

## Supplementary information

### Reversible 1,4-cycloaddition of singlet oxygen to *N*-substituted 2-pyridones: 1,4-endoperoxide as a versatile chemical generator of singlet oxygen

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**Synthesis of *N*-benzyl-2-pyridone (1a) (typical procedure):** A solution of sodium salt of 2-hydroxypyridine (0.95g, 1.0 mmol) in tetrahydrofuran (THF) (9 mL) was prepared by the use of 2-hydroxypyridine and NaH. To the solution, benzyl bromide was added and heated at refluxing temperature under N<sub>2</sub> atmosphere. After 1h, the reaction mixture was cooled, poured into aq. NH<sub>4</sub>Cl solution, and then extracted with AcOEt. The organic layer was dried over MgSO<sub>4</sub>, and concentrated. The residue was chromatographed on silica gel and eluted with AcOEt to give *N*-benzyl-2-pyridone (**1a**) as colorless crystals in 91 % yield.

**1a:** colorless granules melted at 68.0-68.5 °C (from AcOEt-hexane)

<sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 5.15 (s, 2H), 6.15 (t, J = 6.7 Hz, 1H), 6.62 (d, J = 9.2 Hz, 1H), 7.25 – 7.36 (m, 7H) ppm; <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 51.8, 106.0, 121.1, 127.8, 128.0, 128.7, 136.2, 137.1, 139.2, 162.5 ppm; IR (KBr): 3071, 3032, 1657, 1588, 1535, 1143 cm<sup>-1</sup>; Mass (EI, %): 185 (M<sup>+</sup>, 74), 91 (100), 79 (24), 65 (20).

**Synthesis of endoperoxide of *N*-benzyl-2-pyridone (2a) (typical procedure):** A solution of *N*-benzyl-2-pyridone (**1a**) (253 mg) in dichloromethane (10 mL) was irradiated in the presence of a catalytic amount of TPP (0.8 mg) with 960 W Na lamp under O<sub>2</sub> atmosphere at -78 °C for 2h. The photolysate was concentrated *in vacuo*, and the residue was chromatographed on silica gel with dichloromethane-AcOEt (10 : 1) to give endoperoxide (**2a**) as a colorless solid in 84 % yield.

**2a:** colorless granules melted at 67-68 °C (dec) (from dichloromethane-hexane)

<sup>1</sup>HNMR (400 MHz, CDCl<sub>3</sub>): δ<sub>H</sub> 4.42(d, J = 15.3 Hz, 2H), 4.87 (d, J = 15.3 Hz, 1H), 5.08 (ddd, J = 5.8, 2.1, 0.6 Hz, 1H), 5.53 (ddd, J = 5.2, 2.1, 0.6 Hz, 1H), 6.71 (ddd, J = 7.8, 5.2, 2.1 Hz, 1H), 6.76 (ddd, J = 7.8, 5.8, 2.1 Hz, 1H), 7.19-7.24 (m, 3H), 7.28-7.39 (m, 3H) ppm; <sup>13</sup>CNMR (100 MHz, CDCl<sub>3</sub>): δ<sub>C</sub> 46.9, 78.0, 83.2, 127.8, 127.9, 128.6, 128.8, 134.2, 135.1, 167.9 ppm; IR (KBr): 3089, 3031, 2932, 1691, 1426, 1350, 1158 cm<sup>-1</sup>; Mass (EI, %): 217 (M<sup>+</sup>, 25), 201 (70), 185 (76), 184 (34), 106 (34), 91 (100), 79 (19), 65 (20).

**Preparation of 2-pyridone supported on Merrifield's resin (1f):** 2-Hydroxypyridine (2.88 g, 30.3 mmol) was added to a suspension of NaH (275 mg) in DMF (15 mL) under N<sub>2</sub> atmosphere at ice-cooled temperature. To this solution, Merrifield's resin (5.09 g, 1% cross-linked polystyrene; 200-400 mesh, 1.2 mmol Cl<sup>-</sup> / g) was added and stirred at 60 °C for 5 h. After cooling to room temperature, the reaction mixture was filtered, and the solid was washed thoroughly with water and methanol, and then dried under reduced pressure to give the desired resin (**1f**) (5.38 g). IR (KBr): 3058, 3025, 2921, 2849, 1661, 1593, 1537 cm<sup>-1</sup>.

**Preparation of endoperoxide of 2-pyridone supported on Merrifield's resin (2f):** A suspension of 2-pyridone supported on Merrifield's resin (**1f**) (207 mg) in dichloromethane (10 mL) containing TPP (0.8 mg) was irradiated with 960 W Na lamp under O<sub>2</sub> atmosphere at -78 °C for 3 h. The resin was washed thoroughly with dichloromethane and methanol, and then dried under reduced pressure to give the desired resin (**2f**) (209 mg). IR (KBr): 3058, 3015, 2920, 2850, 1710, 1599, 1491 cm<sup>-1</sup>.

**Thermal decomposition of endoperoxide of N-benzyl-2-pyridone (2a) (typical procedure):** Endoperoxide (**2a**) (1.5 x 10<sup>-2</sup> M) and 2,3-dimethylbut-2-ene (7.5 x 10<sup>-2</sup> M) were heated in CDCl<sub>3</sub>. The time course of thermolysis was examined by means of <sup>1</sup>H NMR spectra, in which the area of peaks (A) (δ<sub>H</sub> = 4.97 and 5.01 ppm) due to protons of olefinic methylene in a hydroperoxide (**8**), that of peak (B) (dd at 5.51-5.53) due to an endoperoxide (**2a**), and that of peak (C) (d at 6.62) due to a 2-pyridone (**1a**) were monitored, at 30, 40, and 50 °C. Conversion of **2a** was estimated from the ratio between the area of peak (B) and that of peak (C), while yield of <sup>1</sup>O<sub>2</sub> was estimated from the ratio between the area of peak (A) and that of peak (C).