ESI

Diversity-Oriented Synthesis of Tetrathia[8]circulenes by Sequential C–H Borylation and Annulation

Shohei Kato,† Yuma Serizawa,† Daisuke Sakamaki,‡ Shu Seki,‡ Yoshihiro Miyake,*,† and Hiroshi Shinokubo†

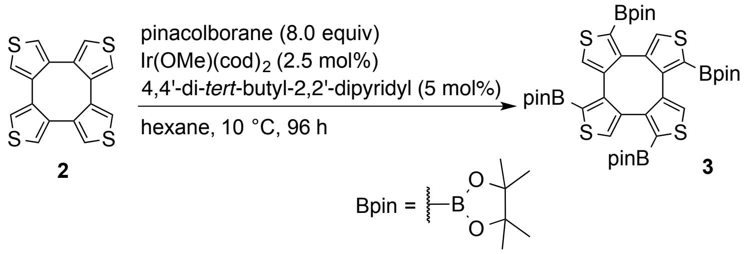
†Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya, 464-8603, Japan.

‡Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan.

Instrumentation and Materials

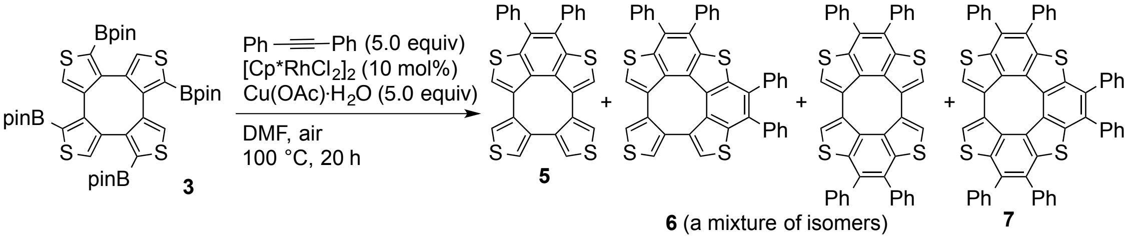
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ ($\delta = 7.260$ ppm) for ^{1}H NMR, and $CDCl_3$ ($\delta = 77.0$ ppm) for ^{13}C NMR. UV/vis absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V670 spectrometer. Mass spectra were recorded on a Bruker microTOF using positive mode ESI-TOF and APCI-TOF method for acetonitrile solutions. Melting points were measured by a SRS MPA100 OptiMelt Automated Melting Point System. Gel permeation chromatography (GPC) was performed using a JAI model LC-928 recycling preparative HPLC equipped either with JAIGEL-2H-40 and -2.5H-40 columns (40 x 600 mm x 2) with $CHCl_3$ as eluent. Solvents were dried by the general methods, and degassed before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Cyclic tetrathiophene **2**,[S1] diarylalkynes **4a-4c**,[S2] dialkylalkynes **4g-4i**,[S3] and **4j**[S4] were prepared according to the literature procedures.

Borylation of cyclic tetrathiophene 2.



In a 50 mL Schlenk flask were placed $[Ir(OMe)(cod)]_2$ (16.6 mg, 2.5 mol%) and pinacolborane (1.16 mL, 8.0 equiv) under N_2, and then a hexane solution of 4,4'-di-*tert*-butyl-2,2'-dipyridyl (13.4 mg, 5 mol% / 5 mL) was added at room temperature. After stirring for 15 min, **2** (329 mg, 1.00 mmol) was added to the solution. Then, the reaction mixture was stirred for 96 h at 10 °C. After the solution was concentrated *in vacuo*, the residue was purified by column chromatography (florisil) with CH_2Cl_2 to give a colorless oil. The resulting oil was purified by GPC with $CHCl_3$ as an eluent to give a white solid. After recrystalization from heptane, **3** was obtained as white crystals (273 mg, 0.329 mmol, 33% yield), m.p. 264.5 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 4H), 1.22 (s, 24H), 1.21 (s, 24H). ^{13}C NMR ($CDCl_3$) δ 145.6, 139.3, 132.3, 83.6, 25.1, 24.4. HRMS (APCI) Calcd. for $C_{40}H_{53}B_4O_8S_4$ [M+H]: 833.3016. Found: 833.3053.

Rh-Catalyzed Annulation of 3 with diphenylacetylene



In a Schlenk flask were placed **3** (60 mg, 72.1 mmol), diphenylacetylene (64.2 mg, 5.0 equiv), $[Cp^*RhCl_2]_2$ (4.5 mg, 10 mol%), $Cu(OAc)_2 \cdot H_2O$ (14.4 mg, 5.0 equiv) and DMF (1.0 mL) under air. The reaction mixture was stirred for 20 h at 100 °C. The suspension was poured into 2 N aq. HCl and the resulting mixture was extracted with $CHCl_3$ (15 mL x 3). The combined organic layer was washed with 2 N aq. HCl and brine, then dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2) with hexane/$CHCl_3$ to give **5** (7.9 mg, 15.7 μmol, 22% yield), **6** (10.5 mg, 15.4 μmol, 21% yield) and **7** (10.0 mg, 11.7 μmol, 16%).

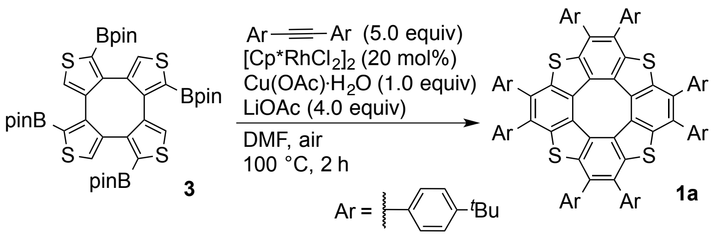
5: A white solid, m.p. 161.5 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 7.61 (s, 2H), 7.42 (d, J = 3.8 Hz, 2H), 7.28 (br, 10H), 7.10 (d, J = 3.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 141.7, 138.6, 137.5, 136.0, 134.6, 131.8, 131.7, 128.3, 127.9, 127.7, 126.0, 125.2. HRMS (APCI) Calcd. for $C_{30}H_{17}S_4$ [M+H]: 505.0208. Found:

505.0220.

6: A white solid, m.p. 174.3 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 7.83 (s), 7.57 (s), 7.50 (br), 7.39 (br), 7.31 (br), 7.29 (br), 7.28 (s), 7.19 (br), 6.99 (br). ^{13}C NMR ($CDCl_3$) δ 142.2, 141.9, 138.64, 138.59, 135.9, 134.5, 132.7, 132.01, 131.96, 131.44, 131.38, 130.6, 130.3, 130.0, 128.4, 128.3, 128.1, 127.74, 127.69, 126.3. HRMS (APCI) Calcd. for $C_{44}H_{25}S_4$ [M+H]: 681.0834. Found: 681.0800.

7: A white solid, m.p. > 400 °C. ^{1}H NMR ($CDCl_3$ / CS_2 = 10 / 1) δ 7.84 (s, 2H), 7.32-7.18 (m, 30H). ^{13}C NMR ($CDCl_3$ / CS_2 = 10 / 1) δ 141.7, 141.5, 141.3, 138.7, 138.6, 138.5, 134.5, 133.5, 133.0, 132.0, 131.4, 131.0, 130.7, 130.5, 130.4, 128.7, 128.30, 128.25, 128.2, 127.74, 127.70. HRMS (APCI) Calcd. for $C_{58}H_{33}S_4$ [M+H]: 857.1460. Found: 857.1421.

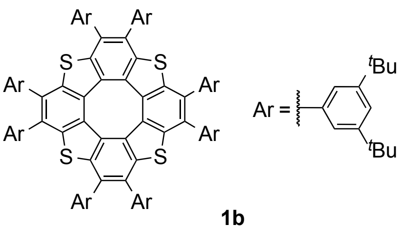
Rh-Catalyzed Annulation of 3 with alkynes 4.



Typical procedure for rhodium-catalyzed annulation of **3** with an alkyne is described below. In a Schlenk flask were placed **3** (40 mg, 48.1 μmol), bis(*p*-tert-butylphenyl)acetylene (**4a**) (70.0 mg, 5.0 equiv), $[Cp^*RhCl_2]_2$ (5.9 mg, 20 mol%), $Cu(OAc)_2 \cdot H_2O$ (9.6 mg, 1.0 equiv), LiOAc (12.7 mg, 4.0 equiv) and DMF (1.0 mL) under air. The reaction mixture was stirred for 2 h at 100 °C. The suspension was poured into 2 N aq. HCl and the resulting mixture was extracted with $CHCl_3$ (15 mL x 3). The combined organic layer was washed with 2 N aq. HCl and brine, then dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2) with hexane/$CHCl_3$ to give a yellow solid. After recrystalization from $CHCl_3$/hexane, **1a** was obtained (19.4 mg, 13.1 μmol, 27% yield).

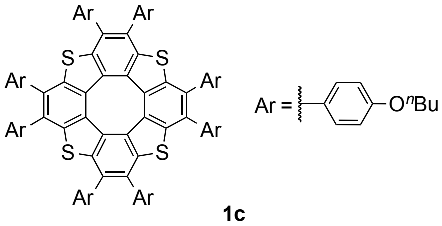
1a: A yellow solid, m.p. > 400 °C. ^{1}H NMR ($CDCl_3$) δ 7.19 (s, 32H), 1.24 (s, 72H). ^{13}C NMR ($CDCl_3$) δ 150.2, 140.8, 136.1, 134.1, 130.5, 130.3, 124.7, 34.6, 31.4. HRMS (APCI) Calcd. for $C_{104}H_{105}S_4$ [M+H]: 1482.7126. Found: 1482.7109.

Isolated yields and spectroscopic data of other products are as follows:



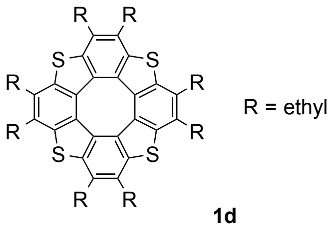
1b

1b: 26% yield (DMF (5 mL) was used as a solvent.). A yellow solid, m.p. > 400 °C. ^{1}H NMR ($CDCl_3$) δ 7.18-7.15 (m, 24H), 1.12 (s, 144H). ^{13}C NMR ($CDCl_3$) δ 150.0, 140.9, 138.4, 134.6, 130.4, 125.5, 120.8, 34.8, 31.5. HRMS (APCI) Calcd. for $C_{136}H_{169}S_4$ [M+H]: 1931.2135. Found: 1931.2082.



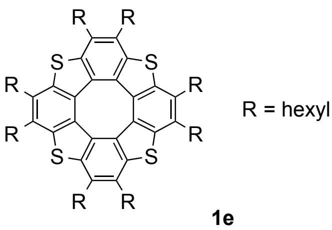
1c

1c: 23% yield. A yellow solid, m.p 264.5 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 7.10 (d, J = 7.5 Hz, 16H), 6.62 (br, 16H), 3.80 (br, 16H), 1.74 (quint, J = 7.3 Hz, 16H), 1.48 (sext, J = 7.3 Hz, 16H), 0.97 (t, J = 7.3 Hz, 24H). ^{13}C NMR ($CDCl_3$) δ 158.3, 141.3, 133.7, 131.9, 131.2, 130.2, 114.1, 31.6, 19.4, 14.1. HRMS (ESI) Calcd. for $C_{104}H_{104}O_8S_4Na$ [M+Na]: 1632.6539. Found: 1632.6548.



1d

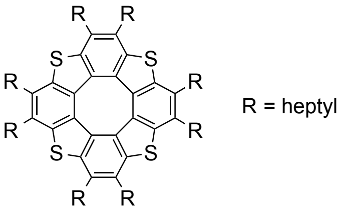
1d: 33% yield. A yellow solid, m.p. 325.2 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 3.34 (q, J = 7.8 Hz, 16H), 1.53 (t, J = 7.8 Hz, 24H). ^{13}C NMR ($CDCl_3$) δ 137.8, 133.1, 130.3, 25.6, 14.3. HRMS (APCI) Calcd. for $C_{40}H_{41}S_4$ [M+H]: 649.2086. Found: 649.2055.



1e

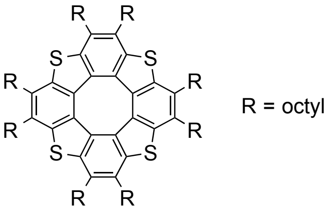
1e: 33% yield. A yellow solid, m.p. 262.3 °C (decomp.). ^{1}H NMR ($CDCl_3$) δ 3.25 (t, J = 7.6 Hz, 16H), 1.89 (quint, J = 7.6 Hz, 16H), 1.63 (quint, J = 7.6 Hz, 16H), 1.43 (m, 32H), 0.96 (t, J = 7.6 Hz, 24H). ^{13}C NMR ($CDCl_3$) δ 138.0, 132.2, 130.2, 32.7, 31.8, 30.1, 29.8, 22.8, 14.3. HRMS (APCI) Calcd. for

$C_{72}H_{105}S_4$ [M+H]: 1097.7094. Found: 1097.7064.



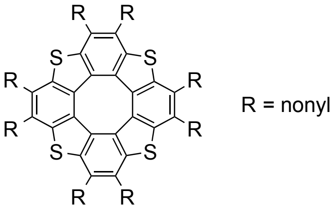
1f

1f: 25% yield. A yellow solid, m.p. 212.2 °C (decomp.). ^1H NMR ($CDCl_3$) δ 3.24 (t, J = 7.6 Hz, 16H), 1.88 (quint, J = 7.6 Hz, 16H), 1.61 (quint, J = 7.6 Hz, 16H), 1.47 (quint, J = 7.6 Hz, 16H), 1.37 (m, 32H), 0.94 (t, J = 7.6 Hz, 16H). ^{13}C NMR ($CDCl_3$) δ 138.0, 132.2, 130.2, 32.7, 32.0, 30.4, 29.8, 29.3, 23.0, 14.3. HRMS (APCI) Calcd. for $C_{80}H_{121}S_4$ [M+H]: 1209.8346. Found: 1209.8354.



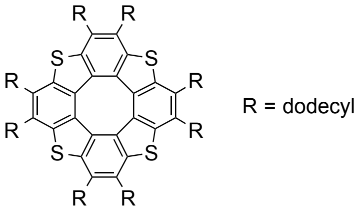
1g

1g: 20% yield. A yellow solid, m.p. 181.4 °C (decomp.). ^1H NMR ($CDCl_3$) δ 3.25 (t, J = 7.5 Hz, 16H), 1.89 (quint, J = 7.5 HZ, 16H), 1.62 (quint, J = 7.5 Hz, 16H), 1.47 (quint, J = 7.5 Hz, 16H) 1.35 (m, 48H), 0.91 (t, J = 7.5 Hz, 24H). ^{13}C NMR ($CDCl_3$) δ 138.0, 132.2, 130.2, 32.7, 32.1, 30.5, 29.8, 29.6, 29.5, 22.9, 14.3. HRMS (APCI) Calcd. for $C_{88}H_{137}S_4$ [M+H]: 1321.9598. Found: 1321.9577.



