## **Supplementary Material**

Combining hydrogen bonding and metal coordination for controlling topochemical [2+2] cycloaddition from multi-component assemblies.

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## 1. List of Figures

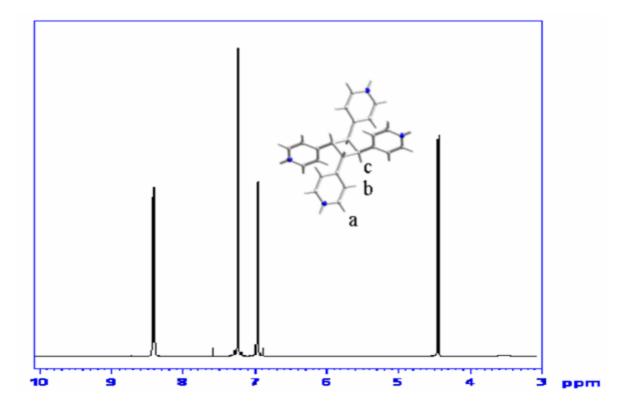
**Figure S1**. <sup>1</sup>H NMR spectrum of the *rctt*-4,4'-tpcb isomer obtained from the photoreaction of compound **2**.

**Figure S2.** <sup>1</sup>H NMR spectrum of the *rctt*-4,4'-tpcb isomer obtained from the photoreaction of compound 3.

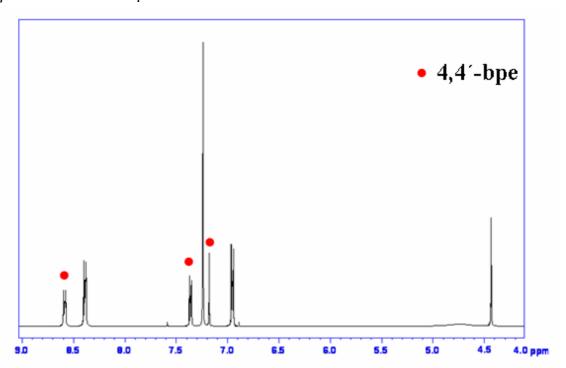
**Figure S3.** <sup>1</sup>H NMR spectrum of the *rctt*-4,4'-tpcb isomer obtained from the photoreaction of compound **4**.

**Figure S4**. (a) <sup>1</sup>H NMR spectrum of the *rctt*-4,4'-tpcb isomer obtained from the photoreaction of the desolvated crystals of **5**. (b) <sup>1</sup>H NMR spectrum of the photoproducts obtained from the photoreaction of compound **5** in its mother-liquor.

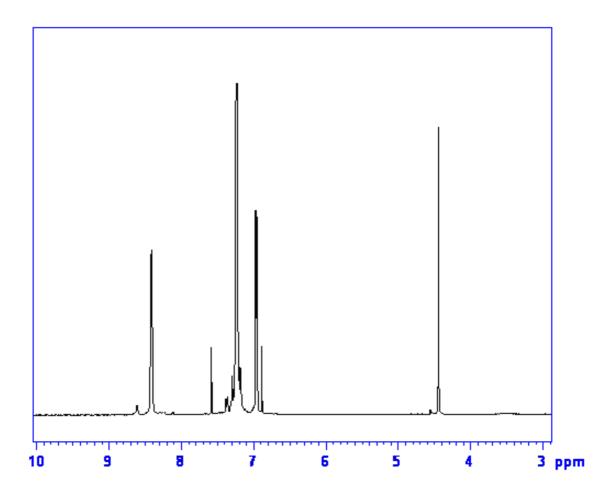
**Figure S1**. <sup>1</sup>H NMR spectrum of the *rctt*-4,4'-tpcb isomer obtained from the photoreaction of compound **2**.



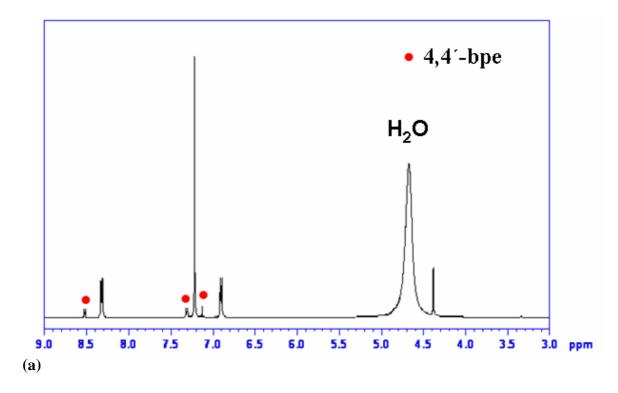
**Figure S2.** <sup>1</sup>H NMR spectrum of the *rctt*-4,4'-tpcb isomer obtained from the photoreaction of compound **3**.

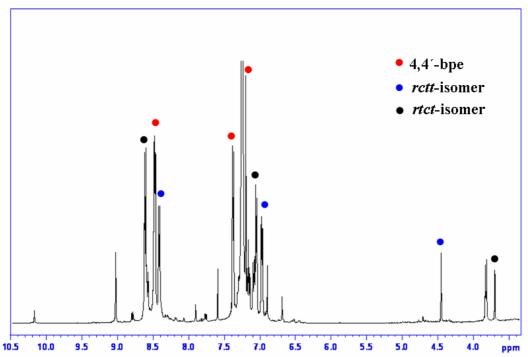


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**Figure S4**. (a) <sup>1</sup>H NMR spectrum of the *rctt*-4,4'-tpcb isomer obtained from the photoreaction of the desolvated crystals of **5**. (b) <sup>1</sup>H NMR spectrum of the photoproducts obtained from the photoreaction of compound **5** in its mother-liquor.





**(b)**