_{44}H_{50}S_3Si_2$ (M^+), 730.2613; found, 730.2607 (error: -0.82 ppm).



27

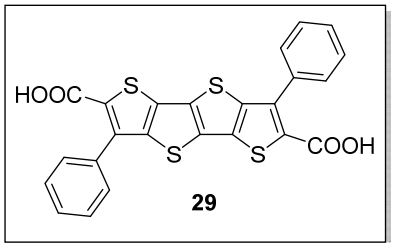
Under argon and anhydrous condition at -78 ^{o}C, *n*-BuLi (1.6 M in hexane, 6.25 mL, 10.00 mmol) was slowly added to a solution of 2,3,5,6-tetrabromothieno[3,2-

b]thiophene (**17**, 2.28 g, 5.00 mmol) in THF (40 mL) and the mixture was stirred for 1 h. Benzaldehyde (1.06 g, 10.00 mmol) was added by syringe at -78 ^{o}C. The reaction was slowly warmed to room temperature and stirred overnight. The reaction was quenched by water at 0 ^{o}C. The organic solvent was removed and the organic precipitate was collected by filtration. The precipitate was washed by hexane to give the white diol intermediate which used for the next step reaction without further purification and characterization.



28

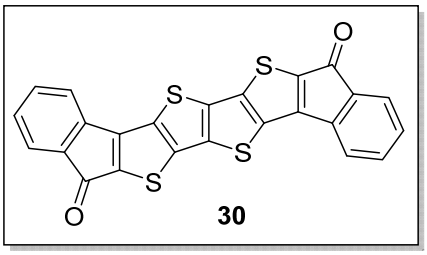
The above diol intermediate was dissolved in 40 mL of DCM. PCC (3.23 g, 15 mmol) was slowly added into the solution by portions. The reaction was stirred overnight at room temperature and the resulting mixture was poured into water and extracted with dichloromethane. The combine extracts were dried (Na_2SO_4), the solvent removed in vacuo and the residue purified by column chromatography (silica gel, hexane: EA = 5: 1). The title compound **28** was obtained as white solid (1.52 g, 60% yield) ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.89 (d, *J* = 7.1 Hz. 2H), 7.66 (m, 1H), 7.53 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 187.80, 142.90, 139.79, 136.97, 133.51, 129.78, 128.60, 107.71. HR MS (EI): calcd for $C_{20}H_{10}Br_2O_2S_2$ (M^+), 505.8468; found, 505.8468 (error: 0 ppm).



29

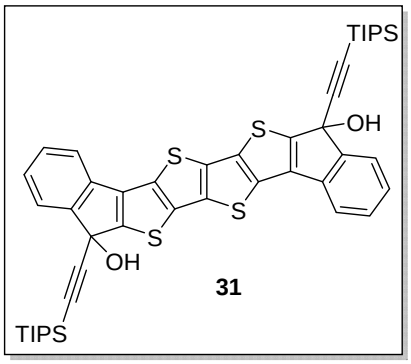
Ethyl mercaptoacetate (300 mg, 2.5 mmol) and compound **28** (506 mg, 1 mmol) were dissolved in 20 mL of ethanol. KOH (224 mg, 5 mmol) was added to the above reaction mixture. The reaction was stirred at room temperature for 2 h then stirred at

50-60 °C overnight. Then excess of KOH (1g) was added and the reaction was heated to reflux for 24 h. After cooling down the alcohol was evaporated and 10% HCl was slowly added. During this period diacid **29** was precipitated. After filtration, a pale yellow solid was obtained. The crude product was purified by washing with hexane (30 mL) and DCM (30 mL) to give a pale yellow solid (453 mg, 92% yield). ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ = 13.28 (br, 1H), 7.65-7.61 (m, 2H), 7.55-7.48 (m, 3H). ^{13}C NMR data were not obtained due to its poor solubility. HR MS (APCI): calcd for $C_{24}H_{13}O_4S_4$ $(M + H)^+$, 492.9697; found, 492.9674 $(M + H)^+$ (error: -4.67 ppm). Anal. Calcd for $C_{24}H_{12}O_4S_4$: C, 58.52; H, 2.46; S, 26.04; found: C, 58.42; H, 2.64; S, 26.32.



30

Compound **29** (492 mg, 1.00 mmol) was added in anhydrous DCM (20 mL), followed by the addition of excess of thionyl chloride (2 mL). To this mixture anhydrous DMF (1-2 drops) was added at room temperature. The resultant mixture was heated at reflux overnight. After cooling down the solvent was removed under reduced pressure to afford crude acid chloride. This intermediate compound was dissolved in anhydrous DCM (20 mL) then anhydrous $AlCl_3$ (533 mg, 4.00 mmol) was added carefully at 0 °C. The resultant mixture was allowed to warm up to room temperature and stirred overnight, then slowly quenched by 10% HCl solution to form a red precipitate. The crude precipitate was rinsed with 10% NaOH, MeOH, DCM and THF until the washings were colorless, giving **30** as an insoluble red solid (329 mg, 72% yield). Both ^{1}H NMR and ^{13}C NMR data were not obtained due to its poor solubility. HR MS (APCI): calcd for $C_{24}H_9O_2S_4$ $(M + H)^+$, 456.9485; found, 456.9480 $(M + H)^+$ (error: -1.09 ppm). Anal. Calcd for $C_{24}H_8O_2S_4$: C, 63.13; H, 1.77; S, 28.09; found: C, 62.85; H, 2.02; S, 27.98.



31

To a solution of triisopropylsilylacetylene (730 mg, 4.00 mmol) in anhydrous THF (30 mL) at 0 ^{o}C was added dropwise *n*-BuLi (1.6 M in hexane, 2.50 ml, 4.00 mmol). The solution was stirred for 30 min at 0 ^{o}C. Then diketone **30** (228 mg, 0.50 mmol) was added as solid in one portion. The mixture was slowly warmed to room temperature and stirred overnight. During this period the insoluble diketone disappeared and the solution became clear with strong blue fluorescence. The reaction was quenched with 10% HCl solution (10 mL) and extracted in ethyl acetate. The combine extracts were dried (Na_2SO_4), the solvent removed under vacuum and the residue was purified by column chromatography (silica gel, hexane: EA = 6: 1). The resulting solid was washed with hexane to obtain the title compound **31** as off-white solid (120 g, 29% yield). The low yield was due to the column chromatography process because the title diol compound was very easily to attach on the silica gel. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, ppm): δ = 7.64 (m, 1H), 7.38-7.23 (m, 3H), 2.90 (s, 1H), 1.10-1.03 (br, 21H). ^{13}C NMR data were not obtained due to its poor solubility. HR MS (APCI): calcd for $C_{46}H_{53}O_2S_4Si_2$ $(M + H)^+$, 821.2467; found, 821.2487 (error: 2.44 ppm). Anal. Calcd for $C_{46}H_{52}O_2S_4Si_2$: C, 67.27; H, 6.38; S, 15.62; found: C, 67.39; H, 6.68; S, 15.30.

2. In situ generation of S4-TIPS

Compound **31** was dissolved in dry toluene (or THF, $CHCl_3$ etc.) and excessive dry $SnCl_2$ was added. The mixture was shacked to facilitate reaction. The reaction was carefully conducted under argon atmosphere and followed by ^{1}H NMR (in dry $CDCl_2CDCl_2$, Fig. S1) and UV-vis-NIR measurements (in dry toluene, Fig. S2). The reaction completed in about 30 mins (Fig. S1 and Fig. S2a) but the products

gradually decomposed simultaneously even under Ar protection (Fig. S2b). The formation of the **S4-TIPS** was confirmed by the MALDI-TOF mass spectrometry for the freshly prepared sample (Fig. S3a). Upon contact with air, it quickly decomposed with the major products as the oxygen addition species (Fig. S3b).

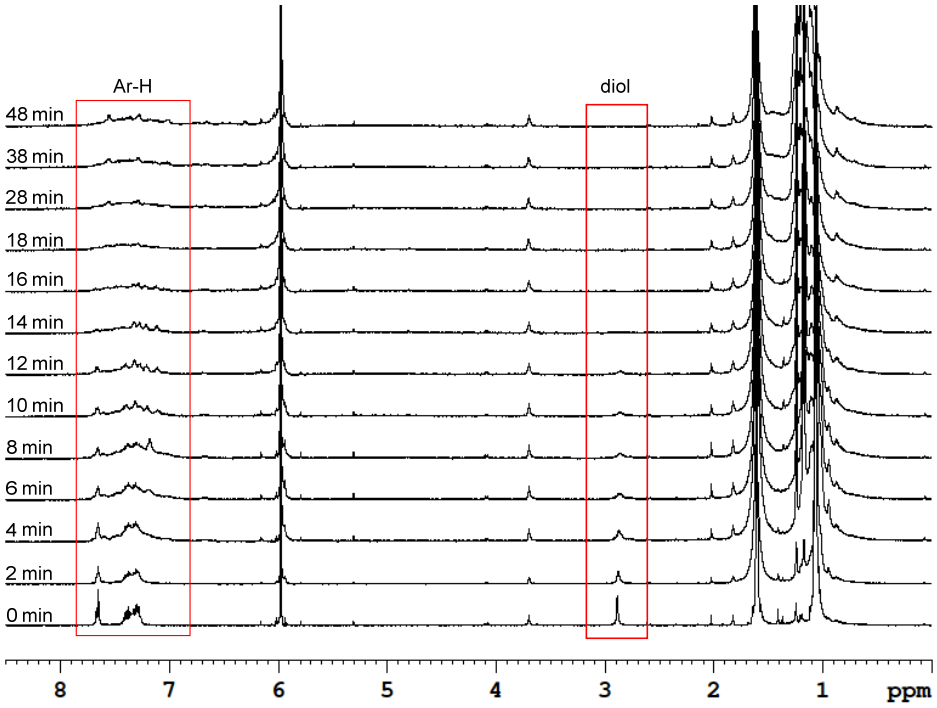


Fig. S1. The in situ generation of **S4-TIPS** by reduction of **31** in $CDCl_2CDCl_2$ under Ar followed by ^1H NMR (500 MHz, $C_2D_2Cl_4$, rt).

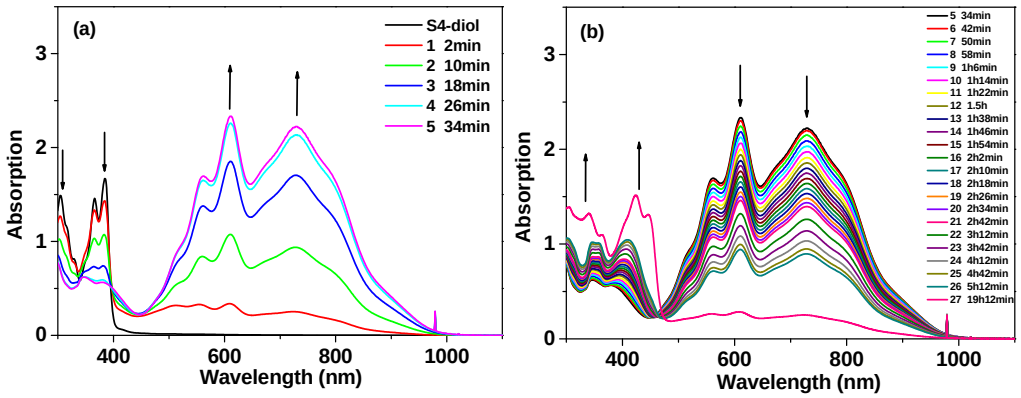


Fig. S2. UV-vis-NIR absorption spectra of **S4-TIPS** during the reduction of compound **31** (concentration: 5 x 10^{-5}M) by $SnCl_2$ in dry toluene under argon atmosphere. The arrows show the changes of the spectra during the reduction reaction. (a) The spectra recorded in 0-34 min after addition of $SnCl_2$. (b) The spectra recorded in 34 min-19 h after addition of $SnCl_2$.

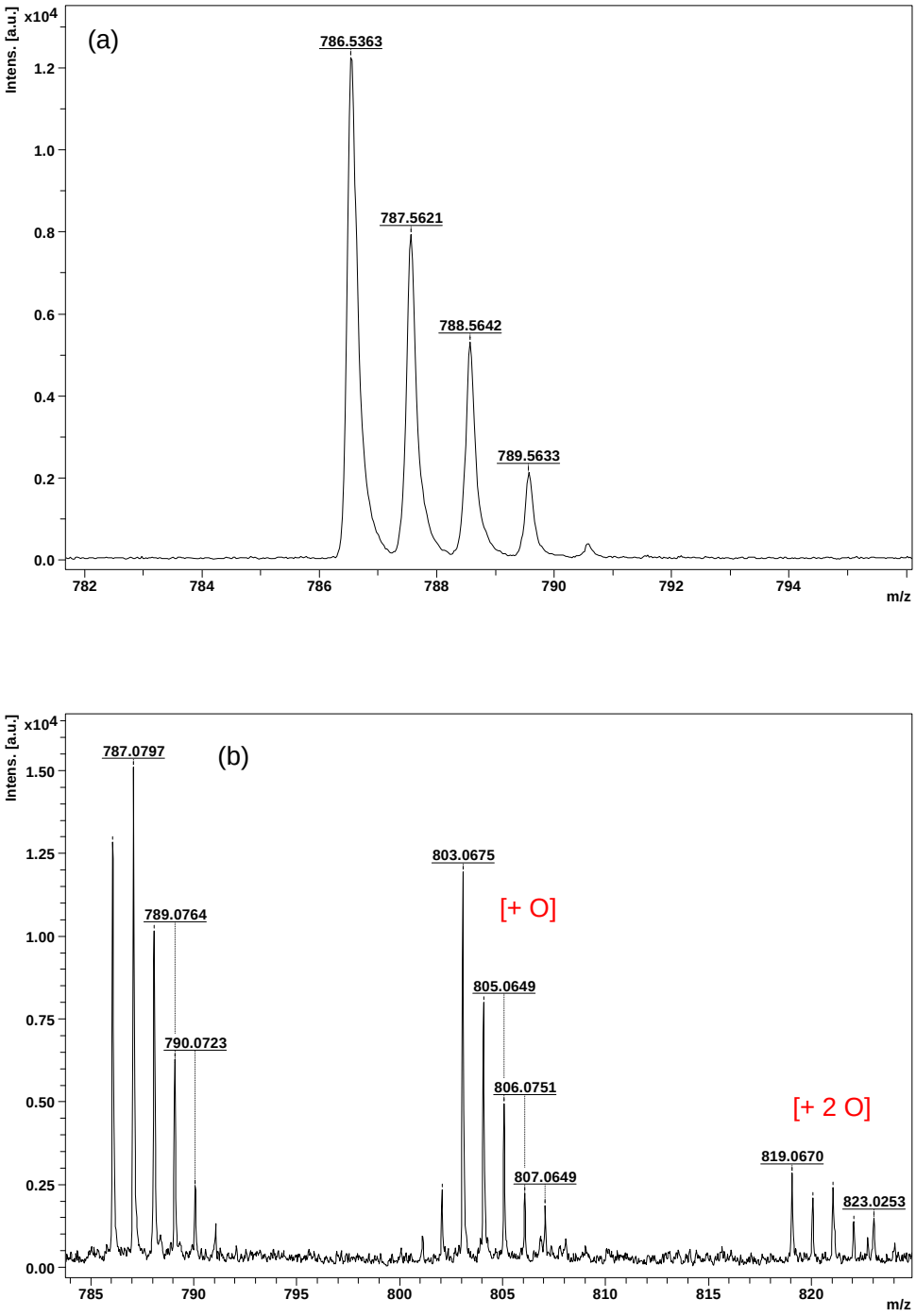


Fig. S3. MALDI-TOF mass spectra of the freshly prepared **S4-TIPS** (a) and its decomposition products (b)**.**

3. TD DFT calculations

DFT calculations have been performed both at the B3LYP/6-31G* level of theory and the UCAM-B3LYP level of theory, as implemented in the Gaussian 09 program package. Molecules **S1-S3** series all showed a closed-shell ground state, but **S4-TIPS** has a singlet biradical ground state. Absorption spectra of **S1-S3** were calculated by TD DFT at B3LYP/6-31G* level. NICS values at the UCAM-B3LYP/6-31G* level using the standard GIAO procedure (NMR pop=NCSall).

Table S1. Selected TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength and compositions of major electronic transitions of **S1-TIPS**.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions
729.7	0.1511	H-0->L+0(+89%) H-1->L+0(+11%)
442.8	0.7393	H-1->L+0(+87%) H-0->L+0(11%)
356.5	0.1460	H-5->L+0(+94%)
299.6	0.4906	H-0->L+1(+93%)

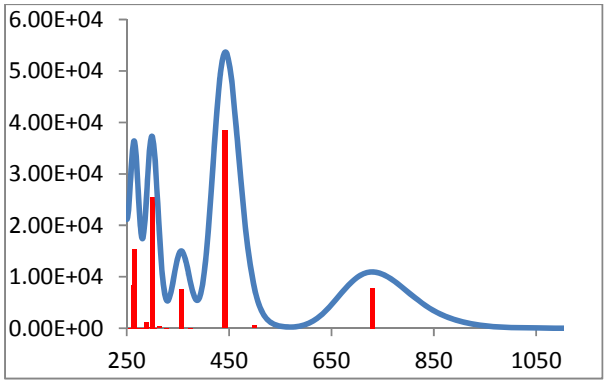


Fig. S4. Calculated (B3LYP/6-31G*) absorption spectrum of **S1-TIPS**.

Table S2. Selected TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength and compositions of major electronic transitions of **S2-TIPS**.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions
634.9	0.6714	H-0->L+0(+89%) H-2->L+0(12%)
452.4	0.6830	H-2->L+0(+87%) H-0->L+0(+12%)
363.7	0.1922	H-6->L+0(+96%)
295.7	0.2056	H-0->L+2(+88%) H-0->L+4(+8%)

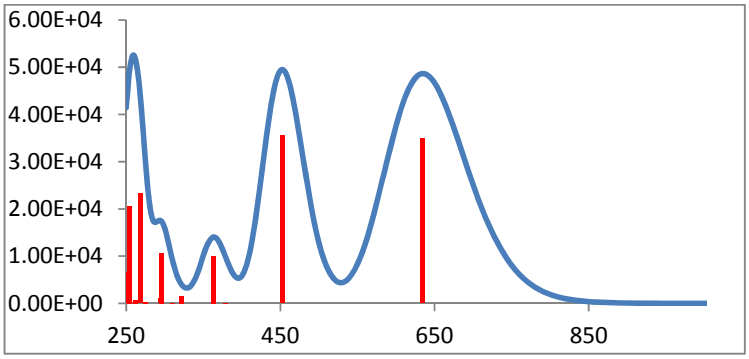


Fig. S5. Calculated (B3LYP/6-31G*) absorption spectrum of **S2-TIPS**.

Table S3. Selected TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength and compositions of major electronic transitions of **S2-Mes**.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions
563.0	0.4219	H-0->L+0(+84%) H-2->L+0(+16%)
421.6	0.4520	H-2->L+0(+58%) H-4->L+0(+31%)
		H-0->L+0(10%)
409.1	0.2577	H-4->L+0(+67%) H-2->L+0(25%)
		H-0->L+0(+6%)
306.8	0.1768	H-8->L+0(+90%)

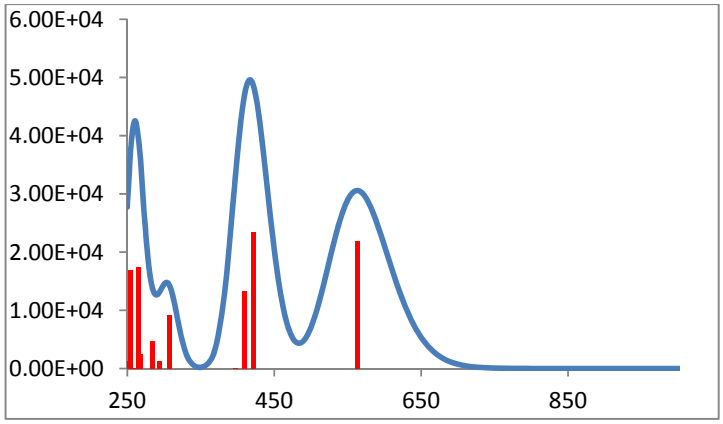


Fig. S6. Calculated (B3LYP/6-31G*) absorption spectrum of **S2-Mes**.

Table S4. Selected TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength and compositions of major electronic transitions of **S2-Ph**.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions

622.1	0.6741	H-0->L+0(+91%) H-2->L+0(10%)
434.6	0.6159	H-2->L+0(+88%) H-0->L+0(+10%)
363.0	0.1471	H-4->L+0(+96%)
305.9	0.3150	H-0->L+2(+86%) H-9->L+0(8%)

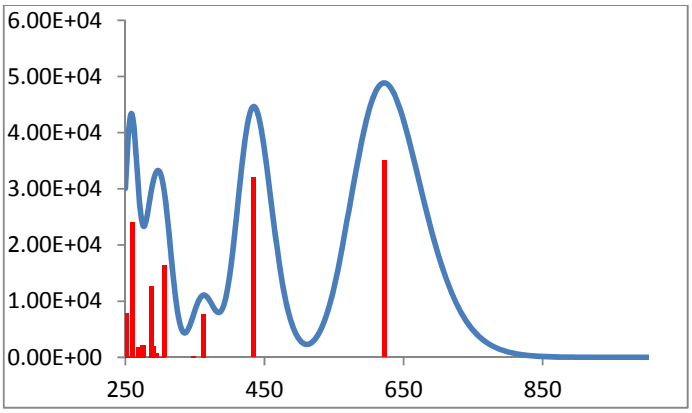


Fig. S7. Calculated (B3LYP/6-31G*) absorption spectrum of **S2-Ph**.

Table S5. Selected TD-DFT (B3LYP/6-31G*) calculated energies, oscillator strength and compositions of major electronic transitions of **S3-TIPS**.

Wavelength (nm)	Osc. Strength (*f*)	Major contributions
720.3	0.6399	H-0->L+0(+79%) H-2->L+0(23%)
530.7	1.0510	H-2->L+0(+76%) H-0->L+0(+24%)
374.9	0.1146	H-7->L+0(+85%) H-5->L+0(6%)
305.7	0.1769	H-0->L+2(+83%) H-0->L+3(10%)

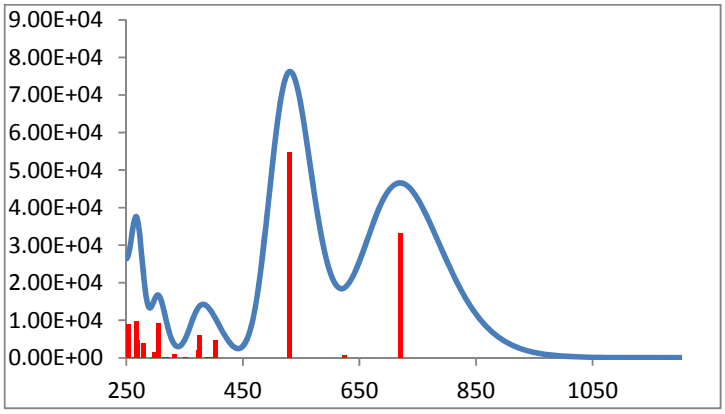
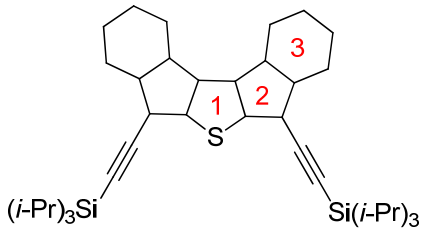


Fig. S8. Calculated (B3LYP/6-31G*) absorption spectrum of **S3-TIPS**.

NICS values at the **UCAM-B3LYP/6-31G*** level using the standard GIAO procedure (NMR pop=NCSall).

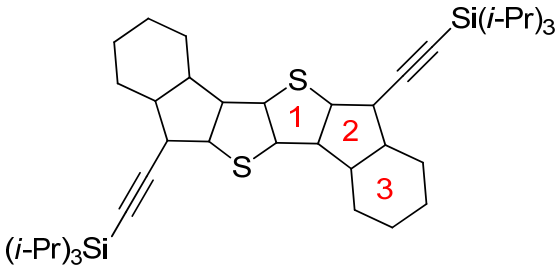
Compound: **S1-TIPS**



Bq distance (Å)	NICS values (sigma zz) ring 1	ring 2	ring 3
0.0000	33.9516	46.2279	-1.8365
0.1000	33.4921	45.8498	-2.3014
0.2000	32.1429	44.7015	-3.6429
0.3000	29.9920	42.7614	-5.6813
0.4000	27.1842	40.0405	-8.1595
0.5000	23.9104	36.6198	-10.7934
0.6000	20.3873	32.6615	-13.3197
0.7000	16.8291	28.3873	-15.5309
0.8000	13.4210	24.0377	-17.2930
0.9000	10.3002	19.8299	-18.5450
1.0000	7.5498	15.9289	-19.2873
1.1000	5.2030	12.4375	-19.5643
1.2000	3.2546	9.4007	-19.4457
1.3000	1.6739	6.8191	-19.0118
1.4000	0.4168	4.6645	-18.3423
1.5000	-0.5651	2.8927	-17.5092
1.6000	-1.3191	1.4541	-16.5735
1.7000	-1.8878	0.2991	-15.5847
1.8000	-2.3080	-0.6178	-14.5808
1.9000	-2.6106	-1.3371	-13.5897
2.0000	-2.8210	-1.8936	-12.6313
2.1000	-2.9598	-2.3171	-11.7185
2.2000	-3.0434	-2.6328	-10.8593
2.3000	-3.0850	-2.8616	-10.0577
2.4000	-3.0951	-3.0209	-9.3149
2.5000	-3.0819	-3.1252	-8.6302
2.6000	-3.0517	-3.1862	-8.0013
2.7000	-3.0094	-3.2135	-7.4254
2.8000	-2.9590	-3.2147	-6.8990
2.9000	-2.9031	-3.1959	-6.4185
3.0000	-2.8439	-3.1620	-5.9802
3.1000	-2.7831	-3.1169	-5.5805

3.2000	-2.7217	-3.0636	-5.2159
3.3000	-2.6606	-3.0045	-4.8833
3.4000	-2.6003	-2.9414	-4.5797
3.5000	-2.5412	-2.8758	-4.3023
3.6000	-2.4835	-2.8088	-4.0486
3.7000	-2.4274	-2.7413	-3.8164
3.8000	-2.3730	-2.6739	-3.6036
3.9000	-2.3203	-2.6073	-3.4084
4.0000	-2.2692	-2.5416	-3.2290
4.1000	-2.2198	-2.4773	-3.0640
4.2000	-2.1720	-2.4146	-2.9120
4.3000	-2.1258	-2.3535	-2.7718
4.4000	-2.0810	-2.2941	-2.6423
4.5000	-2.0376	-2.2366	-2.5225
4.6000	-1.9956	-2.1809	-2.4116
4.7000	-1.9549	-2.1270	-2.3086
4.8000	-1.9154	-2.0750	-2.2130
4.9000	-1.8770	-2.0247	-2.1240
5.0000	-1.8398	-1.9761	-2.0411

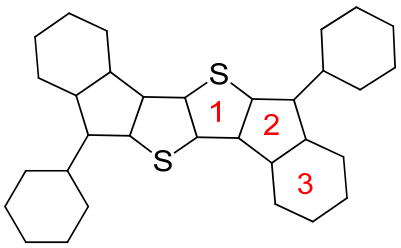
Compound: S2-TIPS



Bq distance (Å)	NICS values (sigma zz)		
	ring 1	ring 2	ring 3
0.0000	30.2717	39.1931	-4.3374
0.1000	29.7376	38.7816	-4.8167
0.2000	28.2855	37.5175	-6.1807
0.3000	26.0279	35.4306	-8.2420
0.4000	23.1368	32.5971	-10.7341
0.5000	19.8252	29.1557	-13.3640
0.6000	16.3221	25.3036	-15.8624
0.7000	12.8438	21.2692	-18.0198
0.8000	9.5686	17.2769	-19.7035
0.9000	6.6224	13.5136	-20.8565
1.0000	4.0751	10.1100	-21.4844
1.1000	1.9477	7.1368	-21.6372
1.2000	0.2245	4.6137	-21.3896
1.3000	-1.1330	2.5232	-20.8262

