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| Journal: | *Organic Chemistry Frontiers* |
| Manuscript ID | QO-RES-02-2021-000223.R4 |
| Article Type: | Research Article |
| Date Submitted by the Author: | 05-May-2021 |
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# Copper-Catalyzed Asymmetric Allylic C-H Amination of Alkenes using *N*-arylhydroxylamines

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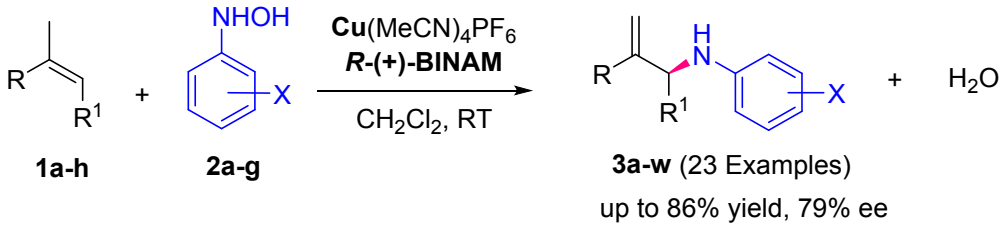
**Abstract**: The first copper-catalyzed asymmetric allylic C-H amination of alkenes using *N*-arylhydroxylamines as aminating agents is disclosed. Enantioselective C-N bond formation reactions are promoted in the presence of $Cu(MeCN)_4PF_6$ as a pre-catalyst and *R*-(+)-BINAM as a chiral ligand. This protocol delivers chiral *N*-aryl allylamines in good yields and enantioselectivities. Data regarding the effect of ligand structure and solvents on the efficiency and enantioselectivity of amination reactions are presented. Furthermore, isolation of metal-ligand-nitroso complex, ESI-MS reaction monitoring analysis and the computational calculations provided additional insights on mechanistic pathway. DFT modeling of the reaction pathway suggests that the stereoselectivity is determined in the conversion of (BINAM)Cu(PhNO)($\eta^2$-alkene)$^+$ to (BINAM)Cu(N-Arylhydroxylamine) via a concerted, asynchronous transition state for C-N bond formation. This catalytic approach features operational simplicity, high product yields with good enantioselectivity, and no byproducts except water.

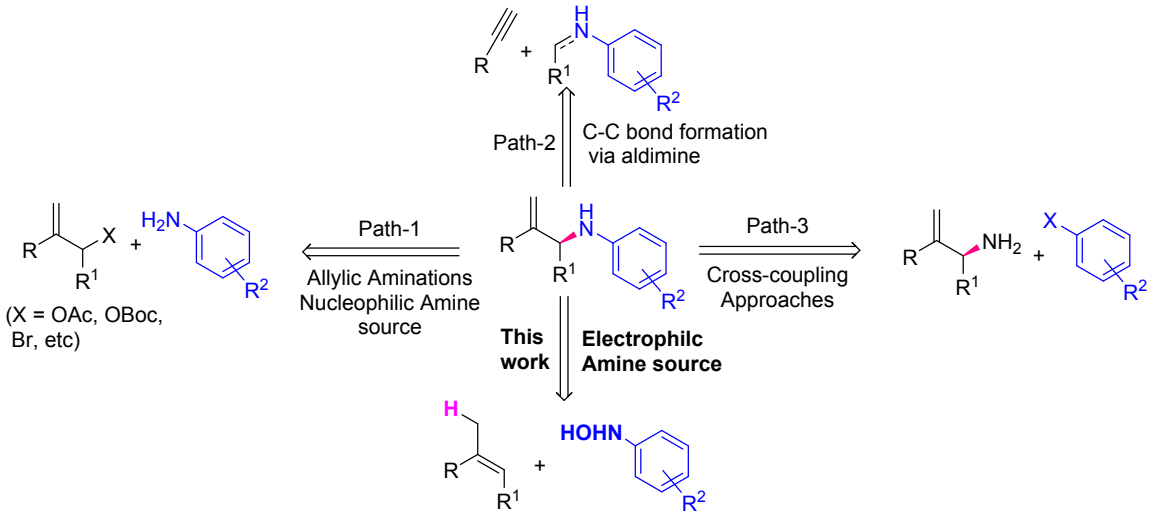



**Introduction**: Chiral allylamines are currently the convenient and vital compounds in organic chemistry and their synthesis is an important industrial and synthetic goal.[1] Often these allylamines are transformed into a range of useful products by oxygenation, amination, reduction, oxidation or metathesis reactions of the double bond. Thus, chiral allylamines have been used as starting

materials for the synthesis of numerous compounds such as chiral amine drugs, chiral amino acids, different alkaloids, and carbohydrate derivatives.[2] Remarkably, the chiral amine frameworks are present in an estimated 45% of pharmaceutical drug candidates. [3] Therefore, considerable effort has been directed toward the asymmetric synthesis of chiral allylamines. In this regard, catalytic enantioselective allylic substitution has emerged as a useful synthetic tool to access chiral amines.[4] However, these traditional approaches rely on nucleophilic substitution of allylic esters or halides, which require a pre-functionalization at the respective allylic-carbon atom. Recently, catalytic enantioselective allylic C–H amination methods[5] have attracted significant attention from the synthetic community due to the unique atom and step economies of such processes.[6]