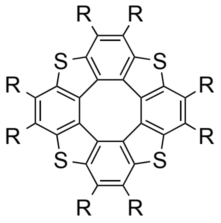
1h

1h: 20% yield. A yellow solid, m.p. 182.2 °C (decomp.). ^1H NMR ($CDCl_3$) δ 3.25 (t, J = 7.5 Hz, 16H), 1.89 (quint, J = 7.5 Hz, 16H), 1.61 (quint, J = 7.5 Hz, 16H), 1.47 (quint, J = 7.5 Hz, 16H), 1.34 (m, 64H), 0.89 (t, J = 7.5 Hz, 24H). ^{13}C NMR ($CDCl_3$) δ 138.0, 132.2, 130.2, 32.7, 32.1, 30.5, 29.8, 29.62, 29.57, 22.9, 14.3. HRMS (APCI) Calcd. for $C_{96}H_{153}S_4$ [M+H]: 1434.0882. Found: 1435.0787.



1i

1i: 16% yield (DMF (5 mL) was used as a solvent.). A yellow solid, m.p. 162.1 °C (decomp.). ^{1}H NMR (CDCl$_3$) δ 3.23 (t, J = 7.5 Hz, 16H), 1.88 (quint, J = 7.5 Hz, 16H), 1.61 (quint, J = 7.5 Hz, 16H), 1.47 (quint, J = 7.5 Hz, 16H), 1.30 (m, 112H), 0.88 (t, J = 7.5 Hz, 24H). ^{13}C NMR (CDCl$_3$) δ 138.0, 132.2, 130.2, 32.7, 32.1, 30.5, 29.94, 29.87, 29.85, 29.8, 29.63, 29.56, 22.9, 14.3. HRMS (APCI) Calcd. for $C_{120}H_{201}S_4$ [M+H]: 1771.4639. Found: 1771.4573.



R = Ph(CH$_2$)$_3$OCH$_2^-$

1j

1j: 19% yield. A yellow solid. ^{1}H NMR (CDCl$_3$) δ 7.22-7.11 (m, 40H), 5.28 (s, 16H), 3.67 (t, J = 7.0, 16H), 2.71 (t, J = 7.0, 16H), 1.96 (quint, J = 7.0, 16H). ^{13}C NMR (CDCl$_3$) δ 142.0, 139.8, 131.3, 129.7, 128.6, 128.4, 125.9, 70.1, 68.9, 32.6, 31.6. HRMS (ESI) Calcd. for $C_{104}H_{104}O_8NaS_4$ [M+Na]: 1632.6539. Found: 1632.6511.

X-Ray Diffraction Analysis

Crystals suitable for X-ray analysis of **1b**, **1d**, **3**, and **5** were obtained by recrystalization from chloroform/methanol, *o*-dichlorobenzene/acetonitrile, heptane and chloroform/hexane. X-ray diffraction data for **1b**, **1d** and **5** were taken on a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71075 Å). X-ray diffraction data for **3** were taken on a Bruker D8 QUEST X-ray diffractometer equipped with PHOTON 100 CMOS active pixel sensor detector and IμS microfocus source using Mo-Kα radiation (λ = 0.71073 Å). All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. Crystallographic data for the structures of **1b**, **1d**, **3**, and **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1405366 (**1b**), CCDC-1405367 (**1d**), CCDC-1416542 (**3**) and CCDC1405368 (**5**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

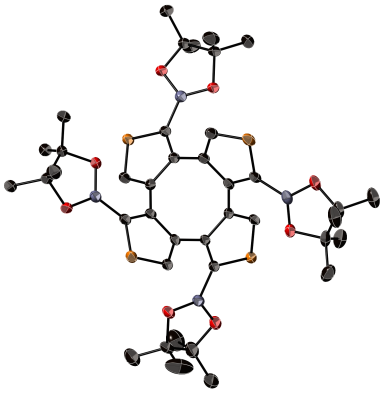


Figure S1. X-ray crystal structure of **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

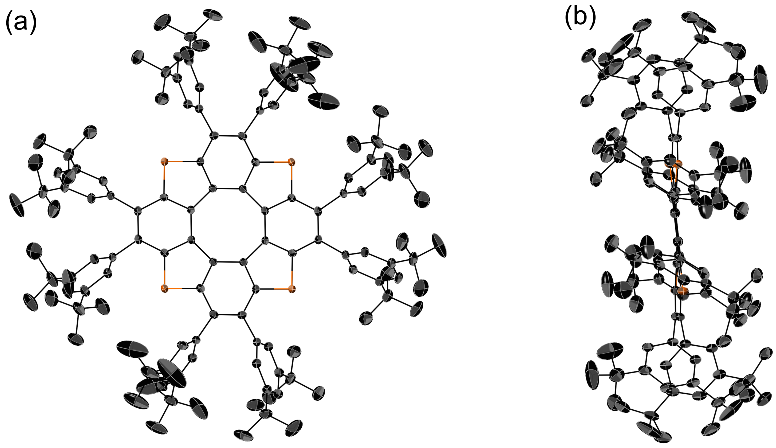


Figure S2. X-ray crystal structure of **1b** (a) top, and (b) side views. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

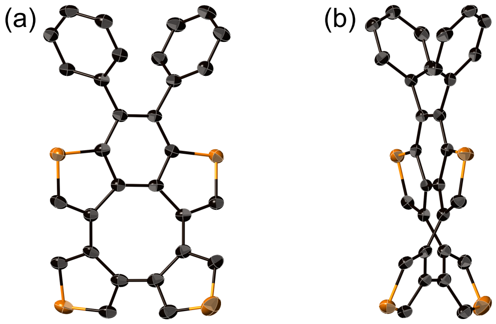


Figure S3. X-ray crystal structure of **5** (a) top, and (b) side views. Hydrogen atoms and chloroform are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

Table S1. Crystallographic data of **3**, **1b**, **1d** and **5**.

compound	**3**	**1b**	**1d**	**5**
Formula	$C_{47}H_{67}B_4O_8S_4$	$C_{140}H_{170.52}Cl_{9.78}S_4$	$C_{40}H_{40}S_4$	$C_{31}H_{18}Cl_2S_4$
Formula weight	931.48	2328.29	648.96	589.59
Crystal system	triclinic	Monoclinic	triclinic	Orthorhombic
Space group	*P*-1	*C*2/c	*P*-1	*P*ca21
Crystal color	Colorless	Yellow	Yellow	Colorless
Crystal description	Prism	Prism	Prism	Prism
a [Å]	12.2323 (6)	42.616 (7)	4.7699 (19)	25.926 (9)
b [Å]	13.9489 (7)	17.397 (3)	13.122 (5)	10.268 (4)
c [Å]	16.2345 (8)	18.769 (3)	14.121 (5)	9.738 (3)
α [°]	76.272 (2)	90	68.200 (14)	90
β [°]	81.959 (2)	98.476 (3)	74.332 (19)	90
γ [°]	78.768 (2)	90	85.09 (2)	90
V [Å^3]	2626.6 (2)	13763 (4)	790.0 (5)	2592.3 (15)
Z	2	4	1	8
d_{calcd} [g cm^{-3}]	1.178	1.124	1.364	1.511
$R1$ ($F^2 < 2\sigma < (F^2)$)	0.0548	0.0598	0.0919	0.0669
Rw (all data)	0.1563	0.1810	0.3208	0.1861
GOF	1.047	1.053	1.065	1.049
Temperature [K]	93	103	103.15	103
Structure solution	SHELXTL	SIR-97	SIR-2002	SIR-97
Structure refinement	SHELXL	SHELXL-97	SHELXL-97	SHELXL-97

Absorption Spectra.

UV/vis absorption spectra were recorded on a Shimadzu UV-2550 (for solution samples) or JASCO V670 spectrometer (for solid sample). Dilute solutions in distilled solvent in a 1 cm square quartz cuvette were used fo the absorption measurements. Absorption spectra of the solid samples were measured using a drop-cast film of **1b**,**1d** and **1f** from a methylcyclohexane suspension deposited onto a quartz substrate.

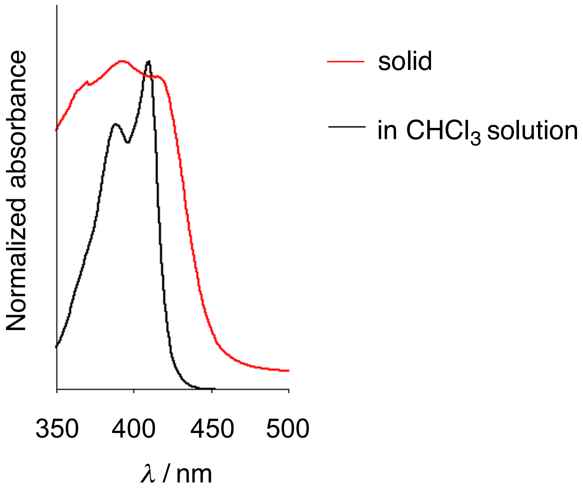


Figure S4. UV/vis absorption spectra of **1f** in solid state and in $CHCl_3$ solution.

Electrochemical Measurement

Electrochemical measurements were recorded on ALS electrochemical analyser 612C. Measurements were performed in freshly distilled dichloromethane and tetrahydrofuran with tetrabutylammonium perchlorate as an electrolyte (0.1 M). A glassy carbon electrode, a platinum wire and $Ag/AgClO_4$ were used as working, conter, and reference electrodes, respectively. The scan rate was 100 mVs^{-1}. The mesurment was performed under nitrogen atmosphere. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

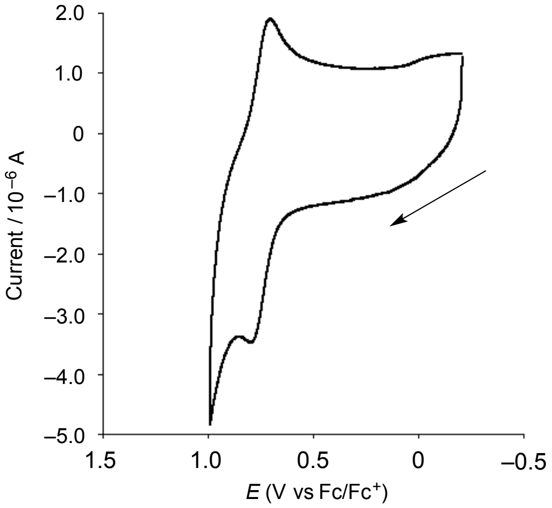


Figure S5. Cyclic voltammogram of **1b** in CH_2Cl_2.

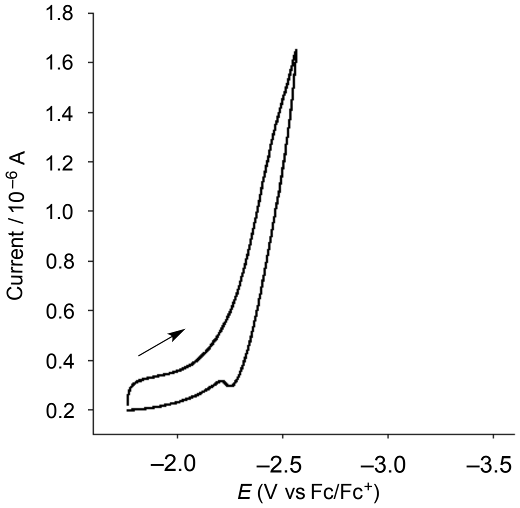


Figure S6. Cyclic voltammogram of **1b** in THF.

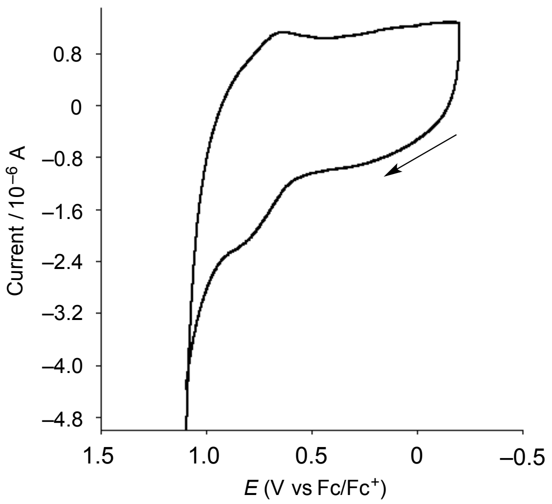


Figure S7. Cyclic voltammogram of **1f** in CH_2Cl_2.

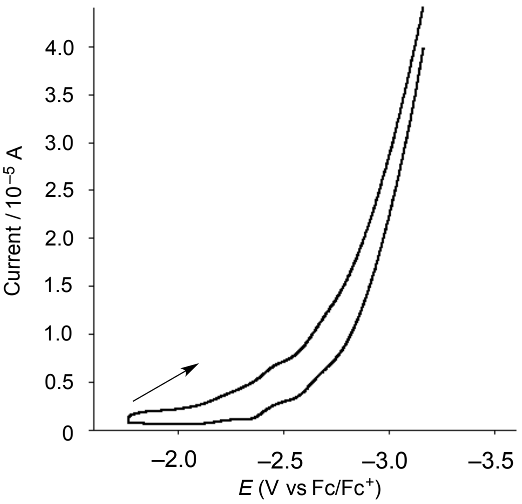


Figure S8. Cyclic voltammogram of **1f** in THF.

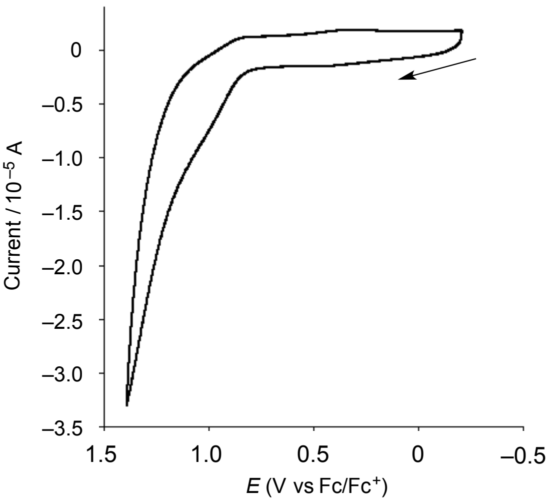


Figure S9. Cyclic voltammogram of **1j** in CH_2Cl_2.

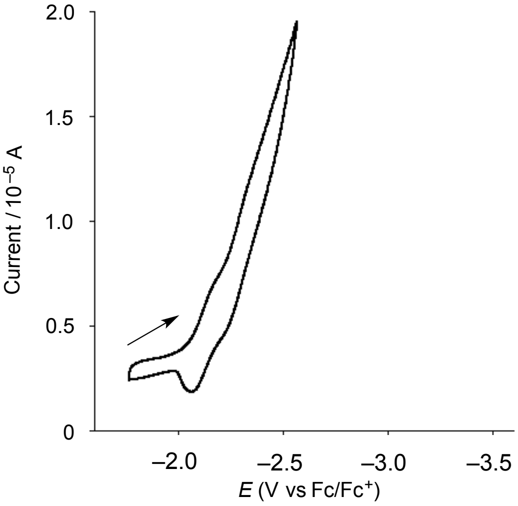


Figure S10. Cyclic voltammogram of **1j** in THF.

