JOC The Journal of Organic Chemistry

Article

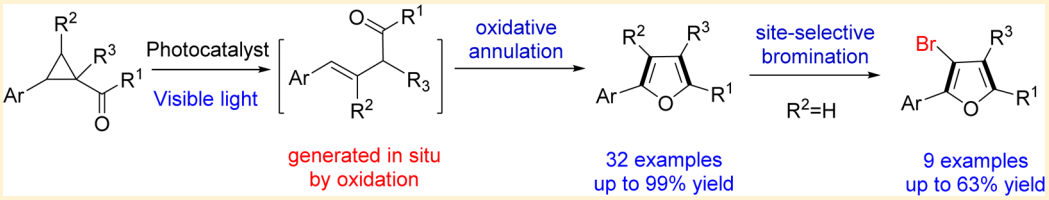
pubs.acs.org/joc

Visible-Light Induced Direct Synthesis of Polysubstituted Furans from Cyclopropyl Ketones

Liyan Feng, Hang Yan, Chao Yang, Dafa Chen, and Wujiong Xia*

State Key Lab of Urban Water Resource and Environment, Shenzhen Graduate School, Harbin Institute of Technology, Harbin 150080 China

Supporting Information



ABSTRACT: In this article, a photoredox protocol for the synthesis of furans via oxidative coupling of olefin generated in situ from cyclopropyl ketones with ketonic oxygen atom is presented. Moreover, bromination of furans in the presence of over-stoichiometric oxidant has been achieved with high regioselectivity.

INTRODUCTION

As one of the most important heterocycles, furan derivatives have exhibited versatile applications in organic synthesis as synthetic intermediates[1] and in the chemical industry to afford commercial products such as pharmaceuticals, pesticides, and functional polymers.[2] Therefore, efficient synthesis of furans, especially in atom-economical pathways, has attracted considerable attention from the realm of organic synthesis.[3] In this regard, transition metal-catalyzed approaches for the assembly of furans meet the criteria well with particular attraction in recent several decades.[4] For instance, a seminal report and subsequent studies on cycloisomerization of allenyl ketones by Marshall lit the way to furan synthesis (Scheme 1, a),[5] followed by Hashmi[6] and Gevorgyan[7] for elaboration. Utimoto[8] and Sheng[9] groups extended the substrate to propargyl ketones (Scheme 1b), and Zhang[10] has developed a series of two-component tandem reactions with high diastereo- and enantioselectivity. Despite the above advances, new methods for direct and regioselective coupling of carbonyl oxygen atom with $C_{sp}{}^2$–H bonds should be potentially of value in constructing furan rings. But a survey of the literature showed that only one report from the Dixneuf group documented the copper catalyzed oxidative coupling to symmetric 2,5-diarylfurans from related unsaturated ketones (Scheme 1c).[11] More recently, a dual catalyst system suitable for efficient construction of C–X bonds by direct addition of heteroatom nucleophiles to alkenes has been established by Nicewicz via a single electron transfer (SET)[12] initiated by visible light irradiation with photosensitizers, which has been well documented as the most effective strategy to activate neutral substrates for bond formation or mesolytic cleavage.[13] Inspired by the pioneering achievement, we are interested in exploiting the photocatalytic protocols for styrene C–H functionalization and discovering new reaction patterns in the oxidative C–O bond formation. In this paper, we present a very intriguing one-pot procedure that consists of the ring opening of aryl cyclopropyl ketones under nonacidic conditions and subsequent direct unimolecular oxidative coupling of the ketonic oxygen atom with $C_{sp}{}^2$–H to deliver polysubstituted furans by visible-light photocatalysis (Scheme 1d).

RESULTS AND DISCUSSION

Our initial investigation was focused on the strategy for transformation of a strained cyclic benzophenone to an unsaturated ketone that was essential for the sequential oxidative coupling reaction. First, **1a** was selected as the model substrate for initial studies. We then introduced carbon tetrabromide as a oxidative quencher that could simultaneously afford bromide ions as an extremely weak base, which was well documented in previous literature.[14] Thus, **1a** was submitted to the typical reaction conditions of CBr_4 (1.0 equiv) and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (5.0 mol %) in CH_3CN under irradiation with a 5 W blue LED. Unexpectedly, a product of 2,5-diphenylfuran **4a** was isolated in 37% yield after reaction for 12 h (Table 1, entry 1). The conversion of compound **1a** to **4a** provides direct access to polysubstituted furans, which stimulated us to explore it in detail.

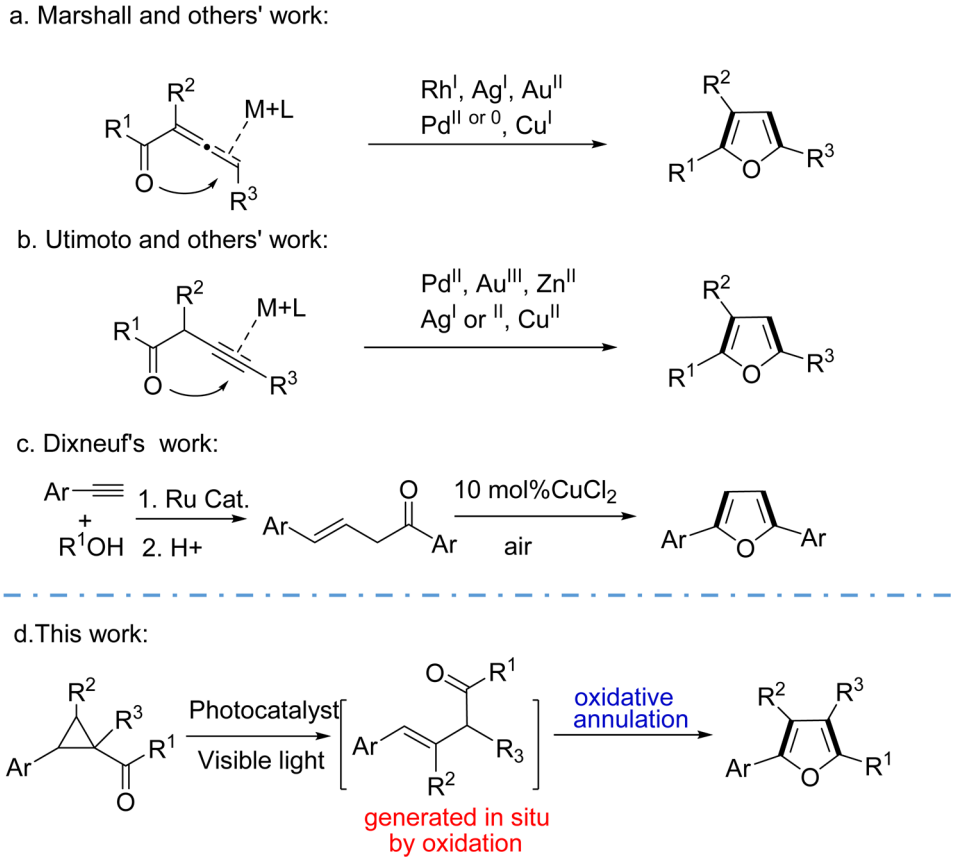
The optimization of the reaction conditions was thus conducted by examination of other oxidative quenchers, such as $Na_2S_2O_8$, but this was ineffective for the reaction unless LiBr was added as an external bromide ion source (Table 1, entries 6 and 8). In addition, the screening of conditions revealed that polar solvents, such as CH_3CN and CH_3NO_2, were more effective possibly owing to their ability to stabilize the distonic radical cations (see SI, Table S2),[15] and $Ru(dtbbpy)_3(PF_6)_2$

Special Issue: Photocatalysis

Received: February 27, 2016
Published: May 11, 2016

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008–7022

Scheme 1. Stepwise Approach to Furans



complex was optimal for this visible-light system (Table 1, entries 7−12).

Moreover, decreasing the concentration of the reagent and halving the stoichiometry of CBr_4 but increasing the amount of LiBr obviously increased the yield of **4a** to 74% (Table 1, entries 13−15). The catalyst loading could be decreased to 1 mol % without loss of effectiveness when a longer time was employed (Table 1, entry 16). Control experiments documented that either light or a photocatalyst was essential for the reaction (Table 1, entries 2 and 3). The oxygen seemed to be friendly for the dehydrogenation, while a tiny amount of water was just opposite (Table 1, entries 4 and 5).

With the optimal conditions in hand, we then investigated the scope of the reaction, and the results are listed in Table 2. As can be seen, electron-donating 2- or 4-substituents of the phenyl ring A were the inevitable choice for the oxidative quenching cycle of the photocatalyst, and various 2,5-diphenylfurans were obtained in moderate to good yields, except for **4v**, which will be discussed later. Electron-donating or -withdrawing substituents including halogen and nitro groups on the other phenyl ring were well tolerated with the reaction conditions. Additionally, the electronic effects of the substituents had a significant influence on reaction time; electron-donating substituents could increase the electron density, which was beneficial to nucleophilicity of the ketonic oxygen atom, and vice versa. For example, the conversion of **4b** and **4c** could be completed in several hours whereas **4i** with CF_3 took a much longer time. On the other hand, different substituents on the furans resulted in different solubility in acetonitrile, which affected the yield due to the sensitivity of furans to light and acidic environments. For instance, **4c** was obtained in good isolated yield since the product was precipitated after reaction.

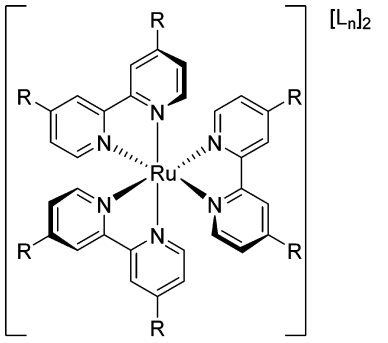
It was particularly noteworthy that the spirocyclopropane was also tolerated with the reaction conditions to contribute a novel dihydronaphthofuran **4t**, but it partly underwent further oxidative dehydrogenation to form **4t′** in a nearly 1:1 ratio. Attempts had been made here to get a single product by examining the amount of CBr_4 and rigorous degassing, but these failed.

Interestingly, a stoichiometric amount of CBr_4 presented a novel bromination pathway of 2,5-unsymmetrically substituted furans with high regioselectivity (see SI, Table S5). Analogous to Fukuzumi's and Nicewicz's studies on selective arene C−H bromination and amination via organic photocatalyst,[16] this electrophilic addition of Br^- was attributed to the orientation of the methoxyl group. Since direct bromination at a certain carbon atom remained a considerable synthetic challenge,[17] we herein disclosed our efforts to develop a radical oxidative sequence to the desired 3-bromofurans. As shown in Table 3, dibromofuran **5c** and the monobromination products **5a**, **5f**, **5g**, **5h**, **5j**, and **5l** were successfully prepared in moderate yields under the standard reaction conditions except for the increased amount of CBr_4 to twice the standard amount. Among these, the progress to afford **5j** did not work out so well even though more oxidant and photocatalyst were employed with a prolonged exposure time to 6 days, yet a higher yield could be achieved by direct irradiation of **4j** in a shorter time. The phenyl ring with an *ortho*-methoxyl group was not ideal for the reaction due to the electronic effect and steric hindrance; for example, **5n** was separated in 53% yield with trace amount of dibromofuran.

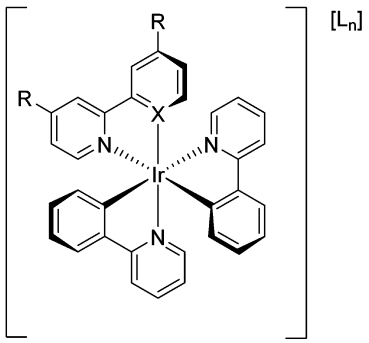
As depicted in the preceding, the coupling reaction to date was limited to aromatic ketones and failed for aliphatic ketones (Table 2, **4v**). To address this drawback, we next devised a

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

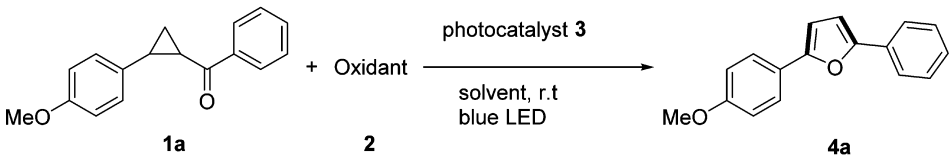
Table 1. Selected Optimization of Reaction Conditions



3a (R= H, Ln = Cl), $Ru(bpy)_3Cl_2$
3b (R = H, Ln = PF_6), $Ru(bpy)_3(PF_6)_2$
3c (R = t-Bu, Ln = PF_6), $Ru(dtbbpy)_3(PF_6)_2$



3d (R= *t*-Bu, X = N, Ln = PF_6), $Ir(ppy)_2(dtbbpy)PF_6$
3e (R = X = H, with no Ln), *fac*-$Ir(ppy)_3$



1a **2** **4a**

2a = CBr_4
2b = $Na_2S_2O_8$

entry[a]	catalyst (mol %)	solvent (M)	oxidant (equiv)	additive (equiv)	*T* (h)	yield[b] (%)
1	**3a** (5)	CH_3CN (0.1)	**2a** (1.0)		12	37
2[c]	**3a** (5)	CH_3CN (0.1)	**2a** (1.0)		24	0
3	--	CH_3CN (0.1)	**2a** (1.0)		24	0
4	**3a** (5)	CH_3CN (0.1)	**2a** (1.0)	H_2O (1.0)	12	16
5[d]	**3a** (5)	CH_3CN (0.1)	**2a** (1.0)		12	23
6	**3a** (5)	CH_3CN (0.1)	**2b** (1.0)		48	0
7	**3a** (5)	CH_3CN (0.1)	**2a** (1.0)	LiBr (1.0)	12	50
8	**3a** (5)	CH_3CN (0.1)	**2b** (1.0)	LiBr (1.0)	12	42
9	**3b** (5)	CH_3CN (0.1)	**2a** (1.0)	LiBr (1.0)	12	32
10	**3c** (5)	CH_3CN (0.1)	**2a** 1.0)	LiBr (1.0)	12	65
11	**3d** (5)	CH_3CN (0.1)	**2a** (1.0)	LiBr (1.0)	12	40
12	**3e** (5)	CH_3CN (0.1)	**2a** (1.0)	LiBr (1.0)	12	42
13	**3c** (5)	CH_3CN (0.1)	**2a** (1.0)	LiBr (0.5)	12	35
14	**3c** (5)	CH_3CN (0.1)	**2a** (0.5)	LiBr (0.5)	12	41
15	**3c** (5)	CH_3CN (0.05)	**2a** (0.5)	LiBr (1.0)	12	74
16	**3c** (1)	CH_3CN (0.05)	**2a** (0.5)	LiBr (1.0)	24	72
17	**3c** (1)	CH_3CN (0.05)	**2a** (0.5)	lutidine	72	0

[a]Reaction conducted under irradiation of a blue LED strip open to air unless otherwise noted. [b]Isolated yields. [c]Without light. [d]Air-free with N_2.

