Supporting information for

# One-dimensional optoelectronic nanostructures derived from the aqueous self-assembly of π-conjugated oligopeptides

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## Materials and Methods
### General Considerations

Reactions were performed in flame-dried glassware under an atmosphere of nitrogen. Non-aqueous solvents were degassed by sparging with nitrogen for 15 minutes prior to use and THF was passed through columns of activated alumina. Tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) was obtained from Strem Chemicals. Chemicals for solid phase peptide synthesis (N-Methylpyrrolidone (NMP), O-(Benzotriazol-1-yl)-N,N,N′,N′-tetramethyluronium hexafluorophosphate (HBTU), Wang resin, Fmoc-Amino acids) were obtained from Advanced ChemTech. All other chemicals were supplied by Sigma-Aldrich or Fisher and used as received. $^1$H-NMR and $^{13}$C-NMR were obtained at 400 MHz and 100 MHz respectively using a Bruker Avance 400 MHz FT-NMR spectrometer. Chemical shifts are reported in parts per million relative to residual protio solvent [$CDCl_3$ $\delta$: 7.26 ($^1$H) and 77.00 ppm ($^{13}$C), DMSO $\delta$: 2.50 ($^1$H) and 40.0 ppm ($^{13}$C), $D_2O$ $\delta$: 4.79 ($^1$H)]. 2,2,5,5-tetramethyl-1-(thiophen-2-ylmethyl)-1,2,5-azadisilolidine (**A**) was prepared by slow addition of 1,2-bis(chlorodimethylsilyl)ethane to a stirring solution of 2-thiophene methylamine and triethylamine at 0$^o$C in $CH_2Cl_2$.[i]

### UV/Vis and Fluorescence

UV-vis absorption spectra were recorded using a Varian Cary 50 Bio UV-Visible spectrophotometer. Solution fluorescence measurements were performed on an ISS K2 multifrequency phase fluorometer (equipped with an ILC Technology Illuminator power supply). A stock solution of peptide (10 mg/mL) was brought to pH 8 by incremental addition of 2 µL of 1M KOH then filtered with

0.45 μm syringe filters. An 11 μM solution of peptide was prepared in both neutral deionized $H_2O$ and concentrated HCl to obtain spectra for the non-aggregated and self-assembled system, respectively. Fluorescence data was collected using samples prepared for UV/Vis.

**Circular Dichroism**

Circular dichroism measurements were carried out at room temperature using a Jasco J-810 spectropolarimeter. A stock solution of peptide (5 mg/mL) was brought to pH 8 by incremental addition of 2 μL of 1M KOH then filtered with 0.45 μm syringe filters. 400 μL of a 3.4 mM solution was then added to a 2.00 mm cuvet to obtain a spectrum of the non-assembled system. A spectrum of the self-assembled system was obtained by adding 100 μL 1M HCl and allowing a self-supporting gel to form.

**Atomic Force Microscopy**

Samples were analyzed by magnetic tapping mode AFM on an Agilent Technologies PicoSPM LE using probes purchased from Micromasch (NSC18 Co/Cr). A stock solution of peptide (10 mg/mL) was brought to pH 8 by incremental addition of 2μL of 1M KOH. The peptide solution was filtered through a 0.45 μm syringe filter. 190μL of peptide solution at a concentration of 0.7 mM was made acidic by the addition of 10μL of 1M HCl. It was immediately vortexed to mix and allowed to sit for 10 minutes to allow it to form a self-supporting gel. The gel was then diluted to 0.07 mM and thoroughly mixed by vortex. A 10 μl aliquot was deposited onto a freshly cleaved mica substrate and allowed to dry for one hour prior to imaging.

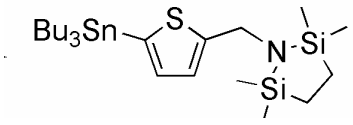
**Infrared Spectroscopy**

Samples of peptide were dried under high vacuum and analyzed by attenuated total reflectance on a Nexus 670 E.S.P. FT-IR.

**Transmission Electron Microscopy**

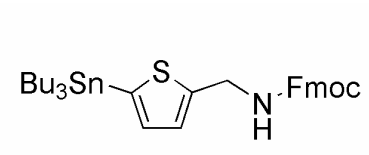
Samples were analyzed on a Philips EM 420 TEM. A stock solution of peptide (10 mg/mL) was brought to pH 8 by incremental addition of 2μL of 1M KOH. The peptide solution was filtered through a 0.45 μm syringe filter. 190μL of peptide solution at a concentration of 0.7 mM was made acidic by the addition of 10μL of 1M HCl. It was immediately vortexed to mix and allowed to sit for 10 minutes to allow it to form a self-supporting gel. The gel was then diluted to 0.07 mM and thoroughly mixed by vortex. A formvar/carbon coated grid was floated on a 10 ul drop of peptide solution. The grid was then floated on water for 10 seconds, floated on 1% PTA for 1 min, and the excess PTA removed by #50 hardened Whatman filter paper. Images were captured using a SIS Megaview III digital CCD, and figures assembled using Adobe Photoshop with only linear adjustments in brightness and contrast.

**Synthetic Procedures**



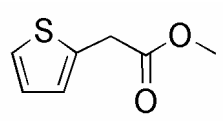

**2,2,5,5-tetramethyl-1-((5-(tributylstannyl)thiophen-2-yl)methyl)-1,2,5-azadisilolidine (B)**. A flame dried Schlenk flask under nitrogen was charged with a solution of STABASE-protected thiophene **A** (1.00 g, 3.91 mmol) in degassed THF (15 mL) and cooled to 0°C. While stirring, a solution of $^{n}$BuLi in

hexanes (2.55 mL, 1.58 M, 4.03 mmol) was added dropwise and the reaction was stirred for 1 hour at 0°C then allowed to warm to RT. $Bu_3SnCl$ (1.09 mL, 4.03 mmol) was then added at once and the reaction was stirred for an additional 1 hour. The reaction was diluted with ether and the organic phase was washed with brine and water, dried with magnesium sulfate, and concentrated by rotovap to yield the crude product as a yellow/orange oil which was used without further purification (2.13 g, 3.91 mmol, crude). $^1H$ NMR ($CDCl_3$) $\delta$: 6.96 (m, 2H), 4.22 (s, 2H), 1.60-1.53 (m, 6H), 1.39-1.32 (m, 6H), 1.08-1.06 (m, 6H), 0.94-0.89 (m, 9H), 0.73 (s, 4H), 0.02 (s, 12H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 154.0, 135.0, 134.7, 125.5, 40.8, 29.0, 27.3, 13.7, 10.8, 8.1, -0.4.

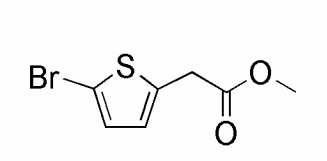



**(9H-fluoren-9-yl)methyl (5-(tributylstannyl)thiophen-2-yl)methylcarbamate (C)**. Stannylated thiophene **B** (7.16 g, 13.1 mmol) was dissolved in EtOAc (33 mL) and stirred with 0.076M HCl (33 mL) for 30 minutes. The reaction was then added to a separation funnel, diluted with EtOAc, and the organic phase was washed with brine and water, dried with magnesium sulfate, and concentrated by rotovap. The resulting oil was taken up in 45 mL of a 1:1 THF:$H_2O$ solution containing sodium bicarbonate (1.44 g, 17.1 mmol). Fmoc-OSu (4.44 g, 13.1 mmol) was then added portionwise over 30 minutes. The reaction was stirred for an additional 3 hours upon which it was diluted with water, acidified (pH=2-3) with 1M HCl, and extracted with EtOAc (3x). The organic phase was then washed with water, dried with magnesium sulfate, concentrated, and purified by

chromatography on a plug of silica (5% EtOAc in hexanes) to yield the product as yellow oil (7.94 g, 12.7 mmol, 97%). $^1$H NMR ($CDCl_3$) $\delta$: 7.80 (d, 2H, *J* = 7.6 Hz), 7.63 (d, 2H, *J* = 7.4 Hz), 7.42 (t, 2H, *J* = 7.2 Hz), 7.33 (t, 2H, *J* = 7.3 Hz), 7.12 (d, 1H, *J* = 2.4 Hz), 7.06 (d, 2H, *J* = 3.0 Hz), 5.29 (broad, 1H), 4.64 (d, 2H, *J* = 5.8 Hz), 4.47 (d, 2H, *J* = 7.0 Hz), 4.26 (t, 1H, *J* = 6.9 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$: 171.2, 156.2, 146.7, 144.0, 141.4, 137.0, 135.4, 127.7, 127.2, 127.1, 125.1, 120.0, 66.9, 60.4, 47.3, 39.9, 29.0, 28.9, 27.3, 21.1, 14.3, 13.7, 13.7, 10.9.

