Supplementary information

Effect of π-linkers on Phenothiazine Sensitizers for Dye-Sensitized Solar Cells

Audun Formo Buene, Nora Uggerud, Solon P. Economopoulos, Odd R. Gautun, Bård Helge Hoff*

Department of Chemistry, Norwegian University of Science and Technology, Høgskoleringen 5, NO-7491 Trondheim, Norway

* Corresponding author. Tel.: +47 73593973; E-mail address: bard.helge.hoff@chem.ntnu.no (B. H. Hoff).

Absorption and emission

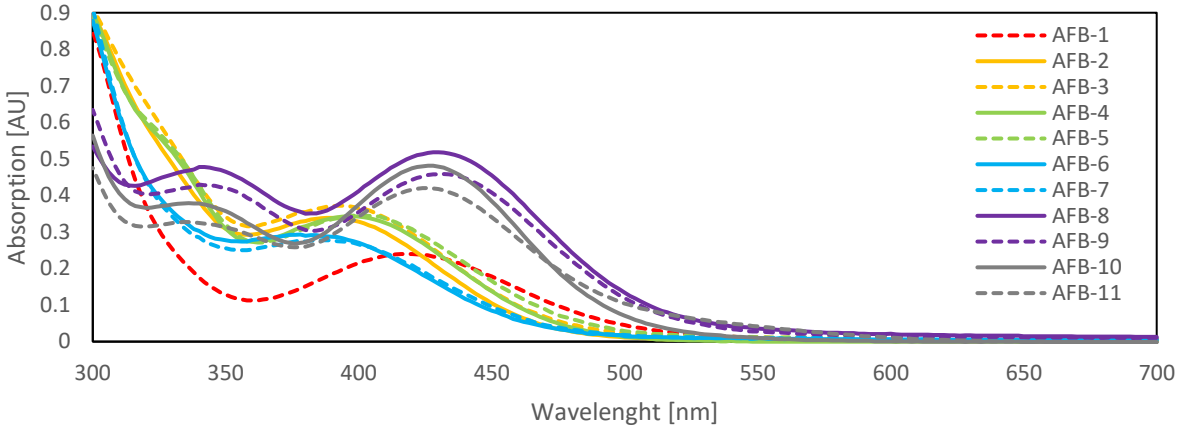


Fig. S1. UV/Visible absorption spectrum of all dyes when deprotonated with triethylamine.

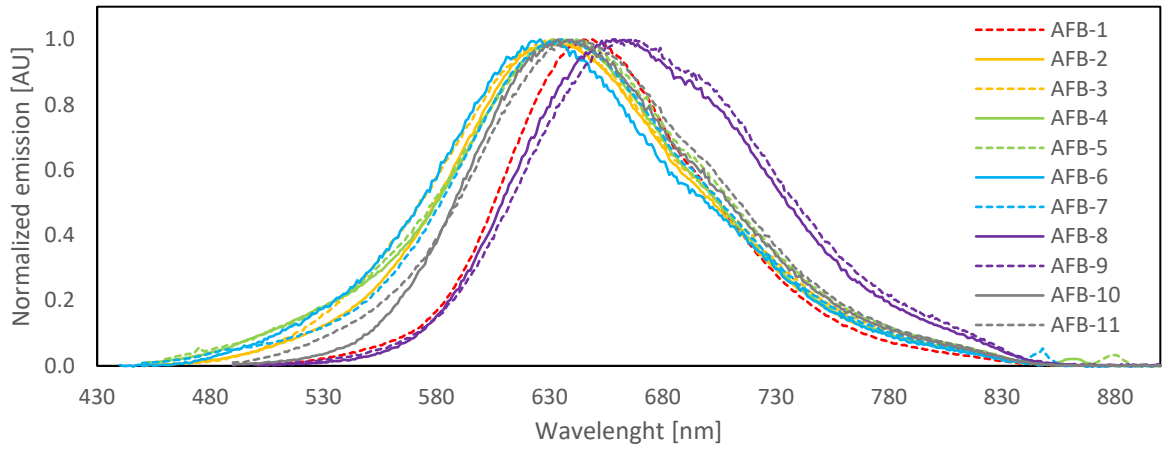


Fig. S2. Normalized emission spectrum of all dyes. Each dye is excited at its ICT transition maximum absorption wavelength.

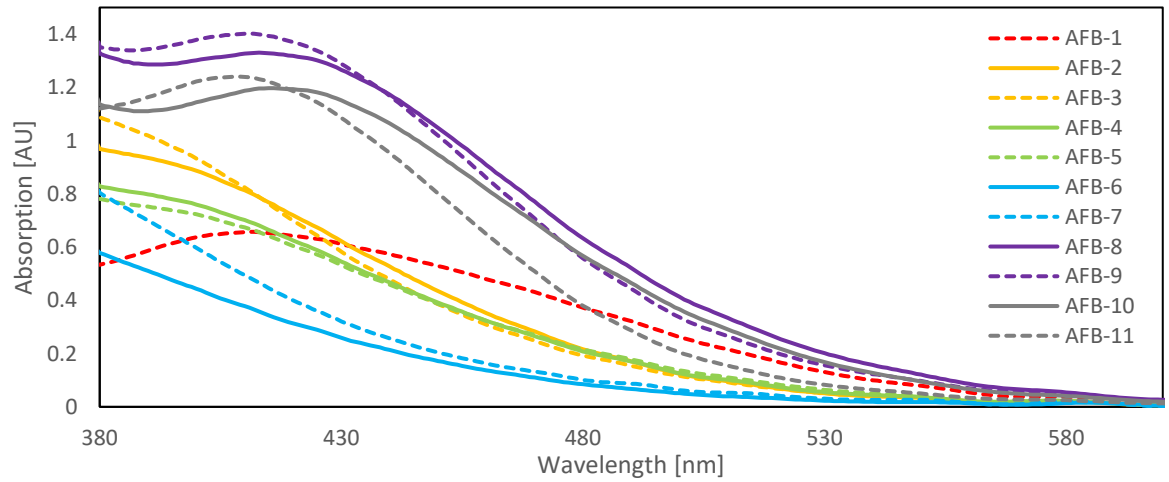


Fig. S3. UV/Visible absorption spectrum of all dyes on TiO_2 films (2.5 µm, 18NR-T, Dyesol).

Tab. S1. Intersection between absorption and the normalized emission spectra in Figure 2, and corresponding band gaps in eV.

Dye	Intersection [nm]	Band gap [eV]
AFB-1	572	2.17
AFB-2	542	2.29
AFB-3	538	2.30
AFB-4	540	2.30
AFB-5	540	2.30
AFB-6	537	2.31
AFB-7	543	2.28
AFB-8	586	2.12
AFB-9	587	2.11
AFB-10	569	2.18
AFB-11	570	2.18

Tab. S1. Photovoltaic properties for all dyes including standard deviation.

Dye[a]	J_{sc} [mA/cm^2]	V_{oc} [V]	FF	PCE [%]
AFB-1	8.64 ± 0.27	0.68 ± 0.01	0.71 ± 0.01	4.15 ± 0.17
AFB-2	7.83 ± 0.25	0.66 ± 0.01	0.68 ± 0.02	3.53 ± 0.04
AFB-3	7.83 ± 0.04	0.66 ± 0.00	0.67 ± 0.03	3.46 ± 0.14
AFB-4	7.63 ± 0.28	0.65 ± 0.01	0.69 ± 0.01	3.43 ± 0.07
AFB-5	7.87 ± 0.05	0.65 ± 0.01	0.67 ± 0.00	3.41 ± 0.05
AFB-6	6.28 ± 0.12	0.65 ± 0.00	0.68 ± 0.01	2.79 ± 0.02
AFB-7	6.77 ± 0.11	0.66 ± 0.00	0.67 ± 0.00	2.96 ± 0.06
AFB-8	9.14 ± 0.45	0.63 ± 0.02	0.68 ± 0.03	3.87 ± 0.08
AFB-9	9.56 ± 0.15	0.62 ± 0.01	0.68 ± 0.01	4.03 ± 0.03
AFB-10	9.44 ± 0.31	0.67 ± 0.01	0.69 ± 0.01	4.34 ± 0.05
AFB-11	9.15 ± 0.07	0.65 ± 0.00	0.67 ± 0.01	3.97 ± 0.05
N719[b]	11.32 ± 0.06	0.69 ± 0.01	0.72 ± 0.01	5.64 ± 0.04

Devices

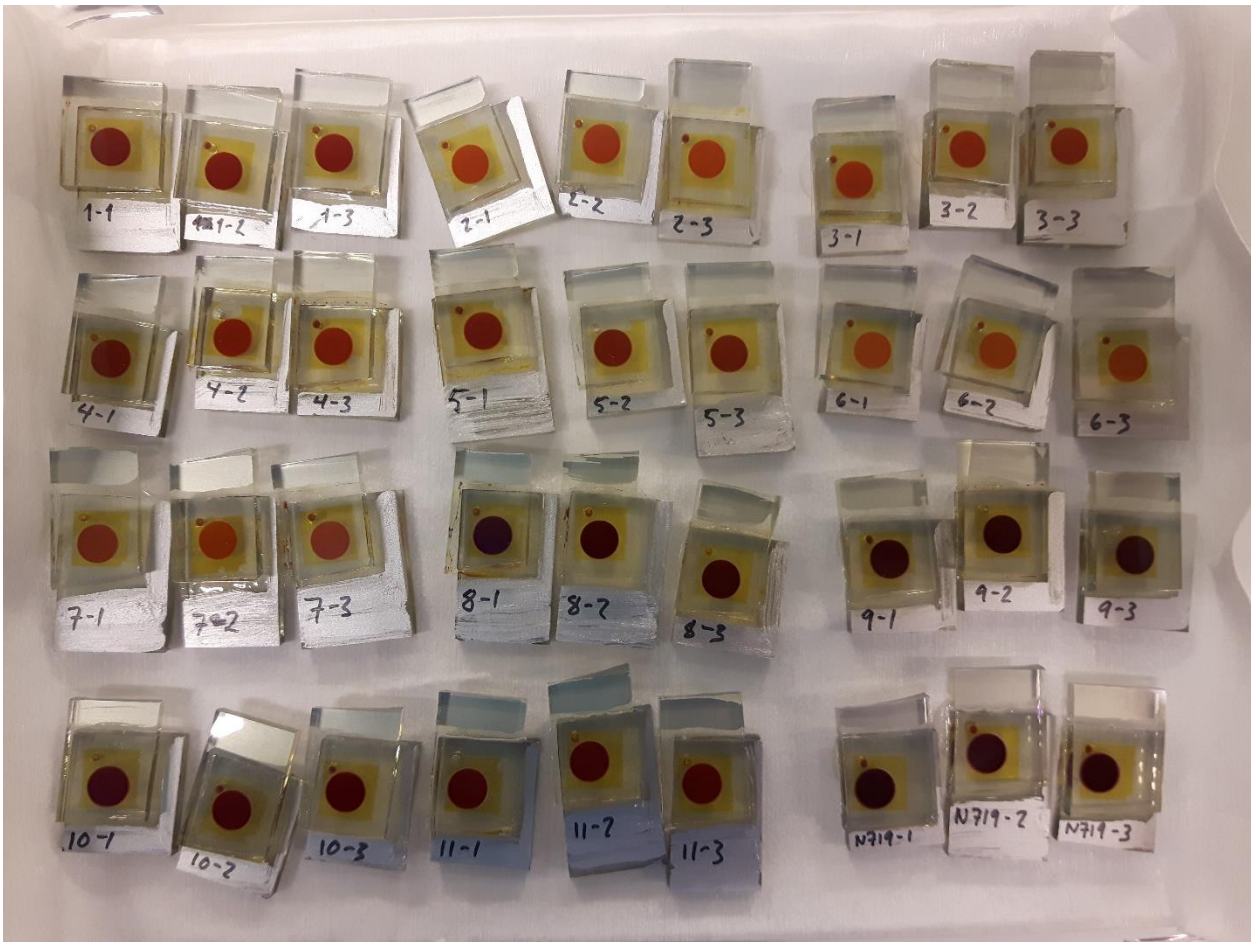


Fig. S4. The fabricated DSSC devices for this study.

Electrochemical measurements

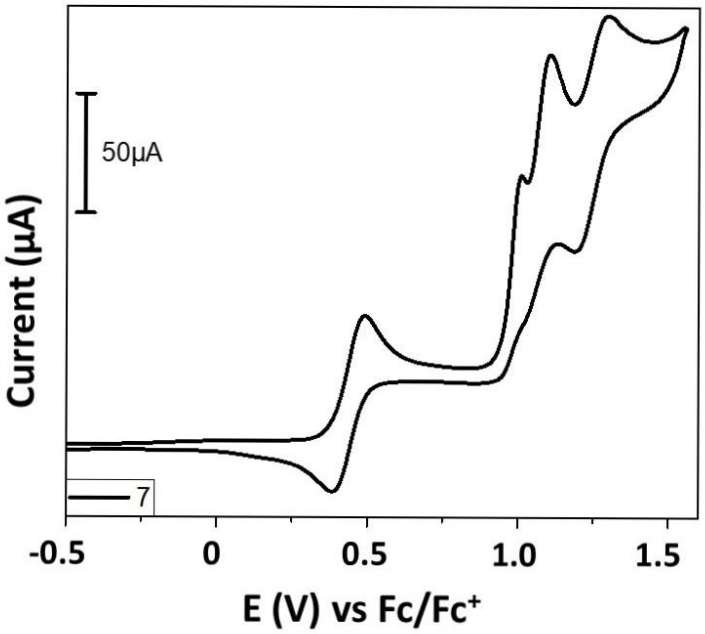


Fig. S5. Cyclic voltammogram of "parent" molecule **7**. *All measurements were run in solution with* $TBAPF_6$ *as supporting electrolyte (0.1 M in DMF). Scan rate 100 mV/s.*

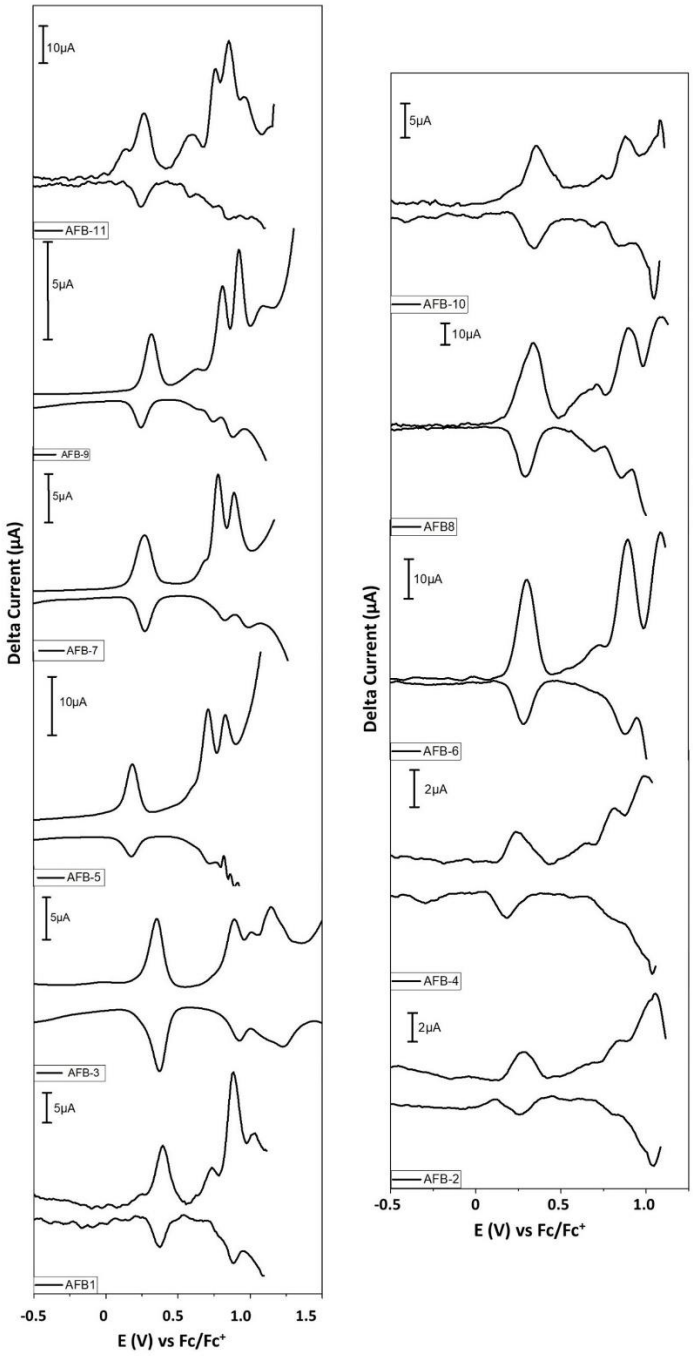


Fig. S6. Differential pulse voltammetry data for the synthesized dyes. The 4-methoxyphenyl series of dyes (left) and the phenyl series of dyes (right). All measurements were run in solution with TBAPF6 as supporting electrolyte (0.1 M in DMF). Experimental: Step height: 25 mV, Step Width: 5 mV, Pulse height: 50 ms, Pulse Width: 100 ms.

