

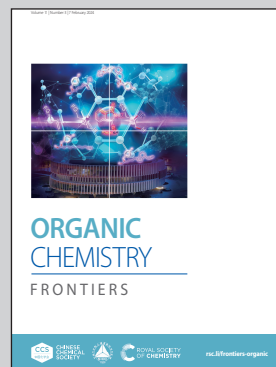


**Showcasing research from the PhotoGreen Lab,
Department of Chemistry, University of Pavia, Pavia, Italy.**

Photoredox catalyzed release of carbon-based radicals from
2-substituted-1,3-imidazolidines

2-Substituted-*N,N*-imidazolidines have been successfully employed as excellent electron donors for the photoredox catalysed release of carbon-centred radicals. Such intermediates have been successfully employed in the alkylation of a wide range of olefins under both batch and continuous flow conditions. Cover designed by Arianna Bini and Elena Mariani.

As featured in:



See Stefano Protti, Maurizio Fagnoni
et al., *Org. Chem. Front.*, 2024, **11**,
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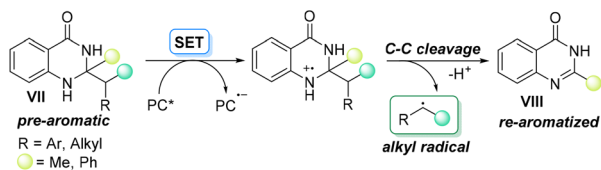
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In this context, a modified DMBI structure (dihydroquinazolinones, **VII**) has emerged as a radical precursor (Scheme 2a).¹² The strategy relies on the aromatic stabilization energy (ASE) of the redox moiety **VIII** when released from the fragmentation of the radical cation.¹³

In such a way, the efficiency in the fragmentation of the radical cation pushed the liberation of a plethora of different radicals by C–C bond cleavage. However, the strategy suffers from some drawbacks such as the poor atom economy of the process (due to the weight of the aromatized fragment **VIII**) and the fact that pre-aromatic derivatives **VII** must be obtained *only* from methyl or phenyl ketones. This is probably due to the fact that the C–C bond cleavage of the other substituents present in position 2 in compounds **VII** must be suppressed thanks to the instability of the methyl/phenyl radicals with respect to the desired radical released (mostly tertiary or, however, stabilized). The radical may, however, be liberated even under photosensitized conditions.¹⁴ Related imidazolidinones have likewise an increased role in dual photocatalytic reactions as chiral bases while remaining, however, photochemically inactive.¹⁵

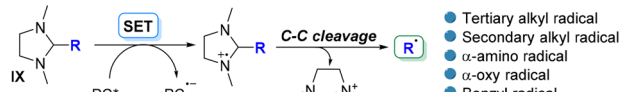
Inspired by these studies and by our achievement in the light induced visible light generation of radical intermediates⁵ we envisioned that simple aminsals such as 2-substituted 1,3-dimethylimidazolidines **IX** (Scheme 2b) could be valid candidates to test the release of carbon radicals *via* C–C bond cleavage by a photoredox SET process. We thus reasoned that the presence of two nitrogen atoms may induce good oxidizability, and noteworthy, the stability of the resulting cation **X** may drive the fragmentation even if this does not evolve into an aromatic derivative. In this work, we report that readily prepared imidazolidines act as more atom-economical (with respect to quinazolidinones) uncharged alkyl radical precursors as detailed below.

a) Dihydroquinazolinones as alkyl radical precursors



- Poor atom economy, mandatory use of methyl and phenyl ketones for the synthesis of VII

b) This work



- Easy synthesis of IX from aldehydes

✓ Light-driven process

✓ Metal-free conditions (organophotocatalyzed)

✓ Yields up to 99%

✓ Suitable under flow conditions

Scheme 2 Photocatalyzed generation of carbon-based radicals from the single electron transfer oxidation of (a) dihydroquinazolinones **VII** and (b) 2-substituted imidazolidines **IX** (this work).

Results and discussion

Different imidazolidines **1a–j** (Fig. S2, see the ESI†) were smoothly prepared by condensation of the corresponding aldehyde with *N,N'*-dimethylethylenediamine. These heterocycles exhibit an oxidation potential of *ca.* 1.0 V *vs.* SCE as shown in Fig. S6† for compound **1c** ($E_{\text{ox}} = 1.16$ V *vs.* SCE). The more accessible E_{ox} allowed us to investigate the use of several colored PCs for the radical addition onto electron-deficient C=C double bonds.