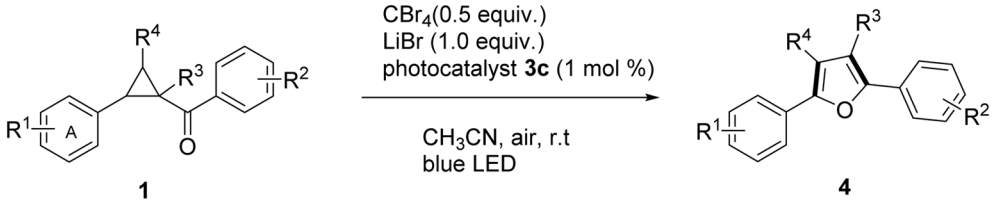
strategy by which the nucleophilicity of alkyl ketone oxygen could be mitigated tactfully by attaching an electron-withdrawing group, such as carbethoxy, to anethene to increase the electrophilicity of the radical cations. However, no reaction was observed when the prepared substrate **6a** (R^2 = H, Table 4) was subjected to the standard conditions. After optimization of the reaction by increasing the amount of CBr_4 (see SI, Table S6), the desired product **7a** was obtained in very high yield (94%). Similarly, other products **7b**−**7h** were also prepared in excellent yield (Table 4). Notably, the reaction conditions were suitable for synthesis of the alkyl substituted furans such as **7i** and **7k** in acceptable yields. The product **7j** containing a hindered group, *tert*-butyl, was also obtained in 95% yield.

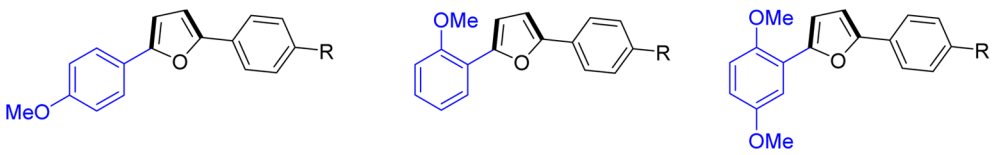
Moreover, this strategy also demonstrated the potential value in the construction of medicinal agents with anticancer activity against breast cancer cell lines and natural product derivatives, such as pallescensin A, a kind of furanosesquiterpene sharing an annulated furan core in common with **7k**.[18]

The mechanism of this transformation was complex and hard to understand. Fortunately, intermediate **B** was isolated from the reaction, which would be useful for the mechanism discussion. But the oxidative ring-opening of **1a** to afford **B** was not found in the literature. To give mechanistic insight into the process, a deuterium substrate, **1a-*d*$_2$**, was treated with $Na_2S_2O_8$, LiBr, and cat. $Ru(bpy)_3Cl_2{\cdot}6H_2O$ under blue LED irradiation. The low deuterium ratio of **B-*d*$_2$** indicated that the process involved both *β*- hydride elimination and intermolecular hydrogen atom transfer (HAT) steps (eq 1). When another substrate, **1w**, was treated under the standard reaction conditions, compound **C** was separated in 38% yield, which suggested the formed radical intermediate without stabilization from a carbonyl group preferred to donate an electron to afford a conjugated alkene (eq 2) or to

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

Table 2. Scope of the 2,5-Diarylfurans Synthesis[a]

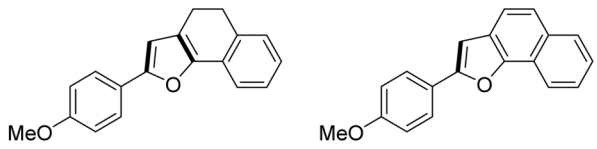




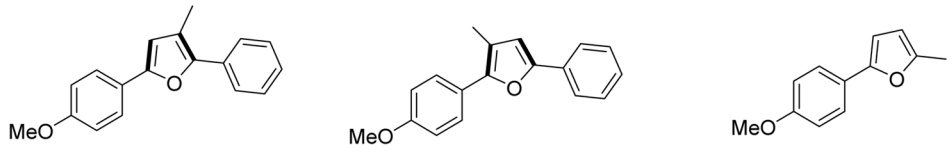
4a: R=H, 12 h, 72%
4b: R=4-Me, 5 h, 68%
4c: R=4-OMe, 21 h, 87%
4d: R=4-t-Bu, 10 h, 73%
4e: R=2,3-butadienyl,7 h, 70%
4f: R=4-F, 20 h, 77%
4g: R=4-Cl, 30 h, 84%
4h: R=4-Br, 30 h, 81%
4i: R=4-CF_3, 20 h, 75%
4j: R=4-NO_2, 16 h, 77%
4k: R=3-OMe, 20 h, 83%
4l: R=3-Cl, 20 h, 82%

4m: R=H, 24 h, 74%
4n: R=4-OMe, 24 h, 75%
4o: R=4-F, 24 h, 69%
4p: R=4-CF_3 24 h, 70%

4q: R=4-F, 20 h, 73%
4r: R=4-CF_3, 24 h, 70%



4t : **4t'** = 1.1:1
28h, 72% yield

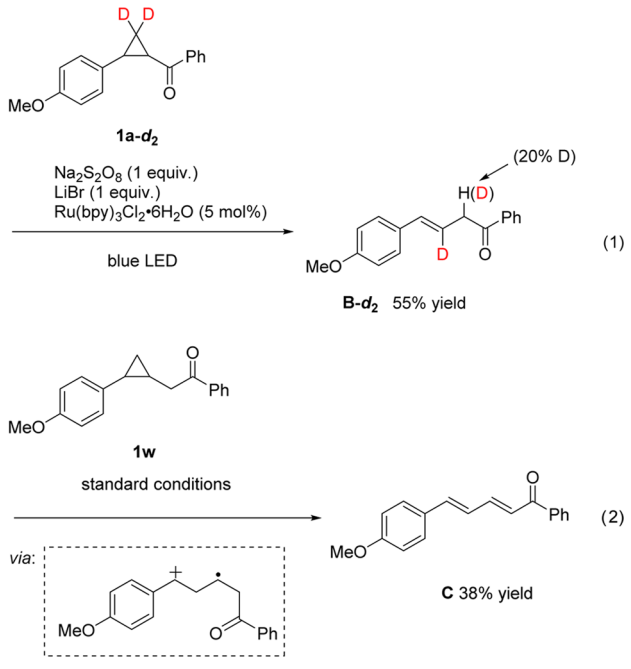


4s
25h, 52% yield

4u
20h, 74% yield

4v
20h, trace

[a]Unless otherwise noted, all reactions were carried out with **1** (50 mg), CBr_4 (0.5 equiv), LiBr (1.0 equiv), and **3c** (1 mol %) in CH_3CN (4 mL) at room temperature under 5 W blue LED. Yields indicated are isolated yields.



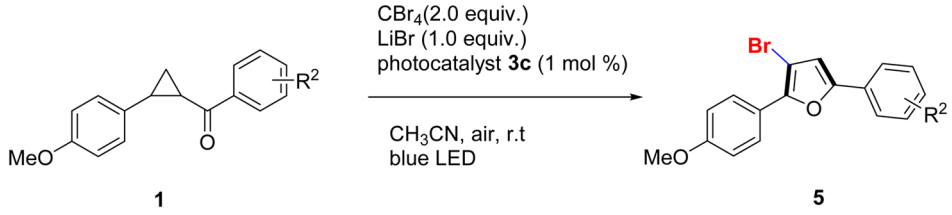
decompose to other products. Moreover, the isolation of **B** was always accompanied by the generation of final product **4a**, which would release HBr to the reaction system. And we proved that the accumulated HBr little by little could facilitate the ring-opening process (Table 5).

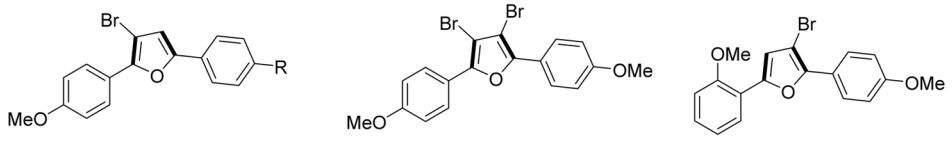
The possible mechanism is shown in Scheme 2. Initially, in pathway A, photoexcited state *$Ru(dtbbpy)_3^{2+}$ was quenched by CBr_4 to form a $Ru(dtbbpy)_3^{3+}$ ($E_{1/2}^{III/II}$ = 1.10 V vs SCE)[19] intermediate, which oxidized anisole **1a-d_2** to radical cation **8**, a species capable of undergoing mesolytic cleavage to afford the distonic radical cation **9**. Previous work in our laboratory demonstrated that these distonic radical cations preferred to eliminate a proton in the presence of 0.3 equiv of CBr_4.[20] The resulting free radical **10** was then reduced by excited *$Ru(dtbbpy)_3^{2+}$ to give **11**, which was acidized to afford **B-d_2**; the high state $Ru(dtbbpy)_3^{3+}$ was utilized for the next cycle. Thus, a catalytic amount of CBr_4 was enough for this process. In pathway B, **1a** was transformed to **B** directly catalyzed by the released HBr in the next step. Here the possible intermediate benzylic cation **12** was also not trapped by Br^-.

Next, the mechanism of the transform from **B** to **4a** was verified by a control experiment. Compound **B** would not

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

Table 3. Scope of 3-Bromofuran Synthesis[a,b]





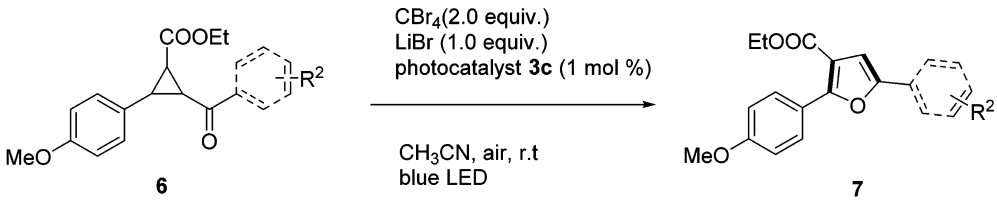
5a: R= H, 52h, 54%
5f: R= 4-F, 85h, 37%
5g: R= 4-Cl, 72h, 55%
5h: R= 4-Br, 82h, 62%
5i: R= 4-CF_3, 60h, 44%
5j[c]: R= 4-NO_2, 6d, 43%
5l: R= 3-Cl, 77h, 63%

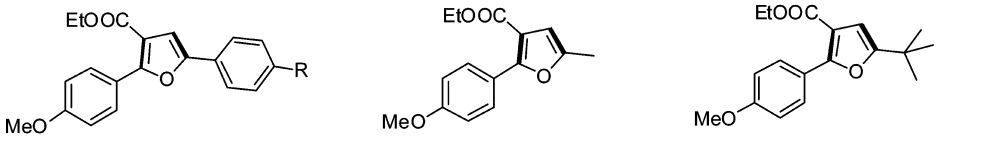
5c: 50h, 63% yield

5n: 53h, 53% yield

[a]Unless otherwise noted, all reactions were carried out with **1** (50 mg), CBr_4 (2.0 equiv), LiBr (1.0 equiv), and **3c** (1 mol %) in CH_3CN (4 mL) at room temperature under 5 W blue LED. [b]Yields indicated are iolated yield. [c]The amount of CBr_4 was increased to 3.0 equiv. to obtain the expected product.

Table 4. Scope of the Furan-3-carboxylate Ethyl Ester Synthesis[a,b]

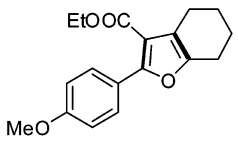




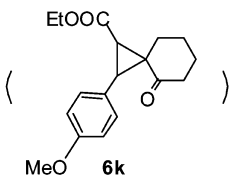
7a: R=H, 34h, 96%
7b: R=4-Me, 29h, 81%
7c: R=4-OMe, 20h, 89%
7d: R=2,3-butadienyl, 37h, 91%
7e: R=4-F, 45h, 99%
7f: R=4-Cl, 58h, 93%
7g: R=4-CF_3, 60h, 80%
7h: R=3-Cl, 52h, 95%

7i: 20h, 63% yield

7j[c]: 24h, 95% yield



7k: 20h, 65% yield



6k

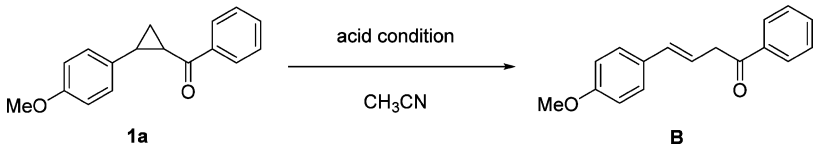
[a]Unless otherwise noted, all reactions were carried out with **6** (100 mg), CBr_4 (2.0 equiv), LiBr (1.0 equiv), and **3c** (1 mol %) in CH_3CN (8 mL) at room temperature under 5 W blue LED. [b]Yields indicated are isolated yield. [c]With cocatalyst 20 mol % TsOH.

transfer to **4a** in acidic conditions under LED irradiation unless oxidative quencher and photocatalyst were added (eqs 3 and 4), which indicated that the aromatic cyclodehydration was an oxidative process. When compound **B** was subjected to the standard conditions, **4a** was isolated in lower yield, and no generation of **5a** was observed (eq 5). These results suggested that all of the 0.5 equiv of CBr_4 was consumed in this oxidative annulation step.

A plausible reaction pathway for the synthesis of furans is illustrated in Scheme 3. The oxidation of the anethene moiety of

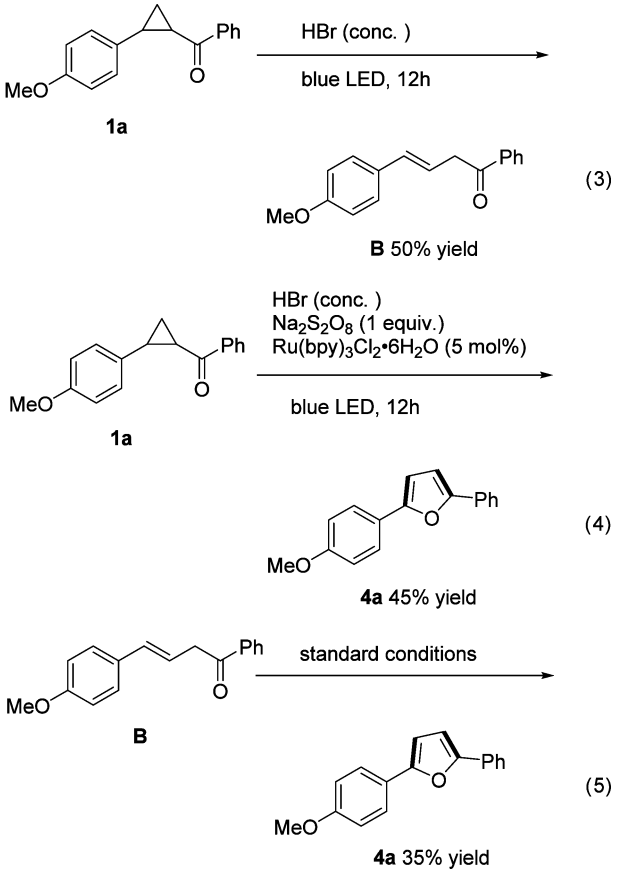
DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

Table 5. Screening of Acids for the Ring Opening[a]



entry	acid (50% mol)	time (min)	yield[b] (%)
1	**HBr (concn)**	**1**	**60**
2	HCl (concn)	1	trace
3	$TsOH·H_2O$	1	20

[a]Acid was added to the solution of **1a** (1 mmol) in CH_3CN (2 mL) with stirring. [b]Isolated yield.



