Ligand-Enabled Carboamidation of Unactivated Alkenes through Enhanced Organonickel Electrophilicity

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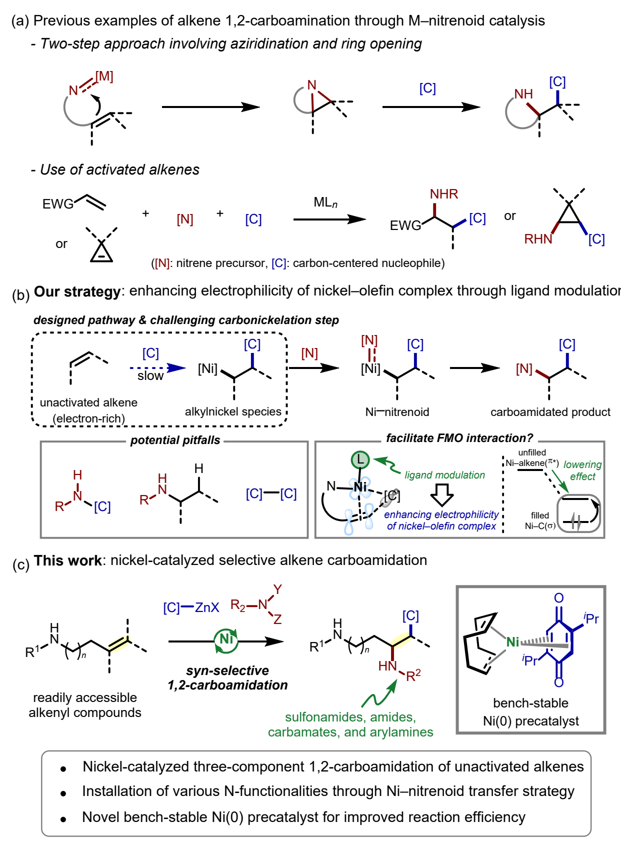
ABSTRACT: Catalytic carboamination of alkenes is a powerful synthetic tool to access valuable amine scaffolds from abundant and readily available alkenes. Although a number of synthetic approaches have been developed to achieve the rapid buildup of molecular complexity in this realm, installation of diverse carbon and nitrogen functionalities onto unactivated alkenes remains underdeveloped. Here we present a ligand design approach to enable nickel-catalyzed three-component carboamidation that is applicable to a wide range of alkenyl amine derivatives via a tandem process involving alkyl migratory insertion and inner-sphere metal–nitrenoid transfer. With this method, various nitrogen functionalities can be installed into both internal and terminal unactivated alkenes, leading to differentially substituted diamines that would otherwise be difficult to access. Mechanistic investigations reveal that the tailored Ni(cod)(BQ^{iPr}) precatalyst modulates the electronic properties of the presumed π-alkene–nickel intermediate via the quinone ligand, leading to enhanced carbonickelation efficiency across the unactivated C=C bond. These findings establish nickel's ability to catalyze multicomponent carboamidation with high efficiency and exquisite selectivity.

Introduction

Olefin difunctionalization is an attractive synthetic strategy for building two distinct chemical bonds in a single operation, enabling rapid access to high-value chemicals.[1-8] Among these transformations, alkene carboamination, in which a nitrogen substituent and a carbon substituent are installed across an olefinic π-system, is particularly appealing to obtain synthetically versatile amine products.[9,10] Traditional carboamination methods have relied on two-component strategies, where two of the three reaction components are integrated into the same molecule.[11-26] For example, intramolecular azacyclization of alkenyl amines is well established under palladium,[27-30] copper,[31,32] and nickel catalysis.[33,34] In addition, several research groups have independently demonstrated that carboamination of alkenes or 1,3-dienes can be achieved using specifically designed bifunctional coupling partners.[35-43] In contrast, three-component approaches remain in their infancy, with the bulk of prior work focused on electronically activated alkenes[44-50] or strained cyclopropenes,[51,52] mainly due to difficulties in controlling regioselectivity and suppressing formation of undesired side products without substrate activation. C–H activation strategies towards alkene carboamination have also been reported, albeit with the carbon coupling partner scope limited to *ortho*-C(aryl)–H bonds adjacent to specific directing groups.[53-56] Recently, an alternative approach involving directed umpolung carboamination of unactivated alkenes using nitrogen-based electrophiles has emerged as a promising means to overcome these limitations.[57-60] However, this approach has been limited to alkyl-amine-derived coupling partners and has not been extended to other synthetically versatile N-functionalities, such as (sulfon)amides and carbamates. This, in turn, limits the scope of accessible products.

