

Electronic Supplementary Information (ESI)

Stereospecific and quantitative photodimerization of terminal olefins in the solid state

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Materials. Silver(I) chlorate ($\geq 99.9\%$), silver(I) perchlorate (99.9%), silver(I) trifluoroacetate ($\geq 99\%$), and silver(I) nitrate ($\geq 99.0\%$), 4-vinylpyridine (95%), acetonitrile (anhydrous, 99.8%) and diethyl ether (anhydrous, ACS reagent, $\geq 99.0\%$) were purchased from Sigma-Aldrich (St. Louis, MO). 4-Vinylpyridine was distilled prior to use, whereas all other materials were used as received.

Crystal growth. Solids **1** and **3a-c** were prepared as follows. The silver salt (0.5 mmol) and 4-vinylpyridine (1.0 mmol) were separately dissolved in acetonitrile (10 ml). The solutions were combined, subsequently filtered through a Millex syringe filter (PVDF, 0.2 μm , 13mm) and left to evaporate at room temperature. Solid **2** was prepared in the same manner using equimolar amounts of the silver salt and **1,2-bpcb** (1.0 mmol). The single crystals were filtered upon formation, washed with diethyl ether and dried at room temperature with exposure to UV light (*i.e.* dark place)

Photoreactivity studies. In a typical photoreaction experiment, 100 mg of the silver complex were gently ground using a mortar and pestle. The obtained powder was placed between two Pyrex glass plates. The plates were transferred in a plastic bag, filled up with $\text{N}_2(\text{g})$ and sealed. The sealed bag was placed in a photoreactor cabinet equipped with a broad-band 450 W medium-pressure Hg-lamp. The powder distributed between the plates was mixed every 10 hours. Importantly, the photoreactive powder should be exposed to air *as less as possible* since the both the photoreactive solids and the photoproducts are air sensitive (*i.e.* they are oxidizing)

Crystallographic studies. The diffraction data were measured on a Nonius Kappa CCD single-crystal X-ray diffractometer at both room and low temperatures using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection, cell refinement and data reduction were performed using *Collect*¹ and *HKL Scalepack/Denzo*,² respectively. Structure solution and refinement were accomplished using SHELXS-97 and SHELXL-97,³ respectively. The heavy-atom sites were in all structures identified using the Patterson method, whereas all other non-hydrogen atoms were identified from the difference Fourier map within several refinement steps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms associated with carbon atoms were refined in geometrically constrained positions. Hydrogen atoms associated with oxygen atoms were calculated in an optimal hydrogen bonding geometry. The details of the structural analysis of all solids are summarized in Table S1.

Table S1 Crystallographic data for **1**, **2** and **3a-c**.

Compound reference	1	1 (low temperature)	2	3a
Chemical formula	C ₁₄ H ₁₄ AgClN ₂ O ₃	C ₃₆ H ₅₆ Ag ₄ Cl ₄ N ₈ O ₁₂	C ₁₄ H ₁₄ AgClN ₂ O ₃	C ₁₄ H ₁₄ AgClN ₂ O ₄
Formula Mass	401.59	1606.37	401.59	417.59
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
<i>a</i> /Å	16.5837(18)	16.0786(17)	18.3059(19)	8.5247(10)
<i>b</i> /Å	11.4570(12)	11.3557(12)	10.9939(12)	9.5750(11)
<i>c</i> /Å	17.1283(18)	17.0932(18)	14.6045(16)	11.3228(12)
α /°	90	90	90	70.075(5)
β /°	101.558(5)	100.711(5)	90.896(5)	88.600(5)
γ /°	90	90	90	68.447(5)
Unit cell volume/Å ³	3188.4(6)	3066.6(6)	2938.8(5)	802.75(16)
Temperature/K	290(2)	150(2)	150(2)	290(2)
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>C2/c</i>	<i>P</i> $\bar{1}$
No. of formula units per unit cell, <i>Z</i>	8	2	8	2
Radiation type	MoK α	MoK α	MoK α	MoK α
Absorption coefficient, μ /mm ⁻¹	1.441	1.499	1.564	1.439
No. of reflections measured	19347	17790	9500	5289
No. of independent reflections	5590	5372	2603	2814
<i>R</i> _{int}	0.0739	0.0336	0.0371	0.0127
Final <i>R</i> _{<i>I</i>} values (<i>I</i> > 2 σ (<i>I</i>))	0.0527	0.0298	0.0357	0.0434
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.1293	0.0837	0.0729	0.1252
Final <i>R</i> _{<i>I</i>} values (all data)	0.1291	0.0457	0.0484	0.0604
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1546	0.1159	0.0784	0.1355
Goodness of fit on <i>F</i> ²	0.908	1.168	1.062	1.092
CCDC number	766415	766416	766417	766418

Table S1 (continued) Crystallographic data for **1**, **2** and **3a-c**.

