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Umpolung synthesis of branched α -functionalized amines from imines *via* photocatalytic three-component reductive coupling reactions†

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A three component reductive coupling reaction of a (hetero)aromatic amine, a (hetero)aromatic aldehyde and an electron deficient olefin catalysed by eosin Y under green LED light irradiation, for the direct generation of γ -amino acid derivatives, is described. This new umpolung synthesis of amines, which exploits the high nucleophilicity of a putative α -amino radical intermediate, generated *via* single electron reduction of the *in situ* generated imine from the Hantzsch ester terminal reductant, is efficient, operationally simple, broad in scope and offers a complementary strategy to existing synthetic approaches.

Chiral α -branched amines and their derivatives are commonplace in pharmaceuticals, agrochemicals and biologically relevant natural products (Fig. 1).¹ Accordingly, the development of new and general methods for their synthesis, through new C–C bond forming processes is important and timely from both academic and industrial perspectives. Furthermore, the possibility to carry out such transformations as multicomponent coupling reactions is attractive for the ready generation of structural analogues in discovery processes.² Such chiral α -branched amine motifs can be accessed from electrophilic imine substrates, through direct addition of carbon-centered nucleophiles such as organometallic reagents and electron rich π -nucleophiles. However, free radical chemistry offers the possibility to reverse the polarity of imine derivatives; the formal addition of a hydrogen atom to the C=N π -bond can generate a nucleophilic α -amino radical able to react with alkenes

and alkynes.³ However, to date these approaches have been limited by the way the radical is generated, typically requiring the specific preparation of radical precursors from imines and subsequent use of, for example, stoichiometric quantities of tin reagents.⁴ Recently, under photoredox catalysis, α -amino radicals have been generated through the decarboxylation of α -amino acids,⁵ α -amino trifluoroborates⁶ or hydrogen atom transfer from protected primary and secondary amines.^{7–9} Also, α -amino radicals have been generated from electron rich tertiary amines by sequential loss of an electron from the nitrogen lone pair, followed by an α -proton. However, the resulting α -amino radical is readily oxidised by the photocatalyst and undergoes a second single-electron oxidation to generate an iminium intermediate which can be subsequently trapped with various nucleophiles.¹⁰ Intercepting the α -amino radical in reactions with, for example, electron poor alkenes is far less common, and to date has been limited to *N*-aryltetrahydroisoquinolines,⁸ and phenyl methyl amines.⁹ Photoredox reactions in which imine moieties have been used as a trap for nucleophilic radicals are limited to a few reports.¹¹

Despite these recent advances we recognised that a direct method for the generation of ‘free’ α -amino radicals would offer a wealth of untapped synthetic potential. Our plan was to identify then develop a new reductive photochemical system that, directly from an *in situ* formed imine, would efficiently generate ‘free’ nucleophilic α -amino radical species capable of undergoing a range of carbon–carbon bond forming processes (Fig. 1). Through its modular design such a process would be useful for library and target synthesis alike and herein we wish to report our findings.

As a model reaction we chose the reductive coupling of benzaldehyde **1a**, anisidine **2a** and sulfone **3a**.¹² Following a series of preliminary studies performed to identify new reactivity, Ru(bpy)₃Cl₂, [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ and [Ir(dtbbpy)(ppy)₂]PF₆, were found to efficiently promote the desired reaction in DMSO under blue LED light irradiation using Hantzsch ester as the terminal reductant. Pleasingly, the use of organic dyes such as eosin Y (EO) and rose bengal (RB) under green LED light irradiation, also promoted the desired reaction with similarly

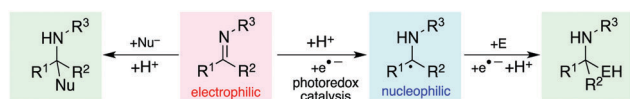


Fig. 1 Concept of umpolung amine synthesis from imines.

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high yields. After further optimisation studies (see ESI†) the allylated product was isolated in 92% yield.

