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Heat- or light-induced acylarylation of unactivated alkenes towards 3-(α-acyl) indolines†

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A heat- or photoredox/iron dual catalysis-enabled dehydrogenative acylarylation of *N*-allyl anilines leading to 2-substituted 3-(α-acyl) indolines with a quaternary stereogenic center is presented, with unactivated alkenic bonds as radical acceptors and simple aldehydes as radical precursors. This reaction features high yields, a broad substrate scope, and a great *exo* selectivity, and gram-scale syntheses could be readily carried out.

Introduction

Indolines are found in the skeletons of many alkaloids and clinical drugs, and exhibit a broad range of important bioactivities.[1,2] However, in the indole chemistry the construction of structurally diverse indoline architectures might be challenging, as compared to other indolic variants. For example, functionalized indoles[3] or oxindoles[4] could be accessed either from acyclic materials or through derivatization of their parent heterocycles, whereas entries to indoline frameworks are mainly restricted to indole dearomatization reactions,[2] leading to 2-substituted indoline derivatives. 2-Unsubstituted indolines might be prepared *via* the reduction of their indole or oxindole counterparts, yet such a transformation suffers from severe functional group-intolerance, especially when a reductant-sensitive motif (*e.g.*, the carbonyl group) is involved. Therefore, it is still urgent to develop general and efficient paradigms for the synthesis of functionalized 2-unsubstituted indolines from readily available acyclic materials.

The introduction and application of the carbonyl motif, due to its versatility, is one of the pillars of classical synthetic chemistry.[5] On the other hand, simple aldehydes are fundamental building blocks in organic synthesis and are bulk chemicals for the chemical industry.[6] It proves that aldehydes could be an ideal acyl source owing to the development of dehydrogenative aldehydic C–H functionalization,[7] which are atom- and step-economic, and categorized into three types: (1) umpolung reactions catalysed by N-heterocyclic carbenes (NHCs)[8] or cyanides,[9] (2) aldehydic C–H activations enabled by noble metal catalysis,[10,11] (3) radical couplings of acyl radicals produced *via* hydrogen atom transfer (HAT).[12–17] In recent years, alkene difunctionalization has emerged as a powerful tool to access molecule complexity,[18] since two functional groups are installed across a double bond in one step. In this regard, great progress has been made towards radical acylation of alkenes with aldehydes, yet the olefins used are mainly restricted to activated ones.[12–15] It is probably because the activating groups, such as aryl,[12] alkoxyacyl,[13] carbamoyl[14] and sulfamoyl functionalities,[15] could significantly stabilize *in situ* generated radical intermediates. Li and co-workers reported the heat-induced radical annulation of aldehydes with olefins towards indolines and dihydropyrans,[13e] and only alkoxyacyl-activated olefins were tested. Acyl radicals and unactivated alkenes are electrophiles and nucleophiles, respectively, and according to polar effects[19] and our experiences in radical chemistry,[20] the addition of acyl radicals to unactivated olefins is polarity-matched and thus might be viable. In addition, a few pioneering works have been reported. Pan, Yu and co-workers[16a] as well as Leng, Wu and co-workers[16b] disclosed 1,2-aryl migration-primed acylarylation of α-hydroxy-α,α-diaryl propylenes, while Duan, Li and co-workers reported the synthesis of dihydroisoquinolinones and indanones through the acylation of *N*-allylbenzamides.[17] However, light-induced acylation of alkenes, either activated[21,22] or unactivated ones,[22] was rarely reported. In 2018, Salles *et al.* presented a visible-light-driven hydroacylation of unactivated olefins with aromatic aldehydes using methylene blue and $K_2S_2O_8$ as the photocatalyst (PC) and the HAT agent, respectively, affording chain-elongated ketone products.[22] Herein, we wish to report an iron-catalysed heat- or light-induced acylarylation of *N*-allyl

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anilines, with unactivated alkenic bonds as radical acceptors and simple aldehydes as radical precursors, affording 3-(α-acyl) indolines with a quaternary stereogenic center as value-added products. This reaction is associated with high yields, a broad substrate scope, and a great *exo* selectivity, and gram-scale syntheses could be readily carried out.

