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Supplementary Information for

Expanded benzo-fused dihydro-azulenoazulenes – Tuning electronic properties

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Contents

General Methods S2
UV-Vis Absorption Spectroscopy S2
Electrochemistry S2
Synthetic Protocols S3
NMR Spectra S7
UV–Vis Absorption Spectroscopy Data S18
Electrochemistry Data S18
X-Ray Crystallography S19
References S40

General Methods

Chemical reagents were purchased from Sigma-Aldrich Co., Canada, Oakwood Products, Inc., or 1PlusChem, Inc. and used as received. Flash column chromatography was performed using silica gel (Silica gel 60 (43–60 μm) purchased from VWR). All solvents used were HPLC grade from VWR. Anh. Tetrahydrofuran (THF) was obtained by distillation from sodium and benzophenone under N_2. NMR spectra were recorded on an Agilent DD2 500 MHz instrument or a Bruker 500 MHz instrument with a cryo-inverse probe. ^{1}H and ^{13}C spectra were recorded at 500 MHz and 126 MHz, respectively. Spectra were recorded at 25 °C and referenced using internal residues: $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.16 ppm), CD_2Cl_2 (δ_H = 5.32 ppm, δ_C = 53.84 ppm), CS_2 with DMSO-d_6 lock tube (δ_H = 2.50 ppm, δ_C = 39.52 ppm). Chemical shift values are referenced to the ppm scale; coupling constants are expressed in Hertz (Hz); and apparent multiplicities are reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), td (triplet of doublets), or m (multiplet). High-resolution mass spectra (HRMS) were recorded using an Agilent 6210 time-of-flight (TOF) LCMS apparatus equipped with an ESI and APPI ion source (Agilent Technologies, Toronto, Canada) or on a Bruker SolariX XR MALDI-FT-ICR instrument with dithranol as a matrix.

UV-Vis Absorption Spectroscopy

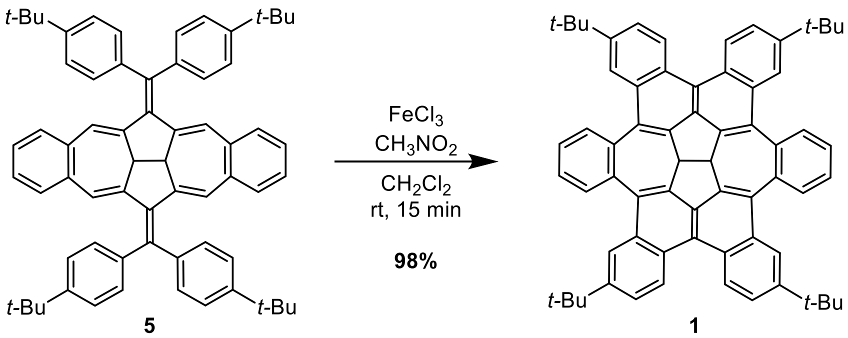
UV–Vis absorption spectra were recorded on a Varian Cary 50 UV–Vis spectrophotometer between 200 and 800 nm. All spectra were recorded in HPLC grade CH_2Cl_2 at room temperature and carried out in a 10 mm quartz cuvettes. Baseline corrections were performed with a blank sample.

Electrochemistry

Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) were performed using an Autolab PGSTAT12 instrument and Nova 1.11 software. A Pt disk electrode (1.6 mm) was used as the working electrode, a Pt wire as the counter electrode, and a Ag wire (isolated by a ceramic frit) as the reference electrode. Measured potentials were referenced to the ferrocene/ferrocenium (Fc/Fc^+) redox couple, measured before and after the experiment for a 1.0 mM solution of Fc. All measurements were carried out using a 0.1 M n-Bu_4NPF_6 solution in HPLC grade CH_2Cl_2 as supporting electrolyte at room temperature with a 0.1 V/s scan rate for CVs. All compounds were measured at 0.50 mM concentrations

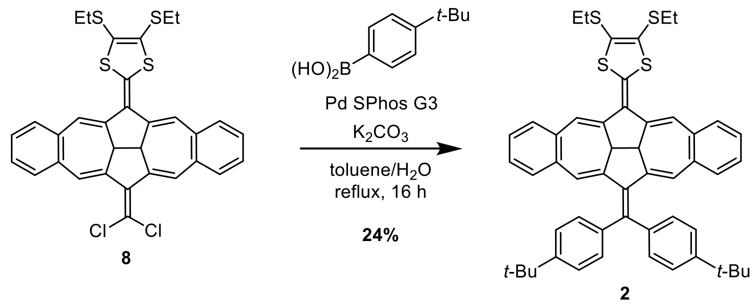
Synthetic Protocols

Compound **1**



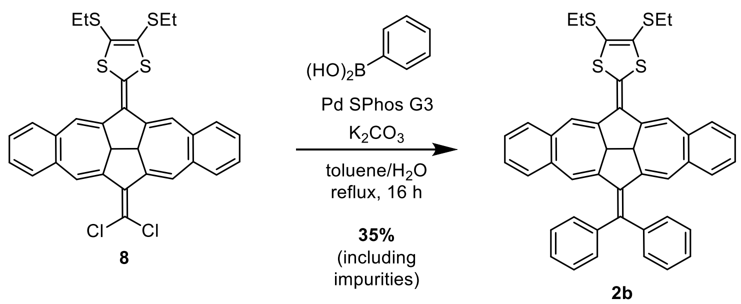
To a flame-dried flask were added $FeCl_3$ (564 mg, 3.49 mmol) in CH_3NO_2 (2.10 mL, 38.4 mmol). To a second flame-dried flask was added compound **5** (300 mg, 0.349 mmol) in anh. CH_2Cl_2 (30 mL). The $FeCl_3$ solution was add to the second flask under vigorous stirring, and a color change from red to blue was observed. The reaction mixture was stirred for 15 min before it was quenched with anh. MeOH (15 mL), and the reaction mixture was stirred for 5 min. Zn powder (114 mg, 1.75 mmol) was added and the reaction was filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, 20 – 30% CH_2Cl_2/*n*-hexane), which yielded compound **1** (294 mg, 0.342 mmol, 98%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.14 (d, J = 8.9 Hz, 4H), 8.60 (d, J = 2.1 Hz, 4H), 8.34 (dd, J = 5.8, 3.4 Hz, 4H), 7.69 (dd, J = 5.8, 3.4 Hz, 4H), 7.67 (dd, J = 8.2, 2.1 Hz, 4H) 5.09 (s, 2H), 1.41 (s, 36H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.25, 147.97, 137.62, 133.51, 132.51, 131.08, 128.91, 127.87, 127.03, 126.13, 124.73, 123.45, 122.71, 50.45, 35.13, 31.48 ppm. HRMS (APPI$^+$): m/z = 868.4916 $[M + NH_4]^+$, calcd. for $[C_{66}H_{62}N^+]$ m/z = 868.4877.

Compound **2**



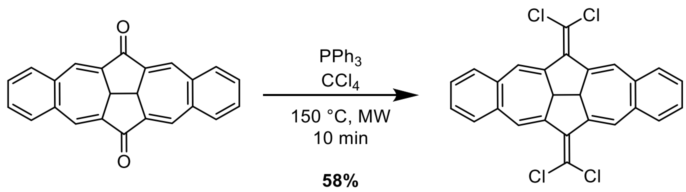
To a solution of compound **6.10** (150 mg, 0.250 mmol) and (4-(*tert*-butyl)phenyl)boronic acid (170 mg, 0.960 mmol) in toluene (20 mL) was added Pd SPhos G3 (40.0 mg, 20 mol%). The solution was degassed for 20 min before degassed aq. K_2CO_3 (1 M, 1.00 mL, 1.00 mmol) was added, and the reaction mixture was heated to reflux for 16 h. The reaction mixture was cooled to room temperature and diluted with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by repeated flash column chromatography (SiO_2, 20 – 30% CH_2Cl_2/*n*-heptane, 10% CH_2Cl_2/*n*-heptane, 20% $CHCl_3$/*n*-heptane), followed by repeated recrystallization from CH_2Cl_2/*n*-heptane, CH_2Cl_2/MeOH and *n*-heptane (three consecutive times). This afforded compound **2** (48.0 mg, 60.0 µmol) in 24% as an orange micro-crystalline solid. ^{1}H NMR (500 MHz, CS_2 with DMSO-d_6 lock tube) δ 7.03 (d, J = 7.7 Hz, 2H), 7.20 – 6.76 (m, 8H), 6.83 (t, J = 7.7 Hz, 2H), 6.72 (t, J = 7.8 Hz, 2H), 6.42 (d, J = 7.8, 1.5 Hz, 2H), 6.28 (s, 2H), 5.67 (s, 2H), 2.75 – 2.62 (m, 4H), 2.68 (s, 2H), 1.13 (td, J = 7.2, 1.4 Hz, 6H), 1.11 (s, 18H) ppm. ^{13}C NMR (126 MHz, CS_2 with DMSO-d_6 lock tube) δ 149.34, 144.91, 143.92, 140.90, 140.39, 136.41, 136.34, 133.43, 132.75, 130.66, 130.37, 128.53, 128.45, 125.04, 125.00, 124.54, 124.18, 122.06, 122.04, 47.43, 33.62, 30.88, 30.74, 14.78 ppm. HRMS (MALDI$^+$ FT-ICR, dithranol): m/z = 802.2796 $[M]^{\bullet+}$, calcd. for $[C_{52}H_{50}S_4^{\bullet+}]$ m/z = 802.2790.

Compound **2b**



To a solution of compound **6.10** (150 mg, 0.250 mmol) and phenylboronic acid (120 mg, 0.990 mmol) in toluene (20 mL) was added Pd SPhos G3 (40.0 mg, 20 mol%). The solution was degassed for 20 min before degassed aq. K_2CO_3 (1 M, 1.00 mL, 1.00 mmol) was added, and the reaction mixture was heated to reflux for 16 h. The reaction mixture was cooled to room temperature and diluted with H_2O (20 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), and the combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by repeated flash column chromatography (SiO_2, 40% CH_2Cl_2/*n*-heptane, 20 – 40% CH_2Cl_2/*n*-heptane, 20% $CHCl_3$/*n*-heptane), followed by repeated recrystallization from CH_2Cl_2/*n*-heptane, *n*-heptane (two consecutive times), and CH_2Cl_2/MeOH. This afforded compound **6.2b** (60.0 mg, 60.0 µmol) in 35% as red crystals; however, the material still contained impurities. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.17 – 6.99 (m, 12H), 6.85 (t, J = 7.4 Hz, 2H), 6.74 (t, J = 7.5 Hz, 2H), 6.48 (d, J = 7.9 Hz, 2H), 6.29 (s, 2H), 5.72 (s, 2H), 2.76 – 2.60 (m, 4H), 2.70 (s, 2H), 1.14 (td, J = 7.4, 2.0 Hz, 7H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6) δ 144.63, 143.95, 143.15, 140.41, 136.45, 136.13, 133.47, 132.97, 130.93, 130.34, 129.23, 128.58, 128.48, 127.90, 126.77, 125.18, 124.65, 124.54, 122.05, 47.42, 30.76, 14.78 ppm. HRMS (MALDI$^+$ FT-ICR, dithranol): m/z = 690.1543 $[M]^{\bullet+}$, calcd. for $[C_{44}H_{34}S_4^{\bullet+}]$ m/z = 690.1538.

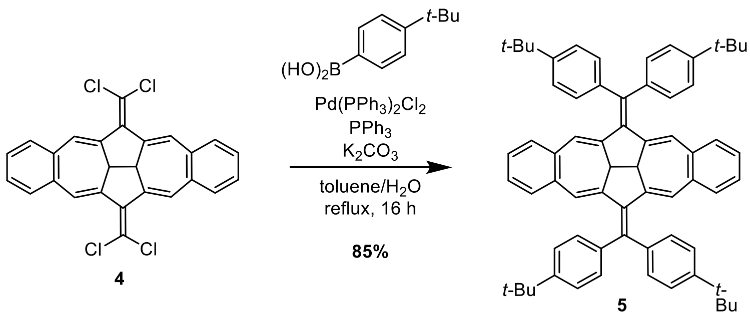
Compound **4**



3 4

To a flame-dried MW vial were added compound **3**[1] (300 mg, 0.897 mmol), PPh_3 (1.88 g, 7.18 mmol) and CCl_4 (7.00 mL, 72.3 mmol), and the suspension was degassed for 30 min. The microwave vial was sealed, and the reaction mixture was heated in a microwave to 150 °C for 10 min. The reaction mixture was filtered through a pad of SiO_2 eluting with CH_2Cl_2 and concentrated *in vacuo*. The product was purified by flash column chromatography (SiO_2, 25 – 90% $CHCl_3$/*n*-hexanes), which yielded compound **4** (242 mg, 0.516 mmol, 58%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 4H), 7.49 (dd, J = 5.9, 3.4 Hz, 4H), 7.33 (dd, J = 5.9, 3.4 Hz, 4H), 2.98 – 2.89 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.15, 137.43, 132.41, 131.68, 127.92, 126.75, 120.91, 47.39 ppm. HRMS (LCMS APPI$^+$): m/z = 468.9918 $[M + H]^+$, calcd. for $[C_{26}H_{14}Cl_4^+]$ m/z = 468.9893.

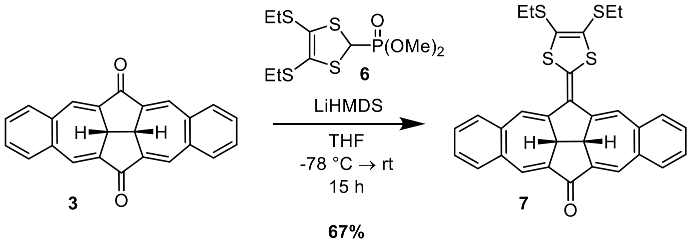
Compound **5**



4 5

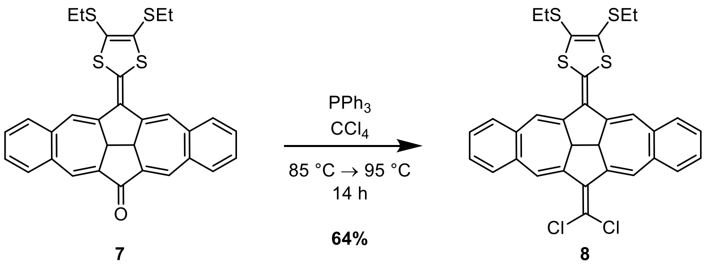
To a solution of compound **4** (396 mg, 0.845 mmol), (4-(*tert*-butyl)phenyl)boronic acid (1.20 g, 6.77 mmol) and PPh_3 (44.0 mg, 0.169 mmol) in toluene (40 mL) were added K_2CO_3 (935 mg, 6.77 mmol) and H_2O (10 mL). The solution was degassed for 20 min before $Pd(PPh_3)_2Cl_2$ (119 mg, 0.169 mmol) was added, and the solution was further degassed for 10 min. The reaction mixture was heated to reflux for 16 h, before it was cooled to room temperature and diluted with H_2O (100 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The reaction was purified by flash column chromatography (SiO_2, 20 – 40% CH_2Cl_2/*n*-hexanes), which yielded compound **5** (625 mg, 0.727 mmol, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, J = 7.5 Hz, 8H), 7.30 (d, J = 7.5 Hz, 8H), 6.98 (dd, J = 5.9, 3.4 Hz, 4H), 6.66 (dd, J = 5.9, 3.4 Hz, 4H), 5.98 (s, 4H), 3.08 (s, 2H), 1.34 (s, 36H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.55, 146.41, 142.08, 141.54, 137.00, 134.93, 130.84, 128.75, 126.04, 125.37, 124.97, 47.44, 34.79, 31.55 ppm. HRMS (ESI$^+$): m/z = 859.5059 $[M + H]^+$, calcd. for $[C_{66}H_{67}^+]$ m/z = 859.5238.

Compound **7**



Synthesized according to a modified literature procedure.[2] To a flame-dried Schlenk flask under a positive flow of N_2 was added phosphonate-ester **6**[3] (795 mg, 2.40 mmol) in anh. THF (18 mL). The solution was degassed and cooled to -78 °C in a dry ice/acetone bath for 30 min. LiHMDS (1 M in toluene, 2.90 mL, 2.90 mmol) was added dropwise, and the reaction mixture was stirred at -78 °C for 1 h. In a separate flame-dried Schlenk flask was added compound **3** (800 mg, 2.40 mmol) in anh. THF (35 mL). The solution was degassed and cooled to -78 °C in a dry ice/acetone bath for 30 min before the solution containing deprotonated **6** was added fast via cannulation. The reaction mixture was stirred for 15 h while slowly reaching rt. The reaction was quenched with aqueous NH_4Cl (sat., 20 mL), washed with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The product was purified by flash column chromatography (70 – 100% CH_2Cl_2/*n*-heptane) followed by precipitation from MeOH. This yielded compound **7** (870 mg, 1.61 mmol, 67%) as a red solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.68 – 7.63 (m, 6H), 7.45 (td, J = 7.6, 1.5 Hz, 2H), 7.36 (td, J = 7.5, 1.3 Hz, 2H), 6.91 (s, 2H), 3.27 – 3.22 (s, 2H), 2.95 (m, 4H), 1.31 (t, J = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 190.39, 144.91, 141.09, 139.29, 137.77, 134.26, 133.21, 132.24, 131.01, 130.17, 128.62, 126.33, 122.63, 121.77, 43.50, 31.38, 15.25. HRMS (MALDI$^+$ FT-ICR, dithranol): m/z = 540.0714 $[M]^{\bullet+}$, calcd. for $[C_{31}H_{24}OS_4^{\bullet+}]$ m/z = 540.0705.

