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Visible-Light-Enabled Decarboxylative Sulfonylation of Cinnamic Acids with Sulfonylhydrazides under Transition-Metal-Free Conditions

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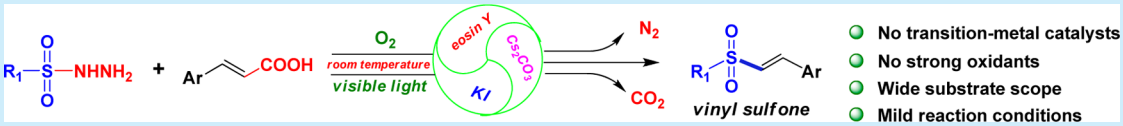
Supporting Information

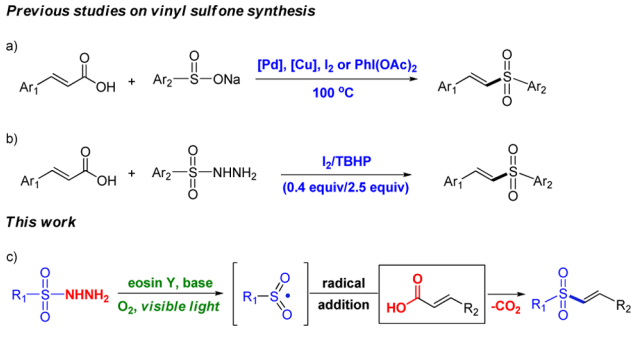


ABSTRACT: Decarboxylative cross-coupling reactions of cinnamic acids with sulfonylhydrazides were explored using oxygen as the sole terminal oxidant, realizing a conceptually novel technology for vinyl sulfone synthesis under the synergistic interactions of visible light irradiation, organic dye-type photocatalyst eosin Y, KI, and Cs_2CO_3 at room temperature.

Visible-light-promoted decarboxylative cross-coupling reactions[1] have emerged as powerful synthetic technologies in organic synthesis because of their potential advantages, e.g., readily available starting materials, simple operation, and nontoxic and easily removed byproduct (CO_2 as the only byproduct), bringing about a range of organic transformations involving various C−N, C−F, and C−C bond formations. A pioneering work by Lei et al. reported an inspirational amide synthesis via visible-light-enabled decarboxylative amidation of α-keto acids and amines.[2] Synergistic combinations of photoredox catalysis with transition metal catalysis were also shown to be effective to afford a new alternative cross-coupling scenario, in which simple, readily available carboxylic acid derivatives could be systematically employed as coupling partners under mild reaction conditions; such activities have been regularly reported.[3] However, the formation of C−S via visible-light-promoted decarboxylation coupling strategy remains an underdeveloped process and continues to capture considerable attention from the synthetic community.

Vinyl sulfones are known to be highly versatile encountered motifs,[4] which have found widespread applications in many biological researches as activity-based protein profiling (ABPP) probes and covalent protease inhibitors.[5] Their important utilities have encouraged considerable synthetic efforts to develop direct, mild, and efficient protocols enabling their preparations. Synthetically, previously described methodologies for accessing vinyl sulfones are to take advantage of the oxidation of the vinyl sulfides, β-elimination of seleno- or halo-sulfones, or condensation of sulfonylacetic acids with aromatic aldehydes.[6] Alternatively, new, more efficient cross-coupling reactions of sulfinate salts and vinyl halides, alkenyl boronic acids, alkenes, or cinnamic acids were also achieved in the presence of strong oxidants or transition metal catalysts.[7] Some examples are depicted in Scheme 1; Guo et al. disclosed vinyl sulfones

Scheme 1. Various Synthetic Routes to Vinyl Sulfones Formation



synthesis via copper-catalyzed decarboxylative sulfonylation of cinnamic acids with sodium sulfinates.[7a] Other transition metal complexes and strong oxidants, e.g., Pd catalyst,[7b] I_2,[7c] and $PhI(OAc)_2$,[7d] were shown effective in similar scenarios (Scheme 1a). Recently, I_2/TBHP-catalyzed decarboxylative sulfonylation of cinnamic acids and sulfonyl hydrazides was reported by Singh et al. for synthesis of vinyl sulfones (Scheme 1b).[7e] However, these established methodologies suffer from one or more drawbacks, e.g., the use of unstable and expensive reagents, harsh reaction conditions, and employment of transition metal catalysts or strong oxidants. It remains highly desirable to