The three-component reductive coupling reaction was found to tolerate a wide range of aromatic aldehydes to afford 4-amino 4-aryl-2-methylene carboxylic esters in very good yields typically within 12 to 15 hours (Table 1). The best results were achieved with electron rich aromatic rings such as *p*-methoxy phenyl (entry 3) or *p*-dimethylamino phenyl (entry 4). A wide range of *ortho* substituents such as methyl (entry 9), bromine (entry 5) and fluorine (entry 6) were well-tolerated as well. Oxygen substitution in the *ortho* position (entries 7 and 8) increased the amount of competing reductive amination. For 2-methoxy substitution (entry 8) this problem could be circumvented by using more powerful LEDs (10 W) in place of normal green LEDs strip. This preferentially accelerated the productive three-component reaction resulting in enhanced product yield.

Pleasingly, electron deficient aromatic aldehydes yielded the desired product (entries 10–13) with acceptable yield although some competing overreduction was observed in all cases. While the reaction with 4-cyanobenzaldehyde generated the product with 54% yield (entry 10), switching the cyano substituent to the *meta* position, thus increasing the electron density of the aldehyde starting material, reduced the reaction time from 7 days to 2 days and the yield recovered to 85% (entry 12). Whereas employing more powerful LEDs had no influence on the reaction of the *p*-cyano substituent, a notable increase in yield was observed for 4-(methoxycarbonyl)phenyl (entry 13, single crystal X-ray diffraction studies of compound **4m** are shown in the ESI†)¹³

Table 1 Aldehyde **1** scope^a

Entry	R	4	Yield ^b (%)
1	Ph	4a	87
2	2-Naphtyl	4b	85
3	4-MeOC ₆ H ₄	4c	80
4	4-Me ₂ NC ₆ H ₄	4d	97
5	2-BrC ₆ H ₄	4e	74
6	2-FC ₆ H ₄	4f	85
7	2-OHC ₆ H ₄	4g	64 ^c
8	2-MeOC ₆ H ₄	4h	57 (86) ^c
9	2-MeC ₆ H ₄	4i	94
10	4-CNC ₆ H ₄	4j	54 ^d
11	4-CF ₃ C ₆ H ₄	4k	0 (82) ^c
12	3-CNC ₆ H ₄	4l	85 ^f
13	4-CO ₂ MeC ₆ H ₄	4m	63 ^e (78) ^c
14	4-Pyridyl	4n	65 ^e
15	3-Pyridyl	4o	83
16	2-Pyridyl	4p	53 ^f
17	2-Furyl	4q	84 ^f
18	2-Thiofuryl	4r	87 ^f
19	1-Methyl-1 <i>H</i> -imidazol-2-yl	4s	79 ^f
20	1 <i>H</i> -Indol-2-yl	4t	52 ^{e,g}

^a Reactions were carried out with 0.2 mmol of **1** and **2a**, 0.3 mmol of Hantzsch ester, 0.5 mmol of **3a** and 2 mol% of catalyst under green strip LEDs irradiation (1 W) in DMF. ^b Isolated yield. ^c Reaction irradiated with green 10 W LEDs. ^d Reaction time: 7 days. ^e Reaction time: 3 days. ^f Reaction time: 2 days. ^g Imine was preformed.

and trifluoromethylphenyl (entry 11). Importantly, heteroaromatic aldehydes, such as pyridine, furan, thiophene, imidazole and indole, also successfully partook in the reaction. As already witnessed with CN substituent, (entries 10 and 12), the position of the heteroatom in the aromatic ring influenced the amount of overreduction observed. While more electron deficient 4- and 2-pyridinecarboxaldehyde produced yields of 50–60% (entries 14 and 16), 3-pyridinecarboxaldehyde improved the product yield to 83% (entry 15). Additionally, the rate of the productive reaction diminished for these substrates and accordingly the reaction time was increased to 3 days (entry 14) or 2 days (entry 16) respectively. Electron-rich 5-membered heterocycles such as furan (entry 17), thiophene (entry 18) and 1-methyl-1*H*-imidazole (entry 19) also required a reaction time of 2 days, yet afforded good yields. Especially noteworthy is the tolerance of indole (entry 20) as the heteroaryl substituent. Although the imine had to be preformed due to the very slow reaction between indole-2-carbaldehyde and *p*-anisidine under standard conditions, a 52% yield was obtained after 3 days before the reaction stalled; a remarkable outcome given that unprotected pyrroles or easily abstracted hydrogens often prove detrimental to photoredox reactions.¹⁴

