Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Selective Photosensitization through AND Logic Response: Optimization of pH and Glutathione Response of Activatable Photosensitizers

Sundus Erbas-Cakmak,[#] Fatma Pir Cakmak,[†]* Seda Demirel Topel,[ᵃ] Taha Bilal Uyar,[#] and Engin U. Akkaya[#, †, *]

[#] UNAM-Institute of Materials Science and Nanotechnology, Bilkent University, Ankara, Turkey, TR-06800. [†] Department of Chemistry, Bilkent University, Ankara, Turkey, TR-06800. [ᵃ]Akdeniz University, Department of Chemistry, Antalya, Turkey, TR-07058.

eua@fen.bilkent.edu.tr

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1. General

All chemicals and solvents purchased from Sigma-Aldrich were used without further purification. Spectra of ^{1}H NMR and ^{13}C NMR were recorded using a Bruker DPX-400 in $CDCl_3$ with TMS as internal reference. Splitting in the spectra are shown as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), and br (broad).

Absorption spectrometry was performed using a Varian spectrophotometer. Steady state fluorescence measurements were conducted using a Varian Eclipse spectrofluorometer. Column chromatography of all products was performed using Merck Silica Gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM). Reactions were monitored by thin layer chromatography using fluorescent coated aluminum sheets. Solvents used for spectroscopy experiments were spectrophotometric grade. Mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS.

The following equation was used for quantum yield calculation,

$$Q = Q_R\,(I/I_R)(A_R/A)\;x\;(n^2/n_R^2) \qquad \text{Equation 1}$$

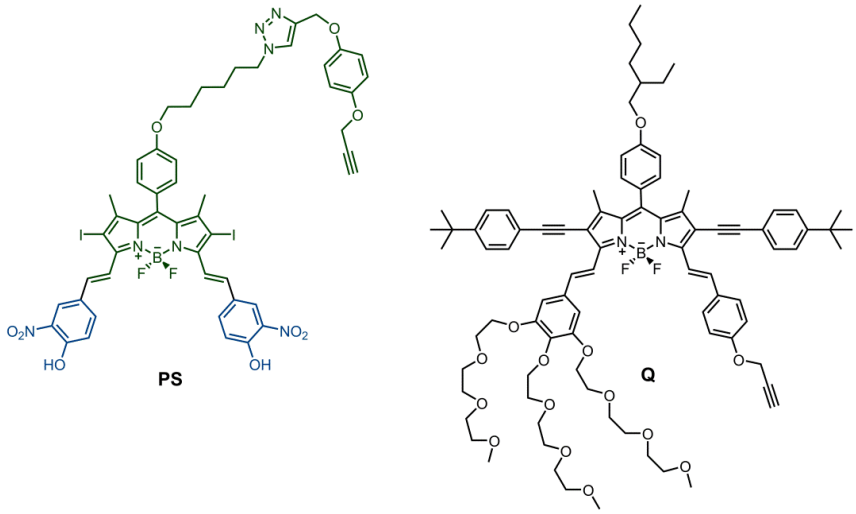
where Q_R is the quantum yield of the reference compound (cresyl violet, 0.78), I and I_R are the integrated areas of the emission spectra for sample and reference, respectively; A and A_R represent absorbance values at the excitation wavelength (610 nm) for sample and standard assuming a path length of 1 cm; and n and n_R refer to refractive indices of the solvents in which the sample and standard compounds were dissolved, respectively.

FRET efficiency was determined using the formula below:

$$E = 1 - \phi_{F(}DA)/\phi_F(D) \qquad \text{Equation 2}$$

where $\phi_F(D)$ and $\phi_{F(}DA)$ refer to fluorescence quantum yields donor (D) alone and donor as a part of EET system respectively.

2. Additional Figures



Scheme S1. Chemical Structures of **PS** and Quencher (**Q**) modules

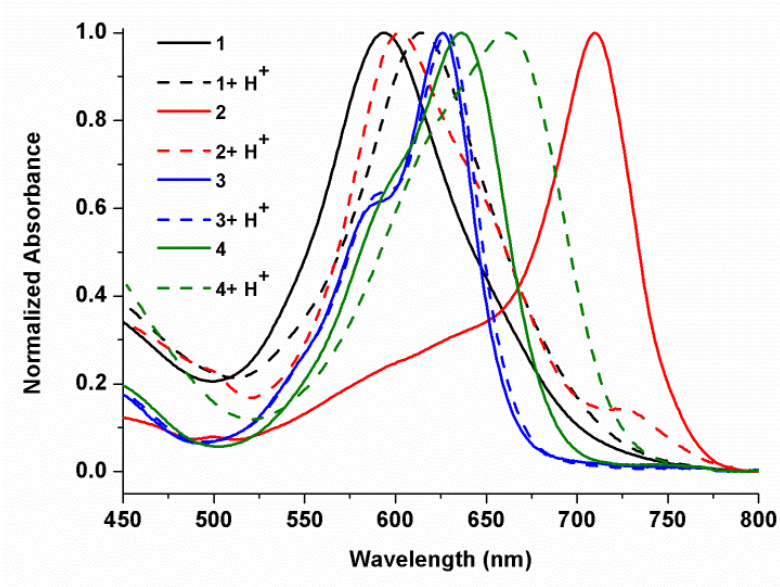


Figure S1. Normalized electronic absorption spectra of compounds **1** (black), **2** (red), **3** (blue) and **4** (green) in their neutral (solid) and protonated (dash) forms. Measurements are done in water for compounds **1** and **2** whereas 40% THF in water was used for others.

Table S1. Summary of protonation dependent absorbance change of compounds 1-5 and BOD1 and their experimental pKa values.[a]

Compound	λ_1[nm]	λ_2[nm]	pKa[b]
1	615	594	3.42
2	601	723	4.21
3	626	628	-[b]
4	660	636	2.62
5	649	731	6.62
PS[c]	649	730	6.92

[a] λ_1 corresponds to maximum absorbance wavelength of compounds in neutral solutions whereas λ_2 corresponds to the value of fully protonated compounds. Values are measured in water for compounds **1**, **2**, **5** and **BOD 1** and in 40% THF in water for compounds **3** and **4**. [b] pKa cannot be determined due to decomposition at high pH. [c] Micellar form of the PS part of **BOD 1** is used to determine the pKa value of **PS** in water.

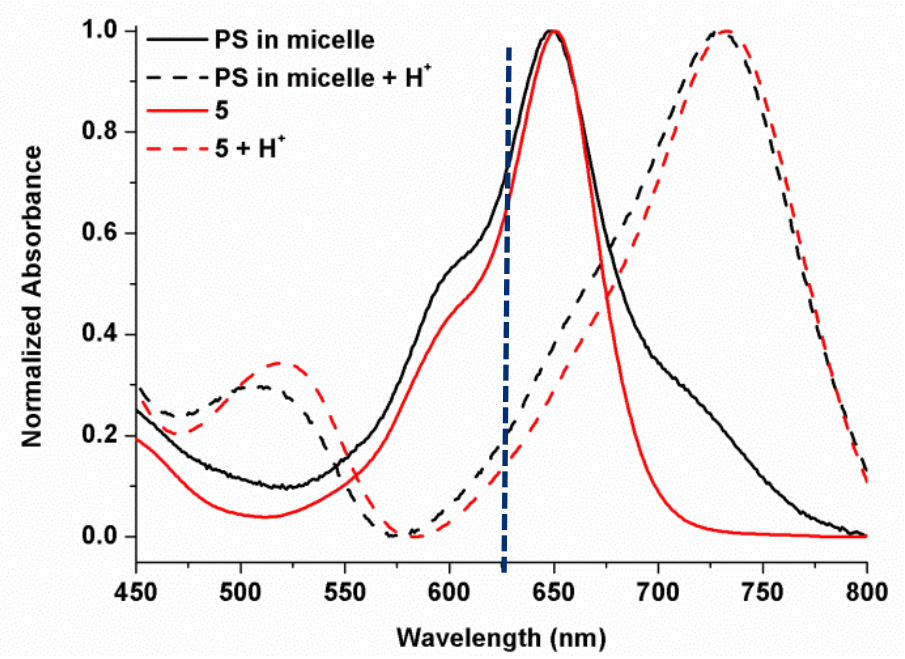


Figure S2. Normalized electronic absorption spectra of neutral (solid) and deprotonated (dash) forms of compounds **5** (red), and micellar form of **PS** module of **BOD 1** (black) in 40% THF/water and water respectively. Wavelength of excitation (625 nm) used for PDT measurements is indicated with blue dashed line.

Table S2. Photophysical characterization of BOD 1, PS and Quencher.[a]

Compound	$\lambda_{1,abs}$[nm]	$\lambda_{2,emm}$[nm]	ε ($M^{-1}cm^{-1}$)	ϕ_Δ
PS	645	667	40000	0.13
	720[b]	-	30000[b]	-
Quencher	685	707	57000	0.76
	685[b]	-	63000[b]	-
BOD 1	640, 685	654, 707	42000[c], 56000[d]	0.24
	687[b]	707[b]	70000[b]	0.15

[a] Values are determined in THF. [b]piperidine is used as a base additive. [c]calculated for absorption at 640 nm. [d]calculated for absorption at 685 nm.

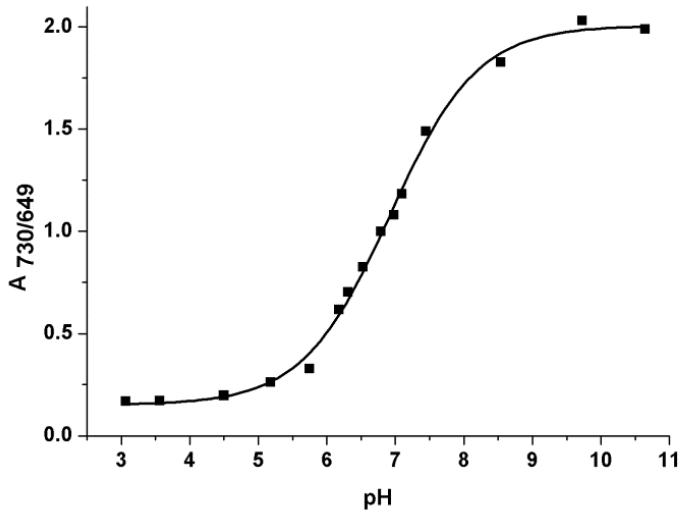


Figure S3. pH dependent change in the ratio of absorbance of **PS** in Cremophor EL micelle at 730 nm with respect to absorbance at 649 nm in water.

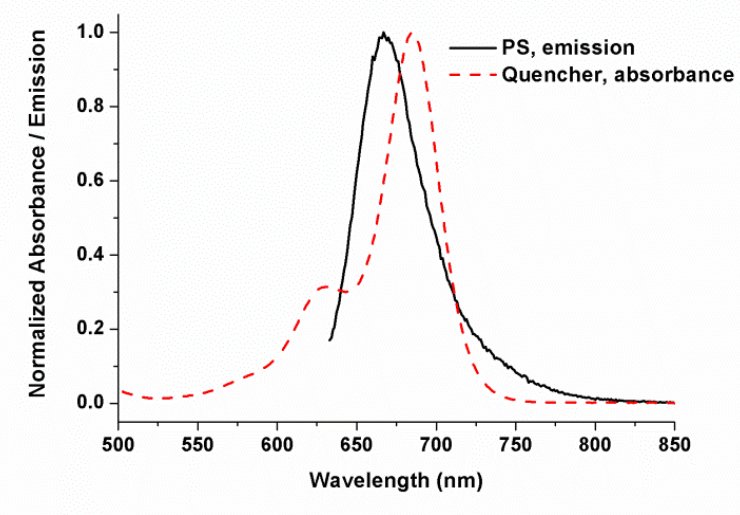


Figure S4. Comparison of normalized emission of PS module (black, solid) and absorption of Quencher module (red, dash) in THF depicting an excellent overlap for electronic energy transfer.

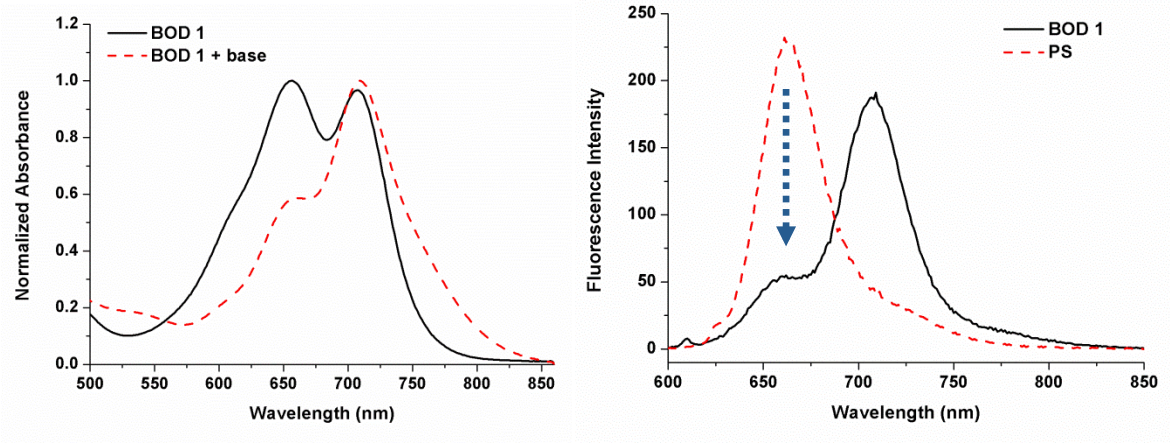


Figure S5. Electronic absorption spectra of neutral (black) and deprotonated (red) forms of micellar **BOD 1** in water (a), and comparison of fluorescence spectra of equally absorbing micellar **PS** (red, dash) and **BOD 1** (black, solid) in water (b, excited at 625 nm).

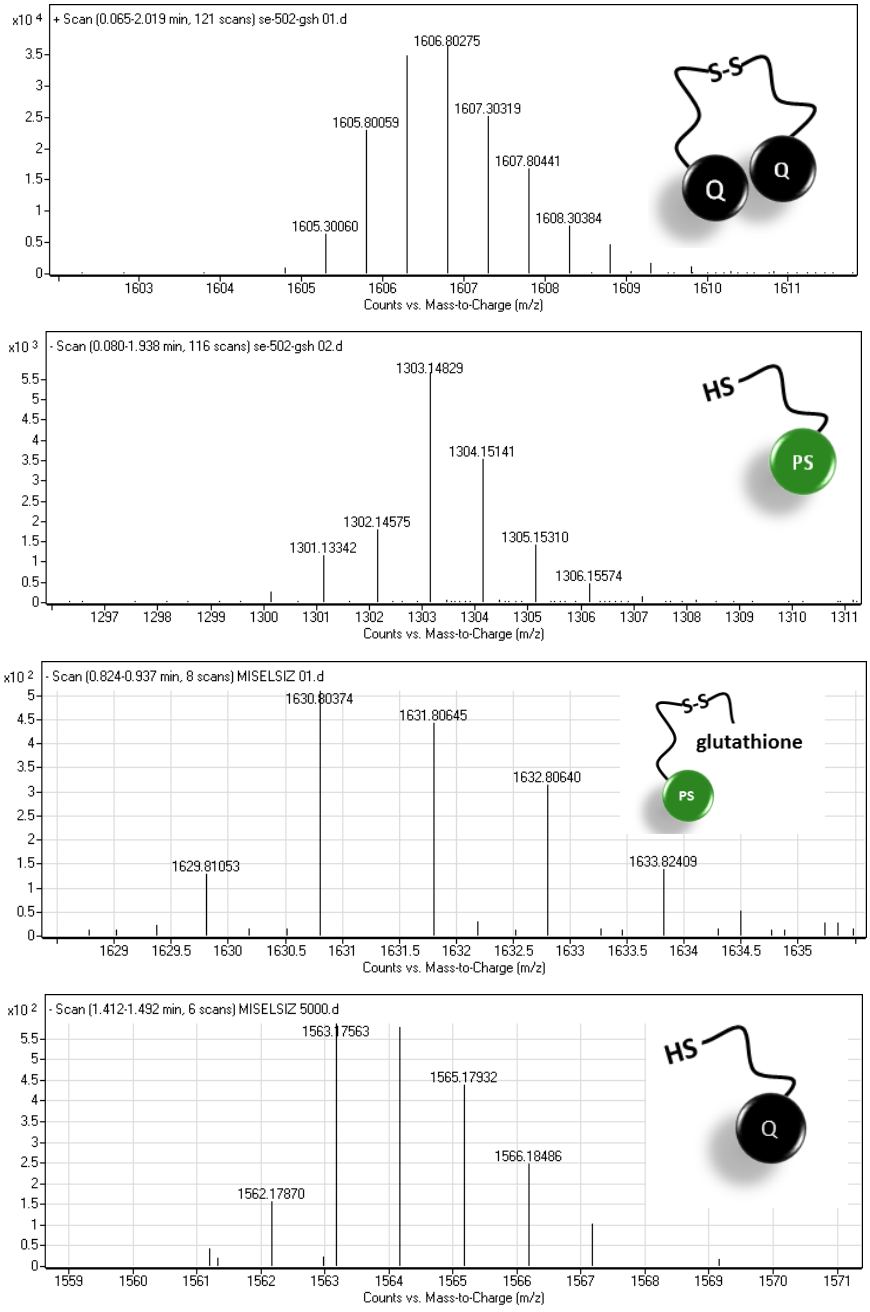


Figure S6. The cleavage of quencher from the photosensitizer in **BOD 1** after incubation with GSH for 12 h as analyzed by HRMS, (Δ = 8.8 ppm for Q-Q disulphide quencher, Δ = 4.65 ppm for thiol photosensitizer). PS-GSH adduct $(M+Na-2H)^-$ and thiol quencher $(M-F)^-$ were detected in micelle free samples.

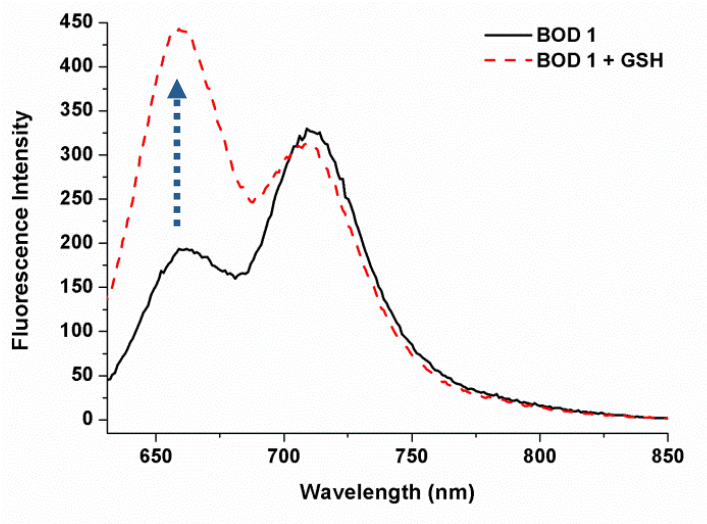


Figure S7. Emission spectra of micellar **BOD 1** at the time of addition of 2.5 equivalents of GSH (black, solid) and after 12h incubation with glutathione (red, dash) in water. The spectrum is taken by excitation at 625 nm.

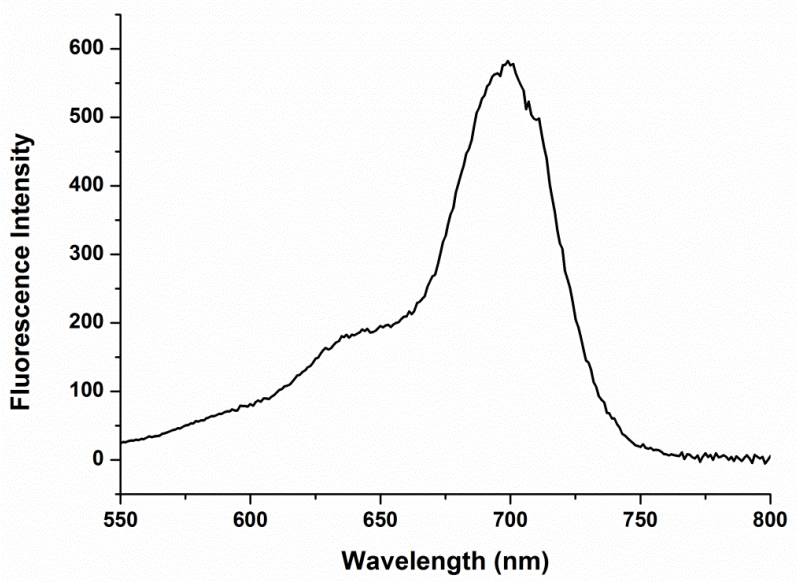


Figure S8. Excitation spectrum of micellar **BOD 1** in water for emission at 715 nm.

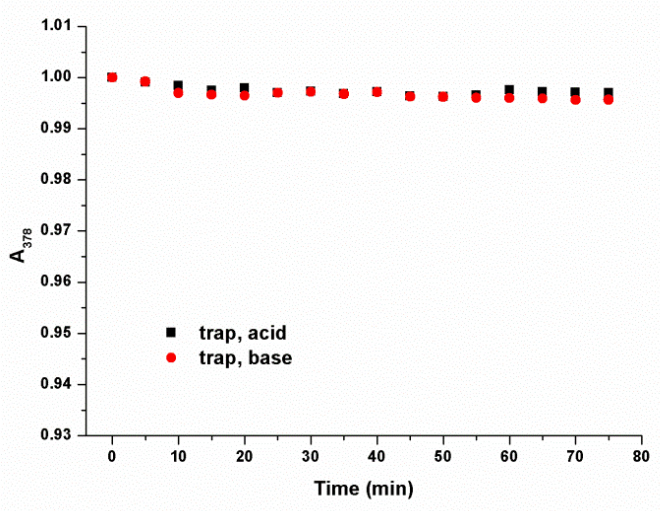


Figure S9. Control experiment with the solution containing the trap molecule only in acidic (black) and basic (red) acqueous conditions

3. Experimental Details

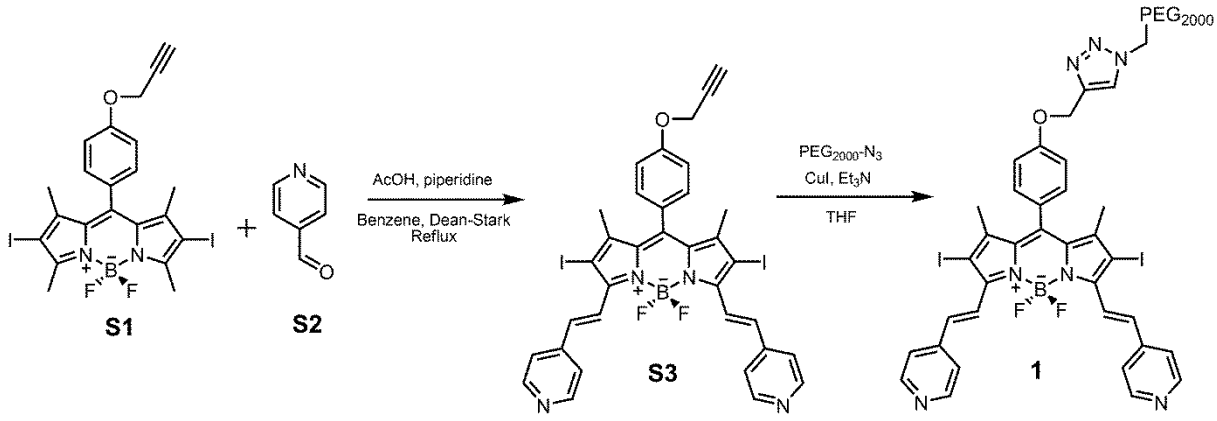
pKa Determination. Aqueous solutions of each compound are prepared and titrated with aliquots of acid (HCl) and base (NaOH) solutions. Each time, pH of the solution is measured with the aid of a pH meter and the spectra are recorded.Since there are two different absorbing species, one protonated/deprotonated and one neutral, two different peak absorbance wavelengths are observed. Plotting pH versus the ratio of absorbance at these two wavelengths and subsequent non-linear curve fit in Origin software gives the experimental pKa values in water. For some compounds 3, 4 and PS 40% THF was used to increase solubility. Since PS is the true module of the target compound (**BOD 1**) and is not soluble in water, the pKa measurements are performed after the formation of micelle.

Micelle Preparation. Micelles of PS module are prepared with Cremophor EL using the procedure in literature.[i] 50 mg Cremophor EL and **PS** (6 mg, 5 μmol) or **BOD 1** (14 mg, 5 μmol) are dissolved in 330 ml freshly distilled tetrahydrofuran. The solution is sonicated for 30 min, while the sonication water bath is kept below 35°C. Then, THF is evaporated under reduced pressure and the remaining compounds are dissolved in water (5 ml). The suspension

is filtered through 0.45 μm PTFE filter. For each measurement micelles are prepared freshly. Concentrations of solutions of the compounds in micelles are predicted using their extinction coefficients in THF. GSH (2.5 equivalent) is added to the solution of **BOD 1** before the preparation of the micelle and the sample is incubated at room temperature for 12 h at room temperature, before HRMS and spectroscopic analysis are performed.

$^1O_2$ Generation Experiments. $^1O_2$ dependent degradation of water soluble trap, 2,2'-(anthracene-9,10-diylbis(methylene) dimalonic acid is used to measure photodynamic activity since the absorption of this compound decreases upon reaction indicating the generation of $^1O_2$.[ii] Since the water solubility of the anthracene-based trap is poor in water, samples are sonicated for 15 min to obtain clear solutions. Measurements are performed using 625 nm LED and samples are irradiated with the light source from a 5 cm distance. All samples are aerated for 5 min prior to experiments. After incubation under dark for 15 min, light is irradiated for 60 min and UV-Vis spectra are recorded at each 5 min intervals. Relative singlet oxygen efficiency is calculated by the percent decrease in trap absorbance at 378 nm within 60 min light irradiation period.

4. Synthesis



Synthesis of Compound S3: Compound **S1**[iii] (120 mg, 0.19 mmol) and 4-pyridinecarboxaldehyde (51 mg, 0.48 mmol) were dissolved in benzene (40 ml). Piperidine (0.4 ml) and acetic acid (0.4 ml) were added. The reaction mixture was refluxed using Dean Stark apparatus until all aldehyde was consumed. After the reaction was completed, it was extracted with $CHCl_3$ and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column

chromatography using $CHCl_3$/MeOH (95:5, v/v). Fraction containing compound **S3** was collected then the solvent was removed under reduced pressure (0.09 mmol, 75 mg, 49%).

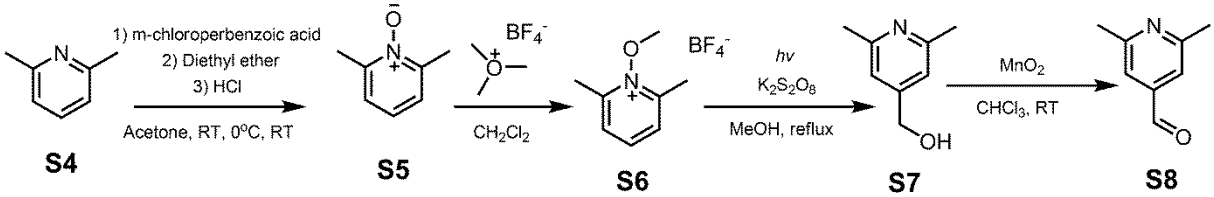
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.69 (4, 2H, J = 6.0 Hz; *CH*), 8.08 (d, 2H, J = 16.7 Hz; ArH), 7.84 (d, 2H, J = 16.7 Hz; *CH*), 7.50 (d, 4H, J = 6.0 Hz; ArH), 7.22 (d, 2H, J = 8.4 Hz; ArH), 7.18 (d, 2H, J = 8.4 Hz; ArH), 4.81 (d, 2H, J = 2.4 Hz; O*CH*$_2$), 2.60 (t, 1H, J = 2.4 Hz; O*CH*$_2$*CH*), 1.50 (s, 6H; Ar*CH*$_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 158.8, 150.3, 149.9, 147.1, 143.7, 141.4, 136.6, 133.9, 129.3, 127.5, 122.8, 121.5, 116.2, 83.7, 77.7, 76.2, 56.1, 17.8.

