

SUPPORTING INFORMATION

BODIPY decorated dendrimeric cyclotriphosphazene photosensitizers: Synthesis and efficient singlet oxygen generators

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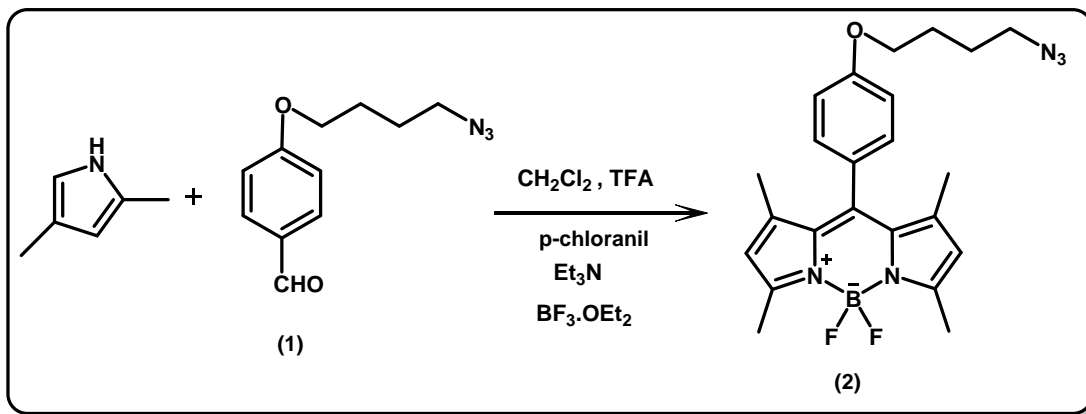
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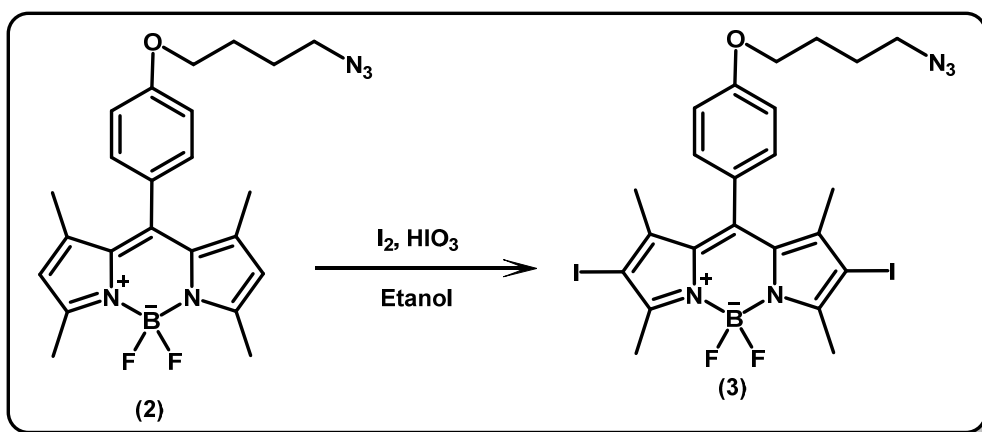
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General methods

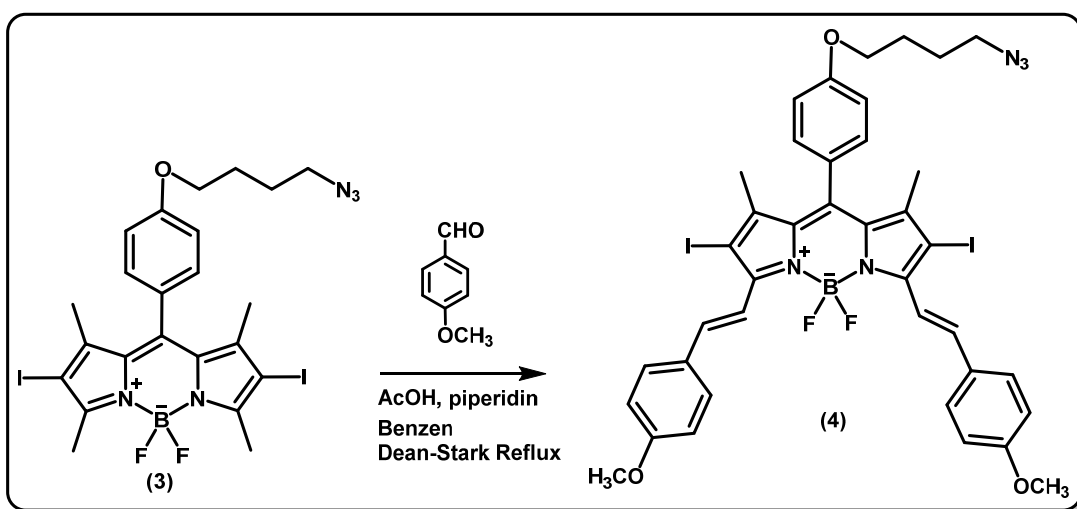
All reagents were purchased from Aldrich and used without further purification and all solvents were obtained from Merck. Reactions were monitored by thin layer chromatography using Merck TLC Silica gel 60 F₂₅₄. Silica gel column chromatography was performed over Merck Silica gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM). Mass analyses were recorded on a Bruker MALDI-TOF (Matrix-Assisted Laser Desorption/Ionization-Time-Of-Flight) spectrometer using 2,5-dihydroxybenzoic acid as a matrix. ¹H, ¹³C and ³¹P NMR spectra were recorded for all compounds in CDCl₃ on a Varian INOVA 500 MHz spectrometer using TMS as an internal reference for ¹H and ¹³C measurements. Electronic absorption spectra in the UV-Vis. region were recorded with a Shimadzu 2101 UV-Vis spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm path length cuvettes at room temperature. Melting points were measured on a Gallenkamp apparatus using a capillary tube. Photo-irradiations were done using a General Electric quartz line lamp (300W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations respectively. An interference filter (Intor, 600 nm with a band width of 40 nm).



