Supporting Information

for

Dry-vortex grinding facilitates a [2 + 2] cycloaddition reaction that triggers a cascade-like reaction that improves the yield under substoichiometric conditions

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1. Materials, General Methods, and Synthesis of the Solids

Materials

The reactant *trans*-1,2-bis(2-pyridyl)ethylene (**2,2-BPE**) along with the template 2,4,6-trifluorophenol (**$C_6H_2F_3OH$**) were both purchased from Sigma-Aldrich Chemical (St. Louis, MO, USA) and used as received.

General Methods

Photoreactions were conducted using UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet. The ground solid that contains the co-crystal 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) was placed between a pair of Pyrex glass plates for irradiation. The photoreactivity of the resulting solid was determined 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. The dry-vortex grinding occurred within a clear 30 mL SmartSnap Grinding Jar along with 2 ball bearings (5 mm diameter) using a VWR Vortex Genie 2.

Synthesis of the Stoichiometric Co-crystal (2:1 Molar Ratio)

The solid containing a stoichiometric amount of the template was synthesized by dry-vortex grinding 81.4 mg of **$C_6H_2F_3OH$** along with 50.0 mg of **2,2-BPE** in a 30 mL SmartSnap Grinding Jar along with 2 ball bearings (5 mm diameter) at a 2:1 molar ratio, respectively. The molecular components were dry-vortex ground for 30 minutes where at both the 10 and 20 minute marks the resulting solid was scraped from the edges before continuing grinding.

Synthesis of the Substoichiometric Co-crystal (1:1 Molar Ratio)

The solid containing a substoichiometric amount of the template was synthesized by dry-vortex grinding 40.7 mg of **$C_6H_2F_3OH$** along with 50.0 mg of **2,2-BPE** in a 30 mL SmartSnap Grinding Jar along with 2 ball bearings (5 mm diameter) at a 1:1 molar ratio, respectively. The molecular components were dry-vortex ground for 30 minutes where at both the 10 and 20 minute marks the resulting solid was scraped from the edges before continuing grinding.

Synthesis of the Substoichiometric Co-crystal (0.5:1 Molar Ratio)

The solid containing a substoichiometric amount of the template was synthesized by dry-vortex grinding 20.3 mg of **$C_6H_2F_3OH$** along with 50.0 mg of **2,2-BPE** in a 30 mL SmartSnap Grinding Jar along with 2 ball bearings (5 mm diameter) at a 0.5:1 molar ratio, respectively. The molecular components were dry-vortex ground for 30 minutes where at both the 10 and 20 minute marks the resulting solid was scraped from the edges before continuing grinding.

2. Powder X-ray Diffraction Diffractogram

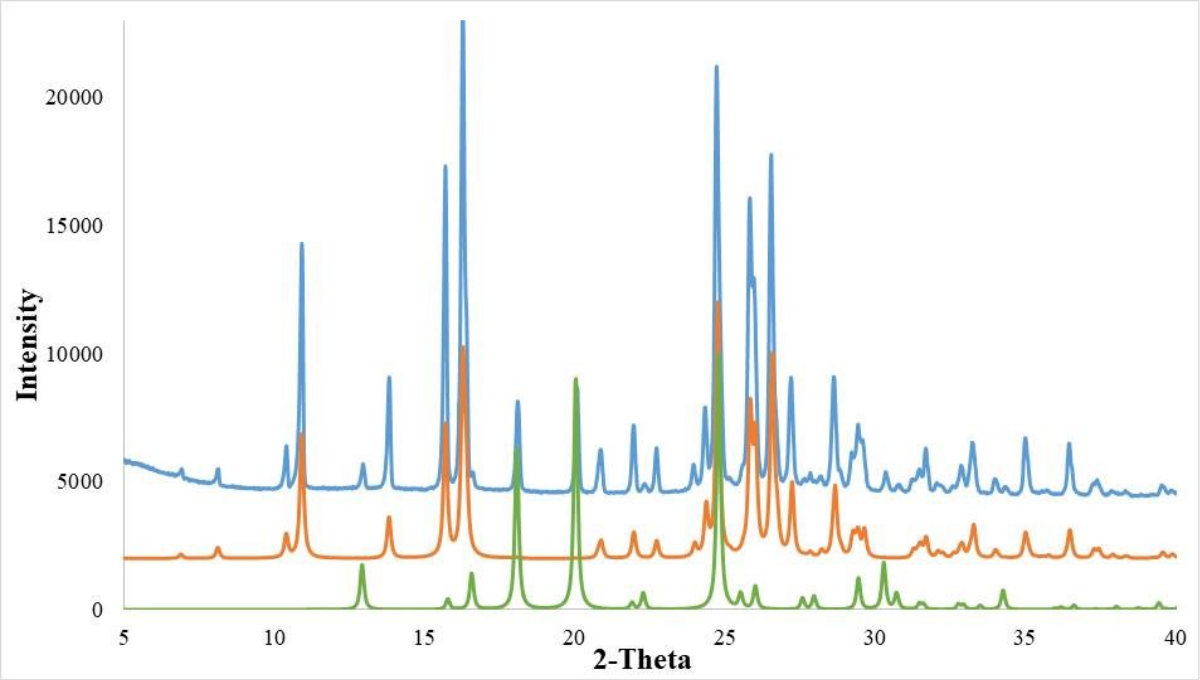

Figure S1. Powder X-ray diffraction data for stoichiometric (2:1 molar ratio) co-crystal sample after a grinding experiment and before photoreaction for the resulting solid (blue) along with the theoretical pattern for 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) (orange) and **2,2-BPE** (green).