HRMS (TOF-ESI): m/z calcd for $C_{34}H_{25}BF_2I_2N_4O$: 809.0252 $[M+H]^+$; found: 809.0290 $[M+H]^+$, Δ = 4.70 ppm.

Synthesis of Compound 1: Compound **S3** (50 mg, 62 μmol) and azide functionalized polyethylene glycol monomethylether (2000MW, 124 mg, 62 μmol) were dissolved in tetrahydrofuran (2 ml). Triethylamine (430 μl) and CuI (24 mg, 0.126 mmol) were added. The reaction mixture was stirred for 12 h at room temperature. After the reaction was completed, it was extracted with $CHCl_3$ and brine. The organic layer was collected and dried over Na_2SO_4, followed by evaporation of the solvent under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$/MeOH (95:5, v/v) as mobile phase. Fraction containing compound **1** was collected then the solvent was removed under reduced pressure (34 μmol, 100 mg, 54%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.62 (4H; *CH*), 8.04 (d, 2H, J = 16.72 Hz; CH), 7.80 (d, 2H, J = 16.80 Hz; *CH*), 7.51 (d, 2H, J = 5.52 Hz; ArH), 7.19 (2H + 2H; ArH), 5.25 (2H; OCH_2), 4.58 (t, 2H, J = 5.08 Hz; N*CH*$_2$), 3.90-3.30 (PEG, O*CH*$_2$*CH*$_2$*O*), 1.50 (s, 6H; Ar*CH*$_3$).



Synthesis of Compound S5^{iv}: 2,6-lutidine (5 g, 47 mmol) was dissolved in 60 ml acetone. m-chloroperbenzoic acid (13 g, 75 mmol) was dissolved in 60 ml acetone and was added to previous mixture dropwise during the course of 10 minutes. The reaction mixture was stirred for 90 min. at room temperature. Then, it was cooled using an ice bath for 30 min. Following this, 20 ml of ice cold diethyl ether was added and HCl gas was bubbled through the reaction for 10 min. The solid produced as a result of bubbling was filtered, washed two times with

ether. Then, salt was dissolved in 20 ml of water; pH was adjusted to be above 10 using $NaHCO_3$. Finally, the solution was extracted with $CHCl_3$, solvent was evaporated to yield liquid colorless compound **S5** (40 mmol, 4.9 g, 85%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.18 (d, 2H, J = 7.24 Hz; Ar*H*), 7.00 (t, 1H, J = 7.56 Hz; ArH), 2.45 (s, 6H; Ar*CH*$_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 148.7, 124.4, 123.8, 18.1.

Synthesis of Compound S6: Compound **S5** (6 g, 32 mmol) was dissolved in 100 ml dichloromethane. Equal amount of trimethyloxonium tetrafluoroborate (32 mmol, 7.05 g) was added and the reaction mixture was stirred for 5h at RT. Solvent was was vacuum evaporated to yield a white solid (quantitative, used without further purification).

^{1}H NMR (D_2O, 400 MHz, δ ppm) 8.18 (t, 1H, J = 7.92 Hz; Ar*H*), 7.75 (d, 2H, J = 7.96 Hz; ArH), 4.22 (s, 3H; OCH_3), 2.81 (s, 6H; Ar*CH*$_3$).

^{13}C NMR (D_2O, 400 MHz, δ ppm) 153.6, 143.8, 128.0, 66.6, 16.7.

Synthesis of Compound S7: Compound **S6** (5.19 g, 23.1 mmol) was dissolved in 65 ml MeOH. Potassium peroxodisulfate (1.53 g, 5.65 mmol) was dissolved in 6 ml H_2O and was added to previous reaction mixture. The solution was refluxed for 30 min while it was irradiated with light. Following this, more of potassium peroxodisulfate (3.06 g, 11.30 mmol) was added and the resction was refluxed for additional 30 min. The excess K2S2O2 was filtered off and the solvent was vacuum evaporated to yield brown oil. The product was further purified by column chromatography using $CHCl_3$:MeOH (90/10; v/v) as mobile phase (yellow oil, 0.86 g, 6.3 mmol, 27%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.48 (s, 2H; ArH), 4.91 (s, 1H; CH_2OH), 2.60 (s, 6H; $ArCH_3$).

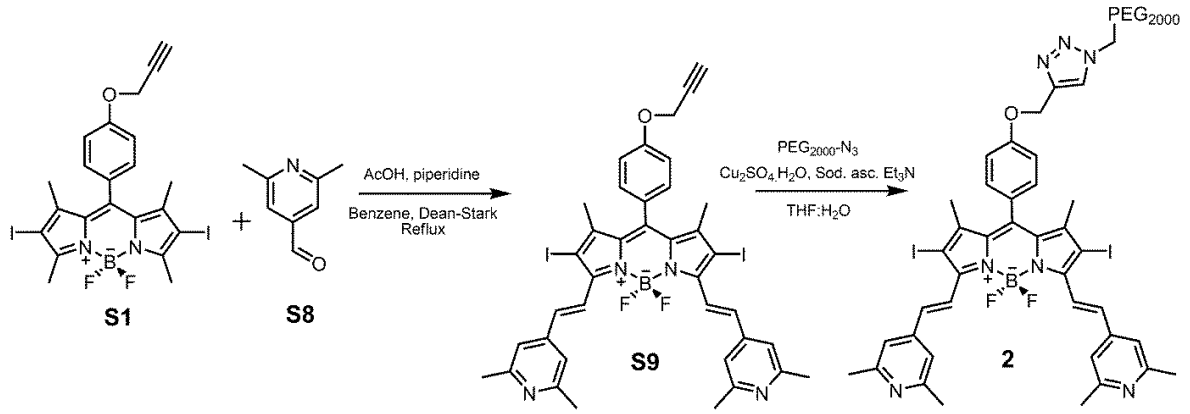
^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 161.6, 152.5, 121.1, 61.5, 18.5.

Synthesis of Compound S8^v: Compound **S7** (864 mg, 6.3 mmol) was dissolved in 2.5 ml $CHCl_3$ and 1 ml methanol. The solution was heated to 35^{o}C to dissolve the compound. Then, 1.1 equivalents of MnO_2 (0.61 g, 7 mmol) was added at RT. After stirring 2h at RT, additional amount of MnO_2 (0.51 g) was added. After 2h, the solid precipitates were removed by filtering over celite. The solvent was removed by vacuum evaporation. Then the product was

prufied further by precipitation of the impurities in $CHCl_3$. (white solid, 101 mg, 0.75 mmol, 12%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 9.93 (s, 1H), 7.30 (s, 2H; ArH), 2.53 (s, 6H; $ArCH_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 192.1, 159.5, 124.1, 119.0, 24.3.



Synthesis of Compound S9: Compound **S1** (93 mg, 0.15 mmol) and 2,6-dimethyl-4-pyridinecarboxaldehyde (**S8**, 60 mg, 0.44 mmol) were dissolved in benzene (15 ml). Piperidine (0.4 ml) and acetic acid (0.4 ml) were added. The reaction mixture was refluxed using Dean Stark apparatus until all aldehyde was consumed. After the reaction was completed, it was extracted with $CHCl_3$ and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$/MeOH (95:5, v/v) as mobile phase. Fraction containing compound **S9** was collected, then the solvent was removed under reduced pressure (0.07 mmol, 61 mg, 47%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.00 (d, 2H, J = 16.73 Hz; CH), 7.78 (d, 2H, J = 16.69 Hz; CH), 7.21 (d, 2H, J = 8.80 Hz; ArH), 7.18 (d,s, 2H + 1H, J = 8.91 Hz; ArH), 4.81 (d, 2H, J = 2.36 Hz; OCH_2), 2.6 (s, 12H, $ArCH_3$), 2.5 (1H, CH), 1.52 (s, 6H, $ArCH_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 158.3, 150.1, 147.0, 144.4, 141.1, 137.2, 133.8, 129.3, 127.5, 122.3, 118.8, 118.4, 116.2, 105.9, 77.8, 76.2, 56.1, 24.1, 17.7.

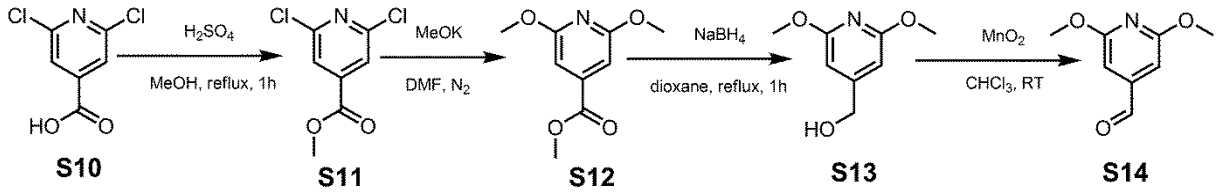
HRMS (TOF-ESI): m/z calcd for $C_{38}H_{34}BF_2I_2N_4O^+$: 865.0878 $[M+H]^+$, found: 865.07406 $[M+H]^+$, Δ = 1.59 ppm.

Synthesis of Compound 2: Compound **S9** (42 mg, 49 μmol) and azide functionalized polyethylene glycol monomethylether (2000MW, 84 mg, 62 μmol) were dissolved in tetrahydrofuran (2 ml) and water (0.1 ml). Triethylamine (50 μl) was added and the reaction was stirred for 5 min. Then, $CuSO_4.5H_2O$ (4 mg, 29 μmol) and sodium ascorbate (6 mg, 29

μmol) were added. The reaction mixture was stirred for 12 h at room temperature. After the reaction was completed, it was extracted with $CHCl_3$ and brine. The organic layer was collected and dried over Na_2SO_4, followed by evaporation of the solvent under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$/MeOH (92:8, v/v) as mobile phase. Fraction containing compound **2** was collected then the solvent was removed under reduced pressure (6 μmol, 18 mg, 12%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.00 (d, 2H, J = 16.73 Hz; ArH), 7.96 (s, 1H; ArH), 7.81 (d, 2H, J = 16.76 Hz; ArH), 7.25-7.15 (m, 2H + 2H + 4H; ArH), 5.29 (s, 2H; OCH_2), 4.12 (t, 2H, J = 4.72 Hz; NCH_2), 2.60 (s, 12H; $ArCH_3$), 1.52 (s, 6H; $ArCH_3$).

HRMS (TOF-ESI): Distribution around 2800 with separation of 44 corresponding to etylene glycole unit.



Synthesis of Compound S11[vi]: 2,6-dichloronicotinic acid (500 mg, 2.6 mmol) was dissolved in 5.2 ml MeOH. 78 μl concentrated H_2SO_4 was added. The reaction mixture was refluxed for 1h. Then, the reaction was cooled to RT and was quenched with $NaHCO_3$. It was extracted with $CHCl_3$ and water. The organic layer was collected and dried over Na_2SO_4, followed by evaporation of the solvent under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$ as mobile phase. Fraction containing compound **S11** was collected then the solvent was removed under reduced pressure (white solid, 2.4 mmol, 490 mg, 92%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.84 (s, 2H; ArH), 4.01 (s, 3H; OCH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 163.2, 151.5, 142.4, 122.6, 53.3.

Synthesis of Compound S12: Compound **S11** (250 mg, 1.21 mmol) was dissolved in 10 ml of anhydrous dimethylformamide. Ar was purged in the solution for 15 min. Potassium methoxide (255 mg, 3.64 mmol, 864 μl) was added to the reaction mixture and it was refluxed for 12h. Then, the reaction mixture was neutralized with HCl solution. It was extracted with $CHCl_3$ and water. The organic layer was collected and dried over Na_2SO_4, followed by evaporation of the solvent under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$/Hexanes (3/2; v/v) as mobile phase. Fraction containing

compound **S12** was collected then the solvent was removed under reduced pressure (white solid, 0.51 mmol, 100 mg, 42%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 6.87 (s, 2H; ArH), 3.96 (s, 6H; $ArOCH_3$), 3.92 (s, 3H; OCH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 165.6, 163.8, 142.7, 101.2, 53.9, 52.5.

Synthesis of Compound S13: Compound **S12** (800 mg, 4.06 mmol) and 2 equivalents of $NaBH_4$ (309 mg, 8.12 mmol) were dissolved in 10 ml dioxane. It was refluxed for 1h. Then, the reaction was cooled to RT and quenched with ice cold water. It was extracted with CH_2Cl_2. The organic layer was collected and dried over Na_2SO_4, followed by evaporation of the solvent under reduced pressure (686 mg, quantitative).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 6.30 (s, 2H, ArH), 4.62 (s, 2H; $ArCH_2$), 3.91 (s, 6H; $ArOCH_3$), 1.93 (b, 1H; $ArCH_2OH$).

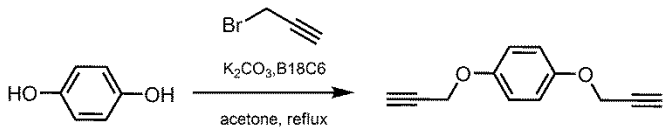
^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 163.5, 155.6, 98.3, 63.8, 53.6.

Synthesis of Compound S14: Compound **S13** (172 mg, 1.02 mmol) was dissolved in 6 ml of $CHCl_3$. 1.1 equivalents of MnO_2 (98 mg, 1.12 mmol) was added, and the reaction mixture was stirred at RT for 12 h. After completion of the reaction as followed by thin layer chromatography, the reaction mixture was filtered over celite to get rid of MnO_2 by products. Solvent was removed under reduced pressure to yield compound **S14** (yellow solid, 118 mg, 68%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 9.94 (s, 1H), 6.73 (s, 2H; ArH), 4.00 (s, 6H; $ArCH_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 191.2, 164.3, 147.5, 100.7, 54.0.

HRMS (TOF-ESI): m/z calcd for $C_8H_{10}NO_3^+$: 168.0655 $[M+H]^+$, found:168.06143 $[M+H]^+$, Δ = 2.42 ppm.



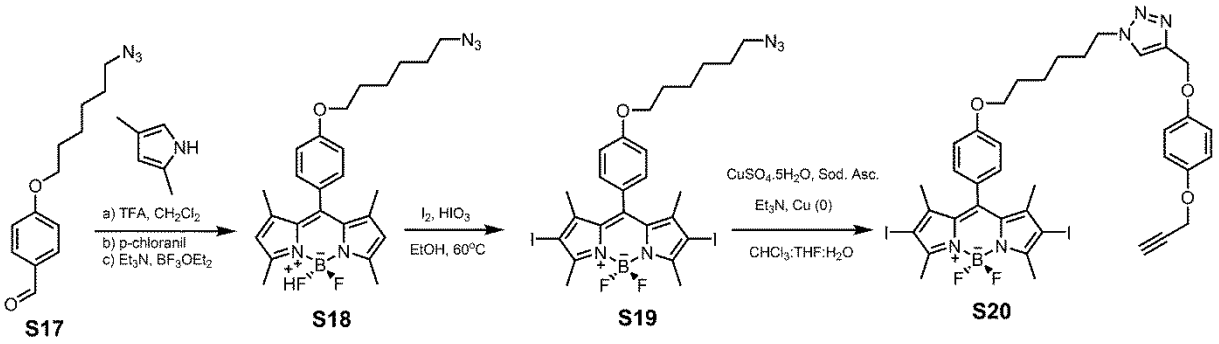
S15 **S16**

Synthesis of Compound 16: Hydroquinone (2 g, 18.2 mmol) was dissolved in 30 ml acetone. 5 equivalents of K_2CO_3 (12.6 g, 91 mmol) was added and the reaction mixture was refluxed for 30 min. Then, 3 equivalents of propargyl bromide (6. 48 g, 54.6 mmol) was added dropwise. The reaction mixture was refluxed for additional 12 h. Then, it was cooled to RT.

Following the extraction with $CHCl_3$, the organic layer was collected and dried over Na_2SO_4, followed by evaporation of the solvent under reduced pressure. Crude product was crystallized in hexanes to yield compound **S16** (white solid, quantitative).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 6.94 (s, 2H; ArH), 4.67 (d, 4H, J = 2.44 Hz; $ArOCH_2$), 2.53 (t, 2H, J = 2.44 Hz; CCH).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 152.4, 116.0, 78.8, 75.4, 56.5.



Synthesis of Compound S18: CH_2Cl_2 (300 ml) was purged with Ar for 30 min. Compound **S17** (1.1 g, 4.45 mmol) and 2,4-dimethyl pyrrole (0.96 ml, 9.4 mmol) were added. The color of the solution turned into red after the addition of 3 drops of trifluoroacetic acid. The reaction mixture was stirred at room temperature for 12h. Then, tetrachloro-1,4-benzoquinone (1.09 g, 4.45 mmol) was added and the reaction mixture was stirred at room temperature for 45 min. Then triethyl amine (5 ml) and boron trifluoride diethyl etherate (5 ml) were added sequencially. After stirring at room temperature for 30 min, it was extracted with water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$. Fraction containing compound **S18** was collected then the solvent was removed under reduced pressure (400 mg, 0.86 mmol, 19%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.20 (d, 2H, J = 8.60 Hz; ArH), 7.01 (d, 2H, J = 8.64 Hz; ArH), 6.00 (s, 2H; ArH), 4.05 (t, 2H, J = 6.44 Hz; OCH_2), 3.31 (t, 2H, J = 6.80 Hz; NCH_2), 2.58 (s, 6H; $ArCH_3$), 1.86 (m, 2H; CH_2), 1.70 (m, 2H; CH_2), 1.55 (m, 4H; CH_2), 1.45 (s, 6H; $ArCH_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 159.6, 155.2, 143.2, 141.9, 131.9, 129.2, 126.9, 121.1, 115.1, 67.9, 51.4, 29.1, 28.8, 26.6, 25.7, 14.6, 14.5.

Synthesis of Compound S19: Compound **S18** (270 mg, 0.58 mmol) and I_2 (368 mg, 1.45 mmol) were dissolved in ethanol (100 ml). Iodic acid, HIO_3 (204 mg, 1.16 mmol) was dissolved in a few drops of water and added into previous solution. The reaction mixture was

stirred at 60°C for a few hours untill all reeactant was consumed. Then, saturated sodium thiosulfate solution was added (50 ml) and it was stirred at rrom temparature for additional 30 min. Then, it was extracted with $CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure (415 mg, quantitative).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.22 (d, 2H, J = 8.68 Hz; ArH), 7.02 (d, 2H, J = 8.68 Hz; ArH), 4.04 (t, 2H, J = 6.36 Hz; OCH_2), 3.30 (t, 2H, J = 6.80 Hz; NCH_2), 2.63 (s, 6H; $ArCH_3$), 1.85 (m, 2H; CH_2), 1.70 (m, 2H; CH_2), 1.55 (m, 4H; CH_2), 1.45 (s, 6H; $ArCH_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 160.1, 156.6, 145.5, 141.6, 131.8, 129.1, 126.6, 115.5, 85.8, 68.0, 51.4, 29.1, 28.8, 26.6, 25.7, 17.2, 16.0.

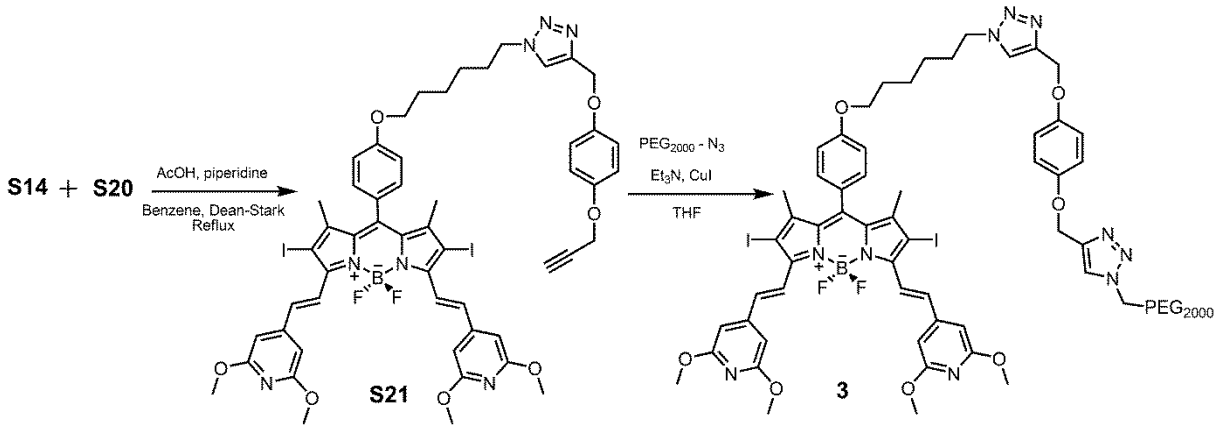
HRMS (TOF-ESI): m/z calcd for $C_{25}H_{27}BF_2I_2N_5O^{-}$ 716.03716 $[M-H]^-$, found: 716.06297 $[M-H]^-$, Δ = 36.0 ppm.

Synthesis of Compound S20: Compound **S16** (519 mg, 2.8 mmol) and compound **S19** (200 mg, 0.28 mmol) were dissolved in $CHCl_3$ (3 ml) and THF (3 ml). Triethylamine (200 μl) was added and the reaction was stirred for 5 min. Then, saturated solutions of $CuSO_4.5H_2O$ (200 μl) and sodium ascorbate (200 μl) were added. Catalytic amount of Cu (0) was added. The reaction mixture was stirred for 12 h at room temperature. After the reaction was completed, it was extracted with $CHCl_3$ and organic layer was evaporatd under reduced pressure. It was purified by silica gel column chromatography using $CHCl_3$ as mobile phase. Fraction containing compound **S20** was collected then the solvent was removed under reduced pressure (0.27 mmol, 241 mg, 96%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.60 (s, 1H; ArH), 7.21 (d, 2H, J = 8.12 Hz; ArH), 7.02 (d, 2H, J = 8.17 Hz; ArH), 6.93 (s, 4H; ArH), 5.16 (s, 2H; OCH_2), 4.62 (d, 2H, J = 1.52 Hz; OCH_2), 4.48 (t, 2H, J = 7.12 Hz; NCH_2), 4.01 (t, 2H, J = 6. 28 Hz; OCH_2), 2.63 (s, 6H; $ArCH_3$), 2.02 (t, 1H, J = 1.40 Hz; CH), 1.96 (m, 2H, CH_2), 1.82 (m, 2H, CH_2), 1.55 (m, 2H, CH_2), 1.44 (s, m, 6H + 2H, $ArCH_3$ + CH_2).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 160.0, 156.5, 153.1, 152.1, 145.4, 144.4, 141.7, 131.7, 129.1, 126.6, 122.5, 116.1, 115.8, 115.4, 78.8, 75.4, 67.9, 62.7, 56.5, 50.3, 30.2, 29.0, 26.3, 25.6, 17.2, 16.0.

HRMS (TOF-ESI): m/z calcd for $C_{37}H_{38}BF_2I_2N_5NaO_3^{+}$: 926.1017 $[M+Na]^+$, found: 926.08227 $[M+Na]^+$, Δ = 20.98 ppm.



Synthesis of Compound S21: Compound **S20** (125 mg, 0.14 mmol) and 2,6-dimethoxy-4-pyridinecarboxaldehyde (**S14**, 92 mg, 0.56 mmol) were dissolved in benzene (30 ml). Piperidine (0.3 ml) and acetic acid (0.3 ml) were added. The reaction mixture was refluxed using Dean Stark apparatus until all aldehyde was consumed. After the reaction was completed, it was extracted with $CHCl_3$ and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$ as mobile phase. Fraction containing compound **S21** was collected, then the solvent was removed under reduced pressure (62 μmol, 75 mg, 44%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.94 (d, 2H, J = 16.68 Hz; CH), 7.72 (d, 2H, J = 16.64 Hz; CH), 7.59 (s, 1H; ArH), 7.16 (d, 2H, J = 8.57 Hz; ArH), 7.04 (d, 2H, J = 8.64 Hz; ArH), 6.93 (s, 4H; ArH), 6.57 (s, 4H; ArH), 5.20 (s, 2H, OCH_2), 4.65 (d, 2H, J = 2.44 Hz; OCH_2), 4.41 (t, 2H, t, J = 7.12 Hz; NCH_2), 4.04 (t, 2H, J = 6.32 Hz; OCH_2), 3.98 (s, 12H, OCH_3), 2.52 (t, 1H, J = 2.42 Hz; CH), 2.01 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 1.62 (s, 6H; $ArCH_3$), 1.48 (m, 4H; CH_2).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 163.8, 160.21, 153.1, 152.2, 150.0, 149.0, 146.7, 144.5, 137.2, 133.8, 129.3, 128.3, 126.6, 122.4, 122.3, 116.1, 115.8, 115.5, 99.3, 78.8, 75.4, 67.9, 62.8, 56.5, 53.7, 50.3, 30.2, 29.0, 26.3, 25.6, 17.8.

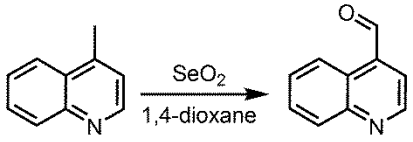
HRMS (TOF-ESI): m/z calcd for $C_{53}H_{52}BF_2I_2N_7NaO_7^+$: 1224.1971 $[M+Na]^+$, found: 1224.1762 $[M+Na]^+$, Δ = 17.07 ppm.

Synthesis of Compound 3: Compound **S21** (17 mg, 14 μmol) and azide functionalized polyethylene glycol monomethylether (2000MW, 31 mg, 16 μmol) were dissolved in $CHCl_3$ (1 ml) and THF (1 ml). Triethylamine (50 μl) was added and the reaction was stirred for 5 min. Then, saturated solutions of $CuSO_4.5H_2O$ (150 μl) and sodium ascorbate (150 μl) were added. Catalytic amount of Cu (0) was added. The reaction mixture was stirred for 12 h at

room temperature. After the reaction was completed, the crude product was applied to silica gel column chromatography using $CHCl_3$/MeOH (90:10, v/v) as mobile phase. Fraction containing compound **3** was collected then the solvent was removed under reduced pressure (8 μmol, 26 mg, 58%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.96 (d, 2H, J = 16.72 Hz; CH), 7.83 (s, 1H; ArH), 7.73 (d, 2H, J = 16.64 Hz; CH), 7.62 (s, 1H; ArH), 7.17 (d, 2H, J = 8.76 Hz; ArH), 7.05 (d, 2H, J = 8.28 Hz; ArH), 6.93 (s, 4H; ArH), 6.54 (s, 4H; ArH), 5.19 (s, 2H; OCH_2), 5.17 (s, 2H; OCH_2), 4.58 (t, 2H, J = 5.00 Hz; NCH_2), 4.41 (t, 2H, t, J = 7.64 Hz; NCH_2), 4.10-3.30 (PEG), 2.01 (m, 2H, CH_2), 1.85 (m, 2H, CH_2), 1.62 (s, 6H; $ArCH_3$), 1.48 (m, 4H; CH_2).

HRMS (TOF-ESI): Distribution around 3000 with separation of 44 corresponding to etylene glycole unit.



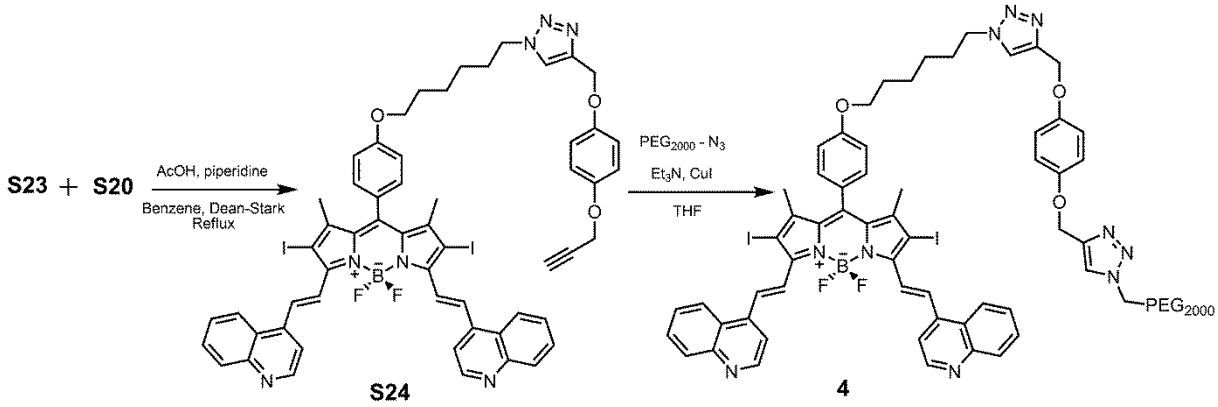
S22 **S23**

Synthesis of Compound S23[vii]: 4-methylquinone (1.32 ml, 10 mmol) was dissolved in 1,4-dioxane (12 ml). Selenium dioxide (1.12 g, 10.12 mmol) was added to the reaction mixture and it was refluxed for 8h. Then, solvent was removed under reduced pressure and the crude product was applied to silica gel column chromatography using ethyl acetate as mobile phase. Fraction containing compound **S23** was collected, then the solvent was removed under reduced pressure (946 mg, 6 mmol, 60%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 10.50 (s, 1H), 9.19 (d, 1H, J = 4.24 Hz; ArH), 9.00 (dt, 1H, J_1 = 0.64 Hz, J_2 = 7.03 Hz; ArH), 8.21 (dt, 1H, J_1 = 0.36 Hz, J_2 = 7.24 Hz; ArH), 7.70-7.85 (m, 3H,; ArCH).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 192.8, 150.4, 149.3, 136.7, 130.2, 130.0, 129.4, 125.8, 124.4, 123.8.

