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# Visible-Light-Induced Intermolecular Dearomative Cyclization of 2-Bromo-1,3-dicarbonyl Compounds and Alkynes: Synthesis of Spiro[4.5]deca-1,6,9-trien-8-ones

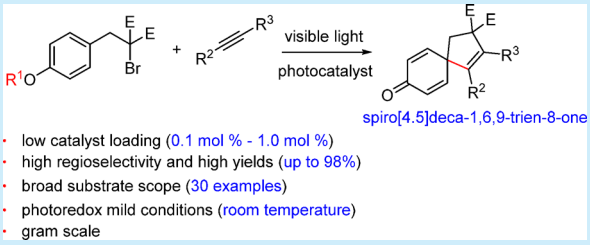
Wuheng Dong,[†] Yao Yuan,[†] Xiaoshuang Gao,[†] Miladili Keranmu,[†] Wanfang Li,[†] Xiaomin Xie,[†] and Zhaoguo Zhang*[,†,‡]

[†]Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

Supporting Information

**ABSTRACT:** A visible-light-induced photocatalytic intermolecular dearomative cyclization of 2-bromo-1,3-dicarbonyl compounds and alkynes afforded biologically important spirocarbocycle structures in moderate to good yields via a 5-exo-dig radical cyclization under mild reaction conditions. A 5.0 mmol scale dearomatization reaction proceeded smoothly with 95% yield even when the catalyst loading was reduced to 0.1 mol %, suggesting that this method was suitable for large-scale synthesis.






Spiro[4,5]decane systems are biologically significant structures, which occur in many biologically active molecules and natural products, such as cDHAs (4′,5-dihydroxy-6′-methoxy-2-methylspiro[cyclohexane-1,1′-indene]-2,5-diene-3′,4(2′′*H*)-dione), DHAs (4′,5-dihydroxy-6′-methoxy-2-methyl-3′*H*-spiro-[cyclohexane-1,1′-isobenzofuran]-2,5-diene-3′,4-dione), schizandrinone, cannabispiradienone, isocannabispiradienone, and carijodienone (Figure 1).[1] For example, schizandrinone is a potential anticancer agent, which has been used for the treatment of cervical, lung, and breast cancer.[1a] Carijodienone, isolated from the Pacific octocoral Carijoa multiflora, shows remarkable antibacterial activity.[1b] Owing to their versatile biological properties and the synthetic challenges with these sterically hindered spiro[4,5]decane substructures, simple and efficient building-up of these scaffolds is of great importance to

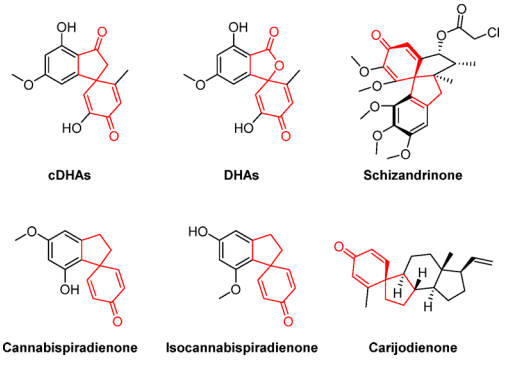
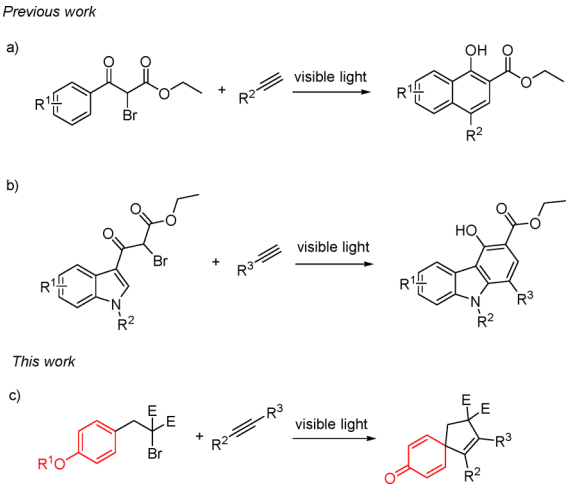



