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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.

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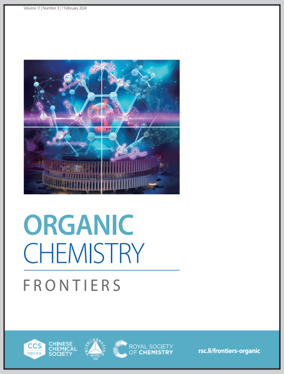

See Stefano Protti, Maurizio Fagnoni *et al.*, *Org. Chem. Front.*, 2024, **11**, 661.

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

Adrián Luguera Ruiz, Elena Mariani, Stefano Protti * and Maurizio Fagnoni *

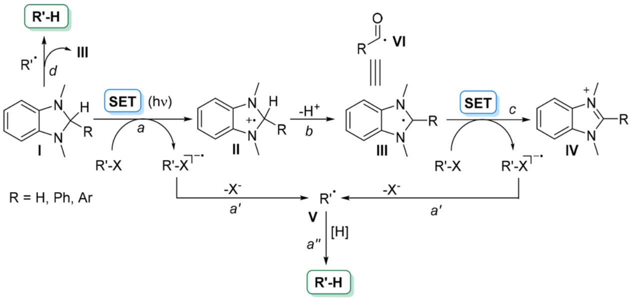
In the frame of developing easily oxidizable compounds for the photorelease of carbon-based radicals, we describe herein the use of 2-substituted-1,3-imidazolidines. These compounds (E_{ox} *ca.* 1 V *vs.* SCE) were used to generate (substituted) alkyl radicals under photoredox conditions. The radicals smoothly added to electron-poor C═C bonds for the forging of C(sp^3)–C(sp^3) bonds under metal-free conditions. Acridinium salts and even 4-CzIPN could be used as photocatalysts thanks to the favorable redox properties of these heterocycles.

Introduction

Carbon based radicals were probably the most used intermediates in synthesis in the past decades.[1] In this context, photoredox catalysis has become the elective method for their generation in a more sustainable and fancy manner than classical synthetic methodologies.[2,3] During the last few years, photoredox generation of alkyl radicals has allowed for the development of protocols for the formation of C(sp^3)–C(sp^3) bonds which is currently a hot topic in organic synthetic chemistry.[2,4] Such a strategy made use of radical precursors bearing redox active moieties that allow their easy oxidation/reduction by a suitable photoexcited catalyst (PC).[2d] Several PCs exhibiting variable oxidation/reduction capability have been designed and investigated for this purpose, but in the case of substrates difficult to oxidize/reduce, the number of suitable PCs strongly decreased.

For these reasons, the redox active moiety is often charged, to shift the radical precursors to a "comfort zone" that allows testing several visible light absorbing PCs. The preparation of these precursors may be in some cases troublesome or impose restrictions to the reaction conditions (the choice of solvent, the compatibility of additives and so on).

The obvious (but not trivial) strategy to overcome such limitations is having recourse to easily oxidizable/reducible uncharged derivatives, and recently, we reported that substituted oxazolidines (E_{ox} *ca.* 1.3 V *vs.* SCE) perfectly fulfill this requirement.[5] We were, however, intrigued to search for further uncharged super electron donors (SEDs)[6] able to release a set of radical intermediates upon oxidation, including tertiary, α-oxy and α-amino carbon-based radicals. In this context, we focused our attention on aminals. The most famous compounds belonging to this class are *N*,*N*-dimethyldihydrobenzoimidazoles (**I**, Scheme 1). 1,3-Dimethyl-2-phenylbenzimidazoline (DMBI) was extensively used to promote a single electron transfer reaction (SET) acting as a reducing agent on compounds R–X with no need of any additives (Scheme 1, path a).[7,8] When R–X is a haloketone, a reductive dehalogenation occurred *via* the fragmentation of the resulting radical anion and hydrogen incorporation from radical **V** (paths a′ and a″).[7d,8b] The radical cation (**II**) formed from the aminal may lose a proton to give radical **III** (path b) again prone to reduce R–X leading to the corresponding benzimidazolium salt **IV** (path c).[9] To strengthen the reducing power of compounds **I** the process was later promoted by light *via* a photoinduced electron transfer reaction (Scheme 1).[10] Interestingly, aminals **I** may also act as efficient hydrogen atom donors to radicals (*e.g.* **V**, path d)[9] More recently, even radical **III** has found application as a surrogate of an acyl radical **VI** in the reaction with styrenes.[11]



Scheme 1 Various pathways in the (photo)chemistry of *N*,*N*-dimethyldihydrobenzoimidazoles **I**.

