

Supplementary Information – Chemical Communications

Oligothiophene-Derivatized Azobenzene as Immobilized Photoswitchable Conjugated Systems

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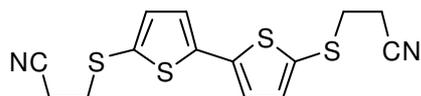
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1) Synthesis

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DRX 500 spectrometer operating at 500.13 and 125.7 MHz respectively ; δ are given in ppm (relative to TMS) and coupling constants (J) in Hz. Mass spectra were recorded under EI mode on a DSQ-Thermolectron mass spectrometer, under MALDI-TOF mode on a MALDI-TOF-MS BIFLEX III Bruker Daltonics spectrometer. IR spectra were recorded on a Perkin-Elmer model 841 spectrophotometer, samples being embedded in KBr discs or thin films between NaCl plates. UV-Vis absorption spectra were recorded on a lambda 950 Perkin-Elmer spectrometer. Melting points were obtained from a Reichert-Jung Thermovar hot-stage microscope apparatus and are uncorrected. Elemental analysis were performed by the Service de Microanalyses of ICSN-CNRS (Gif sur Yvette, France).

The synthesis of *trans*-azo-*p*-toluene¹ and S-4-bromobutyl ethanethioate **5**² has been carried out according to known procedures. The use of *E*-1-(4-(bromomethyl)phenyl)-2-*p*-tolylidiazene **3** has been reported but its synthesis has not been described in the corresponding article.³

5,5'-Bis(2-cyanoethylsulfanyl)-2,2'-bithiophene 2.⁴ Under an inert atmosphere (N_2), a solution of *n*-BuLi 1.6 M in hexane (8 mL, 12.8 mmol, 2.1equiv.) was added dropwise to a solution of 2,2'-bithiophene (1 g, 6 mmol) in anhydrous THF (50 mL) cooled to -78°C . After the lithiated salt precipitated, the reaction mixture was stirred at -78°C for 0.5 h, then allowed to warm to room temperature and stirred at this temperature for 1 h.



¹ (a) A. P. Terent'ev and Y. D. Mogilyanskii, *Dokl. Akad. Nauk S.S.S.R.*, 1955, 10391-10393; (b) B. Jousselme, P. Blanchard, N. Gallego-Planas, E. Levillain, J. Delaunay, M. Allain, P. Richomme and J. Roncali, *Chem. Eur. J.*, 2003, **9**, 5297.

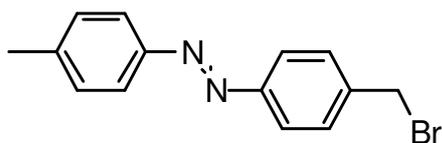
² T.K. Tran, M. Oçafraïn, S. Karpe, P. Blanchard, J. Roncali, S. Lenfant, S. Godey and D. Vuillaume, *Chem. Eur. J.* 2008, **14**, 6237.

³ F. Vögtle, D. Udelhofen, S. Abramson and B. Fuchs, *Journal of Photochemistry and Photobiology A: Chemistry*, 2000, **131**, 41.

⁴ L. Sanguinet, O. Alévêque, P. Blanchard, M. Dias, E. Levillain and D. Rondeau, *J. Mass Spectrom.*, 2006, **41**, 830.

Sulfur (0.41 g, 12.8 mmol, 2.1 equiv.) was added in one portion to the reaction mixture which was further stirred at room temperature for 1 h. After cooling to 0°C, 3-bromopropionitrile (1.15 mL, 13.8 mmol, 2.3 equiv.) was added dropwise and the reaction mixture was left under stirring for 18 h at room temperature. After dilution with CH₂Cl₂ (300 mL), the organic phase was washed with water, dried over MgSO₄ and concentrated under reduced pressure. Purification by chromatography on silica gel (eluent: CH₂Cl₂; the mixture was adsorbed on silica gel before deposition on top of column) gave compound **2** (1.75 g, 87% yields) as a slightly yellow powder. mp 110-111°C. ¹H NMR (500 MHz, CDCl₃): δ = 7.14 (d, 2H, ³J=3.6Hz, H_{thio}); 7.06 (d, 2H, ³J=3.6Hz, H_{thio}); 3.00 (t, 4H, ³J=7.1Hz, CH₂-S); 2.66 (t, 4H, ³J=7.2Hz, CH₂-CN). ¹³C NMR (75 MHz, CDCl₃): δ = 141.4; 136.6; 130.9; 124.6; 117.6 (CN); 33.7; 18.2. UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 339 nm (4.28). Elemental analysis calcd (%) for C₁₄H₁₂N₂S₄: C 49.97, H 3.59, N 8.32; found: C 50.04, H 3.51, N 7.91.

E-1-(4-(bromomethyl)phenyl)-2-p-tolyldiazeno-3. Under an inert atmosphere (N₂), ZrCl₄



(111 mg, 10% mol.)⁵ and *trans*-azo-*p*-toluene¹ (0.87 g, 4.14 mmol) were successively added to a solution of *N*-bromosuccinimide (1.47 g, 2 equiv.) in anhydrous CH₂Cl₂ (80 mL) cooled to

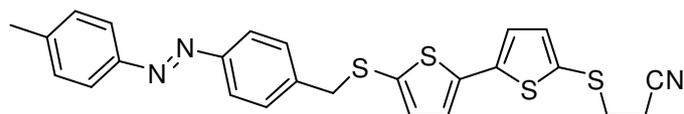
-78°C. The reaction mixture was allowed to warm to room temperature and stirred at this temperature for 18 h. TLC analysis showed the complete consumption of starting material and that formation of the target compound **3** is accompanied with a small amount of bis(bromomethyl) derivative **3'** as by-product. The reaction mixture was washed with a saturated aqueous solution of NaHCO₃ (100 mL) and with water (100 mL). The organic phase was dried over MgSO₄ and concentrated under reduce pressure. Purification by chromatography on silica gel (eluent: Petroleum Ether/CH₂Cl₂ 5:1; the mixture was adsorbed on silica gel before deposition on top of column) gave compound **3** (0.74 g, 62% yields) as an orange powder and compound **3'** (0.23 g, 15% yields) as well as an orange powder.

Compound 3: mp 154-155°C. ¹H NMR (500 MHz, CDCl₃): δ = 7.87 (d, 2H, ³J=8.2Hz, H_{benz}); 7.83 (d, 2H, ³J=8.2Hz, H_{benz}); 7.53 (d, 2H, ³J=8.2Hz, H_{benz}); 7.32 (d, 2H, ³J=8.1Hz, H_{benz}); 4.56 (s, 2H, CH₂); 2.44 (s, 3H, CH₃). ¹³C NMR (125 MHz, CDCl₃): δ = 152.4; 150.7;

⁵ Y. Zhang, K. Shibatomi and H. Yamamoto, *Synlett*, 2005, 2837.

141.9; 140.2; 129.9; 129.8; 123.1; 122.9; 32.8; 21.5. EI MS (70 eV) m/z (I%): 290 and 288 (M⁺, 15), 209 (M-Br, 100). UV/Vis (CH₂Cl₂): λ_{max} = 335 nm (π-π*), 440 nm (n-π*).

