

Supporting Information for:

Spontaneous assembly of aromatic silylethane-thiol derivatives on Au(111): a chemically robust thiol protecting group as precursor for the direct formation of gold thiolate monolayers

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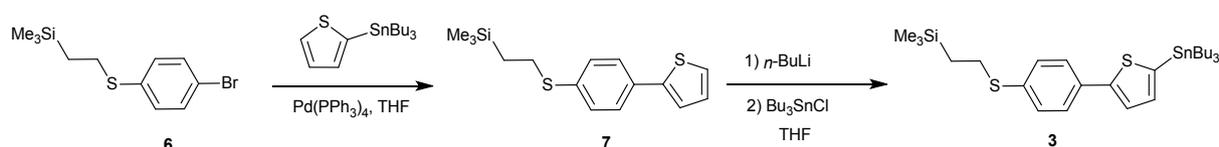
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1. Chemicals and Instrumentation

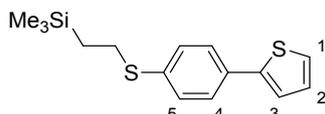
Unless otherwise noted, all chemicals were purchased from Aldrich, Alfa-Aesar or Acros and used without further purification. TLC were performed using aluminium sheet covered by SiO₂ Silica gel 60F₂₅₄ (Merck), and column chromatography using Silica gel 60 (particle size 0.063-0.200 mm, Merck). ¹H-NMR (400 MHz) and ¹³C-NMR (101 MHz) were recorded on Bruker Avance 400. Chemical shifts are given in ppm and coupling constants *J* in Hz. The residual signal of the solvent was taken as internal reference standard. EI-HRMS measurements were made on a Focus DSQ II (Thermo Fischer Scientific) and MALDI-ToF experiments on an Ultraflex III (Bruker) mass spectrometer. Infrared absorption spectra were recorded on a Perkin Elmer 1000 spectrometer. Melting points were measured with a Melting Point M-560 (Büchi) apparatus. Quartz crystal microbalance (QCM) analysis were performed with a Quartz Crystal Analyser QCA922 (Seiko-EG&G, Princeton applied Research) associated to a gold-coated quartz crystal (Biologic). X-ray photoelectron spectroscopy (XPS) data were collected using a Kratos Axis Ultra spectrometer. The X-ray source was monochromatic Al K α working at 1486.6 eV. Spectra were accumulated at a take-off angle of 90° using a spot size of 0.7 x 0.3 mm² at a pressure of less than 10⁻⁸ mbar. High resolution scans (C 1s, S 2s) were carried out with a 0.1 eV step size and a 20 eV pass energy. All spectra were calibrated by taking Au 4f as a reference binding energy of 83.95 and 87.63 eV, without an internal standard. XPS spectra were analyzed with curve-fitting program CASA XPS and involved background subtraction using Shirley function and a subsequent pseudo-Voigt function mixing Gaussian-Lorentzian functions. Atomic ratios of the surfaces were calculated by the normal area divided by the number of scans and the element sensitivity factor. For the elements considered, the sensitivity factors are: C 1s 1.00, O 1s 2.93, S 2p 1.68, Au 4f 17.1, Si 2s 0.95.

2. Experimental Procedure and Characterization Data



Scheme S1: Synthesis of the anchoring agent precursor 3

Trimethyl(2-((4-(thiophen-2-yl)phenyl)thio)ethyl)silane (7)



To a solution of (2-((4-bromophenyl)thio)ethyl)trimethylsilane **6** (10.2 g, 35.3 mmol) in a mixture of THF/DMF (1:1 v/v, 10 mL) were successively added 2-tributylstannylthiophene (13.4 mL, 42.3 mmol), tetrakis(triphenylphosphine) palladium (0) (1.6 g, 1.4 mmol,) and copper iodide (538 mg, 2.8 mmol) under nitrogen. The reaction was stirred at 80°C for 4 days. The reaction mixture was cooled down to room temperature, filtered over a mixture of anhydrous potassium carbonate/silica (1:10 w/w) using CH₂Cl₂ as eluent. The filtrate was concentrated under reduced pressure and dissolved into a mixture of cyclohexane/ether (1:1 v/v, 200 mL). The organic layer was washed with brine (2*150mL),

dried over magnesium sulfate and concentrated under reduced pressure. The crude product obtained was purified by recrystallization in methanol, affording **7** (7.25 g, 70%) as a white solid by filtration.

^1H NMR (400 MHz, C_6D_6): δ (ppm) = 7.42-7.38 (m, 2H, H^4), 7.26-7.23 (m, 2H, H^5), 7.04 (dd, $J = 3.4$ Hz, $J = 1.2$ Hz, 1H, H^1), 6.84 (dd, $J = 5.2$ Hz, $J = 1.2$ Hz, 1H, H^3), 6.77 (dd, $J = 5.2$ Hz, $J = 3.6$ Hz, H^2), 2.84-2.80 (m, 2H, S- CH_2 - CH_2 -), 0.90-0.84 (m, 2H, Si- CH_2 - CH_2 -), -0.09 (s, 9H, Si- CH_3).

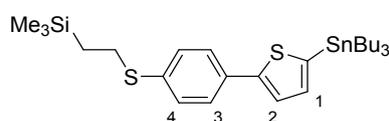
^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 144.1 ($\text{C}_{\text{Th-S}}$), 136.6 ($\text{C}_{\text{Ph-S}}$), 132.1 (C_{Ph}), 129.4 (CH_{Ph}), 128.2 (CH_{Th}), 126.4 (CH_{Ph}), 124.7 (CH_{Th}), 123.0 (CH_{Th}), 29.7 (S- CH_2), 17.0 (Si- CH_2), -1.6 (Si- CH_3).

IR (cm^{-1}): 2952, 2887, 1593, 1488, 1428, 1402, 1245, 1164, 1093, 1011, 824, 809.

HRMS (EI): MH^+ calculated: 293.0848; found: 293.0838.

Mp: 49-50°C.

