Tetraceno[2,1,12,11-*opqra*]tetracene-extended tetrathiafulvalene redox-controlled generation of a large PAH core

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ELECTRONIC SUPPLEMENTARY INFORMATION

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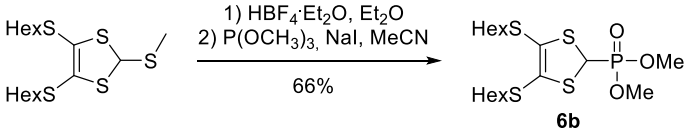
Synthesis

General Procedures

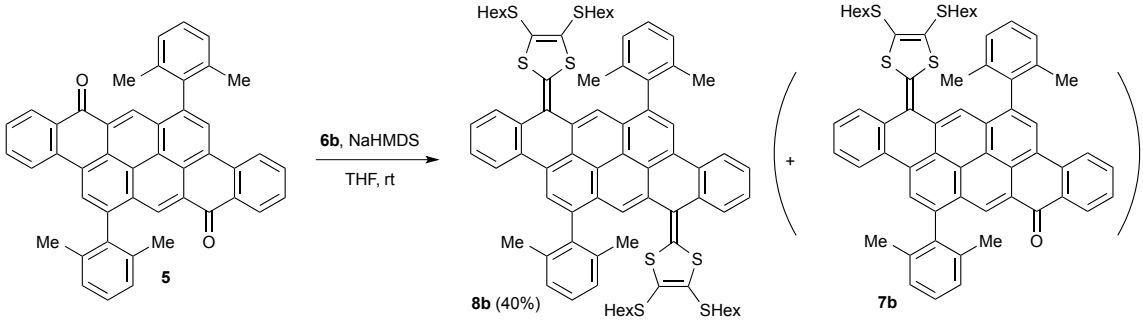
The synthesis of compound **5** will be published elsewhere. All solvents and reagents, unless otherwise stated, were used as received. THF and 1,4-dioxane were purified and dried by distillation from sodium/benzophenone. $CDCl_3$ (unstabilized) was passed through activated Al_2O_3 prior to use. All handling of CS_2 and CCl_4 – including rotary evaporation – was done inside a fumehood. NMR spectra were acquired using a Bruker 500-MHz instrument. All spectroscopic measurements were performed in a 1-cm path length cuvette. UV/Vis absorption spectra were obtained by scanning the wavelength from 1100 to 200 nm.

Protocols



***S*,*S*'-(2-(Dimethoxyphosphoryl)-1,3-dithiole-4,5-diyl) dihexanethioate (6b).** To a solution of *S*,*S*'-(2-(methylthio)-1,3-dithiole-4,5-diyl) dihexanethioate[a)] (5.75 g, 15.0 mmol) in anhydrous diethyl ether (100 mL), was added tetrafluoroboric acid diethyl ether complex (2.3 mL, 17 mmol) and the resulting mixture was stirred for 1.5 h. Additional tetrafluoroboric acid diethyl ether complex (2.3 mL, 17 mmol) was added and the mixture was stirred for a further 45 min. The mixture was concentrated *in vacuo*, redissolved in dry MeCN (100 mL) and trimethyl phosphite (7 mL, 59 mmol) and NaI (5.26, 35.1 mmol) were added. After 2 h of stirring, the mixture was concentrated *in vacuo*, and the residue was purified by flash column chromatography (2% EtOAc/CH_2Cl_2) to afford **6b** as a dark oil (4.44 g, 9.99 mmol, 66%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.73 (d, J = 5.4 Hz, 1H), 3.87 (d, J = 10.7 Hz, 6H), 2.90–2.79 (m, 2H), 2.78–2.70 (m, 2H), 1.72–1.56 (m, 4H), 1.45–1.34 (m, 4H), 1.33–1.22 (m, 8H), 0.87 (t, J = 6.9 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 125.53, 125.52, 54.81, 41.42 (d, J_{PC} = 159.8 Hz), 36.38, 31.47, 29.85, 28.36, 22.68, 14.15 ppm. HR-MS (MALDI$^+$ FT-ICR, dithranol): m/z = 443.0969 $[M\text{-}H]^+$, calcd. for $[C_{17}H_{32}O_3PS_4^+]$: m/z = 443.0966.

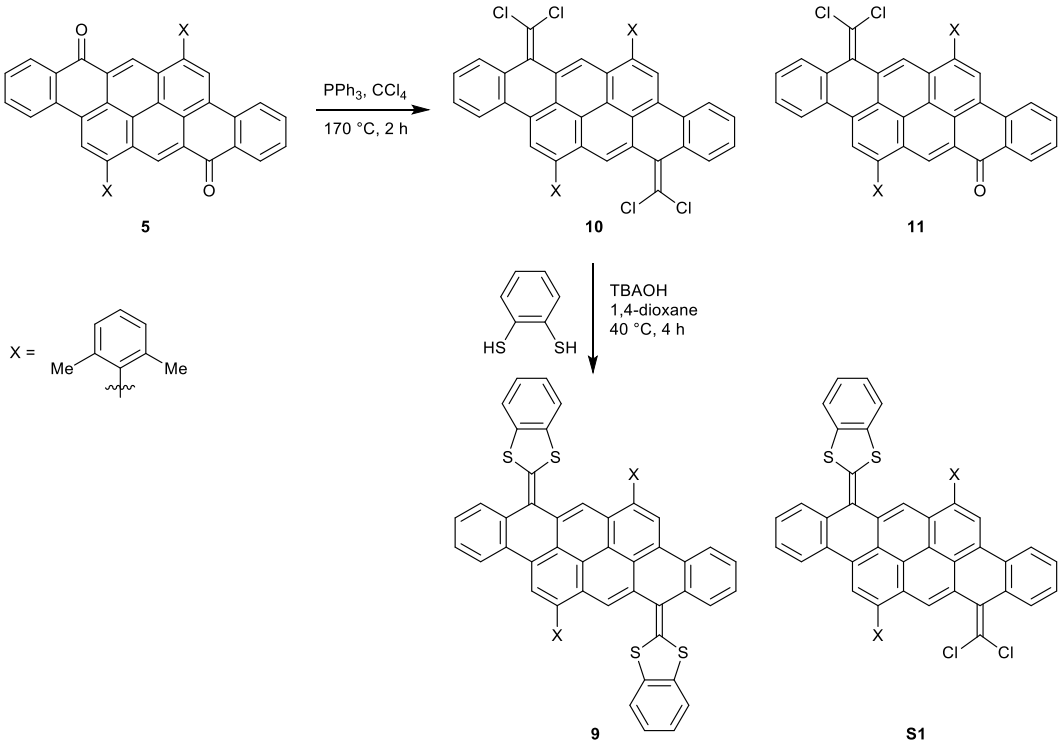
[a)] S. Inoue, S. Mikami, K. Takimiya, T. Otsubo, and Y. Aso, *Heterocycles*, 2007, **71**, 253-268.



2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-opqra]tetracene-8,16-diylidene)bis(4,5-bis(hexylthio)-1,3-dithiole) (8b) and 16-(4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)-6,14-bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-opqra]tetracen-8(16H)-one (7b). To a stirred solution of **6b** (256 mg, 581 µmol, 7 equiv.) and **5**[a)] (51.0 mg, 83.0 µmol) in dry argon-flushed THF (50 mL) at rt, a 0.6 M solution of NaHMDS (0.83 mL, 0.50 mmol, 6 equiv.) in toluene was added drop-wise and the mixture was stirred for 4 h. To the resulting purple reaction mixture was added saturated aqueous NH_4Cl (20 mL) and it was extracted with CH_2Cl_2 (3 x 50 mL). The combined extracts were dried with Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (SiO_2 40 – 63 µm, 15% – 20% CH_2Cl_2 / heptanes to collect **8b**, followed by 20 – 80% CH_2Cl_2 / heptanes to collect **5** and **7b**) gave **8b** as a dark purple oil, the intermediate **7b** as a green to turquois solid, and starting material **5** (26.0 mg, 42.3 µmol, 51%) as an orange to red solid. The sample of **8b** was further purified by flash column chromatography (2% THF / heptanes), which gave **8b** (43.0 mg, 35.4 µmol, 40%) as a dark purple solid. The sample of **7b** was further purified by flash column chromatography (20–60% CH_2Cl_2 / heptanes), which gave **7b** as a dark green solid. [**7b**] ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (s, 1H), 8.75 (s, 1H), 8.60 (s, 1H), 8.57 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.49 (br d, *J* = 8.2 Hz, 1H), 8.28 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.88 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.78 (ddd, *J* = 8.2, 7.1, 1.4 Hz, 1H), 7.57 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 7.53 (ddd, *J* = 7.7, 7.4, 1.2 Hz, 1H), 7.50 (s, 1H), 7.49 (ddd, *J* = 8.1, 7.4, 1.3 Hz, 1H), 7.43–7.39 (m, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 2.77 (q, *J* = 7.3 Hz, 4H), 2.13 (br s, 6H), 2.01 (s, 6H), 1.54 (s, 4H), 1.39–1.18 (m, 12H), 0.84 (dt, *J* = 6.9 Hz, 3H), 0.81 (dt, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.32, 142.52, 139.63, 139.16, 138.51, 138.00, 137.22, 137.08, 136.47, 134.53, 133.76, 133.09, 131.93, 131.26, 130.96, 130.62, 130.38, 129.38, 128.62, 128.45, 128.25, 128.11, 128.07, 128.02, 127.82, 127.55, 127.49, 127.36, 126.67, 125.52, 125.14, 124.92, 124.75, 124.32, 124.03, 123.88, 123.65, 122.98, 122.79, 122.52, 36.73, 36.47, 31.47, 31.40, 29.86, 29.82, 28.38, 28.28, 22.63, 22.63, 21.17, 21.16, 14.13, 14.11 ppm (one signal missing; contains grease). HR-MS (MALDI+ FT-ICR, dithranol): *m/z* = 933.3271 [$M^{\bullet+}$], calcd. for ($C_{61}H_{58}OS_4^{+}$) *m/z* = 933.3287. [**8b**] TLC (15% CH_2Cl_2 / heptanes): R_f = 0.19 (purple). M.p. 144 °C (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 2H), 8.24 – 8.19 (m, 2H), 7.82 – 7.77 (m, 2H), 7.49 – 7.42 (m, 4H), 7.40 (s, 2H), 7.40 – 7.37 (m, 2H), 7.32 (d, *J* = 7.7 Hz, 4H), 2.76 (br t, *J* = 7.4 Hz, 4H), 2.74 (br t, *J* = 7.4 Hz, 4H), 2.11 (s, 11H), 1.58 – 1.51 (m, 11H), 1.38 – 1.13 (m, 8H), 1.28 – 1.18 (m, 8H), 0.84 (br t, *J* = 7.0 Hz, 6H), 0.81 (br t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.00, 137.94, 136.81, 136.21, 134.06, 132.76, 131.77, 128.86, 128.64, 128.03, 127.74, 127.56, 127.52, 127.36, 126.92, 125.49, 125.45, 124.09, 123.89,

122.57, 121.83, 36.67, 36.36, 31.47, 31.40, 29.83, 29.79, 28.38, 28.29, 22.63, 22.63, 21.18, 14.13, 14.11 ppm (one signal missing). HR-MS (MALDI+ FT-ICR, dithranol): *m/z* = 1250.4190 [$M^{\bullet+}$], calcd. for ($C_{76}H_{82}S_8^{\bullet+}$) *m/z* = 1250.4182. Elem anal. calcd. for ($C_{76}H_{82}S_8$) C 72.91, H 6.60; found: C 72.76, H 6.70. UV-Vis (CH_2Cl_2): λ_{max} (ε) = 570.5 (59.9), 535.0 (39.9), 452.0 (14.3), 424.5 (13.7), 397.0 (18.9), 342.5 (50.3), 302.5 (44.9), 253.5 (97.0) nm (x 10^3 M^{-1} cm^{-1}).

[a] The synthesis of **5** is to be reported elsewhere: K. Sbargoud, M. Mamada, Y. Takeda, S. Tokito, A. Yassar, J. Marrot and M. Frigoli, submitted.

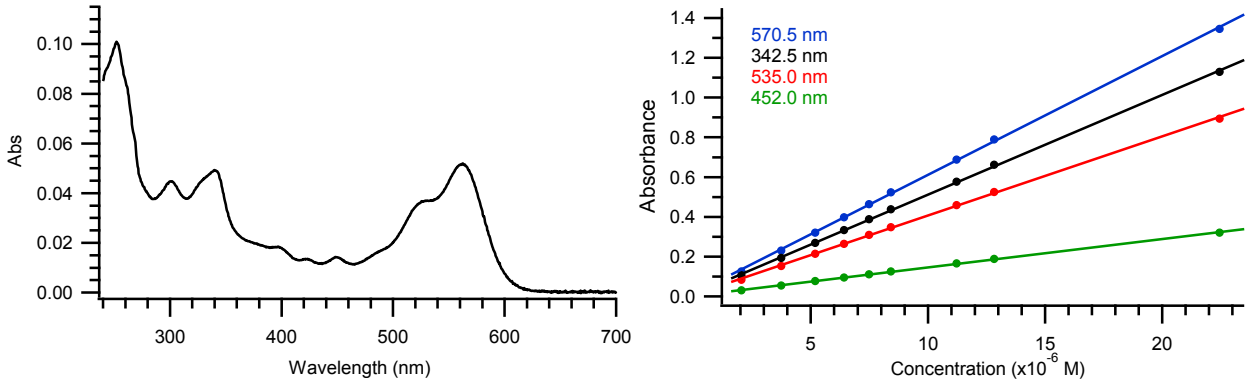


8,16-Bis(dichloromethylene)-6,14-bis(2,6-dimethylphenyl)-8,16-dihydrotetraceno[2,1,12,11-*opqra*]tetracene (10) and 16-(dichloromethylene)-6,14-bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracen-8(16*H*)-one (11). In a capped vial suitable for high-pressure reactions, a stirred suspension of **5** (35.0 mg, 56.9 µmol) and PPh_3 (171.9 mg, 655.4 µmol, 8.8 equiv.) in argon-flushed CCl_4 (10 mL) was exposed to ultrasound for 10 minutes while flushed with argon after which it was stirred at 165–170 °C (pre-heated oil-bath) for 2 h. The resulting black reaction mixture was allowed to cool to rt and then loaded directly onto a silica column and purified by flash column chromatography (20% toluene / heptanes (to collect yellow band) → neat toluene (to collect purple band)) which gave **11** as a purple glassy solid (7.1 mg, 10 µmol, 18%) and **10** (30.7 mg, 41.0 µmol, 72%) as a yellow glassy solid. [**11**] TLC (toluene): R_f = 0.25 (red to purple spot). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.72 (s, 1H), 8.56 (s, 1H),

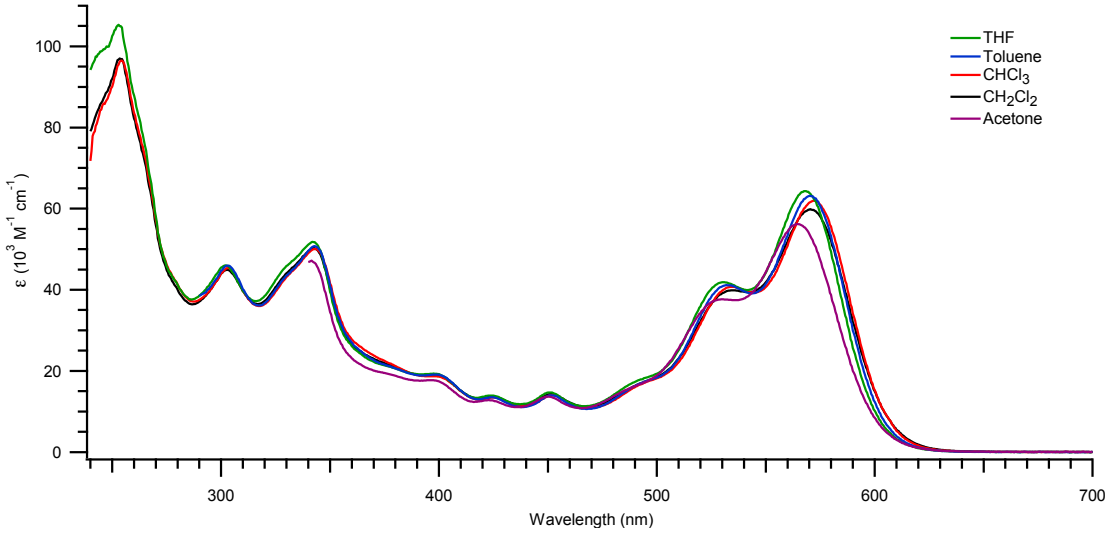
8.55 (dd, J = 7.9, 1.4 Hz, 1H), 8.47 (br d, J = 8.2 Hz, 1H), 8.33 (s, 1H), 8.14 (dd, J = 7.9, 1.2 Hz, 1H), 8.09 (d, J = 8.1, 1.0, 1H), 7.78 (ddd, J = 8.2, 7.2, 1.4 Hz, 1H), 7.58 (ddd, J = 7.9, 7.2, 0.8, 1H), 7.50 (ddd, J = 8.1, 7.3, 1.2 Hz, 1H), 7.43 (ddd, J = 7.9, 7.3, 1.0 Hz, 1H), 7.42 (m, 2H), 7.34 (d, J = 7.5 Hz, 2H), 7.33 (d, J = 7.5 Hz, 2H), 2.03 (s, 6H), 2.01 (s, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.28, 142.58, 139.32, 138.89, 138.28, 137.54, 137.07, 136.99, 133.93, 133.41, 132.70, 132.09, 131.82, 131.52, 130.65, 129.90, 129.59, 129.36, 129.14, 128.71, 128.58, 128.55, 128.40, 128.36, 128.06, 127.69, 127.53, 127.41, 126.82, 126.39, 125.56, 125.37, 124.75, 124.71, 124.59, 124.01, 123.86, 123.23, 121.74, 21.19, 20.99 ppm. HR-MS (MALDI+ FT-ICR, dithranol): m/z = 681.1739 [$M+H^+$], calcd. for ($C_{47}H_{31}Cl_2O^+$) m/z = 681.1747. [**10**] TLC (20% toluene / heptanes): R_f = 0.48 (broad yellow spot). M.p. > 230 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 2H), 8.25 (s, 2H), 8.11 (dd, J = 7.9, 1.1 Hz, 2H), 8.06 (d, J = 8.1 Hz, 2H), 7.47 (m, 2H), 7.43 – 7.35 (m, 4H), 7.32 (d, J = 7.7 Hz, 4H), 2.00 (s, 12H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.51, 138.31, 137.54, 133.78, 133.04, 131.64, 129.85, 129.19, 128.96, 128.82, 128.40, 128.23, 127.61, 126.65, 126.51, 124.81, 124.72, 124.06, 122.43, 120.97, 21.00 ppm. HR-MS (MALDI+ FT-ICR, dithranol): m/z = 748.1085 [$M^{\bullet+}$], calcd. for ($C_{48}H_{30}Cl_4^{\bullet+}$) m/z = 748.1067.

