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Visible-Light-Driven Palladium-Catalyzed Oxy-Alkylation of 2-(1-Arylvinyl)anilines by Unactivated Alkyl Bromides and CO_2: Multicomponent Reactions toward 1,4-Dihydro-2*H*-3,1-benzoxazin-2-ones

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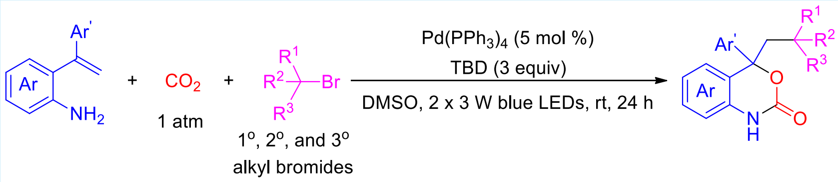
Supporting Information



ABSTRACT: A visible-light-driven palladium-catalyzed radical oxy-alkylation of 2-(1-arylvinyl)anilines with unactivated alkyl bromides and CO_2 has been developed toward 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones. This multicomponent reaction (MCR) starts with (1) carboxylation of an amino by CO_2; (2) formation of Pd(I) and an alkyl radical via visible-light-driven reaction of alkyl bromides and Pd(0); (3) addition of an alkyl radical to the vinyl followed by single electron transfer (SET) oxidation to the carbocation by Pd(I); and (4) cyclization via intramolecular nucleophilic attack of the carboxylate anion to carbocation.

The utilization of CO_2 as a one-carbon source toward value-added chemicals, especially heterocyclic compounds, has received considerable attention in recent years.[1,2] Among which, the carboxylative cyclizations triggered by the reactions of CO_2 with *N*-nucleophile, such as allylamines,[3] propargylamines,[4] and *o*-alkynylanilines,[5] are extremely fascinating, affording useful nitrogen-containing heterocycles with potentially diverse bioactivities. Undoubtedly, the development of such reactions proceeding with either new substrates or new strategies on known substrates would dramatically enlarge the applicable scope of CO_2 fixation, leading to new value-added products with complexity and diversity. With the development of visible-light-driven reactions,[6,7] we have witnessed many elegant examples on visible-light-promoted carboxylative cyclization of allylamines with bromides and CO_2. For instance, He developed the radical-initiated carboxylative cyclization leading to fluorine containing 2-oxazolidinones whereby the sequential radical addition, carboxylation, SET oxidation, and intramolecular cyclization occurred.[8] Afterward, Yu described a similar procedure toward highly functionalized 2-oxazolidinones.[9] However, compared with allylamines, the fixation of CO_2 by *o*-alkenylanilines through a similar procedure has never been investigated before.[10]

Meanwhile, 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones are important structural motifs that widely exist in biologically active natural products and medicines (Scheme 1).[11] Traditional synthetic methods included the cyclization of (2-aminoaryl)-methanols with phosgene or CBr_4 (Scheme 1a),[12a,b] and halo-cyclization reaction of 2-vinylaniline derivatives with 1,3-dichloro-5,5-dimethylhydantoin (Scheme 1b).[13] Nevertheless, to date, the sustainable procedure on the fixation of CO_2 to access such frameworks has been rarely studied.[14] As part of our continuing studies on the chemical conversion of CO_2,[15] we herein present a novel procedure toward 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones, proceeding with a three-component reaction of 2-(1-arylvinyl)anilines, alkyl bromides, and CO_2 promoted by a photoredox and palladium dual-catalysis system at room temperature (Scheme 1c).

