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Regioselective Single-Electron Tsuji−Trost Reaction of Allylic Alcohols: A Photoredox/Nickel Dual Catalytic Approach

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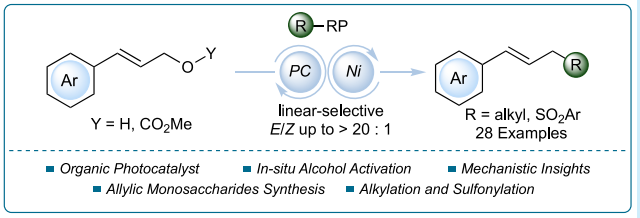
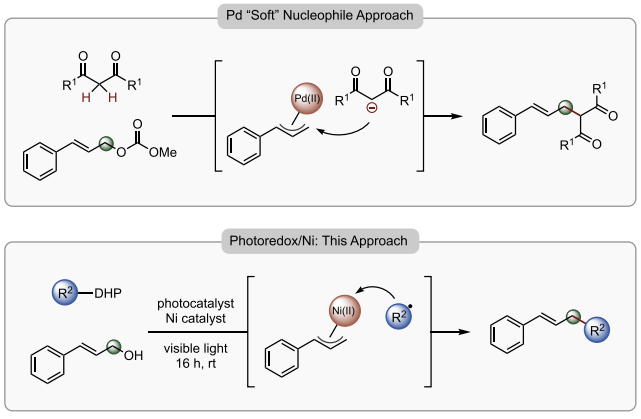
Supporting Information

ABSTRACT: A radical-mediated functionalization of allyl alcohol derived partners with a variety of alkyl 1,4-dihydropyridines via photoredox/nickel dual catalysis is described. This transformation transpires with high linear and *E*-selectivity, avoiding the requirement of harsh conditions (e.g., strong base, elevated temperature). Additionally, using aryl sulfinate salts as radical precursors, allyl sulfones can also be obtained. Kinetic isotope effect experiments implicated oxidative addition of the nickel catalyst to the allylic electrophile as the turnover-limiting step, supporting previous computational studies.



Historically, palladium catalysis has proven to be a powerful means by which C−C bonds can be forged in a regioselective manner.[1] To date, there have been numerous reports utilizing palladium catalysis for coupling allyl alcohol substrates with "soft" (pK_a < 25) enolate nucleophiles (Scheme 1).[2] Other "soft" nucleophiles (e.g., nitrogen- and oxygen-based nucleophiles) have also been employed,[3] and significant advances have been accomplished in the field with the development of stereoselective transformations. By comparison, although known, transformations using "hard" nucleophiles, which coordinate to metal catalysts before reductive elimination, are less studied and often require harsh conditions and/or functional group intolerant reagents.[4]

Scheme 1. Radical-Based Addition to π-Allylnickel Intermediates



In an effort to expand the nucleophile scope of the Tsuji−Trost reaction, reductive allylation strategies have been explored by numerous groups, enabling the employment of "hard" nucleophiles.[5] Notably, Tunge and co-workers pioneered the concept of a radical-based approach.[5a] In this paradigm, utilizing photoredox catalysis, the excited state photocatalyst undergoes a single-electron oxidation of a carboxylate anion substrate. Upon decarboxylation, a carbon-centered alkyl radical is generated and captured by a Pd(II) π-allyl complex, forming a Pd(III) intermediate that reductively eliminates to afford the cross-coupling product.

Although numerous coupling methods using various palladium catalysts have been reported during the past decades, significantly fewer methods have been disclosed utilizing the group 10 base metal, nickel.[6] In addition to the advantage of cost-effectiveness, recent studies have shed light on the complementary reactivity that can arise between nickel and palladium. For example, Fu et al. successfully carried out nickel-catalyzed, enantioselective cross-coupling between allyl chlorides and alkylzinc reagents.[7] Nickel/photoredox dual-catalyzed alkylation of vinyl epoxides has also been developed, with strong evidence of an inner-sphere mechanism.[8]

Inspired by previous work, a Ni-based radical approach to functionalize allylic electrophiles was sought. Herein, alkylation of allyl alcohol derived motifs has been demonstrated by using 4-alkyl 1,4-dihydropyridines (DHPs)[9] as latent radical precursors. Both allyl carbonates and *in situ* activated allyl alcohols have proven effective in the reaction. To highlight the new chemical space, the disclosed reaction was employed for

