Regioselective Deaminative Allylation of Aliphatic Amines via Dual Cobalt and Organophotoredox Catalysis

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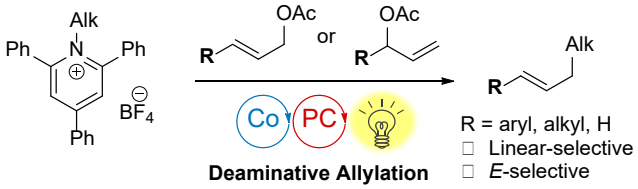
Supporting Information Placeholder



ABSTRACT: Despite the rapid progress in C–C-bond-forming reactions using Katritzky salts, their deaminative allylation remains a challenge. Inspired by the metallaphotoredox-catalyzed allylic substitution regime, here, we report the deaminative allylation of Katritzky salts via cobalt/organophotoredox dual catalysis. This cross-electrophile coupling enables regioselective allylation using a variety of allylic esters, overcoming the substrate limitations of reported protocols. Mechanistic studies indicate the involvement of a π-allyl cobalt complex as a radicalophile that mediates C–C bond formation.

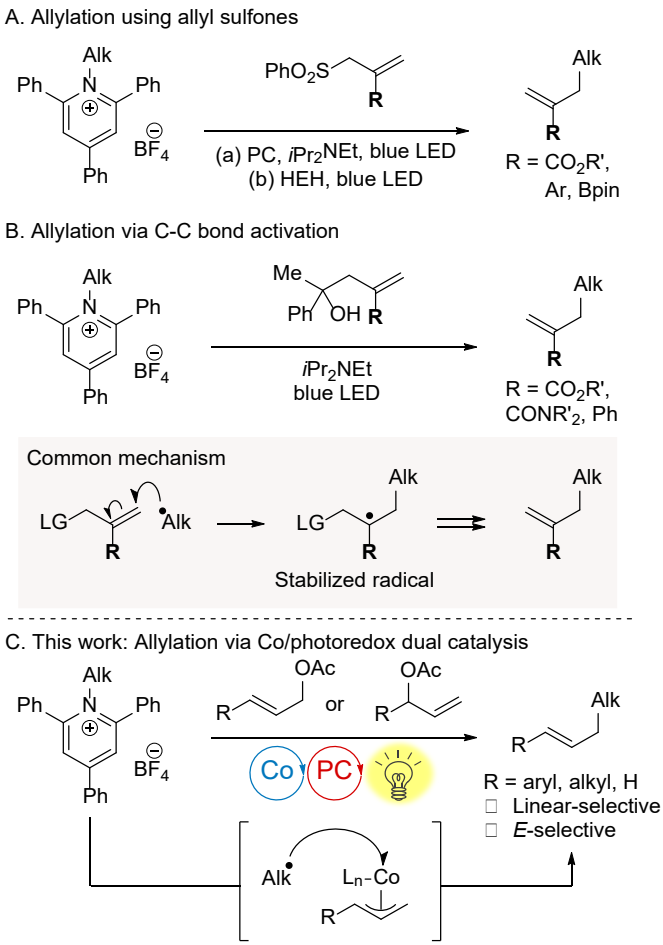
Alkyl amines are ubiquitous structural motifs in commercially available building blocks, drug candidates, and biomolecules. Therefore, the transformation of alkyl amines into further derivatized molecules provides privileged opportunities in chemical synthesis. Since the pioneering work of Watson in 2017,[1] the reactions of Katritzky salts, which are readily synthesized in one step via the condensation of a primary amine with a pyrylium salt, have received intense attention in synthetic chemistry.[2,3] However, in the area of C–C-bond-forming reactions,[4-5] methods to convert amino groups into allylic substituents remain limited.[6] Liu reported a photoredox-catalyzed desulfonylative allylation using allyl sulfones (Scheme 1A(a)),[6a] which was later elaborated into a photocatalyst-free process by Aggarwal (Scheme 1A(b)).[6b] By employing precisely designed homoallylic alcohols, Studer demonstrated a deaminative allylation via C–C bond cleavage (Scheme 1B).[6c] All these allylation reactions share a common mechanism: the alkyl radical reductively generated from the Katritzky salt directly undergoes addition to the olefin, providing the stabilized radical intermediate (Scheme 1, gray inset). Thus, a substituent at the *β*-position of the allylating reagents is required, resulting in limitations in the substrate scope.[7]