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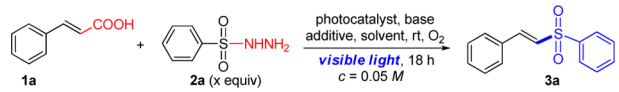
Table 1. Identification of the Optimal Reaction Conditions



1a 2a (x equiv) 3a

entry	2a (equiv)	PC (x mol %)[a]	base (equiv)	solvent (v/v)	additive (equiv)	yield (%)[c]
1	1.5	eosin Y (2)	Na_2CO_3 (2.2)	DMF	KI (1.0)	trace
2	1.5	eosin Y (2)	Cs_2CO_3 (2.2)	DMF	KI (1.0)	31
3	1.5	eosin Y (2)	Cs_2CO_3 (2.2)	DMF/H_2O (8:1)	KI (1.0)	35
4	1.5	eosin Y (2)	Cs_2CO_3 (2.2)	DMF/H_2O (3:1)	KI (1.0)	24
5	1.5	eosin Y (2)	Cs_2CO_3 (2.2)	DMF/H_2O (15:1)	KI (1.0)	42
6	1.5	eosin Y (2)	CsOAc (2.2)	DMF/H_2O (15:1)	KI (1.0)	30
7	1.5	eosin Y (2)	Na_3PO_4 (2.2)	DMF/H_2O (15:1)	KI (1.0)	trace
8	1.5	eosin Y (2)	K_2CO_3 (2.2)	DMF/H_2O (15:1)	KI (1.0)	NR
9	1.5	eosin Y (2)	NaOH (2.2)	DMF/H_2O (15:1)	KI (1.0)	decomp
10	1.5	eosin Y (2)	DBU (2.2)	DMF/H_2O (15:1)	KI (1.0)	36
11	2.2	eosin Y (1)	CS_2CO_3 (3.0)	DMF/H_2O (15:1)	KI (1.0)	73
12	3.0	eosin Y (1)	Cs_2CO_3 (3.5)	DMF/H_2O (15:1)	KI (1.0)	70
13	2.2	eosin Y (1)	Cs_2CO_3 (3.0)	ACN/H_2O (15:1)	KI (1.0)	56
14	2.2	eosin Y (1)	Cs_2CO_3 (3.0)	DMA/H_2O (15:1)	KI (1.0)	58
15	2.2	eosin Y (1)	Cs_2CO_3 (3.0)	EtOH/H_2O (15:1)	KI (1.0)	trace
16[b]	2.2	[Ru] (1)	Cs_2CO_3 (3.0)	DMF/H_2O (15:1)	KI (1.0)	71

[a]Eosin Y was used. [b][Ru] = $Ru(bpy)_3Cl_2·6H_2O$. [c]Yield of isolated product

discover new and straightforward approaches for the facile preparation of vinyl sulfones, with use of less catalysts or oxidants, simpler substrate structures, or milder reaction conditions.

Leveraging recent remarkable achievements in uncovering robust synthetic reactions that relied on visible-light-promoted photocatalysis,[8−10] it is particularly appealing to explore its possible applications in designing and identifying useful paradigms for alternative vinyl sulfones synthesis. As shown in Scheme 1c, we anticipated that an oxidative denitrogenation event might be triggered on sulfonylhydrazide under visible-light-promoted photoredox catalysis, thereby converting it into sulfonyl radical species, which would subsequently undergo a sequence of radical addition, oxidation, and decarboxylation to afford vinyl sulfones. Gratifyingly, an unusually simple and versatile decarboxylative sulfonylation of sulfonyl hydrazides with cinnamic acids was eventually accomplished after careful optimization of reaction conditions.