Experimental information

2.1 Materials and reagents

All reactions were carried out under nitrogen atmosphere, and all synthesis reagents were acquired from Sigma Aldrich.

2.2 Analytical instruments

^{1}H and ^{13}C NMR spectra were recorded at 22 °C on either a Bruker 400 or 600 MHz spectrometer in DMSO-d_6. All chemical shifts are reported in ppm, and the spectra were calibrated using the signal of DMSO at 2.50 ppm (^{1}H) and 39.52 (^{13}C), or that of of TMS (0 ppm) in $CDCl_3$. Infrared absorption (IR) spectra were recorded with a FTIR Thermo Nicolet Nexus FT-IR Spectrometer using a Smart Endurance reflection cell. Reported frequencies were in the range of 4000-400 cm^{-1}. UV/Vis analyses were performed with a Hitachi U-1900 UV/Vis-spectrophotometer using quartz cuvettes (10 mm) and scanning from 300-700 nm. Extinction coefficients were calculated from Lambert-Beer's law. UV/Vis measurements of sensitized TiO_2 films was performed in the same spectrophotometer with a non-stained electrode as the background. Melting points were determined with a Stuart SMP40 automatic melting point instrument. Accurate mass determination in positive and negative mode was performed on a "Synapt G2-S" Q-TOF instrument from Waters™. The samples were ionized by the use of ASAP probe (APCI) or by ESI. Spectra processing was done by Waters™ Software (Masslynx v4.1 SCN871). Fluorescence spectrophotometry was measured with a Varian Cary Eclipse instrument. All dyes were measured in chloroform.

Electrochemistry studies were performed using a standard three-electrode cell under argon atmosphere. All measurements were performed with Ar bubbling into the electrochemical cell for 15 min 10 s prior to the measurements; the Ar was turned to "blanket-mode". Platinum wires (99.99%) were used as working and pseudo-reference electrodes and platinum gauze (55 mesh, 99.9%) as counter electrode. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 98%) was used as the electrolyte and was recrystallized three times from acetone and dried in vacuum at ca 100 °C before each experiment. Measurements were recorded using an EG&G Princeton Applied Research potentiostat/galvanostat Model Verstastat 3 connected to a personal computer running VersaStudio software. The scan rate was kept constant for all CV runs at 100 mV/s while for differential pulse voltammetry measurements, the following parameters were used Step height: 25 mV, Step Width: 5 mV, Pulse height: 50 ms, Pulse Width: 100 ms. All results were calibrated using commercially available ferrocene (purified by sublimation) as internal standard. All samples were studied in anhydrous DMF solution. To calculate HOMO/LUMO levels, using the potentials obtained the following equations from Cardona et al. were used [1]:

$$E_{HOMO} = 2\ (E_{[ox\ vs.\ Fc/Fc+]} + 5.1)\ (eV)$$

$$E_{LUMO} = 2\ (E_{[red\ vs.\ Fc/Fc+]} + 5.1)\ (eV)$$

For HOMO–LUMO estimations, the onset of the peak was considered. For conversions to NHE, a value of -4.5 eV was used as equivalent to 0.0 V vs. NHE. [2]

Device fabrication

The cell fabrication is conducted based on the procedure from Hao et al. [3] TEC-8 FTO glass supplied by Dyesol was washed with Deconex 21 (2 g/L H_2O) in an ultrasonic bath for 45 minutes, and then rinsed with deionized water and ethanol before air drying. Further cleaning was done in a UV-ozone cleaner for 15 minutes (Novascan PSD PRO-UV T6). A blocking layer was deposited by immersion of the FTO glass in an aq. solution of $TiCl_4$ (40 mM) for 30 minutes at 70 °C, rinsing with deionized water and ethanol followed by another immersion for 30 minutes in an aq. solution of $TiCl_4$ (40 mM) at 70 °C, then rinsing with deionized water and ethanol.

Five layers of transparent TiO_2 paste (18NR-T, Dyesol) were screen printed on the FTO glass (mesh count 250, active area 0.238 cm^2). Between each layer, the electrodes were heated to 125 °C for 2-3 minutes. Finally, a scattering layer (WER2-O, Dyesol) was screen printed, and the electrodes were sintered at 500 °C for 30 minutes. The thickness of the sintered TiO_2 was measured to 17.5 μm (12.5 μm + 5 μm) with a profilometer (Veeco, Dektak 150). The electrodes were then post treated with $TiCl_4$ using the same conditions previously described for 30 minutes.

Counter electrodes were fabricated by drilling holes in the FTO glass with a diamond drill bit. The catalytic Pt layer was deposited by dropcasting a 10 mM solution of H_2PtCl_6 in 2-propanol (5 μL/cm^2), followed by firing at 400 °C for 15 minutes. [4]

Before staining, the electrodes were annealed with a hot air gun at 480 °C for 25 minutes. The staining solution had 5×10^{-4} M dye concentration, with a 10-fold amount of CDCA in a mixture of acetonitrile/THF (43:57, v/v). The dielectric constant for this solution is estimated to be around 20 Fm^{-1}, which for Black dye is reported as the optimal dielectric constant. [5] N719 was stained from a 0.5 mM solution in ethanol. The electrodes were stained for 20 hours, then rinsed in acetonitrile for 2 minutes and dried under N_2 flow. The cells were sealed with a 25 μm Surlyn (Solaronix) gasket, melted with a 50 W PTC heat element for 3 × 20 seconds per cell.

The electrolyte was made following a procedure from Demadrille et al. [6], containing 0.5 M 1-butyl-3-methylimidazolium iodide, 0.1 M lithium iodide, 0.05 M I_2 and 0.5 M *tert*-butylpyridine in acetonitrile. This was injected by vacuum backfilling before the filling hole was sealed with Surlyn and a circular glass cover slip. The contacts for the anode and cathode were painted with a conductive silver paint (Electrolube, SCP) before characterization.

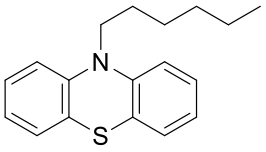
Device characterization

The device's J-V characteristics were measured with a Keithley 2450 under a Sciencetech SP300B solar simulator with an AM 1.5 G filter, calibrated to 100 mW/cm^2 with a Newport Reference Solar Cell and Meter (91150V). All cells were masked with a 0.1547 cm^2 black mask before characterization.

IPCE measurements were obtained from a device fabricated with a halogen lamp (Ocean Optics HL-2000), a monochromator (Spectral Products CM110), connected to the Keithley 2450. The light intensity was determined using a NIST traceable calibrated photodiode (Thorlabs, FDS100-CAL).

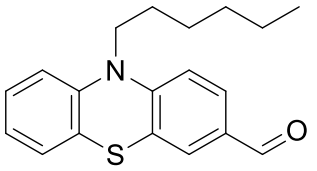
2.3 Synthesis

Synthesis of 10-hexyl-10*H*-phenothiazine (**2**) [7]



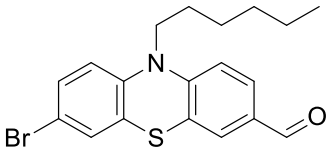
10*H*-Phenothiazine (5.00 g, 25.1 mmol) and NaH (904 mg, 37.7 mmol) were mixed before dry THF (85 mL) was added under N_2 atmosphere. The reaction was left stirring at 22 °C for 15 minutes. 1-Bromohexane (5.29 mL, 6.22 g, 37.7 mmol) was added dropwise over 30 minutes and the mixture was heated to reflux. After 24 hours the reaction was cooled to room temperature and quenched with an aqueous NH_4Cl (50 mL, 5 wt%) solution, and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed in vacuo. The crude product was purified by silica-gel column chromatography (*n*-pentane, R_f = 0.17) to obtain compound **2** as a clear oil (5.12 g, 18.06 mmol, 72%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.20-7.15 (m, 2H), 7.14-7.11 (m, 2H), 6.99-6.96 (m, 2H), 6.94-6.89 (m, 2H), 3.82 (t, *J* = 7.0 Hz, 2H), 1.69-1.609 (m, 2H), 1.39-1.30 (m, 2H), 1.23-1.17 (m, 4H), 0.82-0.77 (m, 3H). ^{1}H NMR recorded in $CDCl_3$ was in accordance with reported data. [8]

Synthesis of 10-hexyl-10*H*-phenothiazine-3-carbaldehyde (**3**) [8]



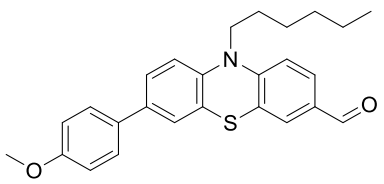
10-Hexyl-10*H*-phenothiazine (**2)** (10.0 g, 35.3 mmol) was dissolved in a mixture of dry 1,2-dichloroethane (300 mL) and DMF (12 mL) followed by cooling to 0 °C. $POCl_3$ (14 mL, 23.0 g, 150 mmol) was added slowly and the mixture heated to reflux and stirred for 12 hours. Water (500 mL) was added, and the aqueous phase was extracted with chloroform (3 × 300 mL). The combined organic phases were dried over anhydrous Na_2SO_4, then filtered and the solvents were removed in vacuo. The crude product was purified by silica-gel column chromatography (hexane:EtOAc, 9:1, R_f = 0.32) to yield compound **3** as a yellow solid (8.24 g, 26.5 mmol, 75%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.58 (s, 1H), 7.18-7.13 (m, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 8.5 Hz, 2H), 3.88 (t, *J* = 7.2 Hz, 2H), 1.84-1.77 (m, 2H), 1.47-1.41 (m, 2H), 1.34-1.27 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{1}H NMR was in accordance with reported literature. [8]

Synthesis of 7-bromo-10-hexyl-10*H*-phenothiazine-3-carbaldehyde (**4**) [8]



Compound **3** (8.40 g, 27.0 mmol) was dissolved in THF (300 mL) and cooled to 0 °C. NBS (5.50 g, 30.9 mmol) was added, the solution was heated to 22 °C, and stirred for 2 hours. Water (300 mL) was added, and the aqueous phase was extracted with dichloromethane (3 × 150 mL). The combined organic phases were dried over anhydrous Na_2SO_4, then filtered and the solvents were removed in vacuo. The crude product was purified by silica-gel column chromatography (CH_2Cl_2) to yield compound **4** as a yellow solid (8.20 g, 21.0 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 7.60 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.19 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.13 (d, *J* = 2.3 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.66 (d, *J* = 8.7 Hz, 1H), 3.79 (t, *J* = 7.2 Hz, 2H), 1.79-1.70 (m, 2H), 1.45-1.36 (m, 2H), 1.33-1.22 (m, 4H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{1}H NMR was in accordance with reported literature. [8]

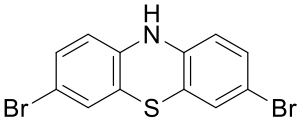
Synthesis of 10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazine-3-carbaldehyde (**5**)



Compound **4** (3.50 g, 8.97 mmol), 4-methoxyphenylboronic acid (1.50 g, 9.86 mmol), $Pd(PPh_3)_4$ (0.11 g, 0.10 mmol) and K_2CO_3 (4.96 g, 35.9 mmol) were mixed. Degassed 1,4-Dioxane (100 mL) and water (100 mL) were added under N_2 atmosphere while stirring. The reaction mixture was heated to 80 °C and left stirring for 2 hours before cooling

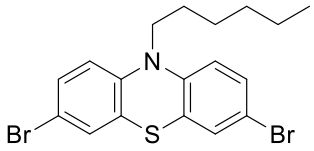
to 22 °C. Water (200 mL) was added to the reaction mixture and CH_2Cl_2 (3 × 150 mL) was used for extraction. The combined organic phases were washed with water and dried over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 9:1, R_f = 0.18) to obtain compound **5** as a brown oil (2.37 g, 5.74 mmol, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.78 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.58 (s, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.92-6.86 (m, 2H), 3.89 (t, *J* = 7.4 Hz, 2H), 1.83 (s, 3H), 1.87-1.80 (m, 2H), 1.49-1.42 (m, 2H), 1.45-1.39 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 190.0, 159.2, 150.6, 142.0, 136.4, 132.2, 131.0, 130.2, 128.4, 127.6 (2C), 125.7, 125.5, 124.6, 124.1, 116.1, 114.7, 114.3 (2C), 55.4, 48.1, 31.4, 26.7, 26.5, 22.6, 14.0; IR (neat, cm^{-1}) ν: 2925 (w), 1683 (m), 1579 (m), 1465 (s), 1236 (s), 1195 (s), 805 (m), 732 (m); HRMS (ASAP+, *m/z*): 417.1763 (calcd. $C_{26}H_{27}NO_2S$: 417.1762 $[M]^+$).

Synthesis of 3,7-dibromo-10*H*-phenothiazine (**6**) [9]



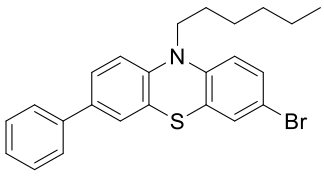
10*H*-Phenothiazine (25.0 g, 125.5 mmol) was suspended in glacial acetic acid (1000 mL) and stirred at 22 °C. Bromine (16.2 mL, 50.3 g, 314.5 mmol) dissolved in glacial acetic acid (400 mL) was added dropwise to the suspension over 90 minutes. After 2.5 hours the reaction mixture was cooled on an ice bath and Na_2SO_3 (31.5 g) and water (15 mL) were added and the mixture was left stirring for 1 hour. By adding aqueous KOH (3 M, 1000 mL), a precipitate was formed and the mixture was left stirring for an additional hour. The precipitate was filtered off, washed with cold 2-propanol (100 mL), and dried to yield a green solid. The crude product was purified by recrystallization from toluene (940 mL) to obtain compound **6** as green crystals (35.89 g, 101.0 mmol, 80%), mp. 185-187 °C (lit. 195.6-196.8 °C [9]) ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.84 (m, 1H), 7.16-7.12 (m, 4H), 6.59-6.57 (m, 2H). ^{1}H NMR was in accordance with reported data. [9]

Synthesis of 3,7-dibromo-10-hexyl-10*H*-phenothiazine (**7**) [7]



Compound **6** (10.00 g, 28.0 mmol) and NaH (1.008 g, 42.0 mmol) were mixed before dry THF (112 mL) was added under N_2 atmosphere. The reaction was left stirring at 22 °C for 20 minutes. 1-Bromohexane (5.90 mL, 6.93 g, 42.0 mmol) was added dropwise over 40 minutes and the mixture was heated to reflux. After 20 hours the reaction was cooled to room temperature and quenched with an aqueous NH_4Cl (50 mL, 5 wt%) solution, and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed in vacuo. The crude product was purified by silica-gel column chromatography (*n*-pentane, R_f = 0.24) to obtain compound **7** as a white solid (11.46 g, 26.0 mmol, 93%), mp. 53-54 °C (lit. 58 °C [10]) ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.37-7.35 (m, 4H), 6.96-6.94 (m, 2H), 3.82-3.79 (m, 2H), 1.66-1.59 (m, 2H), 1.36-1.33 (m, 2H), 1.24-1.22 (m, 4H), 0.83-0.80 (m, 3H). ^{1}H NMR was in accordance with reported data. [7]

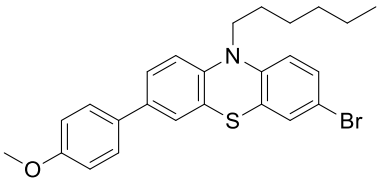
Synthesis of 3-bromo-10-hexyl-7-phenyl-10H-phenothiazine (8)



Compound **7** (2.00 g, 4.53 mmol), phenylboronic acid (608.0 mg, 4.99 mmol), $Pd(PPh_3)_4$ (52.0 mg, 0.045 mmol) and K_2CO_3 (2.506 g, 18.13 mmol) were mixed. Degassed 1,4-Dioxane (15 mL) and water (15 mL) were added under N_2 atmosphere while stirring. The reaction mixture was heated to 80 °C and left stirring for 7.5 hours before cooling to 22 °C. Water (25 mL) was added to the reaction mixture and EtOAc (3 × 30 mL) was used for extraction. The combined organic phases were dried with brine (30 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (*n*-pentane:toluene, 19:1, R_f = 0.22)

to obtain compound **8** as a white solid (921 mg, 2.10 mmol, 46%), mp. 79-80 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.64-7.60 (m, 2H), 7.53-7.49 (m, 1H), 7.45-7.40 (m, 3H), 7.38-7.29 (m, 3H), 7.10-7.07 (m, 1H), 6.98-6.94 (m, 1H), 3.87 (t, J = 6.9 Hz, 2H), 1.72-1.63 (m, 2H), 1.43-1.34 (m, 2H), 1.29-1.21 (m, 4H), 0.85-0.80 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 143.9, 143.6, 138.7, 134.6, 130.1. 128.94, 128.88 (2C), 127.1, 126.0 (3C), 125.8, 125.0, 123.4, 117.4, 116.2, 113.7, 46.6, 30.8, 26.0, 25.8, 22.0, 13.8; IR (neat, cm^{-1}) ν: 2956 (w), 2930 (w), 2847 (w), 1665 (m), 1453 (s), 1407 (m), 1249 (m), 1024 (m), 758 (s), 696 (m); HRMS (ASAP+, m/z): 437.0810 (calcd. $C_{24}H_{24}NS^{79}Br$ 437.0813, $[M]^+$)