2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-opqra]tetracene-8,16-diylidene)bis(benzo[d][1,3]dithiole) (9) and 2-(16-(dichloromethylene)-6,14-bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracen-8(16*H*)-ylidene)benzo[d][1,3]dithiole (S1). A solution of benzene-1,2-dithiol (15.9 mg, 112 μmol, 3 equiv.) in argon-flushed 1,4-dioxane (2 mL) was added to a suspension of **10** (27.9 mg, 37.3 μmol) in argon-flushed 1,4-dioxane (8 mL) and the mixture was flushed with argon for 10 min. To this mixture, a 1 M solution of tetrabutylammonium hydroxide (0.22 mL, 0.22 mmol, 6 equiv) in MeOH was added and the reaction mixture was stirred at 40 °C for 4 h by which the color quickly changed from yellow to red and further to purple. The reaction mixture was poured into MeOH (50 mL), quickly heated to boiling and upon cooling to rt, a dark purple precipitate was collected as a purple powder. The precipitate was taken up in CS_2 and purification by flash column chromatography (CS_2) gave **S1** as a dark red glassy solid and **9** as a purple glassy solid. To remove the grease from the otherwise pure samples of **S1** (1.2 mg, 1.5 μmol, 4%) and **9** (18.0 mg, 20.3 μmol, 55%) the samples were separately passed through several plugs of silica gel (*i*) 30% THF / heptanes and *ii*) 50% $CHCl_3$ / cyclohexane) which ultimately gave pure samples of **S1** and **9**. [**S1**] HR-MS (MALDI+ FT-ICR, dithranol): m/z = 816.1464 [$M^{\bullet+}$], calcd. for ($C_{54}H_{34}Cl_2S_2^{\bullet+}$) m/z = 816.1473. [**9**] M.p. >230 °C (THF/methanol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 2H), 8.24 – 8.21 (m, 2H), 7.99 – 7.95 (m, 2H), 7.63 (s, 2H), 7.53 – 7.48 (m, 4H), 7.40 – 7.36 (m, 2H), 7.34 – 7.31 (m, 4H), 7.17 – 7.15 (m, 2H), 7.11 – 7.09 (m, 4H), 2.14 (br s, 12H) ppm (2H missing, presumably due to misleading integration of signals at δ 7.17 – 7.15 (m, 2H), 7.11 – 7.09 (m, 4H) ppm, but due to low solubility a smooth baseline could not be achieved and acquisition in other solvents was not possible). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.04, 138.02, 137.03, 136.57, 135.05, 134.40, 134.24, 133.03, 132.01, 128.87, 128.12, 127.94 (two signals), 127.60, 127.48, 126.77, 126.09, 126.01, 125.43, 124.88, 124.15, 123.84, 123.16, 121.92, 120.91, 120.77, 21.26 ppm. HR-MS (MALDI+ FT-ICR, dithranol): m/z = 886.1837 [$M^{\bullet+}$], calcd. for ($C_{60}H_{38}S_4^{\bullet+}$) m/z = 886.1851.

UV-Vis Absorption Spectroscopy



Left) UV-Vis absorption spectrum of 8b in MeCN. Right) Absorbance at various wavelengths as a function of concentration ($2.04 \times 10^{-6} – 2.24 \times 10^{-5}$) in CH_2Cl_2.

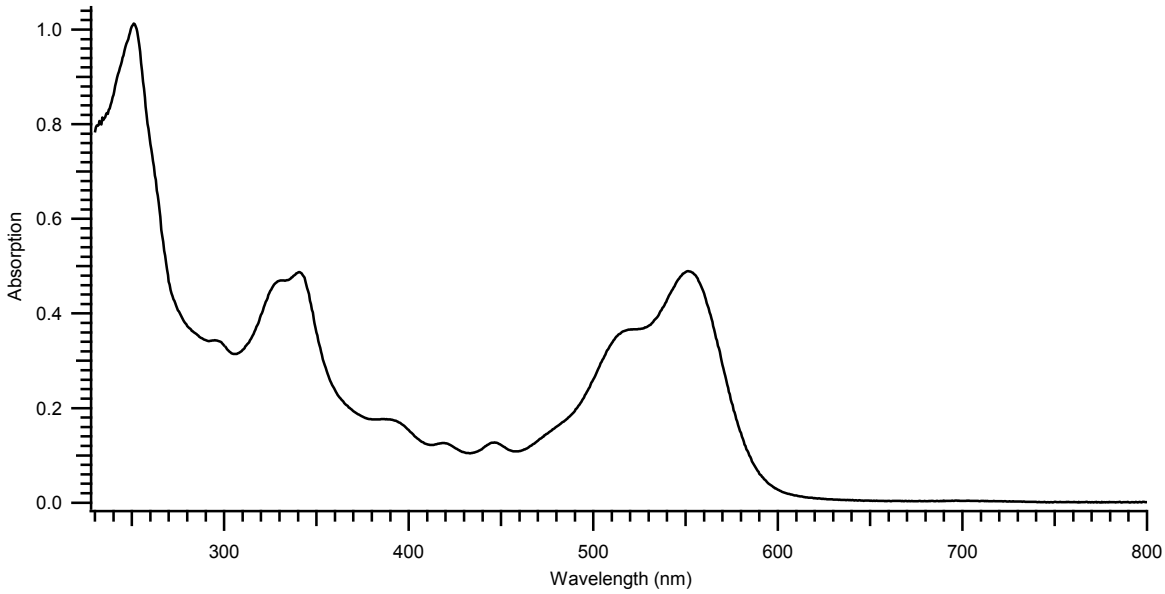


UV-Vis absorption spectrum of 8b in various solvents ($9.63 \times 10^{-6} – 2.24 \times 10^{-5}$ M).

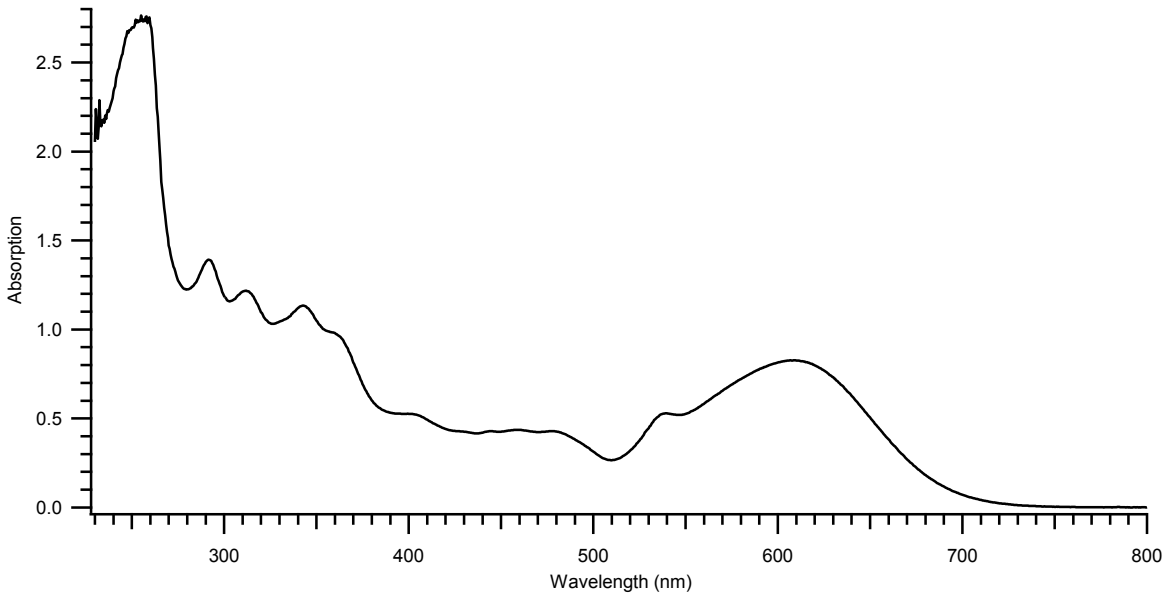
Table 1. Absorption maxima and molar absorptivities for **8b** in various solvents. [λ_{max}] = nm, [ε] = 10^3 M^{-1} cm^{-1}.

	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)	λ_{max} (ε)
THF	567.5	530.0	450.5	423.5	397.5	342.0	302.0	253.0
	(64.3)	(41.9)	(14.7)	(14.0)	(19.3)	(51.8)	(46.0)	(105)
Toluene	570.0	532.5	452.0	424.5	398.0	343.0	303.0	-
	(63.1)	(41.1)	(14.0)	(13.5)	(19.1)	(50.8)	(46.0)	
$CHCl_3$	572.0	534.5	452.0	424.5	398.0	343.5	303.0	254.0
	(61.9)	(40.7)	(14.1)	(13.4)	(18.7)	(50.0)	(45.4)	(95.4)
CH_2Cl_2	570.5	535.0	452.0	424.5	397.0	342.5	302.5	253.5
	(59.9)	(39.9)	(14.3)	(13.7)	(18.9)	(50.3)	(44.9)	(97.0)
Acetone	564.5	529.5	450.0	422.5	396.5	341.5	-	-
	(56.2)	(37.6)	(13.7)	(12.8)	(17.7)	(47.2)		
MeCN[a]	562	525	451	423	399	340	301	253

[a] Due to low solubility, no molar absorptivities are provided. All spectra show a broad shoulder at approximately 490 nm.



UV-Vis absorption spectrum of 9 in CH_2Cl_2 (longest-wavelength absorption maximum at 552 nm).



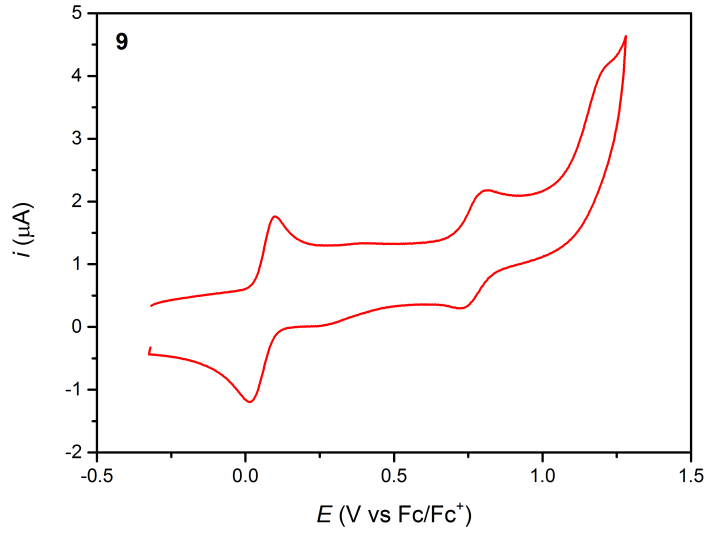
UV-Vis absorption spectrum of 7b in CH_2Cl_2 (longest-wavelength absorption maximum at 609 nm)

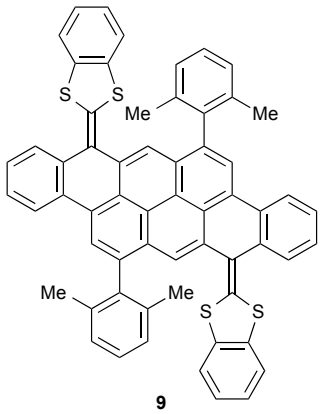
Cyclic Voltammetry

Cyclic voltammetry was carried out in CH_2Cl_2 containing Bu_4NPF_6 (0.1 M) as the supporting electrolyte using an Autolab PGSTAT12 instrument driven by the Nova 1.11 software. The working electrode was circular glassy carbon disk (d = 3 mm), the counter electrode was a platinum wire and the reference electrode was a silver wire immersed in the solvent-supporting electrolyte mixture and physically separated from the solution containing the substrate by a ceramic frit. The potential of the reference electrode was determined *vs* the ferrocene/ferrocenium (Fc/Fc^+) redox couple in separate experiments. The voltage sweep rate was 0.1 V s^{-1}. *iR*-Compensation was used in all experiments. Solutions were purged with argon saturated with CH_2Cl_2 for at least ten minutes before the measurements were made after which a stream of argon was maintained over the solutions. The temperature was 297 K.

The voltammogram for the oxidation of **8b** (1 mM) is shown in the manuscript (Figure 5). For comparison, the voltammograms for the oxidation of **9** (saturated solution) and the model compound, **TTa**, (0.54 mM) are shown below.

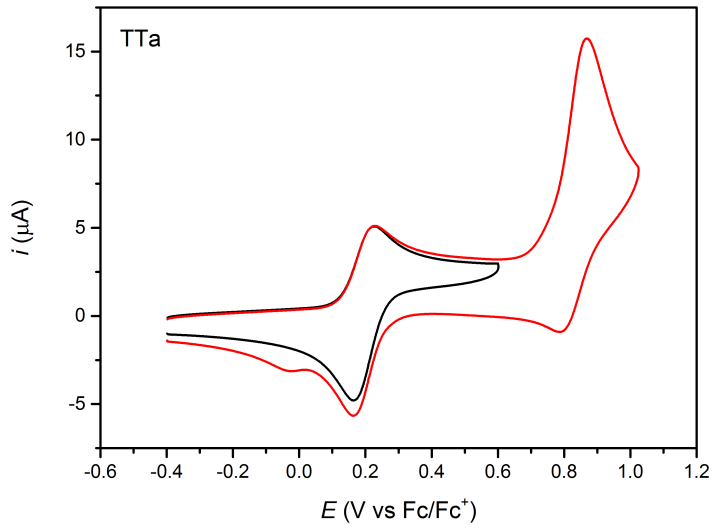
Voltammogram of **9**:

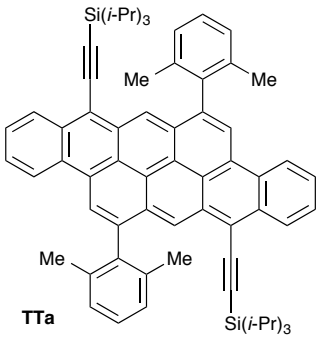




The formal potential for the 1st and 2nd redox couple and the peak potential for the 3rd electron transfer are $E^{o'}(1) = 0.071$, $E^{o'}(2) = 0.768$ and $E_p(3) \approx 1.21$ (V *vs* Fc/Fc^+).

*Voltammogram of **TTa**:*





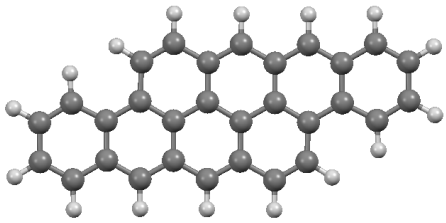
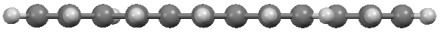
It is seen that the relative peak heights do not reflect accurately those expected for the reversible formation of the radical cation, $\mathbf{TTa}^{\bullet+}$ (1st redox couple) and the subsequent formation of the reactive dication, $\mathbf{TTa}^{2+}$ (2nd electron transfer process). The origin of this behavior was deemed to be beyond the scope of the present study. Still, the voltammogram allows for estimates of the formal potential for the 1st redox couple and the peak potential for the 2nd electron transfer, the values being $E^{o'}(1) = 0.196$ and $E_p(2) = 0.869$ (V *vs* Fc/Fc^+).

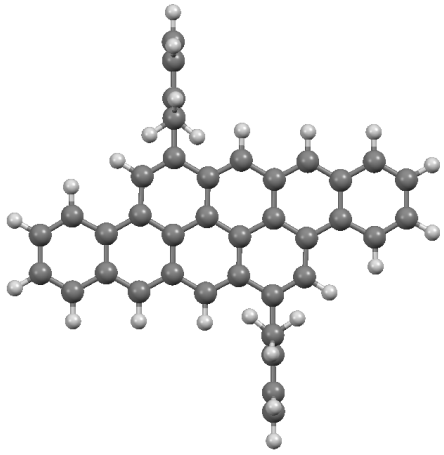
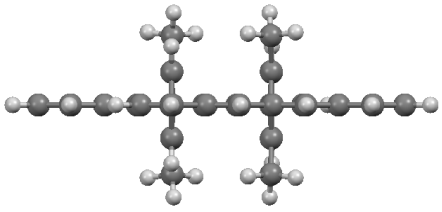
DFT Calculations

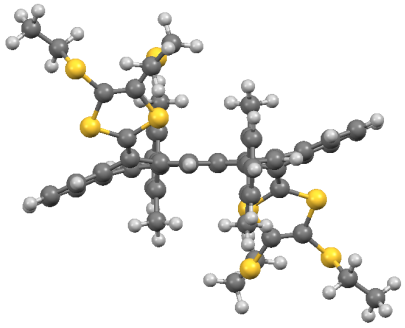
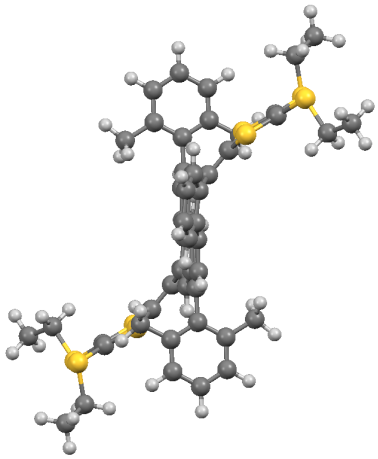
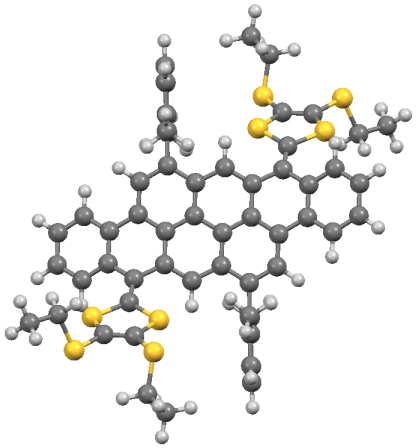
DFT calculations (B3LYP, cc-pVDZ) were carried out using the Gaussian 09 suite of programs.[a)] Structure optimizations were carried out to the opt=tight level and the lack of negative frequencies in the frequency calculations was taken as an indication that true minima had indeed been obtained. In order to save computational time, EtS groups were used as substituents in the DTF substituted derivatives rather than the HexS groups. The effect of the orientation of the EtS groups was not addressed. Π-type bonds are not shown in the figures below.

