# Green Chemistry

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Liu, W. Pan, S. Wu, X. Bu, S. Xin, J. Yu, H. Xu and X. Yang, *Green Chem.*, 2019, DOI: 10.1039/C9GC00022D.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/green-chem

## **Journal Name**



Received 00th January 20xx, Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 01 March 2019. Downloaded by Washington University in St. Louis on 3/1/2019 2:00:33 PM

Visible-light-induced tandem radical addition-cyclization of 2-aryl phenyl isocyanides catalysed by recyclable covalent organic frameworks

Shuyang Liu,<sup>a</sup> Wenna Pan,<sup>a</sup> Songxiao Wu,<sup>a</sup> Xiubin Bu,<sup>a</sup> Shigang Xin,<sup>a</sup> Jipan Yu, \*<sup>c</sup> Hao Xu<sup>\*b</sup> and Xiaobo Yang<sup>\*a</sup>

A visible-light-induced tandem radical addition-cyclization sequence via 2-aryl phenyl isocyanides as the starting material and two-dimensional covalent organic frameworks (2D-COFs) as the photocatalyst was developed, delivering multifarious 6-substituted phenanthridines in high yields. Benefited from the utilization of heterogeneous photocatalyst, this protocol features easy catalyst separation and excellent recyclability. Negligible loss of the catalytic activity was observed after multiple runs. High practicability of this protocol was further demonstrated by continuous flow experiments.

Covalent organic frameworks (COFs), which are prepared from readily available organic units, as a new type of highly ordered porous organic crystalline materials,1 find a variety of applications such as in catalysis<sup>2</sup> and gas storage<sup>3</sup> due to their large surface area and high stabilities. 2D-COFs, possessing extended  $\pi$ -conjugated frameworks and eclipsed stacking, provide ideal channels for exciton separation and charge percolation.<sup>4</sup> Therefore, some well-designed 2D-COFs have proven photoactive and effective in heterogeneous photocatalytic chemical transformations.<sup>5</sup> For example, the groups of Wang,<sup>6a, 6b</sup> Wu<sup>7</sup> and Liu<sup>8a</sup> independently showed the remarkable photocatalytic activity of hydrazone or imine-based 2D-COFs in visible-light-induced cross-dehydrogenative coupling (CDC) reactions. In 2018, Wang and co-workers illustrated the excellent photocatalytic performance of benzoxazole-based COFs in the visible-light-driven aerobic

<sup>a</sup>Institute of Catalysis for Energy and Environment, College of Chemistry & Chemical Engineering, Shenyang Normal University, Shenyang, Liaoning, 110034, P. R. China.

oxidation of arylboronic acids to phenols.<sup>6c</sup> Very recently, Liu reported a visible-light-driven reductive dehalogenation of phenacyl bromides and  $\alpha$ -alkylation of aldehydes catalysed by photoactive imine-based 2D-COFs.<sup>8b</sup> These pioneering works have suggested the great potential catalytic ability of 2D-COFs in heterogeneous visible-light-induced organic transformations, but their applicable organic reaction scope are still limited to visible-light-driven CDC reaction and simple redox reaction. Thus, expanding the boundaries of these heterogeneous visiblelight-induced organic processes with 2D-COFs is highly needed.

The phenanthridine derivatives widely occur in natural products, pharmaceuticals and materials.<sup>9</sup> Consequently, a



Scheme 1 Visible-light-induced tandem radical addition-cyclization of 2-aryl phenyl isocyanides

<sup>&</sup>lt;sup>b</sup>College of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475004, P. R. China.

<sup>&</sup>lt;sup>c</sup> Laboratory of Nuclear Energy Chemistry, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, China.

E-mail: bxy1223@gmail.com; yangxb@synu.edu.cn; xuhao@henu.edu.cn; yujipan@ihep.ac.cn.