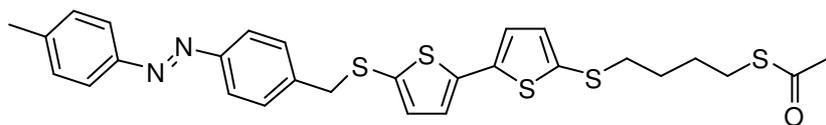
***E*-1-(4-((5'-(2-Cyanoethylsulfanyl)-2,2'-bithiophene-5-sulfanyl)methyl)phenyl)-2-*p*-**



tolyldiazene 4. Under an inert atmosphere (N₂), a solution of CsOH.H₂O (0.26 g, 1.55 mmol) in N₂ degassed MeOH (2 mL) was added

dropwise to a solution of **2** (0.5 g, 1.49 mmol) in N₂ degassed DMF (20 mL) at room temperature. The reaction mixture was stirred for 1 h. After dropwise addition of a solution of bromo derivative **3** (0.47 g, 1.63 mmol) in N₂ degassed DMF (20 mL), the stirring was continued for 4 h. The solvents were evaporated under reduced pressure to give a residue which was diluted with CH₂Cl₂ (150 mL). This solution was washed with water (2 x 50 mL), dried over MgSO₄ and concentrated under reduced pressure. Purification by chromatography on silica gel (eluent: CH₂Cl₂; the mixture was adsorbed on silica gel before deposition on top of column) gave compound **4** (0.44-0.49 g, 60-67% yields) as a yellow-orange powder. mp 135-134°C. ¹H NMR (500 MHz, CDCl₃): δ = 7.82 (d, 4H, ³J=8.3Hz, H_{benz}); 7.31 (d, 4H, ³J=8.3Hz, H_{benz}); 7.11 (d, 1H, ³J=3.8Hz, H_{thio}); 7.00 (d, 1H, ³J=3.6Hz, H_{thio}); 6.95 (d, 1H, ³J=3.7Hz, H_{thio}); 6.82 (d, 1H, ³J=3.6Hz, H_{thio}); 4.03 (s, 2H, Ph-CH₂-S); 2.98 (t, 2H, ³J=7.2Hz, S-CH₂); 2.64 (t, 2H, ³J=7.2Hz, CH₂-CN); 2.44 (s, 3H, CH₃). ¹³C NMR (125 MHz, CDCl₃): δ = 151.8; 150.7; 142.1; 141.7; 140.4; 140.3; 136.7; 135.7; 133.1; 130.2; 129.8; 129.7; 124.4; 124.3; 122.9; 122.8; 117.7 (CN); 43.4; 33.7; 21.5; 18.2. IR (KBr): ν̄ = 2241 cm⁻¹ (CN). EI MS (70 eV) m/z (I%): 491 (M⁺, 15), 209 (100). MALDI MS: 490 (491 for C₂₅H₂₁N₃S₄). UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 339 nm (4.55, π-π*), 437 nm (3.08, n-π*). Elemental analysis calcd (%) for C₂₅H₂₁N₃S₄: C 61.07, H 4.30, N 8.55; found: C 61.14, H 4.53, N 8.41.

***E*-1-(4-((5'-(6-Oxo-5-thiaheptylsulfanyl)-2,2'-bithiophene-5-sulfanyl)methyl)phenyl)-2-*p*-**

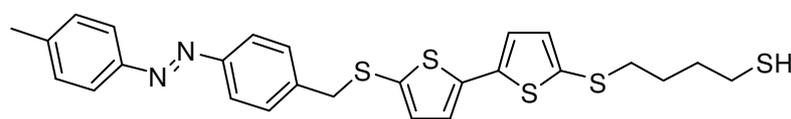


tolyldiazene 1. Under an inert atmosphere (N₂), a solution of CsOH.H₂O

(0.08 g, 0.48 mmol) in N₂ degassed MeOH (1 mL) was added dropwise to a solution of **4** (0.20 g, 0.41 mmol) in N₂ degassed DMF (20 mL) at room temperature. The reaction mixture

was stirred for 1 h. After dropwise addition of a solution of S-4-bromobutyl ethanethioate **5** (0.11 g, 0.52 mmol) in N₂ degassed DMF (2 mL), the stirring was continued for 4 h. The solvents were evaporated under reduced pressure to give a residue which was diluted with CH₂Cl₂ (100 mL). This solution was washed with water (2 x 50 mL), dried over MgSO₄ and concentrated under reduced pressure. Purification by chromatography on silica gel (eluent: Petroleum Ether/CH₂Cl₂ 1:1) gave compound **1** (0.17-0.18 g, 74-78% yields) as a yellow-orange powder. mp 124-125°C. ¹H NMR (500 MHz, CDCl₃): δ = 7.82 (d, 4H, ³J=8.3Hz, H_{benz}); 7.31 (d, 4H, ³J=8.3Hz, H_{benz}); 6.99 (d, 1H, ³J=3.7Hz, H_{thio}); 6.97 (d, 1H, ³J=3.7Hz, H_{thio}); 6.92 (d, 1H, ³J=3.7Hz, H_{thio}); 6.80 (d, 1H, ³J=3.7Hz, H_{thio}); 4.02 (s, 2H, Ph-CH₂-S); 2.87 (t, 2H, ³J=6.7Hz, CH₂-S-CO); 2.80 (t, 2H, ³J=6.7Hz, CH₂-S-Th); 2.44 (s, 3H, CH₃-Ph); 2.32 (s, 3H, CH₃-CO); 1.70 (m, 4H, CH₂-CH₂). ¹³C NMR (125 MHz, CDCl₃): δ = 195.6; 151.9; 150.8; 141.6; 141.1; 140.4; 140.1; 135.6; 134.3; 134.2; 132.5; 129.7; 124.1; 123.9; 122.9; 43.5; 38.3; 30.6; 28.5; 28.3; 21.5. IR (KBr): $\tilde{\nu}$ = 1700 cm⁻¹ (C=O). MALDI MS: 567 (568 for C₂₈H₂₈N₂OS₅). UV/Vis (CH₂Cl₂): λ_{max} (log ε) = 342 nm (4.53, π-π*), 440 nm (3.15, n-π*). Elemental analysis calcd (%) for C₂₈H₂₈N₂OS₅: C 59.12, H 4.96, N 4.92; found: C 59.41, H 4.88, N 4.61.

E-1-(4-((5'-(4-Mercaptobutylsulfanyl)-2,2'-bithiophene-5-sulfanyl)methyl)phenyl)-2-p-



tolyldiazene 1-SH. Under an inert atmosphere (N₂), a solution of CsOH.H₂O (0.04 g, 0.24 mmol) in N₂ degassed MeOH (1 mL) was added dropwise to a solution of **1** (100 mg, 0.18 mmol) in anhydrous and N₂ degassed THF (5 mL) at room temperature. The reaction mixture was stirred for 2 h. After addition of a 1 M aqueous solution of HCl (0.3 mL), the stirring was continued for 2 h. The solvents were evaporated under reduced pressure to give a residue which was diluted with CH₂Cl₂ (40 mL). This solution was washed with water (2 x 20 mL), dried over MgSO₄ and concentrated under reduced pressure. Purification by flash-chromatography on silica gel (solubilization of the residue with CH₂Cl₂; eluent: Petroleum Ether/CH₂Cl₂ 2:1) gave compound **1-SH** (74 mg, 80% yields) as a yellow powder. mp 112-113°C. ¹H NMR (500 MHz, CDCl₃): δ = 7.82 (d, 4H, ³J=8.4Hz, H_{benz}); 7.31 (d, 4H, ³J=8.4Hz, H_{benz}); 6.99 (d, 1H, ³J=3.7Hz, H_{thio}); 6.97 (d, 1H, ³J=3.8Hz, H_{thio}); 6.92 (d, 1H, ³J=3.7Hz, H_{thio}); 6.81 (d, 1H, ³J=3.7Hz, H_{thio}); 4.02 (s, 2H, Ph-CH₂-S); 2.81 (t, 2H, ³J=6.8Hz, CH₂-S-Th); 2.53 (m, 2H, CH₂-SH); 2.44 (s, 3H, CH₃-Ph); 1.74 (m, 4H, CH₂-CH₂); 1.34 (t, 1H,

$^3J=7.9\text{Hz}$, SH). MALDI MS: 526 (526 for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{S}_5$). UV/Vis (CH_2Cl_2): λ_{max} ($\log \epsilon$) = 341 nm (4.53, $\pi-\pi^*$), 435 nm (3.04, $n-\pi^*$).

