Organic LETTERS

Letter

pubs.acs.org/OrgLett

Direct Phosphonation of Quinolinones and Coumarins Driven by the Photochemical Activity of Substrates and Products

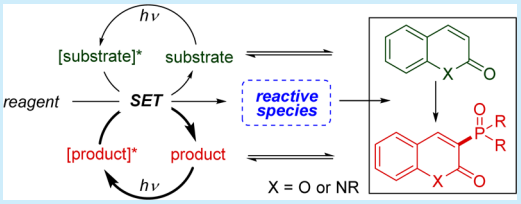
Inwon Kim,[†,‡,§] Minsik Min,[†,‡,§] Dahye Kang,[†,‡] Kiho Kim,[†,‡] and Sungwoo Hong*[,‡,†]

[†]Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

[‡]Center for Catalytic Hydrocarbon Functionalizations, Institute for Basic Science (IBS), Daejeon 305-701, Korea

Supporting Information

ABSTRACT: Light-promoted phosphonation of quinolinones and coumarins was developed without the need for an external photocatalyst. Investigations support a mechanism whereby both starting materials and products act as photosensitizers upon excitation using compact fluorescent light sources to photochemically promote the dissociation of the N−O bond in the pyridinium salt by a single electron transfer pathway. A wide range of quinolinone and coumarin substrates can be utilized in the phosphonation process under mild reaction conditions.



Quinolinones and coumarins are important constituents of numerous naturally occurring compounds[1] and privileged medicinal scaffolds.[2] These derivatives have been extensively investigated as a result of their broad range of biological activities[3] and outstanding optical properties.[4] The direct installations of the phosphoryl groups into the coumarins have been reported based on transition metal-mediated cross-coupling reactions of H-phosphonates and coumarins.[5] Although these approaches have proven valuable for the synthesis of 3-phosphonated coumarins, they suffer from the disadvantages of requiring high temperature, metal catalysts, or toxic reagents.

Strategies using photocatalysts have been intensively investigated to provide straightforward and environmentally friendly synthetic tools under mild conditions.[6] In addition, dual catalytic systems combining photoredox and transition metal catalysis have enabled a diverse array of valuable synthetic transformations in a highly efficient manner.[7] In general, the mode of light-driven photoreactions requires photocatalysts whose excitation by light generates high-energy reactive species. In contrast, the photochemical activity of electron donor−acceptor (EDA) complexes can generate radical species for the synthetically useful transformations without the need for an external photocatalyst.[8] For improving convenience and efficiency, the development of new types of photoreactions using EDA complexes has been the subject of intensive research.[9] Recently, Melchiorre and coworkers demonstrated the ability of chiral enamines to act as photosensitizers to furnish radical species without relying on the formation of photoactive EDA complexes.[10] Fu's group also achieved a photoredox arylthiation of *N*-(acetoxy)phthalimides in the absence of an external photocatalyst.[11]

We were intrigued by the possibility of developing photochemical reactions by employing both substrate[12] and product as effective photosensitizers while avoiding the need for any external photocatalyst. In this study, we have discovered the capability of quinolinone and coumarin moieties excited under household compact fluorescent light (CFL) illumination to trigger the photochemical generation of reactive radical species as effective photosensitizers under mild conditions. Interestingly, the resulting 3-phosphonated products absorb longer-wavelength light to activate reagents efficiently, and the reaction rate is accelerated so that the entire set of chemical reactions are self-sustaining in an autocatalytic fashion (Schemes S2 and S4 and Figure S1).

Recently, Lakhdar's group has reported efficient phosphonation reactions of arylphosphine oxides with alkynes under photocatalytic conditions by using EDA complex formation between eosin Y and *N*-ethoxy-2-methylpyridinium tetrafluoroborate.[13] In the process, the EDA complex exhibits a single electron transfer (SET) event, giving a reactive ethoxy radical to abstract a hydrogen atom from diphenylphosphine oxide. Moreover, Stephenson's group has reported efficient trifluoromethylation under photocatalytic conditions by using EDA complex formation between acylated and nonacylated pyridine N-oxide.[14] The calculated triplet energy (E_T) of pyridinium salt **3a** was ∼80 kcal/mol, which is not congruent with the triplet energy of quinolinone (E_T = 66 kcal/mol). On the other hand, considering that the redox potential of pyridinium salt **3a** is approximately −0.60 V vs the saturated calomel electrode (SCE), quinolinone **1a** might work as an effective photoreductant of **3a** because the redox potential of the oxidation of triplet excited state is estimated to be $\mathbf{1a}^{\bullet+}/\mathbf{1a}^{*}$ = −1.05 V vs SCE (see Figure S8 for details).