Initially, we tested the reaction of 2-(1-phenylvinyl)aniline **1a** (0.2 mmol), 1-bromoadamantane **2o** (0.3 mmol), and atmospheric pressure CO_2 to optimize the reaction conditions. First, during the screening of photocatalysts, only $Pd(PPh_3)_4$ (5 mol %) was efficient under the irradiation of 2 × 3 W blue LEDs in the presence of Cs_2CO_3 (3 equiv) as the base, leading to the annulation product **3a** in 45% yield (Table 1 entries 1−3). Among the tested bases such as KO^tBu (<5%), DBU (58%), TBD (85%), and MTBD (61%), TBD was the best (Table 1, entries 3−7). Notably, the solvent also had a profound effect on the reaction efficiency, and DMSO (85%) was superior to DMF (78%) and MeCN (36%, Table 1, entries 7−9). $Pd(PPh_3)_2Cl_2$ gave a comparable yield (75%). However, $Pd(OAc)_2$ (<5%) and $Pd_2(dba)_3$ (<5%) almost inhibited the reaction (Table 1, entries 7, and 10−12). Additionally, 5 mol % of $Pd(PPh_3)_4$ and 1.5 equiv of 1-bromoadamantane were

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Scheme 1. Representative 1,4-Dihydro-2*H*-3,1-benzoxazin-2-ones and Synthetic Pathways

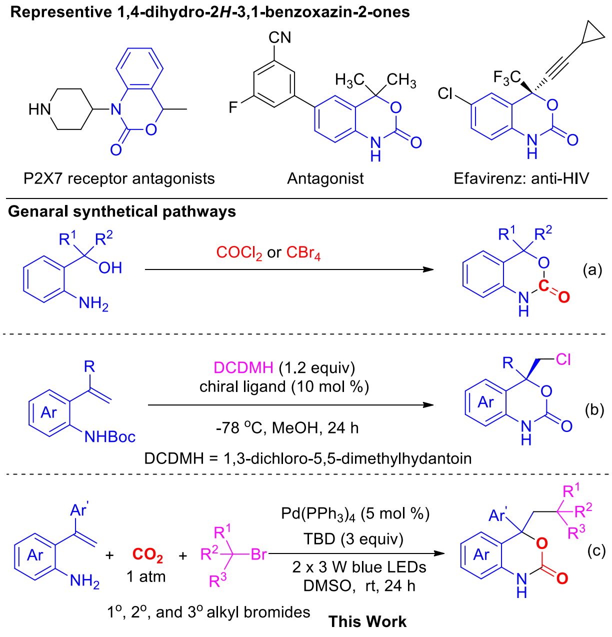
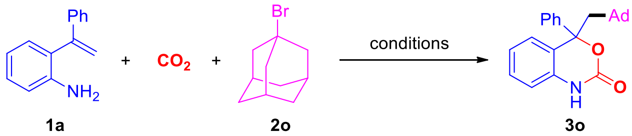


Table 1. Selected Results for Screening the Optimized Reaction Conditions[a]



entry	catalyst	base	solvent	yield[b] (%)
1[c]	*fac*-Ir(ppy)$_3$	Cs_2CO_3	DMSO	N.R.
2[c]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	Cs_2CO_3	DMSO	N.R.
3	Pd(PPh$_3$)$_4$	Cs_2CO_3	DMSO	45
4	Pd(PPh$_3$)$_4$	KO^{t}Bu	DMSO	<5
5	Pd(PPh$_3$)$_4$	DBU	DMSO	58
6	Pd(PPh$_3$)$_4$	MTBD	DMSO	61
7	Pd(PPh$_3$)$_4$	TBD	DMSO	85
8	Pd(PPh$_3$)$_4$	TBD	DMF	78
9	Pd(PPh$_3$)$_4$	TBD	MeCN	36
10	Pd(PPh$_3$)$_2$Cl$_2$	TBD	DMSO	75
11	Pd(OAc)$_2$	TBD	DMSO	<5
12	Pd$_2$(dba)$_3$	TBD	DMSO	<5
13	Pd(PPh$_3$)$_4$	TBD	DMSO	75[d], 81[e], 83[f]
14[g]	Pd(PPh$_3$)$_4$	TBD	DMSO	N.R.
15	Pd(PPh$_3$)$_4$	–	DMSO	N.R.

