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Silicon-Directed Rhenium-Catalyzed Allylic Substitutions with *N*-Hydroxycarbamates, *N*-Hydroxysulfonamides, and Hydroxamic Acids

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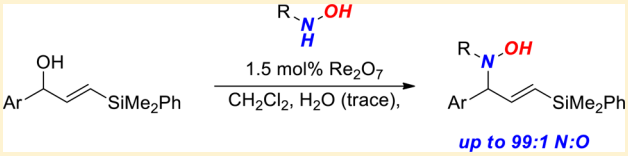
Supporting Information

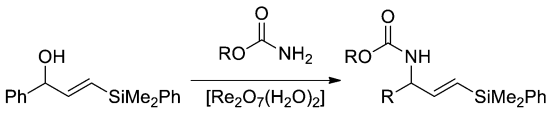
ABSTRACT: A rhenium-catalyzed *N*-selective allylic amination reaction of *N*-hydroxycarbamates has been developed. This reaction occurs with excellent *N*/*O* selectivity and with complete carbon selectivity on the allylic system. The reaction is tolerant of many functional groups and also proceeds with *N*-hydroxysulfonamides and hydroxamic acids.



Allylic aminations are an important class of reactions with their products being versatile intermediates for synthesis.[1] The majority of transition-metal-catalyzed methods proceed via π-allylic intermediates that are intercepted by an exogenous nitrogen nucleophile to form the requisite allyl amine. In particular, palladium[2] and iridium[3] are very common catalysts that provide the linear and branch products, respectively, with high levels of regiocontrol. Alternative metals including ruthenium and rhodium are also effective catalysts, however, less commonly used.[4] Although these methods are excellent when applied to monosubstituted allylic systems, they are much less efficient in the case of unsymmetrical 1,3-disubstituted arrangements that can lead to poor regioselectivity.

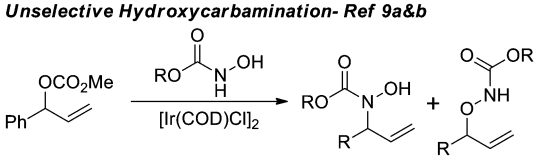
We recently reported the regioselective carbamination of 1,3-substituted allylic alcohols using a rhenium catalyst to provide allylic carbamates as a single regioisomer (eq 1).[5] This method

Regioselective Carbamination - Ref 5



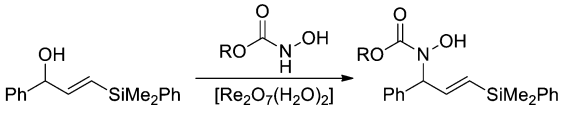
(1)

Unselective Hydroxycarbamination- Ref 9a&b



(2)

Highly Selective Hydroxycarbamination - This Work



(3)

gave exclusively the benzylic, nonconjugated regioisomer in contrast to other published methods that proceed via an allylic cation, which generally provide allylic substitution and conjugated products.[6] We examined the mechanism and found the active catalyst to be perrhenic acid $[Re_2O_7(H_2O)_2]$, which is formed through the reaction of Re_2O_7 with adventitious water in the reaction mixture.[5,7] This was established through a series of control experiments in which moisture was removed from the reaction, which led to no reaction proceeding, suggesting that the trace amount of water from these reactions being performed in an open flask was key. Further evidence was obtained through the complete inhibition of the reaction following the addition of base, thus implying that the active catalyst was in fact perrhenic acid. Following this discovery, we began examining the use of other nucleophiles for this reaction. As basic amine substrates inhibited the reaction, presumably through deprotonation of the acid catalyst, we examined the use of *N*-hydroxycarbamates to investigate their reactivity and regioselectivity.

The use of *N*-hydroxycarbamates and hydroxamic acids to directly form allylamines can be achieved in several ways. These include the nitroso-ene reaction in which a nitroso-carbamate can be generated in situ through the oxidation of the corresponding hydroxylamine.[8] There have also been several reports of transition-metal-catalyzed allylic and propargylic substitution reactions (eq 2).[9] Many of these methods suffer from poor *N*,*O*-selectivity issues, and when 1,3-disubstitution is present on the allylic system, poor carbon regioselectivity is also observed. Herein, we report a highly selective rhenium-catalyzed allylic amination using ambident hydroxylamine nucleophiles (eq 3).

