Visible-Light-Induced C=C Bond Cleavage of Enaminones for the Synthesis of 1,2-Diketones and Quinoxalines in Sustainable Medium

Shuo Cao,^[a] Shanshan Zhong,^[a] Luoting Xin,^[a] Jie-Ping Wan,^{*[a]} and Chengping Wen^{*[b]}

The C=C double bond cleavage of enaminones has been realized under ambient conditions through visible-light catalysis in the presence of Rose Bengal, which leads to the synthesis of a class of 1,2-diketones without using any metal catalyst. In addition, the one-pot synthesis of quinoxalines has also been achieved under identical photocatalytic conditions by making use of the in situ generated 1,2-diketones as intermediates.

Introduction

1,2-Diketones are valuable organic compounds possessing highly enriched reactivity owing to the presence of the characteristic adjacent electron-deficient double carbonyls. Therefore, as the main building blocks, 1,2-diketones have been broadly used in the synthesis of many important organic products such as α -hydroxyl ketone,^[1] N-containing heterocycles,^[2] and carbohydrates.^[3] More notably, the 1,2-diketone fragment has been found to be present in a number of biologically relevant organic molecules.^[4] During the past decades, the efforts of chemists have led to the establishment of several different types of strategies toward the synthesis of 1,2-diketones. Typically, the main synthetic toolbox consists of the oxidation of the α -hydroxyl ketone,^[5] stilbenes,^[6] vicinal dibromoalkanes,^[7] vicinal diols,^[8] enones,^[9] methylene ketones, etc.^[10] And more generally, the oxidative dicarbonylation of internal alkynes has been widely employed to access 1.2-diketones.^[11] Additionally. oxidative cleavage of 1,3-diketones using different oxidants is also known as independently reported by Zhang,^[12] Smonou^[13a] and Yuan.^[13b] On the other hand, new synthetic methods involving unconventional transformation have also been achieved. Jiao and co-workers developed the copper-catalyzed synthesis of 1,2-diketones by the cascade coupling and oxygenation reaction using olefins and hydrazines [Eq. (1) in Scheme 1],^[14] and Yang and Tang et al. reported the 1,2-diketone synthesis using β -ketoaldehydes in the presence of NaClO [Eq. (2) in Scheme 1].^[15] Upon the sustaining efforts, the palla-

[a]	S. Cao, S. Zhong, L. Xin, Dr. JP. Wan
	Key Laboratory of Functional Small Organic Molecules
	Ministry of Education, College of Chemistry and Chemical Engineering
	Jiangxi Normal University
	Nanchang 330022 (P.R. China)
	E-mail: wanjieping@jxnu.edu.cn
[b]	Prof. Dr. C. Wen
	College of Basic Medical Sciences
	Zhejiang Chinese Medical University
	Hangzhou 310053(P.R. China)
	E-mail: cpwen.zcmu@yahoo.com
	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201500139.

ChemCatChem 0000, 00, 0 – 0 Wiley Online Library

These are not the final page numbers! 77

1



Scheme 1. Different routes for the synthesis of 1,2-diketone.

dium-catalyzed bifunctionalization of olefins using nitroalkanes^[16] and the palladium- or copper-catalyzed decarboxylative coupling reactions of aryl propiolic acids and aryl iodides^[17] have also been found as attractive methods for 1,2-diketone synthesis. Generally, most of these known methods encounter one or more limits such as the dependence on transition-metal catalyst, high-temperature heating or employment of additional oxidants. In this context, searching for alternatively sustainable and mild approaches is still highly desirable work in the area of 1,2-diketone synthesis.

