Zitierweise: *Angew. Chem. Int. Ed.* **2022,** *61,* e202204516
Internationale Ausgabe: doi.org/10.1002/anie.202204516
Deutsche Ausgabe: doi.org/10.1002/ange.202204516

Homoallylic Compounds

Synthesis of Homoallylic Amines by Radical Allylation of Imines with Butadiene under Photoredox Catalysis

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Abstract: Ionic ($2e^-$) nucleophilic addition of allylmetal regents to imines dominates the synthesis of homo-allyl amine; however, single electron ($1e^-$) mediated imine allylation with feedstocks butadiene as an alternative allyl source remains unexplored. In this work, we report a conceptually different radical–radical cross-coupling strategy for the synthesis of a homoallyl amine between an α-amino alkyl radical and a transient allylic radical. This metal-free method provided a novel approach for the synthesis of homoallylic amines (>80 examples) from readily available materials with excellent regioselectivity and exceptional broad functional group compatibility.

The development of efficient and sustainable methods that can directly convert industrial raw materials to value-added chemicals represents a critical objective in modern synthetic research.[1–4] Homoallylic amine architectures serve as important organic blocks, crucial to the synthesis of a wide variety of nitrogen-containing natural products and pharmaceuticals (Figure 1d).[5–10] Classical nucleophilic addition of π-allylmetal reagents to imines dominates the synthesis of homoallylic amines (Figure 1a).[11–13] However, the tedious preparation of moisture-sensitive π-allylmetal reagents via oxidative addition to pre-activated allylic halides limited their broad applications, particularly for pharmaceutical endeavors due to difficulties associated with the separation of metal residues from products.[14–16]

Recently, reductive umpolung of imines to generate nucleophilic α-amino alkyl radicals under photoredox conditions offers unique and unconventional synthetic strategies.[17–23] In this regard, the seminal work of polarity-reversed allylation of imines via the addition of α-amino alkyl radicals to electrophilic alkenes was reported by the research groups of Chen and Dixon (Figure 1b).[24–26] However, a radical approach for imine allylation with industrial raw material butadiene remains, to the best of our knowledge unprecedented.

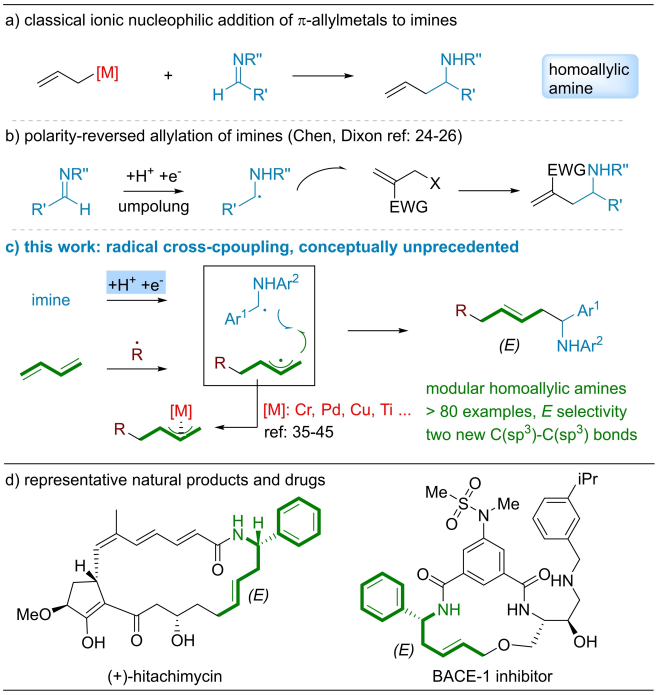

Figure 1. Strategies for imine allylation.

Feedstock butadiene has been frequently used as a promising alternative allyl source for organic synthesis.[27–33] However, radical functionalization of butadiene remains a challenge due to the rapid radical chain polymerization.[34] A few recent successful protocols relied on transition metals that can quickly trap highly reactive allylic radicals to generate the corresponding π-allylmetal species for subsequent transformations (Figure 1c middle-lower).[35–45] To further exploit the synthetic potentials of allyl radical species, we wonder whether an allyl radical could be directly coupled with another radical without the aid of transition metals (Figure 1c). Here, we report a strategically unprecedented approach for the synthesis of homoallylic amines via radical–radical cross-coupling between an α-amino alkyl radical and a transient allylic radical. Specifically, allylic

