

Supporting Information
for
Thiophene-forming one-pot synthesis of three thienyl-bridged oligophenothiazines and their electronic properties

Dominik Urselmann, Konstantin Deilhof, Bernhard Mayer and Thomas J. J. Müller*

Address: Institut für Organische Chemie und Makromolekulare Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany.

Email: Thomas J. J. Müller - ThomasJJ.Mueller@uni-duesseldorf.de

*Corresponding author

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1 General considerations

All reactions were conducted in heat gun-dried glassware under a nitrogen atmosphere. All solvents for reactions were directly used from a MB-SPS 800 solvent drying system (Firma MBraun). Commercially available reagents and catalysts were purchased and employed without further purification.

All reactions were monitored by TLC (silica gel 60, F254, Merck KGaA). The spots were detected with UV light at $\lambda_{\text{max,exc}} = 254 \text{ nm}$ and stained with aqueous potassium permanganate solution. The crude mixtures were adsorbed on Celite[®] 545 (0.02–0.10 mm, Carl Roth GmbH Co.KG) prior to chromatographic purification. Preparative flash column chromatography was conducted with silica gel (0.04 to 0.063 mm, Macherey-Nagel) and a pressure of 2.0 bar was employed.

¹H, ¹³C and 135-DEPT NMR spectra were recorded on Bruker Avance III 600, Bruker Avance DRX 500, or Bruker Avance III 300 in acetone-*d*₆ (¹H δ 2.05, ¹³C δ 29.9) and in CDCl₃ (¹H δ 7.26, ¹³C δ 77.0). As an internal standard for the ¹H NMR the signal of the remaining protons of CDCl₃ (δ 7.26), or tetramethylsilane (δ 0.00) was used. As internal standard for the ¹³C NMR the signal of CDCl₃ (δ 77.00) or acetone-*d*₆ (δ 29.9) was used. The conventional abbreviations were used as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet).

The EI mass spectra were recorded on a Finnigan MAT 8200 apparatus, ESI mass spectra on a Finnigan LCQ Deca Thermo Quest apparatus, and MALDI–TOF spectra on a Bruker Ultraflex spectrometer.

IR spectra were recorded on a Bruker Vector 22 FT-IR apparatus (solids as KBr pellets). The intensities of the absorption bands are indicated by vs (very strong), s (strong), m (medium), and w (weak).

UV–vis spectra were recorded with a Hewlett-Packard HP8452 A spectrometer with CH₂Cl₂ (UVASOL) as a solvent. Fluorescence spectra were measured with a Perkin-Elmer LS-55 spectrometer and the Perkin Elmer software FL Winlab was used for evaluation of the data. For determination of the fluorescence quantum yield Φ_f coumarin 151 in ethanol/water 1:1 (w/w)

with $\Phi_f = 88\%$ at an excitation wavelength $\lambda_{\text{max,exc}} = 380$ nm and emission at $\lambda_{\text{max,em}} = 490$ nm was used.¹ The quantum yield Φ_f was calculated according to equation 1,

$$\Phi_f(\text{sample}) = \Phi_f(\text{coumarin 151}) \cdot \frac{F_{\text{sample}}}{F_{\text{coumarin 151}}} \cdot \frac{A_{\text{coumarin 151}}}{A_{\text{sample}}} \cdot \frac{n_{\text{sample}}^2}{n_{\text{coumarin 151}}^2} \quad (\text{equation 1})$$

where F is the integrated fluorescence intensity, A is the absorbance at identical wavelength, n is the refractive index of the corresponding solvent (n (dichloromethane) = 1.4242, n (ethanol/water 1:1 (w/w)) = 1.3604).

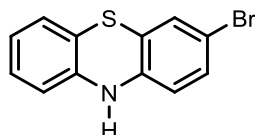
Cyclic voltammetry experiments (EG & G potentiostatic instrumentation) were performed under argon in dry and degassed CH_2Cl_2 at room temperature and at scan rates of 50, 100, 250, 500 mVs^{-1} . The electrolyte was Bu_4NPF_6 (0.025 M). The working electrode was a 1 mm platinum disk, the counter electrode was a platinum wire, and the reference electrode was a Ag/AgCl electrode. The potentials were corrected to the internal standard of Fc/Fc⁺ in CH_2Cl_2 ($E_0^{0/+1} = 450$ mV).²

¹ G. Jones II, W. R. Jackson, C. Y. Choi, W. R. Bergmark, *J. Phys. Chem.* **1985**, 89, 294-300. DOI: [10.1021/j100248a024](https://doi.org/10.1021/j100248a024)

² P. Zanello, Ferrocenes, eds. A. Togni, T. Hayashi, VCH, Weinheim, **1995**, 317-430.

2 Syntheses of 7-Bromo Oligophenothiazines 1

2.1 3-Bromo-10*H*-phenothiazine³

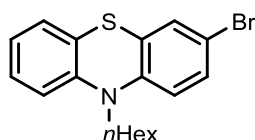


C₁₂H₈BrNS (MW 278.17)

In a nitrogen-flushed 250 mL round-bottom flask with a magnetic stir bar and septum 10*H*-phenothiazine (7.97 g, 40.0 mmol) was dissolved in dry THF (60 mL) under nitrogen. The dark solution was deaerated by a constant stream of nitrogen through a syringe for 10 min and cooled to 0 °C (ice bath/water). *N*-Bromosuccinimide (7.12 g, 40.0 mmol) was slowly added to the reaction mixture under nitrogen, then stirred for 16 h and allowed to come to room temperature. To this solution was added a saturated aqueous solution of sodium sulfite (150 mL) and the aqueous layer was extracted several times with dichloromethane. The combined organic layers were dried with anhydrous magnesium sulfate and filtered. The solvents were removed in vacuo and the residue was adsorbed onto celite® and purified by chromatography on silica gel (*n*-hexane/ethyl acetate 20:1) to give 4.95 g (45%) of 3-bromo-10*H*-phenothiazine as a colorless solid, *R*_f (*n*-hexane/acetone 4:1) = 0.33. The ¹H NMR spectrum was in agreement with the literature.

¹H NMR (CDCl₃, 300 MHz): δ 5.89 (s, br, 1 H), 6.52 (m, 1 H), 6.61 (m, 1 H), 6.83-7.15 (m, 5 H).

2.2 3-Bromo-10-hexyl-10*H*-phenothiazine (1a)



C₁₈H₂₀BrNS (MW 362.33)

In a nitrogen-flushed 250 mL round-bottom flask with a magnetic stir bar and septum 3-bromo-10*H*-phenothiazine (4.95 g, 17.8 mmol) was dissolved in dry THF (50 mL) under nitrogen. The colorless solution was deaerated by a constant stream of nitrogen through a syringe for 10 min

³ H.-H. Lin, S.-Y. Su, C.-C. Chang, *Org. Biomol. Chem.* **2009**, 7, 2036-2039. DOI: 10.1039/B902399B

and cooled to 0 °C (ice bath/water). Potassium *tert*-butanolate (2.40 g, 21.4 mmol) was added to the reaction mixture under nitrogen and the reaction mixture was allowed to come to room temperature and then stirred for 1 h. To this solution 1-bromo hexane (3.00 mL, 21.4 mmol) was slowly added by syringe and stirring at room temp was continued for 16 h. The solvents were removed in vacuo and the residue was adsorbed onto celite® and purified by chromatography on silica gel (*n*-hexane) to give 5.83 g (90%) of 3-bromo-10-hexyl-10*H*-phenothiazine (**1a**) as a yellow resin, *R*_f (*n*-hexane) = 0.43. The NMR spectra were in excellent agreement with the literature.⁴

¹H NMR (300 MHz, acetone-*d*₆): δ = 0.84 (t, ³*J* = 7.1 Hz, 3 H), 1.23-1.33 (m, 4 H), 1.44 (dt, ³*J* = 7.2 Hz, ³*J* = 6.8 Hz, 2 H), 1.77 (dt, ³*J* = 7.5 Hz, ³*J* = 7.5 Hz, 2 H), 3.92 (t, ³*J* = 7.0 Hz, 2 H), 6.95 (d, ³*J* = 8.7 Hz, 2 H), 7.03 (dd, ³*J* = 8.2 Hz, ⁴*J* = 0.9 Hz, 1 H), 7.14 (dd, ³*J* = 7.6 Hz, ⁴*J* = 1.4 Hz, 1 H), 7.21 (ddd, ³*J* = 8.2 Hz, ³*J* = 7.3 Hz, ⁴*J* = 1.6 Hz, 1 H), 7.27 (d, ⁴*J* = 2.2 Hz, 1 H), 7.32 (dd, ³*J* = 8.6 Hz, ⁴*J* = 2.3 Hz, 1 H). - ¹³C NMR (75 MHz, acetone-*d*₆): δ = 14.2 (CH₃), 23.2 (CH₂), 27.0 (CH₂), 27.4 (CH₂), 32.1 (CH₂), 47.9 (CH₂), 114.7 (C_{quat}), 116.9 (CH), 118.1 (CH), 123.6 (CH), 124.7 (C_{quat}), 128.1 (C_{quat}), 128.1 (CH), 128.6 (CH), 130.0 (CH), 130.9 (CH), 145.7 (C_{quat}), 145.9 (C_{quat}).

2.3 General procedure (GP) for the modified BLEBS synthesis of 7-bromo oligophenothiazines 1

In a flame-dried two-necked round-bottom flask with a magnetic stir bar and septum bromo-(oligo)phenothiazine **1** was dissolved in dry THF (2.00 mL/mmol) and the mixture was deaerated by a constant stream of nitrogen through a syringe for 10 min (for experimental details see Table S1). Then the solution was cooled to -78 °C (dry ice/acetone bath) and a 1.60 M solution of *n*-butyllithium in *n*-hexane (1.1 equiv) was slowly added dropwise within 5 min. After stirring for 15 min trimethylborate (1.15 equiv) was added and stirring was continued at -78 °C for 15 min. Then the cooling bath was removed and the reaction mixture was allowed to come to room temperature. 3,7-Dibromo-10-hexyl-10*H*-phenothiazine (**3**, 3 equiv) and Pd(PPh₃)₄ (5.00 mol %) and potassium *tert*-butanolate (1.10 equiv) were added under nitrogen. The reaction mixture was heated at 60 °C for 48 h. After the mixture was cooled to room temperature a dilute aqueous solution of Na₂SO₃ was added. The aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried with

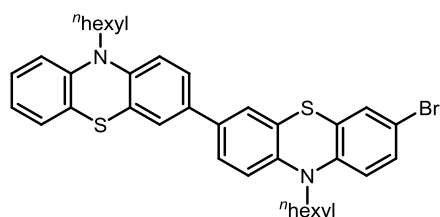
⁴ M. Sailer, A. W. Franz, T. J. J. Müller, *Chem. Eur. J.* **2008**, *14*, 2602-2614. DOI: 10.1002/chem.200701341

anhydrous sodium sulfate, filtered and Celite® was added. The solvents were removed in vacuo and the residue was purified by chromatography on silica gel.

Table S1: Experimental details of the BLEBS synthesis of 7-bromo(oligo)phenothiazines **1**.

Entry	Bromo (oligo)phenothiazine 1	3,7-Dibromo-10-hexyl-10H- phenothiazine (3)	7-Bromo (oligo)phenothiazine 1
1	1.81 g (5.00 mmol) of 1a	6.62 g (15.0 mmol)	2.50 g (3.88 mmol, 78%) of 1b
2	2.12 g (3.29 mmol) of 1b	4.35 g (9.87 mmol)	1.31 g (1.41 mmol, 67%) of 1c

2.3.1 7-Bromo-10,10'-dihexyl-10H,10'H-3,3'-biphenothiazine (**1b**)



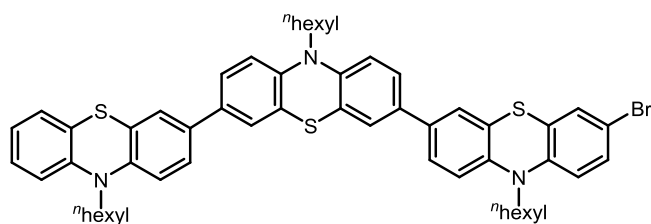
C₃₆H₃₉BrN₂S₂ (MW 643.74)

According to the GP and chromatography on silica gel (*n*-hexane/dichloromethane 10:1) 2.50 g (78%) of compound **1b** was obtained as a yellow resin, *R_f* (*n*-hexane/acetone 50:1) = 0.34. The NMR spectra were in excellent agreement with the literature.⁵

¹H NMR (600 MHz, acetone-d₆): δ 0.81-0.88 (m, 6 H), 1.25-1.35 (m, 8 H), 1.41-1.48 (m, 4 H), 1.74-1.83 (m, 4 H), 3.91-3.98 (m, 4 H), 6.91-7.06 (m, 5 H), 7.14 (dd, ³J = 7.6 Hz, ⁴J = 1.4 Hz, 1 H), 7.17-7.22 (m, 1 H), 7.26-7.33 (m, 2 H), 7.34-7.41 (m, 2 H), 7.41-7.46 (m, 2 H). - ¹³C NMR (125 MHz, acetone-d₆): δ 14.3 (2 CH₃), 23.3 (CH₂), 23.3 (CH₂), 27.1 (CH₂), 27.2 (CH₂), 27.4 (CH₂), 27.5 (CH₂), 32.2 (CH₂), 32.2 (CH₂), 47.8 (CH₂), 48.0 (CH₂), 114.7 (C_{quat}), 116.6 (CH), 116.8 (CH), 117.0 (CH), 118.1 (CH), 123.3 (CH), 125.1 (C_{quat}), 125.1 (C_{quat}), 125.6 (CH), 126.0 (CH), 126.1 (CH), 126.4 (CH), 127.6 (C_{quat}), 128.0 (CH), 128.3 (CH), 130.0 (CH), 131.0 (CH), 134.7 (C_{quat}), 135.3 (C_{quat}), 144.7 (C_{quat}), 145.3 (C_{quat}), 145.5 (C_{quat}), 146.0 (C_{quat}). - MS (MALDI) *m/z*: 644.1 ([⁸¹Br-M]⁺), 642.1 ([⁷⁹Br-M]⁺).

