Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis of novel sulphur–rich BODIPY systems that enable stepwise fluorescent O–atom turn–on responses and H_2O_2 neuronal system probing

Atul P. Singh, Kang Mun Lee, Dhiraj P. Murale, Taehong Jun, Hyunjeong Liew, Yoo–Hun Suh, and David G. Churchill*

Experimental Section

General Considerations. All chemicals used herein were used as received from commercial suppliers (Aldrich, Acros, and Junsei companies). 2',7'–dichlorofluorescein diacetate was obtained from Sigma–Aldrich. The synthetic details for the preparation of the dipyrromethanes and for the BODIPY systems follow literature methods.[1] ^{1}H and ^{13}C NMR spectra were acquired using a Bruker Avance 400 MHz spectrometer. TMS was used as an internal standard. ^{1}H and ^{13}C NMR spectral signals were calibrated internally by the respective protio impurity or carbon resonance of the $CDCl_3$ (^{1}H: δ 7.24; ^{13}C: δ 77.0). A high resolution hybrid tandem LC–MS/MS spectrometer was used for mass data collection by the research support staff at KAIST.

Absorption and Emission Spectroscopy. All compounds were dissolved in acetonitrile; BODIPY solutions of concentration 1 x 10^{-6} M were prepared. UV–vis absorption and emission measurements were obtained using a CARY 300 Bio UV–vis spectrometer and a Shimatzu RF–5301 PC spectrophotometer, respectively. Emission spectra are obtained through the excitation at λ_{max} from the absorption spectrum of each compound. Fluorescein (Φ_F = 0.92) in 0.1 *N* NaOH is used as the standard to calibrate the quantum yield.[2]

Cell culture. Human neuroblast, SH–SY5Y cells were maintained in DMEM medium supplemented with 100 U/mL penicillin, 100 μg/mL streptomycin, 2 mM L–glutamine, and 10% (v/v) heat–inactivated fetal bovine serum at 37 °C and 5% (v/v) CO_2. Every 48 h, cells were sub–cultured with fresh medium.

Determination of ROS species. For determining whether relevant ROS production *in vitro* can be detected by BODIPY system **2**, we induced intracellular superoxide anion formation by H_2O_2 treatment before staining. In short, 2×10^5 SH–SY5Y cells per well were seeded onto coverslip in a six–well plate 24 h before the experiment. After preincubation (18 h) with H_2O_2 to induce ROS production, cells on coverslips were rinsed with ice–cold HBSS quickly followed by fixation for 15 min at room temperature with paraformaldehyde (4% w/v). Compound **2** was incubated for 2 h at 37°C. As a comparison, 30 μM of the H_2O_2–sensitive fluorescent probe 2′,7′–dichlorofluorescein diacetate (DCF–DA) was also used to stain other cells for 2 h at 37°C. Afterwards, the cells were washed with HBSS, and mounted on glass slides in anti–fade mounting media, Fluorsave™ (calcbiochem; La Jolla, CA, USA). Fluorescence staining was visualized using an Olympus fluorescence microscope (New Hyde Park, NY, USA).

Synthetic procedure.

For 1 and **1a.** Synthesis of **1** and **1a** was performed via a typical procedure.[3] Firstly, CuI (0.5 mol %) and benzotriazole (1.0 mol %) were mixed in 2–3 mL DMSO and aryl halide (2.0 g, 7.41 mmol) was further added and stirred the for 10 min. Next, arylthiol (2.02 g, 16.3 mmol) and Cs_2CO_3 (3.38 g, 10.4 mmol) were added and the reaction mixture was stirred for 10–12 h at 90–95 °C. The reaction was monitored by TLC. After completion of the reaction, 30 mL of ethylacetate was added and this layer was washed with water (3 times with 10 mL). The solution was then dried on Na_2SO_4 and the volatiles where pumped away through use of a rotoevaporator. The viscous mass was then subjected to column chromatography (dichloromethane/hexane eluant) to afford the desired compounds, **1**

and **1a**.

1: Yield = 2.14 g, 81%.^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): δ 10.0 (s, 1 H_6), 7.46 (s, 1 H_4), 7.39 (d, $^{3}J_{H–H}$ = 8.2 Hz, 2 H_8), 7.17 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_9), 7.16 (d, $^{3}J_{H–H}$ = 8.2 Hz, 2 H_{13}), 7.07 (d, $^{3}J_{H–H}$ = 8.1 Hz, 2 H_{14}), 2.35 (s, 3 H_{11}), 2.29 (s, 3 H_{16}). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz): 183.7 (C_6), 155.6 (C_3), 139.9 (C_{10}), 138.0 (C_2), 137.4 (C_{15}), 134.3 (C_5), 133.9 (C_4), 132.8 (C_8), 132.5 (C_7), 130.6 (C_9), 130.0 (C_{14}), 129.4 (C_{13}), 129.3 (C_{12}), 21.2 (C_{11}), 21.0 (C_{16}). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = $[M + Na]^+$ = 379.0261 (calc(calc.), 379.0280 (exp.). **1a:** Yield = 0.100 g, 4.3%.^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): δ 9.98 (S, 1H_6), 7.36 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_8), 7.34 (s, 1 H_4), 7.18 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_9), 2.35 (s, 3 H_{11}). ^{13}C ($CDCl_3$, δ 77.0, 400 MHz) = 183.0 (C_6), 151.7 (C_3), 139.7 (C_7), 139.4 (C_2), 132.2 (C_8), 130.6 (C_9), 129.7 (C_{10}), 129.6 (C_4), 112.9 (C_5), 21.2 (C_{11}). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = $[M + Na + H]^+$ = 344.9619 (calc.), 344.9323 (exp.); $[M + MeO–Br]^+$ = 264.0279 (calc.), 263.9664 (exp.).

General procedure of one-pot synthesis of BODIPY. Aldehyde and dimethylpyrrole were added to a two–neck flask in 20 mL of dichloromethane at ice–bath temperature; sparging with nitrogen for 10 min was then undertaken to remove atmospheric oxygen. Trifluoroacetic acid (TFA) is added dropwise, and materials were kept to react under N_2 for ~1 h. Thin layer chromatographic (TLC) assaying revealed the formation of a new spot at R_f = ~ 0.7–0.8 (**2, 2a**) in dichloromethane, ~ 0.05–0.2 (**6, 7, 8**), in dichloromethane/methanol (99:1) and consumption of the starting aldehydes. It signified the formation of dipyrromethane–based species. The resultant solution was neutralized with *N,N*–di–isopropylethylamine to maintain a pH of ~7; the solution volume was maintained to

~50 mL with dichloromethane. The solution temperature was retained at ice–cold temperature and *p*–Chloranil (tetrachloro–*p*–benzoquinone) was added slowly. The solution was stirred for ~3 h to complete the oxidation reaction. The resultant solution was neutralized with *N,N*–di–isopropylethylamine, followed by 10 min of additional stirring. Boron trifluoride dietherate is then added, and the reaction was kept stirring for 2 h at room temperature. A thin layer chromatography (TLC) assay revealed the expected orange–red spot at R_f = ~0.05–0.2 (**6, 7, 8**) in dichloromethane/methanol (99:1), ~0.7–0.8 (**2, 2a, 9**) in neat dichloromethane. Solvent of the reaction mixture was pumped off through the use of rotoevaporation and the crude solid material was used for silica gel column chromatography (eluent: dichloromethane:methanol = 99:1 (**6, 7, 8**); dichloromethane (**2, 2a, 9**). Single crystals suitable for X–ray diffraction study obtained from a solvent system composed of dichloromethane and hexane.

For 2. Compound, **1** (0.622 g, 1.74 mmol), 2,4–dimethylpyrrole (0.40 mL, 3.49 mmol), TFA (0.01 mL, 0.175 mmol), *p*–chloranil (0.472 g, 1.92 mmol), *N,N*–di–isopropylethylamine (3.03 mL, 17.4 mmol) and $BF_3{\cdot}Et_2O$ (2.4 mL, 17.45 mmol) were used in accordance with the general procedure above. Yield = 0.525 g, 52.3%.^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): δ 7.27 (d, $^3J_{H–H}$ = 8.1 Hz, 2 H_{12}), 7.20 (d, $^3J_{H–H}$ = 8.2, 2 H_{17}), 7.07 (d, $^3J_{H–H}$ = 8.2 Hz, 2 H_{18}), 7.01 (d, $^{33}J_{H–H}$ = 7.9 Hz, 2 H_{13}), 6.88 (s, 1 H_{10}) 5.9 (s, 2 H_2), 2.54 (s, 6 H_{21}), 2.30 (s, 3 H_{15}), 2.27 (s, 3 H_{20}), 1.57 (s, 3 H_{22}). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz): 155.9 (C_1), 142.6 (C_4), 139.4 (C_{11}), 138.5 (C_7), 137.4 (C_{14}), 136.7 (C_9), 135.8 (C_6), 134.2 (C_{12}), 134.2 (C_5), 134.1 (C_6), 133.1 (C_{16}), 131.3 (C3), 130.0 (C_{13}, C_{18}), 129.4 (C_{17}), 128.6 (C_{19}), 121.1 (C_2), 21.2 (C_{20}), 21.0 (C_{15}), 14.6 (C_{21}), 13.7 (C_{22}). ^{11}B–NMR ($CDCl_3$, $BF_3.OEt_2$, δ 0.00): 0.74 (t, 32.92 Hz). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = $[M + Na]^+$ = 597.1452

(calc.), 597.1468 (exp.).

For 2a. Compound **1a** (0.050 g, 0.145 mmol), 2,4–dimethylpyrrole (0.03 mL, 0.290 mmol), TFA (0.001 mL, 0.0145 mmol), *p*–chloranil (0.039 g, 0.159 mmol), *N,N*–di–isopropylethylamine (0.25 mL, 1.45 mmol) and $BF_3{\cdot}Et_2O$ (0.20 mL, 1.45 mmol) were used in accordance with general procedure above. Yield = 0.058 g, 75.4%. ^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): 7.26 (dd, $^3J_{H–H}$, $^3J_{H–H}$ = 6.4 Hz, 1.6 Hz, 2H_{12}), 7.0 (dd, $^3J_{H–H}$, $^3J_{H–H}$ = 6.4 Hz = 8.0 Hz, 0.8 Hz, 2 H_{13}), 6.79 (s, 1 H_{10}), 5.94 (s, 2 H_2), 2.55 (s, 6 H_{16}), 2.27 (s, 3 H_{15}), 1.53 (s, 6 H_{17}). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz) = 156.1 (C_1), 142.6 (C_4), 139.4 (C_{11}), 136.9 (C_7), 135.3 (C_{10}), 134.0 (C_{13}), 133.5 (C_6), 131.3 (C_3), 130.7 (C_{14}), 129.9 (C_{12}), 128.6 (C_5), 121.2 (C_2), 114.0 (C_9), 21.1 (C_{15}), 14.6 (C_{16}), 13.6 (C_{17}). ^{11}B NMR ($CDCl_3$, $BF_3{\cdot}OEt_2$, δ 0.00): 0.67 (t, 33.06 Hz). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = $[M + Na + 2H]^+$ = 555.0523 (calc.), 555.0348 (exp.).

Synthetic procedure for 3–5. In a round bottom flask, aldehyde **1** was dissolved in 50 mL dichloromethane and maintained at ice–bath temperature. Further, a solution of *m*–CPBA (77%) in dichloromethane (40 mL) was added in solution of **1** and stirred for the next 2 –3 h. The reaction progress was monitored by TLC. The resulting white precipitate was filtered from the solution and washed with aqueous $NaHCO_3$ solution and dried on $MgSO_4$. Solvent was removed by rotoevaporation and the crude mass was subjected to silica gel column chromatographic purification (eluent: dichloromethane/methanol: 99:1 (**3**); dichloromethane: **4**, **5**).

For 3. Compound **1** (2.0 g, 5.60 mmol) underwent oxidation with *m*–CPBA (*m*–

chloroperoxybenzoic acid) (3.14 g, 14.0 mmol) in accordance with the general procedure above. Yield = 2.18 g, 87.2%.^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): 9.79 (s, 1 H_6), 7.68 (s, 1 H_4), 7.56 (d, $^{3}J_{H–H}$ = 8.1 Hz, 2 H_8), 7.49 (d, $^{3}J_{H–H}$ = 8.1 Hz, 2 H_{13}), 7.21 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_9), 7.12 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_{14}), 2.27 (s, 3 H_{11}), 2.21 (s, 3 H_{16}). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz) = 182.7 (C_6), 164.8 (C_3), 153.2 (C_{10}), 142.6 (C_2), 142.6 (C_{15}), 140.4 (C_5), 140.2 (C_4), 137.9 (C_8), 130.2 (C_7), 130.0 (C_9), 129.7 (C_{14}), 125.1 (C_{13}), 124.1 (C_{12}), 21.1 (C_{11}), 21.0 (C_{16}). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = [M + CH_3OH + Na] = 443.0421 (calc.), 443.0431 (exp.).

For 4. Compound **1** (2.14 g, 6.0 mmol) underwent reaction with *m*–CPBA (*m*–Chloroperoxybenzoic acid) (4.71g, 21.0 mmol) in accordance with the general procedure above. Yield = 0.80 g, 40.0%.^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): 9.85 (s, 1 H_6), 7.91 (s, 1 H_4), 7.84 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_4), 7.7 (d, $^{3}J_{H–H}$ = 7.9 Hz, 2 H_{13}), 7.33 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_9), 7.26 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_{14}), 2.41 (s, 3 H_{11}), 2.35 (s, 3 H_{16}). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz) = 182.6 (C_6), 168.2 (C_3), 147.6 (C_{10}), 145.5 (C_2), 143.4 (C_{15}), 140.2 (C_5), 137.6 (C_4), 137.2 (C_8), 133.5 (C_7), 130.3 (C_9), 130.2 (C_{14}), 127.7 (C_{13}), 125.7 (C_{12}), 21.6 (C_{11}), 21.5 (C_{16}). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = $[M + Me]^+$ = 419.0445 (calc.), 419.0445 (exp.).

For 5. Compound **1** (1.44 g, 4.039 mmol) underwent reaction with *m*–CPBA (*m*–chloroperoxybenzoic acid) (4.07 g, 18.18 mmol) in accordance with general procedure above. Yield = 0.70 g, 41%. ^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): 10.37 (s, 1 H_6), 7.85 (s, 1 H_4), 7.84 (d, $^{3}J_{H–H}$ = 8.4 Hz, 4 $H_{8,13}$), 7.36 (d, $^{3}J_{H–H}$ = 8.5 Hz, 2 H_9), 7.34 (d, $^{3}J_{H–H}$ = 8.0 Hz, 2 H_{14}), 2.42 (s, 6 $H_{11,16}$). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz) = 182.8 (C_6), 155.4 (C_3), 149.4 (C_2),

146.4 (C_7), 146.0 (C_{12}), 140.3 (C_5), 136.8 (C_{10}), 136.8 (C_{15}), 131.7 (C_4), 130.7 (C_9), 130.5 (C_{14}), 128.0 (C_8), 127.9 (C_{13}), 21.7 (C_{11}), 21.7 (C_{16}). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = $[M + Na]^+$ = 443.0058 (calc.), 443.0048 (exp.).

For 6. Compound, **3** (0.270 g, 0.695 mmol), 2,4–dimethylpyrrole (0.14 mL, 1.39 mmol), TFA (0.005 mL, 0.070 mmol),p–chloranil (0.188 g, 0.765 mmol), *N,N*–di–isopropylethylamine (1.2 mL, 6.95 mmol) and $BF_3{\cdot}Et_2O$ (0.94 mL, 6.95 mmol) were used in accordance with the general procedure above. Yield = 0.160 g, 40.0%. ^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): 7.53 (d, $^3J_{H–H}$ = 8.0 Hz, 2H), 7.33 (d, $^3J_{H–H}$ = 7.9 Hz, 2H), 7.29 (d, $^3J_{H–H}$ = 7.9 Hz, 2 H), 7.19 (s, 1 H), 7.09 (d, $^3J_{H–H}$ = 7.9 Hz, 2 H), 6.01 (s, 1 H), 5.78 (s, 1 H), 2.53 (s, 3 H), 2.50 (s, 3 H), 2.39 (s, 3 H), 2.29 (s, 3 H), 1.49 (s, 3 H), 1.02 (s, 3 H). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz) = 157.5, 156.5, 155.5, 152.9, 143.1, 142.7, 142.1, 141.1, 138.8, 134.5, 130.5, 130.3, 130.2, 130.0, 129.9, 124.5, 124.0, 122.1, 121.2, 21.4, 14.7, 14.5, 13.7, 13.5. ^{11}B–NMR ($CDCl_3$, $BF_3.OEt_2$, δ 0.00): 5.22 (t, 32.96 Hz). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = $[M + Na]^+$ = 629.1350 (calc.), 629.1361 (exp.).

For 7. Compound, **4** (0.45 g, 1.11 mmol), 2,4–dimethylpyrrole (0.22 mL, 2.23 mmol), TFA (0.008 mL, 0.111 mmol), *p*–chloranil (0.301 g, 1.23 mmol), *N,N*–di–isopropylethylamine (1.94 mL, 11.1 mmol) and $BF_3{\cdot}Et_2O$ (1.52 mL, 11.1 mmol) were used in accordance with general procedure above. Yield = 0.180 g, 26.0%. ^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): 7.81 (d, $^3J_{H–H}$ = 8.2 Hz, 2 H), 7.39 (s, 1 H), 7.35 (s, $^3J_{H–H}$ = 8.1 Hz, 2 H), 7.31 (s, $^3J_{H–H}$ = 8.1 Hz, 2 H), 7.09 (s, $^3J_{H–H}$ = 8.0 Hz, 2 H), 2.55 (s, 3 H), 2.50 (s, 3 H), 2.42 (s, 3 H), 2.29 (s, 3 H), 1.49 (s, 3 H), 0.86 (s, 3 H). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz) = 157.8, 156.7, 155.7, 148.4, 145.3, 143.5, 142.6, 141.9, 138.2, 137.9, 134.0, 133.3, 130.4, 130.2, 130.0,

129.5, 127.4, 124.8, 122.3, 121.2, 21.6, 21.4, 14.8, 14.5, 13.7, 13.6. ^{11}B–NMR ($CDCl_3$, $BF_3{\cdot}OEt_2$, δ 0.00): 5.29 (t, 39.99 Hz). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = [M + Na]$^+$ = 645.1299 (calc.), 645.1308 (exp.).

For 8 and 9. Compound, **5** (0.418 g, 0.993 mmol), 2,4–dimethylpyrrole (0.20 mL, 1.99 mmol), TFA (0.008 mL, 0.099 mmol),p–chloranil (0.269 g, 1.09 mmol), *N,N*–di–isopropylethylamine (1.73 mL, 9.93 mmol) and $BF_3{\cdot}Et_2O$ (1.35 mL, 9.93 mmol) were used in accordance with general procedure above. **For 8:** Yield = 0.184 g, 29.0%. ^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): 7.81 (d, $^3J_{H–H}$ = 8.3 Hz, 2 H_{12}), 7.50 (d, $^3J_{H–H}$ = 8.3 Hz, 2 H_{17}), 7.36 (s, 1 H_{10}), 7.32 (d, $^3J_{H–H}$ = 8.0 Hz, 2 H_{18}), 7.03 (d, $^3J_{H–H}$ = 8.1 Hz, 2 H_{13}), 5.75 (s, 2 H_2), 2.49 (s, 6 H_{21}), 2.40 (s, 3 H_{15}), 2.26 (s, 3 H_{20}), 1.06 (s, 6 H_{22}). ^{13}C NMR ($CDCl_3$, δ 77.0, 400 MHz) = 156.9, 149.3, 147.1, 145.9, 145.7, 142.2, 137.4, 136.8, 134.1, 133.8, 130.3, 129.4, 128.5, 127.5, 121.5, 21.6, 21.5, 14.6, 13.3. ^{11}B–NMR ($CDCl_3$, $BF_3.OEt_2$, δ 0.00): 5.22 (t, 32.96 Hz). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = [M + Na]$^+$ = 661.1248 (calc.), 661.1249 (exp.).

For 9: Yield = 0.023 g, 9.9%. ^{1}H NMR ($CDCl_3$, δ 7.24, 400 MHz): 7.46 (s, 1H_9), 7.07 (s, 1H_7), 6.68 (s, 1H_2), 6.09 (s, 1H_5), 2.54 (s, 3H_{10}), 2.24 (s, 3H_{11}), 2.10 (s, 3H_{12}). ESI–MS (positive mode, $CHCl_3$ + CH_3OH) = [M + Na]$^+$ = 257.1038 (calc.), 257.1033 (exp.).

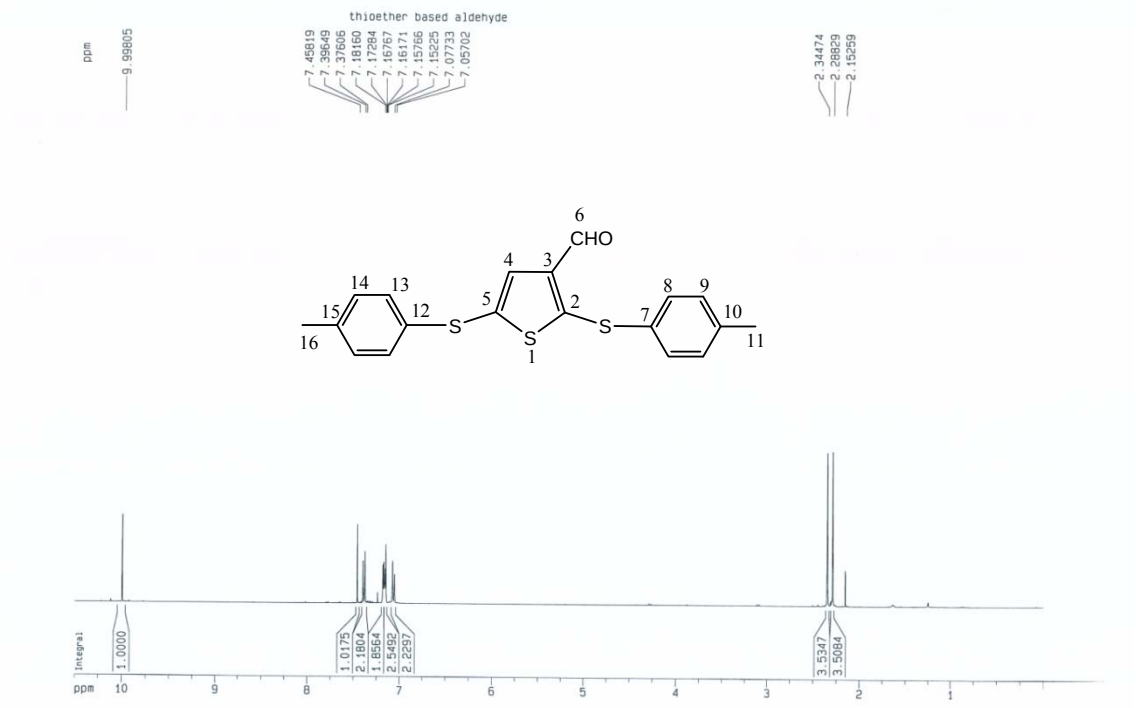

Figure S1.1: ^{1}H NMR spectrum of **1**.

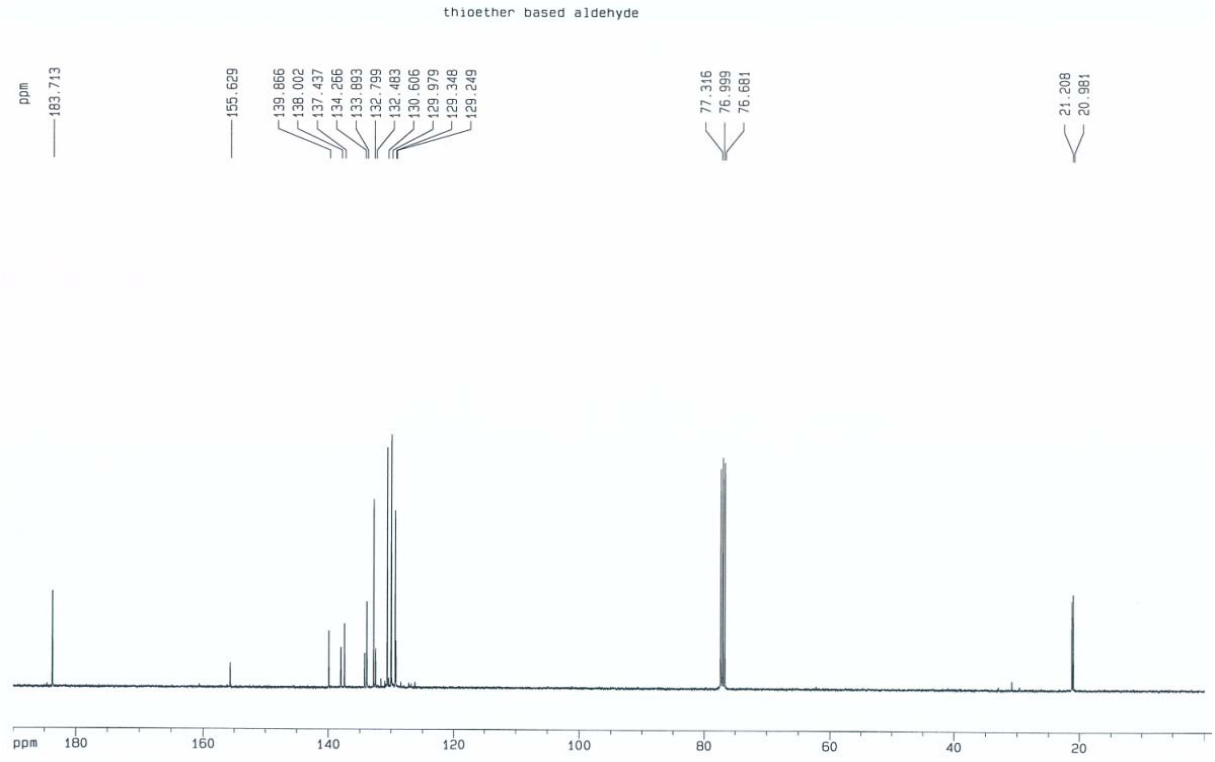

Figure S1.2: ^{13}C NMR spectrum of **1.**

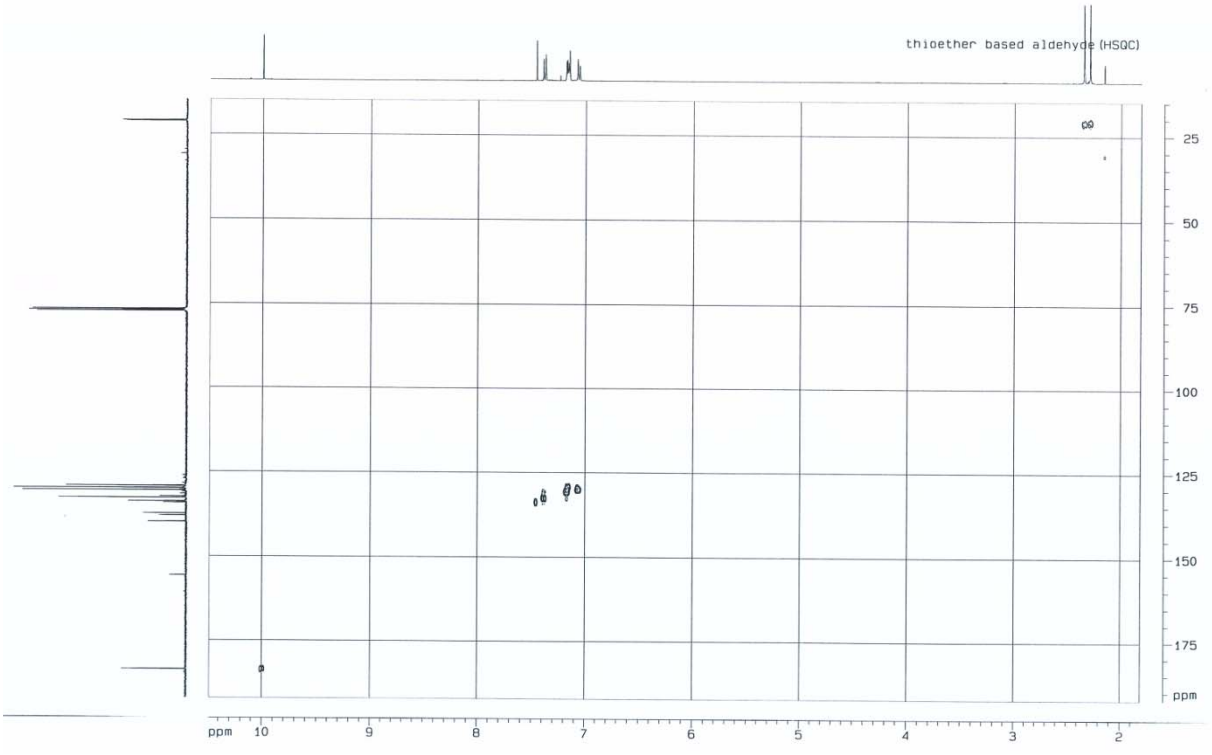

Figure S1.3: $^{1}H–^{13}C$ HSQC NMR spectrum of **1.**

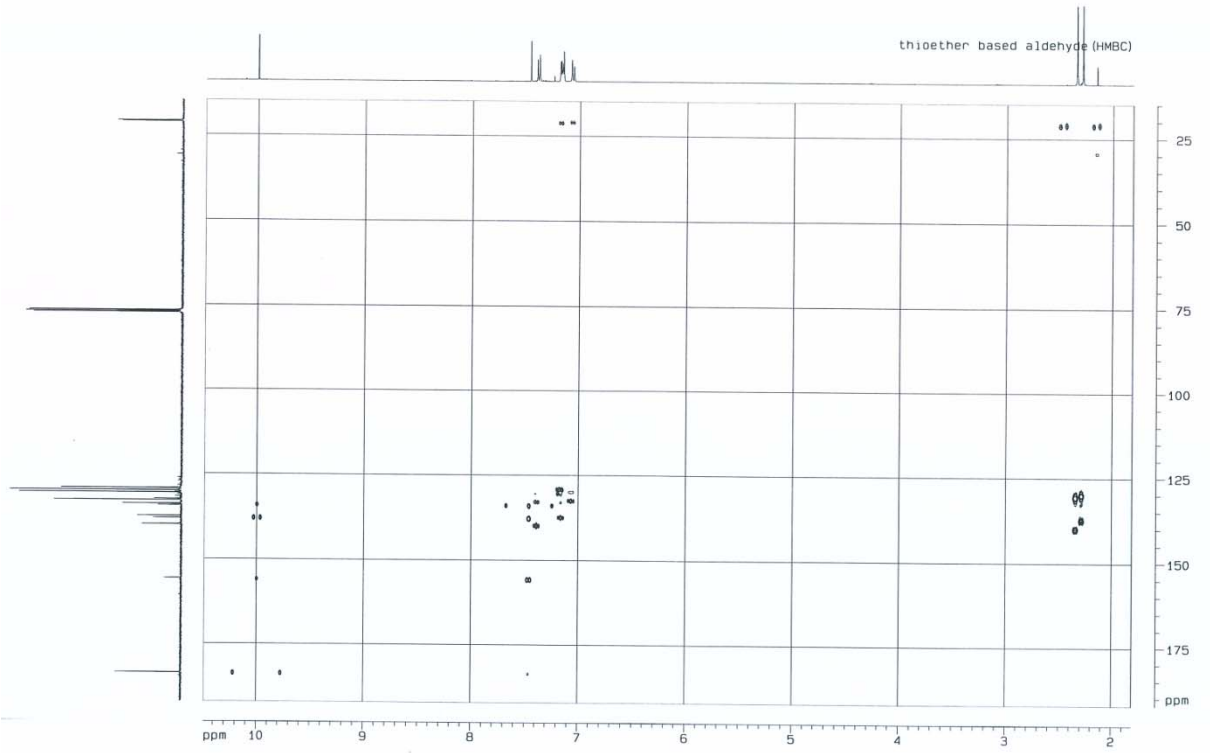

Figure S1.4: HMBC ($^{1}H–^{13}C$) NMR spectrum of **1**.