2) Cyclic Voltammetric and UV-Vis Data

The electrochemical and optical properties of 2,2'-bithiophene derivatives **1**, **1-SH**, **2** and **4**, and **p-diMeAB** in solution have been analyzed by cyclic voltammetry and UV-Vis spectroscopy. Table S1 summarizes experimental conditions and electrochemical and optical data.

Table S1. Cyclic Voltammetric^a and UV-vis^b

Compd	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)		E_{pa}^1 (V)	E_{pa}^2 (V)	E_{pc}^1 (V)	E_{pc}^2 (V)
	$\pi-\pi^*$	$n-\pi^*$				
p-diMeAB	336 (20500)	440 (1300)	-	-	-1.30	1.54
2	339 (18900)	-	1.16	1.29	-	-
4	339 (35700)	437 (1200)	1.09	1.25	-1.46 (sh)	-1.60
1	342 (34100)	440 (1400)	1.00	1.17	-1.48 (sh)	-1.60
1-SH	341 (33700)	435 (1100)	1.04	1.21	-1.57	-1.75

^a Performed with 1 mM of compd in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$ 1:1, scan rate 100 mV/s, Pt electrodes, SCE as reference. ^b In CH_2Cl_2 .

3) Trans-Cis isomerization (UV-vis spectroscopy)

The behavior of thioester compound **1** under irradiation has been investigated by UV-vis spectroscopy. Irradiation was realized with 360 nm (*trans* to *cis*) or 480 nm (*cis* to *trans*) monochromatic lights by using a 150 W xenon lamp with band-pass filters. The measured light intensity at the sample was 0.64 mW cm⁻² for UV light centered at 360 nm and 1.52 mW cm⁻² for visible light centered at 480 nm. The solution of **1** or **2** was directly irradiated in 1 x 1 cm² UV-quartz cuvettes.

A control experiment performed on a 4 x 10⁻⁵ M solution of *p*-diMeAB in dichloromethane shows that, as expected, irradiation with 360 nm causes bleaching of the 336 nm band with a hypsochromic shift of λ_{max} to 298 nm and a slight intensification of the n- π^* transition at 440 nm (Figure S3). The photostationary state was reached after *ca.* 3 h of irradiation at 360 nm. Return to the initial conditions can be achieved by irradiation at 480 nm.

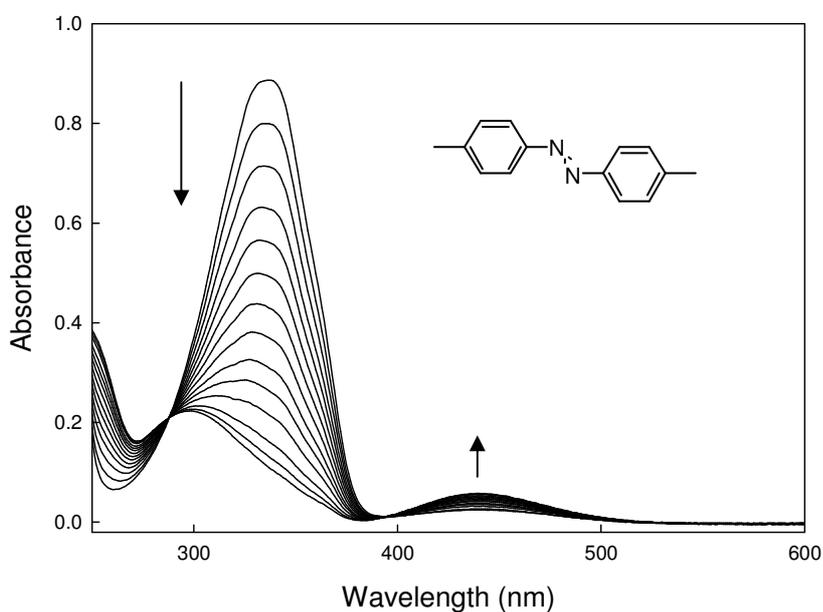


Figure S1. Changes in the UV-vis spectrum of *p*-diMeAB (4 x 10⁻⁵ M in CH₂Cl₂) at 20°C during photoirradiation at 360 nm for 0, 10, 20, 30, 40, 50, 60, 70, 85, 100, 115, 135, 155 and 175 min.

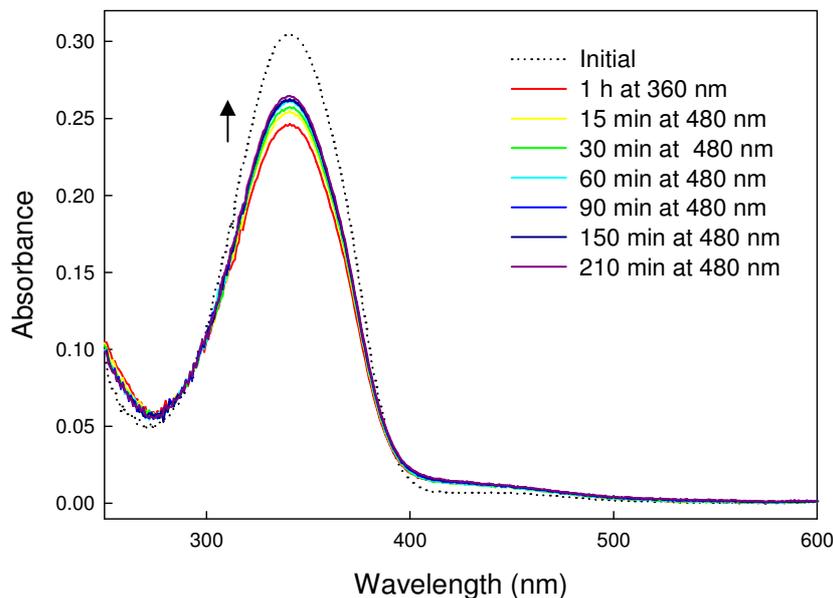


Figure S2: *Cis to Trans* isomerization of **1.** Changes in the UV-vis spectrum of **1** (4×10^{-6} M in CH_2Cl_2) at 20°C after 1 h of irradiation at 360 nm and then increasing time of irradiation at 480 nm for 15, 30, 60, 90, 150 and 210 min.

4) Cyclic voltammetry in solution

Electrochemical experiments were carried out with a PAR 273 potentiostat-galvanostat in a three-electrode single compartment cell equipped with platinum of 2 mm diameter and modified gold disks as working electrodes, a platinum wire counter electrode and a silver wire as pseudo-reference electrode. The ferricinium/ferrocenium couple was used as internal reference ($E^\circ(\text{Fc}^+/\text{Fc}) = 0.405$ V/SCE in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ or CH_2Cl_2). Potentials were then expressed towards a saturated calomel reference electrode (SCE).

