Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.


Supporting Information

for

# Regioselective Photoreactions within a Series of Mixed Co-crystals Containing Isosteric Dihalogenated Resorcinols with 4-Stilbazole

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

### Materials

4,6-dichlororesorcinol (**4,6-diCl res**), 4-stilbazole (**4-SB**) as well as the solvent ethanol were all purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received. 4,6-dibromoresorcinol (**4,6-diBr res**) was formed via a standard literature preparation. All crystallization studies 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. Co-crystals of each were placed between a pair of Pyrex glass plates for irradiation. The overall yield of the photoreaction was determined using $^1$H NMR spectroscopy after 20 hours of UV exposure. $^1$H NMR spectra were collected using a Bruker Avance 400 MHz spectrometer using DMSO-$d_6$ as a solvent. X-ray powder diffraction data was collected at room temperature on a Rigaku Ultima IV X-ray diffractometer between 5˚ to 50˚ two-theta. The melting point was measured using a Mel-Temp Capillary Melting Point Apparatus.

### Synthesis of (4,6-diCl/Br res)•2(4-SB) 25/75

Co-crystals of (**4,6-diCl/Br res**)•2(**4-SB**) were synthesized by dissolving 25.0 mg of **4-SB** in 2 mL of ethanol, which was then combined with a separate 1 mL ethanol solution containing 3.1 mg of **4,6-diCl res** and a separate 1 mL ethanol solution containing 13.9 mg of **4,6-diBr res**. The solution was allowed to evaporate slowly. Following a period of three days, single crystals suitable for X-ray diffraction were formed.

### Synthesis of (4,6-diCl/Br res)•2(4-SB) 50/50

Co-crystals of (**4,6-diCl/Br res**)•2(**4-SB**) were synthesized by dissolving 25.0 mg of **4-SB** in 2 mL of ethanol, which was then combined with a separate 1 mL ethanol solution containing 6.2 mg of **4,6-diCl res** and a separate 1 mL ethanol solution containing 9.3 mg of **4,6-diBr res**. The solution was allowed to evaporate slowly. Following a period of three days, single crystals suitable for X-ray diffraction were formed.

### Synthesis of (4,6-diCl/Br res)•2(4-SB) 75/25

Co-crystals of (**4,6-diCl/Br res**)•2(**4-SB**) were synthesized by dissolving 25.0 mg of **4-SB** in 2 mL of ethanol, which was then combined with a separate 1 mL ethanol solution containing 9.2 mg of **4,6-diCl res** and a separate 1 mL ethanol solution containing 4.6 mg of **4,6-diBr res**. The solution was allowed to evaporate slowly. Following a period of three days, single crystals suitable for X-ray diffraction were formed.

### Formation of the Single Crystals for (4,6-diCl/Br res)•(*ht*-PP)

Each co-crystal was exposure to 20 hours of UV-radiation from a 450 W medium-pressure mercury lamp in a photoreactor and a quantitative yield was reached for each solid. The resulting solid for the 50/50 mixed crystal was then dissolved in 3 ml of ethanol and upon slow evaporation crystals suitable for X-ray diffraction were formed within two days.

## 2. X-ray Diffraction Information, Data Tables and Powder Diffractograms

Single crystal X-ray diffraction data for the co-crystals were collected on a Bruker X8-kappa diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). Intensity data collection and data reduction was performed using the Bruker program, APEX II. A semi-empirical correction for absorption was applied using the program *SADABS*.[1] The *SHELXTL*[2] suite of programs were used for the solution and refinement of the crystal structure. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added in calculated positions. The occupancy of the Cl and Br atoms were refined as free variables to obtain the relative ratio of **4,6-diCl res** to **4,6-diBr res** components in the mixed co-crystals.