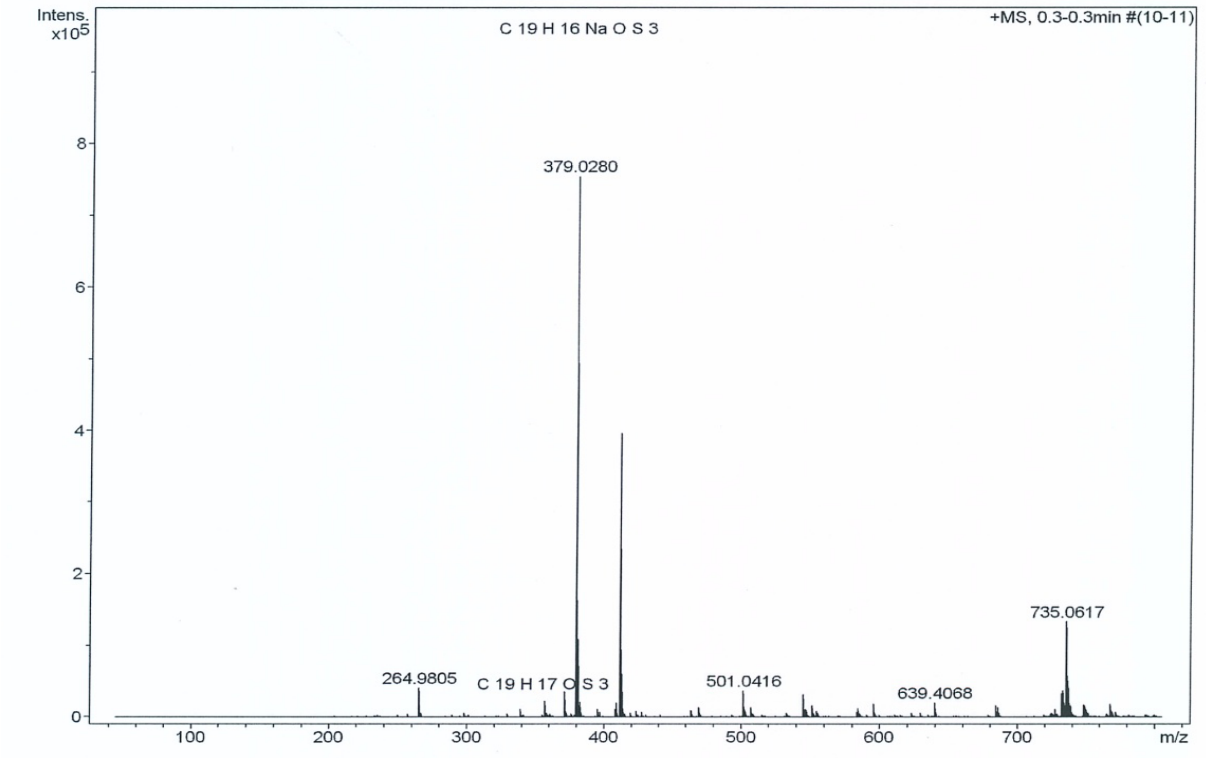

Figure S1.5: Mass spectrum of **1.**

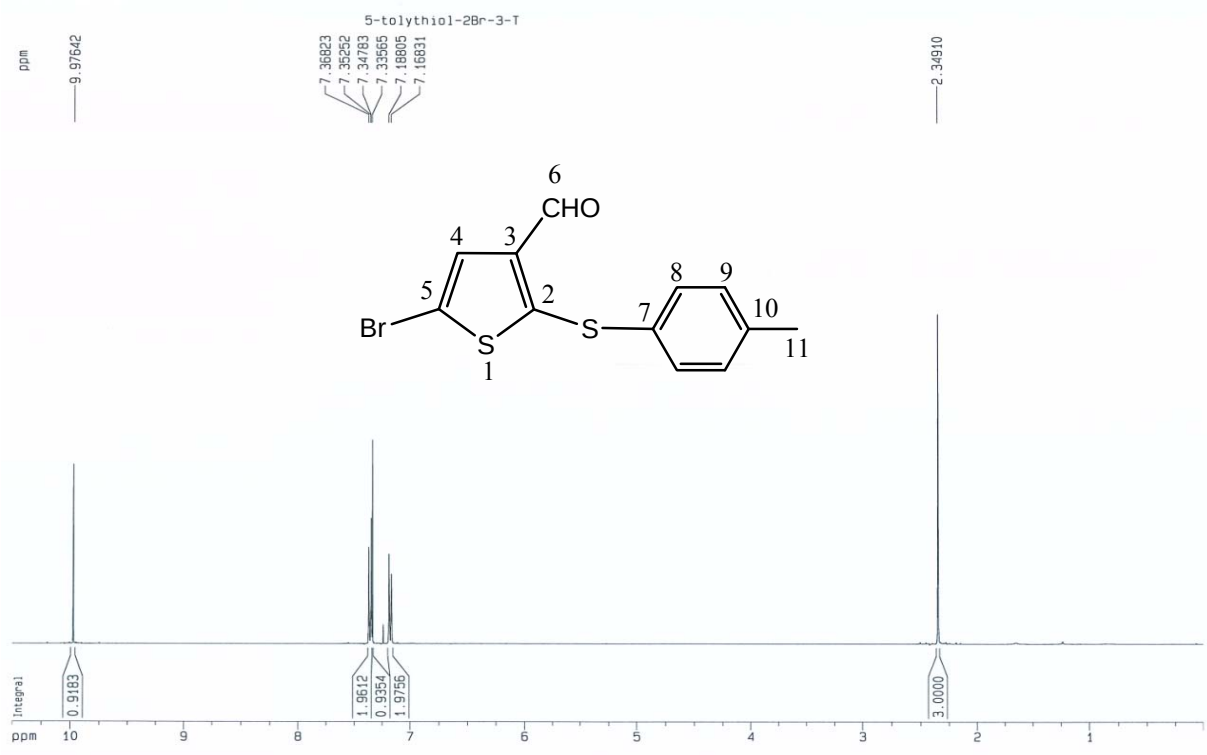

Figure S1a.1: ^{1}H NMR spectrum of **1a.**

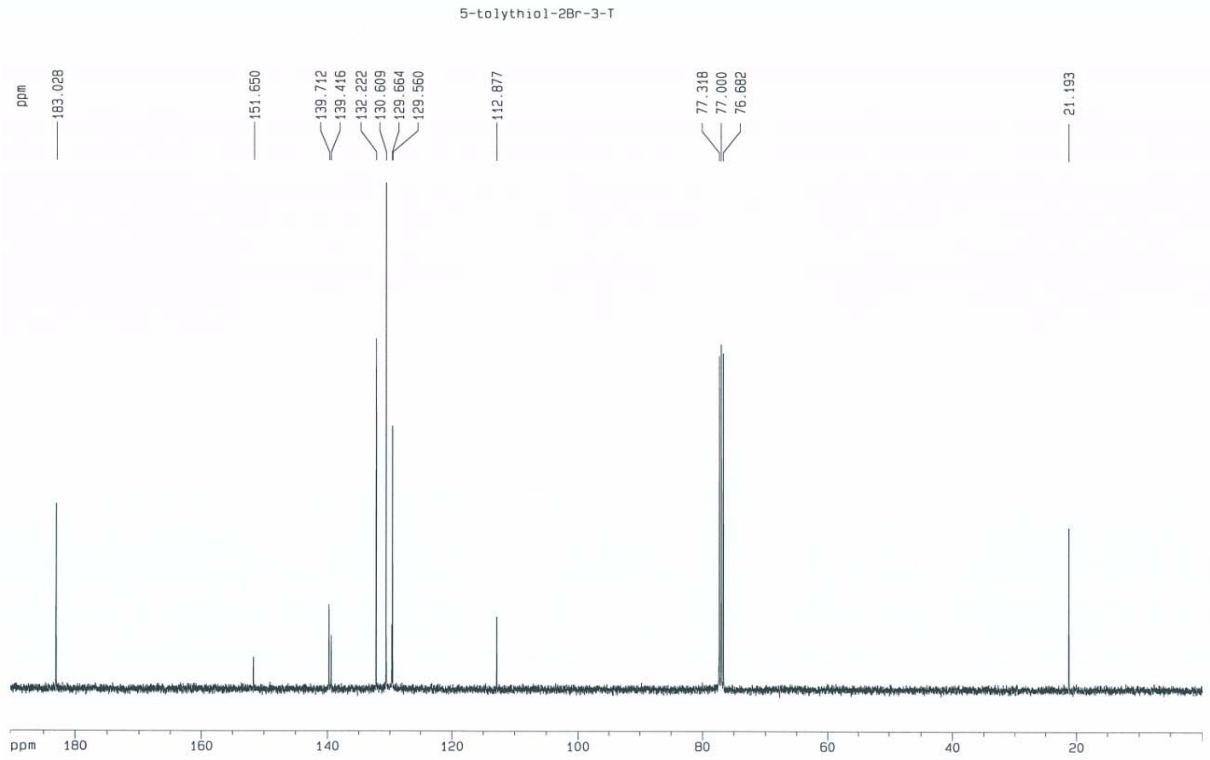

Figure S1a.2: ^{13}C NMR spectrum of **1a.**

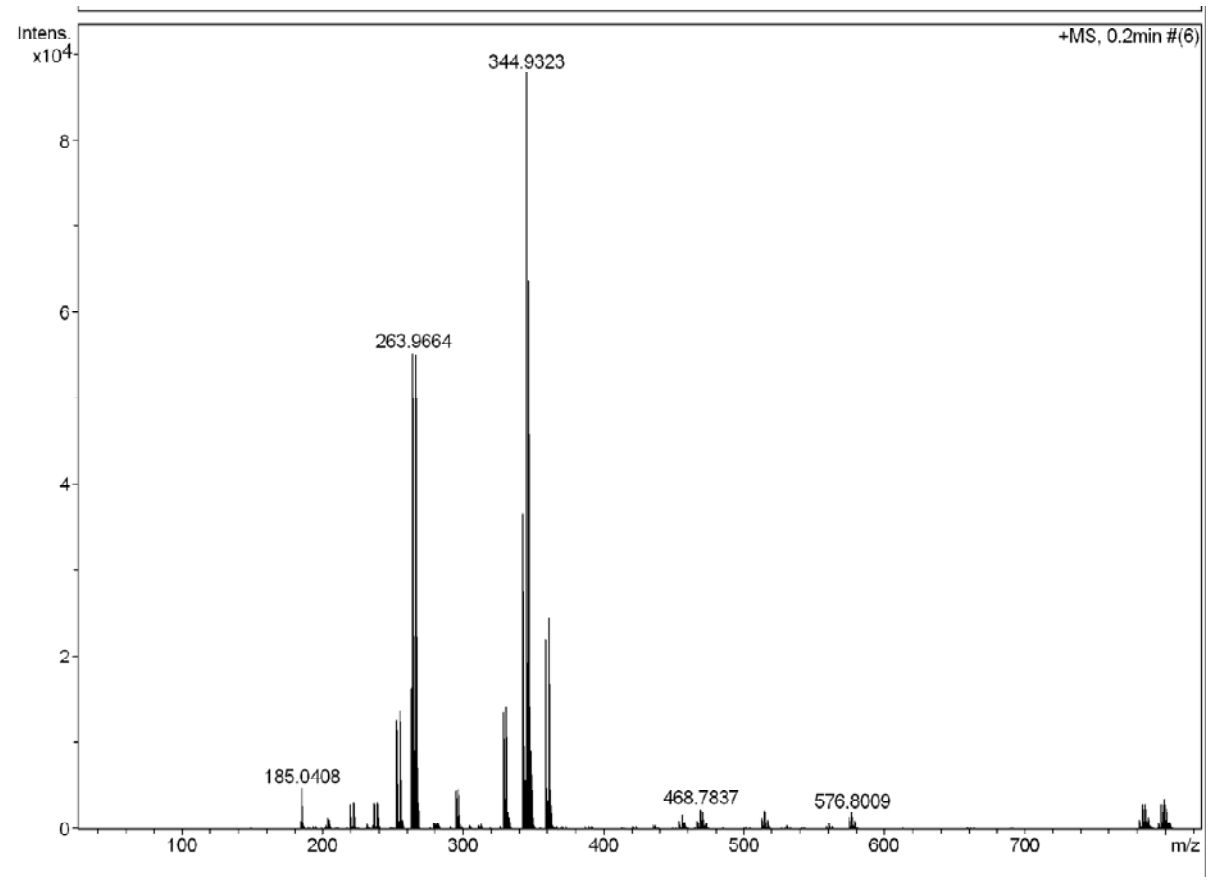

Figure S1a.3: Mass spectrum of **1a**.

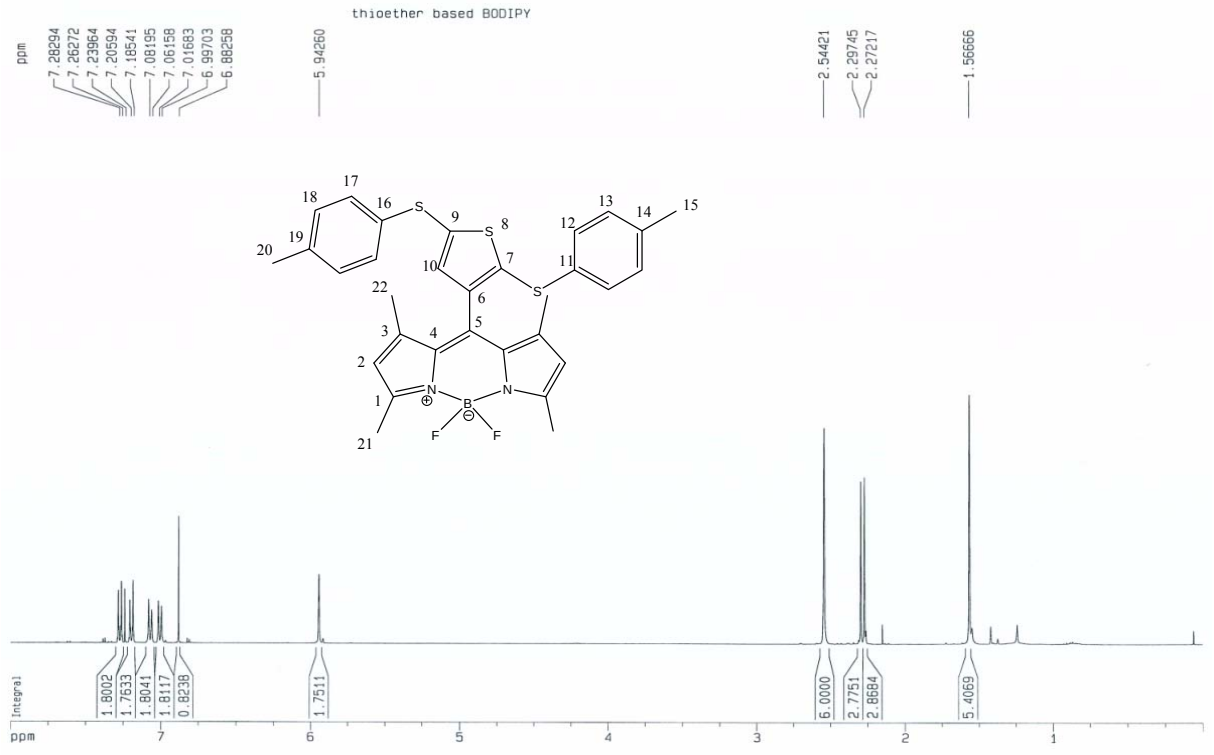

Figure S2.1: ^{1}H NMR spectrum of **2**.

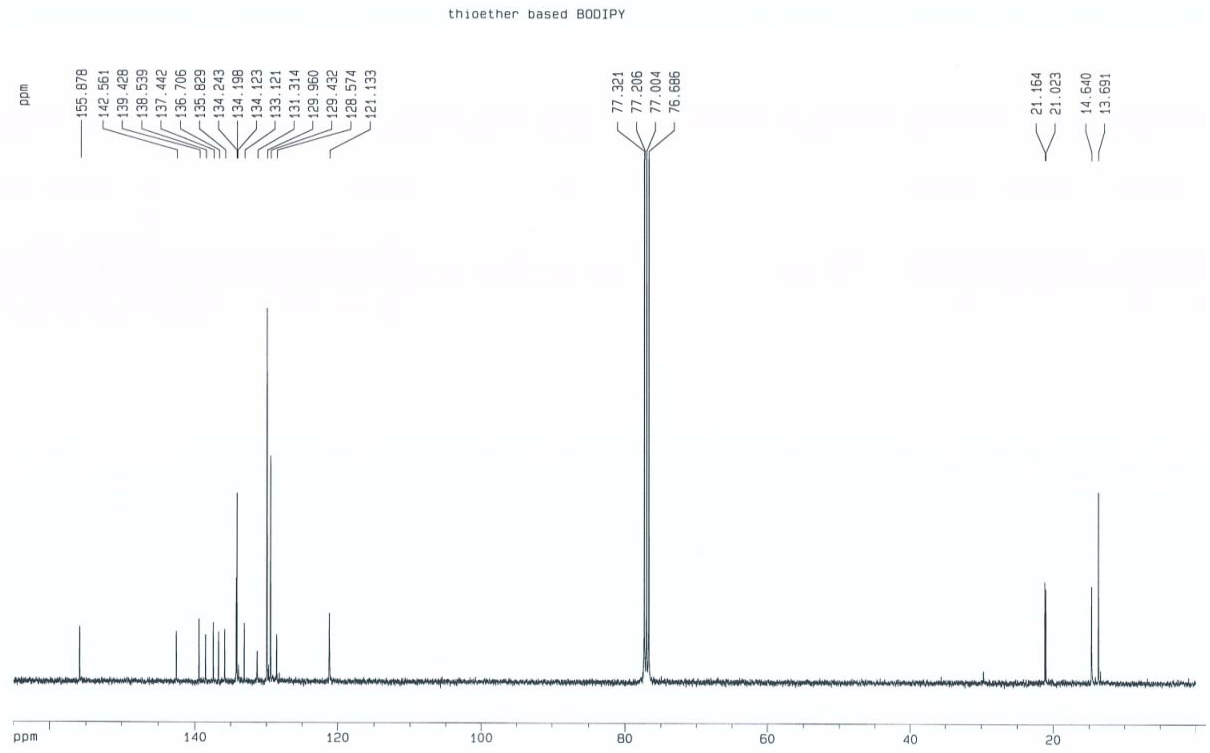

Figure S2.2: ^{13}C NMR spectrum of **2**.

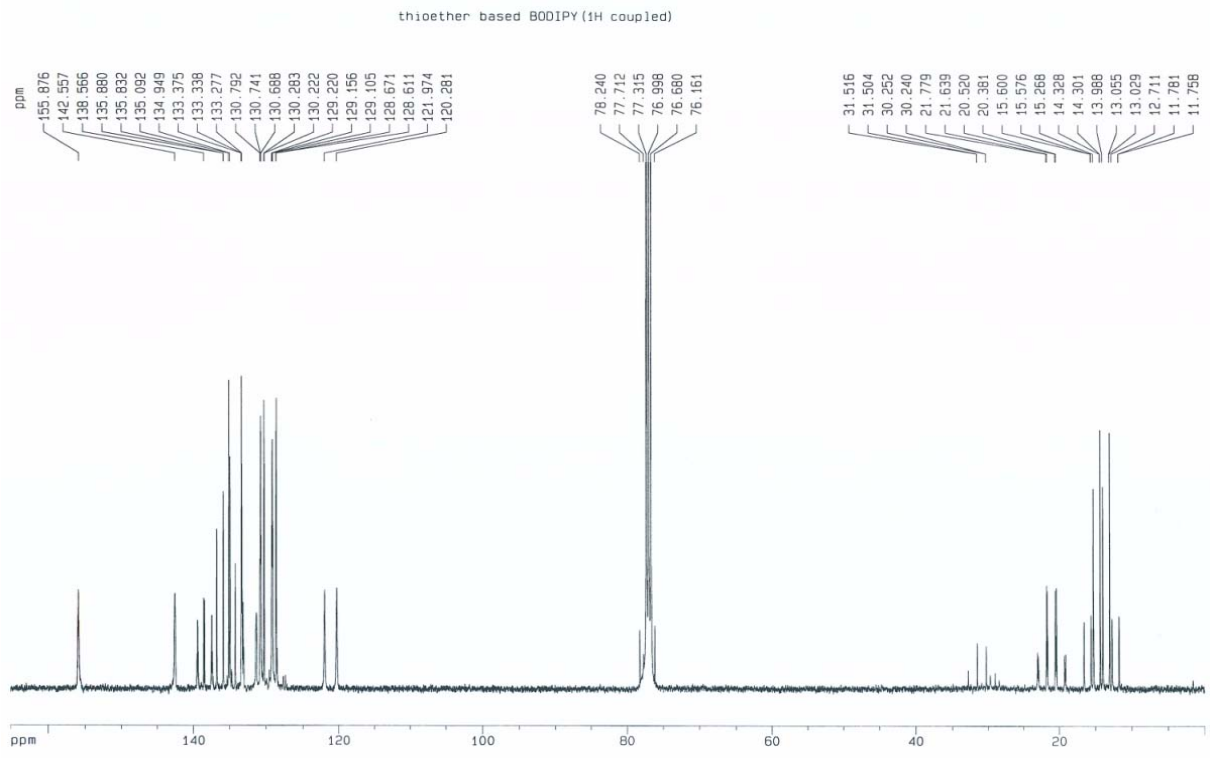

Figure S2.3: $^{13}C\{^{1}H$ coupled$\}$ NMR spectrum of **2**.

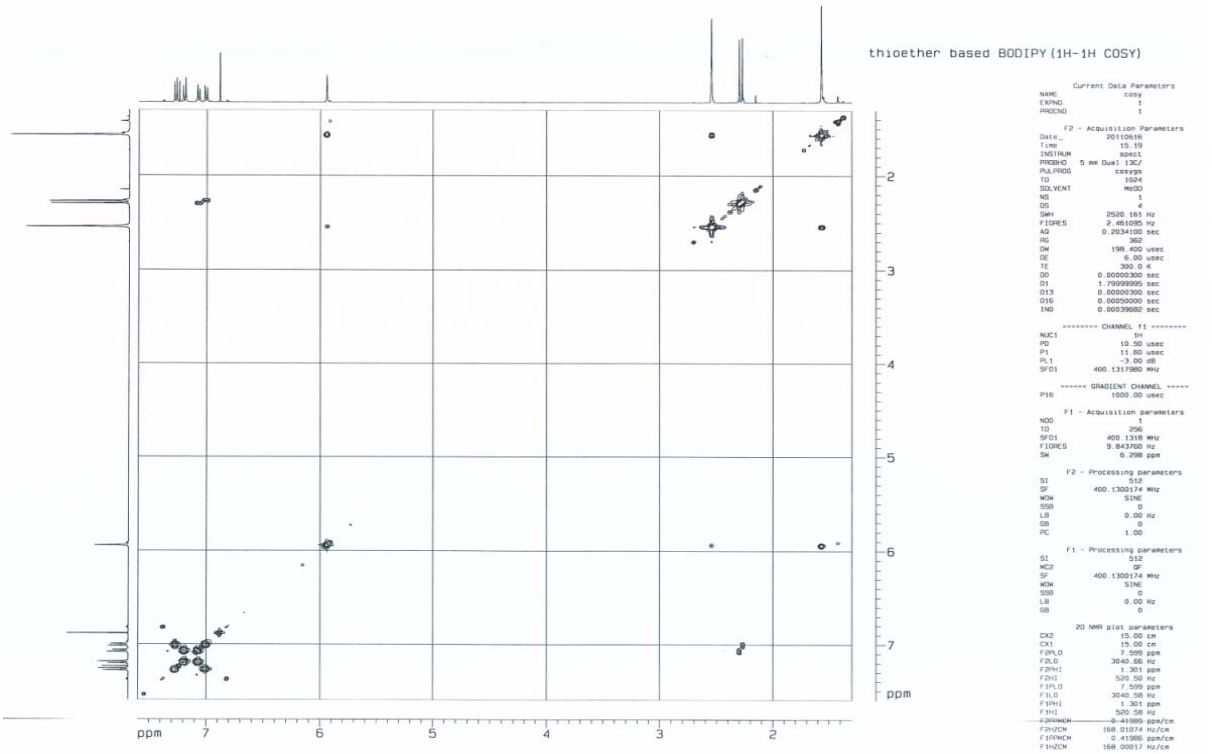

Figure S2.4: COSY(^{1}H–^{1}H) NMR spectrum of **2.**

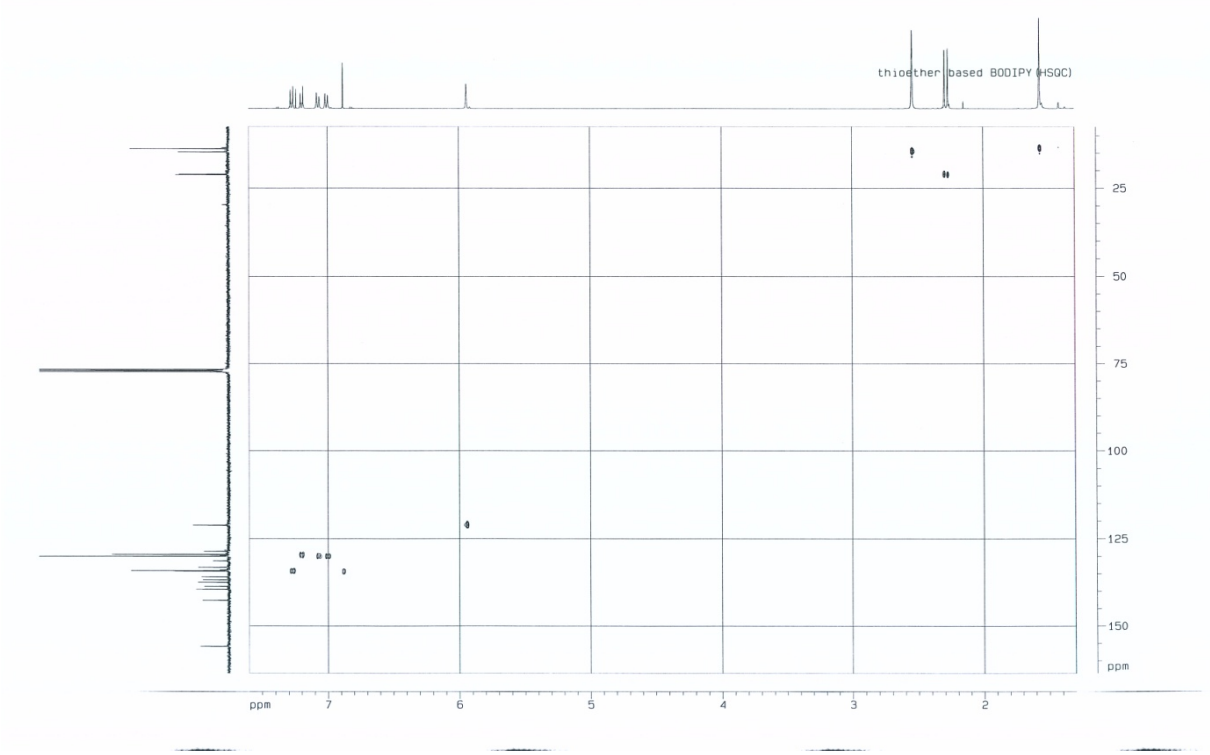

Figure S2.5: $^{1}H–^{13}C$ HSQC NMR spectrum of **2**.

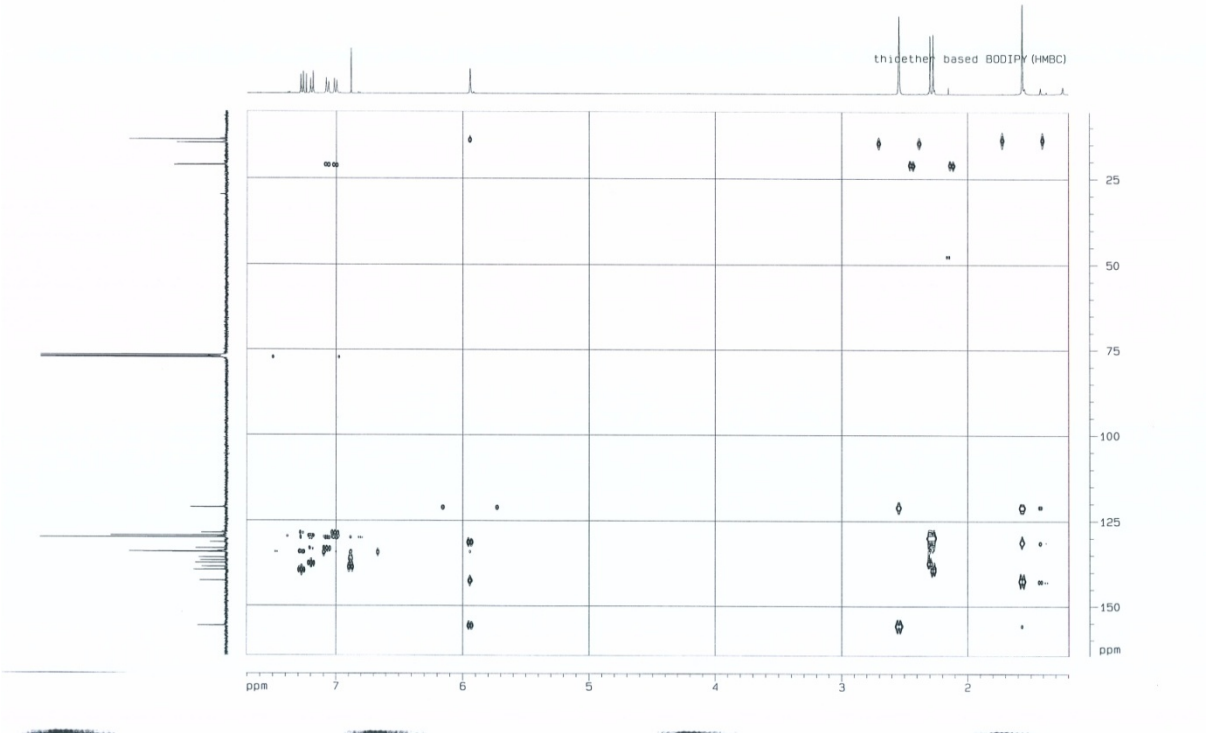

Figure S2.6: HMBC ($^{1}H–^{13}C$) NMR spectrum of **2**.