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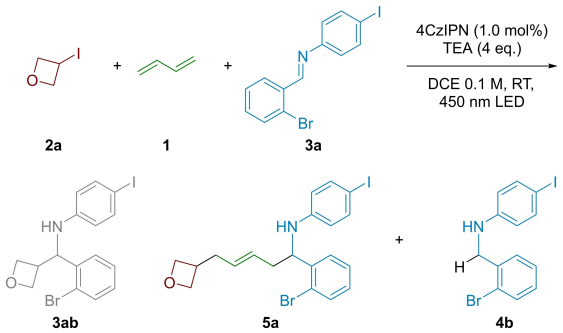
radicals were generated in situ through the addition of various alkyl-radicals to butadiene.

Radical-radical couplings usually are mostly nearly diffusion-controlled and irreversible. Given that alkyl radicals and α-amino alkyl radicals are present simultaneously in the reaction, how to avoid their rapid direct cross-coupling [the coupling rate constant between alkyl radical and α-amino alkyl radical, $k_{R\ im} = 2.1 \times 10^9\ M^{-1} s^{-1}$, Supporting Information S10.2, Eq. (18)] is challenging. Additionally, the dimerization or further reduction of α-amino alkyl radicals may complicate the radical cascade process. In principle, both nucleophilic alkyl radicals and electrophilic α-carbonyl radicals are expected to undergo rapid addition to butadiene, an excellent radical acceptor, generating transient allyl radicals.[46] On the other hand, it might be difficult to add longer-lived and highly nucleophilic α-amino alkyl radicals to butadiene, but they can be readily coupled with allyl radicals.

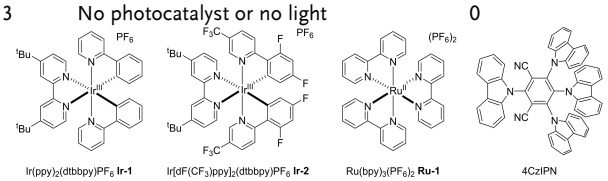
We started our study by examining 3-iodooxetane **2a**, butadiene, and imine **3a** as the model substrates. After a careful variation of reaction parameters, we identified the suitable reaction conditions in which a mixture of low-cost organic dye 4CzIPN, triethylamine (TEA, 4.0 equiv), **1** (2.0 equiv, 2 M in THF), **2a** (2.0 equiv), and **3a** (1.0 equiv), in dichloroethane (DCE) at room temperature under irradiation afforded homoallylic **5a** with a good yield (74 %, Table 1, entry 1). Further screening revealed that $Ir(ppy)_2(dtbbpy)PF_6$ (**Ir-1**) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**Ir-2**) are suitable photocatalysts; both of them led to the full conversion of **3a** and afforded **5a** in decent yields (entries 2 and 3). Increasing the reaction concentration to 0.2 M led to a decreased yield of 41 % (entry 5). The use of other organic electron donors, such as diisopropylethylamine (DIPEA), triethylenediamine (DABCO), and dicyclohexylmethylamine (Cy_2NMe) instead of TEA, resulted in a low conversion of **3a** (entry 6). However, using Hantzsch Esters as the reductant only led to the direct reduction of **3a** to amine **4b** in 86 % yield (entry 7). Irradiation with a white light emitting diode lamp (LED) instead of a 450-nm LED for 20 h produced **5a** in 51 % yield (entry 8). Various solvents were evaluated. Although acetonitrile is suitable for reaction (entry 9), other solvents including dimethyl formamide (DMF), tetrahydrofuran, and toluene gave **5a** in reduced yields (entries 10–12). Notably, the reaction did not proceed in the absence of the photocatalyst or visible light (entry 13). Condition-based sensitivity screening revealed that the reaction is sensitive towards high oxygen concentration (Supporting Information S6).[47]

Having established the optimal conditions, we then systematically investigated the generality of the radical cascade reaction. Impressively, the reaction system showed broad scope and compatibility with sensitive functional groups. As shown in Table 2, various primary (**5r**–**5v**), secondary (**5a**–**5c**), and tertiary (**5q**) alkyl iodides were successfully transformed to the target homoallylic amines in satisfactory yields and regioselectivity. The addition of *tert*-butyl radical to butadiene led to the formation of quaternary carbon centers **5l**, **5q**, and **6r**. Both α-bromo carboxylates and α-bromo amides are capable radical precursors and

Table 1: Reaction optimization.[a,b]