**Table S1**. X-ray data for all mixed co-crystals of (**4,6-diCl/Br res**)•2(**4-SB**).

| Initial Percent **4,6-diCl res** | 25% | 50% | 75% |
|---|---|---|---|
| Observed Percent **4,6-diCl res** | 38% | 50% | 67% |
| chemical formula | $C_{32}H_{26}Br_{1.24}Cl_{.76}N_2O_2$ | $C_{32}H_{26}BrClN_2O_2$ | $C_{32}H_{26}Br_{.66}Cl_{1.34}N_2O_2$ |
| crystal system | Triclinic | Triclinic | Triclinic |
| space group | Pī | Pī | Pī |
| a/Å | 10.9120(17) | 10.9647(8) | 10.9822(13) |
| b/Å | 10.9997(17) | 11.0160(8) | 10.9866(13) |
| c/Å | 11.6021(18) | 11.6107(10) | 11.6040(13) |
| α/° | 91.680(8) | 91.273(4) | 98.151(3) |
| β/° | 97.459(8) | 97.696(4) | 90.796(3) |
| γ/° | 91.733(8) | 91.769(4) | 91.779(4) |
| V/Å$^3$ | 1379.4(4) | 1388.6(2) | 1385.1(3) |
| $\rho_{calc}$/g cm$^{-3}$ | 1.437 | 1.401 | 1.368 |
| T/K | 290 | 290 | 290 |
| Z | 2 | 2 | 2 |
| radiation type | Mo Kα | Mo Kα | Mo Kα |
| absorption coefficient, μ/mm$^{-1}$ | 1.957 | 1.608 | 1.141 |
| no. of reflections measured | 11536 | 15123 | 20026 |
| no. of independent reflections | 4891 | 6367 | 5670 |
| $R_{int}$ | 0.0626 | 0.0280 | 0.0300 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0457 | 0.0354 | 0.0381 |
| $wR(F^2)$ ($I > 2\sigma(I)$) | 0.0689 | 0.0755 | 0.0805 |
| $R_1$ (all data) | 0.1539 | 0.0700 | 0.0726 |
| $wR(F^2)$ (all data) | 0.0910 | 0.0857 | 0.0910 |
| Goodness-of-fit | 0.925 | 1.038 | 1.033 |
| CCDC deposition number | 1867907 | 1867908 | 1867909 |

**Table S2**. X-ray data for (**4,6-diCl/Br res**)•(***ht*-PP**).

| | |
|---|---|
| Initial Percent **4,6-diCl res** | 50% |
| Observed Percent **4,6-diCl res** | 60% |
| Chemical formula | $C_{32}H_{26}Br_{0.80}Cl_{1.20}N_2O_2$ |
| crystal system | Orthorhombic |
| space group | $Pna2_1$ |
| a/Å | 18.9449(8) |
| b/Å | 9.4629(4) |
| c/Å | 14.4914(6) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| V/Å$^3$ | 2597.93(19) |
| $\rho_{calc}$/g cm$^{-3}$ | 1.475 |
| T/K | 100 |
| Z | 4 |
| radiation type | Mo Kα |
| absorption coefficient, μ/mm$^{-1}$ | 1.432 |
| no. of reflections measured | 24687 |
| no. of independent reflections | 5653 |
| $R_{int}$ | 0.0475 |
| $R_1$ ($I > 2\sigma(I)$) | 0.0303 |
| $wR(F^2)$ ($I > 2\sigma(I)$) | 0.0548 |
| $R_1$ (all data) | 0.0380 |
| $wR(F^2)$ (all data) | 0.0567 |
| Goodness-of-fit | 1.021 |
| CCDC deposition number | 1867910 |

| | (**4,6-diCl res**) •2(**4-SB**) | (**4,6-diBr res**) •2(**4-SB**) | (**4,6-diCl/Br res**) •2(**4-SB**) | | |
|---|---|---|---|---|---|
| Initial Percent (Cl/Br) | 100/0 | 0/100 | 75/25 | 50/50 | 25/75 |
| O-H•••N Hydrogen Bond Distances (Å) | 2.690(2)<br>2.692(2) | 2.688(3)<br>2.691(3) | 2.688(2)<br>2.695(2) | 2.690(2)<br>2.690(2) | 2.670(5)<br>2.681(5) |
| Olefin-Olefin Distance within the Assembly (Å) | 4.33 | 4.29 | 4.32 | 4.31 | 4.29 |
| Olefin-Olefin Distance between Assemblies (Å) | 3.99 | 4.10 | 4.02 | 4.04 | 4.04 |
| Regiochemistry of the Photoproduct | head-to-tail | head-to-head | head-to-tail | head-to-tail | head-to-tail |

**Table S3.** Hydrogen bond distances, olefin-olefin distances (centroid-centroid), and the resulting photoproduct for the various pure and mixed co-crystals. Similar values for the pure co-crystals (**4,6-diCl res**)•2(**4-SB**) and (**4,6-diCl res**)•2(**4-SB**) are shown as a comparison.