Continuing our research efforts toward the development of versatile olefin difunctionalization processes, we sought to achieve selective 1,2-carboamination of unactivated alkenes by taking advantage of metal–nitrenoids as key intermediates. This

Scheme 1. Strategies for the Selective 1,2-Carboamination of Unactivated Alkenes



approach would bypass one of the two steps in the classical sequence of olefin aziridination and subsequent ring-opening with carbon nucleophiles (Scheme 1a).[61-77] Rovis and co-workers elegantly demonstrated that direct carboamination of α,β-unsaturated carbonyls and cyclopropenes can be achieved to access either α-amino acid derivatives or cyclopropyl amines under Rh-catalysis.[78,79] Complementing these reports, three-component carboamination that is applicable to a wide range of *unactivated olefins using earth-abundant metal catalysts* would be highly appealing. The key to success in this realm would be to prevent the formation of undesired side products that arise due to slow carbonickelation of electron-rich unactivated alkenes with carbon nucleophiles (Scheme 1b).[80] Indeed, carbon-centered nucleophiles are known to react directly with electrophilic metal–nitrenoids via two-component C–N coupling,[81] which could derail olefin difunctionalization. In addition, hydroaminated side product could also form if the nitrogen-based electrophile reacts solely with the alkene substrate.[82] Moreover, slow migratory insertion of the alkene into the metal–carbon bonds would result in dimerization of the carbon coupling partner without alkene engagement.[83] We envisioned that, upon modification of the ligands, the unfilled π* orbital energy of the presumed nickel–olefin intermediate could be tuned to enhance its electrophilicity, thereby facilitating the orbital interaction with the Ni–C fragment during migratory insertion into an unactivated C=C bond. We predicted that such a tailored catalyst system would avoid the potential pitfalls described above, enabling distinctive selectivity toward the desired multicomponent carboamination.

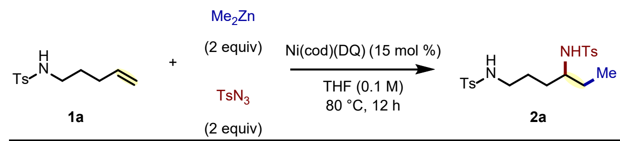
Herein, we present the first example of catalytic three-component carboamidation of unactivated alkenes via Ni–nitrenoid catalysis, which furnishes differentially substituted diamine products in a concise manner (Scheme 1c). A bench-stable Ni(cod)(quinone) catalyst was optimized to facilitate carboamidation of diverse mono-, di-, and tri-substituted olefins. Furthermore, this transformation proceeds with high *syn*-stereoselectivity and provides facile access to a wide range of valuable N-functionalities that are unattainable by conventional alkene carboamination methods. Integrated experimental and computational studies reveal that the principal role of the electron-deficient quinone ligand is to lower the absolute energies of the nickel–olefin complex frontier molecular orbitals, enhancing coupling efficiency between the carbon nucleophile and the alkene and enabling efficient multicomponent carboamidation.

Results and Discussion

Reaction Development. Based on our prior work on three-component Ni-catalyzed coupling of alkenyl amine derivatives with organometallic nucleophiles and alkyl amine electrophiles,[57] we envisioned that we could access a broader scope of potential diamine products through engaging nickel–nitrenoid catalysis. To test the feasibility of our hypothesis, we commenced our study by evaluating a series of nickel catalysts for the proposed three-component carboamination with 4-methyl-*N*-(pent-4-en-1-yl)benzenesulfonamide (**1a**) as the model substrate (Table 1). The reaction was attempted using dimethylzinc and 4-methylbenzenesulfonyl azide (TsN_3)[84] as alkyl nucleophile and nitrene precursor, respectively. In particular, we envisioned that an organic azide would be an attractive nitrene precursor since the amination would then proceed in the absence of external oxidants that could decompose the organozinc coupling partner.[81]

As shown in Table 1, we were pleased to find that 1,4-disulfonamide **2a** was obtained in 45% yield when 15 mol % of bench-stable Ni(cod)(DQ)[85] (cod = 1,5-cyclooctadiene, DQ = duroquinone) catalyst was used at 80 °C in tetrahydrofuran

Table 1. **Optimization of Reaction Parameters**[a]



