supporting information for

Visible-Light-Induced Tandem Reaction of Quinoxalin-2(1H)-ones, Alkenes, and Sulfonyl Chlorides

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1. General procedure for the synthesis of substrates 1a-1q

$$R^{1} \xrightarrow[H]{} NH_{2} + H \xrightarrow[H]{} O \xrightarrow{\text{EtOH, 85 °C}} R^{1} \xrightarrow[H]{} N \xrightarrow{\text{R}^{2}} K_{2}CO_{3}, DMF \xrightarrow{\text{R}^{1}} R^{1} \xrightarrow[H]{} N \xrightarrow{\text{R}^{2}} O \xrightarrow{\text{R}^{2}} K_{2}CO_{3}, DMF \xrightarrow{\text{R}^{2}} R^{1} \xrightarrow{\text{R}^{2}} N \xrightarrow{\text{R}^{2}} O$$

Ethyl 2-oxoacetate (50% in toluene, 4.5g, 22.0 mmol, 1.1 equiv.) was added to a suspension of o-arylenediamine (20.0 mmol, 1.0 equiv.) in ethanol (40 mL, 0.5 M). The reaction mixture was stirred and refluxed in an oil bath for 1 h, then stirred at room temperature for 16 h. Upon completion (as monitored by TLC), the precipitate was filtered and washed with ethanol, then dried to give quinoxalinone. For alkylation, the corresponding halogenoalkane (16 mmol, 1.6 equiv.) was added to a suspension of quinoxalinone (10 mmo, 1.0 equiv.) and potassium carbonate (12 mmo, 1.2 equiv.) in DMF (20.0 mL, 0.5M). The mixture was stirred at room temperature for 16 h. Upon completion (as monitored by TLC), the reaction mixture was washed with saturated solution of ammonium chloride (5.0 mL), ethyl acetate (10.0 mL) and water (10.0 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate $(2 \times 10.0 \text{ mL})$. The combined organic layers were dried with anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The resulting organic residue was purified by flash chromatography column over silica gel (SiO₂) to afford the alkylated quinoxalinone.

2. Reaction optimization

			$(1)^{N}$ + $(1)^{SO}$	2CI PC, Base		, D		
			1a 2a 3a	hv	✓ 'N' 'O 4a	~ `		
Entry	2a (eq.)	3a (eq.)	PC (mol%)	Base (eq.)	Solvent (mL)	Light Source	Time (h)	Yield (%)
1	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	DCE (2.0)	24 W Green	12	0
2	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	DCE (2.0)	24 W White	12	46
3	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	DCE (2.0)	24 W Purple	12	trace
4	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	DCE (2.0)	24 W Blue	12	54
5	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	Toluene (2.0)	24 W Blue	12	15
6	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	MeCN (2.0)	24 W Blue	12	trace
7	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	THF (2.0)	24 W Blue	12	trace
8	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	DMAc (2.0)	24 W Blue	12	34
9	2.0	2.0	4-CzIPN (2.0)	K ₂ HPO ₄ (1.5)	acetone (2.0)	24 W Blue	12	34
10	2.0	2.0	4-CzIPN (2.0)	KF (1.5)	DCE (2.0)	24 W Blue	12	76
11	2.0	2.0	4-CzIPN (2.0)	DBU (1.5)	DCE (2.0)	24 W Blue	12	53
12	2.0	2.0	4-CzIPN (2.0)	K ₂ CO ₃ (1.5)	DCE (2.0)	24 W Blue	12	57
13	2.0	2.0	4-CzIPN (2.0)	Na ₂ CO ₃ (1.5)	DCE (2.0)	24 W Blue	12	34
14	2.0	2.0	4-CzIPN (2.0)	K ₃ PO ₄ (1.5)	DCE (2.0)	24 W Blue	12	89
15	2.0	2.0	4-CzIPN (2.0)	K ₃ PO ₄ (1.0)	DCE (2.0)	24 W Blue	12	83
16	2.0	2.0	4-CzIPN (2.0)	K ₃ PO ₄ (2.0)	DCE (2.0)	24 W Blue	12	84
17	2.0	2.0	PTH (2.0)	K ₃ PO ₄ (1.5)	DCE (2.0)	24 W Blue	12	76
18	2.0	2.0	fac-Ir(ppy) ₃ (2.0)	K ₃ PO ₄ (1.5)	DCE (2.0)	24 W Blue	12	13
19	2.0	2.0	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6(2.0)$	K ₃ PO ₄ (1.5)	DCE (2.0)	24 W Blue	12	32
20	2.0	2.0	Na ₂ Eosin Y (10)	K ₃ PO ₄ (1.5)	DCE (2.0)	24 W Blue	12	0
21	1.5	2.0	4-CzIPN (2.0)	K ₃ PO ₄ (1.5)	DCE (2.0)	24 W Blue	12	82

