Position and Orientation Control of a Photo- and Electrochromic Dithienylethene Using a Tripodal Anchor on Gold Surfaces

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Supporting information

Contents

1. General experimental

UV/vis absorption spectra were recorded using a Analytik Jena Specord S600 UV/vis absorption spectrophotometer and quartz cuvettes (1 cm path length). NMR spectra were recorded on a Varian VXR-300, a Varian Unity AS 400, or a Varian Unity Plus 500, operating at 299.97, 399.93 and 499.85 MHz for ^{1}H NMR, respectively. Chemical shifts are denoted in δ-unit (ppm) relative to $CDCl_3$ (7.26) or CD_2Cl_2 (5.32) for ^{1}H NMR spectra and relative to $CDCl_3$ (77.16) for ^{13}C NMR spectra. The splitting parameters for ^{1}H NMR are denoted as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), dt (double triplet), m (multiplet), and b (broad). For ^{13}C NMR spectroscopy, peaks are assigned as q (primary carbon), t (secondary carbon), d (tertiary carbon), and s (quaternary carbon). Raman and SERS spectra were recorded with a PerkinElmer RamanStation 400F spectrometer at 785 nm. Electrochemical experiments as well as the electrochemical cleaning and roughening of the gold beads were performed with a CHI760 bipotentiostat (CH Instruments). Infrared spectra were recorded with a PerkinElmer Spectrum 400 FT-IR spectrometer equipped with a universal diamond ATR sampling pod. Melting points were determined with a Büchi B-545 melting point apparatus. Low resolution mass spectra were obtained with a Hewlett-Packard HP 6890 Series GC system in combination with a HP 5973 mass spectrometer. High resolution mass spectra were obtained using a Orbitrap XL (Thermo Fisher Scientific) HR/MS with an APPI (Kr lamp) ionization source. UV irradiation was performed with a Spectroline ENB-280C/FE or Vilber VL-4.LC UV lamp, emitting at 365 nm or a 355 nm 10 mW CW laser (Cobalt - Zouk). Visible irradiation was carried out with a Thorlabs OSL1-EC fibre optic illuminator in combination with a > 440 nm longpass filter. Solvents used for spectroscopy and the self-assembly on gold were of UVASOL grade (Merck).

Tetrakis(triphenylphosphine)palladium(0) and bis(triphenylphosphine)palladium(II)dichloride were obtained from Strem Chemicals. Other chemicals and solvents were obtained from Aldrich, Acros, Merck, and Lab-Scan, and used as received. Column chromatography was performed on silica gel (SiliCycle SiliaFlash, 230-400 mesh) using methodology described by Still and coworkers.[1] All reactions were carried out under a nitrogen atmosphere, with the exception of lithium-halogen exchange reactions and Pd-catalysed cross-coupling reactions which were carried out under an argon atmosphere.

1.1 DFT calculation of Raman spectra

DFT calculations were performed with the Firefly 8.0.0 RC QC program,[2] which is based partially on GAMESS (US) source code.[3] Basis sets were obtained from the EMSL basis set exchange (https://bse.pnl.gov/bse/portal). In order to obtain a better correspondence between theoretical and experimental spectra, calculated Raman activities were converted to Raman intensities using the following formula:[4,5]

$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i\left(1 - e^{-\frac{hc\nu_i}{kT}}\right)}$$

where I_i is the Raman intensity, S_i is the Raman activity (Å^4 amu^{-1}), and ν_i is the wavenumber (cm^{-1}) of the *i*-th vibration, ν_0 is the wavenumber (cm^{-1}) of the excitation laser, *h* is the Planck constant (J s), *c* is the speed of light (m s^{-1}), k is the Boltzmann constant (J K^{-1}), *T* is the temperature (K), and *f* is an optional normalization factor. The calculated Raman intensities were convoluted with Lorentzian curves (full width at half maximum = 10 cm^{-1}) in order to obtain the theoretical spectrum. These post-processing steps were performed with the GaussSum 2.2.6.1 program.[6]

1.2 SERS experiments with colloidal gold

Aqueous colloidal gold was prepared from $HAuCl_4$ through reduction using trisodium citrate.[7] This resulted in the formation of aqueous gold colloid consisting of nanoparticles with an average diameter of 18 nm as determined by transmission electron microscopy (TEM). 1 mL of the gold colloid was added to a quartz cuvette, and 5–10 µL of an approx. 10^{-4} M solution of the dithienylethene in toluene/acetonitrile was added and mixed by shaking. 5–10 µL of aqueous 0.2 M NaCl was added, which caused aggregation of the gold colloid, after which the Raman spectrum of the mixture was recorded.

1.3 Preparation of 1 on gold/mica

150 nm thick gold films on mica were prepared by sublimation of gold in a custom-built high-vacuum evaporator (base pressure: 10^{-7} mbar). Prior to deposition, mica sheets were freshly cleaved and annealed at 375 °C for 16 h in order to remove impurities. After evaporation of gold at 375 °C and cooling to 50 °C, the gold/mica substrate obtained was immersed immediately into a 0.5 mM solution of dithienylethene $\mathbf{1_o}$ in DCM and left for 16 h at room temperature (rt). The slide was then removed, rinsed with DCM, and dried with air. The SAMs on gold/mica prepared in this way were used directly for XPS studies.

1.4 Preparation of 1 on gold beads

Gold beads were prepared by melting the tip of a 0.5 mm diameter gold wire (99.995 % Au, SHÖNE EDELMETAAL B.V.) with a butane torch until a bead with a 1–2 mm diameter had formed. The bead was then cleaned electrochemically by cycling between –0.6 V and 1.2 V in 0.5 M H_2SO_4 (aq.) with a Pt wire counter electrode and Hg/$HgSO_4$ reference electrode (CHIstruments), until a stable voltammogram was obtained. The area of the bead was determined after electrochemical cleaning from the AuO reduction wave in the last cleaning cycle (charge density of an AuO surface: 390 µC cm^{-2}). If roughening of the bead was desired, this was performed subsequently using a sweep step function: in 0.1 M aqueous KCl, using a Pt wire counter electrode and SCE reference electrode, the potential was increased from –0.3 V to 1.2 V at 1 V/s, held at 1.2 V for 30 s, and then reduced to –0.3 V at 0.5 V/s. This was repeated at least 24 times, causing the bead to obtain a greyish colour. After successive rinsing with ethanol and DCM, the bead was transferred directly into a 0.5 mM solution of dithienylethene **1** in DCM and left for at least 16 h. The bead was then rinsed with DCM and dried using a flow of nitrogen gas.

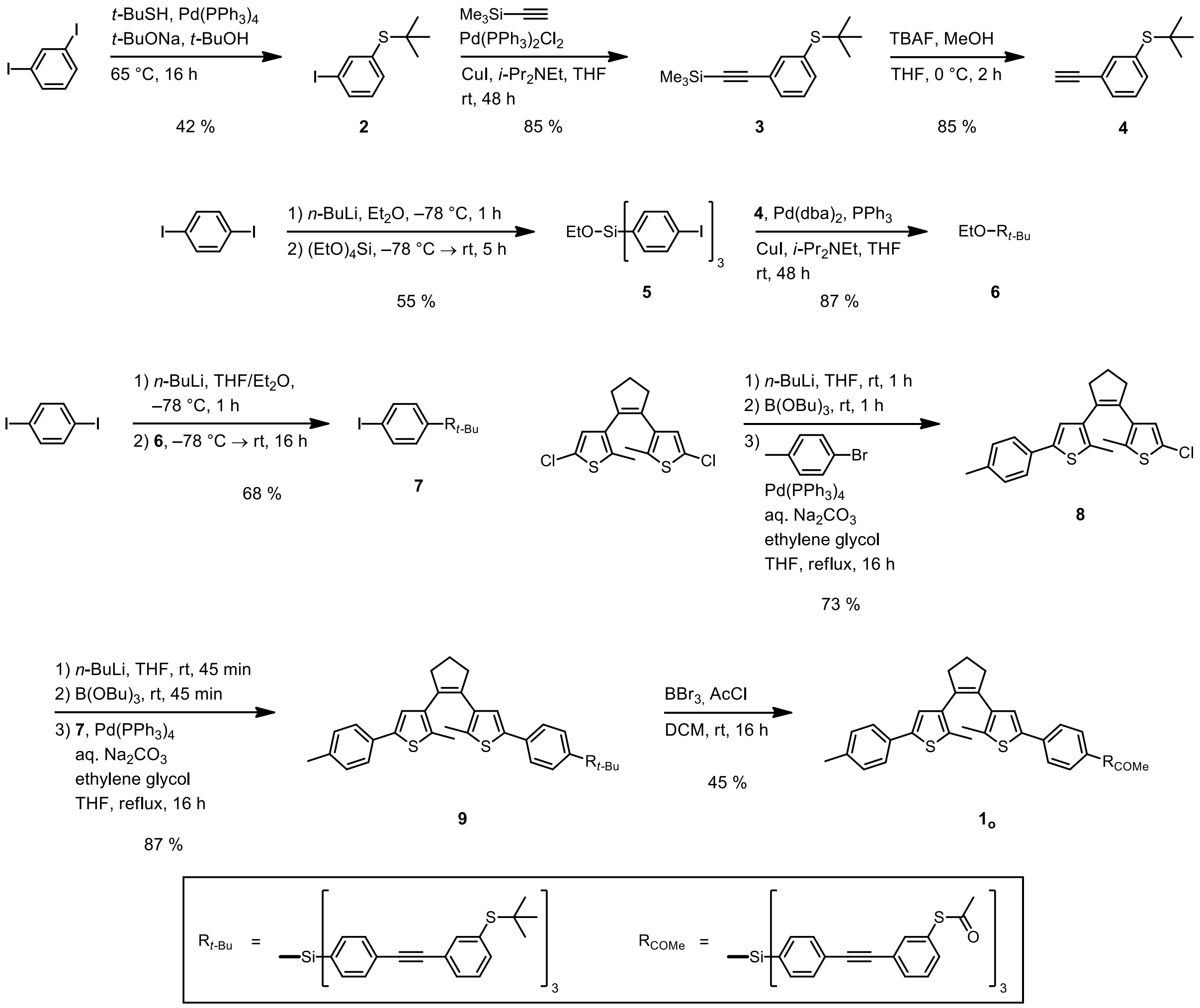
1.5 X-ray photoelectron spectroscopy

XPS was performed using a Surface Science SSX-100 ESCA instrument with a monochromatic Al K_α X-ray source ($h\nu$ = 1486.6 eV). The pressure in the measurement chamber was maintained below 1 × 10^{-9} mbar during data acquisition. The electron take-off angle with respect to the surface normal was 37°. The diameter of the analysed area was 1000 µm; the energy resolution was 1.07 eV (or 1.67 eV for a broad survey scan). XPS spectra were analysed using the least-squares curve fitting program Winspec.[8] Binding energies are reported ±0.1 eV and referenced to the Au $4f_{7/2}$ photoemission peak originating from the substrate, centred at a binding energy of 84 eV.[9] Deconvolution of the spectra included a Shirley[10] (for carbon, gold and oxygen) or linear (for sulfur) baseline subtraction and fitting with a minimum number of peaks consistent with the structure of the molecules on a surface, taking into account the experimental resolution. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. The uncertainty in the peak area determination is 4 % for sulfur and oxygen, and 1 % for carbon and gold. All measurements were carried out on freshly prepared samples. Irradiation of the slide at 365 nm was performed with the sample in XPS vacuum chamber, thus preserving a fixed sample position.

1.6 Cyclic voltammetry

Solution experiments were performed using a Telfon-shrouded glassy carbon working electrode (CH Instruments), a Pt wire counter electrode, and a saturated calomel electrode (SCE) reference in DCM/0.1 $TBAPF_6$. The concentration of the analyte was 0.50 mM. Experiments with SAMs of **1** on gold beads employed the gold bead as the working electrode, a Pt counter electrode, and an SCE reference electrode in DCM/0.1 $TBAPF_6$. iR compensation was employed with scan rates > 0.25 V s^{-1} in order to correct for solution resistance. The surface coverage of $\mathbf{1_c}$ on the gold beads was calculated using the cathodic and anodic parts of both redox waves displayed by $\mathbf{1_c}$.

2. Synthesis and characterisation



Scheme S1. Synthesis of dithienylethene $\mathbf{1_o}$.

Synthesis of *tert*-butyl(3-iodophenyl)sulfane (2)

A mixture of 1,3-diiodobenzene (33.9 g, 103 mmol), 2-methyl-2-propanethiol (11.1 g, 123 mmol), sodium tert-butoxide (23.7 g, 246 mmol), tetrakis(triphenylphosphine)palladium(0) (4.27 g, 3.69 mmol), and tert-butanol (1.3 L) was stirred at 65 °C for 16 h. The mixture was concentrated *in vacuo* and pentane (600 mL) was added. The resulting mixture was washed with water (2 x 300 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Column chromatography (silica gel, heptane + 0.2 % EtOAc, R_f = 0.55) yielded thioether **2** as a colourless solid (12.6 g, 42 %); mp 45–46 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, *J* = 1.7 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 1.29 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.7 (d), 137.7 (d), 136.6 (d), 135.2 (s), 130.1 (d), 94.0 (s), 46.5 (s), 31.1 (q); IR (neat) ν_{max} 2959, 1565, 1550, 1454, 1386, 1362, 1152, 1057, 995, 777, 741, 685, 647 cm^{-1}; Raman (neat) ν_{max} 3054, 2960, 2921, 2895, 1566, 1167, 1102, 1058, 996, 808, 743, 648, 583, 250 cm^{-1}; *m/z* (EI, %): 292 (M^+, 18), 236 (100); HRMS (APPI): calcd for $C_{10}H_{13}IS$: 291.9777, found: 291.9775.

Synthesis of ((3-(*tert*-butylthio)phenyl)ethynyl)trimethylsilane (3)

A mixture of thioether **2** (14.52 g, 49.70 mmol), trimethylsilylacetylene (7.32 g, 74.5 mmol, 10.6 mL), and *N*,*N*-diisopropylethylamine (10.9 g, 84.5 mmol, 14.7 mL) in THF (135 mL) was stirred for 30 min at rt. Bis(triphenylphosphine)palladium(II)dichloride (1.74 g, 2.48 mmol) and copper(I) iodide (473 mg, 2.48 mmol), both degassed *in vacuo* for 1 h, were added and the resulting mixture was stirred for

48 h at rt. Water (150 mL) and diethylether (150 mL) were added, after which the layers were separated and the water layer was extracted with diethylether (150 mL). The combined organic layers were washed with water (150 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by column chromatography (SiO_2, heptane/toluene 10:1, R_f = 0.50) provided thioether **3** as a slightly yellow liquid (11.06 g, 85 %); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (t, J = 1.5 Hz, 1H), 7.50–7.43 (m, 2H), 7.26 (t, J = 7.8 Hz, 1H), 1.29 (s, 9H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6 (d), 137.6 (d), 133.1 (s), 132.3 (d), 128.4 (d), 123.7 (s), 104.5 (s), 94.9 (s), 46.2 (s), 31.1 (q), 0.1 (q); IR (neat) ν_{max} 2961, 2162, 1466, 1364, 1250, 1161, 888, 843, 793, 760, 691 cm^{-1}; Raman (neat) ν_{max} 3060, 2961, 2922, 2898, 2163, 1582, 1217, 997, 646, 604, 593, 572 cm^{-1}; *m/z* (EI, %): 262 (M^+, 12), 206 (53), 191 (100); HRMS (APPI): calcd for $C_{15}H_{23}SSi$ ($[M + H]^+$): 263.1284, found: 263.1280.