With the aim of investigating the feasibility of our proposal, we initially focused on the tertbutylation of dimethylmaleate **2a** (Fig. S1, see the ESI†) by using imidazolidine **1a** as the model reactant. Different reaction parameters were investigated, and these included the nature of the photocatalyst, the reaction media, the stoichiometric ratio, and the influence of oxygen on the reaction outcome (see Table S1 in the ESI† for a detailed description of the experiments). The most representative control experiments are described in Table 1.

Gratifyingly, the desired product **3** was isolated in almost quantitative amount, 99% yield (Table 1, entry 1), when $[\text{Acr-Mes}]^+(\text{BF}_4)^-$ ($E_{\text{RED}}^* > 2.19$ V *vs.* SCE¹⁶) was used as a PC. Similar results were found by employing 4CzIPN ($E_{\text{RED}}^* > 1.38$ V *vs.* SCE¹⁶) under a N_2 atmosphere (entry 2). The 3CzClIPN photocatalyst ($E_{\text{RED}}^* > 1.56$ V *vs.* SCE¹⁶) showed a poor performance (entry 3) whereas the use of both pyrylium salts (entry 4) and $\text{Ir}(\text{ppy})_3$ (entry 5) did not lead to the desired product. A slight decrease in the reaction yield was observed when performing the reaction under a N_2 atmosphere (entry 6). No product formation occurred when the reaction was carried out in polar solvents (entry 7). Alternative halogenated media (*e.g.* DCM) gave a lower tertbutylation yield (entry 8). On-off experiments (Table S3, Fig. S7†) and the absence of light (entry 9) confirmed the photochemical nature of the process. In addition, a decrease of the overall yield to 50% occurred when TEMPO (1 equiv., Table S1,† entry 15) was present in the reaction media.

Table 1 Selected optimization results for the synthesis of succinate **3**

Entry	Deviation from standard conditions	3 (% yield)
1	None	99
2	4CzIPN (10 mol%), N_2 atmosphere	98
3	3CzClIPN (10 mol%), N_2 , dimethylcarbonate	22
4	$\text{Ph}_3\text{pyrylium}^+\text{BF}_4^-$ (10 mol%)	—
5	$\text{Ir}(\text{ppy})_3$ (5 mol%), N_2 atmosphere	—
6	N_2 atmosphere	90
7	MeCN as solvent	—
8	DCM as solvent	84
9	No light	—



In view of these results, we adopted the followed conditions: an air-equilibrated DCE solution of **1a** (1.5 equiv.), **2a** (0.05 M), and Acr-Mes⁺ BF₄⁻ (10 mol%), under irradiation at 405 nm (EvoluChem 18 W LED) for 24 h (Fig. S3, ESI[†]). In some cases (see below), the use of 4CzIPN was considered as a convenient alternative to [Acr-Mes]⁺(BF₄)⁻ as the PC.

We thus explored the scope of the reaction by adding the generated alkyl radicals to electron-poor alkenes and vinyl heteroarenes (Fig. S1[†]) as sketched in Scheme 3. Notably, all *tert*-butylated derivatives **3–11** (including the alkylated 2,3-dihydro-naphthoquinone **11**) were obtained in satisfactory yields, as well as adamantyl derivatives **12–19** that were isolated in up to 99% yield. Interestingly, to the best of our knowledge, the *tert*-butylation of 1,4-naphthoquinone **2i** was previously reported only by using rather toxic organomercury derivatives.¹⁷

A complete regioselectivity was observed when using allyl methacrylate **2j** as the electron-poor olefin, where the