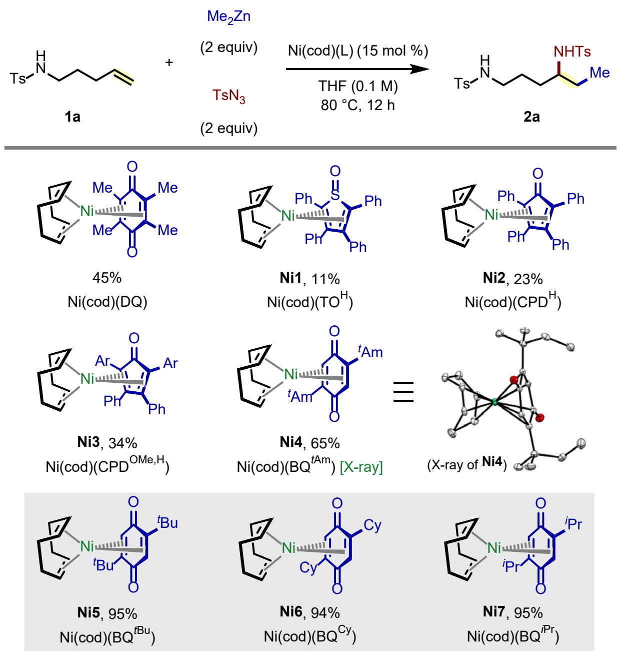
Entry	Deviation from the standard conditions	Yield of **2a** (%)
1	none	45
2	$NiBr_2$·glyme as a catalyst	12 (25)[b]
3	$Ni(acac)_2$ as a catalyst	<5
4	$Ni(cod)_2$ as a catalyst	12
5	$Ni(^{4\text{-}t\mathrm{Bu}}stb)_3$ as a catalyst	11
6	w/o Ni catalyst	<2
7	cyclohexane as solvent	21
8	MeCN as solvent	15
9	0.1 M to 0.2 M	28
10	7.5 mol % of Ni(cod)(DQ)	35
11	w/o glovebox	42
12	$NiBr_2$·glyme (15 mol %) as a catalyst with DQ (40 mol %) (w/o glovebox)	40[b]

[a]Reactions were run on a scale of 0.05 mmol, and yields were measured by ^1H NMR spectroscopy with 1,1,2-trichloroethane as an internal standard. [b]PhMe (0.1 M) solvent was

(THF) solvent (entry 1). Notably, carboamidation occurred with excellent regioselectivity (>19:1) to install the new nitrogen functionality at the δ-position with respect to the sulfonamide directing group, and the potentially competing regioisomer was not observed. By comparison, $NiBr_2$·glyme catalyst was an ineffective precatalyst for this carboamidation reaction in both THF and PhMe solvent (entry 2). Similarly, $Ni(acac)_2$ did not give the desired carboamidated product **2a** under otherwise identical conditions (entry 3). $Ni(cod)_2$ exhibited poor reactivity, suggesting that the duroquinone ligand plays an important role in the designed process (entry 4). In addition, a sixteen-electron Ni(0) complex bearing *trans*-stilbene-derived ligands, which was recently revealed to be an effective Ni(0) source,[86] was low-yielding (entry 5), with significant amounts of unreacted starting material **1a** remaining.

Control experiments revealed that reaction did not occur in the absence of the Ni(cod)(DQ) catalyst (entry 6). Furthermore, replacement of THF solvent with cyclohexane or MeCN led to a substantial decrease in reaction efficiency (entries 7 and 8, see the Supporting Information for details). When the concentration of the solution was increased, lower product yield was obtained (entry 9). Reduced loading of the Ni catalyst led to diminished yield (entry 10). Importantly, the bench-stable Ni(cod)(DQ) catalyst allowed the reaction to be performed without an inert-atmosphere glovebox yet with similar results (see the Supporting Information for details). In addition, $NiBr_2$·glyme in combination with DQ ligand could be used in place of Ni(cod)(DQ) with only slightly diminished yield, reinforcing the importance of the quinone ligand.

Table 2. Catalyst Evaluation[a]



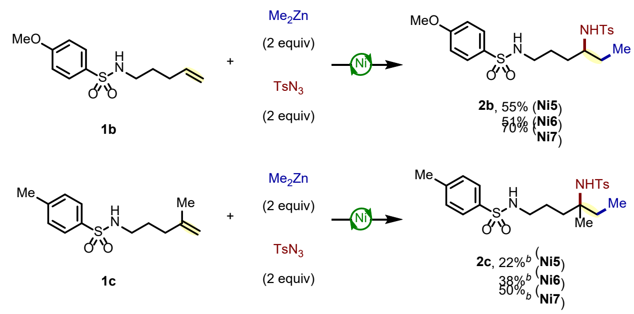
[a]Reactions were run on a scale of 0.05 mmol, and yields were measured by ^{1}H NMR spectroscopy with 1,1,2-trichloroethane as an internal standard. [b]Isolated yield. Ar = 4-OMe(C_6H_4).

The poor reactivity of most conventional nickel catalysts suggested that the initial migratory insertion step to form the corresponding alkylnickel intermediate was inefficient in the absence of the appropriate ligand (see the Supporting Information for details). Considering that the electrophilicity of nickel centers is closely related to the electronic character of the ancillary ligands,[87] the decisive role of duroquinone in promoting this three-component 1,2-carboamidation of alkenyl sulfonamides led us to hypothesize that modification of the π-accepting properties of the ligand would facilitate carbonickelation with a carbon nucleophile by enhancing electrophilicity of the unactivated C=C bond (Scheme 1b).