Most of these methods are associated with the use of complex olefin substrates, catalysts of expensive metals such as Pd, Ir, Rh and toxic chiral phosphine ligands. Hartwig et. al. developed a one-pot sequential dual catalytic approach for allylic substitution which involves Pd-catalyzed allylic C–H bond oxidation to form linear allyl benzoates, followed by Ir-catalyzed allylic substitution.[5d] Additionally, these reported methods use either carbamates or chiral sulfonimidamides[7] as nitrogen reagents and are not useful for obtaining *N*-aryl allylamines in enantioselective fashion. Dauban et. al. developed an interesting Rh-catalyzed asymmetric C-H sulfonimidoyl amidation of alkenes, that requires use of a hypervalent iodine reagent as an oxidizing agent.[7b] Aromatic amines with a stereocenter α to the nitrogen atom are important structural motifs in a number of biologically active compounds.[8] Thus, a procedure to prepare optically active aromatic amines, in particular, an enantioselective route to *N*-aryl allylamines would be useful because of the dual amine and alkene functionality.

Despite the progress in catalytic asymmetric allylic amination, the synthesis of chiral *N*-aryl allylamines through allylic amination has proven to be very challenging and remains largely unexplored. Aromatic amines have not been used commonly in allylic amination,[9] presumably because of their lower nucleophilicity than the more commonly used benzylamine or stabilized anionic nitrogen nucleophiles.[10] A few allylic amination reactions use anilines as a nucleophilic substrate to react with either allylic halides, alcohols or esters as electrophilic substrates. (Scheme 1, path 1) [6i,11] Alternatively, reaction of metal coordinated aryl aldimines with alkynes produce chiral allylamines.[12] (path 2) Additionally, cross-coupling of chiral allylamines and haloarenes have also been reported.[13] (path 3) However, a direct enantioselective allylic *N*-aryl amination reaction using simple alkene has not been reported.




**Scheme 1**. Alternate approaches for making chiral N-aryl allylamines

**Results and Discussion**:

Following the seminal work by Sharpless on stoichiometric amination,[14] several catalytic allylic amination reactions have been developed using ArNHOH, ArNO and $ArNO_2$ as aminating agents by us and others.[15] We have studied mechanistic aspects of this reaction including, isolation of catalytic intermediates, kinetic experiments and computational studies.[16] We have isolated an iron azodioxide and Cu(I)-nitrosoarene complexes, implicated as reactive intermediates in metal catalyzed allylic *N*-aryl amination reactions.[17] Although the non-asymmetric version of this allylic *N*-aryl amination has been known for two decades, surprisingly, no asymmetric variant has been reported to date. Based on our experience on allylic C-H amination chemistry, we hypothesized that the kinetically controlled C-N bond formation would be feasible, in the presence of a suitable metal pre-catalyst and a chiral ligand, if either the alkene or the intermediate nitrosoarene binds to metal center during C-N bond formation. The asymmetric environment or the chiral pocket around the metal center would then favor the selective formation of one of the allylic amine enantiomers. Our hypothesis was examined systematically, and we developed the first catalytic enantioselective synthesis of chiral *N*-aryl allylamines using *N*-arylhydroxylamines and simple alkenes as reaction partners. (Scheme 1) In parallel to this study, we have developed an approach for catalytic asymmetric α-amination of carbonyl compounds.[18]

For initial experimentation, the reaction of 2-methyl-2-pentene (**1b**) and *N*-phenylhydroxylamine (**2a**) was selected as a model amination reaction (Table 1) and screened a

set of privileged chiral ligands[19] with 1:2 metal-ligand ratio using our previously established reaction conditions.[16] (Scheme 1)

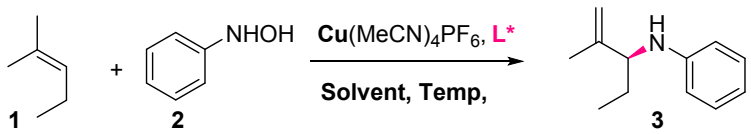
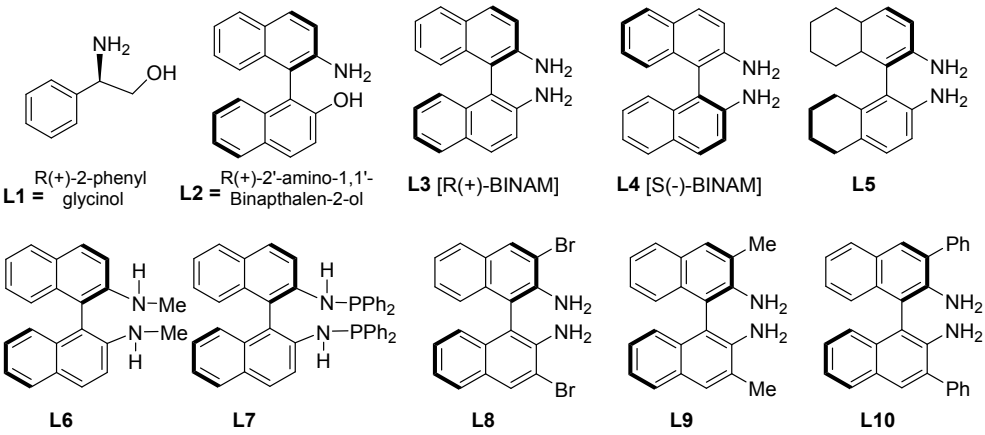