⁵ A. W. Franz, T. J. J. Müller, *Synthesis* **2008**, 1121-1125. DOI: [10.1055/s-2008-1032118](https://doi.org/10.1055/s-2008-1032118)

2.3.2 7-Bromo-10,10',10''-trihexyl-10*H*,10'*H*,10''*H*- [3,3',7',3'']terphenothiazine (**1c**)



C₅₄H₅₈BrN₃S₃ (MW 925.16)

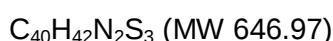
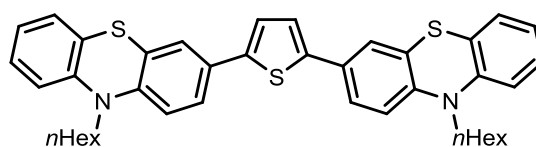
According to the GP and chromatography on silica gel (*n*-hexane/dichloromethane 5:1) 1.31 g (67%) of compound **1c** was obtained as a yellow resin, *R_f* (*n*-hexane/acetone 50:1) = 0.11. The NMR spectra were in excellent agreement with the literature.⁵

¹H NMR (300 MHz, acetone-d₆): δ 0.80-0.88 (m, 9 H), 1.23-1.34 (m, 12 H), 1.40-1.51 (m, 6 H), 1.70-1.87 (m, 6 H), 3.86-4.00 (m, 6 H), 6.90-6.96 (m, 2 H), 6.99-7.05 (m, 4 H), 7.12-7.23 (m, 2 H), 7.27 (d, ⁴*J* = 2.3 Hz, 1 H), 7.31 (dd, ³*J* = 8.6 Hz, ⁴*J* = 2.3 Hz, 1 H), 7.35-7.38 (m, 3 H), 7.39-7.46 (m, 4 H). - ¹³C-NMR (75 MHz, acetone-d₆): δ 14.3 (2 CH₃), 14.3 (CH₃), 23.3 (CH₂), 23.3 (CH₂), 23.3 (CH₂), 27.1 (CH₂), 27.2 (CH₂), 27.2 (CH₂), 27.4 (CH₂), 27.5 (CH₂), 27.5 (CH₂), 32.2 (CH₂), 32.2 (CH₂), 32.2 (CH₂), 47.8 (CH₂), 47.9 (CH₂), 47.9 (CH₂), 114.7 (C_{quat}), 116.6 (CH), 116.7 (2 CH), 116.8 (CH), 117.0 (CH), 118.0 (CH), 123.3 (CH), 125.1 (C_{quat}), 125.1 (C_{quat}), 125.5 (C_{quat}), 125.5 (CH), 125.5 (CH), 125.5 (C_{quat}), 125.6 (CH), 125.6 (CH), 126.0 (C_{quat}), 126.1 (CH), 126.1 (CH), 126.2 (CH), 126.4 (CH), 127.6 (C_{quat}), 128.0 (CH), 128.3 (CH), 130.0 (CH), 130.9 (CH), 134.7 (C_{quat}), 134.9 (C_{quat}), 134.9 (C_{quat}), 135.3 (C_{quat}), 144.7 (C_{quat}), 144.9 (C_{quat}), 145.0 (C_{quat}), 145.2 (C_{quat}), 145.4 (C_{quat}), 146.0 (C_{quat}). - MS (MALDI) *m/z*: 925.2 ([⁸¹Br-M]⁺), 923.2 ([⁷⁹Br-M]⁺).

2.4 General procedure (GP) for the consecutive pseudo five-component synthesis of 2,5-di(oligophenothiazinyl)thiophenes **3**

7-Bromo(oligo)phenothiazine **1** (2.00 mmol) and dry THF (10.0 mL) were placed in a microwave vessel with septum (80 mL) and the mixture was deaerated by a constant stream of nitrogen through a syringe for 10 min. Then PdCl₂(PPh₃)₂ (56.0 mg, 0.08 mmol), CuI (15.0 mg, 0.08 mmol), PPh₃ (21 mg, 0.08 mmol), (trimethylsilyl)acetylene (0.56 mL, 2.00 mmol), and piperidine (5.00 mL, 50.4 mmol) were added. The closed vessel under nitrogen was heated at 55 °C (oil bath) for 16 h. Then, TBAF·3 H₂O (631 mg, 2.00 mmol) was added and the vessel opened to ambient atmosphere was then stirred at room temperature for 16 h. Then, sodium sulfide nonahydrate (960 mg, 4.00 mmol) and potassium hydroxide (224 mg, 4.00 mmol) were added and the reaction mixture in the closed vessel was heated at 120 °C in the microwave cavity for 30 min. After cooling to room temperature the solvents were removed in vacuo and the residue was filtered with THF through a short plug of Celite® and silica gel. The solvents were removed in vacuo and the residue was purified by chromatography on silica gel to give the pure compounds **3**.

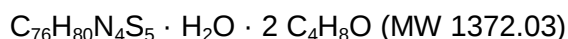
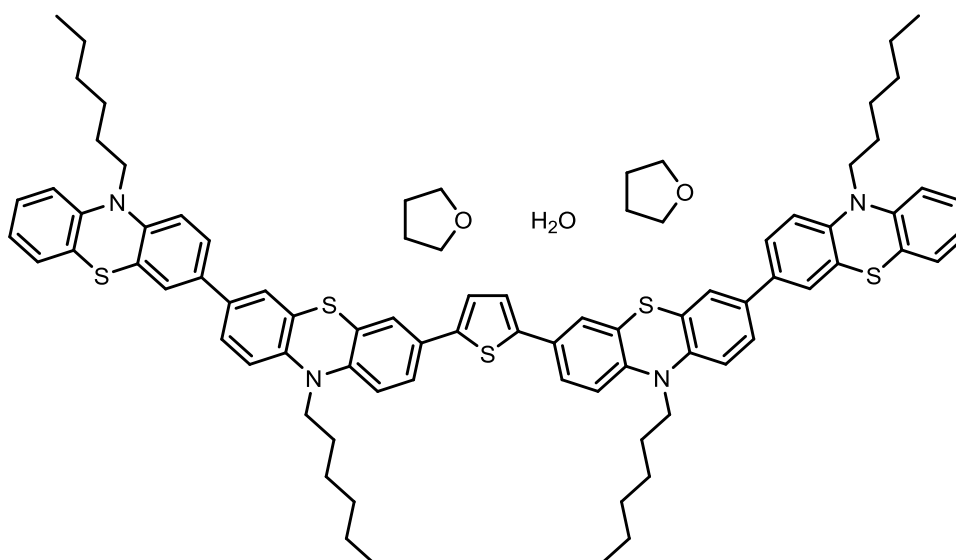
2.4.1 2,5-Bis(10-hexyl-10*H*-phenothiazin-3-yl)thiophene (**3a**)



According to the GP 3-bromo-10-hexyl-10*H*-phenothiazine (**1a**, 725 mg, 2.00 mmol) after chromatography on silica gel (hexane/dichloromethane 10:1) gave 218 mg (34%) of compound **3a** as a yellow greenish resin. *R*_f (hexane/acetone 10:1) = 0.53. - ¹H NMR (300 MHz, acetone-d₆): δ 0.84 (t, ³*J* = 7.1 Hz, 6 H), 1.21-1.33 (m, 8 H), 1.39-1.51 (m, 4 H), 1.78 (quint, ³*J* = 7.5 Hz, 4 H), 3.92 (t, ³*J* = 7.0 Hz, 4 H), 6.90-6.97 (m, 2 H), 6.97-7.03 (m, 4 H), 7.14 (dd, ³*J* = 7.7 Hz, ⁴*J* = 1.5 Hz, 2 H), 7.16-7.23 (m, 2 H), 7.29 (s, 2 H), 7.41 (d, ⁴*J* = 2.1 Hz, 2 H), 7.44 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.2 Hz, 2 H). - ¹H NMR (600 MHz, CDCl₃): δ 0.64-0.91 (m, 6 H), 1.09-1.26 (m, 8 H), 1.26-1.39 (m, 4 H), 1.59-1.81 (m, 4 H), 3.58-3.85 (m, 4 H), 6.70 (d, *J* = 8.7 Hz, 2 H), 6.74 (d, *J* = 8.1 Hz, 2 H), 6.81 (t, *J* = 7.5 Hz, 2 H), 6.97-7.09 (m, 6 H), 7.21-7.30 (m, 4 H). - ¹³C NMR (75 MHz, acetone-d₆): δ 14.3 (CH₃), 23.3 (CH₂), 27.1 (CH₂), 27.5 (CH₂), 32.2 (CH₂), 47.9 (CH₂), 116.7 (CH), 116.8 (CH), 123.4 (CH), 124.4 (CH), 124.5 (CH), 124.8 (C_{quat}), 125.4 (CH), 126.1

(C_{quat}), 128.1 (CH), 128.4 (CH), 129.6 (C_{quat}), 142.5 (C_{quat}), 145.5 (C_{quat}), 145.8 (C_{quat}). - ¹³C NMR (151 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.7 (CH₂), 26.9 (CH₂), 31.5 (CH₂), 47.6 (CH₂), 115.4 (CH), 115.5 (CH), 122.5 (CH), 123.1 (CH), 124.2 (C_{quat}), 124.2 (CH), 124.5 (CH), 125.3 (C_{quat}), 127.3 (CH), 127.5 (CH), 128.8 (C_{quat}), 142.0 (C_{quat}), 144.5 (C_{quat}), 144.9 (C_{quat}). - MS (MALDI) *m/z*: 646.3 ([M]⁺). - UV/Vis (CH₂Cl₂), λ_{max} [nm] (ε): 246 (39600), 261 (39100), 318 (27000), 395 (33100). - IR (KBr) $\tilde{\nu}$ [cm⁻¹]: 3057 (w), 2951 (w), 2926 (w), 2851 (w), 1917 (w), 1597 (w), 1576 (w), 1539 (w), 1489 (w), 1458 (s), 1398 (w), 1362 (w), 1331 (m), 1285 (w), 1248 (m), 1238 (m), 1225 (w), 1192 (w), 1161 (w), 1134 (w), 1103 (w), 1038 (w), 1022 (w), 968 (w), 926 (w), 908 (w), 874 (w), 793 (s), 745 (s), 704 (w), 681 (w), 669 (w), 646 (w), 625 (w). - Anal. calcd. for C₄₀H₄₂N₂S₃ (647.0): C 74.26, H 6.54, N 4.33; Found: C 74.17, H 6.79, N 4.05.

2.4.2 2,5-Bis(10,10'-dihexyl-10*H*,10'*H*-3,3'-biphenothiazin-7-yl)thiophene (3b)



According to the GP 7-bromo-10,10'-dihexyl-10*H*,10'*H*-3,3'-biphenothiazine (**1b**, 1.29 g, 2.00 mmol) after chromatography on silica gel (hexane/THF 20:1) gave 435 mg (36%) of compound **3b** as a yellow greenish resin. - ¹H NMR (600 MHz, CDCl₃): δ 0.65-0.82 (m, 12 H), 1.10-1.23 (m, 16 H), 1.26-1.36 (m, 8 H), 1.62-1.76 (m, 8 H), 3.62-3.79 (m, 8 H), 6.64-6.84 (m, 10 H), 6.93-7.09 (m, 6 H), 7.09-7.26 (m, 12 H). - ¹³C NMR (151 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.7 (CH₂), 26.7 (CH₂), 26.8 (CH₂), 26.9 (CH₂), 31.5 (CH₂), 47.5 (CH₂), 47.6 (CH₂), 115.3 (CH), 115.4 (CH), 115.5 (CH), 115.5 (CH), 122.4 (CH), 123.1 (CH), 124.2 (CH), 124.4 (C_{quat}), 124.4 (C_{quat}), 124.6 (CH), 124.8 (C_{quat}), 125.1 (CH), 125.1 (CH), 125.2 (CH), 125.3 (CH), 127.3 (CH), 127.5 (CH), 128.9 (C_{quat}), 134.2 (C_{quat}), 134.4 (C_{quat}), 141.9 (C_{quat}), 143.7 (C_{quat}), 144.2

(C_{quat}), 144.3 (C_{quat}), 145.1 (C_{quat}). - MS (MALDI) m/z : 1208.5 ([M]⁺). - UV/Vis (CH₂Cl₂), λ_{max} [nm] (ϵ): 266 (52100), 284 (45900), 319 (32500), 404 (27700). - IR (KBr) $\tilde{\nu}$ [cm⁻¹]: 2951 (w), 2922 (w), 2853 (w), 1456 (s), 1416 (w), 1375 (w), 1364 (w), 1331 (m), 1292 (w), 1238 (m), 1192 (w), 1138 (w), 1105 (w), 1063 (w), 1040 (w), 872 (m), 797 (s), 745 (s), 727 (w), 706 (w), 611 (w). - Anal. calcd. for C₇₆H₈₀N₄S₅ · H₂O · 2 C₄H₈O (1209.8 + 18.0 + 144.2): C 73.53, H 7.20, N 4.08; Found: C 73.39; H 7.36; N 4.29. - HPLC (*n*-hexane) t_R [min] (%) = 4.49 (99).