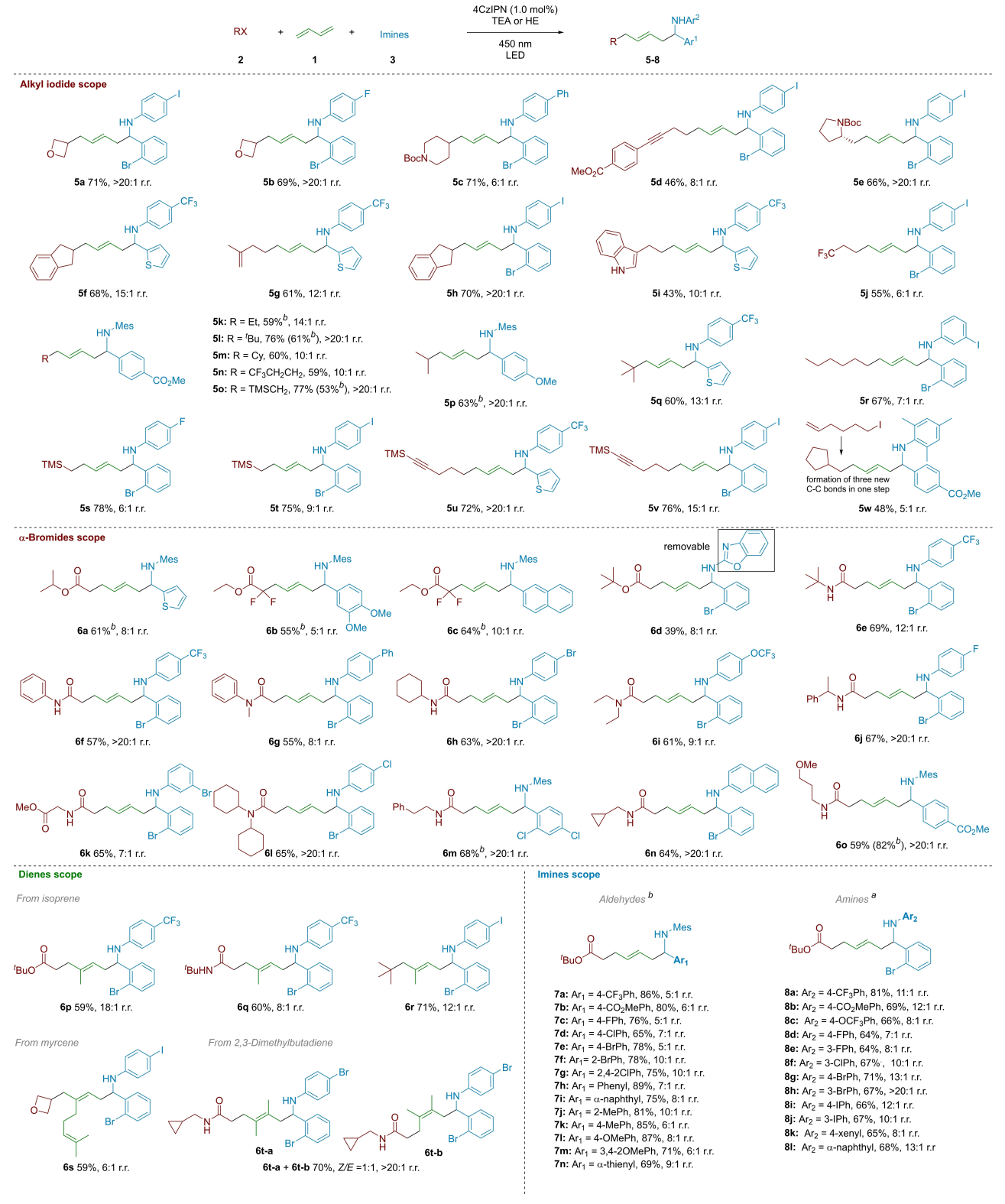
Entry	Variation from standard conditions	Yield of **5a** [%]
1	none	74 [71][c]
2	**Ir-1** instead of 4CzIPN	63
3	**Ir-2** instead of 4CzIPN	55
4	**Ru-1** instead of 4CzIPN	< 5
5	0.2 M instead of 0.1 M	41
6	DIPEA/DABCO/Cy_2NMe instead of TEA	0–26
7	Hantzsch Ester instead of TEA	86 (yield of **4b**)
8	white LED instead 450 nm LED, 20 h	51
9	MeCN instead of DCE	70
10	DMF instead of DCE	66
11	toluene instead of DCE	57
12	THF instead of DCE	25
13	No photocatalyst or no light	0