**Table 1**. Selected screening data toward the catalytic synthesis of chiral *N*-aryl allylamines




| Entry | Ligand | Temp (°C) | Solvent | % Yield[a] | % ee[b] |
|---|---|---|---|---|---|
| 1 | **L1** | RT | Dioxane | 46 | 5 |
| 2 | **L2** | RT | Dioxane | 62 | 9 |
| 3 | **L2** | RT | $CH_2Cl_2$ | 58 | 28 |
| 4 | **L3** | RT | $CH_2Cl_2$ | 62 | 70 |
| 5 | **L3**[c] | RT | $CH_2Cl_2$ | 65 | 62 |
| **6** | **L3**[d] | **RT** | **$CH_2Cl_2$** | **67** | **69** |
| 7 | **L3** | RT | $CHCl_3$ | 54 | 46 |
| 8 | **L3** | 50 | $CH_2Cl_2$ | 68 | 23 |
| 9 | **L3** | 0 | $CH_2Cl_2$ | 6 | ND |
| 10 | **L4** | RT | $CH_2Cl_2$ | 64 | 73 |
| 11 | **L5** | RT | $CH_2Cl_2$ | 62 | 56 |
| 12 | **L6** | RT | $CH_2Cl_2$ | 53 | 14 |
| 13 | **L7** | RT | $CH_2Cl_2$ | 13 | <5 |
| 14 | **L8** | RT | $CH_2Cl_2$ | 64 | 43 |
| 15 | **L9** | RT | $CH_2Cl_2$ | 58 | 46 |
| 16 | **L10** | RT | $CH_2Cl_2$ | 60 | 39 |

[a]Measured by GC-MS [b]Measured by chiral GC [c]1:1 and [d]**1:1.2** Metal-Ligand ratio

Preliminary investigations suggested that the tested privileged chiral ligands are not effective in terms of both the enantioselectivity and the product formation. However, surprisingly, simple amino alcohols such as *R*-(+)-2-phenyl glycinol (**L1**, 5% ee) and *R*- (+)-2'-amino-1'-binapthalen-2-ol (**L2**, 9% ee) induced some enantioselectivity at room temperature. Consequently, we have varied the reaction temperatures and solvents while keeping pre-catalyst and ligand the same. Replacing the 1,4-dioxane with dichloromethane, substantially improved the enantioselectivity (**L2**, 28% ee) without compromising % yield. When we lowered the reaction temperature to 0$^{o}$ C, the % yield of desired allylamine product dropped considerably while the formation of azo and azoxybenzene byproducts significantly increased (entry 9, Table 1). Lowering catalyst loading to 5% led to decrease in yield while maintaining similar % ee. Considering these conditions and the structural features of **L1** and **L2** ligands, we tested some commercially available ligands with diol, amino alcohol, and diamine functionalities including axially chiral compounds. Except *R*-(+)-1,1′-Binaphthyl-2,2′-diamine (BINAM, **L3**, 69% ee, entry 6), none of them improved enantioselectivity. Based on these observations, we anticipated that the structurally modified *R*-(+)-BINAM ligand may improve the electronic and steric effects of the catalytic system thereby enhancing enantioselectivity.[20] Accordingly, ligands **L6**, **L7** and **L9** were acquired commercially and other substituted BINAM ligands (**L5**, **L8** and **L10**) were prepared using catalytic reduction, halogenation, and cross-coupling methods.[21] We have introduced aryl substitutions on ortho-position to the amine group on BINAM. Even though they are equally effective in terms of enantioselectivity, none of them outperformed *R*-(+)-BINAM ligand. With the systematic optimization of ligands, pre-catalysts, metal-ligand ratios and solvents at room temperature, we found that 1:2 ratio of $Cu(MeCN)_4PF_6$ and *R*-(+)-BINAM using dichloromethane as a solvent worked well in terms of product yields and enantioselectivity. The initial results of this work have been patented.[22]