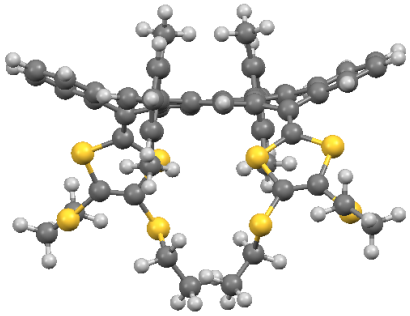
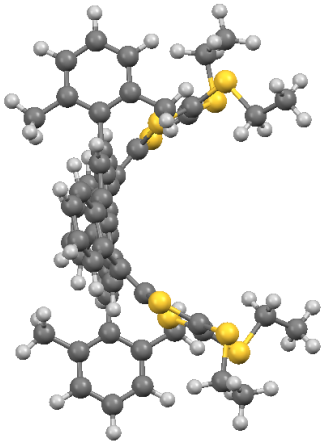
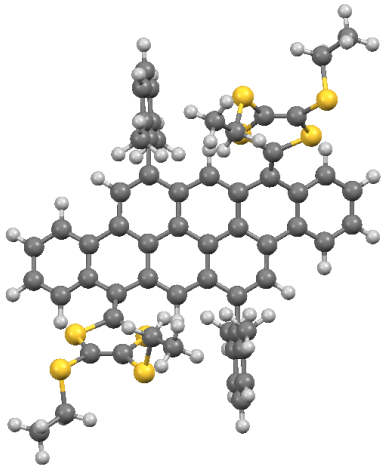
[a)] Gaussian 09, EM64L-G09RevB.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.

1. Structures and properties of the neutral species

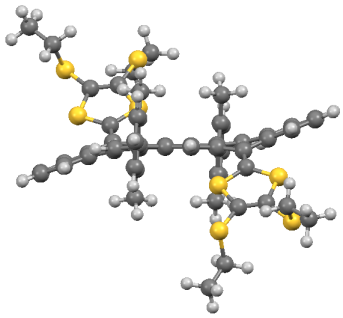
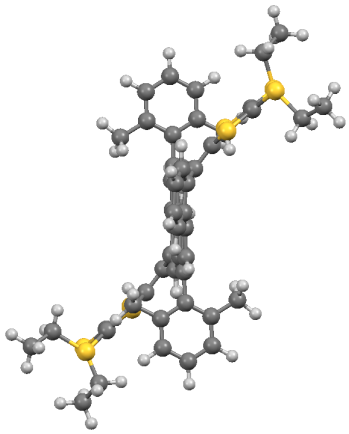
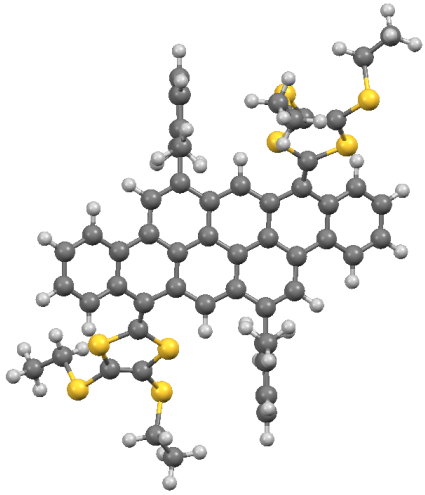
Compound	tetraceno[2,1,12,11-*opqra*]tetracene, **TT**
top view	
side view	
Geometry	planar
E(RB3LYP) (a.u.)	-1152.98683186

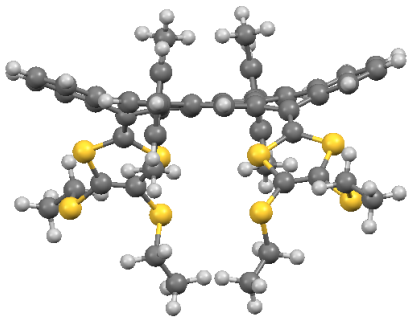
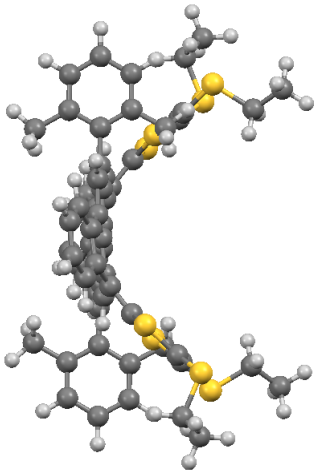
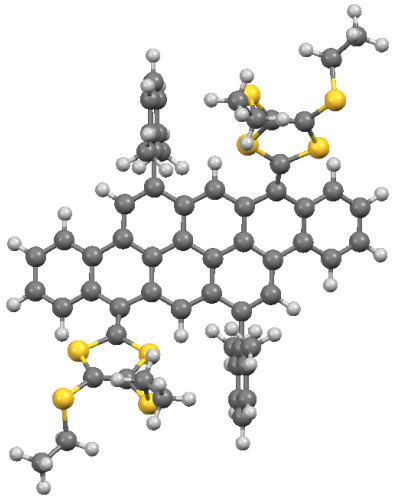
Compound	6,14-bis(2,6-dimethylphenyl)-tetraceno[2,1,12,11-*opqra*]tetracene
top view	
side view	
Core geometry	planar
Aryl-core angles (degrees)	~90
E(RB3LYP) (a.u.)	-1772.38461744

Compound	**8a-*anti***
side view of the core	
view of the orientation of the DTF groups	
top view of the orientation of the 2,6-dimethylphenyl groups	
Core geometry	S-shaped
DTF orientation	anti
Aryl-central core angles (degrees)	~90
E(RB3LYP) (a.u.)	-5502.33749693

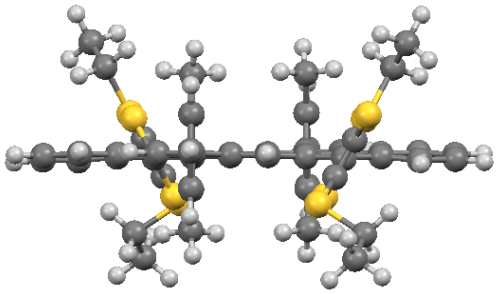
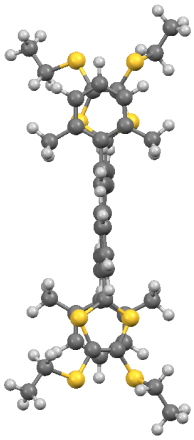
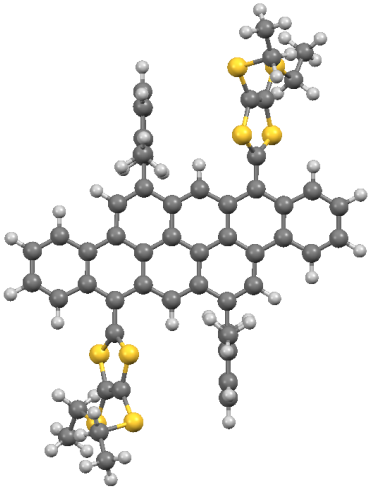
Compound	**8a-*syn***
side view of the core	
view of the orientation of the DTF groups	
top view of the orientation of the 2,6-dimethylphenyl groups	
Core geometry	U-shaped
DTF orientation	syn
Aryl-central core angles (degrees)	~87
E(RB3LYP) (a.u.)	-5502.33808362

2. Structures and properties of $8a^{\cdot+}$

Compound	**$8a^{\cdot+}$-*anti***
side view of the core	
view of the orientation of the DTF groups	
top view of the orientation of the 2,6-dimethylphenyl groups	
Core geometry	S-shaped
DTF orientation	anti
Aryl-central core angles (degrees)	~84
E(UB3LYP) (a.u.)	-5502.13889240

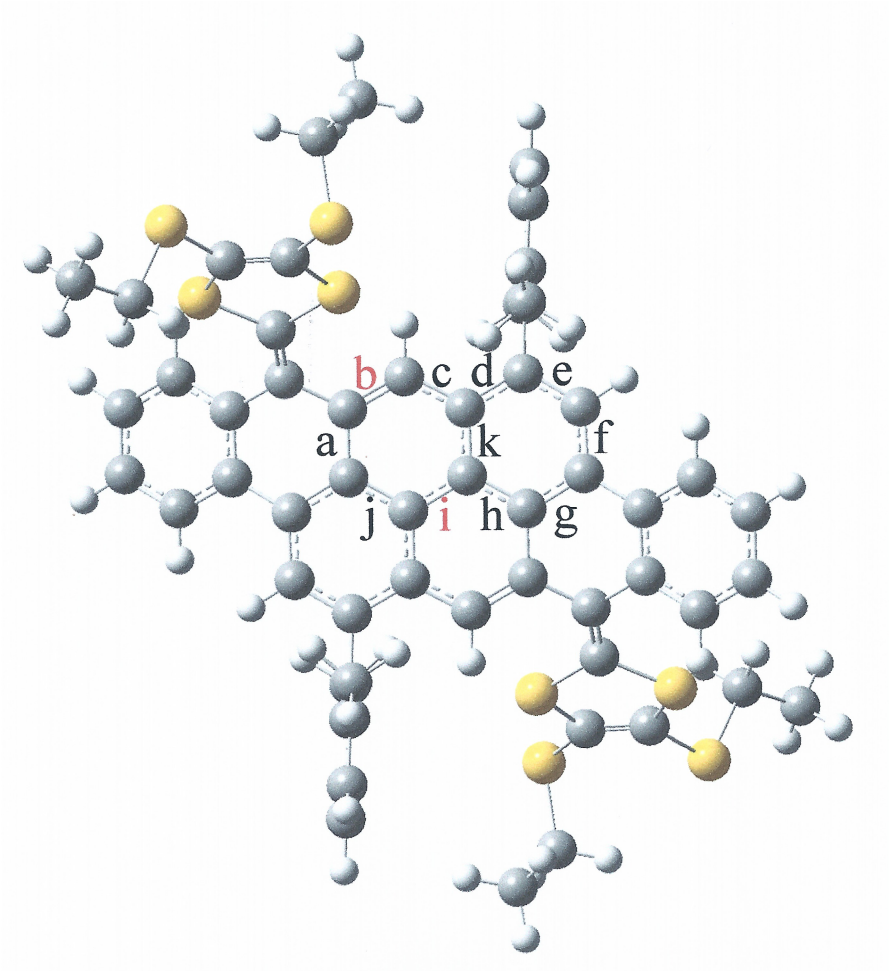
Compound	**8a**$^{\cdot+}$ ***-syn***
side view of the core	
view of the orientation of the DTF groups	
top view of the orientation of the 2,6-dimethylphenyl groups	
Core geometry	U-shaped
DTF orientation	syn
Aryl-central core angles (degrees)	~87
E(UB3LYP) (a.u.)	-5502.13892323

3. Structure and properties of $8a^{2+}$

Compound	$8a^{2+}$
side view of the core	
view of the orientation of the DTF groups	
top view of the orientation of the 2,6-dimethylphenyl groups	
Core geometry	Essentially planar
DTF-central core angles (degrees)	~63
Aryl-central core angles (degrees)	~90
E(RB3LYP) (a.u.)	-5501.86135302

4. Comparison of selected bonds in TT, 8a-*anti* and $8a^{2+}$.

Bond lengths (in Å) resulting from DTF calculations (B3LYP, cc-pVDZ). The bonds to be compared, a-k, are indicated below at the structure of **8a-*anti***. It is clearly seen that the two bonds **b** and **i** are essentially of the same length in the aromatic **TT** and in $\mathbf{8a^{2+}}$, whereas bond **b** is shorter (more double bond character), and bond **i** longer (more single bond character), in **8a-*anti***.



Bond lengths (Å)

	TT	**8a-*anti***	**$8a^{2+}$**
a	1.446	1.448	1.443
b	**1.420**	**1.380**	**1.417**
c	1.387	1.431	1.390
d	1.438	1.422	1.450
e	1.362	1.393	1.369
f	1.442	1.407	1.436
g	1.425	1.417	1.422
h	1.429	1.428	1.430
i	**1.419**	**1.432**	**1.418**
j	1.429	1.428	1.430
k	1.445	1.430	1.440

5. G09 output

a. Neutral species

Tetraceno[2,1,12,11-*opqra*]tetracene (TT)


```
1\1\GINC-SLEJPNER\Freq\RB3LYP\CC-pVDZ\C30H16\HAMMERICH\10-Dec-2015\0\\
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 830598766,0.3872793953,-0.0034819121\C,5.6079509681,-0.3297147916,-0.0
 015984424\C,4.3360118266,0.318500988,-0.0023668563\C,4.3216787331,1.76
 26901975,-0.0052059897\C,5.5635630492,2.4745808905,-0.007106672\C,3.09
 17316605,-0.3936247581,-0.0004662453\C,1.8630286157,0.3278138626,-0.00
 13935354\C,1.8700467717,1.7733733748,-0.0042422361\C,3.0977533989,2.44
 95482339,-0.0060673023\C,0.6110896401,-0.3609350336,0.0004647483\C,-0.
 6110899725,0.3609337165,-0.0004650127\C,-0.5837853079,1.8052774894,-0.
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 .5036519674,0.0041883998\C,0.5837846401,-1.8052788507,0.0033181789\C,-
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 .0042407081\C,-3.097754016,-2.4495491589,0.0060640162\C,-4.3216792251,
 -1.7626905637,0.0052043939\C,-4.3360116044,-0.3185014309,0.0023686944\
 C,-5.5635638846,-2.4745803222,0.0071038527\C,-6.7638035556,-1.80946639
 53,0.0062775261\C,-6.7830590229,-0.387277598,0.0034872288\C,-5.6079495
 769,0.3297157963,0.0016044381\H,7.7038587379,2.365484746,-0.0077502212
 \H,7.7394583478,-0.1400495885,-0.0028247297\H,5.6602371793,-1.41803857
 6,0.0005261719\H,5.5329191972,3.5670429205,-0.0092467932\H,3.102035684
 9,3.5427690864,-0.008222148\H,0.6471965194,3.5635835472,-0.0072745474\
 H,-3.9518750684,2.4101141825,-0.0031562919\H,-1.8270121338,3.596257450
 9,-0.0063446067\H,3.9518736702,-2.4101162239,0.0031574729\H,1.82701102
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 \H,-3.1020368342,-3.5427700575,0.0082162468\H,-5.5329208481,-3.5670424
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 9536\\Version=EM64L-G09RevB.01\State=1-A\HF=-1152.9868319
```

6,14-Bis(2,6-dimethylphenyl)-tetraceno[2,1,12,11-*opqra*]tetracene


```
1\1\GINC-SLEJPNER\Freq\RB3LYP\CC-pVDZ\C46H32\HAMMERICH\12-Mar-2016\0\\
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 75\C,4.3387507774,-5.2250416457,0.0000964931\C,4.0621160477,-3.8764165
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 2,0.0000134662\C,-1.3762236478,-2.1487013262,0.0000362152\C,-1.0283550
 68,1.585735175,-0.0000274577\C,-2.3918118657,1.9924058312,-0.000031840
 6\C,-3.4006189915,0.9660061403,-0.0000132432\C,-3.1109880436,-0.370670
 2315,0.0000081359\C,3.4006189126,-0.9660059619,0.0000134119\C,3.110987
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 9404,4.3624924525,-0.0000719101\C,-2.720525102,3.3884431725,-0.0000543
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 562107,-2.9063263457,0.0000503122\H,-4.4512489567,1.2555832556,-0.0000
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 1561,-0.0000526168\H,-1.1603669759,6.4788702977,-0.0001077431\H,-3.519
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 868477\H,-4.8940084905,3.1728008825,-0.0000476969\C,4.2240702157,1.378
 261878,-0.0000279588\C,4.7484437307,1.8454196806,1.227094071\C,4.74845
 21925,1.845368477,-1.2271658954\C,5.7950324576,2.778684236,1.206642829
 6\C,5.7950413167,2.7786332952,-1.2067463948\C,6.3168732342,3.244475502
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 ,3.1423290547,-2.1536602533\H,7.1318556499,3.9722604419,-0.0000720681\
 C,-4.2240704403,-1.3782617531,0.0000273093\C,-4.7484532009,-1.84541208
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 31855784,-3.9722605421,0.0000774152\C,4.2010486848,1.3541303478,-2.547
 8048728\H,4.3589390733,0.2706816259,-2.6747398581\H,3.1148266177,1.523
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 2.3846174
```

8a-*anti*

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32944009,2.7207140246,-1.7745636088\C,4.314144818,3.31907932,-2.654646
9029\C,1.1924043371,2.802039326,-0.5889595716\C,1.1794345708,1.3867258
148,-0.5226983403\C,2.313973555,0.6104002738,-0.9779669891\C,3.5612659
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\C,-0.0348980787,-0.7151468481,-0.0035795798\C,1.0498226335,-1.4645577
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8a-*syn*


