Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

for

Varying the regiochemistry of a [2 + 2] cycloaddition reaction within isostructural hydrogen bonded co-crystals containing 4-stilbazole

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1. Materials, General Methods and Synthesis of the 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.

Synthesis of (4,6-diCl res)•2(4-SB)

Co-crystals of (**4,6-diCl res**)•2(**4-SB**) was synthesized by dissolving 50.0 mg of **4-SB** in 2 mL of ethanol, which was then combined with a separate 2 mL ethanol solution containing 24.7 mg of **4,6-diCl res** (2:1 molar equivalent). The solution was allowed to evaporate slowly. Following a period of two days, single crystals suitable for X-ray diffraction were formed.

Synthesis of (4,6-diBr res)•2(4-SB)

In a similar way as before, co-crystals of (**4,6-diBr res**)•2(**4-SB**) was synthesized by dissolving 50.0 mg of **4-SB** in 2 mL of ethanol, which was then combined with a separate 2 mL ethanol solution containing 37.0 mg of **4,6-diBr res** (2:1 molar equivalent). The solution was again allowed to evaporate slowly. Following a period of two days, single crystals suitable for X-ray diffraction were formed.

Formation of the Single Crystals for (4,6-diCl res)•(*ht*-PP) and (4,6-diBr res)•(*hh*-PP)

Each co-crystal was exposure to 20 hours of UV-radiation from a 450 W medium-pressure mercury lamp in a photoreactor where a quantitative yield was reached for each solid. Each of the resulting solids 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 Data Tables

Single crystal X-ray diffraction data for the co-crystals were collected on a Bruker PLATFORM three circle 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 were corrected for Lorentz, polarization, and background effects using the Bruker program APEX II. A semi-empirical correction for adsorption was applied using the program *SADABS*.[1] The *SHELXL-2014*[2], series of programs were used for the solution and refinement of the crystal structure. All non-hydrogen atoms were refined anisotropically and 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 (**4,6-diCl res**)•2(**4-SB**) and (**4,6-diCl res**)•(***ht*-PP**).

compound name	**(4,6-diCl res)•2(4-SB)**	**(4,6-diCl res)•(*ht*-PP)**
chemical formula	$C_{32}H_{26}Cl_2N_2O_2$	$C_{32}H_{26}Cl_2N_2O_2$
formula mass	541.45	541.45
crystal system	Triclinic	Orthorhombic
space group	$P\bar{1}$	$Pna2_1$
a/Å	10.9020(5)	18.9319(13)
b/Å	11.0152(5)	9.4899(6)
c/Å	11.5729(5)	14.4526(10)
α/°	80.9869(12)	90
β/°	89.8172(12)	90
γ/°	88.0995(14)	90
$V/Å^3$	1371.85(11)	2596.6(3)
ρ_{calc} /g cm^{-3}	1.311	1.385
T/K	290	100
Z	2	4
radiation type	Mo Kα	Mo Kα
absorption coefficient, μ/mm^{-1}	0.269	0.284
no. of reflections measured	16806	32881
no. of independent reflections	5187	7913
R_{int}	0.0257	0.0792
R_1 ($I > 2\sigma(I)$)	0.0402	0.0532
wR(F^2) ($I > 2\sigma(I)$)	0.0906	0.0962
R_1 (all data)	0.0636	0.0801
wR(F^2) (all data)	0.1034	0.1070
Goodness-of-fit	1.027	1.027
CCDC deposition number	1829786	1829787

Table S2. X-ray data for (**4,6-diBr res**)•2(**4-SB**) and (**4,6-diBr res**)•(***hh*-PP**).