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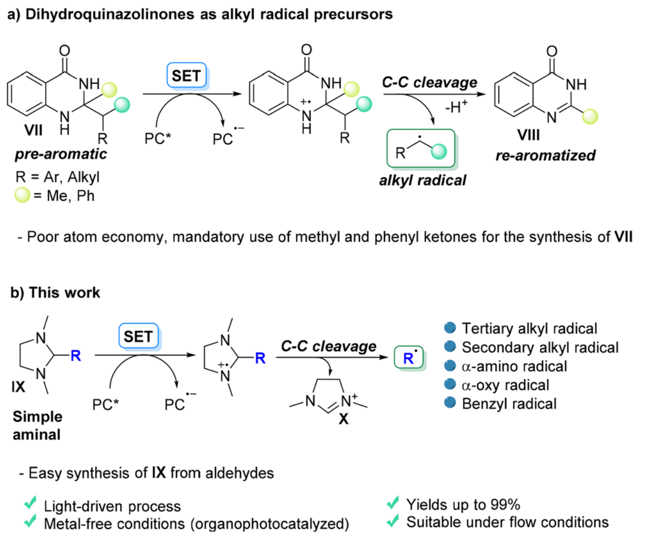
In this context, a modified DMBI structure (dihydroquinazolinones, **VII**) has emerged as a radical precursor (Scheme 2a).[12] The strategy relies on the aromatic stabilization energy (ASE) of the redox moiety **VIII** when released from the fragmentation of the radical cation.[13]

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 intermediates[5] we envisioned that simple aminals 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 noteworthily, 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.



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).

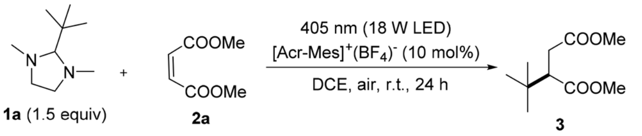
Results and discussion

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_{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 [Acr-Mes]$^+$(BF$_4$)$^-$ ($E^*_{RED} > 2.19$ V *vs.* SCE[16]) was used as a PC. Similar results were found by employing 4CzIPN ($E^*_{RED} > 1.38$ V *vs.* SCE[16]) under a N_2 atmosphere (entry 2). The 3CzClIPN photocatalyst ($E^*_{RED} > 1.56$ V *vs.* SCE[16]) showed a poor performance (entry 3) whereas the use of both pyrylium salts (entry 4) and Ir(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 terbutylation 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**

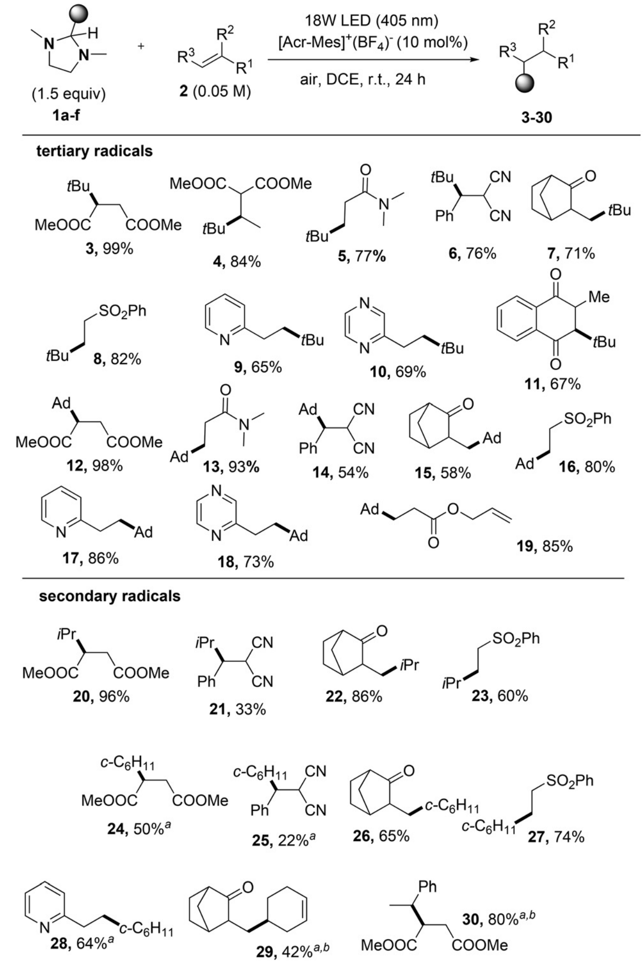


Entry	Deviation from standard conditions	**3** (% yield)
1	None	99
2	4CzIPN (10 mol%), N_2 atmosphere	98
3	3CzClIPN (10 mol%), N_2, dimethylcarbonate	22
4	Ph$_3$pyrylium$^+$ BF$_4^-$ (10 mol%)	—
5	Ir(ppy)$_3$ (5 mol%), N_2 atmosphere	—
6	N_2 atmosphere	90
7	MeCN as solvent	—
8	DCM as solvent	84
9	No 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$^+$ BF_4^- (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 $[Acr\text{-}Mes]^+(BF_4)^-$ 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-dihydronaphthoquinone **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**.