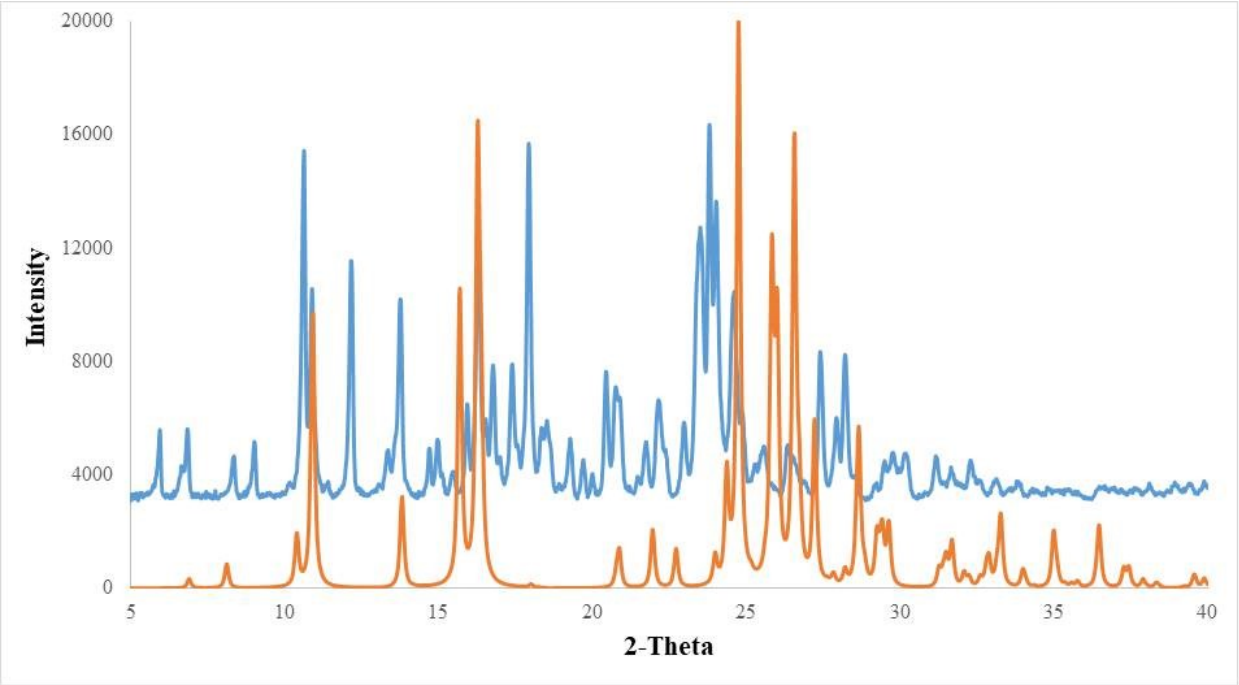

Figure S2. Powder X-ray diffraction data for stoichiometric (2:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) (orange).

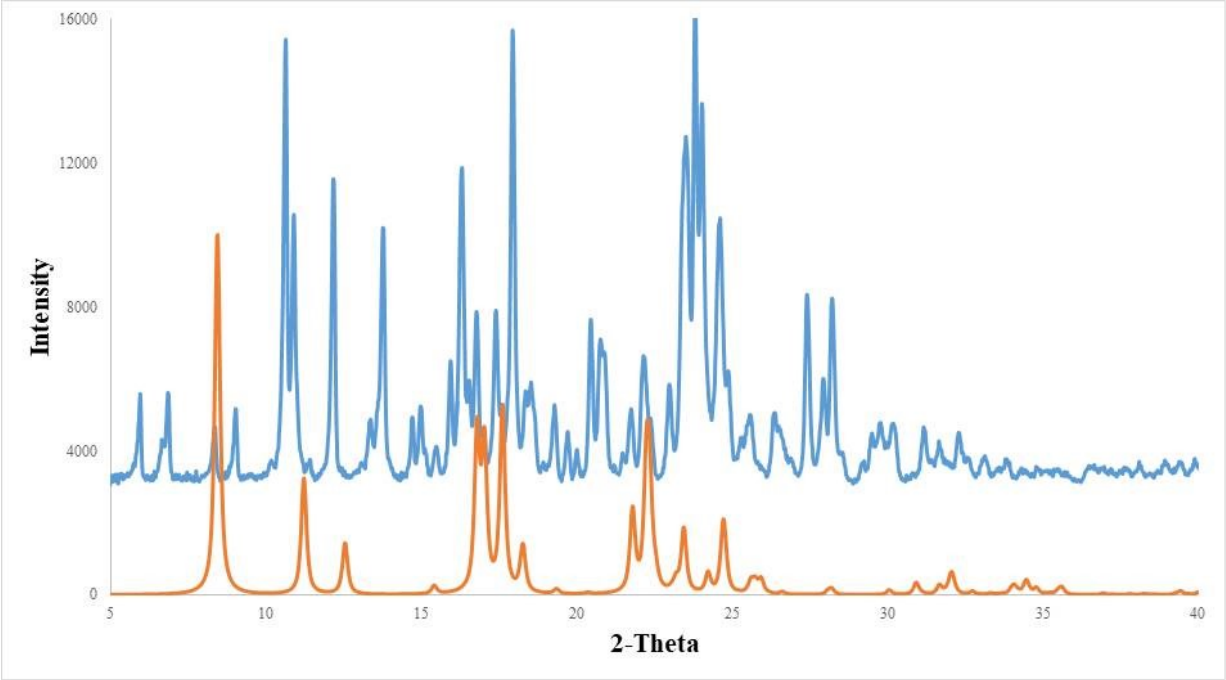

Figure S3. Powder X-ray diffraction data for stoichiometric (2:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for **2,2-TPCB** (orange).

