Electronic Supplementary Information

Effect of furan π-spacer and triethylene oxide methyl ether substituents on performance of phenothiazine sensitizers in dye-sensitized solar cells

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Absorption and emission

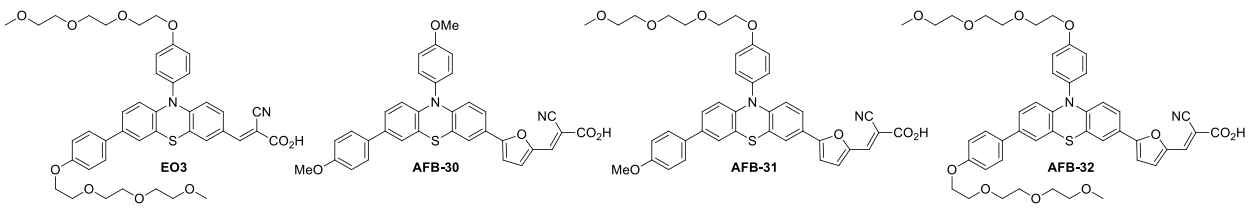


Fig. S1 *Structures of the four sensitizers* ***EO3***, ***AFB-30***, ***AFB-31*** *and* ***AFB-32***.

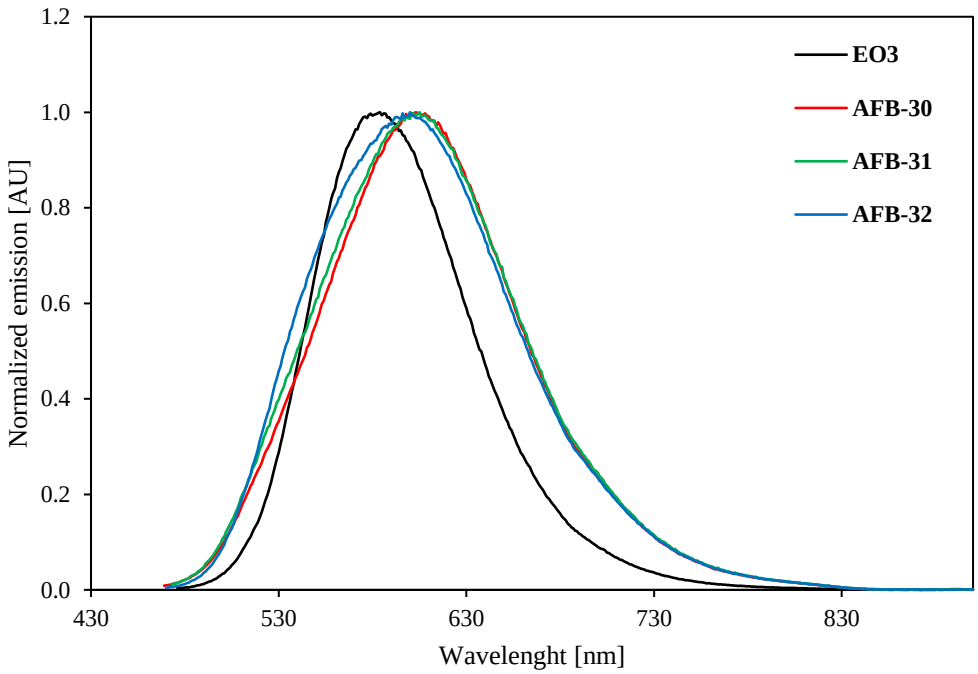


Fig. S2 *Normalized emission spectra of all dyes, recorded in THF. Emission at the wavelength of the ICT peak from the UV/vis absorption.*

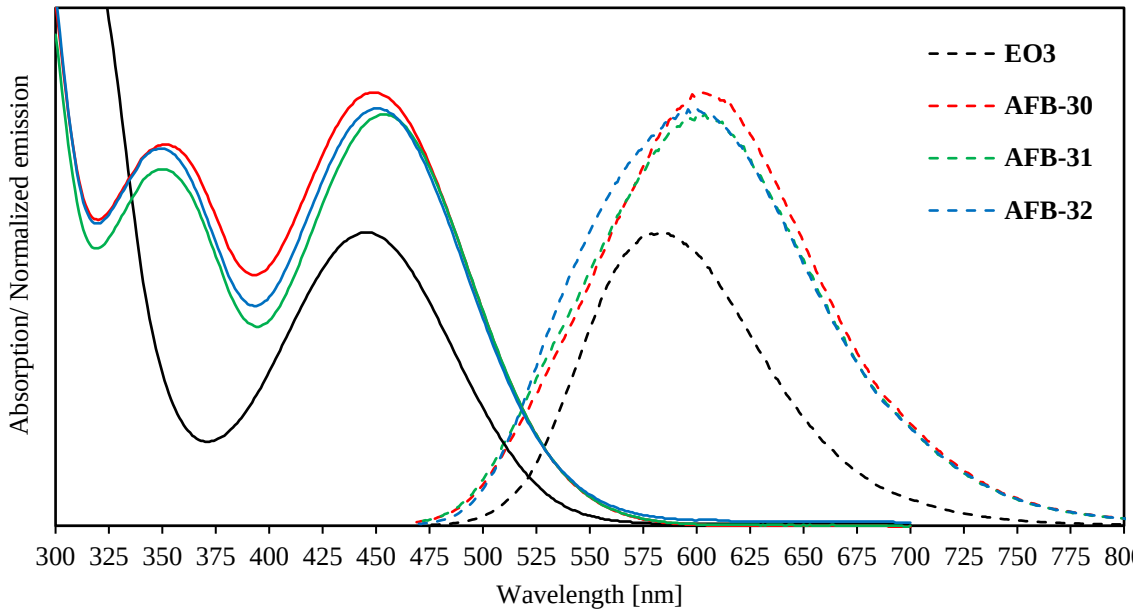


Fig. S3 *Absorption spectra in solution plotted with corresponding normalized emission spectra (dashed lines). The intersects dictates the optical bandgaps. Intersecting wavelengths:* ***EO3*** *521 nm,* ***AFB-30*** *520 nm,* ***AFB-31*** *518 nm and* ***AFB-32*** *518 nm.*

Cyclic voltammetry

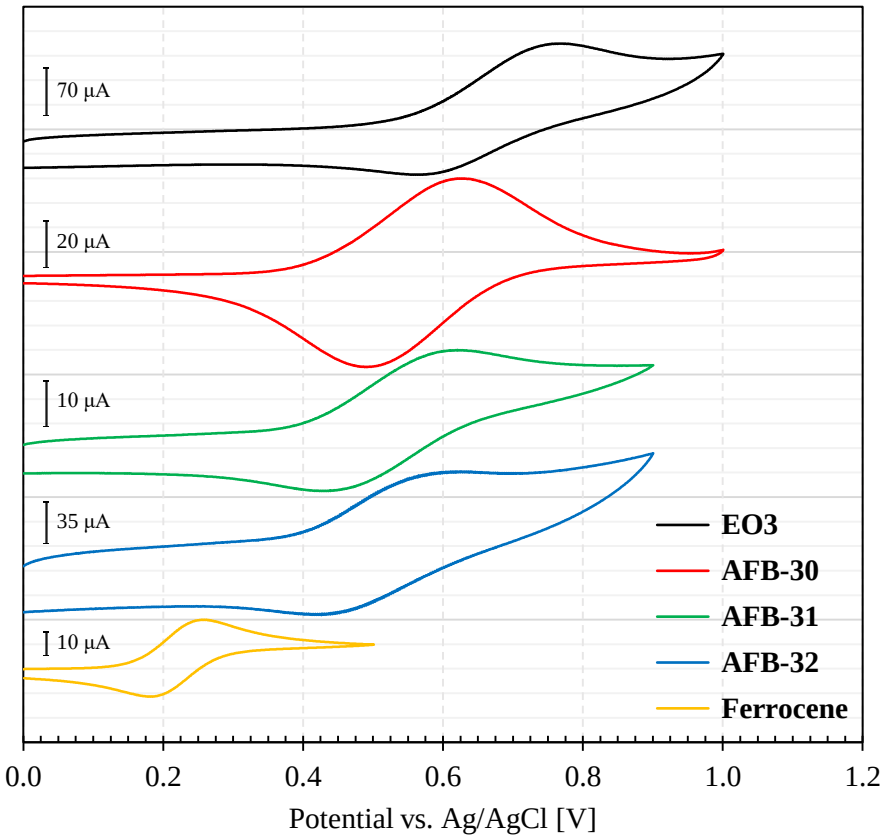


Fig. S4 *Cyclic voltammograms of all dyes on TiO_2 measured in acetonitrile with 0.1 M LiTFSI, with a carbon counter electrode and Ag/AgCl reference electrode. For the measurement of ferrocene, the working electrode was a glassy carbon electrode.*

Photovoltaic performance with aqueous $[Co(bpy\text{-}pz)_2]^{2+/3+}$ electrolyte

