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# Visible-light-promoted syntheses of β-keto sulfones from alkynes and sulfonylhydrazides<sup>†</sup>

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Shunyou Cai,\*<sup>a,b</sup> Danling Chen,<sup>a</sup> Yaohui Xu,<sup>a</sup> Wen Weng,<sup>a</sup> Lihuang Li,<sup>a</sup> Ruijie Zhang<sup>a</sup> and Mingqiang Huang<sup>a</sup>

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A variety of functionalized  $\beta$ -keto sulfones were smoothly prepared through oxysulfonylation of commercially available alkynes with sulfonylhydrazides under the synergistic interactions of visible light irradiation, Ru(bpy)<sub>3</sub>Cl<sub>2</sub> photocatalyst, oxygen, KI, and NaOAc basic additive at very mild reaction conditions.

Owing to their ubiquitous presence in a wide range of molecules<sup>1</sup> which have widely used in pharmaceuticals, material science, and agrochemicals, the synthesis of  $\beta$ -keto sulfones has been extensively explored.<sup>2</sup> As outlined in Scheme 1, traditionally,  $\beta$ -keto sulfones are synthesized by alkylation of sodium sulfinates with acyl halides under basic conditions (Scheme 1a), but the method requires preactivation of ketones by halogenation, which is not a step- and atom-economical process. As a response to this problem, various alternative protocols for  $\beta$ -keto sulfones syntheses, including C–H functionalization strategy, have been continuously reported in recent literature.<sup>3</sup>





formation

In 2013, Lei and co-workers developed an inspirational

triggered oxidative difunctionalization of terminal alkynes with sulfinic acids (Scheme 1b).<sup>3a</sup> The work has subsequently stimulated several other synthetic efforts aimed at exploring new, efficient, and mild methodologies toward their preparations. Within this paradigm, Wang and co-workers reported a practical β-keto sulfones synthesis through coppercatalyzed oxysulfonylations of alkenes with sulfonylhydrazides and dioxygen (Scheme 1c).<sup>3b</sup> AgNO<sub>3</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> catalytic system was proved to be effective in similar context (Scheme 1d).<sup>3c</sup> Alternatively, cross-coupling of ketones and theirs derivates with sodium sulfinates were also investigated in the presence of strong oxidants or transition-metal catalysts. For example, Jiang and co-workers disclosed a practical method for synthesis of sulfone derivatives from readily available sodium sulfinates and oxime acetates by C-H functionalizations (Scheme 1e).<sup>3d</sup> Sreedhar and co-workers developed an one-pot protocol to  $\beta$ -keto sulfones through I<sub>2</sub>-catalyzed coupling of ketones with sodium sulfinates (Scheme 1f).<sup>3e</sup> Although  $\beta$ -keto sulfones have been accessed with existing literature revelations,<sup>3</sup> a practical, mild, and straightforward route for their synthesis utilizing commercially available materials remains highly desirable.

method for constructing β-keto sulfones via dioxygen-



#### Scheme 2. Visible-light-induced photocatalysis strategy to $\beta$ -

#### keto sulfones

We were intrigued by the feasibility of a merge of radical chemistry with visible-light-promoted photoredox catalysis<sup>4-7</sup> to develop a conceptually novel approach for  $\beta$ -keto sulfones synthesis. Our design concept, as described in Scheme 2, envisioned that an oxidative denitrogenation event might be initiated on sulfonylhydrazide under the synergistic actions of photo-catalyst, visible light stimulation, and dioxygen, thereby generating a relatively long-lived sulfonyl radical<sup>8</sup> species, which would subsequent undergo a tandem sulfonyl radical addition, oxygen capture, and peroxide reduction sequence to

<sup>&</sup>lt;sup>a</sup>School of Chemistry and Environment, Fujian Provincial Key Laboratory of Modern Analytical Science and Separation Technology, Minnan Normal University, Zhangzhou, 363000, China. E-mail: <u>caishy05@mnnu.edu.cn</u>

<sup>&</sup>lt;sup>b</sup>Key Laboratory of Chemical Genomics, School of Chemical Biology and

Biotechnology, Peking University, Shenzhen Graduate School, Shenzhen, 518055 China.

