Visible-Light-Driven C−H Imidation of Arenes and Heteroarenes by a Phosphonium Ylide Organophotoredox Catalyst: Application to C−H Functionalization of Alkenes

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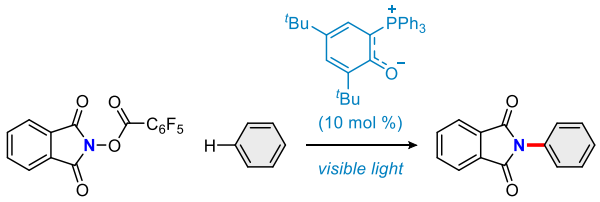
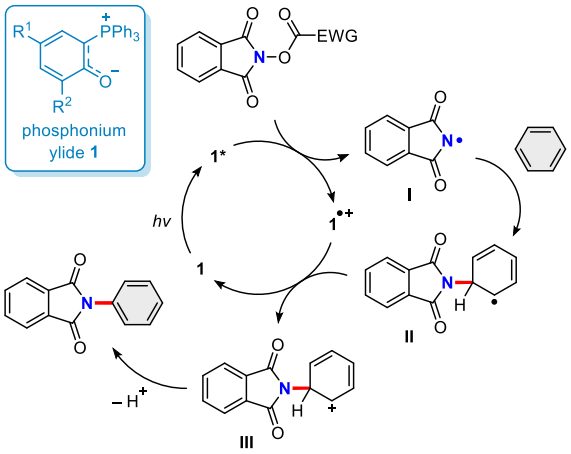
Supporting Information Placeholder



ABSTRACT: Phosphonium ylide catalysis through an oxidative quenching cycle has been developed for visible-light-driven C−H imidation of arenes and heteroarenes. The present protocol could be applied not only to trihalomethylative lactonization reactions involving trifluoromethyl, trichloromethyl, and tribromomethyl radicals but also to the first example of an organophotoredox-catalyzed imidative lactonization reaction involving a nitrogen-centered electrophilic radical species.

Arylamines represent an important class of nitrogen containing compounds, many of which are found in drugs, agrochemicals, and fine chemicals.[1] Cross-coupling reactions by transition metal catalysis are powerful tools for preparing arylamines from aryl (pseudo)halides or aryl boronic acids.[2] Direct intermolecular C−H amination of arenes is an attractive but still challenging strategy, in which the C−H bond of the arene does not have to be prefunctionalized.[3] In particular, since the *N*-phthaloyl group can be readily derivatized to the corresponding anilines, there are several reports on catalytic arene C−H phthalimidation with the use of transition metals.[4,5] Aromatic substitution reactions by nitrogen-centered radicals are also well-known approaches toward the direct C−H amination.[6] Due to growing interest in sustainable chemistry, photocatalytic imidation involving the radical has emerged recently.[7,8] In 2014, Sanford et al. successfully revealed that a phthalimidyl radical could be generated from *N*-acyloxyphthalimide via the single electron transfer mechanism in the presence of $Ir(ppy)_3$ under visible light irradiation.[7a] The electrophilic radical undergoes addition to arenes to afford the C−H imidated products. In the same year, Lee et al. demonstrated N−Cl bond cleavage of *N*-chlorophthalimide for C−H imidation by photoredox catalysis,[7b] while Studer et al. used *N*-amidopyridinium salts as a precursor for the phthalimidyl radical.[7c] In early 2017, the direct catalytic C−H imidation of arenes and heteroarenes using 2-*tert*-butylanthraquinone with visible light was reported by Itoh and co-workers.[7d] The Ooi group reported a thioxanthone catalyst that acts as an excited-state reductant under UV light irradiation, achieving radical aromatic substitution using *N*-acyloxyphthalimide.[7e] By employing a phosphine combined with *N*-hydroxyphthalimide, Ma et al. recently achieved photocatalytic C−H imidation.[7f]

Scheme 1. C−H Imidation of Arenes and Heteroarenes by Organophotoredox Catalysis

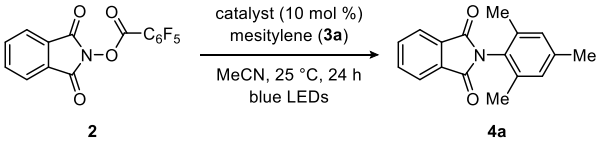


Meanwhile, the discovery of new organocatalysts to achieve green chemical transformations, as alternatives to the use of transition metal catalysts, is an important task in the field of catalysis development. In conjunction with the significant growth of modern photoredox catalysis, organophotoredox catalysis has attracted increasing attention as a powerful tool for sustainable organic synthesis.[9] In 2021, we reported the first example of phosphonium ylide-catalyzed photoredox reactions that proceed under visible light irradiation.[10] Phosphonium ylide **1a** (R^1 = Me, R^2 = H, Ar = Ph)[11] acts as an excited-state

