Supporting Information

for

Expanding the versatility of trihalophenols as molecular templates to achieve a series of [2 + 2] cycloaddition reaction involving 1,2-bis(2-pyridyl)ethylene

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1. Materials, General Methods, and Synthesis of the Co-crystals

Materials

The solvent ethanol (reagent grade), *trans*-1,2-bis(2-pyridyl)ethylene (**2,2-BPE**), 2,4,6-trifluorophenol (**$C_6H_2F_3OH$**), 2,4,6-trichlorophenol (**$C_6H_2Cl_3OH$**), and 2,4,6-tribromophenol (**$C_6H_2Br_3OH$**) were all purchased from Sigma-Aldrich (St. Louis, MO) and were used as received without any further purification. All crystallization experiments were performed in 20 mL scintillation vials.

General Methods

Photoreactions were conducted using UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet. The different co-crystals were dried and placed between a pair of Pyrex glass plates for irradiation. The photoreactivity of each co-crystal were determined before and after UV exposure by using ^{1}H NMR spectroscopy. ^{1}H NMR spectrum was collected using a Bruker Avance 400 MHz spectrometer using DMSO-d_6 as a solvent.

Synthesis of the Co-crystals

Synthesis of 2($C_6H_2F_3OH$)•(2,2-BPE)

The co-crystal 2(**$C_6H_2F_3OH$**)•(**2,2-BPE**) was synthesized by dissolving 40.6 mg of **$C_6H_2F_3OH$** in 2.0 mL of ethanol, which was then combined with a separate 2.0 mL ethanol solution containing 25.0 mg of **2,2-BPE** (2:1 molar equivalent). The resulting solution was allowed to slowly evaporate and within two day, crystals suitable for X-ray diffraction formed.

Synthesis of 2($C_6H_2Cl_3OH$)•(2,2-BPE)

The co-crystal 2(**$C_6H_2Cl_3OH$**)•(**2,2-BPE**) was synthesized by dissolving 54.2 mg of **$C_6H_2Cl_3OH$** in 2.0 mL of ethanol then combined with 25.0 mg of **2,2-BPE** also in 2.0 mL of ethanol (2:1 molar equivalent). The resulting solution was allowed to slowly evaporate and within one day, single-crystals suitable for X-ray diffraction were realized.

Synthesis of 2($C_6H_2Br_3OH$)•(2,2-BPE)

The co-crystal 2(**$C_6H_2Br_3OH$**)•(**2,2-BPE**) was synthesized by dissolving 90.6 mg of **$C_6H_2Br_3OH$** in 2.0 mL of ethanol which was then combined with a 2.0 mL ethanol solution containing 25.0 mg of **2,2-BPE** (2:1 molar equivalent). The combined solution was allowed to slowly evaporate and within one day, crystals suitable for X-ray diffraction formed.

2. Electronic Structure Calculations

To obtain binding energies, density functional theory calculations were performed using the M06-2X density functional as implemented in the Gaussian 16 program.[1] X-ray diffraction data was used to determine the positions of all atoms, with the exception of hydrogen. The hydrogen coordinates were obtained by performing a molecular mechanics[2] optimization with all non-hydrogen atoms frozen at the X-ray diffraction values. An aug-cc-pVTZ basis set, stored internally in the Gaussian program was used for all atoms. The energies were computed using the counterpoise method as implemented in Gaussian. This procedure computes the energy as the difference between the energy of the pair and the energies of the separated molecules. In the case of the separated fragments, the energies are computed using the entire set of orbitals for the molecular pair. For all calculations, the counterpoise correction was rather modest, comprising no more than about 10% of the computed value.

The overall homogenous and face-to-face π-π stacking interaction energy was determined based upon the atomic positions of a pair of the hydrogen-bond donors as determined by single-crystal X-ray diffraction data. Before performing the electronic structure calculation, the positons of the hydrogen atoms were adjusted via a molecular mechanics routine.[2]

3. Single X-ray Diffraction Information and Data Table

Data were collected on a Bruker D8 VENTURE DUO diffractometer equipped with a IμS 3.0 microfocus source operated at 75 W (50 kV, 1.5 mA) to generate Mo Kα radiation (λ = 0.71073 Å) and a PHOTON III detector. Crystals were transferred from the vial and placed on a glass slide in Paratone-N oil. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The selected crystal and a small amount of the oil were collected on a MiTeGen 100-micron MicroLoop and transferred to the instrument. The sample was optically centered with the aid of a video camera to ensure that no translations were observed as the crystal was rotated through all positions. A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database a data collection strategy was calculated by *APEX4*.[3] The crystal was measured for size, morphology, and color.