[a] Reaction conditions: 2-(1-phenylvinyl)aniline **1a** (0.2 mmol), 1-bromoadamantane **2o** (0.3 mmol), catalyst (0.01 mmol, 5 mol %), base (0.6 mmol), solvent (0.1 M), 2 × 3 W blue LEDs, 24 h, in a sealed Schlenk tube under room temperature, unless otherwise noted. [b] Isolated yield. [c] Catalyst (0.002 mmol, 2 mol %). [d] Pd(PPh$_3$)$_4$ (2.5 mol %). [e] Pd(PPh$_3$)$_4$ (10 mol %). [f] 1-Bromoadamantane (0.4 mmol). [g] Without Pd(PPh$_3$)$_4$ or in dark. Ad = adamantan-1-yl. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. TBD = (1,5,7-triazabicyclo[4.4.0]-dec-5-ene). MTBD = 1-methyl-2,3,4,6,7,8-hexahydro-1*H*-pyrimido-[1,2-*a*]pyrimidine. N.R. = no reaction.

sufficient enough for high reaction efficiency (Table 1, entry 13). During the blank experiments, the reaction failed to work in the absence of each reaction parameter (Table 1, entries 14–15).

Having established the optimized reaction conditions, first, the scope and limitation of alkyl bromides were investigated, as summarized in Figure 1. Generally, the catalytic system exhibited a broad substrate scope and high functional group tolerance. Importantly, primary (40–78%, **3a–f**), secondary (61–88%, **3g–n**), and tertiary alkyl bromides (85%, **3o**) all ran smoothly under the optimized conditions. Particularly, ethyl 5-bromopentanoate provided **3d** in 51% yield. Both acyclic (72%, **3e**) and cyclic (78%, **3f**) acetal worked well under the procedure. Notably, the cyclic secondary alkyl bromides, such as 2-bromoadamantane (72%, **3g**), bromocyclopropane (62%, **3h**), bromocyclobutane (88%, **3i**), bromocyclohexane (70%, **3j**), 4-bromo *N*-Boc piperidine (61%, **3k**), and 4-bromotetrahydro-2*H*-pyran (78%, **3l**), all served as good reaction partners. The product **3n** was isolated in 71% yield (dr = 1/1). To our delight, ester (51%, **3d**), acetal (72%–78%, **3e–3f**), *N*-Boc (61%, **3k**), and ether (78%, **3l**) groups, which were handles for potential further functionalization, survived well in this procedure. Additionally, a 1 mmol scale reaction of **1a** with **2o** also ran smoothly under slightly modified conditions to afford **3o** in 73% yield. The structure of **3b** was further confirmed by X-ray crystallography study (CCDC 1920540).