**Figure 1.** Bioactive or natural compounds bearing spiro[4,5]decane systems.

**Scheme 1. Visible Light-Induced Radical Cyclization of Alkynes and 2-Bromo-1,3-dicarbonyl Compounds**




chemists. Dearomatization reactions rank among the most powerful and promising organic transformations, which render a rapid construction of spiro[4,5]decane systems from readily available phenols and their derivatives.[2] In recent decades, acid[3]- and transition-metal-catalyzed dearomative cyclization has been explored intensively and gained outstanding achievements, especially for transition-metal-catalyzed asymmetric dearomatization reactions.[4] In addition, radical cyclization approaches to

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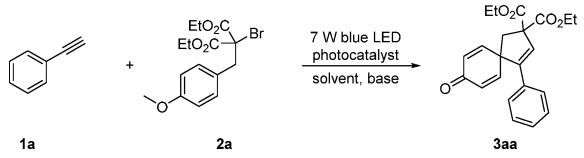
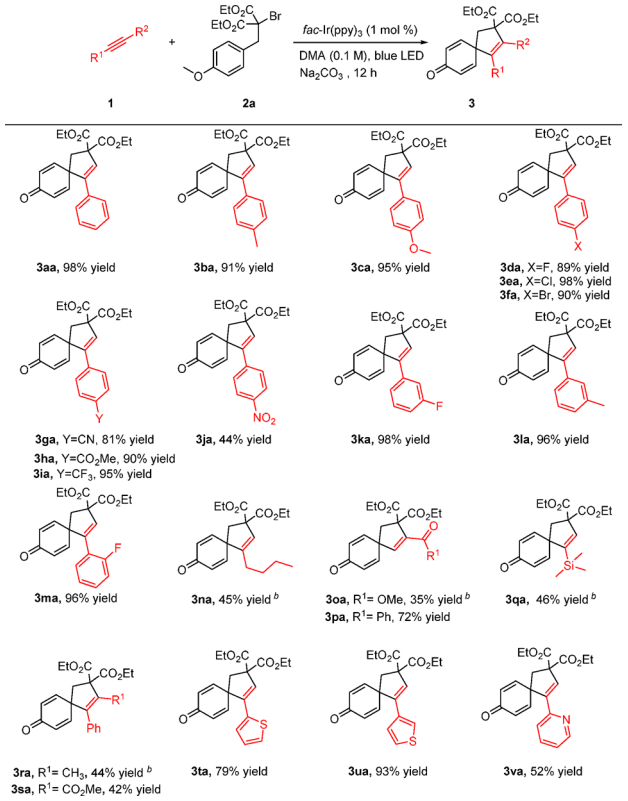
## Table 1. Optimization of Reaction Conditions[a]




| entry | photocatalyst | base | solvent | yield[b](%) |
|---|---|---|---|---|
| 1 | *fac*-Ir(ppy)$_3$ | | $CH_3CN$ | 34 |
| 2 | Ru(bpy)$_3$Cl$_2$.6H$_2$O | | $CH_3CN$ | 0 |
| 3 | EosinY | | $CH_3CN$ | 0 |
| 4 | *fac*-Ir(ppy)$_3$ | $Na_2CO_3$ | $CH_3CN$ | 66 |
| 5 | *fac*-Ir(ppy)$_3$ | $K_2CO_3$ | $CH_3CN$ | 58 |
| 6 | *fac*-Ir(ppy)$_3$ | $Li_2CO_3$ | $CH_3CN$ | 52 |
| 7 | *fac*-Ir(ppy)$_3$ | $iPr_2NEt$ | $CH_3CN$ | 51 |
| 8 | *fac*-Ir(ppy)$_3$ | DBU | $CH_3CN$ | trace |
| 9 | *fac*-Ir(ppy)$_3$ | $Na_2CO_3$ | DCM | 53 |
| 10 | *fac*-Ir(ppy)$_3$ | $Na_2CO_3$ | MeOH | 63 |
| 11 | *fac*-Ir(ppy)$_3$ | $Na_2CO_3$ | DMF | 71 |
| 12 | *fac*-Ir(ppy)$_3$ | $Na_2CO_3$ | DMA | 99 (98[c]) |
| 13[d] | | $Na_2CO_3$ | DMA | 0 |
| 14[e] | *fac*-Ir(ppy)$_3$ | $Na_2CO_3$ | DMA | 0 |