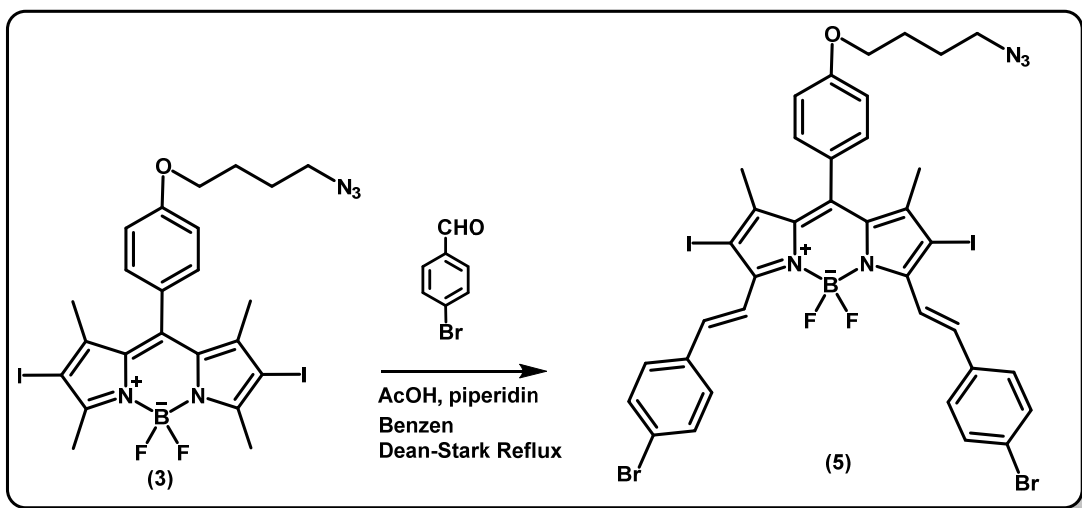
Scheme S1. Synthesis of Compound 2



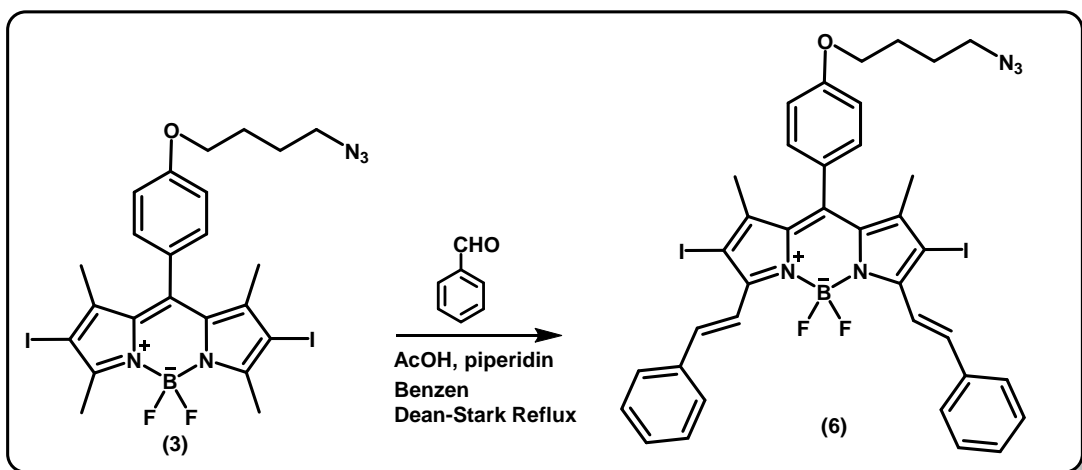
Scheme S2. Synthesis of Compound 3



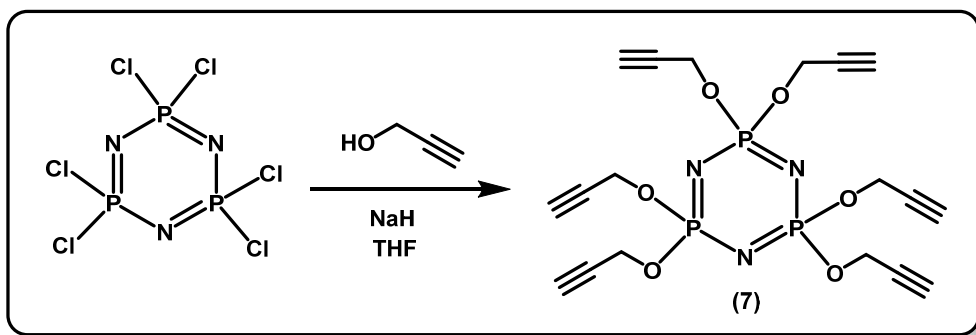
Scheme S3. Synthesis of Compound 4



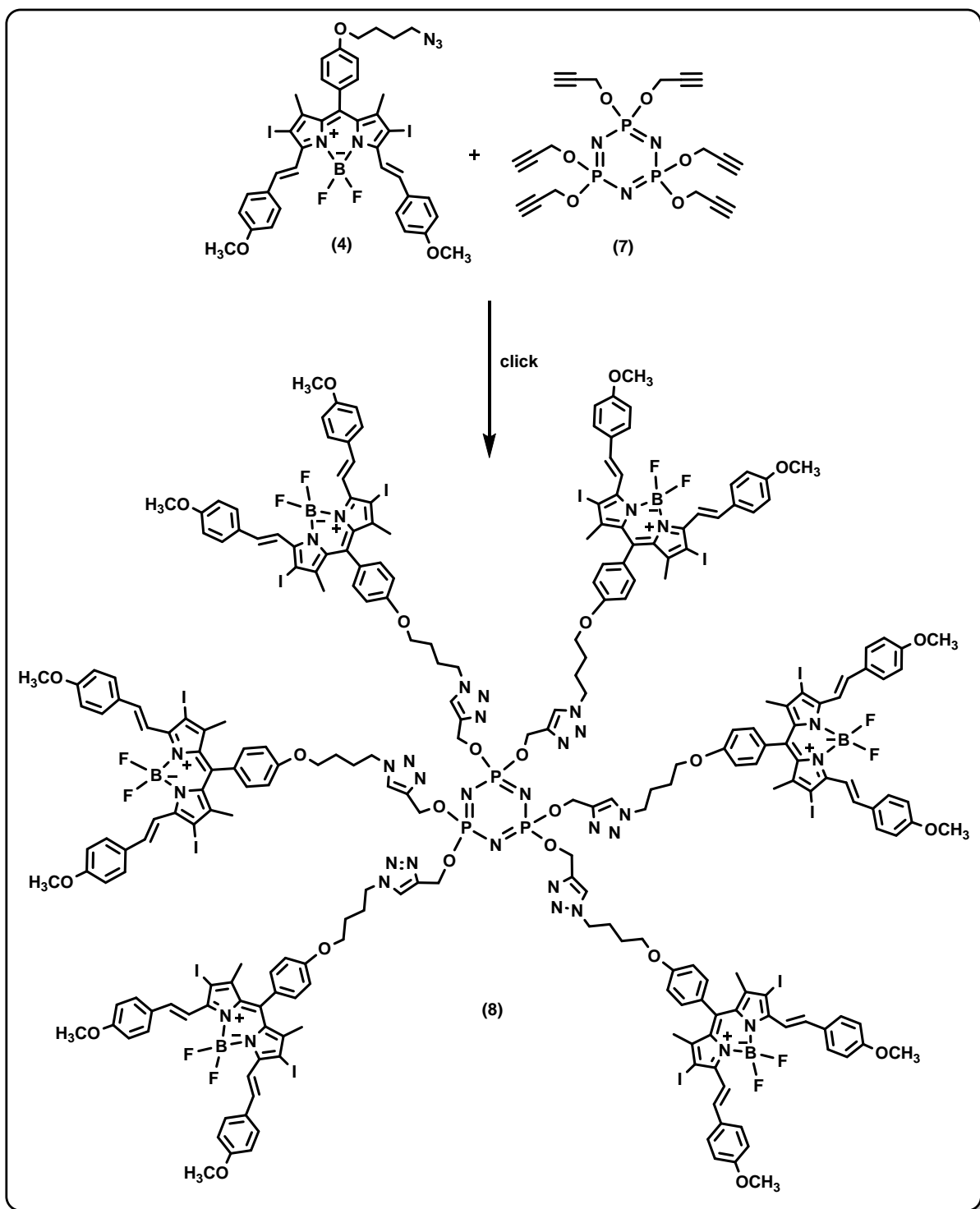
Scheme S4. Synthesis of Compound 5



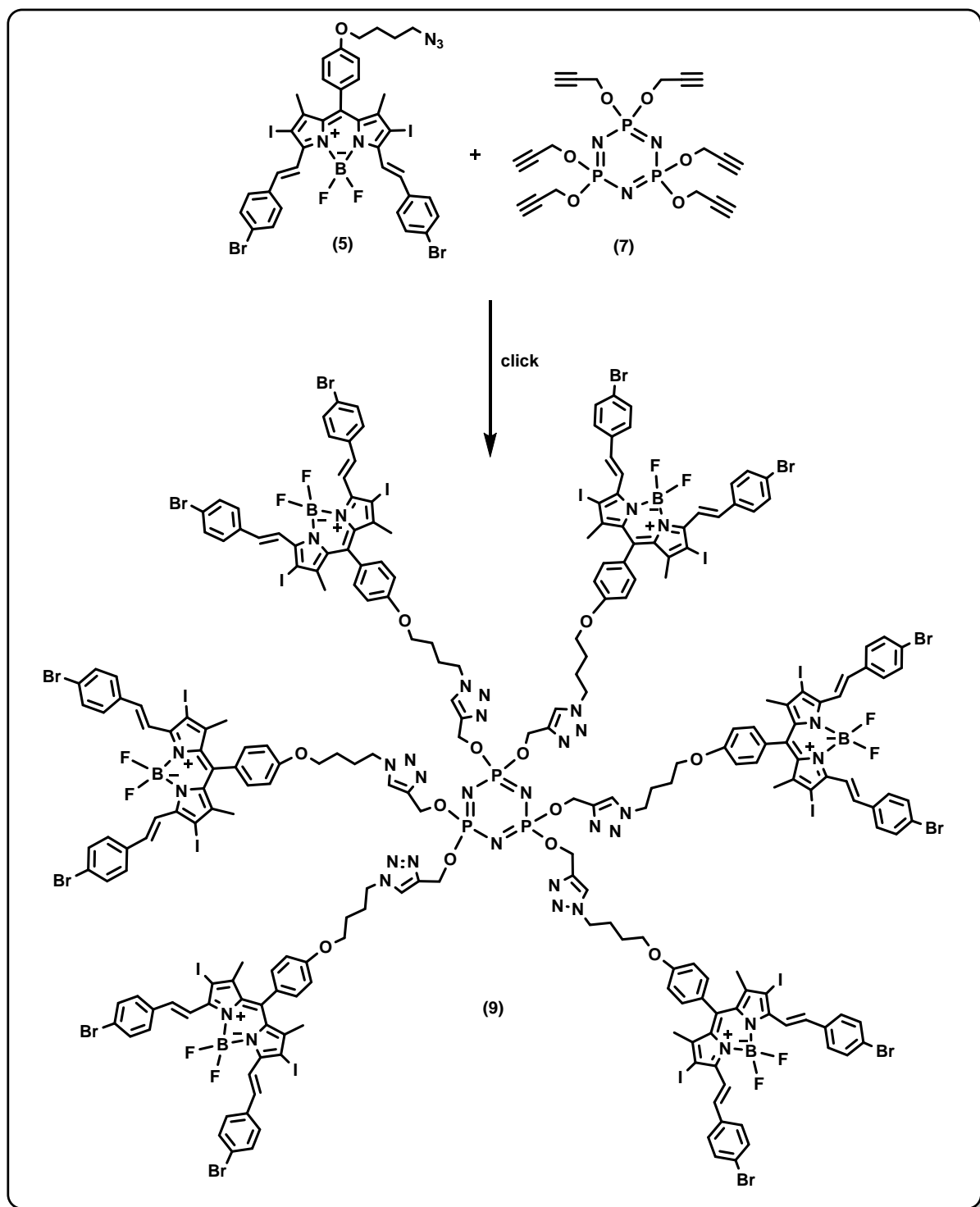
Scheme S5. Synthesis of Compound 6



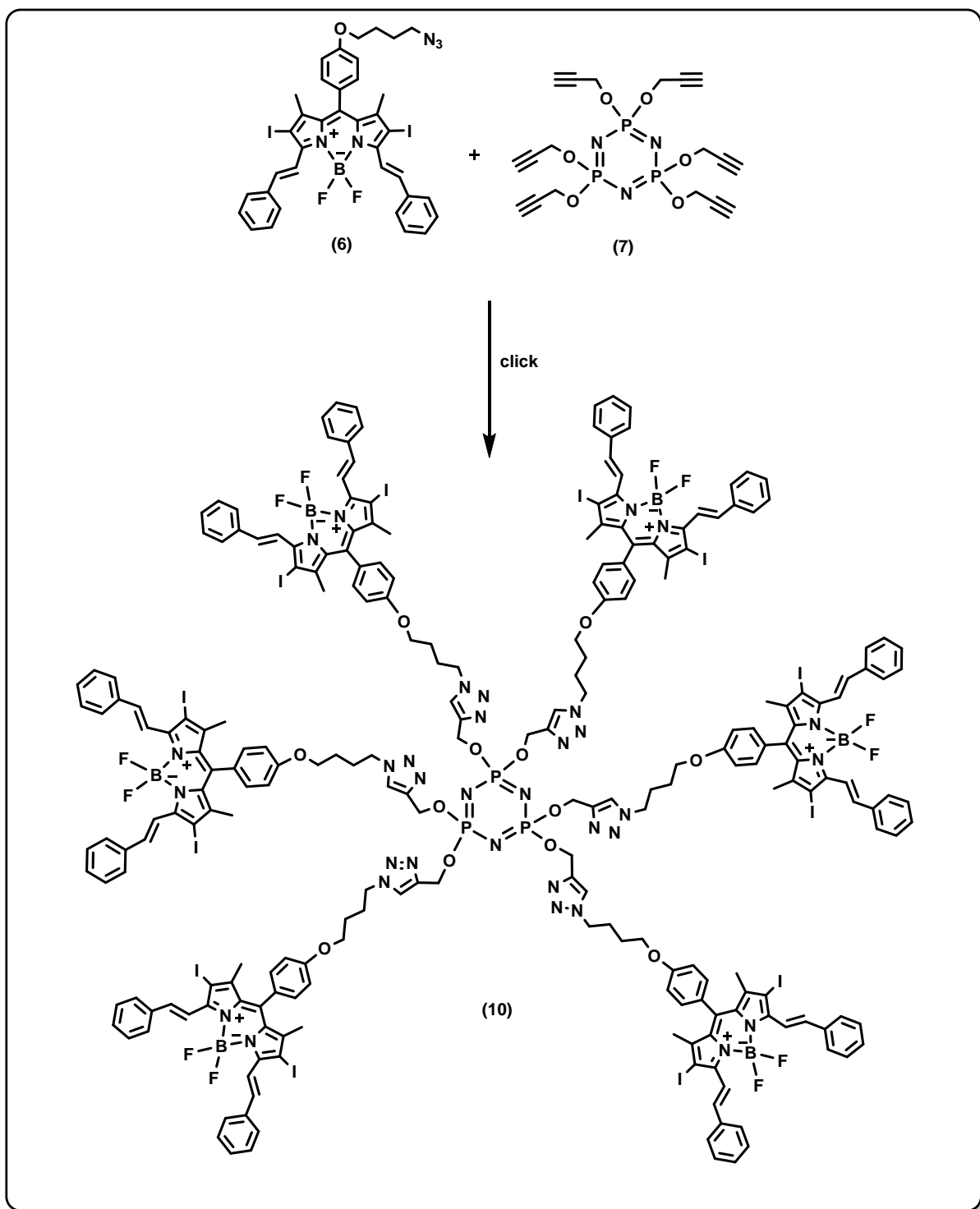
Scheme S6. Synthesis of Compound 7



Scheme S7. Synthesis of Compound 8



Scheme S8. Synthesis of Compound **9**



Scheme S9. Synthesis of Compound **10**

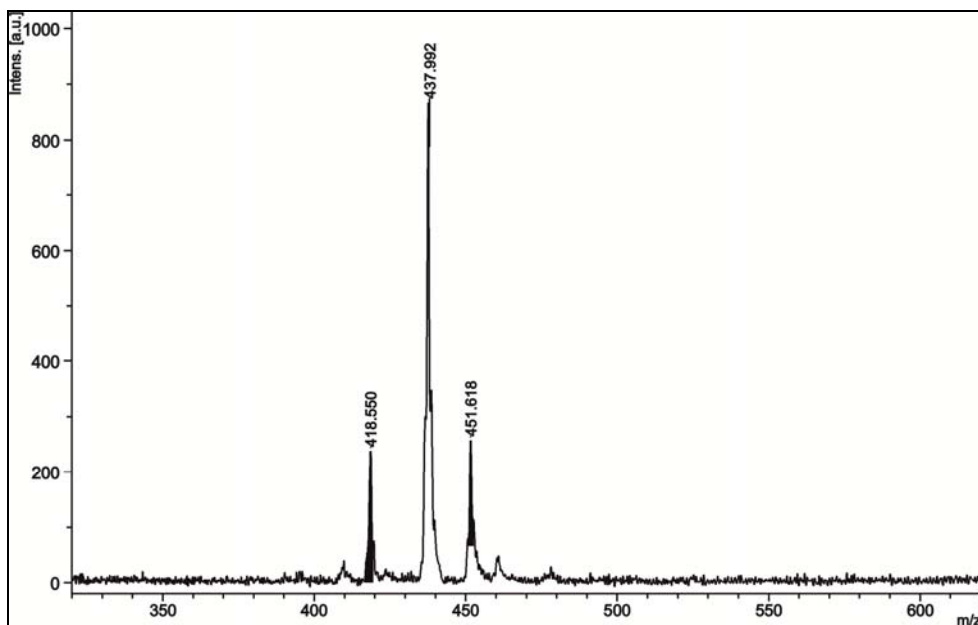


Figure S1: Mass spectrum of compound 2

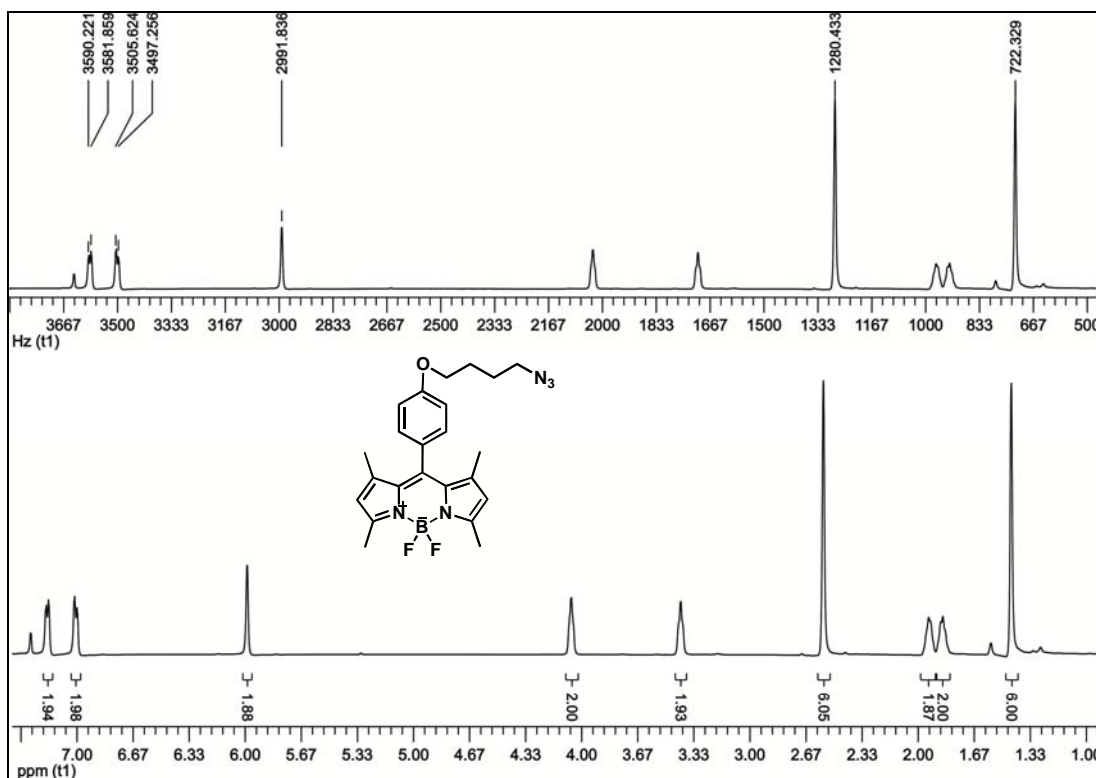


Figure S2: ¹H NMR spectrum of compound 2

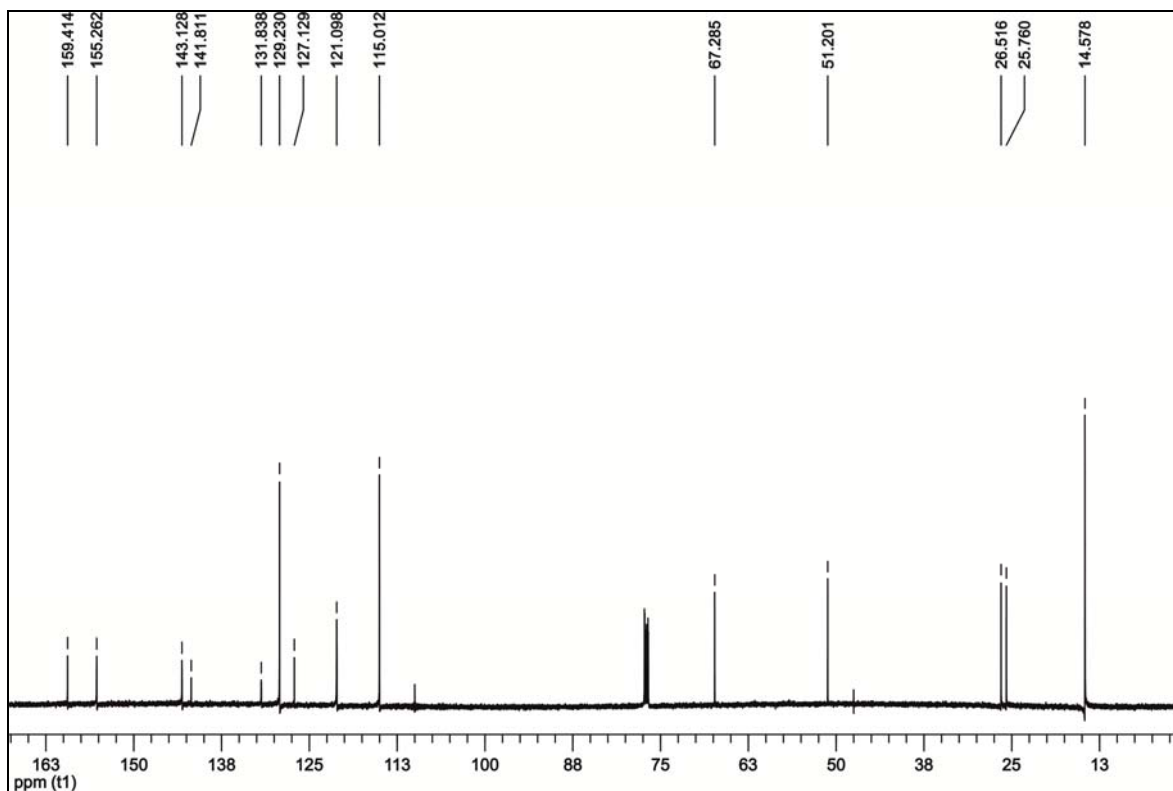


Figure S3: ^{13}C NMR spectrum of compound **2**

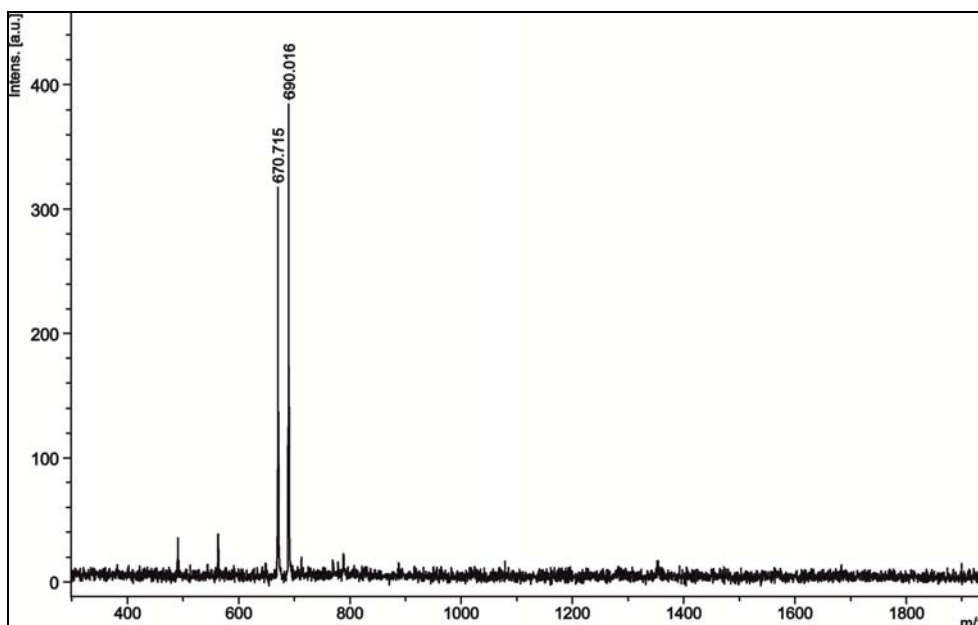


Figure S4: Mass spectrum of compound **3**

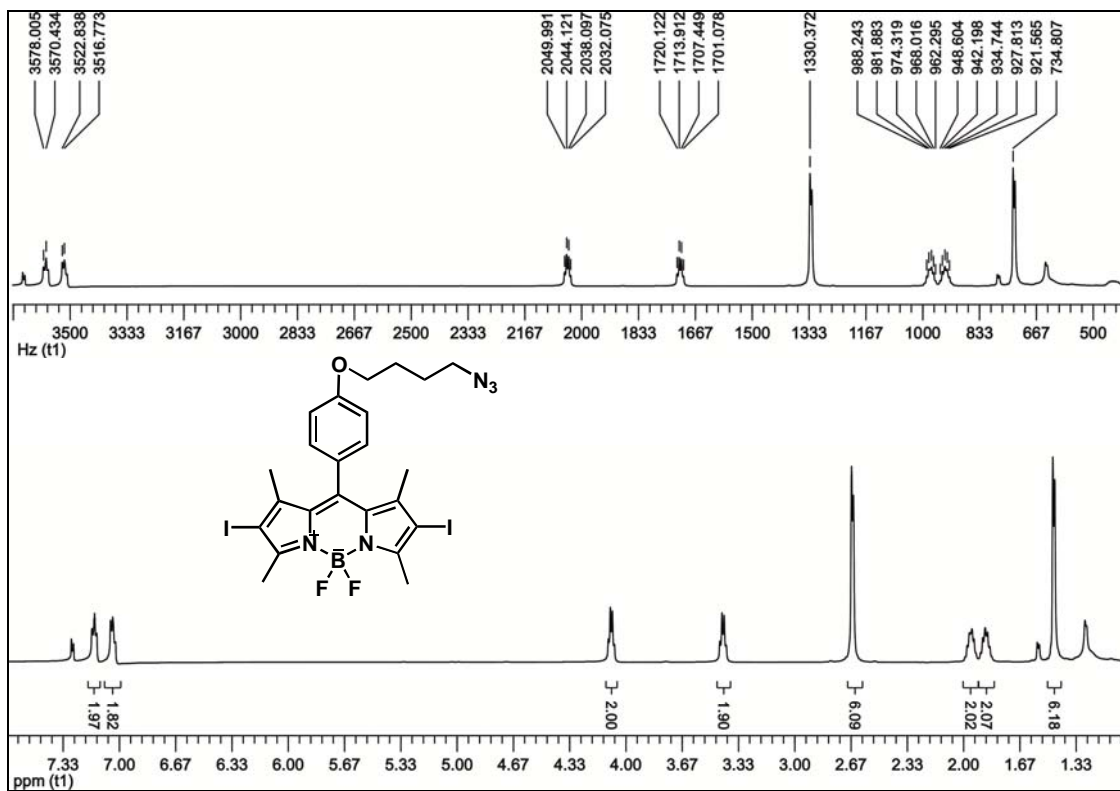


Figure S5: ^1H NMR spectrum of compound **3**

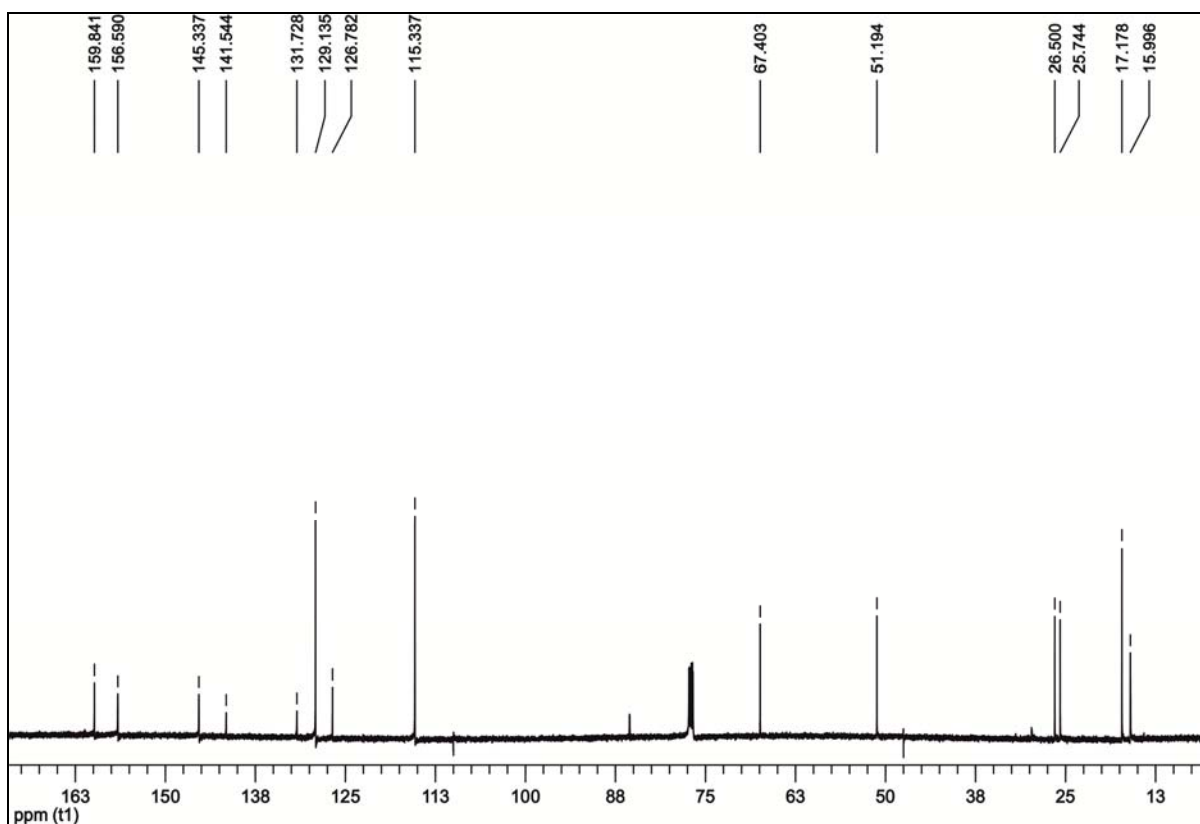


Figure S6: ^{13}C NMR spectrum of compound **3**

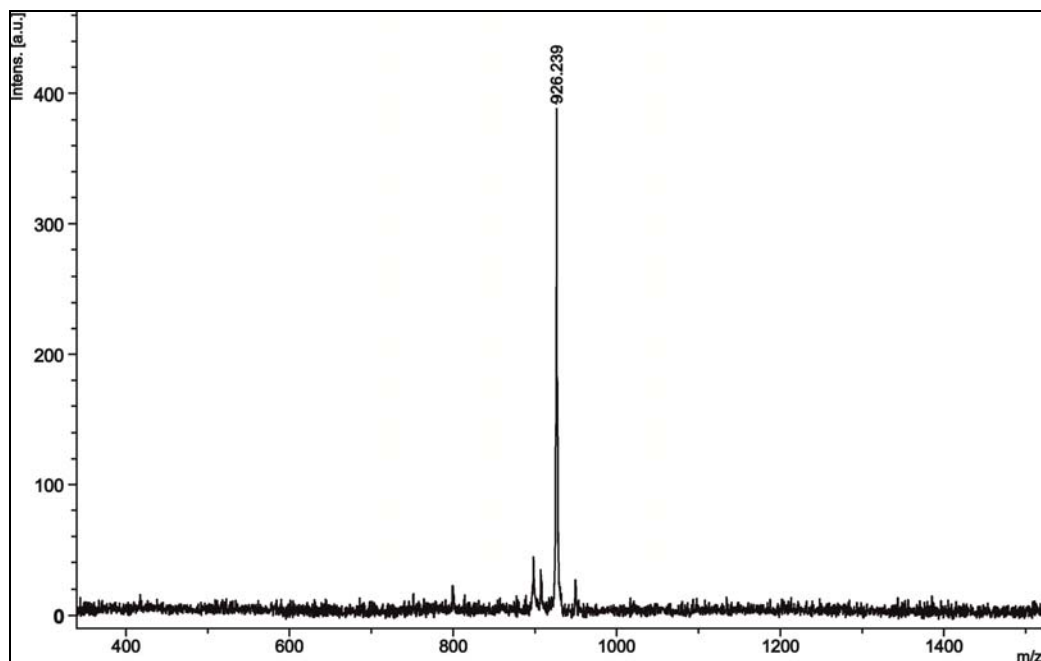


Figure S7: Mass spectrum of compound 4

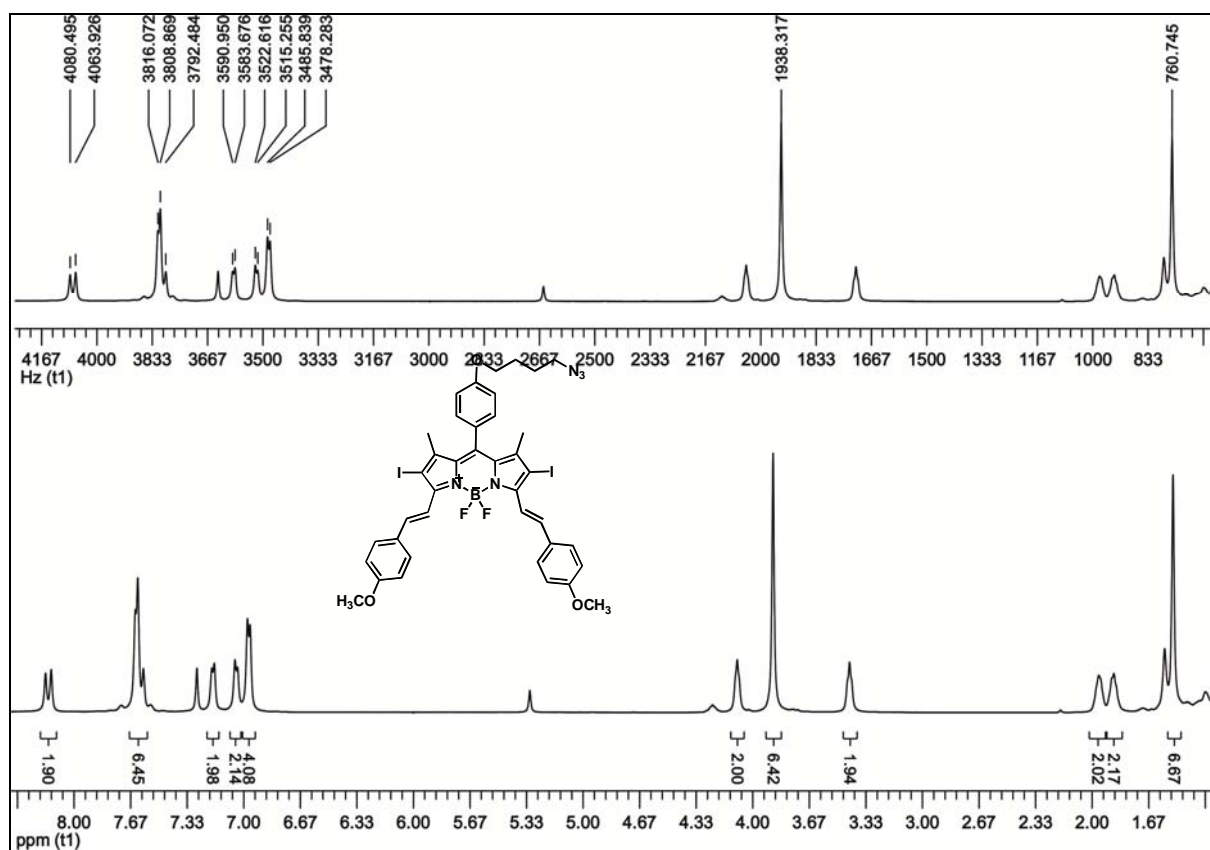


Figure S8: ¹H NMR spectrum of compound 4

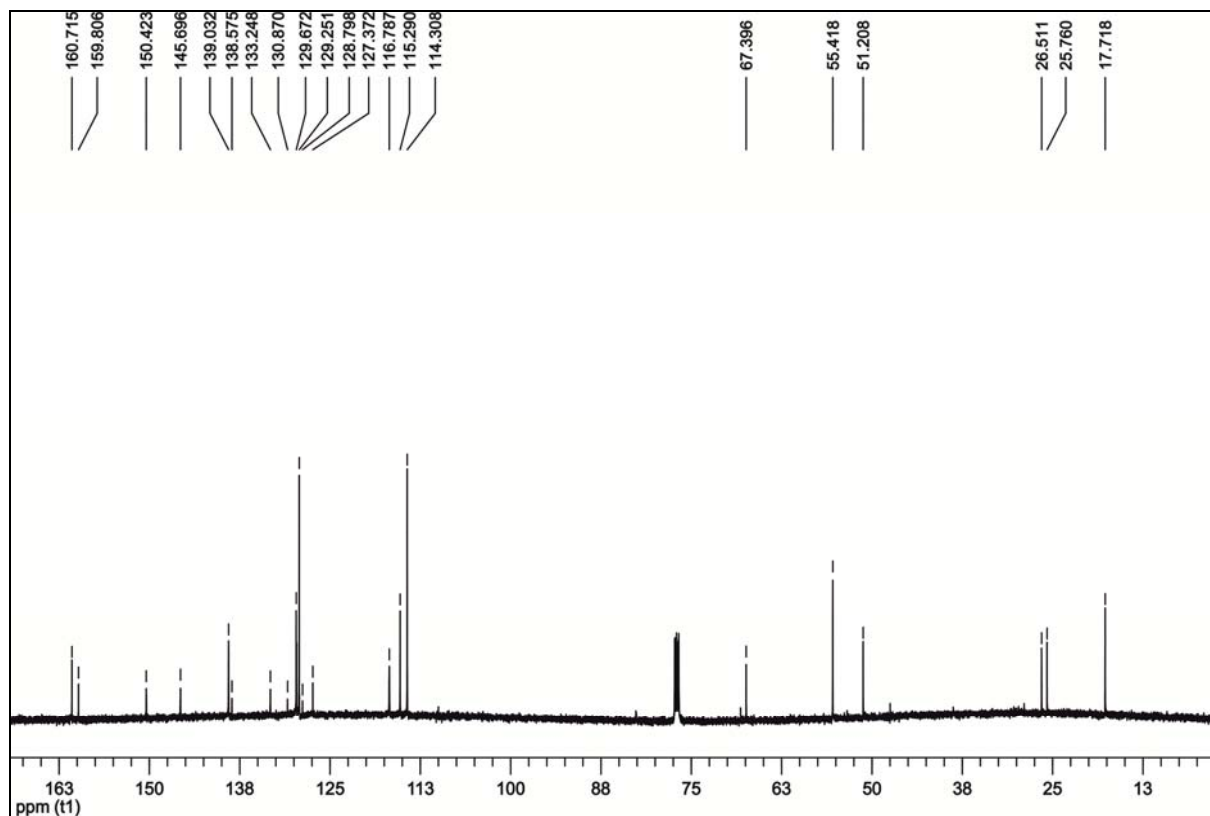


Figure S9. ^{13}C NMR spectrum of compound 4

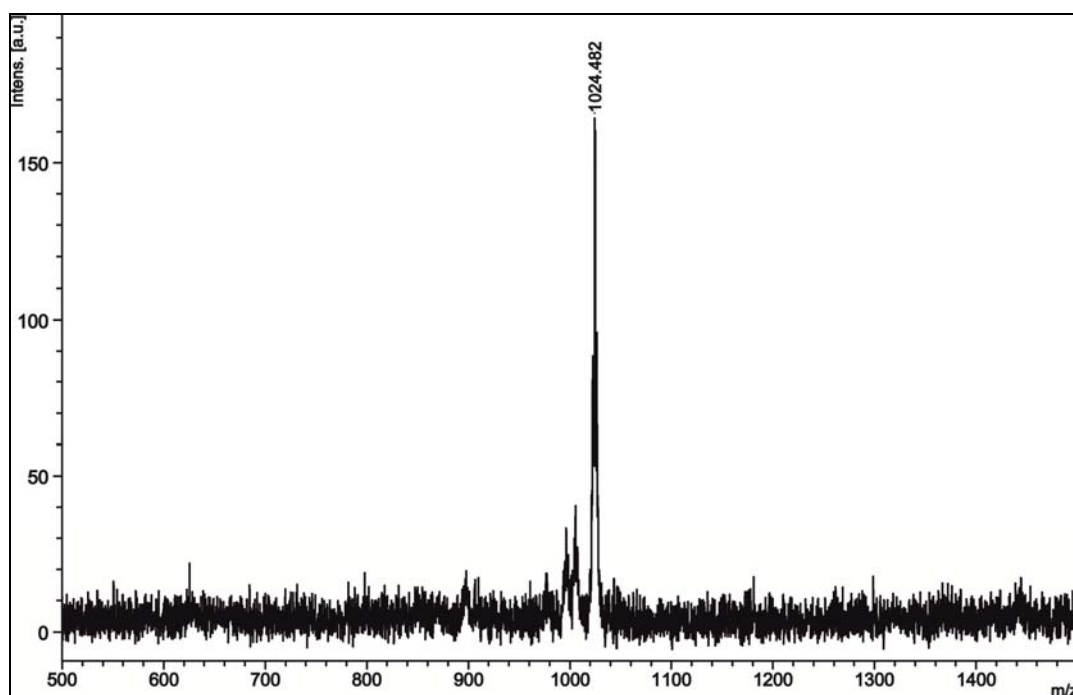


Figure S10. Mass spectrum of compound 5

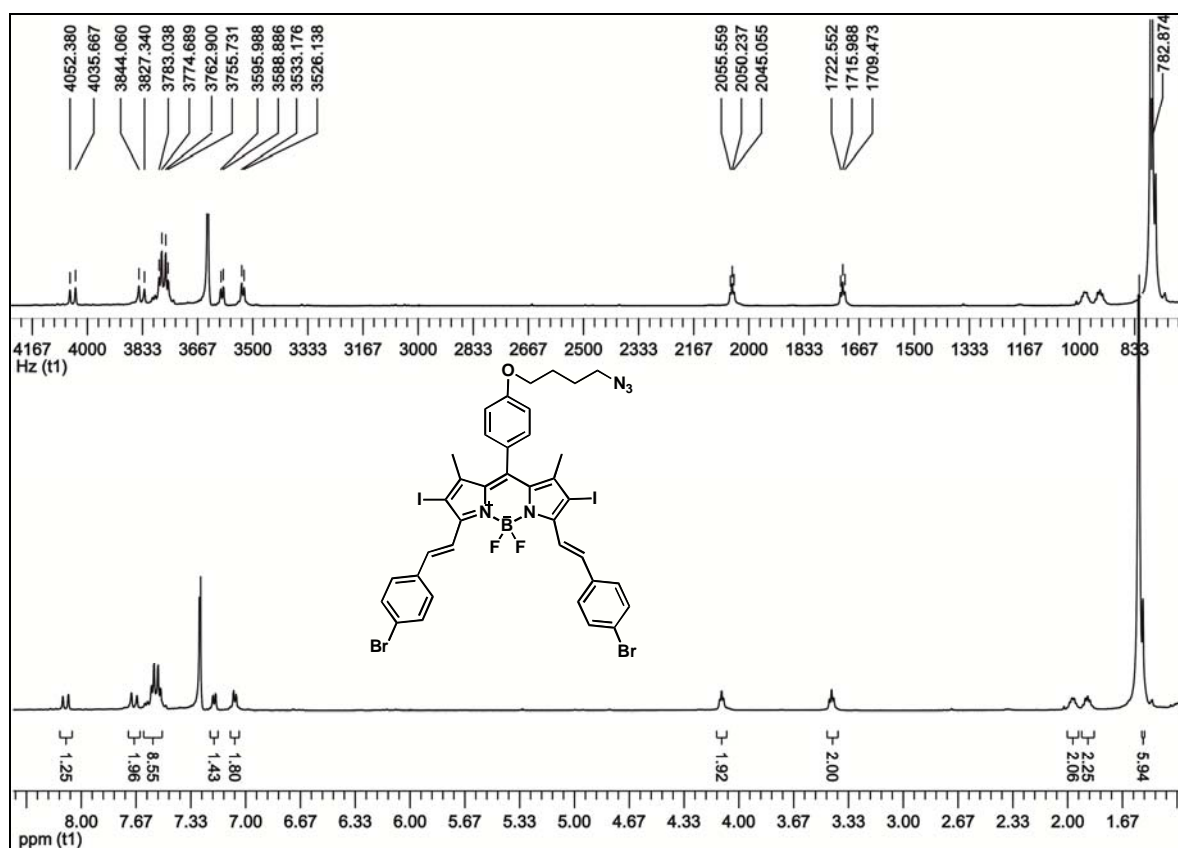


Figure S11. ¹H NMR spectrum of compound 5

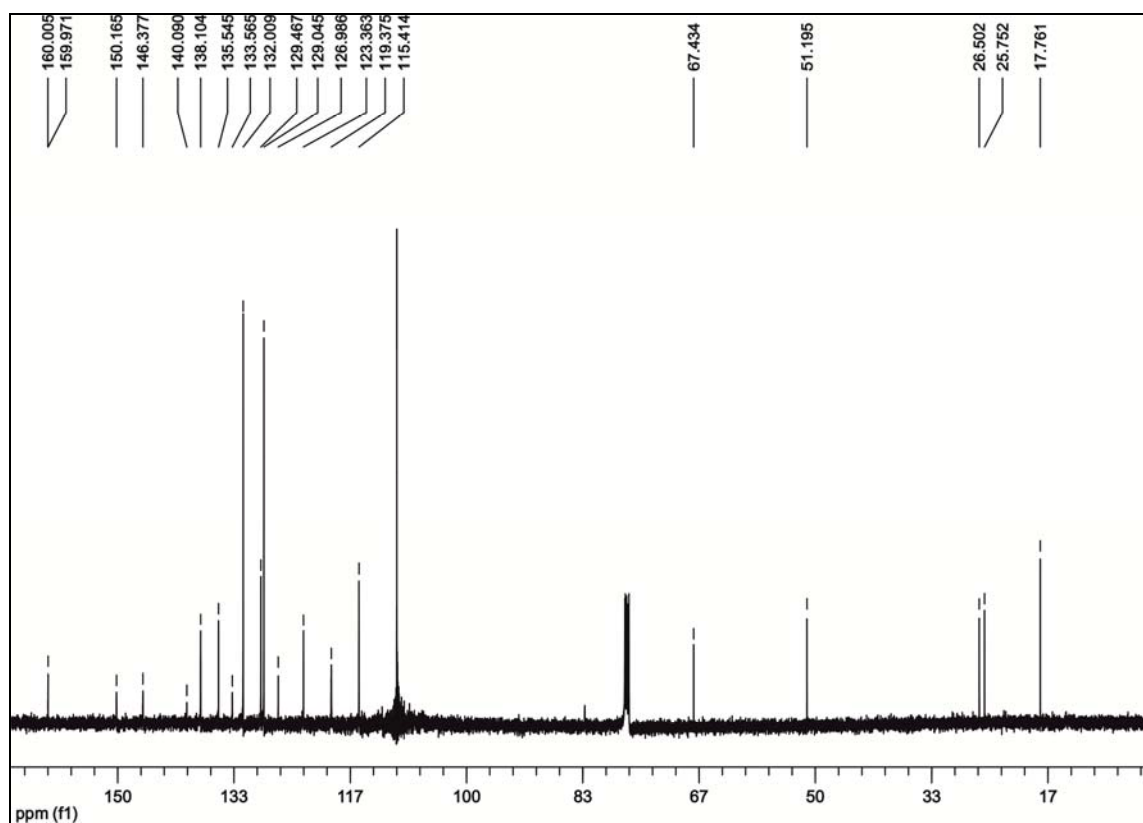


Figure S12. ¹³C NMR spectrum of compound 5