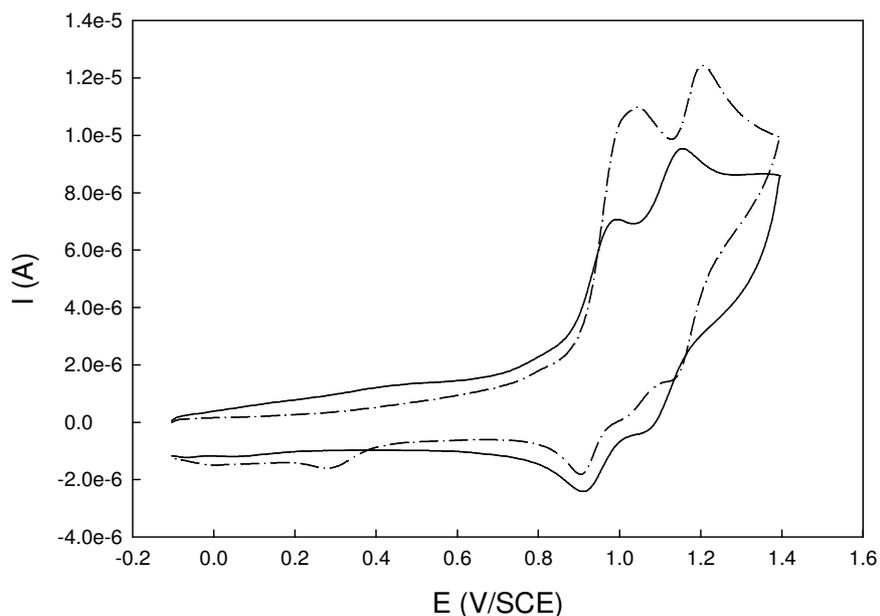


Figure S3. CVs of **1-SH** (dash-dot line) and **1** (10^{-3} M) in 0.1 M $n\text{-Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2\text{-CH}_3\text{CN}$ 1:1, scan rate 100 mV/s.

5) Preparation of SAM and Characterization by Cyclic Voltammetry

The gold electrodes used for cyclic voltammetry consist in homemade gold disks of 0.20 cm^2 diameter on glass. They were prepared by physical vapor deposition of an adhesion layer of chromium of *ca.* 2 nm followed by a layer of gold of *ca.* 30 nm on glass. The electrodes are then annealed at 200°C using a furnace placed in a glove box for 2h30 under argon in order to avoid any pollution. The gold electrodes were subjected to a UV-ozone treatment for 15 min and then immersed in dichloromethane under ultrasounds for 1 min before use.

Monolayers of **1-SH** were obtained by immersion of cleaned gold electrodes in a millimolar solution of compound **1-SH** in CH_2Cl_2 for 96 h in the absence of light to prevent *trans* to *cis* isomerization. The resulting modified electrodes were rinsed with pure CH_2Cl_2 and CH_3CN and were then analyzed by cyclic voltammetry. As depicted in Figure S6, the first CV trace exhibits two one-electron reversible oxidation waves corresponding to the successive formation of the radical-cation and dication of the bithiophene backbone respectively at $E_{pa}^1 = 0.95$ V and at $E_{pa}^2 = 1.29$ V, values which are relatively closed to that measured for **1-SH** in solution using Pt working electrode ($E_{pa}^1 = 1.04$ V and at $E_{pa}^2 = 1.21$

V). However, additional potential sweeps between 0.3 V and 1.3 V/SCE lead to the loss of the monolayer due to oxidation of gold at such positive potentials.

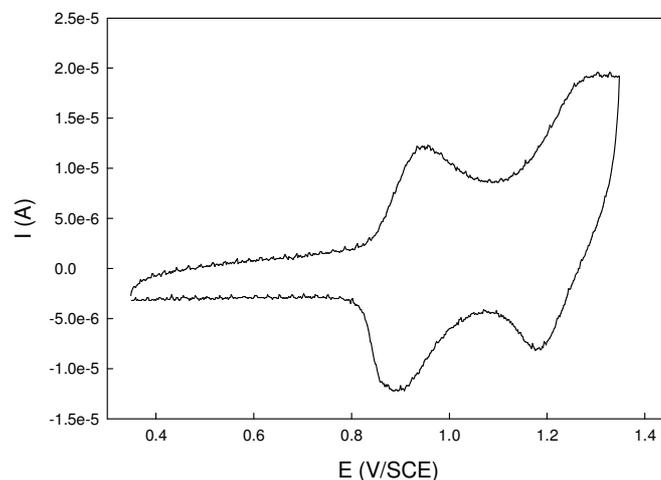


Figure S4. First CV trace of a monolayer of **1-SH** on gold immersed in 0.1 M *n*-Bu₄NPF₆/CH₂Cl₂, scan rate 500 mV/s.

By contrast, a reproducible CV trace was obtained when the upper positive potential value was limited to +1.0 V. Under these conditions (Figure 2) a stable CV trace with a reversible one-electron oxidation wave at $E_{pa}^1 = 0.98$ V was obtained. It is noteworthy that the monolayers of **1-SH** were found more stable when cyclic voltammetry was performed in a CH₂Cl₂/CH₃CN 1:1 mixture than in pure CH₂Cl₂ probably due to favored desorption of molecules of **1-SH** in the later case.

6) Structural characterization of the SAM

Contact-angle measurements. We measured the water contact angle with a remote-computer controlled goniometer system (DIGIDROP by GBX, France). We deposited a drop (10-30 μL) of desionized water ($18\text{M}\Omega\cdot\text{cm}^{-1}$) on the surface and the projected image was acquired and stored by the computer. Contact angles were extracted by contrast contour image analysis software. These angles were determined few seconds after application of the drop. These measurements were carried out in a clean room (ISO 6) where the relative humidity (50%) and the temperature (22°C) are controlled. The precision with these measurements are $\pm 2^\circ$.

Spectroscopic ellipsometry. We recorded spectroscopic ellipsometry data in the visible range using an UVISEL (Jobin Yvon Horiba) Spectroscopic Ellipsometer equipped with a DeltaPsi 2 data analysis software. The system acquired a spectrum ranging from 2 to 4.5 eV (corresponding to 300 to 750 nm) with intervals of 0.1 eV (or 15 nm). Data were taken at an angle of incidence of 70° , and the compensator was set at 45.0° . We fitted the data by a regression analysis to a film-on-substrate model as described by their thickness and their complex refractive indexes. First, we recorded a background before monolayer deposition for the gold coated substrate. Secondly, after the monolayer deposition, we used a 2 layers model (substrate/SAM) to fit the measured data and to determine the SAM thickness. We used the previously measured optical properties of the gold coated substrate (background), and we fixed the refractive index of the organic monolayer at 1.50. The usual values in the literature for the refractive index of organic monolayers are in the range 1.45-1.50.⁶ We can notice that a change from 1.50 to 1.55 would result in less than 1 \AA error for a thickness less than 30 \AA . We estimated the accuracy of the SAM thickness measurements at $\pm 1 \text{\AA}$.

Electrical measurements. We performed current-voltage measurements by conducting-Atomic Force Microscopy (C-AFM) in ambient air (Dimension 3100, Veeco), using a PtIr submitted to coated tip (tip radius of curvature less than 25nm, force constant in the range 0.17-0.2N/m). Placing the conducting tips at a stationary point contact formed nano-junctions. A square grid of 10x10 is defined with a lateral step of 2 nm. At each point, 10 I-V curves are acquired and averaged. Out of the 100 I-V traces, some are eliminated due to lateral drift of

⁶ (a) N. Parikh, A. Allara, I. Ben Azouz and F. Rondelez, *J. Phys. Chem.*, 1994, **98**, 7577-7590; (b) A. Ulman, *An introduction to ultrathin organic films: from Langmuir-Blodgett to self-assembly*, edited by Academic Press, Harcourt Brace Jovanovich, Publishers Boston, 1991.

the C-AFM setup and about 40 I-V "mechanically stable" traces are used for statistics. The load force was adjusted in the range 20-30 nN and measured by force-distance curves with the controlling software of the Dimension 3100. The bias was applied on the Au substrate and the tip was grounded through the input of the current amplifier. We focused the light from a xenon lamp to an optical fiber. We used two dichroic filters centered at 360 nm and 480 nm. At the output of the optical filter, the SAMs were irradiated on about 1 cm² at power density of 70 μW/cm² (at 360 nm) and 250 μW/cm² (at 480nm). Due to the size and design of the Dimension 3100, it is not easily possible to bring the optical fiber close to the AFM tip, thus the light irradiation was not done with the AFM tip contacting the monolayer. We moved the sample mounted on the chuck back and forth between AFM tip area and the illumination area located nearby on the Dimension 3100 platform.