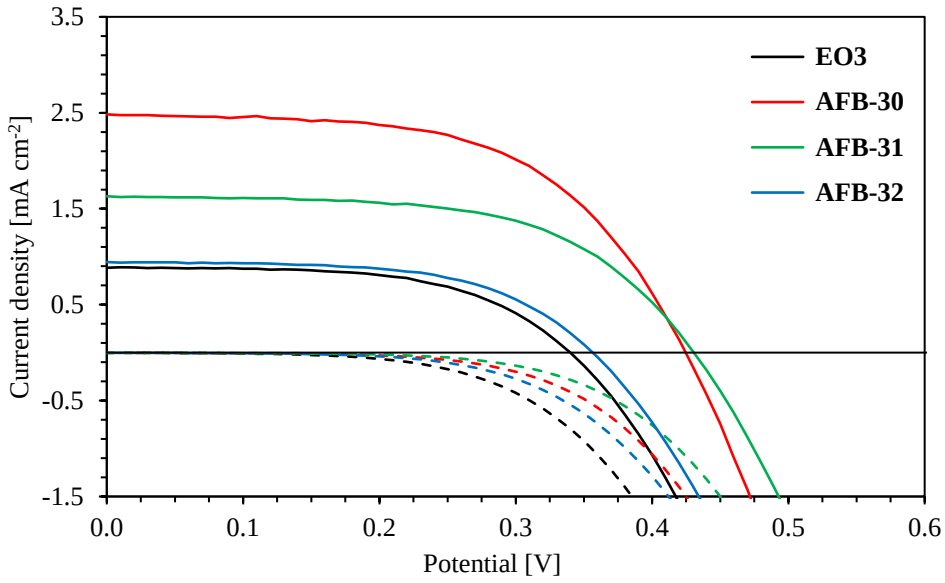


Fig. S5 *J-V characteristics of devices sensitized with* ***EO3*** *and* ***AFB-30*** *to* ***32*** *using the aqueous* $[Co(bpy\text{-}pz)_2]^{2+/3+}$ *electrolyte.*

Table S1 *Photovoltaic performance of dyes* ***AFB-30***, ***31*** *and* ***32*** *with aqueous* $[Co(bpy\text{-}pz)_2]^{2+/3+}$ *electrolyte under 1 sun AM 1.5G illumination. Averages of two devices.*

Dye	J_{SC} (mA cm^{-2})	V_{OC} (mV)	FF	PCE (%)
EO3	0.83 ± 0.08	347 ± 11	0.57 ± 0.01	0.17 ± 0.01
AFB-30	2.36 ± 0.18	430 ± 7	0.58 ± 0.00	0.57 ± 0.03
AFB-31	1.66 ± 0.04	426 ± 7	0.59 ± 0.00	0.40 ± 0.00
AFB-32	0.91 ± 0.05	354 ± 3	0.58 ± 0.00	0.18 ± 0.01

Electrolyte composition 0.13 M $[Co(bpy\text{-}pz)_2]Cl_2$, *0.06 M* $[Co(bpy\text{-}pz)_2]Cl_3$ *and 0.8 M 1-methylbenzimidazole (MBI) in deionized* H_2O.

Synthesis and characterization

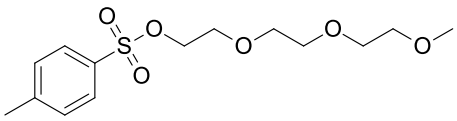
Materials

All reagents were acquired from Sigma Aldrich unless otherwise stated.

Characterization

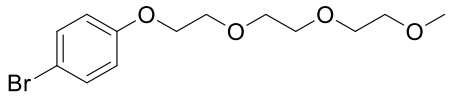
^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on either a Bruker 400 MHz or 600 MHz spectrometer, and all chemical shifts were reported in ppm relative to respective solvent peaks. Accurate mass determination in positive and negative mode was performed on a "Synapt G2-S" Q-TOF instrument from Waters™. UV/Vis spectrometry was measured on a Hitachi U-1900 instrument using quartz cuvettes for the solution measurements, fluorescence measurements on a Cary Eclipse Fluorescence Spectrophotometer and infrared spectra were recorded on an FTIR Thermo Nicolet Nexus FT-IR spectrophotometer with a Smart Endurance reflection cell. Thermogravimetric analyses were performed on a Netzsch STA 449 *F3 Jupiter* instrument, ramping from 20-275 °C with a rate of 5 °C/min and from 275-600 °C with 10 °C/min. The airflow was 50 mL/min.

Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (1)[1]



p-Toluenesulfonyl chloride (10.0 g, 52.5 mmol), dichloromethane (125 mL) and triethylene glycol monomethyl ether (10 mL, 62 mmol) were mixed in a flask. Finely powdered potassium hydroxide (5.97 g, 106 mmol) was added in portions and the reaction mixture was stirred for 2 hours at room temperature before it was quenched with deionized water (100 mL). The aqueous phase was extracted with dichloromethane (100 mL) and the organic phase was washed with deionized water (3 × 150 mL) and brine (150 mL) and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and compound **1** was obtained as a colorless oil (15.7 g, 49.4 mmol, 94%), R_f (ethyl acetate/pentane, 3:1) = 0.30. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.79 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 4.14-4.08 (m, 2H), 3.59-3.54 (m, 2H), 3.51-3.39 (m, 8H), 3.23 (s, 3H), 2.42 (s, 3H); HRMS (ASCI/ASAP, m/z): found 319.1214 (calcd. $C_{14}H_{22}O_6S$, 319.1215, $[M+H]^+$).

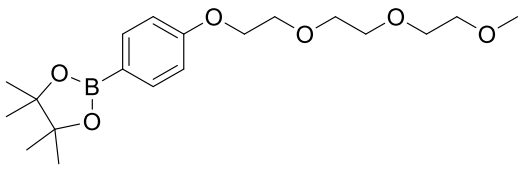
Synthesis of 1-bromo-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (2)[2]



A flask was charged with 4-bromophenol (1.55 g, 8.96 mmol) and K_2CO_3 (4.43 g, 32.1 mmol) and a nitrogen atmosphere was established. Dimethylformamide (30 mL) was added and the mixture was stirred for 15 minutes. 2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (2 mL, 8 mmol) was added and the reaction was stirred at 90 °C for 19 hours before the mixture was diluted with deionized water (50 mL) and dichloromethane (50 mL). The phases were separated and the aqueous phase was extracted with

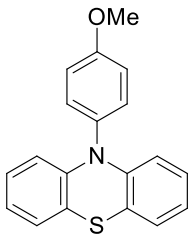
dichloromethane (2 × 50 mL) and the combined organic phases were washed with deionized water (3 × 100 mL) and brine (3 × 100 mL) before it was dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and silica gel column chromatography (gradient: 25-50% ethyl acetate in pentane) afforded compound **2** as a colorless oil (2.46 g, 7.71 mmol, 96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.43 (d, J = 9.1 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 4.10-4.06 (m, 2H), 3.74-3.71 (m, 2H), 3.59-3.56 (m, 2H), 3.54-3.49 (m, 4H), 3.44-3.40 (m, 2H), 3.23 (s, 3H); HRMS (ASCI/ASAP, m/z): found 319.0544 (calcd. $C_{13}H_{19}{}^{79}BrO_4$, 319.0545, $[M+H]^+$).

Synthesis of 2-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3)[3]



To a dry Schlenk flask was added $PdCl_2(CH_3CN)_2$ (68 mg, 0.26 mmol) and SPhos (202 mg, 0.493 mmol). Under nitrogen atmosphere, dry 1,4-dioxane (20 mL) was added through the septum followed by compound **2** (1.95 g, 6.11 mmol), dry NEt_3 (2.6 mL, 19 mmol) and pinacol borane (1.1 mL, 7.6 mmol). The reaction mixture was stirred at 80 °C for 2.5 hours before it was cooled to room temperature and filtered through a pad of Celite with ethyl acetate as eluent. Upon removal of the solvent *in vacuo*, compound **3** was obtained as a dark red oil (2.19 g, 5.98 mmol, 98%). The material was used without further purification, R_f (ethyl acetate/pentane, 3:1) = 0.38. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.59 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 4.13-4.09 (m, 2H), 3.76-3.72 (m, 2H), 3.60-3.57 (m, 2H), 3.54-3.49 (m, 4H), 3.44-3.40 (m, 2H), 3.23 (s, 3H), 1.27 (s, 12H); HRMS (ASCI/ASAP, m/z): found 365.2245 (calcd. $C_{19}H_{31}BO_6$, 365.2250, $[M]^+$)

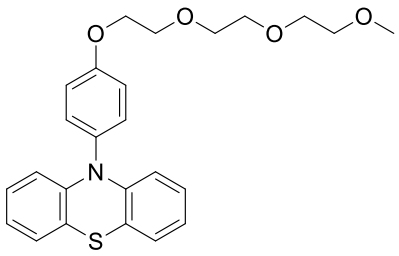
Synthesis of 10-(4-methoxyphenyl)-10*H*-phenothiazine (4)[4]



10*H*-Phenothiazine (11.0 g, 55.3 mmol), $P(Cy)_3$ (0.63 g, 2.3 mmol), sodium *tert*-butoxide (13.0 g, 135 mmol) and $Pd_2(dba)_3$ (2.54 g, 2.8 mmol) were placed in a flask under nitrogen atmosphere. Degassed toluene (200 mL) was then added followed by 4-bromoanisole (9 mL, 71.8 mmol)). The reaction mixture was stirred at reflux for 4 hours before it was cooled to room temperature and the solvent was removed *in vacuo*. The reaction mixture was dissolved in dichloromethane (200 mL) and washed with deionized water (3 × 200 mL) and brine (50 mL), then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*. The crude product was purified by recrystallization from ethyl acetate, which afforded compound **4** as pale yellow crystals (12.2 g, 39.9 mmol, 72%). R_f (ethyl acetate/pentane, 1:20) = 0.32, mp 174-176 ºC (lit.[5] 171-

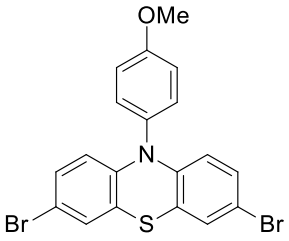
172 ºC). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.34 (d, J = 8.7 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 7.4 Hz, 2H), 6.91 (t, J = 7.3 Hz, 2H), 6.82 (t, J = 7.4 Hz, 2H), 6.14 (d, J = 8.1 Hz, 2H), 3.85 (s, 3H); HRMS (ASAP+, m/z): found 305.0875 (calcd. $C_{19}H_{15}NOS$, 305.0874, $[M]^+$).

