SCIENCE CHINA
Chemistry

•ARTICLES•
SPECIAL ISSUE: 2022 Emerging Investigator Issue

November 2022 Vol.65 No.11: 2231–2237
https://doi.org/10.1007/s11426-022-1331-y

Deoxygenative alkylation of tertiary amides using alkyl iodides under visible light

Feng Zhao[1,2†], Feng Jiang[2,3†] & Xiaoming Wang[2,3*]

[1]*The Education Ministry Key Lab of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, College of Chemistry and Materials Science, Shanghai Normal University, Shanghai 200234, China;*
[2]*State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China;*
[3]*School of Chemistry and Materials Science, Hangzhou Institute for Advanced Study, University of Chinese Academy of Sciences, Hangzhou 310024, China*

Received May 23, 2022; accepted July 11, 2022; published online July 18, 2022

It is an unceasing goal for organic chemists to develop new catalytic methodologies for functional group transformations of widespread molecular structures. Amides are readily available from simple and reliable reactions, which are common structural units found in biologically active compounds. Consequently, they are attractive to be exploited in amine synthesis by reductive cross coupling. However, deoxygenative functionalization of amides is a long-standing challenge owing to the inertness of the resonance-stabilized amide C=O bond. In this work, a deoxygenative alkylation strategy was demonstrated, which combines amides and alkyl iodides to build structurally diverse tertiary alkylamines in a single step. Compared with previous deoxygenative alkylation of amides using organometallic reagents as functional partner, this work uses stable and easily available alkyl halides as functionalization reagents. The versatile and flexible strategy plus structural and functional diversity of readily available amides and alkyl iodides renders it highly appealing for the streamlined synthesis of tertiary amines and would be of much interest in areas such as pharmaceutical and agrochemical research.

deoxygenative alkylation, amide transformation, alkyl radical, alkylamine, visible light

Citation: Zhao F, Jiang F, Wang X. Deoxygenative alkylation of tertiary amides using alkyl iodides under visible light. *Sci China Chem*, 2022, 65: 2231–2237, https://doi.org/10.1007/s11426-022-1331-y

1 Introduction

As nitrogen containing precursors, amides are attractive to be exploited in homologous amine synthesis, which are found widely in nature and utilized broadly in industries (Figure 1a) [1–8]. However, due to their high chemical stability and low inherent reactivity [9–15], the efficient reductive transformation of amides to α-substituted amines remains largely a formidable challenge. Either a stoichiometric amount of strongly electrophilic reagents (such as Tf_2O) [13–15] or Schwartz's reagent (Cp_2ZrHCl) [16] or DIBAL-H [17,18] have been used for pre-activation of the amides (Figure 1b) [19–22]. Alternatively, catalytic deoxygenative functionalization of tertiary amides has been developed by way of the enamine and/or iminium ion intermediates formed from partial reduction of the amide C=O bond [23,24], as demonstrated in the elegant studies by the groups of Nagashima [25], Dixon [26–29], Chida/Sato [30–33], Huang [34,35], Adolfsson [36] and others [37–40]. Despite these remarkable advances, typical nucleophiles are required to introduce coupling partners at the α-position of the resulting amines. For examples, pre-prepared alkyl lithium or Grignard reagents are often used as alkylation reagents in the con-

†These authors contributed equally to this work.
*Corresponding author (email: xiaoming@sioc.ac.cn)

struction of new C–C bond, which can lead to poor chemical selectivity and functional group compatibility problems. Given these severe limitations of the organometallic nucleophiles, development of alternate strategies based on the use of a reactive intermediate generated *in situ* from reaction of a chemically stable compound as the alkyl source is in urgent demand. Notably, Huang and co-workers [41] reported a formal alkylation of tertiary amides, which features a tandem iridium-catalyzed hydrosilation of amides, copper(I)-salt-catalyzed addition of terminal alkyne and Pd/C-catalyzed hydrogenation. Dixon group [27] developed a reductive functionalization of tertiary amides with dehydroalanine acceptors by a dual iridium-catalyzed hydrosilylation and photochemical single electron reduction, leading to the formation of α-functionalized tertiary amine derivatives *via* a key α-amino radical intermediate.