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b. Radical cations

8a$^{\cdot+}$-*anti*


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8a$^{\cdot+}$-*syn*


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c. Dication

$8a^{2+}$


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NMR Spectra

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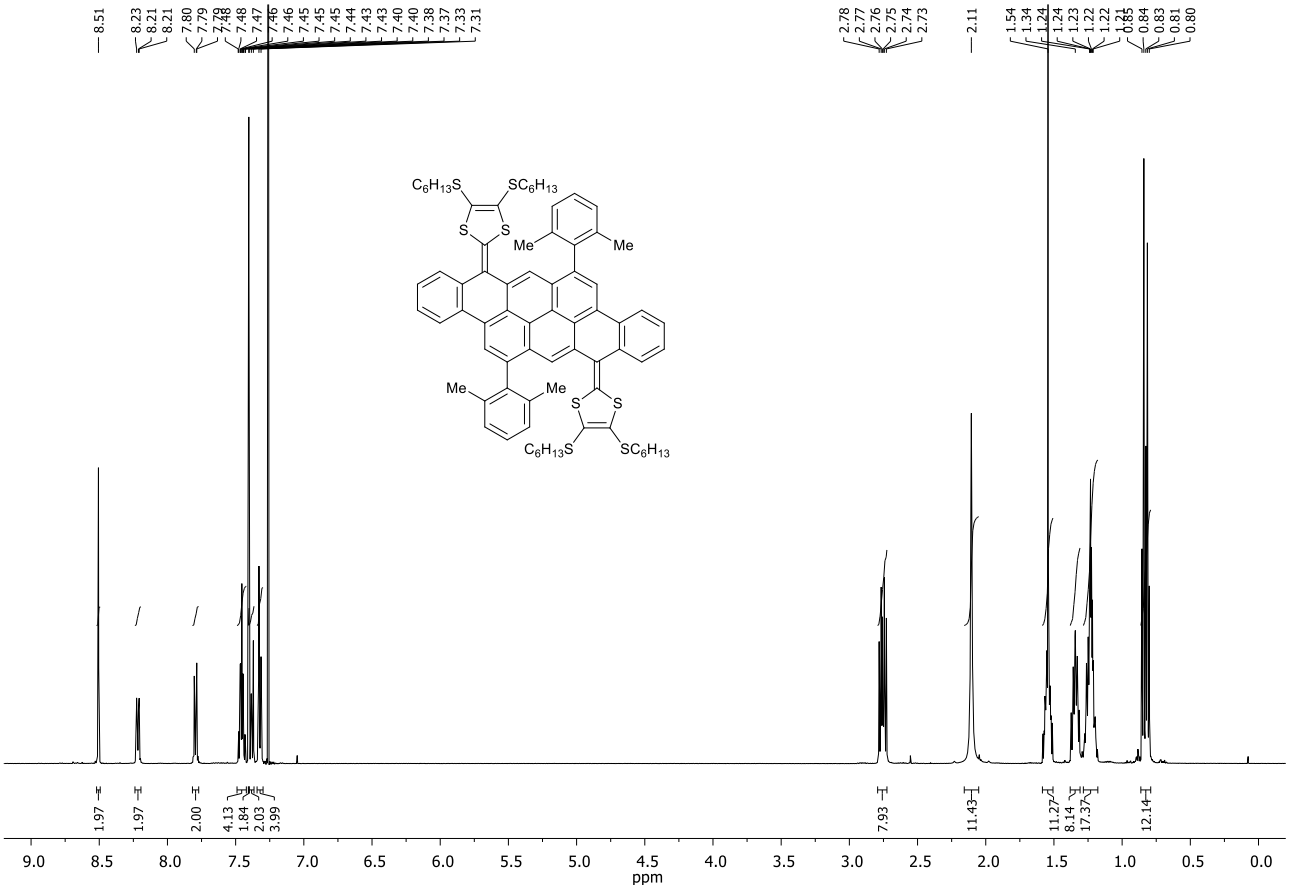
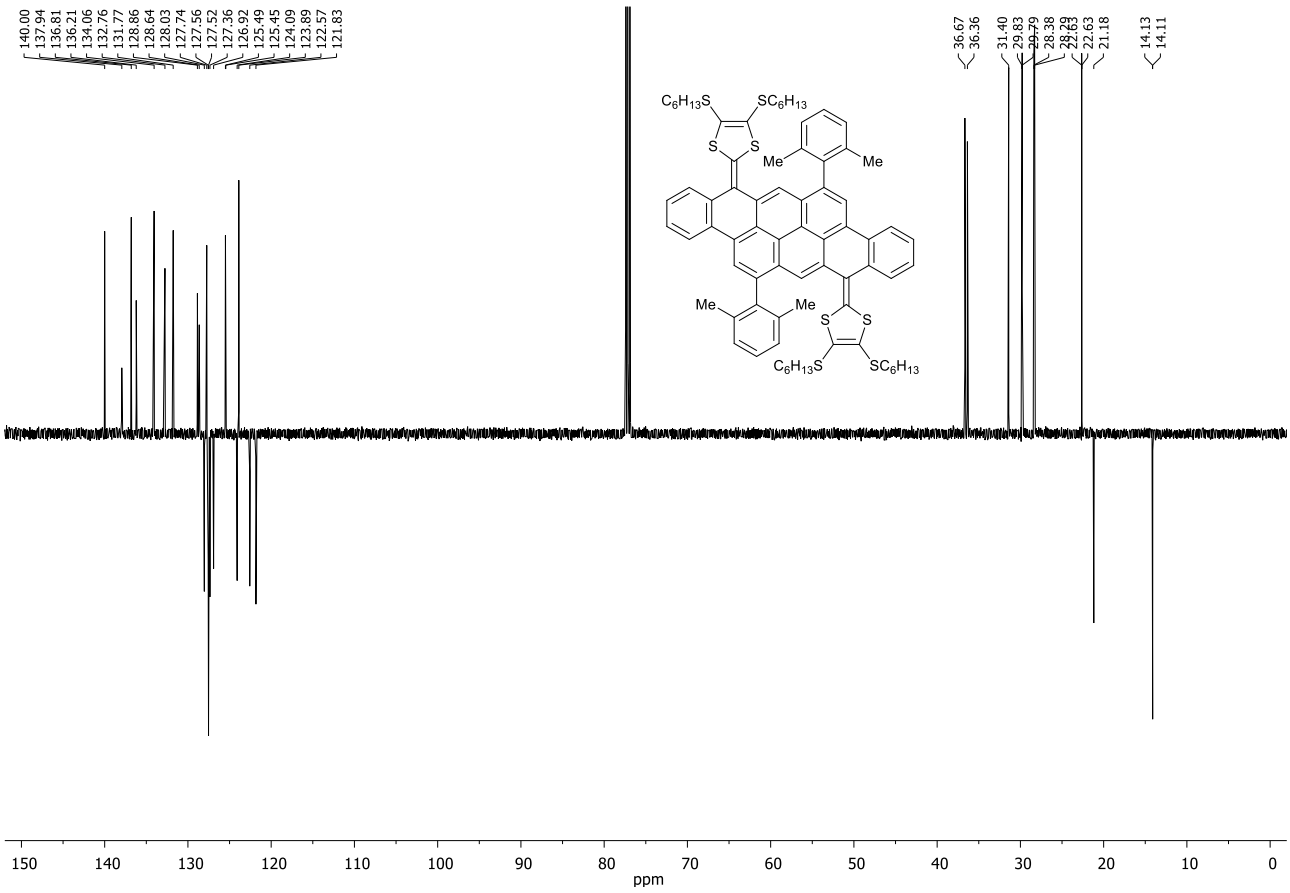


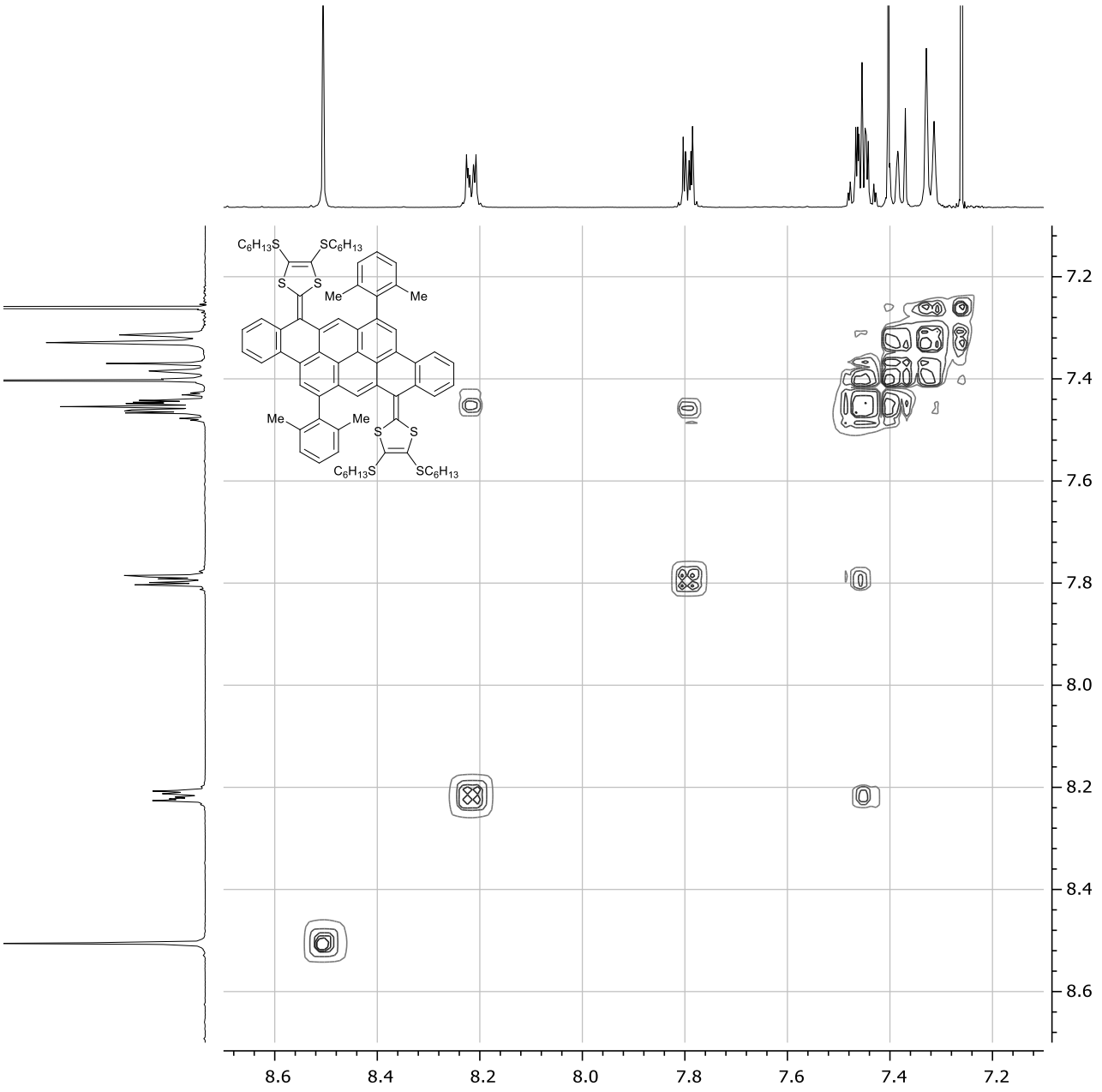
^{1}H NMR spectrum of 8b in $CDCl_3$ (500 MHz).

2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracene-8,16-diylidene)bis(4,5-bis(hexylthio)-1,3-dithiole) (8b).



^{13}C APT NMR spectrum of 8b in $CDCl_3$ (126 MHz).

2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracene-8,16-diylidene)bis(4,5-bis(hexylthio)-1,3-dithiole) (8b).



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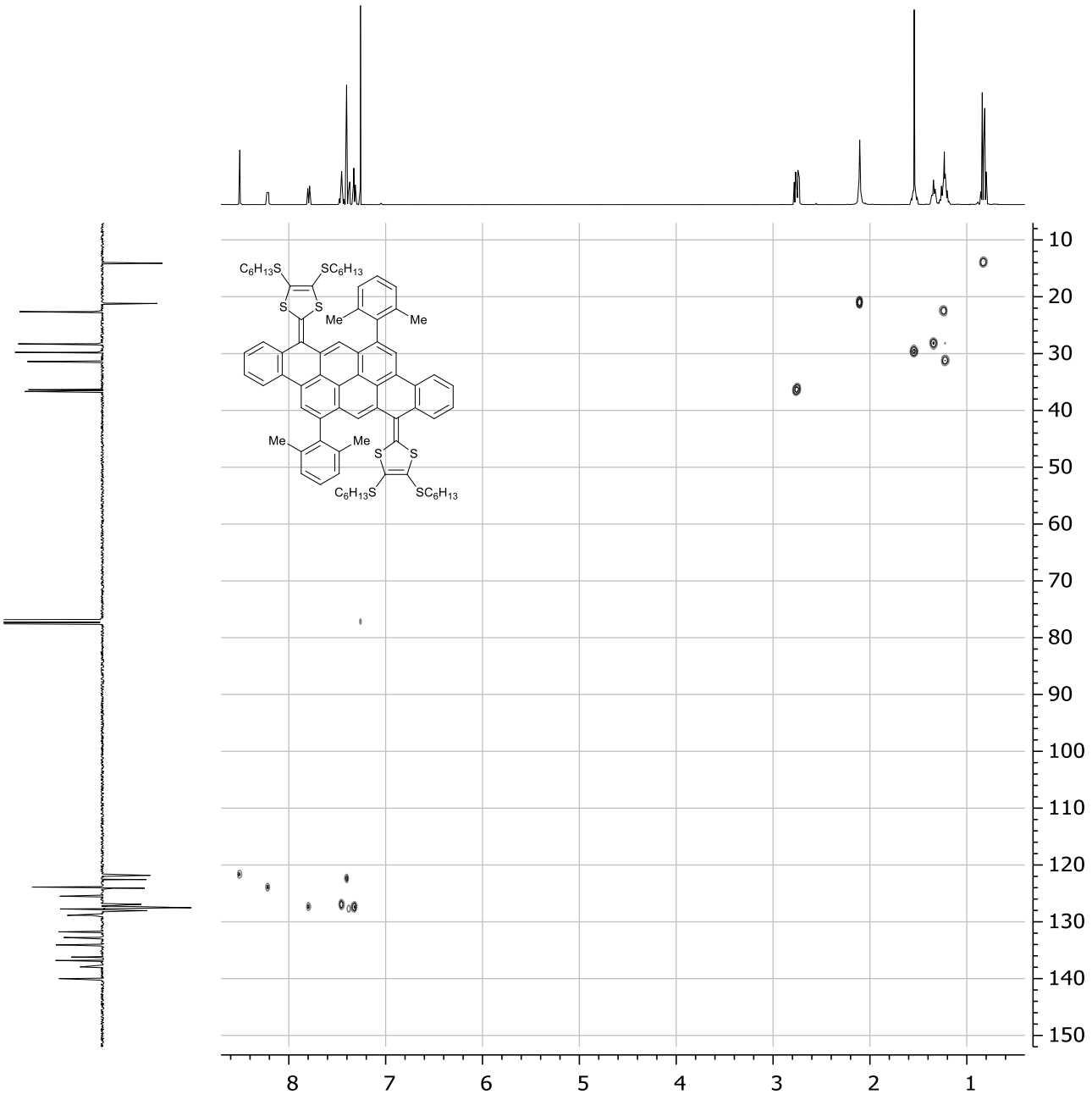
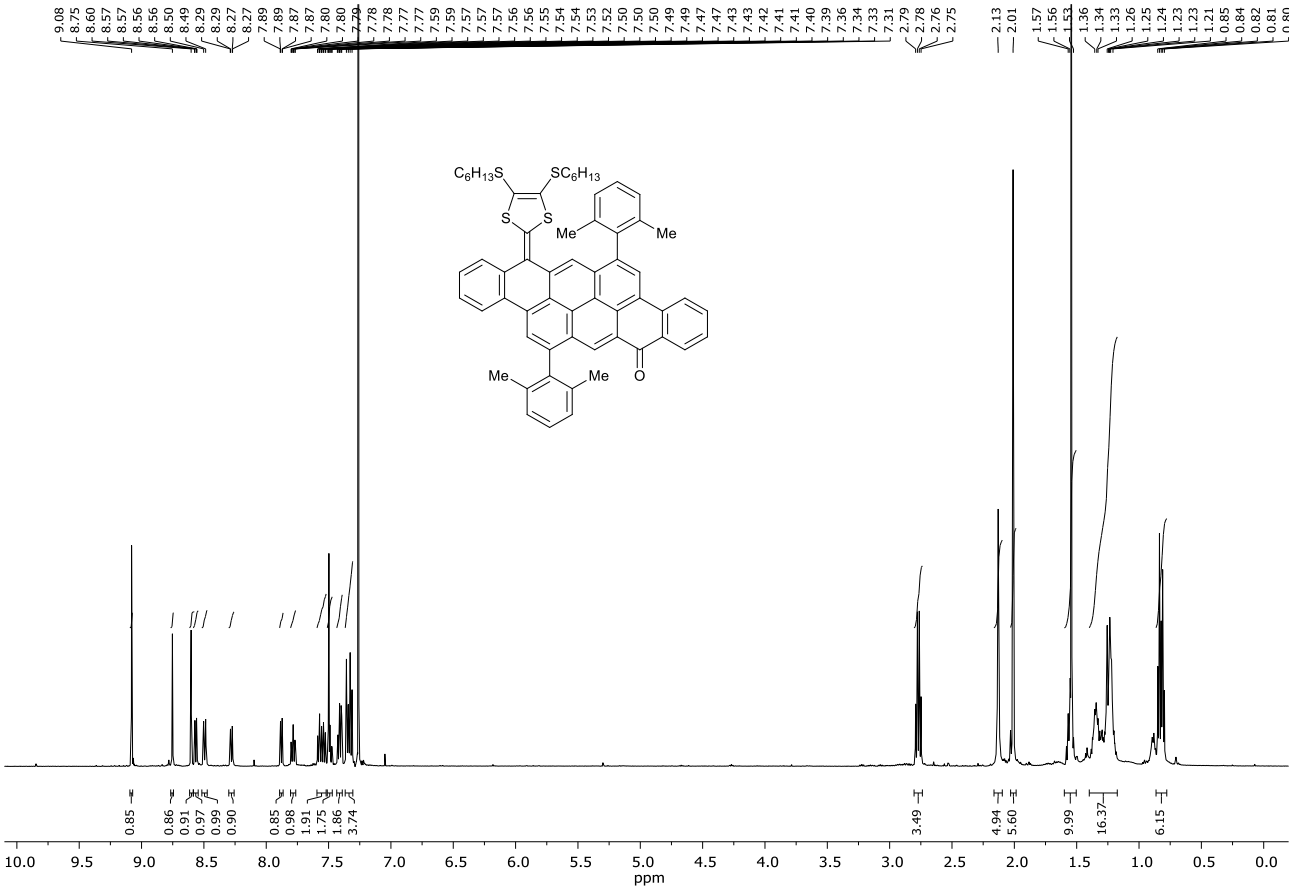
2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracene-8,16-diylidene)bis(4,5-bis(hexylthio)-1,3-dithiole) (8b).



$^{1}H/^{13}C$ HSQC NMR spectrum of 8b in $CDCl_3$ (500/126 MHz).

16-(4,5-Bis(hexylthio)-1,3-dithiol-2-ylidene)-6,14-bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracen-8(16*H*)-one (7b).



^{1}H NMR spectrum of 7b in $CDCl_3$ (500 MHz).

