Electronic Supplementary Information

Auxiliary donors for phenothiazine sensitizers for dye-sensitized solar cells – How important are they really?

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Absorption, emission and dye loading

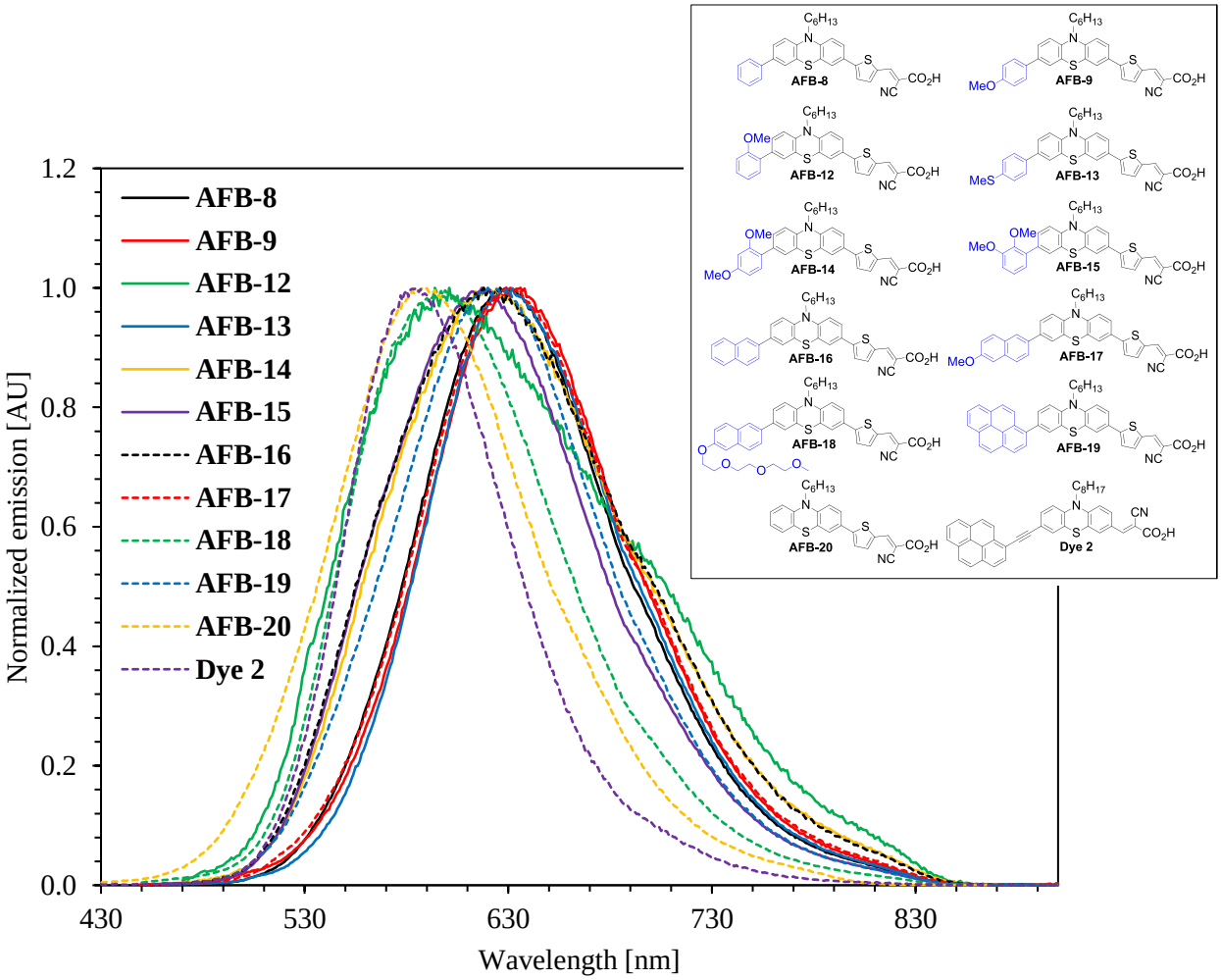


Figure S1. *Normalized emission spectra of all dyes, recorded in THF.*

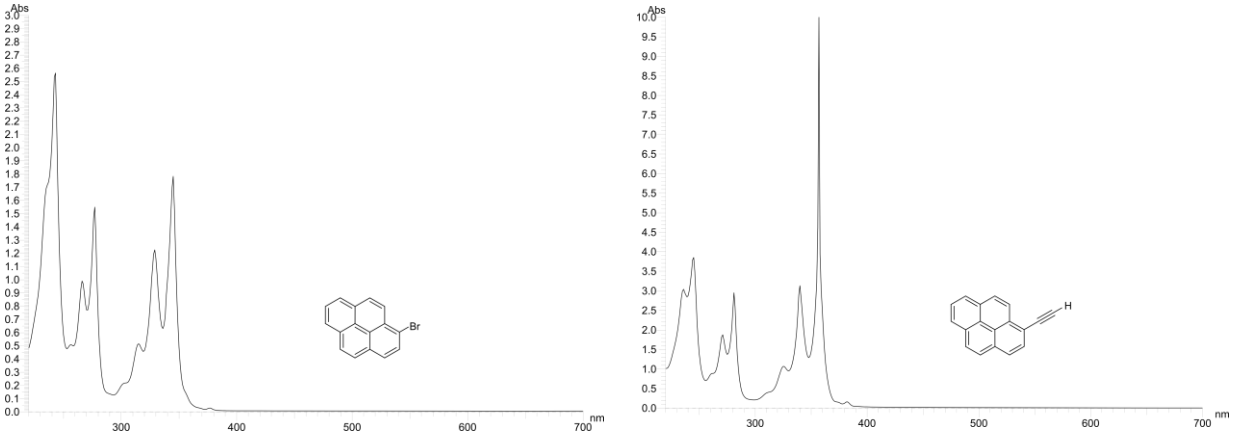


Figure S2. *UV/Vis absorption spectra in THF of pyrene-containing 1-bromopyrene (left) and 1-ethynylpyrene (right).*

Table S1. *Dye loading data for* ***AFB-12****,* ***AFB-19****,* ***AFB-20*** *and* ***Dye 2****.*

Dye	Dye loading (10^{-7} mol cm^{-2})[a]
AFB-12	2.63 ± 0.22
AFB-19	4.89 ± 0.61
AFB-20	2.99 ± 0.15
Dye 2	3.51 ± 0.20

[a] Measured by UV/Vis from the staining solutions with 10-fold amount of CDCA. Averages of three separate staining baths.

Cyclic voltammetry

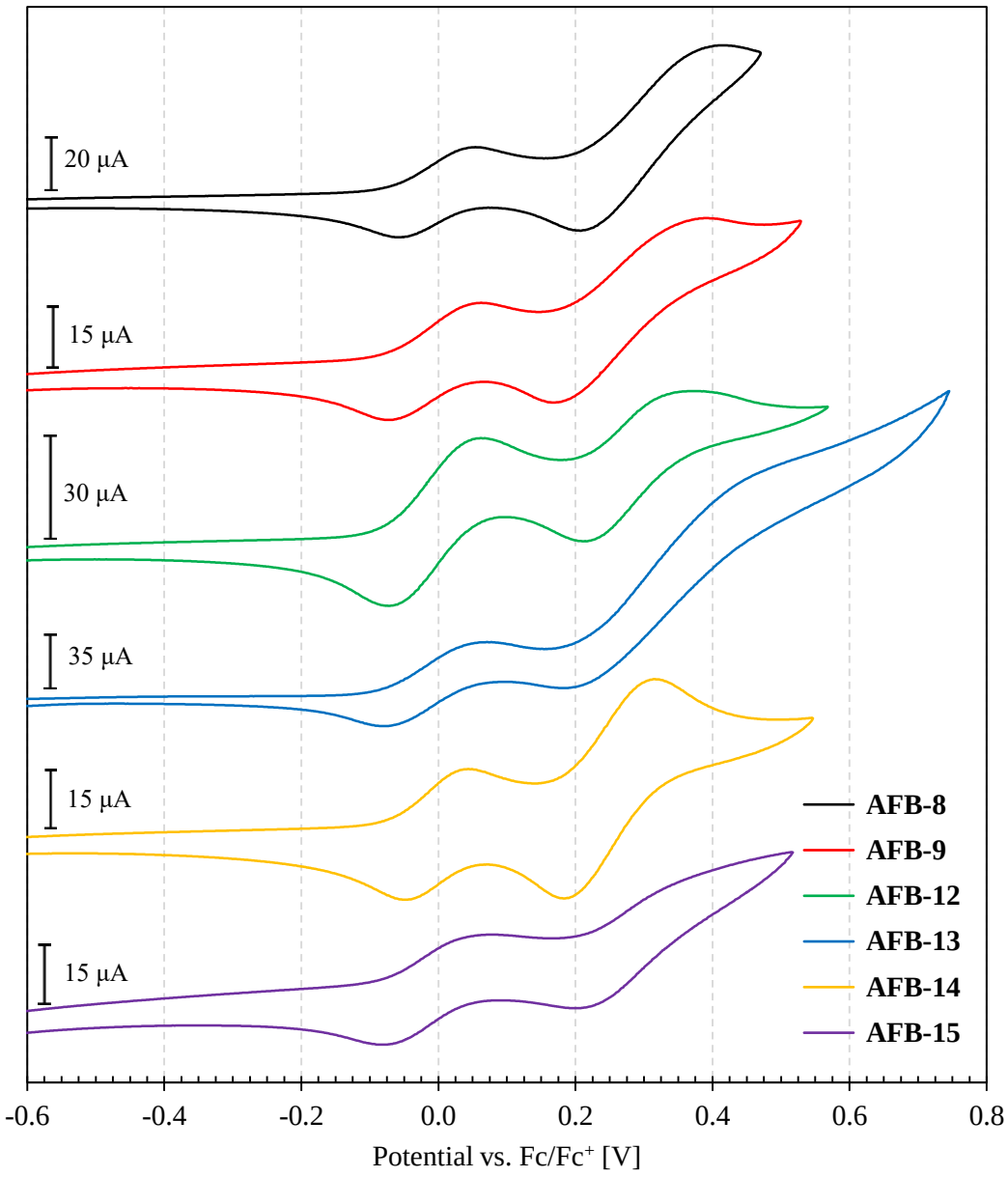


Figure S3. *Cyclic voltammograms of dyes* ***AFB-8***, ***9***, ***12-15*** *in DMF solution.*

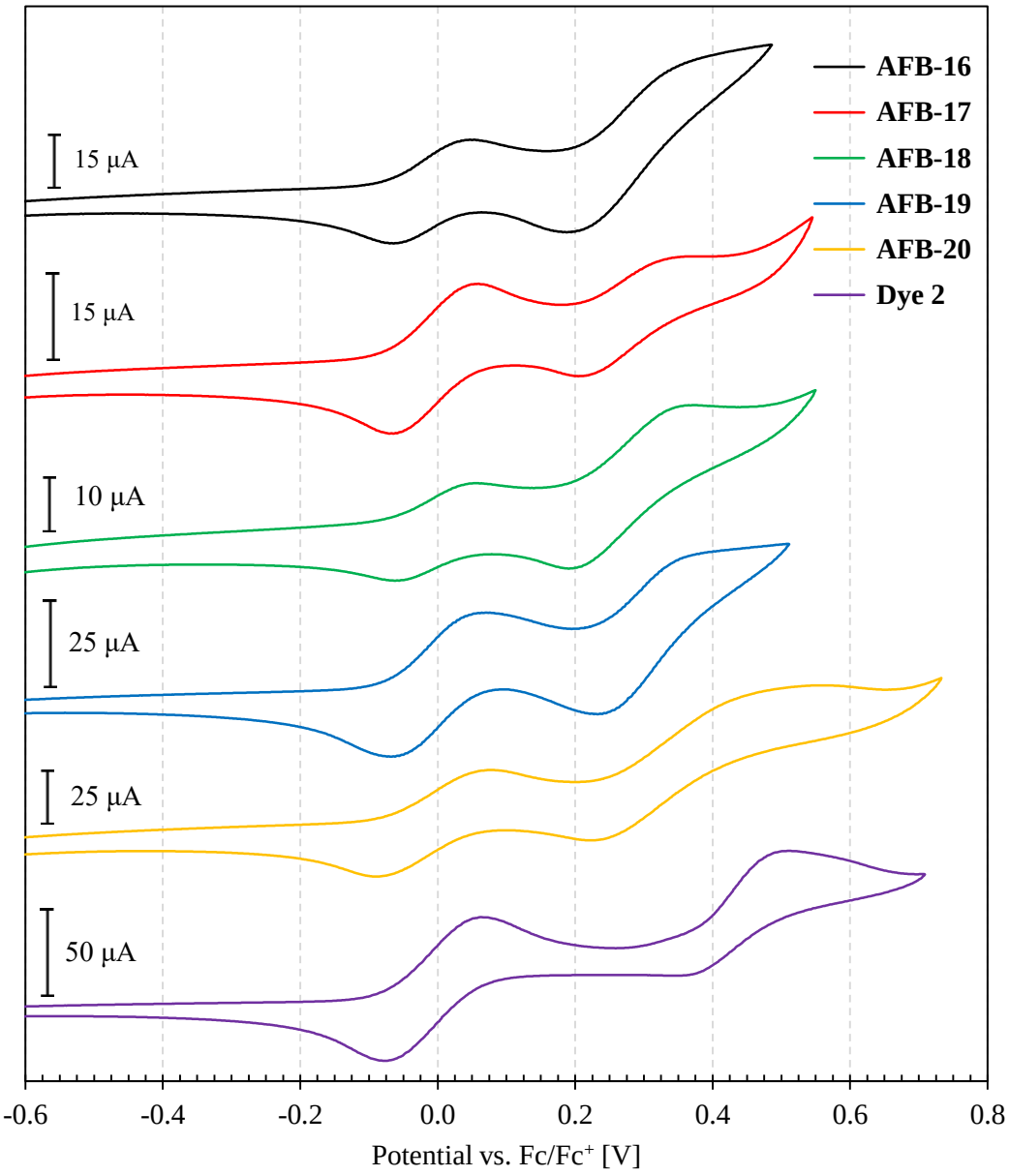


Figure S4. *Cyclic voltammograms of dyes* ***AFB-16*** *to* ***20*** *and* ***Dye 2*** *in DMF solution.*

Copper (II/I) electrolyte for AFB-19

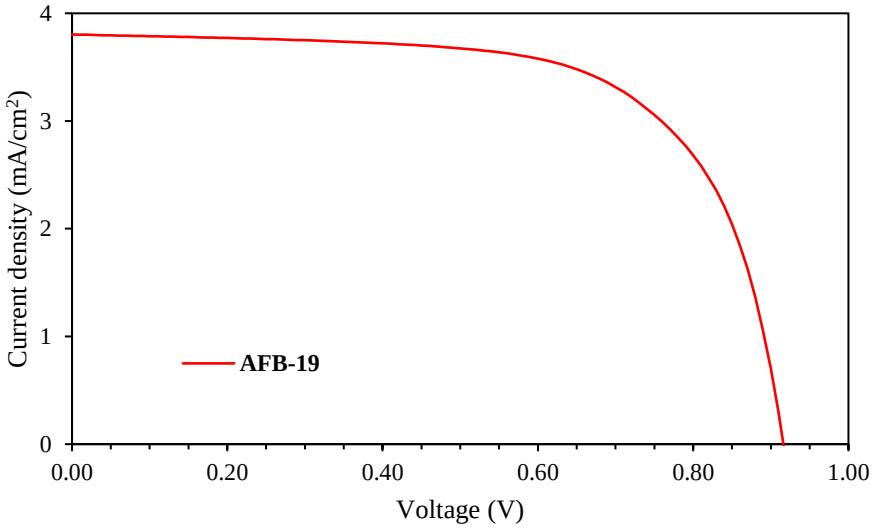


Figure S5. *Current-voltage plot for* ***AFB-19*** *with $Cu^{(II/I)}(tmby)_2TFSI_{2/1}$ electrolyte (similar system as reported by Saygili et al.[1]) under 1 sun AM 1.5G illumination.*

Table S2. *Photovoltaic performance of* ***AFB-19*** *under 1 sun AM 1.5G illumination with the A6141 iodide electrolyte (same data set as in Table 2) and $Cu^{(II/I)}(tmby)_2TFSI_{2/1}$ electrolyte.*

Electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
I^-/I_3^- (A6141)	9.00 ± 0.44	0.78 ± 0.00	0.72 ± 0.02	5.00 ± 0.20
Cu(tmby)	3.82 ± 0.02	0.91 ± 0.01	0.65 ± 0.02	2.27 ± 0.08

Experimental information

Materials and reagents

All reactions were carried out under nitrogen atmosphere, and all synthesis reagents were acquired from Sigma Aldrich. The synthesis of building block **1** was performed as previously reported by our research group.[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 or $CDCl_3$. 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 were 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.