<sup>†</sup> Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

#### COMMUNICATION

Published on 01 March 2019. Downloaded by Washington University in St. Louis on 3/1/2019 2:00:33 PM

wide range of efficient methods have been developed for the synthesis of these scaffolds in the past decades.<sup>10</sup> Among them, visible-light-induced tandem radical addition-cyclization of 2aryl phenyl isocyanides is the most attractive and facile strategy because of its high efficiency and green features.<sup>11</sup> Numerous homogeneous photosensitizers including [Ru] or [Ir] complex<sup>12</sup> and organic dyes<sup>13</sup> have been reported to realize this photocatalytic transformation successfully (Scheme 1a), but the drawbacks of homogeneous photocatalysts, for example, difficult to separate and recycle impairs their practical applications,<sup>14</sup> especially in industrialized synthesis. To address the above practicability issues and maximize the application potentials of 2D-COFs in photocatalytic organic transformations, in the continuation of our interests on photoinduced reactions and construction of N-heterocycles,<sup>15</sup> herein, we wish to report a heterogeneous visible-light-induced tandem radical addition-cyclization process from 2-aryl synthesize diverse 6-substituted phenylisocyanides to phenanthridines, in which hydrazone-based two-dimensional covalent organic frameworks (2D-COF-1) are utilized as the recyclable and reusable heterogeneous photosensitizers (Scheme 1b).

At the outset of our study, the 2D-COF-1 was prepared by the condensation of 2,5-dimethoxyterephthalohydrazide with 1,3,5-triformylbenzene according to a previously reported



**Figure 1** (a) Normalized UV/Vis absorption spectra of 2D-COF-1 (red line), [Acr<sup>+</sup>-Mes]ClO<sub>4</sub><sup>-</sup> (blue line), Eosin B (purple line) and Ir[(ppy)<sub>2</sub>(dtbpy)]PF<sub>6</sub> (green line). (b) Redox potentials (in V vs. SCE) of 2D-COF-1 and reported homogeneous photosensitizers.

Table 1 Visible-light-induced tandem radical addition-cyclization./of.2\_aryl\_phenyl



<sup>o</sup>**1** (0.1 mmol), **2** (0.3 mmol), 2D-COF-1 (0.001 mmol, 4 mg), K<sub>2</sub>CO<sub>3</sub> (0.3 mmol), DMSO (1 mL), 5 W Blue LEDs, under air for 20 h at room temperature. <sup>b</sup>Isolated yield. <sup>c</sup>Hydrazine hydrochlorides were used.

protocol<sup>6</sup> (Scheme S1, see details in ESI). Its structure, porosity and thermostability were confirmed and characterized by FT-IR spectra, <sup>13</sup>C CP/MAS NMR spectra, powder X-ray diffraction, thermogravimetric analysis, nitrogen adsorption-desorption experiments and scanning electron microscopy respectively (Figure S1-S6, Table S1, see details in ESI). The results indicate that the synthesized 2D-COF-1 possesses high crystallinity and good thermostability which are the key features of the suitable heterogeneous catalyst. Subsequently, to verify the feasibility of the above visible-light-induced organic transformation with this 2D-COF, the comparison of UV/Vis absorption and redox potential between 2D-COF-1 and reported homogeneous photosensitizers<sup>16</sup> were conducted (Figure 1, S7, S8), and the potential photocatalytic activity of this 2D-COF material was investigated by electrochemical impedance spectroscopy (EIS) and the photocurrent tests (Figure S9, S10, see details in ESI). All of these results demonstrate that it is qualified to be an effective photocatalyst in the tandem radical additioncyclization of 2-aryl phenyl isocyanides under blue LED light irradiation.

Motivated by the remarkable suitability of 2D-COF-1 in photocatalytic reactions, we further investigated the application of 2D-COF-1 as the heterogeneous photosensitizers for the installation of various radical precursors onto 2-aryl phenyl isocyanides, delivering a wide range of 6-substituted phenanthridines.