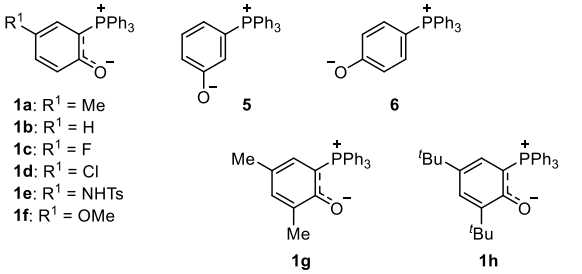
reductant (E^*_{ox} = −2.36 V vs. SCE, τ = 2.0 ns), enabling C−H functionalization reactions, including C−H imidation of arenes, with the use of *N*-acyloxyphthalimide (E_{red} = −1.26 V vs. SCE),[12] via oxidative quenching (Scheme 1). While the potential utility of phosphonium ylides as a visible-light-driven organophotoredox catalyst was disclosed, the improved catalytic activity was only aspirational. Accordingly, we envisioned steric and/or electronic modification of phosphonium ylides **1** by introducing substituents on the ylide moiety.[11c] Although the imidation system inherently requires pre-preparation of *N*-acyloxyphthalimide, it would be beneficial if some novel mechanistic aspects of the organophotoredox catalysts could be invoked. Herein, we describe a phosphonium ylide organophotoredox catalysis that facilitates C−H imidation reactions of arenes and heteroarenes. Trihalomethylative lactonization reactions, involving electrophilic •CF_3, •CCl_3, and •CBr_3 radical intermediates generated through an oxidative quenching cycle, are also demonstrated.[13-15] Moreover, ylide catalysis is satisfactorily extended to unprecedented imidative lactonization reactions of unsaturated carboxylic acids with the phthalimidyl radical.[16]

At the outset of our study, we attempted the imidation of mesitylene (**3a**) using *N*-acyloxyphthalimide **2** (Table 1). Based on our previous report,[10] the reactions were carried out in the presence of phosphonium ylide **1** (10 mol %) using 10 equiv of arene **3a** in acetonitrile (0.02 M) at 25 °C for 24 h under blue LED irradiation. The initial experiment using **1a** afforded a 65% (NMR) yield of the desired product **4a**, along with a 33% (NMR) yield of phthalimide (entry 1). Introduction of a halo group as the R^1 group was somewhat effective, whereas non-substituted **1b** and methoxy-substituted **1f** led to decreased yields (entries 2–6). Interestingly, lower yields were observed with the use of betaines **5** and **6**, implying the privileged structure of ylide **1** (entries 7 and 8). Phosphonium ylide **1h** (E^*_{ox} = −2.38 V vs. SCE, τ = 3.2 ns) bearing two *tert*-butyl groups resulted in the highest yield among those tested. Thus, it was found that steric hindrance around the oxygen atom of **1** was more important than the electronic properties to enhance the catalytic activity (entry 10). It should be noted that CV experiments on **1** provided information about the stability of the radical cations $\mathbf{1}^{\bullet+}$ (see SI for details).[17] Finally, the reaction using 2.0 equiv of arene **3a** successfully provided **4a** in 78% isolated yield (entry 11).

Table 1. Optimization Studies for Phosphonium Ylide-Catalyzed C−H Imidation[a]