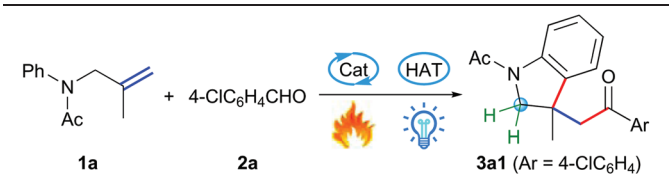
Results and discussion

Our initial attempt was launched with the alkene acylation utilizing *N*-(2-methylallyl) acetanilide **1a** and 4-chlorobenzaldehyde **2a** as model substrates (Table 1; see ESI† for full details). Combining **1a** and 3 equiv. of **2a** together with 5 mol% of $FeCl_2$ and 4 equiv. of di-*tert*-butyl peroxide (DTBP) in chlorobenzene solution at 120 °C furnished the acylated indoline product **3a1** bearing a quaternary stereogenic center in 87% yield after 6 h (entry 1). $FeCl_2$ is a beneficial additive for this transformation, probably due to the abilities of transition-metal salts to stabilize radicals and to facilitate some single-electron transfer (SET) processes, and a compromised yield was obtained in the absence of $FeCl_2$ (entry 2). While beneficial effects were not associated with the inclusion of $FeSO_4$ (entry 3), the use of other tested metal salts, such as $FeCl_3$ (entry 4), CuI (entry 5) and $AgNO_3$ (entry 6), all led to an erosion of the yield. Oxidant DTBP proved to be the optimal HAT agent. While the use of *tert*-butyl hydroperoxide (TBHP, entry 7) or dicumyl peroxide (DCP, entry 8) delivered indoline **3a1** in diminished yields, only trace amounts of **3a1** were observed with benzoyl peroxide (BPO, entry 9) or $K_2S_2O_8$ (entry 10). Then, a survey of a series of solvents was conducted. The use of toluene furnished indoline **3a1** in only 39% yield, probably owing to the competitive HAT from the arylmethane moiety, whereas reactions performed in a polar solvent like 1,2-dichloroethane (DCE, entry 12), CH_3CN (entry 13) or dimethylsulfoxide (DMSO, entry 14) were retarded.

Intrigued by the fact that photoredox catalysis-enabled reactions generally proceed under mild conditions, we subsequently sought to effect the title indoline synthesis in a photocatalytic manner by switching from heating to the combination of a PC and the light-emitting-diode (LED) irradiation (see ESI† for full details). At room temperature rather than 120 °C and under blue-light irradiation, a range of photosensitizers were assessed. To our delight, 3-(α-acyl) indoline product **3a1** was afforded in a moderate yield after 12 h using *fac*-Ir(ppy)$_3$ as the PC (entry 15), whereas $Ru(bpy)_3Cl_2$ (entry 16), Mes-Acr$^+$ClO$_4^-$ (entry 17), eosin Y (entry 19) and rose bengal (entry 20) all proved ineffective. When 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) was used, indoline **3a1** was produced in 62% yield, identifying 4CzIPN as the optimal PC, and the yield was further improved to 70% by prolonging the reaction time to 24 h (entry 18). Interestingly, this photoredox process benefits from the $FeCl_2$ additive as well, and in the absence of it indoline **3a1** was produced in a moderate yield (entry 21).

Thus, we established both the heat-induced (conditions A) and the photoredox conditions (conditions B) for the synthesis of 3-(α-acyl) indolines, and the two protocols are complementary. Both sets of optimal conditions were selected to probe the substrate scope, and the reactions were first extended to a broad collection of allylated anilines **1** (Table 2). 4-Chlorobenzaldehyde **2a** reacted smoothly with *N*-(2-methylallyl) acetanilides bearing a methyl, *tert*-butyl, methoxy, bromo, chloro, trifluoromethyl, ethoxycarbonyl, acetyl, or cyano group at the *para* position of the *N*-aryl group, affording the corresponding 3-(α-acyl) indolines **3a2-10** in moderate to excellent yields. In general, the yields of the heat-induced syntheses are higher than the ones of photocatalysed reactions, and the substrates with an electron-deficient *N*-aryl group are more reactive. In contrast, 5-phenyl indoline **3a11** was furnished in only 45% yield under the heating conditions from allylated biphenyl-4-amine, the origin of which remains unclear at this time. While propionyl- or pivaloyl-protected *N*-(2-methylallyl) anilines were transformed efficiently into the corresponding indoline products **3b1,2**, the *tert*-butyloxy-carbonyl (Boc, **3c1,2**), ethanesulfonyl (**3d1,2**), methanesulfonyl (**3e1**), tosyl (**3e2**) and *o*-tolylsulfonyl *N*-protecting groups (PGs, **3e3**) are all compatible with this transformation. Unfortunately, we failed to isolate any pure product from the complex reaction mixtures of allyl anilines protected by an

