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Supporting Information

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Towards Unimolecular Luminescent Solar Concentrators: Bodipy-Based Dendritic Energy-Transfer Cascade with Panchromatic Absorption and Monochromatized Emission**

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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 spectrometry measurements were done at the Ohio State University Mass Spectrometry and Proteomics Facility, Ohio, U.S.A. For compounds **1**, **8** and **10**, mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS.

Quantum yield measurements and calculations were done using Rhodamine G6 (excitation 488 nm, water), Sulforhodamine 101(excitation 550 nm, ethanol) and Cresyl Violet (excitation 610 nm, methanol) as standard chromophores having quantum yields 0.95, 0.90 and 0.66 respectively. All absorbance values were below 0.1 to avoid self quenching. Following formula was used for calculations: [1]

$$\mathbf{Q = Q_R\ (I/I_R)*(A_R/A)*(n^2/n_R^2)}$$

where Q_R stands for quantum yield of reference, I and I_R for integrated area of emission spectrum for specific wavelength for sample and for standard respectively, A and A_R represents absorbance of corresponding wavelength for sample and standard, n and n_R refer to refractive indices of solvents in

which sample and standard compounds were dissolved respectively. Refractive index values were taken to be 1.333 for water, 1.3624 for ethanol and 1.329 for methanol. All samples except standards were dissolved in chloroform which has an n value of 1.49.

Lifetime measurements were done on a HORIBA Jobin Yvon fluorolog, FL-1057. The dye laser excitation was at 495, 609 and 667 nm NanoLED with pulse width less than 250 ps. The instrument response function was measured with an aqueous Ludox solution. The decays were analyzed with a multiexponential fitting function by iterative reconvolution and chi-square minimization. Results having χ^2's at around 1.0 were taken into consideration.

FRET efficiency was determined using time-resolved approach. Time resolved approach provides more accurate results since inner filter effect or errors associated with integration are lacking here. FRET rate constant and FRET efficiencies were calculated using formulas below:[2, 3]

$$\mathbf{k_{FRET} = 1/\tau_{DA} - 1/\tau_D}$$

$$\mathbf{\varepsilon_{FRET} = 1 - \tau_{DA}/\tau_D}$$

where τ_D and τ_{DA} refer to excited state decay time (lifetime) of donor in the absence and presence of acceptor respectively. For energy transfer from mono-styryl BODIPY steady state approach with following formula was used. ε_{FRET} was calculated from quantum yields.

$$\mathbf{k_{FRET} = 1/\tau_D \left[(1/\varepsilon_{FRET}) - 1\right]^{-1}}$$

2. Theoretical Calculations

We describe the coupled dynamics of the photon field and luminescent centers using a simplified model in terms of rate equations. Three optical centers absorb and emit from the photon density at a particular location as described below

$$\dot{n_1} = \int [P_{in}(\lambda) + P(\lambda)]\, a_1(\lambda)\, d\lambda - n_1 (r_{e,1} + r_{l,1} + r_{F,1\to 2}) \qquad \textbf{Eq.S1}$$

$$\dot{n_2} = \int [P_{in}(\lambda) + P(\lambda)]\, a_2(\lambda)\, d\lambda + n_1 r_{F,1\to 2} - n_2 (r_{e,2} + r_{l,2} + r_{F,2\to 3}) \qquad \textbf{Eq. S2}$$

$$\dot{n_3} = \int [P_{in}(\lambda) + P(\lambda)]\, a_3(\lambda)\, d\lambda + n_2 r_{F,2\to 3} - n_3 (r_{e,3} + r_{l,3}) \qquad \textbf{Eq. S3}$$

$$\dot{P}(\lambda) = -P(\lambda)\left(a_1(\lambda) + a_2(\lambda) + a_3(\lambda)\right) + \left(n_1 r_{e,1} e_1(\lambda) + n_2 r_{e,2} e_2(\lambda) + n_3 r_{e,3} e_3(\lambda)\right)\eta_t \qquad \textbf{Eq. S4}$$

Here, P(λ) shows the wavelength dependent photon number guided in the slab; n_1, n_2 and n_3 denote the number of excited centers; a_1, a_2 and a_3 denote absorption coefficients of corresponding centers; $e_1(\lambda)$, $e_2(\lambda)$ and $e_3(\lambda)$ denote the spectral distribution of light emission. The slab is being excited by an external light field with spectral distribution $P_{in}(\lambda)$ and $\eta_t \sim 0.75$ denotes the efficiency of emission into guided modes of the slab. The excitation is modeled as $P_{in}(\lambda)$ = Plaser if x=0, and $P_{in}(\lambda) = 0$ otherwise. The luminescence and near field energy transfer efficiencies are characterized by rates $r_{e,1}$,$r_{e,2}$,$r_{e,3}$ and $r_{F,1\text{-}2}$, $r_{F,2\text{-}3}$. Non-radiative losses are characterized by the rates $r_{l,1}$,$r_{l,2}$,$r_{l,3}$. The Monte-Carlo simulation is based on Eqs. S1, S2, S3, S4 using Gaussian emission and absorption profiles for individual centers. A narrow spectral distribution $P_{in}(\lambda)$ with a peak around 532 nm and 2 nm spectral width is used to model the laser excitation. Propagation of emitted light is approximated by an average propagation direction parallel to the horizontal axis. In the calculation of the spectra, multiple absorption/emission events occurring not between the excitation and collection points are ignored for sake of simplicity.

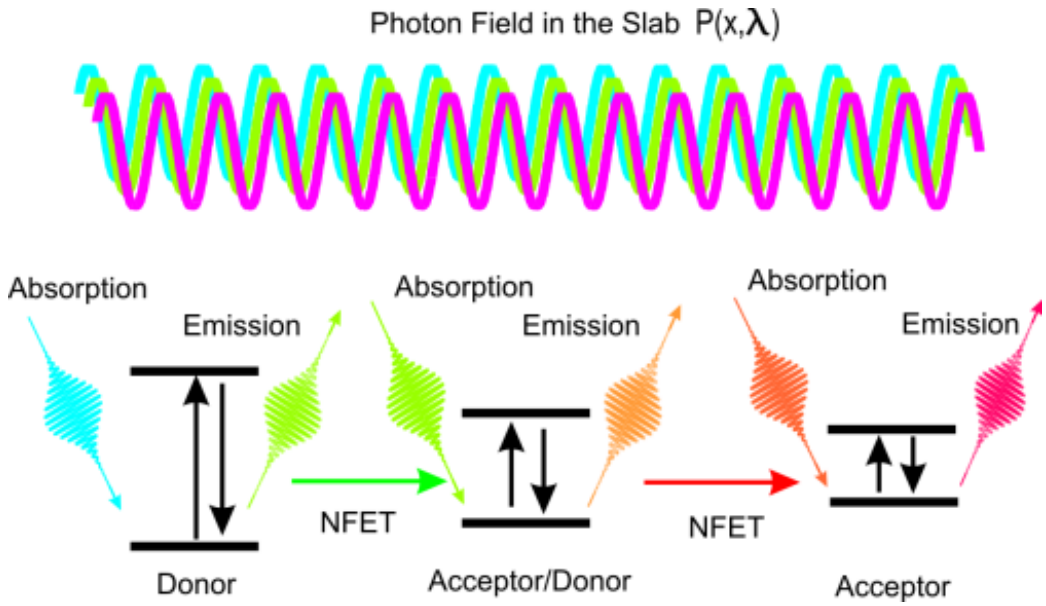


Figure S1. The luminescent centers interact with photon field inside the slab light-guide, as well as with the external excitation. The photon field is characterized by a distribution of energy to wavelengths and wavevectors (directions) as a function of distance. Simplified rate equations describe the dynamics of energy transfer between the photon field and luminescent centers due to absorption, emission and near-field energy transfer effects. In the schematic, non-radiative losses and losses due to escape from the slab are omitted for clarity.

3. Results

Fluorescence intensities of energy transfer cassettes and corresponding elements with equal absorbance at point of excitation were compared. For **ET-1** quenching of donor BODIPY and increase in acceptor distyryl BODIPY emission was shown in Figure 1 and 2, which indicates efficient energy transfer. Excitation at two different wavelengths (525 nm, 585 nm) were compared in Figure 3.

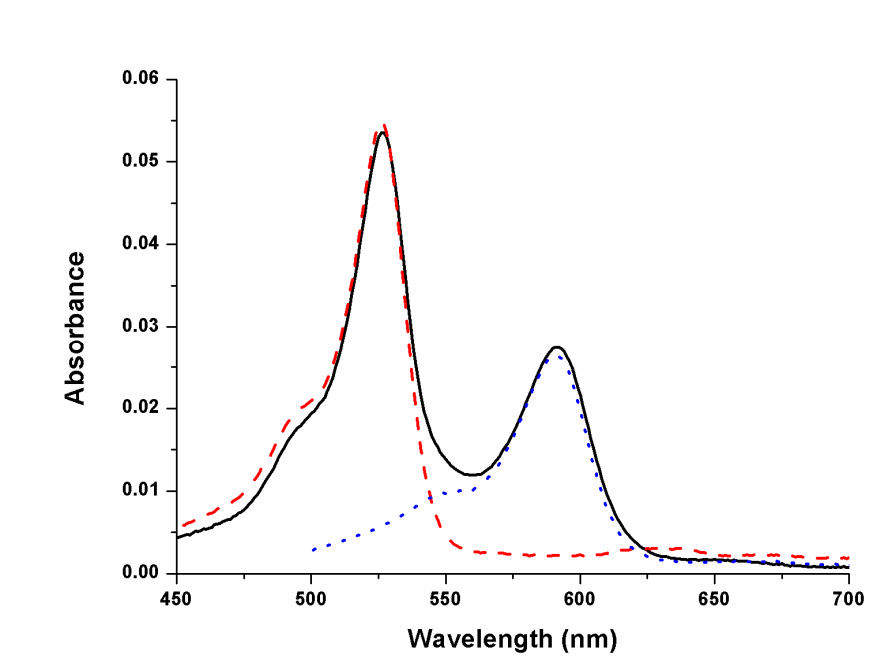


Figure S2. Absorbance spectra of compounds $\mathbf{B_1}$ (dashed), $\mathbf{C_1}$ (dot) and **ET-1** (solid).

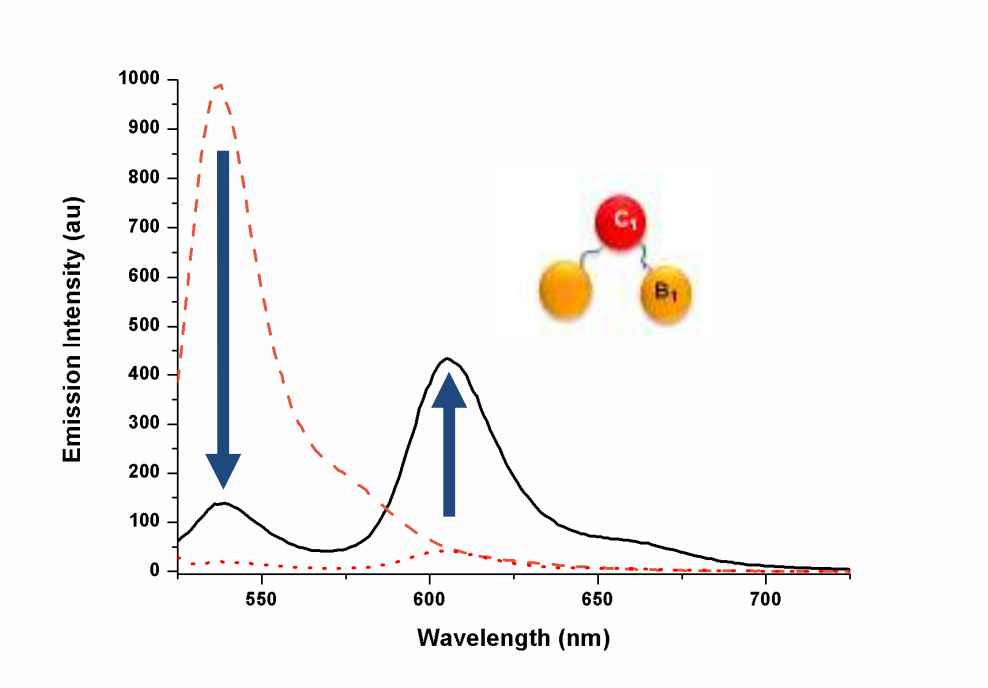


Figure S3. Emission spectra of compounds $\mathbf{B_1}$ (dashed), $\mathbf{C_1}$ (dot) and **ET-1** (solid) with equal absorbance excited at 525 nm.

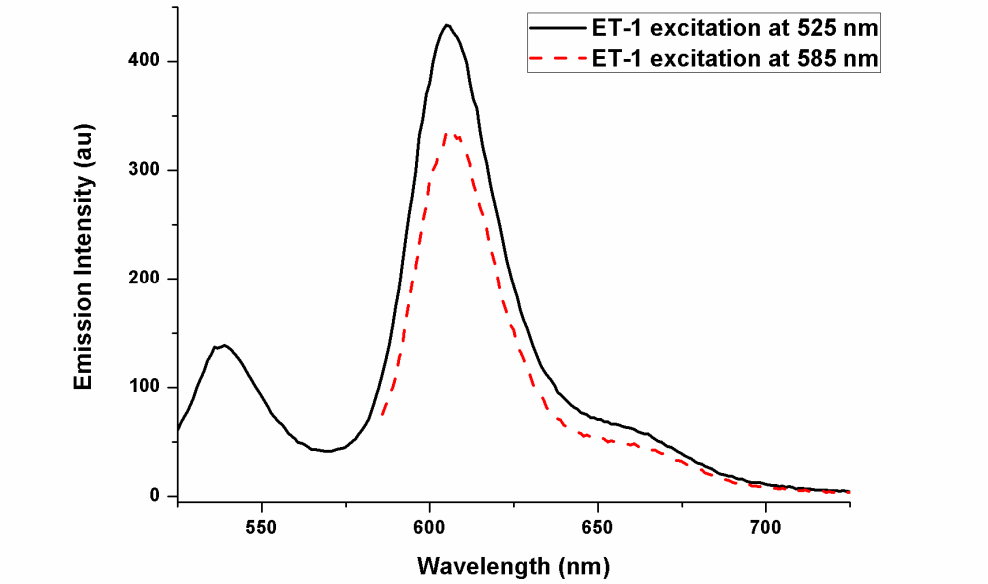


Figure S4. Comparison of emissions of **ET-1** excited at 525(solid line) and 585 nm (dashed line).

For **ET-2** quenching of donor monostyryl-BODIPY and increase in acceptor distyryl BODIPY emission was shown in Figure 4 and 5, which indicates efficient channeling of energy to acceptor chromophore. Excitations at two different wavelengths (585 nm, 645 nm) were compared in Figure 6.

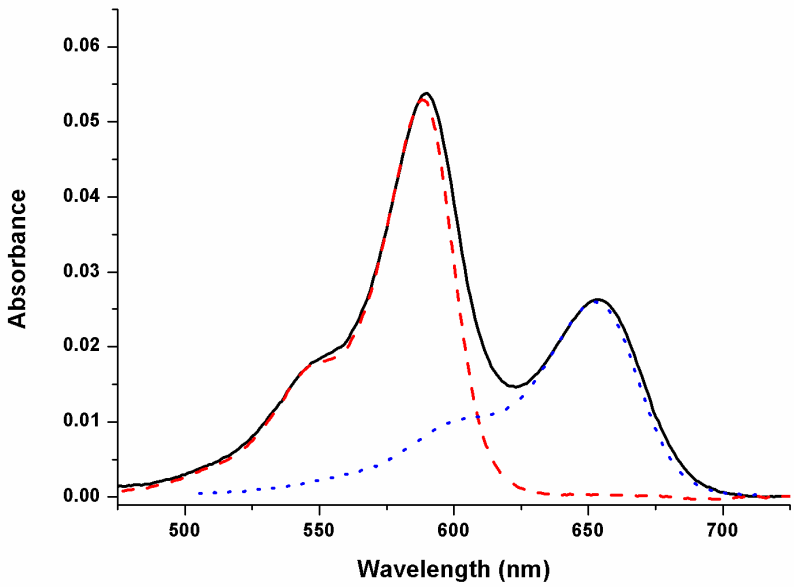


Figure S5. Absorbance spectra of compounds $\mathbf{D_1}$ (dot), $\mathbf{C_2}$ (dashed), **ET-2** (solid).

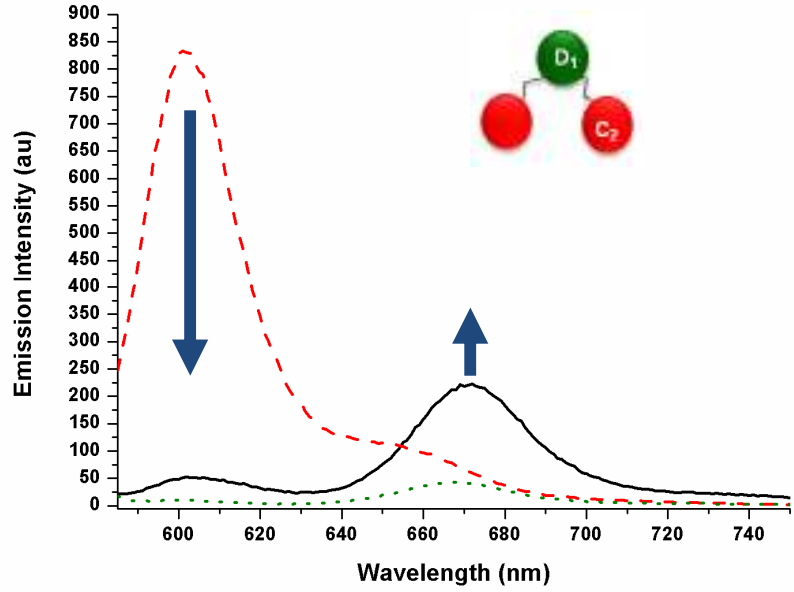


Figure S6. Emission spectra of compounds $\mathbf{D_1}$ (dot), $\mathbf{C_2}$ (dashed) and **ET-2** (solid) with equal absorbance excited at 585 nm.

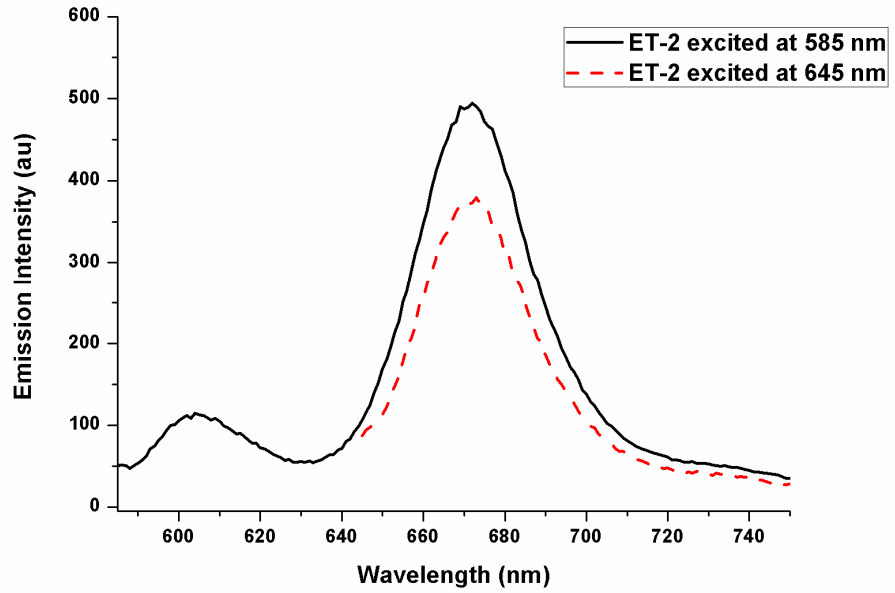


Figure S7. Comparison of emission of **ET-2** excited at 585 nm (solid) and 645 nm (dashed).

For **ET-3** decrease in donor monostyryl-BODIPY and increase in acceptor distyryl BODIPY emission was shown in Figure 7 and 8. Excitations at two different wavelengths (585 nm, 645 nm) were compared in Figure 9.

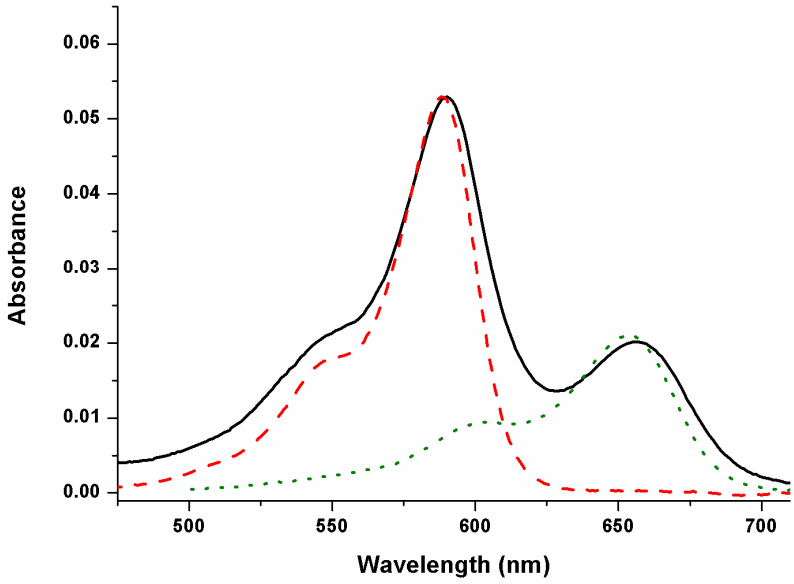


Figure S8. Absorbance spectra of $\mathbf{D_2}$(dot), $\mathbf{C_2}$ (dashed), **ET-2** (solid).

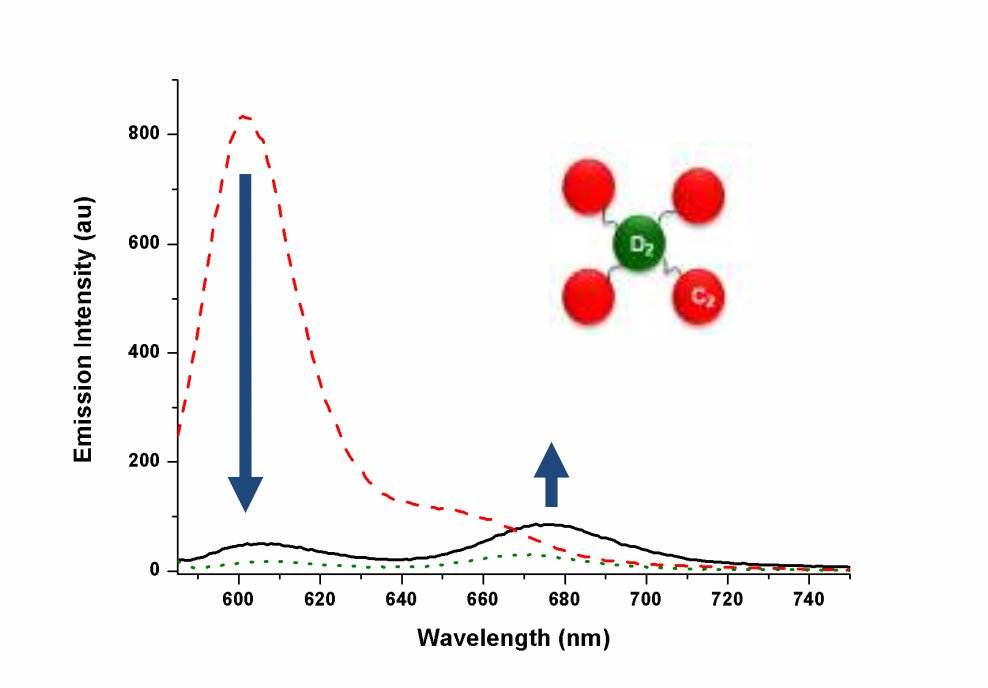


Figure S9. Emission spectra of compounds $\mathbf{D_2}$ (dot), $\mathbf{C_2}$ (dashed), **ET-2** (solid) with equal absorbance excited at 585 nm.

