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Regioselective Oxidative Ring-Opening of Cyclopropenyl Carboxylates by Visible Light Photoredox Catalysis

Qianwen Ye,[a] Hongqiang Ye,[a] Dongping Cheng,*[b] Xiaonian Li,*[a] and Xiaoliang Xu*[a]

[a]*College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China*
[b]*College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, P. R. China*

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ABSTRACT

Catalyzed by Ir(dFCF$_3$ppy)$_2$(dtbbpy)PF$_6$, several aroyl methylidenemalonates were synthesized in good to excellent yields via visible light photoredox-catalyzed the oxidative ring-opening of cyclopropenyl carboxylate derivatives. The possible mechanism of oxidative quenching cycle was proposed.

* Corresponding author. Tel.: +86-571-88320920; e-mail: chengdp@zjut.edu.cn; xnli@zjut.edu.cn; xuxiaoliang@zjut.edu.cn

Introduction

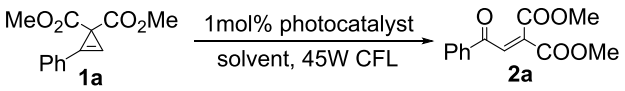
Visible light catalysis has attracted tremendous attention from chemists owing to its wide applications in organic synthesis and its significance in sustainable chemistry.[1] Without stoichiometric activated reagents, this catalytic strategy make it easier to get access to various radical ions and/or radicals by photo-excited single electron-transfer under very mild conditions.[2-3] These highly active *in situ* formed intermediates could participate in the innovative valuable reactions and transform into numerous interesting molecules in a controllable manner.[4] Among the various reactions mediated by visible light catalysis, the oxidation of carbon-carbon double bonds and its subsequent transformation have drawn much attention. For example, Yoon group reported several [2+2] cross-cycloadditions through the photocatalytic oxidation of olefins to give a range of cyclobutane derivatives.[5] Most noteworthy was that the oxidative dehydrogenative coupling of alkenes induced by photo-oxidation was also explored, such as the selective oxidative [4+2] annulation of imine and alkene for the synthesis of substituted dihydroisoquinolines,[6a] the C-H/C-H cross-coupling between electron-rich arenes and styrene derivatives affording various substituted aryl alkenes,[6b] and the cross-coupling of alkenes with alcohols or azoles generating multi-substituted enol ether.[6c]

Cyclopropenes, the smallest unsaturated carbocycles, are readily prepared molecules. Because of the highly strained double bond, they have unique and higher reactivity than olefins, allenes and alkynes.[7] With regard to the many types of cyclopropenes, substituted cyclopropene carboxylates have frequently been the focus of study. They easily undergo intramolecular cyclizations[8] as well as C-C bond cleavage[9] to arouse ring expansion and afford ring-opening products. Substantive studies showed that the 1,3 or 2,3 carbon-carbon bond cleavage of cyclopropene carboxylates is feasible, which gave totally different products. Under the nucleophilic attack of Grignard reagents,[9c] halide ions,[8d,10] organolithium,[8b,9b] organocuprate,[9d] the 2,3 cleavage of cyclopropene carboxylates was attained extensively. In contrast, reports regarding the 1,3 bond cleavage of cyclopropylene carboxylates were very rare. For instance, the tri- and tetrasubstituted alkenes were synthesized by $Fe(acac)_3$-catalyzed ring-opening reactions of cyclopropene carboxylates with trialkylaluminum reagents.[9a] Ma reported the ring-opening cycloisomerization of cyclopropenyldicarboxylates for the synthesis of 2,3,5-trisubstituted furans via tri(2-furanyl)phosphine catalysis.[8a] On the other hand, aroyl methylidenemalonates have found a wide range of applications due to their bioactive[11] and pharmaceutical significance.[12] They can be used as Michael acceptors or starting materials for the synthesis of different compounds such as pyrroles,[13a] furans,[13b] pyridazines,[14] indoles,[15] enonediesters,[16] oxazoles,[17] and etc. Generally, the preparation of aroyl methylidenemalonates was achieved by (1) $BF_3{\cdot}OEt_2$-mediated ring-opening of D-A nitrocyclopropanes;[18a] (2) one-pot reaction of 2-diazomalonate with epoxypropane catalyzed by $Rh_2(OAc)_4$ and subsequently Wittig olefination;[18b] and (3) oxidative radical reaction of aryl-substituted allenes with dimethylmalonate catalyzed by $Mn(OAc)_3$.[18c] Although these procedures are all good, they have also some obvious shortcomings such as multistep reactions, unaccessible starting materials and etc.