Given that electron-deficient diene-type ligands were previously observed to form well-defined 18-electron Ni(cod)(L) complexes,[87] we considered modified quinone ligands as well as other readily tunable diene ligands, including thiophene-S-oxides and cyclopentadienones. As depicted in Table 2, a wide range of Ni complexes bearing functionalized diene ligands were prepared and examined as precatalysts in the carboamidation of **1a**. Compared to DQ, tetraphenyl thiophene-S-oxide (**Ni1**) and tetraarylcyclopentadienone (**Ni2** and **Ni3**) ligands were lower-yielding, with large amounts of unreacted starting material **1a** remaining (see the Supporting Information for details). In stark contrast, 1,4-benzoquinone (BQ) ligands bearing alkyl substituents at the C2 and C5-position dramatically improved yields (**Ni4**–**Ni7**). Whereas Ni catalyst bearing highly bulky bis(*tert*-amyl) groups (**Ni4**) was less effective, catalysts with less bulky and less electron-donating alkyl substituents provided **2a** in excellent yields (**Ni5**–**Ni7**).[88]

Considering that all three catalysts **Ni5**–**Ni7** performed similarly with the standard substrate **1a**, we next sought to identify which catalyst would be most generally applicable across different alkenes (Scheme 2). Comparing the results with two additional substrates with a more electron-donating sulfonamide

Scheme 2. Comparative Studies with Electron-Rich Alkenes[a]

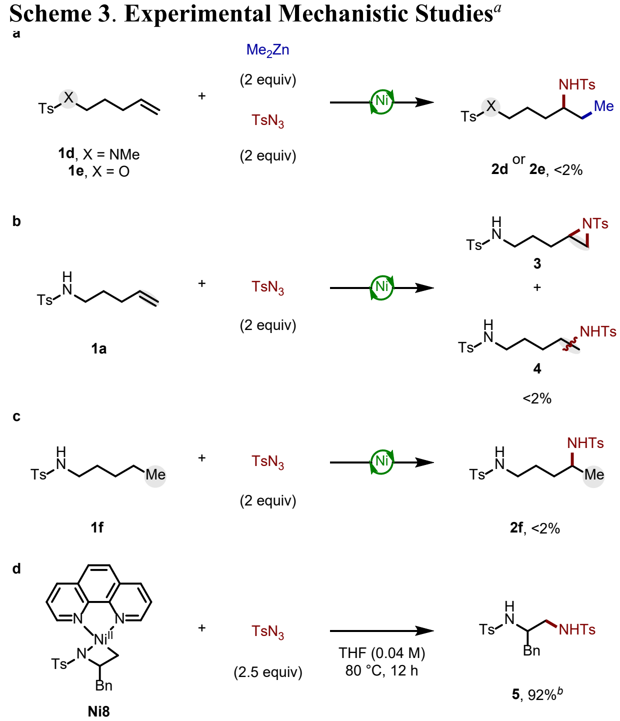


[a]Reactions were run on a scale of 0.05 mmol, and yields were measured by ^{1}H NMR spectroscopy with 1,1,2-trichloroethane as an internal standard. [b]PhMe (0.1 M) was used as

(**1b**) and more highly substituted alkene (**1c**) revealed that BQ^{iPr} ligand complex **Ni7** provided the highest yields in both cases. A plausible explanation based on our mechanistic model is that the less electron-donating isopropyl groups lead the ligand to be more electron-withdrawing, which is especially important in the migratory insertion step with more electron-rich substrates.

Experimental Investigations of the Reaction Pathways. Intrigued by the ligand-enabled reactivity, we next sought to interrogate the mechanistic details of this catalytic system. A series of control experiments were first conducted, as shown in Scheme 3. The observation that carboamidation did not take place with *N*-methylated sulfonamide (**1d**) or bishomoallyl aryl sulfonate (**1e**) reveals the importance of the N–H moiety of the substrate in the catalytic reaction, consistent with X-type coordination (Scheme 3a).[57] Mindful of the potential for olefin aziridination under these conditions,[89-91] we also scrutinized the

Scheme 3. Experimental Mechanistic Studies[a]