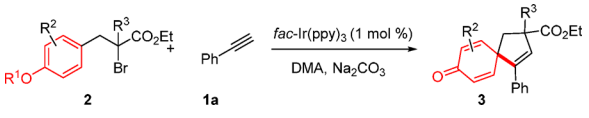
[a]Conditions: **1a** (30.6 mg, 0.3 mmol), **2a** (215.5 mg, 0.6 mmol), photocatalyst (1 mol %), base (0.36 mmol), solvent (3 mL), irradiation with a 7 W blue LED at rt for 12 h. [b]$^1$H NMR yield was reported using benzyl ether as an internal standard. [c]Isolated yield. [d]Without photocatalyst. [e]Reaction was carried out in the dark.

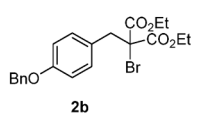
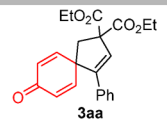
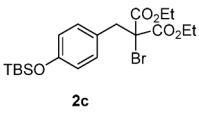
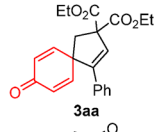
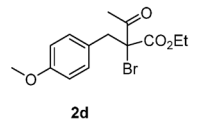
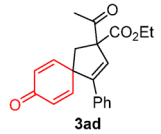
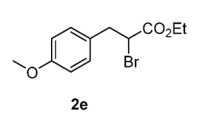
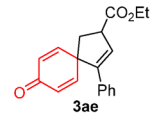
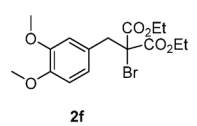
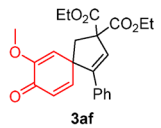
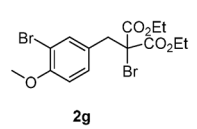
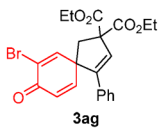
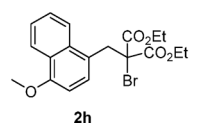
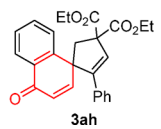
## Scheme 2. Substrate Scope of Alkynes[a]




[a]Conditions: **1** (0.3 mmol), **2a** (215.5 mg, 0.6 mmol), *fac*-Ir(ppy)$_3$ (4.2 mg, 1 mol %), $Na_2CO_3$ (38.2 mg, 0.36 mmol), DMA (3 mL), irradiation with 7 W blue LED at rt for 12 h; isolated yields were given. [b]**1**/**2a** = 5:1.

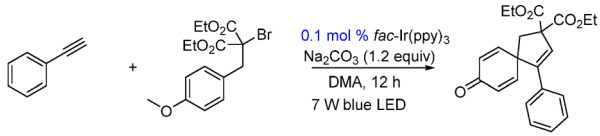
## Table 2. Substrate Scope of 2-Bromo-carbonyl Compounds[a]




| entry | substrate | product | yield |
|---|---|---|---|
| 1 |  **2b** |  **3aa** | 81 |
| 2 |  **2c** |  **3aa** | 98 |
| 3 |  **2d** |  **3ad** | 59 |
| 4 |  **2e** |  **3ae** | 58 |
| 5 |  **2f** |  **3af** | 85 |
| 6 |  **2g** |  **3ag** | 60 |
| 7 |  **2h** |  **3ah** | 83 |

[a]Conditions: **1a** (0.3 mmol), **2** (215.5 mg, 0.6 mmol), *fac*-Ir(ppy)$_3$ (4.2 mg, 1 mol %), $Na_2CO_3$ (38.2 mg, 0.36 mmol), DMA (3 mL), irradiation with 7 W blue LED at rt for 12 h; isolated yields were given.

## Scheme 3. Synthesis of 3aa on Gram-Scale




these spiro-scaffolds have also been reported by several groups.[5] For example, Santi and co-workers disclosed an oxidative cyclization between substituted diethyl benzyl malonates and alkynes for the synthesis of spiro[4,5]decatriene derivatives by using stoichiometric amounts of Mn(OAc)$_3$.[5c] Thus, far, there still an ongoing research interest in developing simple, mild, and efficient methodology for the construction of these biologically relevant spirocarbocycles.