With cinnamic acid **1a** and benzenesulfonohydrazide **2a** as the model substrates, we started the optimization with a catalytic amount of organic dye type eosin Y[11] (2 mol %) as photocatalyst and a 45 W household fluorescent compact bulb as the visible light source. However, only trace amount of desired product was detectable when the reaction was conducted in dimethylformamide (DMF) in the presence of a substoichiometric amount of Na_2CO_3 (2.2 equiv) and KI (1.0 equiv) under a balloon-oxygen atmosphere at room temperature (entry 1, Table 1). Fortunately, a switch of the base Na_2CO_3 to Cs_2CO_3 showed dramatic improvement of the reactivity (31% isolated yield, entry 2). Next, a different volume ratio of DMF/H_2O was explored (entries 3−5), from which a 15:1 mixed solvent of DMF and H_2O explicitly turned out to be optimal (42% yield). Then, a series of bases (CsOAc, Na_3PO_4, K_2CO_3, NaOH, and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU)) were screened (entries 6−10), but all resulted in either a lower product yield or complete inhibition in reactivities. We note that a respectable 73% yield of desired product was recorded by increasing the amount of **2a** (2.2 equiv) and Cs_2CO_3 (3.0 equiv) (entry 11). Further increased loading of **2a** and Cs_2CO_3 was found to be disadvantageous for the product yield (entry 12). The effect of KI was also proven fairly critical (see the Supporting Information). Other attempts employing acetonitrile (ACN), dimethylacetamide (DMA), or EtOH in place of DMF in the mixed solvent were again confirmed to negatively influence the reaction efficiency (entries 13−15). Finally, a transition metal photosensitizer $Ru(bpy)_3Cl_2$ was investigated under otherwise identical reaction conditions; desired product **3** was produced in a slightly lower yield (71%, entry 16). However, in terms of the cost and environmental friendliness, organic dye type eosin Y seems to exhibit a superior alternative to its transition-metal-derived counterpart $Ru(bpy)_3Cl_2$. Together these screenings built up an efficient visible light photoredox decarboxylative sulfonylation of cinnamic acids with sulfonyl hydrazides relying on the synergy of 1 mol % eosin Y photocatalyst, 3.00 equiv of Cs_2CO_3 base, 1.00 equiv of KI additive, and DMF/H_2O (15:1) as the solvent.

With the conditions in hand, a series of cinnamic acids bearing a variety of functional groups were next attempted to react with **2a**; the results were summarized in Scheme 2. Generally, corresponding vinyl sulfone product **3** was smoothly produced in moderate-to-excellent isolated yields (50−92%). Cinnamic acids with a *para*- or *ortho*-methyl substituent on the aromatic ring could be unambiguously converted into the products **3b** and **3c** in 54 and 76% yield, respectively. Some of the frequently encountered functional groups, e.g., bromo (**3d**), chloro (**3e**−**3i**), fluoro (**3j**−**3l**), trifluoromethyl (**3m** and **3n**), nitro (**3o**), and trifluoromethoxy (**3p**), were demonstrated to be well-tolerated in these transformations in terms of isolated yield (50−92%).[12] The electronic characteristics of the cinnamic acid aromatic ring substituents (R_1) were found to have a crucial effect on the reactivity, where complicated mixtures were observed with the substrates carrying R_1, which is an electron-donating group (i.e., R_1 = OMe or thienyl).

To further investigate the substrate scope of this protocol, a range of sulfonylhydrazides **2** were next exposed to the optimal reaction conditions to react with the **1a**. As shown in Scheme 3, sulfonylhydrazides with both the electron-donating (**4a**−**4g**) and electron-withdrawing (**4h**−**4m**) nature of the substituents on the aromatic ring could smoothly undergo this transformation to provide the corresponding products in various isolated yields