Synthesis of *tert*-butyl(3-ethynylphenyl)sulfane (4)

A stirred solution of thioether **3** (11.1 g, 42.1 mmol) in THF (540 mL) and MeOH (8 mL) was cooled to 0 °C. Tetrabutyl ammonium fluoride (1.0 M in THF, 20.6 mmol, 20.6 mL) was added dropwise over 5 min, after which the mixture was stirred for 2 h at 0 °C. The mixture was poured onto saturated aqueous solution of NH_4Cl (500 mL) and extracted with CH_2Cl_2 (2 x 300 mL). The combined organic layers were washed with water (2 x 300 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The resulting oil was filtered over a short column of silica gel (pentane), providing thioether **4** as a slightly yellow liquid (7.35 g, 85 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 3.10 (s, 1H), 1.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8 (d), 137.9 (d), 133.3 (s), 132.4 (d), 128.5 (d), 122.6 (s), 83.1 (s), 77.9 (d), 46.2 (s), 31.1 (q); IR (neat) ν_{max} 3291, 2960, 1585, 1560, 1466, 1457, 1394, 1363, 1158, 1079, 900, 843, 792, 691, 652 cm^{-1}; Raman (neat) ν_{max} 3060, 2962, 2922, 2898, 2112, 1585, 1198, 999, 682, 599, 570, 466, 361 cm^{-1}; *m/z* (EI, %): 190 (M^+, 11), 134 (100).

Synthesis of ethoxytris(4-iodophenyl)silane (5)

A stirred suspension of 1,4-diiodobenzene (50.0 g, 152 mmol) in Et_2O (750 mL) was cooled to –78 °C and *n*-BuLi (1.6 M in hexane, 113.5 mmol, 70.9 mL) was added dropwise over 15 min. The resulting mixture was stirred for 1 h, after which tetraexthoxysilane (7.90 g, 37.9 mmol, 8.5 mL) was added at once and stirring was continued for 1 h. The mixture was allowed to warm to rt and stirred for an additional 4 h. Aqueous HCl (1 M, 125 mL) was added and the layers were separated after which the organic layer was washed with water (2 x 250 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Purification was performed by column chromatography (SiO_2, heptane/toluene 9:1, R_f = 0.45), which provided silane **5** as a white solid (14.20 g, 55 %); m.p. 177–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 6H), 7.28 (d, J = 8.2 Hz, 6H), 3.83 (q, J = 7.0 Hz, 2H), 1.22 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4 (d), 136.8 (d), 132.9 (s), 98.1 (s), 60.1 (t), 18.5 (q); IR (neat) ν_{max} 2967, 1565, 1474, 1373, 1116, 1104, 1077, 1055, 1002, 951, 802, 761, 724 cm^{-1}; Raman (neat) ν_{max} 3042, 1567, 1190, 1106, 1056, 694, 628, 329, 288, 252, 230 cm^{-1}; HRMS (APPI): calcd for $C_{20}H_{18}I_3OSi$ ($[M + H]^+$): 682.8256, found: 682.8242.

Synthesis of tris(4-((3-(*tert*-butylthio)phenyl)ethynyl)phenyl)(ethoxy)silane (6)

A mixture of silane **5** (8.00 g, 11.7 mmol), thioether **4** (13.3 g, 70.1 mmol), bis(dibenzylideneacetone)palladium(0) (1.01 g, 1.76 mmol), triphenylphosphine (1.54 g, 5.87 mmol), copper(I) iodide (302 mg, 1.58 mmol), *N*,*N*-diisopropylethylamine (267 mL), and THF (800 mL) was stirred at rt for 48 h. Water (600 mL) was added, after which the mixture was extracted with diethylether (3 x 750 mL). The combined organic layers were washed with water (2 x 500 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Column chromatography (SiO_2, heptane/toluene 4:3, R_f = 0.45) provided thioether **6** as a yellow sticky oil (5.35 g, 87 %); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (s, 3H), 7.63–7.49 (m, 18H), 7.32 (t, J = 7.7 Hz, 3H), 3.89 (q, J = 6.9 Hz, 2H), 1.31 (s, 27H), 1.26 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.3 (d), 137.6 (d), 135.3 (d), 134.4 (s), 133.3 (s), 131.9 (d), 131.1 (d), 128.5 (d), 125.0 (s), 123.6 (s), 90.2 (s), 89.9 (s), 60.1 (t), 46.2 (s), 31.1 (q), 18.5 (q); IR (neat) ν_{max} 2959, 1594, 1362, 1159, 1106, 1075, 823, 790, 766, 744, 687, 642 cm^{-1}; Raman (neat) ν_{max} 2223, 2189, 1595, 1584, 1150, 1094, 998, 600, 570 cm^{-1}.

Synthesis of tris(4-((3-(*tert*-butylthio)phenyl)ethynyl)phenyl)(4-iodophenyl)silane (7)

A stirred solution of 1,4-diiodobenzene (683 mg, 2.07 mmol) in THF (10 mL) and diethylether (10 mL) was cooled to –78 °C. *n*-Butyl lithium (1.6 M in hexane, 2.28 mmol, 1.4 mL) was added dropwise over 5 min, after which the resulting mixture was stirred at –78 °C for 1 h. A precooled solution of tris(4-((3-(*tert*-butylthio)phenyl)ethynyl)phenyl)(ethoxy)silane (**6**, 1.50 g, 1.73 mmol) in THF (20 mL) was added and the resulting mixture was stirred at –78 °C for 30 min, after which it was allowed to warm to rt overnight. Water (50 mL) and ethyl acetate (50 mL) were added and the layers were separated. The aqueous layer was extracted with ethyl acetate (50 mL), after which the combined organic layers were washed with water (50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Column chromatography (SiO_2, heptane/toluene 4:3) provided thioether **7** as a sticky oil (1.21 g, 68 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.72 (t, J = 1.5 Hz, 3H), 7.58–7.50 (m, 18H), 7.32 (t, J = 7.7 Hz, 3H), 7.27 (d, J = 7.1 Hz, 2H), 1.32 (s, 27H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4 (d), 137.9 (d), 137.6 (d), 137.4 (d), 136.3 (d), 133.6 (s), 133.4 (s), 132.7 (s), 132.0 (d), 131.3 (d), 128.6 (d), 125.0 (s), 123.6 (s), 97.8 (s), 90.4 (s), 89.8 (s), 46.3 (s), 31.2 (q); IR (neat) ν_{max} 2958, 1594, 1455, 1362, 1158, 1103, 1004, 822, 790, 765, 714, 687, 643 cm^{-1}; Raman (neat) ν_{max} 2223, 2190, 1594, 1583, 1150, 1091, 997, 599, 570 cm^{-1}; HRMS (APPI): calcd for $C_{60}H_{55}IS_3Si$: 1026.2274, found: 1026.2264.

Synthesis of 5-chloro-2-methyl-3-(2-(2-methyl-5-(*p*-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophene (8)

n-BuLi (1.6 M solution in hexane, 3.19 mmol, 2.0 mL) was added dropwise to a stirred solution of 1,2-bis(5-chloro-2-methylthiophen-3-yl)cyclopent-1-ene (1.00 g, 3.04 mmol) in THF (40 mL), after which stirring was continued for 1 h. Tributyl borate (978 mg, 4.25 mmol, 1.1 mL) was added dropwise and the resulting mixture was stirred for an additional 1 h. Meanwhile, in a separate flask, a stirred mixture of 4-bromotoluene (779 mg, 4.55 mmol), $Pd(PPh_3)_4$ (105 mg, 91.1 µmol), ethylene glycol (0.4 mL), aqueous Na_2CO_3 (2 M, 16 mL), and THF (24 mL) was heated to 70 °C. The crude boronic ester was added and the resulting mixture was refluxed for 16 h. The mixture was diluted with Et_2O (100 mL) and washed with water (2 x 50 mL). The combined aqueous layers were extracted with Et_2O (50 mL), after which the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2, heptane + 1 % EtOAc, R_f = 0.5) provided dithienylethene **8** as a slightly pink oil (848 mg, 73 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 6.93 (s, 1H), 6.62 (s, 1H), 2.83–2.71 (m, 4H), 2.34 (s, 3H), 2.09–2.00 (m, 2H), 1.98 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1 (s), 137.0 (s), 136.4 (s), 135.5 (s), 135.3 (s), 134.0 (s), 133.7 (s), 133.4 (s), 131.8 (s), 129.6 (d), 127.0 (d), 125.4 (d), 125.1 (s), 123.4 (d), 38.6 (t), 38.5 (t), 23.1 (t), 21.2 (q), 14.5 (q), 14.29 (q); IR (neat) ν_{max} 2916, 2842, 1512, 1437, 1164, 1004, 828, 810, 750 cm^{-1}; Raman (neat) ν_{max} 2916, 1634, 1612, 1556, 1514, 1470, 1378, 1245, 1211, 1186, 793, 704 cm^{-1}; HRMS (APPI): calcd for $C_{22}H_{22}ClS_2$ ([M + H]$^+$): 385.0846, found: 385.0840.

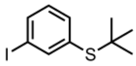
Synthesis of tris(4-((3-(*tert*-butylthio)phenyl)ethynyl)phenyl)(4-(5-methyl-4-(2-(2-methyl-5-(*p*-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)phenyl)silane (9)

5-Chloro-2-methyl-3-(2-(2-methyl-5-(*p*-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophene (**8**, 725 mg, 1.88 mmol) was dissolved in THF (20 mL). *n*-BuLi (1.6 M solution in hexane, 2.07 mmol, 1.3 mL) was added dropwise, after which stirring was continued for 45 min. Tributyl borate (476 mg, 2.07 mmol, 0.56 mL) was added dropwise and stirring was continued for 45 min. Meanwhile, in a separate flask, a stirred mixture of tris(4-((3-(tert-butylthio)phenyl)ethynyl)phenyl)(4-iodophenyl)silane (**7**, 1.45 g, 1.41 mmol), $Pd(PPh_3)_4$ (65.2 mg, 56.4 µmol), ethylene glycol (0.20 mL), aqueous Na_2CO_3 (2 M, 12 mL), and THF (8 mL) was heated to 70 °C. The crude boronic ester was added and the resulting mixture was refluxed for 16 h. The mixture was diluted with pentane (50 mL) and washed with water (2 x 50 mL). The combined aqueous layers were extracted with pentane (50 mL), after which the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Column chromatography (SiO_2, heptane/toluene 4:3) provided dithienylethene **9** as a light grey sticky oil (1.53 g, 87 %); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (s, 3H), 7.57–7.49 (m, 22H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.10 (s, 1H), 6.99 (s, 1H), 2.87–2.81 (m, 4H), 2.34 (s, 3H), 2.11–2.04 (m, 2H), 2.01 (s, 3H), 1.98 (s, 3H), 1.31 (s, 27H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4 (d), 140.0 (s), 139.2 (s), 137.6 (d), 137.1 (s), 136.95 (d), 136.92 (s), 136.6 (s), 136.3 (d), 136.2 (s), 135.4 (s), 135.1 (s), 134.5 (s), 134.3 (s), 134.0 (s), 133.4 (s), 132.0 (d), 131.9 (s), 131.4 (s), 131.2 (d), 129.6 (d), 128.6 (d), 125.4 (d), 125.0 (d), 124.9 (d), 124.8 (s), 123.7 (s), 123.6 (d), 90.2 (s), 89.9 (s), 46.3 (s), 38.64 (t), 38.59 (t), 31.2 (q), 23.2 (t), 21.3 (q), 14.7 (q), 14.5 (q); IR (neat) ν_{max} 2957, 1593, 1455, 1392, 1362, 1159, 1103, 821, 812, 790,764, 737, 686, 644 cm^{-1}; Raman (neat) ν_{max} 2223, 2189, 1594, 1583, 1502, 1465, 1149, 1091, 997 cm^{-1}; HRMS (APPI): calcd for $C_{82}H_{76}S_5Si$: 1271.4212, found: 1271.4224.

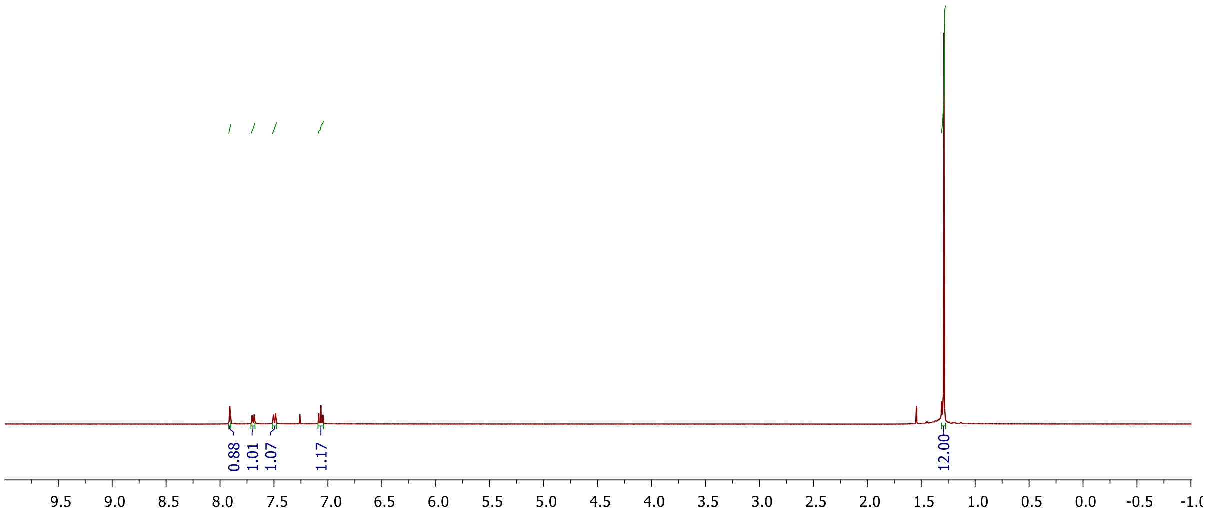
Synthesis of *S,S',S''*-(((((4-(5-methyl-4-(2-(2-methyl-5-(*p*-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)phenyl)silanetriyl)tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))tris(benzene-3,1-diyl)) triethanethioate (1)

Tris(4-((3-(*tert*-butylthio)phenyl)ethynyl)phenyl)(4-(5-methyl-4-(2-(2-methyl-5-(*p*-tolyl)thiophen-3-yl)cyclopent-1-en-1-yl)thiophen-2-yl)phenyl)silane (**9**, 1.50 g, 1.20 mmol) was dissolved in dichloromethane (60 mL) and acetyl chloride (2.83 g, 36.0 mmol, 2.6 mL) was added. Boron tribromide (1.0 M in CH_2Cl_2, 3.96 mmol, 4.0 mL) was added dropwise over 5 min, after which the resulting mixture was stirred for 16 h. Water (50 mL) and ethyl acetate (50 mL) were added and the layers were separated. The inorganic layer was extracted with ethyl acetate (50 mL), after which the combined organic layers were washed with water (50 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Column chromatography (SiO_2, heptane/ethyl acetate 67:1) provided dithienylethene **1** as a brown sticky oil (659 mg, 45 %); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 3H), 7.59–7.49 (m, 19H), 7.43–7.37 (m, 8H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 1H), 6.99 (s, 1H), 2.84 (t, *J* = 7.5 Hz, 4H), 2.44 (s, 9H), 2.34 (s, 3H), 2.13–2.04 (m, 2H), 2.01 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.6 (s), 134.0 (s), 139.2 (s), 137.5 (d), 137.1 (s), 137.0 (d), 136.6 (s), 136.3 (d), 136.2 (s), 135.4 (s), 135.0 (s), 134.5 (d), 134.3 (s), 134.0 (s), 132.7 (d), 131.9 (s), 131.2 (d), 129.6 (d), 129.3 (d), 128.4 (s), 125.4 (d), 125.0 (d), 124.8 (d), 124.6 (s), 124.5 (s), 123.6 (d), 90.5 (s), 89.7 (s), 38.65 (t), 38.61 (t), 30.4 (q), 23.2 (t), 21.3 (q), 14.7 (q), 14.6 (q); IR (neat) ν_{max} 2915, 1705, 1593, 1497, 1101, 1018, 946, 884, 820, 787, 765, 737, 684 cm^{-1}; Raman (neat) ν_{max} 2224, 2190, 1586, 1502, 1466, 1152, 1090, 996 cm^{-1}; HRMS (APPI): calcd for $C_{76}H_{59}O_3S_5Si$ ([M + H]$^+$): 1207.2832, found: 1207.2804.