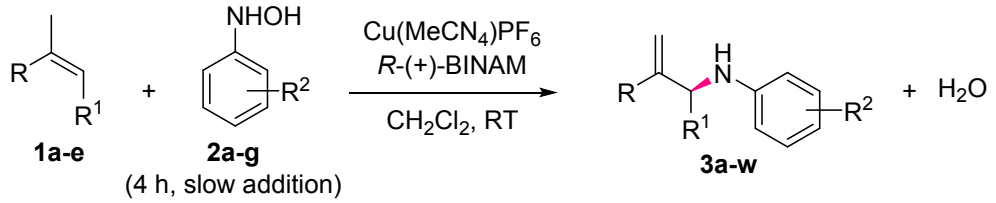
With these optimized conditions, the scope of the substrate structure was investigated. The initial focus was set on variations of the alkenes (**1a-1h**) using *N*-phenyl hydroxylamine (**2a**) as an amine source. (Table 2) Along with the 2-methyl-2-pentene (**1b**), we have considered a set of homologous alkenes to check the effect of chain length and substitutions (**1a, 1c, 1d, 1e**). Even though the product yields are comparable, enantioselectivities slightly increased on going from methyl to a higher chain length. Keeping the alkene partners same, we chose a set of substituted *N*-aryl hydroxylamines (**2b**-**2g**) having methyl and halo-substituents at different positions on ring.

Both electron-deficient and electron-rich aryl hydroxylamine partners reliably delivered desired chiral allylamine products (**3f-3t**) (Table 2). Compared to phenylhydroxylamine (**2a**) and *p*-tolyl hydroxylamine (**2b**), haloaryl hydroxylamines (**2c**-**2f**) produced relatively higher yields and enantioselectivities of desired *N*-aryl allylamines (**3j**-**3q, 3s, 3t**). However, when compared to the *N*-aryl allylamines **2c** (*p*-iodo) and **2e** (*m*-iodo), presence of large 'iodo' group at ortho-position (**2f**) negatively impacted the enantioselectivity as well as isolated yield. Moreover, the *N*-aryl hydroxylamine with para-withdrawing group (*p*-CN, **2g**) led to low conversion as well as poor enantioselectivity. It should be noted here, the chiral allylamine products with halo substituent can undergo further cross-coupling reactions for the elaboration of more complex chiral amine compounds.[23]

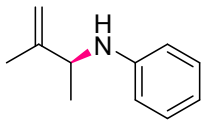
We have previously reported non-asymmetric amination approaches for making highly functionalized *N*-aryl aza Baylis-Hillman adducts[15k] and aminomethyl dienes/trienes.[17b] With that knowledge, we extended the current asymmetric catalytic approach to new substrates such as ethyl tiglate (**1f**), 3-methylpent-1,3-diene (**1g**), 2,6-dimethyloct-2,4,6-triene (**1h**). The α,β-unsaturated ester **1f** produced the corresponding chiral amine (**3u**) in good yield but with low enantioselectivity. However, enantioselectivity was increased from 23% to 51% when the same reaction performed in presence of ligand **L10**. Additionally, the diene **1g** and triene **1h** also produced the corresponding allylamines (**3v**, **3w**) with moderate enantioselectivities. (Table 2) Overall, this catalytic allylic C-H amination method works well with simple alkenes and *N*-aryl hydroxylamines.

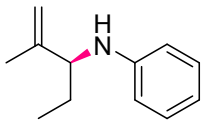
Having developed the optimized catalytic method, we turned our attention to studying mechanistic aspects of the reaction. Metal-nitroso (M-ONR) complexes are highly electrophilic in nature and are reactive toward the nucleophilic olefin via nitroso-ene reactions which is the basis for allylic amination of olefins. We have previously studied mechanistic aspects of this reaction including isolation of intermediate Fe- and Cu-complexes, kinetic experiments and computational studies.[15-17] A Cu(I)-nitrosoarene complex, i.e. $\{Cu[N(O)Ar]_3\}^+$, was synthesized and characterized by us.[16,17a] Implication of this complex has been established in the allylic amination reaction. Similarly, a recent report by Warren et al.[19] on the synthesis of Cu(I)-β-ketiminate C-nitroso complexes reveals both Cu-(N-O) and Cu-N(O) bonding modes in complexes $[L_nCu(\eta^2\text{-}ONAr)]$ and $\{L_nCu[\eta^1\text{-}N(O)Ar]\}$.[24] In contrast to Warren's study, the use of tetradentate ligand ($Me_6$tren) leads to formation of $\{L_nCu[\eta^1\text{-}O(N)Ar]\}$ in which oxygen is coordinated to copper.[25]

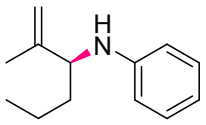
**Table 2.** Asymmetric Allylic Amination of Olefins by *N*-Hydroxylamines[a, b, c, d]