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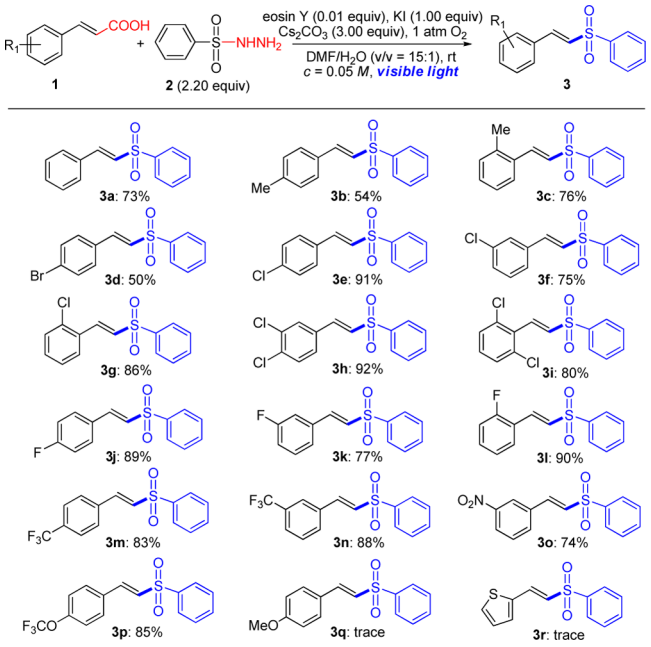
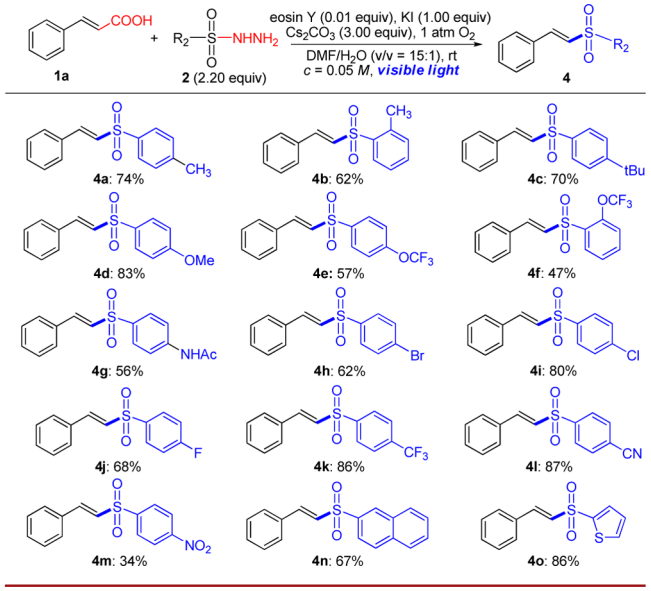
Scheme 2. Reactivity Screenings on Cinnamic Acid 1



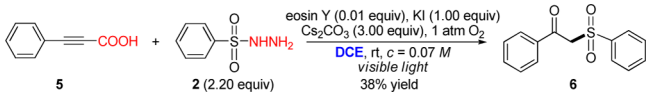
Scheme 3. Reactivity Screenings on Sulfonylhydrazides 2



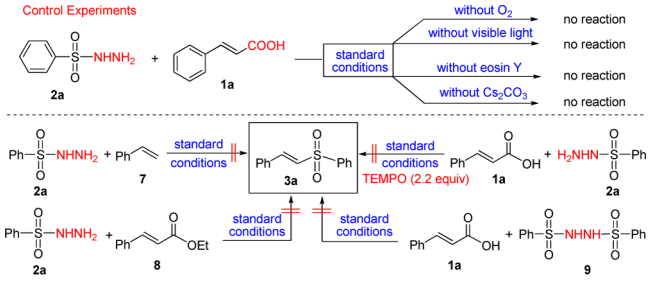
(34−87%). Substrates possessing a naphthalenyl (**4n**) or a thienyl (**4o**) group were also accommodated in the transformations.

Finally, it is interesting that when 3-phenylpropiolic acid **5** was employed as the substrate, only *β*-keto sulfone **6** was obtained in 38% isolated yield by using 1,2-dichloroethane (DCE) as the solvent under otherwise identical reaction conditions (Scheme 4).[13]

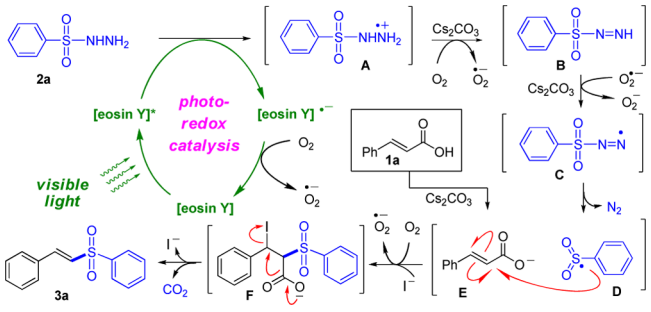
Scheme 4. Decarboxylative Oxysulfonylation of 3-Phenyl-Propiolic Acid with Benzenesulfonohydrazide



