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Visible-light-driven palladium-catalyzed Dowd–Beckwith ring expansion/C–C bond formation cascade†

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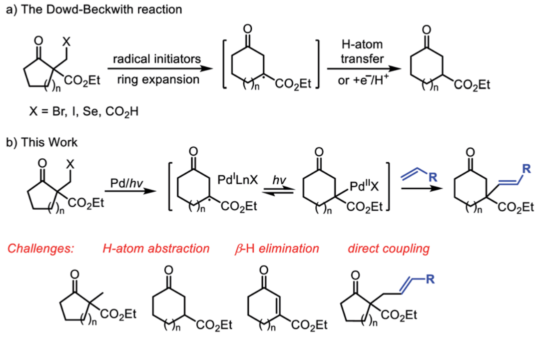
A visible-light-induced palladium-catalyzed Dowd–Beckwith ring expansion/C–C bond formation cascade is described. A range of six to nine-membered β-alkenylated cyclic ketones possessing a quaternary carbon center were accessed under mild conditions. Besides styrenes, the electron-rich alkenes such as silyl enol ethers and enamides were also compatible, providing the desired β-alkylated cyclic ketones in moderate to good yields.

Introduction

The medium-sized carbocycles constitute the core frameworks of many natural products, valuable pharmaceutical compounds and so on.[1] Given their widely recognized importance, continuous efforts from chemists have been devoted to construct the related skeletons.[1,2] In addition to the cyclization reactions, the ring-expansion reactions represent complementary and useful strategy to access these frameworks.[3] Different methods including fragmentation of the zero bridge in fused bicyclic units, inter- and intramolecular carbon-insertion reactions and others have been developed to achieve the ring-expansion.[4] In this field, the ring expansion of cycloalkanones provided an efficient strategy for the medium-sized cyclic ketones' construction.[3c–e] The ring expansion of unstrained cyclic ketones, particularly five- and six-membered rings is more challenging and attractive due to the relatively much weaker ring strain. Recently, Dong's group presented an elegant Rh-catalyzed strategy based on the installation of temporary directing group to activate the C–C bond, followed by carbon insertion to enlarge the cyclic ketones.[3b,3f,5] Unfortunately, this strategy is limited to cyclopentanones. The development of ring-expansion reactions to form functionalized medium-sized carbonyl compounds still remains highly demanding.

The Dowd–Beckwith reaction and variants represent an important class of radical ring-expansion reaction, which offers useful alternative to obtain the medium-sized cyclic ketones. Since the seminal pioneering works of Dowd and Beckwith,[3,6] a variety of radical initiating systems, especially photocatalytic systems have been established for this transformation (Scheme 1, eqn a).[7] Although many progress have been made in the reaction system, the ring expansion/H-atom abstraction is still the mainstream transformation, which limited its application in the radical cascade.[8] Recently, the light-induced transition-metal catalysis has emerged as a versatile platform to realize transformations that are otherwise difficult to achieve. In this field, the groups of Gevorgyan, Fu, Yu and others recently demonstrated a series of fantastic chemical transformations through visible light-induced Pd-catalyzed alkyl couplings, wherein the hybrid alkyl Pd(I)-radical species enabled the alkyl couplings achievable.[9] As a part of our interest in radical chemistry and transition-metal catalysis,[10] we hope to explore an intermolecular Dowd–Beckwith ring-expansion/Heck-type coupling cascade (Scheme 1, eqn b). Challenges for developing such cascade include the fast competitive H-atom abstraction, the possible β-H elimination and other side reactions due to several different reactive radical species involved. Herein, we report the first visible light induced, Pd-catalyzed



Scheme 1 The classical Dowd–Beckwith reactions and our design on the Dowd–Beckwith ring-expansion/Heck-type coupling cascade.