Cyclic voltammetry was performed in a three-electrode cell with platinum wire electrodes in DMF with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). A Princeton Applied Research Versastat 3 potensiostat was used along with the VersaStudio software. The scan rate was 100 mV/s for all measurements. Calculation of the E_{HOMO} vs. SHE was done according to the following equation where a conversion constant of 624 mV of Fc^{+}/Fc vs. SHE is used.[3]

$$E_{HOMO} = E_{1/2}\,(dye) - E_{1/2}(Fc) + 0.624$$

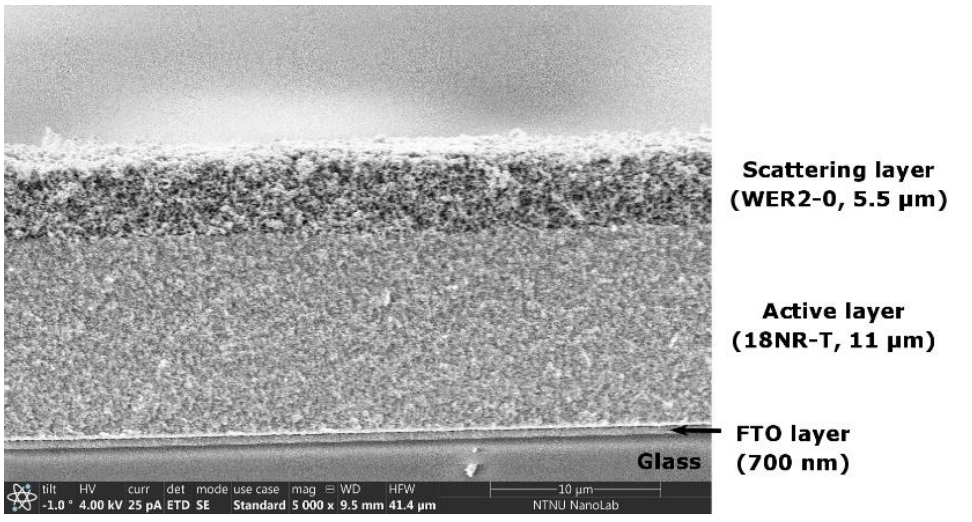


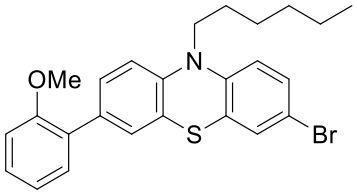
Figure S6. *Cross-section scanning electron microscopy image of the screen-printed electrodes. The complete cross section is shown, with glass, FTO, active 18NR-T TiO_2 and scattering WER2-0 TiO_2. A white compact layer on top of the FTO is most likely the TiO_2 blocking layer formed by hydrothermal deposition.*

Synthesis

General procedure for Suzuki coupling

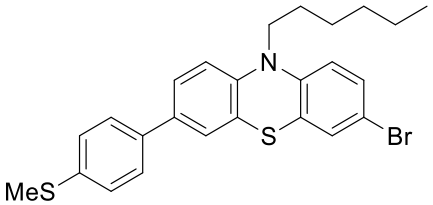
3,7-Dibromo-10-hexyl-10*H*-phenothiazine (**1**) (1 eq.), boronic acid containing the desired donor group (1.0-1.1 eq.), $Pd(PPh_3)_4$ (0.01 eq.) and potassium carbonate (4 eq.) were mixed. The system was evacuated and backflushed with N_2. 1,4-Dioxane and water (1:1, v:v, 6.6 mL/mmol) were degassed and added, and the reaction mixture was stirred at 80 °C until desired conversion. Water was added to the reaction mixture, and the aqueous phase extracted using ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The product was purified by silica gel column chromatography.

3-Bromo-10-hexyl-7-(2-methoxyphenyl)-10*H*-phenothiazine (2)



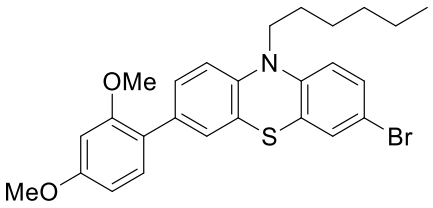
The synthesis was performed as described in the general procedure, starting with compound **1** (200 mg, 0.453 mmol), 2-methoxyphenylboronic acid (69 mg, 0.453 mmol), $Pd(PPh_3)_4$ (5.2 mg, 4.5 μmol) and K_2CO_3 (251 mg, 1.813 mmol). The reaction time was 16 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/toluene, 5:1, R_f = 0.17), to yield compound **2** as a yellow oil (80 mg, 0.171 mmol, 38%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.37-7.34 (m, 2H), 7.33-7.29 (m, 2H), 7.26 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 7.00 (td, *J* = 7.5, 1.0 Hz, 1H), 6.98-6.95 (m, 1H), 3.86 (t, *J* = 7.0 Hz, 2H), 3.76 (s, 3H), 1.70-1.65 (m, 2H), 1.40-1.38 (m, 2H), 1.31-1.26 (m, 4H), 0.84-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 156.0, 144.0, 143.2, 132.7, 130.1, 130.0, 129.0, 128.9, 128.7, 128.4, 127.7, 126.0, 122.1, 120.8, 117.4, 115.5, 113.6, 111.7, 55.5, 46.5, 30.8, 26.1, 25.8, 22.0, 13.8; IR (neat, cm^{-1}) ν: 3065 (w, br), 2951 (m, br), 2914 (m, br), 2947 (m), 1595 (m), 1465 (s), 1247 (s), 1023 (m), 800 (m), 738 (s); HRMS (TOF MS ASAP+, *m/z*): found 467.0919 (calcd. $C_{25}H_{26}NOS^{79}Br$: 467.0918, $[M]^+$).

3-Bromo-10-hexyl-7-(4-(methylthio)phenyl)-10*H*-phenothiazine (3)



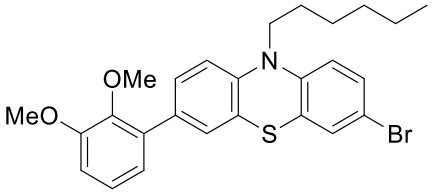
The synthesis was performed as described in the general procedure, starting with compound **1** (1.00 g, 2.266 mmol), (4-methylthio)phenyl)boronic acid (419 mg, 2.493 mmol), $Pd(PPh_3)_4$ (26 mg, 0.022 mmol) and K_2CO_3 (1.25 g, 9.07 mmol). The reaction time was 8 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/toluene, 9:1, R_f = 0.12), to yield compound **3** as an off-white solid (560 mg, 1.156 mmol, 51%), mp 69-70 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.59-7.55 (m, 2H), 7.48 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 1H), 7.36-7.32 (m, 2H), 7.31-7.28 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.96-6.93 (m, 1H), 3.85 (t, *J* = 6.9 Hz, 2H), 2.49 (s, 3H), 1.70-1.61 (m, 2H), 1.41-1.32 (m, 2H), 1.27-1.20 (m, 4H), 0.84-0.79 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 143.9, 143.5, 137.1, 135.3, 134.0, 130.1, 128.9, 126.5 (2C), 126.4 (2C), 125.8, 125.7, 124.7, 123.4, 117.4, 116.2, 113.7, 46.6, 30.8, 26.0, 25.8, 22.1, 14.7, 13.8; IR (neat, cm^{-1}) ν: 2952 (w), 2919 (w), 2852 (w), 1455 (s), 1248 (s), 1097 (m), 802 (s); HRMS (TOF MS ASAP+, *m/z*): found 484.0767 (calcd. $C_{25}H_{27}NOS_2^{79}Br$: 484.0768, $[M+H]^+$).

3-Bromo-7-(2,4-dimethoxyphenyl)-10-hexyl-10*H*-phenothiazine (4)



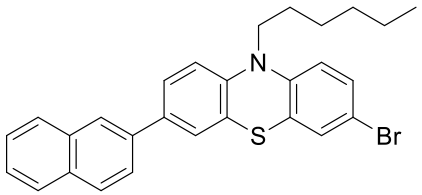
The synthesis was performed as described in the general procedure, starting with compound **1** (200 mg, 0.453 mmol), 2,4-dimethoxyphenylboronic acid (82 mg, 0.453 mmol), $Pd(PPh_3)_4$ (5.2 mg, 4.5 μmol) and K_2CO_3 (251 mg, 1.813 mmol). The reaction time was 1.5 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/toluene, 4:1, R_f = 0.14), to yield compound **4** as a yellow oil (110 mg, 0.221 mmol, 49%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.36-7.34 (m, 2H), 7.26 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.19 (s, 1H), 7.18 (d, *J* = 6.4 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.97-6.94 (m, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 6.58 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.85 (t, *J* = 6.9 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 1.70-1.65 (m, 2H), 1.41-1.37 (m, 2H), 1.26-1.17 (m, 4H), 0.84-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 160.0, 157.0, 144.1, 142.7, 132.6, 130.4, 130.1, 128.9, 128.5, 127.5, 126.0, 122.1, 121.1, 117.3, 115.5, 113.5, 105.3, 98.9, 55.5, 55.3, 46.5, 30.8, 26.1, 25.8, 22.0, 13.8; IR (neat, cm^{-1}) ν: 2956 (m), 2925 (m), 2852 (m), 2369 (w), 1610 (m), 1455 (s), 1242 (s), 1205 (s), 1163 (s), 795 (s); HRMS (TOF MS ASAP+, *m/z*): found 497.1017 (calcd. $C_{26}H_{28}NO_2S^{79}Br$: 497.1024, $[M]^+$).

3-Bromo-7-(2,3-dimethoxyphenyl)-10-hexyl-10*H*-phenothiazine (5)



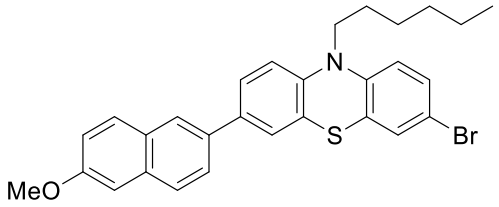
The synthesis was performed as described in the general procedure, starting with compound **1** (200 mg, 0.453 mmol), 2,3-dimethoxyphenylboronic acid (82 mg, 0.453 mmol), $Pd(PPh_3)_4$ (5.2 mg, 4.5 μmol) and K_2CO_3 (251 mg, 1.813 mmol). The reaction time was 16 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/toluene, 5:1, R_f = 0.13), to yield compound **5** as a yellow oil (120 mg, 0.241 mmol, 53%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.36-7.34 (m, 2H), 7.33-7.32 (m, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 7.11-7.06 (m, 2H), 7.02-7.02 (m, 1H), 6.98-6.95 (m, 1H), 6.89-6.87 (m, 1H), 3.87 (t, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 3.53 (s, 3H), 1.71-1.66 (m, 2H), 1.40-1.38 (m, 2H), 1.27-1.25 (m, 4H), 0.84-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 152.8, 145.8, 143.9, 143.4, 133.6, 132.3, 130.1, 129.0, 128.5, 127.3, 125.9, 124.2, 122.3, 121.7, 117.4, 115.6, 113.7, 111.9, 60.1, 55.8, 46.6, 30.8, 26.1, 25.8, 22.0, 13.8. IR (neat, cm^{-1}) ν: 2945 (w, br), 2925 (m, br), 2852 (w, br), 1574 (m), 1444 (s), 1397 (m), 1252 (s), 1117 (s), 790 (s), 748 (s); HRMS (TOF MS ASAP+, *m/z*): found 497.1019 (calcd. $C_{26}H_{28}NO_2S^{79}Br$: 497.1024, $[M]^+$).

3-Bromo-10-hexyl-7-(naphthalen-2-yl)-10*H*-phenothiazine (6)



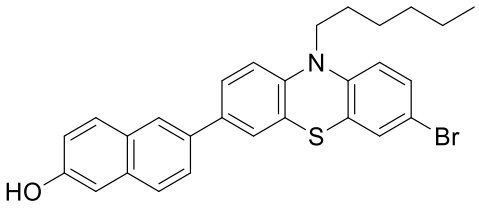
The synthesis was performed as described in the general procedure, starting with compound **1** (203 mg, 0.460 mmol), naphthalen-2-ylboronic acid (79 mg, 0.460 mmol), $Pd(PPh_3)_4$ (5.3 mg, 4.60 μmol) and K_2CO_3 (254 mg, 1.840 mmol). The reaction time was 19 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/toluene, 20:1, R_f = 0.13), to yield compound **6** as a yellow oil (94 mg, 0.192 mmol, 42%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.18 (s, 1H), 7.98-7.94 (m, 2H), 7.91 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.81 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.66 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.61 (d, *J* = 2.2 Hz, 1H), 7.55-7.47 (m, 2H), 7.37-7.34 (m, 2H), 7.12 (d, *J* = 8.6 Hz, 1H), 6.98-6.94 (m, 1H), 3.88 (t, *J* = 6.9 Hz, 2H), 1.73-1.64 (m, 2H), 1.43-1.34 (m, 2H), 1.27-1.21 (m, 4H), 0.85-0.79 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 143.9, 143.7, 136.0, 134.4, 133.3, 132.1, 130.1, 128.9, 128.4, 128.1, 127.4, 126.4, 126.2, 125.9, 125.8, 125.3, 124.6, 124.4, 123.5, 117.4, 116.3, 113.7, 46.6, 30.8, 26.0, 25.7, 22.0, 13.8; IR (neat, cm^{-1}) ν: 3054 (br), 2924 (m), 2853 (m), 1600 (m), 1453 (s), 1264 (m), 805 (m); HRMS (TOF MS ASAP+, *m/z*): found 488.1043 (calcd. $C_{28}H_{27}NS^{79}Br$: 488.1048, $[M+H]^+$).

3-Bromo-10-hexyl-7-(6-methoxynaphthalen-2-yl)-10*H*-phenothiazine (7)



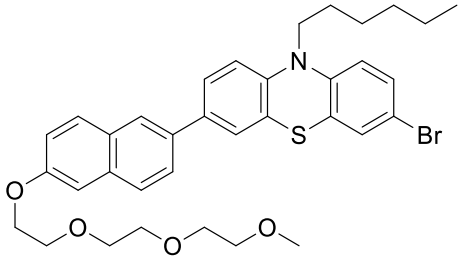
The synthesis was performed as described in the general procedure, starting with compound **1** (200 mg, 0.453 mmol), (6-methoxynaphthalen-2-yl)boronic acid (92 mg, 0.453 mmol), $Pd(PPh_3)_4$ (5.2 mg, 4.5 μmol) and K_2CO_3 (251 mg, 1.813 mmol). The reaction time was 16 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate, 77.5:2.5, R_f = 0.11), to yield compound **7** as a yellow oil (90 mg, 0.174 mmol, 38%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8. 11 (d, *J* = 1.6 Hz, 1H), 7.89-7.84 (m, 2H), 7.79-7.75 (m, 1H), 7.63 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.38-7.34 (m, 2H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.12 (d, *J* = 8.6 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 1H), 3.91-3.86 (m, 5H), 1.73-1.65 (m, 2H), 1.42-1.36 (m, 2H), 1.26-1.24 (m, 4H), 0.85-0.81 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 157.3, 143.9, 143.4, 134.5, 133.7, 133.3, 130.1, 129.6, 128.9, 128.7, 127.3, 126.0, 125.8, 125.0, 124.9, 123.4, 118.9, 117.4, 116.3, 113.7, 108.6, 105.7, 55.2, 46.6, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 3065 (br), 2953 (m), 1628 (m), 1456 (s), 1391 (m), 1245 (s), 1029 (m), 799 (m); HRMS (TOF MS ASAP+, *m/z*): found 518.1148 (calcd. $C_{29}H_{29}NOS^{79}Br$: 518.1141, $[M+H]^+$).

6-(7-Bromo-10-hexyl-10*H*-phenothiazin-3-yl)naphthalen-2-ol (8)



The synthesis was performed as described in the general procedure, starting with compound **1** (1.22 g, 2.77 mmol), (6-((tertbutyldimetylsilyl)oxy)naphthalen-2-yl)boronic acid (836 mg, 2.77 mmol), $Pd(PPh_3)_4$ (32 mg, 0.028 mmol) and K_2CO_3 (1.53 g, 11.07 mmol). The reaction time was 72 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/toluene, 10:1, R_f = 0.23), to yield compound **8** as a green solid (710 mg, 1.407 mmol, 51%), mp 96-100 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.77 (s, 1H), 8.04 (s, 1H), 7.80 (d, *J* = 8.8 Hz, 1H), 7.74-7.66 (m, 2H), 7.59 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.37-7.33 (m, 2H), 7.13-7.07 (m, 3H), 6.95 (d, *J* = 8.5 Hz, 1H), 3.86 (t, *J* = 7.0 Hz, 2H), 1.72-1.65 (m, 2H), 1.43-1.36 (m, 2H), 1.26-1.21 (m, 4H), 0.84-0.80 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 155.4, 144.0, 143.3, 134.8, 133.7, 132.9, 130.1, 129.7, 128.9, 128.0, 126.6, 125.9, 125.9, 124.9, 124.7, 124.3, 123.4, 119.0, 117.3, 116.3, 113.6, 108.4, 46.6, 30.8, 26.0, 25.8, 22.0, 13.8; IR (neat, cm^{-1}) ν: 3326 (w, br), 2921 (m), 1697 (m), 1496 (m), 1455 (s), 1246 (m), 1145 (m), 797 (m); HRMS (TOF MS ASAP+, *m/z*): found 504.0996 (calcd. $C_{28}H_{27}NOSBr$: 504.0997, $[M+H]^+$).