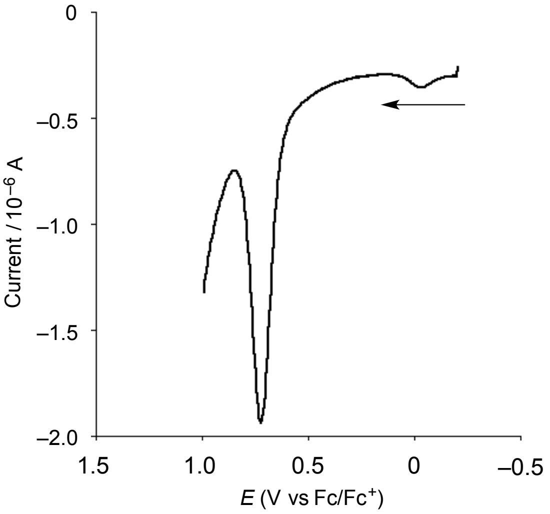


Figure S11. Differential-pulse voltammogram of **1b** in CH_2Cl_2.

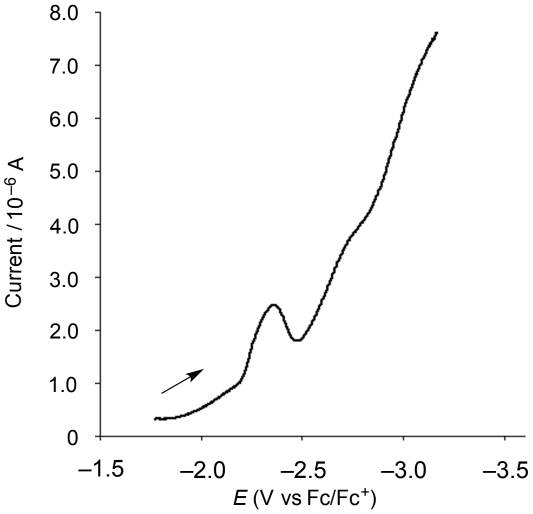


Figure S12. Differential-pulse voltammogram of **1b** in THF.

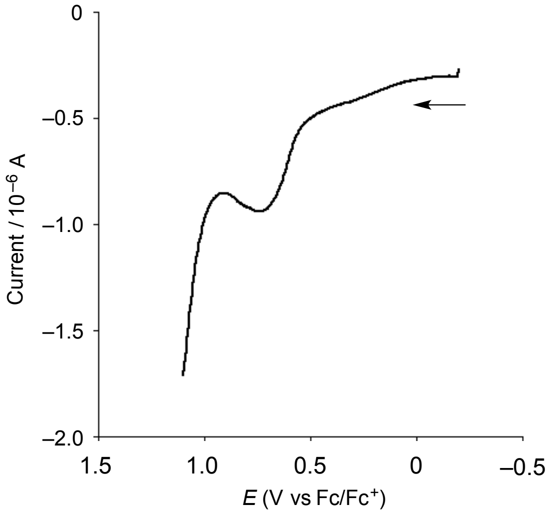


Figure S13. Differential-pulse voltammogram of **1f** in CH_2Cl_2.

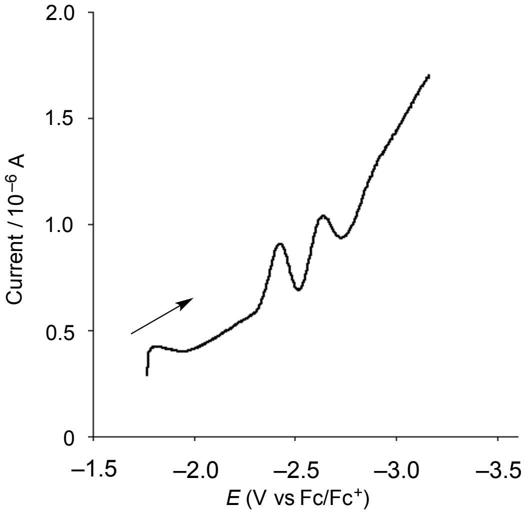


Figure S14. Differential-pulse voltammogram of **1f** in THF.

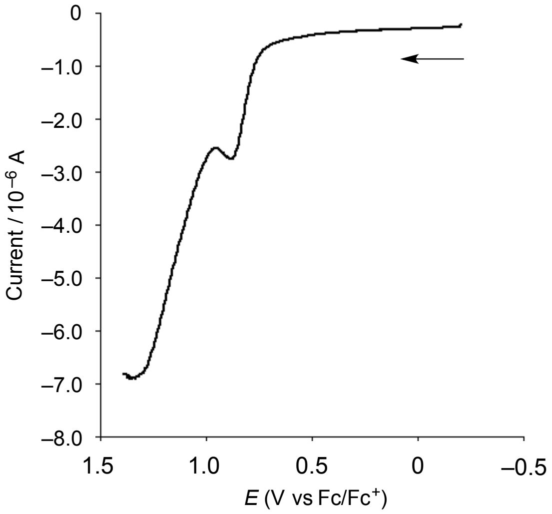


Figure S15. Differential-pulse voltammogram of **1j** in CH_2Cl_2.

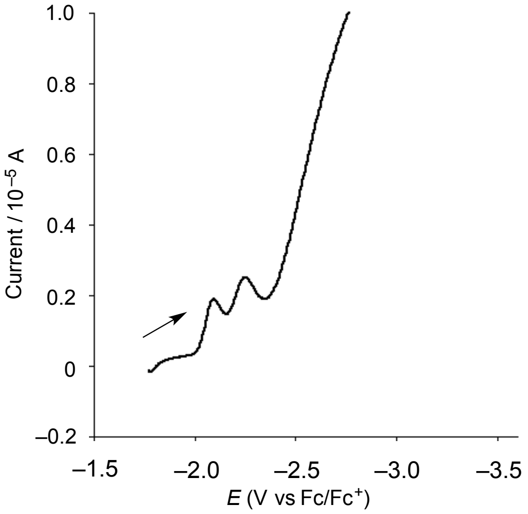


Figure S16. Differential-pulse voltammogram of **1j** in THF.

Table S2. Summary of redox potentials (V vs Fc/Fc^+).

compound	E_{ox}	E_{red}^1	E_{red}^2	ΔE
1b	0.723	–2.36	-	3.08
1f	0.738	–2.43	–2.64	3.17
1j	0.883	–2.10	–2.25	2.98

ADF Calculations.

Calculations of electronic couping (V) between neighboring molecules in the crysytalline state were performed using PW91 functional with the DZP basic set implemented in the ADF2014 program,[S5] and the results were summarized in Figures S16 and S17.

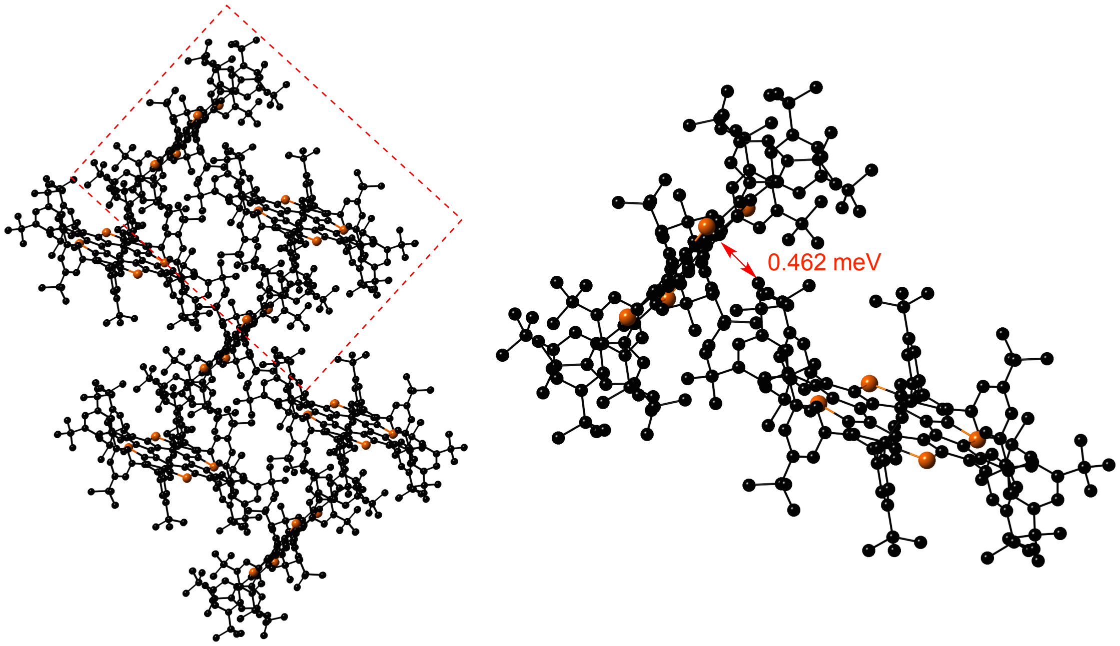


Figure S17. X-ray crystal structure and electron coupling of **1b**.

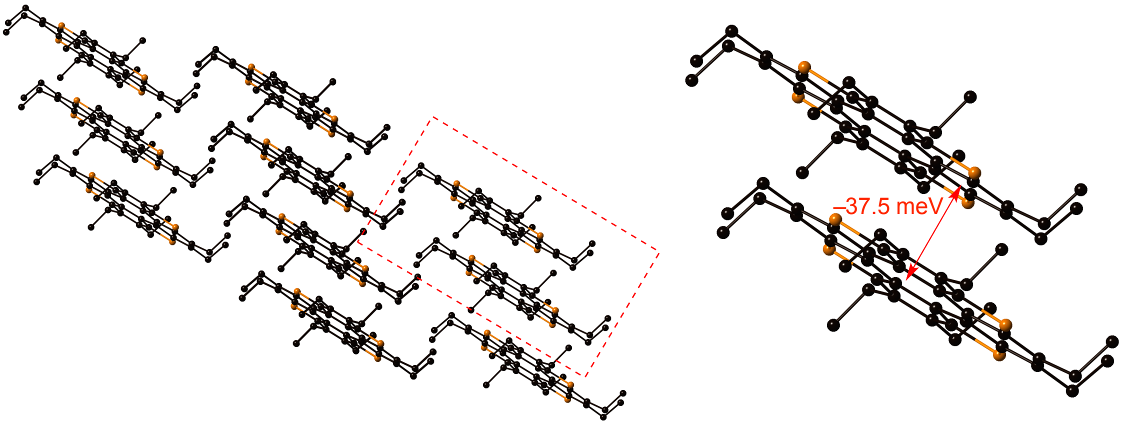


Figure S18. X-ray crystal structure and electron coupling of **1d**.

Flash-Photolysis Time Resolved Microwave Conductivity Measurements

FP-TRMC measurements were conducted, using solid samples of **1** covered with a PVA film onto quartz substrates. The probing microwave was led into a TE-mode microwave cavity, and the microwave power and frequency were set at 3 mW and ~ 9.1 GHz, respectively. The charge carriers were injected into the samples via photo-ionization by direct excitation with a third harmonic generation (λ = 355 nm) light pulses from a Nd: YAG laser (spectra Physics, INDI-HG). The excitation density was tuned at 9.1×10^{15} cm^{-2} photons per pulse. The TRMC signal from a diode was recorded on a digital oscilloscope (Tektronix, TDS 3032B).

According to the Slater's theory and formulations on microwave cavities[S6], reflected power change ratio ($\Delta P_r/P_r$) of microwave from the cavity is in relation with the total loss ($\Delta(1/Q)$) of microwave by the photo-induced transient species in the cavity as follows:

$$\frac{\Delta P_{\mathrm{r}}}{P_{\mathrm{r}}} = \frac{\left(\frac{1}{Q}\right)}{\left(\frac{\Delta\omega}{\omega_0}\right)^2 + \left(\frac{1}{2Q}\right)^2}\,\Delta\left(\frac{1}{Q}\right) \qquad (1),$$

where, ω_0 and $\Delta\omega$ are the resonant frequency of microwave and its shift by the photo-induced transient species. The loss and the frequency shift of the microwave are expressed as a function of complex conductivity ($\Delta\sigma_r + i\Delta\sigma_i$) of the transient species by:

$$\Delta\left(\frac{1}{Q}\right) - i\frac{2\Delta\omega}{\omega_0} = F\left(\Delta\sigma_{\mathrm{r}} + i\Delta\sigma_{\mathrm{i}}\right) \qquad (2),$$

where F is a calibration factor derived from the measurements of total loss of microwave in the cavity loaded with materials with well-known conductivity values. Thus, in case of negligibly small $\Delta\omega$, eqs (1) and (2) give the following relation between $\Delta P_r/P_r$ and the sum of the mobilities ($\Sigma\mu$) of charged species:

$$\Delta\sigma_{\mathrm{r}} = N\phi\sum\mu = \mathrm{A}\frac{\Delta P_{\mathrm{R}}}{P_{\mathrm{R}}} \qquad (3),$$

where N, ϕ, and A are the number of absorbed photons, photo-carrier separation quantum yield, and a sensitivity factor (constant), respectively. Details of the experimental setup are described in the literature.[S7]

To determine the values of ϕ, we conducted transient optical absorption spectroscopy at using a drop-cast film of **1f** from a $CHCl_3$ solution deposited onto a quartz substrate.[S8] Transmittance of excitation light pulses was measured by a PE25 power meter of Ophir Optronics Ltd. Time-dependent absorption spectral changes were monitored by Hamamatsu C7700 streak camera via a Hamamatsu C5094 spectrometer upon direct excitation of the film using a third harmonic generation (λ = 355 nm) light pulses from a Nd: YAG laser (Spectra Physics, INDI-HG). The excitation density was tuned at 9.1 × 10^{15} cm^{-2} photons per pulse. To correct a 2-dimensional time-wavelength correlation data of the transient absorption, the streak scope images were averaged over 1600 images. The transient optical absorption spectra are shown in Figure S18. The change of the molar extinction coefficients of **1f**$^{+\cdot}$ from the neutral state was determined by subtracting the absorption spectrum of a CH_2Cl_2 solution of **1f** from the spectrum of **1f**$^{+\cdot}$ generated by chemical oxidation with tris(4-bromophenyl) aminium hexachloroantimonate (Figures S20 and S19). By using the change of the molar extinction coefficient at 432 nm, the value of ϕ was determined at as $\phi = 3.8 \times 10^{-2}$. The sum of the mobility values in the fiber **1f** was calculated based on the conductivity transient with the ϕ value as 2.66×10^{-3} $cm^2V^{-1}s^{-1}$.

