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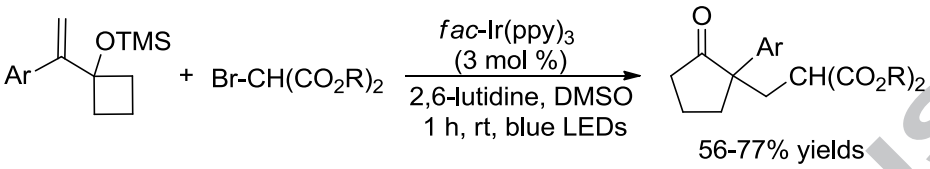

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ABSTRACT

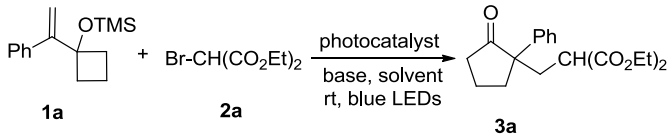
A visible light-mediated photocatalytic bis(alkoxycarbonyl)methylation/ring expansion of alkenyl cyclobutanols is described. This approach provides a mild and operationally simple access to the synthesis of bis(alkoxycarbonyl)methyl-substituted cyclic ketones from the coupling reaction of 1-(1-arylvinyl)cyclobutanols with aryl bromomalonates.

The difunctionalization of alkenes has become a powerful strategy for the synthesis of useful building blocks of natural products and biologically active compounds through introduction of two functional groups across double bond.[1] Until now, considerable studies have been conducted on the difunctionalization of alkenes with the aim of developing novel and efficient methods.[2] Recently, a novel application of visible light-mediated photoredox catalysis was described for chemical transformations in synthetic organic chemistry and has proven to be a powerful tool with a host of attractive features such as mild reaction condition, excellent functional group tolerance, and high reactivity.[3] With the use of suitable radical sources, the visible light-mediated photocatalytic difunctionalization of alkenes mediated by visible light offers a viable option for obtaining functionalized molecules.[4] Since the pioneer work on the visible light-induced difunctionalization of alkenes with alkyl radical species generated from bromomalonates disclosed by Stephenson in 2010,[5] a number of photocatalytic systems for the difunctionalization of alkenes with electron-deficient alkyl bromides have been reported.[6] Among the known alkylation reactions, the introduction of a bis(alkoxycarbonyl)methyl group (-CH(COOEt)$_2$) is a highly appealing topic owing to the high possibility for post-functionalization of ester groups.[7] Recently, several groups reported the radical addition and 1,2-aryl migration sequences of α,α-diaryl allylic alcohol derivatives with various radicals including phophoryl, sulfonyl, trifluoromethyl, and alkyl radicals using metal-free oxidation and metal- or photo-mediated oxidation.[8] Quite recently, the Xia group has reported visible light mediated arylalkylation of α,α-diaryl allylic alcohols through concomitant 1,2-aryl migration.[9] However, to the best of our knowledge, visible light-mediated photoredox alkylation and 1,2-carbon migration sequences of 1-(1-arylvinyl)cyclobutanols with bromomalonate derivatives has not been reported.

As part of a research program related to redox reaction and cyclization sequences, we recently reported the internal redox reaction via C-H bond functionalization[10] and photoredox-catalytic fluoroalkylation/ring expansion.[11] In this communication, we wish to describe visible light-mediated photocatalytic bis(alkoxycarbonyl)methylation/ring expansion via 1,2-carbon migration of 1-(1-arylvinyl)cyclobutanol derivatives.