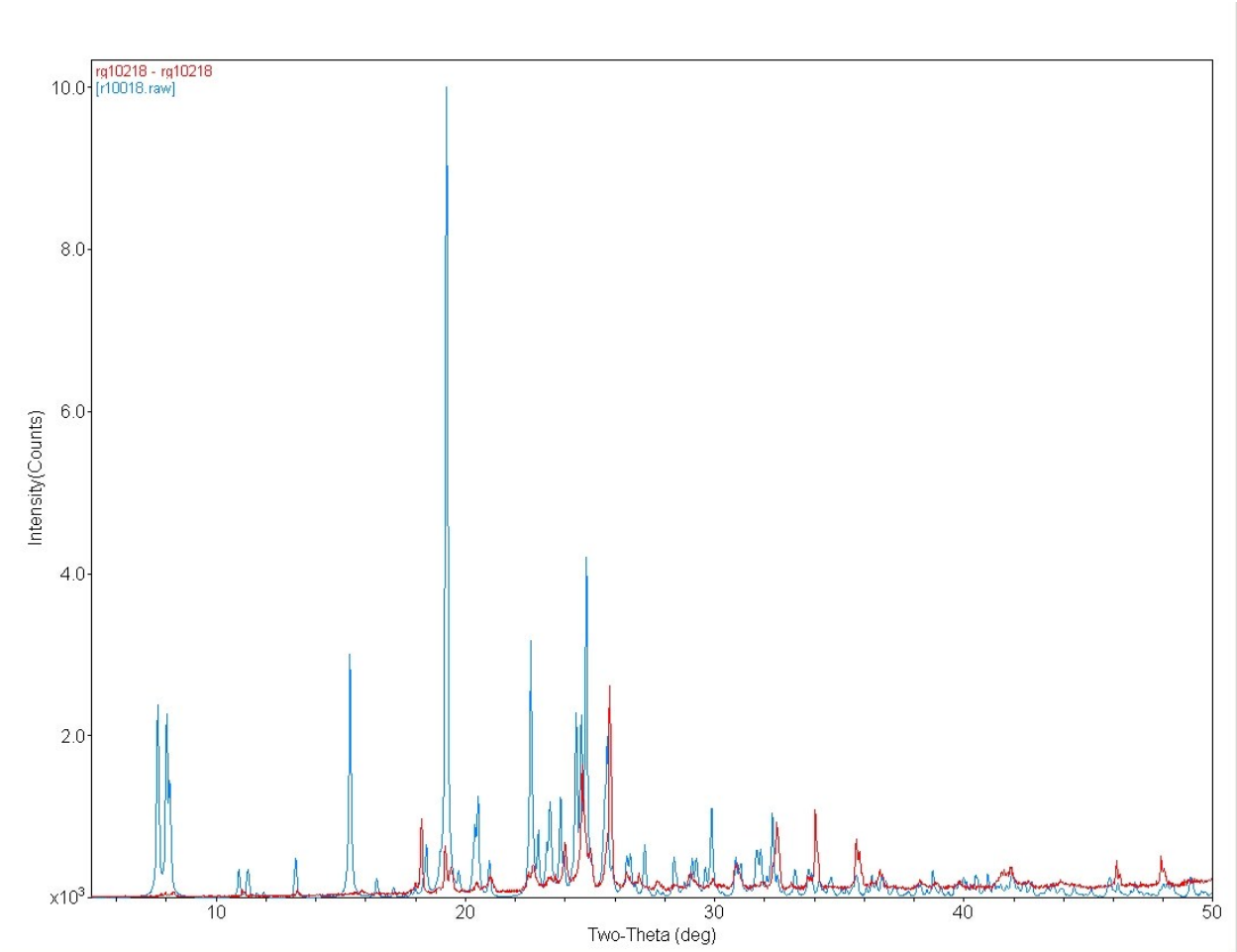


**Figure S1:** Powder X-ray diffraction data for (**4,6-diCl/Br res**)•2(**4-SB**) before photoreaction (red) and calculated (blue) based upon 25% **4,6-diCl res** and 75% **4,6-diBr res**.