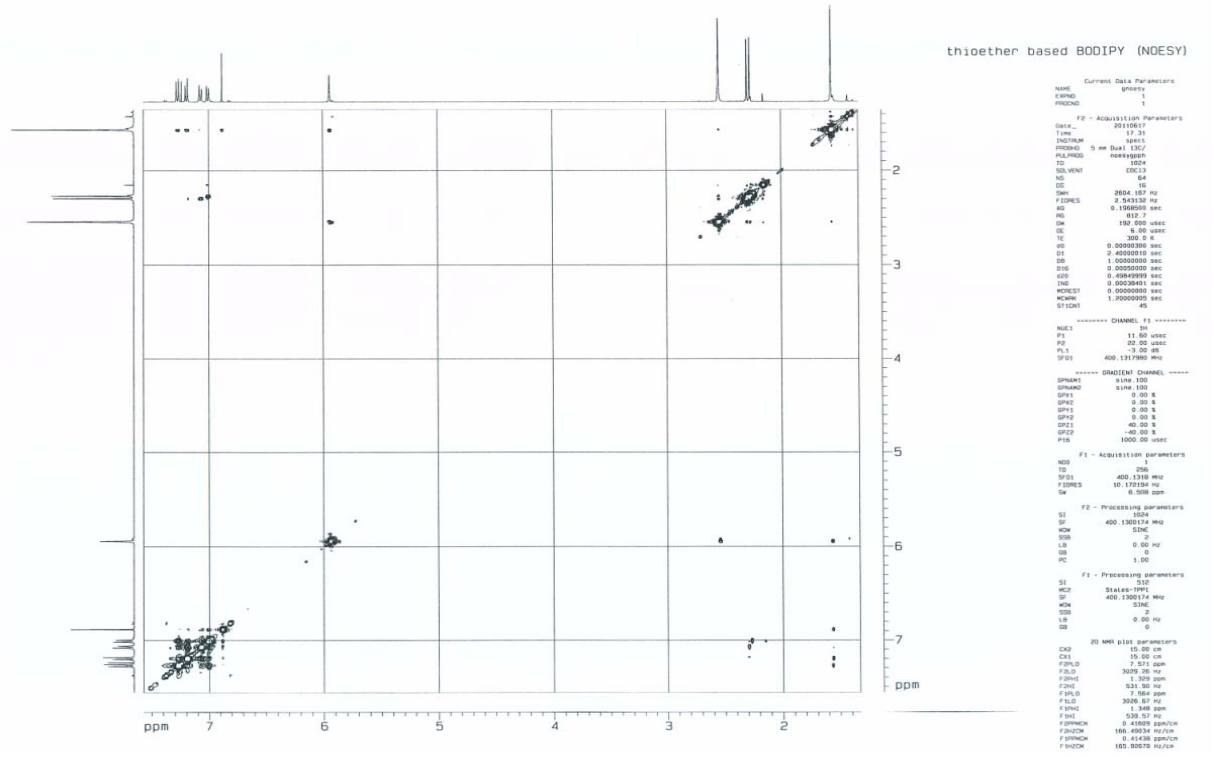

Figure S2.7: NOESY NMR spectrum of **2**.

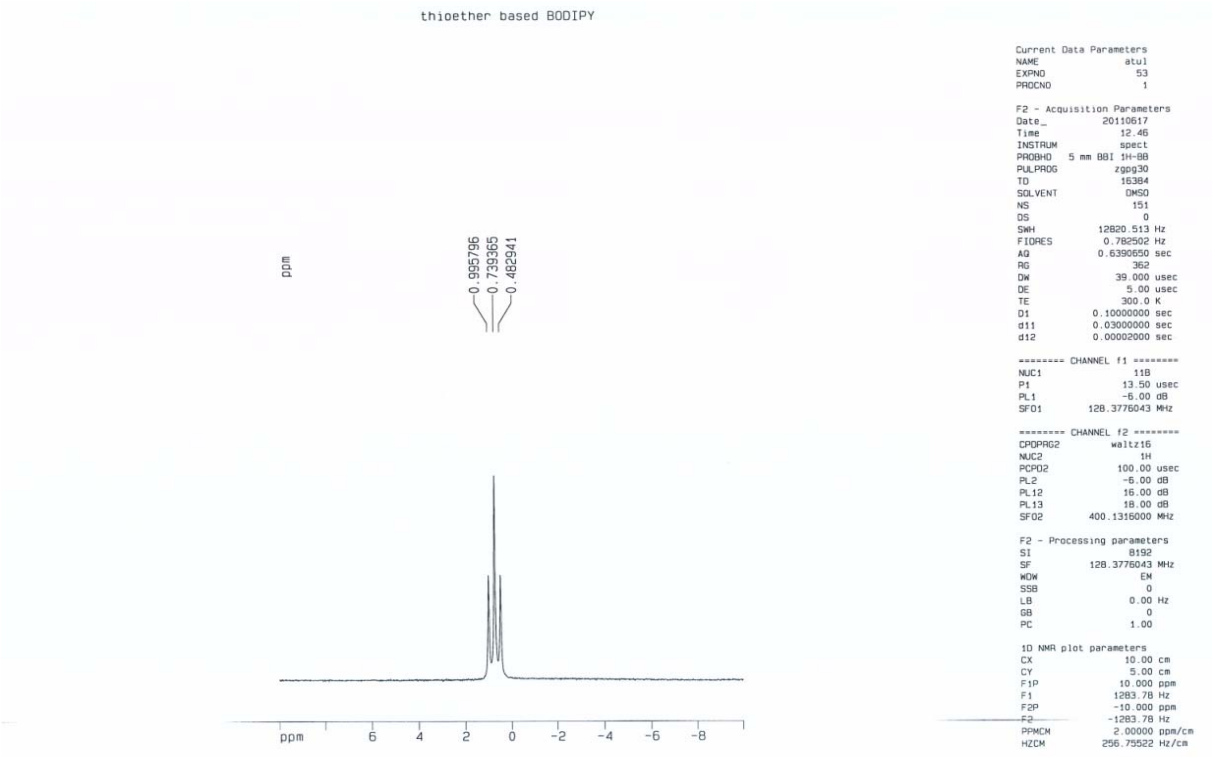

Figure S2.8: ^{11}B NMR spectrum of **2.**

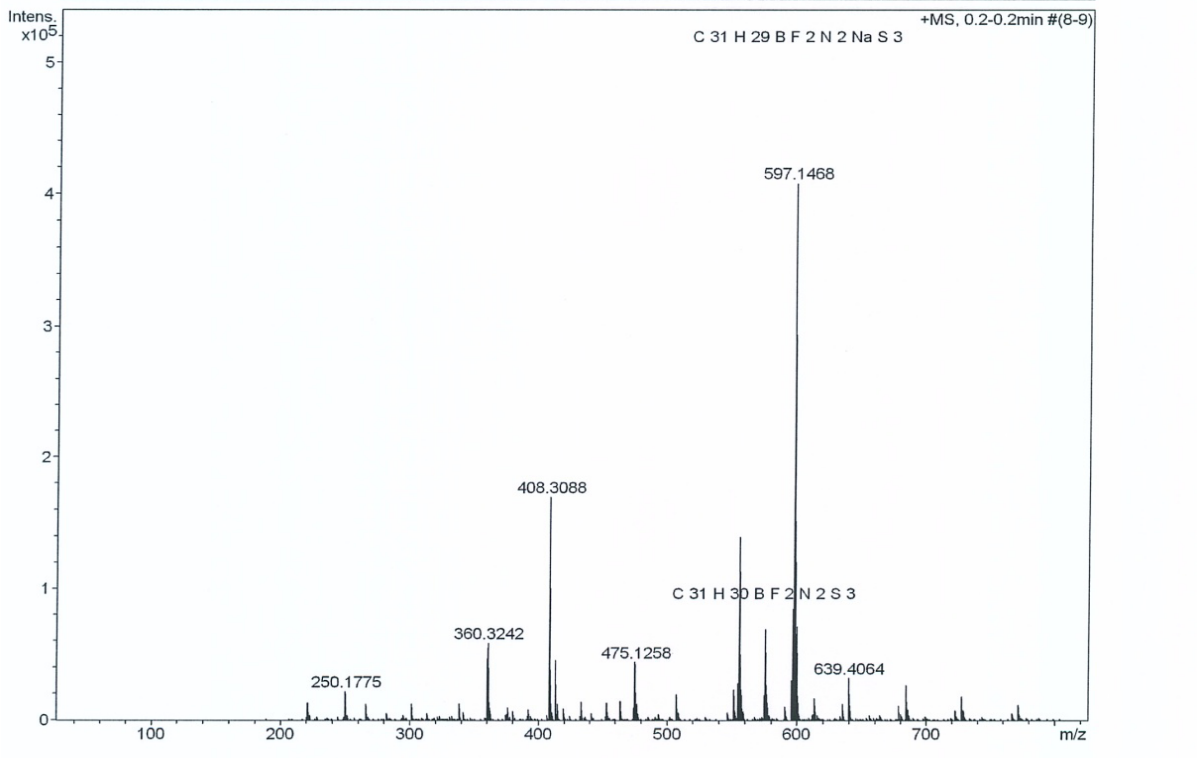

Figure S2.9: Mass spectrum of **2**.

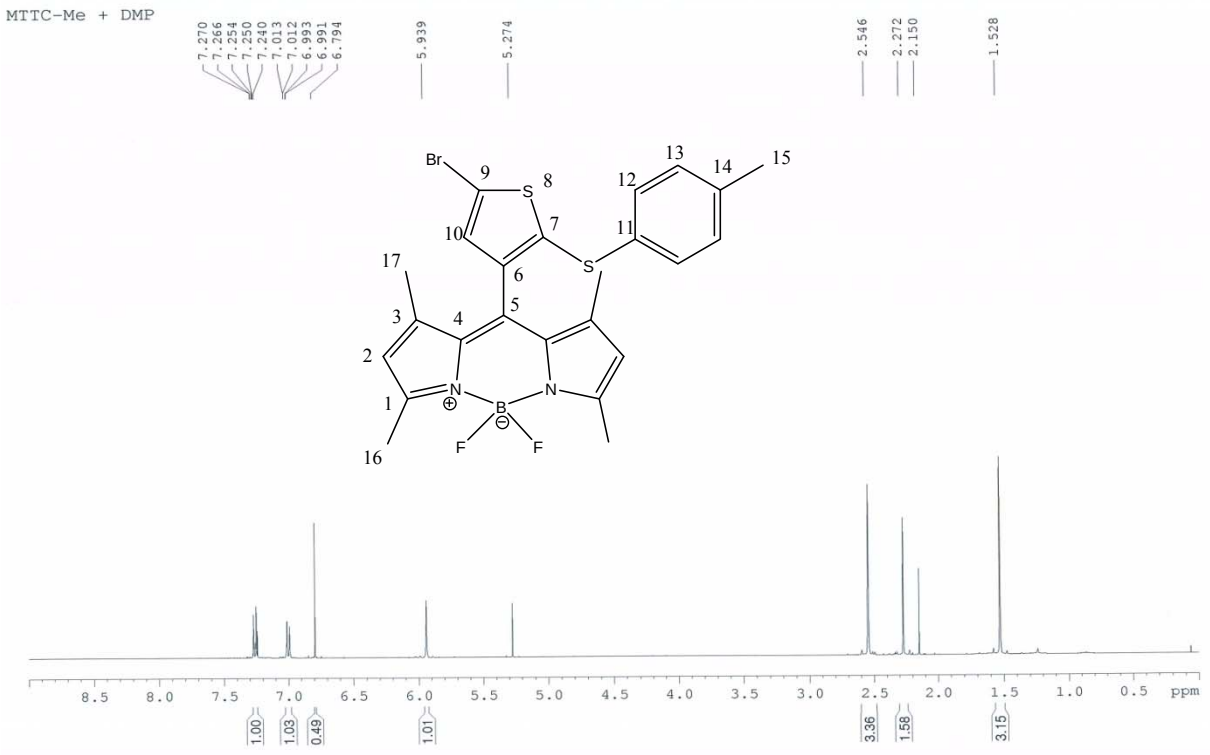

Figure S2a.1: ^{1}H NMR spectrum of **2a**.

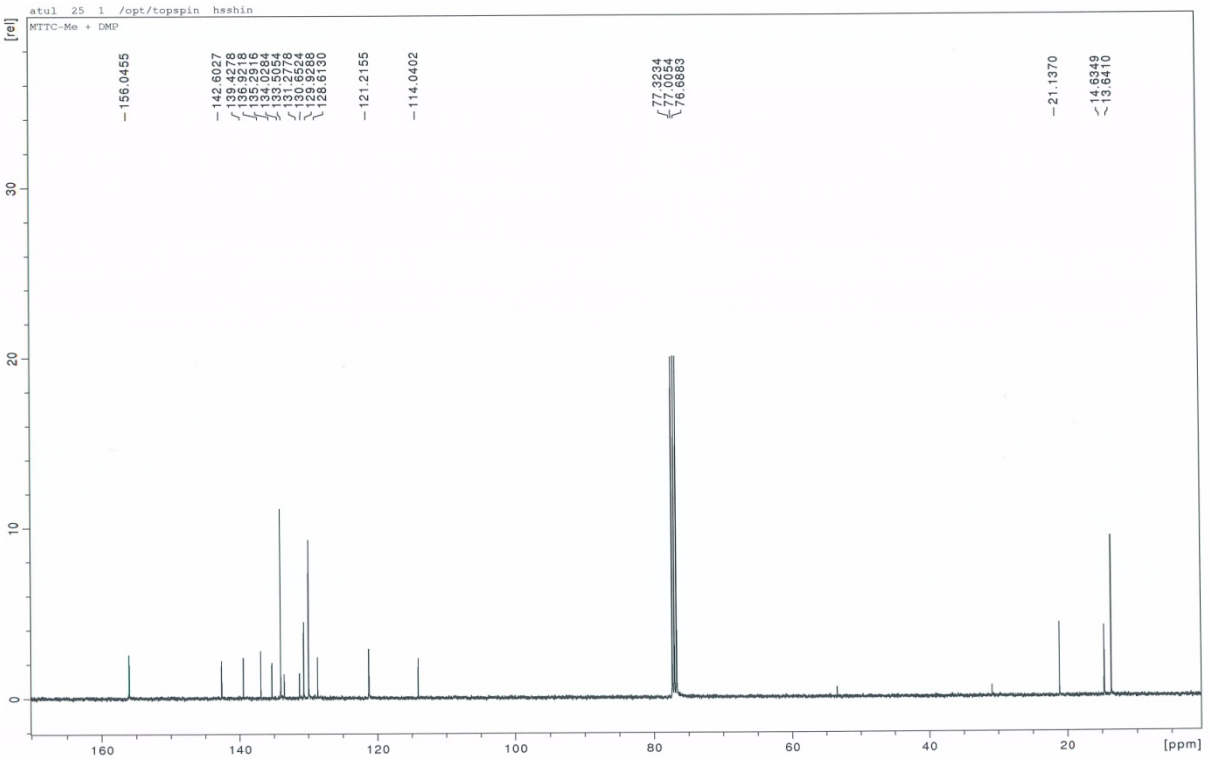

Figure S2a.2: ^{13}C NMR spectrum of **2a**.

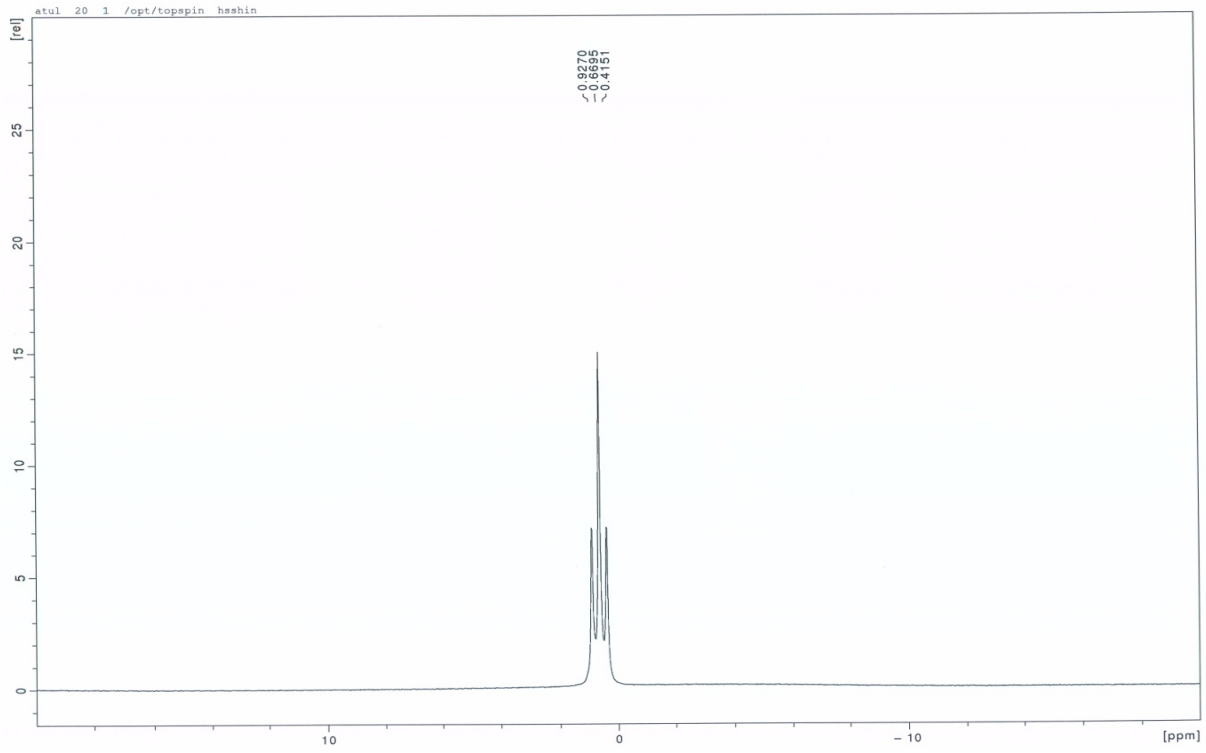

Figure S2a.3: ^{11}B NMR spectrum of **2a.**

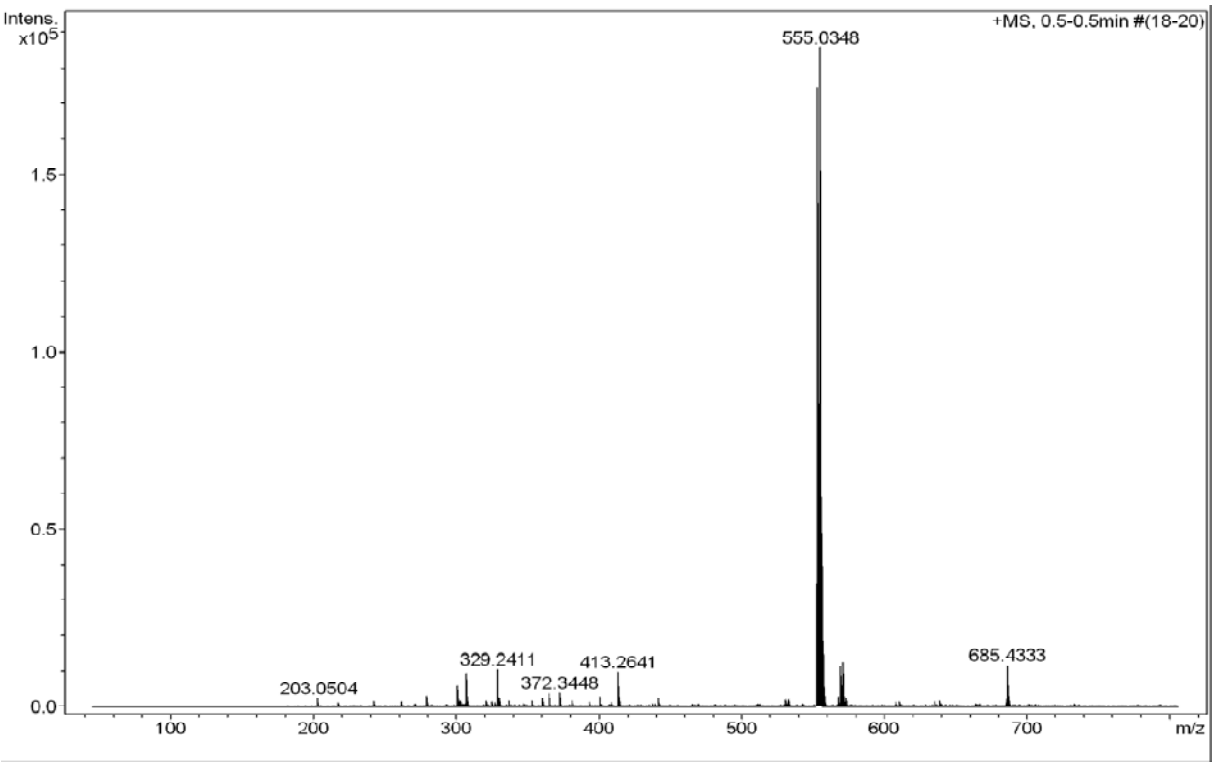

Figure S2a.4: Mass spectrum of **2a**.

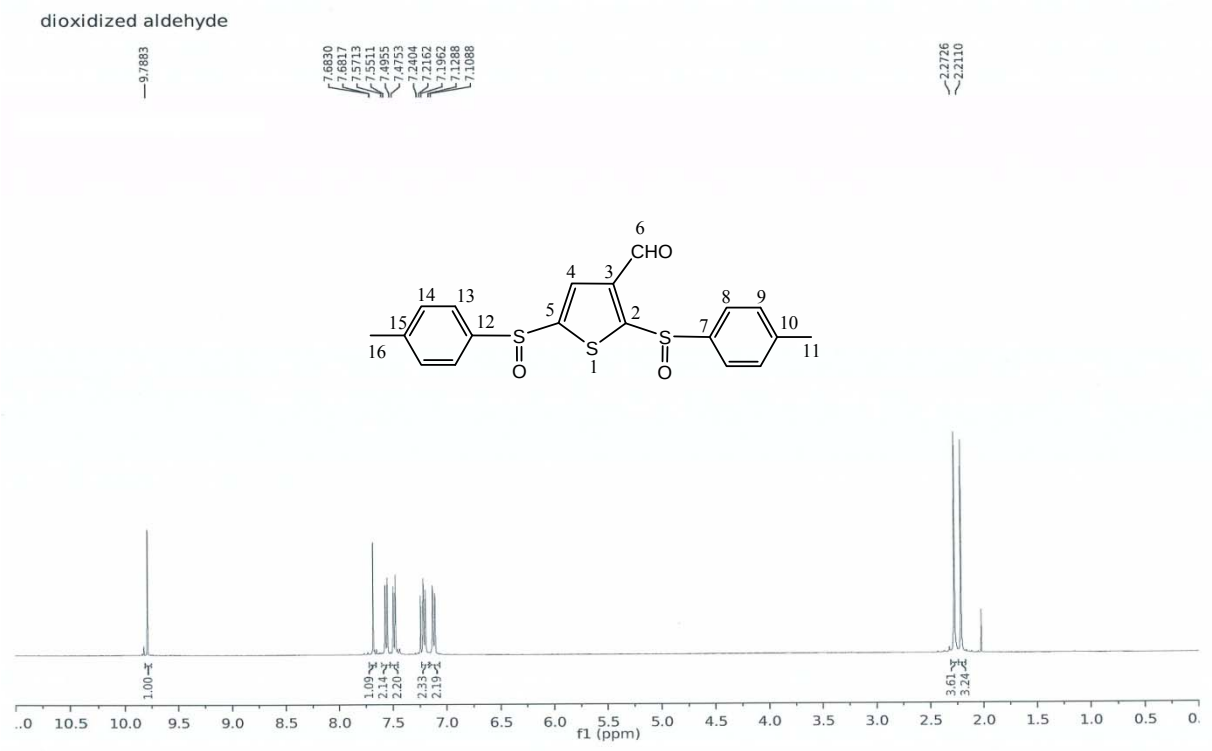

Figure S3.1: ^{1}H NMR spectrum of **3**.

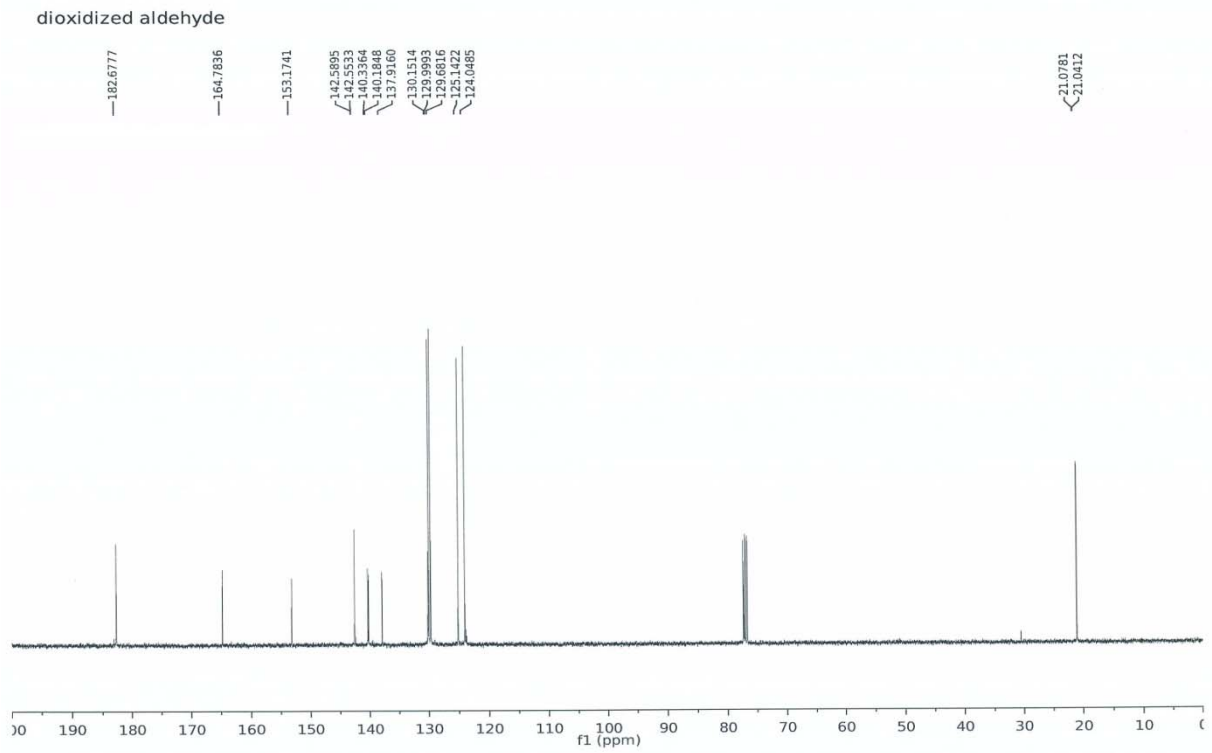

Figure S3.2: ^{13}C NMR spectrum of **3**.

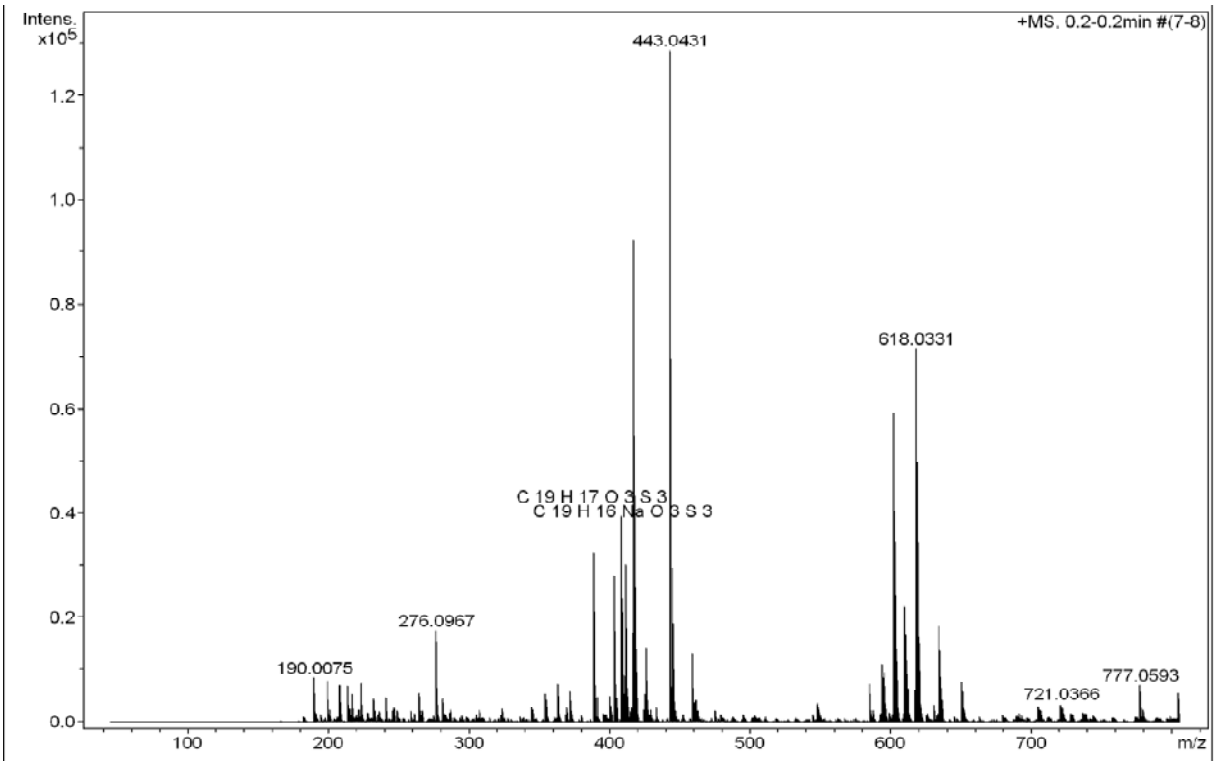

Figure S3.3: Mass spectrum of **3**.

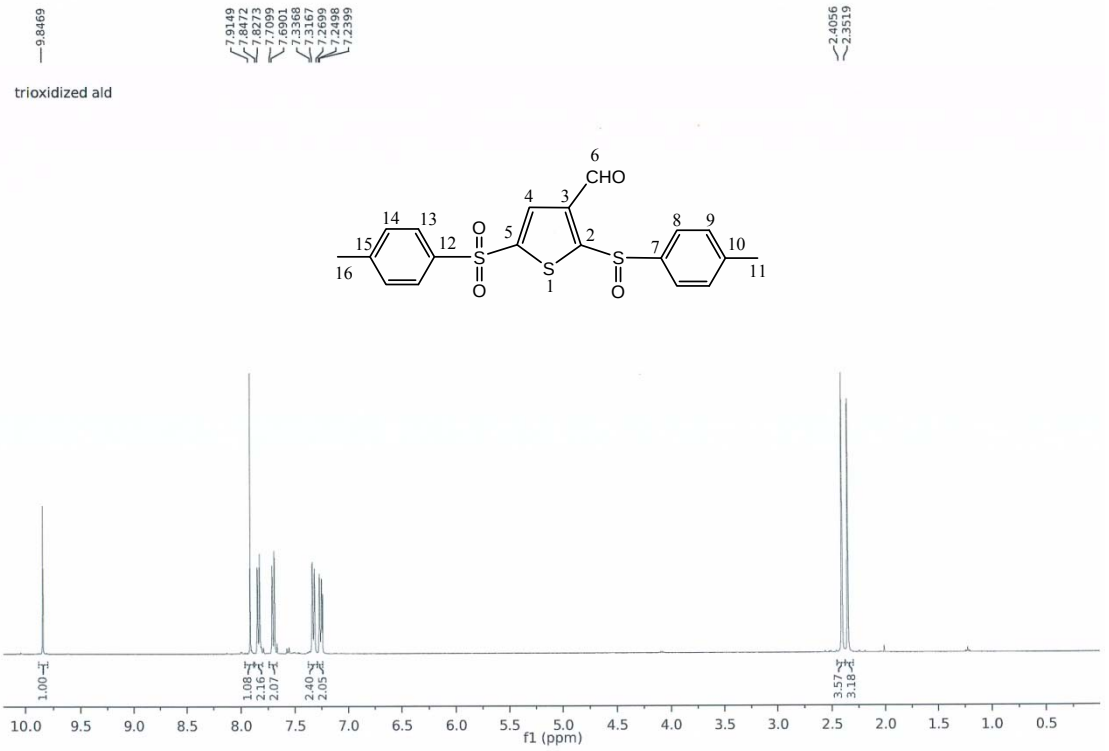

Figure S4.1: ^{1}H NMR spectrum of **4**.