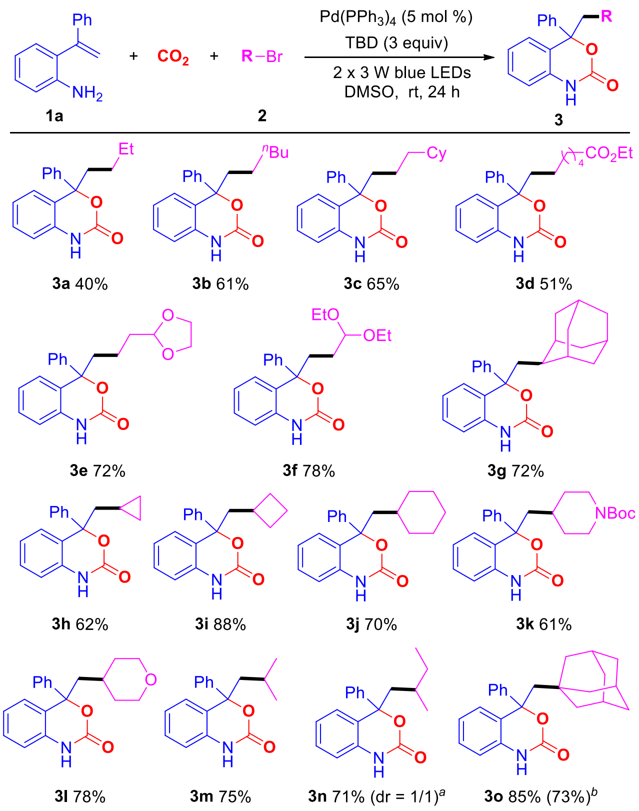


Figure 1. Scope of Alkyl Bromides. Reaction conditions: 2-(1-phenylvinyl)aniline **1a** (0.2 mmol), alkyl bromide **2** (0.3 mmol), Pd(PPh$_3$)$_4$ (0.01 mmol, 5 mol %), and TBD (0.6 mmol) in DMSO (2.0 mL) were irradiated with 2 × 3 W blue LEDs for 24 h in a sealed Schlenk tube at room temperature, unless otherwise noted. [a] Determined by ^{1}H NMR. [b] 2-(1-Phenylvinyl)aniline **1a** (1.0 mmol), 1-bromoadamantane **2o** (2.0 mmol), Pd(PPh$_3$)$_4$ (0.1 mmol, 10 mol %), and TBD (3.0 mmol) in DMSO (10.0 mL) were irradiated with 2 × 3 W blue LEDs for 24 h in a 25 mL Schlenk tube with a CO_2 balloon at room temperature.

Subsequently, the substrates scope of 2-(1-arylvinyl)anilines was also investigated as shown in Figure 2. As expected, the substituted 2-(1-arylvinyl)anilines proceeded smoothly with bromocyclobutane **2i** and atmospheric pressure CO_2 to afford 6-, 7-, and 8-substituted 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones in moderate to good yields. The electronic properties of the substituents on the phenyl ring of the aniline moiety had some effect on the reaction. For example, the substrates bearing electron-donating (**4a**−**4f**, 75%−80%) and weak electron-withdrawing groups (**4i**−**4j**, 66%−81%) worked well. However, for substrates possessing a strong electron-withdrawing group on the aniline moiety, no desired product **4k** could be detected. Notably, some functional groups, such as methyl (**4a**, 66%), methoxy (**4b**, 76%), methylthio (**4e**, 67%), fluoro (**4i**, 80%), and chloro (**4j**, 66%) groups, all remained untouched under these reactions. Importantly, by replacing the phenyl with 2-thiophenyl, 2-furanyl, and 2-naphthyl, the desired products **4m**, **4n**, and **4o** could be isolated in 65%, 26%, and 23% yields, respectively. Unfortunately, introducing a methyl to vinyl resulted in the low yield (**4p**, 28%, dr = 1/1.15), which would be attributed to the steric hindrance.

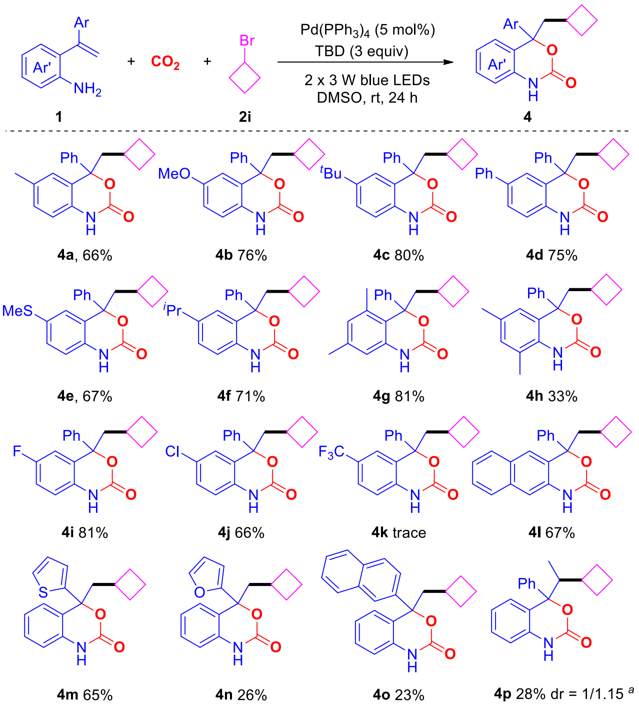
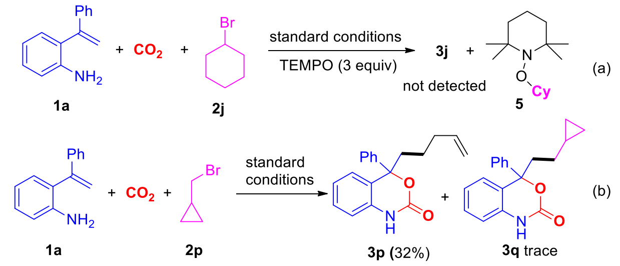