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furnish  $\beta$ -keto sulfones. Within this design scenario, we were pleased to report herein that, via careful optimizations of reaction conditions cultivating these strategic events, an unusually versatile and straightforward methodology was finally established for rapidly approaching to various functionalized  $\beta$ -keto sulfones under mild reaction conditions.

Table 1. Identification of the optimal reaction conditions

| cı—             | _>-=           | + Me-   | O<br>III<br>III<br>O c =               | photocatalyst, base,<br>dditive, solvent, r.t., O <sub>2</sub><br>= 0.07 <i>M, visible light</i> |               | S<br>S<br>S<br>S                |
|-----------------|----------------|---|--|--|---------------|---------------------------------|
| 1               | la             | <b>2a</b> (x eq)  |  | C  | 3a            | ~ 'M                            |
| Entry           | <b>2a</b> (eq) | [Ru] (mol%) <sup>a</sup>  | base (eq)                              | solvent (v/v)  | additive (eq) | yie <b>l</b> d (%) <sup>c</sup> |
| 1               | 1.5            | 5   | 1                                      | MeCN   | /             | NR                              |
| 2               | 1.5            | 5   | Na <sub>2</sub> CO <sub>3</sub> (1.5)  | MeCN   | /             | trace                           |
| 3               | 1.5            | 5   | Na <sub>2</sub> CO <sub>3</sub> (1.5)  | MeCN/H <sub>2</sub> O (3:1)  | /             | trace                           |
| 4               | 1.5            | 5   | Na <sub>2</sub> CO <sub>3</sub> (1.5)  | MeCN/H <sub>2</sub> O (3:1)  | KBr (1.5)     | decomp                          |
| 5               | 1.5            | 5   | Na <sub>2</sub> CO <sub>3</sub> (1.5)  | MeCN/H <sub>2</sub> O (3:1)  | KI (1.5)      | 35                              |
| 6               | 1.5            | 5   | NaOAc (1.5)                            | MeCN/H <sub>2</sub> O (3:1)  | KI (1.5)      | 42                              |
| 7               | 1.5            | 5   | NaOAc (1.5)                            | DMF/H <sub>2</sub> O (3:1)   | KI (1.5)      | 47                              |
| 8               | 1.5            | 5   | Na <sub>2</sub> HPO <sub>4</sub> (1.5) | DMF/H <sub>2</sub> O (3:1)   | KI (1.5)      | 41                              |
| 9               | 1.5            | 5   | Cs <sub>2</sub> CO <sub>3</sub> (1.5)  | DMF/H <sub>2</sub> O (3:1)   | KI (1.5)      | decomp                          |
| 10              | 1.5            | 5   | DBU (1.5)                              | DMF/H <sub>2</sub> O (3:1)   | KI (1.5)      | decomp                          |
| 11              | 1.5            | 5   | NaOAc (1.5)                            | DMF/H <sub>2</sub> O (3:1)   | KI (1.0)      | 56                              |
| 12              | 1.5            | 5   | NaOAc (1.5)                            | DMF/H <sub>2</sub> O (3:1)   | KI (0.5)      | 52                              |
| 13              | 2.2            | 5   | NaOAc (2.2)                            | DMF/H <sub>2</sub> O (3:1)   | KI (1.0)      | 72                              |
| 14              | 2.2            | 5   | NaOAc (2.2)                            | DMF/H <sub>2</sub> O (8:1)   | KI (1.0)      | 68                              |
| 15              | 2.2            | 2   | NaOAc (2.2)                            | DMF/H <sub>2</sub> O (5:1)   | KI (1.0)      | 84                              |
| 16              | 2.2            | 2   | NaOAc (2.2)                            | DMSO/H <sub>2</sub> O (5:1)  | KI (1.0)      | trace                           |
| 17              | 2.2            | 2   | NaOAc (2.2)                            | EtOH/H2O (5:1)   | KI (1.0)      | 48                              |
| 18 <sup>b</sup> | 2.2            | Eosin   | NaOAc (2.2)                            | DMF/H <sub>2</sub> O (5:1)   | KI (1.0)      | 78                              |
| ²[Ri            | u] = Ru(bp     | /) <sub>3</sub> Cl <sub>2</sub> • 6H <sub>2</sub> O. <sup>b</sup> 2 | 2 mol% of Eosin Y                      | was used. <sup>c</sup> Yield of isol   | ated product. |                                 |