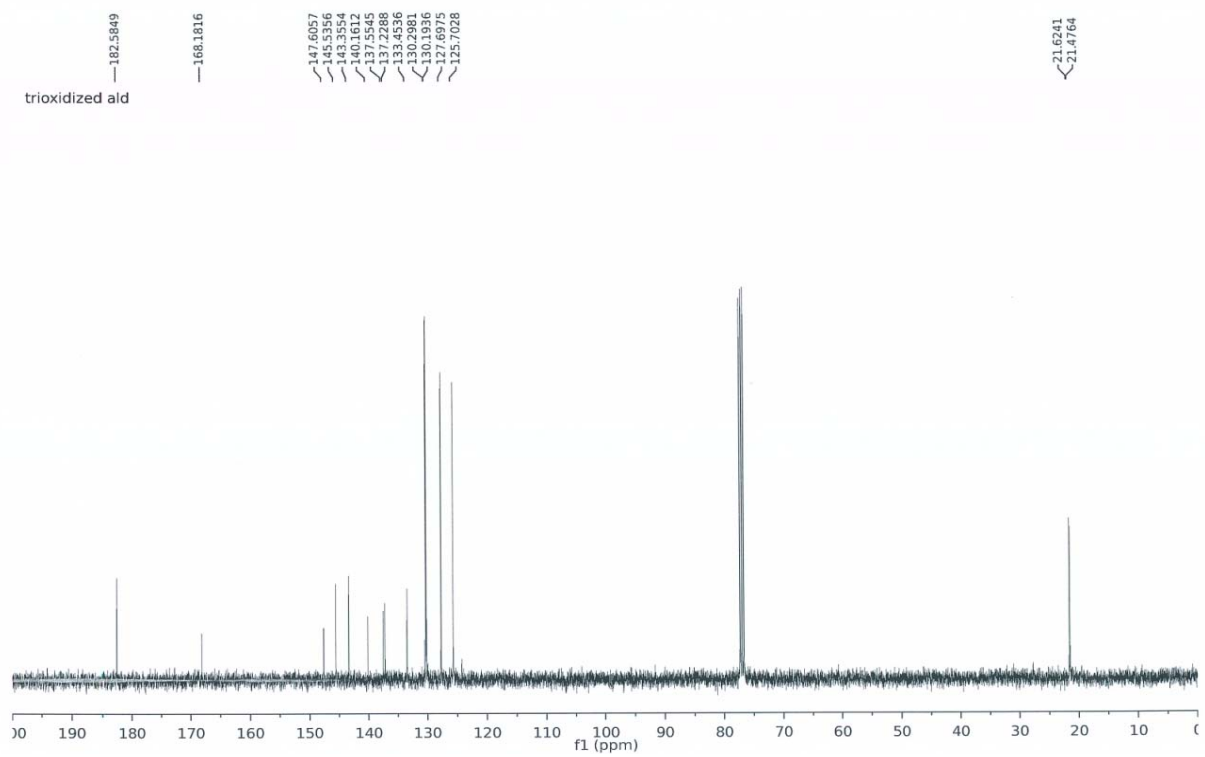

Figure S4.2: ^{1}H NMR spectrum of **4**.

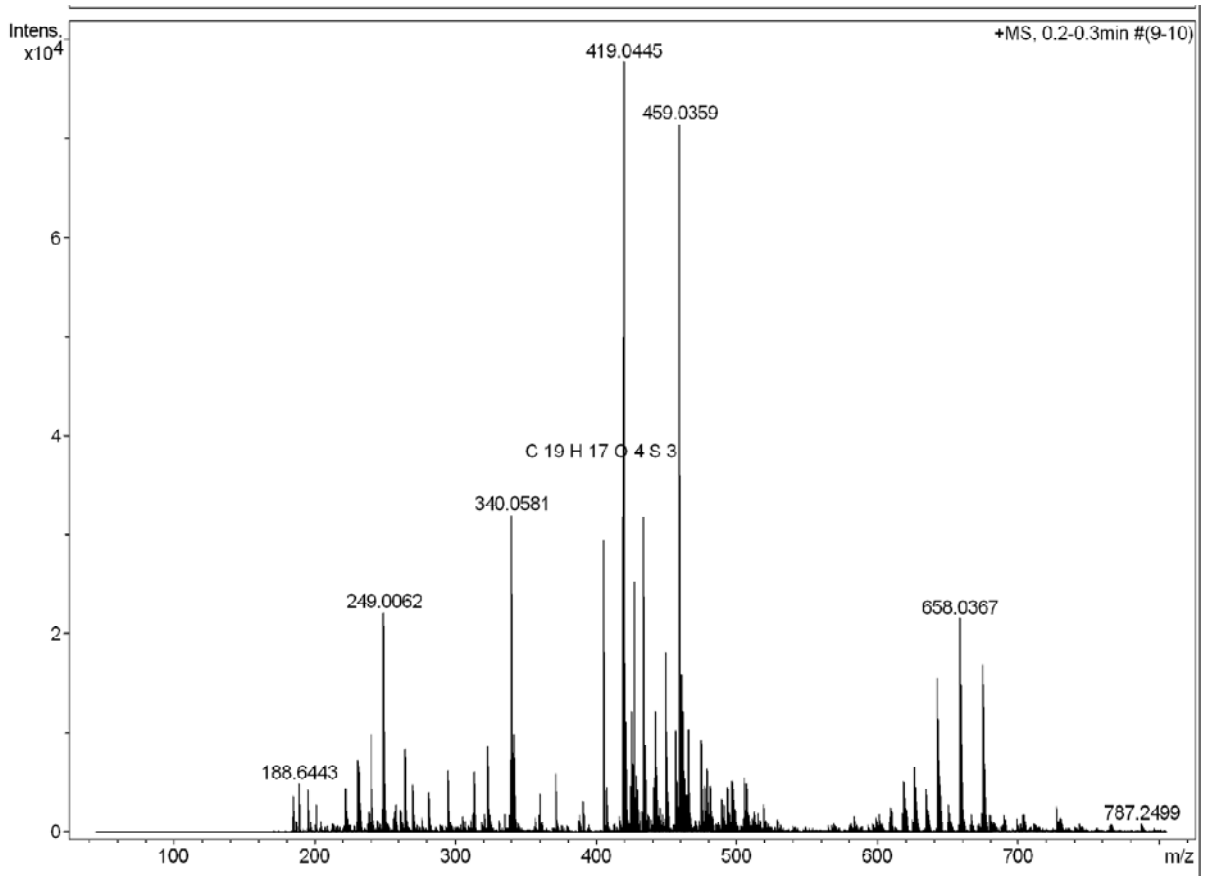

Figure S4.3: Mass spectrum of **4.**

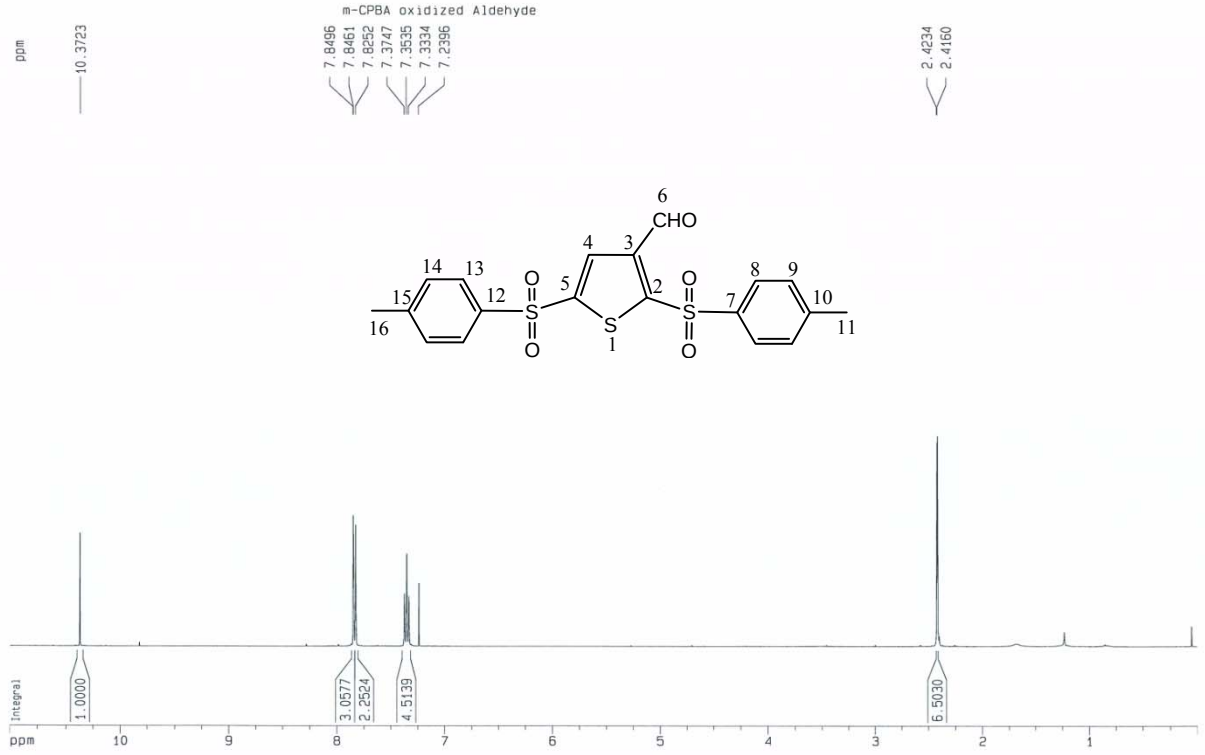

Figure S5.1: ^{1}H NMR spectrum of **5.**

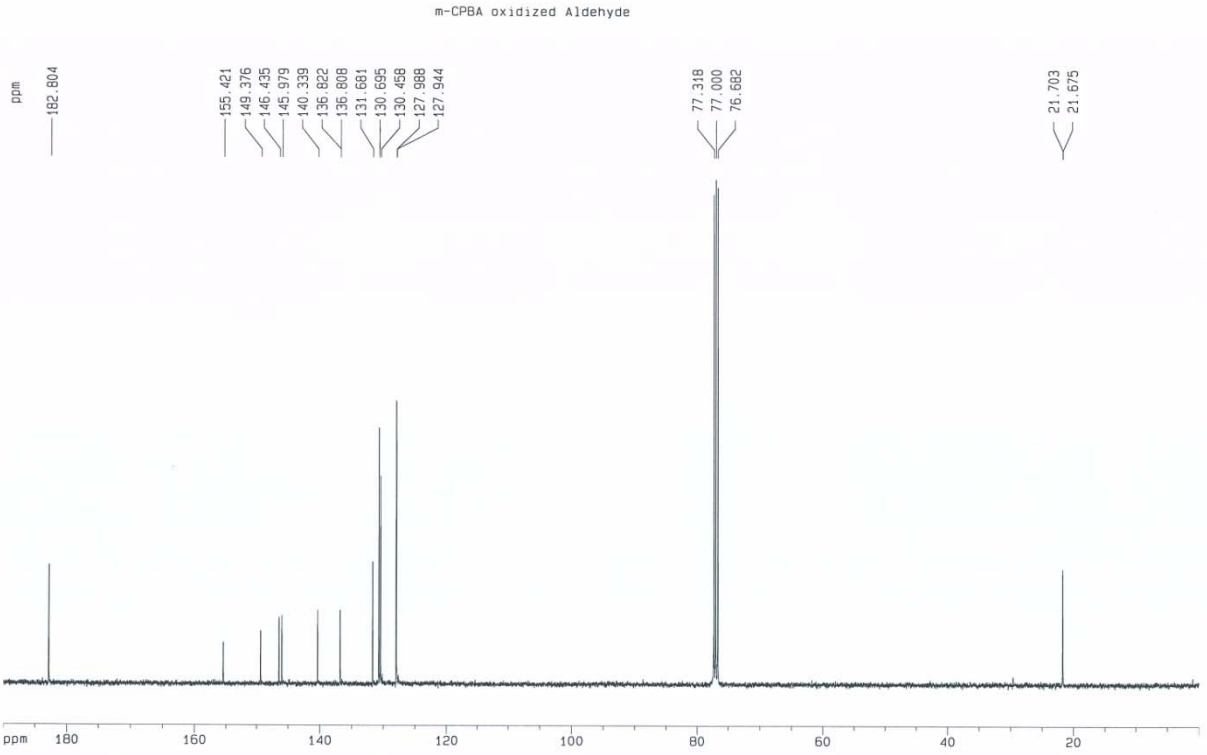

Figure S5.2: ^{13}C NMR spectrum of **5**.

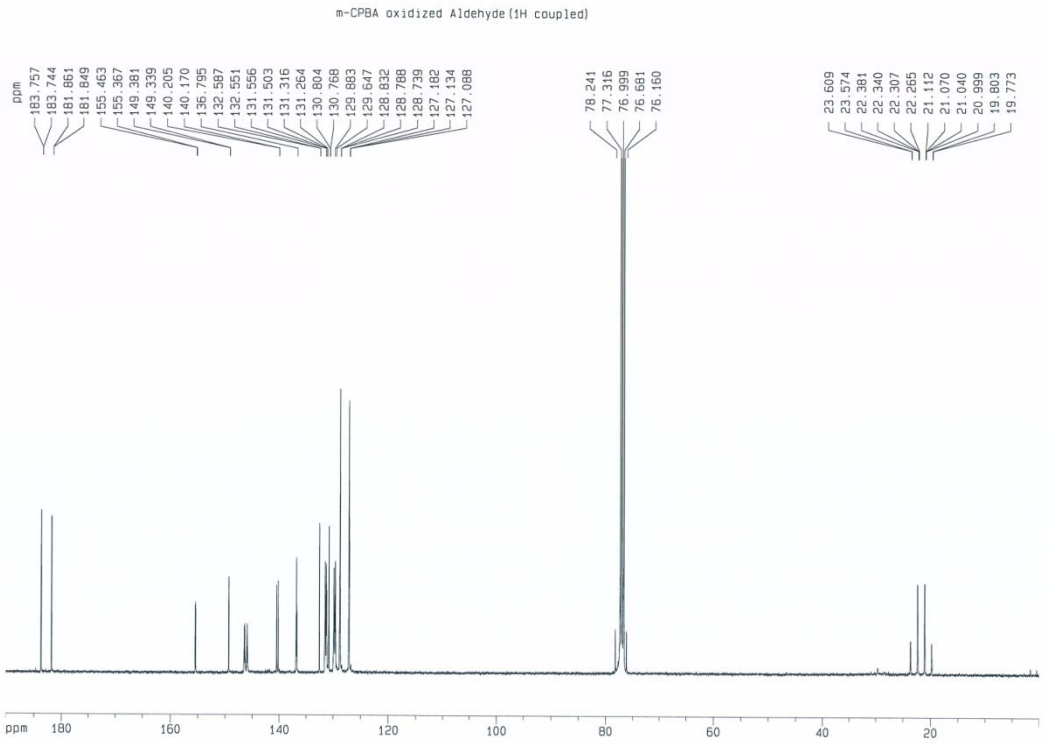

Figure S5.3: $^{13}C\{^{1}H$ coupled$\}$ NMR spectrum of **5**.

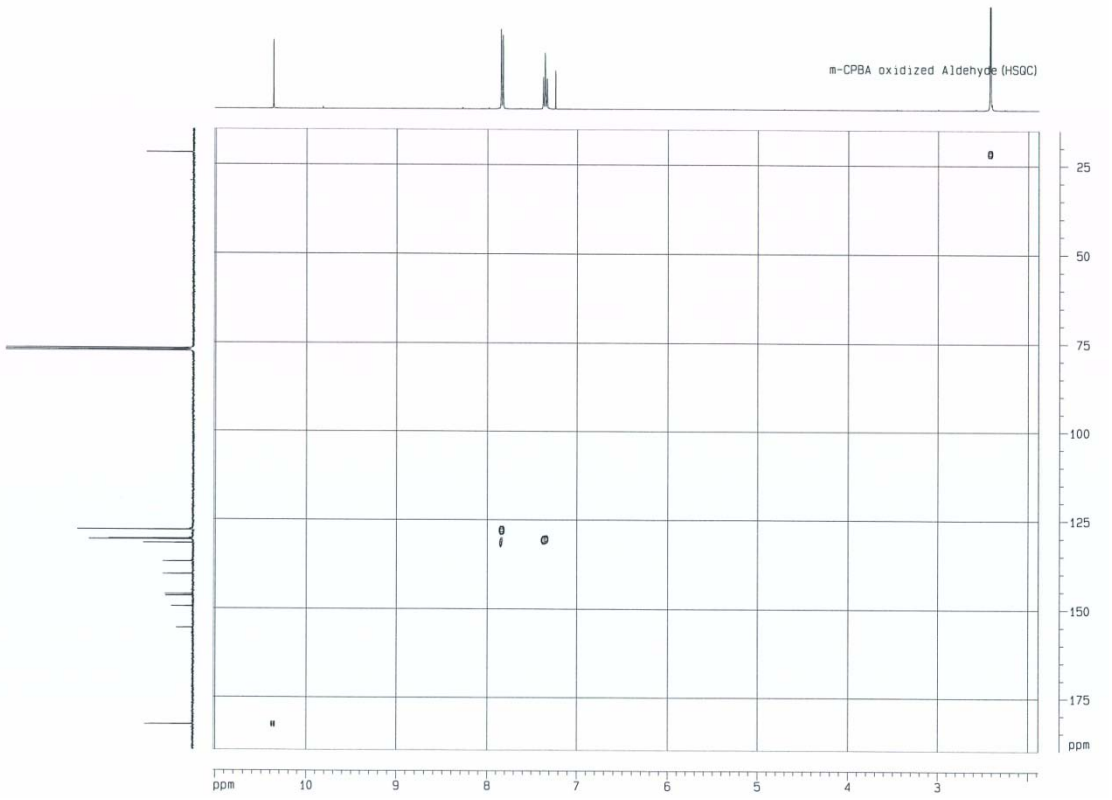

Figure S5.4: $^{1}H–^{13}C$ HSQC NMR spectrum of **5**.

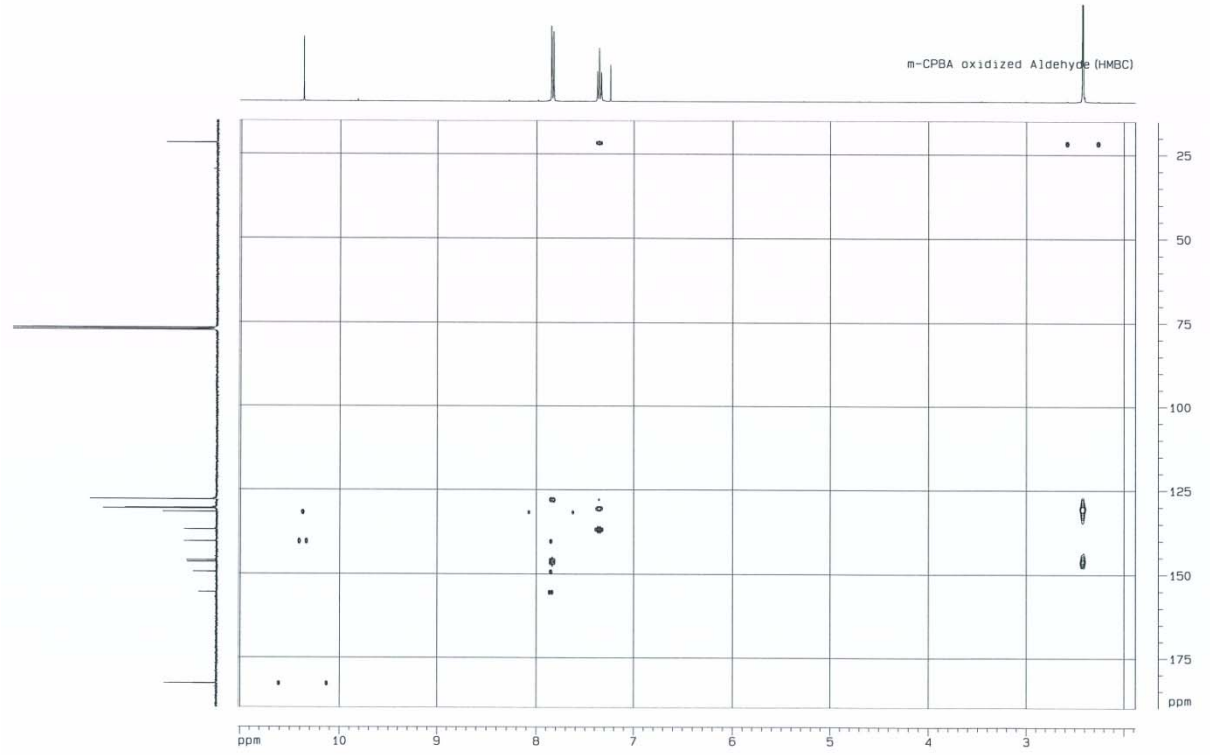

Figure S5.5: HMBC (^{1}H–^{13}C) NMR spectrum of **5**.

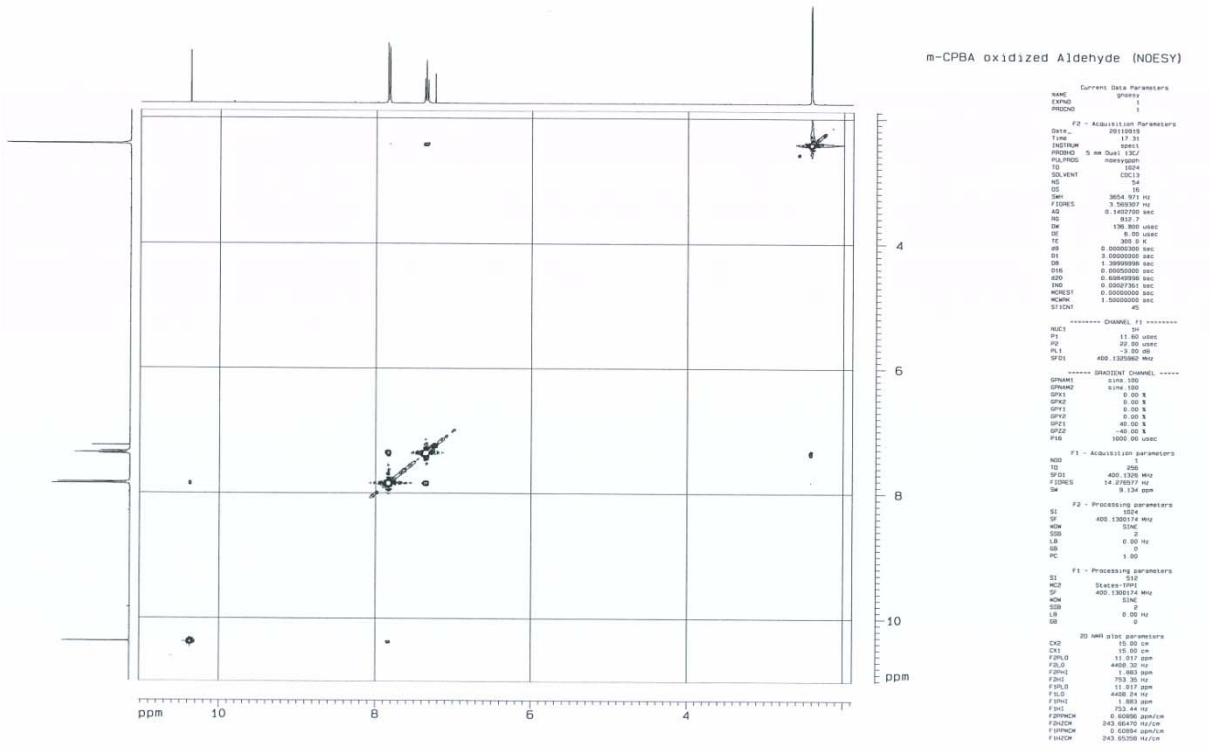

Figure S5.6: NOESY NMR spectrum of **5**.

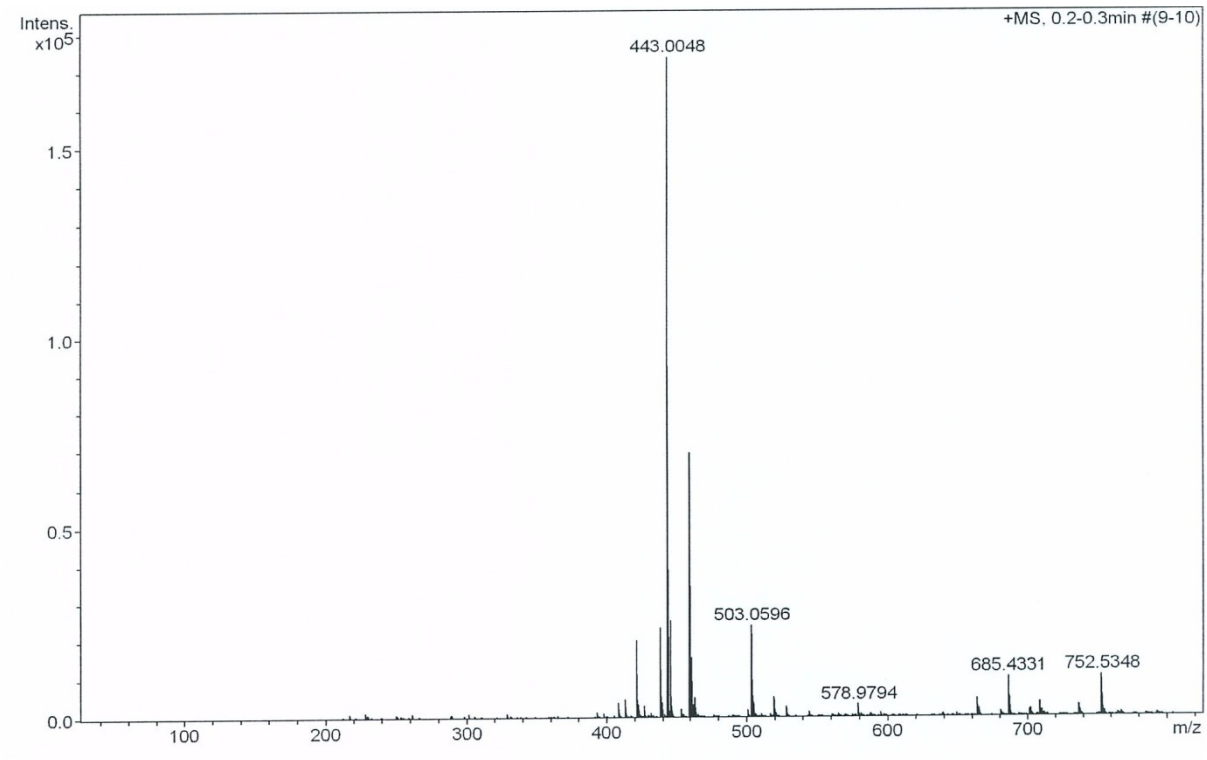

Figure S5.7: Mass spectrum of **5**.

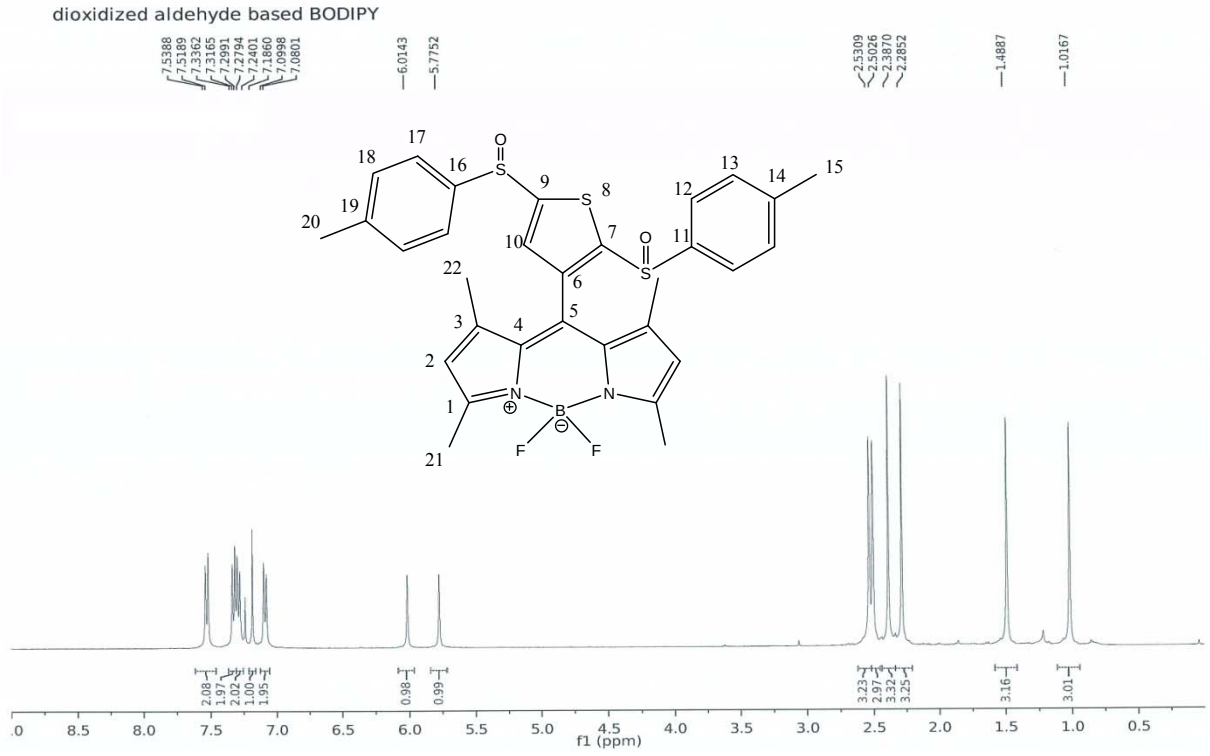

Figure S6.1: ^{1}H NMR spectrum of **6**.