HRMS (TOF-ESI): m/z calcd for $C_{10}H_8NO^+$: 158.0600 $[M+Na]^+$, found: 158.05593 $[M+Na]^+$, Δ = 25.75 ppm.



Synthesis of Compound S24: Compound **S20** (91 mg, 0.1 mmol) and quinoline-4-carboxaldehyde, compound **S23** (40 mg, 0.25 mmol) were dissolved in benzene (25 ml). Piperidine (0.3 ml) and acetic acid (0.3 ml) were added. The reaction mixture was refluxed using Dean Stark apparatus until all aldehyde was consumed. After the reaction was completed, it was extracted with $CHCl_3$ and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc as mobile phase. Fraction containing compound **S24** was collected, then the solvent was removed under reduced pressure (84 μmol, 99 mg, 84%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 9.01 (d, 2H, J = 4.64 Hz; ArH), 8.96 (d, 2H, J = 16.56 Hz; CH), 8.32 (d, 2H, J = 8.40 Hz; ArH), 8.18 (d, 2H, J = 8.36 Hz; ArH), 7.94 (d, 2H, J = 16.53 Hz; CH), 7.81 (d, 2H, J = 4.60 Hz; ArH), 7.77 (t, 2H, 7.48 Hz; ArH), 7.62 (t, 2H, j = 7.76 Hz; ArH), 7.22 (d, 2H, J = 8.41 Hz, ArH), 7.09 (d, 2H, J = 8.44 Hz; ArH), 6.95 (s, 4H; ArH), 5.20 (s, 2H; OCH_2), 4.64 (d, 2H, J = 2.04 Hz; OCH_2), 4.43 (t, 2H, J = 7.12 Hz; NCH_2), 4.05 (t, 2H, J = 6.17 Hz; OCH_2), 2.52 (t, 1H, J = 1. 84 Hz; CH), 2.02 (m, 2H; CH_2), 1.88 (m, 2H, CH_2), 1.60 (m, 8H, $ArCH_3 + CH_2$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 163.8, 160.2, 153.1, 152.2, 150.0, 149.0, 146.7, 144.5, 137.2, 133.8, 129.3, 128.3, 126.6, 122.4, 122.3, 116.1, 115.8, 115.5, 99.3, 78.8, 75.4, 67.9, 62.8, 56.5, 53.7, 50.3, 30.2, 29.0, 26.3, 25.6, 17.8.

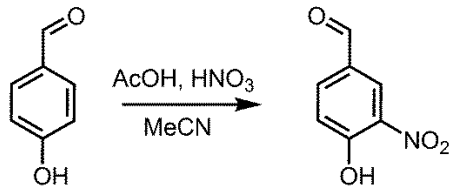
HRMS (TOF-ESI): m/z calcd for $C_{57}H_{48}BF_2I_2N_7NaO_3^+$: 1204.1861 $[M+Na]^+$, found: 1204.1620 $[M+Na]^+$, Δ = 20.01 ppm.

Synthesis of Compound 4: Compound **S24** (20 mg, 17 μmol) and azide functionalized polyethylene glycol monomethylether (2000MW, 37 mg, 19 μmol) were dissolved in $CHCl_3$ (2 ml) and THF (2 ml). Triethylamine (150 μl) was added and the reaction was stirred for 5 min. Then, saturated solutions of $CuSO_4.5H_2O$ (250 μl) and sodium ascorbate (250 μl) were

added. Catalytic amount of Cu (0) was added. The reaction mixture was stirred for 12 h at room temperature. After the reaction was completed, the crude product was applied to octadecyl functionalized silica gel column chromatography using $CHCl_3$ as mobile phase. The mobile phase was changed to CH_2Cl_2/MeOH (80:20; v/v) after the starting compound was eluted from the column. Fraction containing compound **4** was collected then the solvent was removed under reduced pressure (13 μmol, 40 mg, 76%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 9.02-8.9 (m, 2H + 2H; ArH), 8.31 (d, 2H, J = 8.17 Hz; ArH), 8.17 (d, 2H, J = 8.16 Hz; ArH), 7.93 (d, 2H, J = 16.85 Hz; ArH), 7.85-7.70 (m, 2H + 2H + 1H; ArH), 7.60 (s + d, 1H + 2H; J = 8.24 Hz; ArH), 7.20 (d, 2H, J = 8.16 Hz; ArH), 7.09 (d, 2H, J = 8.37 Hz; ArH), 6.92 (s, 4H, ArH), 5.16 (s, 2H; OCH_2), 5.13 (s, 2H; OCH_2), 4.54 (t, 2H, J = 4.76 Hz; NCH_2), 4.40 (t, 2H, J = 6.92 Hz; NCH_2), 3.90-3.30 (PEG), 2.00 (m, 2H; CH_2), 1.85 (m, 2H; CH_2), 1.40 (m, 4H; CH_2), 1.30 (s, 6H; $ArCH_3$).

HRMS (TOF-ESI): Distribution around 3000 with separation of 44 corresponding to etylene glycole unit.

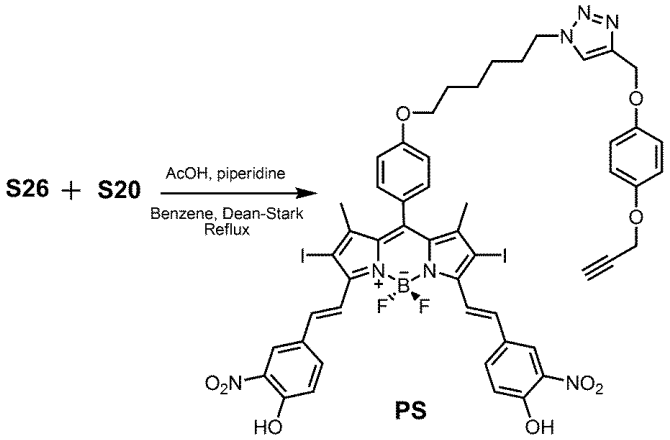


S25 **S26**

Synthesis of Compound S26[viii]: 4-hydroxybenzaldehyde (1.22 g, 10 mmol) was dissolved in 20 ml acetonitrile. Acetic acid (10 ml) and nitric acid (0.75 ml) were added and the reaction was refluxed for 3h. Then, it was cooled to RT and extracted with EtOAc and water. Organic layer was collected and dried with Na_2SO_4, solvent was evaporated under reduced pressure. (9.1 mmol, 1.52 g, 91%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 11.05 (s, 1H; ArOH), 9.98 (s, 1H), 8.68 (s, 1H, ArH), 8.17 (d, 1H, J = 8.61 Hz; ArH), 7.34 (d, 1H, J = 8.68 Hz; ArH).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 188.7, 159.3, 136.4, 128.6, 126.2, 121.3, 115.7.

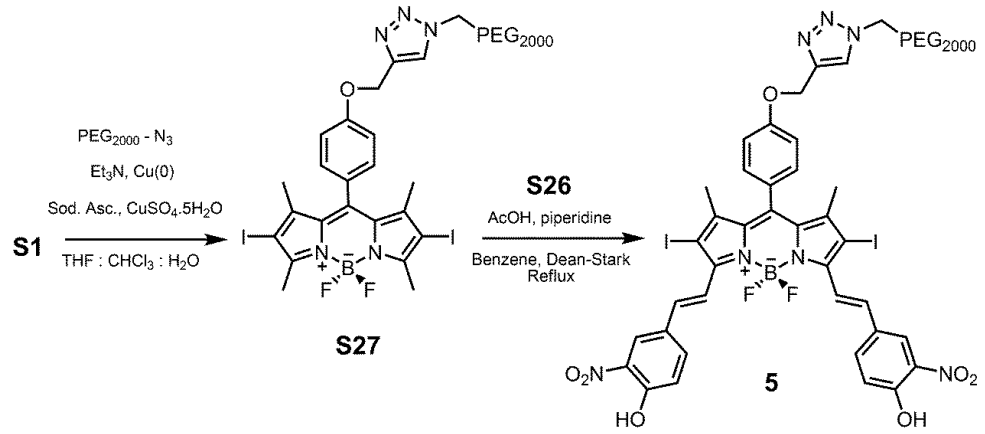


Synthesis of Compound PS: Compound **S20** (200 mg, 0.22 mmol) and 4-hydroxy-3-nitrobenzaldehyde, compound **S26** (110 mg, 0.66 mmol) were dissolved in benzene (20 ml). Piperidine (0.3 ml) and acetic acid (0.3 ml) were added. The reaction mixture was refluxed using Dean Stark apparatus until all aldehyde was consumed. After the reaction was completed, it was extracted with CH_2Cl_2 and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc as mobile phase. After the impurities are eluted from the column, the mobile phase was changed to CH_2Cl_2/MeOH/AcOH (90/5/5; v/v). Fraction containing compound **PS** was collected, then the solvent was removed under reduced pressure (0.15 mmol, 180 mg, 68%).

^{1}H NMR (**PS** + AcOH: $CDCl_3$, 400 MHz, δ ppm) 8.79 (s, 2H; ArH), 8.19 (d, 2H, J = 16.81 Hz; ArH), 7.97 (d, 2H, J = 8.80 Hz; ArH), 7.60 (d + s, 2H + 1H, J = 16.65 Hz; ArH), 7.23 (d, 2H, J = 8.80 Hz; ArH), 7.19 (d, 2H, J = 7.44 Hz; ArH), 7.05 (d, 2H, J = 8.24 Hz; ArH), 6.93 (s, 4H; ArH), 5.20 (s, 2H; OCH_2), 4.64 (s, 2H; OCH_2), 4.41 (t, 2H, J = 7.12 Hz; NCH_2), 4.05 (t, 2H, J = 5.84 Hz; OCH_2), 2.52 (s, 1H; CH), 1.85 (m, 2H, CH_2), 1.60-1.40 (m, 12H, CH_2 + $ArCH_3$).

^{13}C NMR cannot be recorded due to poor solubility.

HRMS (TOF-ESI): m/z calcd for $C_{51}H_{43}BF_2I_2N_7O_9$- 1200.1278 $[M-H]^-$, found: 1200.13078 $[M-H]^-$, Δ = 2.48 ppm.



Synthesis of Compound S27: Compound **S1** (127 mg, 0.2 mmol) and azide functionalized polyethylene glycol monomethylether (2000MW, 800 mg, 0.4 mmol) were dissolved in tetrahydrofuran (2 ml). Triethylamine (1.4 ml) and CuI (77 mg, 0.4 mmol) were added. The reaction mixture was stirred for 12 h at room temperature. After the reaction was completed, the crude product was purified by silica gel column chromatography using $CHCl_3$/MeOH (93:7, v/v) as mobile phase. Fraction containing compound **S27** was collected then the solvent was removed under reduced pressure (red oil, 0.11 mmol, 300 mg, 55%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.93 (s, 1H, ArH), 7.12 (b, 2H + 2H), 5.24 (s, 2H; OCH_2), 4.58 (t, J = 4.84 Hz; NCH_2), 3.90-3.40 (PEG), 3.35 (s, 3H; OCH_3), 2.60 (s, 6H; $ArCH_3$), 1.40 (s, 6H; $ArCH_3$).

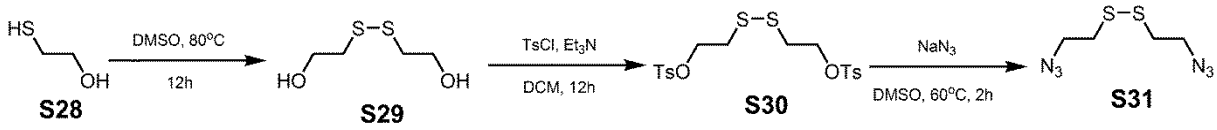
HRMS (TOF-ESI): Distribution around 2500 with separation of 44 corresponding to etylene glycole unit.

Synthesis of Compound 5: Compound **S27** (120 mg, ~45 μmol) and compound **S26** (23 mg, 135 μmol) were dissolved in benzene (25 ml). Piperidine (0.2 ml) and acetic acid (0.2 ml) were added. The reaction mixture was refluxed using Dean Stark apparatus until all aldehyde was consumed. After the reaction was completed, the crude product was purified by silica gel column chromatography using CH_2Cl_2/MeOH (85/15; v/v) as mobile phase. Fraction containing compound **5** was collected, then the solvent was removed under reduced pressure (30 μmol, 90 mg, 66%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.24 (s, 2H; ArH), 8.06 (d, 2H, J = 16.72 Hz; ArH), 7.93 (m, 2H + 2H; ArH), 7.56 (d, 2H, J = 16.69 Hz; ArH), 7.20 (m, 2H + 2H + 2H; ArH), 5.28 (s, 2H, OCH_2), 4.60 (t, 2H, J = 4.36 Hz; NCH_3), 3.90-3.40 (PEG), 3.35 (s, 3H; OCH_3), 1.50 (s, 6H; $ArCH_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 159.6, 155.8, 149.8, 146.7, 143.2, 140.4, 136.2, 135.3, 133.7, 129.5, 127.2, 124.5, 124.4, 120.7, 119.3, 115.9, 94.3, 83.6, 72.0, 70.6, 69.6, 62.2, 59.0, 50.7, 50.4, 17.7.

HRMS (TOF-ESI): Distribution around 2800 with separation of 44 corresponding to etylene glycole unit.



S28 **S29** **S30** **S31**

Synthesis of Compound S29[ix]: mercaptoethanol (5 g, 64 mmol) was dissolved in DMSO (20 ml). The reaction mixture was stirred at 80oC for 12h. Then, it was cooled to RT and was extracted with brine and EtOAc. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using Hexanes/EtOAc 75/25; v/v) as mobile phase. Fraction containing compound **s9** was collected, then the solvent was removed under reduced pressure (29 mmol, 4.5 g, 86%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 3.90 (t, 4H, J = 5.84 Hz; OCH_2), 7.30 (t, 4H, J = 5.88 Hz; SCH_2).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 60.4, 41.3.

Synthesis of Compound S30[160]***:*** 2-hydroxyethyldisulfide, compound S**29** (1 g, 6.5 mmol) was dissolved in 20 ml CH_2Cl_2 and 2 ml Et_3N. In a dropper, p-toluene sulfonyl chloride (1.44 g, 13 mmol) was dissolved in CH_2Cl_2 10 ml and was added to the previous solution dropwise while the reaction mixture was being cooled with ice bath. It was stirred for 12h. After the extraction with water, organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$ as mobile phase. Fraction containing compound S**30** was collected, then the solvent was removed under reduced pressure (white solid, 6.5 mmol, 3 g, quantitative).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.83 (d, 4H, J = 8.04 Hz; ArH), 7.38 (d, 4H, J = 7.93 Hz; ArH), 4.21 (t, 4H, J = 6.61 Hz; OCH_2), 2.85 (t, 4H, J = 6.53 Hz; SCH_2), 2.48 (s, 6H, $ArCH_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 145.2, 130.0, 128.0, 67.5, 36.9, 21.7.

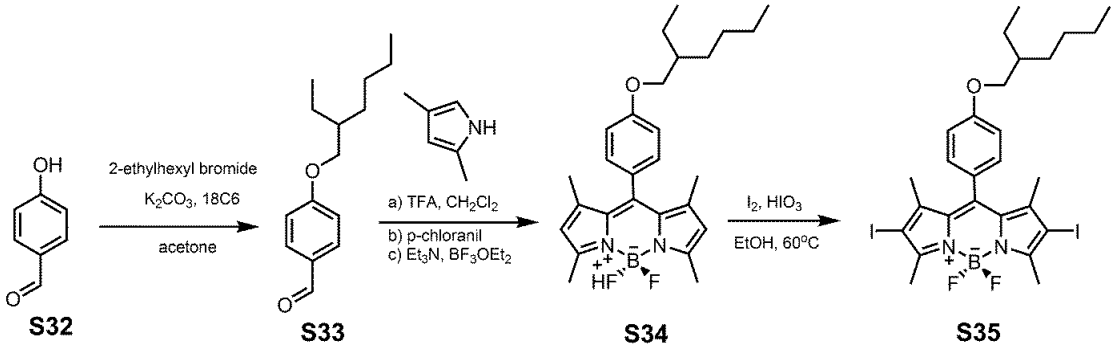
HRMS (TOF-ESI): m/z calcd for $C_{18}H_{22}NaO_6S_4^+$ 485.0191 $[M+Na]^+$, found: 485.0104 $[M+Na]^+$, Δ = 17.94 ppm.

Synthesis of Compound S31: Compound S**30** (1.2 g, 2.6 mmol) was dissolved in 10 ml DMSO and sodium azide (12 mmol, 780 mg) was added to the reaction mixture. It was stirred

2h at 60 oC. After cooling to RT, it was extracted with EtOAc. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. (yellow oil, 2.47 mmol, 0.5 g, 95%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 3.63 (t, 4H, J = 6.76 Hz; NCH_2), 2.89 (t, 4H, J = 6.76 Hz; SCH_2).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 49.9, 37.6.



Synthesis of Compound S33: 4-hydroxybenzaldehyde (4 g, 33 mmol), 2-ethylhexyl bromide (6.7 ml, 36 mmol) and catalytic amount of benzo-18-crown-6 were dissolved in 60 ml acetonitrile. K_2CO_3 (13.6 g, 98 mmol) was added and the reaction mixture was refluxed for 12 h. The solvent was evaporated under reduced pressure and the crude product was extracted with CH_2Cl_2. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. (yellow oil, 7.7 g, quantitative).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 9.88 (s, 1H), 7.83 (d, 2H, J = 8.24 Hz; ArH), 7.01 (d, 2H, J = 8.33 Hz; ArH), 3.94 (d, 2H, J = 5.64 Hz; OCH_2), 1.77 (m, 1H; CH), 1.45 (m, 4H; CH_2), 1.32 (m, 4H; CH_2), 0.93 (m, 6H; CH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 190.7, 164.5, 131.9, 129.7, 114.8, 70.9, 39.3, 30.4, 29.0, 23.8, 23.0, 14.0, 11.1.

HRMS (TOF-ESI): m/z calcd for $C_{15}H_{23}O_2^+$ 235.16926 $[M+H]^+$, found: 235.17327 $[M+H]^+$, Δ = 17.1 ppm.

Synthesis of Compound S34: CH_2Cl_2 (400 ml) was purged with Ar for 30 min. Compound **S33** (2.4 g, 10.24 mmol) and 2,4-dimethyl pyrrole (2.3 ml, 22.53 mmol) were added. The color of the solution turned into red after the addition of 3 drops of trifluoroacetic acid. The reaction mixture was stirred at room temperature for 12 h. Then, tetrachloro-1,4-benzoquinone (2.52 g, 10.24 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. Then triethyl amine (9 ml) and boron trifluoride diethyl etherate (9 ml) were added sequencially. After stirring at room temperature for 1 h, it was extracted with

water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$ and then EtOAc/Hexanes (20/80; v/v) as mobile phase. Fraction containing compound **S34** was collected then the solvent was removed under reduced pressure (810 mg, 1.8 mmol, 18%).

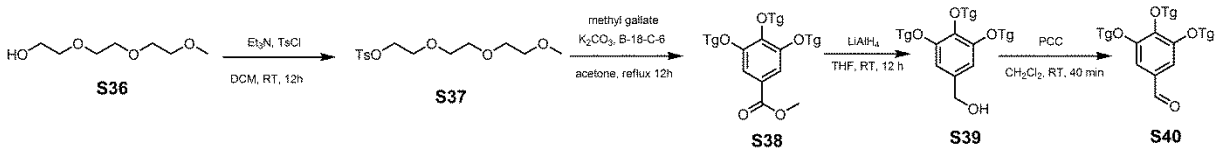
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.17 (d, 2H, J = 8.76 Hz; ArH), 7.01 (d, 2H, j = 8.80 Hz; ArH), 5.99 (s, 2H; ArH), 3.92 (d, 2H, J = 5.93 Hz, OCH_2), 2.55 (s, 6H, $ArCH_3$), 1.79 (m, 1H, CH), 1.60-1.40 (m, s, 4H + 6H; CH_2 + $ArCH_3$), 1.37 (m, 4H; CH_2), 0.96 (m, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 160.0, 155.2, 143.2, 142.1, 131.9, 129.1, 126.8, 121.1, 114.8, 70.9, 39.4, 30.6, 29.1, 23.9, 23.0, 14.6, 14.1, 11.2.

Synthesis of Compound S35: Compound S**34** (330 mg, 0.73 mmol) and I_2 (389 mg, 1.53 mmol) were dissolved in ethanol (200 ml). Iodic acid, HIO_3 (256 mg, 1.46 mmol) was dissolved in a few drops of water and added into previous solution. The reaction mixture was stirred at 60^{o}C for 1 h untill all reeactant was consumed. Then, saturated sodium thiosulfate solution was added (50 ml) and it was stirred at room temparature for additional 30 min. Then, it was extracted with $CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and compound S**35** was obtained by evaporation of the solvent under reduced pressure (514 mg, quantitative).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.12 (d, 2H, J = 8.68 Hz; ArH), 7.03 (d, 2H, j = 8.72 Hz; ArH), 3.92 (d, 2H, J = 5.88 Hz, OCH_2), 2.64 (s, 6H, $ArCH_3$), 1.79 (m, 1H, CH), 1.60-1.40 (m, s, 4H + 6H; CH_2 + $ArCH_3$), 1.36 (m, 4H; CH_2), 0.96 (m, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 160.2, 156.7, 145.8, 142.1, 132.1, 129.8, 126.8, 115.8, 85.9, 71.2, 39.6, 31.0, 24.3, 17.6, 16.3, 14.3, 11.7.



S36 S37 S38 S39 S40

Synthesis of Compound S37: triethyleneglycol monomethyl ether (10 g, 61 mmol) was dissolved in 100 ml CH_2Cl_2 and 13 ml Et_3N. In a dropper, p-toluene sulfonyl chloride (12 g, 63 mmol) was dissolved in CH_2Cl_2 (20 ml) and was added to the previous solution dropwise while the reaction mixture was being cooled with ice bath. It was stirred for 12 h. After the extraction with water, organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. (yellow oil, 55 mmol, 17.5 g, 90%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.78 (d, 2H; J = 8.24 Hz; ArH), 7.32 (d, 2H, J = 8.04 Hz; ArH) 4.15 (t, 2H; J = 4.77 Hz; OCH_2), 3.67 (m, 4H; OCH_2), 3.60 (m, 4H; OCH_2), 3.51 (m, 2H; OCH_2). 3.34 (s, 3H; OCH_3), 2.42 (s, 3H; $ArCH_3$).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 144.8, 133.0, 129.8, 127.9, 71.9, 70.7, 70.5, 70.5, 69.3, 68.6, 59.0, 21.6.

HRMS (TOF-ESI): m/z calcd for $C_{14}H_{22}NaO_6S^+$ 341.1029 $[M+Na]^+$, found: 341.10639 $[M+Na]^+$, Δ = 10.23 ppm.

Synthesis of Compound S38: methyl-3,4,5-trihydroxybenzoate (2.75 g, 15 mmol), compound **S37** (15g, 47 mmol) and catalytic amount of benzo-18-crown-6 were dissolved in 60 ml acetone. K_2CO_3 (8.3 g, 60 mmol) were added and the reaction mixture was refluxed for 18 h. Then, solvent was removed under reduced pressure and the crude product was extracted with EtOAc and brine. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc as mobile phase. Fraction containing compound **S38** was collected then the solvent was removed under reduced pressure (colorless liquid, 6 g, 9.6 mmol, 64%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.30 (s, 2H; ArH), 4.22 (m, 2H + 4H; OCH_2), 3.88 (m, 4H + 3H; OCH_3 + OCH_2), 3.80 (m, 2H; OCH_2), 3.74 (m, 6H; OCH_2). 3.65 (m, 12H; OCH_2), 3.56 (m, 6H; OCH_2), 3.38 (s, 9H; OCH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 166.5, 152.3, 142.6, 124.9, 109.0, 72.4, 71.9, 70.8, 70.7, 70.6, 70.5, 69.6, 68.8, 52.1.

Synthesis of Compound S39: Compound S38 (3 g, 4.8 mmol) was dissolved in freshly distilled THF (20 ml) while rhe flask was being cooled within ice bath. To this solution, $LiAlH_4$ (347 mg, 9.6 mmmol) was added portionwise. Then the reaction mixture was stirred 12 h at RT. The excess $LiAlH_4$ was carefully quenched with cold water and it was extracted with EtOAc and brine. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc as mobile phase. Fraction containing compound **S39** was collected then the solvent was removed under reduced pressure (colorless liquid, 2.5 g, 4.2 mmol, 88%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 6.63 (s, 2H; ArH), 4.58 (s, 2H; OCH_2), 4.15 (m, 2H + 4H; OCH_2), 3.84 (t, 4H, J = 5.29 Hz; OCH_2), 3.79 (t, 2H, J = 5.44 Hz; OCH_2), 3.73 (m, 6H; OCH_2). 3.65 (m, 12H; OCH_2), 3.54 (m, 6H; OCH_2), 3.38 (s, 9H; OCH_3).

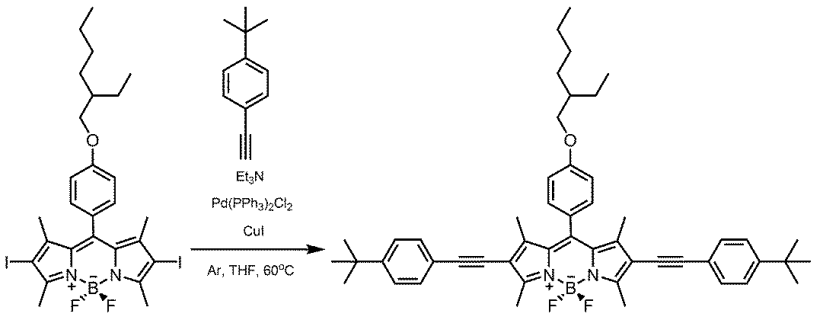
^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 152.7, 137.8, 136.7, 106.6, 72.3, 71.9, 70.8, 70.7, 70.5, 69.8, 68.9, 65.2, 59.0.

Synthesis of Compound S40: Compound **S39** (2.4 g, 4 mmol) was dissolved in CH_2Cl_2 (25 ml). Pyridinium chlorochromate (2.15 g, 10 mmol) was added to the reaction mixture and it was stirred for 40 min ar RT. Then, it was directly applied to silica column chromatography using EtOAc/MeOH (95/5; v/v) as mobile phase. Fraction containing compound **S40** was collected then the solvent was removed under reduced pressure (colorless oil, 2.37 g, quantitative).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 9.82 (s, 1H), 7.14 (s, 2H; ArH), 4.21 (m, 6H; OCH_2), 3.89 (m, 4H; OCH_2), 3.82 (m, 2H; OCH_2), 3.80-3.50 (m, 24H; OCH_2), 3.38 (s, 9H; OCH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 191.0, 153.0, 144.1, 131.6, 109.0, 72.5, 71.9, 70.8, 70.7, 70.6, 70.5, 69.6, 68.9, 59.0.

HRMS (TOF-ESI): m/z calcd for $C_{28}H_{48}NaO_{13}^+$ 615.2987 $[M+Na]^+$, found: 615.28633 $[M+Na]^+$, Δ = 20.10 ppm.