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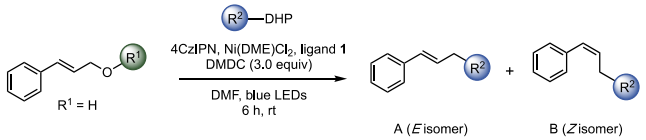
the synthesis of allylated monosaccharides. Heteroatomic radical sources, such as aryl sulfinates, were also used as partners in this reaction. Finally, from a mechanistic standpoint, various factors influencing regioselectivity (e.g., the ligand on the nickel center) were demonstrated, in addition to kinetic isotope effect studies that support oxidative addition as the turnover-limiting step.

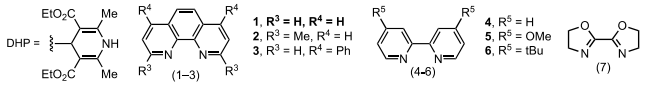
At the outset of the synthetic studies, optimization was conducted using isopropyl DHP as the radical precursor, and the best results were observed with allyl methyl carbonate as the electrophile. This result provided an opportunity to use dimethyl dicarbonate (DMDC) as an activator, which had proven to be compatible in previous studies (Table 1, entry 2).[10] To confirm the necessity of photocatalyst 4CzIPN (2,4,5,6-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene), nickel catalyst, and light, control experiments were performed (Table 1, entries 3–5). For each control experiment, no desired product was observed. Using high-throughput experimentation, further optimizations were carried out to identify a set of suitable reaction conditions (e.g., photocatalyst, Ni source, solvent, and ligand; see Supporting Information for further details). To investigate the regioselectivity (linear/branched) and stereoselectivity (E/Z) of the reaction further, a series of bipyridine ligands were screened (entries 6–12). Most of the ligands led to highly selective linear product formation, although further investigations showed a substrate dependence on the linear/branched selectivity (see Supporting Information for further details). 1,10-Phenanthroline was identified as a suitable ligand, rendering almost exclusively E-selective product with a high yield (entry 6). Further reactions were therefore carried out using the preformed complex, Ni(phen)Cl_2, as the precatalyst.

Table 1. Control Studies and Ligand Optimization[a]



entry	deviation from standard conditions	yield (%)	E/Z ratio (A:B)
1	**R^1 = CO_2Me, R^2 = *i*-Pr, No DMDC**	**83**	**>20:1**
2	**none, R^2 = *i*-Pr**	**66**	**>20:1**
3	no light, R^2 = *i*-Pr	trace	–
4	no photocatalyst, R^2 = *i*-Pr	0	–
5	no Ni catalyst, R^2 = *i*-Pr	0	–
6	**none, R^2 = Cyclohexyl**	**87**	**>20:1**
7	Ni **2**, R^2 = Cyclohexyl	26	7:1
8	Ni **3**, R^2 = Cyclohexyl	66	>20:1
9	Ni **4**, R^2 = Cyclohexyl	8	*E* only
10	Ni **5**, R^2 = Cyclohexyl	10	1.3:1
11	Ni **6**, R^2 = Cyclohexyl	73	1:1.2
12	Ni **7**, R^2 = Cyclohexyl	21	2:1

[a]Reaction conditions: Allyl alcohol or carbonate (1.0 equiv, 0.1 mmol), DHP (1.5 equiv, 0.15 mmol), 4CzIPN (3 mol %), Ni catalyst (5 mol %), DMDC (3.0 equiv), and DMF (0.1 M) thoroughly degassed followed by stirring near blue LEDs for 16 h. Overall yields and regioselectivity were determined by GC, and E/Z isomer ratios were determined by NMR.



With suitable conditions in hand, an investigation of the stereoelectronic effects of the aryl moiety on the reaction was begun. Similar to reactivity trends reported for Tsuji–Trost reactions,[11] electron-withdrawing groups (**2d**) did not significantly decrease overall reaction efficiency (Figure 1).