Synthesis of 3-bromo-10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazine (**9**)

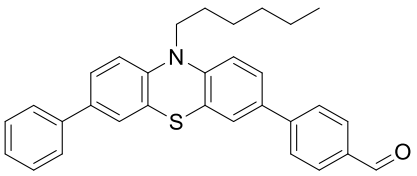


Compound **7** (2.01 g, 4.56 mmol), (4-methoxyphenyl)boronic acid (0.761 g, 5.01 mmol), $Pd(PPh_3)_4$ (53.0 mg, 0.046 mmol) and K_2CO_3 (2.52 g, 18.22 mmol) were mixed. Degassed 1,4-Dioxane (15 mL) and water (15 mL) were added under N_2 atmosphere while stirring. The reaction mixture was heated to 80 °C and left stirring for 19 hours before cooling to room temperature. Water (25 mL) was added to the reaction mixture and EtOAc (3 × 25 mL) was used for extraction. The combined organic phases were dried with brine (25 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (*n*-pentane:toluene, 19:1, R_f = 0.17) to obtain compound **9** as a yellow oil (1.09 g, 2.32 mmol, 51%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.58-7.56 (m, 2H), 7.47-7.44 (m, 1H), 7.40-7.39 (m, 1H) 7.36- 7.34 (m, 2H), 7.08-7.05 (m, 1H), 6.98-6.95 (m, 3H), 3.88-3.85 (m, 2H), 3.79 (s, 3H), 1.71-1.64 (m, 2H), 1.41-1.35 (m, 2H), 1.28-1.24 (m, 4H), 0.88-0.82 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 158.7, 144.0, 143.0, 134.4, 131.2, 130.1, 128.9, 127.1 (2C), 125.8, 125.5, 124.5, 123.3, 117.3, 116.2, 114.3 (2C), 113.6, 55.1, 46.6, 30.8, 26.0, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2951 (m), 2929 (m), 2846 (m), 1610 (m), 1490 (m), 1464 (s), 1231 (m), 1179 (m), 873 (m), 800 (s); HRMS (ASAP+, m/z): 467.0919 (calcd. $C_{25}H_{27}NS^{79}Br$ 467.0918, $[M+H]^+$).

General procedure for Suzuki coupling of **7** or **8**

The phenothiazines **8** or **9** (1 eq.), arylboronic acid (1.5 eq.), $Pd(OAc)_2$ (0.02 eq.), SPhos (0.04 eq.) and K_2CO_3 (4 eq.) were mixed. 1,4-Dioxane and water (1:1, v:v) were then degassed and added under N_2 atmosphere. The reactions were heated to 80 °C and stirred until full conversion (1-16 hours). Then the reaction mixture was cooled to room temperature before water was added and EtOAc was used for extraction. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude products were purified by silica-gel column chromatography.

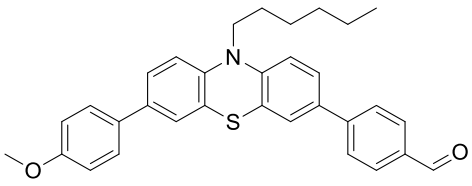
Synthesis of 4-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)benzaldehyde (**10**)



The synthesis was done in accordance with the general procedure starting with compound **8** (306 mg, 0.698 mmol), (4-formylphenyl)boronic acid (157 mg, 1.047 mmol), $Pd(OAc)_2$ (3.13 mg, 0.014 mmol), SPhos (11.5 mg, 0.028 mmol) and K_2CO_3 (386 mg, 2.79 mmol). The reaction was left stirring at 80 °C for 4 hours before cooling and extraction of the reaction mixture with EtOAc (3 × 20 mL). The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 7:1, R_f = 0.39) to obtain compound **10** as a yellow solid (294 mg, 0.635 mmol, 91%), mp. 80-82 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.02 (s, 1H), 7.97-7.87 (m, 4H), 7.66-7.57 (m, 4H), 7.53-7.49 (m, 1H), 7.47-7.40 (m, 3H), 7.35-7.30 (m, 1H), 7.15-7.08 (m, 2H), 3.93 (t, J = 6.9 Hz, 2H), 1.77-1.68 (m, 2H), 1.46-1.37 (m, 2H), 1.32-1.21 (m, 4H), 0.87-0.80 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.6, 144.8, 144.5, 143.4, 138.8, 134.7, 134.6, 132.7, 130.1 (2C), 128.9 (2C), 127.1, 126.49 (2C), 126.47, 126.0 (2C), 125.9, 125.4, 125.0, 123.8, 123.5, 116.2, 116.1, 46.6, 30.8, 26.2, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2951 (w), 2919 (w), 2852

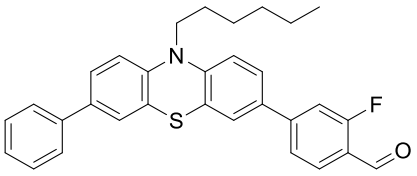
(w), 1690 (m), 1600 (m), 1462 (s), 1247 (m). 1212 (m), 1168 (m), 807 (s), 759 (s), 696 (s); HRMS (ASAP+, *m/z*): 463.1964 (calcd. $C_{31}H_{29}NOS$ 463.1970, $[M]^+$).

Synthesis of 4-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)benzaldehyde (**11**)



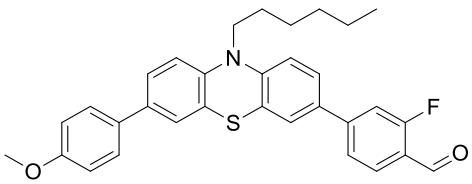
The synthesis was done in accordance with the general procedure starting with compound **9** (500 mg, 1.07 mmol), (4-formylphenyl)boronic acid (240 mg, 1.60 mmol), $Pd(OAc)_2$ (4.79 mg, 0.021 mmol), SPhos (17.5 mg, 0.043 mmol) and K_2CO_3 (590 mg, 4.27 mmol). The reaction was left stirring at 80 °C for 16 hours before cooling and extraction of the reaction mixture with EtOAc (3 × 30 mL). The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 4:1, R_f = 0.35) to obtain compound **11** as an orange solid (431 mg, 0.873 mmol, 82%) mp. 71-73 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.02 (s, 1H), 7.96-7.87 (m, 4H), 7.65-7.61 (m, 1H), 7.59-7.55 (m, 3H), 7.47-7.43 (m, 1H), 7.41-7.39 (m, 1H), 7.13-7.06 (m, 2H), 7.01-7.67 (m, 2H), 3.93 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 1.77-1.68 (m, 2H), 1.46-1.37 (m, 2H), 1.31-1.22 (m, 4H), 0.87-0.81 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 192.5, 158.7, 144.9, 144.5, 142.7, 134.7, 134.4, 132.5, 131.2, 130.1 (2C), 127.1 (2C), 126.46 (2C), 126.45, 126.42, 125.4, 124.5, 123.8, 123.4, 116.1, 116.0, 114.3 (2C), 55.1, 46.6, 30.8, 26.2, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2956 (w), 2925 (w), 2842 (w), 1692 (m), 1600 (m), 1462 (s), 1239 (s), 1213 (m), 1168 (s), 805 (s), 790 (s); HRMS (ASAP+, *m/z*): 493.2076 (calcd. $C_{32}H_{31}NO_2S$ 493.2075, $[M]^+$).

Synthesis of 2-fluoro-4-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)benzaldehyde (**12**)



The synthesis was done in accordance with the general procedure starting with compound **8** (350 mg, 0.798 mmol), (3-fluoro-4-formylphenyl)boronic acid (201 mg, 1.197 mmol), $Pd(OAc)_2$ (3.58 mg, 0.016 mmol), SPhos (13.11 mg, 0.032 mmol) and K_2CO_3 (441 mg, 3.19 mmol). The reaction was left stirring at 80 °C for 3 hours before cooling and extraction of the reaction mixture with EtOAc (3 × 25 mL). The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 5:1, R_f = 0.48) to obtain compound **12** as a yellow solid (314.3 mg, 0.653 mmol, 82%), mp. 91-92 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.21 (s, 1H), 7.88-7.83 (m, 1H), 7.76-7.60 (m, 6H), 7.53-7.48 (m, 1H), 7.46-7.40 (m, 3H), 7.34-7.29 (m, 1H), 7.12-7.07 (m, 2H), 3.92 (t, *J* = 6.9 Hz, 2H), 1.76-1.66 (m, 2H), 1.45-1.36 (m, 2H), 1.30-1.21 (m, 4H), 0.86-0.79 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 187.2 (d, *J* = 4.7 Hz), 163.9 (d, *J* = 256.6 Hz), 147.0 (d, *J* = 9.2 Hz), 145.3, 143.2, 138.8, 134.7, 131.3, 129.8 (d, *J* = 2.2 Hz), 128.9 (2C), 127.1, 126.6, 126.0 (2C), 125.9, 125.5, 125.0, 123.8, 123.4, 122.2 (d, *J* = 2.5 Hz), 122.0 (d, *J* = 8.6 Hz), 116.1 (d, *J* = 26.2 Hz), 113.6, 113.4, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2949 (w), 2926 (w), 2848 (w), 1686 (m), 1614 (m), 1462 (m), 1252 (s), 820 (m), 763 (s), 690 (m); HRMS (ASAP+, *m/z*): 481.1870 (calcd. $C_{31}H_{28}NOFS$ 481.1876, $[M]^+$).

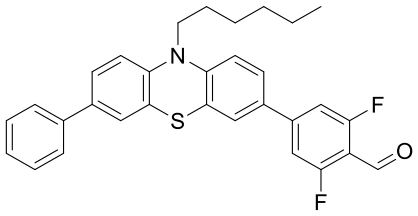
Synthesis of 2-fluoro-4-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)benzaldehyde (**13**)



The synthesis was done in accordance with the general procedure starting with compound **9** (500 mg, 1.07 mmol), (3-fluoro-4-formylphenyl)boronic acid (269 mg, 1.60 mmol), $Pd(OAc)_2$ (4.79 mg, 0.021 mmol), SPhos (17.5 mg, 0.043 mmol) and K_2CO_3 (590 mg, 4.27 mmol). The reaction was left stirring at 80 °C for 16 hours before cooling and extraction of the reaction mixture with EtOAc (3 × 35 mL). The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 4:1, R_f = 0.43) to obtain compound **13** as a red solid (422 mg, 0.865 mmol, 81%), mp. 71-73 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.21 (s, 1H), 7.88-7.83 (m, 1H), 7.76-7.64

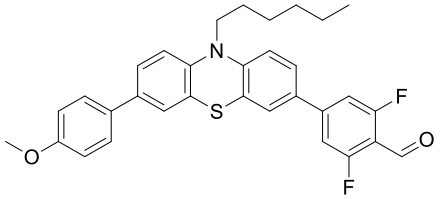
(m, 3H), 7.63-7.62 (m, 1H), 7.58-7.54 (m, 2H), 7.46-7.42 (m, 1H), 7.40-7.38 (m, 1H), 7.11-7.04 (m, 2H), 7.00-6.96 (m, 2H), 3.92 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 1.75-1.66 (m, 2H), 1.45-1.36 (m, 2H), 1.30-1.21 (m, 4H), 0.86-0.80 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 187.2 (d, *J* = 4.2 Hz), 163.9 (d, *J* = 256.4 Hz), 158.7, 147.0 (d, *J* = 9.0 Hz), 145.4, 142.5, 134.5, 131.2 (d, *J* = 3.6 Hz), 129.8 (d, *J* = 2.2 Hz), 127.2 (2C), 126.6, 125.4 (d, *J* = 10.3 Hz), 124.5, 123.8, 123.3, 122.2 (d, *J* = 3.0 Hz), 122.0, 121.9, 116.2, 115.8, 114.3 (2C), 113.6, 113.3, 55.1, 46.6, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 3029 (w), 2925 (m), 2847 (m), 2847 (m), 1688 (s), 1610 (s), 1465 (s), 1382 (m), 1242 (s), 1174 (s), 1117 (m), 1029 (m), 805 (s); HRMS (ASAP+, *m/z*): 511.1982 (calcd. $C_{32}H_{30}NO_2FS$ 511.1981, $[M]^+$).

Synthesis of 2,6-difluoro-4-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)benzaldehyde (**14**)



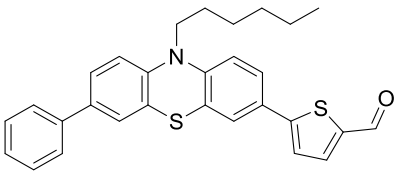
The synthesis was done in accordance with the general procedure starting with compound **8** (350 mg, 0.798 mmol), (3,5-difluoro-4-formylphenyl)boronic acid (223 mg, 1.20 mmol), $Pd(OAc)_2$ (3.58 mg, 0.016 mmol), SPhos (13.11 mg, 0.032 mmol) and K_2CO_3 (441 mg, 3.19 mmol). The reaction was left stirring at 80 °C for 2.5 hours before cooling and extraction of the reaction mixture with EtOAc (3 × 25 mL). The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 5:1, R_f = 0.51) to obtain compound **14** as a red solid (318 mg, 0.636 mmol, 80%), mp. 69-71 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.19 (s, 1H), 7.73-7.67 (m, 2H), 7.66-7.61 (m, 4H), 7.53-7.49 (m, 1H), 7.46-7.40 (m, 3H), 7.34-7.30 (m, 1H), 7.12-7.07 (m, 2H), 3.93 (t, *J* = 6.9 Hz, 2H), 1.75-1.67 (m, 2H), 1.45-1.36 (m, 2H), 1.30-1.22 (m, 4H), 0.86-0.80 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 184.3, 162.7 (dd, *J* = 258.3 Hz, 7.6 Hz, 2C), 147.2 (t, *J* = 11.5 Hz), 145.8, 143.0, 138.7, 134.8, 130.1, 128.9 (2C), 127.1, 126.7, 126.0, 126.0 (2C), 125.6, 125.0, 123.8, 123.3, 116.3, 115.8, 111.7 (t, *J* = 11.6 Hz), 109.5 (d, *J* = 24.5 Hz, 2C), 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2956 (w), 2925 (w), 2857 (w), 1694 (m), 1624 (s), 1460 (s), 1245 (m), 1195 (s), 1037 (m), 809 (m), 759 (s), 696 (m); HRMS (ASAP+, *m/z*): 499.1776 (calcd. $C_{31}H_{27}NOF_2S$ 499.1781, $[M]^+$)

Synthesis of 2,6-difluoro-4-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)benzaldehyde (**15**)



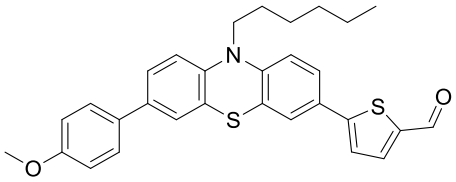
The synthesis was done in accordance with the general procedure starting with compound **9** (500 mg, 1.10 mmol), (3,5-diflouro-4-formylphenyl)boronic acid (300 mg, 1.60 mmol), $Pd(OAc)_2$ (6 mg, 0.02 mmol), SPhos (19 mg, 0.05 mmol) and K_2CO_3 (610 mg, 4.40 mmol). Full conversion was obtained after 1 hour. The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 14:1, R_f = 0.27) to obtain compound **15** as a red oil (440 mg, 0.84 mmol, 76%); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.20 (s, 1H), 7.74-7.70 (m, 1H), 7.69-7.68 (m, 1H), 7.66-7.63 (m, 2H), 7.58-7.56 (m, 2H), 7.46-7.44 (m, 1H), 7.40-7.39 (m, 1H), 7.10-7.09 (m, 1H), 7.08-7.06 (m, 1H), 7.00-6.98 (m, 2H), 3.95-3.91 (m, 2H), 3.78 (s, 3H), 1.75-1.67 (m, 2H), 1.43-1.37 (m, 2H), 1.29-1.23 (m, 4H), 0.85-0.84 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 189.0, 184.3 (d, *J* = 4.1 Hz), 163.0 (d, *J* = 278.0 Hz), 158.7, 147.2 (d, *J* = 3.7 Hz), 145.9, 142.4, 134.6, 131.4 (d, *J* = 1.5 Hz), 131.2, 127.2 (2C), 126.7, 125.6, 125.4, 124.5, 123.8, 123.2, 116.3 (2C), 115.8 (d, *J* = 48.1 Hz), 114.3 (2C), 109.5 (d, *J* = 23.6 Hz, 2C), 55.1, 46.6, 30.8, 26.1, 25.8, 20.8, 13.8; IR (neat, cm^{-1}) ν: 2951 (w), 2879 (w), 2847 (w), 2774 (w), 1699 (s), 1625 (s), 1460 (s), 1242 (s), 1029 (s), 816 (s); HRMS (ASAP+, *m/z*): 529.1888 (calcd. $C_{32}H_{29}F_2NO_2S$: 529.1887, $[M]^+$).

