

A Comprehensive Study of Extended Tetrathiafulvalene Cruciform Molecules for Molecular Electronics: Synthesis and Electrical Transport Measurements

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Summary of Photophysical Properties

Table S1. Photophysical properties (UV-Vis absorption and fluorescence data; sh = shoulder; Q. Y. = quantum yield).

Compound	$\lambda_{\text{max}} / \text{nm}$ ($\epsilon / 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{exc, max}} / \text{nm}$	$\lambda_{\text{em, max}} / \text{nm}$	Q. Y.
OPE3 1	250 (12.7), 319 (63.8, sh), 332 (80.0), 352 (52.0), 380 (1.5, sh)	344, 355	366, 382	0.38
OPE5 2	230 (43.3), 289 (30.7), 362 (123.6), 384 (89.9, sh)	244, 292, 356	400, 421	0.61
OPE3 3	334 (72.4), 397 (14.8, sh)	334, 351	370, 386	8.6×10^{-3}
OPE5 5	292 (38.1), 351 (108.6)	288, 366	394, 416	0.13
OPE3 6	250 (36.0), 301 (31.6), 345 (72.6), 412 (38.8), 436 (36.4, sh)	337, 394	478	5×10^{-4}
OPE3 7	250 (39.1), 311 (29.2), 367 (76.7), 408 (52.0), 431 (47.4, sh)		No emission	
OPE3 8	336 (68), 417 (49), 425 (48, sh)			
OPE3 9	250 (43.6), 320 (50.0, sh), 340 (73.9), 359 (58.3), 408 (8.2)		No emission	
OPE5 10	316 (57.2, sh), 365 (115.5), 427 (39.3)	356	497	2×10^{-4}
OPE5 11	360 (117.2)	244, 260, 360, 383	410, 426	6×10^{-3}
12a	255 (16.8), 400 (37.9), 413 (35.6)	420	478	1.0×10^{-3}
OPE3 13a	250 (32.0), 403 (97.0), 419 (87.9, sh)	424	461	1.3×10^{-3}
OPE3 14a	250 (37.9), 331 (42.3), 408 (91.7), 436 (68.5, sh)	428	486	1.2×10^{-3}
OPE3 15a	250 (42.1), 336 (37.7), 401 (100.3), 449 (58.5, sh)	410	488	5×10^{-4}
OPE3 26	250 (31.0), 302 (32.8), 346 (73.0), 364 (61.8, sh.), 403 (17.6)		No emission	
OPE3 54	250 (20.8), 357 (70.5), 375 (59.6)	363	405	0.1
OPE3 55	250 (33.0), 318 (41.0), 358 (74.5), 409 (36.2), 445 (27.0, sh)	400	459	5×10^{-4}

UV-Vis Absorption Spectra

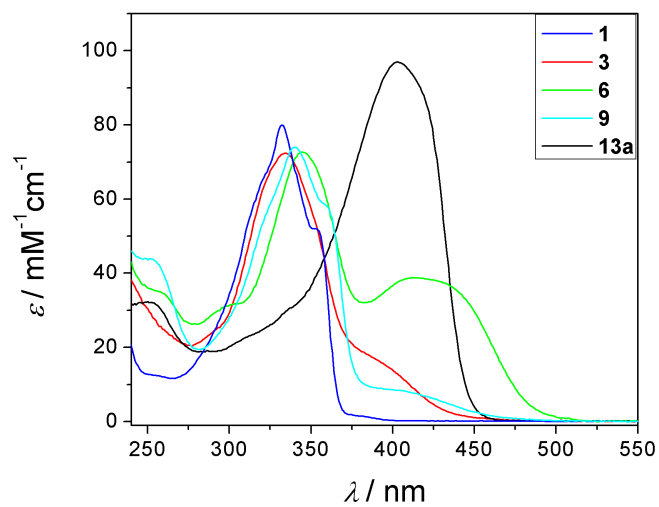


Figure S1. UV-Vis absorption spectra of **1** [0.0], **3** [0.1], **6** [0.2], **9** [0.2], and **13a** [2.0] in CH_2Cl_2 .

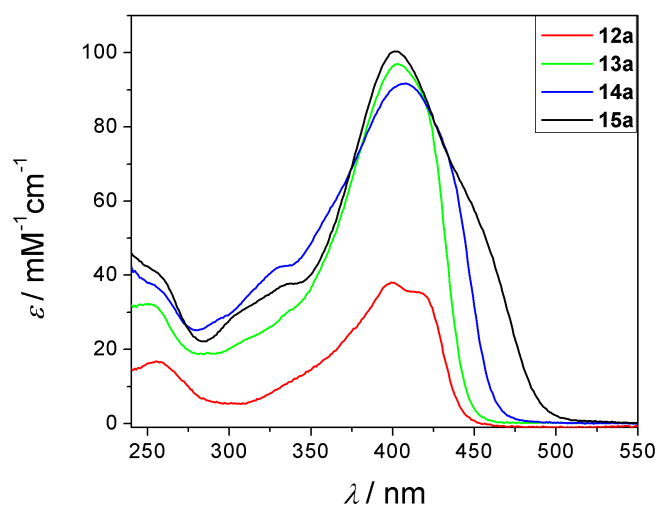


Figure S2. UV-Vis absorption spectra of **12a** [2.0], **13a** [2.0], **14a** [2.1], and **15a** [2.2] in CH_2Cl_2 .

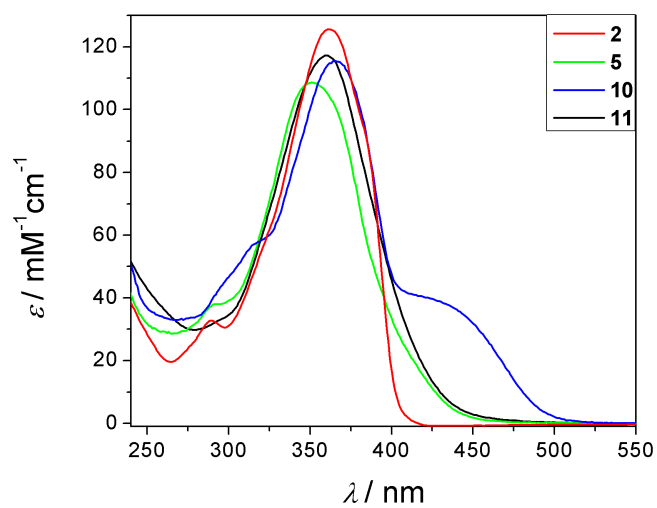


Figure S3. UV-Vis absorption spectra of **2** [0.0], **5** [0.1], **10** [0.2], and **11** [0.2] in CH_2Cl_2 .

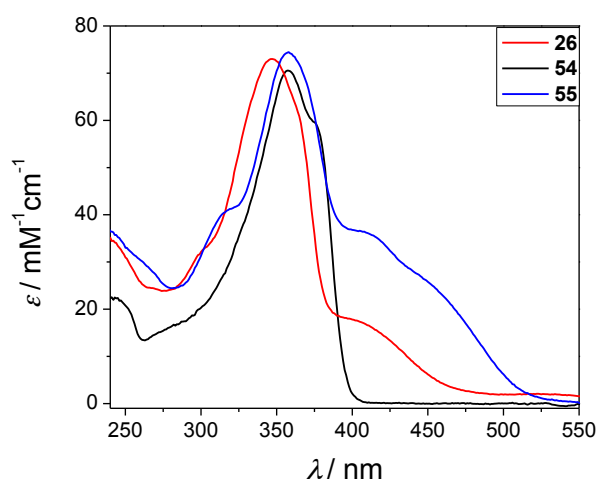


Figure S4. UV-Vis absorption spectra of OPE3 di-aldehyde compounds **54** [0.0], **26** [0.1], and **55** [0.2] in CH_2Cl_2 .

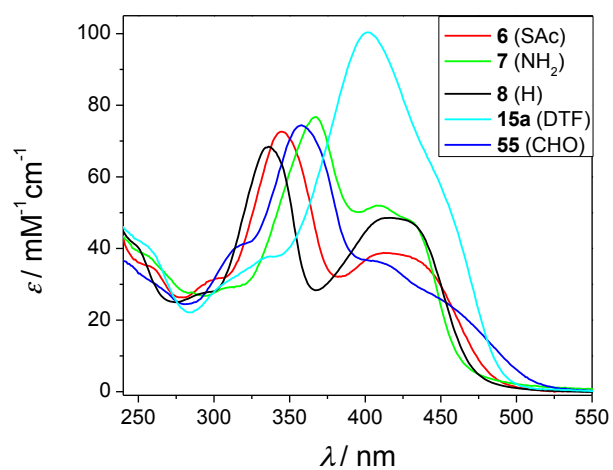


Figure S5. UV-Vis absorption spectra of OPE3 cruciforms [0.2] with different termini: **6** (SAc), **7** (NH₂), **8** (H), **15a** {DTF(SCH₂CH₂CN)₂}, and **55** (CHO) in CH₂Cl₂.

Electrochemistry

Table S2. Cyclic Voltammetry and Differential Pulse Voltammetry data of compounds in CH₂Cl₂ with 0.1 M [NBu₄]PF₆ as a supporting electrolyte.^{a)} Potentials vs Fc/Fc⁺.

Compound	Cyclic Voltammetry				Differential Pulse Voltammetry			
	E_{ox}^1 / V	E_{ox}^2 / V	E_{red}^1 / V	E_{red}^2 / V	E_{ox}^1 / V	E_{ox}^2 / V	E_{red}^1 / V	Other
1	+1.26 ⁱ							
3 (very dilute)	+0.57 ^{b)}				+0.53	+0.88		
6	+0.49 ⁱ	+0.85 ⁱ	-1.93 ⁱ sh	-2.00 ⁱ	+0.46	+0.85	-1.80	-1.94
8	+0.49 ⁱ	+0.85 ⁱ	-2.12 ⁱ					
9	+0.74 ⁱ		-2.34 ⁱ					
12a	+0.25 ⁱ	+0.47 ⁱ	-2.48 ⁱ		+0.23	+0.45	-2.36	
15a	+0.42 ⁱ	+0.85 ⁱ	-2.17 ⁱ		+0.30	+0.74	-1.85	-2.05
21	+0.75 ⁱ	+0.86 ⁱ sh	-1.96 ⁱ	-2.43 ⁱ	+0.70	+0.84	-1.81	-2.36, -2.45
37	+0.54 ⁱ (+0.45) ^{c)}	+0.62 ⁱ sh (+0.59 sh) ^{c)}	-1.83 ⁱ		+0.51	+0.64	-1.74	+0.89
37^{d)}	+0.59 ⁱ sh (+0.47) ^{c)}	+0.66 ⁱ (+0.58) ^{c)}						
43	+0.72		-1.97 ⁱ		+0.73		-1.86	

^{a)} Conditions: Approximately 1 mM solutions of the compounds, except for compound **3**, the solution of which was very dilute. Glassy-carbon working electrode, silver reference electrode and platinum counter electrode, scan rate 100 mV/s. ^{b)} $E_{\text{pa}} = +0.61$ and $E_{\text{pc}} = +0.53$ V; seems reversible, even after eight cycles. ^{c)} Value in () is the corresponding E_{pc} . ^{d)} Scan rate 1 V/s. ⁱ = Irreversible electron transfer so only E_{pc} (reduction) or E_{pa} (oxidation) listed. sh = shoulder.

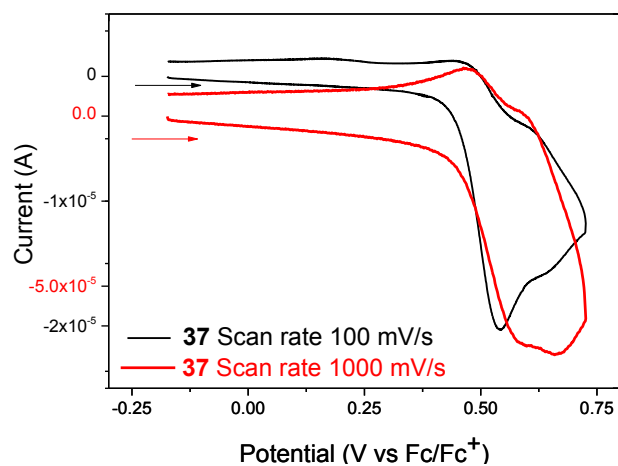


Figure S6. Cyclic voltammograms of compound **37** at scan rates of 100 mV/s (black trace) and 1000 mV/s (red trace).

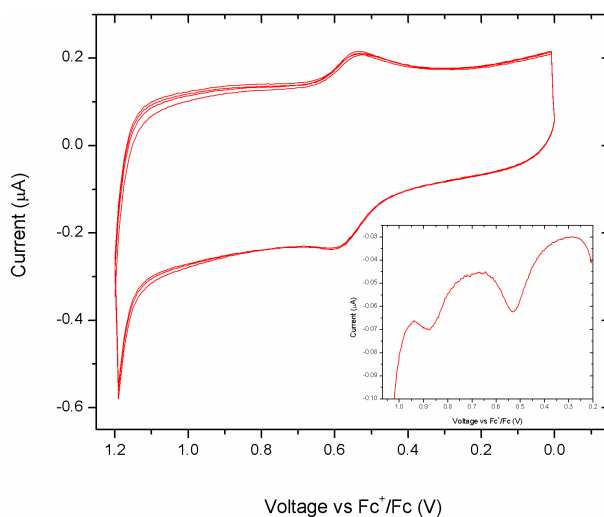


Figure S7. Cyclic Voltammogram of **3** under dilute conditions, cycled eight times to show the reversibility under dilute conditions, recorded in CH₂Cl₂ with 0.1 M Bu₄NPF₆. Inset shows Differential Pulse Voltammogram of the compound in the same solvent.

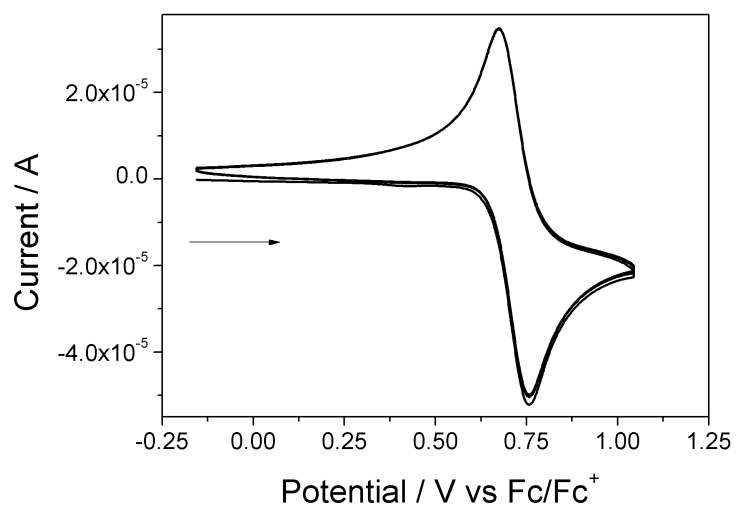


Figure S8. Cyclic voltammogram of **43** showing 10 cycles highlighting the reversibility at the scan rate of 100 mV/s.

X-Ray Crystallography

Crystals of **43** were grown by vapour diffusion of MeOH into a CH₂Cl₂ solution. Single crystal X-ray diffraction studies were performed using a Bruker D8 Venture diffractometer monochromated with a doubly curved silicon crystal (Mo K α). The datasets were collected and processed using Bruker's Apex2, with the SAINT [Bruker (2007). *Apex2*, *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA] and SADABS [Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.] programs and refined using Olex2 [Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341]. All hydrogens were added using a riding model and refined with an isotropic displacement factor of $1.2U_{eq}$ of the parent atom.

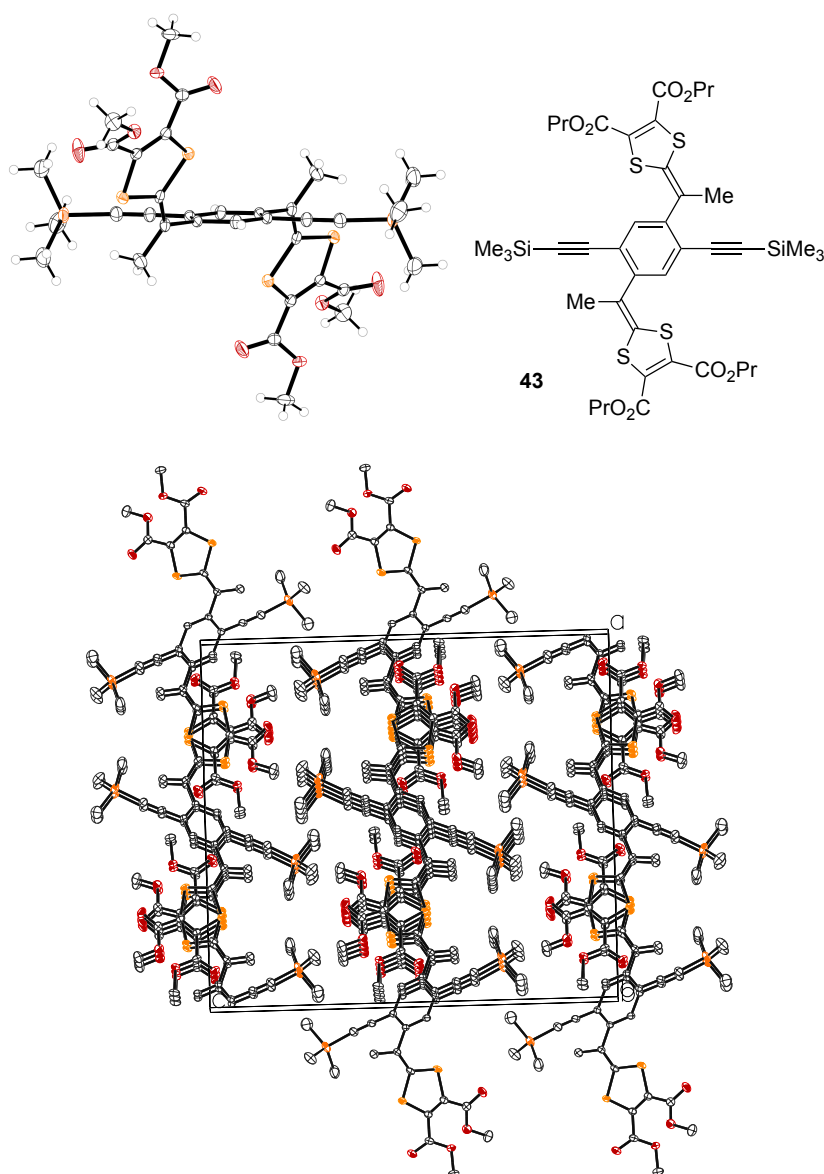


Figure S9. ORTEP plot showing the molecular structure of **43** (top) and crystal packing (bottom, H-atoms are omitted for clarity). Crystals were grown by vapour diffusion of MeOH into a CH₂Cl₂ solution.

Table S3. Crystallographic data for compound **43**.

Compound	43
Formula	C ₃₄ H ₃₈ O ₈ S ₄ Si ₂
<i>M</i> (g mole ⁻¹)	759.11
Crystal size (mm ³)	0.28×0.17×0.08
Crystal system	Orthorhombic
Space group	Pbca
<i>a</i> (Å)	20.3534(10)
<i>b</i> (Å)	8.3596(5)
<i>c</i> (Å)	22.6457(11)
α (°)	90
β (°)	90
γ (°)	90
<i>U</i> (Å ³)	3853.1(4)
<i>Z</i>	4
<i>D_x</i> (g cm ⁻³)	1.3085
<i>T</i> (K)	122(1)
μ	0.355
No. measured / unique reflections	49188 / 4097
Parameters refined	222
Final <i>R</i> 1	0.0426
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0856
<i>R</i> 1, <i>wR</i> ₂ (all data)	0.0750, 0.0981
<i>S</i> (GoF)	1.043

CP-AFM Studies on SAMs

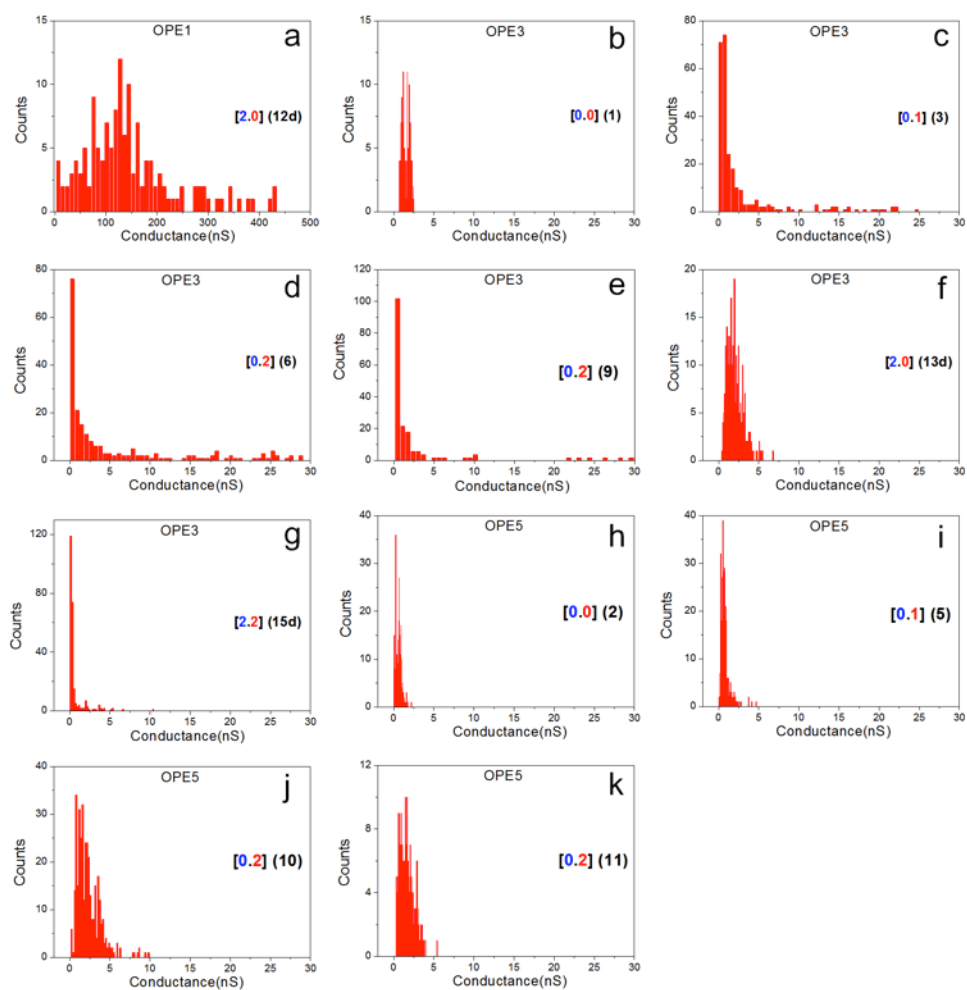


Figure S10. CP-AFM conductance histograms of the OPE molecular junctions (SAMs).

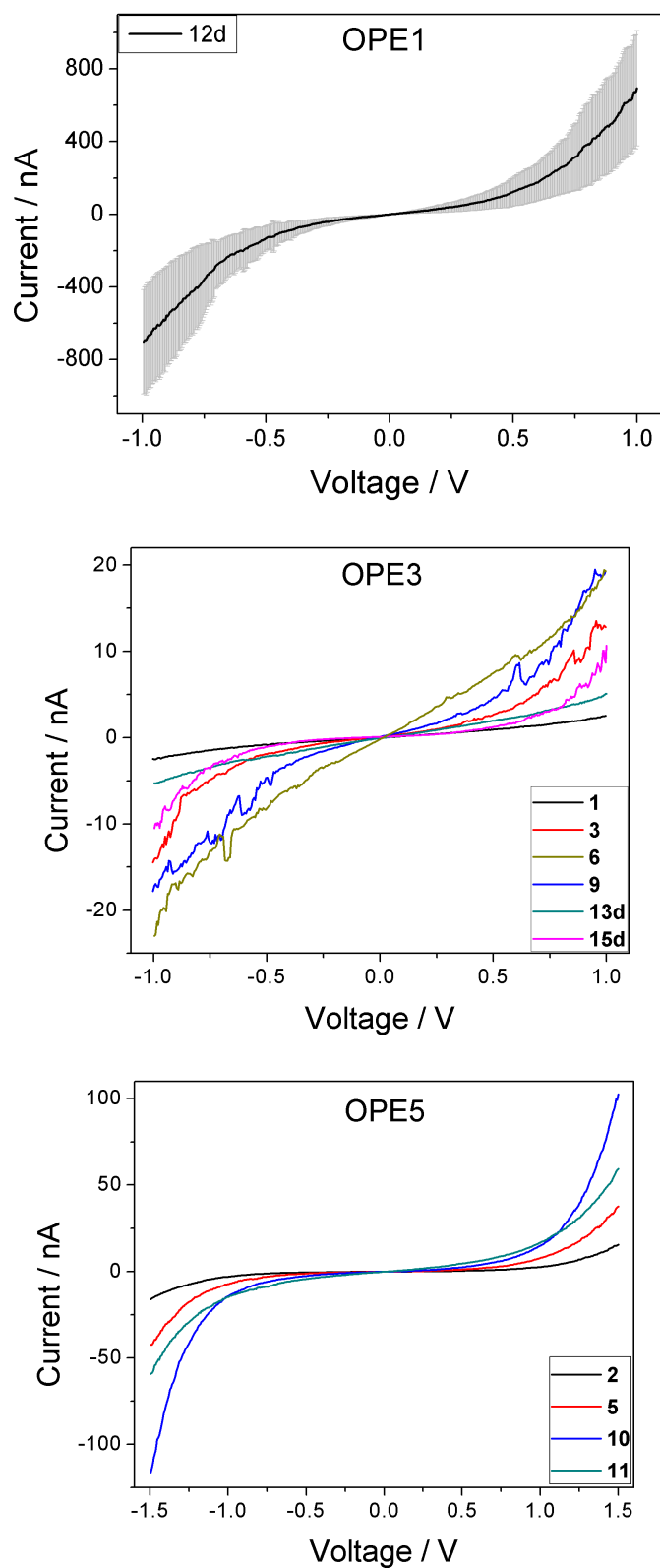


Figure S11. Average I - V curves of molecular junctions based on the OPE SAMs measured by CP-AFM. Standard deviation (error bars) is included in the curve for the “OPE1” **12d** (top).

Single-Molecule Conductance Studies

STM-BJ

Table S4. The data in the table corresponds to the experimental run with the largest

Compound	Highest % of Plateaus Observed	N _{Total}	N _{Plateaus}	Mean Plateau Length (nm)	Log Histogram max (Log(G/G ₀))	Log Histogram max (G/G ₀)	Linear Histogram max (G/G ₀)
1	26	10486	2696	1.28±0.37	-3.82±0.88	1.5 x 10 ⁻⁴	5.2 x 10 ⁻⁵
3	18	15944	2862	1.25±0.41	-3.85±1.04	1.4 x 10 ⁻⁴	5.0 x 10 ⁻⁵
6	12	13551	1603	1.21±0.46	-3.80±1.28	1.6 x 10 ⁻⁴	3.0 x 10 ⁻⁵
9	20	3115	295	1.06±0.49	-4.49±1.14	3.2 x 10 ⁻⁵	7.4 x 10 ⁻⁶
7	17	3188	754	1.13±0.46	-3.74±1.12	1.8 x 10 ⁻⁴	6.3 x 10 ⁻⁵
15c	3	4231	129	1.22±0.58	-4.54±1.34	2.9 x 10 ⁻⁵	5.0 x 10 ⁻⁶
2	22	2737	594	2.00±0.89	-6.03±0.59	9.3 x 10 ⁻⁷	6.7 x 10 ⁻⁷
10	24	5825	1401	2.17±0.64	-6.14±0.82	7.2 x 10 ⁻⁷	3.3 x 10 ⁻⁷

percentage of plateaus observed in any run. This is the same data from the same runs we present in the main text. N_{Total} and N_{Plateaus} are the total number of recorded traces and the number displaying a plateau respectively in the particular run. The mean plateau lengths are taken as the maximum from the fitted Gaussian curve to the distributions shown in Figure S6. The error quoted is the full width at half maximum (FWHM). The conductance values are taken from fitting the conductance histograms shown in Figure S13 with single Gaussian curves. The error is the FWHM. The linear conductance histogram maximum is calculated from the Gaussian fit to the log histogram.

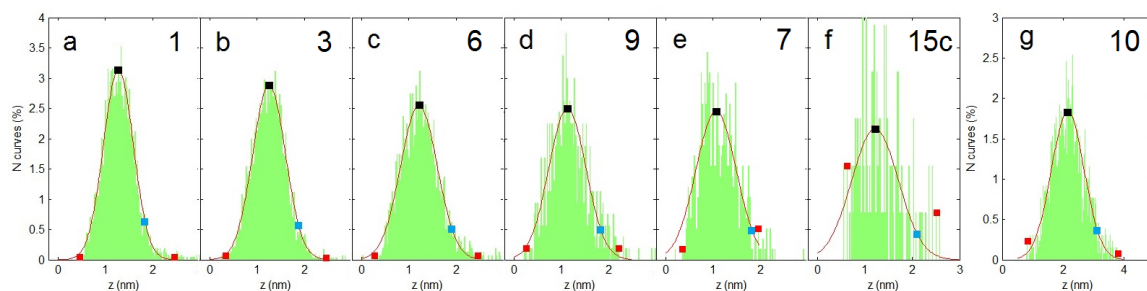


Figure S12. (a-g). Histograms of the plateau lengths measured in each $G(z)$ trace determined to contain a plateau. The plateau length of each trace is calculated as the total displacement Δz needed to change the junction conductance from 0.5 to $1 \times 10^{-5} G_0$ for compounds **1**, **2**, **4** and **7**. For the others, the lower limit was changed according to the position of the conductance peak. The black square represents the mean value whilst the blue square shows the 95th percentile.

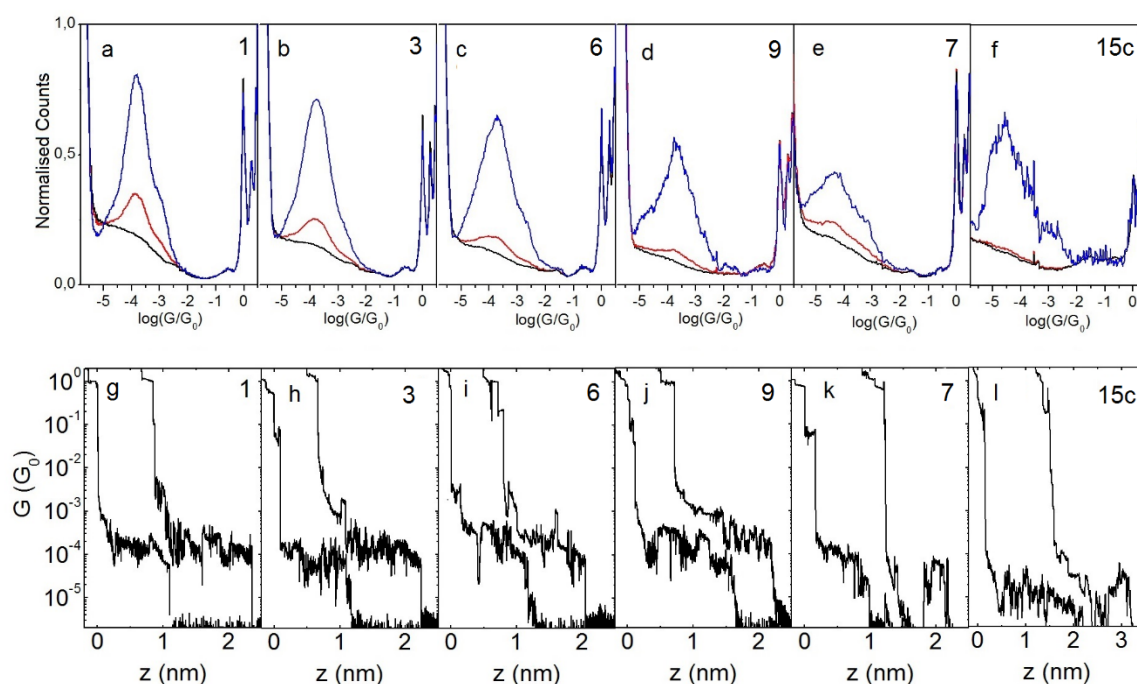


Figure S13. (a-f) One-dimensional (1D) conductance histograms for OPE3 compounds **1**, **3**, **6**, **9**, **7**, **15c**, obtained in air after exposing a substrate to a 1 mM dichlorometane solution for 30 minutes followed by rinsing with ethanol. The red, blue and black histograms represent all the traces, traces with plateaus and traces without plateaus respectively. **(g-l)** Further examples of individual $G(z)$ traces showing plateaus used to build the blue histograms in a-f.

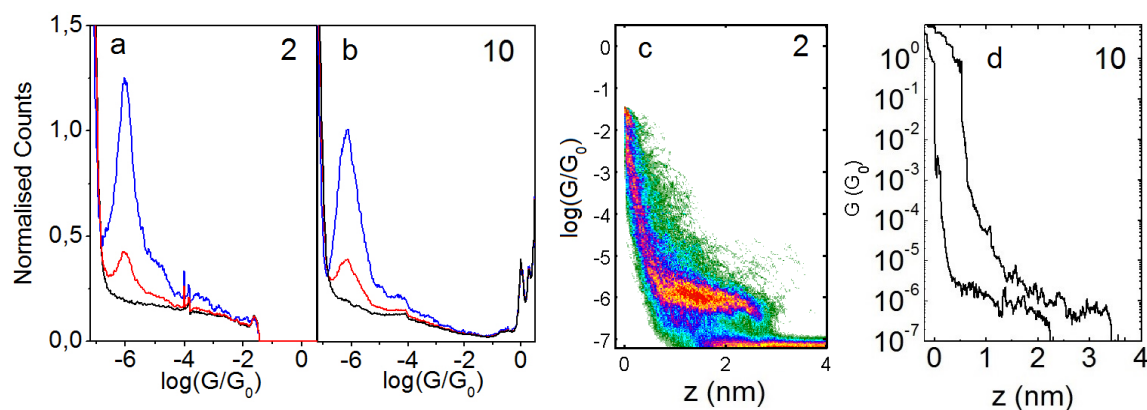


Figure S14. (a and b) One-dimensional (1D) conductance histograms for OPE5 compounds **2** and **10** obtained in air after exposing a substrate to a 1 mM dichloromethane solution for 30 minutes followed by rinsing with ethanol. **(c)** 2D histogram of compound **2** built from the same 594 traces displaying plateaus as for the blue 1D in **a**. **(d)** Examples of individual $G(z)$ traces of compound **10** showing plateaus used to build the blue histogram in **b**.

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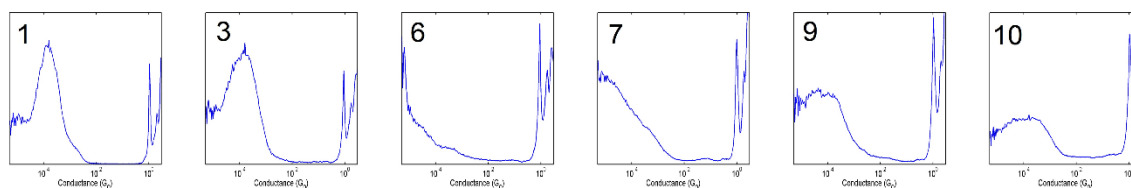


Figure S15. (a-f) One-dimensional (1D) conductance histograms for OPE compounds **1**, **3**, **6**, **7**, **9**, and **10**, obtained in air after exposing the MCBJ device to a 1 mM dichlorobenzene solution containing the molecule of interest.

Sulfur-Sulfur Distances

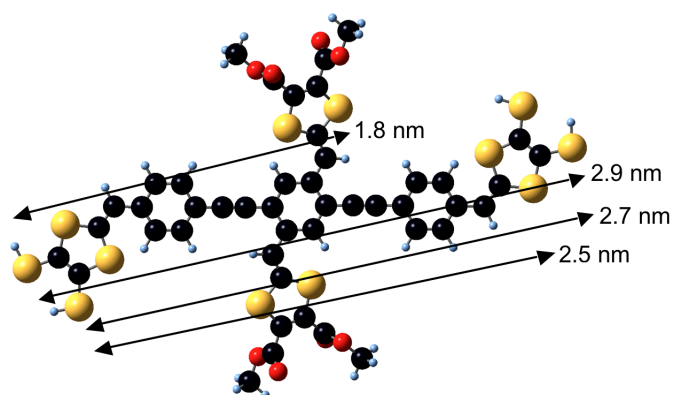


Figure S16. PM3 geometry-optimized structure of [2.2] OPE3 cruciform (with peripheral SH groups on the DTF termini and CO₂Me groups on the central DTF groups) and selected S-S distances.

Isomerism – Overview

Compounds with asymmetrically substituted DTF groups:

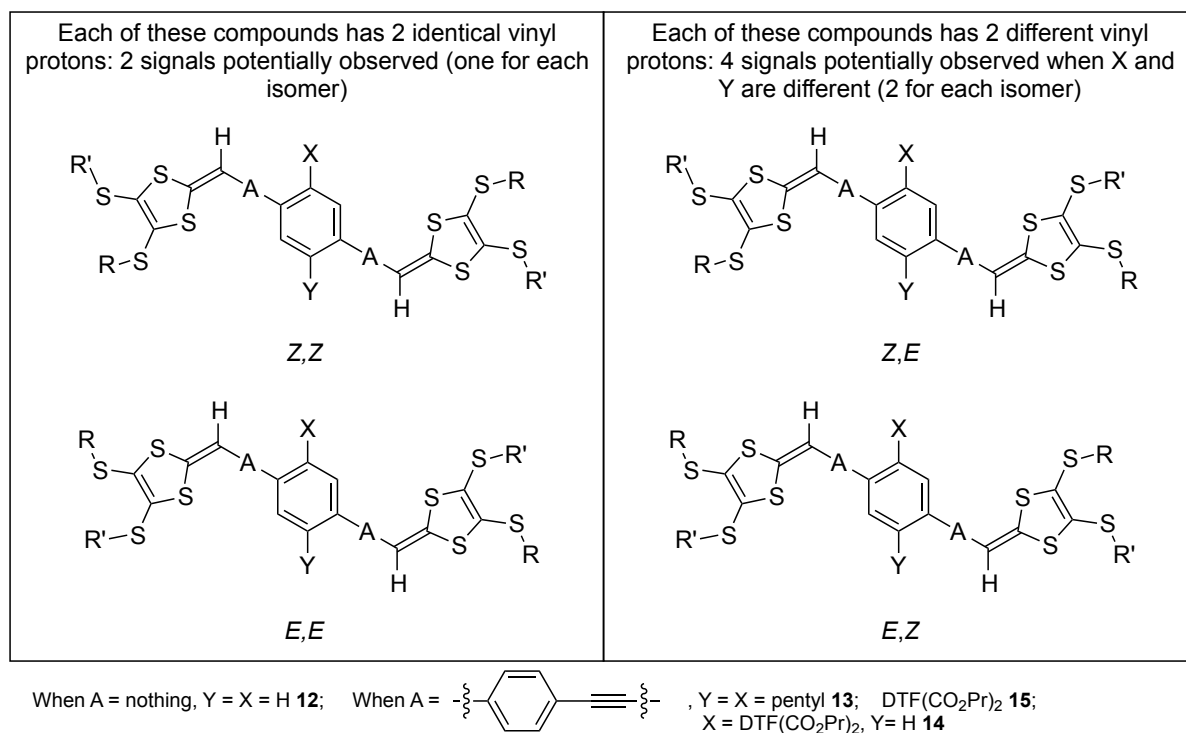


Figure S17. A mixture of isomers for **12-15b-d** (*Z,Z* / *E,E* / *Z,E* / *E,Z* – *Z,E* and *E,Z* are identical for X = Y) and **52b,d** (*Z/E*) are obtained when the substituents on the DTF are different ($R \neq R'$, Priority: $R > R'$).

Experimental

UV-Vis Absorption and Fluorescence Measurements. Optical spectra were recorded at rt using a quartz cell of 1 cm path. Room temperature fluorescence spectra were recorded on a spectrofluorometer using an integration time of 0.5 s and a band width of 3 nm. Emission and excitation spectra were corrected for the instrumental function and the analyzed data represent the average of at least 5 independent measurements.

Electrochemistry. Electrochemical samples were measured in CH₂Cl₂ containing 0.1 M [NBu₄][PF₆] as the supporting electrolyte. External reference: FeCp₂ / [FeCp₂]⁺ (*E* = 0.00 V) scanned at 100 mV/s. A glassy carbon disk electrode was used as working electrodes, a platinum wire as counter electrode and a silver electrode soaked in the electrolyte solution was used as reference

Formation and Characterization of SAMs. The OPE compounds were dissolved at 0.25 mM in 15% Et₃N in THF which had been purged of O₂ with a steady flow of Ar. Freshly stripped ultraflat gold substrates were immediately immersed into the solutions. The containers were filled with Ar and sealed, then left in absence of light for 48 h at room temperature to grow the SAMs. After removal from the solutions, the sample was extensively rinsed with ethanol and then dried under a stream of N₂ before all measurements. The SAMs were studied by conventional cyclic voltammetry measurements using a three-electrode cell containing a Au work electrode (~0.4 cm²), a platinum electrode, and a Ag/AgCl reference electrode in 5.0 mM K₃Fe(CN)₆/K₄Fe(CN)₆ solution with 1 M KNO₃ as supporting electrolyte. XPS experiments were performed using a monochromated Al K α (h ν =1486.6 eV, power=150 W) X-ray source. The base pressure in the chamber was 5 x 10⁻¹⁰ mbar and never exceeds 5 x 10⁻⁹ mbar during an experiment. A pass energy (PE) of 160 eV was used for wide scan and PE=10 eV for high resolution scan. All samples were energy calibrated using the Au 4f7/2 line at 84 eV.

CP-AFM Measurements. CP-AFM measurements were performed at room temperature in air. A tip (spring constant: 2 N/m) with a 30 nm Au coating was used. The current-voltage (*I*-*V*) characteristics of the SAM were measured by a tunneling current AFM application mode. The conductive tip in contact with SAM was the top electrode and the Au substrate at the bottom of SAM was connected with a conducting wire as one external electrode. The load force was maintained at about 4 nN to achieve a soft contact. *I*-*V* curves were recorded using the same tip and at different places (at least 100~200 places and 2 cyclic measurements at each place). The voltage range was 1 to -1 V or 1.5 to -1.5 V, and at each point, the adding voltage was swept in both directions.

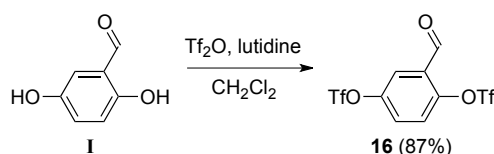
STM-BJ Methods. The molecules were deposited onto a freshly flame-annealed gold substrate from a 1 mM dichloromethane solution, using an immersion time of 30 minutes. After, the sample was rinsed copiously with ethanol to remove unbound material and blown dry with a stream of nitrogen. The sample was mounted directly in the microscope and allowed to dry further for 1-2 hours. All measurements were carried out in air using a bias voltage *V*_{bias} = 0.2 V and a retraction rate of approximately 40 nms⁻¹ with a resolution of 1 pm. We recorded approximately ten thousand opening and closing traces per sample. During a measurement sequence we varied the location of the tip over the surface by pausing the experiment and manually rotating the head of the microscope. In the analysis we focus on the opening stages of the cycle, and search for conductance versus distance plateaus, which are the typical signal of molecular junction formation. We separated traces containing such plateaus using an automated routine after completion of the measurements. The criteria used

depend slightly on the molecule as the plateau appearance varies from molecule to molecule. For molecules **1**, **2**, **4** and **7** a trace was judged to contain a plateau whenever an elongation δz larger than 0.18 nm is needed to produce a decay in conductance of $\delta \log (G/G_0)=0.2$ at any conductance below 0.5 G_0 .

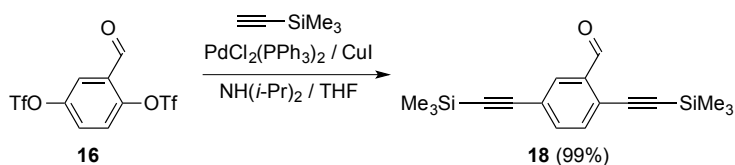
MCBJ Methods. The MCBJ device was mounted in the setup in a three-point bending configuration and the gold wire electrically contacted. The gold nano-electrodes were firstly formed, by breaking the gold wire, and then few thousands opening and closing traces were recorded. All the measurements were performed in air at room temperature, the bias voltage was $V_{\text{bias}} = 0.1$ V and the electrode separation speed $v_{\text{electrode}} = 5$ nm/s. After the characterization of the clean gold sample, we deposited the molecule of interest by drop-casting 2 μL of a 1 mmol/L solution (dichlorobenzene) onto the device. For each molecule, we record between one and two thousands conductance traces, during the opening and closing cycles.

General Synthesis Methods and Characterization Techniques. 2,5-Dihydroxybenzaldehyde, methyl 2,5-dihydroxybenzoate, trimethylsilylacetylene, phenylacetylene, (triisopropylsilyl)acetylene, 4-iodoaniline, terephthalaldehyde, triethyl phosphite $\text{P}(\text{OEt})_3$, and 4-iodobenzaldehyde were commercially available. *Literature references for synthesis of starting materials:* **17** (Wang, L.-G.; Zhan, T.-G.; Zhao, X.; Jiang, X.-K.; Li, Z.-T. *Tetrahedron* **2012**, 68, 5303-5310), **20** (Sato, M.; Gonnella, N. C.; Cava, M. P. *J. Org. Chem.* **1979**, 44, 930-934), **23** (Jennum, K.; Vestergaard, M.; Pedersen, A. H.; Fock, J.; Jensen, J.; Santella, M.; Led, J. J.; Kilså, K.; Bjørnholm, T.; Nielsen, M. B. *Synthesis* **2011**, 539-548), **30** (Stuhr-Hansen, N.; Sørensen, J. K.; Moth-Poulsen, K.; Christensen, J. B.; Bjørnholm, T.; Nielsen, M. B. *Tetrahedron* **2005**, 61, 12288-12295), **38** and **40** (Sørensen, J. K.; Vestergaard, M.; Kadziola, A.; Kilså, K.; Nielsen, M. B. *Org. Lett.* **2006**, 8, 1173-1176; Jennum, K.; Vestergaard, M.; Pedersen, A. H.; Fock, J.; Jensen, J.; Santella, M.; Led, J. J.; Kilså, K.; Bjørnholm, T.; Nielsen, M. B. *Synthesis* **2011**, 539-548), **42** (Baffreau, J.; Dumur, F.; Hudhomme, P. *Org. Lett.* **2006**, 8, 1307-1310), **51a** and **51b** (Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Synthesis* **1994**, 809-812; Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mørk, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1996**, 407-418), **IV** (Hu, L.-Y.; Ryder, T. R.; Rafferty, M. F.; Taylor, C. P.; Feng, M. R.; Kuo, B.-S.; Lotarski, S. M.; Miljanich, G. P.; Millerman, E.; Siebers, K. M.; Szoke, B. G. *Bioorg. Med. Chem.* **2000**, 8, 1203-1212). 1-Propanol was dried over molecular sieves (4 Å), THF was either distilled over Na / benzophenone or obtained from a solvent drying tower, DMF was obtained from a solvent drying tower. When amine bases (NEt_3 , $\text{NH}(i\text{-Pr})_2$) were used as a major component in a solvent they were passed through basic Al_2O_3 just prior to use. Sonogashira couplings were performed under inert atmosphere with the solvents carefully flushed beforehand with inert gas. $\text{CsOH}\cdot\text{H}_2\text{O}$ was easily dissolved in 1-propanol to form a ca. 0.17 M (ca. 25 mg in 1 mL) solution; at higher concentrations solubility became an issue. $\text{NaOPr}/1\text{-PrOH}$ was freshly prepared by addition of Na into 1-PrOH under inert atmosphere. *Standard washing procedure* for substituting cyanoethyl groups in DMF: 5 min after the electrophile (MeI or AcCl) was added to the thiolate the solution was diluted with CH_2Cl_2 (50 mL) and then it was washed with water (5-10 x 50 mL) to remove the DMF. The organic phase was then dried (Na_2SO_4) and the solvent removed before the residue was loaded onto a column. Compounds with DTF-SAc anchoring groups are quite sensitive and can degrade on silica and in solution for prolonged period (a more expensive brand of silica is milder on these compounds and does not cause a large amount of degradation during column chromatography or darkening and degradation once the compound is off the column). For NMR analysis, CDCl_3 should be avoided or at least passed through a plug of basic alumina prior to use; better alternatives are CD_2Cl_2 or C_6D_6 , if the compound is soluble enough in the

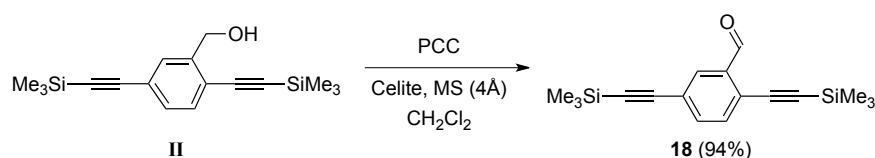
latter. If there is only a minor impurity in the sample after the column chromatography, it can often be purified by taking it up in minimal CH_2Cl_2 and triturating the compound in either MeOH or heptanes and then collecting the precipitate and washing with pentane. A mixture of isomers are obtained for compounds with different peripheral groups on the DTFs (**12-15b-d** *Z,Z* / *Z,E* / *E,Z* / *E,E* and **52b,d** *Z/E*), which complicates the NMR spectra by increasing the number of peaks. In general, there is some overlap in signals in the ^1H and ^{13}C NMR spectra. There is also a possibility that some of the quaternary carbons are not observed when relaxing too slowly, especially on the DTF groups. Missing carbon resonances based on the number of different carbon atoms, whether due to overlap or due to too weak intensities, are indicated for all compounds except for the *Z/E* isomeric compounds. IR spectra were obtained using the attenuated total reflectance (ATR) method on either neat oils or on a solution of the compound being dropped onto the diamond and waiting for the solvent to evaporate off and measuring on a thin film. The relative peak intensities were recorded, where vw = very weak, w = weak, m = medium, s = strong, vs = very strong, br = broad, sh = shoulder. Mass spectrometry (MS) was performed using either Electrospray Ionization (ESI), Matrix Assisted Laser Desorption Ionization (MALDI), Fast Atom Bombardment (FAB), or using a gas chromatograph coupled with a mass selective detector (GC); HR = High Resolution. Elemental analysis was either performed at University of Copenhagen or at London Metropolitan University. Melting points are uncorrected.



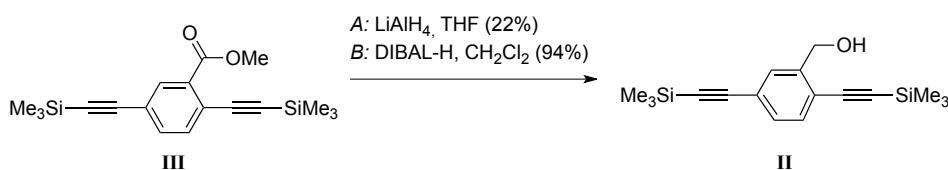
Compound 16. To a solution of 2,5-dihydroxybenzaldehyde (**I**) (1.00 g, 7.24 mmol) in CH_2Cl_2 (50 mL) was added 2,6-lutidine (2.5 mL). The mixture was cooled to 0 °C and then triflic anhydride (6.13 g, ~3.7 mL, 21.7 mmol) was added dropwise. The reaction mixture was then stirred for 30 min before the solvents were removed under reduced pressure and the remaining solids were redissolved in Et_2O (100 mL). The ether was then washed with water (2 x 50 mL), brine (50 mL) and dried over Na_2SO_4 . The solvent was then evaporated off and the red oily crude was poured through a short plug (SiO_2 , heptane / CH_2Cl_2 2:1). Fractions containing the product were collected and concentrated to a white powder (2.55 g, 87%). Mp 53-54 °C. Anal. Calcd ($\text{C}_9\text{H}_4\text{F}_6\text{O}_7\text{S}_2$): C, 26.87; H, 1.00. Found: C, 26.65; H, 0.68. ^1H NMR (500 MHz, CDCl_3) δ 10.26 (s, 1H), 7.91 (d, J = 3.1 Hz, 1H), 7.64 (dd, J = 9.1, 3.1 Hz, 1H), 7.56 (d, J = 9.1 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 184.33, 148.77, 148.76, 130.33, 128.70, 125.01, 123.12, 118.79 (q, $J_{\text{C-F}}$ = 321 Hz), 118.73 (q, $J_{\text{C-F}}$ = 321 Hz). MS (GC-MS) m/z : 402 $[\text{M}]^+$.



Compound 18. Compound **16** (1.00 g, 2.49 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (175 mg, 0.25 mmol, 10 mol%), CuI (48 mg, 0.25 mmol, 10 mol%), and trimethylsilylacetylene (733 mg, ~ 1.1 mL, 7.46 mmol) were dissolved in argon degassed, dry THF (8 mL) and $\text{NH}(i\text{-Pr})_2$ (2 mL). The reaction mixture was then stirred for 1 h at rt and then at 45 °C for 15 min before it was cooled to rt and Et_2O (100 mL) was added. The ether phase was washed with saturated aqueous NH_4Cl (100 mL) and brine (100 mL) before it was dried over Na_2SO_4 and concentrated *in vacuo*. The oily crude was then subjected to flash column chromatography (SiO_2 , CH_2Cl_2 / petroleum spirit 1:2) giving the product as white powder (739 mg, 99%).

