# **Supporting Information**

# Photooxidation of oxazolidine molecular switches: uncovering intramolecular ionization facilated cyclization process

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### 1. General experimental information

### Materials

Phenylhydrazine (98 %), 4-Nitrophenylhydrazine (98 %), 4-Methoxyphenylhydrazine hydrochloride (98 %), 4-Dimethylaminobenzaldehyde (99 %) and Diethyl malonate (99 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). 3-Methyl-2-butanone (98 %), 2-Bromoethanol (98 %), Anisic aldehyde (99 %) and 4- (Diethylamino)salicylaldehyde (98 %) were purchased from Energy Chemical (Shanghai, China). Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and phosphoryl chloride (POCl<sub>3</sub>) were purchased from Beijing Chemical Factory (Beijing, China). Solvents: Dimethyl sulfoxide (DMSO, HPLC) was purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China); dimethylformamide (DMF), acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), dichloromethane (DCM), ethyl acetate (EtOAc) and toluene (PhMe) were purchased from Beijing Chemical Factory (Beijing, China). Unless otherwise stated, all reagents were used without further purification.

### Instruments

The UV-Vis absorption spectra were measured using a 0.25 cm quartz cuvette on a Shimadzu UV-2550 PC double-beam spectrophotometer. The LC-HRMS (ESI) analysis was performed on an Agilent 1290-micro TOF-Q II mass spectrometer. The infrared spectra were measured using a Brucker VERTEX 80V. The IR sample of **OXA-1-R** was prepared by repeatedly dropping the red DMSO solution of **OXA-1** ( $1.0 \times 10^{-4}$  M) (irradiation by sunlight for 6 days) on KBr and drying the sample. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (126 MHz) spectra were recorded on a Bruker AVANCE500 at room temperature and were reported in ppm and determined with tetramethylsilane (TMS) or respect to residual signals of the deuterated solvents as internal standards (TMS, 0.00; CDCl<sub>3</sub>, 7.26; DMSO-*d*<sub>6</sub>, 2.50 for <sup>1</sup>H NMR and CDCl<sub>3</sub>, 77.0; DMSO-*d*<sub>6</sub>, 39.5 for <sup>13</sup>C NMR). HPLC spectra were recorded on Waters 1525 Binary HPLC Pump. Melting point was determined using a SGW X-4B microscopy melting point apparatus. pH of various solvents after irradiation were measured with Sartorius basic pH-Meter PB-20 after addition of the same volume of water. While, for water immiscible solvents (i.e., EtOAc, CH<sub>2</sub>Cl<sub>2</sub> and PhMe), their extract from water phase were measured.

## 2. Synthesis of OXA-1 to OXA-6



Scheme S1. General synthesis procedure of OXA-1 ~ OXA-4.

The compounds **OXA-1** ~ **OXA-4** were synthesized according to a reported procedure shown in Scheme S1 and analytical data were consistent with reported values.  $^{S1, S2}$ 



Scheme S2. General synthesis procedure of OXA-5 and OXA-6.

The compound **6** was synthesized according to a reported procedure shown in Scheme S2 and analytical data were consistent with reported values.<sup>S3</sup>



1-(2-hydroxyethyl)-2,3,3-trimethyl-3H-indol-1-ium bromide (3, 4.2 mmol, 1.19 g) and 4-(dimethylamino)benzaldehyde (6, 5.04 mmol, 1.23 g) were dissolved in ethanol solvent (10 mL) and refluxed for 10 h under  $N_2$  atmosphere. After cooled down to room temperature and placed overnight, black solid