The maximum transient conductivity ($\phi\Sigma\mu$) of **1b**, **1d**-**i** are shown in Figure S21, and the result of quenching experiments in an SF_6 environment is also shown in Figure S22.

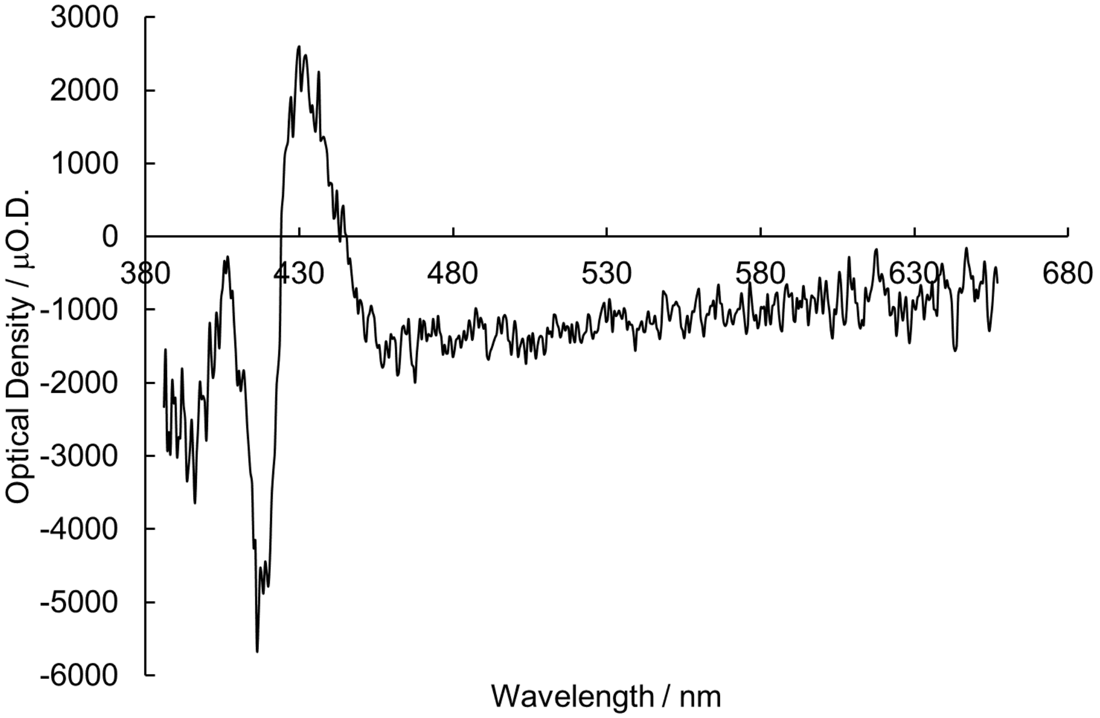


Figure S19. Transient absorption spectra of a **1f** film observed upon excitation at 355 nm, 9.1 × 10^{15} photons cm^{-2} under ambient condition.

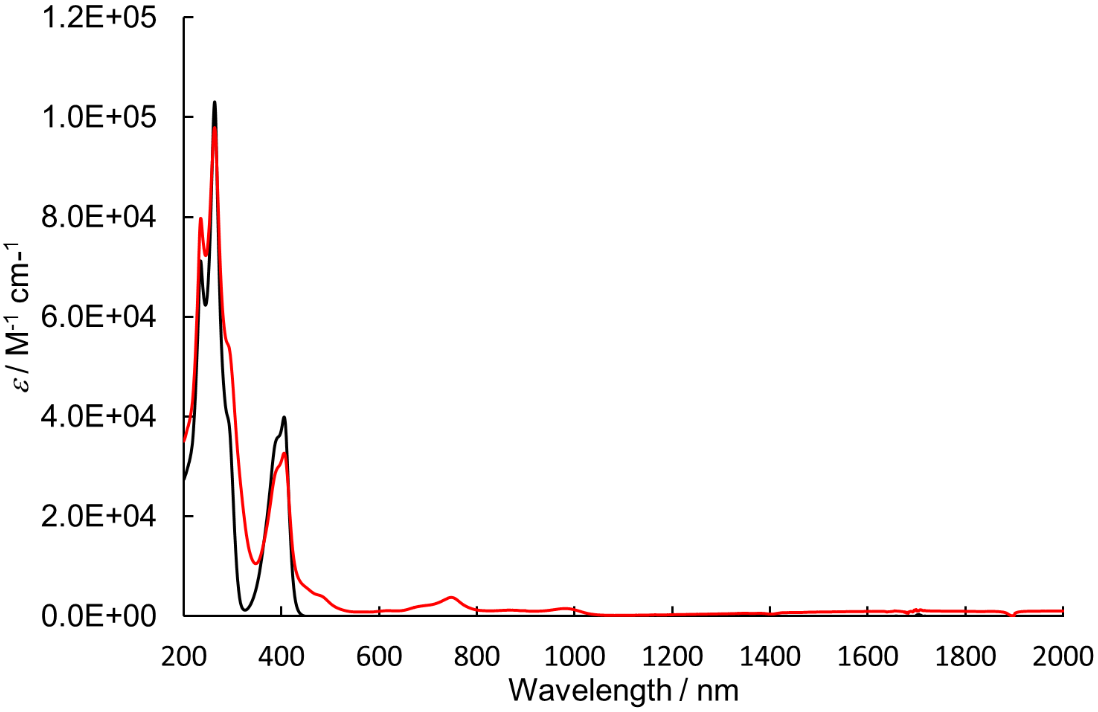


Figure S20. Absorption spectra of **1f** (black) and **1f**$^{+\cdot}$ (red) in CH_2Cl_2 solution.

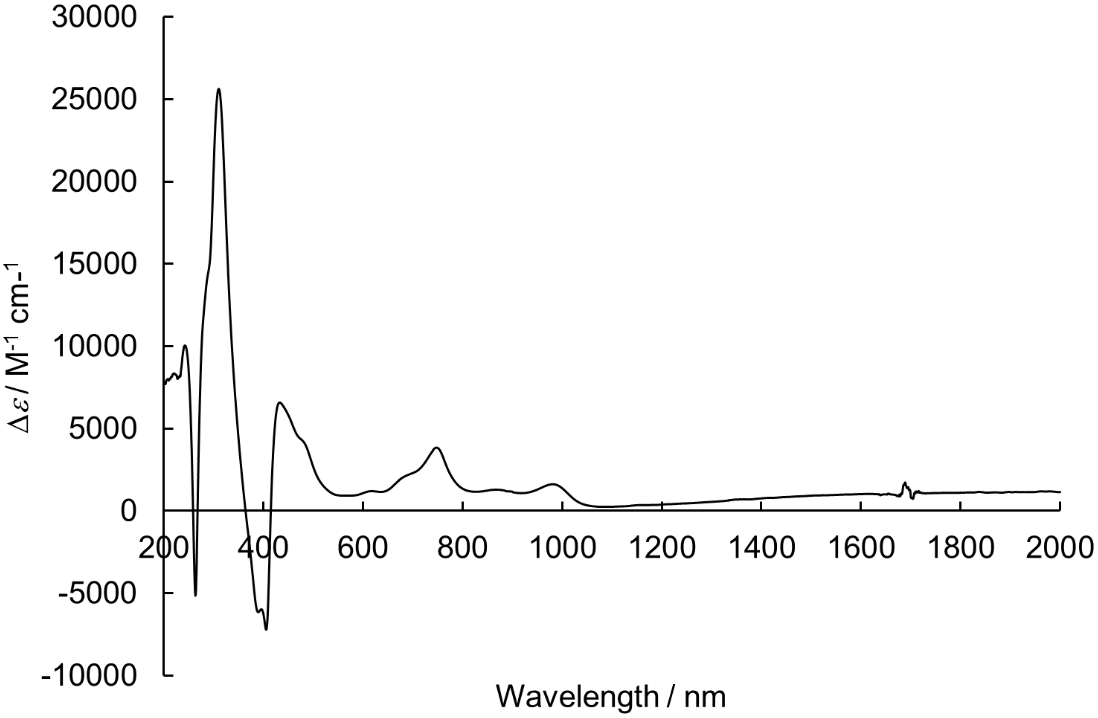


Figure S21. Subtraction spectrum between **1f** and **1f**$^{+\cdot}$ in CH_2Cl_2 solution.

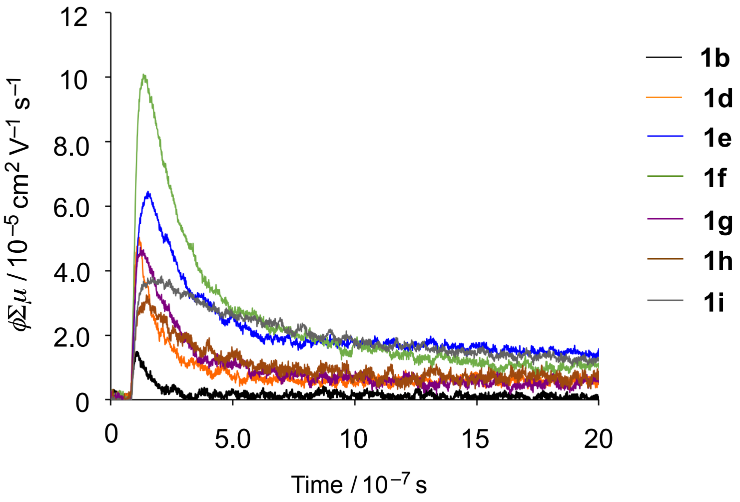


Figure S22. Time-resolved microwave conductivities of solid samples of **1b**, **1d**-**i**.

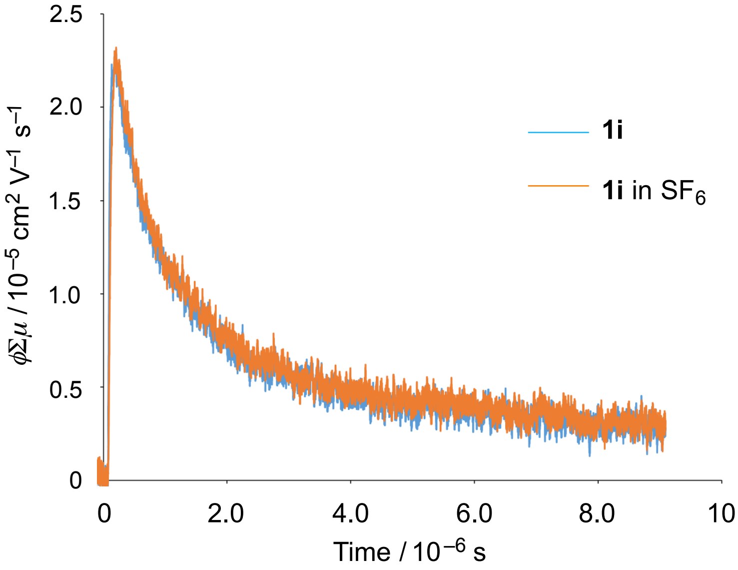


Figure S23. Time-resolved microwave conductivities of **1i** and **1i** in SF$_6$.

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[S5] ADF2014, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com

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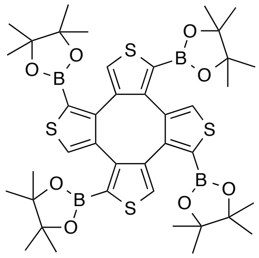

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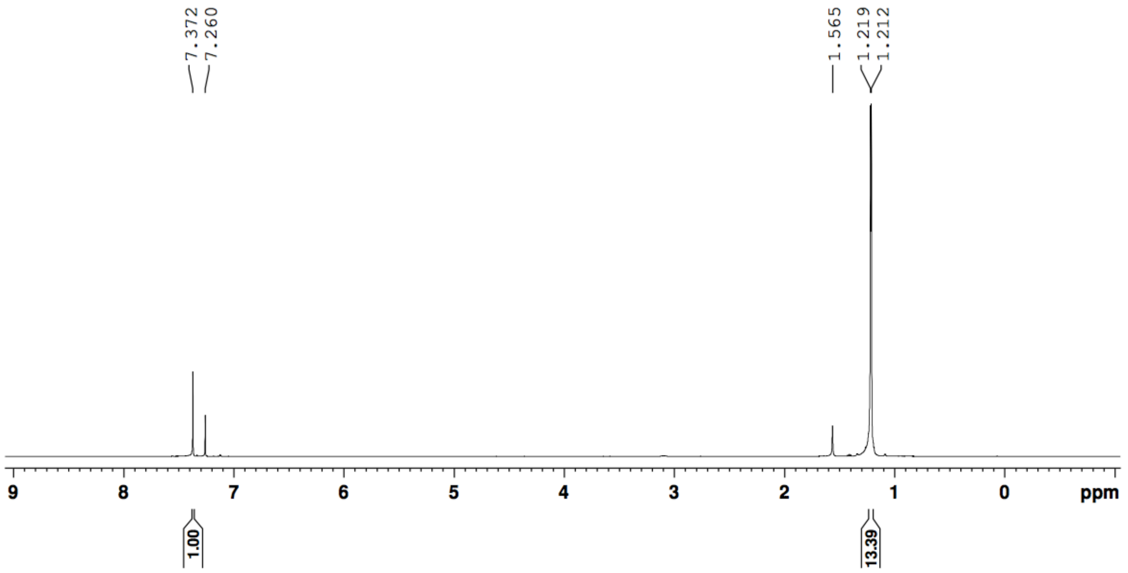