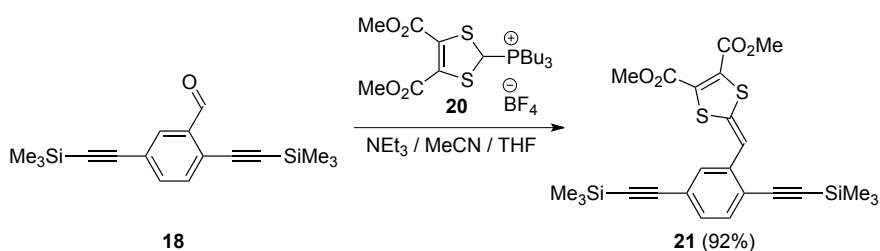


Compound 18. To a solution of the alcohol **II** (1.26 g, 4.2 mmol) in dry CH_2Cl_2 (100 mL) was added 4 Å molecular sieves (2.57 g), Celite (1.25 g) and PCC (1.48 g, 6.87 mmol). The reaction mixture changed color from yellow to black. After 2 h, further PCC (0.11 g, 0.51 mmol) was added. The crude was run through a short plug (SiO_2 , CH_2Cl_2) to give the product as a thick, slightly yellow oil that slowly solidified (1.18 g, 94%) Mp 54-55 °C. ^1H NMR (500 MHz, CDCl_3) δ 10.49 (s, 1H), 7.97 (dd, $J = 1.7, 0.5$ Hz, 1H), 7.59 (dd, $J = 8.0, 1.7$ Hz, 1H), 7.50 (dd, $J = 8.0, 0.5$ Hz, 1H), 0.28 (s, 9H), 0.25 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.17, 136.51, 135.98, 133.49, 130.56, 126.27, 124.00, 104.41, 103.23, 99.78, 98.04, -0.09, -0.16. MS (GC-MS) m/z : 298 $[\text{M}]^+$.

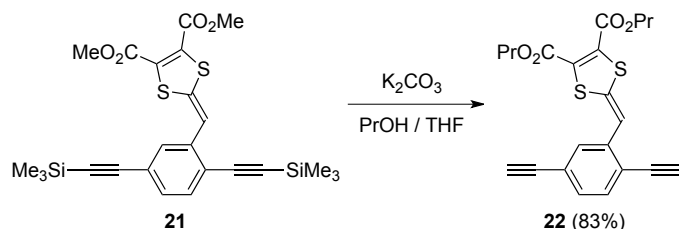


Compound II. *Method A:* Compound **III** (1.966 g, 6.08 mmol) was weighed off in a dried round-bottomed flask, put under argon atmosphere and then dry THF (15 mL) was added. LiAlH_4 (6.1 mL, 6.1 mmol, 1 M in THF) was added to the yellow solution, this made the solution change color to black, which after 15 min slowly changed back to yellow. Any excess LiAlH_4 was neutralized by dropwise addition of H_2O (0.5 mL). The reaction mixture was poured into CH_2Cl_2 (15 mL) and saturated aqueous NH_4Cl (20 mL) was added. The water phase was extracted with CH_2Cl_2 (50 mL) and the combined organic phases were washed with H_2O (50 mL) and dried with Na_2SO_4 . The solvents were removed under reduced pressure and the crude product was purified by flash column chromatography (SiO_2 , CH_2Cl_2). After removal of solvents *in vacuo* the product was isolated as a thick oil which solidified to a white solid (0.40 g, 22%). *Method B:* Compound **III** (1.474 g, 4.49 mmol) was weighed off in a dried round-bottomed flask, put under argon atmosphere, dissolved in dry CH_2Cl_2 (10 mL), and DIBAL-H (11.2 mL, 11.2 mmol, 1 M in CH_2Cl_2) was then added to the yellow

solution. After 45 min, the reaction mixture was poured into saturated aqueous NH_4Cl (50 mL) and ice, which resulted in a thick gel. After extensive extraction with CH_2Cl_2 (5 x 100 mL), the combined organic phases were washed with H_2O (50 mL), dried over Na_2SO_4 and the solvents were removed *in vacuo* giving the product as a yellow oil (1.262 g, 94%). Mp 75.1-76.7 °C. Anal. Calcd ($\text{C}_{17}\text{H}_{24}\text{OSi}_2$): C, 67.94; H, 8.05. Found: C, 67.98; H, 8.03. ^1H NMR (500 MHz, CDCl_3) δ 7.54 - 7.53 (m, 1H), 7.38 (d, J = 7.9 Hz, 1H), 7.32 (dd, J = 7.9, 1.6 Hz, 1H), 4.78 (d, J = 6.3 Hz, 2H), 2.13 (t, J = 6.3 Hz, 1H), 0.26 (s, 9H), 0.24 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 143.23, 132.35, 130.77, 130.60, 123.73, 121.17, 104.63, 102.20, 101.72, 96.61, 63.75, 0.04, 0.02. MS (GC-MS) m/z : 300 $[\text{M}]^+$.

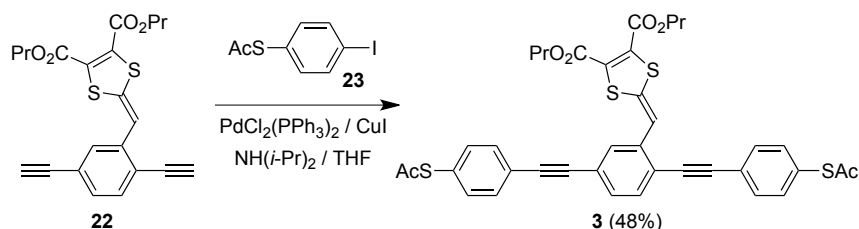


Compound 21. Aldehyde **18** (0.751 g, 2.52 mmol) and phosphonium salt **20** (1.92 g, 3.77 mmol) were dissolved in dry degassed MeCN (9 mL) and THF (36 mL), which gave a yellow colored solution. NEt_3 (0.7 mL, 5.03 mmol) was then added to the solution, which made the solution turn to an orange color. After stirring for 2 h, the solution was poured into CH_2Cl_2 and washed with H_2O (3 x 50 mL). The aqueous phase was extracted with CH_2Cl_2 (50 mL), the combined organic phases were dried with Na_2SO_4 and the solvent removed *in vacuo*. The crude product was purified with flash column chromatography (SiO_2 , CH_2Cl_2) and the major orange band was collected and removal of solvents *in vacuo* yielded the product as an orange solid (1.165 g, 92%). Mp 166.1-167.7 °C. Anal. Calcd ($\text{C}_{24}\text{H}_{28}\text{O}_4\text{S}_2\text{Si}_2$): C, 57.56; H, 5.64. Found: C, 57.87; H, 5.53. ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 1.5 Hz, 1H), 7.22 (dd, J = 8.0, 1.5 Hz, 1H), 6.86 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 0.26 (s, 9H), 0.26 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 160.18, 160.08, 137.49, 133.46, 132.68, 131.08, 129.89, 129.87, 127.95, 123.53, 121.36, 113.20, 104.41, 102.85, 102.45, 96.83, 53.69 - 53.54 (m, 2C, due to incomplete decoupling), 0.05; 1 signal missing due to overlap (SiMe_3). MS (ESP+) m/z : 501 $[\text{M}+\text{H}]^+$.

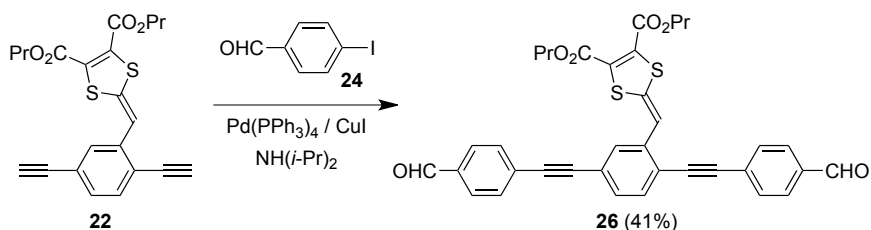


Compound 22. Compound **21** (0.502 g, 1.00 mmol) was dissolved in THF (20 mL) and 1-propanol (60 mL), and then K_2CO_3 (1.504 g, 10.88 mmol) was added to this stirring orange colored solution. After stirring for 24 h, the reaction mixture was poured into CH_2Cl_2 (150 mL) and run through a short silica plug (SiO_2 , CH_2Cl_2). The silica was further extracted with CH_2Cl_2 (3 x 100 mL), solvents were removed *in vacuo* to give an orange colored oil, which solidified after 1 week as an orange solid (345 mg, 83%). Mp 49.3-52.1 °C. Anal. Calcd ($\text{C}_{22}\text{H}_{20}\text{O}_4\text{S}_2$): C, 64.05; H, 4.89. Found: C, 63.67; H, 4.83. ^1H NMR (500 MHz, CDCl_3) δ

7.47 (d, $J = 1.5$ Hz, 1H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.26 (dd, $J = 7.9, 1.5$ Hz, 1H), 6.87 (s, 1H), 4.21, 4.21 (2 x t, $J = 6.6$ Hz, 4H), 3.43 (s, 1H), 3.19 (s, 1H), 1.73 (m, 4H), 0.98, 0.97 (2 x t, $J = 7.4, 6$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 159.73, 159.60, 137.98, 134.64, 133.31, 131.26, 129.82, 129.70, 128.51, 122.96, 120.78, 112.30, 84.49, 83.11, 81.49, 79.44, 68.49, 68.45, 21.93, 21.92, 10.46, 10.44. MS (ESP+) m/z : 413 $[\text{M}+\text{H}]^+$.

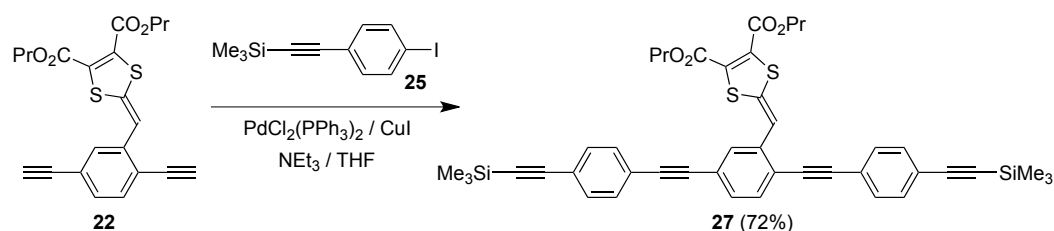


Compound 3. A mixture of **22** (166 mg, 597 μmol), CuI (11 mg, 58 μmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (16 mg, 23 μmol) was dissolved in THF (15 mL) and stirred. To this solution was added $\text{NH}(i\text{-Pr})_2$ (1 mL) followed 5 min later by **23** (152 mg, 368 μmol) and a further portion of **23** (151 mg, 543 μmol). After 3 h, the reaction mixture had turned an orange color and after an additional 1 h, Ac_2O (0.1 mL, 1 mmole) was added. After stirring for 30 min, the reaction mixture was poured into CH_2Cl_2 (55 mL), washed with water saturated with NH_4Cl (55 mL) and then washed with brine (50 mL). The water phases were extracted with CH_2Cl_2 (30 mL) and the combined organic phases were dried with Na_2SO_4 and the solvents were removed *in vacuo*. The crude product was purified by flash column chromatography (SiO_2 , CH_2Cl_2); the first band was unreacted **23** while the second major orange band gave the product as an orange solid (127 mg, 48%). Mp 139.3-141.4 $^\circ\text{C}$. Anal. Calcd ($\text{C}_{38}\text{H}_{32}\text{O}_6\text{S}_4$): C, 64.02; H, 4.52. Found: C, 63.68; H, 4.28. ^1H NMR (500 MHz, CDCl_3) δ 7.59 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.3$ Hz, 2H), 7.54 - 7.50 (m, 2H), 7.43 (d, $J = 1.4$ Hz, 2H), 7.42 - 7.40 (m, 2H), 7.34 (dd, $J = 8.1, 1.4$ Hz, 1H), 6.94 (s, 1H), 4.22, 4.21 (2 x t, $J = 6.7$ Hz, 4H), 2.45 (s, 3H), 2.44 (s, 3H), 1.73 (m, 4H), 0.99, 0.98 (2 x t, $J = 7.3$ Hz, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 193.50, 193.46, 159.71, 159.67, 137.58, 134.44, 134.37, 132.80, 132.42, 132.26, 131.11, 130.04, 129.49, 128.72, 128.60, 128.12, 124.27, 124.20, 123.50, 121.25, 112.63, 95.97, 90.90, 90.75, 89.15, 68.49, 68.45, 30.46 (2x), 21.92, 10.48, 10.44; 2 signals missing. MS (ESP+) m/z : 713 $[\text{M}+\text{H}]^+$.

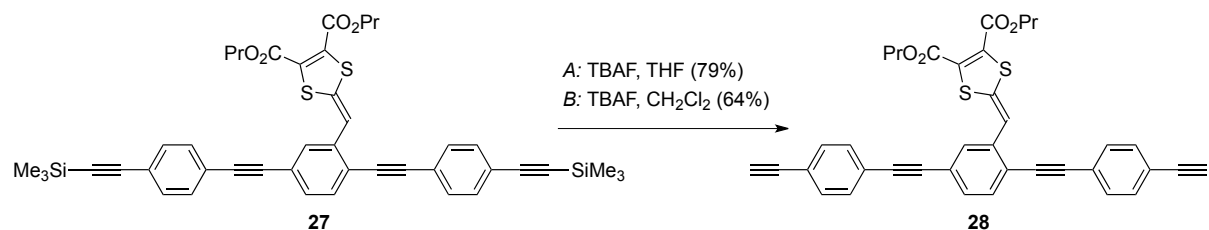


Compound 26. Compounds **22** (290 mg, 703 μmol), 4-iodobenzaldehyde **24** (421 mg, 1.81 mmol), $\text{Pd}(\text{PPh}_3)_4$ (84 mg, 73 μmol) and CuI (14 mg, 72 μmol) were weighed off in a round-bottomed flask and put under Ar atmosphere. The solids were dissolved in degassed $\text{NH}(i\text{-Pr})_2$ (100 mL) and the reaction mixture was sonicated at 40 $^\circ\text{C}$ for 40 min and was then stirred at rt. After 21 h, the amine was evaporated off *in vacuo* and the crude product was redissolved in toluene and filtered through cotton. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO_2 , CH_2Cl_2). The fourth

band was orange and gave **26** as an orange solid (180 mg, 41%). Mp 142.7-143.9 °C. Anal. Calcd (C₃₆H₂₈O₆S₂): C, 69.66; H, 4.55. Found: C, 69.23; H, 4.33. IR(ATR, cm⁻¹): ν = 2967w, 2879vw, 2842vw, 2741vw, 2210vw (C≡C), 1733m sh (CO₂Pr), 1702vs (CH=O), 1599m, 1560m, 1508vw, 1466w, 1412vw, 1388w, 1349vw, 1300m, 1283m sh, 1239s, 1205s. ¹H NMR (500 MHz, CD₂Cl₂) δ 10.03 (s, 2H), 7.91 – 7.88 (m, 4H), 7.75 – 7.71 (m, 4H), 7.61 – 7.59 (m, 2H), 7.42 – 7.40 (m, 1H), 7.00 (s, 1H), 4.20, 4.20 (2 x t, J = 6.7 Hz, 4H), 1.76-1.68 (m, 4H), 0.97, 0.97 (2 x t, J = 7.4 Hz, 6H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 191.82, 191.78, 160.07, 159.90, 138.28, 136.47, 136.43, 135.54, 133.52, 132.80, 132.65, 131.76, 130.09, 130.05, 129.98, 129.42, 129.34, 128.61, 123.94, 121.63, 112.61, 96.35, 92.96, 91.43, 91.26, 69.01, 68.91, 22.35, 22.34, 10.64; 2 signals missing. HR-MS (MALDI) m/z : 620.1317 [M]⁺; calcd for C₃₆H₂₈O₆S₂⁺: 620.1322.

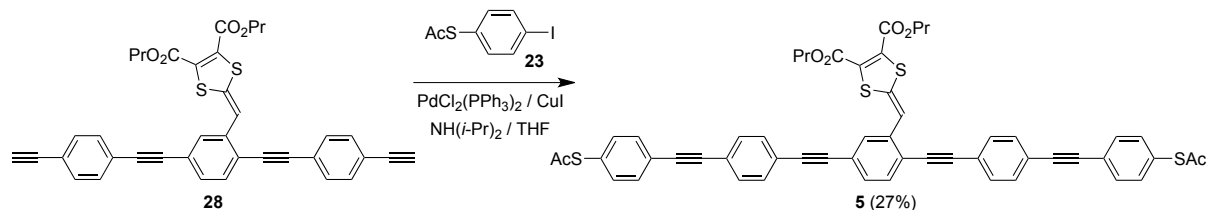


Compound 27. A mixture of **22** (407 mg, 987 μ mol), **25** (891 mg, 2.97 mmol), PdCl₂(PPh₃)₂ (70 mg, 0.10 mmol) and CuI (19 mg, 0.10 mmol) was dissolved in dry argon degassed THF (20 mL), and 1 min later argon degassed NEt₃ (1.38 mL, 9.87 mmol) was added whereupon the reaction mixture turned black. After stirring for 7 h, the solvent was evaporated *in vacuo* and the crude was purified by flash chromatography (SiO₂, heptane / CH₂Cl₂ 1:3); collection of the first major orange band gave the product **27** as an orange solid (535 mg, 72%). Mp 153.4-155.7 °C. Anal. Calcd (C₄₄H₄₄O₄S₂Si₂): C, 69.80; H, 5.86. Found: C, 69.51; H, 5.62. ¹H NMR (500 MHz, CDCl₃) δ 7.50 - 7.45 (m, 12H), 7.32 (dd, J = 8.0, 1.5 Hz, 1H), 6.94 (s, 1H), 4.22, 4.21 (2 x t, J = 6.7 Hz, 4H), 1.73 (m, 4H), 0.99, 0.98 (2 x t, J = 7.4 Hz, 6H), 0.26 (s, 9H), 0.26 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 159.74, 159.69, 137.46, 134.24, 132.77, 132.13, 132.08, 131.66, 131.49, 131.10, 130.06, 129.44, 128.06, 123.52, 123.51, 123.39, 123.08, 123.00, 121.31, 112.73, 104.73, 104.69, 96.80, 96.68, 96.43, 91.33, 91.04, 89.45, 68.51, 68.46, 21.93, 10.48, 10.45, 0.07; 2 signals missing. MS (ESP+) m/z : 757 [M+H]⁺.

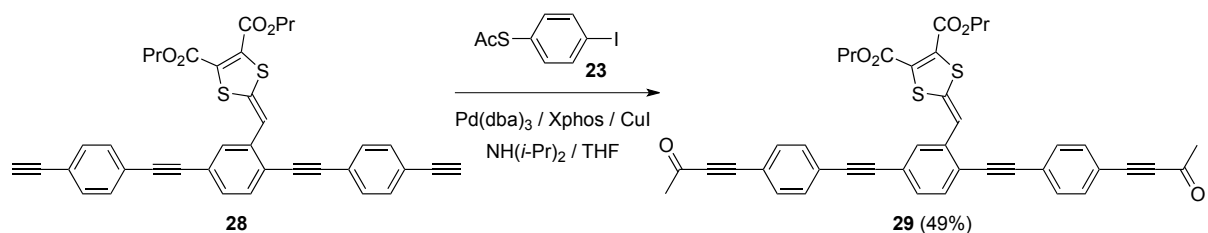


Compound 28. *Method A:* In a dried round-bottomed flask, **27** (90 mg, 119 μ mol) was weighed off and dissolved in THF (20 mL) after which TBAF•3H₂O (130 mg, 412 μ mol) was added. The reaction mixture went from an orange color to black. After stirring for 4.5 h, the reaction mixture was diluted with CH₂Cl₂ (50 mL) and washed with saturated aqueous NH₄Cl (2 x 50 mL). The water phase was extracted with CH₂Cl₂ (50 mL) and the combined organic phases were run through a short silica column (SiO₂, CH₂Cl₂). Concentration *in vacuo* yielded the pure product **28** as an orange solid (57.5 mg, 79%). *Method B:* Using CH₂Cl₂ as

solvent for the reaction under otherwise similar conditions, the product was obtained in a yield of 64%. Mp 119.7-122.4 °C. Anal. Calcd (C₃₈H₂₈O₄S₂): C, 74.48; H, 4.61. Found: C, 74.56; H, 4.18. ¹H NMR (500 MHz, CDCl₃) δ 7.55 - 7.49 (m, 11H), 7.33 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.93 (s, 1H), 4.22, 4.21 (2 x t, *J* = 6.7 Hz, 4H), 3.20 (s, 1H), 3.19 (s, 1H), 1.73 (m, 4H), 0.99, 0.98 (2 x t, *J* = 7.4 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 159.74, 159.70, 137.52, 134.33, 132.79, 132.32, 132.26, 131.75, 131.59, 131.09, 130.07, 129.47, 128.10, 123.51, 123.44, 122.48, 122.37, 121.28, 112.68, 96.22, 91.14, 91.09, 89.50, 83.38, 83.35, 79.35, 79.26, 68.52, 68.47, 21.93, 10.47, 10.45; 2 signals missing. MS (ESP+) *m/z*: 613 [M+H]⁺.

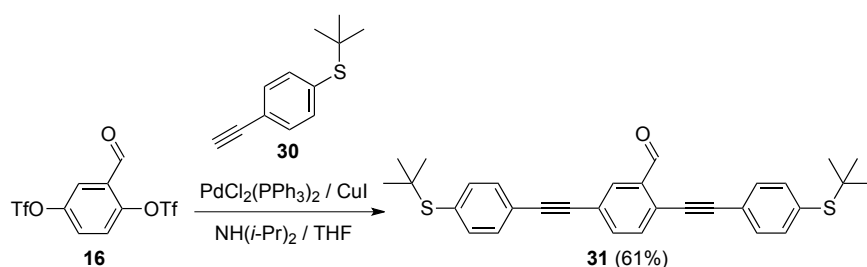


Compound 5. To a mixture of **28** (69 mg, 113 μmol), **23** (102 mg, 367 μmol) and PdCl₂(PPh₃)₂ (10 mg, 14 μmol) was added dry argon degassed THF (14 mL). This was followed by addition of NH(*i*-Pr)₂ (0.4 mL), and 5 min later, CuI (8 mg, 42 μmol) was added. After stirring for 22 h, the reaction mixture was diluted with CH₂Cl₂ (100 mL), washed with saturated aqueous NH₄Cl (2 x 75 mL) and the water phase was extracted with CH₂Cl₂ (25 mL). The combined organic phases were dried with Na₂SO₄ and the solvent was evaporated *in vacuo*. The crude product was purified by flash column chromatography (SiO₂, CH₂Cl₂); the first two bands gave starting materials **23** and **28**, respectively, while the third band gave the OPE5 **5** as an orange solid (28 mg, 27%). ¹H NMR (500 MHz, CDCl₃) δ 7.58 - 7.52 (m, 14H), 7.41 (d, *J* = 8.0 Hz, 4H), 7.35 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.96 (s, 1H), 4.22, 4.22 (2 x t, *J* = 6.7 Hz, 4H), 2.44 (s, 6H), 1.74 (m, 4H), 0.99, 0.98 (2 x t, *J* = 7.4 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 193.54, 159.75, 159.71, 137.52, 134.40, 134.30, 132.80, 132.35, 131.86, 131.85, 131.81, 131.68, 131.10, 130.08, 129.48, 128.53, 128.50, 128.10, 124.40, 124.37, 123.55, 123.31, 123.20, 123.17, 123.09, 121.33, 112.73, 96.48, 91.38, 91.18, 90.90, 90.86, 90.83, 90.81, 89.59, 68.53, 68.48, 30.47, 21.94, 10.48, 10.47; 5 signals missing. HR-MS (MALDI) *m/z*: 912.1690 [M]⁺; calcd for C₅₄H₄₀O₆S₄⁺: 912.1702.

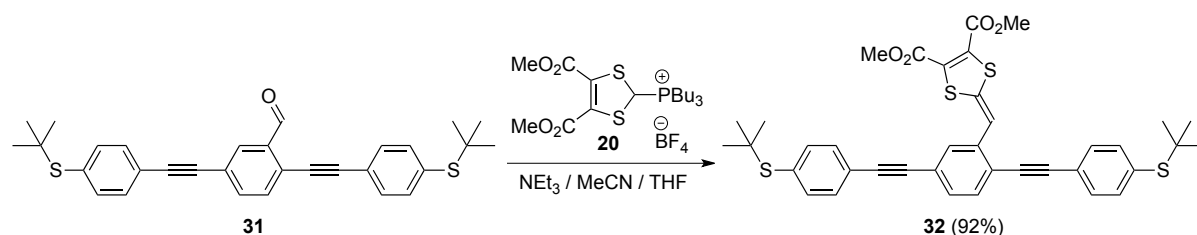


Compound 29. A mixture of **28** (128 mg, 209 μmol), **23** (240 mg, 862 μmol), CuI (4.3 mg, 22.6 μmol), Xphos (19.8 mg, 41.5 μmol) and Pd₂(dba)₃ (11.2 mg, 12.2 μmol) was dissolved in THF (5 mL), and 5 min later, NH(*i*-Pr)₂ (1 mL) was added. After stirring for 20 h, the reaction mixture was diluted with CH₂Cl₂ and the solvent was evaporated *in vacuo*. The crude product was purified by flash column chromatography (SiO₂, CH₂Cl₂); the third band was orange and gave **29** as a slightly impure product as an orange solid. The product was dissolved in a minimal amount of CH₂Cl₂ and triturated by MeOH (60 mL) and the fine orange powder was collected (71 mg, 49%). Mp 121-124 °C. Anal. Calcd (C₄₂H₃₂O₆S₂): C,

72.39; H, 4.63. Found: C, 72.20; H, 4.52. IR(ATR, cm^{-1}): ν = 2967m, 2936w, 2879w, 2855w, 2199vs, 2164w, 2136w (3 x $\text{C}\equiv\text{C}$), 1732m (CO_2Pr), 1667vs (CO), 1599m, 1583m, 1550w, 1531w, 1509m, 1464w, 1408w, 1390w, 1559m, 1282s, 1239s. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.62 – 7.55 (m, 10H), 7.38 (dd, J = 7.9, 1.6 Hz, 1H), 6.98 (s, 1H), 4.20, 4.20 (2 x t, J = 6.7 Hz, 4H), 2.44, 2.44 (2 x s, 6H), 1.75 – 1.70 (m, 4H), 0.97, 0.97 (2 x t, J = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 184.67, 160.07, 159.91, 138.14, 135.32, 133.55, 133.51, 133.40, 132.39, 132.24, 131.72, 130.12, 129.90, 128.51, 125.81, 125.74, 123.90, 121.63, 120.60, 120.51, 112.71, 96.39, 92.41, 91.27, 90.87, 90.09, 90.04, 89.39, 89.35, 68.99, 68.90, 33.18, 22.34, 10.64; 4 signals missing. MS (FAB) m/z : 697 $[\text{M}+\text{H}]^+$.

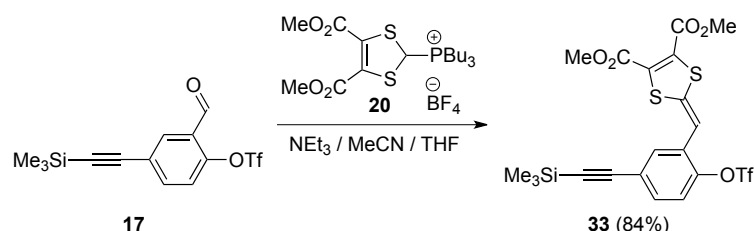


Compound 31. Compound **16** (380 mg, 0.94 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (70 mg, 0.10 mmol, 10 mol%), CuI (19 mg, 0.10 mmol, 10 mol%), and **30** (539 mg, 2.83 mmol) were dissolved in argon degassed dry THF (8 mL) and $\text{NH}(i\text{-Pr})_2$ (2 mL). The reaction mixture was then stirred for 16 h at 50 °C before it was diluted with CH_2Cl_2 (100 mL) and washed with saturated aqueous NH_4Cl (100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude was then subjected to flash column chromatography (SiO_2 , CH_2Cl_2 / petroleum spirit 2:3) giving the product **31** as a yellow powder (276 mg, 61%). Mp 153–155 °C. Anal. Calcd ($\text{C}_{31}\text{H}_{30}\text{OS}_2$): C, 77.14; H, 6.26. Found: C, 76.80; H, 6.15. ^1H NMR (500 MHz, CDCl_3) δ 10.61 (s, 1H), 8.09 (dd, J = 1.8, 0.5 Hz, 1H), 7.71 (dd, J = 8.0, 1.8 Hz, 1H), 7.63 (dd, J = 8.0, 0.5 Hz, 1H), 7.57 – 7.48 (m, 8H), 1.32 (s, 9H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 190.91, 137.48, 137.43, 136.34, 135.97, 134.89, 134.28, 133.45, 131.75, 131.74, 130.77, 126.04, 124.06, 122.97, 122.54, 97.59, 92.14, 89.44, 86.35, 46.90, 46.79, 31.18, 31.17. MS (MALDI-TOF) m/z : 483 $[\text{M}+\text{H}]^+$.

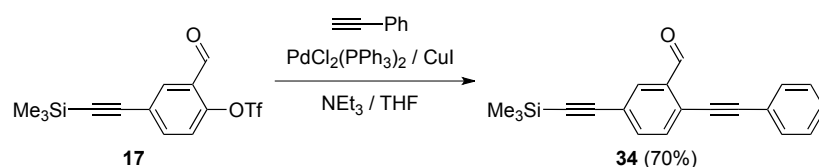


Compound 32. Compound **31** (55 mg, 0.11 mmol) and phosphonium salt **20** (173 mg, 0.33 mmol) were dissolved in THF (2 mL) and MeCN (1 mL). NEt_3 (0.2 mL) was added and the mixture stirred for 30 min before water (10 mL) was added. The mixture was then extracted with CH_2Cl_2 (15 mL) and the red organic layer was dried over Na_2SO_4 and the volatile removed under reduced pressure. The residue was then subjected to flash column chromatography (SiO_2 , CH_2Cl_2) giving the product as an orange solid (69 mg, 92%). Mp 145–147 °C. Anal. Calcd ($\text{C}_{38}\text{H}_{36}\text{O}_4\text{S}_4$): C, 66.63; H, 5.30. Found C, 66.33; H, 5.23. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.55 – 7.50 (m, 10H), 7.37 (dd, J = 8.0, 1.5 Hz, 1H), 7.00 (s, 1H), 3.85

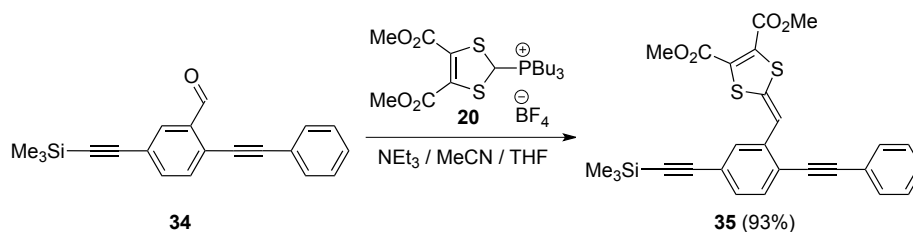
(s, 3H), 3.83 (s, 3H), 1.31 (2 x s, 18H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.53, 160.23, 137.90, 137.84, 137.81, 134.69, 134.65, 134.56, 133.22, 132.12, 131.96, 131.87, 129.97, 129.88, 128.35, 123.95, 123.66, 123.60, 121.81, 113.30, 96.71, 91.48, 90.75, 89.18, 53.87, 47.05, 47.01, 31.34; 2 signals missing. MS (FAB) m/z : 685 $[\text{M}]^+$.



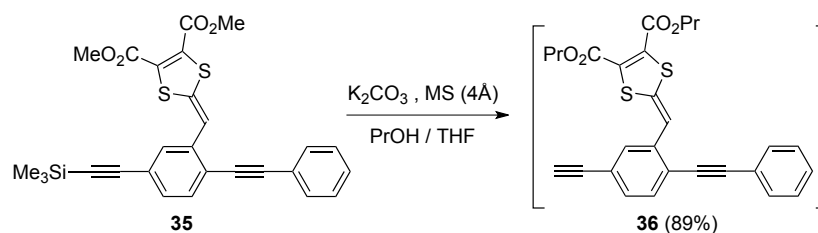
Compound 33. Compounds **17** (1.55 g, 4.42 mmol) and **20** (2.32 g, 4.6 mmol) were dissolved in Ar degassed THF (60 mL) and MeCN (20 mL). NEt_3 (0.8 mL) was then added whereupon the solution turned to a red color. After stirring for 2 h, the reaction mixture was diluted with CH_2Cl_2 (200 mL), washed with H_2O (2 x 100 mL), brine (200 mL), dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2 , CH_2Cl_2 / heptane 4:1) to provide the product as a red oil which slowly crystallized to an orange solid (2.05 g, 84%). Mp 101.3-102.3 $^\circ\text{C}$. Anal. Calcd ($\text{C}_{20}\text{H}_{19}\text{F}_3\text{O}_7\text{S}_3\text{Si}_2$): C, 43.47; H, 3.47. Found: C, 43.46; H, 3.34. ^1H NMR (500 MHz, CDCl_3) δ 7.53 (d, J = 2.0 Hz, 1H), 7.35 (dd, J = 8.5, 2.0 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), 6.44 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 0.27 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 159.81, 159.79, 145.20, 137.84, 131.75, 131.41, 130.47, 129.85, 129.61, 124.18, 122.00, 118.70 (q, $J_{\text{C-F}}$ = 321 Hz), 105.84, 102.84, 97.18, 53.66, 53.61, -0.03. MS (FAB) m/z : 553 $[\text{M}+\text{H}]^+$.



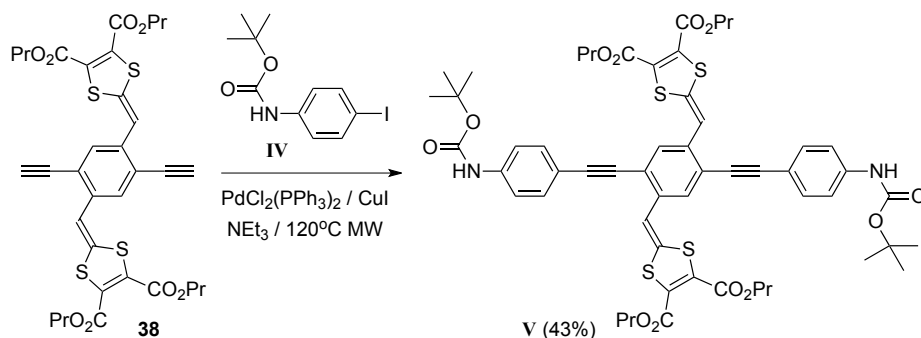
Compound 34. Compound **17** (0.40 g, 1.14 mmol) was dissolved in Ar degassed dry THF (6 mL) and Ar degassed NEt_3 (2 mL) under Ar atmosphere; then $\text{PdCl}_2(\text{PPh}_3)_2$ (74 mg, 0.10 mmol) and CuI (20 mg, 0.11 mmol) were added. Phenylacetylene (0.3 mL, 0.3 mmol) was added, and the mixture turned black. After stirring for 15 min, the reaction mixture was diluted with Et_2O (50 mL), washed with saturated aqueous NH_4Cl (100 mL), brine (100 mL), dried with Na_2SO_4 and evaporated under vacuum. The compound was purified by repeated flash column chromatography (SiO_2 , pentane / CH_2Cl_2 1:1; then petroleum spirit / EtOAc 10:1) to give **34** as a white solid (240 mg, 70%). Mp 63-64 $^\circ\text{C}$. Anal. Calcd ($\text{C}_{20}\text{H}_{18}\text{OSi}$): C, 79.42; H, 6.00. Found: C, 79.60; H, 5.58. ^1H NMR (500 MHz, CDCl_3) δ 10.59 (s, 1H), 8.02 (d, J = 1.8 Hz, 1H), 7.64 (dd, J = 8.0, 1.8 Hz, 1H), 7.59 – 7.55 (m, 3H), 7.40 – 7.39 (m, 3H), 0.26 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.00, 136.62, 135.78, 133.24, 131.88, 131.07, 129.43, 128.73, 126.43, 123.88, 122.28, 103.38, 98.10, 98.04, 84.90, -0.04. MS (GC-MS) m/z : 302 $[\text{M}]^+$.



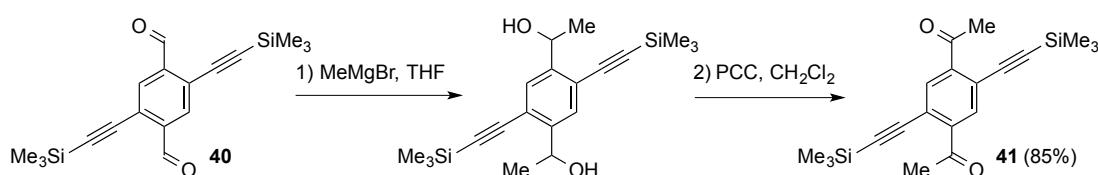
Compound 35. A mixture of **34** (130 mg, 0.43 mmol) and **20** (0.49 g, 0.96 mmol) was dissolved in Ar degassed dry THF (6 mL) and MeCN (3 mL), then NEt₃ (1 mL) was added whereupon the reaction mixture turned red. After stirring for 30 min, the reaction mixture was diluted with CH₂Cl₂ (100 mL), washed with H₂O (2 x 100 mL), brine (100 mL), dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, petroleum spirit / CH₂Cl₂ 1:1) to give the product as an orange solid (202 mg, 93%). Mp 144-145 °C. Anal. Calcd (C₂₇H₂₄O₄S₂Si): C, 64.25; H, 4.79. Found: C, 64.47; H, 4.75. ¹H NMR (500 MHz, CDCl₃) δ 7.53 – 7.51 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 1.5 Hz, 1H), 7.37 – 7.36 (m, 3H), 7.28 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.94 (d, *J* = 0.6 Hz, 1H), 3.87 (s, 6H), 0.28 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 160.15, 160.08, 137.21, 133.56, 132.52, 131.70, 131.07, 130.12, 129.97, 128.84, 128.61, 128.27, 123.43, 122.97, 121.71, 113.37, 104.55, 96.80 (2 x alkyne-C), 87.46, 53.58, 53.53, 0.10. MS (FAB) *m/z*: 505 [M+H]⁺.



Compound 36. Compound **35** (151 mg, 0.30 mmol) was dissolved in THF (10 mL) and 1-propanol (15 mL). Molecular sieves (10 sieves, 4Å) and K₂CO₃ (0.5 g, 3.6 mmol) were added. After stirring for 5 h, the reaction mixture was filtered on a short plug (SiO₂, CH₂Cl₂) and concentrated under reduced pressure to give the product as an orange solid (130 mg, 89%). This compound was used immediately for further reaction. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.57 – 7.50 (m, 4H), 7.41 – 7.38 (m, 3H), 7.31 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.99 (s, 1H), 4.20 (2 x t, *J* = 6.7 Hz, 4H), 3.29 (s, 1H), 1.77 – 1.69 (m, 4H), 0.99 (2 x t, *J* = 7.4, 6H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 160.08, 159.85, 137.77, 134.77, 133.08, 132.09, 131.72, 130.19, 130.03, 129.33, 129.03, 128.91, 123.29, 122.71, 122.41, 112.95, 97.23, 87.61, 83.51, 79.66, 68.90, 68.82, 22.35, 22.33, 10.68, 10.65.

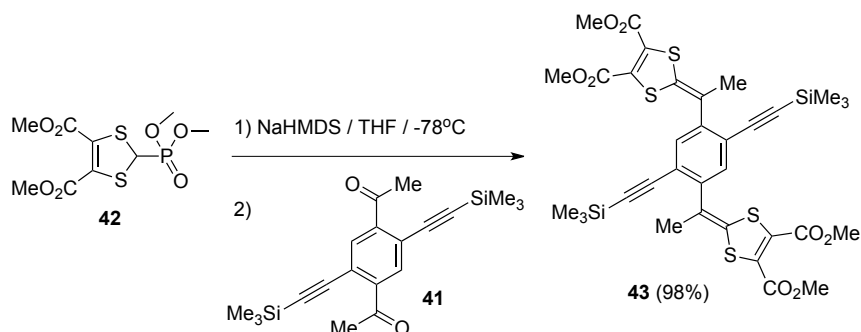


Compound V. In a microwave vial were placed $\text{PdCl}_2(\text{PPh}_3)_2$ (15 mg, 0.02 mmol), CuI (4 mg, 0.02 mmol), **38** (100 mg, 0.14 mmol) and **IV** (110 mg, 0.35 mmol). The vial was sealed and filled with an inert atmosphere of Ar. Then dry argon degassed DMF (4 mL) was added. To the resulting mixture was then added NEt_3 (1.5 mL) and the vial was placed inside a microwave reactor. After stirring for 5 min inside the microwave reactor the temperature was raised to 120 °C and the mixture was heated for 30 min. To the resulting solution was added 0.2 M HCl (10 mL) and it was extracted with Et_2O (3 x 20 mL). The organic phase was further washed with NaHCO_3 (2 x 15 mL), H_2O (2 x 15 mL) and dried over MgSO_4 , filtered and the solvent was removed *in vacuo* to yield the crude product. The crude material was purified by dry column vacuum chromatography (SiO_2 , 12.6 cm², 0 – 50% heptanes / EtOAc , 4% steps, 40 mL fractions) to yield pure **V** as a red solid (65 mg, 43%). Mp 184-189 °C. Anal. Calcd ($\text{C}_{56}\text{H}_{60}\text{N}_2\text{O}_{12}\text{S}_4$): C, 62.20; H, 5.59; N, 2.59. Found: C, 61.71; H, 5.52; N, 2.78. ^1H NMR (500 MHz, CDCl_3) δ 7.50 – 7.48 (m, 6H), 7.39 (d, $J = 8.6$ Hz, 4H), 6.94 (s, 2H), 6.55 (s, 2H), 4.22, 4.21 (2 x t, $J = 7.0$ Hz, 8H), 1.73 (m, 8H), 1.54 (s, 9H), 0.99, 0.98 (2 x t, $J = 7.0$ Hz, 12H). ^{13}C NMR (125 MHz, CDCl_3) δ 159.78, 159.69, 152.46, 139.00, 134.77, 133.41, 132.71, 131.20, 131.02, 130.19, 128.95, 128.66, 121.65, 118.19, 117.19, 112.78, 96.61, 86.93, 68.48, 68.42, 38.88, 28.47, 21.93, 10.48, 10.46. MS (FAB, *m*-NBA) m/z : 1080 $[\text{M}]^+$.

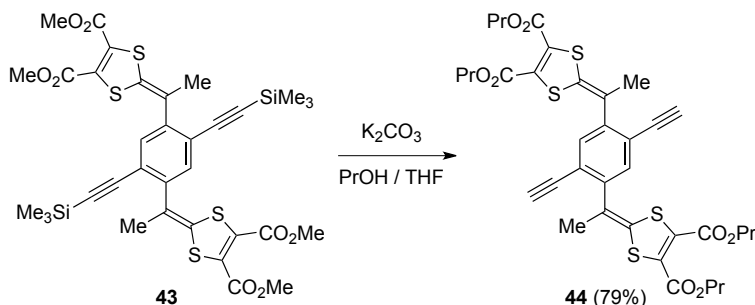


Compound 41. The dialdehyde **40** (225 mg, 0.69 mmol) was dissolved in dry THF (10 mL), placed under an Ar atmosphere and cooled to 0 °C. Methylmagnesium bromide solution (0.7 mL, 2.07 mmol, 3 M in Et_2O) was added and the mixture left to stir for 30 min at rt. The mixture was poured onto 2 M HCl (25 mL) and extracted with Et_2O (50 mL). The ether phase was dried over Na_2SO_4 and concentrated under reduced pressure into an off-white solid (~270 mg). The mixture of diol stereoisomers was subsequently reacted with pyridinium chlorochromate (PCC) (594 mg, 2.76 mmol) in CH_2Cl_2 (15 mL) under argon. After 1 h of stirring, Celite (0.5 g) was added and the mixture was stirred for additional 5 h at rt. The mixture was then poured through a short plug of silica (SiO_2 , CH_2Cl_2) to remove the black tar formed under the reaction. The solvent was removed under reduced pressure and the product **41** was isolated after column chromatography (SiO_2 , pentane / CH_2Cl_2 1:2) as white powder (207 mg, 85%). Mp 74-76 °C. Anal. Calcd ($\text{C}_{20}\text{H}_{26}\text{O}_2\text{Si}_2$): C, 67.74; H, 7.39. Found: C,

67.37; H, 7.50. ^1H NMR (500 MHz, CDCl_3) δ 7.83 (s, 2H), 2.73 (s, 6H), 0.26 (s, 18H). ^{13}C NMR (125 MHz, CDCl_3) δ 199.44, 142.93, 134.45, 121.43, 104.40, 102.59, 30.18, -0.31. MS (GC-MS) m/z : 354 $[\text{M}]^+$.

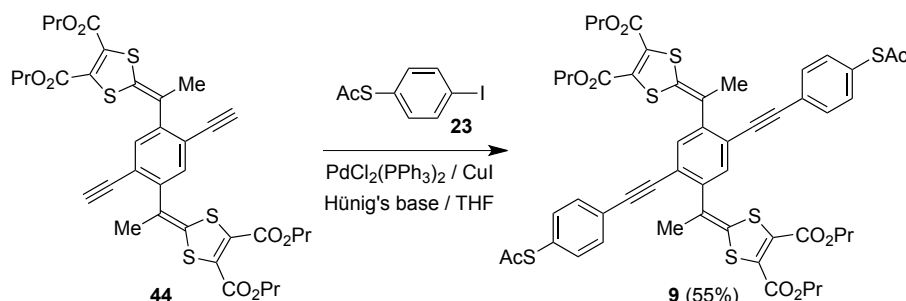


Compound 43. The phosphonate ester **42** (231 mg, 0.71 mmol) was dissolved in dry THF (10 mL), placed under argon and cooled to -78 °C. Sodium bis(trimethylsilyl)amide solution (NaHMDS) (1.1 mL, 0.7 mmol, 0.6 M in toluene) was added and the mixture left to stir for 20 min at -78 °C. Hereafter, a solution of the diketone **41** (100 mg, 0.28 mmol) in dry THF (10 mL) was cannulised into the purple colored ylide solution. The entire mixture was allowed to warm up to rt over approximate 30 min, whereupon the mixture adopted an orange color. The mixture was then poured onto aqueous NH_4Cl (25 mL) and extracted with CH_2Cl_2 (50 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure into a red solid. The product was isolated after column chromatography (SiO_2 , CH_2Cl_2) as an orange powder (208 mg, 98%). Crystals suitable for single-crystal X-Ray diffraction studies were grown from vapour diffusion of MeOH into a CH_2Cl_2 solution. Mp 236-238 °C (decomp.). Anal. Calcd ($\text{C}_{34}\text{H}_{38}\text{O}_8\text{S}_4\text{Si}_2$): C, 53.80; H, 5.05. Found: C, 54.09; H, 5.01. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.34 (s, 2H), 3.81 (s, 6H), 3.76 (s, 6H), 1.99 (s, 6H), 0.23 (s, 18H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.89, 160.66, 144.61, 133.29, 132.35, 130.11, 128.28, 122.92, 121.67, 102.92, 101.86, 53.72 (OMe; the other signal masked by solvent), 22.88, 0.00. MS (MALDI-TOF) m/z : 766 $[\text{M}+\text{Li}]^+$.

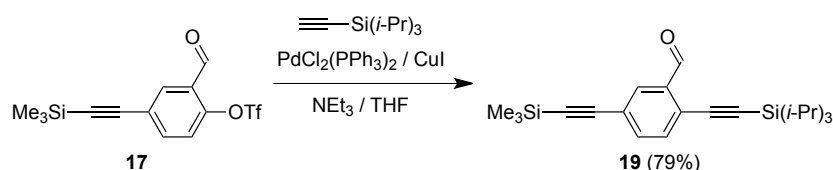


Compound 44. Compound **43** (200 mg, 0.26 mmol) was dissolved in THF (7 mL); then 1-propanol (25 mL) and K_2CO_3 (500 mg, 3.62 mmol) were added. The reaction was monitored by TLC and after 3 h of stirring, the mixture was poured through a short plug (SiO_2 , CH_2Cl_2) and the yellow filtrate collected. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2 , CH_2Cl_2) to yield the product **44** as an orange solid (150 mg, 79%). Mp 144-145 °C. Anal. Calcd. ($\text{C}_{36}\text{H}_{38}\text{O}_8\text{S}_4$): C, 59.48; H, 5.27. Found: C, 59.50; H, 4.91. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.43 (s, 2H), 4.16 (t, J = 6.7

Hz, 4H), 4.10 (t, $J = 6.7$ Hz, 4H), 3.41 (s, 2H), 2.01 (s, 6H), 1.74 – 1.62 (m, 8H), 0.97 (t, $J = 7.4$ Hz, 6H), 0.91 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.49, 160.24, 144.75, 134.28, 132.25, 130.21, 128.76, 122.41, 121.06, 83.65, 81.46, 68.70, 68.64, 22.98, 22.35, 22.27, 10.65, 10.58. MS (MALDI-TOF) m/z : 726 $[\text{M}]^+$.

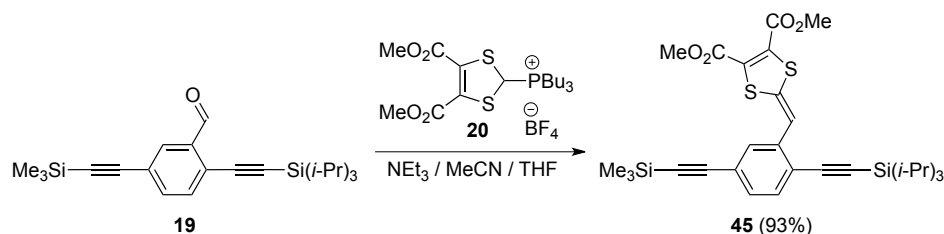


Compound 9. Compound **44** (140 mg, 0.19 mmol) was mixed with **23** (214 mg, 0.77 mmol), CuI (4 mg, 0.02 mmol, 10 mol%), and $\text{PdCl}_2(\text{PPh}_3)_2$ (14 mg, 0.02 mmol, 10 mol%) in a flame-dried flask. The mixture was placed under argon before argon degassed dry THF (5 mL) and Hünig's base (2 mL) were added. The reaction mixture was stirred for 5 h at 45 °C before it was poured onto an aqueous NH_4Cl solution (20 mL) and extracted with CH_2Cl_2 (50 mL). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure into a red oil. The product was isolated after column chromatography (SiO_2 , CH_2Cl_2) as a red oil, which slowly turned into a solid after cooling (110 mg, 55%). Mp 48–49 °C. Anal. Calcd. ($\text{C}_{52}\text{H}_{50}\text{O}_{10}\text{S}_6$): C, 60.79; H 4.91. Found: C 60.71, H 4.95. IR (ATR, cm^{-1}) $\nu = 2967\text{m}$, 2936w, 2895w, 2879w, 2216vw ($\text{C}\equiv\text{C}$), 1709vs ($\text{C}=\text{O}$), 1591m, 1497m, 1463m, 1390m, 1350m, 1310w, 1238vs. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.57 (d, $J = 8.5$ Hz, 4H), 7.53 (s, 2H), 7.43 (d, $J = 8.5$ Hz, 4H), 4.17 (t, $J = 6.7$ Hz, 4H), 4.10 (t, $J = 6.7$ Hz, 4H), 2.43 (s, 6H), 2.11 (s, 6H), 1.75 – 1.60 (m, 8H), 0.97 (t, $J = 7.4$ Hz, 6H), 0.89 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 193.72, 160.55, 160.22, 144.36, 134.97, 133.36, 132.66, 132.53, 130.05, 129.60, 128.83, 124.47, 122.76, 121.40, 95.21, 89.47, 68.68, 68.63, 30.70, 23.18, 22.36, 22.26, 10.67, 10.57. MS (MALDI-TOF) m/z : 1026 $[\text{M}]^+$.