B by $Ru(dtbbpy)_3^{3+}$ resulted in the formation of the radical cation **13**. Nucleophilic addition of ketone oxygen to benzyl carbocation followed by deprotonation gave a radical **15**, which would be oxidated by O_2 to afford the end furan adduct **4a** and released a new oxidative quencher at the same time according to Huo's report.[21]

In the presence of an excess amount of CBr_4, 4-methoxylphenyl could be oxidized by $Ru(dtbbpy)_3^{3+}$ to afford the radical cation **16**, which would undergo charge delocalization to the furan ring. The more stable dihydrofuran radical cation **17** enabled selective addition of Br^- to a certain carbon atom. Analogously, the brominated furan radical **18** was apt to lose an electron to afford **19**, which released a proton to form the 3-bromofuran **5a** (Scheme 4).

CONCLUSION

In summary, we have developed a novel protocol for synthesis of substituted furans from easily accessible cyclopropyl ketones via oxidative C−C bond cleavage and C−O bond formation under mild conditions. The bromofurans could also be achieved with high regioselectivity by employment of an excess amount of CBr_4. We believe that this general SET coupling method will find potential application in natural product and biologically active compound synthesis.

EXPERIMENTAL SECTION

General Information. Unless otherwise stated, all reactions were carried out in air and using distilled solvent, without any precautions to exclude air and moisture unless otherwise noted. All reagents were purchased from commercial suppliers and used without further purification. Melting points were uncorrected. Reactions were monitored by thin-layer chromatography (TLC) carried out on commercial silica gel plates (GF254) using UV light as a visualizing agent. Flash chromatography was performed on silica gel 60 (200−300 mesh). ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on 400 or 600 MHz instrument. Chemical shifts for ^1H NMR spectra were reported in δ ppm referenced to an internal tetramethylsilane (TMS) standard. Chemical shifts for ^{13}C NMR spectra were reported in parts per million relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm. Abbreviations for signal couplings are s, singlet; d, doublet; t, triplet; m, multiplet. Coupling constants (J) are reported in hertz and refer to apparent peak multiplications. High resolution mass spectra (HRMS) were obtained on an iFunnel Q-TOF (ESI) mass spectrometer. GC-MS analysis was performed on a spectrometer with an EI source.

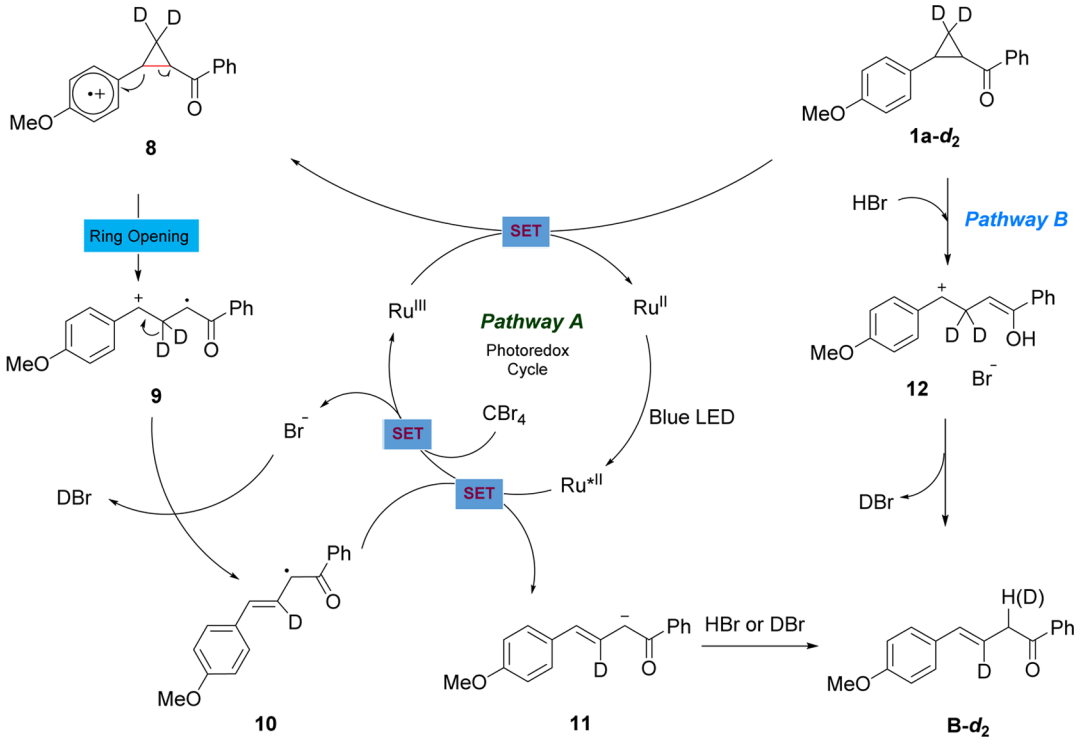
General Procedure for the Synthesis of 1a−1t.[22] Taking substrate **1a** as an example, to a mixture of 4.8 mmol of trimethyloxosulfonium iodide and 1 equiv of NaH (60% mineral oil dispersion) in a two-neck round-bottom flask under N_2 atmosphere, 3 mL of anhydrous THF was added to remove the mineral oil. Anhydrous DMSO (20 mL) was introduced dropwise via syringe, which resulted in vigorous evolution of hydrogen. After being stirred for nearly 30 min, the mixture was clear and no gas bubbled off; 10 mL of a DMSO solution of 4.8 mmol of chalcone was added at 0 °C in an ice bath. The mixture was warmed to room temperature with vigorous stirring for another 20 min and then quenched with 20 mL of sat. aq NH_4Cl, followed by 20 mL of ethyl acetate. The mixture was transferred to a 250 mL separatory funnel, and the organic phase was separated. The aqueous layer was extracted with 3 × 20 mL of ethyl acetate. All organic portions were combined and washed with 3 × 100 mL of brine to remove DMSO, dried over magnesium sulfate, and filtered, and the solvent was removed under vacuum to give a pale yellow oil, which was further purified by flash chromatography (hexane/ethyl acetate = 15:1) to obtain **1a** as a colorless oil.

*(2-(4-Methoxyphenyl)cyclopropyl)(phenyl)methanone (**1a**).* ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00−7.98 (m, 2H), 7.57−7.53 (m, 1H), 7.47−7.44 (m, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.83 (ddd, J = 8.0, 5.2, 4.1 Hz, 1H), 2.66 (ddd, J = 9.1, 6.7, 4.0 Hz, 1H), 1.89 (ddd, J = 9.1, 5.2, 4.1 Hz, 1H), 1.51 (ddd, J = 8.0, 6.7, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.6, 158.4, 137.79, 132.8, 132.4, 128.5, 128.1, 127.4, 114.0, 55.3, 29.6, 29.2, 18.9. HRMS m/z: calcd for $C_{17}H_{16}O_2$ $[M + H]^+$ 253.1224, found 253.1222.

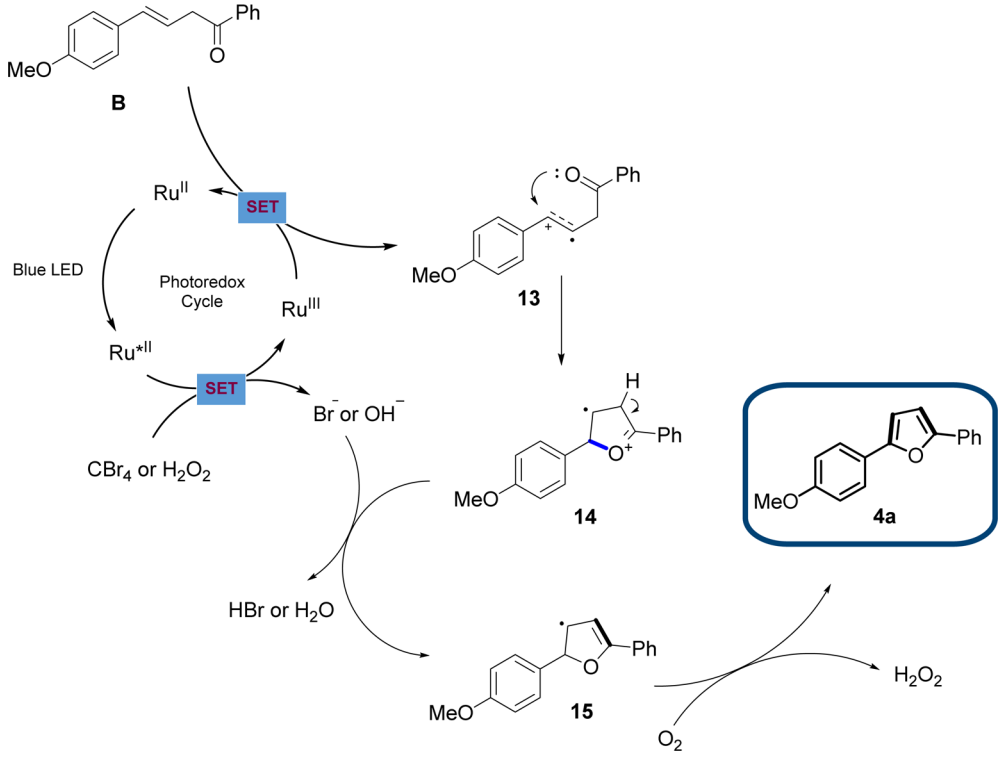
*(2-(4-Methoxyphenyl)cyclopropyl)(p-tolyl)methanone (**1b**).* ^1H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H),

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

Scheme 2. Mechanism for Ring Opening



Scheme 3. Mechanism for Oxidative Annulation

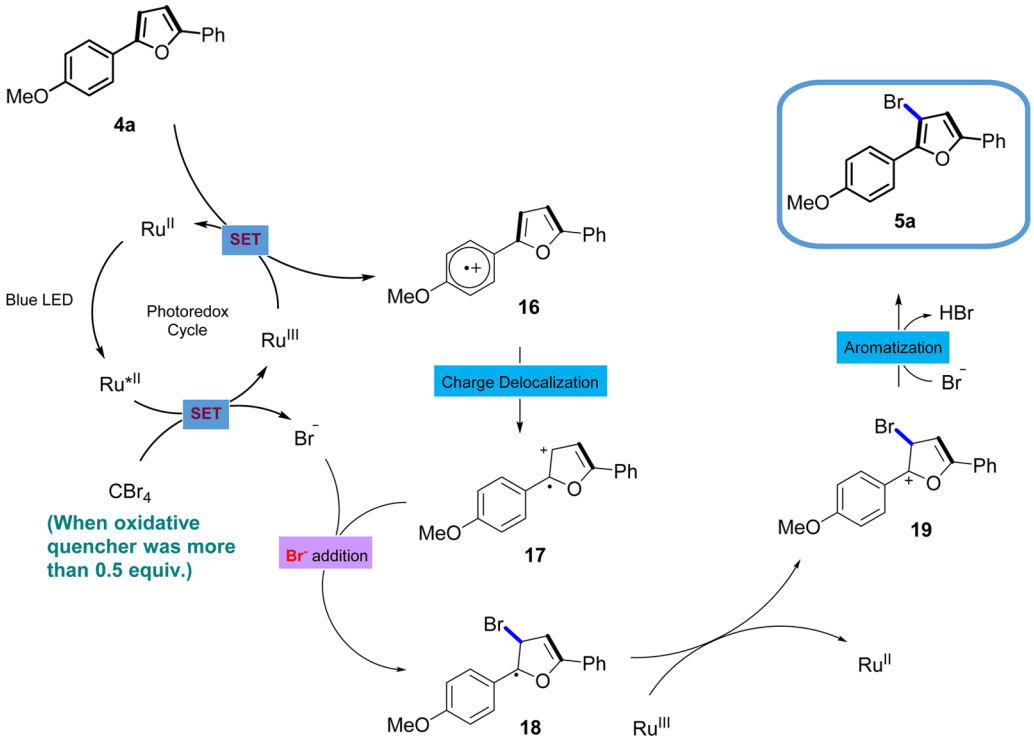


7.11 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 2.80 (ddd, J = 8.1, 5.2, 4.1 Hz, 1H), 2.64 (ddd, J = 9.1, 6.6, 4.0 Hz, 1H), 2.41 (s, 3H), 1.87 (ddd, J = 9.2, 5.2, 4.1 Hz, 1H), 1.48 (ddd, J = 8.0, 6.7, 4.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.2, 158.3, 143.6, 135.2, 132.6, 129.2, 128.2, 127.4, 113.9, 55.3, 29.4, 29.0, 21.6, 18.8. HRMS m/z: calcd for $C_{18}H_{18}O_2$ $[M + H]^+$ 267.1380, found 267.1388.

*(4-Methoxyphenyl)(2-(4-methoxyphenyl)cyclopropyl)methanone (**1c**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 2.78 (ddd, J = 8.3, 5.0, 4.3 Hz, 1H) 2.63 (ddd, J = 9.3, 6.6, 4.0 Hz, 1H), 1.86 (ddd, J = 9.1, 5.1, 4.2 Hz, 1H), 1.47 (ddd, J = 8.0, 6.6, 4.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.1, 163.4, 158.3, 132.7, 130.8, 130.3, 127.4, 113.9, 113.7, 55.5, 55.3, 29.1, 28.8, 18.6. HRMS m/z: calcd for $C_{18}H_{18}O_3$ $[M + H]^+$ 283.1329, found 283.1329.

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

Scheme 4. Mechanism for Regioselective Bromination of Furan



2-(4-Methoxyphenyl)cyclopropyl(4-tert butylpheny)lmethanone (***1d***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.82 (ddd, J = 8.4, 5.1, 4.3 Hz, 1H), 2.63 (ddd, J = 8.6, 6.7, 4.2 Hz, 1H), 1.88 (ddd, J = 9.1, 5.0, 4.3 Hz, 1H), 1.48 (ddd, J = 7.8, 6.8, 4.2 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 158.4, 156.5, 135.2, 132.6, 128.0, 127.4, 125.4, 114.0, 55.3, 35.0, 31.1, 29.4, 29.0, 18.6. HRMS m/z: calcd for $C_{21}H_{24}O_2$ $[M + H]^+$ 309.1850, found 309.1847.