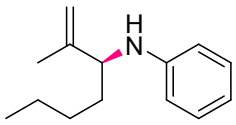


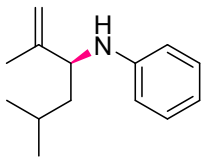

**1a-e** + **2a-g** (4 h, slow addition) → **3a-w**

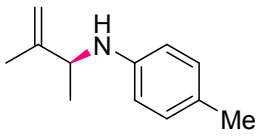

**3a** (58%), 53% *ee*

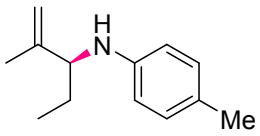

**3b** (67%), 69% *ee*

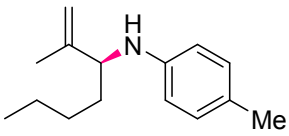

**3c** (61%), 63% *ee*

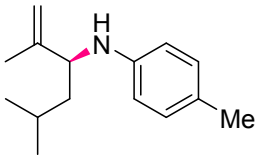

**3d** (59%), 61% *ee*

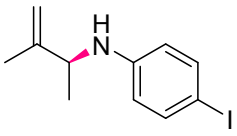

**3e** (65%), 67% *ee*

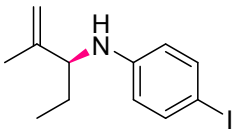

**3f** (55%), 53% *ee*

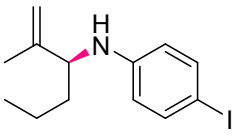

**3g** (58%), 72% *ee*

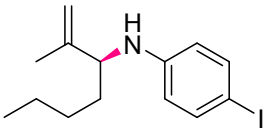

**3h** (62%), 66% *ee*

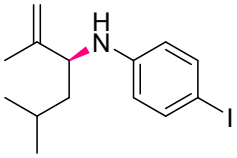

**3i** (65%), 46% *ee*

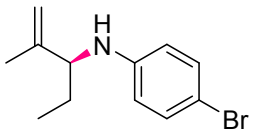

**3j** (76%), 70% *ee*

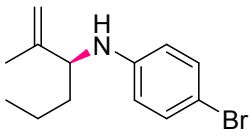

**3k** (86%), 79% *ee*

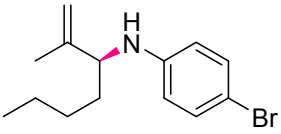

**3l** (78%), 60% *ee*

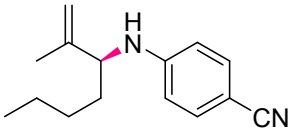

**3m** (81%), 73% *ee*

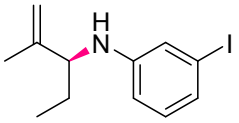

**3n** (73%), 61% *ee*

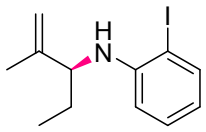

**3o** (79%), 48% *ee*

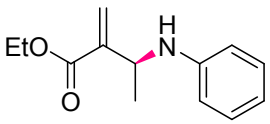

**3p** (71%), 63% *ee*

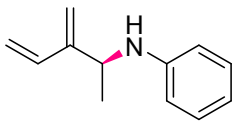

**3q** (68%), 60% *ee*

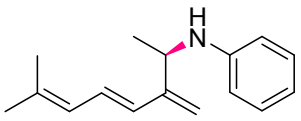

**3r** (35%), 26% *ee*


**3s** (82%), 75% *ee*


**3t** (68%), 29% *ee*


**3u** (54%), 23% *ee*
(57%), 51% *ee*[e]


**3v** (48%), 40% *ee*


**3w** (58%), 39% *ee*

[a] Reaction conditions: ArNHOH (0.5 mmol), olefin (1.5 mmol), $Cu(MeCN)_4PF_6$ (10 mol %), *R*-(+)-BINAM (12 mol %), dichloromethane (6 mL), T = 25 °C, 5-8 h. [b] Yields were reported after isolation from silica column. [c] Azoxybenzene is commonly observed as a sideproduct. [d] Enantiomeric excess (*ee*) was measured by chiral HPLC. [e] Used **L10** as a chiral ligand.

With that knowledge on various metal-nitroso binding modes and mechanisms, we made attempts in identifying and isolating chiral metal-nitroso complexes to understand the mechanistic aspects. Over the past decade, various methodologies have been developed to enhance the ability of ESI-MS to continuously monitor catalytic reactions as they proceed which helped in determining the mechanistic pathways of several homogenous catalytic mechanisms.[26] We adopted an ESI-MS online reaction monitoring analysis approach to identify intermediate complexes and determine their catalytic behavior. We pursued online monitoring ESI-MS analysis in a sequential manner by injecting sample after adding each reagent. A solution of $Cu(CH_3CN)_4PF_6$ and *R*-(+)-BINAM (**L3**) in dichloromethane was stirred for 10 min, and then monitored by ESI(+)-MS. As shown in table 3, four clusters identified and are attributed to $[Cu(BINAM)]^+$, $[Cu(H_2O)(BINAM)]^+$, $[Cu(CH_3CN)(BINAM)]^+$, and $[Cu(BINAM)_2]^+$ respectively. The ESI(+)-MS/MS of first three complexes (entries C1-C3) have a 1:1 metal-ligand ratio, whereas the fourth one (entry C4) has 1:2 metal-ligand ratio. After 10 minutes of mixing $Cu(CH_3CN)_4PF_6$ and *R*-(+)-BINAM, 2-methyl-2-pentene (**1b**) was added followed by slow addition of phenyl hydroxylamine (**2a**) over an hour and the sample collected for ESI(+)-MS analysis. (Table 3) After 1 hour, the ESI(+)-MS showed two new clusters (entries C5 and C6) at *m/z* 522 and 537, and they could be attributed to [Cu(**3b**)(BINAM)]+ and [Cu(BINAM)(1b+PhNO-H)]+ respectively.