Compound reference	3a (low temperature)	3b	3b (low temperature)	3c
Chemical formula	C ₁₄ H ₁₄ AgClN ₂ O ₄	C ₃₂ H ₂₈ Ag ₂ F ₆ N ₄ O ₄	C ₃₂ H ₂₈ Ag ₂ F ₆ N ₄ O ₄	C ₁₄ H ₁₄ AgN ₃ O ₃
Formula Mass	417.59	862.32	862.32	380.15
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
<i>a</i> /Å	8.2375(9)	13.4624(14)	12.8602(14)	11.0503(12)
<i>b</i> /Å	9.2898(10)	15.2237(16)	15.1102(16)	10.9201(12)
<i>c</i> /Å	11.4161(12)	16.9018(18)	17.0170(18)	12.8477(14)
<i>α</i> /°	71.026(5)	90	90	90
<i>β</i> /°	89.128(5)	90	90	94.835(5)
<i>γ</i> /°	71.020(5)	90	90	90
Unit cell volume/Å ³	777.22(14)	3464.0(6)	3306.7(6)	1544.8(3)
Temperature/K	190(2)	290(2)	150(2)	290(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
No. of formula units per unit cell, <i>Z</i>	2	4	4	4
Radiation type	MoK α	MoK α	MoK α	MoK α
Absorption coefficient, μ /mm ⁻¹	1.487	1.204	1.261	1.317
No. of reflections measured	5256	21109	28524	8702
No. of independent reflections	2702	6079	7569	2697
<i>R</i> _{int}	0.0108	0.0279	0.0232	0.0308
Final <i>R</i> _I values (<i>I</i> > 2 σ (<i>I</i>))	0.0281	0.0475	0.0277	0.0418
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.0734	0.1352	0.0862	0.1186
Final <i>R</i> _I values (all data)	0.0297	0.0755	0.0358	0.053
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0743	0.1476	0.1051	0.1261
Goodness of fit on <i>F</i> ²	1.064	1.103	1.012	1.068
CCDC number	766419	766420	766421	766422

¹H NMR studies. ¹H NMR data were collected on an AVANCE Bruker NMR spectrometer operating at 300 MHz using DMSO-*d*₆ as solvent. Figures S1-S4 depict the ¹H NMR spectra of **1** and **3a-c** before and after UV irradiation, respectively.