Result and discussion

Herein we wish to report a facile access to aroyl methylidenemalonate derivatives via visible light photocatalytic regioselective ring-opening reaction of cyclopropenyl carboxylates.

Table 1: Optimization of the reaction conditions[a]



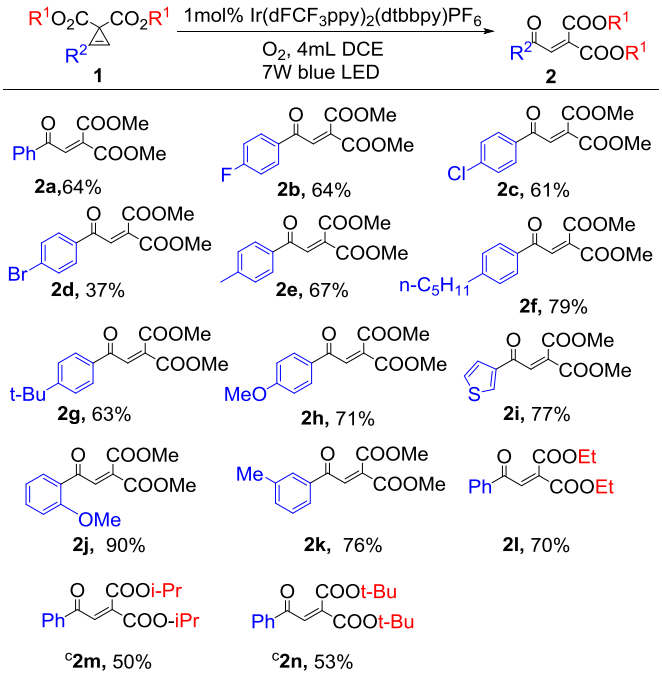
entry	photocatalyst	oxidant	time/h	Yield (%)[b]
1	$Ir(ppy)_3$	PhN_2BF_4	14	36
2	$Ir(ppy)_3$	-	4	16
3	$Ir(ppy)_3$	CBr_4	10	65
4	$Ir(ppy)_3$	CCl_4	14	65
5	$Ir(ppy)_3$	$Na_2S_2O_8$	24	67
6	$Ir(ppy)_3$	$K_2S_2O_8$	24	26
7	$Ir(ppy)_3$	$(NH_4)_2S_2O_8$	24	trace
8	$Ru(bpy)_3(BF_4)_2$	$Na_2S_2O_8$	2	48
9	$Ru(bpy)_3Cl_2$-$6H_2O$	$Na_2S_2O_8$	2	46
10	$Ru(bpz)_3(PF_6)_2$	O_2	24	20
11	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	O_2	5	52
12[c]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	O_2	36	trace
13[d]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	O_2	6	63
14[e]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	-	36	trace
15[f]	$Ir(dFCF_3ppy)_2(dtbbpy)PF_6$	O_2	10	see footnote

[a] **1a** (0.3mmol), oxidant (0.3mmol), photocatalyst (0.003mmol, 1mol%), 4mL DCE (AR), 45W compact fluorescent light (CFL) irradiation under O_2 at room temperature unless otherwise noted. [b]Yield of isolated product based on **1a**. [c]No photocatalyst or no light. [d]7W blue LED instead of 45W CFL. [e]Under N_2 atmosphere. [f]Distilled water (1eq, 2eq, 3eq) was added to absolute DCE to give the product in 70%, 73%, 74% yield respectively.