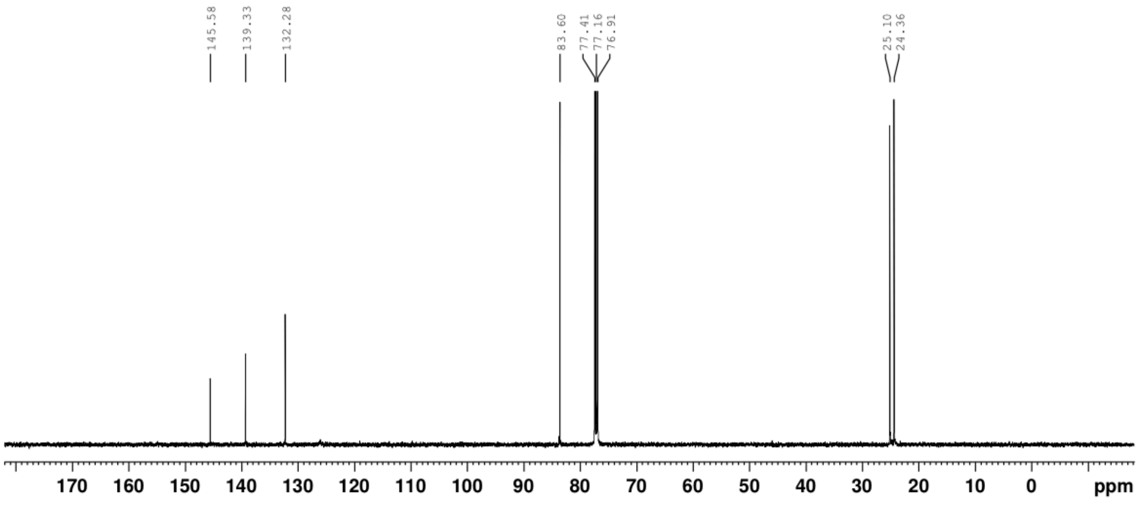

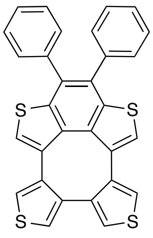
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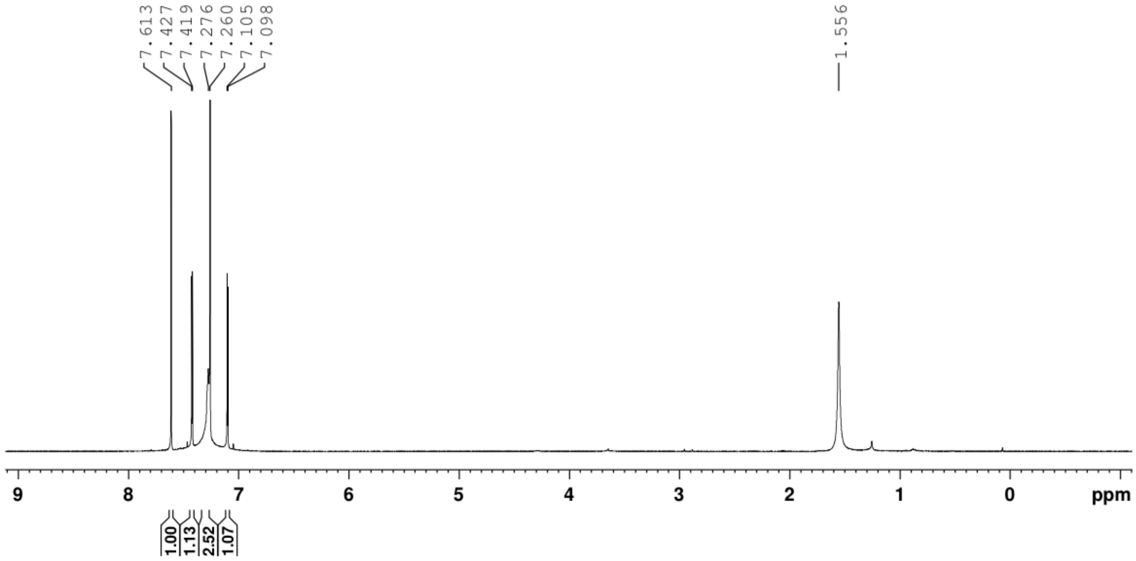
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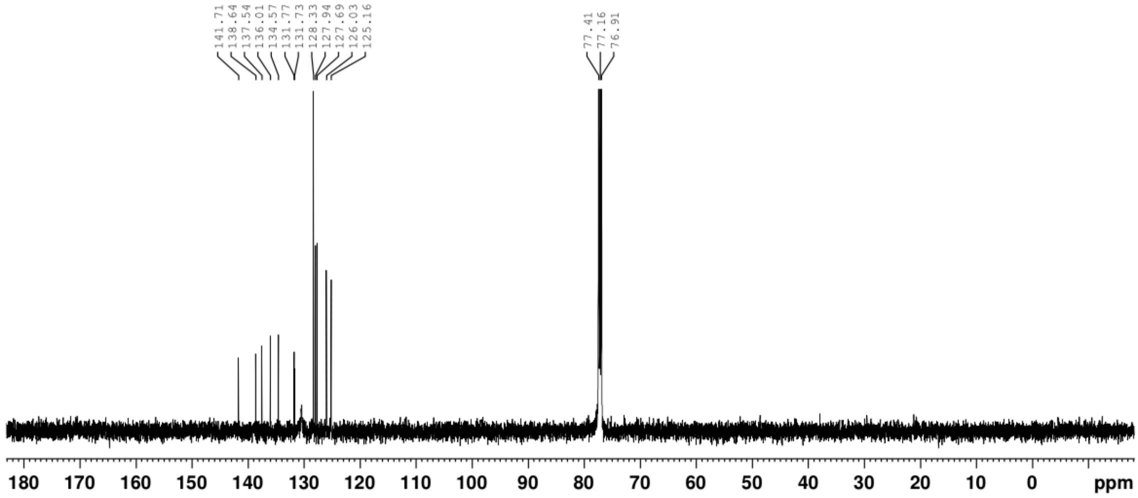
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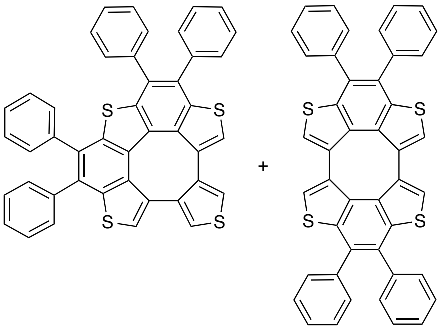
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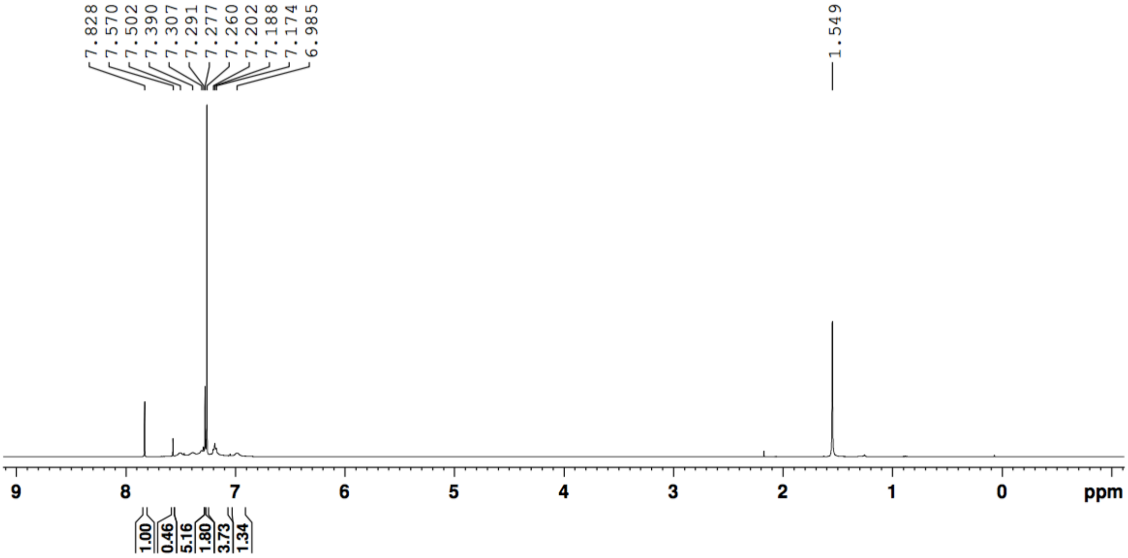
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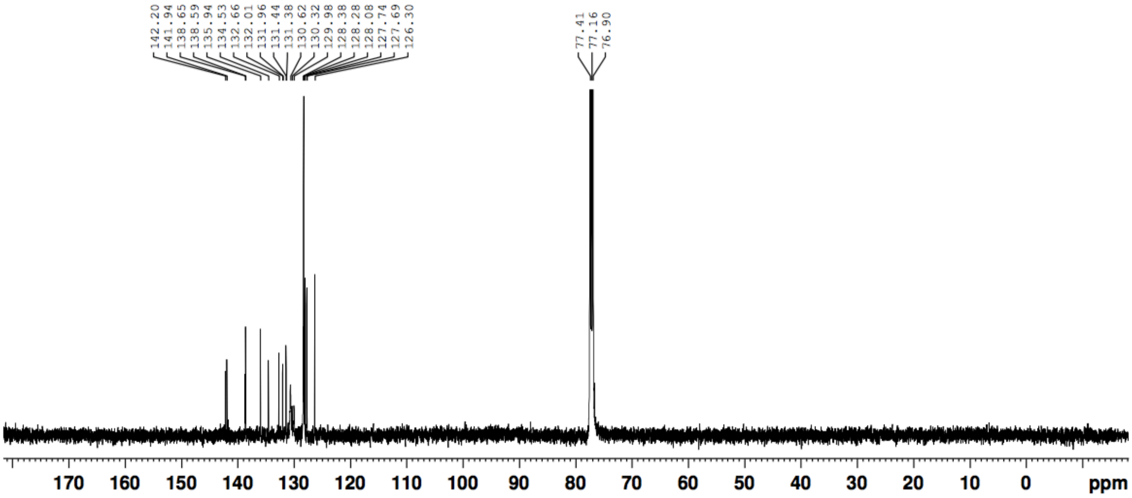
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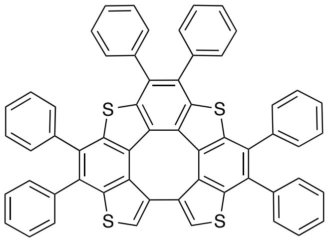
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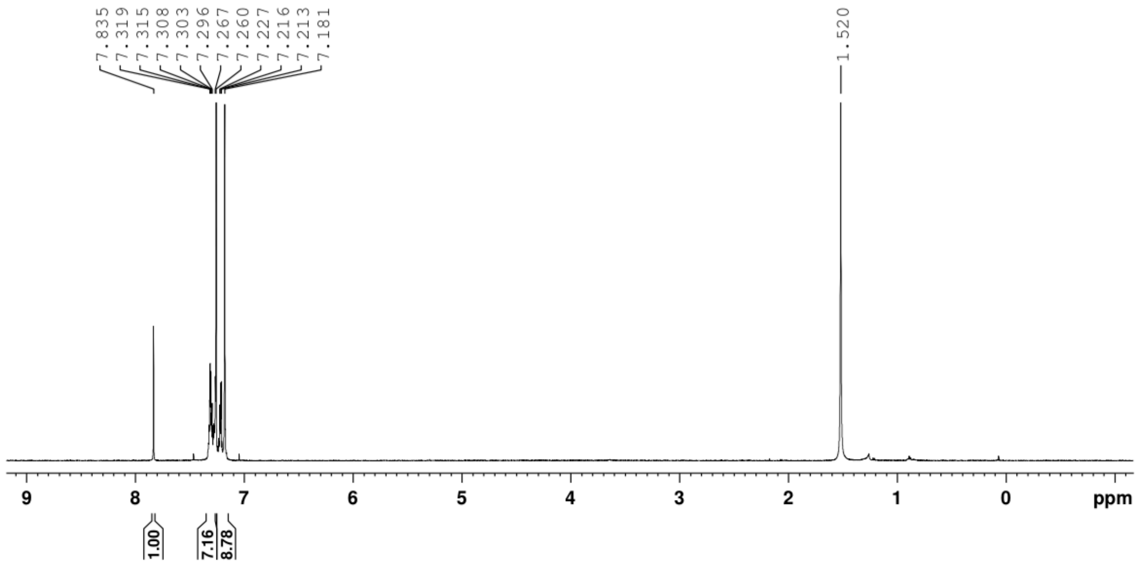
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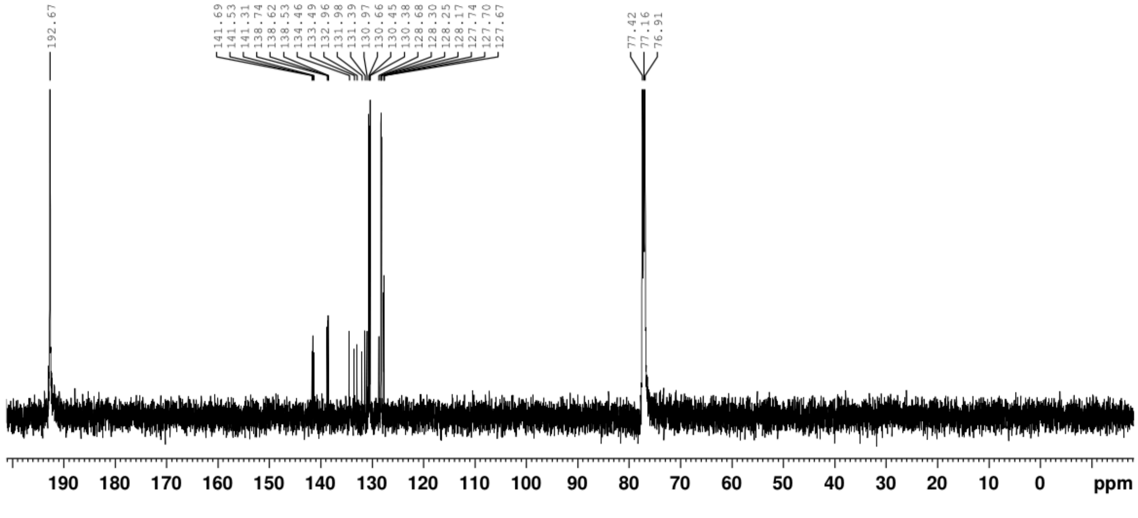
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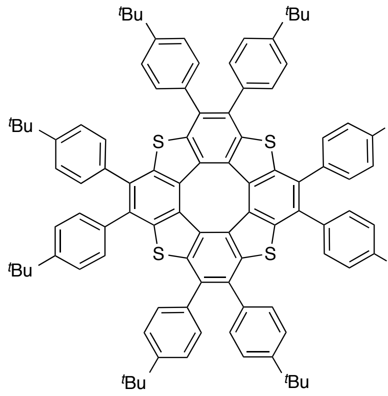
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tBu
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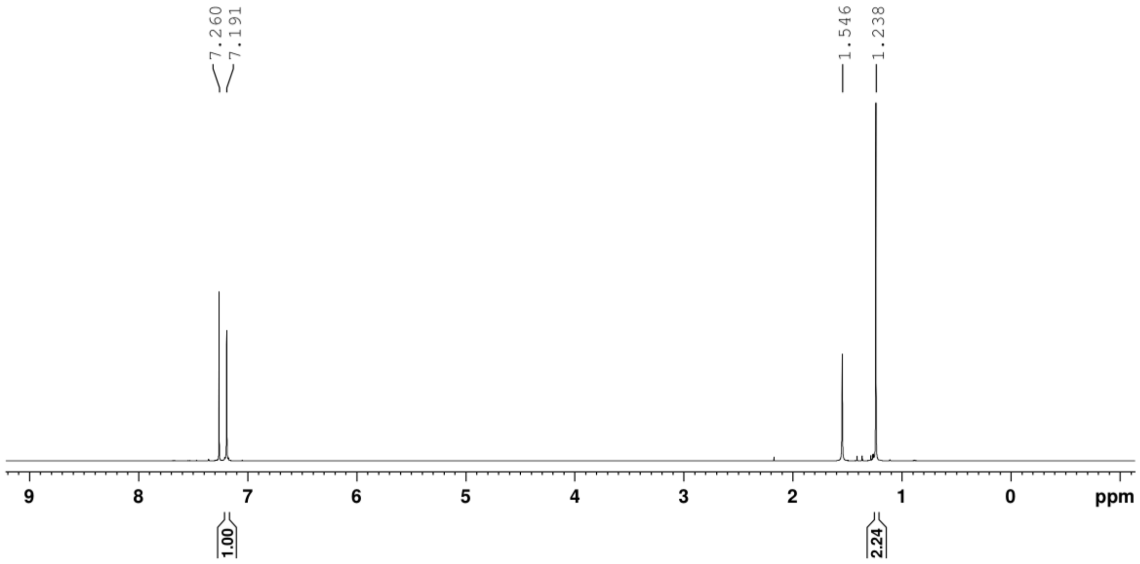
1a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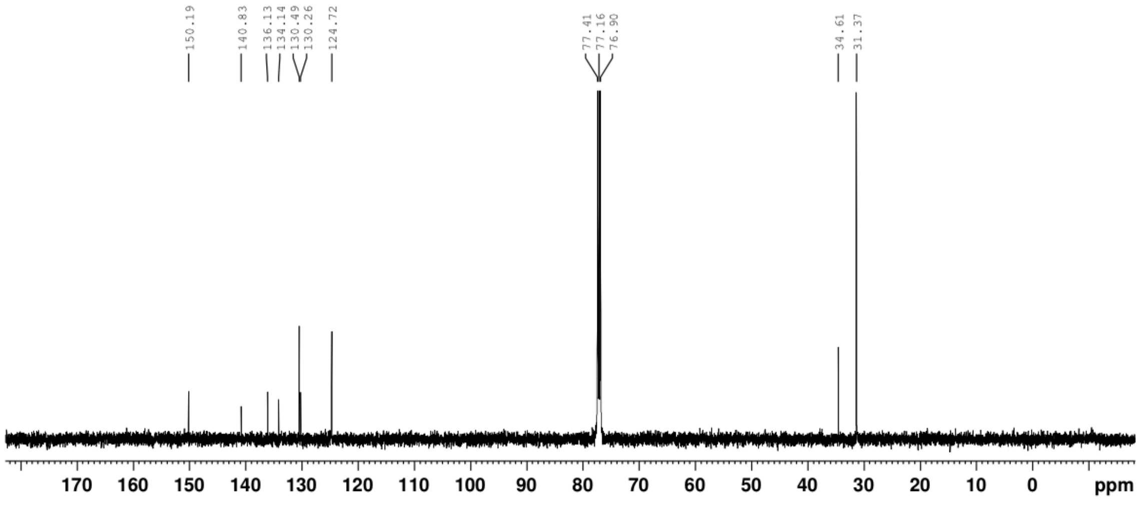
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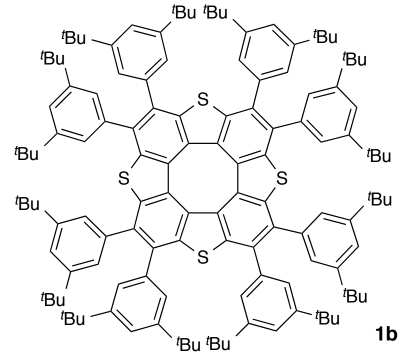