were deposited. The residue was washed with ethyl acetate for several times to give the pure black solid. Then the black solid were dissolved in mixed solution of saturated solution of Na<sub>2</sub>CO<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>, and were stirred for 5 h. Then the organic phase were rotary evaporation to obtain the product as a green solid **OXA-5** (769 mg, Yield: 42.5 %). m.p. 168.1 – 169.0 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.59 (s, 1H), 7.27 (d, *J* = 9.0 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 15.6 Hz, 1H), 6.58 (d, *J* = 9.0 Hz, 1H), 6.50 (s, 1H), 3.50 – 3.80 (m, 4H), 3.42 (q, *J* = 7.2 Hz, 4H), 1.45 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 6H), 1.18 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  161.2, 155.9, 150.8, 150.6, 139.9, 128.9, 128.1, 127.6, 126.8, 122.4, 121.6, 117.0, 112.1, 110.2, 109.1, 108.9, 97.2, 63.6, 50.2, 48.0, 44.9, 28.6, 20.5, 12.6; LC-HRMS (ESI): m/z calculated for [*M* + H]<sup>+</sup> 431.2329, found 431.2331.



1-(2-hydroxyethyl)-2,3,3-trimethyl-5-nitro-3H-indol-1ium bromide (**3**, 2 mmol, 568 mg) and 4-(dimethylamino)benzaldehyde (2.2 mmol, 539 mg) were dissolved in ethanol solvent (5 mL) and refluxed for 10 h under  $N_2$  atmosphere. After cooled down to room

temperature and placed overnight, black solid were deposited. The residue was washed with ethyl acetate for several times to give the pure black solid. Then the black solid were dissolved in mixed solution of saturated solution of Na<sub>2</sub>CO<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>, and were stirred for 5 h. Then the organic phase were rotary evaporation to obtain the product as a yellow solid **OXA-6** (380 mg, Yield: 39.9 %). m.p. 181.3 – 181.5 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.13 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.95 (d, *J* = 2.4 Hz, 1H), 7.60 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 15.9 Hz, 1H), 6.78 (d, *J* = 8.7, 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (dd, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (dd, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (dd, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (dd, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (dd, *J* = 2.4 Hz, 1H), 6.50 (dd, *J* = 2.4 Hz, 1H), 3.50 – 3.87 (m, 4H), 3.43 (q, 1H), 6.59 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.50 (dd, *J* = 2.4 Hz, 1H), 6.50 (dd

J = 7.2 Hz, 4H), 1.47 (s, 3H), 1.22 (t, J = 7.2 Hz, 6H), 1.20 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  161.2, 157.3, 156.0, 150.8, 142.6, 141.1, 140.3, 129.1, 127.7, 126.3, 125.2, 118.9, 116.3, 111.2, 110.3, 109.2, 108.7, 97.1, 63.7, 49.5, 47.5, 44.9, 20.4, 12.6; LC-HRMS (ESI): m/z calculated for  $[M + H]^+$  476.2180, found 476.2190.

# 3. LC-HRMS and <sup>1</sup>H NMR spectra for photooxidation products of OXA-1 and ROF-Br-1



Figure S1. LC-HRMS spectra for (a) OXA-1 and (b) ROF-Br-1 in DMSO after irradiation with sunlight.



Figure S2. <sup>1</sup>H NMR spectra for (a) OXA-1 and (c) ROF-Br-1 in DMSO- $d_6$ , and (b) OXA-1 and (d) ROF-Br-1 in DMSO- $d_6$  after irradiation with high pressure mercury lamp for 2 hrs and 10 hrs, respectively.

By comparing spectrum b with spectra c and d, a little ring-open form (indicated by blue dash line) and traces of photooxidation products (indicated by green dash line) could be observed for **OXA-1** after irradiation by high pressure mercury lamp.



**Figure S3.** <sup>1</sup>H NMR spectra of **ROF-Br-1** (12 mg in 0.5 mL DMSO- $d_6$ ) before and after irradiation by a high pressure mercury lamp for 24 hrs.

The <sup>1</sup>H NMR spectra showed a 100% transformation of **ROF-Br-1** in DMSO solution with irradiation of high pressure mercury lamp.