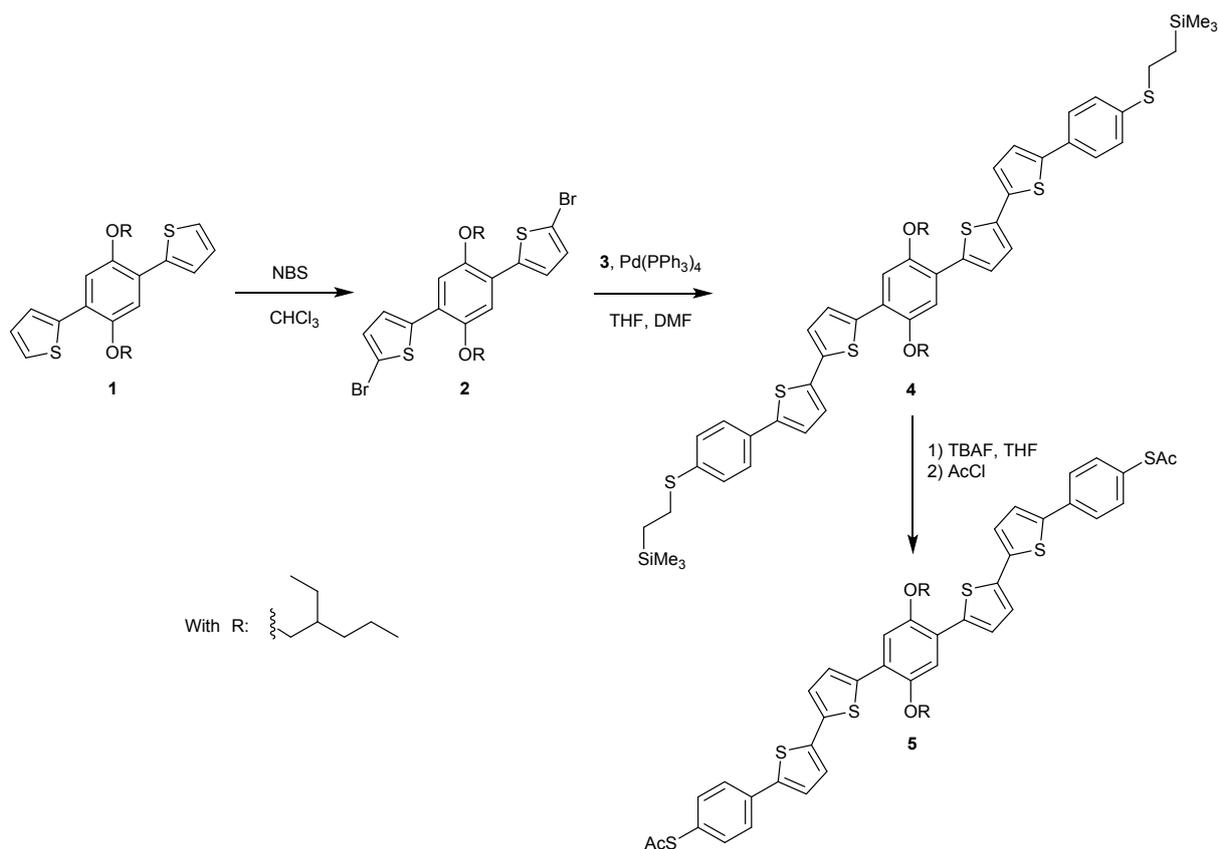
Trimethyl(2-((4-(5-(tributylstannyl)thiophen-2-yl)phenyl)thio)ethyl)silane (**3**)



To a solution of **7** (2.05 g, 7.0 mmol) in anhydrous THF (20 mL) was added dropwise *n*-butyllithium (1.6 M in hexanes, 4.8 mL, 7.7 mmol) at -78°C and under nitrogen. The mixture was slowly warmed to 0°C over a period of 2h. It was then cooled to -10°C before the addition of tributyltin chloride (2.09 mL, 7.7 mmol) in one portion. The reaction mixture was allowed to warm to room temperature overnight. It was then concentrated under reduced pressure, diluted with dichloromethane and filtered over celite. The filtrate was concentrated under reduced pressure, to give **3** as a brown oil which was used in the next step without further purification.

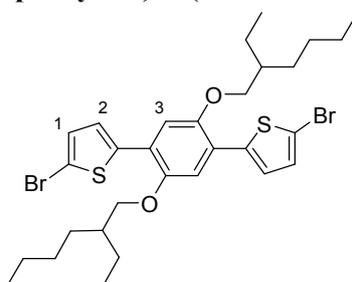
^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.56-7.54 (m, 2H, H^3), 7.40 (d, $J = 3.2$ Hz, 1H, H^2), 7.32-7.28 (m, 2H, H^4), 7.13 (d, $J = 3.2$ Hz, 1H, H^1), 3.0-2.9 (m, 2H, S- CH_2 - CH_2 -), 1.7-1.5 (m, 6H, Sn- CH_2 - CH_2 -), 1.4-1.3 (m, 6H, Sn- CH_2 - CH_2 -), 1.2-1.1 (m, 6H, - CH_2 - CH_3), 1.0-0.9 (m, 11H, Si- CH_2 - CH_2 - and - CH_2 - CH_3), -0.095 (s, 9H, Si- CH_3).

^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 149.6, 136.9, 136.6, 136.0, 132.3, 129.4, 126.3, 124.2, 29.8, 29.1, 27.4, 17.0, 13.8, 11.0, -1.6.



Scheme S2: Synthesis of the SAMs precursors **4** and **5**

5,5'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)bis(2-bromothiophene) (2**)**



To a solution of **1** (4.0 g, 8.0 mmol.) in CH_2Cl_2 (20 mL) was added N-bromosuccinimide (3.2 g, 18 mmol.) at room temperature and under nitrogen. The reaction mixture was protected from light and stirred at room temperature for two hours. The reaction mixture was then diluted in CH_2Cl_2 (30 mL), washed with an aqueous sodium thiosulfate solution (1N, 2*50 mL) and brine (2*50 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated under reduced pressure, to give **2** (3.8 g, 72%) as a yellow solid.

^1H NMR (400 MHz, CDCl_3): δ (ppm) = 7.26 (d, J = 4.0 Hz, 2H, H^1), 7.16 (s, 2H, H^3), 7.05 (d, J = 4.0 Hz, H^2), 4.00-3.92 (m, 4H, $\text{O}-\text{CH}_2-\text{CH}-$), 1.91-1.81 (m, 2H, $\text{O}-\text{CH}_2-\text{CH}-$), 1.65-1.39 (m, 8H, $-\text{CH}-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}-\text{CH}_2-\text{CH}_2-$), 1.39-1.29 (m, 8H, $-\text{CH}-\text{CH}_2-\text{CH}_3$ and $-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 0.96 (t, J = 7.5 Hz, 6H, $-\text{CH}-\text{CH}_2-\text{CH}_3$), 0.94-0.89 (m, 6H, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$).

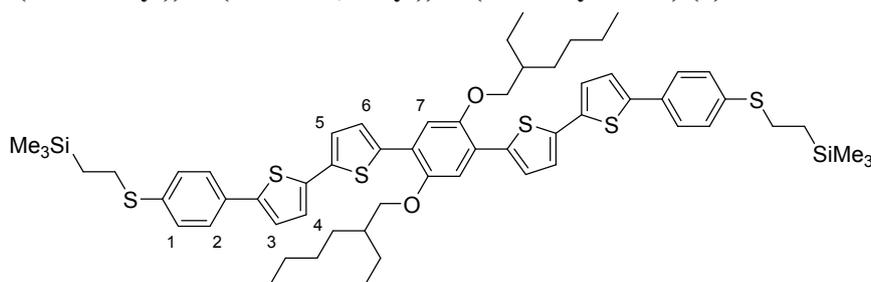
^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 149.3 ($\text{C}_{\text{Ph-O}}$), 140.5 (C_{Th}), 129.4 (CH_{Th}), 124.9 (CH_{Th}), 122.5 (C_{Ph}), 113.2 (C-Br), 111.5 (CH_{Ph}), 72.2 (O-CH_2), 39.7 (CH), 30.8 (CH_2), 29.3 (CH_2), 24.2 (CH_2), 23.2 (CH_2), 14.3 (CH_3), 11.3 (CH_3).

IR (cm^{-1}): 2957, 2922, 2871, 2855, 1724, 1541, 1495, 1458, 1403, 1336, 1277, 1207, 1080, 1035, 1018, 959, 842, 777.

HRMS (EI): M^+ calculated: 654.0836, found: 654.0842.

Mp: 98-99°C.

(((2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)bis([2,2'-bithiophene]-5',5'-diyl))bis(4,1-phenylene))bis(sulfanediy))bis(ethane-2,1-diyl))bis(trimethylsilane) (4)



To a solution of **2** (1.12 g, 1.4 mmol) in a mixture of THF/DMF (1:1 v/v, 10 mL) were successively introduced tributylstannyl derivative **3** (1.74 g, 3.0 mmol), tetrakis(triphenylphosphine) palladium (0) (138 mg, 0.12 mmol) and copper iodide (45 mg, 0.24 mmol) under nitrogen. The reaction mixture was stirred at 80°C overnight. It was then cooled down to room temperature and filtered over dicalite using CH_2Cl_2 as eluent. The organic layer was washed with brine (3*150 mL), dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product obtained was purified by column chromatography on silica gel (eluent: gradient cyclohexane/ CH_2Cl_2 , going from 100:0 to 60:40 v/v), to give **4** (0.89 g, 55%) as an orange solid.