**Table 3**. List of clusters identified from ESI(+)-MS (5 eV) analysis.

| Entry | Proposed structures | Formula | Calculated | Found |
|---|---|---|---|---|
| C1 | $[Cu(BINAM)]^+$ | $C_{20}H_{16}CuN_2$ | 347.0609 | 347.0612 |
| C2 | $[Cu(H_2O)(BINAM)]^+$ | $C_{20}H_{18}CuN_2O$ | 365.0715 | 365.0706 |
| C3 | $[Cu(CH_3CN)(BINAM)]^+$ | $C_{22}H_{19}CuN_3$ | 388.0875 | 388.0863 |
| C4 | $[Cu(BINAM)_2]^+$ | $C_{40}H_{32}CuN_4$ | 631.1923 | 631.1934 |
| C5 | [Cu(**3**)(BINAM)]+ | $C_{32}H_{32}N_3Cu$ | 522.1970 | 522.1981 |
| C6 | [Cu(BINAM)(1b+PhNO-H)]+ | $C_{32}H_{32}N_3OCu$ | 537.1841 | 537.1844 |

As shown in table 3, the HRMS confirmed the formula of predicted structures (**Figure 1**). Based on these observations, we can conclude that there are two types of complexes formed in the reaction with different metal-ligand ratios i.e. 1:1 and 1:2. However, 1:1 metal-ligand complex seems to be responsible for asymmetric induction in C-N bond formation.

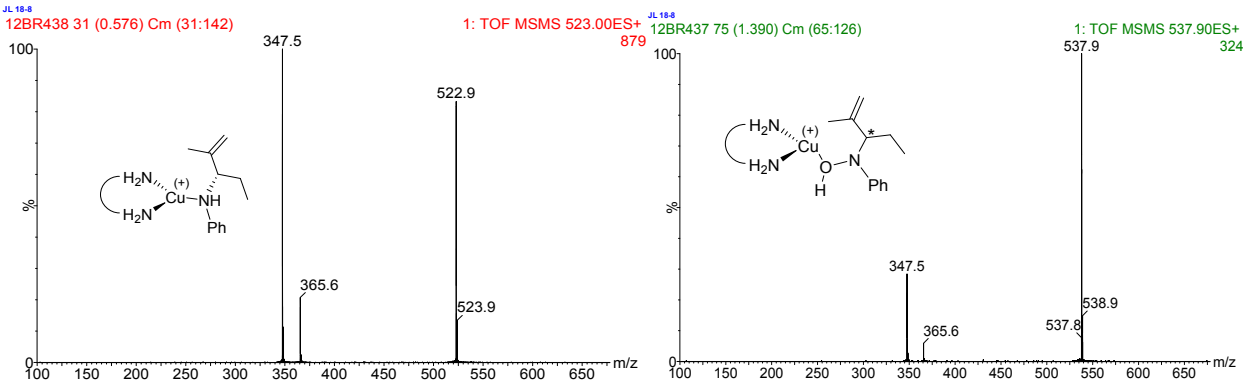
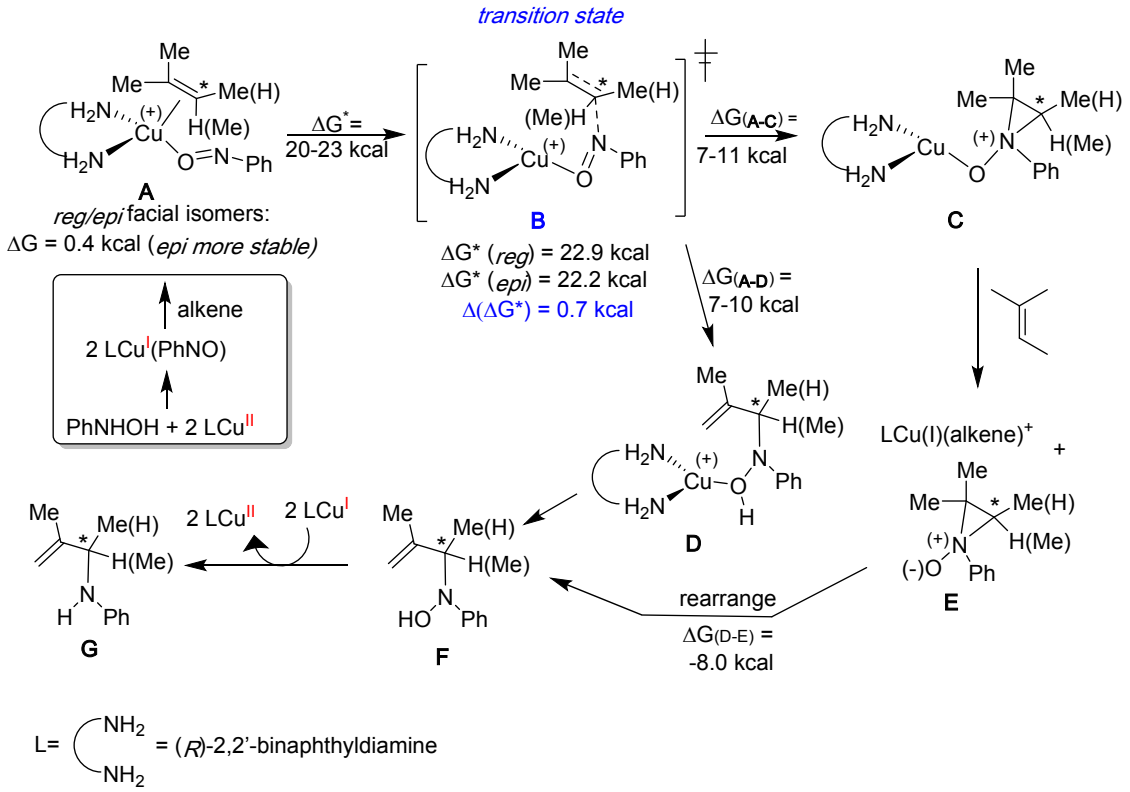