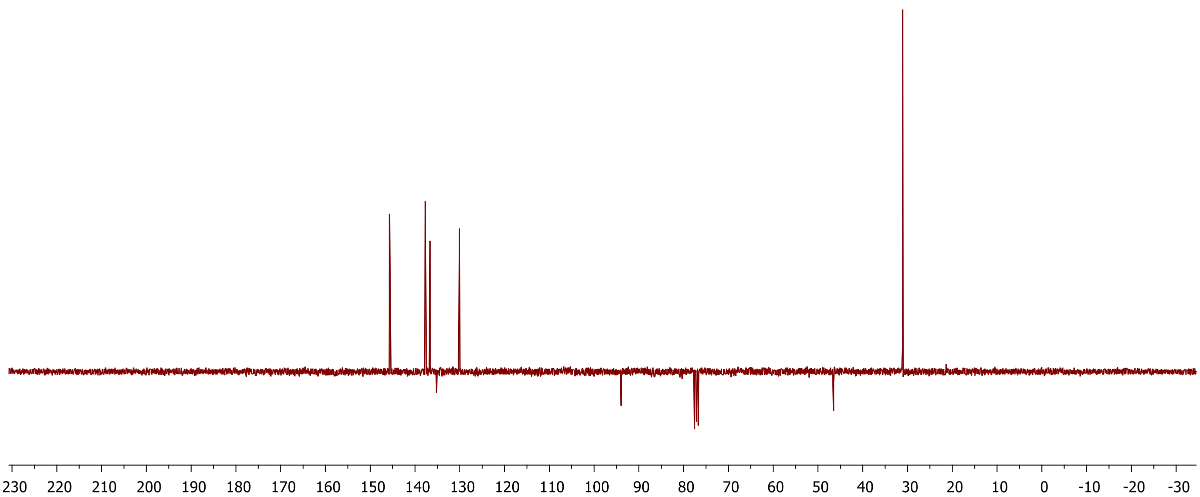
3. **NMR spectra of 1 and its precursors**

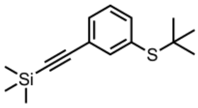


^{1}H NMR (400 MHz, $CDCl_3$):

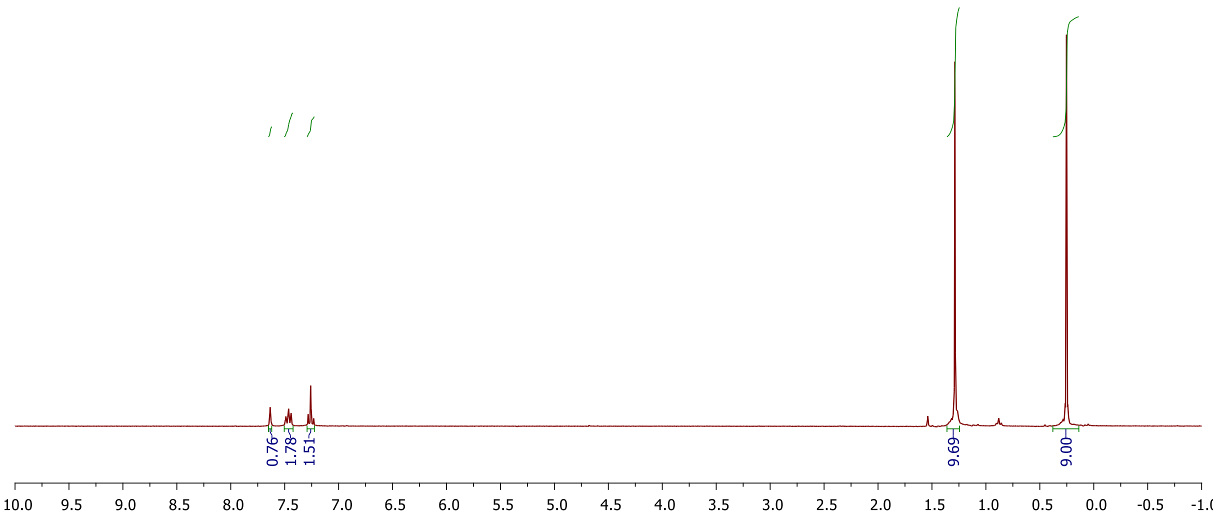


APT (75 MHz, $CDCl_3$):

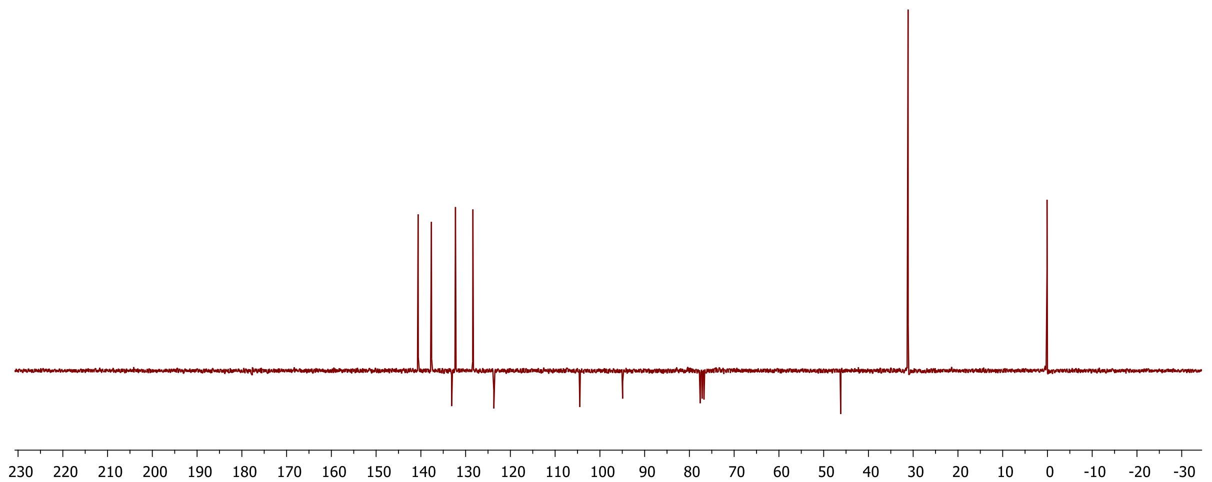


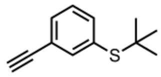


^{1}H NMR (300 MHz, $CDCl_3$):

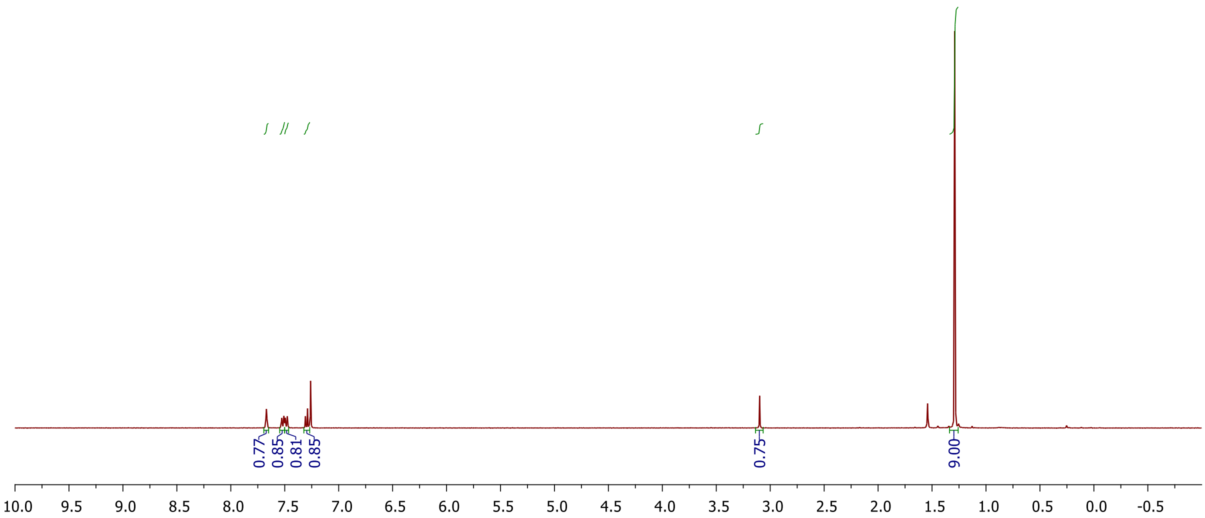


APT (75 MHz, $CDCl_3$):

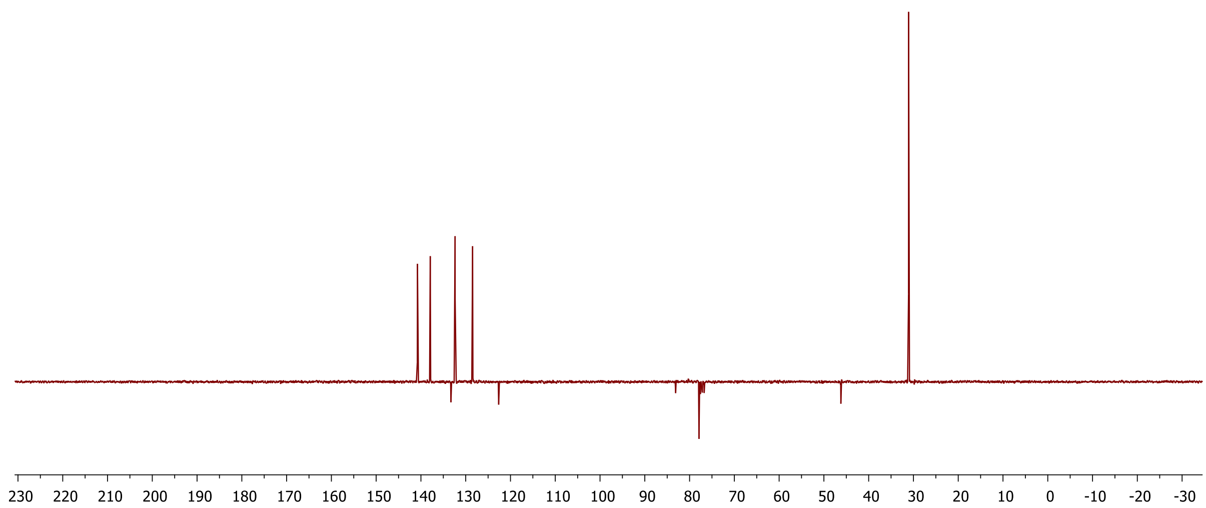


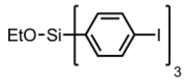


^{1}H NMR (400 MHz, $CDCl_3$):

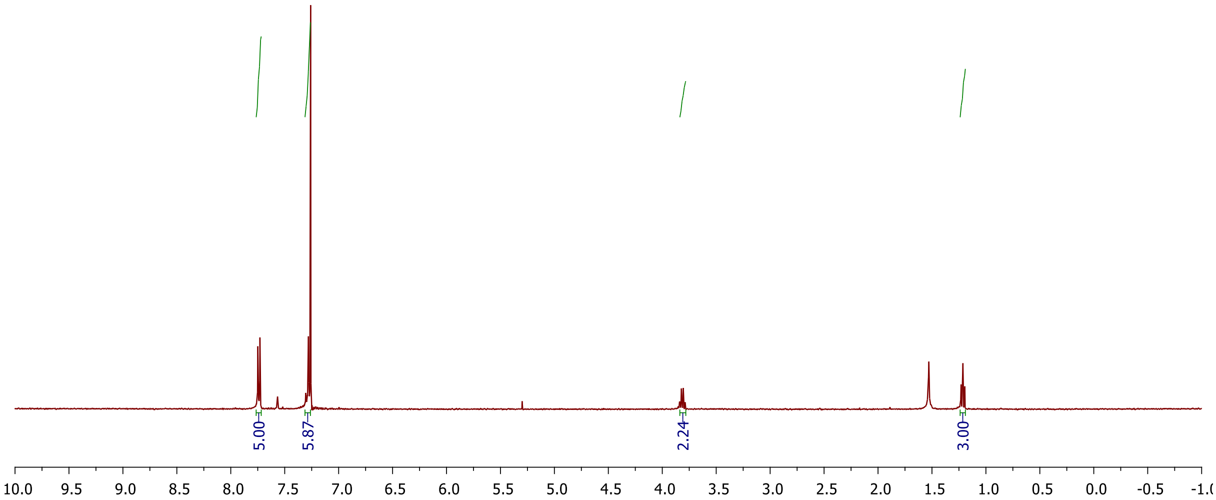


APT (75 MHz, $CDCl_3$):