compound name	**(4,6-diBr res)•2(4-SB)**	**(4,6-diBr res)•(*hh*-PP)**
chemical formula	$C_{32}H_{26}Br_2N_2O_2$	$C_{32}H_{26}Br_2N_2O_2$
formula mass	630.37	630.37
crystal system	Triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/c$
a/Å	10.9175(2)	17.251(2)
b/Å	11.1262(2)	9.2852(11)
c/Å	11.6716(2)	17.340(2)
α/°	92.504(1)	90
β/°	96.840(1)	97.350(3)
γ/°	91.789(1)	90
V/Å^3	1405.37(4)	2754.7(6)
ρ_{calc} /g cm^{-3}	1.490	1.520
T/K	290	100
Z	2	4
radiation type	Mo Kα	Mo Kα
absorption coefficient, μ/mm^{-1}	2.916	2.975
no. of reflections measured	33870	23779
no. of independent reflections	5736	5589
R_{int}	0.0576	0.0760
R_1 ($I > 2\sigma(I)$)	0.0362	0.0693
wR(F^2) ($I > 2\sigma(I)$)	0.0844	0.1532
R_1 (all data)	0.0699	0.1206
wR(F^2) (all data)	0.0960	0.1735
Goodness-of-fit	0.958	1.060
CCDC deposition number	1829784	1829785