We began examining 1-phenyl-3-silyl propenol **1a**,[10] which we had previously reported with the carbamination reaction. This substrate provided a single regioisomer with the benzylic carbamate being formed as the sole product (eq 1). A range of protected *N*-hydroxycarbamates were tested, and to our delight, excellent reactivity was observed in all cases (Table 1). The choice of protecting group was key to the regioselectivity. When Cbz protected hydroxylamine was used, the corresponding *N*-hydroxycarbamate **2a** was formed in a 99:1 mixture of *N* to *O*-isomers.[11] This was in contrast to the Boc derivative, which

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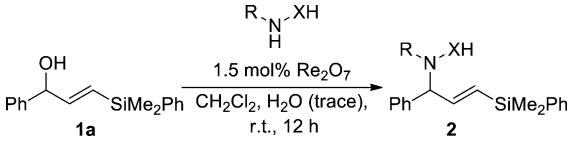
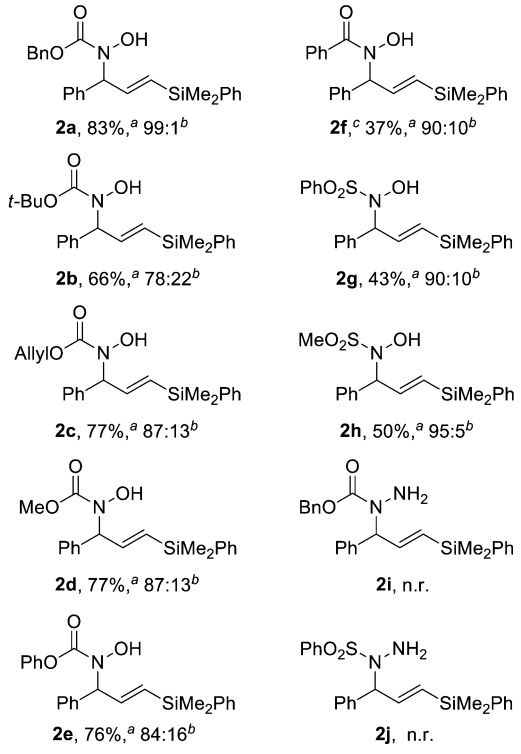
Table 1. Scope of Nucleophile[a,b,c]



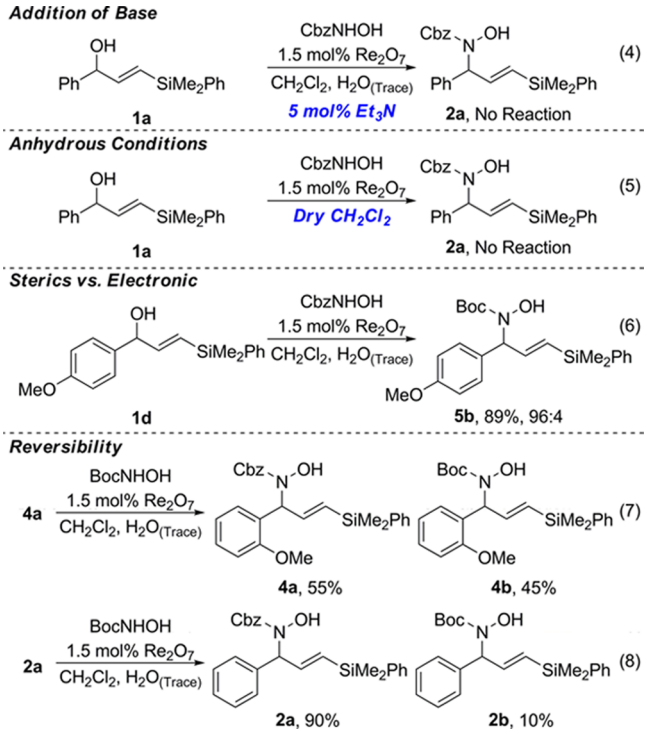


[a]Isolated yield of a single *N*-isomer. [b]*N*/*O* ratios determined by ^{1}H NMR of the crude reaction mixture. [c]Reaction performed at 45 °C.

provided a much lower selectivity of **2b** (78:22), and all other carbamates tested (allyl, methyl, and phenyl) **2c**–**e** provided inferior regioselectivities in the region of 85:15. We also examined hydroxamic acids and found a 90:10 ratio of products, albeit in lower yields. A similar scenario was found when *N*-hydroxysulfonamides were used with moderate yields and good to excellent selectivity observed. Hydrazides were also examined; however, both tosylhydrazide and Cbz-hydrazide gave no reaction with quantitative recovery of starting materials. This is presumably due to the inhibition of the catalyst by the basic nitrogen.