^1H NMR (400 MHz, C_6D_6): δ (ppm) = 7.56 (d, J = 3.8 Hz, 2H, H^6), 7.42-7.39 (m, 6H, H^7 and H^2), 7.28-7.26 (m, 4H, H^1), 7.23 (d, J = 3.8 Hz, 2H, H^3), 7.17 (d, J = 3.8 Hz, 2H, H^4), 6.96 (d, J = 3.8 Hz, 2H, H^5), 3.89 (d, J = 5.2 Hz, 4H, $\text{O-CH}_2\text{-CH-}$), 2.87-2.82 (m, 4H, $\text{S-CH}_2\text{-CH}_2\text{-}$), 1.9-1.8 (m, 2H, $\text{O-CH}_2\text{-CH-}$), 1.7-1.4 (m, 8H, $\text{-CH-CH}_2\text{-CH}_2\text{-}$ and $\text{-CH-CH}_2\text{-CH}_2\text{-}$), 1.35-1.4 (m, 8H, $\text{-CH-CH}_2\text{-CH}_3$ and $\text{-CH}_2\text{-CH}_2\text{-CH}_3$), 0.95-0.85 (m, 16H, $\text{Si-CH}_2\text{-CH}_2\text{-}$, $\text{-CH-CH}_2\text{-CH}_3$ and $\text{-CH}_2\text{-CH}_2\text{-CH}_3$), -0.07 (s, 18H, Si-CH_3).

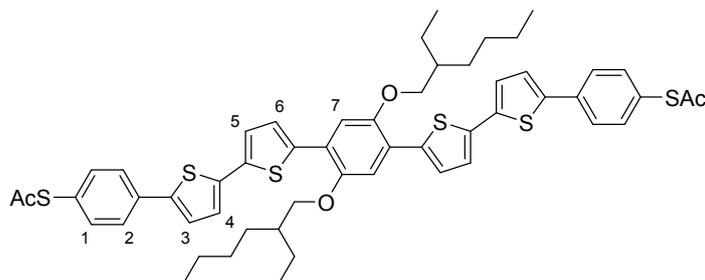
^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 149.4 ($\text{C}_{\text{Ph-O}}$), 142.5 ($\text{C}_{\text{Ph-S}}$), 138.3 (C_{Th}), 137.3 (C_{Th}), 137.0 (C_{Th}), 136.8 (C_{Th}), 131.7 (C_{Ph}), 129.2 (CH_{Ph}), 126.0 (CH_{Ph}), 125.9 (CH_{Th}), 124.2 (CH_{Th}), 123.7 (CH_{Th}), 123.4 (CH_{Th}), 122.6 (C_{Ph}), 111.7 (CH_{Ph}), 72.0 (O-CH_2), 39.9 (CH), 30.9 (CH_2), 29.6 (S-CH_2), 29.4 (CH_2), 24.2 (CH_2), 23.3 (CH_2), 16.9 (Si-CH_2), 14.3 (CH_3), 11.5 (CH_3), -1.6 (Si-CH_3).

IR (cm^{-1}): 2953, 2861, 1526, 1486, 1451, 1403, 1261, 1248, 1210, 1162, 1093, 1032, 1009, 854, 829, 799.

MS (MALDI) m/z (%): 1078.4 (M^+).

Mp: 154-155°C.

((2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)bis([2,2'-bithiophene]-5',5-diyl))bis(4,1-phenylene) diethanethioate (5)



In a two-necked round bottom flask were successively introduced **4** (100 mg, 0.093 mmol) and a 1M solution of tetrabutylammonium fluoride in THF (6.5 mL, 6.5 mmol) under nitrogen. The reaction mixture was stirred at room temperature for one hour. Freshly distilled acetyl chloride (0.4 mL, 5.6 mmol) was then added dropwise to the reaction mixture at room temperature. The mixture was stirred further for 30 min at room temperature. It was then diluted with CH₂Cl₂ (100 mL) before being neutralized by the addition of an aqueous saturated solution of NaHCO₃ (100 mL). The product was extracted with CH₂Cl₂ (2*30 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product obtained was purified by column chromatography on silica gel (eluent: gradient cyclohexane/CH₂Cl₂, going from 100:0 to 60:40 v/v), to give **5** (60 mg, 67%) as an orange powder.

¹H NMR (400 MHz, C₆D₆): δ (ppm) = 7.55 (d, J = 3.8 Hz, 2H, H⁶), 7.42 (s, 2H, H⁷), 7.41-7.37 (m, 4H, H²), 7.35-7.30 (m, 4H, H¹), 7.23 (d, J = 3.8 Hz, 2H, H³), 7.14 (d, J = 3.8 Hz, 2H, H⁴), 6.93 (d, J = 3.8 Hz, 2H, H⁵), 3.90 (d, J = 5.5 Hz, 4H, O-CH₂-CH-), 1.89 (s, 6H, CO-CH₃), 1.86 - 1.78 (m, 2H, O-CH₂-CH-), 1.73-1.40 (m, 8H, -CH-CH₂-CH₂- and -CH-CH₂-CH₂-), 1.39-1.25 (m, 8H, -CH-CH₂-CH₃ and -CH₂-CH₂-CH₃), 0.99-0.87 (m, 12H, -CH-CH₂-CH₃ and -CH₂-CH₂-CH₃).

¹³C NMR (101 MHz, C₆D₆): δ (ppm) = 192.4 (CO), 150.5 (C_{Ph}-O), 142.6 (C_{Ph}-S), 139.5 (C_{Th}), 138.7 (C_{Th}), 138.1 (C_{Th}), 135.7 (CH_{Th}), 135.6 (C_{Th}, C_{Ph}), 128.7 (CH_{Ph}), 127.1 (CH_{Th}), 126.7 (CH_{Ph}), 125.1 (CH_{Th}), 124.5 (CH_{Th}), 123.8 (C_{Ph}), 113.0 (CH_{Ph}), 72.5 (O-CH₂), 40.5 (CH), 31.6 (CH₂), 30.1 (COCH₃), 30.0 (CH₂), 24.9 (CH₂), 23.9 (CH₂), 14.7 (CH₃), 11.9 (CH₃).

IR (cm⁻¹): 2953, 2924, 2861, 1693, 1591, 1528, 1502, 1483, 1451, 1399, 1319, 1278, 1209, 1114, 1083, 1026, 951, 850, 821.

MS (MALDI) m/z (%): 962.3 (M⁺).

Mp: 165-166°C.