3. ^{1}H NMR Spectroscopic Data

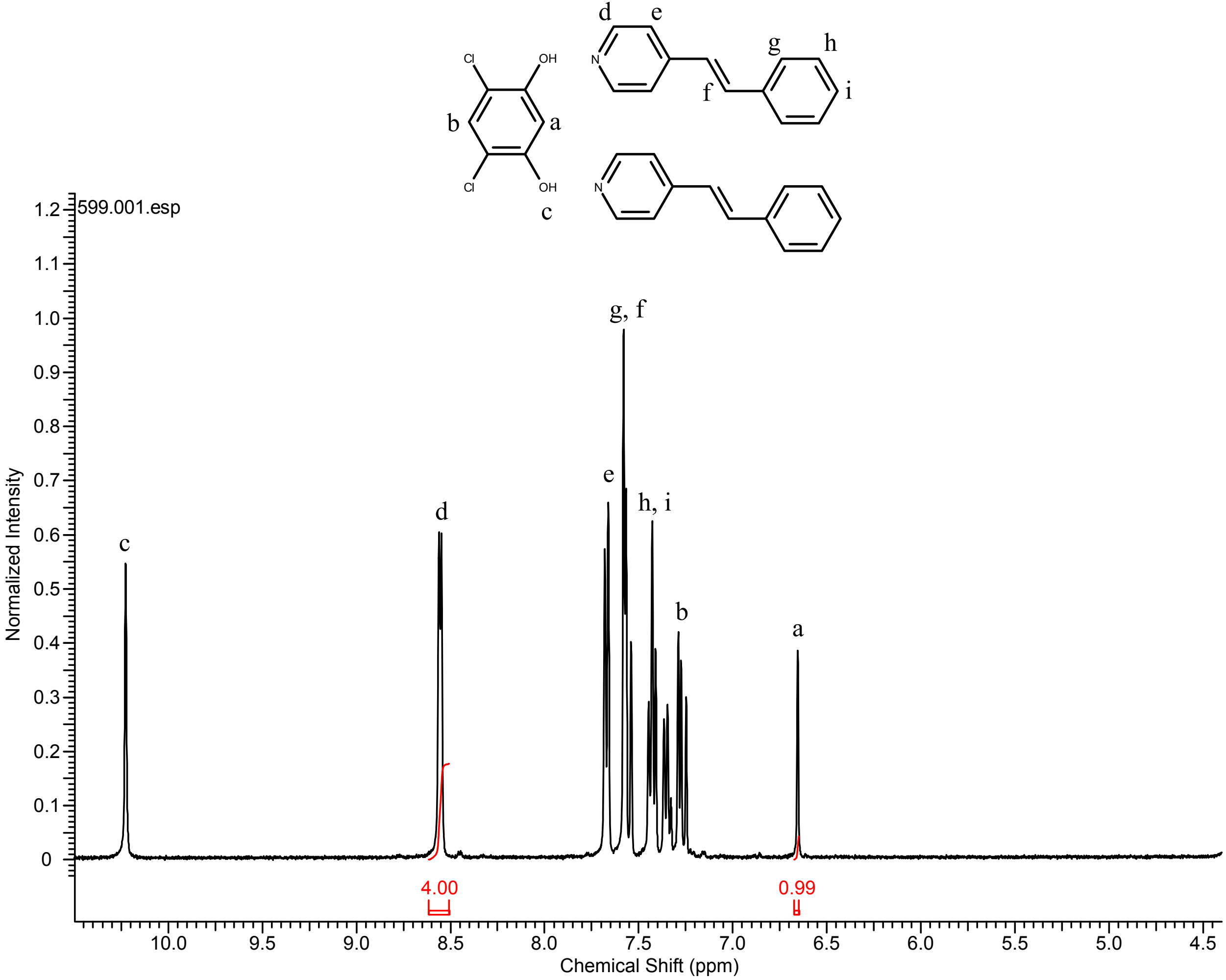

Figure S1: ^{1}H NMR spectrum of (**4,6-diCl res**)•2(**4-SB**) before photoreaction (400 MHz, DMSO-d_6).