Page 2 of 7

Published on 01 March 2019. Downloaded by Washington University in St. Louis on 3/1/2019 2:00:33 PM

#### COMMUNICATION

#### Journal Name

Initially, we chose phenylhydrazine 2a as the phenyl radical precursor to synthesize 6-aryl phenanthridines under visiblelight irradiation in the presence of 10 mol% 2D-COF-1. To our delight, after the optimization and adjustments of the reaction conditions (Table S2, see details in ESI), the desired product 3aa was obtained in 77% yield. Then we examined the generality of this photocatalytic transformation by using different 2-aryl phenyl isocyanides and hydrazines. As shown in the Table 1, all of the selected 2-aryl phenyl isocyanides participated the reactions well regardless of the position or type of the substituted group. Halogenated aryl isocyanides also gave the corresponding products in high yield, providing a chance for further derivatization and modification (3ba, 3bc, 3dc, 3ec, 3gc, 3jc). Apart from phenylhydrazines, tert-butyl hydrazine 2c is also compatible with this reaction, producing the target molecules in excellent yields (3ac-3jc). Compared with previous work using the homogeneous photosensitizer, there is no

**Table 2** Visible-light-induced tandem radical addition-cyclization of 2-aryl phenyl isocyanides (1) with  $CF_3SO_2Na$  (4) <sup>*a,c*</sup>, diphenylphosphine oxide (5)<sup>*b,c*</sup> by using 2D-COF-1 as the photosensitizer



 $^o\mathbf{1}$  (0.1 mmol), 4 (0.2 mmol), 2D-COF-1 (0.001 mmol, 4 mg),  $K_2S_2O_8$  (0.2 mmol),  $Na_2CO_3$  (0.2 mmol), EA (1 mL), 34 W Blue LED, under  $N_2$  for 36 h at room temperature.  $^b\mathbf{1}$  (0.1 mmol), 5 (0.3 mmol), 2D-COF-1 (0.001 mmol, 4 mg),  $K_2S_2O_8$  (0.3 mmol), CSF (0.2 mmol), EA (1 mL), 34 W Blue LED, under  $N_2$  for 12 h at room temperature.  $^c$ Isolated yield.



 $^{o}1$  (0.1 mmol), 6 (0.2 mmol), 2D-COF-1 (0.001 mmol, 4 mg), DTBP (0.2 mmol), EA (1 mL), 5 W Blue LEDs, under N $_{2}$  for 24h at room temperature.  $^{b}$ Isolated yield.

# Scheme 2 Visible-light-induced tandem radical addition-cyclization of 2-aryl phenyl isocyanides (1) with diphenyl disulfide (6) by using 2D-COF-1 as the photosensitizer



Scheme 3 (a) Recycling experiments (b) Reactions in continuous flow

obvious diminishing reaction efficiency.<sup>5a</sup>

Next, the scope of this strategy was expanded by installing trifluoromethyl radical and P-centered radical onto 2-aryl phenyl isocyanides (Table 2). Under the modified reaction conditions (Table S3, S4, see details in ESI), CF<sub>3</sub>SO<sub>2</sub>Na and diphenylphosphine oxide were both smoothly converted to the corresponding radicals respectively under the blue LED light irradiation with the photocatalyst 2D-COF-1, producing a series of 6-trifluoromethyl phenanthridines and 6-phosphorylated phenanthridines in good to excellent yields. The electronic effect and substituent type are not the key factors of this reaction. Notably, in the reactions towards the above two types of phenanthridines, ethyl acetate (EA), as a greener solvent, was employed instead of environmental-unfriendly DMF, which was used in previous works.<sup>10c</sup> More importantly, because of the excellent porosity and photoactivity of the 2D-COF-1, the corresponding product yields of these two heterogeneous photocatalytic transformations are comparable with reported

#### Journal Name

homogeneous photocatalysis. In some cases, it is even higher than previous protocols.