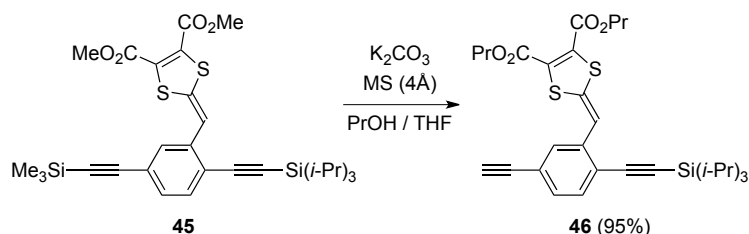


Compound 19. Compound **17** (1.1 g, 3.1 mmol) was dissolved in a solution of Ar degassed THF (15 mL) and NEt_3 (5 mL) under an Ar atmosphere; then $\text{PdCl}_2(\text{PPh}_3)_2$ (113 mg, 0.15 mmol) and CuI (28 mg, 0.15 mmol) were added. Triisopropylsilylacetylene (1.1 mL, 5 mmol) was added whereupon the solution darkened into a black color. After stirring for 10 min, the reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with saturated aqueous NH_4Cl (100 mL), brine (100 mL), dried with Na_2SO_4 and concentrated under reduced pressure. The compound was purified by repeated flash column chromatography (SiO_2 , pentane / CH_2Cl_2 1:1) to a light yellow oil (0.95 g, 79%). ^1H NMR (500 MHz, CDCl_3) δ 10.55 (s, 1H), 7.99 (dd, $J = 1.8, 0.6$ Hz, 1H), 7.58 (dd, $J = 8.0, 1.8$ Hz, 1H), 7.51 (dd, $J = 8.0,$

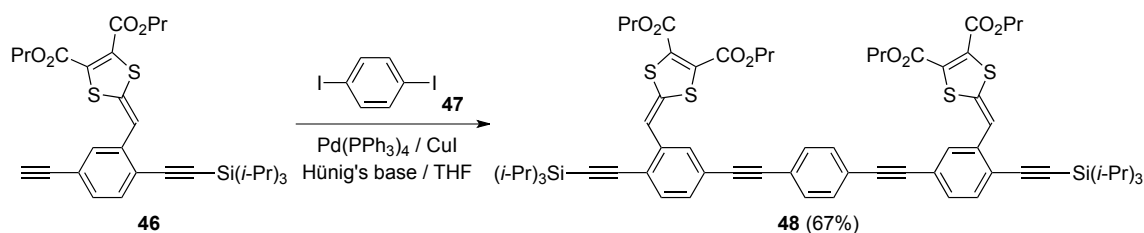
0.6 Hz, 1H), 1.14 (m, 21H), 0.26 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.05, 136.47, 136.16, 133.86, 130.65, 126.61, 123.97, 103.33, 101.79, 101.35, 98.00, 18.81, 11.41, -0.05. MS (GC-MS) m/z : 367 $[\text{M}-\text{CH}_3]^+$ (30%), 339 $[\text{M}-(i\text{-Pr})]^+$ (100%), 297 (80%), 269 (85%).



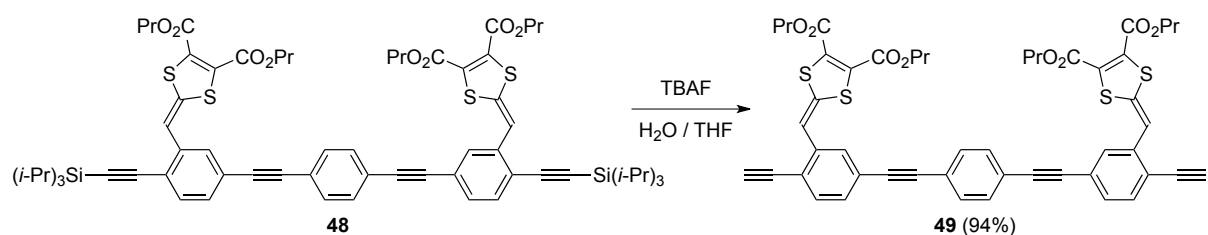
Compound 45. The compounds **19** (0.60 g, 1.6 mmol) and **20** (1.2 g, 2.4 mmol) were dissolved in Ar degassed dry THF (10 mL) and MeCN (5 mL). The solution was then treated with NEt_3 (2 mL), whereupon the mixture turned red. After stirring for 20 min, the reaction mixture was diluted with CH_2Cl_2 (50 mL), washed with H_2O (2 x 50 mL), brine (50 mL), dried with Na_2SO_4 and evaporated under reduced pressure. The compound was purified by flash column chromatography (SiO_2 , petroleum spirit / CH_2Cl_2 1:1) to give compound **45** as an orange oil (865 mg, 94%). Anal. Calcd. ($\text{C}_{30}\text{H}_{40}\text{O}_4\text{S}_2\text{Si}_2$): C, 61.60; H 6.89. Found: C 61.50, H 7.20. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.43 (d, J = 8.0 Hz, 1H), 7.38 (d, J = 1.5 Hz, 1H), 7.23 (dd, J = 8.0, 1.5 Hz, 1H), 6.97 (s, 1H), 3.84, 3.84 (2 x s, 6H), 1.15 – 1.14 (m, 21H), 0.26 (s, 9H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.59, 160.24, 138.17, 134.25, 133.24, 131.95, 130.17, 129.72, 128.21, 123.89, 122.34, 113.39, 105.00, 104.66, 99.60, 97.19, 53.97, 53.87, 19.04, 11.90, 0.11. HR-MS (ESP+) m/z : 585.1967 $[\text{M}+\text{H}]^+$; calcd for $\text{C}_{30}\text{H}_{41}\text{O}_4\text{S}_2\text{Si}_2^+$: 585.1979.



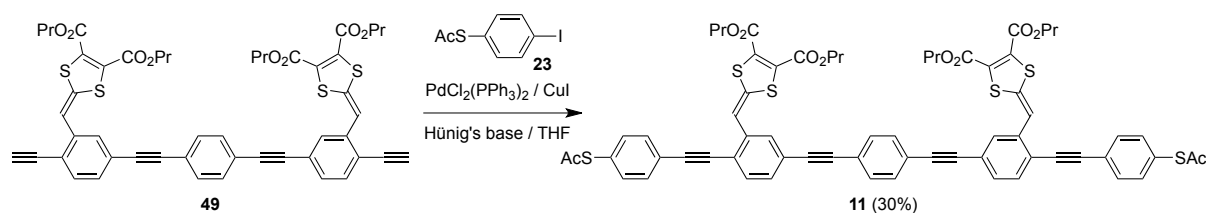
Compound 46. Compound **45** (720 mg, 1.2 mmol) was dissolved in THF (20 mL) and then 1-propanol (40 mL), molecular sieves (1 g, 4Å) and K_2CO_3 (1.5 g, 1.1 mmol) were added. After stirring for 5 h, the reaction mixture was filtered through a short plug (SiO_2 , CH_2Cl_2) and concentrated under reduced pressure to give a yellow colored oil (650 mg, 93%), which was immediately used for further reaction. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.46 – 7.44 (m, 2H), 7.26 (dd, J = 7.8, 1.6 Hz, 1H), 6.98 (s, 1H), 4.19 (2 x t, J = 6.7 Hz, 4H), 3.26 (s, 1H), 1.74 – 1.69 (m, 4H), 1.15 (s, 21H), 0.97 (2 x t, J = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.20, 159.86, 138.30, 134.74, 133.29, 131.98, 130.05, 129.76, 128.71, 122.74, 122.67, 112.98, 104.86, 99.70, 83.44, 79.57, 68.94, 68.84, 22.35, 22.31, 19.03, 11.89, 10.61; one signal missing. HR-MS (ESP+) m/z : 591.2027 $[\text{M}+\text{Na}]^+$; calcd for $\text{C}_{31}\text{H}_{40}\text{O}_4\text{S}_2\text{SiNa}^+$: 591.2029.



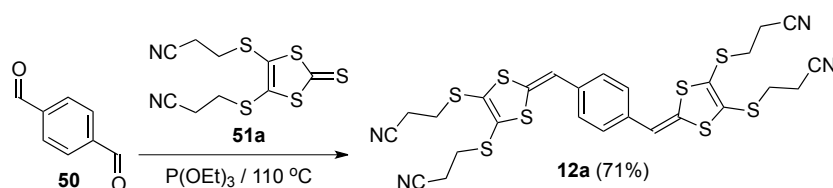
Compound 48. Compound **46** (569 mg, 1.00 mmol) was dissolved in Ar degassed dry THF (15 mL) and Hünig's base (5 mL) under Ar atmosphere; then Pd(PPh₃)₄ (125 mg, 0.1 mmol), CuI (20 mg, 0.1 mmol) and 1,4-diiodobenzene **47** (165 mg, 0.50 mmol) were added to the mixture. The temperature was raised to 40 °C. After stirring for 20 h, the reaction mixture was diluted with CH₂Cl₂ (50 mL) and washed with saturated aqueous NH₄Cl (50 mL), brine (50 mL), dried with Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO₂, CH₂Cl₂ / petroleum spirit 2:1) to give **48** as a dark red oil (405 mg, 67%). Anal. Calcd (C₆₈H₈₂O₈S₄Si₂): C, 67.40; H, 6.82. Found: C, 67.14; H, 6.90. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.57 (s, 4H), 7.51 (d, *J* = 1.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.33 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.02 (s, 2H), 4.19 (2 x t, *J* = 6.7 Hz, 8H), 1.76 - 1.68 (m, 8H), 1.16 (s, 42H), 0.97 (2 x t, *J* = 7.4 Hz, 12H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 160.20, 159.91, 138.38, 134.62, 133.37, 132.24, 131.95, 129.87, 129.65, 128.14, 123.70, 123.60, 122.31, 113.12, 105.09, 99.71, 91.47, 91.45, 68.94, 68.84, 22.36, 22.32, 19.05, 11.92, 10.64, 10.62. MS (MALDI) *m/z*: 1211 [M+H]⁺.



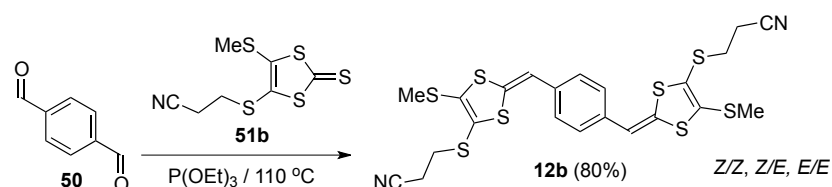
Compound 49. Compound **48** (100 mg, 0.0825 mmol) was dissolved in THF (3 mL) and two drops of H₂O were added, followed by Bu₄NF (53 mg, 0.20 mmol). After stirring for 30 min, the reaction mixture was diluted with CH₂Cl₂ (10 mL) and filtered on a short plug (SiO₂, CH₂Cl₂) and concentrated under reduced pressure to an orange oil (70 mg, 94%), which was immediately used for further reaction. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.56 (s, 4H), 7.50 (d, *J* = 1.5 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.32 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.01 (s, 2H), 4.19 (2 x t, *J* = 6.7 Hz, 8H), 1.75-1.67 (m, 8H), 0.97, 0.97 (2 x t, *J* = 7.4 Hz, 12H).



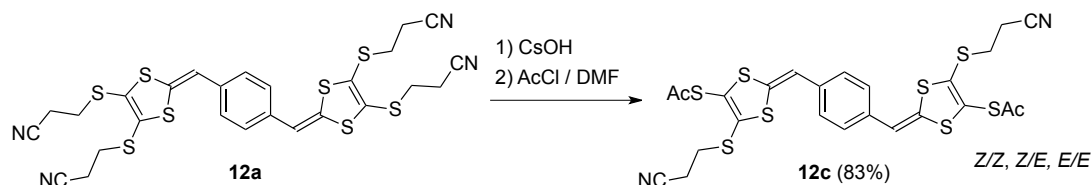
Compound 11. $\text{PdCl}_2(\text{PPh}_3)_2$ (6.5 mg, 9 μmol) was mixed with Ar degassed Hünig's base (3 mL) and stirred for 10 min under Ar atmosphere, followed by addition of compound **23** (178 mg; 0.64 mmol) and CuI (2.5 mg, 0.013 mmol). Compound **49** (70 mg, 0.078 mmol) was dissolved in Ar degassed dry THF (4 mL) and was transferred via cannula into the reaction mixture. After stirring for 2.5 h, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed with saturated aqueous NH_4Cl (50 mL), brine (50 mL), dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by repeated flash column chromatography (SiO_2 , eluent 1% EtOAc in CH_2Cl_2 , last flash column was 6 cm and neat CH_2Cl_2 was used as the eluent) to furnish the product as a thick orange oil (28 mg, 30%). Mp 168–170 $^\circ\text{C}$. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.59 – 7.54 (m, 12H), 7.45 – 7.36 (m, 6H), 7.00 (s, 2H), 4.20 (2 x t, J = 6.7 Hz, 8H), 2.43 (s, 6H), 1.76 – 1.69 (m, 8H), 0.98 (2 x t, J = 7.4 Hz, 12H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 193.72, 160.10, 159.92, 138.03, 135.00, 134.96, 133.30, 132.56, 132.26, 131.73, 130.11, 129.83, 129.53, 128.39, 124.47, 124.00, 123.60, 121.62, 112.91, 96.35, 91.68, 91.47, 89.45, 68.94, 68.86, 30.71, 22.35, 22.33, 10.66; one signal missing. MS (MALDI) m/z : 1199 $[\text{M}+\text{H}]^+$. HR-MS (MALDI) m/z : 1198.2021 $[\text{M}]^+$; calcd for $\text{C}_{66}\text{H}_{54}\text{O}_{10}\text{S}_6$: 1198.2036.



Compound 12a. A degassed suspension of terephthalaldehyde **50** (200 mg, 1.49 mmol), thione **51a** (1.818 mg, 5.97 mmol) and $\text{P}(\text{OEt})_3$ (8 mL) was heated to 110 $^\circ\text{C}$ under an Ar atmosphere. The mixture turned into a red color and most of the solids dissolved before a yellow solid started to form. After stirring for about 150 min, the suspension was allowed to cool to rt and MeOH (25 mL) was added to precipitate more of the product and help remove the pungent phosphite. The solid was isolated by filtration and washed with MeOH (25 mL) and petroleum spirit (3 x 30 mL or until the phosphite smell was gone) to give a dark orange-yellow colored solid which was not quite pure (according to NMR). The solid was dissolved in CH_2Cl_2 and purified by flash column chromatography (SiO_2 , initially CH_2Cl_2 then a gradient to CH_2Cl_2 / EtOAc 1:1). First there was a yellow band, followed by a darker orange band, which contained the product **12a** (686 mg, 71%) as an orange-yellow solid. Mp 141.5–144 $^\circ\text{C}$ (darkens and melts). Anal. Calcd ($\text{C}_{26}\text{H}_{22}\text{N}_4\text{S}_8$): C, 48.27; H, 3.43; N, 8.66. Found: C, 48.07; H, 2.96; N, 8.51. IR(ATR, cm^{-1}): ν = 2990w, 2953w, 2928w, 2249m (CN), 1569s, 1547m, 1505m, 1410s, 1322m, 1278m, 1232m, 1209m, 1165w. ^1H NMR (500 MHz, CDCl_3) δ 7.20 (s, 4H), 6.50 (s, 2H), 3.12 – 3.08 (m, 8H), 2.79 – 2.74 (m, 8H). ^{13}C NMR (125 MHz, CDCl_3) δ 133.92, 130.02, 127.88, 127.31, 125.16, 117.63, 117.54, 116.36, 31.23, 31.19, 19.13, 19.08. MS (MALDI) m/z : 646 $[\text{M}]^+$.

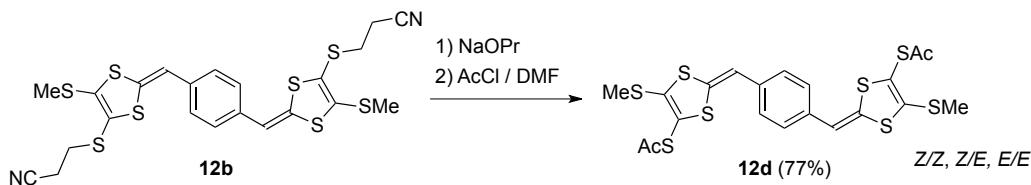


Compound 12b. A degassed suspension of terephthalaldehyde **50** (100 mg, 0.75 mmol), thione **51b** (791 mg, 2.99 mmol) and $\text{P}(\text{OEt})_3$ (4 mL) was heated to 110 °C under an Ar atmosphere. The solution turned a red color and most of the solids dissolved before a yellow precipitate started to form. After stirring for about 150 min, the suspension was allowed to cool to rt and MeOH (15 mL) was added to precipitate more compound. The solid was filtered and washed with MeOH (15 mL) and petroleum spirit (3 x 20 mL or until the pungent phosphite smell was gone) to give an orange-yellow colored solid which contains some minor impurities. This crude compound can be purified by flash column chromatography (SiO_2 , CH_2Cl_2). There were two minor yellow bands before the major yellow band (closely followed by a minor orange band) which contained **12b** as a yellow solid (339 mg, 80%). Mp 141.5–143.5 °C (melts and darkens). Anal. Calcd ($\text{C}_{22}\text{H}_{20}\text{N}_2\text{S}_8$): C, 46.44; H, 3.54; N, 4.92. Found: C, 46.00; H, 3.25; N, 4.86. IR(ATR, cm^{-1}): $\nu = 3020\text{w}$, 2990w , 22920m , 2248m (CN), 1568vs , 1545s , 1504s , 1494s , 1411s , 1339m , 1317m , 1281m , 1229m , 1213m , 1183w , 1165w , 1135w . ^1H NMR (500 MHz, CD_2Cl_2) δ 7.22 – 7.21 (m, 4H), 6.50 Br, 6.49 Br (2 x s, 2H), 3.04 / 3.04 (2 x t, $J = 7.1$ Hz, 4H), 2.73 (2 x t, $J = 7.1$ Hz, 4H), 2.49, 2.48 (2 x s, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 135.20, 135.16, 134.31, 134.27, 132.74, 132.72, 131.77, 131.76, 131.62, 131.61, 127.50, 120.77, 120.72, 118.33, 118.26, 117.67, 117.64, 115.54, 115.38, 31.74, 19.44, 19.31, 19.19. MS (MALDI) m/z : 568 $[\text{M}]^+$.

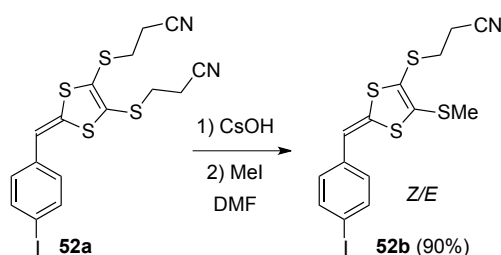


Compound 12c. A Schlenk flask containing a degassed solution of **12a** (50 mg, 0.077 mmol) in DMF (7 mL) was treated with $\text{CsOH} \cdot \text{H}_2\text{O}$ solution (0.98 mL, 0.165 M in PrOH, 0.162 mmol) over a period of 90 s and the yellow solution turned into a bronze-red color. After stirring for 20 min, acetyl chloride (16 μL , 0.23 mmol) was added and the solution immediately turned orange, and material started to precipitate. After stirring for 5 min, CH_2Cl_2 (50 mL) was added and the solution was washed with water (ca. 5–10 x 50 mL to remove DMF), dried over Na_2SO_4 and concentrated *in vacuo*. Flash column chromatography (SiO_2 , gradient 1–10 % EtOAc in CH_2Cl_2) gave **12c** as a dark yellow solid (40 mg, 83%). Mp ca. 165–167 °C (darkens at 155 °C). Anal. Calcd ($\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_8$): C, 46.12; H, 3.23; N, 4.48. Found: C, 45.84; H, 2.90; N, 4.44. IR(ATR, cm^{-1}): $\nu = 3022\text{vw}$, 2987vw , 2956vw , 2924w , 2853vw , 2249w (CN), 1727vs , 1708vs (2 x CO), 1569vs , 1546m , 1506m , 1413s , 1352m , 1324w , 1281m , 1229w , 1213w , 1165w , 1113vs . ^1H NMR (500 MHz, CD_2Cl_2) δ 7.23, 7.21, 7.21, 7.18 (4 x s of different isomers, 4H), 6.51, 6.51, 6.50, 6.50 (4 x s of different isomers, 2H), 3.03, 3.03 (2 x t, $J = 7.0$ Hz, 4H), 2.71–2.66 (m, 4H), 2.44 (s, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 191.69, 191.67, 191.45, 134.32, 134.30, 134.26, 132.53, 131.46, 131.39, 131.35,

130.91, 127.60, 127.58, 127.53, 127.51, 123.66, 121.94, 118.23, 118.19, 116.00, 115.98, 115.90, 31.92, 31.84, 30.36, 30.33, 19.20, 19.17. MS (MALDI) m/z : 624 $[M]^+$.

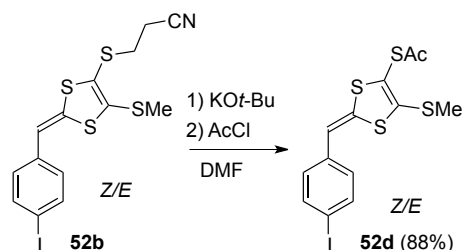


Compound 12d. To a solution of **12b** (61 mg, 0.11 mmol) in DMF (10 mL) was added a solution of sodium propoxide (0.50 mL, 0.652 M in 1-PrOH, 0.33 mmol). The solution immediately turned red and was stirred for 30 min at rt. Acetyl chloride (32 μ L, 0.45 mmol) was added whereupon the color changed to light orange. After stirring for 5 min, CH₂Cl₂ (150 mL) was added and the standard washing procedure used. Purification by flash column chromatography (SiO₂, gradient 50 – 70% CH₂Cl₂ in petroleum spirit) and the first major yellow band gave **12d** as a yellow solid (45 mg, 77%). Mp ca. 168 °C (darkens at 162 °C). Anal. Calcd (C₂₀H₁₈O₂S₈): C, 43.92; H, 3.32. Found: C, 44.30; H, 3.22. IR(ATR, cm⁻¹): ν = 3020w, 2993w, 2920m, 2851w, 1729vs, 1708vs (2 x CO), 1598w, 1568s, 1545s, 1503m, 1410m, 1351m, 1316m, 1282w, 1219m, 1184w, 1166w, 1110vs. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.24, 7.21, 7.20, 7.18 (4 x s, 4H), 6.50, 6.49, 6.49, 6.47 (4 x s, 2H), 2.44, 2.44 br, 2.43 (3 x s, 6H), 2.42, 2.42 br, 2.41 (3 x s, 6H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 191.98, 191.62, 137.67, 135.95, 135.93, 134.36, 134.32, 134.28, 134.24, 132.18, 132.15, 132.12, 127.52, 127.49, 127.45, 127.43, 116.27, 116.16, 115.32, 115.31, 115.14, 115.13, 113.77, 30.26, 30.21, 19.45, 19.43, 19.29; pentane residuals observed in NMR spectra. MS (MALDI) m/z : 546 [M]⁺.

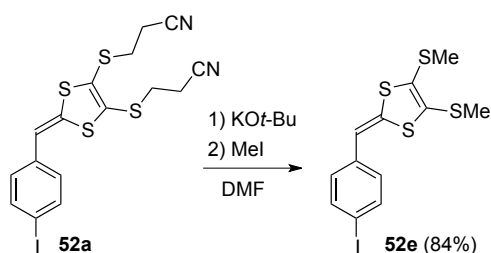


Compound 52b. To a stirring degassed solution of **52a** (1.0 g, 2.05 mmol) in DMF (20 mL) was added a degassed methanolic solution (ca. 5 mL) containing CsOH•H₂O (379 mg, 2.26 mmol) dropwise over 1-2 min, upon which the color of the solution darkened. After stirring for 20 min, MeI (0.64 mL, 10.25 mmol) was added and the solution rapidly lightened to a transparent dark orange color. After 5 min, the solution was diluted with CH₂Cl₂ (ca. 100 mL) and washed with water (ca. 10 x 100 mL to remove the DMF). The CH₂Cl₂ solution was dried (Na₂SO₄), filtered and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO₂, petroleum spirit / CH₂Cl₂ 1:3) and the first minor yellow-brown fraction gave **52e** (25 mg, 3%) as an orange-brown oil. The next major yellow-brown band gave **52b** as a tan yellow solid (826 mg, 90%) which had a slightly unpleasant sulphurous odour. Data **52b**: Mp 94-96 °C. Anal. Calcd (C₁₄H₁₂INS₄): C, 37.42; H, 2.69; N, 3.12. Found: C, 37.55; H, 2.55; N, 3.06. IR(ATR, cm⁻¹): ν = 3044vw, 2990vw, 2956vw, 2921w, 2864vw, 2247w (CN), 2228w (CN), 1567vs, 1541vs, 1491s, 1477s, 1420vs,

1390vs, 1314s, 1272m. ^1H NMR (500 MHz, CDCl_3) δ 7.66 (d, J = 8.5 Hz, 2H), 6.94, 6.92 (2 x d, J = 8.5 Hz, 2H), 6.40, 6.39 (2 x s, 1H), 3.02 (q, J = 7.3 Hz, 2H), 2.72 (q, J = 7.3 Hz, 2H), 2.48, 2.46 (2 x s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.73, 135.51, 135.49, 134.95, 132.60, 132.46, 132.38, 128.59, 120.05, 117.70, 117.63, 116.83, 114.60, 114.49, 91.11, 91.07, 31.16, 19.12, 18.88, 18.87, 18.85. MS (FAB) m/z : 449 $[\text{M}]^+$.

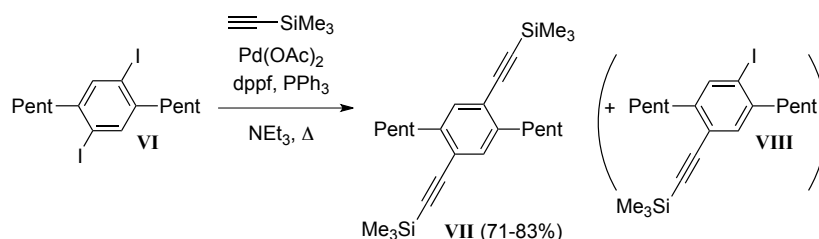


Compound 52d. To a stirring solution of **52b** (100 mg, 0.22 mmol) in dry, degassed DMF (5 mL) was added $\text{KO}^t\text{-Bu}$ (37 mg, 0.33 mmol), which caused the color of the solution to change from faint yellow to a darker yellow-brown. After 15 min, AcCl (32 μL , 0.44 mmol) was added which caused the solution to turn into a light orange color. After stirring for 5 min, the reaction was quenched by first adding CH_2Cl_2 (50 mL) and then water (100 mL). The organic phase was washed with water (ca. 50 mL x 5-10) to remove the DMF and then dried with Na_2SO_4 . The solvent was removed and the crude oily solid was purified by flash column chromatography (SiO_2 , initially 2:3 then 1:1 petroleum spirit / CH_2Cl_2). There was a faint band before a major pale yellow band, which contained the desired compound **52d** (86 mg, 88%) as an oil, which solidified to a pale yellow solid. Mp 90-92 $^\circ\text{C}$. IR(ATR, cm^{-1}): ν = 2995w, 2918m, 2851w, 1728vs, 1704vs (2 x CO), 1570vs, 1543vs, 1494m, 1479s, 1420m, 1395s, 1349m, 1315m, 1203m. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.69 – 7.67 (m, 4H), 6.99 – 6.98 (m, 2H), 6.96 – 6.95 (m, 2H), 6.43 (s, 1H), 6.42 (s, 1H), 2.44 (s, 3H), 2.42 (s, 3H), 2.41 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 191.84, 191.49, 138.12, 138.09, 137.72, 136.16, 136.10, 135.77, 133.91, 133.89, 129.02, 128.96, 116.45, 114.36, 114.16, 113.73, 91.11, 91.06, 30.28, 30.22, 19.45, 19.29. HR-MS (MALDI) m/z : 437.8732 $[\text{M}]^+$; calcd for $\text{C}_{13}\text{H}_{11}\text{IOS}_4^+$: 437.8732.



Compound 52e. To a stirring degassed solution of **52a** (200 mg, 0.41 mmol) in DMF (5 mL) was added $\text{KO}^t\text{-Bu}$ (184 mg, 1.64 mmol), which caused the solution to instantly turn from transparent dark orange to dark cherry red. After stirring for 15 min, MeI (0.15 mL, 2.46 mmol) was added and the solution turned orange and a white precipitate also formed. After 5 min, the solution was diluted with CH_2Cl_2 (ca. 50 mL) and was washed with water (up to 10 x 50 mL). The CH_2Cl_2 solution was dried (Na_2SO_4), filtered and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (SiO_2 , petroleum spirit / CH_2Cl_2 1:1) and the first yellow-brown fraction gave the product **52e** as an

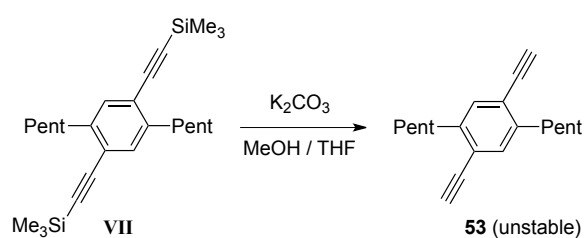
orange colored viscous oil (141 mg, 84%), which had a slight sulphurous odour. IR(ATR, cm^{-1}): $\nu = 3042\text{vw}$, 2988w , 2915m , 2848vw , 2821vw , 1568vs , 1542vs , 1496s , 1478s , 1418s , 1391s , 1311m . ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 2H), 6.37 (s, 1H), 2.43 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 137.64, 135.79, 133.70, 128.53, 127.65, 124.38, 113.61, 90.63, 19.17, 19.03. MS (FAB) m/z : 410 $[\text{M}]^+$, 411 $[\text{M}+\text{H}]^+$. HR-MS (MALDI) m/z : 409.8784 $[\text{M}]^+$; calcd for $\text{C}_{12}\text{H}_{11}\text{IS}_4^+$: 409.8783.



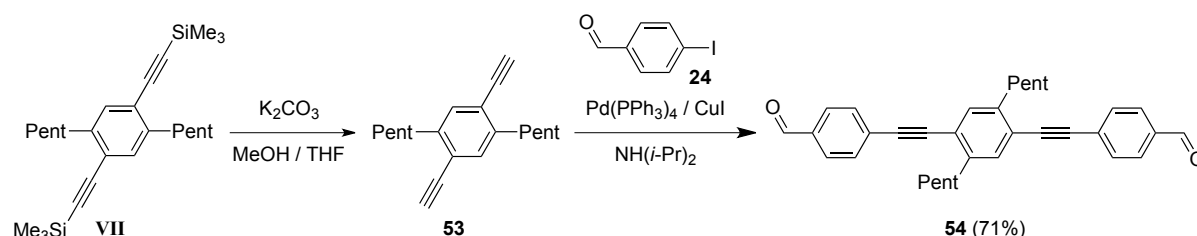
The coupling of **VI**, incorporating solubilizing pentyl groups, with trimethylsilylacetylene was quite difficult; methods with THF as solvent and minimal amine base only gave, even upon heating, trace amounts of **VII**, and some of the monoethynyl derivative **VIII**, along with mostly starting material **VI**. Instead, by heating in PhMe/ NEt_3 with $\text{Pd}(\text{OAc})_2$, dppf, PPh_3 and CuI , the reaction slowly proceeded to completion. Most couplings reactions in literature involving silyl-protected acetylenes with diiodobenzenes containing alkyl chains (greater than butyl) use amine bases in high concentration or as neat solvent: a) Kukula, H.; Veit, S.; Godt, A. *Eur. J. Org. Chem.* **1999**, 277-286. b) Nielsen, K. T.; Spanggaard, H.; Krebs, F. C. *Macromolecules* **2005**, 38, 1180-1189. c) Lebouch, N.; Garreau, S.; Louarn, G.; Belletête, M.; Durocher, G.; Leclerc, M. *Macromolecules* **2005**, 38, 9631-9637. d) Werz, D. B.; Fischer, F. R.; Kornmayer, S. C.; Rominger, F.; Gleiter, R. *J. Org. Chem.* **2008**, 73, 8021-8029. e) Mössinger, D.; Jester, S.-S.; Sigmund, E.; Müller, U.; Höger, S. *Macromolecules* **2009**, 42, 7974-7978. f) Jenny, N. M.; Wang, H.; Neuburger, M.; Fucjs, H.; Chi, L.; Mayor, M. *Eur. J. Org. Chem.* **2013**, 2738-2747.

Compounds VII and VIII. To a mixture of **VI** (355 mg, 0.76 mmol), CuI (14 mg, 0.076), $\text{Pd}(\text{OAc})_2$ (17 mg, 0.076 mmol), dppf (42 mg, 0.76 mmol) and PPh_3 (99 mg, 0.38 mmol) was added a degassed solution of toluene (35 mL), NEt_3 (14 mL) and trimethylsilylacetylene (0.63 mL, 4.53 mmol). The reaction was performed under two different reaction conditions: (a) to 85°C and stirred for 12 h in a screw cap Schlenck tube or (b) 45°C for 3 d. The reaction was then monitored by TLC (petroleum spirit $40-65^\circ\text{C}$, showing no more starting material or mono adduct) and the solvent was removed. The residue was dissolved in heptanes and filtered through cotton wool. This solution was then reduced to 2-3 mL and purified by flash column chromatography (SiO_2 , petroleum spirit). The first UV active bands in order of appearance can be either starting material **VI**, $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$, the mono adduct **VIII** ($R_f = 0.6$) and **VII** as the major band ($R_f = 0.4$ in petroleum spirit $40-65^\circ\text{C}$). The product **VII** was obtained as a clear oil which quickly solidified to an off-white waxy crystalline solid ((a): 220 mg, 71% at 85°C for 12 h; (b) 83% at 45°C for 3 d). Data for **VII**: Mp $44-48^\circ\text{C}$. Anal. Calcd ($\text{C}_{26}\text{H}_{42}\text{Si}_2$): C, 76.02; H, 10.31. Found: C, 76.08; H, 10.63. IR(ATR, cm^{-1}): $\nu = 2955\text{s}$, 2927s , 2857m , 2152s ($\text{C}\equiv\text{C}$), 1487m , 1464m , 1428m , 1374m , 1248s , 1197m , 894m , 863s , 836vs , 758s , 731s , 698s , 623s . ^1H NMR (500 MHz, CDCl_3) δ 7.25 (s, 2H), 2.70 – 2.66 (m, 4H), 1.64 – 1.55 (m, 4H), 1.35 – 1.33 (m, 8H), 0.90 (t, $J = 7.0$ Hz, 6H), 0.25 (s, 18H). ^{13}C NMR (125 MHz, CDCl_3) δ 142.80, 132.61, 122.70, 104.08, 99.03, 34.22, 31.92, 30.43, 22.69, 14.23, 0.12. MS (ESP) m/z : 411 $[\text{M}+\text{H}]^+$, 433 $[\text{M}+\text{Na}]^+$. MS (FAB) m/z : 410 $[\text{M}]^+$. The monoadduct **VIII** can be contaminated with $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ when isolated by column chromatography, but this impurity can be

removed by sublimation or even on the rotary evaporator at about 60 °C, leaving **VIII** as a colorless oil in the flask. Data for **VIII**: IR(ATR, cm^{-1}): $\nu = 2955\text{s}, 2926\text{s}, 2857\text{m}, 2153\text{m}$ ($\text{C}\equiv\text{C}$), $1466\text{m}, 1374\text{m}, 1248\text{s}, 1217\text{m}, 1140\text{m}, 890\text{m}, 841\text{vs}, 759\text{s}, 726\text{m}, 699\text{m}, 663\text{s}$. ^1H NMR (500 MHz, CDCl_3) δ 7.62 (s, 1H), 7.23 (s, 1H), 2.66 – 2.59 (m, 4H), 1.63 – 1.53 (m, should be 4H but on top of the H_2O signal), 1.40 – 1.30 (m, 8H), 0.91, 0.90 (2 x t, $J = 7.0$ Hz, 6H), 0.25 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 144.76, 142.78, 139.53, 132.58, 122.74, 103.47, 101.27, 98.68, 40.27, 33.97, 31.90, 31.69, 30.41, 30.07, 22.65 (2 overlapping signals), 14.22, 14.19, 0.09. HR-MS (MALDI) m/z : 440.1391 $[\text{M}]^+$; calcd for $\text{C}_{21}\text{H}_{33}\text{ISi}^+$: 440.1391.

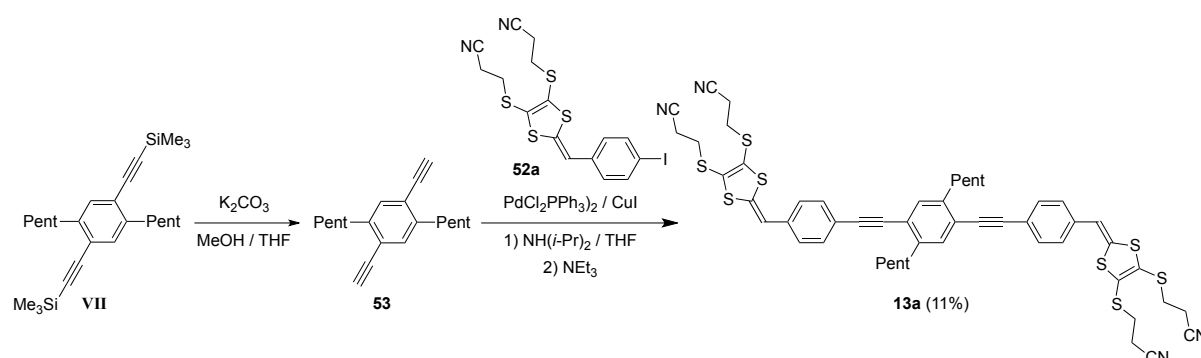


Compound 53. General procedure for desilylation of **VII** to **53**: Compound **VII** (0.1 mmol) was dissolved in THF (2 mL) and MeOH (3 mL). K_2CO_3 (1.5 mmol) was added, and the mixture was stirred for 15 min before the reaction was complete (TLC: product has a slightly higher R_f than starting material in petroleum spirit). The mixture was passed through a plug of SiO_2 (CH_2Cl_2). Removal of the solvent gave the terminal alkyne, which was immediately used for further reaction because of instability. When concentrated and heated above 35 °C or when neat for a short while, the oily film turned a purple color which darkened in time. This color can be removed by passing the compound through a short plug (SiO_2 , petroleum spirit). IR(ATR, cm^{-1}): $\nu = 3311\text{m}$ ($\text{C}\equiv\text{CH}$), $2955\text{s}, 2925\text{vs}, 2857\text{s}, 2104\text{w}$ ($\text{C}\equiv\text{C}$), $1489\text{m}, 1465\text{m}, 1378\text{w}, 1211\text{m}, 897\text{m}, 644\text{m}, 606\text{m}$. ^1H NMR (500 MHz, CDCl_3) δ 7.30 (s, 2H), 3.29 (s, 2H), 2.73 – 2.70 (m, 4H), 1.65 – 1.59 (m, 4H), 1.35 – 1.32 (m, 8H), 0.92 – 0.89 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 142.84, 133.09, 122.06, 82.40, 81.67, 33.88, 31.75, 30.30, 22.63, 14.17. MS (GC-MS) m/z : 266 $[\text{M}]^+$.

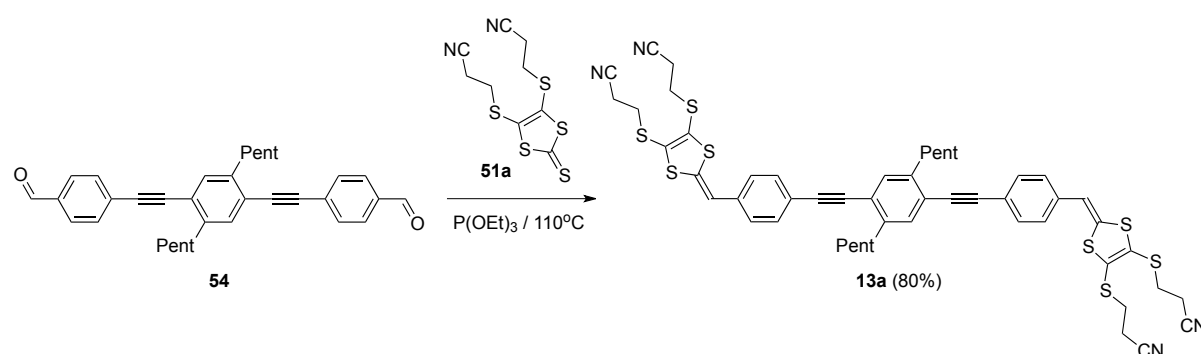


Compound 54. Compound **VII** (136 mg, 0.331 mmol) was desilylated to the unstable bisacetylene **53**, as described above, and the residue was reacted straight away. To a Schlenk flask containing the residue of **53** was added 4-iodobenzaldehyde **24** (192 mg, 0.829 mmol), $\text{Pd}(\text{PPh}_3)_4$ (38 mg, 0.033 mmol) and CuI (6.3 mg, 0.033 mmol) and then dried and degassed $\text{NH}(i\text{-Pr})_2$ (20 mL) was added. The compounds took some time to dissolve but after 5 h of stirring at rt, **53** had been consumed (TLC). After stirring for 20 h, the solvent was removed and the residue was loaded onto a flash column (SiO_2 , initially petroleum spirit then a

gradient up to petroleum spirit / CH₂Cl₂ 1:1). The first major band was the starting material **24**, followed by a minor band and the third band, which was highly luminescent under UV light, gave **54** (112 mg, 71%) as an off-white waxy solid. Mp 115-117 °C. Anal. Calcd (C₃₄H₃₄O₂): C, 86.04; H, 7.22. Found: C, 85.98; H, 7.14. IR(ATR, cm⁻¹): ν = 2951m, 2923m, 2855m, 2814w, 2726w (CHO), 2211w (C≡C), 1697vs (CHO), 1597vs, 1560m, 1509w, 1485w, 1456w, 1409w, 1384w, 1301m, 1285w, 1204s, 1166m, 1135w. ¹H NMR (500 MHz, CDCl₃) δ 10.03 (s, 2H), 7.88 (d, *J* = 8.1 Hz, 4H), 7.67 (d, *J* = 8.1 Hz, 4H), 7.41 (s, 2H), 2.82 (dd, *J* = 8.9, 6.4 Hz, 4H), 1.75 – 1.69 (m, 4H), 1.42-1.37 (m, 8H), 0.93 – 0.90 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 191.49, 142.81, 135.59, 132.78, 132.09, 129.79, 129.76, 122.64, 93.48, 92.50, 34.23, 31.85, 30.48, 22.69, 14.20. MS (FAB) *m/z*: 474 [M]⁺, 475 [M+H]⁺.

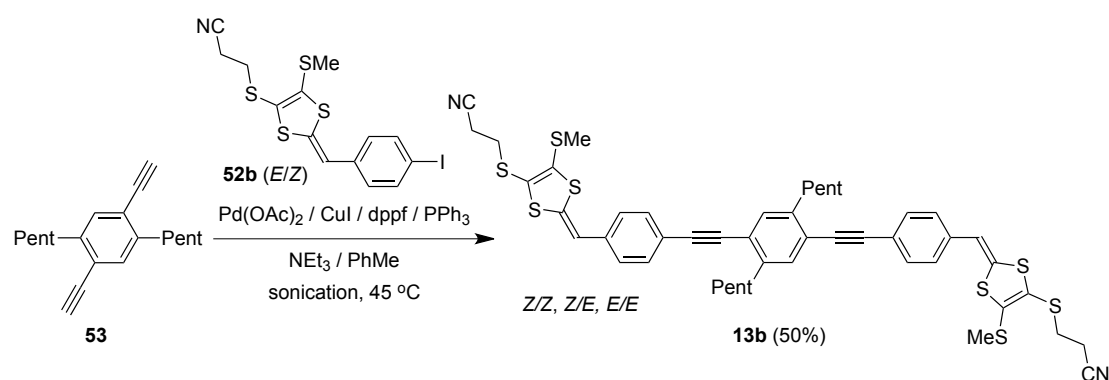


Compound 13a. Method A: Compound **VII** (118 mg, 0.287 mmol) was desilylated to the bisacetylene **53**, as described above. The crude diyne was dissolved in degassed THF (6 mL) and NH(*i*-Pr)₂ (2.5 mL). Compound **52a** (280 mg, 0.574 mmol), PdCl₂(PPh₃)₂ (10 mg, 0.014 mmol) and CuI (3 mg, 0.016 mmol) were added. The mixture was stirred for 20 h including 4 h of sonication. The reaction did not look like it was proceeding well so the solvent was evaporated, and the residue was dissolved in degassed NEt₃. PdCl₂(PPh₃)₂ (10 mg, 0.014 mmol) and CuI (3 mg, 0.016 mmol) were added. After 6 h of stirring, the solvent was removed. Flash column chromatography (SiO₂, CH₂Cl₂) gave compound **13a** as a yellow solid (31 mg, 11%).

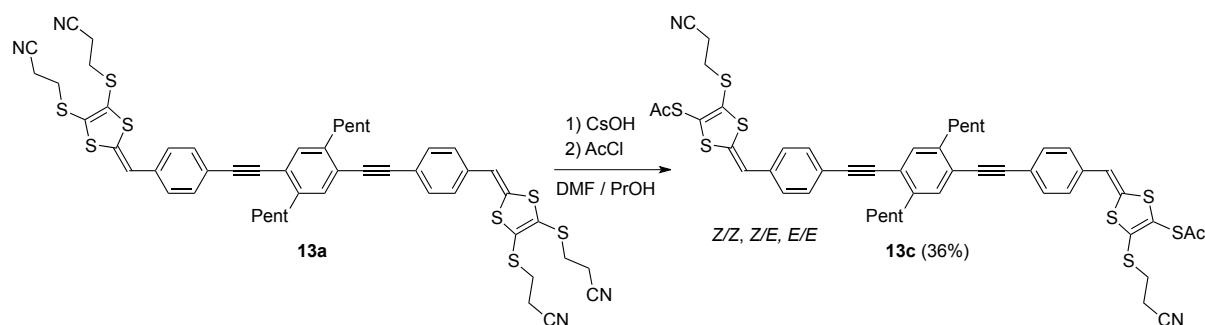


Compound 13a. Method B: A suspension of thione **51a** (180 mg, 0.590 mmol) and compound **54** (70 mg, 0.147 mmol) in P(OEt)₃ (3 mL) was degassed with Ar for 15 min and kept under an Ar atmosphere and then heated to 110 °C. Within 10 min, a yellow precipitate started to form; the reaction was stirred for 3 h and then allowed to cool to ambient temperature. MeOH (ca. 15 mL) was added to the suspension which was then poured onto a

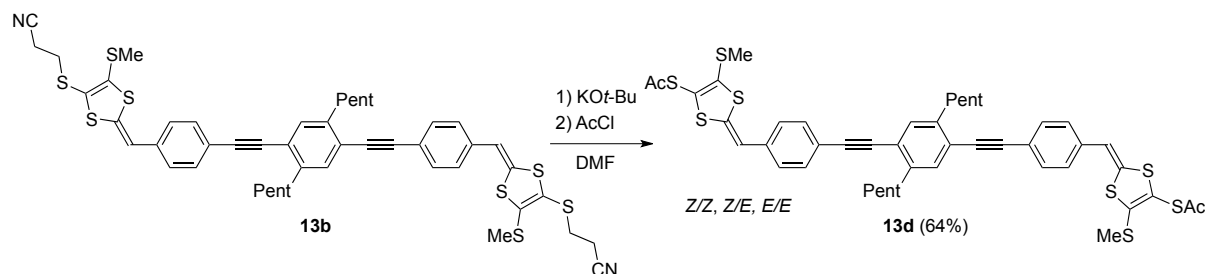
sintered glass funnel (pore 3) and washed with MeOH (2 x 15 mL) and petroleum (3 x 15 mL) to remove the malodorous $\text{P}(\text{OEt})_3$. It is recommended to dissolve the near pure solid in minimal CH_2Cl_2 and then triturate the compound in stirring MeOH (ca. 60 mL) before collecting the solid and purifying this by flash column chromatography (SiO_2 , load in CH_2Cl_2 then increase to 1% EtOAc to remove the first minor yellow band and then increased to 3% to remove the major yellow band). The solvent was removed to give **13a** as a bright yellow solid (117 mg, 80%). Mp 170-172 °C. Anal. Calcd ($\text{C}_{52}\text{H}_{50}\text{N}_4\text{S}_8$): C, 63.25; H, 5.10; N, 5.67. Found: C, 63.14; H, 4.78; N, 5.65. IR(ATR, cm^{-1}): $\nu = 3026\text{vw}$, 2952s , 2927s , 2865m , 2251m (CN), 2201vw ($\text{C}\equiv\text{C}$), 1599vw , 1567vs , 1540s , 1509s , 1495m , 1460m , 1409s , 1377w , 1324m , 1279m , 1232w . ^1H NMR (500 MHz, CD_2Cl_2) δ 7.53 (dd, $J = 8.4$ Hz, 4H), 7.38 (s, 2H), 7.23 (dd, $J = 8.4$ Hz, 4H), 6.56 (s, 2H), 3.12, 3.12 (2 x t, $J = 7.0$ Hz, 8H), 2.85 – 2.75 (m, 12H), 1.74 – 1.68 (m, 4H), 1.44 – 1.35 (m, 8H), 0.96 – 0.86 (m, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 142.92, 136.28, 132.82, 132.28, 132.20, 128.53, 127.38, 125.76, 123.09, 121.54, 118.20, 118.13, 115.97, 94.63, 89.83, 34.61, 32.30, 31.83, 31.79, 30.93, 23.14, 19.52, 19.48, 14.42. MS (FAB) m/z : 986 $[\text{M}]^+$.



Compound 13b. To a mixture of **53** (60 mg, 0.23 mmol), **52b** (246 mg, 0.55 mmol), CuI (4.3 mg, 0.023 mmol), $\text{Pd}(\text{OAc})_2$ (5.1 mg, 0.023 mmol), dppf (13 mg, 0.023 mmol) and PPh_3 (30 mg, 0.11 mmol) was added a degassed solution of toluene (12 mL) and NEt_3 (4 mL). The solution was stirred at rt for 17 h, and then it was sonicated at 45 °C for 24 hr. The solvent was removed and the residue was purified by flash column chromatography (SiO_2 , gradient from 1:1 to 1:2 petroleum spirit / CH_2Cl_2). The first major band was the starting material **52b**, then a minor yellow band followed major yellow band which contained slightly crude **13b**. The residue was dissolved in minimal CH_2Cl_2 (ca. 10 mL) and then was triturated in MeOH (ca. 60 mL) to give a bright yellow precipitate (103 mg, 50%). Mp 134 °C starts to melt, 140-143 °C finishes melting and darkens. Anal. Calcd ($\text{C}_{48}\text{H}_{48}\text{N}_2\text{S}_8$): C, 63.39; H, 5.32; N, 3.08. Found: C, 63.16; H, 5.33; N, 3.00. IR(ATR, cm^{-1}): $\nu = 3028\text{vw}$, 2952m , 2925s , 2857m , 2248w (CN), 2190vw ($\text{C}\equiv\text{C}$), 1599w , 1567vs , 1541s , 1509s , 1465m , 1408s , 1320m , 1277m . ^1H NMR (500 MHz, CDCl_3) δ 7.51 – 7.49 (m, 4H), 7.36 (s, 2H), 7.21 – 7.17 (m, 4H), 6.50 (s, 1H), 6.49 (s, 1H), 3.06 – 3.03 (m, 4H), 2.82 – 2.79 (m, 4H), 2.75 – 2.72 (m, 4H), 2.49 (s, 3H), 2.49 (s, 3H), 1.72 – 1.68 (m, 4H), 1.41 – 1.36 (m, 8H), 0.93 – 0.90 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 142.35, 135.88, 135.12, 132.60, 132.57, 132.44, 132.41, 131.81, 126.86, 122.66, 121.05, 121.00, 117.74, 117.66, 116.96, 115.17, 115.03, 94.30, 89.49, 34.26, 31.90, 31.21, 30.46, 22.72, 19.18, 18.91, 18.88, 14.25. MS (MALDI) m/z : 908 $[\text{M}]^+$.

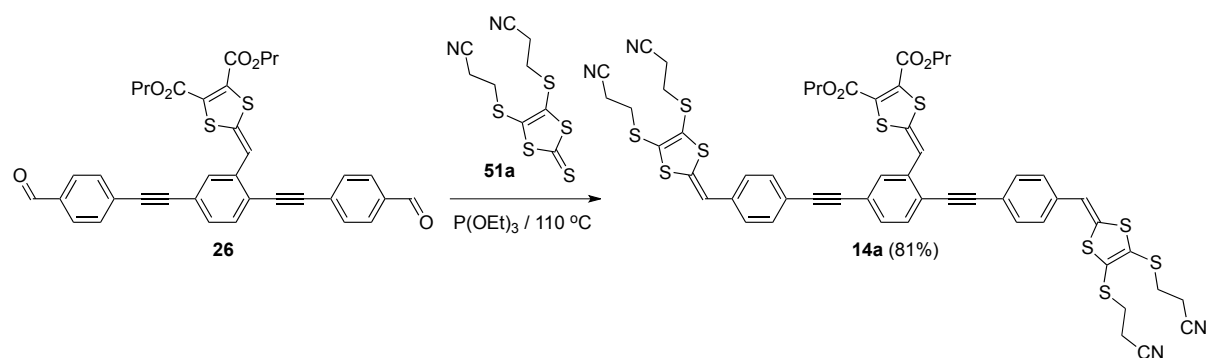


Compound 13c. A solution of **13a** (43 mg, 0.044 mmol) in DMF (8 mL) was treated with a propanolic solution of CsOH•H₂O (0.52 mL, 177 mM) over the period of 1 min upon which the yellow solution turned red and then black. After stirring for 25 min, AcCl (ca. 9 μ L, 0.13 mmol) was added until the solution returned to a transparent yellow color and it was stirred for a further 5 min. The solution was then diluted with CH₂Cl₂ (ca. 50 mL) and then washed with H₂O (ca. 5-10 x 70 mL to remove the DMF from the organic phase). The yellow organic phase was dried with Na₂SO₄ and the solvent removed under reduced pressure. The yellow residue was purified by flash chromatography (SiO₂, CH₂Cl₂), the third yellow-orange band (major) gave the desired compound as a yellow solid (15 mg, 36%). Mp 129-133 °C (decomp.). Anal. Calcd (C₅₀H₄₈N₂O₂S₈): C, 62.21; H, 5.01; N, 2.90. Found: C, 62.38; H, 4.84; N, 2.83. IR(ATR, cm⁻¹): ν = 3029vw, 2953s, 2926s, 2856s, 2251vw (CN), 2204vw (C \equiv C), 1730s (C=O), 1709s (C=O), 1598w, 1567vs, 1541s, 1509s, 1463m, 1409m, 1377w, 1352m, 1327w, 1277m, 1233w, 1208w, 1186w, 1165w, 1113vs. ¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 2.3 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.55 (s, 1H), 6.54 (s, 1H), 3.05 (t, *J* = 6.9 Hz, 2H), 3.04 (t, *J* = 6.9 Hz, 2H), 2.83 – 2.80 (m, 4H), 2.71 (t, *J* = 6.9 Hz, 2H), 2.69 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 2.45 (s, 3H), 1.73 – 1.70 (m, 4H), 1.43 – 1.38 (m, 8H), 0.93 – 0.90 (m, 6H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 191.64, 191.41, 142.91, 136.36, 136.32, 133.07, 132.96, 132.81, 132.68, 132.19, 130.93, 127.35, 127.28, 123.98, 123.09, 122.08, 121.46, 121.40, 118.22, 118.17, 115.63, 115.52, 94.66, 89.77, 34.61, 32.31, 31.95, 31.89, 30.93, 30.39, 30.34, 23.14, 19.22, 19.18, 14.42. HR-MS (MALDI) *m/z*: 964.1469 [M]⁺; calcd for C₅₀H₄₈N₂O₂S₈⁺: 964.1476.

