# **Supporting Information**

# Direct construction of 4-aryl tetralones via visible-light-induced cyclization of styrenes with molecular oxygen

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# 1. Comparison of different transformations to 4-aryl tetralones

Correlated method	Compound treated	Reaction conditions	<b>Comparative results</b>
Klumpp' method (Ref. 1)	СО2Н	TfOH, benzene	Not readily available starting material, especially for 2- phenylcyclopropanecarboxylic acid, only 12% yield was obtained.
Miyano's method (Ref. 2)		AlCl <sub>3</sub> , benzene, 5h, then (COCl) <sub>2</sub> , 6 h; and then AlCl <sub>3</sub> , r.t., 8 h	Not readily available starting material and require multiple steps.
Murphy's method (Ref. 3)		SnCl <sub>4,</sub> 18 h	Not readily available starting material, need poisonous metal salts and only 17% yield was obtained.
Koltunov and Sommer's method and they refered methods (Ref. 4)	OH	AlCl <sub>3</sub> , benzene, 20 °C, 16 h HF-SbF <sub>5</sub> , 0 °C, 2 h HUSY, benzene, 130 °C, 70 h HUSY/HCl, benzene, 130 °C, 40 h	Although given good yields, but require acid medium, long reaction time and a higher reaction temperature or used environmentally-unfriendly expensive metal salts
This method	+ O <sub>2</sub>	Mes-Acr <sup>+</sup> , blue LED, r.t., 16 h	Only catalytic amount of Mes- Acr <sup>+</sup> was used as catalyst, commercial available starting materials, green oxygen source, clean energy, facile and easily operative reaction conditions.

#### Table S1. Comparison of different transformations to 4-aryl tetralones

References:

1. R. Rendy, Y. Zhang, A. McElrea, A. Gomez and D. A. Klumpp, J. Org. Chem., 2004, 69, 2340.

2. S. Miyano, T. Tatsuoka, K. Suzuki, K. Imao, F. Satoh, T. Ishihara, I. Hirotsu, T. Kihara, M. Hatta, Y. Horikawa and K. Sumoto, *Chem. Pharm. Bull.*, 1990, **38**, 1570.

3. W. S. Murphy and K. Hantawong, J. Chem. Soc., Perkin Trans. 1, 1983, 817.

4. K. Y. Koltunov, S. Walspurger and J. Sommer, *Chem. Commun.*, 2004, 1754 and references cited therein.

# 2. UV-Vis experiments

The UV-Vis measurement was performed with a  $CH_3CN$  solution of different dyes (100  $\mu$ M) and the results were listed in Figure S1.



Figure S1 UV-Vis absorbance spectra of the dyes

#### 3. Quantum yield study

Light intensity was determined by a silicon diode (S1337-1010BQ, Hamamatsu, Japan) calibrated in National Institute of Metrology, China. A curvilinear relationship of the generation number of photons of blue LED ( $\lambda$  = 455 nm) with distance (between blue LED source with measure point) was obtained (d = 20 mm, I<sub>0</sub> = 1.8456 × 10<sup>16</sup> cm<sup>-2</sup>s<sup>-1</sup>). Further, transmission rate of solution of 4-methylstyrene (0.50 mmol) in 2 mL of CH<sub>3</sub>CN is 0% under  $\lambda$  = 455 nm light source irradiated by UV-Vis analysis. On the other hand, the CH<sub>3</sub>CN solution of 4-methylstyrene (0.50 mmol) was exposure to blue LED at a distance of 2 cm under air in a quartz cuvette (10 mm), and the yields of different reaction times (0.5, 1, 2, 4, 5, 8 and 10 h) were obtained by <sup>1</sup>H NMR analysis with adding DCE (0.25 mmol) as standard. The reaction rate (R) is about 1.5515 × 10<sup>-6</sup> mmol/s, as shown Figure S2 (B). Meanwhile, pink area indicated that the reaction was in the photoinitiation stage, leading to a nonlinear relationship. At last, the quantum yield ( $\Phi$ ) was found to be approximately 5% according to the linear results and reaction mechanism. So, the quantum yield of the reaction would exceed 5% under O<sub>2</sub> instead of air.



Figure S2 Study linear relationship to give approximately quantum yield of the reaction.

### 4. EPR studies

The EPR studies were tested for using different photocatalysts (Mes-Acr<sup>+</sup>, Methylene blue and Rose Bengal) under following conditions: EPR spectrums of a solution of photocatalysts ( $2\times10^{-3}$  mol/L), **1a** ( $8\times10^{-2}$  mol/L), and DMPO ( $3.4\times10^{-2}$  mol/L) or TEMP ( $2.4\times10^{-2}$  mol/L) in air-saturated CH<sub>3</sub>CN under blue LED irradiation for 30 s.



### 5. Cyclic voltammetry (CV) measurements

The cyclic voltammetry (CV) measurements were tested using tetrabutylammonium tetrafluoroborate (0.1 M in MeCN) as electrolyte and selected styrenes as 0.01 M in MeCN. Comparing the excited state oxidation potentials (2.08–2.18 V) of acridinium salts (Mes-Acr<sup>+</sup>) as photocatalysts (reported by König, *Chem. Commun.*, 2015, **15**, 6568) with our tested oxidation potentials for selected styrenes, we feel that Mes-Acr<sup>+</sup> can photooxidize them (related study, see: D. A. Nicewicz and D. S. Hamilton, *Synlett*, 2014, **25**, 1191).



#### 6. Control experiment with TMEPO

To prove the formation of intermediate **C**, as shown in Scheme 4 of revised manuscript, a control experiment was conducted by addition of 2.0 equiv of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) to a mixture of **1a** and 5.0 mol % of Mes-Acr<sup>+</sup> in CH<sub>3</sub>CN, then the reaction mixture was stirred under  $O_2$  with blue LED irradiation to capture the radical generated during the reaction. After 16 h, only a trace amount of desired product **2a** was observed, along with the products **I** and **II**, which were detected by HRMS. Based on the above results, the intermediate **C** and **D** would react with TEMPO to give **I** and **II**, respectively.





## 7. HRMS spectra for detection of <sup>18</sup>O-2a and aldehydes as byproduct

# 8. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the products





































9. <sup>1</sup>H NMR spectra for analysis of yields on different times







