



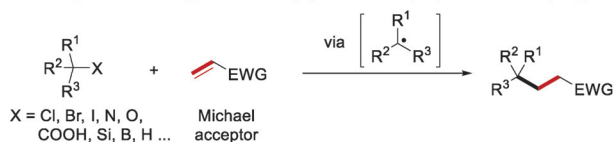
Carboamination of Unactivated Alkenes through Three-Component Radical Conjugate Addition

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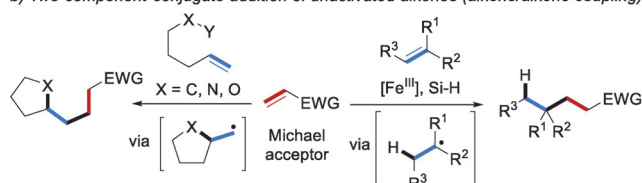
Abstract: Two-component Giese type radical additions are highly practical and established reactions. Herein, three-component radical conjugate additions of unactivated alkenes to Michael acceptors are reported. Amidyl radicals, oxidatively generated from α -amido oxy acids using redox catalysis, act as the third reaction component which add to the unactivated alkenes. The adduct radicals engage in Giese type additions to Michael acceptors to provide, after reduction, the three-component products in an overall alkene carboamination reaction. Transformations which can be conducted under practical mild conditions feature high functional group tolerance and broad substrate scope.

The reductive conjugate radical addition of an alkyl halide to an electron deficient alkene, known as the Giese reaction, represents a valuable transformation in organic synthesis.^[1] Along with halides,^[2] amine,^[3] and alcohol,^[4] carboxylic acid derivatives,^[5] among other compound classes, have been used as radical precursors in such additions (Scheme 1a).^[6–8] Notably, the Giese reaction allows for construction of quaternary carbons under mild and practical conditions.^[9] If alkenes are used as precursors of nucleophilic C-radicals, Giese reactions allow the reductive coupling of unactivated alkenes with electron-poor alkenes. Such two-component alkene couplings have been achieved following two different strategies: A) A widely reported approach uses radical cascades comprising an initial cyclization with subsequent intermolecular conjugate addition (Scheme 1b, left),^[10] and B) Baran realized a hydroalkylation of alkenes through radical additions, in which the nucleophilic C-radicals are generated by addition of a Fe–H species to the alkene (Scheme 1b, right).^[11] However, three-component radical additions of unactivated alkenes to Michael acceptors where the C-radicals are generated by intermolecular C–X bond formation leading to alkene 1,2-difunctionalization products have not been reported.^[12]

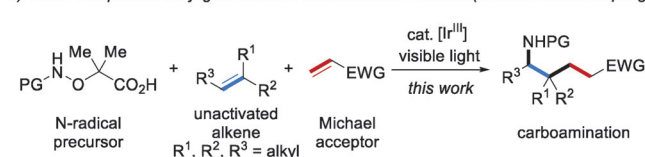
a) Two-component Giese type radical conjugate addition (alkyl-X/alkene coupling)



b) Two-component conjugate addition of unactivated alkenes (alkene/alkene coupling)



c) Three-component conjugate addition of unactivated alkenes (alkene/alkene coupling)



Scheme 1. Giese reaction and its application to radical alkene/alkene coupling (EWG = electron withdrawing group).

As part of our program on N-radical chemistry,^[13] we intended to achieve three-component carboamination of unactivated alkenes providing valuable δ -amino ketone/ester derivatives where the C-radical required for the Giese reaction is generated through amidyl radical addition to an unactivated alkene (Scheme 1c).^[14] Carboamination of activated alkenes including styrenes and acrylates has gained attention recently,^[15] but the herein disclosed strategy shoutable for unactivated alkenes has not been established to date.^[16] As N-radical precursors, we used readily prepared α -amido-oxy acids^[17] where the N-protecting group can be varied and radical generation is known to be achieved by single electron oxidation using a redox catalyst.^[18]