The combination of photoredox and transition-metal catalysis, or metallaphotoredox catalysis, is a rapidly growing research area.[8] Relevant to the present work, a radical-based approach to transition-metal-catalyzed allylic alkylation[9] has been recognized as a complementary strategy to established protocols employing soft carbanion equivalents. Furthermore, metallaphotoredox catalysis has been proved to be a viable strategy for cross-electrophile coupling,[10] enabling selective coupling of two different electrophiles without the use of a stoichiometric metal reductant.[11] Inspired by these precedents, we hypothesized that π-allyl Co complexes, which are key intermediates in Co/photoredox-catalyzed allylic substitution,[12-14] might serve as potent radicalophiles[15] and realize a new deaminative allylation with a broader scope in terms of allylating reagents (Scheme 1C).

Our reaction design for the deaminative allylation is outlined in Scheme 2. Under irradiation with visible light, the photoredox catalyst (PC) in its excited state (PC*) oxidizes an electron donor (D). The reduced photocatalyst ($PC^{\bullet-}$) and Co(II) undergo single electron transfer (SET), affording a Co(I) complex (Scheme 2A). Similarly, photoredox-induced SET between the reduced photocatalyst and Katritzky salts would afford an alkyl radical (Scheme 2B), which enters the dual Co and photoredox catalytic cycle (Scheme 2C). The low-valent Co(I) complex engages with an allylic acetate to form a π-allyl Co(III) intermediate. SET between the π-allyl Co(III) intermediate and the reduced photocatalyst yields a π-allyl Co(II) complex and the ground state photocatalyst. The alkyl radical from the Katritzky pyridinium salt is intercepted by the π-allyl Co(II) complex. Reductive elimination proceeds to afford the desired cross-coupled product and regenerate the Co(I) catalyst.

The results of our initial examination of the desired cross-electrophilic coupling based on this reaction proposal are summarized in Table 1. We attempted the deaminative

Scheme 1. Deaminative Allylation Reactions



Scheme 2. Reaction Design

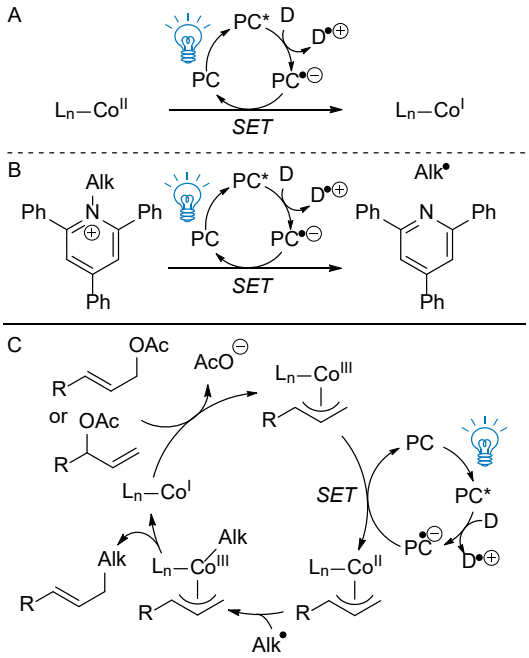
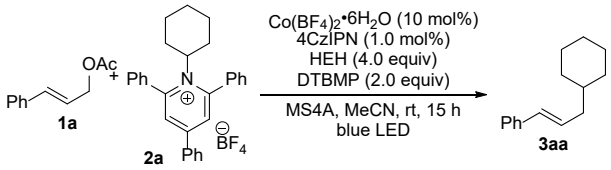
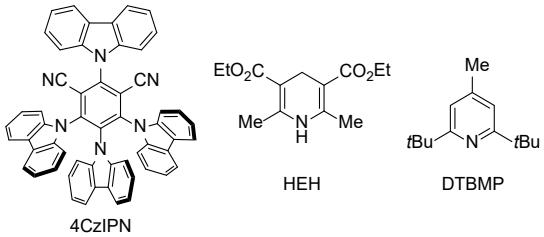