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the *APEX4*.[3] A numerical absorption correction was applied based on a Gaussian integration over a multifaceted crystal and followed by a semi-empirical correction for adsorption applied using *SADABS*.[3] The program *SHELXT*[4] was used for the initial structure solution and *SHELXL*[5] was used for refinement of the structure. Both programs were utilized within the OLEX2 software.[6] Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

Table S1. X-ray data for 2($C_6H_2F_3OH$)•(2,2-BPE), 2($C_6H_2Cl_3OH$)•(2,2-BPE), and 2($C_6H_2Br_3OH$)•(2,2-BPE).

compound name	2($C_6H_2F_3OH$)•(2,2-BPE)	2($C_6H_2Cl_3OH$)•(2,2-BPE)	2($C_6H_2Br_3OH$)•(2,2-BPE)
chemical formula	$C_{24}H_{16}F_6N_2O_2$	$C_{24}H_{16}Cl_6N_2O_2$	$C_{24}H_{16}Br_6N_2O_2$
formula mass	478.39	577.09	843.85
crystal system	Monoclinic	Triclinic	Monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a/Å	16.4149(11)	3.8425(3)	15.2907(6)
b/Å	3.8067(4)	11.4827(8)	4.0298(2)
c/Å	17.2311(14)	13.8828(9)	22.1448(7)
α/°	90	94.128(2)	90
β/°	99.309(2)	94.256(2)	106.3530(10)
γ/°	90	95.001(2)	90
V/Å^3	1062.53(16)	606.63(7)	1309.33(9)
ρ_{calc}/g cm^{-3}	1.495	1.580	2.140
T/K	290.00	290.00	290.00
Z	2	1	2
radiation type	Mo Kα	Mo Kα	Mo Kα
absorption coefficient, μ/mm^{-1}	0.132	0.735	9.225
no. of reflections measured	24075	19706	35054
no. of independent reflections	2171	2566	3113
R_{int}	0.0660	0.0681	0.0640
R_1 (I > 2σ(I))	0.0418	0.0395	0.0299
$wR(F^2)$ (I > 2σ(I))	0.1073	0.0959	0.0683
R_1 (all data)	0.0579	0.0549	0.0428
$wR(F^2)$ (all data)	0.1199	0.1072	0.0739
Goodness-of-fit	1.067	1.035	1.021
CCDC deposition number	2337585	2337583	2337582