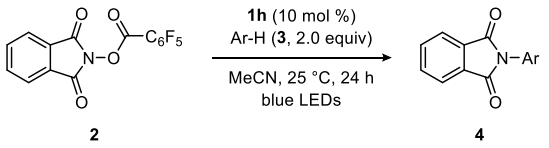
2 **4a**



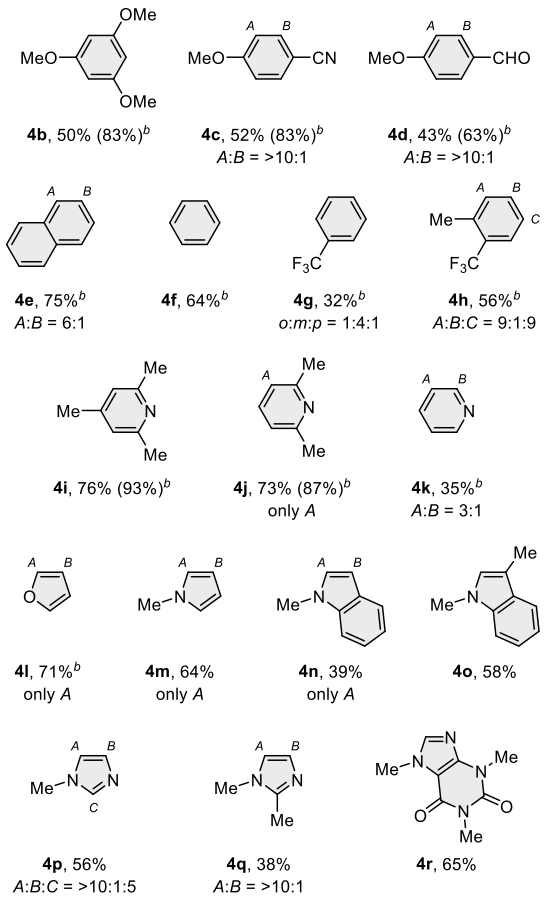
entry	catalyst	conv. of **2** (%)[b]	yield of **4a** (%)[b]
1	**1a**	>95	65
2	**1b**	74	39
3	**1c**	>95	70
4	**1d**	>95	80
5	**1e**	>95	73
6	**1f**	77	30
7	**5**	55	11
8	**6**	32	9
9	**1g**	>95	75
10	**1h**	>95	85
11[c]	**1h**	>95	78 (78)

[a]Unless otherwise noted, all reactions were carried out using **2** (0.1 mmol), arene **3a** (1.0 mmol, 10 equiv), and catalyst (10 mol%) in MeCN (0.02 M) at 25 °C for 24 h under blue LED irradiation. [b]Determined by ^{1}H NMR analysis. Isolated yield of **4a** is shown in parentheses. [c]2.0 equiv of arene **3a** was used.

Table 2. Substrate Scope for C−H Imidation of Arenes and Heteroarenes[a]



2 **4**



[a]Reaction conditions: 0.1 mmol of **2**, arene **3** (2.0 equiv), phosphonium ylide **1h** (10 mol%), MeCN (0.02 M), 25 °C, 24 h, under blue LED irradiation. Isolated yields of **4** are shown. [b]10 equiv of arene **3** was used.

Table 2 summarizes the scope of C−H imidation of arenes and heteroarenes by organophotoredox catalysis. The imidations of trimethoxybenzene (**3b**), *p*-anisonitrile (**3c**), and *p*-anisaldehyde (**3d**) proceeded smoothly to give the products in moderate to good yields. Naphthalene (**3e**), benzene (**3f**), benzotrifluoride (**3g**), and 2-methylbenzotrifluoride (**3h**) were also tolerated with the use of 10 equiv of arenes. 2,4,6-Collidine (**3i**) and 2,6-lutidine (**3j**) were highly reactive substrates while a lower yield was obtained by the reaction of pyridine (**3k**). Electron-rich heterocycles such as furan (**3l**), 1-methylpyrrole (**3m**), and indoles **3n** and **3o** underwent C2 selective C−H imidation in relatively good yields. Imidazole derivatives **3p**−**3r** were also viable substrates, affording the corresponding products under our optimal conditions.

Once C−H imidation of (hetero)arenes was established, we became interested in the alteration of the electrophilic radical precursor to explore the versatile synthetic potential of the photoexcited phosphonium ylide catalysis (Table 3). First, trifluoromethylative lactonization of **7** using **9** was investigated due to its importance in pharmaceuticals.[13] To our delight, not only five-membered lactones **8a**–**8d** but also six-membered lactone **8e** were furnished in modest to good yields. Urea **7'** was applicable to alkene functionalization as well as carboxylic acids **7**. The methodology to introduce a trichloromethyl group was next demonstrated to empower phosphonium ylides as distinguished organophotoredox catalysts because trichloromethylative functionalization via a radical pathway has been unexploited to date.[14] As a result, the desired lactones **8f**–**8j** bearing a trichloromethyl group were successfully obtained in up to 79% yield when carbon tetrachloride was used as a •CCl_3 radical precursor. In addition, tribromomethylative lactonization of **7** was proven to form the products **8k** and **8l**, although bromolactonization competed. These fruitful results suggested that phthalimidyl radical addition to alkenes may occur faster than that to arenes. Thus, the reaction of alkenes bearing a carboxylic moiety with the phthalimidyl radical is expected to provide the corresponding lactones, the efficient synthesis of which remains a serious challenge.[16] We lastly found that 4-pentenoic acids **7a** and **7b** underwent visible-light-driven imidative lactonization in the presence of catalyst **1h** to afford the desired products **8m** and **8n** in moderate yields. Similarly, not only 2-vinyl benzoic acid derivatives **7c** and **7d** but also 5-phenylhex-5-enoic acid (**7e**) were tolerated.