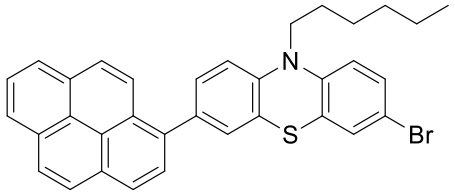
3-Bromo-10-hexyl-7-(6-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphthalen-2-yl)-10*H*-phenothiazine (9)



Compound **8** (401 mg, 0.794 mmol) and K_2CO_3 (330 mg, 2.388 mmol) were mixed, under N_2-atmosphere. DMF (32 mL) was added, and the mixture was stirred for 1 hour. 2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (504 mg, 1.583 mmol) was added, and the reaction was stirred at 130 °C for 20 hours. The reaction mixture was stirred with water (200 mL) for 30 minutes, followed by an extraction of the aqueous phase with ethyl acetate (2 × 100 mL) and the resulting organic phase was washed with water (4 × 100 mL). The organic phase was dried over Na_2SO_4, filtered and solvents were removed *in vacou*. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-pentane, 1:1, R_f = 0.15), to yield compound **9** as a yellow oil (377 mg, 0.580 mmol, 73%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.11 (s, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.85-7.83 (m, 1H), 7.77-7.75 (m, 1H), 7.63 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.57 (d, *J* = 1.8 Hz, 1H),

7.37-7.33 (m, 3H), 7.19 (dd, *J* = 9.1, 2.0 Hz, 1H), 7.11 (d, *J* = 8.6, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 4.23-4.21 (m, 2H), 3.88 (t, *J* = 7.0 Hz, 2H), 3.82-3.81 (m, 2H), 3.63-3.61 (m, 2H), 3.56-3.55 (m, 2H), 3.53-3.52 (m, 2H), 3.42-3.42 (m, 2H), 3.23 (s, 3H), 1.71-1.66 (m, 2H), 1.42-1.37 (m, 2H), 1.27-1.25 (m, 4H), 0.85-0.82 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 156.5, 143.9, 143.4, 134.6, 133.8, 133.3, 130.1, 129.7, 128.9, 128.8, 127.3, 126.0, 125.8, 125.0, 124.9, 124.3, 123.5, 119.1, 117.4, 116.3, 113.6, 106.5, 71.2, 70.0, 69.8, 69.6, 69.9, 67.2, 54.9, 46.6, 30.8, 26.0, 25.7, 22.0, 13.8; IR (neat, cm^{-1}) ν: 2923 (m), 2869 (m), 1604 (m), 1457 (s), 1391 (m), 1246 (s), 1105 (m), 803 (m); HRMS (TOF MS ASAP+, *m/z*): found 649.1854 (calcd. $C_{35}H_{40}NO_4SBr$: 649.1861, $[M]^+$).

3-Bromo-10-hexyl-7-(pyren-1-yl)-10*H*-phenothiazine (10)



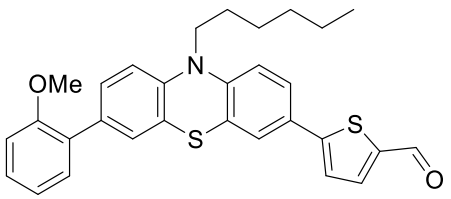
The synthesis was performed as described in the general procedure, starting with compound **1** (800 mg, 1.813 mmol), pyren-1-ylboronic acid (491 mg, 1.994 mmol), $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) and K_2CO_3 (1.00 g, 7.25 mmol). 1,4-Dioxane (6 mL) and water (6 mL) were added, and the reaction was stirred at 80 °C for 14 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/Et_2O, 20:1, R_f = 0.34), to yield compound **10** as a yellow solid (409 mg, 0.726 mmol, 40%), mp 95-97 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.35-8.31 (m, 2H), 8.28 (d, *J* = 7.3 Hz, 1H), 8.22 (s, 2H), 8.18-8.15 (m, 1H), 8.13-8.07 (m, 2H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.47 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.42-7.39 (m, 3H), 7.25 (d, *J* = 8.4 Hz, 1H), 7.05-7.02 (m, 1H), 3.95 (t, *J* = 6.9 Hz, 2H), 1.79-1.73 (m, 2H), 1.48-1.42 (m, 2H), 1.33-1.26 (m, 4H), 0.88-0.84 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 144.0, 143.8, 135.9, 134.8, 131.0, 130.4, 130.2, 130.1, 129.9, 129.1, 128.6, 127.7, 127.6, 127.5, 127.40, 127.36, 126.4, 125.9, 125.4, 124.98, 124.95, 124.5, 124.2, 124.0, 123.1, 117.6, 116.0, 113.8, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2945 (w), 2919 (w), 2849 (w), 1598 (w), 1454 (s), 1245 (m), 1103 (m), 842 (m); HRMS (TOF MS ASAP+, *m/z*): found 562.1195 (calcd. $C_{34}H_{29}NSBr$: 562.1204, $[M+H]^+$).

General procedure for borylation and subsequent Suzuki coupling

The reaction procedure performed was based on a description by Billingsley and Buchwald.[4] The selected building block (**2**-**10**, 1 eq.) was mixed with dichlorobis(acetonitrile)palladium(II) (0.02 eq.) and SPhos (0.08 eq). The system was sealed, evacuated and backflushed with N_2. Dry and degassed 1,4-dioxane and triethylamine were added, followed by addition of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.5 eq.). The reaction was stirred at 80 °C until full conversion. The reaction solution was cooled, and filtered through a pad of Celite with ethyl acetate. The crude product was concentrated *in vacuo*.

$Pd(OAc)_2$ (0.02 eq.), SPhos (0.08 eq.) and K_2CO_3 (4 eq.) were added to the crude borylation products (1 eq.), before the Schlenk tubes were sealed, evacuated and backflushed with N_2. Water (194 eq.) and 1,4-dioxane (40 eq.) were degassed and added through the septum followed by 5-bromothiophene-2-carbaldehyde (1.5 eq.). The reaction was stirred at 80 °C until full conversion, followed by extraction by ethyl acetate (3 × 30 mL), drying of the combined organic phased with brine (30 mL) and drying over anhydrous Na_2SO_4. The solvents were removed *in vacuo* and the crude was purified by silica gel column chromatography.

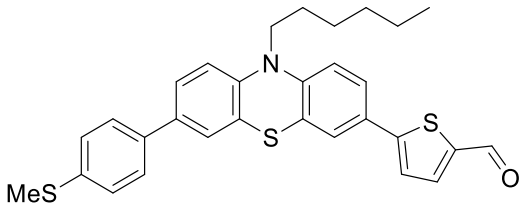
5-(10-Hexyl-7-(2-methoxyphenyl)-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (11)



The reaction was performed as described in the general procedure for borylation and subsequent Suzuki cross-coupling, starting with compound **2** (400 mg, 0.854 mmol), SPhos (28 mg, 0.068 mmol), pinacol borane (164 mg, 1.281 mmol) and dichlorobis(acetonitrile)palladium(II) (4.4 mg, 0.017 mmol), achieving full conversion in 1.5 hours. The crude material (380

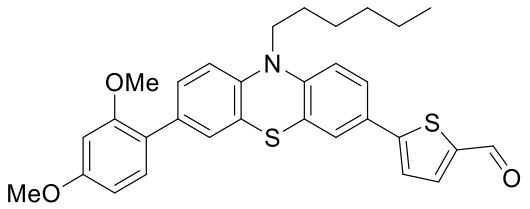
mg) was subjected to the above mentioned Suzuki reaction conditions with SPhos (12.1 mg, 0.029 mmol), $Pd(OAc)_2$ (3.3 mg, 0.015 mmol), K_2CO_3 (408 mg, 2.95 mmol) and 5-bromothiophene-2-carbaldehyde (211 mg, 1.106 mmol) in water and 1,4-dioxane. The product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate, 1:10, R_f = 0.23), to yield compound **11** as a red solid (210 mg, 0.420 mmol, 57%), mp 81-84 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 8.00 (d, *J* = 3.9 Hz, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.63-7.59 (m, 2H), 7.34-7.30 (m, 2H), 7.28 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 7.11-7.07 (m, 3H), 7.01 (td, *J* = 7.4, 1.0 Hz, 1H), 3.93 (t, *J* = 7.0 Hz, 2H), 3.76 (s, 3H), 1.73-1.71 (m, 2H), 1.43-1.41 (m, 2H), 1.28-1.27 (m, 4H), 0.85-0.83 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 184.7, 156.0, 151.9, 145.5, 142.6, 141.1, 139.4, 132.8, 129.9, 128.7, 128.7, 128.4, 127.7, 126.7, 125.8, 124.4, 124.3, 124.1, 121.9, 120.8, 116.0, 115.5, 111.7, 55.5, 46.6, 30.8, 26.2, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 1951 (w, br), 2925 (m, br), 2847 (w), 1662 (s), 1584 (m), 1470 (m), 1429 (s), 1221 (s), 800 (s), 748 (s); HRMS (TOF MS ASAP+, *m/z*): found 499.1640 (calcd. $C_{30}H_{29}NO_2S_2$: 499.1640, $[M]^+$).

5-(10-Hexyl-7-(4-(methylthio)phenyl)-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (12)



The reaction was performed as described in the general procedure for borylation and subsequent Suzuki cross-coupling, starting with compound **3** (300 mg, 0.619 mmol), SPhos (20.3 mg, 0.05 mmol), pinacol borane (119 mg, 0.929 mmol) and dichlorobis(acetonitrile)palladium(II) (3.2 mg, 0.012 mmol), achieving full conversion in 2 hours. The crude material (329 mg) was subjected to the above mentioned Suzuki reaction conditions with SPhos (10.16 mg, 0.025 mmol), $Pd(OAc)_2$ (2.8 mg, 0.012 mmol), K_2CO_3 (342 mg, 2.476 mmol) and 5-bromothiophene-2-carbaldehyde (177 mg, 0.928 mmol) in water and 1,4-dioxane. The product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate, 6:1, R_f = 0.14), to yield compound **12** as a red solid (167 mg, 0.323 mmol, 52%), mp 95-96 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.67 (d, *J* = 3.9 Hz, 1H), 7.62-7.57 (m, 4H), 7.49 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.44 (d, *J* = 2.1 Hz, 1H), 7.33-7.28 (m, 2H), 7.10-7.05 (m, 2H), 3.91 (t, *J* = 7.0 Hz, 2H), 2.50 (s, 3H), 1.74-1.66 (m, 2H), 1.44-1.35 (m, 2H), 1.29-1.22 (m, 4H), 0.86-0.80 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.8, 151.9, 145.4, 142.9, 141.1, 139.4, 137.1, 135.2, 134.1, 126.7, 126.5 (2C), 126.4 (2C), 125.9, 125.6, 124.7, 124.41, 124.36, 123.9, 123.1, 116.3, 116.0, 46.7, 30.8, 26.1, 25.8, 22.1, 14.7, 13.8; IR (neat, cm^{-1}) ν: 2921 (w), 2851 (w), 1661 (s), 1472 (m), 1437 (s), 1226 (m), 804 (m); HRMS (TOF MS ASAP+, *m/z*): found 516.1489 (calcd. $C_{30}H_{30}NOS_3$: 516.1490, $[M+H]^+$).

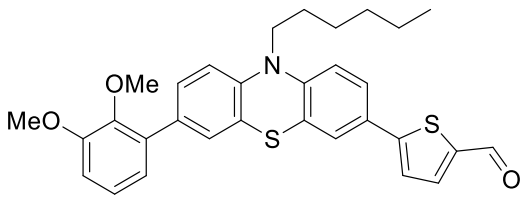
5-(7-(2,4-Dimethoxyphenyl)-10-hexyl-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (13)



The reaction was performed as described in the general procedure for borylation and subsequent Suzuki cross-coupling, starting with compound **4** (280 mg, 0.562 mmol), SPhos (18.5 mg, 0.045 mmol), pinacol borane (108 mg, 0.843 mmol) and dichlorobis(acetonitrile)palladium(II) (2.9 mg, 0.011 mmol), achieving full conversion in 1.5 hours. The crude material (300 mg) was subjected to the above mentioned Suzuki reaction conditions with SPhos (10.9 mg, 0.027 mmol), $Pd(OAc)_2$ (3.8 mg, 0.017 mmol), K_2CO_3 (313 mg, 2.265 mmol) and 5-bromothiophene-2-carbaldehyde (158 mg, 0.825 mmol) in water and 1,4-dioxane. The product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate, 1:10, R_f = 0.20), to yield compound **13** as a red solid (170 mg, 0.321 mmol, 58%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.67 (d, *J* = 4.0 Hz, 1H), 7.62-7.58 (m, 2H), 7.27 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.21-7.18 (m, 2H), 7.07 (d, *J* = 8.6 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 6.64 (d, *J* = 2.5 Hz, 1H), 6.59 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.91 (t, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 1.72-1.70 (m, 2H), 1.41-1.40 (m, 2H), 1.28-1.26 (m, 4H),

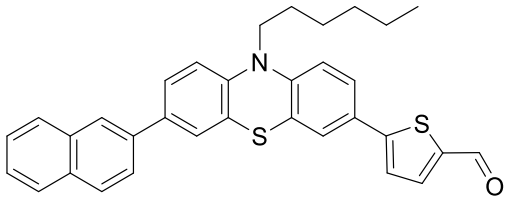
0.85-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.7, 160.0, 157.0, 152.0, 145.6, 142.1, 141.0, 139.4, 132.8, 130.4, 128.5, 127.5, 126.6, 125.8, 124.4, 124.3, 124.1, 121.8, 121.1, 115.9, 114.5, 105.3, 98.9, 55.5, 55.3, 46.6, 30.8, 26.2, 25.8, 22.0, 13.8; IR (neat, cm^{-1}) ν: 2951 (m, br), 2930 (m, br), 2852 (w, br), 1652 (s), 1605 (m), 1434 (s), 1226 (s), 1205 (s), 1060 (s), 795 (s); HRMS (TOF MS ASAP+, *m/z*): found 529.1744 (calcd. $C_{31}H_{31}NO_3S_2$: 529.1745, $[M]^+$).

5-(7-(2,3-Dimethoxyphenyl)-10-hexyl-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (14)



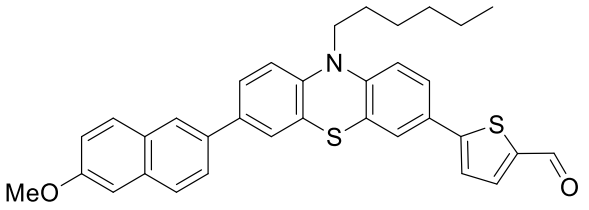
The reaction was performed as described in the general procedure for borylation and subsequent Suzuki cross-coupling, starting with compound **5** (400 mg, 0.802 mmol), SPhos (26.4 mg, 0.064 mmol), pinacol borane (154 mg, 1.204 mmol) and dichlorobis(acetonitrile)palladium(II) (4.2 mg, 0.016 mmol), achieving full conversion in 4 hours. The crude material (438 mg) was subjected to the above mentioned Suzuki reaction conditions with SPhos (13.2 mg, 0.032 mmol), $Pd(OAc)_2$ (3.6 mg, 16.0 μmol), K_2CO_3 (444 mg, 3.21 mmol) and 5-bromothiophene-2-carbaldehyde (230 mg, 1.204 mmol) in water and 1,4-dioxane. The product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate, 20:1, R_f = 0.10), to yield compound **14** as a red solid (106 mg, 0.200 mmol, 25%), mp 89-91 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 8.00 (d, J = 4.1 Hz, 1H), 7.67 (d, J = 3.9 Hz, 1H), 7.63-7.59 (m, 2H), 7.34 (dd, J = 8.4, 1.8 Hz, 1H), 7.25 (d, J = 1.8 Hz, 1H), 7.12-7.07 (m, 3H), 7.05-7.02 (m, 1H), 6.90 (d, J = 7.6 Hz, 1H), 3.93 (t, J = 7.0 Hz, 2H), 3.83 (s, 3H), 3.54 (s, 3H), 1.74-1.70 (m, 2H), 1.44-1.39 (m, 2H), 1.28-1.24 (m, 4H), 0.85-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.7, 152.8, 151.9, 145.8, 145.4, 142.8, 141.1, 139.4, 133.6, 132.5, 128.5, 127.3, 126.7, 125.8, 124.4, 124.3, 124.2, 124.0, 122.0, 121.7, 116.1, 115.6, 112.2, 60.1, 55.8, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2928 (m), 2854 (w), 1657 (s), 1580 (m), 1434 (s), 1258 (m), 1224 (m), 1120 (m), 802 (m), 735 (m); HRMS (TOF MS ASAP+, *m/z*): found 530.1818 (calcd. $C_{31}H_{32}NO_3S_2$: 530.1824, $[M+H]^+$).