7) ^1H and ^{13}C NMR spectra

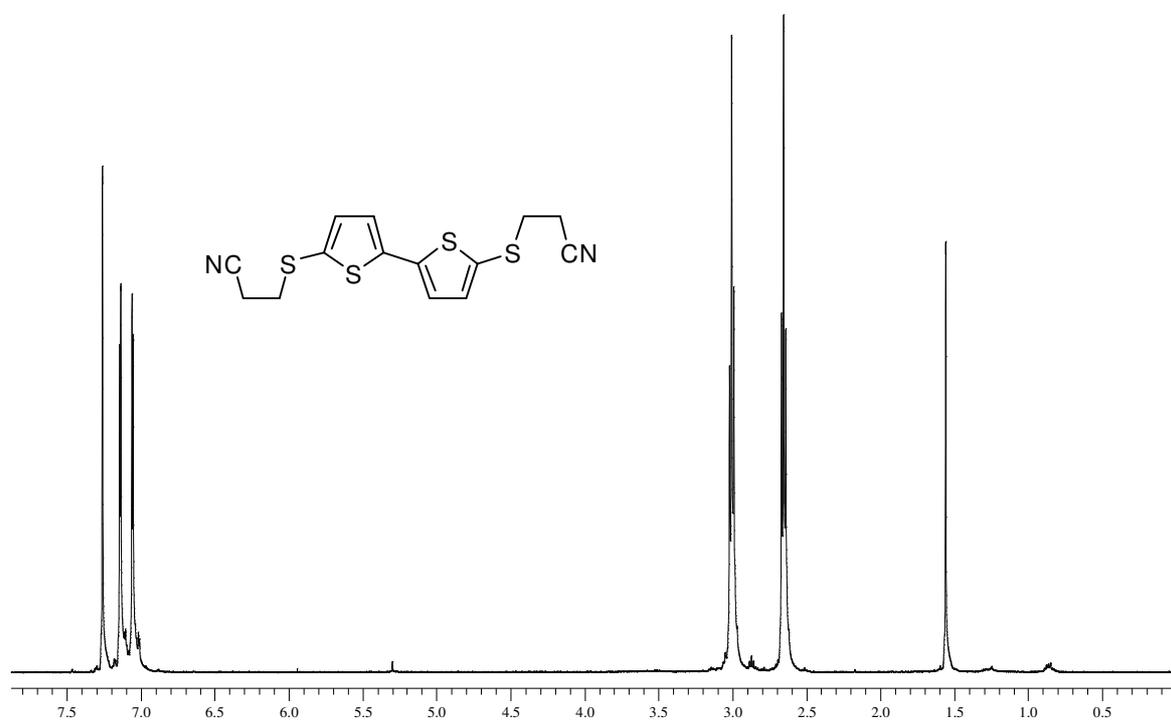


Figure S5. ^1H NMR (500 MHz) spectrum of **2** in CDCl_3 .

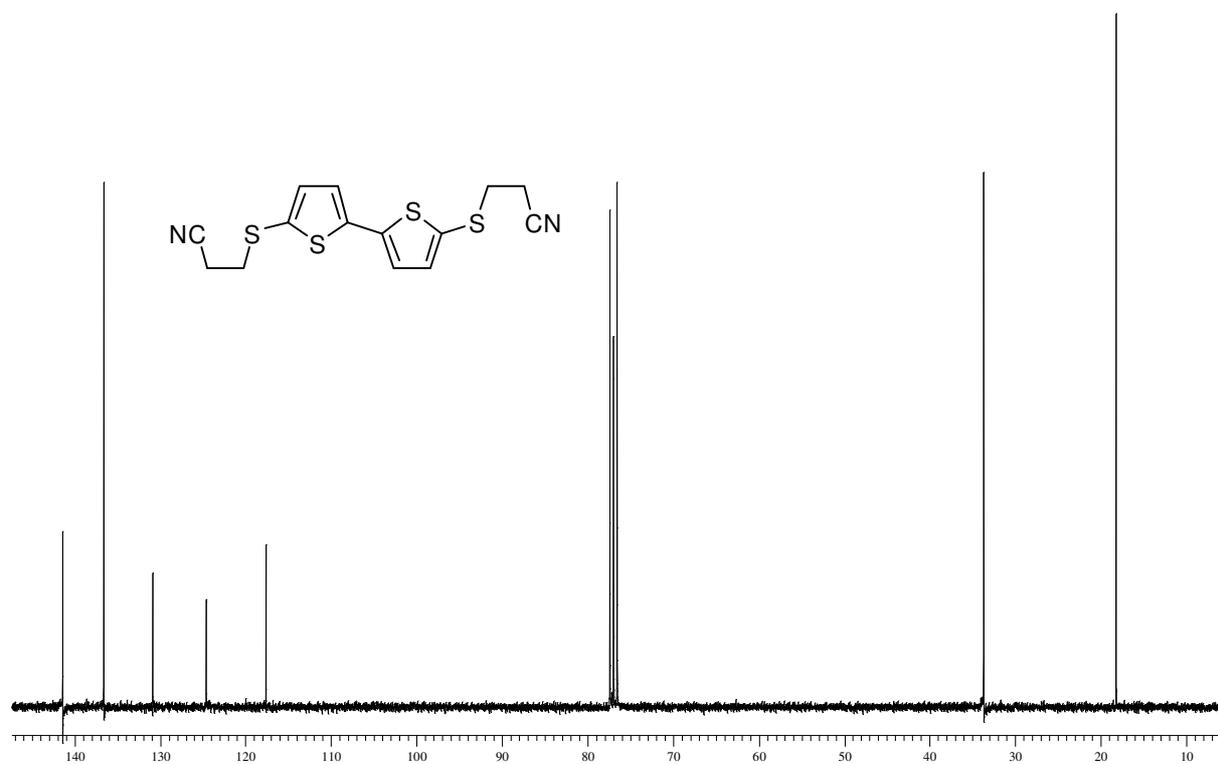


Figure S6. ^{13}C NMR (75 MHz) spectrum of **2** in CDCl_3 .