S35 **S41**

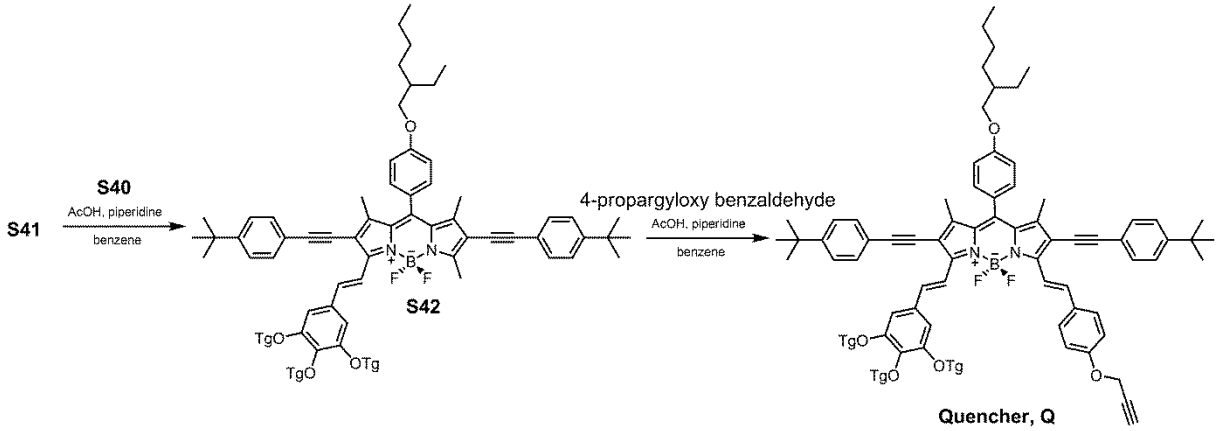
Synthesis of Compound S41: Compound **S35** (100 mg, 0.14 mmol) was dissolved in tetrahydrofuran (30 ml) and triethylamine (5 ml). Argon was purged for 30 min. Then, 15% mole equivalent of $Pd(PPh_3)_4$ (24 mg, 21 μmol) was added. 4-(Tert-butyl)phenylacetylene (88 μl, 0.49 mmol) was added via syringe and the reaction mixture was stirred 12 h at 60^{o}C. After it was cooled to RT, it was extracted with CH_2Cl_2 and brine. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc/Hexanes (10/90; v/v) as mobile phase. Fraction containing compound **S41** was collected then the solvent was removed under reduced pressure (92 mg, 0.12 mmol, 86%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 7.43 (d, 4H, J = 8.16 Hz; ArH), 7.37 (d, 4H, j = 8.48 Hz; ArH), 7.18 (d, 2H, J = 8.52 Hz; ArH), 7.06 (d, 2H, J = 8.61 Hz; ArH), 3.95 (d, 2H, J = 5.76

Hz, OCH_2), 2.73 (s, 6H, $ArCH_3$), 1.80 (m, 1H, CH), 1.60-1.30 (m, 4H + 6H + 18H; CH_2 + $ArCH_3$ + CCH_3), 0.96 (m, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 160.3, 158.1, 151.4, 143.9, 142.7, 131.7, 131.1, 129.1, 126.2, 125.4, 120.4, 116.2, 115.4, 96.5, 81.0, 70.9, 39.4, 34.8, 31.2, 30.6, 29.2, 23.9, 23.1, 14.1, 13.7, 13.6, 11.2.

HRMS (TOF-ESI): m/z calcd for $C_{51}H_{60}BF_2N_2O^+$ 765.4761 $[M+H]^+$, found: 765.4540 $[M+H]^+$, Δ = 28.87 ppm.



Synthesis of Compound S42: Compound **S41** (150 mg, 0.2 mmol) and compound **S40** (100 mg, 0.17 mmol) were dissolved in benzene (45 ml). Piperidine (0.3 ml) and acetic acid (0.3 ml) were added. The reaction mixture was refluxed using Dean Stark apparatus until all aldehyde was consumed. After the reaction was completed, it was extracted with CH_2Cl_2 and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc/MeOH (85/15; v/v) as mobile phase. Fraction containing compound **S42** was collected, then the solvent was removed under reduced pressure (41 μmol, 55 mg, 21%).

^1H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.34 (d, 1H, J = 16.24 Hz; ArH), 7.62 (d, 1H, J = 16. 21 Hz; ArH), 7.50-7.30 (m, 8H; ArH), 7.21 (d, 2H, J = 8.60 Hz; ArH), 7.06 (d, 2H, J = 8.65 Hz; ArH), 6.87 (s, 2H; ArH), 4.25 (m, 6H; OCH_2), 3.95 (d, 2H, J = 4.56 Hz; OCH_2), 3.90 (t, 4H, J = 5.37 Hz; OCH_2), 3.85 (t, 2H, J = 4.40 Hz; OCH_2), 3.80-3.50 (m, 24H; OCH_2), 3.38 (s, 9H; OCH_3), 2.77 (s, 3H; $ArCH_3$), 1.8 (m, 1H; CH), 1.65 (s, 3H; $ArCH_3$), 1.63 (s, 3H; $ArCH_3$), 1.60-1.40 (m, 6H; CH_2), 1.40-1.20 (m, 18H + 2H; CH_3 + CH_2), 0.95 (m, 3H + 3H; CH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 160.3, 152.9, 151.7, 151.5, 141.4, 140.0, 138.8, 132.5, 131.1, 130.8, 129.3, 126.4, 125.5, 125.4, 120.5, 120.4, 115.4, 107.5, 98.1, 96.7, 83.3, 81.0, 72.5, 72.0, 71.9, 71.0, 70.9, 70.7, 70.6, 69.8, 69.0, 59.0, 39.4, 34.8, 31.2, 30.6, 29.2, 23.9, 23.0, 14.1, 13.7, 13.4, 11.2.

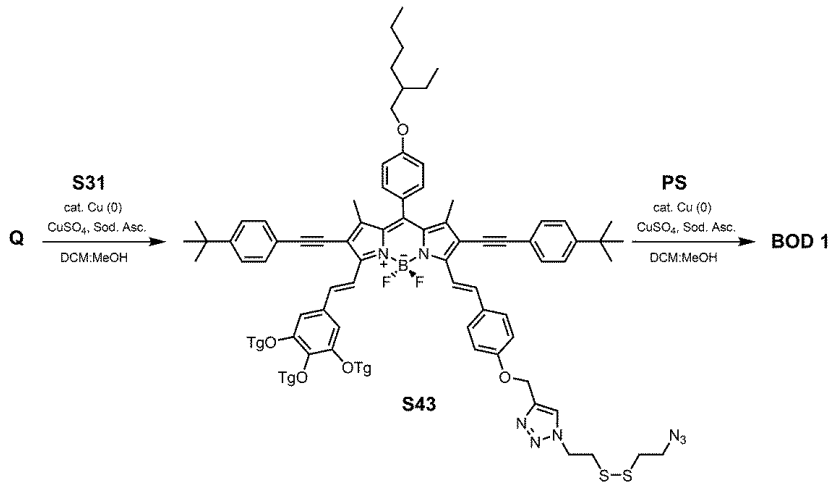
HRMS (TOF-ESI): m/z calcd for $C_{79}H_{105}BF_2N_2NaO_{13}^+$ 1361.7570 $[M+Na]^+$, found: 1361.7296 $[M+Na]^+$, Δ = 20.12 ppm.

Synthesis of Quencher Module, Q: Compound **S42** (45 mg, 30 μmol) and 4-propargyloxy benzaldehyde (9 mg, 56 μmol) were dissolved in benzene (25 ml). Piperidine (0.2 ml) and acetic acid (0.2 ml) were added. The reaction mixture was refluxed using Dean Stark apparatus until all aldehyde was consumed. After the reaction was completed, it was extracted with CH_2Cl_2 and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc/MeOH (90/10; v/v) as mobile phase. Fraction containing compound **Q** was collected, then the solvent was removed under reduced pressure (27 μmol, 40 mg, 90%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.49 (d, 1H, J = 16.24 Hz; ArH), 8.34 (d, 1H, J = 16.16 Hz; ArH), 7.74 (d, 1H, J = 16.60 Hz; ArH), 7.65 (s + d + d, 1H + 2H + 2H; ArH), 7.50-7.30 (m, 8H; ArH), 7.21 (d, 2H, J = 8.09 Hz; ArH), 7.10-7.00 (m, 2H + 2H; ArH), 6.90 (s, 2H; ArH), 4.77 (2H; OCH_2), 4.25 (m, 6H; OCH_2), 4.00- 3.50 (m, 32H; OCH_2), 3.40 (s, 3H; OCH_3), 3.37 (s, 6H; OCH_3), 2.60 (1H; CH), 1.80-1.20 (m, 23H; CH_3 + CH_2), 0.98 (m, 3H + 3H; CH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 160.3, 158.6, 152.9, 151.7, 145.3, 140.2, 139.7, 138.8, 132.7, 130.8, 130.7, 129.6, 129.2, 126.6, 125.6, 125.5, 120.6, 120.5, 115.3, 107.9, 98.4, 98.2, 83.4, 83.1, 77.4, 77.1, 76.7, 75.9, 72.5, 72.0, 71.9, 69.9, 69.2, 59.0, 59.0, 59.0, 55.9, 39.4, 34.8, 31.2, 30.6, 29.2, 23.9, 23.1, 14.1, 11.2.

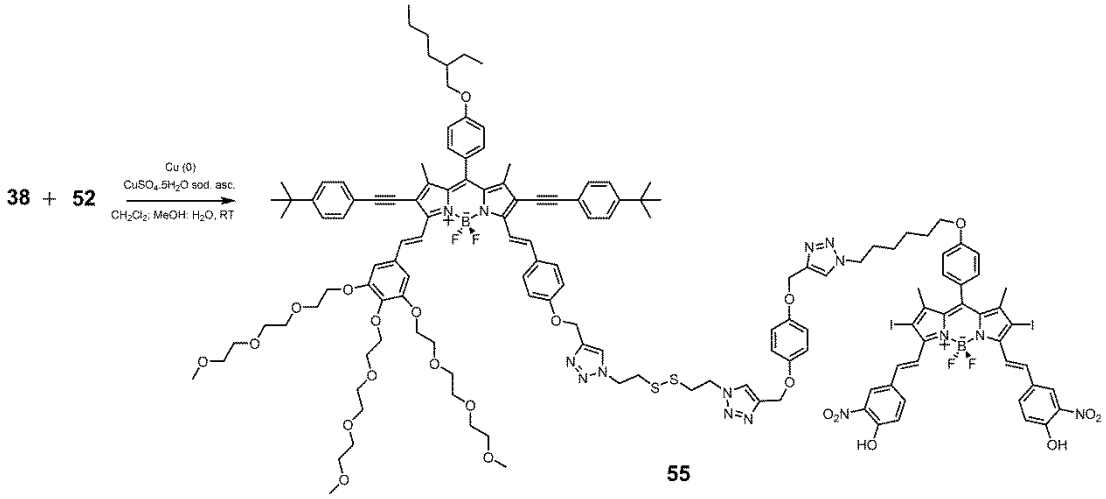
HRMS (TOF-ESI): m/z calcd for $C_{89}H_{111}BF_2N_2NaO_{14}^+$ 1503.7989 $[M+Na]^+$, found: 1503.7684 $[M+Na]^+$, Δ = 20.28 ppm.



Synthesis of Compound S43: Compound **Q** (45 mg, 30 μmol) and compound **S31** (62 mg, 300 μmol) were dissolved in CH_2Cl_2 (6 ml) and MeOH (3 ml). Saturated solutions of $CuSO_4.5H_2O$ (100 μl) and sodium ascorbate (100 μl) were added. Catalytic amount of Cu (0) was added. The reaction mixture was stirred for 12 h at room temperature. After the reaction was completed, it was extracted with CH_2Cl_2 and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc/MeOH (85/15; v/v) as mobile phase. Fraction containing compound **S43** was collected, then the solvent was removed under reduced pressure (18 μmol, 30 mg, 60%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.48 (d, 1H, J = 16.32 Hz; ArH), 8.34 (d, 1H, J = 16.28 Hz; ArH), 7.75-7.60 (d+ s + d + d, 2H + 1H + 1H + 2H; ArH), 7.50-7.30 (m, 8H; ArH), 7.21 (d, 2H, J = 8.33 Hz; ArH), 7.08 (d, 2H, J = 3.49 Hz; ArH), 7.05 (d, 2H, J = 3.40 Hz; ArH), 6.91 (s, 2H; ArH), 5.31 (s, 2H; OCH_2), 4.73 (t, 2H, J = 6.64 Hz; NCH_2), 4.25 (m, 6H; OCH_2), 4.00- 3.50 (m, 32H; OCH_2), 3.40 (s, 3H; OCH_3), 3.37 (s, 6H; OCH_3), 3.22 (t, 2H, J = 6.64 Hz; NCH_2), 2.89 (m, 2H + 2H; SCH_2), 1.80-1.20 (m, 23H; CH_3 + CH_2), 0.98 (m, 3H + 3H; CH_3).

^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 160.3, 159.3, 153.0, 151.8, 145.3, 144.4, 140.1, 139.6, 138.9, 133.4, 132.7, 132.2, 131.9, 130.8, 130.4, 129.6, 128.6, 126.7, 125.5, 123.6, 120.6, 118.4, 117.1, 116.1, 115.3, 114.0, 107.9, 107.2, 98.4, 98.2, 83.3, 72.5, 71.9, 70.9, 70.8, 70.7, 70.5, 70.4, 69.8, 69.2, 68.9, 62.1, 59.0, 49.9, 48.9, 39.5, 37.7, 34.9, 31.3, 30.6, 29.2, 23.9, 23.1, 14.1, 13.5.



Synthesis of BOD 1: Compound **S43** (40 mg, 24 μmol) and compound **PS** (45 mg, 37 μmol) were dissolved in CH_2Cl_2 (6 ml) and MeOH (3 ml). Saturated solutions of $CuSO_4.5H_2O$ (100 μl) and sodium ascorbate (100 μl) were added. Catalytic amount of Cu (0) was added. The reaction mixture was stirred for 12 h at room temperature. After the reaction was completed, it

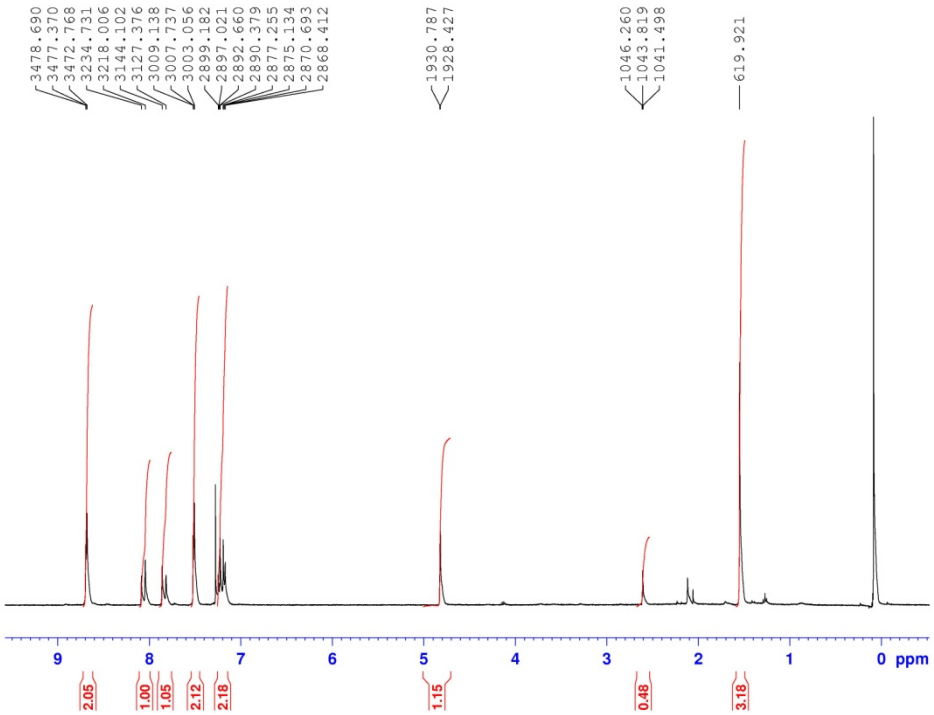
was extracted with CH_2Cl_2 and water. Organic layer was collected and dried with Na_2SO_4, evaporated under reduced pressure. The product was purified by silica gel column chromatography using EtOAc/MeOH (85/15; v/v) as mobile phase. Fraction containing compound **BOD 1** was collected, then the solvent was removed under reduced pressure (12 μmol, 35 mg, 50%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 8.48 (d, 1H, J = 15.92 Hz; ArH), 8.32 (d, 1H, J = 15.84 Hz; ArH), 8.29 (s, 2H; ArH), 8.09 (d, J = 16.52 Hz, 2H; ArH), 7.95 (d, J = 8.04 Hz, 2H; ArH), 7.8-7.5 (m, 10H; ArH), 7.50-7.30 (m, 10H; ArH), 7.25-7.10 (m, 6H; ArH), 7.10-7.0 (m, 5H; ArH), 6.90 (m, 6H; ArH), 5.30 (s, 2H, OCH_2), 5.15 (s, 4H, OCH_2), 4.65 (s, 4H, NCH_2), 4.40 (m, 2H, OCH_2), 4.2 (m, 6H; OCH_2), 4.10-3.50 (m, 36H, OCH_2), 3.30 (s + s, 6H + 3H; OCH_3), 3.15 (m, 4H; SCH_2), 2.05 (m, 18H; CH_3), 1.8 (m, 4H), 1.60-1.0 (21H), 0.95 (m, 6H).

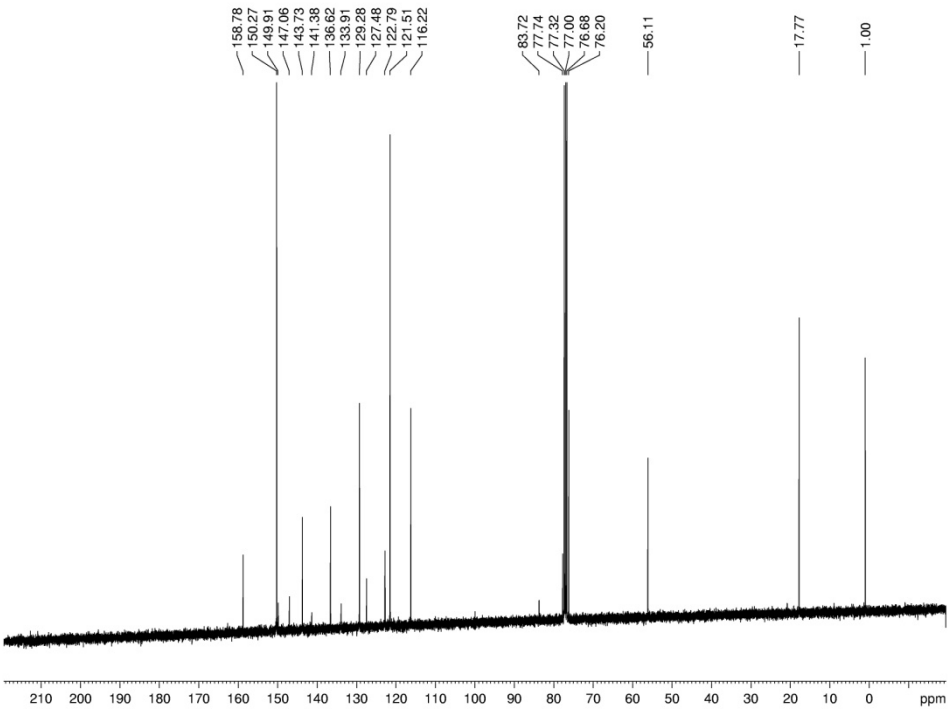
^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm) 167.8, 160.3, 160.2, 159.2, 158.6, 155.6, 152.8, 151.7, 149.8, 146.6, 138.8, 136.2, 135.4, 133.7, 132.7, 130.8, 130.3, 129.6, 129.5, 129.4, 129.3, 126.6, 125.6, 125.5, 124.4, 123.7, 120.7, 120.4, 119.4, 115.9, 115.8, 115.5, 115.3, 107.8, 72.4, 71.9, 70.9, 70.8, 70.6, 70.5, 69.8, 69.1, 59.0, 58.9, 48.9, 40.6, 39.4, 31.2, 30.6, 30.2, 29.2, 26.3, 25.6, 23.9, 23.0, 17.8, 14.1, 13.5, 11.2.

HRMS (TOF-ESI): m/z calcd for $C_{144}H_{162}B_2F_4I_2N_{15}O_{23}S_2^-$ 2884.9 $[M-H]^-$, found: 2884.9 $[M-H]^-$