5-(10-Hexyl-7-(naphthalen-2-yl)-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (15)



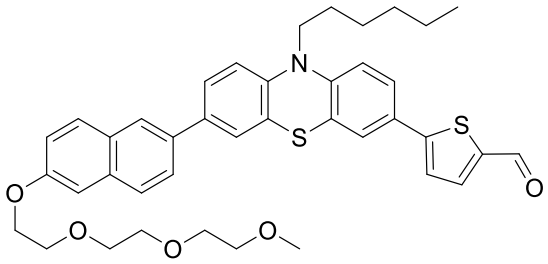
The reaction was performed as described in the general procedure for borylation and subsequent Suzuki cross-coupling, starting with compound **6** (400 mg, 0.819 mmol), SPhos (26.9 mg, 0.066 mmol), pinacol borane (157 mg, 1.228 mmol) and dichlorobis(acetonitrile)palladium(II) (4.3 mg, 0.016 mmol), achieving full conversion in 4.5 hours. The crude material (439 mg) was subjected to the above mentioned Suzuki reaction conditions with SPhos (13.5 mg, 0.033 mmol), $Pd(OAc)_2$ (3.7 mg, 0.016 mmol), K_2CO_3 (453 mg, 3.28 mmol) and 5-bromothiophene-2-carbaldehyde (235 mg, 1.230 mmol) in water and 1,4-dioxane. The product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate, 20:1, R_f = 0.11), to yield compound **15** as a red solid (183 mg, 0.352 mmol, 43%), mp 129-131 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.88 (s, 1H), 8.20 (s, 1H), 8.01 (d, J = 4.0 Hz, 1H), 7.97 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 7.9 Hz, 1H), 7.84 (dd, J = 8.6, 1.3 Hz, 1H), 7.70-7.67 (m, 2H), 7.64-7.61 (m, 3H), 7.55-7.48 (m, 2H), 7.16 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 8.3 Hz, 1H), 3.96 (t, J = 7.0 Hz, 2H), 1.77-1.71 (m, 2H), 1.46-1.40 (m, 2H), 1.30-1.25 (m, 4H), 0.86-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.8, 151.9, 145.4, 143.2, 141.1, 139.4, 136.0, 134.5, 133.3, 132.1, 128.4, 128.1, 127.4, 126.8, 126.4, 126.3, 126.0, 125.9, 125.3, 124.6, 124.43, 124.40 (2C), 123.9, 123.3, 116.4, 116.1, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2913 (w), 2851 (w), 1659 (s), 1580 (m), 1433 (s), 1229 (m), 1057 (m), 801 (s); HRMS (TOF MS ASAP+, *m/z*): found 520.1761 (calcd. $C_{33}H_{30}NOS_2$: 520.1769, $[M+H]^+$).

5-(10-Hexyl-7-(6-methoxynaphthalen-2-yl)-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (16)



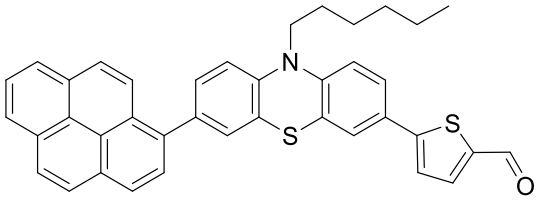
The reaction was performed as described in the general procedure for borylation and subsequent Suzuki cross-coupling, starting with compound **7** (350 mg, 0.675 mmol), SPhos (22.2 mg, 0.054 mmol), pinacol borane (130 mg, 1.013 mmol) and dichlorobis(acetonitrile)palladium(II) (3.5 mg, 0.014 mmol), achieving full conversion in 5 hours. The crude material (382 mg) was subjected to the above mentioned Suzuki reaction conditions with SPhos (11.1 mg, 0.027 mmol), $Pd(OAc)_2$ (3.0 mg, 0.014 mmol), K_2CO_3 (373 mg, 2.70 mmol) and 5-bromothiophene-2-carbaldehyde (194 mg, 1.013 mmol) in water and 1,4-dioxane. The product was purified by silica gel column chromatography (CH_2Cl_2/*n*-pentane, 4:1, R_f = 0.18), to yield compound **16** as a red solid (226 mg, 0.411 mmol, 61%), mp 174-176 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.88 (s, 1H), 8.12 (s, 1H), 8.00 (d, *J* = 3.9 Hz, 1H), 7.89-7.86 (m, 2H), 7.78 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.68 (d, *J* = 3.9 Hz, 1H), 7.65-7.60 (m, 3H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 7.10 (d, *J* = 8.3 Hz, 1H), 3.95 (t, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 1.76-1.70 (m, 2H), 1.45-1.40 (m, 2H), 1.30-1.25 (m, 4H), 0.86-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.8, 157.3, 151.9, 145.4, 142.9, 141.1, 139.4, 134.7, 133.7, 133.4, 129.6, 128.8, 127.3, 126.7, 126.0, 125.9, 125.0, 124.9, 124.42, 124.37, 124.3, 123.9, 123.2, 118.9, 116.3, 116.1, 105.7, 55.2, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2918 (w), 2852 (w), 1661 (s), 1600 (m), 1433 (s), 1372 (m), 1230 (m), 799 (s); HRMS (TOF MS ASAP+, *m/z*): found 550.1869 (calcd. $C_{34}H_{32}NO_2S_2$: 550.1874, $[M+H]^+$).

5-(10-Hexyl-7-(6-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphthalen-2-yl)-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (17)



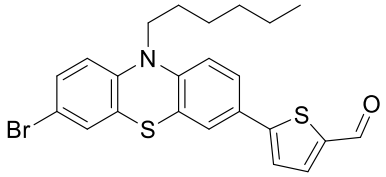
The reaction was performed as described in the general procedure for borylation and subsequent Suzuki cross-coupling, starting with compound **9** (378 mg, 0.581 mmol), SPhos (19.1 mg, 0.046 mmol), pinacol borane (112 mg, 0.871 mmol) and dichlorobis(acetonitrile)palladium(II) (3.0 mg, 0.012 mmol), achieving full conversion in 24 hours. The crude material (405 mg) was subjected to the above mentioned Suzuki reaction conditions with SPhos (9.5 mg, 0.023 mmol), $Pd(OAc)_2$ (2.6 mg, 0.012 mmol), K_2CO_3 (321 mg, 2.322 mmol) and 5-bromothiophene-2-carbaldehyde (166 mg, 0.871 mmol) in water and 1,4-dioxane. The product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate, 3:2, R_f = 0.07), to yield compound **17** as a red oil (216 mg, 0.316 mmol, 55%). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 8.12 (s, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.86-7.83 (m, 1H), 7.78-7.76 (m, 1H), 7.68 (d, *J* = 4.0 Hz, 1H), 7.65-7.60 (m, 3H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 4.24-4.21 (m, 2H), 3.94 (t, *J* = 7.0 Hz, 2H), 3.82-3.81 (m, 2H), 3.63-3.60 (m, 2H), 3.57-3.51 (m, 4H), 3.44-3.41 (m, 2H), 3.23 (s, 3H), 1.76-1.70 (m, 2H), 1.45-1.39 (m, 2H), 1.30-1.24 (m, 4H), 0.86-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.7, 156.5, 151.9, 145.4, 142.9, 141.1, 139.4, 134.7, 133.8, 133.4, 129.7, 128.8, 127.3, 126.7, 126.0, 125.9, 125.0, 124.9, 124.41, 124.36, 124.3, 123.9, 123.2, 119.1, 116.3, 116.0, 106.5, 71.3, 70.0, 69.8, 69.6, 68.9, 67.2, 58.0, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2952 (m), 1725 (w), 1658 (s), 1602 (m), 1434 (s), 1269 (m), 1103 (m), 798 (m); HRMS (TOF MS ASAP+, *m/z*): found 682.2659 (calcd. $C_{40}H_{44}NO_5S_2$: 682.2661, $[M+H]^+$).

5-(10-Hexyl-7-(pyren-1-yl)-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (18)



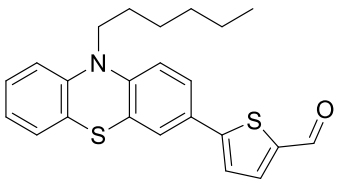
The reaction was performed as described in the general procedure for borylation and subsequent Suzuki cross-coupling, starting with compound **10** (250 mg, 0.444 mmol), SPhos (14.6 mg, 0.036 mmol), pinacol borane (85 mg, 0.667 mmol) and dichlorobis(acetonitrile)palladium(II) (2.3 mg, 8.89 μmol), achieving full conversion in 2 hours. The crude material (271 mg) was subjected to the above mentioned Suzuki reaction conditions with SPhos (7.3 mg, 0.018 mmol), $Pd(OAc)_2$ (2.0 mg, 8.89 μmol), K_2CO_3 (246 mg, 1.778 mmol) and 5-bromothiophene-2-carbaldehyde (127 mg, 0.667 mmol) in water and 1,4-dioxane. The product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate, 3:1, R_f = 0.32), to yield compound **18** as a red solid (153 mg, 0.257 mmol, 58%), mp 122-125 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 9.88 (s, 1H), 8.36-8.26 (m, 3H), 8.22 (s, 2H), 8.19-8.07 (m, 3H), 8.03-7.99 (m, 2H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.67-7.63 (m, 2H), 7.47 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 8.9 Hz, 1H), 4.01 (t, *J* = 6.9 Hz, 2H), 1.84-1.75 (m, 2H), 1.51-1.43 (m, 2H), 1.34-1.24 (m, 4H), 0.89-0.84 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.8, 151.9, 145.5, 143.2, 141.1, 139.4, 135.8, 134.9, 131.0, 130.4, 130.1, 129.9, 128.6, 127.7, 127.6, 127.5, 127.39, 127.35 (2C), 126.9, 126.4, 125.9, 125.3, 125.0, 124.9, 124.5, 124.4, 124.2, 124.0, 122.8, 116.2, 116.0, 54.9, 46.8, 30.8, 26.2, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2923 (w), 1658 (s), 1582 (m), 1433 (s), 1224 (m), 1056 (w), 845 (m); HRMS (TOF MS ASAP+, *m/z*): found 594.1921 (calcd. $C_{39}H_{32}NOS_2$: 594.1925, $[M+H]^+$).

5-(7-Bromo-10-hexyl-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (19)[5]



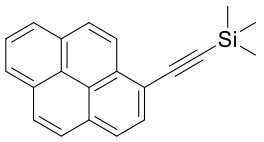
Compound **1** (1.00 g, 2.266 mmol), (5-formylthiophen-2-yl)boronic acid (530 mg, 3.40 mmol), $Pd(OAc)_2$ (10.2 mg, 0.045 mmol), SPhos (37 mg, 0.091 mmol) and K_2CO_3 (1.25 g, 9.07 mmol) were mixed in a Schlenk tube which was sealed with a septum, then evacuated and backflushed with N_2 three times. 1,4-Dioxane (6 mL) and water (6 mL) were degassed and added, and the reaction was stirred at 80 °C for 16 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/EtOAc, 3:1, R_f = 0.38), to yield compound **19** as a red solid (350 mg, 0.741 mmol, 33%), mp 77-78 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 7.99 (d, *J* = 4.0 Hz, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.62-7.57 (m, 2H), 7.37-7.33 (m, 2H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.97 (d, *J* = 9.4 Hz, 1H), 3.86 (t, *J* = 6.9 Hz, 2H), 1.69-1.61 (m, 2H), 1.40-1.32 (m, 2H), 1.26-1.20 (m, 4H), 0.84-0.79 (m, 3H). ^{1}H NMR data are in accordance with that reported by Lin et al.[5]

5-(10-Hexyl-10*H*-phenothiazin-3-yl)thiophene-2-carbaldehyde (20)[6]



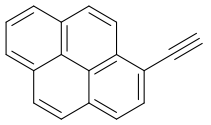
Compound **19** (300 mg, 0.635 mmol), $Pd(OAc)_2$ (2.9 mg, 0.013 mmol), triphenylphosphine (13.3 mg, 0.051 mmol) and K_2CO_3 (176 mg, 1.270 mmol) were mixed in a Schlenk tube which was sealed with a septum, then evacuated and backflushed with N_2 three times. *n*-Butanol (2 mL) was degassed and added, and the reaction was stirred at 100 °C for 2 hours. The crude product was purified by silica gel column chromatography (*n*-pentane/EtOAc, 9:1, R_f = 0.21), to yield compound **20** as a red oil (151 mg, 0.384 mmol, 60%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.87 (s, 1H), 8.00 (d, *J* = 4.0 Hz, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.62-7.57 (m, 2H), 7.24-7.19 (m, 1H), 7.16 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.09-7.03 (m, 2H), 6.99-6.94 (m, 1H), 3.90 (t, *J* = 6.9 Hz, 2H), 1.73-1.64 (m, 2H), 1.43-1.34 (m, 2H), 1.28-1.21 (m, 4H), 0.85-0.79 (m, 3H). ^{1}H NMR data are in accordance with that reported by Huang et al.[6]

Trimethyl(pyren-1-ylethynyl)silane (21)[7]



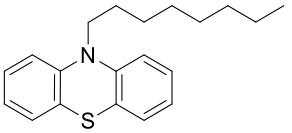
1-Bromopyrene (1.12 g, 4.00 mmol), ethynyltrimethylsilane (480 mg, 0.70 mL, 4.95 mmol), $Pd(PPh_3)_2Cl_2$ (347 mg, 0.494 mmol), CuI (42 mg, 0.221 mmol) were mixed with dry Et_3N (60 mL) and stirred at 85 °C for 24 hours under nitrogen. The reaction mixture was quenched with distilled water (100 mL) and extracted with CH_2Cl_2 (3 × 60 mL). The combined organic phase was dried with brine (50 mL) and over anhydrous Na_2SO_4 and filtered. The solvent was removed and the crude product was purified using column chromatography (*n*-pentane, R_f = 0.20). The product **21** was obtained as a yellow solid (851 mg, 2.850 mmol, 71%), mp 100-103 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.32-8.28 (m, 1H), 8.22-8.17 (m, 3H), 8.12-8.07 (m, 2H), 8.05-7.97 (m, 3H), 0.37 (s, 9H). ^{1}H NMR analysis of **19** in $CDCl_3$ was in accordance with previously reported values.[7]

1-Ethynylpyrene (22)[7]



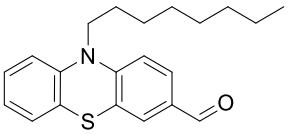
Compound **21** (1.00 g, 3.35 mmol), potassium carbonate (1.41 g, 10.2 mmol), MeOH (17 mL) and THF (40 mL) were mixed at room temperature for 1 hours. The reaction mixture was quenched with water (50 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was washed with water (50 mL) before it was dried with brine (50 mL) and then over anhydrous Na_2SO_4. The solvent was removed after filtration and the crude product was purified using column chromatography (*n*-pentane, R_f = 0.21). The product **22** was a brown solid (627 mg, 2.77 mmol, 82%), mp 112-113 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.49 (d, *J* = 9.1 Hz, 1H), 8.40-8.34 (m, 3H), 8.29 (d, *J* = 9.3 Hz, 1H), 8.27 (d, *J* = 10.4 Hz, 1H), 8.24-8.19 (m, 2H), 8.14 (t, *J* = 7.6 Hz, 1H), 4.81 (s, 1H). ^{1}H NMR analysis of **22** in $CDCl_3$ was in accordance with previously reported values.[7]

10-Octyl-10*H*-phenothiazine (23)[8]



10*H*-Phenothiazine (5.08 g, 25.5 mmol) and sodium hydride (0.91 g, 37.9 mmol) were mixed and nitrogen atmosphere was established. Dry, degassed THF (85 mL) was added and the mixture was stirred at room temperature until the color changed from green to yellow. 1-Bromooctane (3.9 mL, 22.6 mmol) was added dropwise using a syringe pump over 20 minutes, after which the reaction mixture was heated at reflux for 5 hours. A 5% aqueous sol. of NH_4Cl (50 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 50 mL). The combined organic layer was dried with brine (50 mL) and over anhydrous Na_2SO_4. Solvents was removed under reduced pressure. The crude product was purified using column chromatography (*n*-pentane, R_f = 0.21). The product **23** was a colourless liquid (6.47 g, 19.1 mmol, 84%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.18-7.13 (m, 2H), 7.11 (dd, *J* = 7.6, 1.5 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.89 (td, *J* = 7.4, 0.9 Hz, 2H), 3.80 (t, *J* = 6.9 Hz, 2H), 1.68-1.59 (m, 2H), 1.36-1.28 (m, 2H), 1.22–1.10 (m, 8H), 0.81-0.76 (m, 3H). ^{1}H NMR analysis of **23** in $CDCl_3$ was in accordance with previously reported values.[8]