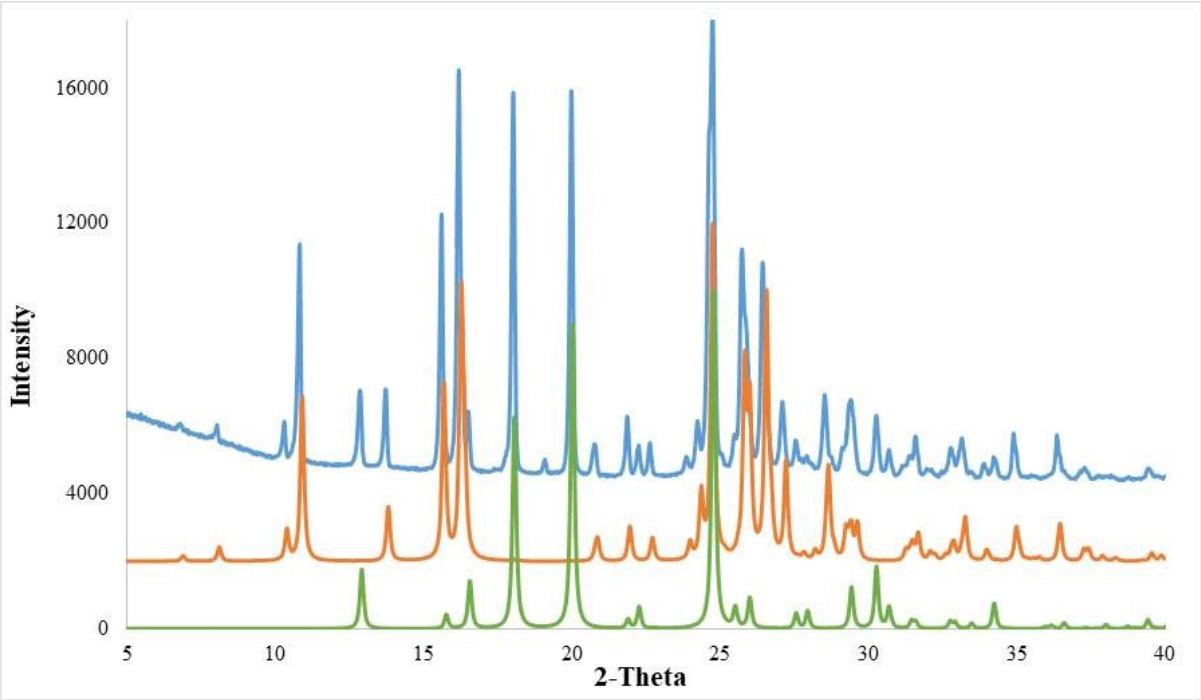

Figure S4. Powder X-ray diffraction data for substoichiometric (1:1 molar ratio) co-crystal sample after a grinding experiment and before photoreaction for the resulting solid (blue) along with the theoretical pattern for 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) (orange) and **2,2-BPE** (green).

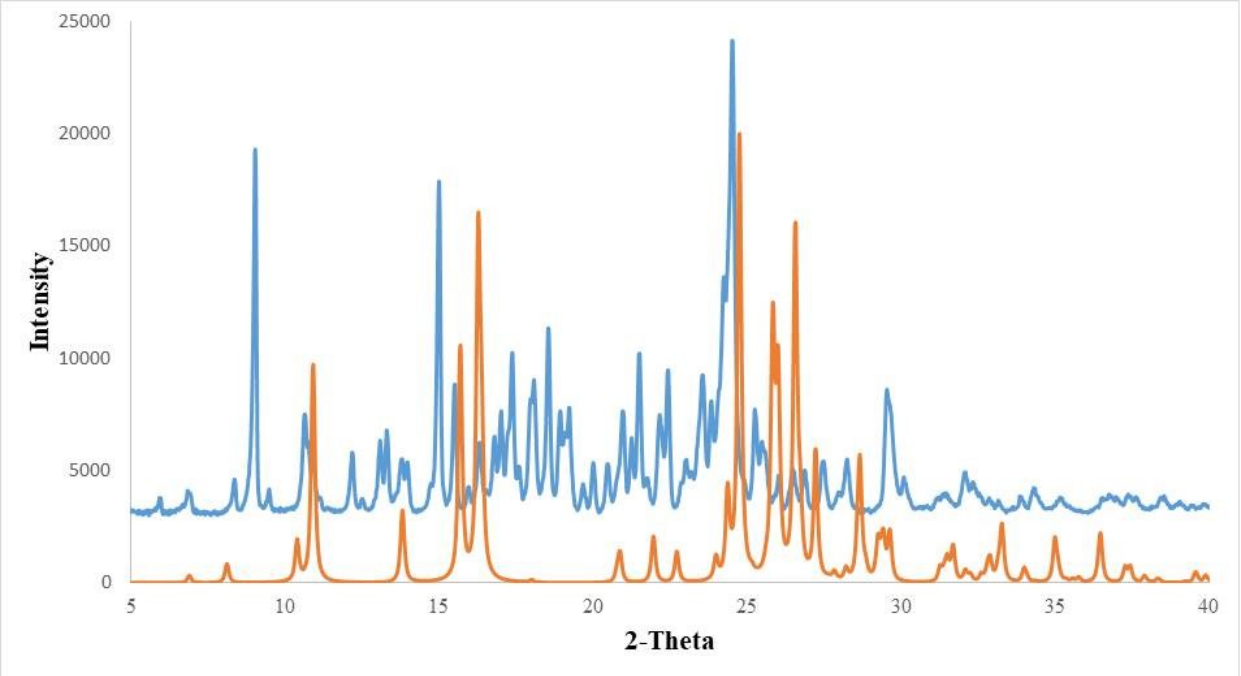

Figure S5. Powder X-ray diffraction data for substoichiometric (1:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) (orange).