Synthesis of 10-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazine (5)[6]



To a dry flask was added $Pd(OAc)_2$ (79 mg, 0.35 mmol), XPhos (418 mg, 0.88 mmol), 10*H*-phenothiazine (6.99 g, 35.1 mmol), compound **2** (7.00 g, 21.9 mmol) and Cs_2CO_3 (8.93 g, 27.4 mmol), an atmosphere of nitrogen was made followed by injection of toluene (35 mL) and *tert*-butanol (7 mL) through the septum. The reaction mixture was stirred at reflux for 22 hours. The solvent was removed *in vacuo* and the crude material was dissolved in dichloromethane (200 mL) and washed with deionized water (3 × 200 mL) and brine (200 mL), then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*. Silica gel column chromatography (ethyl acetate/pentane, 1:1, R_f = 0.26) afforded compound **5** as an off-white solid (9.12 g, 20.8 mmol, 95%), mp 67-70 °C (lit.[6] oil). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.30 (d, J = 8.9 Hz, 2H), 7.20 (d, J = 8.9 Hz, 2H), 7.02 (dd, J = 7.5, 1.6 Hz, 2H), 6.88 (td, J = 7.4, 1.6 Hz, 2H), 6.81 (td, J = 7.4, 1.3 Hz, 2H), 6.14 (dd, J = 8.2, 1.1 Hz, 2H), 4.19-4.15 (m, 2H), 3.81-3.77 (m, 2H), 3.63-3.59 (m, 2H), 3.57-3.50 (m, 4H), 3.45-3.40 (m, 2H), 3.24 (s, 3H); HRMS (ASCI/ASAP, m/z): found 437.1660 (calcd. $C_{25}H_{27}NO_4S$, 437.1661, $[M]^+$)

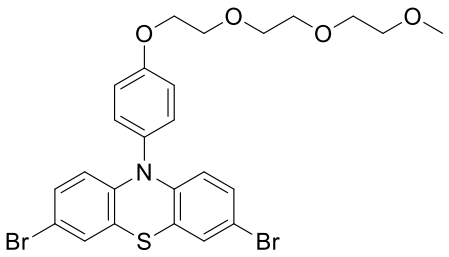
Synthesis of 3,7-dibromo-10-(4-methoxyphenyl)-10*H*-phenothiazine (6)[7]



Compound **1** (8.95 g, 29.3 mmol) was dissolved in chloroform (250 mL) and acetic acid (250 mL). The solution was degassed for 15 minutes. *N*-Bromosuccinimide (10.5 g, 59.2 mmol) was added in portions giving a purple solution. The reaction mixture was stirred for 1 hour before it was quenched with deionized water (250 mL). The aqueous phase was extracted with dichloromethane (2 × 150 mL) and the combined organic phases were washed with deionized water (2 × 150 mL) and brine (150 mL), then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*. Purification by silica gel column chromatography (pentane/ethyl acetate, 25:1) afforded compound **6** as a yellow solid (9.15 g, 19.75 mmol, 67%). R_f (ethyl

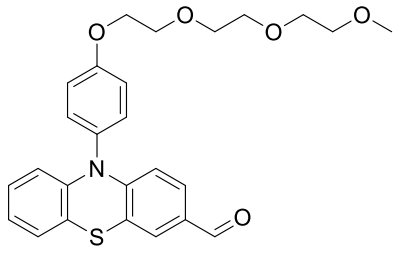
acetate/pentane, 1:3) = 0.63, mp 155-156 ºC (lit.[7] 157-158 ºC). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.34 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 2.1 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 7.08 (dd, J = 8.8, 2.2 Hz, 2H), 6.00 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H); HRMS (ASAP+, m/z): found 460.9087 (calcd. $C_{19}H_{13}{}^{79}Br_2NOS$, 460.9085, $[M]^+$).

Synthesis of 3,7-dibromo-10-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazine (7)



Compound **3** (3.00 g, 6.86 mmol) was dissolved in chloroform (45 mL) and acetic acid (45 mL). The solution was degassed for 15 minutes before *N*-bromosuccinimide (2.56 g, 14.4 mmol) was added. The reaction mixture was stirred at room temperature for 5 hours before it was quenched with deionized water (100 mL). The aqueous phase was extracted with dichloromethane (50 mL) and the organic phase was washed with deionized water (2 × 100 mL) and brine (100 mL) and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and silica gel column chromatography (ethyl acetate/pentane, 1:1, R_f = 0.31) afforded compound **7** as a light brown solid (4.08 g, 6.03 mmol, 88%), mp 74-75 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.33 (d, J = 8.9 Hz, 2H), 7.25 (d, J = 2.3 Hz, 2H), 7.21 (d, J = 9.0 Hz, 2H), 7.07 (dd, J = 8.8, 2.3 Hz, 2H), 6.00 (d, J = 8.8 Hz, 2H), 4.20-4.16 (m, 2H), 3.81- 3.76 (m, 2H), 3.63-3.59 (m, 2H), 3.57-3.51 (m, 4H), 3.45-3.41 (m, 2H), 3.24 (s, 3H); HRMS (ASCI/ASAP, m/z): found 592.9865 (calcd. $C_{25}H_{25}{}^{79}Br_2NO_4S$, 592.9871, $[M]^+$).

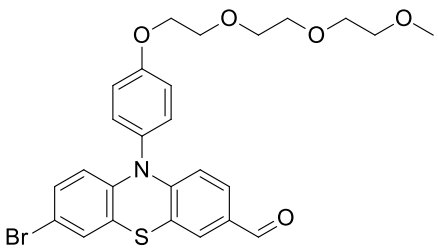
Synthesis of 10-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazine-3-carbaldehyde (8)[6]



Compound **5** (2.19 g, 5.01 mmol) was dissolved in a mixture of anhydrous dimethylformamide (1.5 mL) and 1,2-dichloroethane (25 mL) followed by cooling in an water-ice bath. Slowly, $POCl_3$ (1.75 mL) was added to the reaction mixture over 30 minutes using a syringe. The mixture was heated to 80 °C and left stirring overnight. The reaction was quenched by addition of deionized water (100 mL) followed by extraction with chloroform (3 × 100 mL). The combined organic phases were washed with deionized water

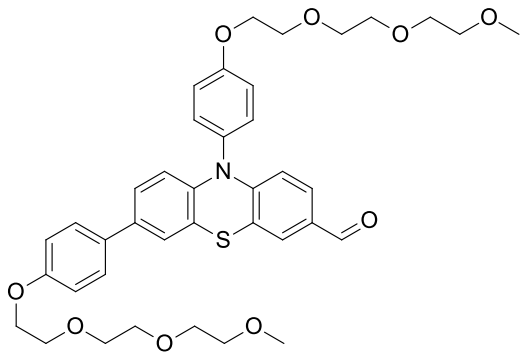
(100 mL), then dried with brine (100 mL) and over anhydrous Na_2SO_4. The solvents were removed *in vacuo* and the crude product was purified using silica gel column chromatography (*n*-pentane/ethyl acetate, 1:1, R_f = 0.14). Compound **8** was obtained as a yellow solid (1.46 g, 3.14 mmol, 63%), mp 77-78 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.69 (s, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.42 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.06 (dd, *J* = 7.2, 1.9 Hz, 1H), 6.95-6.86 (m, 2H), 6.20 (d, *J* = 8.6 Hz, 1H), 6.11 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.20 (t, *J* = 4.5 Hz, 2H), 3.80 (t, *J* = 4.5 Hz, 2H), 3.64-3.60 (m, 2H), 3.57-3.52 (m, 4H), 3.46-3.42 (m, 2H), 3.24 (s, 3H); HRMS (ASAP+, *m*/*z*): found 466.1688 (calcd. $C_{26}H_{28}NO_5S$, 466.1696, $[M+H]^+$).

Synthesis of 7-bromo-10-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazine-3-carbaldehyde (9)[6]



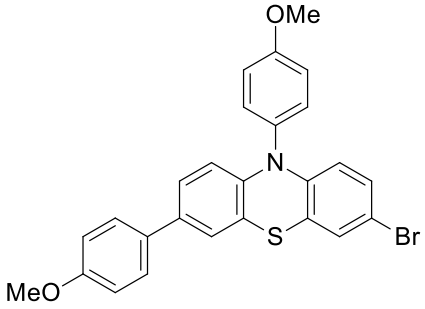
Compound **8** (1.18 g, 2.53 mmol) was dissolved in acetic acid (10 mL). *N*-Bromosuccinimide (457 mg, 2.57 mmol) was added and the reaction mixture was stirred at room temperature for 30 minutes. The reaction was quenched by addition of deionized water (100 mL) followed by extraction with diethyl ether (3 × 100 mL). The organic phases were collected and washed with deionized water (100 mL), then dried with brine (100 mL) and over anhydrous Na_2SO_4. The solvents were removed *in vacuo* and the crude product was purified using silica gel column chromatography (*n*-pentane/ethyl acetate, 1:2, R_f = 0.31). Compound **9** was obtained as a yellow solid (982 mg, 1.80 mmol, 70%), mp 75-77 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.70 (s, 1H), 7.50 (d, *J* = 1.9 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.37 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 2.3 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 2H), 7.09 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.19 (d, *J* = 8.5 Hz, 1H), 6.01 (d, *J* = 8.5 Hz, 1H), 4.20 (t, *J* = 4.4 Hz, 2H), 3.79 (t, *J* = 4.4 Hz, 2H), 3.64-3.60 (m, 2H), 3.57-3.52 (m, 4H), 3.45-3.42 (m, 2H), 3.24 (s, 3H); HRMS (ASAP+, *m*/*z*): found 544.0793 (calcd. $C_{26}H_{27}{}^{79}BrNO_5S$, 544.0786, $[M+H]^+$).