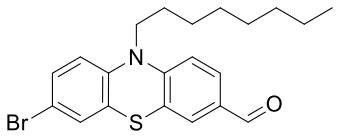
10-Octyl-10*H*-phenothiazine-3-carbaldehyde (24)[9]



Compound **23** (6.14 g, 19.7 mmol) was dissolved in DMF (6.00 mL, 5.68 g, 77.8 mmol) and 1,2-dichloroethene (120 mL). The mixture was cooled using an ice bath. $POCl_3$ (7.00 mL, 74.9 mmol) was added to the reaction mixture using a syringe pump over 45 minutes. The reaction was heated to reflux and left to stir over night. The reaction mixture was quenched with water and extracted with $CHCl_3$ (3 × 100 mL). The combined organic layer was washed with water (100 mL) and then dried with brine (100 mL) and over anhydrous Na_2SO_4. Solvents were removed *in vacuo* and the product purified using column chromatography (*n*-pentane/ethyl acetate 6:1, R_f = 0.45). This gave **24 as** a yellow liquid (4.84 g, 14.2 mmol, 72%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.78 (s, 1H), 7.70 (dd, *J* = 6.4, 1.9 Hz, 1H), 7.58 (d, *J* =

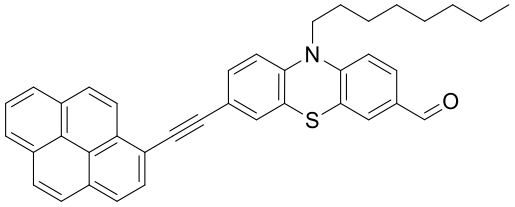
2.0 Hz, 1H), 7.24-7.19 (m, 1H), 7.16-7.12 (m, 2H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.99 (td, *J* = 7.5, 0.9 Hz, 1H), 3.92 (t, *J* = 6.9 Hz, 2H), 1.70-1.62 (m, 2H), 1.40-1.31 (m, 2H), 1.24–1.14 (m, 8H), 0.82-0.77 (m, 3H). ^{1}H NMR analysis of **24** in $CDCl_3$ was in accordance with previously reported values.[9]

7-Bromo-10-octyl-10*H*-phenothiazine-3-carbaldehyde (25)[10]



Compound **24** (1.01 g, 2.97 mmol) was dissolved in dry THF (100 mL) and cooled in an ice bath. NBS (0.84 g, 4.72 mmmol) was added, and the reaction mixture was left to stir in room temperature for 2 days. The reaction mixture was quenched with water (100 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with water (100 mL) and then dried with brine (100 mL) and over anhydrous Na_2SO_4. The crude product was purified using column chromatography (ethyl acetate, R_f = 0.70). The product **25** was obtained as a brown oil (1.17 g, 2.80 mmol, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.79 (s, 1H), 7.72 (dd, *J* = 6.6, 2.1 Hz, 1H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.38–7.34 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.02–6.98 (m, 1H), 3.90 (t, *J* = 6.8 Hz, 2H), 1.69-1.60 (m, 2H), 1.39-1.31 (m, 2H), 1.25–1.15 (m, 8H), 0.83-0.77 (m, 3H); HRMS TOF MS ASAP+, *m/z*): found 418.0839 (calcd. $C_{21}H_{25}NOSBr$: 418.0840, $[M+H]^+$). ^{1}H NMR analysis of **25** in $CDCl_3$ was in accordance with previously reported values.[10]

10-Octyl-7-(pyren-1-ylethynyl)-10*H*-phenothiazine-3 -carbaldehyde (26)[11]

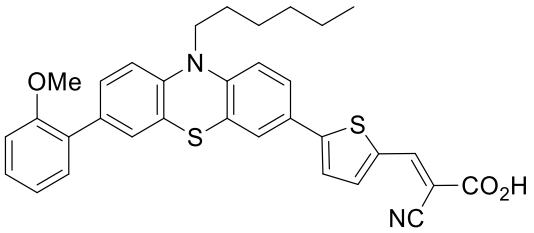


Compound **25** (196 mg, 0.469 mmol), compound **20** (206 mg, 0.912 mmol), $Pd(PPh_3)_2Cl_2$ (49 mg, 0.691 mmol), and CuI (10 mg, 0.050 mmol) were mixed with dry triethylamine (7.5 mL), and heated (80 °C) for 24 hours under nitrogen atmosphere. The reaction mixture was quenched with distilled water (15 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried with with brine (15 mL) and then over anhydrous Na_2SO_4 and filtered. The solvent was removed and the crude product was purified using column chromatography (*n*-pentane/ethyl acetate 8:7, R_f = 0.41). The product **26** was obtained as an orange solid (172 mg, 0.306 mmol, 65%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.82 (s, 1H), 8.63 (d, *J* = 9.2 Hz, 1H), 8.42–8.21 (m, 7H), 8.14 (t, *J* = 7.7 Hz, 1H), 7.76 (dd, *J* = 6.6, 1.9 Hz, 1H), 7.67–7.58 (m, 3H), 7.24–7.17 (m, 2H), 4.01 (t, *J* = 6.9 Hz, 2H), 1.77-1.69 (m, 2H), 1.46-1.37 (m, 2H), 1.30–1.20 (m, 8H), 0.86-0.80 (m, 3H); HRMS (TOF MS ASAP+, *m/z*): found 564.2361 (calcd. $C_{39}H_{34}NOS$: 564.2350, $[M+H]^+$). ^{1}H NMR analysis of **26** was in accordance with previously reported values.[11]

General procedure for Knoevenagel condensation

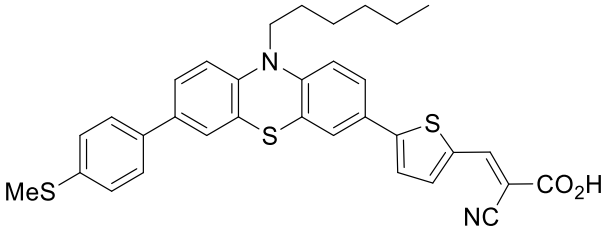
The aldehyde (1 eq.) was mixed with cyanoacetic acid (20 eq.) and dissolved in degassed acetonitrile under nitrogen atmosphere, then piperidine (12 eq.) was added, and the mixture was refluxed until full conversion. The reaction was quenched with HCl (2 M, 100-150 mL) before ethyl acetate was added, the phases separated and the aqueous was washed with water (5 × 200 mL). The organic phase was dried with brine (50 mL) and over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was further purified by silica gel column chromatography.

(*E*)-2-Cyano-3-(5-(10-hexyl-7-(2-methoxyphenyl)-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-12)



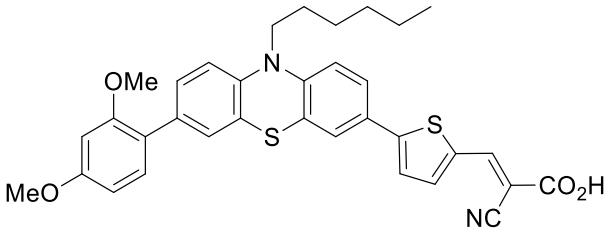
The synthesis was performed according to the general procedure, starting with compound **11** (200 mg, 0.400 mmol) and cyanoacetic acid (681 mg, 8.01 mmol) and piperidine (409 mg, 4.80 mmol) in acetonitrile (48 mL) for 2 hours. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield compound **AFB-12** as a dark red solid (190 mg, 0.335 mmol, 84%), mp 160-163 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.66 (s, 1H), 8.42 (s, 1H), 7.95 (d, J = 3.9 Hz, 1H), 7.69 (d, J = 4.1 Hz, 1H), 7.60-7.57 (m, 2H), 7.34-7.30 (m, 2H), 7.28 (dd, J = 7.5, 1.6 Hz, 1H), 7.26 (d, J = 2.0 Hz, 1H), 7.11-7.07 (m, 3H), 7.00 (t, J = 7.3 Hz, 1H), 3.93 (t, J = 7.3 Hz, 2H), 3.77 (s, 3H), 1.75-1.70 (m, 2H), 1.45-1.40 (m, 2H), 1.30-1.25 (m, 4H), 0.86-0.83 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 165.6, 163.6, 156.0, 145.6, 145.5, 142.5, 141.1, 134.0, 132.9, 129.9, 128.8, 128.7, 128.4, 127.7, 126.6, 125.8, 124.3, 124.2, 124.1, 121.8, 120.8, 116.1, 115.8, 115.5, 111.7, 55.5, 46.7, 30.8, 26.2, 25.8, 24.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2951 (m), 2930 (m), 2841 (m), 2577 (w), 2499 (w), 2213 (w), 1730 (w), 1678 (m), 1553 (s), 1397 (s), 1242 (s), 1221 (s), 1060 (s), 805 (s); HRMS (TOF MS ASAP+, *m/z*): found 522.1798 (calcd. $C_{32}H_{30}N_2OS_2$: 522.1800, $[M\text{-}CO_2]^+$); UV (THF, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 459 (19050 M^{-1} cm^{-1}).

(*E*)-2-Cyano-3-(5-(10-hexyl-7-(4-(methylthio)phenyl)-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-13)



The synthesis was performed according to the general procedure, starting with compound **12** (150 mg, 0.291 mmol) and cyanoacetic acid (495 mg, 5.82 mmol) and piperidine (297 mg, 3.49 mmol) in acetonitrile (35 mL) for 3 hours. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield compound **AFB-13** as a dark red solid (115 mg, 0.197 mmol, 68%), mp 253 °C (dec.). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.19 (s, 1H), 7.74 (d, J = 4.1 Hz, 1H), 7.59-7.55 (m, 3H), 7.52-7.45 (m, 3H), 7.42 (d, J = 2.2 Hz, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.04 (t, J = 8.5 Hz, 2H), 3.87 (t, J = 6.7 Hz, 2H), 2.49 (s, 3H), 1.72-1.63 (m, 2H), 1.42-1.33 (m, 2H), 1.27-1.20 (m, 4H), 0.84-0.79 (m, 3H) (COO<u>H</u> proton not visible); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.9, 148.3, 144.9, 143.0, 141.7, 137.2, 137.1, 135.2, 135.1, 134.0, 127.1, 126.45 (2C), 126.38 (2C), 125.6, 125.5, 124.7, 124.0, 123.9, 123.8, 123.2, 118.8, 116.2, 116.1, 106.7, 46.7, 30.8, 26.1, 25.8, 22.1, 14.7, 13.8; IR (neat, cm^{-1}) ν: 3395 (br), 2952 (w), 2920 (w), 2852 (w), 2215 (w), 1574 (m), 1470 (m), 1386 (s), 1248 (s), 800 (s); HRMS (TOF-ESI negative mode, *m/z*): found 581.1392 (calcd. $C_{33}H_{29}N_2O_2S_2$: 581.1391, $[M\text{-}H]^-$); UV (THF, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 442 (23250 M^{-1} cm^{-1}).

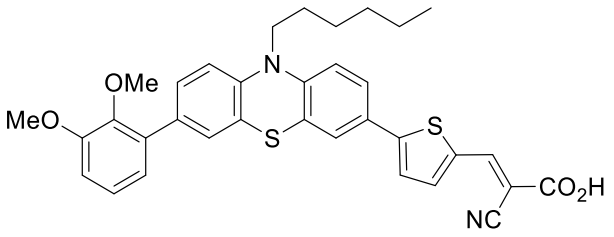
(*E*)-2-Cyano-3-(5-(7-(2,4-dimethoxyphenyl)-10-hexyl-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-14)



The synthesis was performed according to the general procedure, starting with compound **13** (170 mg, 0.321 mmol) and cyanoacetic acid (546 mg, 6.42 mmol) and piperidine (328 mg, 3.85 mmol) in acetonitrile (38 mL) for 1.5 hours. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield compound **AFB-14** as a dark red

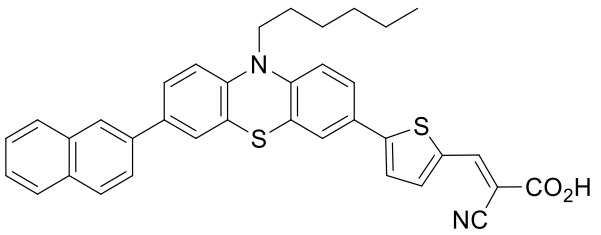
solid (121 mg, 0.202 mmol, 63%), mp 200 °C (dec.). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.83 (s, 1H), 8.38 (s, 1H), 7.91 (d, *J* = 3.8 Hz, 1H), 7.66 (d, *J* = 4.0 Hz, 1H), 7.59-7.55 (m, 2H), 7.27 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.21-7.18 (m, 2H), 7.08 (d, *J* = 8.6 Hz, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.64 (d, *J* = 2.3 Hz, 1H), 6.59 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.91 (t, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 1.74-1.69 (m, 2H), 1.43-1.39 (m, 2H), 1.28-1.23 (m, 4H), 0.85-0.83 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.6, 160.0, 157.0, 151.1, 145.6, 145.1, 142.1, 140.4, 134.1, 132.8, 130.4, 128.5, 127.5, 126.6, 125.8, 124.3, 124.14, 124.10, 121.8, 121.1, 117.2, 116.0, 115.5, 105.3, 99.9, 98.9, 55.5, 55.3, 46.6, 30.8, 26.2, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2956 (w), 2930 (m), 2842 (w), 2358 (m), 2213 (w), 1673 (m), 1610 (m), 1558 (s), 1397 (s), 1241 (s), 1205 (s), 1158 (s), 1070 (s), 800 (s); HRMS (TOF MS ASAP+, *m/z*): found 552.1904 (calcd. $C_{33}H_{32}N_2O_2S_2$: 552.1905, $[M\text{-}CO_2]^+$); UV (THF, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 457 (22600 M^{-1} cm^{-1}).

(*E*)-2-Cyano-3-(5-(7-(2,3-dimethoxyphenyl)-10-hexyl-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-15)



The synthesis was performed according to the general procedure, starting with compound **14** (140 mg, 0.264 mmol) and cyanoacetic acid (450 mg, 5.29 mmol) and piperidine (270 mg, 3.17 mmol) in acetonitrile (31 mL) for 1 hour. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield compound **AFB-15** as a dark red solid (122 mg, 0.204 mmol, 77%), mp 183-186 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.24 (s, 1H), 7.80 (d, *J* = 3.5 Hz, 1H), 7.61 (d, *J* = 3.8 Hz, 1H), 7.56-7.53 (m, 2H), 7.34 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.12-7.07 (m, 3H), 7.05-7.02 (m, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 3.92 (t, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 3.54 (s, 3H), 1.75-1.70 (m, 2H), 1.44-1.39 (m, 2H), 1.30-1.25 (m, 4H), 0.85-0.82 (m, 3H) (COO<u>H</u> proton not visible); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.5, 152.8, 149.3, 145.8, 145.1, 142.9, 138.4, 134.8, 133.6, 132.4, 128.4, 127.3, 127.0, 125.6, 124.2, 124.15, 124.06, 123.9, 122.1, 121.7, 118.2, 116.1, 115.6, 112.2, 60.1, 55.8, 54.9, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8 (one ^{13}C shift missing); IR (neat, cm^{-1}) ν: 2954 (w), 2214 (w), 1716 (w), 1574 (s), 1464 (m), 1391 (s), 1254 (s), 798 (m), 742 (m); HRMS (TOF MS ASAP+, *m/z*): 553.1984 (calcd. $C_{33}H_{33}N_2O_2S_2$: found 553.1982, $[M\text{-}CO_2+H]^+$); UV (THF, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 443 (22600 M^{-1} cm^{-1}).