[a] Reaction scale: **3a** (0.5 mmol). [b] Yields were determined by ^1H NMR spectroscopy vs. an internal standard (1,2,3-trimethoxybenzene). [c] Isolated yield.

afforded diverse γ,δ-unsaturated esters/amides which are important synthetic building blocks.[48] The mild conditions are compatible with a variety of functional groups, including trimethylsilyl **5s**–**5v**, alkyne **5u**–**5v**, alkene **5g**, and iodobenzene **5t**, providing an effective platform for further synthetic elaborations. When 6-iodohex-1-ene was used as an alkyl radical precursor, the cyclized product **5w** was successfully obtained, and three new C–C bonds were created in only one step. Small strained ring cyclopropane **6n** and **6t** and 3-oxetanone **5a**,**b** and **6s** were preserved, and heterocycles thiophene **6a**, benzoxazole **6d**, and unprotected indole **5i** were kept intact under the mild conditions. Particularly, the benzoxazole group in **6d** can be readily removed to afford free primary amine. Next, the scope of imines was evaluated. It was found that sterically hindered imines derived from 2,4,6-trimethylaniline **7a**–**7n** were inert to current conditions and can be recycled. Fortunately, this was resolved by simply using Hantzsch ester as the reducing reagent. Furthermore, the aromatic substituents of imines have no obvious effect on the reaction. Both electron-poor (**7a** and **8c**) and electron-rich (**7j**–**7n**) aryl groups were tolerated, thus delivering the desired homoallylic amines. Several different commercially available dienes were tested including iso-

Table 2: Scope of allylation with butadiene.[a]



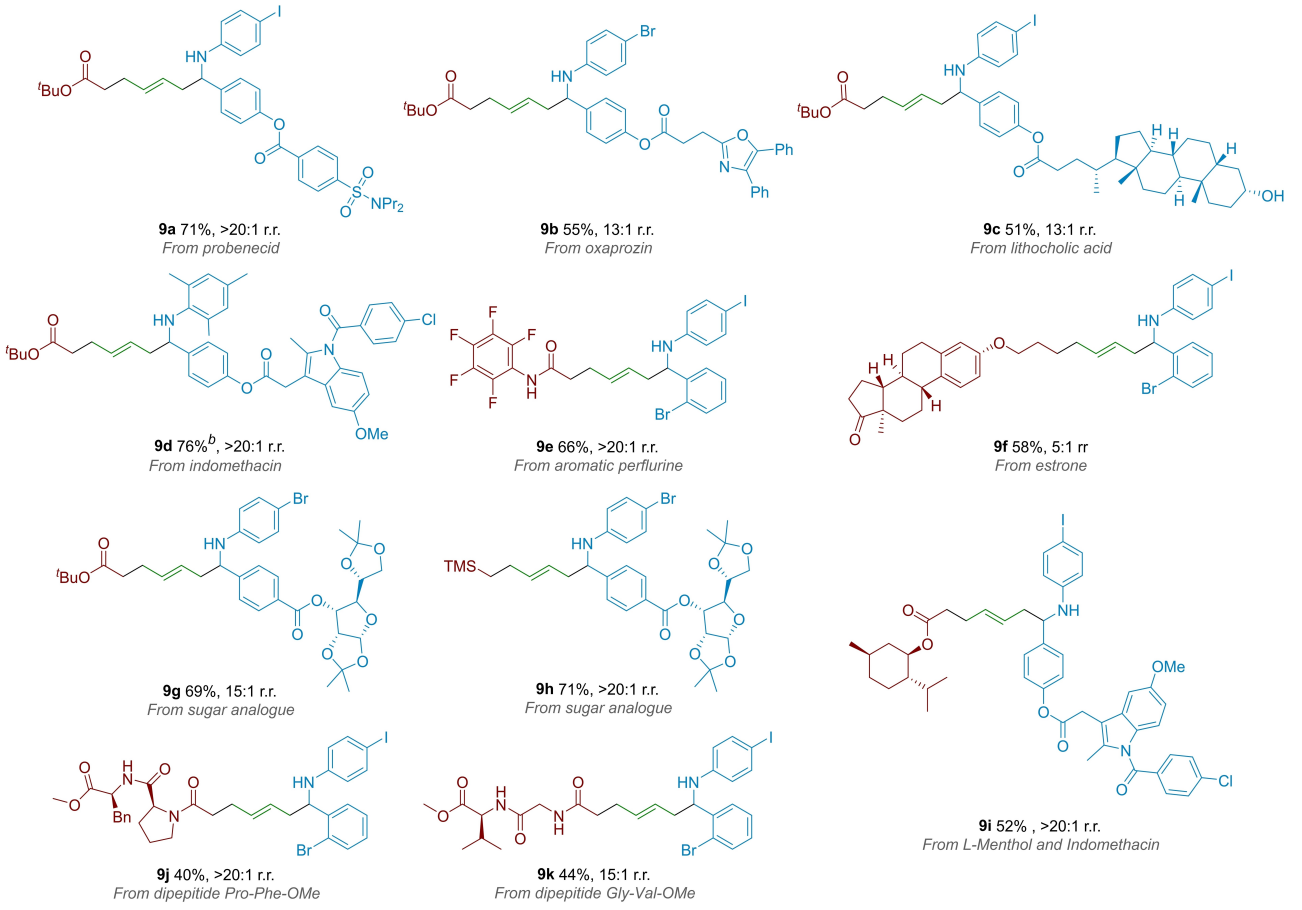
Reported yields are those of the isolated products. [a] Reactions were performed on a 0.5-mmol scale of imine **3** (DCE 0.1 M); Conditions **A**: 4CzIPN (1.0 mol%), TEA (4 equiv), butadiene (2 equiv), RX **2** (2 equiv), 450 nm LED, 5 h. [b] Conditions **B**: Except for HE (2 equiv) instead of TEA (4 equiv), others are identical to conditions **A**.