Table 1 Optimization of the reaction conditions[a]

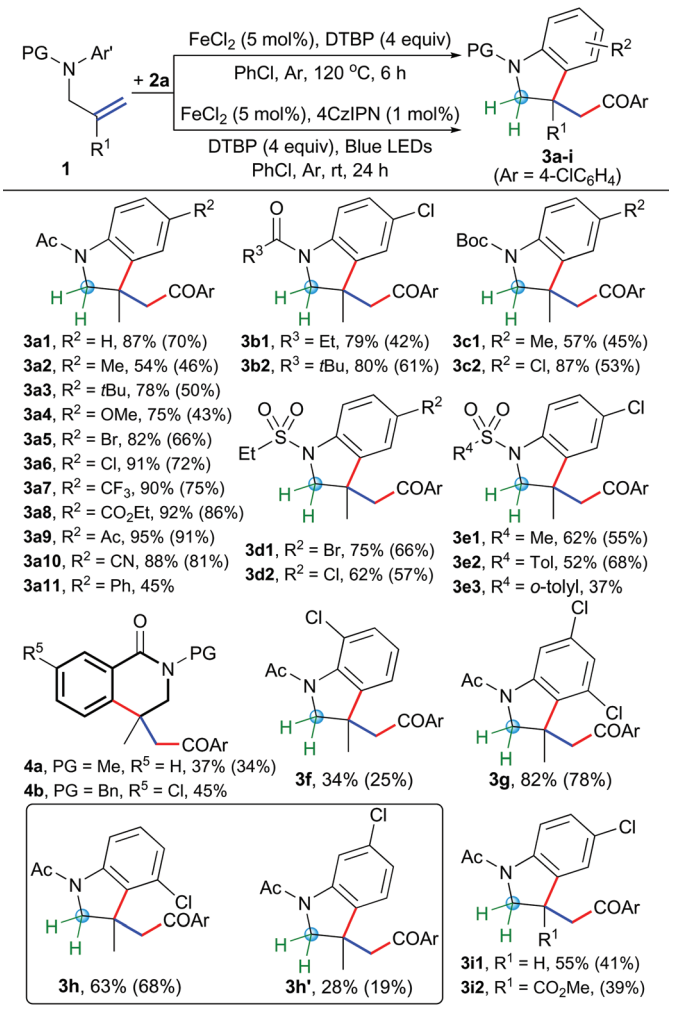


1a **2a** **3a1** (Ar = 4-ClC$_6$H$_4$)

Entry	Catalyst	Oxidant	PC[b] (mol%)	Solvent	Yield (%)
1	$FeCl_2$	DTBP	—	PhCl	87
2	—	DTBP	—	PhCl	68
3	$FeSO_4$	DTBP	—	PhCl	69
4	$FeCl_3$	DTBP	—	PhCl	57
5	CuI	DTBP	—	PhCl	41
6	$AgNO_3$	DTBP	—	PhCl	18
7	$FeCl_2$	TBHP[c]	—	PhCl	53
8	$FeCl_2$	DCP	—	PhCl	71
9	$FeCl_2$	BPO	—	PhCl	Trace
10	$FeCl_2$	$K_2S_2O_8$	—	PhCl	Trace
11	$FeCl_2$	DTBP	—	Toluene	39
12	$FeCl_2$	DTBP	—	DCE	11
13	$FeCl_2$	DTBP	—	CH_3CN	0
14	$FeCl_2$	DTBP	—	DMSO	0
15	$FeCl_2$	DTBP	*fac*-Ir(ppy)$_3$ (1)	PhCl	52
16	$FeCl_2$	DTBP	$Ru(bpy)_3Cl_2$ (1)	PhCl	Nr
17	$FeCl_2$	DTBP	Mes-Acr$^+$ClO$_4^-$ (1)	PhCl	Trace
18	$FeCl_2$	DTBP	4CzIPN (1)	PhCl	62 (70)[d]
19	$FeCl_2$	DTBP	Eosin Y (5)	PhCl	Nr
20	$FeCl_2$	DTBP	Rose bengal (5)	PhCl	Nr
21	—	DTBP	4CzIPN (1)	PhCl	51

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (3.0 equiv), catalyst (5 mol%), oxidant (4.0 equiv.), solvent (2.0 mL), Ar, 120 °C (for entries 1–14) or room temperature (for entries 15–21), 6 h (for entries 1–14) or 12 h (for entries 15–21). [b] 6 W Blue LEDs were used to excite the PCs. [c] 5.0–6.0 mol L^{-1} in decane. [d] The reaction time was prolonged to 24 h.