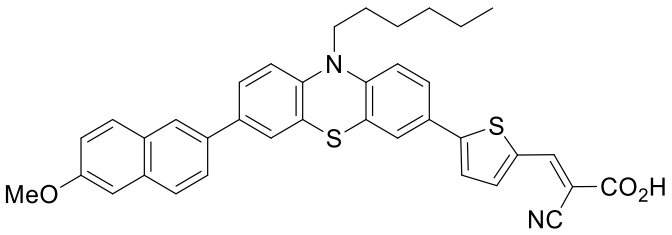
(*E*)-2-Cyano-3-(5-(10-hexyl-7-(naphthalen-2-yl)-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-16)



The synthesis was performed according to the general procedure, starting with compound **15** (135 mg, 0.260 mmol) and cyanoacetic acid (442 mg, 5.20 mmol) and piperidine (265 mg, 3.12 mmol) in acetonitrile (31 mL) for 1.5 hours. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield compound **AFB-16** as a dark red solid (86 mg, 0.147 mmol, 56%), mp 211-213 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.84 (s, 1H), 8.39 (s, 1H), 8.20 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.94-7.90 (m, 2H), 7.83 (d, *J* = 8.7 Hz, 1H), 7.69-7.65 (m, 2H), 7.62 (s, 1H), 7.60-7.57 (m, 2H), 7.55-7.48 (m, 2H), 7.15 (d, *J* = 8.7 Hz, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 3.95 (t, *J* = 3.8 Hz, 2H), 1.76-1.70 (m, 2H), 1.45-1.40 (m, 2H), 1.30-1.24 (m, 4H), 0.86-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 165.5, 163.6, 151.1, 145.3, 143.1, 140.5, 136.0, 134.5, 134.1, 133.3, 132.1, 128.4, 128.1, 127.4, 126.8, 126.4, 126.3, 125.9, 125.8, 125.3, 124.6, 124.4, 124.3, 124.2, 124.0, 123.2, 117.1, 116.4, 116.2, 116.0, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 3051 (m), 2487 (w, br), 2216 (m), 1681 (m), 1557 (s), 1360 (s), 1212 (m), 1061 (m), 796 (m); HRMS (TOF

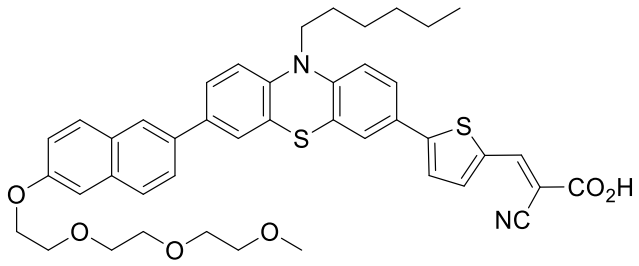
MS ASAP+, *m/z*): found 543.1928 (calcd. $C_{35}H_{31}N_2S_2$: 543.1929, $[M\text{-}CO_2+H]^+$); UV (THF, 2×10^{-5} M, 22 °C) λ_{max} (nm): 455 (21350 M^{-1} cm^{-1}).

(*E*)-2-Cyano-3-(5-(10-hexyl-7-(6-methoxynaphthalen-2-yl)-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-17)



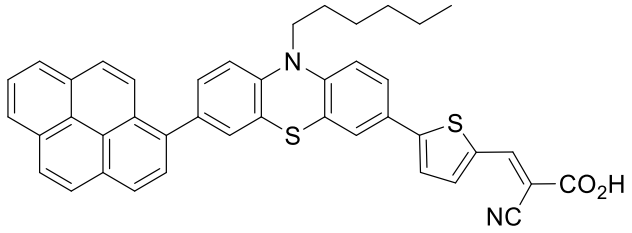
The synthesis was performed according to the general procedure, starting with compound **16** (150 mg, 0.273 mmol) and cyanoacetic acid (464 mg, 5.46 mmol) and piperidine (279 mg, 3.27 mmol) in acetonitrile (33 mL) for 1.5 hours. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield compound **AFB-17** as a dark red solid (110 mg, 0.178 mmol, 65%), mp 218-224 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.89 (s, 1H), 8.28 (s, 1H), 8.12 (s, 1H), 7.90-7.86 (m, 2H), 7.84 (d, *J* = 3.5 Hz, 1H), 7.77 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.66-7.62 (m, 2H), 7.59-7.55 (m, 3H), 7.33 (d, *J* = 2.2 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 7.11-7.09 (m, 1H), 3.94 (t, *J* = 6.9 Hz, 2H), 3.89 (s, 3H), 1.76-1.71 (m, 2H), 1.45-1.40 (m, 2H), 1.30-1.24 (m, 4H), 0.86-0.82 (m, 3H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.5, 157.3, 149.8, 145.2, 143.7, 142.9, 139.0, 134.7, 134.6, 133.7, 133.4, 129.6, 128.8, 127.3, 126.9, 126.0, 125.7, 125.0, 124.9, 124.3, 124.2, 124.0, 123.9, 123.2, 122.8, 118.9, 117.9, 116.3, 116.1, 105.7, 55.2, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8; IR (neat, cm^{-1}) ν: 2921 (w, br), 2853 (w, br), 2216 (w), 1564 (s), 1392 (s), 1243 (s), 1064 (m), 797 (m); HRMS (TOF MS ASAP+, *m/z*): found 573.2028 (calcd. $C_{36}H_{33}N_2OS_2$: 573.2034, $[M\text{-}CO_2+H]^+$); UV (THF, 2×10^{-5} M, 22 °C) λ_{max} (nm): 450 (19850 M^{-1} cm^{-1}).

(*E*)-2-Cyano-3-(5-(10-hexyl-7-(6-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)naphthalen-2-yl)-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-18)



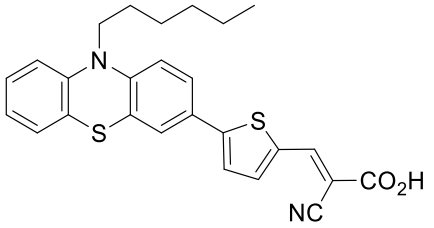
The synthesis was performed according to the general procedure, starting with compound **17** (160 mg, 0.235 mmol) and cyanoacetic acid (399 mg, 4.69 mmol) and piperidine (240 mg, 2.82 mmol) in acetonitrile (28 mL) for 1.5 hours. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield compound **AFB-18** as a dark red solid (136 mg, 0.182 mmol, 77%), mp 200-202 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.18 (s, 1H), 8.12 (s, 1H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.78-7.75 (m, 2H), 7.63 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.61 (d, *J* = 3.9 Hz, 1H), 7.59-7.57 (m, 1H), 7.56-7.53 (m, 2H), 7.34 (d, *J* = 1.6 Hz, 1H), 7.19 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 7.09 (d, *J* = 9.2 Hz, 1H), 4.24-4.21 (m, 2H), 3.94 (t, *J* = 6.8 Hz, 2H), 3.83-3.80 (m, 2H), 3.63-3.61 (m, 2H), 3.57-3.55 (m, 2H), 3.54-3.51 (m, 2H), 3.44-3.41 (m, 2H), 3.23 (s, 3H), 1.76-1.69 (m, 2H), 1.45-1.39 (m, 2H), 1.31-1.25 (m, 4H), 0.86-0.82 (m, 3H) (COO<u>H</u> proton not visible); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.1, 156.6, 145.0, 142.9, 141.8, 137.5, 135.1, 134.7, 133.8, 133.4, 129.7, 128.8, 127.3, 127.1, 126.8, 126.0, 125.6, 125.0, 124.9, 124.3, 124.1, 124.0, 123.9, 123.3, 119.1, 118.6, 116.3, 116.1, 106.5, 71.3, 70.0, 69.8, 69.6, 68.9, 67.2, 58.0, 46.7, 30.8, 26.1, 25.8, 22.1, 13.8. IR (neat, cm^{-1}) ν: 2914 (w), 2212 (w), 1713 (w), 1574 (s), 1435 (m), 1360 (s), 1243 (s), 1103 (m), 797 (s); HRMS (TOF MS ASAP+, *m/z*): found 705.2813 (calcd. $C_{42}H_{45}N_2O_4S_2$: 705.2821, $[M\text{-}CO_2+H]^+$); UV (THF, 2×10^{-5} M, 22 °C) λ_{max} (nm): 437 (20200 M^{-1} cm^{-1}).

(*E*)-2-Cyano-3-(5-(10-hexyl-7-(pyren-1-yl)-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-19)



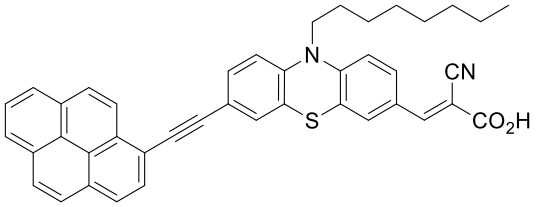
The synthesis was performed according to the general procedure, starting with compound **18** (120 mg, 0.202 mmol) and cyanoacetic acid (344 mg, 4.04 mmol) and piperidine (206 mg, 2.425 mmol) in acetonitrile (24 mL) for 2 hours. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield compound **AFB-19** as a dark red solid (101 mg, 0.154 mmol, 76%), mp 198-203 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.34-8.22 (m, 4H), 8.20 (s, 2H), 8.17-8.10 (m, 2H), 8.08 (t, J = 7.6 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 4.0 Hz, 1H), 7.62 (d, J = 4.0 Hz, 1H), 7.59-7.55 (m, 2H), 7.45 (dd, J = 8.1, 1.9 Hz, 1H), 7.40 (d, J = 1.9 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 7.12 (d, J = 9.1 Hz, 1H), 3.97 (t, J = 6.7 Hz, 2H), 1.81-1.72 (m, 2H), 1.48-1.40 (m, 2H), 1.34-1.21 (m, 4H), 0.87-0.81 (m, 3H) (COOH proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.5, 149.2, 145.1, 143.3, 142.8, 138.2, 135.9, 134.9, 131.0, 130.4, 130.1, 129.9, 128.6, 127.7, 127.6, 127.5, 127.40, 127.39, 127.2, 126.4, 125.7, 125.4, 125.0 (2C), 124.6, 124.25, 124.19, 124.1 (2C), 124.0, 122.9, 118.4, 116.2, 115.9, 105.2, 46.8, 30.9, 26.2, 25.9, 22.1, 13.9; IR (neat, cm^{-1}) ν: 2946 (w), 2855 (w), 2210 (w), 1715 (m), 1574 (s), 1404 (s), 1215 (s), 1131 (s), 1064 (s), 846 (m); HRMS (TOF MS ASAP+, *m/z*): found 617.2076 (calcd. $C_{41}H_{33}N_2S_2$: 617.2085, [M-CO_2+H]$^+$); UV (THF, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 441 (24450 M^{-1} cm^{-1}).

(*E*)-2-Cyano-3-(5-(10-hexyl-10*H*-phenothiazin-3-yl)thiophen-2-yl)acrylic acid (AFB-20)[12]



The synthesis was performed according to the general procedure, starting with compound **20** (115 mg, 0.292 mmol) and cyanoacetic acid (497 mg, 5.84 mmol) and piperidine (299 mg, 3.51 mmol) in acetonitrile (35 mL) for 30 min. The crude product was purified by silica gel column chromatography (gradient: 0-20% MeOH in CH_2Cl_2) to yield compound **AFB-20** as a dark red solid (113 mg, 0.245 mmol, 84%), mp 190 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.21 (s, 1H), 7.76 (d, J = 3.9 Hz, 1H), 7.59 (d, J = 3.9 Hz, 1H), 7.54-7.49 (m, 2H), 7.24-7.18 (m, 1H), 7.17-7.13 (m, 1H), 7.07-7.01 (m, 2H), 6.99-6.93 (m, 1H), 3.88 (t, J = 6.8 Hz, 2H), 1.72-1.63 (m, 2H), 1.42-1.33 (m, 2H), 1.27-1.20 (m, 4H), 0.85-0.78 (m, 3H) (COOH proton not visible); UV (THF, 2 × 10^{-5} M, 22 °C) λ_{max} (nm): 436 (20050 M^{-1} cm^{-1}). ^{1}H NMR data are in accordance with that reported by Yang et al.[12]

2-Cyano-3-(10-octyl-7-(pyren-1-ylethynyl)-10*H*-phenothiazin-3-yl)acrylic acid (Dye 2)[11]



The synthesis was performed according to the general procedure, starting with compound **26** (150 mg, 0.266 mmol) and cyanoacetic acid (453 mg, 5.32 mmol) and piperidine (272 mg, 3.19 mmol) in acetonitrile (32 mL) for 18 hours. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2) to yield sensitizer **Dye 2** as a dark red solid (109 mg, 0.172 mmol, 65%), mp 198 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.61 (d, J = 9.3 Hz, 1H), 8.40–8.18 (m, 7H), 8.12 (t, J = 7.6 Hz, 1H), 7.92 (s, 1H), 7.79 (dd, J = 7.0, 1.7 Hz, 1H), 7.70 (d, J = 1.73 Hz, 1H), 7.60–7.54 (m, 2H), 7.12 (t, J = 7.8 Hz, 2H), 3.93 (t, J = 6.6 Hz, 2H), 1.73-1.64 (m, 2H), 1.42-1.34 (m, 2H), 1.29–1.14 (m, 9H), 0.83-0.77 (m, 3H) (COOH proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.0, 147.7, 146.7, 144.3, 131.8, 131.4, 131.2, 131.2, 130.5, 130.2, 129.9, 129.2, 128.7, 128.4, 128.0, 127.7, 127.2, 126.4 (2C), 125.4 (2C), 124.1, 123.9, 123.4, 123.1, 119.5, 117.4 (2C), 116.6 (2C), 95.0, 89.0, 47.3, 31.6, 29.0, 28.9, 26.5, 26.4, 22.5, 14.1; IR (neat, cm^{-1}) ν: 2915 (m), 2846 (m), 2212 (w), 1356 (s),

1272 (s), 806 (s), 714 (s); HRMS (TOF-ESI negative mode, *m/z*): found 629.2263 (calcd. $C_{42}H_{33}N_2O_2S$: 629.2256, $[M-H]^-$). ^1H and ^{13}C NMR analysis of **Dye 2** is in accordance with previously reported values.[11]