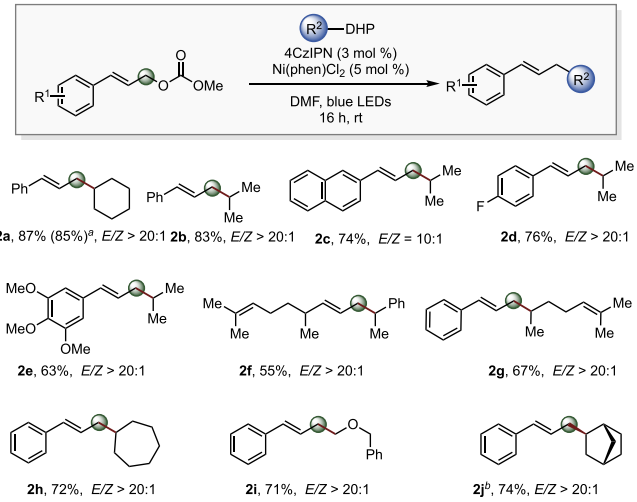


Figure 1. Exploring alkylation scope with carbonates. Reaction conditions: Allyl methyl carbonate (1.0 equiv, 0.30 mmol), DHP (1.5 equiv, 0.45 mmol), 4CzIPN (3 mol %), Ni(phen)Cl_2 (5 mol %), and DMF (3 mL, 0.1 M) thoroughly degassed followed by stirring near blue LEDs for 16 h. E/Z ratios were determined by ^{1}H NMR of the isolated product. [a] 1 mmol scale. [b] *dr* > 20:1.

Conversely, electron-donating moieties (**2e**) led to slightly diminished yields (63%). Furthermore, exploration of alkyl-substituted electrophilic partners was of interest. Notably, **2f** was successfully isolated from the corresponding dienol derivative, albeit in lower yield. As a general note, alkyl-substituted allyl carbonates suffered from diminished reactivity and, in some cases, no reactivity. This occurrence may result from a decrease in electrophilicity, hampering π-allyl nickel complex formation.

Next, attention was focused on incorporating a wider range of DHPs, beginning with cyclic carbon-centered radicals (**2a**, **2h**, and **2j**). Functional groups such as alkenes (**2g**) and activated hydrogens (**2i**) are also compatible, providing good yields of the desired products. A 1 mmol scale reaction was also attempted for **1a**, and a comparable 85% yield was obtained.

Although allyl carbonates are both commercially available and easily accessed, conditions were sought to improve step economy by alkylating allylic alcohols in a single-step, one-pot reaction. With DMDC identified as the most efficient activator, the scope of this approach was examined with various cinnamyl alcohol derivatives and functionally diverse DHPs (Figure 2). Comparing previous yields with allyl carbonates and the newly developed allyl alcohol conditions, comparable results were achieved (**2a** and **2b** versus **3a** and **3b**). Therefore, investigation of the scope of the functional group breadth for the allyl alcohol and DHP pieces was continued. Similar compatibility for substitutions about the aryl motif was observed (**3c**–**3g**). Nitrogen- (**3k**) and oxygen-containing (**3i**) heterocyclic DHPs were successfully incorporated into the reaction manifold, with moderate to good yield. Notably, a hydroxymethyl radical was successfully applied in this transformation, with a 57% yield of β-hydroxyl product **3l** isolated.

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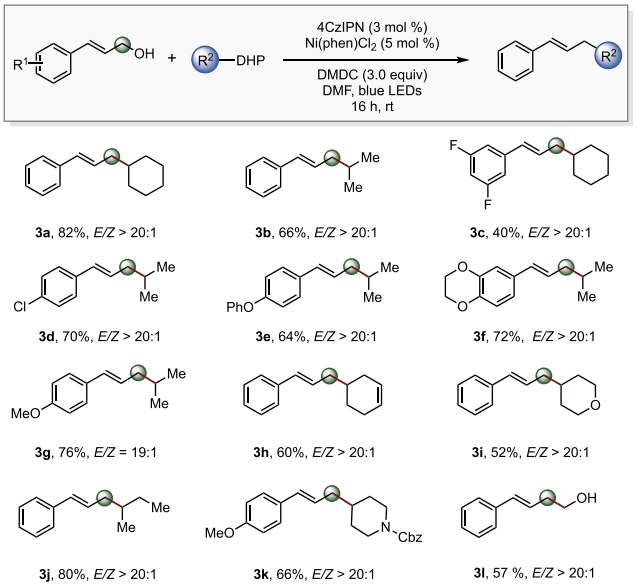
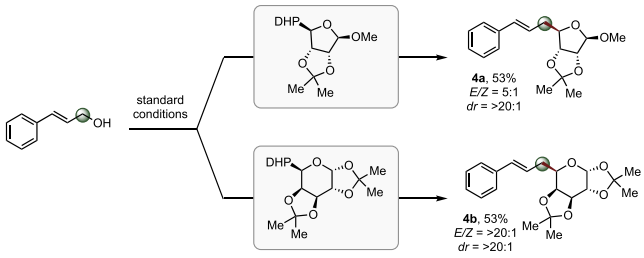