Synthesis of 5-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (**16**)



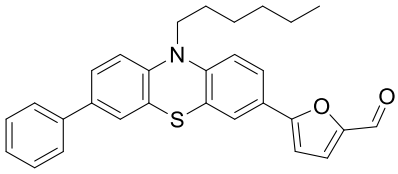
Compound **8** (390 mg, 0.890 mmol) was mixed with dichlorobis(acetonitrile)palladium (II) (4.62 mg, 0.018 mmol) and SPhos (29.2 mg, 0.071 mmol). Dry 1,4-dioxane (0.7 mL) and triethylamine (0.5 mL) were added under N_2 atmosphere and pinacol borane (170 mg, 193 µL, 1.335 mmol) was added to the mixture dropwise. The reaction mixture was stirred 80 °C for 1 hour before cooling, filtration through a Celite plug and removal of solvents in vacuo. This gave a light brown oil. To the crude product, $Pd(OAc)_2$ (3.70 mg, 0.016 mmol), SPhos (13.53 mg, 0.033 mmol) and K_2CO_3 (455.0 mg, 3.30 mmol) was added. Under N_2 atmosphere, degassed 1,4-dioxane (3 mL) and water (3 mL) were added, followed by 5-bromothiophene-2-carbaldehyde (236 mg, 1.24 mmol). The reaction was stirred at 80 °C for 18 hours before cooling and extraction of the reaction mixture with EtOAc (3 × 30 mL). The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 5:1, R_f = 0.33) to obtain compound **16** as a red solid (228 mg, 0.486 mmol, 55%), mp. 66-68 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 8.00 (d, J = 4.0 Hz, 1H), 7.67 (d, J = 4.0 Hz, 1H), 7.65-7.58 (m, 4H), 7.53-7.49 (m, 1H), 7.46-7.40 (m, 3H), 7.35-7.29 (m, 1H), 7.12-7.06 (m, 2H), 3.92 (t, J = 3.9 Hz, 2H), 1.75-1.66 (m, 2H), 1.445-1.36 (m, 2H), 1.29-1.21 (m, 4H), 0.86-0.80 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 183.8, 151.9, 145.4, 143.1, 141.1, 139.4, 138.8, 134.8, 128.9 (2C), 127.2, 126.8, 126.1 (2C), 126.0, 125.9, 125.0, 124.43, 124.38, 124.0, 123.2, 116.3, 116.1, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2956 (w), 2914 (w), 2847 (w), 1656 (s), 1433 (s), 1400 (m), 1223 (s), 1055 (m). 799 (m), 758 (s), 696 (m); HRMS (ASAP+, *m/z*): 469.1530 (calcd. $C_{29}H_{27}NOS_2$ 469.1534, $[M]^+$).

Synthesis of 5-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (**17**)



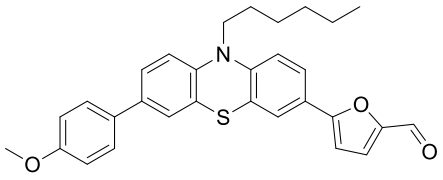
Compound **9** (300 mg, 0.640 mmol) was mixed with dichlorobis(acetonitrile)palladium (II) (3.32 mg, 0.013 mmol) and SPhos (21.03 mg, 0.051 mmol). Dry 1,4-dioxane (0.4 mL) and triethylamine (0.3 mL) were added under N_2 atmosphere. Then pinacol borane (123 mg, 139 µL, 0.961 mmol) was added dropwise. The reaction mixture was stirred 80 °C for 1 hour before cooling, filtration through a Celite plug and removal of solvents in vacuo. This gave a light brown oil. To the crude intermediate product, $Pd(OAc)_2$ (2.61 mg, 0.012 mmol), SPhos (9.56 mg, 0.023 mmol) and K_2CO_3 (322 mg, 2.33 mmol) were added. Under N_2 atmosphere, degassed 1,4-dioxane (2 mL) and water (2 mL) were added, then 5-bromothiophene-2-carbaldehyde (167 mg, 0.873 mmol). The reaction was stirred at 80 °C for 18 hours before cooling and extraction of the reaction mixture with EtOAc (3 × 30 mL). The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 5:1, R_f = 0.31) to obtain compound **17** as a red solid (209 mg, 0.419 mmol, 72%), mp. 70-72 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 7.99 (d, J = 3.9 Hz, 1H), 7.66 (d, J = 3.9 Hz, 1H), 7.61-7.53 (m, 4H), 7.46-7.42 (m, 1H), 7.40-7.38 (m, 1H), 7.08-7.02 (m, 2H), 7.00-6.95 (m, 2H), 3.89 (t, J = 6.9 Hz, 2H), 3.78 (s, 3H), 1.73-1.64 (m, 2H), 1.43-1.34 (m, 2H), 1.27-1.20 (m, 4H), 0.85-0.79 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 183.7, 158.7, 152.0, 145.5, 142.4, 141.1, 139.4, 134.6, 131.2, 127.2 (2C), 126.6, 125.8, 125.4, 124.5, 124.4, 124.3, 123.9, 123.1, 116.2, 115.9, 114.3 (2C), 55.1, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 3033 (w), 2950 (m), 2924 (m), 2852 (m), 1657 (s), 1429 (s), 1226 (s), 1179 (s), 805 (s), 675 (s) HRMS (ASAP+, *m/z*): 499.1637 (calcd. $C_{30}H_{29}NO_2S_2$ 499.1640, $[M+H]^+$).

Synthesis of 5-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)furan-2-carbaldehyde (**18**)



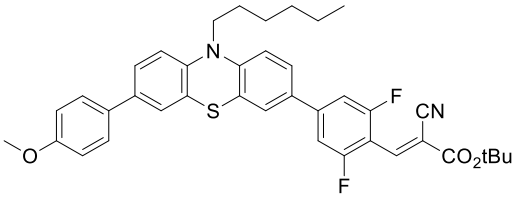
The synthesis was done in accordance with the general procedure starting with compound **8** (298 mg, 0.680 mmol), (5-formylfuran-2-yl)boronic acid (144 mg, 1.02 mmol), $Pd(OAc)_2$ (3.05 mg, 0.014 mmol), SPhos (11.17 mg, 0.027 mmol) and K_2CO_3 (376.0 mg, 2.72 mmol). The reaction was left stirring at 80 °C for 2 hours before cooling and extraction of the reaction mixture with EtOAc (3 × 30 mL). The crude product was purified by silica-gel column chromatography (*n*-pentane:EtOAc, 5:1, R_f = 0.31) to obtain compound **18** as a brown solid (282 mg, 0.621 mmol, 91%), mp. 58-61 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.56 (s, 1H), 7.70-7.66 (m, 1H), 7.65-7.61 (m, 4H), 7.53-7.49 (m, 1H), 7.46-7.40 (m, 3H), 7.35-7.30 (m, 1H), 7.20 (d, *J* = 3.8 Hz, 1H), 7.14-7.09 (m, 2H), 3.93 (t, *J* = 6.9 Hz, 2H), 1.75-.167 (m, 2H), 1.45-1.36 (m, 2H), 1.29-1.21 (m, 4H), 0.85-0.80 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 177.3, 157.7, 151.3, 145.6, 143.0, 138.7, 134.8, 128.9 (2C), 127.2, 126.1 (2C), 126.0, 125.8, 125.0, 124.7, 123.8, 123.5, 123.2, 122.9, 116.4, 116.0, 107.8, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2945 (w), 2909 (w), 2847 (w), 1461 (s), 1251 (m), 1242 (m), 802 (m), 757 (s), 697 (s); HRMS (ASAP+, *m/z*): 453.1760 (calcd. $C_{29}H_{27}NO_2S$ 453.1762, $[M]^+$).

Synthesis of 5-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)furan-2-carbaldehyde (**19**)



The synthesis was done in accordance with the general procedure starting with compound **9** (540 mg, 1.15 mmol), 5-formylfuran-2-boronic acid (240 mg, 1.73 mmol), $Pd(OAc)_2$ (5.8 mg, 0.02 mmol), SPhos (19.8 mg, 0.05 mmol) and K_2CO_3 (640 mg, 4.60 mmol). Full conversion was obtained after 1 hour. The crude product was purified by silica-gel column chromatography (gradient: 10-33% EtOAc in *n*-pentane) to obtain compound **19** as a red oil (300 mg, 0.62 mmol, 54%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.56 (s, 1H), 7.69-7.68 (m, 1H), 7.65-7.64 (m, 1H), 7.63-7.62 (m, 1H), 7.58-7.57 (m, 2H), 7.47-7.45 (m, 1H), 7.41-7.40 (m, 1H), 7.21-7.20 (m, 1H), 7.14-7.12 (m, 1H), 7.10-7.08 (m, 1H), 7.00-6.98 (m, 2H), 4.03-4.02 (m, 2H), 3.78 (s, 3H), 1.74-1.69 (m, 2H), 1.44-1.39 (m, 2H), 1.28-1.26 (m, 4H), 0.85-0.84 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 177.3, 158.7, 157.8, 151.3, 145.7, 142.4, 134.7, 131.1, 127.2 (2C), 125.5, 124.7, 124.5, 123.8, 123.5, 123.2, 122.8, 122.6, 116.3, 116.0, 114.3 (2C), 107.8, 55.1, 46.7, 30.8, 26.1, 25.7, 22.0, 13.8; IR (neat, cm^{-1}) ν: 3122 (w), 2925 (w), 2857 (w), 1662 (s), 1600 (m), 1460 (s), 1402 (m), 1237 (s), 1179 (m), 1018 (s), 790 (s); HRMS (ASAP+, *m/z*): 483.1862 (calcd. $C_{30}H_{29}NO_3S$: 483.1868, $[M]^+$).

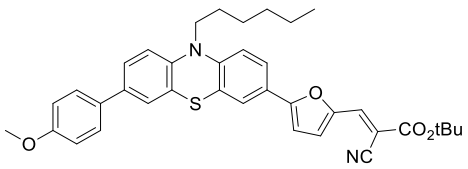
Synthesis of *tert*-butyl *(E)*-2-cyano-3-(2,6-difluoro-4-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)phenyl)acrylate (**20**)



Compound **15** (410 mg, 0.80 mmol) and ammonium acetate (240 mg, 3.10 mmol) were mixed before acetic acid (4.5 mL) and *tert*-butyl 2-cyanoacetate (0.44 mL, 3.10 mmol) were added under N_2 atmosphere. The reaction mixture was heated to 75 °C and left stirring for 1 hour. Water (30 mL) was added to the solution and the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. Purification by silica-gel column chromatography (*n*-pentane:EtOAc, 14:1, R_f = 0.24) gave compound **20** as a dark red oil (450 mg, 0.69 mmol, 89%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.19 (s, 1H), 7.73-7.68 (m, 4H), 7.58-7.56 (m, 2H), 7.46-7.44 (m, 1H), 7.41-7.40 (m, 1H), 7.09-7.07 (m, 2H), 7.00-6.98 (m, 2H), 3.95-3.90 (m, 2H), 3.78 (s, 3H), 1.75-1.68 (m, 2H), 1.43 (s, 9H), 1.41-1.37 (m, 2H), 1.29-1.24 (m, 4H), 0.85-0.82 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.3, 159.8 (2C), 158.7, 145.7, 145.3 (d, *J* = 2.0 Hz), 142.42, 142.37, 134.5, 131.2, 130.3, 127.2 (2C), 125.4, 124.5, 123.8, 123.3, 116.4, 115.5 (d, *J* = 55.8 Hz), 114.3 (2C), 111.5, 109.4

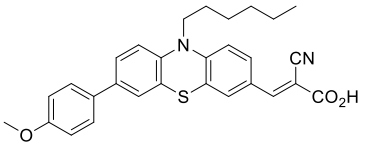
(d, *J* = 24.4 Hz, 2C), 84.0, 82.7, 55.1, 46.7, 30.8, 27.5 (3C), 27.4, 26.1, 25.8, 22.0, 13.8 (2 shifts missing); IR (neat, cm^{-1}) ν: 3065 (w), 2925 (w), 2852 (w), 1740 (s), 1719 (s), 1470 (s), 1273 (s), 1242 (s), 1148 (s), 1023 (s), 816 (s); HRMS (ASAP+, *m/z*): 652.2566 (calcd. $C_{39}H_{38}F_2N_2O_3S$: 652.2571, $[M]^+$).

Synthesis of compound *tert*-butyl *(E)*-2-cyano-3-(5-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)furan-2-yl)acrylate (**21**)



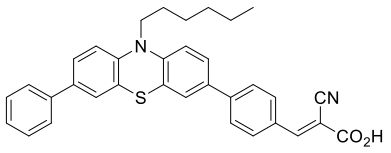
Compound **19** (170 mg, 0.40 mmol) and ammonium acetate (110 mg, 1.40 mmol) were mixed before acetic acid (2.0 mL) and *tert*-butyl 2-cyanoacetate (0.20 mL, 1.40 mmol) were added under N_2 atmosphere. The reaction mixture was heated to 75 °C and left stirring for 1 hour. Water (30 mL) was added to the solution and the aqueous phase was extracted with EtOAc (3 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. Purification by silica-gel column chromatography (*n*-pentane: EtOAc, 19:1, R_f = 0.49) gave compound **21** as a dark red oil (120 mg, 0.198 mmol, 55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.99 (s, 1H), 7.75-7.74 (m, 1H), 7.71-7.70 (m, 1H), 7.59-7.57 (m, 2H), 7.56-7.55 (m, 1H), 7.47-7.45 (m, 1H), 7.42-7.41 (m, 1H), 7.31-7.30 (m, 1H), 7.17-7.15 (m, 1H), 7.10-7.09 (m, 1H), 7.00-6.98 (m, 2H), 3.96-3.90 (m, 2H), 3.78 (s, 3H), 1.74-1.69 (m, 2H), 1.43 (s, 9H), 1.43-1.41 (m, 2H), 1.27-1.25 (m, 4H), 0.85-0.82 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.3, 158.6, 158.5, 147.1, 144.8, 143.2, 137.2, 134.0, 130.7, 127.4 (2C), 127.2, 125.1, 124.8, 124.6, 123.2, 123.0, 122.62, 122.61, 116.43, 116.42, 116.1, 114.7 (2C), 109.4, 95.0, 83.6, 55.1, 46.6, 30.8, 27.6 (3C), 26.1, 25.7, 22.0, 13.8; IR (neat, cm^{-1}) ν: 3138 (w), 2977 (w), 2930 (w), 2870 (w), 2262 (w), 2218 (w), 1740 (s), 1714 (s), 1610 (s), 1583 (s), 1456 (s), 1236 (s), 1152 (s), 1028 (s), 798 (s), 587 (m); HRMS (ASAP+, *m/z*): 606.2548 (calcd. $C_{37}H_{38}N_2O_4S$: 606.2552, $[M]^+$).