3. ^1H and ^{13}C NMR spectra

Figure. S1: ^1H NMR spectra of **7** in C_6D_6

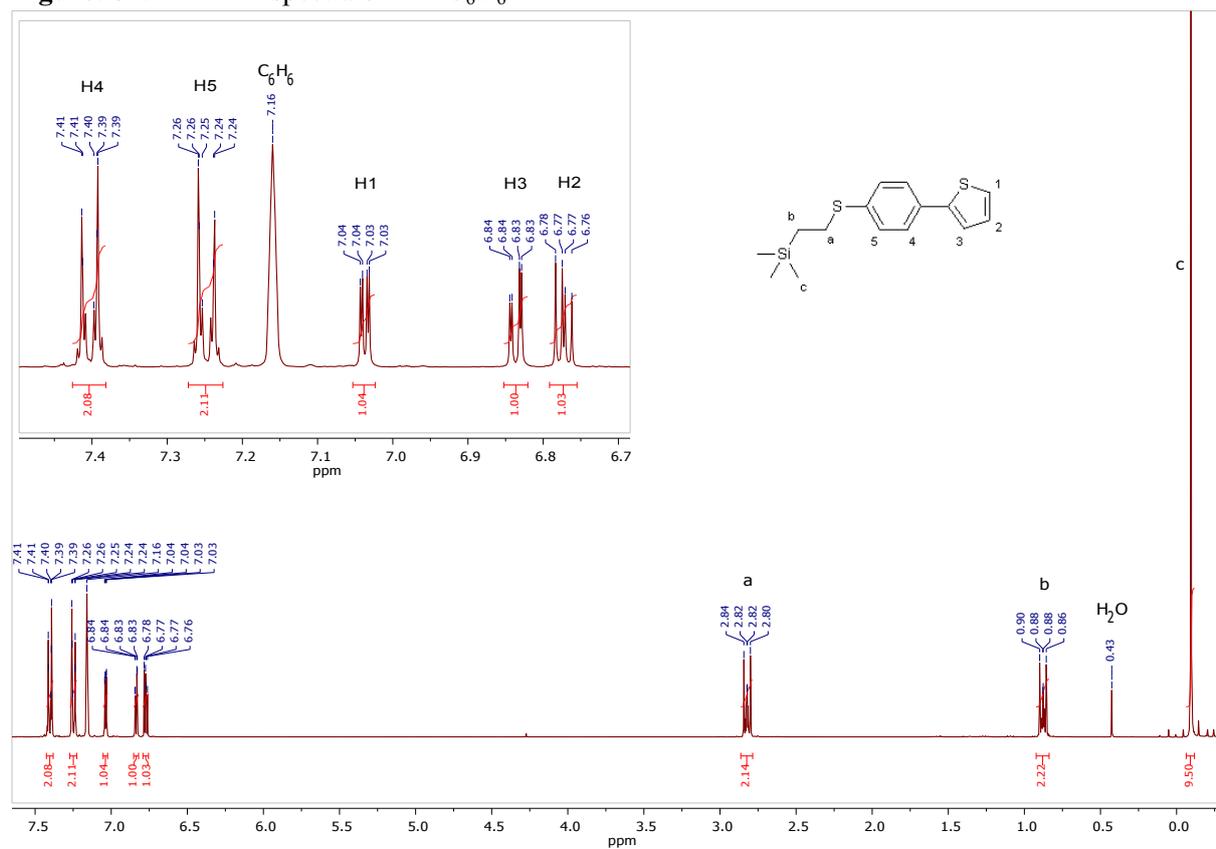


Figure. S2: ^{13}C NMR spectra of **7** in CDCl_3

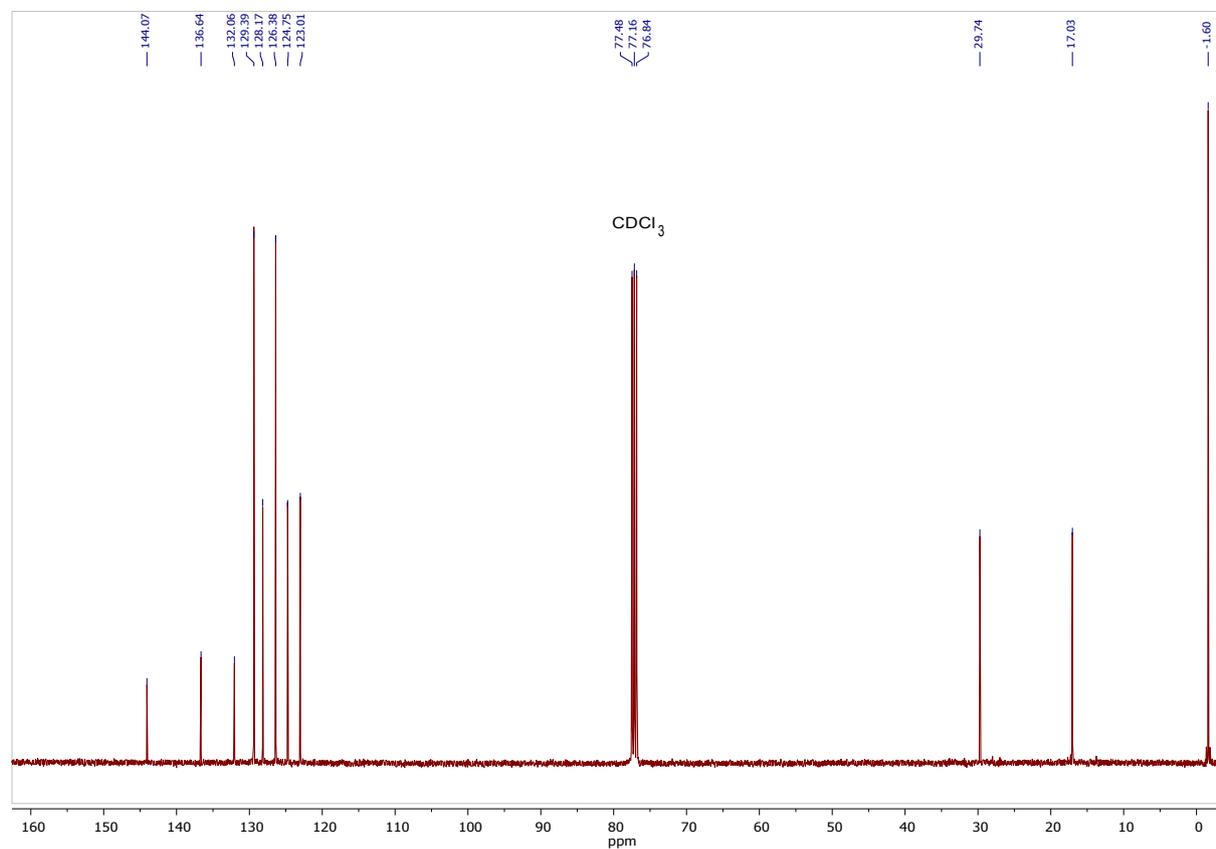