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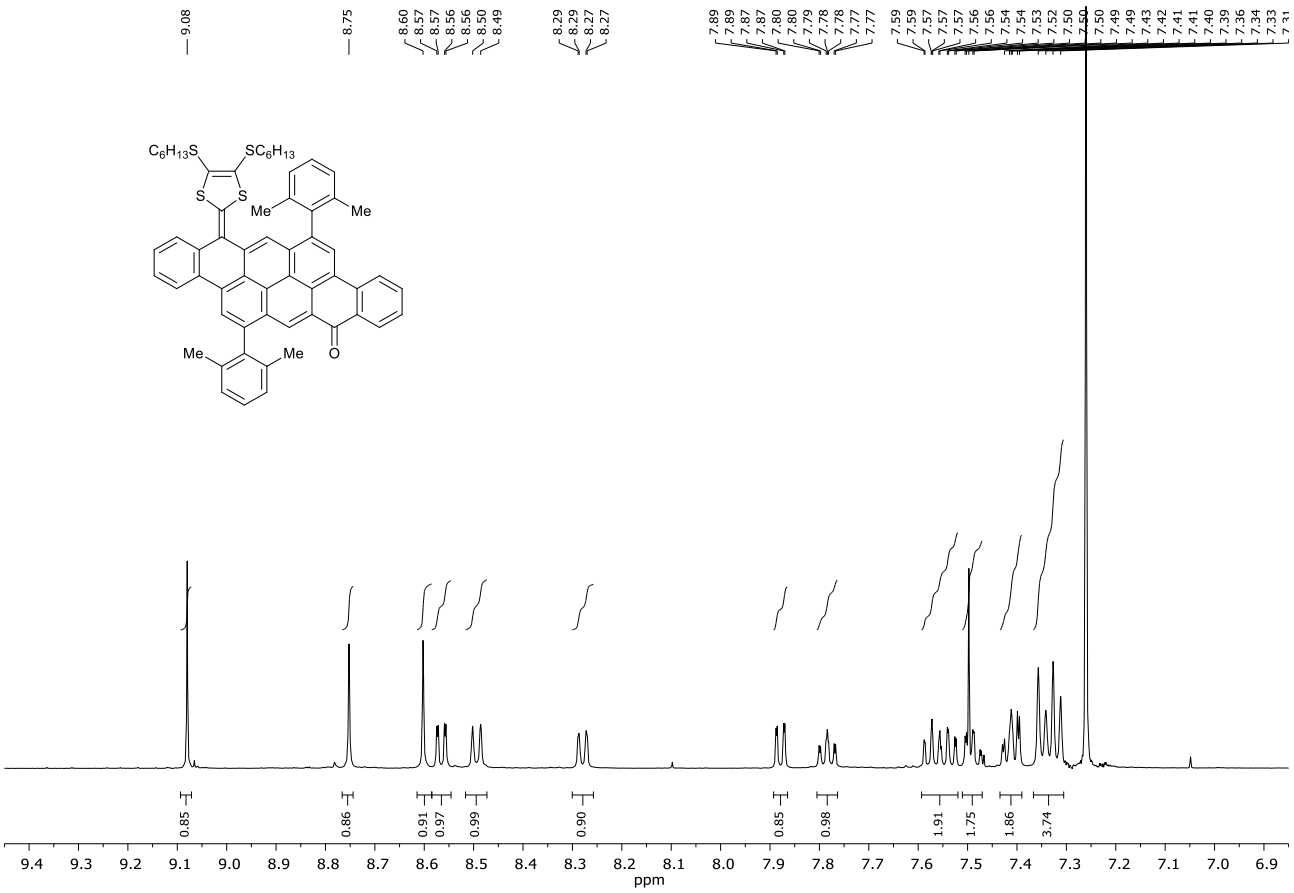

^{1}H NMR spectrum of 7b in $CDCl_3$ (500 MHz).

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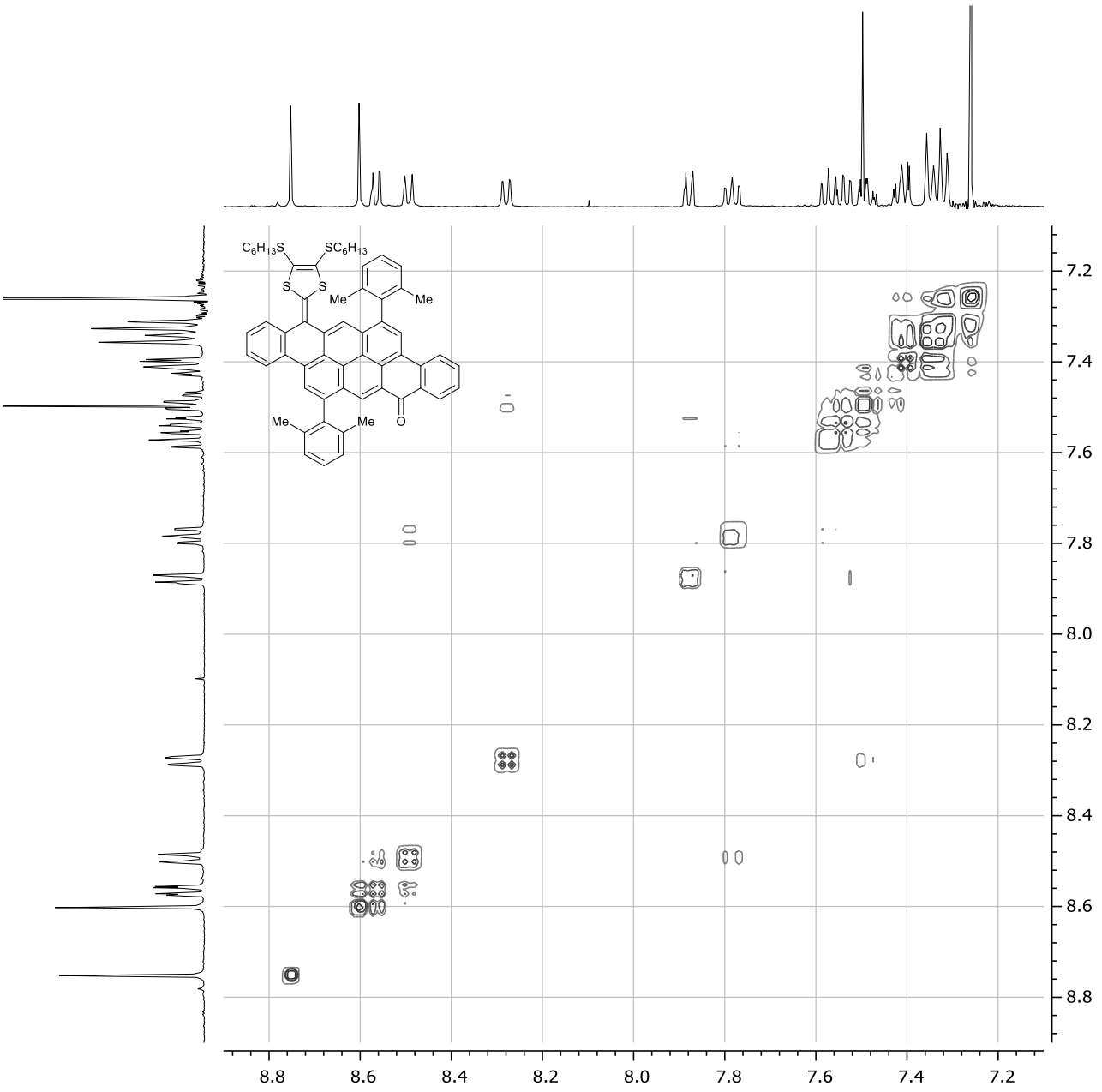

^{1}H/^{1}H NMR spectrum of 7b in $CDCl_3$ (500 MHz).

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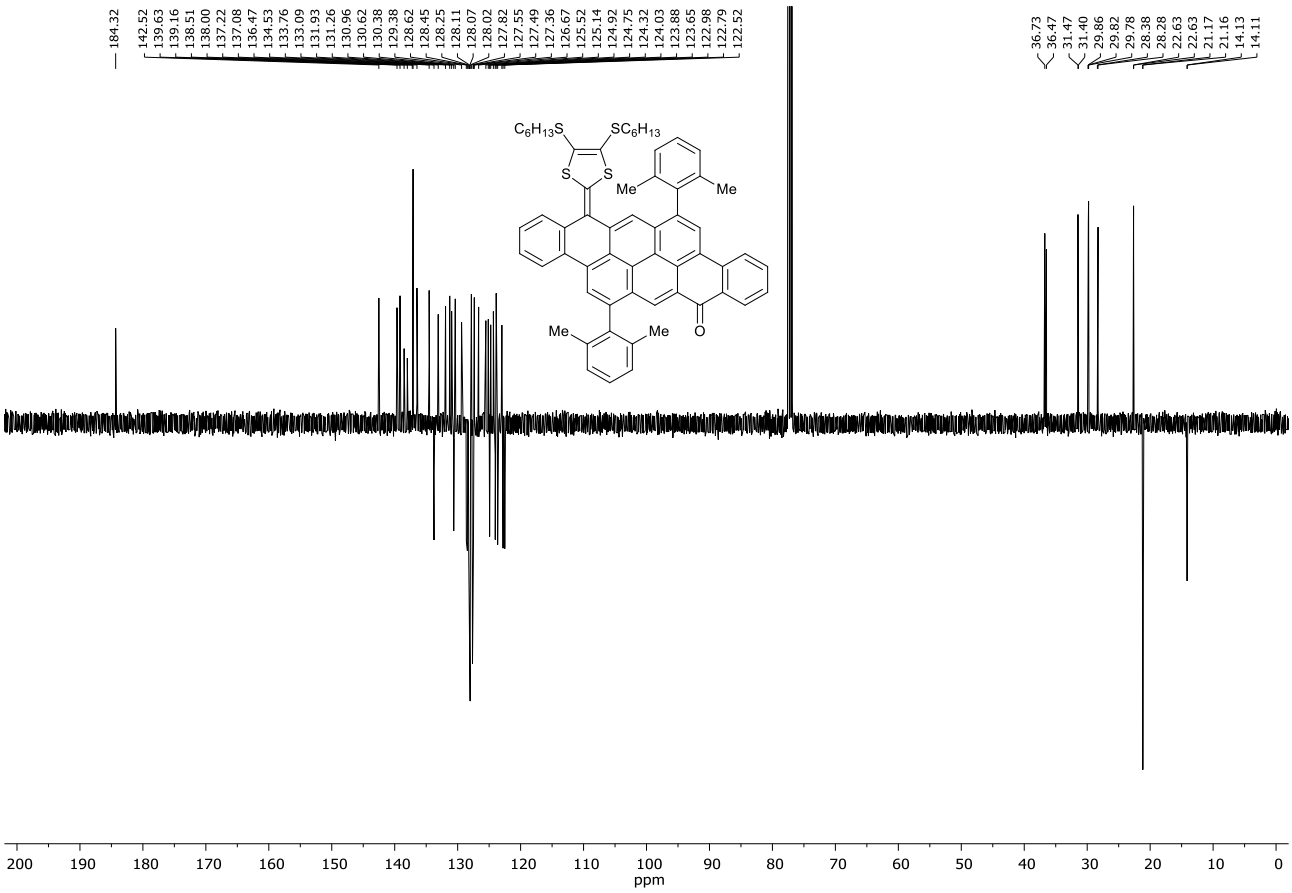
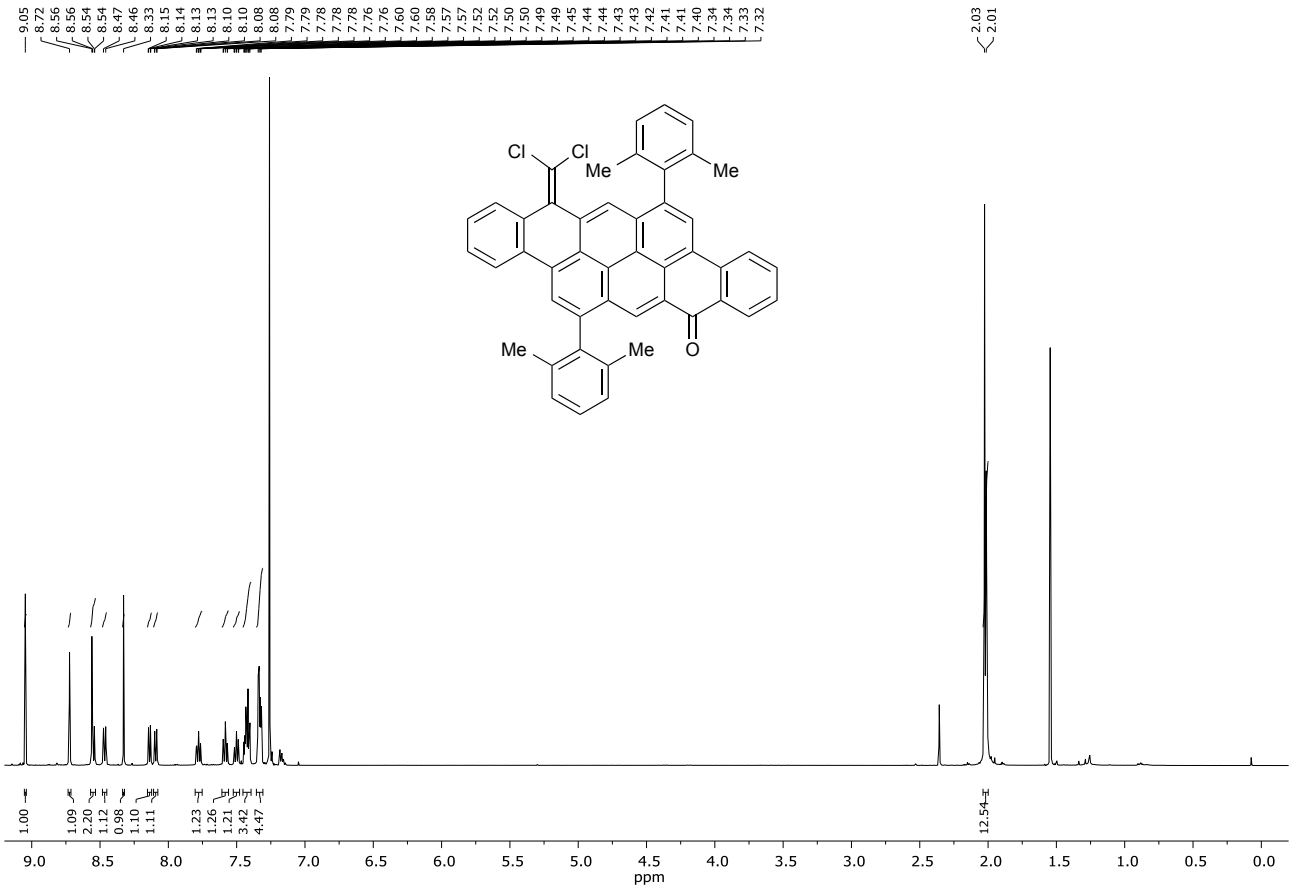


^{13}C APT NMR spectrum of 7b in $CDCl_3$ (126 MHz).

16-(Dichloromethylene)-6,14-bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracen-8(16*H*)-one (11).



^{1}H NMR spectrum of 11 in $CDCl_3$ (500 MHz).