NMR
AFB-12

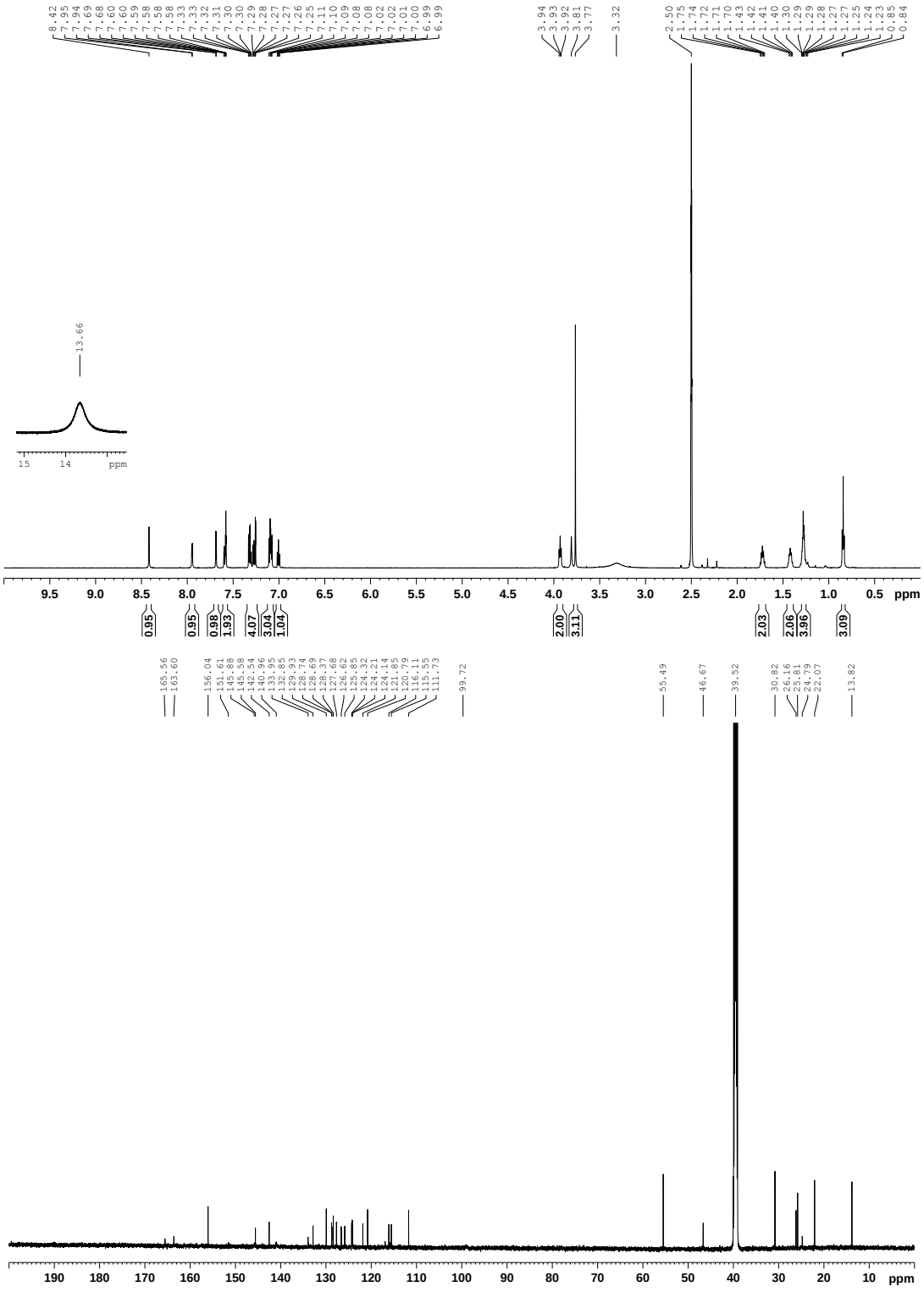


Figure S7. *^{1}H and ^{13}C NMR spectra for* ***AFB-12****.*

AFB-13

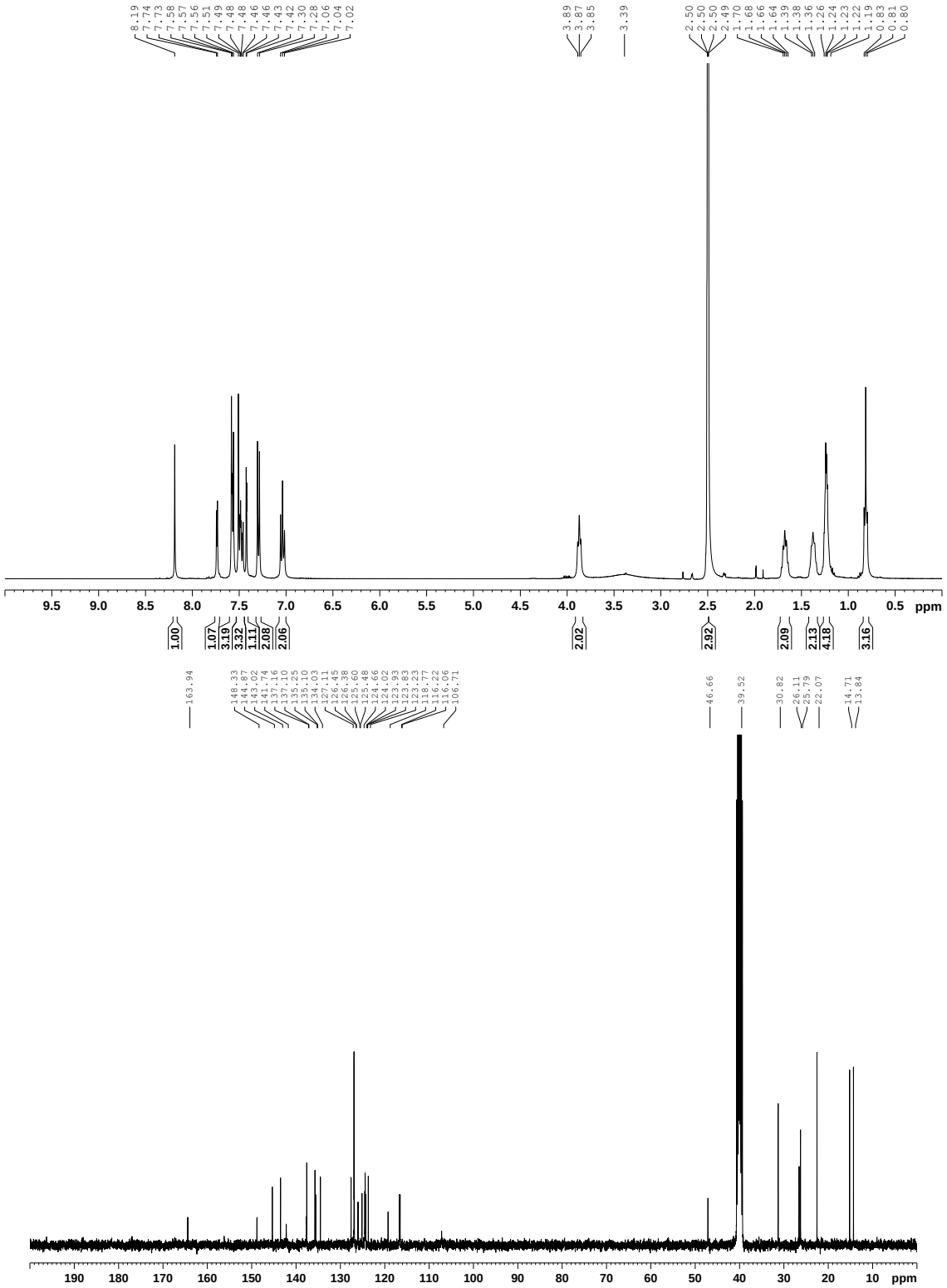


Figure S8. *^{1}H and ^{13}C NMR spectra for* ***AFB-13****.*

AFB-14

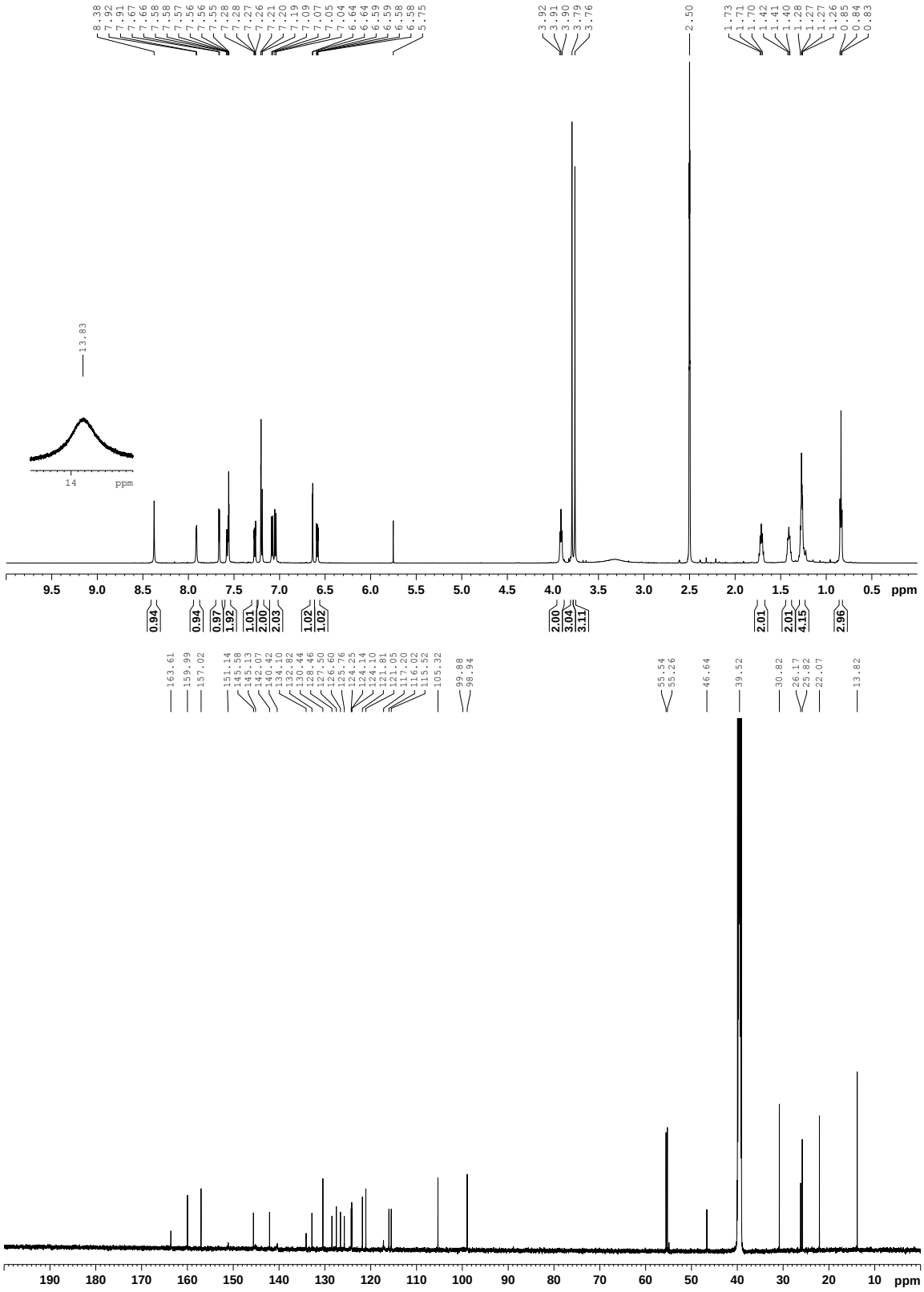


Figure S9. *^{1}H and ^{13}C NMR spectra for* ***AFB-14****.*

AFB-15

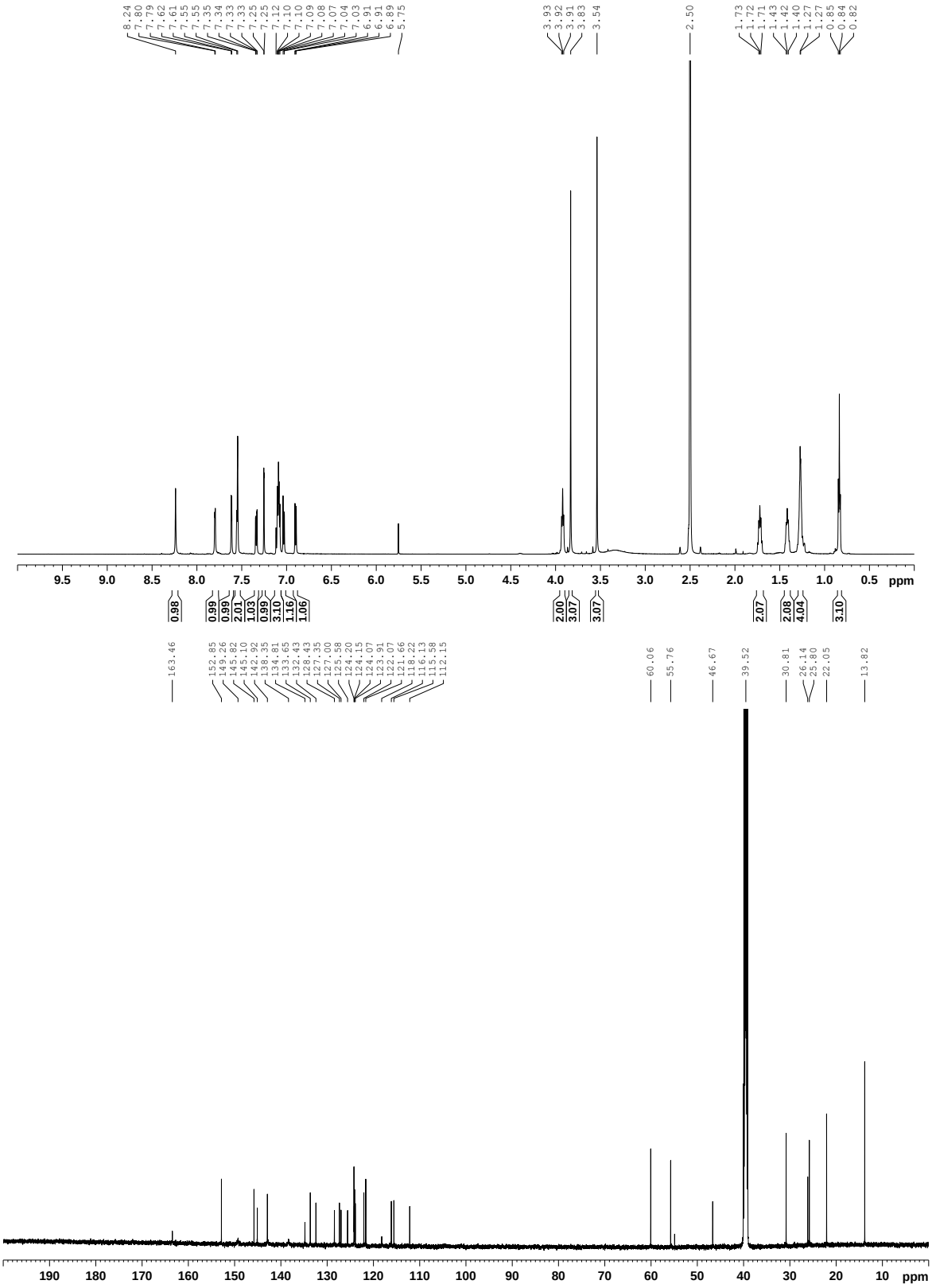


Figure S10. *^{1}H and ^{13}C NMR spectra for* ***AFB-15****.*

AFB-16

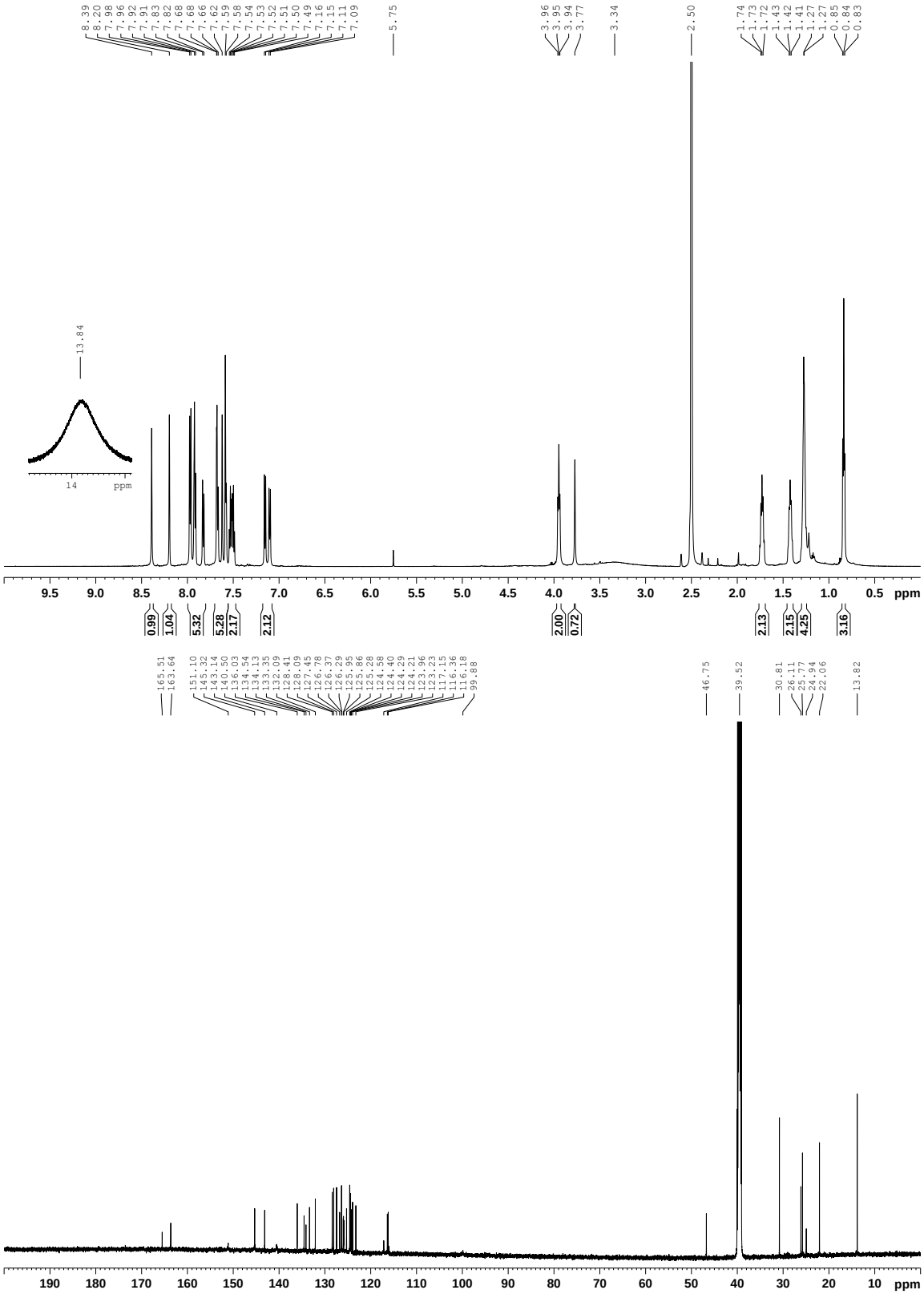


Figure S11. *^{1}H and ^{13}C NMR spectra for* ***AFB-16****.*

AFB-17