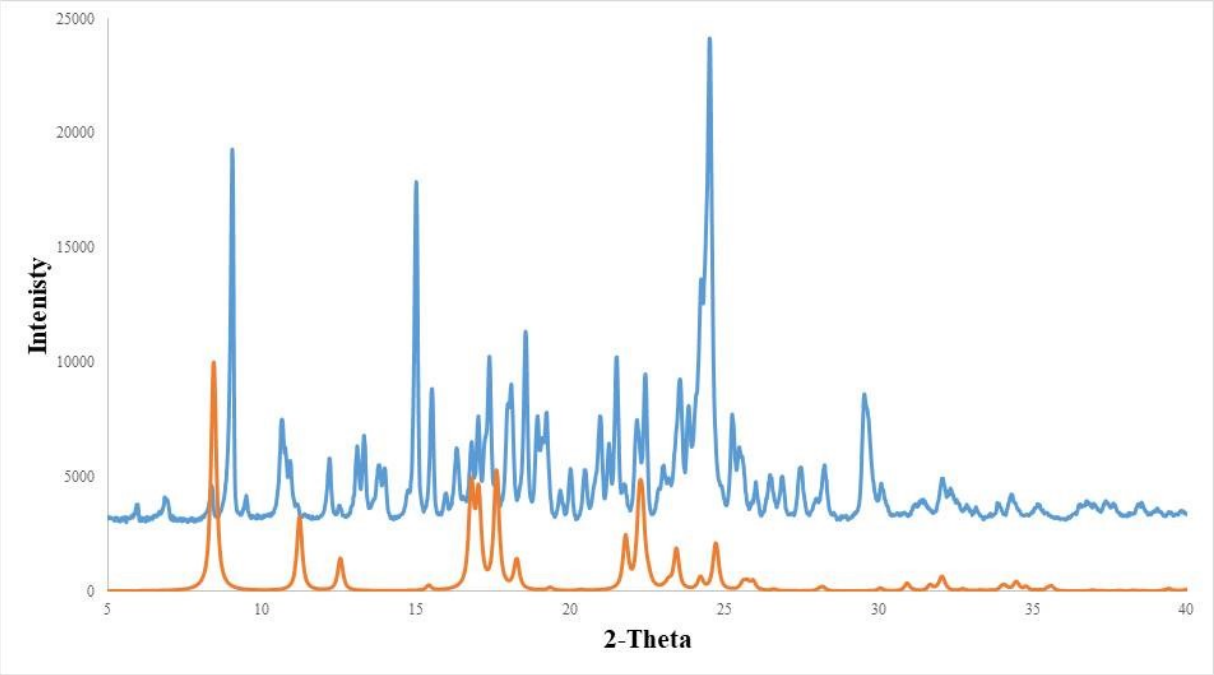

Figure S6. Powder X-ray diffraction data for substoichiometric (1:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for **2,2-TPCB** (orange).

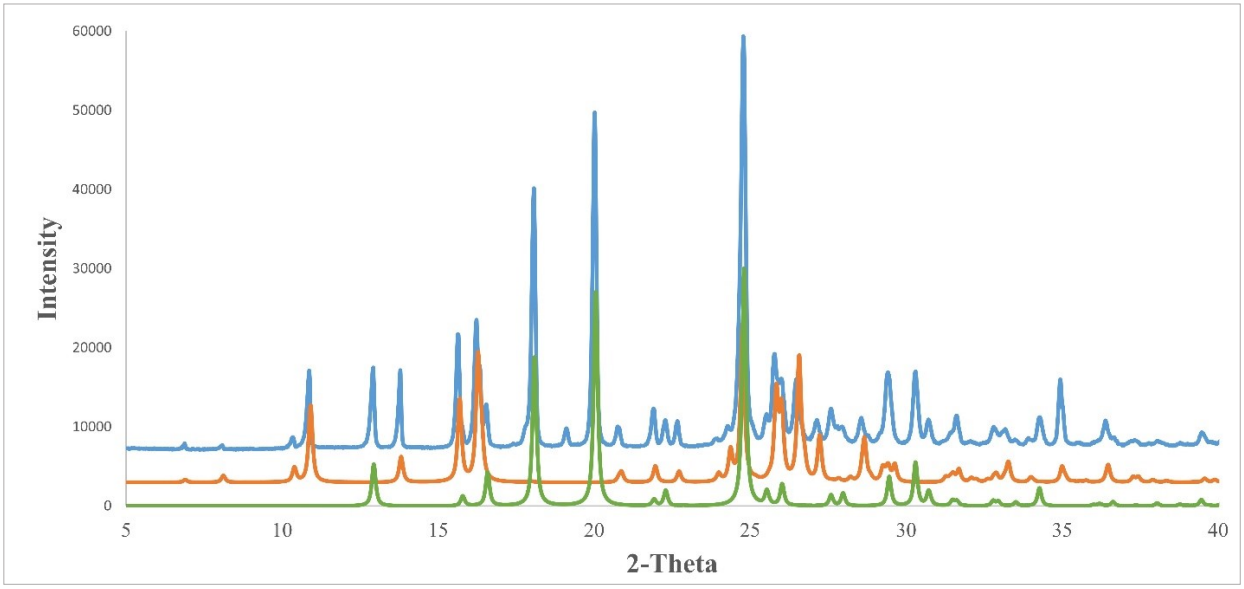

Figure S7. Powder X-ray diffraction data for substoichiometric (0.5:1 molar ratio) co-crystal sample after a grinding experiment and before photoreaction for the resulting solid (blue) along with the theoretical pattern for 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) (orange) and **2,2-BPE** (green).