Figure. S3: ^1H NMR spectra of **3** in CDCl_3

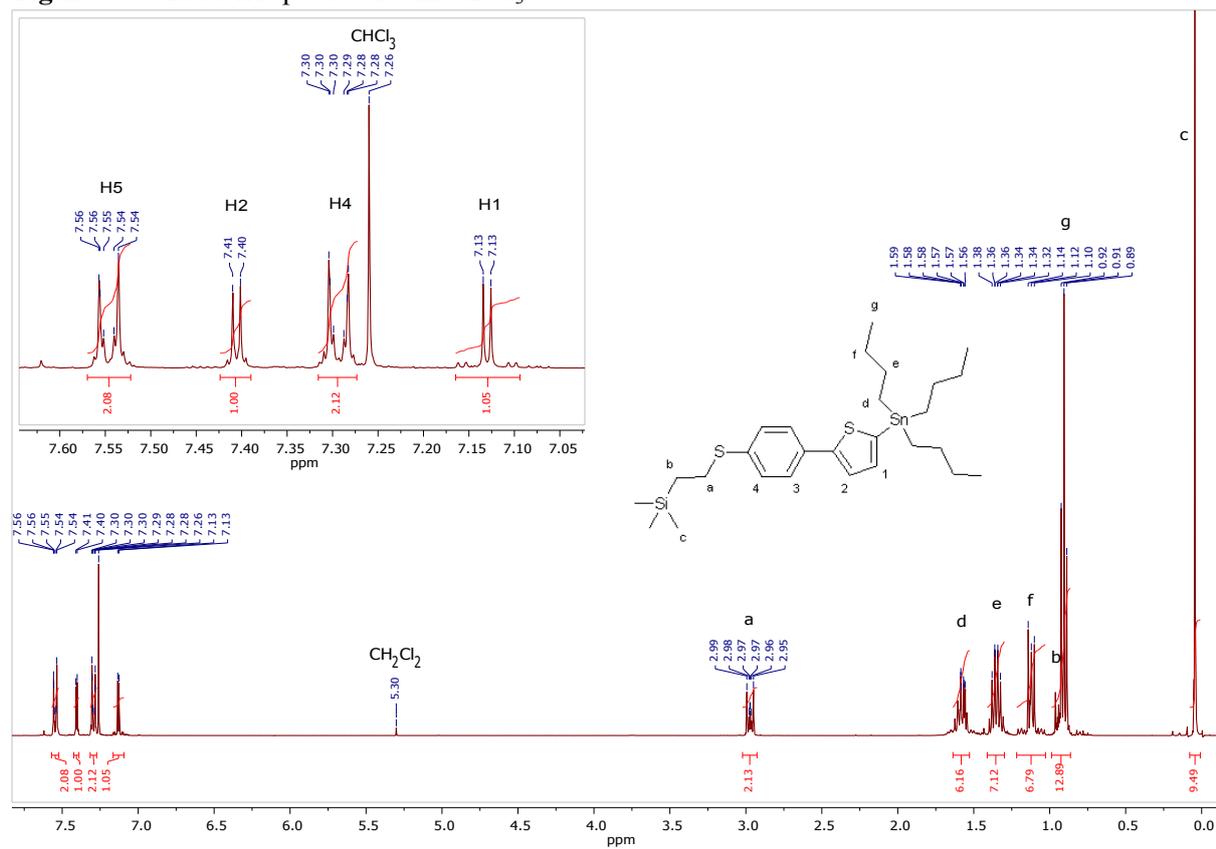


Figure. S4: ^{13}C NMR spectra of **3** in CDCl_3

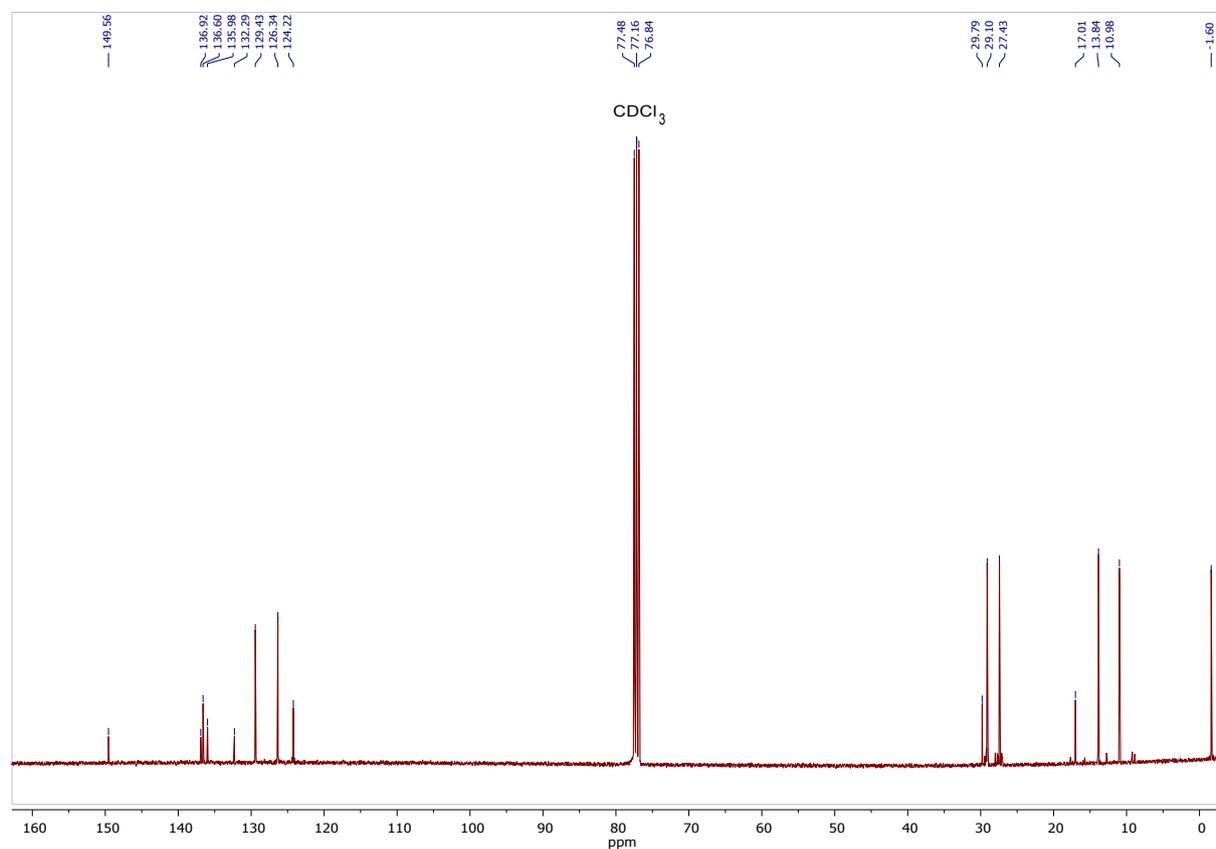


Figure. S5: ^1H NMR spectra of **2** in CDCl_3