Enaminones are a class of broadly investigated organic compounds in organic synthesis. Owing to their easy availability and highly versatile reactivity, enaminones have been extensively employed as main building blocks for the synthesis of a great variety of organic products.^[18] Predominantly, most enaminone- and similar enamine-based organic syntheses utilize one or more of enaminones' reactive sites such as the amino



group, the nucleophilic α -carbon, the electrophilic β -carbon, and the ketone carbonyl, etc.^[19] Interestingly, rather rare reports on enaminone-based synthesis involving the functionalization of the C=C double bond have been known. During our research efforts on the enaminone and analogous substrates participated organic synthesis,^[20] we have recently disclosed that the enaminones are able to undergo the C=C bond cleavage to take part in the construction of pyridines by acting as C4 building block.^[21] Inspired by this transformation, we have conducted investigation on the catalytic production of 1,2-diketones by making use of the C=C bond cleavage-based transformation of proper enaminone substrates. Primary attempts by Wasserman and Ives have revealed that the 1,2-diketones are accessible from enaminones under catalytic conditions of 650 W lamp heating and -78°C to room temperature operation.^[22a,b] This method has been seriously restricted from practical synthetic application by the inconvenient and harsh conditions. Therefore, an operationally practical catalytic protocol of improved applicability is urgently required to complement this type of 1,2-diketone synthesis. Herein, we report the synthesis of 1,2-diketones based on the C=C bond cleavage of enaminones under sustainable catalytic conditions consist of Rose Bengal assistance (metal-free), visible-light radiation and roomtemperature stirring in bio-based ethyl lactate (EL) medium [Eq. (3) in Scheme 1].^[23] Notably, this catalytic transformation also allows the direct one-pot synthesis of useful quinoxalines^[24] by employing o-phenylenediamines as reaction partners without any modification on the reaction conditions [Eq. (4) in Scheme 1].

Results and Discussion

Initially, enaminone 1 a was selected as the model substrate to optimize the reaction parameters. At first, control experiments in the absence of visible light and/or photocatalyst (Rose Bengal) were conducted. The results demonstrated that in the absence of either visible light or Rose Bengal no production of expected 1,2-diketone product 2a occurred (entries 1-3, Table 1). On the other hand, the conditions with both visiblelight radiation and Rose Bengal presence allowed successful C=C bond cleavage to produce diketone 2a with moderate yield (entry 4, Table 1). On the basis of the result, prolonging the reaction time to 48 h gave the highest yield (entries 5-7, Table 1). Notably, further attempts in improving the reaction efficiency by varying the reaction medium using different candidates such as water, lactic acid (LA), ethanol, EL, DMF, and AcOH proved that EL, which was well known as a nontoxic, biomass-available, cheap, and easily degradable green organic solvent,^[25] was found as the best medium for the reaction by providing a yield of 92% (entries 8-13, Table 1). Finally, the favorable loading of Rose Bengal was found as 5 mol% according to the data provided by the entries using different amounts of Rose Bengal (entries 14-15, Table 1).

With the results from the systematic optimization in hand, the application scope of this photocatalytic protocol on the synthesis of different 1,2-diketones was then explored by subjecting various enaminone substrates **1**. According to the re-



[a] General conditions: enaminone **1a** (0.3 mmol), Rose Bengal sodium salt (5 mol%) in 2 mL solvent, radiation with 15 W LED bulb at room temperature (EL=ethyl lactate, LA=lactic acid). [b] Yield of isolated product. [c] Reaction in black. [d] Reaction without Rose Bengal. [e] 2.5 mol% Rose Bengal. [f] 7.5 mol%Rose Bengal.

Table 2. Scope of metal-free photocatalytic 1,2-diketone synthesis.O15 W white LED bulbO Ar^1 $Rose Bengal$ Ar^1 Ar^2 $Rose Bengal$ Ar^1 Ar^2 $Rose Bengal$ Ar^1 Ar^2 $Rose Bengal$ Ar^2 $Ar^$				
Ar ¹	Ar ²	Product	Yield [%] ^[a]	
Ph	Ph	2 a	92	
4-BrC ₆ H₄	Ph	2 b	94	
4-CIC ₆ H ₄	Ph	2 c	95	
4-MeC ₆ H₄	Ph	2 d	80	
2,5-(Me) ₂ C ₆ H ₃	Ph	2 e	75	
4-MeOC ₆ H ₄	Ph	2 f	85	
4-CIC ₆ H ₄	$4-FC_6H_4$	2 g	77	
4-CH ₃ OC ₆ H ₄	$4-FC_6H_4$	2 h	61	
4-CH ₃ C ₆ H ₄	$4-FC_6H_4$	2i	83	
4-BrC ₆ H ₄	$4-FC_6H_4$	2j	76	
2,5-(Me) ₂ C ₆ H ₃	$4-FC_6H_4$	2 k	75	
4- <i>i</i> PrC ₆ H ₄	$4-FC_6H_4$	21	68	
4-CH ₃ OC ₆ H ₄	$4-CH_3OC_6H_4$	2 m	27	
naphthyl	Ph	2 n	63	
[a] Yield of isolated product.				