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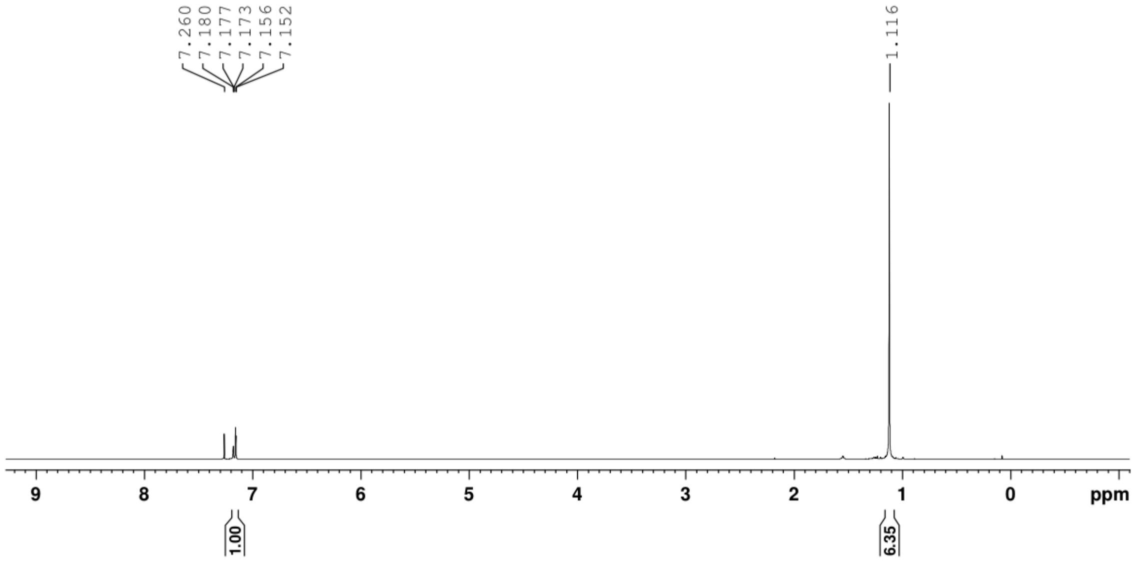

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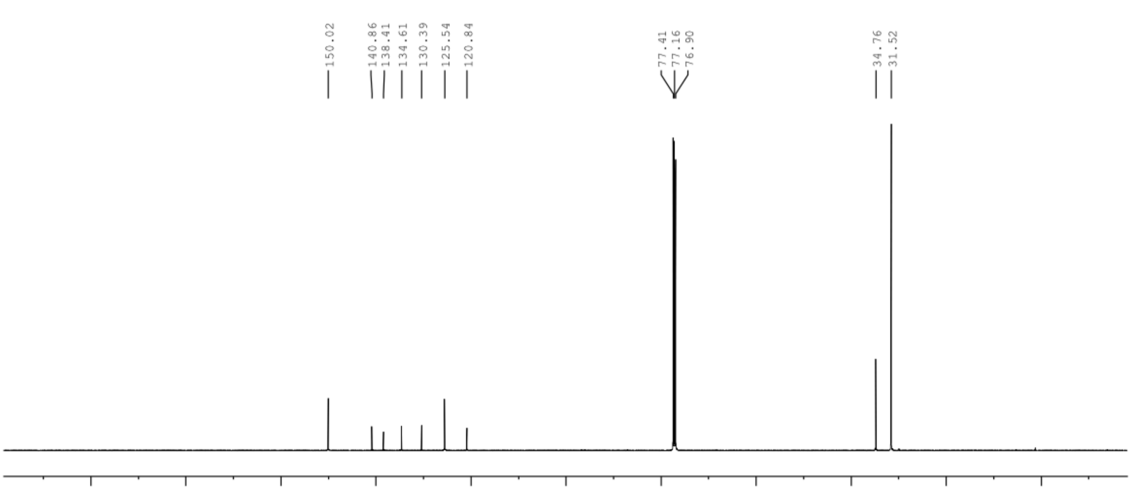

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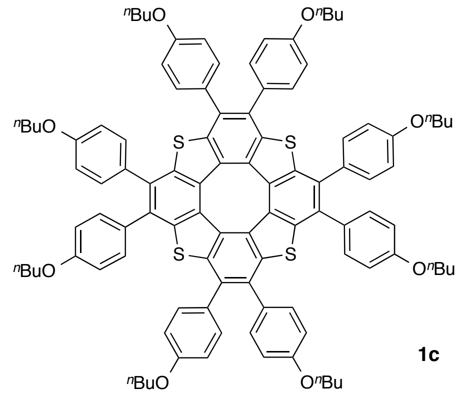

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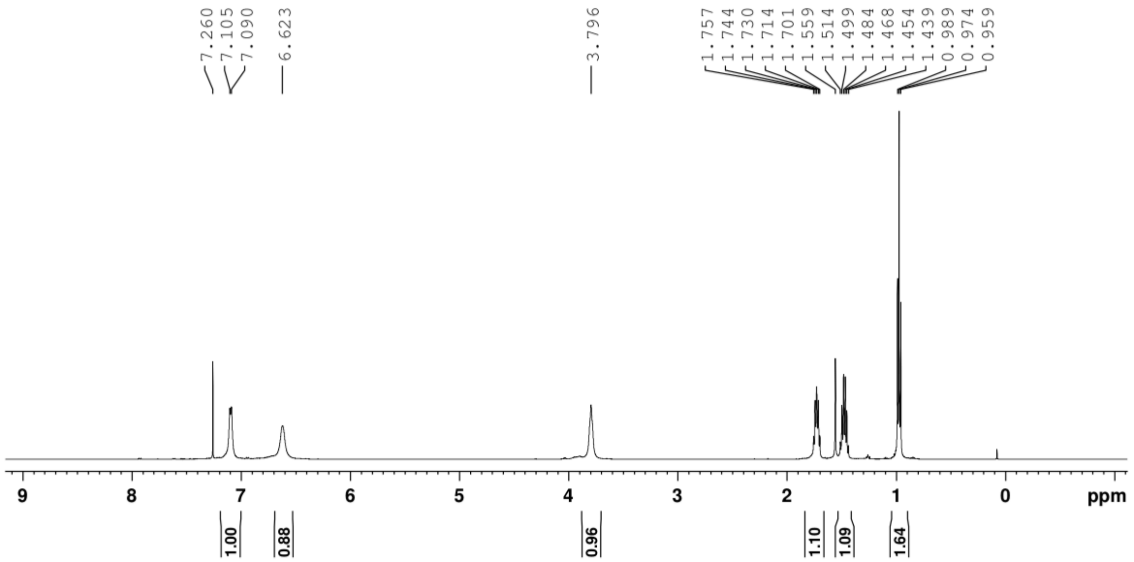
OⁿBu

1c



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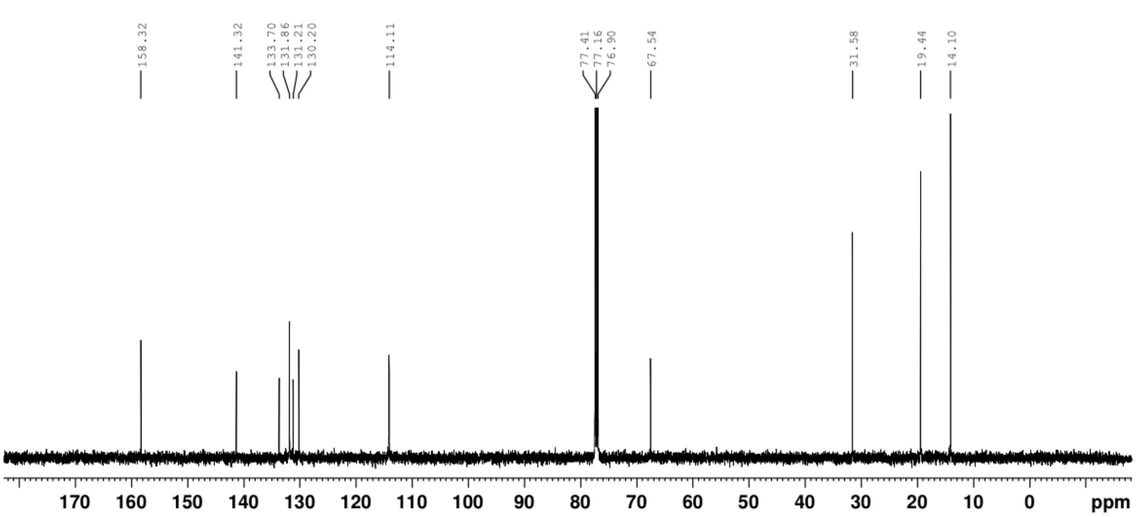