1.4000	-2.1745	0.8259	-20.0298
1.5000	-2.9520	-0.5283	-19.0746
1.6000	-3.5149	-1.5911	-18.0234
1.7000	-3.9069	-2.4113	-16.9263
1.8000	-4.1648	-3.0324	-15.8216
1.9000	-4.3193	-3.4917	-14.7376
2.0000	-4.3948	-3.8207	-13.6936
2.1000	-4.4110	-4.0456	-12.7024
2.2000	-4.3835	-4.1879	-11.7714
2.3000	-4.3242	-4.2654	-10.9041
2.4000	-4.2426	-4.2926	-10.1012
2.5000	-4.1459	-4.2811	-9.3614
2.6000	-4.0396	-4.2404	-8.6820
2.7000	-3.9278	-4.1780	-8.0597
2.8000	-3.8135	-4.0997	-7.4907
2.9000	-3.6990	-4.0103	-6.9709
3.0000	-3.5860	-3.9134	-6.4963
3.1000	-3.4754	-3.8118	-6.0630
3.2000	-3.3680	-3.7076	-5.6674
3.3000	-3.2643	-3.6025	-5.3061
3.4000	-3.1645	-3.4976	-4.9758
3.5000	-3.0687	-3.3940	-4.6736
3.6000	-2.9769	-3.2924	-4.3969
3.7000	-2.8891	-3.1931	-4.1433
3.8000	-2.8052	-3.0966	-3.9106
3.9000	-2.7250	-3.0030	-3.6968
4.0000	-2.6483	-2.9126	-3.5002
4.1000	-2.5749	-2.8254	-3.3190
4.2000	-2.5048	-2.7414	-3.1520
4.3000	-2.4377	-2.6606	-2.9978
4.4000	-2.3734	-2.5829	-2.8552
4.5000	-2.3119	-2.5083	-2.7231
4.6000	-2.2529	-2.4367	-2.6007
4.7000	-2.1963	-2.3680	-2.4871
4.8000	-2.1419	-2.3021	-2.3815
4.9000	-2.0897	-2.2389	-2.2832
5.0000	-2.0395	-2.1782	-2.1916

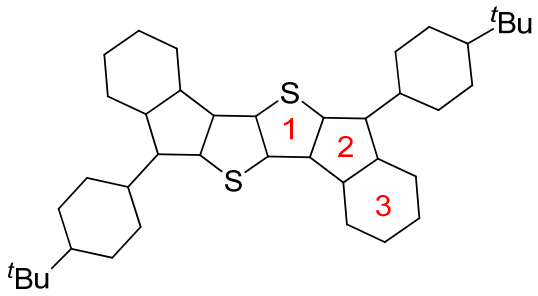
Compound: **S2-Mes**



Bq distance (Å)	NICS values (sigma zz) ring 1	ring 2	ring 3
0.0000	29.1530	37.1357	-5.0010
0.1000	28.5714	36.7836	-5.5039
0.2000	27.0913	35.5849	-6.8851
0.3000	24.8319	33.5668	-8.9559
0.4000	21.9684	30.8053	-11.4488
0.5000	18.7130	27.4414	-14.0706
0.6000	15.2902	23.6749	-16.5531
0.7000	11.9092	19.7371	-18.6881
0.8000	8.7410	15.8540	-20.3446
0.9000	5.9046	12.2130	-21.4676
1.0000	3.4649	8.9439	-22.0642
1.1000	1.4397	6.1157	-22.1856
1.2000	-0.1884	3.7460	-21.9073
1.3000	-1.4585	1.8151	-21.3144
1.4000	-2.4201	0.2811	-20.4898
1.5000	-3.1250	-0.9083	-19.5080
1.6000	-3.6219	-1.8073	-18.4317
1.7000	-3.9540	-2.4672	-17.3109
1.8000	-4.1579	-2.9339	-16.1842
1.9000	-4.2640	-3.2475	-15.0795
2.0000	-4.2967	-3.4422	-14.0164
2.1000	-4.2757	-3.5470	-13.0076
2.2000	-4.2165	-3.5861	-12.0606
2.3000	-4.1314	-3.5796	-11.1790
2.4000	-4.0297	-3.5441	-10.3634
2.5000	-3.9189	-3.4926	-9.6127
2.6000	-3.8042	-3.4351	-8.9241
2.7000	-3.6897	-3.3790	-8.2944
2.8000	-3.5782	-3.3292	-7.7196
2.9000	-3.4716	-3.2885	-7.1957
3.0000	-3.3710	-3.2578	-6.7186
3.1000	-3.2771	-3.2368	-6.2843
3.2000	-3.1900	-3.2243	-5.8890
3.3000	-3.1095	-3.2182	-5.5292
3.4000	-3.0352	-3.2163	-5.2014
3.5000	-2.9667	-3.2162	-4.9026
3.6000	-2.9034	-3.2160	-4.6300

3.7000	-2.8445	-3.2137	-4.3809
3.8000	-2.7896	-3.2078	-4.1531
3.9000	-2.7380	-3.1974	-3.9442
4.0000	-2.6891	-3.1816	-3.7525
4.1000	-2.6424	-3.1601	-3.5762
4.2000	-2.5975	-3.1329	-3.4137
4.3000	-2.5540	-3.1000	-3.2636
4.4000	-2.5115	-3.0620	-3.1247
4.5000	-2.4699	-3.0192	-2.9958
4.6000	-2.4289	-2.9721	-2.8759
4.7000	-2.3882	-2.9214	-2.7642
4.8000	-2.3479	-2.8675	-2.6598
4.9000	-2.3078	-2.8112	-2.5620
5.0000	-2.2679	-2.7529	-2.4703

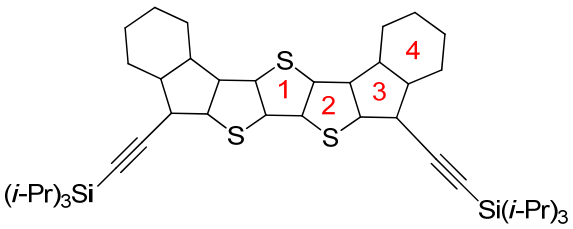
Compound: **S2-Ph**



Bq distance (Å)	NICS values (sigma zz)		
	ring 1	ring 2	ring 3
0.0000	29.7970	39.3052	-4.3257
0.1000	29.2384	38.7551	-4.7239
0.2000	27.7518	37.3387	-6.0137
0.3000	25.4572	35.1038	-8.0117
0.4000	22.5353	32.1437	-10.4537
0.5000	19.2067	28.6091	-13.0476
0.6000	15.7044	24.7017	-15.5236
0.7000	12.2441	20.6487	-17.6707
0.8000	9.0006	16.6680	-19.3538
0.9000	6.0945	12.9381	-20.5137
1.0000	3.5901	9.5811	-21.1536
1.1000	1.5041	6.6603	-21.3213
1.2000	-0.1822	4.1899	-21.0901
1.3000	-1.5087	2.1488	-20.5435
1.4000	-2.5256	0.4950	-19.7635
1.5000	-3.2849	-0.8224	-18.8242
1.6000	-3.8351	-1.8557	-17.7880

1.7000	-4.2192	-2.6535	-16.7051
1.8000	-4.4733	-3.2588	-15.6142
1.9000	-4.6270	-3.7083	-14.5433
2.0000	-4.7045	-4.0328	-13.5121
2.1000	-4.7247	-4.2576	-12.5336
2.2000	-4.7025	-4.4037	-11.6151
2.3000	-4.6495	-4.4878	-10.7602
2.4000	-4.5749	-4.5239	-9.9696
2.5000	-4.4854	-4.5229	-9.2420
2.6000	-4.3863	-4.4936	-8.5747
2.7000	-4.2815	-4.4431	-7.9643
2.8000	-4.1738	-4.3768	-7.4069
2.9000	-4.0654	-4.2991	-6.8985
3.0000	-3.9577	-4.2131	-6.4350
3.1000	-3.8518	-4.1216	-6.0124
3.2000	-3.7483	-4.0265	-5.6270
3.3000	-3.6476	-3.9293	-5.2753
3.4000	-3.5501	-3.8311	-4.9542
3.5000	-3.4558	-3.7329	-4.6606
3.6000	-3.3646	-3.6352	-4.3920
3.7000	-3.2767	-3.5387	-4.1457
3.8000	-3.1919	-3.4436	-3.9198
3.9000	-3.1100	-3.3504	-3.7122
4.0000	-3.0310	-3.2590	-3.5211
4.1000	-2.9548	-3.1699	-3.3450
4.2000	-2.8811	-3.0829	-3.1824
4.3000	-2.8099	-2.9982	-3.0320
4.4000	-2.7411	-2.9159	-2.8927
4.5000	-2.6744	-2.8359	-2.7635
4.6000	-2.6099	-2.7582	-2.6434
4.7000	-2.5474	-2.6829	-2.5317
4.8000	-2.4868	-2.6099	-2.4275
4.9000	-2.4280	-2.5391	-2.3303
5.0000	-2.3710	-2.4706	-2.2393

Compound: **S3-TIPS**

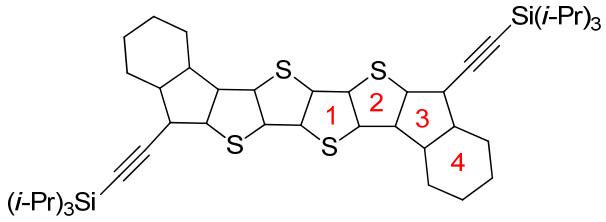


Bq distance (Å)	NICS values (sigma zz)			
	ring 1	ring 2	ring 3	ring 4
0.0000	23.5971	26.1709	39.2581	-3.7475
0.1000	23.0469	25.6666	38.8292	-4.2156
0.2000	21.4826	24.1648	37.5604	-5.5633
0.3000	19.0597	21.8043	35.4780	-7.6069
0.4000	16.0085	18.7967	32.6526	-10.0838
0.5000	12.5976	15.3951	29.2169	-12.7051
0.6000	9.0947	11.8587	25.3629	-15.2041
0.7000	5.7324	8.4190	21.3169	-17.3724
0.8000	2.6845	5.2552	17.3034	-19.0766
0.9000	0.0578	2.4832	13.5113	-20.2583
1.0000	-2.1032	0.1575	10.0742	-20.9208
1.1000	-3.8040	-1.7178	7.0658	-21.1119
1.2000	-5.0834	-3.1735	4.5084	-20.9044
1.3000	-5.9982	-4.2605	2.3864	-20.3811
1.4000	-6.6114	-5.0376	0.6612	-19.6236
1.5000	-6.9839	-5.5634	-0.7166	-18.7053
1.6000	-7.1703	-5.8908	-1.7986	-17.6886
1.7000	-7.2167	-6.0655	-2.6340	-16.6232
1.8000	-7.1606	-6.1253	-3.2666	-15.5475
1.9000	-7.0317	-6.1003	-3.7340	-14.4897
2.0000	-6.8530	-6.0145	-4.0682	-13.4694
2.1000	-6.6420	-5.8861	-4.2959	-12.4994
2.2000	-6.4119	-5.7294	-4.4389	-11.5875
2.3000	-6.1721	-5.5549	-4.5154	-10.7373
2.4000	-5.9296	-5.3705	-4.5401	-9.9498
2.5000	-5.6894	-5.1819	-4.5250	-9.2237
2.6000	-5.4549	-4.9934	-4.4797	-8.5568
2.7000	-5.2282	-4.8078	-4.4119	-7.9458
2.8000	-5.0108	-4.6272	-4.3278	-7.3869
2.9000	-4.8034	-4.4529	-4.2321	-6.8763
3.0000	-4.6063	-4.2855	-4.1285	-6.4101
3.1000	-4.4195	-4.1255	-4.0200	-5.9844
3.2000	-4.2429	-3.9730	-3.9087	-5.5957
3.3000	-4.0759	-3.8279	-3.7965	-5.2407
3.4000	-3.9183	-3.6901	-3.6845	-4.9161
3.5000	-3.7695	-3.5594	-3.5737	-4.6191
3.6000	-3.6291	-3.4352	-3.4648	-4.3472
3.7000	-3.4965	-3.3175	-3.3585	-4.0978
3.8000	-3.3711	-3.2057	-3.2549	-3.8690
3.9000	-3.2527	-3.0996	-3.1545	-3.6587
4.0000	-3.1406	-2.9988	-3.0572	-3.4652
4.1000	-3.0344	-2.9030	-2.9634	-3.2869
4.2000	-2.9338	-2.8119	-2.8728	-3.1224
4.3000	-2.8384	-2.7252	-2.7857	-2.9704

4.4000	-2.7478	-2.6426	-2.7018	-2.8298
4.5000	-2.6617	-2.5638	-2.6212	-2.6996
4.6000	-2.5798	-2.4887	-2.5438	-2.5788
4.7000	-2.5018	-2.4170	-2.4695	-2.4666
4.8000	-2.4274	-2.3485	-2.3981	-2.3622
4.9000	-2.3565	-2.2830	-2.3295	-2.2650
5.0000	-2.2888	-2.2203	-2.2637	-2.1743

Compound: **S4-TIPS**

<S**2>= 0.8808



Bq distance (Å)	NICS values (sigma zz) ring 1	ring 2	ring 3	ring 4
0.0000	18.7560	23.3058	41.1880	-2.5373
0.1000	18.1870	22.7590	40.7828	-3.0065
0.2000	16.5406	21.1763	39.5718	-4.3474
0.3000	14.0024	18.7179	37.5621	-6.3814
0.4000	10.8416	15.6221	34.7995	-8.8518
0.5000	7.3635	12.1649	31.3952	-11.4754
0.6000	3.8612	8.6221	27.5271	-13.9900
0.7000	0.5773	5.2303	23.4179	-16.1887
0.8000	-2.3176	2.1661	19.2972	-17.9378
0.9000	-4.7291	-0.4636	15.3646	-19.1762
1.0000	-6.6296	-2.6153	11.7653	-19.9047
1.1000	-8.0418	-4.2974	8.5855	-20.1672
1.2000	-9.0197	-5.5511	5.8569	-20.0336
1.3000	-9.6323	-6.4360	3.5703	-19.5843
1.4000	-9.9516	-7.0170	1.6915	-18.8986
1.5000	-10.0444	-7.3571	0.1734	-18.0490
1.6000	-9.9689	-7.5119	-1.0346	-17.0966
1.7000	-9.7729	-7.5285	-1.9821	-16.0909
1.8000	-9.4947	-7.4450	-2.7133	-15.0701
1.9000	-9.1636	-7.2912	-3.2669	-14.0622
2.0000	-8.8016	-7.0904	-3.6762	-13.0872
2.1000	-8.4250	-6.8598	-3.9689	-12.1582
2.2000	-8.0453	-6.6126	-4.1681	-11.2832
2.3000	-7.6709	-6.3581	-4.2931	-10.4663
2.4000	-7.3071	-6.1031	-4.3597	-9.7087

2.5000	-6.9574	-5.8522	-4.3806	-9.0097
2.6000	-6.6240	-5.6086	-4.3665	-8.3671
2.7000	-6.3078	-5.3743	-4.3257	-7.7780
2.8000	-6.0093	-5.1504	-4.2649	-7.2390
2.9000	-5.7281	-4.9376	-4.1894	-6.7464
3.0000	-5.4638	-4.7360	-4.1033	-6.2965
3.1000	-5.2156	-4.5453	-4.0100	-5.8856
3.2000	-4.9828	-4.3653	-3.9119	-5.5104
3.3000	-4.7643	-4.1954	-3.8110	-5.1676
3.4000	-4.5594	-4.0352	-3.7089	-4.8541
3.5000	-4.3670	-3.8841	-3.6066	-4.5673
3.6000	-4.1863	-3.7414	-3.5050	-4.3045
3.7000	-4.0165	-3.6067	-3.4048	-4.0602
3.8000	-3.8568	-3.4794	-3.3065	-3.8390
3.9000	-3.7065	-3.3590	-3.2105	-3.6355
4.0000	-3.5648	-3.2449	-3.1169	-3.4481
4.1000	-3.4313	-3.1368	-3.0259	-3.2754
4.2000	-3.3053	-3.0343	-2.9377	-3.1159
4.3000	-3.1862	-2.9370	-2.8523	-2.9684
4.4000	-3.0736	-2.8445	-2.7698	-2.8318
4.5000	-2.9667	-2.7564	-2.6900	-2.7052
4.6000	-2.8658	-2.6724	-2.6130	-2.5875
4.7000	-2.7700	-2.5924	-2.5387	-2.4781
4.8000	-2.6792	-2.5160	-2.4671	-2.3761
4.9000	-2.5929	-2.4432	-2.3981	-2.2810
5.0000	-2.5108	-2.3734	-2.3316	-2.1921

4. Additional TA spectra and decay curves

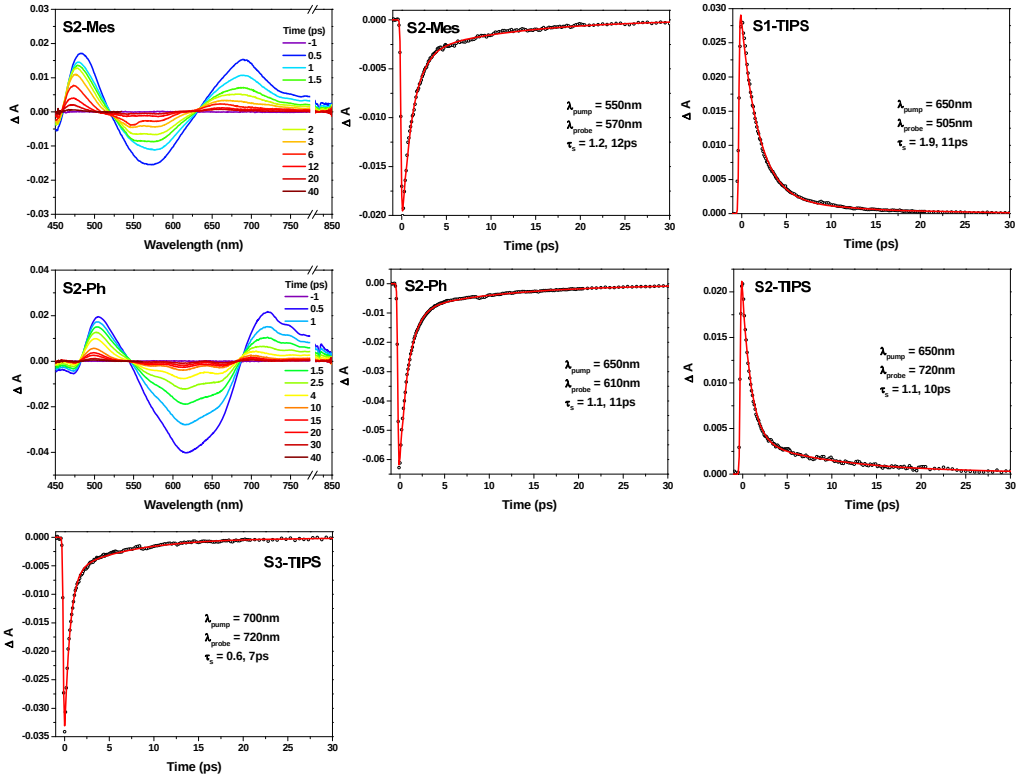


Fig. S9. Additional TA spectra of **S2-Mes** and **S2-Ph**, and all time decay profiles.

5. Z-scan curves

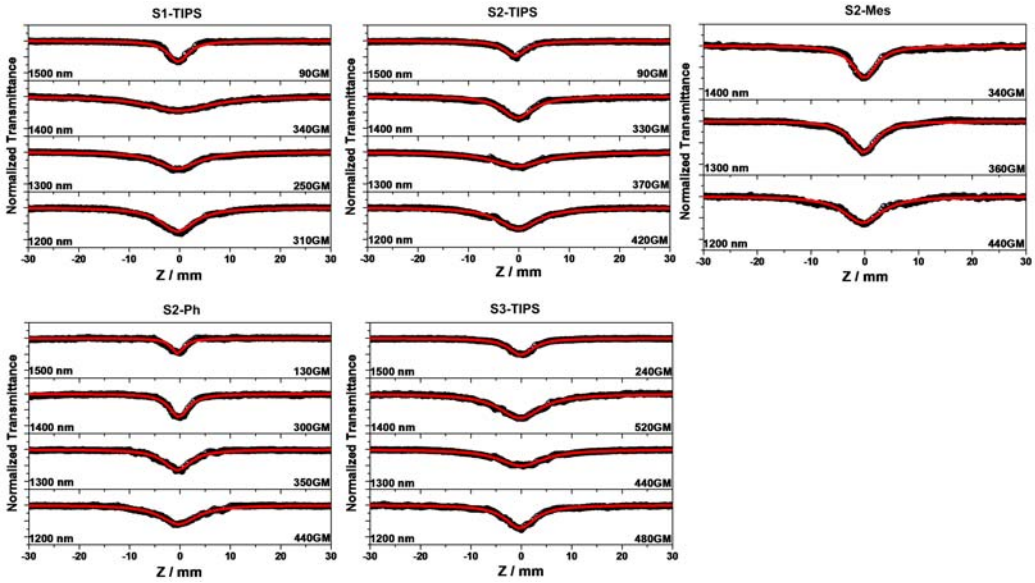


Fig. S10. Z-scan curves by photoexcitation in the range of 1200-1500 nm. We have always confirmed our experimental condition using Styryl-9M as a reference molecule before proceeding to actual measurements. Also, in every measurement we have ensured that the Rayleigh ranges, even though with fluctuations, reside in a certain range.

6. **OFET characterizations of compound S2-TIPS**

Top-contact, bottom-gate structure was used for the FET devices. A heavily n^+-doped silicon wafer (Silicon Quest International, resistivity < 0.005 Ωcm^{-1}) with a 200-nm thermal silicon dioxide (SiO_2) was used as the substrate/gate electrode, with the SiO_2 layer serving as the gate dielectric. The SiO_2/Si substrate was cleaned with acetone, IPA. It was then immersed in a piranha solution ($V(H_2SO_4)$: $V(H_2O_2)$ = 2:1) for 20 minutes, followed by rinsing with deionized water, and then re-immersed in a 3 mM solution of octadecyltrichlorosilane (OTS) in hexadecane at room temperature for 16 h in N_2 glove box. It was then rinsed with $CHCl_3$, IPA, DI water, and then blow dried with nitrogen gas. The semiconductor layer of **S2-TIPS** was deposited on top of the OTS-modified substrates by drop casting the 1wt% solution in chloroform with a covered OTS-treated wafer to control the thin film formation. Subsequently, gold source/drain electrode pairs were deposited by thermal evaporation through a metal shadow mask to create a series of TFTs with various channel length (W/L = 10/20) dimensions. The FET devices were then characterized using a Keithley SCS-4200 probe station under N_2.

Table S6. OFET characteristics of **S2-TIPS**.

Surface treatment	Annealing temperature	In N_2			In air		
		μ[$cm^2V^{-1}s^{-1}$]	**V_T [V]**	**On/off**	**μ[$cm^2V^{-1}s^{-1}$]**	**V_T [V]**	**On/off**
OTS-S	As-spun	0.016±0.004	-10	10^5-10^6	0.01±0.004	-25	10^4-10^5
OTS-S	150 °C	0.007	-12	10^5-10^6	0.004	-6	10^4-10^5

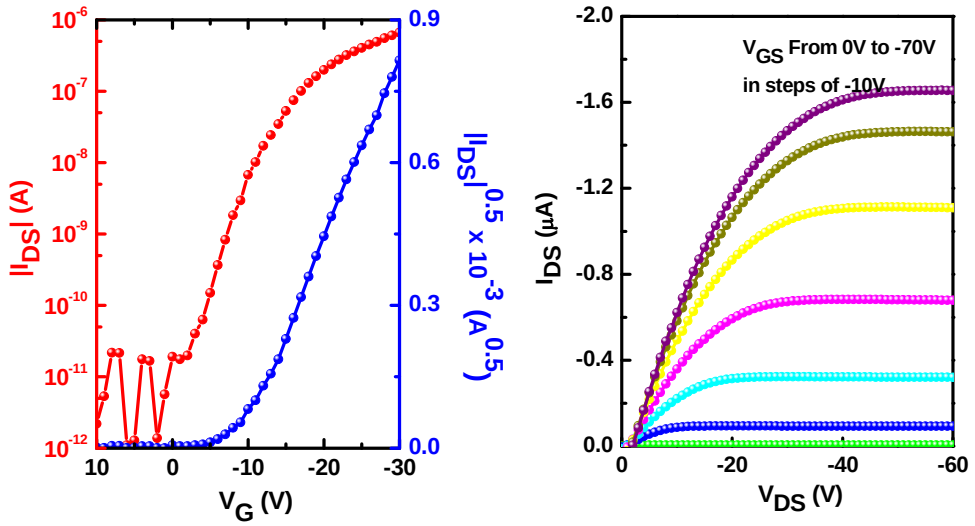


Fig. S11. Transfer and output characteristics of FET devices fabricated by solution casting of **S2-TIPS** on OTS-treated substrates when operated in N_2.

7. Combined ^{1}H NMR spectra of S1-TIPS - S3-TIPS

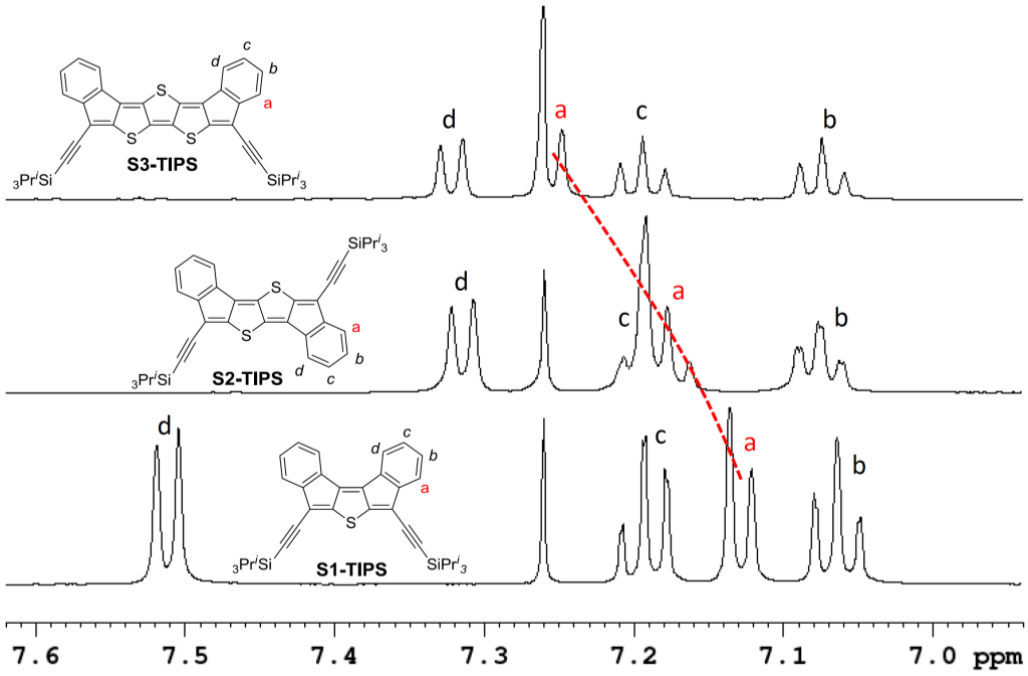


Fig. S12. Combined ^{1}H NMR spectra (aromatic region) of **S1-TIPS**, **S2-TIPS** and **S3-TIPS** in $CDCl_3$ (500 MHz). The resonance for proton "*d*" in **S1-TIPS** located at low field mainly due to the de-shielding effect from the second terminal benzene ring.

8. Variable temperature ESR spectra of S4-TIPS

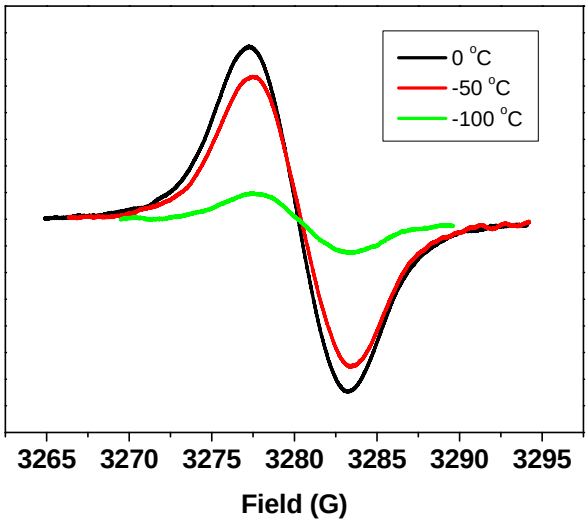


Fig. S13. VT ESR spectra of the *in situ* generated **S4-TIPS** in dry toluene.