Table 1. Optimization of Reaction Conditions[a]



entry	Deviation from above	yield (%)[b]
1	None	79[c]
2	$CoBr_2$ (99.99% purity)	63
3	$Ir(ppy)_2(dtbbpy)PF_6$	30
4	2.0 equiv HEH	59
5	**1a** (2.0 equiv) and **2a** as the limiting reagent	72[c]
6	Mn or Zn (4.0 equiv) instead of 4CzIPN and HEH at 40 °C without blue LED irradiation	0



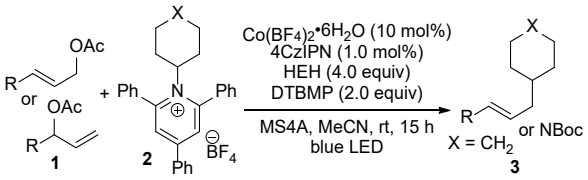
[a]**1a** (0.050 mmol), **2a** (2.0 equiv), $Co(BF_4)_2 \cdot 6H_2O$ (10 mol%), 4CzIPN (1.0 mol%), HEH (4.0 equiv), DTBMP (2.0 equiv), and MS4A (200 g/mol) in MeCN (0.050 M to **1a**) at room temperature for 15 hours under blue LED irradiation unless otherwise noted. Regioselectivity and *E*/*Z* ratios were determined using GC-MS or ^{1}H NMR analysis of the crude mixture. For all cases, the linear/branched ratio was >20:1 and the *E*/*Z* ratio was >20:1. [b]Determined by ^{1}H NMR. [c]Isolated yield in 0.15 mmol scale.

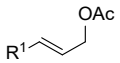
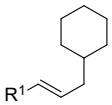
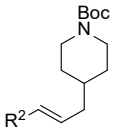
allylation of cyclohexyl Katritzky salt **2a** using (*E*)-cinnamyl acetate **1a** as the allylating reagent. After intensive investigation of the reaction conditions, the combination of 10 mol% of $Co(BF_4)_2 \cdot 6H_2O$, 1.0 mol% of 4CzIPN as the organic PC, 4.0 equivalents of Hantzsch ester (HEH) as the electron donor, and 2.0 equivalents of 2,6-di-*tert*-butyl-4-methylpyridine (DTBMP) as the base in the presence of MS4A in acetonitrile under blue LED irradiation provided the best result, furnishing **3aa** in 79% isolated yield with an excellent linear selectivity and *E*-selectivity (Table 1, entry 1).[16] Interestingly, no additional ligands for Co were required for the reaction. Comparable results were obtained when $CoBr_2$ with 99.99% purity on a trace metal basis was used, clearly indicating that the reaction is mediated by cobalt and not by other metallic impurities (entry 2). The organophotocatalyst 4CzIPN proved to be more suitable for this metallaphotoredox system than iridium-centered photocatalysts (entry 3). The reaction proceeded in synthetically useful yield when the amount of HEH was reduced to 2.0 equiv (entry 4). It is noteworthy that comparable yield of **3aa** was observed when **2a** was used as a limiting reagent (entry 5). Metal reductants Mn and Zn did not promote the reaction, suggesting that photoredox conditions are uniquely effective for this type of cross-electrophilic allylation (entry 6).[17]

With the optimized conditions in hand, we investigated the substrate scope of this reaction with respect to allylating reagents (Table 2). In all the cases examined, the allylated products were obtained with exclusive linear selectivity and high *E*-selectivity. From linear aromatic allyl esters, the products were obtained in good yield

irrespective of steric or electronic effects on the arene ring (**3aa–3ja**). Also, from branched aliphatic allyl acetates, linear products were obtained (**3kb–3mb**[18]), indicating that the regioselectivity of the products is not affected by the structure of the allylating reagents.[19] An unsubstituted allylic acetate was also applicable to the deaminative reaction, delivering the terminal alkene **3nb** in 66% yield.