Scheme 5. Experimental Probes on Reaction Parameters



Scheme 6. Mechanistic Proposal



Several control experiments on reaction parameters were next carried out to shed light on the potential reaction pathways; the results were compiled in Scheme 5. Reactions conducted without the oxygen, visible light irradiation, eosin Y, or Cs_2CO_3 only led to complete inhibition of the reactivity, thereby confirming explicitly that the reproducible formation of **3a** requires all of these. When 2.2 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was purposefully introduced into the reaction system as a radical scavenger, the reaction was found to be totally inhibited, suggesting a radical pathway is involved in this reaction. Styrene **7** or ethyl cinnamate **8** was subsequently subjected to the standard reaction conditions to couple with **2a**; no desired vinly sulfone product **3a** was detected at all. Finally, a switch of **2a** to protected sulfonohydrazide **9** also resulted in failure.

To determine whether the excited photocatalyst was quenched by iodine anion or **2a** in this transformation, a number of fluorescence quenching (Stern−Volmer) experiments on eosin Y were therefore conducted (see the Supporting Information). A notable decrease of fluorescence intensity of eosin Y was recorded with the increase in the concentration of **2a**, which strongly indicated that **2a** should participate in single-electron transfer with the photocatalyst under the standard reaction conditions.[8b]

To account for the above investigations and the observed reactivities, a plausible mechanistic network was proposed in Scheme 6. Upon exposure to visible light stimulation, sulfonylhydrazide **2a** would be intercepted by the excited-state species eosin Y to produce a highly active radical **A**, which should undergo subsequent electron transfer with oxygen, followed by a sequential N−H abstractions, thereby giving rise to the key sulfonyl radical **D**[14] with the release of nitrogen. Then, a sequence of radical addition, oxidation, and iodine anion capture would take place to afford intermediate **F**.[15] Finally, intermediate **F** would undergo the elimination of carbon dioxide and iodine anion to yield the final (*E*)-*α*,*β*-unsaturated phenyl sulfone product, **3a**.

Stimulated by the original design concept of exploring a novel technology for vinyl sulfone formation by means of visible-light photoredox catalysis, we have disclosed herein that a diverse

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series of vinyl sulfones having numerous useful functionalities could be smoothly produced in good-to-excellent yields with oxygen as the sole terminal oxidant, and only nitrogen and carbon dioxide as the byproducts under considerably mild reaction conditions. We note that the established methodology, by contrast with the previous approaches,[6,7] refrains from using transition metal catalysts and strong oxidants and operates efficiently at room temperature. Because of the broadly appreciated importance of vinyl sulfone substances in biological and pharmaceutical contexts, it is envisioned that this discovery would find wider applications and motivate further studies in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01353.

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Xuan, J.; Zhang, Z.-G.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2015**, *54*, 15632. (b) Shen, C.; Zhang, P.; Sun, Q.; Bai, S.; Hor, T. S. A.; Liu, X. *Chem. Soc. Rev.* **2015**, *44*, 291. (c) Weaver, J. D.; Recio, A., III; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846. (d) Rodríguez, N.; Gooßen, L. J. *Chem. Soc. Rev.* **2011**, *40*, 5030. (e) Gooßen, L. J.; Rodríguez, N.; Gooßen, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 3100.

(2) Liu, J.; Liu, Q.; Yi, H.; Qin, C.; Bai, R.; Qi, X.; Lan, Y.; Lei, A. *Angew. Chem., Int. Ed.* **2014**, *53*, 502.

(3) For selected examples of combining photoredox catalysis with transition metal catalysis, see (a) Ventre, S.; Petronijevic, F. R.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2015**, *137*, 5654. (b) Xuan, J.; Zeng, T.-T.; Feng, Z.-J.; Deng, Q.-H.; Chen, J.-R.; Lu, L.-Q.; Xiao, W.-J.; Alper, H. *Angew. Chem., Int. Ed.* **2015**, *54*, 1625. (c) Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science* **2014**, *345*, 433. (d) Kalyani, D.; McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18566.