To determine suitable reaction conditions for the visible light-mediated photocatalytic bis(alkoxycarbonyl)methylation/ring expansion of 1-(1-arylvinyl)cyclobutanols, we examined the visible light-mediated photocatalytic reaction of (1-(1-phenylvinyl)cyclobutoxy)trimethylsilane (**1a**) with diethyl bromomalonate (**2a**) in the presence of 5 mol % of *fac*-Ir(ppy)$_3$ under visible light irradiation with blue LEDs (5 W, λ_{max} = 455 nm) in DMF at room temperature (Table 1). By screening photocatalysts in DMF (entries 1-5), we found that *fac*-Ir(ppy)$_3$ was the best photocatalyst for this bis(alkoxycarbonyl)methylation/1,2-carbon migration, affording the corresponding product **3a** in 64% yield (Table 1, entry 1). Among the solvents evaluated (Table 1, entries 1 and 6-9), the best result was achieved when the reaction was conducted in DMSO (Table 1, entry 9). Next, we examined effect of bases in DMSO (Table 1, entries 9-14). A survey of different bases indicates that 2,6-lutidine gave the highest yield (Table 1, entry 9). The present catalytic system tolerates photocatalyst loading down to 3 mol % without compromising the yield. However, reducing the photocatalyst loading to 1 mol % slightly reduced the product yield (Table 1, entries 15-16). When a 1-(1-phenylvinyl)cyclobutanol was utilized as the substrate instead of **1a**, reduced yield was obtained (Table 1, entry 17). Without 2,6-lutidine, a longer reaction time was needed for the complete

Table 1. Optimization of the reaction conditions [a]



1a 2a 3a

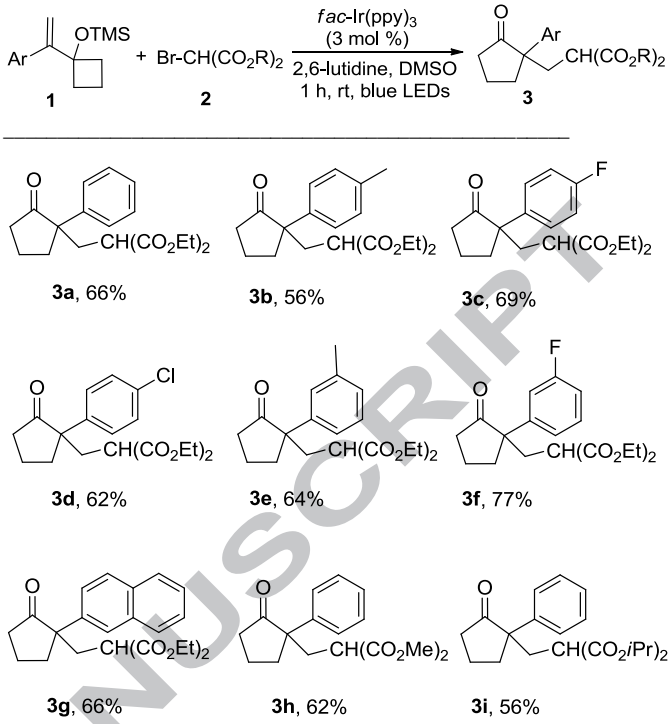
entry	photocatalyst	base	solvent	time (h)	yield (%)[b]
1	*fac*-Ir(ppy)$_3$	2,6-lutidine	DMF	1	64
2	Ru(bpy)$_3$Cl$_2$·6H$_2$O	2,6-lutidine	DMF	5	n.r.
3	Ru(Phen)$_3$Cl$_2$·H$_2$O	2,6-lutidine	DMF	5	n.r.
4	Fluorecein	2,6-lutidine	DMF	5	n.r.
5	Eosin Y	2,6-lutidine	DMF	5	n.r.
6	*fac*-Ir(ppy)$_3$	2,6-lutidine	CH_2Cl_2	1	48
7	*fac*-Ir(ppy)$_3$	2,6-lutidine	CH_3CN	12	42
8	*fac*-Ir(ppy)$_3$	2,6-lutidine	THF	12	34
9	*fac*-Ir(ppy)$_3$	2,6-lutidine	DMSO	1	66
10	*fac*-Ir(ppy)$_3$	DIPEA	DMF	9	n.r.
11	*fac*-Ir(ppy)$_3$	Et_3N	DMF	2	20
12	*fac*-Ir(ppy)$_3$	K_2CO_3	DMF	5	25
13	*fac*-Ir(ppy)$_3$	K_2HPO_4	DMF	5	22
14	*fac*-Ir(ppy)$_3$	DTBMP	DMF	5	22
15[c]	*fac*-Ir(ppy)$_3$	2,6-lutidine	DMSO	1	66
16[d]	*fac*-Ir(ppy)$_3$	2,6-lutidine	DMSO	3	62
17[e]	*fac*-Ir(ppy)$_3$	2,6-lutidine	DMSO	1	59
18	*fac*-Ir(ppy)$_3$	-	DMSO	3	58
19	-	2,6-lutidine	DMSO	3	n.r.
20[f]	*fac*-Ir(ppy)$_3$	2,6-lutidine	DMSO	3	n.r.