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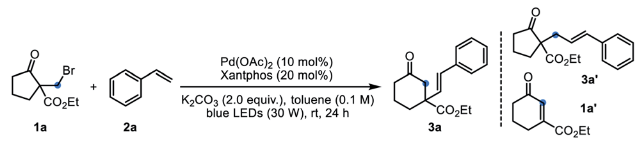
intermolecular Dowd–Beckwith ring-expansion/C–C bond formation cascade. A range of medium-sized β-alkenylated cyclic ketones bearing a quaternary carbon centre were obtained under mild conditions with good yields and excellent stereoselectivity.

Results and discussion

Inspired by the pioneering works on visible-light induced Pd-catalyzed alkyl-Heck coupling reactions,[11] we envisioned that photoirradiation might facilitate the SET event between Pd(0) complex and Dowd–Beckwith halides to initiate the ring expansion process. The interaction of the tertiary radical species and Pd(I) complex generated *in situ* would provide opportunities for further transformation (Scheme 1, eqn b). To check this hypothesis, we set to examine the reaction of α-bromomethyl β-keto ester **1a** and styrene **2a** in the presence of Pd(0) complex under visible light irradiation. To our delight, treatment of **1a** and **2a** with 10 mol% of $Pd(OAc)_2$, 20 mol% of 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) and K_2CO_3 (2.0 equiv.) in toluene under blue LEDs irradiation afforded the desired ring-expansion/alkenylation product **3a** in 66% yield (Table 1, entry 1). Other palladium catalysts such as $Pd(TFA)_2$, $PdCl_2$ and $Pd(PPh_3)_4$ also displayed some catalytic activity, but gave lower yields than $Pd(OAc)_2$ (entries 2 and 3). When $Ni(OAc)_2$ was used instead of $Pd(OAc)_2$ as the catalyst, no reaction occurred (entry 4). The ligand proved to be crucial for this reaction. Except for Xantphos, other phosphine ligands neither bidentate (DPEPhos, BINAP) nor monodentate ($P(o\text{-}MeOC_6H_4)_3$) were effective (entries 5 and 6). Both inorganic and organic bases were examined, and K_2CO_3 turned out to be the optimal one (entries 7 and 8). Solvent screening reveals that $PhCF_3$, xylene and DCE were inferior to toluene, while polar solvents such as CH_3CN and DMF were completely unsuitable (entries 9 and 10). Lowering the loading of Pd/Xantphos to 5/10 mol% resulted in a diminished yield of **3a** (entry 1). Control experiments indicated that catalyst, ligand and base were all essential for this reaction (entry 11). Furthermore, visible light irradiation was also required (entry 12). Without irradiation, the reaction did not work even heating up to 80 °C (entry 13). It is noteworthy that some amount of the direct alkyl-Heck coupling product **3a′** (without ring-expansion) and ring-expansion/β-H elimination product **1a′** were also observed during the reaction. Under the optimal conditions, the byproduct **3a′** was isolated in 10% yield and the **1a′** was obtained in 5% yield. Finally, to demonstrate the utility of this procedure, the reaction of **1a** and **2a** was conducted on a 1.0 mmol scale, and 62% yield of **3a** was still obtained.

With the optimized reaction conditions in hand, the generality of this reaction with respect to alkenes was evaluated (Table 2). A variety of *para*-, *meta*-, and *ortho*-substituted styrenes reacted with **1a** smoothly to afford the desired six-membered products **3b–3p** in 15–76% yields. In general, styrenes with electron-donating groups gave better yields than