(2-(4-Methoxyphenyl)cyclopropyl)(naphthalen-1-yl)methanone (***1e***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.49 (d, J = 9.1 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.94−7.80 (m, 2H), 7.53 (dtd, J = 14.1, 6.9, 1.5 Hz, 2H), 7.49 (t, J = 8.2 Hz, 1H), 7.13 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.78 (dddd, J = 12.0, 8.1, 5.9, 4.0 Hz, 2H), 2.03 (ddd, J = 9.2, 5.3, 4.1 Hz, 1H), 1.57 (ddd, J = 9.4, 8.1, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.4, 158.4, 137.4, 133.8, 132.2, 132.1, 129.9, 128.4, 127.5, 127.4, 127.3, 126.3, 125.7, 124.5, 114.0, 55.3, 33.4, 30.3, 19.6. HRMS m/z: calcd for $C_{21}H_{18}O_2$ $[M + H]^+$ 303.1380, found 303.1377.

(4-Fluorophenyl)(2-(4-methoxyphenyl)cyclopropyl)methanone (***1f***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, J = 8.8, 5.4 Hz, 2H), 7.12 (t, J = 8.8 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 2.76 (ddd, J = 8.1, 5.0, 4.2 Hz, 1H), 2.65 (ddd, J = 9.2, 6.7, 4.0 Hz, 1H), 1.89 (ddd, J = 9.2, 5.1, 4.3 Hz, 1H), 1.52 (ddd, J = 7.8, 6.8, 4.2 Hz, 1H), 1.52 (ddd, J = 7.8, 6.8, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.0, 165.6 (d, J = 254.3 Hz), 158.4, 134.1 (d, J = 2.9 Hz), 132.3, 130.6 (d, J = 9.2 Hz), 127.3, 115.6 (d, J = 21.8 Hz), 114.0, 55.3, 29.7, 29.1, 18.9. HRMS m/z: calcd for $C_{17}H_{15}FO_2$ $[M + H]^+$ 271.1129, found 271.1132.

(4-Chlorophenyl)-2-(4-methoxyphenyl)cyclopropylmethanone (***1g***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 2.75 (ddd, J = 8.1, 5.1, 4.2 Hz, 1H), 2.65 (ddd, J = 8.9, 6.7, 4.0 Hz, 1H), 1.89 (ddd, J = 9.2, 5.0, 4.3 Hz, 1H), 1.52 (ddd, J = 7.9, 6.8, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.3, 158.4, 139.2, 136.0, 132.1, 129.4, 128.8, 127.3, 114.0, 55.3, 29.9, 29.2, 19.0. HRMS m/z: calcd for $C_{17}H_{15}ClO_2$ $[M + H]^+$ 287.0834, found 287.0833.

(4-Bromophenyl)-2-(4-methoxyphenyl)cyclopropylmethanone (***1h***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 2.75 (ddd, J = 8.1, 5.1, 4.2 Hz, 1H), 2.66 (ddd, J = 9.4, 6.7, 4.0 Hz, 1H), 1.89 (ddd, J = 9.2, 5.1, 4.3 Hz, 1H), 1.53 (ddd, J = 7.9, 6.8, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 158.5, 136.5, 132.2, 131.8, 129.6, 128.0, 127.4, 114.1, 55.3, 29.9, 29.2, 19.1. HRMS m/z: calcd for $C_{17}H_{15}BrO_2$ $[M + H]^+$ 331.0329, found 331.0334.

4-(Trifluoromethyl)phenyl)-2-(4-methyloxyphenyl)-cycloprylmethanone (***1i***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 3.80 (s, 3H), 2.80 (ddd, J = 8.1, 5.1, 4.1 Hz, 1H), 2.80 (ddd, J = 8.1, 5.1, 4.1 Hz, 1H), 2.70 (ddd, J = 9.3, 6.8, 4.0 Hz, 1H), 1.94 (ddd, J = 9.2, 4.9, 4.4 Hz, 1H), 1.58 (ddd, J = 7.8, 6.9, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 158.6, 140.5 (d, J = 1.0 Hz), 134.1 (q, J = 32.7 Hz), 131.9, 128.4, 127.4, 125.6 (q, J = 3.7 Hz), 123.6 (q, J = 272.6 Hz), 114.1, 55.3, 30.4, 29.6, 19.3. HRMS m/z: calcd for $C_{18}H_{15}F_3O_2$ $[M + H]^+$ 321.1097, found 321.1091.

[2-(4-Methoxyphenyl)cyclopropyl](4-nitrylphenyl)methanone (***1j***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J = 8.9 Hz, 2H), 8.12 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 2.80 (ddd, J = 8.0, 5.1, 4.0 Hz, 1H), 2.73 (ddd, J = 9.2, 6.9, 3.9 Hz, 1H), 1.97 (ddd, J = 9.3, 5.1, 4.4 Hz, 1H), 1.63 (ddd, J = 7.8, 6.9, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.2, 158.7, 150.1, 142.3, 131.6, 129.0, 127.3, 123.8, 114.1, 55.3, 30.9, 30.1, 19.7. GC-MS (EI)m/z: 297, 147, 132, 115, 104, 91, 76.

2-(4-Methoxyphenyl)cyclopropyl(3-methoxy-phenyl)methanone (***1k***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.10 (t, J = 7.9 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 3H), 2.80 (ddd, J = 8.1, 5.1, 4.2 Hz, 1H), 2.66 (ddd, J = 9.2, 6.7, 4.0 Hz, 1H), 1.88 (ddd, J = 9.1, 5.1, 4.2 Hz, 1H), 1.51 (ddd, J = 7.9, 6.7, 4.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.5, 159.8, 158.4, 139.1, 132.4, 129.5, 127.4, 120.8, 119.3, 114.0, 112.3, 55.4, 55.3, 29.8, 29.308, 19.0. HRMS m/z: calcd for $C_{18}H_{18}O_3$ $[M + H]^+$ 283.1329, found 283.1322.

(3-Chlorophenyl)-2-(4-methoxyphenyl)cyclopropylmethanone (***1l***). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (dd, J = 7.5, 1.5 Hz, 1H), 7.38 (td, J = 7.2, 1.6 Hz, 1H), 7.38 (dd, J = 7.5, 1.5 Hz, 1H), 7.31 (td, J = 7.2, 1.6 Hz, 1H), 7.09 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 3.78 (s, 3H), 2.75 (ddd, J = 9.1, 6.9, 4.0 Hz, 1H), 2.67 (ddd, J = 8.1, 5.1, 4.1 Hz, 1H), 1.93 (ddd, J = 9.2, 5.1, 4.3 Hz, 1H) 1.55 (ddd, J = 7.8,

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

7.0, 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5, 158.4, 139.9, 132.0, 131.7, 131.3, 130.4, 129.2, 127.34 126.9, 113.9, 55.3, 33.6, 31.1, 20.2. HRMS *m*/*z*: calcd for $C_{17}H_{15}ClO_2$ $[M + H]^+$ 287.0834, found 287.0836.

*2-(2-Methoxyphenyl)cyclopropylphenylmethanone (**1m**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04−7.99 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 2.86 (ddd, *J* = 8.8, 7.0, 4.2 Hz, 1H), 2.80 (ddd, *J* = 7.9, 5.1, 4.3 Hz, 1H), 1.89 (ddd, *J* = 9.0, 5.2, 4.0 Hz, 1H), 1.55 (ddd, *J* = 7.9, 7.0, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 158.5, 138.1, 132.6, 128.7, 128.4, 128.1, 127.7, 126.2, 120.4, 110.3, 55.3, 27.8, 25.5, 17.3. HRMS *m*/*z*: calcd for $C_{17}H_{16}O_2$ $[M + H]^+$ 253.1224, found 253.1222.

*(2-Methoxyphenyl)cyclopropyl(4-methoxyphenyl)methanone (**1n**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.9 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.92 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H), 2.83 (ddd, *J* = 8.8, 7.0, 4.3 Hz, 1H), 2.76 (ddd, *J* = 7.9, 5.2, 4.3 Hz, 1H), 1.86 (ddd, *J* = 9.0, 5.1, 4.0 Hz, 1H), 1.50 (ddd, *J* = 7.7, 7.0, 3.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.6, 163.2, 158.5, 131.1, 130.4, 129.0, 127.6, 126.2, 120.4, 113.6, 110.3, 55.4, 55.3, 27.4, 24.9, 17.1. HRMS *m*/*z*: calcd for $C_{18}H_{18}O_3$ $[M + H]^+$ 283.1329, found 283.1334.

*(4-Fluorophenyl)-2-(2-methoxyphenyl)cyclopropylmethanone (**1o**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 2.83 (ddd, *J* = 8.7, 7.2, 4.2 Hz, 1H), 2.74 (ddd, *J* = 7.9, 5.0, 4.2 Hz, 1H), 1.89 (ddd, *J* = 9.1, 5.1, 4.1 Hz, 1H), 1.56 (ddd, *J* = 7.7, 7.0, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 165.6 (d, *J* = 253.9 Hz), 158.5, 134.4 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 9.2 Hz), 128.6, 127.8, 126.3, 120.4, 115.5 (d, *J* = 21.8 Hz), 110.3, 55.3, 27.7, 25.6, 17.2. HRMS *m*/*z*: calcd for $C_{17}H_{15}FO_2$ $[M + H]^+$ 271.1134, found 271.1139.

*4-(Trifluoromethyl)phenyl-2-(2-methyloxyphenyl)-cycloprylmethanone (**1p**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 3H), 2.86 (ddd, *J* = 8.7, 7.2, 4.2 Hz, 1H), 2.75 (ddd, *J* = 7.8, 5.0, 4.4 Hz, 1H), 1.94 (ddd, *J* = 9.1, 5.1, 4.1 Hz, 1H), 1.62 (ddd, *J* = 7.6, 7.2, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.5, 158.5, 140.8 (d, *J* = 1.0 Hz), 133.9 (q, *J* = 32.6 Hz), 128.4, 128.3, 128.0, 126.4, 125.5 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.6 Hz) 120.4, 110.3, 55.3, 28.2, 26.5, 17.4. HRMS *m*/*z*: calcd for $C_{18}H_{15}F_3O_2$ $[M + H]^+$ 321.1097, found 321.1103.

*(4-Fluorophenyl)[2-(2,5-dimethoxyphenyl)cyclopropyl]-methanone (**1q**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.74 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.61 (d, *J* = 2.9 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 2.83 (ddd, *J* = 8.9, 7.0, 4.2 Hz, 1H), 2.75 (ddd, *J* = 8.0, 5.1, 4.4 Hz, 1H), 1.89 (ddd, *J* = 9.1, 5.1, 4.1 Hz, 1H), 1.53 (ddd, *J* = 7.6, 7.1, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 165.6 (d, *J* = 254.0 Hz), 153.6, 152.7, 134.4 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.2 Hz), 130.0, 115.5 (d, *J* = 21.8 Hz), 113.1, 111.4, 111.3, 56.0, 55.7, 27.9, 25.5, 17.4. HRMS *m*/*z*: calcd for $C_{18}H_{17}FO_3$ $[M + H]^+$ 301.1240, found 301.1249.

*[4-(Trifluoromethyl)phenyl)]-2-[(2,5-dimethyloxyphenyl)-cyclopryl]methanone (**1r**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.75 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.63 (s, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 2.86 (ddd, *J* = 7.6, 6.2, 3.5 Hz, 1H), 2.77 (ddd, *J* = 12.0, 5.9, 3.4 Hz, 1H), 1.93 (ddd, *J* = 9.1, 5.4, 1.4 Hz, 1H), 1.60 (ddd, *J* = 7.7, 5.0, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.3, 153.6, 152.7, 140.7 (d, *J* = 0.8 Hz), 134.0 (q, *J* = 32.6 Hz), 129.6, 128.4, 125.5 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 272.5 Hz), 113.3, 111.5, 111.3, 55.9, 55.7, 28.4, 26.3, 17.6. HRMS *m*/*z*: calcd for $C_{19}H_{17}F_3O_3$ $[M + H]^+$ 351.1208, found 351.1208.

*(2-(4-Methoxyphenyl)-1-methylcyclopropyl)(phenyl)methanone (**1s**).* ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.82−7.70 (m, 2H), 7.53−7.47 (m, 1H), 7.48−7.40 (m, 2H), 7.24−7.15 (m, 2H), 6.96−6.88 (m, 2H), 3.82 (s, 3H), 2.62 (dd, *J* = 9.2, 6.9 Hz, 1H), 1.98 (dd, *J* = 9.2, 4.8 Hz, 1H), 1.20 (dd, *J* = 6.9, 4.8 Hz, 1H), 1.15 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 203.82, 158.41, 137.48, 131.64, 129.89, 128.68, 128.27, 128.23, 113.77, 113.54, 55.22, 32.53, 31.09, 18.24, 16.68. HRMS *m*/*z*: calcd for $C_{18}H_{18}O_2$ $[M + H]^+$ 267.1385, found 267.1389.

*2-(4-Methoxyphenyl)-3′,4′-dihydro-1′H-spiro(cyclopropane-1,2′-naphthalen)-1′-one (**1t**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 7.2 Hz, 1H), 7.43 (td, *J* = 7.2, 1.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.95 (dd, *J* = 8.5, 7.7 Hz, 1H), 2.78−2.65 (m, 2H), 1.89 (ddd, *J* = 13.8, 8.8, 4.6 Hz, 2H), 1.64 (ddd, *J* = 13.8, 6.4, 4.9 Hz, 1H), 1.31 (dd, *J* = 7.1, 4.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.2, 158.4, 143.9, 133.0, 132.7, 130.1, 128.8, 128.4, 126.9, 126.5, 113.5, 55.1, 34.1, 34.0, 27.8, 26.4, 20.4. HRMS *m*/*z*: calcd for $C_{19}H_{18}O_2$ $[M + H]^+$ 279.1385, found 279.1385.

General Procedure for the Synthesis of 1u. A mixture of anethene (3.4 g, 23 mmol) and $Rh_2(OAc)_4$ (35.5 mg, 0.08 mmol) was dispersed in dried DCM under N_2 atmosphere, a solution of diazoacetate (2.7 mL, 23 mmol) was introduced via a pressure-compensated dropping funnel over a period of 12 h, and then the reaction stood for another 12 h. The mixture was then concentrated, and the residue was directly purified by flash chromatography (petroleum ether/ethyl acetate = 15:1) to afford the cyclopropane derivative as colorless oil in 65% yield.

To the mixed solution in MeOH (20 mL) and THF (10 mL) of the cyclopropane derivative (3.5 g, 15 mmol) was added 10 mL of NaOH (aqueous 3 M solution), and the mixture was refluxed for 3 h. The mixture was then concentrated under vacuum to remove MeOH and THF. The residue then acidified to pH 3 (with aqueous 1 M HCl solution), extracted with ethyl acetate (3 × 20 mL), and washed with brine. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated in vacuum to give the crude carboxylic acid. The acid was purified by flash chromatography (petroleum ether/EtOAc = 5:1) to obtain cyclopropyl acid as white solid in 90% yield.