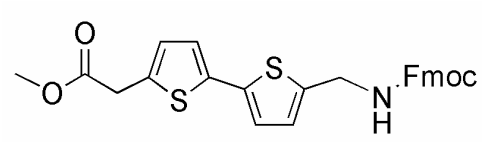



**Methyl 2-(thiophen-2-yl)acetate**. Thiophene acetic acid (27.3 g, 192 mmol) was treated with a solution of $H_2SO_4$ (5.76 mL, 108 mmol) in MeOH (384 mL) at reflux for 1 hour. The reaction was then cooled to room temperature, concentrated by rotovap, diluted with ether, washed with 5% sodium bicarbonate and brine. The organic phase was then dried with magnesium sulfate and concentrated by rotovap to yield the product as a yellow oil (27.4 g, 176 mmol, 91%) which was used without further purification. The product matches data for commercially available 19432-68-9.



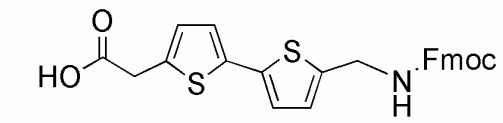

**Methyl 2-(5-bromothiophen-2-yl) acetate (D)**. A solution of methyl 2-(thiophen-2-yl) acetate (27.44 g, 175.7 mmol) was dissolved in DMF (500 mL) and stirred in the dark as NBS (37.52 g, 210.8 mmol) was added portionwise. The reaction

was stirred for 3 hours at which TLC indicated completion of the reaction. The reaction was diluted with ether and the organic phase was washed with ammonium chloride and water, then dried with magnesium sulfate and concentrated by rotovap. The resulting crude oil was purified by triturating with hexanes, decanting off the organic phase above the oil, then subjecting the oil to chromatography on a gradient plug of silica gel (hexanes to 10% EtOAc in hexanes) to yield the product as a yellow oil (33.90 g, 144.2 mmol, 82%). The product matches literature data.[ii] $^1$H NMR ($CDCl_3$) $\delta$: 6.89 (d, $J$ = 4.0 Hz, 1H), 6.69 (dt, $J$ = 4.0 Hz, 1H), 3.76 (s, 2H), 3.72 (s, 3H).




**Methyl 2-(5'-((((9H-fluoren-9-yl)methoxy)carbonylamino)methyl)-2,2'-bithiophen-5-yl)acetate (E).** A flame dried Schlenk flask was charged with $Pd(PPh_3)_4$ (0.220 g, 0.191 mmol), evacuated and placed under $N_2$. Degassed dioxane (21.0 mL) was cannulated in to a flame-dried round bottom flask containing stannylated and Fmoc-protected thiophene **C** (7.94 g, 12.7 mmol), which was dissolved and then cannulated into the Schlenk flask. Brominated thiophene methyl ester **D** (1.49 g, 6.36 mmol) was then added at once and the reaction heated to 90$^o$C and stirred for 18 hours. The reaction was cooled to room temperature, diluted with ether, and filtered through celite. The organic phase was then washed with brine and water, dried with magnesium sulfate, and concentrated by rotovap. The crude oil was taken into $CH_2Cl_2$ and purified on a

plug of silica using $CH_2Cl_2$ as the mobile phase and the eluents were concentrated by rotovap. The resulting oil was triturated with hexanes and the solids that formed were filtered and rinsed with hexanes to yield the product as faint pink/tan solid (2.16 g, 4.41 mmol, 69%). $^1$H NMR ($CDCl_3$) $\delta$: 7.76 (d, 2H, *J* = 7.6 Hz), 7.59 (d, 2H, *J* = 8.8Hz), 7.39 (t, 2H, *J* = 7.4 Hz), 7.30 (t, 2H, *J* = 7.4 Hz), 6.96 (m, 2H), 6.82 (m, 2H), 5.17 (broad, 1H), 4.51 (d, 2H, *J* = 5.9 Hz), 4.46 (d, 2H, *J* = 7.1 Hz), 4.23 (t, 1H, *J* = 6.7 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$: 170.6, 156.1, 143.8, 141.3, 140.2, 137.15, 137.0, 134.1, 127.7, 127.6, 127.0, 126.4, 125.0, 123.3, 123.2, 123.2, 123.1, 120.0, 66.8, 52.3, 47.2, 40.0, 35.4, 29.7. HRMS (FAB) m/z calculated for $(C_{27}H_{23}NO_4S_2)^+$ 489.1068, found 489.1069.



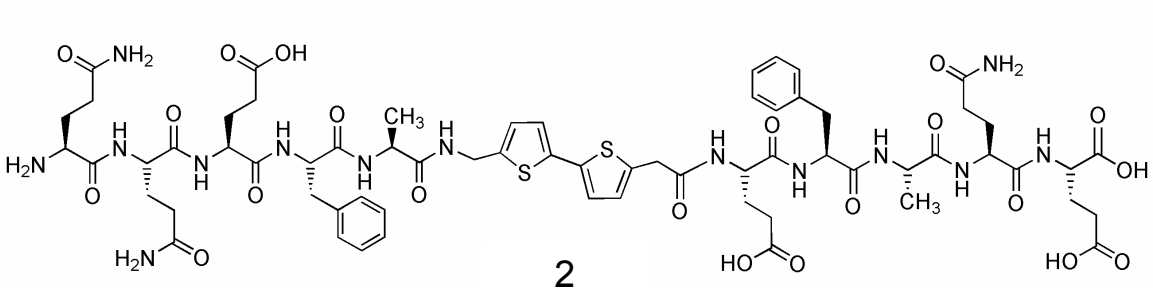

**2-(5'-((((9H-fluoren-9-yl)methoxy)carbonylamino)methyl)-2,2'-bithiophen-5-yl)acetic acid (1)**. Bithiophene amino ester **E** (2.16 g, 4.41 mmol) was dissolved in a 0.8 M $CaCl_2$ solution of $^i$PrOH:$H_2O$ (7:3) (110mL). The solution was then treated with NaOH (0.212 g, 5.29 mmol) and stirred for 18 hours at room temperature. The reaction was then heated to 40$^o$C and stirred for an additional 6 hours. The reaction was then neutralized with 1M HCl and diluted with EtOAc. The organic phase was then washed with water, dried with magnesium sulfate, and concentrated by rotovap. The crude oil was then dissolved in minimum amount of hot EtOAc and then precipitated by the addition of excess hexanes. The solids were filtered and rinsed with hexanes to provide the product isolated as tan solid (1.90 g, 4.00 mmol, 90%). $^1$H NMR (DMSO-d6) $\delta$: 7.99 (t, 1H, *J* =

5.9 Hz), 7.87 (d, 2H, *J* = 7.4 Hz), 7.69 (d, 2H, *J* = 7.4Hz), 7.41 (t, 2H, *J* = 7.6 Hz), 7.32 (t, 2H, *J* = 7.4 Hz), 7.05 (d, 2H, *J* = 3.4Hz), 6.88 (d, 1H, *J* = 3.8Hz), 6.86 (d, 1H, *J* = 3.4Hz), 4.36 (d, 2H, *J* = 7.0Hz), 4.32 (d, 2H, *J* = 5.7Hz), 4.24 (t, 1H, *J* = 6.8Hz), 3.82 (s, 2H). $^{13}$C NMR (DMSO-d6) $\delta$: 172.0, 156.6, 144.3, 142.5, 141.2, 136.3, 136.1, 136.0, 128.2, 128.1, 127.4, 126.6, 125.6, 123.4, 120.6, 65.9, 47.2, 35.5. HRMS (FAB) m/z calculated for $(C_{26}H_{21}NO_4S_2)^+$ 475.0912, found 475.0914.