4. ^{1}H NMR Spectroscopic Data
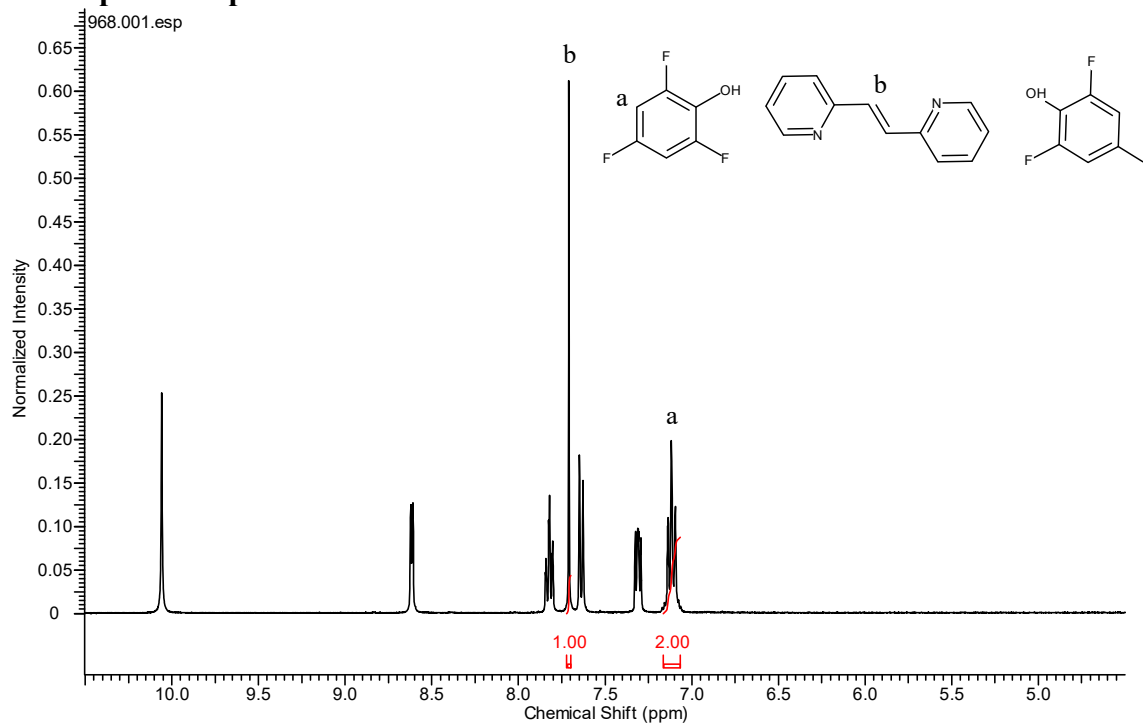
Figure S1: ^{1}H NMR spectrum of the co-crystal 2(**C$_6$H$_2$F$_3$OH**)•(**2,2-BPE**) before UV irradiation (400 MHz, DMSO-d_6).
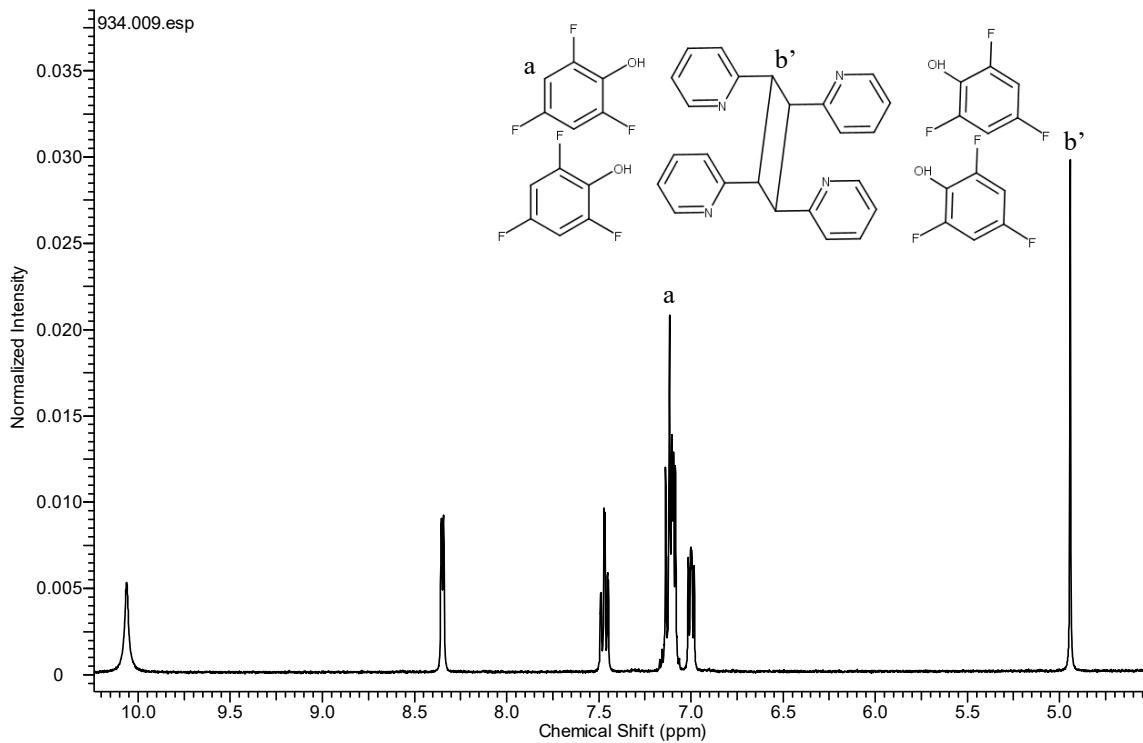