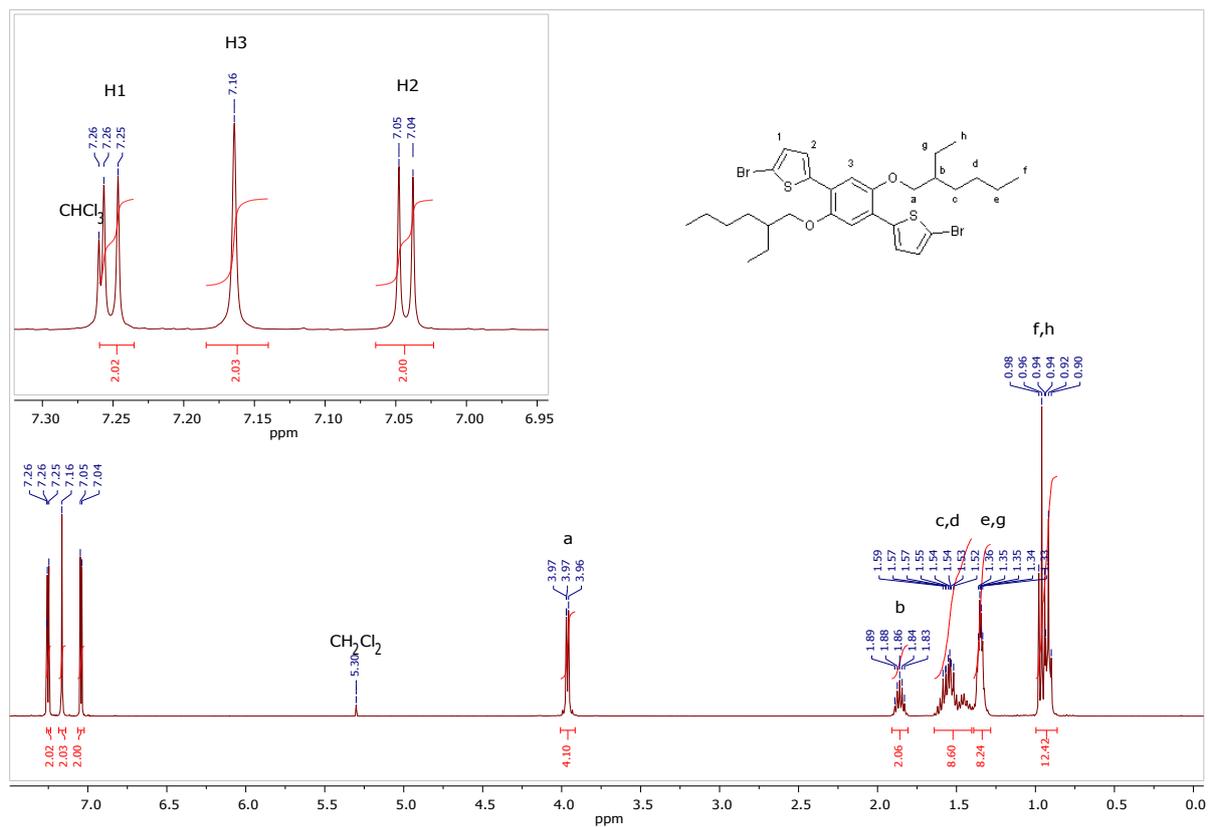


Figure. S6: ^{13}C NMR spectra of **2** in CDCl_3

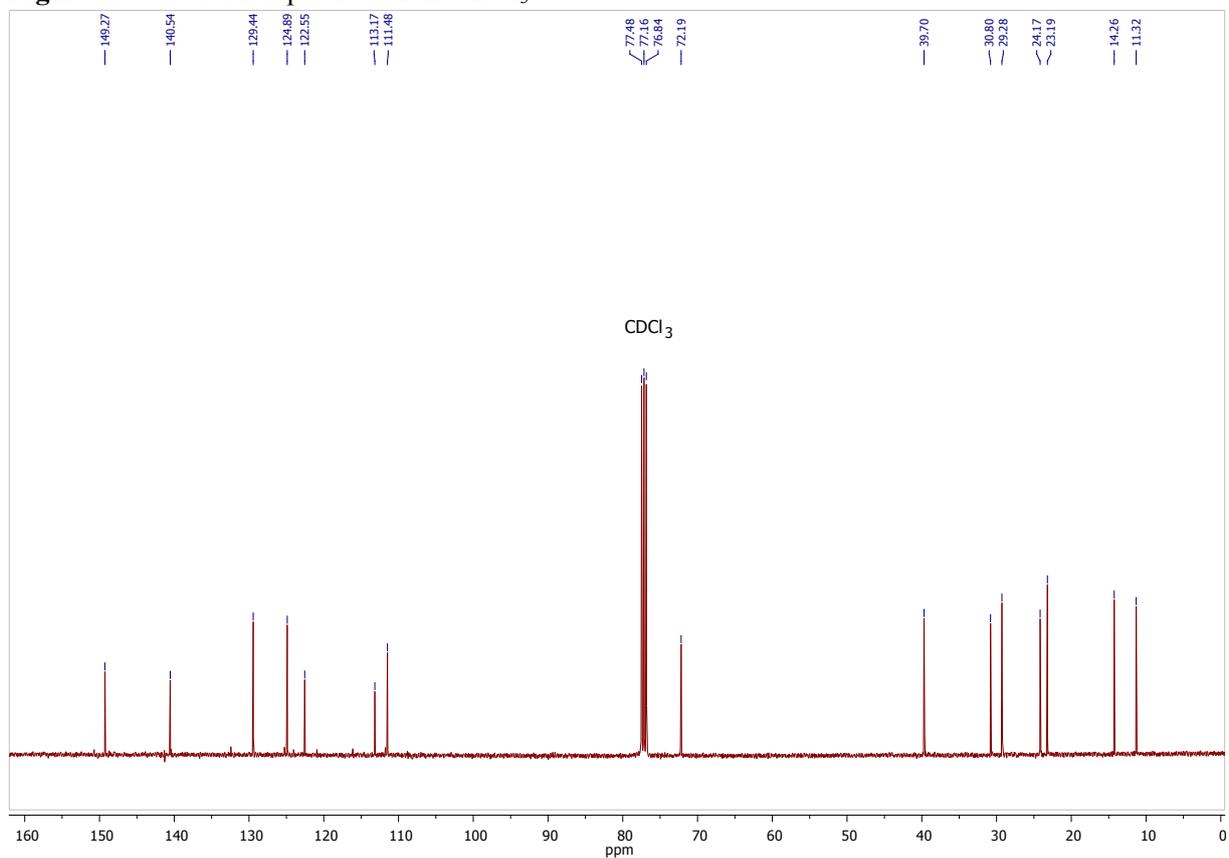


Figure. S7: ^1H NMR spectra of **4** in C_6D_6

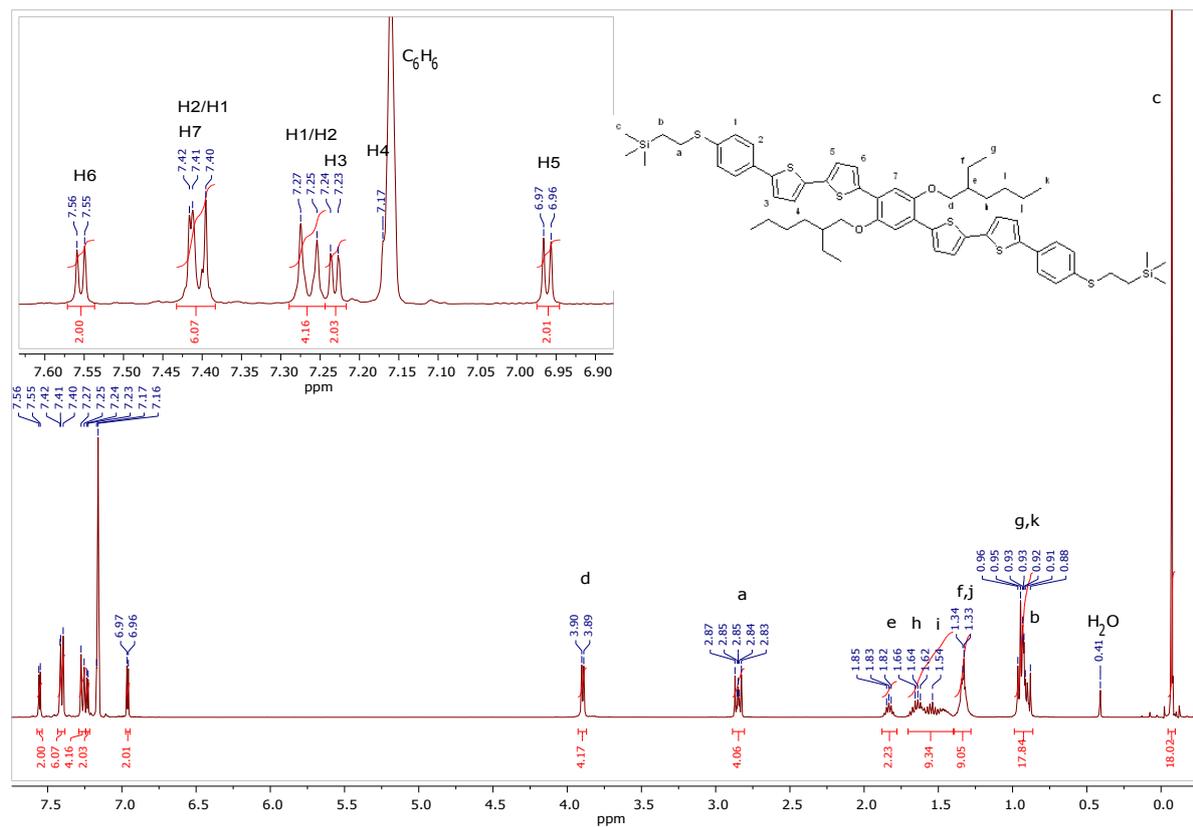