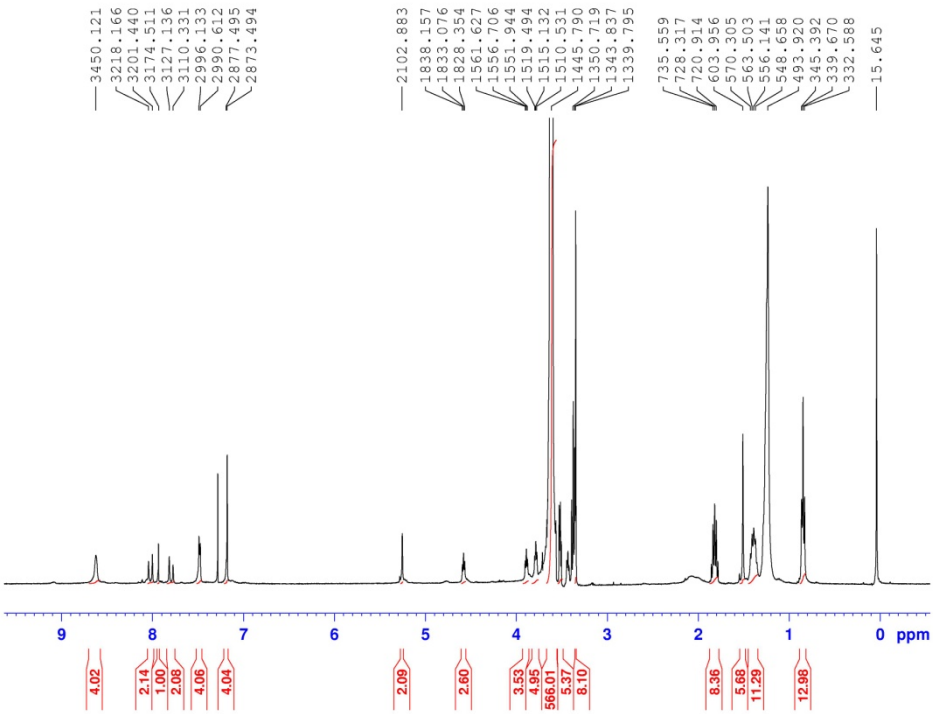
5. NMR Spectra



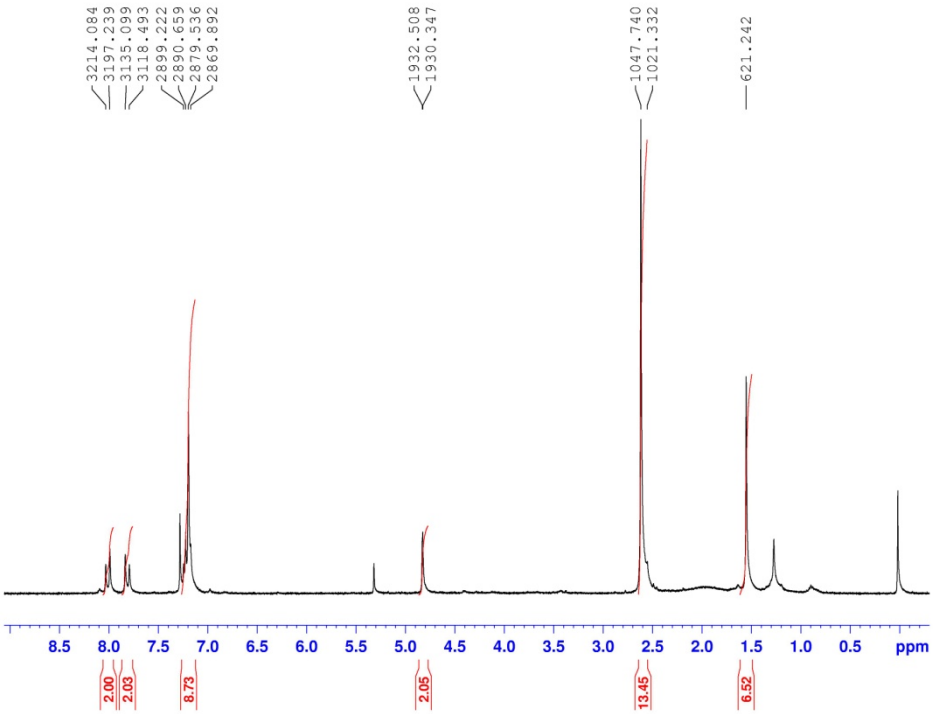
^{1}H NMR of compound S3



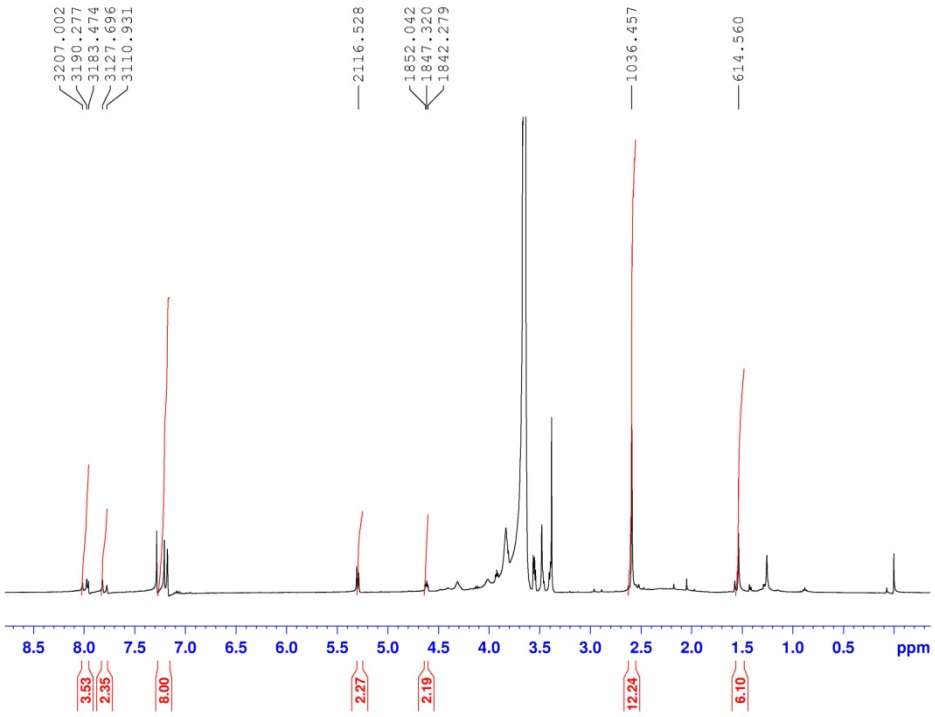
^{13}C NMR of compound S3



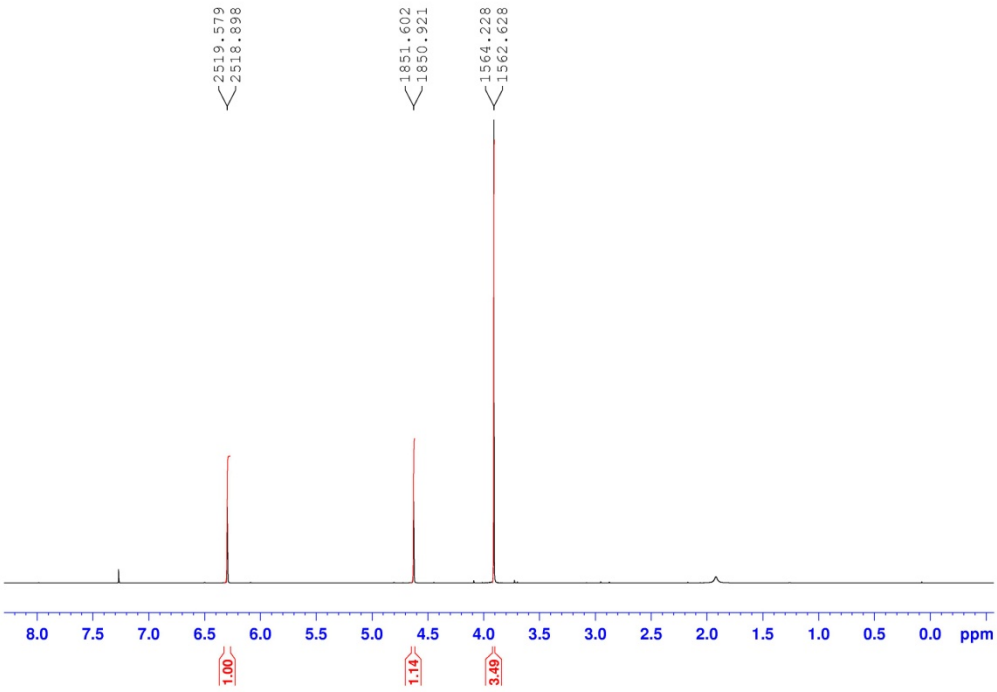
^{1}H NMR of compound 1



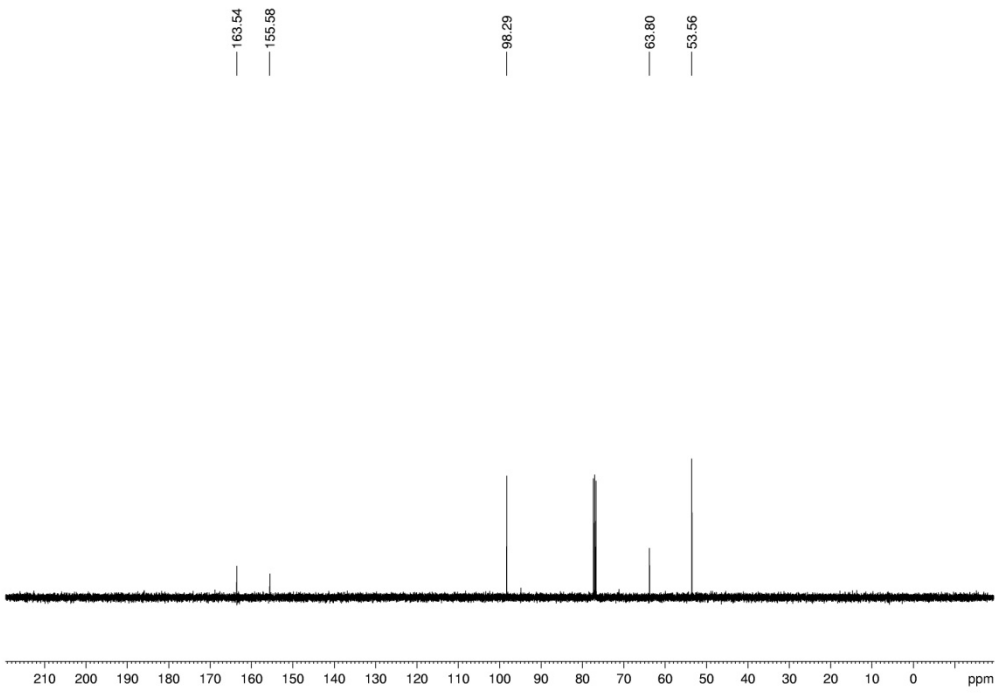
^{1}H NMR of compound **1**



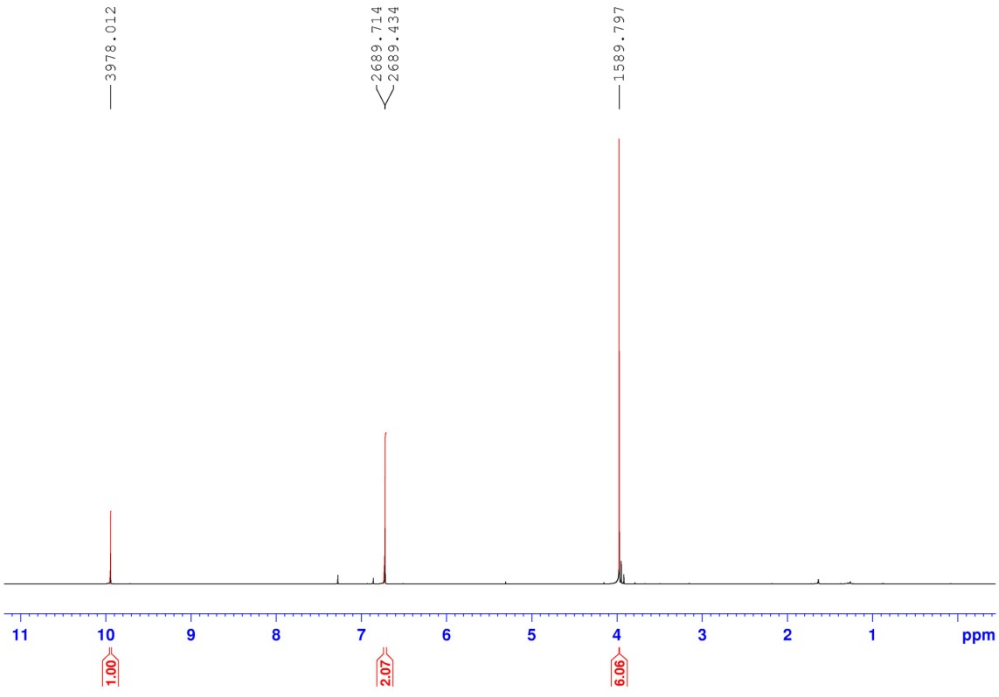
^{1}H NMR of compound **2**



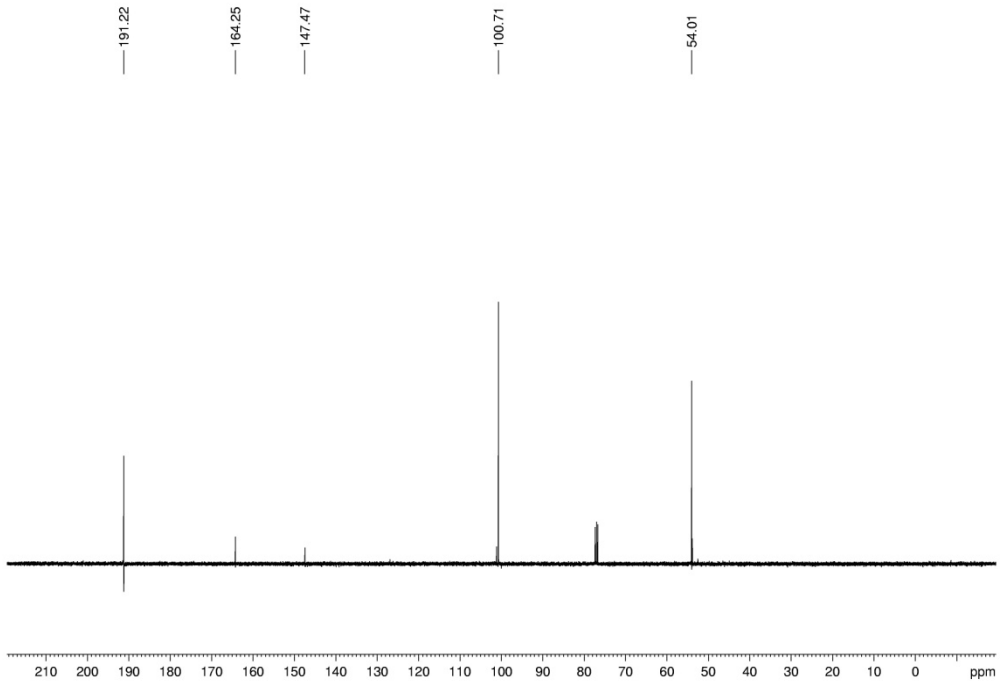
^{1}H NMR of compound **S13**



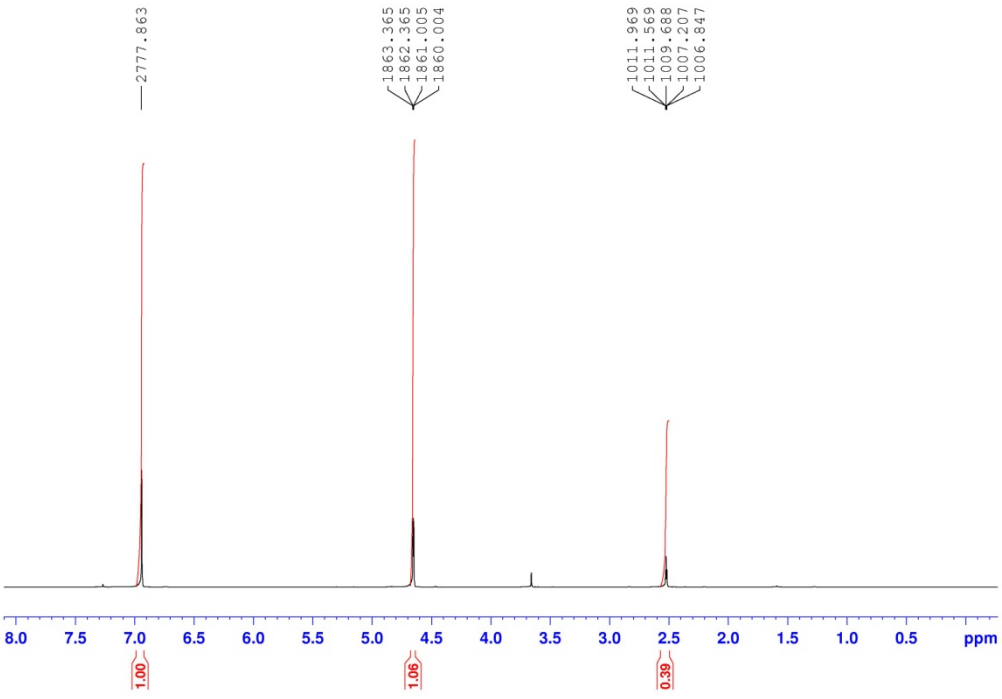
^{13}C NMR of compound S13



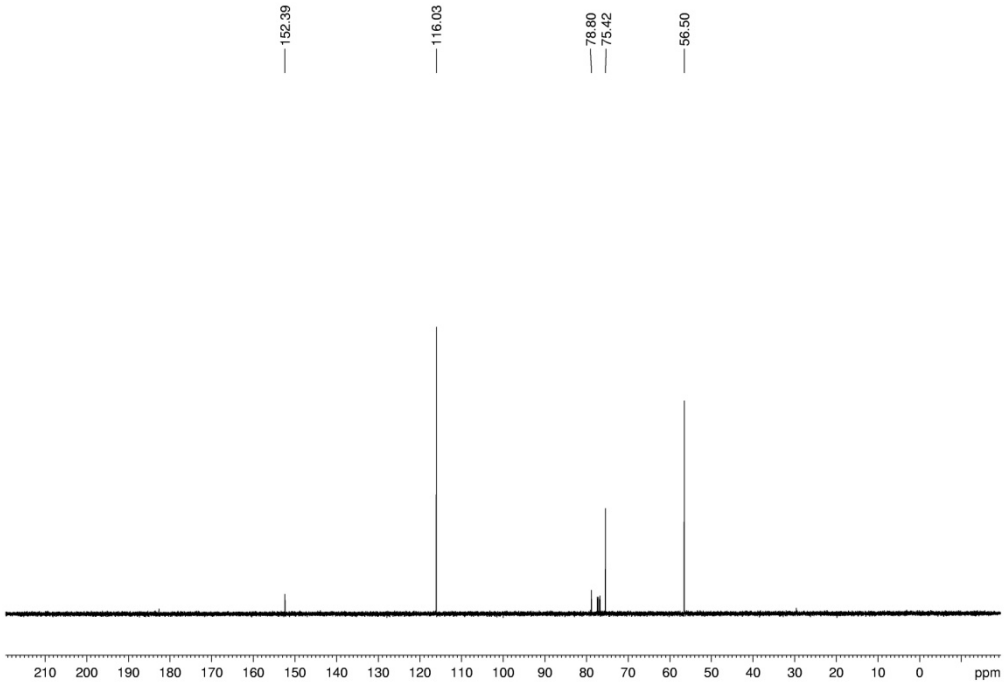
^{1}H NMR of compound **S14**



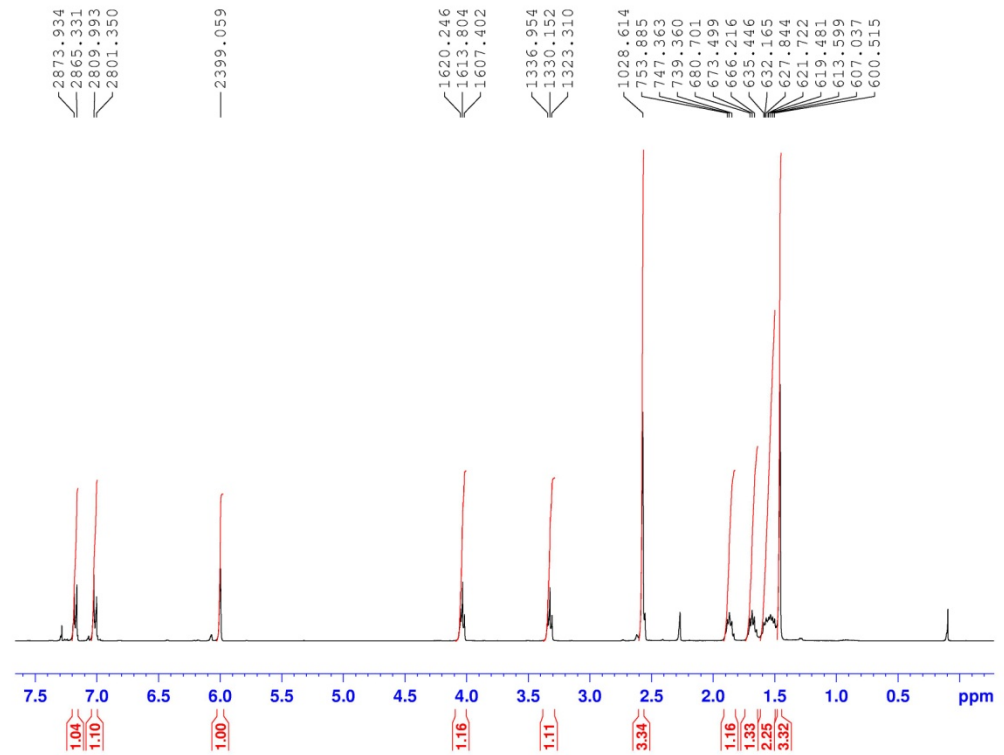
^{13}C NMR of compound S14



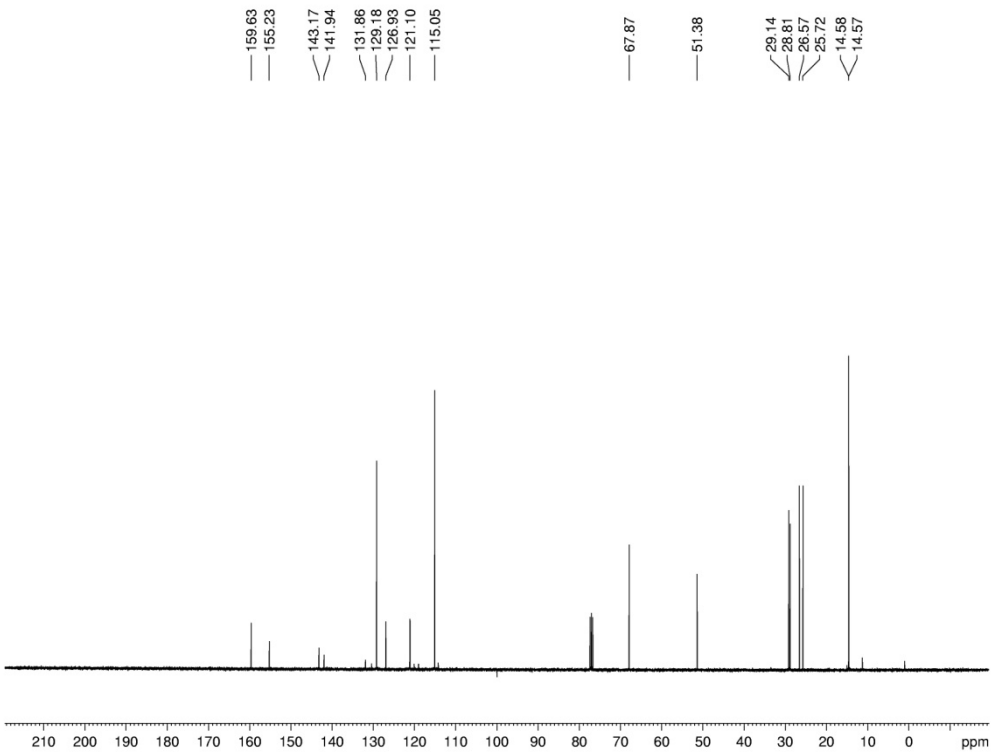
^{1}H NMR of compound **S16**



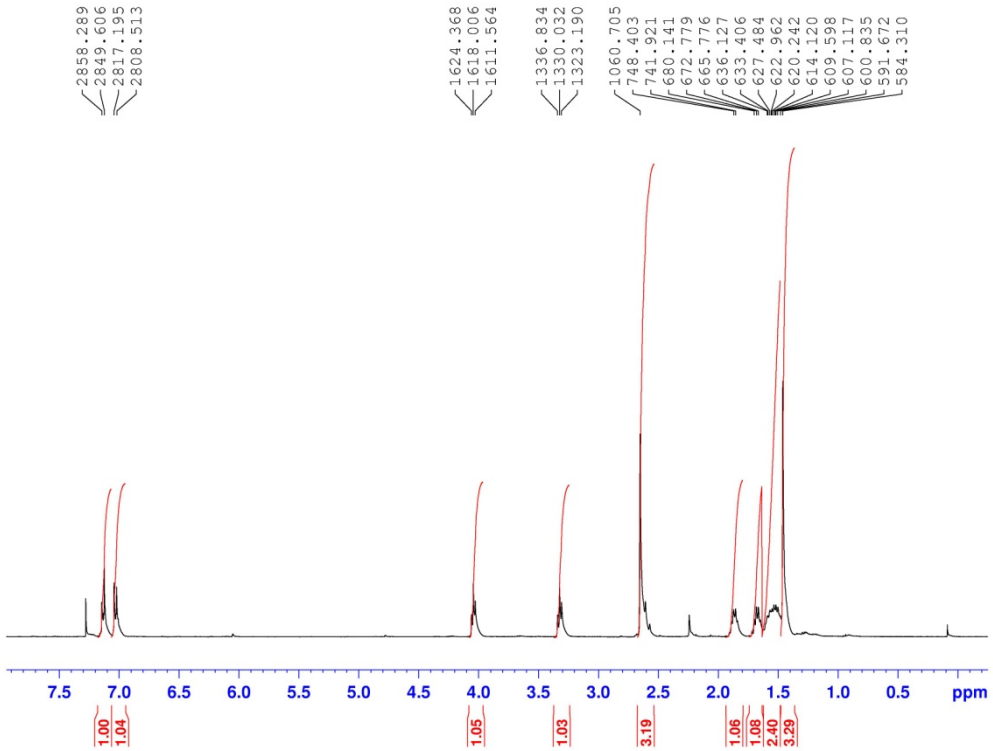
^{13}C NMR of compound S16



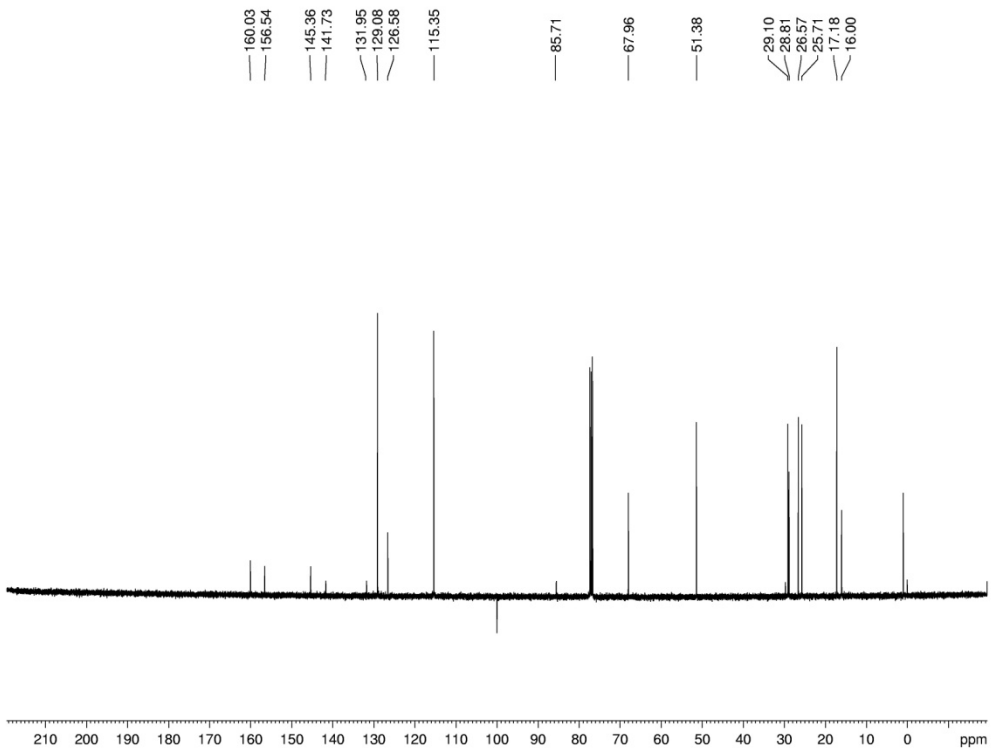
^{1}H NMR of compound **S18**



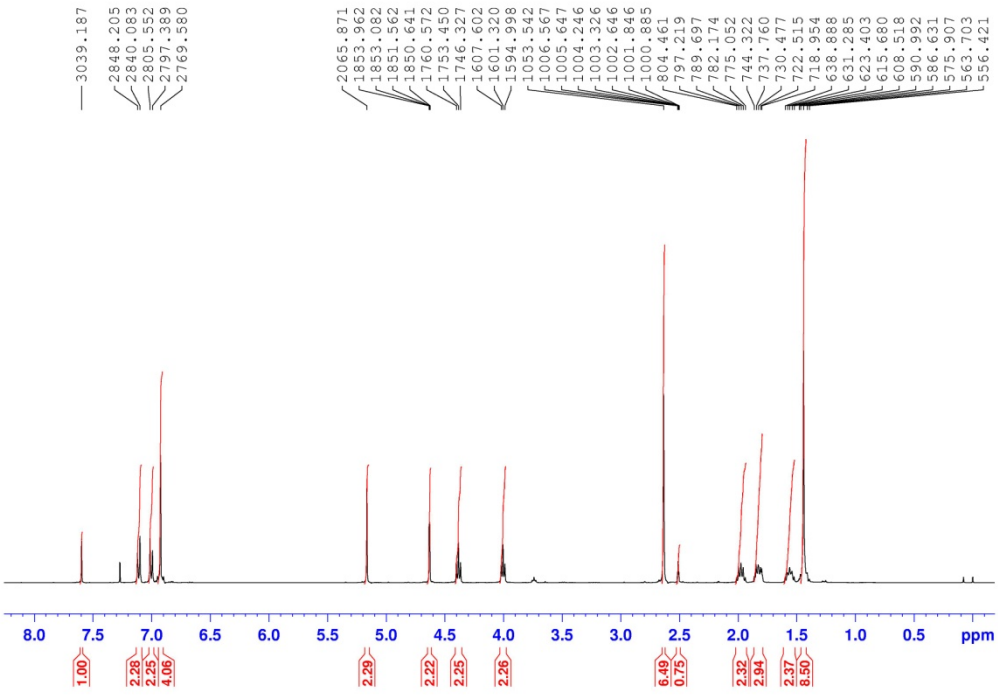
^{13}C NMR of compound S18