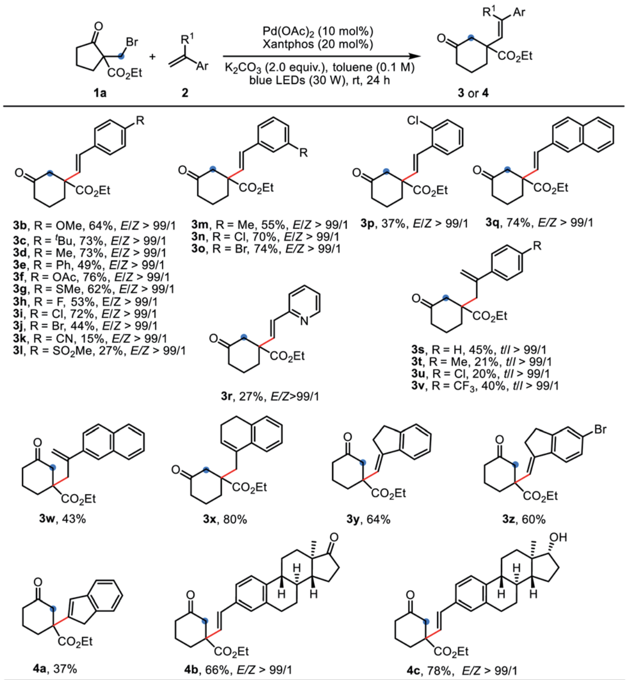
Table 1 Optimization of reaction conditions[a]



Entry	Variants from standard conditions	Yield (%)
1	None	66 (55)[b]
2	$Pd(TFA)_2$, or $PdCl_2$ as the catalyst	14, 16
3	$Pd(PPh_3)_4$ as the catalyst	33
4	$Ni(OAc)_2$ as the catalyst	n.r.[c]
5	DPEPhos or BINAP as the ligand	Trace, n.r.[c]
6	$P(o\text{-}MeOC_6H_4)_3$	n.r.[c]
7	Cs_2CO_3, Li_2CO_3 or KOAc as the base	50, 16, 48
8	Et_3N or DIPEA as the base	12, 28
9	$PhCF_3$, xylene or DCE as the solvent	39, 43, 20
10	CH_3CN or DMF as the solvent	n.r.[c]
11	Without catalyst or ligand or base	n.r.[c] or trace
12	In the dark	n.r.[c]
13	Without irradiation, heating to 80 °C	n.r.[c]

[a] Reaction conditions **A**: **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL) were irradiated with 30 W blue LEDs at room temperature for 24 h under N_2. Yields of isolated product were given. [b] 5 mol% of $Pd(OAc)_2$ and 10 mol% of Xantphos were used. [c] n.r. = no reaction.

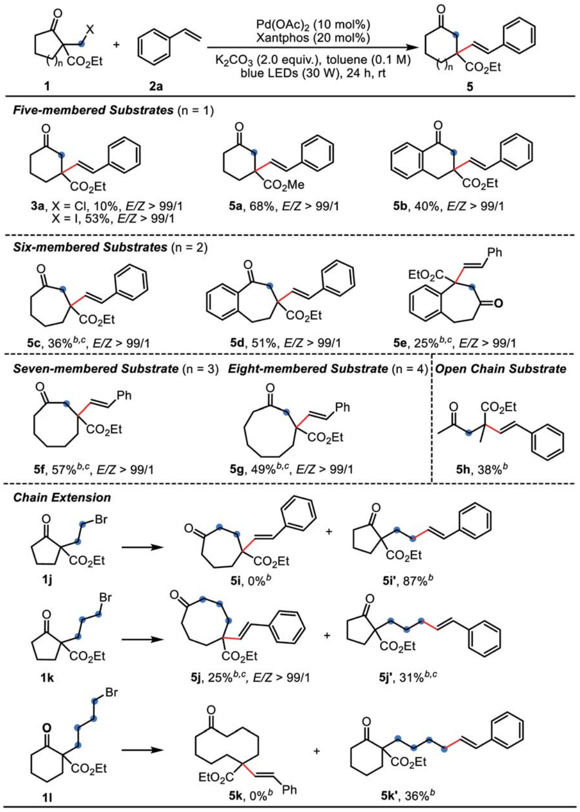
Table 2 Scope of the alkenes[a]