sults showing in Table 2, α -aryl enaminones were generally applicable for the synthesis of enaminones **2** through photocatalysis. A variety of different functional groups, including alkyl, alkoxyl, and halogen in both Ar¹ and Ar² tolerated the synthesis of corresponding 1,2-diketones well. The effect of substituent in aryls was not observed, and most products were provided



in good to excellent yields. The attempts on running identical synthesis using alkyl functionalized enaminones were not successful. As extended investigation, an entry directly using 1,2diphenylethanone as starting material was also run under the standard reaction conditions, however, no reaction was observed, demonstrating the special reactivity of enaminone 1 for the phtotocatalytic synthesis of 1,2-diketone.

Considering the versatile reactivity of 1,2-ketones, we envisioned that this photocatalytic generation of 1,2-diketones could be employed as a key step for running cascade synthesis of more complex molecules. Under the inspiration, we attempted to subject o-phenylenediamine 3 together with the enaminone under the standard reaction conditions in hope of achieving the direct synthesis of guinoxaline. However, the direct operation gave no expect transformation probably because of the interaction between enaminone 1 and diamine 3 before the formation of diketone. Therefore, we modified the operation by running the first step of 1,2-diketone synthesis before employing diamine 3. To our delight, synthesis of quinoxalines was realized by using the modified operation without employing any other catalyst or additive. The results on the quinoxaline synthesis were given in Table 3. It could be seen from the products that the scope of the synthesis was broad and reliable synthesis of quinoxalines containing different substructures was allowed. Functional groups of different properties such as electron-donating group and electron-withdrawing groups were compatible both to this one-pot synthetic protocol. Generally, relatively lower yields of corresponding products were

observed if o-phenylenediamines containing electron-withdrawing groups such as nitro and halogen were used (4k, 4l, 4r) because of their weaker amino nucleophilicity. Good to excellent yields of guinoxalines were afforded by all other entries.

According to known literature on both the Rose Bengalbased photocatalysis and the enaminone C=C double-bond cleavage, we proposed the reaction mechanism as shown in Scheme 2. Firstly, the inducement of the photon to Rose Bengal (RB) provides the excited state of RB as RB* which returns to the stage of RB by promoting the production of singlet oxygen.^[26]

The singlet oxygen then incorporates to the enaminone to afford peroxide intermediates 5 as described by Wasserman and lves and others.^[22] The automatic decomposition of 5 provides the 1,2-diketones 2, which could be captured in situ by 3







to give guinoxalines 4. The good effect of EL, as observed in previous studies, may be attributed to its special property in solving oxvaen.^[25c,d]

Conclusions

A photocatalytic synthesis of 1,2diketones through the cleavage of enaminones has been achieved under mild and metalfree conditions. Besides offering a sustainable synthetic option in the field of vicinal diketone synthesis, the present catalytic protocol is also applicable for the sustainable one-pot synthesis of quinoxalines by simply employing o-phenylenediamine as the reaction partner. The simplicity in operation and easy availability of all reagents ensure the present work as useful complement to known methods for both the synthesis of 1,2-diketones and quinoxaline heterocycles.