In summary, we have developed visible-light-driven C−H imidation of various arenes and heteroarenes by a phosphonium ylide organophotoredox catalyst. Introduction of bulky substituents into the catalyst structure of **1** led to improved catalytic activity. This protocol could be expanded to the trihalomethylative lactonization of alkenes bearing a carboxylic moiety. This method enables the installation of trifluoromethyl, trichloromethyl, and tribromomethyl groups into unsaturated carboxylic acids. In addition, based on the mechanism via oxidative quenching of phosphonium ylide **1**, the first organocatalytic imidative lactonization reactions were demonstrated for the synthesis of aminoalcohol derivatives. Further investigation to develop fascinating radical reactions by phosphonium ylide catalysis are currently underway in our laboratory.

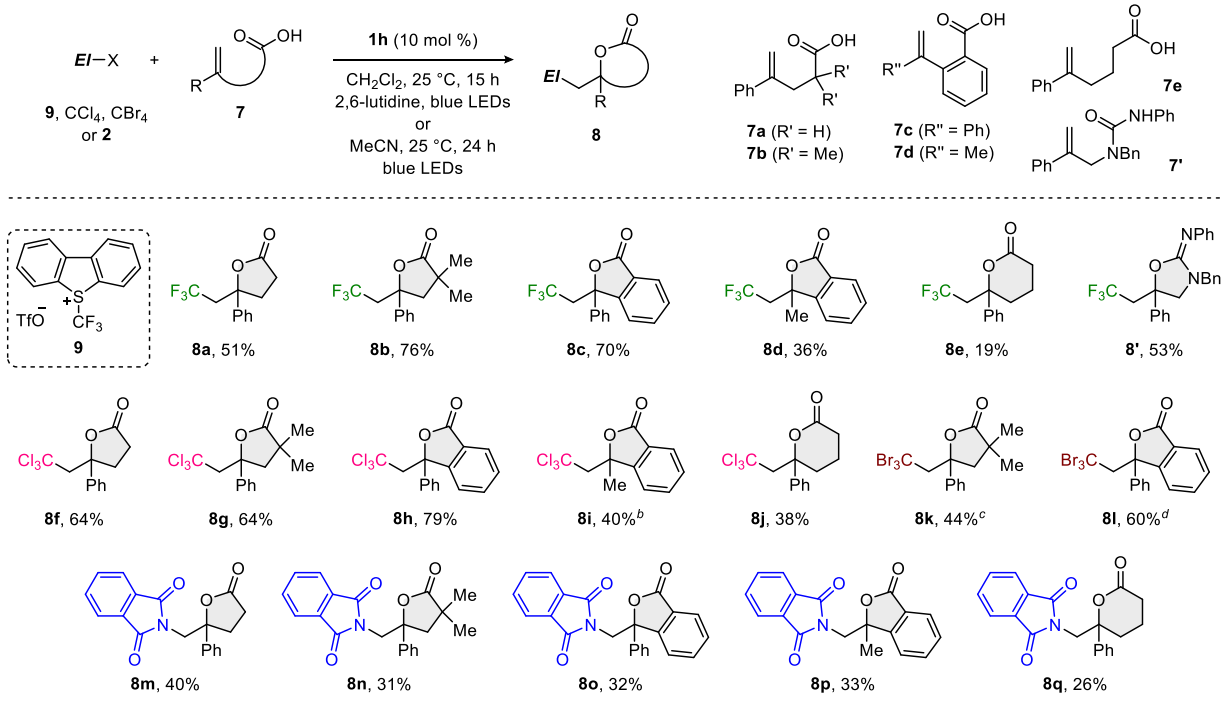
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and spectroscopic data for all new compounds (PDF).

Table 3. Reaction Scope[a]



[a]Reaction conditions for trihalomethylative lactonization: 0.1 mmol of **7**, trihalomethylating reagent (1.2−3.0 equiv). Reaction conditions for imidative lactonization: 0.1 mmol of **2**, alkene **7** (2.0 equiv). Isolated yields of **8** are shown. See SI for details. [b]6% of chlorolactone was included. [c]11% of bromolactone was included. [d]4% of bromolactone was included.

Accession Codes

CCDC 2254825 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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