With 1-chloro-4-ethynylbenzene 1a and 4methylbenzenesulfonohydrazide 2a as the model substrates, no desired product was observed when the reaction was carried out in acetonitrile (MeCN) with a catalytic amount of photocatalyst Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (5 mol %) and visible-light irradiation from a 45 W household bulb under a balloon-oxygen atmosphere for 24 h at room temperature (entry 1, Table 1). Next, performing the reaction with 1.5 equiv of  $Na_2CO_3$  in MeCN or a mixed solvent (MeCN/H<sub>2</sub>O) also resulted in failures (entry 2-3). Fortunately, a subsequent significant observation was made when two reactions using 1.50 equiv of KBr (entry 4) or  $KI^{9}$  (entry 5) in conjunction with Na<sub>2</sub>CO<sub>3</sub>, respectively, were performed in parallel; the comparative results showed the latter to be a better reaction promoter than the former (35% yield vs trace amount of 3a). Furthermore, the utilization of a weaker basic NaOAc was found to be advantageous to the transformation (42% yield, entry 6). When the dimethylformamide (DMF) was used in place of MeCN in the mixed solvent under otherwise comparable reaction conditions, a respectable 47% yield of product was recorded (entry 7). Thus, a number of bases, such as Na<sub>2</sub>HPO<sub>4</sub>, Cs<sub>2</sub>CO<sub>3</sub>, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), were subsequently screened under similar reaction conditions (entry 8-10), from which the use of other bases was found to have negatively influenced the desired product formation. In some above cases, a major byproduct 1-chloro-4-(1-iodo-2tosylvinyl)benzene was observed along with unreacted 1chloro-4-ethynylbenzene 1a. We envisioned that an increase in the amount of 4-methylbenzenesulfonohydrazide 2a and basic NaOAc, as well as a decrease of amount of KI might be helpful in improving the reaction yield. Indeed, the yield of 3a was 

Scheme 3. Substrate scope of alkyne substrates 1

With the above optimal reaction conditions in hand, a range of terminal alkynes carrying a variety of electron-withdrawing and electron-donating substituents were next attempted to react with benzenesulfonohydrazide 2a, and the results were depicted in Scheme 3. In most cases, the reactivity appeared to be quite general, delivering smoothly the corresponding  $\beta$ keto sulfone product 3 in moderate-to-excellent isolated yields. A closer inspection revealed that the electronic characteristics of the substituents on the aryl rings on the alkynes 1 posed an influence on the catalysis efficiency: when R<sup>1</sup> was an electronwithdrawing group, such as Cl (3a), F (3b-3d), CO<sub>2</sub>Me (3e), the corresponding products were obtained in relatively low yields (59-84%); when  $R^1$  was H or electron-donating in nature (i.e.,  $R^1$  = Me, Et, *n*Pr, *n*Bu, or OMe), presumably due to the conjugation-enhanced radical stabilization effects, the reactions proceeded smoothly to provide the corresponding products **3f-3l** in excellent yields (84-93%). Interestingly, the R<sup>2</sup> substituent on the benzenesulfonohydrazide 2 also played a

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crucial role in affecting the reaction; from **3m** to **3n** and **3o**, a decrease of product yield was recorded with the increase in the electronic negativity of  $R^2$ .

To further explore the substrate scope of the established methodology, direct oxysulfonylations of a series of structurally variable sulfonylhydrazides 2 and the 4methoxyphenylacetylene 1l were next examined. As compiled in Scheme 4, the corresponding  $\beta$ -keto sulfones 4a-40 were generally produced in good-to-excellent isolated yields (up to 93%). These results confirmed that neither the aryl ring sizes (4a, 4b) nor electrondonating or -withdrawing properties on the aryl ring (4c-4l) on sulfonylhydrazides 2 appeared to have had a significant influence on the reaction efficiency, except in the case of 4m (32%) wherein the presence of a nitro group seemed to retard the reaction to some extent. The reaction was also successful with alkyl-substituted sulfonylhydrazide (i.e.,  $R^3 = nBu$ ), and the  $\beta$ -keto sulfone **4n** was thus delivered in 86% yield. Moreover, the substrate bearing a heterocyclic group (4o) was demonstrated to be accommodated in this transformation in terms of product yield (67%).