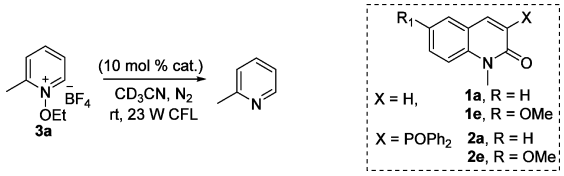
To corroborate this scenario, the feasibility of photolysis of **3a** by quinolinones was investigated in the model reactions. Indeed, illuminating the reaction mixture of quinolinones (10 mol %) and **3a** using a household 23 W CFL bulb provided significant amounts of photolytic product 2-methylpyridine (Table 1), representing the first example of quinolinone-induced photoreactions. Notably, 3-phosphonated quinolinone **2e** displayed

Received: January 27, 2017

© XXXX American Chemical Society

DOI: 10.1021/acs.orglett.7b00299
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Photolysis of Pyridinium Salt by Quinolinones and Photocatalysts[a]



entry	photocat. (10 mol %)	base (10 mol %)	yield (%)[b]
1	**1a**	$NaHCO_3$	5
2	**2a**	$NaHCO_3$	10
3	**1e**	$NaHCO_3$	34
4	**2e**	$NaHCO_3$	63
5	**2e**		62
6	eosin Y	$NaHCO_3$	20
7	eosin Y		6
8	benzophenone		trace
9	benzil		trace
10		$NaHCO_3$	trace

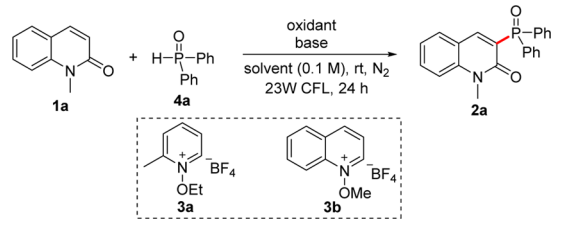
[a]Reactions were carried out in CD_3CN at rt under N_2 for 14 h with light irradiation using a 23 W CFL bulb. [b]Yields were determined by ^1H NMR.

superior photocatalytic activity at room temperature, allowing efficient production of reactive radical species under both basic and neutral conditions. Eosin Y proved to be less efficient than **2e** in this model reaction. It is noteworthy that only trace amounts of photolytic product were observed with the use of benzophenone (E_T = 69 kcal/mol) or benzil (E_T = 52 kcal/mol), which are known to be effective triplet sensitizers.

On this basis, we investigated the proposed direct phosphonation of *N*-methylquinolinone (**1a**) with diphenylphosphine oxide (**4a**) under 23 W CFL irradiation at room temperature (Table 2). With respect to the required capability, the external oxidant candidates (**3a** and **3b**) were selected based on the low bond dissociation energies of their N−O bonds[15] and relevant redox potentials. To our delight, the use of pyridinium salt **3a** was found to initiate the C3 phosphonation of quinolinone **1a**, thus highlighting that the overall process was operating effectively. Among the solvents screened, acetonitrile was most efficient in this reaction, and the desired product was obtained in 81% yield (entry 5). The properties of the oxidant were also critical to the efficiency of the transformation, and only 11% yield of product was obtained with the use of **3b** (entry 6). In the absence of $NaHCO_3$, only 23% of the product was formed, presumably due to acidification of the medium in the reaction (entry 4). Control experiments confirmed the essential role of light in this reaction (entry 8). The complete inhibition of the reactivity in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (entry 10) supports a radical mechanism being operative. No beneficial effects were observed upon the addition of external photocatalysts, such as $Ir(ppy)_3$ and eosin Y, which are known to promote efficient photoredox catalysis (entries 11 and 12).