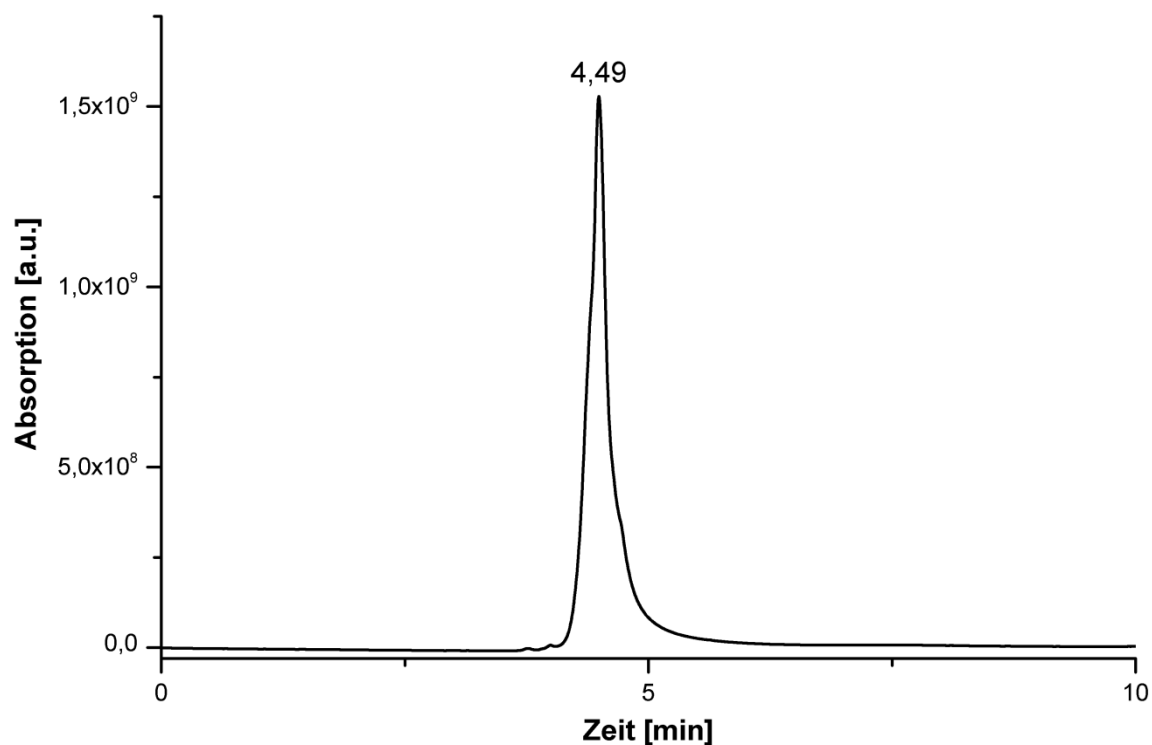
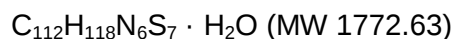
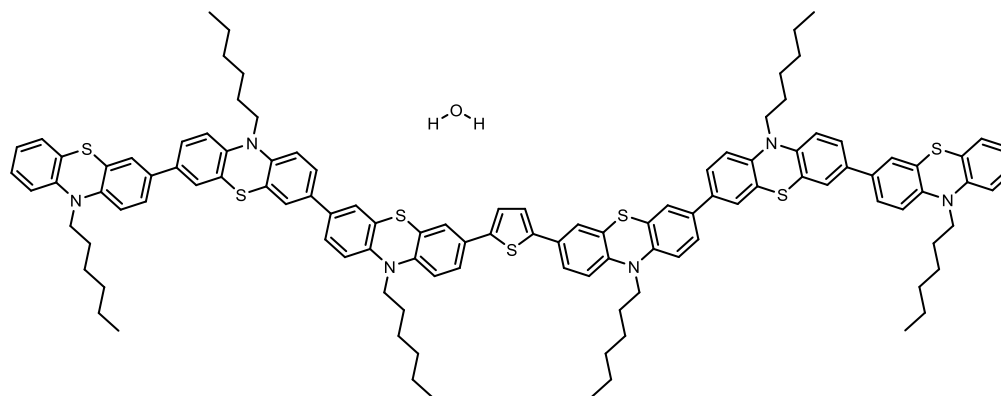


Figure S1: HPLC chromatogram of compound **3b** (column: YMC-Pack SIL-ASP, 150 × 6.0 mm, S-5 μ m, 60 Å; eluent: *n*-hexane, 1.5 mL/min, UV-detection at 254 nm).

2.4.3 2,5-Bis(10,10',10''-trihexyl-10H,10'H,10''H-3,3',3''-triphenothiazin-7-yl)thiophene (3c)



According to the GP 7-bromo-10,10',10''-trihexyl-10H,10'H,10''H-[3,3',7',3'']terphenothiazin (**1c**) (1.85 g 2.00 mmol) after chromatography on silica gel (hexane/THF 7:1 to 3:1) gave 955 mg (54%) of compound **3c** as a yellow greenish resin. – 1H NMR (600 MHz, $CDCl_3$): δ 0.75-0.88 (m, 18 H), 1.08-1.33 (m, 24 H), 1.31-1.40 (m, 12 H), 1.66-1.81 (m, 12 H), 3.60-3.89 (m, 12 H), 6.68-6.88 (m, 14 H), 7.00-7.11 (m, 6 H), 7.13-7.37 (m, 20 H). – ^{13}C NMR (151 MHz, $CDCl_3$): δ 14.05 (CH_3), 14.06 (CH_3), 22.64 (CH_2), 22.66 (CH_2), 26.69 (CH_2), 26.72 (CH_2), 26.8 (CH_2), 26.88 (CH_2), 26.90 (CH_2), 31.5 (CH_2), 47.5 (CH_2), 47.6 (CH_2), 47.63 (CH_2), 115.31 (CH), 115.37 (CH), 115.42 (CH), 115.46 (CH), 115.48 (CH), 122.3 (CH), 123.1 (CH), 124.2 (CH), 124.42 (C_{quat}), 124.44 (C_{quat}), 124.57 (CH), 124.68 (C_{quat}), 124.72 (C_{quat}), 124.8 (CH), 125.12 (CH), 125.14 (CH), 125.18 (CH), 125.19 (CH), 125.25 (CH), 125.29 (CH), 127.25 (CH), 127.5 (CH), 128.9 (C_{quat}), 134.18 (C_{quat}), 134.23 (C_{quat}), 134.30 (C_{quat}), 134.37 (C_{quat}), 141.9 (C_{quat}), 143.7 (C_{quat}), 143.9 (C_{quat}), 144.0 (C_{quat}), 144.20 (C_{quat}), 144.22 (C_{quat}), 145.1 (C_{quat}). – MS (MALDI) m/z : 1770.7 ($[M]^+$). – UV/Vis (CH_2Cl_2), λ_{max} [nm] (ϵ): 267 (103000), 283 (116200), 327 (61000), 379 (51900). – IR (KBr) $\tilde{\nu}$ [cm^{-1}]: 3024 (w), 2951 (w), 2922 (w), 2851 (w), 1603 (w), 1574 (w), 1454 (s), 1416 (w), 1377 (w), 1331 (w), 1294 (w), 1238 (m), 1190 (w), 1140 (w), 1105 (w), 1063 (w), 1038 (w), 968 (w), 928 (w), 910 (w), 872 (w), 802 (s), 745 (m), 729 (w), 691 (w). – Anal. calcd. for $C_{112}H_{118}N_6S_7 \cdot H_2O$ (1772.63 + 18.0): C 75.13, H 6.76, N 4.69; Found: C 74.89, H 6.50, N 4.53. – HPLC (*n*-hexane/THF 99.5:0.5) t_R [min] (%) = 2.92 (99).

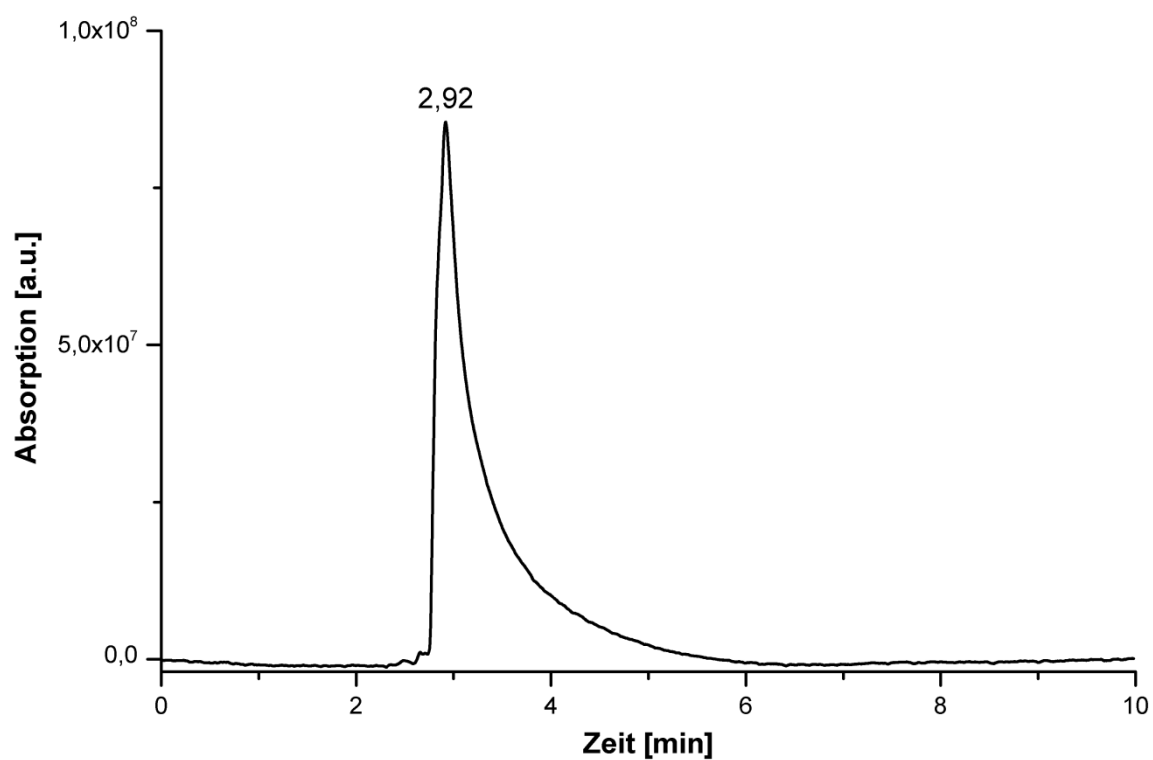
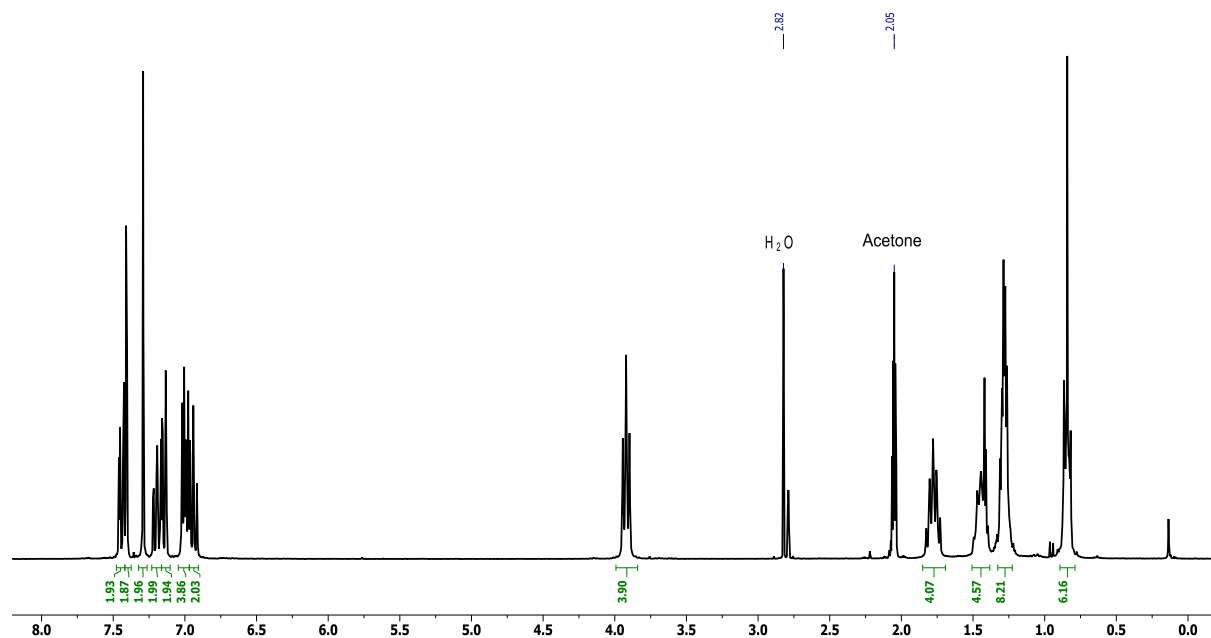