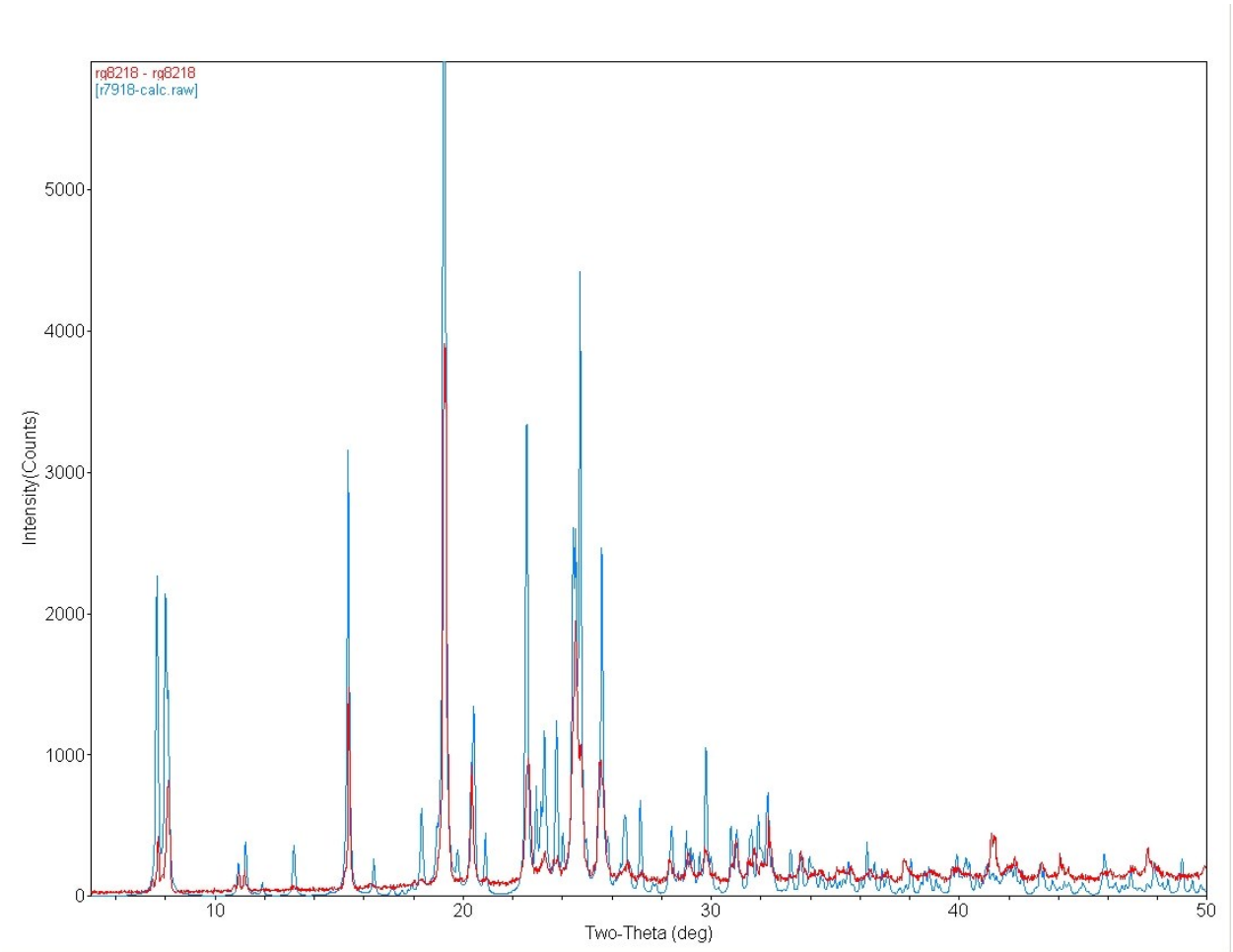


**Figure S2:** Powder X-ray diffraction data for (**4,6-diCl/Br res**)•2(**4-SB**) before photoreaction (red) and calculated (blue) based upon 50% **4,6-diCl res** and 50% **4,6-diBr res**.