In recent years, free radical chemistry has been developed rapidly and active radical intermediates have been generated in various ways and widely used in the carbon-carbon and carbon-heteroatom bond-forming reactions [42–44]. Particularly, some free radical reactions can be effectively initiated by visible light and have demonstrated the advantages of mild conditions and environmental beingness [45–49]. It is worth noting that an imine or iminium ion can be prone to the attack of a free nucleophilic radical, thus resulting the formation of an α-functionalized amine [50–55]. For examples, Gaunt group [54,55] reported an elegant work on the 1,2-addition of alkyl radicals to aldiminium ions, which were generated *in situ* from the condensation of secondary amines with alkyl aldehydes. Recently, we have developed an efficient synthesis of β-substituted amines *via* the reaction of electrophilic radicals with enamine intermediates generated from Ir-catalyzed reduction of amides [40]. We envisioned that the facile addition of a nucleophilic alkyl radical, instead of organometallic nucleophiles, onto the iminium ion intermediate formed *in situ via* Ir-catalyzed partial reduction of a tertiary amide, can constitute an effective way for deoxygenative alkylation of amides and might offer a general and attractive alternative to α-alkylated tertiary amine synthesis (Figure 1c). However, several competitive pathways might occur concurrently, which can severely compromise the presumed amide reduction and photo-induced radical process [40]. In this scenario, the residual reductant and Ir catalyst from the amide reduction may interfere with the ensuing photo-induced radical process. Furthermore, the interception of the iminiumion intermediate by the alkyl radical must proceed with adequate efficiency to compete favorably with the otherwise over-reduction of the amide. Finally, the radical reducing agent for hydrogen atom transfer (HAT), such as tris(trimethylsilyl)silane [56,57] should be compatible with the residual Ir catalyst.

Herein, we report an unprecedented deoxygenative alkylation of amides *via* merging Ir catalyzed amides reduction with a visible light induced radical generation from alkyl iodides (Figure 1c). The inert amide is activated by an Ir-catalyzed partial reduction to form a reactive iminium ion intermediate, while a highly active alkyl radical is generated from alkyl iodide under visible light. The facile combination of the reactive species led to rapid construction of a large variety of tertiary amines in moderate to good yields. A key part of this protocol is the successful incorporation of the above two activation strategies through the radical addition to iminium ion, leading to the formation of the new C–C bond. Benefitted from the two accessible feedstocks and mild reaction conditions, we anticipate that this platform will be an attractive alternative method to facilitate rapid access to α-branched tertiary alkylamines, which are likely to be important for synthetic and medicinal chemistry.

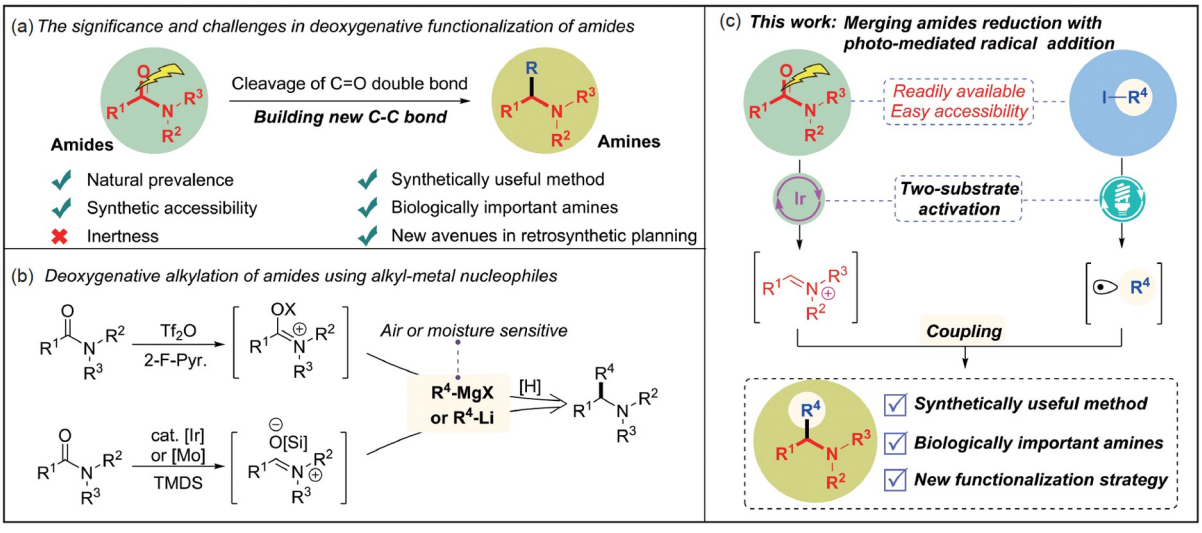

Figure 1 Deoxygenative alkylation of amides for the synthesis of α-alkylated tertiary amines (color online).