Table 2 Scope of *N*-allyl anilines[a,b]

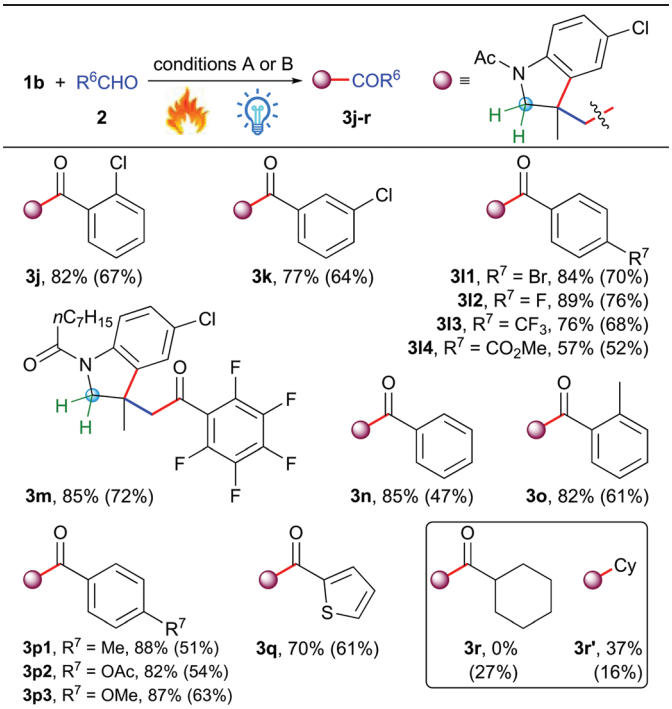


[a] Reaction conditions A: **1** (0.5 mmol), **2a** (1.5 mmol), $FeCl_2$ (0.025 mmol), DTBP (2.0 mmol), degassed chlorobenzene (2.0 mL), Ar, 120 °C, 6 h; reaction conditions B: **1** (0.5 mmol), **2a** (1.5 mmol), $FeCl_2$ (0.025 mmol), 4CzIPN (0.005 mmol), DTBP (2.0 mmol), chlorobenzene (2.0 mL), Ar, 6 W Blue LEDs, 24 h. [b] The yields of reactions under conditions B are shown in parenthesis.

aroyl substituent, probably because both phenyl rings might serve as the inbuilt radical trap during reaction. Allylated benzamides, however, could undergo a similar acylarylation reaction with **2a** to afford the 3,4-dihydroisoquinolin-1-ones **4a,b**, albeit in modest yields, and in the case of *N*-benzyl-3-chloro-*N*-(2-methylallyl)benzamide, the cyclizative arylation process occurred on the benzoyl ring as well and at the less hindered position (**4b**). Substantial steric effects were observed in the reaction of the *ortho*-substituted anilide, and the 7-chloro indoline **3f** was obtained in only poor yields. Whereas a 3,5-dichloro anilide reacted with aldehyde **2a** to give the 4,6-dichloro indoline **3g** in high yields, the 4-chloroindoline **3h** and regioisomeric 6-chloroindoline **3h′** were produced simultaneously from a 3-chloro aniline substrate. Interestingly, more encumbered isomer **3h** is the major product, and such a regioselectivity might be associated with the intermediate stability. Variations of the R^1 branch have also been performed, and the non- or methoxycarbonyl-branched substrates participated in this transformation as well, delivering the corresponding indoline products **3i1,2** albeit with a depreciation in yield.

Both the heat-induced and the photoredox conditions are also applicable to a range of aldehydes (Table 3). 2- or 3-Chlorobenzaldehyde are both usable acyl radical precursors, and their reactions with *N*-(4-chlorophenyl)-*N*-(2-methylallyl) acetamide **1b** under either conditions afforded the indoline products **3j,k** in moderate to high yields. Whereas high yields were obtained using 4-bromo (**3l1**) or 4-fluoro benzaldehyde (**3l2**), aldehydes with a strongly electron-withdrawing substituent (*e.g.*, trifluoromethyl or methoxycarbonyl group) reacted with **1b** to afford the indolines **3l3,4** in diminished yields, indicating that the use of electron-deficient aromatic aldehydes might have adverse effects on the title reaction. Nonetheless, the reactions of pentafluorobenzaldehyde with a long-chain acyl-protected allyl aniline proceeded to give the 3-(α-acyl) indoline **3m** in high yields. While non-substituted (**3n**) or 2-methyl-substituted benzaldehydes (**3o**) are both excellent acyl sources for this transformation, electron-donating substituents, such as the methyl (**3p1**), acetoxy (**3p2**), and methoxy groups (**3p3**), at the *para*-position of the aldehydic aryl group were well-tolerated as well. Noteworthy is the compatibility of

Table 3 Scope of aldehydes[a,b]



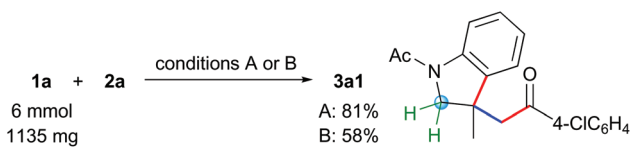
[a] Reaction conditions A: **1b** (0.5 mmol), **2** (1.5 mmol), $FeCl_2$ (0.025 mmol), DTBP (2.0 mmol), degassed chlorobenzene (2.0 mL), Ar, 120 °C, 6 h; reaction conditions B: **1b** (0.5 mmol), **2** (1.5 mmol), $FeCl_2$ (0.025 mmol), 4CzIPN (0.005 mmol), DTBP (2.0 mmol), chlorobenzene (2.0 mL), Ar, 6 W Blue LEDs, 24 h. [b] The yields of reactions under conditions B are shown in parenthesis.

2-thenaldehyde, with the corresponding product **3q** isolated in 70% (conditions A) or 61% yield (conditions B). Interestingly, when cyclohexanecarbaldehyde and **1b** were subjected to the heating conditions, decarbonylation occurred, furnishing the cyclohexylated indoline **3r′** albeit in a poor yield. Under the mild irradiation conditions, however, both the acylated indoline **3r** and the decarbonylative product **3r′** were produced. It is worthy of notice that an *exo* selectivity was achieved in all of the above reactions, and a formal 6-*endo-trig* product was not observed.

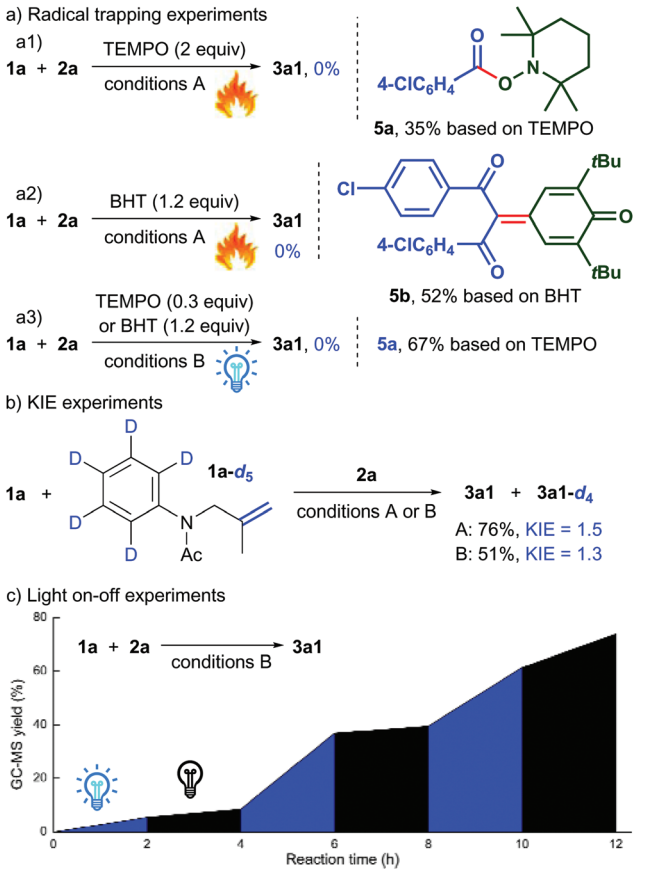
The present syntheses of 3-(α-acyl) indolines under either the heating or the photoredox conditions could be readily carried out on a gram-scale with only a slight loss in yield (Scheme 1), rendering them practical protocols. The relatively modest yield obtained under the photoredox conditions might reflect the insufficient irradiation as a result of the microphotoreaction setup we used (see ESI† for full details).

To gain further insight into the mechanisms, a series of mechanistic investigations were performed (Scheme 2). Upon addition of either 2 equiv. of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, Scheme 2a1) or 1.2 equiv. of butylated hydroxytoluene (BHT, Scheme 2a2) to the model reactions induced by heat, both reactions were completely suppressed, and the aldehyde-TEMPO and the aldehyde-BHT adducts **5a,b** were isolated in 35% and 52% yields, respectively. The model reactions under the photoredox conditions doped with 0.3 equiv. of TEMPO or 1.2 equiv. of BHT did not proceed either, with the aldehyde-TEMPO adduct **5a** furnished in 67% yield in the TEMPO experiment (Scheme 2a3). These results suggest that radical processes might be involved in this transformation, and acyl radicals might be the key open-shell intermediates.

The kinetic isotope effect (KIE) experiments between **1a** and the aryl-deuterated substrate **1a-*d*$_5$** under both sets of optimal conditions were conducted (Scheme 2b), giving minor KIE values of 1.5 (conditions A) and 1.3 (conditions B), respectively. These results indicate that the C–H bond cleavage of the *N*-aryl moiety is probably not involved in the rate-limiting step. Finally, light on–off experiments showed that during light off-cycles the photoredox reaction was retarded, and that a constant irradiation is necessary for it to reach completion (Scheme 2c). A radical chain might exist,[23] yet the chain length is short. These were further supported by measuring the quantum yield, which was found to be 0.24 (see ESI† for full details). Interestingly, there seems to be an induction period, which might be explained by the requirement to access an Fe(III) species from the Fe(II) catalyst, facilitating the key SET process from the dearomatized aryl radical **B**.

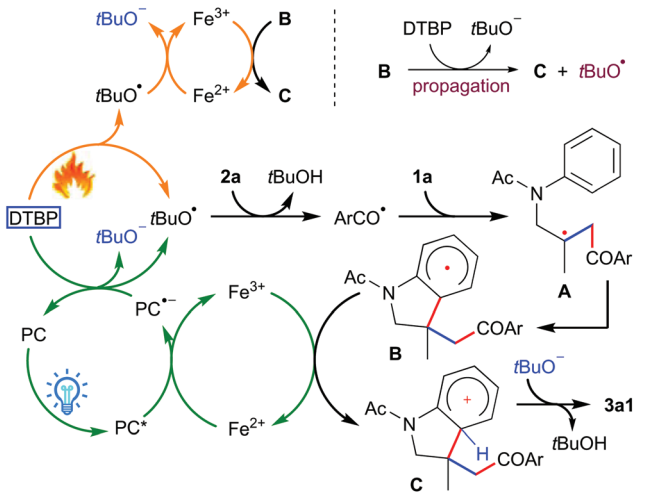


Scheme 1 Gram-scale syntheses.



Scheme 2 Mechanistic investigations.

Based on the above experimental results and literature reports, plausible reaction mechanisms were proposed (Scheme 3). Under the photoredox conditions, the PC, 4CzIPN, is transferred to its highly oxidizing excited state (PC*) by absorbing photons, and the excited-state species PC* would then be reductively quenched by an Fe(II) species, affording an



Scheme 3 Proposed mechanisms.

Fe(III) complex and the reduced photosensitizer $PC^{\bullet-}$. The later reduces the oxidant DTBP to produce the *tert*-butanolate anion and a *tert*-butoxyl radical, as well as the regenerated PC. HAT from the aldehydic C–H bond to the *tert*-butoxyl radical affords an acyl radical, the addition of which across the tethered double bond leads to the radical intermediate **A**. **A** is highly active, and the rapid intramolecular radical trapping by the *N*-aryl moiety ensues, delivering the dearomatized aryl radical intermediate **B**. Subsequent SET from **B** to an Fe(III) complex gives the dearomatized cationic intermediate **C** and regenerates the Fe(II) catalyst. Finally, deprotonation of **C** by the *tert*-butanolate anion furnishes the 3-(α-acyl) indoline **3a1**. As for the heat-induced reaction, the *tert*-butoxyl radical was produced by the thermal decomposition of DTBP, and this radical could oxidize the Fe(II) catalyst to give an Fe(III) complex. The direct SET from aryl radical **B** to DTBP might occur as well,[23] enabling a propagation process as a minor reaction pathway observed in the light on–off experiments.

Conclusions

To conclude, a heat- or photoredox/iron dual catalysis-enabled synthesis of 3-(α-acyl) indolines bearing a quaternary stereogenic center has been developed, with unactivated alkenic bonds as radical acceptors and simple aldehydes as radical precursors. This reaction is associated with high yields, a broad substrate scope, and a great *exo* selectivity, and gram-scale syntheses could be readily carried out.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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