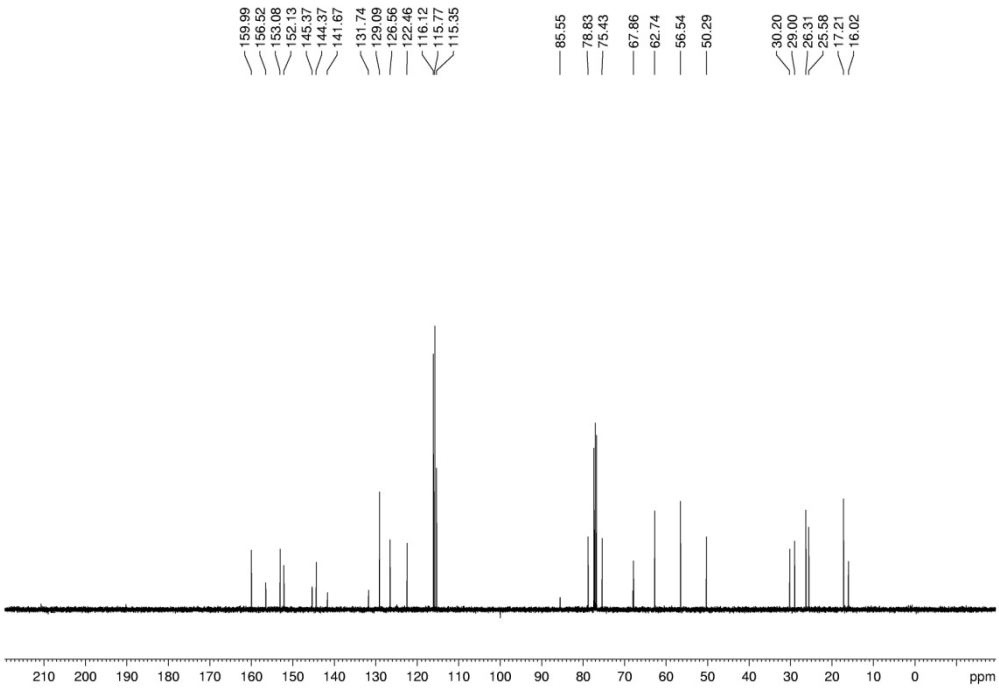
^{1}H NMR of compound **S19**



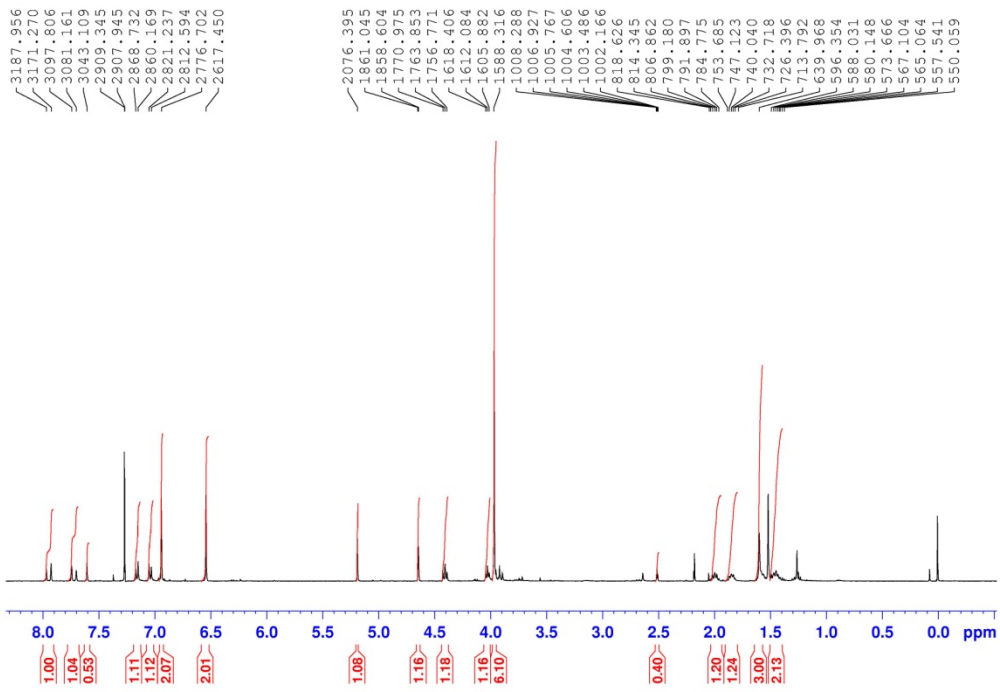
^{13}C NMR of compound S19



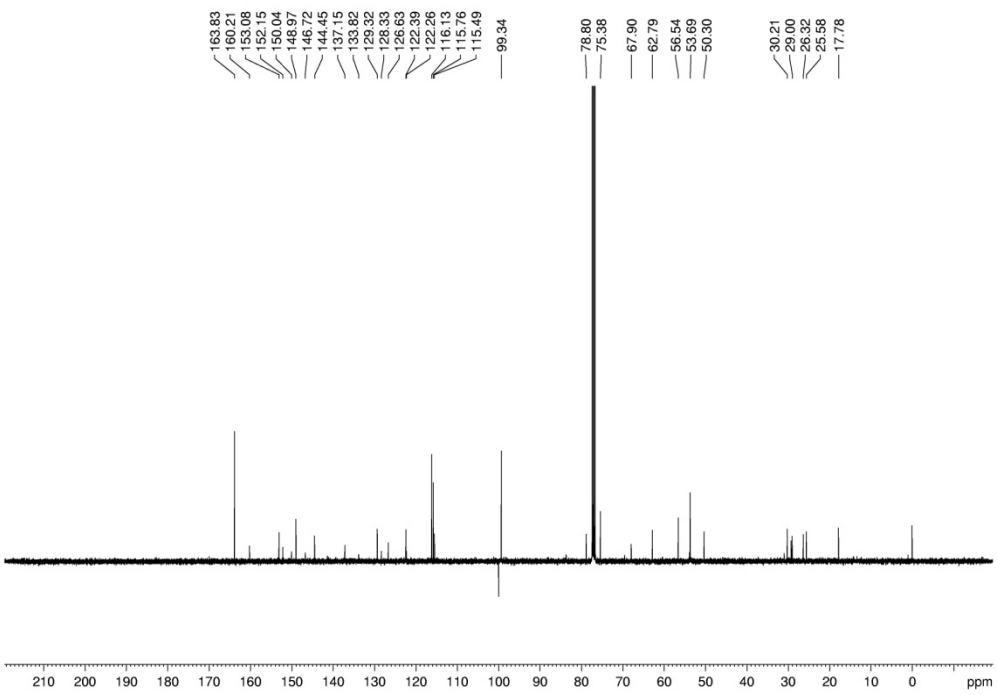
^{1}H NMR of compound **S20**



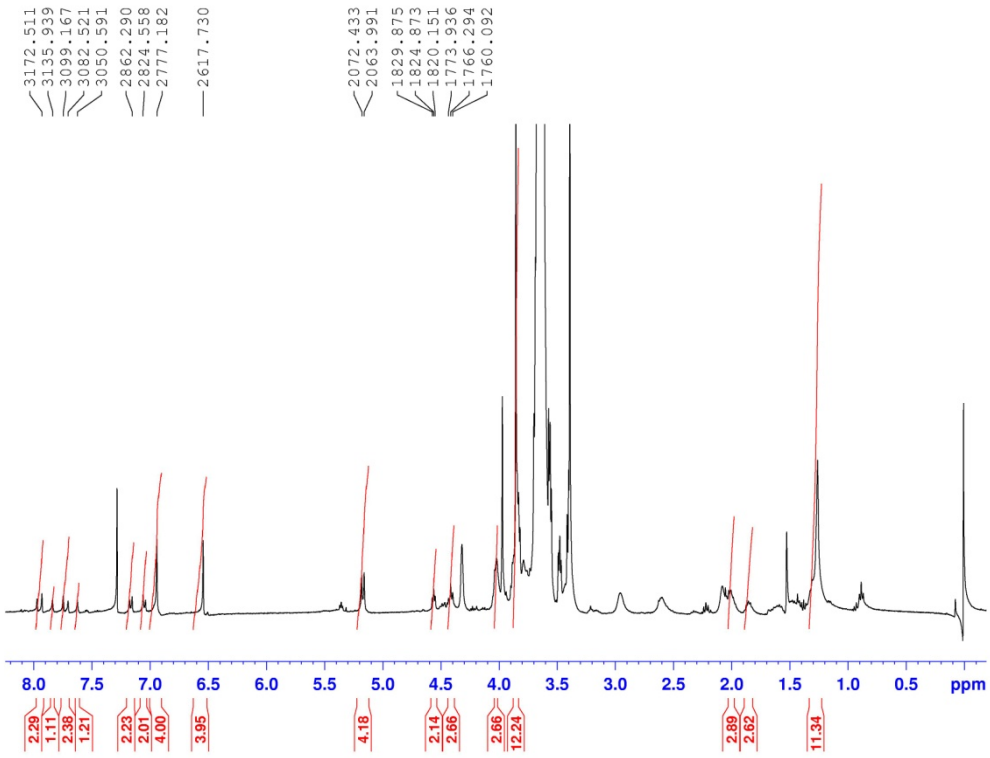
^{13}C NMR of compound S20



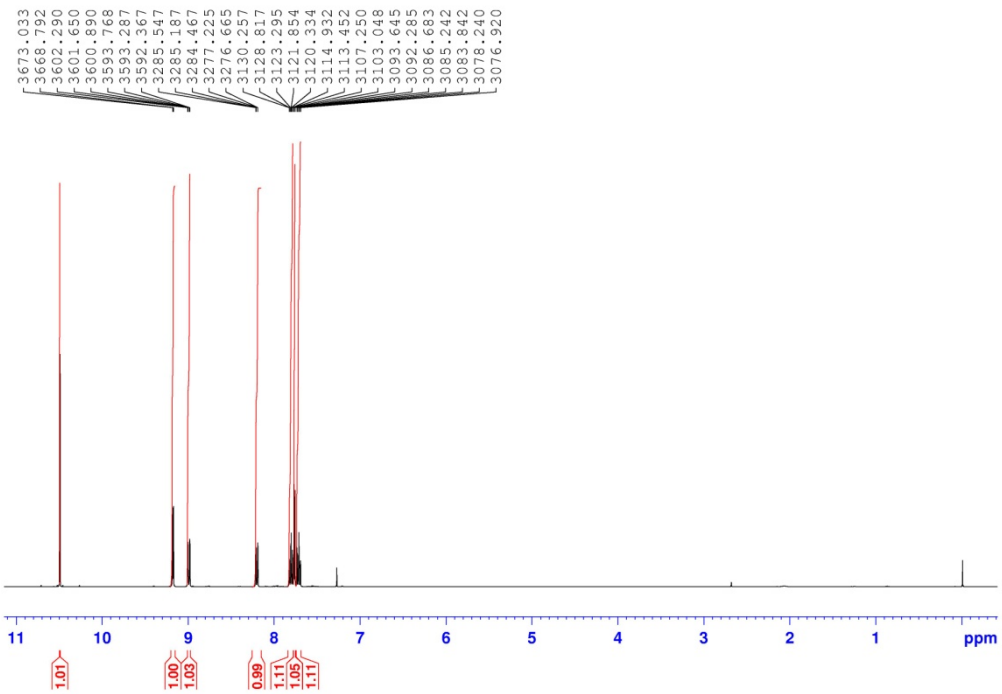
^{1}H NMR of compound **S21**



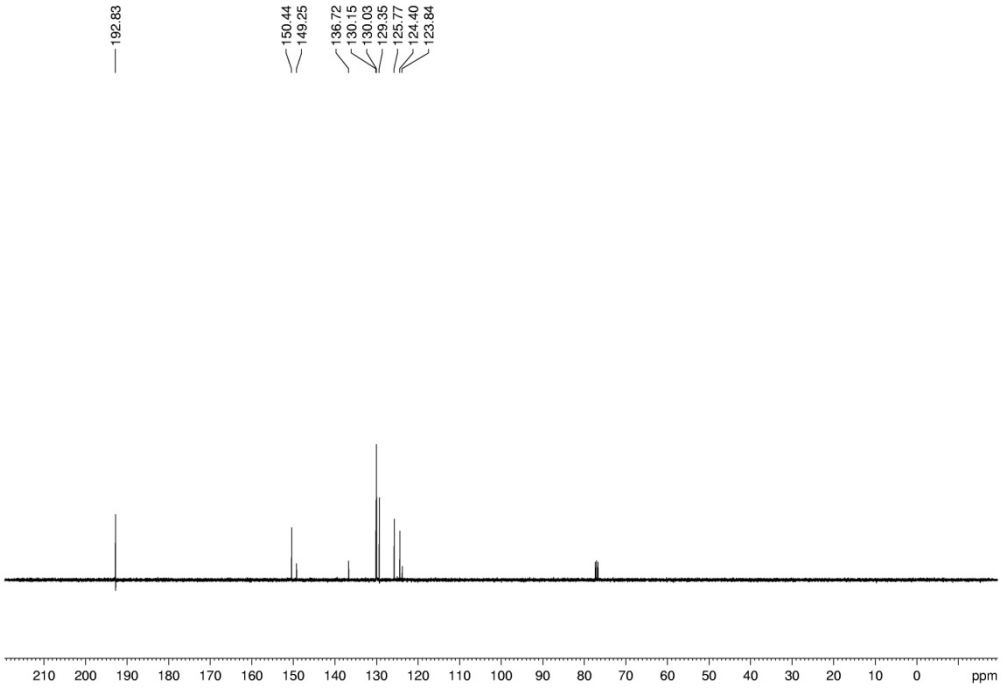
^{13}C NMR of compound S21



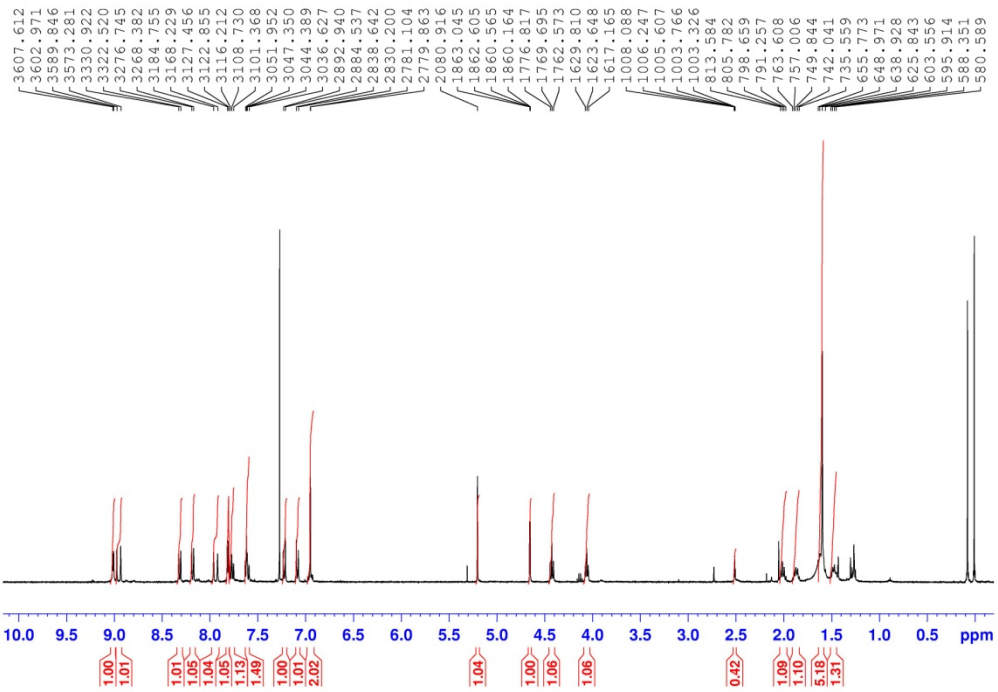
^{1}H NMR of compound **3**



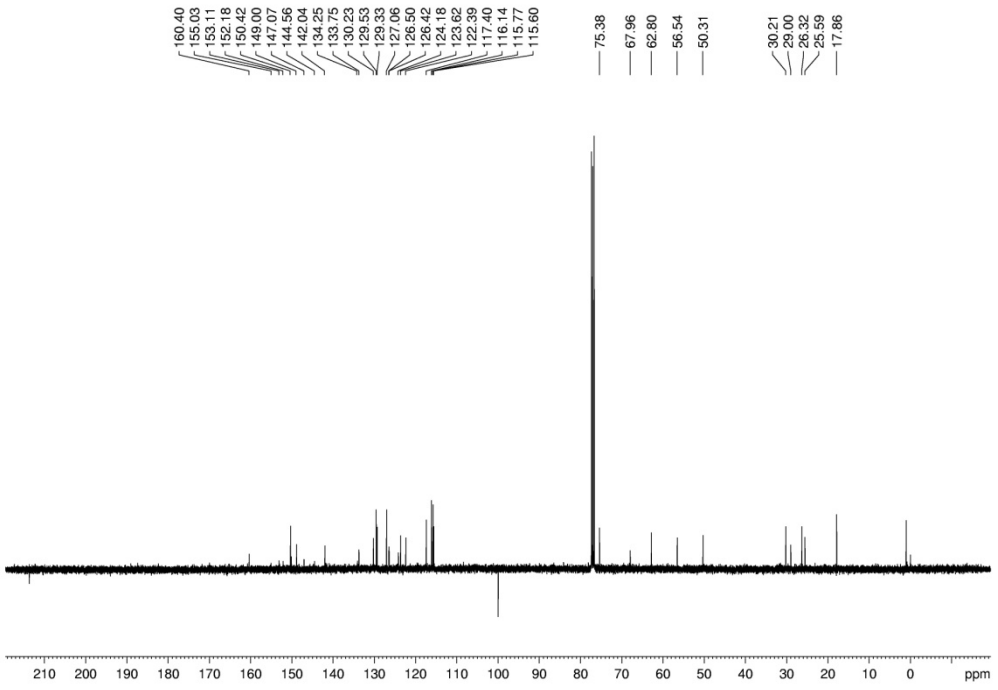
^{1}H NMR of compound **S23**



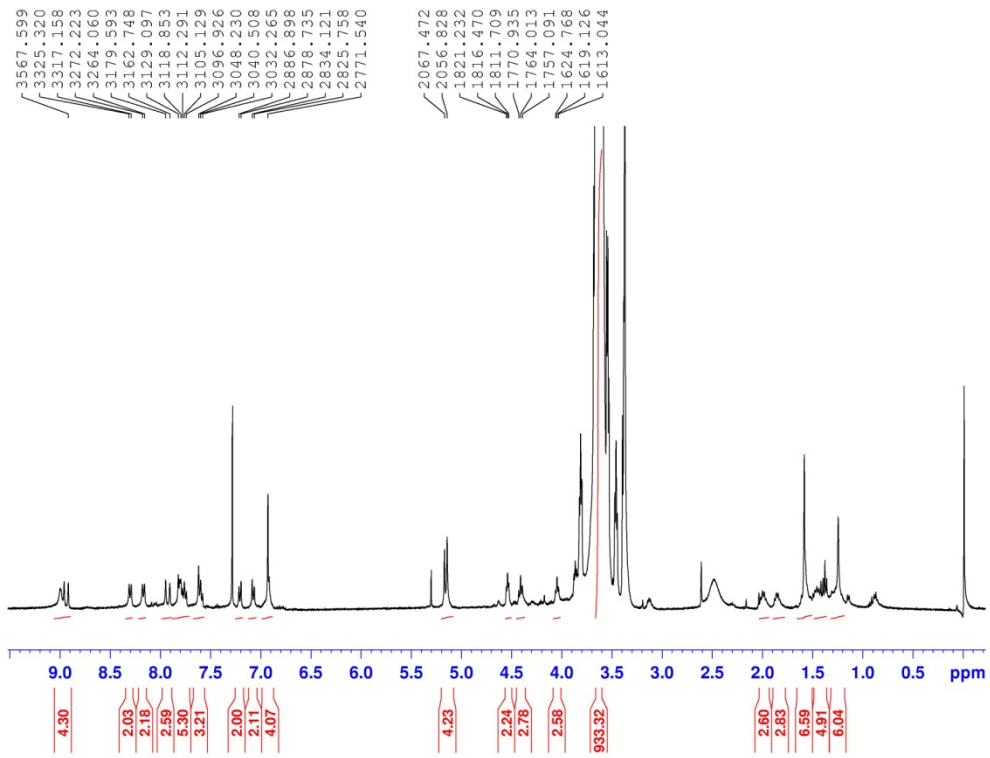
^{13}C NMR of compound S23



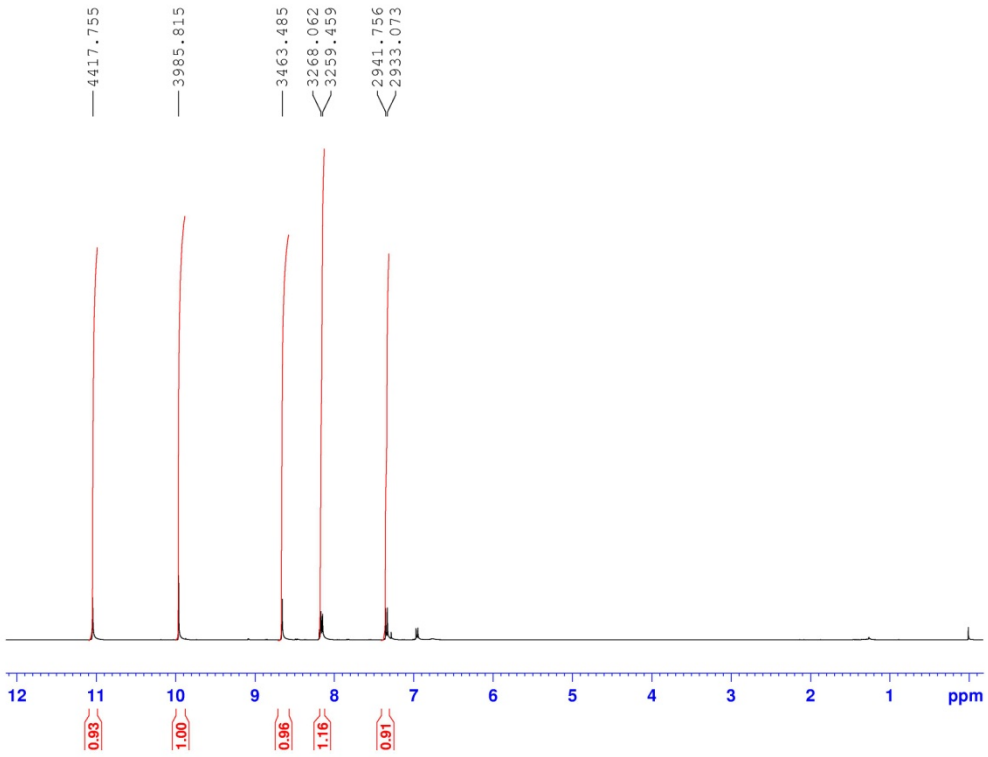
^{1}H NMR of compound **S24**



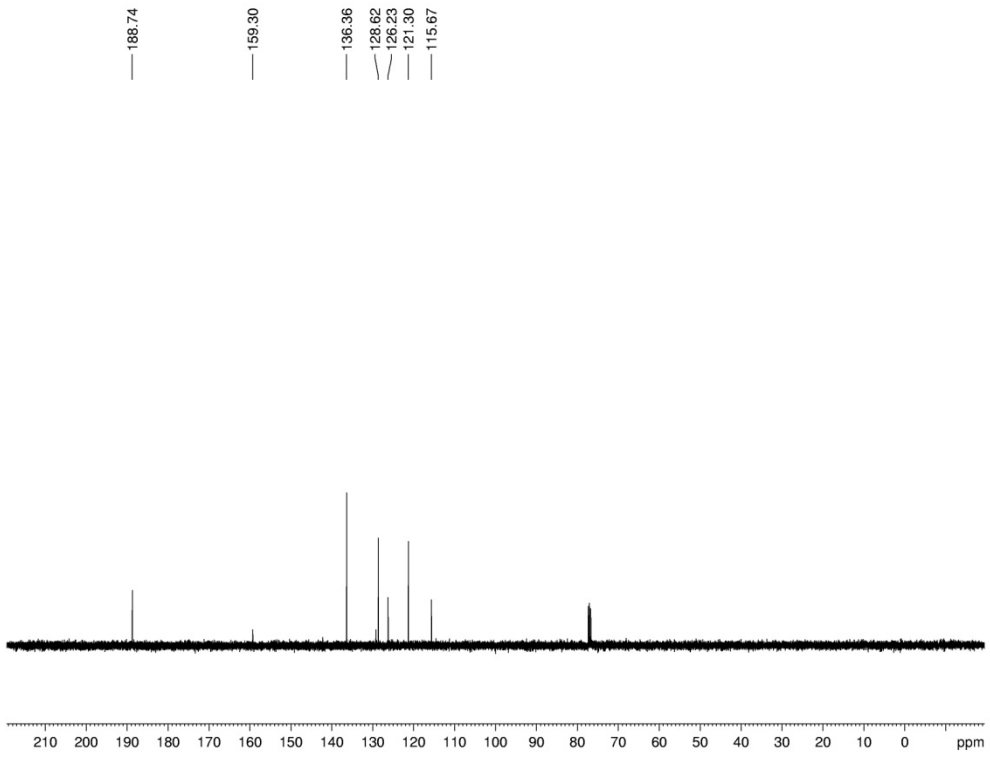
^{13}C NMR of compound S24



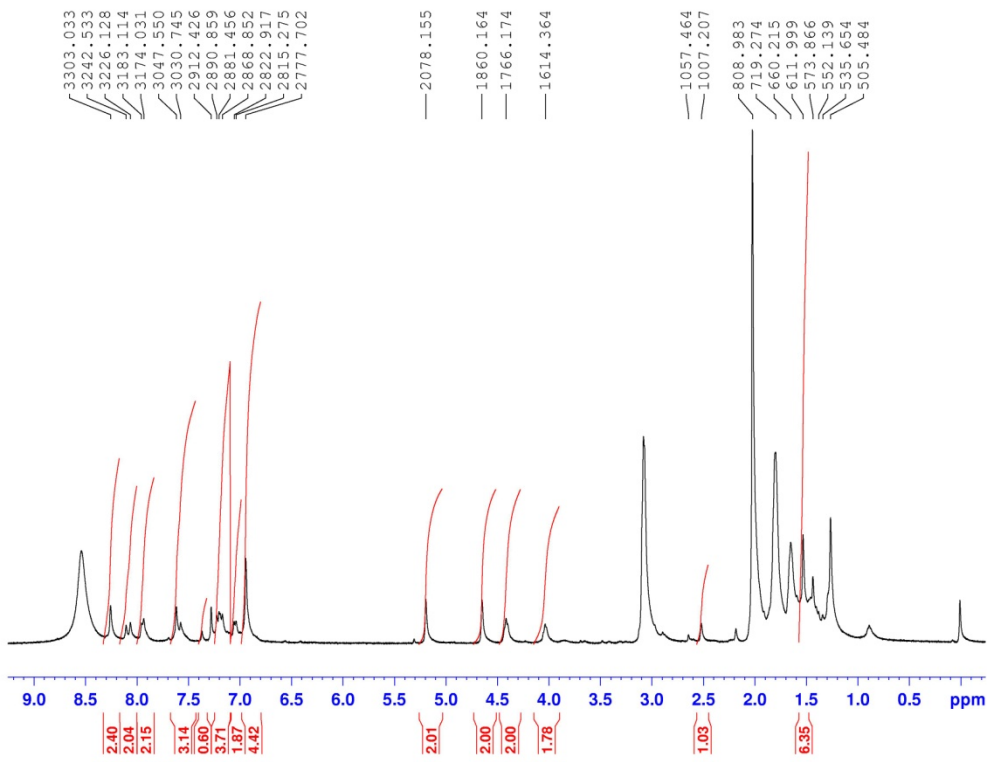
^{1}H NMR of compound **4**



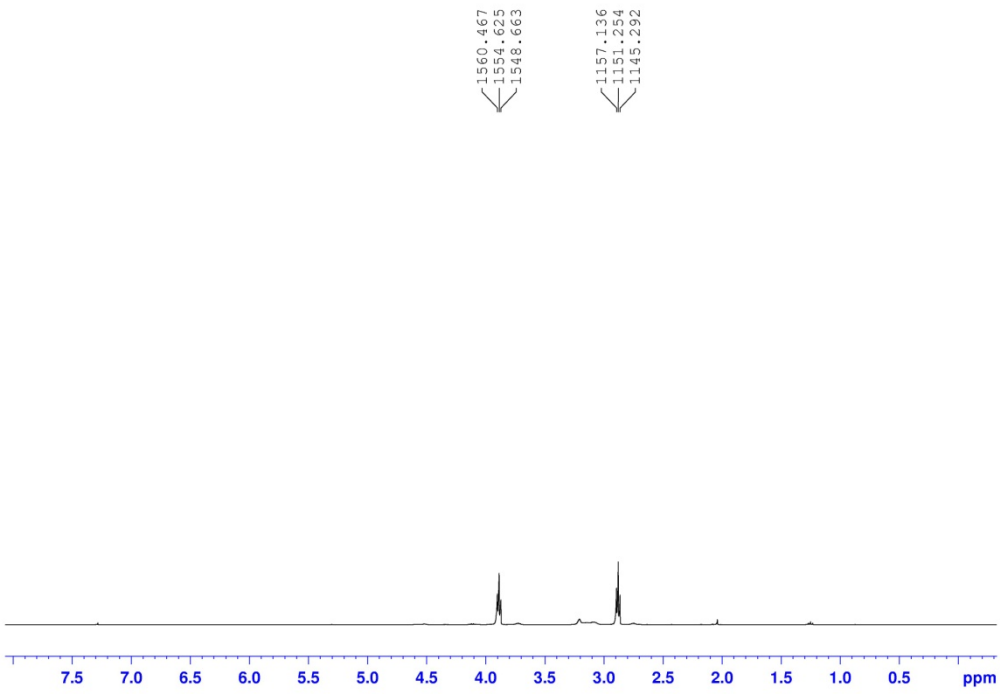
^{1}H NMR of compound **S26**



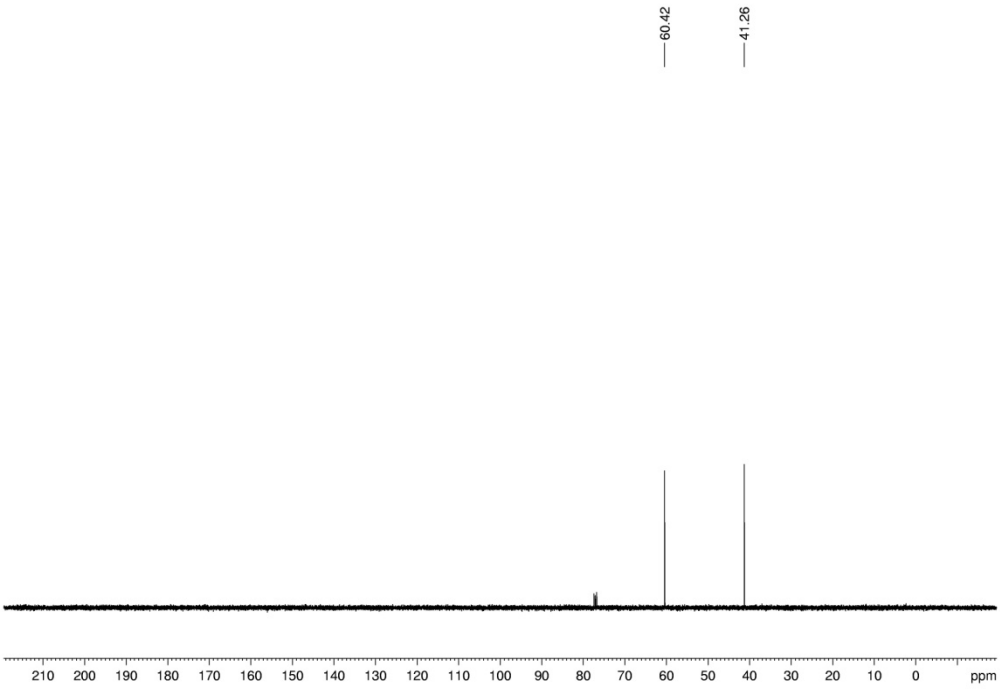