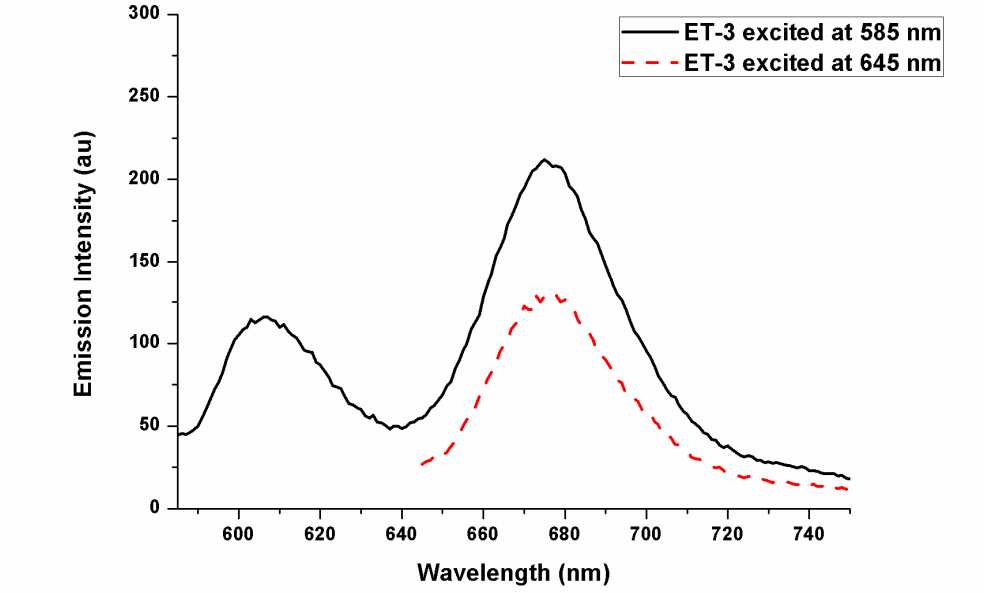


Figure S10. Comparison of emission of **ET-3** excited at 585 nm (solid line), 645 nm (dashed line).

For **SC-1** decrease in donor BODIPY, monostyryl-BODIPY and increase in acceptor distyryl BODIPY emission was shown in Figure 10, 11 and 12. Excitations at three different wavelengths (525 nm, 585 nm, 645 nm) were compared in Figure 13.

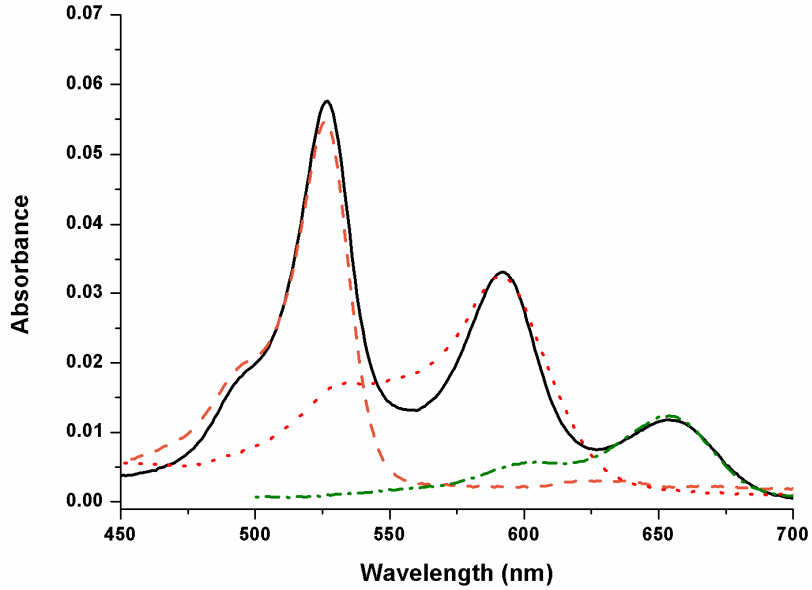


Figure S11. Absorbance spectra of compounds $\mathbf{B_1}$ (dashed), $\mathbf{C_2}$ (dot), $\mathbf{D_2}$ (dot-dashed), **SC-1** (solid).

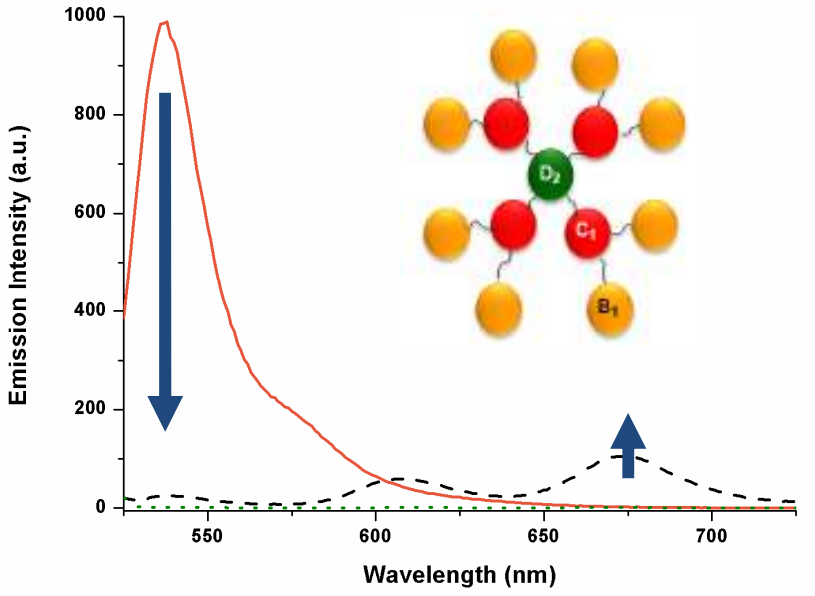


Figure S12. Emission spectra of compounds $\mathbf{B_1}$ (solid), $\mathbf{D_2}$ (dot), **SC-1** (dashed) with equal absorbance excited at 525 nm.

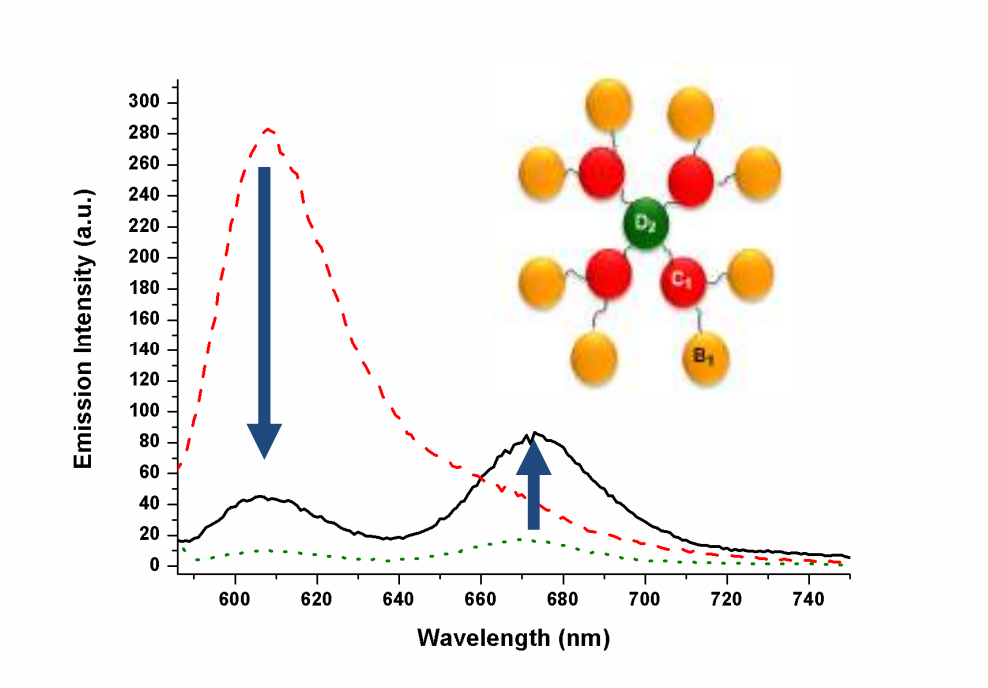


Figure S13. Emission spectra of compounds $\mathbf{C_1}$ (dashed), $\mathbf{D_2}$ (dot), **SC-1** (solid) with equal absorbance excited at 585 nm.

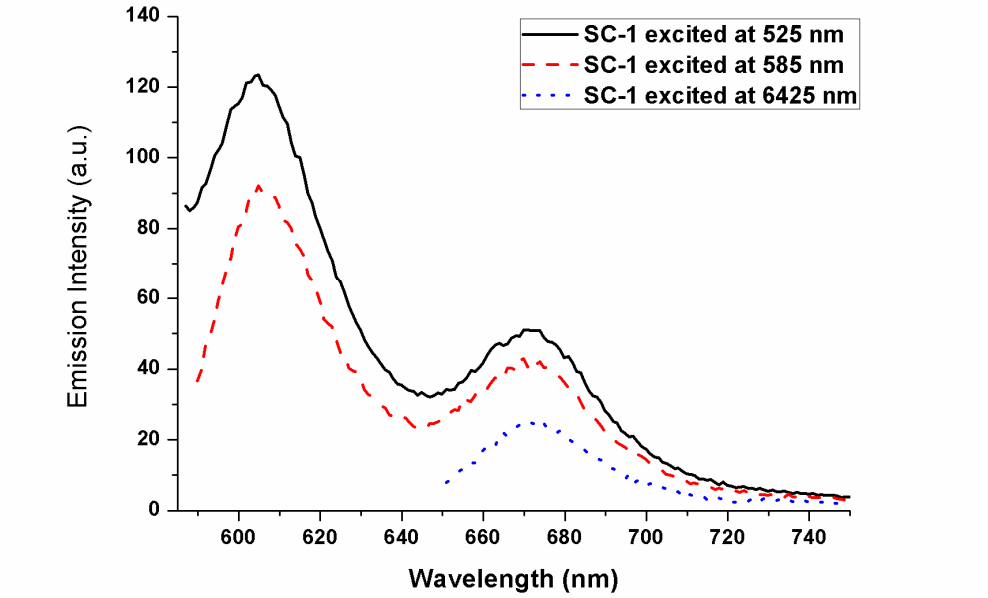
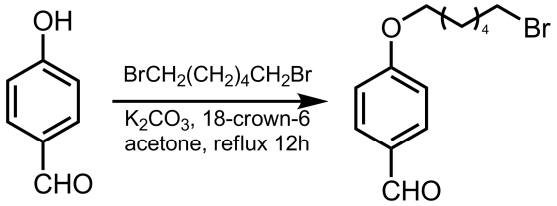


Figure S14. Comparison of emission of **SC-1** excited at 525 nm (solid), 585 nm (dashed) and 645 nm (dot).

4. Synthesis

4.1 Synthesis of 4-(6-bromohexoxy)benzaldehyde (1)

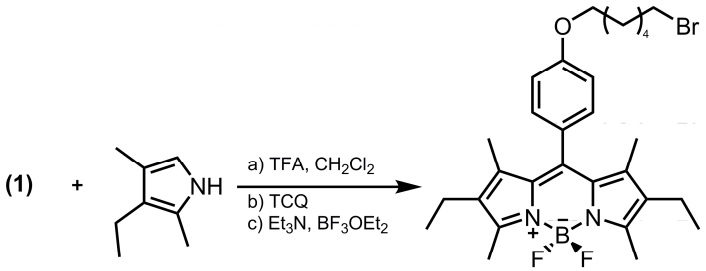


(1)

4-hydroxybenzaldehyde (5 g, 41 mmol) and 1, 6 dibromohexane (2 g, 82 mmol) were dissolved in acetone (150 ml). K_2CO_3 (17.2 g, 123 mmol) and catalytic amount of benzo-18-crown-6 were added. The reaction mixture was refluxed for 12h. Then, acetone was evaporated in vacuo and extracted with water and chloroform. Organic layer was dried with Na_2SO_4 and evaporated in vacuo**.** The product was purified by silica gel column chromatography using $CHCl_3$/Hexane (75:25, v/v). Fraction containing compound **1** was collected then the solvent was removed under reduced pressure (6.7 mmol, 1.906 g, 16%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.35 (m, 4H), 1.65 (m, 4H), 3.4 (t, *J*= 6.68 Hz, 2H), 3.88 (t, *J*= 6.4 Hz, 2H), 6. 82 (d, *J*= 8.76 Hz, 2H), 7.68 (d, *J*= 8.64 Hz, 2H), 9.7 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 25.24, 26.51, 28.83, 32.39, 44.91, 68.09, 114.68, 129.73, 131.86, 164.08, 190.58. HRMS (TOF-ESI): m/z calcd for $C_{13}H_{17}BrO_2$: 285.04902 $[M+H]^+$; found: 285.05413 $[M+H]^+$, Δ = 17.9 ppm.

4.2 Synthesis of Compound 2



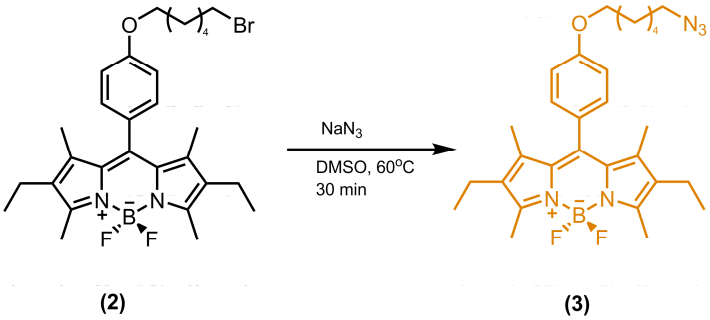
(2)

CH_2Cl_2 (300 ml) was purged with Ar for 30 min. 4-(6-bromohexoxy)benzaldehyde **1** (1.089 g, 3.82 mmol) and 2,4-dimethyl pyrrole (0.94 g, 7.7 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 (0.93 g, 3.82 mmol) was added and the reaction mixture was stirred at room temperature for 45 min. Then triethyl amine (8 ml) and boron trifluoride diethyl etherate (8 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 $CHCl_3$ as mobile phase. Fraction containing compound **2** was collected then the solvent was removed under reduced pressure (670 mg, 1.2 mmol, 31%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (t, J= 7.52, 6H), 1.35 (s, 6H), 1.58 (m, 4H), 1.85 (m, 4H), 2.3 (q, J= 7.56, 4H), 2.55 (s, 6H), 3.59 (t, *J*= 6.64 Hz, 2H), 4.05 (t, *J*= 6.45 Hz, 2H), 7.0 (d, *J*= 8.56 Hz, 2H), 7.15 (d, *J*= 8.56 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.84, 12.46, 14.61, 17.06, 25.43, 26.67, 29.11, 32.48, 44.96, 67.87, 114.95, 127.78, 129.44, 130.10, 132.60, 138.43, 140.0, 153.46, 159.47.

4.3 Synthesis of Compound 3

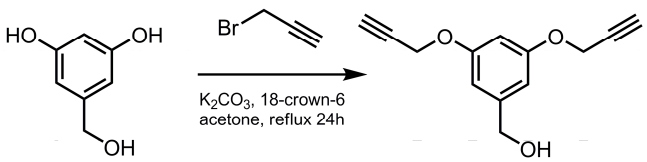


(2) (3)

Compound **2** (190 mg, 0.34 mmol) was dissolved in 20 ml DMSO. Excess amount of sodium azide (600 mg, 9.23 mmol) was added. The reaction mixture was stirred for 30 minutes at 60°C. After 30 minutes, sample was extracted with water and $CHCl_3$ a few times to get rid of DMSO and excess NaN_3. Organic layer containing compound **3** was dried with Na_2SO_4 and evaporated under reduced pressure No further purification was required.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (t, J= 7.52 Hz, 6H), 1.35 (s, 6H), 1.54 (m, 4H), 1.68 (m, 2H), 1.85 (m, 2H), 2.3 (q, J= 7.56 Hz, 4H), 2.55 (s, 6H), 3.32 (t, *J*= 6.64 Hz, 2H), 4.05 (t, *J*= 6.45 Hz, 2H), 7.0 (d, *J*= 8.56 Hz, 2H), 7.15 (d, *J*= 8.56 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.84, 12.46, 14.62, 17.07, 25.71, 26.56, 28.80, 29.13, 51.38, 67.86, 114.95, 127.77, 129.44, 131.19, 132.61, 138.43, 140.33, 153.46, 159.46. HRMS-ESI: calculated for M+H 522.3216, found 522.3240, Δ= 0.8 ppm.

4.4 Synthesis of Compound 4



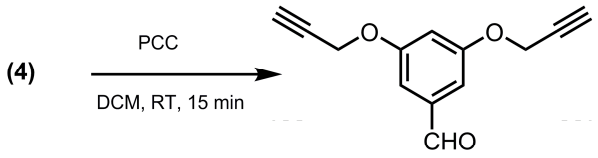
(4)

5-(hydroxymethyl)benzene-1,3-diol (5 g, 35.7 mmol) was dissolved in 200 ml acetone in round bottom flask. K_2CO_3 (5 g, 35.7 mmol) and catalytic amount of 18-crown-6 were added. Propargyl

bromide (10.5 g, 71.4 mmol) was added to the flask and the reaction mixture was refluxed for 24h. Then, acetone was evaporated in vacuo and extracted with water and chloroform. Organic layer was dried with Na_2SO_4 and evaporated in vacuo**.** The product was purified by silica gel column chromatography using $CHCl_3$/Methanol (97:3, v/v). Fraction containing compound **4** was collected then the solvent was removed under reduced pressure (30.5 mmol, 6.6 g, 86%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 2.45 (s, 2H), 4.60 (s, 6H), 6.49 (s, 1H), 6.51 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 55.92, 65.12, 75.67, 78.37, 101.52, 106.23, 143.59, 158.86 as reported elsewhere.[4]

4.5 Synthesis of Compound 5

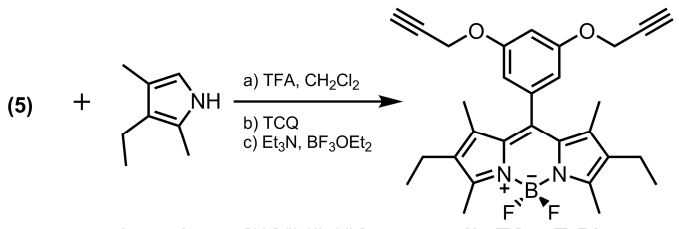


(5)

Compound **4** (1 g, 4.625 mmol) was dissolved in 50 ml dichloromethane. Pyridinium chlorochromat (2 g, 9.25 mmol) was added and the reaction mixture was stirred at room temperature. After 15 minutes all of the compound **4** was converted to compound **5** as followed by TLC. Dichloromethane was evaporated in vacuo and the product was purified by silica gel column chromatography using $CHCl_3$ as mobile phase. Fraction containing compound **5** was collected then the solvent was removed under reduced pressure.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 2.58 (t, J=2.36 Hz, 2H), 4.73 (d, J=2.40 Hz, 4H), 6.85 (t, J= 2.32 Hz, 1H), 7.1 (d, J=2.36 Hz, 2H), 9.9 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 56.15, 76.27, 77.78, 108.8, 138.39, 159.09, 191.42.

4.6 Synthesis of Compound 6



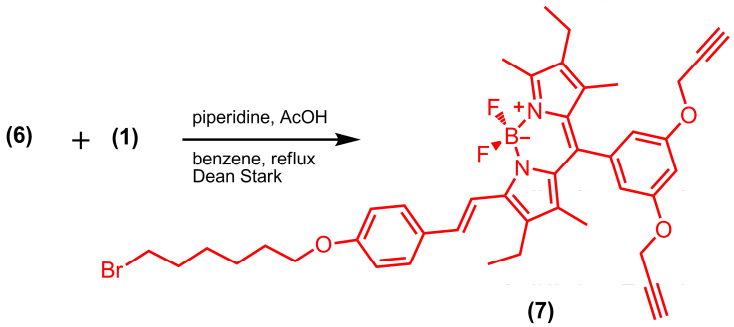
(6)

CH_2Cl_2 (300 ml) was purged with Ar for 30 minutes. Compound **5** (1.0 g, 4.6 mmol) and 2,4-dimethyl pyrrole (1.141 g, 9.2 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 (1.12 g, 4.6 mmol) was added and the reaction mixture was stirred at room temperature for 45 min. Then triethyl amine (8 ml) and boron trifluoride diethyl etherate (8 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 $CHCl_3$: Hexane (66:33, v/v) as mobile phase. Fraction containing compound **6** was collected then the solvent was removed under reduced pressure (470 mg, 0.96 mmol, 21%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (t, J= 7.48 Hz, 6H), 1.44 (s, 6H), 2.3 (q, J=7.56 Hz, 4H), 2.5-2.55 (m, 6H+2H), 4.69 (d, J=2.08 Hz, 4H), 6.6 (d, J=2.28 Hz, 2H), 6.7 (t, J=2.28 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.54, 12.50, 14.63, 17.07, 56.04, 75.94, 78.10, 103.50, 107.93, 130.39, 132.80, 137.56, 138.40, 139.18, 153.89, 159.35. HRMS-ESI: calculated for M+Na 489.2525, found 489.2509, Δ= -3.2 ppm.

4.7 Synthesis of Compound 7



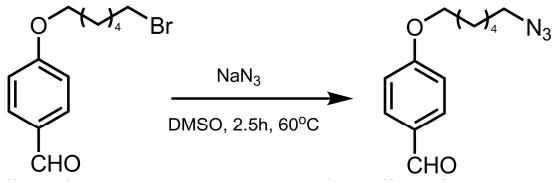
Compound **1** (72 mg, 0.25 mmol) and compound **6** (122 mg, 0.25 mmol) were dissolved in benzene (45 ml). Piperidine (0.2 ml) and glacial acetic acid (0.2 ml) were added. The solution was refluxed using Dean-Stark apparatus. When the solution was concentrated, reaction was followed by TLC until purple-colored product became the major product. Then, benzene was evaporated in vacuo. It was extracted with $CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using Ethyl Acetate: Hexane (25:75, v/v) as mobile phase. Fraction containing compound **7** was collected then the solvent was removed under reduced pressure (78 mg, 0.1 mmol, 29%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (t, J= 6.48 Hz, 3H), 1.18 (t, J= 7.56 Hz), 1.45-1.55 (m, 3H + 3H + 4H), 1.82 (m, 4H), 2.33 (q, J=7.52 Hz, 2H), 2.5-2.65 (m, 3H + 2H + 2H), 3.6 (t, J= 6.68 Hz, 2H), 4.05 (t, J= 6.44 Hz, 2H), 4.69 (s, 4H), 6.6 (d, J=2.32 Hz, 2H), 6.7 (t, J=2.32 Hz, 1H), 6.9 (d, J= 8.6 Hz, 2H), 7.19 (d, J= 16.69 Hz, 1H), 7.5 (d, J= 8.72 Hz, 2H), 7.62 (d, J= 16.72 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.27, 11,61, 12.75, 14.10, 14.56, 17.12, 18.33, 25.41, 26.66, 29.08, 30.32, 32.52, 44.99, 56.07,

67.84, 75.91, 78.09, 103.57, 108.14, 114.74, 117.89, 128.61, 130.19, 135.00, 137.73, 159.35, 159.58. HRMS-ESI: calculated for M+Na 755.2831, found 755.2811, Δ= 2.6 ppm.