2 Experimental

To an over dried Schlenk tube equipped with a magnetic stir bar was added amide **1** (0.2 mmol, 1.0 equiv.) and IrCl(CO)-$(PPh_3)_2$ (0.002 mmol, 1.0 mol%, 1.6 mg) in a nitrogen filled glovebox. Then the tube was removed from the glovebox. To this mixture, anhydrous dichloromethane (DCM, 2.0 mL) and 1,1,3,3-tetramethyldisiloxane (TMDS, 2.0 equiv., 0.4 mmol, 71 μL) were added *via* a gastight syringe under argon atmosphere. The mixture was allowed to stir for 30 min in the air-conditioned room of 25 °C. A solution of alkyl iodide **2** (0.6 mmol, 3.0 equiv.), tris(trimethylsilyl)silane (TTMSS, 0.4 mmol, 2.0 equiv., 123 μL), and TBSOTf (0.2 mmol, 1.0 equiv., 46 μL) in DCM (3 mL) was added *via* a gastight syringe under argon atmosphere. The resulting mixture in Schlenk tube was allowed to stir for 8.0 h under irradiation with 24 W blue light-emitting diodes (LEDs; with fan, ca. 25 °C) in the air-conditioned room of 25 °C. The reaction mixture was transferred into a 25 mL round bottom flask, and the solvent was removed *in vacuo*. Then 5 mL petroleum ether was added and removed *in vacuo*. The resulting mixture was washed with hexane (3 × 5 mL) under ultrasound to remove the silane and pour out upper oil phase carefully. The residue was redissolved in 5 mL DCM, and NaOH solid was added and stirred vigorously for 2 h. The resulting suspension is filtered out of the solid, and the solvent was removed on a rotary evaporator. The crude product was purified by flash chromatography on basic aluminum oxide using petroleum ether/EtOAc as eluant.

3 Results and discussion

3.1 Reaction development

As shown in Table 1, we began our studies on the deoxygenative alkylation of amide **1a** and 2-iodopropane **2a**. An careful assessment of the reaction parameters revealed an optimal procedure for the reaction, *i.e.*, aging a dichloromethane solution of amide **1a**, IrCl(CO)$(PPh_3)_2$ (Vaska's complex, 1.0 mol%) and 1,1,3,3-tetramethyldisiloxane (TMDS, 2.0 equiv.) at r.t. for 30 min in a typical run, before addition of a dichloromethane solution of 2-iodopropane **2a**, tris(trimethylsilyl) silane (TTMSS, 2.0 equiv.) and trifuloromethanesulfonate (TBSOTf, 1.0 equiv.), and the resulting mixture was stirred at r.t. for 8.0 h under visible light irradiation. Under these conditions, *N*,*N*-dibenzyl-4-methyl-1-phenylpentan-3-amine (**3aa**) was obtained in 82% yield (Table 1, entry 1) with a few over-reduced amines **4** (11% yield). Subsequent survey of reaction parameters was then carried out on the effects of the amount of reductant and Ir catalyst, solvent and so on. Reducing the loading of TMDS to 1.0 equiv. in the reaction afforded the desired product **3aa** in 66% yield and the by-product **4** in 6%

Table 1 Optimization of the reaction conditions for **3aa** [a]

Entry	Changes to standard conditions	**3aa** (%) [b]	**4** (%) [b]
1	None	89 (82) [c]	11
2	TMDS (1 equiv.)	66	6
3	CH_3CN instead of DCM	6	29
4	Toluene instead of DCM	47	28
5	DCE instead of DCM	81	18
6	No TBSOTf	35	43
7	No TTMSS	<1	93

a) Reaction conditions: a mixture of **1a** (0.2 mmol), TMDS (0.4 mmol), IrCl(CO)$(PPh_3)_2$ (1.0 mol%) and DCM (2 mL) was pre-mixed for 30 min. Then a solution of **2a** (0.6 mmol), TTMSS (0.4 mmol) and TBSOTf (0.2 mmol) in DCM (3 mL) was added. The resulting mixture was stirred under the irradiation of 24 W blue LED at r.t. for 8 h. b) Determined by gas chromatograph (GC) using mesitylene as the internal standard. c) Isolated yield.

yield, indicating that an excess amount of the reductant is necessary for the deoxygenative reduction of amide (entry 2). Screening of the solvent revealed that dichloromethane was the optimal solvent for the reaction as compared to toluene, acetonitrile or 1,2-dichloroethane (DCE) (entry 1 *vs.* 3–5). In the absence of a Lewis acid, the yield of **3aa** was found to decrease to 35% (entry 6) and amine **4** was found to be the main product in 43% yield. This result highlighted the role of TBSOTf in the reaction, which may promote the formation of iminium ion intermediate in the process of amide reduction [23,24], and may also protect the amine product as its ammonium salt [58]. TTMSS seems to play an important role in the radical process, including the radical initiation, hydrogen-atom transfer with the generated *in situ* aminium radical cation and the radical chain propagation process [54–57]. As expected, without the addition of TTMSS, only over-reduced amine **4** was formed as the major product (93% yield, entry 7) without the alkylation process.

3.2 Reaction scope

With the optimal reaction conditions having been established, the substrate scope of the deoxygenative alkylation with respect to the amides was explored firstly. As shown in Figure 2, the reactions of 2-iodopropane **2a** with a range of amides derived from a variety of linear carboxylic acids, respectively, proceeded smoothly to give the corresponding α-branched alkylamines in moderate to good yields (**3aa**–**3ra**). The amides with phenyl groups tethered by alkyl chains of different lengths were well tolerated (**3aa**–**3ca**), and the longer alkyl chains seem to be more favorable for the alkylation (**3aa** and **3ba** *vs.* **3ca**). Meanwhile, the alkylation

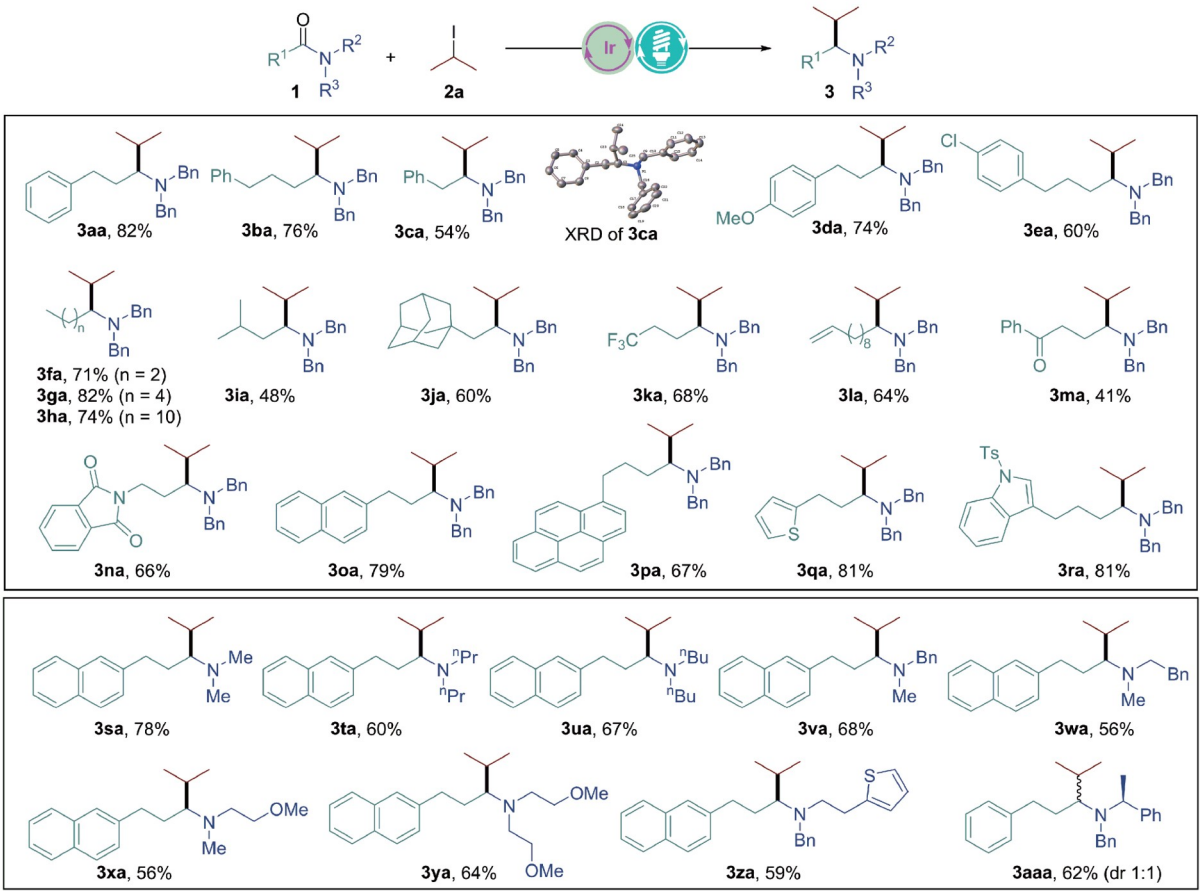

Figure 2 Substrate scope of the amides. For reaction conditions, see entry 1, Table 1 (color online).

tolerated amides with a phenyl group bearing either an electron-donating or -withdrawing substituent (**3da**, **3ea**), affording the expected products in 74% and 60% yields, respectively. Next, examination of various non-functionalized alkyl groups, including linear- (**3fa**–**3ha**), branched- (**3ia**), and cyclo-alkyl (**3ja**), showed that the amides exhibited favorable reactivity. Furthermore, alkyl amides bearing an additional functional group also underwent the reaction to give the corresponding tertiary alkylamines successfully. For examples, trifluoromethyl in **1k** (a group relevant to bioactivities), alkylene in **1l**, a ketone in **1m**, and a *O*-phthalimide group in **1n** were well tolerated in the reaction, to give the corresponding alkylation products in 68%, 64%, 41%, and 66% yields, respectively. Likewise, the reactions involving the amides linked by fused aromatic ring as the starting material provided the desired products (**3oa** and **3pa**) in 79% and 67% yields, respectively. It is worth noting that reactions of aromatic heterocyclic liner amides also work well in the reaction (**3qa** and **3ra**, both in 81% yields), showing a good toleration towards heterocyclic cycles. Apart from carboxamides derived from various carboxylic acids above, we found that amides derived from diverse secondary amines were also compatible with the process (**3sa**–**3aaa**). For amides **1sa**–**1ua**, derived from non-functionalized dialkylamines, the alkylation reactions gave the targeted products **3sa**–**3ua** in 60%–78% yields. Amides from *N*-methylbenzylamine (**1va**) and *N*-methylphenethylamine (**1wa**) proceeded well under the standard conditions, giving the alkylamines **3va** and **3wa** in 68% and 56% yields, respectively. Furthermore, carboxamides from methoxy substituted secondary amines were applicable to this reaction (**3xa** and **3ya**). *N*-benzyl-3-(naphthalen-2-yl)-*N*-(2-(thiophen-2-yl)ethyl)propenamide was tested in the reaction and the terminal amine was obtained in 59% yield (**3za**). Finally, when chiral amide (**1aa**) was used in this transformation, the corresponding product (**3aaa**) was obtained in 62% yield with 1:1 diastereoisomer ratio, suggesting the stereoselectivity seems difficult to control in this reaction. It should be highlighted that the approach exhibited high functional group tolerance, since products bearing various synthetic handles, such as OMe (**3da**), aryl chloride (**3ea**), terminal olefin (**3la**), ketone (**3ma**), *O*-phthalimide (**3na**) and heterocycles (**3qa**, **3ra**, and **3za**) were obtained in good yields, thus offering good opportunities for downstream transformations. The structure of **3ca** was unambiguously determined by single-crystal X-ray diffraction.

We then sought to explore the scope of alkyl iodide in the deoxygenative alkylation reaction with *N*,*N*-dibenzyl-3-phenylpropanamide **1a**. As shown in (Figure 3a), both simple and functionalized secondary alkyl iodides were competent substrates, and the reactions gave the corresponding amines **3ab**–**3an** in synthetically useful yields. Cycloalkyl iodides of different ring sizes were compatible in this reaction, and the α-cycloalkyl tertiary amines (**3ab**–**3ae**) were obtained in 62%–78% yields. For 2-iodo-2,3-dihydro-1*H*-indene, this alkylation method worked effectively as well (**3af**). The alkyl iodide bearing 2*H*-pyranyl ring was well tolerated in this reaction, giving a 57% yield of tertiary amine **3ag**. The 8-iodo-1,4-dioxaspiro[4.5]decane was also a suitable substrate for the alkylation, producing the amine (**3ah**) in 51% yield. The iodide bearing a synthetically useful ester group was also tolerated under standard conditions, yielding the corresponding product (**3ai**) in 46% yield. Secondary iodides with longer chain were tested subsequently. Alkylation with 5-iodononane had a yield of 49% (**3aj**), and the reaction of 2-iodobutane gave a 65% yield of **3ak** with a diastereomeric ratio of 1.2:1. Besides, the reaction of 1-iodopropane as a primary iodide produced the corresponding product (**3al**) in 40% yield. Lastly, we evaluated the reactivity of tertiary iodide. 2-Iodo-2-methylpropane (**2m**) and 1-iodoadamantane (**2n**) were demonstrated to be compatible in the alkylation process, providing the corresponding products in 23% (**3am**) and 47% (**3an**) yields, respectively. Unfortunately, when isopropyl bromide or isopropyl chloride was tested in the reaction with amide **1a** under the standard conditions, no desired product **3aa** was detected.

3.3 Late-stage modification of complex architectures

α-Branched alkylamines are ubiquitous structural units found in a wide range of small-molecule drugs and preclinical drug candidates. To show the applicability of the reaction developed herein on the synthesis of relatively complex tertiary alkylamines, amides derived from biologically active amines or carboxylic acids were prepared and subjected to the reactions with **2a** under standard conditions (Figure 3a). To our delight, amides derived from Maprotiline, a tetracyclic antidepressant, from Chlorambucil, an anticancer drug, and from Eicosapentaenoic acid, a ω-3 fatty acid which plays an important role in the human diet and in human physiology were also found compatible to the reaction, affording the corresponding alkylamines (**5a**–**5c**) in synthetically useful yields. In addition, alkylation of the iodide derived from hydrogenated Cholesterol proceeded efficiently, giving the corresponding product **5d** in 88% yield with 1:1 diastereoisomer ratio. The successful deoxygenative alkylation of the complex amide substrates, derived from natural products or pharmaceutical agents, further attests the practicality of this process for access to functionalized α-branched alkylamines.