Synthesis of *(E)*-2-cyano-3-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)acrylic acid (**AFB-1**)



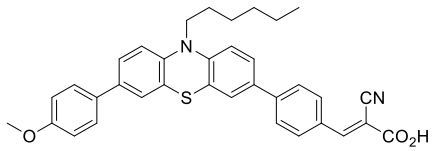
Compound **5** (200 mg, 0.479 mmol) and cyanoacetic acid (815 mg, 9.58 mmol) were dissolved in degassed acetonitrile (55 mL) under N_2-atmosphere. Piperidine (569 µL, 489 mg, 5.75 mmol) was added and the reaction was heated to 80 °C for 40 minutes before cooling to 22 °C and quenched in aqueous HCl (2 M, 150 mL). EtOAc (50 mL) was added and the organic phase was washed with water (8 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-1** as a dark solid (215 mg, 0.444 mmol, 93%), mp. 204-208 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.72 (s, 1H), 8.15 (s, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.82 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.39 (s, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 1.74-1.64 (m, 2H), 1.45-1.35 (m, 2H), 1.31-1.20 (m, 4H), 0.82 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.8, 158.8, 152.5, 148.6, 141.1, 135.3, 131.7, 130.9, 129.1, 127.2 (2C), 125.5, 125.4, 124.6, 122.7, 122.5, 116.8, 116.7, 115.5, 114.3 (2C), 99.4, 55.1, 47.0, 30.8, 26.0, 25.7, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2909 (w), 1683 (m), 1558 (m), 1470 (s), 1184 (s), 826 (m); HRMS (ASAP+, *m/z*): 484.1815 (calcd. $C_{29}H_{28}N_2O_3S$: 484.1821 $[M]^+$); UV (CH_2Cl_2, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 305.5 (26200), 475.0 (14000)

Synthesis of *(E)*-2-cyano-3-(4-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)phenyl)acrylic acid (**AFB-2**)



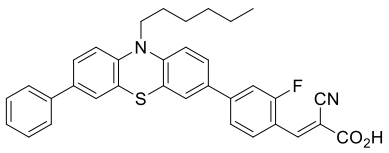
Compound **10** (294 mg, 0.634 mmol) and cyanoacetic acid (1.079 g, 12.7 mmol) were dissolved in degassed acetonitrile (60 mL) under N_2-atmosphere. Piperidine (753 µL, 648.0 mg, 7.61 mmol) was added and the reaction was heated to 80 °C for 45 minutes before cooling 22 °C and quenched in aqueous HCl (2 M, 150 mL). EtOAc (50 mL) was added and the organic phase was washed with water (8 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-2** as a dark brown solid (164 mg, 0.308 mmol, 49%), mp. 246 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.05 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.65-7.61 (m, 2H), 7.59 (dd, *J* = 8.5 Hz, 2.1, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.50 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.46 (d, *J* = 2.3 Hz, 1H), 7.44-7.40 (m, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.09 (dd, *J* = 8.7, 2.1 Hz, 2H), 3.92 (t, *J* = 6.9 Hz, 2H), 1.74-1.68 (m, 2H), 1.44-1.38 (m, 2H), 1.28-1.23 (m, 4H), 0.85-0.81 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.4, 147.9, 144.4, 143.5, 141.2, 138.8, 134.5, 132.9, 131.6, 130.2 (2C), 128.9 (2C), 127.1, 126.3 (2C), 126.1, 126.0 (2C), 125.9, 125.1, 125.0, 123.7, 123.5, 118.9, 116.1, 116.0, 111.4, 46.6, 30.8, 26.2, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2961 (w), 2925 (w), 2852 (w), 2218 (w), 1600 (m), 1579 (m), 1464 (m), 1393 (m), 1247 (m), 1189 (m), 808 (m), 758 (s), 696 (m); HRMS (ASAP+, *m/z*): 486.2127 (calcd. $C_{33}H_{30}N_2S$: 486.2130, $[M\text{-}CO_2+H]^+$); UV (CH_2Cl_2, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 425.0 (11350)

Synthesis of *(E)*-2-cyano-3-(4-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)phenyl)acrylic acid (**AFB-3**)



Compound **11** (190 mg, 0.385 mmol) and cyanoacetic acid (655 mg, 7.70 mmol) were dissolved in degassed acetonitrile (46 mL) under N_2 atmosphere. Piperidine (457 µL, 393 mg, 4.62 mmol) was added and the reaction was heated to 80 °C for 15 minutes before cooling to 22 °C and quenched in aqueous HCl (2 M, 100 mL). EtOAc (50 mL) was added and the organic phase was washed with water (8 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-3** as a dark brown solid (186 mg, 0.331 mmol, 86%), mp. 237 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.03 (s, 1H), 7.97-7.93 (m, 2H), 7.80-7.76 (m, 2H), 7.60-7.53 (m, 4H), 7.46-7.42 (m, 1H), 7.41-7.39 (m, 1H), 7.10-7.03 (m, 2H), 7.00-6.96 (m, 2H), 3.91 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 1.76-1.66 (m, 2H), 1.45-1.36 (m, 2H), 1.29-1.21 (m, 4H), 0.86-0.80 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.2, 158.7, 147.9, 144.5, 142.8, 141.2, 134.3, 132.8, 131.6, 131.3, 130.2 (2C), 127.2 (2C), 126.3 (2C), 126.1, 125.3, 125.0, 124.5, 123.8, 123.5, 119.0, 116.1, 116.0, 114.3 (2C), 111.0, 55.2, 46.6, 30.9, 26.2, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 3033 (w, br), 2925 (w), 2847 (w), 2223 (w), 1719 (m), 1693 (m), 1574 (s, br), 1460 (s), 1242 (s), 1179 (s), 1242 (s), 1179 (s), 1023 (m), 805 (s); HRMS (ASAP+, *m/z*): 516.2228 (calcd. $C_{34}H_{32}N_2OS$: 516.2235 $[M\text{-}CO_2]^+$); UV (CH_2Cl_2, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 429.5 (12700).

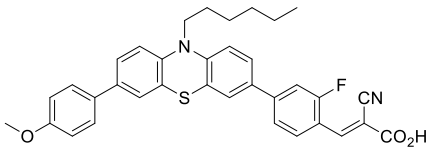
Synthesis of *(E)*-2-cyano-3-(2-fluoro-4-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)phenyl)acrylic acid (**AFB-4**)



Compound **12** (205 mg, 0.425 mmol) and cyanoacetic acid (722 mg, 8.49 mmol) were dissolved in degassed acetonitrile (50 mL) under N_2 atmosphere. Piperidine (504 µL, 434 mg, 5.10 mmol) was added and the reaction was heated to 80 °C for 25 minutes before cooling to 22 °C and quenched in aqueous HCl (2 M, 100 mL). EtOAc (50 mL) was added and the organic phase was washed with water (6 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The

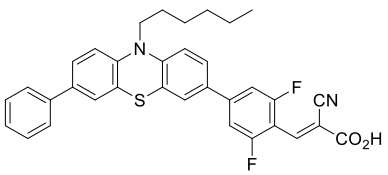
crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-4** as a dark red solid (200 mg, 0.365 mmol, 86%), mp. 214 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.19 (t, *J* = 8.2 Hz, 1H), 8.14 (s, 1H), 7.70-7.57 (m, 6H), 7.53-7.48 (m, 1H), 7.47-7.39 (m, 3H), 7.35-7.29 (m, 1H), 7.12-7.05 (m, 2H), 3.92 (t, *J* = 6.9 Hz, 2H), 1.76-1.66 (m, 2H), 1.45-1.36 (m, 2H), 1.29-1.21 (m, 4H), 0.86-0.80 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.4, 160.9 (d, *J* = 251 Hz), 144.9, 143.5 (d, *J* = 10.7 Hz), 143.35, 138.8, 134.6, 131.8 (d, *J* = 3.8 Hz), 131.7, 130.2, 128.9 (2C), 128.6 (d, *J* = 2.0 Hz), 127.1, 126.2, 126.1 (2C), 125.9, 125.2, 125.0, 123.7, 123.4, 122.1 (d, *J* = 2.1 Hz), 119.3 (d, *J* = 12.0 Hz), 118.5, 116.0 (d, *J* = 21.3 Hz), 113.0, 112.7, 46.6, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2951 (w), 2935 (w), 2862 (w), 2218 (w), 1579 (m), 1465 (s), 1393 (m), 1257 (m), 808 (m), 758 (s), 696 (m); HRMS (ASAP+, *m/z*): 504.2035 (calcd. $C_{33}H_{29}FN_2S$: 505.2035, $[M\text{-}CO_2]^+$); UV (CH_2Cl_2, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 431.5 (12950).

Synthesis of *(E)*-2-cyano-3-(2-fluoro-4-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)phenyl)acrylic acid (**AFB-5**)



Compound **13** (186 mg, 0.364 mmol) and cyanoacetic acid (618 mg, 7.27 mmol) were dissolved in degassed acetonitrile (44 mL) under N_2 atmosphere. Piperidine (432 µL, 371 mg, 4.36 mmol) was added and the reaction was heated to 80 °C for 20 minutes before cooling to 22 °C and quenched in aqueous HCl (2 M, 125 mL). EtOAc (50 mL) was added and the organic phase was washed with water (8 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-5** as a dark red solid (121 mg, 0.209 mmol, 58%), mp. 220 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.18 (t, *J* = 8.0 Hz, 1H), 8.12 (s, 1H), 7.70-7.65 (m, 2H), 7.63 (dd, *J* = 8.5 Hz, 2.2, 1H), 7.60-7.55 (m, 3H), 7.45 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.40 (d, *J* = 2.2 Hz, 1H), 7.07 (t, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.91 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 1.75-1.67 (m, 2H), 1.45-1.36 (m, 2H), 1.30-1.21 (m, 4H), 0.86-0.81 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.4, 160.8 (d, *J* = 251.1 Hz), 158.7, 145.0, 143.4 (d, *J* = 9.6 Hz), 142.7, 138.3, 134.4, 131.6, 131.2, 128.5, 127.2 (2C), 126.2, 125.4, 125.1, 124.5, 123.7, 123.4, 122.1 (d, *J* = 2.3 Hz), 119.4 (d, *J* = 11.5 Hz), 118.7, 116.1, 115.8, 114.3 (2C), 112.9, 112.8, 55.2, 46.6, 30.8, 26.2, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 3034 (w, br), 2925 (w), 2847 (w), 2223 (w), 1719 (m), 1693 (m), 1574 (s, br), 1460 (s), 1242 (s), 1179 (s), 1023 (m), 805 (s); HRMS (ASAP+, *m/z*): 534.2139 (calcd. $C_{34}H_{31}N_2OFS$: 534.2141 $[M\text{-}CO_2]^+$); UV (CH_2Cl_2, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 440.5 (12050).

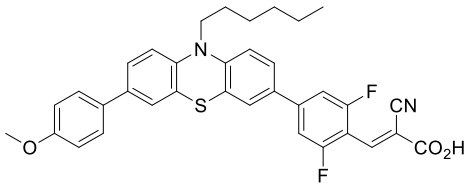
Synthesis of *(E)*-2-cyano-3-(2,6-difluoro-4-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)phenyl)acrylic acid (**AFB-6**)



Compound **14** (228 mg, 0.457 mmol) and cyanoacetic acid (777 mg, 9.13 mmol) were dissolved in degassed acetonitrile (55 mL) under N_2 atmosphere. Piperidine (542 µL, 466 mg, 5.48 mmol) was added and the reaction was heated to 80 °C for 40 minutes before cooling to 22 °C and quenched in aqueous HCl (2 M, 150 mL). EtOAc (50 mL) was added and the organic phase was washed with water (8 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-6** as a red solid (181 mg, 0.319 mmol, 70%), mp. 210 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.85 (s, 1H), 7.68-7.56 (m, 6H), 7.51 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.46 (d, *J* = 2.2 Hz, 1H), 7.45-7.40 (m, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.11-7.06 (m, 2H), 3.92 (t, *J* = 6.8 Hz, 2H), 1.75-1.67 (m, 2H), 1.45-1.36 (m, 2H), 1.29-1.22 (m, 4H), 0.85-0.80 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.7, 159.9 (dd, *J* = 251.6, 8.1 Hz, 2C), 145.1, 143.2, 143.0, 138.8, 135.5, 134.6, 130.8,

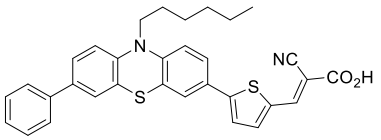
128.9 (2C), 127.1, 126.3, 126.0 (2C), 125.9, 125.2, 125.0, 123.7, 123.4, 121.5, 117.2, 116.1, 115.8, 109.7, 109.1 (d, *J* = 25.1 Hz, 2C), 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2956 (w), 2925 (w), 2847 (w), 2229 (w), 1627 (m), 1463 (m), 1392 (m), 1197 (m), 1024 (m), 808 (m), 758 (s), 696 (m); HRMS (ASAP+, *m/z*): 522.1937 (calcd. $C_{33}H_{28}N_2F_2S$: 522.1941 $[M\text{-}CO_2]^+$); UV (CH_2Cl_2, 2×10^{-5} M, 22 °C) λ_{max} (nm): 419.5 (10650).

Synthesis of *(E)*-2-cyano-3-(2,6-difluoro-4-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)phenyl)acrylic acid (**AFB-7**)



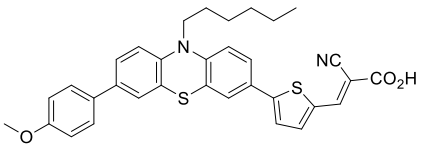
Compound **20** (300 mg, 0.45 mmol) was stirred in TFA (28 mL) for 1 hour, then the reaction mixture was poured into water (40 mL) and the precipitate that formed was filtered off. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-7** as a dark red solid (190 mg, 0.30 mmol, 76%), mp. 115-120 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.86 (s, 1H), 7.65-7.55 (m, 6H), 7.44 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.90 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 1.73-1.67 (m, 2H), 1.43-1.37 (m, 2H), 1.28-1.22 (m, 4H), 0.85-0.80 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.2, 160.1 (d, *J* = 268.3 Hz, 2C), 158.8, 147.5 (d, *J* = 3.1 Hz), 145.6, 142.5, 140.0, 134.5, 131.2, 130.1, 127.2 (2C), 126.4, 125.4, 125.3, 124.5, 123.8, 123.3, 117.4, 116.2, 116.0 (d, *J* = 41.6 Hz), 115.8, 114.3 (2C), 109.1 (d, *J* = 24.9 Hz, 2C), 98.0, 55.1, 46.6, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2966 (w, br), 2925 (w), 2857 (w), 1703 (m, br), 1631 (s, br), 1465 (s), 1195 (s), 1018 (s), 805 (s); HRMS (ASAP+, *m/z*): 552.2045 (calcd. $C_{34}H_{30}F_2N_2OS$: 552.2047 $[M\text{-}CO_2]^+$); UV (CH_2Cl_2, 2×10^{-5} M, 22 °C) λ_{max} (nm): 424.0 (9650).

Synthesis of *(E)*-2-cyano-3-(5-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (**AFB-8**)



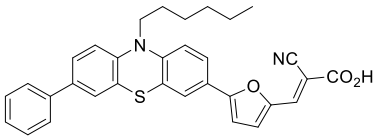
Compound **16** (222 mg, 0.472 mmol) and cyanoacetic acid (803 mg, 9.44 mmol) were dissolved in degassed acetonitrile (55 mL) under N_2 atmosphere. Piperidine (561 µL, 482 mg, 5.66 mmol) was added and the reaction was heated to 80 °C for 30 minutes before cooling to 22 °C and quenched in aqueous HCl (2 M, 150 mL). EtOAc (50 mL) was added and the organic phase was washed with water (8 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-8** as a dark solid (224 mg, 0.417 mmol, 88%), mp. 209 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.18 (s, 1H), 7.68 (d, *J* = 4.1 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 3.8 Hz, 1H), 7.54-7.49 (m, 3H), 7.46-7.40 (m, 3H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 3.91 (t, *J* = 6.9 Hz, 2H), 1.73-1.67 (m, 2H), 1.43-1.37 (m, 2H), 1.28-1.22 (m, 4H), 0.84-0.80 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.6, 148.6, 144.9, 143.2, 141.9, 138.8, 137.5, 135.1, 134.7, 128.9 (2C), 127.2, 127.1, 126.1 (2C), 126.0, 125.5, 125.0, 124.1, 124.0, 123.9, 123.2, 118.6, 116.2, 116.1, 106.6, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8**;** IR (neat, cm^{-1}) ν: 2956 (w), 2909 (w), 2852 (w), 2213 (w), 1574 (m), 1470 (m), 1389 (s), 1247 (s), 1060 (m), 798 (s), 758 (s), 695 (m); HRMS (ASAP+, *m/z*): 492.1690 (calcd. $C_{31}H_{28}N_2S_2$: 492.1694 $[M\text{-}CO_2]^+$); UV (CH_2Cl_2, 2×10^{-5} M, 22 °C) λ_{max} (nm): 356.5 (19000), 466.5 (18050).