9. Additional cyclic voltammograms

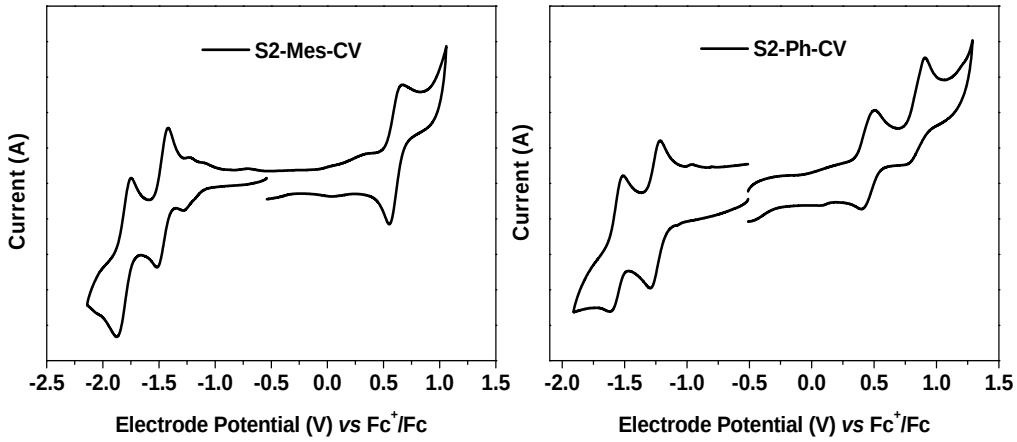


Fig. S14. Cyclic voltammograms of **S2-Mes** and **S2-Ph** in dry dichloromethane containing 0.1 M Bu_4NPF_6 as the supporting electrolyte, AgCl/Ag as the reference electrode, Au as the working electrode, Pt wire as the counter electrode, and a scan rate of 50 mV s^{-1}. The potential was externally calibrated against the ferrocene/ferrocenium couple.

10. Crystallographic data

Table S7. Crystal data and structure refinement for **S1-TIPS**.

Empirical formula	C40 H50 S Si2
Formula weight	619.04
Temperature	153(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 18.8584(12) A alpha = 90 deg.
	b = 12.3701(8) A beta = 104.724(4) deg.
	c = 15.9959(11) A gamma = 90 deg.
Volume	3609.0(4) $Å^3$
Z	4
Calculated density	1.139 Mg/m^3
Absorption coefficient	1.611 mm^{-1}
F(000)	1336
Crystal size	0.40 x 0.08 x 0.04 mm
Theta range for data collection	4.32 to 65.08 deg.
Limiting indices	-22<=h<=19, -14<=k<=14, -18<=l<=18
Reflections collected / unique	11612 / 3024 [R(int) = 0.0481]
Completeness to theta = 65.08	97.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9383 and 0.5650
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3024 / 0 / 201
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.1386
R indices (all data)	R1 = 0.0685, wR2 = 0.1511
Largest diff. peak and hole	0.555 and -0.261 e.A^-3

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **S1-TIPS**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	0	7289(1)	7500	37(1)
Si(1)	1675(1)	5736(1)	10991(1)	29(1)
C(1)	294(2)	8296(2)	8279(2)	32(1)
C(2)	160(1)	9384(2)	7934(2)	30(1)
C(3)	430(1)	10118(2)	8660(2)	30(1)
C(4)	443(2)	11235(2)	8729(2)	35(1)
C(5)	729(2)	11698(2)	9536(2)	41(1)
C(6)	994(2)	11062(2)	10257(2)	40(1)
C(7)	993(2)	9938(2)	10196(2)	36(1)
C(8)	712(1)	9478(2)	9397(2)	32(1)
C(9)	635(1)	8319(2)	9142(2)	32(1)

C(10)	909(2)	7452(2)	9708(2)	33(1)
C(11)	1188(1)	6751(2)	10211(2)	33(1)
C(12)	1107(2)	5559(2)	11795(2)	35(1)
C(13)	333(2)	5154(2)	11337(2)	46(1)
C(14)	1058(2)	6611(2)	12285(2)	44(1)
C(15)	2628(2)	6272(2)	11491(2)	39(1)
C(16)	2971(2)	5779(3)	12382(2)	53(1)
C(17)	2674(2)	7509(3)	11531(2)	52(1)
C(18)	1708(2)	4444(2)	10375(2)	36(1)
C(19)	2198(2)	3592(2)	10932(2)	56(1)
C(20)	1941(2)	4632(3)	9537(2)	51(1)

Table S9. Bond lengths [A] and angles [deg] for **S1-TIPS**.

S(1)-C(1)#1	1.750(2)
S(1)-C(1)	1.750(2)
Si(1)-C(11)	1.842(2)
Si(1)-C(12)	1.884(3)
Si(1)-C(18)	1.887(2)
Si(1)-C(15)	1.892(3)
C(1)-C(9)	1.366(4)
C(1)-C(2)	1.453(3)
C(2)-C(2)#1	1.366(5)
C(2)-C(3)	1.459(3)
C(3)-C(4)	1.386(4)
C(3)-C(8)	1.408(3)
C(4)-C(5)	1.390(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.381(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.394(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.377(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.487(3)
C(9)-C(10)	1.415(3)
C(10)-C(11)	1.208(4)
C(12)-C(14)	1.535(4)
C(12)-C(13)	1.540(4)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(17)	1.533(4)
C(15)-C(16)	1.534(4)
C(15)-H(15)	1.0000
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800

C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-C(19)	1.530(4)
C(18)-C(20)	1.531(4)
C(18)-H(18)	1.0000
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

C(1)#1-S(1)-C(1)	89.21(16)
C(11)-Si(1)-C(12)	105.68(12)
C(11)-Si(1)-C(18)	107.48(11)
C(12)-Si(1)-C(18)	110.94(12)
C(11)-Si(1)-C(15)	107.69(12)
C(12)-Si(1)-C(15)	113.33(12)
C(18)-Si(1)-C(15)	111.34(12)
C(9)-C(1)-C(2)	110.9(2)
C(9)-C(1)-S(1)	135.79(19)
C(2)-C(1)-S(1)	113.33(18)
C(2)#1-C(2)-C(1)	112.06(14)
C(2)#1-C(2)-C(3)	141.57(13)
C(1)-C(2)-C(3)	106.4(2)
C(4)-C(3)-C(8)	119.9(2)
C(4)-C(3)-C(2)	132.7(2)
C(8)-C(3)-C(2)	107.3(2)
C(3)-C(4)-C(5)	118.7(2)
C(3)-C(4)-H(4)	120.7
C(5)-C(4)-H(4)	120.7
C(6)-C(5)-C(4)	120.9(2)
C(6)-C(5)-H(5)	119.6
C(4)-C(5)-H(5)	119.6
C(5)-C(6)-C(7)	121.1(2)
C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4
C(8)-C(7)-C(6)	118.1(2)
C(8)-C(7)-H(7)	121.0
C(6)-C(7)-H(7)	121.0
C(7)-C(8)-C(3)	121.3(2)
C(7)-C(8)-C(9)	129.9(2)
C(3)-C(8)-C(9)	108.8(2)
C(1)-C(9)-C(10)	129.2(2)
C(1)-C(9)-C(8)	106.6(2)
C(10)-C(9)-C(8)	124.1(2)
C(11)-C(10)-C(9)	175.5(3)
C(10)-C(11)-Si(1)	175.9(2)
C(14)-C(12)-C(13)	110.2(2)
C(14)-C(12)-Si(1)	111.63(18)
C(13)-C(12)-Si(1)	110.29(17)
C(14)-C(12)-H(12)	108.2
C(13)-C(12)-H(12)	108.2
Si(1)-C(12)-H(12)	108.2
C(12)-C(13)-H(13A)	109.5

C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(17)-C(15)-C(16)	110.6(2)
C(17)-C(15)-Si(1)	113.9(2)
C(16)-C(15)-Si(1)	112.6(2)
C(17)-C(15)-H(15)	106.4
C(16)-C(15)-H(15)	106.4
Si(1)-C(15)-H(15)	106.4
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(19)-C(18)-C(20)	110.4(3)
C(19)-C(18)-Si(1)	112.00(19)
C(20)-C(18)-Si(1)	112.51(18)
C(19)-C(18)-H(18)	107.2
C(20)-C(18)-H(18)	107.2
Si(1)-C(18)-H(18)	107.2
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+3/2

Table S10. Anisotropic displacement parameters (A^2 x 10^3) for **S1-TIPS**. The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	50(1)	22(1)	35(1)	0	5(1)	0
Si(1)	33(1)	26(1)	28(1)	1(1)	6(1)	2(1)
C(1)	40(1)	24(1)	33(1)	1(1)	9(1)	0(1)
C(2)	32(1)	25(1)	34(1)	1(1)	8(1)	2(1)
C(3)	29(1)	29(1)	32(1)	-1(1)	7(1)	2(1)
C(4)	38(1)	27(1)	36(1)	0(1)	5(1)	3(1)
C(5)	48(2)	30(1)	43(1)	-7(1)	8(1)	-2(1)
C(6)	44(2)	42(1)	32(1)	-8(1)	5(1)	-1(1)
C(7)	36(1)	41(1)	29(1)	0(1)	6(1)	3(1)
C(8)	32(1)	30(1)	35(1)	0(1)	10(1)	0(1)
C(9)	35(1)	29(1)	31(1)	2(1)	8(1)	0(1)
C(10)	39(1)	29(1)	31(1)	0(1)	10(1)	-1(1)
C(11)	37(1)	29(1)	32(1)	2(1)	7(1)	1(1)
C(12)	40(2)	34(1)	32(1)	5(1)	10(1)	4(1)
C(13)	45(2)	52(2)	43(2)	2(1)	16(1)	-8(1)
C(14)	49(2)	43(2)	44(2)	-3(1)	18(1)	4(1)
C(15)	34(1)	46(2)	36(1)	-7(1)	8(1)	-2(1)
C(16)	42(2)	71(2)	42(2)	-4(1)	-1(1)	4(2)
C(17)	49(2)	52(2)	56(2)	-12(1)	14(1)	-14(1)
C(18)	42(2)	29(1)	38(1)	-5(1)	8(1)	0(1)
C(19)	74(2)	35(1)	56(2)	-1(1)	10(2)	19(2)
C(20)	65(2)	48(2)	42(2)	-11(1)	19(1)	3(2)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **S1-TIPS**.

	x	y	z	U(eq)
H(4)	259	11675	8234	42
H(5)	743	12463	9592	49
H(6)	1179	11396	10804	48
H(7)	1181	9502	10692	43
H(12)	1348	4999	12225	42
H(13A)	36	5101	11756	69
H(13B)	369	4441	11084	69
H(13C)	103	5663	10879	69
H(14A)	860	7187	11871	66
H(14B)	1548	6815	12628	66
H(14C)	734	6503	12670	66
H(15)	2941	6036	11105	47
H(16A)	3484	6010	12580	80
H(16B)	2950	4989	12340	80
H(16C)	2699	6023	12794	80
H(17A)	2364	7782	11892	78
H(17B)	2503	7806	10946	78
H(17C)	3183	7730	11781	78
H(18)	1199	4143	10210	44

H(19A)	2147	2904	10618	84
H(19B)	2051	3495	11473	84
H(19C)	2710	3830	11063	84
H(20A)	2437	4936	9674	76
H(20B)	1600	5137	9168	76
H(20C)	1936	3943	9233	76

Table S12. Torsion angles [deg] for **S1-TIPS**.

C(1)#1-S(1)-C(1)-C(9)	-178.3(4)
C(1)#1-S(1)-C(1)-C(2)	0.30(13)
C(9)-C(1)-C(2)-C(2)#1	178.1(3)
S(1)-C(1)-C(2)-C(2)#1	-0.9(4)
C(9)-C(1)-C(2)-C(3)	-1.3(3)
S(1)-C(1)-C(2)-C(3)	179.74(16)
C(2)#1-C(2)-C(3)-C(4)	1.9(7)
C(1)-C(2)-C(3)-C(4)	-179.0(3)
C(2)#1-C(2)-C(3)-C(8)	-179.0(4)
C(1)-C(2)-C(3)-C(8)	0.1(3)
C(8)-C(3)-C(4)-C(5)	-0.7(4)
C(2)-C(3)-C(4)-C(5)	178.3(3)
C(3)-C(4)-C(5)-C(6)	-0.3(4)
C(4)-C(5)-C(6)-C(7)	1.1(4)
C(5)-C(6)-C(7)-C(8)	-0.8(4)
C(6)-C(7)-C(8)-C(3)	-0.2(4)
C(6)-C(7)-C(8)-C(9)	-179.3(3)
C(4)-C(3)-C(8)-C(7)	1.0(4)
C(2)-C(3)-C(8)-C(7)	-178.3(2)
C(4)-C(3)-C(8)-C(9)	-179.7(2)
C(2)-C(3)-C(8)-C(9)	1.0(3)
C(2)-C(1)-C(9)-C(10)	-174.9(3)
S(1)-C(1)-C(9)-C(10)	3.7(5)
C(2)-C(1)-C(9)-C(8)	1.9(3)
S(1)-C(1)-C(9)-C(8)	-179.5(2)
C(7)-C(8)-C(9)-C(1)	177.4(3)
C(3)-C(8)-C(9)-C(1)	-1.8(3)
C(7)-C(8)-C(9)-C(10)	-5.5(4)
C(3)-C(8)-C(9)-C(10)	175.2(2)
C(1)-C(9)-C(10)-C(11)	130(3)
C(8)-C(9)-C(10)-C(11)	-46(3)
C(9)-C(10)-C(11)-Si(1)	-6(6)
C(12)-Si(1)-C(11)-C(10)	127(3)
C(18)-Si(1)-C(11)-C(10)	-115(3)
C(15)-Si(1)-C(11)-C(10)	5(3)
C(11)-Si(1)-C(12)-C(14)	-62.3(2)
C(18)-Si(1)-C(12)-C(14)	-178.52(19)
C(15)-Si(1)-C(12)-C(14)	55.4(2)
C(11)-Si(1)-C(12)-C(13)	60.6(2)
C(18)-Si(1)-C(12)-C(13)	-55.6(2)
C(15)-Si(1)-C(12)-C(13)	178.29(18)
C(11)-Si(1)-C(15)-C(17)	29.0(2)
C(12)-Si(1)-C(15)-C(17)	-87.5(2)
C(18)-Si(1)-C(15)-C(17)	146.6(2)

C(11)-Si(1)-C(15)-C(16)	156.0(2)
C(12)-Si(1)-C(15)-C(16)	39.5(2)
C(18)-Si(1)-C(15)-C(16)	-86.4(2)
C(11)-Si(1)-C(18)-C(19)	171.5(2)
C(12)-Si(1)-C(18)-C(19)	-73.4(3)
C(15)-Si(1)-C(18)-C(19)	53.8(3)
C(11)-Si(1)-C(18)-C(20)	46.4(2)
C(12)-Si(1)-C(18)-C(20)	161.5(2)
C(15)-Si(1)-C(18)-C(20)	-71.3(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+3/2

Table S13. Crystal data and structure refinement for **S2-TIPS**.

Empirical formula	C42 H50 S2 Si2
Formula weight	675.12
Temperature	123(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.402(6) A alpha = 73.693(15) deg. b = 14.535(11) A beta = 83.913(16) deg. c = 18.955(14) A gamma = 77.680(14) deg.
Volume	1910(3) $Å^3$
Z	2
Calculated density	1.174 Mg/m^3
Absorption coefficient	0.230 mm^{-1}
F(000)	724
Crystal size	0.40 x 0.22 x 0.02 mm
Theta range for data collection	1.12 to 25.68 deg.
Limiting indices	-9<=h<=8, -17<=k<=17, -22<=l<=23
Reflections collected / unique	26316 / 7205 [R(int) = 0.2133]
Completeness to theta = 25.68	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9954 and 0.9136
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7205 / 0 / 427
Goodness-of-fit on F^2	0.996
Final R indices [I>2sigma(I)]	R1 = 0.0719, wR2 = 0.1581
R indices (all data)	R1 = 0.1814, wR2 = 0.2103
Largest diff. peak and hole	0.522 and -0.390 e.A^-3

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **S2-TIPS**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)

S(1)	3729(2)	4966(1)	6066(1)	26(1)
S(2)	1369(2)	4874(1)	3975(1)	25(1)
Si(1)	183(2)	7640(1)	7768(1)	30(1)
Si(2)	4669(2)	7346(1)	1381(1)	31(1)
C(1)	4733(7)	4598(3)	5297(2)	26(1)
C(2)	3933(7)	6164(3)	5620(2)	23(1)
C(3)	3461(7)	7052(3)	5771(2)	23(1)
C(4)	4081(7)	7776(3)	5124(2)	25(1)
C(5)	3945(7)	8763(3)	5000(3)	27(1)
C(6)	4649(8)	9283(3)	4319(3)	32(1)
C(7)	5428(7)	8819(3)	3789(3)	28(1)
C(8)	5576(7)	7817(3)	3913(3)	27(1)
C(9)	4897(7)	7296(3)	4579(3)	24(1)
C(10)	4814(7)	6270(3)	4884(2)	24(1)
C(11)	2504(7)	7274(3)	6412(3)	26(1)
C(12)	1646(8)	7475(3)	6946(3)	31(1)
C(13)	27(8)	8915(4)	7805(3)	36(1)
C(14)	-1235(11)	9188(5)	8456(4)	73(2)
C(15)	1863(10)	9262(4)	7761(3)	53(2)
C(16)	1279(9)	6659(4)	8564(3)	40(2)
C(17)	15(10)	6456(5)	9242(3)	66(2)
C(18)	3179(9)	6780(4)	8718(3)	53(2)
C(19)	-2161(8)	7446(4)	7629(3)	37(1)
C(20)	-3157(9)	8263(4)	7006(3)	51(2)
C(21)	-2064(10)	6449(4)	7478(4)	55(2)
C(22)	316(7)	4575(3)	4856(2)	23(1)
C(23)	972(7)	6097(3)	3986(2)	21(1)
C(24)	1371(7)	6948(3)	3524(2)	24(1)
C(25)	632(7)	7724(3)	3907(2)	23(1)
C(26)	632(7)	8706(3)	3687(3)	29(1)
C(27)	-155(7)	9275(3)	4159(3)	28(1)
C(28)	-915(8)	8859(3)	4848(3)	28(1)
C(29)	-942(7)	7868(3)	5075(2)	24(1)
C(30)	-182(7)	7307(3)	4600(2)	22(1)
C(31)	42(7)	6264(3)	4663(2)	24(1)
C(32)	2357(7)	7100(3)	2827(3)	25(1)
C(33)	3220(8)	7236(3)	2242(3)	31(1)
C(34)	3594(9)	8492(4)	697(3)	46(2)
C(35)	1575(11)	8539(5)	561(4)	82(3)
C(36)	4724(11)	8730(5)	-36(3)	68(2)
C(37)	4821(9)	6168(4)	1123(3)	46(2)
C(38)	3003(11)	5958(5)	995(4)	76(2)
C(39)	6257(10)	6068(4)	492(3)	53(2)
C(40)	7048(9)	7465(4)	1574(3)	46(2)
C(41)	7980(9)	6561(4)	2143(3)	52(2)
C(42)	6988(11)	8405(5)	1814(3)	58(2)

Table S15. Bond lengths [A] and angles [deg] for **S2-TIPS**.

S(1)-C(1)	1.732(5)
S(1)-C(2)	1.740(5)
S(2)-C(23)	1.744(5)

S(2)-C(22)	1.745(5)
Si(1)-C(12)	1.842(6)
Si(1)-C(13)	1.853(5)
Si(1)-C(19)	1.873(6)
Si(1)-C(16)	1.878(5)
Si(2)-C(33)	1.843(6)
Si(2)-C(34)	1.878(5)
Si(2)-C(37)	1.887(6)
Si(2)-C(40)	1.889(7)
C(1)-C(10)#1	1.364(6)
C(1)-C(1)#1	1.468(9)
C(2)-C(3)	1.366(6)
C(2)-C(10)	1.456(7)
C(3)-C(11)	1.422(7)
C(3)-C(4)	1.477(6)
C(4)-C(5)	1.371(6)
C(4)-C(9)	1.418(7)
C(5)-C(6)	1.410(7)
C(5)-H(5)	0.9500
C(6)-C(7)	1.374(7)
C(6)-H(6)	0.9500
C(7)-C(8)	1.391(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.383(7)
C(8)-H(8)	0.9500
C(9)-C(10)	1.453(6)
C(10)-C(1)#1	1.364(6)
C(11)-C(12)	1.211(7)
C(13)-C(15)	1.534(8)
C(13)-C(14)	1.557(8)
C(13)-H(13)	1.0000
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(17)	1.505(8)
C(16)-C(18)	1.522(8)
C(16)-H(16)	1.0000
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(21)	1.540(7)
C(19)-C(20)	1.540(7)
C(19)-H(19)	1.0000
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800

C(22)-C(31)#2	1.361(6)
C(22)-C(22)#2	1.456(9)
C(23)-C(24)	1.371(6)
C(23)-C(31)	1.447(6)
C(24)-C(32)	1.424(7)
C(24)-C(25)	1.487(6)
C(25)-C(26)	1.370(6)
C(25)-C(30)	1.412(6)
C(26)-C(27)	1.387(7)
C(26)-H(26)	0.9500
C(27)-C(28)	1.391(7)
C(27)-H(27)	0.9500
C(28)-C(29)	1.387(6)
C(28)-H(28)	0.9500
C(29)-C(30)	1.380(7)
C(29)-H(29)	0.9500
C(30)-C(31)	1.461(6)
C(31)-C(22)#2	1.361(6)
C(32)-C(33)	1.206(7)
C(34)-C(35)	1.527(9)
C(34)-C(36)	1.535(8)
C(34)-H(34)	1.0000
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-C(38)	1.500(9)
C(37)-C(39)	1.531(8)
C(37)-H(37)	1.0000
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-C(41)	1.530(7)
C(40)-C(42)	1.546(8)
C(40)-H(40)	1.0000
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800

C(1)-S(1)-C(2)	90.0(2)
C(23)-S(2)-C(22)	90.0(2)
C(12)-Si(1)-C(13)	107.6(2)
C(12)-Si(1)-C(19)	106.5(2)
C(13)-Si(1)-C(19)	109.8(3)
C(12)-Si(1)-C(16)	105.8(3)
C(13)-Si(1)-C(16)	116.0(3)
C(19)-Si(1)-C(16)	110.6(3)

C(33)-Si(2)-C(34)	107.7(3)
C(33)-Si(2)-C(37)	105.8(2)
C(34)-Si(2)-C(37)	116.0(3)
C(33)-Si(2)-C(40)	108.3(3)
C(34)-Si(2)-C(40)	109.0(3)
C(37)-Si(2)-C(40)	109.7(3)
C(10)#1-C(1)-C(1)#1	111.9(5)
C(10)#1-C(1)-S(1)	135.2(4)
C(1)#1-C(1)-S(1)	112.9(5)
C(3)-C(2)-C(10)	110.0(4)
C(3)-C(2)-S(1)	136.9(4)
C(10)-C(2)-S(1)	113.1(3)
C(2)-C(3)-C(11)	127.9(4)
C(2)-C(3)-C(4)	107.1(4)
C(11)-C(3)-C(4)	125.0(4)
C(5)-C(4)-C(9)	120.7(4)
C(5)-C(4)-C(3)	130.2(5)
C(9)-C(4)-C(3)	109.0(4)
C(4)-C(5)-C(6)	118.1(4)
C(4)-C(5)-H(5)	120.9
C(6)-C(5)-H(5)	120.9
C(7)-C(6)-C(5)	121.2(5)
C(7)-C(6)-H(6)	119.4
C(5)-C(6)-H(6)	119.4
C(6)-C(7)-C(8)	121.0(4)
C(6)-C(7)-H(7)	119.5
C(8)-C(7)-H(7)	119.5
C(9)-C(8)-C(7)	118.5(5)
C(9)-C(8)-H(8)	120.7
C(7)-C(8)-H(8)	120.7
C(8)-C(9)-C(4)	120.5(4)
C(8)-C(9)-C(10)	132.9(5)
C(4)-C(9)-C(10)	106.5(4)
C(1)#1-C(10)-C(9)	140.7(5)
C(1)#1-C(10)-C(2)	112.0(4)
C(9)-C(10)-C(2)	107.2(4)
C(12)-C(11)-C(3)	178.2(5)
C(11)-C(12)-Si(1)	172.1(5)
C(15)-C(13)-C(14)	109.7(5)
C(15)-C(13)-Si(1)	116.7(4)
C(14)-C(13)-Si(1)	114.2(4)
C(15)-C(13)-H(13)	105.0
C(14)-C(13)-H(13)	105.0
Si(1)-C(13)-H(13)	105.0
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5

H(15B)-C(15)-H(15C)	109.5
C(17)-C(16)-C(18)	113.5(5)
C(17)-C(16)-Si(1)	114.2(4)
C(18)-C(16)-Si(1)	113.5(4)
C(17)-C(16)-H(16)	104.7
C(18)-C(16)-H(16)	104.7
Si(1)-C(16)-H(16)	104.7
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(21)-C(19)-C(20)	109.5(5)
C(21)-C(19)-Si(1)	111.8(4)
C(20)-C(19)-Si(1)	112.5(4)
C(21)-C(19)-H(19)	107.6
C(20)-C(19)-H(19)	107.6
Si(1)-C(19)-H(19)	107.6
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(31)#2-C(22)-C(22)#2	112.7(6)
C(31)#2-C(22)-S(2)	135.1(4)
C(22)#2-C(22)-S(2)	112.2(4)
C(24)-C(23)-C(31)	110.8(4)
C(24)-C(23)-S(2)	136.2(4)
C(31)-C(23)-S(2)	113.0(3)
C(23)-C(24)-C(32)	129.1(4)
C(23)-C(24)-C(25)	106.3(4)
C(32)-C(24)-C(25)	124.5(4)
C(26)-C(25)-C(30)	120.1(4)
C(26)-C(25)-C(24)	130.5(4)
C(30)-C(25)-C(24)	109.3(4)
C(25)-C(26)-C(27)	118.9(5)
C(25)-C(26)-H(26)	120.5
C(27)-C(26)-H(26)	120.5
C(26)-C(27)-C(28)	120.8(4)
C(26)-C(27)-H(27)	119.6
C(28)-C(27)-H(27)	119.6

C(29)-C(28)-C(27)	120.9(5)
C(29)-C(28)-H(28)	119.6
C(27)-C(28)-H(28)	119.6
C(30)-C(29)-C(28)	118.1(5)
C(30)-C(29)-H(29)	121.0
C(28)-C(29)-H(29)	121.0
C(29)-C(30)-C(25)	121.1(4)
C(29)-C(30)-C(31)	132.4(4)
C(25)-C(30)-C(31)	106.5(4)
C(22)#2-C(31)-C(23)	112.1(4)
C(22)#2-C(31)-C(30)	140.8(5)
C(23)-C(31)-C(30)	107.1(4)
C(33)-C(32)-C(24)	178.6(6)
C(32)-C(33)-Si(2)	175.2(4)
C(35)-C(34)-C(36)	110.5(5)
C(35)-C(34)-Si(2)	114.2(4)
C(36)-C(34)-Si(2)	114.1(4)
C(35)-C(34)-H(34)	105.7
C(36)-C(34)-H(34)	105.7
Si(2)-C(34)-H(34)	105.7
C(34)-C(35)-H(35A)	109.5
C(34)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(34)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(34)-C(36)-H(36A)	109.5
C(34)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(34)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(38)-C(37)-C(39)	112.2(6)
C(38)-C(37)-Si(2)	115.1(5)
C(39)-C(37)-Si(2)	112.1(4)
C(38)-C(37)-H(37)	105.5
C(39)-C(37)-H(37)	105.5
Si(2)-C(37)-H(37)	105.5
C(37)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(37)-C(39)-H(39A)	109.5
C(37)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(37)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(41)-C(40)-C(42)	111.0(5)
C(41)-C(40)-Si(2)	111.5(4)
C(42)-C(40)-Si(2)	111.7(4)
C(41)-C(40)-H(40)	107.5
C(42)-C(40)-H(40)	107.5

Si(2)-C(40)-H(40)	107.5
C(40)-C(41)-H(41A)	109.5
C(40)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(40)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(40)-C(42)-H(42A)	109.5
C(40)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(40)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1