[a] Reaction conditions: (1-(1-phenylvinyl)cyclobutoxy)trimethylsilane (**1a**, 0.3 mmol), Br-CH(CO$_2$Et)$_2$ (**2**, 0.6 mmol), base (0.6 mmol), photocatalyst (0.015 mmol), solvent (5.0 mL) at room temperature under visible light irradiation. [b] Isolated yield. [c] 3 mol % photocatalyst loading. [d] 1 mol % photocatalyst loading. [e] 1-(1-phenylvinyl)cyclobutanol was utilized as the substrate instead of **1a**. [f] The reaction was performed in the dark.

reaction with a slight decrease in yield (Table 1, entry 18). The control experiment showed that the reaction could not proceeded in the absence of a photocatalyst and visible light (Table 1, entries 19-20).

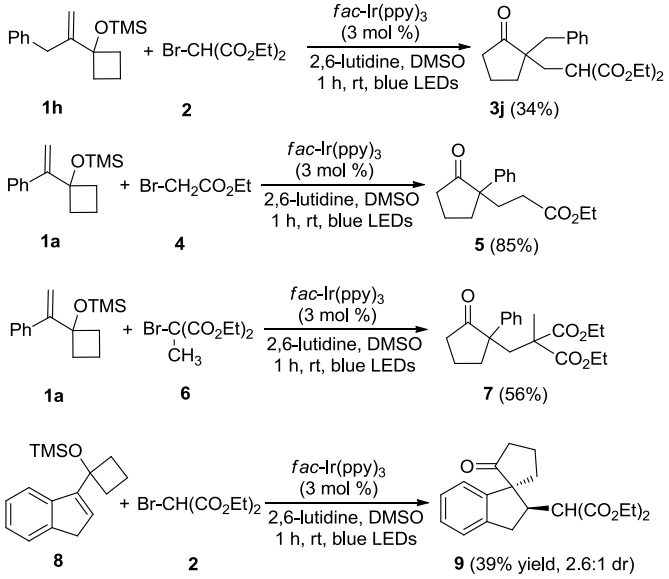
With the optimal reaction conditions in hand, we investigated the scope of this visible light-mediated photocatalytic bis(alkoxycarbonyl)methylation/ring expansion via the 1,2-carbon migration sequence of (1-(1-arylvinyl)cyclobutoxy)trimethyl-silanes **1** with dialkyl bromomalonate (**2**) in the presence of 3 mol % of *fac*-Ir(ppy)$_3$ under light irradiation with blue LEDs in DMSO at room temperature for 1 h.[12] As shown in Table 2, various (1-(1-arylvinyl)cyclobutoxy)trimethylsilanes **1** with electron-withdrawing or electron-donating aryl groups furnished the corresponding migration products with moderate to good yields (Table 2, **3a**–**3g**). Additionally, dimethyl malonate (**2b**) and diisopropyl malonate (**2c**) were found to be effective for this process (Table 2, **3h**-**3i**). (1-(3-Phenylprop-1-en-2-yl)cyclobutoxy)trimethylsilane (**1h**) as an aliphatic alkene substrate provided the desired product **3j** with 34% yield under the same reaction conditions (Scheme 1).