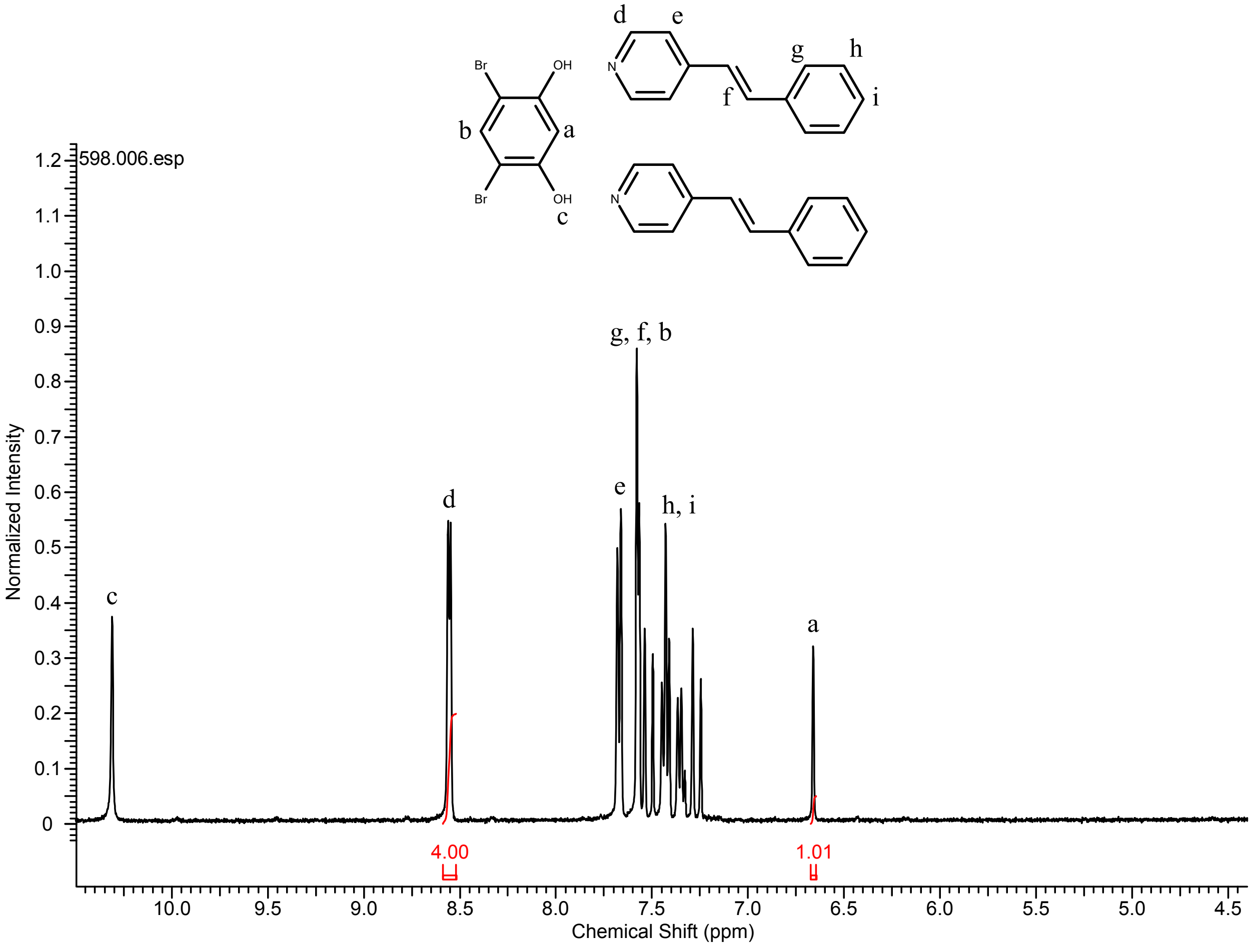

Figure S2: ^{1}H NMR spectrum of (**4,6-diBr res**)•2(**4-SB**) before photoreaction (400 MHz, DMSO-d_6).

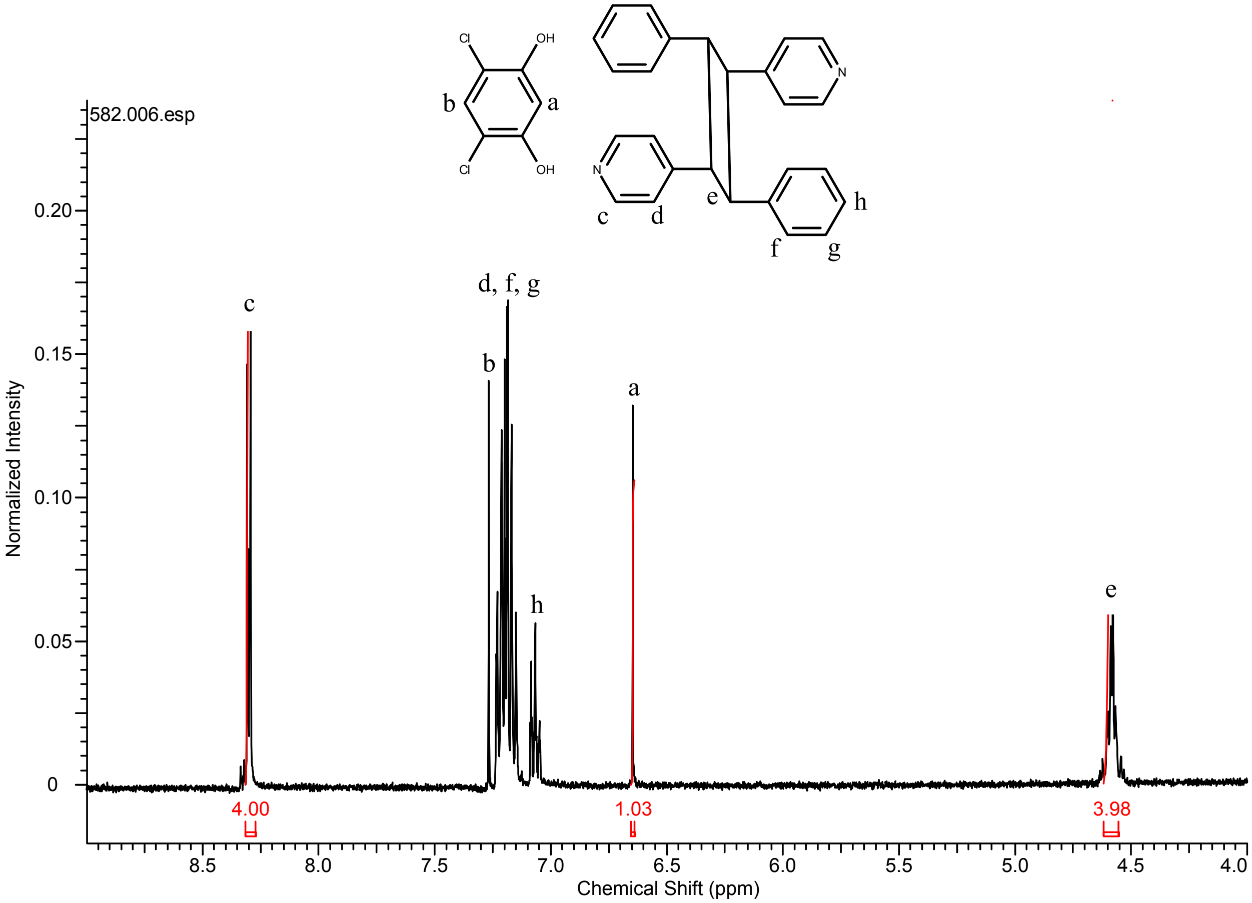

Figure S3: ^{1}H NMR spectrum of (**4,6-diCl res**)•(***ht*-PP**) after 20 hours of UV irradiation with a quantitative yield for the [2+2] cycloaddition reaction (400 MHz, DMSO-d_6).