(4) (a) Back, T. G.; Clary, K. N.; Gao, D. *Chem. Rev.* **2010**, *110*, 4498. (b) Choi, J.; Martín-Gago, P.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *136*, 12161. (c) Alba, A.-N. R.; Companyó, X.; Rios, R. *Chem. Soc. Rev.* **2010**, *39*, 2018. (d) Ettari, R.; Tamborini, L.; Angelo, I. C.; Micale, N.; Pinto, A.; De Micheli, C.; Conti, P. *J. Med. Chem.* **2013**, *56*, 5637. (e) Dunny, E.; Doherty, W.; Evans, P.; Malthouse, J. P. G.; Nolan, D.; Knox, A. J. S. *J. Med. Chem.* **2013**, *56*, 6638.

(5) (a) Chauhan, P.; Hadad, C.; López, A. H.; Silvestrini, S.; La Parola, V.; Frison, E.; Maggini, M.; Prato, M.; Carofiglio, T. *Chem. Commun.* **2014**, *50*, 9493. (b) van der Westhuyzen, R.; Strauss, E. *J. Am. Chem. Soc.* **2010**, *132*, 12853.

(6) (a) Matteucci, M.; Bhalay, G.; Bradley, M. *Org. Lett.* **2003**, *5*, 235. (b) Huang, X.; Duan, D.; Zheng, W. *J. Org. Chem.* **2003**, *68*, 1958. (c) Nair, V.; Augustine, A.; Suja, T. D. *Synthesis* **2002**, 2259. (d) Qian, H.; Huang, X. *Synlett* **2001**, *2001*, 1913. (e) Vollhardt, J.; Gais, H.; Lukas, K. L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 696. (f) Ley, S. V.; Simpkins, N. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1281. (g) Hopkins, P. B.; Fuchs, P. L. *J. Org. Chem.* **1978**, *43*, 1208. (h) Posner, G. H.; Brunelle, D. J. *J. Org. Chem.* **1972**, *37*, 3547. (i) Chodroff, S.; Whitmore, W. F. *J. Am. Chem. Soc.* **1950**, *72*, 1073.

(7) (a) Jiang, Q.; Xu, B.; Jia, J.; Zhao, A.; Zhao, Y.; Li, Y.; He, N.; Guo, C. *J. Org. Chem.* **2014**, *79*, 7372. (b) Guo, R.; Gui, Q.; Wang, D.; Tan, Z. *Catal. Lett.* **2014**, *144*, 1377. (c) Gao, J.; Lai, J.; Yuan, G. *RSC Adv.* **2015**, *5*, 66723. (d) Katrun, P.; Hlekhlai, S.; Meesin, J.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Org. Biomol. Chem.* **2015**, *13*, 4785. (e) Singh, R.; Allam, B. K.; Singh, N.; Kumari, K.; Singh, S. K.; Singh, K. N. *Org. Lett.* **2015**, *17*, 2656. (f) Xu, Y.; Tang, X.; Hu, W.; Wu, W.; Jiang, H. *Green Chem.* **2014**, *16*, 3720. (g) Huang, F.; Batey, R. A. *Tetrahedron* **2007**, *63*, 7667. (h) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Parisi, L. M.; Bernini, R. *J. Org. Chem.* **2004**, *69*, 5608.

(8) For selected reviews on photoredox catalysis, see (a) Hari, D. P.; König, B. *Chem. Commun.* **2014**, *50*, 6688. (b) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322. (c) Xuan, J.; Xiao, W.-J. *Angew. Chem., Int. Ed.* **2012**, *51*, 6828.