Figure 2. Coupling allyl alcohols with DHPs. Reaction conditions: Allyl alcohol (1.0 equiv, 0.30 mmol), DHP (1.5 equiv, 0.45 mmol), 4CzIPN (3 mol %), $Ni(phen)Cl_2$ (5 mol %), DMDC (3.0 equiv, 0.90 mmol), and DMF (3 mL, 0.1 M) thoroughly degassed followed by stirring near blue LEDs for 16 h. *E*/*Z* ratios were determined by ^1H NMR of the isolated product.

To broaden the scope and demonstrate the utility of this alkylation of allyl alcohol pro-electrophiles, attention was turned toward more challenging scaffolds, specifically monosaccharides.[12] Functionalization of carbohydrates has proven to be pivotal in many fields, including labeling technologies,[13] cyclodextrin-mediated catalysis,[14] and carbohydrate drug development.[15] Notably, few *C*-allyl glycoside syntheses have been reported, most of which are restricted to *C*-1 alkylation of the carbohydrate and further limited to unsubstituted propenyl electrophiles.[16] Upon treating both furanose (**4a**) and pyranose (**4b**) DHPs under the standard reaction conditions, the nontraditional *C*-allyl glycosides were isolated in acceptable yields and excellent regio- and diastereoselectivities (Scheme 2). Notably, structurally similar organometallic saccharide partners cannot be accessed owing to rapid β-alkoxy elimination. During the course of these studies, Mazet and co-workers published a complementary approach, using a one-pot isolation/C−O arylation strategy with a glycoside-derived allyl electrophile and Grignard reagents, rendering similar motifs albeit with less functional group tolerance anticipated in the aryl subunit.[17]

Scheme 2. Direct Allylation of Monosaccharides[a]



[a]Reaction conditions: Allyl alcohol (1.0 equiv, 0.30 mmol), DHP (1.5 equiv, 0.45 mmol), 4CzIPN (3 mol %), $Ni(phen)Cl_2$ (5 mol %), DMDC (3.0 equiv, 0.90 mmol), and DMF (3 mL, 0.1 M) thoroughly degassed, followed by stirring near blue LEDs for 16 h. *E*/*Z* ratios were determined by ^1H NMR of the isolated product.

To extend the functional group repertoire of allyl alcohol derived electrophiles further, other carbon- or heteroatom-centered radical sources were tested. Although toolboxes such as alkyltrifluoroborates,[18] Ikylsilicates,[19] and *N*-centered radicals[20] were incompatible, aryl sulfinate salts were coupled with allyl carbonates to generate allyl aryl sulfones (Figure 3).[21]

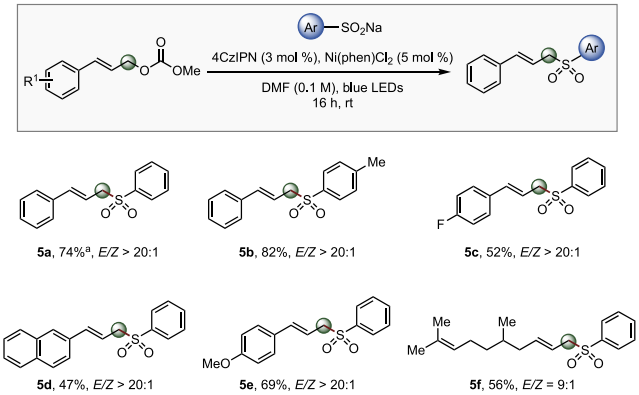


Figure 3. Demonstrating latent radical breadth. Reaction conditions: Allyl methyl carbonate (1.0 equiv, 0.30 mmol), DHP (1.5 equiv, 0.45 mmol), 4CzIPN (3 mol %), $Ni(phen)Cl_2$ (5 mol %), and DMF (3 mL, 0.1 M) thoroughly degassed followed by stirring near blue LEDs for 16 h. *E*/*Z* ratios were determined by ^1H NMR of the isolated product. [a] Sample was contaminated with hexane, EtOAc, and H_2O.