Synthesis of 7,10-bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazine-3-carbaldehyde (10)[6]



Compound **9** (420 mg, 0.771 mmol), compound **3** (583 mg, 1.59 mmol), $Pd(OAc)_2$ (12 mg, 0.053 mmol), SPhos (35 mg, 0.085 mmol), K_2CO_3 (431 mg, 3.12 mmol) were added to a round-bottom flask. 1,4-Dioxane (6 mL), followed by deionized water (6 mL), were added to the flask, and the mixture was stirred at 80 °C for 1 hour. The reaction was quenched with deionized water (100 mL) followed by extraction with ethyl acetate (3 × 100 mL). The combined organic phases were washed with deionized water (100 mL), and then dried with brine (100 mL) and over anhydrous Na_2SO_4. Excess solvent was removed under reduced pressure. The crude product was purified using silica gel column chromatography (3% methanol in dichloromethane, R_f = 0.35). Compound **10** was obtained as a yellow oil (476 mg, 0.676 mmol, 88%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.70 (s, 1H), 7.50 (d, J = 8.8 Hz, 1H), 7.42 (dd, J = 8.8, 2.0 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 2.2 Hz, 1H), 7.26 (d, J = 8.8 Hz, 2H), 7.18 (dd, J = 8.7, 2.2 Hz, 1H), 7.00–6.90 (m, 4H), 6.19 (d, J = 8.6 Hz, 1H), 6.13 (d, J = 8.6 Hz, 1H), 4.21 (t, J = 4.4 Hz, 2H), 4.11 (t, J = 4.4 Hz, 2H), 3.81 (t, J = 4.4 Hz, 2H), 3.77–3.72 (m, 2H), 3.64-3.49 (m, 12H), 3.46-3.40 (m, 4H), 3.24 (s, 3H), 3.23 (s, 3H); HRMS (ASAP+, m/z): found 704.2893 (calcd. $C_{39}H_{46}NO_9S$, 704.2888, $[M+H]^+$).

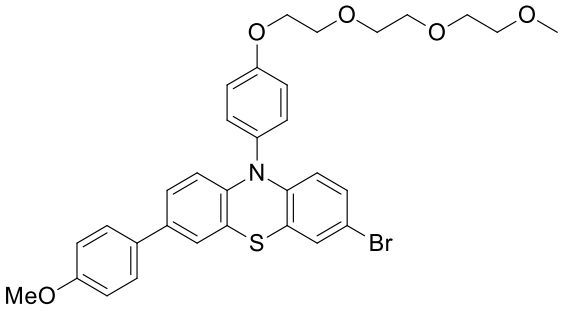
Synthesis of 3-bromo-7,10-bis(4-methoxyphenyl)-10*H*-phenothiazine (11)[7]



Compound **2** (1.51 g, 3.3 mmol), $Pd(PPh_3)_4$ (0.34 g, 0.3 mmol) and K_2CO_3 (1.82 g, 13.2 mmol) were added to a flask and a nitrogen atmosphere was established. 1,4-Dioxane (30 mL) and deionized water (30 mL) were added and the mixture was stirred at 40 ºC for 30 minutes. Then (4-methoxyphenyl)boronic acid (0.53 g, 3.5 mmol) dissolved in 1,4-dioxane (5 mL) was added dropwise to the reaction mixture which was then stirred at 80 ºC for 24 hours before it was quenched with deionized water (50 mL) and dichloromethane (50

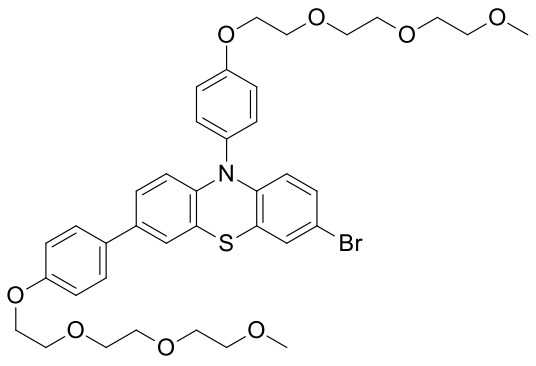
mL), and the phases separated. The aqueous phase was extracted with dichloromethane (50 mL) and the combined organic phases were washed with deionized water (50 mL) and brine (30 mL). The solvent was removed *in vacuo*, and the crude product was filtered through a silica plug (dichloromethane/pentane, 2:3) and afterwards purified by silica gel column chromatography (gradient: 2.5-5% acetone in pentane) which afforded compound **11** as a fluffy yellow powder (0.51 g, 1.040 mmol, 32%), R_f (pentane/ethyl acetate, 3:1) = 0.51, mp 130-133 ºC (lit.[7] 126-127 ºC). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.50 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 1H), 7.26 (s, 1H), 7.22 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 9.1 Hz, 1H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.13 (d, *J* = 8.5 Hz, 1H), 6.02 (d, *J* = 10.4 Hz, 1H), 3.86 (s, 3H), 3.76 (s, 3H) ; ^{13}C NMR (150 MHz, DMSO-d_6) δ: 159.1, 158.7, 143.2, 142.1, 134.4, 132.1, 131.8 (2C), 131.0, 129.7, 128.2, 127.0 (2C), 125.1, 123.9, 121.0, 118.4, 116.9, 116.4 (2C), 116.0, 114.3 (2C), 113.5, 55.5, 55.2; HRMS (ASAP+, m/z): found 489.0393 (calcd. $C_{26}H_{20}{}^{79}BrNO_2S$, 489.0398, $[M]^+$).

Synthesis of 3-bromo-10-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-7-(4-methoxyphenyl)-10*H*-phenothiazine (12)



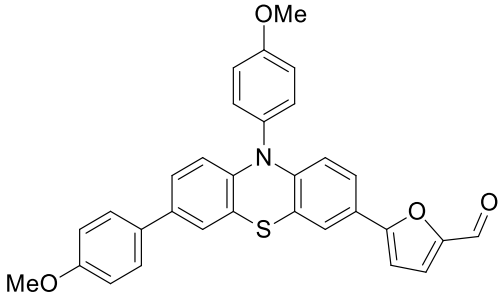
To a Schlenk flask compound **4** (2.07 g, 3.48 mmol), $Pd(PPh_3)_4$ (356 mg, 0.308 mmol), and K_2CO_3 (1.70 g, 13.9 mmol) were added, and a nitrogen atmosphere established. Degassed 1,4-dioxane (20 mL) and deionized water (20 mL) were added through the septum. The mixture was stirred at 40 °C for 30 minutes before (4-methoxyphenyl)boronic acid (519 mg, 3.42 mmol) dissolved in 1,4-dioxane (0.5 mL) was added dropwise through the septum. The reaction mixture was stirred at 80 °C for 22 hours before deionized water (80 mL) and dichloromethane (80 mL) were added and the phases separated. The aqueous phase was extracted with dichloromethane (80 mL). The combined organic phases were washed with deionized water (2 × 100 mL) and brine (100 mL), then dried over anhydrous Na_2SO_4. The solvents were removed *in vacuo*, and silica gel column chromatography (15% acetone in pentane) afforded compound **12** as a yellow oil (0.730 g, 1.173 mmol, 34%), R_f (pentane/acetone, 3:1) = 0.24. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.48 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.9 Hz, 2H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.21 (d, *J* = 9.0 Hz, 2H), 7.15 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.05 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.13 (d, *J* = 8.7 Hz, 1H), 6.01 (d, *J* = 8.8 Hz, 1H), 4.21-4.16 (m, 2H), 3.82-3.77 (m, 2H), 3.76 (s, 3H), 3.64-3.59 (m, 2H), 3.57-3.51 (m, 4H), 3.46-3.41 (m, 2H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 158.7, 158.4, 143.2, 142.1, 134.4, 132.1, 131.7 (2C), 130.9, 129.7, 128.2, 127.0 (2C), 125.0, 123.8, 120.9, 118.4, 116.9, 116.8 (2C), 116.0, 114.3 (2C), 113.5, 71.3, 69.9, 69.8, 69.6, 68.9, 67.5, 58.0, 55.1; HRMS (ASCI/ASAP, m/z): found 621.1180 (calcd. $C_{32}H_{32}{}^{79}BrNO_5S$, 621.1185, $[M]^+$).