The development of C−C bond formation via visible-light-promoted photoredox catalysis has recently received much attention owing to its inherent green and sustainable features.[6]



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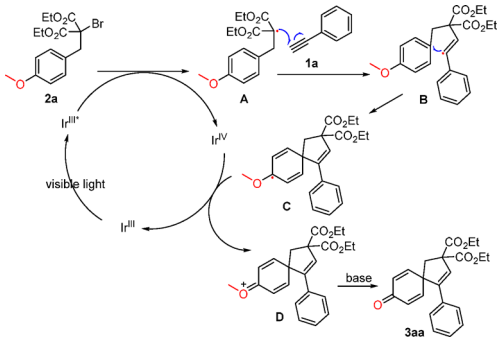
**Scheme 4. Proposed Mechanism for the Catalysis**




Numerous efforts have been devoted to the synthesis of complex compounds through this powerful tool. Specifically, the reactions between $\alpha$-carbonyl alkyl radicals and double or triple C−C bonds, including inter- and intramolecular additions, have been widely explored by many groups.[7] Recently, Yu developed an efficient coupling of alkynes and 2-bromo-1,3-dicarbonyl compounds for the synthesis of functionalized naphthols and furans by using photoredox catalyst (Scheme 1a).[8] A similar Ir(III)-catalyzed formal [4 + 2] cycloaddition of indole-derived bromides and alkynes to synthesize carbazoles was reported by Xiao and co-workers (Scheme 1b).[9] Our group has recently developed a photocatalytic dearomative cyclization of $\alpha$-bromo-*N*-benzyl-alkylamide for the efficient preparation of 2-azaspiro[4.5]decanes.[10] Herein, we describe an efficient and regioselective formation of interesting spirocarbocycle via visible light-induced intermolecular dearomative reaction between 2-bromo-1,3-dicarbonyl compounds and alkynes (Scheme 1c).

To initiate our study, ethynylbenzene (**1a**) and 2-bromo-2-(4-methoxybenzyl)malonate (**2a**) were chosen as model substrates to examine the dearomatization reaction. Fortunately, a 34% yield of the desired spiro[4,5]decane compound (**3aa**) was obtained when using 1 mol % of *fac*-Ir(ppy)$_3$ as the photocatalyst in $CH_3CN$ at room temperature (Table 1, entry 1). Other types of photocatalyst like Ru(bpy)$_3$Cl$_2$·6H$_2$O or EosinY proved to be futile because no desired products were detected (Table 1, entries 2 and 3). To drive the dearomative cyclization to complete, external base is required to neutralize the hydrobromic acid generated thereof. When $Na_2CO_3$ was added, the yield was significantly increased to 66% (Table 1, entry 4). Encouraged by this result, various bases were examined (Table 1, entries 5−8). Inorganic bases, such as $K_2CO_3$ and $Li_2CO_3$, resulted in moderate conversions. Organic bases such as $^i$Pr$_2$NEt and DBU led to even much lower yields. Considering the different solubility of inorganic bases in varies organic solvent, we next examined different solvents (Table 1, entries 9−12). To our delight, the isolated yield was remarkably increased to 98% when DMA was used as solvent (Table 1, entry 12). Finally, control experiments showed that both photocatalyst and irradiation were essential, and no reaction occurred if photocatalyst or visible light irradiation was omitted (Table 1, entries 13 and 14).