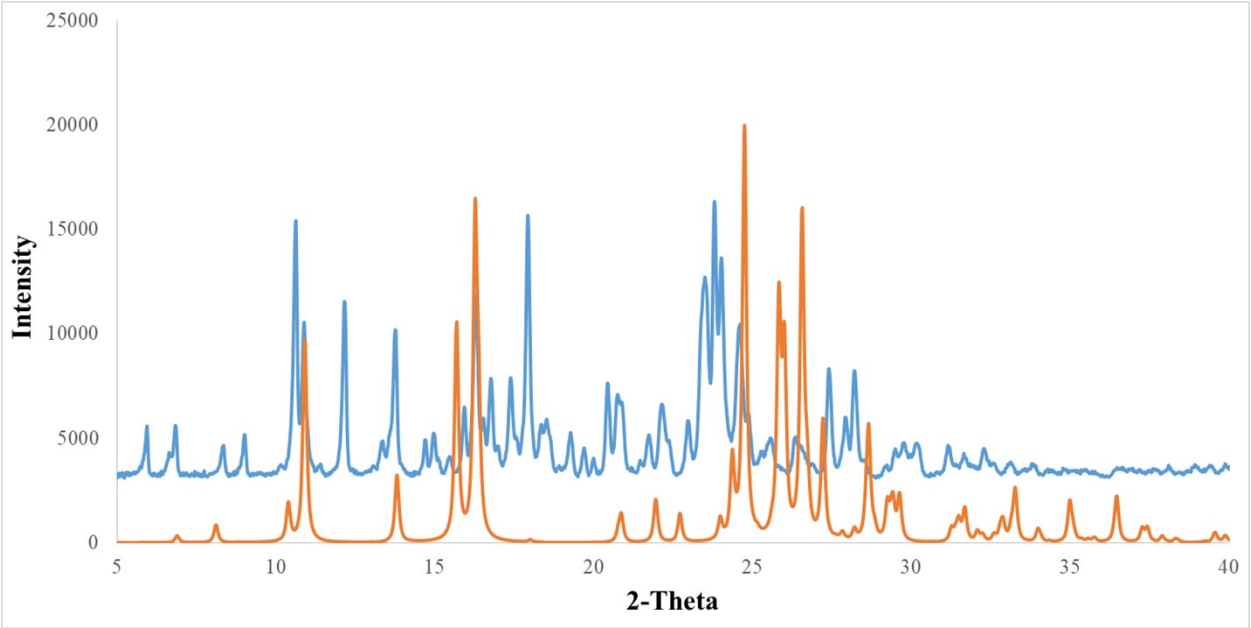

Figure S8. Powder X-ray diffraction data for substoichiometric (0.5:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) (orange).

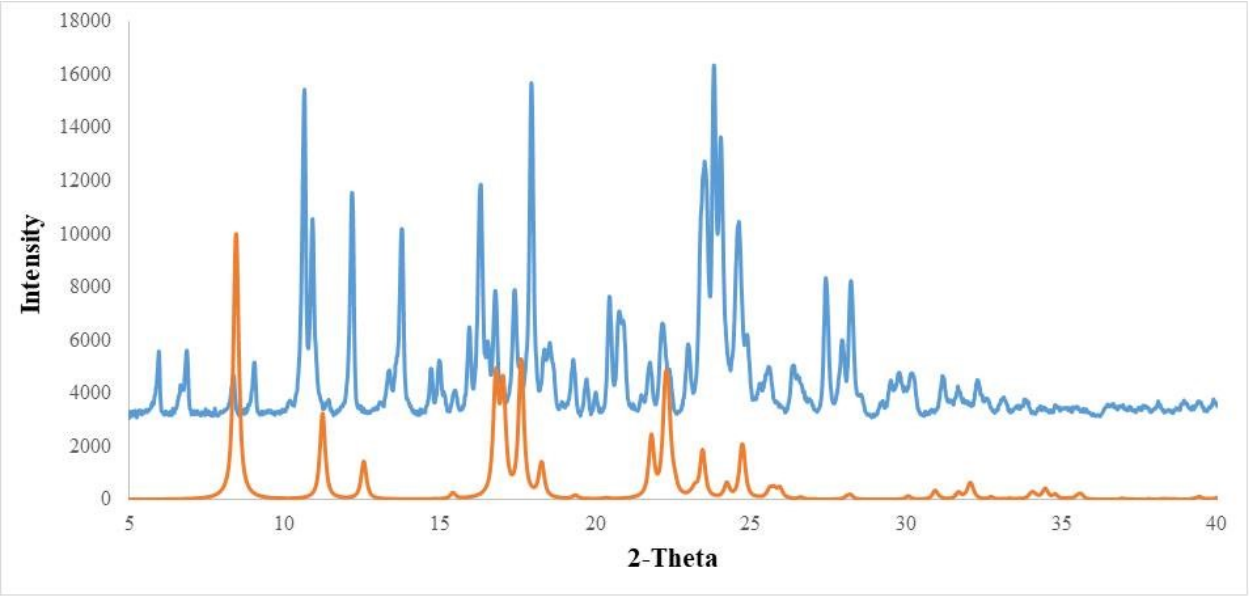

Figure S9. Powder X-ray diffraction data for substoichiometric (0.5:1 molar ratio) co-crystal sample after a grinding experiment and after photoreaction for the resulting solid (blue) along with the theoretical pattern for **2,2-TPCB** (orange).