Synthesis of 3-bromo-7,10-bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazine (13)



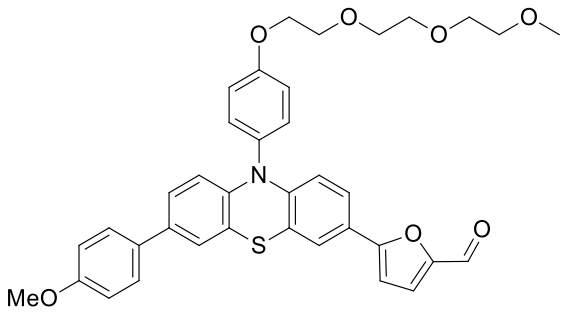
Compound **4** (1.00 g, 1.68 mmol), $Pd(PPh_3)_4$ (0.184 g, 159 mmol) and K_2CO_3 (0.894 g, 6.47 mmol) were added to a flask and a nitrogen atmosphere established. Degassed toluene (6 mL) and degassed deionized water (6 mL) were added, and the mixture was stirred at 40 °C for 30 minutes before compound **5** (604 mg, 1.65 mmol) was added through the septum. The reaction mixture was stirred at 80 °C for 21 hours before it was diluted with deionized water (40 mL) and dichloromethane (40 mL). The phases were separated and the aqueous phase was extracted with more dichloromethane (40 mL). The combined organic phase were washed with deionized water (80 mL) and brine (80 mL), then dried over Na_2SO_4. The solvent was removed *in vacuo*, and silica gel column chromatography (gradient: 25-50% acetone in pentane) afforded compound **13** as a yellow oil (0.568 g, 0.753 mmol, 45%), R_f (acetone/pentane, 1:1) = 0.67. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.48 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.9 Hz, 2H), 7.28 (d, J = 1.9 Hz, 1H), 7.24 (d, J = 2.3 Hz, 1H), 7.22 (d, J = 8.9 Hz, 2H), 7.16 (dd, J = 8.7, 2.2 Hz, 1H), 7.06 (dd, J = 8.8, 2.4 Hz, 1H), 6.96 (d, J = 8.8 Hz, 2H), 6.13 (d, J = 8.6 Hz, 1H), 6.01 (d, J = 8.8 Hz, 1H), 4.21-4.16 (m, 2H), 4.11-4.07 (m, 2H), 3.82-3.77 (m, 2H), 3.75-3.71 (m, 2H), 3.64-3.39 (m, 16H), 3.24 (s, 3H), 3.23 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 158.4, 157.9, 143.2, 142.1, 134.4, 132.1, 131.7 (2C), 131.0, 129.7, 128.2, 127.0 (2C), 125.1, 123.9, 120.9, 118.4, 116.9, 116.8 (2C), 116.0, 114.8 (2C), 113.5, 71.3, 71.3, 69.9, 69.9, 69.8, 69.8, 69.6, 69.6, 68.9, 68.9, 67.5, 67.2, 58.0, 58.0; HRMS (ASCI/ASAP, m/z): found 753.1961 (calcd. $C_{38}H_{44}{}^{79}BrNO_8S$, 753.1971, $[M]^+$).

Synthesis of 5-(7,10-bis(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)furan-2-carbaldehyde (14)



Compound **3** (376 mg, 0.77 mmol), SPhos (19.6 mg, 0.048 mmol), (5-formyl-2-furanyl)boronic acid (299 mg, 2.1 mmol), $Pd(OAc)_2$ (8.5 mg, 0.038 mmol) and K_2CO_3 (416 mg, 3.0 mmol) were added to a flask which was then evacuated and flushed with N_2 to obtain an inert atmosphere. Degassed 1,4-dioxane (12 mL) and deionized water (12 mL) were added and the reaction mixture was stirred at 80 °C for 2 hours before it was diluted with dichloromethane (50 mL) and deionized water (50 mL). The aqueous phase was extracted with dichloromethane (50 mL) and the combined organic phases were washed with deionized water (30 mL) and brine (30 mL), then dried over anhydrous Na_2SO_4 before the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (gradient: 15-25% ethyl acetate in pentane) and compound **14** was obtained as an orange foam (327 mg, 0.647 mmol, 84%), R_f (ethyl acetate/pentane, 1:4) = 0.16. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.52 (s, 1H), 7.56 (d, *J* = 3.8 Hz, 1H), 7.50 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.38-7.32 (m, 3H), 7.27 (d, *J* = 2.2 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 2H), 7.13 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.08 (d, *J* = 3.8 Hz, 1H,), 6.94 (d, *J* = 8.9 Hz, 2H), 6.16 (d, *J* = 8.7 Hz, 1H), 6.11 (d, *J* = 8.9 Hz, 1H) 3.86 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 177.1, 159.1, 158.7, 157.6, 151.3, 144.6, 141.6, 134.6, 131.9, 131.7 (2C), 130.9, 127.0 (2C), 124.9, 124.2, 123.8, 122.9, 122.8, 119.3, 118.5, 116.3 (2C), 116.2, 115.5, 114.2 (2C), 112.1, 107.6, 55.4, 55.1. HRMS (ASAP+, m/z): found 505.1344 (calcd. $C_{31}H_{23}NO_4S$, 505.1348, $[M]^+$).

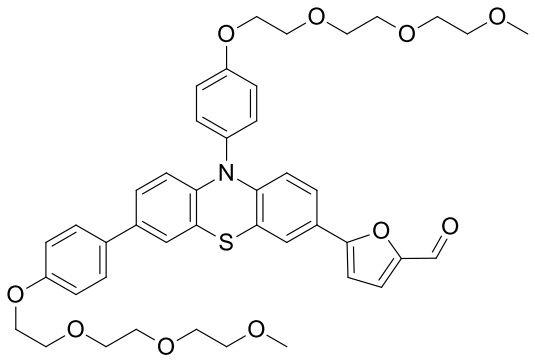
Synthesis of 5-(10-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-7-(4-methoxyphenyl)-10*H*-phenothiazin-3- yl)furan-2-carbaldehyde (15)



SPhos (50.1 mg, 0.122 mmol), $Pd(OAc)_2$ (18.3 mg, 0.0815 mmol), K_2CO_3 (650 mg, 4.70 mmol) and 5-formyl-2-furanylboronic acid (260 mg, 1.86 mmol) were added to a flask which then was evacuated and flushed with nitrogen. 1,4-Dioxane (25 mL) and deionized water (25 mL) were added through the septum followed by compound **10** (700 mg, 1.12 mmol) dissolved in 1,4-dioxane (1 mL). The reaction mixture was stirred at 80 °C for 3 hours before it was diluted with dichloromethane (30 mL) and deionized water (20 mL). The phases were separated and the aqueous phase was further extracted with dichloromethane (50 mL) and the combined organic phases were washed with deionized water (2 × 100 mL) and brine (100 mL). Silica gel column chromatography (gradient: 25-50% acetone in pentane) afforded compound **15** as a yellow foam (475 mg, 0.745 mmol, 66%). R_f (acetone/pentane, 3:5) = 0.21. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.53 (s, 1H), 7.60 (d, *J* = 3.8 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.41-7.35 (m, 3H), 7.31 (d, *J* = 2.1 Hz, 1H), 7.25 (d, *J* = 8.9 Hz, 2H), 7.16 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.13 (d, *J* = 3.8 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.18 (d, *J* = 8.6 Hz, 1H), 6.12 (d, *J* = 8.6 Hz, 1H), 4.23-4.18 (m, 2H), 3.82-3.78 (m, 2H), 3.77 (s, 3H), 3.65-3.61 (m, 2H), 3.58-3.52 (m, 4H), 3.46-3.42 (m, 2H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 177.3, 158.7, 158.5, 157.6, 151.3, 144.6, 141.7, 134.7, 132.0, 131.7 (2C),

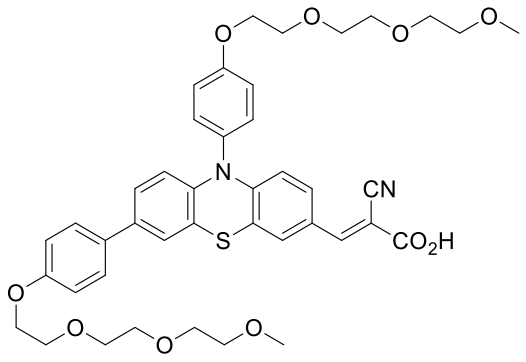
130.9, 127.1 (2C), 125.8, 125.0, 124.2, 123.9, 122.9, 122.8, 119.2, 118.5, 116.9 (2C), 116.2, 115.6, 114.3 (2C), 107.7, 71.3, 70.0, 69.8, 69.6, 68.9, 67.5, 58.1, 55.2; HRMS (ASCI/ASAP, m/z): found 638.2205 (calcd. $C_{37}H_{36}NO_7S$, 638.2212, $[M+H]^+$).

Synthesis of 5-(7,10-bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazin-3-yl)furan-2- carbaldehyde (16)



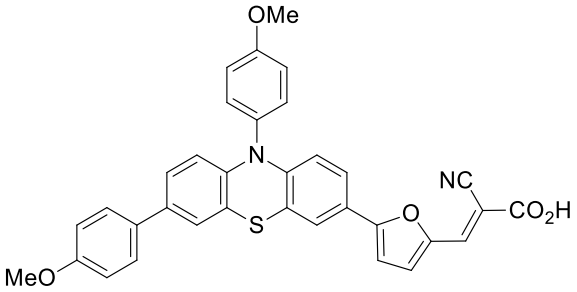
SPhos (15.3 mg, 0.0373 mmol), $Pd(OAc)_2$ (10.6 mg, 0.0472 mmol), K_2CO_3 (220 mg, 1.59 mmol) and 5-formyl-2-furanylboronic acid (70.8 mg, 0.506 mmol) were added to a flask which then was evacuated and flushed with nitrogen. 1,4-Dioxane (8 mL) and deionized water (8 mL) were added through the septum followed by compound **6** (240 mg, 0.318 mmol) dissolved in 1,4-dioxane (1 mL). The reaction mixture was stirred at 80 °C for 3.5 hours before it was diluted with dichloromethane (30 mL) and deionized water (30 mL). The phases were separated and the aqueous phase was extracted with dichloromethane (20 mL) and the combined organic phases were washed with deionized water (2 × 30 mL) then brine (30 mL). Silica gel column chromatography (gradient: 25-50% acetone in pentane) afforded compound **16** as a yellow oil (147 mg, 0.191 mmol, 60%), R_f (pentane/acetone, 1:1) = 0.20. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.52 (s, 1H), 7.58 (d, J = 3.7 Hz, 1H), 7.52 (d, J = 2.1 Hz, 1H), 7.48 (d, J = 8.8 Hz, 2H), 7.38-7.31 (m, 3H), 7.29 (d, J = 2.2 Hz, 1H), 7.22 (d, J = 8.9 Hz, 2H), 7.14 (dd, J = 8.7, 2.2 Hz, 1H), 7.11 (d, J = 3.7 Hz; 1H), 6.95 (d, J = 8.8 Hz, 2H), 6.16 (d, J = 8.7 Hz, 1H), 6.11 (d, J = 8.5 Hz, 1H), 4.21-4.16 (m, 2H), 4.11-4.06 (m, 2H), 3.81-3.77 (m, 2H), 3.75-3.71 (m, 2H), 3.64-3.39 (m, 16H), 3.24 (s, 3H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 177.2, 158.4, 157.9, 157.6, 151.3, 144.6, 141.6, 134.6, 132.0, 131.7 (2C), 131.0, 127.0 (2C), 125.7, 124.9, 124.2, 123.8, 122.9, 122.8, 119.2, 118.5, 116.8 (2C), 116.2, 115.5, 114.8 (2C), 107.7, 71.3, 71.3, 70.0, 69.9, 69.8, 69.8, 69.6, 69.6, 68.9, 68.9, 67.5, 67.2, 58.0, 58.0; HRMS (ASCI/ASAP, m/z): found 770.2989 (calcd. $C_{43}H_{48}NO_{10}S$, 770.2999, $[M+H]^+$).