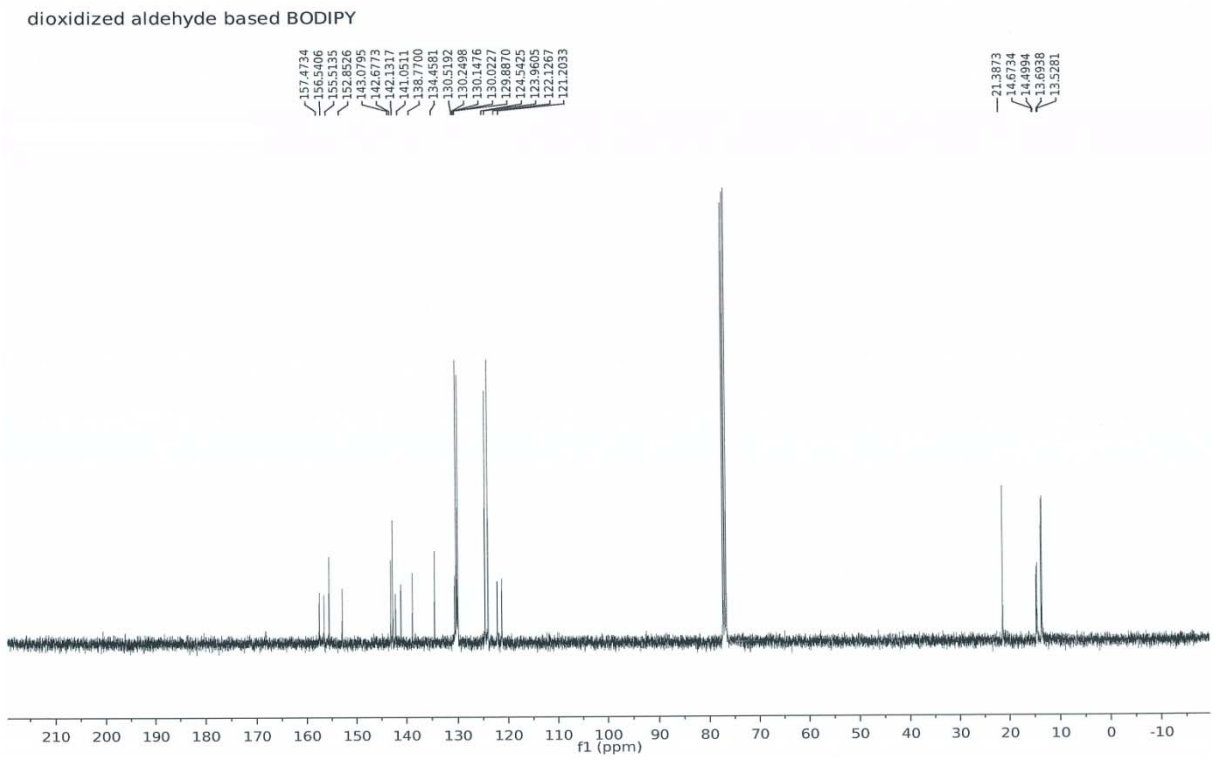

Figure S6.2: ^{13}C NMR spectrum of **6**.

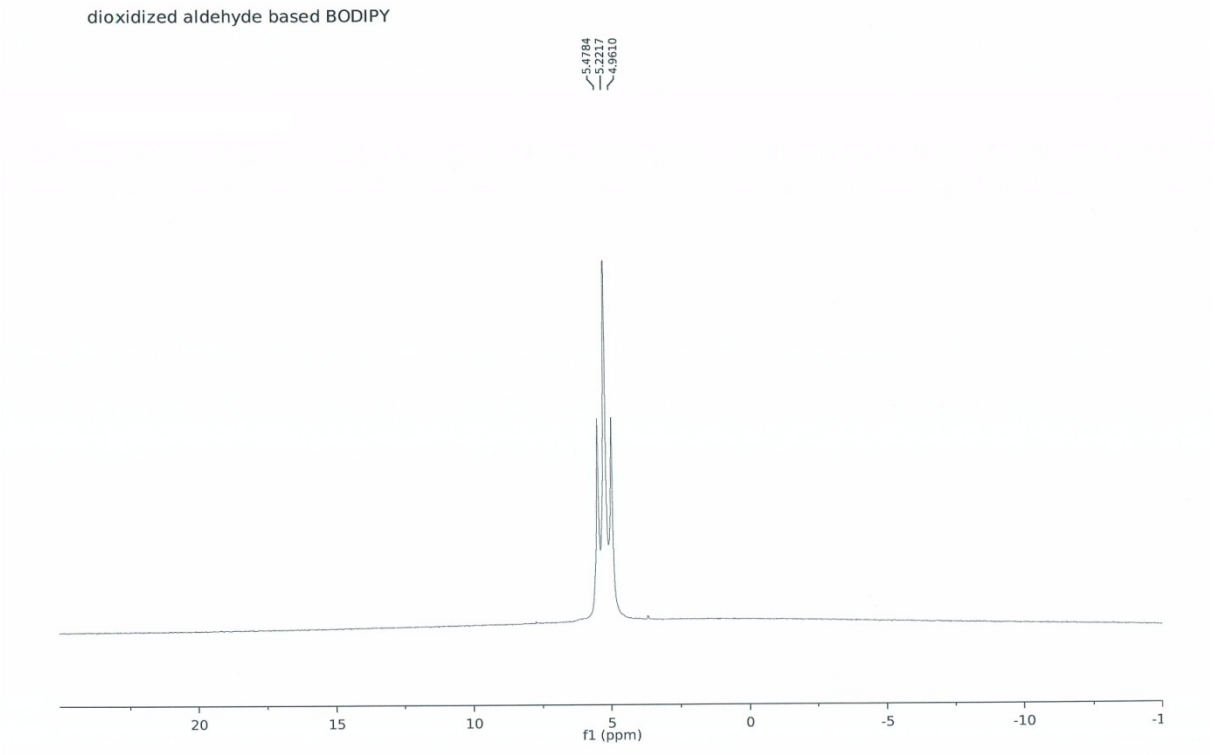

Figure S6.3: ^{11}B NMR spectrum of **6.**

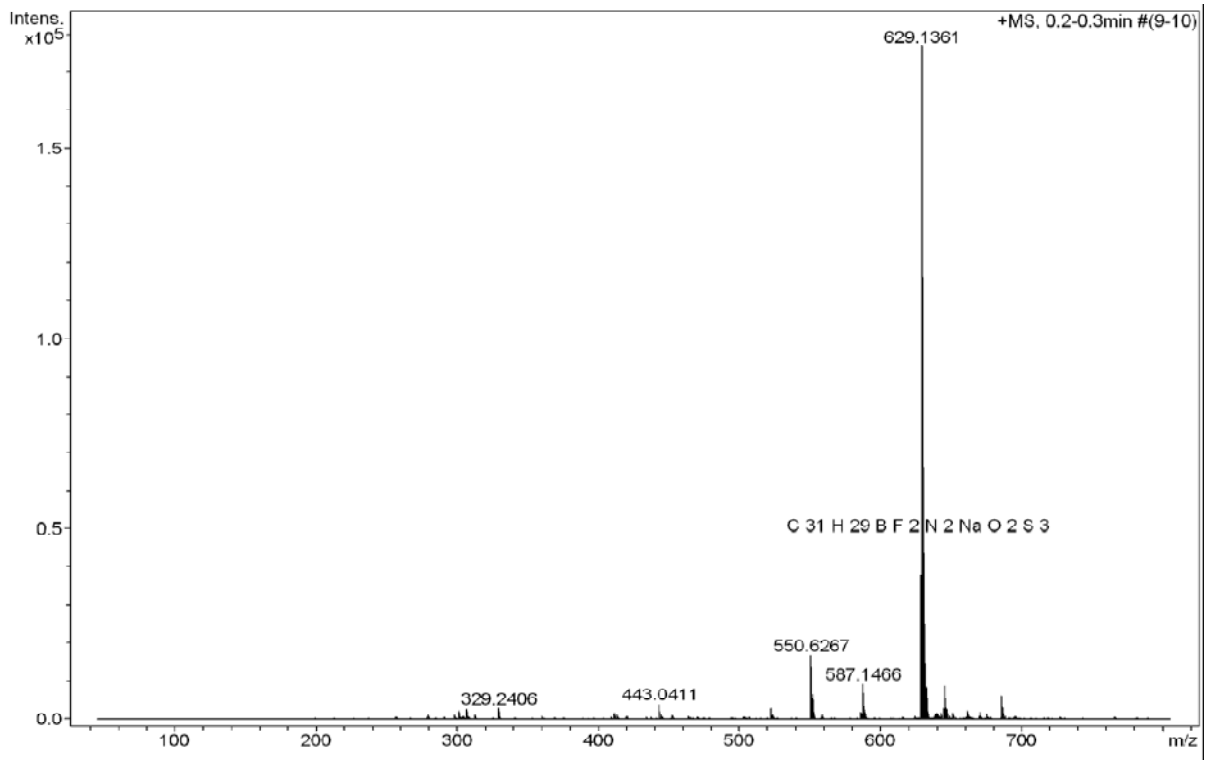

Figure S6.4: Mass spectrum of **6**.