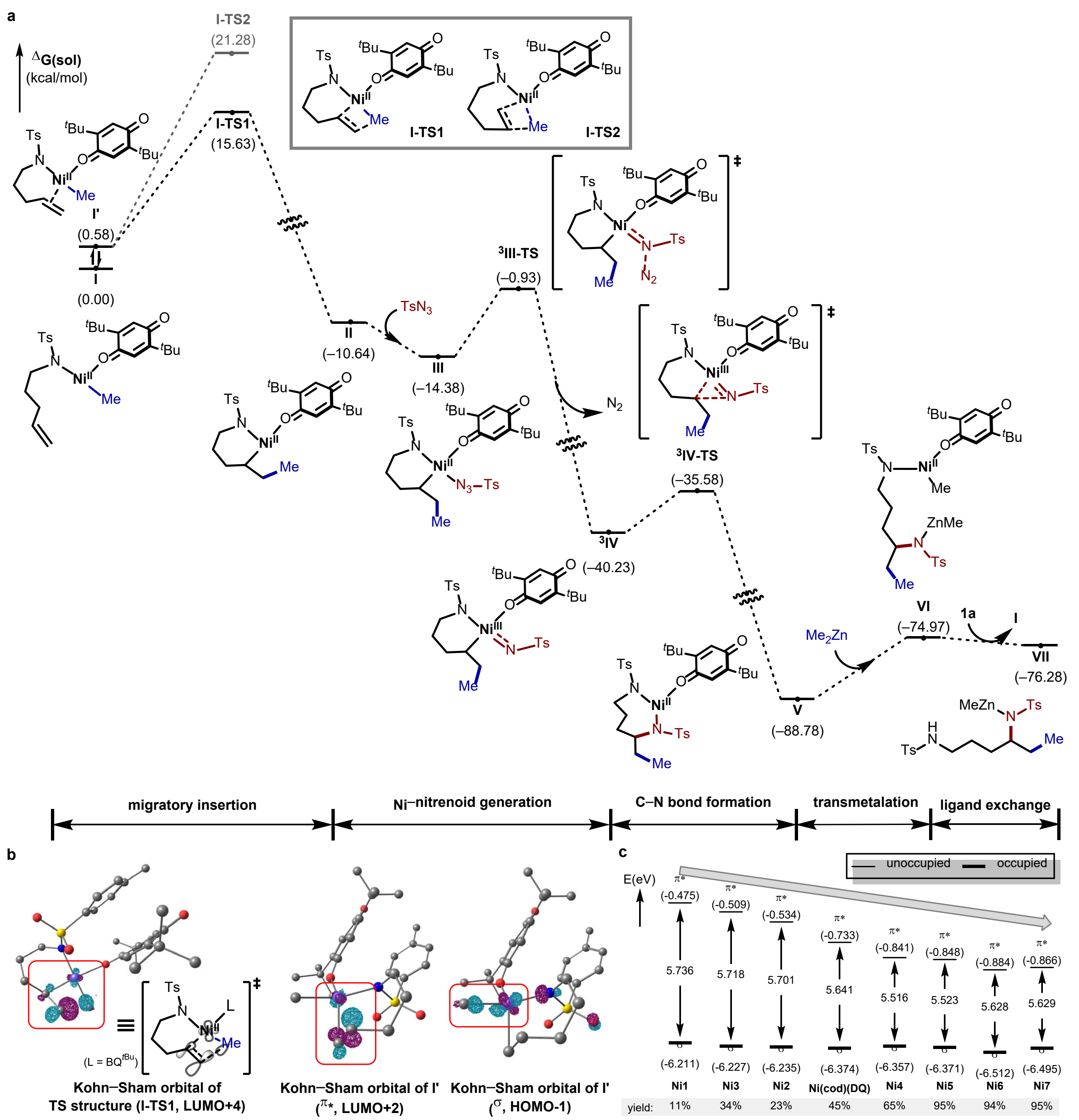


[a]Reactions were run on a scale of 0.05 mmol with **Ni7** (15 mol %) as a catalyst, and yields were measured by ^{1}H NMR spectroscopy with 1,1,2-trichloroethane as an internal standard. [b]Isolated yield

possibility of initial aziridination followed by ring-opening involving a carbon nucleophile (Scheme 3b). However, aziridination of **1a** did not take place under the standard reaction conditions in the absence of nucleophile. Chang and co-workers reported that nickel-catalyzed intermolecular C(sp^3)–H amidation of carboxamides can be promoted by a bidentate directing group.[92] To test the viability of a pathway involving hydroalkylation[93] followed by C–H amidation, we treated 4-methyl-*N*-pentylbenzenesulfonamide **1f** with TsN_3 under the standard conditions yet found no detectable quantities of amidated products (Scheme 3c). To acquire additional insights into the C–N bond-forming step in the present carboamidation reaction, we conducted stoichiometric amidation reactions with independently synthesized Ni(II) complex (**Ni8**),[94] as shown in Scheme 3d. When complex **Ni8** was mixed with TsN_3 (2.5 equiv) in THF, the corresponding amidated product **5** was obtained in 92% yield. This finding establishes the competency of an metalacyclic alkylnickel(II) intermediate in C–N bond formation.