**Figure 1**. ESI(+)-MS/MS of clusters at *m/z* 522 and *m/z* 537.

To foster further understanding of catalytic activity and reaction pathway, we made attempts to isolate and characterize a Cu-BINAM complex. Although we were not successful in obtaining a single crystal of $Cu^{I}(MeCN)_4PF_6$/ *R*-(+)BINAM (**4a**), our attempt with $Cu^{II}OTf_2$- *R*-(+)BINAM produced {$[Cu(BINAM)_2OTf_2]$, (**4b**) which was characterized by X-ray crystallography. As can be seen from the crystal structure provided in supplementary information (Figure **S1**), the metal-ligand ratio of the isolated complex is 1:2. We treated this complex **4b** with nitrosobenzene and p-*N,N'*-dimethyl nitrosobenzene in two separate reactions. However, we were only able to isolate the metal-ligand-nitrosoarene complex $[Cu(BINAM)_2$(p-N,N'-$Et_2PhNO)_2OTf_2]$, (**4c**) with *p-N,N'*-diethyl nitrosobenzene. The X-ray crystallographic analysis of **4c** clearly indicates that two molecules of p-*N,N'*-dimethyl nitrosobenzene coordinated to the metal with the *trans*-octahedral geometry. (Figure **S2**, SI) It is noteworthy that **4c** has Cu(II) and that the ArNO unit is O-bound to Cu. Later we tested the catalytic activity of complex **4b** for the reaction of *N*-phenylhydroxylamine (**2a**) and 2-methyl-2-pentene (**1b**). Although the expected allylamine was produced, the very low enantioselectivity (<5% ee) of the product indicates the complex **4b** is probably not responsible for the asymmetric induction. We also treated the isolated complex **4c** with 2-methyl-2-pentene, but no allylamine product was observed. We have previously established that p-*N,N'*-diethylnitrosobenzene is less reactive towards alkenes to produce allylamine.[16,17] Nevertheless, the crystal structure of metal-ligand-nitrosoarene complex (**4c**) provides some important aspects of binding modes of ligand and nitrosoarene, and the nitroso-activation for the amination reactions. To probe the possible metal-nitroso intermediate complexes formation, we performed a control experiment replacing *N*-phenylhydroxylamine with nitrosobenzene under same experimental conditions which resulted in the formation of product **3a** (52% yield) with slightly reduced enantioselectivity (47%).

The results of ESI-MS reaction monitoring analysis and isolation of copper-complexes prompted us to consider a computational investigation to predict possible intermediates and the reaction pathway for the asymmetric allylic amination. A potential reaction pathway that accounts for the enantioselectivity was addressed with the DFT-B3LYP method (SMD solvent model for $CH_2Cl_2$). Various $(diamine)_xCu(I,II)(alkene)(PhNO)^+$ species were evaluated for the reaction of *N*-phenyl hydroxylamine (**2a**) with 2-methyl-2-butene (**1b**) using *R*-(+)-BINAM (**L3**) as the chiral ligand. An energetically viable pathway for the asymmetric amination that affords the corresponding chiral allylamine ($\Delta G_{calc}$= -23.7 kcal) was found starting with {*R*-(+)-BINAM)Cu(I)(alkene)(PhNO)}$^+$ **A** as a key intermediate (Scheme 2).