Figure. S8: ^{13}C NMR spectra of **4** in CDCl_3

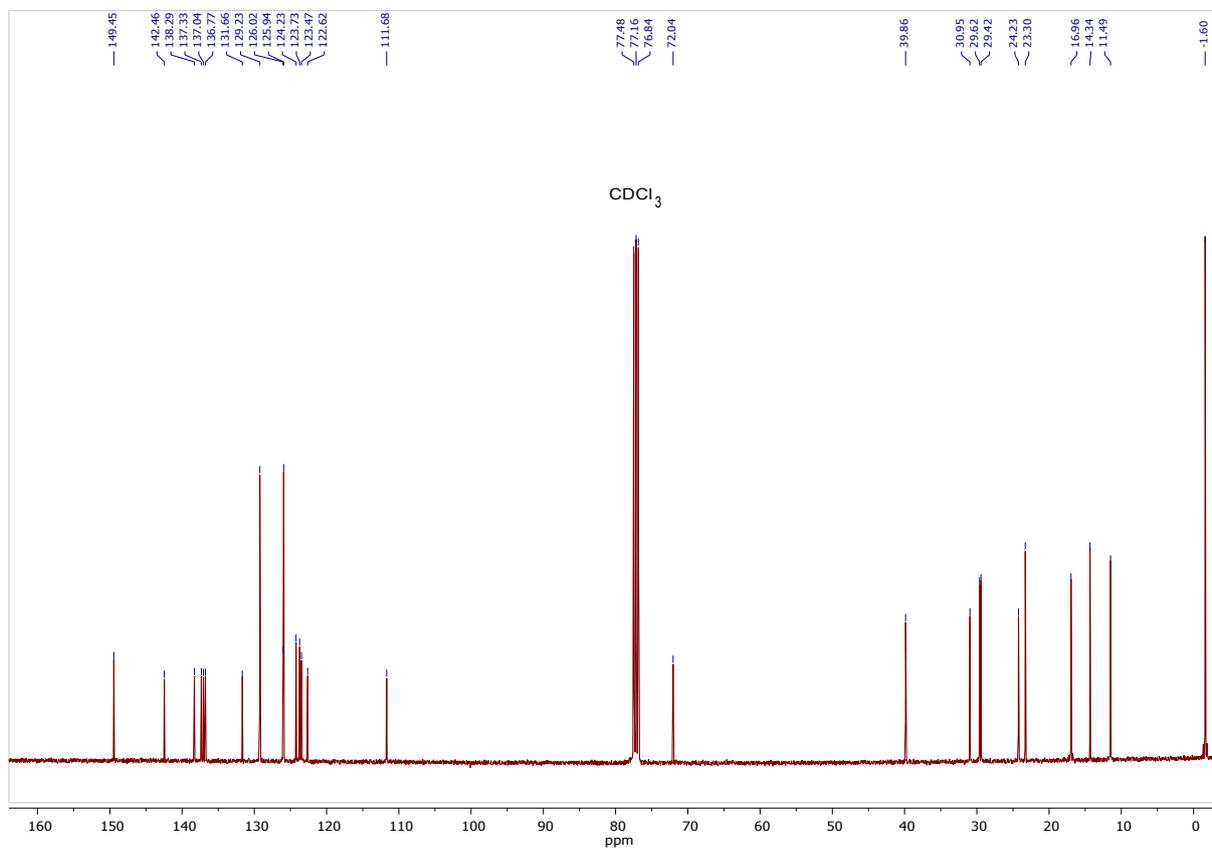


Figure. S9: ^1H NMR spectra of **5** in C_6D_6

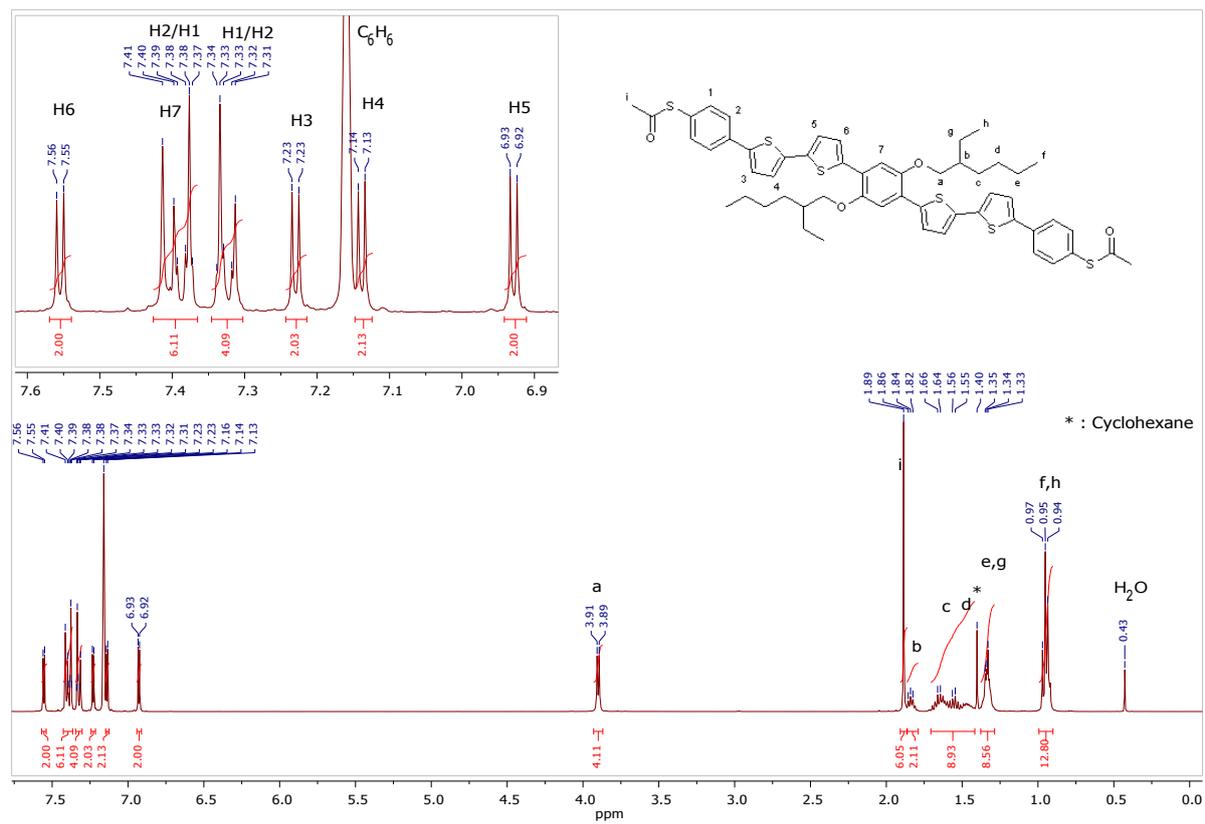
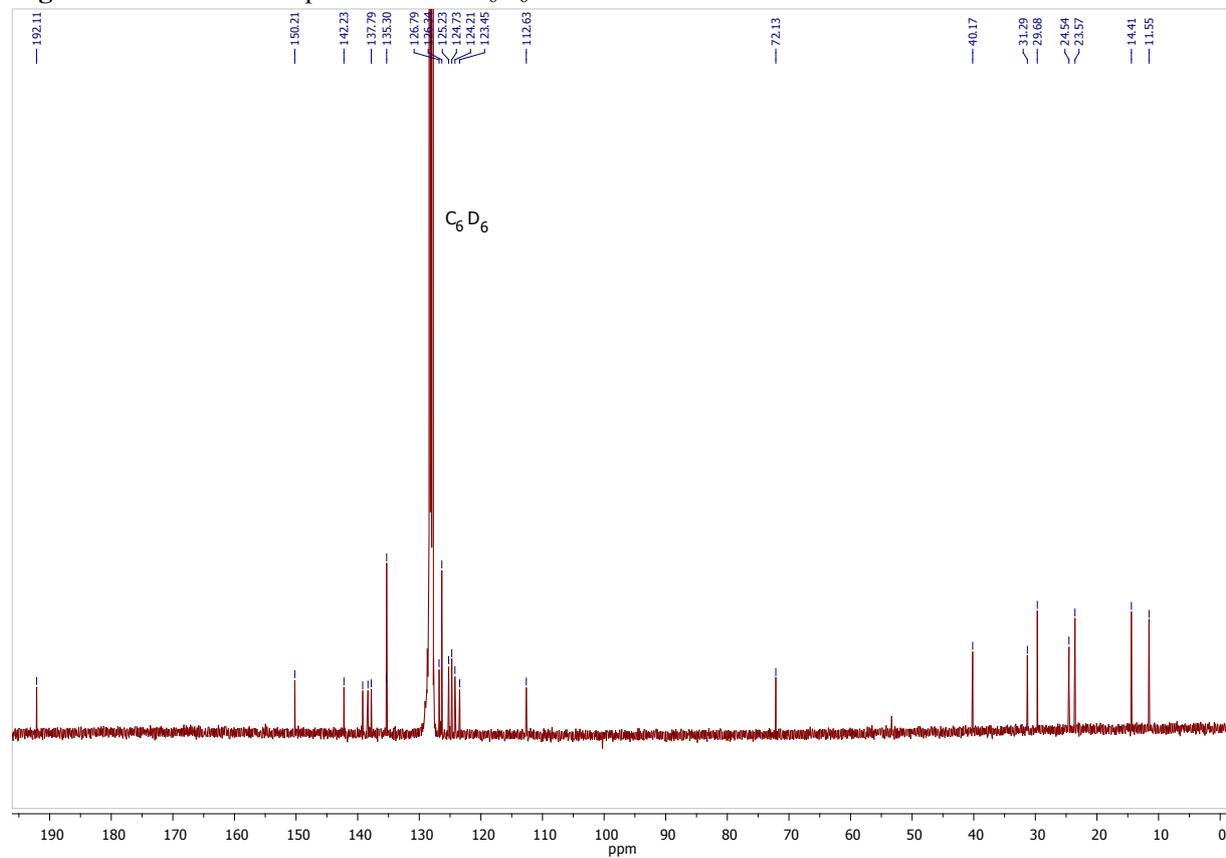