**General synthesis of peptides:**

All peptides were synthesized using standard solid phase 9-fluorenylmethoxycarbonyl (Fmoc) chemistry on a Wang resin preloaded with Fmoc-Glu (O-$^t$Bu). Fmoc deprotection was performed by mixing the resin in a piperidine/DMF (2:8) solution for 10 minutes (2x), then rinsing with DMF, MeOH, and DCM. For all standard amino acid couplings, 3.0 eq. (relative to the resin substitution) of Fmoc-protected amino acid was activated externally with 2.9 eq. of O-Benzotriazole-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU) and 10 eq. of diisopropylethylamine (DIPEA). The activated Fmoc-protected amino acid was then added to a peptide chamber containing the Wang resin and mixed for 3 hours. The resin was then drained and rinsed with NMP, MeOH, and DCM then allowed to dry. All coupling and deprotection steps were monitored by performing a Kaiser test on a few resin beads which were removed from the peptide chamber after drying. The resin was prepared for cleavage by washing with acetic acid, DCM, and MeOH then drying under high vacuum. Cleavage from the resin and removal of side-chain protecting groups was accomplished by stirring the resin with 20 mL of trifluoroacetic acid (TFA), water, and

triisopropylsilane (TIPS) (95:2.5:2.5) for 3 hours. The resin was removed by filtration and washed with 5 mL of the cleavage mixture. The filtrate volume was then reduced by half by rotovap and the peptide was precipitated by the addition of 200 mL cold diethyl ether. The precipitate was filtered and rinsed with cold diethyl ether to obtain the crude peptide. The crude peptide was then eluted off the filter with ammonium hydroxide, condensed by rotovap, and dried under high vacuum. The peptide was then triturated with acetonitrile and the solids filtered to yield the final product.



2

**2**. For coupling of **1**: 0.178 g (0.374 mmol) of **1** and 0.135 g (0.355 mmol) of HBTU was added to Wang-EQAFE-$NH_2$ and dissolved in 1:2 NMP:DCM, then 0.326 mL of DIPEA (1.87 mmol) was added and the reaction was mixed for 3 hours. Peptide **9** underwent two rounds of coupling to fully incorporate **1**. Fmoc-deprotection, peptide elongation (A, F, E, Q, Q), and final cleavage from the resin was performed as described above. Final peptide was obtained as a brown powder. $^1$H NMR ($D_20$) $\delta$: 7.23-6.97 (m, 12H), 6.81 (broad, 1H), 6.76 (broad, 1H), 4.47 (broad, 2H), 4.37 (d, *J* = 6.9 Hz, 2H), 4.21-3.91 (m, 10H), 3.62 (m, 2H), 2.98-2.72 (broad, 4H), 2.28-1.68 (broad, 29H), 1.24-1.16 (m, 6H). MS (ESI -) m/z

calculated for $(C_{65}H_{82}N_{14}O_{21}S_2)^{2-}/2$ : 729.79, found 729.55; m/z calculated for $(C_{65}H_{81}N_{14}O_{21}S_2)^{3-}/3$ : 486.19, found 486.05.

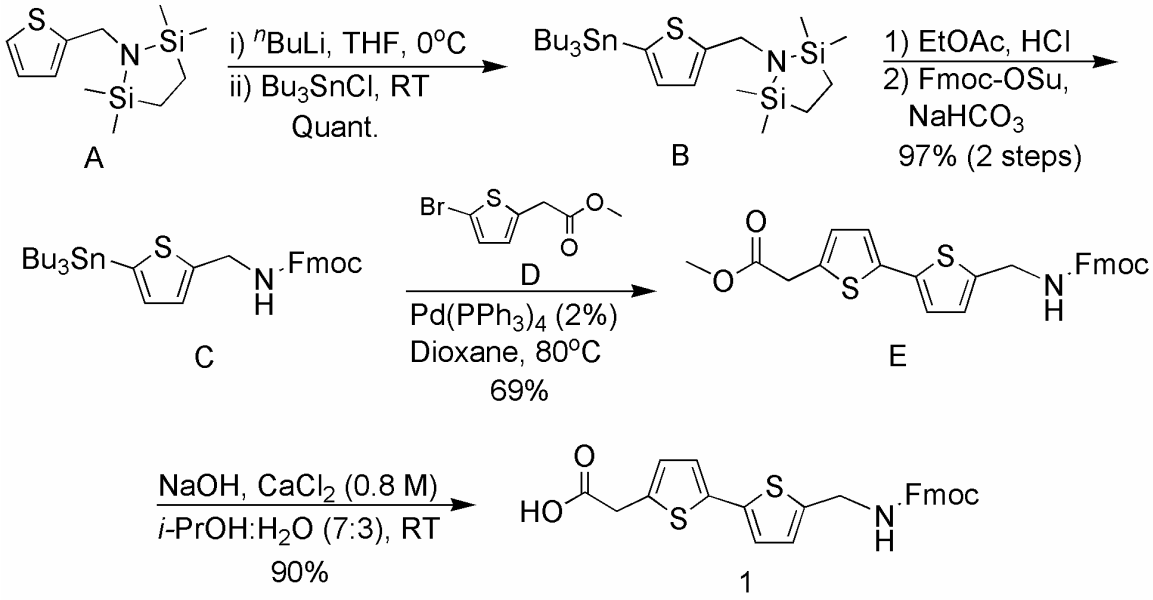



**Figure S1**: Total synthesis of bithiophene-based amino acid **1.**

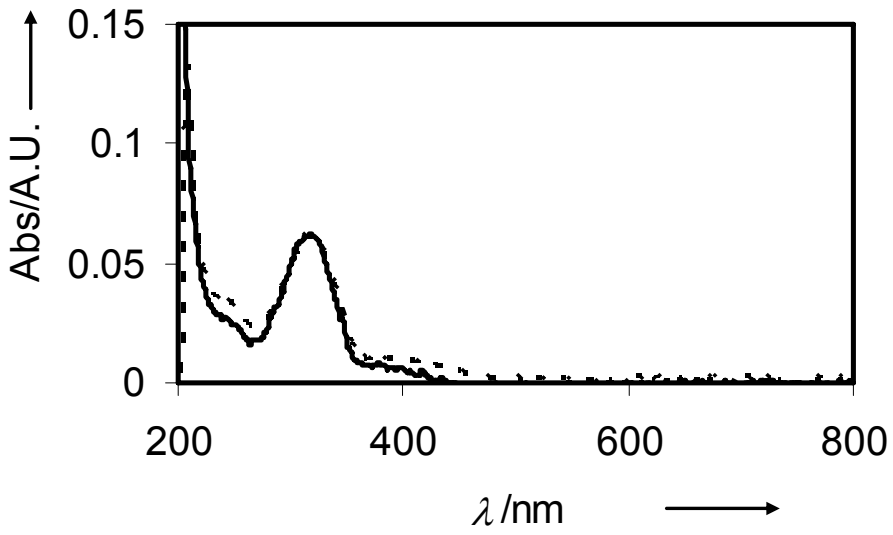



**Figure S2**: UV-Vis spectra of **2** taken in basic water (conditions that foster dissolution, pH 7, solid line) and acidic water (conditions that foster aggregation, pH -1, dashed line).