Table S16. Anisotropic displacement parameters (A^2 x 10^3) for **S2-TIPS**. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	30(1)	28(1)	20(1)	-6(1)	0(1)	-8(1)
S(2)	28(1)	29(1)	19(1)	-6(1)	-1(1)	-10(1)
Si(1)	37(1)	32(1)	22(1)	-7(1)	2(1)	-12(1)
Si(2)	37(1)	37(1)	21(1)	-8(1)	5(1)	-16(1)
C(1)	25(3)	33(3)	19(2)	-5(2)	1(2)	-8(2)
C(2)	20(3)	31(3)	22(3)	-9(2)	-3(2)	-9(2)
C(3)	19(3)	34(3)	20(3)	-9(2)	-5(2)	-8(2)
C(4)	24(3)	29(3)	22(3)	-6(2)	-4(2)	-8(2)
C(5)	26(3)	32(3)	28(3)	-16(2)	-3(2)	-3(2)
C(6)	39(4)	23(3)	36(3)	-9(2)	-4(3)	-10(2)
C(7)	35(4)	31(3)	19(3)	-4(2)	-1(2)	-12(2)
C(8)	26(3)	32(3)	24(3)	-8(2)	-3(2)	-8(2)
C(9)	22(3)	31(3)	24(3)	-10(2)	-6(2)	-7(2)
C(10)	23(3)	27(3)	22(3)	-6(2)	-3(2)	-8(2)
C(11)	29(3)	21(3)	26(3)	-4(2)	-8(2)	-3(2)
C(12)	38(4)	31(3)	25(3)	-6(2)	-1(3)	-13(2)
C(13)	37(4)	34(3)	38(3)	-9(2)	8(3)	-13(2)
C(14)	99(7)	57(4)	69(5)	-39(4)	32(5)	-19(4)
C(15)	64(5)	37(3)	63(4)	-13(3)	-3(4)	-20(3)
C(16)	41(4)	49(3)	27(3)	-1(2)	5(3)	-14(3)
C(17)	70(6)	76(5)	35(4)	7(3)	6(4)	-13(4)
C(18)	40(4)	62(4)	45(4)	4(3)	-9(3)	-5(3)
C(19)	42(4)	49(3)	23(3)	-15(2)	8(3)	-14(3)
C(20)	40(4)	72(4)	46(4)	-17(3)	-12(3)	-13(3)
C(21)	55(5)	64(4)	63(4)	-30(3)	6(4)	-33(3)
C(22)	21(3)	24(2)	23(3)	-5(2)	-3(2)	-4(2)
C(23)	22(3)	27(3)	15(2)	-5(2)	-2(2)	-5(2)

C(24)	25(3)	29(3)	19(3)	-4(2)	-2(2)	-8(2)
C(25)	22(3)	29(3)	18(2)	-7(2)	-5(2)	-5(2)
C(26)	30(4)	33(3)	25(3)	-2(2)	-5(2)	-12(2)
C(27)	38(4)	17(2)	30(3)	-3(2)	-8(3)	-9(2)
C(28)	32(3)	28(3)	25(3)	-9(2)	-4(2)	-7(2)
C(29)	26(3)	33(3)	17(2)	-8(2)	-1(2)	-12(2)
C(30)	22(3)	27(3)	19(3)	-4(2)	-6(2)	-8(2)
C(31)	22(3)	32(3)	21(3)	-8(2)	-4(2)	-9(2)
C(32)	26(3)	23(2)	28(3)	-6(2)	-7(2)	-7(2)
C(33)	35(4)	36(3)	22(3)	-8(2)	3(2)	-13(2)
C(34)	58(5)	43(3)	34(3)	-5(3)	2(3)	-10(3)
C(35)	62(6)	86(5)	77(5)	13(4)	-32(5)	-4(4)
C(36)	101(7)	63(4)	32(4)	1(3)	7(4)	-21(4)
C(37)	43(4)	48(4)	53(4)	-20(3)	17(3)	-22(3)
C(38)	63(6)	101(6)	88(6)	-53(5)	15(4)	-41(4)
C(39)	56(5)	57(4)	51(4)	-25(3)	17(3)	-18(3)
C(40)	42(4)	69(4)	33(3)	-16(3)	14(3)	-30(3)
C(41)	37(4)	75(4)	45(4)	-12(3)	-4(3)	-17(3)
C(42)	71(6)	73(5)	45(4)	-20(3)	4(4)	-41(4)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **S2-TIPS**.

	x	y	z	U(eq)
H(5)	3392	9088	5362	33
H(6)	4583	9967	4224	38
H(7)	5872	9189	3331	34
H(8)	6131	7497	3548	32
H(13)	-612	9330	7352	43
H(14A)	-715	8785	8924	109
H(14B)	-2480	9072	8430	109
H(14C)	-1303	9879	8425	109
H(15A)	1615	9970	7696	79
H(15B)	2639	9105	7343	79
H(15C)	2507	8933	8217	79
H(16)	1519	6048	8397	49
H(17A)	689	5949	9636	99
H(17B)	-1053	6231	9131	99
H(17C)	-413	7055	9402	99
H(18A)	3049	7357	8903	80
H(18B)	3962	6860	8262	80
H(18C)	3751	6199	9087	80
H(19)	-2929	7451	8095	44
H(20A)	-2321	8370	6567	77
H(20B)	-3522	8867	7163	77
H(20C)	-4262	8072	6892	77
H(21A)	-3313	6373	7410	83
H(21B)	-1535	5926	7897	83
H(21C)	-1282	6413	7032	83

H(26)	1162	8992	3219	35
H(27)	-175	9958	4010	34
H(28)	-1422	9260	5168	33
H(29)	-1469	7584	5544	29
H(34)	3583	9037	923	56
H(35A)	1048	9196	269	123
H(35B)	872	8390	1034	123
H(35C)	1509	8061	293	123
H(36A)	4721	8238	-298	102
H(36B)	6000	8728	60	102
H(36C)	4171	9376	-337	102
H(37)	5310	5637	1560	55
H(38A)	2488	6431	549	114
H(38B)	2140	6009	1418	114
H(38C)	3192	5296	933	114
H(39A)	6263	5459	365	79
H(39B)	7486	6059	645	79
H(39C)	5941	6623	61	79
H(40)	7824	7515	1105	55
H(41A)	9217	6641	2224	78
H(41B)	8088	5982	1962	78
H(41C)	7233	6481	2607	78
H(42A)	6138	8408	2247	88
H(42B)	6557	8978	1411	88
H(42C)	8231	8424	1936	88

Table S18. Torsion angles [deg] for **S2-TIPS**.

C(2)-S(1)-C(1)-C(10)#1	179.7(6)
C(2)-S(1)-C(1)-C(1)#1	1.4(5)
C(1)-S(1)-C(2)-C(3)	177.7(6)
C(1)-S(1)-C(2)-C(10)	-1.3(4)
C(10)-C(2)-C(3)-C(11)	176.9(5)
S(1)-C(2)-C(3)-C(11)	-2.1(9)
C(10)-C(2)-C(3)-C(4)	-1.3(5)
S(1)-C(2)-C(3)-C(4)	179.7(4)
C(2)-C(3)-C(4)-C(5)	-179.8(5)
C(11)-C(3)-C(4)-C(5)	2.0(8)
C(2)-C(3)-C(4)-C(9)	1.2(6)
C(11)-C(3)-C(4)-C(9)	-177.0(5)
C(9)-C(4)-C(5)-C(6)	-0.4(7)
C(3)-C(4)-C(5)-C(6)	-179.3(5)
C(4)-C(5)-C(6)-C(7)	0.9(8)
C(5)-C(6)-C(7)-C(8)	-1.1(8)
C(6)-C(7)-C(8)-C(9)	0.9(7)
C(7)-C(8)-C(9)-C(4)	-0.4(7)
C(7)-C(8)-C(9)-C(10)	179.6(5)
C(5)-C(4)-C(9)-C(8)	0.2(7)
C(3)-C(4)-C(9)-C(8)	179.3(5)
C(5)-C(4)-C(9)-C(10)	-179.8(4)
C(3)-C(4)-C(9)-C(10)	-0.7(5)
C(8)-C(9)-C(10)-C(1)#1	-1.0(11)

C(4)-C(9)-C(10)-C(1)#1	179.0(6)
C(8)-C(9)-C(10)-C(2)	179.9(5)
C(4)-C(9)-C(10)-C(2)	-0.1(5)
C(3)-C(2)-C(10)-C(1)#1	-178.5(4)
S(1)-C(2)-C(10)-C(1)#1	0.8(6)
C(3)-C(2)-C(10)-C(9)	0.9(5)
S(1)-C(2)-C(10)-C(9)	-179.9(3)
C(2)-C(3)-C(11)-C(12)	-107(16)
C(4)-C(3)-C(11)-C(12)	71(17)
C(3)-C(11)-C(12)-Si(1)	77(17)
C(13)-Si(1)-C(12)-C(11)	-158(3)
C(19)-Si(1)-C(12)-C(11)	-41(3)
C(16)-Si(1)-C(12)-C(11)	77(3)
C(12)-Si(1)-C(13)-C(15)	-52.6(5)
C(19)-Si(1)-C(13)-C(15)	-168.1(4)
C(16)-Si(1)-C(13)-C(15)	65.6(5)
C(12)-Si(1)-C(13)-C(14)	177.7(5)
C(19)-Si(1)-C(13)-C(14)	62.2(5)
C(16)-Si(1)-C(13)-C(14)	-64.1(6)
C(12)-Si(1)-C(16)-C(17)	-161.7(5)
C(13)-Si(1)-C(16)-C(17)	79.1(5)
C(19)-Si(1)-C(16)-C(17)	-46.7(5)
C(12)-Si(1)-C(16)-C(18)	66.0(5)
C(13)-Si(1)-C(16)-C(18)	-53.2(5)
C(19)-Si(1)-C(16)-C(18)	-179.0(4)
C(12)-Si(1)-C(19)-C(21)	55.2(4)
C(13)-Si(1)-C(19)-C(21)	171.5(4)
C(16)-Si(1)-C(19)-C(21)	-59.2(4)
C(12)-Si(1)-C(19)-C(20)	-68.5(4)
C(13)-Si(1)-C(19)-C(20)	47.8(5)
C(16)-Si(1)-C(19)-C(20)	177.1(4)
C(23)-S(2)-C(22)-C(31)#2	-179.8(5)
C(23)-S(2)-C(22)-C(22)#2	-0.2(5)
C(22)-S(2)-C(23)-C(24)	177.4(6)
C(22)-S(2)-C(23)-C(31)	0.1(4)
C(31)-C(23)-C(24)-C(32)	176.2(5)
S(2)-C(23)-C(24)-C(32)	-1.1(9)
C(31)-C(23)-C(24)-C(25)	-1.2(6)
S(2)-C(23)-C(24)-C(25)	-178.5(4)
C(23)-C(24)-C(25)-C(26)	-178.9(5)
C(32)-C(24)-C(25)-C(26)	3.6(8)
C(23)-C(24)-C(25)-C(30)	0.5(6)
C(32)-C(24)-C(25)-C(30)	-177.0(5)
C(30)-C(25)-C(26)-C(27)	0.9(7)
C(24)-C(25)-C(26)-C(27)	-179.8(5)
C(25)-C(26)-C(27)-C(28)	0.7(8)
C(26)-C(27)-C(28)-C(29)	-1.4(8)
C(27)-C(28)-C(29)-C(30)	0.5(7)
C(28)-C(29)-C(30)-C(25)	1.2(7)
C(28)-C(29)-C(30)-C(31)	179.0(5)
C(26)-C(25)-C(30)-C(29)	-1.9(7)
C(24)-C(25)-C(30)-C(29)	178.7(4)
C(26)-C(25)-C(30)-C(31)	179.8(4)
C(24)-C(25)-C(30)-C(31)	0.3(5)
C(24)-C(23)-C(31)-C(22)#2	-177.9(4)

S(2)-C(23)-C(31)-C(22)#2	0.1(5)
C(24)-C(23)-C(31)-C(30)	1.4(5)
S(2)-C(23)-C(31)-C(30)	179.4(3)
C(29)-C(30)-C(31)-C(22)#2	-0.1(10)
C(25)-C(30)-C(31)-C(22)#2	178.0(6)
C(29)-C(30)-C(31)-C(23)	-179.1(5)
C(25)-C(30)-C(31)-C(23)	-1.0(5)
C(23)-C(24)-C(32)-C(33)	-121(22)
C(25)-C(24)-C(32)-C(33)	56(22)
C(24)-C(32)-C(33)-Si(2)	83(23)
C(34)-Si(2)-C(33)-C(32)	177(6)
C(37)-Si(2)-C(33)-C(32)	53(6)
C(40)-Si(2)-C(33)-C(32)	-65(6)
C(33)-Si(2)-C(34)-C(35)	-55.9(6)
C(37)-Si(2)-C(34)-C(35)	62.4(6)
C(40)-Si(2)-C(34)-C(35)	-173.2(5)
C(33)-Si(2)-C(34)-C(36)	175.7(5)
C(37)-Si(2)-C(34)-C(36)	-66.1(6)
C(40)-Si(2)-C(34)-C(36)	58.4(5)
C(33)-Si(2)-C(37)-C(38)	60.2(5)
C(34)-Si(2)-C(37)-C(38)	-59.1(6)
C(40)-Si(2)-C(37)-C(38)	176.8(5)
C(33)-Si(2)-C(37)-C(39)	-169.9(4)
C(34)-Si(2)-C(37)-C(39)	70.7(5)
C(40)-Si(2)-C(37)-C(39)	-53.3(5)
C(33)-Si(2)-C(40)-C(41)	61.7(5)
C(34)-Si(2)-C(40)-C(41)	178.7(4)
C(37)-Si(2)-C(40)-C(41)	-53.3(5)
C(33)-Si(2)-C(40)-C(42)	-63.1(4)
C(34)-Si(2)-C(40)-C(42)	53.8(5)
C(37)-Si(2)-C(40)-C(42)	-178.1(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x,-y+1,-z+1

Table S19. Crystal data and structure refinement for **S2-Mes**.

Empirical formula	C38 H30 S2
Formula weight	550.74
Temperature	173(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.0732(12) A alpha = 83.771(13) deg. b = 7.9974(14) A beta = 88.008(13) deg. c = 12.843(2) A gamma = 79.973(14) deg.
Volume	711.1(2) $Å^3$
Z	1
Calculated density	1.286 Mg/m^3
Absorption coefficient	1.881 mm^{-1}
F(000)	290
Crystal size	0.04 x 0.02 x 0.01 mm
Theta range for data collection	3.46 to 61.15 deg.

Limiting indices	-5<=h<=8, -9<=k<=9, -14<=l<=14
Reflections collected / unique	9077 / 2144 [R(int) = 0.1118]
Completeness to theta = 61.15	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9814 and 0.9286
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2144 / 0 / 185
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0811, wR2 = 0.2103
R indices (all data)	R1 = 0.1262, wR2 = 0.2501
Extinction coefficient	0.018(4)
Largest diff. peak and hole	0.398 and -0.487 e.A^-3

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **S2-Mes**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	5723(2)	2908(1)	1172(1)	56(1)
C(1)	5896(7)	4366(5)	71(4)	49(1)
C(2)	3397(7)	3947(5)	1445(4)	51(1)
C(3)	2774(7)	5404(5)	669(4)	47(1)
C(4)	842(7)	6128(5)	989(4)	50(1)
C(5)	-472(8)	7487(6)	560(4)	57(1)
C(6)	-2253(8)	7859(7)	1057(4)	65(2)
C(7)	-2702(8)	6888(7)	1952(4)	68(2)
C(8)	-1361(8)	5511(6)	2403(4)	61(2)
C(9)	380(7)	5133(6)	1916(4)	50(1)
C(10)	2060(7)	3774(5)	2195(4)	50(1)
C(11)	2193(6)	2569(5)	3164(4)	47(1)
C(12)	2344(7)	3187(6)	4137(4)	54(1)
C(13)	2483(7)	2047(7)	5049(4)	60(1)
C(14)	2501(7)	347(7)	5032(4)	59(2)
C(15)	2390(7)	-261(6)	4058(4)	61(2)
C(16)	2228(7)	827(6)	3130(4)	54(1)
C(17)	2456(10)	5036(6)	4211(5)	77(2)
C(18)	2671(8)	-863(7)	6019(4)	78(2)
C(19)	2027(10)	98(7)	2118(5)	79(2)

Table S21. Bond lengths [A] and angles [deg] for **S2-Mes**.

S(1)-C(1)	1.747(4)
S(1)-C(2)	1.751(5)
C(1)-C(3)#1	1.335(7)
C(1)-C(1)#1	1.482(9)
C(2)-C(10)	1.340(7)

C(2)-C(3)	1.465(6)
C(3)-C(1)#1	1.335(7)
C(3)-C(4)	1.452(6)
C(4)-C(5)	1.380(6)
C(4)-C(9)	1.419(7)
C(5)-C(6)	1.392(7)
C(5)-H(5)	0.9500
C(6)-C(7)	1.376(8)
C(6)-H(6)	0.9500
C(7)-C(8)	1.408(7)
C(7)-H(7)	0.9500
C(8)-C(9)	1.363(7)
C(8)-H(8)	0.9500
C(9)-C(10)	1.489(6)
C(10)-C(11)	1.483(6)
C(11)-C(16)	1.394(6)
C(11)-C(12)	1.407(7)
C(12)-C(13)	1.399(7)
C(12)-C(17)	1.508(7)
C(13)-C(14)	1.360(7)
C(13)-H(13)	0.9500
C(14)-C(15)	1.400(8)
C(14)-C(18)	1.504(6)
C(15)-C(16)	1.392(6)
C(15)-H(15)	0.9500
C(16)-C(19)	1.502(8)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800

C(1)-S(1)-C(2)	90.9(2)
C(3)#1-C(1)-C(1)#1	113.2(5)
C(3)#1-C(1)-S(1)	135.7(4)
C(1)#1-C(1)-S(1)	111.1(5)
C(10)-C(2)-C(3)	111.9(4)
C(10)-C(2)-S(1)	136.3(3)
C(3)-C(2)-S(1)	111.8(4)
C(1)#1-C(3)-C(4)	141.2(4)
C(1)#1-C(3)-C(2)	113.1(4)
C(4)-C(3)-C(2)	105.7(4)
C(5)-C(4)-C(9)	120.5(5)
C(5)-C(4)-C(3)	132.3(5)
C(9)-C(4)-C(3)	107.2(4)
C(4)-C(5)-C(6)	118.5(5)
C(4)-C(5)-H(5)	120.8
C(6)-C(5)-H(5)	120.8
C(7)-C(6)-C(5)	120.9(5)
C(7)-C(6)-H(6)	119.6
C(5)-C(6)-H(6)	119.6

C(6)-C(7)-C(8)	121.0(5)
C(6)-C(7)-H(7)	119.5
C(8)-C(7)-H(7)	119.5
C(9)-C(8)-C(7)	118.4(5)
C(9)-C(8)-H(8)	120.8
C(7)-C(8)-H(8)	120.8
C(8)-C(9)-C(4)	120.7(4)
C(8)-C(9)-C(10)	130.7(5)
C(4)-C(9)-C(10)	108.6(4)
C(2)-C(10)-C(11)	128.7(4)
C(2)-C(10)-C(9)	106.5(4)
C(11)-C(10)-C(9)	124.7(4)
C(16)-C(11)-C(12)	119.1(4)
C(16)-C(11)-C(10)	121.6(4)
C(12)-C(11)-C(10)	119.3(4)
C(13)-C(12)-C(11)	119.3(4)
C(13)-C(12)-C(17)	119.4(5)
C(11)-C(12)-C(17)	121.3(4)
C(14)-C(13)-C(12)	122.4(5)
C(14)-C(13)-H(13)	118.8
C(12)-C(13)-H(13)	118.8
C(13)-C(14)-C(15)	117.9(4)
C(13)-C(14)-C(18)	121.7(5)
C(15)-C(14)-C(18)	120.4(5)
C(16)-C(15)-C(14)	121.8(5)
C(16)-C(15)-H(15)	119.1
C(14)-C(15)-H(15)	119.1
C(15)-C(16)-C(11)	119.6(5)
C(15)-C(16)-C(19)	118.9(4)
C(11)-C(16)-C(19)	121.5(4)
C(12)-C(17)-H(17A)	109.5
C(12)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(12)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(14)-C(18)-H(18A)	109.5
C(14)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(14)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table S22. Anisotropic displacement parameters (A^2 x 10^3) for **S2-Mes**.

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	62(1)	46(1)	51(1)	6(1)	11(1)	6(1)
C(1)	60(3)	39(2)	43(3)	1(2)	7(2)	0(2)
C(2)	58(3)	38(2)	52(3)	-1(2)	9(2)	-2(2)
C(3)	54(3)	40(2)	44(3)	-3(2)	2(2)	-3(2)
C(4)	59(3)	42(2)	46(3)	-9(2)	6(2)	0(2)
C(5)	70(4)	46(2)	49(3)	-3(2)	0(2)	2(2)
C(6)	61(4)	63(3)	64(4)	-11(3)	2(3)	10(3)
C(7)	59(3)	70(3)	69(4)	-14(3)	13(3)	8(3)
C(8)	61(3)	62(3)	55(3)	-5(2)	13(2)	0(2)
C(9)	55(3)	45(2)	46(3)	-4(2)	5(2)	-3(2)
C(10)	55(3)	44(2)	47(3)	-4(2)	6(2)	-1(2)
C(11)	45(3)	46(2)	45(3)	-2(2)	11(2)	2(2)
C(12)	57(3)	52(3)	50(3)	-5(2)	12(2)	1(2)
C(13)	58(3)	71(3)	44(3)	-7(2)	14(2)	1(3)
C(14)	45(3)	69(3)	53(3)	12(3)	10(2)	0(2)
C(15)	59(3)	48(3)	70(4)	7(3)	6(3)	-4(2)
C(16)	53(3)	48(3)	58(3)	-3(2)	3(2)	-4(2)
C(17)	107(5)	59(3)	63(4)	-13(3)	0(3)	-3(3)
C(18)	64(4)	91(4)	66(4)	32(3)	11(3)	-2(3)
C(19)	108(5)	54(3)	74(4)	-10(3)	-7(3)	-11(3)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **S2-Mes**.

	x	y	z	U(eq)
H(5)	-169	8154	-61	68
H(6)	-3171	8796	775	78
H(7)	-3935	7150	2271	82
H(8)	-1663	4861	3031	73
H(13)	2568	2476	5704	72
H(15)	2427	-1448	4028	73
H(17A)	3501	5363	3755	116
H(17B)	2701	5197	4937	116
H(17C)	1238	5751	3988	116
H(18A)	4030	-1256	6180	117
H(18B)	2064	-1846	5921	117
H(18C)	2028	-275	6599	117
H(19A)	2088	-1140	2254	118
H(19B)	3071	341	1634	118
H(19C)	790	617	1806	118

Table S24. Torsion angles [deg] for **S2-Mes**.

C(2)-S(1)-C(1)-C(3)#1	-179.8(6)
C(2)-S(1)-C(1)-C(1)#1	-0.8(5)
C(1)-S(1)-C(2)-C(10)	-177.4(6)
C(1)-S(1)-C(2)-C(3)	0.7(4)
C(10)-C(2)-C(3)-C(1)#1	178.2(5)
S(1)-C(2)-C(3)-C(1)#1	-0.4(6)
C(10)-C(2)-C(3)-C(4)	-1.6(6)
S(1)-C(2)-C(3)-C(4)	179.7(3)
C(1)#1-C(3)-C(4)-C(5)	1.3(11)
C(2)-C(3)-C(4)-C(5)	-178.9(5)
C(1)#1-C(3)-C(4)-C(9)	-179.4(7)
C(2)-C(3)-C(4)-C(9)	0.3(5)
C(9)-C(4)-C(5)-C(6)	0.1(8)
C(3)-C(4)-C(5)-C(6)	179.3(5)
C(4)-C(5)-C(6)-C(7)	-0.5(8)
C(5)-C(6)-C(7)-C(8)	1.3(9)
C(6)-C(7)-C(8)-C(9)	-1.7(9)
C(7)-C(8)-C(9)-C(4)	1.3(8)
C(7)-C(8)-C(9)-C(10)	-179.7(5)
C(5)-C(4)-C(9)-C(8)	-0.6(8)
C(3)-C(4)-C(9)-C(8)	-179.9(5)
C(5)-C(4)-C(9)-C(10)	-179.8(5)
C(3)-C(4)-C(9)-C(10)	0.9(5)
C(3)-C(2)-C(10)-C(11)	-174.1(5)
S(1)-C(2)-C(10)-C(11)	4.0(10)
C(3)-C(2)-C(10)-C(9)	2.2(6)
S(1)-C(2)-C(10)-C(9)	-179.7(4)
C(8)-C(9)-C(10)-C(2)	179.0(6)
C(4)-C(9)-C(10)-C(2)	-1.9(6)
C(8)-C(9)-C(10)-C(11)	-4.5(9)
C(4)-C(9)-C(10)-C(11)	174.6(5)
C(2)-C(10)-C(11)-C(16)	-71.4(7)
C(9)-C(10)-C(11)-C(16)	112.9(5)
C(2)-C(10)-C(11)-C(12)	106.7(6)
C(9)-C(10)-C(11)-C(12)	-69.0(7)
C(16)-C(11)-C(12)-C(13)	-1.4(7)
C(10)-C(11)-C(12)-C(13)	-179.5(4)
C(16)-C(11)-C(12)-C(17)	175.6(5)
C(10)-C(11)-C(12)-C(17)	-2.5(7)
C(11)-C(12)-C(13)-C(14)	0.8(8)
C(17)-C(12)-C(13)-C(14)	-176.2(5)
C(12)-C(13)-C(14)-C(15)	0.5(8)
C(12)-C(13)-C(14)-C(18)	179.4(5)
C(13)-C(14)-C(15)-C(16)	-1.2(8)
C(18)-C(14)-C(15)-C(16)	179.8(5)
C(14)-C(15)-C(16)-C(11)	0.6(8)
C(14)-C(15)-C(16)-C(19)	-177.3(5)
C(12)-C(11)-C(16)-C(15)	0.7(7)
C(10)-C(11)-C(16)-C(15)	178.8(5)
C(12)-C(11)-C(16)-C(19)	178.6(5)
C(10)-C(11)-C(16)-C(19)	-3.4(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z

Table S25. Crystal data and structure refinement for **S2-Ph**.

Empirical formula	C40 H34 S2
Formula weight	578.79
Temperature	123(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 24.0560(10) A alpha = 90 deg. b = 16.0276(10) A beta = 122.105(4) deg. c = 18.3518(16) A gamma = 90 deg.
Volume	5993.7(7) $Å^3$
Z	8
Calculated density	1.283 Mg/m^3
Absorption coefficient	1.810 mm^{-1}
F(000)	2448
Crystal size	0.20 x 0.06 x 0.01 mm
Theta range for data collection	3.51 to 68.11 deg.
Limiting indices	-28<=h<=28, -19<=k<=19, -18<=l<=21
Reflections collected / unique	24423 / 5317 [R(int) = 0.2779]
Completeness to theta = 68.11	97.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9821 and 0.7135
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5317 / 0 / 385
Goodness-of-fit on F^2	1.156
Final R indices [I>2sigma(I)]	R1 = 0.1245, wR2 = 0.3045
R indices (all data)	R1 = 0.1843, wR2 = 0.3754
Largest diff. peak and hole	1.199 and -0.988 e.A^-3

Table S26. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **S2-Ph**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	4258(1)	3446(1)	8647(1)	41(1)
S(2)	5640(1)	5186(1)	8769(1)	40(1)
C(1)	4043(3)	4442(3)	8807(3)	39(1)
C(2)	3560(3)	4773(3)	8898(3)	39(1)
C(3)	3690(3)	5683(3)	9026(3)	39(1)
C(4)	3355(3)	6344(3)	9122(3)	45(1)
C(5)	3609(4)	7150(4)	9224(4)	53(2)
C(6)	4170(4)	7315(3)	9233(4)	49(2)

C(7)	4514(4)	6670(3)	9124(3)	45(1)
C(8)	4268(3)	5873(3)	9014(3)	36(1)
C(9)	4496(3)	5076(3)	8876(3)	33(1)
C(10)	4977(3)	4765(3)	8776(3)	40(1)
C(11)	4933(3)	3862(3)	8664(3)	42(1)
C(12)	5440(3)	3548(3)	8627(3)	38(1)
C(13)	5718(4)	2740(3)	8604(3)	44(1)
C(14)	5496(3)	1934(3)	8554(3)	42(1)
C(15)	5884(4)	1280(3)	8549(3)	50(2)
C(16)	6448(4)	1448(3)	8565(4)	50(2)
C(17)	6672(3)	2258(3)	8613(3)	46(1)
C(18)	6298(3)	2920(3)	8635(3)	40(1)
C(19)	6412(3)	3838(3)	8687(3)	40(1)
C(20)	5887(3)	4184(3)	8677(3)	38(1)
C(21)	3007(3)	4334(3)	8843(3)	40(1)
C(22)	2722(3)	3647(3)	8311(3)	41(1)
C(23)	2203(3)	3220(3)	8259(3)	42(1)
C(24)	1944(4)	3459(3)	8747(3)	44(1)
C(25)	2230(3)	4150(3)	9292(3)	44(1)
C(26)	2750(3)	4573(3)	9341(3)	43(1)
C(27)	1360(4)	3034(4)	8697(4)	48(2)
C(28)	1559(4)	2666(4)	9582(4)	56(2)
C(29)	814(4)	3678(4)	8426(4)	53(2)
C(30)	1095(4)	2324(4)	8043(5)	63(2)
C(31)	6956(3)	4281(3)	8714(3)	37(1)
C(32)	6863(3)	5044(3)	8294(3)	41(1)
C(33)	7371(3)	5451(3)	8294(3)	43(1)
C(34)	8005(3)	5118(3)	8730(3)	44(2)
C(35)	8103(3)	4376(3)	9187(3)	42(1)
C(36)	7600(3)	3980(3)	9185(3)	41(1)
C(37)	8563(3)	5510(3)	8689(4)	45(1)
C(38)	9179(4)	5646(4)	9582(4)	58(2)
C(39)	8364(4)	6372(4)	8243(4)	55(2)
C(40)	8746(4)	4939(4)	8173(4)	53(2)

Table S27. Bond lengths [A] and angles [deg] for **S2-Ph**.