In order to obtain optimal conditions for the synthesis of aroyl methylidenemalonate derivatives, a variety of conditions were attempted (Table 1). Firstly dimethyl 2-phenylcycloprop-2-ene-1,1-dicarboxylate **1a** with 1eq of PhN_2BF_4 in the presence of 1mol% $Ir(ppy)_3$ was illuminated under air by a 45W white CFL at room temperature (entry 1). To our delight, the reaction afforded the desired **2a** in 36% yield. Without PhN_2BF_4, the reaction turned to be complicated and several unidentified by-products could be observed (entry 2). Then several oxidants were examined. CBr_4, CCl_4 and $Na_2S_2O_8$ all worked (entries 3-5). And 67% yield of **2a** could be obtained when $Na_2S_2O_8$ was used as an oxidant (entry 5). However, the reaction did not proceed well with $K_2S_2O_8$ or $(NH_4)_2S_2O_8$ (entries 6-7). Catalyzed by $Ru(bpy)_3(BF_4)_2$ or $Ru(bpy)_3Cl_2$, moderate yield of **2a** was obtained with $Na_2S_2O_8$ as the oxidant (entries 8-9). It ocurred to us that if the oxidizing ability of the photocatalyst was strong enough, the desired transformation may proceed as well even in the absence of extra oxidant. Based on the redox potential values of the photocatalysts,[19] $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ ($E_{1/2}III^*/II$=+1.21V vs SCE in CH_3CN) and $Ru(bpz)_3(PF_6)_2$ ($E_{1/2}III/II$=+1.86V vs SCE in CH_3CN) were attempted under O_2 atmosphere (entries 10-11). To our delight, the desired target product could be obtained in 52% yield with $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as the catalyst (entry11). Almost no **2a** was observed in the absence of light or photocatalyst (entry12). Under the illumination of 7W blue LED for 6hrs the target product was isolated in 63% yield (entry13). The reaction could not proceed under N_2 atmosphere (entry14). When the reaction was carried out in DMSO, DMF and THF, only complicated mixtures were obtained. Other solvents such as DCM, diethyl ether, toluene, MeCN, or acetone, could give **2a** in 42%, 10%, 50%, 52% and 53% yield respectively. Moreover,

when 1-3 equiv. of water was added to the absolute DCE, the yield is almost same as the results of entries 3-5 which the AR grade DCE was used as the solvent (entry15).

Scheme 1: Regioselective ring-opening reaction of cyclopropenyl carboxylates[a,b]



[a]**1**(0.5 mmol), $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (0.005 mmol, 5.6mg, 1mol%), 10hrs, 7W blue LED, O_2, 4mL DCE (AR), r.t. [b]Yield of isolated product. [c]CBr_4 (1eq).

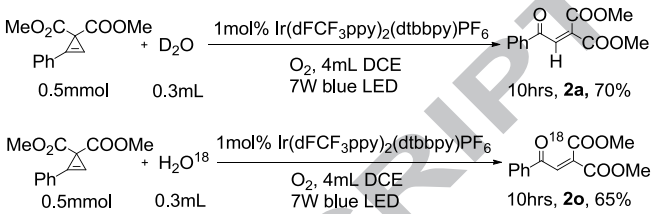
To explore the scope of the reaction, a series of cyclopropenyl carboxylates were tested under the optimized conditions (Scheme 1). The *para*-halogen on the aryl of **1** generated the corresponding products **2b**, **2c** or **2d** in moderate to reasonalbe yields. Substrates **1** with an aryl substituted by electron-donating group at the para position, such as Me, n-C_5H_{11}, *t*-Bu or MeO, afforded good yields (**2e-2h**). The target product **2j** was isolated in 90% yield when the substrate bearing 2-MeO on the phenyl ring was used, which showed no obvious steric effect on the reaction. Especially heterocyclic substituted dimethyl 2-(3-thienyl)cycloprop-2-ene-1,1-dicarboxylate **1i** also underwent the reaction smoothly to afford **2i** in 77% yield. When the ethyl, i-propyl and t-butyl esters were used as the substrates, moderate yields were also obtained (**2l-2n**). Unfortunately alkyl substituted substrate dimethyl 2-n-hexylcycloprop-2-ene-1,1-dicarboxylate is inert in this reaction, which was in accordance with the results reported.[20]