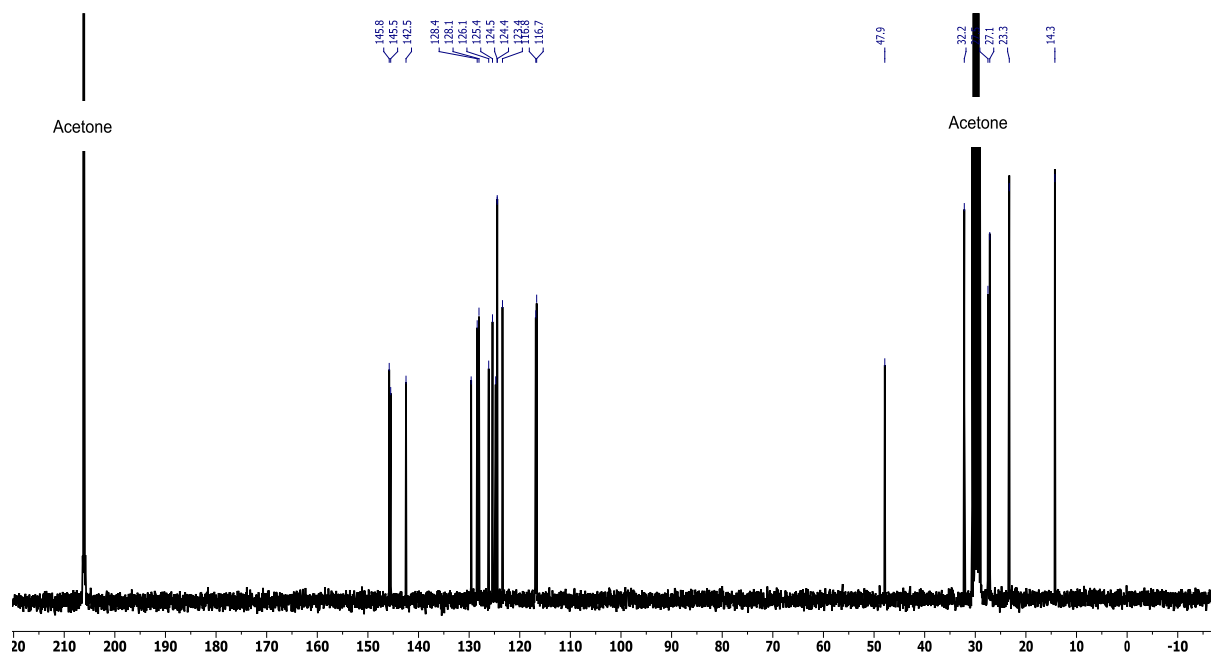
Figure S2: HPLC chromatogram of compound **3c** (column: YMC-Pack SIL-ASP, 150 x 6.0 mm, S-5 μm , 60 Å; eluent: *n*-hexane/THF 99.5:0.5, 1.5 mL/min, UV-detection at 254 nm).

3 ^1H and ^{13}C NMR spectra of compounds 3

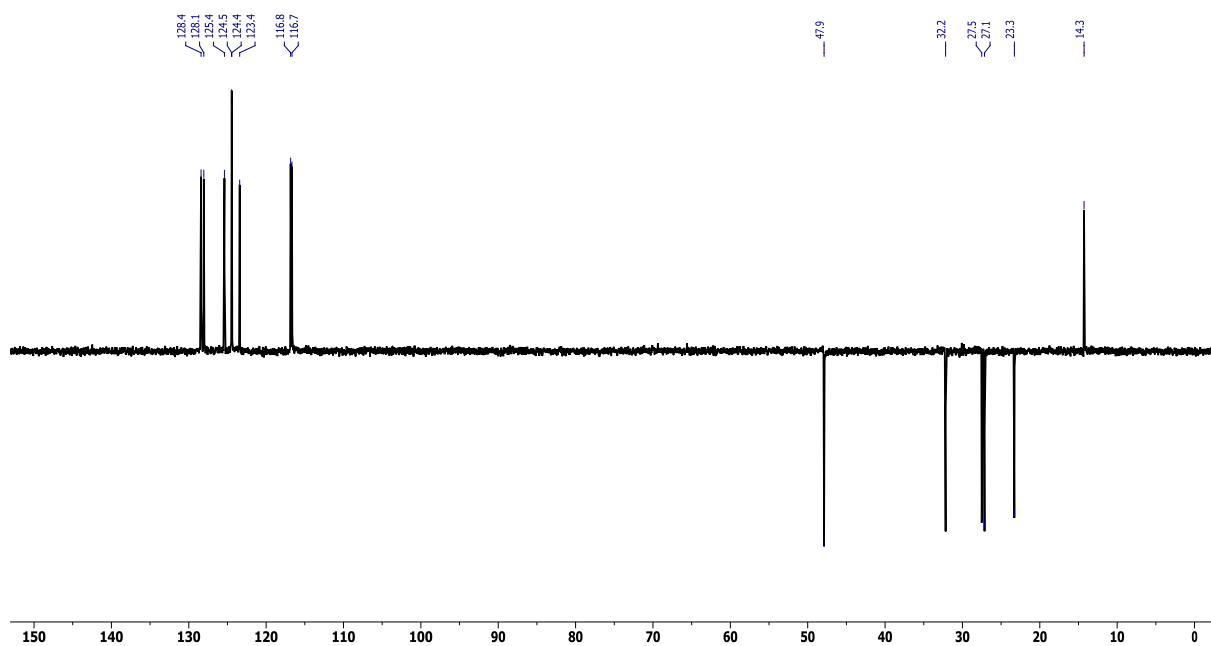
3.1 ^1H and ^{13}C NMR spectra of compound 3a



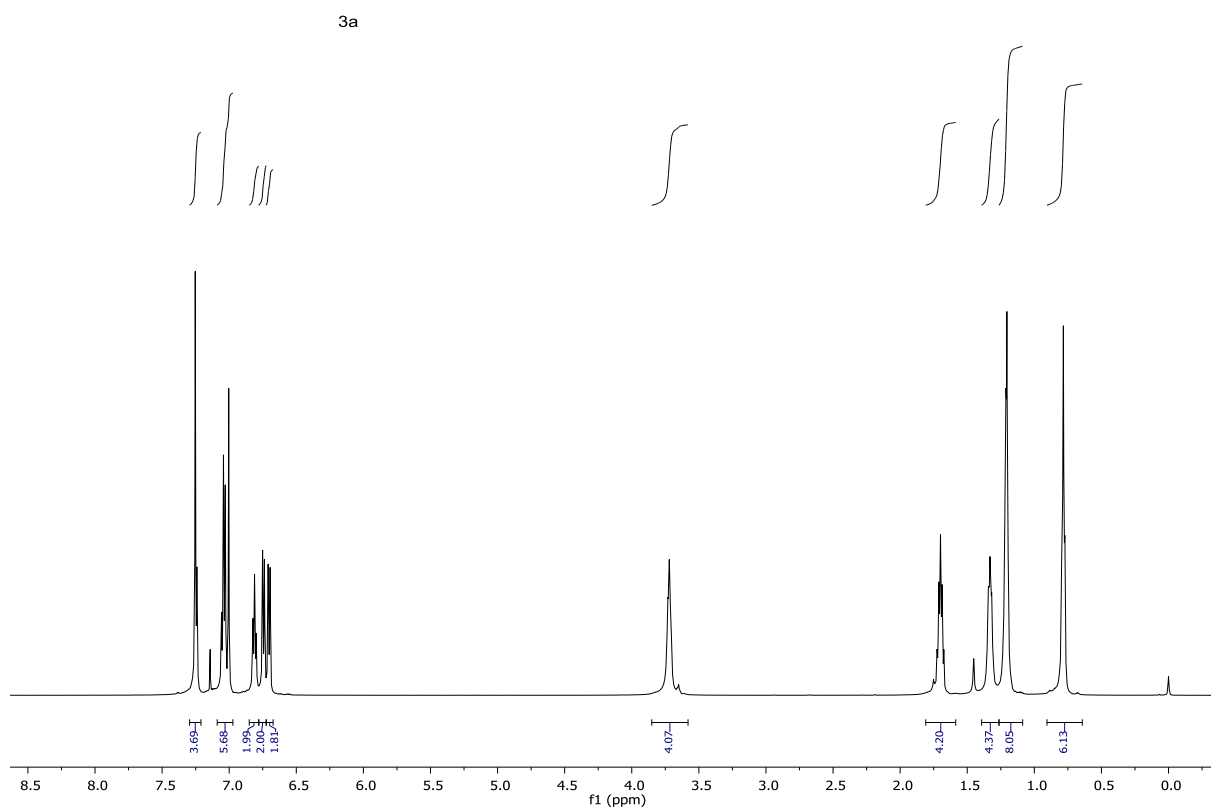
^1H NMR of **3a** in acetone- d_6 at $T = 298\text{ K}$ (δ in ppm).



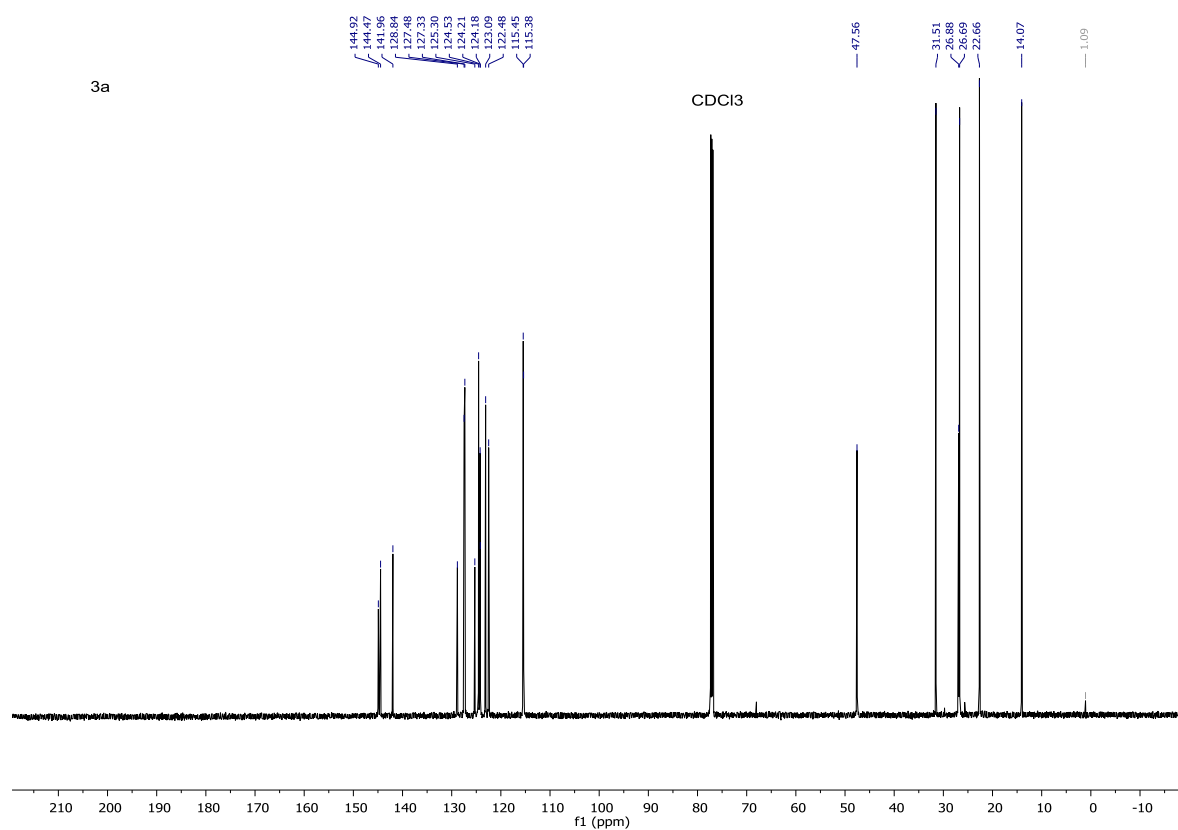
^{13}C NMR of **3a** in acetone- d_6 at $T = 298\text{ K}$ (δ in ppm).