Table S1 Reaction Optimization^a

81	12	24 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.5	22
83	12	24 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	1.5	2.0	23
81	12	24 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.5	2.0	24
85	12	24 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (1.5)	2.0	2.0	25
87	12	24 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.5)	2.0	2.0	26
84	12	24 W Blue	DCE (1.5)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	27
86	12	24 W Blue	DCE (2.5)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	28
81	12	18 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	29
84	12	30 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	30
0	12	24 W Green	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	31
46	12	24 W White	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	32
trace	12	24 W Purple	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	33
0	12	24 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	-	2.0	2.0	34
0	12	24 W Purple	DCE (2.0)	K ₃ PO ₄ (1.5)	-	2.0	2.0	35
0(air)	12	24 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	36
0(dark)	12	24 W Blue	DCE (2.0)	K ₃ PO ₄ (1.5)	4-CzIPN (2.0)	2.0	2.0	37

^{*a*} **1a** (0.20 mmol), **2a** (0.30-0.50 mmol), **3a** (0.30-0.50 mmol), photocatalyst (0.003-0.02 mmol), base (0.20-0.40 mmol) in solvent (1.5-2.5 mL) under the irradiation of LEDs for 12 h at 40 °C.

3. Larger-scale experiments

To a 100.0 mL flame-dried round Schlenk tube equipped with a magnetic stir bar was added quinoxalin-2(1H)-ones **1a** (0.64 g, 4.0 mmol), styrene **2a** (0.83 g, 8.0 mmol) and tosyl chloride **3a** (1.53 g, 8.0 mmol), K₃PO₄ (1.27 g, 6.0 mmol), 4CzIPN (64.0 mg, 0.08 mmol) and dry DCE (40.0 mL). The resulting mixture was charged with argon. Then, the solution was stirred under the irradiation of 24 W blue LEDs at 40 °C for about 12 h under argon atmosphere. The organic phase was evaporated under reduced pressure to give a residue, which was then purified with chromatography column on silica gel (PE : EA = 3 : 1) to give the corresponding products **4a** as a white solid (1.38 g, 83%).



Figure S1. The setup for the blue LEDs-driven large-scale reaction

4. Radical trapping experiments



To a solution of **1a** (0.20 mol), **2a** (0.40 mmol), **3a** (0.40 mmol), K_3PO_4 (0.30 mmol), 4CzIPN (2 mol%), TEMPO (0.4 mmol) and dry DCE (2.0 mL). The reaction mixture was evacuated and with argon for three times and stirred under the irradiation of 24 W blue LEDs at 40 °C for about 12 h under argon atmosphere. The reaction was completely inhibited, no desired product was obtained and TEMPO-trapped complex (5) was detected by LC-MS analysis. HRMS ESI (m/z): [M+H]⁺ calcd for C₂₄H₃₄NO₃S⁺ 416.2254, found: 416.2272.



5. Fluorescence quenching studies

The fluorescence emission intensity of the reaction solution was recorded using a Cary Eclipse Fluorescence spectrophotometer (Agilent Technologies, USA). The emission wavelength was 537 nm. The samples were prepared by mixing 4CzIPN (1.0 \times 10⁻³ mol/L) and different amounts of quinoxalin-2(*H*)-one (**1a**) in DCE (total volume = 2.0 mL) in an optical path quartz fluorescence cuvette. The concentration of quinoxalin-2(*H*)-one (**1a**) solution in DCE was 1.0×10^{-3} mol/L. In each quenching experiment, a different amount of quinoxalin-2(H)-one solution was titrated into 0.02 mL of 4CzIPN mixed solution (total volume = 2.0 mL). The emission intensity was then collected and the results are shown in Figure S1.



Figure S1. Quenching of 4CzIPN fluorescence emission in the presence of quinoxalin-2(*H*)-one.

An indeed fluorescence quenching phenomenon of 4CzIPN under various concentrations of quinoxalin-2(*H*)-one **1a** was demonstrated in a curve of $[I_0/I]$ vs C [**1a**], as shown in Figure S2 (Stern-Volmer plots).



Figure S2. Stern-volmer plots. I_0 is the inherent fluorescence intensity of 4-CzIPN. I is the fluorescence intensity of 4-CzIPN in the presence of 1a

The fluorescence emission intensity of the reaction solution was recorded using a Cary Eclipse Fluorescence spectrophotometer (Agilent Technologies, USA). The emission wavelength was 537 nm. The samples were prepared by mixing 4CzIPN (1.0 \times 10⁻³ mol/L) and different amounts of p-toluenesulfonyl chloride (**3a**) in DCE (total volume = 2.0 mL) in an optical path quartz fluorescence cuvette. The concentration of p-Toluenesulfonyl chloride solution in DCE was 1.0×10^{-3} mol/L. In each quenching experiment, a different amount of p-toluenesulfonyl chloride (**3a**) solution was titrated into 0.02 mL of 4CzIPN mixed solution (total volume = 2.0 mL). The emission intensity was then collected and the results are shown in Figure S3.



Figure S3. Quenching of 4CzIPN fluorescence emission in the presence of 3a.

An indeed fluorescence quenching phenomenon of 4CzIPN under various concentrations of p-toluenesulfonyl chloride (**3a**) was demonstrated in a curve of $[I_0/I]$ vs C [**3a**], as shown in Figure S2 (Stern-Volmer plots).



Figure S4. Stern-volmer plots. I_0 is the inherent fluorescence intensity of 4-CzIPN. I is the fluorescence intensity of 4-CzIPN in the presence of **3a**

6. Unsuitable substrates



Figure S5. Unsuitable substrates



7. Copies of ¹H N













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