Synthesis of *(E)*-2-cyano-3-(5-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (**AFB-9**)



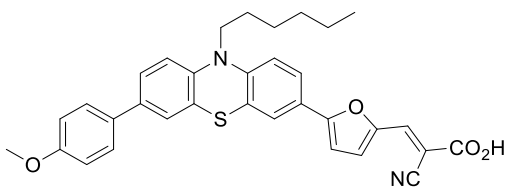
Compound **17** (189 mg, 0.379 mmol) and cyanoacetic acid (644 mg, 7.57 mmol) were dissolved in degassed acetonitrile (45 mL) under N_2 atmosphere. Piperidine (450 µL, 387 mg, 4.54 mmol) was added and the reaction was heated to 80 °C for 30 minutes before cooling to 22 °C and quenched in aqueous HCl (2 M, 150 mL). EtOAc (50 mL) was added and the organic phase was washed with water (8 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-9** as a dark solid (165 mg, 0.290 mmol, 77%), mp. 233 °C (dec.); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.16 (s, 1H), 7.73 (d, *J* = 3.9 Hz, 1H), 7.58 (d, *J* = 4.1 Hz, 1H), 7.57-7.54 (m, 2H), 7.52-7.49 (m, 2H), 7.44 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.39 (d, *J* = 2.2 Hz, 1H), 7.07-7.03 (m, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.89 (t, *J* = 7.0 Hz, 2H), 3.78 (s, 3H), 1.72-1.66 (m, 2H), 1.42-1.36 (m, 2H), 1.28-1.22 (m, 4H), 0.85-0.80 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.7, 158.7, 148.2, 145.0, 142.5, 141.5, 137.1, 135.1, 134.5, 131.2, 127.2 (2C), 127.0, 125.5, 125.4, 124.5, 124.01, 123.98, 123.8, 123.2, 118.8, 116.2, 116.0, 114.3 (2C), 106.6, 55.2, 46.6, 30.8, 26.1, 25.8, 22.1, 13.8**;** IR (neat, cm^{-1}) ν: 2950 (w, br), 2924 (w), 2852 (w), 1709 (m), 1688 (m, br), 1579 (s), 1444 (s), 1408 (s), 1236 (s), 1179 (s), 1060 (m), 800 (s); HRMS (ASAP+, *m/z*): 566.1691 (calcd. $C_{33}H_{30}N_2O_3S_2$: 566.1698 [M]$^+$); UV (CH_2Cl_2, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 360 (16800), 471.0 (15200).

Synthesis of *(E)*-2-cyano-3-(5-(10-hexyl-7-phenyl-10*H*-phenothiazin-3-yl)furan-2-yl)acrylic acid (**AFB-10**)



Compound **18** (264 mg, 0.583 mmol) and cyanoacetic acid (992 mg, 11.7 mmol) were dissolved in degassed acetonitrile (60 mL) under N_2 atmosphere. Piperidine (693 µL, 596 mg, 6.99 mmol) was added and the reaction was heated to 80 °C for 15 minutes before cooling to 22 °C and quenched in aqueous HCl (2 M, 150 mL). EtOAc (50 mL) was added and the organic phase was washed with water (8 × 100 mL), then dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed in vacou. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-10** as a dark solid (149 mg, 0.285 mmol, 49%), mp. 154 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.89 (s, 1H), 7.72 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.51 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 3.5 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 3.94 (t, *J* = 6.9 Hz, 2H), 1.74-1.68 (m, 2H), 1.44-1.38 (m, 2H), 1.28-1.22 (m, 4H), 0.85-0.81 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.0, 156.8, 147.7, 145.2, 143.1, 138.7, 135.3, 134.8, 128.9 (2C), 127.2, 126.1 (2C), 126.0, 125.0, 124.4, 123.7, 123.2, 123.1 (2C), 118.0, 116.3, 116.1, 108.5, 102.0, 46.7, 30.8, 26.1, 25.7, 22.1, 13.8 (1 shift is missing); IR (neat, cm^{-1}) ν: 2955 (w), 2917 (w), 2849 (w), 2215 (w), 1686 (w), 1580 (m), 1454 (s), 1390 (m), 1233 (m), 1023 (m), 791 (m), 759 (s), 695 (m); HRMS (ASAP+, *m/z*): 476.1922 (calcd. $C_{31}H_{28}N_2OS$: 476.1922 [M-CO_2]$^+$); UV (CH_2Cl_2, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 363.0 (14850), 479.5 (19150).

Synthesis of *(E)*-2-cyano-3-(5-(10-hexyl-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)furan-2-yl)acrylic acid (**AFB-11**)



Compound **21** (120 mg, 0.19 mmol) was stirred in TFA (12 mL) for 10 minutes until full conversion was observed. The reaction mixture was poured into water (40 mL) and the precipitate that formed was filtered off. The crude product was purified by silica-gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to obtain **AFB-11** as a black solid (83 mg, 0.15 mmol, 79%), mp. 155-160 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.83 (s, 1H), 7.70 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.66 (d, *J* = 2.1 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.45 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.41 (d, *J* = 2.1 Hz, 1H), 7.27 (d, *J* = 3.6 Hz, 1H), 7.18 (d, *J* = 3.6 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.92 (t, *J* = 6.9 Hz, 2H), 3.78 (s, 3H), 1.75-1.66 (m, 2H), 1.45-1.36 (m, 2H), 1.29-1.21 (m, 4H), 0.85-0.80 (m, 3H) (carboxylic acid proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.0, 158.7, 156.1, 147.9, 145.1, 142.5, 134.6, 131.2, 127.2 (2C), 125.5, 125.4, 124.5, 124.2, 123.7, 123.3, 123.1, 122.9, 118.7, 116.3, 116.0, 114.3 (2C), 113.6, 108.2, 95.4, 55.2, 46.7, 30.8, 26.1, 25.7, 22.1, 13.8; IR (neat, cm^{-1}) ν: 3132 (w, br), 2956 (w), 2919 (w), 2847 (w), 2213 (w), 1683 (s, br), 1579 (s), 1455 (s), 1418 (s), 1236 (s), 1034 (s), 935 (w), 790 (s); HRMS (ASAP+, *m/z*): 506.2024 (calcd. $C_{32}H_{30}N_2O_4S$: 506.2028 $[M\text{-}CO_2]^+$); UV (CH_2Cl_2, 2×10^{-5} M, 22 °C): λ_{max} (nm): 362.5 (14200), 473.0 (14800).