Compound **8**



To a flame-dried microwave vial were added compound **7** 50 (409 mg, 0.756 mmol) and PPh_3 (1.54 g, 5.87 mmol) and CCl_4 (6.00 mL, 46.8 mmol), and the suspension was degassed for 30 min. The microwave vial was sealed and the reaction mixture was heated to 80 °C using conventional heating. After 1 h, the temperature was increased to 95 °C, and the reaction mixture was stirred for 14 h before it was cooled to rt. The reaction mixture was filtered through a plug of SiO_2 (CH_2Cl_2) and concentrated *in vacuo* to afford compound **8** (294 mg, 0.484 mmol) in 64% yield as a red solid, without further purification needed. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.83 (s, 2H), 7.53

– 7.49 (m, 4H), 7.33 (td, J = 7.5, 1.6 Hz, 2H), 7.29 (td, J = 7.4, 1.5 Hz, 2H), 6.75 (s, 2H), 3.04 – 3.00 (m, 2H), 2.99 – 2.86 (m, 4H), 1.31 (t, J = 7.3 Hz, 6H) ppm. ^{13}C NMR (126 MHz, CD_2Cl_2) δ 146.03, 142.94, 138.30, 136.76, 135.35, 133.25, 132.10, 131.47, 129.70, 128.15, 126.94, 125.90, 122.29, 121.48, 120.13, 48.43, 31.31, 15.30 ppm. HRMS (MALDI$^+$ FT-ICR, dithranol): m/z = 606.0141 $[M]^{\bullet+}$, calcd. for $[C_{32}H_{24}Cl_2S_4^{\bullet+}]$ m/z = 606.0133.

NMR Spectra

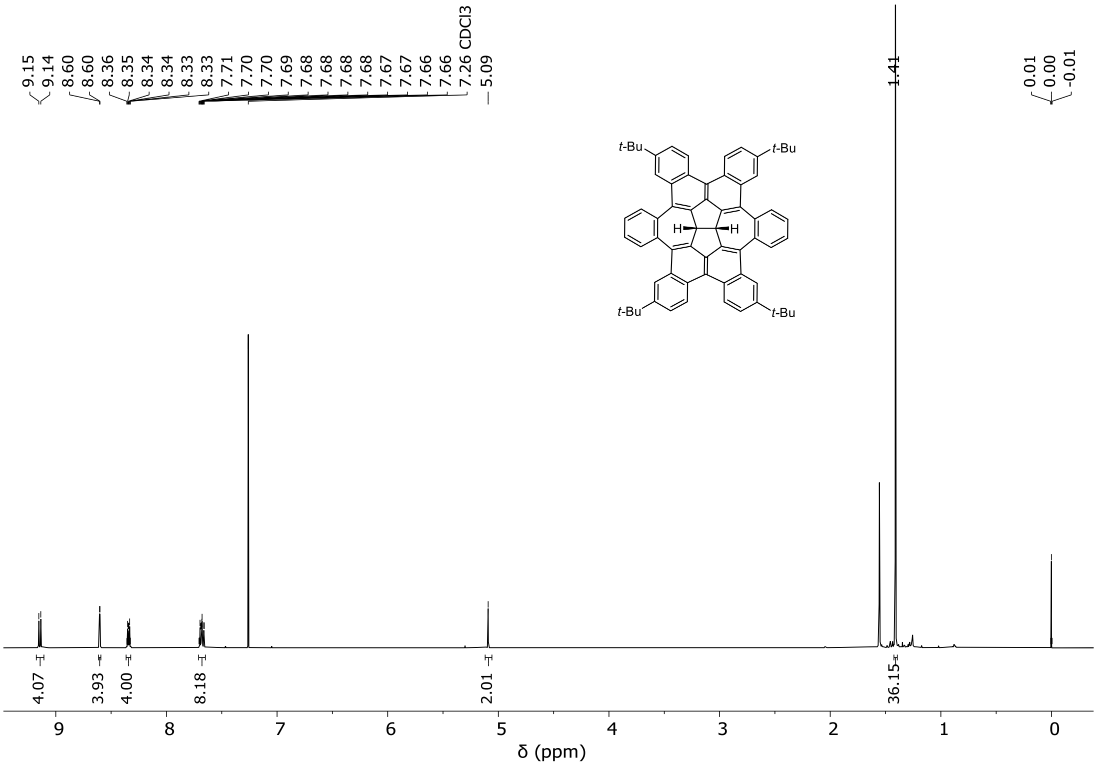


Fig. S1 ^{1}H NMR (500 MHz) spectrum of compound **1** in $CDCl_3$.

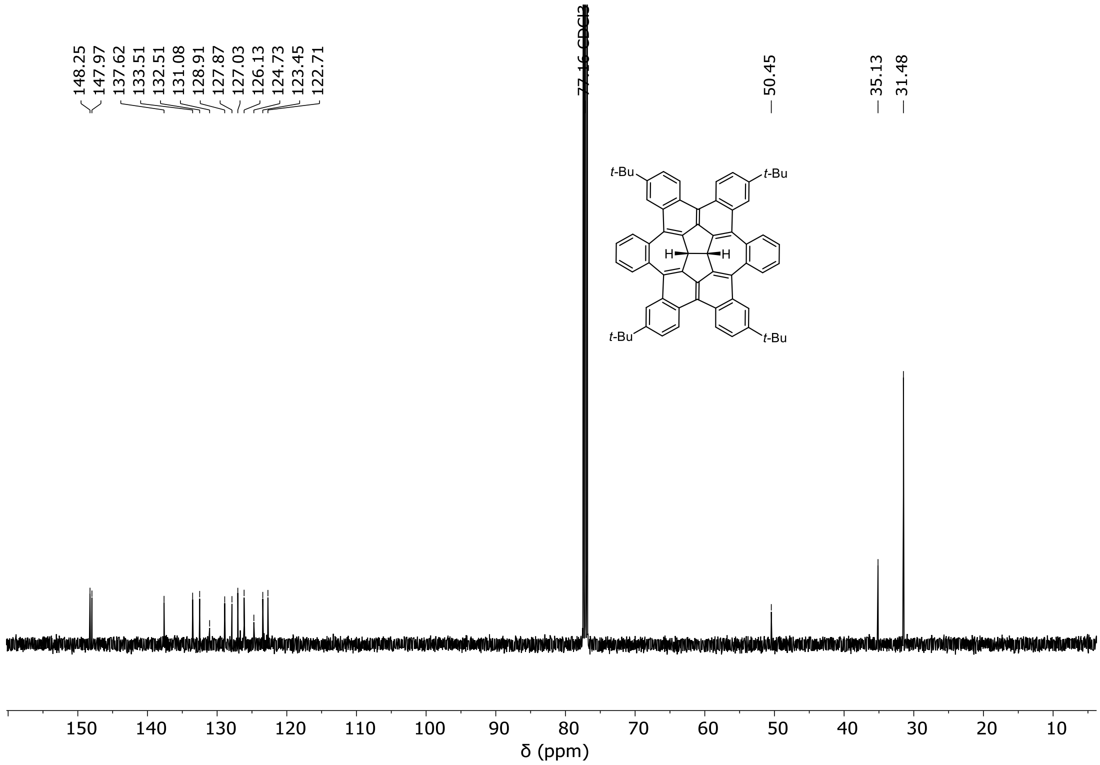


Fig. S2 ^{13}C NMR (126 MHz) spectrum of compound **1** in $CDCl_3$.

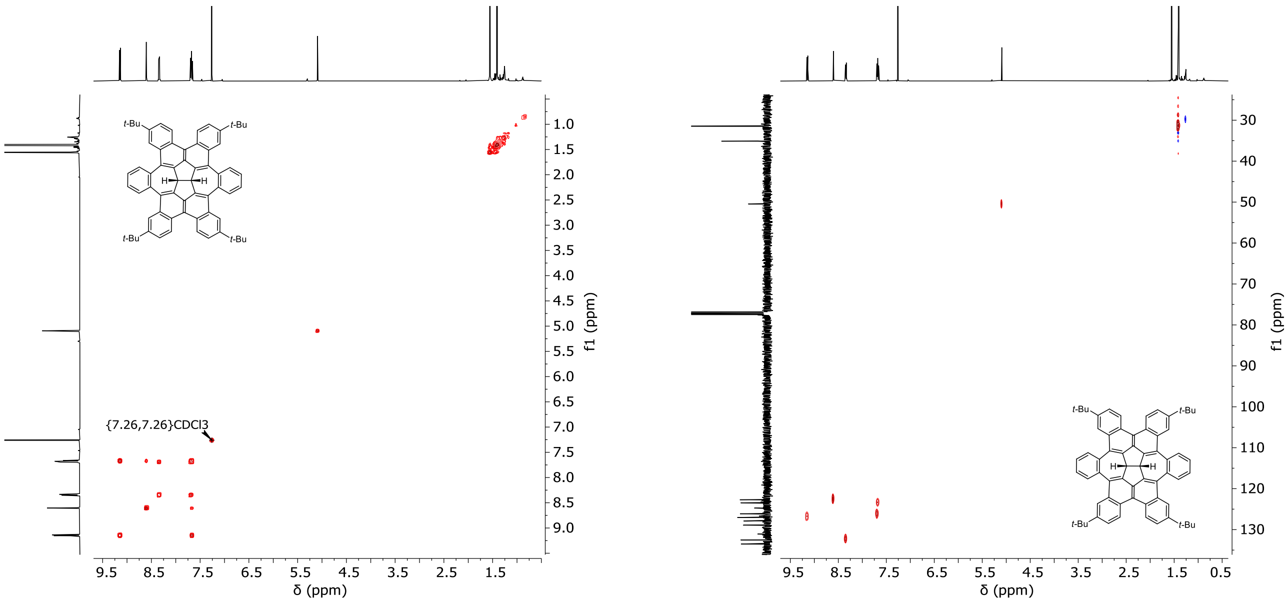


Fig. S3 Left: ^{1}H–^{1}H COSY NMR (500 MHz) of compound **1** in $CDCl_3$. Right: ^{1}H–^{13}C HSQC NMR (500/126 MHz) of compound **1** in $CDCl_3$.

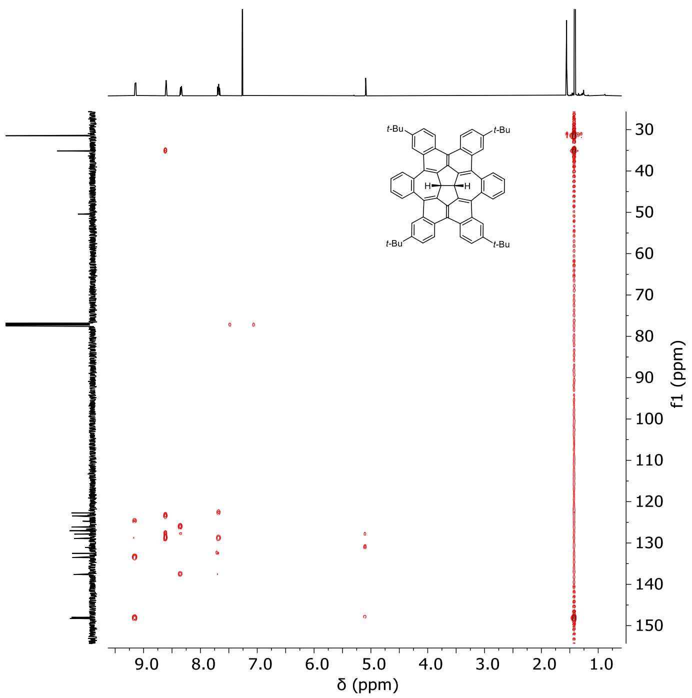


Fig. S4 ^{1}H–^{13}C HMBC NMR (500/126 MHz) of compound **6.1** in $CDCl_3$.

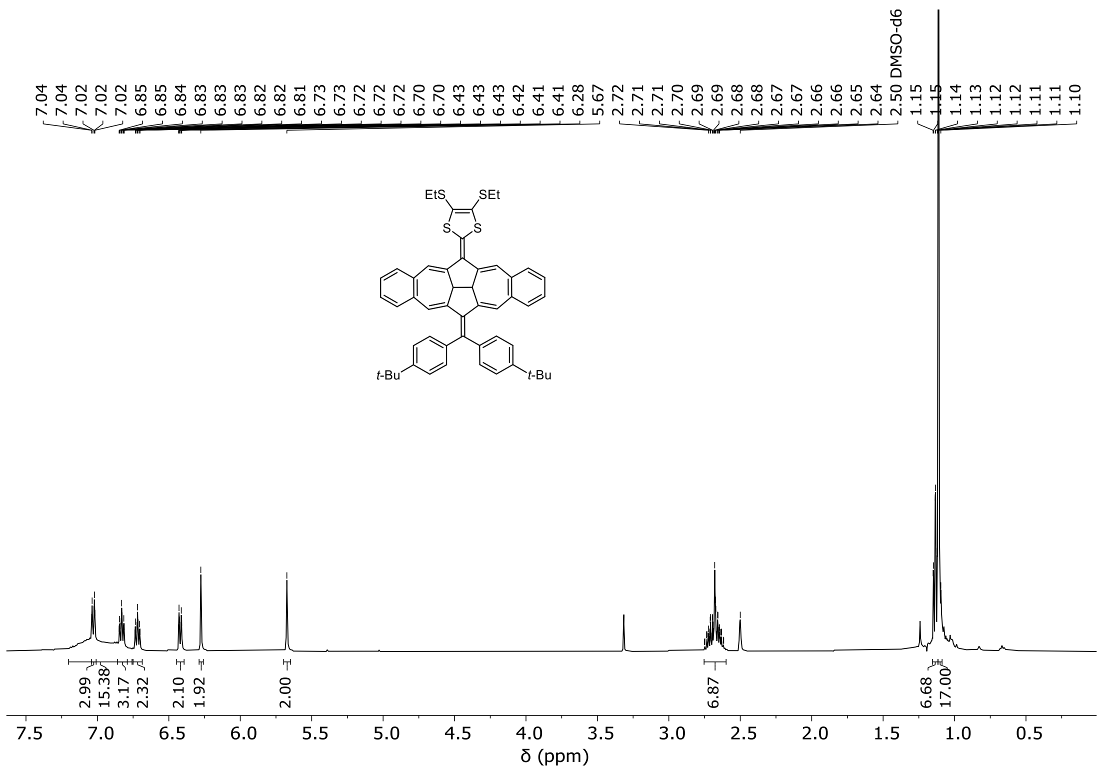


Fig. S5 ^{1}H NMR (500 MHz) spectrum of compound **2** in CS_2 with DMSO-d_6 lock tube.

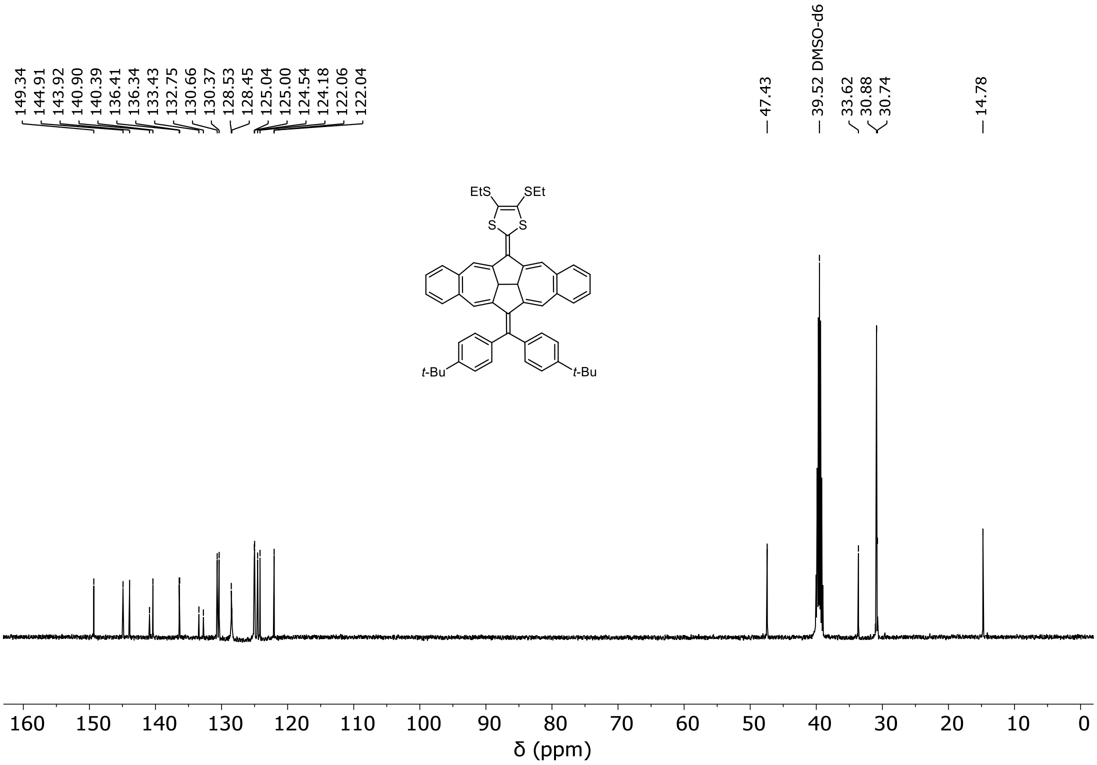


Fig. S6 ^{13}C NMR (126 MHz) spectrum of compound **2** in CS_2 with DMSO-d_6 lock tube.