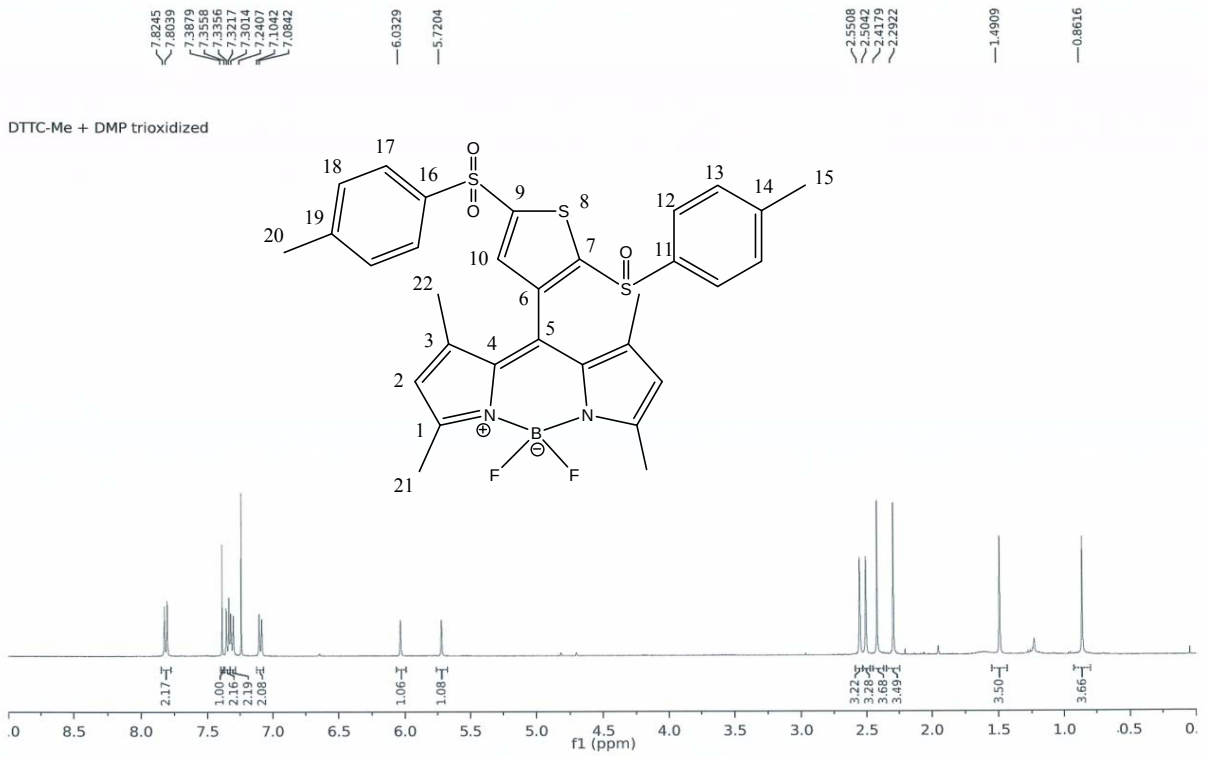

Figure S7.1: ^{1}H NMR spectrum of **7.**

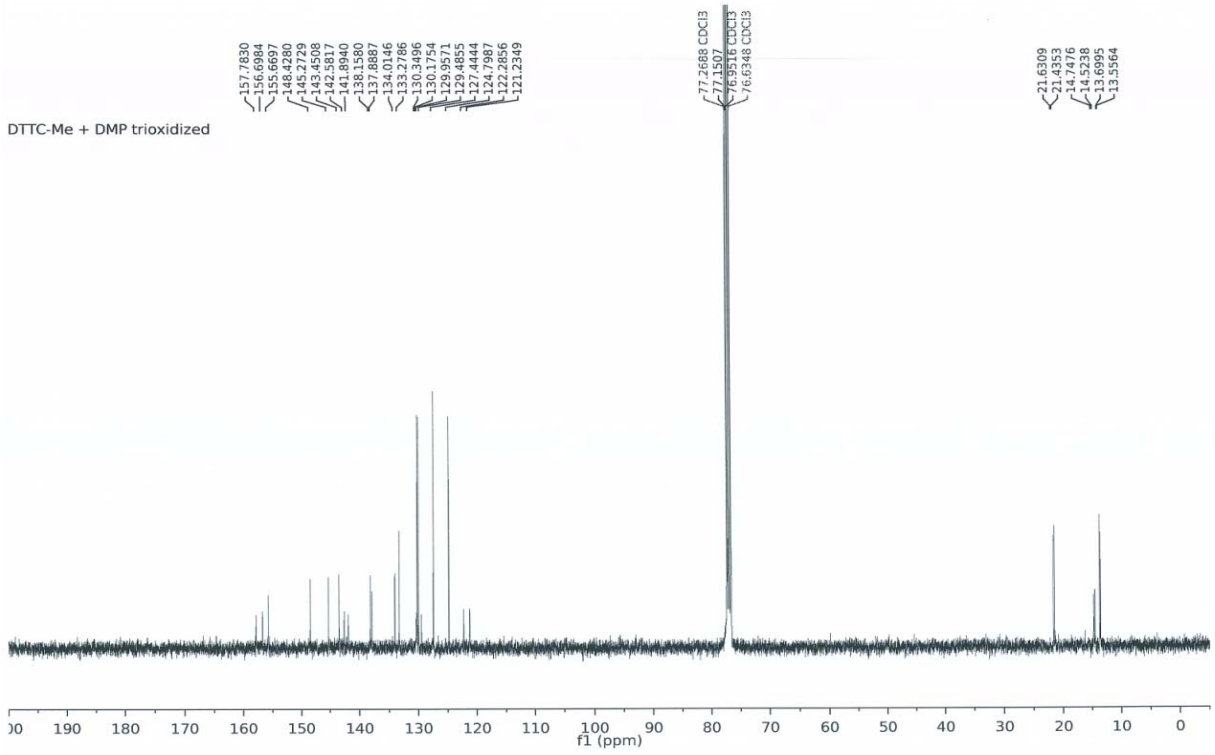

Figure S7.2: ^{13}C NMR spectrum of **7.**

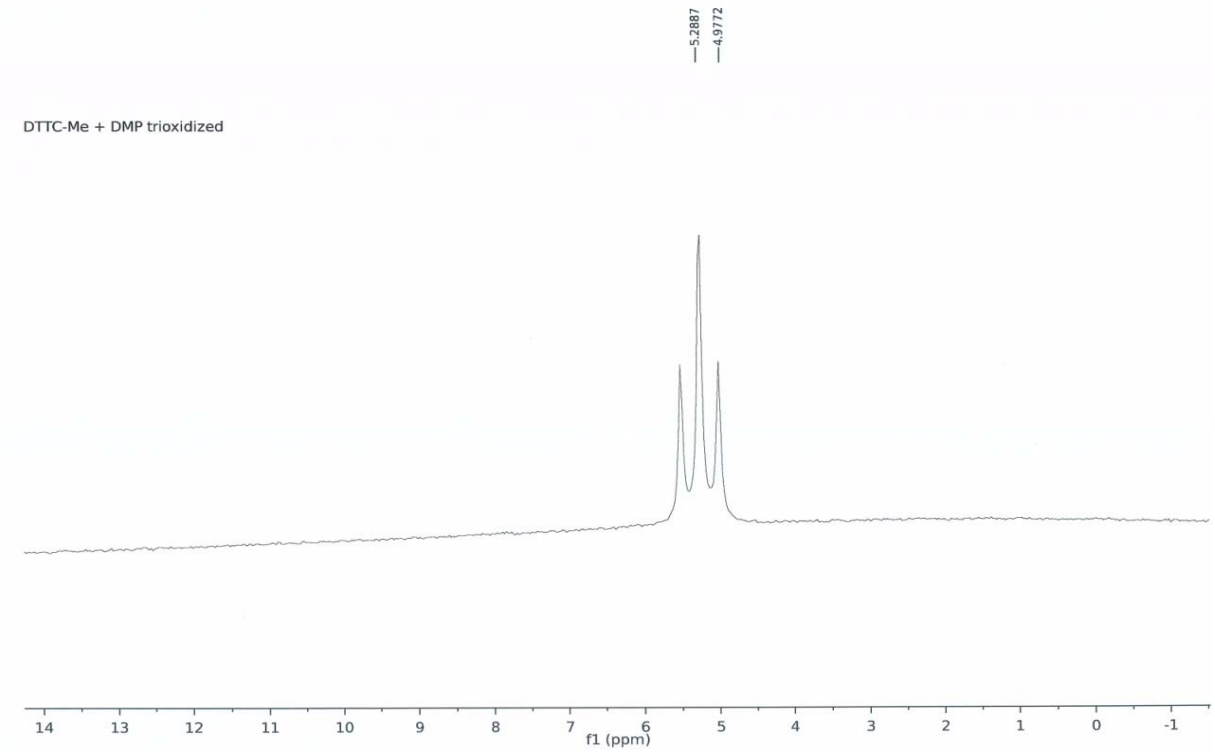

Figure S7.3: ^{11}B NMR spectrum of **7.**

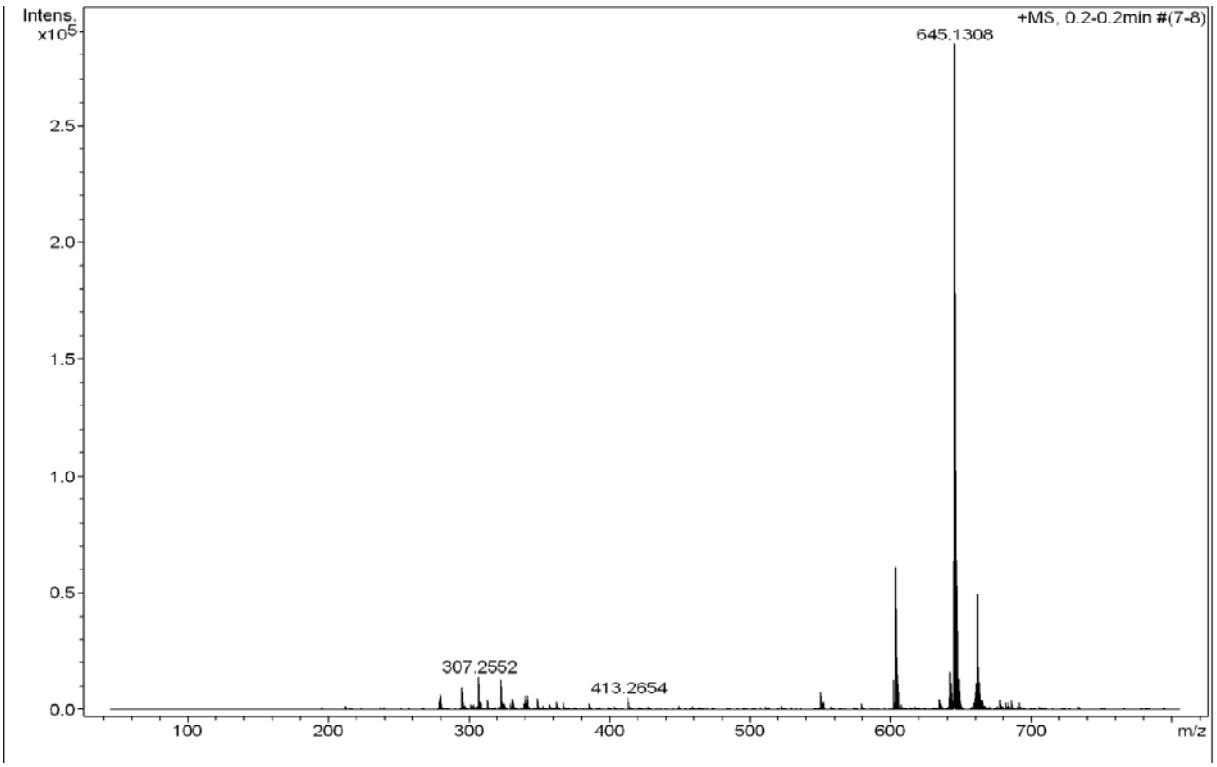

Figure S7.4: Mass spectrum of **7.**

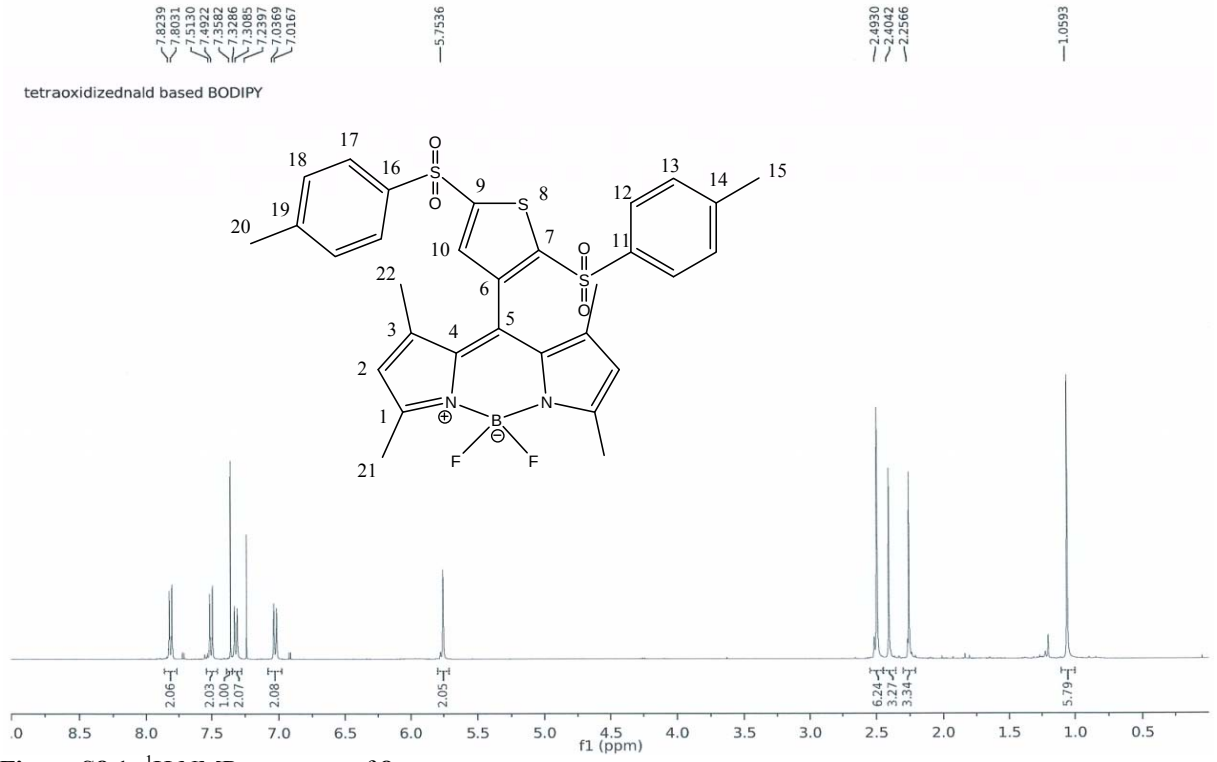

Figure S8.1: ^{1}H NMR spectrum of **8.**

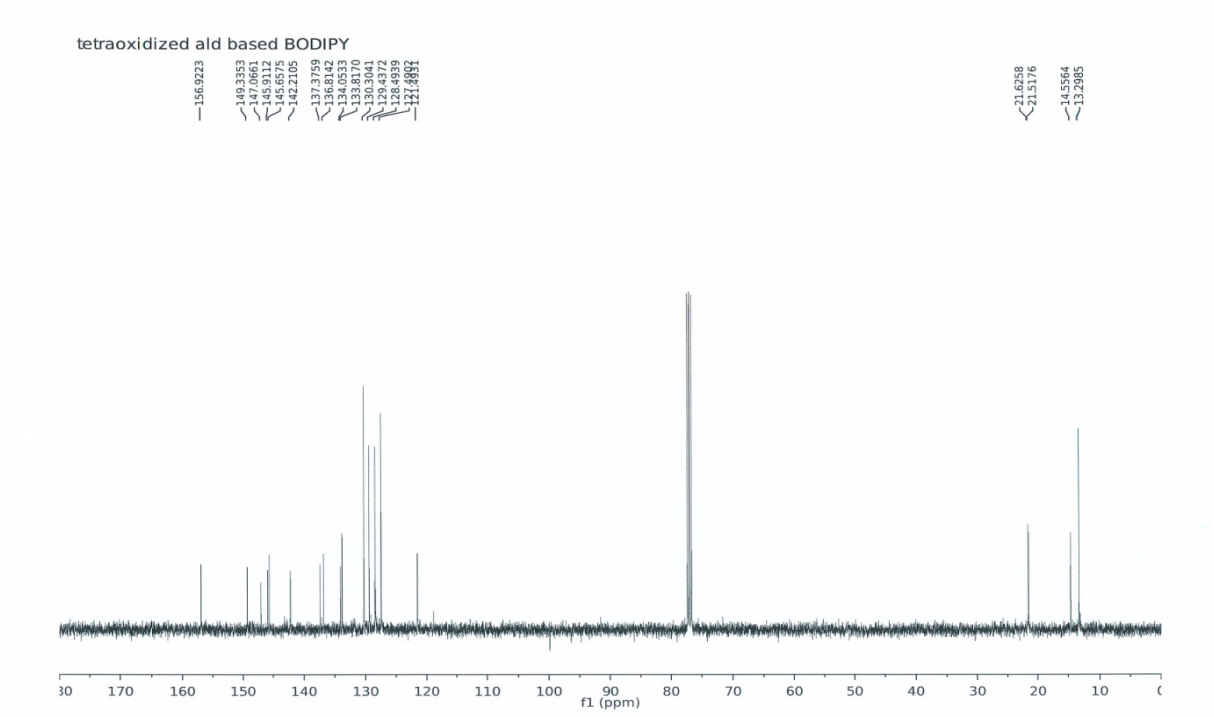

Figure S8.2: ^{13}C NMR spectrum of **8.**

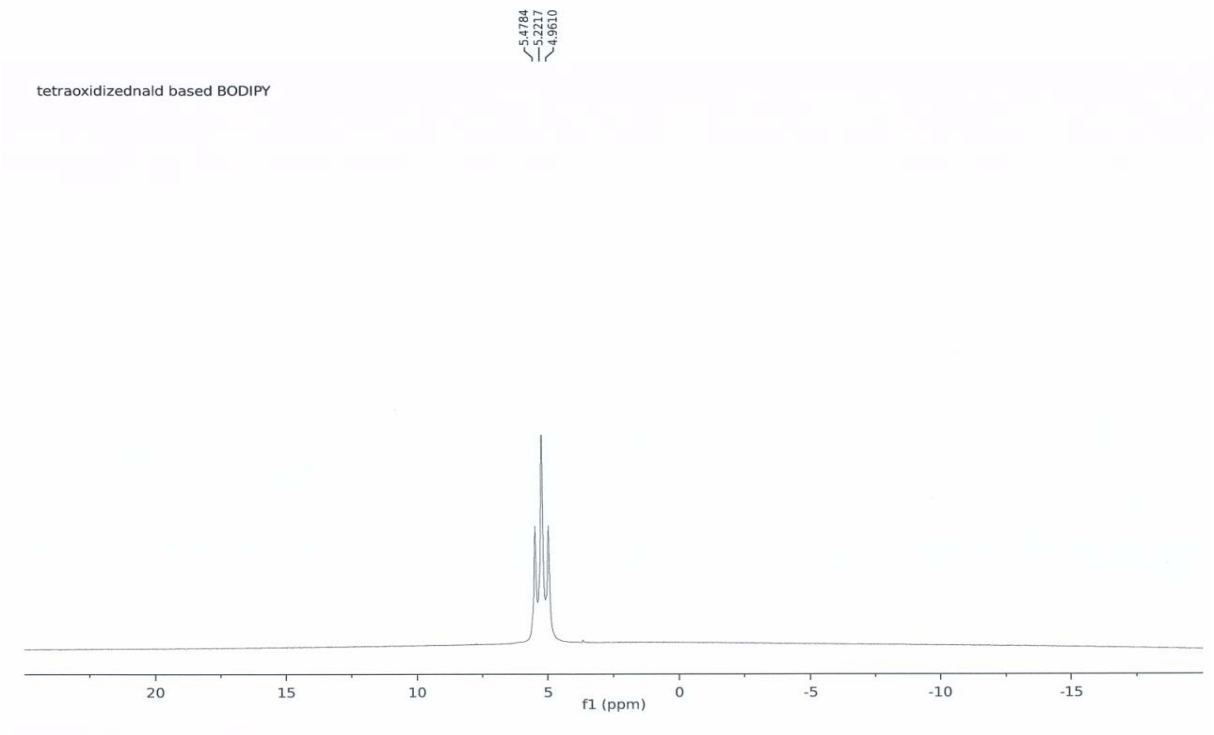

Figure S8.3: ^{11}B NMR spectrum of **8.**

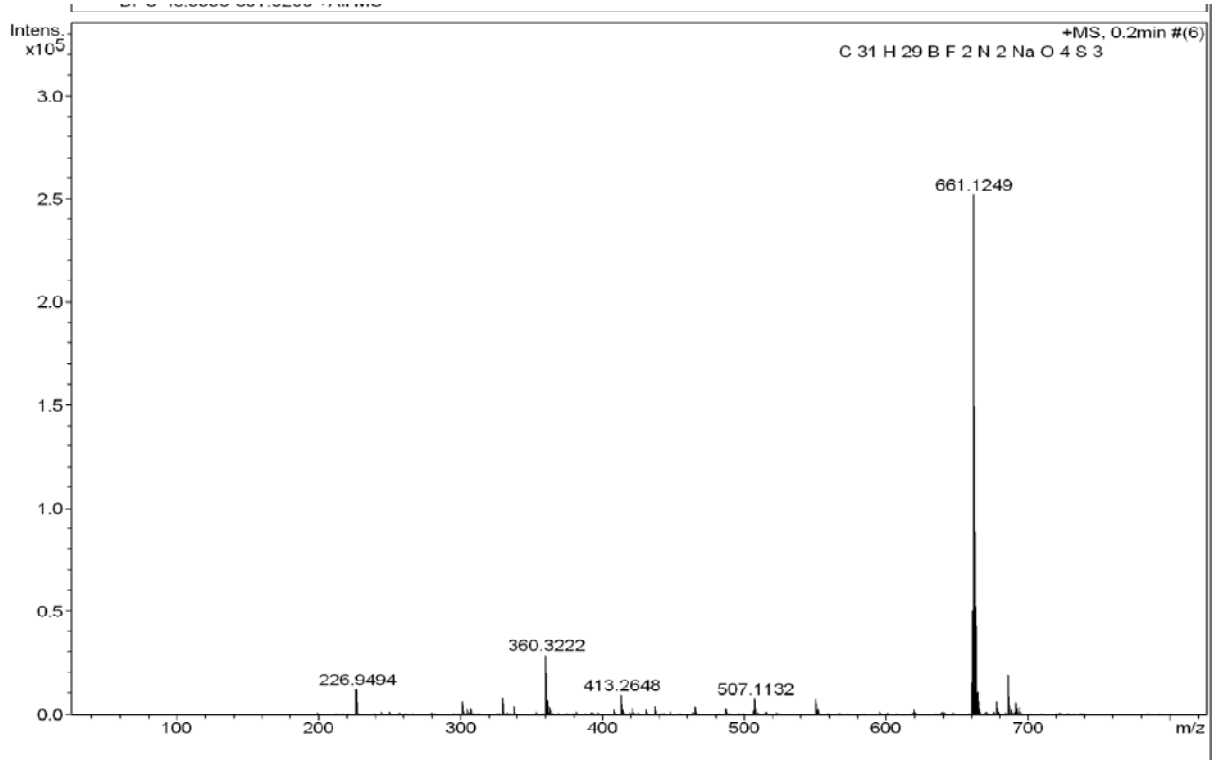

Figure S8.4: Mass spectrum of **8.**

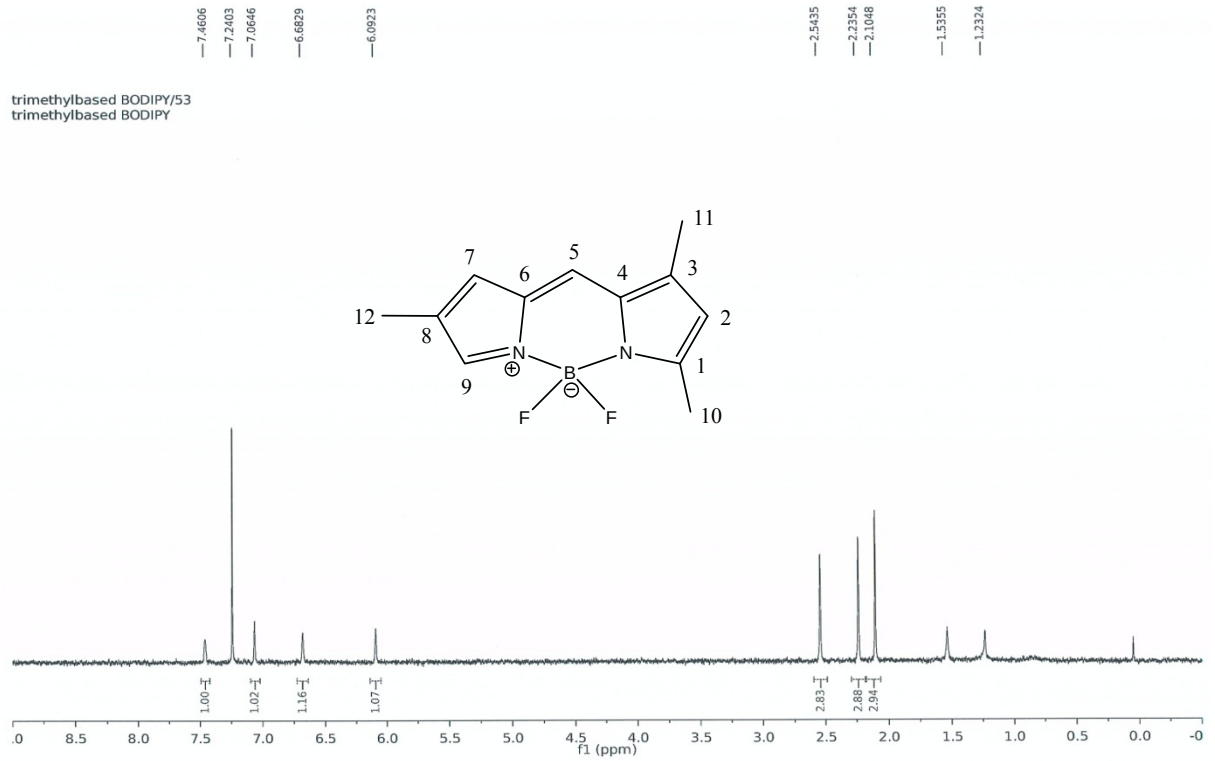

Figure S9.1: ^{1}H NMR spectrum of **9.**

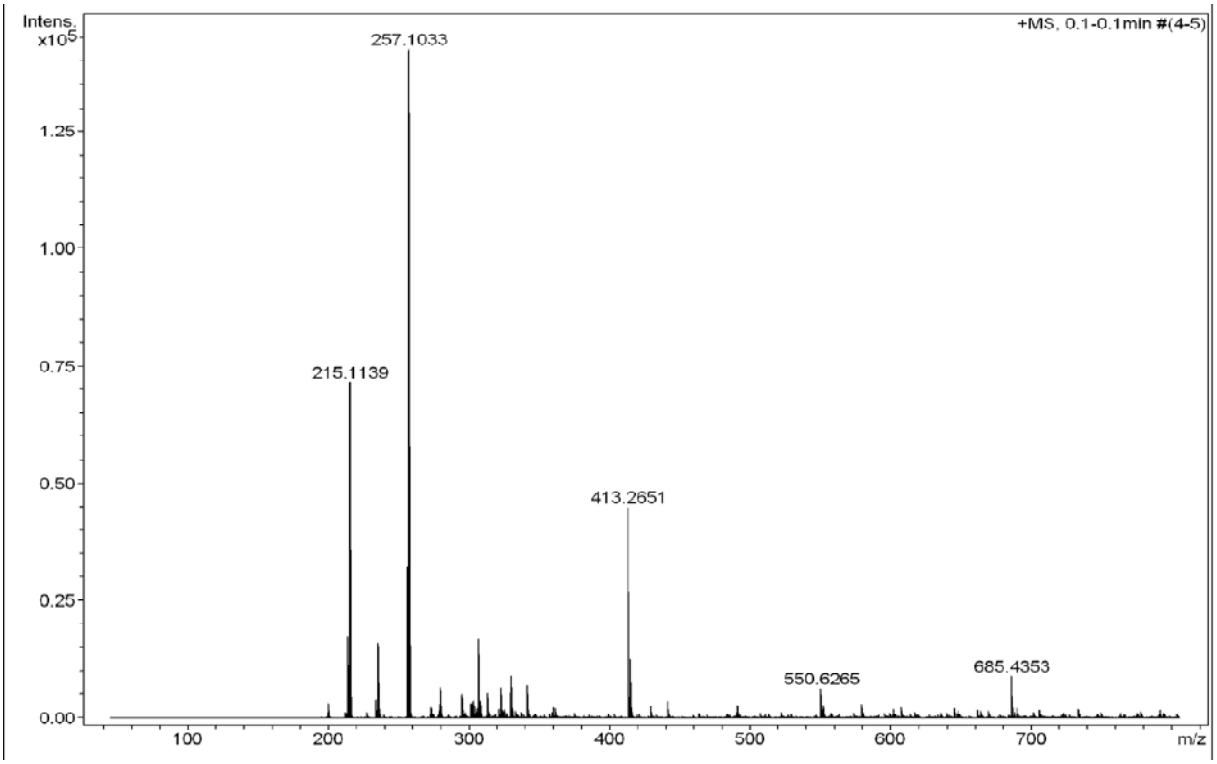

Figure S9.2: Mass spectrum of **9.**

Crystal Structures:

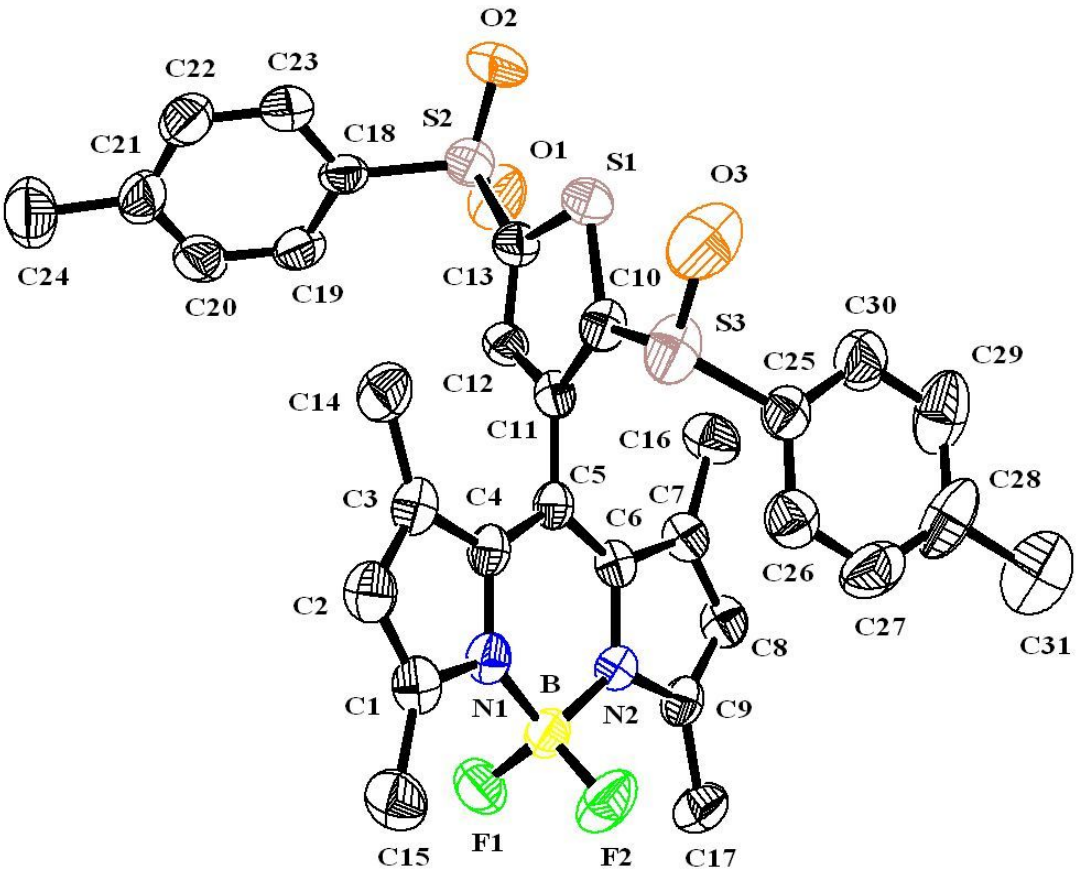

Figure S10a. Crystal structure of **7**. Hydrogen atoms are omitted for clarity, percentage of thermal ellipsoids = 30%.

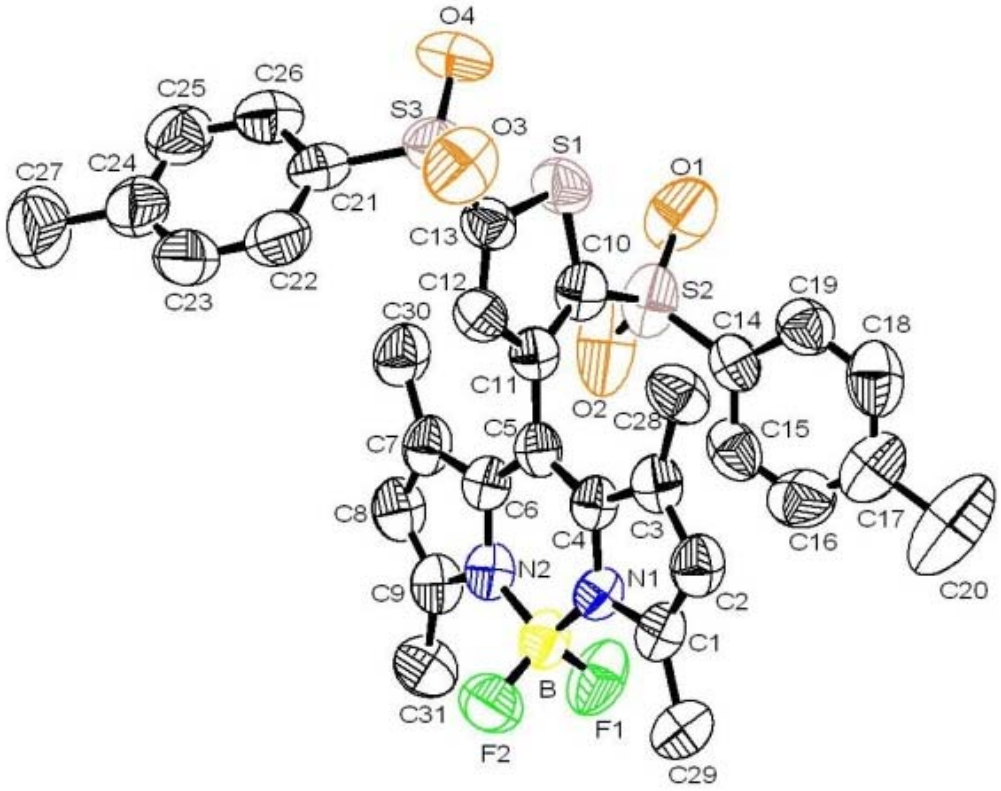

Figure S10b. Crystal structure of **8**. Hydrogen atoms are omitted for clarity, percentage of thermal ellipsoids = 30%.

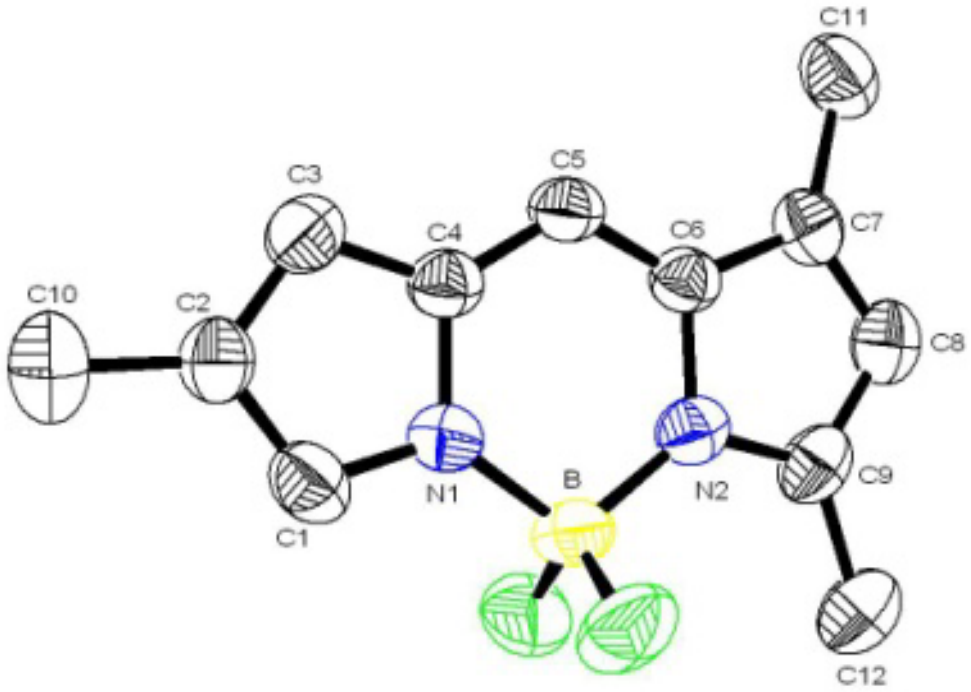

Figure S10c. Crystal structure of **9**. Hydrogen atoms are omitted for clarity, percentage of thermal ellipsoide = 30%.

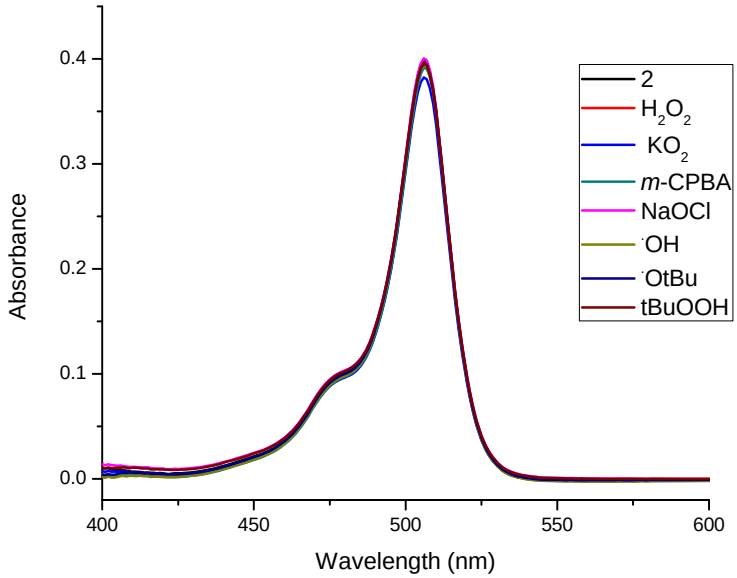

Figure S11a. Absorbance spectra of compound **2** (1×10^{-6} M, 3.0 mL) with (1×10^{-2} M, 50 μL, ~50 equiv) of *m*–CPBA, KO_2, H_2O_2, NaOCl, *t*–BuOOH, ·OH, ·O*t*–Bu.

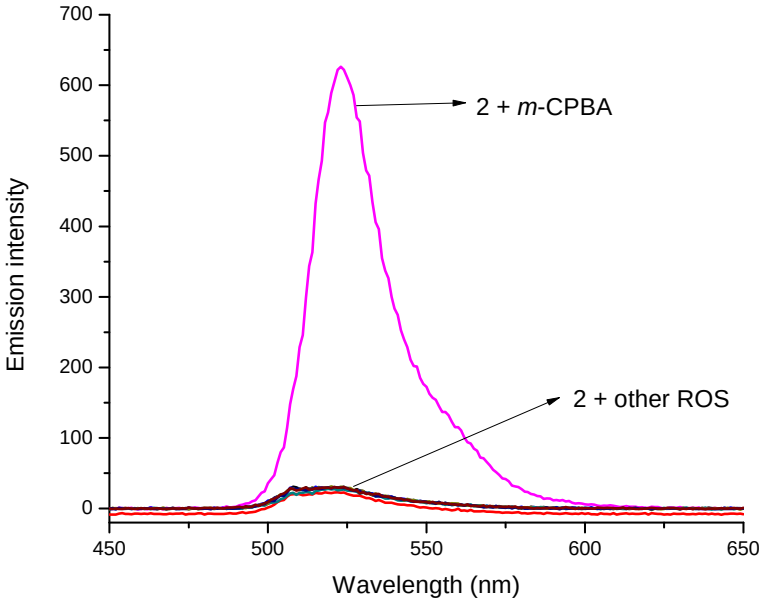

Fig. S11b: Emission spectra of compound **2** (1×10^{-6} M, 3.0 mL) with (1×10^{-2} M, 50 μL, ~50 equiv) of *m*–CPBA, KO_2, H_2O_2, NaOCl, *t*–BuOOH, ·OH, ·O*t*–Bu.

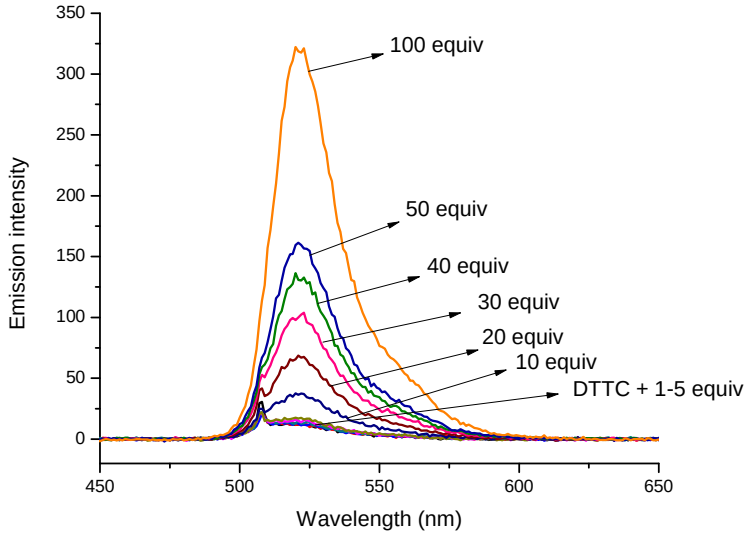

Figure S12. Emission spectra of compound **2** (1×10^{-6} M, 3 mL) with increasing concentration of *m*–CPBA (1, 2, 3, 4, 5, 10, 20, 30, 40, 50 and 100 equiv) in acetonitrile after 2 h.

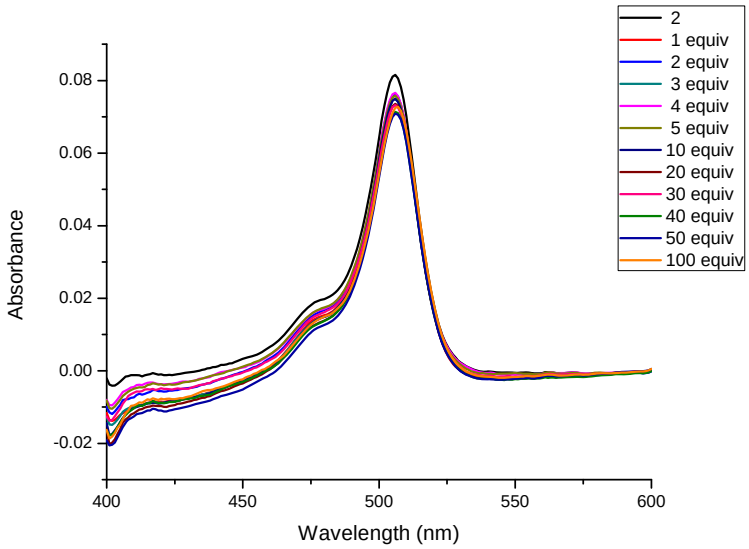

Figure S13. Absorbance spectra of compound **2** (1×10^{-6} M, 3 mL) with increasing concentration of *m*–CPBA (1, 2, 3, 4, 5, 10, 20, 30, 40, 50 and 100 equiv) in acetonitrile after 2 h.

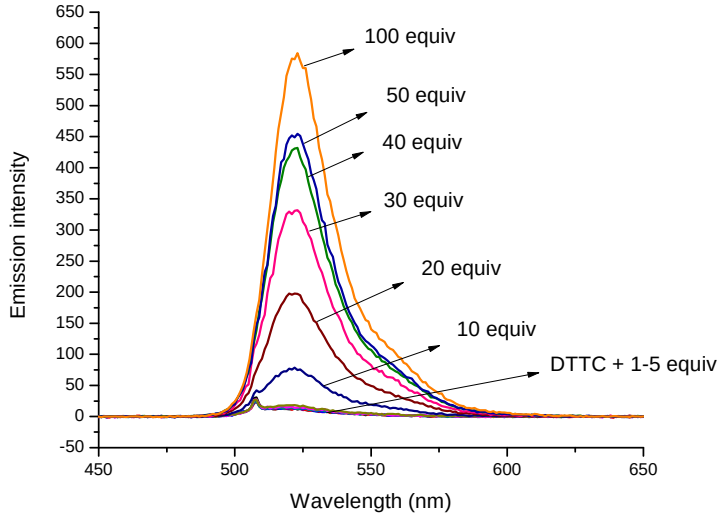

Figure S14. Emission spectra of compound **2** (1 × 10^{-6} M, 3.0 mL) with increasing concentration of *m*–CPBA (1, 2, 3, 4, 5, 10, 20, 30, 40, 50 and 100 equiv) in acetonitrile after 15 h.

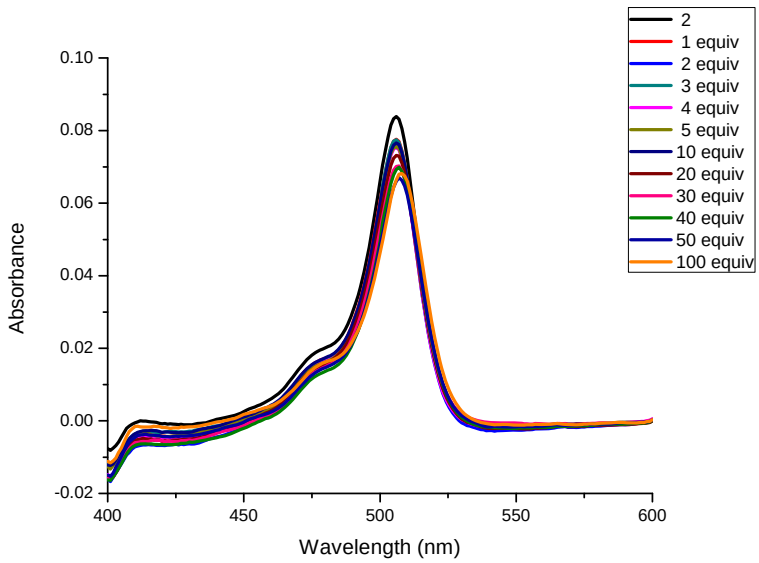

Figure S15. Absorbance spectra of compound **2** (1×10^{-6} M, 3.0 mL) with increasing concentration of *m*–CPBA (1, 2, 3, 4, 5, 10, 20, 30, 40, 50 and 100 equiv) in acetonitrile after 15 h.

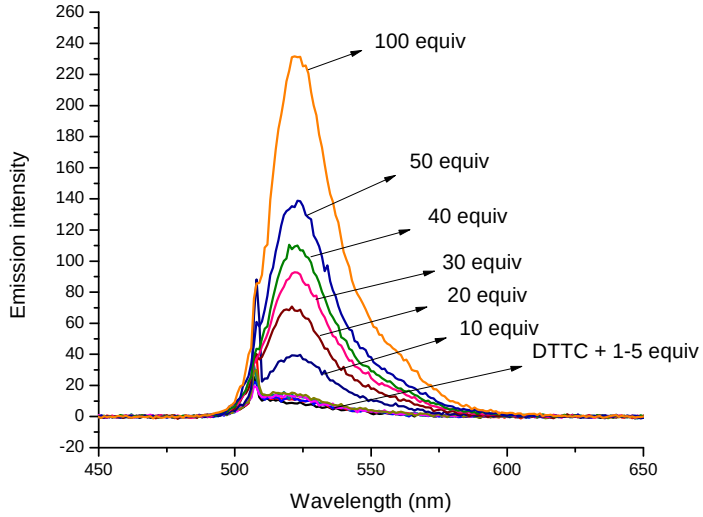

Figure S16. Emission spectra of compound **2** (1×10^{-6} M, 3.0 mL) with increasing concentration of *m*–CPBA (1–5, 10, 20, 30, 40, 50 and 100 equiv) in acetonitrile:water (70:30) after 2 h.

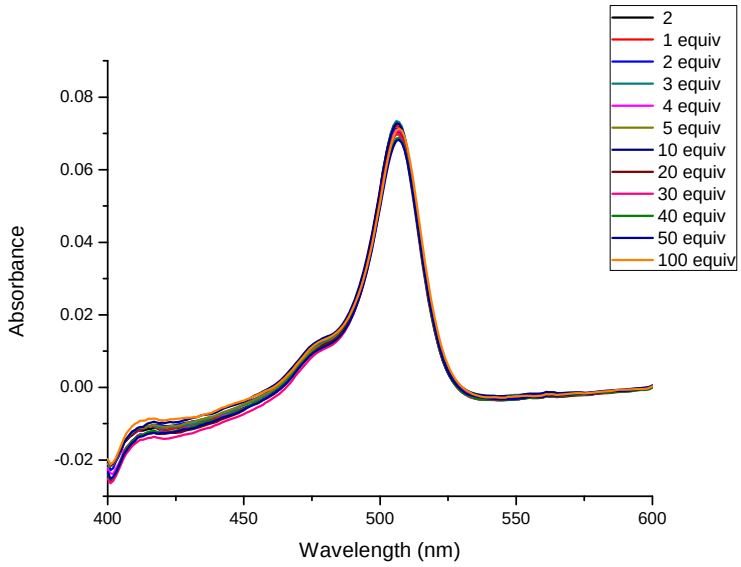

Figure S17. Absorbance spectra of compound **2** (1×10^{-6} M, 3.0 mL) with increasing concentration of *m*–CPBA (1–5, 10, 20, 30, 40, 50 and 100 equiv) in acetonitrile:water (70:30) after 2 h.

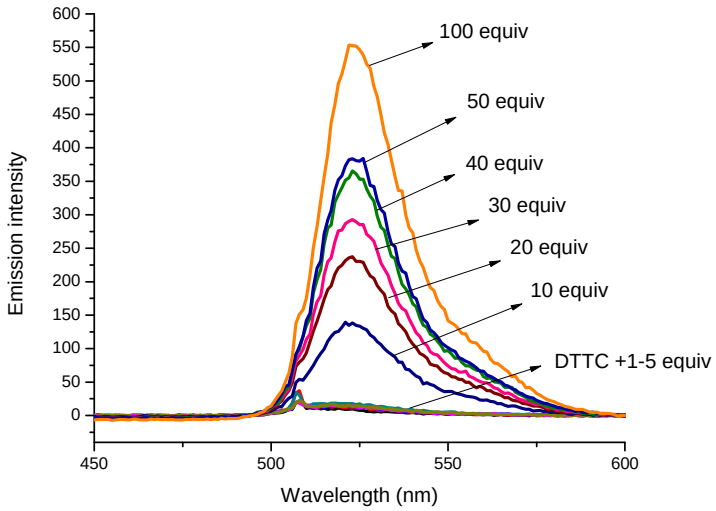

Figure S18. Emission spectra of compound **2** (1×10^{-6} M, 3.0 mL) with increasing concentration of *m*–CPBA (1–5, 10, 20, 30, 40, 50 and 100 equiv) in acetonitrile:water (70:30) after 15 h.

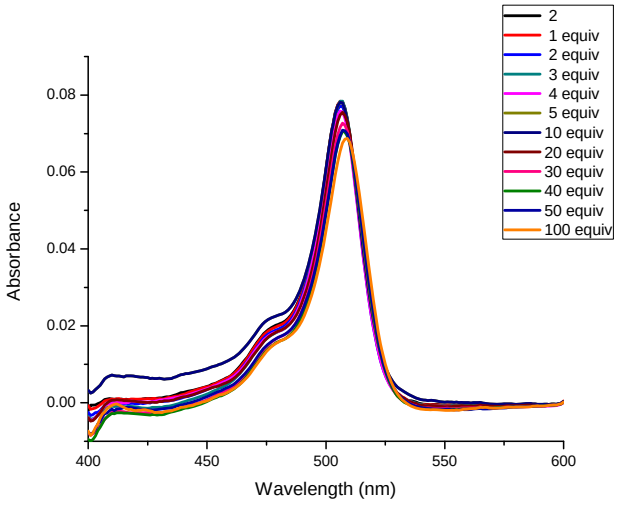

Figure S19. Absorbance spectra of compound **2** (1×10^{-6} M, 3.0 mL) with increasing concentration of *m*–CPBA (1–5, 10, 20, 30, 40, 50 and 100 equiv) in acetonitrile:water (70:30) after 15 h.

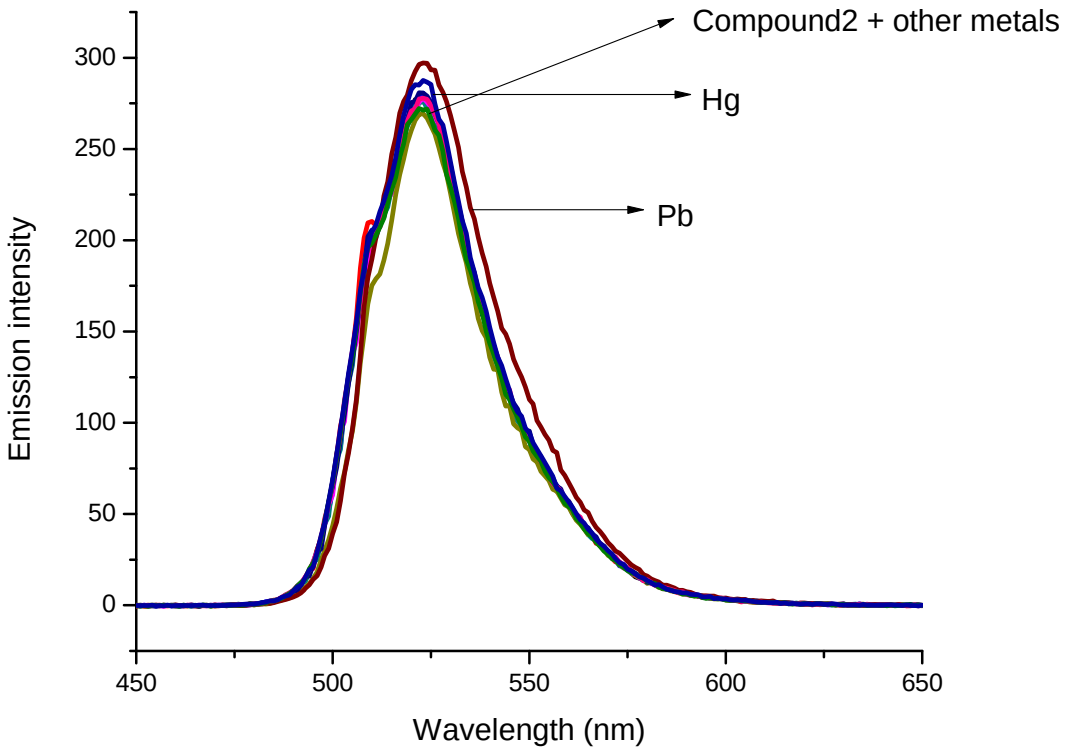

Figure S20. Emission spectra of compound **2** (1×10^{-6} M, 3.0 mL) with (1×10^{-2} M, 50 μL, ~50 equiv) of Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, and Zn^{2+}.