As excellent regioselectivities were achieved, we began to examine the scope of the reaction using CbzNHOH (Table 2). We found that the reaction was tolerant of a wide range of functional groups, including arylhalides, ethers, and alkenes, in the allylic alcohol **1**. In particular, electron-rich aromatic substrates gave both high yields and almost complete selectivity for the *N*-allylated isomers **2a**–**11a**. As the electron-rich substrates performed better, we reexamined the use of other nucleophiles (demonstrated in Table 1) with 2-methoxy substrate **1c**. Using the alternative carbamates, the yields and regioselectivities improved, providing the corresponding products **4b**–**e**, generally in around 90% isolated yield and >90:10 regioselectivity. When the hydroxamic acids and *N*-hydroxysulfonamides were used, similar improvements were observed with increased yields and selectivities of the *N*-allylated products **4f**–**h**.

The iridium-catalyzed allylic substitution of *N*-hydroxycarbamated described by Takemoto proved moderately regioselective (3:2) when electron-deficient substrates were used.[9b] This indicated no inherent bias for *N*-allylation versus *O*-allylation. We believe the excellent *N*-selectivity observed in our case is due to the acidic nature of the reaction mixture. *N*-Hydroxycarbamates contain a relatively acidic proton with a pK_a of around 10.[12] Under neutral or mildly basic conditions, a proportion of the nucleophile could be present in the deprotonated form. As deprotonated *N*-hydroxycarbamates and hydroxamic acids exist in a dynamic equilibrium between *O*- and *N*-deprotonated forms,[12a] either of these anions can react with the allylic cation. This can lead to poor selectivity as the deprotonated form is more nucleophilic than its neutral counterpart. In our case, the reaction is mildly acidic, which counteracts this effect and ensures that the *N*-hydroxycarbamate is always present as the fully protonated form. To test this, we attempted the reaction with the addition of a base; however, this led to a complete inhibition of the reaction (eq 4). This is consistent with our previous findings with carbamate nucleophiles and further strengthens our argument that perrhenic acid $[Re_2O_7(H_2O)_2]$ is the active catalysts. We also performed the reaction under anhydrous conditions, and once again found no reaction occurring, thus suggesting that the adventitious water in the system is forming perrhenic acid (eq 5).



We were also intrigued by the enhancement of the *N*/*O* selectivity when the 2-methoxy substrate **1c** was used, and we examined the origin of this improved selectivity. This could be due to kinetic factors based on the sterics/electronics, or the more electron-rich nature of the substrate could lead to reversibility and a thermodynamic ratio being obtained. First, we examined the effect of sterics by reacting 4-methoxy substrate **1d** with BocNHOH, and the same ratio was obtained as in the 2-methoxy case, thus suggesting electronics as the main factor (eq 6). To further probe the nature of the electronic effect, we performed a series of crossover experiments by independently

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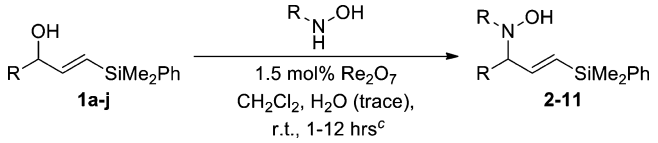
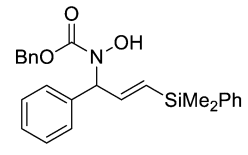
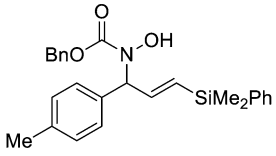
Table 2. Scope of Substrates[a,b,c]

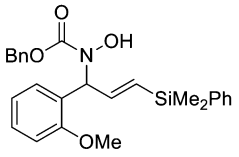




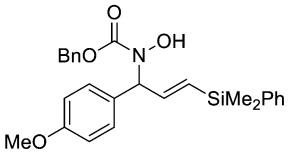
2a, 83%,[a] 99:1[b]



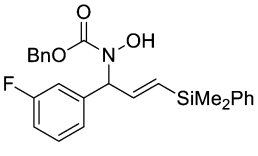
3a, 93%,[a] 98:2[b]



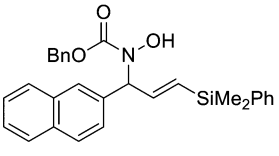
4a, 91%,[a] 98:2[b]