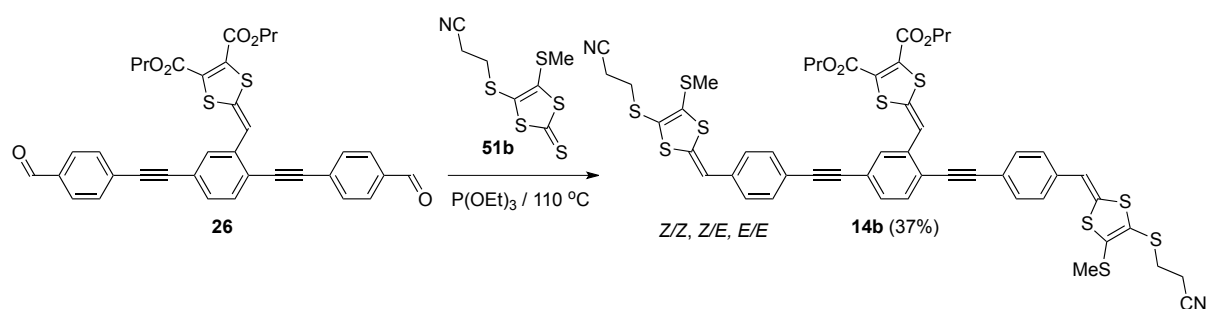


Compound 13d. To a stirred solution of **13b** (61 mg, 0.067 mmol) in DMF (12 mL; brief heating may be needed to get the compound into solution but it should be ensured that the solution is at ambient temperature when adding the base) was added KO*t*-Bu (17 mg, 0.148 mmol). This caused the yellow colored solution to rapidly turn dark red. The solution was stirred for a further 12 min before AcCl (14.3 μ L, 0.201 mmol) was added, reverting the solution back to a yellow color within 30 s. The solution was stirred for a further 10 min, it

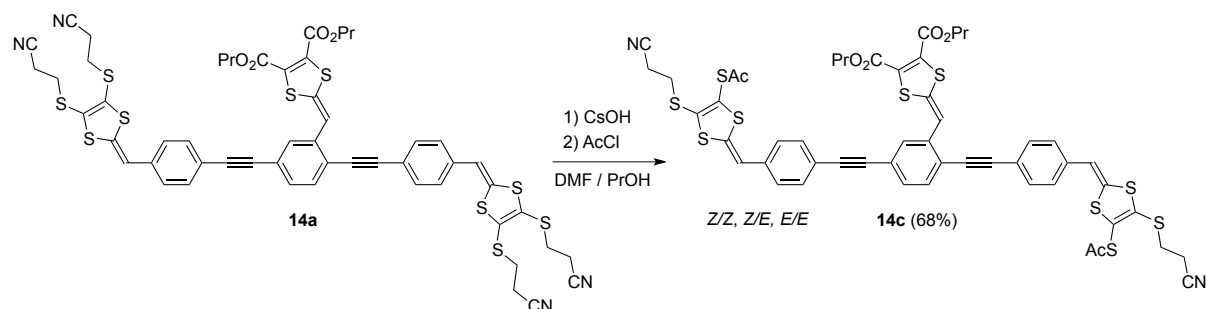
was then diluted with CH₂Cl₂ (ca. 50 mL) and then washed with H₂O (approximately 5-10 times to remove the DMF from the organic phase). The yellow organic phase was dried with Na₂SO₄ and the solvent removed under reduced pressure. The residue was purified by flash column chromatography (SiO₂, petroleum spirit / CH₂Cl₂ 1:1) and the first yellow fraction gave **13d** as a yellow solid (38 mg, 64%), which had a slightly oily texture on glass. Mp 139-142 °C (decomposes to a black color and melts after 142 °C). Anal. Calcd (C₄₈H₄₈N₂S₈): C, 62.26; H, 5.22. Found: C, 61.93; H, 4.86. IR(ATR, cm⁻¹): ν = 3028w, 2953m, 2924s, 2855m, 2199vw (C≡C), 1732s (C=O), 1710m (C=O), 1567s, 1540m, 1508m, 1457w, 1428w, 1408m, 1351w, 1273w, 1111s. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.37 (t, *J* = 2.6 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.53 (s, 1H), 6.52 (s, 1H), 2.83 – 2.79 (m, 4H), 2.45 (s, 3H), 2.45 (s, 3H), 2.42 (s, 6H), 1.72 – 1.69 (m, 4H), 1.41 – 1.38 (m, 8H), 0.93 – 0.90 (m, 6H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 191.88, 191.52, 142.89, 137.84, 136.59, 136.54, 135.94, 134.03, 134.01, 132.79, 132.16, 132.13, 127.28, 127.21, 123.10, 123.09, 121.17, 121.08, 116.61, 114.85, 114.66, 113.89, 94.74, 89.66, 89.64, 34.62, 32.31, 30.94, 30.30, 30.24, 23.15, 19.48, 19.31, 14.42. MS (MALDI) *m/z*: 886 [M]⁺.



Compound 14a. In a dried round-bottomed flask containing **26** (75 mg, 121 μmol) and thione **51a** (148 mg, 486 μmol) under Ar atmosphere was added P(OEt)₃ (1.5 mL) degassed for 20 min. The suspension was heated to 110 °C for 3 h and then was allowed to cool to rt. Then MeOH (10 mL) was added, causing product to crash out, and the solid was filtered and washed with MeOH (2 x 10 mL) and petroleum spirit (2 x 10 mL). The crude was purified by flash chromatography (SiO₂, 3% EtOAc in CH₂Cl₂) and the major orange fraction gave **14a**, but it contained a minor impurity so the residue was dissolved in minimal CH₂Cl₂ and the addition of heptane caused the product to crash out. The solid was washed with heptane (2 x 10 mL), which gave pure product as an orange-red solid (111 mg, 81%). Mp 71.2 – 72.5 °C. Anal. Calcd (C₅₄H₄₄N₄O₄S₁₀): C, 57.21; H, 3.91; N, 4.94. Found: C, 57.05; H, 3.67; N, 4.92. IR(ATR, cm⁻¹): ν = 2967m, 2933m, 2880w, 2855w, 2251w (CN), 2205w (C≡C), 1709vs (CO₂R), 1580s sh, 1568s, 1541s, 1507m, 1464m, 1411m, 1390m, 1361m, 1312m, 1266s sh, 1238s, 1222vs. ¹H NMR (500 MHz, CDCl₃) δ 7.58 – 7.53 (m, 6H), 7.36 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.24 (dd, *J* = 8.5, 2.3 Hz, 4H), 7.01 (s, 1H), 6.56 (s, 2H), 4.20, 4.19 (2 x t, *J* = 6.7 Hz, 4H), 3.12, 3.12 (2 x t, *J* = 7.1 Hz, 8H), 2.78, 2.77 (2 x t, *J* = 7.1 Hz, 8H), 1.76 – 1.68 (m, 4H), 0.98, 0.97 (2 x t, *J* = 7.4 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃) 160.14, 159.97, 137.87, 136.67, 136.57, 134.66, 133.12, 132.68, 132.56, 132.48, 132.34, 131.62, 130.17, 129.83, 128.54, 128.53, 128.33, 127.40, 127.37, 125.83, 125.81, 123.95, 121.80, 120.95, 120.87, 118.19, 118.13, 115.89, 115.85, 113.19, 97.33, 92.10, 90.35, 88.80, 68.95, 68.87, 31.83, 31.80, 22.35, 22.34, 19.52, 19.49, 10.65; 7 signals missing.

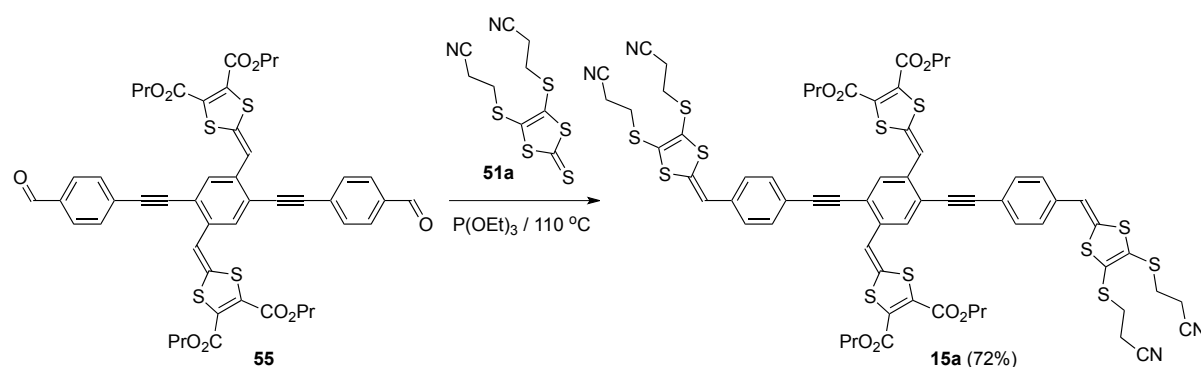


Compound 14b. A suspension of dialdehyde **26** (67 mg, 0.11 mmol), thione **51b** (115 mg, 0.43 mmol) in $\text{P}(\text{OEt})_3$ (2.5 mL) was degassed for 15 min with Ar and kept under an Ar atmosphere. The orange suspension was heated up to 110 °C, the solid dissolved and the mixture turned red. After stirring for 3 h, the reaction mixture was allowed to cool and an orange precipitate formed. MeOH (15 mL) was added to the solution to cause more product to precipitate, it was filtered through a sintered glass funnel and washed with MeOH (2 x 20 mL) and petroleum spirit (3 x 20 mL). The precipitate was purified by column chromatography (SiO_2 , gradient elution of EtOAc 0-3% in CH_2Cl_2) and the major orange band gave **14b** (42 mg, 37%) as an orange solid. Anal. Calcd ($\text{C}_{50}\text{H}_{42}\text{N}_2\text{O}_4\text{S}_{10}$): C, 56.89; H, 4.01; N, 2.65. Found: C, 56.61; H, 3.71; N, 2.70. IR(ATR, cm^{-1}): 3027w, 2965m, 2922m, 2878m, 2853w, 2250w (CN), 2205w ($\text{C}\equiv\text{C}$), 1710s (CO_2Pr), 1564vs, 1539vs, 1505s, 1464s, 1408s, 1389m, 1346m, 1311m, 1230vs. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.60 – 7.48 (m, 6H), 7.35 (dd, J = 8.0, 1.6 Hz, 1H), 7.26 – 7.19 (m, 4H), 7.01 (s, 1H), 6.54 / 6.52 (2 x s, 2H), 4.20, 4.19 (2 x t, J = 6.7 Hz, 4H), 3.06, 3.05 (2 x t, J = 7.1 Hz, 4H), 2.74, 2.74 (2 x t, J = 7.1 Hz, 4H), 2.50 (s, 6H), 1.80 – 1.63 (m, 4H), 0.98, 0.97 (2 x t, J = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.13, 159.96, 137.81, 136.88, 136.78, 135.46, 134.57, 133.94, 133.81, 133.78, 133.65, 133.09, 132.93, 132.90, 132.43, 132.34, 132.29, 131.63, 131.61, 130.17, 129.81, 128.29, 127.27, 127.25, 123.93, 121.80, 120.98, 120.94, 120.62, 120.56, 120.54, 120.48, 118.31, 118.24, 117.78, 117.76, 115.06, 115.02, 114.90, 114.86, 113.22, 97.43, 92.19, 90.24, 88.70, 68.94, 68.85, 31.79, 31.78, 22.35, 22.33, 19.46, 19.33, 19.20, 10.65. MS (MALDI) m/z : 1054 $[\text{M}]^+$.

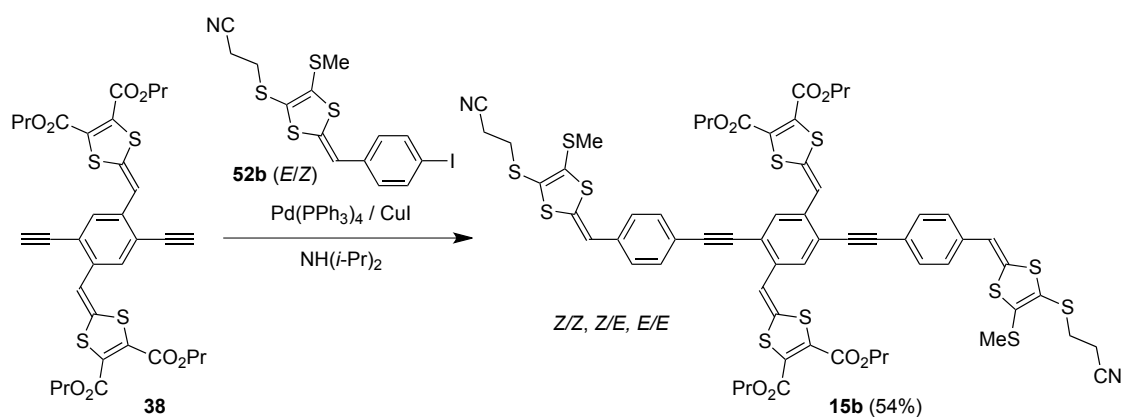


Compound 14c. A solution of **14a** (83 mg, 0.073 mmol) in DMF (16 mL) was treated with a propanolic solution of $\text{CsOH}\cdot\text{H}_2\text{O}$ (0.93 mL, 165 mM) over the period of 90 s, which caused the solution to turn from yellow-orange to a dark red (burgundy) colour. After stirring for 20 min, AcCl (20 μL , 0.22 mmol) was added and the solution turned a yellow colour again and after a further 5 min, it was diluted with CH_2Cl_2 (50 mL) and washed with H_2O (ca. 7 x 50 mL), the organic fraction dried with Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by flash chromatography (SiO_2 , 0.5% EtOAc in CH_2Cl_2); two minor

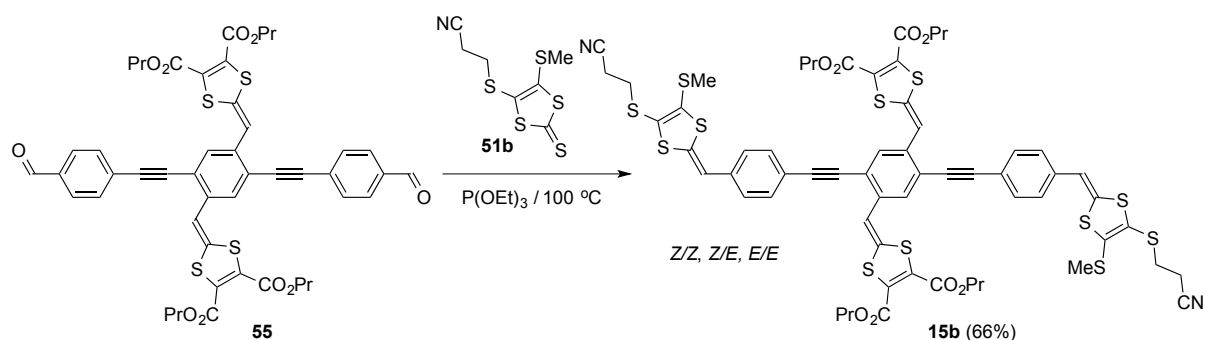
yellow/orange bands came through before the major orange band (product) came through. This gave **14c** as an orange solid (55 mg, 68%). Mp 115-118 °C (darkens). Anal. Calcd (C₅₂H₄₂N₂O₆S₁₀): C, 56.19; H, 3.81; N, 2.52. Found: C, 55.87; H, 4.10; N, 2.52. IR(ATR, cm⁻¹): 3029w, 2967m, 2933m, 2879w, 2855w, 2251w (CN), 2207w (C≡C), 1729vs (C=O), 1712vs (C=O), 1568vs, 1541s, 1507m, 1465m, 1409m, 1389m, 1351m, 1310m, 1241vs, 1112s. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.60 – 7.48 (m, 6H), 7.39 – 7.30 (m, 1H), 7.28 – 7.15 (m, 4H), 7.04 – 6.94 (m, 1H), 6.54, 6.54 (2 x s, 2H), 4.23 – 4.17 (m, 4H), 3.11 – 3.01 (m, 4H), 2.78 – 2.63 (m, 4H), 2.45 (s, 6H), 1.83 – 1.62 (m, 4H), 1.04 – 0.89 (m, 6H). ¹³C NMR (125 MHz, CD₂Cl₂) δ 191.64, 191.63, 191.40, 160.13, 159.96, 137.83, 136.73, 136.69, 136.63, 136.59, 134.61, 133.47, 133.35, 133.23, 133.10, 132.71, 132.46, 132.43, 132.32, 132.30, 131.64, 131.62, 130.96, 130.94, 130.17, 130.15, 129.81, 128.30, 127.35, 127.32, 127.28, 127.25, 124.00, 123.93, 122.12, 122.10, 121.79, 120.85, 120.80, 120.77, 120.72, 118.21, 118.17, 115.54, 115.51, 115.43, 115.39, 113.19, 97.36, 92.13, 90.31, 90.28, 88.74, 68.93, 68.85, 31.95, 31.89, 30.39, 30.35, 22.35, 22.33, 19.21, 19.18, 10.65. HR-MS (MALDI) *m/z*: 1110.0237 [M]⁺; calcd for C₅₂H₄₂N₂O₆S₁₀⁺: 1110.0244.



Compound 15a. Compound **15a** has previously been reported (Parker, C. R.; Wei, Z.; Arroyo, C. R.; Jennum, K.; Li, T.; Santella, M.; Bovet, N.; Zhao, G.; Hu, W.; van der Zant, H. S. J.; Vanin, M.; Solomon, G. S.; Laursen, B. W.; Nørgaard, K.; Nielsen, M. B. *Adv. Mater.* **2013**, *25*, 405-40; Schou, S. S.; Parker, C. R.; Lincke, K.; Jennum, K.; Vibenholt, J.; Kadziola, A.; Nielsen, M. B. *Synlett* **2013**, *24*, 231-235), but we have found that when the number of equivalents of thione **51a** was increased from 3.3 to 4 equivalents, the yield of **15a** increased to 72% compared to the previously reported 63%

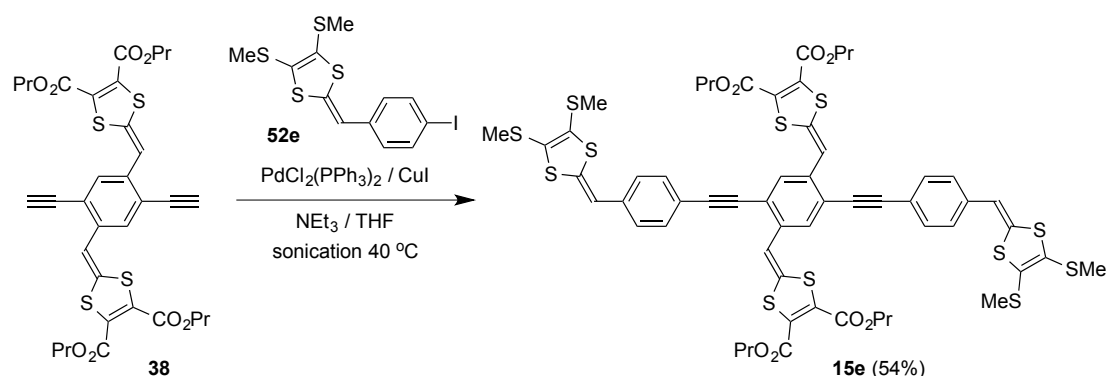


Compound 15b. *Method A:* To a mixture of **38** (84 mg, 0.12 mmol), **52b** (168 mg, 0.37 mmol), Pd(PPh₃)₄ (12.4 mg, 0.011 mmol), and CuI (2.0 mg, 0.011 mmol) was added a degassed solution of NH(*i*-Pr)₂ (25 mL) and the suspension was vigorously stirred at rt. The color of the suspension and solution started orange yellow and turned into a thicker orange red suspension over a day. TLC indicated the presence of mono-adduct so the solution was stirred for a further day. The solution was then diluted with CH₂Cl₂ (ca. 50 mL) and passed through a plug of silica. The solvent was removed and the residue was purified by flash chromatography (SiO₂, gradient 1-5% EtOAc in CH₂Cl₂); from the second pale yellow band starting material **52b** (75 mg, 0.17 mmol) was recovered, the third band which was orange gave what was suspected to be a mono adduct (5 mg, 5%), the fourth and major dark orange band gave the desired compound **15b** (87 mg, 54%) as a dark red solid.



Method B: To a mixture of **55** (70 mg, 0.077 mmol) and **51b** (95 mg, 0.358 mmol) was added P(OEt)₃ (2.5 mL) and the mixture was degassed with Ar for 10 min and kept under an Ar atmosphere. The red suspension was heated to 100 °C for 150 min under stirring, during which a dark red precipitate formed. The suspension was allowed to cool to rt and diluted with MeOH (ca. 20 mL) and filtered through a sintered funnel. The dark red solid was washed with MeOH (2 x 15 mL) and petroleum spirit (3 x 15 mL) which removed the pungent smelling P(OEt)₃. NMR of the rather insoluble crude red solid indicated there was still an aldehyde present (δ_H 10.03; δ_C 191.79 in CD₂Cl₂) along with the desired product. So to the crude mixture (85 mg) and an additional portion of thione (50 mg, 0.19 mmol) was added P(OEt)₃ (4 mL) and the mixture was degassed. The suspension was then heated to 110 °C for 4 h and worked up as before. The rather insoluble precipitate was then passed through a short flash column (SiO₂, first CH₂Cl₂ and then EtOAc 1-5% gradient elution); there was a minor yellow band which was followed by a major orange-red band which gave **15b** as a dark

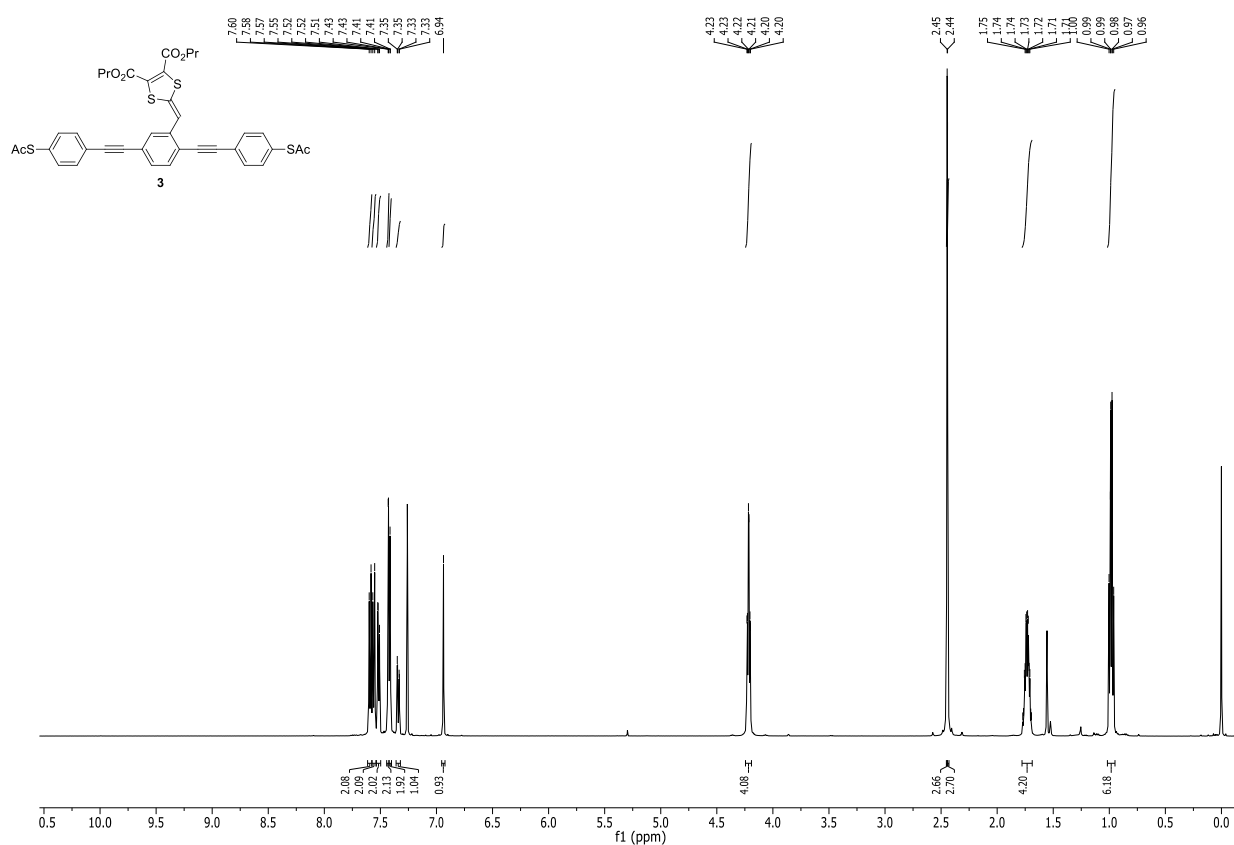
red solid (68 mg, 66%). The spectral data of this sparingly soluble compound have been reported previously.^{8f}



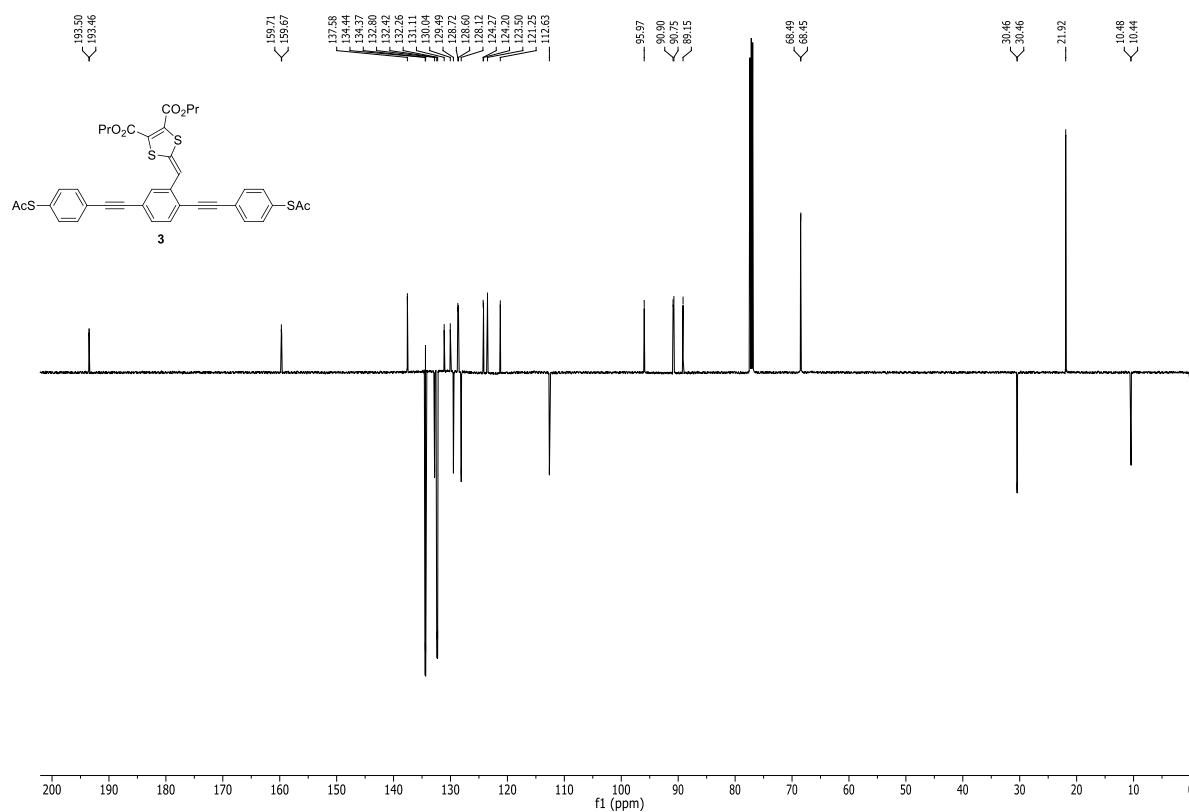
Compound 15e. To a mixture of **38** (50 mg, 0.072 mmol), **52e** (69 mg, 0.168 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (5 mg, 0.0072 mmol) and CuI (1.4 mg, 0.0072 mmol) was added a degassed solution of THF (7 mL) and NEt_3 (0.2 mL). The reaction mixture was stirred for 1 d, then sonicated at 40°C for 7 h during which time the red colored mixture darkened. The solvent was removed and the residue was purified by flash column chromatography (SiO_2 , initially in petroleum spirit / CH_2Cl_2 1:3). The first pale yellow band was unreacted starting material **52e** (29 mg), followed by a minor yellow-orange band, which was discarded, then a major orange band which contained **15e** (49 mg, 54%) as a dark red solid. Mp $112\text{--}116^\circ\text{C}$. Anal. Calcd ($\text{C}_{58}\text{H}_{54}\text{O}_8\text{S}_{12}$): C, 55.12; H, 4.31. Found: C, 54.71; H, 3.92. IR(ATR, cm^{-1}): $\nu = 2967\text{m}$, 2921w , 2878w , 2200w ($\text{C}\equiv\text{C}$), 1735s (CO_2Pr), 1582s , 1567s , 1539m , 1507m , 1470w , 1430w , 1408w , 1389w , 1311m , 1238vs . ^1H NMR (500 MHz, CD_2Cl_2) δ 7.56 (d, $J = 8.3$ Hz, 4H), 7.53 (s, 2H), 7.24 (d, $J = 8.3$ Hz, 4H), 7.00 (s, 2H), 6.52 (s, 2H), 4.20 (2 x t, $J = 6.7$ Hz, 8H), 2.45, 2.45 (2 x s, 6H) 1.78 – 1.65 (m, 8H), 0.98, 0.97 (2 x t, $J = 7.4$ Hz, 12H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 159.94, 159.76, 137.02, 135.06, 134.80, 134.15, 132.19, 131.59, 130.13, 128.92, 128.12, 127.00, 124.86, 121.84, 119.92, 114.00, 112.68, 97.28, 88.35, 68.77, 68.68, 22.18, 22.16, 19.26, 19.14, 10.48. MS (MALDI) m/z : 1262 $[\text{M}]^+$.

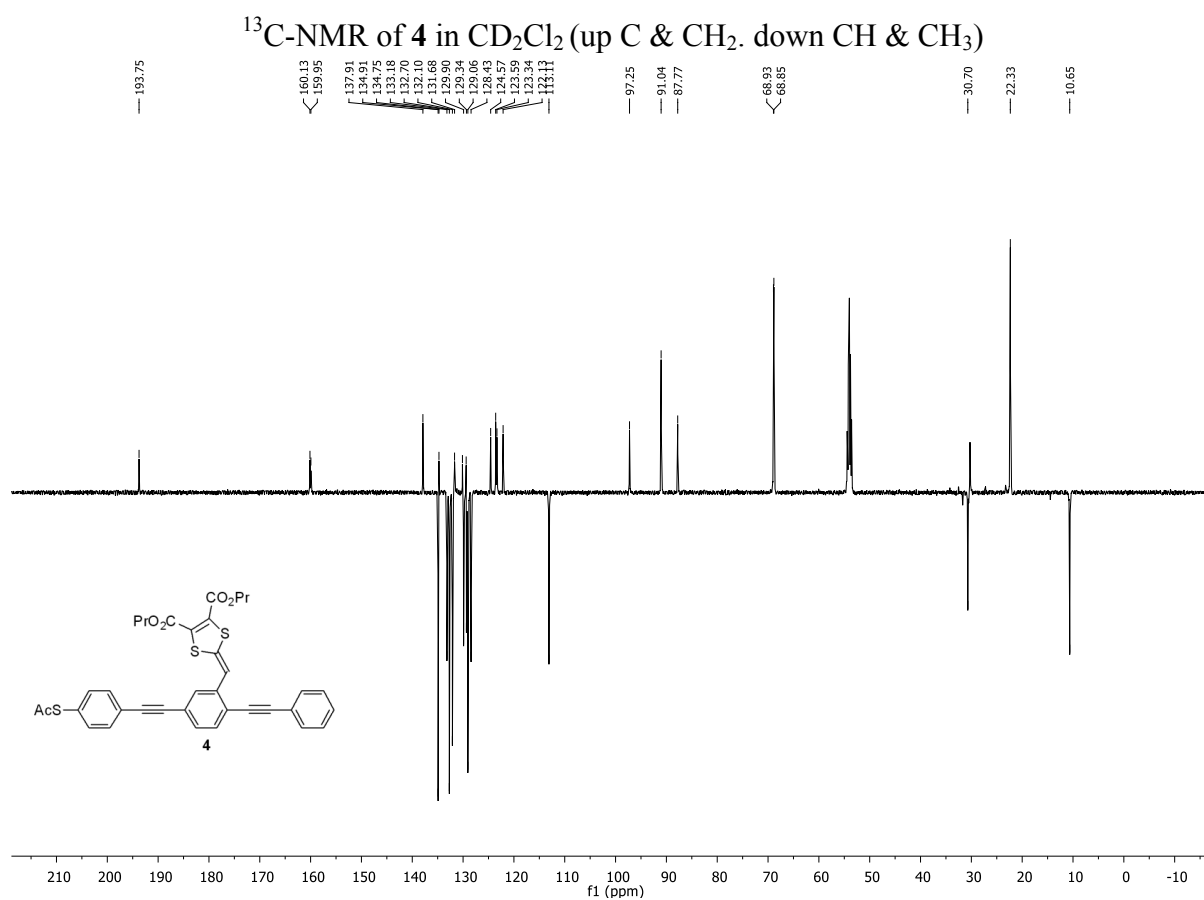
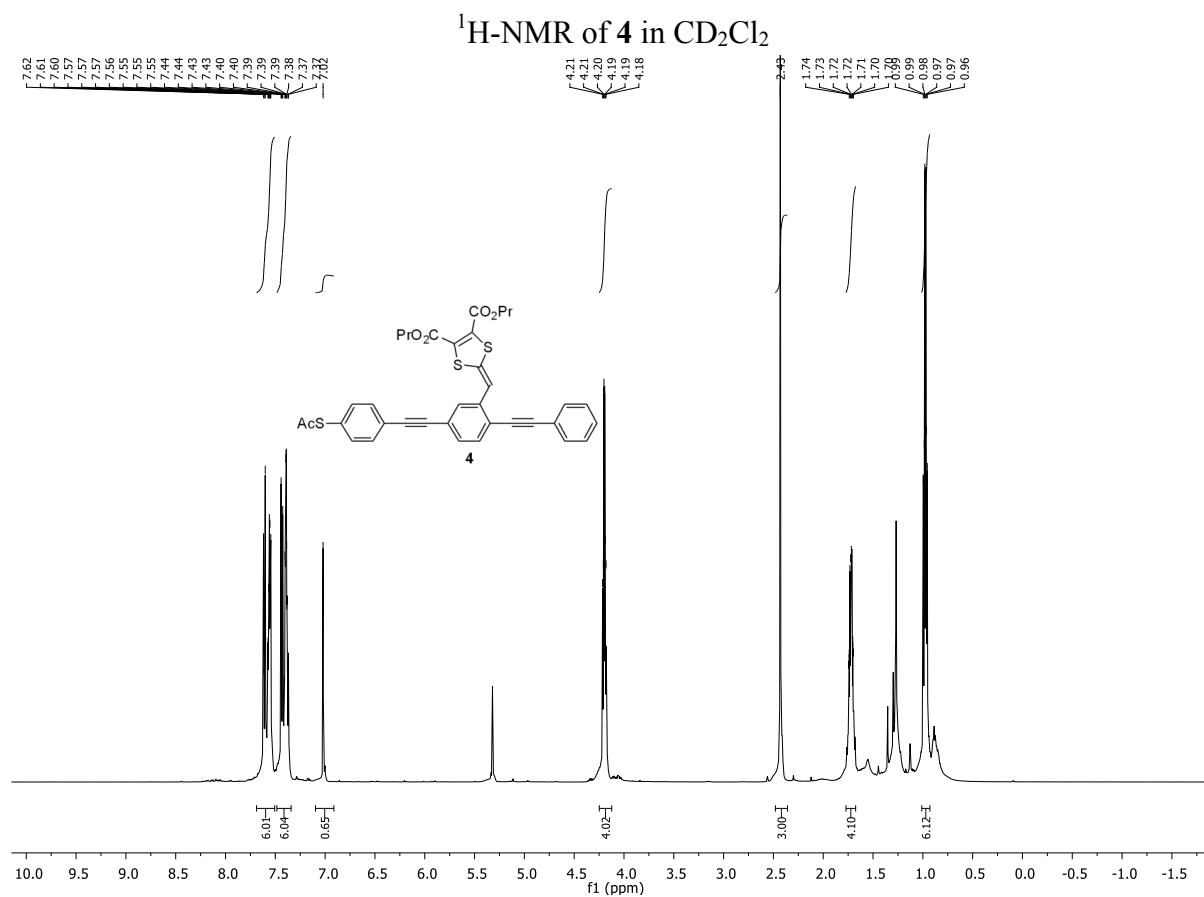
NMR Spectra

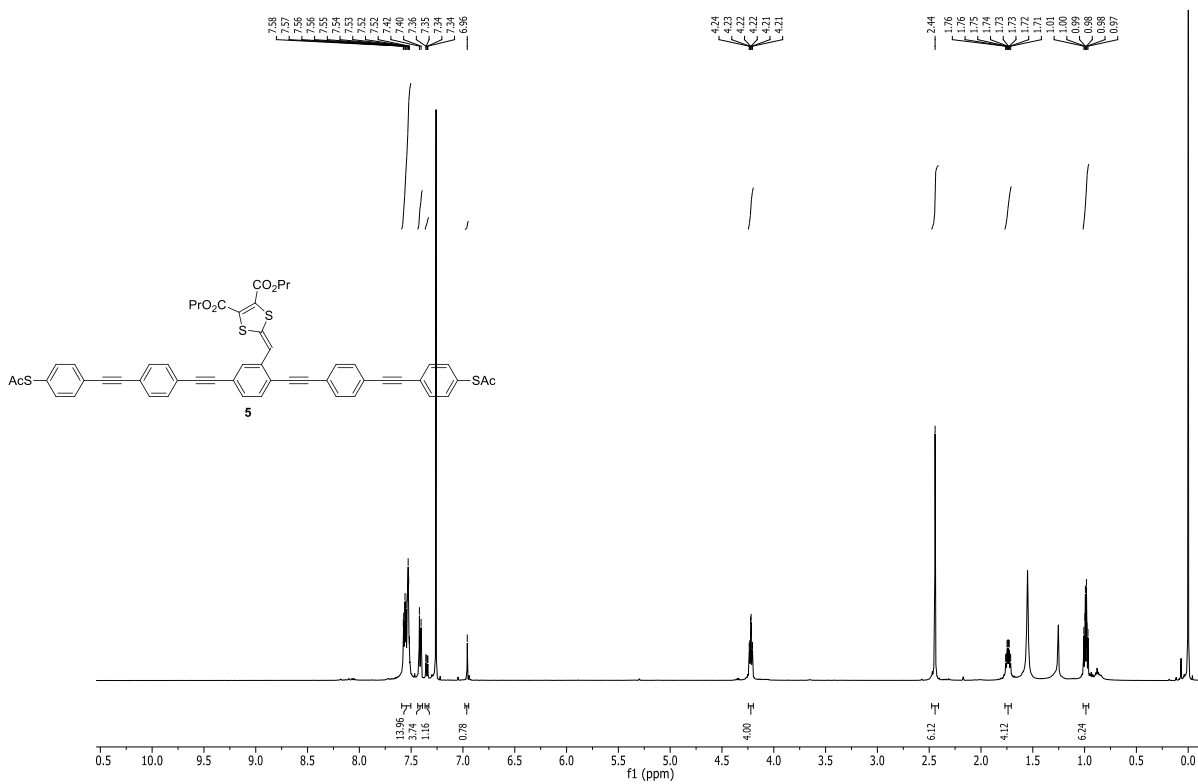
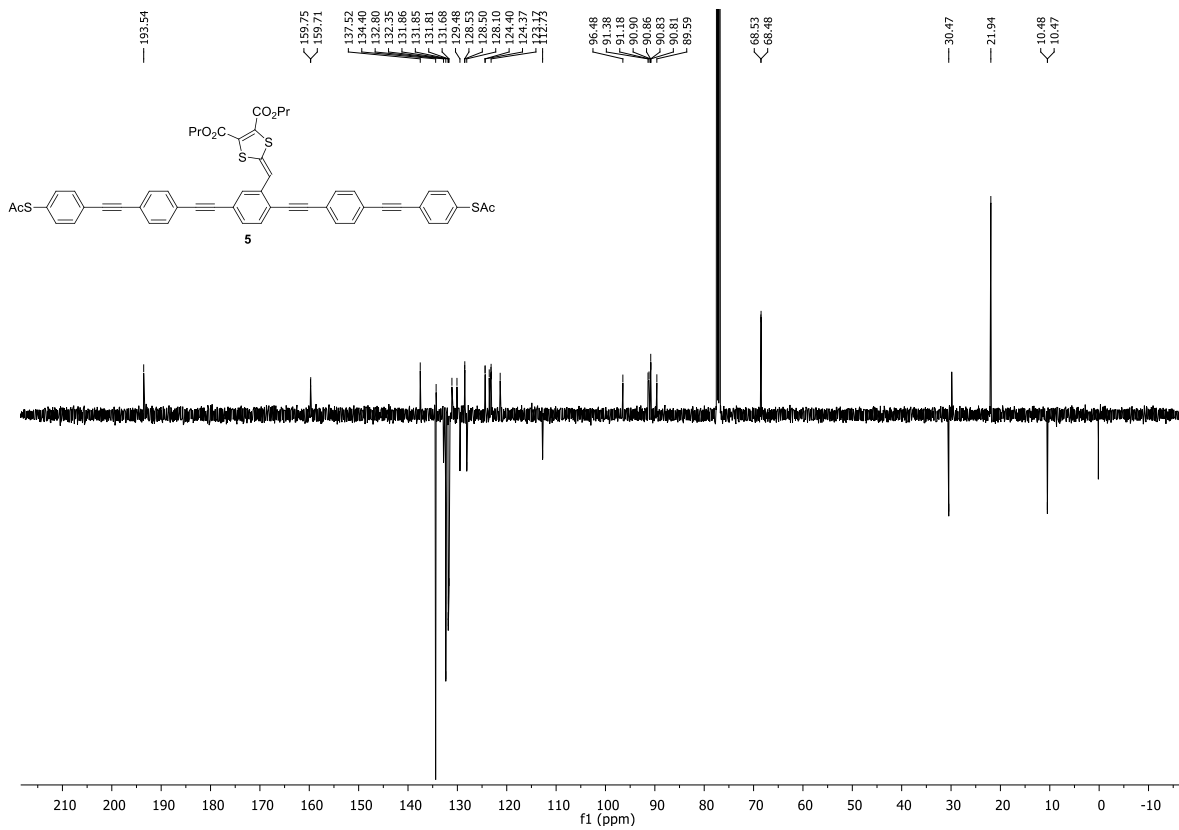
¹H-NMR of **3** in CDCl₃

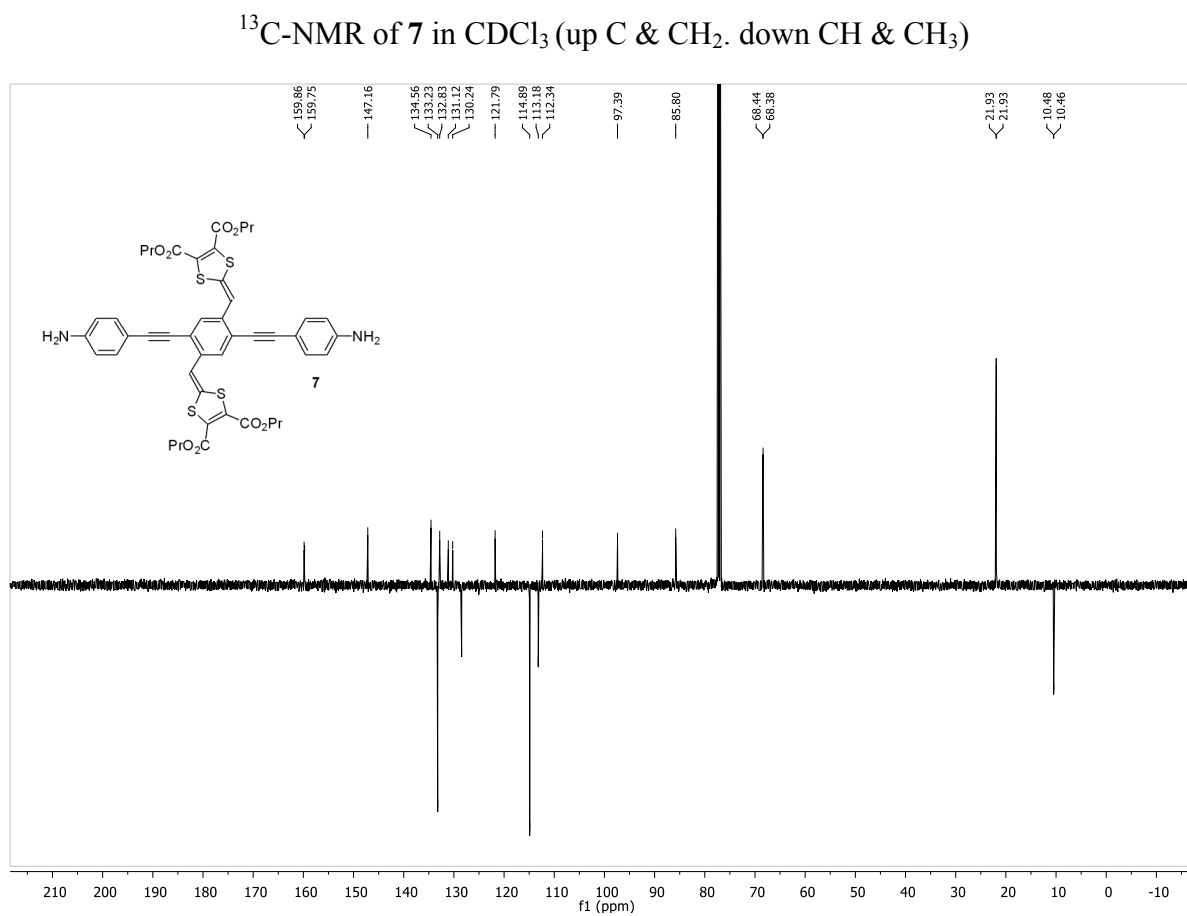
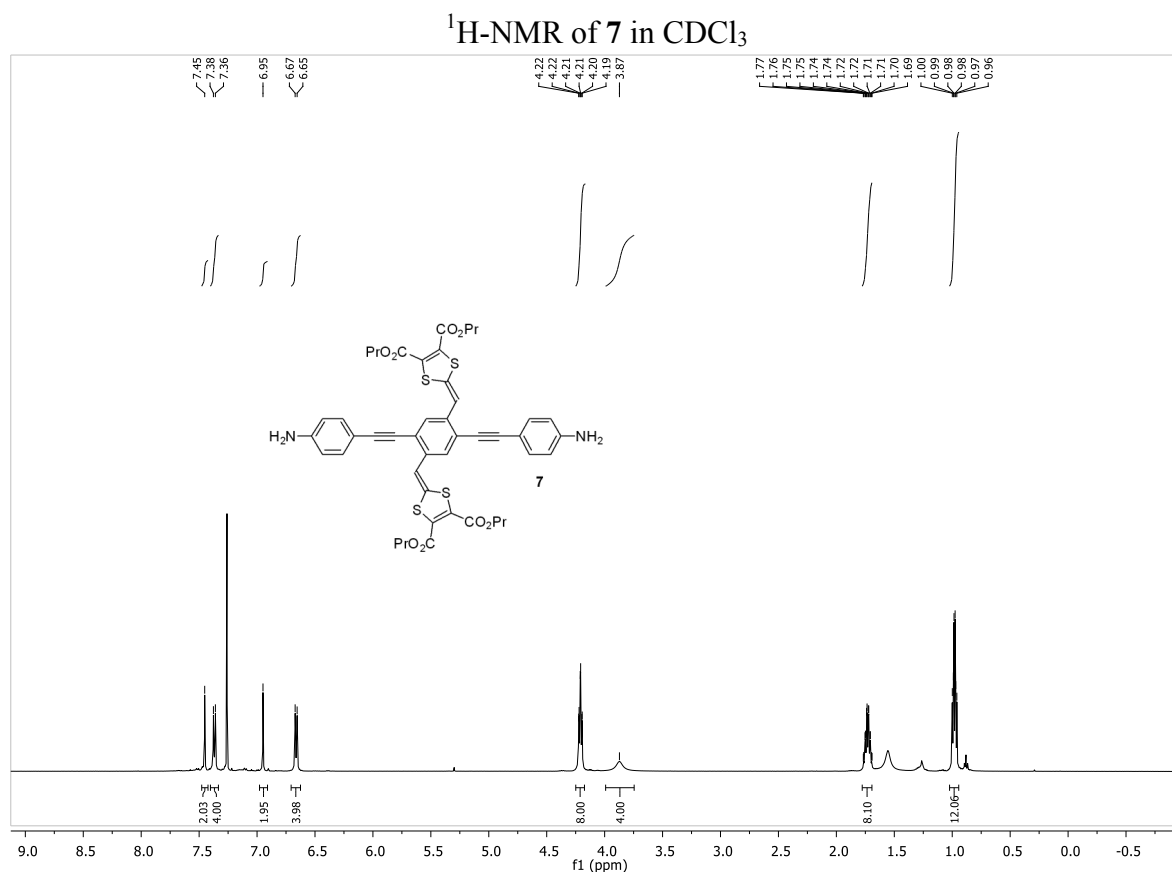


¹³C-NMR of **3** in CDCl₃ (up C & CH₂. down CH & CH₃)