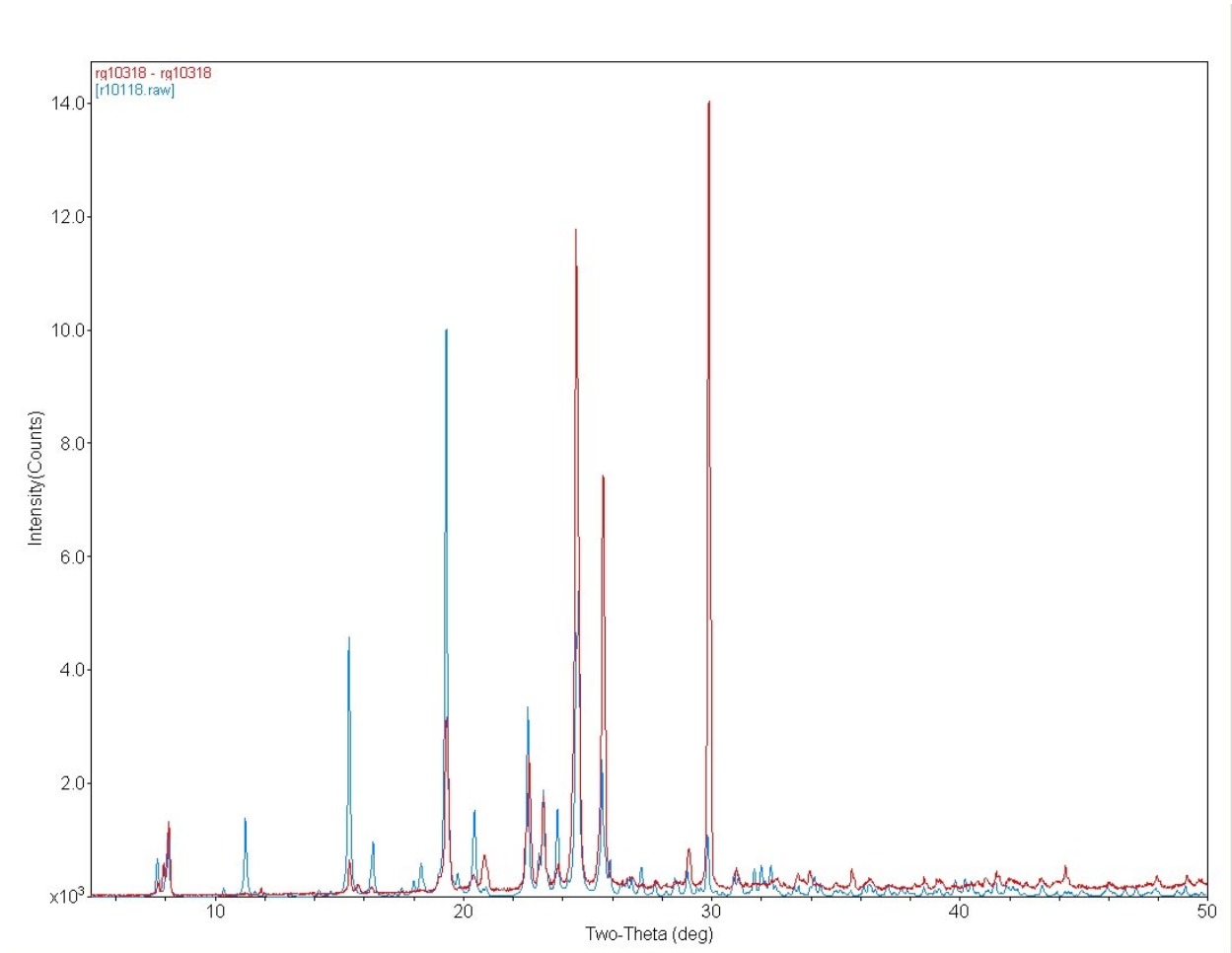


**Figure S3:** Powder X-ray diffraction data for (**4,6-diCl/Br res**)•2(**4-SB**) before photoreaction (red) and calculated (blue) based upon 75% **4,6-diCl res** and 25% **4,6-diBr res**.