4.8 Synthesis of Compound 8

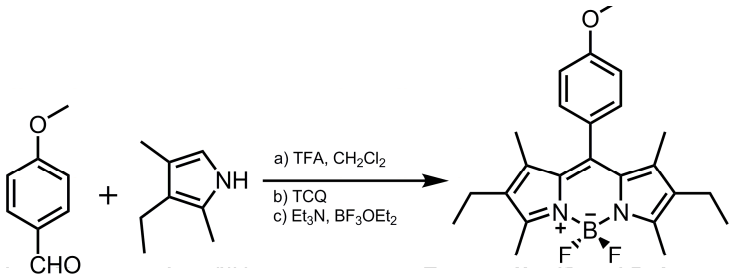
Compound **1** (1.5 g, 5.3 mmol) was dissolved in 25 ml DMSO. Sodium azide (1.37 g, 21.2 mmol) was added and the reaction mixture was stirred at 60°C for 2.5 hours. Then, it was extracted with water and $CHCl_3$ a few times and organic layer was collected, dried with Na_2SO_4 and evaporated under reduced pressure. No further purification was required.



(1) **(8)**

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.4-1.55 (m, 4H), 1.55-1.65 (m, 2H), 1.75-1.85 (m, 2H), 3.28 (t, J=6.80 Hz, 2H), 4.05 (t, J=6.40 Hz, 2H), 7.00 (d, J=8.76 Hz, 2H), 7.82 (d, J= 7.86 Hz, 2H), 9.86 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 25.57, 26.43, 28.74, 28.89, 51.31, 68.12, 114.73, 129.80, 131.96, 164.14, 190.75. HRMS (TOF-ESI): m/z calcd for $C_{13}H_{17}N_3O_2$: 248.13990 $[M+H]^+$; found: 248.14573 $[M+H]^+$, Δ = 23.5 ppm.

4.9 Synthesis of Compound 9



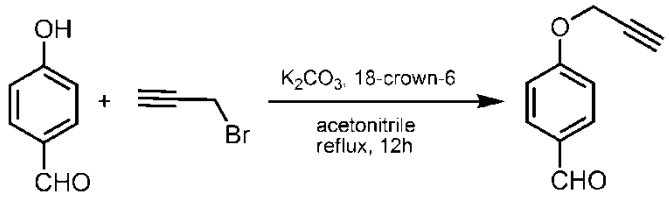
(9)

CH_2Cl_2 (300 ml) was purged with Ar for 30 min. 4-methoxy benzaldehyde (394 mg, 2.89 mmol) and 2,4-dimethyl pyrrole (0.75 g, 5.78 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 (0.72 g, 2.89 mmol) was added and the reaction mixture was stirred at room temperature for 45 min. Then triethyl amine (6 ml) and boron trifluoride diethyl etherate (6 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 $CHCl_3$ as mobile phase. Fraction containing compound **9** was collected then the solvent was removed under reduced pressure (412 mg, 1 mmol, 35%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (t, J= 7.52 Hz, 6H), 1.35 (s, 6H), 2.3 (q, J=7.56 Hz, 4H), 2.52 (s, 6H), 3.90 (s, 3H), 7.00 (d, J=8.76 Hz, 2H), 7.16 (d, J= 8.76 Hz, 2H), ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.81, 12.46, 14.61, 17.06, 55.30, 114.42, 127.87, 129.46, 131.19, 132.62, 138.43, 140.27, 153.48, 159.99. HRMS-ESI: calculated for M+H 411.2419, found 411.2424, Δ= 0.2 ppm.

4.10 Synthesis of Compound 10



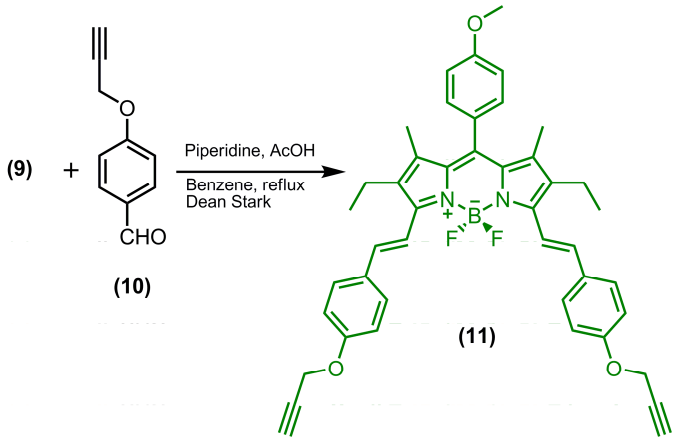
4-hydroxybenzaldehyde (4.9 g, 40 mmol) and propargyl bromide (5 g, 60 mmol) were dissolved in 100 ml acetonitrile. K_2CO_3 (11 g, mmol) and a few crystals of benzo-18-crown-6 were added. The reaction was refluxed until all 4-hydroxybenzaldehyde was consumed. The solvent was evaporated, extracted with water and $CHCl_3$. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$/Hexane (50:50, v/v). Fraction containing compound **10** was collected then the solvent was removed under reduced pressure (5.8 g, 91%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 9.92 (s, 1H), 7.87 (d, *J*=8.92 Hz, 2H), 7.11 (d, *J*=8.72 Hz, 2H), 4.80 (d, *J*=2.44 Hz, 2H), 2.58 (t, *J*=2.48 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 55.94, 76.35, 77.54, 115.18, 130.00, 131.88, 162.37, 190.74. HRMS-ESI: calculated for M+Na 183.0422, found 183.0422, Δ= 0 ppm.

4.11 Synthesis of Compound 11

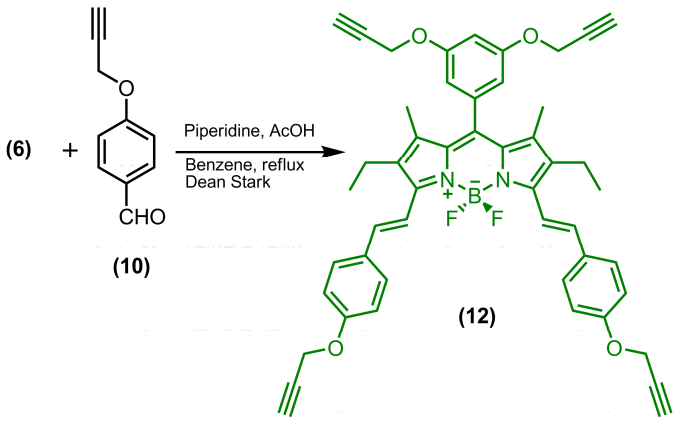
Compound **9** (100 mg, 0.24 mmol) and Compound **10** (98 mg, 0.6 mmol) dissolved in benzene (45 ml). Piperidine (0.4 ml) and glacial acetic acid (0.4 ml) were added. The solution was refluxed using Dean-Stark apparatus. When the solution was concentrated, reaction was followed by TLC until green-colored product became the major product. Then, benzene was evaporated in vacuo. It was extracted with

$CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using Ethyl Acetate:Hexane (25:75, v/v) as mobile phase. Fraction containing compound **11** was collected then the solvent was removed under reduced pressure (150 mg, 0.22 mmol, 90%).



^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.15 (t, J= 7.48 Hz, 6H), 1.38 (s, 6H), 2.55-2.65 (m, 4H+2H), 3.90 (s, 3H), 4.75 (d, J=2.36 Hz, 4H), 7.00-7.06 (m, 4H + 2H), 7.17-7.24 (m, 2H+2H), 7.06 (d, J=8.76 Hz, 4H), 7.70 (d, J=16.56 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.67, 14.04, 18.00, 55.58, 56.04, 75.50, 78.10, 115.20, 116.00, 118.50, 127.50, 128.69, 129.50, 130.00, 133.50, 158.00, 159.50. HRMS-ESI: calculated for M+Na 717.3076, found 717.3060, Δ= -2.2 ppm.

4.12 Synthesis of Compound 12

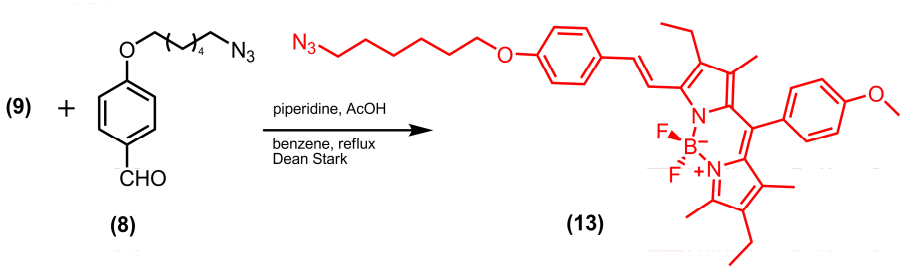


Compound **6** (200 mg, 2.05 mmol) and compound **10** (800.9 mg, 5 mmol) dissolved in benzene (45 ml). Piperidine (0.5 ml) and glacial acetic acid (0.5 ml) were added. The solution was refluxed using Dean-Stark apparatus. When the solution was concentrated, reaction was followed by TLC until green-colored product became the major product. Then, benzene was evaporated in vacuo. It was extracted with $CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The

product was purified by silica gel column chromatography using Ethyl Acetate:Hexane (20:80, v/v) as mobile phase. Fraction containing compound **12** was collected then the solvent was removed under reduced pressure.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.15 (t, J= 7.44 Hz, 6H), 1.5 (s, 6H), 2.52 (t, J=2.36 Hz, 2H), 2.55 (t, J=2.36 Hz, 2H), 2.63 (q, J=7.56 Hz, 4H), 4.70 (d, J=2.4 Hz, 4H), 4.75 (d, J= 2.36 Hz, 4H), 6.63 (d, J=2.32 Hz, 2H), 6.72 (t, J=2.28 Hz, 1H), 7.05 (d, J=8.80 Hz, 4H), 7.21 (d, J=16.77 Hz, 2H), 7.60 (d, J=8.80 Hz, 4H), 7.68 (d, J= 16.73 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.37, 14.04, 18.39, 55.89, 56.08, 75.73, 75.94, 78.10, 103.61, 108.32, 115.22, 118.58, 128.73, 130.00, 131.17, 135.26, 137.86, 158.04, 159.37. HRMS-ESI: calculated for M+Na 795.3182, found 795.3199, Δ= 2.2 ppm.

4.13 Synthesis of Compound 13

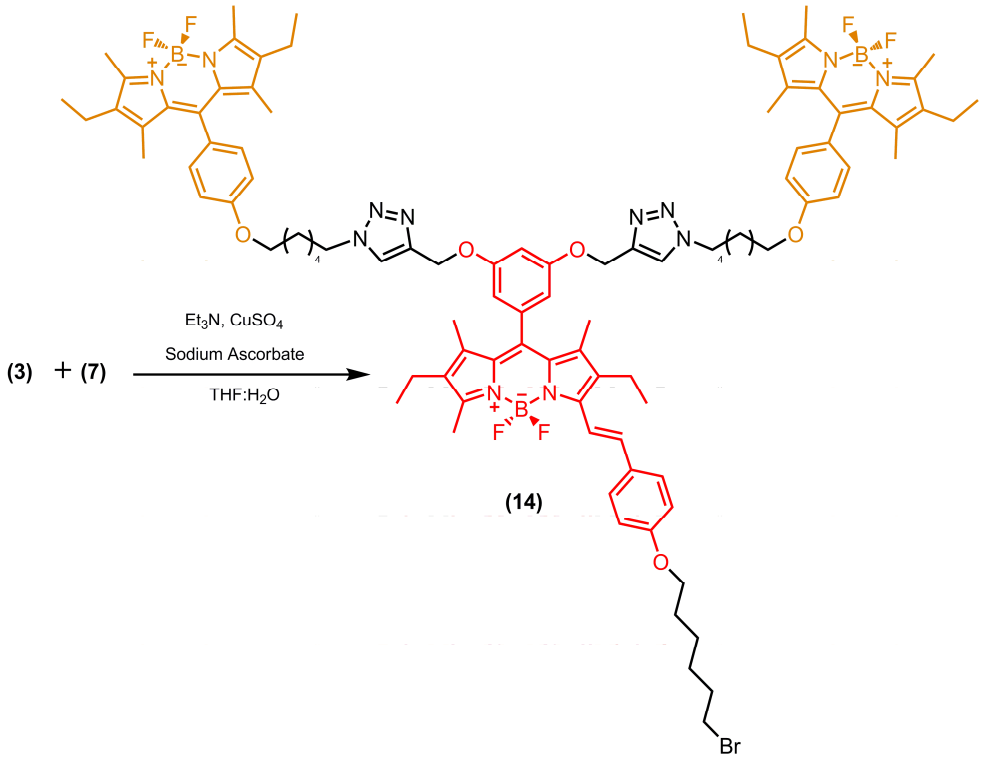


Compound **9** (410 mg, 1 mmol) and 4-(6-azidohexoxy) benzaldehyde **8** (120 mg, 0.49 mmol) dissolved in benzene (45 ml). Piperidine (0.5 ml) and glacial acetic acid (0.5 ml) were added. The solution was refluxed using Dean-Stark apparatus. When the solution was concentrated, reaction was followed by TLC until purple-colored product became the major product. Then, benzene was evaporated in vacuo. It was extracted with $CHCl_3$ and water. Organic layer was taken, dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using Ethyl Acetate:Hexane (20:80, v/v) as mobile phase. Fraction containing **13** was collected then the solvent was removed under reduced pressure (100 mg, 0.16 mmol, 16 %)

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (t, J= 7.48 Hz, 3H), 1.15 (t, J= 7.56 Hz, 3H), 1.36 (s, 3H), 1.38 (s, 3H), 1.50 (m, 4H), 1.68 (m, 2H), 1.84 (m, 2H), 2.34 (q, J= 7.48 Hz, 2H), 2.58 (m, 2H+3H), 3.32 (t, J= 6.84 Hz, 2H), 3.90 (s, 3H), 4.02 (t, J=6.32 Hz, 2H), 6.91 (d, J=8.72 Hz, 2H), 7.03 (d, J=8.68 Hz, 2H), 7.15-7.22 (m, 2H+1H), 7.54 (d, J=8.76 Hz, 2H), 7.62 (d, J=16.69 Hz, 1H) ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.58, 11.91, 12.71, 14.11, 14.56, 17.11, 18.32, 25.68, 26.52, 28.81, 29.11, 51.40, 55.33, 67.81, 114.44, 114.72, 118.00, 128.03, 128.57, 129.65, 130.27, 134.73, 138.63, 149.90, 155.00, 159.49, 160.02. HRMS-ESI: calculated for M+Na 640.3634, found 640.3604, Δ= -4.8 ppm.

4.14 Synthesis of Compound 14

Synthesis was done according to literature.[5] Compound **3** (107 mg, 0.21 mmol) and compound **7** (78 mg, 0.1 mmol) were dissolved in 8 ml THF. A few drops of Et_3N was added and the reaction mixture was stirred for 5 minutes at room temperature. In a viel, $CuSO_4.5H_2O$ (30% mole equavalent of compound **7**, 7.5 mg, 0.03 mmol) was dissolved in 4 ml water separately. Sodium ascorbate (60% mole equavalent of compound **7**, 11.88 mg, 0.06 mmol) was dissolved in 4 ml water in another viel. Solutions of sodium ascorbate and $CuSO_4$ were added to the first reaction mixture sequantially and the resultant mixture was stirred at room temperature untill all compound **7** was consumed, as followed by TLC. Then, it was extracted with $CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$ as mobile phase. Fraction containing compound **14** was collected then the solvent was removed under reduced pressure (65 mg, 0.035mmol, 35 %).



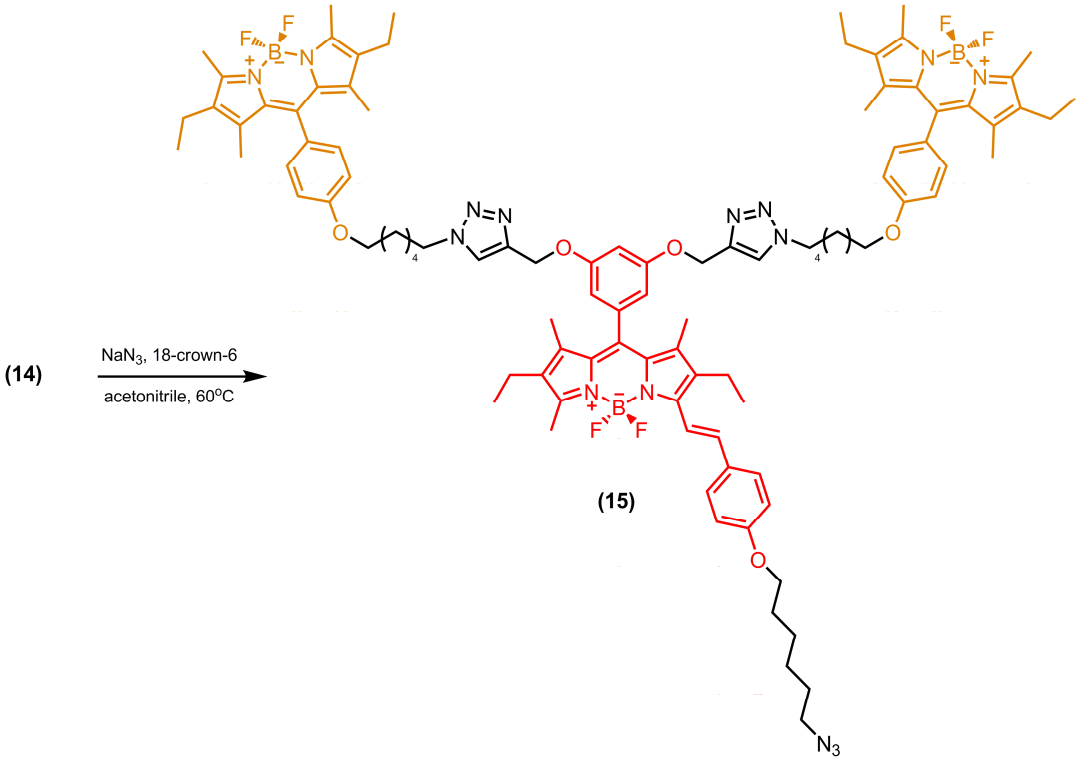
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (m, 15H), 1.16 (t, J= 7.40 Hz, 3H), 1.34 (s, 12H), 1.42-1.62 (m, 3H + 3H + 12H), 1.84 (m, 8H), 2.00 (m, J= 8H), 2.3 (m, 8H + 2H), 2.54 (s, 12H), 2.58-2.64 (m, 2H+3H), 3.58 (t, J=6.68 Hz, 2H), 4.01 (m, 6H), 4.42 (t, J=7.12 Hz, 4H), 5.20 (s, 4H), 6.61 (d, J=2.20, 2H), 6.78 (t, J=2.20 Hz, 1H), 6.90 (d, J= 8.76 Hz, 2H), 6.98 (d, J=8.60 Hz, 4H), 7.15 (d, J=8.52, 4H), 7.19 (d, J=16.286 Hz, 1H), 7.54 (d, J=8.72 Hz, 2H), 7.61 (d, J=16.85 Hz, 1H), 7.66 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.32, 11.66, 11.85, 12.46, 14.10, 14.57, 14.62, 17.06, 25.40, 25.61, 26.37, 26.66, 29.08, 30.25, 32.51, 44.99, 50.36, 62.27, 67.75, 67.84, 100.00, 102.00, 108.00, 114.75, 114.91, 122.64,

127.83, 128.61, 129.46, 130.13, 132.62, 135.05, 137.86, 138.40, 140.27, 143.44, 153.49, 159.41, 160.22. MALDI: calculated for compound **14** 1782.8871, found 1755.

4.15 Synthesis of Compound 15

Compound **14** (40 mg, 0.022 mmol) and sodium azide (7.23 mg, 0.11 mmol) was dissolved in 15 ml acetonitrile. Catalytic amount of 18-crown-6 was added and the reaction mixture was stirred 2 days at 60°C. Then, it was extracted with ethyl acetate and water. Organic layer was collected, dried with Na_2SO_4 and evaporated under reduced pressure. No further purification was required. Compound **15** was used immediately after synthesized.

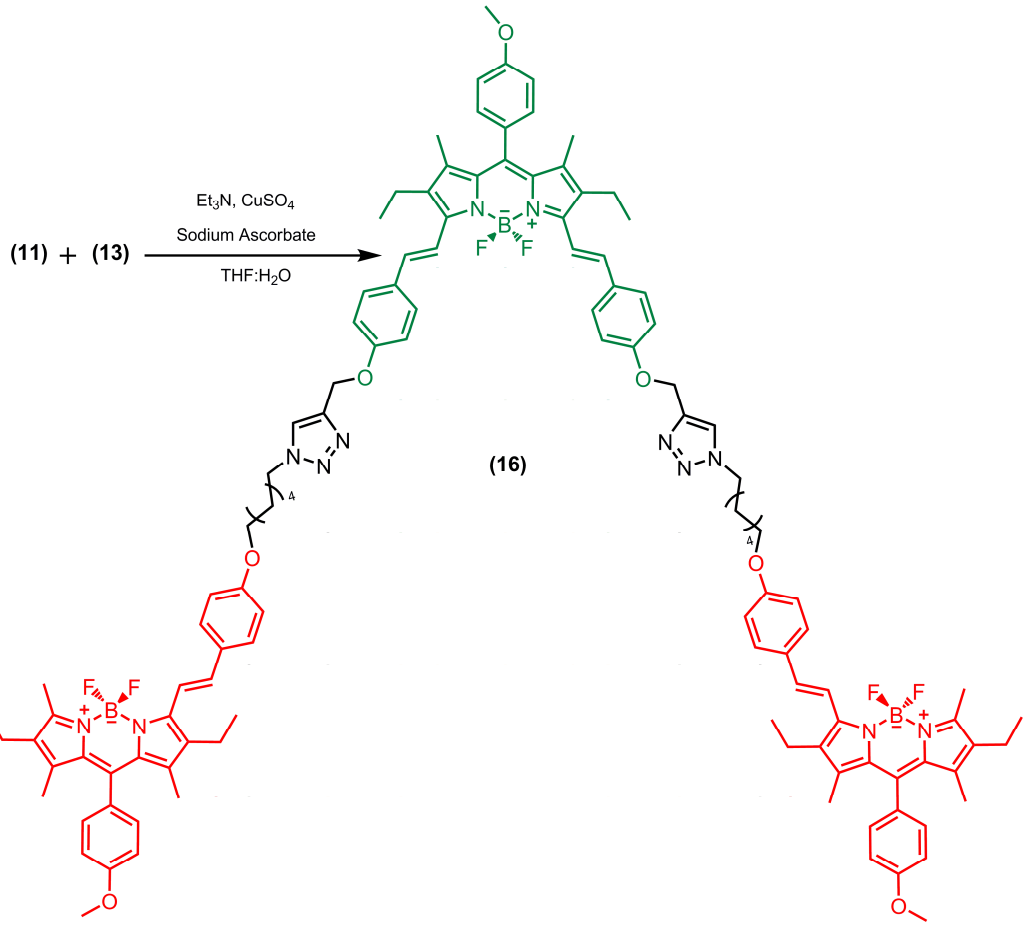
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (m, 15H), 1.16 (t, J= 7.16 Hz, 3H), 1.34 (s, 12H), 1.42-1.62 (m, 3H + 3H + 12H), 1.84 (m, 8H), 2.00 (m, 8H), 2.3 (m, 8H + 2H), 2.50-2.65 (m, 12H+2H+3H), 3.30 (t, J=6.84 Hz, 2H), 4.05 (m, 6H), 4.42 (t, J=7.12 Hz, 4H), 5.20 (s, 4H), 6.61 (d, J=1.68, 2H), 6.78 (t, J=2.20 Hz, 1H), 6.90 (d, J= 8.56 Hz, 2H), 6.98 (d, J=8.28 Hz, 4H), 7.15-7.20 (m,4H+1H), 7.54 (d, J=8.60 Hz, 2H), 7.61 (d, J=16.53 Hz, 1H), 7.66 (s, 2H).