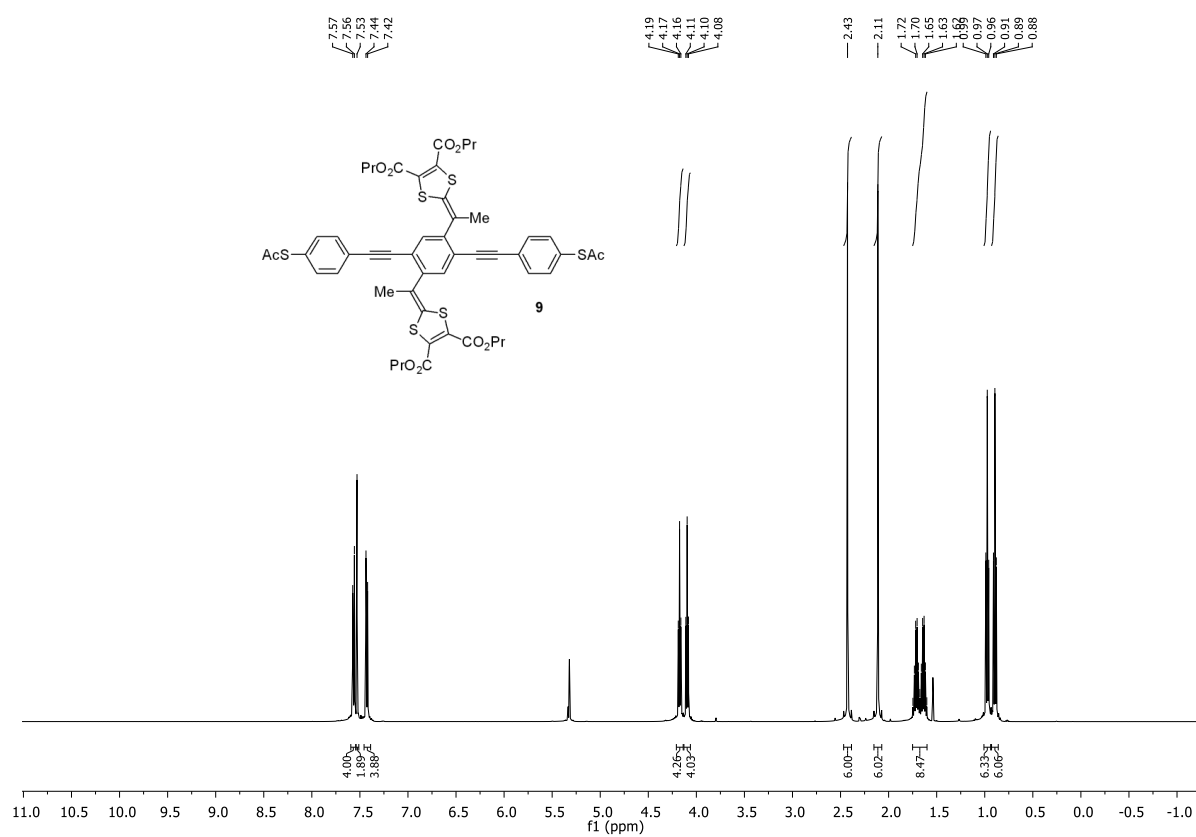




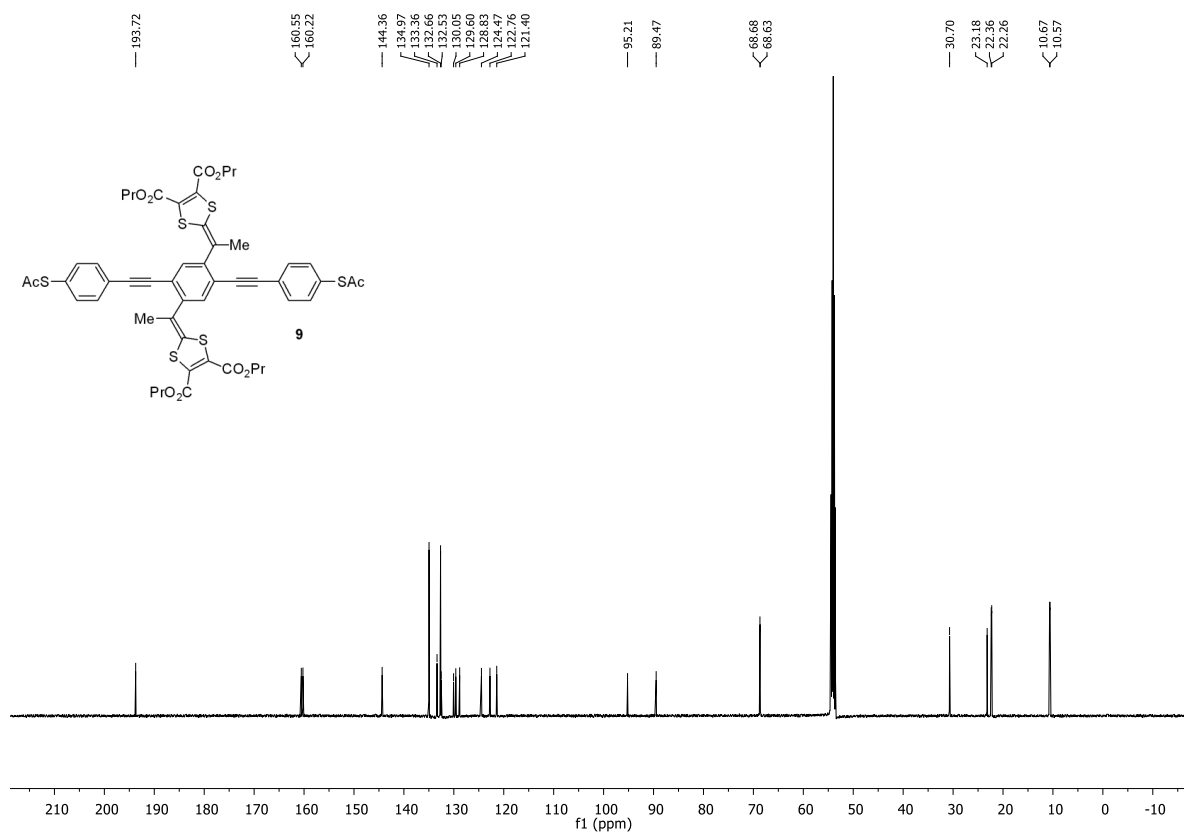
$^1\text{H-NMR}$ of **5** in CDCl_3  ^{13}C -NMR of **5** in CDCl_3 (up C & CH_2 . down CH & CH_3)

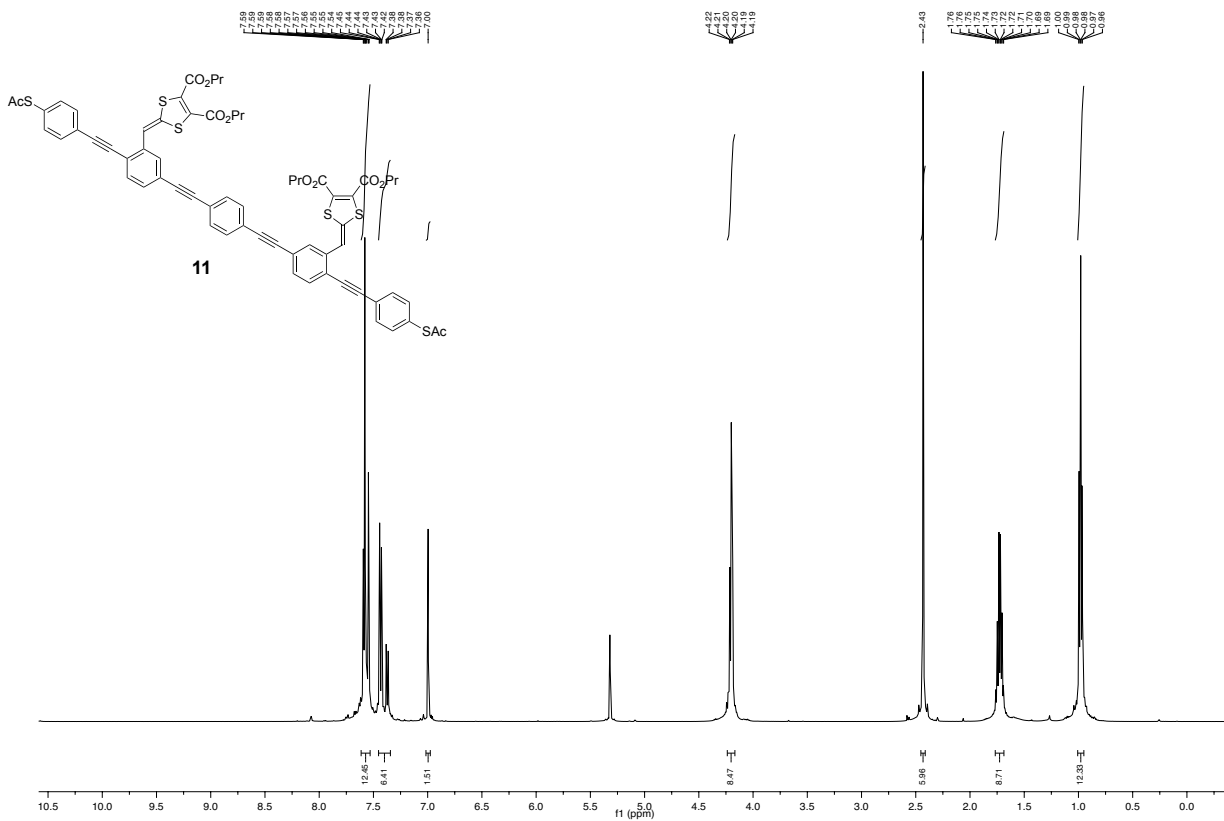
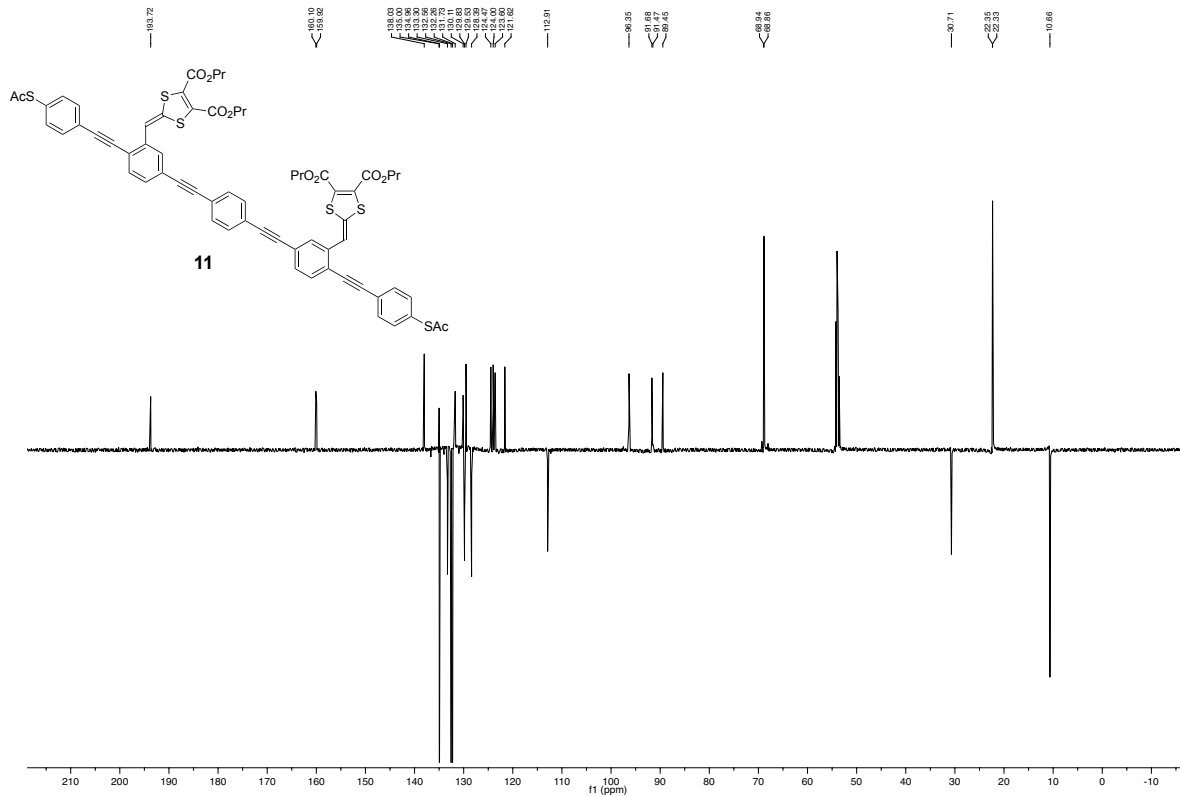


¹H-NMR of **9** in CD₂Cl₂

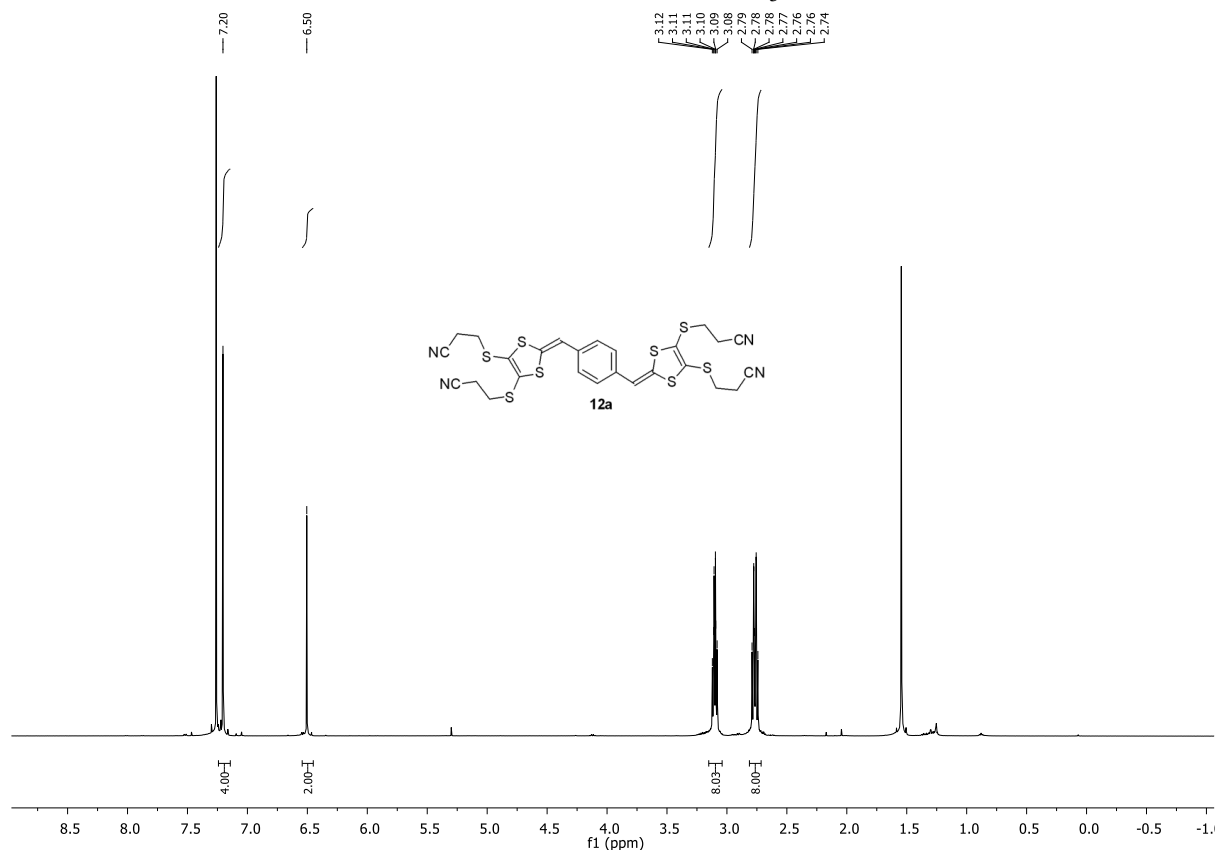


¹³C-NMR of **9** in CD₂Cl₂

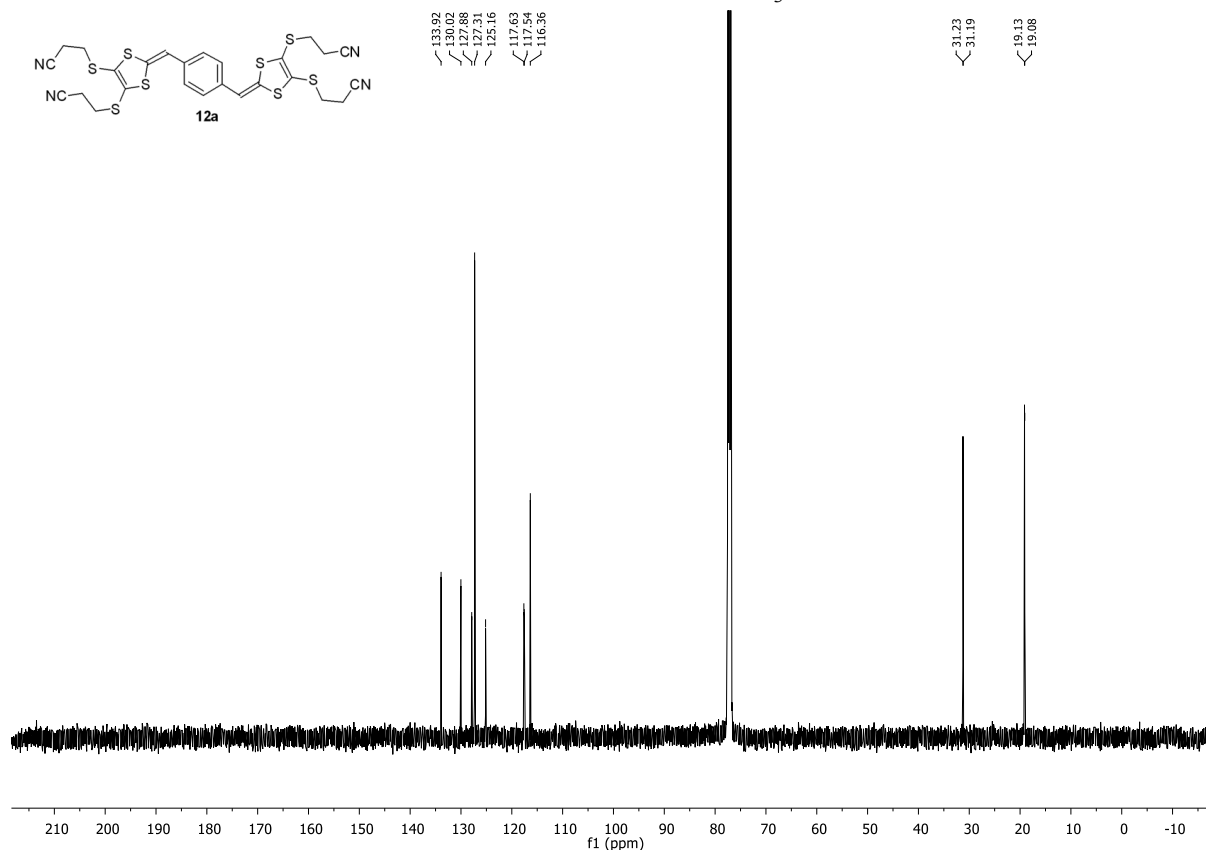


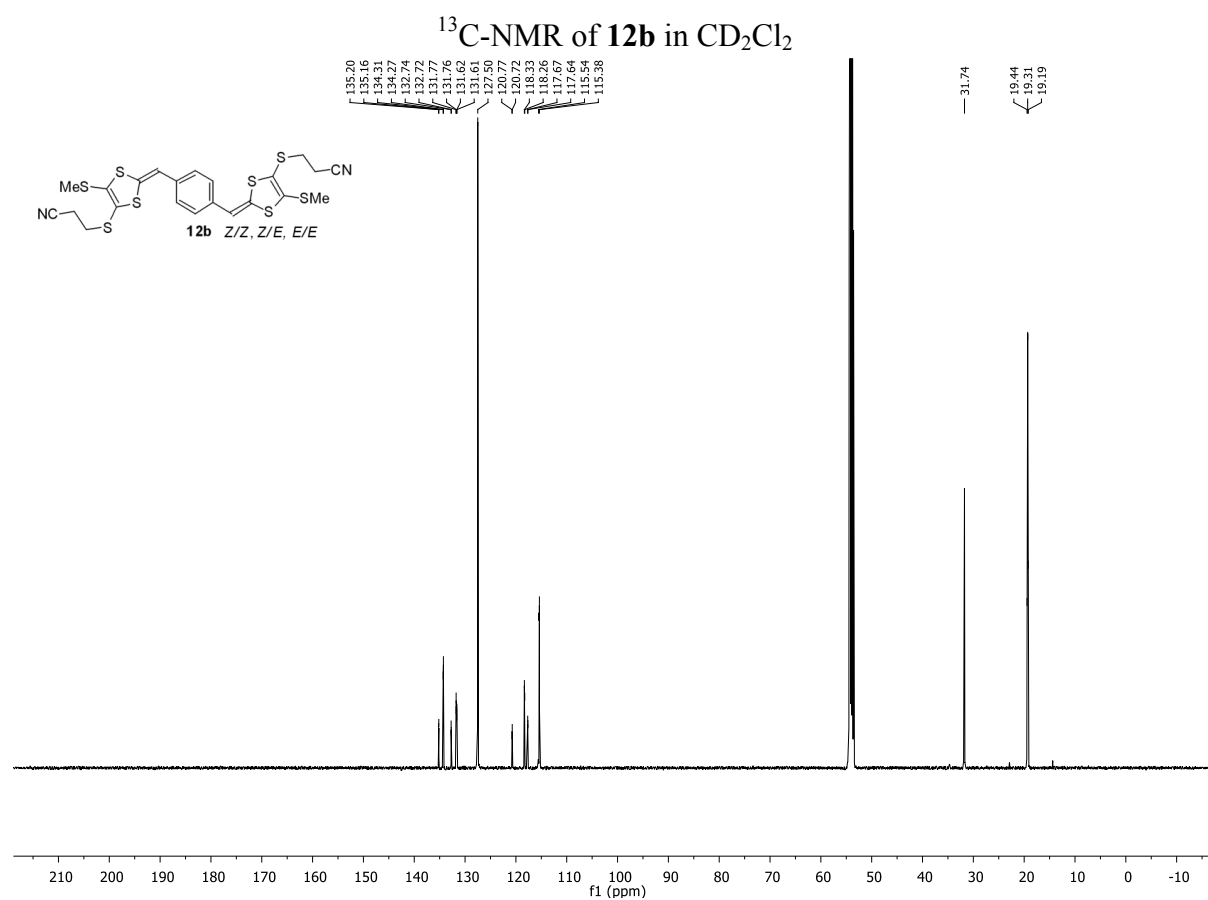
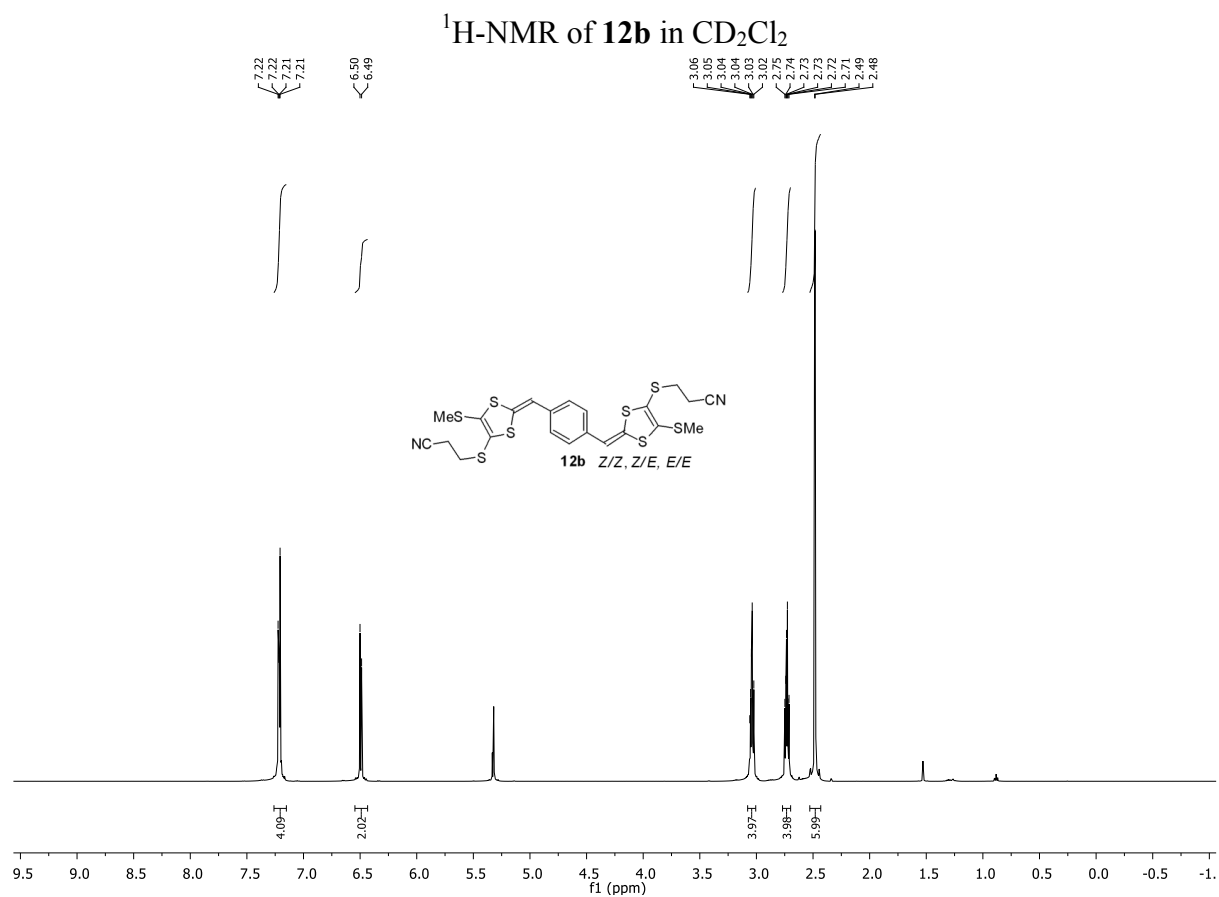
¹H-NMR of **11** in CD₂Cl₂¹³C-NMR of **11** in CD₂Cl₂ (up C & CH₂. down CH & CH₃)

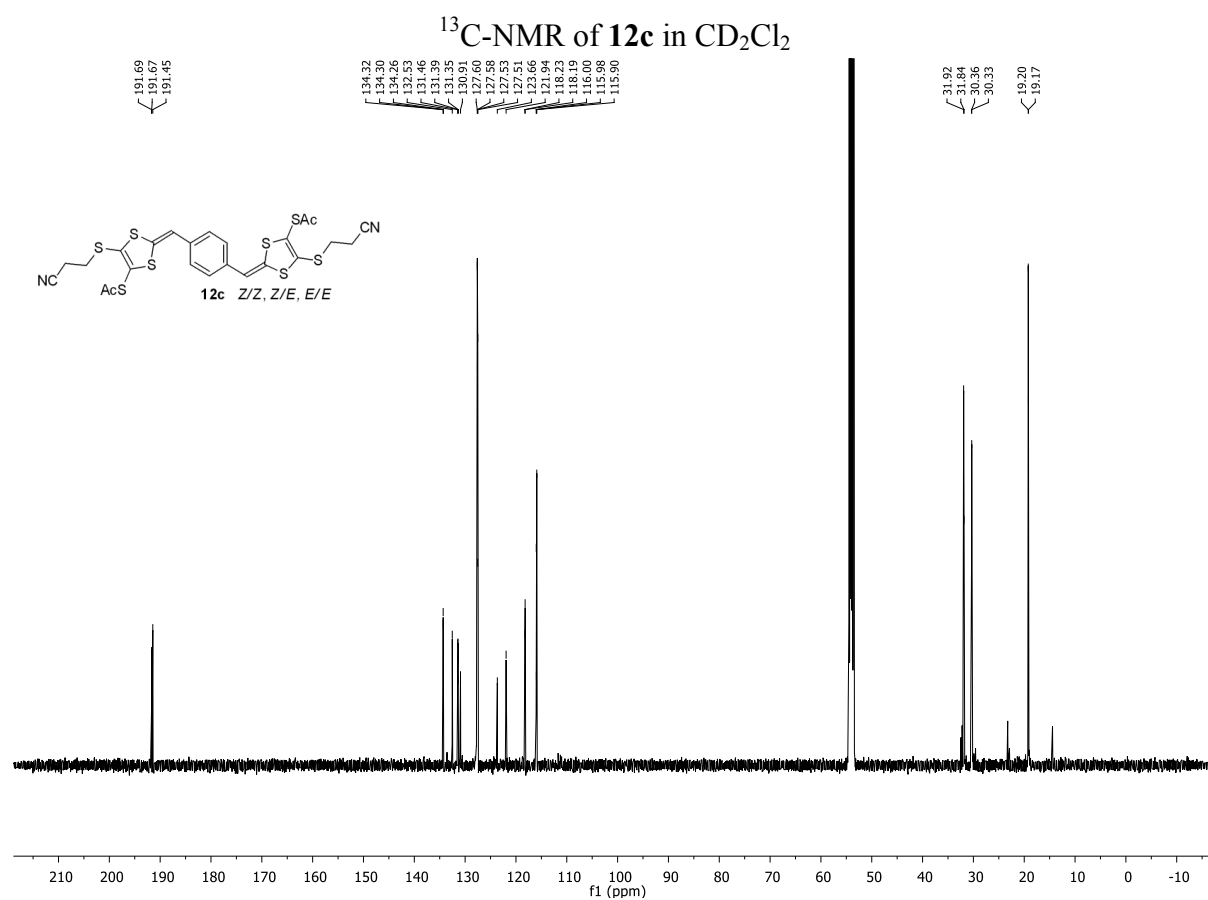
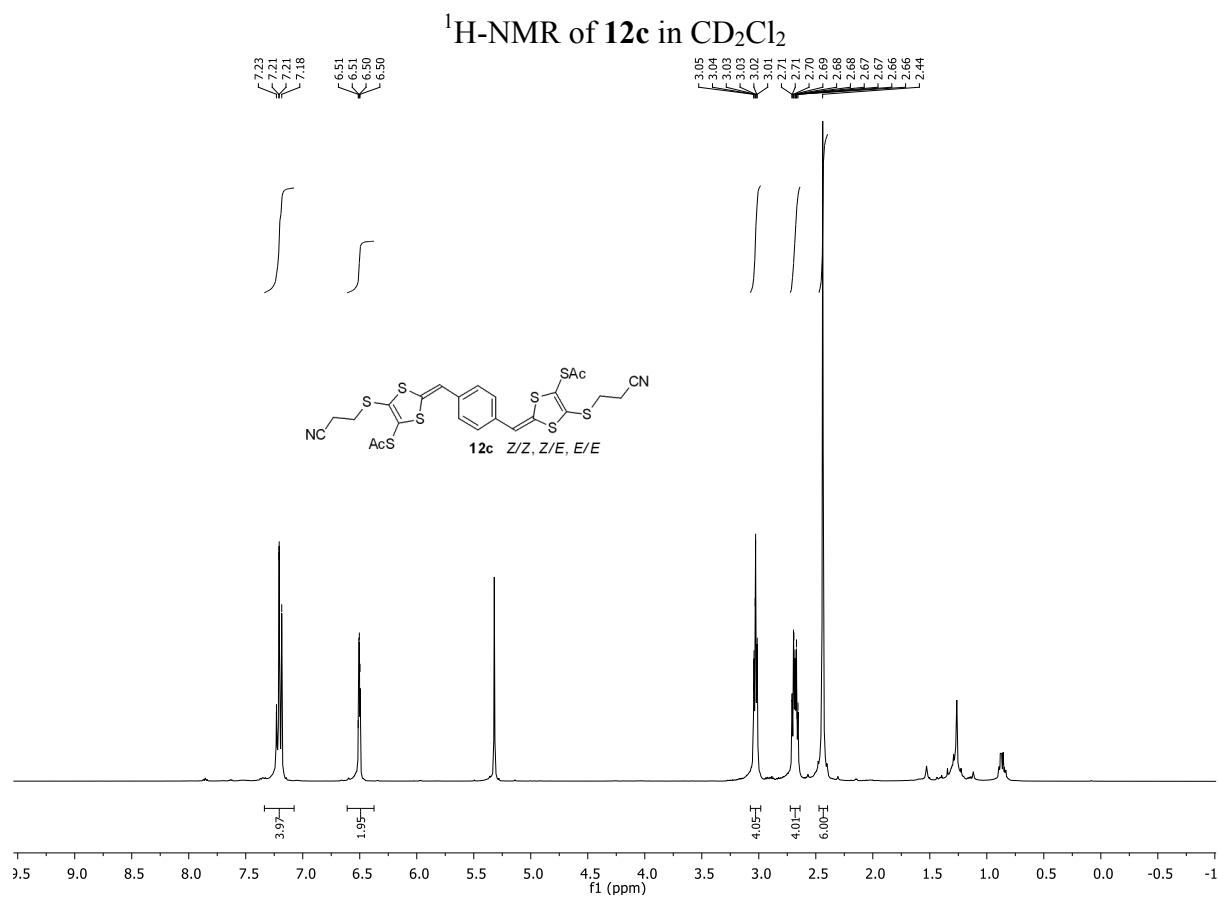
¹H-NMR of **12a** in CDCl₃

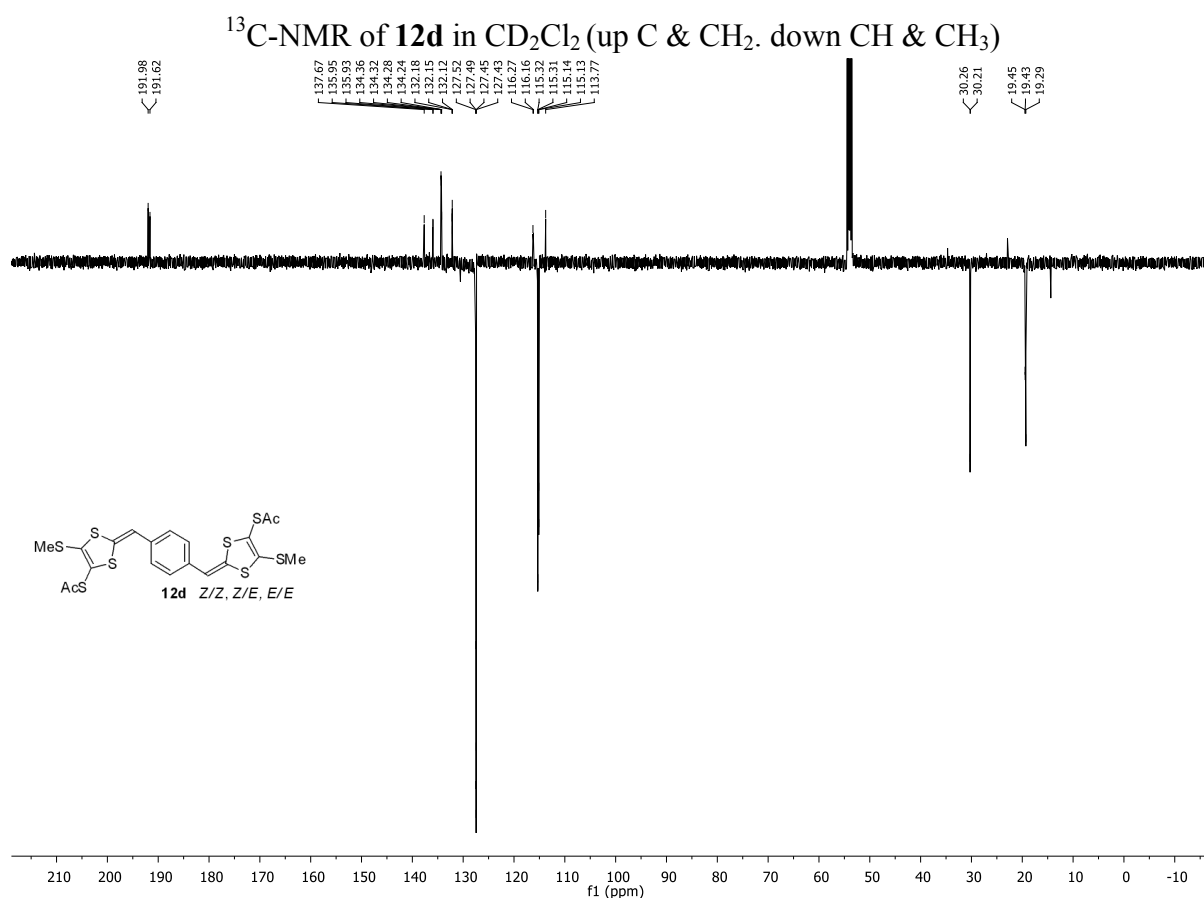
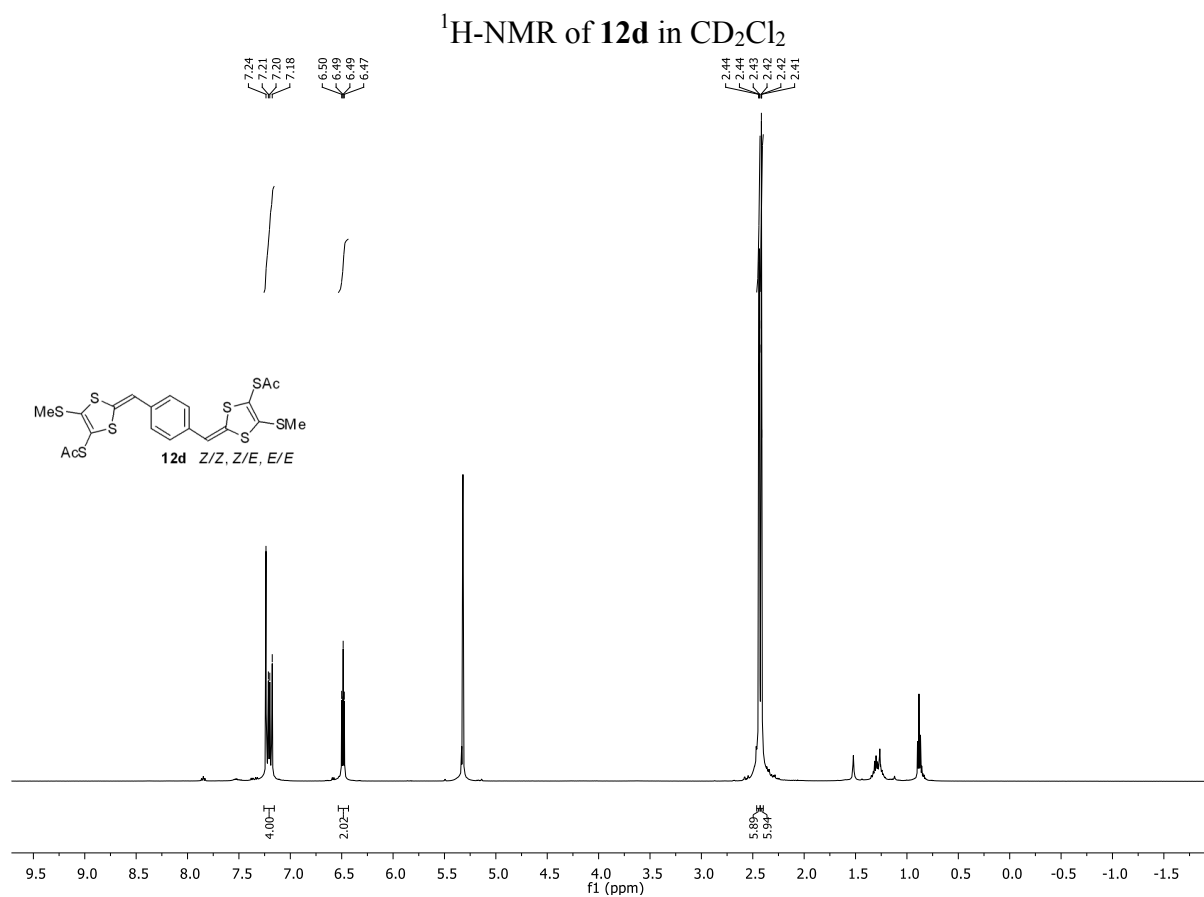


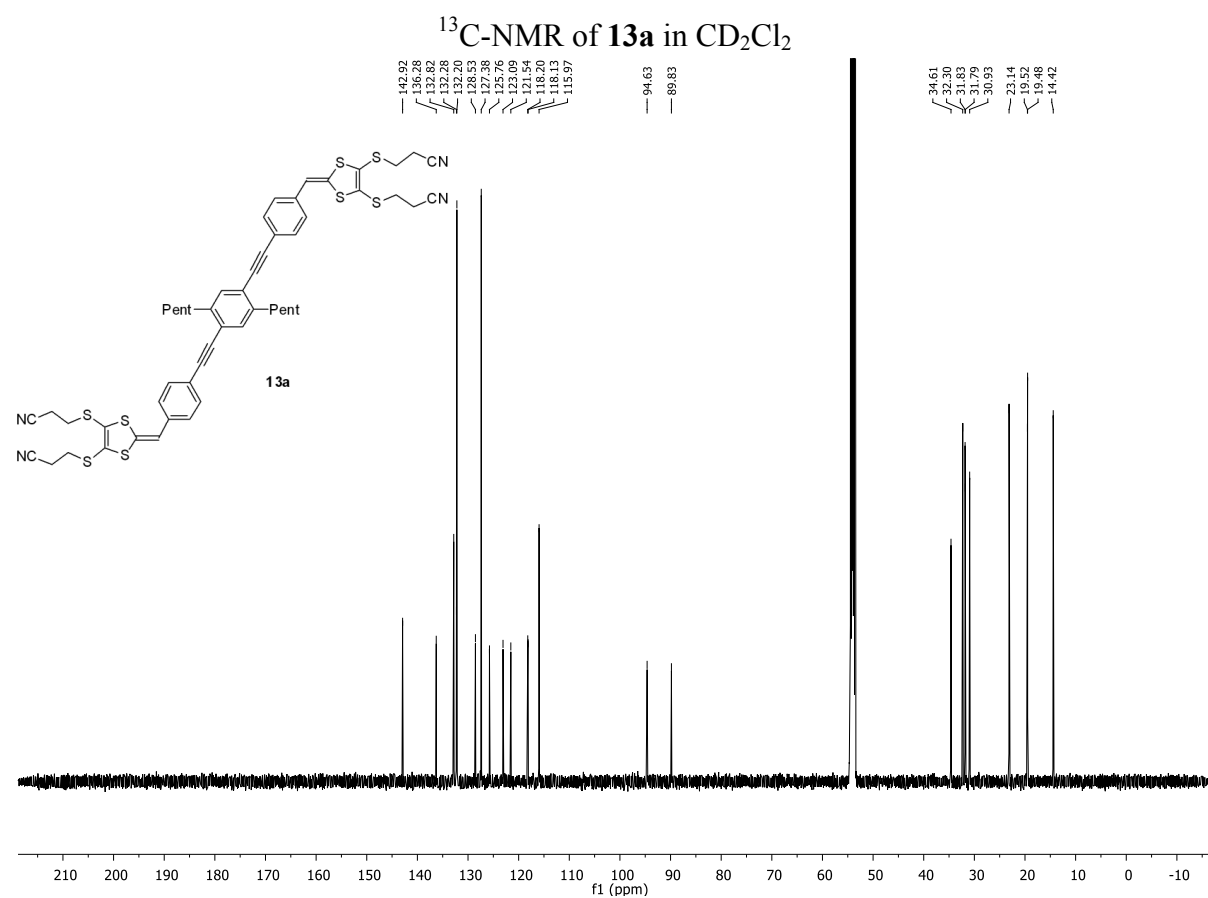
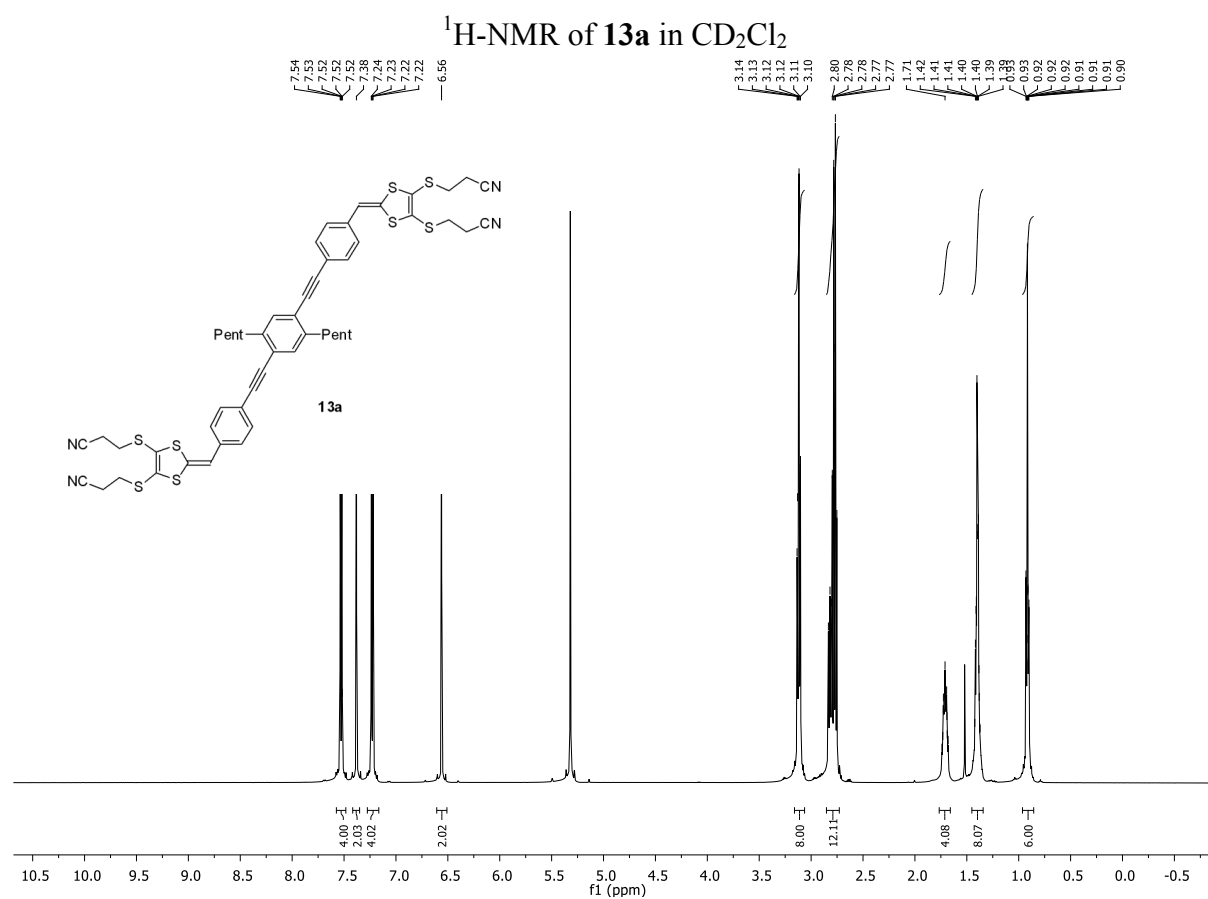
¹³C-NMR of **12a** in CDCl₃

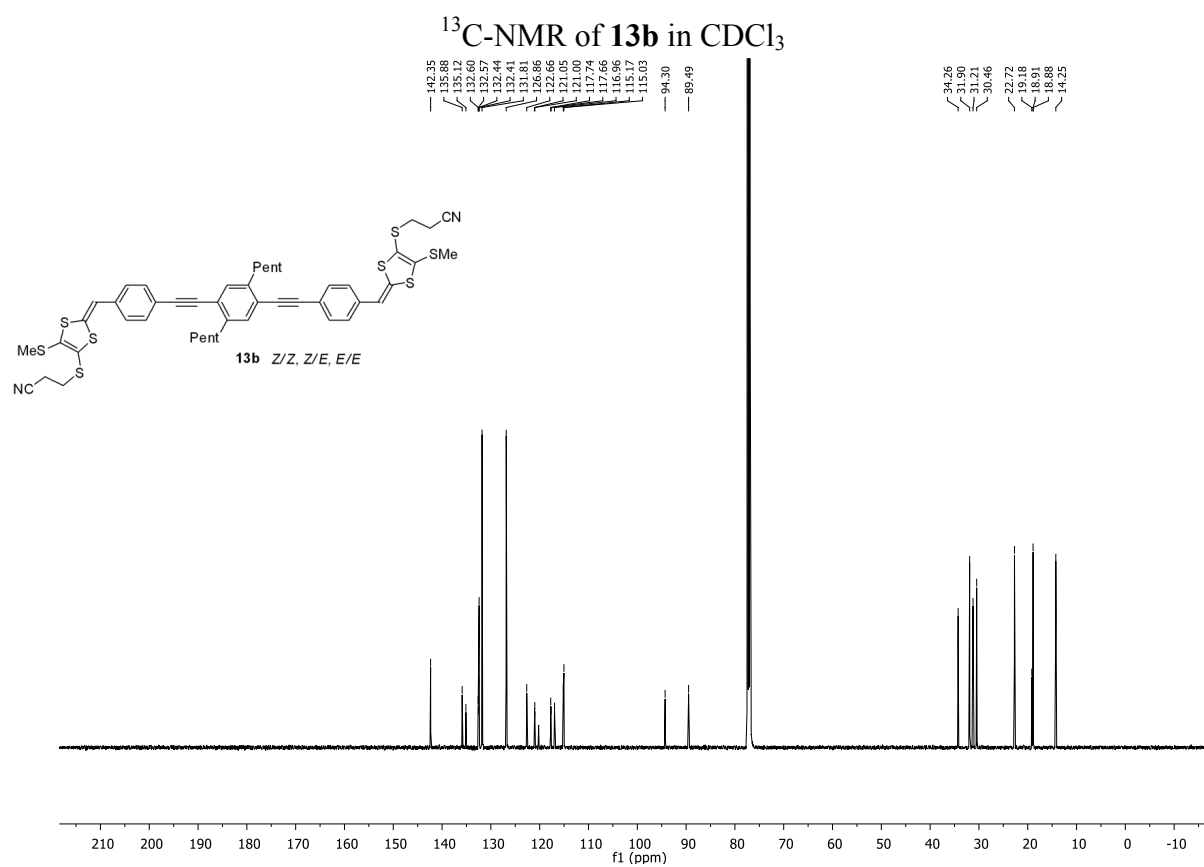
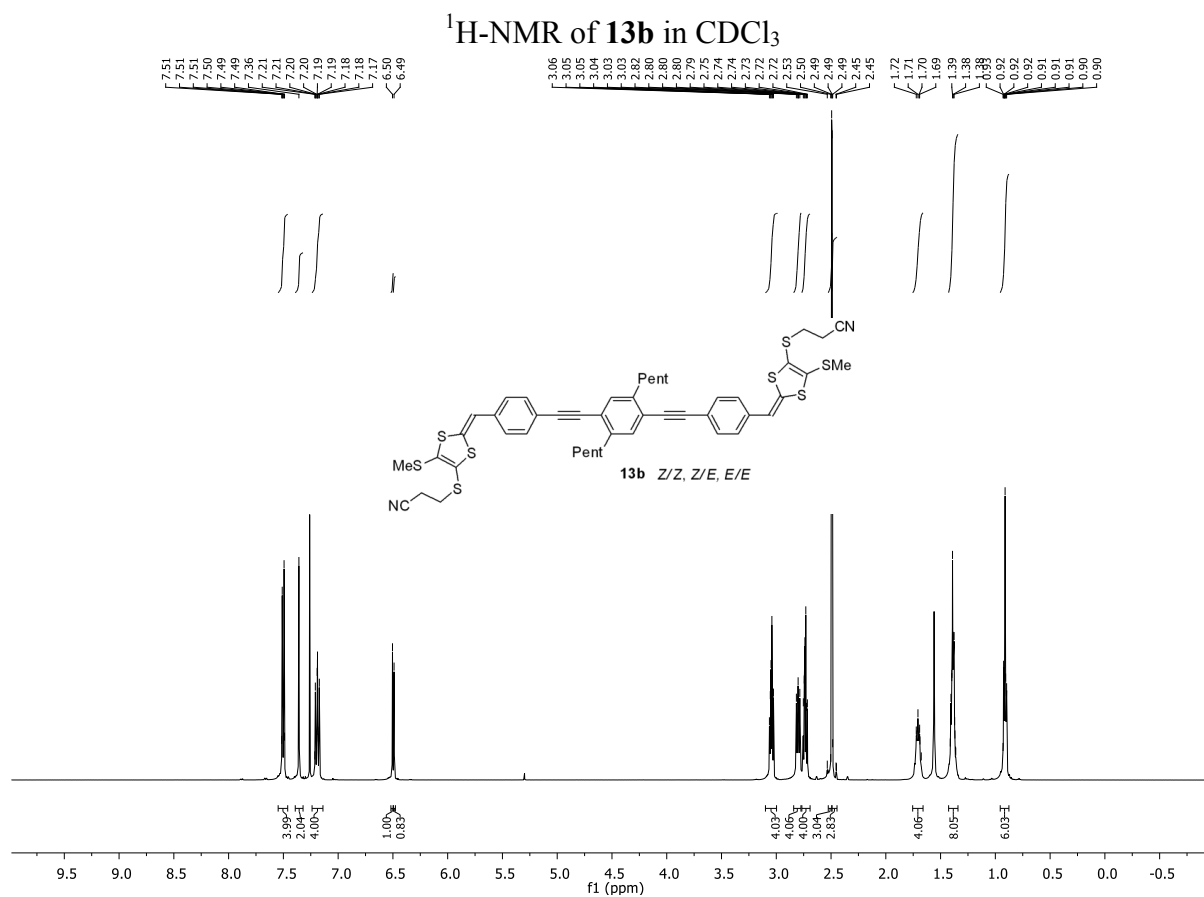