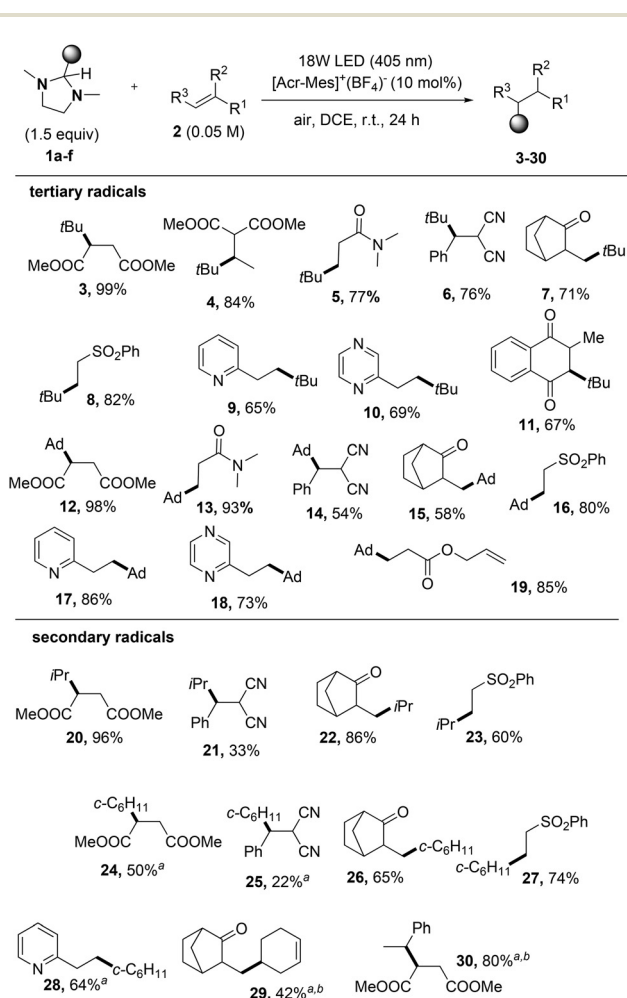
electrophilic C=C bond was exclusively derivatized to form product **19**.

The release of secondary radicals (*iso*-propyl, cyclohexyl and 3-cyclohexenyl) from imidazolidines **1c–e** was next tested. Even in this case, the corresponding alkylated compounds **20–29** were obtained in a satisfactory yield with the only exception of dicyano derivatives **21** and **25**. When releasing secondary radicals, the adoption of 4CzIPN as the photoredox catalyst was beneficial for the successful outcome of the reaction (see the results obtained for compounds **24**, **28**, and **29**). The 4CzIPN photocatalyzed benzylation of dimethyl maleate by using **1f** afforded the benzylated derivative **30** as a mixture of diastereoisomers. Unfortunately, any attempts to perform alkylation of olefins with primary alkyl radicals starting from imidazolidine **1g** were ineffective.

The synthesis of **3** was also optimized under flow conditions by using a lab-made flow photoreactor (see Fig. S4 and S5, ESI[†] for details). In this case, we were able to use less toxic dichloromethane (DCM) in place of DCE as the solvent. To this aim, different parameters were considered, including the light source and its intensity, the residence time and the concentration of the substrates. A complete list of the experiments is included in Table S2[†] but the most representative results are shown in Table 2 (accompanied by the corresponding Space Time Yield (STY) values).

Gratifyingly, as depicted in entry 1, when the reaction was carried out in DCM, compound **3** was isolated in quantitative yield with a residence time of only 2 h. Interestingly, the light source could be replaced with a 390 nm Kessil lamp without a significant decrease of the yield (entry 2). It is also possible to scale up the reaction from 0.1 M to 0.4 M (1 mmol **2a**) with no clogging problems and no precipitate formation inside the reactor tubing (entry 3, 92% yield with a STY of 3.07 mmol L⁻¹ min⁻¹).

On the other hand, an increase in the flow rate (when using either a 405 nm or a 390 nm LED lamp) resulted in a significant lowering of the reaction yield (entries 4 and 5).



Scheme 3 Imidazolidines for the photocatalyzed alkylation of C=C bonds. Conditions: **1a–f** (0.075 M, 1.5 equiv., 0.375 mmol), **2** (0.25 mmol), [Acr-Mes]⁺(BF₄)⁻ (10 mol%), DCE (5 mL), air, under 18 W LED irradiation (405 nm) at r.t. for 24 h. Isolated yields. Ad = adamantyl. ^a 4CzIPN (10 mol%) was used as the PC under a nitrogen atmosphere. ^b Mixture of two diastereoisomers (dr 1 : 1).