ChemCatChem 0000, 00, 0 – 0 www.chemcatchem.org These are not the final page numbers! 77

3



General procedure for the photocatalytic synthesis of 1,2-diketones

Enaminone **1** (0.3 mmol) and Rose Bengal (0.015 mmol) were charged in a 25 mL round-bottom flask equipped with a stirring bar. EL (2 mL) was added and the mixture was stirred at RT and open-air atmosphere for 48 h under visible-light irradiation (15 W white LED bulb). After completion of the reaction, water (5 mL) was added, and the resulting mixture was extracted with ethyl acetate (3×8 mL). The organic layers were combined and washed with water for 3 times (3×20 mL). The acquired solution was dried overnight with anhydrous MgSO₄. After filtration and removing the solvent under reduced pressure, the residue was subjected to silica gel column chromatography to provide pure products.

Benzil (**2a**).^[13b] Yield: 58 mg, 92%; yellow solid; m.p. 93–96 °C; ¹H NMR (400 MHz, CDCl₃): δ =7.97 (d, J=7.6 Hz, 4H), 7.66 (t, J= 7.6 Hz, 2H), 7.51 ppm (t, J=7.6 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ =194.6, 134.9, 133.0, 129.9, 129.0 ppm.

General procedure for the one-pot synthesis of quinoxalines

Enaminone **1** (0.3 mmol) and Rose Bengal (0.015 mmol) were charged in a 25 mL round-bottom flask equipped with a stirring bar. EL (2 mL) was added. The resulting mixture was stirred at RT and open-air atmosphere for 48 h under irradiation of light (15 W white LED bulb). Subsequently, *o*-phenylenediamine **3** (0.3 mmol) was employed and further stirring of 24 h under identical light irradiation was performed. Upon reaction completion, water (5 mL) was added, and the resulting mixture was extracted with ethyl acetate (3×8 mL). The collected organic layer was then washed with water for 3 times (3×20 mL). The organic solution was dried overnight with anhydrous MgSO₄. After filtration and removing the solvent under reduced pressure, the residue was subjected to silica gel column chromatography to provide pure products.

2,3-Diphenylquinoxaline (**4a**).^[24a] Yield: 68 mg, 80%; white solid; m.p. 120–122 °C; ¹H NMR (400 MHz, CDCl₃): δ =8.17 (q, *J*=3.2 Hz, 2H), 7.74 (q, *J*=3.2 Hz, 2H), 7.51 (d, *J*=7.6 Hz, 4H), 7.32 ppm (d, *J*=7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ =153.5, 141.3, 139.1, 130.0, 129.9, 129.2, 128.9, 128.3 ppm.

Acknowledgements

The work is financially supported by the National Natural and Science Foundation of China (no. 21102059) and a research project from The Department of Education of Jiangxi Province (GJJ13245). C. Wen thanks the support from the National Basic Research Program "973" of China (No. 2014CB5430).

Keywords: amines · ketones · photochemistry · reaction mechanism · sustainable chemistry

- a) P. Hoyos, J. V. Sinisterra, F. Molinari, A. R. Alcántara, P. Domínguez de Maria, Acc. Chem. Res. 2010, 43, 288; b) T. Koike, K. Murata, T. Ikariya, Org. Lett. 2000, 2, 3833; c) P. P. Giovannini, G. Fantin, A. Massi, V. Venturi, P. Pedrini, Org. Biomol. Chem. 2011, 9, 8038.
- [2] a) S. E. Wolkenberg, D. D. Wisnoski, W. H. Leister, Y. Wang, Z. Zhao, C. W. Lindsley, Org. Lett. 2004, 6, 1453; b) X. Deng, N. S. Mani, Org. Lett. 2006, 8, 269; c) J. M. KcKenna, F. Halley, J. E. Souness, I. M. McLay, S. D. Pickett, A. J. Collis, K. Page, I Ahmed, J. Med. Chem. 2002, 45, 2173; d) A. Cab-

rera, P. Sharma, M. Ayala, L. Rubio-Perez, M. Amézquita-Valencia, *Tetra*hedron Lett. **2011**, *52*, 6758.