COMMUNICATION

Sulfur-containing compounds, as an important class of chemicals, play the key role in the pharmaceutical industry and materials science.<sup>17</sup> Although a number of excellent methods for their synthesis have been reported,<sup>18</sup> there is still extremely necessary for the development of more practical and environmentally benign methods to construct them. Hence, diphenyl disulfide was introduced to generate the S-radical with the 2D-COF-1 via a visible-light- enabled process. As depicted in Scheme 2, two sulfur contained phenylhydrazines were synthesized in moderated yields under the established reaction conditions (Table S5, see details in ESI). To the best of our knowledge, the present approach illustrates the first method to prepare 6-phenylthiophenanthridines via visible-light-induced tandem radical addition-cyclization, avoiding the high reaction temperature in the previous report.<sup>10f</sup>

As a heterogeneous photosensitizer, the recyclability and reusability are crucial features in practical process. In this context, the recycling experiment was performed using 2-isocyano-4'-methoxy-1,1'-biphenyl (1a) and tert-butyl hydrazine (2c) as the substrates with 10 mol% 2D-COF-1 under the standard conditions. As shown in Scheme 3a, it displays almost unchanged reaction efficiency after six runs. Furthermore, inspired by the pioneer work on heterogeneous transformations<sup>19</sup>, the reaction between 2-isocyano-4'-methoxy-1,1'-biphenyl (1a) and diphenyl disulfide **6** was conducted and scaled-up in continuous flow by using a modified continuous-flow photoreactor (see details in ESI), giving the desired product **9a** in 79% yield (Scheme 3b). All of these experiments suggest the great potential of 2D-COF-1 as the photocatalyst to generate radicals with visible light as the driving force.

To gain the mechanistic insights of this photoinduced reaction, several trapping experiments were conducted. As shown in Scheme 4a, in the four model reaction systems, the radical addition-cyclization reactions were significantly suppressed with the addition of TEMPO (common radical scavenger), suggesting that a radical process should be involved. Furthermore, in Scheme 4b, the apparent quantum efficiency (450 nm) values for the four model reactions were calculated to be 9.5%, 5.4%, 17.6% and 6.8% respectively (see details in ESI, part VIII), which indicate that this radical process should present a closed photoredox cycle without chain propagation.

(a) Radical trapping experiments





Based on the above experiments, the measurement of the redox potential for the 2D-COF-1 and previous Peports<sup>103</sup>, CaCplausible reaction mechanism was proposed as depicted in Scheme 5. Initially, under the visible-light irradiation, the excited-state 2D-COF-1\* reduces the oxidant with the formation of radical anion **A**. It abstracts one electron from the radical precursor to generate the key radical **B**. Then, intermediate I is formed via the intermolecular addition from **B** and the substrate **1**. Subsequently, the intramolecular cyclization delivers a cyclohexadienyl-type radical **II**, which is oxidized by 2D-COF-1\* to afford the cation intermediate **III** with the regeneration of the photocatalyst 2D-COF-1. Finally, in the presence of base, the deprotonation of intermediate **III** produces the desired 6-substituted phenanthridine.



Scheme 5 A plausible mechanism

#### Conclusions

Overall, we have described a practical protocol toward the synthesis of diverse 6-substituted-phenanthridines from 2-aryl phenyl isocyanides via visible-light-induced tandem radical addition-cyclization under very mild conditions, in which the 2D-COF-1 hydrazone-based was employed as the heterogeneous photosensitizer. The reaction shows good functional-group compatibility and efficiency. The recycling experiments and continuous flow experiments suggest that the use of heterogeneous photosensitizer 2D-COF-1 exhibits excellent recyclability and practicability. Studies on other visible-light-induced organic transformations with photoactive 2D-COFs are currently ongoing.

#### Acknowledgements

We acknowledge funding from the National Natural Science Foundation of China (Grant No. 21402126, 21502042, 21806167), Natural Science Foundation of Liaoning Province (20180550882), the Program for Creative Talents in University of Liaoning Province, the Basic Scientific Project of the Universities in Liaoning Province (LFW201701), the Program for Young Creative Talents in Shenyang City (RC170189), the Engineering Technology Research Centre of Catalysis for Energy and Environment-Major Platform for Science and Technology of Accepted

#### Journal Name

the Universities in Liaoning Province. We acknowledge Dr. Wenbo Liu, Dr. Minghua Bai, Dr. Ling Zhang and Dr. Lijing Zhou for valuable suggestions and experimental assistance.