Table 2 Selected optimization results for the synthesis of **3** under flow conditions

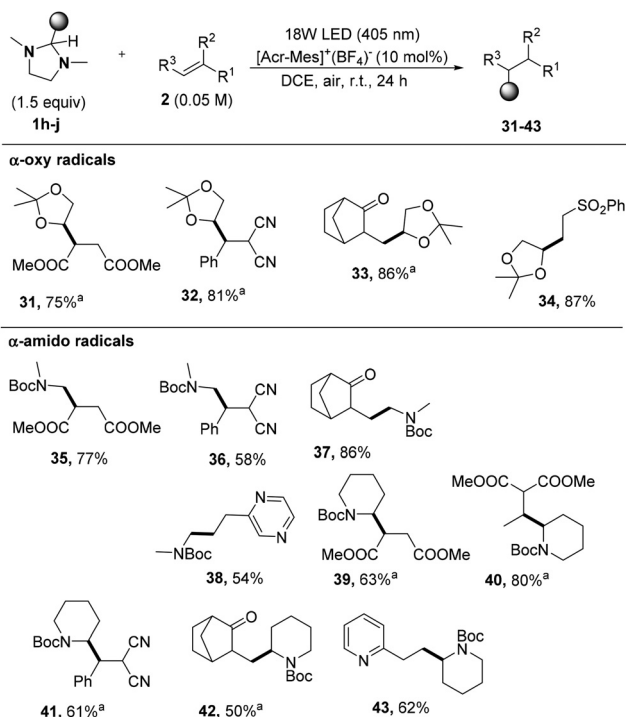
Entry	Deviation from standard conditions	3 , % yield (STY, mmol L ⁻¹ min ⁻¹)
1	None	99 (0.825)
2	390 nm (100% power), flow rate: 0.8 mL min ⁻¹ , 2 h	96 (0.80)
3	2a (0.4 M), 1a (1.5 equiv.), 405 nm (100% power), flow rate: 0.8 mL min ⁻¹ , 2 h	92 (3.07)
4	Flow rate: 1.6 mL min ⁻¹ , 1 h	43 (0.72)
5	390 nm (Kessil 40 W LED) (50% power), flow rate: 1.2 mL min ⁻¹ , 1.5 h	65 (0.72)



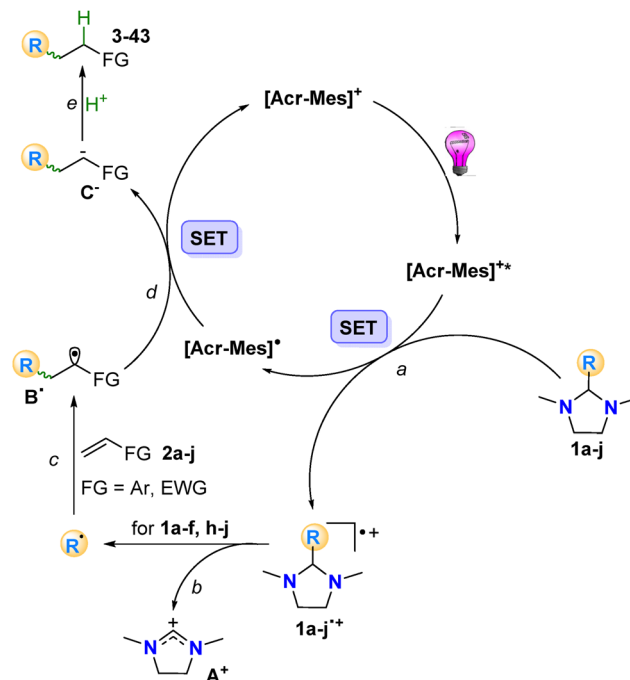
We then turned our attention to electron-rich carbon centered radicals bearing heteroatom-based substituents (N, O) starting from suitably functionalized imidazolidines **1h–j** and the results are summarized in Scheme 4. Thus, when using the dioxolane derivative **1h**, the desired products **31–34** were isolated in up to 97% yield (mostly as a 1 : 1 mixture of diastereoisomers). Analogously, α -amido radicals (photogenerated from **1i** and **1j**) were exploited to incorporate cyclic and acyclic *N*Boc protected amines **35–43** in a different range of electron-poor olefins with yields ranging from 50 to 86%.

In the mechanism suggested, reductive quenching of the photoexcited acridinium catalyst $[\text{Acr-Mes}]^{+*}$ (or 4CzIPN^{+*}) with the concomitant oxidation of imidazolidines **1a–j** to generate the corresponding radical cations **1a–j^{•+}** occurred (Scheme 5, path a). The radical species R^\bullet was formed upon fragmentation of the C–C bond in **1a–f**, **h–j^{•+}** releasing a stable iminium ion A^+ (path b). The nucleophilic R^\bullet was trapped by electron-poor olefins **2a–j** (path c) and the resulting adduct radical B^\bullet underwent mono-electronic reduction by Acr-Mes^\bullet to generate the corresponding anion C^- while restoring the starting photocatalyst. Protonation of C^- (path e) by adventitious water afforded the desired products **3–43**. Hydrogen abstraction from the solvent by radical B^\bullet was safely excluded by deuteration experiments (see the ESI, section 4[†]).