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), $[Acr\text{-}Mes]^+$ (BF_4^-) (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).

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).

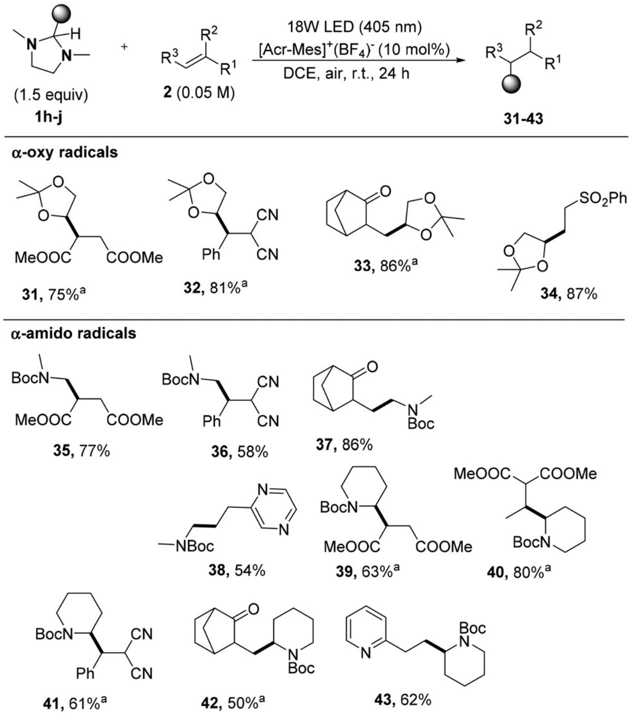
Table 2 Selected optimization results for the synthesis of **3** under flow conditions

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)

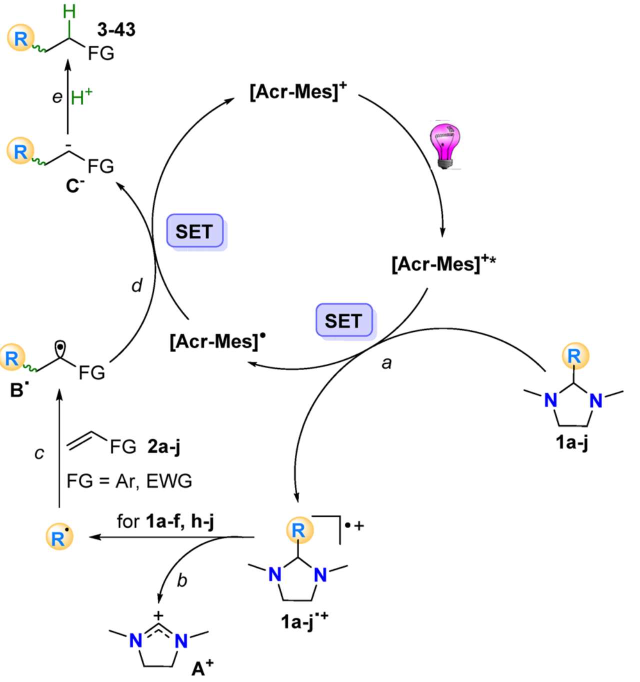
We then turned our attention to electron-rich carbon centered radicals bearing heteroatom-based substituents (N, O) starting from suitably functionalized imidazolidines **1h–j** and the results are summarized in Scheme 4. Thus, when using the dioxolane derivative **1h**, the desired products **31–34** 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 $\mathbf{1a\text{–}j}^{\bullet+}$ occurred (Scheme 5, path a). The radical species $R^{\bullet}$ was formed upon fragmentation of the C–C bond in **1a–f**, $\mathbf{h\text{–}j}^{\bullet+}$ releasing a stable iminium ion $\mathbf{A}^{+}$ (path b). The nucleophilic $R^{\bullet}$ was trapped by electron-poor olefins **2a–j** (path c) and the resulting adduct radical $\mathbf{B}^{\bullet}$ underwent monoelectronic reduction by Acr-Mes$^{\bullet}$ to generate the corresponding anion $\mathbf{C}^{-}$ while restoring the starting photocatalyst. Protonation of $\mathbf{C}^{-}$ (path e) by adventitious water afforded the desired products **3–43**. Hydrogen abstraction from the solvent by radical $\mathbf{B}^{\bullet}$ 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., 0.375 mmol), **2** (0.25 mmol), $[\text{Acr-Mes}]^{+}$ (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 C(sp^3)–C(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 oxidazability 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 $MgSO_4$ (25 mg $mmol^{-1}$) and the corresponding aldehyde (1 equiv.) in Et_2O (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 $[Acr\text{-}Mes]^+(BF_4)^-$ 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 SiO_2 cartridge (eluant: cyclohexane/ethyl acetate mixture except where indicated).

Conflicts of interest

There are no conflicts to declare.

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