Figure S2: ^{1}H NMR spectrum of the co-crystal 2(**C$_6$H$_2$F$_3$OH**)•(**2,2-BPE**) after 25 hours of UV irradiation reaching a quantitative yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO-d_6).
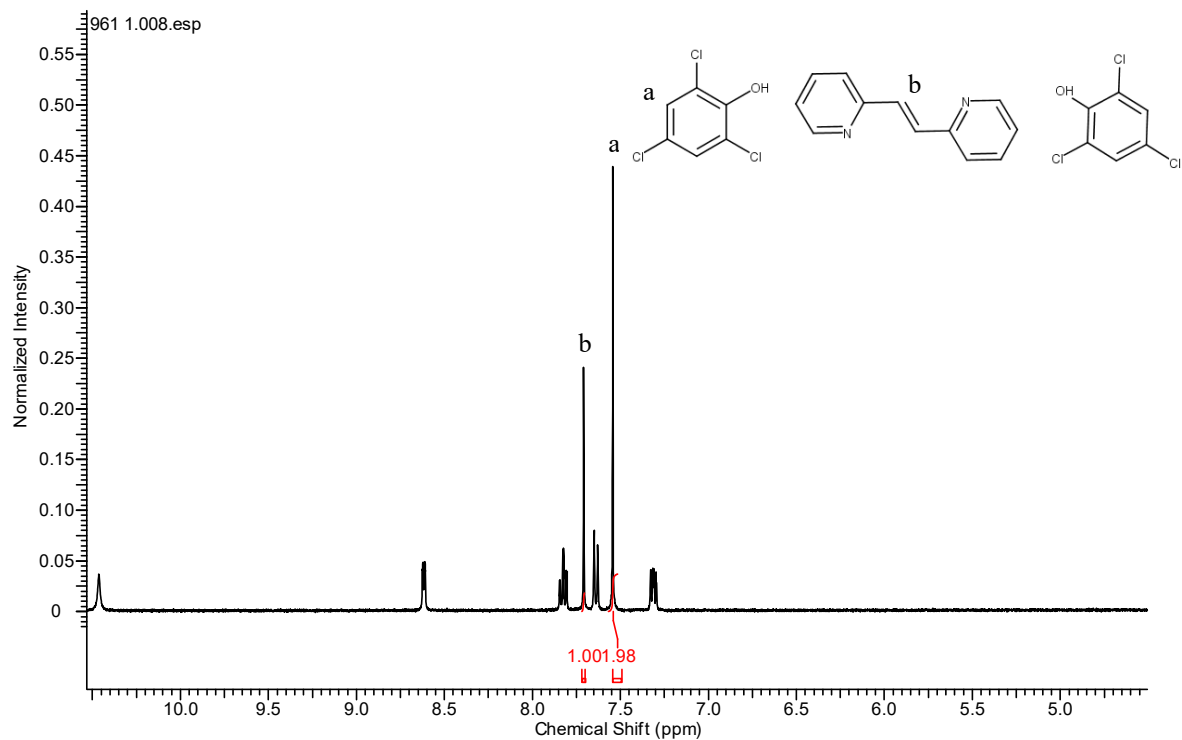
Figure S3: ^{1}H NMR spectrum of the co-crystal 2(**C₆H₂Cl₃OH**)•(**2,2-BPE**) before