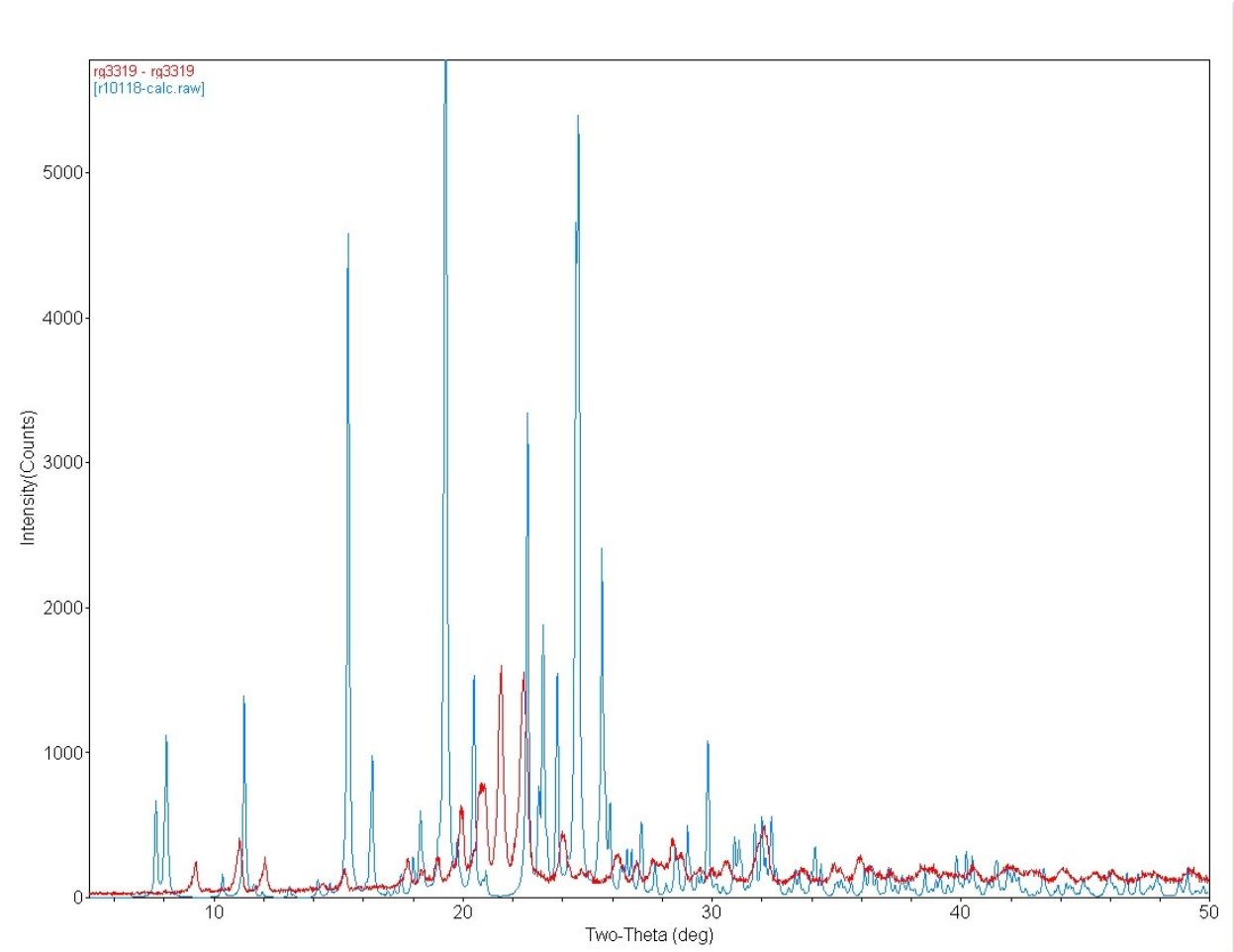


**Figure S4:** Powder X-ray diffraction data for (**4,6-diCl/Br res**)•(***ht*-PP**) (red) and (**4,6-diCl/Br res**)•2(**4-SB**) calculated (blue) based upon **75% 4,6-diCl res** and **25% 4,6-diBr res**.