(9) (a) Hari, D. P.; Schroll, P.; König, B. *J. Am. Chem. Soc.* **2012**, *134*, 2958. (b) Hari, D. P.; Hering, T.; König, B. *Org. Lett.* **2012**, *14*, 5334. (c) Zhang, J.; Wang, L.; Liu, Q.; Yang, Z.; Huang, Y. *Chem. Commun.* **2013**, *49*, 11662. (d) Rueping, M.; Zhu, S.; Koenigs, R. M. *Chem. Commun.* **2011**, *47*, 8679. (e) Zhu, S.; Rueping, M. *Chem. Commun.* **2012**, *48*, 11960. (f) Srivastava, V. P.; Yadav, A. K.; Yadav, L. D. S. *Synlett* **2013**, *24*, 465. (g) Rueping, M.; Vila, C. *Org. Lett.* **2013**, *15*, 2092. (h) Yoo, W.; Tsukamoto, T.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2015**, *54*, 6587. (i) Li, J.; Zhang, J.; Tan, H.; Wang, D. Z. *Org. Lett.* **2015**, *17*, 2522. (j) Meyer, A. U.; Jager, S.; Prasad Hari, D.; König, B. *Adv. Synth. Catal.* **2015**, *357*, 2050. (k) Reckenthäler, M.; Griesbeck, A. G. *Adv. Synth. Catal.* **2013**, *355*, 2727. (l) Cai, S.; Chen, D.; Xu, Y.; Weng, W.; Li, L.; Zhang, R.; Huang, M. *Org. Biomol. Chem.* **2016**, *14*, 4205.

(10) (a) Cai, S.; Zhao, X.; Wang, X.; Liu, Q.; Li, Z.; Wang, D. Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 8050. (b) Wallentin, C. J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875. (c) Liu, Q.; Li, Y.-N.; Zhang, H.; Chen, B.; Tung, C.; Wu, L. *Chem. - Eur. J.* **2012**, *18*, 620. (d) Kalyani, D.; McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18566. (e) Zou, Y. Q.; Lu, L. Q.; Fu, L.; Chang, N. J.; Rong, J.; Chen, J. R.; Xiao, W. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 7171. (f) Yu, J.; Zhang, L.; Yan, G. *Adv. Synth. Catal.* **2012**, *354*, 2625. (g) Xuan, J.; Feng, Z.-J.; Duan, S.-W.; Xiao, W.-J. *RSC Adv.* **2012**, *2*, 4065. (h) Ischay, M. A.; Lu, Z.; Yoon, T. P. *J. Am. Chem. Soc.* **2010**, *132*, 8572. (i) Rueping, M.; Zhu, S.; Koenigs, R. M. *Chem. Commun.* **2011**, *47*, 12709. (j) Cai, S.; Zhang, S.; Zhao, Y.; Wang, D. Z. *Org. Lett.* **2013**, *15*, 2660. (k) Majek, M.; von Wangelin, A. J. *Chem. Commun.* **2013**, *49*, 5507.

(11) (a) Cantillo, D.; de Frutos, O.; Rincón, J. A.; Mateos, C.; Kappe, C. O. *Org. Lett.* **2014**, *16*, 896. (b) Meng, Q. Y.; Zhong, J.; Liu, Q.; Gao, X.; Zhang, H.; Lei, T.; Li, Z. J.; Feng, K.; Chen, B.; Tung, C.; Wu, L. *J. Am. Chem. Soc.* **2013**, *135*, 19052. (c) Neumann, M.; Füldner, S.; König, B.; Zeitler, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 951. (d) Hari, D. P.; König, B. *Org. Lett.* **2011**, *13*, 3852. (e) Majek, M.; Filace, F.; von Wangelin, A., J. *Beilstein J. Org. Chem.* **2014**, *10*, 981.

(12) The decarboxylative sulfonylation could be conveniently performed at gram-scale; see the Supporting Information for details.

(13) For the mechanistic proposal for β-keto sulfone **6** formation, see the Supporting Information.

(14) (a) Li, X.; Xu, X.; Hu, P.; Xiao, X.; Zhou, C. *J. Org. Chem.* **2013**, *78*, 7343. (b) Taniguchi, T.; Sugiura, Y.; Zaimoku, H.; Ishibashi, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 10154. (c) Li, X.; Shi, X.; Fang, M.; Xu, X. *J. Org. Chem.* **2013**, *78*, 9499.

(15) (a) Nair, V.; Augustine, A.; George, T. G.; Nair, L. G. *Tetrahedron Lett.* **2001**, *42*, 6763. (b) Zhang, N.; Yang, D. S.; Wei, W.; Yuan, L.; Cao, Y. J.; Wang, H. *RSC Adv.* **2015**, *5*, 37013.

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