#### **Conflicts of interest**

There are no conflicts to declare.

#### Notes and references

- (a) A. P. Côté, A. I. Benin, N. W. Ockwig, M. O'Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166; (b) X. Feng, X. Ding and D. Jiang, *Chem. Soc. Rev.*, 2012, **41**, 6010; (c) S.-Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548; (d) S. Das, P. Heasman, T. Ben and S. Qiu, *Chem. Rev.*, 2017, **117**, 1515; (e) S. M. J. Rogge, A. Bavykina, J. Hajek, H. Garcia, A. I. Olivos-Suarez, A. Sepúlveda-Escribano, A. Vimont, G. Clet, P. Bazin, F. Kapteijn, M. Daturi, E. V. Ramos-Fernandez, F. X. Llabrés i Xamena, V. Van Speybroeck and J. Gascon, *Chem. Soc. Rev.*, 2017, **46**, 3134; (f) Y. Jin, Y. Hu and W. Zhang, *Nat. Rev. Chem.*, 2017, **1**, 0056; (g) C. S. Diercks and O. M. Yaghi, *Science*, 2017, **355**, eaal1585; (h) W. Zhao, L. Xia and X. Liu, *CrystEngComm*, 2018, **20**, 1613.
- For selected examples: (a) S.-Y. Ding, J. Gao, Q. Wang, Y. Zhang, W.-G. Song, C.-Y. Su and W. Wang, J. Am. Chem. Soc. 2011, 133, 19816; (b) H. Xu, J. Gao and D. Jiang, Nat. Chem., 2015, 7, 905; (c) X. Wang, X. Han, J. Zhang, X. Wu, Y. Liu and Y. Cui, J. Am. Chem. Soc., 2016, 138, 12332; (d) Z.-F. Pang, S.-Q. Xu, T.-Y. Zhou, R.-R. Liang, T.-G. Zhan and X. Zhao, J. Am. Chem. Soc., 2016, 138, 4710; (e) Q. Sun, B. Aguila, J. Perman, N. Nguyen and S. Ma, J. Am. Chem. Soc., 2016, 138, 15790.
- For selected examples: (a) S. S. Han, H. Furukawa, O. M. Yaghi and W. A. Goddard, J. Am. Chem. Soc., 2008, 130, 11580; (b) H. Furukawa and O. M. Yaghi, J. Am. Chem. Soc., 2009, 131, 8875; (c) C. J. Doonan, D. J. Tranchemontagne, T. G. Glover, J. R. Hunt and O. M. Yaghi, Nat. Chem., 2010, 2, 235.
- 4 (a) X. Ding, L. Chen, Y. Honsho, X. Feng, O. Saengsawang, J. Guo, A. Saeki, S. Seki, S. Irle, S. Nagase, V. Parasuk and D. Jiang, J. Am. Chem. Soc., 2011, 133, 14510; (b) S. Patwardhan, A. A. Kocherzhenko, F. C. Grozema and L. D. A. Siebbeles, J. Phy. Chem. C, 2011, 115, 11768; (c) L. Chen, K. Furukawa, J. Gao, A. Nagai, T. Nakamura, Y. Dong and D. Jiang, J. Am. Chem. Soc., 2014, 136, 9806.
- 5 For selected examples: (a) L. Stegbauer, K. Schwinghammer and B. V. Lotsch, *Chem. Sci.*, 2014, **5**, 2789; (b) V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld and B. V. Lotsch, *Nat.Commun.*, 2015, **6**, 8508; (c) R. K. Yadav, A. Kumar, N.-J. Park, K.-J. Kong and J.-O. Baeg, *J. Mater. Chem. A*, 2016, **4**, 9413; (d) T. Banerjee, F. Haase, G. Savasci, K. Gottschling, C. Ochsenfeld and B. V. Lotsch, *J. Am. Chem. Soc.*, 2017, **139**, 16228; (e) X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W.-H. Zhu, R. Clowes, Y. Yan, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *Nat. Chem.*, 2018, **10**, 1180; (f) L. Stegbauer, S. Zech, G. Savasci, T. Banerjee, F. Podjaski, K. Schwinghammer, C. Ochsenfeld and B. V. Lotsch, *Adv. Energy Mater.*, 2018, **8**, 1703278.
- 6 (a) H.-Z. Wang, M.S. Thesis, Lanzhou University, Lanzhou, China, 2014; (b) Chinese Patent Application 201410010008.6, 2014; (c) P.-F. Wei, M.-Z. Qi, Z.-P. Wang, S.-Y. Ding, W. Yu, Q. Liu, L.-K. Wang, H.-Z. Wang, W.-K. An and W. Wang, J. Am. Chem. Soc., 2018, 140, 4623.
- 7 W. Liu, Q. Su, P. Ju, B. Guo, H. Zhou, G. Li and Q. Wu, *ChemSusChem*, 2017, **10**, 664.
- 8 (a) Y. Zhi, Z. Li, X. Feng, H. Xia, Y. Zhang, Z. Shi, Y. Mu and X. Liu, *J. Mater. Chem. A*, 2017, **5**, 22933; (b) Z. Li, Y. Zhi, P. Shao,