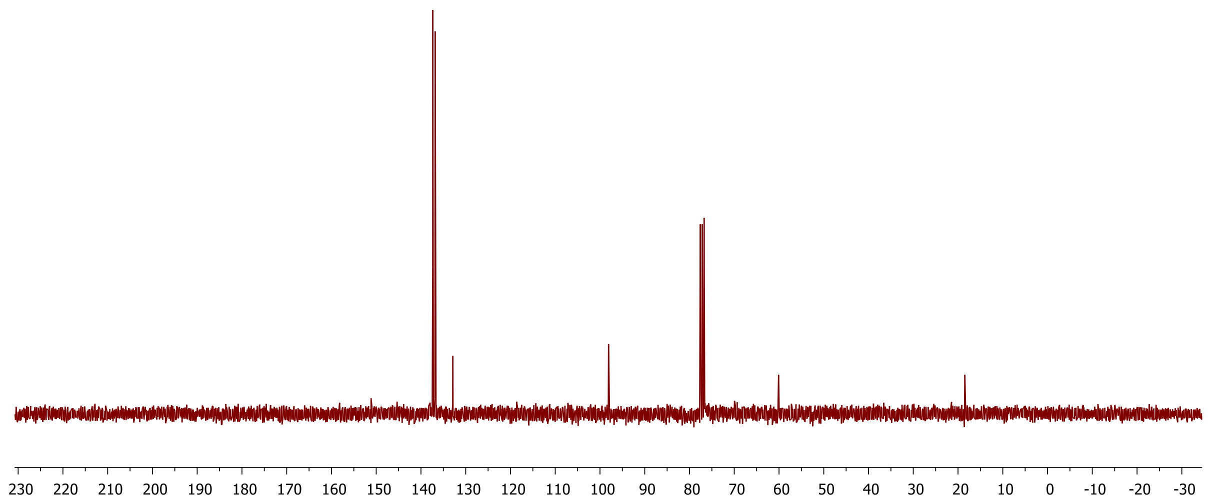


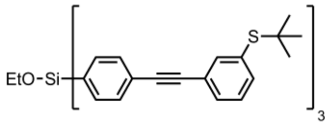


^1H NMR (400 MHz, $CDCl_3$):

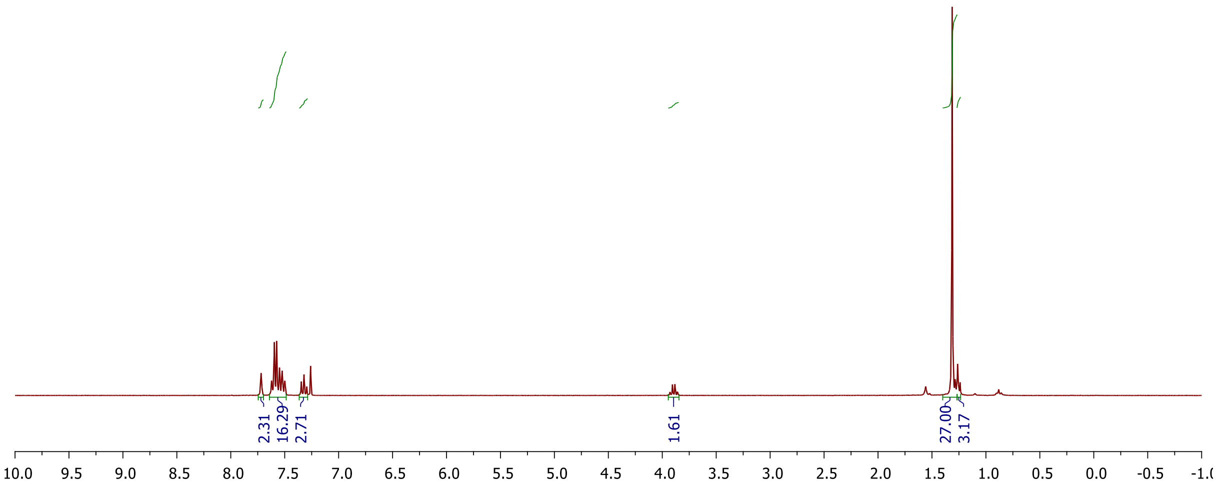


^{13}C NMR (75 MHz, $CDCl_3$):

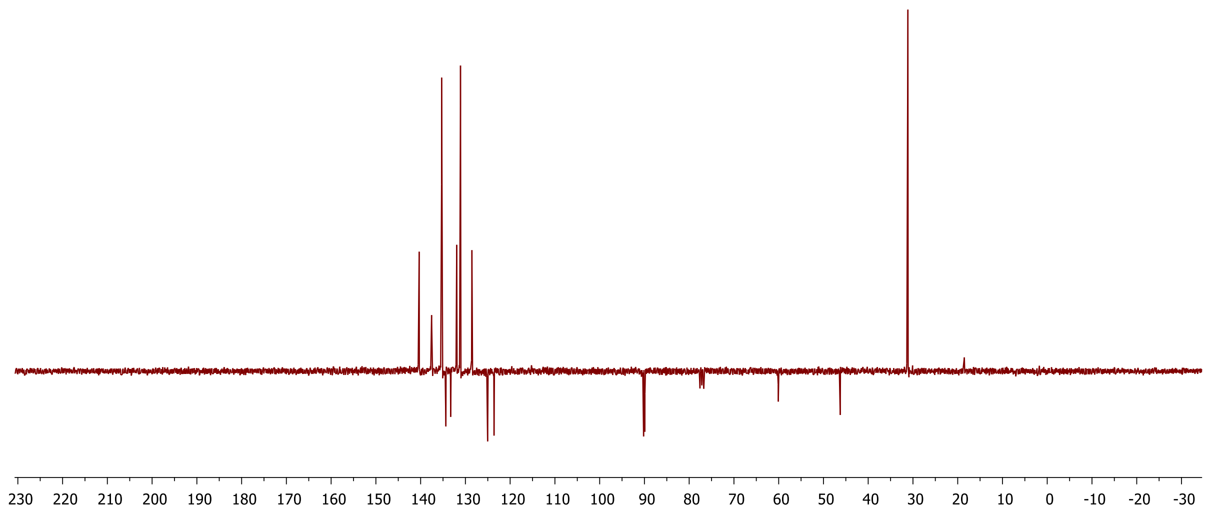


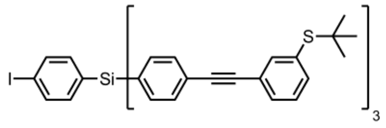


^{1}H NMR (300 MHz, $CDCl_3$):

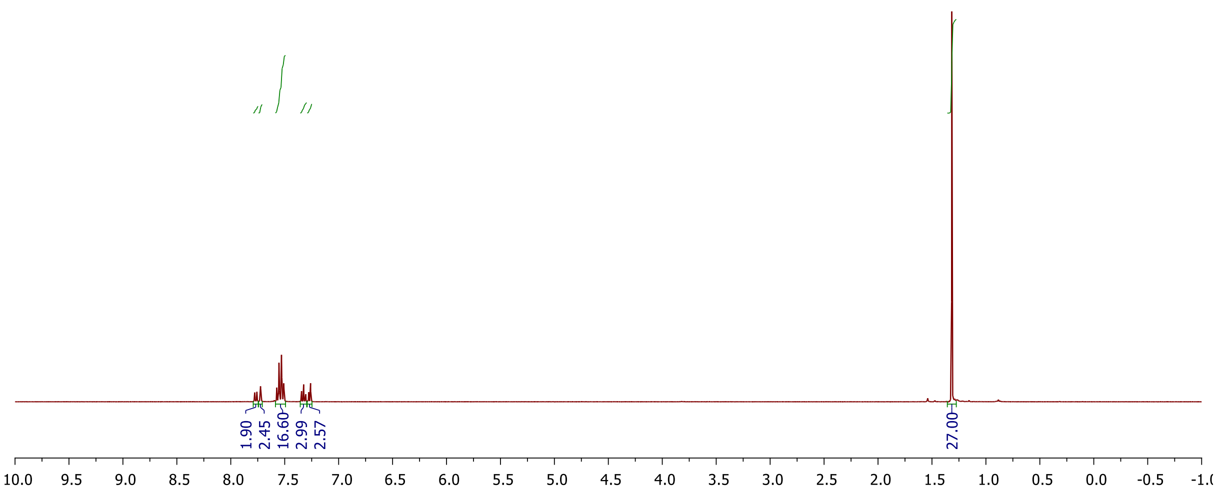


APT (75 MHz, $CDCl_3$):

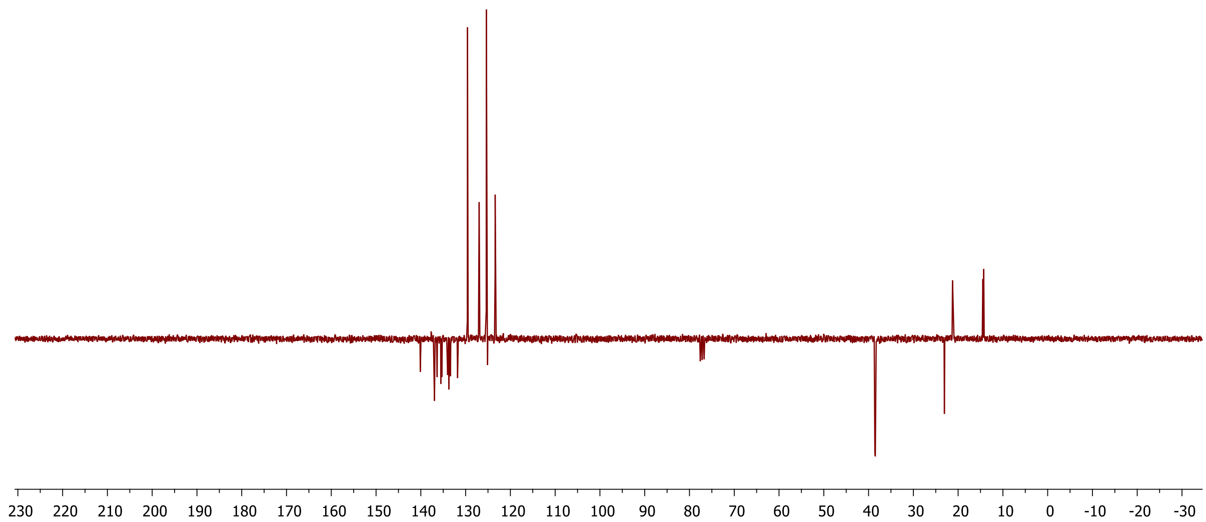


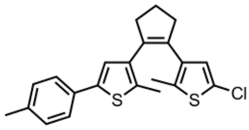


^{1}H NMR (400 MHz, $CDCl_3$):

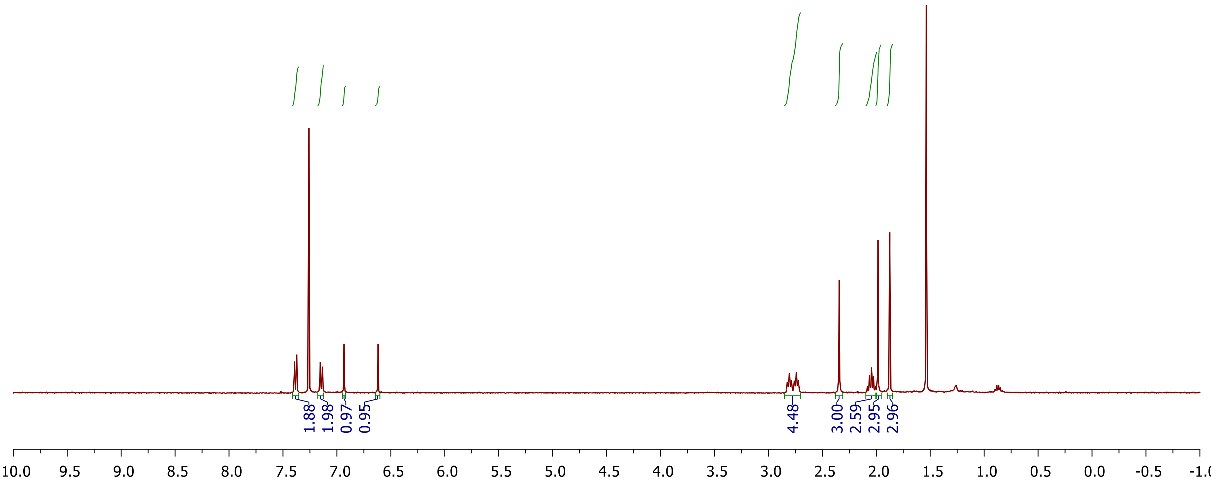


APT (75 MHz, $CDCl_3$):

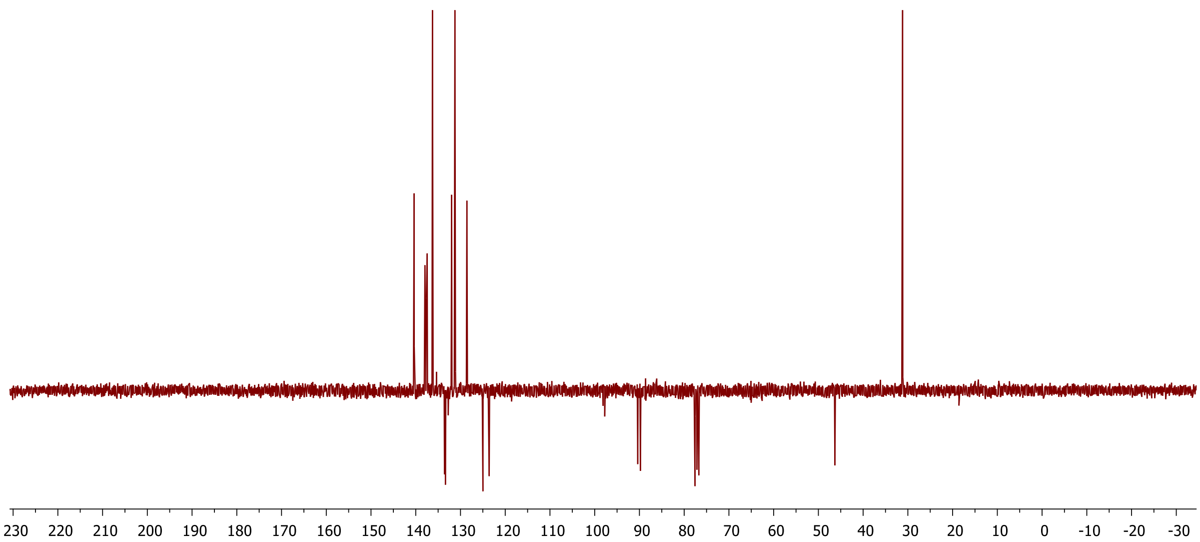


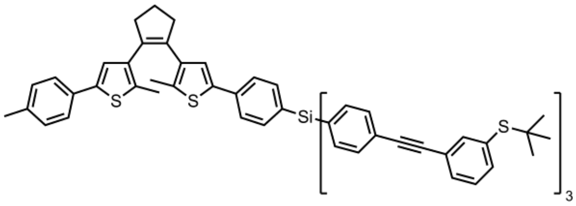


^{1}H NMR (400 MHz, $CDCl_3$):