Scheme 2: The oxidative ring-opening reaction of **3**

It is worth mentioning that methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate **3** could not give the corresponding oxidative ring-opening product (Scheme 2). Instead, the 2-oxo-2-phenylacetic acid methyl ester **4** and methyl benzoate **5** were obtained in 63% and 12% yields, respectively, which may be formed by the oxidative cleavage of ring opening product and subsequent intermolecular transesterification. Without additional oxidant CBr_4, the reaction could not proceed.

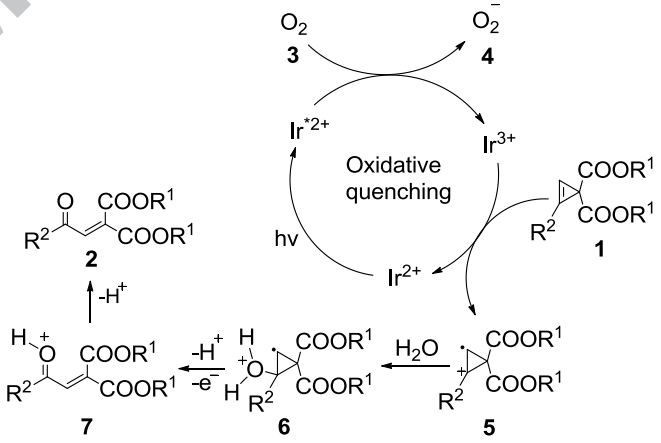
In order to elucidate the mechanism, two control experiments were conducted (Scheme 3). When D_2O was added, **2a** was isolated in 70% yield and the deuterium product was not found. The replacement of H_2O with H_2O^{18}, the heavy oxygen substituted product **2o** was obtained in 65% yield. Moreover, when TEMPO was added as radical scavenger, the product was obtained in 10% yield for 24hrs.

Scheme 3: The control experiments with D_2O and H_2O^{18}



Based on the literatures[21] and the above experiments, a plausible mechanism was proposed in Scheme 4. At first, illumination by a 7W blue LED, the ground state of Ir^{2+} was excited to provide Ir^{*2+}. Then Ir^{3+} was formed by the oxidation of Ir^{*2+} by O_2. Ir^{3+} captures one electron from substrate **1** to give the radical cation **5**, which itself was reduced to the initial photocatalyst Ir^{2+}. The nucleophilic attack of H_2O to **5** provides intermediate **6**, which subsequently losses one electron and one proton by the oxidation of Ir^{3+}, and then undergoes ring opening to give the intermediate **7**. At last **7** loses one proton and affords product **2**.

Scheme 4: A plausible mechanism



Conclusions

In summary, a visible-light photoredox catalyzed aerobic oxidative ring-opening of cyclopropenyl carboxylates has been developed for the synthesis of aroyl methylidene malonates. The simple and mild conditions make the method attractive, especially the visible light as a clean and renewable energy source makes it as a good substitute for the existing conventional synthetic reagents. Further investigations on the interesting reactivity of cyclopropenes are ongoing in our laboratory.