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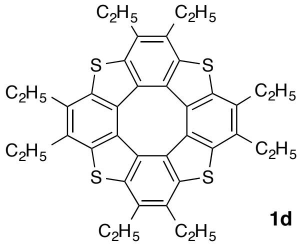
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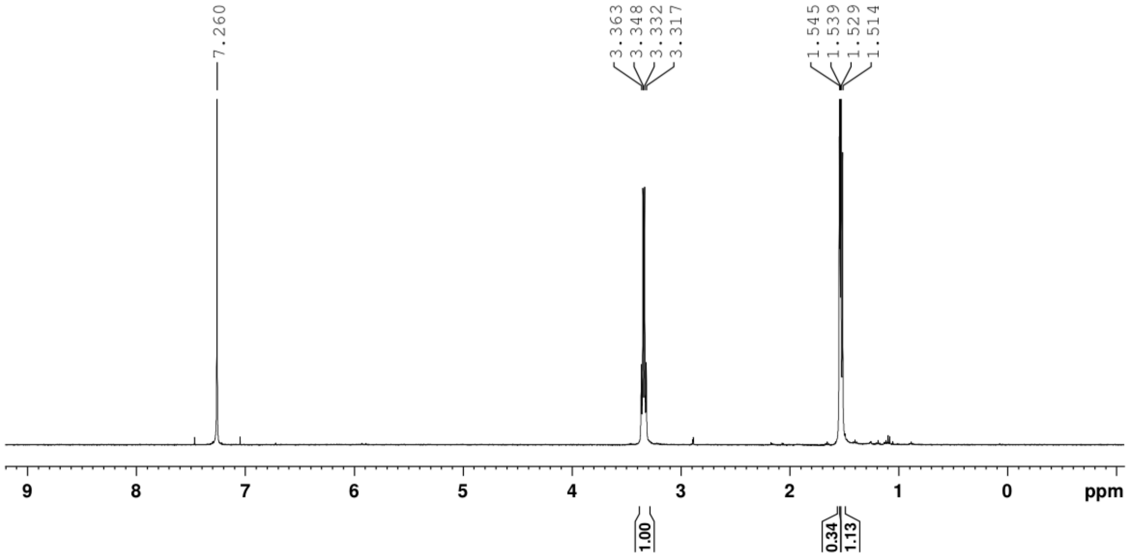
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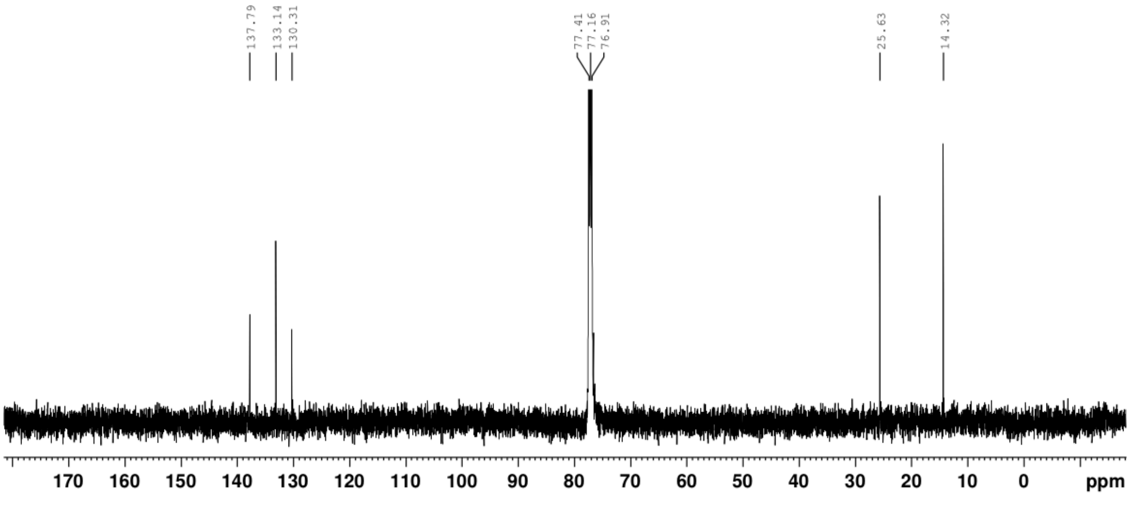
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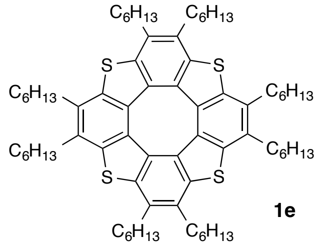
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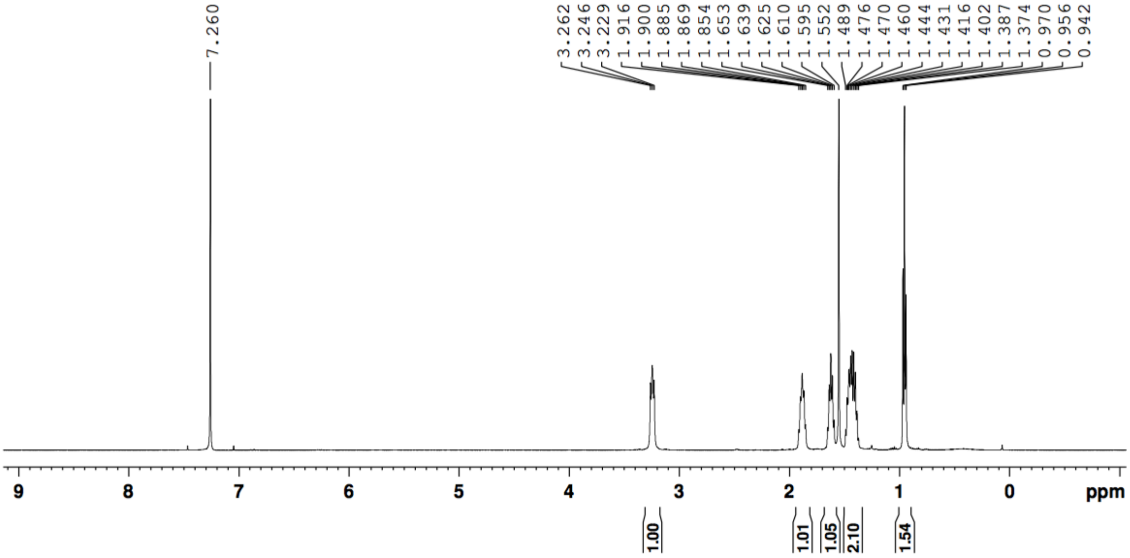
1e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1.885
1.869
1.854
1.653
1.639
1.625
1.610
1.595
1.552
1.489
1.476
1.470
1.460
1.444
1.431
1.416
1.402
1.387
1.374
0.970
0.956
0.942
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6
5
4
3
2
1
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1.00
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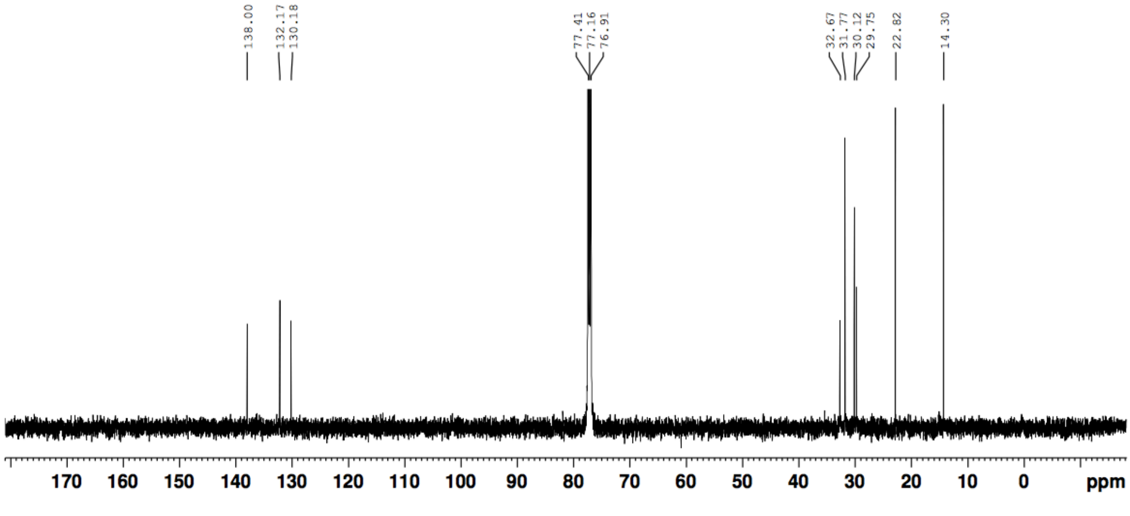
1.05
2.10
1.54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77.41
77.16
76.91
32.67
31.77
30.12
29.75
22.82
14.30
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160
150
140
130
120
110
100
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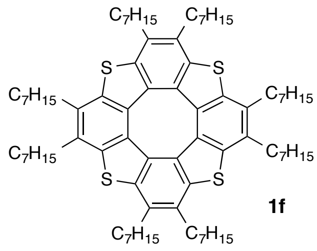
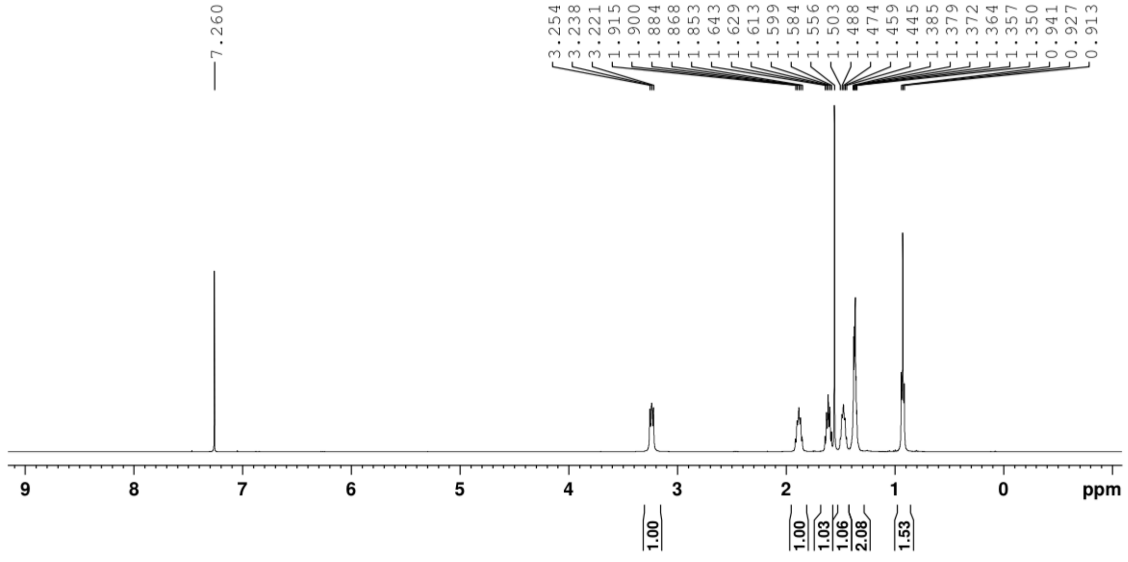

C$_7$H$_{15}$
S

1f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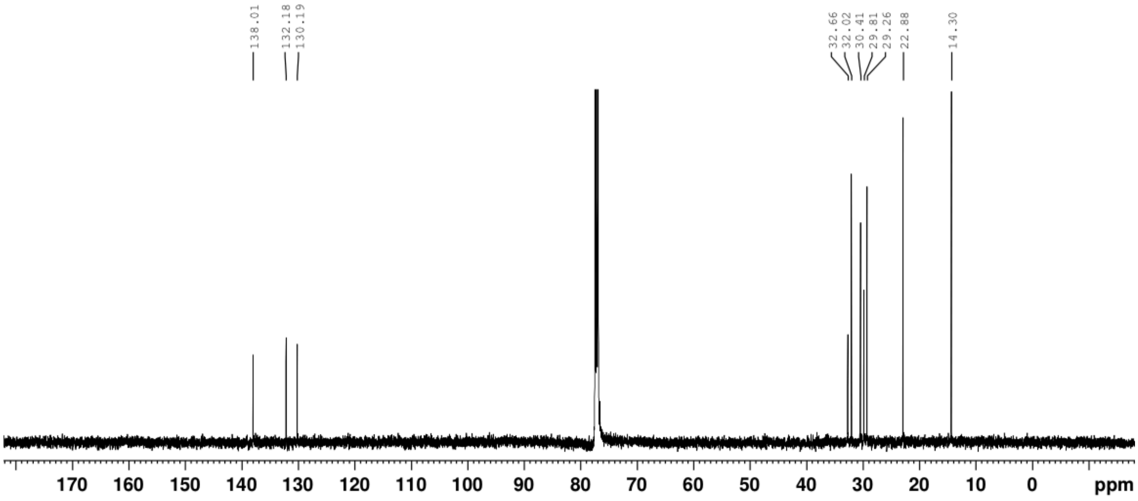
3.238
3.221
1.915
1.900
1.884
1.868
1.853
1.643
1.629
1.613
1.599
1.584
1.556
1.503
1.488
1.474
1.459
1.445
1.385
1.379
1.372
1.364
1.357
1.350
0.941
0.927
0.913
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.03
1.06
2.08
1.53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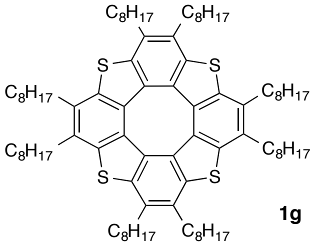
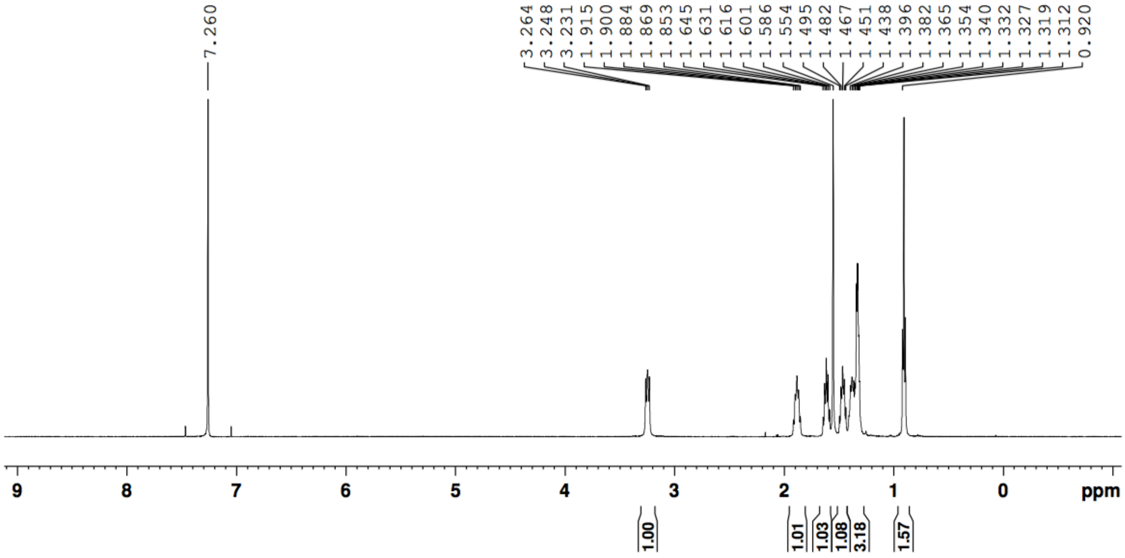
132.18
130.19
32.66
32.02
30.41
29.81
29.26
22.88
14.30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