Table 2. Variation of substrates **1**[a,b]



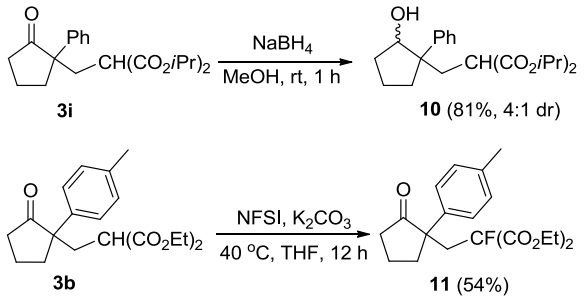
[a] Reaction conditions: (1-(1-arylvinyl)cyclobutoxy)trimethylsilane **1** (0.3 mmol), BrCH$_2$CO$_2$Et (**2**, 0.6 mmol), 2,6-lutidine (0.6 mmol), *fac*-Ir(ppy)$_3$ (0.009 mmol), DMSO (5.0 mL) at room temperature under visible light irradiation. [b] Isolated yield.

In addition to ethyl bromomalonate (**4**) and ethyl bromopropionate (**6**) could undergo photoredox-catalytic alkylation/ring expansion under optimum reaction conditions. Furthermore, (1-(1*H*-inden-3-yl)cyclobutoxy)trimethylsilane (**8**) was used as a substrate in this visible light-mediated photoredox reaction. It was found that the corresponding product **9** was obtained in 39% yield with 2.6:1 dr (Scheme 1).



Scheme 1. Visible light-mediated photoredox alkylation/ring expansion of ethyl bromoesters (**4** and **6**) and cyclobutoxy trimethylsilane derivatives (**1h** and **8**).

To illustrated synthetic utility, we further conducted some functional group transformation. The cyclopentanone derivative **3i** was reduced the corresponding cyclopentanol **10** with 81% yield and 4:1 diastereoselectivity. Ttreatment of the cyclopentanone **3b** with the *N*-fluorobenzensulfonimide at the base conditions led to the formation of the fluorinated ketone **11** in 54% yield (Scheme 2).



Scheme 2. Transformation of cyclopentanone derivatives **3**.

To obtain mechanistic insights into this transformation, some preliminary experiments were performed. The absence of either the photocatalyst *fac*-$Ir^{3+}(ppy)_3$ or visible light shut down the reactivity completely, thus suggesting a crucial role for both of these elements in the transformation (Table 1, entries 17-18). A trace of the product was detected in the presence of a radical scavenger 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO). We propose the reaction mechanism shown in Figure 1 based on the results. The presence of visible light induces a metal to ligand charge transfer in the photocatalyst *fac*-$Ir^{3+}(ppy)_3$, resulting in the excited state *fac*-$Ir^{3+}(ppy)_3^*$. Afterward, a single electron transfer to ethyl bromomalonate (**2**) generates *fac*-$Ir^{4+}(ppy)_3$ and a bis(alkoxycarbonyl)methyl radical **I**. Radical **I** then reacts with (1-(1-arylvinyl)cyclobutoxy)trimethylsilanes **1,** yielding intermediate **II**, which undergoes single electron transfer from *fac*-$Ir^{4+}(ppy)_3$ to generate cation **III**. 1,2-carbon migration of cation **III** leads to a ring expansion that yields the product **3**.