H. Xia, G. Li, X. Feng, X. Chen, Z. Shi and X. Liu, Avel, Catal, B 2019, 245, 334. DOI: 10.1039/C9GC00022D

- 9 (a) T. Nakanishi, M. Suzuki, A. Saimoto and T. Kabasawa, J. Nat. Prod., 1999, 62, 864; (b) I. Kock, D. Heber, M. Weide, U. Wolschendorf and B. Clement, J. Med. Chem., 2005, 48, 2772; (c) N. Stevens, N. O'Connor, H. Vishwasrao, D. Samaroo, E. R. Kandel, D. L. Akins, C. M. Drain and N. J. Turro, J. Am. Chem. Soc., 2008, 130, 7182.
- 10 For selected examples and reviews: (a) D. A. Candito and M. Lautens, Angew. Chem. Int. Ed., 2009, 48, 6713; (b) M. Tobisu, K. Koh, T. Furukawa and N. Chatani, Angew. Chem. Int. Ed., 2012, 51, 11363; (c) B. Zhang, C. G. Daniliuc and A. Studer, Org. Lett., 2014, 16, 250; (d) J.-J. Cao, T.-H. Zhu, S.-Y. Wang, Z.-Y. Gu, X. Wang and S.-J. Ji, Chem. Commun., 2014, 50, 6439; (e) J. Liu, C. Fan, H. Yin, C. Qin, G. Zhang, X. Zhang, H. Yi and A. Lei, Chem. Commun., 2014, 50, 2145; (f) H. Fang, J. Zhao, P. Qian, J. Han and Y. Pan, Asian J. Org. Chem., 2014, **3**, 1266; (g) C. Pan, H. Zhang, J. Han, Y. Cheng and C. Zhu, Chem.Commun., 2015, 51, 3786; (h) B. Zhang and A. Studer, Chem. Soc. Rev., 2015, 44, 3505; (i) W.-L. Chen, C.-Y. Chen, Y.-F. Chen and J.-C. Hsieh, Org. Lett., 2015, 17, 1613; (j) X. Tang, S. Song, C. Liu, R. Zhu and B. Zhang, RSC Adv., 2015, 5, 76363; (k) J. Lei, J. Huang and Q. Zhu, Org. Biomol. Chem., 2016, 14, 2593; (I) J.-T. Yu and C. Pan, Chem. Commun., 2016, 52, 2220; (m) H.-B. Zhao, Z.-J. Liu, J. Song and H.-C. Xu, Angew. Chem. Int. Ed., 2017, 56, 12732; (*n*) Q. Yao, X. Zhou, X. Zhang, C. Wang, P. Wang and M. Li, Org. Biomol. Chem., 2017, 15, 957; (o) J. Li, C. A. D. Caiuby, M. W. Paixão and C.-J. Li, Eur. J. Org. Chem., 2018, 20-21, 2498.
- (a) M. H. Shaw, J. Twilton and D. W. C. MacMillan, J. Org. Chem., 2016, **81**, 6898; (b) N. A. Romero and D. A. Nicewicz, Chem. Rev., 2016, **116**, 10075; (c) Q. Liu and L.-Z. Wu, Natl. Sci. Rev., 2017, **4**, 359; (d) C. Michelin and N. Hoffmann, ACS Catal., 2018, **8**, 12046; (e) I. K. Sideri, E. Voutyritsa and C. G. Kokotos, Org. Biomol. Chem., 2018, **16**, 4596.