Both electron-rich (**5e**) and electron-deficient (**5c**) allyl carbonates performed well, and an aliphatic allyl carbonate was applicable with good regioselectivity (**5f**), providing the desired product in 56% yield with a 9:1 *E*/*Z* ratio.

Finally, to shed some light on the mechanism, several preliminary experiments were carried out, including Stern−Volmer quenching experiments. Although significant fluorescent quenching with alkyl DHPs has been previously reported,[22] neither $Ni(phen)Cl_2$ nor allyl methyl carbonate quenched the fluorescence of 4CzIPN. This finding suggests that the reductive generation of the allylic radical is not occurring by interaction with the photocatalyst or the low-valent Ni species. To determine the turnover-limiting step, we investigated the kinetic isotope effect by comparing reaction rates of α-deuterated cinnamyl methyl carbonate vs its nondeuterated form. A significant secondary isotope effect (k_H/k_D = 1.15 ± 0.07) was observed, indicating a change in hybridization of the allyl carbonate substrate in the turnover-determining step, suggesting oxidative addition of allyl carbonate to the nickel complex as the turnover-limiting step. The regioselectivity would then most likely be dictated by energy differences between the corresponding transition structures involved in the reductive elimination step, which is consistent with previous computational studies.[8,23] Based on these results and previous mechanistic studies, a plausible mechanism is proposed (Scheme 3): upon excitation, the photocatalyst oxidizes the radical precursors to generate alkyl or sulfonyl radicals, which are subsequently captured by Ni(0). Allyl methyl carbonate then oxidatively adds to the Ni(I) intermediate to generate the active Ni(III) species, followed by reductive elimination to form C_{sp^3}−C_{sp^3} or C_{sp^3}−S bonds. The resulting Ni(I) species is reduced by the radical anion of 4CzIPN, closing both catalytic cycles.

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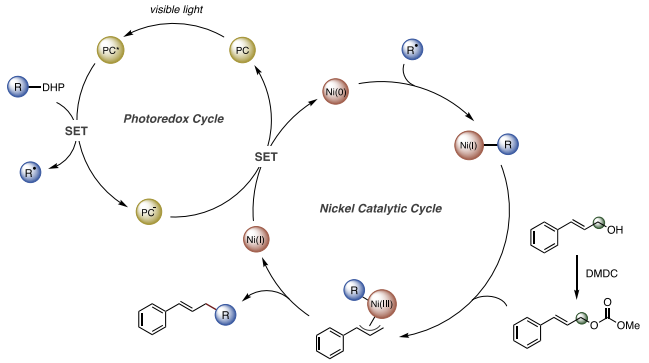
Scheme 3. Putative Radical-Based Mechanism



In conclusion, the *in situ* activation and radical-mediated alkylation of cinnamyl alcohol scaffolds in a photoredox/nickel-mediated transformation has been disclosed. During the course of these studies, reaction conditions (e.g., ligand, solvent) to favor the regioselective linear product and *E*-isomer have been pinpointed. Furthermore, the range of "nucleophilic" partners has been expanded. By either prefunctionalization or *in situ* activation with DMDC, radical precursors such as alkyl DHPs and aryl sulfinates can be engaged in the reaction, rendering alkylated or sulfonylated species in a highly stereoselective and regioselective manner. Notably, monosaccharide-derived DHPs have been coupled in the reaction to prepare nontraditional *C*-allylated glycosides. As a complementary approach for allyl-alkyl/sulfone coupling, the disclosed transformation extends the scope of allylic functionalization, while at the same time extending the range of Ni-catalyzed photoredox transformations, providing a useful synthetic tool for elaboration of readily available electrophilic partners.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02473.

Detailed experimental procedures, mechanistic investigations, characterization data, and NMR spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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