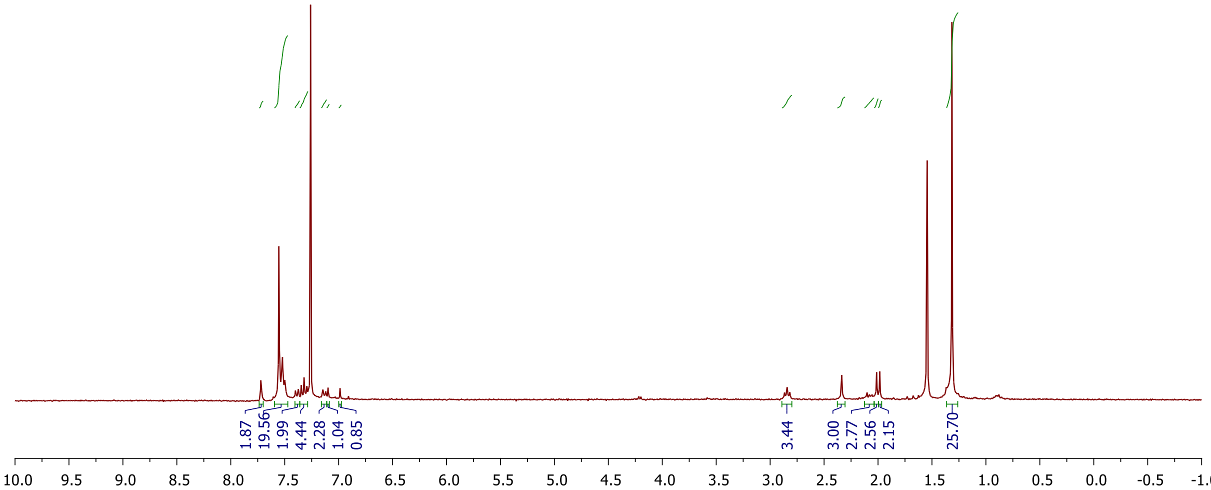


APT (75 MHz, $CDCl_3$):

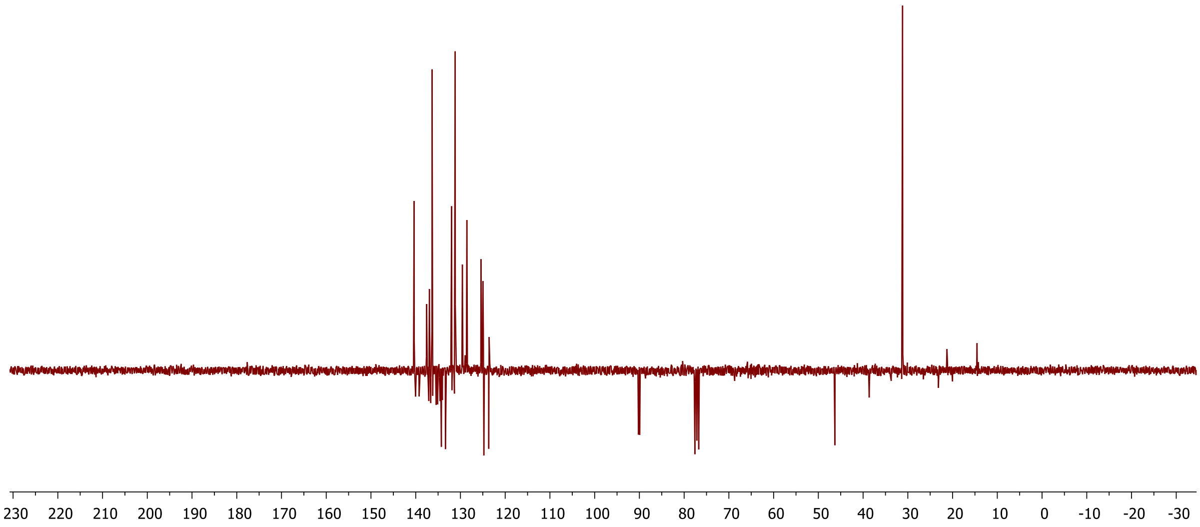


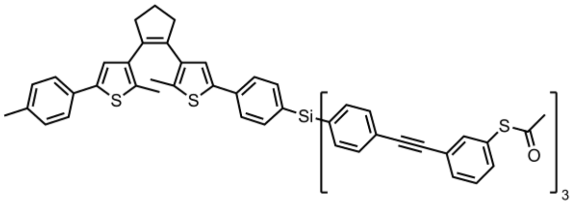


[1]H NMR (300 MHz, $CDCl_3$):

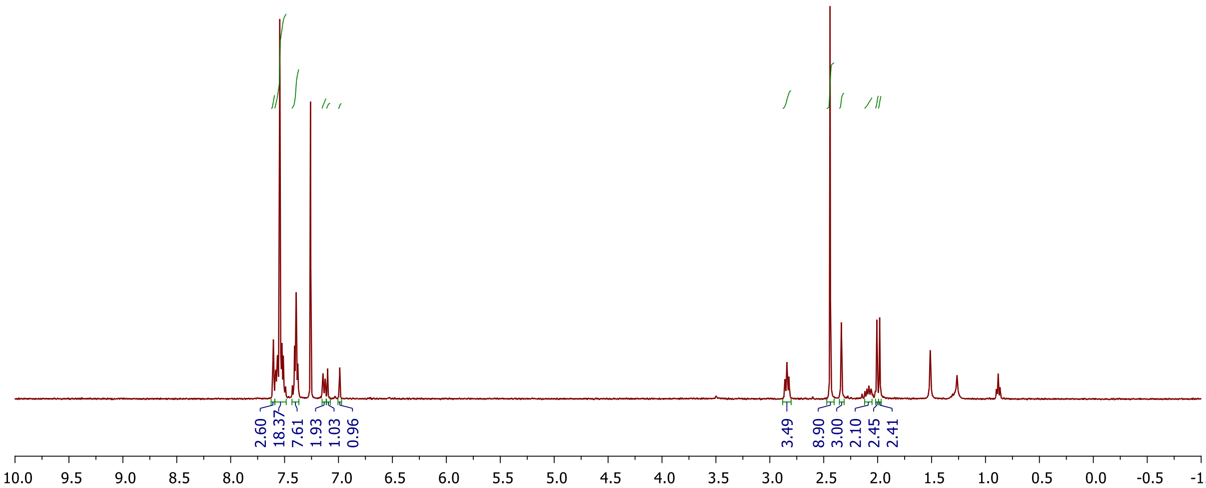


APT (75 MHz, $CDCl_3$):

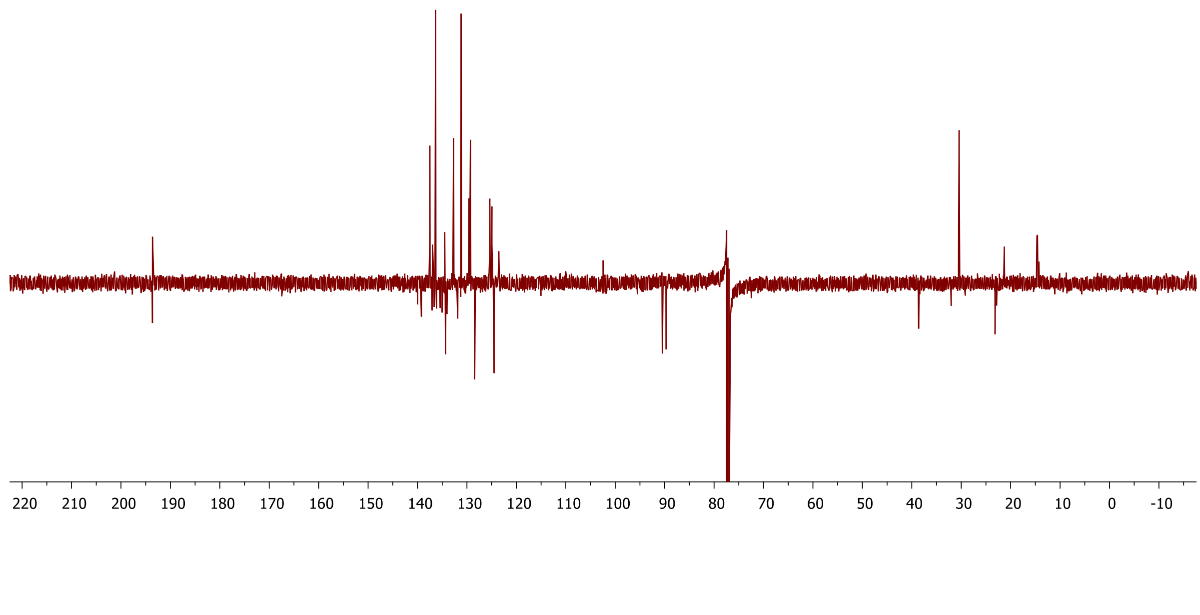




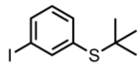
^{1}H NMR (400 MHz, $CDCl_3$):



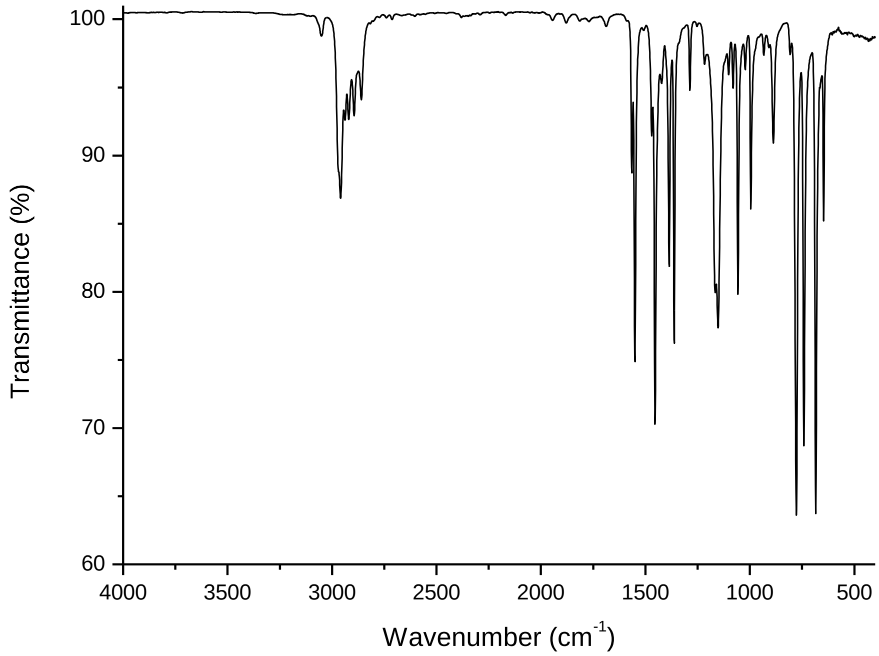
APT (126 MHz, $CDCl_3$):



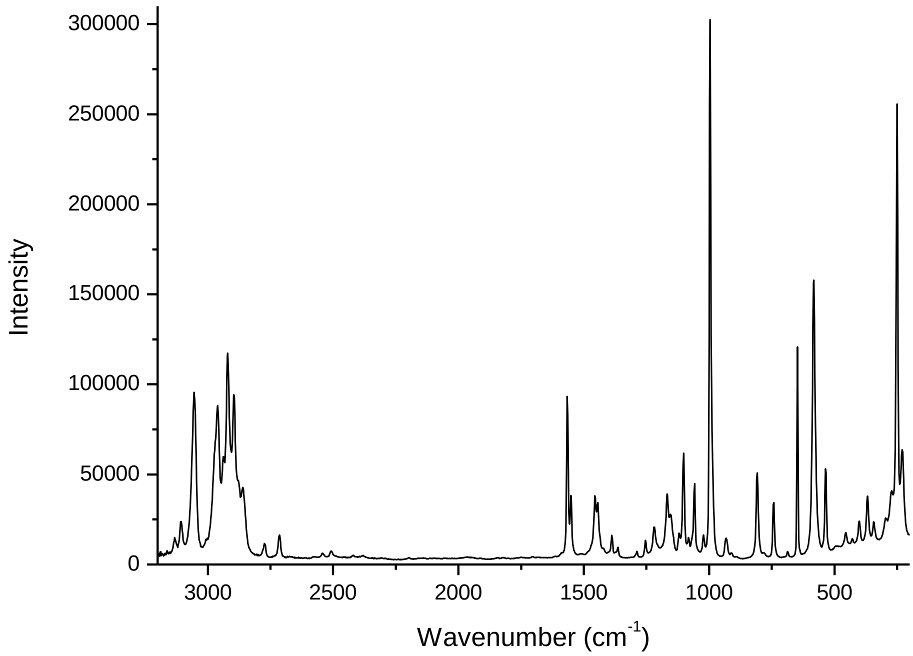
4. **Infrared absorption spectra and Raman spectra of 1 and its precursors**

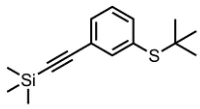


IR spectrum (neat):

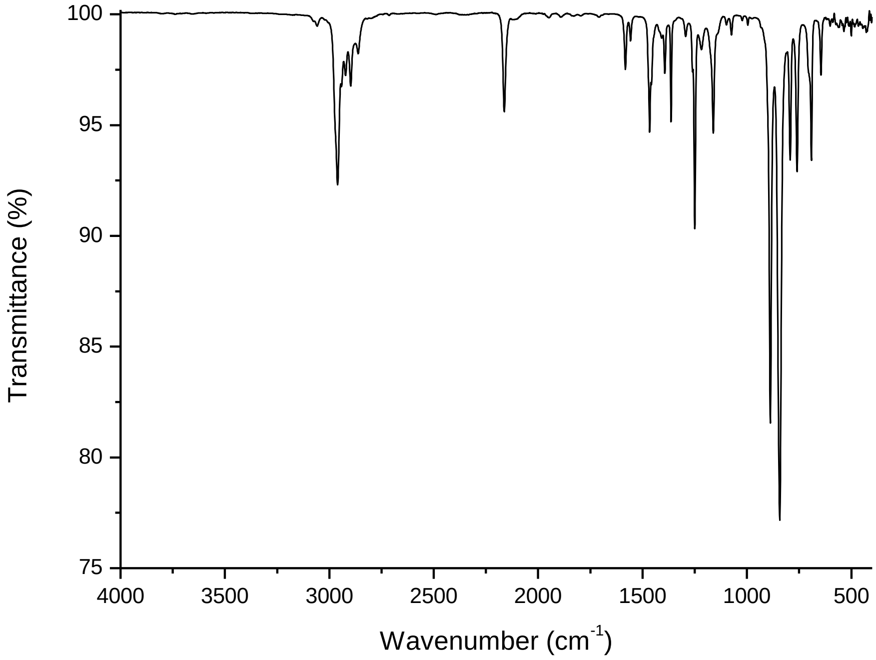


Raman spectrum (neat):