4.16 Synthesis of Compound 16

Compound **11** (22 mg, 0.03 mmol) and compound **13** (60 mg, 0.094 mmol) were dissolved in 3 ml THF. A few drops of Et_3N was added and the reaction mixture was stirred for 5 minutes at room temperature. In a viel, $CuSO_4.5H_2O$ (30% mole equavalent of compound **11**, 2.3 mg, 0.009 mmol) was dissolved in 1.5 ml water separately. Sodium ascorbate (60% mole equavalent of compound **11**, 3.6 mg,

0.018 mmol) was dissolved in 1.5 ml water in another viel. Solutions of sodium ascorbate and $CuSO_4$ were added to the first reaction mixture sequantially and the resultant mixture was stirred at room temperature untill all compound **11** was consumed, as followed by TLC. Then, it was extracted with $CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$:Methanol (95:5, v/v) as mobile phase. Fraction containing compound **16** was collected then the solvent was removed under reduced pressure.

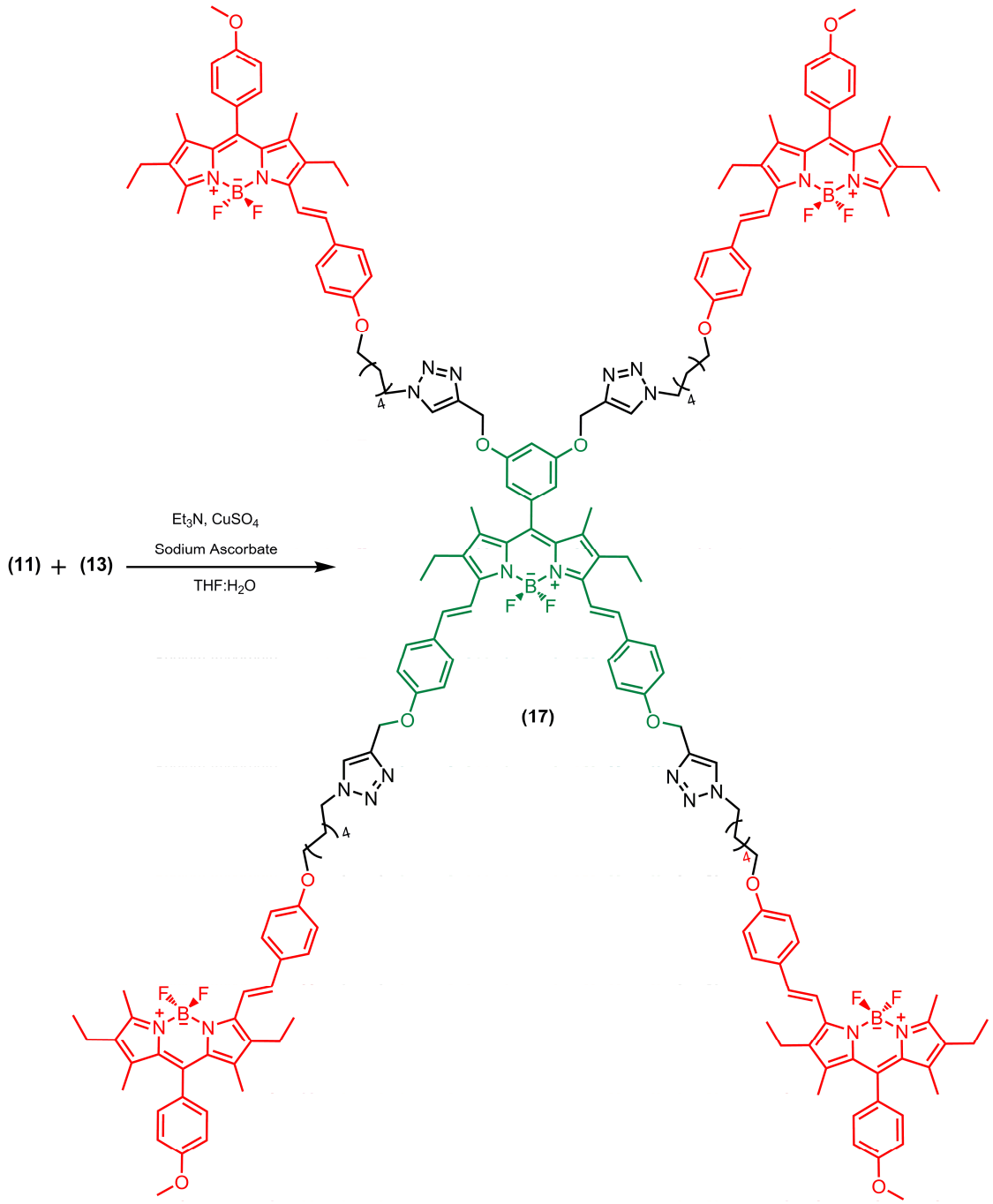


^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (t, J= 7.52 Hz, 6H), 1.15 (M, 12H), 1.35 (m, 12H+6H+2H), 1.54 (m, 4H), 1.78 (m, 4H), 1.98 (m, 4H), 2.32 (m, 4H), 2.55-2.65 (m, 6H+8H), 3.9 (s, 9H), 3.98 (t, J= 6.20 Hz, 4H), 4.4 (m, 4H), 5.3 (s, 4H), 6.88 (d, J= 8.80 Hz, 4H), 7.03 (m, 4H+2H+4H), 7.12-7.24 (m, 4H+2H+4H), 7.52 (d, J= 8.72 Hz, 4H), 7.55-7.65 (m, 2H+4H+2H), 7.68 (d, J= 16.61 Hz, 2H) ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm) 11.91, 12.72, 14.06, 14.11, 14.57, 17.11, 18.32, 18.38, 25.50, 26.23, 28.97, 30.19, 50.33, 55.33, 62.19, 67.68, 114.44, 114.47, 114.72, 115.15, 122.58, 128.02, 128.55, 128.77, 129.65, 129.85, 130.24, 130.86, 134.73, 158.72, 159.47, 160.02, 160.06. MALDI: calculated for compound **16** 1973.0291, found 1973.

4.17 Synthesis of Compound 17

Compound **12** (13.3 mg, 0.017 mmol) and compound **13** (55 mg, 0.086 mmol) were dissolved in 3 ml THF. A few drops of Et_3N was added and the reaction mixture was stirred for 5 minutes at room temperature. In a viel, $CuSO_4.5H_2O$ (21.5 mg, 0.086 mmol) was dissolved in 1.5 ml water separately. Sodium ascorbate (25.6 mg, 0.129 mmol) was dissolved in 1.5 ml water in another viel. Solutions of sodium ascorbate and $CuSO_4$ were added to the first reaction mixture sequantially and the resultant mixture was stirred at room temperature untill all compound **12** was consumed, as followed by TLC. Then, it was extracted with $CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$ as mobile phase and then $CHCl_3$:Methanol (98:2, v/v) as mobile phase. Fraction containing compound **17** was collected then the solvent was removed under reduced pressure.

^1H NMR ($CDCl_3$, 400 MHz, δ ppm) 0.8-1.65 (m, 24H+24H+8+8+8+6+6), 1.75 (m, 8H), 1.95 (m, 8H), 2.32 (m, 8H), 2.6 (m, 20H+4H), 3.9 (s, 12H), 4.00 (m, 8H), 4.40 (m, 8H), 5.2 (m, 8H), 6.6 (d, J= 3.84 Hz, 2H), 6.9 (m, 8H+4H+1H), 7.00 (m, 8H+4H), 7.1-7.25 (m, 8H+ 4H + 2H), 7.45-7.70 (m, 4H+8H+2H+4H+4H). MALDI: calculated for compound **17**, 3329.7508, found 3329.

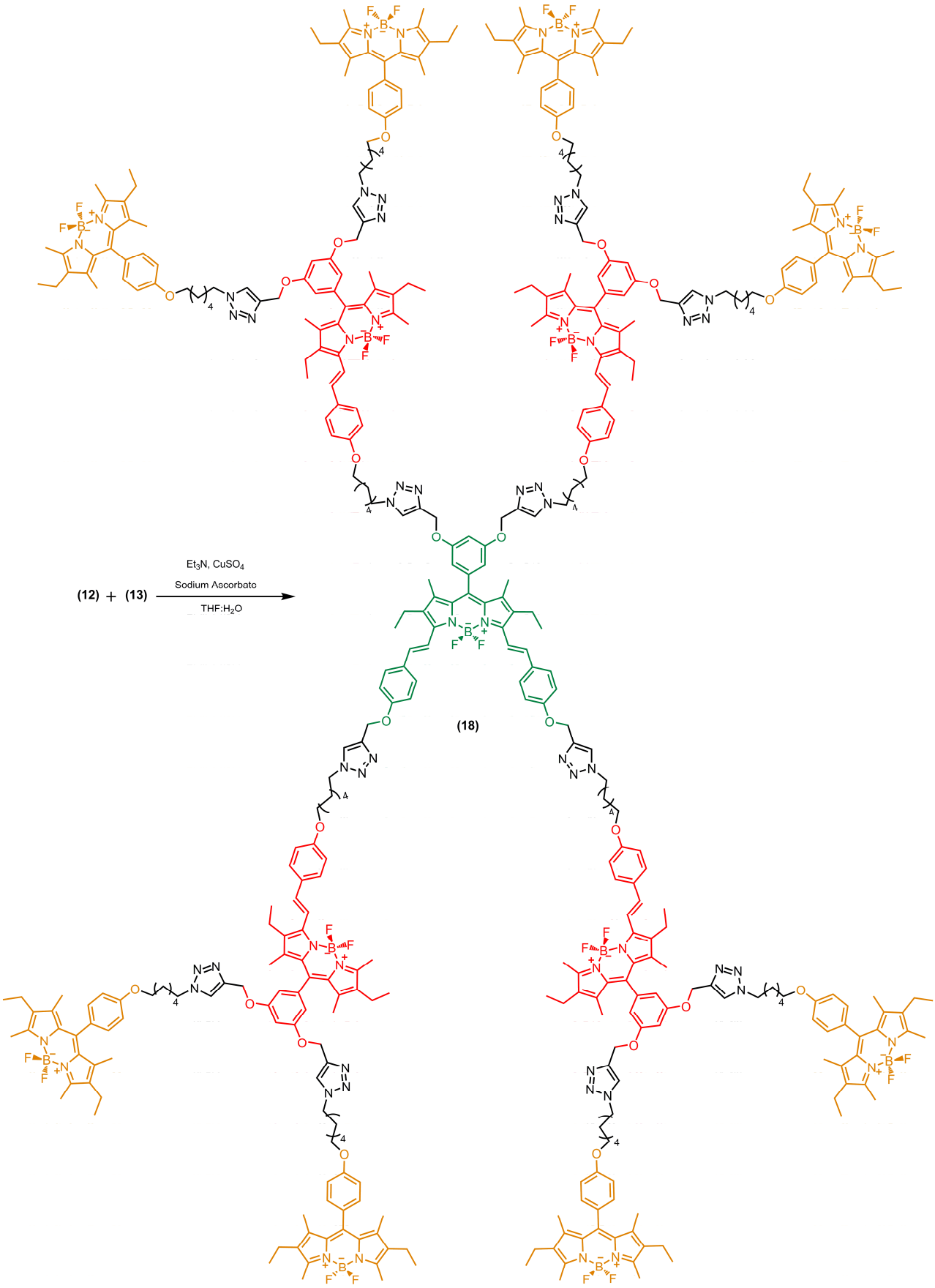


4.18 Synthesis of Compound 18

Compound **12** (4.39 mg, 0.0057 mmol) and compound **15** (50 mg, 0.028 mmol) were dissolved in 3 ml THF. A few drops of Et_3N was added and the reaction mixture was stirred for 5 minutes at room temperature. In a viel, $CuSO_4.5H_2O$ (19 mg, 0.076 mmol) was dissolved in 0.75 ml water separately. Sodium ascorbate (35.1 mg, 0.177 mmol) was dissolved in 0.75 ml water in another viel. Solutions of sodium ascorbate and $CuSO_4$ were added to the first reaction mixture sequantially and the resultant mixture was stirred at room temperature untill all compound **12** was consumed, as followed by TLC. Then, it was extracted with $CHCl_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated under reduced pressure. The product was purified by silica gel column chromatography using $CHCl_3$: Methanol

(95:5, v/v) as mobile phase. Fraction containing compound **18** was collected then the solvent was removed under reduced pressure.

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm) 1.0 (m, 60H), 1.18 (m, 12H+6H), 1.22-1.70 (m, 120H + 6H + 8H), 1.82 (m, 32H), 2.00 (m, 24H), 2.34 (m, 40H), 2.5-2.64 (m, 12H+8H+48H+4H), 4.00 (m, 16H+8H), 4.40 (m, 16H+8H), 5.2 (m, 16H+8H), 6.6 (8H+2H), 6.79 (4H+1H), 6.86 (8H), 7.00(16H+4H), 7.18 (16H+4H+2H), 7.48-7.62 (8H+4H+4H+2H), 7.65 (8H+4H). MALDI: calculated for compound **18**, 7812.3031, found 7794.


Et3N, CuSO4
Sodium Ascorbate
THF:H2O
(12) + (13)
(18)

5. Preparation of Dendrimer-doped Epoxy Resin

Epoxy resin (25.0 g, Specifix) was taken; dendrimer in acetone was added to the resin with final concentration 2.5 μM. Following the addition of hardener (3.0 g) the sample was stirred rigorously for a few minutes and then poured into a small container. It was dried *in vacuo* until all bubbles have disappeared. Then samples were left overnight and sliced into mm-sized cylindrical slabs.

6. References

[1] Lakowicz, J.R. *Principles of Fluorescence Spectroscopy*, Kluwer Acadamic, Plenum Publishers, **1999**.

[2] Valeur, B. *Molecular Fluorescence, Principles and Applications*, Wiley-WC, **2002**.

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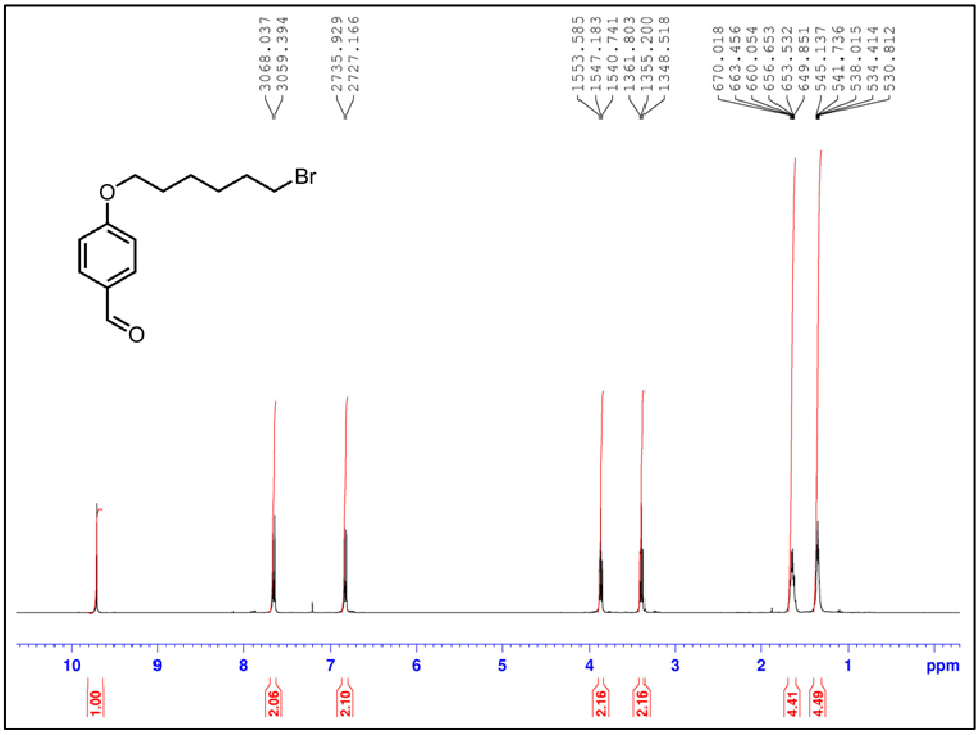
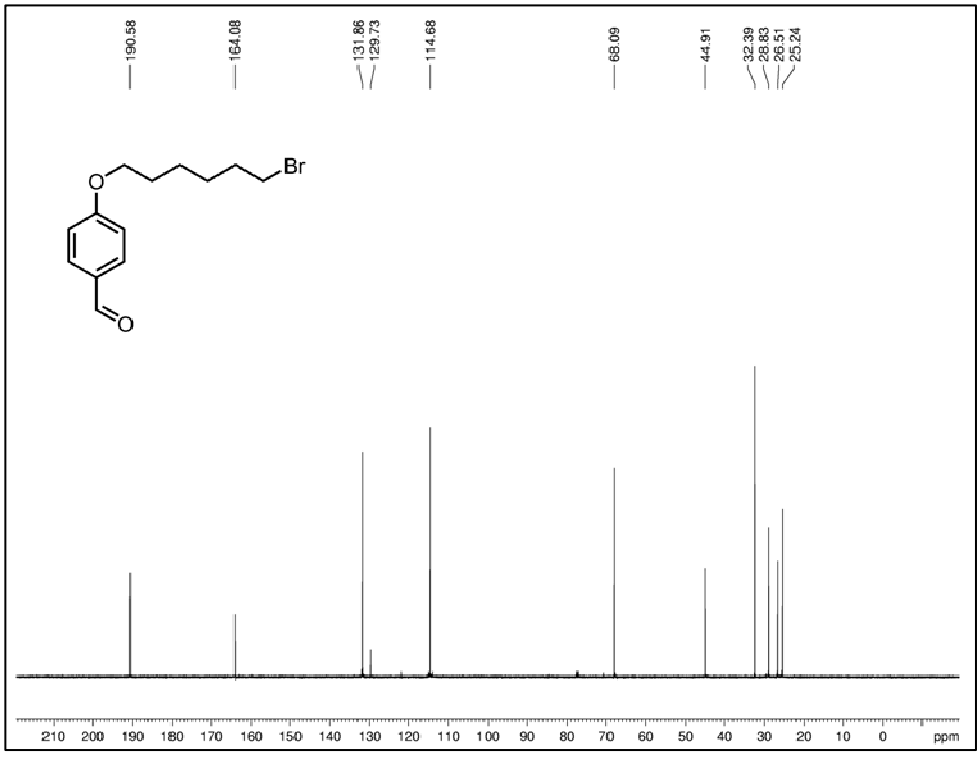
[4] *Pat*. 424 165. 2008. *USPTO*., 20080233047.

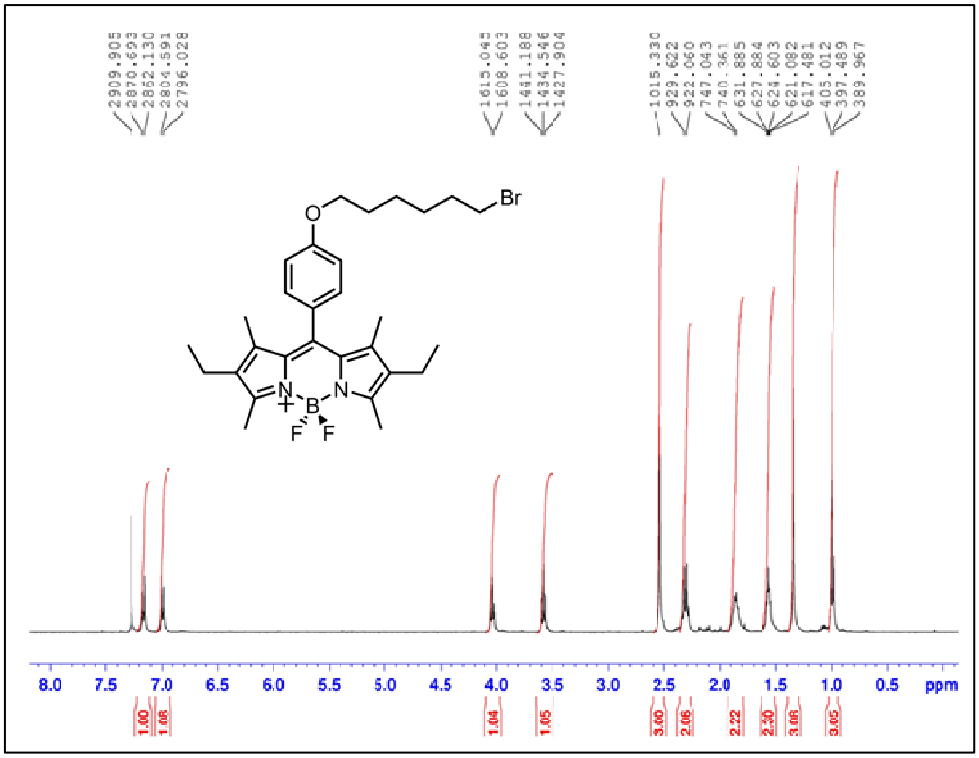
[5] Wyszogrodzka, M.; Haag, R. *Chem. Eur. J*., **2008**, 14, 9202.