[a] Reaction conditions **A**: **1a** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL) were irradiated with 30 W blue LEDs at room temperature for 24 h under N_2. Yields of isolated product were given. *E*/*Z* and t/l ratios of products were determined by ^1H NMR analysis: t = terminal and l = linear.

those bearing strong electron-withdrawing groups (**3b–3g** *vs.* **3k** and **3l**), probably due to the polarity-matching of radicals. In these cases, most of the substrate **1a** was recovered. Remarkably, excellent stereoselectivity was observed for all these reactions, and only *E*-isomers were obtained as sole products. 2-Vinylpyridine was also efficient for this reaction, providing the desired product **3r** in 27% yield. 1,1-Disubstituted alkenes participated in this reaction to deliver the corresponding products **3s–3z** in moderate yields. Satisfactorily, the exocyclic alkenes derived from 1-tetralone and 1-indanones furnished the products **3x–3z** in 60–80% yields. It is worth noting that the bromo groups in styrenes were retained in this palladium catalytic system (**3j**, **3o**, **3z**), thereby providing opportunity for further derivatization. Besides terminal alkenes, the 1*H*-indene containing an internal alkene also gave the product **4a**, albeit with somewhat low yield due to poor conversion. Notably, the estrone-derived olefins underwent this reaction efficiently to give the products **4b** and **4c** in satisfied yields, which highlighted the potential of this method in late-stage functionalization of complex molecules. Unfortunately, aliphatic alkenes, allylbenzene and acrylate esters were inert under the standard conditions.

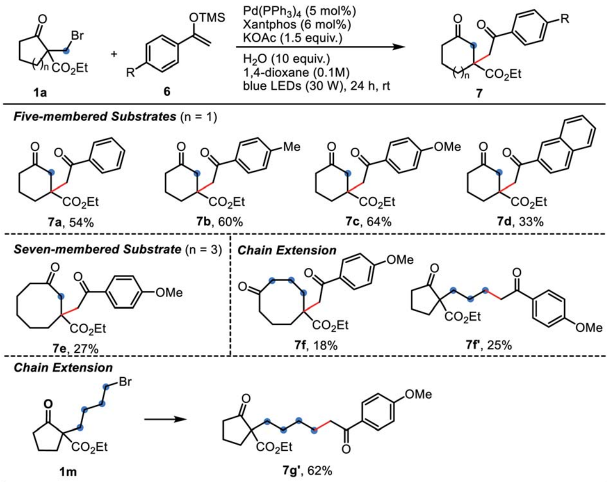
Table 3 Scope of the β-keto esters[a]



Subsequently, the scope and limitations of β-keto esters **1** were examined using **2a** as the coupling partner (Table 3). Besides the α-bromomethyl substrate **1a**, the homologous chloride and iodide gave the product **3a** in 10% and 53% yield, respectively. A range of α-bromomethyl substrates containing five-to eight-membered ring could react smoothly to afford the one-carbon extended products **5a–5g**. For six-, seven-, eight-membered or other substrates, $PdCl_2(PPh_3)_2$ was found as optimal catalyst (conditions **B**). The relatively strained five-membered substrates displayed much better reaction efficiency, giving the six-membered products **5a** and **5b** in good yields. It is a pity that some of the yields were unsatisfied due to the low conversion even after prolonged reaction time. Therein, the Dowd–Beckwith bromides could be recovered. When the substrate **1k** bearing a three-carbon side chain was subjected to the reaction, the anticipated product **5j** was formed in a low yield, along with the by-product **5j'** in 31% isolated yield. Substrates with two- or four-carbon side chain (**1j** and **1l**) failed to give any expected products, delivering 87% and 36% of the direct coupling by-products, respectively.[3a] The 2-phenyl cycloheptanone only afforded trace amount of the desired product (not shown).