We commenced the study by using the Cbz-protected N-radical precursor **1a** in combination with 2-ethylbutene **2a** and methyl vinyl ketone (**3a**) applying photoredox catalysis. Extensive experimentation revealed that the cascade is best conducted with Ir(dFCF₃ppy)₂(dtbbpy)PF₆ as the photocatalyst (**PC**, 0.5 mol %) in combination with Cs₂CO₃ (1.5 equiv) and H₂O (2 equiv) as an additive in dichloromethane (DCM) at room temperature for 24 hours under blue light irradiation. Targeted **4aa** was isolated in 87 % yield by using an excess of both **1a** (1.5 equiv) and **2a** (2 equiv). A lower yield (61 %) was obtained upon decreasing the amount of **PC** to 0.2 mol %. The use of H₂O as an additive, which role is not understood, is essential to get a high yield: the water free reaction delivered **4aa** in only 17 % yield. Control experiments showed the

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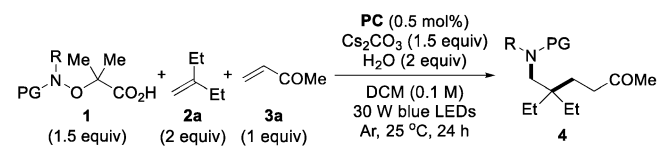
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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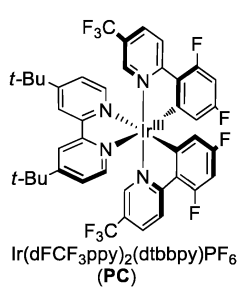
necessity of photocatalyst, base, and light irradiation (see Supporting Information for details on reaction optimization).

With optimal conditions in hand, we varied the N-protecting group (Table 1). Commonly used carbamate

Table 1: Carboamination of **2a** using different N-radical precursors and **3a**.



No.	PG	R	Yield [%] ^[a]
4aa	Cbz	H	87, 61 ^[b] , 17 ^[c]
4ab	Boc	H	85
4ac	Fmoc	H	83
4ad	Alloc	H	89
4ae	Teoc	H	82
4af	Moc	H	85
4ag	Troc	H	47
4ah	Phth	H	trace
4ai	Bz	H	13
4aj	Ac	H	88
4ak	Cbz	Me	n.d.
4al	Troc	Me	65
4am	Tfoc	Me	71

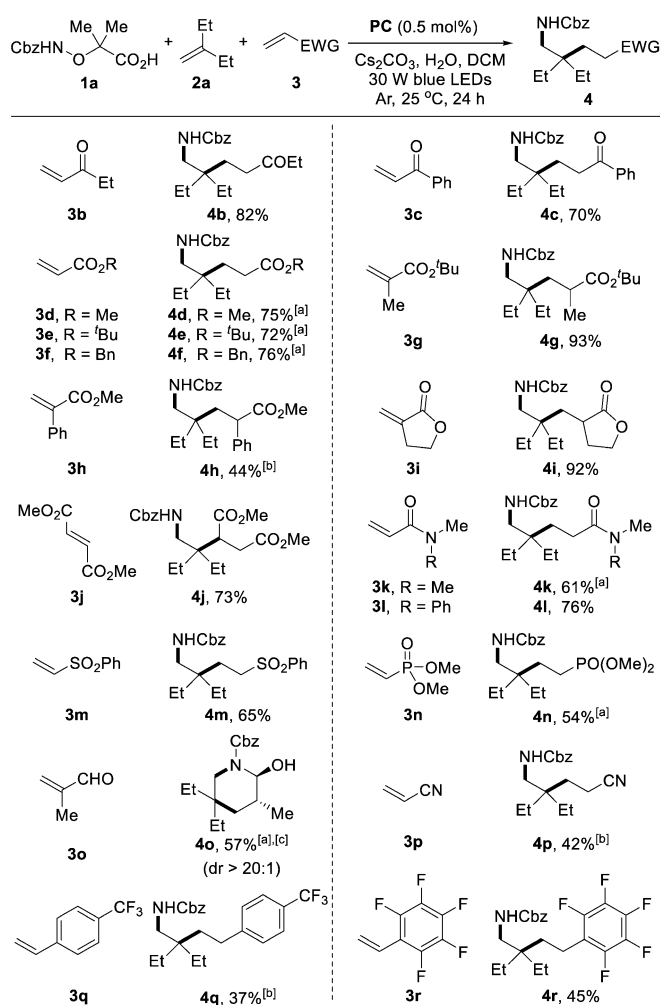


Ir(dFCF₃ppy)₂(dtbbpy)PF₆ (PC)