**Scheme 2**. Plausible mechanistic pathway of Cu-catalyzed asymmetric allylic amination

Two alkene facial isomers of **A** were optimized (*pro-R* and *pro-S*) with the *pro-S* isomer being more stable by 0.4 kcal/mol. Two isomeric C-N bond-forming transition states (TS) **B**, generated from the facial isomers of **A**, could be located with activation energies of 22.2 and 22.9 kcal/mol, a difference (ΔΔG*) of 0.7 kcal. The lower activation energy from the *pro-S* isomer predicts the stereoselective formation of the (*S*)-allylamine with approximately 54% ee with the *R*-(+)-BINAM ligand, in good agreement with our experimental results (see supporting

information) showing the (*S*)-allylamine (**3a**) as the major enantiomer with 53% ee. A comparison of the diastereomeric transition state free energies for **B** with the B3LYP and M06 functionals gave very similar differences of 1.1 and 1.0 kcal/mol, again leading to the experimentally favored *S*-product. This supports the validity of the proposed intermediates, the mechanistic pathway and the calculational methods employed.

The transition state **B** shows that C-N bond formation is initiated asynchronously before C-H bond-breaking (Figure 2). The preferred regioselectivity for attack at the less-substituted alkene **C** is previewed by the differing C-N distances (1.84 vs. 2.6 Å) in the TS. As C-N bond formation completes from TS **B**, two intermediates of comparable energy, **C** or **D**, may form; **C** is a Cu-coordinated aziridine *N*-oxide and **D** is a Cu-complexed *N*-allyl hydroxylamine. In the next step, the free aziridine *N*-oxide **E** detaches from complex **C**, while the (BINAM)Cu+ fragment associates with alkene to generate {(*R*-(+)-BINAM)Cu(alkene)}$^{+}$. Rapid rearrangement of the aziridine *N*-oxide **E** via H-transfer and ring opening, a known process that occurs stereospecifically,[28] would produce the allyl hydroxylamine **F**. Alternatively, the hydroxylamine **F** could form via dissociation from complex **D**. Subsequent Cu(I) reduction of **F** would give the allylamine **G** and (BINAM)Cu(II) that can re-enter the catalytic cycle after one-electron reduction.[16,17a] The stepwise nature of the conversion of **A** to allyl hydroxylamine **F** can be compared to the stepwise, diradical pathway implicated for the uncatalyzed ArNO/alkene ene-reaction.[29]

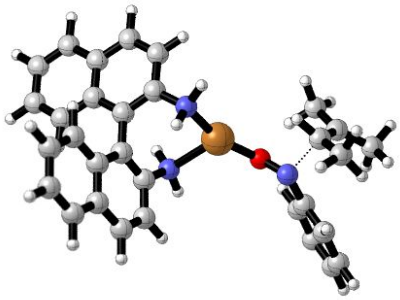


**Figure 2**. Favored *pro*-S transition state for the reaction of (*R(+)*-BINAM)Cu(PhNO)($\eta^2$-2-methyl-2-butene)$^{+}$ leading to the (*S*)-hydroxylamine **F**; N-C3 = 1.84 Å, N-C2 = 2.46 Å; C=grey, H=white, N=blue, O=red, Cu=bronze.

**Conclusions**:

We have developed a novel catalytic asymmetric allylic C-H amination approach for the amination of simple alkenes with *N*-arylhydroxylamines. This procedure can be operated without

any special precautions as it works at room temperature utilizing an *in situ* generated copper catalytic system i.e. the combination of $Cu(CH_3CN)_4PF_6$ and *R*-(+)-BINAM. We have extended this approach to access other useful chiral amine compounds employing α,β-unsaturated carbonyl compound, diene and triene as alkene partners. We have also established the configuration of major enantiomers obtained in this reaction. To gain additional insights on the reaction mechanism, we have monitored the reaction with ESI-MS analysis, isolated metal complexes, performed control experiment with nitrosobenzene, and predicted the possible intermediates based on computational studies. Overall, this simple and straight forward methodology marks a significant step forward in the synthesis of the chiral *N*-aryl allylamine scaffolds. DFT modeling of the reaction pathway suggests that the stereoselectivity is determined in the conversion of (BINAM)Cu(PhNO)($\eta^2$-alkene)$^+$ to (BINAM)Cu(N-Ar hydroxylamine) via a concerted, asynchronous transition state for C-N bond formation.

**Author Contributions**:

S. M., K. M. N., R. S. S.: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Project administration, Resources, Software, Supervision, Validation, Writing – original draft Writing – review & editing. S. M., B. D. M., R. B., D. H., J. L. B., F. F.: Methodology, Data curation, Investigation, Writing.

**Conflicts of Interest**:

There are no conflicts of interest.

**Acknowledgements**:

We thank Dr. Sushant Sahu for helping us with the HPLC data collection for the control experiments. We are grateful for financial support from the NSF (CHE1566561 to RSS and SM) and NIH-NIGMS (1R15GM120663-01 to RSS), LBRN Full Project Award (to SM) from IDeA Networks of Biomedical Research Excellence (INBRE-NIGMS/NIH P2O GM103424-19). KN acknowledges support from the National Science Foundation (CHE 1566213), an A.C. Cope Scholar award and generous computer time from the OU Supercomputing Center for Education and Research (O.S.C.E.R.).

**Electronic Supporting Information Available:** Experimental procedures and structural characterization data including $^{1}$H- and $^{13}$C-NMR, HR-MS, HPLC, and X-ray crystallography analysis available for the synthesized compounds.

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