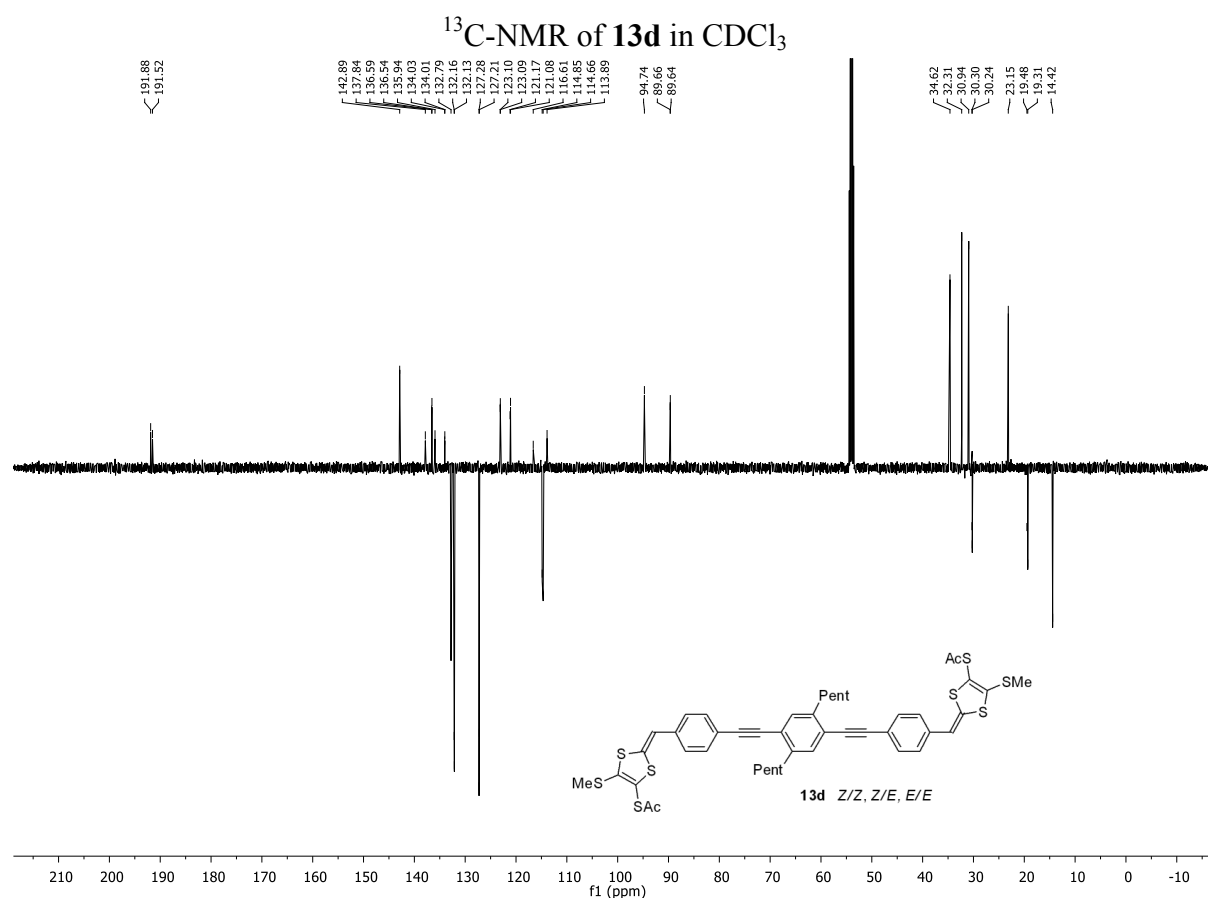
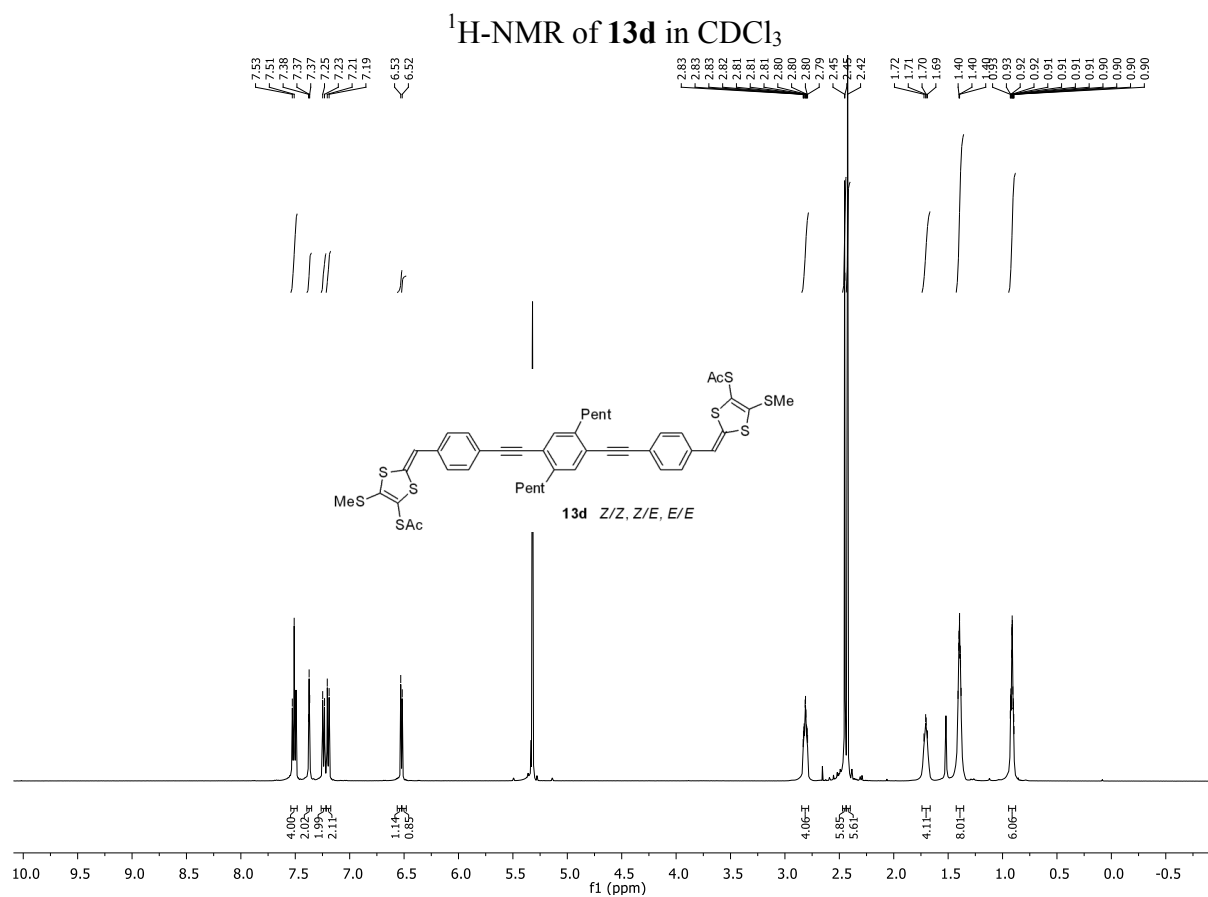




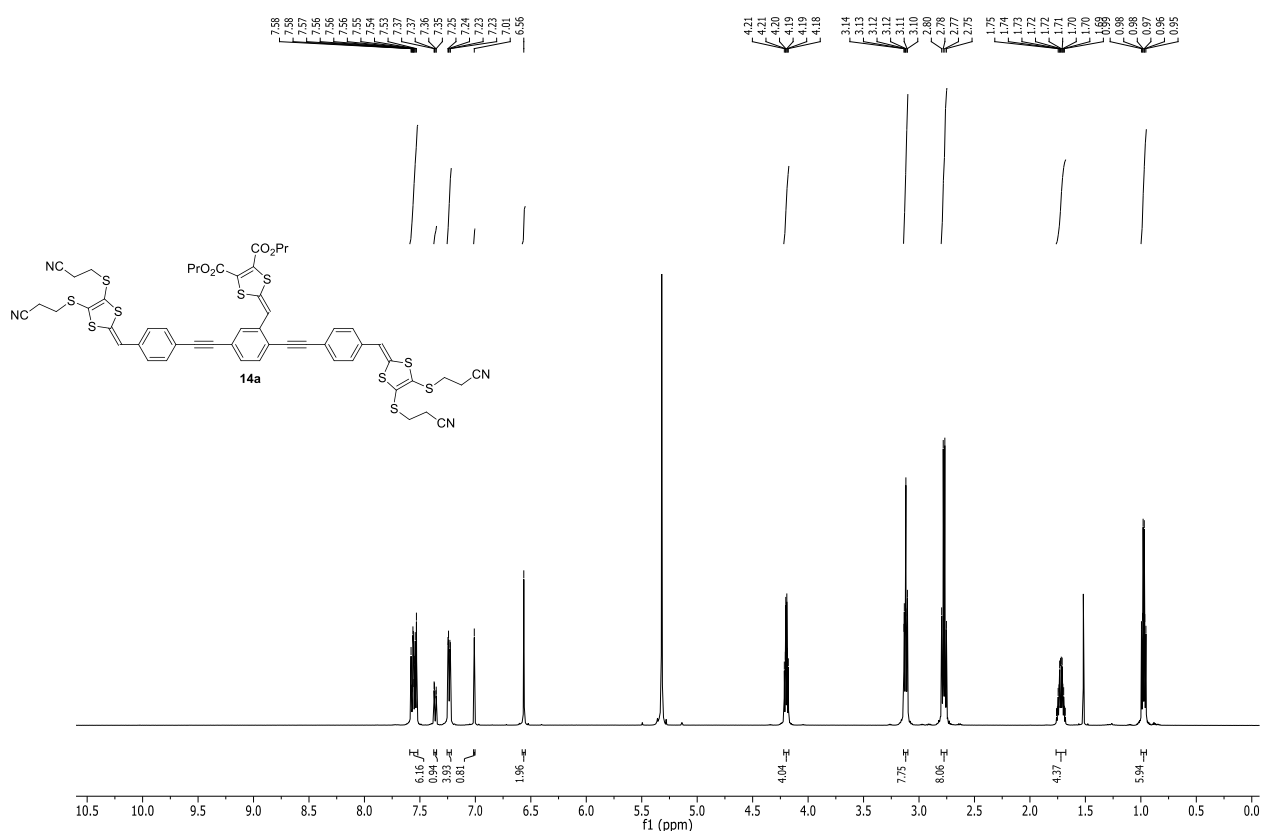




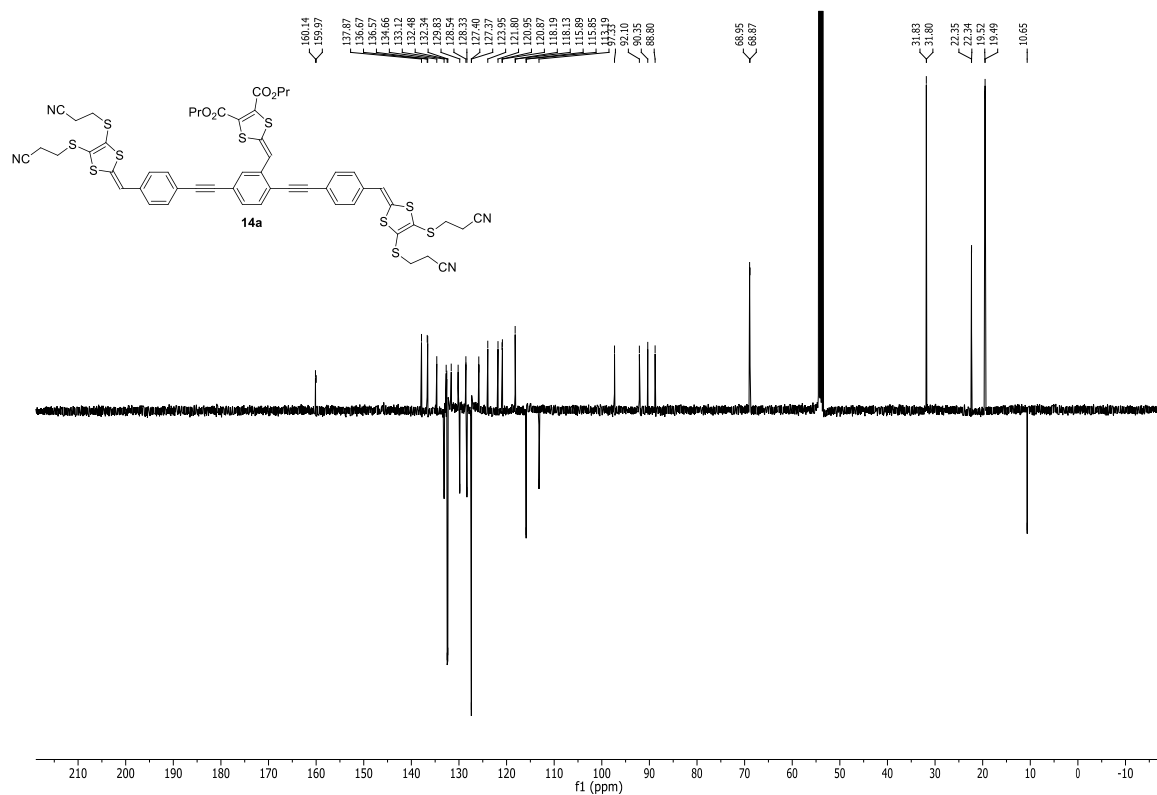


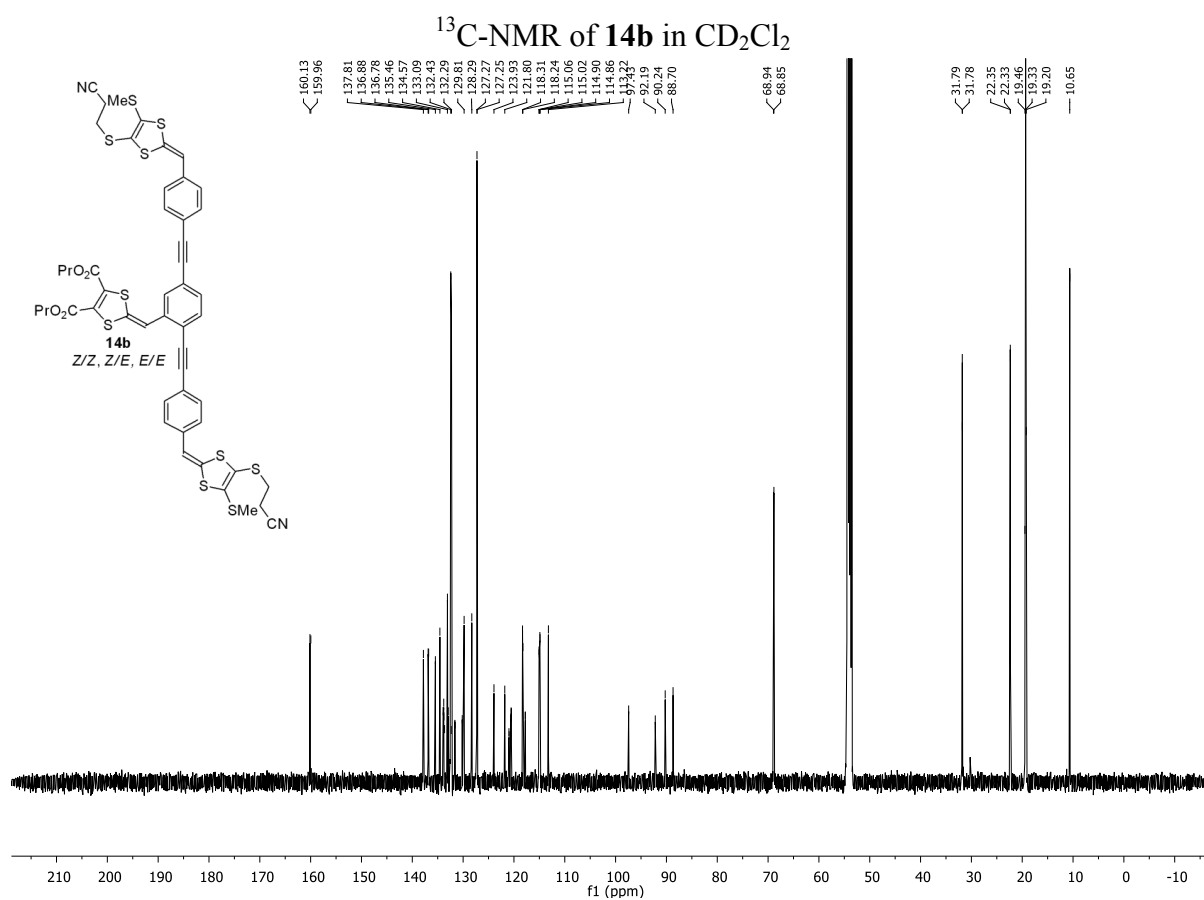
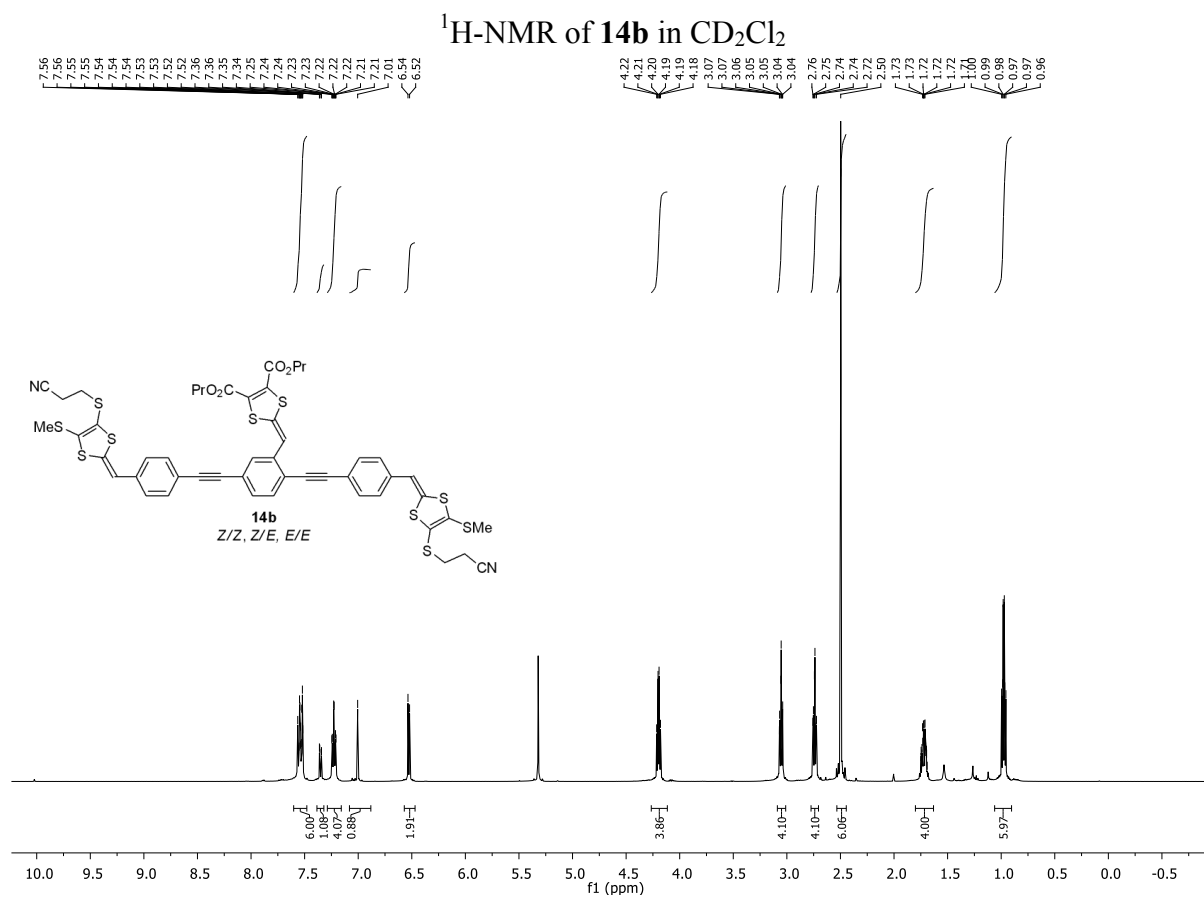


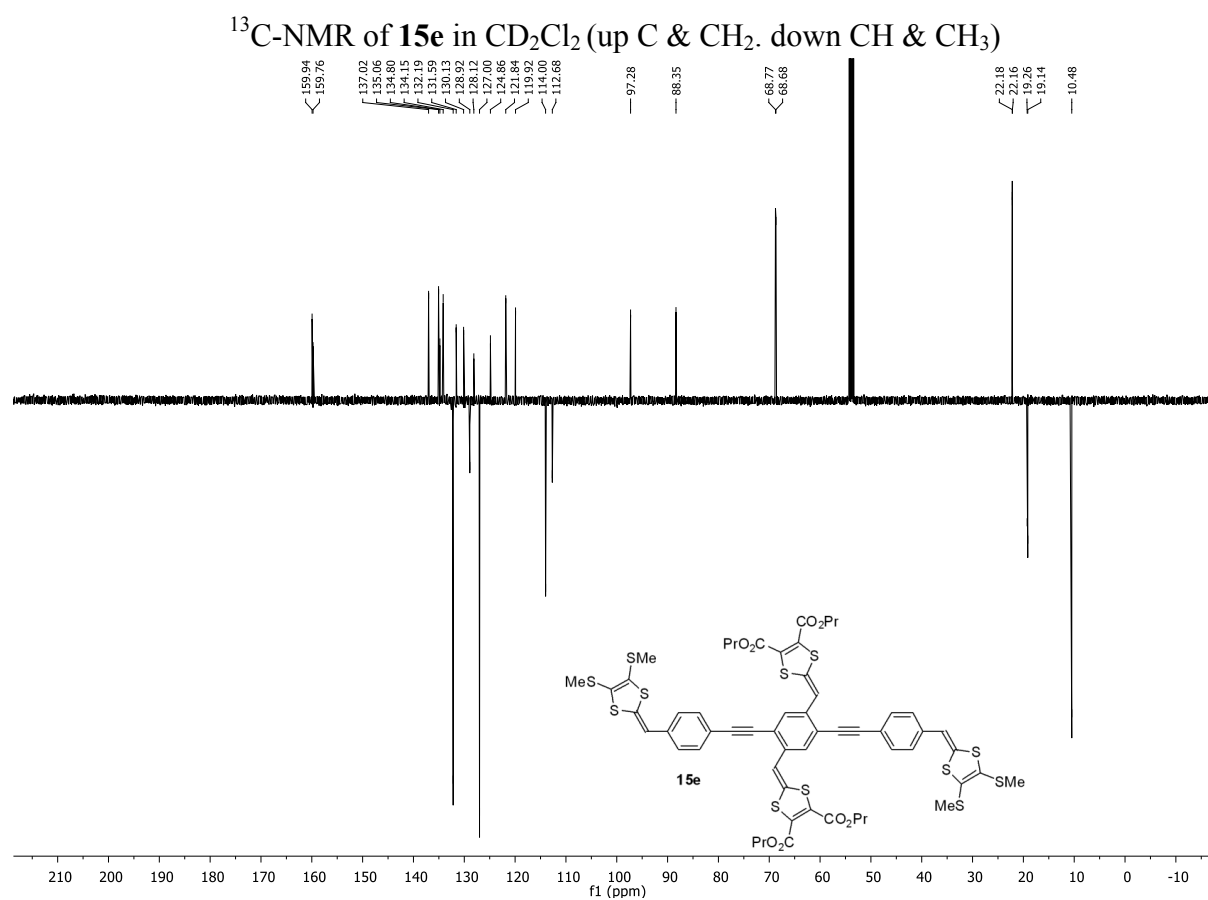
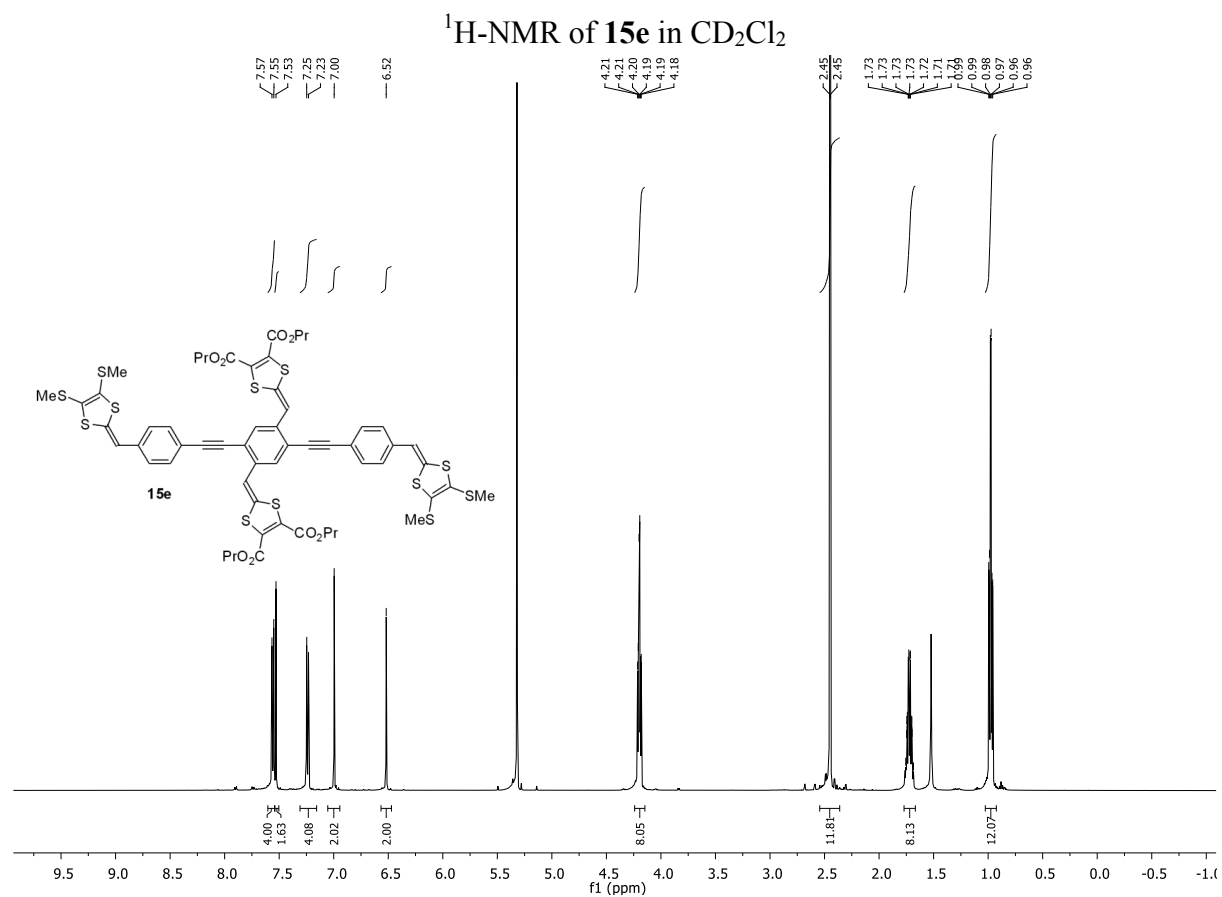
$^1\text{H-NMR}$ of **14a** in CD_2Cl_2



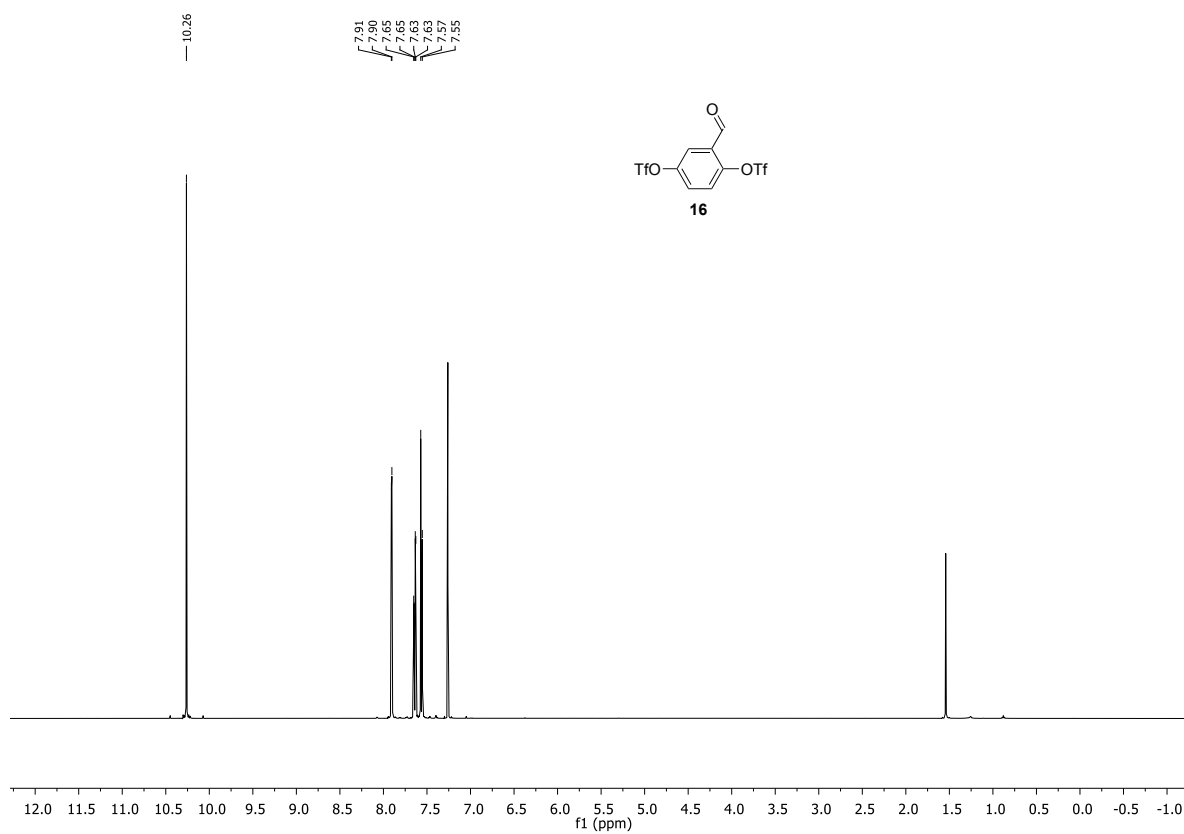
$^{13}\text{C-NMR}$ of **14a** in CD_2Cl_2 (up C & CH_2 . down CH & CH_3)



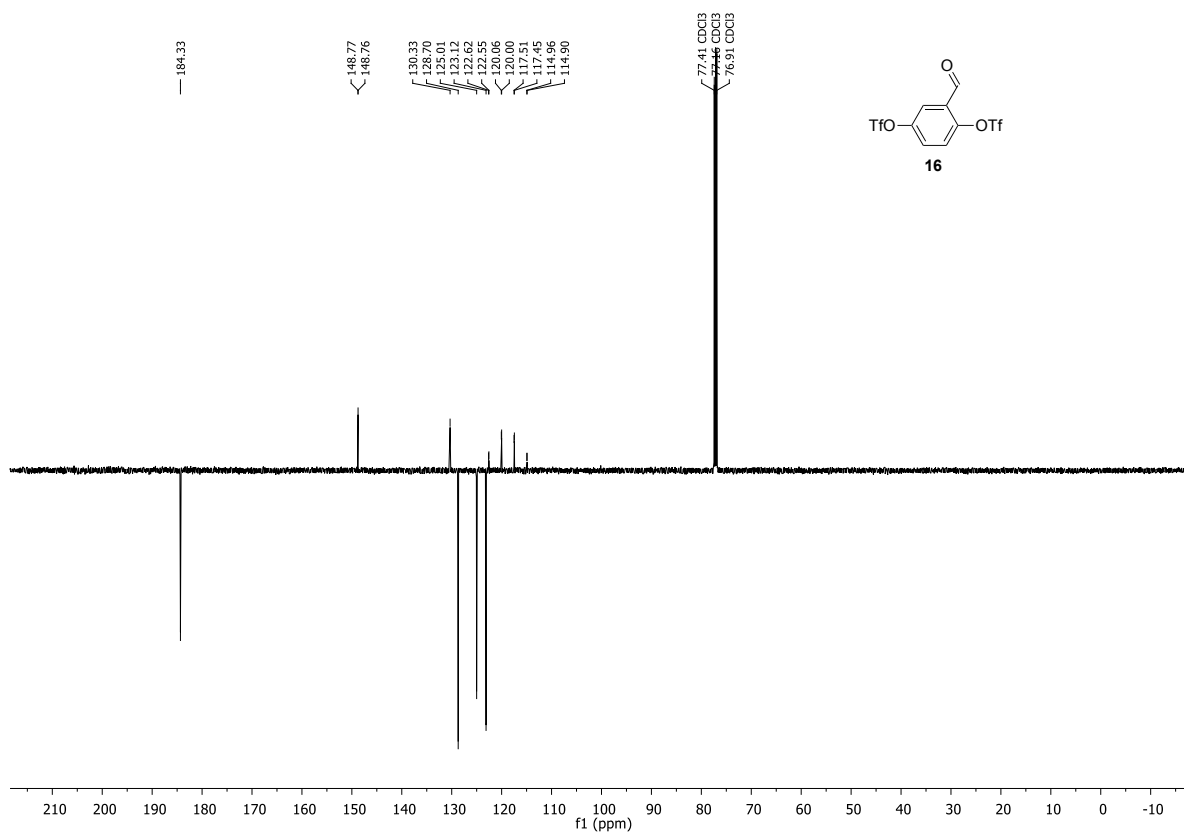




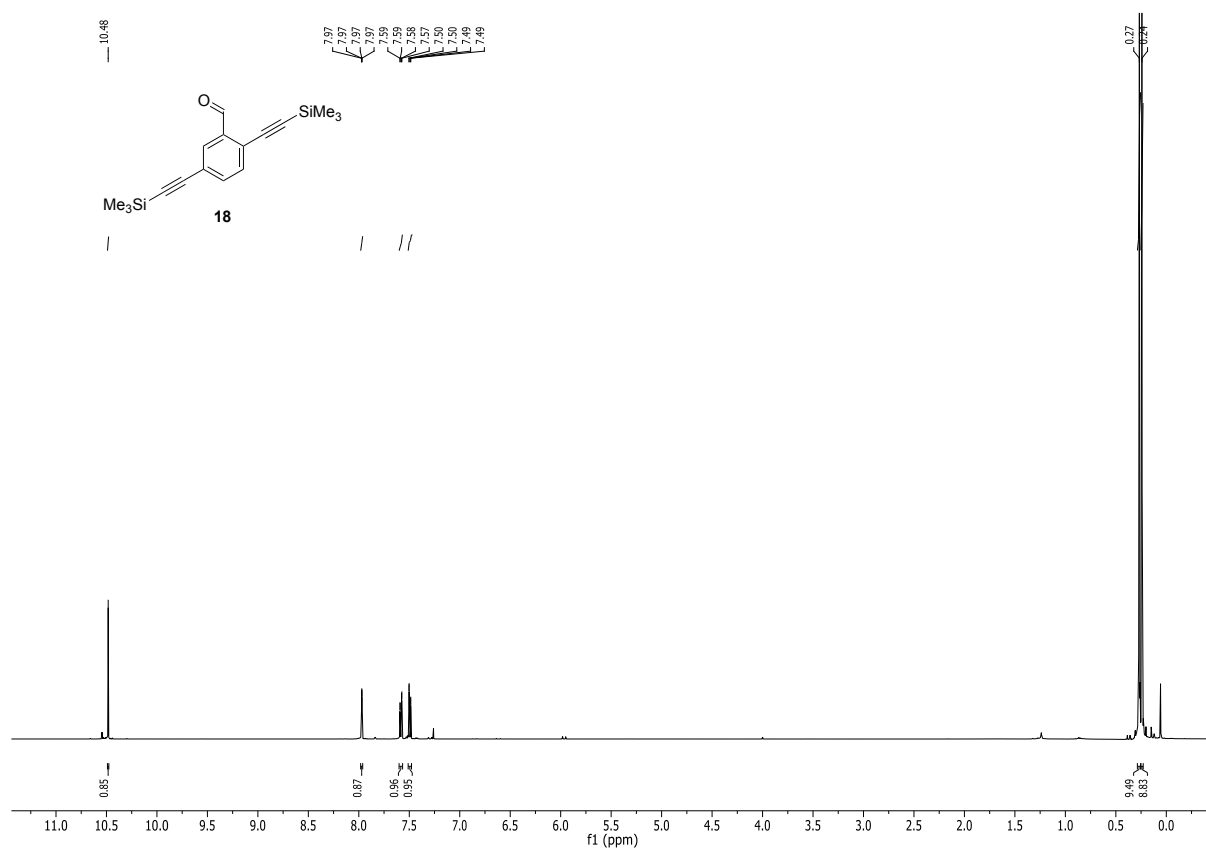
¹H-NMR of **16** in CDCl₃



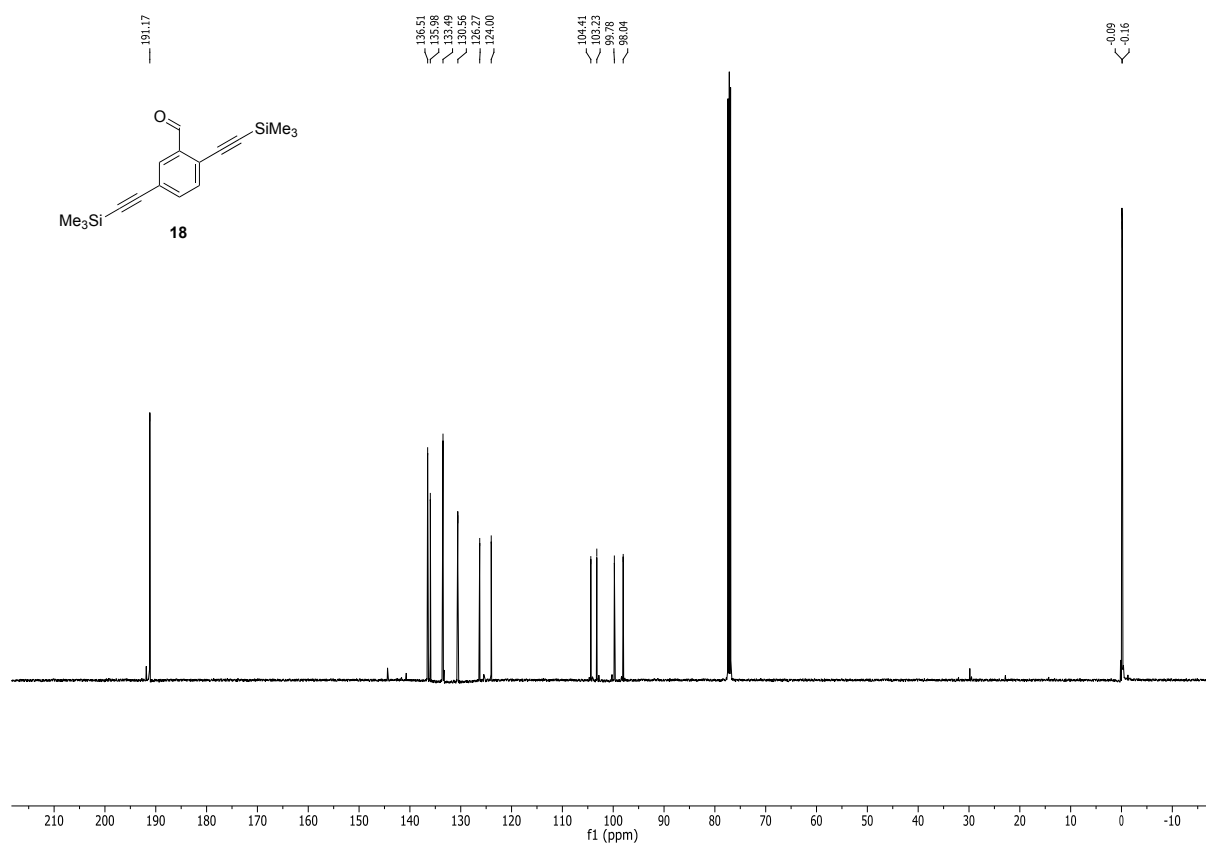
¹³C-NMR of **16** in CDCl₃ (up C & CH₂. down CH & CH₃)



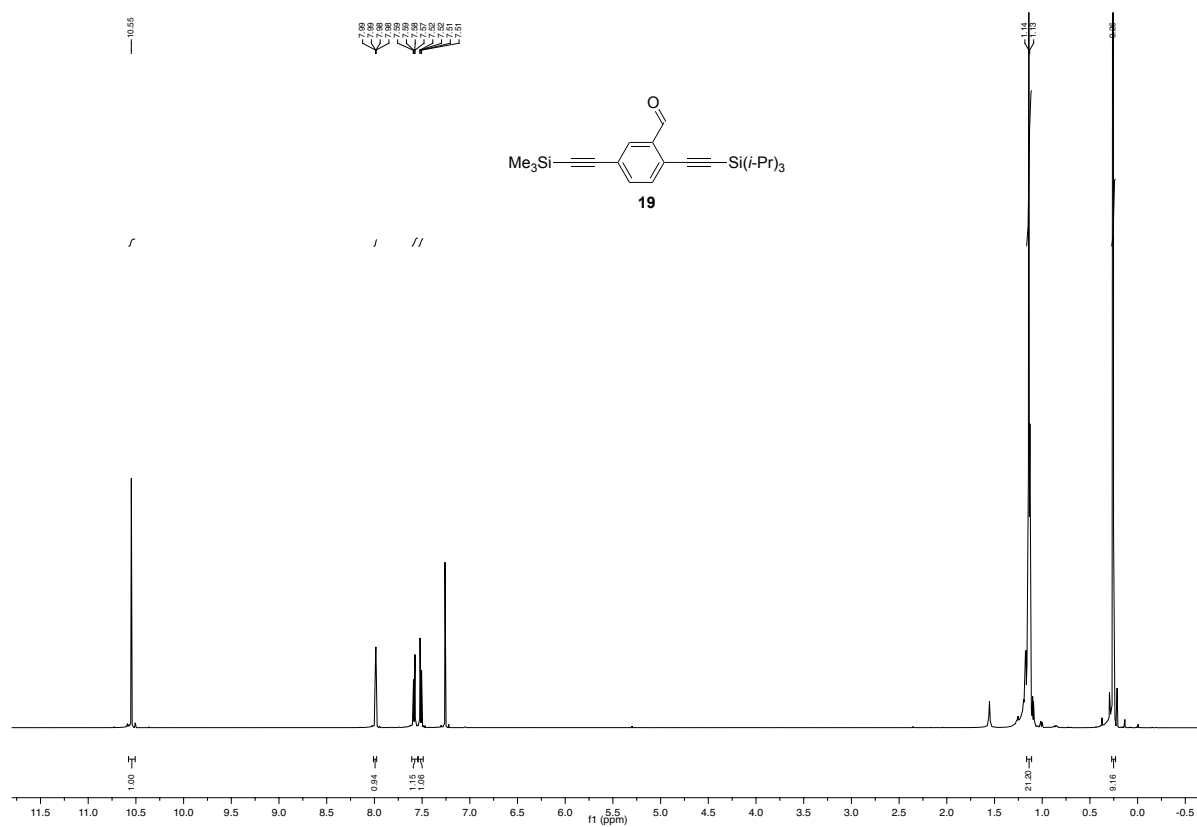
¹H-NMR of **18** in CDCl₃



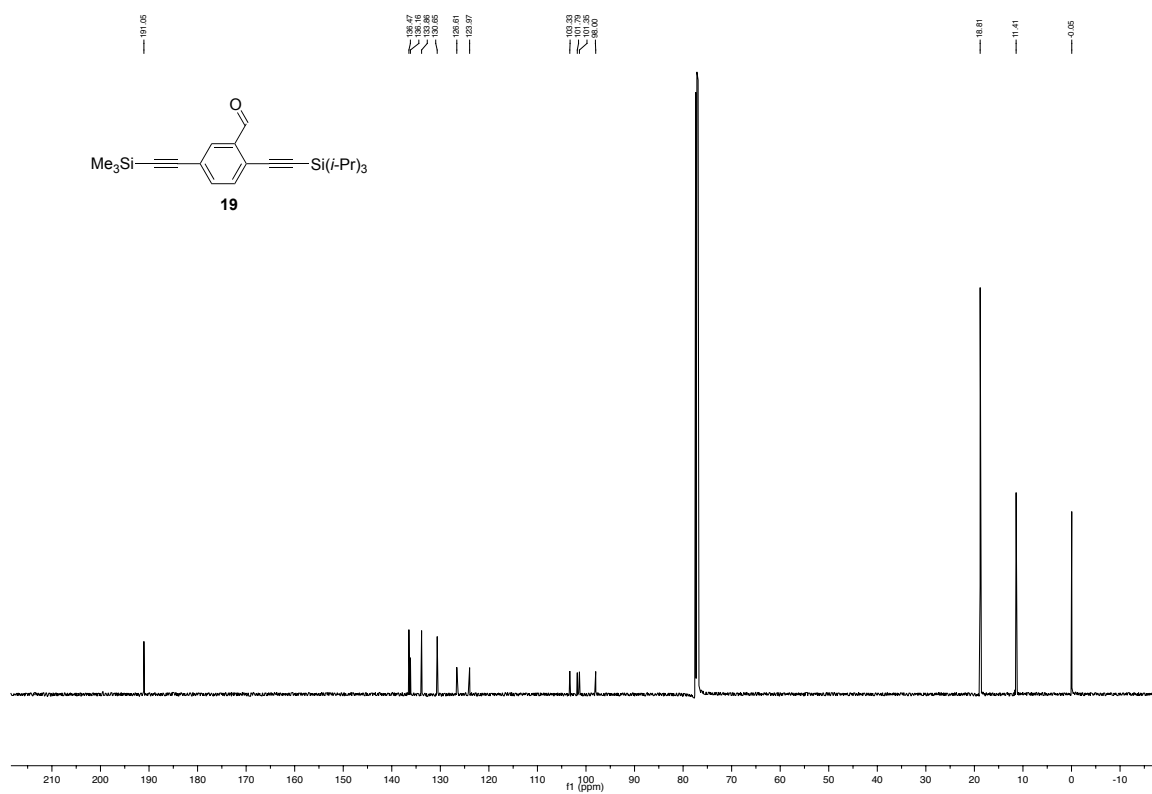
¹³C-NMR of **18** in CDCl₃

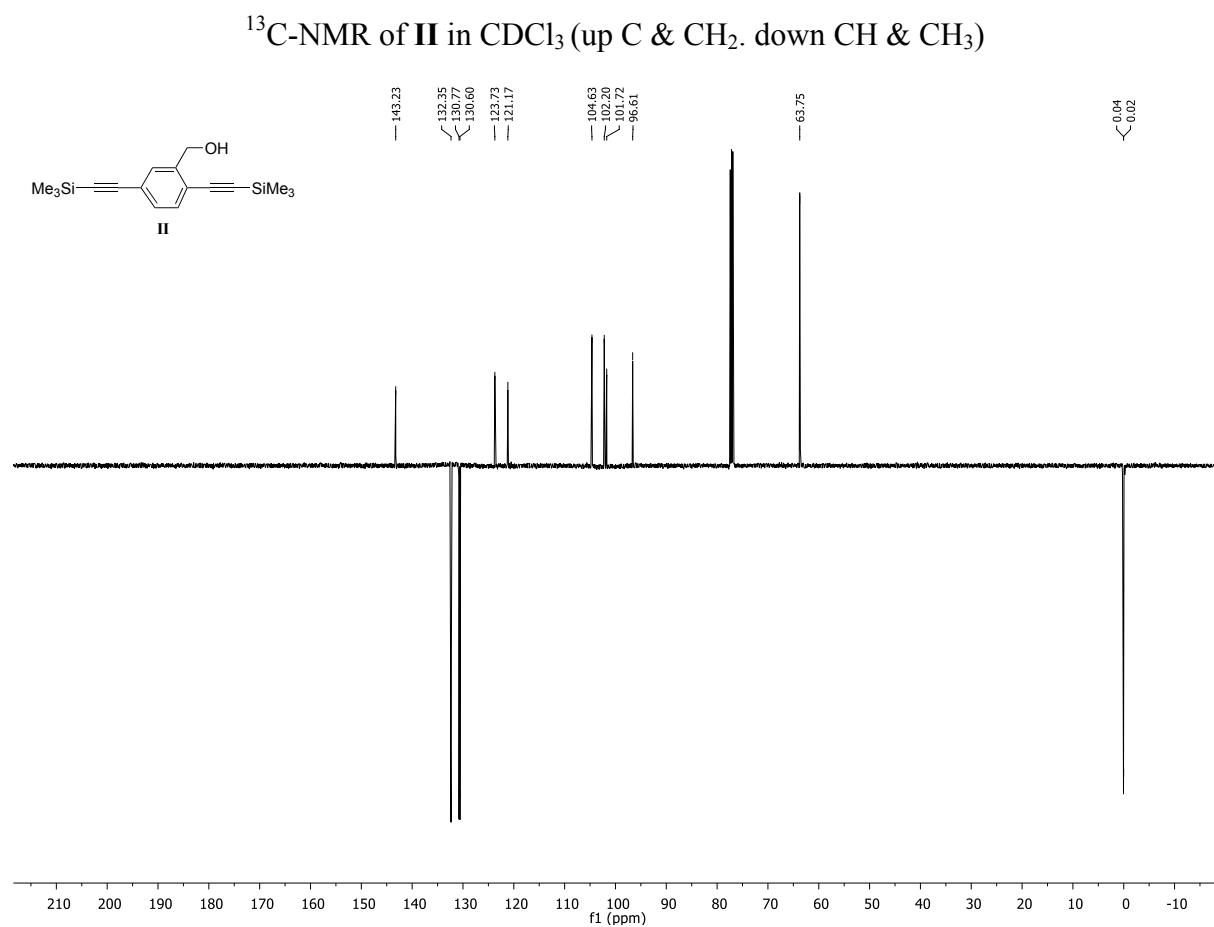
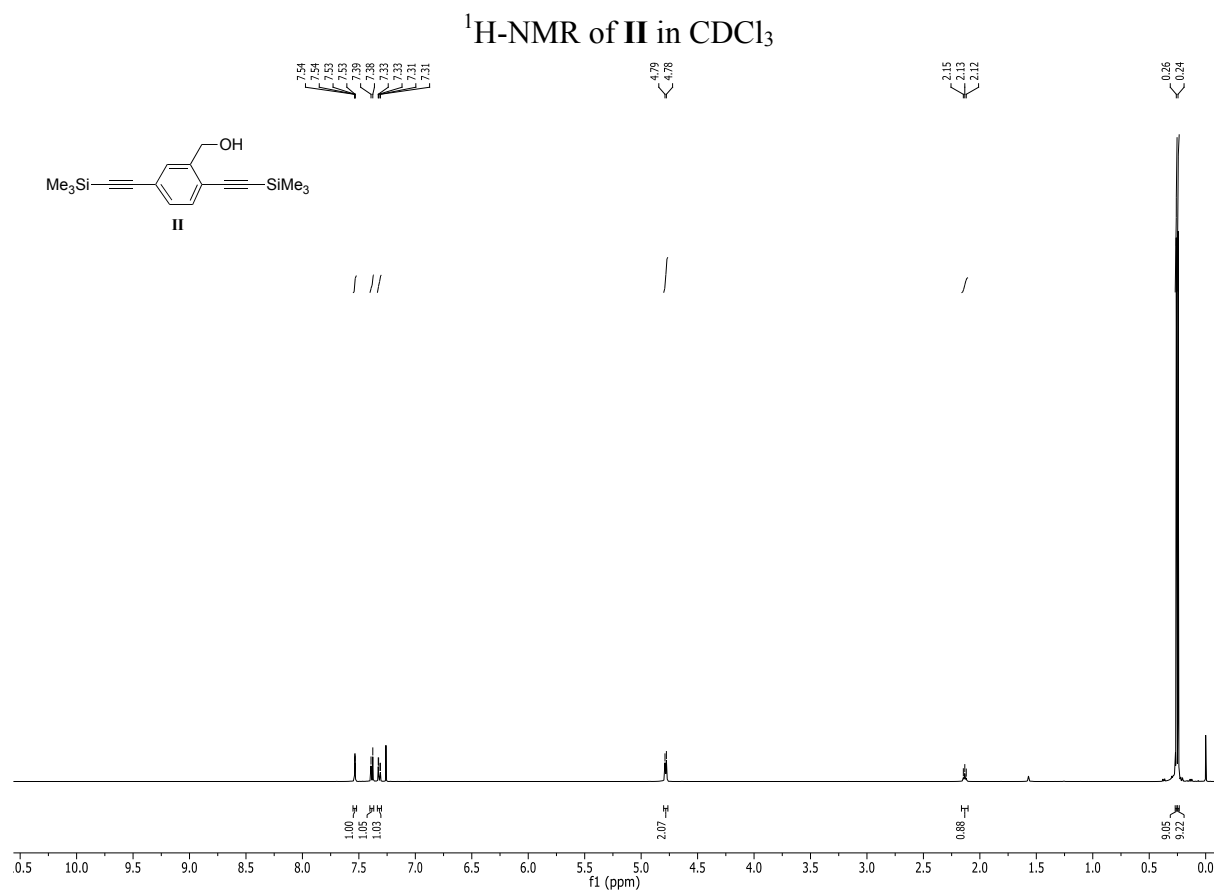