^{13}C NMR of compound S26



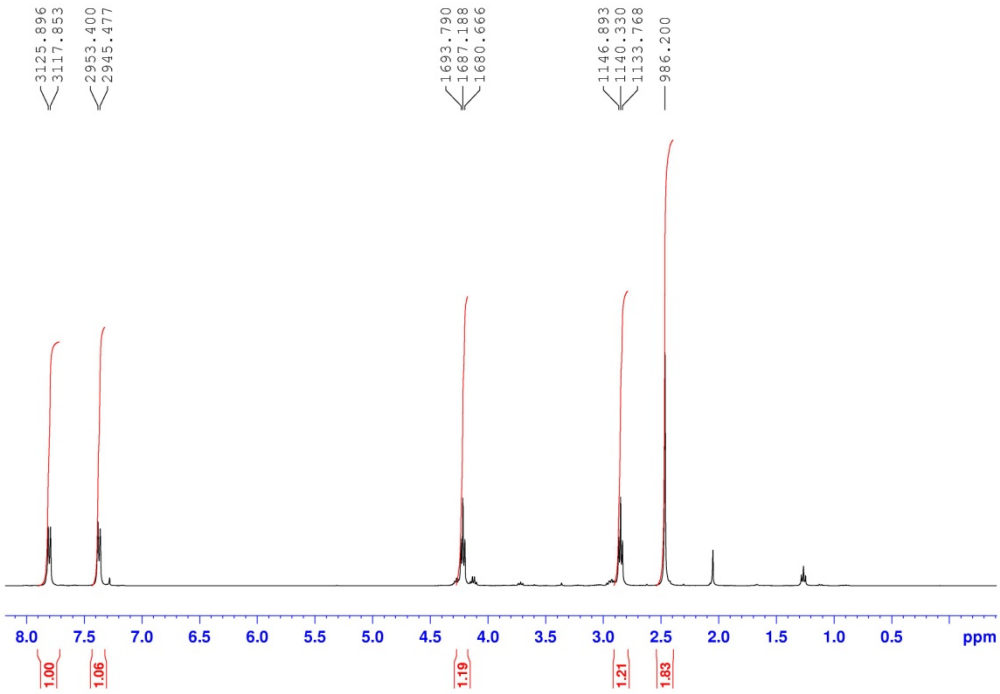
^{1}H NMR of compound **PS** + AcOH



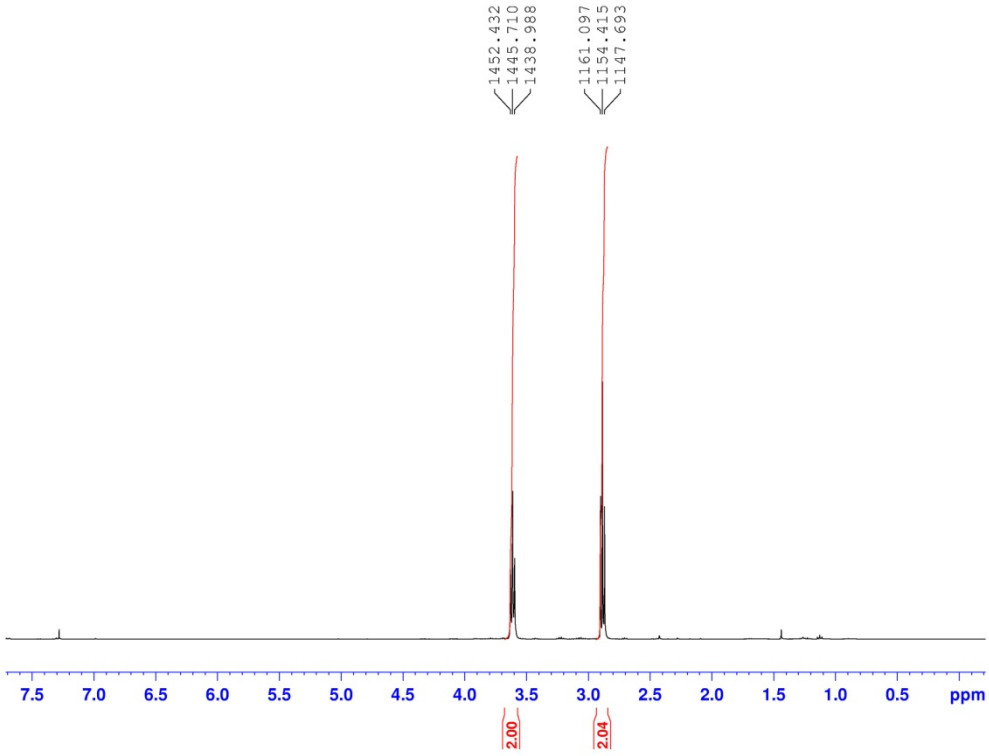
^{1}H NMR of compound **S29**



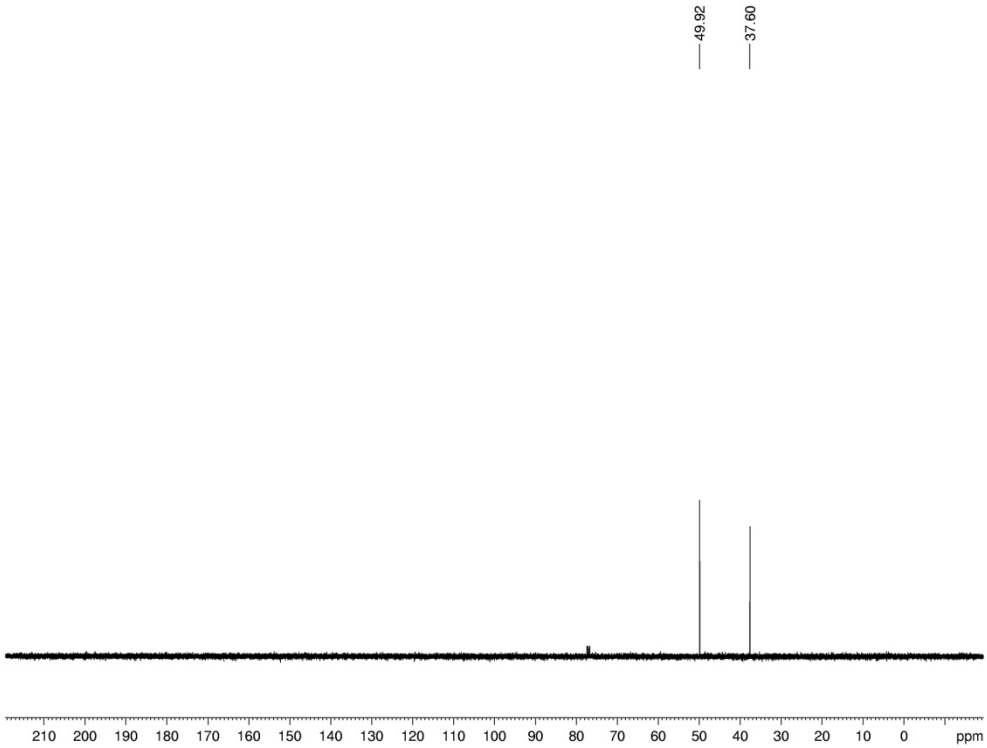
^{13}C NMR of compound S29



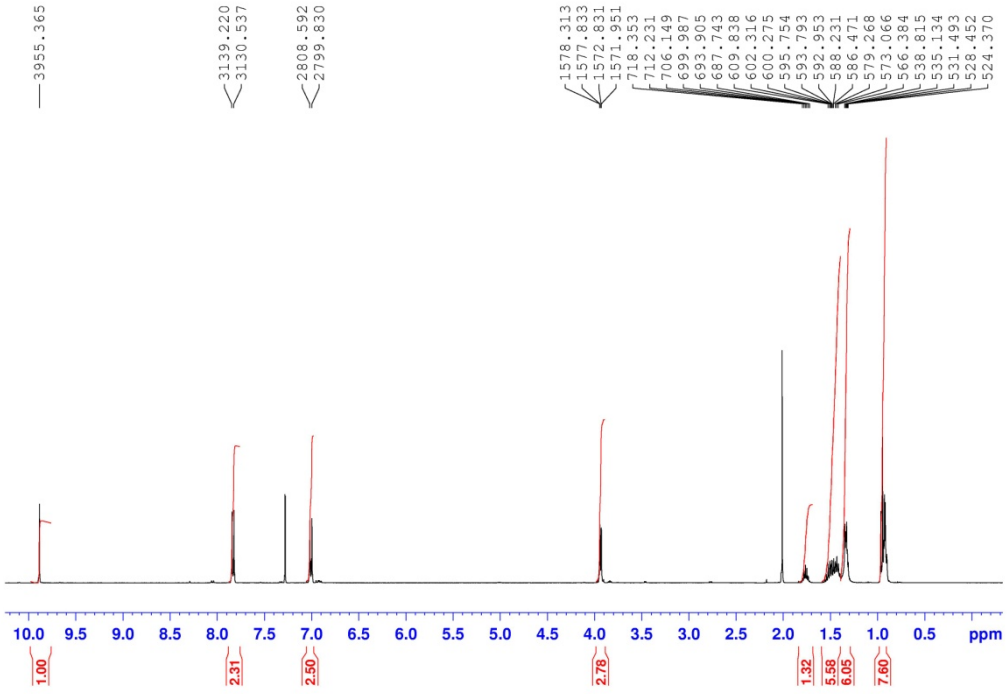
^{1}H NMR of compound **S30**



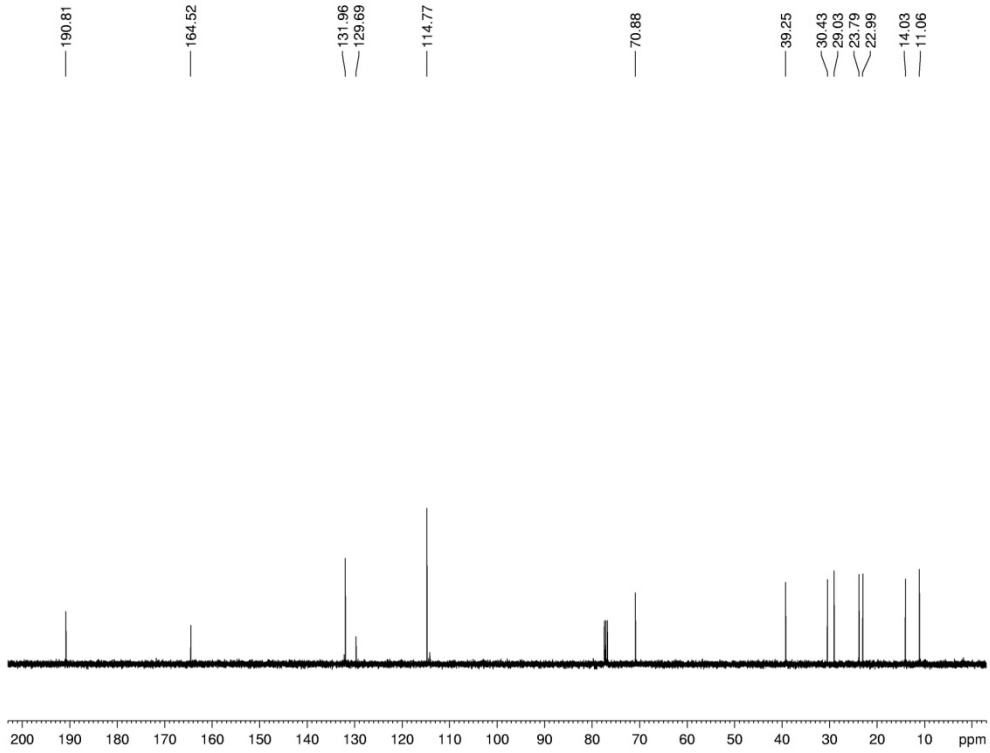
^{1}H NMR of compound **S31**



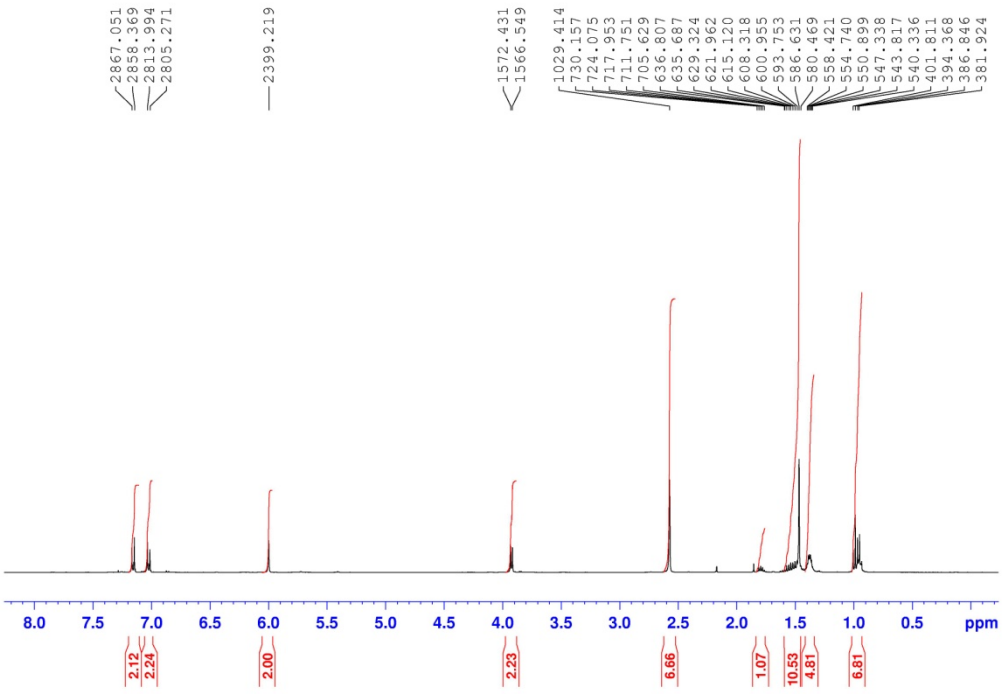
^{13}C NMR of compound S31



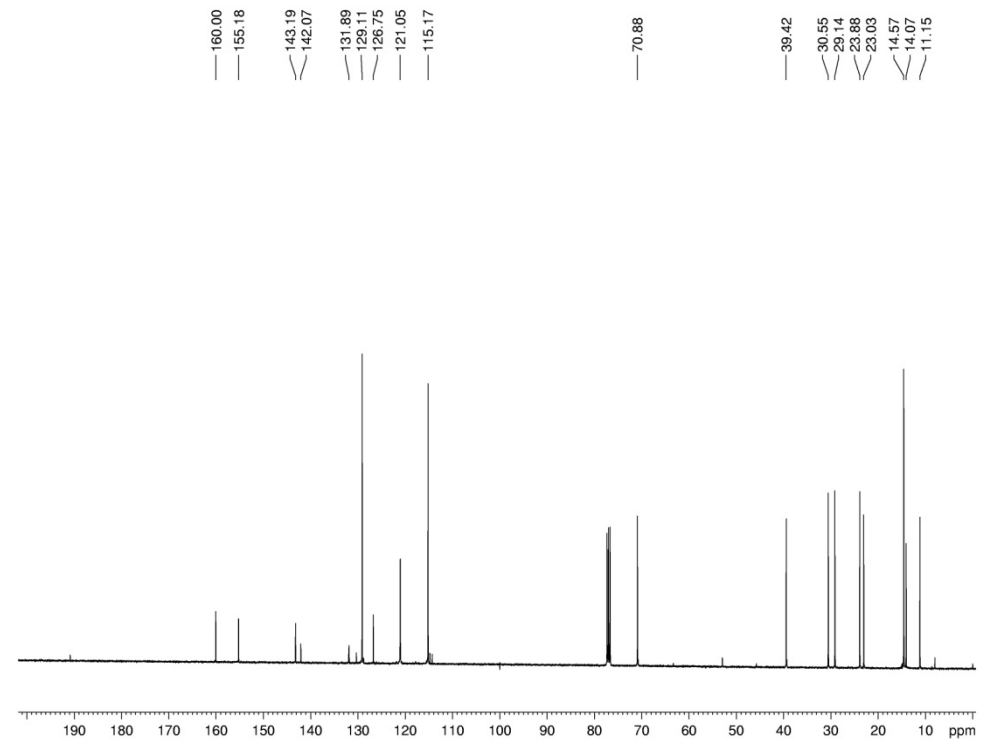
^{1}H NMR of compound **S33**



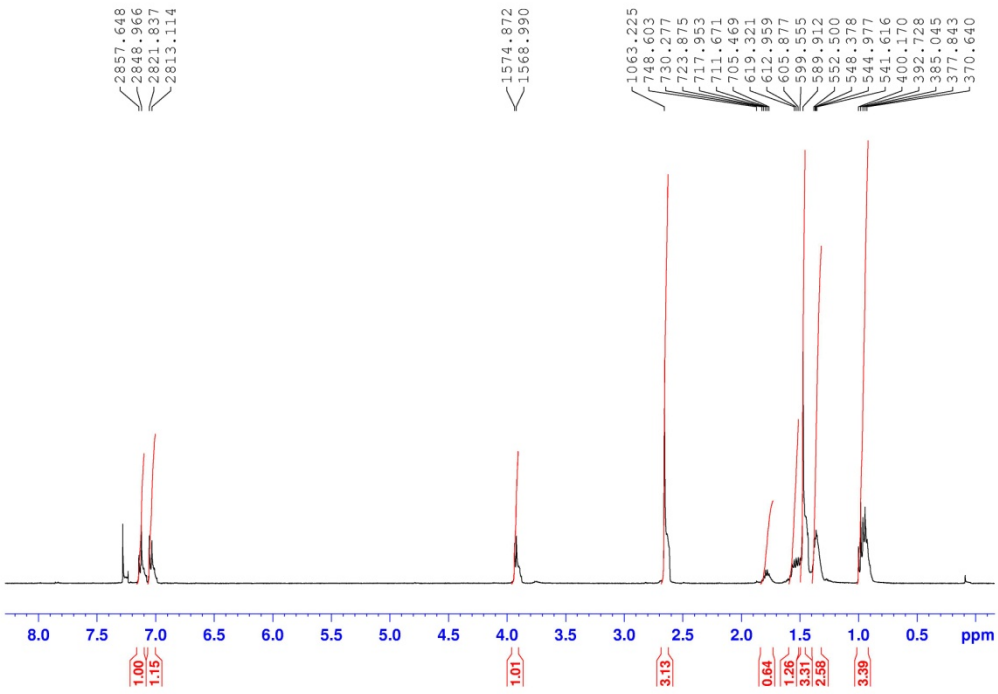
^{13}C NMR of compound **S33**



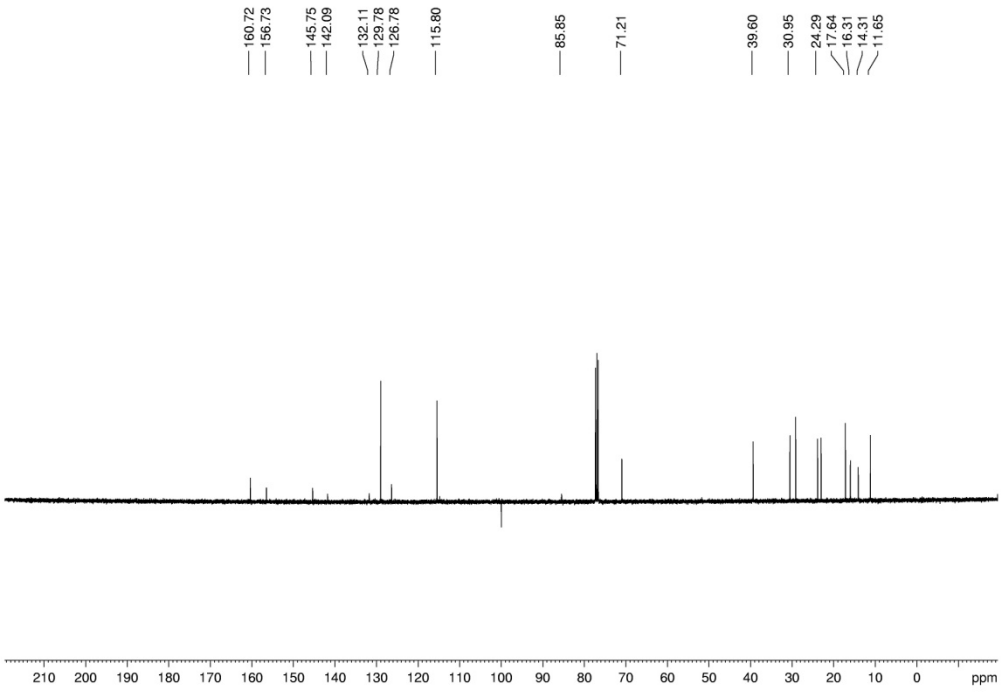
^{1}H NMR of compound **S34**



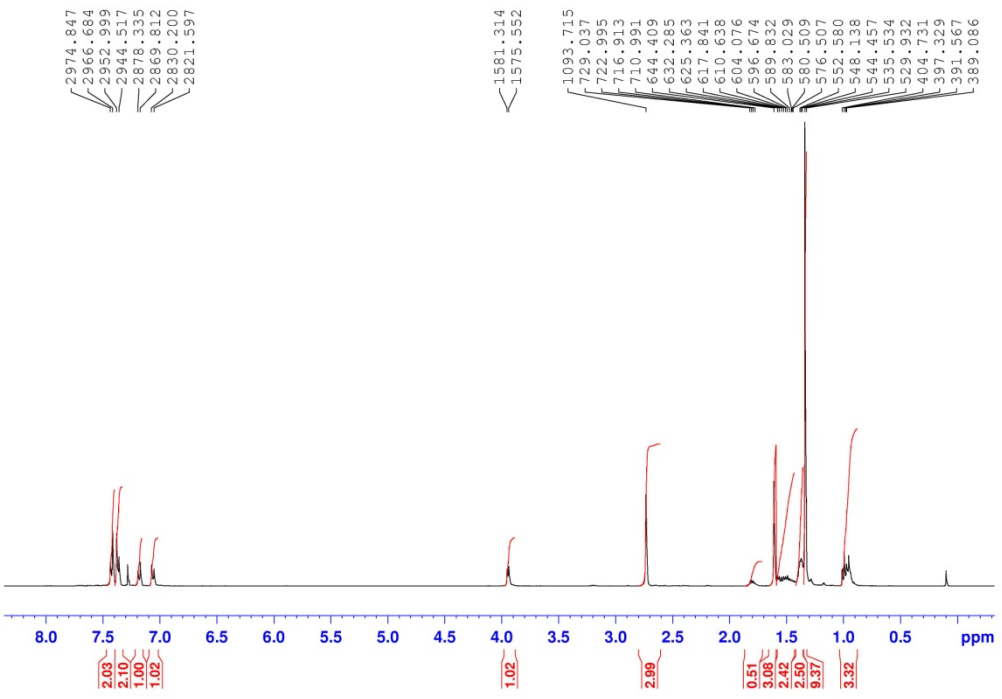
^{13}C NMR of compound **S34**



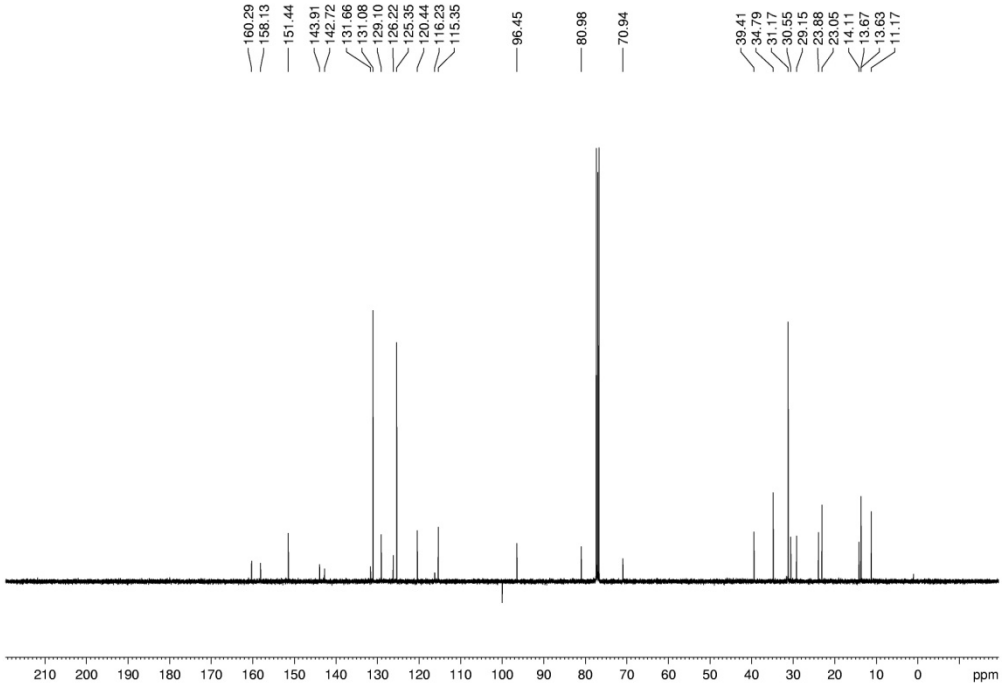
^{1}H NMR of compound **S35**



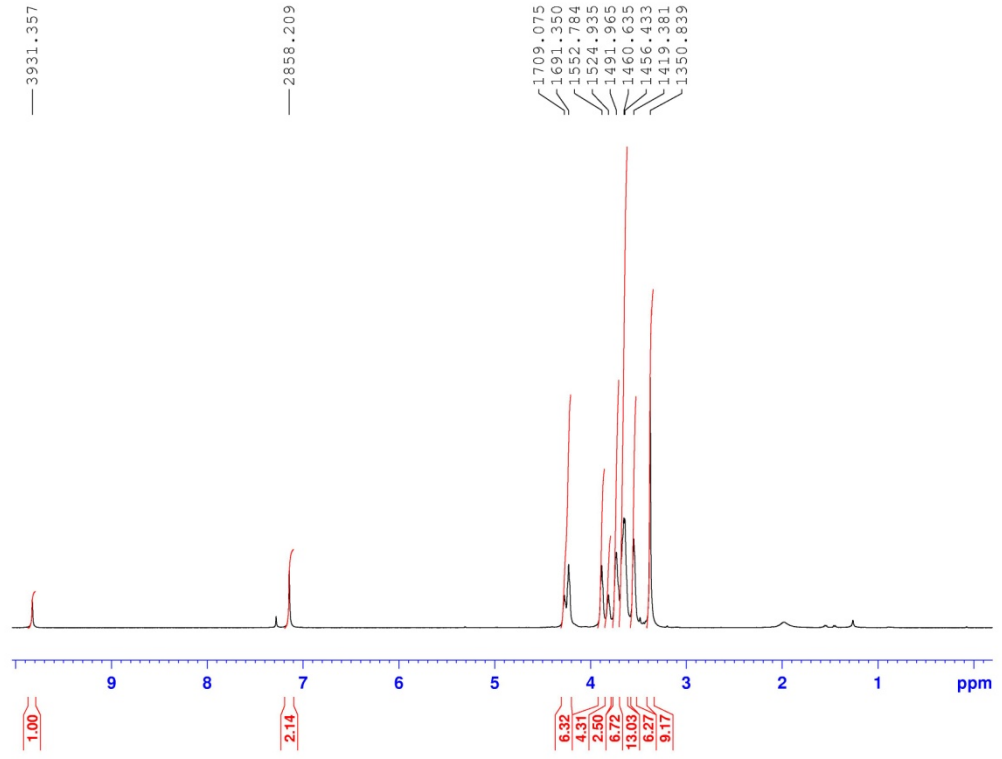
^{13}C NMR of compound **S35**



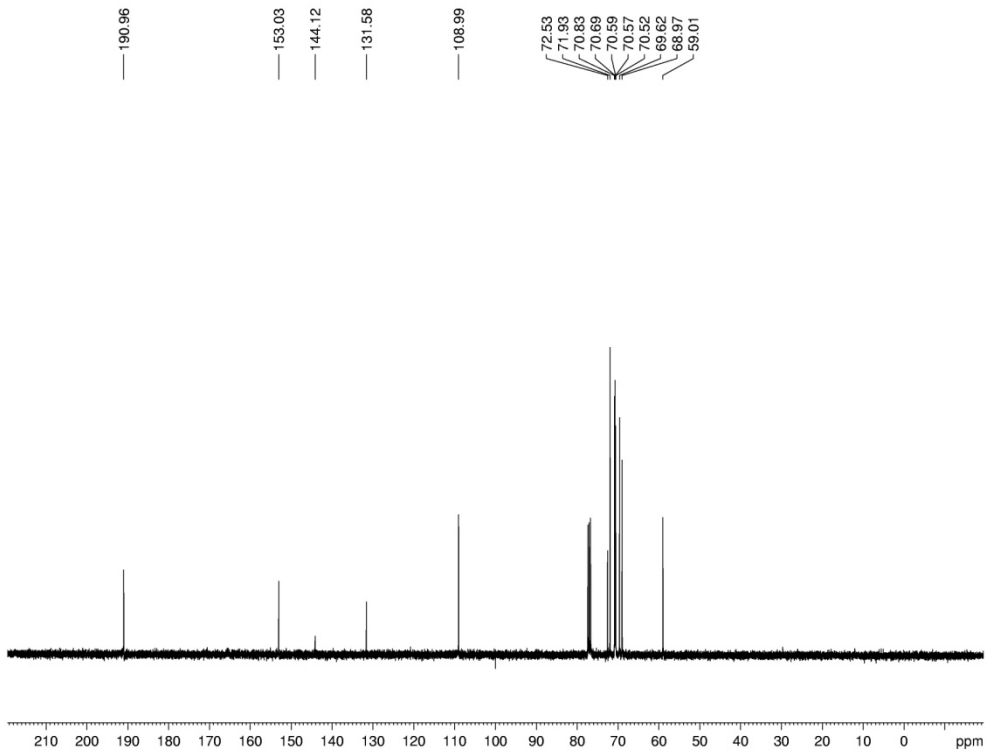
^{1}H NMR of compound **S41**