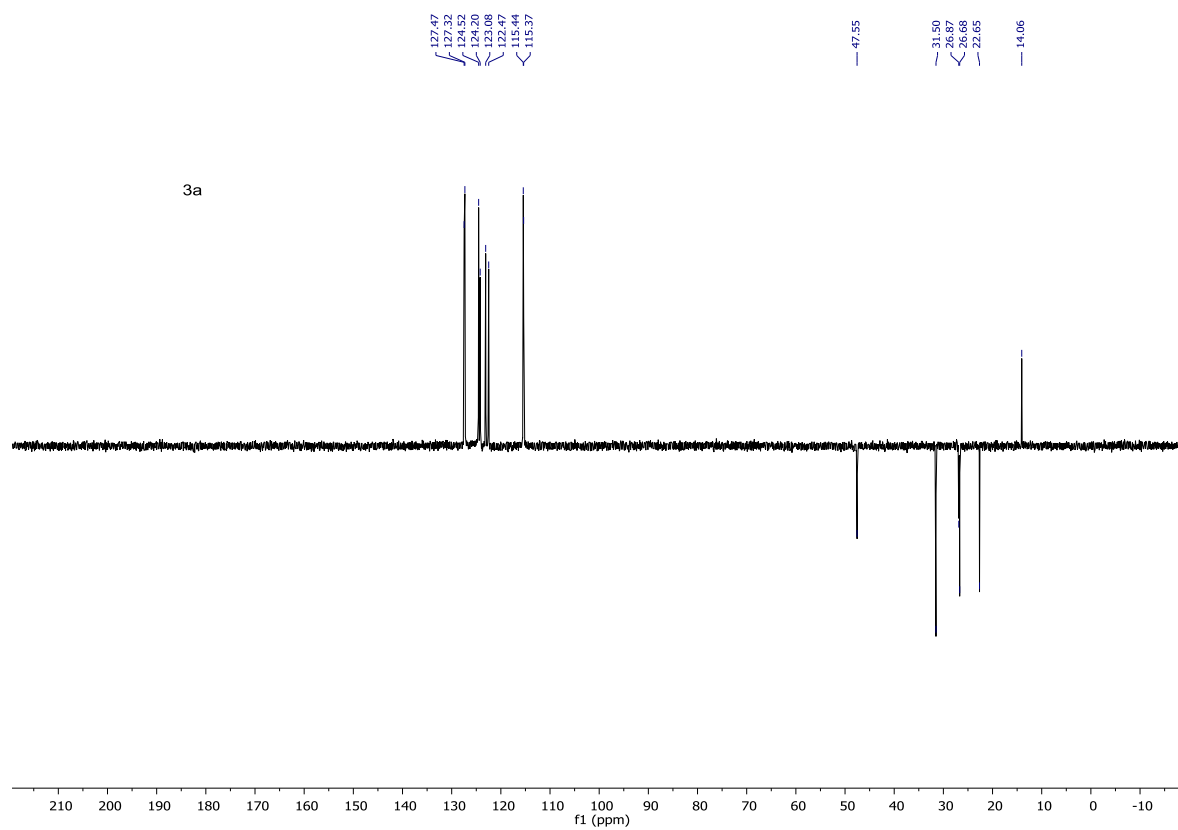
¹³C DEPT 135-NMR of **3a** in acetone-d₆ at *T* = 298 K (δ in ppm).



¹H NMR of **3a** CDCl₃ at *T* = 298 K (δ in ppm).

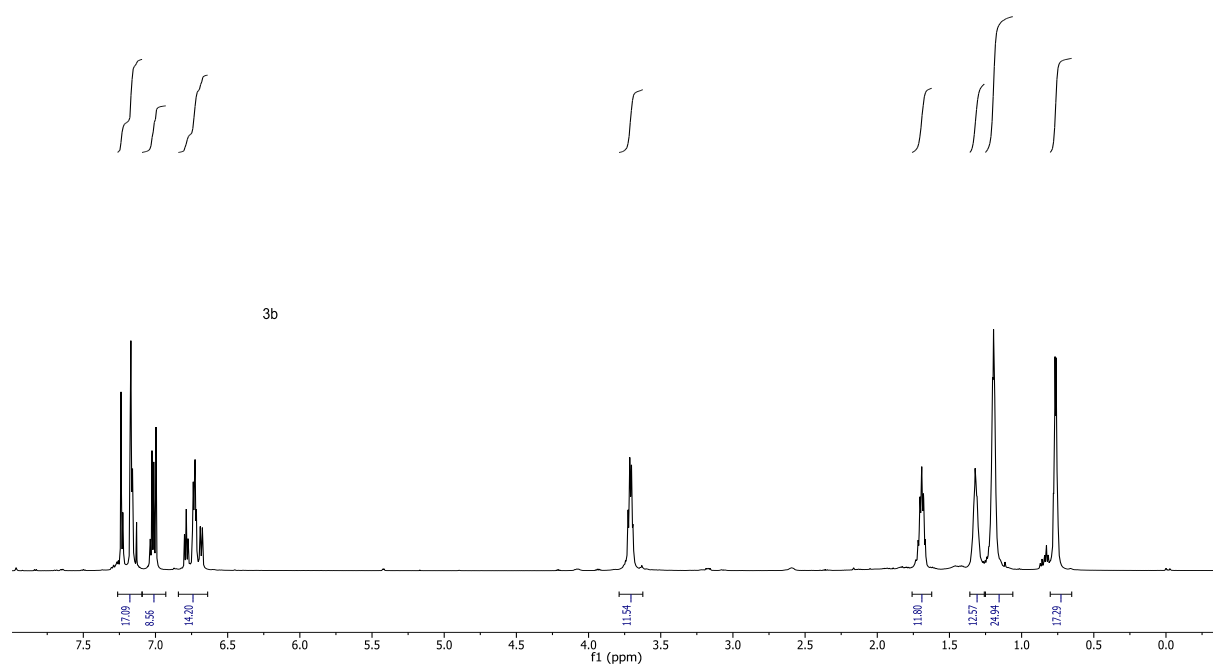


¹³C NMR of **3a** in CDCl₃ at $T = 298$ K (δ in ppm).

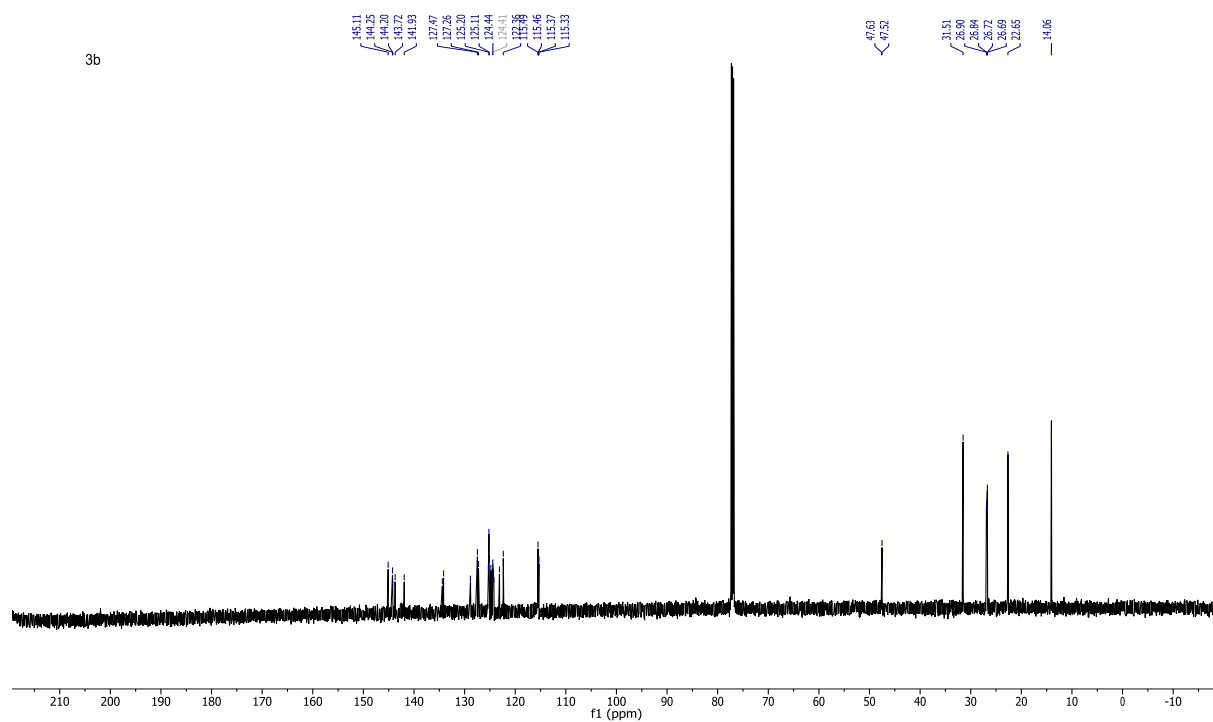


¹³C DEPT 135-NMR of **3a** in CDCl₃ at $T = 298$ K (δ in ppm).

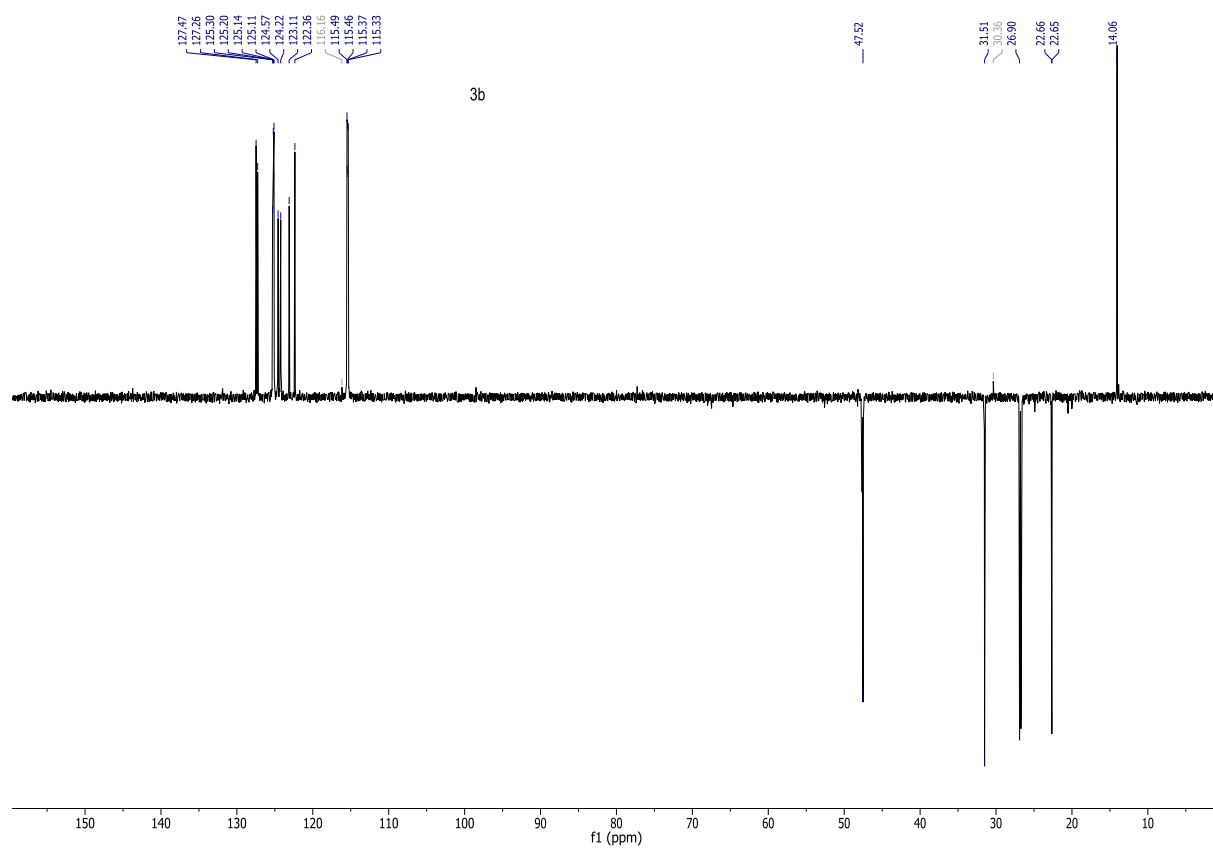
3.2 ^1H and ^{13}C NMR spectra of compound **3b**



^1H NMR of **3b** in CDCl_3 at $T = 298\text{ K}$ (δ in ppm).