¹H-NMR of **19** in CDCl₃

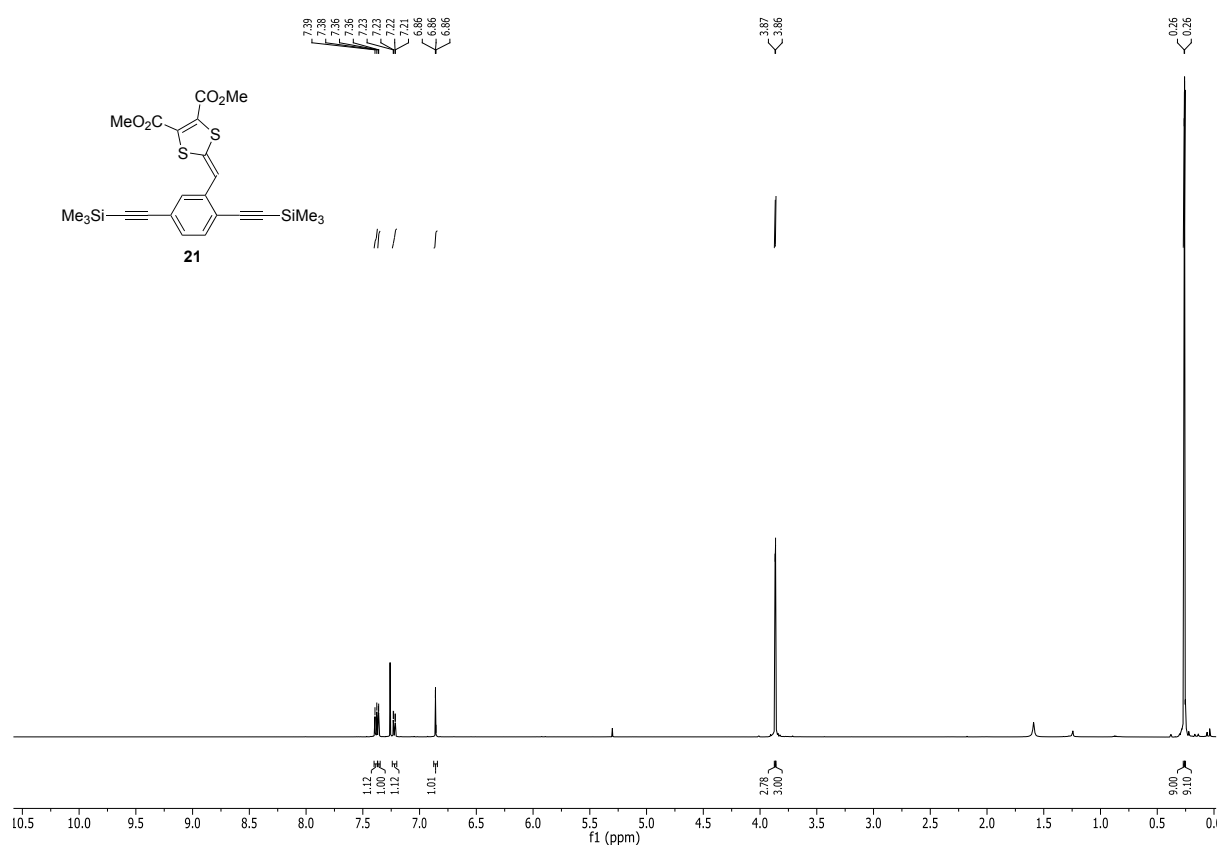


¹³C-NMR of **19** in CDCl₃

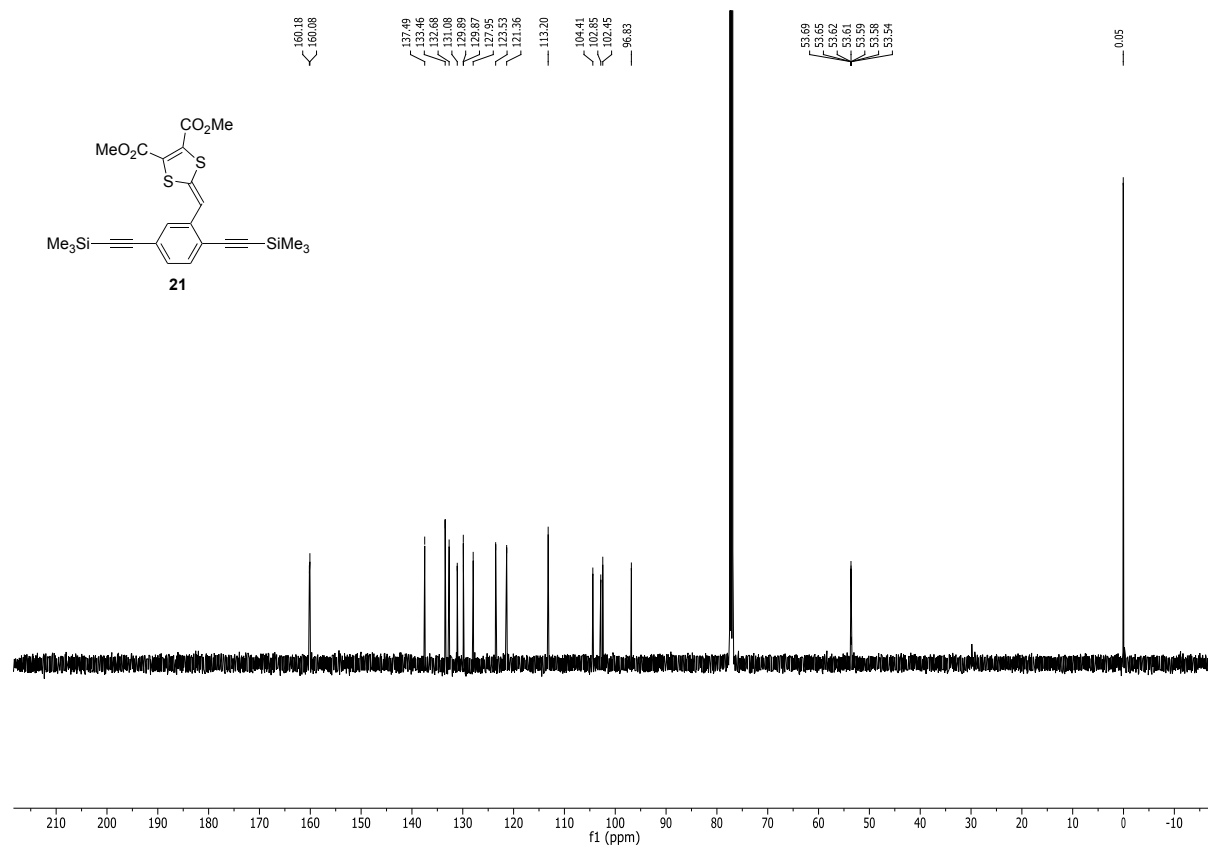




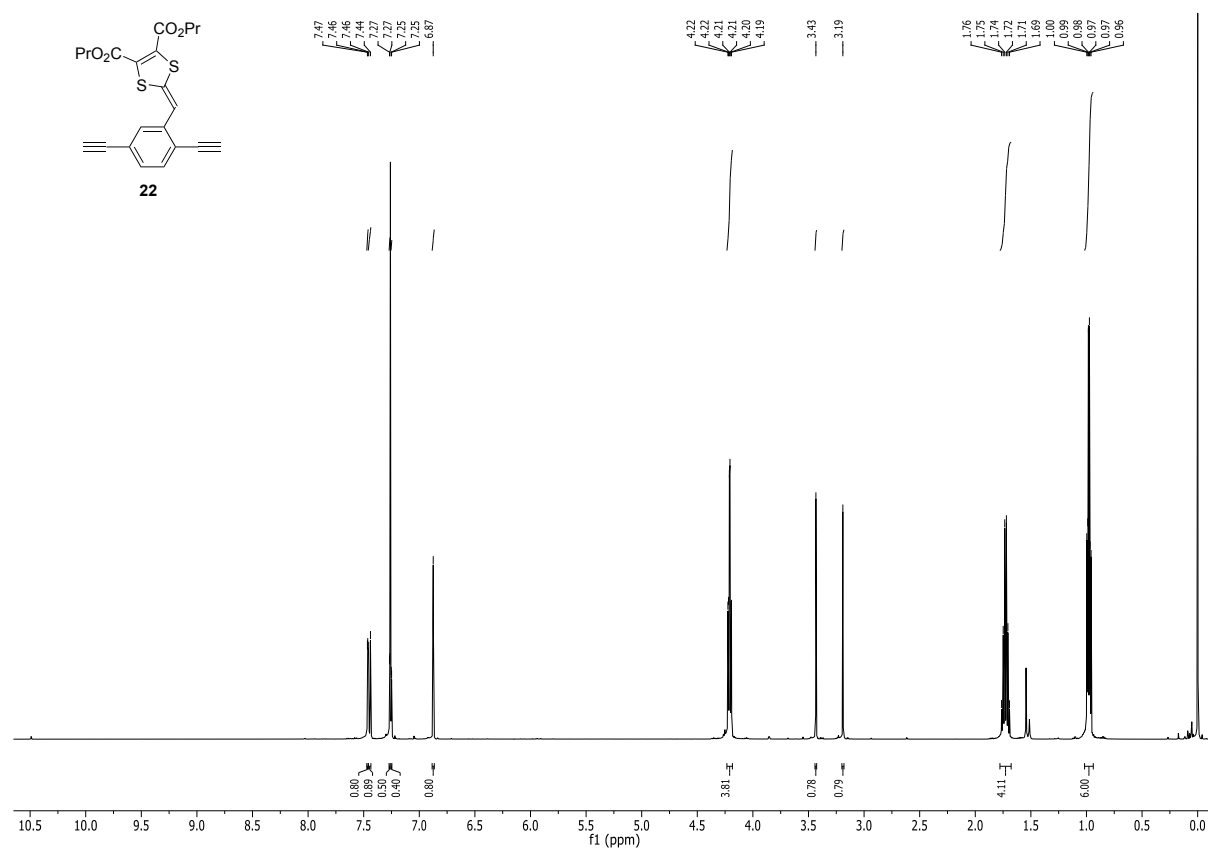
$^1\text{H-NMR}$ of **21** in CDCl_3



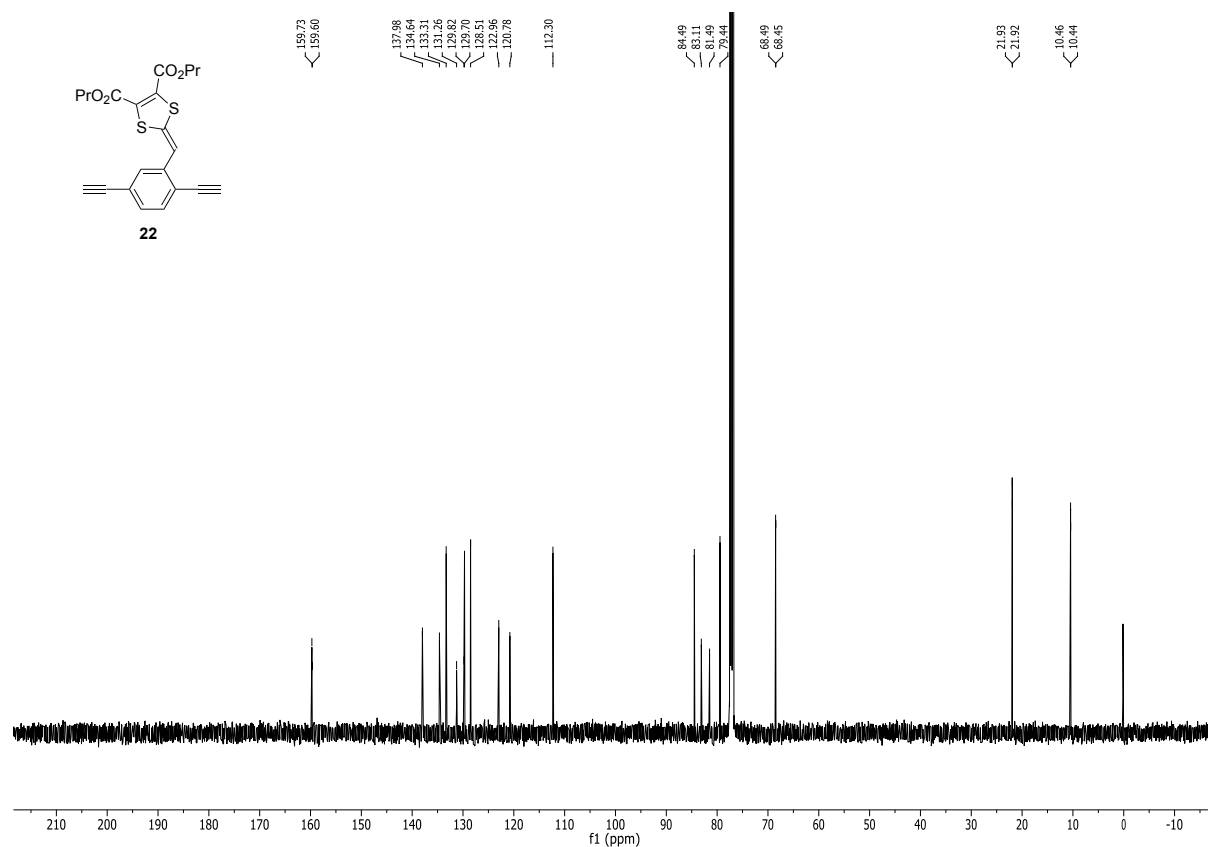
$^{13}\text{C-NMR}$ of **21** in CDCl_3



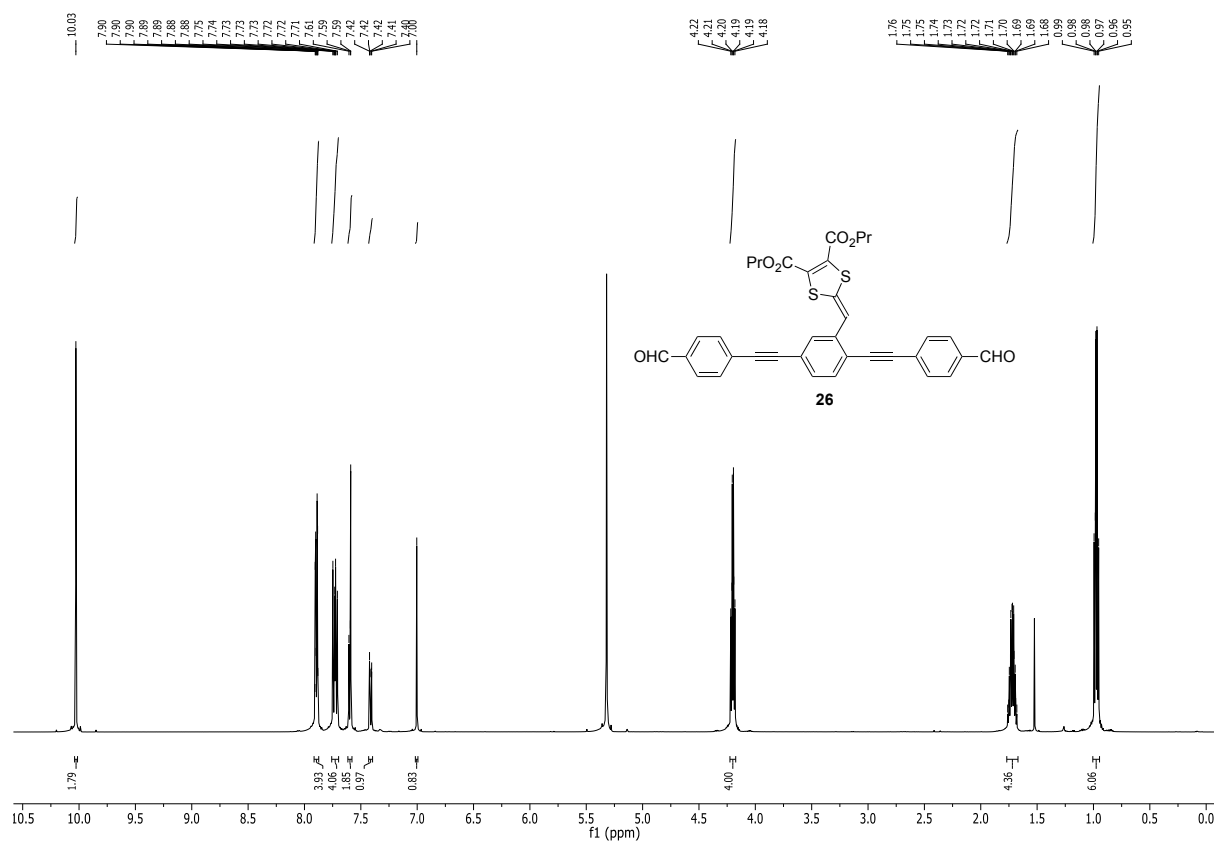
¹H-NMR of **22** in CDCl₃



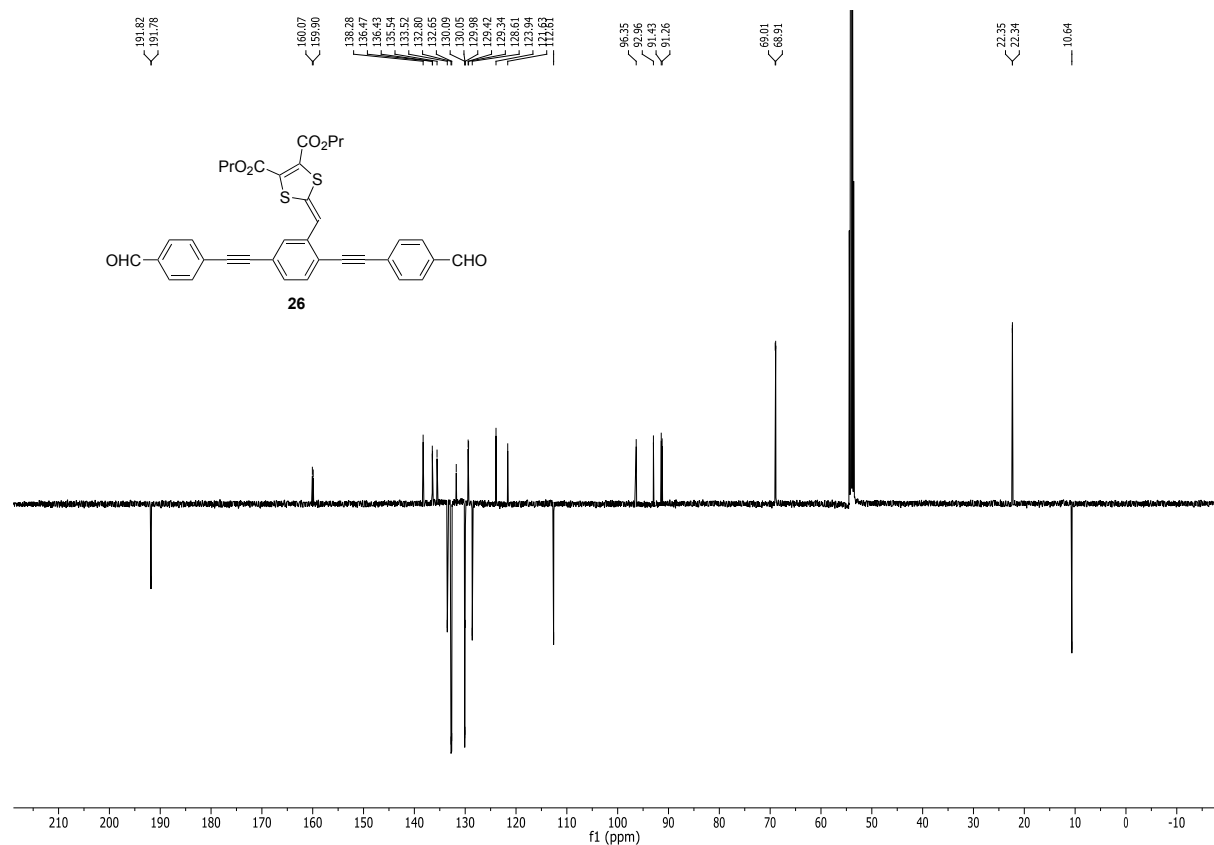
¹³C-NMR of **22** in CDCl₃



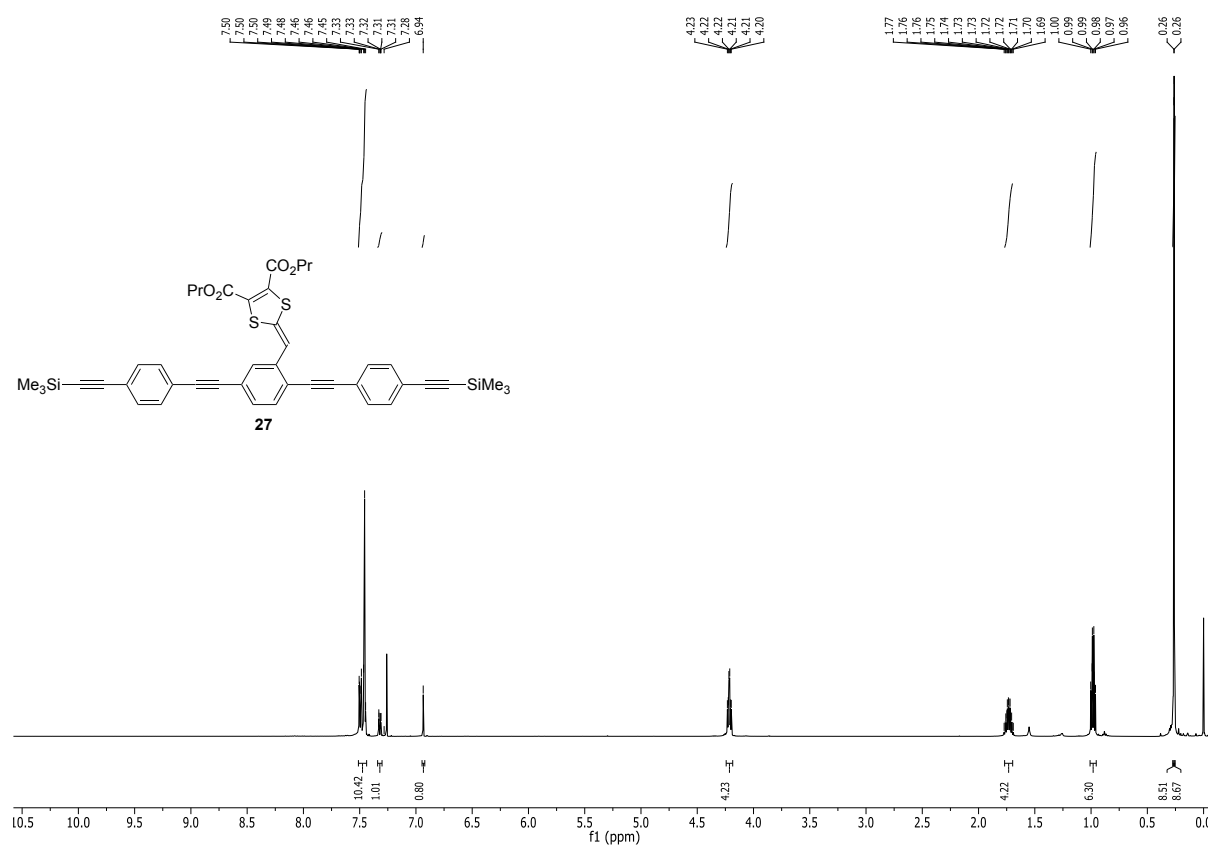
¹H-NMR of **26** in CD₂Cl₂



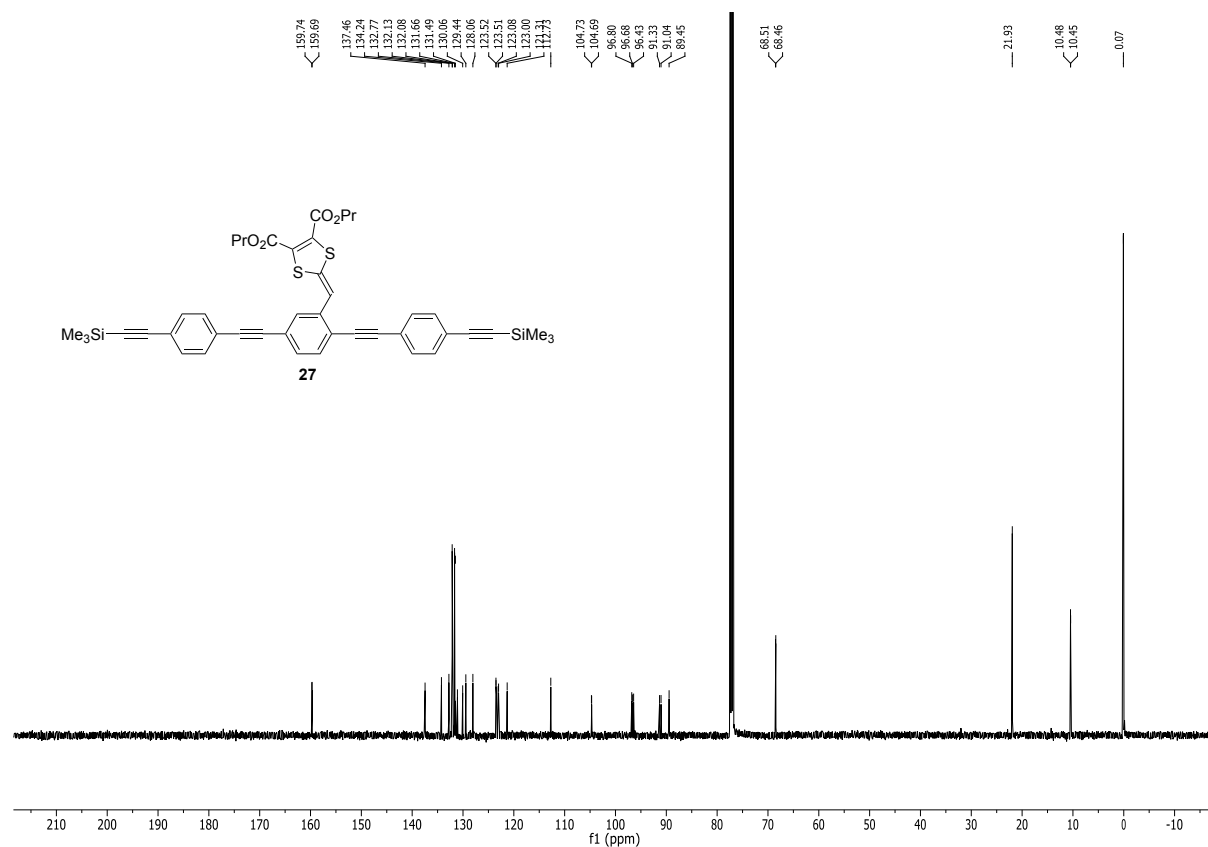
¹³C-NMR of **26** in CD₂Cl₂ (up C & CH₂. down CH & CH₃)



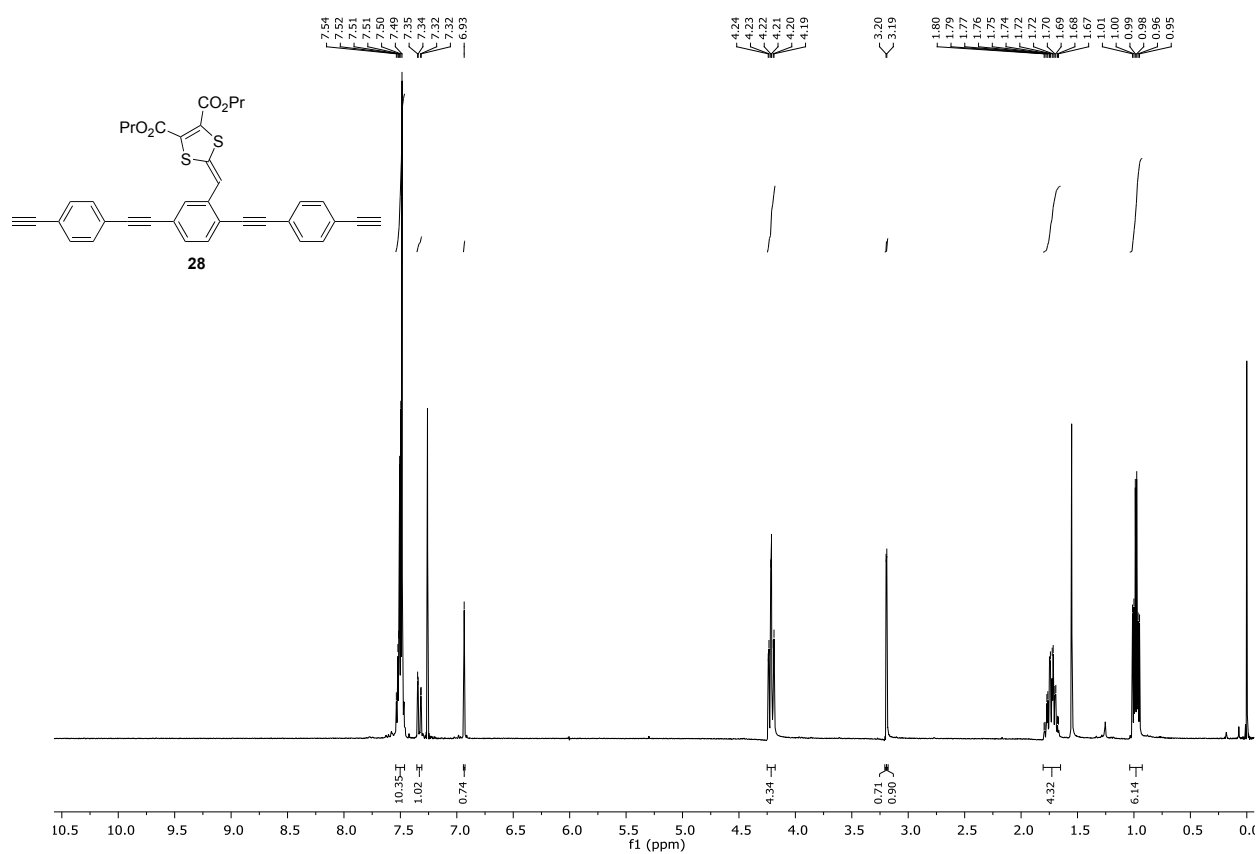
¹H-NMR of **27** in CDCl₃



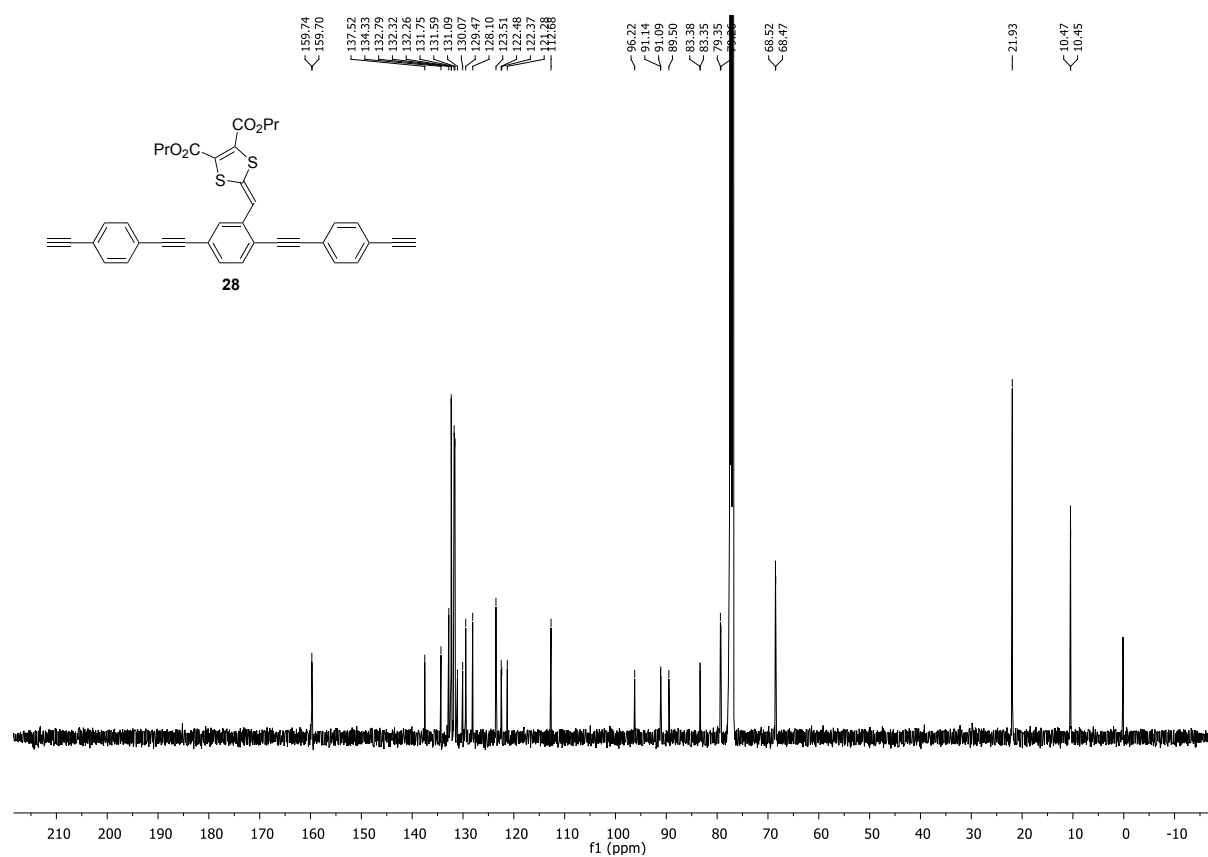
¹³C-NMR of **27** in CDCl₃



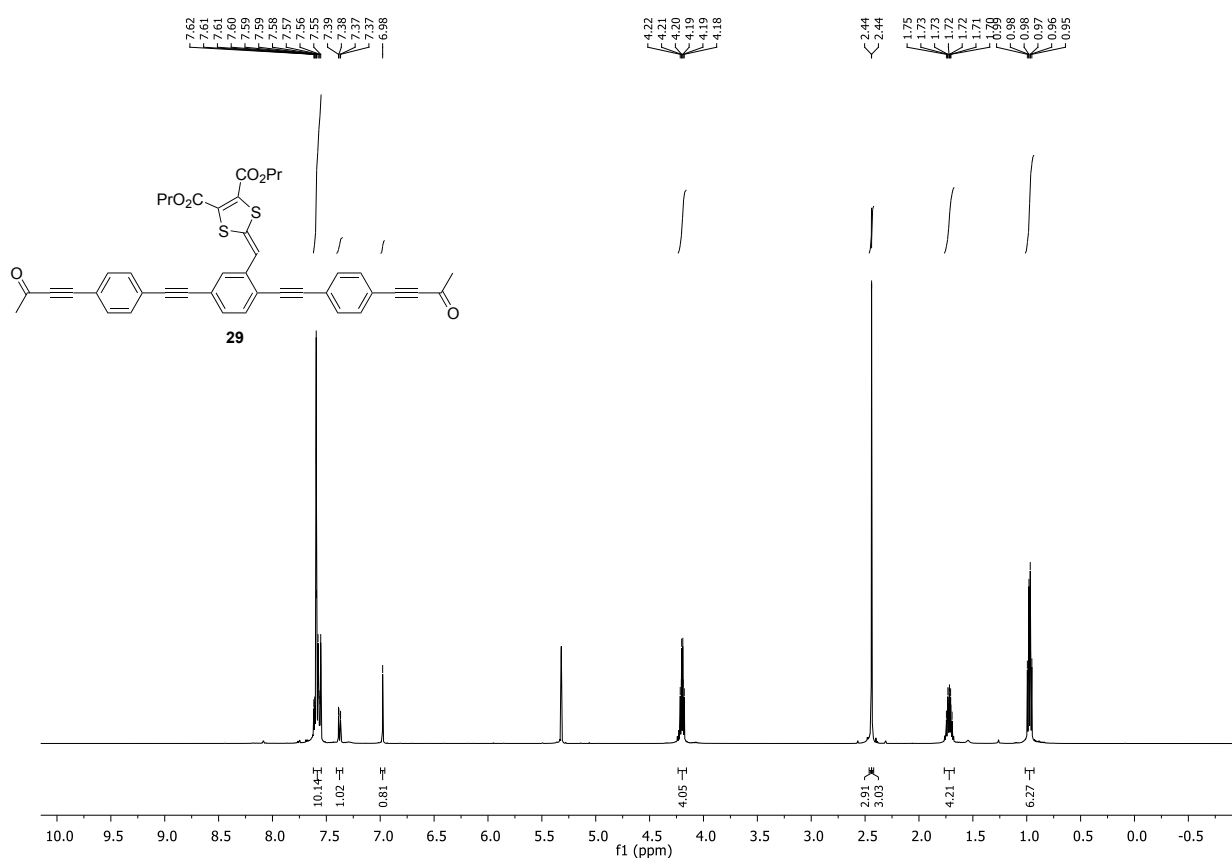
^1H -NMR of **28** in CDCl_3



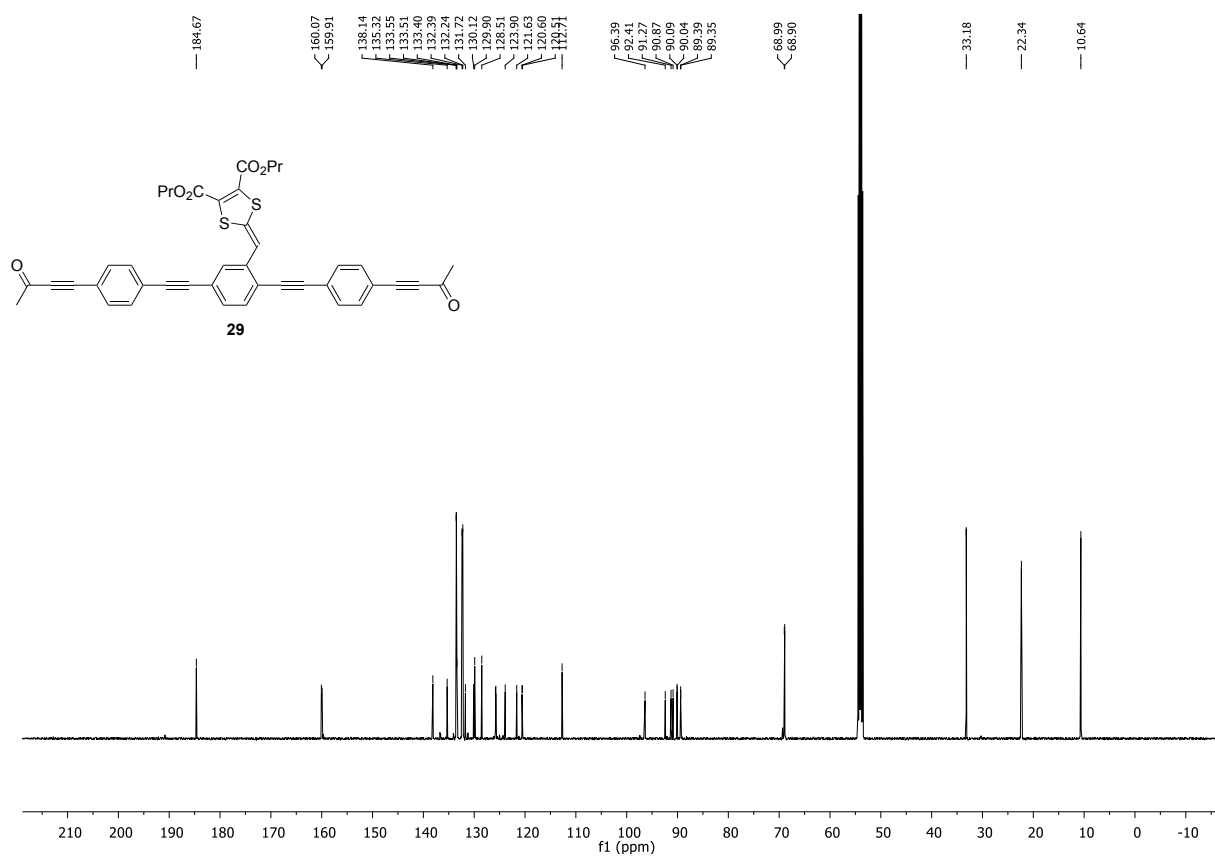
^{13}C -NMR of **28** in CDCl_3

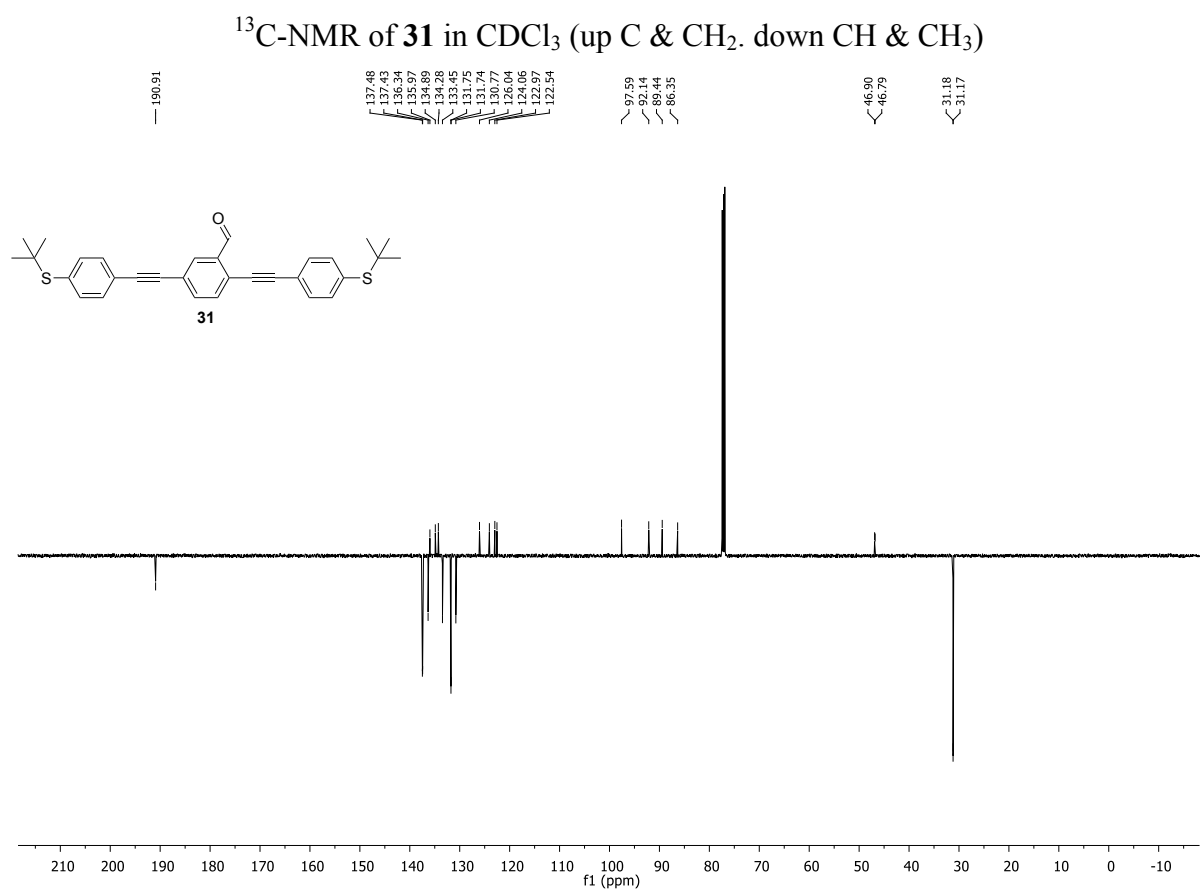
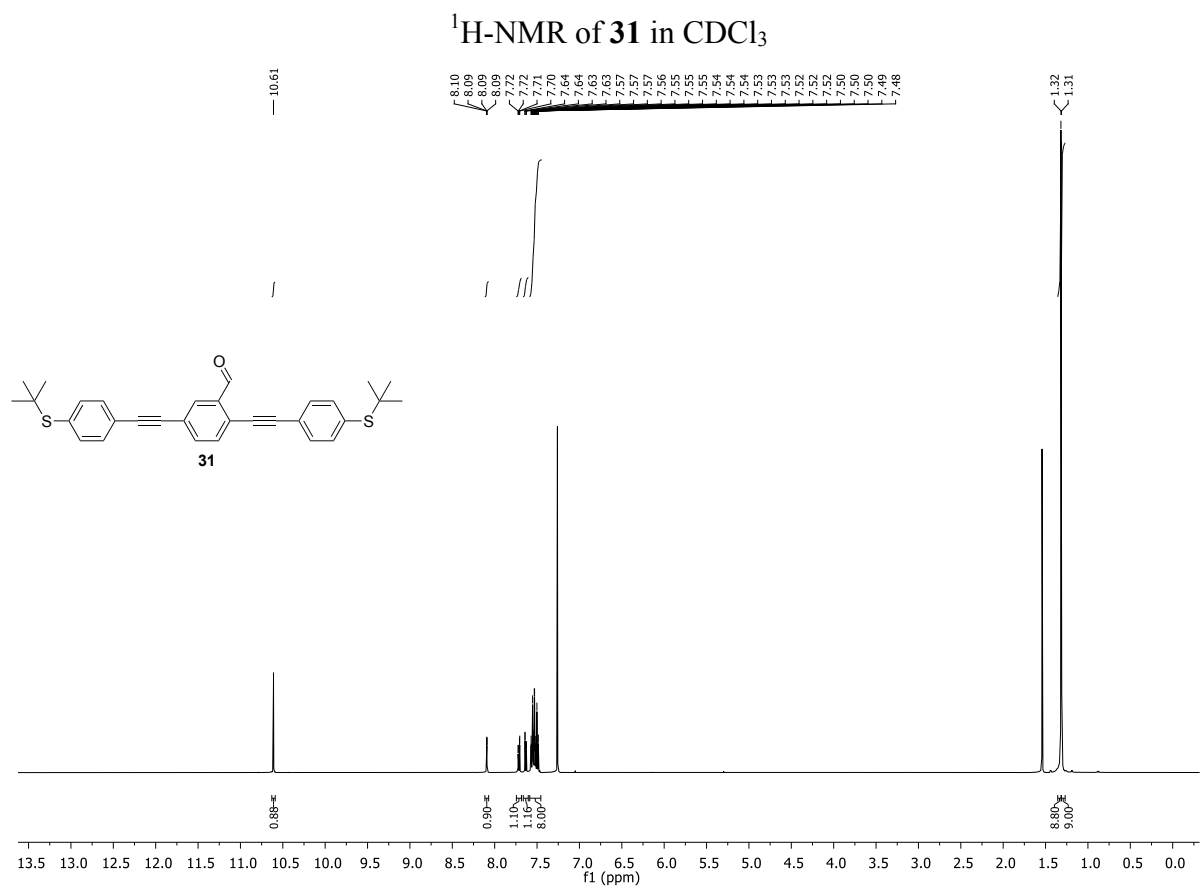


¹H-NMR of **29** in CD₂Cl₂

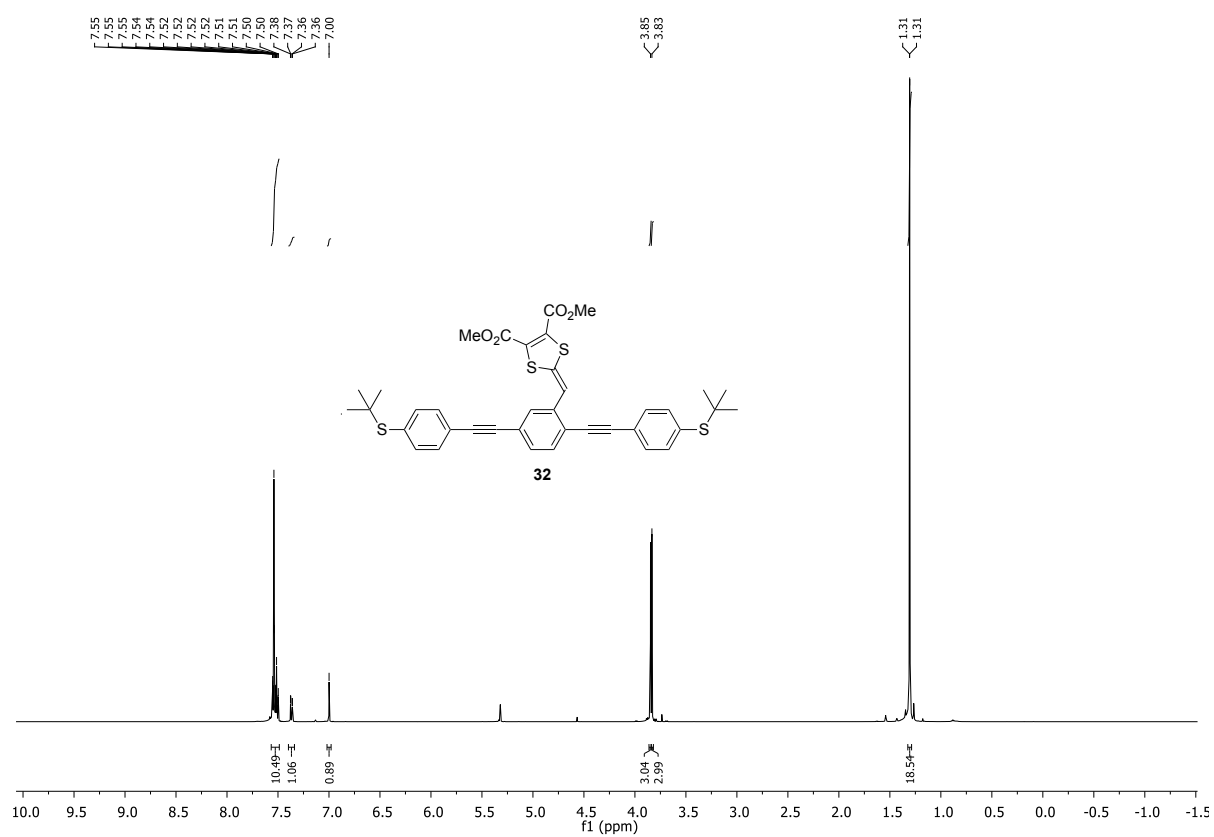


¹³C-NMR of **29** in CD₂Cl₂

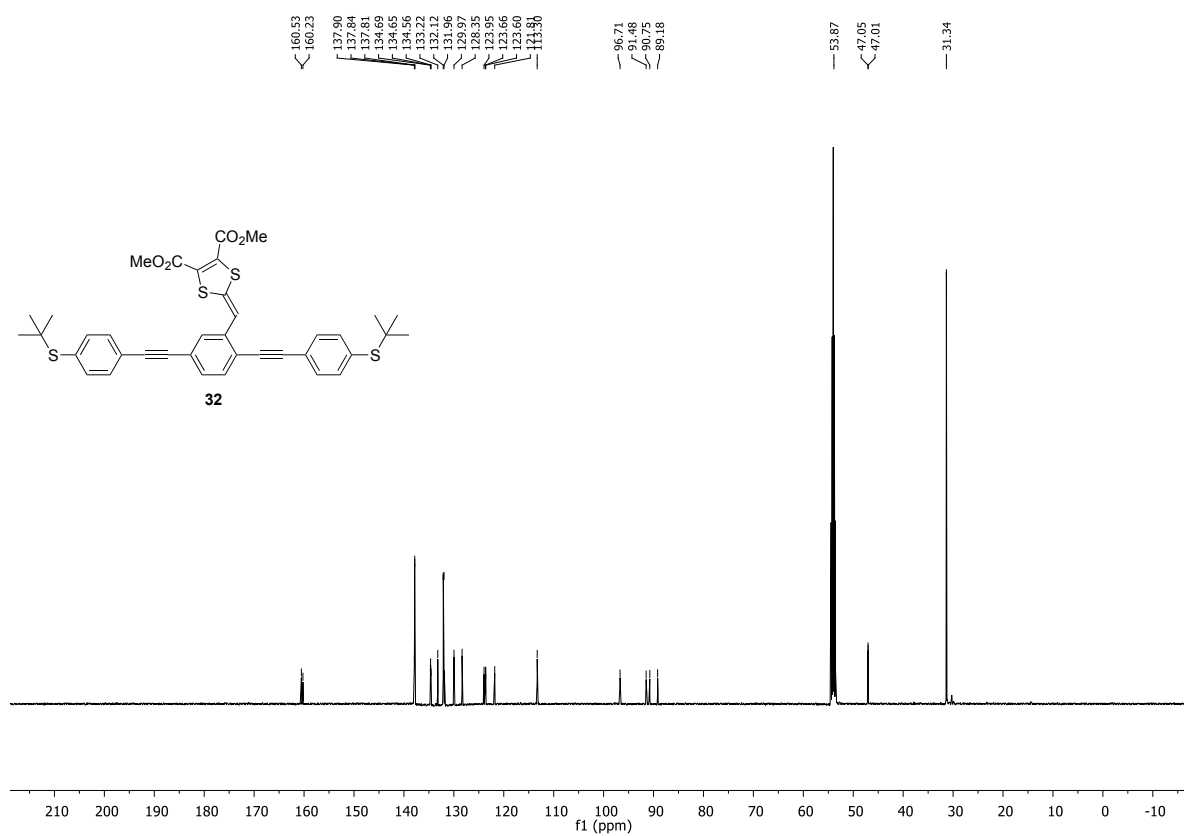




¹H-NMR of **32** in CD₂Cl₂



¹³C-NMR of **32** in CD₂Cl₂



33

^1H NMR spectrum (CDCl_3) of compound **33**. The spectrum shows peaks at δ 7.53, 7.52, 7.51, 7.38, 7.36, 7.34, 7.32, 7.29, 7.27, 7.21, 6.44, 3.97, 3.96, 1.52, 0.92, and 0.00 ppm. Integration values are shown below the peaks: 0.86, 1.05, 1.05, 0.80, 0.80, 2.80, 2.80, 1.00, and 8.80.