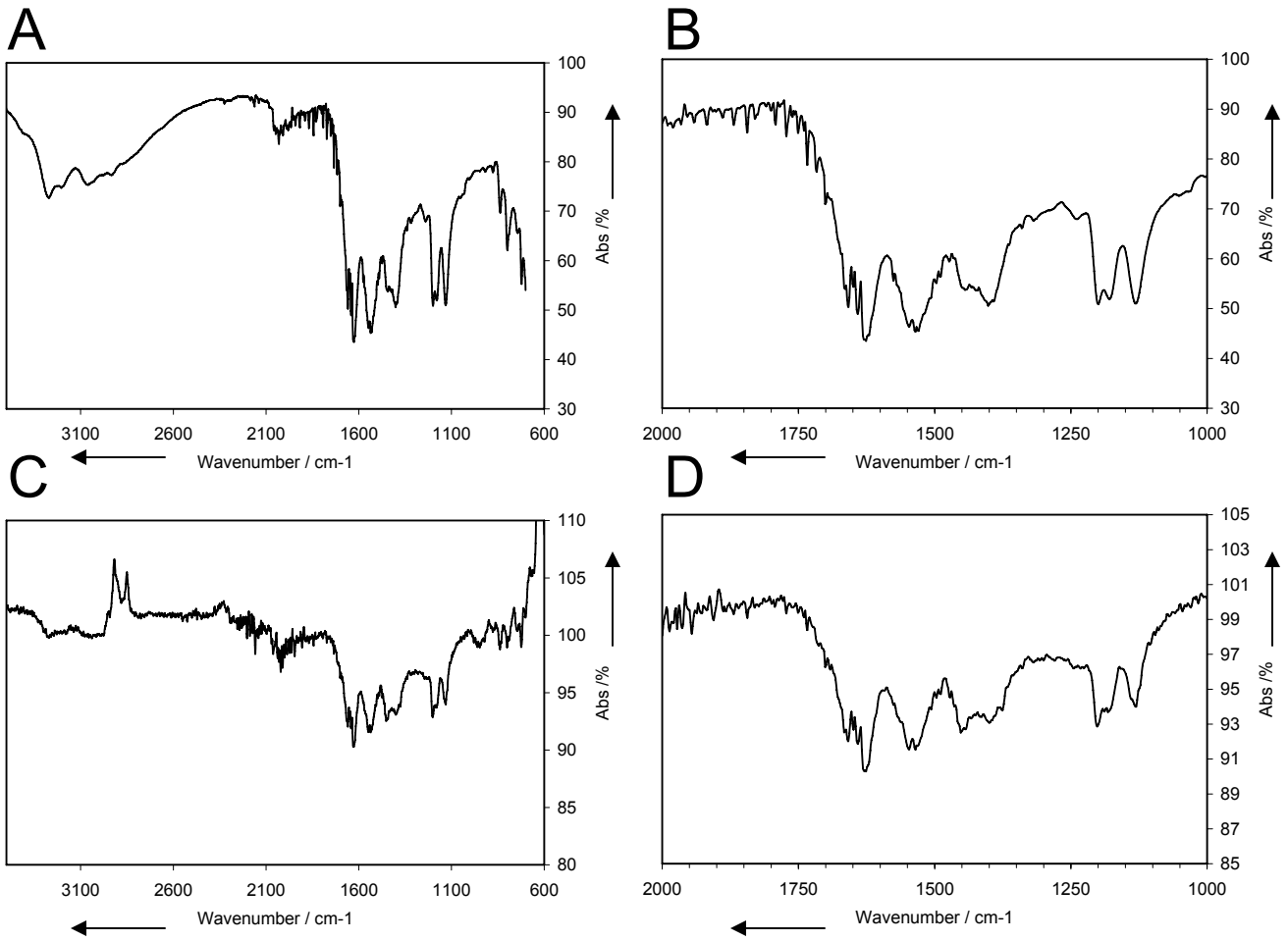



**Figure S3**: Attenuated total reflectance IR spectra of **2** in the solid state (A and B) and mineral oil mull (C and D).

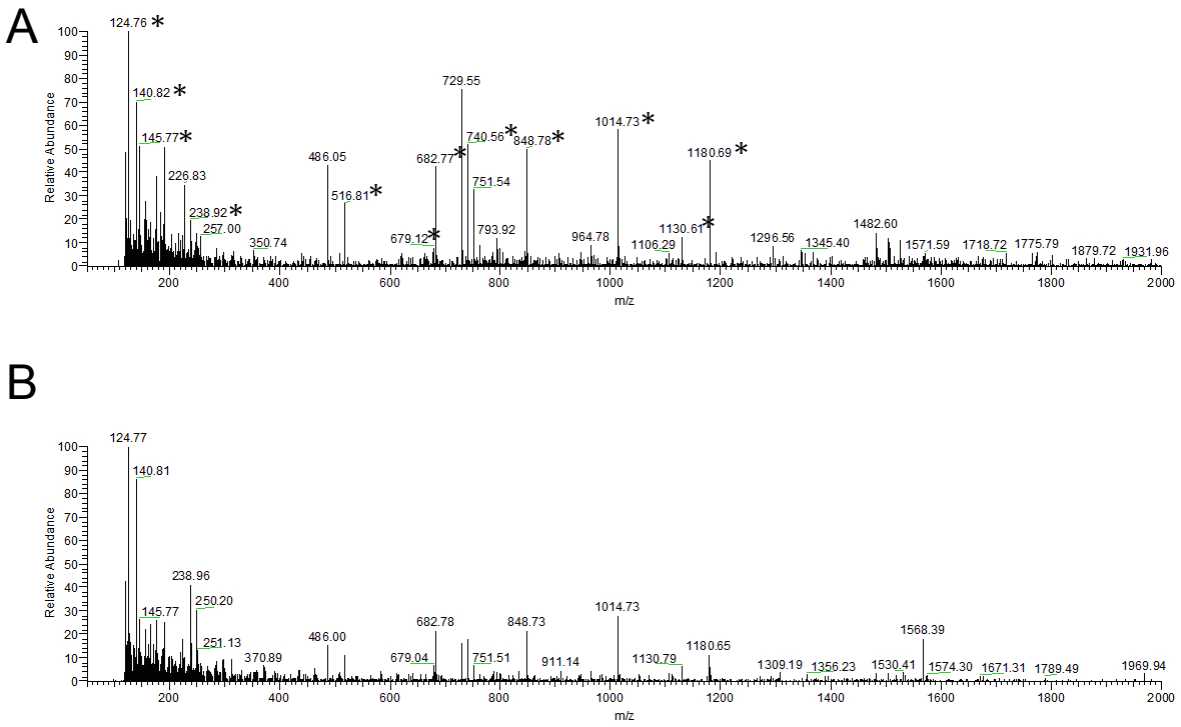



**Figure S4**: Mass spec (ESI -) of **2** (A). Asterisks' indicate mass peaks which are observable in background spectra. Background spectrum for **2** (B) is shown because of a large number of background peaks.