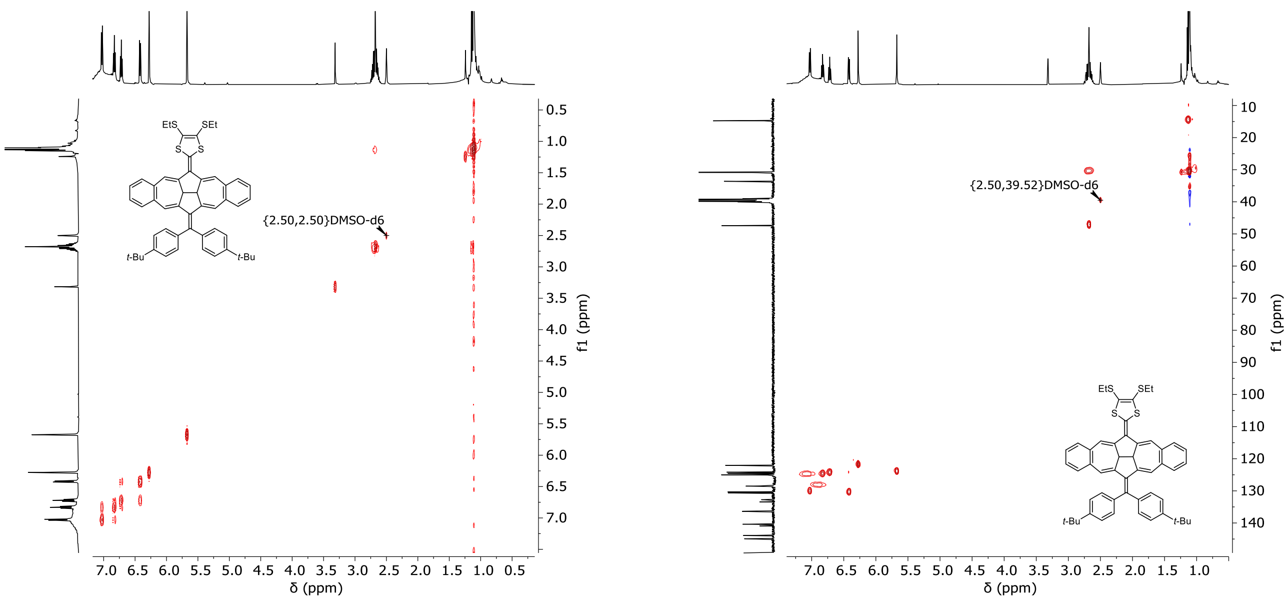


Fig. S7 Left: ^{1}H–^{1}H COSY NMR (500 MHz) of compound **2** in CS_2 with DMSO-d_6 lock tube. Right: ^{1}H–^{13}C HSQC NMR (500/126 MHz) of compound **2** in CS_2 with DMSO-d_6 lock tube.

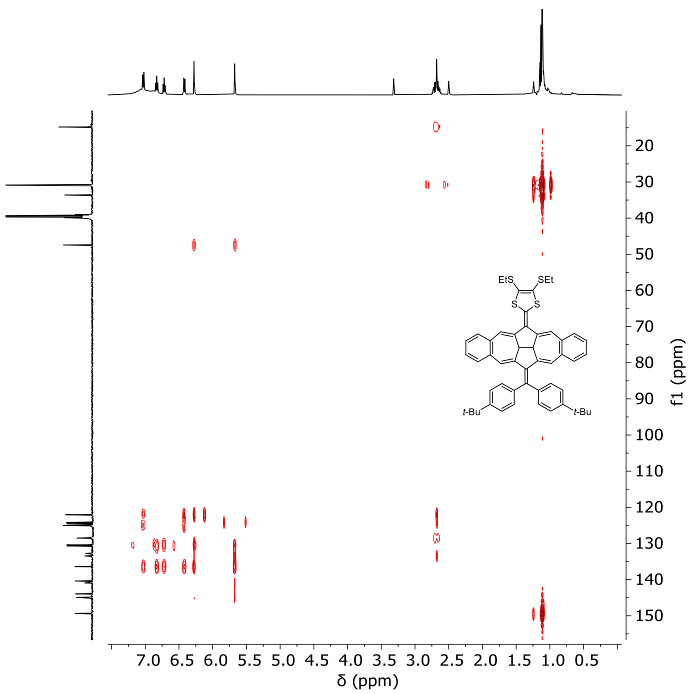


Fig. S8 ^{1}H–^{13}C HMBC NMR (500/126 MHz) of compound **2** in CS_2 with DMSO-d_6 lock tube.

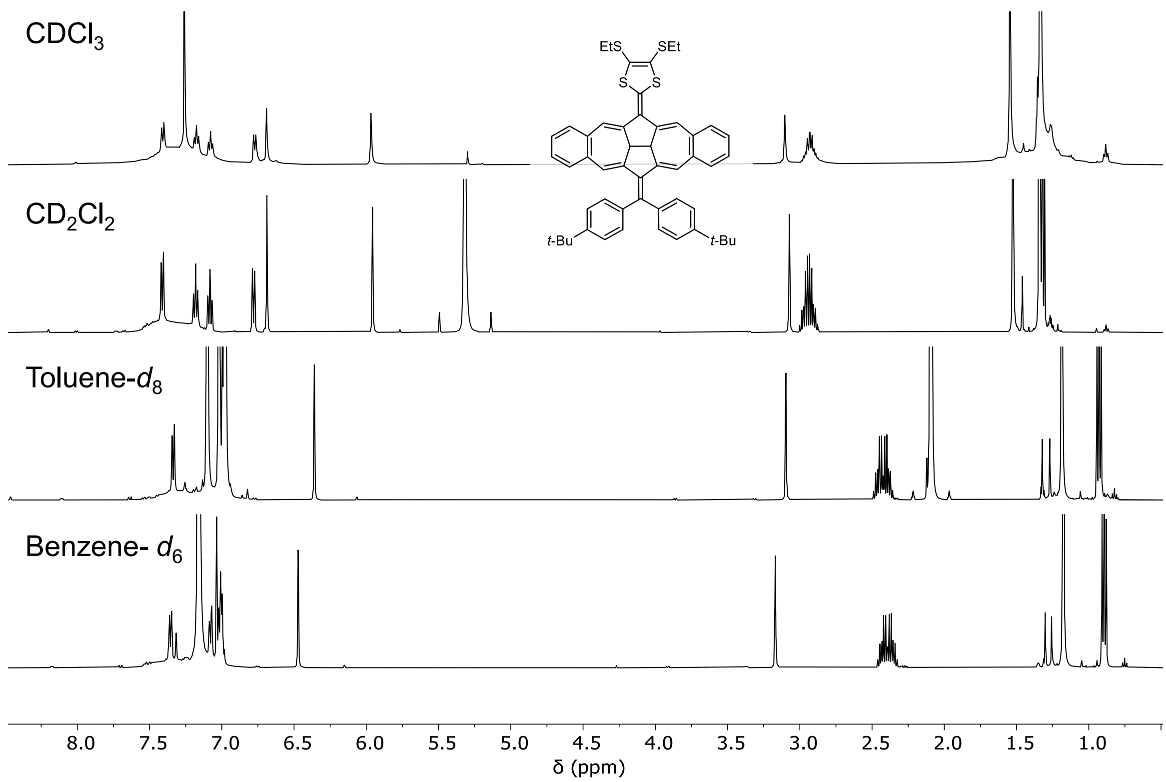


Fig. S9 ^{1}H NMR (500 MHz) spectra of compound **2** in different solvents (from the top): $CDCl_3$, CD_2Cl_2, toluene-d_8, and benzene-d_6.

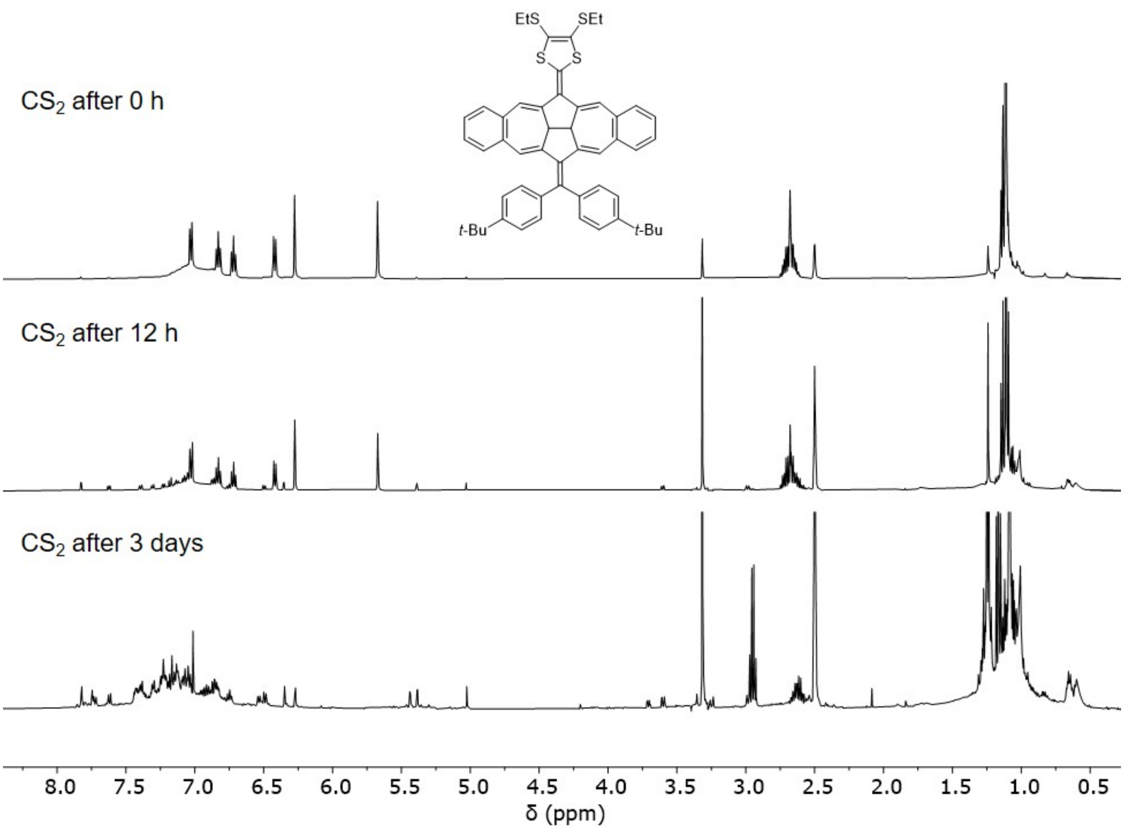


Fig. S10 [1]H NMR spectra of compound **2** recorded in CS_2 (with DMSO-*d*$_6$ lock tube) right after preparing the sample (top), after 12 h (middle), and after 3 days (bottom) at 25 °C.

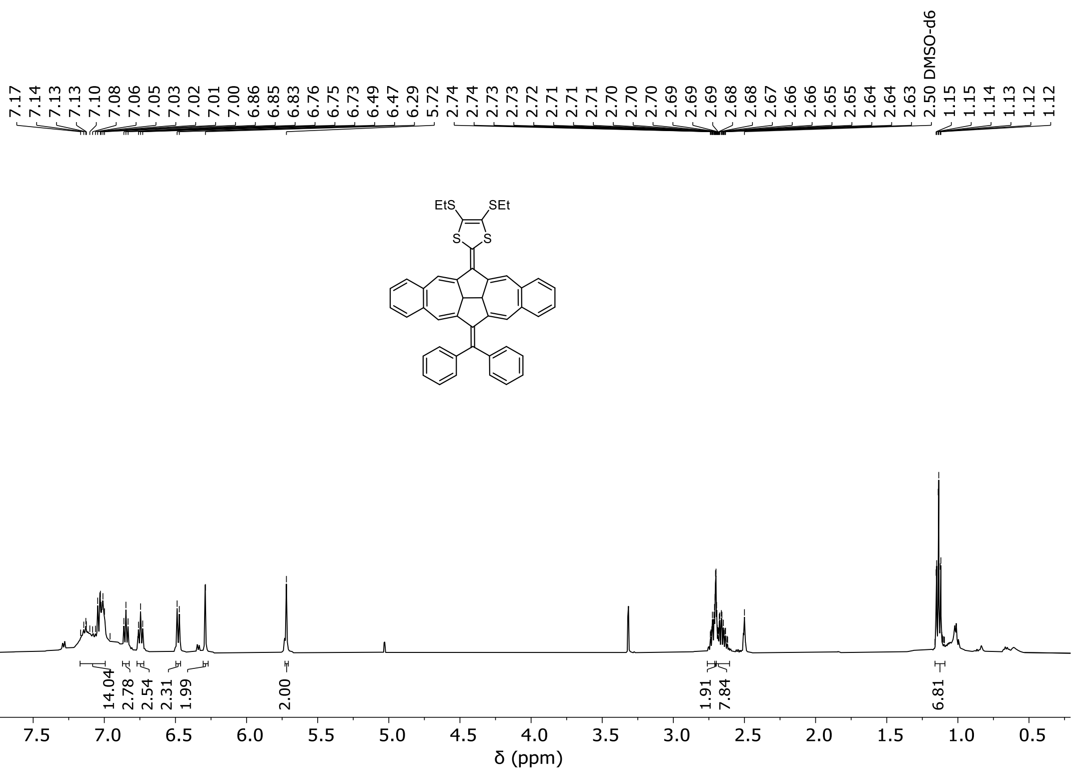


Fig. S11 [1]H NMR (500 MHz) spectrum of compound **2b** including impurities in CS_2 with DMSO-*d*$_6$ lock tube.

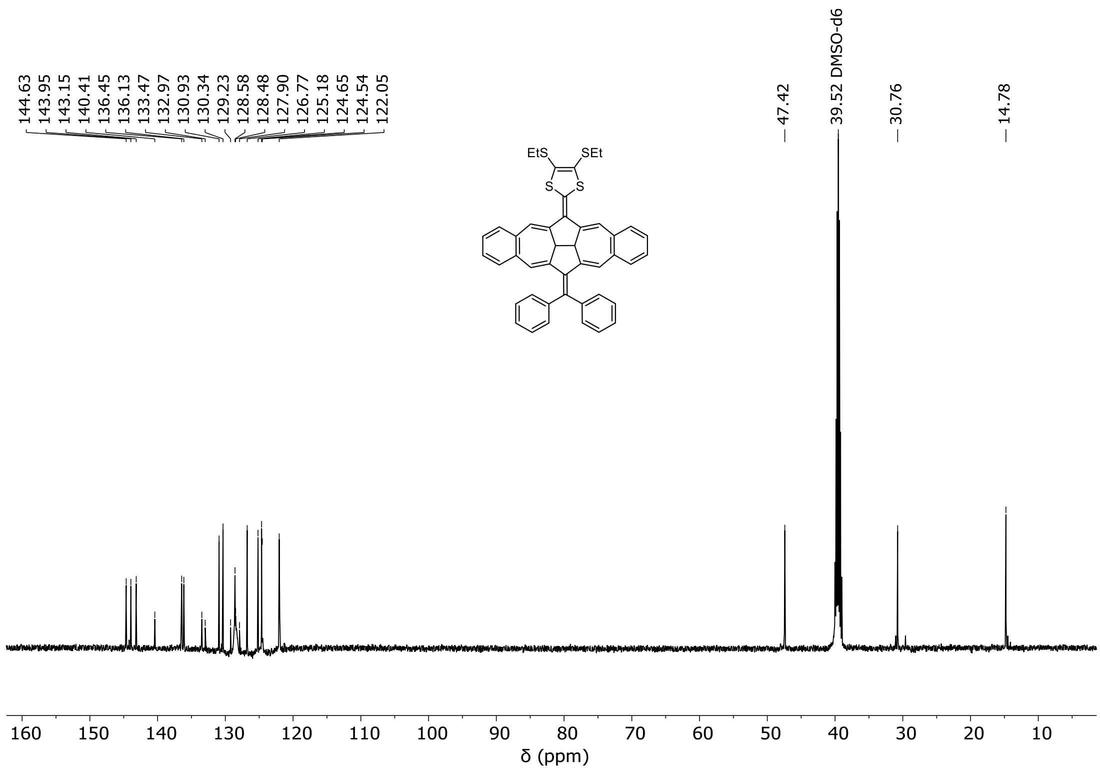


Fig. S12 ^{13}C NMR (126 MHz) spectrum of compound **2b** including impurities in CS_2 with DMSO-d_6 lock tube.