After optimizing the reaction conditions, we next investigated the scope of both quinolinones and phosphine oxides to extend the utility and generality of this methodology (Scheme 1). We were pleased to observe that quinolinones bearing either electron-rich or -deficient groups (methyl, methoxy, fluoro, chloro, bromo, and trifluoromethyl) reacted with diphenylphosphine oxides **4** to provide the desired products under the reaction conditions. Notably, chloro and bromo groups were intact under the reaction conditions to provide the desired products (**2g** and **2h**), enabling further functionalization. In a similar fashion, 4-hydroxyquinolinone is also a viable substrate for obtaining phosphonated product **2j**. Importantly, employment of dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide resulted in the formation of the corresponding phosphonated product (**2k**). The scope of the phosphine oxides was subsequently examined, and a relatively broad range of phosphine oxides worked well in the optimized system (**2l**−**2p**).

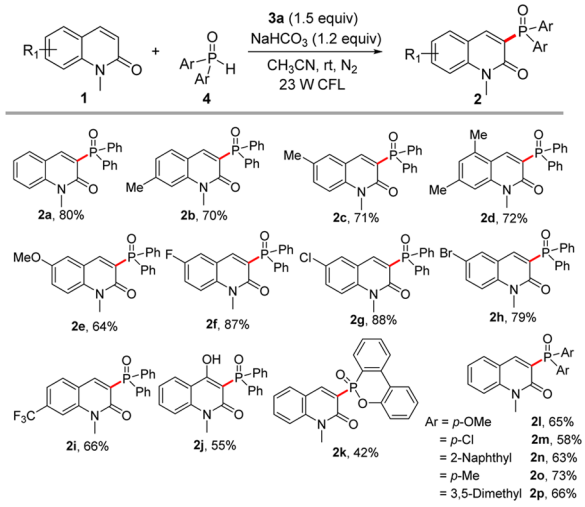
Table 2. Optimization of the Reaction Conditions[a]



entry	photocat. (4 mol %)	oxidant	base	solvent	yield (%)[b]
1		$K_2S_2O_8$	$NaHCO_3$	CH_3CN	trace
2		**3a**	$NaHCO_3$	1,2-DCE	45
3		**3a**	$NaHCO_3$	DMSO	36
4		**3a**		CH_3CN	23
5		**3a**	**$NaHCO_3$**	**CH_3CN**	**81**
6		**3b**	$NaHCO_3$	CH_3CN	11
7		**3a**	NaOAc	CH_3CN	62
8[c]		**3a**	$NaHCO_3$	CH_3CN	0
9[d]		**3a**	$NaHCO_3$	CH_3CN	trace
10[e]		**3a**	$NaHCO_3$	CH_3CN	trace
11	$Ir(ppy)_3$	**3a**	$NaHCO_3$	CH_3CN	76
12	eosin Y	**3a**	$NaHCO_3$	CH_3CN	80

[a]Reactions were performed using **1a** (0.1 mmol), **4a** (2.0 equiv), oxidant (1.5 equiv), base (1.2 equiv), and solvent (1.0 mL) under light irradiation using a 23 W compact fluorescent light bulb at rt for 24 h. [b]Yields were determined by ^1H NMR. [c]Reaction was conducted in the dark. [d]Reaction was conducted under air atmosphere. [e]TEMPO (1.2 equiv) was added.

Scheme 1. Substrate Scope for the Phosphonation of Quinolinones[a]



[a]Reactions were performed using **1** (1.0 equiv), **4** (2.0 equiv), **3a** (1.5 equiv), $NaHCO_3$ (1.2 equiv), and CH_3CN (2.0 mL) at rt under N_2 for 24−36 h with light irradiation using a 23 W CFL bulb. Yields of isolated products.