C$_8$H$_{17}$
C$_8$H$_{17}$
S
S
C$_8$H$_{17}$
C$_8$H$_{17}$
C$_8$H$_{17}$
C$_8$H$_{17}$
S
S
C$_8$H$_{17}$
C$_8$H$_{17}$

1g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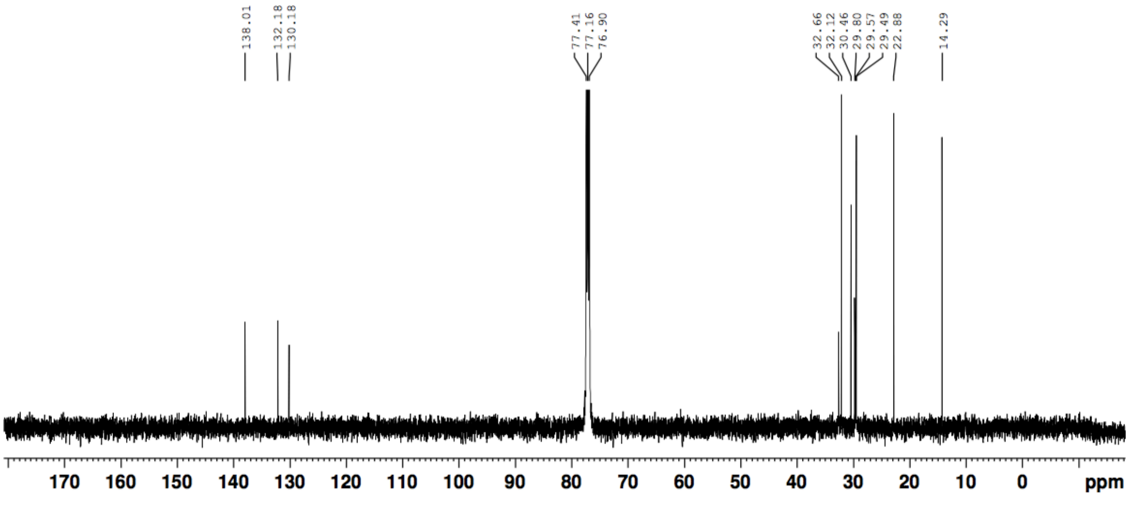
3.248
3.231
1.915
1.900
1.884
1.869
1.853
1.645
1.631
1.616
1.601
1.586
1.554
1.495
1.482
1.467
1.451
1.438
1.396
1.382
1.365
1.354
1.340
1.332
1.327
1.319
1.312
0.920
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.03
1.08
3.18
1.57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76.90
32.66
32.12
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29.80
29.57
29.49
22.88
14.29
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160
150
140
130
120
110
100
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80
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60
50
40
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20
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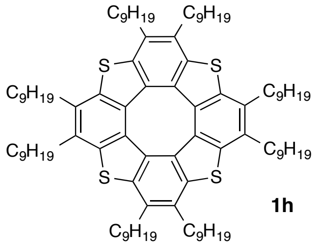
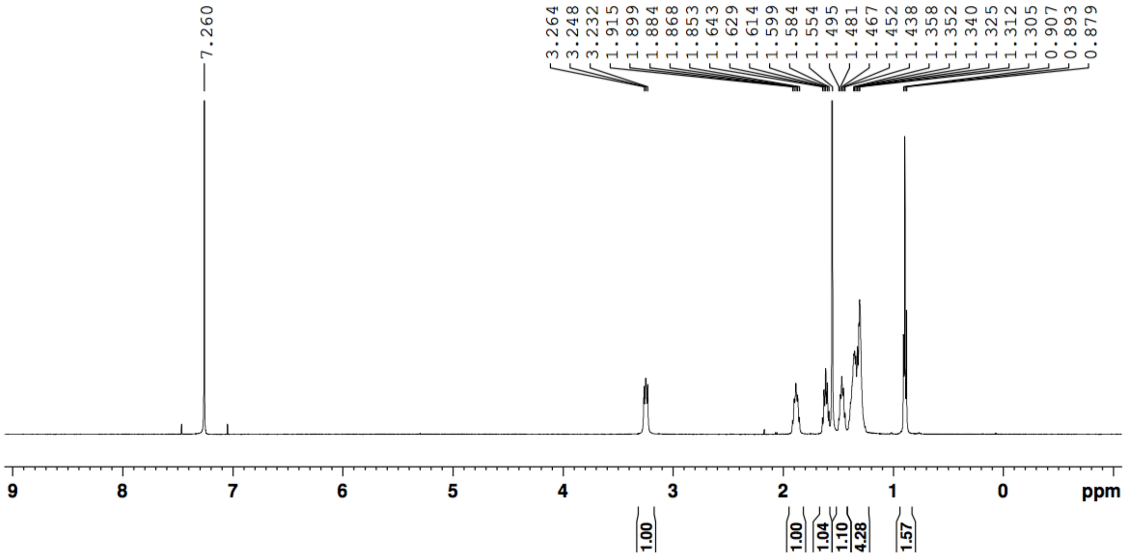
0
ppm


C9H19
C9H19
C9H19
C9H19
C9H19
C9H19
C9H19
C9H19
S
S
S
S

1h


7.260
3.264
3.248
3.232
1.915
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1.884
1.868
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1.643
1.629
1.614
1.599
1.584
1.554
1.495
1.481
1.467
1.452
1.438
1.358
1.352
1.340
1.325
1.312
1.305
0.907
0.893
0.879
9
8
7
6
5
4
3
2
1
0
ppm
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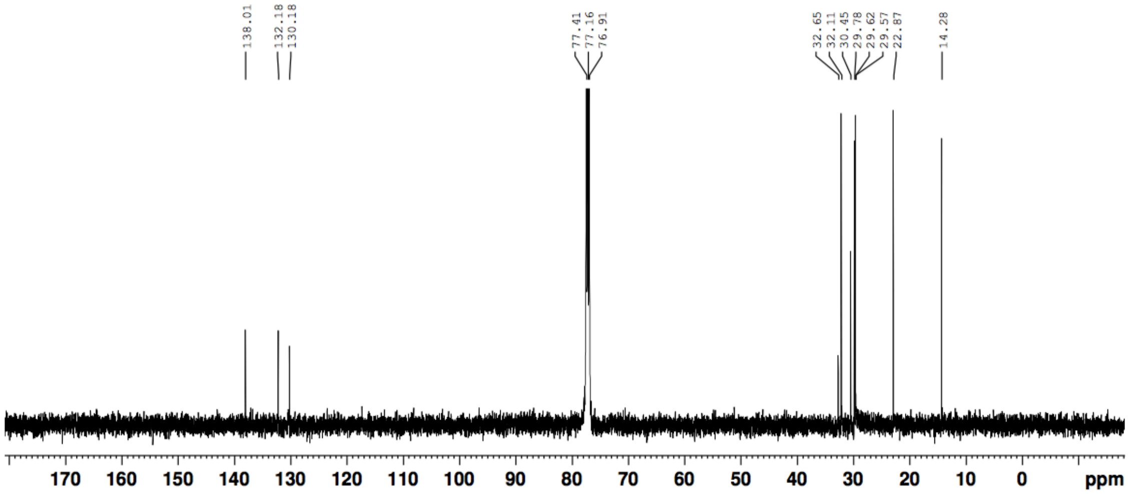
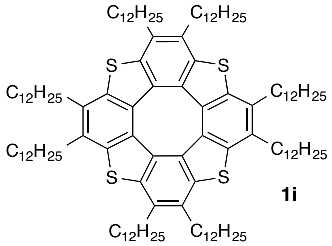
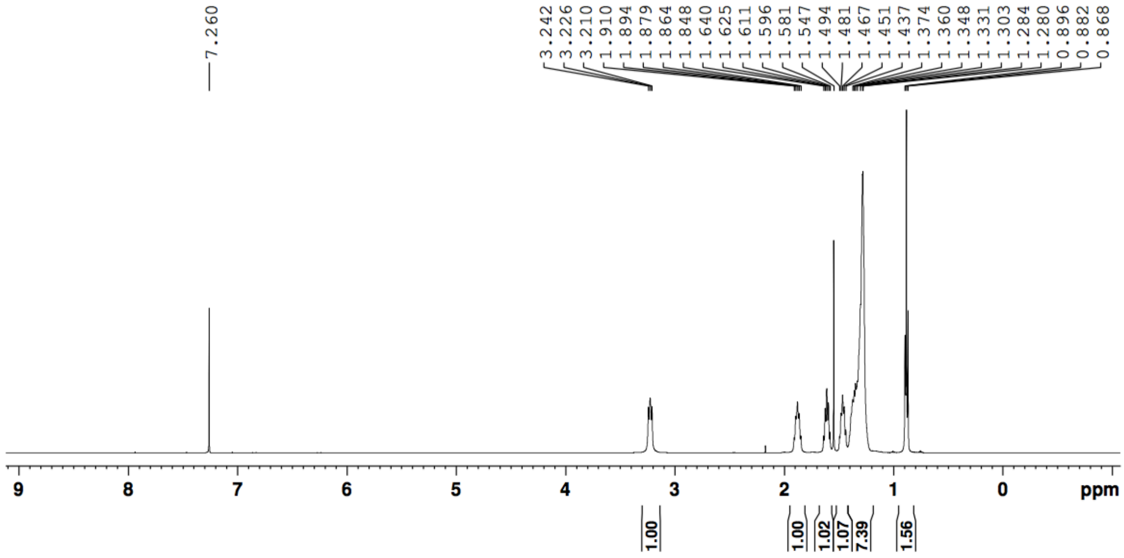
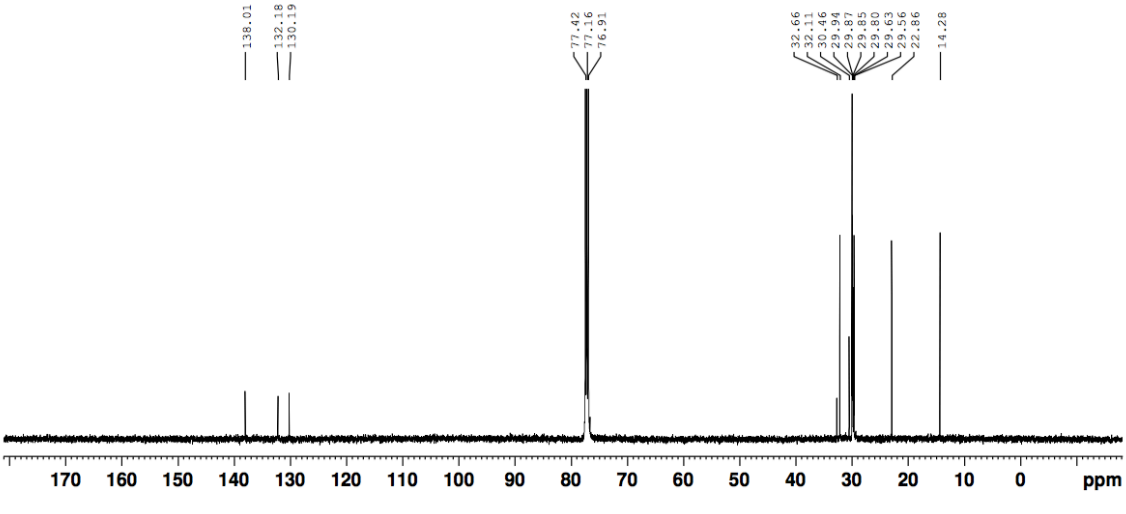
1.00
1.04
1.10
4.28
1.57

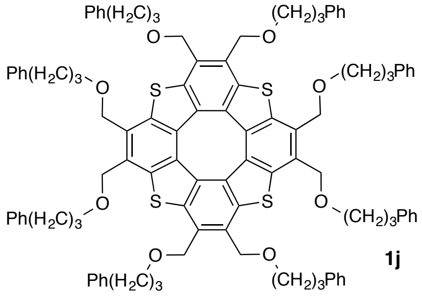

138.01
132.18
130.18
77.41
77.16
76.91
32.65
32.11
30.45
29.78
29.62
29.57
22.87
14.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


C12H25
C12H25
S
S
C12H25
C12H25
C12H25
C12H25
S
S
C12H25
C12H25

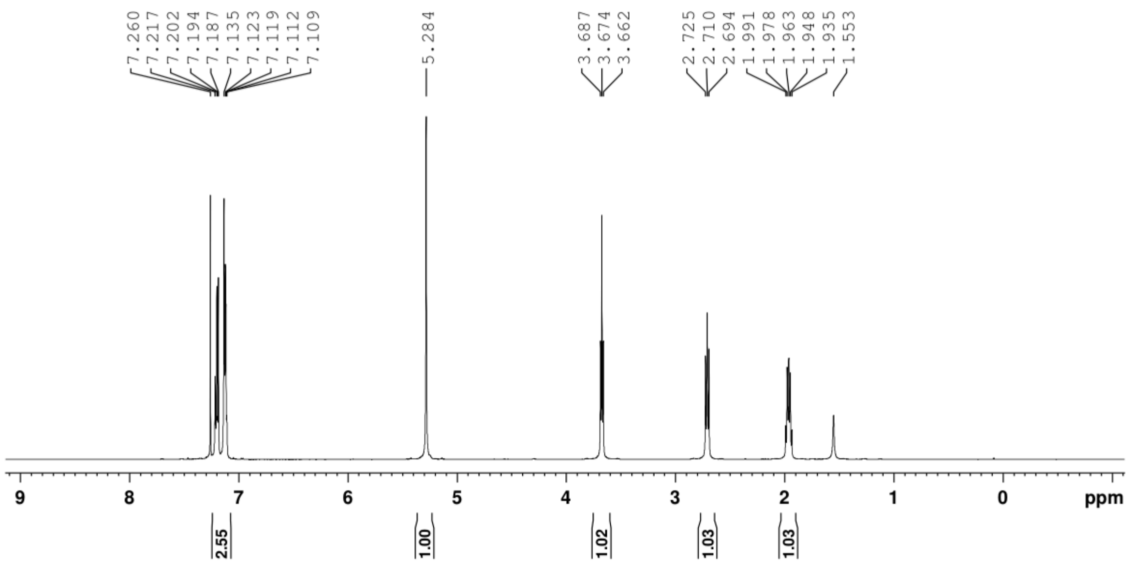
1i

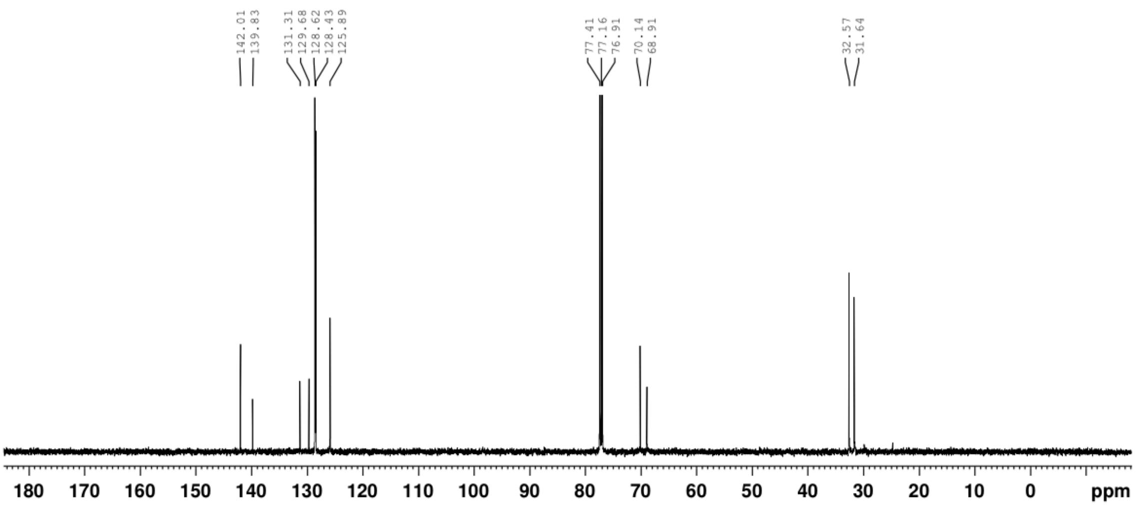

7.260
3.242
3.226
3.210
1.910
1.894
1.879
1.864
1.848
1.640
1.625
1.611
1.596
1.581
1.547
1.494
1.481
1.467
1.451
1.437
1.374
1.360
1.348
1.331
1.303
1.284
1.280
0.896
0.882
0.868
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.02
1.07
7.39
1.56


138.01
132.18
130.19
77.42
77.16
76.91
32.66
32.11
30.46
29.94
29.87
29.85
29.80
29.63
29.56
22.86
14.28
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Ph(H2C)3
(CH2)3Ph
O
S

1j


7.260
7.217
7.202
7.194
7.187
7.135
7.123
7.119
7.112
7.109
5.284
3.687
3.674
3.662
2.725
2.710
2.694
1.991
1.978
1.963
1.948
1.935
1.553
9
8
7
6
5
4
3
2
1
0
ppm
2.55
1.00
1.02
1.03
1.03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128.62
128.43
125.89
77.41
77.16
76.91
70.14
68.91
32.57
31.64
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm