Supporting Information

for

Solvent-free synthesis and purification of a photoproduct via sublimation of a tetrahalogenated template

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Materials

1,2,4,5-tetrabromobenzene **($C_6H_2Br_4$)**, 1,2,4,5-tetrachlorobenzene **($C_6H_2Cl_4$)**, 1,2-dibromo-4,5-difluorobenzene **($C_6H_2Br_2F_2$)**, and *trans*-1,2-bis(4-pyridyl)ethylene **(4,4'-BPE)** were each purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. All reagents were used without further purification. The dry vortex grinding was done utilizing 20 mL glass scintillation vials with two two steel BBs (5 mm diameter) per vial.

General Methods

Photoreactions were conducted using UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet. Co-crystals of each were placed between a pair of Pyrex glass plates for irradiation. The overall yield of the photoreaction was monitored using ^{1}H NMR spectroscopy in 24 hour intervals of UV exposure. Due to manufacturing recommendations and supervision of the photoreactor's water flow rate the co-crystals were only exposed to UV light for six hours per day for 12 consecutive days. ^{1}H NMR spectra were collected using a Bruker Avance 400 MHz spectrometer using DMSO-d_6 as a solvent. X-ray powder diffraction data were collected at room temperature on a Rigaku Ultima IV X-ray diffractometer between 5˚ to 40˚ two-theta.

Synthesis of the Co-crystals

Each co-crystal was synthesized by grinding 50 mg of **4,4-BPE** with either 108 mg of **$C_6H_2Br_4$**, 59 mg of **$C_6H_2Cl_4$**, or 75 mg of **$C_6H_2Br_2F_2$** (1:1 molar equivalents). Each sample was ground using a VWR Vortex Genie 2 for a total of 15 minutes with scraping the sides of the vial every 5 minutes. Pure photoproduct **4,4'-TPCB** was achieved by simple sublimation of **$C_6H_2Br_2F_2$** during the length of the experiment.

^{1}H NMR Spectroscopic Data

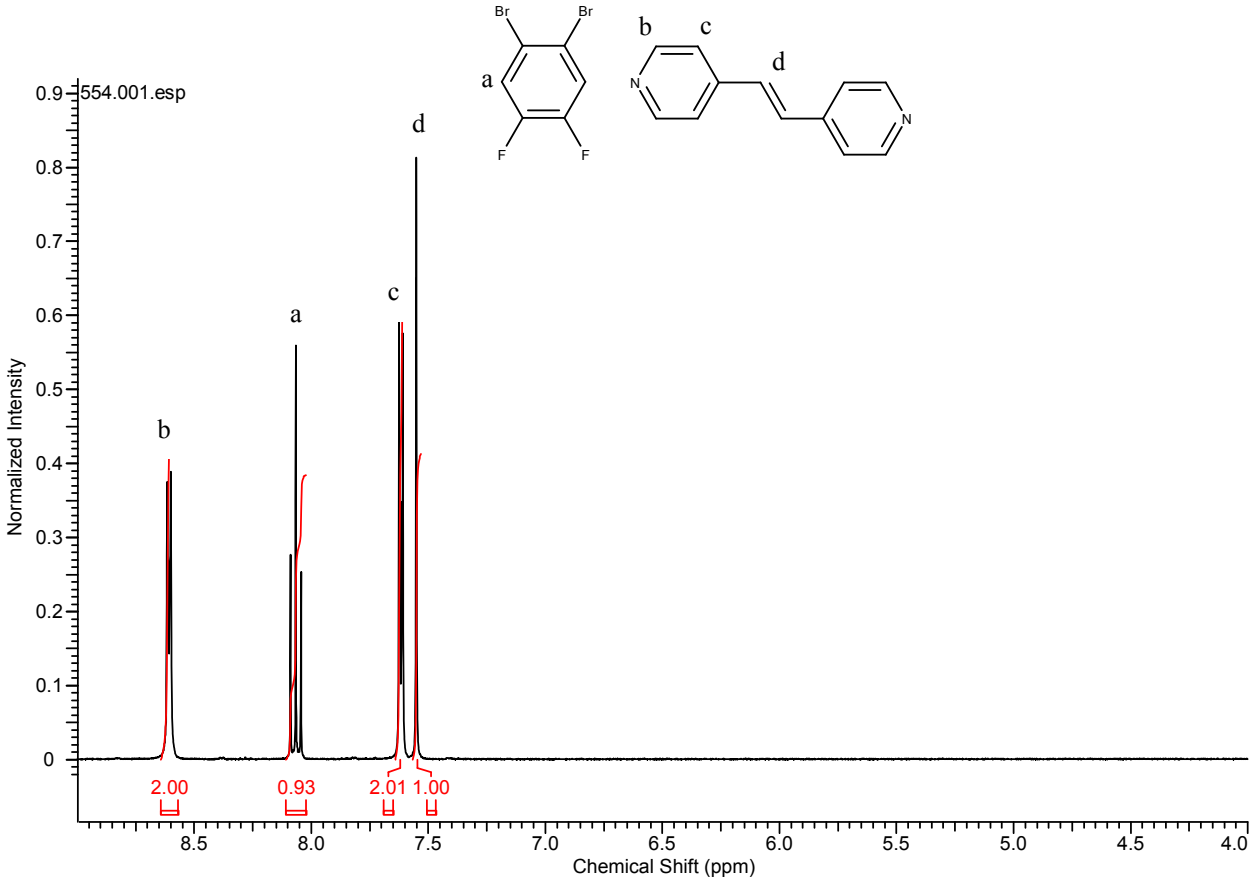

Figure S1: ^{1}H NMR spectrum of the co-crystal containing both $\mathbf{C_6H_2Br_2F_2}$ and **4,4'-BPE** after 15 minutes of dry vortex grinding and before photoreaction (400 MHz, DMSO-d_6).

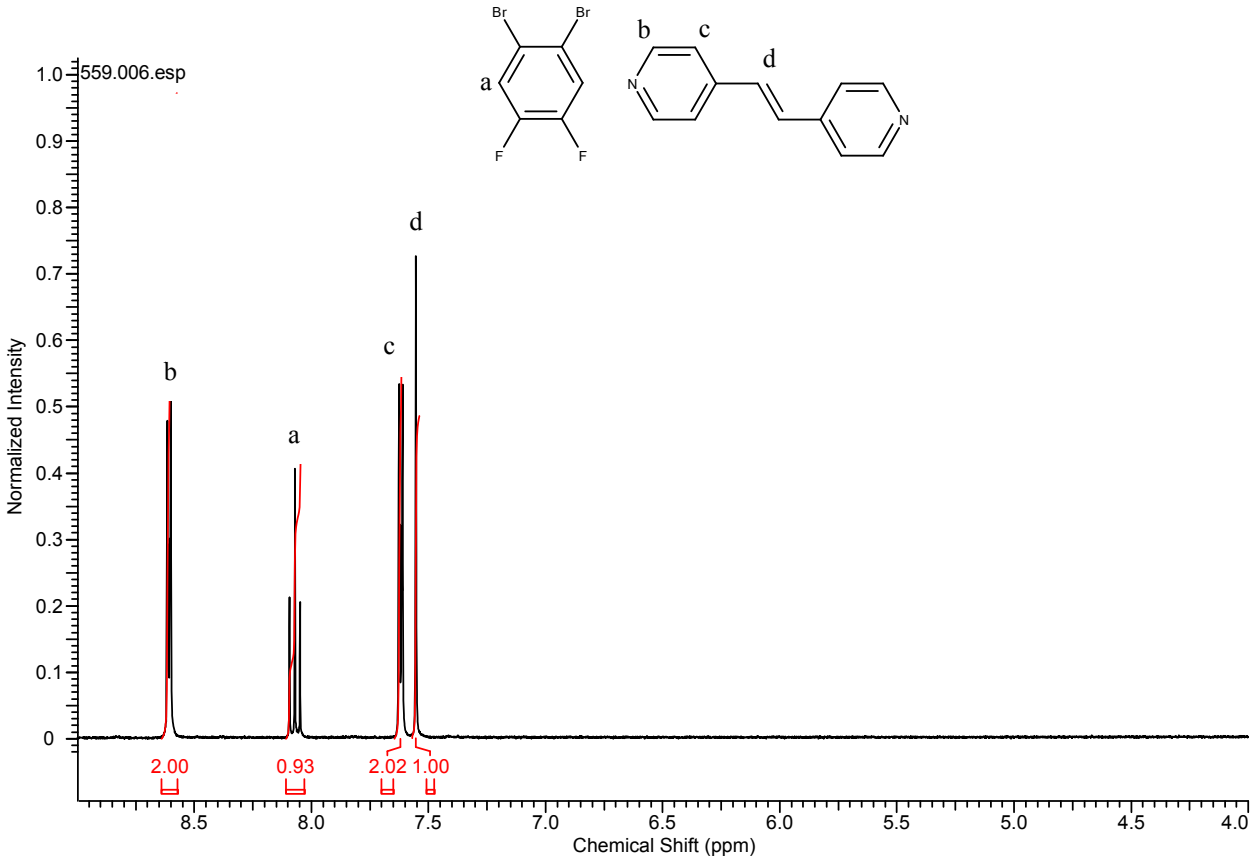

Figure S2: ^{1}H NMR spectrum of the co-crystal containing both $\mathbf{C_6H_2Br_2F_2}$ and **4,4'-BPE** one week after the initial 15 minutes of dry vortex grinding and before photoreaction indicting no additional loss of the template (400 MHz, DMSO-d_6).

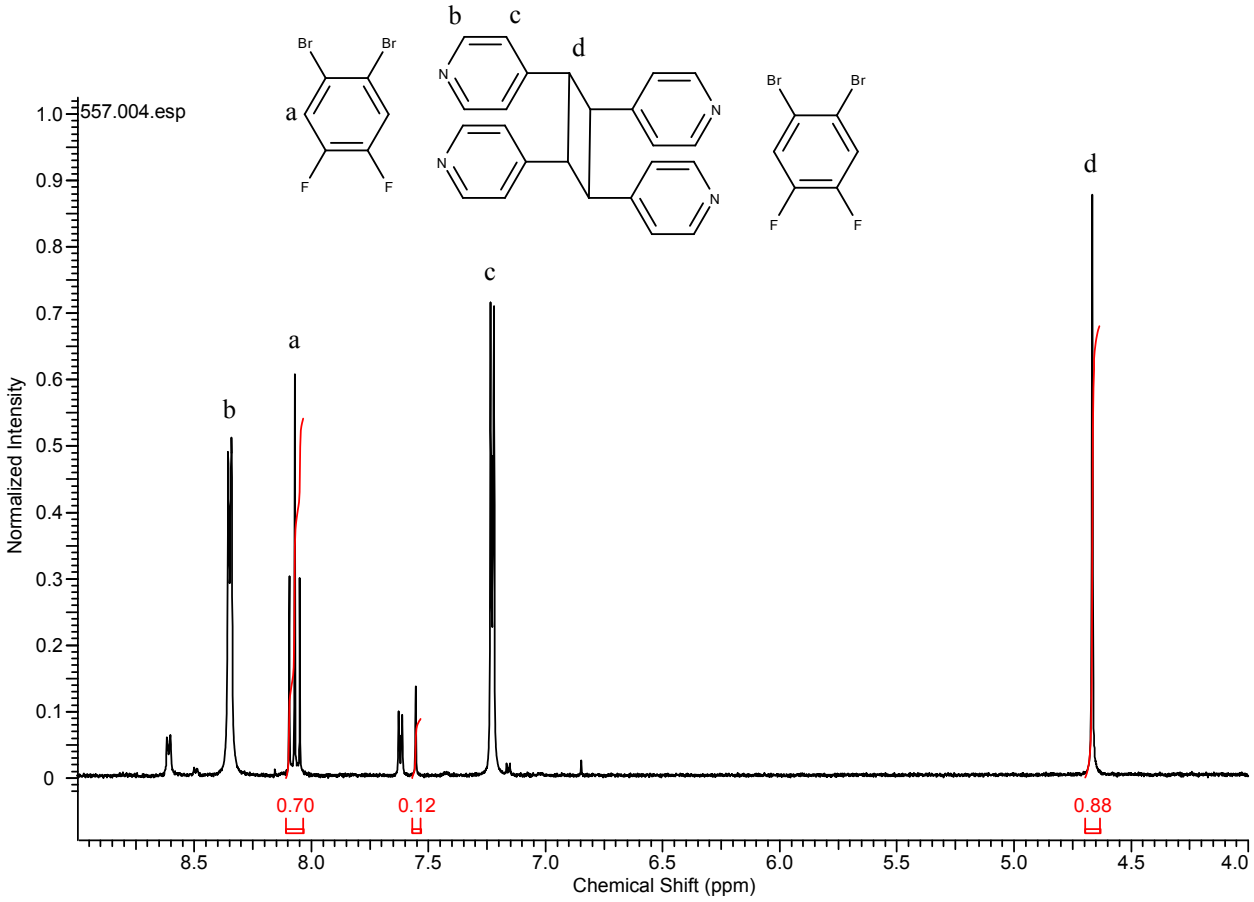

Figure S3: ^{1}H NMR spectrum of the co-crystal containing both $\mathbf{C_6H_2Br_2F_2}$ and **4,4'-BPE** after 24 hours of UV irradiation with an overall yield of 88% for the [2+2] cycloaddition reaction. A loss of the template is observed. (400 MHz, DMSO-d_6).

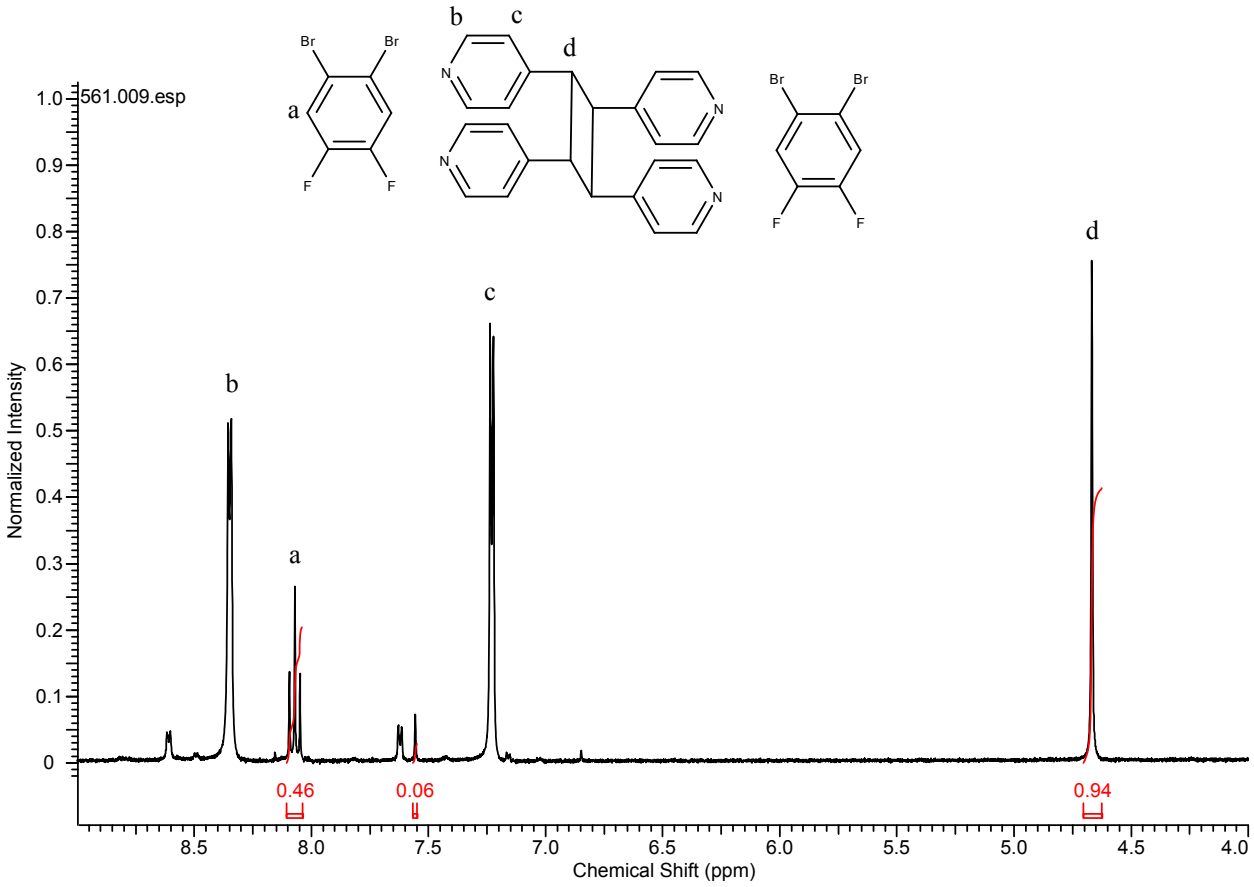

Figure S4: ^{1}H NMR spectrum of the co-crystal containing both $\mathbf{C_6H_2Br_2F_2}$ and **4,4'-BPE** after 48 hours of UV irradiation with an overall yield of 94% for the [2+2] cycloaddition reaction. An additional loss of template is observed. (400 MHz, DMSO-d_6).

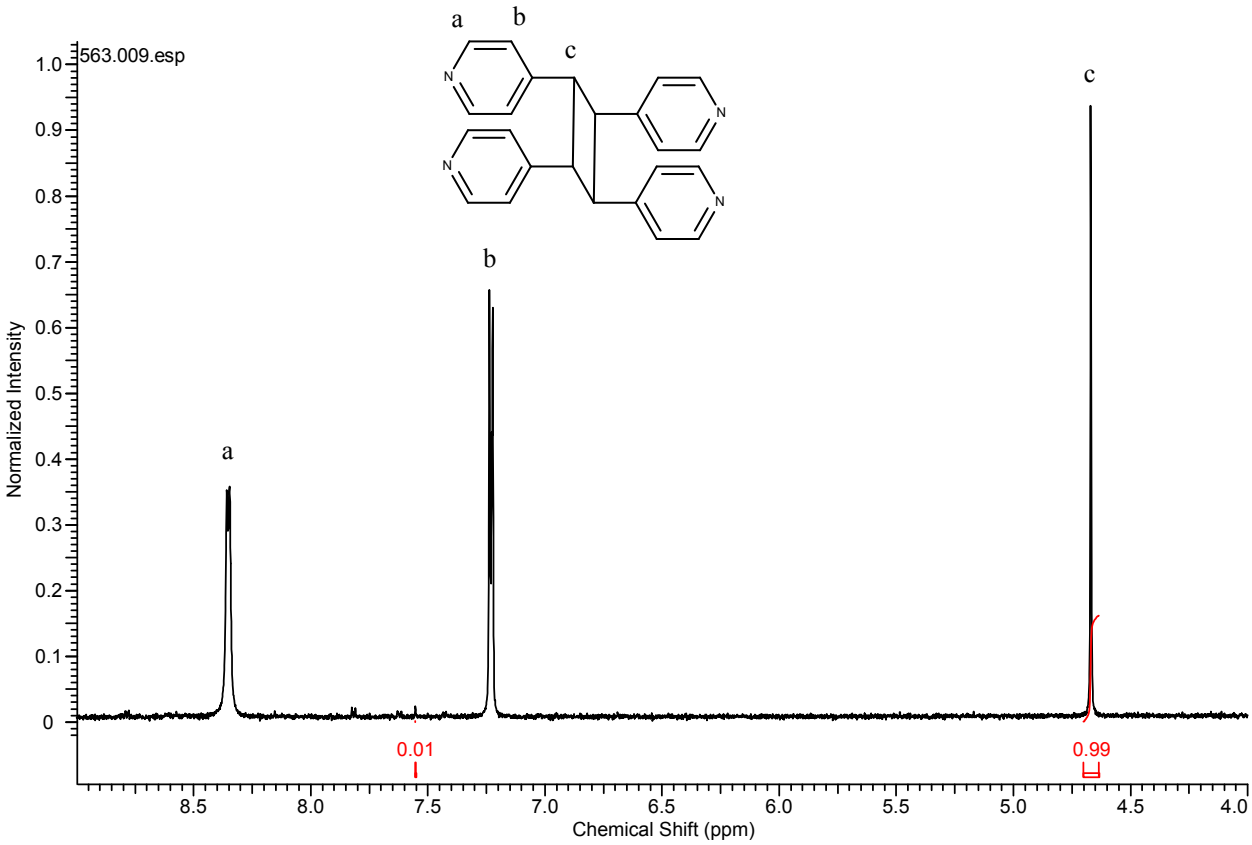

Figure S5: ^{1}H NMR spectrum of **4,4'-TPCB** after 72 hours of UV irradiation with an overall yield of >99% for the [2+2] cycloaddition reaction with complete loss of template observed. (400 MHz, DMSO-d_6).

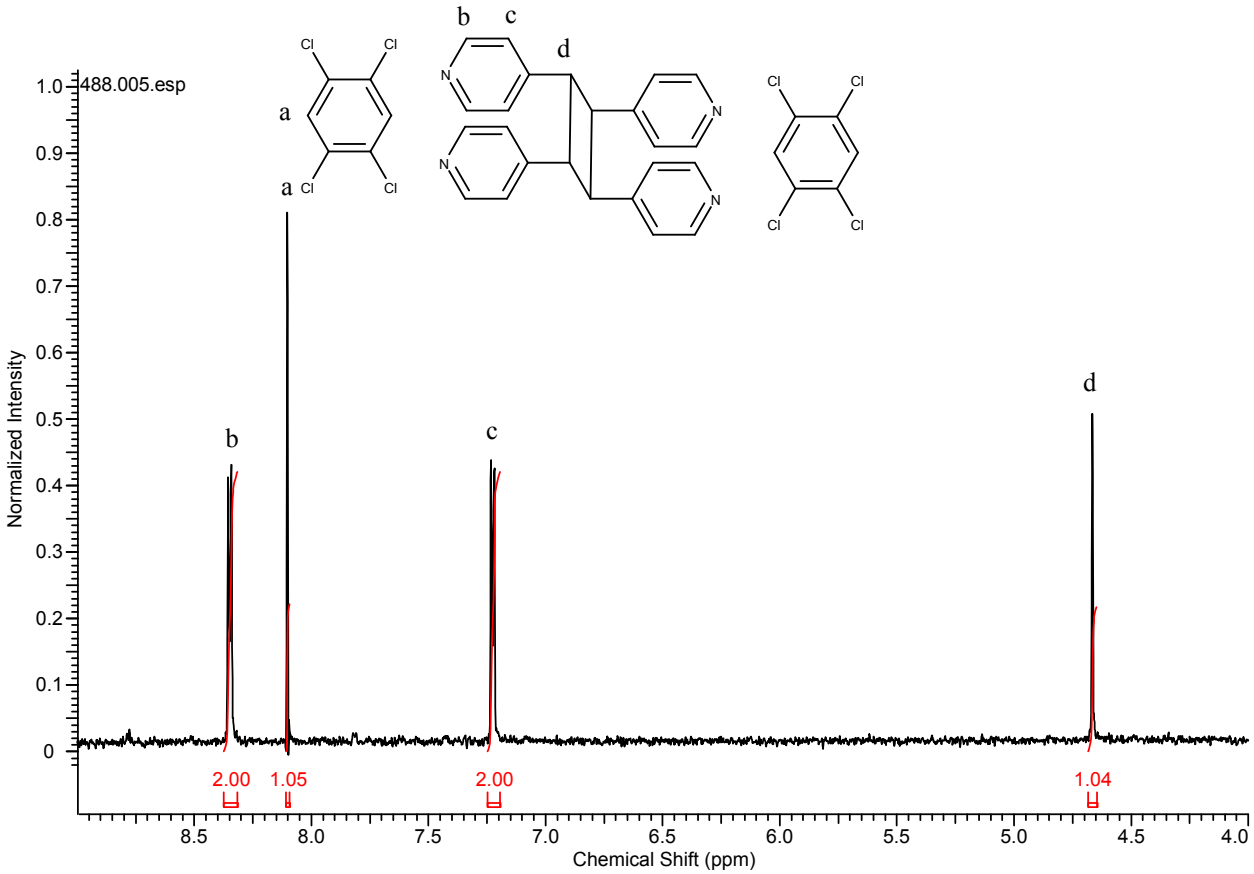

Figure S6: ^{1}H NMR spectrum of **($C_6H_2Cl_4$)•(4,4'-BPE)** after 36 hours of UV irradiation with an overall yield of 100% for the [2+2] cycloaddition reaction after 15 minutes of vortex grinding. (400 MHz, DMSO-d_6).

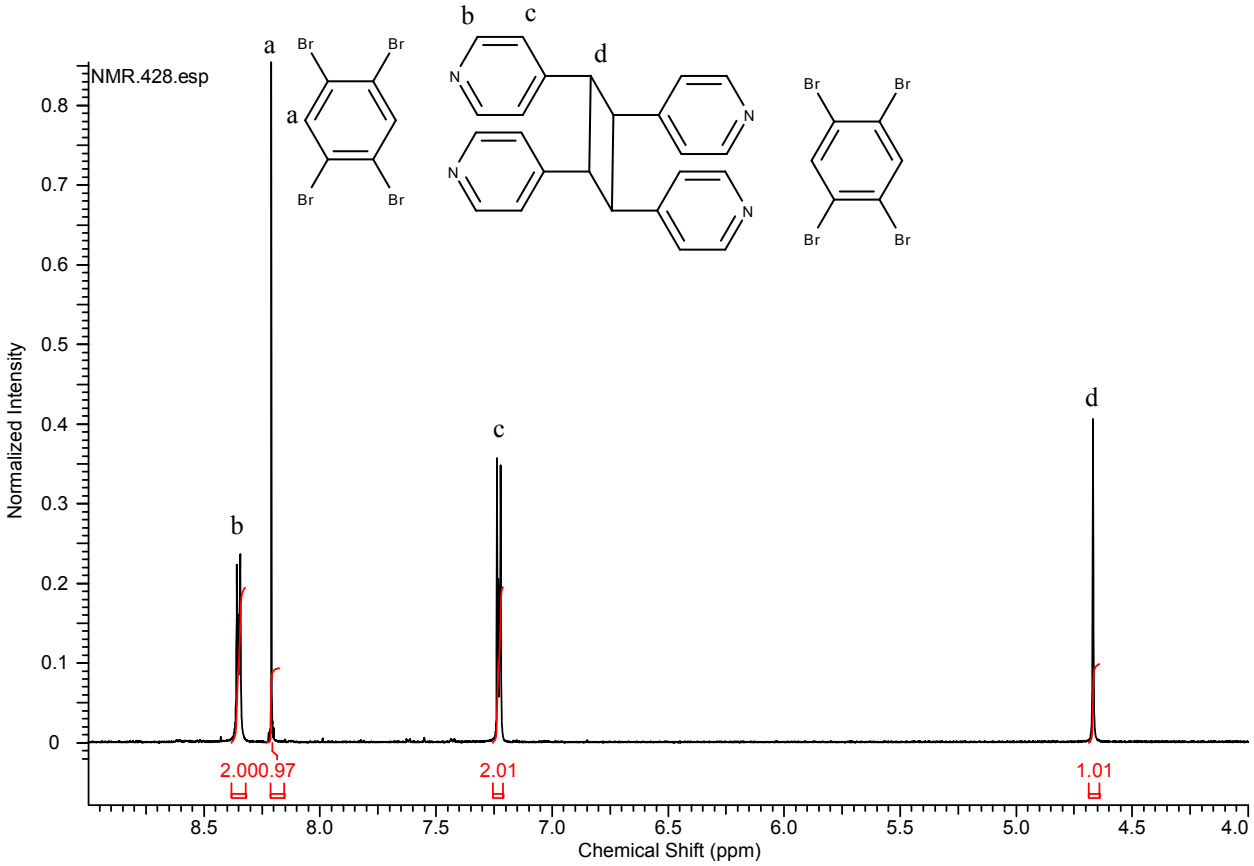

Figure S7: ^{1}H NMR spectrum of **($C_6H_2Br_4$)•(4,4'-BPE)** after 36 hours of UV irradiation with an overall yield of 100% for the [2+2] cycloaddition reaction after 15 minutes of vortex grinding. (400 MHz, DMSO-d_6).

X-ray Powder Diffraction Data

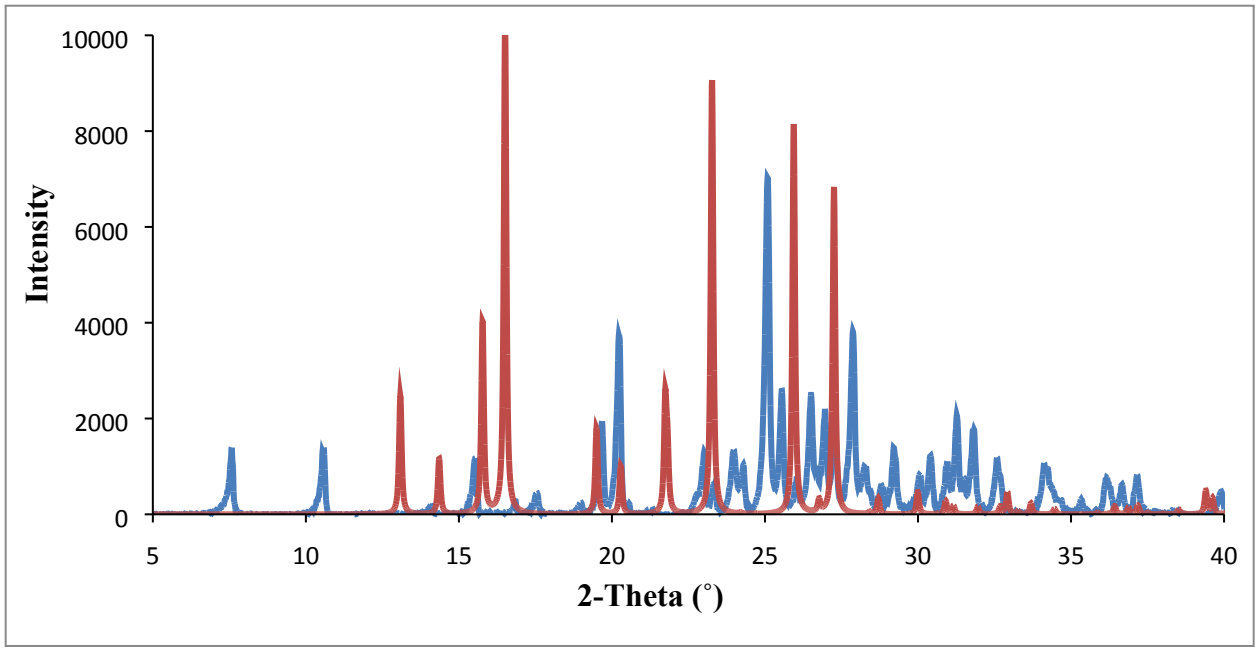

Figure S8: Powder X-ray diffraction data for the co-crystal containing both $C_6H_2Br_2F_2$ and **4,4'-BPE** (blue) and the calculated powder pattern for pure **4,4'-BPE** (red).

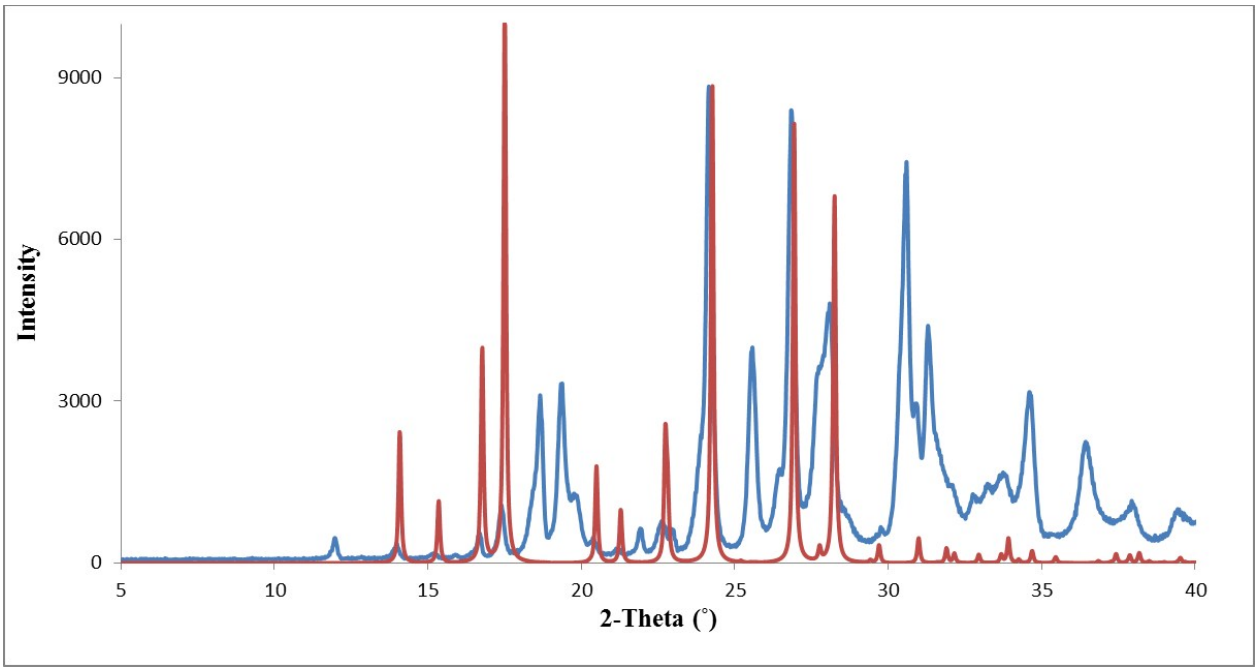

Figure S9: Powder X-ray diffraction data for the co-crystal containing both $C_6H_2Br_4$ and **4,4'-BPE** (blue) and the calculated powder pattern for pure **4,4'-BPE** (red).

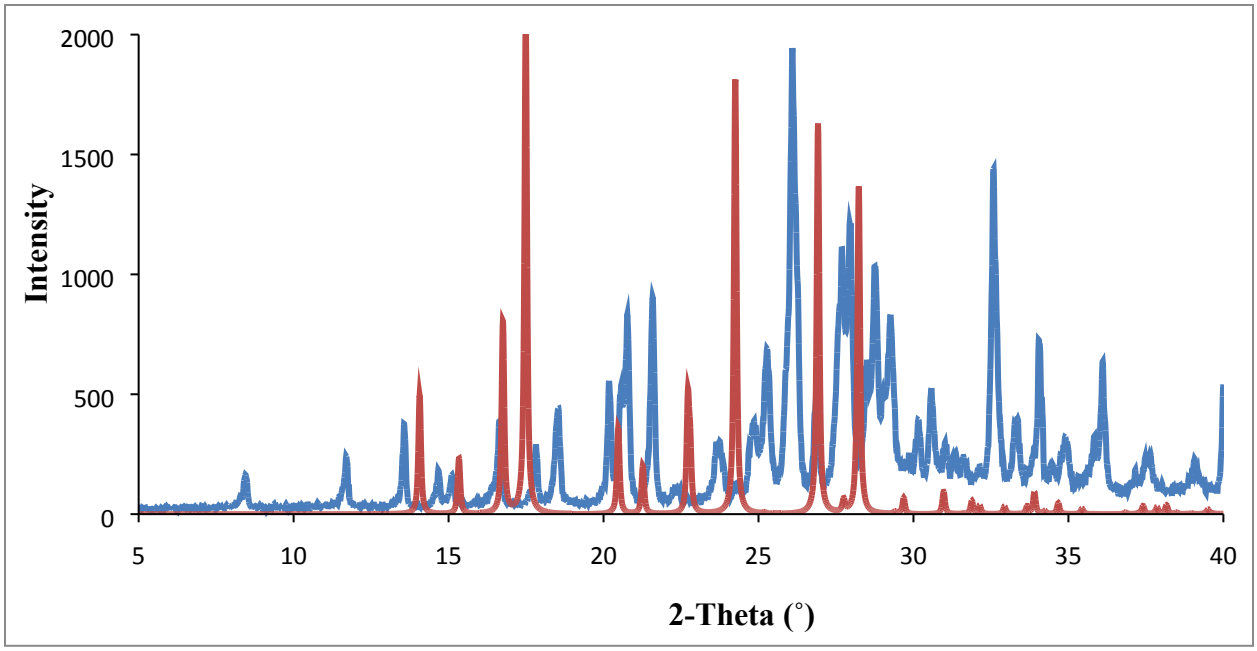

Figure S10: Powder X-ray diffraction data for the co-crystal containing both $C_6H_2Cl_4$ and **4,4'-BPE** (blue) and the calculated powder pattern for pure **4,4'-BPE** (red).