[a] Reaction conditions: A mixture of **1** (1.5 equiv), **2a** (2 equiv), **3a** (1 equiv), **PC** (0.5 mol%), Cs₂CO₃ (1.5 equiv), H₂O (2 equiv), and DCM (0.1 M) was irradiated by 30 W blue LEDs at 25 °C for 24 h. Yields of isolated products are provided. [b] 0.2 mol% **PC** was used. [c] Reaction performed without H₂O. Abbreviations: n.d. = not detected, PG = protecting group, Cbz = benzyloxycarbonyl, Boc = *tert*-butoxycarbonyl, Fmoc = fluorenylmethyloxycarbonyl, Alloc = allyloxycarbonyl, Teoc = 2-(trimethylsilyl)ethoxycarbonyl, Moc = methoxycarbonyl, Troc = 2,2,2-trichloroethoxycarbonyl, Phth = phthaloyl, Bz = benzoyl, Ac = acetyl, Tfoc = 2,2,2-trifluoroethoxycarbonyl.

protecting groups including Boc, Fmoc, Alloc, Teoc, and Moc provided the desired **4ab–4af** in high yields (82–89%) except for the Troc-protected congener **4ag** (47%). The phthaloyl system afforded only traces of **4ah**, but the *N*-acetyl protected N-radical worked well to give **4aj** (88%). In contrast, the benzoyl derivate **1i** provided **4ai** in only 13% yield. The *N*-methyl-Cbz-protected acid **1k** leading to a sterically more hindered N-radical did not afford the targeted **4ak** and CbzNHMe was identified as the major product. However, charged with the more electron deficient Troc and Tfoc protecting groups, carboamination was achieved and **4al** and **4am** were isolated in 65% and 71% yields.

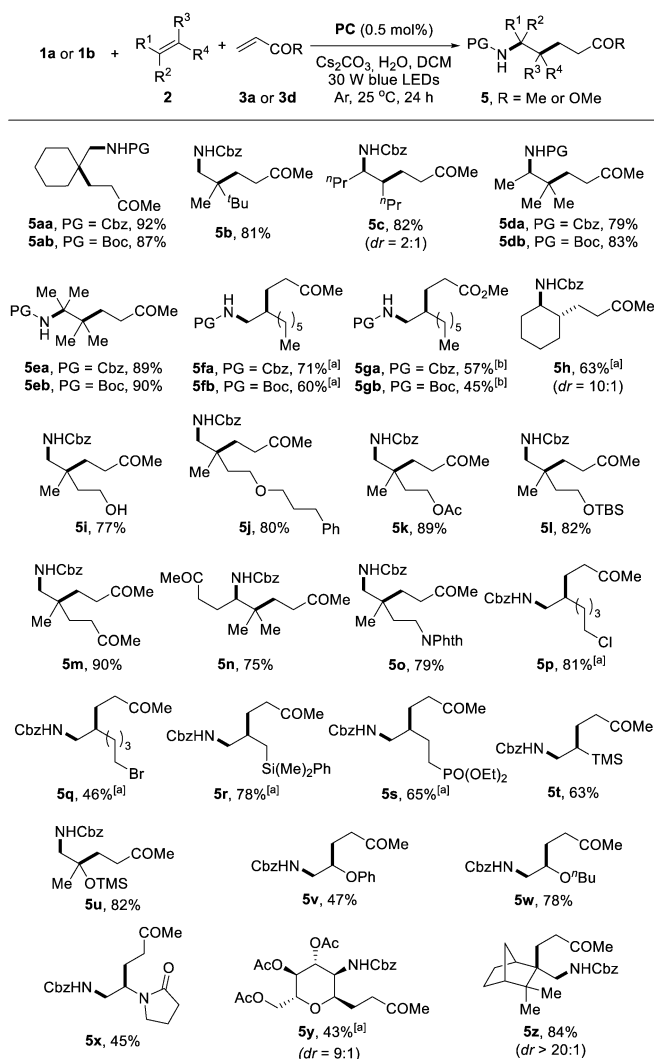
The Cbz-protected **1a** was chosen to examine reaction scope with respect to the Michael acceptor (Scheme 2). Ethyl vinyl ketone (**3b**) and phenyl vinyl ketone (**3c**) gave the δ -amino ketones **4b** (82%) and **4c** (70%) in good yields. Methyl, *tert*-butyl, and benzyl acrylate are also competent substrates providing **4d–4f** (72–76%). 2-Methyl acrylate (**3g**) gave **4g** in excellent 93% yield. However, 2-phenyl acrylate (**3h**) provided a significantly lower yield (**4h**, 44%) and dimethyl fumarate (**3j**) afforded **4j** in 73% yield. Other electron-deficient alkenes including acrylamides (**3k** and **3l**), phenyl vinyl sulfone (**3m**), dimethyl vinylphosphonate (**3n**),