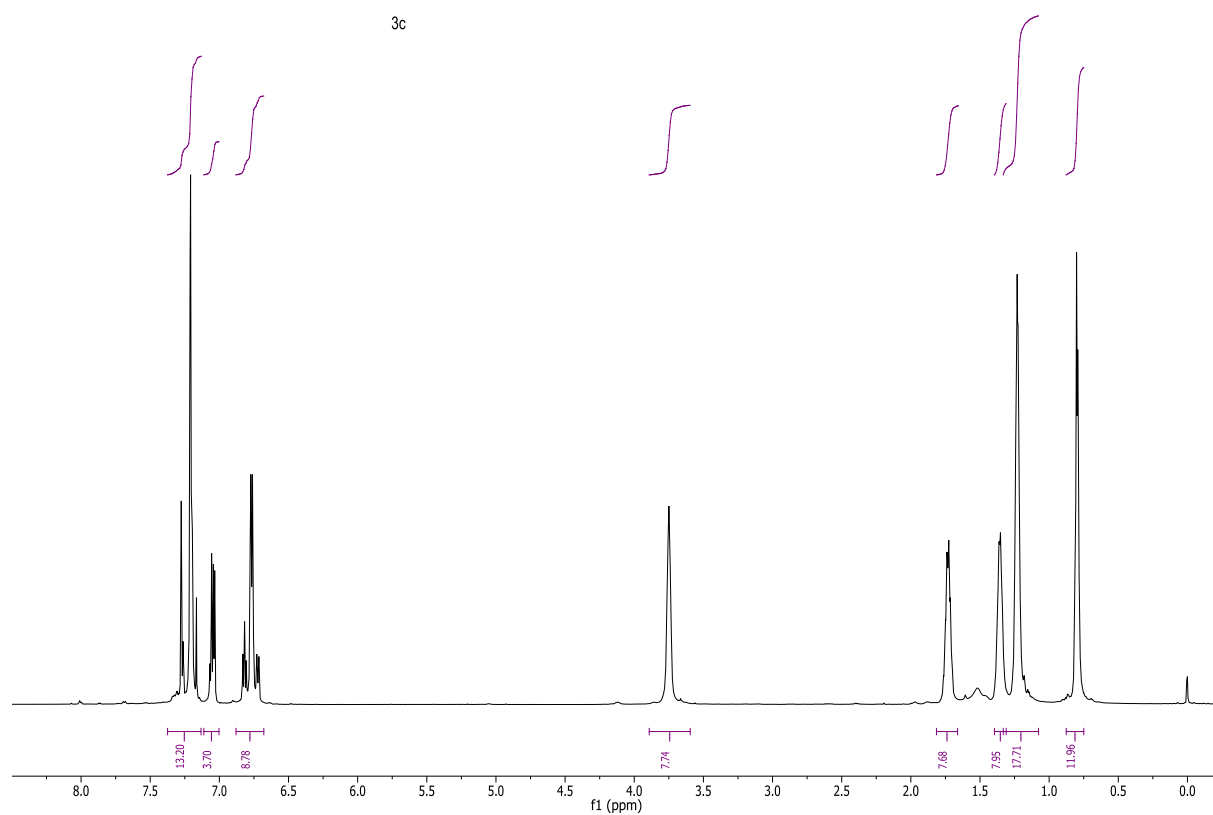


^{13}C NMR of **3b** in CDCl_3 at $T = 298\text{ K}$ (δ in ppm).

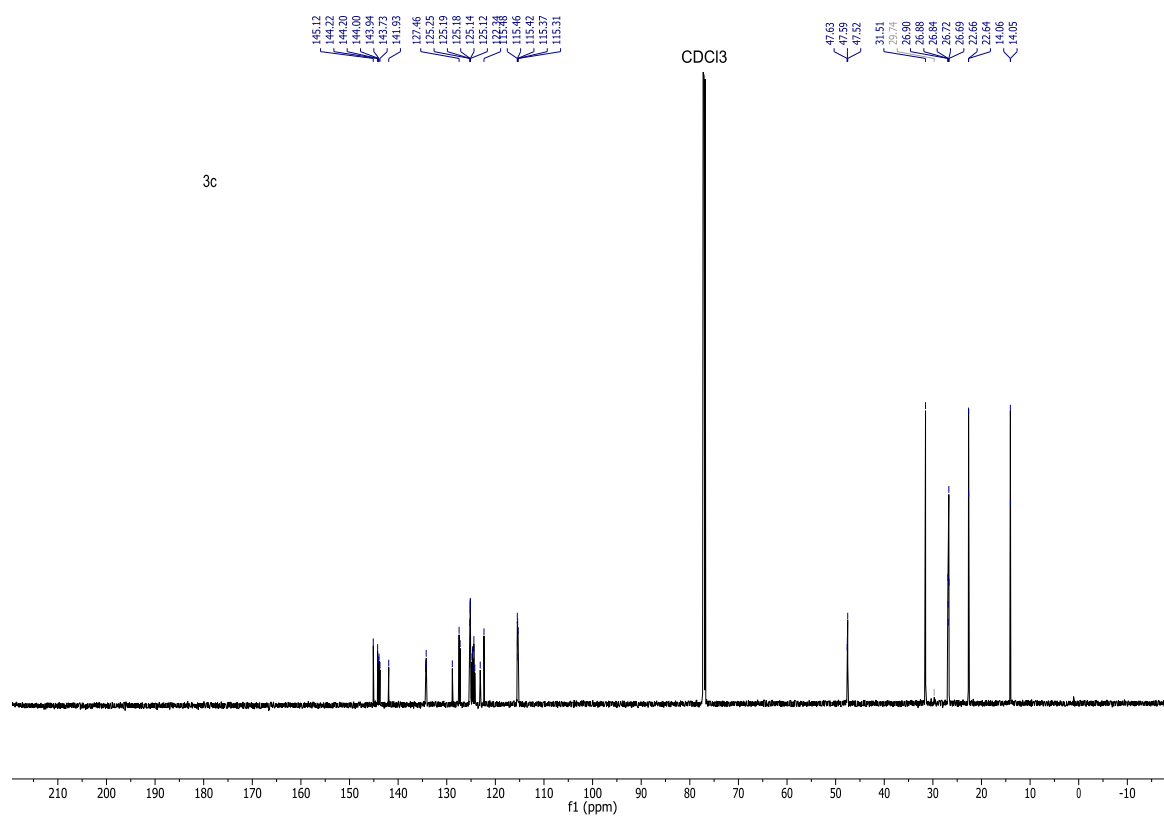


¹³C DEPT 135-NMR of **3b** in CDCl₃ at T = 298 K (δ in ppm).

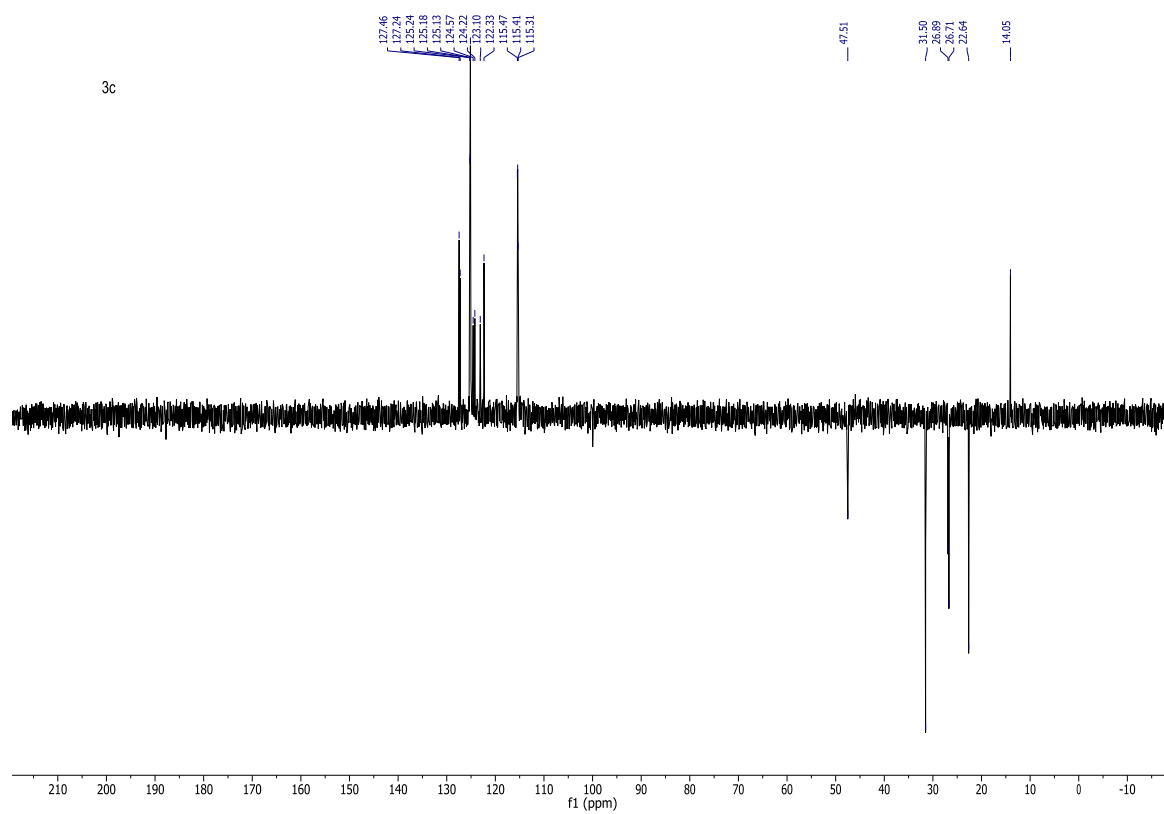
3.3 ^1H and ^{13}C NMR spectra of compound **3c**



^1H NMR of **3c** in CDCl_3 at $T = 298\text{ K}$ (δ in ppm).



¹³C NMR of **3c in CDCl₃ at *T* = 298 K (δ in ppm).**



¹³C DEPT 135-NMR of **3c in CDCl₃ at *T* = 298 K (δ in ppm).**

4 Lambert-Beer Plots of Compounds 3b and 3c

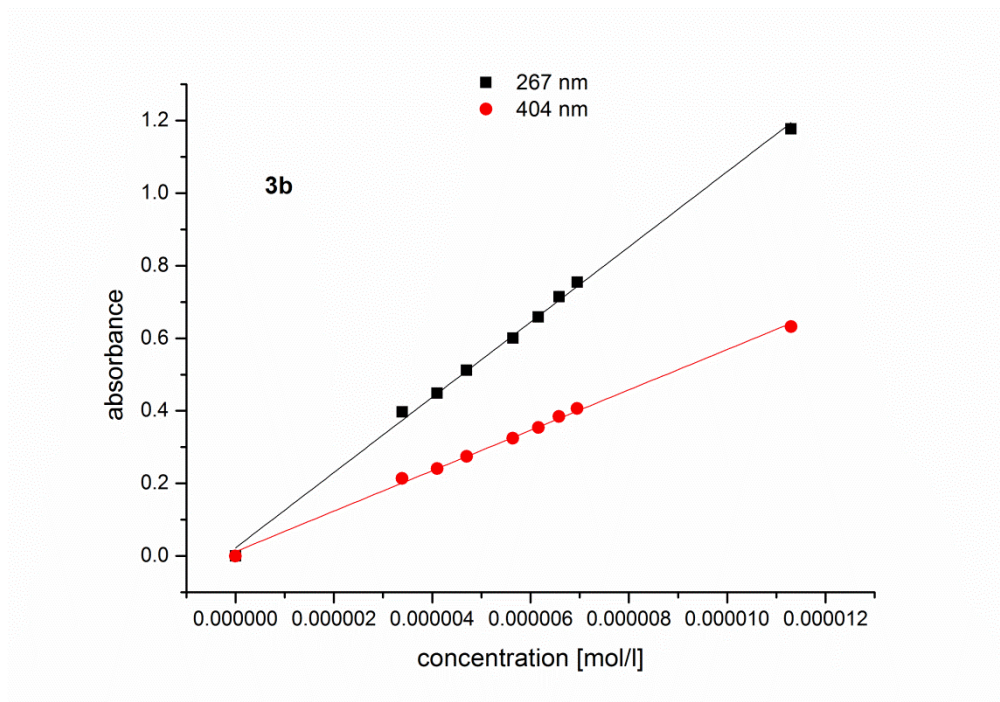


Figure S3: Lambert–Beer plot of compound **3b** at various concentrations in dichloromethane at $T = 298\text{ K}$ ($\lambda_{\text{max}} = 267\text{ nm}$; $\lambda_{\text{max}} = 404\text{ nm}$).

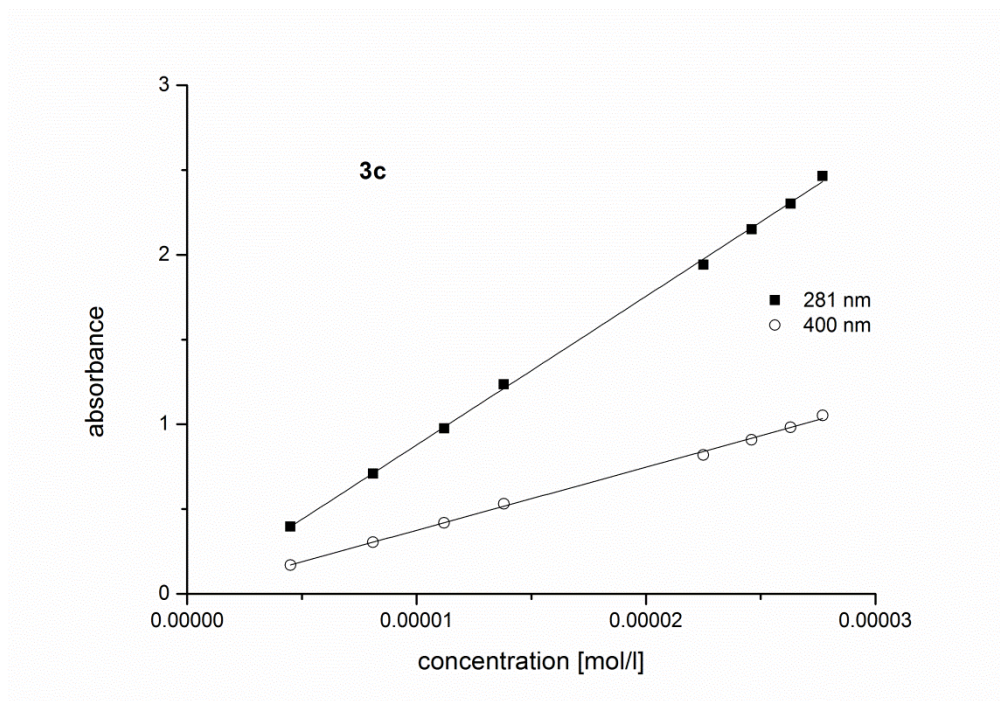


Figure S4: Lambert–Beer plot of compound **3c** at various concentrations in dichloromethane at $T = 298\text{ K}$ ($\lambda_{\text{max}} = 281\text{ nm}$; $\lambda_{\text{max}} = 400\text{ nm}$).