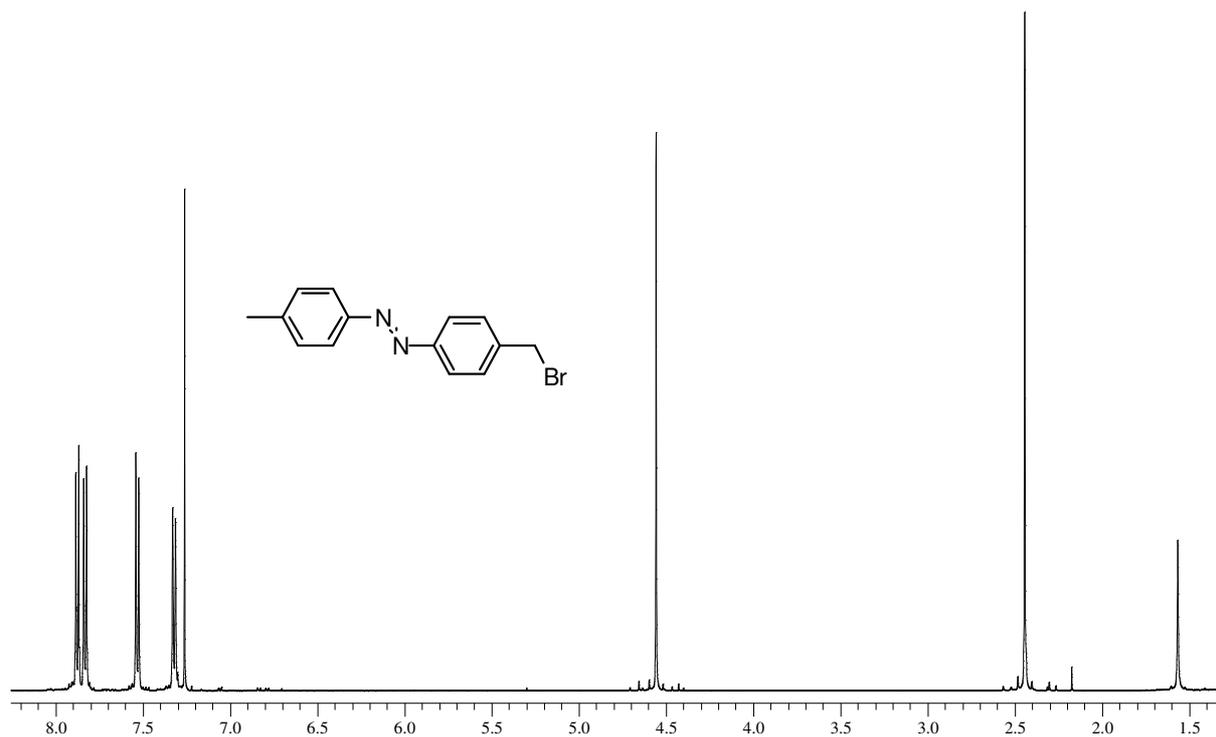


Figure S7. ¹H NMR (500 MHz) spectrum of **3** in CDCl₃.

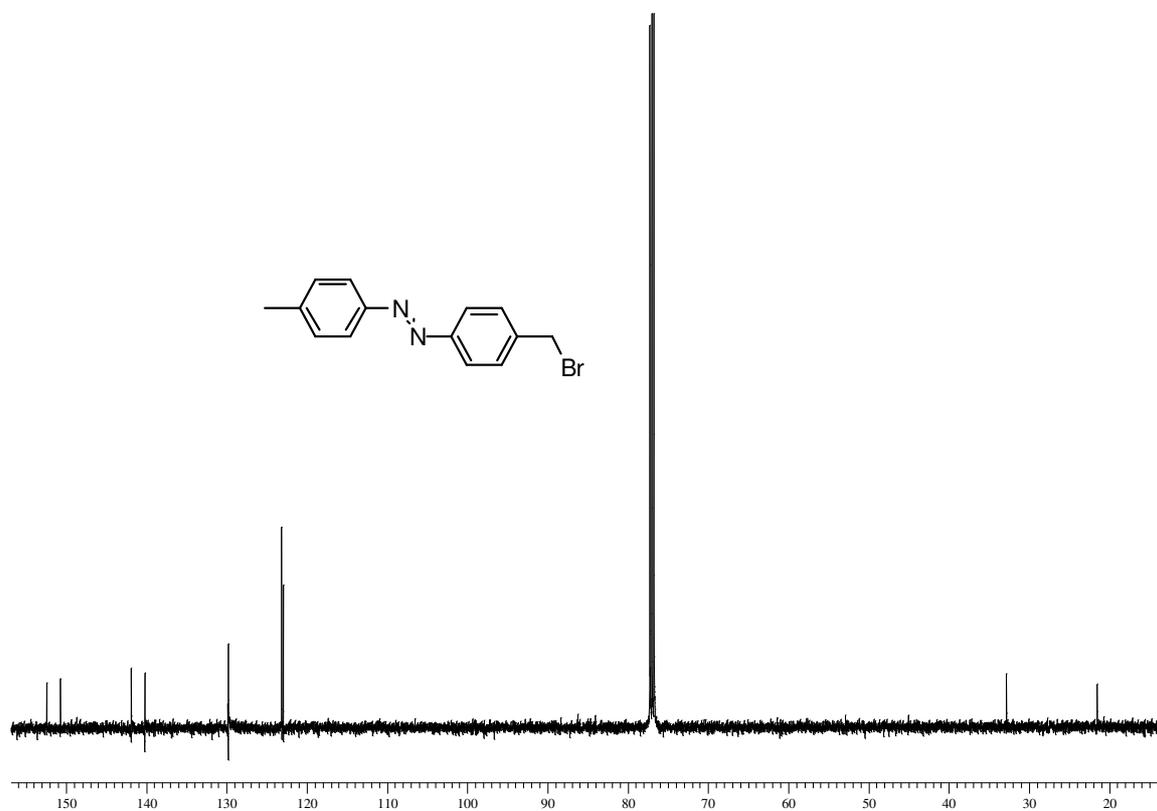


Figure S8. ¹³C NMR (125 MHz) spectrum of **3** in CDCl₃.

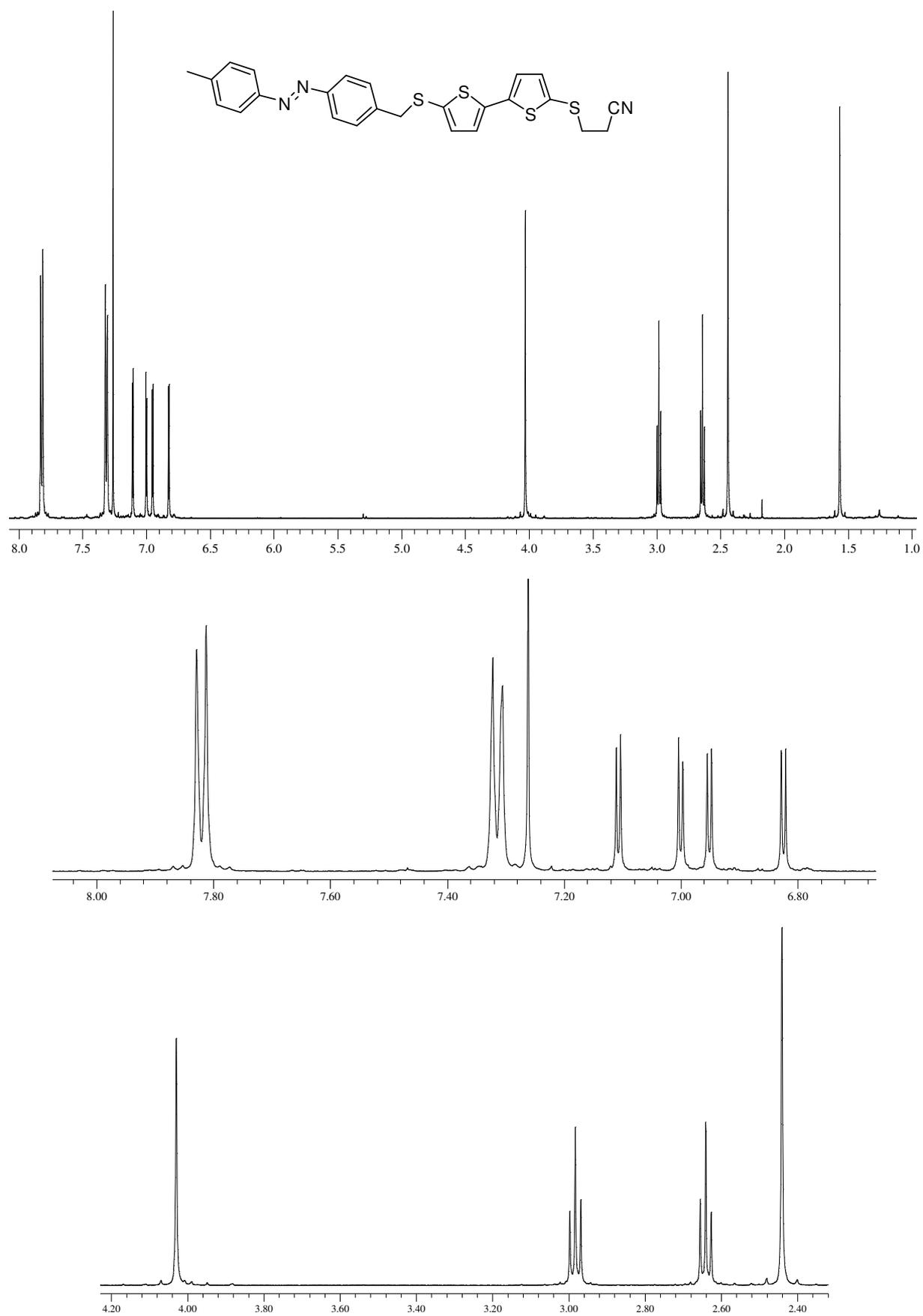


Figure S9. ^1H NMR (500 MHz) spectrum of **4** in CDCl_3 .