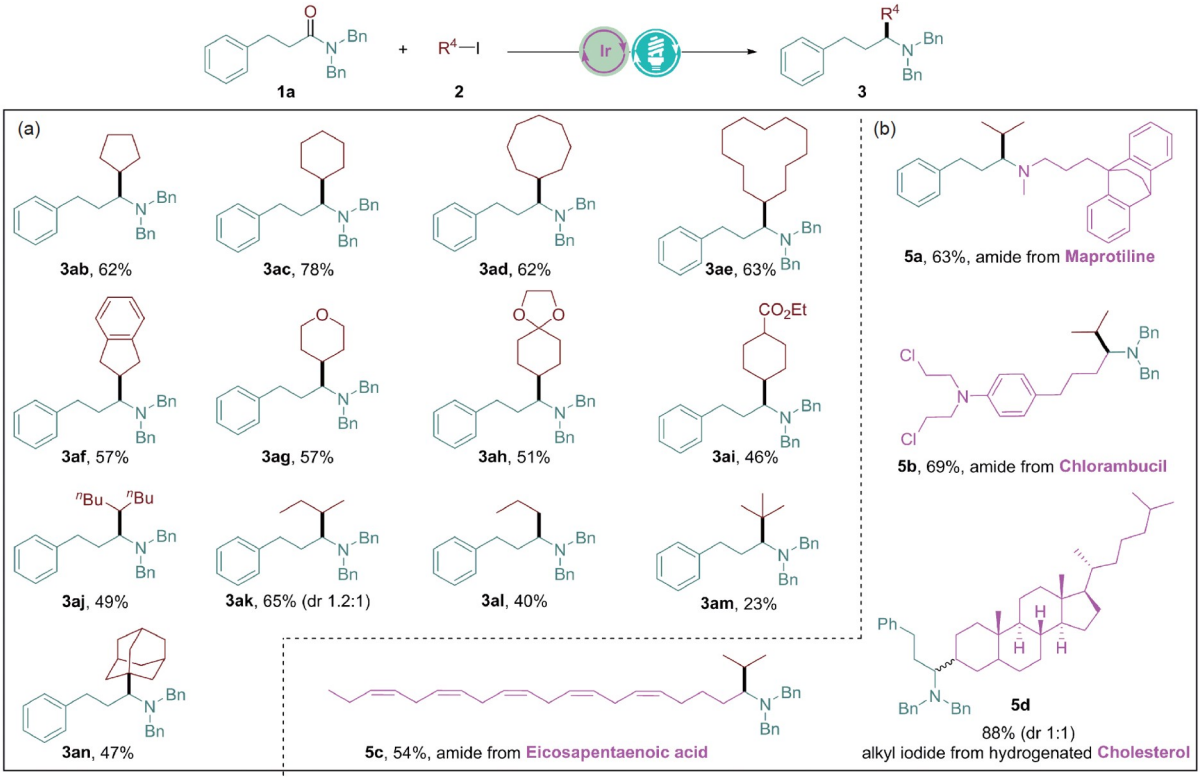

Figure 3 Substrate scope of alkyl iodide (a), and reactions of substrates derived from natural products or drugs (b). For reaction conditions, see entry 1, Table 1 (color online).

3.4 Mechanistic investigations

To explore the reaction mechanism for this deoxygenative alkylation reaction, ^{1}H NMR analysis of the reaction mixture was performed firstly to probe into the nature of the intermediate generated by the iridium-catalyzed reduction of amide **1a**, and the signals assigned to the newly generated enamine intermediate **I** as the major species were clearly visible in the ^{1}H NMR spectrum, which is likely to be produced via the intermediacy of silylhemiaminal (more details see Figure S1 in the Supporting Information online). Besides, some control experiments were also conducted on the alkylation reaction (Figure 4a). For the reaction of model substrate performed in the absence of blued LEDs irradiation, no alkylation product **3aa** was detected, while the over-reduce amine **4** was observed as the major species (71% yield) (Figure 4a-i). Besides, the deoxygenative alkylation was completely inhabited when stoichiometric 2,2,6,6-tetramethyl-1-poperidinyloxy (TEMPO), a radical scavenger, was used in the reaction (Figure 4a-ii). Instead, the relevant TEMPO-adduct **6** was detected by HRMS, suggesting the possible involvement of an isopropyl radical in this process [54,55]. The presence of alkyl radicals was further corroborated by radical clock experiment of iodomethylcyclopropane **2o** with amide **1a** under the standard conditions (Figure 4a-iii), and in this case the ring-opened alkenyl product **7** was isolated in 63% yield.

Based on the above experimental results and previous reports [54–57], we proposed a plausible reaction mechanism shown in Figure 4b. The Ir-catalyzed deoxygenative reduction of the amide gives enamine **I** as the incipient intermediate, which is in equlibrium with iminium ion **II** by the action of a Lewis acid [23,24]. On the other hand, blue-light irradiation on the mixture of alkyl iodide and $(TMS)_3Si$-H induced the generation of the $(TMS)_3Si$• radical **III**, which abstracts iodine atom from alkyl iodide, leading to the formation of alkyl radical **IV**. Subsquent attack of the alkyl radical **IV** on the iminium ion **II** furnishes the aminium radical cation **V** [50–3], which on an HAT process with $(TMS)_3SiH$ affords the desired C–C bond coupling product **VI** [54–57], along with a regenerated silyl radical **III**, which enters chain propagation. Finally, deprotonation of **VI** by a base delivers alkylation product **3**. In the reaction, Lewis acid might promote the formation of iminium ions **II** and protect the products as the corresponding ammonium salts [58].