Regarding the amine component, reactivity was witnessed in the presence of both electron-rich and electron-poor aromatic amines as well as heteroaromatic amines (Table 2, entries 1–4). Although *ortho* substituents were well-tolerated, with *O*-methoxyphenyl (entry 1) and 2-pyridyl substituents (entry 4) the preformation of the imine was necessary but the standard reaction conditions still afforded the desired products in excellent yields in both cases. Preformation of the imine was also necessary when electron poor *p*-nitroaniline was used as amine component; although in this case the reaction yield was diminished to 46%.

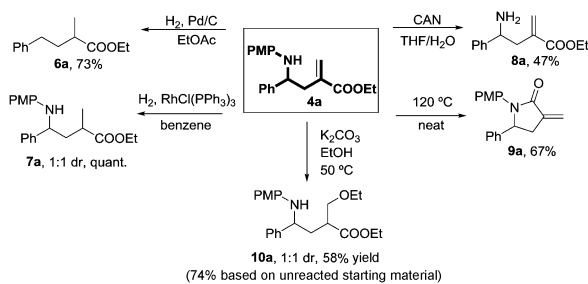
Next, we explored the range of allyl sulfones that were tolerated in the reaction (Table 2, entries 5–7). A *tert*-butyl ester derivative (entry 5) performed in the reaction without significant loss of yield (82%). However, other carbonyl groups such as ketones, carboxylic acids or carboxamides all failed to afford the product (ESI†). Interestingly, other electron withdrawing groups such as cyano (entry 6) and diethylphosphonate (entry 7) performed in the reaction well, yielding the expected product with moderate yield. The developed reaction proved to be robust to scale up; a gram scale synthesis of **4a** proceeded in a yield of

Table 2 Aniline **2** and sulfone **3** scope

Entry	R ₁	R ₂	5	Yield (%)
1	2-MeOC ₆ H ₄	COOEt	5a	99 ^a
2	Ph	COOEt	5b	86
3	4-NO ₂ C ₆ H ₄	COOEt	5c	46 ^a
4	2-Pyridyl	COOEt	5d	93 ^a
5	4-MeOC ₆ H ₄	COO ^t Bu	5e	82
6	4-MeOC ₆ H ₄	CN	5f	47
7	4-MeOC ₆ H ₄	PO(OEt) ₂	5g	49

^a Imine was preformed.



Fig. 2 Derivatization of compound **4a**.

95% which represents an improvement when compared to the reaction performed on 0.2 mmol scale.

Three-component coupling product **4a** is a versatile and modifiable building block rich in synthetic potential (Fig. 2).¹⁵ α -Methyl- γ -phenyl carboxylic compounds (**6a**) are easily accessible through simple hydrogenolysis and some derivatives have been studied as agonists for antimicrobial peptide systems.¹⁶ The PMP protecting group could be easily removed under standard conditions to provide the parent α -phenyl- γ -aminoesters that could find application in medicinal chemistry programmes as γ -aminobutyric acid (GABA) derivatives. Also, α -alkylidene γ -lactam **9a** can be formed simply by heating compound **4a** in the absence of solvent. Such lactams have already shown potential as inhibitors of homoserine transacetylase (HTA)¹⁷ and have been studied as less toxic alternatives to α -methylene γ -lactones in cancer treatment.¹⁸ Our new methodology allows a fast and easy approach to the synthesis of libraries of α -methylene γ -lactams in only two steps. The double bond can be further manipulated through hydrogenation to give **7a** or through addition of nucleophiles such as ethanol yielding **10a**.

To interrogate the reaction pathway to the three-component coupling product, control and cross-over experiments were performed. LED irradiation and eosin Y were necessary for the reaction to proceed. Also, the reaction was inhibited when TEMPO was added, supporting the participation of radical intermediates in the transformation (ESI[†]). As phenyl benzyl amines have been used in photoredox catalysis as reductive quenchers,¹⁹ the appearance of the overreduction product in the photoredox reactions with the less reactive imines²⁰ raised the possibility that this compound could be, in fact, a potential species suffering single electron oxidation by eosin Y to generate an alpha amino radical^{21,22} ready to add into allyl sulfone **3a**. However, subjection of a mixture of reductive amination product **11**, allyl sulfone **3a** and eosin Y in DMSO to green LED light irradiation gave no reaction, ruling out a tandem reductive then oxidative pathway to **4a** (Fig. 3). Interestingly, a similar reaction set-up but in the presence [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ as photocatalyst and blue LED light irradiation, afforded the reaction product as expected in 63% NMR yield.