Computational Studies. To gain further insight into the mechanism of this catalytic carboamidation and elucidate the role of the ligand in enhancing reaction efficiency, energy profiles of the proposed pathways were evaluated by density functional theory (DFT) calculations (Scheme 4a).[95] Due to the potentially hemilabile nature of the quinone-type ligands,[96-98] a careful conformational analysis was performed. The O-bound geometries are calculated to be energetically more stable than η^2-olefin-binding modes (>7kcal/mol), presumably due to steric

Scheme 4. Computational Analysis of the Nickel-Catalyzed Three-Component Carboamidation



repulsion with the *tert*-butyl substituents at the C2 and C5-position of the ligand (see the Supporting Information for details). Based on the experimental mechanistic studies on the Ni-catalyzed carboamidation (Scheme 3), the present reaction is assumed to start with a catalyst–substrate adduct **I**, where alkenyl sulfonamide **1a** is bound to the coordinatively unsaturated nickel species. Upon coordination of the alkene to the nickel center, the resultant π-alkene complex **I'** traverses **I-TS1** via migratory insertion to deliver the methyl group to the terminal alkene position with a 15.1 kcal/mol barrier, thus generating the six-membered nickelacycle **II**.[99] In contrast, the competing carbonickelation at the internal position of alkene (**I-TS2**) is calculated to be less accessible, thus corroborating the high experimentally measured regioselectivity (Table 1). Subsequent binding of TsN_3 as the nitrenoid source takes place to lead to the corresponding adduct **III**. Importantly, adduct **III** is able to form the triplet Ni(III)–nitrenoid species ^{3}**IV** by extruding N_2 through a transition state ^{3}**III-TS**, with a 13.5 kcal/mol kinetic barrier. We then postulate that the highly electrophilic nature of the Ni–nitrenoid fragment allows for favorable interaction with a Ni–C bond to form intermediate **V**. Indeed, TS calculations revealed that the inner-sphere C–N coupling traverses ^{3}**IV-TS** with a low barrier of 4.7 kcal/mol. Finally, the alkylnickel(II) species **VI** is regenerated in situ by the dimethylzinc reagent, and the desired carboamidated product **VII** is released through the subsequent ligand exchange with another alkenyl sulfonamide substrate **1a**.

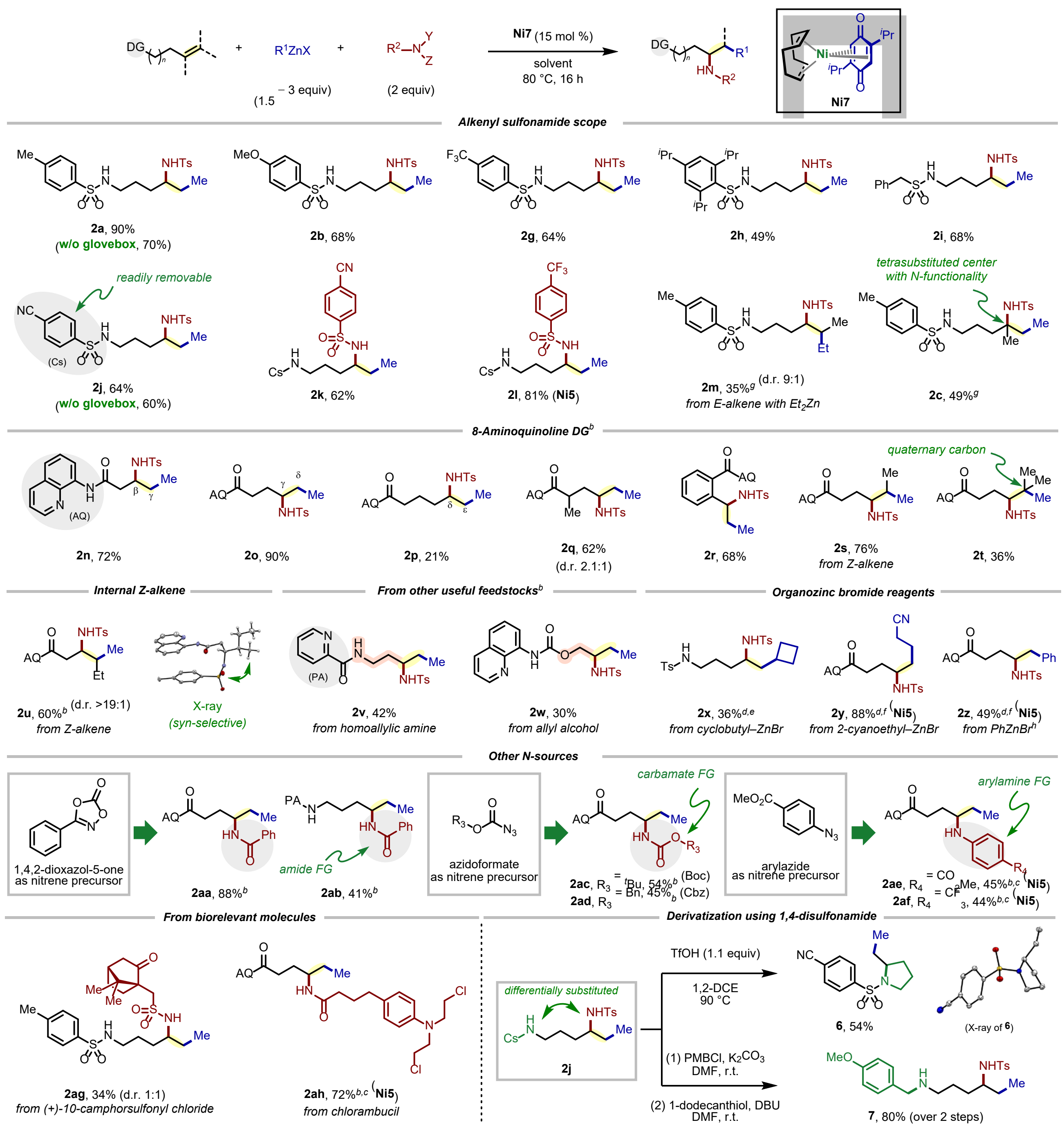
With experimental evidence that yield is strongly influenced by the ancillary ligand (Table 2), we sought to understand the relationship between the electronic properties of the π-alkene–nickel intermediate and those of the diene ligand. Our hypothesis was that ligands that generated a more electron-poor π-alkene–nickel intermediate would exhibit enhanced reactivity in the key migratory insertion. First, a Kohn–Sham orbital analysis was conducted to investigate the electronic structure of the nickel species during the key carbonickelation process (Scheme 4b). Examination of the transition state **I-TS1** revealed that the LUMO+4 is responsible for the alkyl migratory insertion into the C=C bond. In addition, it was found that the π-alkene and Ni–C fragments of the LUMO+4 of the transition state exhibit similar shapes and orientation to LUMO+2 (unfilled Ni–alkene π*) and HOMO-1 (filled Ni–C σ) of the nickel π-alkene intermediate **I'**, suggesting participation in the migratory insertion process (see the Supporting Information for details).