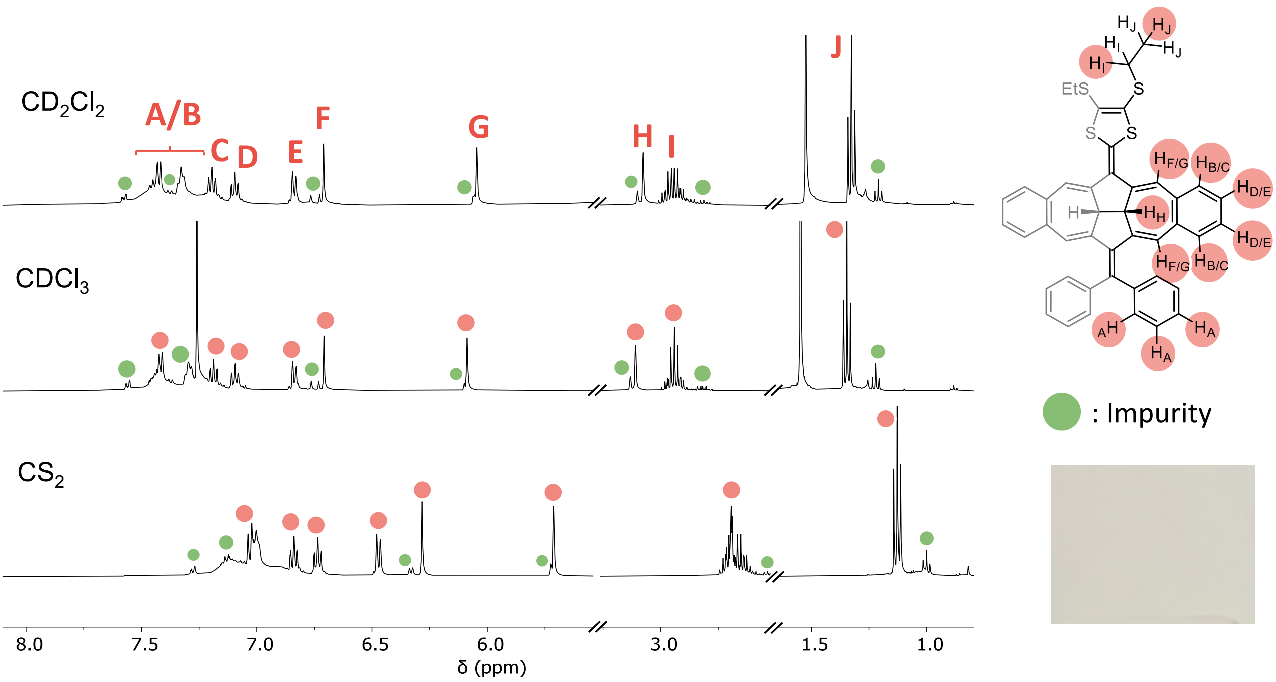


Fig S13 ^{1}H NMR spectra of compound **2b** including impurities, recorded in CD_2Cl_2 (top), $CDCl_3$ (middle), and CS_2 (with DMSO-d_6 lock tube, bottom) at 25 °C. Insert: photograph of isolated crystalline material.

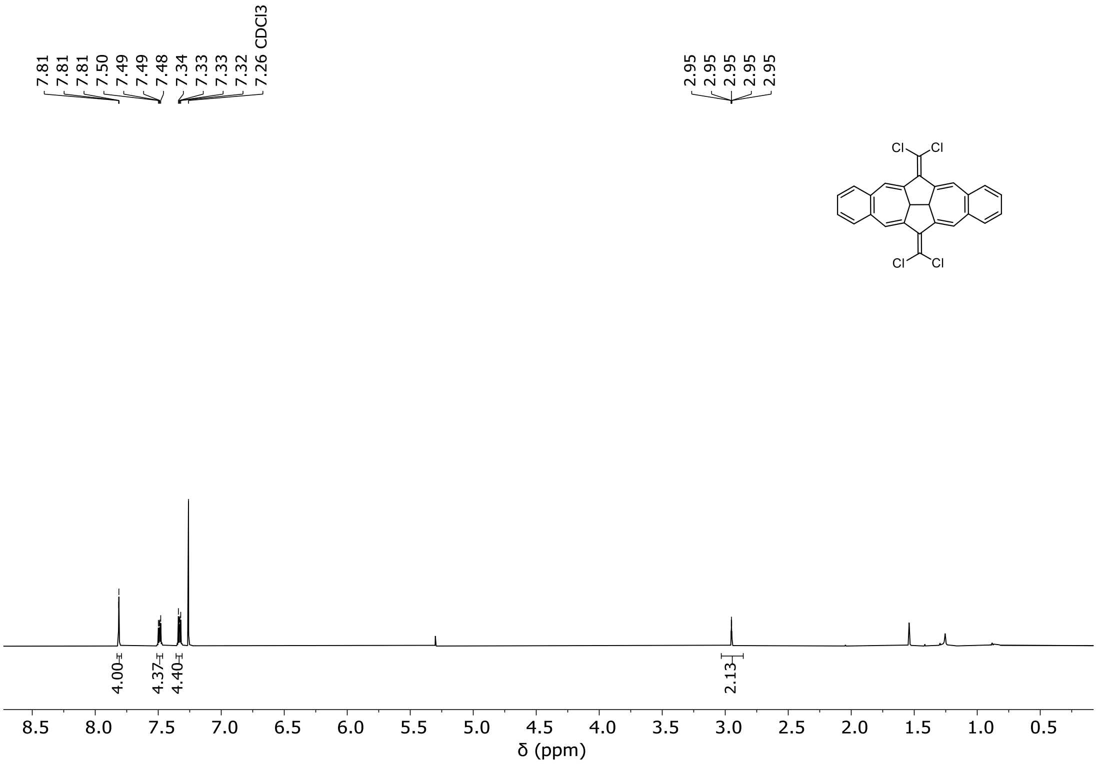


Fig. S14 ^{1}H NMR (500 MHz) spectrum of compound **4** in $CDCl_3$.

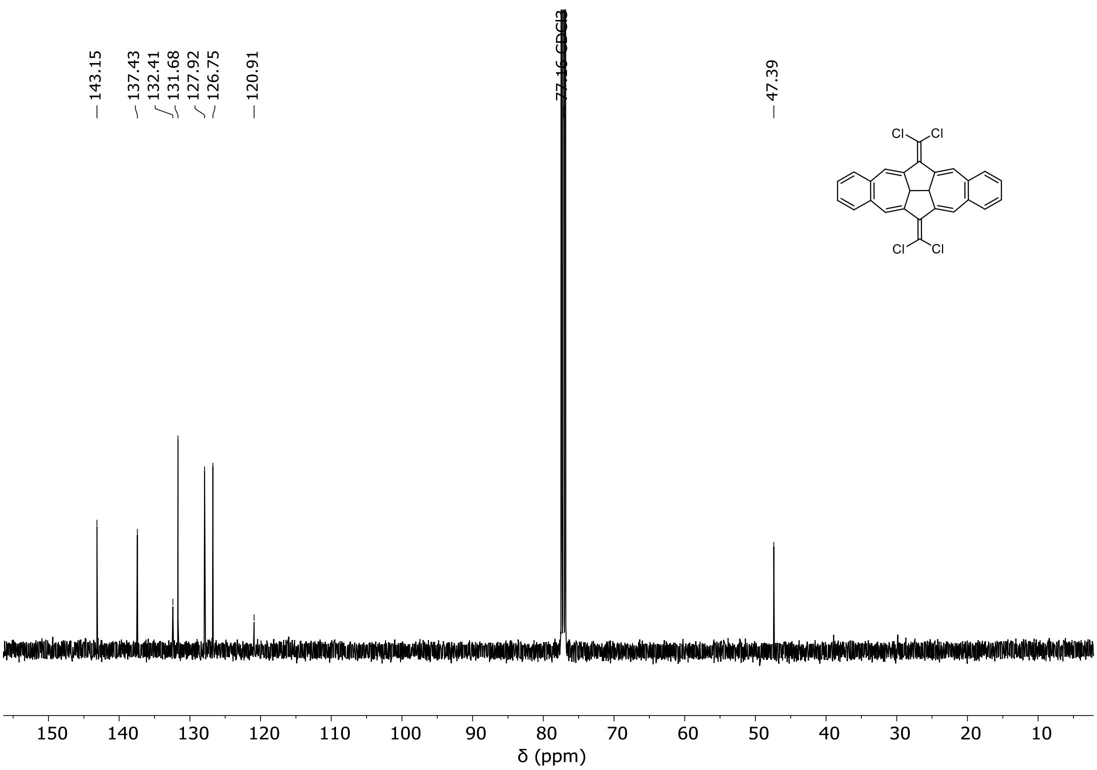


Fig. S15 ^{13}C NMR (126 MHz) spectrum of compound **4** in $CDCl_3$.

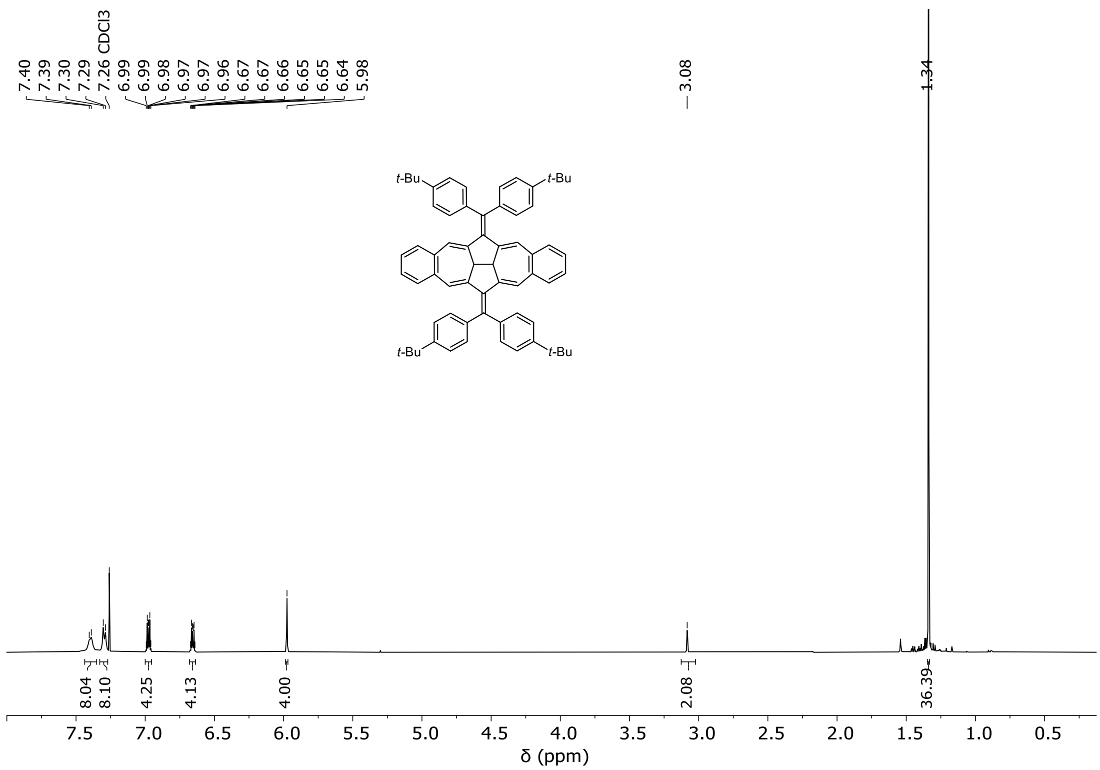


Fig. S16 ^{1}H NMR (500 MHz) spectrum of compound **5** in $CDCl_3$.

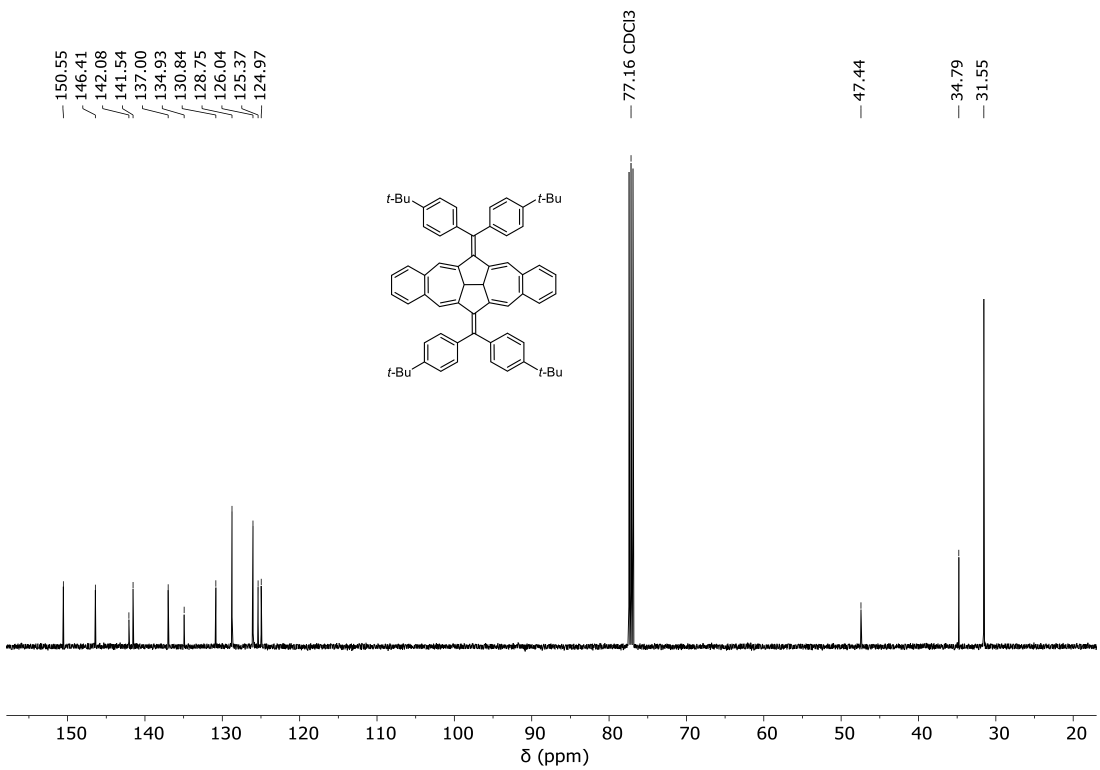


Fig. S17 ^{13}C NMR (126 MHz) spectrum of compound **5** in $CDCl_3$.