4 Conclusions

In summary, we have developed a deoxygenative alkylation of amides with alkyl iodides via merging amides reduction

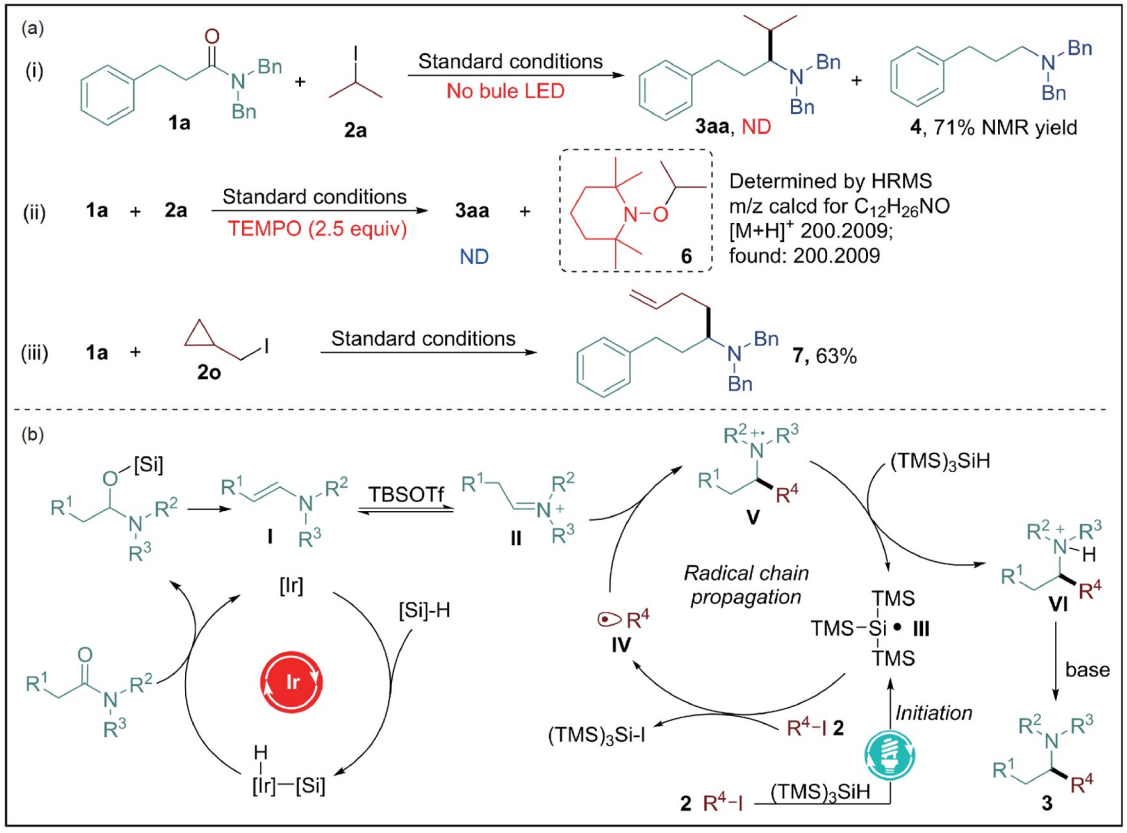

Figure 4 Mechanistic investigations. (a) Control experiments; (b) proposed mechanism (color online).

with photo-mediated radical addition. The reactions are operationally simple and proceed under mild conditions, affording a series of α-branched alkylamines in moderate to good yields. The present methodology obviates the use of highly sensitive Grignard or lithium nucleophiles and can be used in the late-stage diversification of several complex architectures derived from drugs or natural products. Noteworthily, the present strategy of dual activation of both substrates of a reaction would pave the way for the design of novel, efficient and practical transformations of amides and other types of intrinsically inert chemicals.

Acknowledgements This work was supported by the National Natural Science Foundation of China (22171278, 21821002).

Conflict of interest The authors declare no conflict of interest.

Supporting information The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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