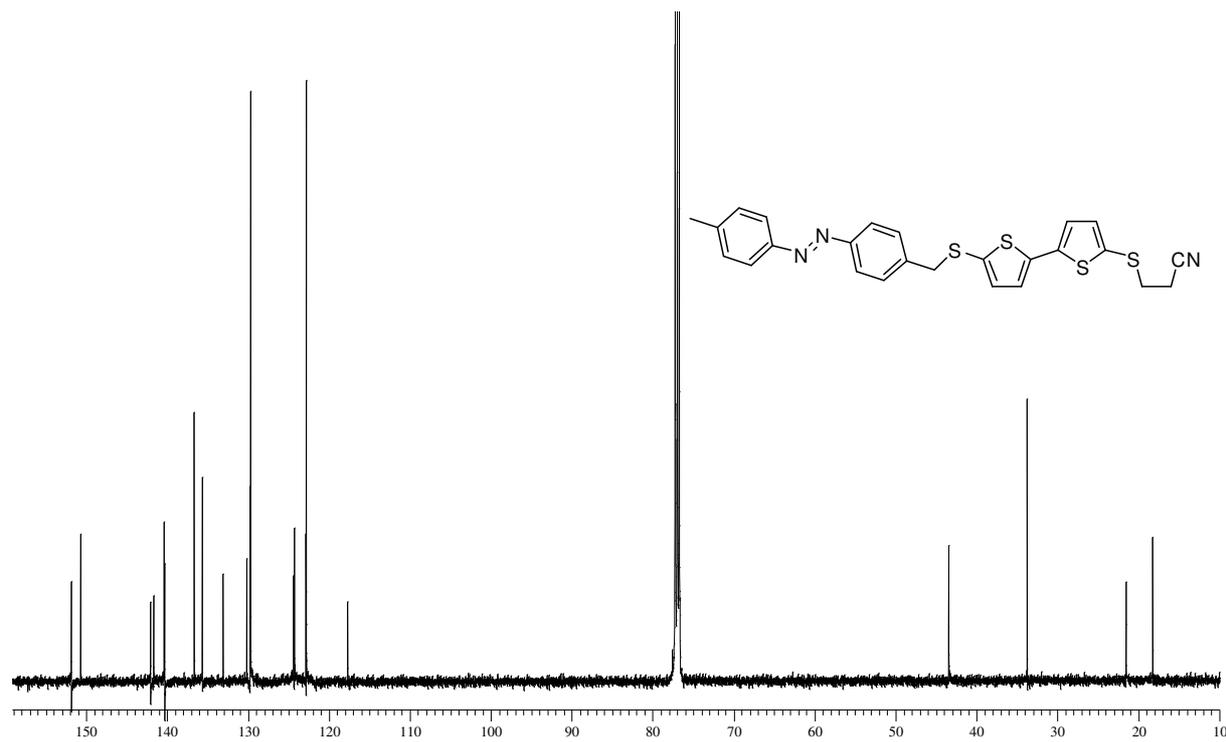


Figure S10. ^{13}C NMR (125 MHz) spectrum of **4** in CDCl_3 .

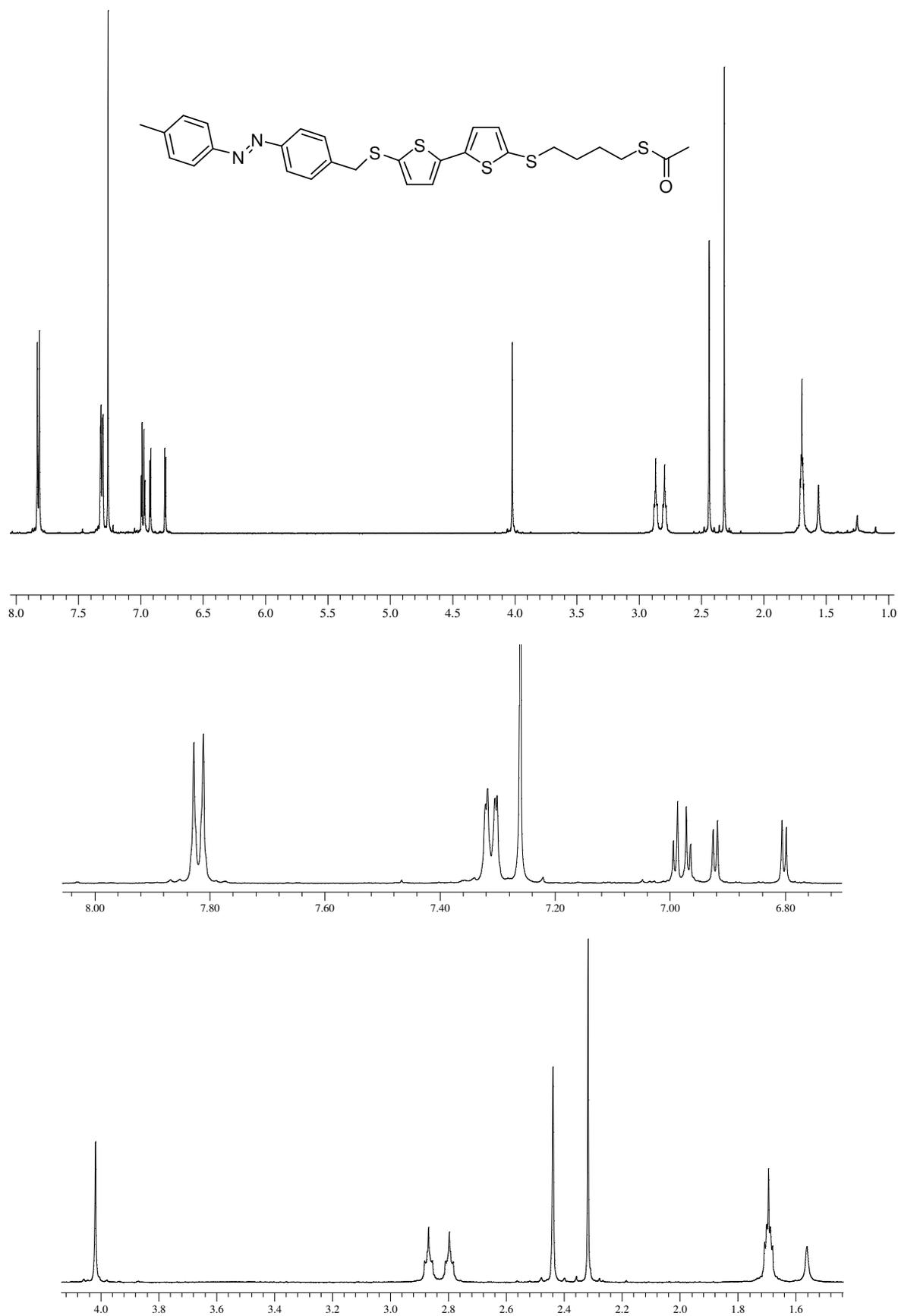


Figure S11. ^1H NMR (500 MHz) spectrum of **1** in CDCl_3 .