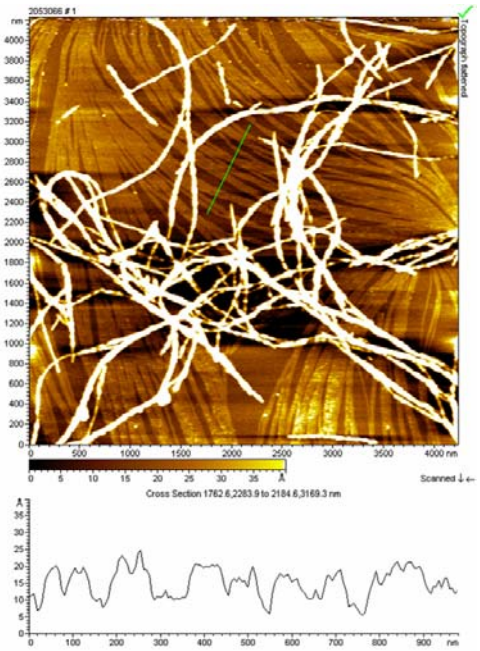


**Figure S5**: AFM image of **2** on mica substrate showing the formation of 1-D nanostructures on top of a surface passivated with flat tape-like structures. The height profile of the tape-like structures shows heights of approximately 1 nm.

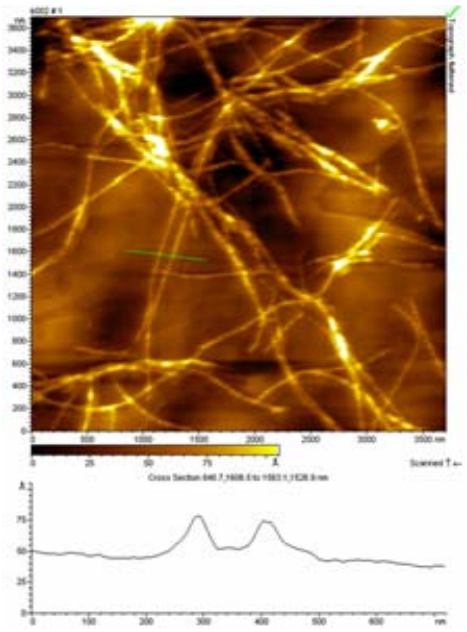


**Figure S6**: AFM image of **2** on graphite substrate showing the formation of 1-D nanostructures and lack of flat tape-like structures.

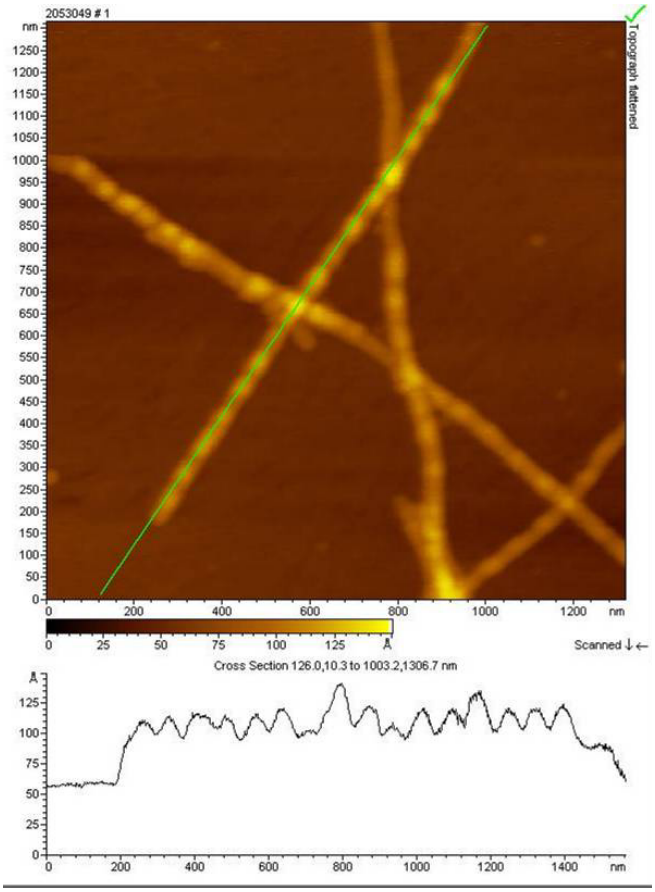



**Figure S7**: Height profile along the long axis of 1-D nanostructures derived from **2** which show regular height fluctuations. Average spacing of height fluctuations of indicated structures is 76 nm.

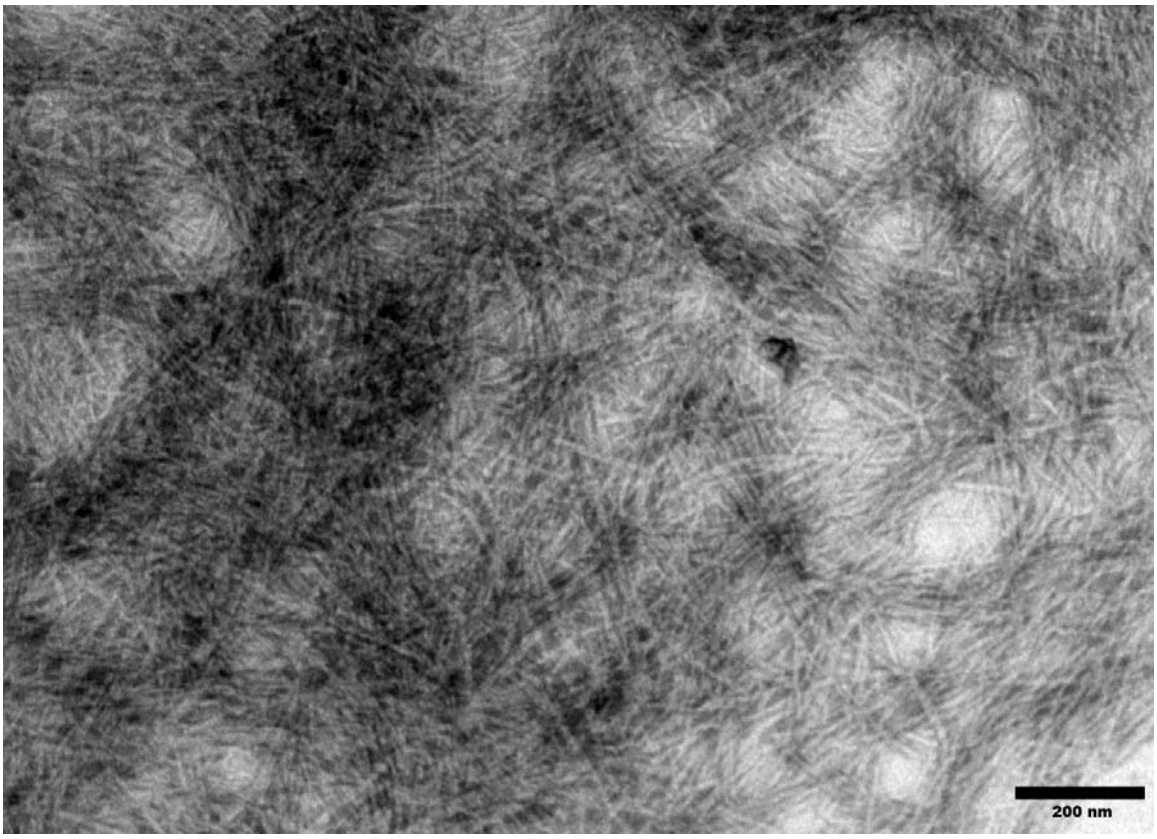



**Figure S8**: TEM image of **2** on formvar/carbon coated grids showing the formation of 1-D nanostructures. Sample was analyzed at 100 kV and a magnification of 86000x.