To the solution of cyclopropyl acid (2.8 g, 12.1 mmol) and cat. DMF in DCM was introduced oxalyl chloride (1.85 g, 14.5 mmol) via syringe slowly with vigorous stirring over 10 min at room temperature. The resulting mixture was stirred for another 1 h, and then the solution and excess oxalyl chloride was removed under vacuum to afford a yellow residue, which was dissolved in another 30 mL of DCM, followed by addition of *N*,*O*-dimethylhydroxylamine hydrochloride (1.77 g, 18.2 mmol) and pyridyl (3.8 g, 48 mmol). The reaction was quenched with aqueous 1 M HCl solution to pH 7, extracted with ethyl acetate, washed with brine, dried with $MgSO_4$, filtered, and concentrated to give the crude Weinreb formamide, which was purified by flash chromatography (petroleum ether/EtOAc = 5:1) to afford colorless oil in 85% yield.

Phenylmagnesium bromide (1.0 M in THF, 6.0 mmol) was added via syringe dropwise to the solution of the Weinreb formamide (1.0 g, 4.0 mmol) in THF under N_2 atmosphere at room temperature, and the reaction was stirred for an additional 4 h, quenched with sat. aq NH_4Cl, and extracted with ethyl acetate. The combined organic layers were washed with sat. aq. NH_4Cl and brine, dried ($MgSO_4$), and concentrated to give crude product that was subjected to chromatography on a short silica column (petroleum ether/EtOAc = 15:1) to obtain **1u** in 95% yield.

*(2-(4-Methoxyphenyl)-3-methylcyclopropyl)(phenyl)methanone (**1u**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07−7.98 (m, 2H), 7.60−7.54 (m, 1H), 7.51−7.42 (m, 2H), 7.15−7.07 (m, 2H), 6.88−6.80 (m, 2H), 3.79 (s, 3H), 2.92 (dd, *J* = 9.2, 5.0 Hz, 1H), 2.78 (dd, *J* = 6.7, 5.0 Hz, 1H), 2.00 (dp, *J* = 9.2, 6.3 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.56, 158.14, 138.77, 132.91, 132.62, 128.48, 128.00, 127.38, 113.88, 77.21, 77.00, 76.79, 55.31, 34.49, 32.44, 28.61, 11.63. HRMS *m*/*z*: calcd for $C_{18}H_{18}O_2$ $[M + H]^+$ 267.1385, found 267.1391.

General Procedure for the Synthesis of 1w. Cyclopropyl alcohol was prepared according to literature. To a solution of cyclopropyl alcohol in DCM was added PCC (1.5 equiv) at room temperature under N_2. After complete conversion in about 1.5 h, Celite was added followed by petroleum ether, and then the mixture was filtered and concentrated *in vacuo*. The residue was purified on short silica column to afford the target compound. To a solution of the aldehyde in dry THF was added PhMgBr solution (1.0 M in THF, 1.3 equiv) dropwise at 0 °C.

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

After stirring at room temperature for 5 h, the reaction then quenched with sat. aq. NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography to give the desired benzyl alcohol, which could be oxidated smoothly to **1w** by PCC yielding a white solid.

*2-(2-(4-Methoxyphenyl)cyclopropyl)-1-phenylethan-1-one (**1w**).* ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.03−7.92 (m, 2H), 7.61−7.53 (m, 1H), 7.47 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.09−7.00 (m, 2H), 6.85−6.77 (m, 2H), 3.77 (s, 3H), 3.14 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.98 (dd, *J* = 16.5, 7.0 Hz, 1H), 1.76 (dt, *J* = 9.3, 5.0 Hz, 1H), 1.48−1.38 (m, 1H), 0.99 (dt, *J* = 8.5, 5.2 Hz, 1H), 0.84 (dt, *J* = 8.7, 5.3 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.43, 157.69, 136.82, 134.65, 133.05, 128.62, 128.14, 127.26, 113.73, 55.30, 43.41, 22.31, 17.79, 14.93. HRMS *m*/*z*: calcd for $C_{18}H_{19}O_2$ $[M + H]^+$ 267.1385, found 267.1371.

General Procedure for the Synthesis of 6a−6k.[23] Taking substrate **6a** as an example, a solution of chalcone (2.0 g, 8.4 mmol) and ethyl (dimethylsulfuranylidene)acetate (1.87 g, 13 mmol) in DCM was held overnight at 50 °C. The mixture was concentrated and eluted through a silica gel (petroleum ether/EtOAc = 5:1) to give a mixture of diastereoisomers, separated by flash chromatography (petroleum ether/EtOAc = 20:1 to 5:1), and recrystallized from ethyl acetate/hexanes to give the desired cyclopropane derivative.

*Ethyl-2-benzoyl-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6a**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.18−7.13 (m, 2H), 6.90−6.84 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.32 (t, *J* = 6.2 Hz, 1H), 3.03 (dd, *J* = 9.5, 6.4 Hz, 1H), 2.58 (dd, *J* = 9.5, 6.0 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.81, 169.24, 158.71, 136.90, 133.20, 129.97, 128.55, 128.30, 127.67, 114.07, 60.99, 55.27, 34.94, 31.48, 29.18, 13.99. HRMS *m*/*z*: calcd for $C_{20}H_{20}O_4$ $[M + H]^+$ 325.1434, found 325.1435.

*Ethyl-2-(4-methoxyphenyl)-3-(4-methylbenzoyl)cyclopropane-1-carboxylate (**6b**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 3.30 (t, *J* = 6.2 Hz, 1H), 3.01 (dd, *J* = 9.5, 6.5 Hz, 1H), 2.56 (dd, *J* = 9.5, 6.0 Hz, 1H), 2.40 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.39, 169.34, 158.69, 144.04, 134.48, 130.13, 129.38, 129.25, 128.56, 128.45, 127.69, 114.07, 60.97, 55.30, 34.95, 31.41, 29.11, 21.66, 14.02. HRMS *m*/*z*: calcd for $C_{21}H_{22}O_4$ $[M + H]^+$ 339.1591, found 339.1595.

*Ethyl-2-(4-methoxybenzoyl)-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6c**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.03−7.98 (m, 2H), 7.17−7.13 (m, 2H), 6.95−6.90 (m, 2H), 6.88−6.84 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.85 (d, *J* = 1.5 Hz, 3H), 3.79 (d, *J* = 1.5 Hz, 3H), 3.29 (t, *J* = 6.2 Hz, 1H), 2.99 (dd, *J* = 9.5, 6.5 Hz, 1H), 2.54 (dd, *J* = 9.5, 5.9 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.21, 169.41, 163.57, 158.67, 130.63, 130.19, 130.05, 127.68, 114.06, 113.72, 60.96, 55.45, 55.30, 34.88, 31.27, 29.02, 14.04. HRMS *m*/*z*: calcd for $C_{21}H_{22}O_5$ $[M + H]^+$ 355.1540, found 355.1541.

*Ethyl-2-(1-naphthoyl)-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6d**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 8.6 Hz, 1H), 8.05 (dd, *J* = 7.2, 1.0 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.59 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 7.50 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.18−7.14 (m, 2H), 6.89−6.86 (m, 2H), 4.18−4.11 (m, 2H), 3.80 (s, 3H), 3.44 (t, *J* = 6.2 Hz, 1H), 3.10 (dd, *J* = 9.5, 6.2 Hz, 1H), 2.66 (dd, *J* = 9.5, 6.3 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 197.45, 169.06, 158.75, 135.54, 133.86, 133.04, 130.23, 129.97, 128.63, 128.33, 128.01, 127.64, 126.48, 125.92, 124.34, 114.12, 61.18, 55.33, 37.75, 32.95, 30.38, 14.12. HRMS *m*/*z*: calcd for $C_{24}H_{22}O_4$ $[M + H]^+$ 375.1591 found 375.1599

*Ethyl-2-(4-fluorobenzoyl)-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6e**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.09−8.03 (m, 2H), 7.19−7.10 (m, 4H), 6.92−6.85 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.31 (t, *J* = 6.2 Hz, 1H), 2.98 (dd, *J* = 9.4, 6.4 Hz, 1H), 2.58 (dd, *J* = 9.5, 6.0 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.23, 169.20, 166.63, 164.94, 158.77, 133.37, 133.35, 130.98, 130.92, 129.80, 127.66, 115.79, 115.64, 114.12, 61.08, 55.30, 34.85, 31.41, 29.18, 14.03. HRMS *m*/*z*: calcd for $C_{20}H_{19}FO_4$ $[M + H]^+$ 343.1340, found 343.1345.

*Ethyl-2-(4-chlorobenzoyl)-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6f**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 3.30 (t, *J* = 6.2 Hz, 1H), 2.97 (dd, *J* = 9.4, 6.4 Hz, 1H), 2.58 (dd, *J* = 9.4, 6.0 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.63, 169.13, 158.78, 139.65, 135.23, 129.71, 129.69, 128.90, 127.65, 114.11, 61.09, 55.29, 34.81, 31.47, 29.22, 14.02. HRMS *m*/*z*: calcd for $C_{20}H_{19}ClO_4$ $[M + H]^+$ 359.1045, found 359.1042.

*Ethyl-2-(4-methoxyphenyl)-3-(4-(trifluoromethyl)benzoyl)-cyclopropane-1-carboxylate (**6g**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.19−7.13 (m, 2H), 6.92−6.86 (m, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.33 (t, *J* = 6.2 Hz, 1H), 3.00 (dd, *J* = 9.4, 6.4 Hz, 1H), 2.63 (dd, *J* = 9.4, 6.0 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.05, 169.07, 158.88, 139.57, 134.50 (q, *J* = 32.6 Hz), 129.52, 128.63, 127.69, 125.73 (q, *J* = 3.5 Hz), 123.58 (q, *J* = 272.8 Hz), 114.18, 61.22, 55.33, 34.95, 31.66, 29.46, 14.03. HRMS *m*/*z*: calcd for $C_{21}H_{19}F_3O_4$ $[M + H]^+$ 393.1308, found 393.1306.

*Ethyl-2-(3-chlorobenzoyl)-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6h**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63−7.56 (m, 1H), 7.43−7.36 (m, 2H), 7.32 (ddd, *J* = 7.6, 5.7, 2.9 Hz, 1H), 7.14−7.08 (m, 2H), 6.88−6.82 (m, 2H), 4.18 (qd, *J* = 7.1, 4.2 Hz, 2H), 3.78 (s, 3H), 3.36 (t, *J* = 6.4 Hz, 1H), 3.04 (dd, *J* = 9.4, 6.1 Hz, 1H), 2.61 (dd, *J* = 9.4, 6.5 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 196.71, 168.72, 158.67, 138.74, 132.08, 131.52, 130.39, 129.92, 129.86, 129.67, 127.57, 127.49, 126.85, 113.97, 61.11, 55.21, 37.88, 33.64, 31.27, 14.10. HRMS *m*/*z*: calcd for $C_{20}H_{19}ClO_4$ $[M + H]^+$ 359.1045, found 359.1050.

*Ethyl-2-acetyl-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6i**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09−7.03 (m, 2H), 6.87−6.81 (m, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.14 (t, *J* = 6.2 Hz, 1H), 2.48 (dd, *J* = 9.5, 6.3 Hz, 1H), 2.39 (dd, *J* = 9.5, 6.3 Hz, 1H), 2.32 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 202.78, 169.09, 158.68, 129.88, 129.81, 127.66, 127.51, 114.01, 61.14, 55.28, 37.66, 31.83, 30.82, 29.69, 14.11. HRMS *m*/*z*: calcd for $C_{15}H_{18}O_4$ $[M + H]^+$ 263.1283, found 263.1279.

*(E)-Ethyl-2-(4-methoxyphenyl)-3-pivaloylcyclopropane-1-carboxylate (**6j**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.13−7.04 (m, 2H), 6.91−6.81 (m, 2H), 4.23−4.11 (m, 2H), 3.79 (s, 3H), 3.13 (t, *J* = 6.2 Hz, 1H), 2.65 (dd, *J* = 9.4, 6.0 Hz, 1H), 2.43 (dd, *J* = 9.4, 6.5 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 209.26, 168.94, 158.62, 130.19, 127.63, 114.01, 60.99, 55.28, 44.27, 33.01, 32.16, 30.91, 29.51, 26.23, 14.16. HRMS *m*/*z*: calcd for $C_{18}H_{24}O_4$ $[M + H]^+$ 305.1747, found 305.1755.

*(Z)-Ethyl-2-(4-methoxyphenyl)-3-pivaloylcyclopropane-1-carboxylate (**6j′**).* ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 3.27 (t, *J* = 5.5 Hz, 1H), 2.91 (dd, *J* = 9.8, 6.2 Hz, 1H), 2.56 (dd, *J* = 9.9, 4.7 Hz, 1H), 1.28 (s, 9H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 211.93, 168.91, 158.69, 129.86, 126.77, 113.62, 60.78, 55.22, 44.39, 34.21, 31.64, 28.62, 26.08, 14.11. HRMS *m*/*z*: calcd for $C_{18}H_{24}O_4$ $[M + H]^+$ 305.1747, found 305.1755.

*Ethyl-2-(4-methoxyphenyl)-4-oxospiro[2.5]octane-1-carboxylate (**6k**).* ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.04 (d, *J* = 8.4 Hz, 2H), 6.78 (d, *J* = 8.3 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.31 (d, *J* = 6.8 Hz, 1H), 2.91 (d, *J* = 6.8 Hz, 1H), 2.30 (dd, *J* = 14.8, 1.9 Hz, 1H), 2.23 (dd, *J* = 7.8, 2.8 Hz, 1H), 2.03 (ddd, *J* = 15.3, 7.4, 3.4 Hz, 2H), 1.90−1.81 (m, 2H), 1.78−1.68 (m, 1H), 1.65 (td, *J* = 14.2, 5.8 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 205.91, 169.81, 158.50, 129.78, 126.75, 113.63, 60.87, 55.15, 43.73, 41.53, 33.94, 32.35, 31.65, 26.21, 23.80, 14.12. HRMS *m*/*z*: calcd for $C_{18}H_{22}O_4$ $[M + H]^+$ 303.1591, found 303.1598.

General Procedure for the Synthesis of 2,5-Diarylfurans 4a−4v. The mixture of ((2-aryl)cyclopropyl)(aryl)methanone (**1**, 50 mg), **2** (0.5 equiv), LiBr (1.0 equiv), and photocatalyst **3** (1 mol %) in 4 mL of dry CH_3CN was stirred under irradiation with a 100 cm blue LED round strip at room temperature. Upon completion of the reaction (monitored via TLC), it was quenched by saturated

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

Na_2CO_3 (5 mL) and then extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the title compound **4**.

*2-(4-Methoxyphenyl)-5-phenylfuran (**4a**).*[24] Yield 36 mg, 72% (12 h) as white solid, mp = 115.2−116.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, J = 7.9 Hz, 2H), 7.70−7.65 (m, 2H), 7.39 (t, J = 7.7 Hz, 2H), 7.27−7.22 (m, 1H), 6.96−6.91 (m, 2H), 6.71 (d, J = 3.4 Hz, 1H), 6.59 (d, J = 3.4 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$):δ = 159.08, 153.44, 152.67, 130.90, 128.65, 127.06, 125.17, 123.89, 123.53, 114.17, 107.17, 105.63, 55.31. GC-MS (EI) m/z: 250, 235, 207, 178, 125, 77.