- 12 For the synthesis of phenanthridine derivatives using [Ru] or [Ir] complex as photoredox catalysts, see: (a) H. Jiang, Y. Cheng, R. Wang, M. Zheng, Y. Zhang and S. Yu, Angew. Chem. Int. Ed., 2013, 52, 13289; (b) X. Sun and S. Yu, Org. Lett., 2014, 16, 2938; (c) S. Wang, W.-L. Jia, L. Wang and Q. Liu, Eur. J. Org. Chem., 2015, 31 6817; (d) Z. Zhang, X. Tang and W. R. Dolbier, Org. Lett., 2015, 17, 4401; (f) J. Rong, L. Deng, P. Tan, C. Ni, Y. Gu and J. Hu, Angew. Chem. Int. Ed., 2016, 55, 2743; (g) H. Zhou, X. Z. Deng, A. H. Zhang and R. X. Tan, Org. Biomol. Chem., 2016, 14, 10407; (h) C.-X. Li, D.-S. Tu, R. Yao, H. Yan and C.-S. Lu, Org. Lett., 2016, 18, 4928.
- 13 For the synthesis of phenanthridine derivatives using organic dyes as photoredox catalysts, see: (a) T. Xiao, L. Li, G. Lin, Q. Wang, P. Zhang, Z.-w. Mao and L. Zhou, *Green Chem.*, 2014, 16, 2418; (b) J. Fang, W.-G. Shen, G.-Z. Ao and F. Liu, *Org. Chem. Front.*, 2017, 4, 2049; (c) M. Singh, A. K. Yadav, L. D. S. Yadav and R. K. P. Singh, *Synlett*, 2018, 29, 176.
- 14 (a) X. Lang, X. Chen and J. Zhao, *Chem. Soc. Rev.*, 2014, 43, 473; (b) J. Chen, J. Cen, X. Xu and X. Li, *Catal. Sci. Technol.*, 2016, 6, 349; (c) D. Friedmann, A. Hakki, H. Kim, W. Choi and D. Bahnemann, *Green Chem.*, 2016, 18, 5391; (d) J. Z. Bloh and R. Marschall, *Eur. J. Org. Chem.*, 2017, 15, 2085.
- (a) H. Xu, S. Ma, Y. Xu, L. Bian, T. Ding, X. Fang, W. Zhang and Y. Ren, J. Org. Chem., 2015, **80**, 1789; (b) X. Yang, W. Liu, L. Li, W. Wei and C.-J. Li, Chem. -Eur J., 2016, **22**, 15252; (c) W. Liu, X. Yang, Y. Gao and C.-J. Li, J. Am. Chem. Soc., 2017, **139**, 8621; (d) L. Pan, Z. Li, T. Ding, X. Fang, W. Zhang, H. Xu and Y. Xu, J. Org. Chem., 2017, **82**, 10043; (e) W. Liu, X. Yang, Z.-Z. Zhou and C.-J. Li, Chem, 2017, **2**, 688; (f) S. Liu, J. Jie, J. Yu and X. Yang, Adv. Syn. Catal., 2018, **360**, 267; (g) Z. Lai, Z. Li, Y. Liu, P. Yang, X. Fang, W. Zhang, B. Liu, H. Chang, H. Xu and Y. Xu, J. Org. Chem., 2018, **83**, 145.
- 16 (a) S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko and H. Lemmetyinen, J. Am. Chem. Soc., 2004, **126**, 1600; (b)