With the optimal conditions in hand, we next investigated the generality of this visible-light-induced intermolecular dearomative cyclization by exploring the scope of alkynes. First, a variety of substituted aryl acetylenes smoothly coupled with 2-bromo-2-(4-methoxybenzyl)malonate (**2a**) under standard reaction conditions to produce the target product **3** in excellent yields. Except for the nitro group, various aryl acetylenes with electron-donating or electron-withdrawing group on the *para*-position of the benzene ring showed that the electronic nature of the substituents has hardly any effect on chemical yields, affording the corresponding spiro[4.5]deca-1,6,9-trien-8-ones in generally high yields (Scheme 2, **3aa**−**3ja**). As expected, the substituents at *meta*- or *ortho*-position for the phenyl ring also worked well; **3ka**−**3ma** were obtained in approximately quantitative yields. In addition, linear and functionalized aliphatic alkynes were also compatible with the reaction and moderate yields of the corresponding products were obtained (Scheme 2, **3na**−**3pa**). It is noteworthy that methyl propargylate and propiolophenone witnessed a reversed regioselectivity (**3oa** and **3pa**) wherein the carbonyl groups end up in the $\beta$-position of the newly formed spirocarbon centers. Gratifyingly, sterically hindered TMS-acetylene was also amenable to this reaction albeit in lower yield (**3qa**, 46%). Internal alkynes were also applicable in this dearomative cyclization. For example, 1-phenylpropyne (**1r**) and methyl phenylpropiolate (**1s**) participated in this transformation to give the desired product **3ra** and **3sa** in 44% and 42% yield, respectively. Unfortunately, diphenyl acetylene and dimethyl acetylenedicarboxylate showed no reactivity in this reaction, and the starting materials were fully recovered. Finally, a variety of heteroaryl acetylenes containing the thiophene and pyridine rings were all compatible with the transformation (**3ta**−**3va**).

To further diversify the protocol, different 2-bromo-1,3-dicarbonyl compounds **2** were screened in the annulation with phenyl acetylene (**1a**) (Table 2). As expected, when the phenol hydroxyl was protected with benzyl or TBDMS (*tert*-butyldimethylsilanoxy) group, the dearomatization reaction still proceeded, and good yields were also obtained (Table 2, entries 1 and 2). Under the optimal conditions, **2d** proved to be a viable substrate to give product **3ad** in moderate yield. It is noteworthy that secondary bromide **2e** could also successfully afford the desired product in 58% yield (**3ae**). In the case of 3,4-dimethoxy substituted $\alpha$-bromomalonate (**2f**), the target product **3af** was obtained in a good yield of 85%. Notably, a bromo substituent on the phenyl ring was sustained under the reaction conditions, and the desired product **3ag** was isolated in 60% yield. Moreover, the substrate with a naphthalene ring yielded the corresponding product in 83% yield (Table 2, entry 7).

To further demonstrate the synthetic potential of this synthetic method, a gram-scale reaction with **1a** and **2a** was carried out. The intermolecular dearomatization reaction of **1a** on a 5.0 mmol scale gave the desired product **3aa** in 95% yield with a catalyst loading of 0.1 mol % (Scheme3).

On the basis of the control experiments and related reports,[10] a possible mechanism was proposed for the reaction as shown in Scheme 4. First, excitation of the metal catalyst under visible light generated the excited Ir$^{III}$* species, which underwent a SET oxidation by 2-bromo-2-(4-methoxybenzyl)malonate (**2a**) to give Ir$^{IV}$, whereby radical **A** was formed. Subsequently, **A** underwent a rapid addition with ethynylbenzene (**1a**) to provide the radical intermediate **B**. The following key C−C bond formation was finalized through an intramolecular 5-exo-trig radical cyclization. The resultant radical **C** could be oxidized by Ir$^{IV}$ metal complex to oxynium cation **D**. Finally, the desired product **3aa** was released from intermediate **D** in the presence of a base.[7h,10]

In conclusion, we have developed an efficient visible light-induced intermolecular dearomative 5-exo-trig radical cyclization between 2-bromo-1,3-dicarbonyl compounds and alkynes under mild reaction conditions, affording the biologically



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important spirocarbocycle structures in moderate to good yields. Further studies toward expanding the application of photoredox catalysis to other dearomatization reactions are currently underway in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02463.

Preparation of substrates, general procedure, characterization data, and $^{1}H$ and $^{13}C$ NMR spectra (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Author

*Fax: (+86)-21-5474-8925. Phone: (+86)-21-5474-8925. E-mail: zhaoguo@sjtu.edu.cn.

### ORCID

Xiaomin Xie: 0000-0002-5798-291X

Zhaoguo Zhang: 0000-0003-3270-6617


### Notes

The authors declare no competing financial interest.

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## ■ DEDICATION

Dedicated to Professor Xiyan Lu on the occasion of his 90th birthday.

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