Figure 2. Scope of 2-(1-Arylvinyl)anilines. Reaction conditions: 2-(1-arylvinyl)aniline **1** (0.2 mmol), bromocyclobutane **2i** (0.3 mmol), $Pd(PPh_3)_4$ (0.01 mmol, 5 mol %), and TBD (0.6 mmol) in DMSO (2.0 mL) were irradiated with 2 × 3 W blue LEDs for 24 h in a sealed Schlenk tube at room temperature, unless otherwise noted. [a] Determined by ^1H NMR.

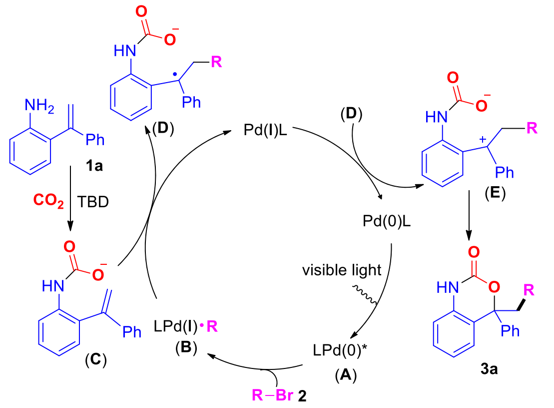
Some control experiments were conducted to gain insight into this transformation. In the presence of radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3 equiv), the reaction was totally inhibited, and radical adduct **5** was detected by GC-MS (Scheme 2a; for details, please see Supporting Information). Thus, this reaction may involve a radical pathway. Moreover, a radical clock experiment was conducted by using cyclopropylmethyl bromide **2p** as the alkylation reagent. As expected, the reaction of **1a**, CO_2, and **2p** formed the rearranged product **3p** in 32% yield (Scheme 2b). This result further confirmed the involvement of a radical pathway during the procedure.

Scheme 2. Preliminary Mechanism Study



On the basis of the aforementioned results and some relative previous studies, a tentative mechanism is outlined in Scheme 3.[6g−l,9,16] First, the excited state $Pd(PPh_3)_4$ **A** is formed under light irradiation, which is oxidized by alkyl bromide **2** to generate active Pd(I) species **B** and an alkyl radical. Meanwhile, with the assistance of TBD, the *o*-alkenylaniline **1a** reacts with CO_2 rapidly, leading to carbamate **C**. Meanwhile, the addition of the radical to the alkene in carbamate **C** produces a more stabilized benzylic radical **D**. Then, the SET between Pd(I) species and intermediate **D** regenerates the Pd(0) catalyst and delivers the stabilized carbon-cation species **E**. Finally, intramolecular nucleophilic attack of intermediate **E** affords 1,4-dihydro-2*H*-3,1-benzoxazin-2-one **3a**.

Scheme 3. Proposed Mechanism



In conclusion, we have developed a visible-light-driven palladium catalyzed radical oxy-alkylation of 2-(1-arylvinyl)-anilines with unactivated alkyl bromides and CO_2, affording a series of 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones in moderate to excellent yields. This procedure starts with the carboxylation of an amino by CO_2. Then, under visible light, the reaction of alkyl bromides and a palladium catalyst produces an alkyl radical, which undergoes the addition to the vinyl to form a new radical species. After the single electron transfer (SET) oxidation of the newly formed radical species to a carbocation, the cyclization takes place whereby intramolecular nucleophilic attack of the carboxylate anion to the carbocation occurs. Thus, it represents an efficient method for incorporation of CO_2 into heterocycles.

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■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02700.

Experimental procedures along with copies of spectra (PDF)

Accession Codes

CCDC 1920540 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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