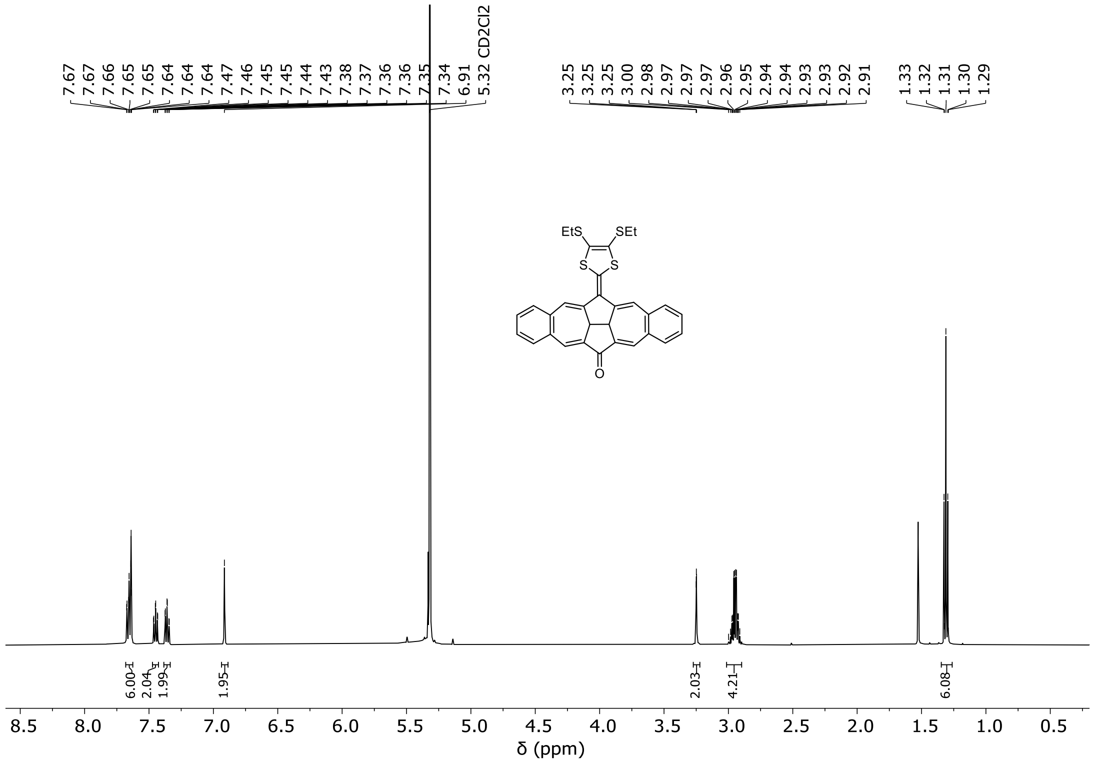


Fig. S18 ^{1}H NMR (500 MHz) spectrum of compound **7** in CD_2Cl_2

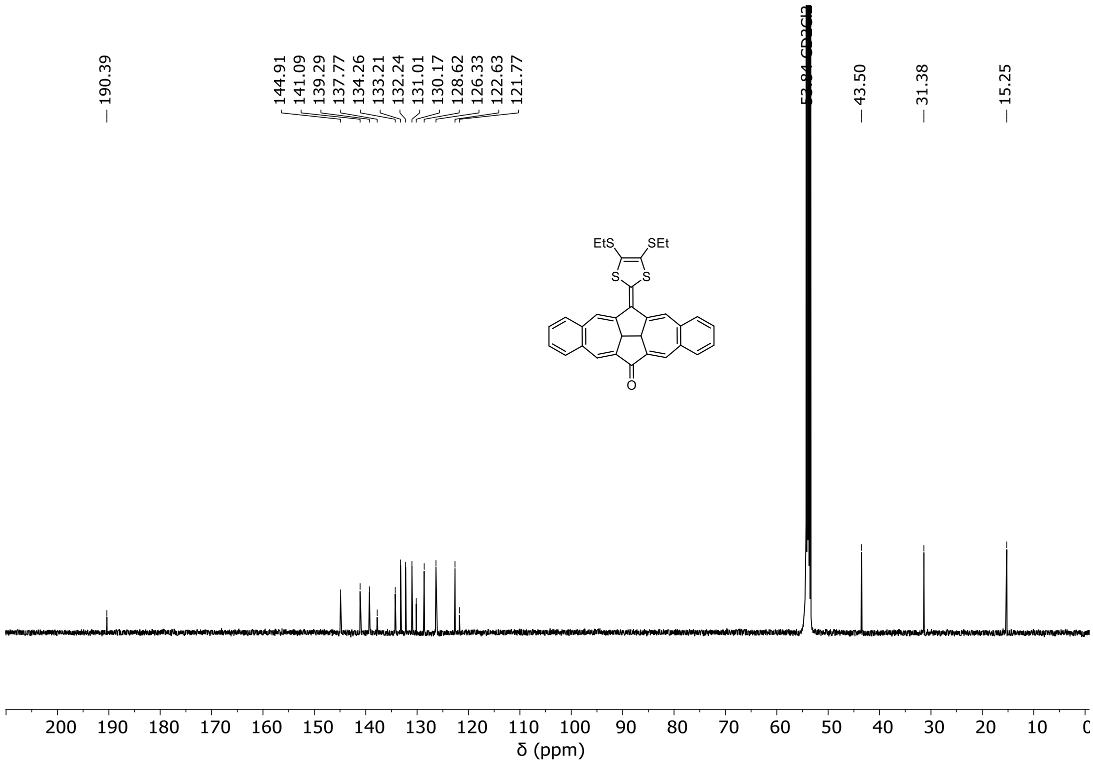


Fig. S19 ^{13}C NMR (126 MHz) spectrum of compound **7** in CD_2Cl_2.

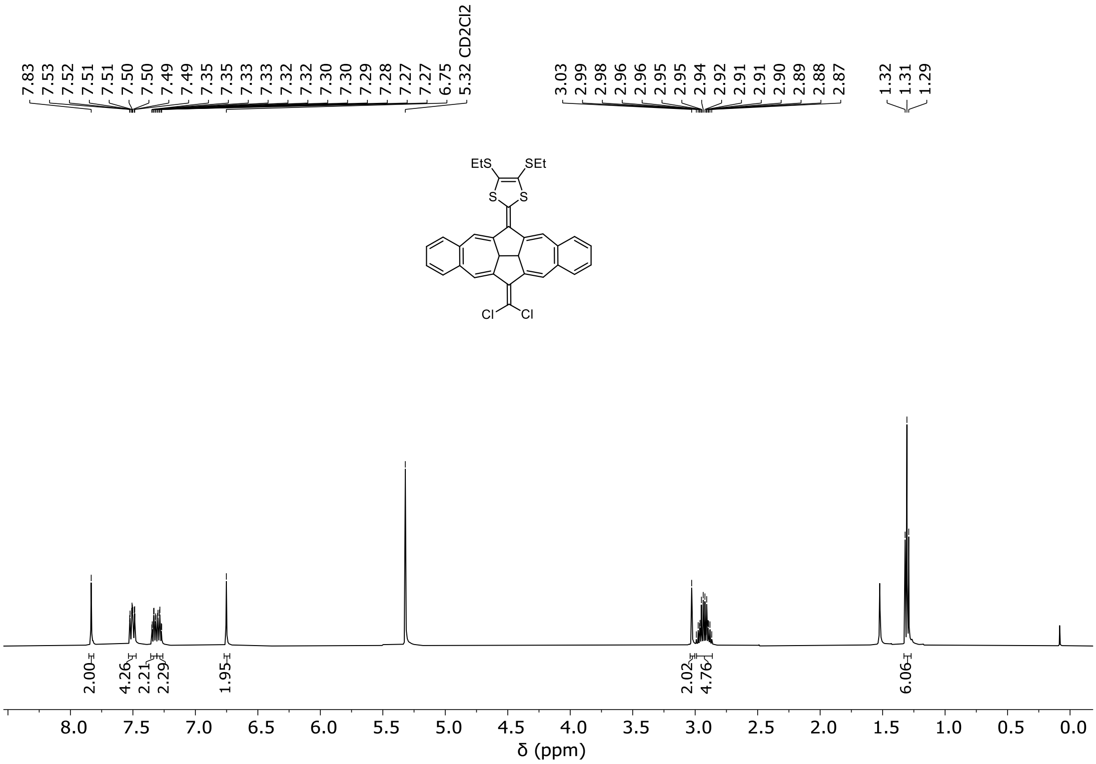


Fig. S20 ^{1}H NMR (500 MHz) spectrum of compound **8** in CD_2Cl_2.

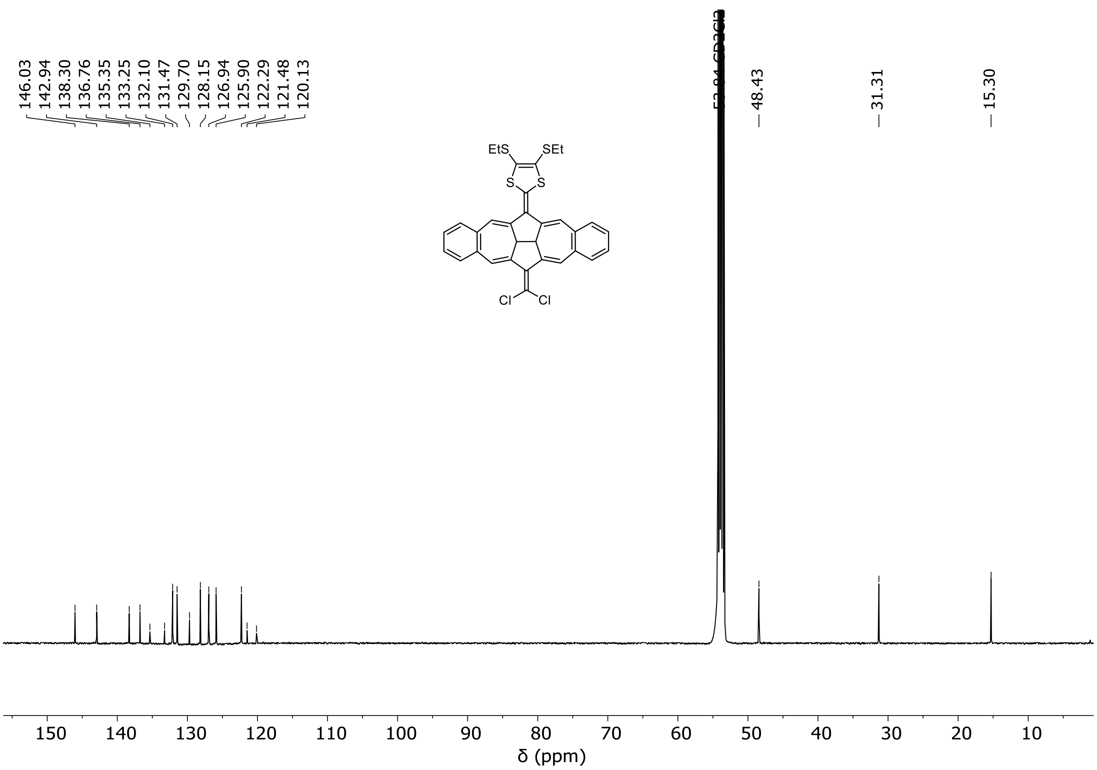


Fig. S21 ^{13}C NMR (126 MHz) spectrum of compound **8** in $CDCl_3$

UV–Vis Absorption Spectroscopy Data

Table S1. Absorption maxima and extinction coefficients for compounds **1**, **5**, **2**, and **7** in CH_2Cl_2, at room temperature

Compound	λ_{max} (nm), (ε /10^4 $cm^{-1}\cdot M^{-1}$)
1	397 (1.1), 375 (0.9), 355 (2.7), 340 (4.0), 302 (12.3), 293 (12.2), 253 (*sh*, 6.6), 244 (7.0)
5	386 (1.6), 276 (7.7)
2	450 (2.8), 379 (1.9), 356 (1.9), 332 (*sh*, 2.0), 287 (9.4)
7	545 (0.9), 419 (1.5), 392 (*sh*, 1.5), 364 (1.6), 315 (6.9)

Electrochemistry Data

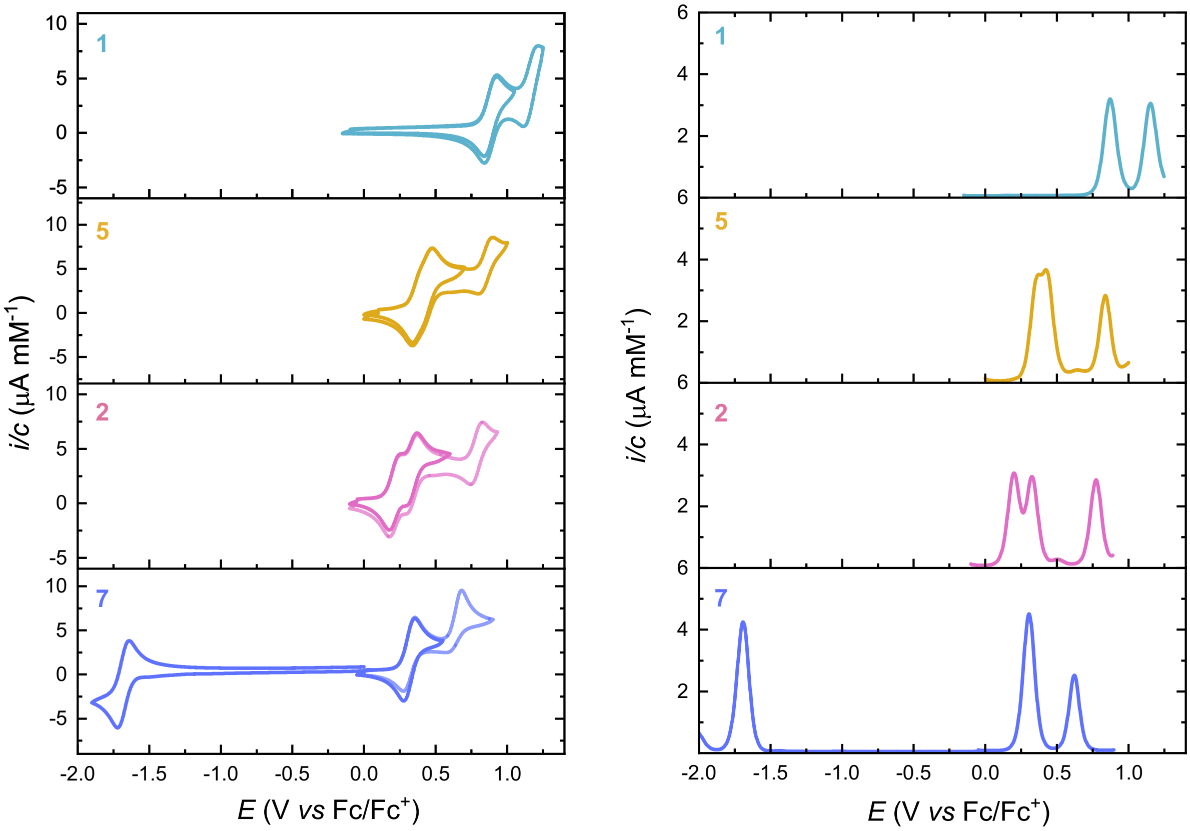


Fig. S22 Cyclic voltammograms (left) and differential pulse voltammograms (right) of **1** (cyan), **5** (yellow), **2** (pink), and **7** (purple). The experiments were recorded in CH_2Cl_2 with *n*-Bu_4NPF_6 (0.1 M) as supporting electrolyte at room temperature, analyte concentrations at 0.5mM and a scan rate of 0.1 $V\cdot s^{-1}$.

X-Ray Crystallography

X-Ray crystal data obtained for mo_d8v7146_1_ (compound 2b) including disorder

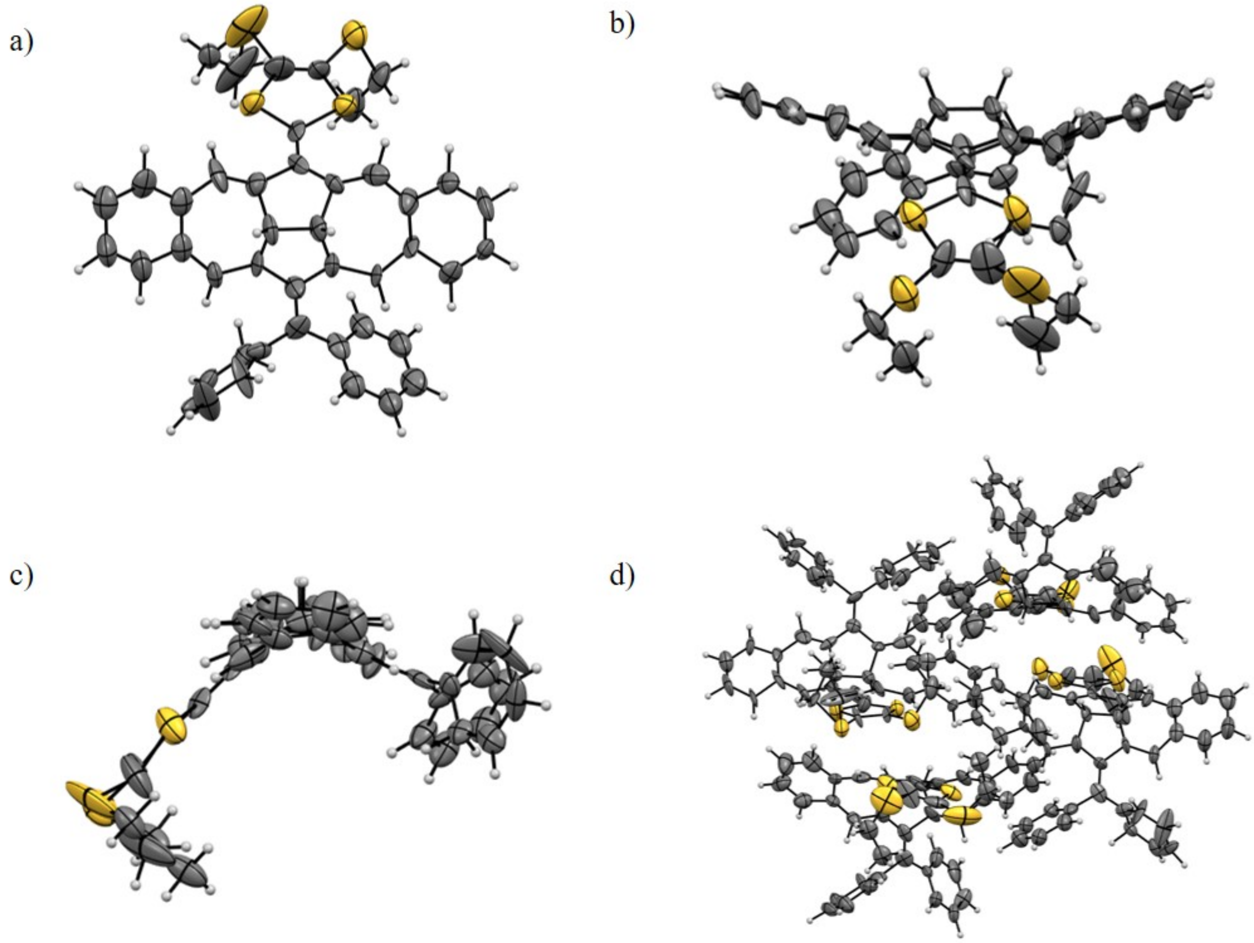


Fig. S23 Crystal structure obtained for compound **2b** determined by X-ray diffraction data shown as 50% probability thermal ellipsoids. a) Top view, b) front view, c) side view, d) packing. Atoms are colored grey (carbon), yellow (sulfur), and white (hydrogen).