Scheme 2. Variation of the Michael acceptor. Reactions were performed under the optimized conditions unless otherwise specified and yields of isolated products are provided. [a] 3 equiv **2a** were used. [b] 3 equiv **2a** and 1 mol% **PC** were used. [c] **4o** was formed via half acetal formation of intermediate δ -amido aldehyde formed by using methacrolein (**3o**) as the radical acceptor.

methacrolein (**3o**), and acrylonitrile (**3p**) are also eligible acceptors to provide the corresponding products **4k–4p** in 42–76% yield. Notably, electron-deficient styrene derivatives can also be used as documented by the successful preparation of **4q** and **4r**, albeit yield decreased (37–45%).

Next, we examined the scope with respect to the second alkene component using **1a** or **1b** in combination with methyl vinyl ketone or methyl acrylate (Scheme 3). 1,1-Disubstituted alkenes (**5aa**) including a sterically hindered *tert*-butyl congener (**5b**), an internal non-cyclic alkene (**5c**), a trisubstituted alkene (**5da**), even a tetra-substituted alkene (**5ea**) and less nucleophilic terminal alkenes (**5fa**, **5ga**) engaged in the cascade with **1a** to give the products in satisfactory to good yields. By replacing Cbz with Boc (see **1b**), the desired Boc-protected amines **5ab**, **5db**, **5eb**, **5fb**, and **5gb** were obtained. Cyclohexene provided with **1a** the targeted **5h** with high *trans* selectivity (10:1, 63%). We found that different functionalities including free alcohol (**5i**), ether (**5j**), ester (**5k**), silyl

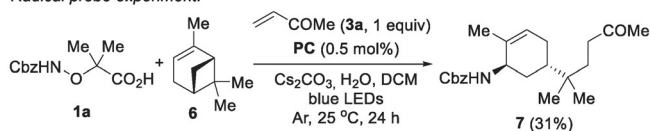


Scheme 3. Variation of the alkene component **2**. Reactions were performed under the optimized conditions unless otherwise specified and yields of isolated products are provided. [a] 1 mol% PC was used. [b] 3 equiv of alkene **2** and 1 mol% PC were used.