UV irradiation (400 MHz, DMSO-d_6).
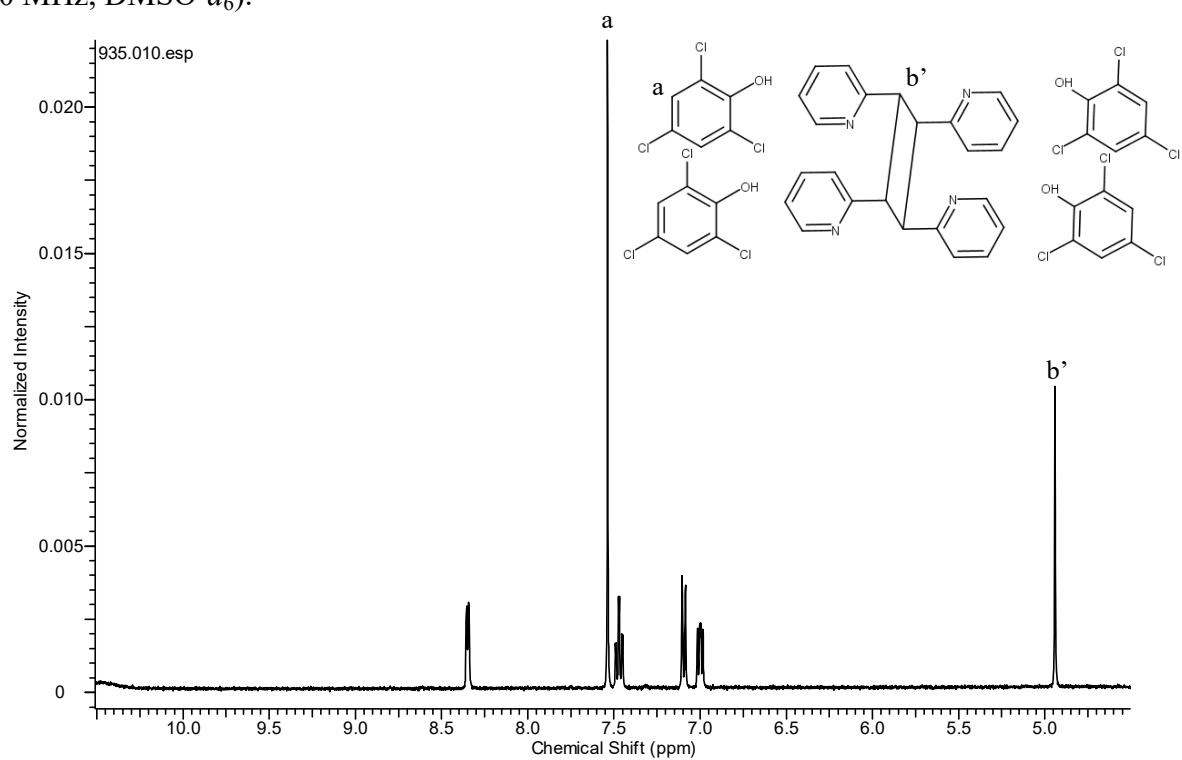
Figure S4: ^{1}H NMR spectrum of the co-crystal 2(**C₆H₂Cl₃OH**)•(**2,2-BPE**) after 5 hours of UV irradiation reaching a quantitative yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO-d_6).