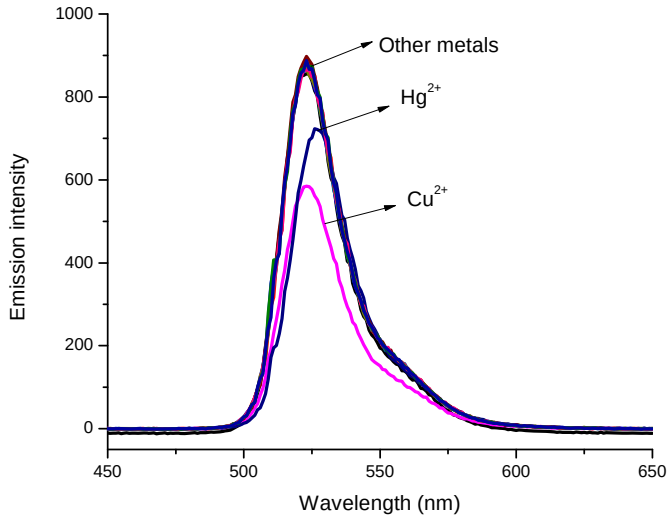

Figure S21. Emission spectra of compound **6** (1×10^{-6} M, 3.0 mL) with (1×10^{-2} M, 50 μL, ~50 equiv) of Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Pb^{2+}, and Zn^{2+}.

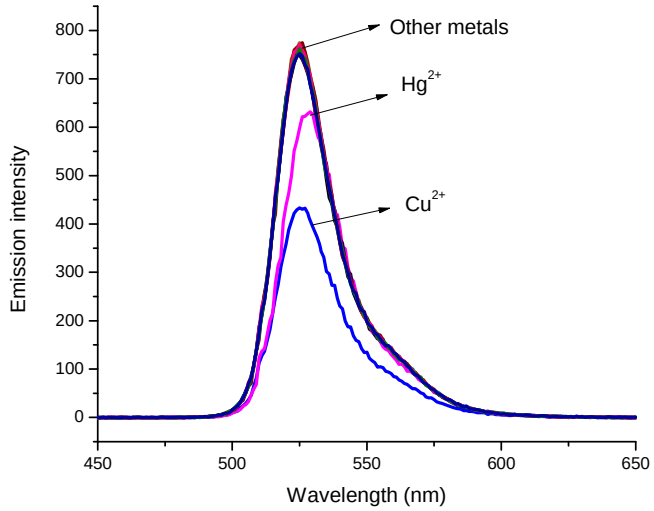

Figure S22. Emission spectra of compound **7** (1×10^{-6} M, 3.0 mL) with (1×10^{-2} M, 50 μL, ~50 equiv) of Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Pb^{2+}, and Zn^{2+}.

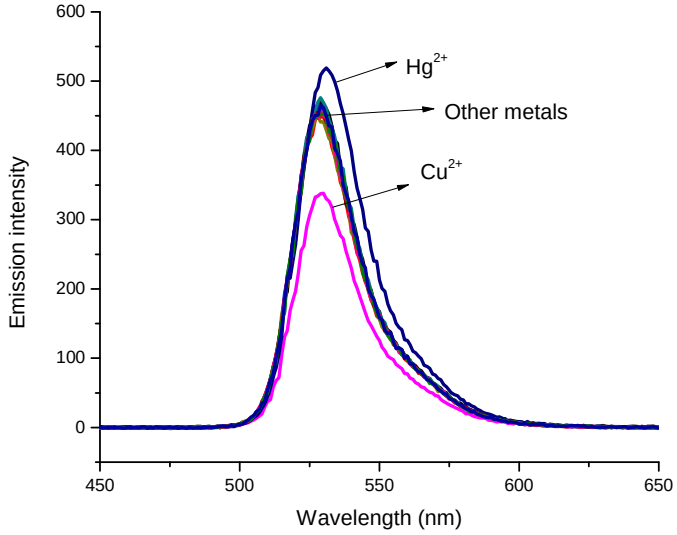

Figure S23. Emission spectra of compound **8** (1×10^{-6} M, 3.0 mL) with (1×10^{-2} M, 50 μL, ~50 equiv) of Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Pb^{2+}, and Zn^{2+}.

Table S1. Selected photophysical data for **2**, **2a**, and **6–9** in CH_3CN.

Compound	**λ_{abs}, max (nm)**	**λ_{em}, max (nm)**	**Stoke's Shift (nm)**	**Absorption coefficient (ε = M^{-1} cm^{-1})**	**Flurorescence quantum yield (Φ_F)**
2a	506	524	678.9	65820	0.060 ± 0.003
2	506	532	965.9	74590	0.010 ± 0.003
6	509	523	525.9	51700	1.020 ± 0.059
7	512	524	447.3	45440	1.067 ± 0.022
8	515	527	442.1	53690	0.588 ± 0.012
9	508	523	564.6	22760	0.98 ± 0.06

Cellular Assays.

The cellular permeable probe 2',7' –dichlorofluorescein diacetate (DCFDA) was studied and compared to compound **2**. DCFDA is a fluorogenic dye that measures hydroxyl, peroxyl and other reactive oxygen species (ROS) activity in the cell. All treatment was in 24 hours. Compound **2** and DCFDA were 1 x 10^{-5} M after 30 min. Conclusions from this work include (*i*) *m*–CPBA is somewhat more weakly detected than H_2O_2 by **2** in case of ROS induction. Also (*ii*) Compound **2** is more sensitive to ROS detection than DCFDA. The images below relate to the following conditions:

i. No dye & instrumental resting.

ii. No dye, with H_2O_2.

iii. DCFDA instrumental resting: control experiment.

iv. Compound **2** instrumental resting: control experiment.

v. DCFDA (5×10^{-5} M) treated with H_2O_2.

vi. Compound **2** (5×10^{-5} M) treated with H_2O_2.

vii. DCFDA (5×10^{-5} M) treated with *m*–CPBA.

viii. Compound **2** (5×10^{-5} M) treated with *m*–CPBA.

Figure S24. No dye & instrumental resting.

Figure S25. No dye, with H_2O_2.

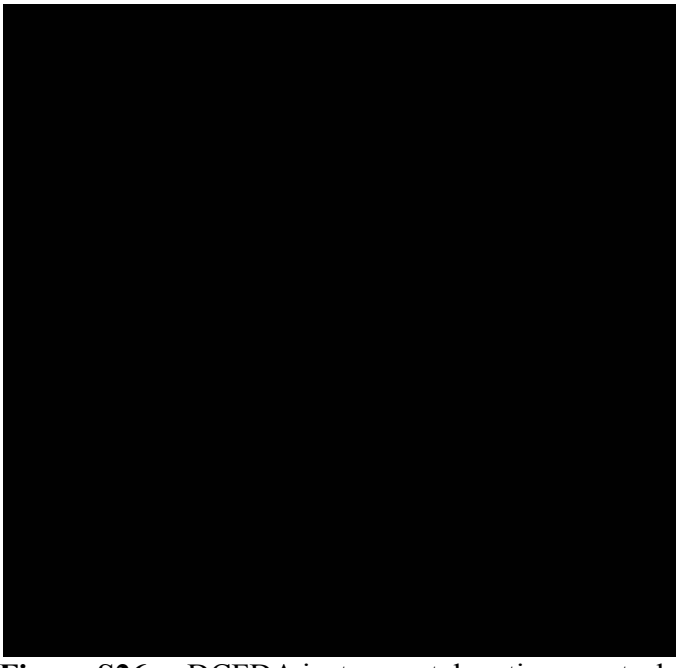

Figure S26. DCFDA instrumental resting: control experiment.

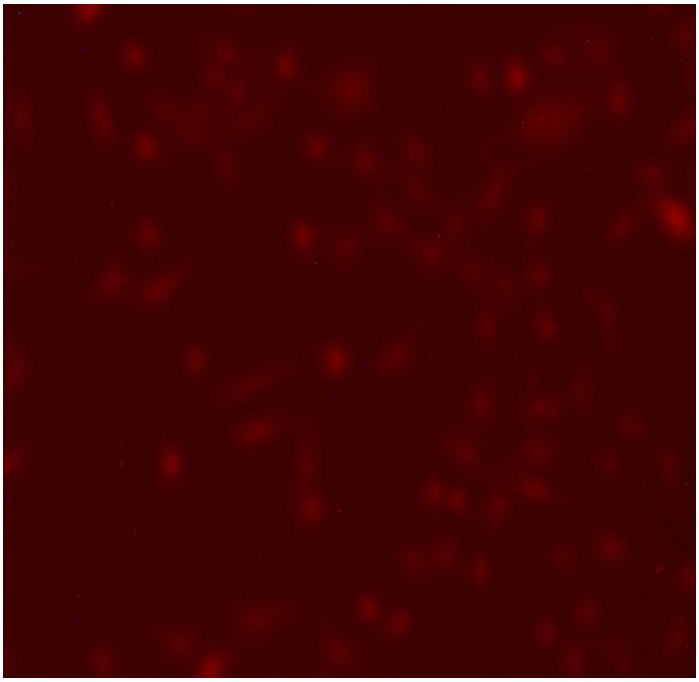

Figure S27. DCFDA instrumental resting: control experiment.

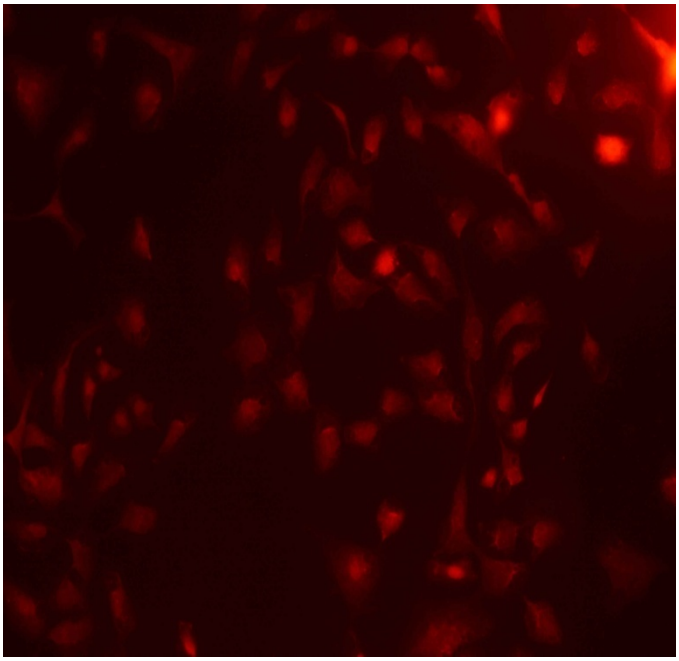

Figure S28. Compound **2** instrumental resting: control experiment.

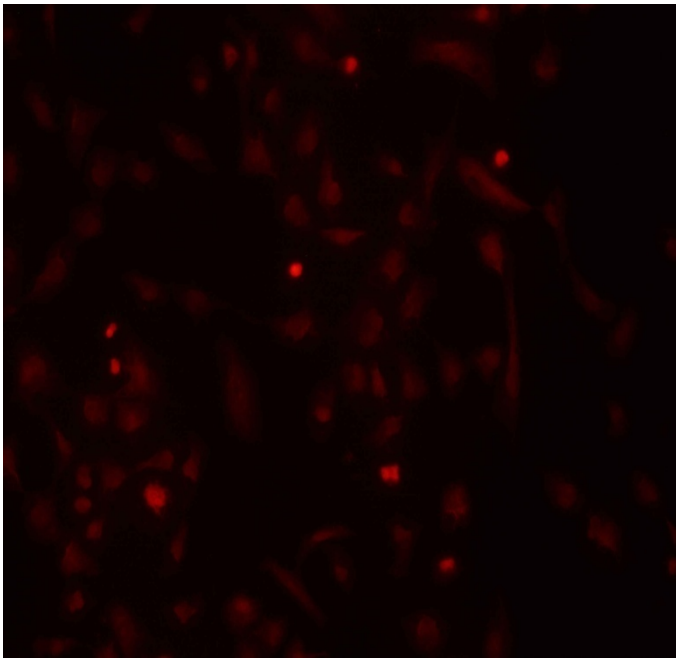

Figure S29. Compound **2** instrumental resting: control experiment.

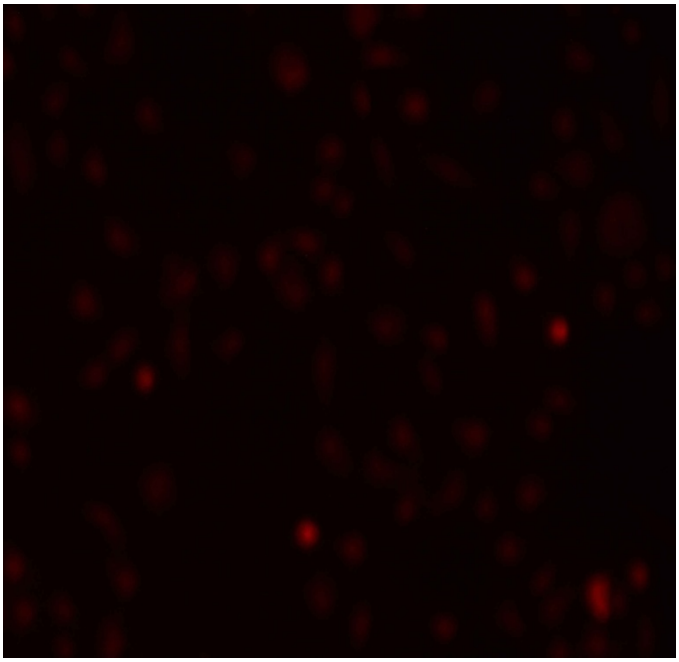

Figure S30. Compound **2** instrumental resting: control experiment.

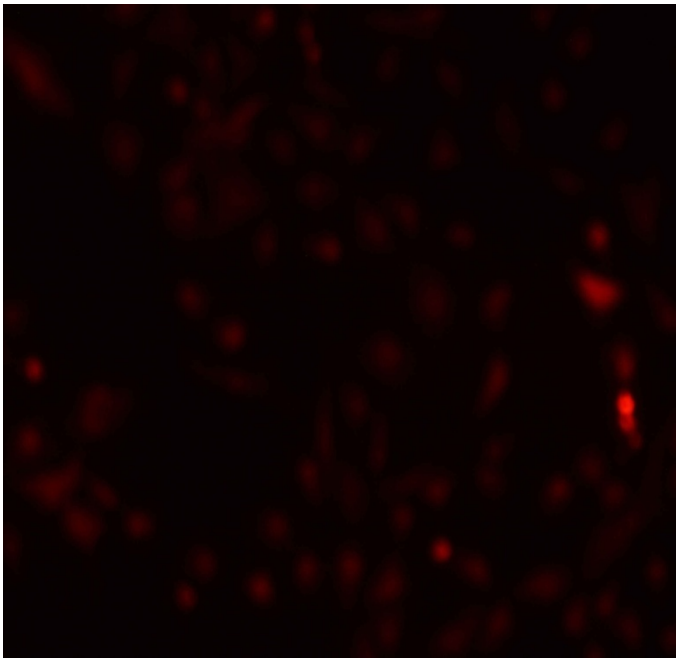

Figure S31. Compound **2** instrumental resting: control experiment.

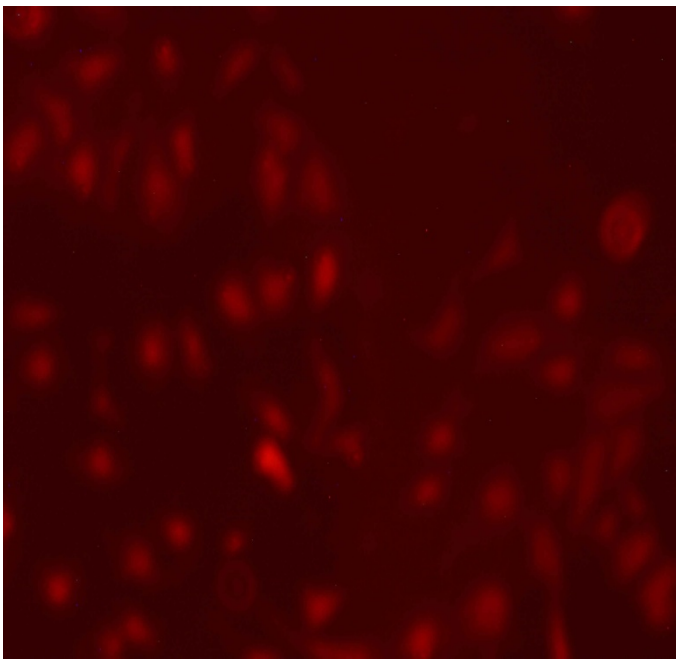

Figure S32. DCFDA (5×10^{-5} M) treated with H_2O_2.

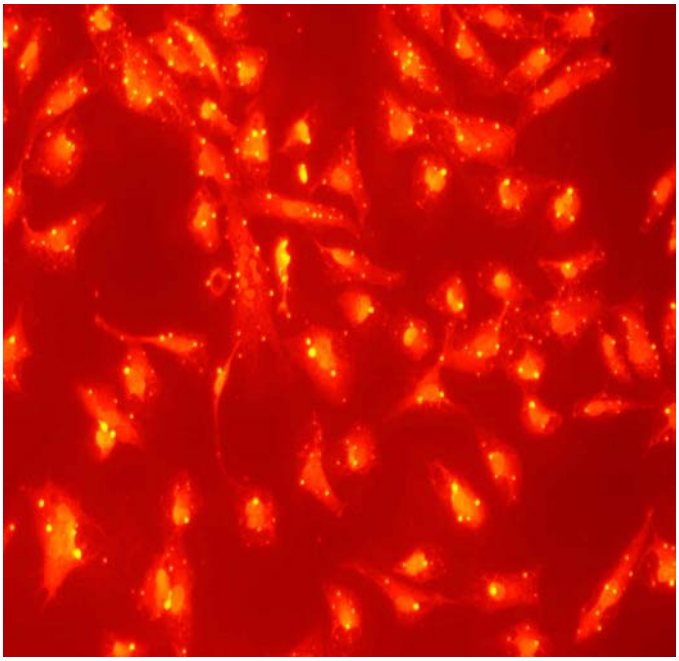

Figure S33. Compound **2** (5×10^{-5} M) treated with H_2O_2.

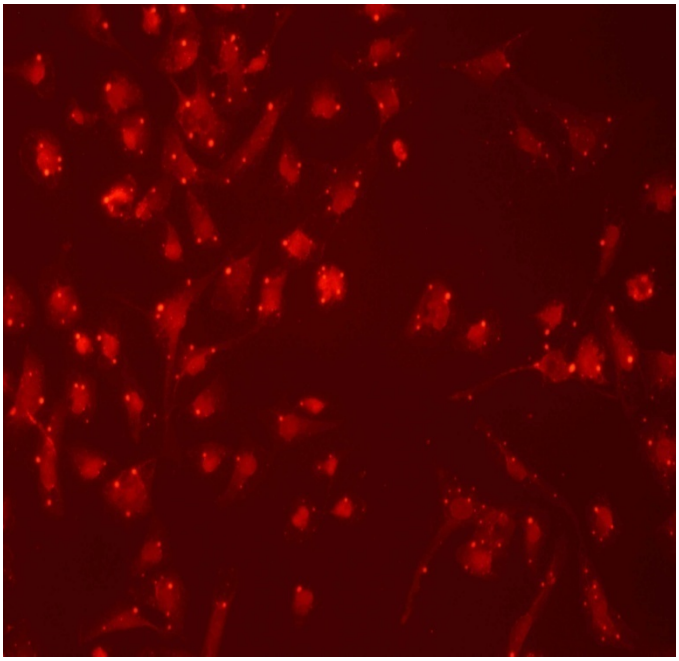

Figure S34. Compound **2** (5×10^{-5} M) treated with H_2O_2.

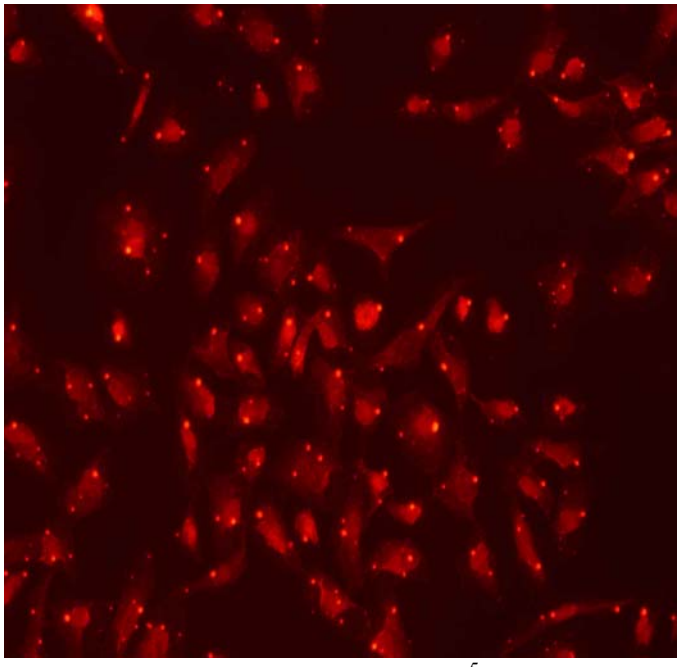

Figure S35. Compound **2** (5×10^{-5} M) treated with H_2O_2.

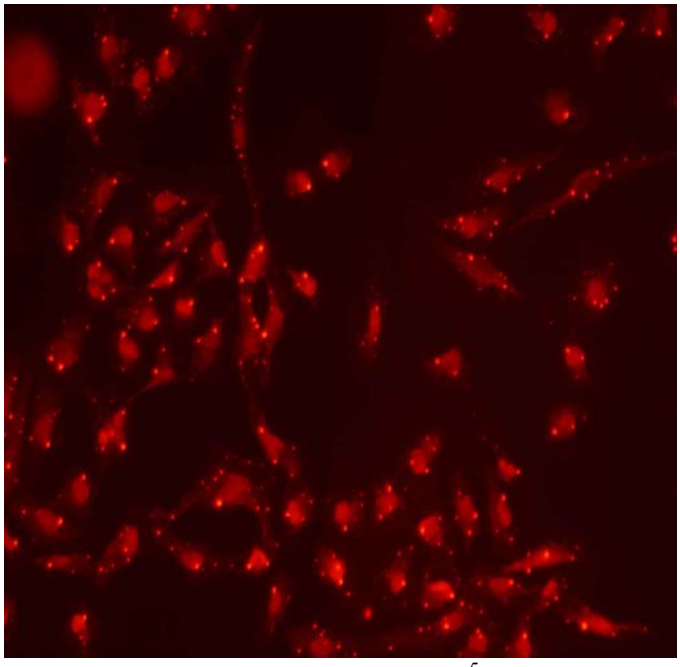

Figure S36. Compound **2** (5×10^{-5} M) treated with H_2O_2.

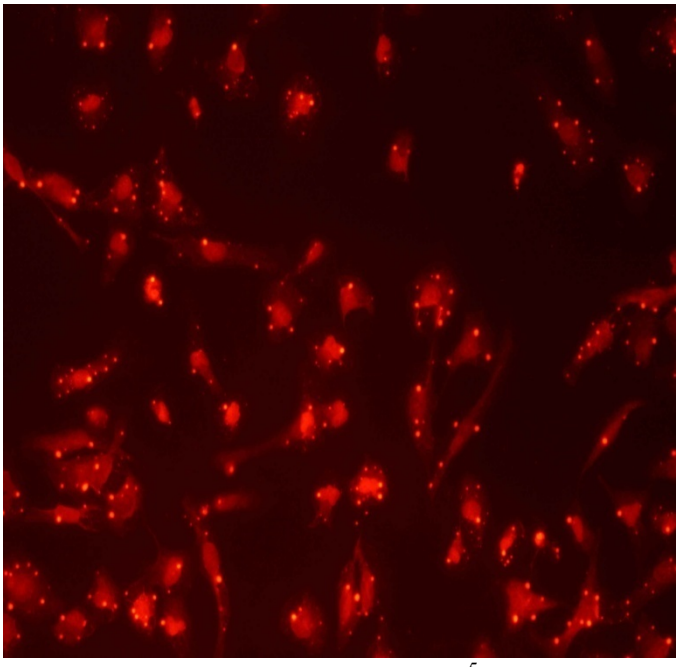

Figure S37. Compound **2** (5×10^{-5} M) treated with H_2O_2.

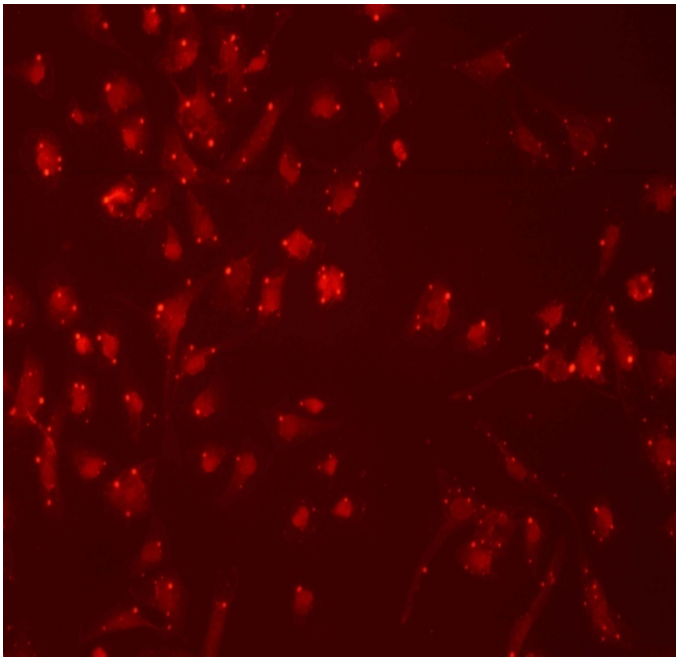

Figure S38. Compound **2** (5×10^{-5} M) treated with H_2O_2.

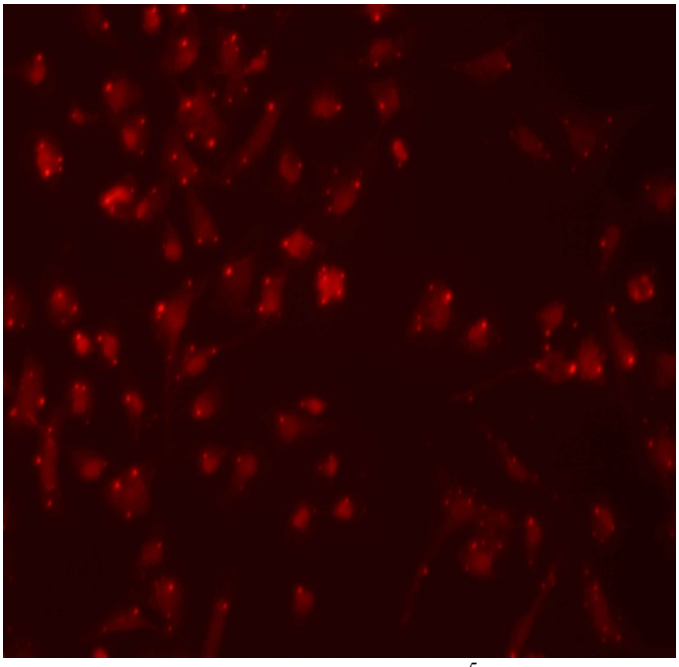

Figure S39. Compound **2** (5×10^{-5} M) treated with H_2O_2.

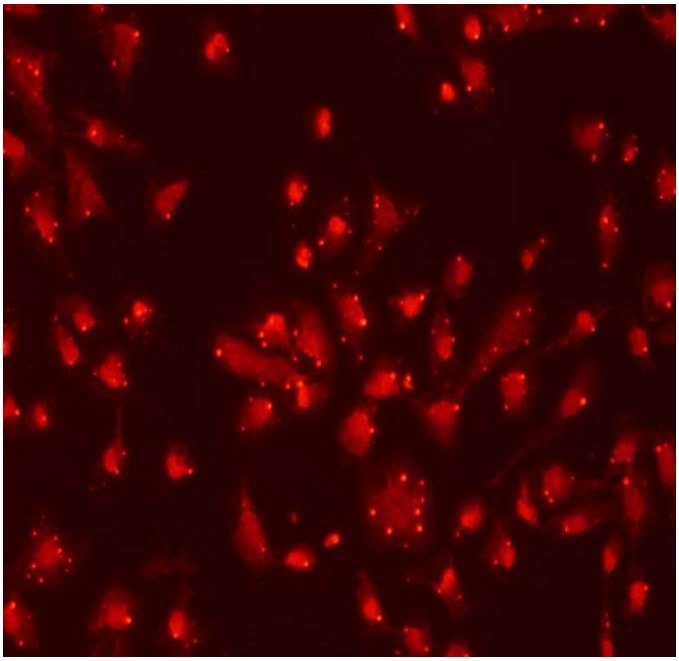

Figure S40. Compound **2** (5×10^{-5} M) treated with H_2O_2.

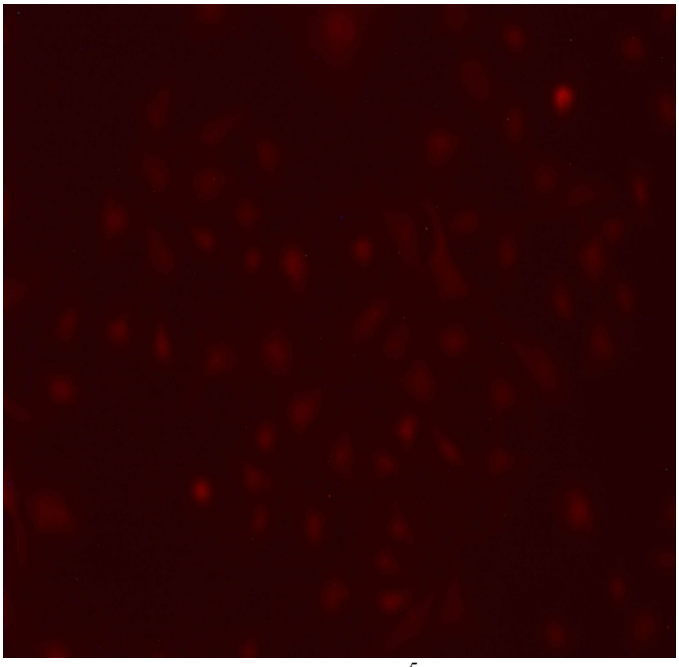

Figure S41. DCFDA (5×10^{-5} M) treated with *m*–CPBA.