The key role of the carbon centered intermediate R^\bullet has been further evidenced by the detrimental effect of TEMPO when present in the reaction mixture (Table S1, entry 15[†]).



Scheme 4 Functionalization of C=C bonds via photogenerated α -oxy and α -amido alkyl radicals. Conditions: **1h–j** (0.075 M, 1.5 equiv.), **2** (0.25 mmol), $[\text{Acr-Mes}]^+(\text{BF}_4^-)$ (10 mol%), DCE (5 mL), air, under 18 W LED irradiation (405 nm) at r.t. for 24 h. Isolated yields. ^a Mixture of two diastereoisomers (dr 1 : 1).



Scheme 5 Proposed mechanism for the synthesis of compounds **3–43**.

As hinted above, the forging of $\text{C}(\text{sp}^3)\text{--}\text{C}(\text{sp}^3)$ bonds is a current hot topic in organic synthesis. In the present work, we highlighted the potential of imidazolidines **1** (smoothly prepared from commercially available aldehydes and 1,2-diamines) as appealing alternatives to both uncharged (including among others, 1,3-dioxolanes,¹⁸ 1,3-oxazolidines,⁵ Barton esters,¹⁹ *N*-(acyloxy)phthalimides,^{4f,20a} substituted Hantzsch ester)^{20b,c} and charged (alkyl tetrafluoro borates,^{2d} alkyl carboxylates,^{2d} alkyl *N*-phthalimidoyl oxalates^{2d}) known radical precursors.

The protocol presented here offers the chance to generate a wide range of carbon-based radicals, including tertiary, secondary, benzyl, α -oxy and α -amido, by exploiting the easy oxidizability of the radical precursors. The latter point has the consequence of both allowing the use of metal-free PCs having poor oxidizing power in the excited state (e.g. 4CzIPN) and liberating a stable iminium ion in the fragmentation of the thus formed radical cation, which is the driving force of the reaction. Contrary to dihydroquinazolinones, there is no possible competitive release of other radicals upon fragmentation, overcoming the requirement to have an aromatic leaving group that strongly affected the atom economy of the process.

Furthermore, such a methodology exhibited excellent functional group tolerance, allowing for the alkylation of differently decorated olefins bearing carbonyl and carboxylic groups, sulfones and even of heteroarenes.

Conclusions

Summing up, we developed the application of 2-substituted-*N*, *N*-imidazolidines as uncharged carbon centered precursors



under photoredox catalyzed conditions, for the versatile functionalization of a large variety of C=C bonds. The adoption of super-donors for the liberation of radicals is of urgent importance since it may allow the use of mild oxidative conditions limiting the interference of other reagents/additives that may be oxidized as well in the process when using powerful oxidizing PCs. Furthermore, the data presented herein also evidenced the chance of applying imidazolidines in alkylation strategies under continuous flow conditions.

Experimental

General procedure for the synthesis of 2-substituted *N,N'*-dimethylimidazolidines 1a-j

The desired imidazolidines **1a-j** (Fig. S2†) were synthesized by adapting a procedure previously described for the synthesis of 1,3-oxazolidines.⁵ *N,N'*-Dimethylethylenediamine (1 equiv.) was added to a suspension of MgSO₄ (25 mg mmol⁻¹) and the corresponding aldehyde (1 equiv.) in Et₂O (1.7 mL mmol⁻¹). The reaction mixture was refluxed and stirred overnight, and the resulting residue was diluted with DCM, filtered, and concentrated *in vacuo* to yield the desired imidazolidine that was employed for the photocatalytic step without any further purification.

General procedure for the photoredox catalyzed preparation of compounds 3-43

A solution of the chosen imidazolidine **1a-j** (1.5 equiv.), olefin **2a-j** (1 equiv.) and [Acr-Mes]⁺(BF₄)⁻ in DCE (5 mL) was prepared in a Pyrex glass vessel (see Fig. S3†). The solution was irradiated for 24 h at 405 nm by means of an 18 W EvoluChem lamp. The resulting solution was then concentrated *in vacuo* and the residue was purified by flash column chromatography using an Isolera apparatus (Biotage) and a SiO₂ cartridge (eluant: cyclohexane/ethyl acetate mixture except where indicated).

Conflicts of interest

There are no conflicts to declare.

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