Acknowledgments

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Supplementary Material

Supplementary data (^{1}H NMR, ^{13}C NMR data and ^{1}H NMR, ^{13}CNMR spectra of all compounds) associated with this article can be found, in the online version, at

References and notes

1. (a) Johnston, C. P.; Smith, R. T.; Allmendinger. S.; MacMillan, D. W. C. *Nature* 2016, **536,** 322; (b) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* 2010, **2,** 527; (c) Bosque, I.; Magallanes, G.; Rigoulet, M.; Karkas, M. D.; Stephenson, C. R. J. *ACS Cent. Sci*. 2017, **3,** 621; (d) Reckenthaler, M.; Griesbeck, A. G. *Adv. Synth. Catal.* 2013, **355,** 2727; (e) Zhao, Q. Q.; Chen, J.; Yan, D. M.; Chen J. R.; Xiao, W. J. *Org. Lett.* 2017, **19,** 3620; (f) Wang, L.; Lv, J.; Li, S.; Luo, S. Z. *Org. Lett.* 2017, **19,** 3366.
2. Reviews on photocatalysis: (a) Levin, M. D.; Kim, S.; Toste, F. D. *ACS. Cent. Sci.* 2016, **2,** 293; (b) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* 2016, **116,** 10075; (c) Schultz, D. M.; Yoon, T. P. *Science.* 2014, **343,** 1239176; (d) Hoffmann, N.; *J. Photochem. Photobiol*. 2008, **9,** 43; (e) Ravelli, D.; Fagnoni, M.; Albini, A. *Chem. Soc. Rev*. 2013, **42,** 97; (f) Hari, D. P.; Konig, B. *Chem. Commun.* 2014, **50,** 6688; (g) Zhang, N.; Samanta, S. R.; Rosen, B. M.; Percec, V. *Chem. Rev.* 2014, **114,** 5848; (h) Shi, L.; Xia, W. *Chem. Soc. Rev.* 2012, **41,** 7687; (i) Narayanam, J. M. R.; Stephenson, C. R. J. *Chem. Soc. Rev.* 2011, **40,** 102. (j) Xuan, J.; Xiao, W. J. *Angew. Chem., Int. Ed*. **2012**, *51*, 6828. (k) Twilton, J.; Le, C.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W. C. *Nat. Rev. Chem.* **2017**, *1*, 0052.
3. (a) Lin, S. S.; Lies, S. D.; Gravatt, C. S.; Yoon, T. P. *Org. Lett.* 2017, **19,** 368; (b) Miyake, Y.; Ashida, Y.; Nakajima, K.; Nishibayashi, Y. *Chem. Commun.* 2012, **48,** 6966; (c) Rono, L. J.; Yayla, H. G.; Wang, D. Y.; Armstrong, M. F.; Knowles, R. R. *J. Am. Chem. Soc.* 2013, **135,** 17735.
4. (a) Huo, H.; Wang, C.; Harms, K.; Meggers, E. *J. Am. Chem. Soc.* 2015, **137,** 9551; (b) Liu, W. Q.; Lei, T.; Song, Z. Q.; Yang, X. L.; Wu, C.; Jiang, X.; Chen, B.; Tung, C. H.; Wu, L. Z. *Org. Lett.* 2017, **19,** 3251; (c) Jia, K.; Pan, Y.; Chen, Y. *Angew. Chem. Int. Ed.* 2017, **56,** 2478; (d) Huang, H.; Jia, K.; Chen, Y. *ACS Catal.* 2016, **6,** 4983.