Table 2. Reaction Scope with Respect to Allylating Reagents[a]

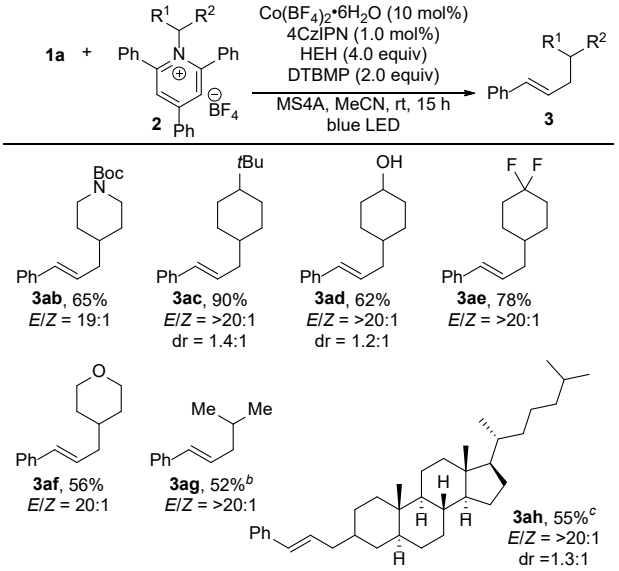


entry	allylating reagent **1**	product **3**	yield (%)	E/Z[b]
				
1	R^1 = Ph (**1a**)	**3aa**	79 (84)[c]	>20:1
2	R^1 = 4-Me-C_6H_4 (**1b**)	**3ba**	79	>20:1
3	R^1 = 3-Me-C_6H_4 (**1c**)	**3ca**	85	>20:1
4	R^1 = 2-Me-C_6H_4 (**1d**)	**3da**	83	>20:1
5	R^1 = 4-*t*Bu-C_6H_4 (**1e**)	**3ea**	83	>20:1
6	R^1 = 4-OMe-C_6H_4 (**1f**)	**3fa**	60	14:1
7	R^1 = 4-CF_3-C_6H_4 (**1g**)	**3ga**	73	>20:1
8	R^1 = 4-F-C_6H_4(**1h**)	**3ha**	79	>20:1
9	R^1 = 4-Cl-C_6H_4 (**1i**)	**3ia**	81	>20:1
10[d]	R^1 = 2-naphthyl (**1j**)	**3ja**	71	4.6:1
				
11	R^2 = Me (**1k**)	**3kb**	76	>20:1
12	R^2 = Et (**1l**)	**3lb**	81	>20:1
13	R^2 = Cy (**1m**)	**3mb**	75	>20:1
14	R^2 = H (**1n**)	**3nb**	66	-

[a]**1** (0.15 mmol), **2** (2.0 equiv), $Co(BF_4)_2 \cdot 6H_2O$ (10 mol%), 4CzIPN (1.0 mol%), HEH (4.0 equiv), DTBMP (2.0 equiv), and MS4A (200 g/mol) in MeCN (0.050 M to **1**) at room temperature for 15 hours under blue LED irradiation. Regioselectivity was determined using GC-MS or ^{1}H NMR analysis of the crude mixture. For all cases, the linear/branched ratio was >20:1. Isolated yields. [b]Determined by ^{1}H NMR analysis of the isolated product. [c]1.0 mmol scale. [d]**2** (1.6 equiv).

The substrate scope in terms of Katritzky pyridinium salts was also examined (Scheme 3). In essence, high regio- and geometrical selectivity was observed in all the cases examined (**3ab–3ah**). When diastereomerically pure Katritzky salt **2d** was employed as a starting material, almost no diastereoselectivity was observed in **3ad**, indicating the intermediacy of the alkyl radical.[20] An acyclic alkyl unit, namely, an isopropyl group, also participated in the cross-electrophilic allylation (**3ag**). The late-stage deaminative allylation of a steroid derivative successfully proceeded (**3ah**),

Scheme 3. Reaction Scope with Respect to Katritzky Salts[a]

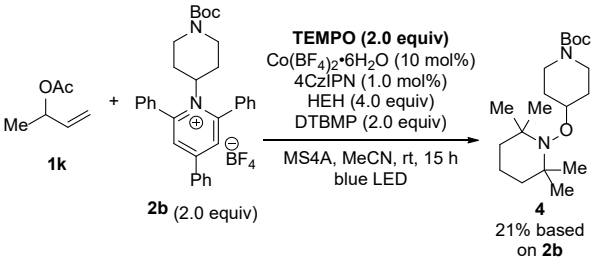


[a]As in **Table 2** (0.15 mmol scale). Regioselectivity was determined by GC-MS or ^{1}H NMR analysis of the crude mixture. For all cases, the linear/branched ratio was >20:1. Isolated yields. E/Z ratios were determined by ^{1}H NMR analysis of the isolated product. [b]GC yield. [c]0.10 mmol scale.

demonstrating the potential applicability of this approach in the derivatization of complex amines. [21]

To support our mechanistic proposal, the intermediacy of alkyl radicals was assessed by performing the reaction in the presence of TEMPO (Scheme 4). In this case, the TEMPO-trapped alkyl radical **4** was unequivocally obtained, and no cross-coupled product **3kb** was observed. This result, along with the loss of stereochemistry in **3ad** (Scheme 3), supports the involvement of an alkyl radical generated from the Katritzky salt.[22]

Scheme 4. Intermediacy of alkyl radicals[a]



[a]As in **Table 2** (0.050 mmol scale). ^{1}H NMR yield.

In summary, we have developed a cobalt/photoredox-catalyzed deaminative cross-electrophilic coupling of allylic acetates and Katritzky pyridinium salts. The dual catalytic system accommodated both linear and branched allylic esters irrespective of the nature of the substituents on the allyl unit, highlighting the synthetic advantages of the present system compared to known deaminative allylations. The intermediacy of a π-allyl Co complex is proposed based on preliminary mechanistic studies, which shed new light on metallaphotoredox-catalyzed allylic substitution reactions. Comprehensive investigations into the applicability of the

Co/photoredox-catalyzed allylation protocol to other radical-based bond-forming reactions, as well as further mechanistic studies including quantum chemical calculations,[23] are currently under investigation in our group.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/@@@@@@.
Experimental details and copies of spectroscopic data of the synthesized compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(15) Capture of alkyl radicals by π-allylcobalt complexes has been proposed in previous reports in the literature. For examples, see 10c and 14b.
(16) The reaction did not occur in the absence of cobalt salt, 4CzIPN, or light. See Table S1 in the Supporting Information for details.
(17) See section 3 in the Supporting Information for additional investigations of the reaction conditions including the effect of other cobalt salts and ratio of **1** and **2**.
(18) This system showed superior performance for the synthesis of **3mb** compared to the reported nickel/photoredox-catalyzed protocol. See Scheme S1 in the Supporting Information for details.
(19) The convergence in the regioselectivity is in line with the intermediacy of π-allyl cobalt complexes. See also Scheme S2 in the Supporting Information for additional investigations.
(20) See Scheme S3 in the Supporting Information for details.
(21) Installation of primary alkyl group was not successful under the developed conditions. See section 4-3 of the Supporting Information for details.
(22) The TEMPO adduct **4** was also obtained when the linear allylic ester **1a** was used instead of **1k**. See Scheme S4 in the Supporting Information for details.
(23) See section 6-3 in the Supporting Information for preliminary investigations using DFT.