## 3. $^1$H NMR Spectroscopic Data

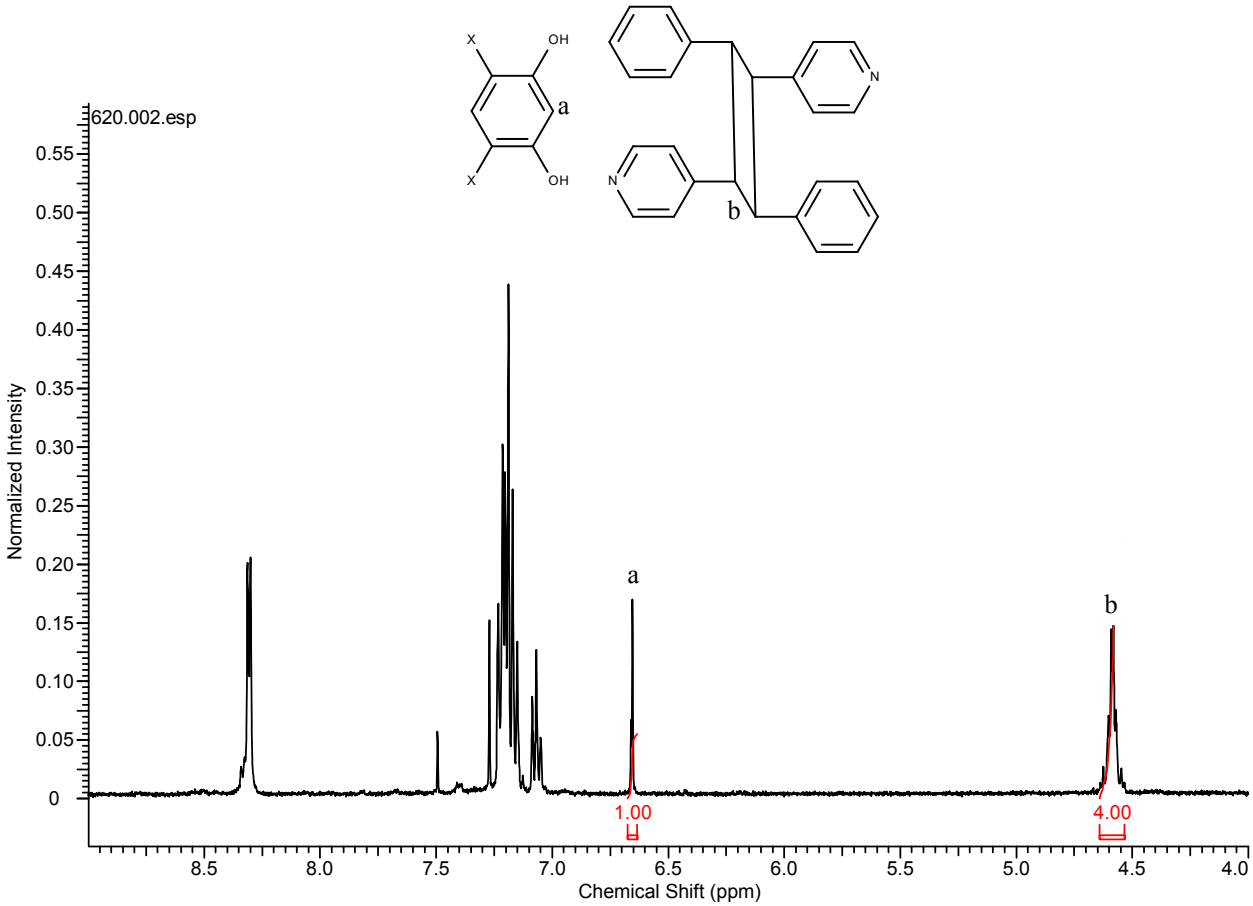


**Figure S5:** $^1$H NMR spectrum of (**4,6-diCl/Br res**)•(***ht*-PP**) after 20 hours of UV irradiation with a quantitative yield for the [2+2] cycloaddition reaction based upon 25% **4,6-diCl res** and 75% **4,6-diBr res** (400 MHz, DMSO-$d_6$).