5 DFT calculations of the structures 3a, 3b, and 3c

The ground state geometries of structures **3a**, **3b**, and **3c** (the *n*-hexyl substituents were truncated to ethyl groups for reducing the computational time) were optimized in a DFT calculation with the B3LYP functional and the 6-311G(d,p) basis set in the program package Gaussian09. The minima structures were confirmed by analytical frequency analysis.

XYZ-coordinates for **3a**

C	-7.353982	3.349588	0.184060
C	-7.159302	2.235864	1.226790
N	-6.782968	0.912526	0.714671
C	-7.805328	0.047156	0.260984
C	-9.103648	0.512434	-0.002949
C	-10.109099	-0.347768	-0.439372
C	-9.843097	-1.693112	-0.657289
C	-8.560189	-2.173115	-0.407621
C	-7.563613	-1.327871	0.071639
S	-6.019045	-2.044701	0.585409
C	-4.948302	-0.660644	0.264359
C	-3.617131	-0.914006	-0.032104
C	-5.422453	0.654556	0.448080
C	-4.469224	1.682472	0.375715
C	-3.129131	1.421124	0.114779
C	-2.670116	0.119672	-0.112498
C	-1.272790	-0.178741	-0.429008
S	0.036132	0.820281	0.170880
C	-0.765272	-1.215071	-1.175638
C	0.647448	-1.204699	-1.286095
C	1.250772	-0.161260	-0.625559
C	2.677202	0.154451	-0.525346
C	3.636836	-0.867640	-0.614364
C	3.142621	1.461940	-0.332984
C	4.501105	1.740785	-0.237475
C	5.459811	0.729845	-0.382389
C	4.994693	-0.584267	-0.573172
S	6.188900	-1.885619	-0.820628
C	7.426963	-1.301150	0.322608
C	8.186370	-2.203693	1.061706
C	9.216648	-1.749110	1.881555
C	9.453876	-0.382297	1.983837
C	8.671188	0.526662	1.275297
C	7.654871	0.082772	0.419502
N	6.850446	0.975535	-0.329125
C	7.356197	2.318152	-0.630259
C	8.622705	2.292340	-1.489316
H	-6.443250	3.547537	-0.382231
H	-7.642673	4.274323	0.692371
H	-8.133735	3.104110	-0.537491
H	-6.391286	2.532479	1.944308
H	-8.077323	2.106671	1.803816
H	-9.346213	1.555555	0.131390
H	-11.100293	0.051527	-0.621185
H	-10.616393	-2.363118	-1.012935

H	-8.327741	-3.220903	-0.560665
H	-3.299872	-1.942751	-0.154716
H	-4.764754	2.711269	0.514940
H	-2.439963	2.255253	0.052500
H	-1.395839	-1.943238	-1.669030
H	1.203299	-1.924978	-1.872028
H	3.320104	-1.898886	-0.711215
H	2.434744	2.279008	-0.255700
H	4.811202	2.760384	-0.049666
H	7.974178	-3.263568	0.981400
H	9.818917	-2.456856	2.438512
H	10.243439	-0.012542	2.628034
H	8.857258	1.586402	1.390315
H	7.518808	2.905987	0.284282
H	6.575649	2.828738	-1.192152
H	9.455093	1.796862	-0.988406
H	8.928637	3.316111	-1.721866
H	8.430086	1.766620	-2.426808

SCF Done: E(RB3LYP) = -2539.53071966 A.U. after 1 cycles
Sum of electronic and zero-point Energies -2539.036031
Sum of electronic and thermal Energies -2539.004561
Sum of electronic and thermal Enthalpies -2539.003617
Sum of electronic and thermal Free Energies -2539.101122

XYZ-coordinates for **3b**

C	-13.344776	4.498418	3.092946
C	-13.619026	4.816615	1.621144
N	-13.879778	3.616367	0.821476
C	-14.898384	3.644512	-0.161174
C	-15.356555	4.834926	-0.741336
C	-16.384742	4.820437	-1.681582
C	-16.947761	3.617688	-2.094661
C	-16.471373	2.422506	-1.560621
C	-15.471542	2.434425	-0.592407
S	-14.942853	0.914245	0.17745
C	-13.214465	1.318727	0.353681
C	-12.242543	0.338026	0.195597
C	-12.866802	2.63726	0.692812
C	-11.508964	2.924551	0.876685
C	-10.543688	1.930449	0.757875
C	-10.885739	0.616652	0.415458
C	-9.856171	-0.439955	0.283217
C	-8.599346	-0.162891	-0.272738
C	-10.086794	-1.752046	0.705105
C	-9.104213	-2.731849	0.607019
C	-7.845082	-2.458872	0.050823
N	-6.844531	-3.448987	-0.058755
C	-7.227309	-4.85675	0.104501
C	-7.298627	-5.389581	1.545104
C	-7.62964	-1.14693	-0.414385
S	-6.167455	-0.762284	-1.353071
C	-5.025988	-1.871274	-0.557012
C	-3.680428	-1.534425	-0.548236
C	-5.473922	-3.118695	-0.075678
C	-4.486858	-4.016111	0.360373

C	-3.13696	-3.686886	0.336644
C	-2.69746	-2.434151	-0.104478
C	-1.284778	-2.053631	-0.106494
S	-0.014695	-3.255704	-0.227943
C	-0.731609	-0.797137	-0.032379
C	0.685272	-0.79071	-0.052079
C	1.246755	-2.042218	-0.140522
C	2.662521	-2.410367	-0.172714
C	3.618906	-1.525221	-0.69639
C	3.129756	-3.635398	0.314656
C	4.483619	-3.948749	0.311308
C	5.445327	-3.06425	-0.201458
N	6.819808	-3.377136	-0.20747
C	7.226441	-4.767054	0.033594
C	7.341617	-5.2058	1.502787
C	4.967314	-1.849307	-0.734461
S	6.066607	-0.776759	-1.63352
C	7.567021	-1.093531	-0.730451
C	8.533771	-0.096904	-0.690132
C	7.810621	-2.371129	-0.190342
C	9.088548	-2.596292	0.34411
C	10.065039	-1.606011	0.344578
C	9.81146	-0.327988	-0.161451
C	10.839173	0.738108	-0.144994
C	12.193745	0.440387	-0.354245
C	10.502046	2.077254	0.088219
C	11.468878	3.076526	0.109864
C	12.816155	2.782447	-0.132529
C	13.158543	1.439641	-0.366574
S	14.854396	1.053043	-0.765761
C	15.632332	2.212332	0.34536
C	16.827452	1.886521	0.980043
C	17.48174	2.826109	1.773663
C	16.90731	4.079001	1.959724
C	15.691232	4.396323	1.358187
C	15.044263	3.478182	0.520394
N	13.82543	3.772155	-0.136251
C	13.460951	5.169501	-0.388173
C	12.849901	5.378444	-1.775788
H	-14.191398	3.961202	3.525482
H	-13.204439	5.429644	3.64875
H	-12.45164	3.88735	3.228288
H	-12.804068	5.419927	1.19593
H	-14.517599	5.42959	1.568789
H	-14.905377	5.779673	-0.467816
H	-16.729338	5.757508	-2.103815
H	-17.740266	3.604005	-2.833264
H	-16.882755	1.473205	-1.883817
H	-12.547353	-0.654491	-0.114586
H	-11.197098	3.929807	1.127988
H	-9.507099	2.182112	0.949294
H	-8.386144	0.829956	-0.651847
H	-11.03533	-2.01246	1.160012
H	-9.333174	-3.718104	0.982022
H	-8.195562	-4.983786	-0.384297
H	-6.517045	-5.451208	-0.47413
H	-8.023875	-4.843926	2.14966
H	-6.338097	-5.322153	2.05733
H	-7.59793	-6.441654	1.526641
H	-3.387007	-0.567727	-0.939819

H	-4.762787	-4.989705	0.736218
H	-2.420047	-4.412647	0.702556
H	-1.328105	0.099146	0.076858
H	1.277727	0.110096	0.041379
H	3.299533	-0.583971	-1.127862
H	2.432925	-4.347784	0.7406
H	4.783356	-4.898406	0.727649
H	6.510949	-5.406281	-0.488064
H	8.183905	-4.912373	-0.470939
H	6.392203	-5.122672	2.033031
H	8.070339	-4.609748	2.05328
H	7.660347	-6.251511	1.543908
H	8.29935	0.866266	-1.128544
H	9.337416	-3.553094	0.778025
H	11.028387	-1.82926	0.787745
H	12.498824	-0.580665	-0.550972
H	9.471985	2.342706	0.29568
H	11.167503	4.093316	0.32567
H	17.248912	0.898047	0.837857
H	18.42232	2.57401	2.24861
H	17.393286	4.81362	2.591598
H	15.24293	5.362102	1.551593
H	12.794471	5.563282	0.39253
H	14.381252	5.748772	-0.330657
H	11.916495	4.829712	-1.90576
H	13.547781	5.046975	-2.547501
H	12.641872	6.441034	-1.928686

SCF Done: E(RB3LYP) = -4525.98854736 A.U. after 1 cycles
Sum of electronic and zero-point Energies -4525.066429
Sum of electronic and thermal Energies -4525.007192
Sum of electronic and thermal Enthalpies -4525.006247
Sum of electronic and thermal Free Energies -4525.168705

XYZ-coordinates for **3c**

C	21.573347	-0.713948	2.588561
C	20.945165	-1.933511	3.284011
N	20.555284	-3.056231	2.423134
C	21.538841	-4.002931	2.057312
C	22.90892	-3.750789	2.234102
C	23.873154	-4.692124	1.880002
C	23.503271	-5.902531	1.308897
C	22.149773	-6.170413	1.12116
C	21.180004	-5.253031	1.515012
S	19.472987	-5.750491	1.465575
C	18.719579	-4.159034	1.214785
C	17.501572	-4.10274	0.548285
C	19.299693	-3.006403	1.778346
C	18.557723	-1.818574	1.684268
C	17.315644	-1.780079	1.059638
C	16.760556	-2.91587	0.463538
C	15.44698	-2.875887	-0.219723
C	15.048194	-1.750114	-0.955078
C	14.546964	-3.945829	-0.143186
C	13.307444	-3.899877	-0.772188
C	12.927747	-2.792137	-1.540584
N	11.68957	-2.71563	-2.218933

C	10.981078	-3.951217	-2.565144
C	10.362625	-3.904897	-3.96428
C	13.825464	-1.712577	-1.613038
S	13.399487	-0.316152	-2.640057
C	11.652076	-0.279537	-2.282024
C	10.979985	0.932839	-2.181545
C	10.969858	-1.500434	-2.144063
C	9.588968	-1.45199	-1.918016
C	8.91466	-0.237159	-1.859473
C	9.591975	0.981516	-1.987234
C	8.877525	2.277421	-1.906628
C	7.815085	2.461267	-1.010132
C	9.224314	3.359638	-2.72389
C	8.548328	4.573014	-2.648788
C	7.518399	4.770666	-1.720166
N	6.830665	5.999171	-1.587406
C	7.475444	7.238776	-2.031711
C	7.278921	8.393139	-1.045995
C	7.160921	3.682052	-0.905462
S	5.905067	3.918965	0.339706
C	4.840044	5.002715	-0.593375
C	3.461542	4.922052	-0.446834
C	5.426747	5.96505	-1.43353
C	4.571582	6.855067	-2.09672
C	3.196043	6.805197	-1.908206
C	2.60696	5.834138	-1.085923
C	1.152805	5.773531	-0.919582
S	0.424731	5.12346	0.535708
C	0.170642	6.180288	-1.790809
C	-1.146007	5.980663	-1.306076
C	-1.199328	5.413311	-0.055279
C	-2.376473	5.055751	0.739723
C	-3.591255	4.741872	0.108056
C	-2.34409	5.007016	2.139914
C	-3.468943	4.659818	2.878406
C	-4.690317	4.386775	2.250582
N	-5.857666	4.044642	2.969215
C	-5.980194	4.444473	4.374511
C	-5.970937	5.963764	4.559518
C	-4.728781	4.444615	0.845904
S	-6.289629	4.180756	0.023886
C	-6.913726	2.897391	1.095779
C	-7.693731	1.87224	0.57611
C	-6.657095	2.988123	2.475147
C	-7.20443	1.998977	3.301981
C	-8.012864	0.994778	2.780406
C	-8.280196	0.908199	1.408858
C	-9.135396	-0.166621	0.852405
C	-10.264016	-0.623505	1.548545
C	-8.857231	-0.760122	-0.384794
C	-9.667845	-1.76164	-0.908397
C	-10.774112	-2.240939	-0.196543
N	-11.613136	-3.267129	-0.688854
C	-11.096265	-4.198548	-1.695925
C	-9.909806	-5.021237	-1.187984
C	-11.051727	-1.654037	1.049868
S	-12.407651	-2.298281	2.01373
C	-13.53269	-2.620032	0.666129
C	-14.90048	-2.453955	0.843193
C	-13.010458	-3.107488	-0.544801