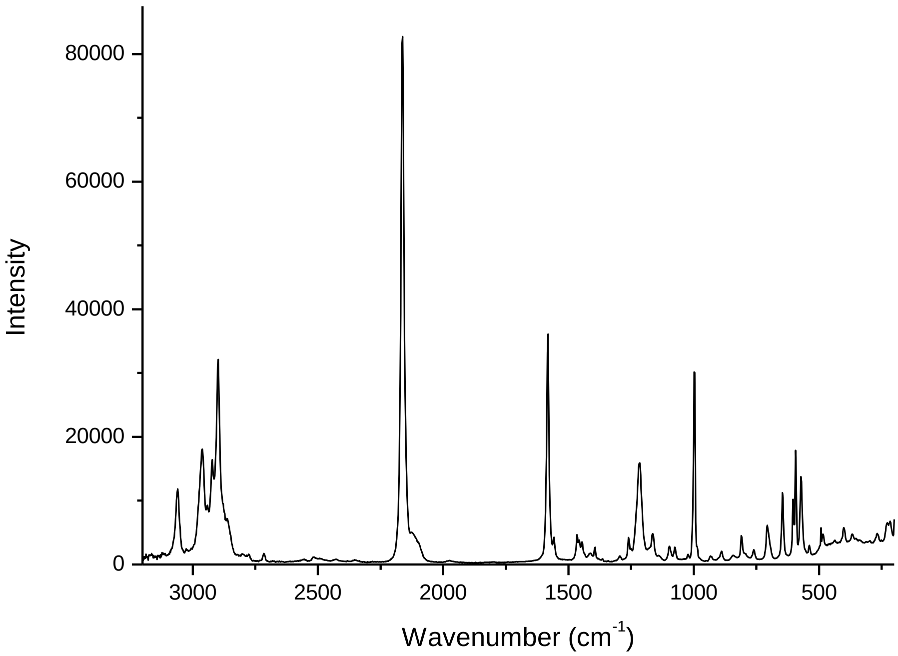


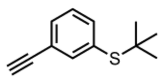


IR spectrum (neat):

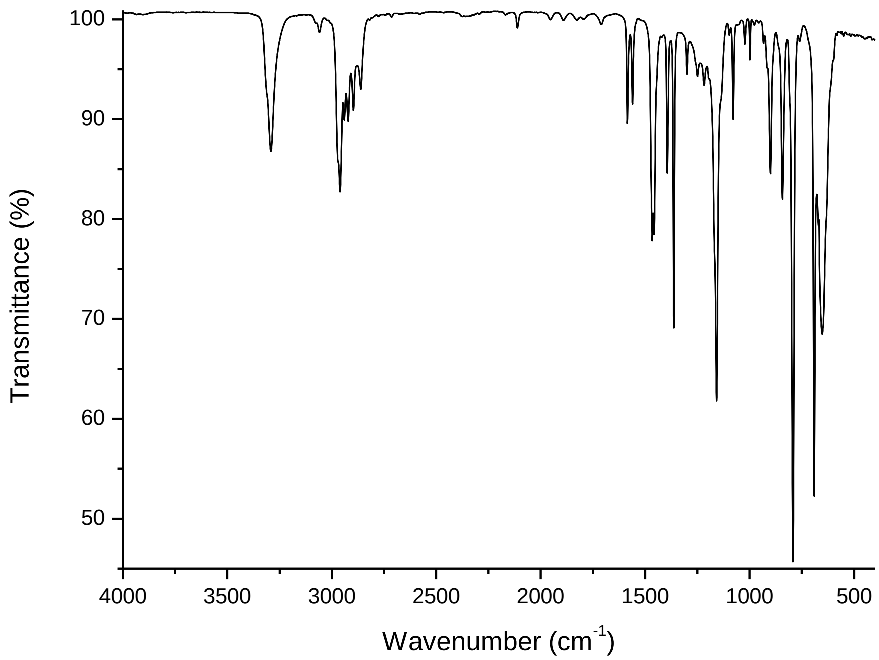


Raman spectrum (neat):

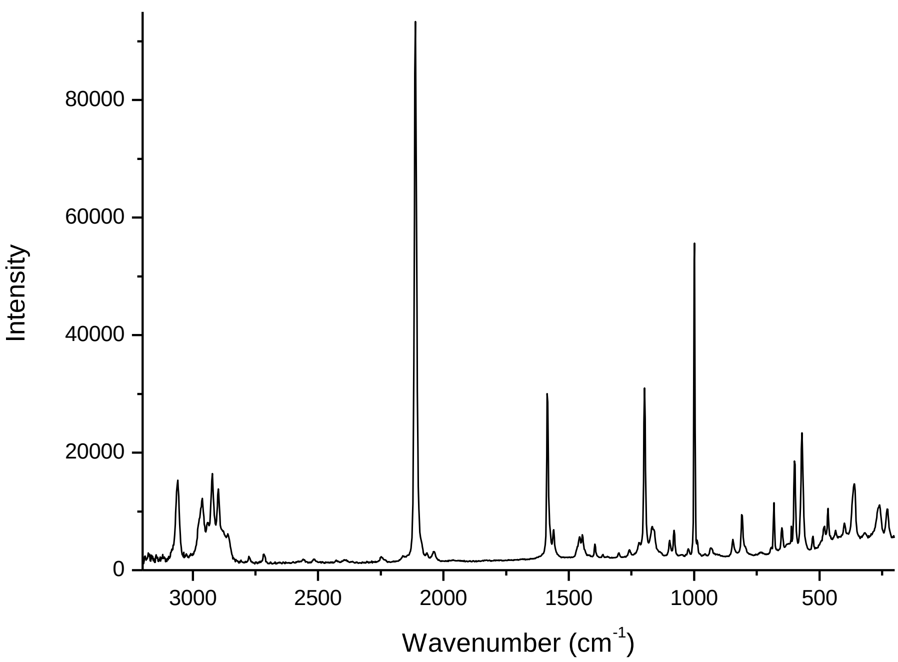


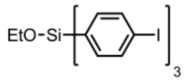


IR spectrum (neat):

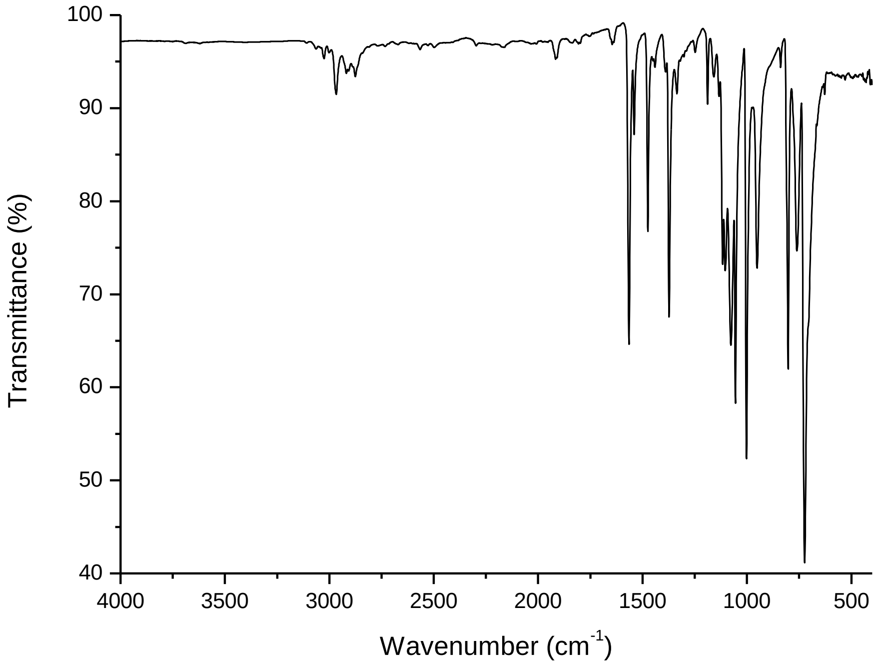


Raman spectrum (neat):

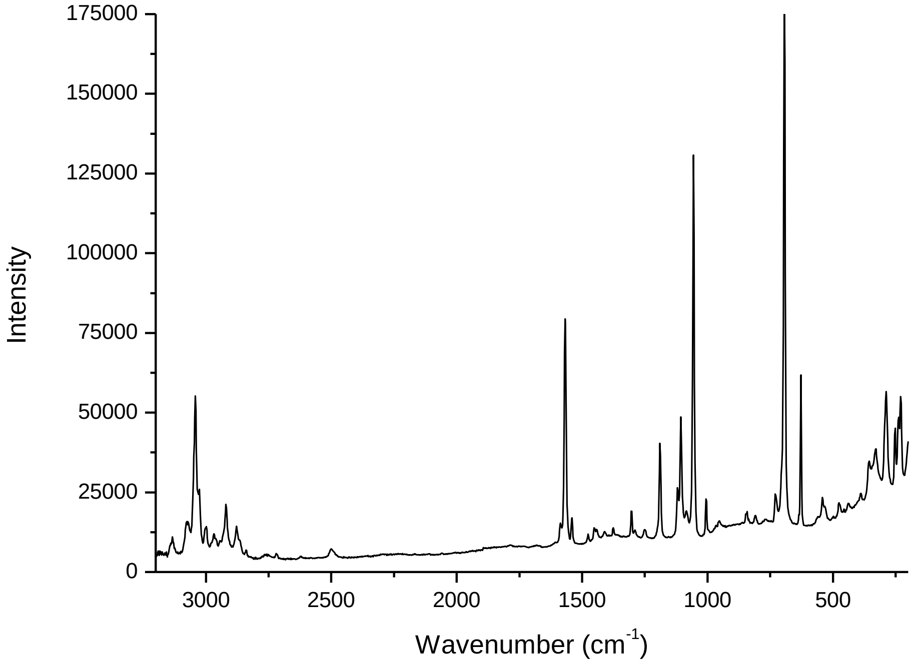


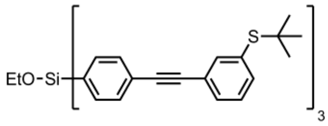


IR spectrum (neat):

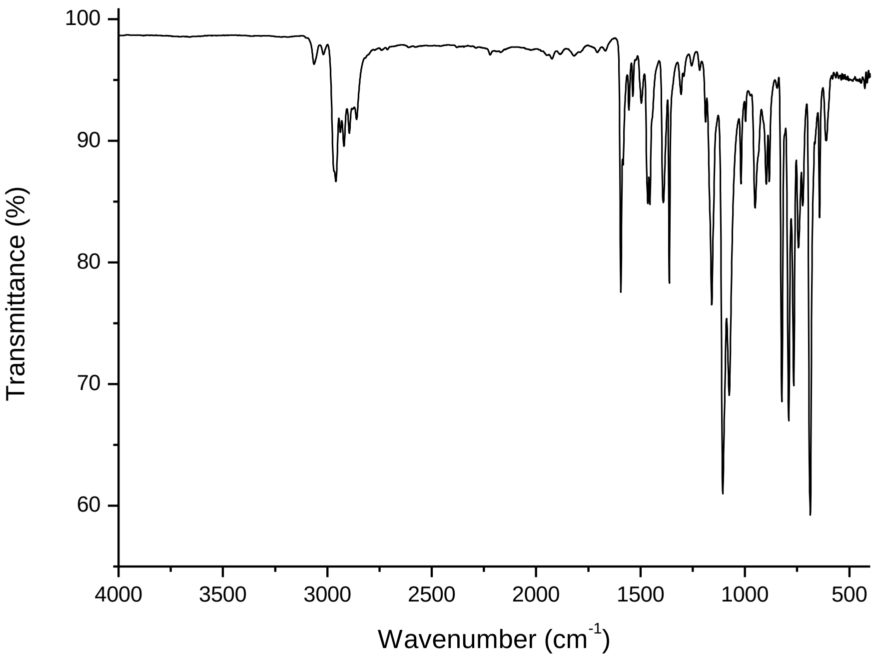


Raman spectrum (neat):

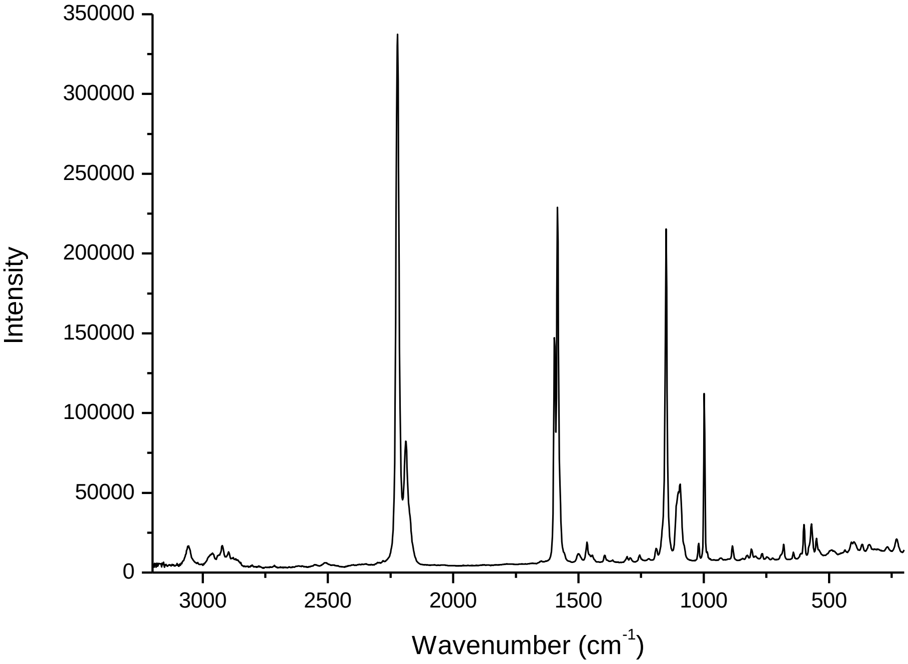


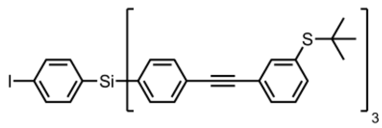


IR spectrum (neat):



Raman spectrum (neat):





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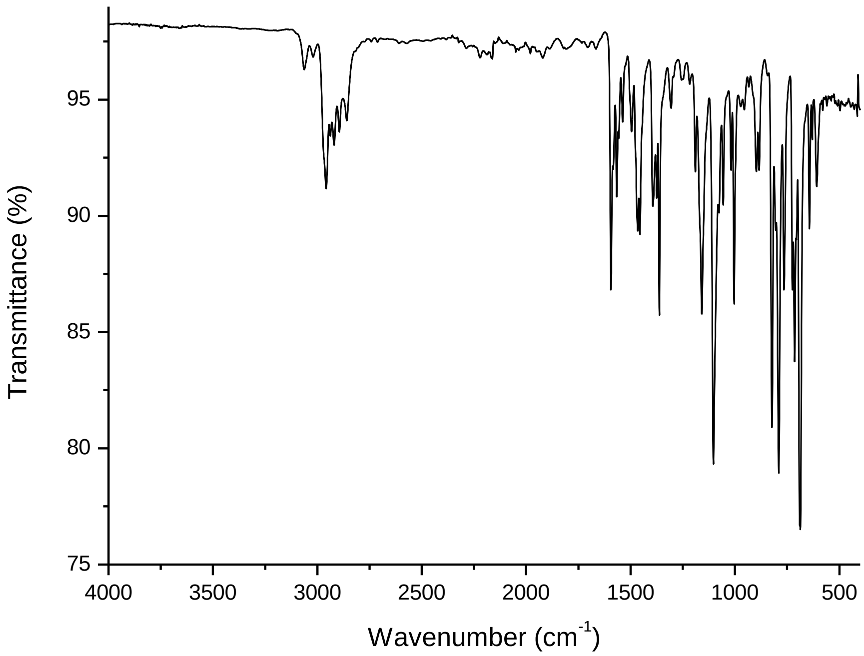