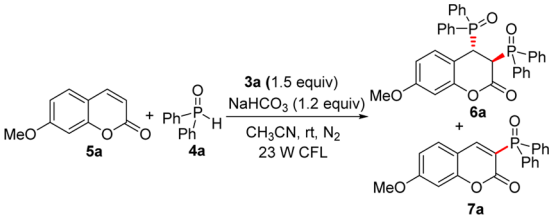
DOI: 10.1021/acs.orglett.7b00299
Org. Lett. XXXX, XXX, XXX−XXX

Two possible ways of quinolinones interacting with light could be considered: (i) involvement of photon-absorbing EDA complex activation or (ii) direct photoexcitation of the quinolinone substrate. We did not detect any color change in the reaction mixture or any photoabsorbing band of the ground-state EDA complex by spectroscopic and absorption measurements (see the SI for detail). Moreover, the addition of a large excess of the reaction components did not change the absorption spectra, excluding any EDA association in the ground state. The only photoabsorbing compound above 360 nm was the quinolinone, indicating that the direct photoexcitation of quinolinone triggers the radical generation from **3a**. We also performed a series of Stern−Volmer quenching experiments by increasing amounts of pyridinium salt **3a**, which revealed that **3a** effectively quenched the excited sate of quinolinone (Figures S4 and S54).

When the product distribution was monitored, we observed that the reaction rate was dramatically accelerated once the 3-phosphonylated product was generated (see the SI). This might be because the 3-phosphonylated products, such as **2e** whose absorption spectrum exhibits a bathochromic displacement reaching up to 440 nm (Figure S1), allow for more effective photocatalysis in the course of the reaction. The results are also consonant with photolysis of pyridinium ion **3a**, where 3-phosphonated quinolinone **2e** displayed superior photocatalytic activity (Table 1, entries 4 and 5).

We next turned our attention to the potential application of our method to valuable coumarin derivatives. When 7-methoxycoumarin (**5a**) was subjected to the optimized conditions (Table 3), a mixture of mono- and bisphosphonated

Table 3. Optimization of the Reaction Conditions for the Phosphonation of Coumarins[a]



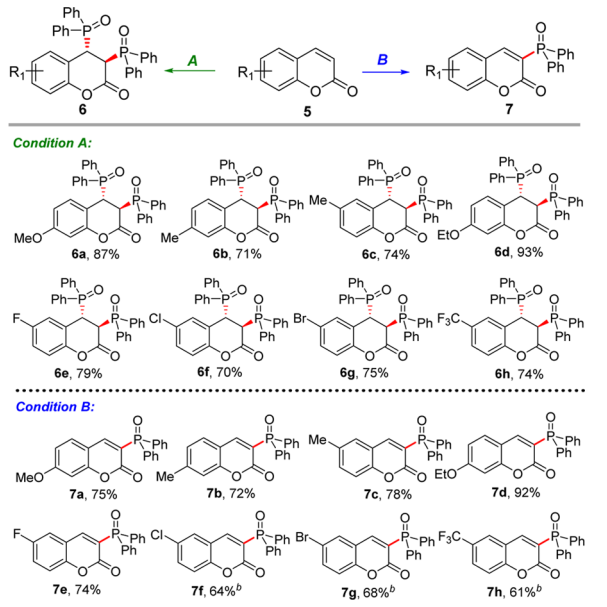
			yield (%)[b]	
entry	**4a** (equiv)	temp/time	**6a**	**7a**
1	1.5	rt/24 h	35	26
2	3.5	rt/24 h	78	14
3	**3.5**	**rt/36 h**	**88**	**trace**
4[c]	**3.5**	**rt/24 h; 90 °C/12 h**	**trace**	**78**

[a]Reactions were performed using **5a** (0.1 mmol), **3a** (1.5 equiv), **4a**, $NaHCO_3$, and CH_3CN (1.0 mL) at rt under N_2 with visible light irradiation using a 23 W CFL bulb. [b]Yields were determined by ^1H NMR. [c]After 24 h, the reaction mixture was treated with paraformaldehyde (2.0 equiv) and $NaHCO_3$ (2.0 equiv) and stirred at 90 °C under N_2 for 12 h.

