Supporting Information

Ms Title: Regioselective Photocycloaddition of Pyridine Derivatives to Electron-rich Alkenes

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X-Structural report of compound **7a**

The cage product **7a** gave colorless prismatic crystals of $C_{12}H_{16}N_2O_3$, monoclinic space group $P-1$, $a=7.320(4)$ Å, $b=9.327(5)$ Å, $c=10.009(5)$ Å, $\alpha=95.736(7)^\circ$, $\beta=107.392(5)^\circ$, $\gamma=94.547(7)^\circ$, $V=644.4(5)$ Å³, $Z=2$, $\rho=1.217$ g/cm³, $\mu(\text{MoK}\alpha)=0.88$ cm⁻¹. The structure was solved by the direct method and refined by the full-matrix least-squares method, where the final R and R_w were 0.080 and 0.086 for 1267 reflections.

Figure S-1. ORTEP drawing of **7a**

X-Structural report of compound **9**

The adduct **9** gave colorless prismatic crystals of $C_{13}H_{18}N_2O_3$, monoclinic space group $P2_1/n$, $a = 10.184(1) \text{ \AA}$, $b = 11.459(1) \text{ \AA}$, $c = 11.709(1) \text{ \AA}$, $\beta = 93.629(9)^\circ$, $V = 1363.8(3) \text{ \AA}^3$, $Z = 4$, $\rho = 1.219 \text{ g/cm}^3$, $\mu(\text{CuK}\alpha) = 0.717 \text{ cm}^{-1}$. The structure was solved by the direct method and refined by the full-matrix least-squares method, where the final R and R_w were 0.072 and 0.081 for 2747 reflections.

Figure S-2. ORTEP drawing of **9**