Scheme 4. Substrate scope of sulfonylhydrazides 2

In order to shed light on the potential reaction pathways, several control experiments were therefore subsequently conducted. As summarized in Scheme 5, oxysulfonylation of alkyne 1f and sulfonylhydrazides 2a was again chose as the model reaction. Performing the reaction in the absence of  $O_{2}$ , visible light, Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, or NaOAc, explicitly resulted in complete inhibition of the reactivity. It should be mentioned that when the reaction was conducted in a 3:1 mixed solvent of MeCN and H<sub>2</sub>O, vinyl iodine 5 was produced in 11% yield. Moreover, the reaction was totally inhibited by employing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a radical scavenger. The result, in conjunction with the aforementioned vinyl iodine 5 formation, strongly implied that radical intermediates should be involved in this reaction. Next, 1-(2iodo-2-phenylvinylsulfonyl)-4-methylbenzene 5, 1-phenyl-2tosylvinyl acetate 6, or 1-phenyl-2-tosylethanol 7 prepared

according to the reported literature<sup>11</sup> were subsequently subjected to the standard reaction conditions<sup>10</sup> and desired<sup>1</sup> between the standard reactions<sup>10</sup> and desired<sup>10</sup> between the standard reactions<sup>10</sup> and desired<sup>10</sup> between the standard reaction conditions<sup>10</sup> between the standard reactions<sup>10</sup> betw



Scheme 5. Experimental probes on reaction parameters

Based on both of the above investigations and the observed reactivities, as well as the relevant results reported,<sup>12</sup> a plausible mechanistic network was proposed in Scheme 6. Under visible light stimulation, the initially generated iodine radical<sup>13</sup> should capture an electron from the nitrogen lone pair in sulfonylhydrazide 2, followed by a sequential N-H abstraction, converting it into the sulfonyl radical **B**. Addition to alkyne 1 would thus generate the key vinyl radical species C, which may participate in two competing pathways, i.e., couple with iodine radical to furnish the vinyl iodine 5, or incorporate with molecular oxygen to product a peroxyl radical intermediate **D**.<sup>3a,8a</sup> The intermediate **D** would further go through single electron transfer (SET), proton transfer (PT), and reduction process successively with Ru(I) intermediate, proton, and iodine anion to lead to the final  $\beta$ -keto sulfone product. It merits a note that the beneficial roles of KI and NaOAc in the context are possibly attributable to their assistances of sulfonyl radical formation.



Scheme 6. Proposed mechanistic network

In summary, we have successfully established a visible-lightpromoted oxysulfonylation of alkynes with sulfonylhydrazides. A diverse range of  $\beta$ -keto sulfones bearing multiple useful functionalities could be smoothly prepared in good-to-

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excellent yields under unusually mild and energy-wise reaction conditions. Preliminary mechanistic investigations revealed that a radical pathway was possibly involved in this transformation. Further studies on this reaction mechanism, reaction scope, and synthetic application will thus be continuously pursued in our laboratory and the results will be disclosed in due course.