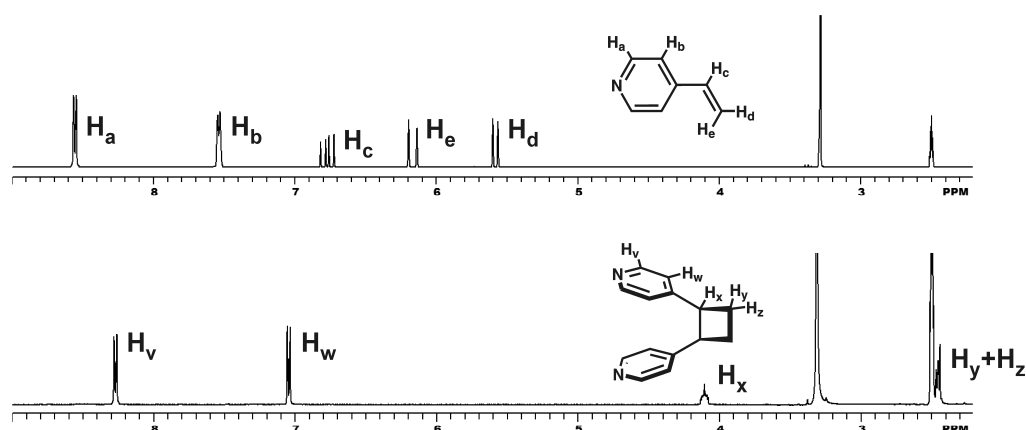


Figure S1. ¹H NMR spectra of **1** before UV irradiation (above) [DMSO-*d*₆, δ /ppm: 8.56 (dd, 8H), 7.54 (dd, 8H), 6.82-6.72 (dd, 4H), 6.20-5.56 (dd, 8H)], and ¹H NMR spectra of **1** after UV irradiation (below) [DMSO-*d*₆, δ /ppm: 8.27 (dd, 8H), 7.06 (dd, 8H), 4.13-4.08 (m, 4H), 2.47-2.44 (m, 8H)].

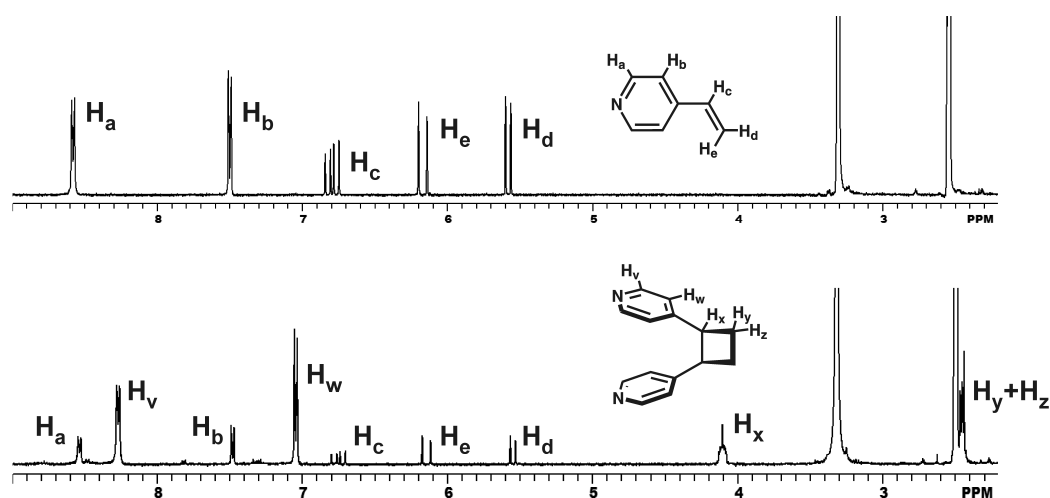


Figure S2. ^1H NMR spectra of **3a** before UV irradiation (above) [DMSO- d_6 , δ /ppm: 8.54 (dd, 8H), 7.46 (dd, 8H), 6.80-6.70 (dd, 4H), 6.16-5.52 (dd, 8H)], and ^1H NMR spectra of **3a** after UV irradiation (below) [DMSO- d_6 , δ /ppm: 8.54 (dd, 1.9H), 8.27 (dd, 6.1H), 7.48 (dd, 1.9H), 7.05 (dd, 6.1H), 6.80-6.71 (dd, 0.95H), 6.17-5.53 (dd, 1.9H), 4.13-4.08 (m, 3.05H), 2.47-2.44 (m, 6.1H)]. The small peaks at 8.8 ppm and 7.8 ppm are corresponding to oxidized pyridyl functional groups that start to form once the photoreaction in the solid state stops proceeding.