The lack of long-range order, which is persistent across different crystallization protocols for **2b**, would yield diffraction data of poor quality as earlier described. The best diffracting crystals were obtained by recrystallisation from dichloromethane and methanol. A clear orange, block-shaped crystal was mounted on the goniometer. Data for mo_d8v7146_1_a were collected from a shock-cooled single crystal at 100.00 K on a Bruker D8 Venture and a Photon III 28 detector. The diffractometer used MoK_α radiation (λ = 0.71073 Å). All data were integrated with SAINT V8.40B and a multi-scan absorption correction using TWINABS 2012/1 was applied.[4,5] The structure was solved by dual methods with SHELXT 2018/2 and refined by full-matrix least-squares methods against F^2 using SHELXL 2019/3.[6,7] All non-hydrogen atoms were refined with anisotropic displacement parameters. Due to poor data quality. This report was partially generated using FinalCif.[8]

The diffraction data clearly indicated the presence of two domains which were considered during the data reduction via TWINABS 2012/1.[4,5] A suitable model was obtained to confirm the overall connectivity and expected geometry of **2b**, by applying a large number of constraints and restraints. In spite of these, the ADPs are large and, furthermore, the bond lengths and angles are not reliable enough to be reported. During the modeling the dispersed F_{obs} vs F_{calc} graph clearly indicated the possibility of other twin domains caused by further merohedral twinning within the two domains. Upon adding the merohedral twin law to the model, the *R*-factor was reduced further. This clearly indicates the lack of long-range order within the crystal. A full table of structure refinement is excluded due to the model being incomplete.

Table S2. Crystal data and structure refinement for compound **2b**

Empirical formula	$C_{88}H_{68}S_8$
Formula weight	1381.90
Temperature [K]	100.00
Crystal system	monoclinic
Space group (number)	*Pn* (7)
a [Å]	11.320(4)
b [Å]	18.967(5)
c [Å]	31.825(8)
α [°]	90
β [°]	91.206(10)
γ [°]	90
Volume [Å^3]	6831(3)
Z	4
Crystal size [mm^3]	0.08×0.153×0.478
Crystal colour	clear orange
Crystal shape	block
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	3.34 to 50.00 (0.84 Å)
Index ranges	−13 ≤ h ≤ 13 −22 ≤ k ≤ 22 −35 ≤ l ≤ 37
Reflections collected	118650
Independent reflections	22940 R_{int} = 0.1145 R_{sigma} = 0.1401
Completeness to θ = 24.999°	99.6 %
Data / Restraints / Parameters	22940 / 241 / 1639
Absorption correction T_{min}/T_{max} (method)	0.2389 / 0.7452 (multi-scan)

Crystal structure of mo_d8v6978_1 (compound 7)

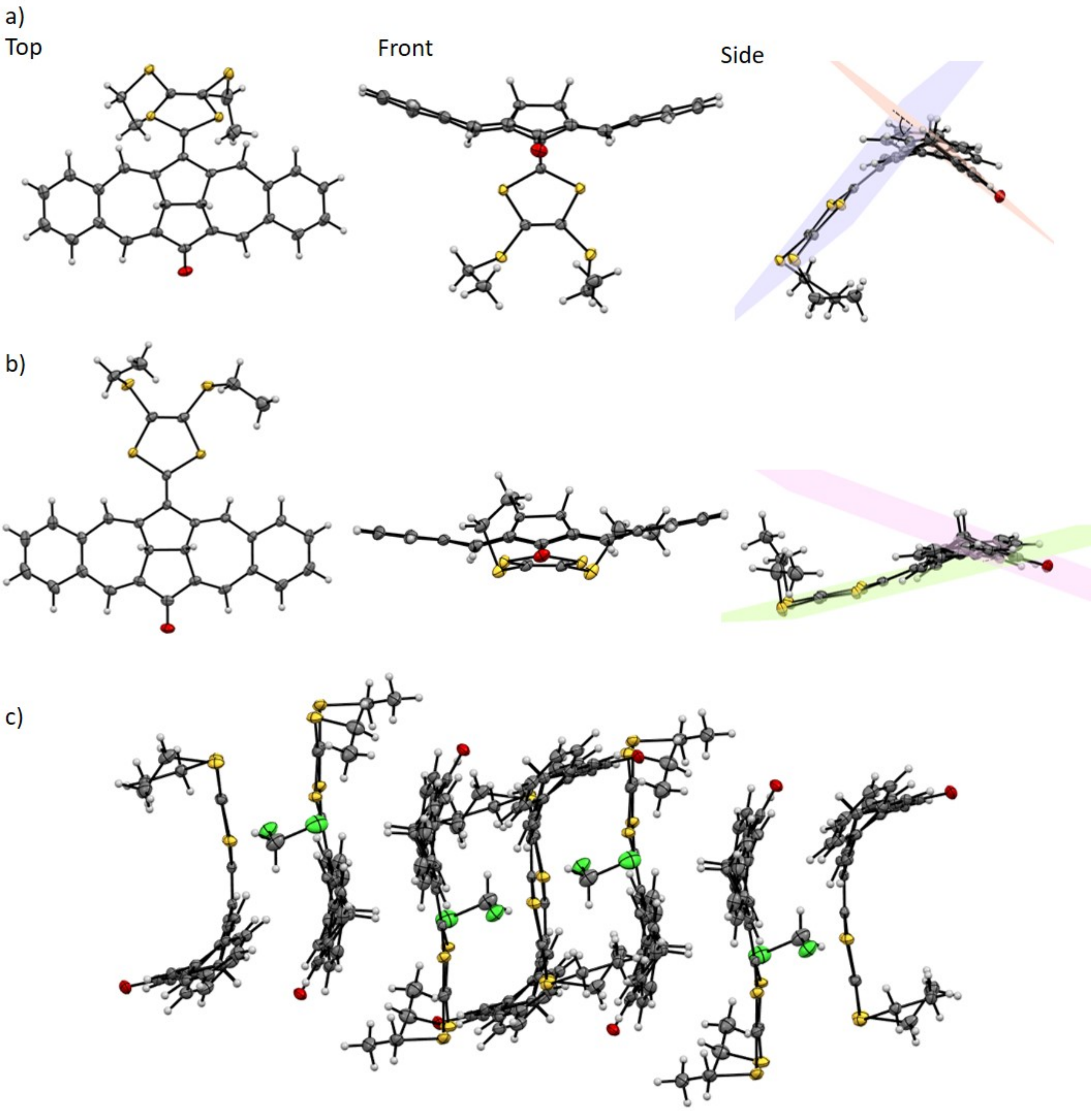


Fig. S24 Molecular structures of **7** obtained by X-ray crystallography shown as 50% probability thermal ellipsoids of two different molecular conformers within the asymmetric unit (a and b), shown from the top view, front view and side view. c) Packing of compound **7** with co-crystallized CH_2Cl_2 shown. Atoms are colored grey (carbon), yellow (sulfur), red (oxygen), white (hydrogen), and green (chlorine).

Single crystals were grown from recrystallization from CH_2Cl_2 and MeOH. A clear violet, needle-shaped crystal was mounted on the goniometer. Data for mo_d8v6978_1 were collected from a shock-cooled single crystal at 100.00 K on a Bruker D8 Venture diffractometer equipped with a Mo Kα high-brilliance IμS radiation source (λ = 0.71073 Å), a multilayer X-ray mirror and a PHOTON 100 CMOS detector, and an Oxford Cryosystems low temperature device. All data were integrated with SAINT V8.40B and a multi-scan absorption correction using SADABS 2016/2 was applied.[4,5]

The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares methods against F^2 using SHELXL 2019/3.[6,7] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[9] CCDC 2548863 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[8]

Table S3. Crystal data and structure refinement for mo_d8v6978_1 (compound **7**).

CCDC number	2548863
Empirical formula	$C_{63}H_{50}Cl_2O_2S_8$
Formula weight	1166.41
Temperature [K]	100.00
Crystal system	triclinic
Space group (number)	$P\overline{1}$ (2)
a [Å]	13.649(3)
b [Å]	14.877(4)
c [Å]	14.912(3)
α [°]	76.215(6)
β [°]	69.224(4)
γ [°]	71.805(7)
Volume [Å^3]	2661.5(10)
Z	2
ρ_{calc} [gcm^{-3}]	1.455
μ [mm^{-1}]	0.483
F(000)	1212
Crystal size [mm^3]	0.063×0.066×0.234
Crystal colour	clear violet
Crystal shape	needle
Radiation	MoK_α (λ=0.71073 Å)
2θ range [°]	4.92 to 53.40 (0.79 Å)
Index ranges	$-17 \leq h \leq 17$ $-18 \leq k \leq 18$ $-18 \leq l \leq 18$
Reflections collected	116216
Independent reflections	11252 R_{int} = 0.1115 R_{sigma} = 0.0524
Completeness to θ = 25.242°	99.9 %
Data / Restraints / Parameters	11252 / 0 / 680
Absorption correction T_{min}/T_{max} (method)	0.6638 / 0.7456 (multi-scan)
Goodness-of-fit on F^2	1.060
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0458 wR_2 = 0.1116
Final R indexes [all data]	R_1 = 0.0722 wR_2 = 0.1223
Largest peak/hole [eÅ^{-3}]	1.04/−0.73

Table S4. Atomic coordinates and U_{eq} [Å^2] for mo_d8v6978_1

Atom	***x***	***y***	***z***	U_{eq}
S1	0.74953(6)	0.87812(5)	0.17831(5)	0.02737(16)
S2	0.52381(5)	0.86110(5)	0.26765(5)	0.01995(14)
S3	0.75146(5)	0.77907(5)	−0.00523(5)	0.02200(15)
S4	0.51766(5)	0.78157(5)	0.10994(4)	0.01926(14)
S5	0.92989(6)	0.64133(6)	0.29891(6)	0.03126(18)
S6	0.69363(5)	0.64961(5)	0.35344(5)	0.02150(15)
S7	0.71677(5)	0.55441(5)	0.19571(5)	0.02245(15)
S8	0.95601(6)	0.52875(5)	0.11381(5)	0.02860(17)
Cl9	0.36768(8)	1.18592(8)	0.32212(7)	0.0555(3)
Cl10	0.41438(7)	1.13533(6)	0.50827(6)	0.0411(2)
O1	0.04347(16)	1.12533(14)	0.20865(14)	0.0306(5)
O2	0.09819(15)	0.68963(14)	0.42978(15)	0.0290(4)
C1	0.6397(3)	1.0651(2)	0.1175(3)	0.0401(8)
H1A	0.647168	1.123313	0.071040	0.060
H1B	0.619210	1.079548	0.183464	0.060
H1C	0.583611	1.040876	0.111408	0.060
C2	0.7466(3)	0.9899(2)	0.0968(2)	0.0351(7)
H2A	0.803155	1.017200	0.098778	0.042
H2B	0.765856	0.976149	0.029998	0.042
C3	0.6405(2)	0.84642(19)	0.16862(19)	0.0206(5)
C4	0.4444(2)	0.82501(17)	0.22043(17)	0.0175(5)
C5	0.3343(2)	0.83645(17)	0.26244(18)	0.0178(5)
C6	0.2599(2)	0.82338(18)	0.21936(18)	0.0187(5)
C7	0.2783(2)	0.77930(19)	0.14293(18)	0.0207(5)
H7	0.350732	0.745944	0.114050	0.025
C8	0.1971(2)	0.7786(2)	0.10135(18)	0.0216(6)
C9	0.2173(2)	0.6985(2)	0.05616(19)	0.0248(6)
H9	0.281722	0.649338	0.055072	0.030
C10	0.1472(2)	0.6888(2)	0.01358(19)	0.0286(6)
H10	0.161370	0.632108	−0.012652	0.034
C11	0.0552(2)	0.7626(2)	0.0092(2)	0.0319(7)
H11	0.006373	0.756904	−0.020173	0.038
C12	0.6501(2)	0.9410(2)	−0.1124(2)	0.0294(6)
H12A	0.705720	0.971223	−0.115425	0.044
H12B	0.587505	0.956163	−0.055304	0.044
H12C	0.627468	0.965113	−0.171026	0.044
C13	0.6959(2)	0.83307(19)	−0.10538(19)	0.0238(6)
H13A	0.753527	0.818352	−0.166690	0.029
H13B	0.637742	0.803234	−0.098739	0.029
C14	0.6388(2)	0.80891(18)	0.09567(18)	0.0201(5)
C15	0.1452(2)	0.86989(18)	0.27432(18)	0.0196(5)
H15	0.099311	0.823020	0.300844	0.023
C16	0.1532(2)	0.91140(18)	0.35533(18)	0.0197(5)
H16	0.108911	0.885928	0.420270	0.024
C17	0.1143(2)	1.01804(19)	0.33438(19)	0.0234(6)
C18	0.1133(2)	1.07875(19)	0.3887(2)	0.0246(6)
H18	0.084997	1.144971	0.370525	0.030
C19	0.1519(2)	1.05165(19)	0.47278(19)	0.0220(6)
C20	0.1062(2)	1.1149(2)	0.5428(2)	0.0265(6)
H20	0.053786	1.172295	0.532041	0.032
C21	0.1356(2)	1.0957(2)	0.6259(2)	0.0278(6)

H21	0.102396	1.138713	0.672301	0.033
C22	0.2138(2)	1.0131(2)	0.6417(2)	0.0266(6)
H22	0.232345	0.998266	0.700129	0.032
C23	0.2646(2)	0.95250(19)	0.57221(19)	0.0225(6)
H23	0.320856	0.898132	0.582249	0.027
C24	0.2355(2)	0.96892(18)	0.48737(18)	0.0198(5)
C25	0.3032(2)	0.90549(18)	0.41474(18)	0.0196(5)
H25	0.376043	0.877179	0.414486	0.023
C26	0.2716(2)	0.88367(17)	0.34840(18)	0.0182(5)
C27	0.0787(2)	1.04418(19)	0.24633(19)	0.0241(6)
C28	0.0978(2)	0.9541(2)	0.21003(19)	0.0228(6)
C29	0.0758(2)	0.9440(2)	0.13251(19)	0.0255(6)
H29	0.039830	0.999763	0.098934	0.031
C30	0.1032(2)	0.8540(2)	0.09614(18)	0.0248(6)
C31	0.0364(2)	0.8440(2)	0.0482(2)	0.0292(6)
H31	−0.024373	0.895337	0.042334	0.035
C32	0.8453(3)	0.6351(3)	0.5051(3)	0.0442(8)
H32A	0.770723	0.646040	0.505007	0.066
H32B	0.862514	0.696664	0.494926	0.066
H32C	0.852965	0.599239	0.567589	0.066
C64	0.9221(3)	0.5784(3)	0.4246(2)	0.0403(8)
H64A	0.899807	0.518891	0.432965	0.048
H64B	0.995495	0.559724	0.431734	0.048
C34	0.8260(2)	0.61187(19)	0.2779(2)	0.0235(6)
C35	0.6287(2)	0.59859(18)	0.30287(18)	0.0181(5)
C36	0.5237(2)	0.59169(17)	0.34472(18)	0.0172(5)
C37	0.4666(2)	0.54755(17)	0.30671(18)	0.0182(5)
C38	0.4919(2)	0.52436(18)	0.21764(18)	0.0211(5)
H38	0.557171	0.536633	0.171909	0.025
C39	0.4300(2)	0.48235(19)	0.18355(19)	0.0226(6)
C40	0.4899(3)	0.4253(2)	0.1096(2)	0.0287(6)
H40	0.566688	0.411889	0.089173	0.034
C41	0.4405(3)	0.3880(2)	0.0657(2)	0.0333(7)
H41	0.483504	0.347864	0.017660	0.040
C42	0.3290(3)	0.4088(2)	0.0913(2)	0.0359(7)
H42	0.295125	0.383775	0.060535	0.043
C43	0.8357(2)	0.56789(19)	0.2048(2)	0.0238(6)
C44	0.9800(2)	0.3995(2)	0.1491(2)	0.0309(7)
H44A	0.914015	0.380386	0.156541	0.037
H44B	1.039231	0.368011	0.096340	0.037
C45	1.0095(3)	0.3640(2)	0.2419(2)	0.0375(7)
H45A	1.023047	0.294163	0.255288	0.056
H45B	0.949719	0.392104	0.295326	0.056
H45C	1.074813	0.382544	0.235331	0.056
C46	0.2674(3)	0.4664(2)	0.1619(2)	0.0317(7)
H46	0.190723	0.482529	0.177816	0.038
C47	0.3154(2)	0.50199(19)	0.2113(2)	0.0247(6)
C48	0.2426(2)	0.56395(19)	0.2829(2)	0.0249(6)
H48	0.173635	0.597377	0.275287	0.030
C49	0.2644(2)	0.57783(18)	0.35832(19)	0.0211(5)
C50	0.1916(2)	0.64499(18)	0.4267(2)	0.0224(6)
C51	0.2507(2)	0.64791(18)	0.49135(18)	0.0201(5)
C52	0.3574(2)	0.57418(17)	0.47216(18)	0.0172(5)
H52	0.359834	0.524754	0.530544	0.021