5. (a) Miller, Z. D.; Lee, B. J.; Yoon, T. P. *Angew. Chem. Int. Ed.* 2017, **56,** 11891. (b) Hurtley, A. E.; Lu, Z.; Yoon, T. P. *Angew. Chem. Int. Ed.* 2014, **53,** 8991; (c) Du, J.; Skubi, K. L.; Schultz, D. M.; Yoon, T. P. *Science* 2014, **344,** 392; (d) Ischay, M. A.; Ament, M. S.; Yoon, T. P. *Chem. Sci.* 2012, **3**, 2807; (e) Ischay, M. A.; Lu, Z.; Yoon, T. P. *J. Am. Chem. Soc.* 2010, **132,** 8572; (f) Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* 2008, **130,** 12886.
6. (a) Hu, X.; Zhang, G.; Bu, F.; Lei, A.; *Angew. Chem. Int. Ed.* 2018, **57,** 1286. (b) Hu, X.; Zhang, G.; Bu, F.; Luo, X.; Yi, K.; Zhang, H.; Lei, A.; *Chem. Sci.* DOI:10.1039/C7SC04634K; (c) Yi, H.; Niu, L.; Song, C.; Li, Y.; Dou, B.; Singh, A. K.; Lei, A. *Angew. Chem. Int. Ed.* 2017, **56**, 1120.
7. (a) Baird, M. S. *Cyclopropenes: Transformations. InHouben-Weyl;* Thieme, Stuttgart, Germany, 1997, Vol. E17d/2, pp 2781; (b) Back, R. D.; Dmitrenko, O. *J. Am. Chem. Soc*. 2004, **126**, 4444; (c) Rubin, M.; Rubina, M.; Gevorgyan, V. *Chem. Rev.* 2007, **107**, 3117; (d) Fox, J. M.; Yan, N. *Curr. Org. Chem.* 2005, **9**, 719; (e) Archambeau, A.; Miege, F.; Meyer, C.; Cossy, J. *Acc. Chem. Res.* 2015, **48**, 1021; (f) Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* 2003, **125,** 7198.
8. (a) Chen, J.; Ni, S.; Ma, S. *Synlett.* 2011, **7**, 931; (b) Liu, Y.; Ma, Y. *Org. Lett*. 2012, **14**, 720; (c) Patel, P. R.; Boger, D. L. *J. Am. Chem. Soc*. 2010, **132**, 8527; (d) Ma, S.; Zhang, J. *J. Am. Chem. Soc.* 2003, **125**, 12386;(e) Song, C.; Sun, D.; Peng, X.; Bai, J.; Zhang, R.; Hou, S.; Wang, J.; Xu, Z. *Chem. Commun.* 2013, **49**, 9167; (f) Zhu, P. L.; Tang, X. Y.; Shi, M. *Chem. Commun.* 2016, **52**, 7245.
9. (a) Wang, Y.; Fordyce, E. A. F.; Chen, F. Y.; Lam, H. W. *Angew. Chem. Int. Ed*. 2008, **47**, 7350; (b) Liu, Y.; Yu, Q.; Ma, S. *Eur. J. Org. Chem.* 2013, 3033;(c) Liu, Y.; Ma, S. *Chem. Sci*. 2011, **2**, 811; (d) Song, C.; Sun, D.; Peng, X.; Bai, J.; Zhang, R.; Hou, S.; Wang, J.; Xu, Z. *Chem. Commun.* 2013, **49**, 9167; (e) Chuprakov, S.; Malyshev, D. A.; Trofimov, A.; Gevorgyan, V. *J. Am. Chem. Soc.* 2007, **129**, 14868.
10. (a) Wang, Y.; Lam, H. W. *J. Org. Chem.*, 2009, **74**, 1353; (b) Ma, S.; Zhang, J.; Cai, Y.; Lu, L. *J. Am. Chem. Soc.* 2003,**125**, 13954; (c) Chen. J.; Ma, S. M. *J. Org. Chem.* 2009, **74**, 5595; (d) Ma, S.; Zhang, J.; Lu, L.; Jin, X.; Cai, Y.; Hou, H. *Chem. Commun.* 2005, 909; (e) Chen, S.; Ren, J.; Wang, Z. *Tetrahedron* 2009, **65**, 9146.
11. (a) Gazar, H. A.; Bedir, E.; Takamatsu, S.; Ferreira, D.; Khan, I. A. *Phytochemistry* 2004, **65**, 2499; (b) Yamazaki, S.; Morikawa, S.; Iwata, Y.; Yamamoto, M.; Kuramoto, K. *Org. Biomol. Chem.* 2004, **2**, 3134; (c) Hermanson, J. R.; Gunther, M. L.; Belletire, J. L.; Pinhas, A. R. *J. Org. Chem.* 1995, **60**, 1900.
