Supporting Information

Synthesis of sulfone-functionalized chroman-4-ones and chromans through the visible-light-induced cascade radical cyclization under transition-metal-free conditions

Yousheng Mei,^{a,b} Lulu Zhao,^b Qi Liu,^b Shuchen Ruan,^b Lei Wang*,^{a,b} and Pinhua Li*,^b

^a Advanced Research Institute and Department of Chemistry, Taizhou University, Taizhou, Zhejiang, 318000, P. R.China; E-mail: *leiwang@chnu.edu.cn*^b Key Laboratory of Green and Precise Synthetic Chemistry and Applications, Ministry of Education; Department of chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China; E-mail: *pphuali@126.com*

Table of Contents for Supporting Information

1. General considerations	.2
2. Procedures for the representative transformations	2
3. Mechanism investigation	4
4. ¹ H and ¹³ C NMR spectra of the products	8

1. General considerations

All ¹H NMR and ¹³C NMR spectra were recorded on 400 MHz or 600 MHz Bruker FT-NMR spectrometer (400 MHz or 100 MHz and 600 MHz or 150 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI).

2-allyloxyarylaldehyde were prepared according to the reported method [L. Tang, Z. Yang, X. Chang, J. Jiao, X. Ma, W. Rao, Q. Zhou and L. Zheng, *Org. Lett.*, 2018, **20**, 6520]. The chemicals and solvents were purchased from commercial suppliers either from Aldrich (USA) or Shanghai Chemical Company (China) without further purification. All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO₂.

2. Procedures for the representative transformations

2.1 Representative procedure for the model reaction



2-(allyloxy)benzaldehyde (**1a**, 0.20 mmol), 4-methylbenzenesulfinic acid (**2a**, 0.40 mmol), (NH₄)₂S₂O₈ (0.30 mmol) and DMSO:H₂O (1:1, 2.0 mL) were sequence added to an oven-dried reaction vessel equipped with magnetic stirring bar. Then the reaction vessel was irradiated using blue LED (410-415 nm, 3 W) under air atmosphere at room temperature for 12 h. After the reaction was completed, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5/1) to give the desired product **3a** in 84% yield as a white solid.

2.2 Gram-scale synthesis of 3a and 5a and their chemical transformations.



Gram-scale synthesis of 3a: A 50 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(allyloxy)benzaldehyde (**1a**, 5.0 mmol), 4-methylbenzenesulfinic acid (**2a**, 10.0 mmol), (NH₄)₂S₂O₈ (1.5 equiv) and DMSO:H₂O (1:1, 20.0 mL). The reaction vessel was exposed to blue LED (410-415 nm, 3 W) irradiation at room temperature in air with stirring for 24 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give the product **3a** (1.074 g, 68% yield).

The transformation of 3a to 6: A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 3a (0.316 g, 1.0 mmol), phenylhydrazine (0.216 g, 2.0 mmol), acetic acid (20 mol%) and EtOH (5.0 mL). and then the mixture was stirred at 75 °C for 12 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give the product 6 (0.369 g, 91% yield).

Gram-scale synthesis of 5a: A 50 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(but-3-en-1-yloxy)benzaldehyde (**4a**, 5.0 mmol), 4-methylbenzenesulfinic acid (**2a**, 10.0 mmol), $(NH_4)_2S_2O_8$ (1.5 equiv) and DMSO:H₂O (1:1, 20.0 mL). The reaction vessel was exposed to blue LED (410-415 nm, 3 W) irradiation at room temperature in air with stirring for 24 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silicagel, petroleum ether/ethyl acetate = 5:1) to give the product **5a** (0.990 g, 60% yield).

The transformation of 5a to 8 and 9: A 10 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 5a (0.330, 1.0 mmol), malononitrile (0.079g, 1.2 mol) or diethyl malonate (0.192g, 1.2 mol), Pyridine (5 mol%) and EtOH (5.0 mL). the mixture was stirred at room temperature for 12 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silicagel, petroleum ether/ethyl acetate = 9:1) to give the product 8 (0.370 g, 98% yield) and 9 (0.368 g, 78% yield).

3. Mechanism investigation

3.1 Free radical-trapping experiment (I)



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(allyloxy)benzaldehyde (**1a**, 0.20 mmol), 4-methylbenzenesulfinic acid (**2a**, 0.40 mmol), (NH₄)₂S₂O₈ (0.30 mmol), TEMPO (93.6 mg, 0.60 mmol) and DMSO:H₂O (1:1, 2.0 mL). The reaction vessel was exposed to blue LED (410-415 nm, 3 W) irradiation in air at room temperature with stirring for 12 h. The reaction was completely inhibited, indicating a radical pathway involved in the reaction.

3.2 Free radical-trapping experiment (II)



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(allyloxy)benzaldehyde (**1a**, 0.20 mmol), 4-methylbenzenesulfinic acid (**2a**, 0.40 mmol), (NH₄)₂S₂O₈ (0.30 mmol), 1,1-diphenylethylene (72.0 mg, 0.40 mmol) and DMSO:H₂O (1:1, 2.0 mL). The reaction vessel was exposed to blue LED (410-415 nm, 3 W) irradiation in air at room temperature with stirring for 12 h. After the reaction was completed, the products were detected by TLC and HPLC-HRMS. The product **3a** was isolated in 57% yield, and small amount of compound **11** was detected by HPLC-HRMS analysis, as shown in **Figure S1**, which is a radical trapping product.



Figure S1. HRMS analysis of reaction mixture

3.3 Free radical-trapping experiment (III)



A radical scavenger (2,2,6,6-tetramethylpiperidinoxy, TEMPO, 3.0 equiv) was added to the reaction solution of **1a** with **2a** under the standard reaction conditions. After 12 h, the crude reaction mixture was detected by HRMS (ESI), and products **10** were detected, as shown in **Figure S2**.



Figure S2. HRMS analysis of the adduct of C-radical and O-radical with TEMPO

3.4 Free radical-trapping experiment (IV)



A radical scavenger (1,1-diphenylethylene, 2.0 equiv) was added to the reaction solution of **1a** with **2a** under the standard reaction conditions. After 12 h, the crude reaction mixture was detected by HRMS (ESI), and products **12** were detected, as shown in **Figure S3**.



Figure S3. HRMS analysis of the adduct of C-radical and O-radical with

1,1-diphenylethylene

4. ¹H and ¹³C NMR spectra of the products











































200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

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