*5-(4-Methoxyphenyl)-2-(4-tolyl)furan (**4b**).*[25] Yield 34 mg, 68% (5 h) as white solid, mp = 150.3−152.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68−7.64 (m, 2H), 7.62 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.96−6.90 (m, 2H), 6.64 (d, J = 3.4 Hz, 1H), 6.58 (d, J = 3.4 Hz, 1H), 3.83 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.93, 153.01, 152.90, 136.90, 129.33, 128.21, 125.07, 123.97, 123.50, 114.12, 106.42, 105.56, 55.30, 21.27. GC-MS (EI) m/z: 264, 249, 221, 178, 132, 91.

*2,5-Bis(4-methoxyphenyl)furan (**4c**).*[25] Yield 43 mg, 87% (21 h) as white solid, mp = 197.0−198.0.°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68−7.63 (m, 4H), 6.96−6.91 (m, 4H), 6.57 (s, 2H), 3.84 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.86, 152.75, 124.98, 124.03, 114.12, 105.56, 55.31. GC-MS (EI) m/z: 280, 265, 250, 222, 194, 165, 140.

*2-(4-tert-Butyl phenyl)-5-(4-methoxyphenyl)furan (**4d**).* Yield 37 mg, 73% (10 h) as white solid, mp = 129.7−130.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69−7.64 (m, 4H), 7.44−7.40 (m, 2H), 6.96−6.92 (m, 2H), 6.66 (d, J = 3.4 Hz, 1H), 6.58 (d, J = 3.4 Hz, 1H), 3.84 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.9, 153.1, 152.9, 150.2, 128.2, 125.6, 125.1, 124.0, 123.4, 114.1, 106.6, 105.6, 55.3, 34.6, 31.3. GC-MS (EI) m/z: 306, 291, 276, 261, 250, 235, 145, 131, 77. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.15; H, 7.43.

*2-(4-Methoxyphenyl)-5-naphylfuran (**4e**).* Yield 35 mg, 70% (7 h) as pale yellow solid, mp = 92.3−92.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, J = 8.1 Hz, 1H), 7.91−7.87 (m, 1H), 7.82 (t, J = 7.8 Hz, 2H), 7.74−7.69 (m, 2H), 7.58−7.50 (m, 3H), 6.98−6.94 (m, 2H), 6.80 (d, J = 3.4 Hz, 1H), 6.71 (d, J = 3.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 153.9, 152.3, 134.0, 128.6, 128.5, 128.3, 126.5, 125.9, 125.8, 125.6, 125.4, 125.2, 123.9, 114.2, 111.4, 105.4, 55.3. GC-MS (EI) m/z: 300, 285, 257, 288, 202, 150, 127, 77. Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 83.85; H, 5.64.

*2-(4-Fluorophenyl)-5-(4-methoxyphenyl)furan (**4f**).*[25] Yield 38 mg, 77% (20 h) as white solid, mp = 133.3−134.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71−7.64 (m, 4H), 7.12−7.05 (m, 2H), 6.96−6.92 (m, 2H), 6.64 (d, J = 3.4 Hz, 1H), 6.58 (d, J = 3.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.78, 161.14, 159.08, 153.44, 151.81, 127.28, 127.26, 125.25, 125.20, 125.14, 123.75, 115.76, 115.61, 114.17, 106.81, 105.62, 55.35, 55.31. GC-MS (EI) m/z: 268, 225, 196, 145, 133, 123, 95, 75.

*2-(4-Chlorophenyl)-5-(4-methoxyphenyl)furan (**4g**).*[25] Yield 42 mg, 84% (30 h) as white solid, mp = 171.5−172.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68−7.62 (m, 4H), 7.38−7.33 (m, 2H), 6.96−6.92 (m, 2H), 6.69 (d, J = 3.5 Hz, 1H), 6.59 (d, J = 3.5 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.18, 153.75, 151.56, 132.59, 129.36, 128.86, 125.22, 124.69, 123.62, 114.18, 107.66, 105.71, 55.33. GC-MS (EI) m/z: 286, 284(1:3), 271, 269(1:3), 241, 178, 142, 111, 102, 75.

*2-(4-Bromophenyl)-5-(4-methoxyphenyl)furan (**4h**).*[26] Yield 40.5 mg, 81% (30 h) as white solid, mp = 193.0−194.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69−7.64 (m, 2H), 7.61−7.56 (m, 2H), 7.54−7.47 (m, 2H), 6.98−6.92 (m, 2H), 6.72 (d, J = 3.5 Hz, 1H), 6.60 (d, J = 3.5 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 153.9, 151.6, 131.8, 129.8, 125.3, 125.0, 123.6, 120.7, 114.2, 107.8, 105.7, 55.3. GC-MS (EI) m/z: 330, 328(1:1), 315, 313(1:1), 205, 178, 165, 76.

*2-(4-Trifluoromethylphenyl)-5-(4-methoxyphenyl)furan (**4i**).*[27] Yield 38 mg, 75% (20 h) as white solid, mp = 163.4−164.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.2 Hz, 2H), 7.70−7.65 (m, 2H), 7.62 (d, J = 8.3 Hz, 2H), 6.98−6.91 (m, 2H), 6.81 (d, J = 3.5 Hz, 1H), 6.61 (d, J = 3.5 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.45, 154.58, 151.12, 133.97, 133.96, 129.03, 128.71, 128.38, 128.28, 128.06, 125.74, 125.70, 125.67, 125.63, 125.58, 125.42, 123.42, 123.40, 122.88, 120.18, 114.26, 109.26, 105.86, 55.33. GC-MS (EI) m/z: 318, 303, 275, 178, 159, 145, 102, 75.

*2-(4-Methoxyphenyl)-5-(4-nitrophenyl)furan (**4j**).* Yield 38 mg, 77% (16 h) as orange solid, mp = 168.0−170.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 3.5 Hz, 1H), 6.67 (d, J = 3.5 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 155.8, 150.3, 146.0, 136.4, 125.7, 124.4, 123.4, 123.0, 114.3, 111.5, 106.4, 55.4. GC-MS (EI) m/z: 295, 280, 265, 249, 234, 206, 178, 76.

*2-(3-Methoxyphenyl)-5-(4-methoxyphenyl)furan (**4k**).* Yield 41 mg, 83% (20 h) as white solid, mp = 123.8−124.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69−7.64 (m, 2H), 7.34−7.29 (m, 2H), 7.28−7.26 (m, 1H), 6.96−6.91 (m, 2H), 6.80 (dt, J = 6.2, 2.6 Hz, 1H), 6.70 (d, J = 3.4 Hz, 1H), 6.59 (d, J = 3.4 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 159.1, 153.5, 152.5, 132.2, 129.7, 125.2, 123.8, 116.2, 114.2, 112.6, 109.1, 107.5, 105.6, 55.3, 55.3. GC-MS (EI) m/z: 280, 265, 237, 222, 194, 165, 135, 77. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.95; H, 5.91.

*2-(3-Chlorophenyl)-5-(4-methoxyphenyl)furan (**4l**).* Yield 41 mg, 82% (20 h) as white solid, mp = 86.0−86.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.20 (d, J = 3.5 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 3.5 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 153.5, 148.9, 130.8, 129.8, 129.2, 127.6, 127.5, 126.8, 125.4, 123.6, 114.2, 113.2, 105.7, 55.3. GC-MS (EI) m/z: 286, 284(1:3), 271, 269(1:3), 243, 241, 243, 205, 178. Anal. Calcd for $C_{17}H_{13}ClO_2$: C, 71.71; H, 4.60. Found: C, 71.57; H, 4.83.

*2-(2-Methoxyphenyl)-5-phenylfuran (**4m**).* Yield 37 mg, 74% (24 h) as white solid, mp = 84.5−86.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, J = 7.7, 1.4 Hz, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.28−7.22 (m, 2H), 7.06 (t, J = 8.0 Hz, 1H), 7.03 (d, J = 3.4 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 6.76 (d, J = 3.4 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 152.3, 149.8, 130.9, 128.7, 128.0, 127.2, 125.8, 123.7, 120.8, 119.8, 112.2, 111.0, 107.4, 55.4. GC-MS (EI) m/z: 250, 207, 178, 145, 125, 115, 105, 77. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.49; H, 5.85.

*2-(2-Methoxyphenyl)-5-(4-methoxyphenyl)furan (**4n**).* Yield 37 mg, 75% (24 h) as white solid, mp = 107.5−108.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (dd, J = 7.7, 1.6 Hz, 1H), 7.69 (d, J = 8.9 Hz, 2H), 7.26−7.20 (m, 1H), 7.04 (td, J = 7.7, 0.9 Hz, 1H), 7.00 (d, J = 3.4 Hz, 1H), 6.95 (t, J = 8.8 Hz, 3H), 6.62 (d, J = 3.4 Hz, 1H), 3.95 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 155.3, 152.4, 149.1, 127.7, 125.6, 125.2, 124.1, 120.7, 119.9, 114.1, 112.2, 110.9, 105.8, 55.3, 55.3. GC-MS (EI) m/z: 280, 265, 237, 222, 194, 135, 77. Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.02; H, 5.81.

*2-(4-Fluorophenyl)-5-(2-methoxyphenyl)furan (**4o**).* Yield 34 mg, 69% (24 h) as white solid, mp = 94.9−96.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 7.7 Hz, 1H), 7.71 (dd, J = 8.8, 5.4 Hz, 2H), 7.28−7.22 (m, 1H), 7.10 (d, J = 8.7 Hz, 2H), 7.07−7.03 (m, 1H), 7.01 (d, J = 3.4 Hz, 1H), 6.97 (d, J = 8.3 Hz, 1H), 6.68 (d, J = 3.4 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.0 (d, J = 246.9 Hz), 155.5, 151.4, 149.8, 128.0, 127.3 (d, J = 3.3 Hz), 125.7, 125.5 (d, J = 8.0 Hz), 120.8, 119.7, 115.71 (d, J = 21.9 Hz), 112.2, 111.0, 107.01 (d, J = 1.3 Hz), 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.46. GC-MS (EI) m/z: 268, 225, 196, 145, 133, 95, 75. Anal. Calcd for $C_{17}H_{13}FO_2$: C, 76.11; H, 4.88. Found: C, 75.73; H, 5.09.

*2-(4-Trifluoromethylphenyl)-5-(2-methoxyphenyl)furan (**4p**).* Yield 35 mg, 70% (24 h) as white solid, mp = 96.7−98.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (dd, J = 7.8, 1.6 Hz, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.30−7.25 (m, 1H), 7.09−7.04 (m, 2H), 6.98 (d, J = 8.3 Hz, 1H), 6.86 (d, J = 3.5 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 150.9, 150.7, 134., 128.6 (q, J = 32.4 Hz), 128.5, 126.0, 125.7 (q, J = 3.9 Hz), 124.2 (q, J = 271.7 Hz).

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

123.6, 120.8, 119.4, 112.4, 111.1, 109.4, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.35. GC-MS (EI) *m/z*: 318, 299, 275, 178, 159, 145, 115, 77. Anal. Calcd for $C_{18}H_{13}F_3O_2$: C, 67.92; H, 4.12. Found: C, 67.79; H, 4.45.

*2-(4-Fluorophenyl)-5-(2,5-dimethoxyphenyl)furan (**4q**).* Yield 36 mg, 73% (20 h) as white solid, mp = 102.9−104.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72−7.66 (m, 2H), 7.50 (d, *J* = 3.0 Hz, 1H), 7.07 (t, *J* = 8.7 Hz, 2H), 7.03 (d, *J* = 3.5 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 1H), 6.77 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.66 (d, *J* = 3.5 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1 (d, *J* = 246.9 Hz), 153.7, 151.5, 150.0, 149.5, 127.2 (d, *J* = 3.3 Hz), 125.5 (d, *J* = 8.0 Hz), 120.3, 115.73 (d, *J* = 21.9 Hz), 112.7, 112.6, 112.1, 111.4, 107.8 (d, *J* = 1.3 Hz), 55.8, 55.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.36. GC-MS (EI) *m/z*: 298, 283, 255, 240, 212, 186, 149, 123, 75. Anal. Calcd for $C_{18}H_{15}FO_3$: C, 72.47; H, 5.07. Found: C, 72.33; H, 5.24.

*2-(4-Trifluoromethylphenyl)-5-(2,5-dimethoxyphenyl)furan (**4r**).* Yield 35 mg, 70% (24 h) as white solid, mp = 107.0−107.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 3.0 Hz, 1H), 7.08 (d, *J* = 3.6 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 1H), 6.87 (d, *J* = 3.6 Hz, 1H), 6.82 (dd, *J* = 8.9, 3.0 Hz, 1H), 3.92 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.7, 150.8, 150.7, 150.2, 133.9 (d, *J* = 1.3 Hz), 128.7 (q, *J* = 32.5 Hz), 125.7 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.8 Hz), 123.7, 120.1, 113.2, 112.7, 112.26, 111.7, 109.5, 55.9, 55.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.40. GC-MS (EI) *m/z*: 348, 333, 305, 290, 262, 174, 145. Anal. Calcd for $C_{19}H_{15}F_3O_3$: C, 65.52; H, 4.34. Found: C, 65.38; H, 4.47.

*5-(4-Methoxyphenyl)-3-methyl-2-phenylfuran (**4s**).*[28] Yield 26 mg, 52% (25 h) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.0 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 2H), 6.48 (s, 1H), 3.84 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.94, 151.73, 147.46, 131.86, 128.51, 126.39, 125.09, 125.02, 123.86, 118.60, 114.11, 109.28, 55.32, 12.15. GC-MS(EI) *m/z*: 264, 249, 221, 178,, 132, 105, 77.

*2-(4-Methoxyphenyl)-4,5-dihydronaphtho[1,2-b]furan (**4t**).* Yield 18 mg, 36% (28 h) as white solid, mp = 103.5−105.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.49 (s, 1H), 3.84 (s, 3H), 2.98 (t, *J* = 7.8 Hz, 2H), 2.76 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.9, 153.3, 149.0, 134.5, 128.1, 127.9, 126.7, 126.0, 125.1, 124.1, 121.5, 118.9, 114.2, 105.0, 55.3, 29.0, 21.1. GC-MS (EI) *m/z*: 276, 261, 247, 231, 215, 202, 138, 115, 101, 89, 77. Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.49; H, 5.93.

*2-(4-Methoxyphenyl)naphtho[1,2-b]furan (**4t′**).*[29] Yield 18 mg, 36% (28 h) as white solid, mp = 111−112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.64 (s, 2H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.7, 155.5, 149.9, 131.2, 128.4, 126.3, 126.2, 125.0, 124.8, 123.7, 123.5, 121.3, 119.9, 119.5, 114.3, 100.9, 55.4. GC-MS (EI) *m/z*: 274, 259, 231, 202, 137, 101, 88, 75.

*2-(4-Methoxyphenyl)-3-methyl-5-phenylfuran (**4u**).*[28] Yield 32 mg, 64% (20 h) as white solid, mp = 94.5−95.1. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72−7.67 (m, 2H), 7.66−7.61 (m, 2H), 7.40−7.34 (m, 2H), 7.25−7.21 (m, 1H), 7.00−6.95 (m, 2H), 6.59 (s, 1H), 3.85 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.44, 151.03, 148.27, 130.87, 128.61, 126.92, 126.67, 124.71, 123.47, 116.97, 114.01, 110.64, 55.30, 11.96. HRMS *m/z*: calcd for $C_{18}H_{16}O_2$ $[M]^+$ 264.1150, found 264.1137.