12. (a) DeMartino, M. P.; Chen, K.; Baran, P. S. *J. Am. Chem. Soc.* 2008, **130**, 11546. (b) Zhu, Y.; Cai, Q.; Gao, Q.; Jia, F.; Liu, M.; Gao, M.; Wu, A. *Tetrahedron* 2013, **69**, 6392;(c) Yu, J. Q.; Corey, E. J. *J. Am. Chem. Soc.* 2003, **125**, 3232; (d) Fouad, M.; Edrada, R. A.; Ebel, R.; Wray, V.; Muller, W. E. G.; Lin, W. H.; Proksch, P. J. *Nat. Prod.* 2006, **69**, 211.
13. (a) Morikawa, S.; Yamazaki, S.; Furusaki, Y.; Amano, N.; Zenke, K.; Kakiuchi, K. *J. Org. Chem.* 2006, **71**, 3540; (b) Morikawa, S.; Yamazaki, S.; Tsukada, M.; Izuhara, S.; Morimoto, T.; Kakiuchi, K. *J. Org. Chem.* 2007, **72**, 6459.
14. Gao, Q.; Zhu, Y.; Lian, M.; Liu, M.; Yuan, J.; Yin, G.; Wu, A. *J. Org. Chem.* 2012, **77**, 9865.
15. (a) Weng, J. Q.; Fan, R. J.; Deng, Q. M.; Liu, R. R.; Gao, J. R.; Jia, Y. X. *J. Org. Chem.* 2016, **81**, 3023; (b) Yamazaki, S.; Iwata, Y. *J. Org. Chem.* 2006, **71**, 739.
16. Horwitz, M. A.; Fulton, J. L.; Johnson, J. S. *Org. Lett.* 2017, **19**, 5783.
17. Selvi, T.; Srinivasan, K. *Chem. Commun.* 2014, **50**, 10845.
18. (a) Selvi, T.; Srinivasan, K. *J. Org. Chem.* 2014, **79**, 3653; (b) Horwitz, M. A.; Fulton, J. L.; Johnson, J. S. *Org. Lett.* 2017, **19**, 5783; (c) Wu, Z.; Huang, X. *Synthesis* 2007, **1**, 45; (d) Iesce, M. R.; Cermola, F.; Piazza, A.; Scarpati, R.; Graziano, M. L. *Synthesis* 1995, 439. (e) Hermanson, J. R.; Gunther, M. L.; Belletire, J. L.; Pinhas, A. R. *J. Org. Chem.* 1995, **60**, 1900.
19. (a) Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* 2012, **77,** 1617-1622; (b) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D. Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* 2005, **17,** 5712-5719.
20. Dange, N. S.; Jatoi, A. H.; Robert, F.; Landais, Y. Org. Lett. 2017, 19, 3652.
21. (a) Karkas, M. D.; Bosque, I.; Matsuura, B. S.; Stephenson, C. R. J. *Org. Lett*. 2016, **18,** 5166-5169.; (b) Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc.* 2011, **133,** 4160.

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Regioselective Oxidative Ring-Opening of Cyclopropenyl Carboxylates by Visible Lightphotoredox Catalysis

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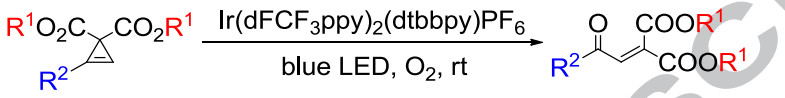

Highlights

1. Regioselective oxidative ring-opening of cyclopropenyl carboxylate derivatives via visible light photoredox catalysis.
2. A variety of aroyl methylidenemalonates were obtained in good to excellent yields.
3. The reaction has the advantage of simple operation and mild conditions.