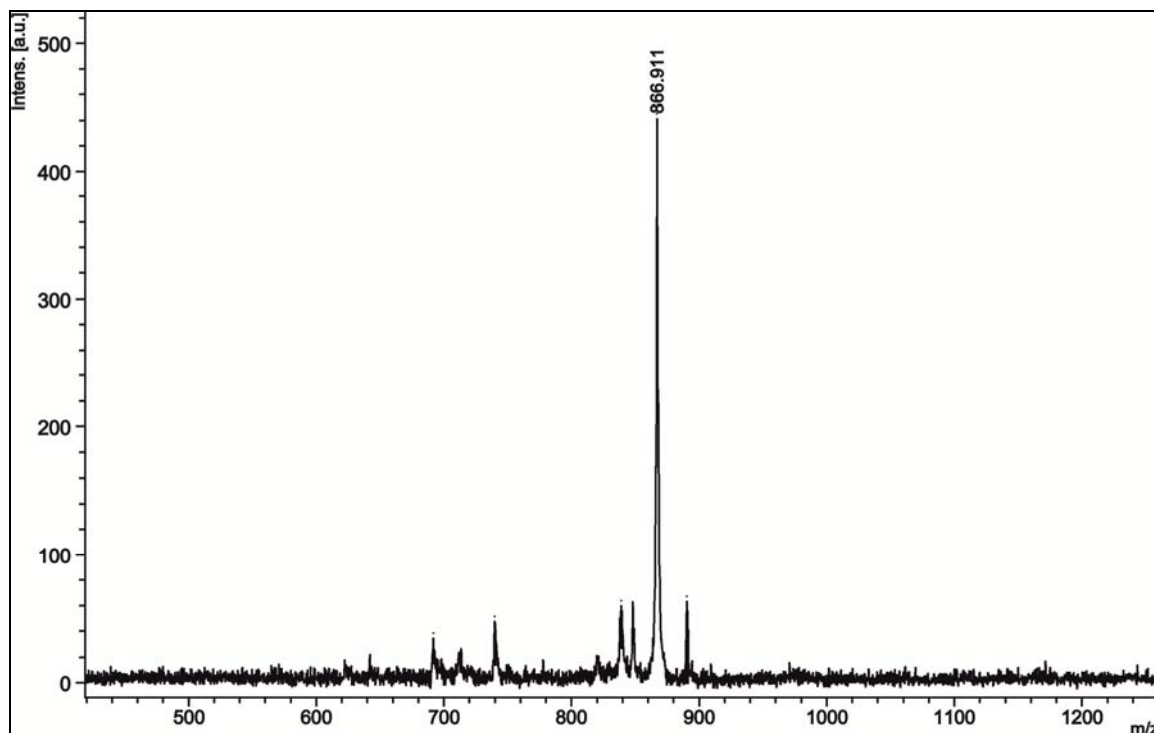


Figure S13. Mass spectrum of compound 6

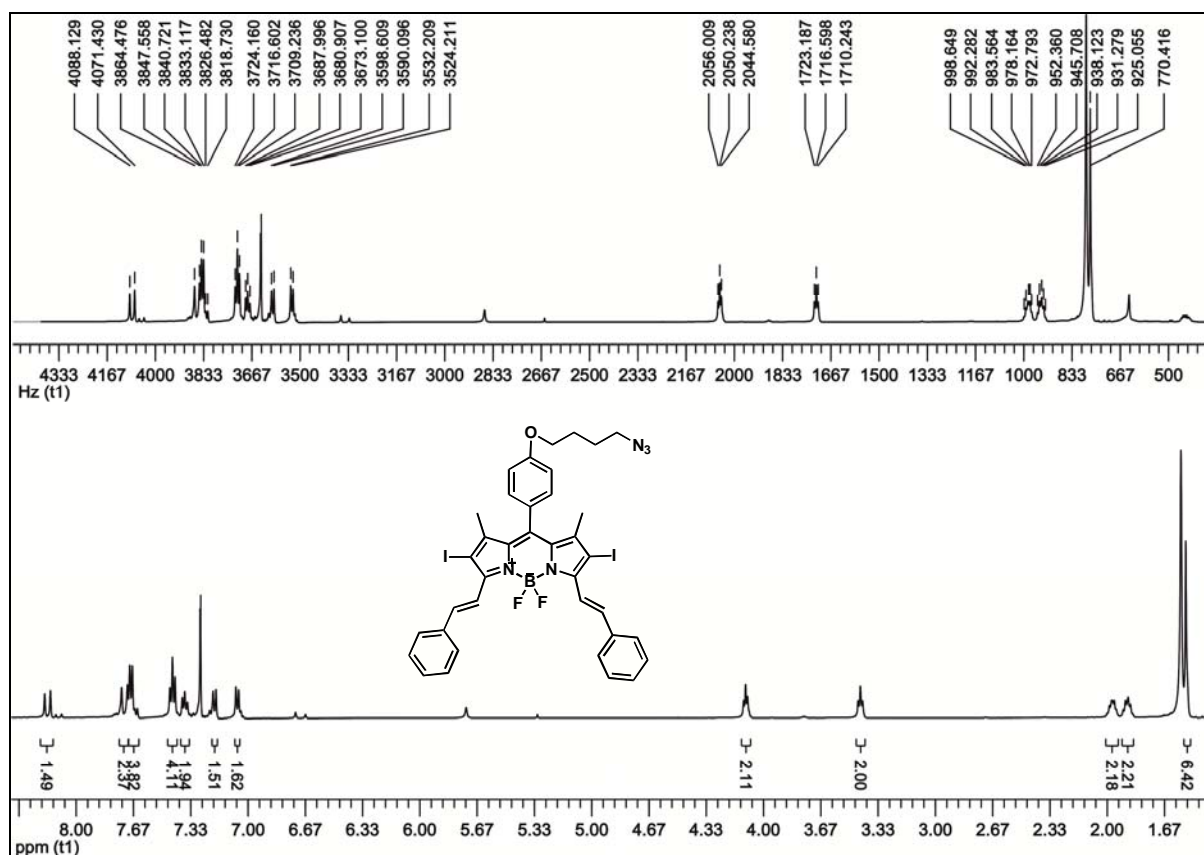


Figure S14. ¹H NMR spectrum of compound 6

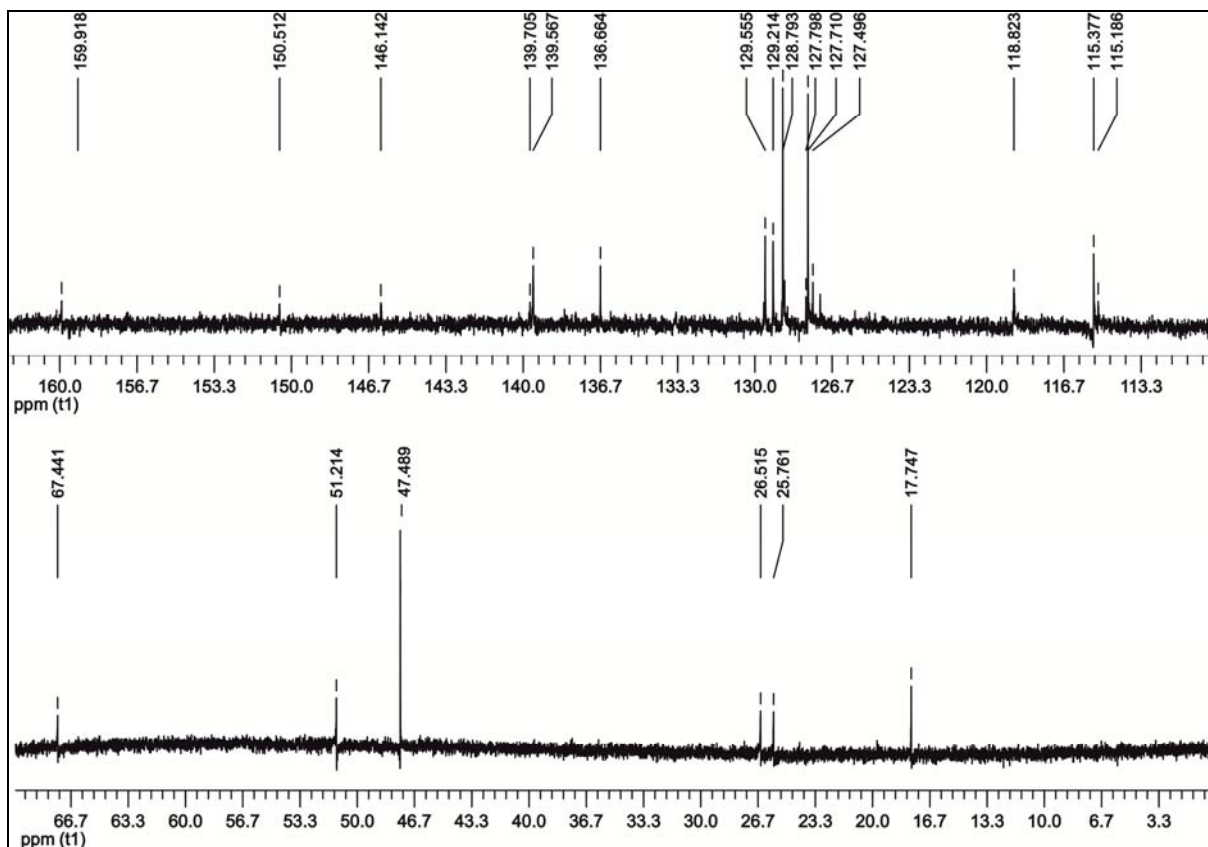


Figure S15. ^{13}C NMR spectrum of compound **6**

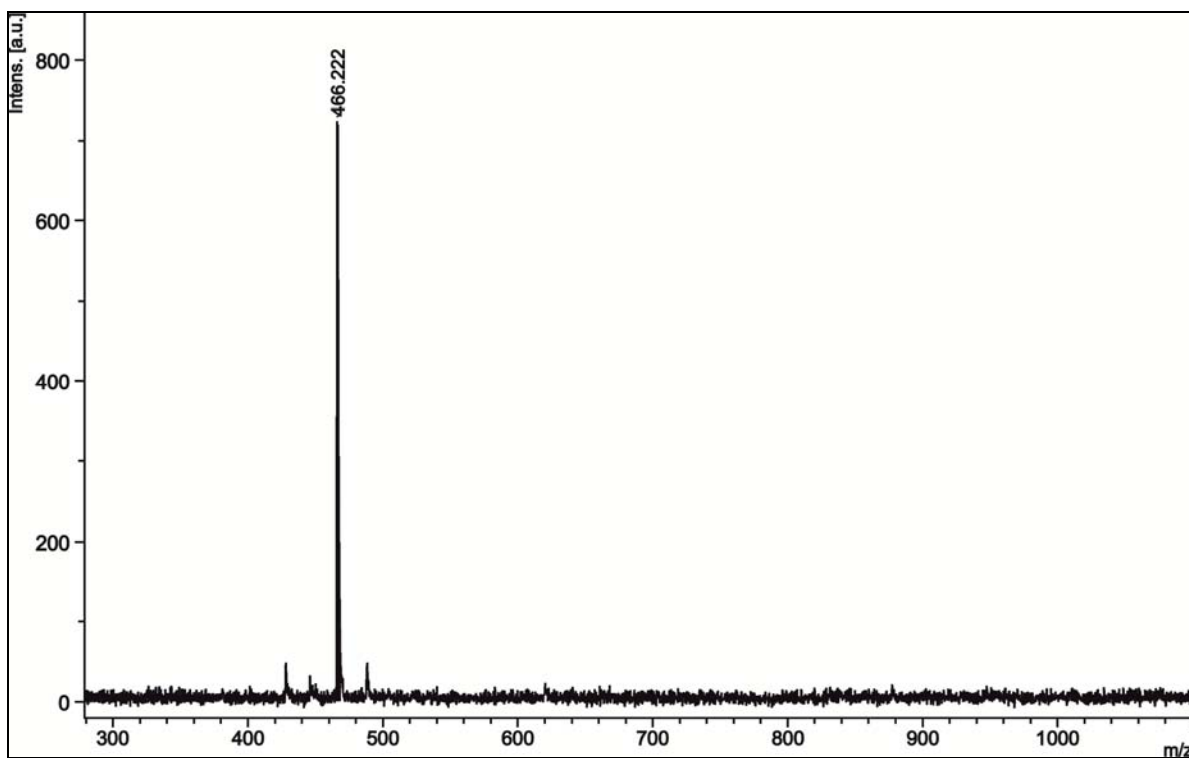


Figure S16: Mass spectrum of compound **7**

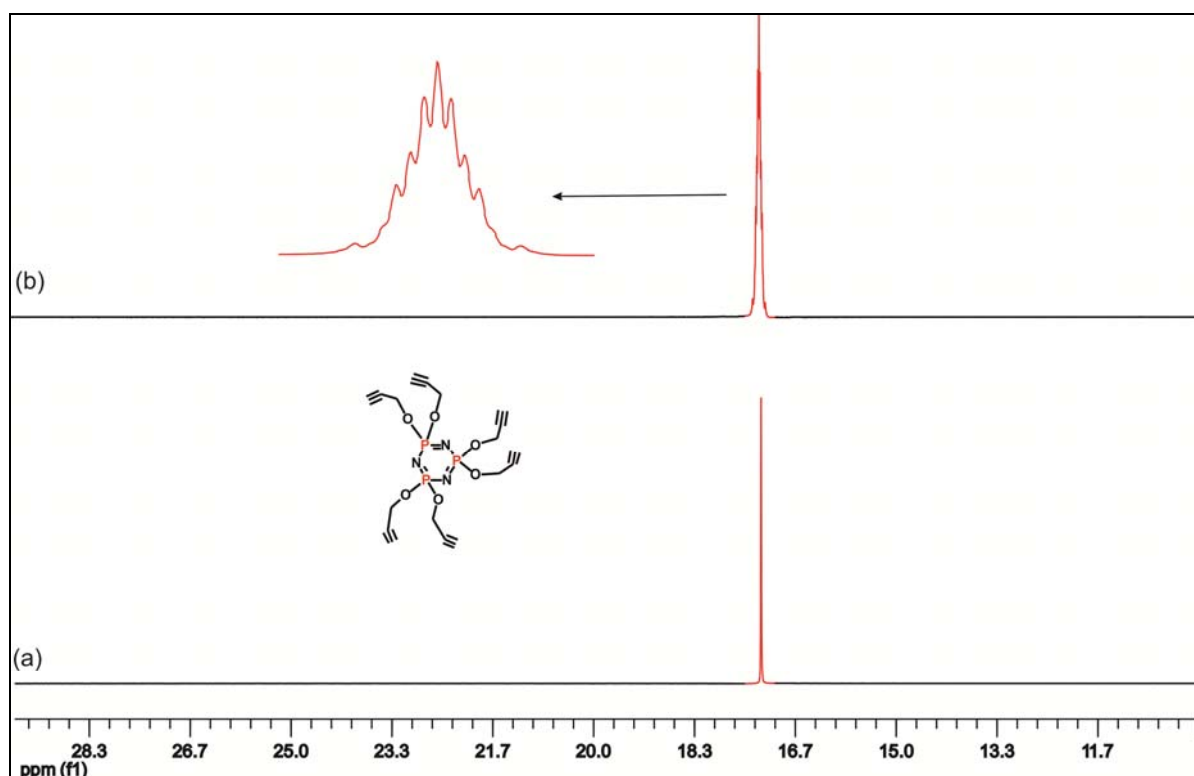


Figure S17: a) The proton decoupled ^{31}P NMR spectrum of the compound **7** b) The proton coupled ^{31}P NMR spectrum of the compound **7**

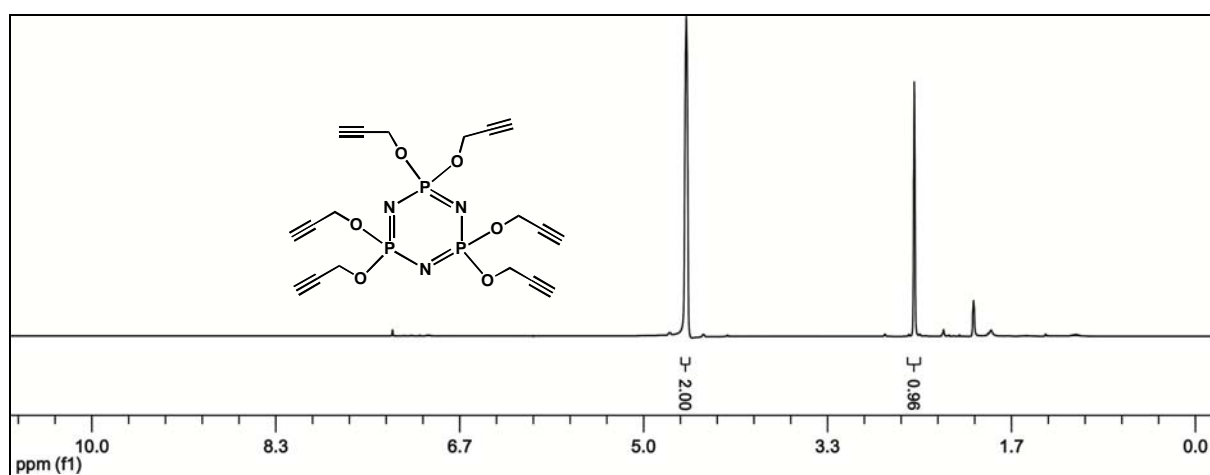


Figure S18: ^1H NMR spectrum of compound **7**

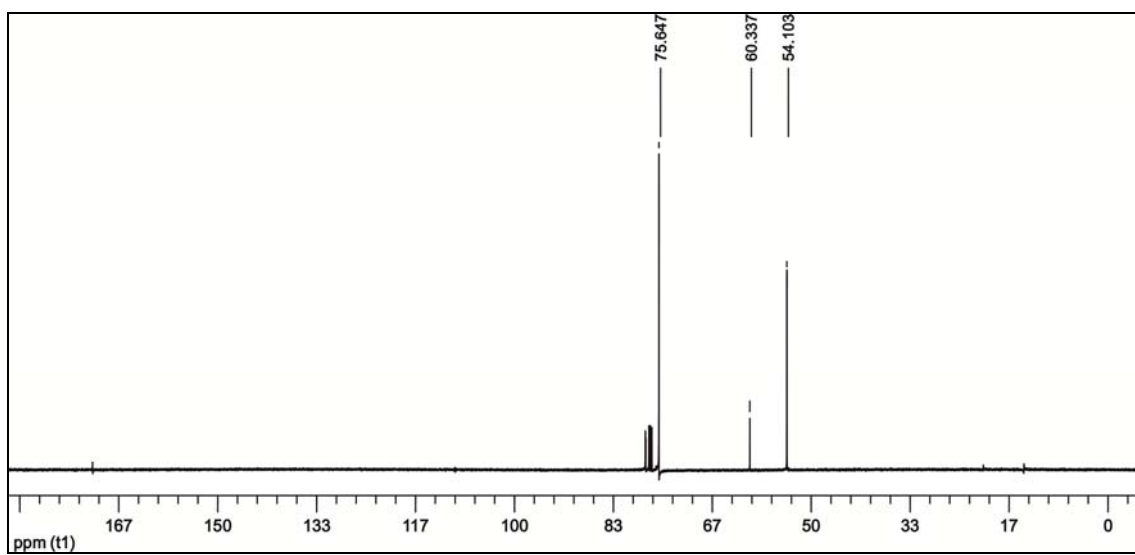


Figure S19. ^{13}C NMR spectrum of compound **7**

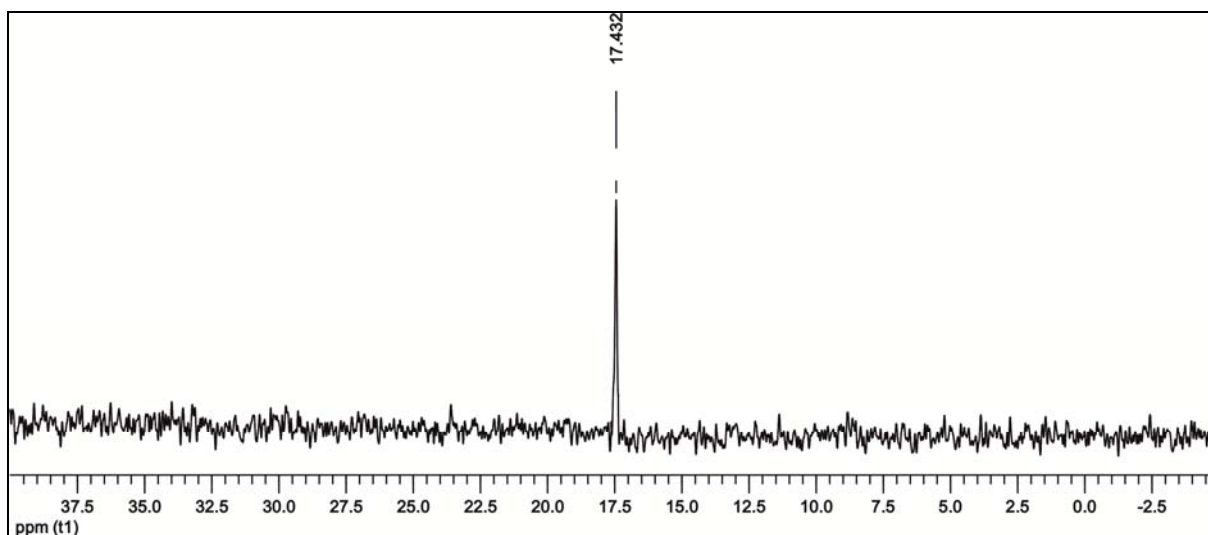


Figure S20: The proton decoupled ^{31}P NMR spectrum of the compound **8**

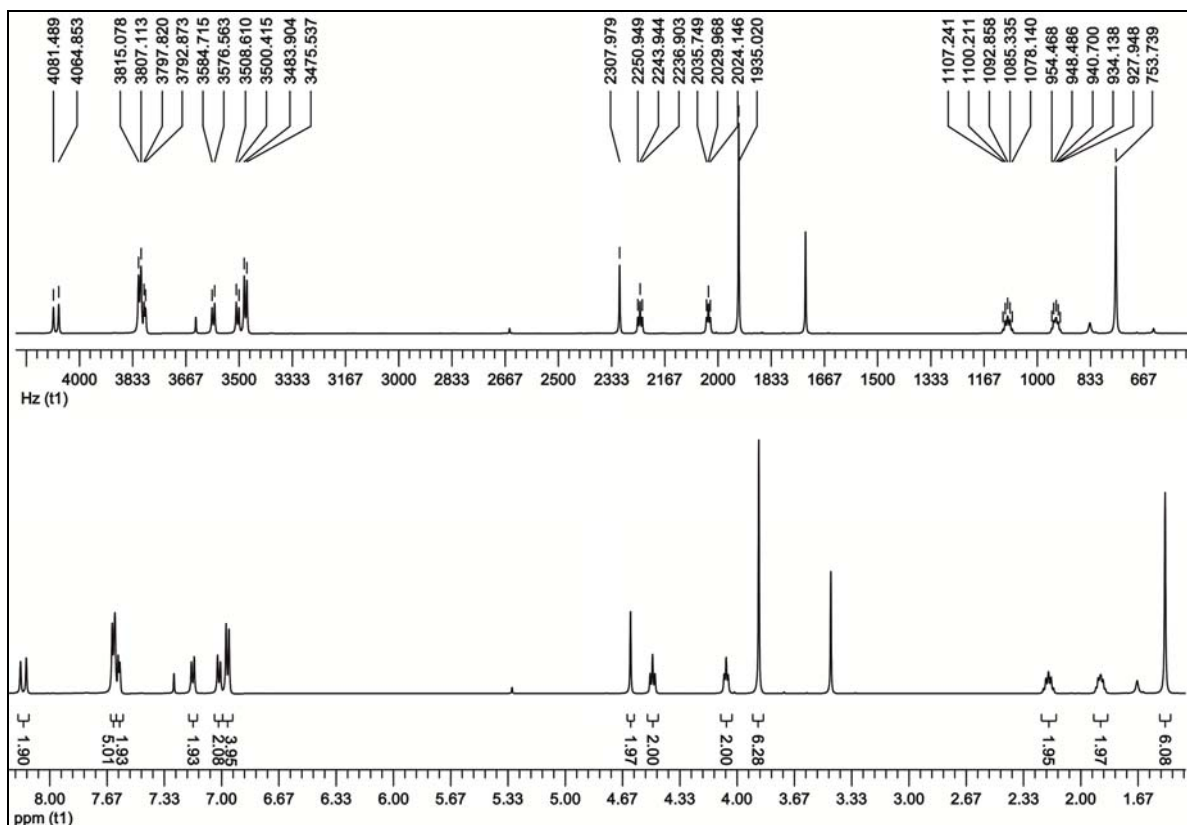


Figure S21. ^1H NMR spectrum of compound **8**

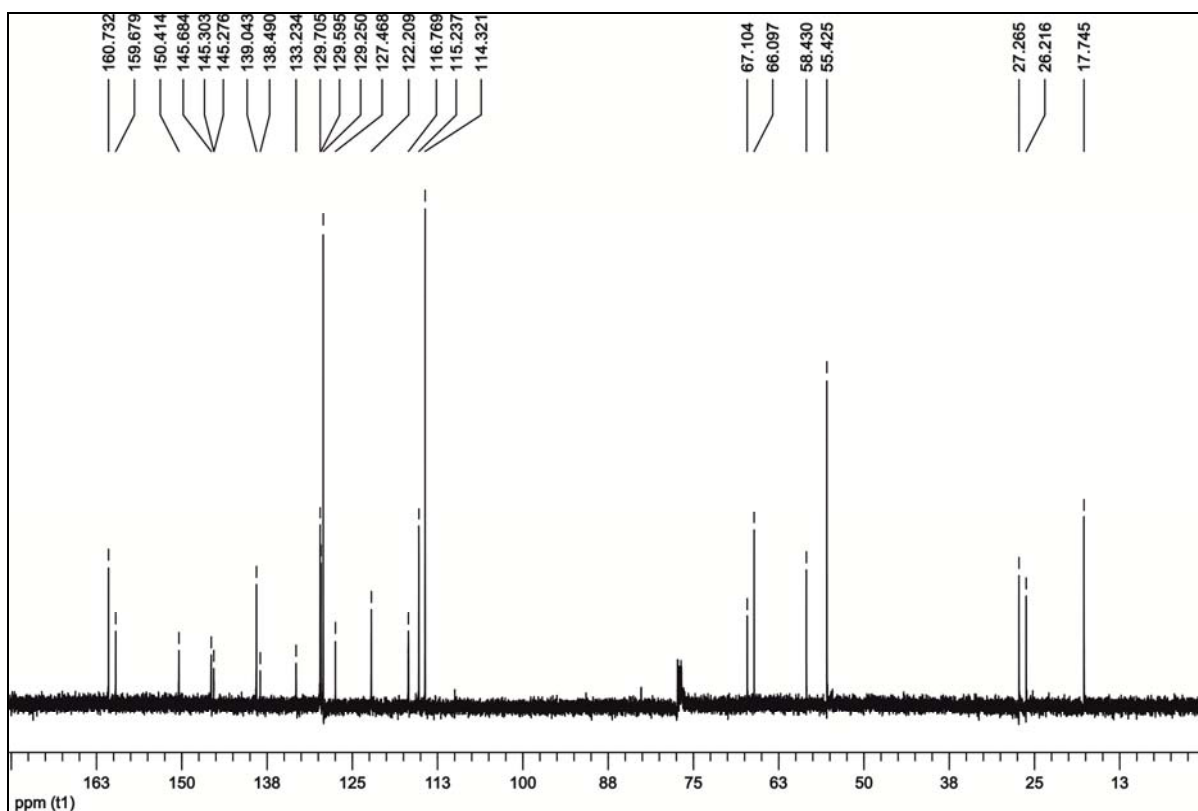


Figure S22. ^{13}C NMR spectrum of compound **8**

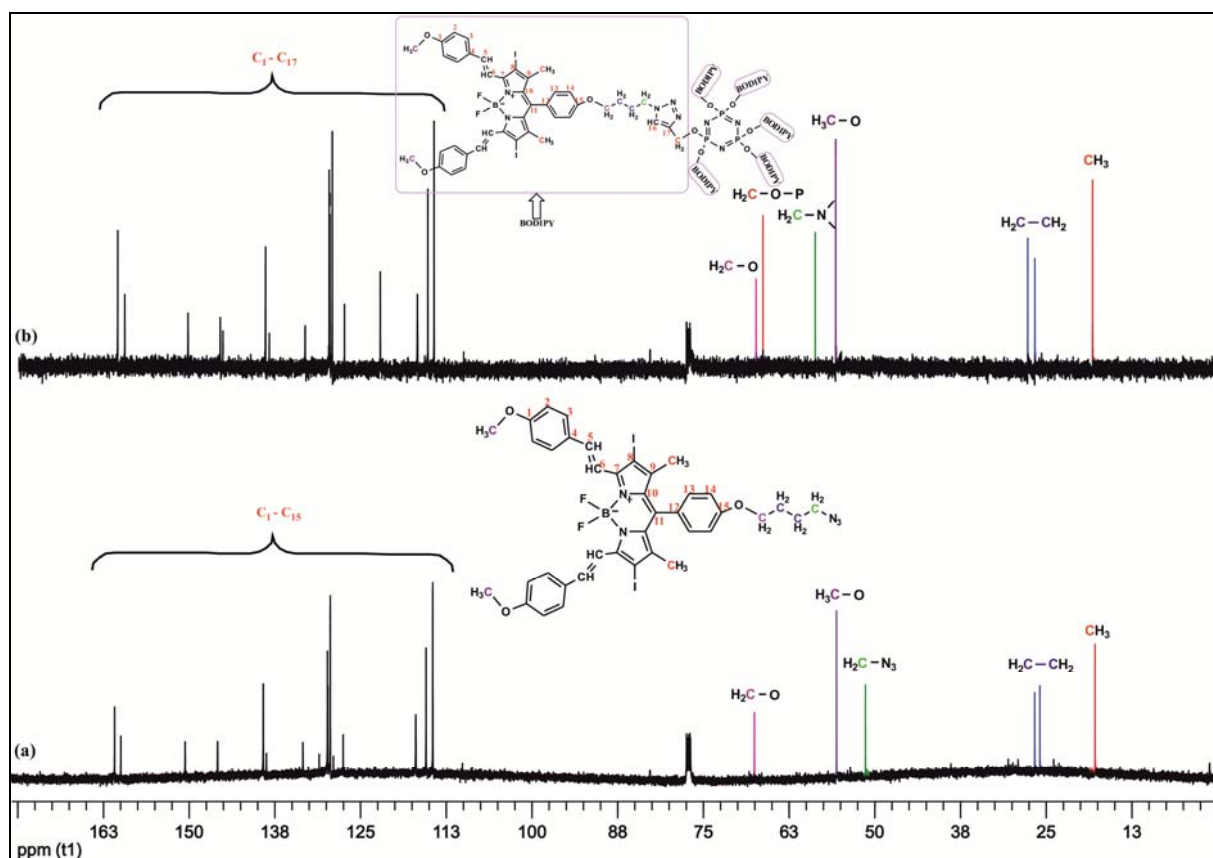


Figure S23. ^{13}C NMR spectrum of Compound 4 b) ^{13}C NMR spectrum of Compound 8.

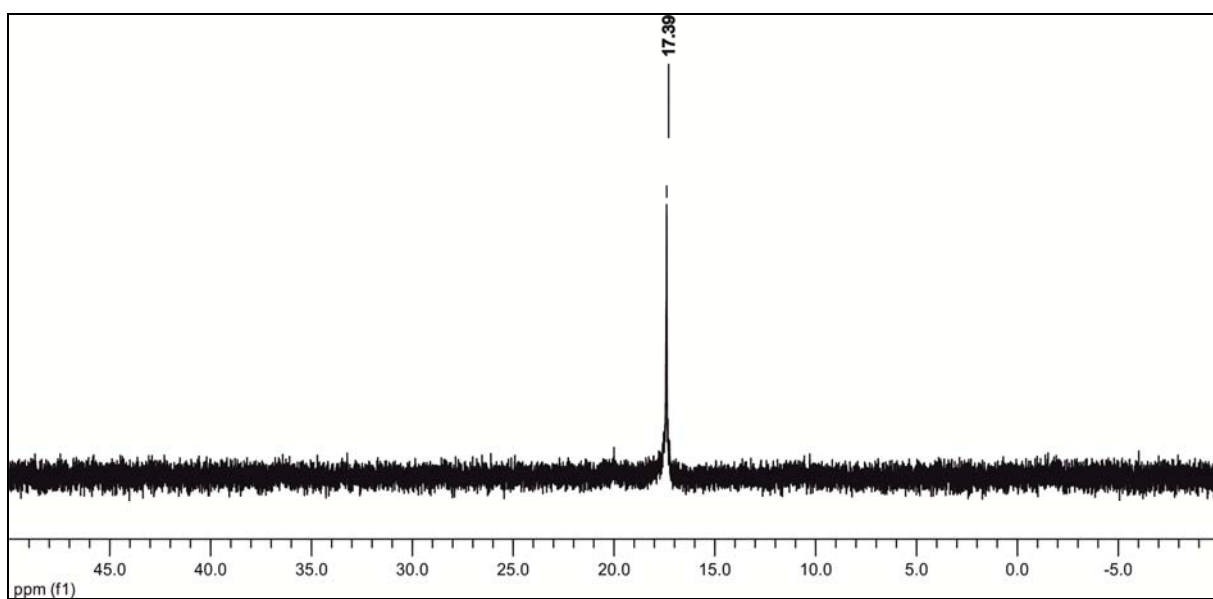


Figure S24: The proton decoupled ^{31}P NMR spectrum of the compound 9

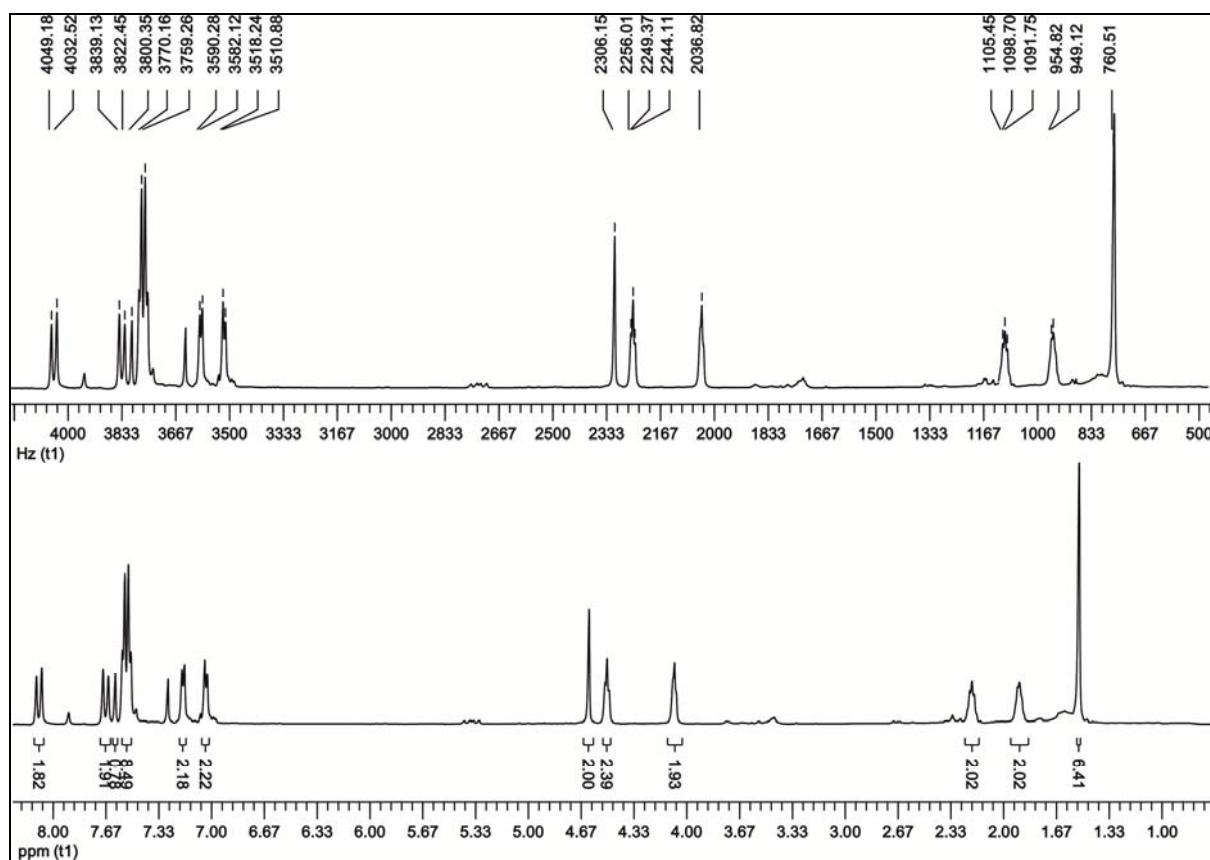


Figure S25. ¹H NMR spectrum of compound **9**

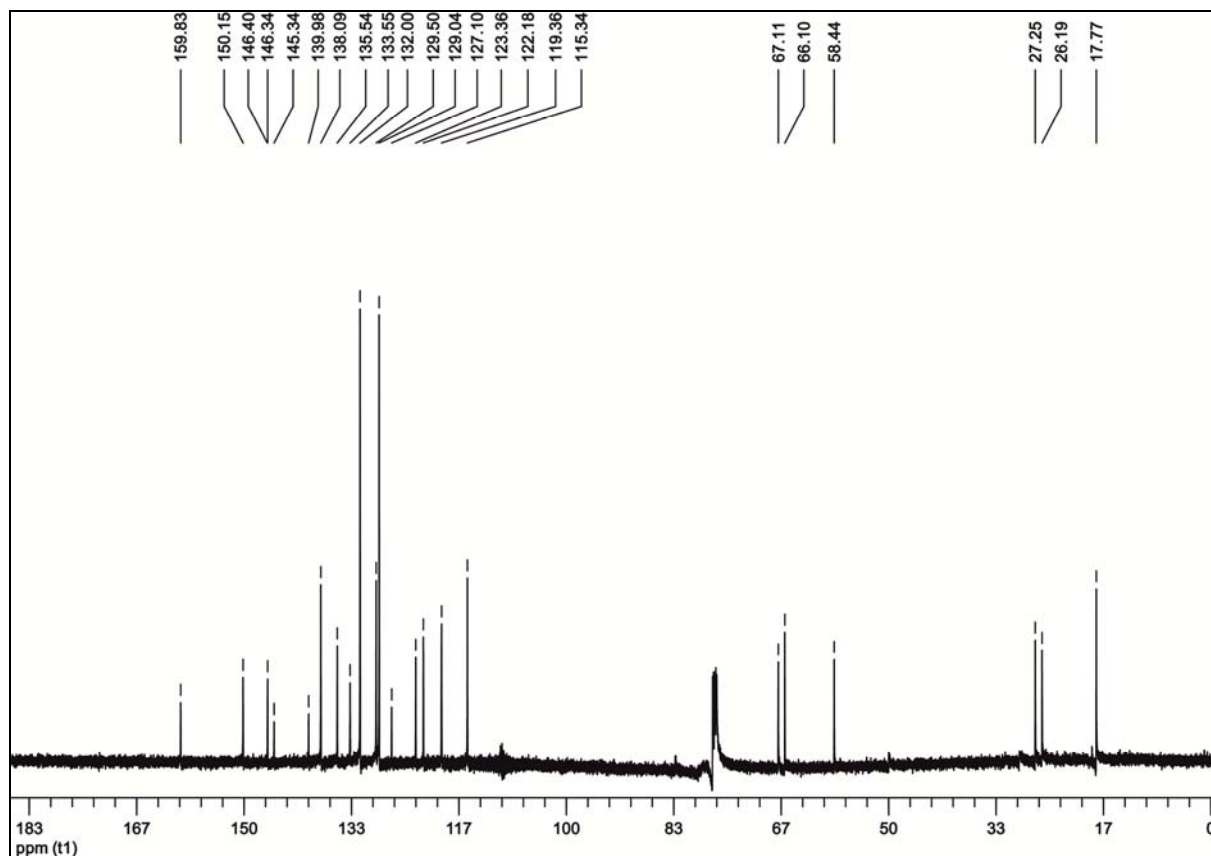


Figure S26. ^{13}C NMR spectrum of compound **9**

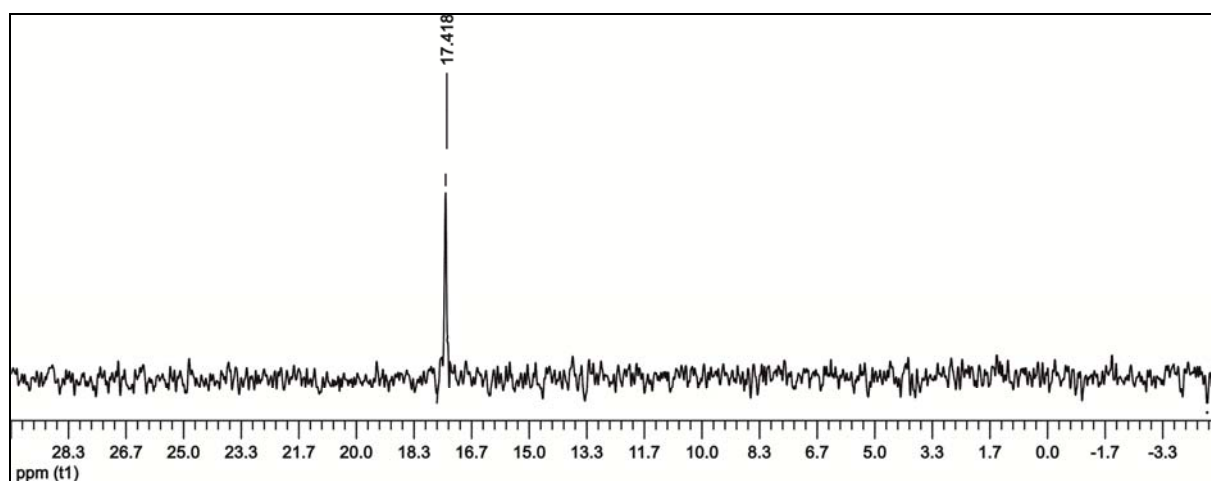


Figure S27: The proton decoupled ^{31}P NMR spectrum of the compound **10**

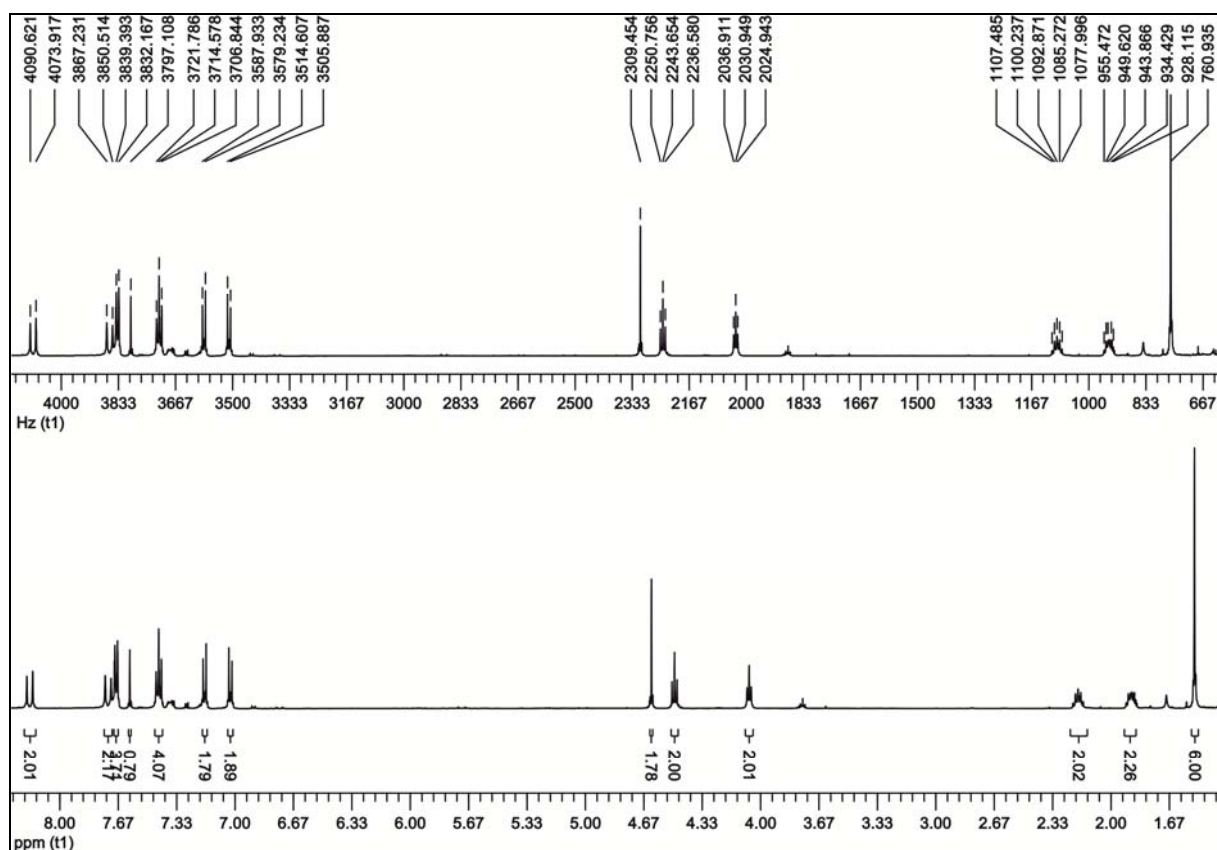


Figure S28. ^1H NMR spectrum of compound **10**

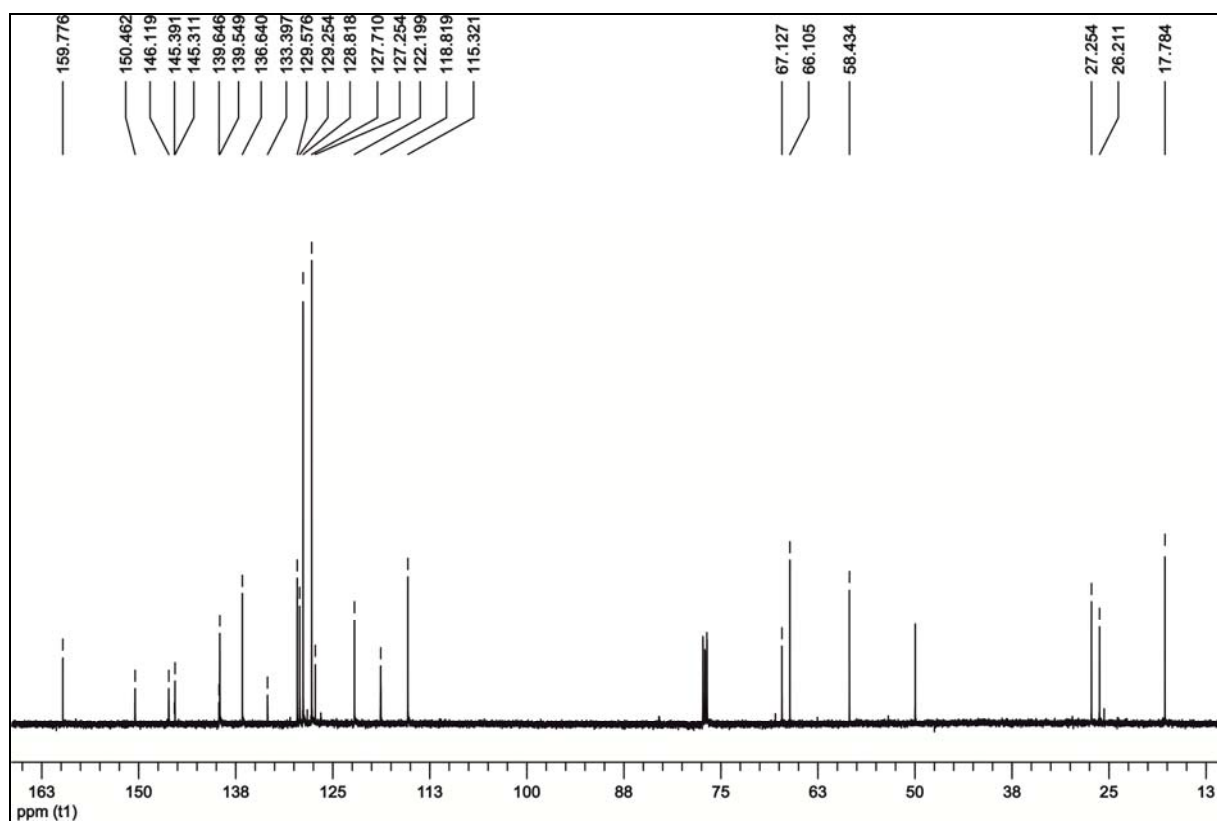


Figure S29. ^{13}C NMR spectrum of compound **10**

Photophysical Measurements

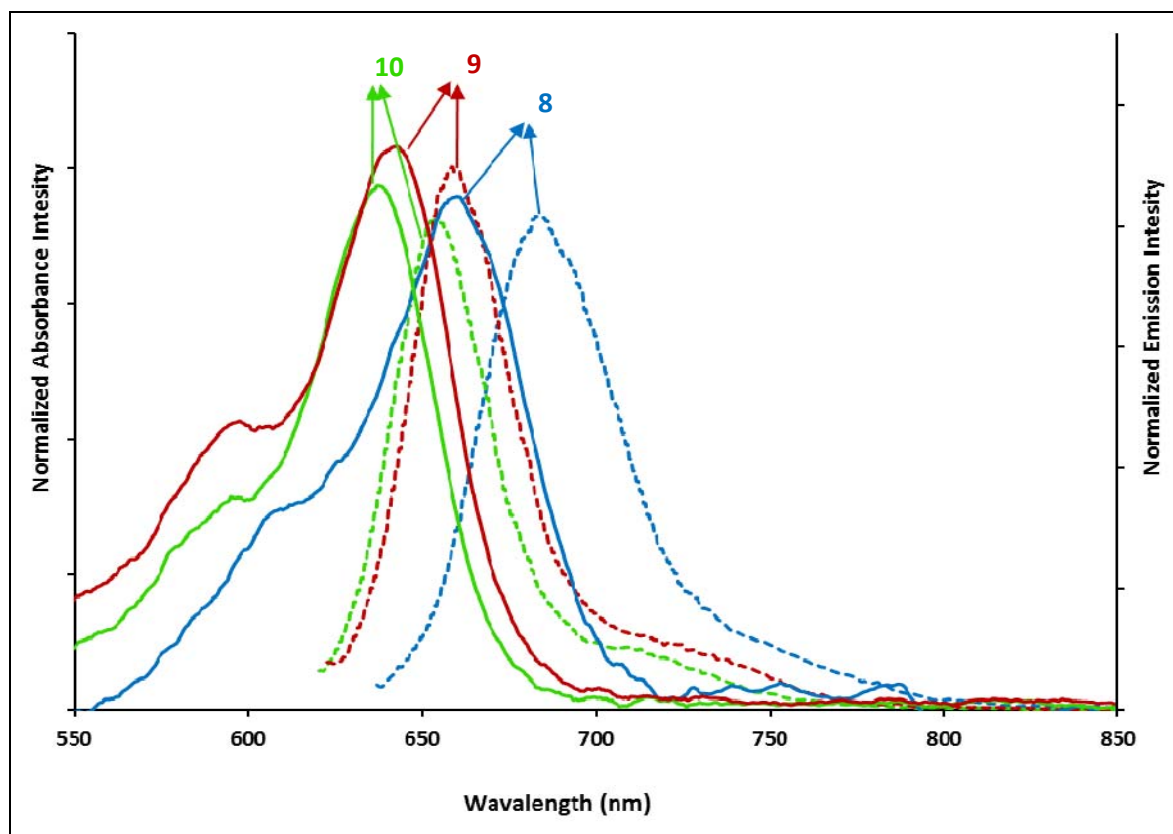


Figure S30. Normalized absorption (solid lines) and emission spectra (dashed lines) of compounds (**8–10**) in dichloromethane.

Singlet Oxygen Measurements:

Singlet oxygen quantum yields (ϕ_{Δ}) were calculated according to the literature.^{14,36} The relative quantum yields were calculated with reference to Methylene Blue (MB) in dichloromethane as 0.57.³⁶ Air saturated DCM was obtained by bubbling air for 15 minutes. The absorbance of DPBF was adjusted around 1.1-1.2 in air saturated dichloromethane. Then, the compound (**8, 9, 10**) was added to cuvette and compound's absorbance was adjusted around 0.2-0.3. After, taking some measurements in dark, we exposed the cuvette to 300 W quartz lamp, filtered to remove light with $\lambda < 600$ nm, at the peak absorption wavelength for 5 second. Absorbance was measured for several times after each irradiation. The graphics are

given in Figure 5 and Figs. S29 and S30. Then, slope of absorbance maxima of DPBF at 414 nm versus time graph for each compound was calculated. Singlet oxygen quantum yield was calculated according to the equation:

$$\phi_{\Delta}(\text{comp}) = \phi_{\Delta}(\text{ref}) \times [m(\text{comp})/m(\text{ref})] \times [F(\text{ref})/F(\text{comp})] \times [PF(\text{ref})/PF(\text{comp})]$$

where comp and ref designate 'Compound **8**, **9**, **10** and 'Methylene Blue' respectively. m is the slope of difference in change in absorbance of DPBF (414 nm) with the irradiation time, F is the absorption correction factor, which is given by $F = 1 - 10^{-OD}$ (OD at the irradiation wavelength), and PF is absorbed photonic flux ($\mu\text{Einstein dm}^{-3} \text{ s}^{-1}$).

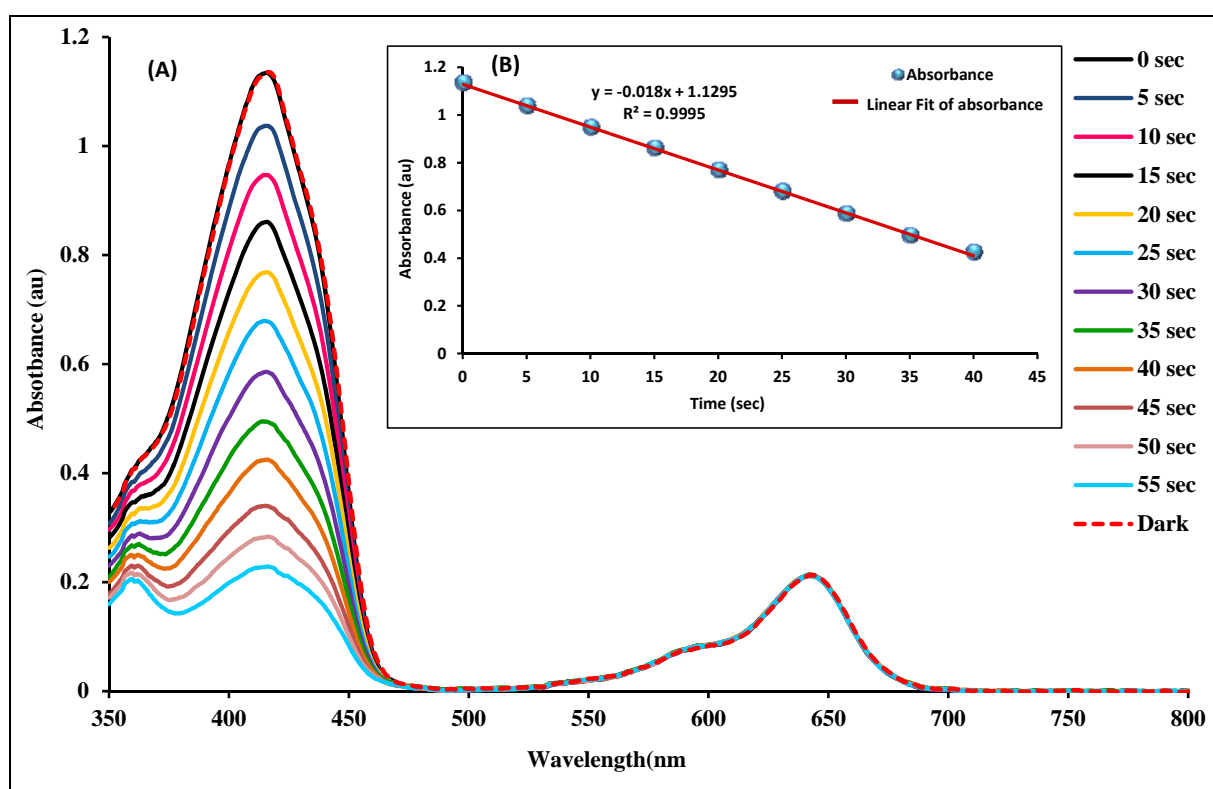


Figure S31. **A)** Decrease in absorbance spectrum of DPBF in the presence of compound **9** (0.5 μM) in dichloromethane. **B)** Absorbance decrease of DPBF at 414 nm with time in dichloromethane in the presence of compound **9**.

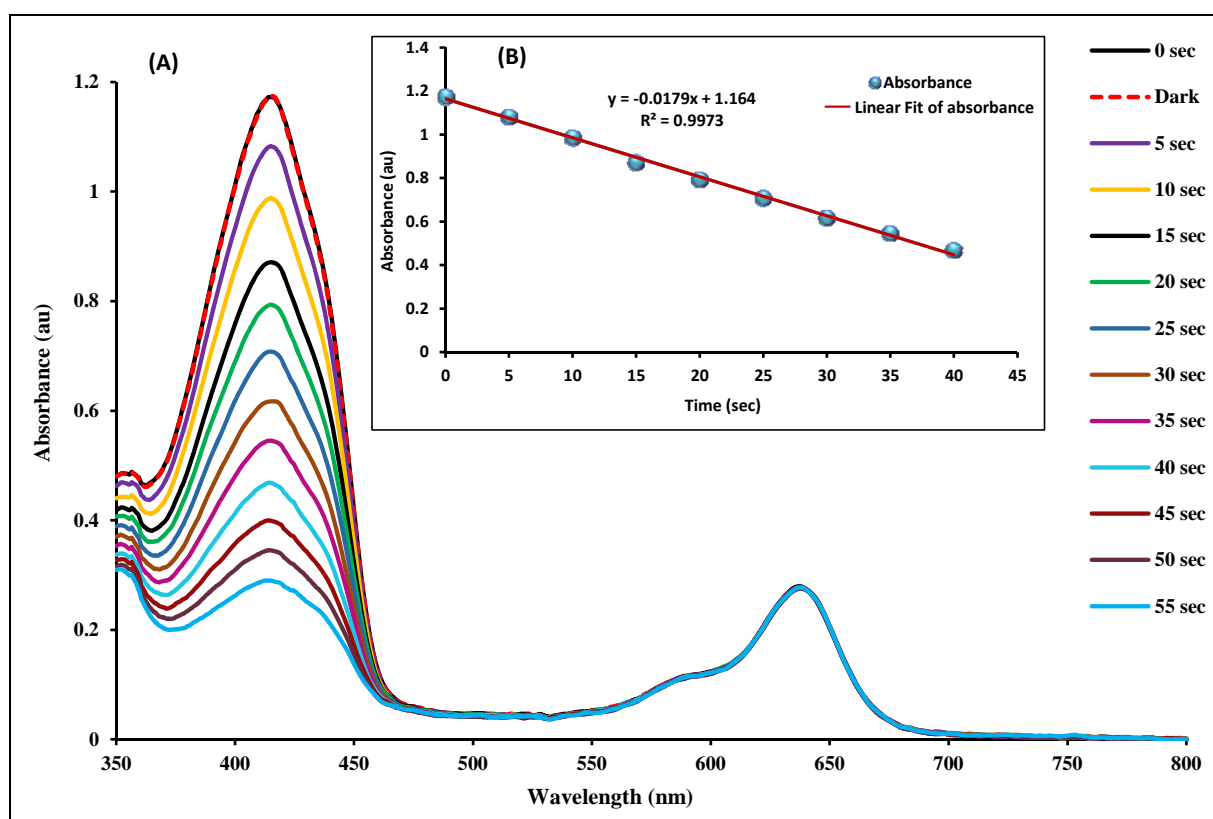


Figure S32. **A)** Decrease in absorbance spectrum of DPBF in the presence of compound **10** ($0.5\mu\text{M}$) in dichloromethane. **B)** Absorbance decrease of DPBF at 414 nm with time in dichloromethane in the presence of compound **10**.

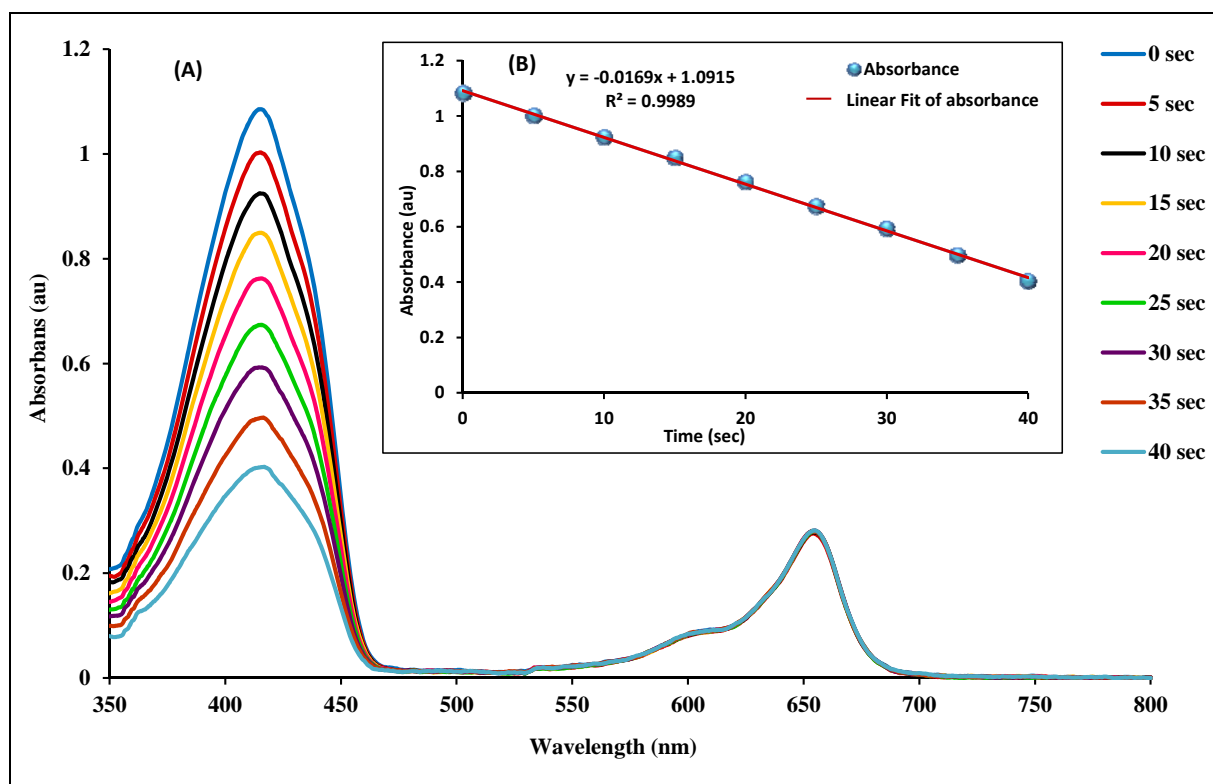


Figure S33. **A)** Decrease in absorbance spectrum of trap molecule DBPF in the presence of methylene blue (4 μM) in dichloromethane. **B)** Absorbance decrease of DPBF at 414 nm with time in dichloromethane in the presence of methylene blue (reference).

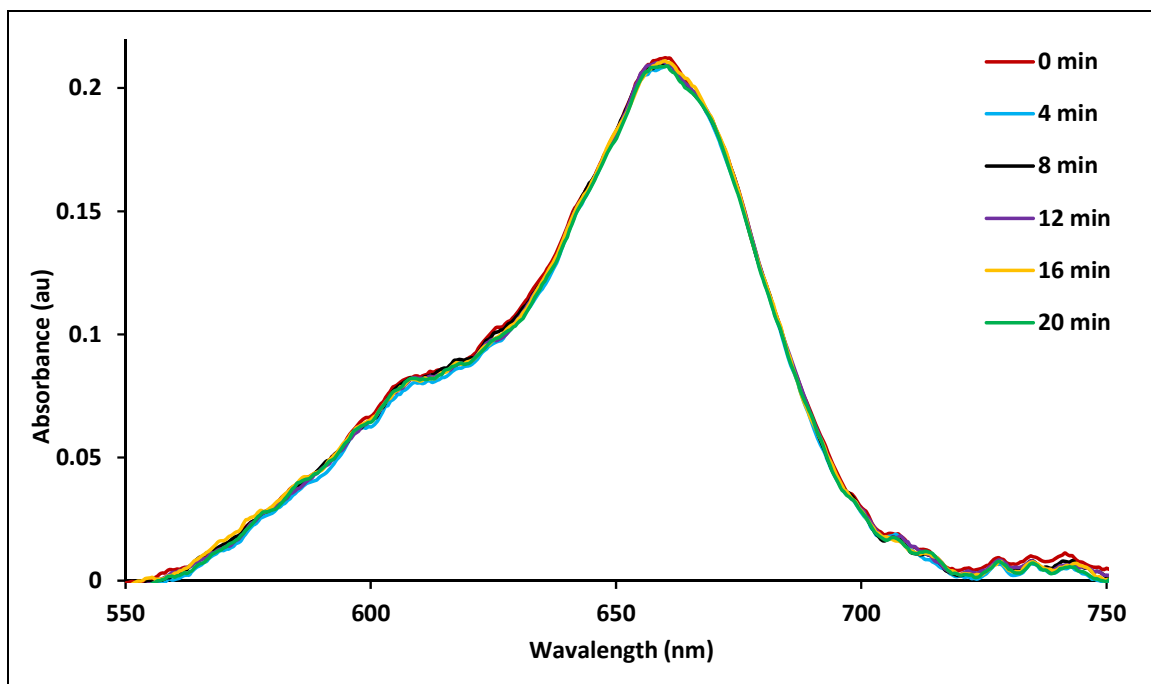


Figure S34. Absorbance spectrum of compound **8** ($0.5\mu\text{M}$) for photodegradation study in DCM under the light from 300 W quartz lamp, filtered to remove light with $\lambda < 600$ nm.

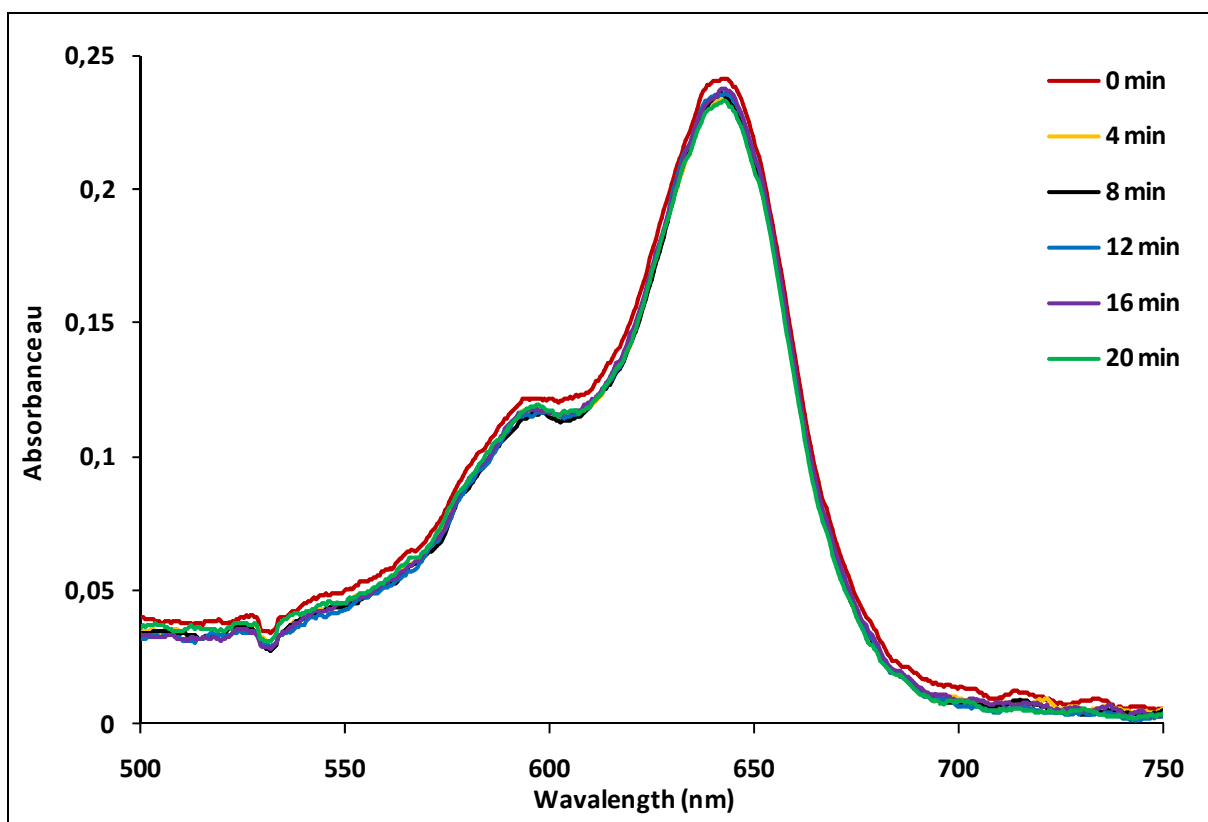


Figure S35. Absorbance spectrum of compound **9** ($0.5\mu\text{M}$) for photodegradation study in DCM under the light from 300 W quartz lamp, filtered to remove light with $\lambda < 600$ nm.

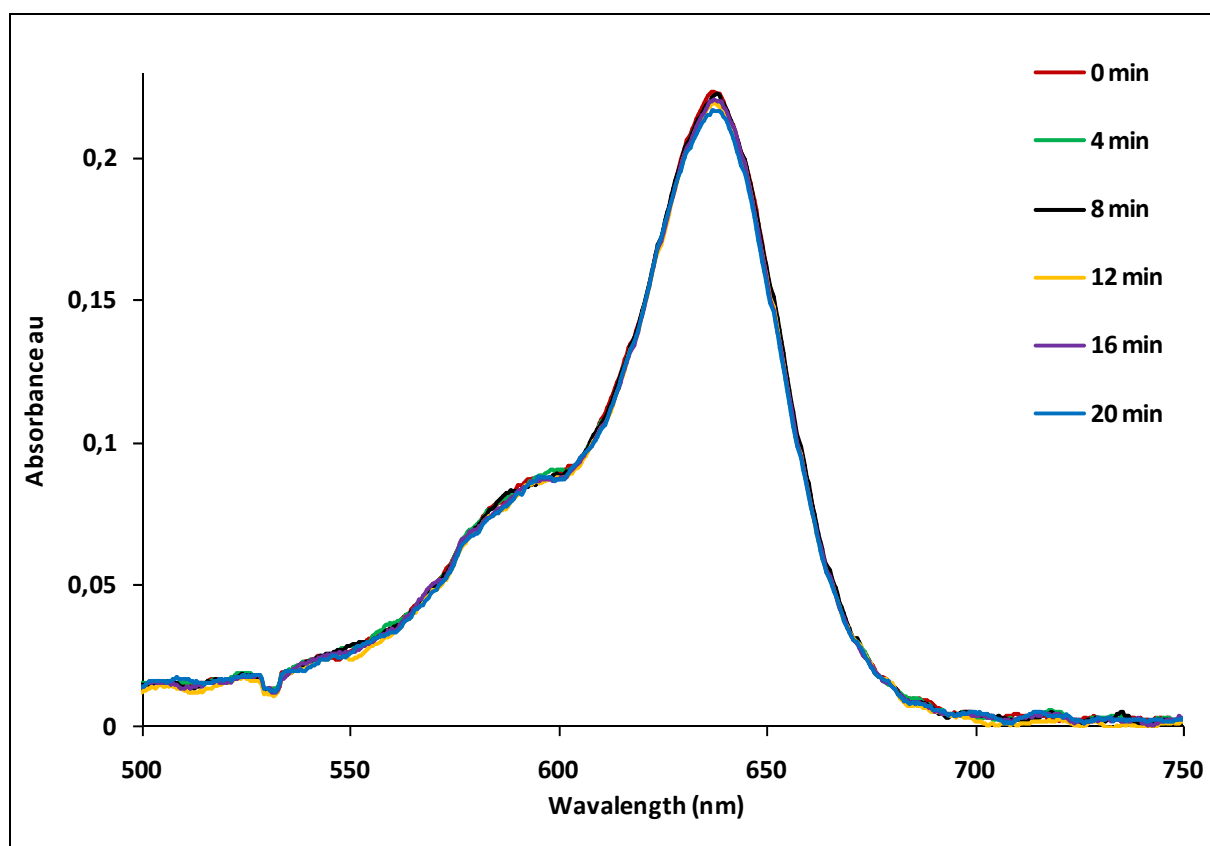


Figure S36. Absorbance spectrum of compound **10** (0.5 μM) for photodegradation study in DCM under the light from 300 W quartz lamp, filtered to remove light with $\lambda < 600$ nm.