General Procedure for the Synthesis of 3-Bromo-2,5-diarylfurans. The mixture of ((2-aryl)cyclopropyl)(aryl)methanone (**1**, 50 mg), **2** (2.5 equiv unless otherwise stated), LiBr (1.0 equiv), and photocatalyst **3** (1.0 mol % unless otherwise stated) in 4 mL of dry CH_3CN was stirred and irradiated by a 100 cm blue LED round strip at room temperature. Upon completion of the reaction (monitored by TLC), it was quenched by saturated Na_2CO_3 (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the title products **5**.

*3-Bromo-2-(4-methoxyphenyl)-5-phenylfuran (**5a**).* Yield 35 mg, 54% (52 h) as white solid, mp = 74.5−76.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01−7.95 (m, 2H), 7.68 (d, *J* = 7.7 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.00−6.95 (m, 2H), 6.75 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.33, 151.98, 148.22, 129.78, 128.76, 127.86, 127.00, 123.67, 122.60, 113.94, 111.12, 96.35, 77.21, 77.00, 76.79, 55.31. GC-MS (EI) *m/z*: 330, 328(1:1), 315, 313(1:1), 287, 285(1:1), 221, 178, 165, 105, 77.

*3,4-Dibromo-2,5-bis(4-methoxyphenyl)furan (**5c**).*[30] Yield 49 mg, 63% (50 h) as white solid, mp = 139.6−140.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00−7.91 (m, 4H), 7.02−6.95 (m, 4H), 3.86 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.7, 147.7, 127.1, 122.1, 114.0, 100.7, 55.4. GC-MS (EI) *m/z*: 440, 438, 437(1:2:1), 425, 423, 421(1:2:1), 331, 329(1:1), 235, 219, 135, 77.

*3-Bromo-5-(4-fluorophenyl)-2-(4-methoxyphenyl)furan (**5f**).* Yield 31 mg, 47% (85 h) as white solid, mp = 80.5−82.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.4 Hz, 2H), 7.67−7.59 (m, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.67 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 162.4 (d, *J* = 248.1 Hz), 159.4, 151.1, 148.2, 126.2 (d, *J* = 3.2 Hz), 126.1, 125.5 (d, *J* = 8.1 Hz), 122.5, 115.9 (d, *J* = 22.0 Hz), 114.0, 110.8, 96.3, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.56. GC-MS (EI) *m/z*: 348, 346(1:1), 333, 331(1:1), 305, 303(1:1), 346, 339, 223, 176, 123, 95, 75. Anal. Calcd for $C_{17}H_{12}BrFO_2$: C, 58.81; H, 3.48. Found: C, 58.60; H, 3.60.

*3-Bromo-5-(4-chlorophenyl)-2-(4-methoxyphenyl)furan (**5g**).* Yield 35 mg, 55% (72 h) as white solid, mp = 95.1−96.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.73 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.5, 150.9, 148.6, 133.5, 129.0, 128.3, 127.1, 124.9, 122.4, 114.0, 111.6, 96.4, 55.3. GC-MS (EI) *m/z*: 366, 364, 362(1:3:2), 351, 349, 347(1:3:2), 323, 321, 319(1:3:2), 255, 182, 139, 111, 75. Anal. Calcd for $C_{17}H_{12}BrClO_2$: C, 56.15; H, 3.33. Found: C, 56.03; H, 3.57.

*3-Bromo-5-(4-bromophenyl)-2-(4-methoxyphenyl)furan (**5h**).* Yield 38 mg, 62% (82 h) as white solid, mp = 96.4−97.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.9 Hz, 2H), 7.53 (s, 4H), 6.98 (d, *J* = 8.9 Hz, 2H), 6.76 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 151.0, 148.7, 132.0, 128.7, 127.1, 125.1, 122.4, 121.7, 114.0, 111.7, 96.4, 76.7, 55.3. GC-MS (EI) *m/z*: 410, 408, 406(1:2:1), 395, 393, 391(1:2:1), 301, 299(1:1), 205, 176, 155. Anal. Calcd for $C_{17}H_{12}Br_2O_2$: C, 50.03; H, 2.96. Found: C, 49.86; H, 3.23.

*3-Bromo-2-(4-methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)-furan (**5i**).* Yield 28 mg, 44% (60 h) as white solid, mp = 74.5−75.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.80 (s, 1H), 3.84 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.68, 150.36, 149.31, 132.84, 129.34 (q, *J* = 32.5 Hz), 127.18, 125.80 (q, *J* = 3.8 Hz), 124.10 (q, *J* = 271.8 Hz), 123.60, 122.18, 114.04, 113.06, 96.53, 55.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.57. GC-MS (EI) *m/z*: 398, 396(1:1), 383, 381(1:1), 355, 353(1:1), 289, 173, 145. Anal. Calcd for $C_{18}H_{12}BrF_3O_2$: C, 54.43; H, 3.05. Found: C, 54.27; H, 3.36.

*3-Bromo-2-(4-methoxyphenyl)-5-(4-nitrophenyl)furan (**5j**).* Yield 34 mg, 53% (6 d) as orange solid, mp = 160−162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.98 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.97, 150.48, 149.55, 146.58, 135.27, 127.39, 124.45, 123.74, 121.80, 114.95, 114.11, 96.92, 77.21, 77.00, 76.79, 55.38. GC-MS (EI) *m/z*: 375, 373(1:1), 360, 358(1:1), 345, 343(1:1), 329, 327(1:1), 314, 312(1:1), 205, 176. Anal. Calcd for $C_{17}H_{12}BrNO_4$: C, 54.57; H, 3.23; N, 3.74. Found: C, 54.32; H, 3.48; N, 3.70.

*3-Bromo-5-(3-chlorophenyl)-2-(4-methoxyphenyl)furan (**5l**).* Yield 40 mg, 63% (77 h) as white solid, mp = 103.0−103.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.6 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.24 (s, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.5, 148.3, 148.2, 130.8, 130.1, 128.4, 128.2, 127.5, 127.2, 126.9, 122.3, 116.9, 114.0, 96.2, 55.3. GC-MS (EI) *m/z*: 366, 364, 362(1:3:2), 351, 349, 347(1:3:2), 323, 321, 319(1:3:2), 255,

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

176, 139. Anal. Calcd for $C_{17}H_{12}BrClO_2$: C, 56.15; H, 3.33. Found: C, 56.04; H, 3.57.

*3-Bromo-5-(2-methoxyphenyl)-2-(4-methoxyphenyl)furan (**5n**).* Yield 34 mg, 53% (53 h) as white solid, mp = 105.4−107.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 6.8 Hz, 1H), 7.05 (s, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.96 (t, J = 7.3 Hz, 3H), 3.95 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 159.2, 155.5, 148.3, 147.1, 128.5, 127.0, 125.6, 122.8, 120.7, 118.8, 116.0, 113.9, 110.9, 96.5, 55.4, 55.3. GC-MS (EI) m/z: 360, 358(1:1), 345, 343(1:1), 317, 315(1:1), 302, 300(1:1), 274, 275(1:1), 135, 77. Anal. Calcd for $C_{18}H_{15}BrO_3$: C, 60.19; H, 4.21. Found: C, 60.05; H, 4.38.

General Procedure for the Synthesis of 7a−7h. The mixture of ethyl-2-benzoyl-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6**, 100 mg), **2** (2.0−2.5 equiv), LiBr (1.0 equiv), and photocatalyst **3** (1.0 mol %) in 8 mL of dry CH_3CN was stirred and irradiated by a 100 cm blue LED round strip at room temperature. Upon completion of the reaction (monitored by TLC), it was quenched by saturated Na_2CO_3 (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the title products **7a−7h**.

*Ethyl 2-(4-Methoxyphenyl)-5-phenylfuran-3-carboxylate (**7a**).* Yield 95 mg, 96% (34 h) as white solid, mp = 95.5−96.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.12−8.04 (m, 2H), 7.72 (d, J = 7.4 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H), 7.06 (s, 1H), 7.02−6.96 (m, 2H), 4.33 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.67, 160.42, 156.78, 151.62, 129.93, 129.87, 128.74, 127.83, 123.83, 122.44, 114.46, 113.52, 107.77, 60.49, 55.31, 14.30. HRMS m/z: calcd for $C_{20}H_{18}O_4$ $[M + H]^+$ 323.1283, found 323.1285.

*Ethyl 2-(4-Methoxyphenyl)-5-(p-tolyl)furan-3-carboxylate (**7b**).* Yield 81 mg, 81% (29 h) as white solid, mp = 84.3−84.5 °C. ^{1}H NMR (400 MHz, chloroform-d): δ = 8.06 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.22 (d, J = 7.7 Hz, 2H), 7.03−6.92 (m, 3H), 4.32 (q, J = 7.0 Hz, 2H), 3.87 (s, 3H), 2.38 (s, 3H), 1.37 (t, J = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.79, 160.37, 156.48, 151.92, 137.83, 129.92, 129.46, 127.21, 123.85, 122.58, 114.43, 113.54, 107.04, 60.48, 55.35, 21.34, 14.33. HRMS m/z: calcd for $C_{21}H_{20}O_4$ $[M + H]^+$ 337.1440, found 337.1437.

*Ethyl 2,5-Bis(4-methoxyphenyl)furan-3-carboxylate (**7c**).* Yield 89 mg, 89% (20 h) as white solid, mp = 64.0−65.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07−8.02 (m, 2H), 7.68−7.63 (m, 2H), 7.00−6.97 (m, 2H), 6.96−6.93 (m, 2H), 6.93 (s, 1H), 4.32 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.81, 160.29, 159.41, 156.21, 151.77, 129.85, 125.36, 122.90, 122.60, 114.41, 114.21, 113.51, 106.13, 60.46, 55.35, 55.34, 14.32. HRMS m/z: calcd for $C_{21}H_{20}O_5$ $[M + H]^+$ 353.1389, found 353.1397.

*Ethyl 2-(4-Methoxyphenyl)-5-(naphthalen-1-yl)furan-3-carboxylate (**7d**).* Yield 91 mg, 91% (37 h) as white solid, mp = 81.8−82.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.45 (d, J = 8.5 Hz, 1H), 8.14−8.07 (m, 2H), 7.91 (d, J = 7.9 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 7.1 Hz, 1H), 7.58 (ddd, J = 8.5, 6.7, 1.5 Hz, 1H), 7.56−7.51 (m, 2H), 7.15 (s, 1H), 7.03−6.98 (m, 2H), 4.36 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.76, 160.43, 157.20, 151.15, 133.88, 130.15, 130.09, 129.96, 129.01, 128.61, 127.44, 126.85, 126.81, 126.38, 126.28, 126.03, 125.24, 125.17, 122.42, 114.22, 113.73, 113.55, 112.01, 60.53, 55.29, 14.33. HRMS m/z: calcd for $C_{24}H_{20}O_4$ $[M + H]^+$ 373.1440, found 373.1436.

*Ethyl 5-(4-Fluorophenyl)-2-(4-methoxyphenyl)furan-3-carboxylate (**7e**).* Yield 99 mg, 99% (45 h) as white solid, mp = 122.4−122.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11−8.00 (m, 2H), 7.69 (ddd, J = 8.3, 5.3, 2.2 Hz, 2H), 7.10 (td, J = 8.8, 2.3 Hz, 2H), 7.04−6.94 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.59, δ 162.44 (d, J = 248.0 Hz), 160.46, 156.80, 150.79, 129.92, 126.30 (d, J = 3.2 Hz), 125.71 (d, J = 8.1 Hz), 122.32, 115.90 (d, J = 22.0 Hz), 114.48, 113.55, 107.44, 60.54, 55.34, 14.30. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.55. HRMS m/z: calcd for $C_{20}H_{17}FO_4$ $[M + H]^+$ 341.1189, found 341.1195.

*Ethyl 5-(4-Chlorophenyl)-2-(4-methoxyphenyl)furan-3-carboxylate (**7f**).* Yield 93 mg, 93% (58 h) as white solid, mp = 119.1−119.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.05 (s, 1H), 6.98 (d, J = 8.4 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.51, 160.54, 157.05, 150.55, 133.52, 129.97, 128.99, 128.37, 125.05, 122.22, 114.55, 113.57, 108.26, 60.58, 55.35, 14.30. HRMS m/z: calcd for $C_{20}H_{17}ClO_4$ $[M + H]^+$ 357.0894, found 357.0899.

*Ethyl 2-(4-Methoxyphenyl)-5-(4-(trifluoromethyl)phenyl)furan-3-carboxylate (**7g**).* Yield 80 mg, 80% (60 h) as white solid, mp = 88.9−89.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.8, 2H), 7.83 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.21 (s, 1H), 7.07−6.96 (m, 2H), 4.36 (q, J = 6.9 Hz, 2H), 3.90 (s, 3H), 1.40 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.35, 160.71, 157.69, 150.02, 133.00, 130.07, 129.43 (q, J = 32.6 Hz), 125.83 (q, J = 4.0 Hz), 124.08 (q, J = 271.9 Hz), 123.81, 122.02, 114.68, 113.61, 109.84, 60.66, 55.35, 14.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ −113.29. HRMS m/z: calcd for $C_{21}H_{17}F_3O_4$ $[M + H]^+$ 391.1157, found391.1159.

*Ethyl 5-(3-Chlorophenyl)-2-(4-methoxyphenyl)furan-3-carboxylate (**7h**).* Yield 95 mg, 95% (52 h) as white solid, mp = 100.2−100.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.46 (d, J = 7.9 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.6 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.37 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.61, 160.56, 156.81, 147.93, 130.80, 130.31, 130.07, 128.48, 128.28, 127.77, 126.90, 122.18, 114.44, 113.59, 113.57, 60.56, 55.34, 14.33. HRMS m/z: calcd for $C_{20}H_{17}ClO_4$ $[M + H]^+$ 357.0894, found 357.0897.

General Procedure for the Synthesis of 7i and 7k. The mixture of ethyl-2-benzoyl-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6**, 100 mg), **2** (1.0 equiv), LiBr (1.0 equiv), and photocatalyst **3** (1.0 mol %) in 8 mL of dry CH_3CN was stirred and irradiated by a 100 cm blue LED round strip at room temperature. Upon completion of the reaction (monitored by TLC), it was quenched with saturated Na_2CO_3 (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was directly purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1) to afford the title products **7i** and **7k**.

*Ethyl 2-(4-Methoxyphenyl)-5-methylfuran-3-carboxylate (**7i**).*[31] Yield 63 mg, 63% (20 h) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.99−7.91 (m, 2H), 6.98−6.91 (m, 2H), 6.40 (d, J = 1.1 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 2.33 (d, J = 0.9 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 163.90, 160.05, 156.21, 150.33, 129.64, 122.76, 113.38, 113.18, 108.50, 60.20, 55.27, 14.27, 13.30. HRMS m/z: calcd for $C_{15}H_{16}O_4$ $[M + H]^+$ 261.1127, found 261.1119.