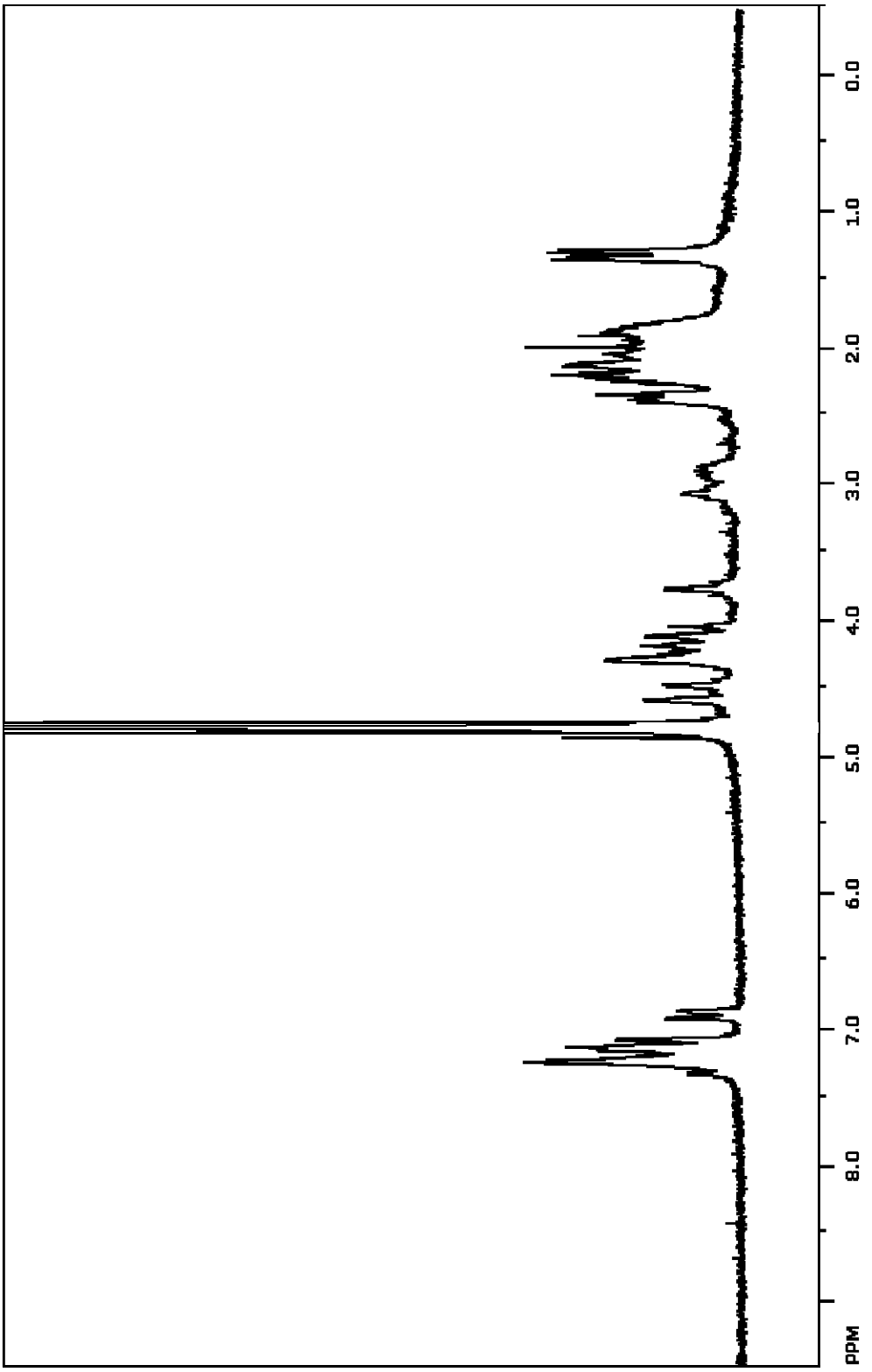



**Figure S9**: $^{1}H$ (400 MHz, $D_2O$) NMR of **2.**

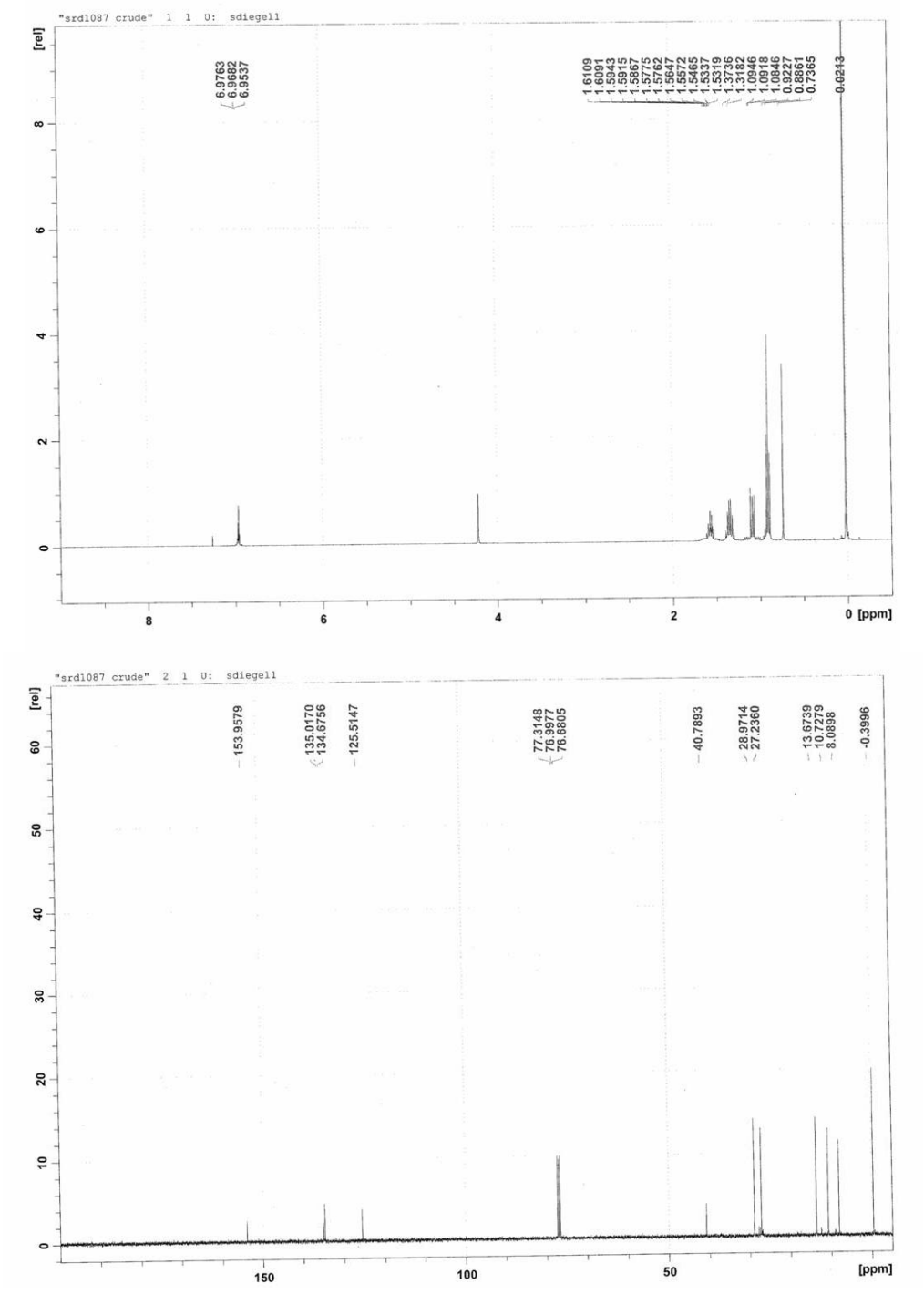



**Figure S10**: $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR of stannylated thiophene **B.**

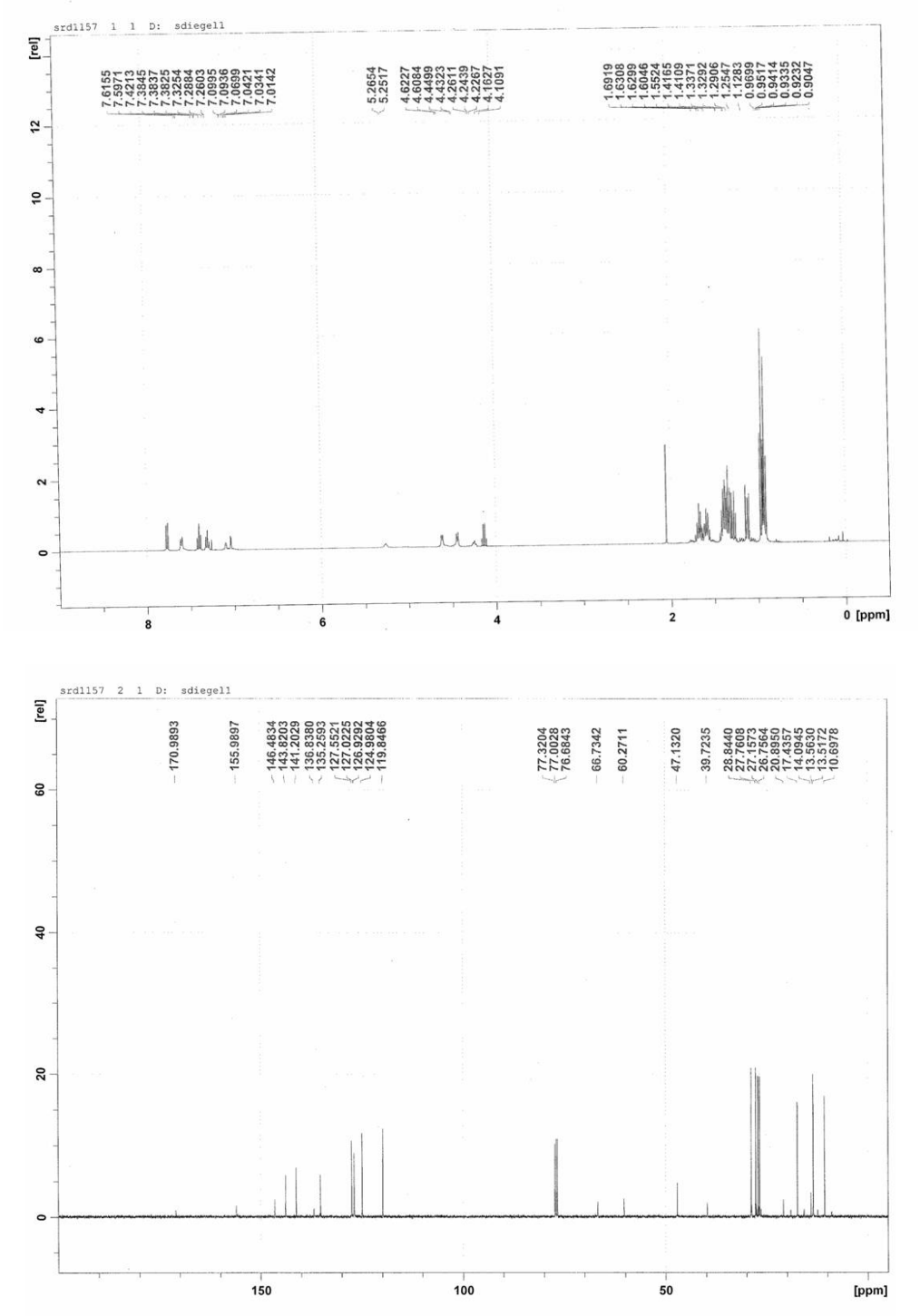



**Figure S11**: $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR of stannylated and Fmoc-protected thiophene **C.**