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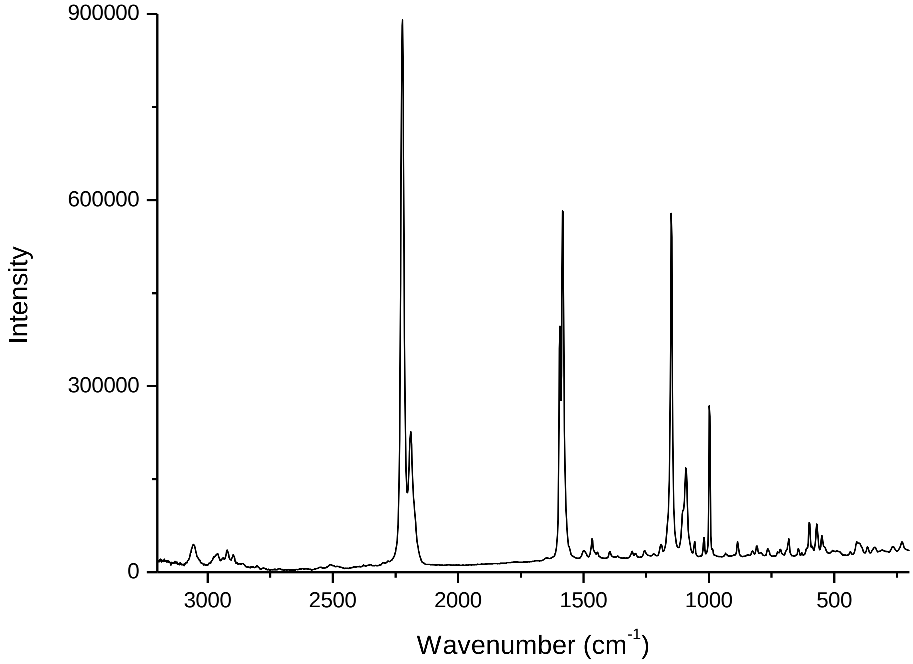
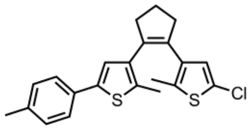
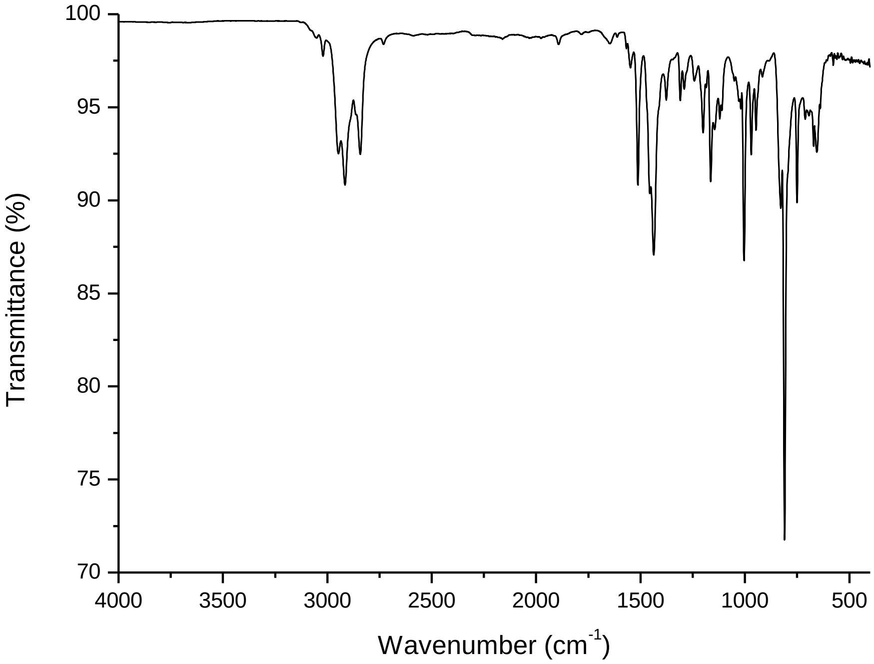




IR spectrum (neat):



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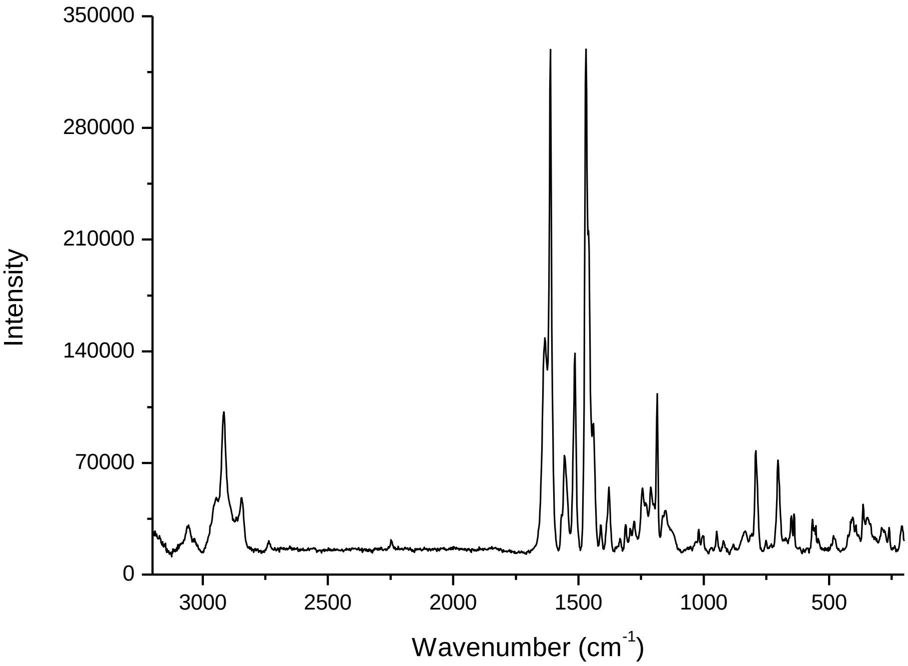
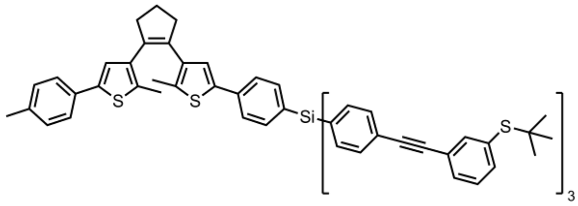
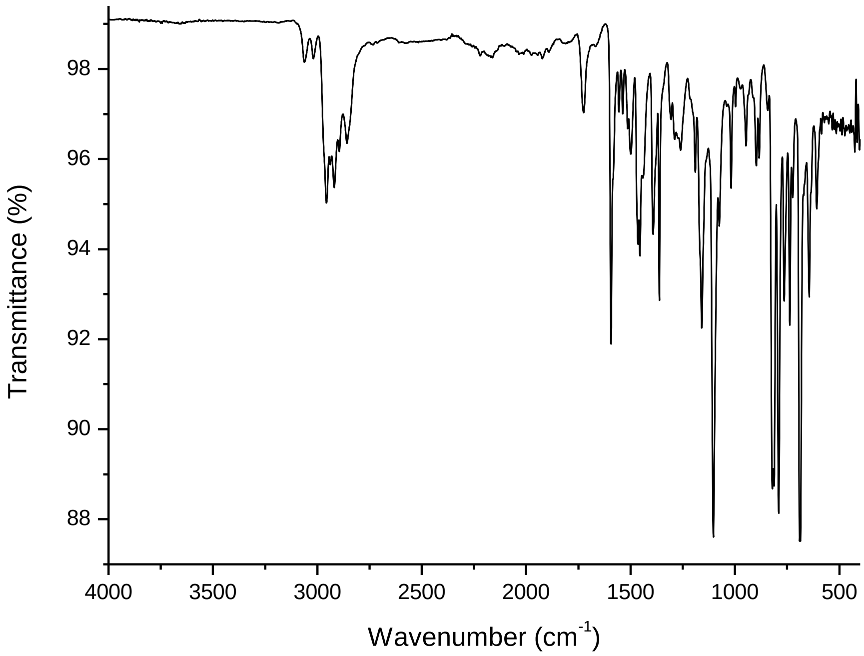
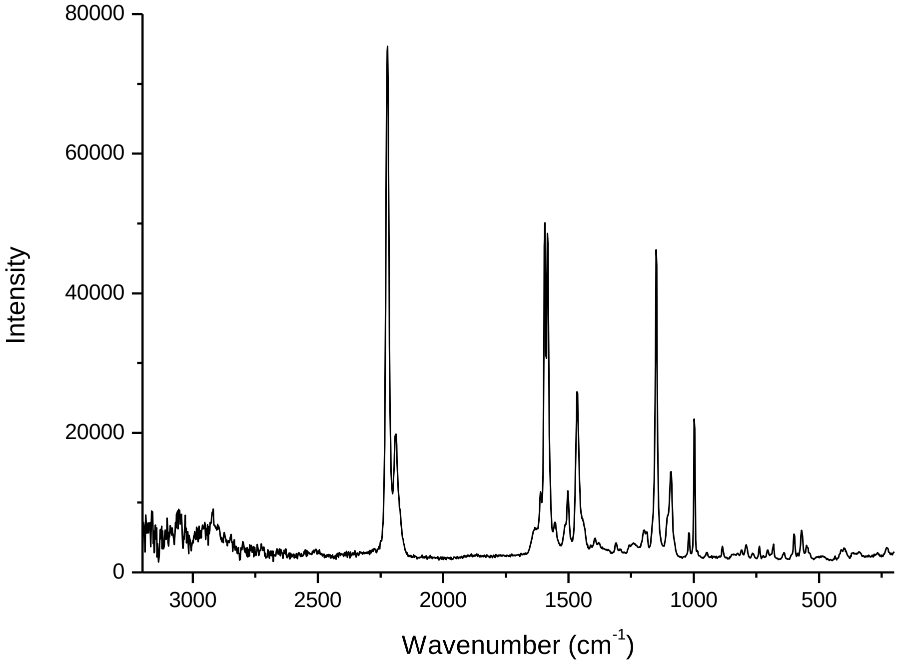


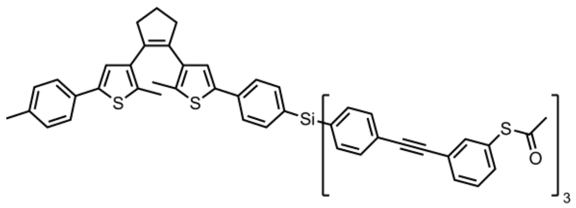


IR spectrum (neat):

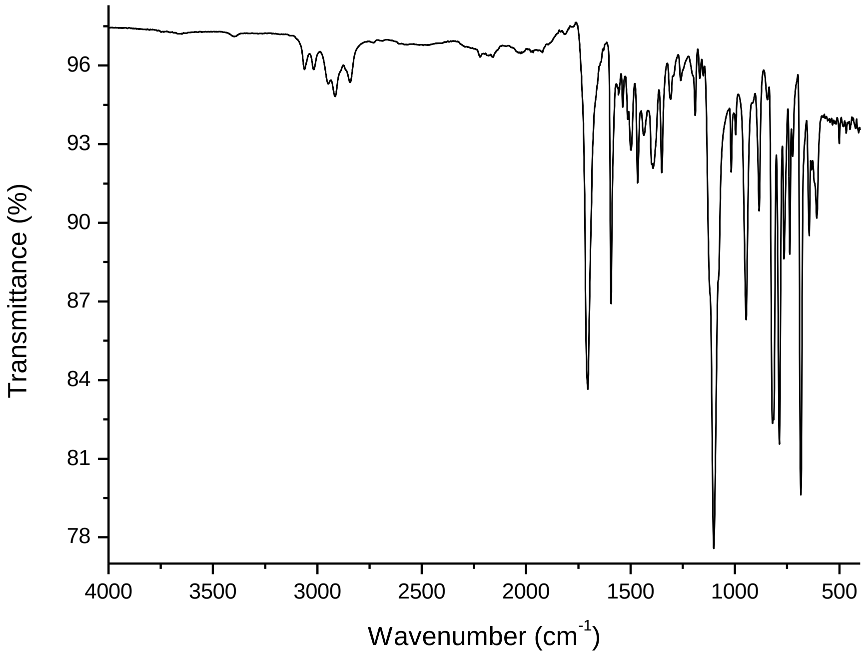


Raman spectrum (neat):

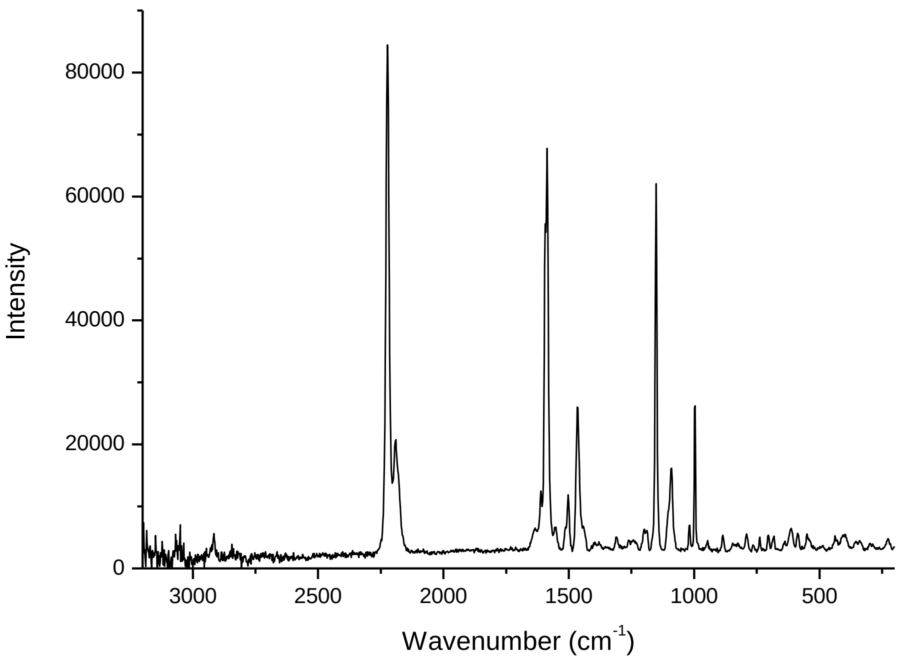




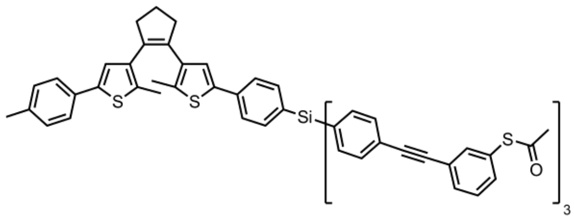
IR spectrum (neat):



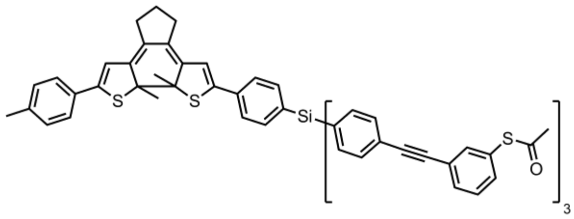
Raman spectrum (neat):



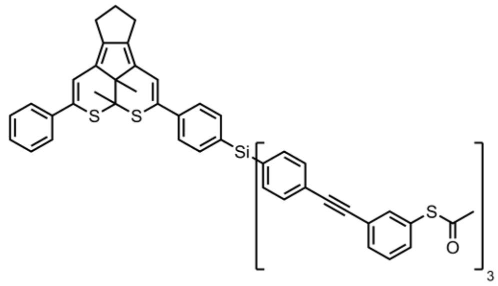
5. ^{1}H NMR spectral data for 1_o, 1_c, and 1_{byprod}



Dithienylethene $\mathbf{1_o}$: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.62–7.50 (m, 22H), 7.46–7.37 (m, 8H), 7.15–7.12 (m, 3H), 7.01 (s, 1H), 2.84 (t, J = 7.3 Hz, 4H), 2.43 (s, 9H), 2.32 (s, 3H), 2.13–2.05 (m, 2H), 2.03 (s, 3H), 1.99 (s, 3H).