S(1)-C(11)	1.739(6)
S(1)-C(1)	1.751(5)
S(2)-C(10)	1.737(6)
S(2)-C(20)	1.752(5)
C(1)-C(2)	1.366(8)
C(1)-C(9)	1.445(7)
C(2)-C(21)	1.463(8)
C(2)-C(3)	1.483(7)
C(3)-C(4)	1.398(8)
C(3)-C(8)	1.433(8)
C(4)-C(5)	1.398(9)
C(4)-H(4)	0.9500
C(5)-C(6)	1.367(10)
C(5)-H(5)	0.9500
C(6)-C(7)	1.404(8)

C(6)-H(6)	0.9500
C(7)-C(8)	1.378(8)
C(7)-H(7)	0.9500
C(8)-C(9)	1.465(7)
C(9)-C(10)	1.358(8)
C(10)-C(11)	1.458(8)
C(11)-C(12)	1.355(8)
C(12)-C(20)	1.448(8)
C(12)-C(13)	1.469(7)
C(13)-C(14)	1.383(8)
C(13)-C(18)	1.395(9)
C(14)-C(15)	1.408(8)
C(14)-H(14)	0.9500
C(15)-C(16)	1.368(10)
C(15)-H(15)	0.9500
C(16)-C(17)	1.391(8)
C(16)-H(16)	0.9500
C(17)-C(18)	1.405(8)
C(17)-H(17)	0.9500
C(18)-C(19)	1.491(7)
C(19)-C(20)	1.372(8)
C(19)-C(31)	1.467(8)
C(21)-C(22)	1.387(8)
C(21)-C(26)	1.401(7)
C(22)-C(23)	1.382(9)
C(22)-H(22)	0.9500
C(23)-C(24)	1.389(8)
C(23)-H(23)	0.9500
C(24)-C(25)	1.404(8)
C(24)-C(27)	1.520(9)
C(25)-C(26)	1.382(9)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(27)-C(30)	1.526(8)
C(27)-C(29)	1.531(9)
C(27)-C(28)	1.545(7)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-C(32)	1.397(7)
C(31)-C(36)	1.398(9)
C(32)-C(33)	1.387(9)
C(32)-H(32)	0.9500
C(33)-C(34)	1.397(9)
C(33)-H(33)	0.9500
C(34)-C(35)	1.400(7)
C(34)-C(37)	1.521(9)
C(35)-C(36)	1.366(8)
C(35)-H(35)	0.9500

C(36)-H(36)	0.9500
C(37)-C(38)	1.531(10)
C(37)-C(40)	1.540(7)
C(37)-C(39)	1.546(8)
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800

C(11)-S(1)-C(1)	90.2(3)
C(10)-S(2)-C(20)	90.2(3)
C(2)-C(1)-C(9)	111.5(4)
C(2)-C(1)-S(1)	136.2(4)
C(9)-C(1)-S(1)	112.3(4)
C(1)-C(2)-C(21)	127.4(5)
C(1)-C(2)-C(3)	106.3(5)
C(21)-C(2)-C(3)	126.3(5)
C(4)-C(3)-C(8)	118.0(5)
C(4)-C(3)-C(2)	132.7(6)
C(8)-C(3)-C(2)	109.3(5)
C(3)-C(4)-C(5)	118.5(6)
C(3)-C(4)-H(4)	120.7
C(5)-C(4)-H(4)	120.7
C(6)-C(5)-C(4)	122.6(5)
C(6)-C(5)-H(5)	118.7
C(4)-C(5)-H(5)	118.7
C(5)-C(6)-C(7)	120.6(6)
C(5)-C(6)-H(6)	119.7
C(7)-C(6)-H(6)	119.7
C(8)-C(7)-C(6)	117.6(6)
C(8)-C(7)-H(7)	121.2
C(6)-C(7)-H(7)	121.2
C(7)-C(8)-C(3)	122.7(5)
C(7)-C(8)-C(9)	131.5(5)
C(3)-C(8)-C(9)	105.8(4)
C(10)-C(9)-C(1)	112.8(5)
C(10)-C(9)-C(8)	140.1(5)
C(1)-C(9)-C(8)	107.1(5)
C(9)-C(10)-C(11)	112.3(5)
C(9)-C(10)-S(2)	135.2(4)
C(11)-C(10)-S(2)	112.5(4)
C(12)-C(11)-C(10)	112.1(6)
C(12)-C(11)-S(1)	135.5(4)
C(10)-C(11)-S(1)	112.4(5)
C(11)-C(12)-C(20)	113.2(5)
C(11)-C(12)-C(13)	140.0(5)
C(20)-C(12)-C(13)	106.7(5)
C(14)-C(13)-C(18)	122.6(5)
C(14)-C(13)-C(12)	131.2(6)
C(18)-C(13)-C(12)	106.1(5)

C(13)-C(14)-C(15)	117.4(6)
C(13)-C(14)-H(14)	121.3
C(15)-C(14)-H(14)	121.3
C(16)-C(15)-C(14)	120.5(5)
C(16)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7
C(15)-C(16)-C(17)	122.1(6)
C(15)-C(16)-H(16)	118.9
C(17)-C(16)-H(16)	118.9
C(16)-C(17)-C(18)	118.3(6)
C(16)-C(17)-H(17)	120.9
C(18)-C(17)-H(17)	120.9
C(13)-C(18)-C(17)	119.0(5)
C(13)-C(18)-C(19)	110.6(5)
C(17)-C(18)-C(19)	130.4(6)
C(20)-C(19)-C(31)	127.2(5)
C(20)-C(19)-C(18)	105.1(5)
C(31)-C(19)-C(18)	127.6(5)
C(19)-C(20)-C(12)	111.4(5)
C(19)-C(20)-S(2)	136.6(4)
C(12)-C(20)-S(2)	111.9(4)
C(22)-C(21)-C(26)	117.0(6)
C(22)-C(21)-C(2)	121.4(5)
C(26)-C(21)-C(2)	121.6(5)
C(23)-C(22)-C(21)	122.0(5)
C(23)-C(22)-H(22)	119.0
C(21)-C(22)-H(22)	119.0
C(22)-C(23)-C(24)	121.2(5)
C(22)-C(23)-H(23)	119.4
C(24)-C(23)-H(23)	119.4
C(23)-C(24)-C(25)	117.3(6)
C(23)-C(24)-C(27)	123.7(5)
C(25)-C(24)-C(27)	119.0(5)
C(26)-C(25)-C(24)	121.2(5)
C(26)-C(25)-H(25)	119.4
C(24)-C(25)-H(25)	119.4
C(25)-C(26)-C(21)	121.3(5)
C(25)-C(26)-H(26)	119.3
C(21)-C(26)-H(26)	119.3
C(24)-C(27)-C(30)	111.5(5)
C(24)-C(27)-C(29)	108.9(5)
C(30)-C(27)-C(29)	108.6(6)
C(24)-C(27)-C(28)	110.4(5)
C(30)-C(27)-C(28)	108.0(5)
C(29)-C(27)-C(28)	109.4(5)
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(27)-C(29)-H(29A)	109.5
C(27)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(27)-C(29)-H(29C)	109.5

H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(27)-C(30)-H(30A)	109.5
C(27)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(27)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(32)-C(31)-C(36)	116.4(5)
C(32)-C(31)-C(19)	121.7(5)
C(36)-C(31)-C(19)	121.9(4)
C(33)-C(32)-C(31)	121.9(6)
C(33)-C(32)-H(32)	119.1
C(31)-C(32)-H(32)	119.1
C(32)-C(33)-C(34)	120.9(5)
C(32)-C(33)-H(33)	119.5
C(34)-C(33)-H(33)	119.5
C(33)-C(34)-C(35)	116.9(6)
C(33)-C(34)-C(37)	122.4(5)
C(35)-C(34)-C(37)	120.6(6)
C(36)-C(35)-C(34)	121.7(6)
C(36)-C(35)-H(35)	119.1
C(34)-C(35)-H(35)	119.1
C(35)-C(36)-C(31)	122.0(5)
C(35)-C(36)-H(36)	119.0
C(31)-C(36)-H(36)	119.0
C(34)-C(37)-C(38)	112.6(5)
C(34)-C(37)-C(40)	109.4(5)
C(38)-C(37)-C(40)	108.2(6)
C(34)-C(37)-C(39)	111.3(5)
C(38)-C(37)-C(39)	106.9(5)
C(40)-C(37)-C(39)	108.4(5)
C(37)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(37)-C(39)-H(39A)	109.5
C(37)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(37)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(37)-C(40)-H(40A)	109.5
C(37)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(37)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S28. Anisotropic displacement parameters (A^2 x 10^3) for **S2-Ph**. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	66(1)	28(1)	47(1)	-3(1)	42(1)	-1(1)
S(2)	62(1)	28(1)	44(1)	0(1)	39(1)	2(1)
C(1)	65(4)	30(2)	34(2)	0(2)	34(3)	-7(2)
C(2)	58(4)	38(3)	33(2)	1(2)	31(3)	1(2)
C(3)	60(4)	30(2)	36(2)	4(2)	32(3)	9(2)
C(4)	67(4)	35(3)	45(3)	-2(2)	37(3)	4(3)
C(5)	87(5)	32(3)	59(3)	1(2)	52(4)	11(3)
C(6)	80(5)	32(3)	51(3)	1(2)	45(3)	7(3)
C(7)	74(4)	31(3)	44(3)	3(2)	41(3)	4(3)
C(8)	56(4)	27(2)	36(2)	-1(2)	32(3)	6(2)
C(9)	44(3)	31(2)	36(2)	-1(2)	30(2)	2(2)
C(10)	65(4)	31(3)	35(2)	5(2)	34(3)	5(2)
C(11)	71(4)	30(3)	36(2)	-1(2)	37(3)	-2(2)
C(12)	60(4)	31(3)	37(2)	-1(2)	36(3)	2(2)
C(13)	81(4)	28(2)	41(2)	-1(2)	45(3)	4(3)
C(14)	63(4)	35(3)	40(2)	1(2)	34(3)	5(3)
C(15)	88(5)	29(2)	44(3)	-1(2)	44(3)	1(3)
C(16)	91(5)	28(2)	46(3)	-1(2)	48(3)	9(3)
C(17)	74(4)	38(3)	42(3)	0(2)	42(3)	8(3)
C(18)	69(4)	31(2)	34(2)	1(2)	36(3)	5(2)
C(19)	62(4)	33(3)	36(2)	1(2)	34(3)	4(2)
C(20)	57(4)	33(2)	37(2)	0(2)	33(3)	-4(2)
C(21)	61(4)	32(3)	38(2)	6(2)	35(3)	9(2)
C(22)	62(4)	37(3)	40(2)	0(2)	38(3)	4(3)
C(23)	61(4)	30(2)	41(2)	-2(2)	32(3)	-2(2)
C(24)	74(4)	31(3)	39(3)	2(2)	38(3)	3(3)
C(25)	71(4)	34(3)	41(2)	1(2)	40(3)	6(3)
C(26)	66(4)	34(3)	42(2)	-1(2)	37(3)	3(3)
C(27)	77(5)	40(3)	45(3)	5(2)	44(3)	3(3)
C(28)	75(5)	50(3)	56(3)	13(3)	44(4)	0(3)
C(29)	67(5)	47(3)	52(3)	7(2)	36(3)	5(3)
C(30)	83(5)	51(4)	77(4)	-20(3)	58(4)	-22(4)
C(31)	59(4)	31(2)	36(2)	2(2)	35(3)	8(2)
C(32)	56(4)	40(3)	41(3)	2(2)	35(3)	7(3)
C(33)	68(4)	33(2)	39(2)	3(2)	37(3)	0(3)
C(34)	78(5)	35(3)	37(2)	-1(2)	41(3)	1(3)
C(35)	56(4)	39(3)	42(3)	1(2)	33(3)	3(3)
C(36)	64(4)	30(2)	47(3)	2(2)	41(3)	3(2)
C(37)	66(4)	36(3)	43(3)	-4(2)	37(3)	1(3)
C(38)	78(5)	57(4)	57(3)	-8(3)	47(4)	-8(3)
C(39)	91(5)	34(3)	64(3)	-3(3)	58(4)	-6(3)
C(40)	87(5)	39(3)	61(3)	-7(2)	58(4)	-6(3)

Table S29. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **S2-Ph**.

	x	y	z	U(eq)
H(4)	2964	6248	9118	54
H(5)	3382	7601	9289	63
H(6)	4329	7871	9315	59
H(7)	4903	6780	9125	54
H(14)	5096	1826	8525	51
H(15)	5754	718	8535	59
H(16)	6695	997	8544	60
H(17)	7067	2362	8629	55
H(22)	2890	3464	7971	49
H(23)	2020	2755	7883	50
H(25)	2064	4331	9633	52
H(26)	2937	5036	9720	52
H(28A)	1774	3098	10025	84
H(28B)	1863	2200	9719	84
H(28C)	1166	2467	9564	84
H(29A)	441	3414	8412	79
H(29B)	672	3892	7853	79
H(29C)	978	4139	8839	79
H(30A)	700	2091	7996	94
H(30B)	1429	1888	8231	94
H(30C)	985	2538	7481	94
H(32)	6439	5290	8001	50
H(33)	7288	5963	7993	51
H(35)	8531	4143	9508	51
H(36)	7689	3484	9513	49
H(38A)	9526	5891	9521	88
H(38B)	9329	5109	9881	88
H(38C)	9077	6024	9914	88
H(39A)	8721	6593	8192	82
H(39B)	8277	6757	8586	82
H(39C)	7968	6313	7669	82
H(40A)	8370	4892	7580	79
H(40B)	8862	4384	8438	79
H(40C)	9120	5177	8172	79

Table S30. Torsion angles [deg] for **S2-Ph**.

C(11)-S(1)-C(1)-C(2)	-179.0(6)
C(11)-S(1)-C(1)-C(9)	-0.4(4)
C(9)-C(1)-C(2)-C(21)	178.2(5)
S(1)-C(1)-C(2)-C(21)	-3.2(9)
C(9)-C(1)-C(2)-C(3)	0.7(6)
S(1)-C(1)-C(2)-C(3)	179.3(4)
C(1)-C(2)-C(3)-C(4)	177.3(5)
C(21)-C(2)-C(3)-C(4)	-0.2(9)

C(1)-C(2)-C(3)-C(8)	-0.5(5)
C(21)-C(2)-C(3)-C(8)	-178.0(5)
C(8)-C(3)-C(4)-C(5)	-1.6(7)
C(2)-C(3)-C(4)-C(5)	-179.3(5)
C(3)-C(4)-C(5)-C(6)	0.0(9)
C(4)-C(5)-C(6)-C(7)	1.1(9)
C(5)-C(6)-C(7)-C(8)	-0.5(8)
C(6)-C(7)-C(8)-C(3)	-1.3(8)
C(6)-C(7)-C(8)-C(9)	179.2(5)
C(4)-C(3)-C(8)-C(7)	2.3(7)
C(2)-C(3)-C(8)-C(7)	-179.5(5)
C(4)-C(3)-C(8)-C(9)	-178.0(4)
C(2)-C(3)-C(8)-C(9)	0.1(5)
C(2)-C(1)-C(9)-C(10)	-179.1(4)
S(1)-C(1)-C(9)-C(10)	1.9(5)
C(2)-C(1)-C(9)-C(8)	-0.6(6)
S(1)-C(1)-C(9)-C(8)	-179.6(3)
C(7)-C(8)-C(9)-C(10)	-2.3(10)
C(3)-C(8)-C(9)-C(10)	178.1(6)
C(7)-C(8)-C(9)-C(1)	179.8(5)
C(3)-C(8)-C(9)-C(1)	0.3(5)
C(1)-C(9)-C(10)-C(11)	-2.7(6)
C(8)-C(9)-C(10)-C(11)	179.4(6)
C(1)-C(9)-C(10)-S(2)	178.7(4)
C(8)-C(9)-C(10)-S(2)	0.9(10)
C(20)-S(2)-C(10)-C(9)	175.7(6)
C(20)-S(2)-C(10)-C(11)	-2.9(4)
C(9)-C(10)-C(11)-C(12)	-175.6(4)
S(2)-C(10)-C(11)-C(12)	3.3(6)
C(9)-C(10)-C(11)-S(1)	2.5(6)
S(2)-C(10)-C(11)-S(1)	-178.6(2)
C(1)-S(1)-C(11)-C(12)	176.3(6)
C(1)-S(1)-C(11)-C(10)	-1.1(4)
C(10)-C(11)-C(12)-C(20)	-1.9(6)
S(1)-C(11)-C(12)-C(20)	-179.3(4)
C(10)-C(11)-C(12)-C(13)	172.9(6)
S(1)-C(11)-C(12)-C(13)	-4.5(11)
C(11)-C(12)-C(13)-C(14)	5.2(11)
C(20)-C(12)-C(13)-C(14)	-179.8(5)
C(11)-C(12)-C(13)-C(18)	-175.3(6)
C(20)-C(12)-C(13)-C(18)	-0.3(6)
C(18)-C(13)-C(14)-C(15)	0.9(8)
C(12)-C(13)-C(14)-C(15)	-179.6(5)
C(13)-C(14)-C(15)-C(16)	-2.0(8)
C(14)-C(15)-C(16)-C(17)	1.9(9)
C(15)-C(16)-C(17)-C(18)	-0.7(8)
C(14)-C(13)-C(18)-C(17)	0.3(8)
C(12)-C(13)-C(18)-C(17)	-179.3(4)
C(14)-C(13)-C(18)-C(19)	-179.9(5)
C(12)-C(13)-C(18)-C(19)	0.5(6)
C(16)-C(17)-C(18)-C(13)	-0.4(7)
C(16)-C(17)-C(18)-C(19)	179.8(5)
C(13)-C(18)-C(19)-C(20)	-0.5(5)
C(17)-C(18)-C(19)-C(20)	179.3(5)
C(13)-C(18)-C(19)-C(31)	-178.7(5)

C(17)-C(18)-C(19)-C(31)	1.1(9)
C(31)-C(19)-C(20)-C(12)	178.5(5)
C(18)-C(19)-C(20)-C(12)	0.3(5)
C(31)-C(19)-C(20)-S(2)	-5.9(9)
C(18)-C(19)-C(20)-S(2)	175.9(4)
C(11)-C(12)-C(20)-C(19)	176.5(4)
C(13)-C(12)-C(20)-C(19)	0.0(6)
C(11)-C(12)-C(20)-S(2)	-0.2(6)
C(13)-C(12)-C(20)-S(2)	-176.7(3)
C(10)-S(2)-C(20)-C(19)	-173.8(6)
C(10)-S(2)-C(20)-C(12)	1.8(4)
C(1)-C(2)-C(21)-C(22)	-31.6(8)
C(3)-C(2)-C(21)-C(22)	145.4(5)
C(1)-C(2)-C(21)-C(26)	146.8(5)
C(3)-C(2)-C(21)-C(26)	-36.2(8)
C(26)-C(21)-C(22)-C(23)	0.9(8)
C(2)-C(21)-C(22)-C(23)	179.4(5)
C(21)-C(22)-C(23)-C(24)	-0.5(9)
C(22)-C(23)-C(24)-C(25)	0.1(8)
C(22)-C(23)-C(24)-C(27)	177.9(5)
C(23)-C(24)-C(25)-C(26)	-0.2(8)
C(27)-C(24)-C(25)-C(26)	-178.1(5)
C(24)-C(25)-C(26)-C(21)	0.7(9)
C(22)-C(21)-C(26)-C(25)	-1.0(8)
C(2)-C(21)-C(26)-C(25)	-179.4(5)
C(23)-C(24)-C(27)-C(30)	-0.6(8)
C(25)-C(24)-C(27)-C(30)	177.2(6)
C(23)-C(24)-C(27)-C(29)	-120.4(6)
C(25)-C(24)-C(27)-C(29)	57.4(6)
C(23)-C(24)-C(27)-C(28)	119.5(6)
C(25)-C(24)-C(27)-C(28)	-62.7(7)
C(20)-C(19)-C(31)-C(32)	-34.9(7)
C(18)-C(19)-C(31)-C(32)	142.9(5)
C(20)-C(19)-C(31)-C(36)	142.7(5)
C(18)-C(19)-C(31)-C(36)	-39.5(7)
C(36)-C(31)-C(32)-C(33)	4.5(7)
C(19)-C(31)-C(32)-C(33)	-177.8(4)
C(31)-C(32)-C(33)-C(34)	-1.2(8)
C(32)-C(33)-C(34)-C(35)	-2.2(7)
C(32)-C(33)-C(34)-C(37)	175.3(5)
C(33)-C(34)-C(35)-C(36)	2.1(7)
C(37)-C(34)-C(35)-C(36)	-175.4(5)
C(34)-C(35)-C(36)-C(31)	1.3(8)
C(32)-C(31)-C(36)-C(35)	-4.5(7)
C(19)-C(31)-C(36)-C(35)	177.7(5)
C(33)-C(34)-C(37)-C(38)	129.3(5)
C(35)-C(34)-C(37)-C(38)	-53.3(7)
C(33)-C(34)-C(37)-C(40)	-110.4(6)
C(35)-C(34)-C(37)-C(40)	67.0(7)
C(33)-C(34)-C(37)-C(39)	9.3(7)
C(35)-C(34)-C(37)-C(39)	-173.3(5)

Symmetry transformations used to generate equivalent atoms:

Table S31. Crystal data and structure refinement for **S3-TIPS**.

Empirical formula	C44 H50 S3 Si2
Formula weight	731.20
Temperature	153(2) K
Wavelength	1.54178 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.5100(3) A alpha = 73.205(2) deg.
	b = 14.0747(6) A beta = 81.761(2) deg.
	c = 20.3192(9) A gamma = 82.646(2) deg.
Volume	2026.41(15) $Å^3$
Z	2
Calculated density	1.198 Mg/m^3
Absorption coefficient	2.451 mm^-1
F(000)	780
Crystal size	0.40 x 0.08 x 0.02 mm
Theta range for data collection	2.29 to 62.38 deg.
Limiting indices	-7<=h<=8, -16<=k<=16, -23<=l<=23
Reflections collected / unique	14925 / 6144 [R(int) = 0.0760]
Completeness to theta = 62.38	95.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9526 and 0.4405
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6144 / 453 / 508
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0974, wR2 = 0.2475
R indices (all data)	R1 = 0.1142, wR2 = 0.2663
Largest diff. peak and hole	0.975 and -1.058 e.A^-3

Table S32. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **S3-TIPS**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	5839(2)	8636(1)	6547(1)	22(1)
S(2)	6699(1)	7866(1)	4861(1)	21(1)
S(3)	7947(1)	10780(1)	4752(1)	20(1)
Si(1)	4214(2)	7853(1)	9408(1)	34(1)
Si(2)	7663(2)	5141(1)	3154(1)	24(1)
C(1)	6671(6)	9210(3)	5696(2)	19(1)
C(2)	6980(6)	8935(3)	5099(2)	18(1)
C(3)	7538(5)	8437(3)	4011(2)	20(1)
C(4)	7890(6)	8168(3)	3404(2)	21(1)
C(5)	8617(6)	9037(3)	2870(2)	21(1)
C(6)	9203(6)	9161(3)	2180(3)	28(1)

C(7)	9890(7)	10055(4)	1805(3)	32(1)
C(8)	9986(6)	10809(4)	2106(3)	30(1)
C(9)	9373(6)	10701(3)	2796(2)	25(1)
C(10)	8683(5)	9804(3)	3191(2)	19(1)
C(11)	8007(6)	9441(3)	3905(2)	17(1)
C(12)	7696(5)	9709(3)	4511(2)	17(1)
C(13)	7120(5)	10216(3)	5605(2)	20(1)
C(14)	6814(6)	10489(3)	6207(2)	18(1)
C(15)	6976(6)	11320(3)	6489(2)	20(1)
C(16)	7646(6)	12240(3)	6190(3)	25(1)
C(17)	7657(6)	12864(3)	6616(3)	30(1)
C(18)	7025(7)	12567(3)	7308(3)	33(1)
C(19)	6357(7)	11640(3)	7618(3)	28(1)
C(20)	6360(6)	11013(3)	7200(2)	24(1)
C(21)	5827(6)	9981(3)	7382(2)	20(1)
C(22)	6103(6)	9707(3)	6781(2)	20(1)
C(23)	5277(6)	9379(3)	8042(2)	24(1)
C(24)	4857(7)	8810(4)	8609(3)	31(1)
C(25)	6419(17)	7018(10)	9682(6)	45(3)
C(26)	7651(15)	7620(11)	9910(5)	62(4)
C(27)	7417(12)	6559(7)	9118(7)	52(3)
C(25A)	6010(40)	7390(20)	9839(16)	34(6)
C(26A)	7050(40)	8140(30)	10057(15)	45(7)
C(27A)	7150(40)	6810(30)	9440(20)	42(7)
C(28)	3373(19)	8391(9)	10113(6)	38(3)
C(29)	1906(18)	9207(11)	9894(7)	57(4)
C(30)	2708(19)	7666(11)	10790(7)	49(3)
C(28A)	2510(30)	8640(13)	9947(10)	43(4)
C(29A)	3170(30)	9655(12)	9911(10)	65(5)
C(30A)	2090(30)	8080(16)	10695(11)	61(5)
C(31)	2661(7)	7054(4)	9197(3)	33(1)
C(32)	2558(8)	6025(4)	9727(3)	49(2)
C(33)	3058(11)	6934(5)	8467(4)	63(2)
C(34)	7742(6)	7218(3)	3308(2)	22(1)
C(35)	7667(6)	6405(3)	3244(2)	26(1)
C(36)	8347(9)	5192(4)	2220(3)	44(1)
C(37)	6988(12)	5839(6)	1751(3)	71(2)
C(38)	10277(10)	5525(6)	1976(4)	71(2)
C(39)	9418(7)	4310(4)	3694(3)	38(1)
C(40)	9696(10)	3262(5)	3607(5)	74(2)
C(41)	9102(10)	4316(7)	4462(4)	77(2)
C(42)	5281(6)	4780(3)	3423(2)	25(1)
C(43)	4997(8)	3790(4)	3304(3)	44(1)
C(44)	4559(7)	4799(4)	4162(3)	37(1)

Table S33. Bond lengths [A] and angles [deg] for **S3-TIPS**.