33

COC(=O)c1cc(s1)/C=C/c2ccc(C#CC[Si](C)(C)C)c2OC(F)(F)F

158.81 158.75 145.30 137.84 131.75 131.71 131.67 128.85 128.81 122.82 122.80 122.78 122.76 122.74 122.72 122.70 122.68 122.66 122.64 122.62 122.60 122.58 122.56 122.54 122.52 122.50 122.48 122.46 122.44 122.42 122.40 122.38 122.36 122.34 122.32 122.30 122.28 122.26 122.24 122.22 122.20 122.18 122.16 122.14 122.12 122.10 122.08 122.06 122.04 122.02 122.00 121.98 121.96 121.94 121.92 121.90 121.88 121.86 121.84 121.82 121.80 121.78 121.76 121.74 121.72 121.70 121.68 121.66 121.64 121.62 121.60 121.58 121.56 121.54 121.52 121.50 121.48 121.46 121.44 121.42 121.40 121.38 121.36 121.34 121.32 121.30 121.28 121.26 121.24 121.22 121.20 121.18 121.16 121.14 121.12 121.10 121.08 121.06 121.04 121.02 121.00 120.98 120.96 120.94 120.92 120.90 120.88 120.86 120.84 120.82 120.80 120.78 120.76 120.74 120.72 120.70 120.68 120.66 120.64 120.62 120.60 120.58 120.56 120.54 120.52 120.50 120.48 120.46 120.44 120.42 120.40 120.38 120.36 120.34 120.32 120.30 120.28 120.26 120.24 120.22 120.20 120.18 120.16 120.14 120.12 120.10 120.08 120.06 120.04 120.02 120.00 119.98 119.96 119.94 119.92 119.90 119.88 119.86 119.84 119.82 119.80 119.78 119.76 119.74 119.72 119.70 119.68 119.66 119.64 119.62 119.60 119.58 119.56 119.54 119.52 119.50 119.48 119.46 119.44 119.42 119.40 119.38 119.36 119.34 119.32 119.30 119.28 119.26 119.24 119.22 119.20 119.18 119.16 119.14 119.12 119.10 119.08 119.06 119.04 119.02 119.00 118.98 118.96 118.94 118.92 118.90 118.88 118.86 118.84 118.82 118.80 118.78 118.76 118.74 118.72 118.70 118.68 118.66 118.64 118.62 118.60 118.58 118.56 118.54 118.52 118.50 118.48 118.46 118.44 118.42 118.40 118.38 118.36 118.34 118.32 118.30 118.28 118.26 118.24 118.22 118.20 118.18 118.16 118.14 118.12 118.10 118.08 118.06 118.04 118.02 118.00 117.98 117.96 117.94 117.92 117.90 117.88 117.86 117.84 117.82 117.80 117.78 117.76 117.74 117.72 117.70 117.68 117.66 117.64 117.62 117.60 117.58 117.56 117.54 117.52 117.50 117.48 117.46 117.44 117.42 117.40 117.38 117.36 117.34 117.32 117.30 117.28 117.26 117.24 117.22 117.20 117.18 117.16 117.14 117.12 117.10 117.08 117.06 117.04 117.02 117.00 116.98 116.96 116.94 116.92 116.90 116.88 116.86 116.84 116.82 116.80 116.78 116.76 116.74 116.72 116.70 116.68 116.66 116.64 116.62 116.60 116.58 116.56 116.54 116.52 116.50 116.48 116.46 116.44 116.42 116.40 116.38 116.36 116.34 116.32 116.30 116.28 116.26 116.24 116.22 116.20 116.18 116.16 116.14 116.12 116.10 116.08 116.06 116.04 116.02 116.00 115.98 115.96 115.94 115.92 115.90 115.88 115.86 115.84 115.82 115.80 115.78 115.76 115.74 115.72 115.70 115.68 115.66 115.64 115.62 115.60 115.58 115.56 115.54 115.52 115.50 115.48 115.46 115.44 115.42 115.40 115.38 115.36 115.34 115.32 115.30 115.28 115.26 115.24 115.22 115.20 115.18 115.16 115.14 115.12 115.10 115.08 115.06 115.04 115.02 115.00 114.98 114.96 114.94 114.92 114.90 114.88 114.86 114.84 114.82 114.80 114.78 114.76 114.74 114.72 114.70 114.68 114.66 114.64 114.62 114.60 114.58 114.56 114.54 114.52 114.50 114.48 114.46 114.44 114.42 114.40 114.38 114.36 114.34 114.32 114.30 114.28 114.26 114.24 114.22 114.20 114.18 114.16 114.14 114.12 114.10 114.08 114.06 114.04 114.02 114.00 113.98 113.96 113.94 113.92 113.90 113.88 113.86 113.84 113.82 113.80 113.78 113.76 113.74 113.72 113.70 113.68 113.66 113.64 113.62 113.60 113.58 113.56 113.54 113.52 113.50 113.48 113.46 113.44 113.42 113.40 113.38 113.36 113.34 113.32 113.30 113.28 113.26 113.24 113.22 113.20 113.18 113.16 113.14 113.12 113.10 113.08 113.06 113.04 113.02 113.00 112.98 112.96 112.94 112.92 112.90 112.88 112.86 112.84 112.82 112.80 112.78 112.76 112.74 112.72 112.70 112.68 112.66 112.64 112.62 112.60 112.58 112.56 112.54 112.52 112.50 112.48 112.46 112.44 112.42 112.40 112.38 112.36 112.34 112.32 112.30 112.28 112.26 112.24 112.22 112.20 112.18 112.16 112.14 112.12 112.10 112.08 112.06 112.04 112.02 112.00 111.98 111.96 111.94 111.92 111.90 111.88 111.86 111.84 111.82 111.80 111.78 111.76 111.74 111.72 111.70 111.68 111.66 111.64 111.62 111.60 111.58 111.56 111.54 111.52 111.50 111.48 111.4

Chemical structure of **34** is shown in the top left corner. The structure is a benzene ring substituted with a trimethylsilyl group (Me_3Si), a carbonyl group ($\text{C}=\text{O}$), and a phenylethynyl group ($\text{C}\equiv\text{C}$).

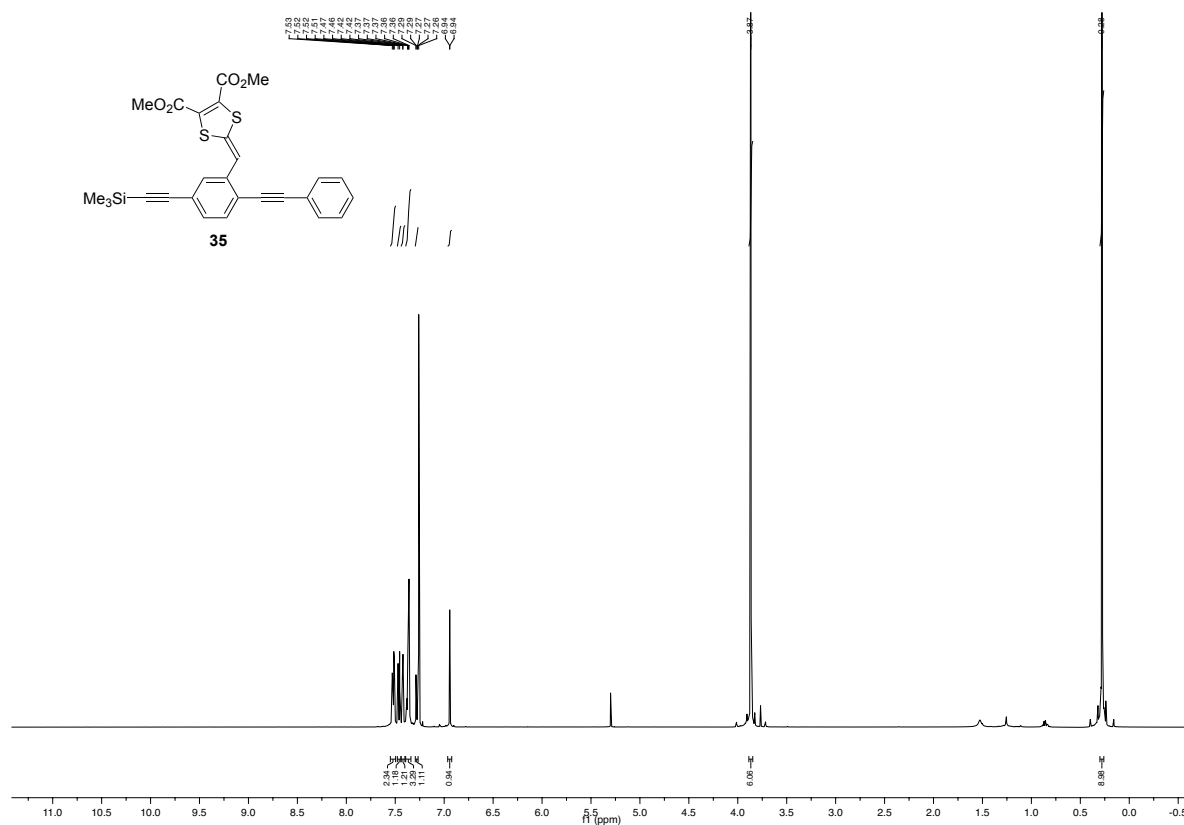
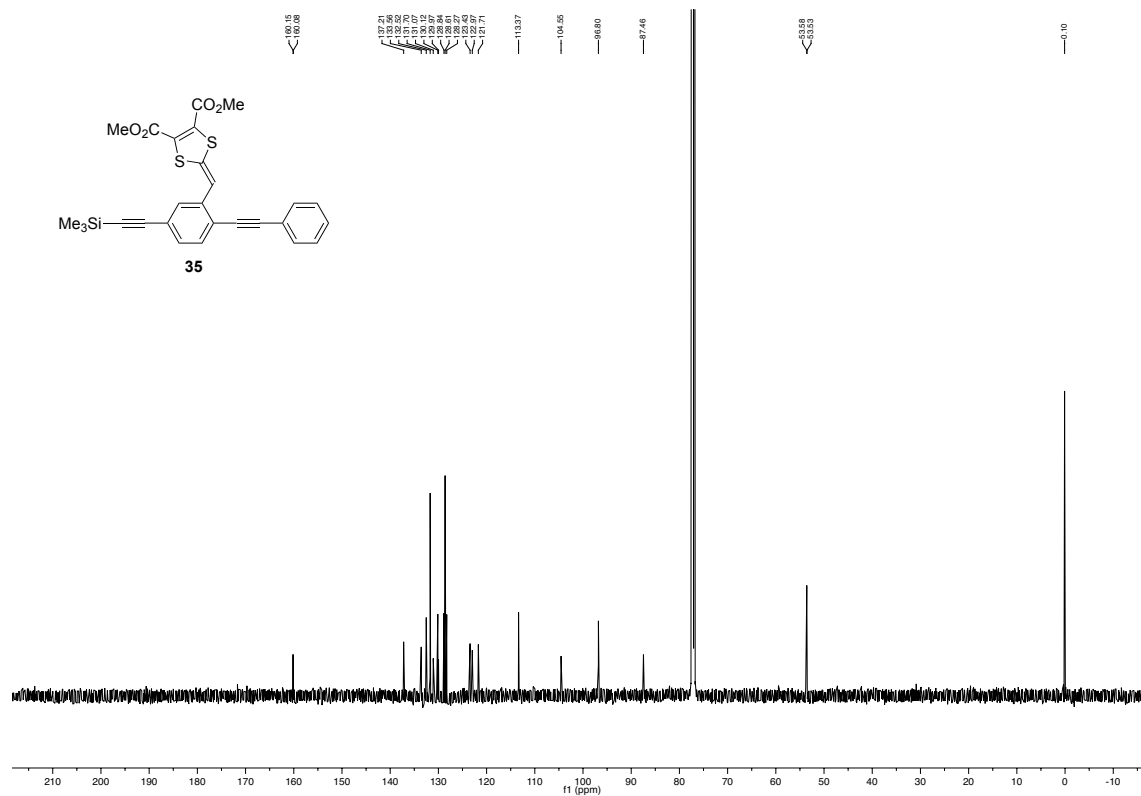
The ^1H NMR spectrum (400 MHz, CDCl_3) shows the following peaks and integrations:

- Peak at δ 10.59 (s, 1H, integration 1.00).
- Peak at δ 7.7 (s, 1H, integration 0.90).
- Peak at δ 7.5 (s, 1H, integration 0.90).
- Peak at δ 7.3 (s, 1H, integration 0.90).
- Peak at δ 7.2 (s, 1H, integration 0.90).
- Peak at δ 7.1 (s, 1H, integration 0.90).
- Peak at δ 1.5 (s, 9H, integration 9.00).
- Peak at δ 0.1 (s, 9H, integration 9.00).

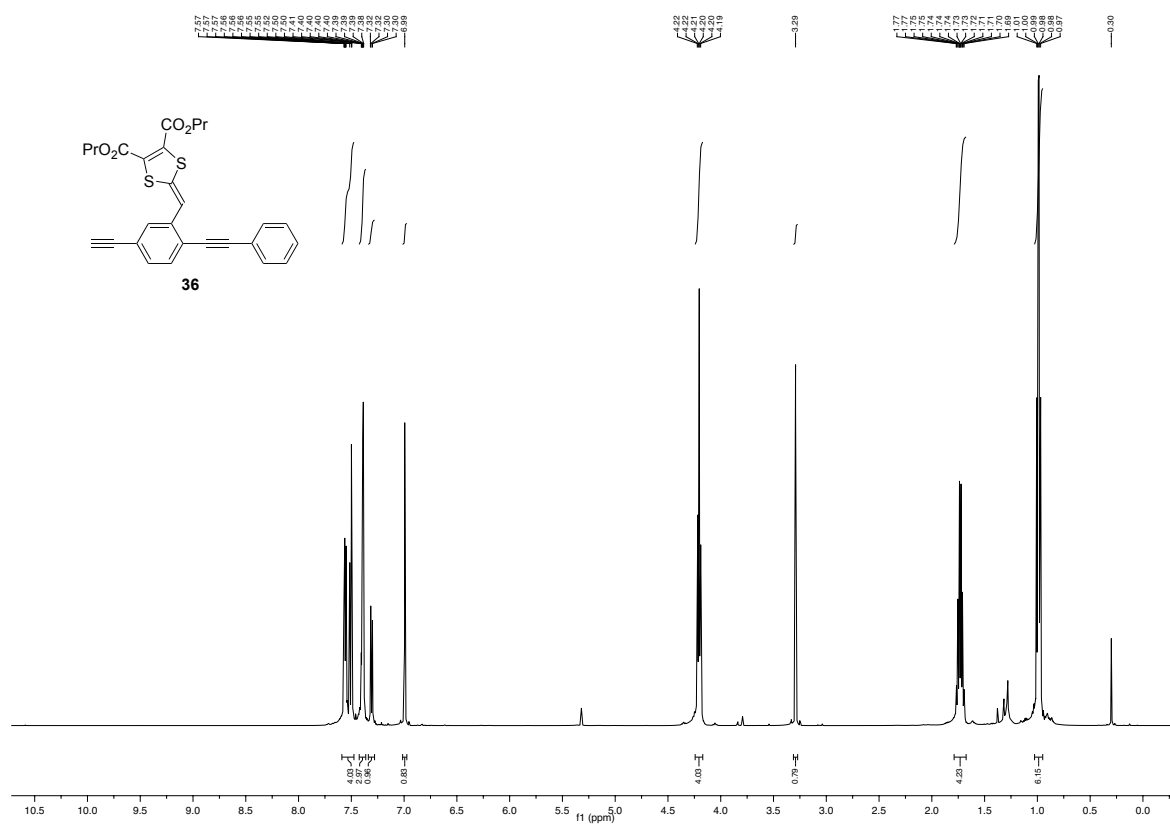
34

C[Si](C)(C)C#Cc1ccc(cc1C#Cc2ccccc2)C(=O)c3ccccc3

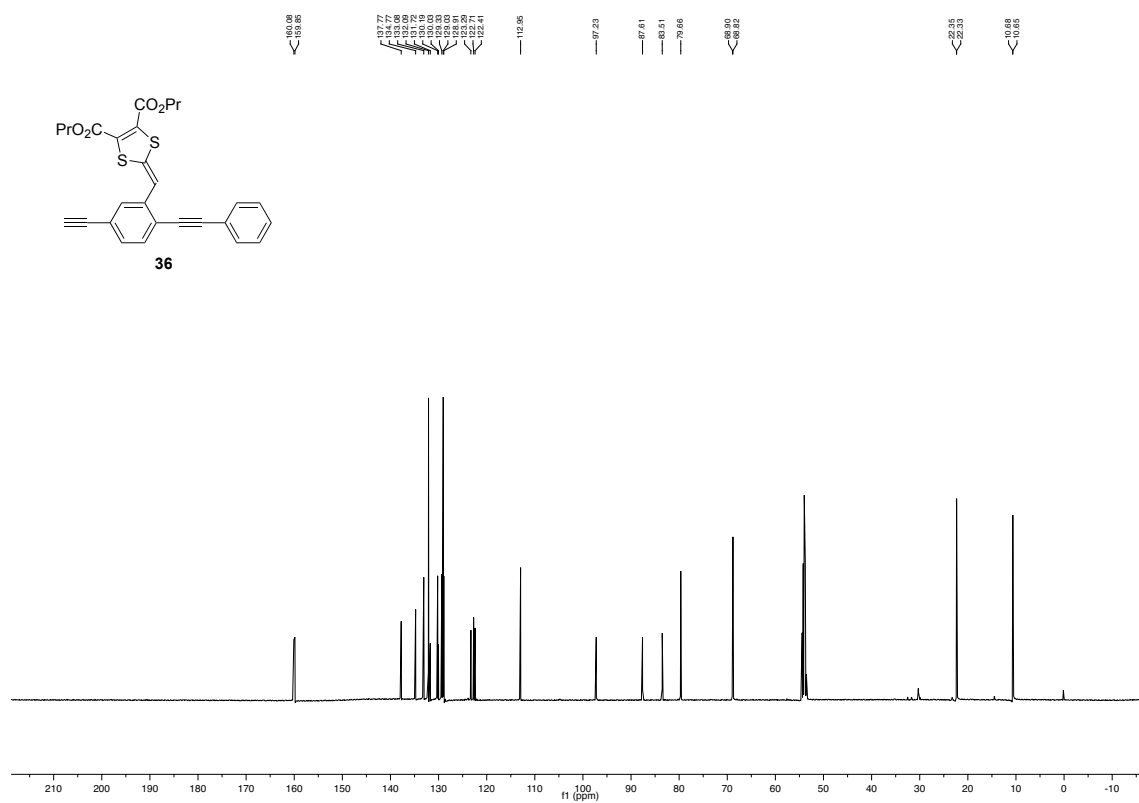
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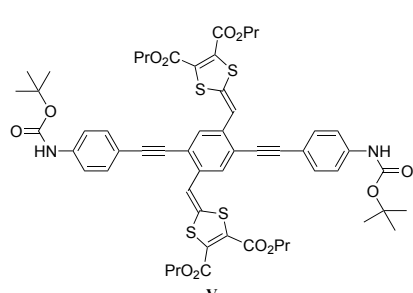
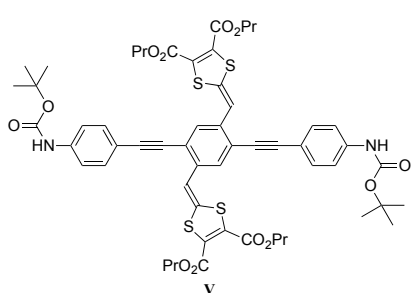
¹H-NMR of **35** in CDCl₃ ^{13}C -NMR of **35** in CDCl_3 

¹H-NMR of **36** in CD₂Cl₂

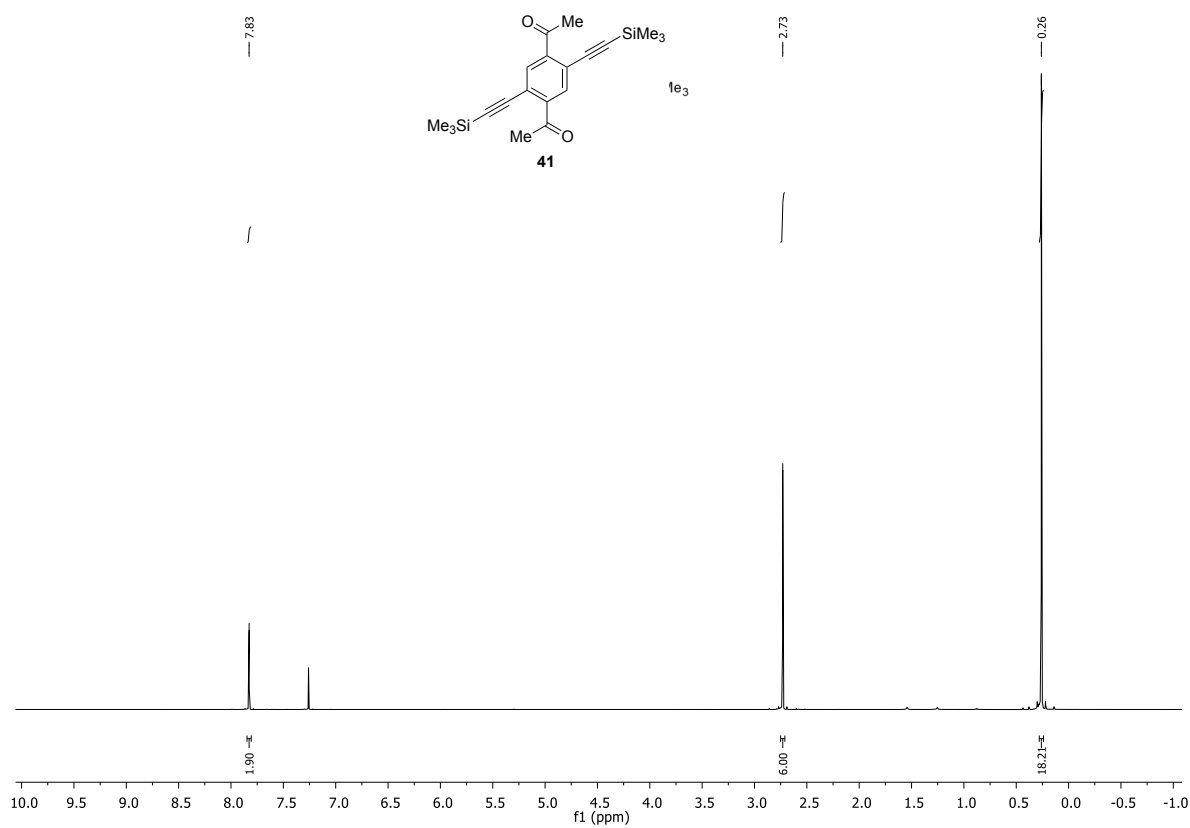


¹³C-NMR of **36** in CD₂Cl₂

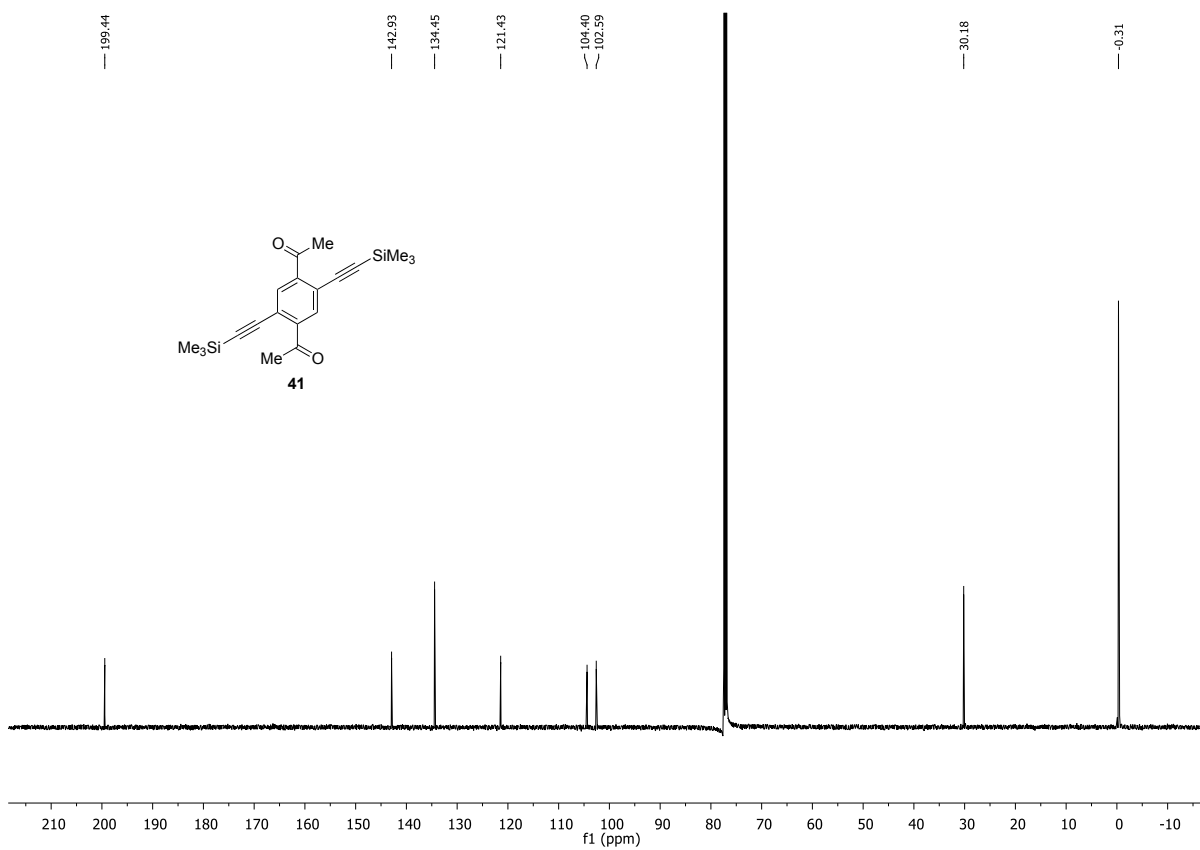




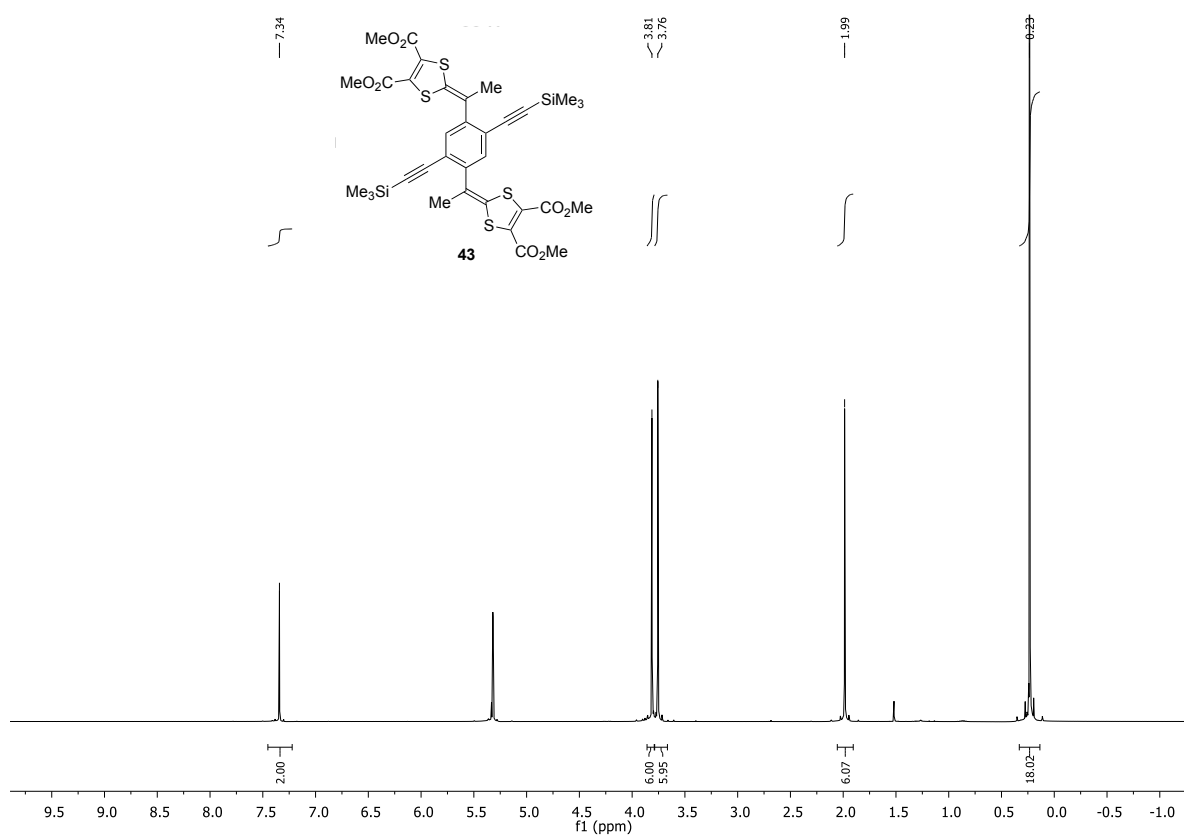
¹H-NMR of **41** in CDCl₃



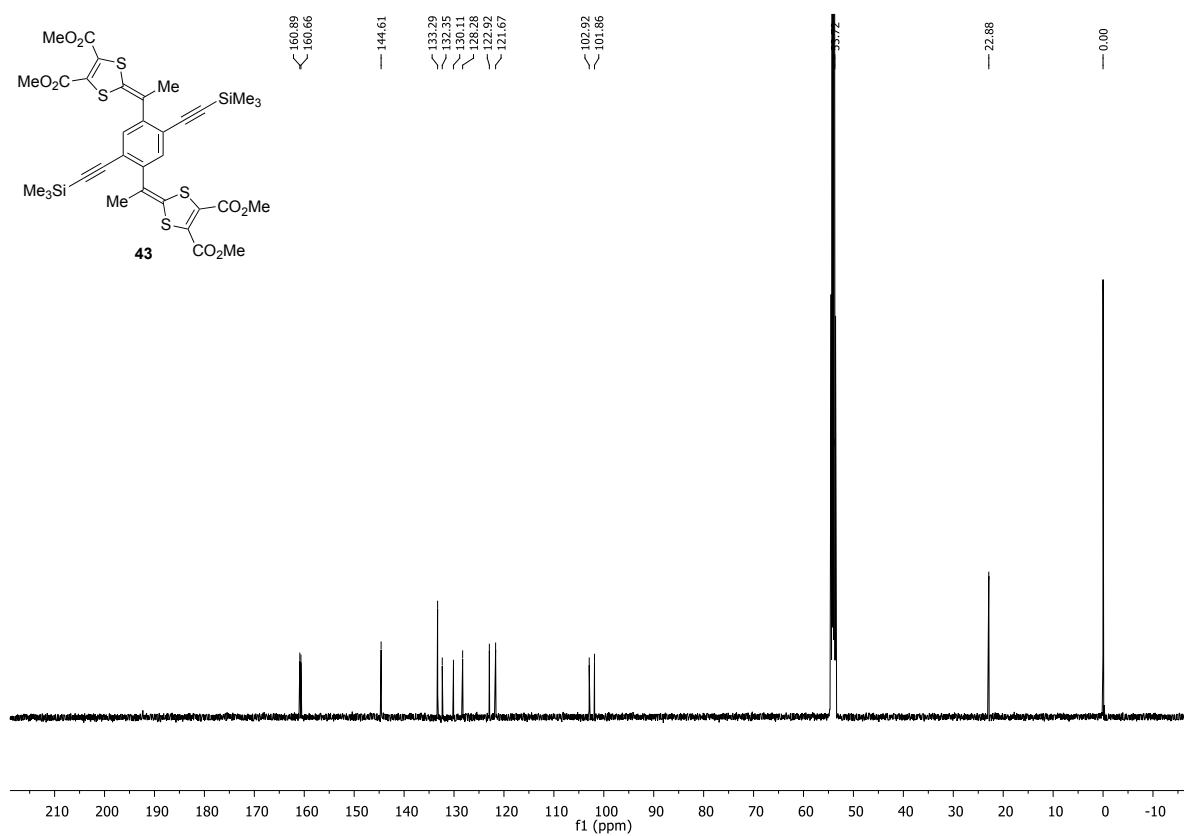
¹³C-NMR of **41** in CDCl₃



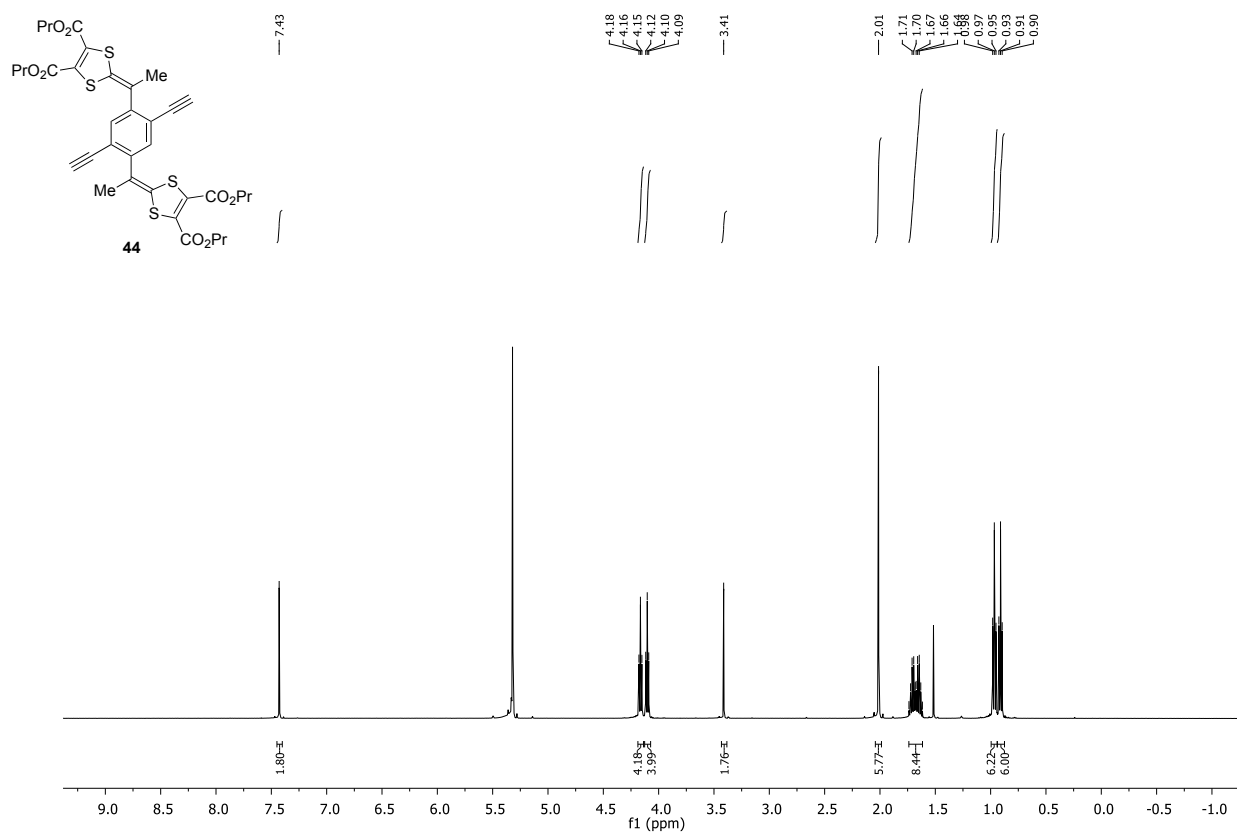
¹H-NMR of **43** in CD₂Cl₂



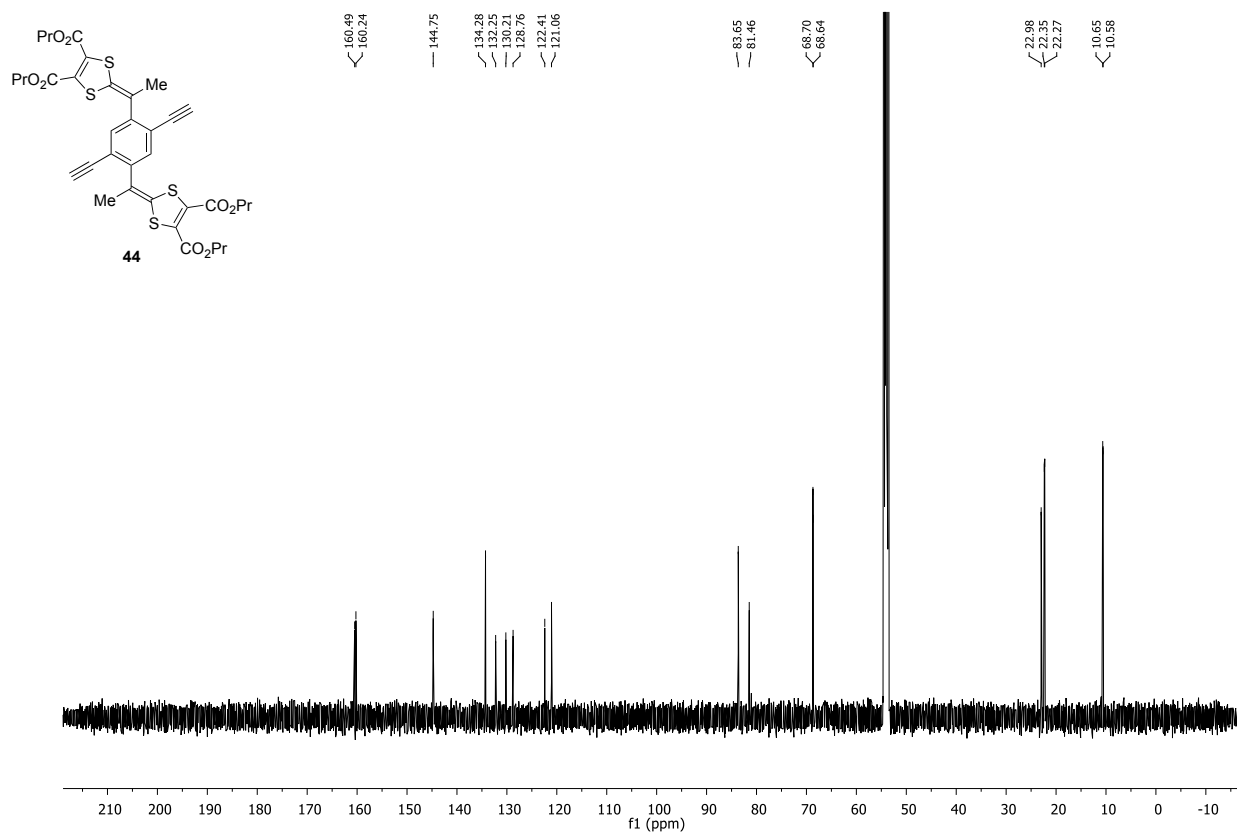
¹³C-NMR of **43** in CD₂Cl₂

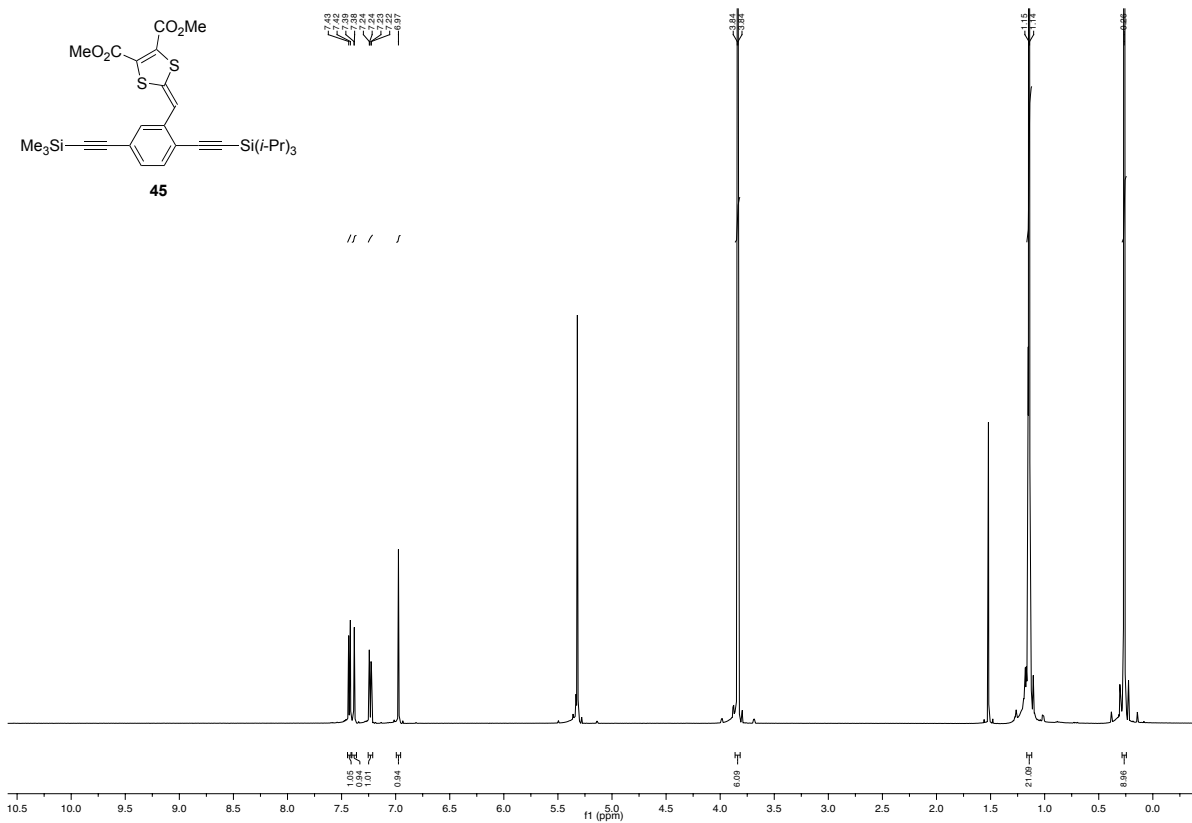


¹H-NMR of **44** in CD₂Cl₂

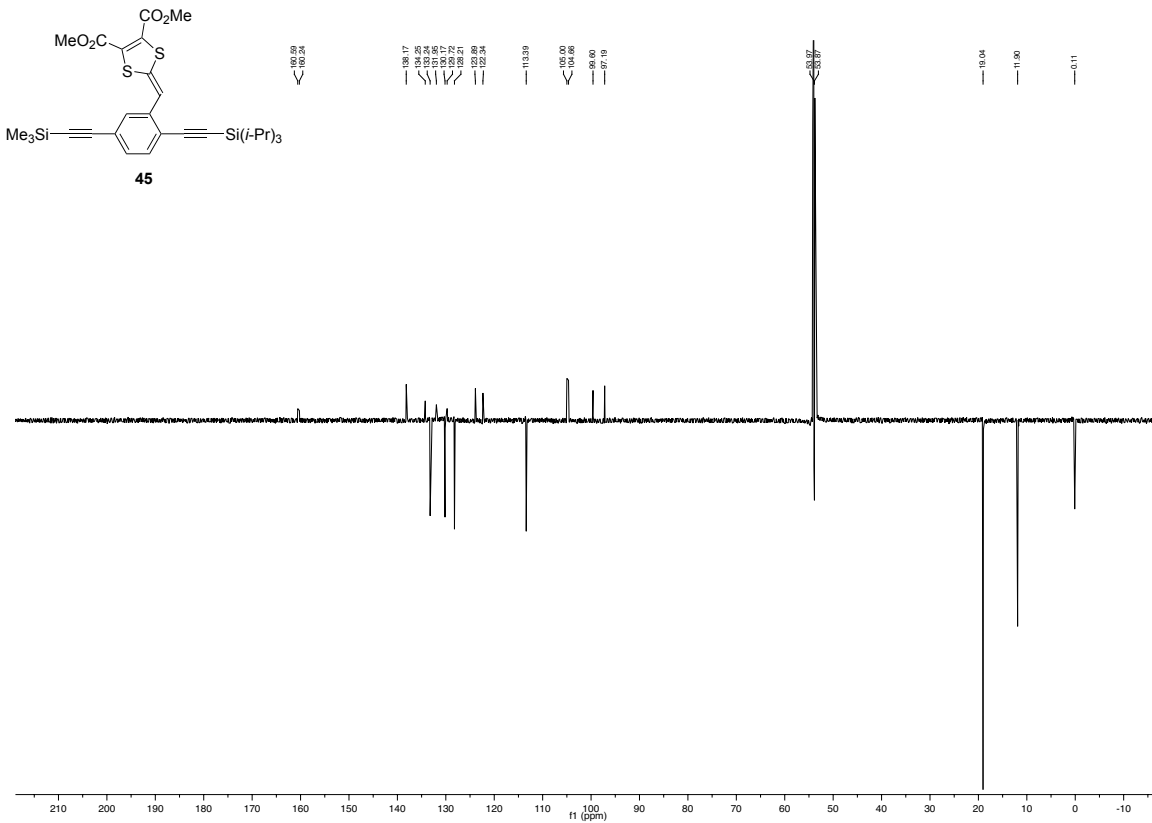


¹³C-NMR of **44** in CD₂Cl₂

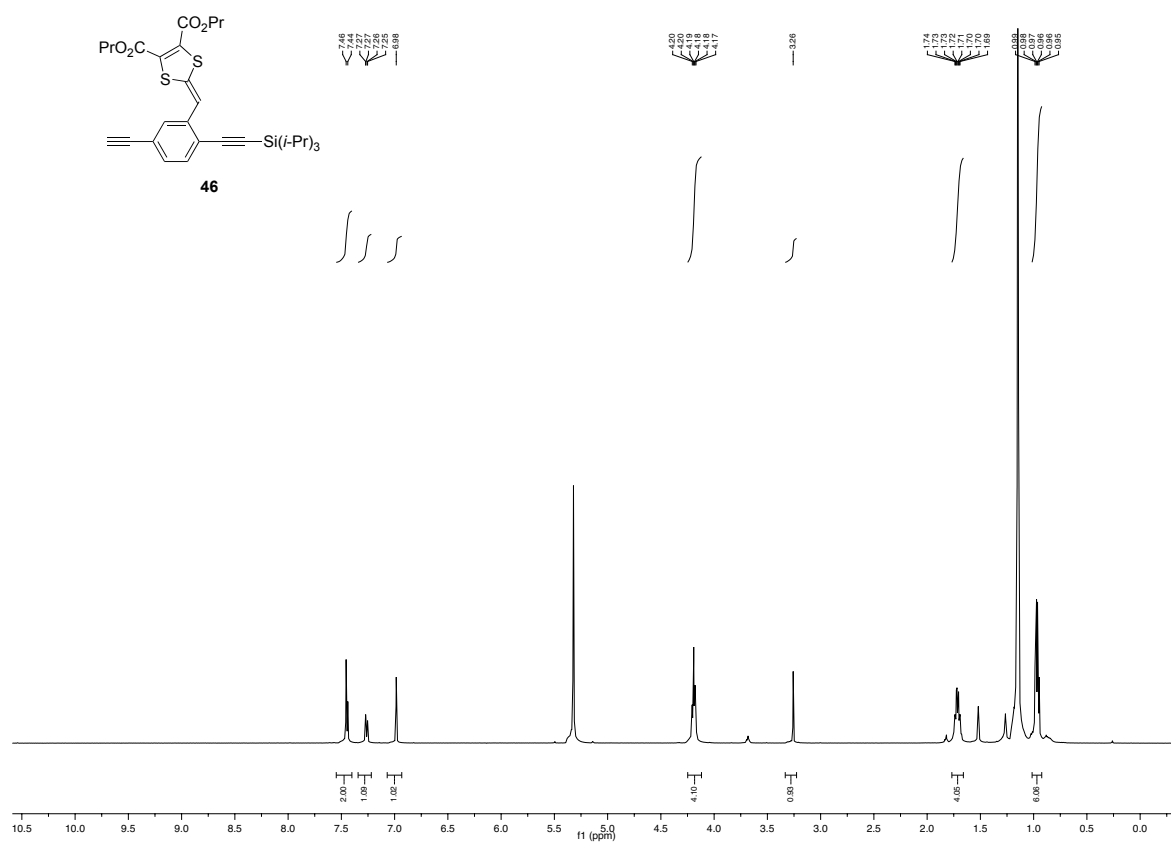


¹H-NMR of **45** in CD₂Cl₂

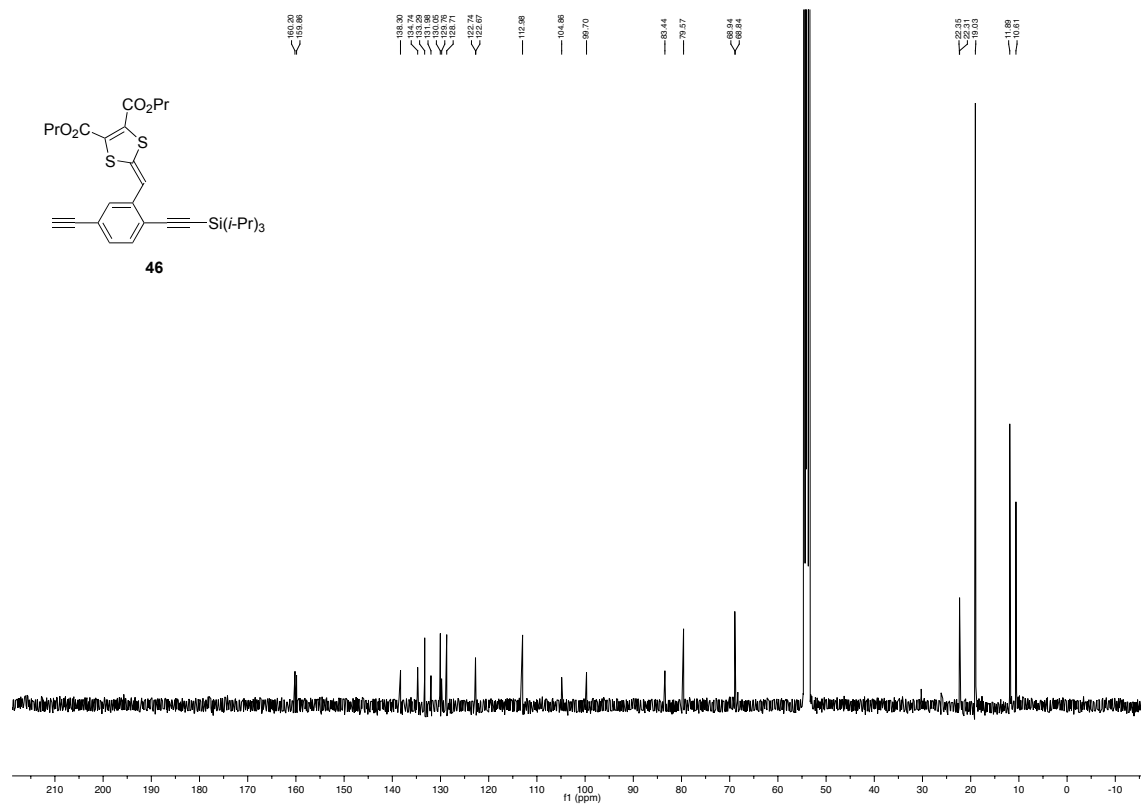
¹³C-NMR of **45** in CD₂Cl₂ (up C & CH₂. down CH & CH₃)

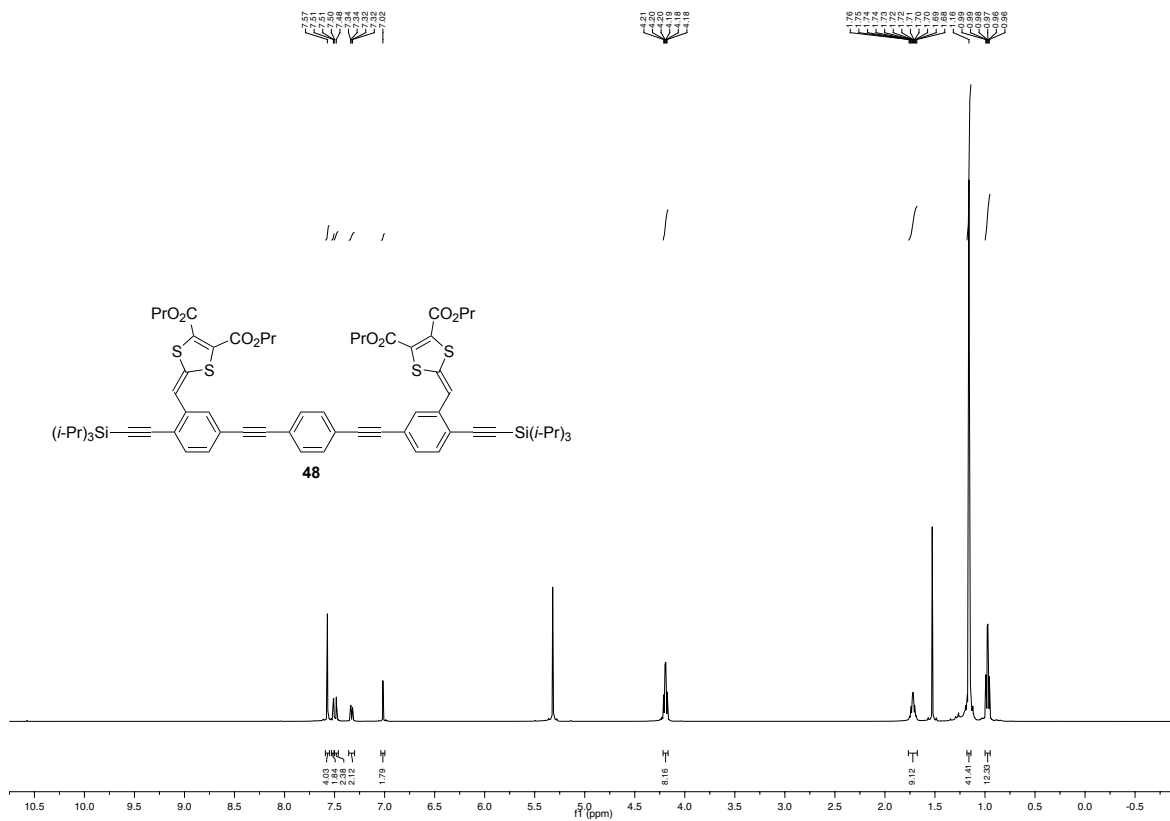


¹H-NMR of **46** in CD₂Cl₂



¹³C-NMR of **46** in CD₂Cl₂



¹H-NMR of **48** in CD₂Cl₂¹³C-NMR of **48** in CD₂Cl₂ (up C & CH₂. down CH & CH₃)