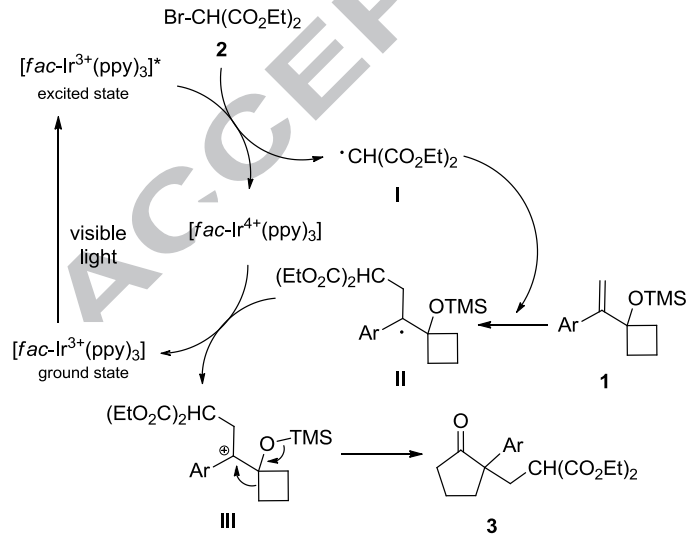


Figure 1. Proposed reaction mechanism.

In conclusion, we achieved visible light-mediated photoredox-catalyzed bis(alkoxycarbonyl)methylation/ring expansion through 1,2-carbon migration of (1-(1-arylvinyl)cyclobutoxy)trimethylsilanes **1** with bromomalonate (**2**). The reaction was completed after a short period in the presence of 3 mol % of *fac*-$Ir(ppy)_3$. The proposed technique is an efficient option for synthesizing bis(alkoxycarbonyl)methyl-substituted cyclic ketone derivatives. A follow-up study is ongoing involving the asymmetric version of the visible light-mediated photoredox-catalyzed bis(alkoxycarbonyl)methylation /ring expansion.

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12. *General procedure for the visible-light-induced photocatalytic alkylation/1,2-carbon migration sequences for the synthesis of bis(alkoxycarbonyl)methyl-substituted cyclic ketones:* An oven-dried Schlenk tube was equipped with a magnetic stir bar, trimethyl(1-(1-arylvinyl)cyclobutoxy)silane **1** (0.3 mmol), *fac*-$Ir(ppy)_3$ (0.009 mmol), $BrCH(CO_2Et)_2$ (**2**, 0.6 mmol), 2,6-lutidine (0.6 mmol) and DMSO (5 mL). The mixture was degassed by the freeze-pump-thaw procedure. The reaction mixture was allowed to stir for 1 h under irradiation of blue LEDs (5 W). After the reaction was finished, the mixture was added ammonium chloride and extracted with ethyl acetate. The organic layers were dried over Na_2SO_4, concentrated in vacuum and purified by chromatography on silica gel (ethyl acetate:*n*-hexane = 1:20) to afford the alkylation-substituted cyclic ketones **3**. **Diethyl 2-((2-oxo-1-phenylcyclopentyl)methyl)malonate (3a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.31 (m, 4 H), 7.25-7.23 (m, 1 H), 4.17-4.04 (m, 2H), 3.98 (q, *J* = 7.2 Hz, 2 H), 3.17 (dd, *J* = 7.2 Hz, 6.0 Hz, 1 H), 2.68 (dd, *J* = 14.6 Hz, 6.0 Hz, 1H), 2.62-2.58 (m, 1H), 2.31-2.26 (m, 3H), 2.01-1.91 (m, 2H), 1.83-1.71 (m, 1H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.3, 169.7, 169.1, 137.3, 128.7, 127.3, 127.2, 61.5, 61.4, 55.7, 48.6, 36.9, 36.
8, 34.4, 18.5, 14.0, 13.9; IR (film) 1727 cm^{-1}; ESI-HRMS : m/z calcd for $C_{19}H_{25}O_5$ $[M+H]^+$: 333.1702; found 333.1706.

Supplementary Material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org

Highlight

1. We have developed the photocatalyzed alkylation/ring expansion of 1-(1-arylvinyl)cyclobutanol derivatives.
2. Moderate to high yields (**3a-3i**, 56-77%) observed.
3. This reaction requires short reaction time and has broad substrate scope.