We next examined the influence of different diene ligands on the frontier orbital energies of filled σ and unfilled π* orbitals of the putative π-alkene–nickel intermediates for several of the precatalysts tested experimentally (Scheme 4c). Analysis of the absolute energies of the relevant frontier molecular orbitals (FMOs) reveals an intriguing trend that the coordinated ligand substantially perturbs the FMO energies and further that the energy difference (specifically the π* orbital level of the presumed π-alkene–nickel intermediates) correlates to the product yield. 2,5-Disubstituted quinone ligands (**Ni4**–**Ni7**) show the lowest energies. Presumably the additional carbonyl group compared to other ligands studied leads to more electron-withdrawing character. This absolute energies of the unfilled π* orbitals are lowered more than those of the filled σ orbitals. In particular, the two best performing catalysts bearing secondary alkyl groups (**Ni6** and **Ni7**) displayed the lowest π* orbital energies among all catalysts examined. This computational outcome strongly suggests that our mechanistically guided approach toward quinone ligand design strategy is fruitful in the context of challenging multicomponent catalytic couplings that proceed via organonickel migratory insertion.

Substrate Scope. We next explored the generality of the current approach to access 1,2-carboamidated scaffolds employing a range of unactivated alkenes, nitrene precursors, and organozinc reagents (Scheme 5). To our delight, this protocol was effective over a broad range of alkenyl sulfonamide substrates irrespective of electronic and steric properties of the sulfonyl substituents, thus furnishing 1,4-disulfonamides **2a**, **2b**, and **2g–2j** with excellent regioselectivity. It should be mentioned that the bench-stable nature of precatalyst **Ni7** allows the reaction to be performed without an inert-atmosphere glovebox, furnishing carboamidated products **2a** and **2j** in good yields (70% and 60%, respectively). In particular, a 4-cyanobenzenesulfonamide (Cs) is an attractive directing group, since the Cs group in the differentially substituted diamine products can be subsequently converted to diverse N-functionalities (*vide infra*). Moreover, we were pleased to observe that the method tolerates other sulfonyl azides, including stronger electron-withdrawing cyano- and CF_3 groups, giving 1,4-disulfonamides **2k** and **2l**, respectively. Considering that catalytic three-component carboamination of sterically demanding disubstituted alkenes is known to be more challenging,[57] we wondered whether our newly developed catalytic system would be applicable in these setting, in which case it would offer access to more diverse diamine scaffolds with distinctive substitution patterns. Intriguingly, the reaction of alkenyl sulfonamide bearing internal (*E*)-olefin was found to afford the desired carboamidated product **2m** with high diastereoselectiviy, which contains two stereogenic centers at the δ,ε-position to the sulfonamide moiety. As we examined, 1,1-disubstituted alkene underwent carboamidation to give the desired product **2c**, demonstrating the ability of this approach to forge a tetrasubstituted carbon center bearing a nitrogen functional group.[100]

Next, we investigated whether our newly developed catalytic carboamidation approach could be applied to other alkene substrates. To this end, we examined a series of easily accessible alkenyl amides having an aminoquinoline (AQ) directing group with increasing number of methylene linkers. Pleasingly, this carboamidation tolerates β,γ- (**2n**), γ,δ- (**2o**), and δ,ε-alkenes (**2p**) to provide the corresponding carboamidated products, albeit in low yield with three methylene linkers. Moreover, a variety of unactivated terminal and internal γ,δ-alkenes underwent carboamidation under the standard conditions to selectively provide the corresponding diamine scaffolds (**2q–2s**). In general, inner-sphere catalytic olefin difunctionalization of tri-substituted alkenes is challenging as it involves formation of hindered bonds.[58] Gratifyingly, in this case, trisubstituted alkene also delivered the corresponding product (**2t**) with excellent regioselectivity, albeit in moderate yield. It is worth mentioning that carboamidation took place in a highly *syn*-selective manner, as evidenced by X-ray crystallographic analysis of **2u**.