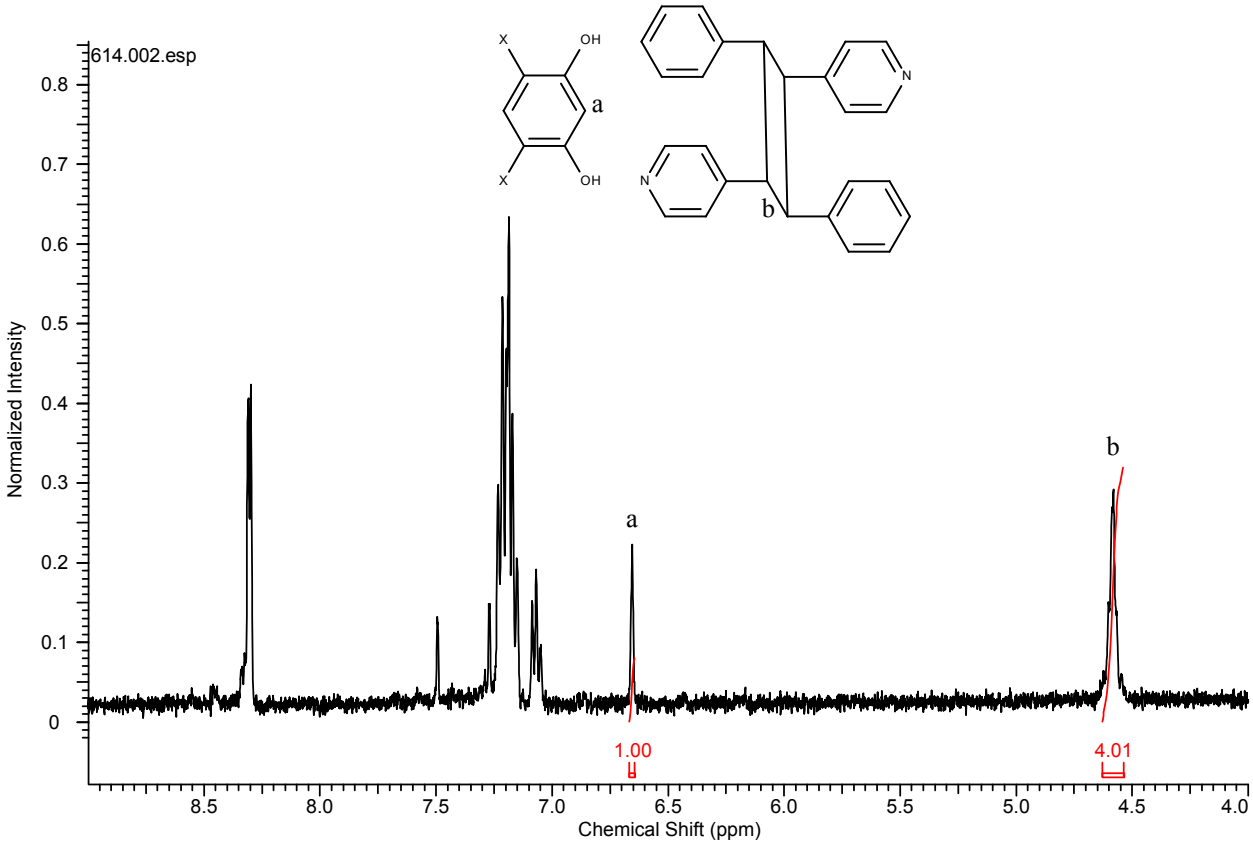


**Figure S6:** $^{1}$H NMR spectrum of (**4,6-diCl/Br res**)•(***ht*-PP**) after 20 hours of UV irradiation with a quantitative yield for the [2+2] cycloaddition reaction based upon 50% **4,6-diCl res** and 50% **4,6-diBr res** (400 MHz, DMSO-$d_6$).

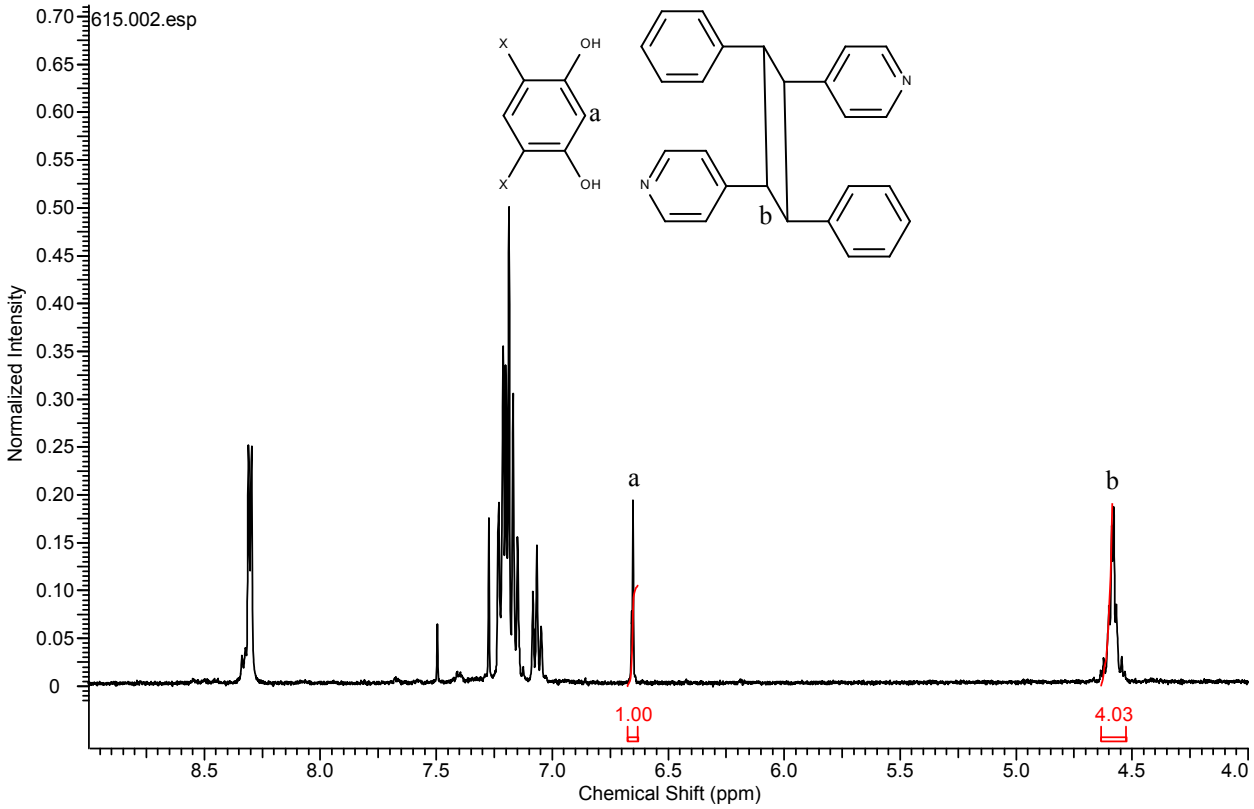


**Figure S7:** $^{1}$H NMR spectrum of (**4,6-diCl/Br res**)•(***ht*-PP**) after 20 hours of UV irradiation with a quantitative yield for the [2+2] cycloaddition reaction based upon 75% **4,6-diCl res** and 25% **4,6-diBr res** (400 MHz, DMSO-$d_6$).

## References

1. Krause *et al.*, (2015) SADABS v 2016/2.

2. Sheldrick, G. M. *Acta Crystallogr.*, **2015**, *C71*, 3.