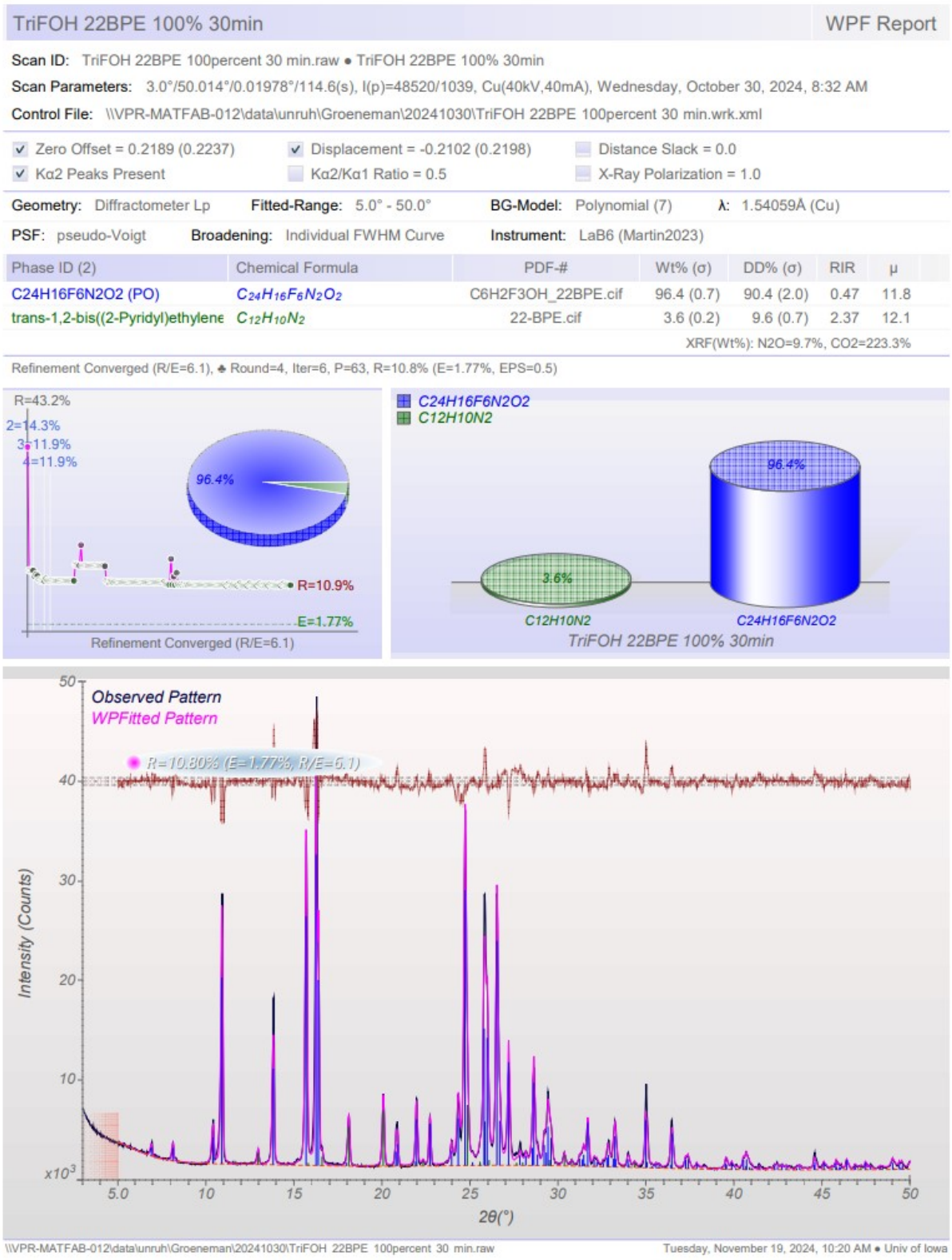

Figure S10: Powder X-ray diffraction Rietveld refinement (Whole Pattern Fitting) within Jade Pro to determine the amount of the co-crystal 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) and **2,2-BPE** in the diffractogram.

3. ^{1}H NMR Spectroscopic Data

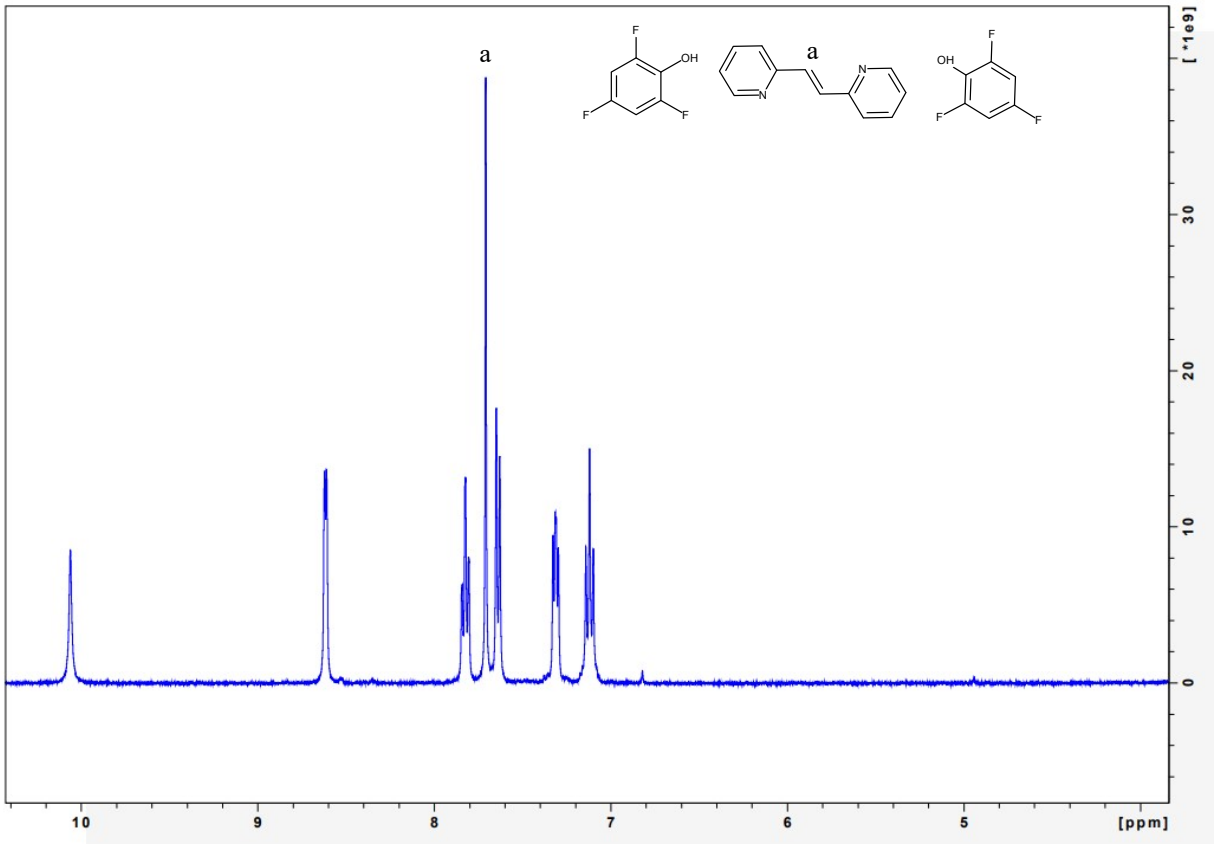

Figure S11. ^{1}H NMR spectrum of the co-crystal 2(**$C_6H_2F_3OH$**)·(**2,2-BPE**) before the [2 + 2] cycloaddition reaction (400 MHz, DMSO-d_6).