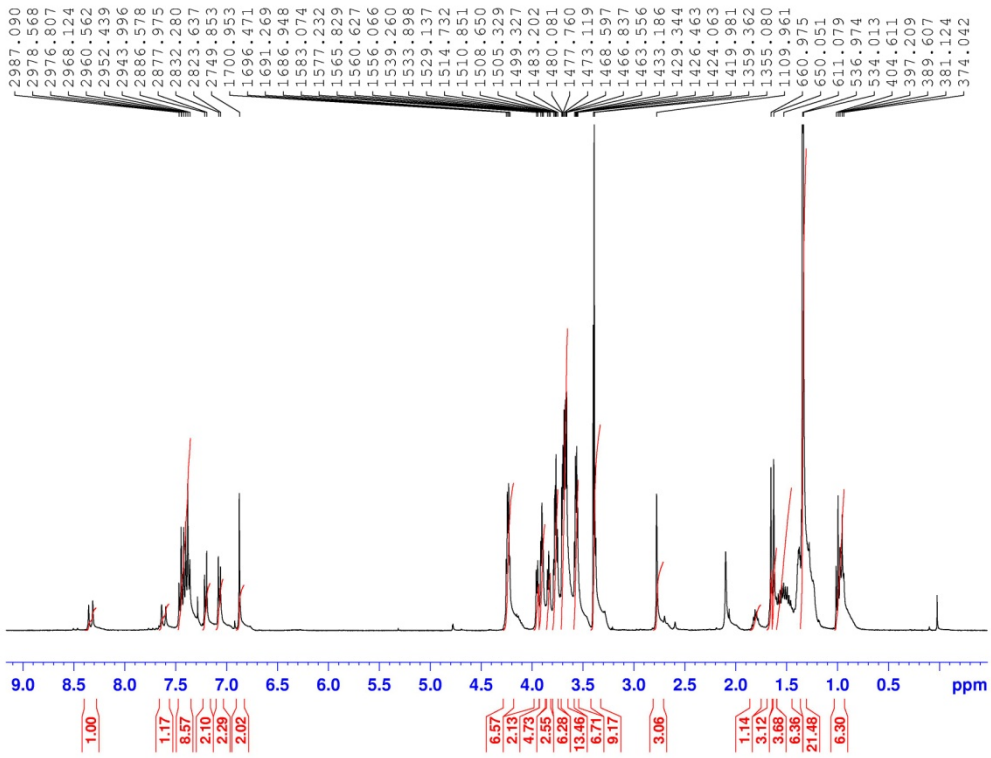
^{13}C NMR of compound **S41**



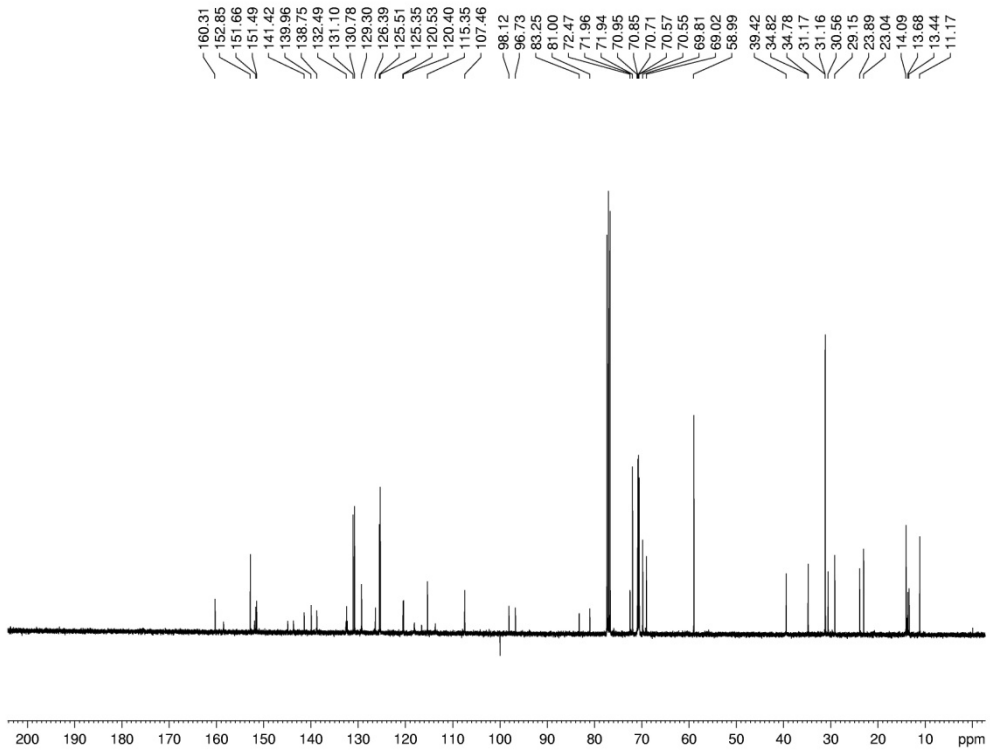
^{1}H NMR of compound **S40**



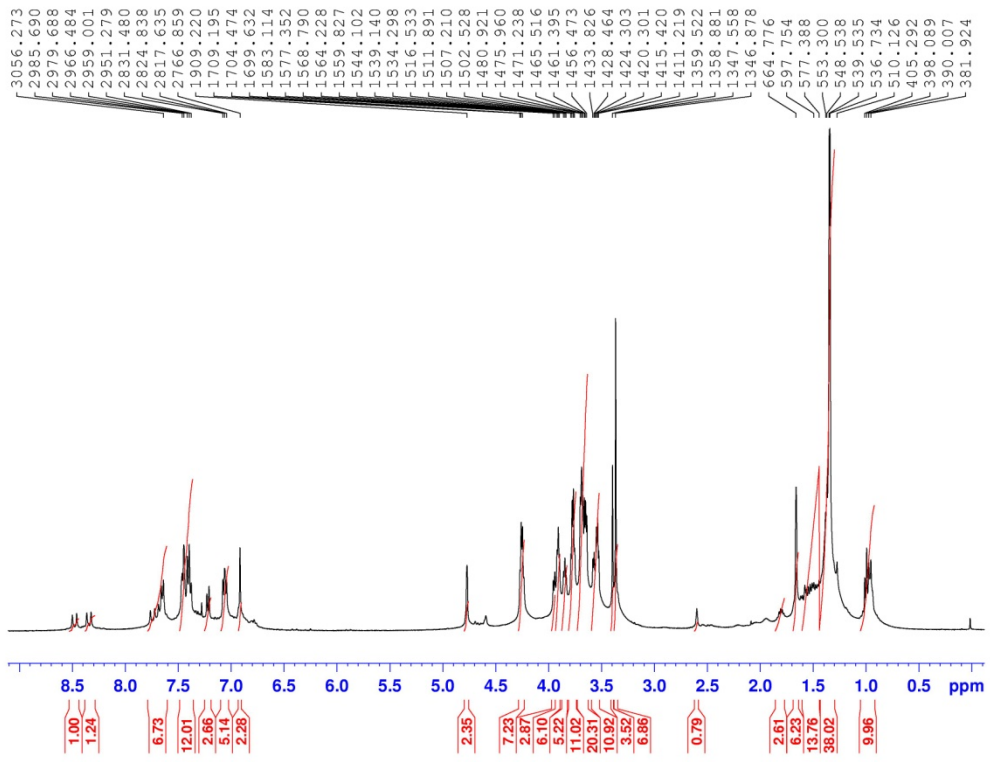
^{13}C NMR of compound S40



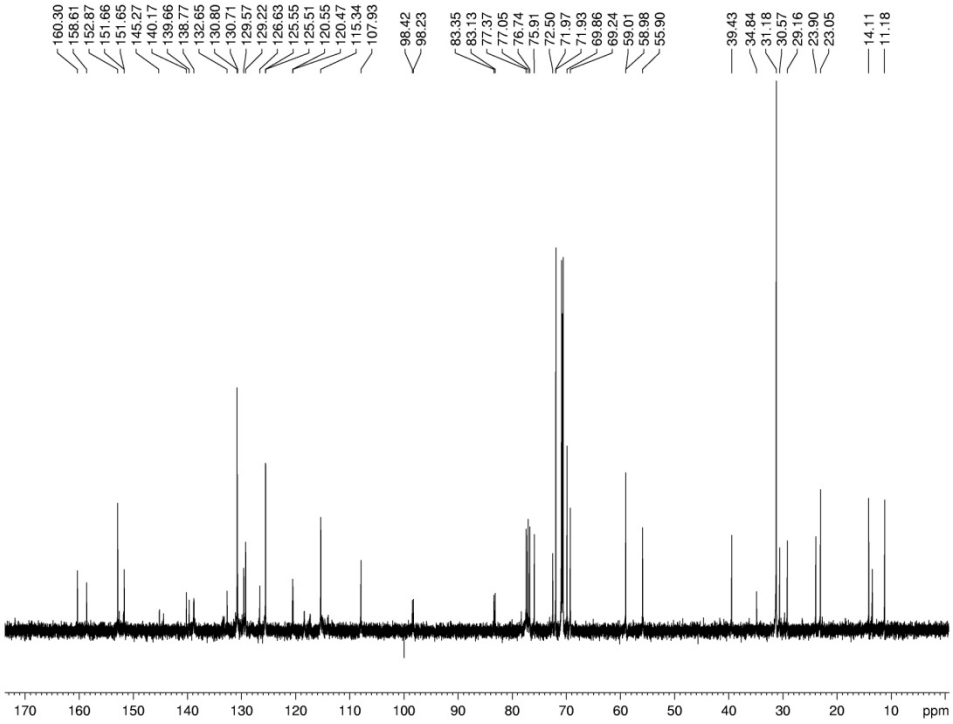
^{1}H NMR of compound **S42**



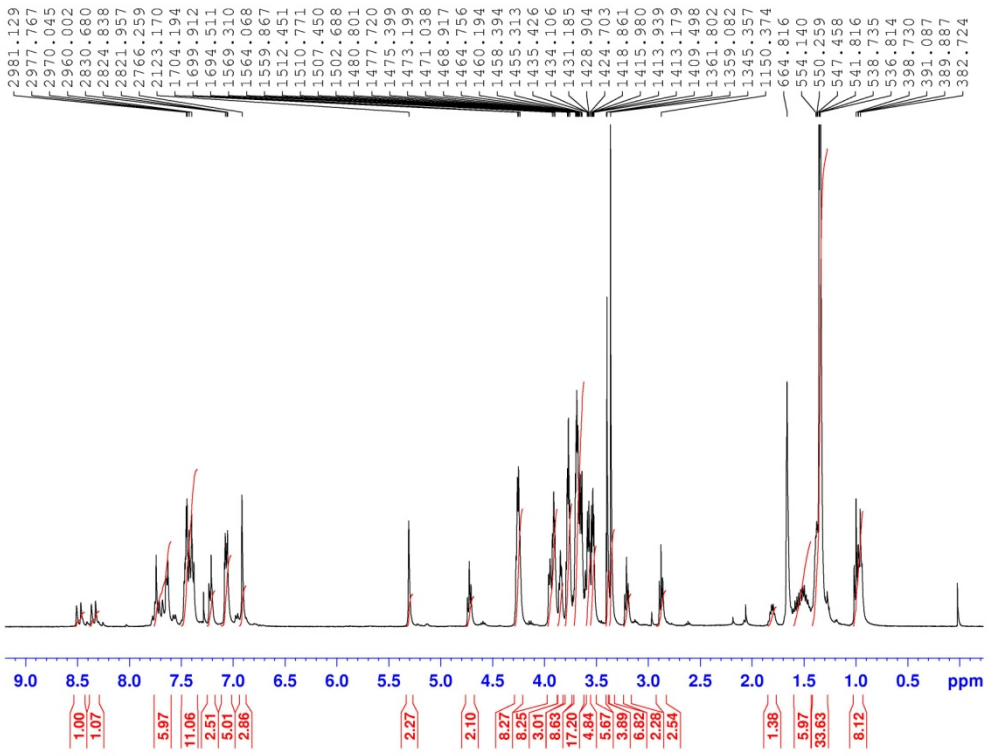
^{13}C NMR of compound **S42**



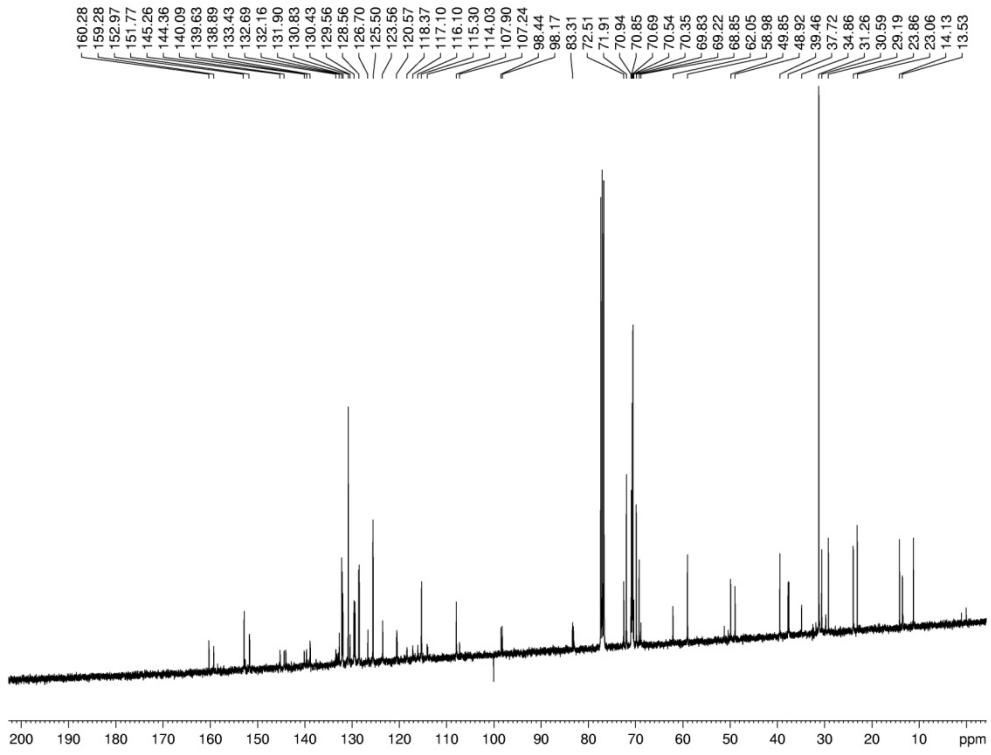
^{1}H NMR of compound **Q**



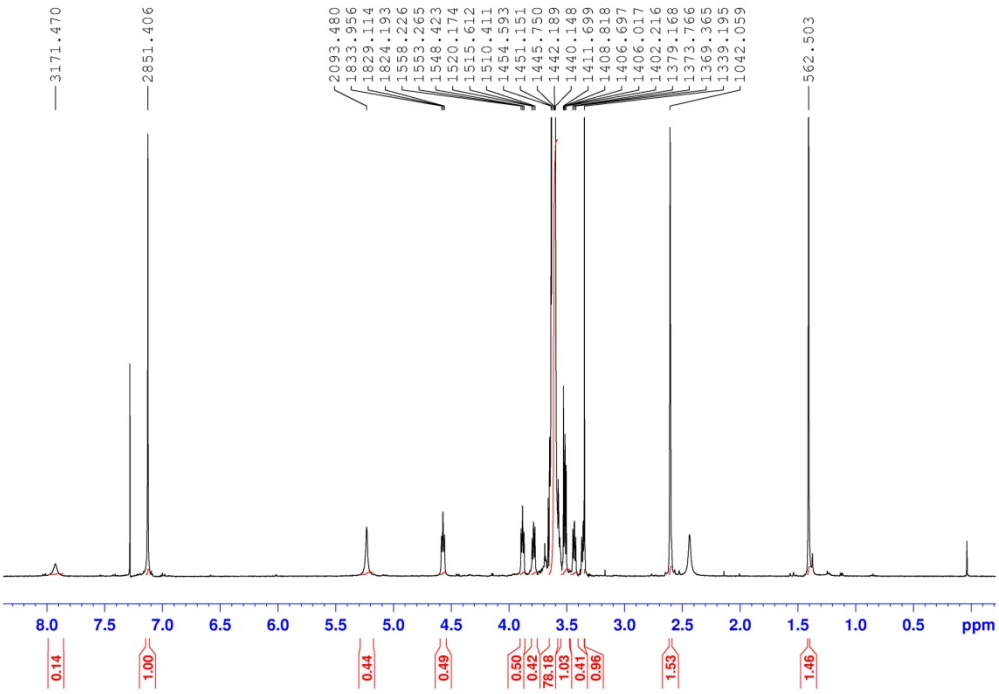
^{13}C NMR of compound **Q**



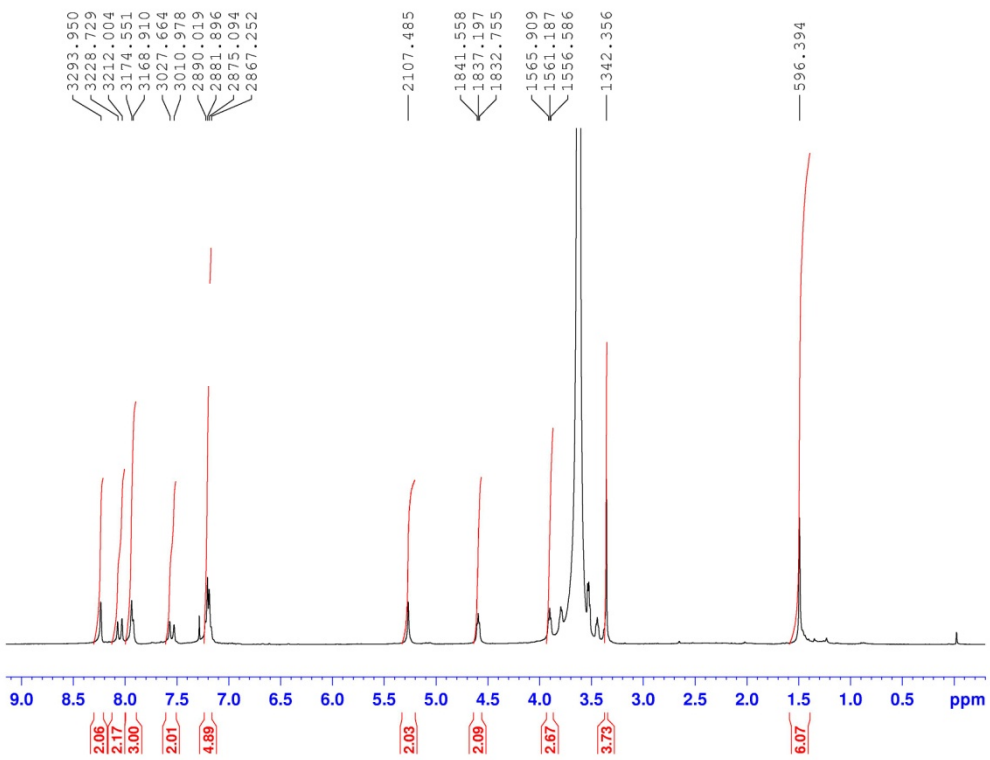
^{1}H NMR of compound **S43**



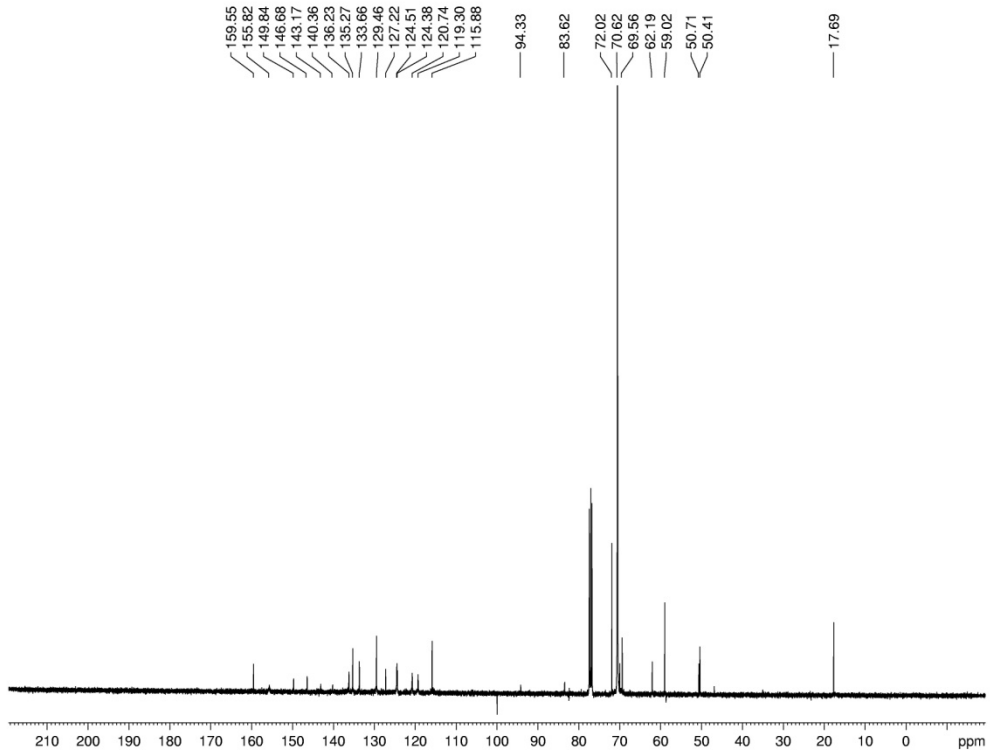
^{13}C NMR of compound **S43**



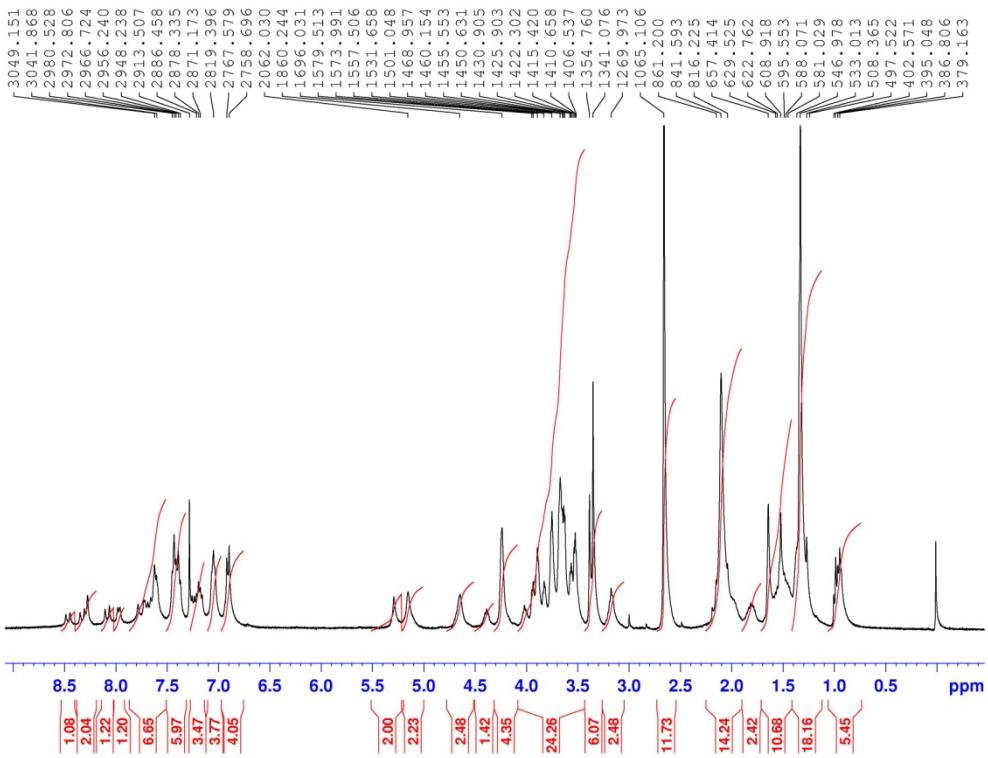
^{1}H NMR of compound **S27**



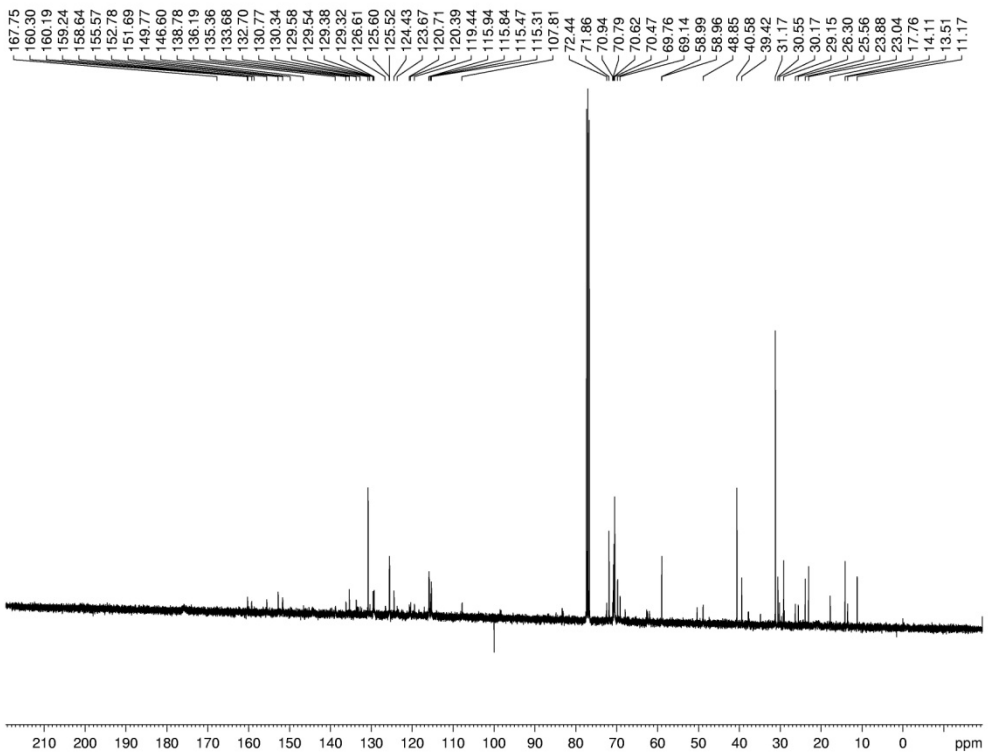
^{1}H NMR of compound **5**



^{13}C NMR of compound **5**



^{1}H NMR of compound **BOD 1**



^{13}C NMR of compound **BOD 1**

6. References

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