- [3] A. J. Herrera, M. Rondón, E. Suárez, J. Org. Chem. 2008, 73, 3384.
- [4] a) R. Maurya, R. Singh, M. Deepak, S. S. Handa, P. P. Yadav, P. K. Mishra, *Phytochemistry* **2004**, *65*, 915; b) R. M. Wadkins, J. L. Hyatt, X. Wei, K. J. P. Yoon, M. Wierdl, C. C. Edwards, C. L. Morton, J. C. Obenauer, K. Damodaran, P. Beroza, M. K. Danks, P. M. Potter, *J. Med. Chem.* **2005**, *48*, 2906; c) B. T. Ngadjui, S. F. Kouam, E. Dongo, G. W. F. Kapche, B. M. Abegaz, *Phytochemistry* **2000**, *55*, 915.
- [5] a) B. Karimi, S. Abedi, J. H. Clark, V. Budarin, Angew. Chem. Int. Ed. 2006, 45, 4776; Angew. Chem. 2006, 118, 4894; b) Y. Uozumi, R. Nakao, Angew. Chem. Int. Ed. 2003, 42, 194; Angew. Chem. 2003, 115, 204; c) Y-M. Zhong, H.-C. Ma, J.-X. Wang, X.-J. Jia, W.-F. Li, Z.-Q. Lei, Catal. Sci. Technol. 2011, 1, 927; d) B. Karimi, F. K. Esfahani, Chem. Commun. 2009, 5555; e) J. E. Steves, S. S. Stahl, J. Am. Chem. Soc. 2013, 135, 15742.
- [6] H.-P. Jia, D. R. Dreyer, C. W. Bielawski, Tetrahedron 2011, 67, 4431.
- [7] D. Villemin, M. Hammadi, Synth. Commun. 1995, 25, 3145.
- [8] a) A. Al-Hunaiti, T. Niemi, A. Sibaouih, P. Pihko, M. Leskelä, T. Repo, *Chem. Commun.* **2010**, *46*, 9250; b) S. Verma, J. L. Bras, S. L. Jain, J. Muzart, *Appl. Catal. A* **2013**, *468*, 334.
- [9] a) A. McKillop, B. P. Swann, E. C. Taylor, *Tetrahedron Lett.* **1970**, *11*, 5281;
 b) Z. Li, J. Yin, G. Wen, T. Li, X. Shen, *RSC Adv.* **2014**, *4*, 32298.
- [10] a) E. J. Corey, J. P. Schaefer, J. Am. Chem. Soc. 1960, 82, 917; b) C. Qi, H. Jiang, L. Huang, Z. Chen, H. Chen, Synthesis 2011, 387.
- [11] a) S. Baskaran, J. Das, S. Chandrasekaran, J. Org. Chem. 1989, 54, 5182;
 b) Y. Ishii, Y. Sakata, J. Org. Chem. 1990, 55, 5545; c) C.-M. Che, W.-Y. Yu, P.-M. Chan, W.-C. Cheng, S.-M. Peng, K.-C. Lau, W.-K. Li, J. Am. Chem. Soc. 2000, 122, 11380; d) A. Gao, F. Yang, J. Li, Y. Wu, Tetrahedron 2012, 68, 4950; e) Y. Xu, X.-B. Wan, Tetrahedron Lett. 2013, 54, 642; f) S. Kobayashi, H. Miyamura, R. Akiyama, T. Ishida, J. Am. Chem. Soc. 2005, 127, 9251;
 g) C.-F. Xu, M. Xu, Y-X. Jia, C.-Y. Li, Org. Lett. 2011, 13, 1556; h) S. Trosien, S. R. Waldvogel, Org. Lett. 2012, 14, 2976; i) Z. Wan, C. D. Jones, D. Mitchell, J. Y. Pu, T. Y. Zhang, J. Org. Chem. 2006, 71, 826; j) W. Ren, Y. Xia, S.-J. Ji, Y. Zhang, X. Wan, J. Zhao, Org. Lett. 2009, 11, 1841.
- [12] L. Huang, K. Cheng, B. Yao, Y. Xie, Y. Zhang, J. Org. Chem. 2011, 76, 5732.