C53	0.4525(2)	0.61811(18)	0.43998(18)	0.0176(5)
C54	0.4625(2)	0.67025(18)	0.49758(18)	0.0193(5)
H54	0.525271	0.694160	0.474210	0.023
C55	0.3874(2)	0.69411(18)	0.59197(18)	0.0208(5)
C56	0.4335(2)	0.70921(19)	0.65609(19)	0.0235(6)
H56	0.510038	0.696055	0.639227	0.028
C57	0.3705(3)	0.7428(2)	0.7433(2)	0.0281(6)
H57	0.403972	0.750454	0.786082	0.034
C58	0.2588(2)	0.7650(2)	0.7678(2)	0.0286(6)
H58	0.215186	0.788889	0.826916	0.034
C59	0.2113(2)	0.75224(19)	0.7059(2)	0.0272(6)
H59	0.134520	0.769141	0.722541	0.033
C60	0.2727(2)	0.71494(18)	0.61859(18)	0.0212(5)
C61	0.2144(2)	0.70710(19)	0.55768(19)	0.0230(6)
H61	0.143606	0.747828	0.565460	0.028
C62	0.3662(2)	0.52843(18)	0.38598(17)	0.0175(5)
H62	0.372710	0.458152	0.404938	0.021
C63	0.4400(3)	1.1000(3)	0.3951(2)	0.0440(8)
H63A	0.518463	1.088954	0.360213	0.053
H63B	0.419948	1.038919	0.406430	0.053

U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Table S5. Anisotropic displacement parameters [Å^2] for mo_d8v6978_1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + \ldots + 2hka^*b^*U_{12}\ ]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.0216(3)	0.0334(4)	0.0314(4)	−0.0128(3)	−0.0047(3)	−0.0107(3)
S2	0.0184(3)	0.0212(3)	0.0208(3)	−0.0081(3)	−0.0032(2)	−0.0049(3)
S3	0.0175(3)	0.0238(3)	0.0220(3)	−0.0082(3)	−0.0012(2)	−0.0032(3)
S4	0.0178(3)	0.0197(3)	0.0209(3)	−0.0076(2)	−0.0032(2)	−0.0051(3)
S5	0.0198(4)	0.0311(4)	0.0444(4)	−0.0131(3)	−0.0039(3)	−0.0095(3)
S6	0.0171(3)	0.0208(3)	0.0264(3)	−0.0099(3)	−0.0022(3)	−0.0047(3)
S7	0.0208(3)	0.0234(3)	0.0212(3)	−0.0086(3)	−0.0006(3)	−0.0056(3)
S8	0.0231(4)	0.0226(4)	0.0308(4)	−0.0082(3)	0.0057(3)	−0.0058(3)
Cl9	0.0504(6)	0.0775(7)	0.0495(5)	−0.0110(5)	−0.0199(4)	−0.0241(5)
Cl10	0.0489(5)	0.0452(5)	0.0331(4)	−0.0102(3)	−0.0026(3)	−0.0252(4)
O1	0.0271(11)	0.0208(10)	0.0334(11)	0.0007(8)	−0.0062(9)	0.0015(9)
O2	0.0202(10)	0.0224(10)	0.0430(12)	−0.0036(9)	−0.0113(9)	−0.0020(8)
C1	0.0427(19)	0.0278(17)	0.0461(19)	−0.0059(14)	−0.0044(15)	−0.0138(15)
C2	0.0378(18)	0.0395(18)	0.0307(16)	−0.0109(14)	0.0012(13)	−0.0222(15)

C3	0.0174(13)	0.0192(13)	0.0238(13)	−0.0063(10)	−0.0037(10)	−0.0033(10)
C4	0.0214(13)	0.0127(12)	0.0180(12)	−0.0026(9)	−0.0062(10)	−0.0032(10)
C5	0.0174(12)	0.0130(12)	0.0209(12)	−0.0018(10)	−0.0051(10)	−0.0024(10)
C6	0.0171(13)	0.0154(12)	0.0203(12)	−0.0009(10)	−0.0032(10)	−0.0039(10)
C7	0.0194(13)	0.0194(13)	0.0216(13)	−0.0016(10)	−0.0043(10)	−0.0059(11)
C8	0.0201(13)	0.0262(14)	0.0175(12)	0.0013(10)	−0.0035(10)	−0.0106(11)
C9	0.0259(14)	0.0273(15)	0.0210(13)	−0.0007(11)	−0.0049(11)	−0.0111(12)
C10	0.0330(16)	0.0360(17)	0.0217(14)	−0.0007(12)	−0.0075(12)	−0.0189(14)
C11	0.0296(16)	0.0458(19)	0.0250(15)	−0.0017(13)	−0.0076(12)	−0.0193(14)
C12	0.0283(15)	0.0222(15)	0.0307(15)	−0.0009(12)	−0.0032(12)	−0.0058(12)
C13	0.0254(14)	0.0232(14)	0.0210(13)	−0.0043(11)	−0.0038(11)	−0.0063(12)
C14	0.0187(13)	0.0185(13)	0.0215(13)	−0.0049(10)	−0.0027(10)	−0.0048(10)
C15	0.0162(13)	0.0196(13)	0.0203(12)	−0.0011(10)	−0.0029(10)	−0.0053(10)
C16	0.0154(12)	0.0185(13)	0.0216(13)	−0.0038(10)	−0.0015(10)	−0.0033(10)
C17	0.0173(13)	0.0206(14)	0.0252(14)	−0.0033(11)	−0.0011(11)	−0.0013(11)
C18	0.0194(13)	0.0154(13)	0.0309(15)	−0.0028(11)	−0.0002(11)	−0.0020(11)
C19	0.0192(13)	0.0170(13)	0.0269(14)	−0.0054(11)	−0.0002(11)	−0.0071(11)
C20	0.0193(14)	0.0187(14)	0.0372(16)	−0.0091(12)	0.0017(12)	−0.0072(11)
C21	0.0253(15)	0.0270(15)	0.0302(15)	−0.0146(12)	0.0029(12)	−0.0106(12)
C22	0.0272(15)	0.0248(15)	0.0299(15)	−0.0106(12)	−0.0037(12)	−0.0101(12)
C23	0.0231(14)	0.0189(13)	0.0242(13)	−0.0071(11)	−0.0021(11)	−0.0066(11)
C24	0.0175(13)	0.0169(13)	0.0215(13)	−0.0060(10)	0.0016(10)	−0.0058(10)
C25	0.0168(12)	0.0148(12)	0.0240(13)	−0.0048(10)	−0.0024(10)	−0.0025(10)
C26	0.0169(12)	0.0124(12)	0.0219(13)	−0.0017(10)	−0.0027(10)	−0.0034(10)
C27	0.0169(13)	0.0217(14)	0.0241(14)	−0.0010(11)	0.0006(11)	−0.0013(11)
C28	0.0133(12)	0.0266(15)	0.0229(13)	−0.0010(11)	−0.0005(10)	−0.0050(11)
C29	0.0172(13)	0.0269(15)	0.0248(14)	0.0016(11)	−0.0034(11)	−0.0024(11)
C30	0.0232(14)	0.0304(15)	0.0171(13)	0.0029(11)	−0.0036(10)	−0.0095(12)
C31	0.0209(14)	0.0393(17)	0.0235(14)	0.0026(12)	−0.0058(11)	−0.0088(13)

C32	0.045(2)	0.047(2)	0.045(2)	−0.0043(16)	−0.0145(16)	−0.0175(17)
C64	0.0345(18)	0.049(2)	0.0427(19)	−0.0132(16)	−0.0164(15)	−0.0077(16)
C34	0.0195(13)	0.0175(13)	0.0289(14)	−0.0055(11)	−0.0005(11)	−0.0045(11)
C35	0.0210(13)	0.0142(12)	0.0180(12)	−0.0034(10)	−0.0042(10)	−0.0039(10)
C36	0.0195(13)	0.0122(12)	0.0192(12)	−0.0033(9)	−0.0052(10)	−0.0030(10)
C37	0.0194(13)	0.0132(12)	0.0209(12)	−0.0022(10)	−0.0057(10)	−0.0033(10)
C38	0.0241(14)	0.0195(13)	0.0198(13)	−0.0015(10)	−0.0058(10)	−0.0076(11)
C39	0.0310(15)	0.0182(13)	0.0213(13)	−0.0004(10)	−0.0095(11)	−0.0098(12)
C40	0.0386(17)	0.0262(15)	0.0244(14)	−0.0052(11)	−0.0098(12)	−0.0108(13)
C41	0.052(2)	0.0264(16)	0.0273(15)	−0.0058(12)	−0.0141(14)	−0.0143(14)
C42	0.058(2)	0.0255(16)	0.0389(17)	0.0003(13)	−0.0268(16)	−0.0209(15)
C43	0.0211(14)	0.0176(13)	0.0288(14)	−0.0053(11)	−0.0011(11)	−0.0057(11)
C44	0.0250(15)	0.0218(15)	0.0377(16)	−0.0112(12)	0.0030(12)	−0.0036(12)
C45	0.0326(17)	0.0283(17)	0.051(2)	−0.0014(14)	−0.0102(15)	−0.0124(14)
C46	0.0418(18)	0.0238(15)	0.0406(17)	0.0005(13)	−0.0226(14)	−0.0154(14)
C47	0.0340(16)	0.0166(13)	0.0269(14)	0.0018(11)	−0.0133(12)	−0.0101(12)
C48	0.0210(14)	0.0207(14)	0.0350(15)	0.0001(11)	−0.0110(12)	−0.0080(11)
C49	0.0210(13)	0.0145(13)	0.0287(14)	0.0002(10)	−0.0090(11)	−0.0067(11)
C50	0.0212(14)	0.0136(12)	0.0300(14)	0.0030(10)	−0.0076(11)	−0.0059(11)
C51	0.0180(13)	0.0161(13)	0.0228(13)	0.0003(10)	−0.0028(10)	−0.0057(10)
C52	0.0180(12)	0.0128(12)	0.0191(12)	−0.0024(9)	−0.0030(10)	−0.0046(10)
C53	0.0165(12)	0.0144(12)	0.0195(12)	−0.0008(9)	−0.0058(10)	−0.0016(10)
C54	0.0183(13)	0.0163(13)	0.0223(13)	−0.0041(10)	−0.0061(10)	−0.0022(10)
C55	0.0250(14)	0.0147(12)	0.0184(12)	−0.0036(10)	−0.0026(10)	−0.0028(11)
C56	0.0255(14)	0.0181(13)	0.0241(13)	−0.0055(11)	−0.0054(11)	−0.0025(11)
C57	0.0408(17)	0.0202(14)	0.0219(14)	−0.0053(11)	−0.0097(12)	−0.0040(13)
C58	0.0357(16)	0.0204(14)	0.0217(14)	−0.0064(11)	0.0028(12)	−0.0066(12)
C59	0.0263(15)	0.0183(14)	0.0274(14)	−0.0045(11)	0.0040(12)	−0.0057(12)
C60	0.0214(13)	0.0147(13)	0.0223(13)	−0.0045(10)	0.0004(10)	−0.0043(11)

C61	0.0165(13)	0.0156(13)	0.0287(14)	−0.0014(11)	0.0016(11)	−0.0039(10)
C62	0.0195(13)	0.0132(12)	0.0192(12)	−0.0025(10)	−0.0046(10)	−0.0045(10)
C63	0.050(2)	0.049(2)	0.0385(18)	−0.0125(16)	−0.0060(16)	−0.0241(18)

Table S6. Bond lengths and angles for compound **7**

Atom–Atom	Length [Å]
S1–C2	1.810(3)
S1–C3	1.756(3)
S2–C3	1.741(3)
S2–C4	1.745(3)
S3–C13	1.817(3)
S3–C14	1.754(3)
S4–C4	1.751(2)
S4–C14	1.753(3)
S5–C64	1.867(3)
S5–C34	1.752(3)
S6–C34	1.753(3)
S6–C35	1.760(3)
S7–C35	1.753(2)
S7–C43	1.751(3)
S8–C43	1.753(3)
S8–C44	1.824(3)
Cl9–C63	1.762(4)
Cl10–C63	1.770(3)
O1–C27	1.229(3)
O2–C50	1.230(3)
C1–H1A	0.9800
C1–H1B	0.9800
C1–H1C	0.9800
C1–C2	1.516(5)
C2–H2A	0.9900
C2–H2B	0.9900
C3–C14	1.345(4)
C4–C5	1.379(4)
C5–C6	1.459(4)
C5–C26	1.464(3)
C6–C7	1.357(4)
C6–C15	1.511(3)
C7–H7	0.9500
C7–C8	1.453(4)
C8–C9	1.413(4)
C8–C30	1.428(4)
C9–H9	0.9500
C9–C10	1.379(4)
C10–H10	0.9500
C10–C11	1.396(4)
C11–H11	0.9500
C11–C31	1.381(4)
C12–H12A	0.9800
C12–H12B	0.9800
C12–H12C	0.9800
C12–C13	1.523(4)
C13–H13A	0.9900
C13–H13B	0.9900
C15–H15	1.0000
C15–C16	1.531(4)
C15–C28	1.507(4)
C16–H16	1.0000
C16–C17	1.501(4)
C16–C26	1.509(3)
C17–C18	1.343(4)
C17–C27	1.484(4)
C18–H18	0.9500
C18–C19	1.452(4)
C19–C20	1.416(4)
C19–C24	1.427(4)
C20–H20	0.9500
C20–C21	1.374(4)

C21–H21	0.9500
C21–C22	1.387(4)
C22–H22	0.9500
C22–C23	1.383(4)
C23–H23	0.9500
C23–C24	1.402(4)
C24–C25	1.466(3)
C25–H25	0.9500
C25–C26	1.346(4)
C27–C28	1.478(4)
C28–C29	1.343(4)
C29–H29	0.9500
C29–C30	1.455(4)
C30–C31	1.400(4)
C31–H31	0.9500
C32–H32A	0.9800
C32–H32B	0.9800
C32–H32C	0.9800
C32–C64	1.513(5)
C64–H64A	0.9900
C64–H64B	0.9900
C34–C43	1.349(4)
C35–C36	1.371(4)
C36–C37	1.473(3)
C36–C53	1.471(3)
C37–C38	1.349(4)
C37–C62	1.513(3)
C38–H38	0.9500
C38–C39	1.466(4)
C39–C40	1.407(4)
C39–C47	1.420(4)
C40–H40	0.9500

C40–C41	1.381(4)
C41–H41	0.9500
C41–C42	1.381(5)
C42–H42	0.9500
C42–C46	1.379(4)
C44–H44A	0.9900
C44–H44B	0.9900
C44–C45	1.506(4)
C45–H45A	0.9800
C45–H45B	0.9800
C45–H45C	0.9800
C46–H46	0.9500
C46–C47	1.413(4)
C47–C48	1.456(4)
C48–H48	0.9500
C48–C49	1.335(4)
C49–C50	1.474(4)
C49–C62	1.506(4)
C50–C51	1.474(4)
C51–C52	1.504(3)
C51–C61	1.339(4)
C52–H52	1.0000
C52–C53	1.510(3)
C52–C62	1.544(3)
C53–C54	1.351(4)
C54–H54	0.9500
C54–C55	1.464(3)
C55–C56	1.406(4)
C55–C60	1.421(4)
C56–H56	0.9500
C56–C57	1.389(4)
C57–H57	0.9500

C57–C58	1.384(4)
C58–H58	0.9500
C58–C59	1.376(4)
C59–H59	0.9500
C59–C60	1.409(4)
C60–C61	1.447(4)
C61–H61	0.9500
C62–H62	1.0000
C63–H63A	0.9900
C63–H63B	0.9900
Atom–Atom–Atom	**Angle [°]**
C3–S1–C2	100.74(14)
C3–S2–C4	96.93(12)
C14–S3–C13	102.24(13)
C4–S4–C14	96.85(12)
C34–S5–C64	101.52(14)
C34–S6–C35	97.89(13)
C43–S7–C35	97.22(13)
C43–S8–C44	100.73(13)
H1A–C1–H1B	109.5
H1A–C1–H1C	109.5
H1B–C1–H1C	109.5
C2–C1–H1A	109.5
C2–C1–H1B	109.5
C2–C1–H1C	109.5
S1–C2–H2A	108.3
S1–C2–H2B	108.3
C1–C2–S1	115.8(2)
C1–C2–H2A	108.3
C1–C2–H2B	108.3
H2A–C2–H2B	107.4