Synthesis of *(E)*-3-(7,10-bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazin-3-yl)-2-cyanoacrylic acid (EO3)[6]



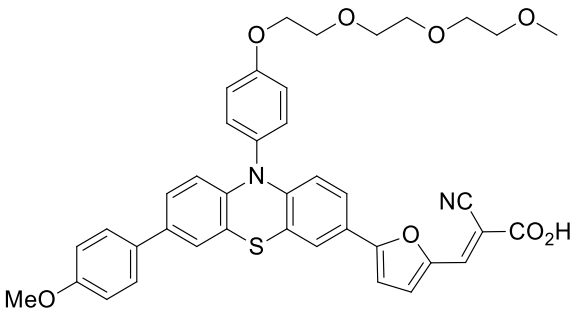
Compound **10** (62 mg, 0.088 mmol) was dissolved in acetonitrile (17 mL). Cyanoacetic acid (198 mg, 2.33 mmol) and piperidine (0.14 mL, 1.38 mmol) were added to the reaction mixture, followed by stirring at 80 °C for 2 hours. The reaction was quenched with HCl (1 M, 50 mL) followed by extraction with ethyl acetate (2 × 50 mL). The organic phases were collected and washed with deionized water (6 × 100 mL), then dried with brine (100 mL) and over anhydrous Na_2SO_4. The solvents were removed *in vacuo* and the crude product was purified using silica gel column chromatography (gradient: 0-15% methanol in dichloromethane), R_f (methanol/dichloromethane, 1:9) = 0.27). The product was dissolved in dichloromethane, filtered and the solvent was removed *in vacuo* to yield sensitizer **EO3** as a red solid (42 mg, 0.054 mmol, 62%), mp 125-127 °C, 170 °C (dec.). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.78 (s, 1H), 7.61 (d, *J* = 1.5 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.39 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.17 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.12 (d, *J* = 2.5 Hz, 1H), 6.11 (d, *J* = 2.9 Hz, 1H), 4.19 (t, *J* = 3.7 Hz, 2H), 4.09 (t, *J* = 4.4 Hz, 2H), 3.79 (t, *J* = 4.4 Hz, 2H), 3.73 (t, *J* = 4.5 Hz, 2H), 3.63-3.61 (m, 2H), 3.59-3.49 (m, 10H), 3.45-3.41 (m, 4H), 3.24 (s, 3H), 3.23 (s, 3H) (COO<u>H</u> proton not visible); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 164.0, 158.5, 158.0, 146.5, 145.6, 141.3, 134.8, 131.8, 131.6 (2C), 130.9, 129.8, 127.1, 127.0 (2C), 126.8, 125.0, 123.8, 119.2, 118.5 (2C), 116.9 (2C), 116.3, 115.1, 114.8 (2C), 109.4, 71.3, 69.95, 69.93, 69.83, 69.78, 69.62, 69.59, 68.92, 68.87, 67.5, 67.2, 58.1, 58.0. (1C missing due to overlapping peaks); UV (THF, 2 × 10^{-5} M, 20 °C) λ_{max} (nm): 451 (14448 M^{-1} cm^{-1}); HRMS (ESI-, *m*/*z*): found 769.2795 (calcd. $C_{42}H_{45}N_2O_{10}S$, 769.2786, $[M-H]^-$).

Synthesis of (*E*)-3-(5-(7,10-bis(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)furan-2-yl)-2-cyanoacrylic acid (AFB-30)



Compound **14** (224 mg, 0.443 mmol) and cyanoacetic acid (754 mg, 8.87 mmol) were added to a flask and dissolved in acetonitrile (59 mL) under a nitrogen atmosphere. Piperidine (0.53 mL, 5.4 mmol) was added and the reaction mixture was stirred at 70 °C for 30 minutes before it was cooled to room temperature and poured into an HCl solution (2 M, 100 mL). After stirring for 15 minutes, ethyl acetate (200 mL) was added. The phases were separated and the organic phase was washed with deionized water (5 × 150 mL) and brine (150 mL), then dried over anhydrous Na_2SO_4. Silica gel column chromatography (gradient: 0-20% methanol in ethyl acetate) afforded the sensitizer **AFB-30** as a dark purple solid (99.1 mg, 39%). R_f (ethyl acetate/methanol, 3:1) = 0.15, mp 264 °C (dec.). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.79 (s, 1H), 7.56 (d, J = 2.0 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.42-7.38 (m, 3H), 7.33 (d, J = 2.2 Hz, 1H), 7.26-7.22 (m, 3H), 7.18 (dd, J = 8.7, 2.2 Hz, 1H), 7.09 (d, J = 3.7 Hz, 1H), 6.96 (d, J = 8.9 Hz, 2H), 6.15 (d, J = 6.9 Hz, 1H), 6.14 (d, J = 6.7 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H) (COO<u>H</u> proton not visible); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.7, 159.2, 158.7, 155.7, 147.9, 144.1, 141.8, 134.0, 133.9, 132.0, 131.7 (2C), 131.0, 127.5, 127.0 (2C), 125.0, 123.9, 123.7, 123.3, 122.3, 119.1, 118.7, 118.5, 116.4 (2C), 116.1, 115.5, 114.5, 114.3 (2C), 108.0, 55.5, 55.2; UV (THF, 2 × 10^{-5} M, 20 °C) λ_{max} (nm): 446 (20634 M^{-1} cm^{-1}); IR (neat, cm^{-1}) ν: 3474 (w, br), 3041 (w), 2956 (w), 2836 (w), 2357 (w), 2214 (w), 1606 (m), 1448 (s), 1382 (s), 1247 (w), 1026 (m), 791 (m); HRMS (TOF MS ASAP+, *m/z*): found 528.1502 (calcd. $C_{33}H_{24}N_2O_3S$, 528.1508, [M-CO_2]$^+$).

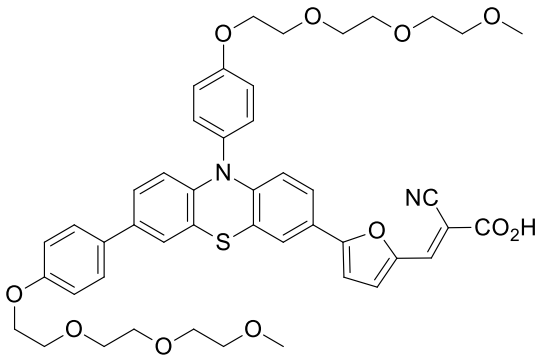
Synthesis of (*E*)-2-cyano-3-(5-(10-(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-7-(4-methoxyphenyl)-10*H*-phenothiazin-3-yl)furan-2-yl)acrylic acid (AFB-31)



Compound **15** (404 mg, 0.633 mmol) and cyanoacetic acid (518 mg, 6.09 mmol) were added to a flask and dissolved in acetonitrile (37 mL) under nitrogen atmosphere. Piperidine (0.36 mL, 3.6 mmol) was added

and the reaction mixture was stirred at 70 °C for 40 minutes before it was cooled to room temperature and poured into an HCl solution (2 M, 100 mL). After stirring for 15 minutes, ethyl acetate (150 mL) was added. The phases were separated and the organic phase was washed with deionized water (2 × 150 mL) and brine (150 mL) and dried over anhydrous Na_2SO_4. Silica gel column chromatography (gradient: 0-25% methanol in ethyl acetate) afforded the sensitizer **AFB-31** as dark purple crystals (377 mg, 0.535 mmol, 84%), R_f (ethyl acetate/methanol, 5:3) = 0.40, mp 145 °C (dec.). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.80 (s, 1H), 7.56 (d, J = 2.1 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.40-7.37 (m, 3H), 7.33 (d, J = 2.2 Hz, 1H), 7.26-7.23 (m, 3H), 7.17 (dd, J = 8.6, 2.2 Hz, 1H), 7.09 (d, J = 3.6 Hz, 1H), 6.96 (d, J = 8.9 Hz, 2H), 6.15 (d, J = 6.8 Hz, 1H), 6.14 (d, J = 6.7 Hz, 1H), 4.23-4.19 (m, 2H), 3.82-3.79 (m, 2H), 3.77 (s, 3H), 3.64-3.43 (m, 8H), 3.25 (s, 3H) (COOH proton not visible); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 164.9, 158.7, 158.4, 155.6, 147.9, 144.0, 141.7, 134.6, 132.0, 131.7 (2C), 131.0, 127.1, 127.0 (2C), 125.0, 123.9, 123.6, 123.4, 122.3, 121.6, 119.1, 118.5, 118.0, 116.9 (2C), 116.2, 115.5, 114.3 (2C), 108.1, 106.8, 71.3, 70.0, 69.8, 69.6, 68.9, 67.5, 58.1, 55.2; IR (neat, cm^{-1}) ν: 3416 (w, br), 3049 (w), 2932 (w), 2214 (w), 1606 (m), 1459 (s), 1382 (s), 1235 (s), 1023 (m), 798 (m), 721 (m); UV (THF, 2 × 10^{-5} M, 20 °C) λ_{max} (nm): 454 (19844 M^{-1} cm^{-1}); HRMS (TOF MS ASAP+, *m/z*): found 660.2289 (calcd. $C_{39}H_{36}N_2O_6S$, 660.2294, $[M\text{-}CO_2]^+$).