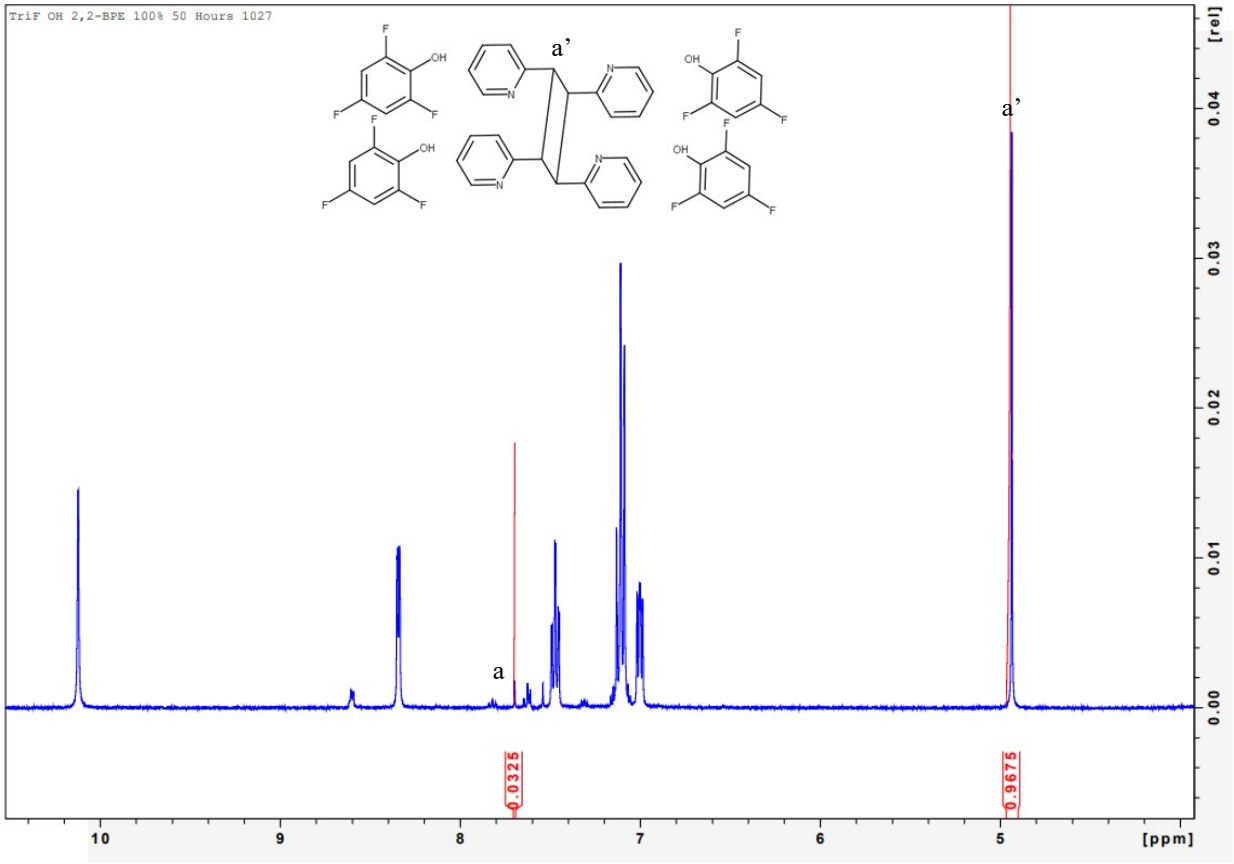

Figure S12. ^{1}H NMR spectrum of the stoichiometric (2:1 molar ratio) solid after dry-vortex grinding along with 50 hours of UV exposure resulting in a 97% yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO-d_6).