prene, myrcene, and 2,3-dimethylbutadiene, and converted into the corresponding homoallylic amines in good yields and regioselectivity (**6p–6t**).

To showcase the robustness and utility of the current strategy, transformations of various structurally complex imines and alkyl halides derived from natural products and drugs were examined (Table 3). Structurally complex architectures bearing multiple functional groups, such as probenecid (**9a**), indomethacin (**9d** and **9i**), oxaprozin (**9b**), (−)-menthol (**9i**) and aromatic perfluorinated scaffold (**9e**) were all tolerated. Reaction is not sensitive to the sterically hindered substrates such as lithocholic acid (**9c**) and estrone (**9f**) derivatives. Pleasingly, acid-sensitive glucose-derived substrates survived (**9g,h**). Dipeptides Pro-Phe-OMe (**9j**) and Gly-Val-OMe (**9k**) were used as radical precursors, and no racemization of chiral carbon center was observed under photo conditions.

There are few possible pathways for the reaction (Figure 2a), including the addition of α-amino alkyl radicals to butadiene followed by cascade coupling with alkyl radicals (path **I**), addition of allylic radicals to imines (path **II**) or cross-coupling with α-amino alkyl radicals (path **III**, same as Figure 1c). The model reaction was performed under the standard conditions in the presence 2,2,6,6-tetramethyl-1-piperinedinyloxy (TEMPO) as a radical scavenger (Figure 2b). In this case, the formation of homoallylic amine **5a** was suppressed; instead, two TEMPO adducts **2a–3** and **2a–4** were detected (Supporting Information Figure S6). These results revealed that alkyl radical **2a–1** and allylic radical **2a–2** were indeed generated in the reaction. When the model reaction was carried out in the absence of **2a**, diamine **4c** was obtained in high yield with a reduced amount of amine **4b** (Figure 2c). This indicated that the addition rate of α-amino alkyl radicals to butadiene is much slower than their dimerization.[49] Therefore, the addition of α-amino alkyl radicals to butadiene (path **I**) could be ruled out. Next, it is necessary to clarify whether the reaction proceeds via the addition of allyl radicals to imine (path **II**), or radical cross-coupling (path **III**). Imine **3b** was selected as a suitable reactant because we found that it could be reduced via single electron transfer (SET) using HE as the electron donor but remained intact when using TEA. With this in mind, a reaction was performed with α-bromo carboxylates **10**, imine **3b**, and butadiene (Figure 2d). When TEA was used as the electron donor, imine **3b** was recycled, and dimer **10a** was obtained in 85 % yield. This is probably

Table 3: Late-stage functionalization of structurally complex molecules.[a]



Reported yields are those of the isolated products. [a] Reactions were performed on a 0.5-mmol scale of imine **3** (DCE 0.1 M); Condition **A**: 4CzIPN (1.0 mol %), TEA (4 equiv), butadiene (2 equiv), RX **2** (2 equiv), 450 nm LED, 5 h.