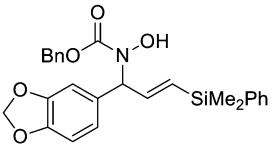
5a, 89%,[a] 99:1[b]



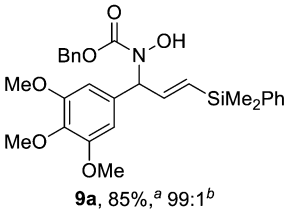
6a, 79%,[a] 99:1[b]



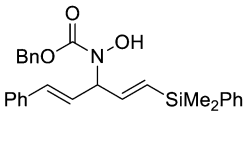
7a, 86%,[a] 99:1[b]



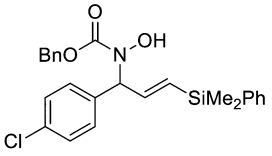
8a, 87%,[a] 99:1[b]



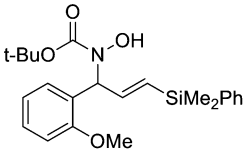
9a, 85%,[a] 99:1[b]



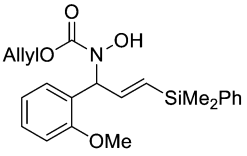
10a, 83%,[a] 99:1[b]



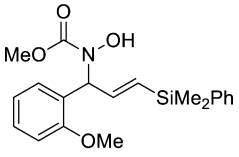
11a, 84%,[a] 92:8



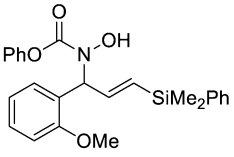
4b, 87%,[a] 96:4[b]



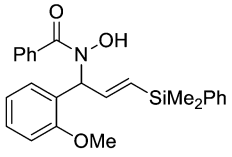
4c, 86%,[a] 96:4[b]



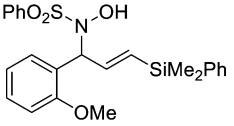
4d, 82%,[a] 89:11[b]



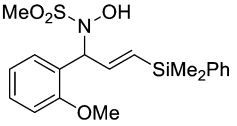
4e, 82%,[a] 92:8[b]



4f,[c] 58%,[a] 94:6[b]



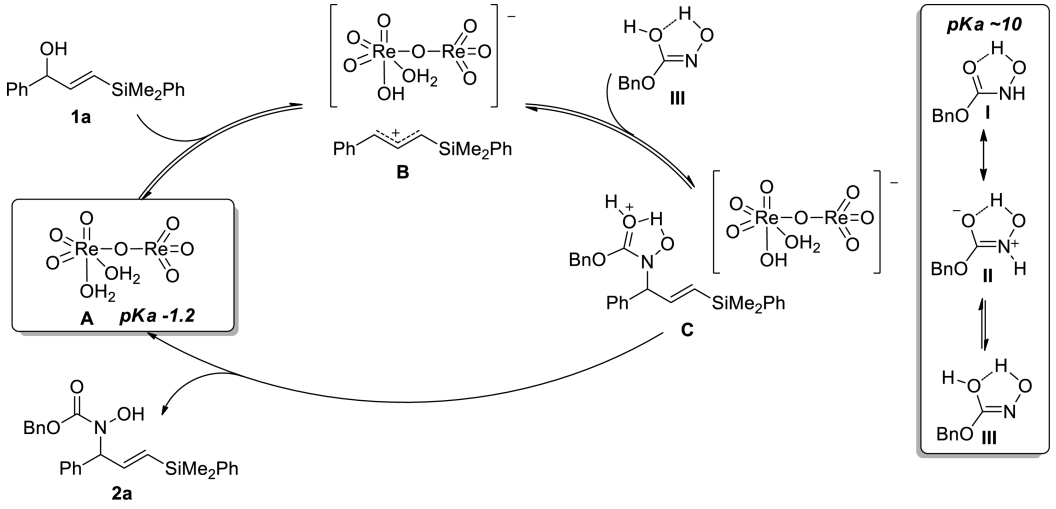
4g, 58%,[a] 94:6[b]



4h, 58%,[a] 96:4[b]

[a]Isolated yield of a single *N*-isomer. [b]*N*/*O* ratios determined by ^{1}H NMR of the crude reaction mixture. [c]See the Experimental Section for details.