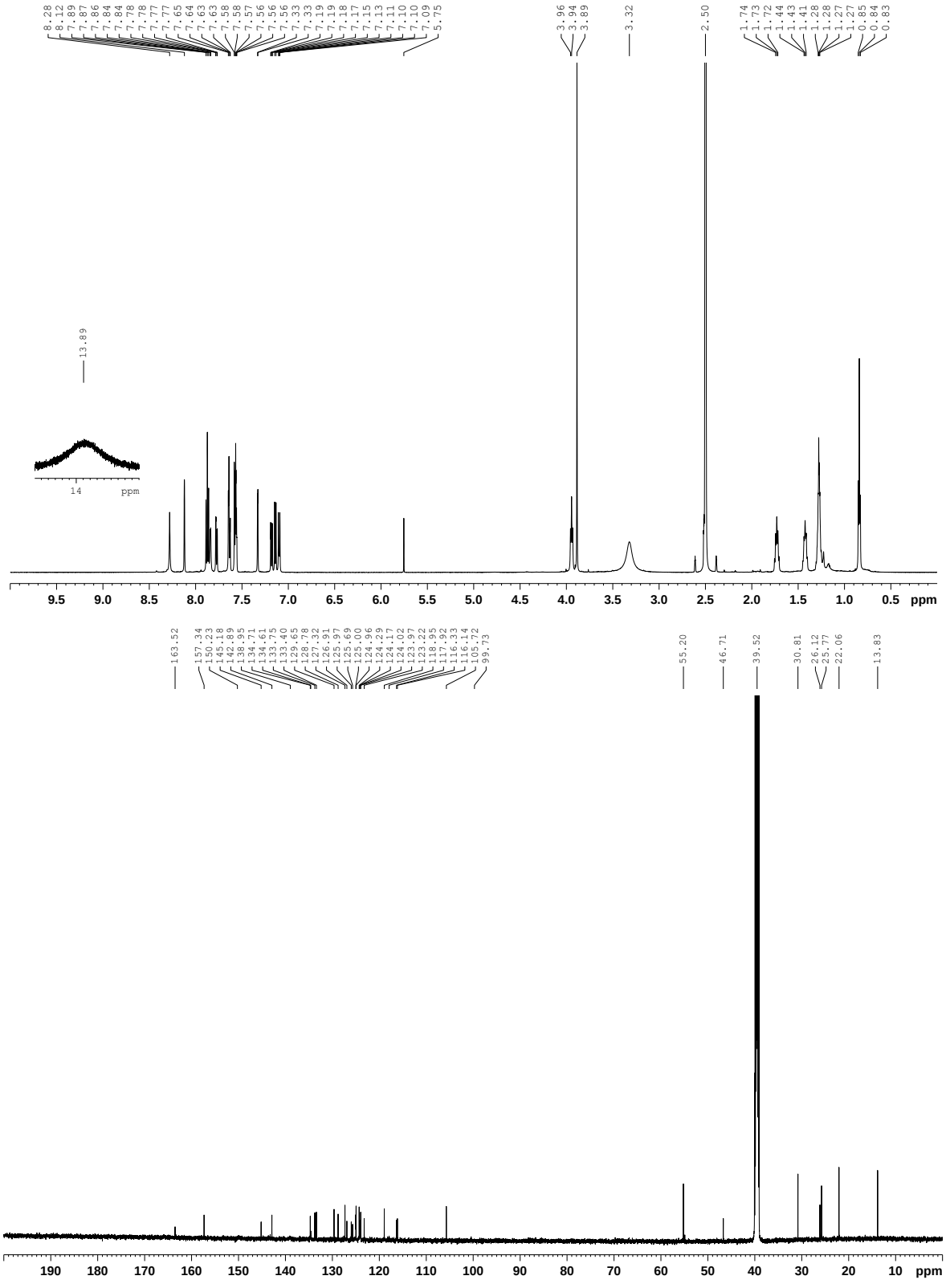


Figure S12. *^{1}H and ^{13}C NMR spectra for* ***AFB-17****.*

AFB-18

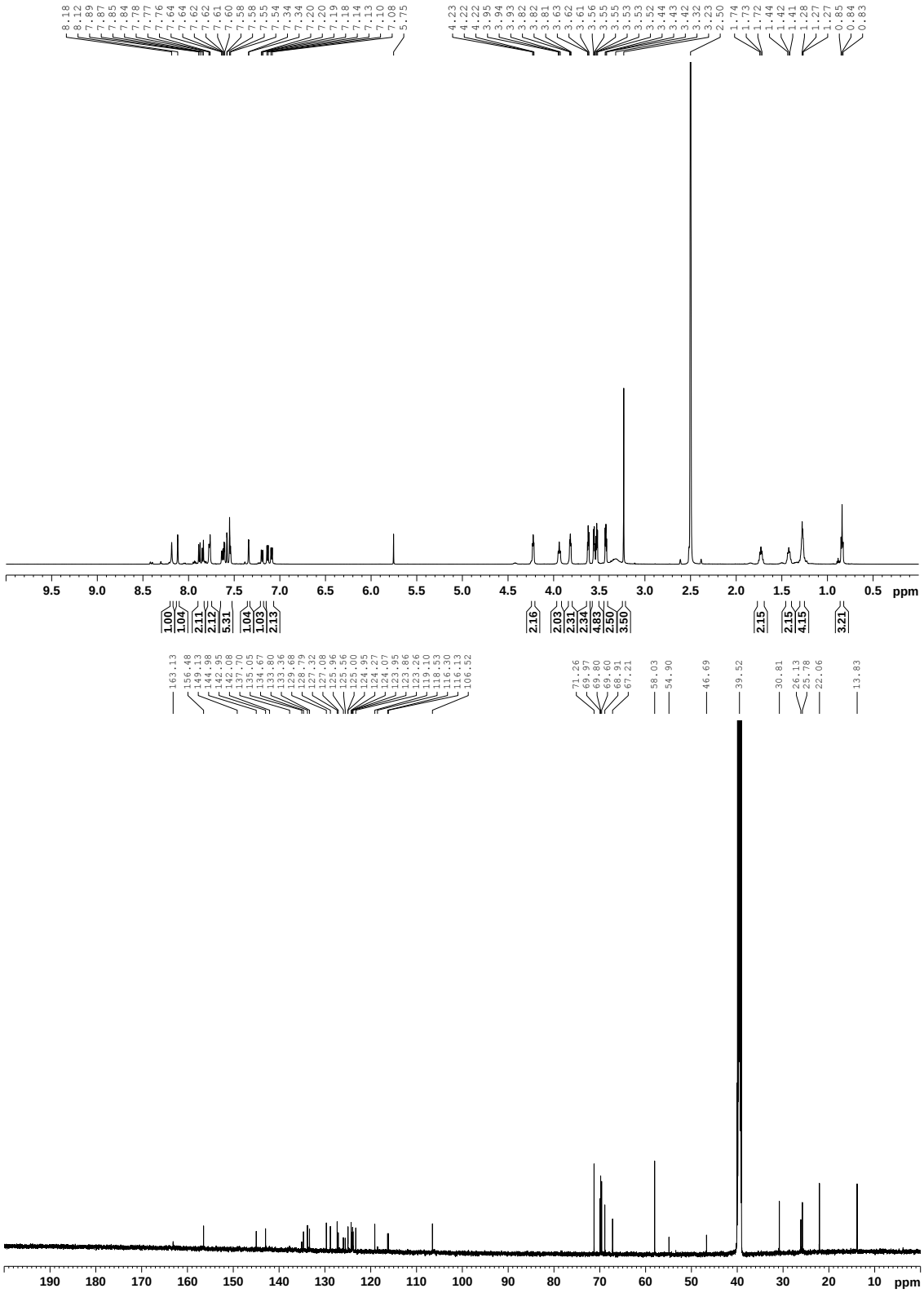


Figure S13. *^{1}H and ^{13}C NMR spectra for* ***AFB-18****.*

AFB-19

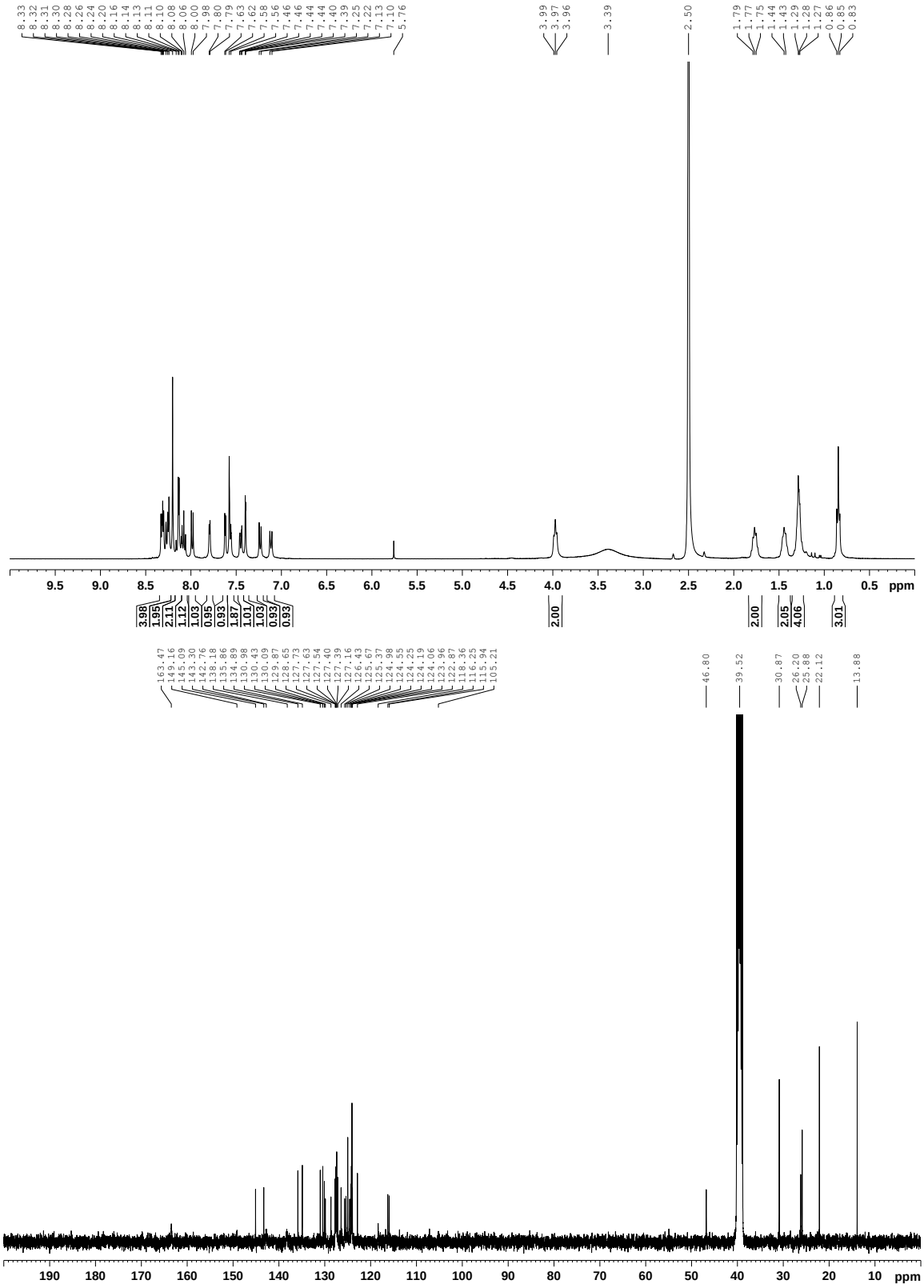


Figure S14. *^{1}H and ^{13}C NMR spectra for* ***AFB-19****.*

AFB-20

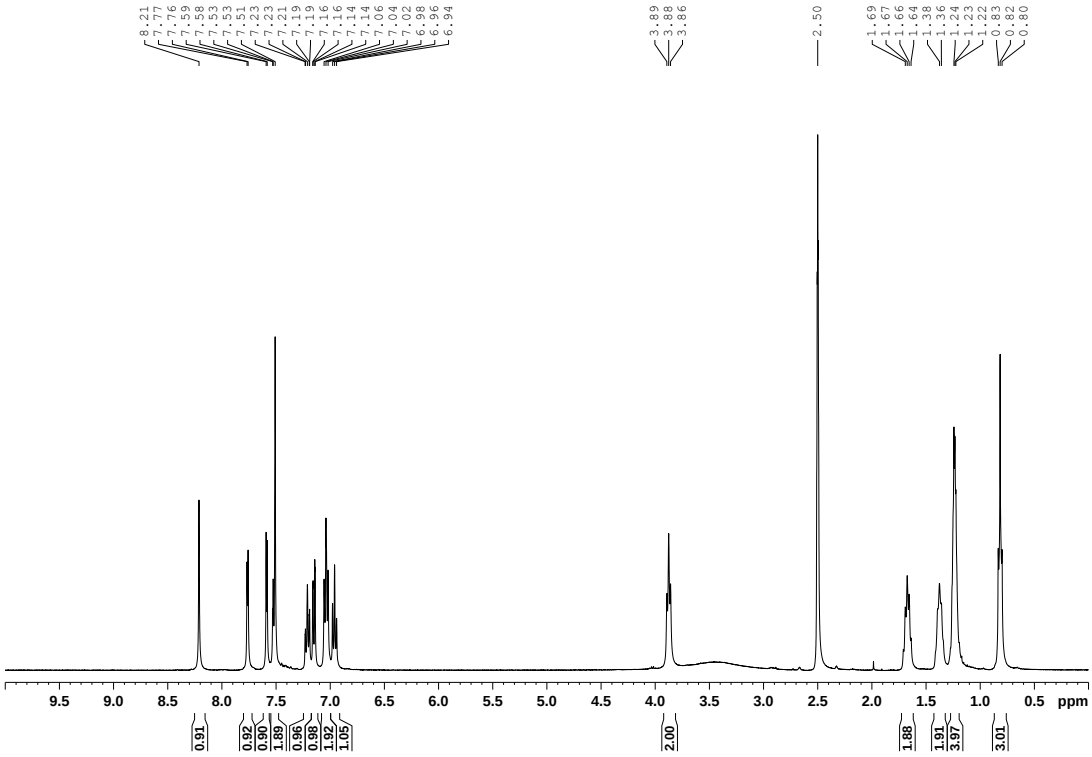


Figure S15. *^{1}H NMR spectra for* ***AFB-20****.*

Dye 2

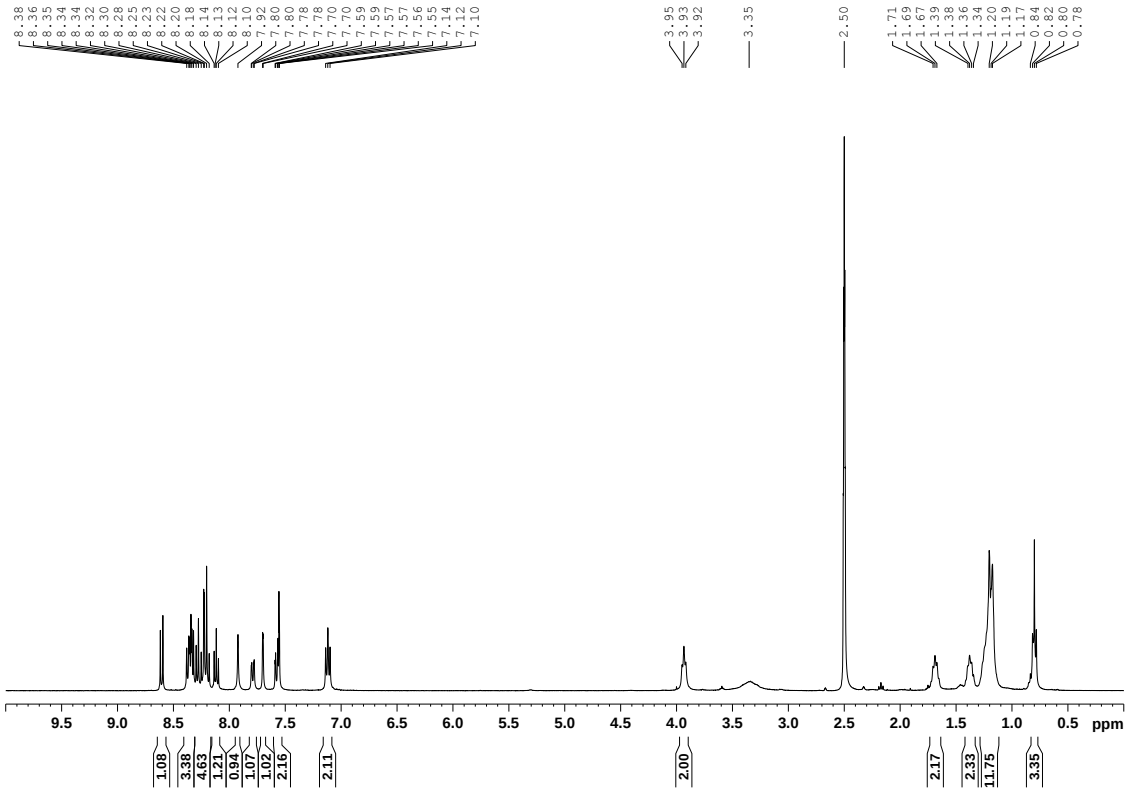


Figure S16. *^{1}H NMR spectra for* ***Dye 2****.*

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