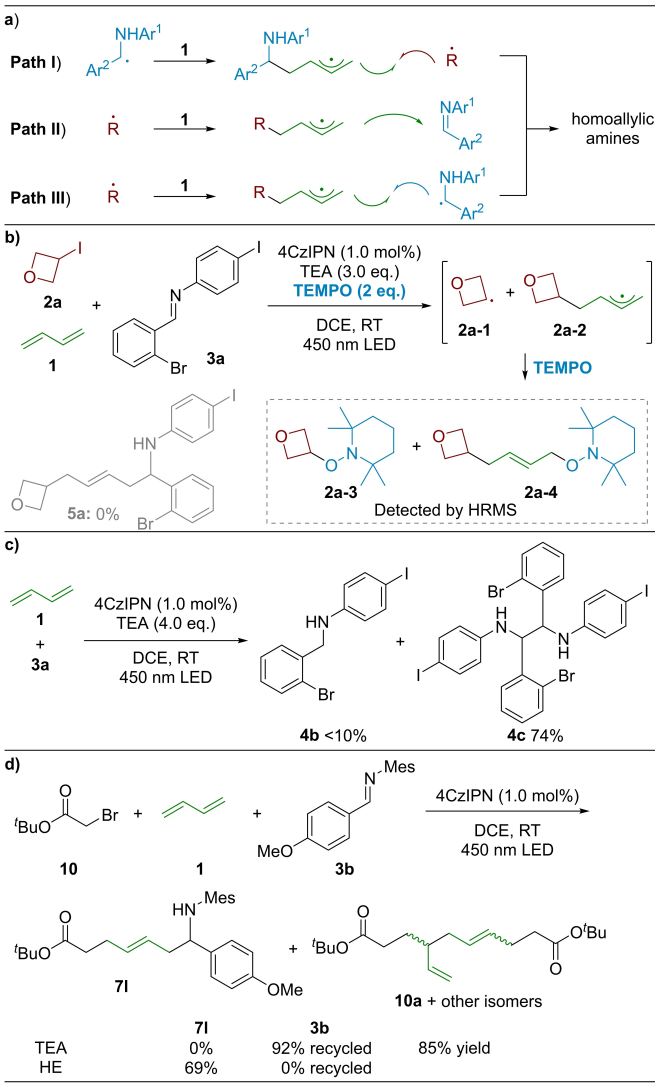


Figure 2. Studies of reaction mechanism. TEMPO: 2,2,6,6-Tetramethyl-1-piperidinyloxy.

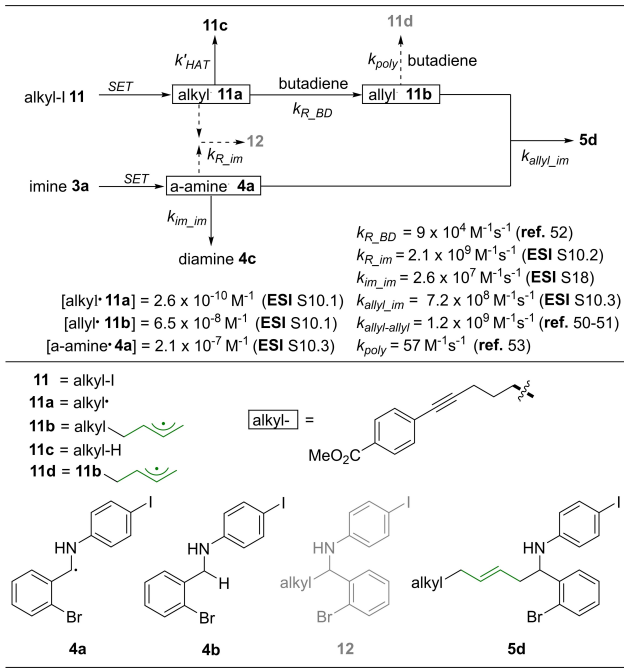


Figure 3. Concentrations of key intermediates and critical rate constants.

because the rate of allylic radical dimerization ($k_{\text{allyl allyl}}=1.2\times10^{9}\,\text{M}^{-1}\text{s}^{-1}$)[50,51] is much faster than its addition to imine. Therefore, path **II** is unlikely. In contrast, the same reaction but in the presence of HE gave γ,δ-unsaturated esters **7l** in 69 % yield. Thus, the cross-coupling between α-amino alkyl radical and allylic radical (path **III**) should operate in the reaction.