## 4. 1D and 2D NMR spectra for OXA-1-R from oxidation of OXA-1



**Figure S4.** <sup>1</sup>H NMR spectrum of **ROF-Br-1** (12 mg in 0.5 mL DMSO- $d_6$ ) after irradiation by a high pressure mercury lamp for 24 hrs.

According to the chemical shift and integral number of hydrogen on **OXA-1-R**, except H9, other hydrogen could be determined as shown in Figure S4. The singlet signal at  $\sim$  6.7 ppm could be H9 if O atom connected to C10 or H10 if O atom connected to C9.



**Figure S5.** <sup>13</sup>C NMR spectrum of **ROF-Br-1** (12 mg in 0.5 mL DMSO- $d_6$ ) after irradiation by a high pressure mercury lamp for 24 hrs.



**Figure S6.** HMQC spectrum of **ROF-Br-1** (12 mg in 0.5 mL DMSO- $d_6$ ) after irradiation by a high pressure mercury lamp for 24 hrs.



**Figure S7.** HMBC spectrum of **ROF-Br-1** (12 mg in 0.5 mL DMSO- $d_6$ ) after irradiation by a high pressure mercury lamp for 24 hrs.

### 5. Influence of oxygen on photooxidation of ROF-Br-1



**Figure S8.** UV-Vis spectra for **ROF-Br-1** ( $2.0 \times 10^{-4}$  M) in (a) MeOH and (b) DMSO before (black line) and after irradiation with high pressure mercury lamp for 2 hrs under Ar (red line) or air (cyan line) condition, respectively.

Solutions of **ROF-Br-1** in MeOH and DMSO were irradiated by a high pressure mercury lamp under Ar and air atmosphere, respectively. For MeOH solution, after irradiation under Ar condition, there is only a slight fall of absorption band around 588 nm; while after irradiation under air condition for the same time, an obvious absorption band around 530 nm belonging to OXA-1-R appeared with further decrease of the absorption band around 588 nm. For DMSO solution, after irradiation by high pressure mercury lamp, new absorption bands around 524 nm, belonging to photooxidation product OXA-1-R, generated both under Ar and air condition, but the amount of generated **OXA-1-R** in air is larger than in Ar. These indicate oxygen plays an important role in photooxidation of ROF-Br-1 to OXA-1-R. For why ROF-Br-1 still suffered oxidations in MeOH and DMSO under Ar condition, on one hand, it might be due to the oxygen for Ar condition was not removed very strictly. The Ar condition was provided by just burbling these solutions with Ar and kept Ar above without vacuum-pumping. That is because **ROF-Br-1** would close ring in a vacuum, which may result from the dynamic balance shifts from its ring-open form to ring-closed form as HBr was pumped out under vacuum condition. While, compared with in MeOH, ROF-Br-1 in DMSO produces much more OXA-1-R under Ar condition. This is might due to UV photolysis of DMSO may generate oxygen, which is another reason for causing the oxidation of OXA-1 in Ar condition. This conjecture was confirmed by a fact that a disgusting smell (similar to dimethyl sulfide) can be smelt after irradiating the DMSO solution with a high pressure mercury lamp for 2 hrs.



**Figure S9.** (a) Plot of fluorescence intensity at 460 nm with irradiation time (by a 365 nm handheld UV lamp) for DPBF in DMSO ( $\lambda_{ex} = 405$  nm,  $2.8 \times 10^{-5}$  M) with mixing different concentrations of **OXA-1**. (b) Normalized fluorescence spectra of (a).



**Figure S10.** UV-Vis spectra of **ROF-Br-1** ( $1.0 \times 10^{-4}$  M) dissolved in different concentration of O<sub>2</sub><sup>--</sup> DMSO solutions (KO<sub>2</sub> : 18-Crown-6 = 1 : 4.2).