S(1)-C(1)	1.745(5)
S(1)-C(22)	1.748(4)
S(2)-C(3)	1.745(5)
S(2)-C(2)	1.752(4)
S(3)-C(13)	1.743(5)

S(3)-C(12)	1.753(4)
Si(1)-C(25A)	1.67(3)
Si(1)-C(28)	1.808(11)
Si(1)-C(24)	1.833(5)
Si(1)-C(31)	1.888(5)
Si(1)-C(25)	1.955(13)
Si(1)-C(28A)	2.001(17)
Si(2)-C(35)	1.841(4)
Si(2)-C(36)	1.877(6)
Si(2)-C(42)	1.884(5)
Si(2)-C(39)	1.895(5)
C(1)-C(2)	1.358(6)
C(1)-C(13)	1.451(6)
C(2)-C(12)	1.455(6)
C(3)-C(4)	1.373(6)
C(3)-C(11)	1.448(6)
C(4)-C(34)	1.426(6)
C(4)-C(5)	1.485(6)
C(5)-C(6)	1.375(7)
C(5)-C(10)	1.422(6)
C(6)-C(7)	1.388(7)
C(6)-H(6)	0.9500
C(7)-C(8)	1.384(7)
C(7)-H(7)	0.9500
C(8)-C(9)	1.381(7)
C(8)-H(8)	0.9500
C(9)-C(10)	1.404(6)
C(9)-H(9)	0.9500
C(10)-C(11)	1.433(6)
C(11)-C(12)	1.369(6)
C(13)-C(14)	1.367(6)
C(14)-C(22)	1.445(6)
C(14)-C(15)	1.468(5)
C(15)-C(16)	1.387(6)
C(15)-C(20)	1.409(7)
C(16)-C(17)	1.402(6)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.378(7)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.398(7)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.391(6)
C(19)-H(19A)	0.9500
C(20)-C(21)	1.483(6)
C(21)-C(22)	1.365(6)
C(21)-C(23)	1.401(7)
C(23)-C(24)	1.223(7)
C(25)-C(26)	1.531(12)
C(25)-C(27)	1.533(15)
C(25)-H(25)	1.0000
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800

C(27)-H(27C)	0.9800
C(25A)-C(27A)	1.43(4)
C(25A)-C(26A)	1.58(4)
C(25A)-H(25A)	1.0000
C(26A)-H(26D)	0.9800
C(26A)-H(26E)	0.9800
C(26A)-H(26F)	0.9800
C(27A)-H(27D)	0.9800
C(27A)-H(27E)	0.9800
C(27A)-H(27F)	0.9800
C(28)-C(29)	1.500(18)
C(28)-C(30)	1.520(17)
C(28)-H(28)	1.0000
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(28A)-C(30A)	1.50(3)
C(28A)-C(29A)	1.55(2)
C(28A)-H(28A)	1.0000
C(29A)-H(29D)	0.9800
C(29A)-H(29E)	0.9800
C(29A)-H(29F)	0.9800
C(30A)-H(30D)	0.9800
C(30A)-H(30E)	0.9800
C(30A)-H(30F)	0.9800
C(31)-C(33)	1.524(8)
C(31)-C(32)	1.538(7)
C(31)-H(31)	1.0000
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(34)-C(35)	1.197(6)
C(36)-C(37)	1.522(9)
C(36)-C(38)	1.549(9)
C(36)-H(36)	1.0000
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-C(40)	1.521(8)
C(39)-C(41)	1.546(9)
C(39)-H(39)	1.0000
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800

C(41)-H(41C)	0.9800
C(42)-C(43)	1.526(6)
C(42)-C(44)	1.529(7)
C(42)-H(42)	1.0000
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800

C(1)-S(1)-C(22)	89.8(2)
C(3)-S(2)-C(2)	89.9(2)
C(13)-S(3)-C(12)	90.8(2)
C(25A)-Si(1)-C(28)	86.0(14)
C(25A)-Si(1)-C(24)	110.3(10)
C(28)-Si(1)-C(24)	111.6(4)
C(25A)-Si(1)-C(31)	123.5(11)
C(28)-Si(1)-C(31)	116.3(4)
C(24)-Si(1)-C(31)	107.7(2)
C(25A)-Si(1)-C(25)	20.6(11)
C(28)-Si(1)-C(25)	105.8(6)
C(24)-Si(1)-C(25)	107.1(4)
C(31)-Si(1)-C(25)	108.0(4)
C(25A)-Si(1)-C(28A)	108.6(15)
C(28)-Si(1)-C(28A)	22.6(5)
C(24)-Si(1)-C(28A)	102.2(5)
C(31)-Si(1)-C(28A)	102.2(6)
C(25)-Si(1)-C(28A)	128.3(8)
C(35)-Si(2)-C(36)	107.9(2)
C(35)-Si(2)-C(42)	106.9(2)
C(36)-Si(2)-C(42)	110.3(2)
C(35)-Si(2)-C(39)	107.3(2)
C(36)-Si(2)-C(39)	109.2(3)
C(42)-Si(2)-C(39)	114.9(2)
C(2)-C(1)-C(13)	112.7(4)
C(2)-C(1)-S(1)	134.7(3)
C(13)-C(1)-S(1)	112.6(3)
C(1)-C(2)-C(12)	113.1(4)
C(1)-C(2)-S(2)	135.1(4)
C(12)-C(2)-S(2)	111.7(3)
C(4)-C(3)-C(11)	110.5(4)
C(4)-C(3)-S(2)	135.7(3)
C(11)-C(3)-S(2)	113.8(3)
C(3)-C(4)-C(34)	127.3(4)
C(3)-C(4)-C(5)	106.5(4)
C(34)-C(4)-C(5)	125.9(4)
C(6)-C(5)-C(10)	121.2(4)
C(6)-C(5)-C(4)	130.6(4)
C(10)-C(5)-C(4)	108.2(4)
C(5)-C(6)-C(7)	118.1(4)
C(5)-C(6)-H(6)	120.9
C(7)-C(6)-H(6)	120.9
C(8)-C(7)-C(6)	121.8(5)
C(8)-C(7)-H(7)	119.1

C(6)-C(7)-H(7)	119.1
C(9)-C(8)-C(7)	120.8(4)
C(9)-C(8)-H(8)	119.6
C(7)-C(8)-H(8)	119.6
C(8)-C(9)-C(10)	118.8(4)
C(8)-C(9)-H(9)	120.6
C(10)-C(9)-H(9)	120.6
C(9)-C(10)-C(5)	119.3(4)
C(9)-C(10)-C(11)	133.1(4)
C(5)-C(10)-C(11)	107.6(4)
C(12)-C(11)-C(10)	141.8(4)
C(12)-C(11)-C(3)	110.9(4)
C(10)-C(11)-C(3)	107.2(4)
C(11)-C(12)-C(2)	113.7(4)
C(11)-C(12)-S(3)	135.1(3)
C(2)-C(12)-S(3)	111.3(3)
C(14)-C(13)-C(1)	112.5(4)
C(14)-C(13)-S(3)	135.4(3)
C(1)-C(13)-S(3)	112.0(3)
C(13)-C(14)-C(22)	112.0(4)
C(13)-C(14)-C(15)	141.7(4)
C(22)-C(14)-C(15)	106.3(4)
C(16)-C(15)-C(20)	121.3(4)
C(16)-C(15)-C(14)	132.0(4)
C(20)-C(15)-C(14)	106.6(4)
C(15)-C(16)-C(17)	117.7(5)
C(15)-C(16)-H(16A)	121.2
C(17)-C(16)-H(16A)	121.2
C(18)-C(17)-C(16)	120.8(4)
C(18)-C(17)-H(17A)	119.6
C(16)-C(17)-H(17A)	119.6
C(17)-C(18)-C(19)	122.1(4)
C(17)-C(18)-H(18A)	118.9
C(19)-C(18)-H(18A)	118.9
C(20)-C(19)-C(18)	117.4(5)
C(20)-C(19)-H(19A)	121.3
C(18)-C(19)-H(19A)	121.3
C(19)-C(20)-C(15)	120.7(4)
C(19)-C(20)-C(21)	129.9(5)
C(15)-C(20)-C(21)	109.5(4)
C(22)-C(21)-C(23)	126.5(4)
C(22)-C(21)-C(20)	106.1(4)
C(23)-C(21)-C(20)	127.3(4)
C(21)-C(22)-C(14)	111.5(4)
C(21)-C(22)-S(1)	135.4(4)
C(14)-C(22)-S(1)	113.0(3)
C(24)-C(23)-C(21)	176.4(5)
C(23)-C(24)-Si(1)	173.6(4)
C(26)-C(25)-C(27)	111.3(9)
C(26)-C(25)-Si(1)	109.4(8)
C(27)-C(25)-Si(1)	113.3(6)
C(26)-C(25)-H(25)	107.5
C(27)-C(25)-H(25)	107.5
Si(1)-C(25)-H(25)	107.5
C(27A)-C(25A)-C(26A)	113(3)

C(27A)-C(25A)-Si(1) 106(2)
C(26A)-C(25A)-Si(1) 118(2)
C(27A)-C(25A)-H(25A) 106.1
C(26A)-C(25A)-H(25A) 106.1
Si(1)-C(25A)-H(25A) 106.1
C(25A)-C(26A)-H(26D) 109.5
C(25A)-C(26A)-H(26E) 109.5
H(26D)-C(26A)-H(26E) 109.5
C(25A)-C(26A)-H(26F) 109.5
H(26D)-C(26A)-H(26F) 109.5
H(26E)-C(26A)-H(26F) 109.5
C(25A)-C(27A)-H(27D) 109.5
C(25A)-C(27A)-H(27E) 109.5
H(27D)-C(27A)-H(27E) 109.5
C(25A)-C(27A)-H(27F) 109.5
H(27D)-C(27A)-H(27F) 109.5
H(27E)-C(27A)-H(27F) 109.5
C(29)-C(28)-C(30) 109.5(11)
C(29)-C(28)-Si(1) 109.9(8)
C(30)-C(28)-Si(1) 115.9(8)
C(29)-C(28)-H(28) 107.1
C(30)-C(28)-H(28) 107.1
Si(1)-C(28)-H(28) 107.1
C(30A)-C(28A)-C(29A) 108.6(15)
C(30A)-C(28A)-Si(1) 113.3(14)
C(29A)-C(28A)-Si(1) 113.2(11)
C(30A)-C(28A)-H(28A) 107.1
C(29A)-C(28A)-H(28A) 107.1
Si(1)-C(28A)-H(28A) 107.1
C(28A)-C(29A)-H(29D) 109.5
C(28A)-C(29A)-H(29E) 109.5
H(29D)-C(29A)-H(29E) 109.5
C(28A)-C(29A)-H(29F) 109.5
H(29D)-C(29A)-H(29F) 109.5
H(29E)-C(29A)-H(29F) 109.5
C(28A)-C(30A)-H(30D) 109.5
C(28A)-C(30A)-H(30E) 109.5
H(30D)-C(30A)-H(30E) 109.5
C(28A)-C(30A)-H(30F) 109.5
H(30D)-C(30A)-H(30F) 109.5
H(30E)-C(30A)-H(30F) 109.5
C(33)-C(31)-C(32) 109.9(5)
C(33)-C(31)-Si(1) 114.5(4)
C(32)-C(31)-Si(1) 113.1(3)
C(33)-C(31)-H(31) 106.2
C(32)-C(31)-H(31) 106.2
Si(1)-C(31)-H(31) 106.2
C(31)-C(32)-H(32A) 109.5
C(31)-C(32)-H(32B) 109.5
H(32A)-C(32)-H(32B) 109.5
C(31)-C(32)-H(32C) 109.5
H(32A)-C(32)-H(32C) 109.5
H(32B)-C(32)-H(32C) 109.5
C(31)-C(33)-H(33A) 109.5
C(31)-C(33)-H(33B) 109.5

H(33A)-C(33)-H(33B)	109.5
C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(35)-C(34)-C(4)	177.5(5)
C(34)-C(35)-Si(2)	177.3(4)
C(37)-C(36)-C(38)	111.3(6)
C(37)-C(36)-Si(2)	112.4(5)
C(38)-C(36)-Si(2)	111.5(4)
C(37)-C(36)-H(36)	107.1
C(38)-C(36)-H(36)	107.1
Si(2)-C(36)-H(36)	107.1
C(36)-C(37)-H(37A)	109.5
C(36)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(36)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(36)-C(38)-H(38A)	109.5
C(36)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(36)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(40)-C(39)-C(41)	112.6(6)
C(40)-C(39)-Si(2)	112.8(4)
C(41)-C(39)-Si(2)	113.4(4)
C(40)-C(39)-H(39)	105.7
C(41)-C(39)-H(39)	105.7
Si(2)-C(39)-H(39)	105.7
C(39)-C(40)-H(40A)	109.5
C(39)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(39)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(39)-C(41)-H(41A)	109.5
C(39)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
C(39)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
C(43)-C(42)-C(44)	110.6(4)
C(43)-C(42)-Si(2)	113.6(3)
C(44)-C(42)-Si(2)	113.8(3)
C(43)-C(42)-H(42)	106.0
C(44)-C(42)-H(42)	106.0
Si(2)-C(42)-H(42)	106.0
C(42)-C(43)-H(43A)	109.5
C(42)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
C(42)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(42)-C(44)-H(44A)	109.5

C(42)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(42)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S34. Anisotropic displacement parameters (A^2 x 10^3) for **S3-TIPS**. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
S(1)	39(1)	12(1)	18(1)	-3(1)	-16(1)	-2(1)
S(2)	37(1)	11(1)	18(1)	-3(1)	-16(1)	-2(1)
S(3)	33(1)	11(1)	18(1)	-2(1)	-17(1)	-1(1)
Si(1)	52(1)	39(1)	18(1)	-5(1)	-15(1)	-16(1)
Si(2)	41(1)	13(1)	20(1)	-4(1)	-15(1)	-2(1)
C(1)	23(2)	16(2)	22(3)	-4(2)	-15(2)	0(2)
C(2)	28(2)	13(2)	18(2)	-5(2)	-18(2)	2(2)
C(3)	24(2)	17(2)	20(2)	-3(2)	-15(2)	2(2)
C(4)	29(2)	13(2)	23(3)	-3(2)	-17(2)	1(2)
C(5)	28(2)	17(2)	19(3)	-1(2)	-17(2)	3(2)
C(6)	41(3)	22(2)	25(3)	-9(2)	-14(2)	4(2)
C(7)	41(3)	33(3)	18(3)	1(2)	-11(2)	3(2)
C(8)	38(2)	20(2)	29(3)	4(2)	-11(2)	-1(2)
C(9)	36(2)	16(2)	23(3)	-2(2)	-14(2)	0(2)
C(10)	24(2)	15(2)	19(2)	-3(2)	-18(2)	4(2)
C(11)	26(2)	13(2)	14(2)	-5(2)	-14(2)	4(2)
C(12)	24(2)	11(2)	18(2)	-1(2)	-17(2)	2(2)
C(13)	18(2)	14(2)	28(3)	-4(2)	-18(2)	3(2)
C(14)	26(2)	14(2)	17(2)	-5(2)	-18(2)	2(2)
C(15)	31(2)	13(2)	21(3)	-6(2)	-21(2)	2(2)
C(16)	34(2)	18(2)	25(3)	-2(2)	-24(2)	4(2)
C(17)	41(3)	15(2)	40(3)	-5(2)	-28(2)	0(2)
C(18)	52(3)	21(2)	38(3)	-17(2)	-34(2)	6(2)
C(19)	42(3)	24(2)	25(3)	-11(2)	-22(2)	3(2)
C(20)	33(2)	16(2)	25(3)	-5(2)	-23(2)	4(2)
C(21)	31(2)	16(2)	19(2)	-5(1)	-20(1)	1(1)
C(22)	31(2)	16(2)	19(2)	-5(1)	-20(1)	1(1)
C(23)	36(2)	23(2)	20(3)	-11(2)	-19(2)	3(2)
C(24)	45(3)	29(3)	25(3)	-10(2)	-16(2)	-5(2)
C(25)	48(5)	52(6)	31(5)	0(4)	-15(4)	-6(5)
C(26)	54(5)	82(7)	52(6)	-3(5)	-29(4)	-21(5)
C(27)	46(4)	42(5)	58(6)	-2(4)	-10(4)	10(4)
C(25A)	28(9)	40(10)	34(10)	-4(7)	-12(7)	-5(7)
C(26A)	35(10)	54(11)	48(11)	-2(8)	-31(7)	-9(8)
C(27A)	40(11)	32(10)	42(11)	6(7)	-6(8)	8(8)
C(28)	55(6)	35(5)	31(5)	-16(4)	-12(4)	-5(5)
C(29)	59(7)	65(7)	47(6)	-19(5)	-14(5)	6(5)

C(30)	59(6)	66(7)	25(5)	-20(5)	-7(5)	0(5)
C(28A)	46(7)	38(7)	48(7)	-20(6)	-3(6)	-3(6)
C(29A)	89(9)	50(7)	68(8)	-38(6)	9(7)	-15(6)
C(30A)	77(9)	63(8)	50(7)	-26(6)	-3(7)	-15(7)
C(31)	48(3)	25(2)	31(3)	-8(2)	-23(2)	0(2)
C(32)	55(3)	32(3)	59(4)	-6(3)	-19(3)	-7(2)
C(33)	97(5)	52(4)	57(4)	-23(3)	-32(4)	-19(3)
C(34)	32(2)	19(2)	19(3)	-4(2)	-15(2)	0(2)
C(35)	37(2)	20(2)	24(3)	-9(2)	-13(2)	-1(2)
C(36)	80(4)	31(3)	29(3)	-15(2)	-8(3)	-11(3)
C(37)	114(5)	68(4)	30(4)	-8(3)	-26(3)	-2(4)
C(38)	86(5)	74(5)	57(4)	-31(4)	22(4)	-31(4)
C(39)	34(2)	25(3)	50(4)	-1(2)	-18(2)	2(2)
C(40)	63(4)	31(3)	126(6)	-7(4)	-43(4)	10(3)
C(41)	66(4)	104(6)	42(4)	9(4)	-31(3)	19(4)
C(42)	37(2)	17(2)	22(3)	-3(2)	-19(2)	1(2)
C(43)	49(3)	34(3)	60(4)	-20(3)	-22(3)	-9(2)
C(44)	47(3)	29(3)	35(3)	-9(2)	-10(2)	-5(2)

Table S35. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **S3-TIPS**.

	x	y	z	U(eq)
H(6)	9141	8651	1967	34
H(7)	10304	10151	1328	38
H(8)	10479	11407	1836	36
H(9)	9418	11225	2999	30
H(16A)	8082	12441	5712	30
H(17A)	8104	13500	6425	36
H(18A)	7045	13007	7584	39
H(19A)	5917	11446	8095	34
H(25)	6063	6457	10092	54
H(26A)	8699	7184	10091	94
H(26B)	6981	7900	10273	94
H(26C)	8061	8163	9514	94
H(27A)	7730	7091	8699	78
H(27B)	6635	6127	9013	78
H(27C)	8522	6165	9280	78
H(25A)	5551	6907	10278	41
H(26D)	7933	7760	10369	68
H(26E)	6185	8546	10295	68
H(26F)	7673	8569	9644	68
H(27D)	7510	7238	8980	63
H(27E)	6501	6272	9404	63
H(27F)	8236	6524	9675	63
H(28)	4393	8708	10206	45
H(29A)	786	8914	9900	85
H(29B)	2263	9616	9425	85

H(29C)	1711	9625	10214	85
H(30A)	2365	8022	11146	73
H(30B)	3673	7139	10937	73
H(30C)	1656	7369	10726	73
H(28A)	1346	8787	9736	51
H(29D)	2827	9803	10357	98
H(29E)	2617	10181	9547	98
H(29F)	4489	9622	9806	98
H(30D)	3195	7941	10924	91
H(30E)	1611	7451	10725	91
H(30F)	1188	8484	10923	91
H(31)	1421	7407	9226	40
H(32A)	1605	5685	9633	73
H(32B)	2285	6109	10195	73
H(32C)	3720	5627	9693	73
H(33A)	4245	6565	8417	95
H(33B)	3055	7593	8131	95
H(33C)	2129	6566	8383	95
H(36)	8376	4498	2180	53
H(37A)	6862	6517	1800	106
H(37B)	5816	5561	1881	106
H(37C)	7413	5854	1269	106
H(38A)	10556	5595	1479	106
H(38B)	11151	5023	2228	106
H(38C)	10345	6166	2066	106
H(39)	10588	4608	3505	45
H(40A)	10730	2895	3843	112
H(40B)	9928	3299	3114	112
H(40C)	8609	2918	3809	112
H(41A)	8030	3971	4688	115
H(41B)	8918	5006	4490	115
H(41C)	10157	3975	4694	115
H(42)	4504	5301	3114	30
H(43A)	5672	3245	3617	66
H(43B)	5430	3800	2824	66
H(43C)	3708	3690	3395	66
H(44A)	3251	4752	4234	55
H(44B)	4816	5423	4237	55
H(44C)	5149	4233	4490	55

Table S36. Torsion angles [deg] for **S3-TIPS**.

C(22)-S(1)-C(1)-C(2)	-179.9(5)
C(22)-S(1)-C(1)-C(13)	-0.6(3)
C(13)-C(1)-C(2)-C(12)	0.3(5)
S(1)-C(1)-C(2)-C(12)	179.7(3)
C(13)-C(1)-C(2)-S(2)	-178.8(3)
S(1)-C(1)-C(2)-S(2)	0.5(8)
C(3)-S(2)-C(2)-C(1)	179.8(5)
C(3)-S(2)-C(2)-C(12)	0.7(3)
C(2)-S(2)-C(3)-C(4)	178.4(5)
C(2)-S(2)-C(3)-C(11)	-0.8(3)
C(11)-C(3)-C(4)-C(34)	174.8(4)

S(2)-C(3)-C(4)-C(34)	-4.5(7)
C(11)-C(3)-C(4)-C(5)	-0.3(5)
S(2)-C(3)-C(4)-C(5)	-179.6(4)
C(3)-C(4)-C(5)-C(6)	179.1(4)
C(34)-C(4)-C(5)-C(6)	3.9(7)
C(3)-C(4)-C(5)-C(10)	0.5(5)
C(34)-C(4)-C(5)-C(10)	-174.7(4)
C(10)-C(5)-C(6)-C(7)	0.9(7)
C(4)-C(5)-C(6)-C(7)	-177.6(5)
C(5)-C(6)-C(7)-C(8)	-0.2(7)
C(6)-C(7)-C(8)-C(9)	-0.9(7)
C(7)-C(8)-C(9)-C(10)	1.3(7)
C(8)-C(9)-C(10)-C(5)	-0.6(6)
C(8)-C(9)-C(10)-C(11)	177.7(4)
C(6)-C(5)-C(10)-C(9)	-0.5(6)
C(4)-C(5)-C(10)-C(9)	178.3(4)
C(6)-C(5)-C(10)-C(11)	-179.2(4)
C(4)-C(5)-C(10)-C(11)	-0.5(5)
C(9)-C(10)-C(11)-C(12)	-0.1(9)
C(5)-C(10)-C(11)-C(12)	178.4(5)
C(9)-C(10)-C(11)-C(3)	-178.2(5)
C(5)-C(10)-C(11)-C(3)	0.3(4)
C(4)-C(3)-C(11)-C(12)	-178.7(4)
S(2)-C(3)-C(11)-C(12)	0.7(5)
C(4)-C(3)-C(11)-C(10)	0.0(5)
S(2)-C(3)-C(11)-C(10)	179.5(3)
C(10)-C(11)-C(12)-C(2)	-178.3(5)
C(3)-C(11)-C(12)-C(2)	-0.2(5)
C(10)-C(11)-C(12)-S(3)	2.1(9)
C(3)-C(11)-C(12)-S(3)	-179.8(3)
C(1)-C(2)-C(12)-C(11)	-179.7(4)
S(2)-C(2)-C(12)-C(11)	-0.4(5)
C(1)-C(2)-C(12)-S(3)	0.0(5)
S(2)-C(2)-C(12)-S(3)	179.33(19)
C(13)-S(3)-C(12)-C(11)	179.4(5)
C(13)-S(3)-C(12)-C(2)	-0.2(3)
C(2)-C(1)-C(13)-C(14)	-179.8(4)
S(1)-C(1)-C(13)-C(14)	0.7(5)
C(2)-C(1)-C(13)-S(3)	-0.5(5)
S(1)-C(1)-C(13)-S(3)	-180.0(2)
C(12)-S(3)-C(13)-C(14)	179.4(4)
C(12)-S(3)-C(13)-C(1)	0.4(3)
C(1)-C(13)-C(14)-C(22)	-0.5(5)
S(3)-C(13)-C(14)-C(22)	-179.6(3)
C(1)-C(13)-C(14)-C(15)	178.4(5)
S(3)-C(13)-C(14)-C(15)	-0.6(9)
C(13)-C(14)-C(15)-C(16)	-2.2(9)
C(22)-C(14)-C(15)-C(16)	176.8(5)
C(13)-C(14)-C(15)-C(20)	-179.4(5)
C(22)-C(14)-C(15)-C(20)	-0.4(4)
C(20)-C(15)-C(16)-C(17)	-1.2(6)
C(14)-C(15)-C(16)-C(17)	-178.1(4)
C(15)-C(16)-C(17)-C(18)	0.1(7)
C(16)-C(17)-C(18)-C(19)	0.2(7)
C(17)-C(18)-C(19)-C(20)	0.5(7)

C(18)-C(19)-C(20)-C(15)	-1.5(7)
C(18)-C(19)-C(20)-C(21)	176.8(4)
C(16)-C(15)-C(20)-C(19)	2.0(7)
C(14)-C(15)-C(20)-C(19)	179.6(4)
C(16)-C(15)-C(20)-C(21)	-176.7(4)
C(14)-C(15)-C(20)-C(21)	0.9(5)
C(19)-C(20)-C(21)-C(22)	-179.6(5)
C(15)-C(20)-C(21)-C(22)	-1.1(5)
C(19)-C(20)-C(21)-C(23)	-3.7(8)
C(15)-C(20)-C(21)-C(23)	174.8(4)
C(23)-C(21)-C(22)-C(14)	-175.1(4)
C(20)-C(21)-C(22)-C(14)	0.8(5)
C(23)-C(21)-C(22)-S(1)	3.6(8)
C(20)-C(21)-C(22)-S(1)	179.4(4)
C(13)-C(14)-C(22)-C(21)	179.1(4)
C(15)-C(14)-C(22)-C(21)	-0.3(5)
C(13)-C(14)-C(22)-S(1)	0.1(5)
C(15)-C(14)-C(22)-S(1)	-179.2(3)
C(1)-S(1)-C(22)-C(21)	-178.4(5)
C(1)-S(1)-C(22)-C(14)	0.3(3)
C(22)-C(21)-C(23)-C(24)	39(7)
C(20)-C(21)-C(23)-C(24)	-136(7)
C(21)-C(23)-C(24)-Si(1)	-42(10)
C(25A)-Si(1)-C(24)-C(23)	104(4)
C(28)-Si(1)-C(24)-C(23)	-162(4)
C(31)-Si(1)-C(24)-C(23)	-33(4)
C(25)-Si(1)-C(24)-C(23)	83(4)
C(28A)-Si(1)-C(24)-C(23)	-140(4)
C(25A)-Si(1)-C(25)-C(26)	-34(3)
C(28)-Si(1)-C(25)-C(26)	-50.5(8)
C(24)-Si(1)-C(25)-C(26)	68.6(8)
C(31)-Si(1)-C(25)-C(26)	-175.6(6)
C(28A)-Si(1)-C(25)-C(26)	-53.0(10)
C(25A)-Si(1)-C(25)-C(27)	-159(3)
C(28)-Si(1)-C(25)-C(27)	-175.4(7)
C(24)-Si(1)-C(25)-C(27)	-56.3(7)
C(31)-Si(1)-C(25)-C(27)	59.5(7)
C(28A)-Si(1)-C(25)-C(27)	-177.9(7)
C(28)-Si(1)-C(25A)-C(27A)	178(2)
C(24)-Si(1)-C(25A)-C(27A)	-71(2)
C(31)-Si(1)-C(25A)-C(27A)	59(2)
C(25)-Si(1)-C(25A)-C(27A)	14(2)
C(28A)-Si(1)-C(25A)-C(27A)	178.2(18)
C(28)-Si(1)-C(25A)-C(26A)	-54(2)
C(24)-Si(1)-C(25A)-C(26A)	58(3)
C(31)-Si(1)-C(25A)-C(26A)	-172.8(17)
C(25)-Si(1)-C(25A)-C(26A)	143(5)
C(28A)-Si(1)-C(25A)-C(26A)	-53(2)
C(25A)-Si(1)-C(28)-C(29)	162.4(13)
C(24)-Si(1)-C(28)-C(29)	52.1(10)
C(31)-Si(1)-C(28)-C(29)	-71.9(9)
C(25)-Si(1)-C(28)-C(29)	168.3(8)
C(28A)-Si(1)-C(28)-C(29)	-16.7(15)
C(25A)-Si(1)-C(28)-C(30)	-72.9(13)
C(24)-Si(1)-C(28)-C(30)	176.9(8)

C(31)-Si(1)-C(28)-C(30)	52.8(11)
C(25)-Si(1)-C(28)-C(30)	-67.0(10)
C(28A)-Si(1)-C(28)-C(30)	108(2)
C(25A)-Si(1)-C(28A)-C(30A)	-50.4(17)
C(28)-Si(1)-C(28A)-C(30A)	-49.5(17)
C(24)-Si(1)-C(28A)-C(30A)	-167.0(12)
C(31)-Si(1)-C(28A)-C(30A)	81.6(13)
C(25)-Si(1)-C(28A)-C(30A)	-43.4(15)
C(25A)-Si(1)-C(28A)-C(29A)	73.8(18)
C(28)-Si(1)-C(28A)-C(29A)	74.7(19)
C(24)-Si(1)-C(28A)-C(29A)	-42.8(15)
C(31)-Si(1)-C(28A)-C(29A)	-154.2(13)
C(25)-Si(1)-C(28A)-C(29A)	80.9(16)
C(25A)-Si(1)-C(31)-C(33)	-98.0(15)
C(28)-Si(1)-C(31)-C(33)	158.5(6)
C(24)-Si(1)-C(31)-C(33)	32.4(5)
C(25)-Si(1)-C(31)-C(33)	-82.9(6)
C(28A)-Si(1)-C(31)-C(33)	139.6(7)
C(25A)-Si(1)-C(31)-C(32)	28.9(15)
C(28)-Si(1)-C(31)-C(32)	-74.6(6)
C(24)-Si(1)-C(31)-C(32)	159.3(4)
C(25)-Si(1)-C(31)-C(32)	44.0(6)
C(28A)-Si(1)-C(31)-C(32)	-93.4(7)
C(3)-C(4)-C(34)-C(35)	-62(13)
C(5)-C(4)-C(34)-C(35)	112(13)
C(4)-C(34)-C(35)-Si(2)	-28(21)
C(36)-Si(2)-C(35)-C(34)	-90(10)
C(42)-Si(2)-C(35)-C(34)	151(10)
C(39)-Si(2)-C(35)-C(34)	27(10)
C(35)-Si(2)-C(36)-C(37)	-64.3(5)
C(42)-Si(2)-C(36)-C(37)	52.1(5)
C(39)-Si(2)-C(36)-C(37)	179.4(4)
C(35)-Si(2)-C(36)-C(38)	61.5(5)
C(42)-Si(2)-C(36)-C(38)	177.9(4)
C(39)-Si(2)-C(36)-C(38)	-54.8(5)
C(35)-Si(2)-C(39)-C(40)	-174.0(5)
C(36)-Si(2)-C(39)-C(40)	-57.3(5)
C(42)-Si(2)-C(39)-C(40)	67.2(5)
C(35)-Si(2)-C(39)-C(41)	56.5(5)
C(36)-Si(2)-C(39)-C(41)	173.2(5)
C(42)-Si(2)-C(39)-C(41)	-62.3(5)
C(35)-Si(2)-C(42)-C(43)	173.8(4)
C(36)-Si(2)-C(42)-C(43)	56.7(4)
C(39)-Si(2)-C(42)-C(43)	-67.3(4)
C(35)-Si(2)-C(42)-C(44)	-58.5(4)
C(36)-Si(2)-C(42)-C(44)	-175.5(3)
C(39)-Si(2)-C(42)-C(44)	60.5(4)

Symmetry transformations used to generate equivalent atoms:

11. ^{1}H and ^{13}C NMR spectra of all new compounds

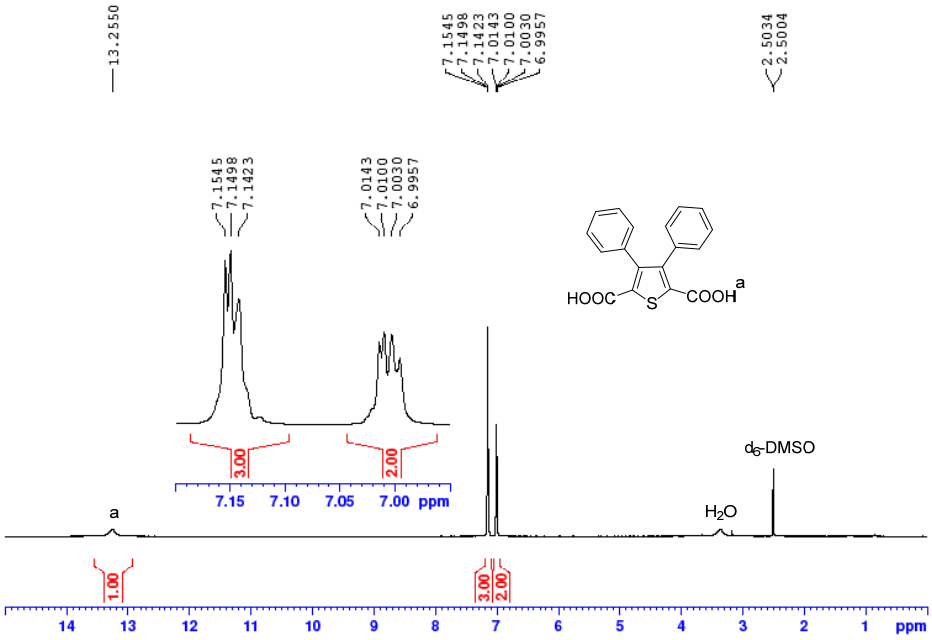


Fig. S15. ^{1}H NMR spectrum of compound **15** (500 MHz, d_6-DMSO, rt).