*Ethyl 2-(4-Methoxyphenyl)-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (**7k**).* Yield 65 mg, 65% (20 h) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 4.26 (q, J = 7.0 Hz, 2H), 3.84 (s, 3H), 2.64 (dt, J = 21.5, 5.9 Hz, 4H), 1.85 (p, J = 5.7 Hz, 2H), 1.76 (p, J = 6.8, 6.2 Hz, 2H), 1.31 (t, J = 7.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.69, 159.91, 156.05, 150.19, 129.81, 123.25, 118.88, 113.31, 112.34, 59.99, 55.28, 23.05, 22.93, 22.68, 22.63, 14.24. HRMS m/z: calcd for $C_{18}H_{20}O_4$ $[M + H]^+$ 301.1440, found 301.1446.

General Procedure for the Synthesis of 7j. The mixture of ethyl-2-benzoyl-3-(4-methoxyphenyl)cyclopropane-1-carboxylate (**6**, 100 mg), **2** (1.0 equiv), LiBr (1.0 equiv), p-TSA·H_2O (20 mol %), and photocatalyst **3** (1.0 mol %) in 8 mL of dry CH_3CN was stirred and irradiated by a 100 cm blue LED round strip at room temperature. Upon completion of the reaction (monitored by TLC), it was quenched by saturated Na_2CO_3 (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was directly purified by flash column chromatography (petroleum ether/ethyl acetate =20:1) to afford the title product **7j**.

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

*Ethyl 5-(tert-Butyl)-2-(4-methoxyphenyl)furan-3-carboxylate (**7j**).* Yield 95 mg, 95% (30 h) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03−7.89 (m, 2H), 6.99−6.89 (m, 2H), 6.38 (s, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 1.33 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.10, 162.31, 160.11, 155.89, 129.71, 122.99, 113.44, 112.78, 105.04, 60.26, 55.32, 32.58, 28.89, 14.37. HRMS m/z: calcd for $C_{18}H_{22}O_4$ $[M + H]^+$ 303.1591, found 303.1615.

Mechanistic Studies. *General Procedure for the Synthesis of Deuterium Compound **1a-d$_2$**. ((Z)-2-(4-Methoxyphenyl)cyclopropyl-3,3-d$_2$)(phenyl)methanone, **1a-d$_2$**.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−7.98 (m, 2H), 7.61−7.55 (m, 1H), 7.53−7.46 (m, 2H), 7.17−7.10 (m, 2H), 6.91−6.84 (m, 2H), 3.83 (s, 3H), 2.84 (d, J = 4.0 Hz, 1H), 2.68 (d, J = 4.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.61, 158.35, 137.71, 132.79, 132.35, 128.48, 128.02, 127.33, 113.92, 55.26, 29.52, 29.04, 18.25 (q, J = 26.0, 25.4 Hz). HRMS m/z: calcd for $C_{17}H_{14}D_2O_2$ $[M + H]^+$ 255.1354, found 255.1321.

*((E)-2-(4-Methoxyphenyl)cyclopropyl-3,3-d$_2$)(phenyl)methanone, **1a-d$_2$**.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.87 (m, 2H), 7.57−7.50 (m, 1H), 7.48−7.40 (m, 2H), 7.22−7.09 (m, 2H), 6.84−6.70 (m, 2H), 3.74 (s, 3H), 3.08 (d, J = 9.2 Hz, 1H), 2.87 (d, J = 9.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.32, 158.23, 138.70, 132.48, 130.10, 128.51, 128.42, 128.00, 127.87, 113.37, 55.10, 28.95, 26.91, 26.83, 11.46−10.84 (m).

*General Procedure for Oxidative Ring Opening of **1a** and **1a-d$_2$**.* The mixture of **1a** or **1a-d$_2$** (50 mg), $Na_2S_2O_8$ (1.0 equiv), LiBr (1.0 equiv), and $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1 mol %) in 4 mL of dry CH_3CN was stirred under irradiation with a 100 cm blue LED round strip at room temperature. After most of the material was converted to the unsaturated ketone (monitored via TLC), the reaction was quenched with saturated Na_2CO_3 (5 mL) and then extracted with EtOAc (3 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL), dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 50:1) to afford the mixture of cyclopropyl and β,γ-unsaturated benzophenone, which was further separated by thin-layer chromatography.

(E)-4-(4-Methoxyphenyl)-1-phenylbut-3-en-1-one.[32] Yield 26 mg, 52% as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.84 (d, J = 8.2 Hz, 2H), 6.49 (d, J = 15.9 Hz, 1H), 6.37−6.27 (m, 1H), 3.88 (d, J = 6.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 198.2, 159.1, 136.6, 133.2, 132.9, 129.8, 128.6, 128.3, 127.4, 120.2, 113.9, 55.2, 42.7.

(E)-4-(4-Methoxyphenyl)-1-phenylbut-3-en-1-one-3-d. Yield 25 mg, 50% as a white solid. ^{1}H NMR (400 MHz, chloroform-d) δ 8.04−7.97 (m, 2H), 7.61−7.54 (m, 1H), 7.48 (dd, J = 8.3, 6.9 Hz, 2H), 7.34−7.28 (m, 2H), 6.87−6.80 (m, 2H), 6.48 (s, 1H), 3.88 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.19, 159.06, 136.59, 133.16, 132.82, 129.78, 128.64, 128.32, 127.41, 119.93 (t, J = 23.5 Hz), 113.88, 77.21, 77.00, 76.79, 55.26, 42.63.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00436.

Optimization studies and characterization data of starting materials and products (PDF)

Crystallographic data for compound **5a** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xiawj@hit.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for the financial support from China NSFC (Nos. 21272047, 21372055, and 21472030), SKLUWRE (No. 2015DX01), the Fundamental Research Funds for the Central Universities (Grant No. HIT.BRETIV.201310), and HLJNSF (No. B201406).

■ REFERENCES

(1) (a) Kappe, C. O.; Murphree, S. S.; Padwa, A. *Tetrahedron* **1997**, *53*, 14179−14233. (b) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795−819. (c) Maier, M. Furan as a Building Block in Synthesis. In *Organic Synthesis Highlights II*; Wiley-VCH Verlag GmbH: Berlin, 2008; pp 231−242. (d) Rees, C. W.; Yue, T. Y. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2247−2252. (e) Zhang, H. J.; Padwa, A. *Org. Lett.* **2006**, *8*, 247−250. (f) Lee, H. K.; Chan, K. F.; Hui, C. W.; Yim, H. K.; Wu, X. W.; Wong, H. N. C. *Pure Appl. Chem.* **2005**, *77*, 139−143.

(2) (a) Gandini, A. *Prog. Polym. Sci.* **2013**, *38*, 1−29. (b) Rahmathullah, S. M.; Hall, J. E.; Bender, B. C.; McCurdy, D. R.; Tidwell, R. R.; Boykin, D. W. *J. Med. Chem.* **1999**, *42*, 3994−4000. (c) Lin, S. Y.; Chen, I. W. P.; Chen, C. H.; Lee, C. F.; Chou, C. M.; Luh, T. Y. *J. Phys. Chem. B* **2005**, *109*, 7915−7922. (d) Bai, H. T.; Lin, H. C.; Luh, T. Y. *J. Org. Chem.* **2010**, *75*, 4591−4595. (e) Gandini, A.; Belgacem, M. N. *Prog. Polym. Sci.* **1997**, *22*, 1203−1379. (f) Donnelly, D. M. X.; Meegan, M. J. Furans and their Benzo Derivatives: (iii) Synthesis and Applications. In *Comprehensive Heterocyclic Chemistry*; Rees, A. R. K. W., Ed. Pergamon: Oxford, 1984; Chapter 3.12, pp 657−712.

(3) (a) Hou, X. L.; Cheung, H. Y.; Hon, T. Y.; Kwan, P. L.; Lo, T. H.; Tong, S. Y.; Wong, H. N. C. *Tetrahedron* **1998**, *54*, 1955−2020. (b) Wong, H. N. C.; Hou, X. L.; Yeung, K. S.; Huang, H. Five-Membered Heterocycles: Furan. In *Modern Heterocyclic Chemistry*; Alvarez-Builla, J., Vaquero, J. J., Barluenga, J., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2011; pp 533−592.

(4) (a) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084−213. (b) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395−3442. (c) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994−2009.

(5) Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990**, *55*, 3450−3451.

(6) Hashmi, A. S. K.; Ruppert, T. L.; Knofel, T.; Bats, J. W. *J. Org. Chem.* **1997**, *62*, 7295−7304.

(7) Kim, J. T.; Kel'in, A. V.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2003**, *42*, 98−101.

(8) (a) Utimoto, K. *Pure Appl. Chem.* **1983**, *55*, 1845. (b) Fukuda, Y.; Shiragami, H.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1991**, *56*, 5816−5819.

(9) Sheng, H.; Lin, S.; Huang, Y. *Synthesis* **1987**, *1987*, 1022−1023.

(10) Liu, F.; Yu, Y.; Zhang, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 5505−5508.

(11) Zhang, M.; Jiang, H. F.; Neumann, H.; Beller, M.; Dixneuf, P. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 1681−1684.

(12) (a) Grandjean, J. M.; Nicewicz, D. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 3967−3971. (b) Griffin, J. D.; Zeller, M. A.; Nicewicz, D. A. *J. Am. Chem. Soc.* **2015**, *137*, 11340−11348. (c) Hamilton, D. S.; Nicewicz, D. A. *J. Am. Chem. Soc.* **2012**, *134*, 18577−18580.

(13) (a) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, *2*, 527−532. (b) Narayanam, J. M.; Stephenson, C. R. *Chem. Soc. Rev.* **2011**, *40*, 102−113. (c) Shi, L.; Xia, W. J. *Chem. Soc. Rev.* **2012**, *41*, 7687−97. (d) Xuan, J.; Xiao, W. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 6828−6838. (e) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. *Chem. Rev.* **2013**, *113*, 5322−5363. (f) Nicewicz, D. A.; Nguyen, T. M. *ACS Catal.* **2014**, *4*, 355−360.

(14) (a) Dai, C.; Narayanam, J. M.; Stephenson, C. R. *Nat. Chem.* **2011**, *3*, 140−5. (b) Tucker, J. W.; Narayanam, J. M.; Shah, P. S.; Stephenson, C. R. *Chem. Commun.* **2011**, *47*, 5040−2. (c) Zhao, Y. T.; Li, Z.; Yang, C.; Lin, R.; Xia, W. J. *Beilstein J. Org. Chem.* **2014**, *10*, 622−627. (d) Lin, R.; Sun, H. N.; Yang, C.; Yang, Y. D.; Zhao, X. X.; Xia, W. J. *Beilstein J. Org. Chem.* **2015**, *11*, 31−6.

(15) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401−449.

(16) (a) Ohkubo, K.; Mizushima, K.; Iwata, R.; Fukuzumi, S. *Chem. Sci.* **2011**, *2*, 715−722. (b) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. *Science* **2015**, *349*, 1326−1330.

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022

(17) (a) Sniady, A.; Wheeler, K. A.; Dembinski, R. *Org. Lett.* **2005**, *7*, 1769−1772. (b) Sromek, A. W.; Rubina, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005**, *127*, 10500−10501. (c) Dudnik, A. S.; Sromek, A. W.; Rubina, M.; Kim, J. T.; Kel'in, A. V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2008**, *130*, 1440−1452. (d) Xia, Y. Z.; Dudnik, A. S.; Gevorgyan, V.; Li, Y. H. *J. Am. Chem. Soc.* **2008**, *130*, 6940−6941. (e) Kim, H. Y.; Lee, S.; Kim, S.; Oh, K. *Org. Lett.* **2015**, *17*, 450−453.
(18) (a) Dong, Y. Z.; Shi, Q. A.; Nakagawa-Goto, K.; Wu, P. C.; Bastow, K. F.; Morris-Natschke, S. L.; Lee, K. H. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 6289−6292. (b) Dong, Y. Z.; Shi, Q.; Liu, Y. N.; Wang, X.; Bastow, K. F.; Lee, K. H. *J. Med. Chem.* **2009**, *52*, 3586−3590. (c) Lin, Y. L.; Tsai, Y. L.; Kuo, Y. H.; Liu, Y. H.; Shiao, M. S. *J. Nat. Prod.* **1999**, *62*, 1500−1503. (d) Foot, J. S.; Phillis, A. T.; Sharp, P. P.; Willis, A. C.; Banwell, M. G. *Tetrahedron Lett.* **2006**, *47*, 6817−6820.
(19) Schwalbe, M.; Schäfer, B.; Görls, H.; Rau, S.; Tschierlei, S.; Schmitt, M.; Popp, J.; Vaughan, G.; Henry, W.; Vos, J. G. *Eur. J. Inorg. Chem.* **2008**, *2008*, 3310−3319.
(20) Guo, L.; Yang, C.; Zheng, L. W.; Xia, W. J. *Org. Biomol. Chem.* **2013**, *11*, 5787−5792.
(21) (a) Huo, C. D.; Wu, M. X.; Chen, F. J.; Jia, X. D.; Yuan, Y.; Xie, H. S. *Chem. Commun.* **2015**, *51*, 4708−4711. (b) Huo, C. D.; Xie, H. S.; Wu, M. X.; Jia, X. D.; Wang, X. C.; Chen, F. J.; Tang, J. *Chem. - Eur. J.* **2015**, *21*, 5723−5726.
(22) (a) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1345−1353. (b) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353−1364.
(23) Ratts, K. W.; Yao, A. N. *J. Org. Chem.* **1966**, *31*, 1185−1188.
(24) Schmidt, B.; Geißler, D. *Eur. J. Org. Chem.* **2011**, *2011*, 7140−7147.
(25) Jiang, H. F.; Zeng, W.; Li, Y. B.; Wu, W. Q.; Huang, L. B.; Fu, W. *J. Org. Chem.* **2012**, *77*, 5179−5183.
(26) Kramer, S.; Madsen, J. L. H.; Rottländer, M.; Skrydstrup, T. *Org. Lett.* **2010**, *12*, 2758−2761.
(27) Altınok, E.; Friedle, S.; Thomas, S. W. *Macromolecules* **2013**, *46*, 756−762.
(28) Yang, Y. Z.; Yao, J. Z.; Zhang, Y. H. *Org. Lett.* **2013**, *15*, 3206−3209.
(29) Arias, L.; Vara, Y.; Cossio, F. P. *J. Org. Chem.* **2012**, *77*, 266−275.
(30) Bailey, P. S.; White, H. M.; Colomb, H. O. *J. Org. Chem.* **1965**, *30*, 487−491.
(31) Tsuji, H.; Yamagata, K.; Ueda, Y.; Nakamura, E. *Synlett* **2011**, *2011*, 1015−1017.
(32) Trofimov, B. A.; Schmidt, E. Y.; Zorina, N. V.; Ivanova, E. V.; Ushakov, I. A. *J. Org. Chem.* **2012**, *77*, 6880−6886.

DOI: 10.1021/acs.joc.6b00436
J. Org. Chem. 2016, 81, 7008−7022