products was obtained. Further exploration demonstrated that bisphosphonated product **6a** could be selectively produced with the addition of an excess of **4a**. It is noteworthy because bisphosphonated products are typically difficult to obtain in transition metal-mediated reactions due to preferential poisoning of the metal catalyst by the bisphosphoryl moiety. Control experiments show that **6a** was produced through the conjugate addition of **4a** to monophosphonated product **7a**, whereas the formation of bis-adduct from quinolinone was not detected (Scheme S1). Calculation of partial charge distribution exhibited that the C4 position of 3-phosphonated coumarin is more electron-positive and more reactive to electrophilic attack than that of the corresponding quinolinone (Figures S9 and S10). To further expand the synthetic utility, we next assessed the potential of the approach to selectively afford monophosphonated product **7a**. Gratifyingly, a convenient one-pot reaction proceeded well through the sequential phosphonation and elimination process, thus allowing for the synthesis of monophosphonated product **7a** (78%, entry 4).

After determining the divergent reaction conditions, we next explored the scope of the reactions (Scheme 2). Various

Scheme 2. Substrate Scope for the Phosphonation of Coumarins[a]



[a]Condition A: Reactions were performed using **5** (1.0 equiv), $HP(O)Ph_2$ (3.5 equiv), **3a** (1.5 equiv), $NaHCO_3$ (1.2 equiv), and CH_3CN (2.0 mL) at rt under N_2 for 36 h with visible light irradiation using a 23 W CFL bulb. Condition B: The above reaction mixture was stirred for 36 h at rt. The reaction mixture was treated with paraformaldehyde (2.0 equiv) and $NaHCO_3$ (2.0 equiv) and stirred at 90 °C under N_2 for 7−12 h. Yields of isolated products. [b]Paraformaldehyde (3.0 equiv) and $NaHCO_3$ (3.0 equiv) were used.

functional groups including methoxy, methyl, ethoxy, fluoro, chloro, bromo, and trifluoromethyl groups were viable under the optimized conditions to afford the desired bisphosphonated products. The electronic environment of the substrates was not crucial to the reaction efficiency, and both electron-donating (**6a−6d**) and -withdrawing (**6e−6h**) groups were all tolerable. The trans relationship of the 3- and 4-substituents in **6g** was unambiguously verified by X-ray crystallographic analysis (see the SI for details). Additionally, the utility of the present reaction was further broadened by applying the one-pot process to various coumarins, leading to the formation of monophosphonated coumarins (**7a−7h**).

On the basis of these observations, a plausible mechanism for the process is proposed in Figure 1. Upon light absorption, the substrate can reach an excited state **II** and act as a photosensitizer, thus triggering the bond fission of pyridinium salt **3a** by single electron-transfer reduction to yield ethoxy radical and 2-

DOI: 10.1021/acs.orglett.7b00299
Org. Lett. XXXX, XXX, XXX−XXX

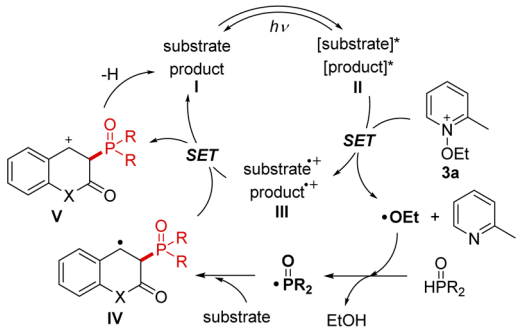


Figure 1. Proposed mechanistic pathway.

methylpyridine. The ethoxy radical undergoes a hydrogen abstraction from diphenylphosphine oxide to afford phosphinoyl radical. Subsequently, the phosphinoyl radical reacts with the quinolinone or coumarin substrates to give radical **IV**, which undergoes a second SET event with strongly oxidizing quinolinone substrate or product radical cations **III** (+1.71 and +1.88 V vs SCE, respectively) to regenerate ground-state substrate or product **I**. The desired product is produced after deprotonation of **V** with base.