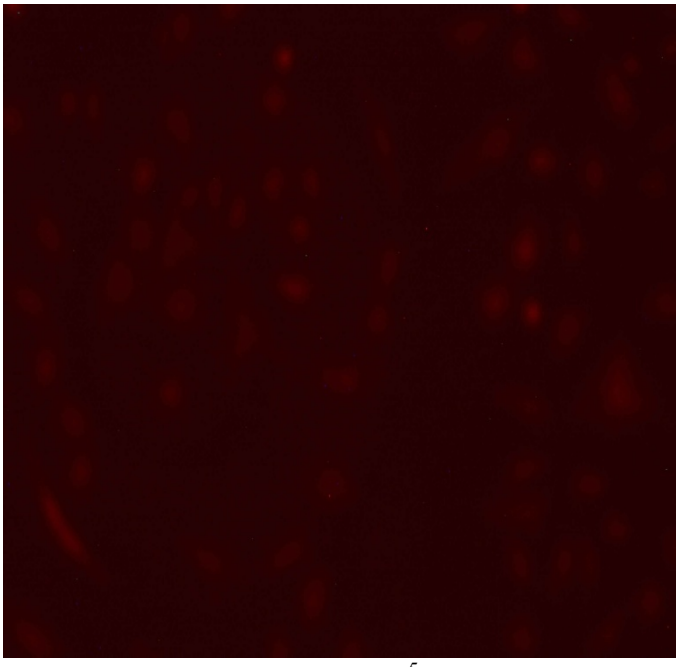

Figure S42. DCFDA (5×10^{-5} M) treated with *m*–CPBA.

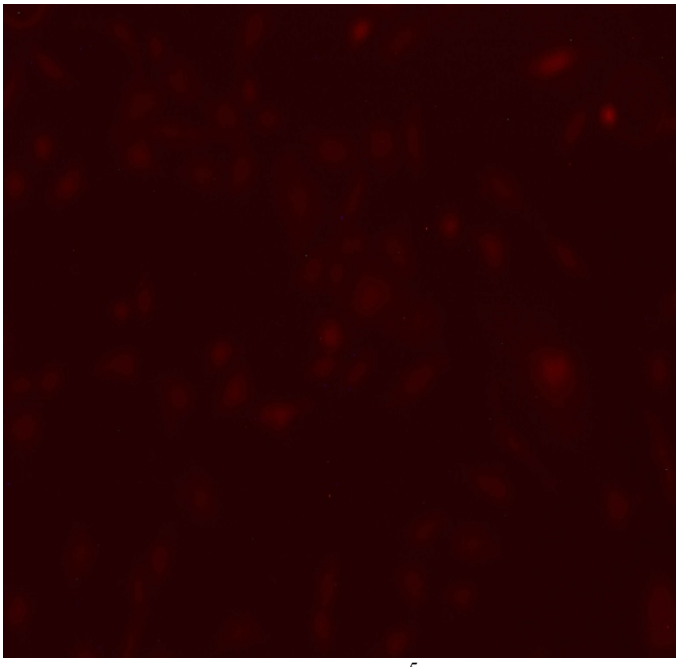

Figure S43. DCFDA (5×10^{-5} M) treated with *m*–CPBA.

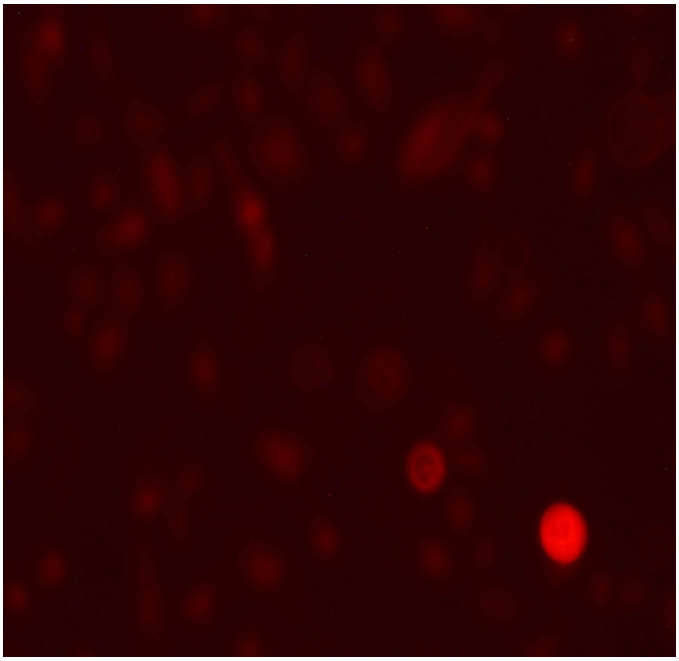

Figure S44. DCFDA (5×10^{-5} M) treated with *m*–CPBA.

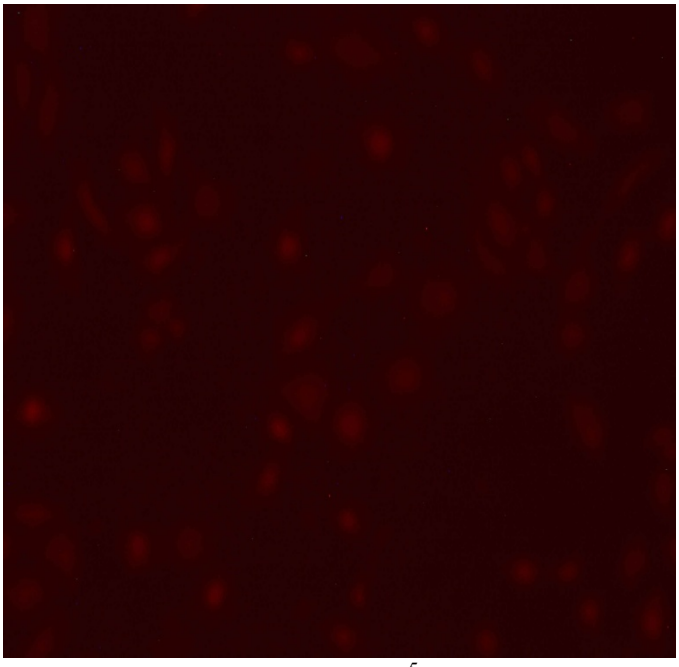

Figure S45. DCFDA (5×10^{-5} M) treated with *m*–CPBA.

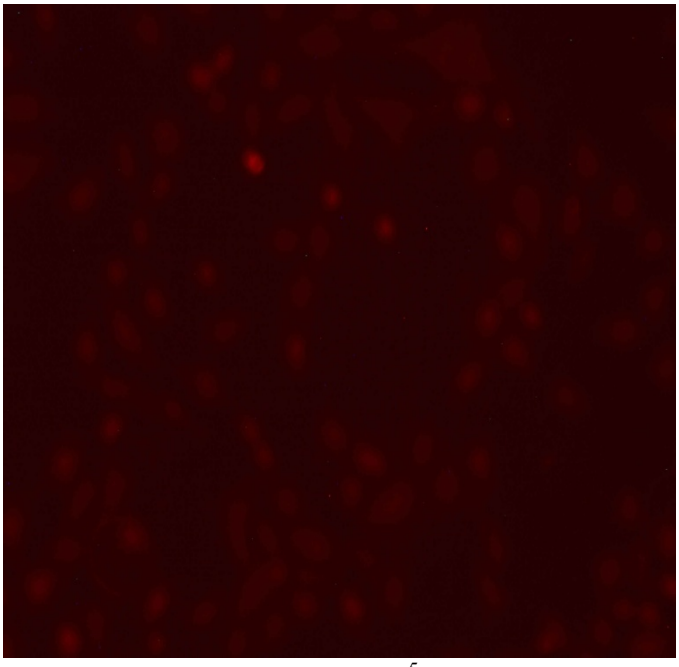

Figure S46. DCFDA (5×10^{-5} M) treated with *m*–CPBA.

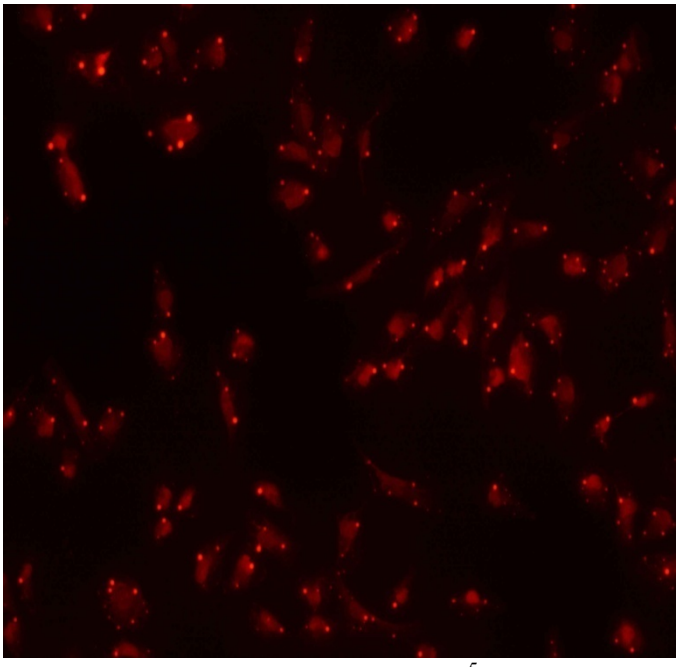

Figure S47. Compound **2** (5×10^{-5} M) treated with *m*–CPBA.

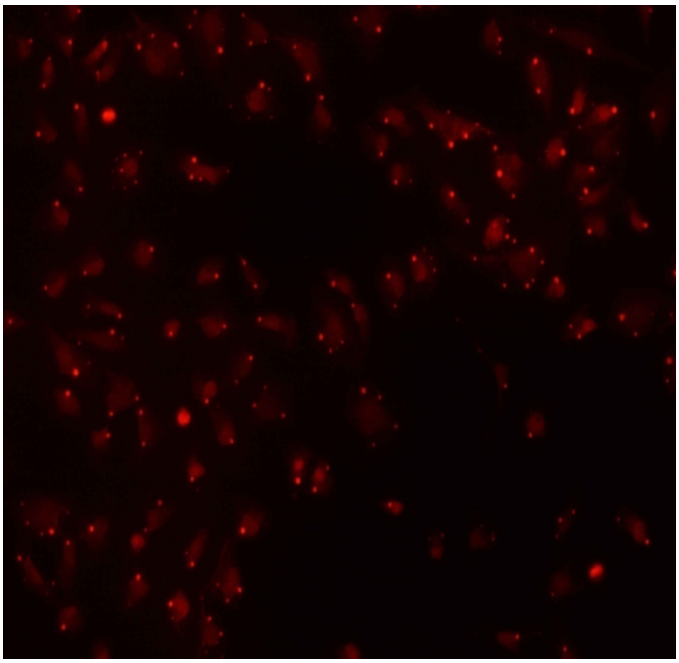

Figure S48. Compound **2** (5×10^{-5} M) treated with *m*–CPBA.

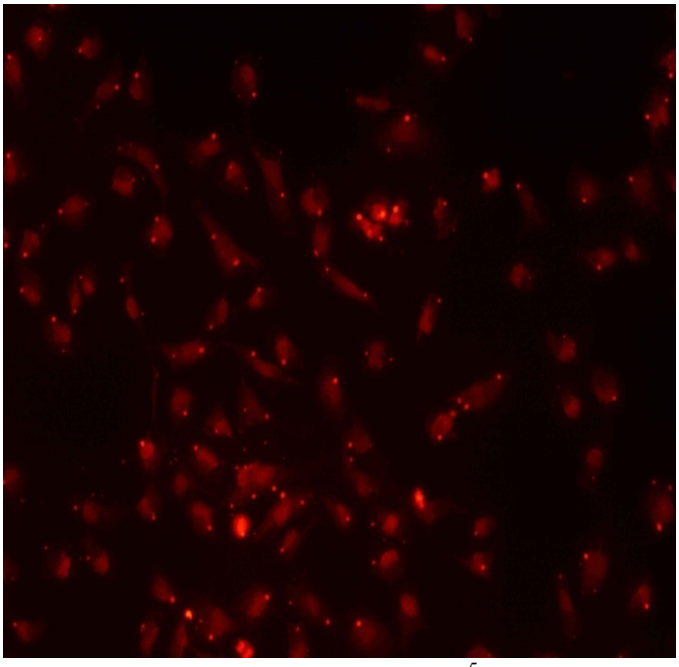

Figure S49. Compound **2** (5×10^{-5} M) treated with *m*–CPBA.

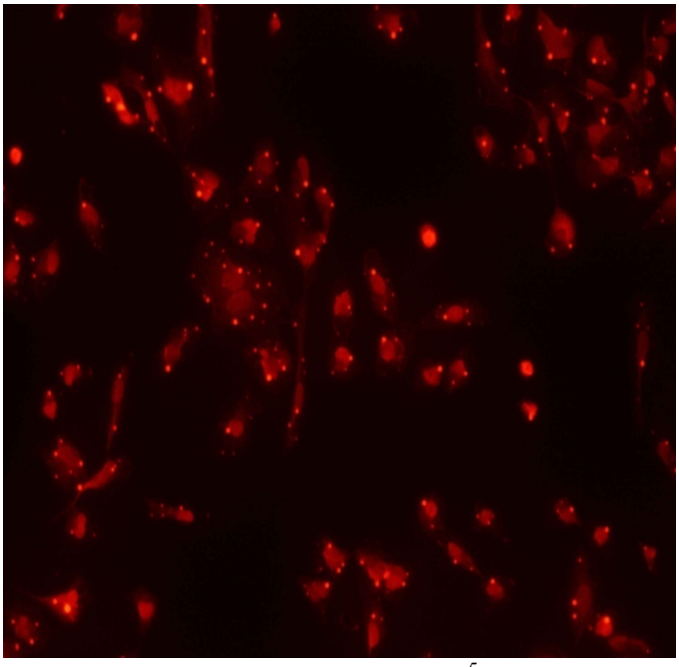

Figure S50. Compound **2** (5×10^{-5} M) treated with *m*–CPBA.

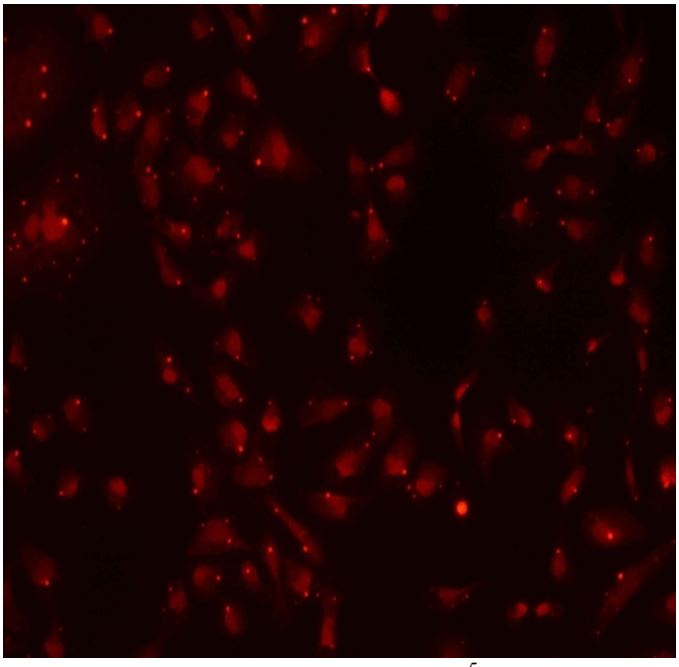

Figure S51. Compound **2** (5×10^{-5} M) treated with *m*–CPBA.

Table S2: Crystallographic data for compounds **7**, **8** and **9**.

Compound Number	**7**	**8**	**9**
empirical formula	$C_{31}H_{29}BF_2N_2O_3S_3$	$C_{31}H_{29}BF_2N_2O_4S_3$	$C_{12}H_{13}B1F_2N_2$
fw	622.55	638.55	234.05
temperature (K)	296(2)	296(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	C2/c	C2/c	P2(1)/c
a (Å)	37.899(9)	38.241(9	6.350(3)
b (Å)	7.743(2)	7.6428(18)	13.032(7)
c (Å)	25.029(7)	25.192(7)	14.253(7)
α (deg)	90.00	90.00	90.00
β (deg)	122.015(11)	121.40(2)	94.75(2)
γ (deg)	90.00	90.00	90.00
V ($Å^3$)	6227(3)	6285(3)	1175.4(10)
Z	8	8	4
density (Mg/m^3)	1.328	1.350	1.323
abs coeff (mm^{-1})	0.285	0.286	0.100
F(000)	2592	2656	488
crystal size	0.3×0.2× 0.15	0.5×0.3×0.2	0.3×0.25× 0.15
θ range for data collection	1.65 −27.90	1.25 – 23.21	2.12 − 32.15
reflns colld	28247	27214	16333
indep reflns	7373	4422	4133
R (*int*)	0.1082	0.0713	0.0857
absorpt correction	multi–scan	multi–scan	multi–scan
max and min transmn	0.941and 0.930	0.941 and 0.930	0.941 and 0.930
data/restraint/parameters	7373/0/ 385	4422/0/ 394	4133/0/ 157
GOF on F^2	1.009	1.005	1.031
final R indices	R1 = 0.0888	R1 = 0.0508	R1 = 0.0992
$[I > 2\sigma(I)]$	wR2 = 0.2208	wR2 = 0.1466	wR2 = 0.2003
R indices	R1 = 0.2123	R1 = 0.0709	R1 = 0.2216
(all data)[a]	wR2 = 0.2866	wR2 = 0.1770	wR2 = 0.2524

Table S3: Bond lengths [Å] for Compound **7** (nchu66–1).

B–F(2)	1.367(6)	C(5)–C(11)	1.479(6)
B–F(1)	1.388(7)	C(6)–C(7)	1.437(6)
B–N(1)	1.535(7)	C(7)–C(8)	1.355(6)
B–N(2)	1.559(7)	C(7)–C(16)	1.501(7)
N(1)–C(1)	1.367(6)	C(8)–C(9)	1.393(7)
N(1)–C(4)	1.392(6)	C(9)–C(17)	1.488(7)
N(2)–C(9)	1.345(6)	C(10)–C(11)	1.356(6)
N(2)–C(6)	1.394(5)	C(11)–C(12)	1.431(6)
S(1)–C(10)	1.715(5)	C(12)–C(13)	1.357(6)
S(1)–C(13)	1.716(6)	C(18)–C(19)	1.370(8)
S(2)–O(1)	1.398(5)	C(18)–C(23)	1.395(7)
S(2)–O(2)	1.436(4)	C(19)–C(20)	1.385(8)
S(2)–C(18)	1.746(5)	C(20)–C(21)	1.365(9)
S(2)–C(13)	1.762(5)	C(21)–C(22)	1.366(10)
S(3)–O(3)	1.457(5)	C(21)–C(24)	1.524(9)
S(3)–C(25)	1.794(6)	C(22)–C(23)	1.362(8)
S(3)–C(10)	1.803(5)	C(25)–C(26)	1.360(8)
C(1)–C(2)	1.388(7)	C(25)–C(30)	1.361(8)
C(1)–C(15)	1.504(7)	C(26)–C(27)	1.349(10)
C(2)–C(3)	1.379(7)	C(27)–C(28)	1.365(11)
C(3)–C(4)	1.437(7)	C(28)–C(29)	1.394(12)
C(3)–C(14)	1.501(7)	C(28)–C(31)	1.535(10)
C(4)–C(5)	1.408(6)	C(29)–C(30)	1.360(10)
C(5)–C(6)	1.398(6)		

Table S4: Bond angles [°] for Compound **7** (nchu66–1).

F(2)–B–F(1)	109.8(5)	C(5)–C(6)–C(7)	132.0(4)
F(2)–B–N(1)	110.9(5)	C(8)–C(7)–C(6)	105.8(4)
F(1)–B–N(1)	110.1(4)	C(8)–C(7)–C(16)	125.0(5)
F(2)–B–N(2)	109.7(4)	C(6)–C(7)–C(16)	129.2(5)
F(1)–B–N(2)	109.1(5)	C(7)–C(8)–C(9)	109.7(4)
N(1)–B–N(2)	107.1(4)	N(2)–C(9)–C(8)	108.8(4)
C(1)–N(1)–C(4)	107.9(4)	N(2)–C(9)–C(17)	122.9(5)
C(1)–N(1)–B	125.9(4)	C(8)–C(9)–C(17)	128.3(5)
C(4)–N(1)–B	126.0(4)	C(11)–C(10)–S(1)	114.3(4)
C(9)–N(2)–C(6)	108.1(4)	C(11)–C(10)–S(3)	127.6(4)
C(9)–N(2)–B	127.1(4)	S(1)–C(10)–S(3)	117.8(3)
C(6)–N(2)–B	124.8(4)	C(10)–C(11)–C(12)	110.1(4)
C(10)–S(1)–C(13)	90.0(2)	C(10)–C(11)–C(5)	125.6(4)
O(1)–S(2)–O(2)	120.2(3)	C(12)–C(11)–C(5)	124.3(4)
O(1)–S(2)–C(18)	108.2(3)	C(13)–C(12)–C(11)	113.0(5)
O(2)–S(2)–C(18)	109.3(3)	C(12)–C(13)–S(1)	112.6(4)
O(1)–S(2)–C(13)	107.3(3)	C(12)–C(13)–S(2)	126.9(4)
O(2)–S(2)–C(13)	106.9(3)	S(1)–C(13)–S(2)	120.6(3)
C(18)–S(2)–C(13)	103.8(2)	C(19)–C(18)–C(23)	119.2(5)
O(3)–S(3)–C(25)	108.3(3)	C(19)–C(18)–S(2)	120.3(4)
O(3)–S(3)–C(10)	103.2(3)	C(23)–C(18)–S(2)	120.4(5)
C(25)–S(3)–C(10)	99.1(2)	C(18)–C(19)–C(20)	118.9(6)
N(1)–C(1)–C(2)	108.9(5)	C(21)–C(20)–C(19)	122.4(6)
N(1)–C(1)–C(15)	122.8(5)	C(20)–C(21)–C(22)	117.6(6)
C(2)–C(1)–C(15)	128.2(5)	C(22)–C(21)–C(24)	121.5(7)
C(3)–C(2)–C(1)	109.4(5)	C(20)–C(21)–C(24)	120.8(8)
C(2)–C(3)–C(4)	105.7(5)	C(23)–C(22)–C(21)	121.9(6)
C(2)–C(3)–C(14)	124.7(5)	C(22)–C(23)–C(18)	119.8(6)
C(4)–C(3)–C(14)	129.6(5)	C(30)–C(25)–C(26)	121.3(6)
N(1)–C(4)–C(5)	119.7(4)	C(26)–C(25)–S(3)	115.8(5)
N(1)–C(4)–C(3)	108.0(4)	C(30)–C(25)–S(3)	122.9(5)
C(5)–C(4)–C(3)	132.3(5)	C(27)–C(26)–C(25)	118.8(6)
C(6)–C(5)–C(4)	121.5(4)	C(26)–C(27)–C(28)	121.9(7)
C(6)–C(5)–C(11)	119.3(4)	C(27)–C(28)–C(29)	118.4(6)
C(4)–C(5)–C(11)	119.1(4)	C(29)–C(28)–C(31)	118.6(10)
N(2)–C(6)–C(5)	120.4(4)	C(27)–C(28)–C(31)	123.0(10)
N(2)–C(6)–C(7)	107.6(4)	C(30)–C(29)–C(28)	119.8(7)
C(25)–C(30)–C(29)	119.8(7)		

Table S5: Bond lengths [Å] for Compound **8** (nchu85–1).

B–F(1)	1.386(6)	C(5)–C(6)	1.403(6)
B–F(2)	1.397(7)	C(5)–C(11)	1.494(6)
B–N(2)	1.536(7)	C(6)–C(7)	1.432(6)
B–N(1)	1.542(7)	C(7)–C(8)	1.380(7)
N(1)–C(1)	1.352(5)	C(7)–C(30)	1.507(7)
N(1)–C(4)	1.404(5)	C(8)–C(9)	1.395(7)
N(2)–C(9)	1.358(6)	C(9)–C(31)	1.492(7)
N(2)–C(6)	1.412(5)	C(10)–C(11)	1.383(6)
S(1)–C(13)	1.706(5)	C(11)–C(12)	1.409(6)
S(1)–C(10)	1.720(5)	C(12)–C(13)	1.368(6)
S(2)–O(2)	1.423(5)	C(14)–C(19)	1.376(7)
S(2)–O(1)	1.465(5)	C(14)–C(15)	1.394(7)
S(2)–C(14)	1.730(5)	C(15)–C(16)	1.350(8)
S(2)–C(10)	1.771(5)	C(16)–C(17)	1.350(8)
S(3)–O(3)	1.419(4)	C(17)–C(18)	1.391(9)
S(3)–O(4)	1.440(4)	C(17)–C(20)	1.535(9)
S(3)–C(21)	1.745(5)	C(18)–C(19)	1.383(8)
S(3)–C(13)	1.765(5)	C(21)–C(26)	1.385(7)
C(1)–C(2)	1.393(6)	C(21)–C(22)	1.388(7)
C(1)–C(29)	1.494(7)	C(22)–C(23)	1.379(8)
C(2)–C(3)	1.377(6)	C(23)–C(24)	1.378(8)
C(3)–C(4)	1.428(6)	C(24)–C(25)	1.382(9)
C(3)–C(28)	1.505(6)	C(24)–C(27)	1.519(8)
C(4)–C(5)	1.396(6)	C(25)–C(26)	1.370(8)

Table S6: Bond angles [°] for Compound **8** (nchu85–1).

F(1)–B–F(2)	109.2(5)	C(6)–C(5)–C(11)	119.1(4)
F(1)–B–N(2)	110.3(4)	C(5)–C(6)–N(2)	119.5(4)
F(2)–B–N(2)	109.6(4)	C(5)–C(6)–C(7)	132.9(5)
F(1)–B–N(1)	110.4(4)	N(2)–C(6)–C(7)	107.6(4)
F(2)–B–N(1)	109.7(4)	C(8)–C(7)–C(6)	106.3(4)
N(2)–B–N(1)	107.7(4)	C(8)–C(7)–C(30)	125.0(5)
C(1)–N(1)–C(4)	108.0(4)	C(6)–C(7)–C(30)	128.7(5)
C(1)–N(1)–B	126.7(4)	C(7)–C(8)–C(9)	109.0(5)
C(4)–N(1)–B	125.3(4)	N(2)–C(9)–C(8)	109.3(4)
C(9)–N(2)–C(6)	107.7(4)	N(2)–C(9)–C(31)	122.5(5)
C(9)–N(2)–B	126.8(4)	C(8)–C(9)–C(31)	128.1(5)
C(6)–N(2)–B	125.5(4)	C(11)–C(10)–S(1)	112.7(3)
C(13)–S(1)–C(10)	90.7(2)	C(11)–C(10)–S(2)	130.8(4)
O(2)–S(2)–O(1)	120.8(3)	S(1)–C(10)–S(2)	116.3(3)
O(2)–S(2)–C(14)	108.8(3)	C(10)–C(11)–C(12)	110.9(4)
O(1)–S(2)–C(14)	108.1(3)	C(10)–C(11)–C(5)	126.1(4)
O(2)–S(2)–C(10)	108.6(3)	C(12)–C(11)–C(5)	123.1(4)
O(1)–S(2)–C(10)	103.1(3)	C(13)–C(12)–C(11)	113.1(4)
C(14)–S(2)–C(10)	106.5(2)	C(12)–C(13)–S(1)	112.6(4)
O(3)–S(3)–O(4)	119.5(2)	C(12)–C(13)–S(3)	128.2(4)
O(3)–S(3)–C(21)	108.9(3)	S(1)–C(13)–S(3)	119.2(3)
O(4)–S(3)–C(21)	108.9(2)	C(19)–C(14)–C(15)	118.9(5)
O(3)–S(3)–C(13)	107.7(2)	C(19)–C(14)–S(2)	120.2(4)
O(4)–S(3)–C(13)	106.3(2)	C(15)–C(14)–S(2)	120.8(4)
C(21)–S(3)–C(13)	104.6(2)	C(16)–C(15)–C(14)	119.5(5)
N(1)–C(1)–C(2)	108.9(4)	C(17)–C(16)–C(15)	123.3(6)
N(1)–C(1)–C(29)	122.5(4)	C(16)–C(17)–C(18)	117.7(6)
C(2)–C(1)–C(29)	128.5(5)	C(16)–C(17)–C(20)	122.7(8)
C(3)–C(2)–C(1)	109.4(4)	C(18)–C(17)–C(20)	119.6(8)
C(2)–C(3)–C(4)	105.8(4)	C(19)–C(18)–C(17)	120.7(5)
C(2)–C(3)–C(28)	124.7(4)	C(14)–C(19)–C(18)	119.8(5)
C(4)–C(3)–C(28)	129.5(4)	C(26)–C(21)–C(22)	119.6(5)
C(5)–C(4)–N(1)	120.1(4)	C(26)–C(21)–S(3)	121.5(4)
C(5)–C(4)–C(3)	132.0(4)	C(22)–C(21)–S(3)	119.0(4)
N(1)–C(4)–C(3)	107.9(4)	C(23)–C(22)–C(21)	118.9(5)
C(4)–C(5)–C(6)	121.9(4)	C(24)–C(23)–C(22)	122.0(6)
C(4)–C(5)–C(11)	119.0(4)	C(23)–C(24)–C(25)	118.3(6)
C(23)–C(24)–C(27)	121.9(8)	C(26)–C(25)–C(24)	120.7(6)
C(25)–C(24)–C(27)	119.8(7)	C(25)–C(26)–C(21)	120.4(6)

Table S7: Bond lengths [Å] for Compound **9** (nchu82–1).

B–F(2)	1.382(4)	C(2)–C(10)	1.502(4)
B–F(1)	1.404(4)	C(3)–C(4)	1.407(4)
B–N(1)	1.542(4)	C(4)–C(5)	1.389(4)
B–N(2)	1.547(4)	C(5)–C(6)	1.376(4)
N(1)–C(1)	1.356(4)	C(6)–C(7)	1.428(4)
N(1)–C(4)	1.395(3)	C(7)–C(8)	1.377(4)
N(2)–C(9)	1.353(3)	C(7)–C(11)	1.497(4)
N(2)–C(6)	1.408(3)	C(8)–C(9)	1.403(4)
C(1)–C(2)	1.390(4)	C(9)–C(12)	1.491(4)
C(2)–C(3)	1.388(4)		

Table S8: Bond angles [°] for Compound **9** (nchu82–1).

F(2)–B–F(1)	108.5(2)	C(2)–C(3)–C(4)	108.6(2)
F(2)–B–N(1)	110.6(3)	C(5)–C(4)–N(1)	119.7(2)
F(1)–B–N(1)	110.0(2)	C(5)–C(4)–C(3)	132.5(2)
F(2)–B–N(2)	110.7(3)	N(1)–C(4)–C(3)	107.8(2)
F(1)–B–N(2)	109.3(2)	C(6)–C(5)–C(4)	122.6(2)
N(1)–B–N(2)	107.8(2)	C(5)–C(6)–N(2)	120.5(2)
C(1)–N(1)–C(4)	106.4(2)	C(5)–C(6)–C(7)	131.3(2)
C(1)–N(1)–B	128.3(2)	N(2)–C(6)–C(7)	108.1(2)
C(4)–N(1)–B	125.3(2)	C(8)–C(7)–C(6)	106.4(2)
C(9)–N(2)–C(6)	107.2(2)	C(8)–C(7)–C(11)	128.4(3)
C(9)–N(2)–B	128.7(2)	C(6)–C(7)–C(11)	125.2(3)
C(6)–N(2)–B	124.1(2)	C(7)–C(8)–C(9)	108.3(3)
N(1)–C(1)–C(2)	112.0(2)	N(2)–C(9)–C(8)	109.9(2)
C(3)–C(2)–C(1)	105.2(2)	N(2)–C(9)–C(12)	122.7(3)
C(3)–C(2)–C(10)	128.7(3)	C(8)–C(9)–C(12)	127.5(3)
C(1)–C(2)–C(10)	126.1(3)		

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