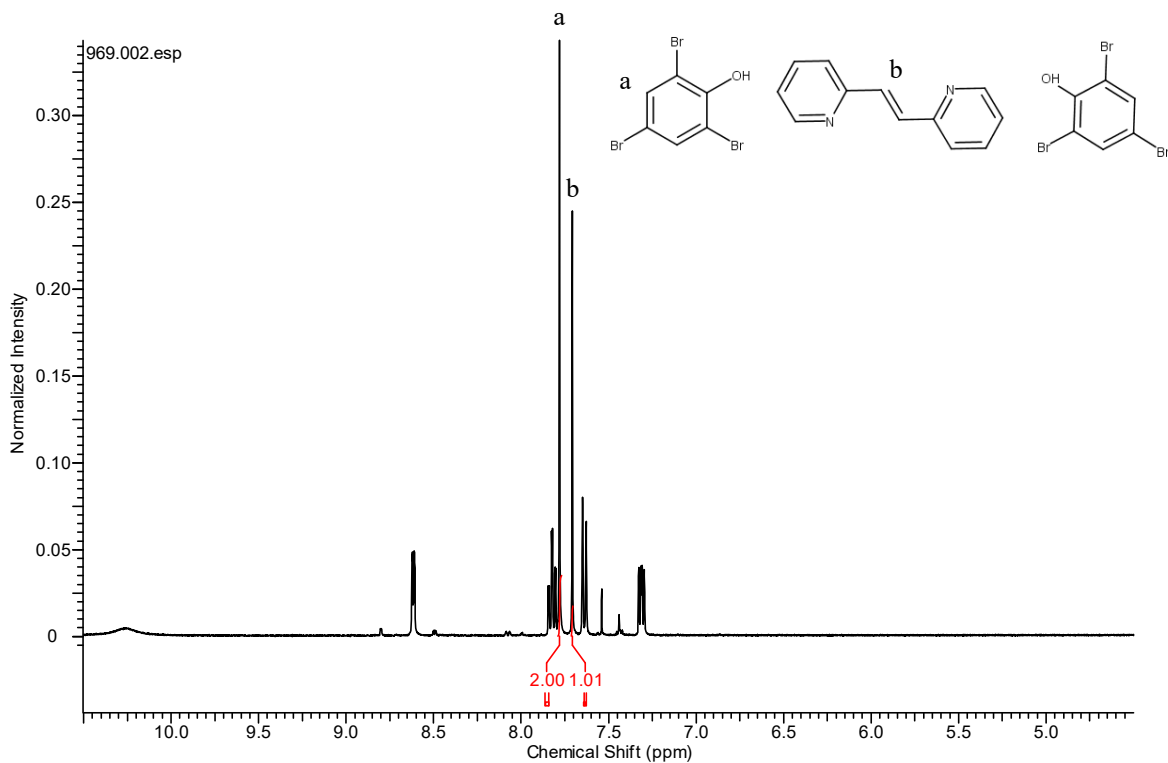**Figure S5:** ^{1}H NMR spectrum of the co-crystal 2(**C₆H₂Br₃OH**)•(**2,2-BPE**) before UV irradiation (400 MHz, DMSO-d_6).
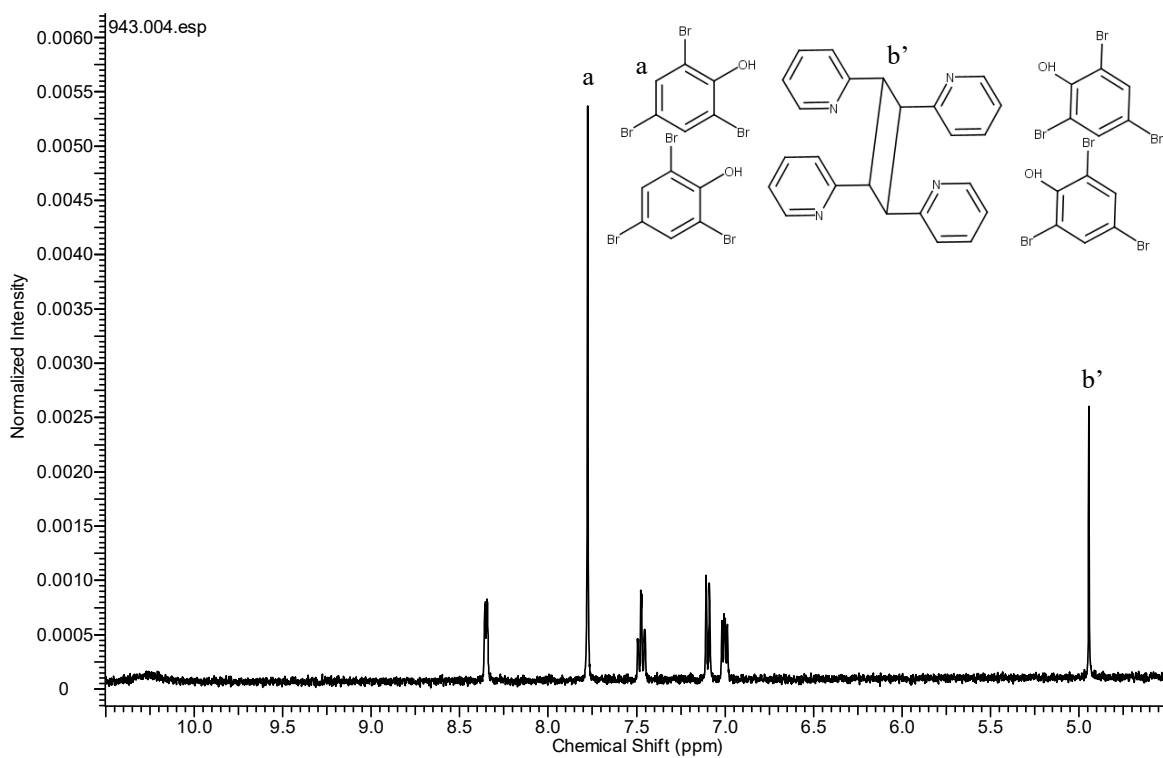
Figure S6: ^{1}H NMR spectrum of the co-crystal 2(**C₆H₂Br₃OH**)•(**2,2-BPE**) after 30 hours of UV irradiation reaching a quantitative yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO-d_6).

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