- [13] a) A. Stergiou, A. Bariotaki, D. Kalaizakis, I. Smonou, J. Org. Chem. 2013, 78, 7268; b) Y. Yuan, H.-T. Zhu, Eur. J. Org. Chem. 2012, 329.
- [14] Y. Su, X. Sun, G. Wu, N. Jiao, Angew. Chem. Int. Ed. 2013, 52, 9808; Angew. Chem. 2013, 125, 9990.
- [15] L. Ruan, M. Shi, N. Li, X. Ding, F. Yang, J. Tang, Org. Lett. 2014, 16, 733.
- [16] A. Wang, H. Jiang, X. Li, J. Org. Chem. 2011, 76, 6958.
- [17] H. Min, T. Palani, K. Park, J. Hwang, S. Lee, J. Org. Chem. 2014, 79, 6279.
- [18] For reviews on the chemistry of enaminones, see: a) A.-Z. A. Elassar, A. A. El-Khair, *Tetrahedron* 2003, *59*, 8463; b) G. Negri, C. Kascheres, A. J. Kascheres, *J. Heterocycl. Chem.* 2004, *41*, 461; c) P. Lue, J. V. Greenhill, *Adv. Heterocycl. Chem.* 1996, *67*, 207.
- [19] a) K. K. Toh, Y.-F. Wang, E. P. J. Ng, S. Chiba, J. Am. Chem. Soc. 2011, 133, 13942; b) S. Würtz, S. Rakshit, J. J. Neumann, T. Dröge, F. Glorius, Angew. Chem. Int. Ed. 2008, 47, 7230; Angew. Chem. 2008, 120, 7340; c) Z.-J. Zhang, Z.-H. Ren, Y.-Y. Wang, Z.-H. Guan, Org. Lett. 2013, 15, 4822; d) X.-L. Lian, Z.-H. Ren, Y.-Y. Wang, Z.-H. Guan, Org. Lett. 2014, 16, 3360; e) J. Weng, Y.-B. Li, R.-B. Wang, G. Lu, ChemCatChem 2012, 4, 1007.
- [20] a) J.-P. Wan, Y. Lin, Q. Huang, Y. Liu, J. Org. Chem. 2014, 79, 7232; b) J.-P.
 Wan, Y. Pan, Chem. Commun. 2009, 2768; c) J.-P. Wan, R. Zhou, Y. Liu, M.
 Cai, RSC Adv. 2013, 3, 2477; d) J.-P. Wan, Y. Lin, Y. Jing, M. Xu, Y. Liu, Tetrahedron 2014, 70, 7874; e) J.-P. Wan, Y. Zhou, K. Jiang, H. Ye, Synthesis 2014, 46, 3256–3262.
- [21] J.-P. Wan, Y. Zhou, S. Cao, J. Org. Chem. 2014, 79, 9872.
- [22] a) H. H. Wasserman, J. L. Ives, J. Am. Chem. Soc. 1976, 98, 7868; b) H. H.
 Wasserman, J. L. Ives, J. Org. Chem. 1985, 50, 3573; c) Q.-Y. Meng, T. Lei,
 L.-M. Zhao, C.-J. Wu, J.-J. Zhong, X.-W. Gao, C.-H. Tung, L.-Z. Wu, Org.
 Lett. 2014, 16, 5968.
- [23] For recent reviews on visible-light photocatalysis, see:a) D. Ravelli, D. Dondi, M. Fagnoni, A. Albini, Chem. Soc. Rev. 2009, 38, 1999; b) D. Ravelli, M. Fagnoni, A. Albini, Chem. Soc. Rev. 2013, 42, 97; c) T. P. Yoon, M. A. Ischay, J. Du, Nat. Chem. 2010, 2, 527; d) J. M. Narayanam, C. R. Stephenson, Chem. Soc. Rev. 2011, 40, 102; e) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, Chem. Rev. 2013, 113, 5322; f) J. Xuan, W.-J. Xiao, Angew. Chem. Int. Ed. 2012, 51, 6828; Angew. Chem. 2012, 124, 6934; g) Y. Xi, H. Yi, A. Lei, Org. Biomol. Chem. 2013, 11, 2387; h) G. Palmisano, E.