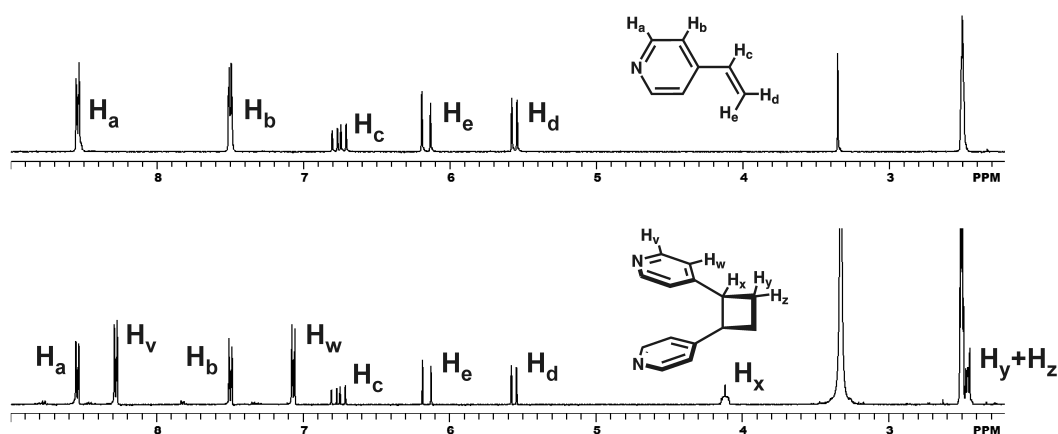


Figure S3. ^1H NMR spectra of **3b** before UV irradiation (above) [DMSO- d_6 , δ /ppm: 8.54 (dd, 8H), 7.50 (dd, 8H), 6.80-6.71 (dd, 4H), 6.19-5.54 (dd, 8H)], and ^1H NMR spectra of **3b** after UV irradiation (below) [DMSO- d_6 , δ /ppm: 8.54 (dd, 3.6H), 8.28 (dd, 4.4H), 7.50 (dd, 3.6H), 7.06 (dd, 4.4H), 6.81-6.71 (dd, 1.8H), 6.18-5.54 (dd, 3.6H), 4.14-4.09 (m, 2.2H), 2.47-2.44 (m, 4.4H)]. The small peaks at 8.8 ppm and 7.8 ppm are corresponding to oxidized pyridyl functional groups that start to form once the photoreaction in the solid state stops proceeding.

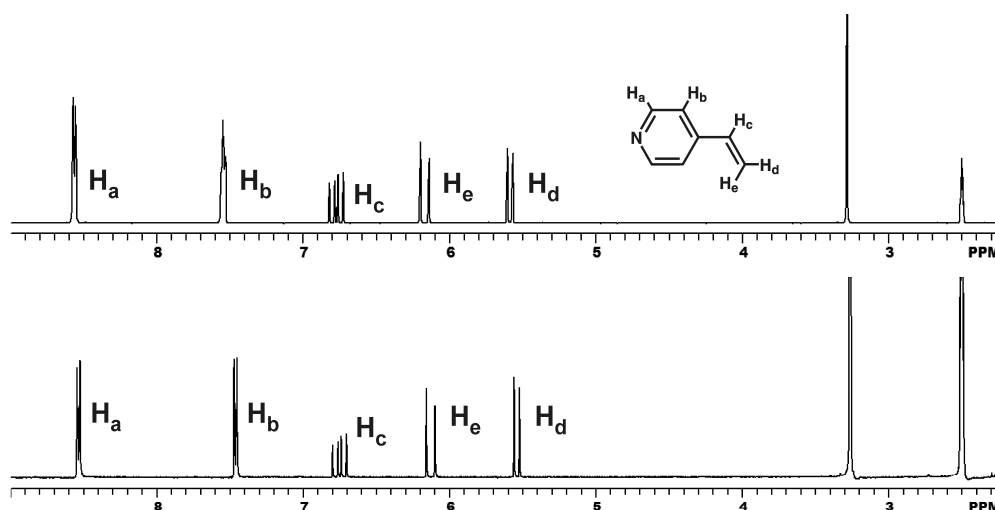


Figure S4. ¹H NMR spectra of **3c** before UV irradiation (above) [DMSO-*d*₆, δ/ppm: 8.56 (dd, 8H), 7.54 (dd, 8H), 6.82-6.73 (dd, 4H), 6.20-5.57 (dd, 8H)], and ¹H NMR spectra of **3c** after UV irradiation (below) [DMSO-*d*₆, δ/ppm: 8.54 (dd, 8H), 7.46 (dd, 8H), 6.80-6.70 (dd, 4H), 6.16-5.52 (dd, 8H)].

References

- ¹ R. W. W. Hoof, Nonius BV, Delft, The Netherlands, 1998.
- ² Z. Otwinowski, W. Minor in *Methods in Enzymology*, ed. C. W. Carter Jr and R. M. Sweet, 1997, Vol. 276 (*Macromolecular Crystallography, Part A*), pp. 307-326.
- ³ G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.