Synthesis of (*E*)-3-(5-(7,10-bis(4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-10*H*-phenothiazin-3-yl)furan-2-yl)- 2-cyanoacrylic acid (AFB-32)



Compound **8** (194 mg, 0.252 mmol) and cyanoacetic acid (480 mg, 5.64 mmol) were added to a flask and dissolved in acetonitrile (30 mL) under nitrogen atmosphere. Piperidine (0.3 mL, 3 mmol) was added and the reaction mixture was stirred at 70 °C for 50 minutes before it was cooled to room temperature and poured into an HCl solution (2 M, 100 mL) where it was stirred for 15 minutes before ethyl acetate (150 mL) was added. The phases were separated and the organic phase was washed with deionized water (2 × 150 mL) and brine (150 mL), then dried over anhydrous Na_2SO_4. Silica gel column chromatography (gradient: 2-25% methanol in ethyl acetate) afforded the sensitizer **AFB-32** as a dark purple solid (148 mg, 0.177 mmol, 70%), R_f (ethyl acetate/methanol, 3:1) = 0.11, mp 123-125 °C, 150 °C (dec.). ^{1}H NMR (600 MHz, DMSO-d_6) δ: 7.75 (s, 1H), 7.56 (d, J = 2.1 Hz, 1H), 7.51 (d, J = 8.8 Hz, 2H), 7.41-7.37 (m, 3H), 7.33 (d, J = 2.2 Hz, 1H), 7.25 (d, J = 8.9 Hz, 2H), 7.21-7.15 (m, 2H), 7.07 (d, J = 3.6 Hz, 1H), 6.97 (d, J = 8.9 Hz, 2H), 6.15 (d, J = 6.5 Hz, 1H), 6.14 (d, J = 6.5 Hz, 1H), 4.25-4.18 (m, 2H), 4.13-4.08 (m, 2H), 3.84-3.78 (m, 2H), 3.76-3.72 (m, 2H), 3.65-3.40 (m, 16H), 3.25 (s, 3H), 3.23 (s, 3H) (COOH proton not visible); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.9, 158.4, 157.9, 155.5, 148.0, 144.0, 141.8, 134.5, 133.9, 132.1, 131.7 (2C), 131.0, 127.0 (2C), 125.0, 123.9, 123.6, 123.4, 122.3, 121.6, 119.1, 118.5, 118.1, 116.9 (2C),

116.2, 115.5, 114.8 (2C), 108.0, 105.9, 71.3, 71.3, 70.0, 69.9, 69.8, 69.8, 69.6, 69.6, 68.9, 68.9, 67.5, 67.2, 58.1, 58.0; IR (neat, cm^{-1}) ν: 3041 (w), 2871 (m, br), 2353 (w), 2209 (w), 1606 (m), 1579 (m), 1452 (s), 1250 (s), 1100 (s), 794 (s); UV (THF, 2×10^{-5} M, 20 °C) λ_{max} (nm): 451 (19385 M^{-1} cm^{-1}); HRMS (TOF MS ASAP+, m/z): found 792.3080 (calcd. $C_{45}H_{48}N_2O_9S$, 792.3081, $[M\text{-}CO_2]^+$).