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#### Notes and references

- (a) C. Curti, M. Laget, A. O. Carle, A. Gellis and P. Vanelle, *Eur. J. Med. Chem.*, 2007, **42**, 880; (b) H. Yang, R. G. Carter and L. N. Zakharov, *J. Am. Chem. Soc.*, 2008, **130**, 9238; (c) M. Artico, R. Silvestri, E. Pagnozzi, B. Bruno, E. Novellino, G. Greco, S. Massa, A. Ettorre, A. G. Loi, F. Scintu and P. L. Coll, *J. Med. Chem.*, 2000, **43**, 1886; (d) J. L. Marco, *J. Org. Chem.*, 1997, **62**, 6575.
- (a) G. E. Vennstra and B. Zwaneburg, *Synthesis* 1975, 519; (b)
  Y.-Y. Xie and Z.-C. Chen, *Synth. Commun.*, 2001, **31**, 3145; (c)
  A. R. Katritzky, A. A. Abdel-Fattah and M. Y. Wang, *J. Org. Chem.*, 2003, **68**, 1443; (d) B. M. Trost and D. P. Curran, *Tetrahedron Lett.*, 1981, **22**, 1287; (e) N. Samakkanad, P. Katrun, T. Techajaroonjit, S. Hlekhlai, M. Pohmakotr, V. Reutrakul, T. Jaipetch, D. Soorukram and C. Kuhakarn, *Synthesis*, 2012, 1693.
- 3 (a) Q. Lu, J. Zhang, G. Zhao, Y. Qi, H. Wang and A. W. Lei, J. Am. Chem. Soc., 2013, 135, 11481; (b) W. Wei, C. Liu, D. Yang, J. Wen, J. You, Y. Suo and H. Wang, Chem. Commun., 2013, 49, 10239; (c) A. K. Singh, R. Chawla and L. D. S. Yadav, Tetrahedron Lett., 2014, 55, 4742; (d) X. Tang, L. Huang, Y. Xu, J. Yang, W. Wu and H. Jiang, Angew. Chem. Int. Ed., 2014, 53, 4205; (e) V. S. Rawat, P. L. M. Reddy and B. Sreedhar, RSC Adv., 2014, 4, 5165; (f) A. K. Singh, R. Chawla, T. Keshari, V. K. Yadav and L. D. S. Yadav, Org. Biomol. Chem., 2014, 12, 8550. (g) H. Jiang, Y. Cheng, Y. Zhang and S. Yu, Eur. J. Org. Chem., 2013, 5485.
- For selected reviews on photo-redox catalysis, see: (a) T. P. Yoon, M. A. Ischay and J. Du, *Nat. Chem.*, 2010, 2, 527; (b) J. M. R. Narayanam and C. R. J. Stephenson, *Chem. Soc. Rev.*, 2011, 40, 102; (c) J. Xuan and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2012, 51, 6828; (d) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, 113, 5322; (e) D. M. Schultz and T. P. Yoon, *Science*, 2014, 343,985; (f) D. Ravelli, D. Dondi, M. Fagnoni and A. Albini, *Chem. Soc. Rev.*, 2009, 38, 1999.
- 5 (a) Q.-Q. Zhou, W. Guo, W. Ding, X. Wu, Xi. Chen, L.-Q. Lu and W.-J. Xiao, Angew. Chem. Int. Ed., 2015, 54, 11196; (b) A. U. Meyer, S. Jager, D. P. Hari and B. König, Adv. Synth. Catal., 2015, 357, 2050; (c) J. Du, K. L. Skubi, D. M. Schultz and T. P. Yoon, Science, 2014, 344, 392; (d) J. D. Nguyen, B. S. Matsuura and C. R. J. Stephenson, J. Am. Chem. Soc., 2014, 136, 1218; (e) A. Noble and D. W. C. MacMillan, J. Am. Chem. Soc., 2014, 136, 11602; (f) W. G. Fan and P. X. Li, Angew. Chem. Int. Ed., 2014, 53, 12201; (g) E. Arceo, E. Montroni and P. Melchiorre, Angew. Chem. Int. Ed., 2014, 53, 12064; (h) S. Cai, K. Yang and D. Z. Wang, Org. Lett., 2014, 16, 2606; (i) S.