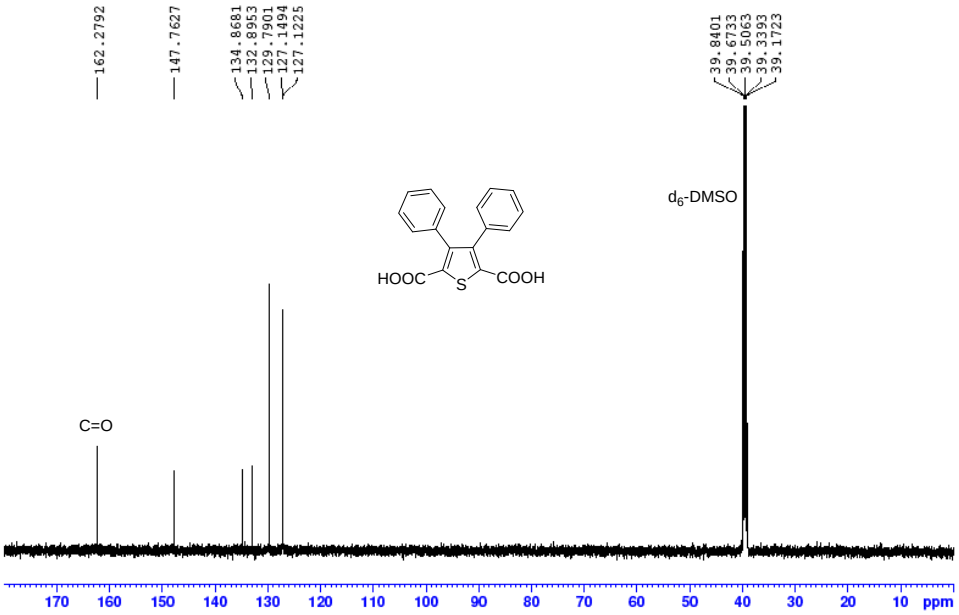


Fig. S16. ^{13}C NMR spectrum of compound **15** (125 MHz, d_6-DMSO, rt).

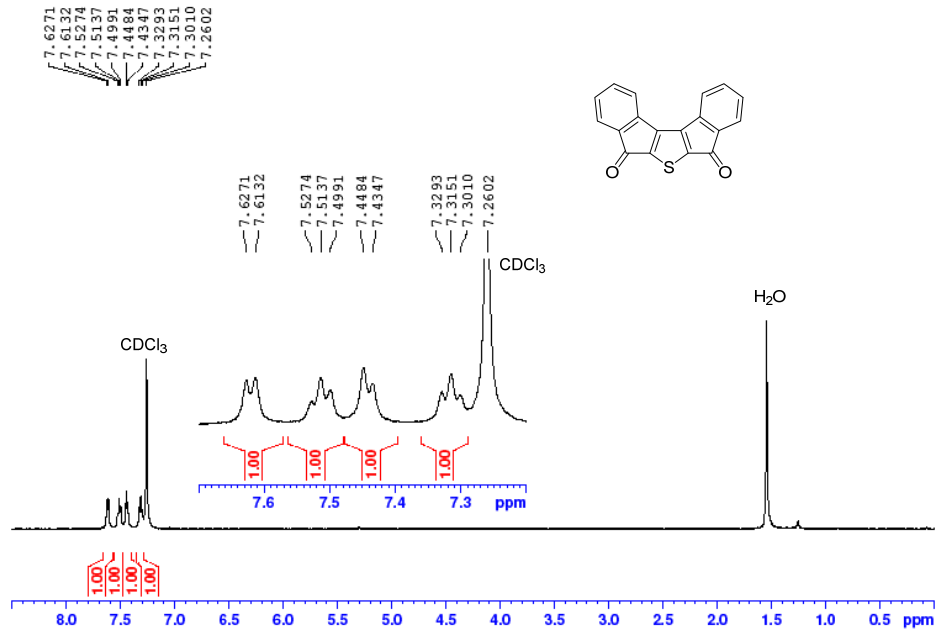


Fig. S17. ^{1}H NMR spectrum of compound **16** (500 MHz, $CDCl_3$, rt).

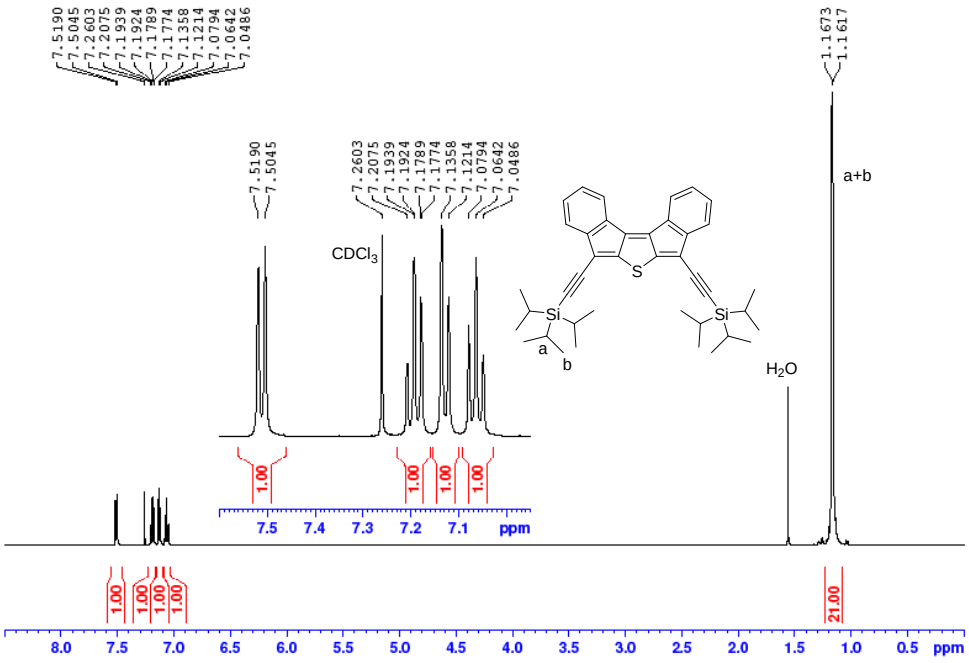


Fig. S18. ^{1}H NMR spectrum of compound **S1-TIPS** (500 MHz, $CDCl_3$, rt).

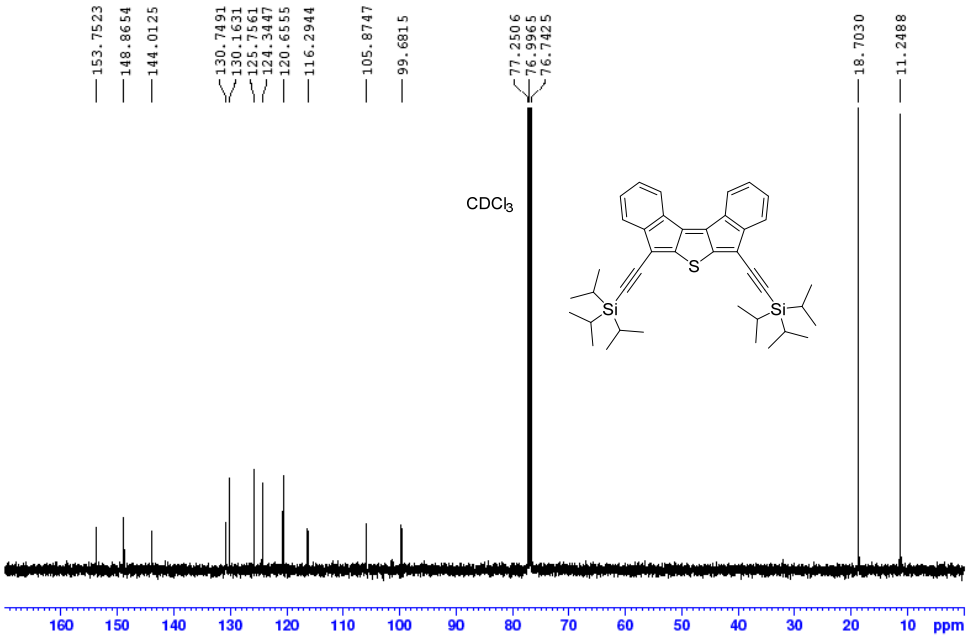


Fig. S19. ^{13}C NMR spectrum of compound **S1-TIPS** (125 MHz, $CDCl_3$, rt).

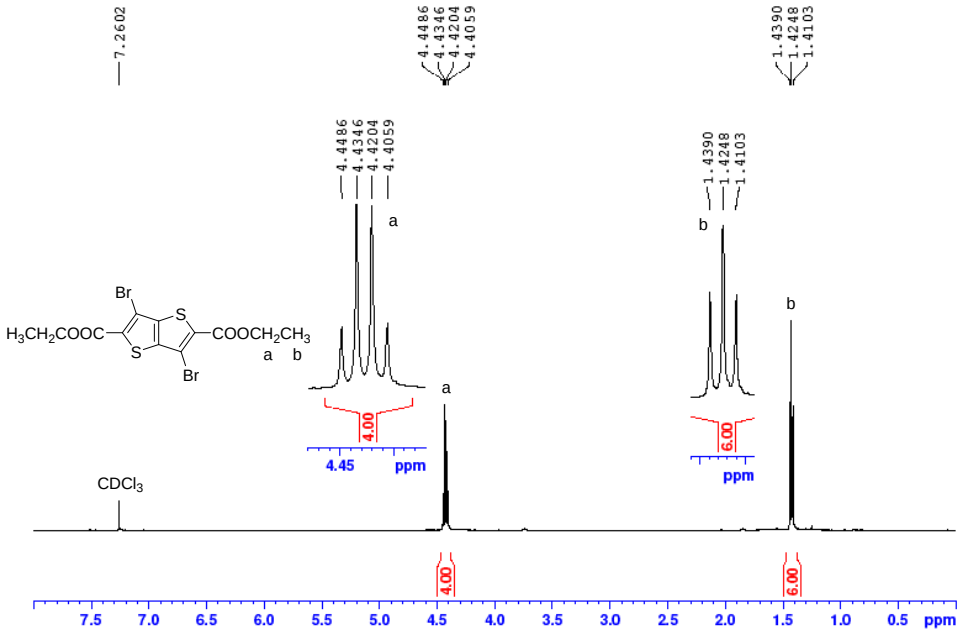


Fig. S20. ^{1}H NMR spectrum of compound **18** (500 MHz, $CDCl_3$, rt).

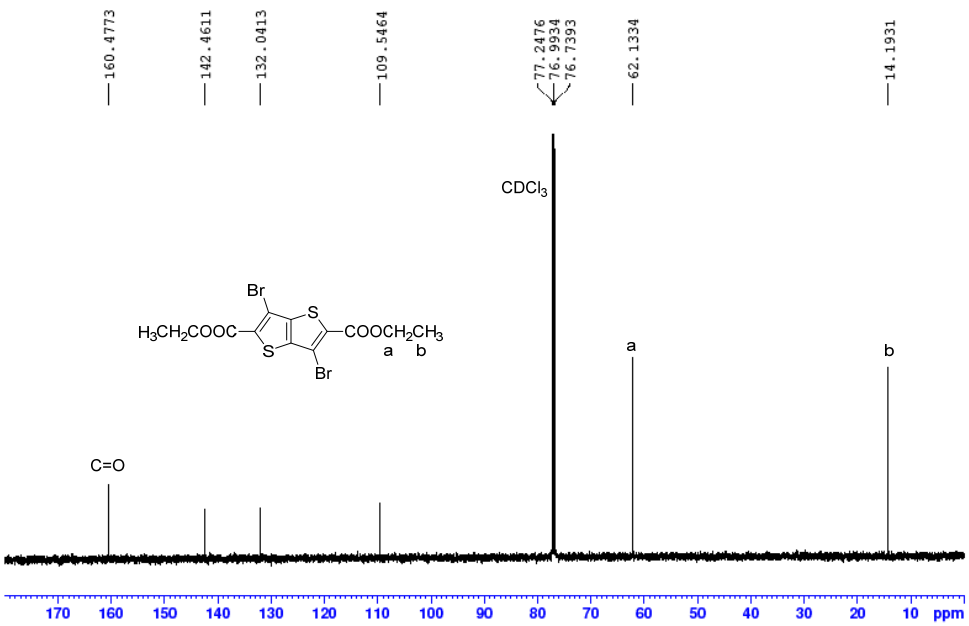


Fig. S21. ^{13}C NMR spectrum of compound **18** (125 MHz, $CDCl_3$, rt).

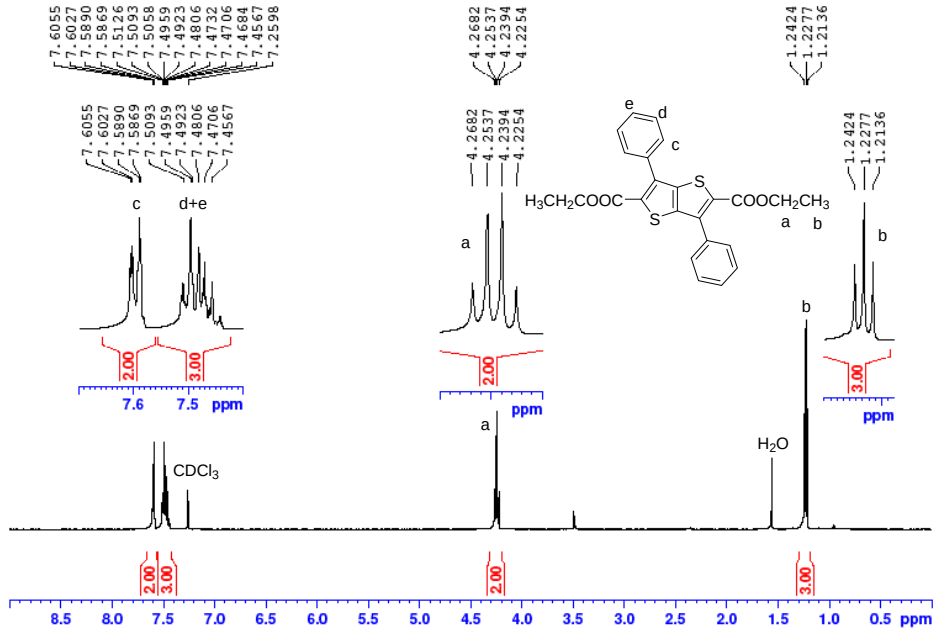


Fig. S22. ^{1}H NMR spectrum of compound **19** (500 MHz, $CDCl_3$, rt).

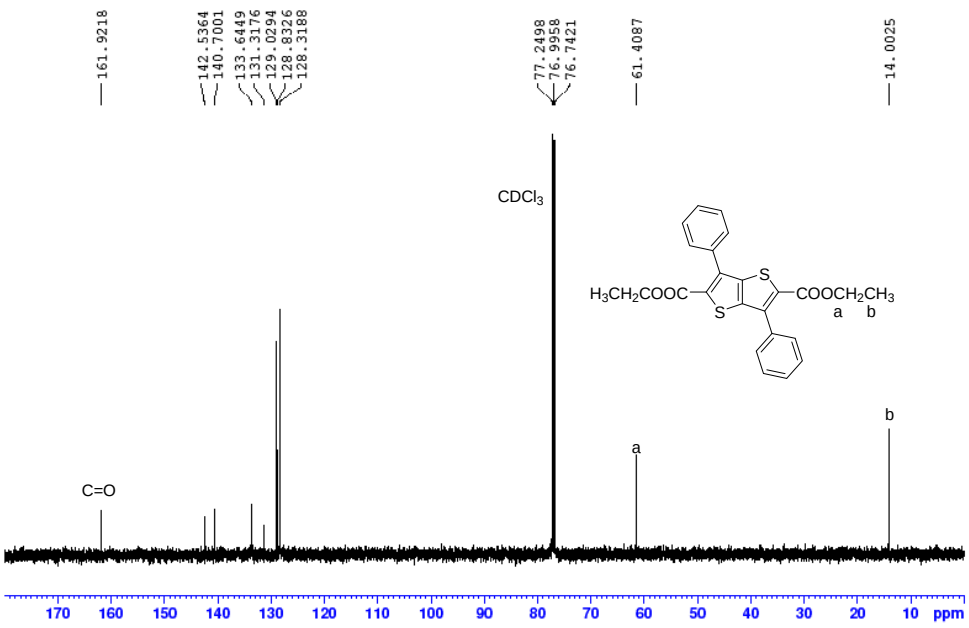


Fig. S23. ^{13}C NMR spectrum of compound **19** (125 MHz, $CDCl_3$, rt).

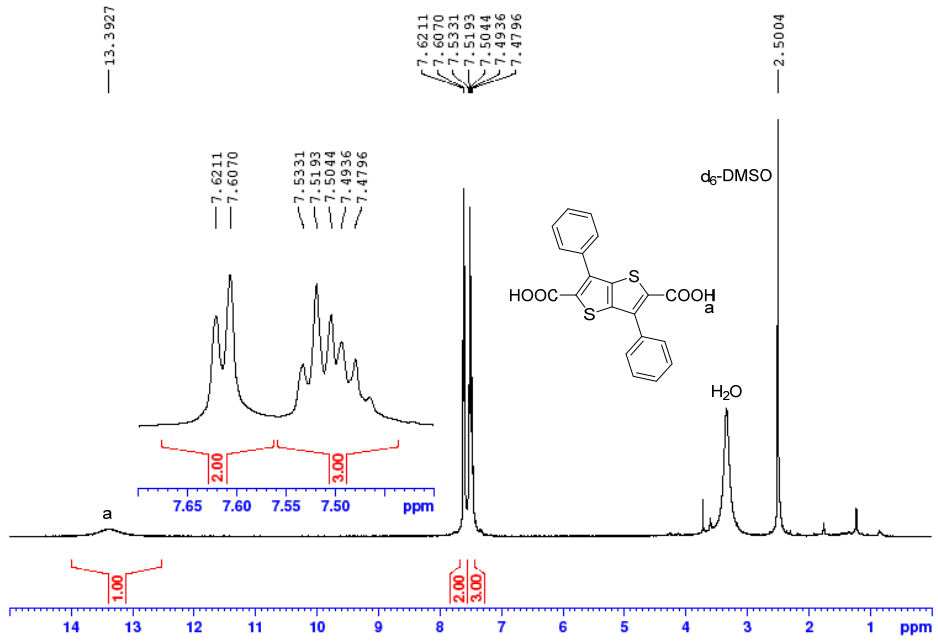


Fig. S24. ^{1}H NMR spectrum of compound **20** (500 MHz, d_6-DMSO, rt).

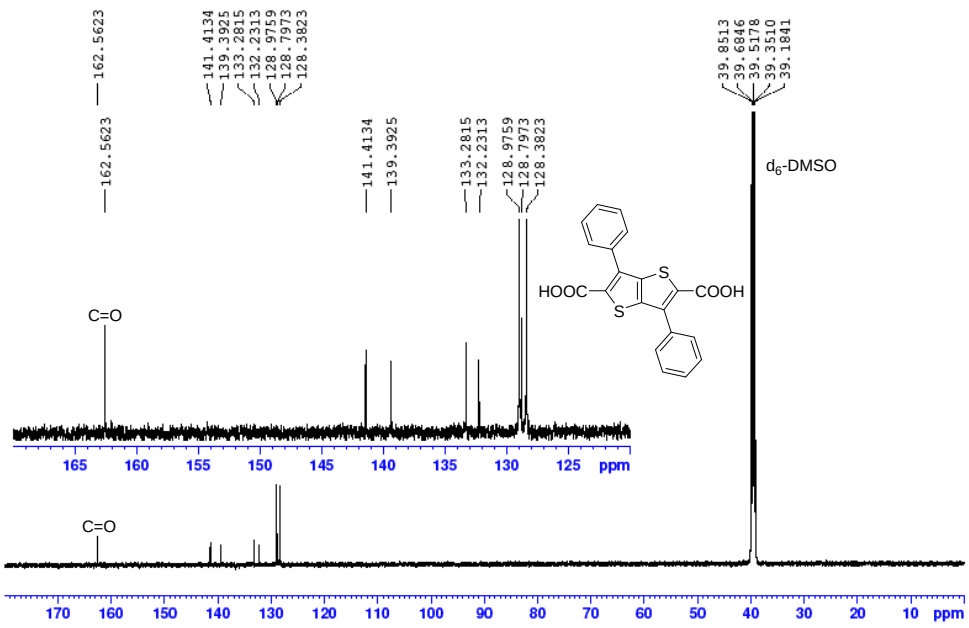


Fig. S25. ^{13}C NMR spectrum of compound **20** (125 MHz, d_6-DMSO, rt).

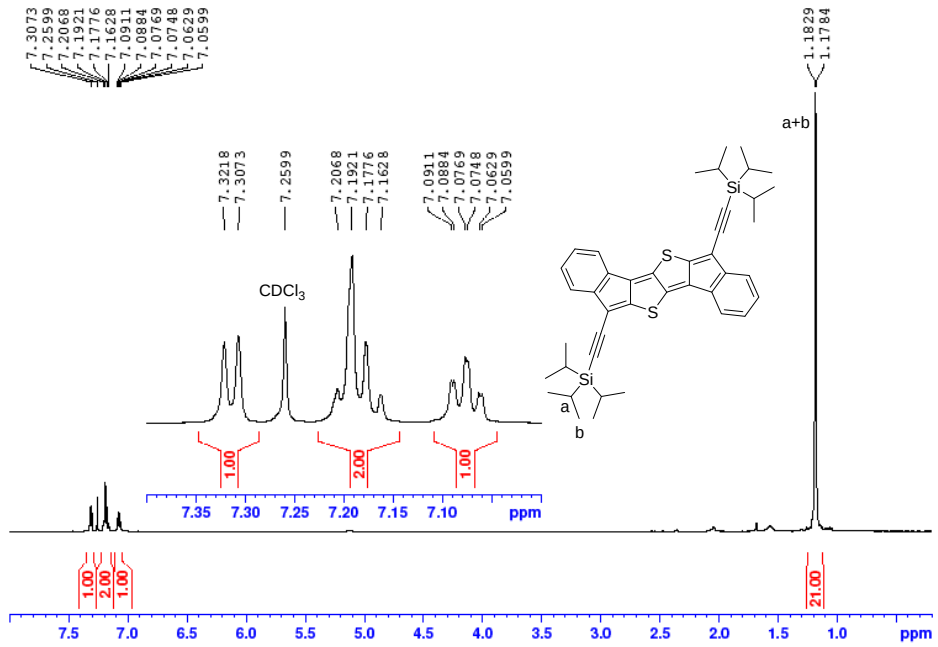


Fig. S26. ^{1}H NMR spectrum of compound **S2-TIPS** (500 MHz, $CDCl_3$, rt).

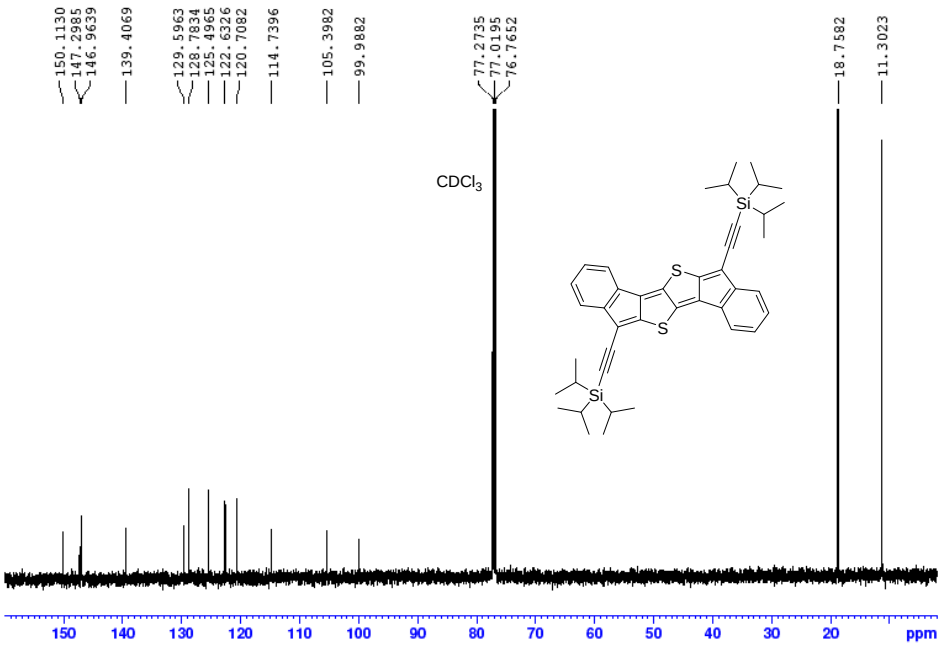


Fig. S27. ^{13}C NMR spectrum of compound **S2-TIPS** (125 MHz, $CDCl_3$, rt).