NMR Spectra
EO3

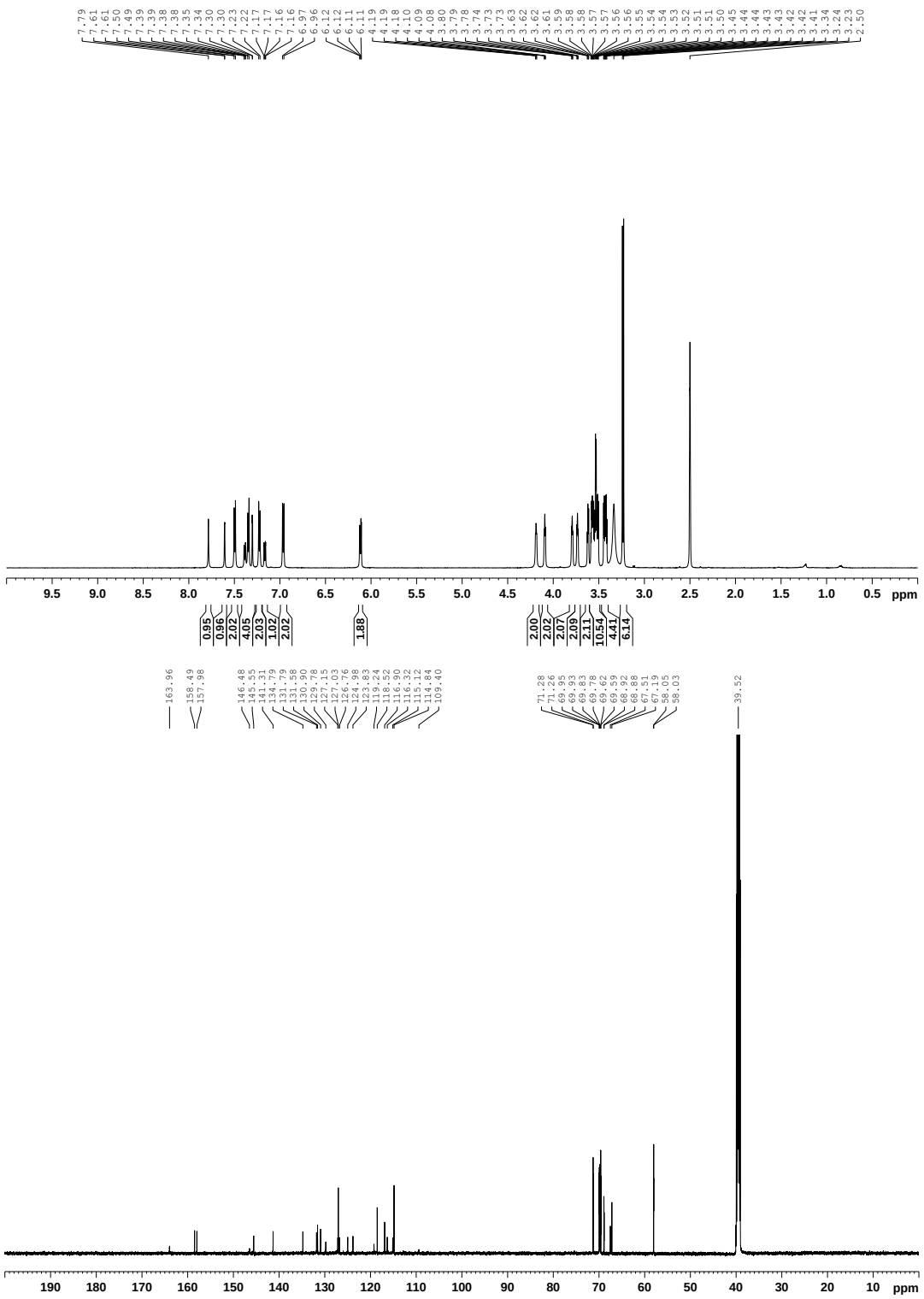


Fig. S6 *^{1}H and ^{13}C NMR spectra for* ***EO3****.*

AFB-30

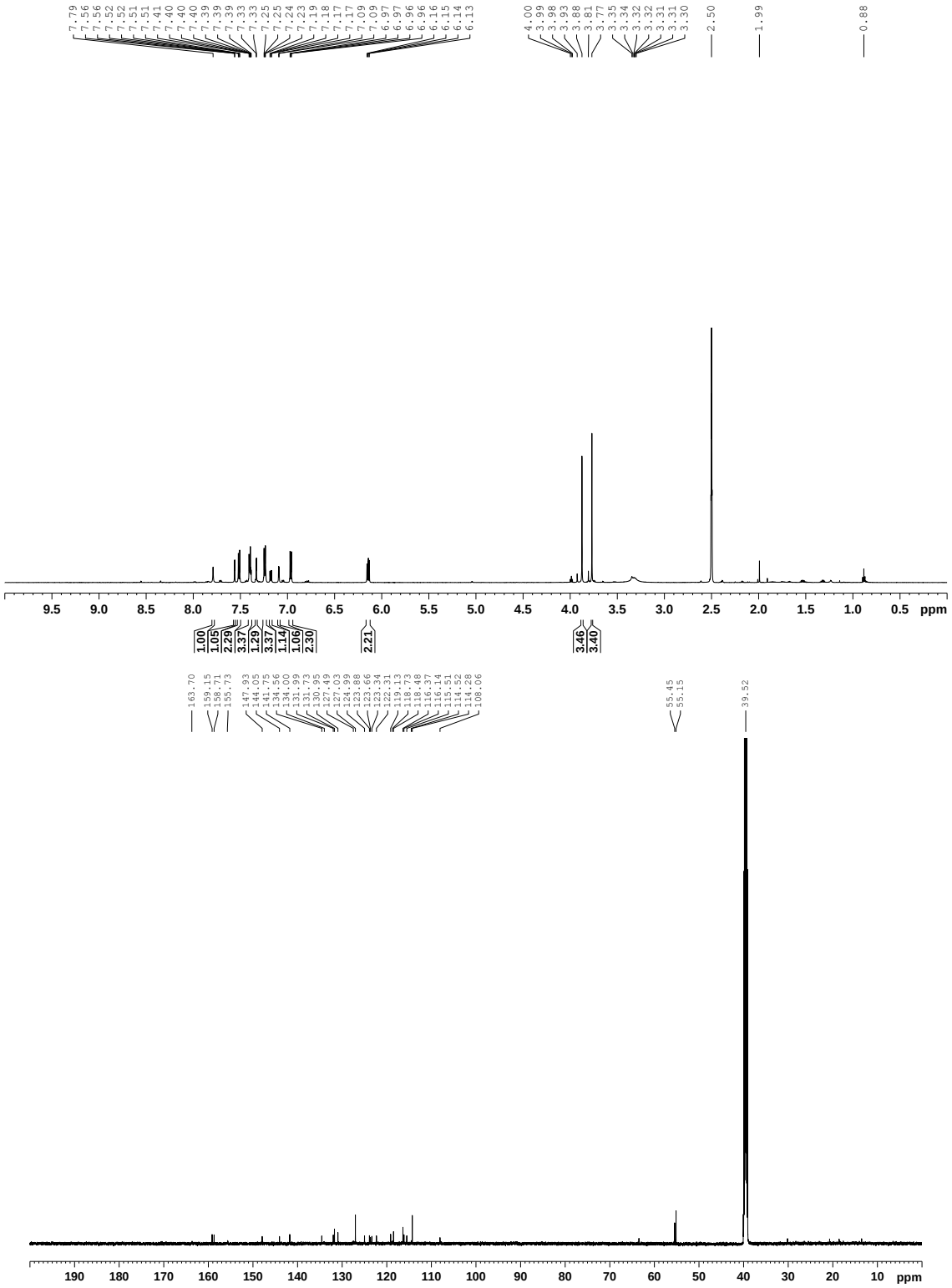


Fig. S7 *^{1}H and ^{13}C NMR spectra for* ***AFB-30****.*

AFB-31

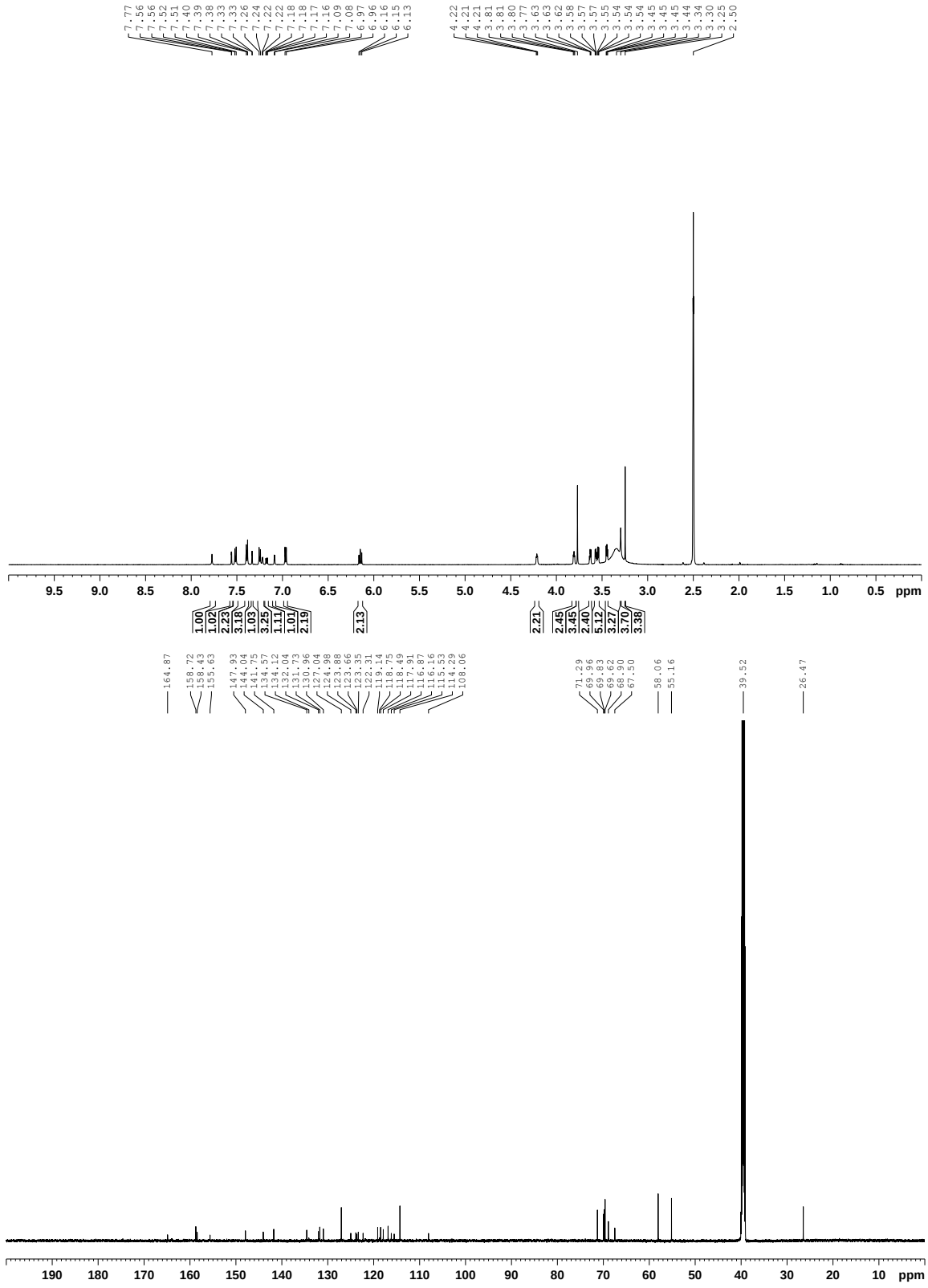


Fig. S8 *^{1}H and ^{13}C NMR spectra for* ***AFB-31****.*

AFB-32

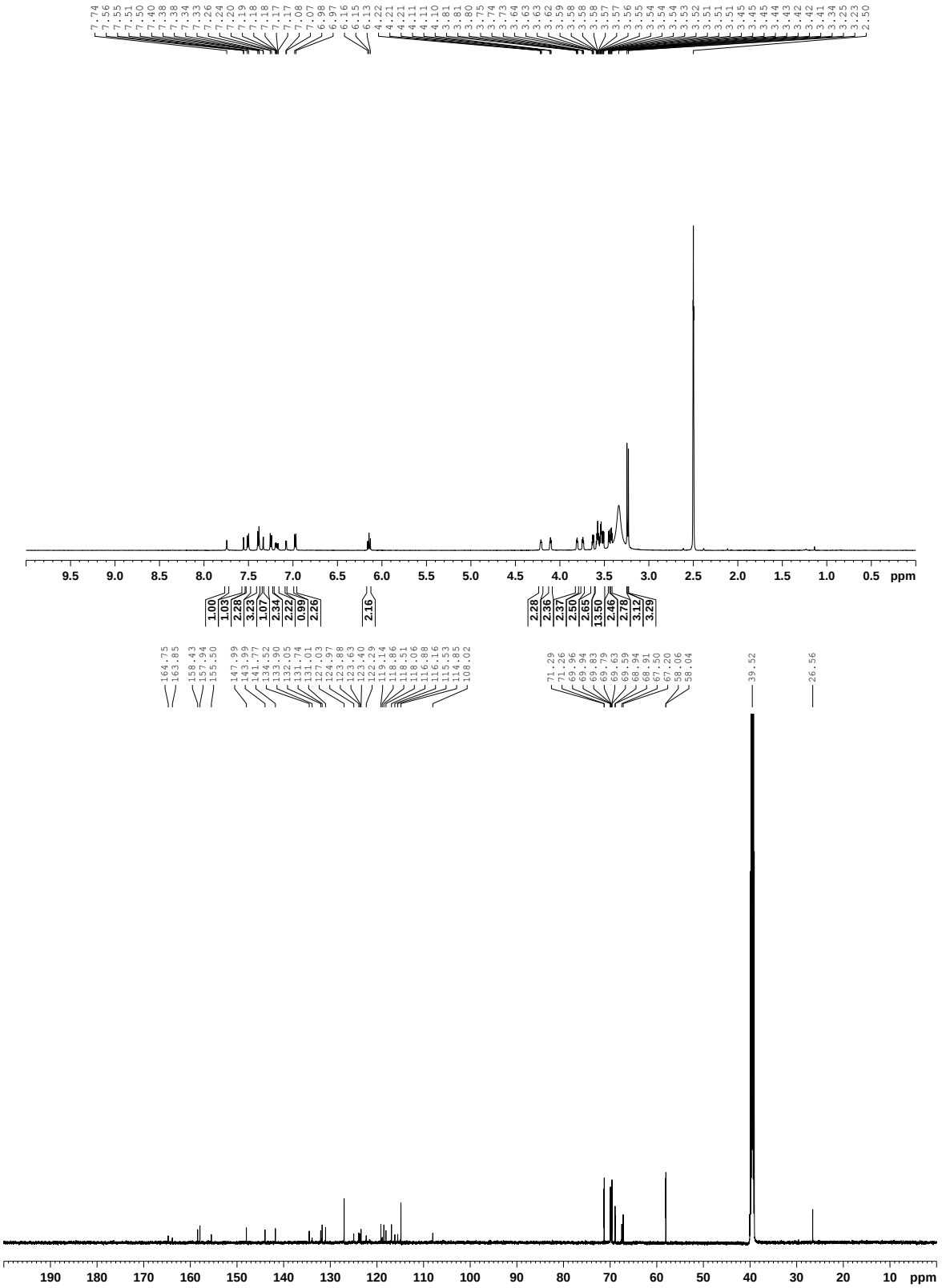


Fig. S9 *^{1}H and ^{13}C NMR spectra for* ***AFB-32****.*

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