Scheme 5. General Applicability of the Carboamidation[a]



[a]Reaction conditions: substrate (0.1 mmol), TsN_3 (2 equiv), Me_2Zn (2 equiv), and Ni catalyst (15 mol %) in THF (1 mL, 0.1 M) at 80 °C for 16 h. [b]PhMe/DMF (0.1 M, 1:1 v/v) solvent was used. [c]1.5 equiv of Me_2Zn was used. [d]3.0 equiv of RZnBr was used. [e]THF (0.25 M) was used. [f]PhMe (0.2 M) was used. [g]PhMe (0.1 M) was used. [h]PhZnBr was prepared from PhMgBr and anhydrous $ZnBr_2$.

Building on these successful results, we sought to extend this strategy toward other synthetically versatile alkene feedstocks, thereby allowing molecular flexibility of starting materials. To our delight, we found that a homoallylic amine bearing a picolinamide (PA) directing auxiliary was also a viable type of substrate in the current catalytic system to produce a desired 1,3-diamine **2v**. Of note, carboamidation was also found to take place with an allyl-alcohol-derived carbamate, as shown in the case of **2w**. Not only can dialkylzinc be employed as a nucleophile but readily available and less reactive organozinc bromide reagents also participate in the reaction, allowing introduction of synthetically useful carbogenic groups, such as cyclobutyl (**2x**), 2-cyanoethyl (**2y**), and phenyl (**2z**).

Next, we wondered whether our newly developed catalytic system could be used with other nitrenoid precursors. To our delight, an amide group could be introduced by the use of 3-phenyl-1,4,2-dioxazol-5-one as a robust acylnitrene precursor (**2aa** and **2ab**).[101,102] In addition, reactions with azidoformates were also successfully applied to the synthesis of **2ac** and **2ad**, which contain a *tert*-butyl (Boc) and benzyl carbamate (Cbz) moiety. Notably, these carbamate functionalities can be readily deprotected, thus leading to the corresponding primary amines.[103] Moreover, aryl azides could also be used to access arylamine-substituted products (**2ae** and **2af**). It should be mentioned that the installation of sulfonamide, amide, carbamate, and arylamine functional groups into unactivated olefinic double bonds is difficult to achieve with previously reported carboamination methods that do not involved a nitrenoid mechanism.[57-60]

Synthetic Applications. The applicability of our current protocol was further explored by employing pharmaceutically relevant molecules. For example, (+)-10-camphorsulfonyl azide could be employed, thus providing a corresponding carboamidated product bearing a terpenoid ketone moiety (**2ag**). Moreover, the reaction of chlorambucil-derived dioxazolone took place smoothly to afford **2ah** in good yield. Synthetic utility of the obtained differentially substituted 1,4-disulfonamide products was briefly examined. Desulfonamidative cyclization of **2j** was effective to provide pyrrolidine **6**, and its solid structure was unambiguously confirmed by X-ray crystallography. Additionally, the Cs protecting group can be utilized in N-diversification, due to its precedented ease of removal by the use of 1-dodecanethiol.[104] Intriguingly, a two-step sequence of *N*-alkylation and chemoselective Cs group deprotection provided *N*-alkyl-*N'*-Ts-protected amine **7** in high yield.

Conclusions

In summary, we present the first example of a catalytic three-component *syn*-carboamidation of unactivated alkenes via a tandem process involving alkyl migratory insertion and inner-sphere Ni–nitrenoid transfer. In particular, the tailored Ni(cod)(quinone) catalyst platform grants access to structurally diverse diamines that are unattainable by the conventional alkene carboamination methods, with excellent compatibility of various substitution patterns and exceptional regioselectivity. Integrated experimental and computational analysis indicate that electronic modulation of key π-alkene–nickel species plays a pivotal role, inducing an alkyl migratory insertion event on the unactivated olefinic double bond for improved carboamidation reactivity. The current method is anticipated to streamline access a wide range of diamine compounds, which are highly sought after in the synthetic and medicinal chemistry communities.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures; characterization data; spectra for all new compounds; crystallographic data; Cartesian coordinates of all computed structures (PDF)
Crystallographic data for **Ni4**
Crystallographic data for **2u**
Crystallographic data for **6**

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Notes

The authors declare no competing financial interest.

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