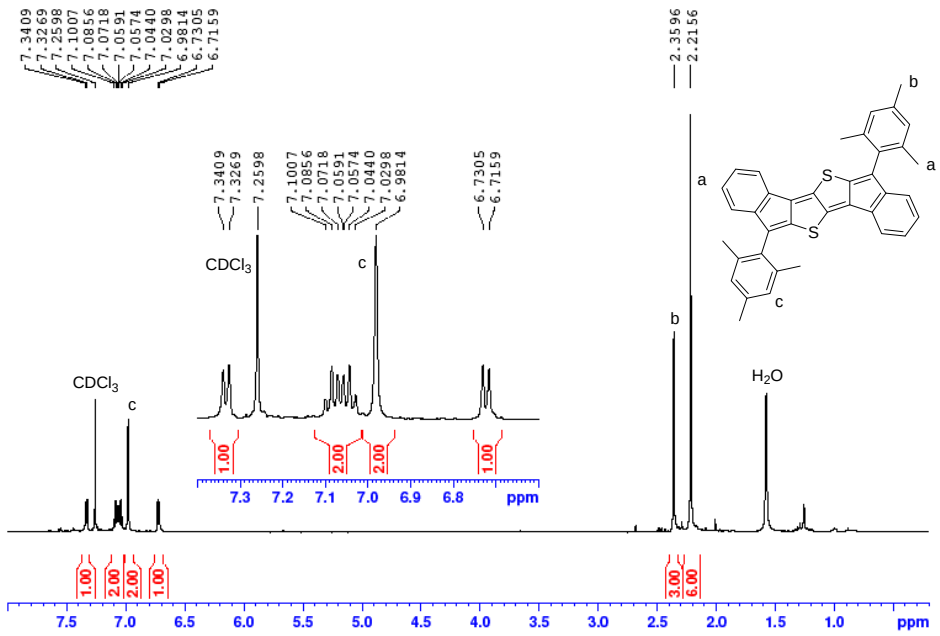


Fig. S28. ^{1}H NMR spectrum of compound **S2-Mes** (500 MHz, $CDCl_3$, rt).

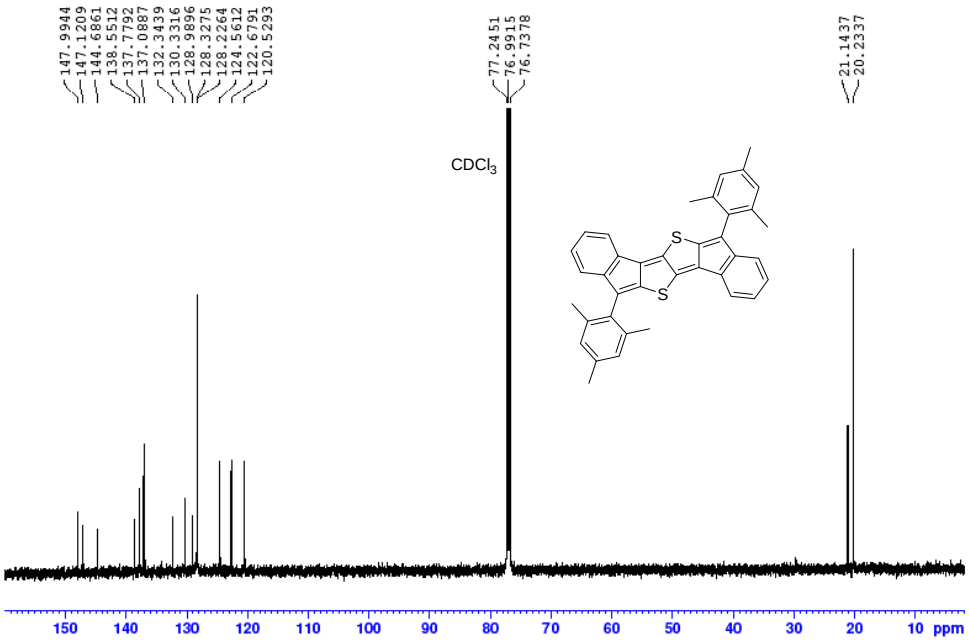


Fig. S29. ^{13}C NMR spectrum of compound **S2-Mes** (125 MHz, $CDCl_3$, rt).

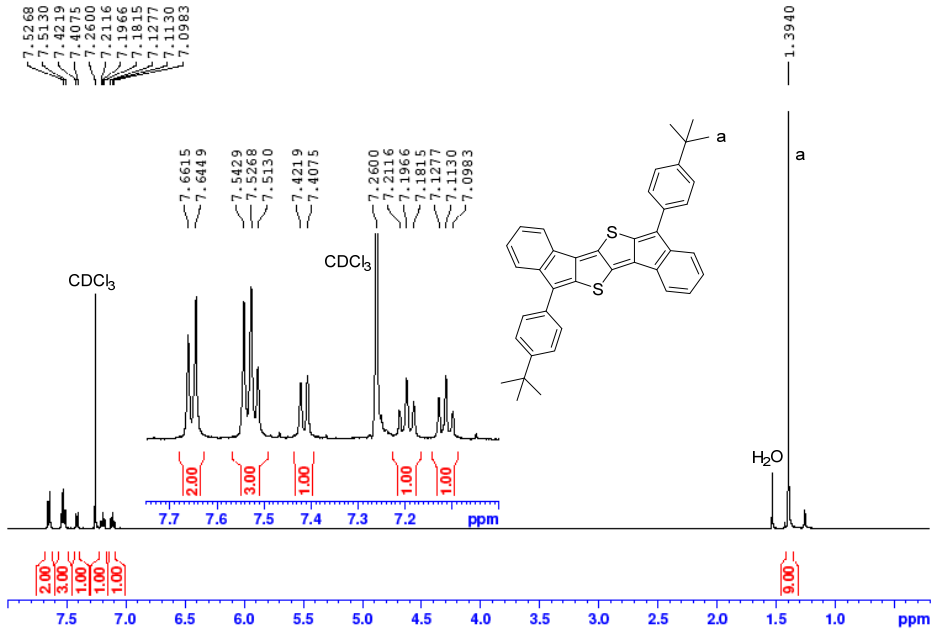


Fig. S30. ^{1}H NMR spectrum of compound **S2-Ph** (500 MHz, $CDCl_3$, rt).

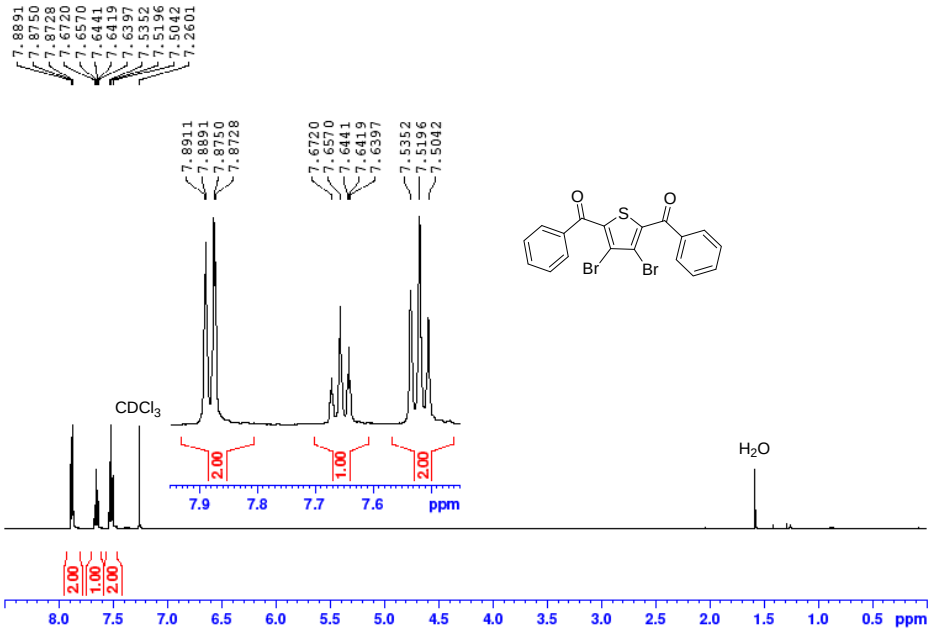


Fig. S31. ^{1}H NMR spectrum of compound **24** (500 MHz, $CDCl_3$, rt).

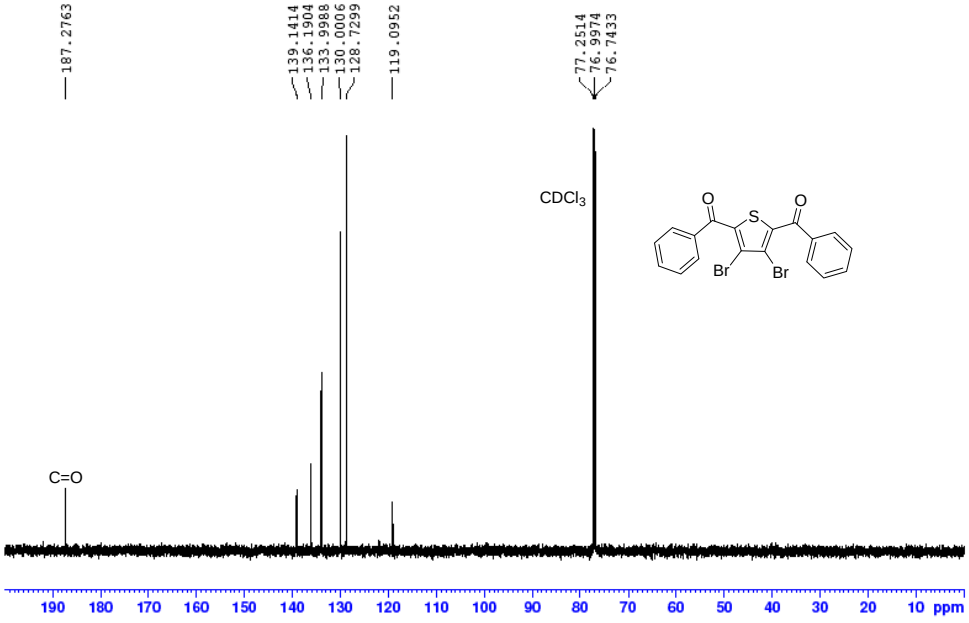


Fig. S32. ^{13}C NMR spectrum of compound **24** (125 MHz, $CDCl_3$, rt).

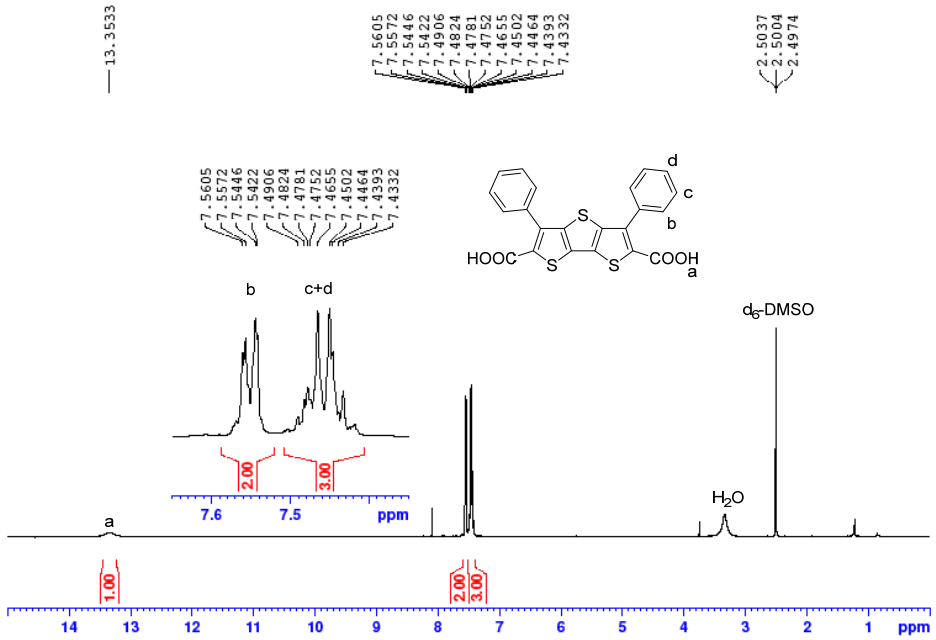


Fig. S33. [1]H NMR spectrum of compound **25** (500 MHz, d_6-DMSO, rt).

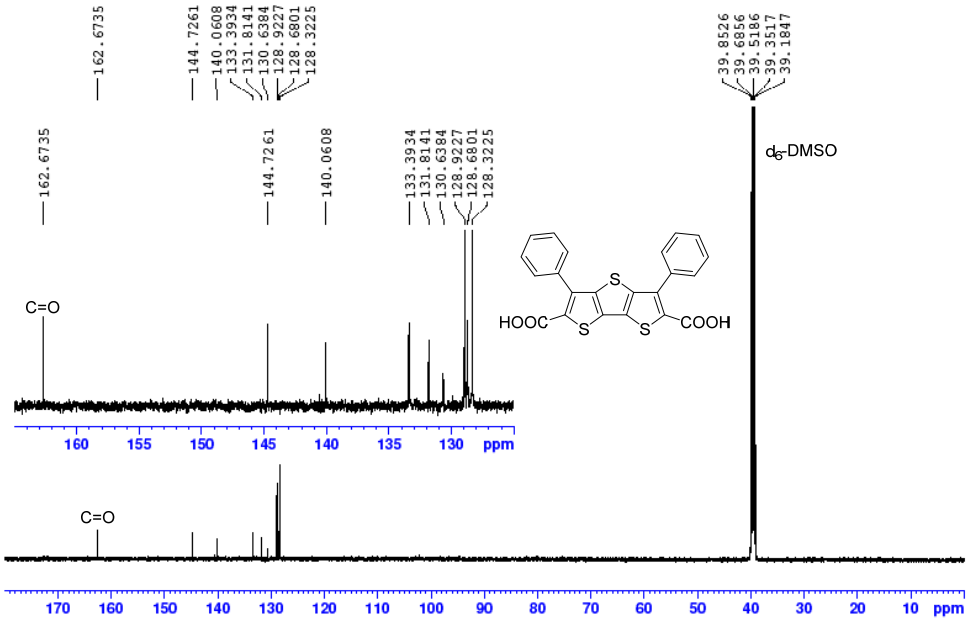


Fig. S34. [13]C NMR spectrum of compound **25** (125 MHz, d_6-DMSO, rt).

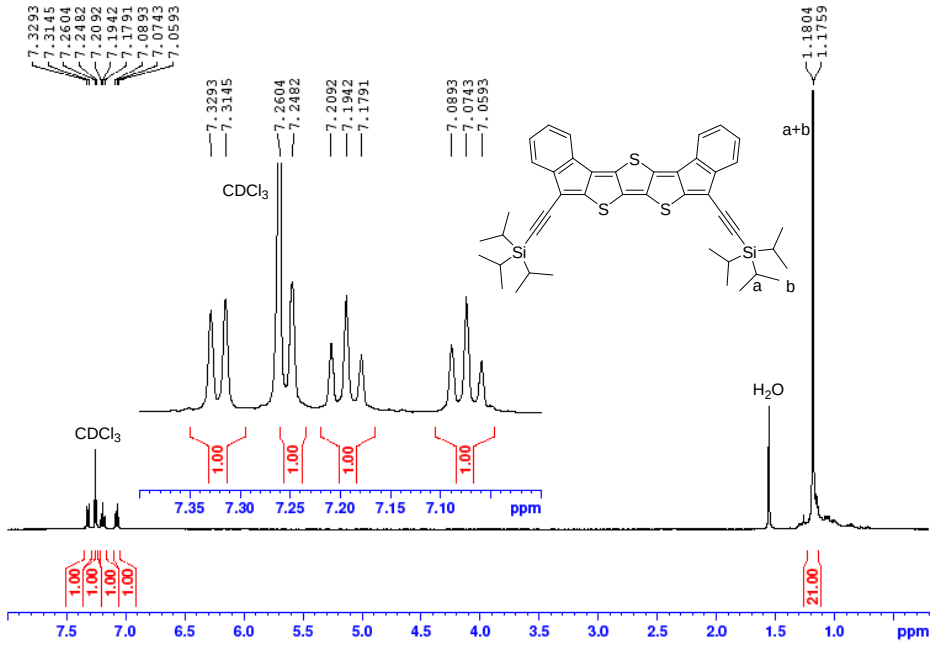


Fig. S35. ^{1}H NMR spectrum of compound **S3-TIPS** (500 MHz, $CDCl_3$, rt).

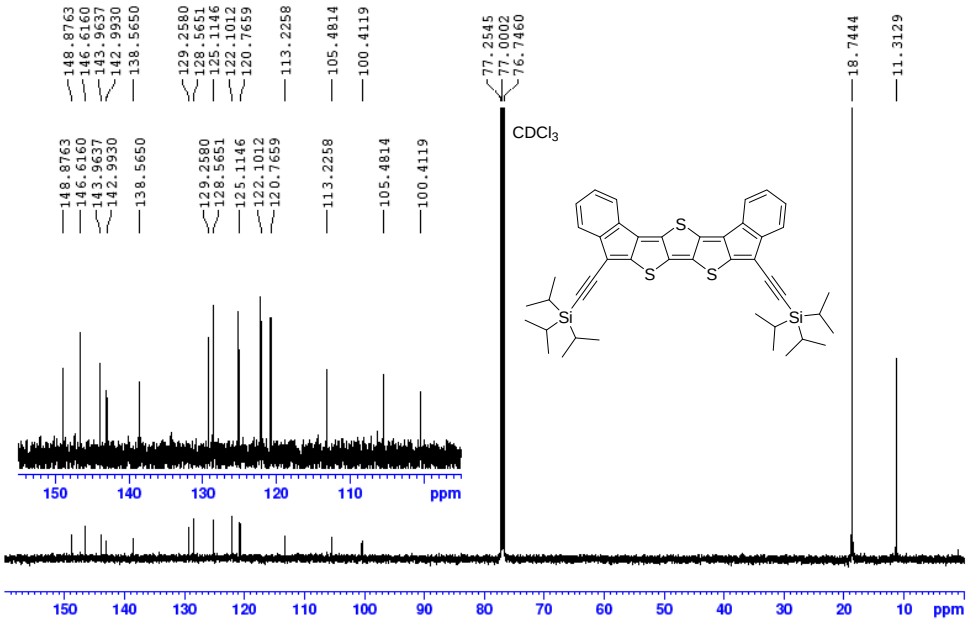


Fig. S36. ^{13}C NMR spectrum of compound **S3-TIPS** (125 MHz, $CDCl_3$, rt).

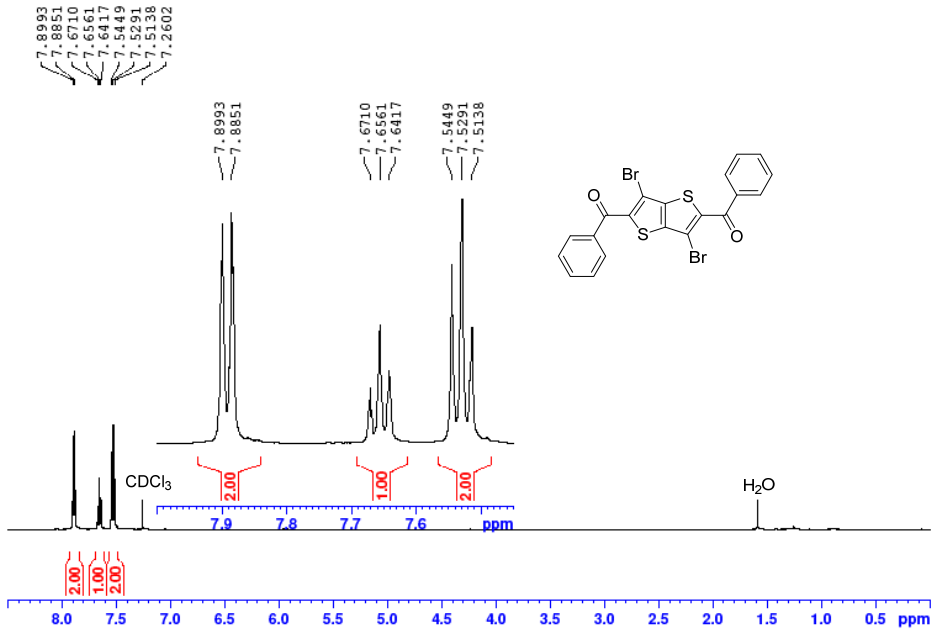


Fig. S37. ^{1}H NMR spectrum of compound **28** (500 MHz, $CDCl_3$, rt).

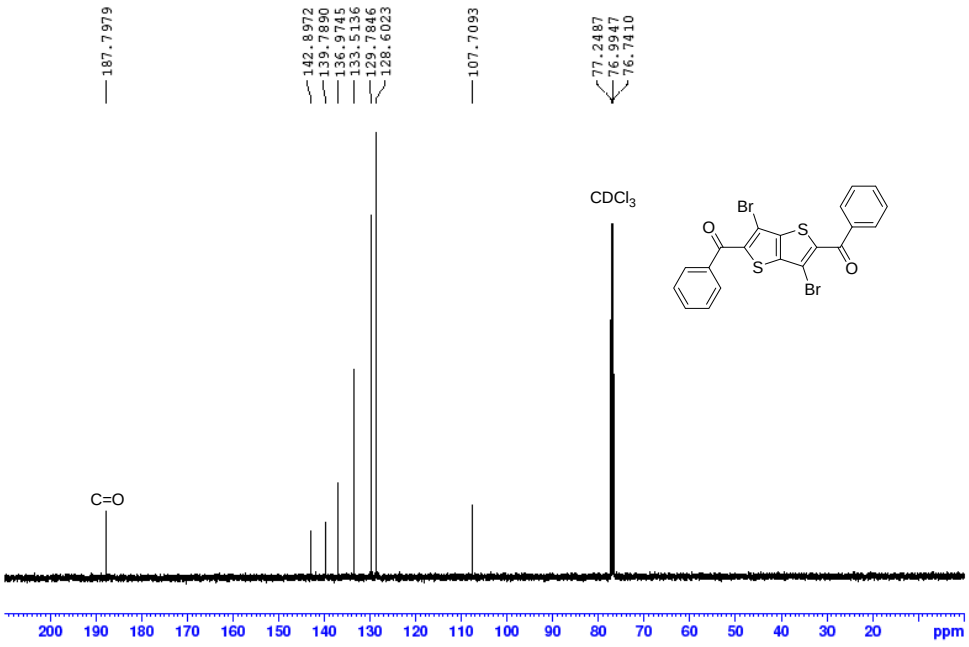


Fig. S38. ^{13}C NMR spectrum of compound **28** (125 MHz, $CDCl_3$, rt).

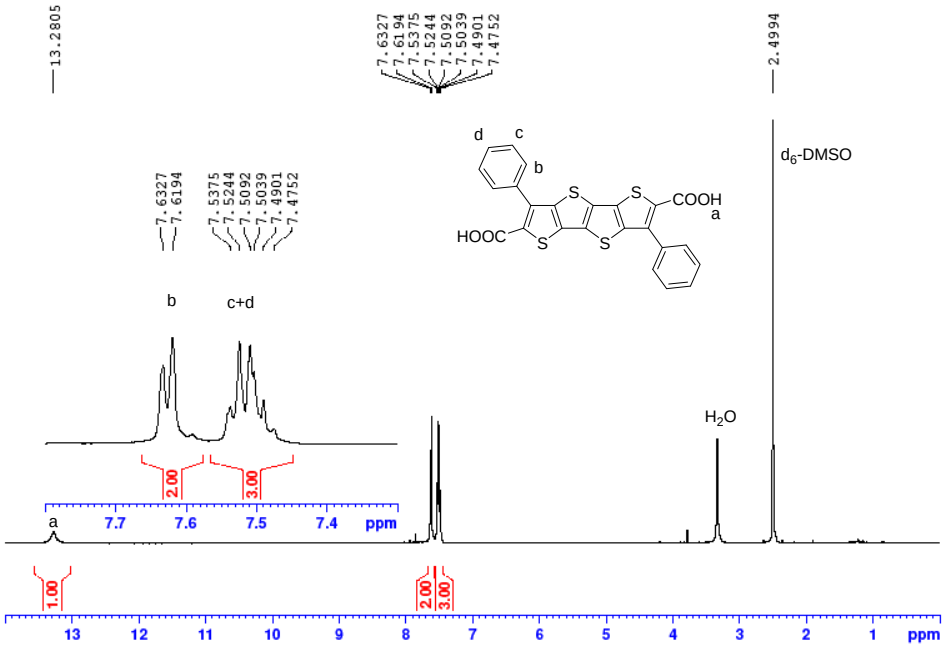


Fig. S39. ^{1}H NMR spectrum of compound **29** (500 MHz, d_6-DMSO, rt).

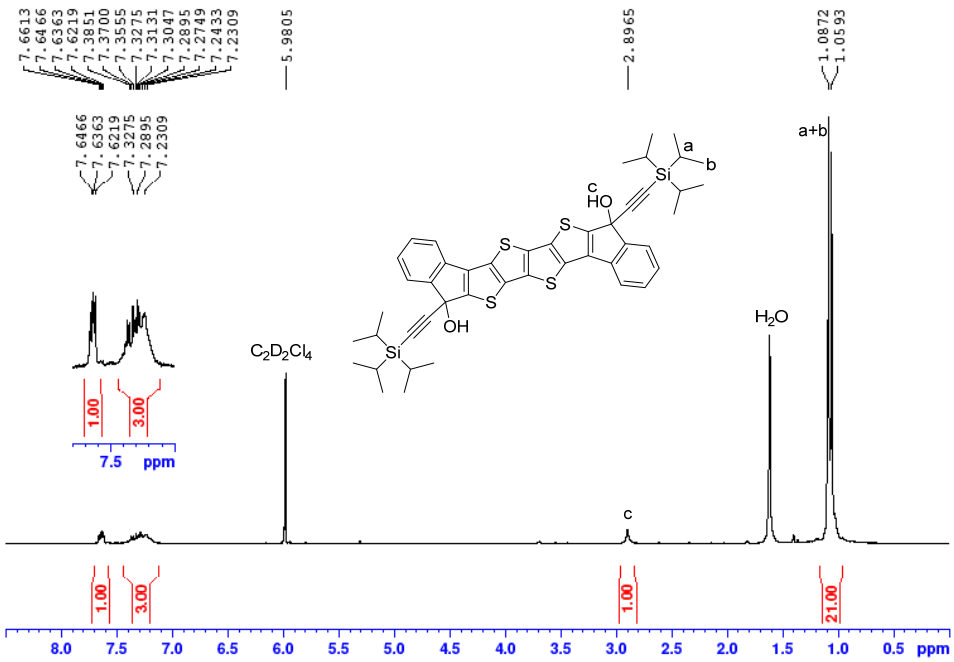


Fig. S40. ^{1}H NMR spectrum of compound **31** (500 MHz, $C_2D_2Cl_4$, rt).

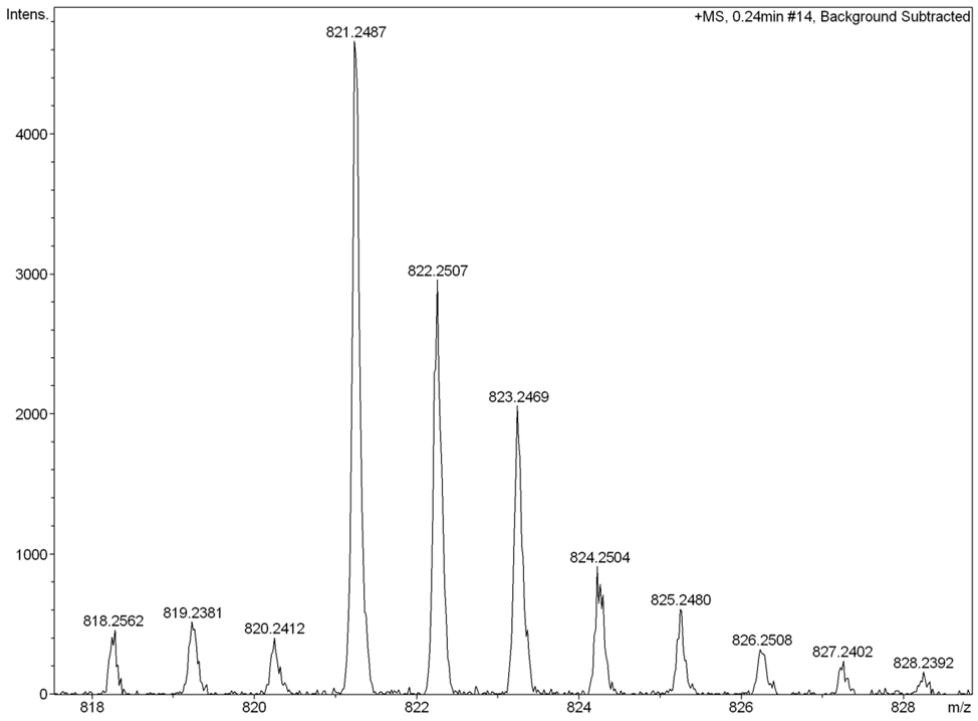


Fig. S41. High resolution mass spectrum (APCI) of compound **31**.