In summary, we developed a regioselective phosphonation of quinolinone and coumarin derivatives using a household CFL bulb without the need for an external photocatalyst. The reaction is initiated by the photochemical activity of substrates, and the resulting products greatly increased the rate through light-mediated autocatalysis. The current method is compatible with a broad range of substituents and allows the rapid generation of 3-phosphonylated derivatives, which are privileged structures in many biologically active compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00299.

Experimental procedure and characterization of new compounds (^{1}H and ^{13}C NMR spectra) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: hongorg@kaist.ac.kr.

ORCID

Sungwoo Hong: 0000-0001-9371-1730

Author Contributions

§I.K. and M.M. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported financially by the Institute for Basic Science (IBS-R010-G1).

■ REFERENCES

(1) Dewick, P. M. *Medicinal natural products: a biosynthetic approach*; John Wiley & Sons, 2002. (d) Michael, J. P. *Nat. Prod. Rep.* **2005**, *22*, 627.

(2) Balderas-Renteria, I.; Gonzalez-Barranco, P.; Garcia, A.; Banik, B. K.; Rivera, G. *Curr. Med. Chem.* **2012**, *19*, 4377.

(3) Zheng, S.; Liu, J.; Wu, Y.; Huang, T. L.; Wang, G. *Future Med. Chem.* **2015**, *7*, 2485.

(4) (a) Yi, L.; Li, H.; Sun, L.; Liu, L.; Zhang, C.; Xi, Z. *Angew. Chem., Int. Ed.* **2009**, *48*, 4034. (b) Xu, Z.; Yoon, J.; Spring, D. R. *Chem. Soc. Rev.* **2010**, *39*, 1996. (c) Chan, J.; Dodani, S. C.; Chang, C. J. *Nat. Chem.* **2012**, *4*, 973. (d) Min, M.; Kim, B.; Hong, S. *Org. Biomol. Chem.* **2012**, *10*, 2692. (e) Kim, N.; Min, M.; Hong, S. *Org. Chem. Front.* **2015**, *2*, 1621. (f) Kim, D.; Min, M.; Hong, S. *Chem. Commun.* **2013**, *49*, 4021.

(5) (a) Mi, X.; Huang, M.; Zhang, J.; Wang, C.; Wu, Y. *Org. Lett.* **2013**, *15*, 6266. (b) Mi, X.; Wang, C.; Huang, M.; Zhang, J.; Wu, Y.; Wu, Y. *Org. Lett.* **2014**, *16*, 3356. (c) Yuan, J.-W.; Li, Y.-Z.; Yang, L.-R.; Mai, W.-P.; Mao, P.; Xiao, Y.-M.; Qu, L.-B. *Tetrahedron* **2015**, *71*, 8178.

(6) For selected recent reviews, see: (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. *Chem. Rev.* **2013**, *113*, 5322. (b) Chatterjee, T.; Iqbal, N.; You, Y.; Cho, E. J. *Acc. Chem. Res.* **2016**, *49*, 2284. (c) Fabry, D. C.; Rueping, M. *Acc. Chem. Res.* **2016**, *49*, 1969. (d) Ghosh, I.; Marzo, L.; Das, A.; Shaikh, R.; Konig, B. *Acc. Chem. Res.* **2016**, *49*, 1566. (e) Hopkinson, M. N.; Tlahuext-Aca, A.; Glorius, F. *Acc. Chem. Res.* **2016**, *49*, 2261. (f) Majek, M.; Jacobi von Wangelin, A. *Acc. Chem. Res.* **2016**, *49*, 2316. (g) Reiser, O. *Acc. Chem. Res.* **2016**, *49*, 1990. (h) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075. (i) Shaw, M. H.; Twilton, J.; MacMillan, D. W. *J. Org. Chem.* **2016**, *81*, 6898. (j) Skubi, K. L.; Blum, T. R.; Yoon, T. P. *Chem. Rev.* **2016**, *116*, 10035. (k) Staveness, D.; Bosque, I.; Stephenson, C. R. *Acc. Chem. Res.* **2016**, *49*, 2295. (l) Yoon, T. P. *Acc. Chem. Res.* **2016**, *49*, 2307. (m) Chen, J. R.; Hu, X. Q.; Lu, L. Q.; Xiao, W. J. *Acc. Chem. Res.* **2016**, *49*, 1911. (n) Chen, J. R.; Hu, X. Q.; Lu, L. Q.; Xiao, W. J. *Chem. Soc. Rev.* **2016**, *45*, 2044.