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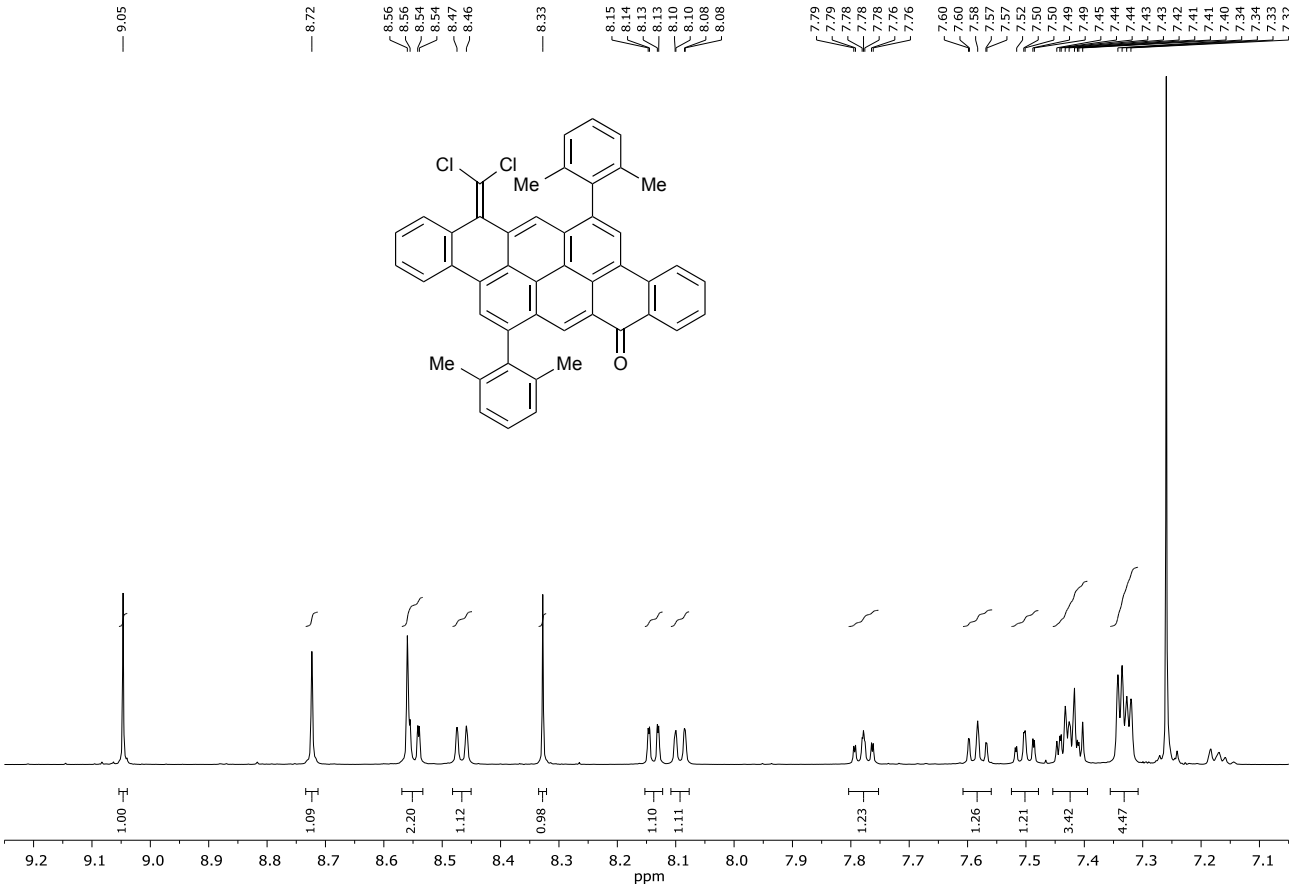
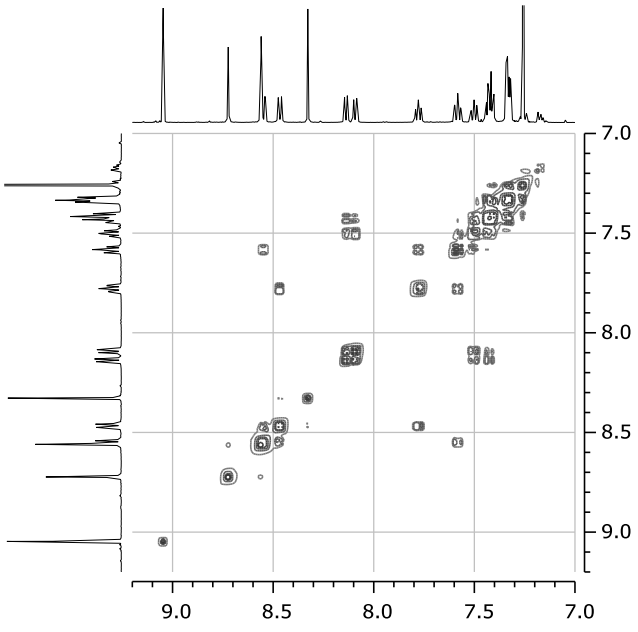
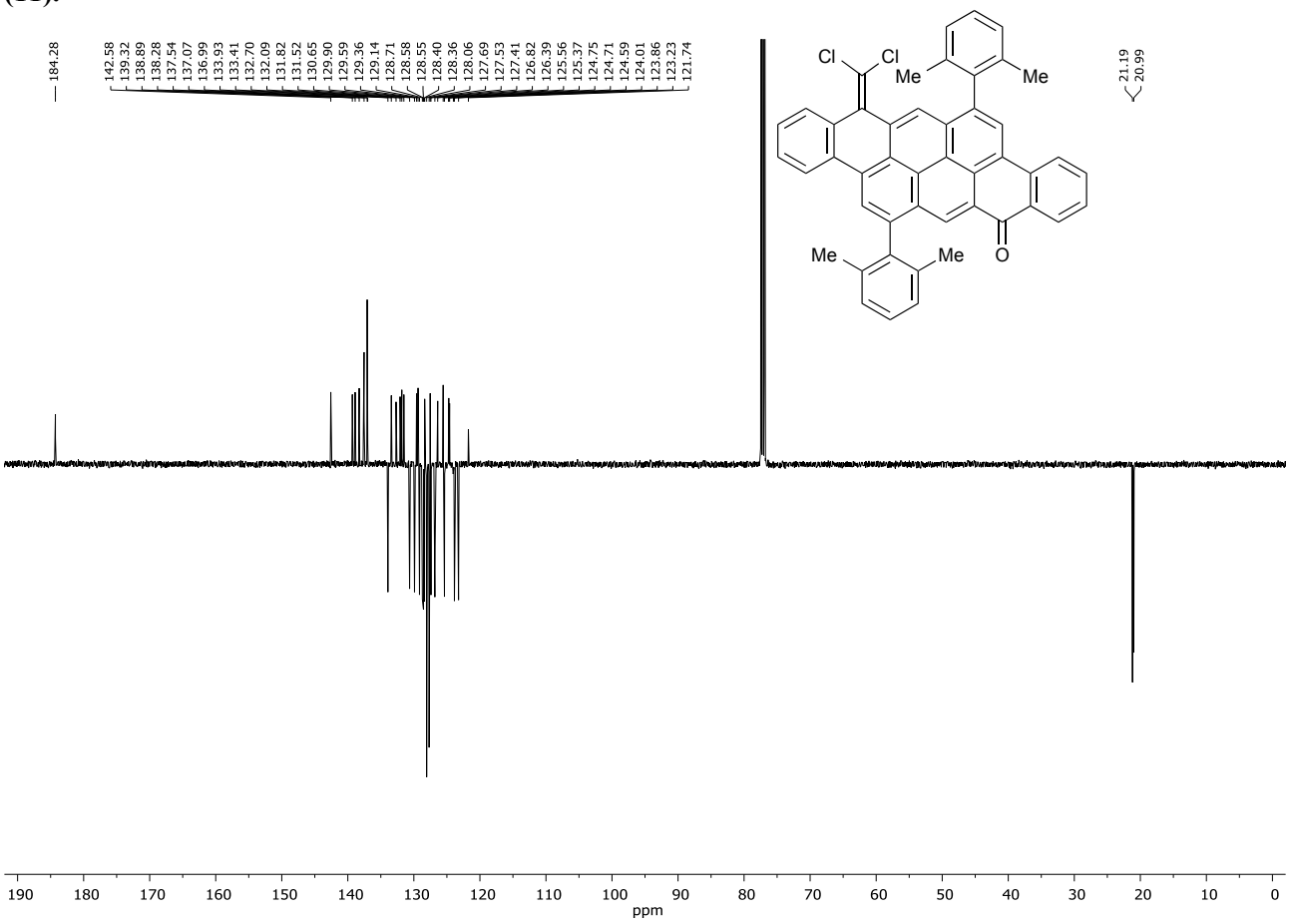


^{1}H NMR spectrum of 11 in $CDCl_3$ (500 MHz).



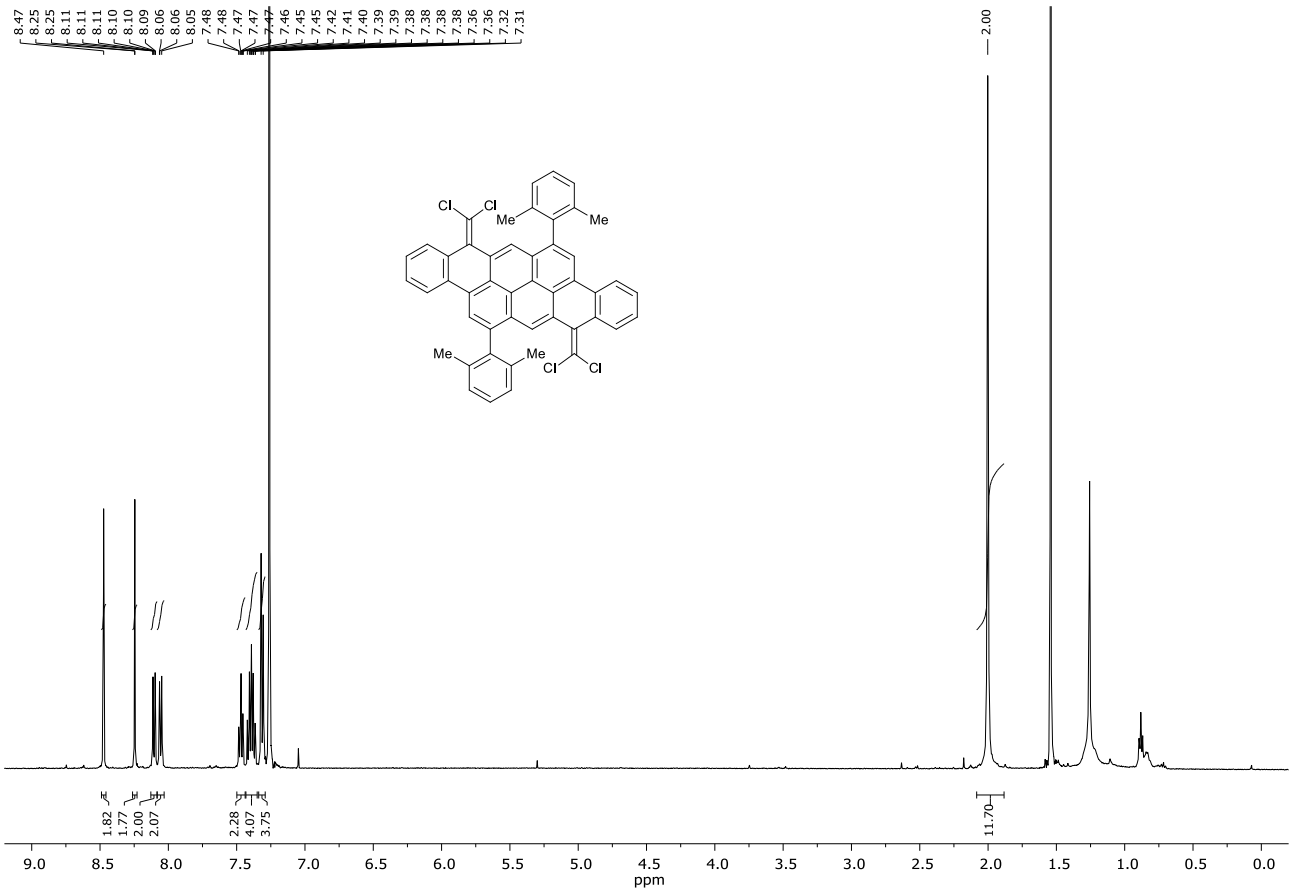
^{1}H/^{1}H COSY NMR spectrum of 11 in $CDCl_3$ (500 MHz).

16-(Dichloromethylene)-6,14-bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracen-8(16*H*)-one (11).



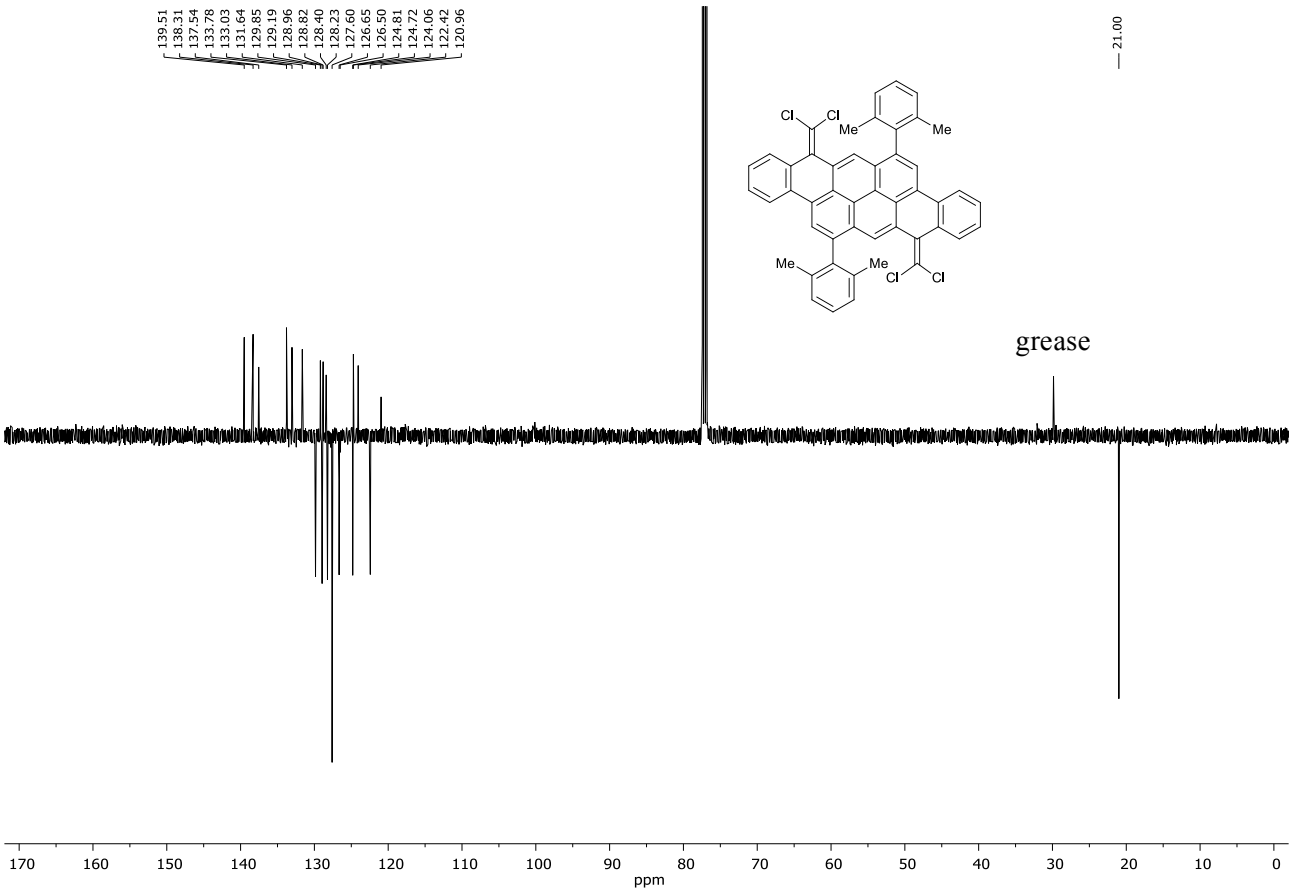
^{13}C APT NMR spectrum of 11 in $CDCl_3$ (126 MHz).

8,16-Bis(dichloromethylene)-6,14-bis(2,6-dimethylphenyl)-8,16-dihydrotetraceno[2,1,12,11-*opqra*]tetracene (10).



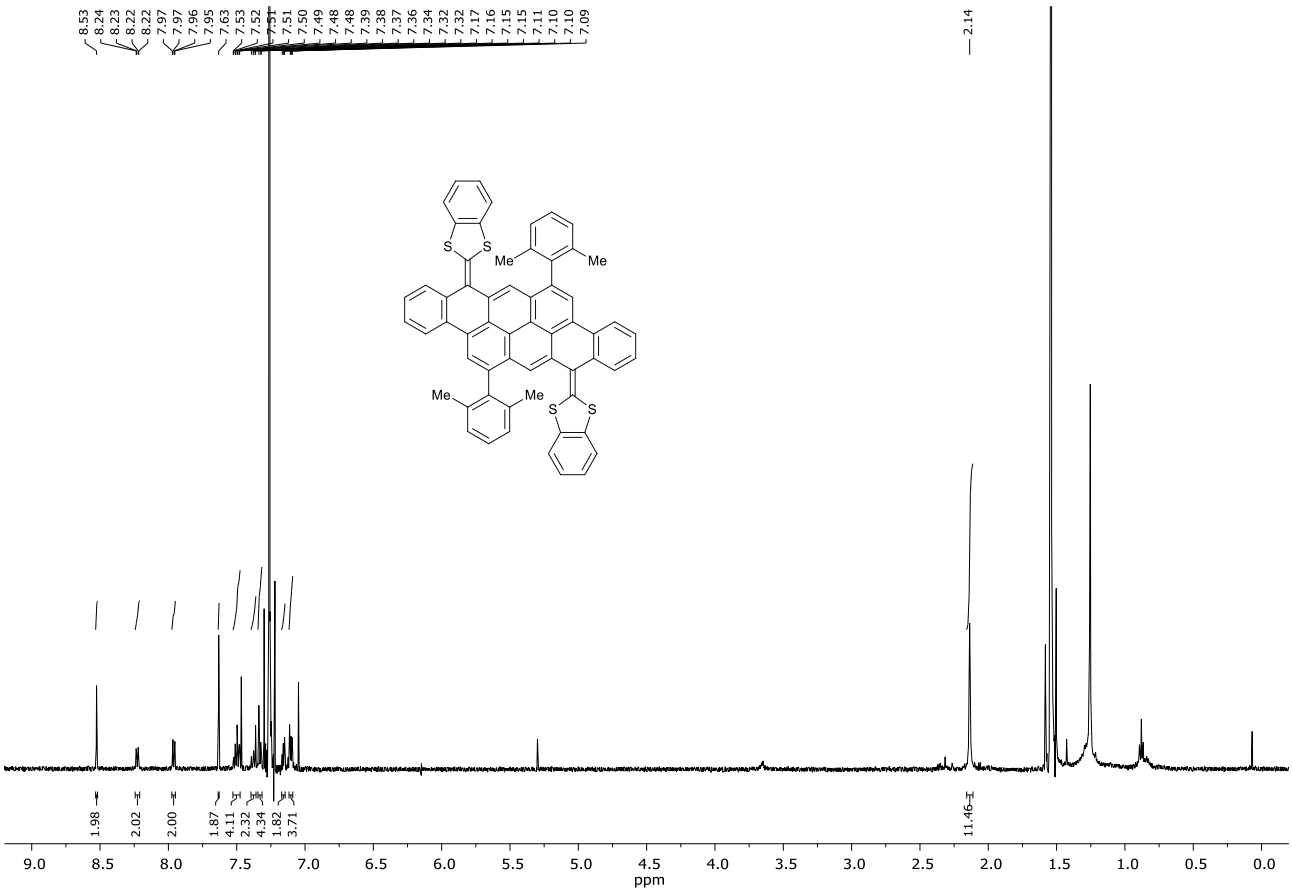
^{1}H NMR spectrum of 10 in $CDCl_3$ (500 MHz).

8,16-Bis(dichloromethylene)-6,14-bis(2,6-dimethylphenyl)-8,16-dihydrotetraceno[2,1,12,11-*opqra*]tetracene (10).



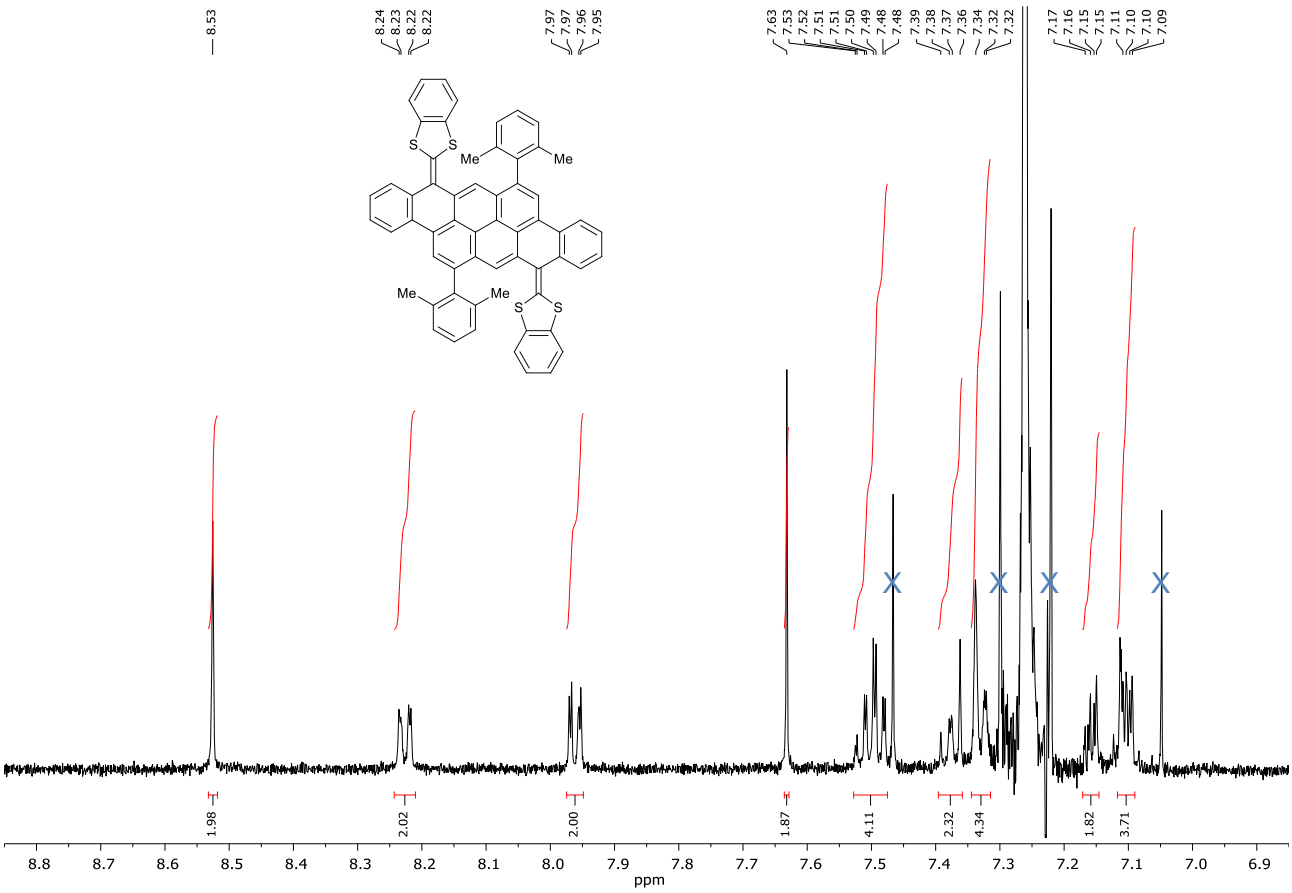
^{13}C APT NMR spectrum of 10 in $CDCl_3$ (126 MHz).

