Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry. This journal is © The Royal Society of Chemistry 2017

> Supplementary Material (ESI) for Organic & Biomolecular Chemistry This journal is (c) The Royal Society of Chemistry 2017

Supporting Information

Visible-light-induced tandem cyclization of 2alkynylanilines with disulfides: A convenient method for accessing benzothiophenes under transition-metal-free and photocatalyst-free conditions

Xiaoyu Xie,^a Pinhua Li,^{*a} Qing Shi,^a and Lei Wang^{*a,b}

^a Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R.

China, Tel: +86-561-3802-069; Fax: +86-561-3090-518

E-mail: pphuali@126.com; leiwang@chnu.edu.cn

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

Table of Contents for Supporting Information

1. General considerations	. 2
2. The control experiments	2
3. ¹ H and ¹³ C NMR spectra of the products	4
4. References	25

1. General considerations

All ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 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).

N-(2-(phenylethynyl)phenyl)acetamide were prepared according to the reported methods.¹ 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. The control experiments

2.1 Free radical-trapping experiment (I)



N-(2-(Phenylethynyl)phenyl)acetamide (**1a**, 0.30 mmol), 1,2-diphenyldisulfane (**2a**, 0.30 mmol), H₂O₂ (0.60 mmol) and 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 0.09 mmol), was added to an oven dried Schlenk tube equipped with magnetic stirring bar, and the reaction tube was irradiated using 3 W blue LED at room temperature under N₂ atmosphere for 15 h. After the reaction was completed, no desired product **3a** was detected by TLC and HPLC-HRMS, indicating that the reaction was completely inhibited. Meanwhile, the corresponding adduct (**4**) of thiyl radical with TEMPO was confirmed by HRMS analysis, as shown in Figure S1.



Figure S1 HRMS analysis of TEMPO with a thiyl radical trapping product 4.

2.2 Free radical-trapping experiment (II)



N-(2-(Phenylethynyl)phenyl)acetamide (**1a**, 0.30 mmol), 1,2-diphenyldisulfane (**2a**, 0.30 mmol), H₂O₂ (0.60 mmol) and 2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO, 0.18 mmol), was added to an ovendried Schlenk tube equipped with magnetic stirring bar, and the reaction tube was irradiated using 3 W blue LED at room temperature under N₂ atmosphere for 15 h. After the reaction was completed, no desired product **3a** was detected by TLC and HPLC-HRMS, indicating that the reaction was completely inhibited. Instead, a small amount of compounds **5** and **6** were detected by HPLC-HRMS analysis, as shown in Figure S2 and Figure S3 . These compounds were possibly generated through the decomposition of the compound **7**, which is a radical trapping product.



Figure S2 HRMS analysis of product 5



Figure S3 HRMS analysis of product 6











8.338 8.338 8.338 8.318 8.318 8.318 8.318 8.338 7.7.873 7.405 7.7.405 7.7.405 7.7.405 7.7.405 7.7.405 7.7.405 7.7.303 7.7.308 7.7.323 7.7.333 7.7.323 7.7.323 7.7.3330 7.7.3333 7.7.333 7.7.3334 7.7.3334 7.7.3334 7.7.334 7.7.3344 7.





































4. References

1 Y. Yan, W. Y. Ma, Z. Chai and G. Zhao, J. Org. Chem. 2007, 72, 5731.