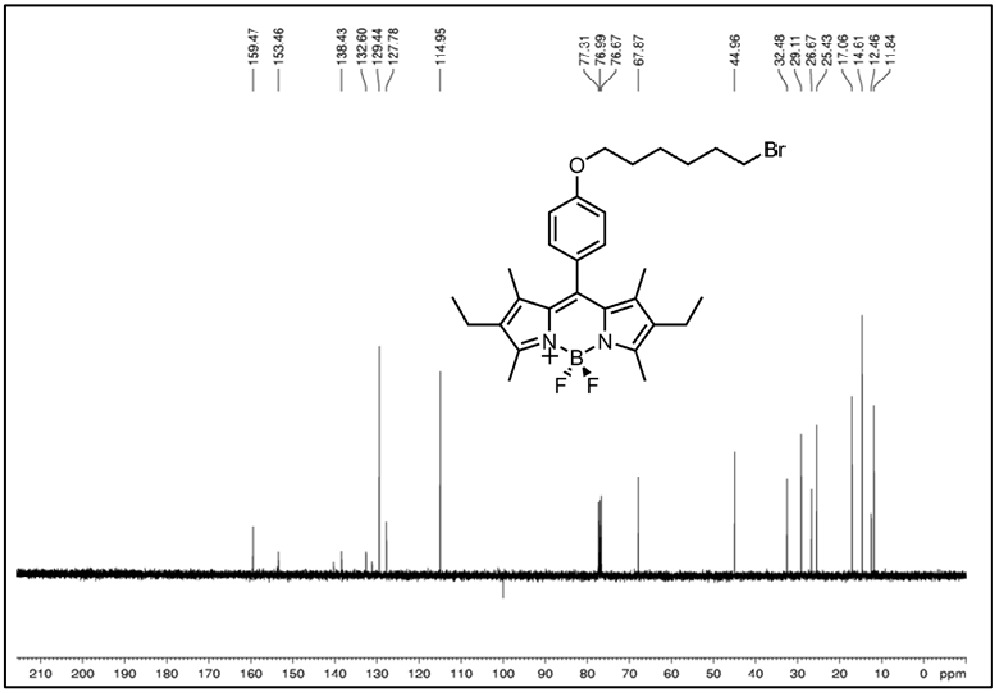
7. NMR Spectra



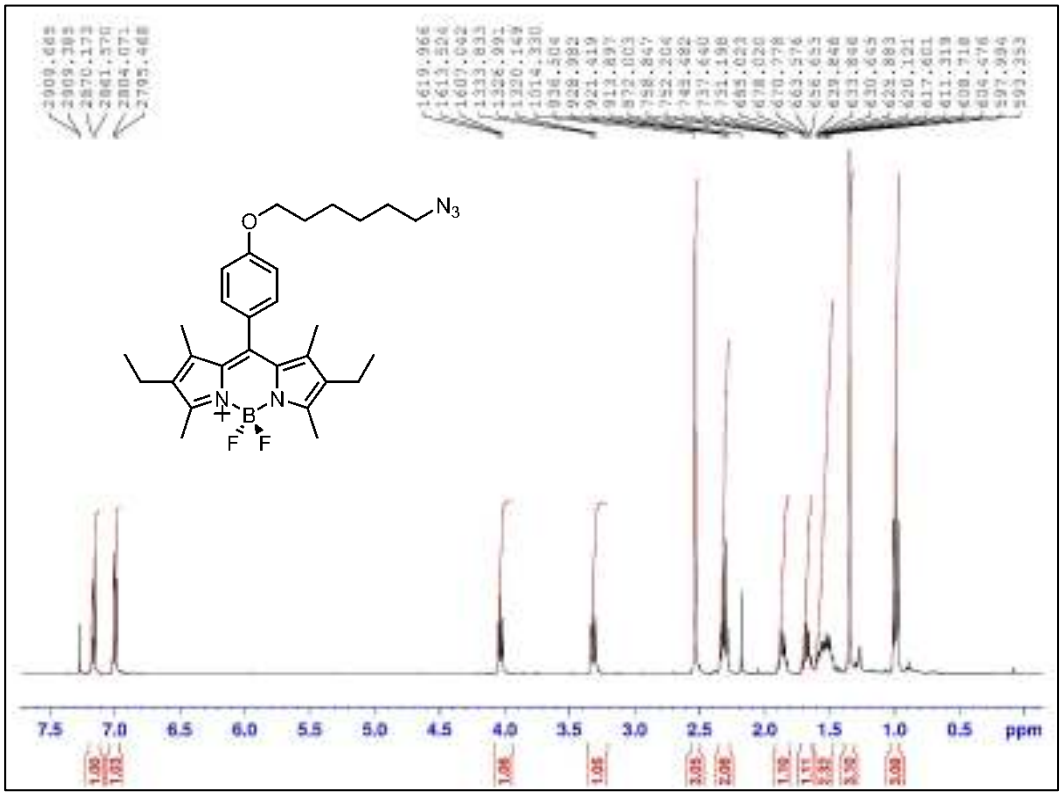


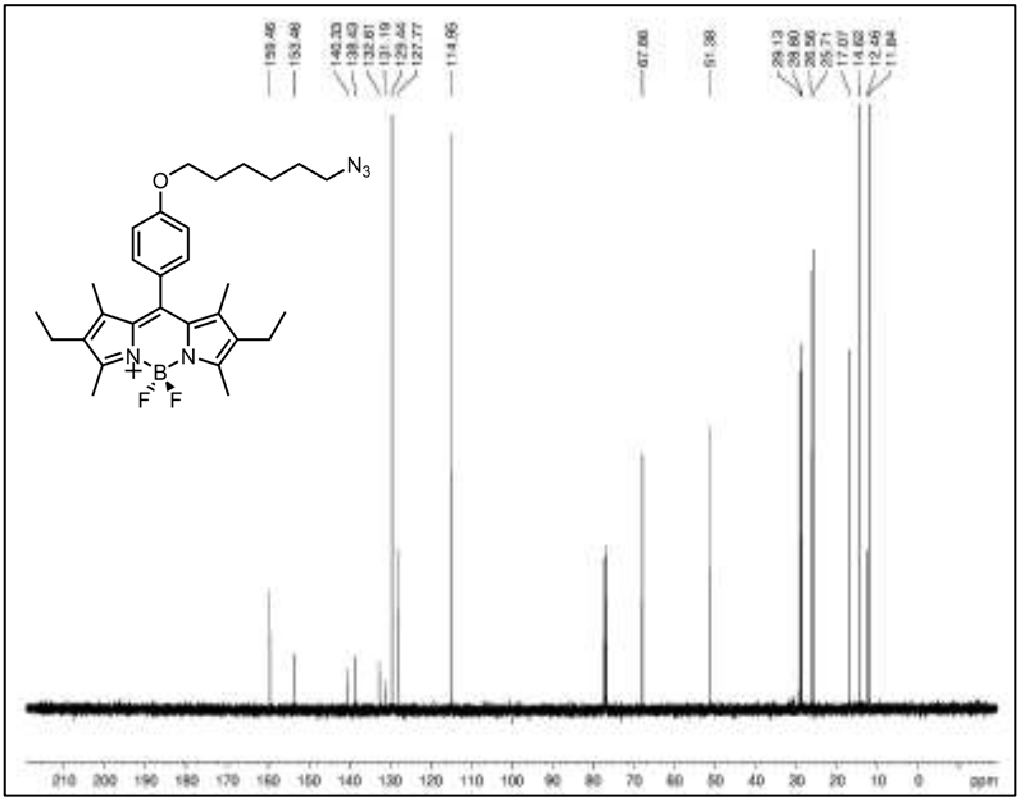
^{1}H and ^{13}C spectra of Compound 1.



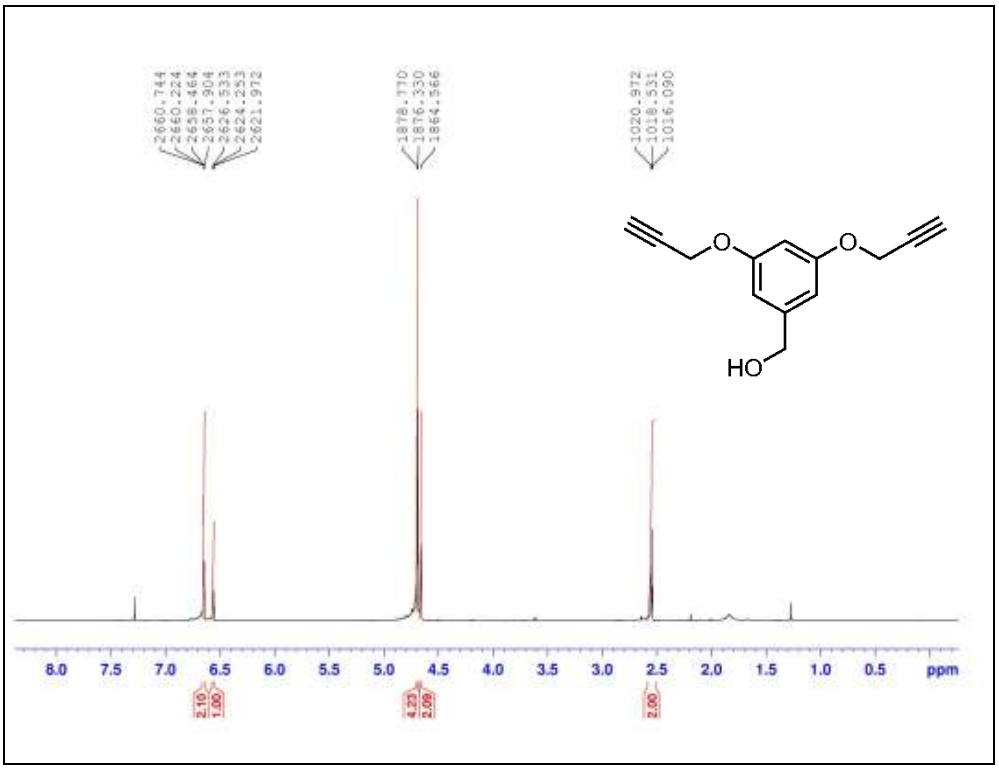


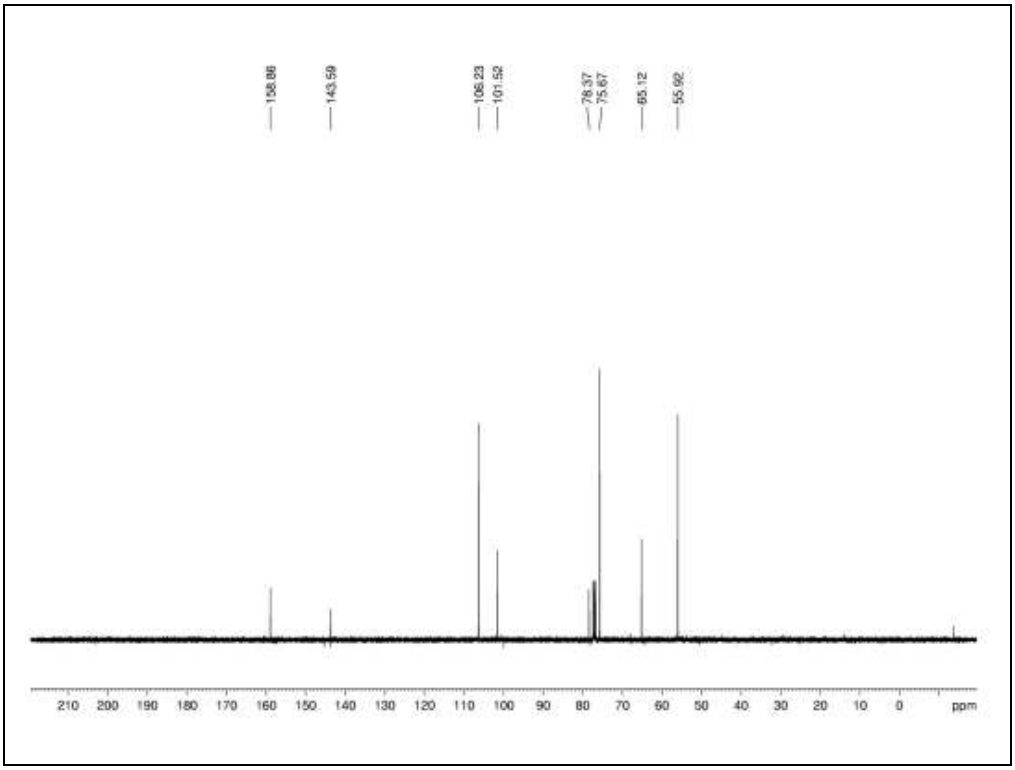
^{1}H and ^{13}C spectra of Compound **2**.



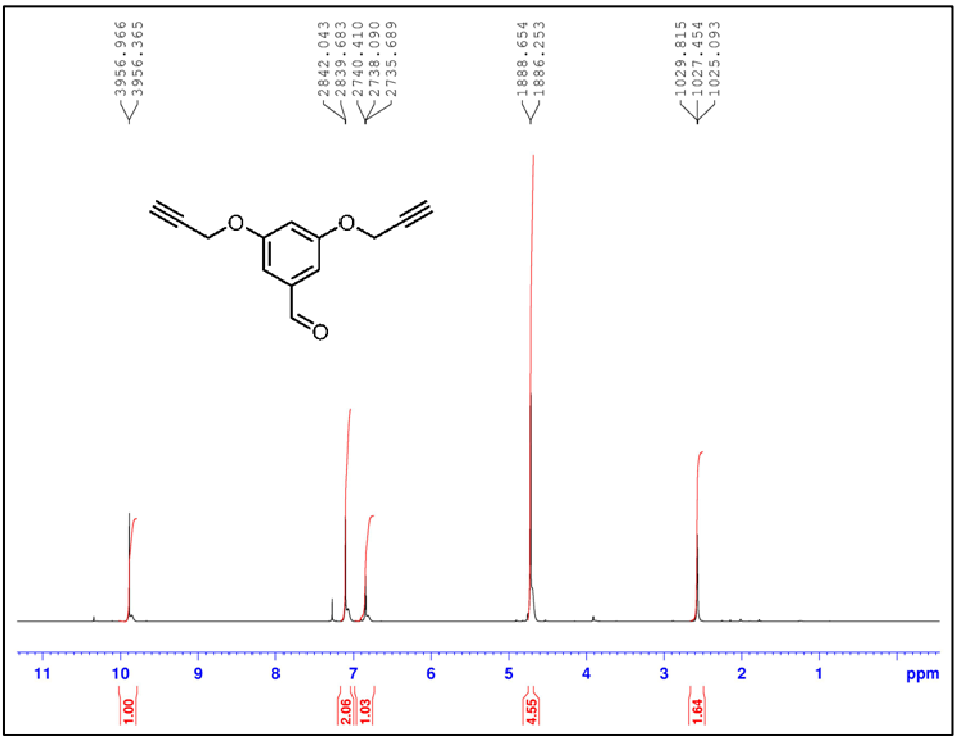


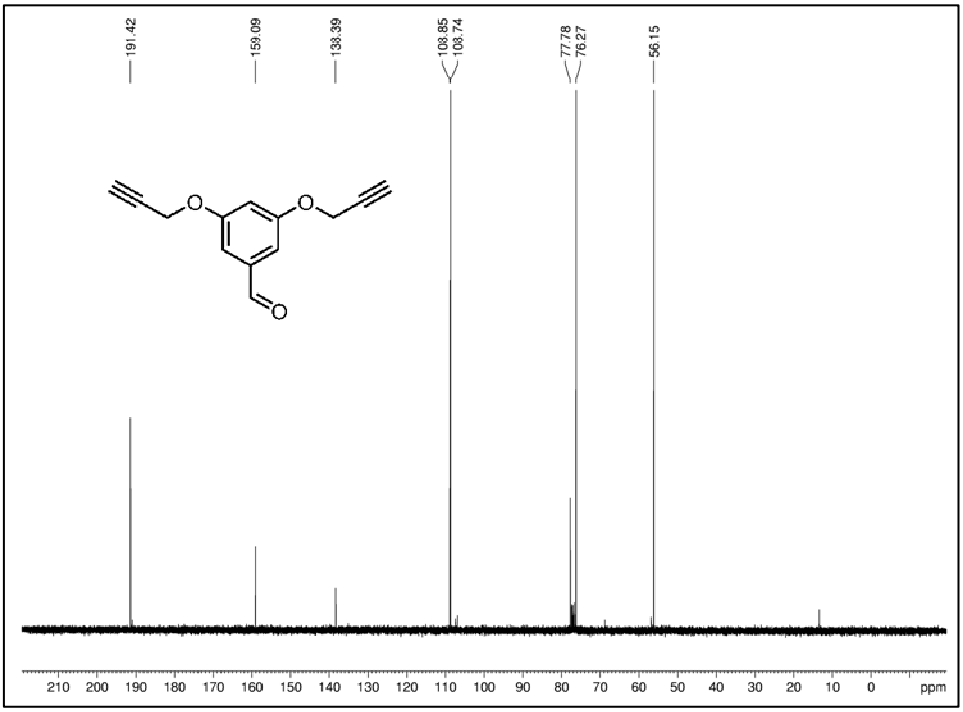
^{1}H and ^{13}C spectra of Compound **3**.



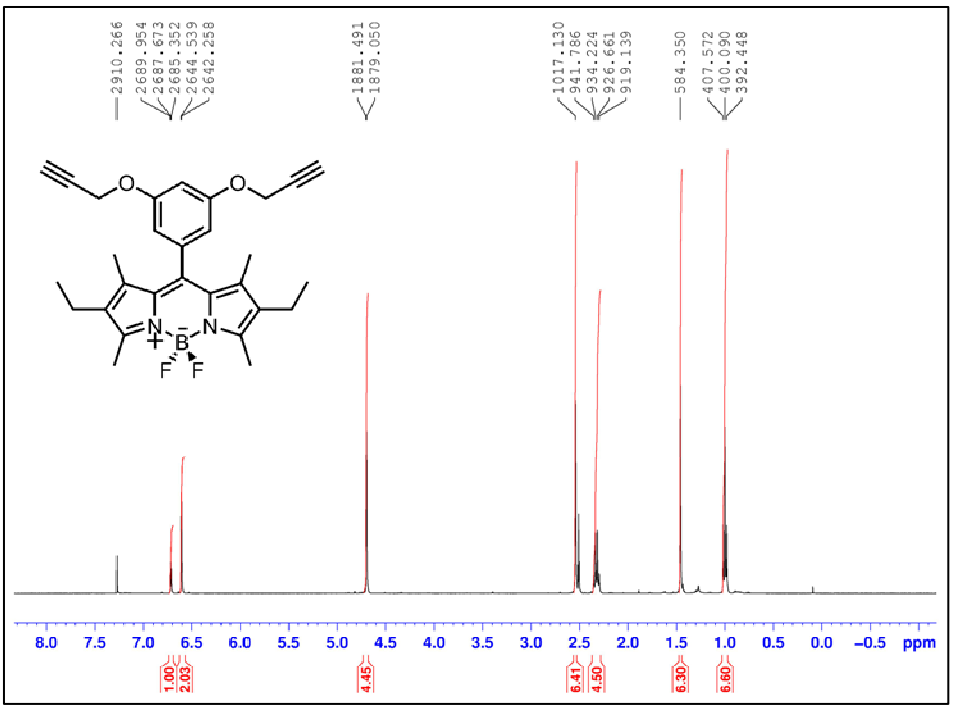


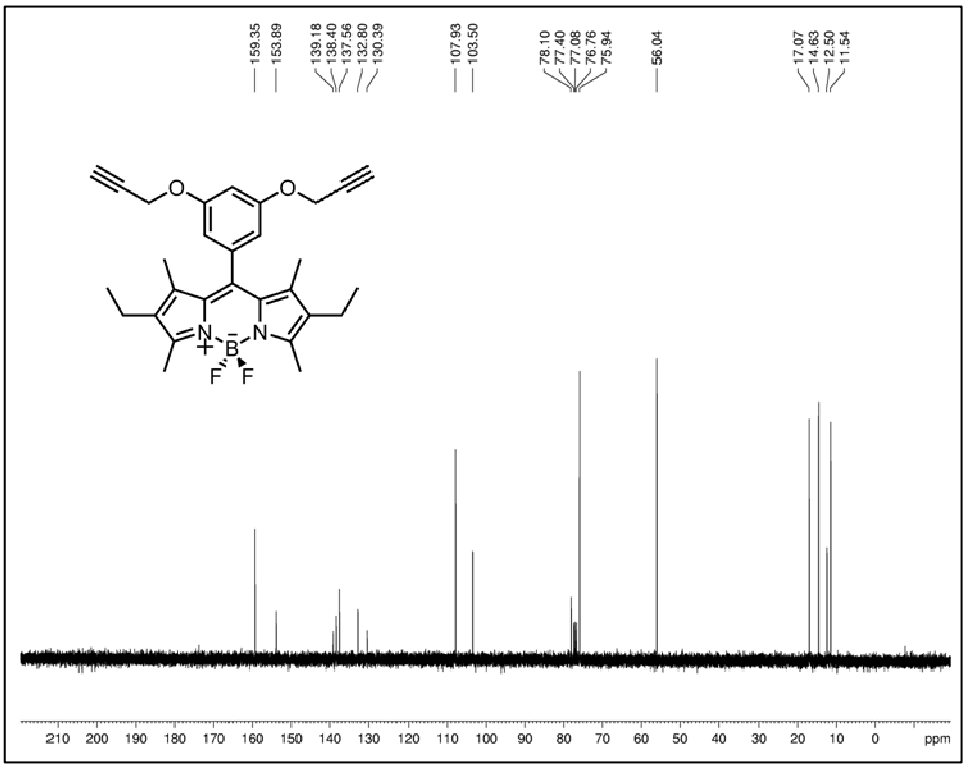
^{1}H and ^{13}C spectra of Compound **4**.



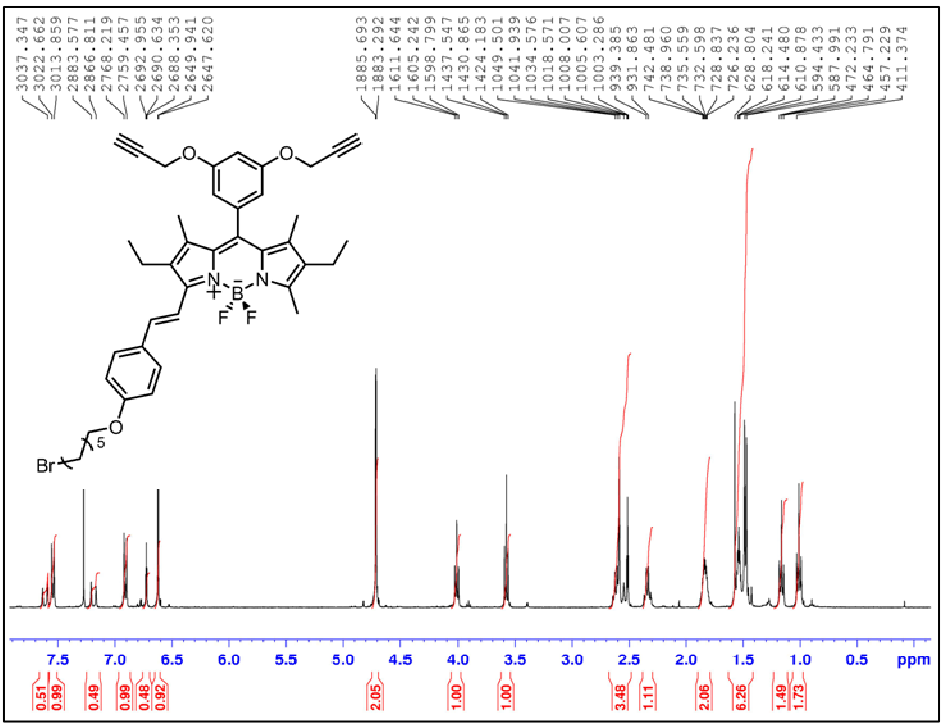


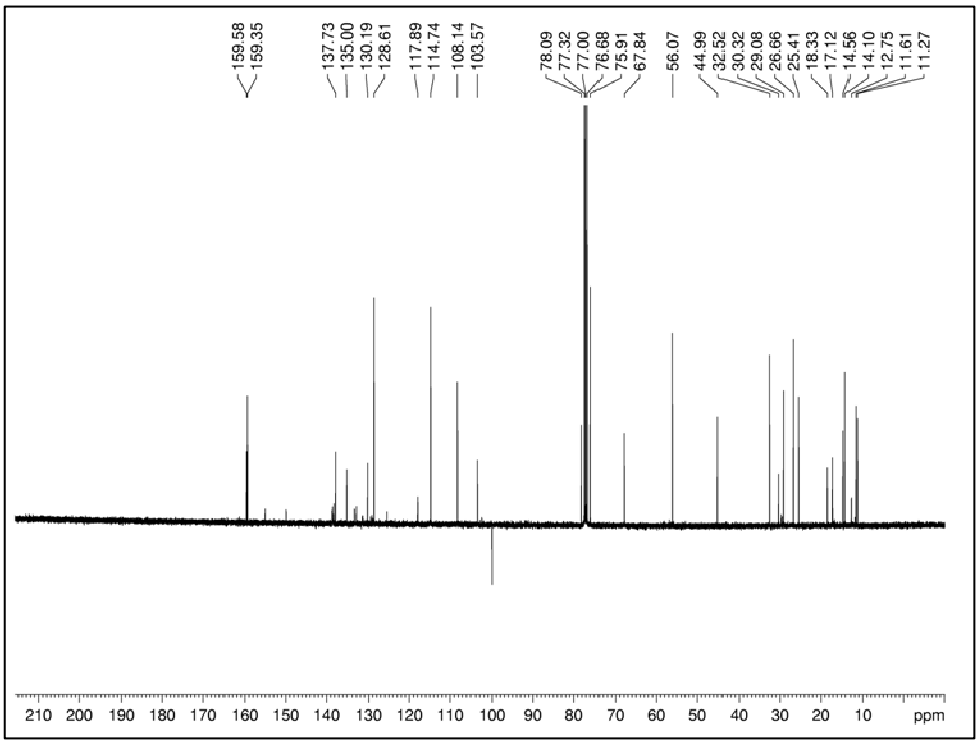
^{1}H and ^{13}C spectra of Compound **5**.