NMR

AFB-1

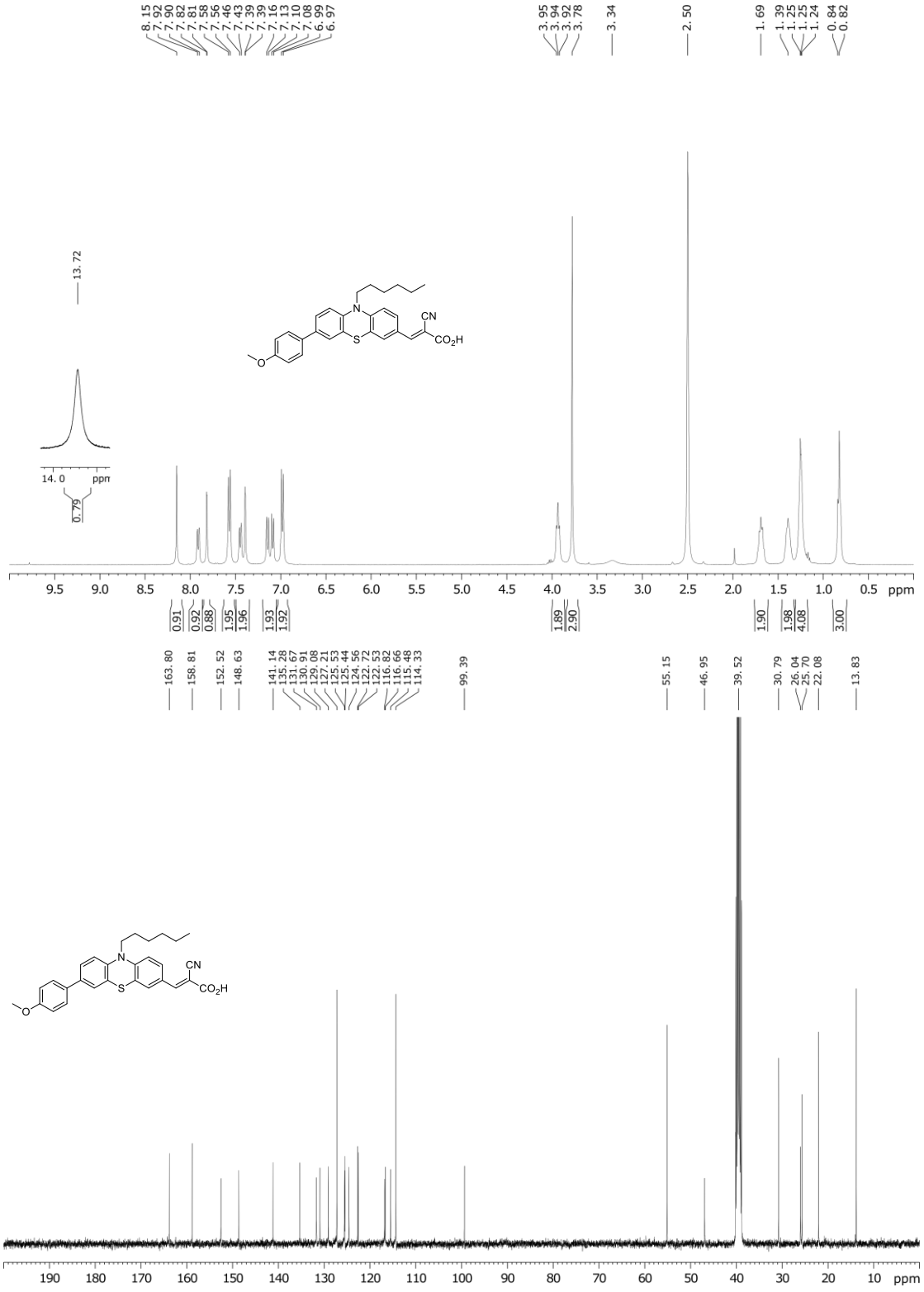


*Fig. S7. ^{1}H and ^{13}C NMR spectra for **AFB-1**.*

AFB-2

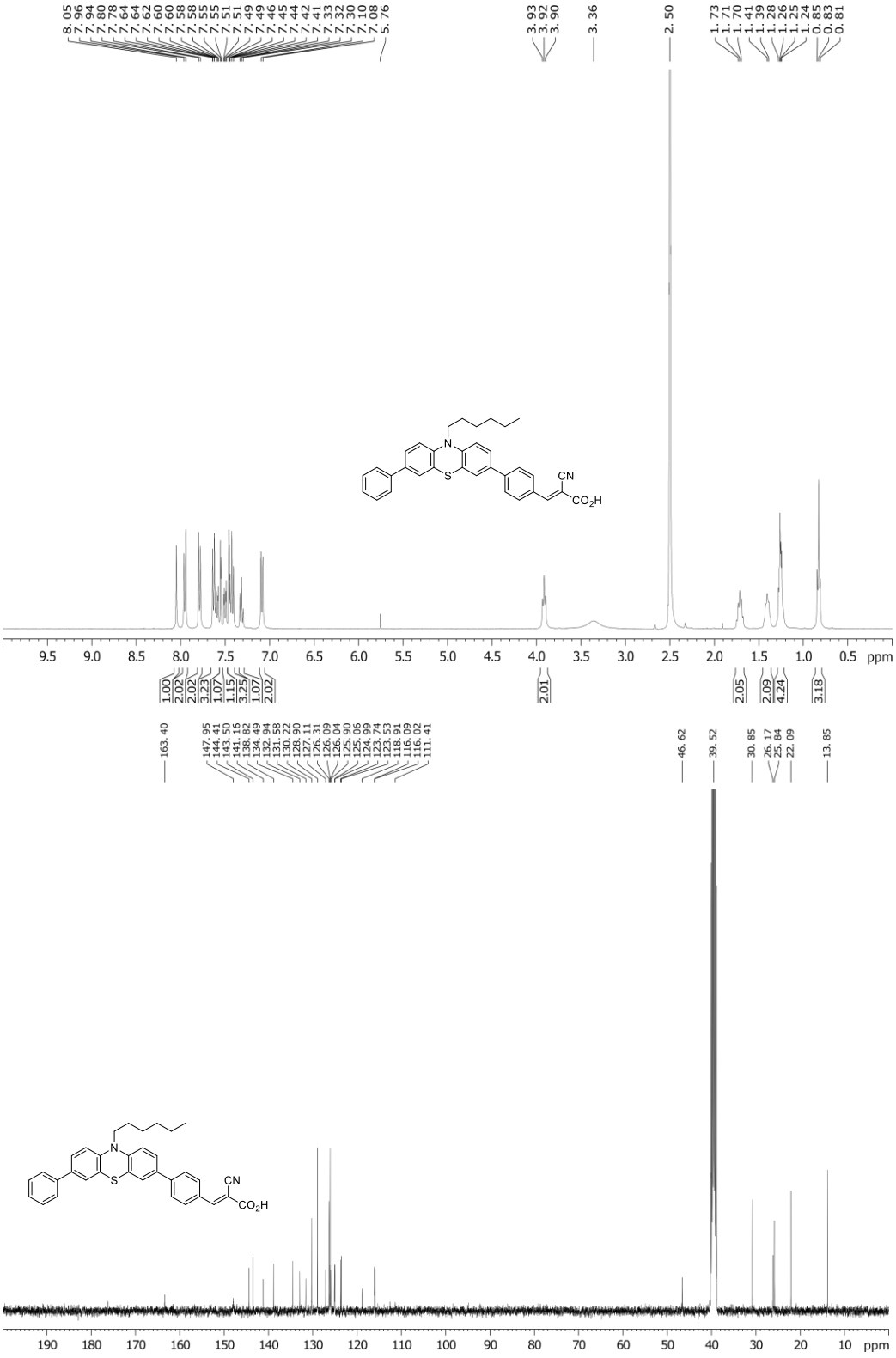


*Fig. S8. ^{1}H and ^{13}C NMR spectra for **AFB-2**.*

AFB-3

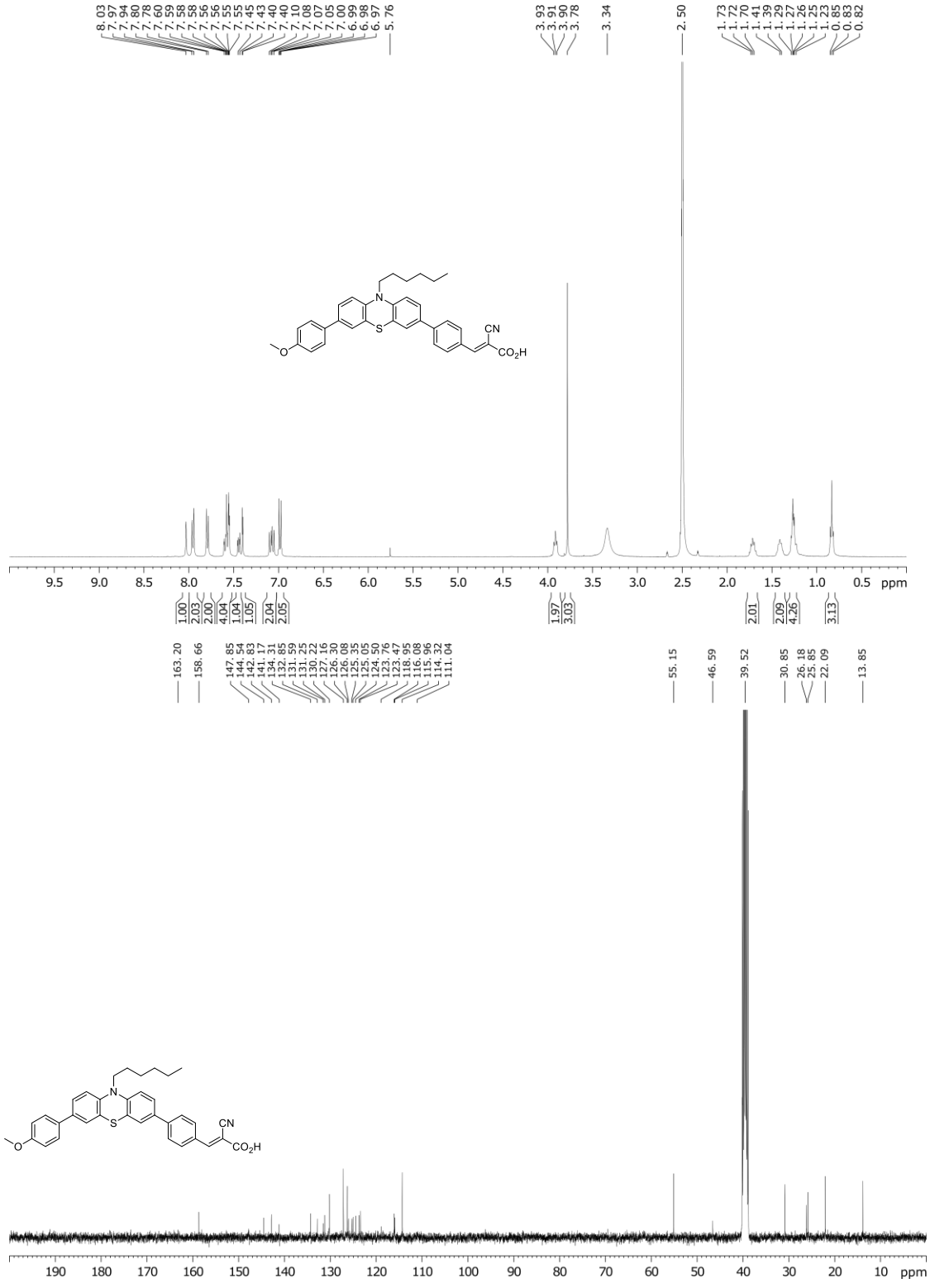


*Fig. S9. ^{1}H and ^{13}C NMR spectra for **AFB-3**.*

AFB-4

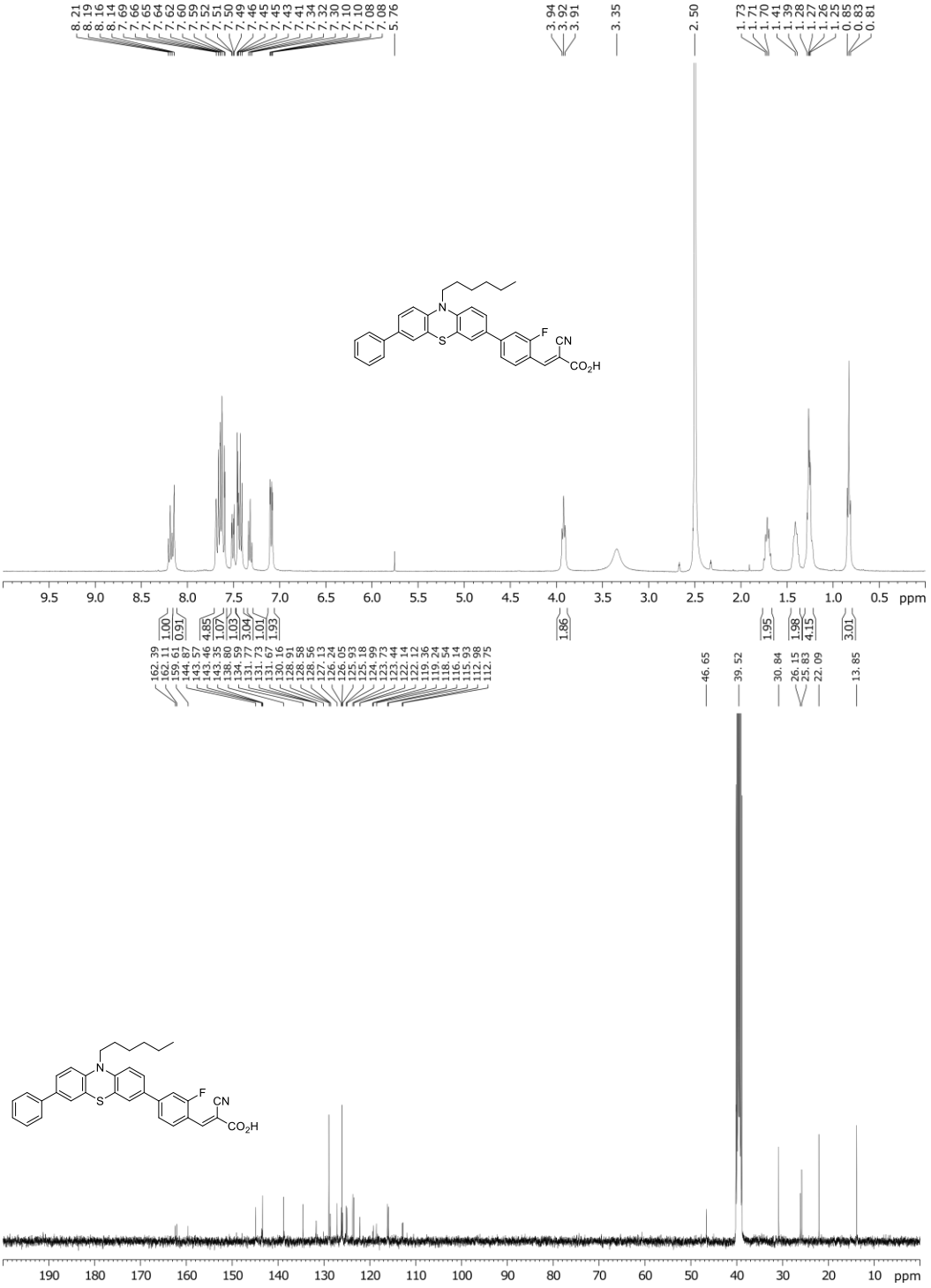


*Fig. S10. ^{1}H and ^{13}C NMR spectra for **AFB-4**.*

AFB-5

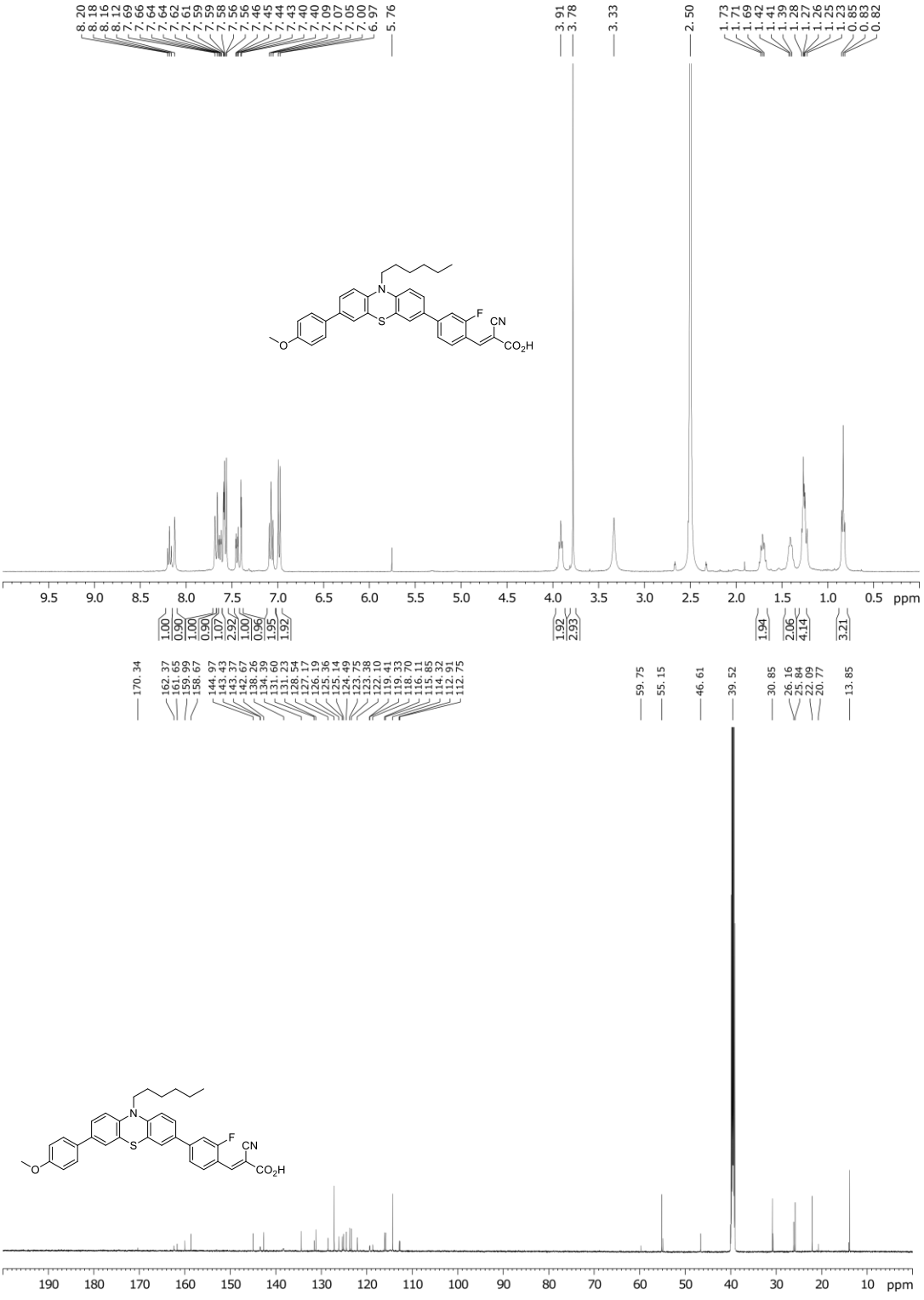


*Fig. S11. ^{1}H and ^{13}C NMR spectra for **AFB-5**.*

AFB-6

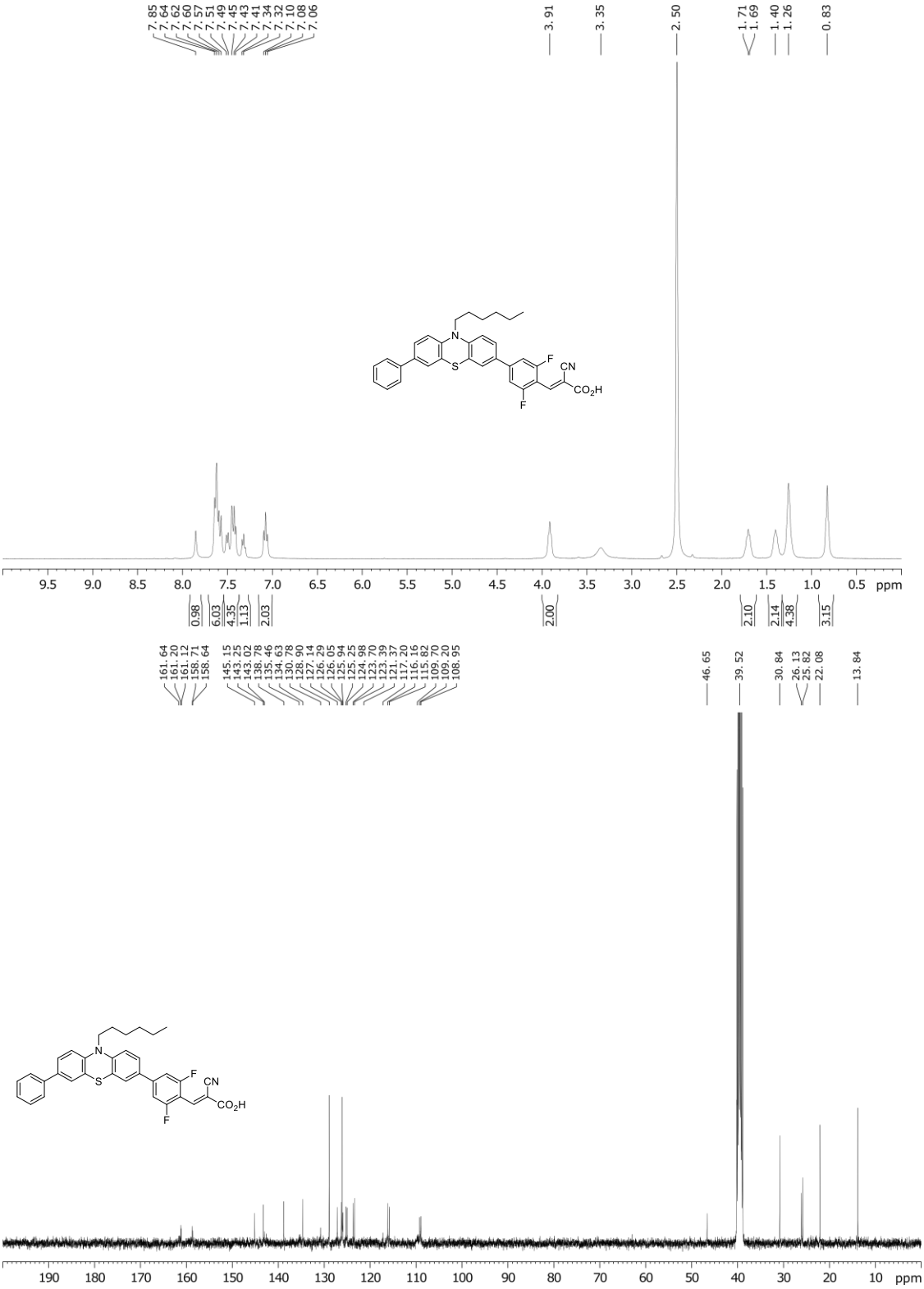


*Fig. S12. ^{1}H and ^{13}C NMR spectra for **AFB-6**.*

AFB-7

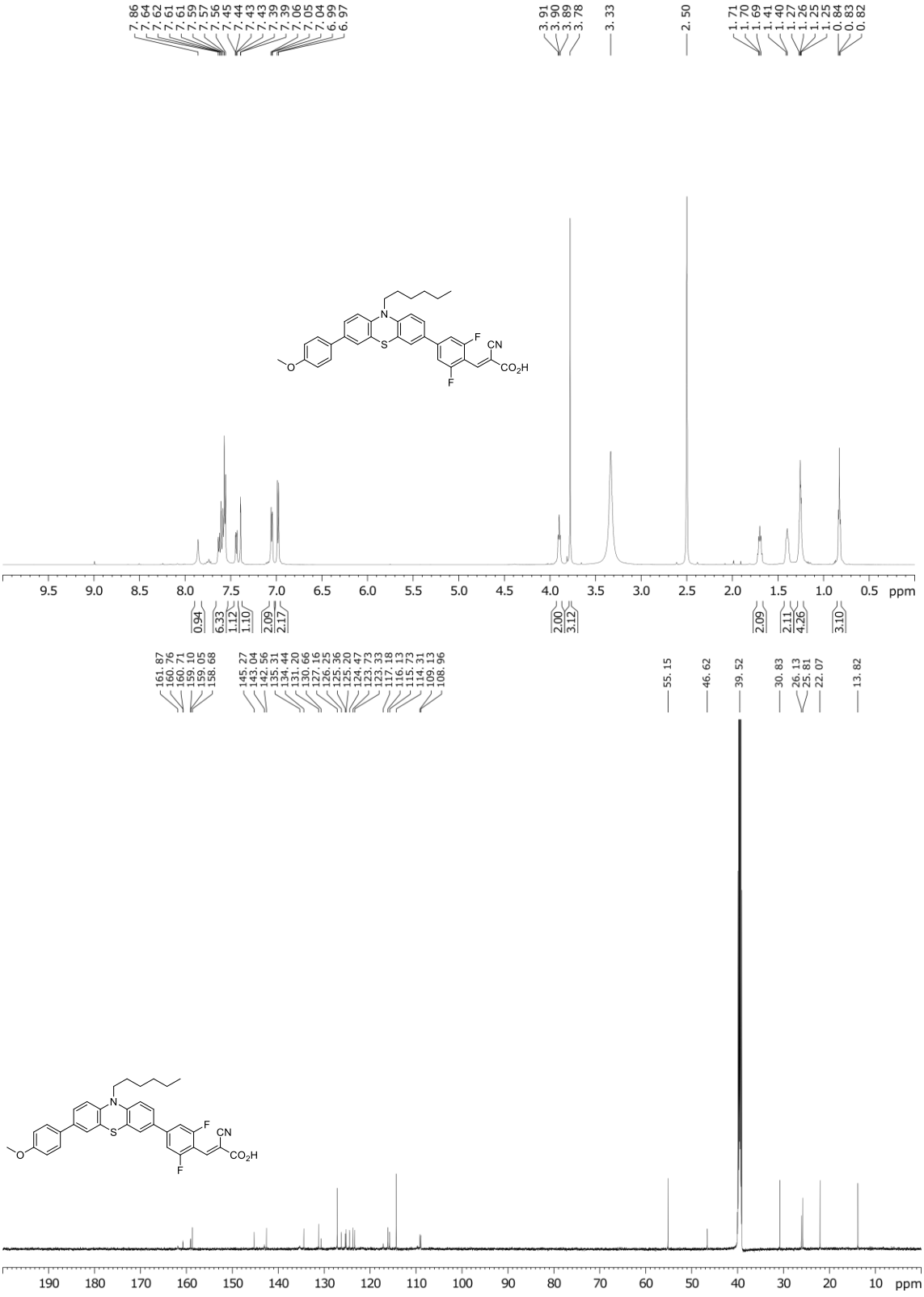


*Fig. S13. ^{1}H and ^{13}C NMR spectra for **AFB-7**.*

AFB-8

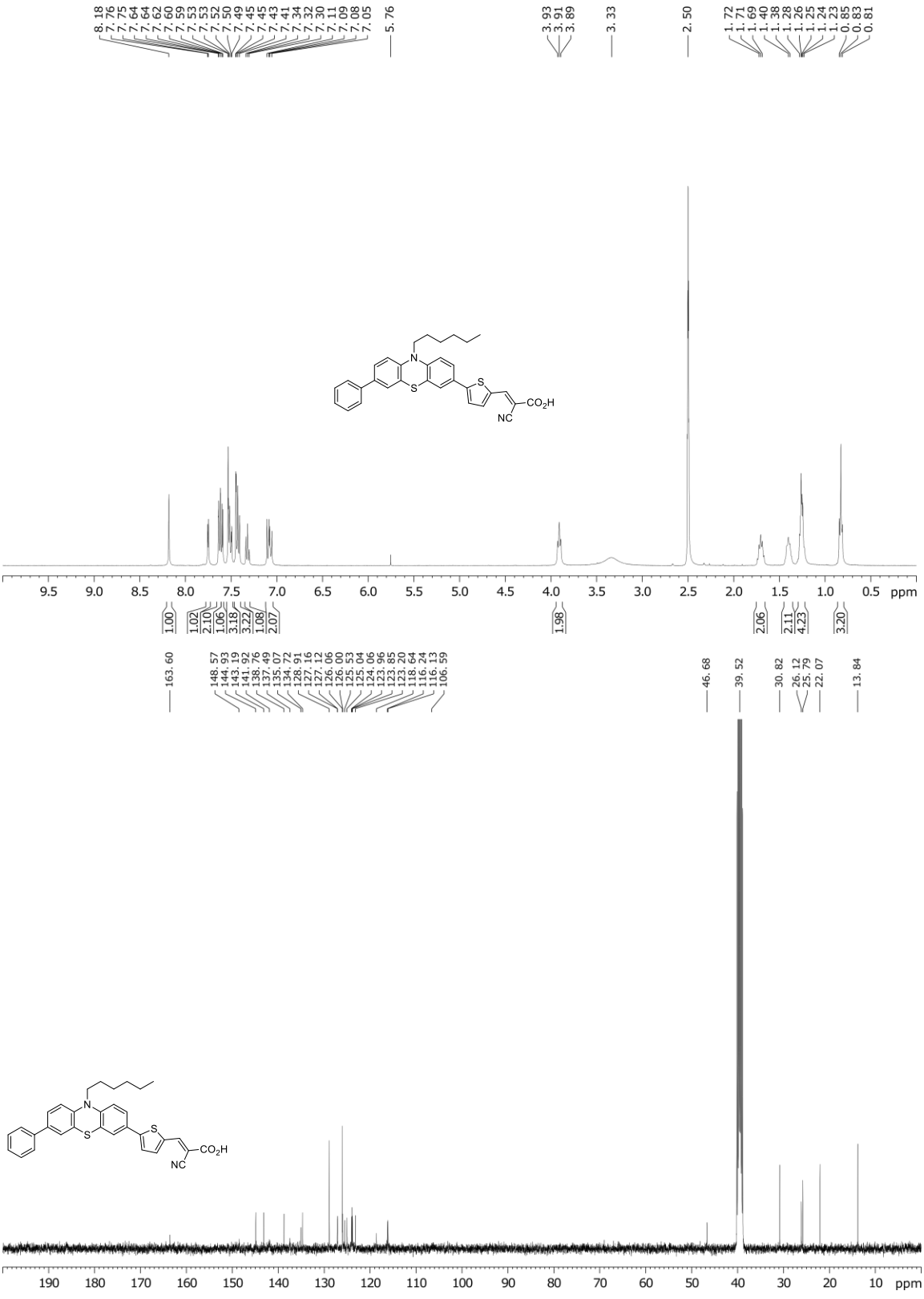


*Fig. S14. ^{1}H and ^{13}C NMR spectra for **AFB-8**.*

AFB-9

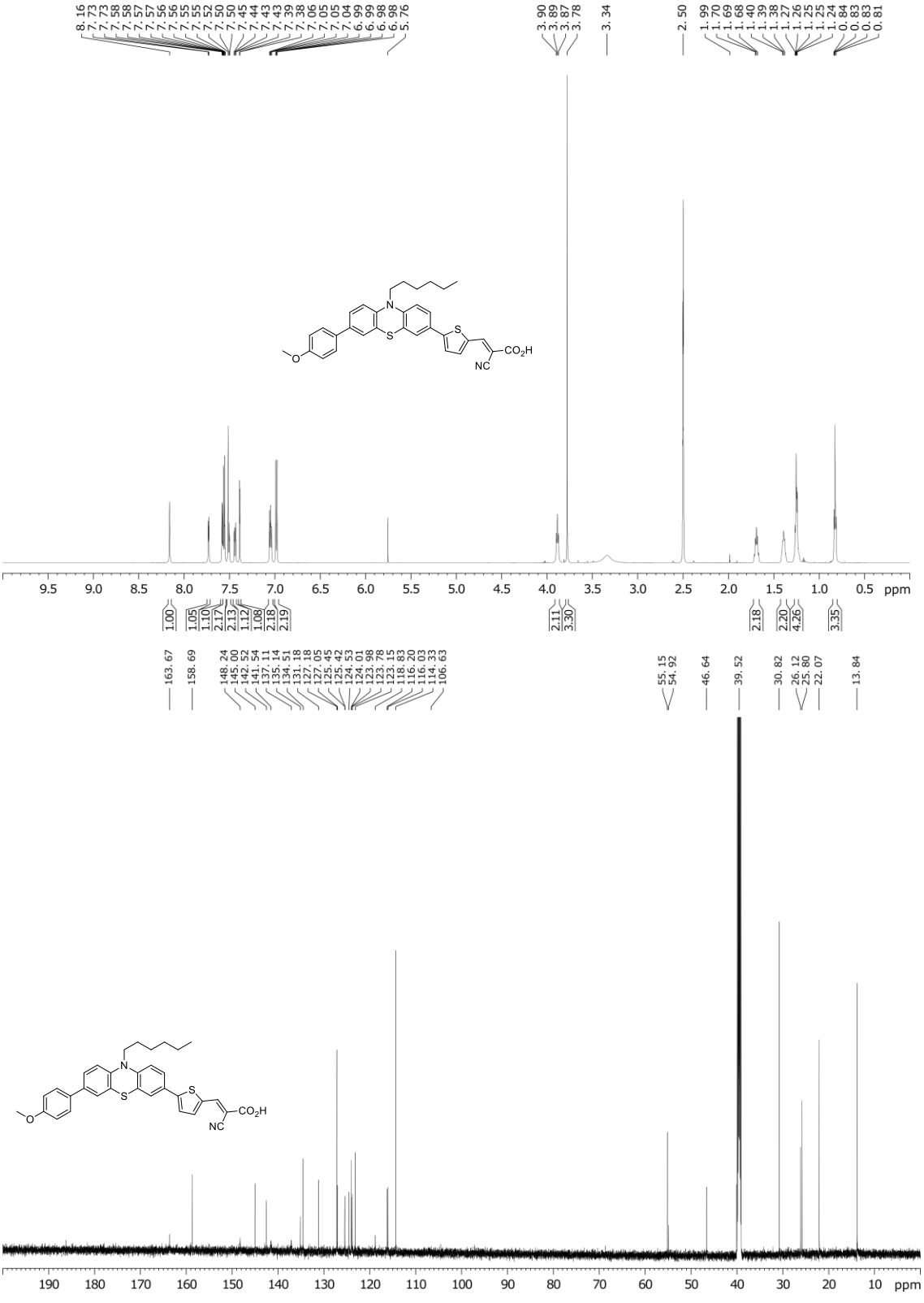


*Fig. S15. ^{1}H and ^{13}C NMR spectra for **AFB-9**.*

AFB-10

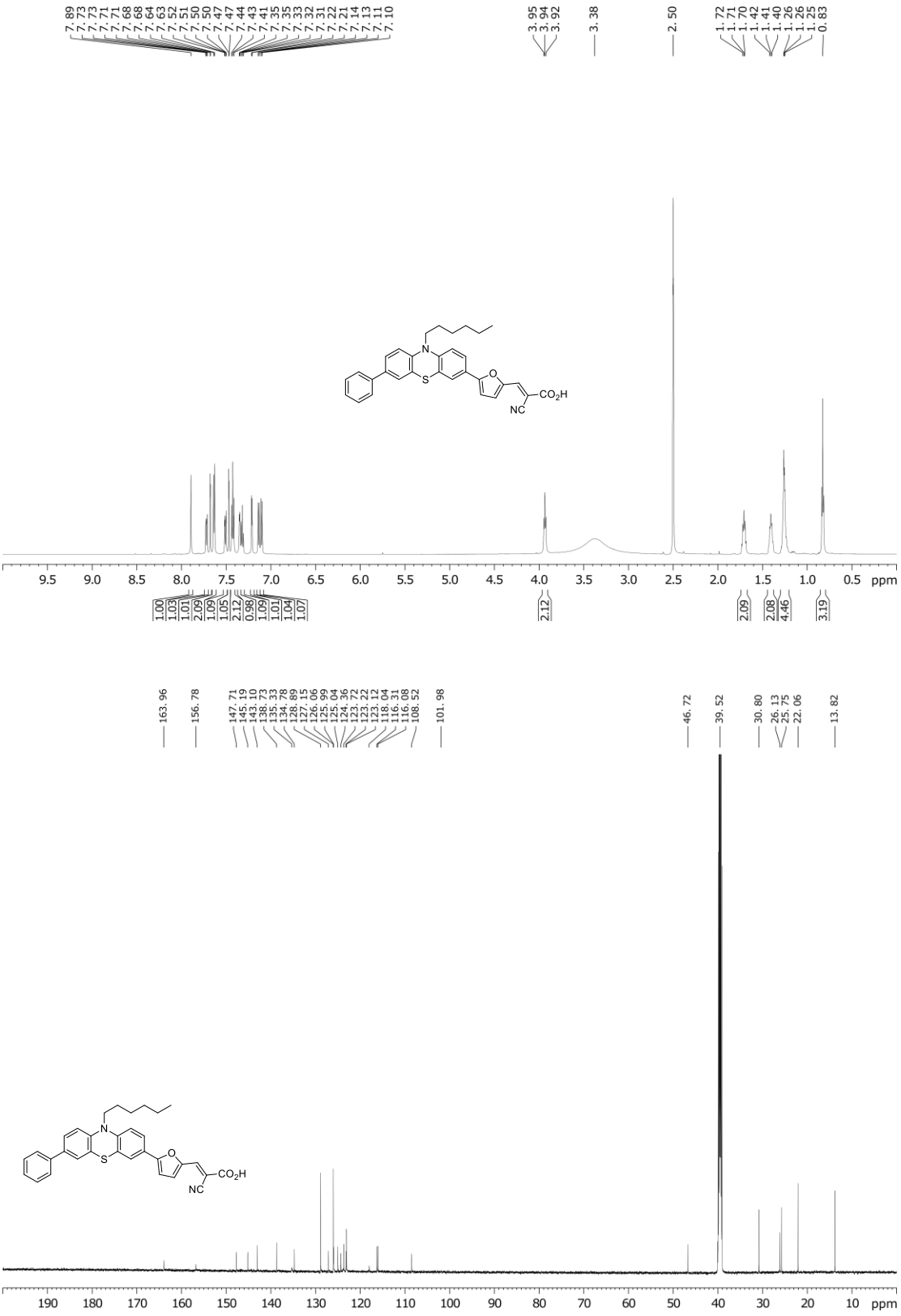


*Fig. S16. ^{1}H and ^{13}C NMR spectra for **AFB-10**.*

AFB-11

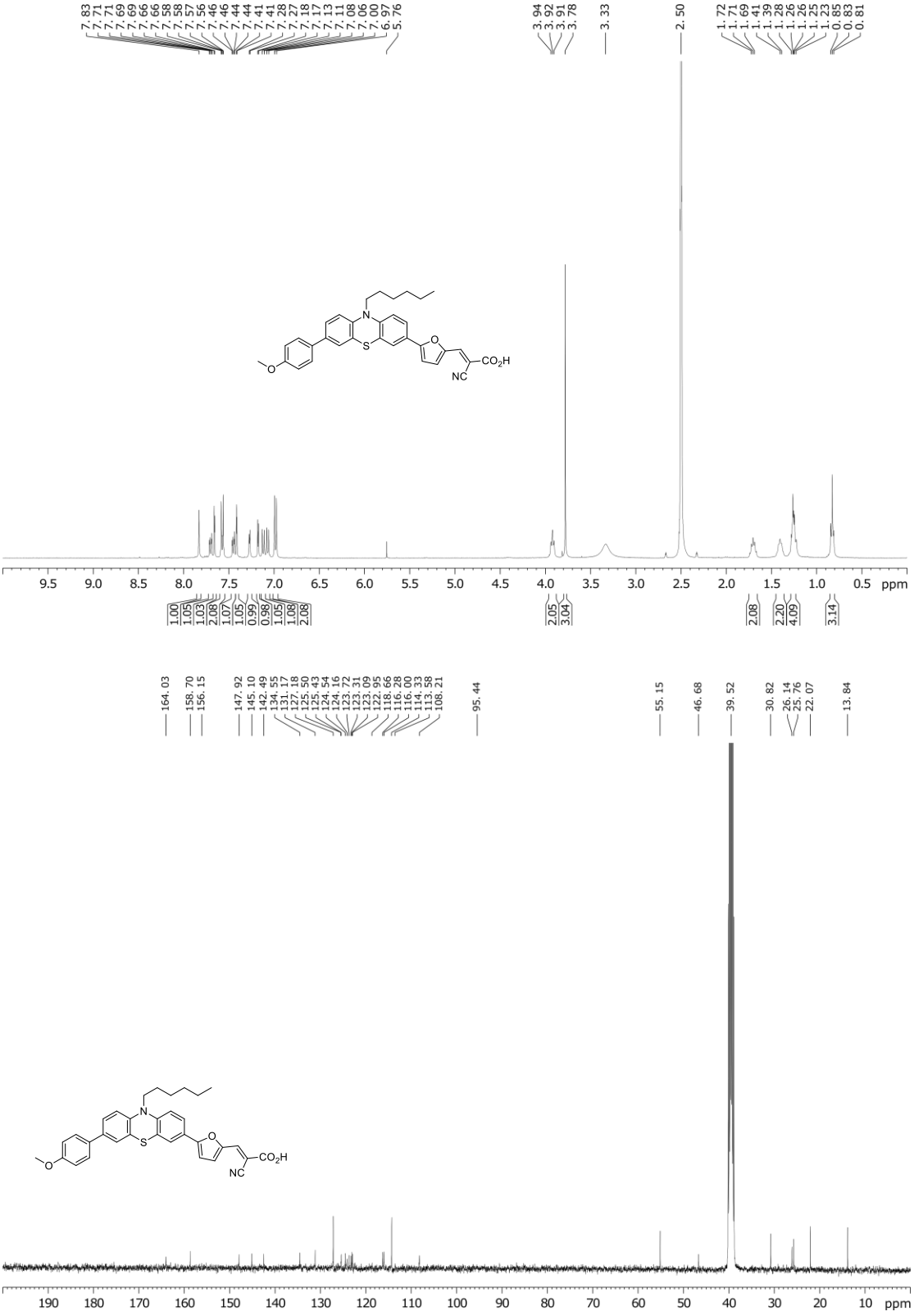


*Fig. S17. ^{1}H and ^{13}C NMR spectra for **AFB-11**.*

References

[1] Cardona C. M., Li W., Kaifer A. E., Stockdale D., Bazan G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. Adv. Mater. 2011;23:2367-2371.
[2] Bard A. J., Faulkner L. R. Electrochemical Methods: Fundamentals and Applications. 2nd edn ed. New York: John Wiley and Sons, 2001.