(7) For selected examples of dual catalysis in photochemical synthesis, see: (a) Ye, Y.; Sanford, M. S. *J. Am. Chem. Soc.* **2012**, *134*, 9034. (b) Sahoo, B.; Hopkinson, M. N.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 5505. (c) Lang, S. B.; O'Nele, K. M.; Tunge, J. A. *J. Am. Chem. Soc.* **2014**, *136*, 13606. (d) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W. *Science* **2014**, *345*, 437. (e) Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science* **2014**, *345*, 433. (f) Shu, X.-Z.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D. *J. Am. Chem. Soc.* **2014**, *136*, 5844. (g) Tasker, S. Z.; Jamison, T. F. *J. Am. Chem. Soc.* **2015**, *137*, 9531. (h) He, Y.; Wu, H.; Toste, F. D. *Chem. Sci.* **2015**, *6*, 1194. (i) 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. (j) Duan, Z.; Li, W.; Lei, A. *Org. Lett.* **2016**, *18*, 4012. (k) Liu, K.; Zou, M.; Lei, A. *J. Org. Chem.* **2016**, *81*, 7088. (l) Shaw, M. H.; Shurtleff, V. W.; Terrett, J. A.; Cuthbertson, J. D.; MacMillan, D. W. *Science* **2016**, *352*, 1304. (m) Tlahuext-Aca, A.; Hopkinson, M. N.; Sahoo, B.; Glorius, F. *Chem. Sci.* **2016**, *7*, 89. (n) Um, J.; Yun, H.; Shin, S. *Org. Lett.* **2016**, *18*, 484.

(8) For recent review on EDA complexes, see: Lima, C. G. S.; Lima, T. D.; Duarte, M.; Jurberg, I. D.; Paixão, M. W. *ACS Catal.* **2016**, *6*, 1389.

(9) (a) Arceo, E.; Jurberg, I. D.; Álvarez-Fernández, A.; Melchiorre, P. *Nat. Chem.* **2013**, *5*, 750. (b) Nappi, M.; Bergonzini, G.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2014**, *53*, 4921. (c) da Silva, G. P.; Ali, A.; da Silva, R. C.; Jiang, H.; Paixão, M. W. *Chem. Commun.* **2015**, *51*, 15110. (d) Kandukuri, S. R.; Bahamonde, A.; Chatterjee, I.; Jurberg, I. D.; Escudero-Adan, E. C.; Melchiorre, P. *Angew. Chem., Int. Ed.* **2015**, *54*, 1485.

(10) Silvi, M.; Arceo, E.; Jurberg, I. D.; Cassani, C.; Melchiorre, P. *J. Am. Chem. Soc.* **2015**, *137*, 6120.

(11) Jin, Y.; Yang, H.; Fu, H. *Chem. Commun.* **2016**, *52*, 12909.

(12) (a) Pratsch, G.; Lackner, G. L.; Overman, L. E. *J. Org. Chem.* **2015**, *80*, 6025. (b) Kim, K.; Min, M.; Hong, S. *Adv. Synth. Catal.* **2016**, 1.

(13) Quint, V.; Morlet-Savary, F.; Lohier, J. F.; Lalevee, J.; Gaumont, A. C.; Lakhdar, S. *J. Am. Chem. Soc.* **2016**, *138*, 7436.

(14) (a) Beatty, J. W.; Douglas, J. J.; Cole, K. P.; Stephenson, C. R. J. *Nat. Commun.* **2015**, *6*, 7919. (b) Beatty, J. W.; Douglas, J. J.; Miller, R.; McAtee, R. C.; Cole, K. P.; Stephenson, C. R. J. *Chem.* **2016**, *1*, 456.

(15) (a) Bockman, T. M.; Lee, K. Y.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1581.

DOI: 10.1021/acs.orglett.7b00299
Org. Lett. XXXX, XXX, XXX−XXX