Scheme 1. Proposed Mechanism



subjecting Cbz products **4a** and **2a** to the reaction conditions with BocNHOH. With the electron-rich methoxy substrate **4a**, a 55:45 mixture of products (**4a** and **4b**) was observed, thus confirming the reversible nature of the reaction (eq 7). In the case of the electron-neutral phenyl substrate **2a**, a much smaller amount of crossover was observed, confirming that this reaction

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is much slower to reverse (eq 8). These results imply that the ratio obtained in the phenyl substrate **1a** is much closer to the kinetic product ratio and the methoxy **1c** is more consistent with the thermodynamic outcome of the reaction.

From our mechanistic studies, we can propose the following mechanism (Scheme 1). *N*-Hydroxycarbamates **I** exist with a strong intramolecular hydrogen bond and can also isomerize to the *N*-nucleophile in acetimidate-type tautomer **III**. When allylic alcohol **1a** reacts with perrhenic acid **A**, an ionization occurs to form allylic cation **B**. This can then undergo an outer-sphere nucleophilic attack by **III** to form protonated *N*-hydroxycarbamate **C**. This protonated species can undergo the reverse reaction to regenerate the allylic cation and **III**. Proton transfer from **C** leads to regeneration of the perrhenic acid catalyst **A** and formation of the substituted *N*-hydroxylcabamate product **2a** (Scheme 1).

In conclusion, we have developed a highly regioselective *N*-selective addition of hydroxylamines to unsymmetrical allylic systems. The reaction proceeds with complete regioselectivity on the allylic portion and with excellent *N*/*O* selectivity. The scope of the reaction is very wide; however, electron releasing substrates are generally superior due to the reversible nature of the reaction.

EXPERIMENTAL SECTION

All reactions were carried out under an atmosphere of argon in oven-dried glassware unless otherwise mentioned elsewhere. All reactions were monitored by thin -layer chromatography (TLC) using Merck TLC silica gel 60 sheets, which were visualized with ultraviolet light and then developed with iodine and basic potassium permanganate or anisaldehyde solution. Flash chromatography was performed on Sigma-Aldrich silica gel 60 as the stationary phase, and the solvents employed were of analytical grade. Unless stated otherwise, all commercially available reagents were used as received. When necessary, commonly used organic solvents were dried prior to use according to standard laboratory practices.[13] NMR spectra were recorded at 400 MHz (^{1}H) and 100 MHz (^{13}C) and were referenced to $CDCl_3$ δ 7.26 and 77.2 ppm, respectively. Infrared spectra were recorded as a thin film on KBr discs. High-resolution mass spectra were obtained on mass spectrometers using electrospray ionization (ESI) or electron impact ionization at 70 eV and TOF analyzers.

General Procedure: Allylic Substitutions of β-Silyl Allylic Alcohols. To a stirred solution of alcohol (1 equiv) and amine (1.2 equiv) in dichloromethane (2 mL) was added Re_2O_7 (1.5 mol %), and the solution was stirred at room temperature or at 20 °C, in a flask open to the atmosphere. After the completion of the reaction, as judged by TLC, 1 mL of saturated ammonium chloride was added and the solution was extracted with dichloromethane (3 × 10 mL). The combined organic extract was dried over anhydrous sodium sulfate, and then the crude product was chromatographed to afford the requisite (*E*)-allylic hydroxylamine.

Benzyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-phenylallyl-*N*-hydroxycarbamate (2a). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 99:1 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **2a** (64 mg, 83%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.27; ν_{max} (thin film)/cm^{-1} 3277, 3030, 2955, 1702, 1402, 1290, 1250, 826, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.48 (m, 2H), 7.37−7.26 (m, 13 H), 6.40 (dd, J = 16.0 Hz, 4.0 Hz, 1H), 6.09−6.03 (m, 2H), 5.78 (dd, J = 4.0, 1.0 Hz, 1H), 5.20−5.12 (m, 2H), 0.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 142.7, 138.2, 137.6, 135.7, 133.8, 132.1, 129.0, 128.5, 128.4, 128.4, 128.3, 128.1, 127.8, 127.8, 68.1, 66.5, −2.5, −2.6; HRMS (ES$^+$) Calcd for $C_{25}H_{28}NO_3Si$ [M + H]$^+$ 418.1838, found 418.1829.