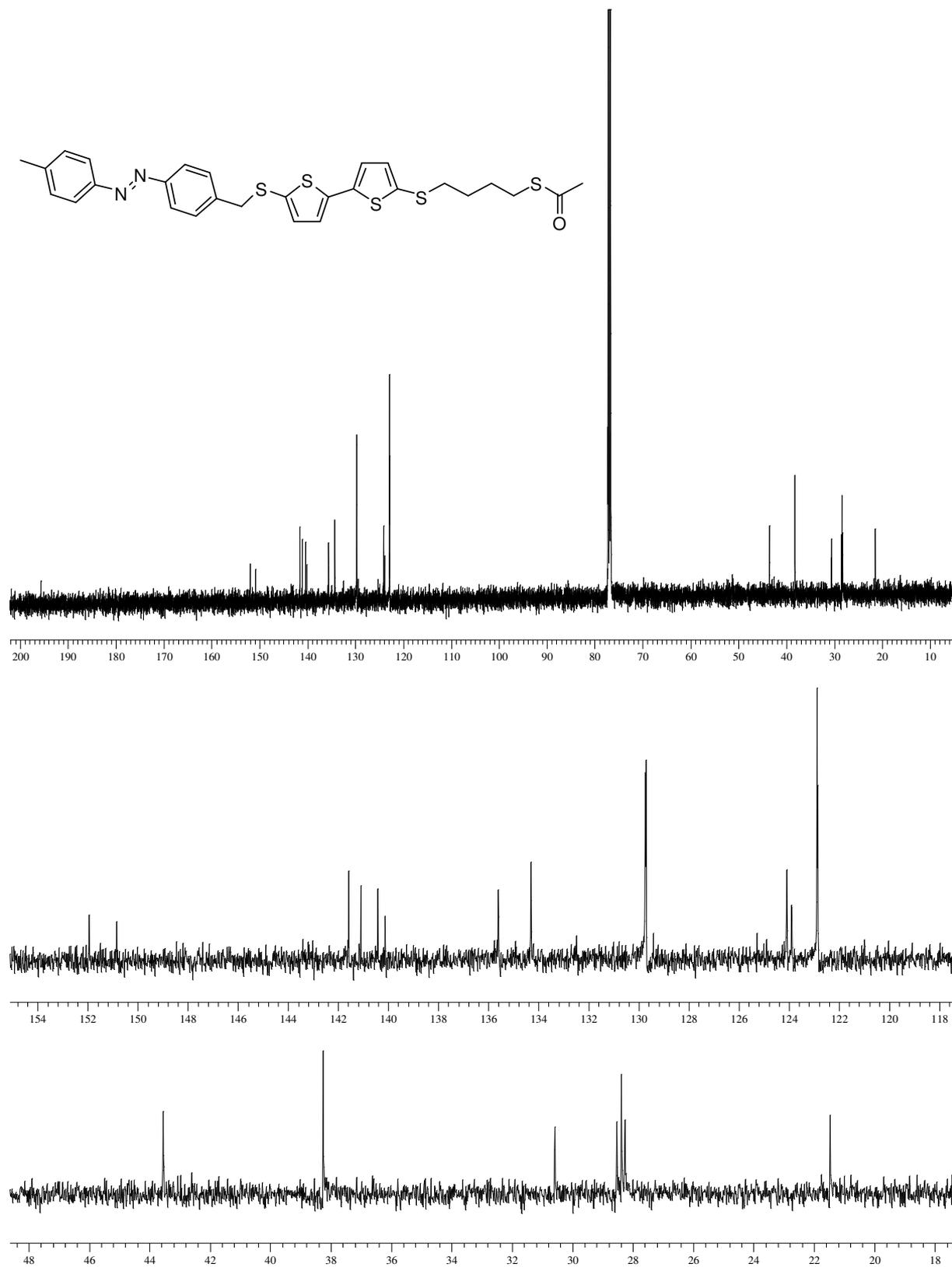


Figure S12. ^{13}C NMR (125 MHz) spectrum of **1** in CDCl_3 .

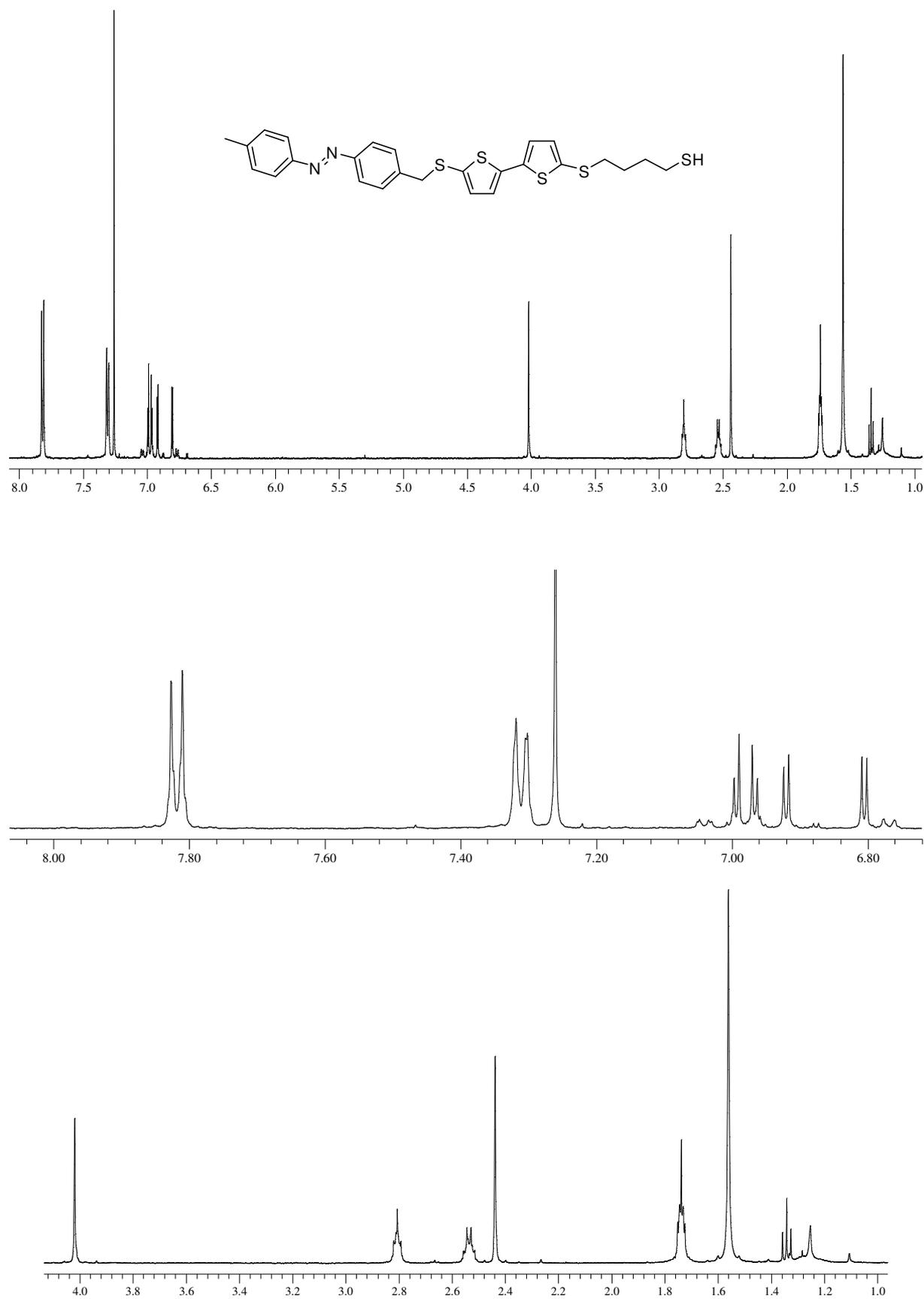


Figure S13. ¹H NMR (500 MHz) spectrum of **1-SH** in CDCl₃.