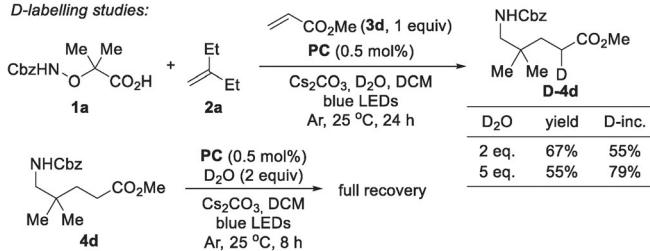
ether (**5l**), ketone (**5m** and **5n**), amine (**5o**), halides (**5p**, **5q**), silane (**5r**), and phosphonate (**5s**) are tolerated and the corresponding Cbz-protected amines were isolated in 46–90% yield. As expected, considering polar effects, activated electron-rich alkenes such as vinyl silanes, silyl enol ethers, vinyl ethers and enamides also react to afford diverse N-protected amines **5t–5x** (45–82%). To our delight, by using a glycol as amidyl radical acceptor, stereoselective formation of the amino-C-glycoside **5y** was achieved in good yield and selectivity. The relative configuration was assigned after derivatization of **5y** by NMR spectroscopy (see Supporting Information). Camphene reacted with **1a** and methyl vinyl ketone to form **5z** which was isolated as a single diastereoisomer in 84% yield.

Several experiments were conducted to elucidate the mechanism. The use of α -pinene as acceptor gave the ring-opening product **7**, supporting the radical nature of the carboamination (Scheme 4). By using 2 equivalents of D₂O in place of H₂O the mono-deuterated D-**4d** was obtained with

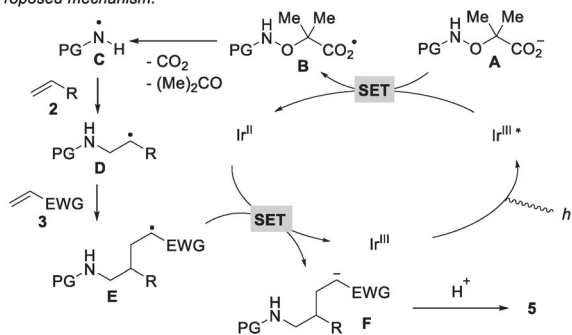
Radical probe experiment:



D-labelling studies:



Proposed mechanism:



Scheme 4. Mechanistic studies and proposed catalytic cycle.

55% D incorporation. 79% D incorporation was achieved upon increasing the amount of D₂O to 5 equivalents, while subjecting product **4d** to the deuteration conditions did not provide any D-incorporation. These labelling experiments illustrate the formation of an enolate prior to protonation.

Based on these results and previous reports, the following mechanism is proposed. The catalytic cycle starts by photoexcitation of Ir^{III} to the excited Ir^{III*} complex which oxidizes carboxylate **A**, formed by deprotonation of **1**, to generate the carboxyl radical **B** and Ir^{II}. Sequential fragmentation of CO₂ and acetone leads to the electrophilic N-radical **C**. Steered by polar effects, the electrophilic N-radical chemoselectively adds to the CC double bond of the electron-rich alkene **2** to provide the adduct radical **D**. Michael acceptor **3** then traps the nucleophilic C-radical **D** to give **E**, which is reduced by the Ir^{II} complex to afford the enolate **F**, closing the catalytic cycle. Protonation eventually gives **5**. Of note, reaction of the nucleophilic C-radical **D** with alkene **2** is slow due to polar mismatch and does not compete with the desired Giese addition. Moreover, the oxy acid moiety in **1a** does not only serve as the radical generating functionality but does also protect CbzNH₂ reacting in an ionic Michael type addition with **3a** and **3b**. In fact, CbzNH₂ efficiently adds to methyl acrylate under the optimized reactions conditions.

In summary, we have established a three-component radical conjugate addition of various unactivated alkenes by photoredox catalysis to furnish alkene carboamination products under mild and practical conditions. Commonly used N-protecting groups, that are valuable moieties considering further elaboration of the products, are installed. These

cascades work with diverse Michael acceptors to give δ -amino ester/ketones mostly in good yields. It is worth mentioning that radical carboamination of a commercial glycol directly delivers an amino-C-glycoside convincingly illustrating the significance of the herein introduced method for the preparation of structurally important amines.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: amidyl radicals · carboamination of alkenes · Giese reaction · photoredox catalysis · radical cascade

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