An attempted cross-over experiment in which both an imine and *p*-tolualdehyde-derived amine **11** were present in the reaction mixture confirmed that under these conditions only the imine was capable of giving rise to the reaction product (Fig. 3).

Stern–Volmer quenching experiments (ESI[†]) showed a significant quenching of eosin Y fluorescence by Hantzsch ester, whereas

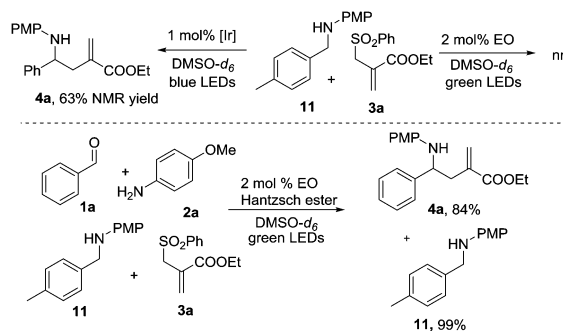


Fig. 3 Control and cross-over experiments.

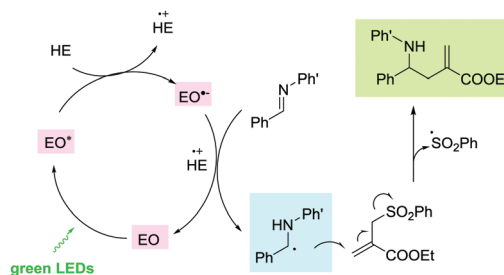


Fig. 4 Proposed reaction mechanism.

sulfone or imine produced a much less pronounced effect. On the basis of these observations, we propose the reaction mechanism as depicted in Fig. 4. Under the reaction conditions, incident light excites EO, which undergoes a rapid intersystem crossing to the lowest energy triplet state,²² thus providing an oxidising species ($E_{1/2}^0 = +0.83$ V vs. SCE in CH₃CN)²² which reduces the Hantzsch ester to the radical cation, HE^{•+}.²³ At this point EO radical-anion, EO^{•-} ($E_{1/2}^0 = -1.06$ vs. SCE in CH₃CN)²² is oxidized by the imine ($E_{1/2}^0 = -1.90$ V vs. SCE in CH₃CN),²⁴ but in order for this process to take place spontaneously, the intervention of transient proton donor is necessary to significantly lower the redox potential of the imine by proton coupled electron transfer (PCET).²⁵ A possible candidate might be Hantzsch ester radical cation (HE^{•+}). In agreement with this hypothesis it was observed that reducing agents other than the Hantzsch ester afforded no product or very low conversion. The generated α -amino-radical would then be poised to add to the sulfone C=C to form the product and benzene sulfinyl radical ($E_{1/2}^0 = +0.40$ vs. SCE)²⁶ which can be further reduced by HE, HE^{•+} or EO^{•-}. On-off light experiments demonstrated that no product formation was occurring in the dark, thus supporting our hypothesis (ESI[†]). However, a short length radical chain mechanism cannot be completely excluded (see ESI[†]).^{27,28}

In summary, we have developed a new three-component reductive coupling reaction of (hetero)arylamines, (hetero)aromatic aldehydes and electron deficient olefins catalysed by eosin Y under green LED light irradiation, employing Hantzsch ester as the terminal reductant.²⁷ The reaction is easy to perform, broad in scope and provides a convenient umpolung alternative to amine synthesis from imines. The Hantzsch ester was found to play a critical role in generating the reactive nucleophilic



radical intermediates and cross-over experiments confirmed the imine – and not the amine resulting from imine reduction – was the source of the α -amino radical. Work to expand the breadth of photochemical umpolung imine coupling reactions is ongoing in our laboratories and the results will be disclosed in due course.

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