To further understand the reactivity of the radical intermediates in the cascade process, extensive kinetic experiments were performed with alkyl iodide **11**, butadiene, and imine **3a**. Figure 3 shows the concentrations of key intermediates and critical rate constants obtained from kinetic experiments (details are shown Supporting Information S10). From these data, several important conclusions can be achieved: 1) Even though the cross-coupling of alkyl radical **11a** and α-amino alkyl radical **4a** [$k_{\text{R im}}=2.1\times10^{9}\,\text{M}^{-1}\text{s}^{-1}$, Supporting Information S10.2, Eq. (18)] is more kinetically favored than its addition to butadiene ($k_{\text{R BD}}=9\times10^{4}\,\text{M}^{-1}\text{s}^{-1}$),[52] due to the much higher concentration of butadiene ($\overline{[\text{BD}]}\approx0.199$ M) than **4a** [$2.1\times10^{-7}\,\text{M}^{-1}$, Supporting Information S10.2, Eq. (16)], most **11a** underwent addition to butadiene rather than coupling [Eq. (1)]. In fact, no formation of **12** was observed under standard conditions; 2) the rate constant of allyl radical **11b** addition to butadiene ($k_{\text{poly}}=57\,\text{M}^{-1}\text{s}^{-1}$)[53] is much slower than its coupling with **4a** [$k_{\text{allyl im}}=7.2\times10^{8}\,\text{M}^{-1}\text{s}^{-1}$, Supporting Information S10.3, Eq. (27)]; therefore, most **11b** underwent cross-coupling with **4a** to produce **5d** rather than further polymerization [Eq. (2)]; 3) given that α-amino alkyl radical **4a** self-coupling ($k_{\text{im im}}=2.6\times10^{7}\,\text{M}^{-1}\text{s}^{-1}$, Supporting Information S8) is slower than that of transient allyl radical **11b** ($k_{\text{allyl allyl}}=1.2\times10^{9}\,\text{M}^{-1}\text{s}^{-1}$),[50,51] the "persistent radical effect" (PRE) should operate in the reaction.[54–59]

The ratio for instantaneous formation rate of **11b** and **12**

$$\frac{k_{\text{R\_BD}}[\mathbf{11a}][\overline{\text{BD}}]}{k_{\text{R\_im}}[\mathbf{11a}][\mathbf{4a}]}=\frac{9\times10^{4}\ \text{M}^{-1}\text{s}^{-1}\times(0.2+0.1)\ \text{M}/2}{2.1\times10^{9}\ \text{M}^{-1}\text{s}^{-1}\times2.2\times10^{-7}\ \text{M}}=29:1 \quad (1)$$

The ratio for instantaneous formation rate of **11d** and **5d**

$$\frac{k_{\text{poly}}[\overline{\text{BD}}]}{k_{\text{allyl\_im}}[\mathbf{4a}]}=\frac{57\ \text{M}^{-1}\text{s}^{-1}\times(0.2+0.1)\ \text{M}/2}{7.2\times10^{8}\ \text{M}^{-1}\text{s}^{-1}\times2.2\times10^{-7}\ \text{M}}=1:19 \quad (2)$$

In summary, we reported a strategically novel and practical synthesis of homoallylic amines through the single-electron mediated radical cross-coupling of allylic radicals and α-amino alkyl radicals. This method provides structurally diverse homoallylic amines from readily available materials. The synthetic value was further demonstrated by

the late-stage functionalization of numerous structurally complex bioactive skeletons.

Acknowledgements

This project is supported by the National Natural Science Foundation of China (2217010858), Open Research Fund of School of Chemistry and Chemical Engineering, Henan Normal University (2020YB03), the Key Scientific Research Projects of Higher Education Institutions in Henan Province (21A150002). We thank WATTCAS CHEM-TECH Co., Ltd. for kindly providing the photoreactors. We acknowledge Hefei Advanced Computing Center for computational resources.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Photoredox Catalysis · Umpolung · Radical Reactions · Dienes · Allylic Compounds

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Manuscript received: March 27, 2022
Accepted manuscript online: May 11, 2022
Version of record online: May 31, 2022