[3] Hao Y., Gabrielsson E., Lohse P. W., Yang W., Johansson E. M. J., Hagfeldt A., et al. Peripheral Hole Acceptor Moieties on an Organic Dye Improve Dye-Sensitized Solar Cell Performance. Adv. Sci. 2015;2:1500174.
[4] Hao Y., Yang W., Zhang L., Jiang R., Mijangos E., Hammarström L., et al. A small electron donor in cobalt complex electrolyte significantly improves efficiency in dye-sensitized solar cells. Nat. Commun. 2016;7:13934.
[5] Ozawa H., Awa M., Ono T., Arakawa H. Effects of Dye-Adsorption Solvent on the Performances of the Dye-Sensitized Solar Cells Based on Black Dye. Chem. Asian. J. 2012;7:156-162.
[6] Joly D., Pellejà L., Narbey S., Oswald F., Chiron J., Clifford J. N., et al. A Robust Organic Dye for Dye Sensitized Solar Cells Based on Iodine/Iodide Electrolytes Combining High Efficiency and Outstanding Stability. Sci. Rep. 2014;4:4033.
[7] Elkassih S. A., Sista P., Magurudeniya H. D., Papadimitratos A., Zakhidov A. A., Biewer M. C., et al. Phenothiazine Semiconducting Polymer for Light-Emitting Diodes. Macromol. Chem. Phys. 2013;214:572-577.
[8] Hua Y., Chang S., Huang D. D., Zhou X., Zhu X. J., Zhao J. Z., et al. Significant Improvement of Dye-Sensitized Solar Cell Performance Using Simple Phenothiazine-Based Dyes. Chem. Mater. 2013;25:2146-2153.
[9] Lin H.-H., Su S.-Y., Chang C.-C. Fluorescent organic nanoparticle formation in lysosomes for cancer cell recognition. Org. Biomol. Chem. 2009;7:2036-2039.
[10] Sailer M., Franz A. W., Müller T. J. J. Synthesis and Electronic Properties of Monodisperse Oligophenothiazines. Chem. Eur. J. 2008;14:2602-2614.