2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracene-8,16-diylidene)bis(benzo[d][1,3]dithiole) (9).



^{1}H NMR spectrum of 9 in $CDCl_3$ (500 MHz).

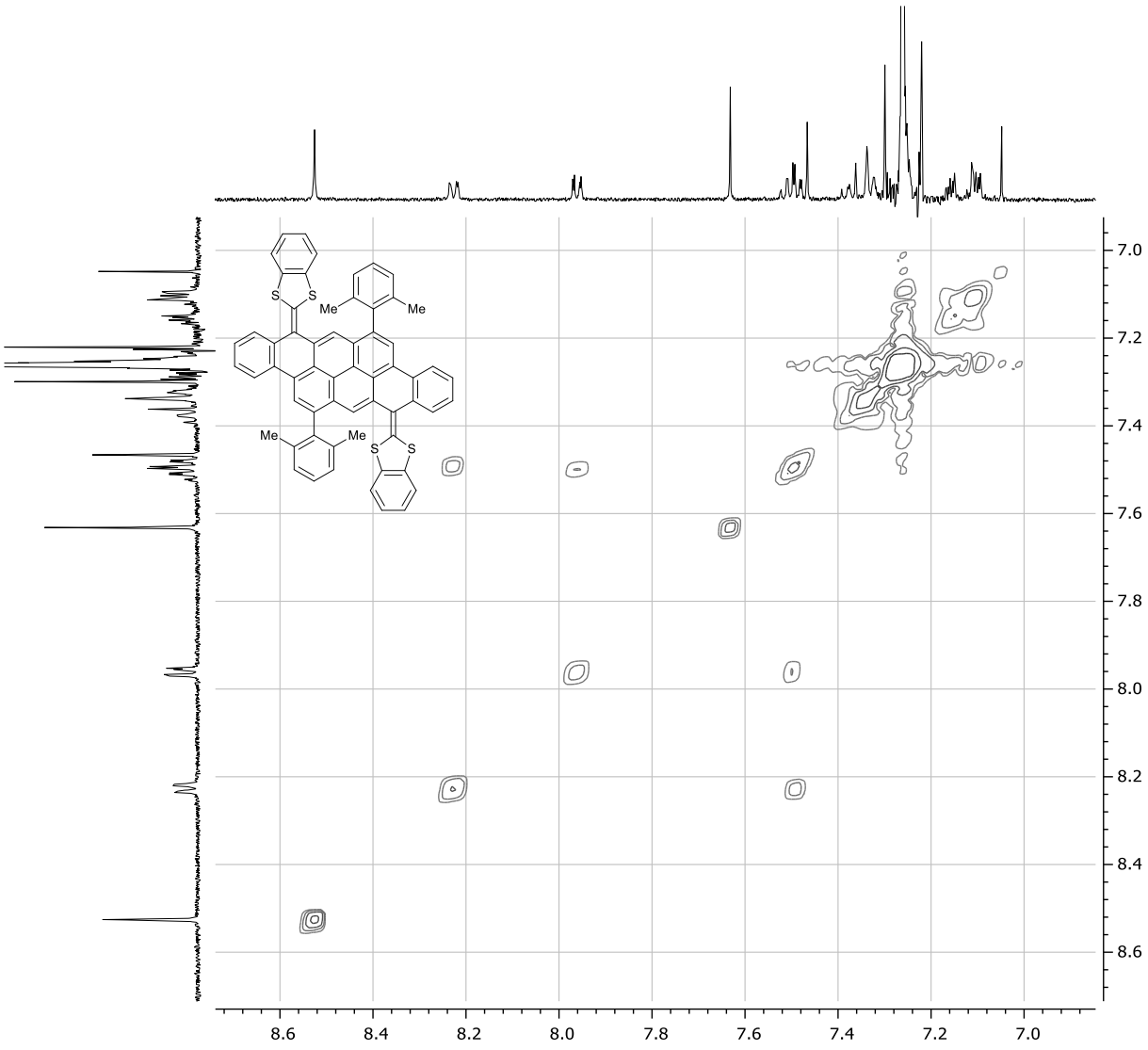
2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracene-8,16-diylidene)bis(benzo[*d*][1,3]dithiole) (9).



^{1}H NMR spectrum of 9 in $CDCl_3$ (500 MHz).

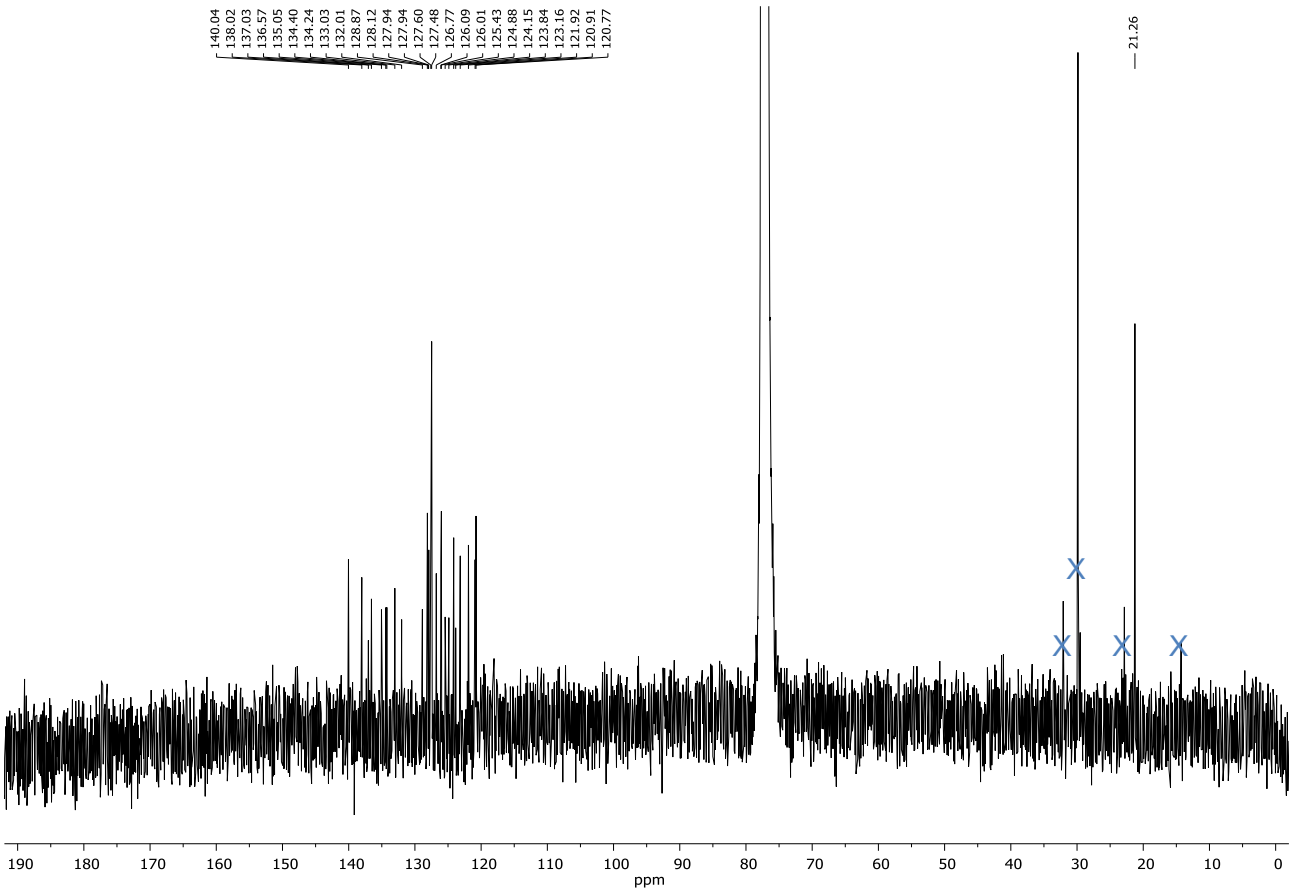
NB. The lines crossed over correspond to spinning sidebands and ^{13}C satellites.

2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracene-8,16-diylidene)bis(benzo[*d*][1,3]dithiole) (9).



^{1}H/^{1}H COSY NMR spectrum of 9 in $CDCl_3$ (500 MHz).

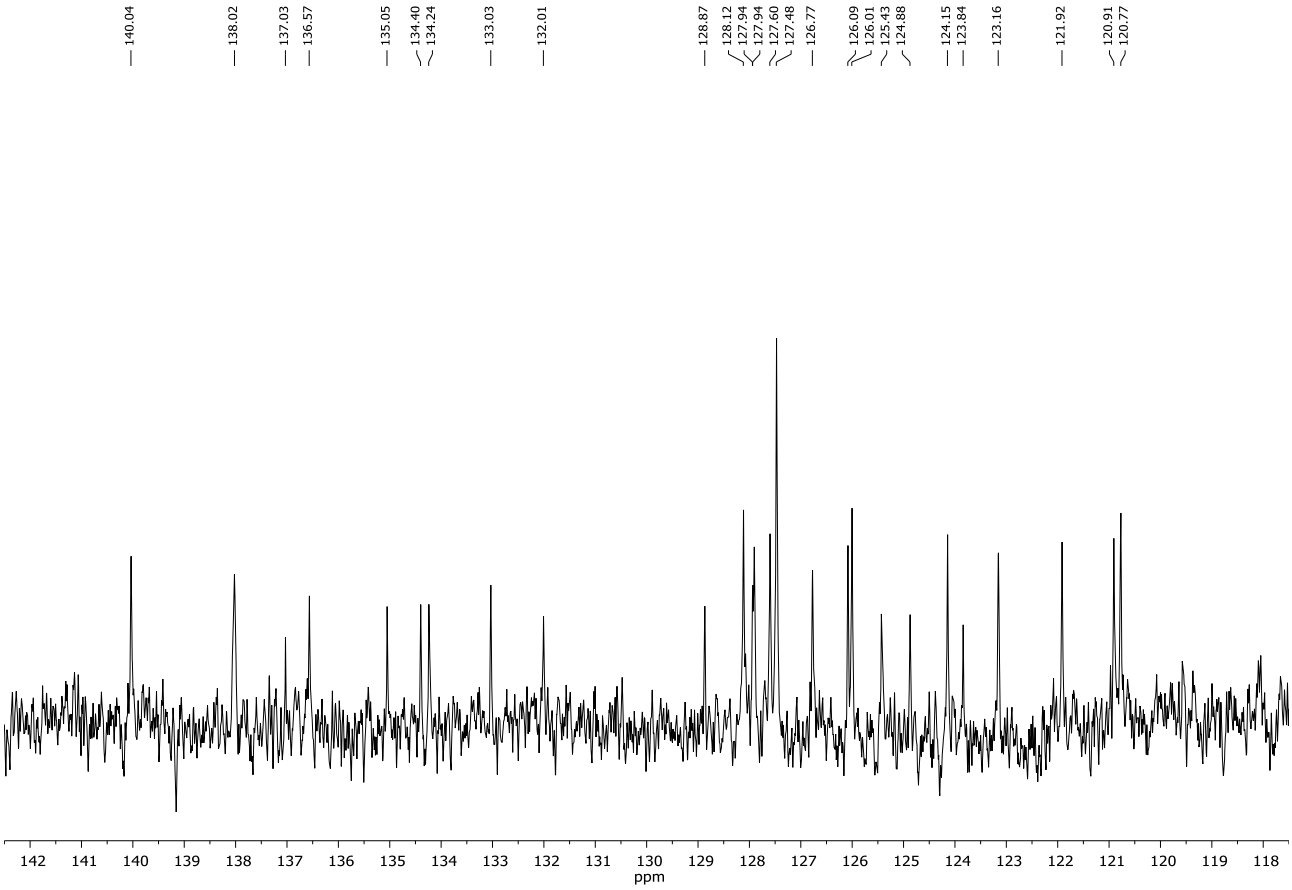
2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracene-8,16-diylidene)bis(benzo[*d*][1,3]dithiole) (9).



^{13}C APT NMR spectrum of 9 in $CDCl_3$ (126 MHz).

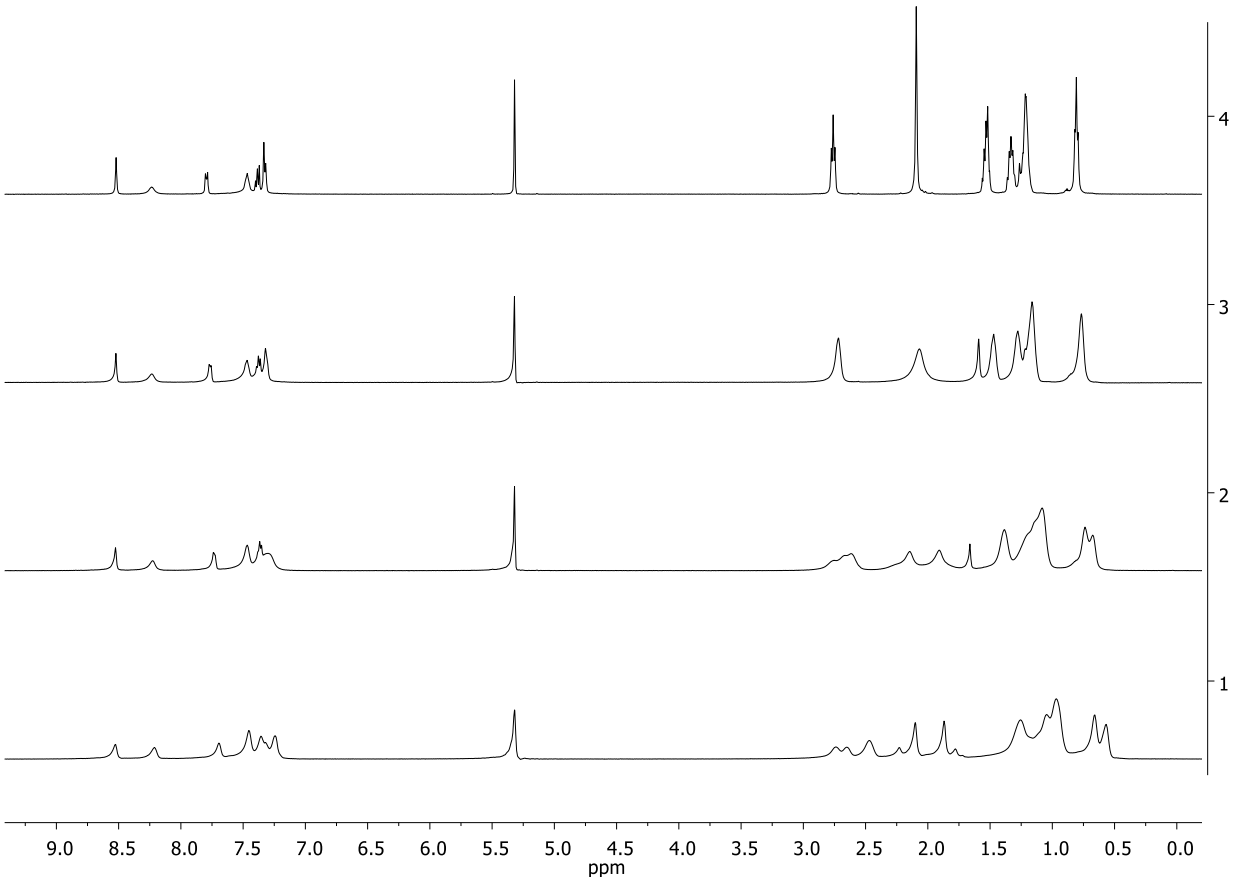
Note: The lines crossed over correspond to residual aliphatic impurities.

2,2'-(6,14-Bis(2,6-dimethylphenyl)tetraceno[2,1,12,11-*opqra*]tetracene-8,16-diylidene)bis(benzo[*d*][1,3]dithiole) (9).