As we know, the Dowd–Beckwith ring-expansion led to a tertiary alkyl radical species bearing an ester group, which is quite electrophilic in nature. Thus, we thought the electron-rich alkenes would be compatible for this tandem transformation. Satisfactorily, the Dowd–Beckwith bromide **1a** reacted smoothly with a series of silyl enol ethers to provide the expected β-alkylated cyclic ketones **7a–7d** in moderate to good yields. Substrate with a three-carbon side chain afforded the desired

Table 4 Scope of the silyl enol ethers[a]



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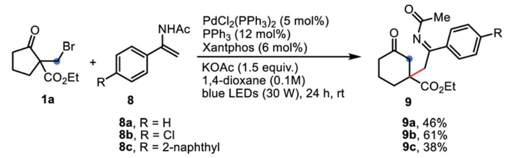
[a] Reaction conditions **A**: **1** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $Pd(OAc)_2$ (10 mol%), Xantphos (20 mol%) and K_2CO_3 (0.4 mmol, 2.0 equiv.) in toluene (2.0 mL) were irradiated with 30 W blue LEDs at room temperature for 24 h under N_2. Yields of isolated product were given. [b] Reaction conditions **B**: **1** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), $PdCl_2(PPh_3)_2$ (5 mol%), PPh_3 (12 mol%), Xantphos (6 mol%) and KOAc (0.3 mmol, 1.5 equiv.) in 1,4-dioxane (2.0 mL) were irradiated with 30 W blue LEDs at room temperature for 24 h under N_2. Yields of isolated product were given. [c] The reactions were irradiated for 48 h.

[a] Reaction conditions **C**: **1** (0.2 mmol, 1.0 equiv.), **6** (0.4 mmol, 2.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), Xantphos (6 mol%) and KOAc (0.3 mmol, 1.5 equiv.) in 1,4-dioxane (2.0 mL) were irradiated with 30 W blue LEDs at room temperature for 24 h under N_2. Yields of isolated product were given.

Table 5 Scope of the enamides[a]



[a] Reaction conditions **B:** **1a** (0.2 mmol, 1.0 equiv.), **8** (0.4 mmol, 2.0 equiv.), $PdCl_2(PPh_3)_2$ (5 mol%), PPh_3 (12 mol%), Xantphos (6 mol%) and KOAc (0.3 mmol, 1.5 equiv.) in 1,4-dioxane (2.0 mL) were irradiated with 30 W blue LEDs at room temperature for 24 h under N_2. Yields of isolated product were given.

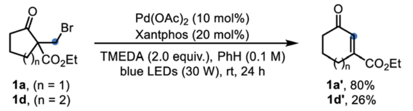


Fig. 1 Ring expansion/β-H elimination reaction.

product **7f** in 18% yield, along with by-product **7f′** in 25% yield. Substrate **1m** with four-carbon side chain didn't undergo the ring-expansion process, only delivering the direct alkylated product **7g′** in 62% yield (Table 4). In addition, the enamides also worked with **1a**, yielding the β-alkylated cyclic ketones **9** in moderate yields (Table 5).

Notably, the byproduct **1a′** formed through ring-expansion/β-H elimination was always observed in above reactions, which is a valuable synthetic intermediate but is hard to obtain in organic synthesis.[12] Thus we hope to amplify this useful transformation (Fig. 1). After several trails, we were delighted to find that the substrate **1a** delivered the desired product **1a′** in 80% yield by using TMEDA as the base and PhH as the solvent. While, the analogue **1d** only afforded the product **1d′** in 26% isolated yield due to incomplete conversion.