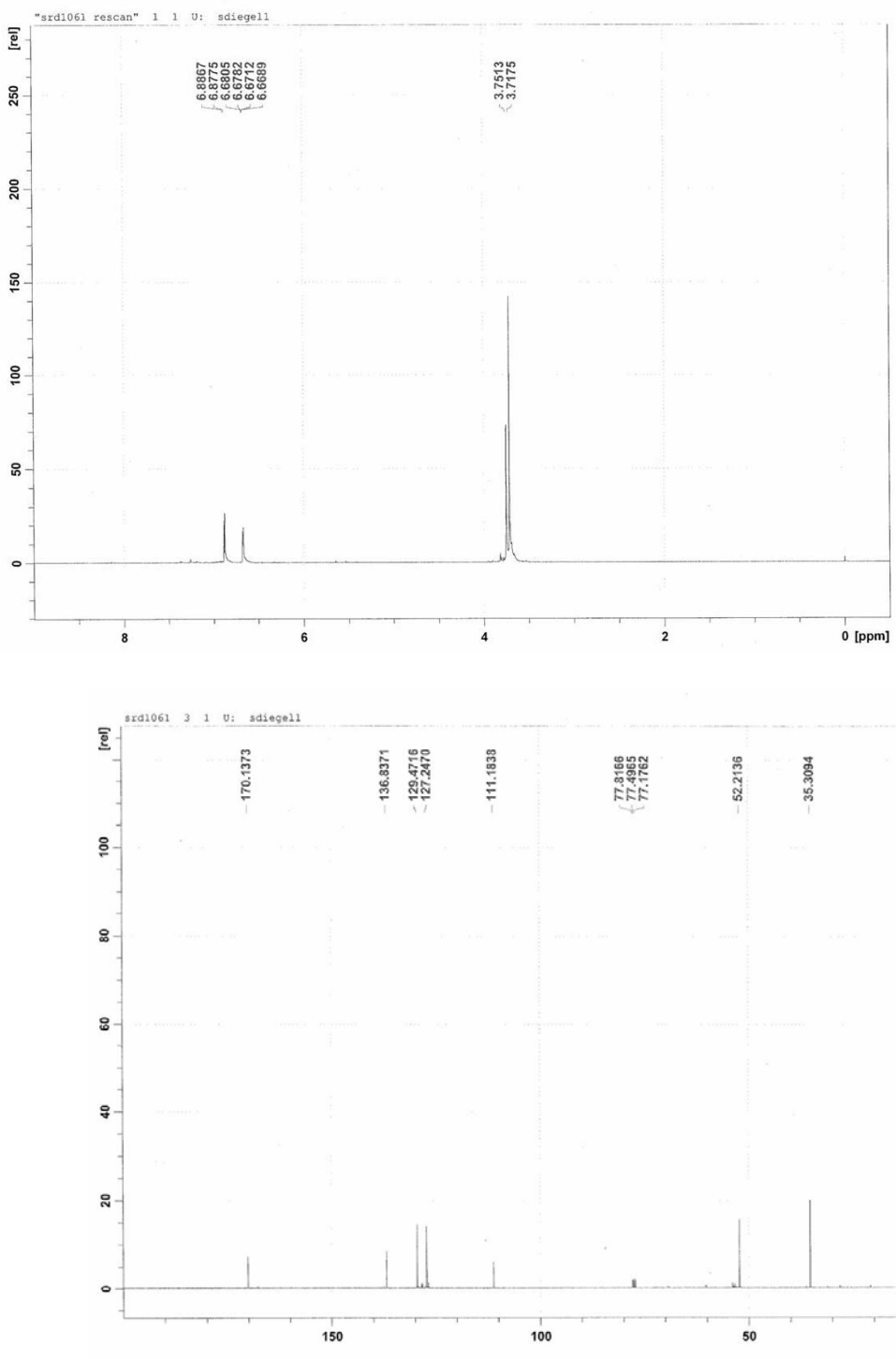



**Figure S12**: $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR of brominated thiophene methyl ester **D.**

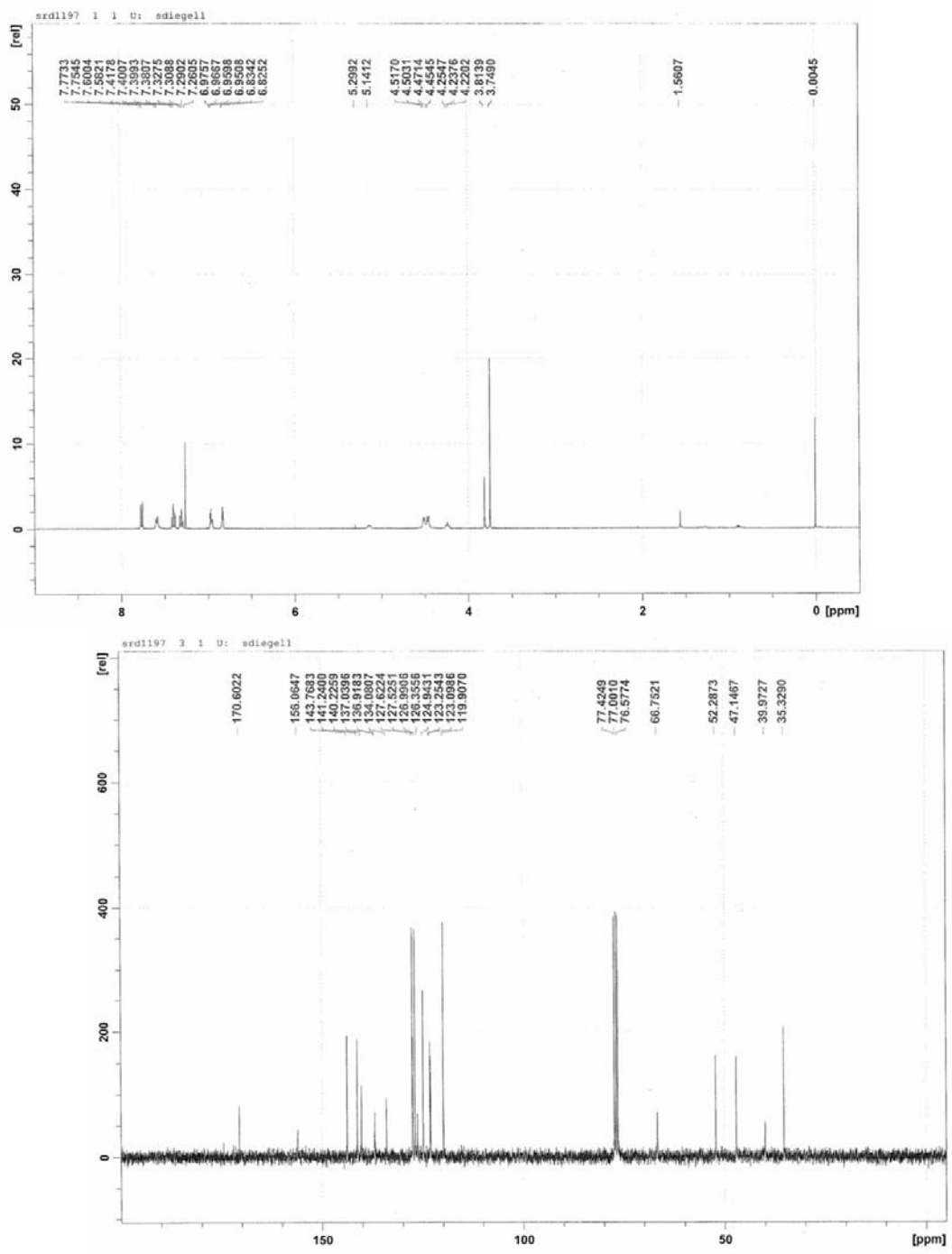



**Figure S13**: $^{1}H$ (400 MHz, $CDCl_3$) and $^{13}C$ (100 MHz, $CDCl_3$) NMR of bithiophene amino ester **E.**

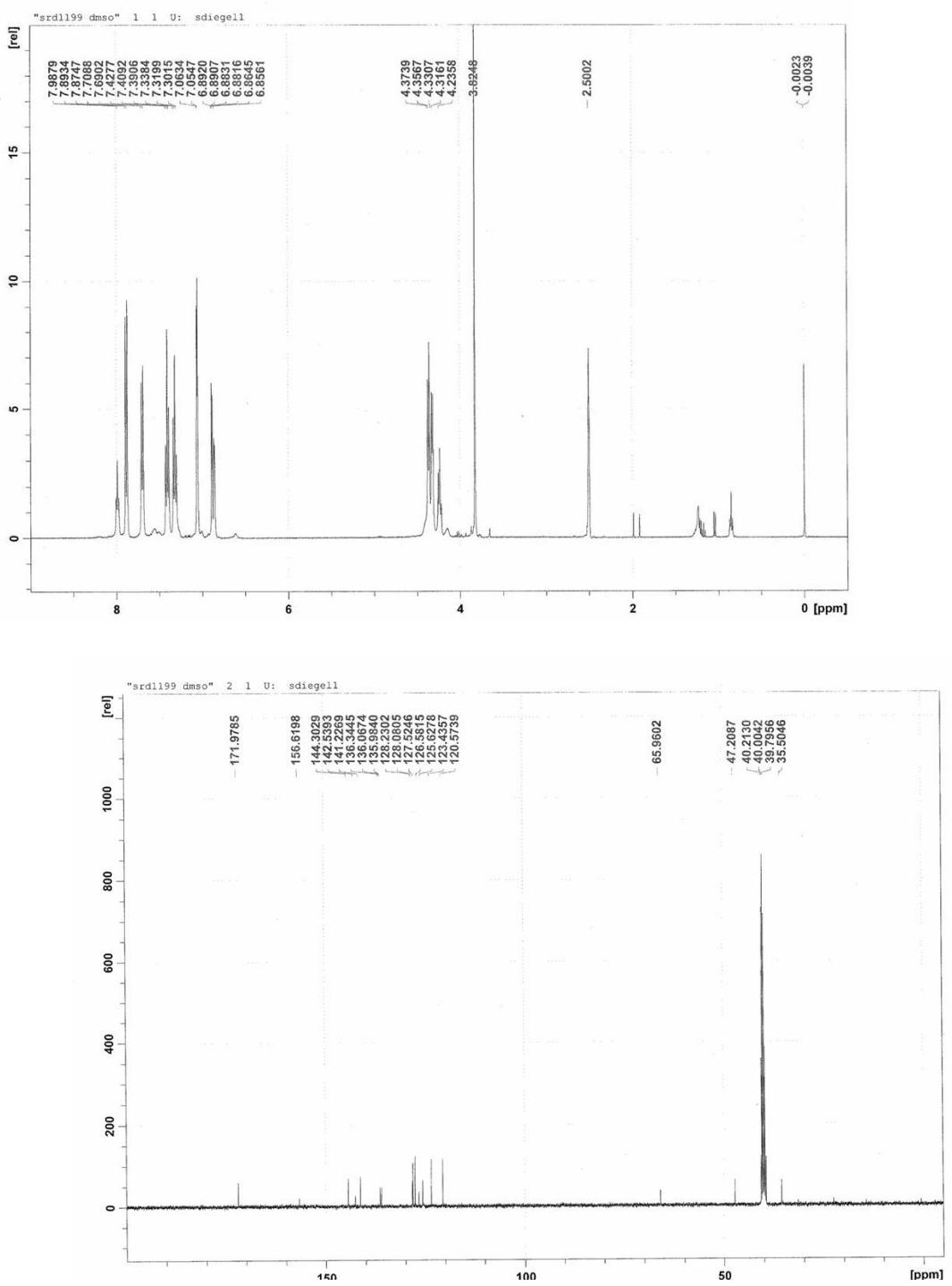



**Figure S14**: $^{1}H$ (400 MHz, DMSO) and $^{13}C$ (100 MHz, DMSO) NMR of bithiophene amino acid **1.**

[i] Mugurama, H., Saito, T., Sasaki, S., Hotta, S., Karube, I. Synthesis and Characterization of α,α'-Bis(aminomethyl)oligo-thiophenes and Their Related Compounds. *J. Heterocyclic Chem*. (**1996**), 33, (1), 173-8

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