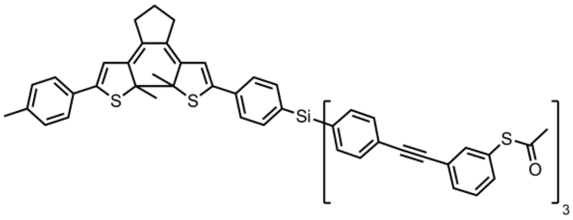


Dithienylethene $\mathbf{1_c}$: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.54 (m, 22H), 7.46–7.39 (m, 8H), 7.15 (d, J = 8.0 Hz, 2H), 6.54 (s, 1H), 6.42 (s, 1H), 2.51–2.46 (m, 4H), 2.43 (s, 9H), 2.358 (s, 3H), 2.00 (s, 6H), 1.93–1.85 (m, 2H).



Dithienylethene $\mathbf{1_{byprod}}$ (partial spectrum): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.56 (s, 1H), 6.43 (S, 1H), 2.55 (s, 3H), 2.50 (s, 3H), 2.33 (s, 3H).

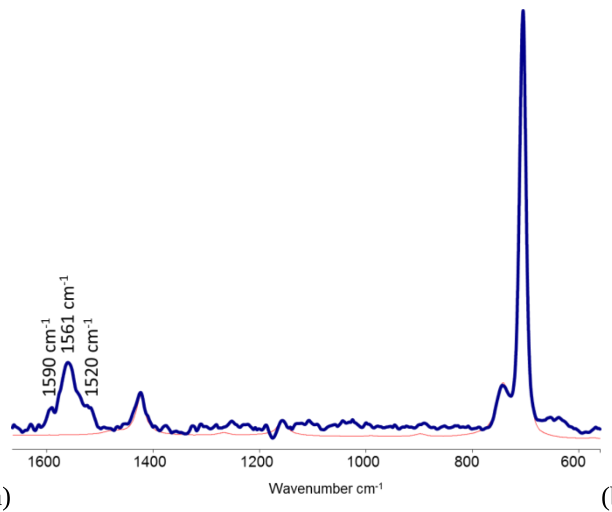
6. Raman shifts for 1_c

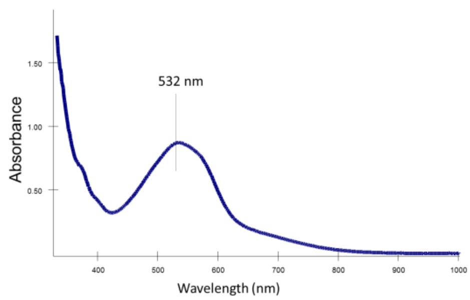


Dithienylethene $\mathbf{1_c}$: Raman (neat) ν_{max} 2224, 1587, 1506, 1312, 1265, 1187, 1151, 1102 cm^{-1}.

7. UV/Vis absorption, Raman, and ^1H NMR spectroscopy of $\mathbf{1_{byprod}}$

We have attempted to record the Raman spectrum of $\mathbf{1_{byprod}}$ (both at 785 nm and 1064 nm) but in both cases sample heating prevented spectral acquisition. In addition, Raman spectra obtained in solution were thwarted by interference by fluorescence at 355 nm, 457 nm, 473 nm, and 633 nm. It was possible to obtain a spectrum at 532 nm, however it should be realized that at this wavelength resonance enhancement is observed and hence the intensity patterns observed are very different from those obtained by SERS or non-resonantly enhanced Raman spectra. Indeed, in part because of the low signal to noise ratio, only the bands centered around 1561 cm^{-1} are observed which is consistent with the calculated spectrum shown in Figure 5.





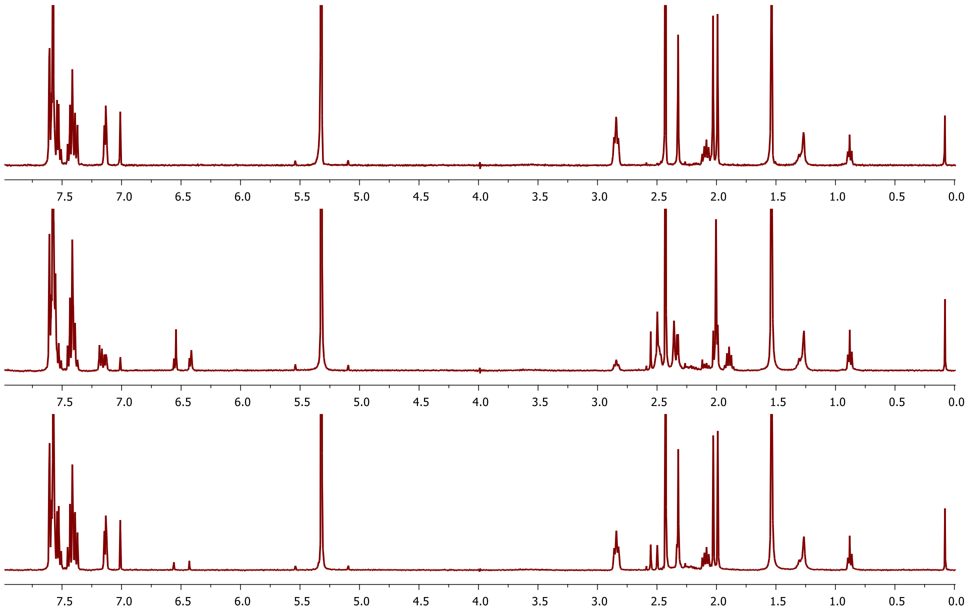
(a) Raman spectrum of $\mathbf{1_{byproduct}}$ in dichloromethane (blue). The spectrum of dichloromethane is shown in red.
(b) UV/Vis absorption spectrum of solution used to record the Raman spectrum.

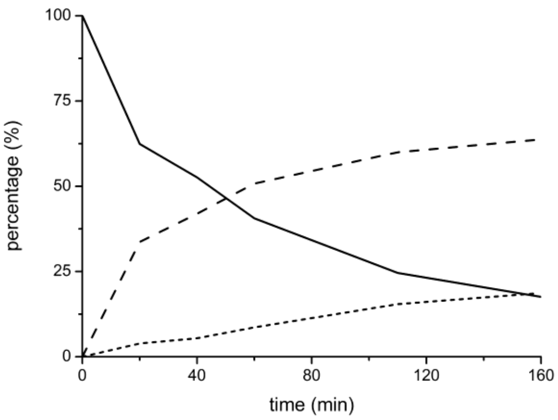
Spectra were recorded on the 400 MHz NMR spectrometer. The NMR sample is a small amount of $\mathbf{1_o}$ dissolved in CD_2Cl_2. The sample was degassed to remove oxygen by three freeze-thaw cycles followed by placing the sample under an atmosphere of Argon. UV irradiation was with a Spectroline ENB-280C/FE lamp; Visible irradiation was performed using an tungsten lamp with a 470 longpass filter.

Irr. time	open form (%)	closed form (%)	by-product (%)
0 min	100.00	0.00	0.00
20 min	62.41	33.69	3.90
40 min	52.61	41.95	5.44
60 min	40.59	50.79	8.62
110 min	24.58	59.98	15.44
160 min	17.57	63.73	18.70
after irr. at > 460 nm	0.00	82.20	17.80

Based on the integration of signals between 6.0 – 7.3 ppm.

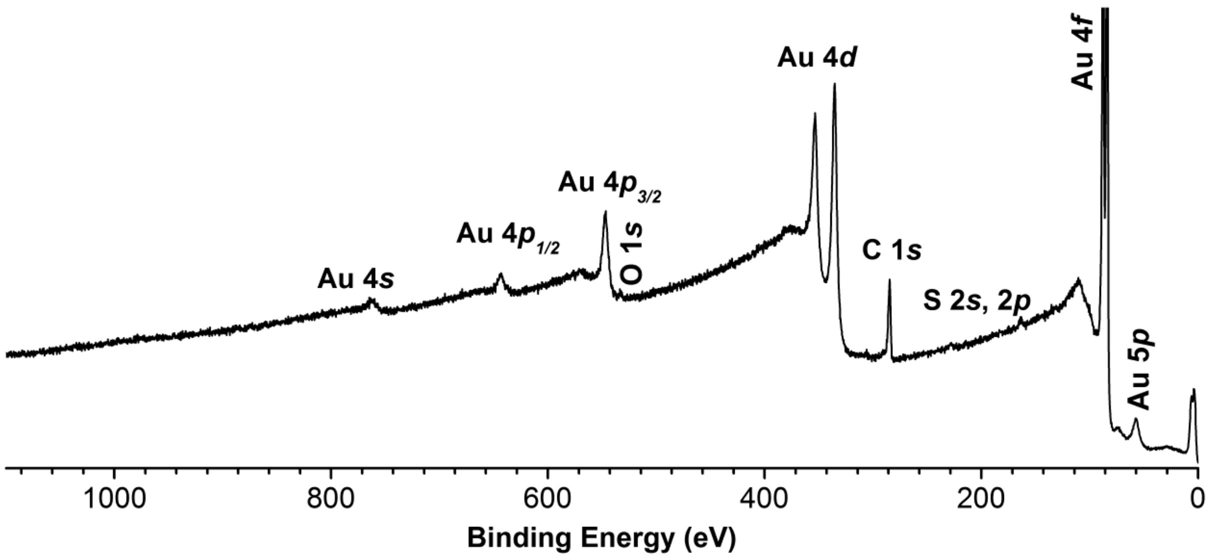
^{1}H NMR spectra of **1$_o$** (top), after 160 min of irradiation at 365 nm (middle), and after subsequent irradiation at > 460 nm (bottom), in CD_2Cl_2.



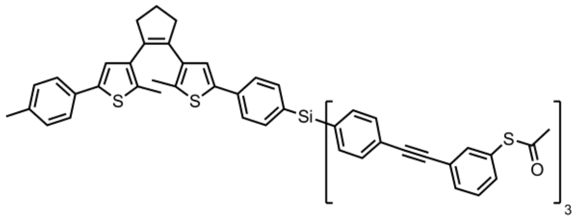


Change in concentration of **1$_o$** (solid line), **1$_c$** (dashed line), and **1$_{byprod}$** (short dashed line), determined by ^{1}H NMR spectroscopy.

8. Full XPS spectrum of 1_o on gold/mica



9. **Cartesian coordinates of DFT optimized geometries**



Dithienylethene $\mathbf{1_o}$ – B97-D3/def2-SVP

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C	-2.088359783139	8.057925968860	1.909266171818
C	-2.182403475120	9.588321354529	2.112749609536
C	-3.323765019776	10.030550343732	1.167463009364
C	-5.486234720197	8.830158485013	0.350487233918
C	-3.952446074109	6.279823159348	1.540103303913
C	-6.481936474246	9.814462794866	0.680562390988
C	-7.670385086835	9.693051880117	-0.022066281965
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C	-5.214937019420	5.851088675250	1.961102195397
S	-5.340746615698	4.111980770314	1.883775486560
C	-3.687085820119	3.927791782438	1.310814051016
C	-3.096378110670	5.177264937737	1.196277775065
C	-8.889561400451	10.507605219227	0.082548015767
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C	-5.190400698768	6.824844070329	-1.307052663893
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C	-11.252450538393	12.114120635296	0.324904886534
C	-9.994020655768	12.592165376788	0.753689325441
C	-8.837901938767	11.814700860726	0.632010543231
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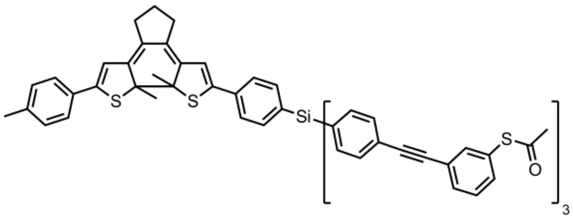

Dithienylethene $\mathbf{1_c}$ – B97-D3/def2-SVP

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C	-6.413258298794	9.461893207515	1.028315664728
C	-7.567762908079	8.850481295268	1.488021519519
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C	1.495681505722	-1.233443249438	-1.628098978950

C	2.356512649937	-1.239496155240	-2.731529197459
C	1.921898776939	-1.761752099892	-3.979797629579
C	0.601328831147	-2.277084336569	-4.075049099839
C	-0.248681954072	-2.261809570664	-2.962814854237
C	-5.534937416914	-5.742126153570	-1.112510977997
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C	2.792369596858	-1.771968415706	-5.108966498291
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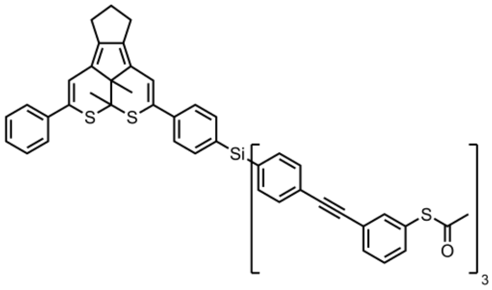

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