**Breen Chemistry Accepted Manuscript** 

#### Journal Name

View Article Online DOI: 10.1039/C9GC00022D

# COMMUNICATION

K. Ohkubo, K. Mizushima, R. Iwata, K. Souma, N. Suzuki and S. Fukuzumi, *Chem. Commun.*, 2010, **46**, 601; (*c*) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, **113**, 5322; (*d*) V. Srivastava and P. P. Singh, *RSC Adv.*, 2017, **7**, 31377.

- 17 (a) E. G. Hope and W. Levason, *Coord. Chem. Rev.*, 1993, 122, 109; (b) N. V. Zyk, E. K. Beloglazkina, M. A. Belova and N. S. Dubinina, *Russ. Chem. Rev.*, 2003, 72, 769; (c) M. D. McReynolds, J. M. Dougherty and P. R. Hanson, *Chem. Rev.*, 2004, 104, 2239; (d) H. Cui, W. Wei, D. Yang, J. Zhang, Z. Xu, J. Wen and H. Wang, *RSC Adv.*, 2015, 5, 84657; (e) X. Liu, H. Cui, D. Yang, S. Dai, T. Zhang, J. Sun, W. Wei and H. Wang, *RSC Adv.*, 2016, 6, 51830; (f) H. Cui, W. Wei, D. Yang, Y. Zhang, H. Zhao, L. Wang and H. Wang, *Green Chem.*, 2017, 19, 3520.
- (a) P.-C. Qian, Y. Liu, R.-J. Song, J.-N. Xiang and J.-H. Li, *Synlett*, 2015, 1213; (b) D.-P. Jin, P. Gao, D.-Q. Chen, S. Chen, J. Wang, X.-Y. Liu and Y.-M. Liang, *Org. Lett.*, 2016, **18**, 3486; (c) W. Wei, H. Cui, D. Yang, H. Yue, C. He, Y. Zhang and H. Wang, *Green Chem.*, 2017, **19**, 5608; (d) M.-H. Huang, W.-J. Hao, G. Li, S.-J. Tu and B. Jiang, *Chem. Commun.* 2018, **54**, 1079; (e) M.-H. Huang, W.-J. Hao and B. Jiang, *Chem. Asian J.* **2018**, *13*, 2958; (f) W. Wei, P. Bao, H. Yue, S. Liu, L. Wang, Y. Li and D. Yang, *Org. Lett.*, 2018, **20**, 5291.
- 19 Y. Cai, Y. Tang, L. Fan, Q. Lefebvre, H. Hou and M. Rueping, ACS Catal., 2018, 8, 9471.

6 | J. Name., 2012, 00, 1-3

Published on 01 March 2019. Downloaded by Washington University in St. Louis on 3/1/2019 2:00:33 PM.

**Graphics abstract** 

# Visible-light-induced tandem radical addition-cyclization of 2-aryl

# phenyl isocyanides catalysed by recyclable covalent organic

### frameworks

Shuyang Liu,<sup>a</sup> Wenna Pan,<sup>a</sup> Songxiao Wu,<sup>a</sup> Xiubin Bu,<sup>a</sup> Shigang Xin,<sup>a</sup> Jipan Yu,<sup>\*c</sup> Hao Xu<sup>\*b</sup>

and Xiaobo Yang\*a



A heterogeneous visible-light-induced tandem radical addition-cyclization of isocyanides by photoactive covalent organic frameworks was developed, delivering diverse phenanthridines with high reaction efficiency and easy catalyst recyclability.