To shed light on the mechanism of this reaction, a series of control experiments were performed (Fig. 2). The addition of TEMPO and BTH, well-known radical scavengers, both inhibited the model reaction significantly (eqn (1) and (2)). When 1.0 equiv. of TEMPO was added, the yield of **3a** was reduced to 20%. Meanwhile, the TEMPO-adduct **10** was isolated in 13% yield. Further increase of the amount of TEMPO led to a higher yield of **10**. These results implied that a radical intermediate might be involved in this reaction. In addition, the reaction of **1a** with 1-(1-cyclopropylvinyl)benzene **2d′**, a radical clock substrate afforded **3x** as the sole product in 55% yield (eqn (3)), which provided clear evidence for radical pathway. Moreover, light on-off studies revealed that constant photoirradiation is essential for this transformation (for details, see the ESI†). The UV-vis analysis indicated that the Pd^0 complex formed in the catalytic system is the photoabsorbing species (for details, see the ESI†).

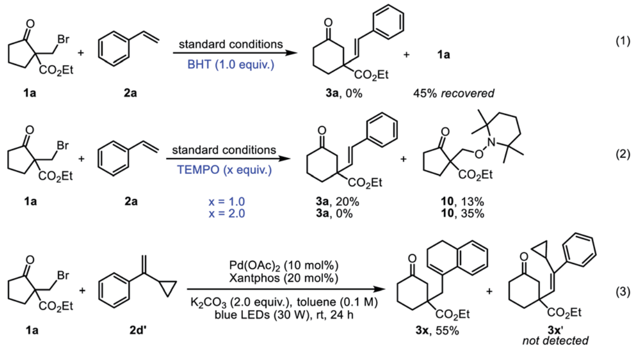
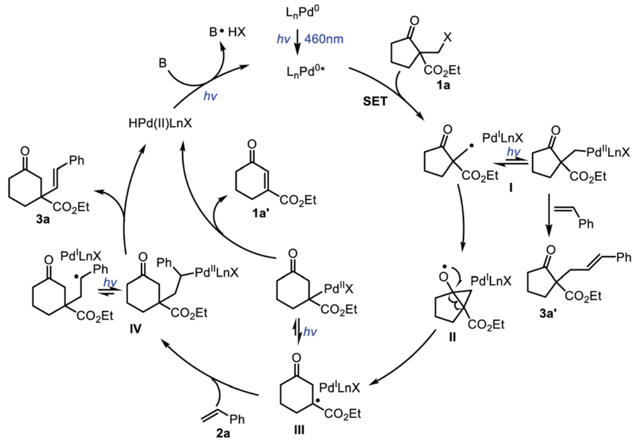


Fig. 2 Control experiments.



Scheme 2 Proposed reaction mechanism.

Based on the above results and literature,[11] a plausible mechanism for this ring-expansion/alkenylation reaction is proposed (Scheme 2). Firstly, the L_nPd^0 complex is photoexcited to form an excited state $L_nPd^{0}*$ species upon irradiation, which promotes a single-electron transfer event with **1a** to generate the putative Pd^I species and a primary alkyl radical **I**. Subsequently, intermediate **I** undergoes intramolecular cyclization of the carbon radical on the carbonyl group, followed by alkoxyl radical triggered C–C bond cleavage to yield the ring extended radical intermediate **III**. Finally, radical addition of **III** to styrene **2a** provides the benzyl radical **IV**, which produces the target product **3a** and regenerates the Pd^0 catalyst through β-H elimination. Due to the equilibrium between hybrid alkyl Pd(I)-radical species and alkyl Pd(II) species,[13] the intermediate **III** could also deliver the product **1a′** and regenerate the Pd^0 catalyst through β-H elimination. In addition, the direct coupling product **3a′** could also be formed during the reaction.

Conclusions

In conclusion, we have developed a Dowd–Beckwith ring expansion/C–C bond formation cascade by light-induced palladium catalysis. A range of five to eight-membered Dowd–Beckwith halides reacted smoothly with styrenes to afford the enlarged β-alkenylated cyclic ketones in moderate to good yields with excellent stereoselectivity. Besides styrenes, the electron-rich alkenes such as silyl enol ethers and enamides were also compatible, providing the desired β-alkylated cyclic ketones. This research would arouse the application of the Dowd–Beckwith reaction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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