- 6 (a) S. Cai, X. Zhao, X. Wang, Q. Liu, Z. Li and D. Z. Wang, Angew. Chem. Int. Ed., 2012, 51, 8050; (b) S. Maity, M. Z. Zhu, R. S. Shinabery and N. Zheng, Angew. Chem. Int. Ed., 2012, 51, 222; (c) Y. Zou, J. Chen, X. Liu, L. Lu, R. Davis, K. A. Jorgensen and W. J. Xiao, Angew. Chem. Int. Ed., 2012, 51, 784; (d) D. A. DiRocco and T. Rovis, J. Am. Chem. Soc., 2012, 134, 8094; (e) M. A. Ischay, M. S. Ament and T. P. Yoon, Chem. Sci., 2012, 3, 2807; (f) S. Lin, M. A. Ischay, C. G. Fry and T. P. Yoon, J. Am. Chem. Soc., 2011, 133, 19350; (i) C. Dai, J. M. R. Narayanam and C. R. J. Stephenson, Nature Chem., 2011, 3, 140; (j) A. McNally, C. K. Prier and D. W. C. MacMillan, Science, 2011, 334, 1114; (k) Y. Q. Zou, L. Q. Lu, L. Fu, N. J. Chang, J. Rong, J. R. Chen and W. J. Xiao, Angew. Chem. Int. Ed., 2011, 50, 7171; (I) D. Kalyani, K. B. McMurtrey, S. R. Neufeldt and M. S. Sanford, J. Am. Chem. Soc., 2011, 133, 18566; (m) M. Rueping, D. Leonori and T. Poisson, Chem. Commun., 2011, 47, 9615; (n) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska and C. R. J. Stephenson, J. Am. Chem. Soc., 2011, 133, 4160; (o) D. A. Nagib and D. W. C. MacMillan, Nature, 2011, 480, 224.
- 7 (a) C. J. Wallentin, J. D. Nguyen, P. Finkbeiner and C. R. J. Stephenson, J. Am. Chem. Soc., 2012, 134, 8875; (b) J. W. Tucker and C. R. J. Stephenson, Org. Lett. 2011, 13, 5468; (c) R. S. Andrews, J. J. Becker and M. R. Gagné, Angew. Chem. Int. Ed., 2010, 49, 7274; (d) J. W. Tucker, J. D. Nguyen, J. M. R. Narayanam, S. W. Krabbe and C. R. J. Stephenson, Chem. Commun., 2010, 46, 4985; (e) H. W. Shih, M. N. Vander Wal, R. L. Grange and D. W. C. MacMillan, J. Am. Chem. Soc., 2010, 132, 13600; (f) A. G. Condie, J. C. González-Gómez and C. R. J. Stephenson, J. Am. Chem. Soc., 2010, 132, 13600; (f) A. G. Condie, J. C. González-Gómez and C. R. J. Stephenson, J. Am. Chem. Soc., 2010, 132, 8572; (h) J. Du and T. P. Yoon, J. Am. Chem. Soc., 2009, 131, 14604; (i) D. A. Nicewicz and D. W. C. MacMillan, Science, 2008, 322, 77.
- (a) Q. Lu, J. Zhang, F. Wei, Y. Qi, H. Wang, Z. Liu and A. W. Lei, Angew. Chem. Int. Ed., 2013, 52, 7156; (b) X. Li, X. Xu, P. Hu, X. Xiao and C. Zhou, J. Org. Chem., 2013, 78, 7343.
- 9 For instructive uses of KI in organic synthesis, see: (a) S. Tang, Y. Wu, W. Liao, R. Bai, C. Liu and A. W. Lei, *Chem. Commun.*, 2014, **50**, 4496; (b) P. Katrun, S. Chiampanichayakul, K. Korworapan, M. Pohmakotr, V. Reutrakul and T. Jaipetch, C. Kuhakarn, *Eur. J. Org. Chem.*, 2010, 5633.
- 10 (a) D. P. Hari and B. König, Org. Lett., 2011, 13, 3852; (b) M. Neumann, S. Füldner, B. König and K. Zeitler, Angew. Chem. Int. Ed., 2011, 50, 951; (c) D. Cantillo, O. de Frutos, J. A. Rincón, C. Mateos and C. O. Kappe, Org. Lett., 2014, 16, 896; (d) Q. Y. Meng, J. J. Zhong, Q. Liu, X. W. Gao, H. H. Zhang, T. Lei, Z. J. Li, K. Feng, B. Chen, C. H. Tung and L. Z. Wu, J. Am. Chem. Soc., 2013, 135, 19052.
- (a) X. Li, X. Xu and X. Shi, *Tetrahedron Lett.*, 2013, 54, 3071;
  (b) V. Nair, A. Augustine and T. D. Suja, *Synthesis*, 2002, 2259;
  (c) A. Kariya, T. Yamaguchi, T. Nobuta, N. Tada, T. Miura and A. Itoh, *RSC Adv.*, 2014, 4, 13191.
- (a) R. Singh, B. K. Allam, N. Singh, K. Kumari, S. K. Singh and K. N. Singh, *Org. Lett.*, 2015, **17**, 2656; (b) S. Handa, J. C. Fennewald and B. H. Lipshutz, *Angew. Chem. Int. Ed.*, 2014, **53**, 3432.
- For visible-light-enabled iodine radical formation, see: (a) J. M. Gardner, M. Abrahamsson, B. H. Farnum and G. J. Meyer,

**4** | J. Name., 2012, **00**, 1-3

#### Journal Name

## J. Am. Chem. Soc., 2009, **131**, 16206; (b) N. S. Lewis and D. G. Nocera, *Proc. Natl. Acad. Sci. U.S.A.*, 2006, **103**, 15729.

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