García-López, G. Marcí, V. Loddo, S. Yurdakal, V. Augugliaro, L. Palmisano, *Chem. Commun.* **2010**, *46*, 7074; i) D. Ravelli, M. Fagnoni, *Chem-CatChem* **2012**, *4*, 169.

- [24] For examples on quinoxaline synthesis, see: a) M. Lian, Q. Li, Y.-P. Zhu, G.-D. Yin, A.-X. Wu, *Tetrahedron* 2012, *68*, 9598; b) B. China Raju, K. V. Prasad, G. Saidachary, B. Sridhar, *Org.Lett.* 2014, *16*, 420; c) F. Zhang, Y. Xi, Y. Lu, L. Wang, L. Liu, J. Li, Y. Zhao, *Chem. Commun.* 2014, *50*, 5771; d) C.-Y. Chen. W.-P. Hu. M.-C. Liu, P.-C. Yan, J.-J. Wang, M.-I. Chung, *Tetrahedron* 2013, *69*, 9735; e) M. M. Heravi, M. Hosseini, H. A. Oskooie, B. Baghernejad, *J. Korean Chem. Soc.* 2011, *55*, 235; f) N. Shah, E. Gravel, D. V. Jawale, E. Doris, I. N. N. Namboothiri, *ChemCatChem* 2015, *7*, 57; g) C. Delpivo, G. Michletti, C. Boga, *Synthesis* 2013, *45*, 1546; h) J.-T. Hou, Y.-H. Liu, Z.-H. Zhang, *J. Heterocycl. Chem.* 2014, *47*, 703; j) W. Wang, Y. Shen, X. Meng, M. Zhao, Y. Chen, B. Chen, *Org. Lett.* 2011, *13*, 4514; j) J.-P. Wan, S.-F. Gan, J.-M. Wu, Y. Pan, *Green Chem.* 2009, *11*, 1633.
- [25] For examples and reviews on EL-mediated sustainable organic synthesis, see: a) J. S. Bennett, K. L. Charles, M. R. Miner, C. F. Heuberger, E. J.

Spina, M. F. Bartels, T. Foreman, *Green Chem.* 2009, *11*, 166; b) J.-P. Wan, C. Wang, R. Zhou, Y. Liu, *RSC Adv.* 2012, *2*, 8789; c) J.-P. Wan, S. Cao, Y. Jing, *Appl. Organometal. Chem.* 2014, *28*, 631; d) Y. Liu, H. Wang, C. Wang, J. Wan, C. Wen, *RSC Adv.* 2013, *3*, 21369; e) G. A. Edwards, M. A. Trafford, A. E. Hamilton, A. M. Buxon, M. C. Bardeaux, J. M. Chalker, *J. Org. Chem.* 2014, *79*, 2094; f) C. S. Pereira, V. M. T. Silva, A. E. Rodrigues, *Green Chem.* 2011, *13*, 2658.

[26] a) Y. Pan, C. W. Kee, L. Chen, C.-H. Tan, *Green Chem.* 2011, *13*, 2682; b) Y.
 Pan, S. Wang, C.-W. Kee, E. Dubuisson, Y. Yang, K. P. Loh, C.-H. Tan, *Green Chem.* 2011, *13*, 3341; c) C. Vila, J. Lau, M. Rueping, *Beilstein J. Org. Chem.* 2014, *10*, 1233.

Received: February 11, 2015 Revised: March 9, 2015 Published online on ■■ ■, 0000

FULL PAPERS

S. Cao, S. Zhong, L. Xin, J.-P. Wan,* C. Wen*

Visible-Light-Induced C=C Bond Cleavage of Enaminones for the Synthesis of 1,2-Diketones and Quinoxalines in Sustainable Medium



6