Figure. S10: ^{13}C NMR spectra of **5** in C_6D_6



4. XPS spectra

Figure. S11: XPS spectra of SAMs prepared from 4 and 5

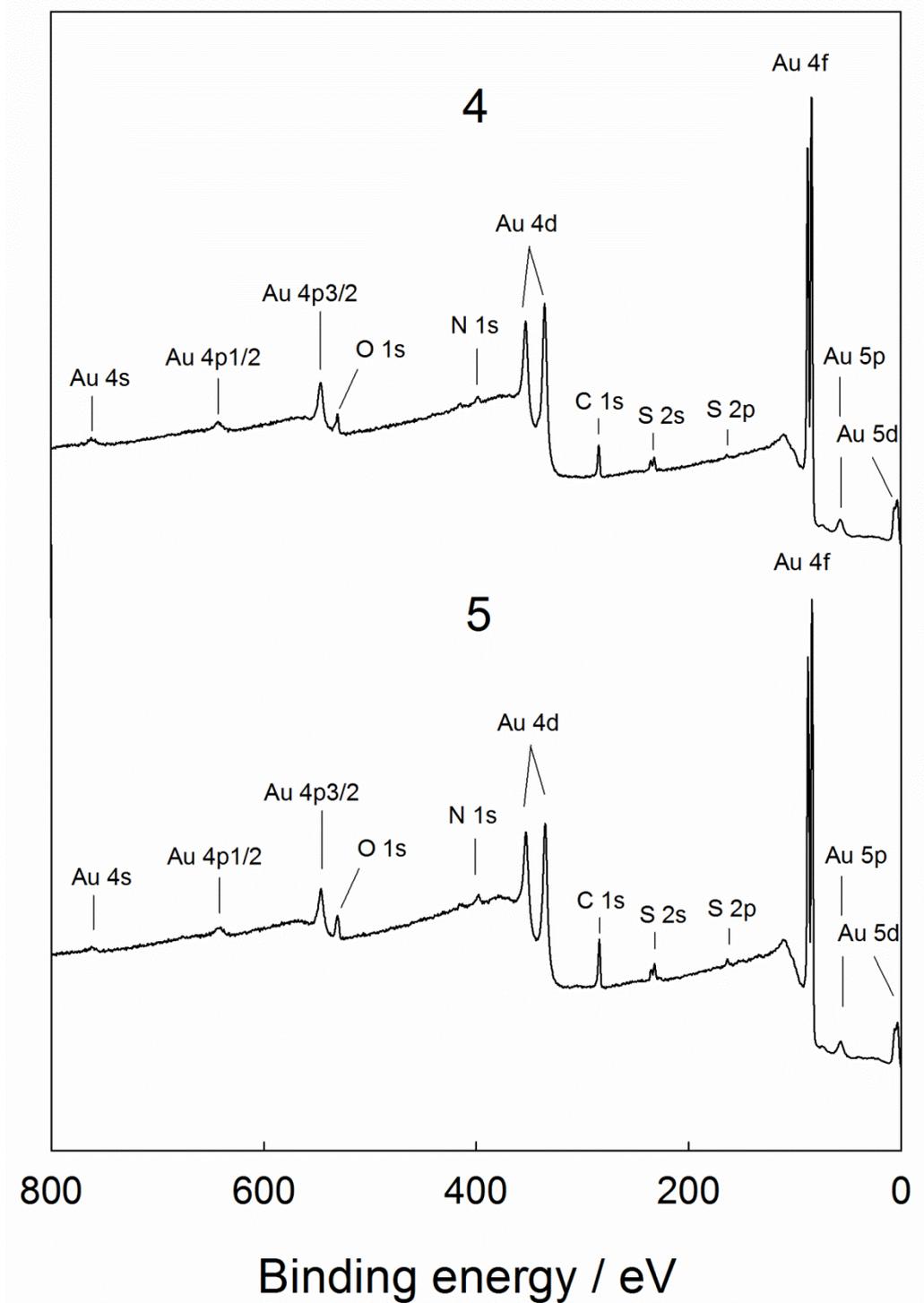


Figure. S12: Si 2p core level spectrum of **4**