C	-13.918674	-3.4019	-1.569679
C	-15.288801	-3.264892	-1.375537
C	-15.813401	-2.793129	-0.16606
C	-17.272228	-2.639758	0.036709
C	-18.181665	-3.549485	-0.521158
C	-17.808668	-1.58951	0.786822
C	-19.18171	-1.436376	0.948062
C	-20.095543	-2.343962	0.390304
C	-19.551553	-3.426009	-0.328833
S	-20.604814	-4.756483	-0.864977
C	-22.086881	-3.826646	-1.187495
C	-22.973504	-4.302292	-2.149171
C	-24.226114	-3.717401	-2.315913
C	-24.571008	-2.634383	-1.518288
C	-23.669918	-2.125098	-0.58553
C	-22.404389	-2.703779	-0.397837
N	-21.489894	-2.199896	0.554763
C	-21.984441	-1.28154	1.587077
C	-22.081509	0.204999	1.203998
H	22.501555	-0.965519	2.074247
H	21.799065	0.052056	3.336376
H	20.90462	-0.274578	1.847581
H	21.635634	-2.327924	4.032686
H	20.051835	-1.625142	3.831306
H	23.23993	-2.813755	2.655383
H	24.9193	-4.459858	2.043151
H	24.24926	-6.631028	1.015407
H	21.832567	-7.111858	0.687154
H	17.124012	-5.007928	0.08722
H	18.936021	-0.903538	2.114645
H	16.768179	-0.844929	1.052493
H	15.716085	-0.901876	-1.048926
H	14.795531	-4.81417	0.455698
H	12.625094	-4.729808	-0.642324
H	10.221965	-4.208519	-1.812772
H	11.719482	-4.751348	-2.546289
H	9.605762	-3.125451	-4.059394
H	9.889233	-4.864951	-4.187706
H	11.136805	-3.717958	-4.711414
H	11.549396	1.852719	-2.242629
H	9.027521	-2.368946	-1.796156
H	7.83957	-0.241993	-1.723418
H	7.517553	1.653172	-0.352182
H	10.007487	3.243197	-3.463982
H	8.818388	5.363852	-3.336388
H	7.14577	7.52769	-3.039672
H	8.541577	7.030418	-2.102832
H	6.22873	8.65912	-0.920409
H	7.811014	9.277691	-1.406844
H	7.679358	8.123739	-0.066441
H	3.048515	4.134273	0.172282
H	4.980835	7.608561	-2.75672
H	2.571733	7.539575	-2.402495
H	0.388614	6.595926	-2.765884
H	-2.032413	6.263166	-1.858894
H	-3.648534	4.722134	-0.973353
H	-1.427645	5.247715	2.666033
H	-3.391827	4.613755	3.956679
H	-5.20905	3.972085	4.999311
H	-6.938593	4.065596	4.725892

H	-5.033758	6.417702	4.235432
H	-6.115069	6.204626	5.616362
H	-6.78278	6.417117	3.986939
H	-7.878246	1.848871	-0.491506
H	-6.98509	1.994763	4.361681
H	-8.405413	0.239935	3.451643
H	-10.541517	-0.16346	2.489513
H	-7.985179	-0.446811	-0.946642
H	-9.423731	-2.180635	-1.875739
H	-10.838745	-3.682133	-2.631661
H	-11.907718	-4.884516	-1.933873
H	-9.051874	-4.399667	-0.9291
H	-9.595218	-5.725999	-1.962624
H	-10.197451	-5.588322	-0.300195
H	-15.261374	-2.090683	1.79828
H	-13.558383	-3.72346	-2.538142
H	-15.95698	-3.488152	-2.199
H	-17.814876	-4.405148	-1.076288
H	-17.150885	-0.846334	1.222049
H	-19.532943	-0.586396	1.513488
H	-22.682431	-5.155271	-2.751687
H	-24.915974	-4.107142	-3.054556
H	-25.541519	-2.163156	-1.623318
H	-23.969099	-1.26824	-0.001099
H	-21.332317	-1.395577	2.455766
H	-22.966167	-1.646567	1.896599
H	-21.113135	0.623559	0.927694
H	-22.463235	0.773347	2.057366
H	-22.754388	0.370239	0.361884

SCF Done: E(RB3LYP) = -6512.44612956 A.U. after 3 cycles
Sum of electronic and zero-point Energies -6511.096684
Sum of electronic and thermal Energies -6511.009730
Sum of electronic and thermal Enthalpies -6511.008786
Sum of electronic and thermal Free Energies -6511.234522

6 Calculation of the UV–vis transitions

Table S2: Experimentally determined (UV/Vis, recorded in CH₂Cl₂, *T* = 298 K) and calculated absorption bands (ZINDO-CI, B3LYP TD-DFT (in vacuo), CAM-B3LYP TD-DFT (in a dichloromethane dielectric) of the thienyl-bridged oligophenothiazines **3**.

Structure	Exp.		ZINDO		B3LYP			CAM-B3LYP		
	λ_{max} (ϵ) [nm]	λ_{max} [nm] (<i>f</i>) ^a	transition (%)	State	λ_{max} [nm] (<i>f</i>) ^a	transition (%)	State	λ_{max} [nm] (<i>f</i>) ^a	transition (%)	State
3a	395 (33100)	387.15 (1.2382)	HOMO→LUMO (85.7)	S ₁	410.53 (0.7422)	HOMO→LUMO (93.5)	S ₁	352.87 (0.9468)	HOMO→LUMO (76.7)	S ₁
	318 (27000)	314.31 (0.0290)	HOMO→LUMO+4 (26.5)	S ₂	371.86 (0.1596)	HOMO-1→LUMO (89.6)	S ₂	316.89 (0.3363)	HOMO-1→LUMO (43.5)	S ₂
		311.37 (0.0080)	HOMO→LUMO+3 (26.4)	S ₃	342.64 (0.0457)	HOMO→LUMO+1 (74.6)	S ₃	296.01 (0.0788)	HOMO→LUMO+1 (25.9)	S ₃
			HOMO→LUMO+1 (26.4)						HOMO→LUMO+3 (51.7)	
			HOMO-1→LUMO (20.0)		329.38 (0.0395)	HOMO→LUMO+2 (36.8)	S ₄	290.32 (0.1736)	HOMO-1→LUMO+1 (21.2)	S ₄
	261 (39100)								HOMO-1→LUMO+2 (17.9)	
	246 (39600)									
3b	404 (27700)	394.90 (1.6110)	HOMO→LUMO (78.3)	S ₁	440.00 (1.2927)	HOMO→LUMO (92.3)	S ₁	370.06 (1.6295)	HOMO→LUMO (70.4)	S ₁
	319 (32500)	329.62 (0.1967)	HOMO→LUMO+1 (18.4)	S ₂	405.77 (0.0364)	HOMO-1→LUMO (77.1)	S ₂	342.38 (0.0588)	HOMO-1→LUMO (34.2)	S ₂
			HOMO-1→LUMO+2 (17.3)	S ₃			S ₃		HOMO→LUMO+1 (29.1)	S ₃
		325.75 (0.3891)	HOMO-1→LUMO (14.7)		369.06 (0.0347)	HOMO→LUMO+1 (72.5)		305.10 (0.2495)	HOMO→LUMO+2 (23.9)	
			HOMO-1→LUMO+1 (31.8)		357.83 (0.0061)	HOMO-2→LUMO (80.1)	S ₄	300.54 (0.2891)	HOMO-1→LUMO+1 (18.4)	S ₄
									HOMO-2→LUMO+1 (12.3)	
									HOMO-2→LUMO+2 (8.6)	
									HOMO-2→LUMO+2 (8.3)	
									HOMO-1→LUMO+4 (7.9)	
	284 (45900)									
	266 (52100)									
3c	379 (51900)	387.87 (1.4718)	HOMO→LUMO (81.4)	S ₁	412.89 (1.4196)	HOMO→LUMO (53.7)	S ₁	348.78 (2.0500)	HOMO-2→LUMO (37.7)	S ₁
	327 (61000)	327.17 (0.7414)	HOMO-1→LUMO+1 (35.4)	S ₂	387.08 (0.1053)	HOMO-2→LUMO (34.1)	S ₂	329.77 (0.1324)	HOMO→LUMO (29.6)	S ₂
			HOMO-2→LUMO+1 (16.4)	S ₃		HOMO-1→LUMO+1 (53.4)	S ₃		HOMO-1→LUMO+1 (16.9)	S ₃
		325.75 (1.4955)	HOMO-2→LUMO+2 (34.9)		377.78 (0.2832)	HOMO-3→LUMO (21.4)		328.34 (0.3130)	HOMO-1→LUMO+2 (12.7)	
			HOMO-1→LUMO+2 (16.2)			HOMO-1→LUMO+1 (34.0)	S ₃		HOMO→LUMO+1 (13.4)	
						HOMO-2→LUMO (13.9)	S ₄		HOMO→LUMO+2 (19.9)	S ₄
						HOMO→LUMO+2 (13.9)			HOMO-1→LUMO+2 (9.6)	
									HOMO-1→LUMO+3 (8.0)	
									HOMO-1→LUMO+1 (7.5)	
					375.71 (0.0768)	HOMO-1→LUMO+2 (26.7)	S ₄	316.84 (0.2084)	HOMO-3→LUMO (15.0)	S ₄
						HOMO→LUMO+1 (14.7)			HOMO→LUMO+3 (11.2)	
						HOMO→LUMO+2 (15.2)			HOMO-5→LUMO (8.8)	
	283 (116200)				373.77 (0.2274)	HOMO-2 → LUMO (38.6)	S ₅	307.85 (0.1977)	HOMO-3→LUMO+1 (11.8)	S ₅
	267 (103000)					HOMO→LUMO (38.6)			HOMO-4→LUMO+2 (11.3)	
									HOMO→LUMO+2 (7.8)	
									HOMO-1→LUMO+1 (7.4)	

^aOscillator strength [a. u.].

Table S3. Frontier molecular orbital (FMO) energies [eV] from ZINDO-CI, B3LYP TD-DFT (in vacuo), and CAM-B3LYP TD-DFT (in a dichloromethane dielectric) calculations of the thienyl-bridged oligophenothiazines **3**.

FMO	ZINDO			B3LYP			CAM-B3LYP		
	3a	3b	3c	3a	3b	3c	3a	3b	3c
LUMO+9	2.120	0.697	0.637	0.617	-0.454	-0.567	1.869	0.694	0.538
LUMO+8	1.367	0.696	0.631	0.570	-0.504	-0.595	1.707	0.632	0.512
LUMO+7	0.769	0.657	0.609	0.044	-0.534	-0.608	1.218	0.588	0.494
LUMO+6	0.722	0.656	0.603	-0.247	-0.568	-0.629	0.904	0.532	0.464
LUMO+5	0.702	0.621	0.576	-0.415	-0.602	-0.663	0.785	0.505	0.428
LUMO+4	0.695	0.620	0.197	-0.495	-0.608	-0.884	0.644	0.493	0.167
LUMO+3	0.648	0.603	0.191	-0.586	-0.654	-0.932	0.535	0.445	0.11
LUMO+2	0.614	0.187	0.153	-0.619	-0.914	-1.095	0.431	0.128	-0.076
LUMO+1	0.525	0.146	0.143	-0.720	-1.093	-1.123	0.358	-0.069	-0.106
LUMO	-0.365	-0.387	-0.377	-1.495	-1.577	-1.534	-0.605	-0.679	-0.628
HOMO	-7.706	-8.045	-7.299	-6.916	-5.389	-4.979	-8.668	-6.891	-6.378
HOMO-1	-8.110	-8.374	-7.493	-7.122	-5.872	-5.059	-8.738	-7.459	-6.476
HOMO-2	-8.677	-8.523	-7.561	-7.202	-6.192	-5.215	-8.781	-7.762	-6.659
HOMO-3	-8.784	-8.750	-7.914	-7.217	-6.202	-5.352	-8.862	-7.774	-6.844
HOMO-4	-8.797	-8.767	-8.041	-7.631	-6.392	-5.483	-9.334	-7.943	-7.007
HOMO-5	-8.997	-8.779	-8.208	-8.126	-6.481	-5.962	-9.954	-8.02	-7.545
HOMO-6	-9.069	-8.866	-8.453	-8.279	-6.798	-6.161	-10.014	-8.353	-7.74
HOMO-7	-9.407	-8.950	-8.640	-8.531	-6.930	-6.167	-10.291	-8.644	-7.747
HOMO-8	-9.870	-9.032	-8.699	-8.802	-7.043	-6.220	-10.508	-8.668	-7.799
HOMO-9	-10.871	-9.038	-8.747	-9.060	-7.154	-6.225	-10.824	-8.755	-7.800