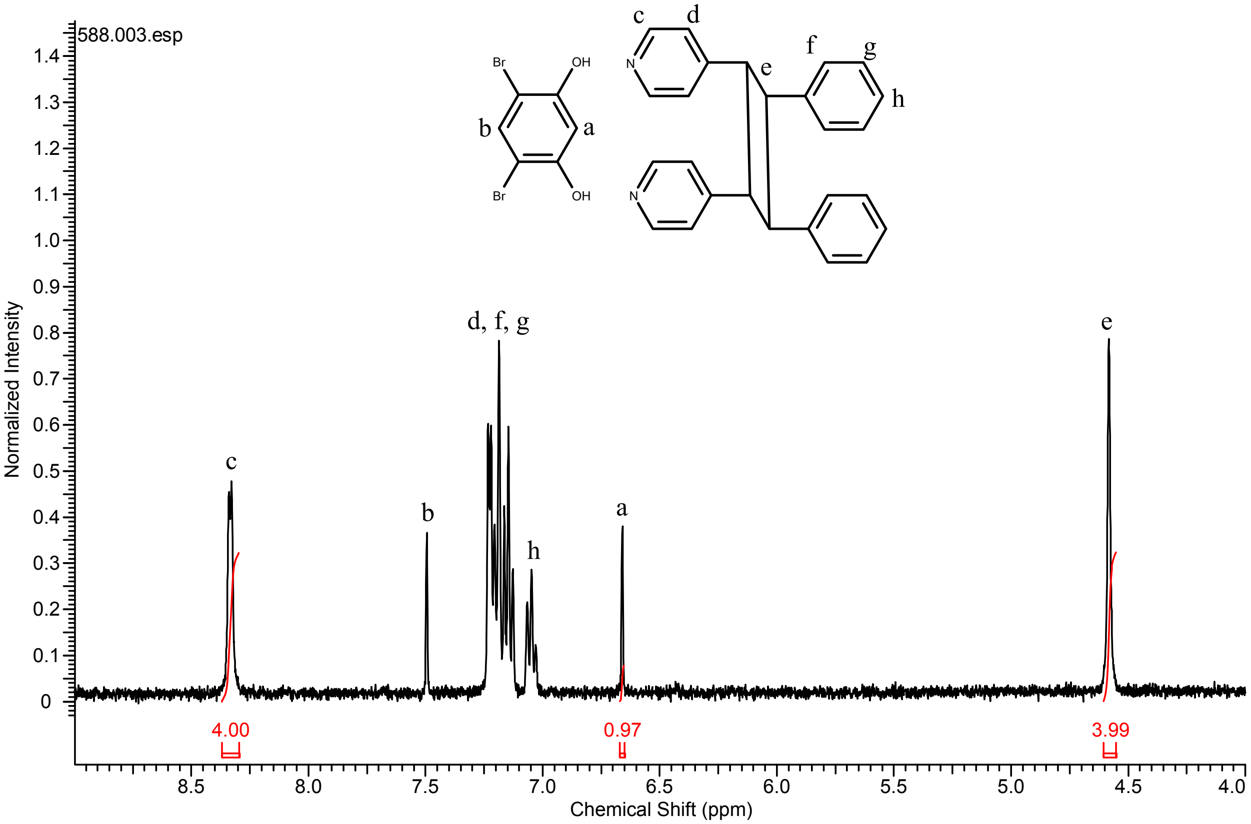

Figure S4: ^{1}H NMR spectrum of (**4,6-diBr res**)•(***hh*-PP**) after 20 hours of UV irradiation with a quantitative yield for the [2+2] cycloaddition reaction (400 MHz, DMSO-d_6).

References

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

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