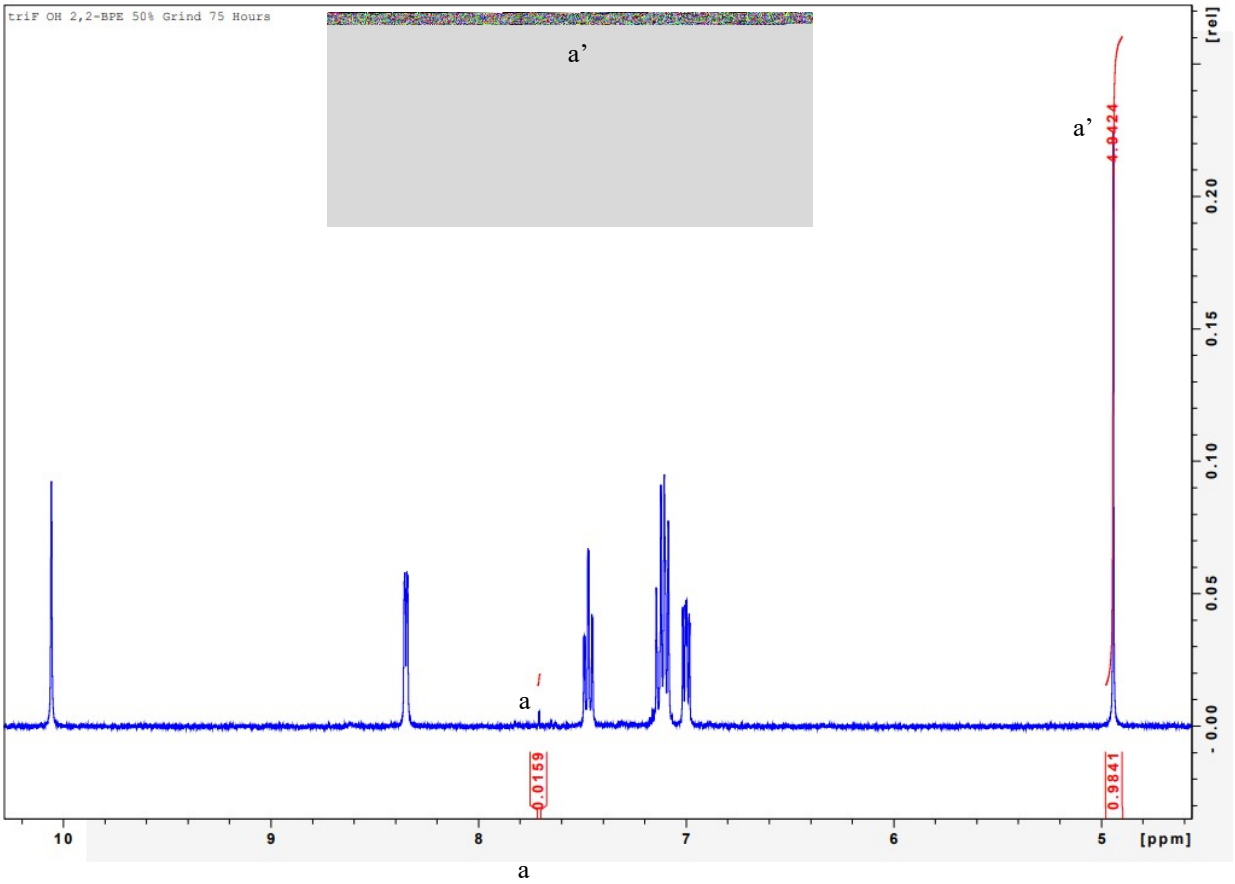

Figure S13. ^{1}H NMR spectrum of the substoichiometric (1:1 molar ratio) solid after dry-vortex grinding along with 75 hours of UV exposure resulting in a 98% yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO-d_6).

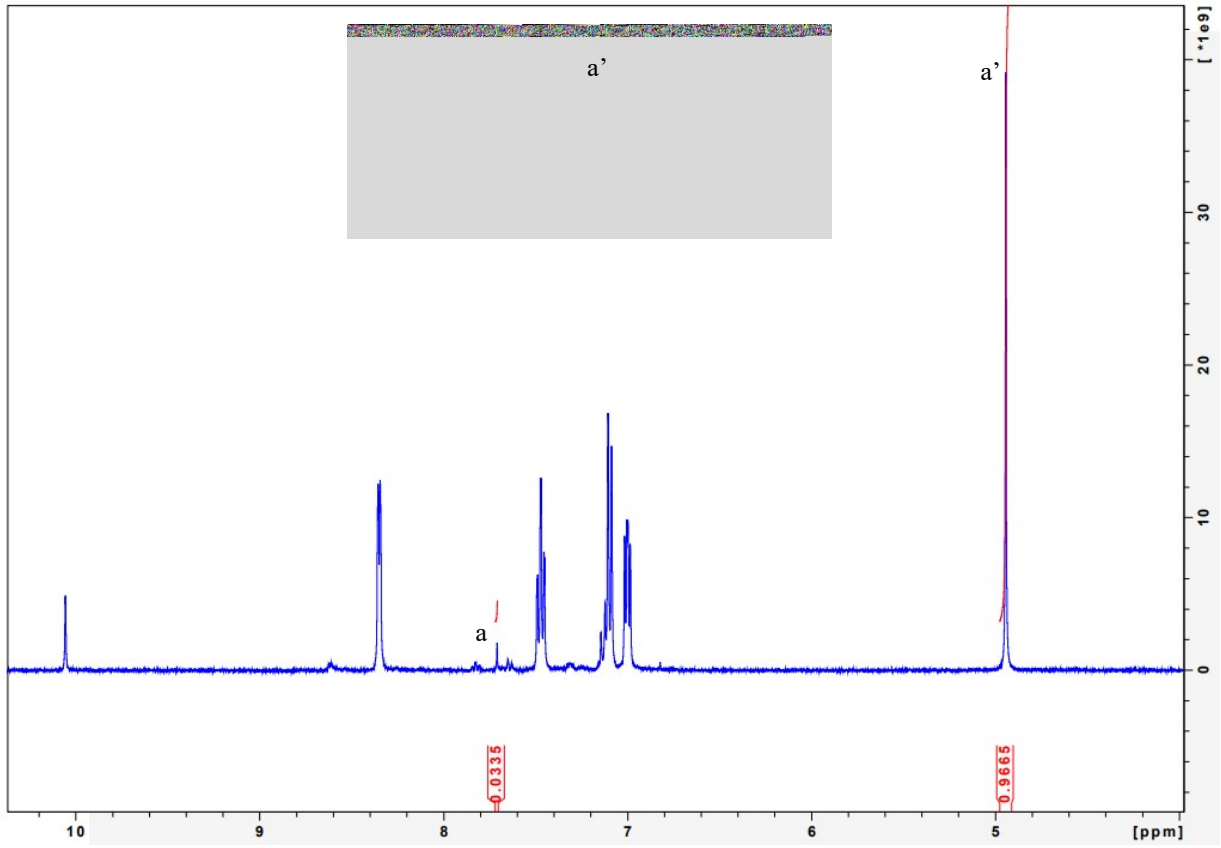

Figure S14. ^{1}H NMR spectrum of the substoichiometric (0.5:1 molar ratio) solid after dry-vortex grinding along with 40 hours of UV exposure resulting in a 97% yield for the [2 + 2] cycloaddition reaction (400 MHz, DMSO-d_6).

4. Pictures of the Experimental Setup for the Dry-Vortex Grinding

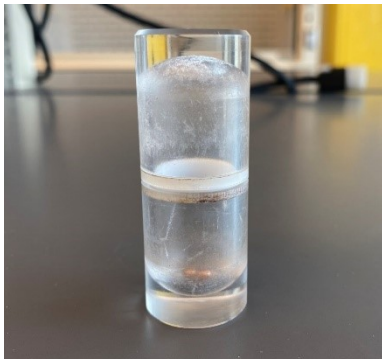

Figure 15. Picture of the 30 mL SmartSnap Grinding Jar.

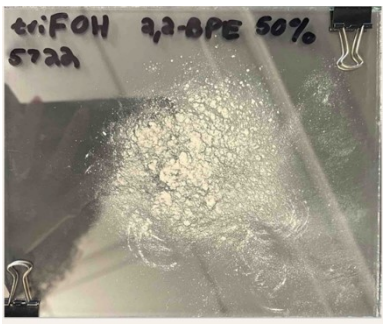

Figure 16. Picture of the glass plates for UV exposure.

Figure 17. Picture of the dry-vortex grinding of the components.