S2–C3–S1	115.49(15)
C14–C3–S1	127.4(2)
C14–C3–S2	117.1(2)
S2–C4–S4	112.66(14)
C5–C4–S2	123.17(19)
C5–C4–S4	124.0(2)
C4–C5–C6	126.3(2)
C4–C5–C26	123.5(2)
C6–C5–C26	109.0(2)
C5–C6–C15	109.1(2)
C7–C6–C5	131.2(2)
C7–C6–C15	119.7(2)
C6–C7–H7	117.1
C6–C7–C8	125.8(2)
C8–C7–H7	117.1
C9–C8–C7	116.6(2)
C9–C8–C30	117.3(2)
C30–C8–C7	126.0(3)
C8–C9–H9	118.7
C10–C9–C8	122.6(3)
C10–C9–H9	118.7
C9–C10–H10	120.1
C9–C10–C11	119.7(3)
C11–C10–H10	120.1
C10–C11–H11	120.6
C31–C11–C10	118.9(3)
C31–C11–H11	120.6
H12A–C12–H12B	109.5
H12A–C12–H12C	109.5
H12B–C12–H12C	109.5
C13–C12–H12A	109.5
C13–C12–H12B	109.5

C13–C12–H12C	109.5
S3–C13–H13A	108.6
S3–C13–H13B	108.6
C12–C13–S3	114.6(2)
C12–C13–H13A	108.6
C12–C13–H13B	108.6
H13A–C13–H13B	107.6
S4–C14–S3	119.76(15)
C3–C14–S3	124.0(2)
C3–C14–S4	116.1(2)
C6–C15–H15	111.5
C6–C15–C16	106.3(2)
C16–C15–H15	111.5
C28–C15–C6	109.8(2)
C28–C15–H15	111.5
C28–C15–C16	105.9(2)
C15–C16–H16	111.1
C17–C16–C15	106.9(2)
C17–C16–H16	111.1
C17–C16–C26	110.1(2)
C26–C16–C15	106.3(2)
C26–C16–H16	111.1
C18–C17–C16	123.7(3)
C18–C17–C27	126.4(3)
C27–C17–C16	109.8(2)
C17–C18–H18	117.3
C17–C18–C19	125.5(3)
C19–C18–H18	117.3
C20–C19–C18	117.0(2)
C20–C19–C24	118.1(3)
C24–C19–C18	124.8(2)
C19–C20–H20	119.0

C21–C20–C19	122.0(3)
C21–C20–H20	119.0
C20–C21–H21	120.1
C20–C21–C22	119.7(3)
C22–C21–H21	120.1
C21–C22–H22	120.1
C23–C22–C21	119.8(3)
C23–C22–H22	120.1
C22–C23–H23	119.0
C22–C23–C24	121.9(3)
C24–C23–H23	119.0
C19–C24–C25	124.7(2)
C23–C24–C19	118.3(2)
C23–C24–C25	116.6(2)
C24–C25–H25	117.0
C26–C25–C24	126.0(2)
C26–C25–H25	117.0
C5–C26–C16	108.9(2)
C25–C26–C5	131.1(2)
C25–C26–C16	119.9(2)
O1–C27–C17	126.7(3)
O1–C27–C28	126.3(3)
C28–C27–C17	107.0(2)
C27–C28–C15	110.4(2)
C29–C28–C15	122.3(3)
C29–C28–C27	127.3(3)
C28–C29–H29	117.6
C28–C29–C30	124.9(3)
C30–C29–H29	117.6
C8–C30–C29	123.8(3)
C31–C30–C8	118.6(3)
C31–C30–C29	117.4(3)

C11–C31–C30	122.7(3)
C11–C31–H31	118.6
C30–C31–H31	118.6
H32A–C32–H32B	109.5
H32A–C32–H32C	109.5
H32B–C32–H32C	109.5
C64–C32–H32A	109.5
C64–C32–H32B	109.5
C64–C32–H32C	109.5
S5–C64–H64A	108.4
S5–C64–H64B	108.4
C32–C64–S5	115.5(3)
C32–C64–H64A	108.4
C32–C64–H64B	108.4
H64A–C64–H64B	107.5
S5–C34–S6	117.90(15)
C43–C34–S5	126.6(2)
C43–C34–S6	115.3(2)
S7–C35–S6	111.35(14)
C36–C35–S6	123.67(19)
C36–C35–S7	124.9(2)
C35–C36–C37	125.8(2)
C35–C36–C53	125.8(2)
C53–C36–C37	108.1(2)
C36–C37–C62	109.3(2)
C38–C37–C36	129.9(2)
C38–C37–C62	120.8(2)
C37–C38–H38	116.4
C37–C38–C39	127.3(2)
C39–C38–H38	116.4
C40–C39–C38	116.3(3)
C40–C39–C47	117.5(3)

C47–C39–C38	125.8(2)
C39–C40–H40	119.0
C41–C40–C39	122.0(3)
C41–C40–H40	119.0
C40–C41–H41	119.8
C40–C41–C42	120.5(3)
C42–C41–H41	119.8
C41–C42–H42	120.4
C46–C42–C41	119.3(3)
C46–C42–H42	120.4
S7–C43–S8	116.87(16)
C34–C43–S7	117.3(2)
C34–C43–S8	125.7(2)
S8–C44–H44A	108.7
S8–C44–H44B	108.7
H44A–C44–H44B	107.6
C45–C44–S8	114.0(2)
C45–C44–H44A	108.7
C45–C44–H44B	108.7
C44–C45–H45A	109.5
C44–C45–H45B	109.5
C44–C45–H45C	109.5
H45A–C45–H45B	109.5
H45A–C45–H45C	109.5
H45B–C45–H45C	109.5
C42–C46–H46	119.2
C42–C46–C47	121.6(3)
C47–C46–H46	119.2
C39–C47–C48	123.9(2)
C46–C47–C39	119.0(3)
C46–C47–C48	116.9(3)
C47–C48–H48	117.2

C49–C48–C47	125.6(3)
C49–C48–H48	117.2
C48–C49–C50	124.5(3)
C48–C49–C62	125.6(2)
C50–C49–C62	109.9(2)
O2–C50–C49	126.1(3)
O2–C50–C51	126.4(3)
C49–C50–C51	107.5(2)
C50–C51–C52	109.9(2)
C61–C51–C50	125.0(3)
C61–C51–C52	125.1(2)
C51–C52–H52	110.6
C51–C52–C53	112.4(2)
C51–C52–C62	106.1(2)
C53–C52–H52	110.6
C53–C52–C62	106.4(2)
C62–C52–H52	110.6
C36–C53–C52	109.2(2)
C54–C53–C36	130.5(2)
C54–C53–C52	120.4(2)
C53–C54–H54	116.3
C53–C54–C55	127.4(2)
C55–C54–H54	116.3
C56–C55–C54	116.0(2)
C56–C55–C60	117.9(2)
C60–C55–C54	125.6(2)
C55–C56–H56	119.0
C57–C56–C55	122.0(3)
C57–C56–H56	119.0
C56–C57–H57	120.1
C58–C57–C56	119.8(3)
C58–C57–H57	120.1
C57–C58–H58	120.2
C59–C58–C57	119.5(3)
C59–C58–H58	120.2
C58–C59–H59	118.9
C58–C59–C60	122.2(3)
C60–C59–H59	118.9
C55–C60–C61	123.8(2)
C59–C60–C55	118.5(3)
C59–C60–C61	117.5(2)
C51–C61–C60	126.2(3)
C51–C61–H61	116.9
C60–C61–H61	116.9
C37–C62–C52	105.9(2)
C37–C62–H62	110.8
C49–C62–C37	112.4(2)
C49–C62–C52	106.0(2)
C49–C62–H62	110.8
C52–C62–H62	110.8
Cl9–C63–Cl10	112.6(2)
Cl9–C63–H63A	109.1
Cl9–C63–H63B	109.1
Cl10–C63–H63A	109.1
Cl10–C63–H63B	109.1
H63A–C63–H63B	107.8

Table S7. Torsion angles for mo_d8v6978_1

Atom–Atom–Atom–Atom	**Torsion Angle [°]**
S1–C3–C14–S3	2.7(4)
S1–C3–C14–S4	178.01(16)
S2–C3–C14–S3	−174.32(15)
S2–C3–C14–S4	0.9(3)
S2–C4–C5–C6	168.9(2)

S2–C4–C5–C26	2.8(4)		C6–C5–C26–C25	175.5(3)
S4–C4–C5–C6	−6.0(4)		C6–C7–C8–C9	−151.7(3)
S4–C4–C5–C26	−172.16(19)		C6–C7–C8–C30	33.0(4)
S5–C34–C43–S7	−175.59(16)		C6–C15–C16–C17	114.9(2)
S5–C34–C43–S8	0.7(4)		C6–C15–C16–C26	−2.8(3)
S6–C34–C43–S7	−0.2(3)		C6–C15–C28–C27	−113.2(2)
S6–C34–C43–S8	176.06(16)		C6–C15–C28–C29	67.8(3)
S6–C35–C36–C37	−178.4(2)		C7–C6–C15–C16	179.5(2)
S6–C35–C36–C53	−5.0(4)		C7–C6–C15–C28	−66.4(3)
S7–C35–C36–C37	−0.9(4)		C7–C8–C9–C10	−179.8(2)
S7–C35–C36–C53	172.5(2)		C7–C8–C30–C29	0.2(4)
O1–C27–C28–C15	178.0(3)		C7–C8–C30–C31	176.1(2)
O1–C27–C28–C29	−3.2(5)		C8–C9–C10–C11	3.8(4)
O2–C50–C51–C52	172.9(2)		C8–C30–C31–C11	2.7(4)
O2–C50–C51–C61	−6.7(4)		C9–C8–C30–C29	−175.2(2)
C2–S1–C3–S2	−105.72(17)		C9–C8–C30–C31	0.8(4)
C2–S1–C3–C14	77.2(3)		C9–C10–C11–C31	−0.2(4)
C3–S1–C2–C1	55.1(3)		C10–C11–C31–C30	−3.0(4)
C3–S2–C4–S4	6.21(16)		C13–S3–C14–S4	52.91(19)
C3–S2–C4–C5	−169.2(2)		C13–S3–C14–C3	−132.0(2)
C4–S2–C3–S1	178.16(15)		C14–S3–C13–C12	60.1(2)
C4–S2–C3–C14	−4.4(2)		C14–S4–C4–S2	−5.82(16)
C4–S4–C14–S3	178.51(16)		C14–S4–C4–C5	169.6(2)
C4–S4–C14–C3	3.0(2)		C15–C6–C7–C8	5.6(4)
C4–C5–C6–C7	16.1(4)		C15–C16–C17–C18	−177.7(2)
C4–C5–C6–C15	−163.5(2)		C15–C16–C17–C27	2.1(3)
C4–C5–C26–C16	162.2(2)		C15–C16–C26–C5	5.4(3)
C4–C5–C26–C25	−16.3(4)		C15–C16–C26–C25	−176.0(2)
C5–C6–C7–C8	−174.0(3)		C15–C28–C29–C30	−5.7(4)
C5–C6–C15–C16	−0.8(3)		C16–C15–C28–C27	1.1(3)
C5–C6–C15–C28	113.3(2)		C16–C15–C28–C29	−177.8(2)
C6–C5–C26–C16	−6.1(3)		C16–C17–C18–C19	1.9(4)

C16–C17–C27–O1	−179.2(3)
C16–C17–C27–C28	−1.4(3)
C17–C16–C26–C5	−110.0(2)
C17–C16–C26–C25	68.6(3)
C17–C18–C19–C20	−154.5(3)
C17–C18–C19–C24	28.7(4)
C17–C27–C28–C15	0.2(3)
C17–C27–C28–C29	179.0(3)
C18–C17–C27–O1	0.6(5)
C18–C17–C27–C28	178.4(3)
C18–C19–C20–C21	179.0(3)
C18–C19–C24–C23	179.5(2)
C18–C19–C24–C25	7.6(4)
C19–C20–C21–C22	1.4(4)
C19–C24–C25–C26	−33.9(4)
C20–C19–C24–C23	2.7(4)
C20–C19–C24–C25	−169.2(2)
C20–C21–C22–C23	2.4(4)
C21–C22–C23–C24	−3.6(4)
C22–C23–C24–C19	0.9(4)
C22–C23–C24–C25	173.5(2)
C23–C24–C25–C26	154.0(3)
C24–C19–C20–C21	−3.9(4)
C24–C25–C26–C5	167.5(3)
C24–C25–C26–C16	−10.8(4)
C26–C5–C6–C7	−176.1(3)
C26–C5–C6–C15	4.3(3)
C26–C16–C17–C18	−62.6(3)
C26–C16–C17–C27	117.2(2)
C27–C17–C18–C19	−177.9(3)
C27–C28–C29–C30	175.5(3)
C28–C15–C16–C17	−1.9(3)

C28–C15–C16–C26	−119.6(2)
C28–C29–C30–C8	−33.0(4)
C28–C29–C30–C31	151.0(3)
C29–C30–C31–C11	178.9(3)
C30–C8–C9–C10	−4.0(4)
C64–S5–C34–S6	61.6(2)
C64–S5–C34–C43	−123.1(3)
C34–S5–C64–C32	−88.5(3)
C34–S6–C35–S7	−9.30(17)
C34–S6–C35–C36	168.5(2)
C35–S6–C34–S5	−178.27(16)
C35–S6–C34–C43	5.9(2)
C35–S7–C43–S8	177.77(16)
C35–S7–C43–C34	−5.6(2)
C35–C36–C37–C38	−16.1(4)
C35–C36–C37–C62	163.7(2)
C35–C36–C53–C52	−163.7(2)
C35–C36–C53–C54	14.7(4)
C36–C37–C38–C39	−178.4(3)
C36–C37–C62–C49	121.8(2)
C36–C37–C62–C52	6.4(3)
C36–C53–C54–C55	179.7(2)
C37–C36–C53–C52	10.6(3)
C37–C36–C53–C54	−171.0(3)
C37–C38–C39–C40	−151.5(3)
C37–C38–C39–C47	35.3(4)
C38–C37–C62–C49	−58.4(3)
C38–C37–C62–C52	−173.8(2)
C38–C39–C40–C41	−174.6(3)
C38–C39–C47–C46	171.1(3)
C38–C39–C47–C48	−3.5(4)
C39–C40–C41–C42	2.3(5)

C39–C47–C48–C49	−29.9(4)
C40–C39–C47–C46	−2.0(4)
C40–C39–C47–C48	−176.6(3)
C40–C41–C42–C46	−0.7(5)
C41–C42–C46–C47	−2.2(4)
C42–C46–C47–C39	3.6(4)
C42–C46–C47–C48	178.6(3)
C43–S7–C35–S6	9.13(16)
C43–S7–C35–C36	−168.6(2)
C43–S8–C44–C45	−68.7(2)
C44–S8–C43–S7	−75.04(19)
C44–S8–C43–C34	108.7(3)
C46–C47–C48–C49	155.4(3)
C47–C39–C40–C41	−0.8(4)
C47–C48–C49–C50	176.5(2)
C47–C48–C49–C62	−3.1(4)
C48–C49–C50–O2	7.6(4)
C48–C49–C50–C51	−173.0(3)
C48–C49–C62–C37	60.1(3)
C48–C49–C62–C52	175.4(3)
C49–C50–C51–C52	−6.4(3)
C49–C50–C51–C61	173.9(2)
C50–C49–C62–C37	−119.5(2)
C50–C49–C62–C52	−4.2(3)
C50–C51–C52–C53	119.7(2)
C50–C51–C52–C62	3.8(3)
C50–C51–C61–C60	−176.7(2)
C51–C52–C53–C36	−122.2(2)
C51–C52–C53–C54	59.2(3)
C51–C52–C62–C37	119.9(2)
C51–C52–C62–C49	0.2(3)

C52–C51–C61–C60	3.7(4)
C52–C53–C54–C55	−2.0(4)
C53–C36–C37–C38	169.6(3)
C53–C36–C37–C62	−10.6(3)
C53–C52–C62–C37	0.0(3)
C53–C52–C62–C49	−119.6(2)
C53–C54–C55–C56	152.0(3)
C53–C54–C55–C60	−36.5(4)
C54–C55–C56–C57	172.6(2)
C54–C55–C60–C59	−169.4(2)
C54–C55–C60–C61	5.7(4)
C55–C56–C57–C58	−1.9(4)
C55–C60–C61–C51	28.1(4)
C56–C55–C60–C59	1.9(4)
C56–C55–C60–C61	177.0(2)
C56–C57–C58–C59	0.9(4)
C57–C58–C59–C60	1.5(4)
C58–C59–C60–C55	−2.9(4)
C58–C59–C60–C61	−178.3(3)
C59–C60–C61–C51	−156.8(3)
C60–C55–C56–C57	0.4(4)
C61–C51–C52–C53	−60.7(3)
C61–C51–C52–C62	−176.6(2)
C62–C37–C38–C39	1.8(4)
C62–C49–C50–O2	−172.8(2)
C62–C49–C50–C51	6.6(3)
C62–C52–C53–C36	−6.5(3)
C62–C52–C53–C54	174.9(2)

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