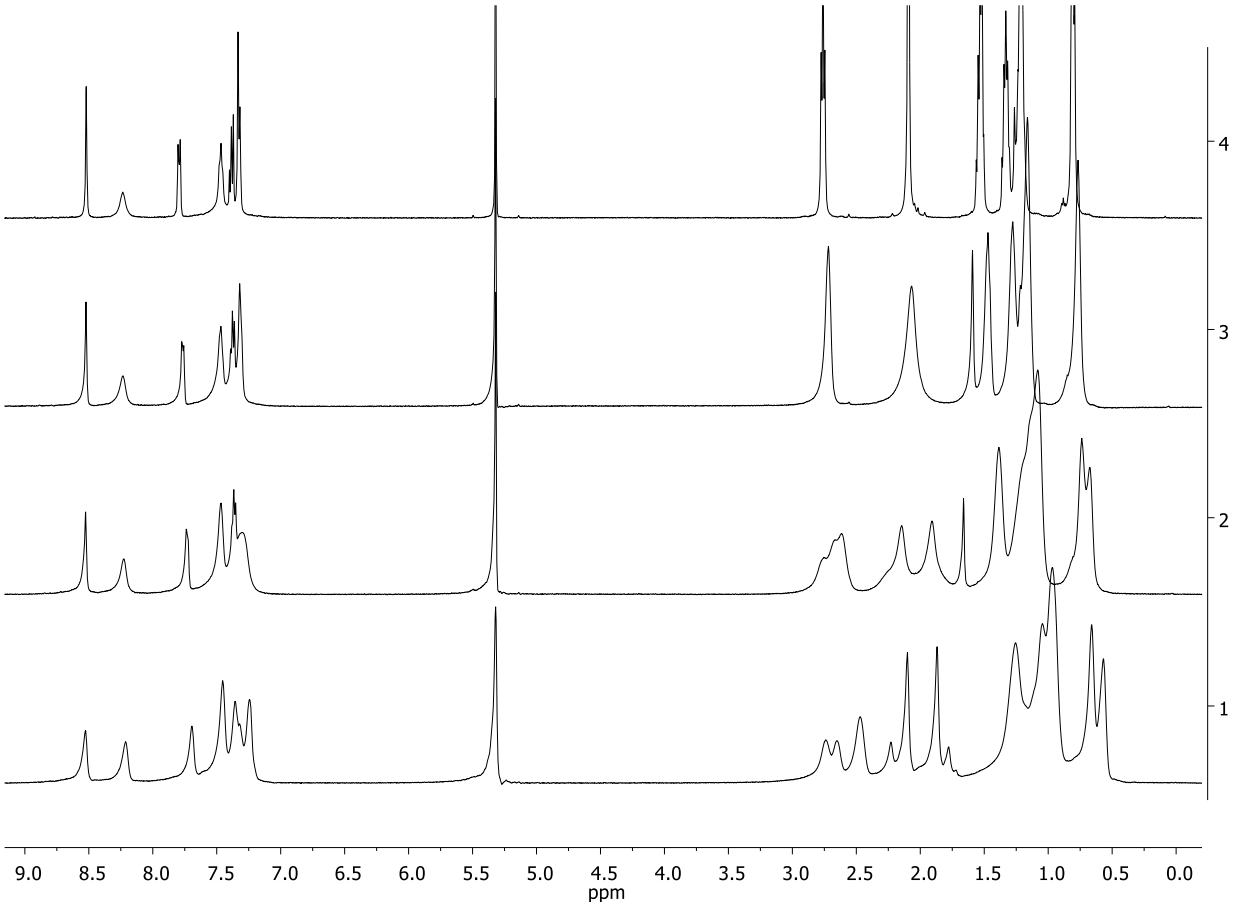


^{13}C APT NMR spectrum of 9 in $CDCl_3$ (126 MHz), zoom of aromatic region (142 – 118 ppm).

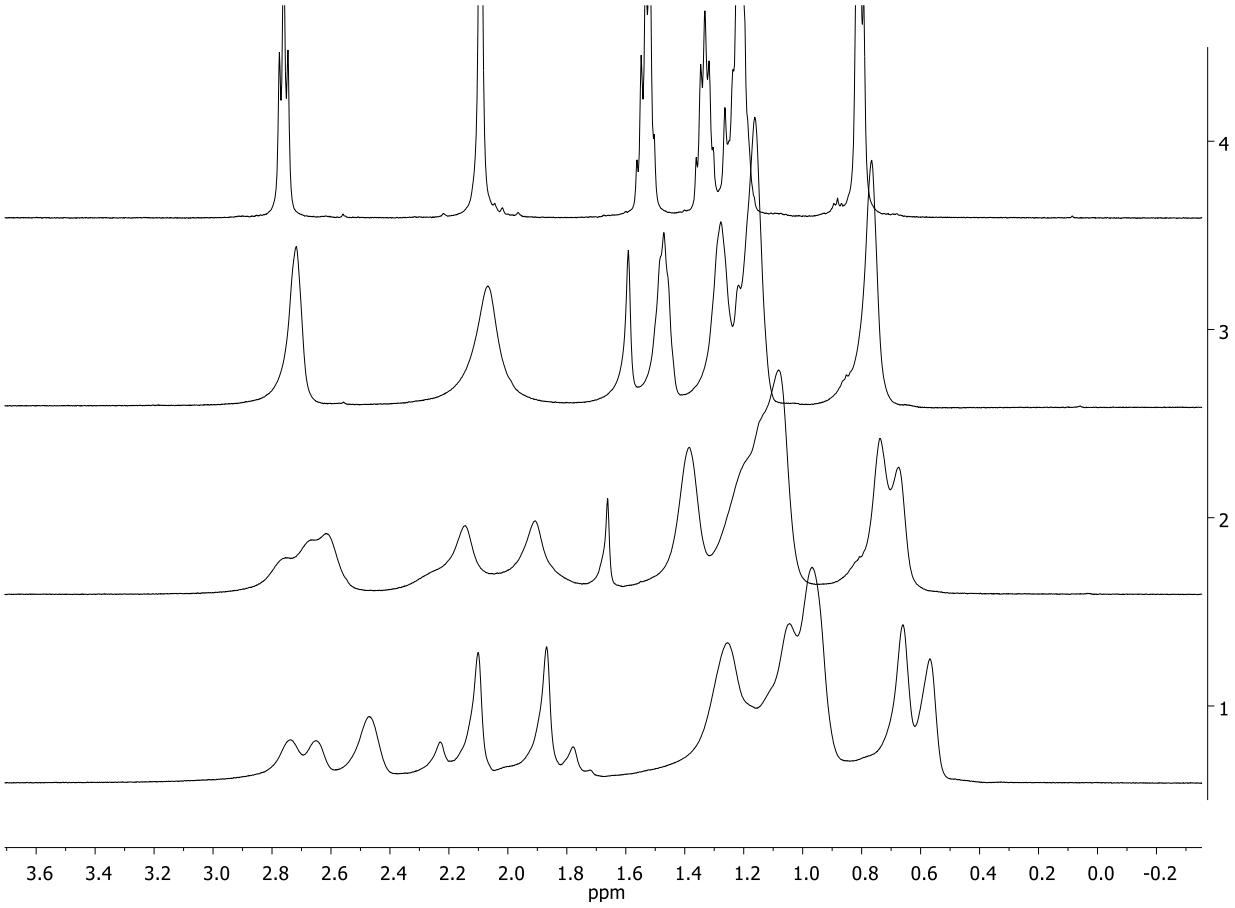
Variable Temperature NMR Experiments



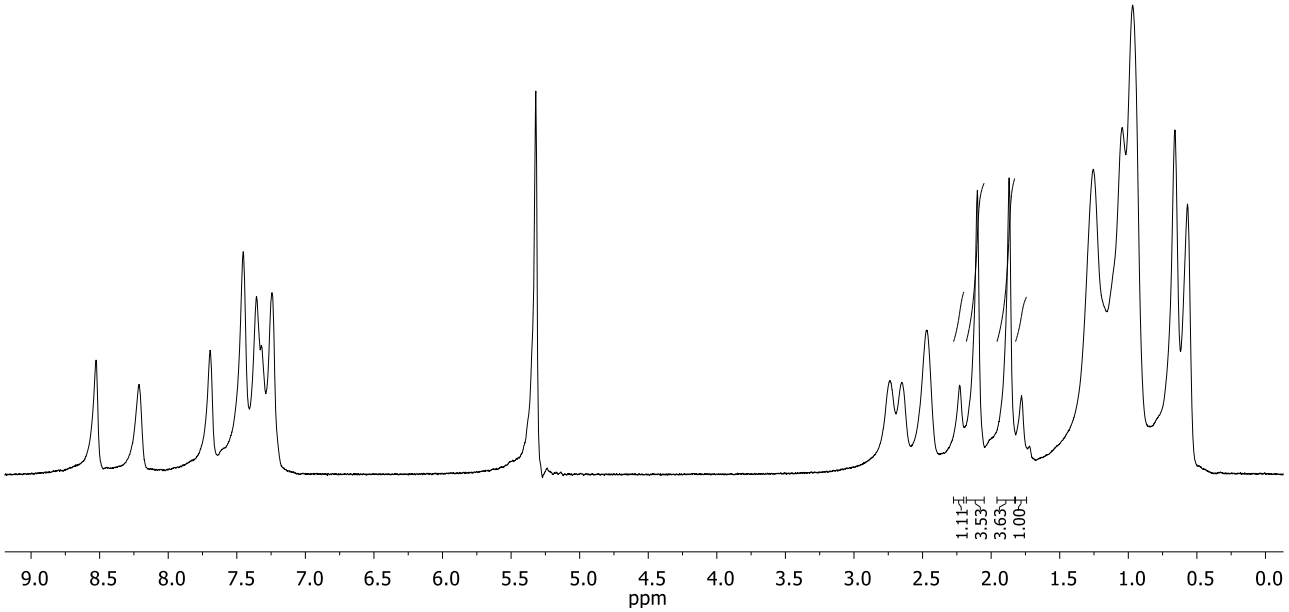
Stacked ^{1}H-NMR spectra (500 MHz) of 8b in CD_2Cl_2, from top to bottom at 300 K, 270 K, 240 K and 211 K.



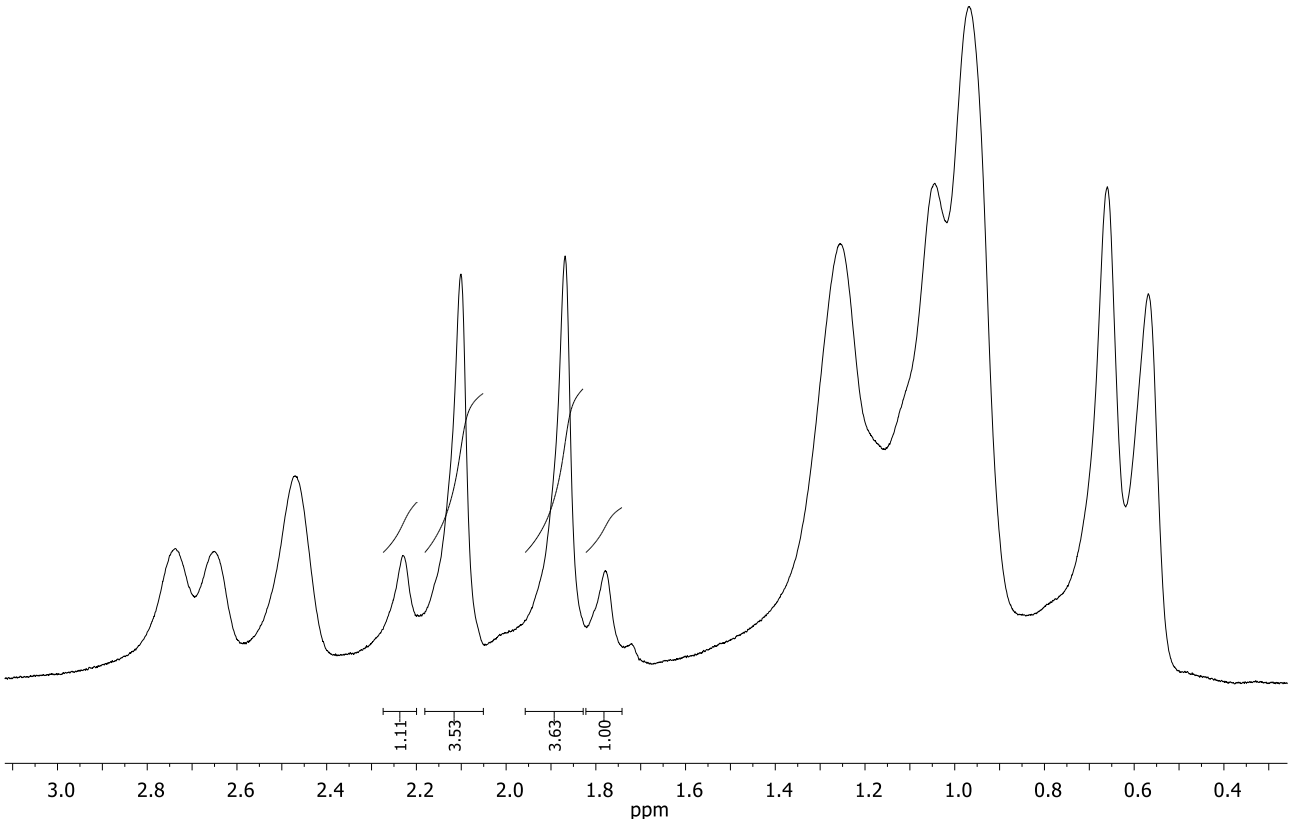
Stacked ^{1}H-NMR spectra (500 MHz) of 8b in CD_2Cl_2, from top to bottom at 300 K (some signals cut off at top), 270 K, 240 K and 211 K.



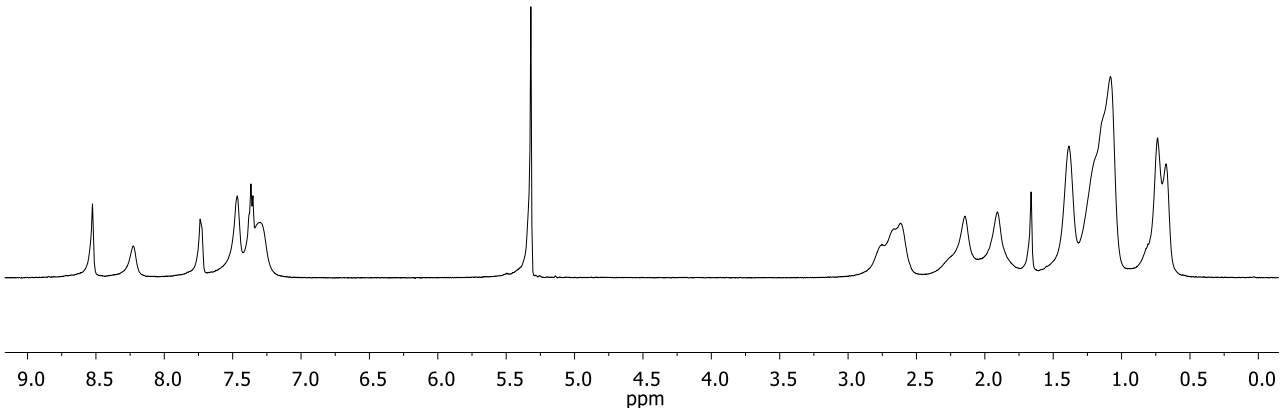
Stacked ^{1}H-NMR spectra (500 MHz) (selected region) of 8b in CD_2Cl_2, from top to bottom at 300 K (signals cut off at top), 270 K, 240 K and 211 K.



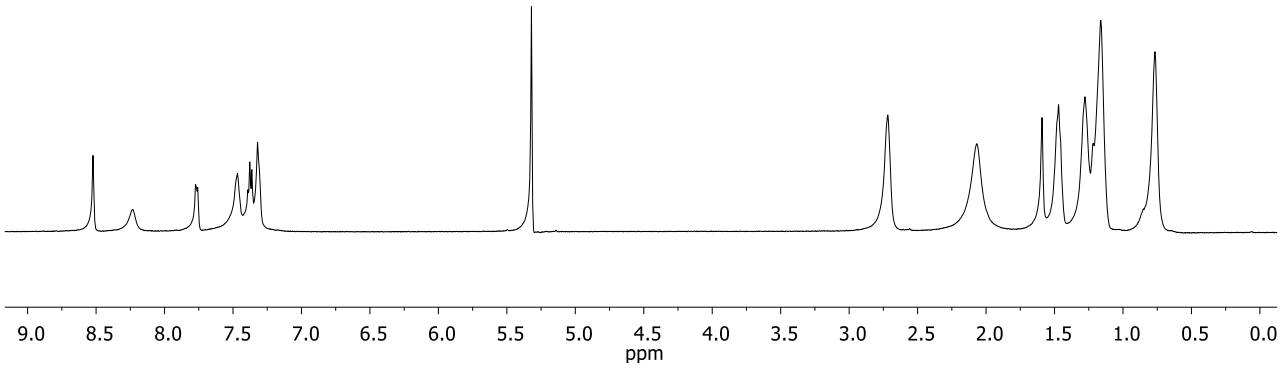
^{1}H-NMR spectrum (500 MHz) of 8b in CD_2Cl_2 at 211 K. The integrated signals are assigned to the Me protons of the 2,6-dimethylphenyl groups.



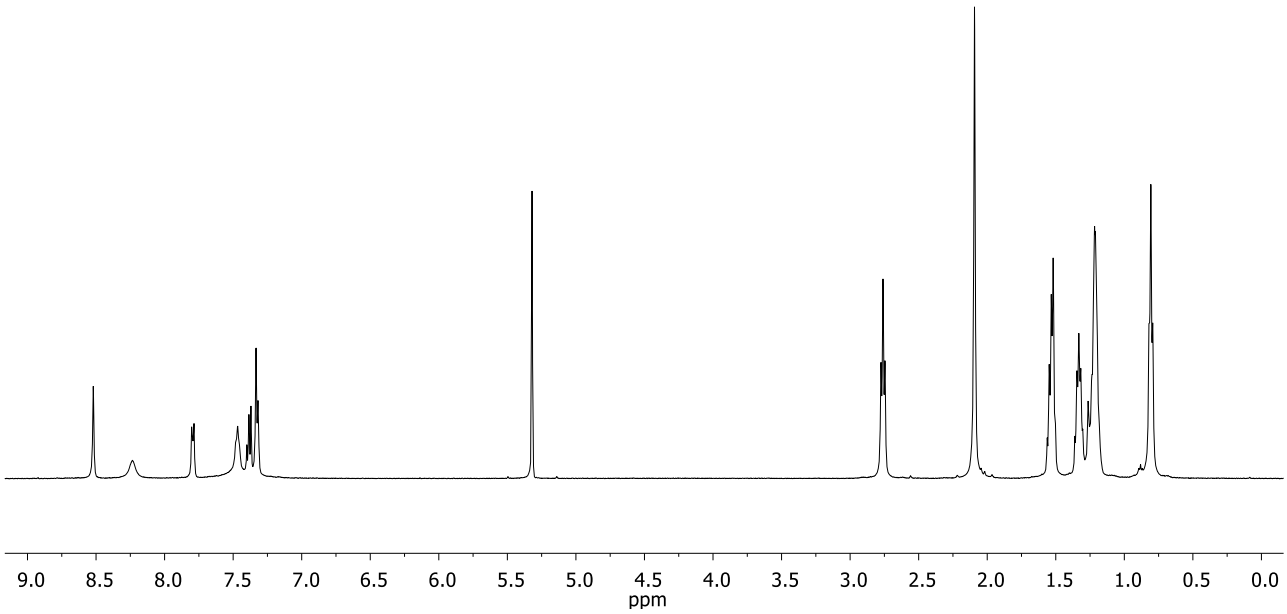
^{1}H-NMR spectrum (500 MHz) of 8b in CD_2Cl_2 at 211 K. The integrated signals are assigned to the Me protons of the 2,6-dimethylphenyl groups.



^{1}H-NMR spectrum (500 MHz) of 8b in CD_2Cl_2 at 240 K.



^{1}H-NMR spectrum (500 MHz) of 8b in CD_2Cl_2 at 270 K.



^{1}H-NMR spectrum (500 MHz) of 8b in CD_2Cl_2 at 300 K.