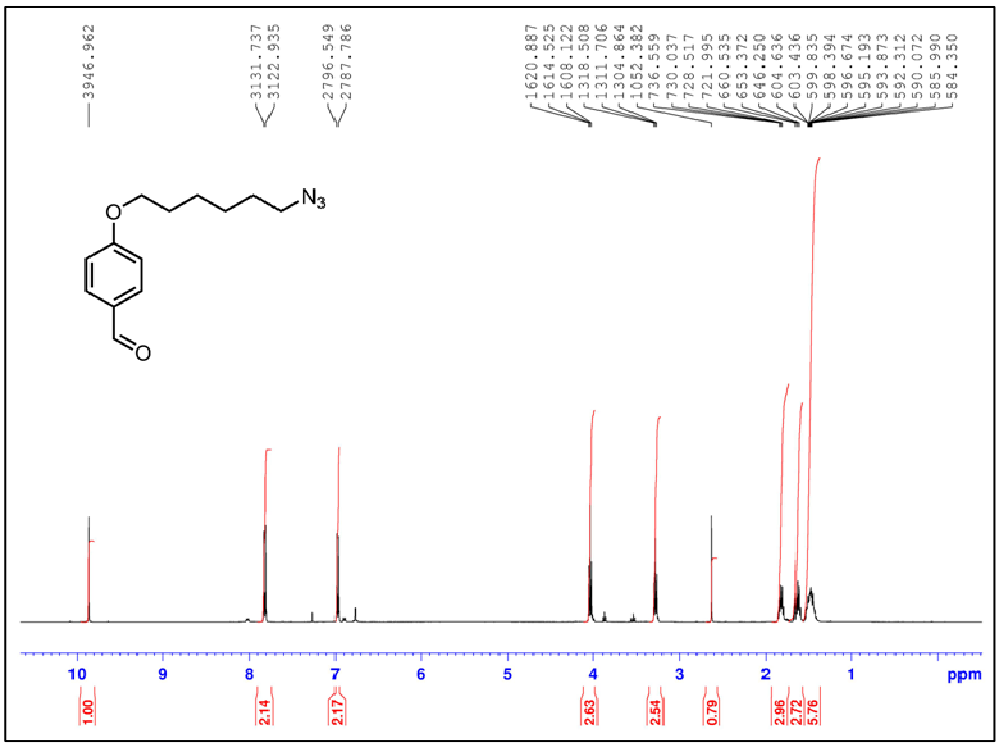


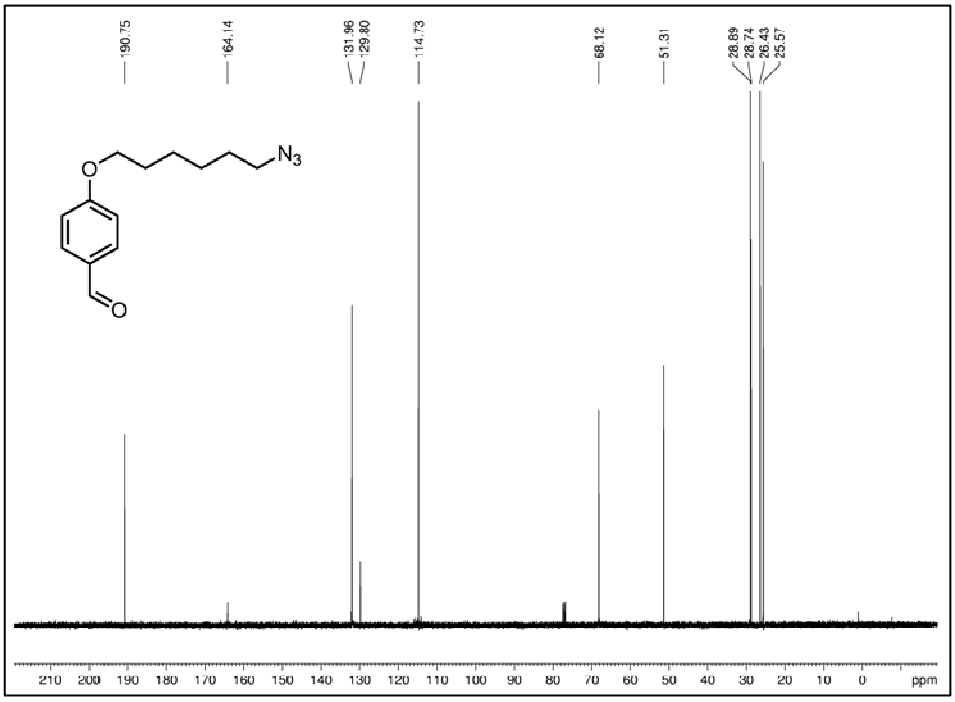
^{1}H and ^{13}C NMR spectra of Compound **6**.



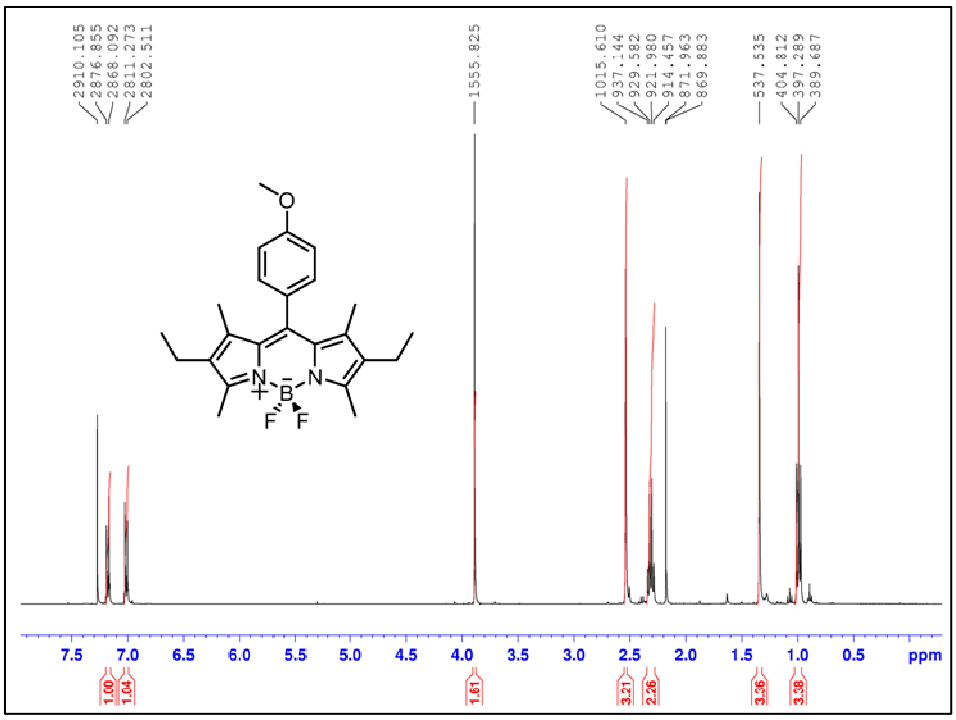


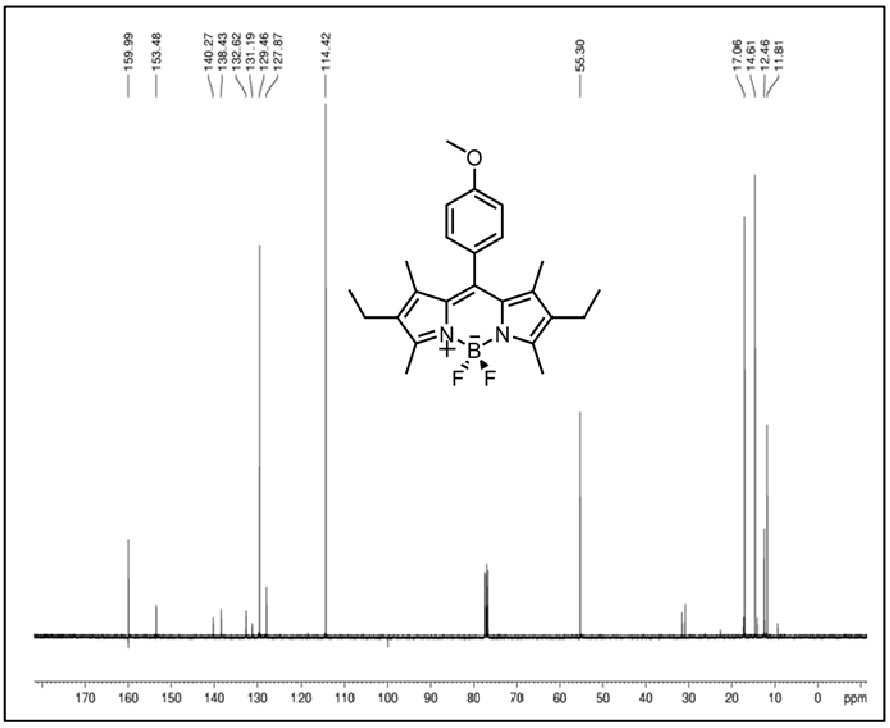
^{1}H and ^{13}C NMR spectra of Compound **7**.



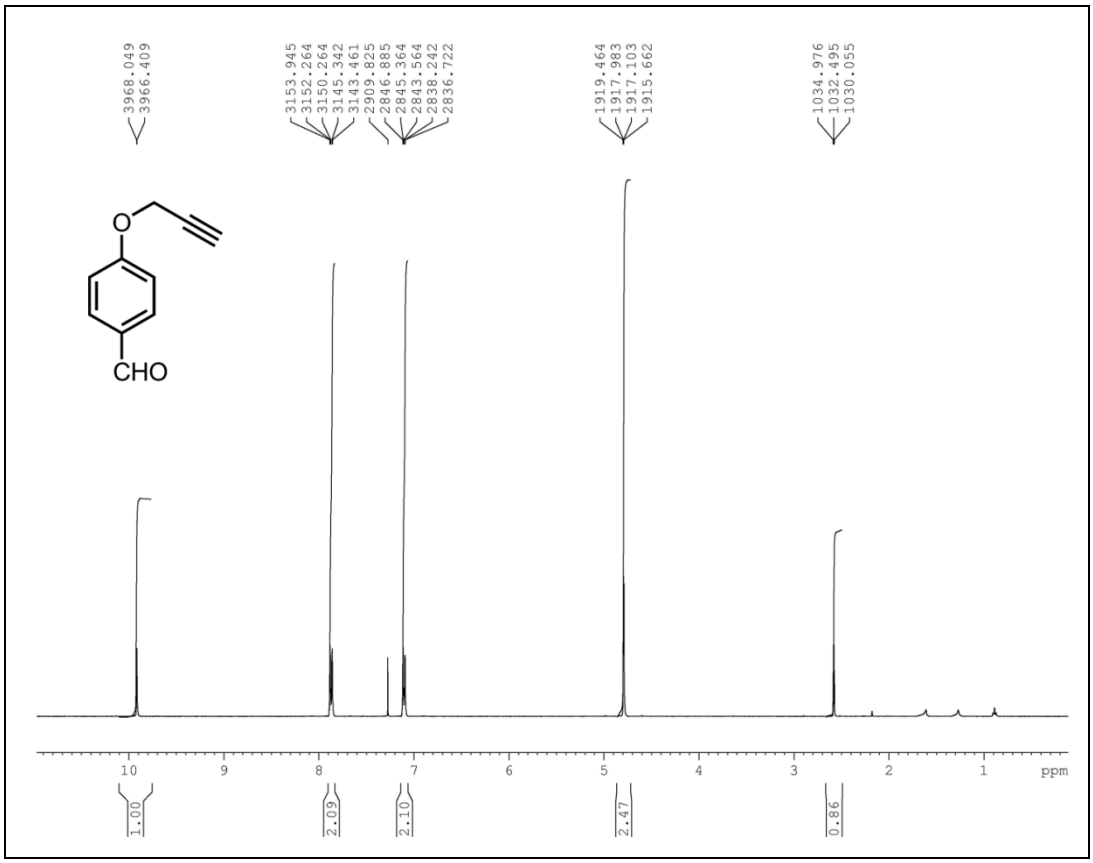


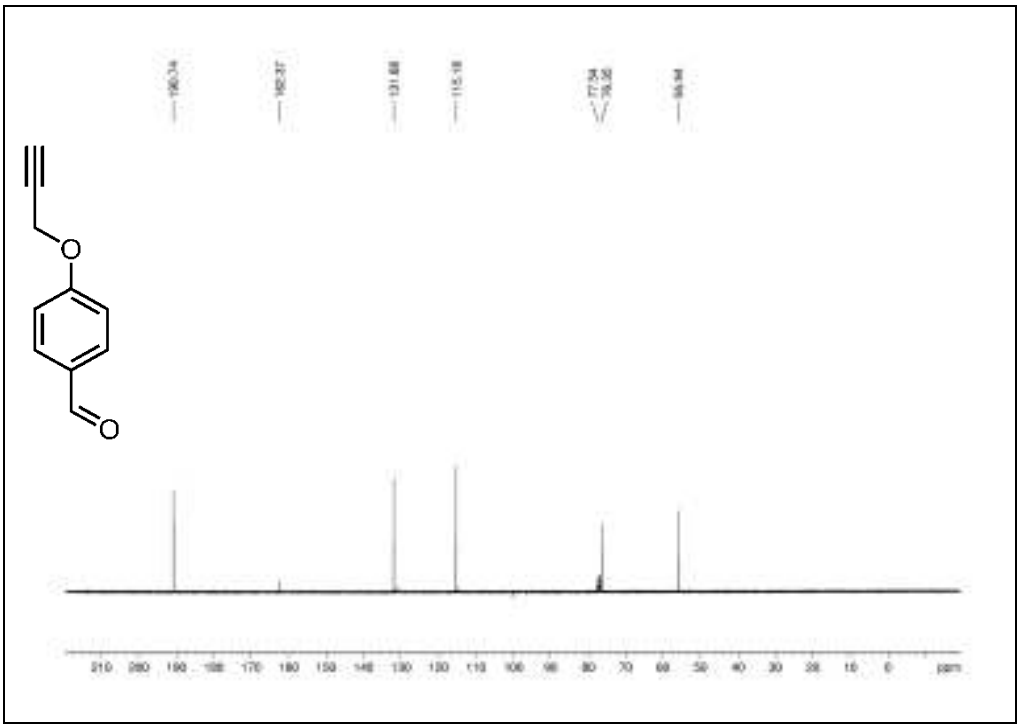
^{1}H and ^{13}C NMR spectra of Compound **8**.



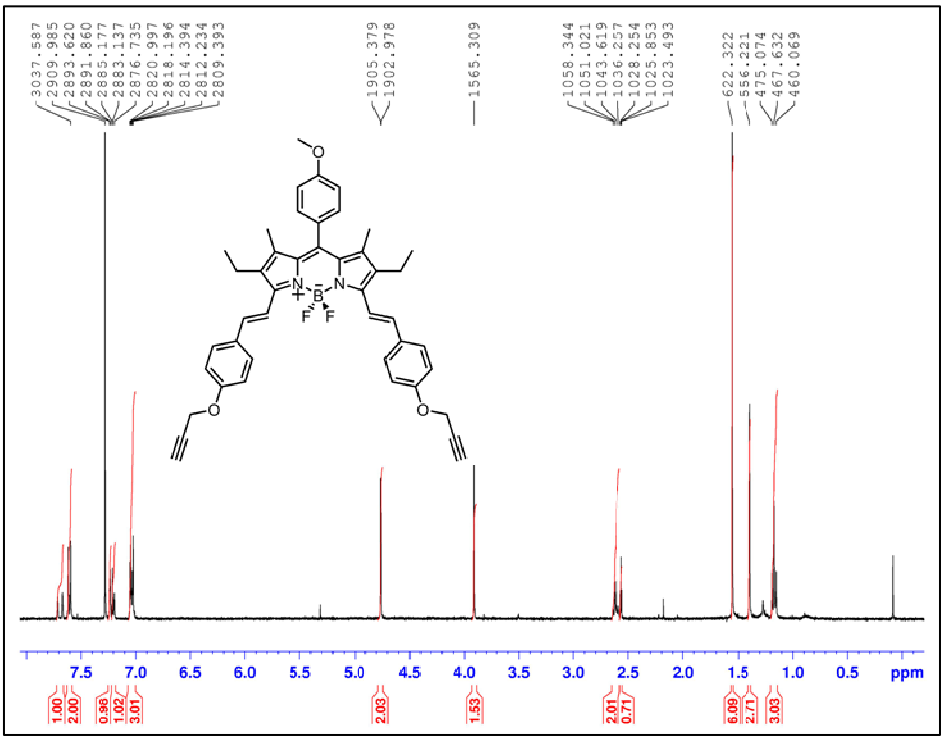


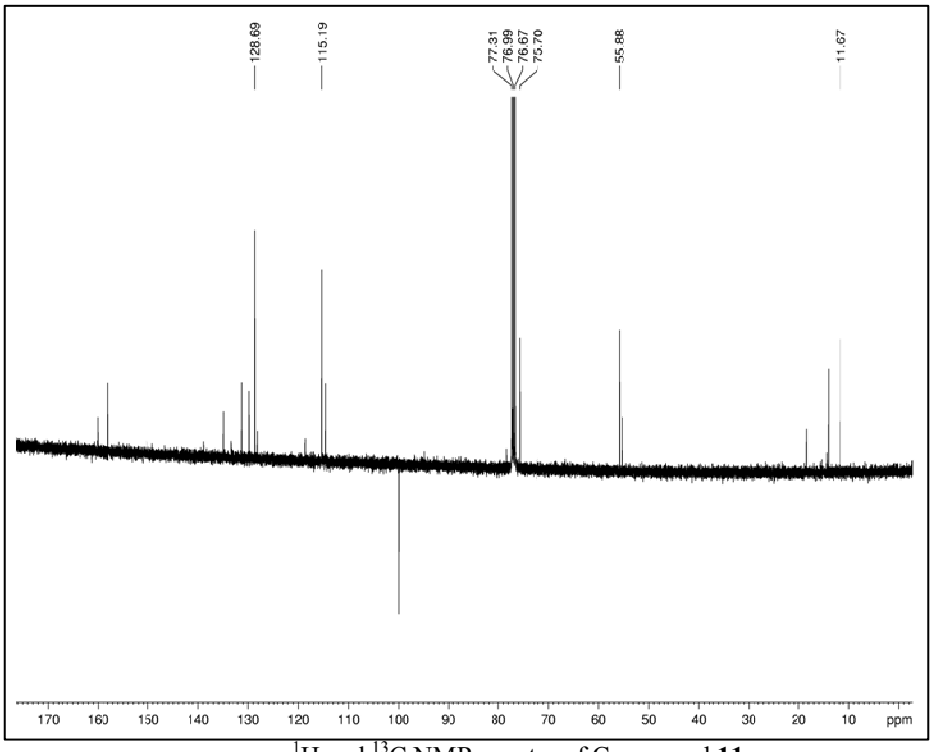
^{1}H and ^{13}C NMR spectra of Compound **9**.



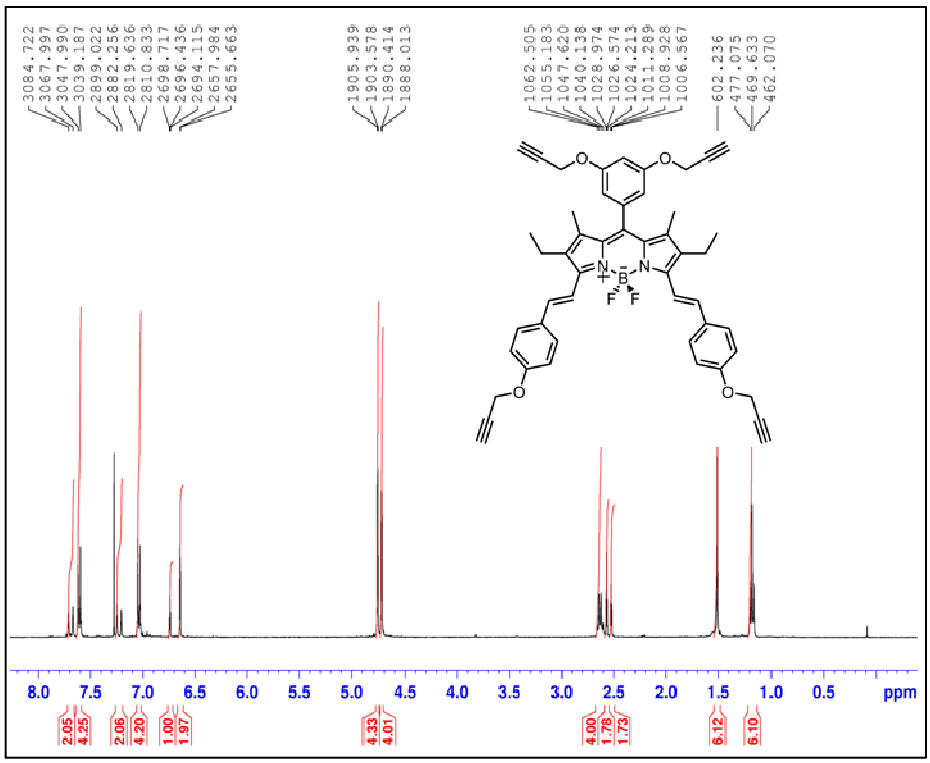


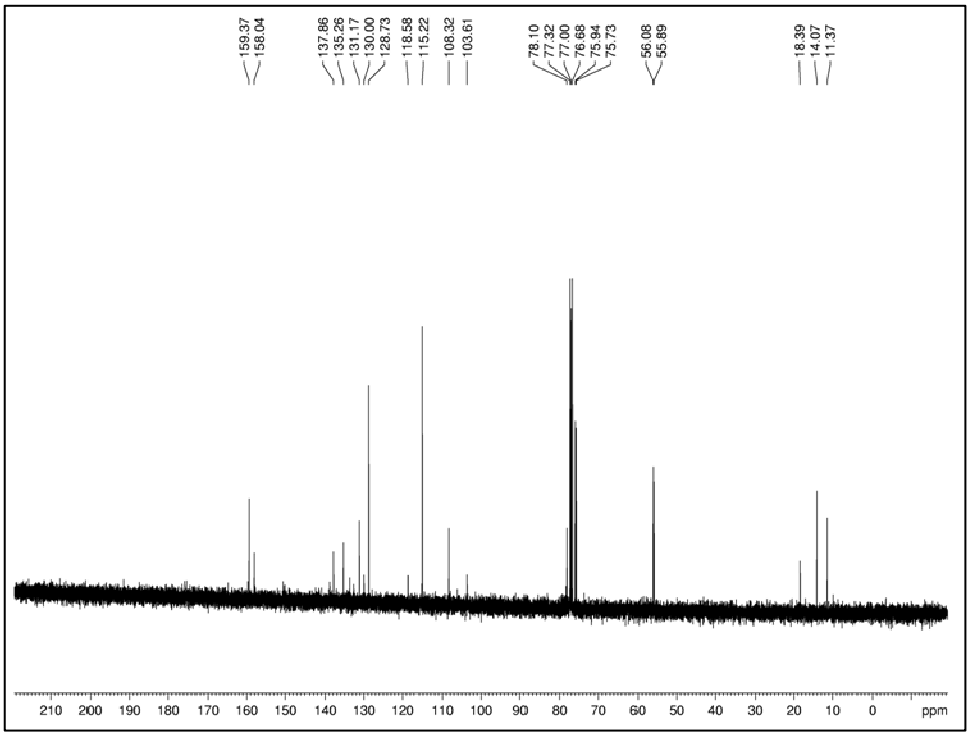
^{1}H NMR spectra of Compound **10**.