When C ( $O_2^{-}$ ) < 2.8 × 10<sup>-7</sup> M, only traces of **ROF-Br-1** transformed to ring-closed form due to the alkaline of KO<sub>2</sub>; When 2.8 × 10<sup>-7</sup> M < C ( $O_2^{-}$ ) < 2.8 × 10<sup>-6</sup> M, all **ROF-Br-1** transformed to ring-closed form; when C ( $O_2^{-}$ ) > 2.8 × 10<sup>-6</sup> M, **ROF-Br-1** was oxidized to other products (green dash box), other than **OXA-1-R**.

#### a) 0d 1d 3d 8d 14d 17d 24d 33d Ms0 (1 M60 Ches 0/150 ( 2×15-4 CM60 b) 0d 1d 3d 8d 14d 17d 24d 33d E404 2×10-4 Eton 1 2×104 Eter Eter 2.

## 6. Influence of solvents on the photooxidation of OXA-1

Figure S11. Photos of solution color change for OXA-1 in (a) DMSO and (b) EtOH (2.0  $\times 10^{-4}$  M) along with irradiation time by sunlight.



Figure S12. MS spectra of OXA-1 in DMF solution  $(1.0 \times 10^{-4} \text{ M})$  after irradiation with sunlight for 7 days.



**Figure S13.** UV-Vis spectra change of **OXA-1** ( $2.0 \times 10^{-4}$  M) with sunlight irradiation time in (a) CH<sub>2</sub>Cl<sub>2</sub>, (b) DMSO, (c) MeOH, (d) EtOH, (e) MeCN, (f) EtOAc, (g) PhMe and (h) DMF, respectively.

As irradiation time increases, **OXA-1** in DCM, DMSO, MeOH, EtOH and MeCN solutions, their absorption bands at around 331 nm decreased, and new absorption bands at around 588 nm belonging to ring-open form of **OXA-1** increased firstly. Then, a new absorption band at around 520 nm belonging to photooxidation product of **OXA-1** increased as a part of absorption bands at around 588 nm decreased. These indicate that **OXA-1** suffered a non-decomposed photooxidation in these solvents. However, in EtOAc, PhMe and DMF, we could only observe the absorption bands around 331 nm decreased, while no new absorption > 400 nm appeared, which indicates a decomposed oxidation happens for **OXA-1** in these solutions.



**Figure S14.** UV-Vis spectra change of **ROF-Br-1** ( $2.0 \times 10^{-4}$  M) with sunlight irradiation time in (a) CH<sub>2</sub>Cl<sub>2</sub>, (b) DMSO, (c) MeOH, (d) EtOH, (e) MeCN and (f) DMF, respectively.

After solutions of **ROF-Br-1** in DMSO, MeOH and EtOH were exposed to sunlight, respectively, new bands around 520 nm appeared, accompanying with decrease of their original absorption bands around 590 nm, which is much easier than transformation of **OXA-1** in these solvents. It indicates that ring-open form is a key intermediate for non-decomposed photooxidation of **OXA-1** in these solutions. For CH<sub>2</sub>Cl<sub>2</sub> solution, **ROF-Br-1** was oxidized very fast. After one day, the solution turned completely to red; while after two days, its absorption around 590 nm fell to nearly zero. For MeCN solution of **ROF-Br-1**, we observed the band around 580 nm decreased and no new peak belonging **OXA-1-R** generated, which indicated most of **ROF-Br-1** suffered a decomposed oxidation in MeCN. Due to that DMF solution is alkaline after UV photolysis, so we only observed a ring-closing process firstly and then a gradually decomposed oxidation. EtOAc and PhMe were not included in this experiment, because **ROF-Br-1** is not soluble in these two solvents.



## 7. LC-HRMS spectra for photooxidation solutions of OXAs

Figure S15. LC-HRMS spectra for (a) OXA-1, (b) OXA-2, (c) OXA-3, (d) OXA-4, (e)OXA-5 and (f) OXA-6 in DMSO after irradiation with sunlight. OXA-Rs were thecorrespondingphotooxidationproductsofOXAs.

## 8. References

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