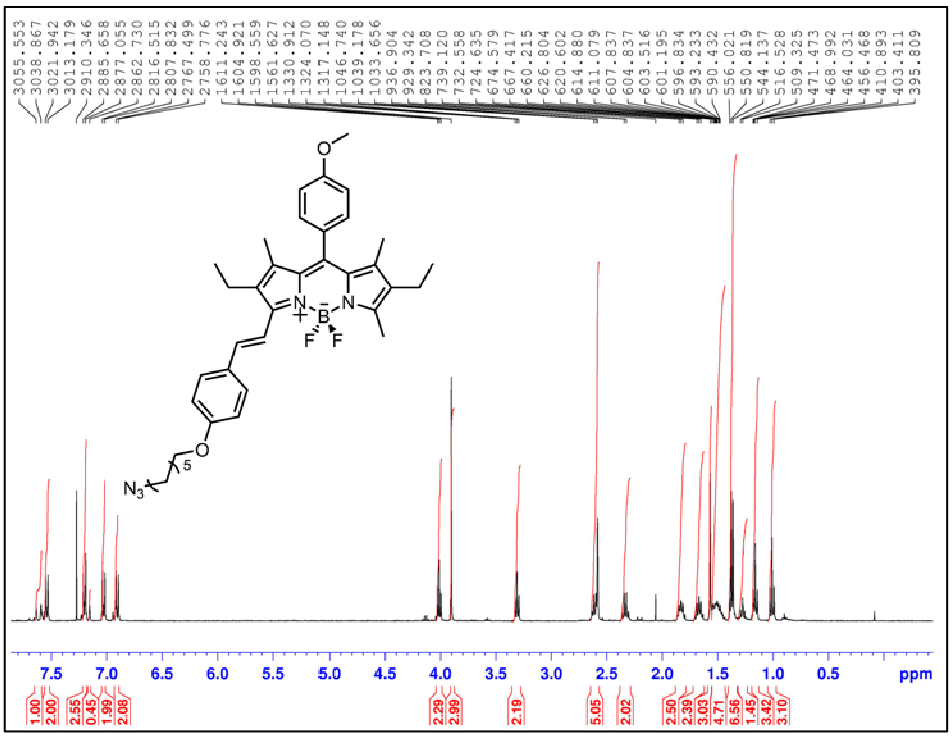


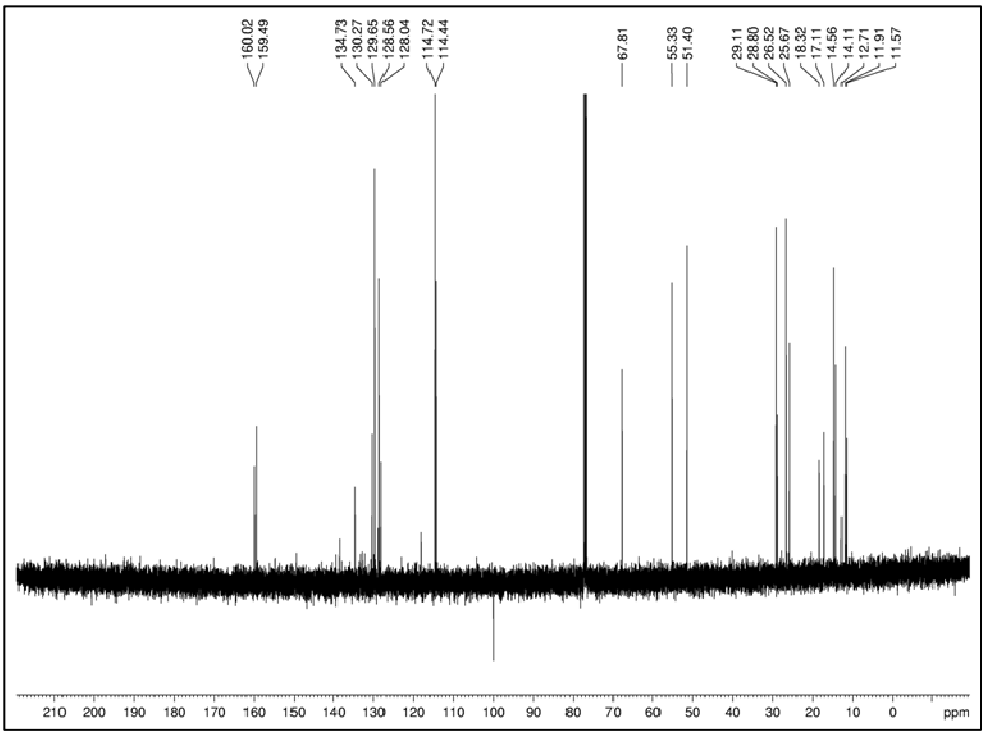
^{1}H and ^{13}C NMR spectra of Compound **11**.



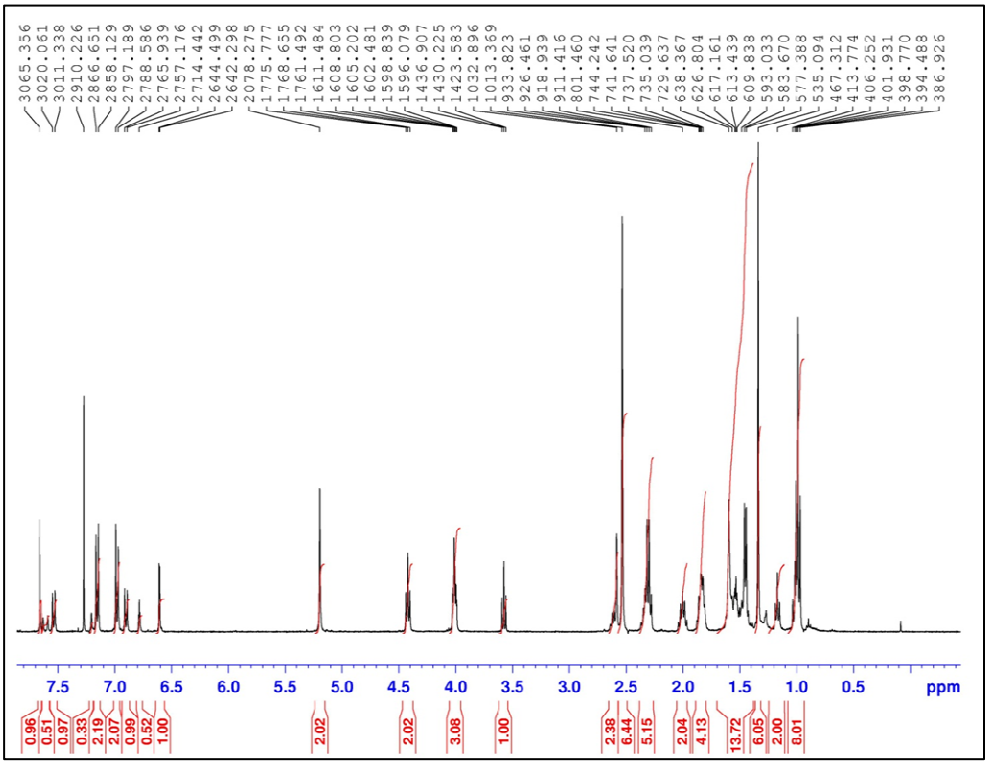


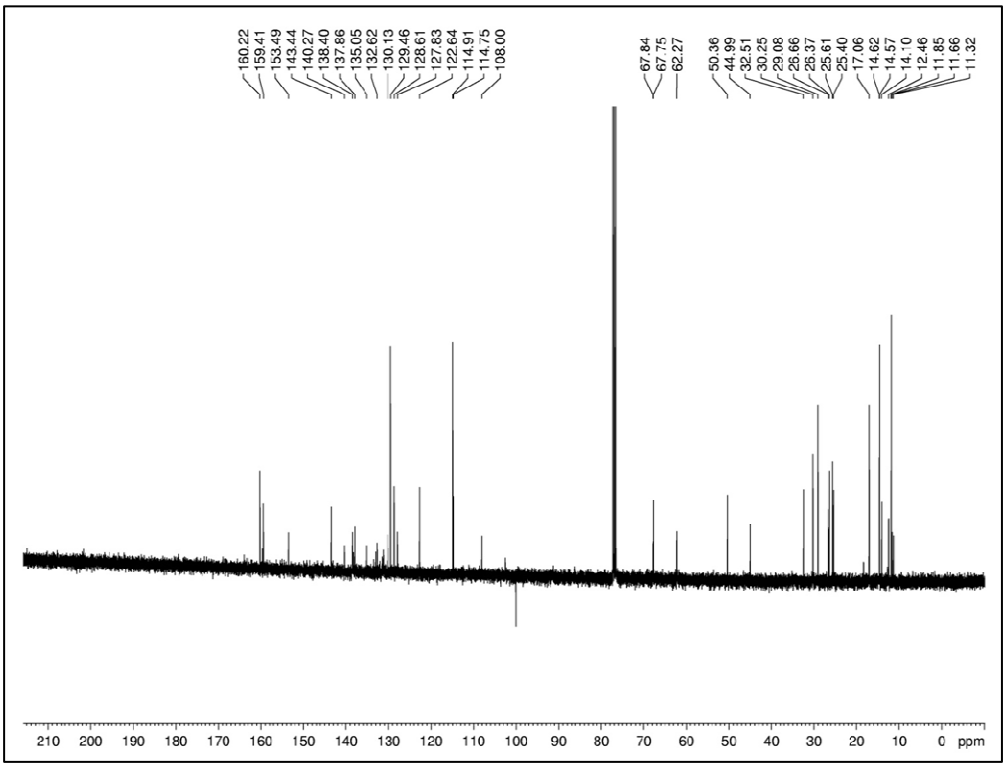
^{1}H and ^{13}C NMR spectra of Compound **12**.



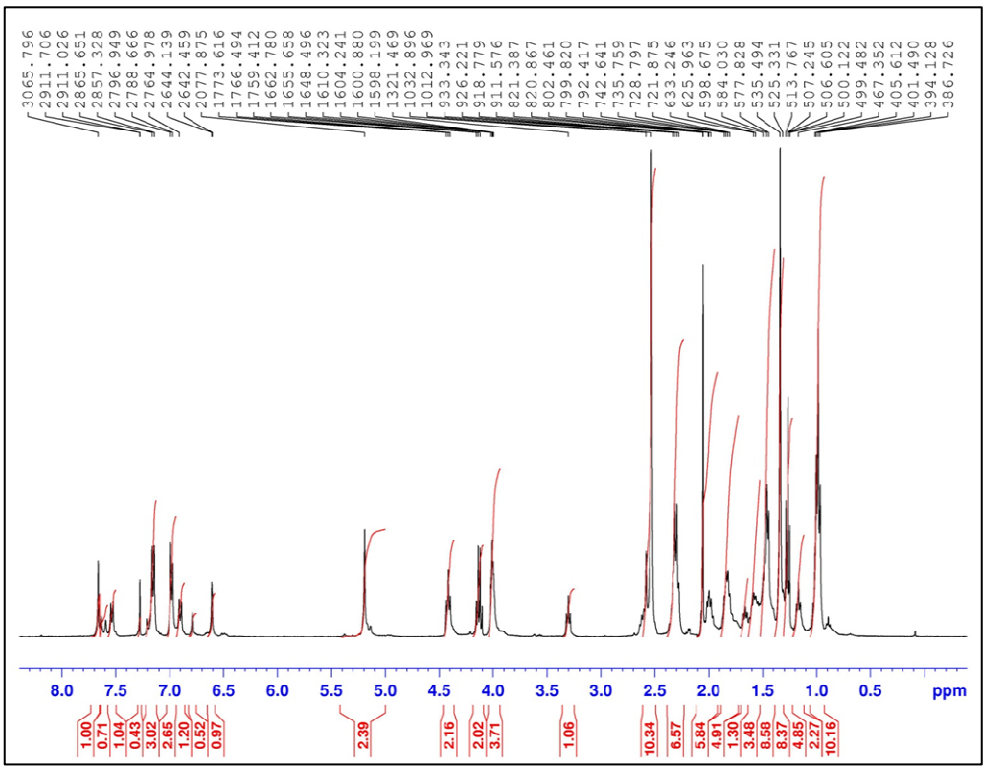


^{1}H and ^{13}C NMR spectra of Compound **13**.

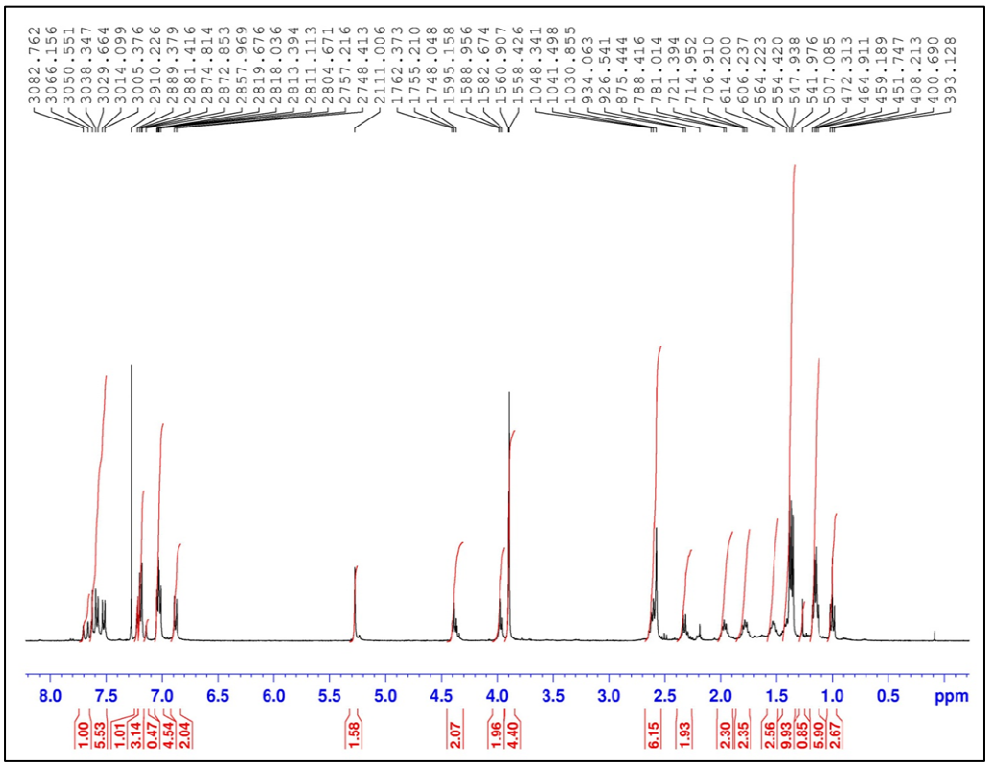


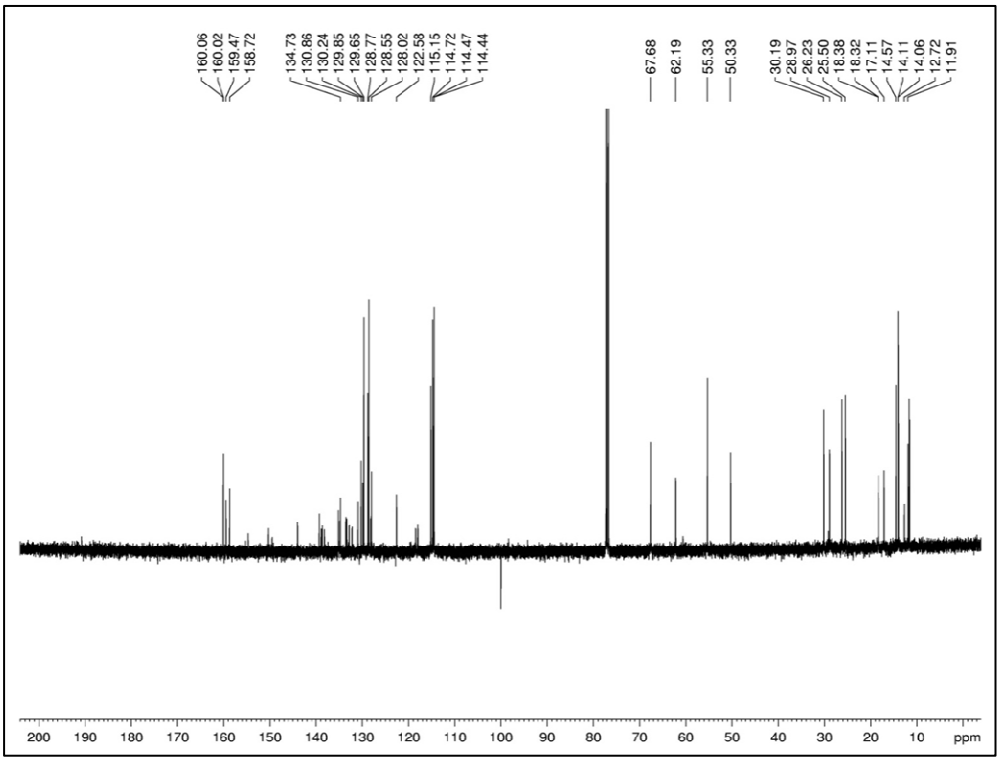


^{1}H and ^{13}C NMR spectra of Compound **14**.



^{1}H NMR spectra of Compound **15**.





^{1}H and ^{13}C NMR spectra of Compound **16**.

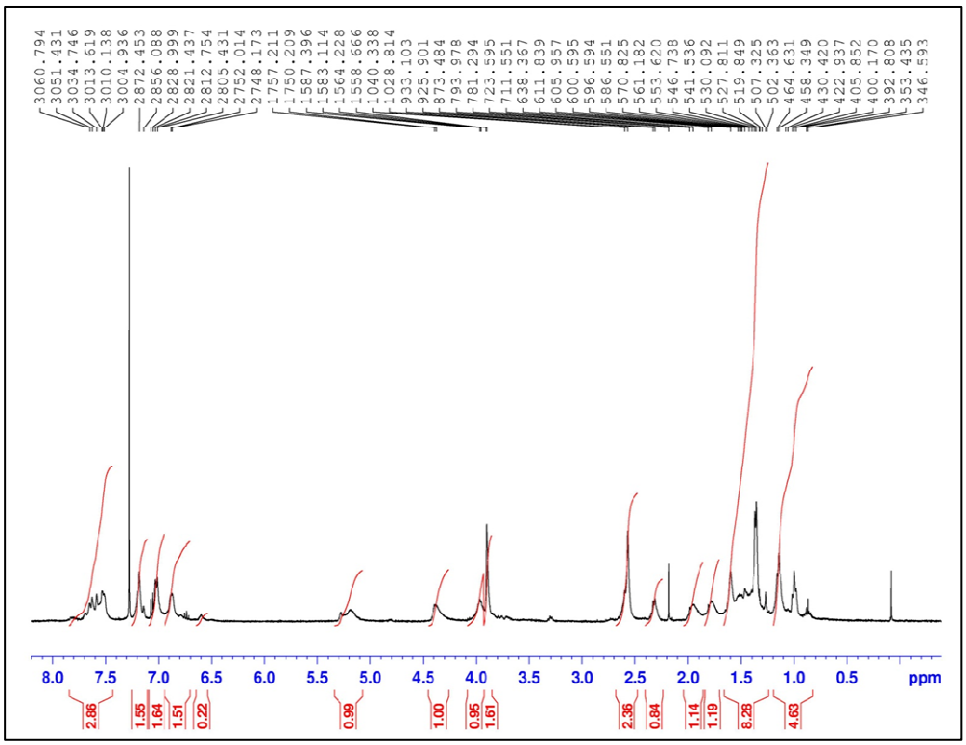
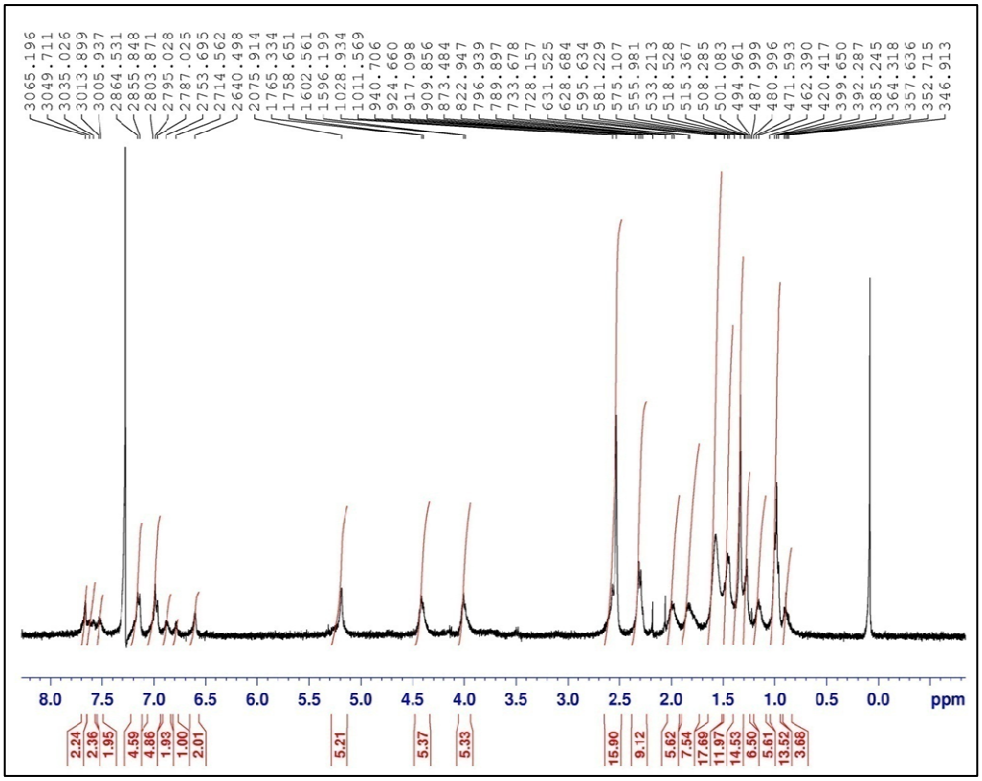
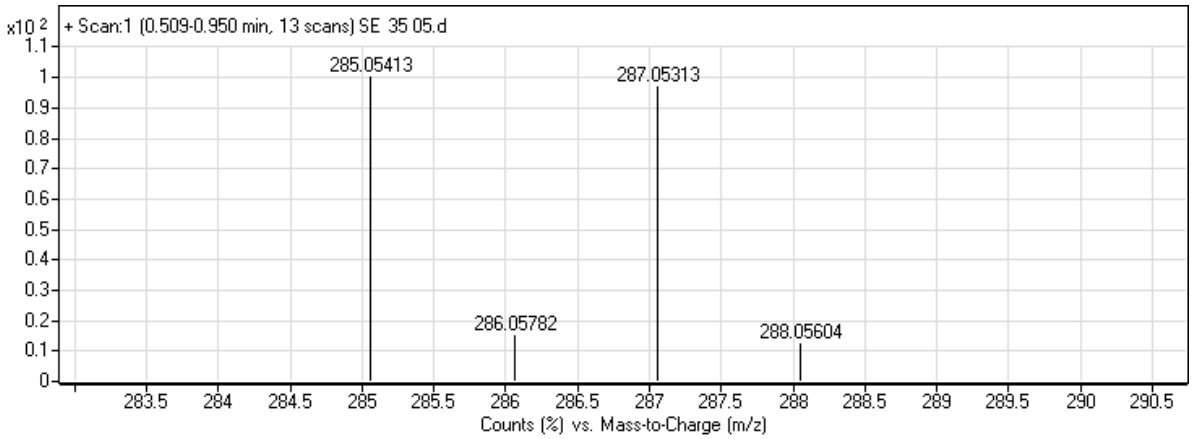


Figure 34. [1]H NMR spectra of Compound **17**.

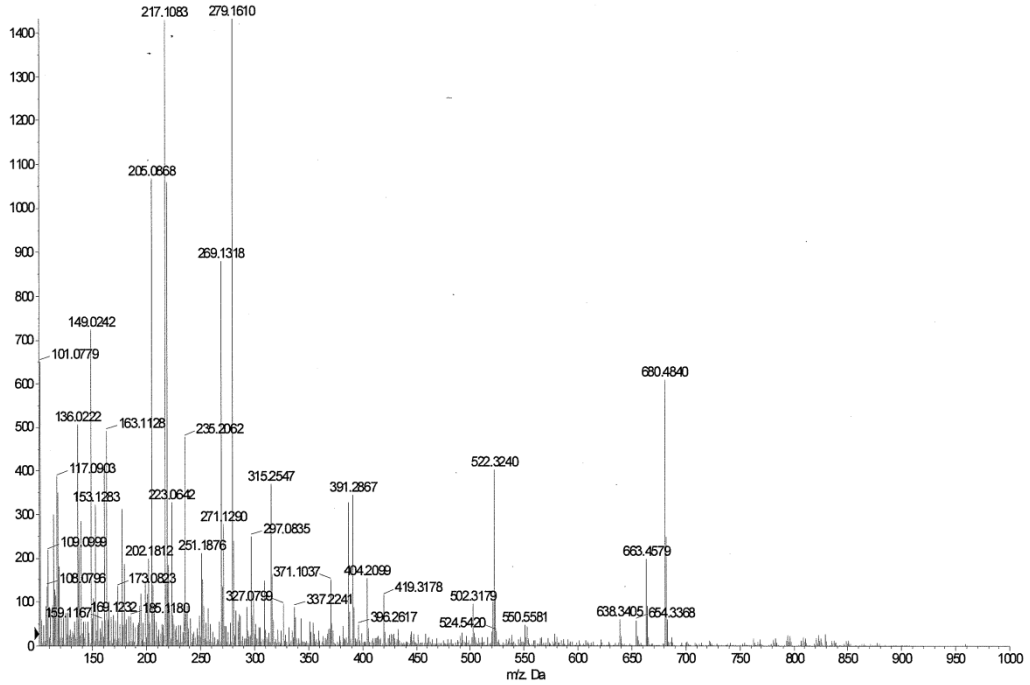


[1]H NMR spectra of Compound **18**.

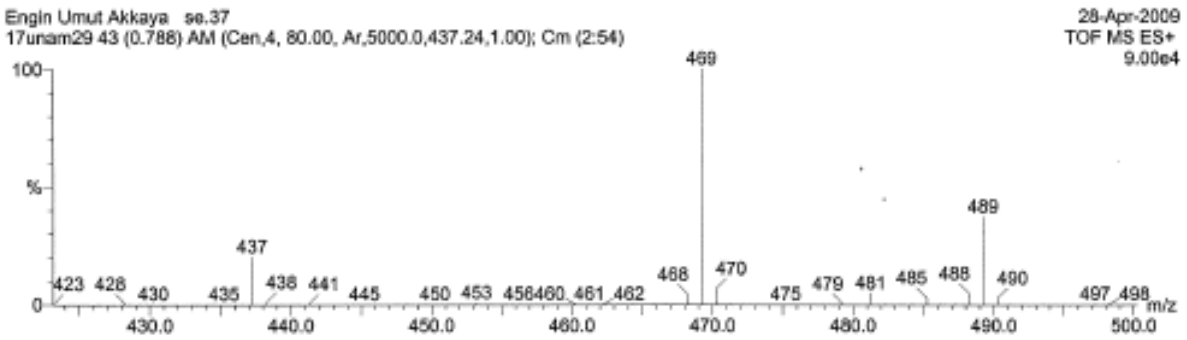
8. MASS Spectra



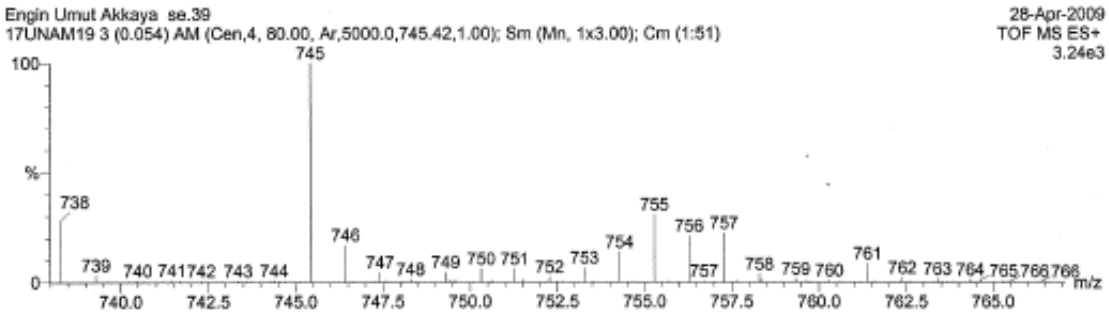
ESI-HRMS of compound **1**.



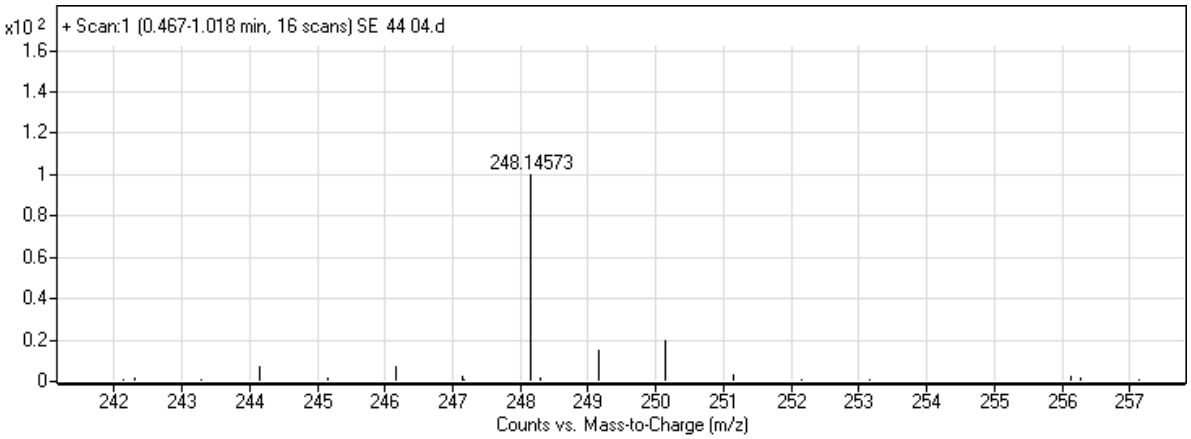
ESI-HRMS of compound **3**.



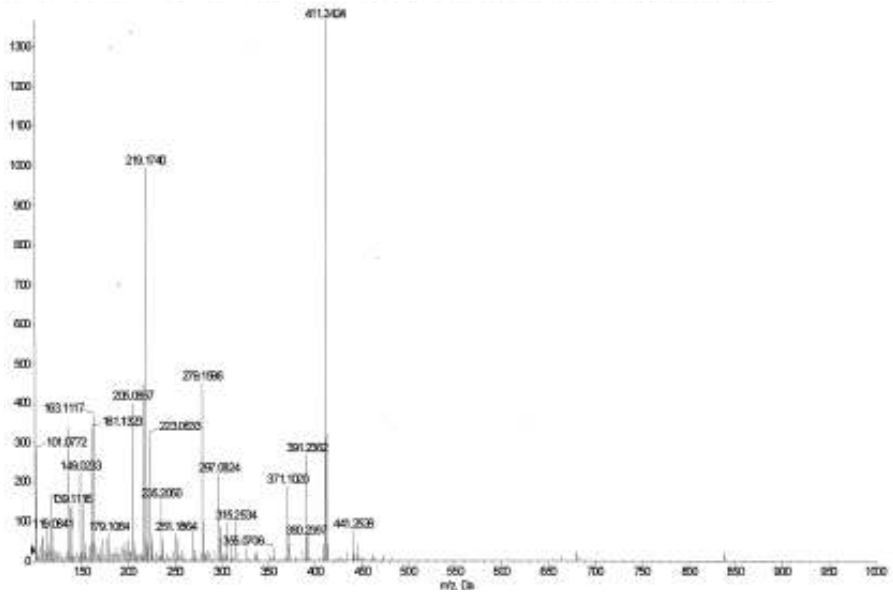
ESI-HRMS of compound **6**.



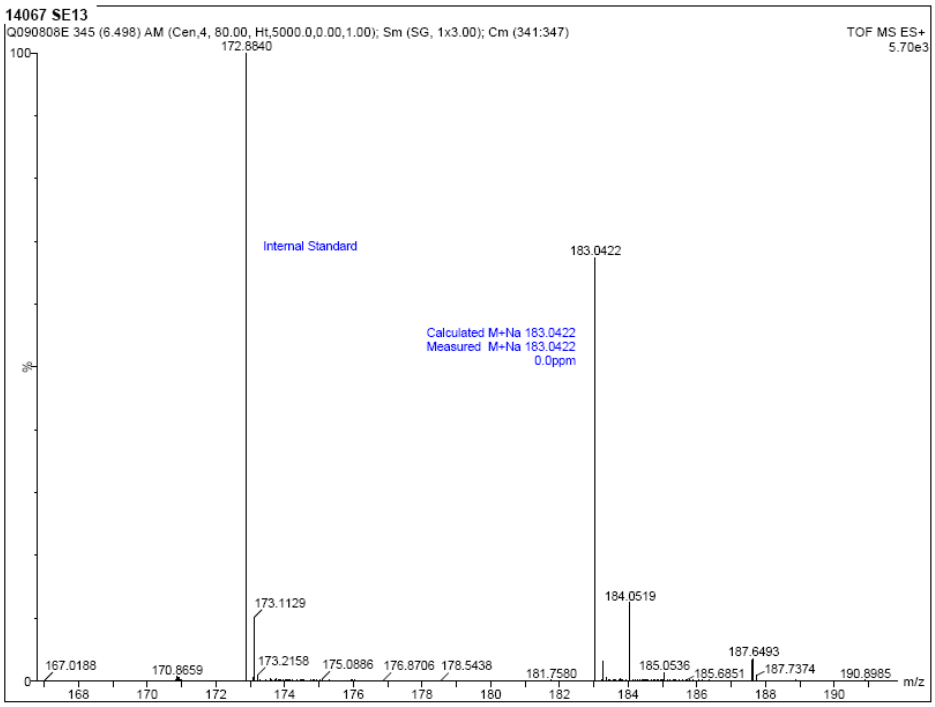
ESI-HRMS of compound **7**.



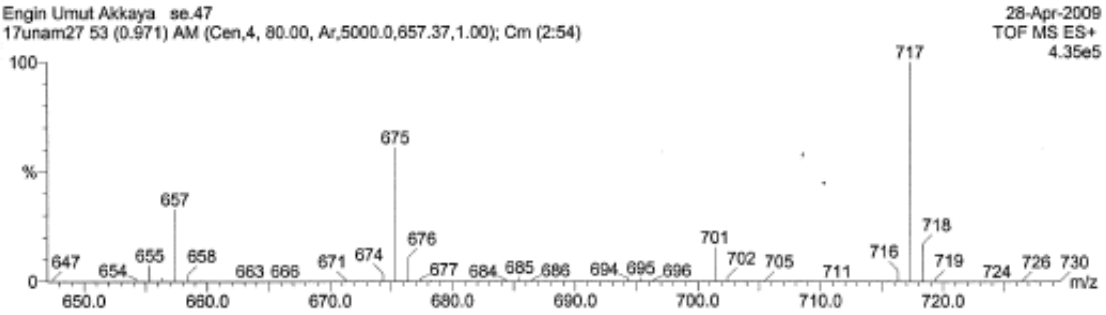
ESI-HRMS of compound **8**.



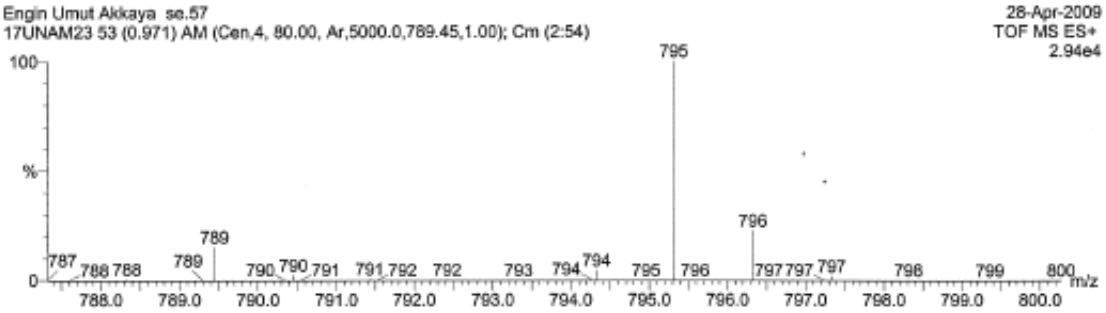
ESI-HRMS of compound **9**.



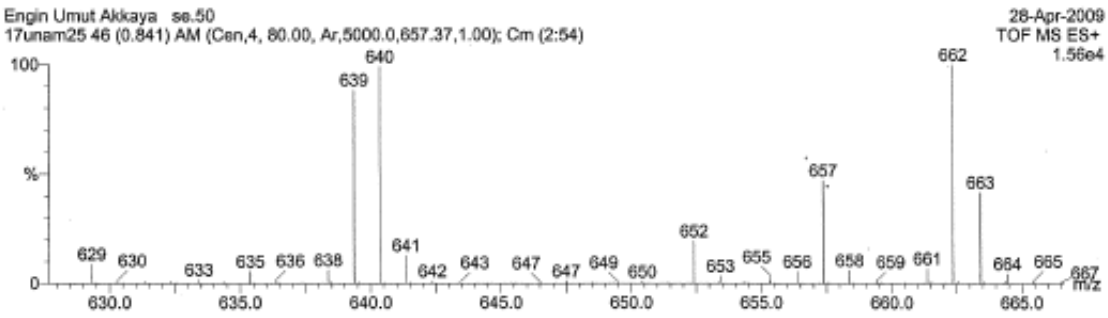
ESI-HRMS of compound **10**.



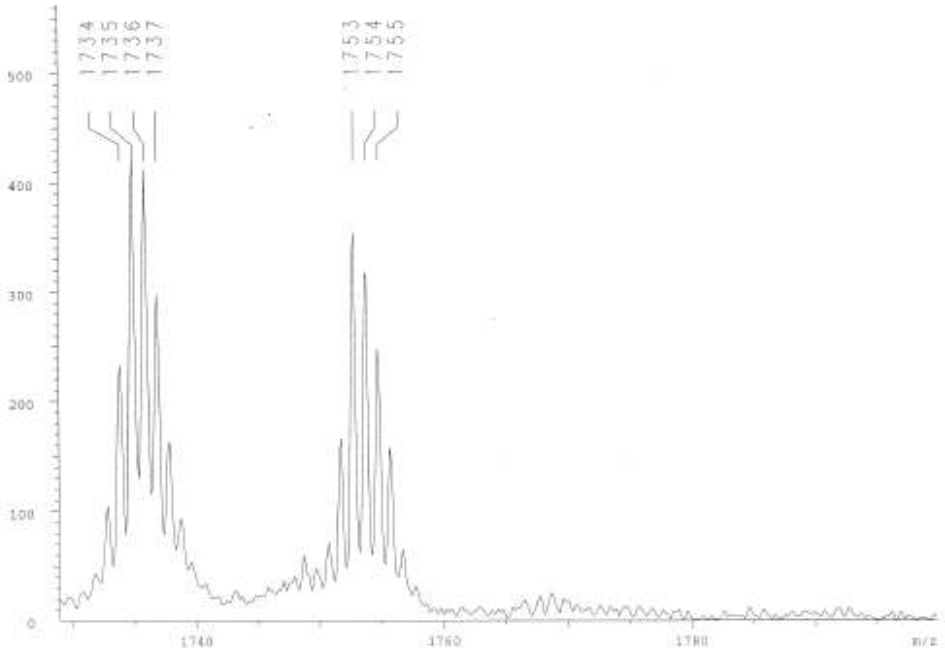
ESI-HRMS of compound **11**.



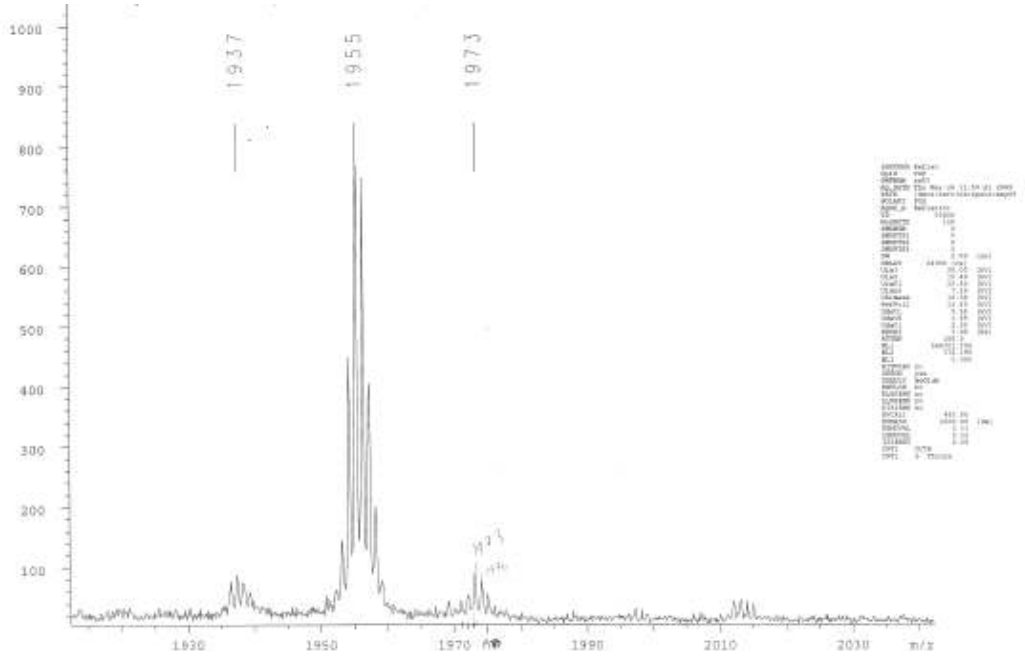
ESI-HRMS of compound **12**.



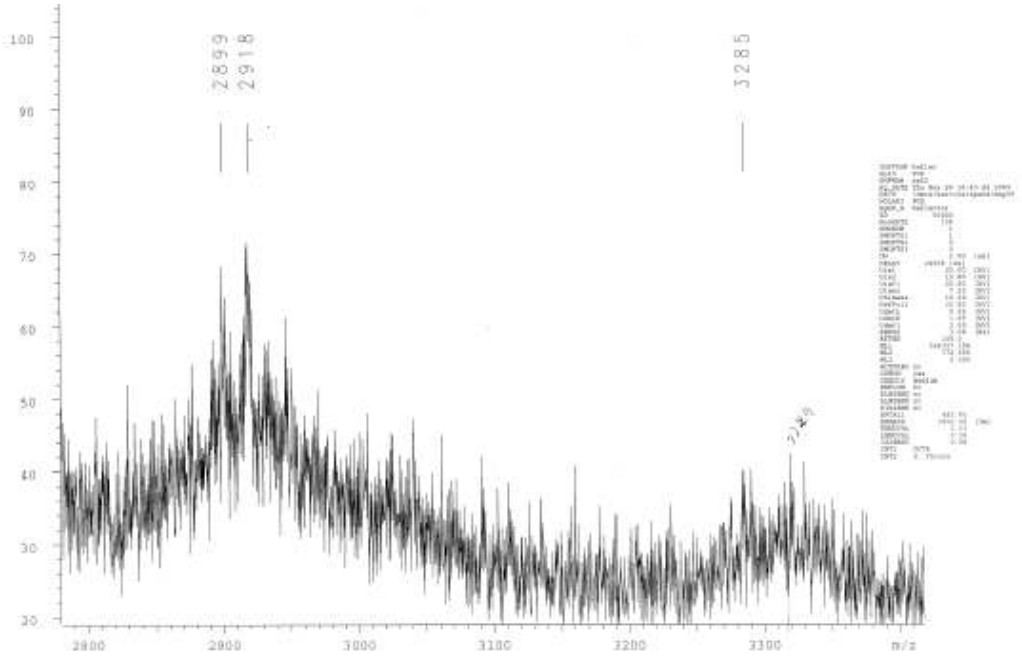
ESI-HRMS of compound **13**.



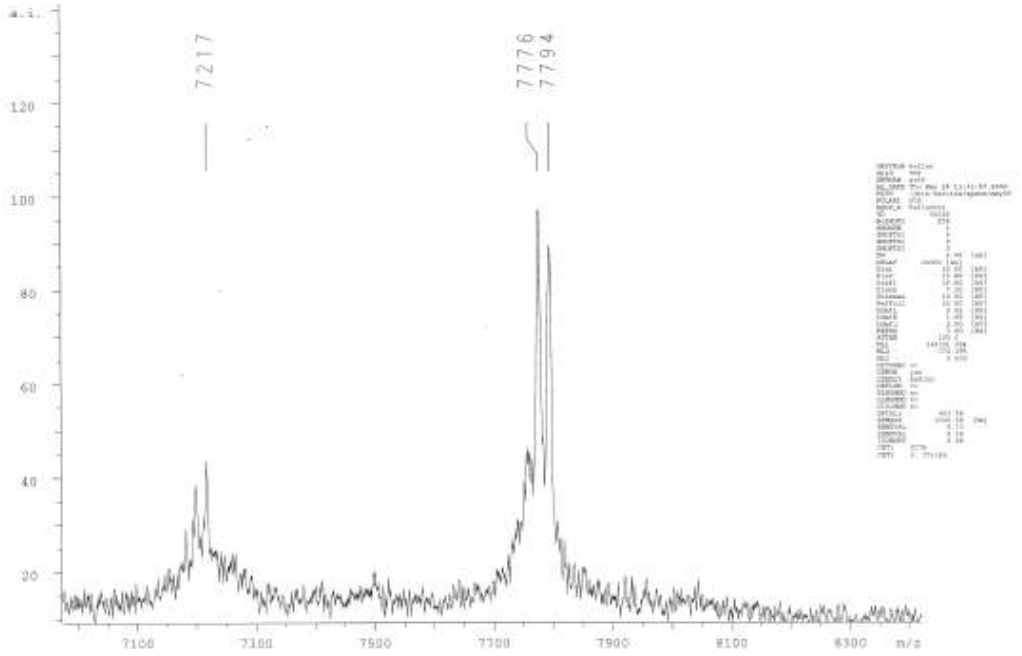
MALDI-MS of compound **14**.



MALDI-MS of compound **16**.



MALDI-MS of compound **17**.



MALDI-MS of compound **18**.