***tert*-Butyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-phenylallyl-*N*-hydroxycarbamate (2b).** After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 78:22 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **2b** (50 mg, 66%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.26; ν_{max} (thin film)/cm^{-1} 3315, 2952, 1693, 1359, 1247, 1163, 829; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.50 (m, 2H), 7.40−7.28 (m, 8 H), 6.43 (dd, J = 18.8, 5.0 Hz, 1H), 6.06 (dd, J = 18.8, 1.5 Hz, 1H), 5.74 (bs, 1H), 5.66 (dd, J = 4.0, 1.2 Hz, 1H), 1.46 (s, 9H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 143.2, 138.3, 138.0, 133.8, 132.0, 129.0, 128.4, 128.3, 127.8, 127.7, 82.4, 66.9, 28.2, −2.6, 2.7; HRMS (ES$^+$) Calcd for $C_{22}H_{33}N_2O_3Si$ [M + NH_4]$^+$ 401.2260, found 401.2250.

Allyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-phenylallyl-*N*-hydroxycarbamate (2c). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 87:13 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **2c** (53 mg, 77%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.26; ν_{max} (thin film)/cm^{-1} 3312, 2957, 1701, 1455, 1247, 1103, 827; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.49 (m, 2H), 7.39−7.27 (m, 8H), 6.42 (dd, J = 18.5, 5.2 Hz, 1H), 6.08 (dd, J = 18.5, 1.7 Hz, 1H), 6.02 (s, 1H), 5.99−5.85 (m, 1H), 5.79 (dd, J = 5.5, 1.4 Hz, 1H), 5.33−5.16 (m, 2H), 4.66−4.62 (m, 2H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 142.7, 138.2, 137.6, 133.8, 132.1, 132.0, 129.0, 128.5, 128.4, 127.9, 127.8, 118.3, 67.0, 66.4, −2.5, −2.6; HRMS (ES$^+$) Calcd for $C_{21}H_{26}NO_3Si$ [M + H]$^+$ 368.1682, found 368.1665.

Methyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-phenylallyl-*N*-hydroxycarbamate (2d). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 87:13 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **2d** (49 mg, 77%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.25; ν_{max} (thin film)/cm^{-1} 3319, 2955, 1702, 1590, 1449, 1275, 1110, 827, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.49 (m, 2H), 7.38−7.28 (m, 8H), 6.41 (dd, J = 18.8, 5.5 Hz, 1H), 6.08 (dd, J = 18.8, 1.5 Hz, 1H), 6.01 (bs, 1H), 5.77 (dd, J = 5.5, 1.5 Hz, 1H), 3.76 (s, 3H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 142.7, 138.2, 137.6, 133.8, 132.1, 129.0, 128.5, 128.4, 127.9, 127.8. 66.3, 53.5, −2.5, −2.6; HRMS (ES$^+$) Calcd for $C_{19}H_{27}N_2O_3Si$ [M + NH_4]$^+$ 359.1791, found 359.1783.

Phenyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-phenylallyl-*N*-hydroxycarbamate (2e). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 84:16 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **2e** (58 mg, 76%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.27; ν_{max} (thin film)/cm^{-1} 3311, 2963, 1697, 1460, 1247, 829; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.50 (m, 2H), 7.46−7.29 (m, 10H), 7.26−7.18 (m, 1H), 7.09−7.03 (m, 2H), 6.48 (dd, J = 18.5, 5.2 Hz, 1H), 6.17 (dd, J = 18.5, 1.4 Hz, 1H), 6.14 (s, 1H), 5.92 (d, J = 5.5 Hz, 1H), 0.39 (s, 3H), 0.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 150.8, 142.4, 138.1, 137.3, 133.8, 132.5, 129.3, 129.1, 128.6, 128.4, 128.0, 127.8, 127.7, 121.4, 66.9, −2.6,-2.6; HRMS (ES$^+$) Calcd for $C_{24}H_{29}N_2O_3Si$ [M + NH_4]$^+$ 421.1947, found 421.1957.

***N*-((*E*)-3-(Dimethyl(phenyl)silyl)-1-phenylallyl)-*N*-hydroxybenzamide (2f).** After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 90:10 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **2f** (27 mg, 37%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.24 ν_{max} (thin film)/cm^{-1} 3290, 3015, 2955, 1690, 1558, 1360, 1145, 826; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.09 (m, 2H), 7.82 (d, J = 7.5 Hz, 1H), 7.68−7.54 (m, 2H), 7.52−7.26 (m, 10H), 6.38 (dd, J = 18.5, 5.2 Hz, 1H), 6.19−6.06 (m, 3H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 148.5, 142.8, 133.7, 133.7, 131.0, 130.0, 129.7, 129.1, 129.0, 128.6, 128.5, 128.3, 128.0, 127.7, 67.7, −2.7,-2.8; HRMS (ES$^+$) Calcd for $C_{24}H_{26}NO_2Si$ [M + H]$^+$ 388.1703, found 388.1715.

Phenyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-phenylallyl-*N*-hydroxysulfonamide (2g). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 90:10 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **2g** (34 mg, 43%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.25; ν_{max} (thin film)/cm^{-1} 3295, 3106, 2966, 1677, 1501, 1440, 1152, 752; ^{1}H NMR (400 MHz, $CDCl_3$)

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δ 7.85−7.76 (m, 2H), 7.57−7.20 (m, 13H), 6.30 (bs, 1H), 6.17 (dd, *J* = 18.0, 3.0 Hz, 1H), 5.82 (dd, *J* = 18.0, 1.2 Hz, 1H), 5.31 (d, *J* = 6.0 Hz, 1H), 0.22 (s, 3H), 0.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 138.0, 137.9, 135.5, 133.7, 133.3, 133.2, 129.4, 129.0, 128.5, 128.4, 127.8, 127.7, 112.0, 69.3, −2.6, −3.0; HRMS (ES$^+$) Calcd for $C_{23}H_{26}NO_3SSi$ $[M + H]^+$ 424.1303, found 424.1311.

Methyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-phenylallyl-*N*-hydroxysulfonamide (2h). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 95:5 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **2h** (34 mg, 50%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.25; ν_{max} (thin film)/cm^{-1} 3293, 2965, 1600, 1540, 1360, 1150, 826; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.49 (m, 2H), 7.48−7.42 (m, 2H), 7.41−7.32 (m, 6H), 6.76 (bs, 1H), 6.51 (dd, *J* = 18.8, 6.2 Hz, 1H), 6.14 (dd, *J* = 18.8, 1.2 Hz, 1H), 5.42 (dd, *J* = 6.2, 1.2 Hz, 1H), 2.55 (s, 3H), 0.40 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 137.7, 136.5, 134.5, 133.7, 129.2, 129.0, 128.5, 128.3, 127.8, 68.6, 34.2, −2.7, −2.8; HRMS (ES$^+$) Calcd for $C_{18}H_{24}NO_3SSi$ $[M + H]^+$ 362.1224, found 362.1228.

Benzyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(4-methylphenyl)-allyl-*N*-hydroxycarbamate (3a). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 98:2 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **3a** (71 mg, 93%) as a yellow oil.

R_f (9:1 hexane−ethyl acetate) = 0.26; ν_{max} (thin film)/cm^{-1} 3317, 3026, 2953, 1706, 1510, 1247, 1114, 834, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.47 (m, 2H), 7.35−7.27 (m, 8H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.39 (dd, *J* = 18.6, 5.2 Hz, 1H), 6.08−6.00 (m, 2H), 5.75 (d, *J* = 4.7 Hz, 1H), 5.16 (s, 2H), 2.32 (s, 3H), 0.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 143.0, 138.2, 137.6, 135.7, 134.5, 133.8, 131.7, 129.1, 129.0, 128.5, 128.4, 128.2, 128.1, 127.7, 68.1, 66.2, 21.0, −2.5, −2.6; HRMS (ES$^+$) Calcd for $C_{26}H_{33}N_2O_3Si$ $[M + NH_4]^+$ 449.2260, found 449.2265.

Benzyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)-allyl-*N*-hydroxycarbamate (4a). After 4 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 98:2 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **4a** (136 mg, 91%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.24; ν_{max} (thin film)/cm^{-1} 3293, 2953, 1698, 1461, 1248, 1111, 822, 758; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.46 (m, 2H), 7.40−7.22 (m, 10H), 6.89 (td, *J* = 8.0, 7.5 Hz, 2H), 6.33 (dd, *J* = 18.5, 4.2 Hz, 1H), 6.32 (bs, 1H), 6.22 (dd, *J* = 4.4, 1.4 Hz, 1H), 5.99 (dd, *J* = 18.5, 1.4 Hz, 1H), 5.18 (d, *J* = 12.5 Hz, 1H), 5.12 (d, *J* = 12.5 Hz, 1H), 3.68 (s, 3H), 0.34 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 156.7, 143.3, 138.5, 136.1, 133.8, 130.5, 129.9, 129.1, 128.9, 128.3, 128.0, 127.8, 127.7, 125.8, 120.4, 110.6, 67.7, 60.5, 55.4, −2.5, −2.5; HRMS (ES$^+$) Calcd for $C_{26}H_{30}NO_4Si$ $[M + H]^+$ 448.1944, found 448.1931.

Benzyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(4-methoxyphenyl)-allyl-*N*-hydroxycarbamate (5a). After 4 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 99:1 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **5a** (94 mg, 89%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.25; ν_{max} (thin film)/cm^{-1} 3212, 2962, 1688, 1490, 1247, 1111, 827, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.47 (m, 2H), 7.40−7.28 (m, 8H), 7.26−7.21 (m, 2H), 6.87−6.81 (m, 2H), 6.37 (dd, *J* = 18.8, 5.2 Hz, 1H), 6.08 (bs, 1H), 6.03 (dd, *J* = 18.8, 1.4 Hz, 1H), 5.74 (dd, *J* = 5.0, 1.2 Hz, 1H), 5.18 (d, *J* = 12.2 Hz, 1H), 5.14 (d, *J* = 12.2 Hz, 1H), 3.77 (s, 3H), 0.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.2, 143.2, 138.2, 135.7, 133.8, 131.5, 129.7, 129.6, 128.5, 128.3, 128.1, 127.8, 127.7, 113.8, 68.1, 65.9, 55.2, −2.5, −2.6; HRMS (ES$^+$) Calcd for $C_{26}H_{33}N_2O_4Si$ $[M + NH_4]^+$ 465.2210, found 465.2228.

Benzyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(3-fluoro phenyl)-allyl-*N*-hydroxycarbamate (6a). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 99:1 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **6a** (120 mg, 79%) as a pale yellow oil.

R_f (9:1 hexane−ethyl acetate) = 0.25; ν_{max} (thin film)/cm^{-1} 3276, 3058, 2955, 1704, 1515, 1402, 1292, 1108, 848, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.46 (m, 2H), 7.38−7.25 (m, 9H), 7.12−7.02 (m, 2H), 6.97 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.60 (bs, 1H), 6.36 (dd, *J* = 18.8, 5.5 Hz, 1H), 6.04 (dd, *J* = 18.8, 1.2 Hz, 1H), 5.73 (d, *J* = 4.0 Hz, 1H), 5.20−5.12 (m, 2H), 0.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 244.0 Hz), 157.3, 142.1, 140.3 (d, J = 6.9 Hz), 138.0, 133.5, 133.7, 133.0, 129.8 (d, *J* = 8.0 Hz), 129.1, 128.5, 128.4, 128.1, 127.8, 123.8 (d, *J* = 3.0 Hz), 115.3 (d, *J* = 22.0 Hz), 114.7 (d, *J* = 21.0 Hz), 68.3, 66.1, −2.6, −2.6; HRMS (ES$^+$) Calcd for $C_{25}H_{30}FN_2O_3Si$ $[M + NH_4]^+$ 453.2010, found 453.1998.

Benzyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(naphthalen-3-yl)allyl-*N*-hydroxycarbamate (7a). After 6 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 99:1 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **7a** (126 mg, 86%) as a pale yellow oil.

R_f (9:1 hexane−ethyl acetate) = 0.29 ν_{max} (thin film)/cm^{-1} 3263, 3047, 2955, 1701, 1548, 1405, 1266, 1104, 823, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.72 (m, 4H), 7.55−7.49 (m, 2H), 7.48−7.43 (m, 3H), 7.37−7.30 (m, 3H), 7.29−7.20 (m, 5H), 6.48 (bs, 1H), 6.51 (dd, *J* = 18.8, 5.2 Hz, 1H), 6.08 (dd, *J* = 18.8, 1.4 Hz, 1H), 5.91 (d, *J* = 4.0 Hz, 1H), 5.13−5.04 (m, 2H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 142.9, 138.2, 135.7, 135.2, 133.8, 133.1, 132.8, 132.3, 129.0, 128.4, 128.2, 128.0, 128.0, 128.0, 127.8, 127.8, 127.5, 126.2, 126.0, 126.0, 68.1, 66.7, −2.5, −2.6; HRMS (ES$^+$) Calcd for $C_{29}H_{33}N_2O_3Si$ $[M + NH_4]^+$ 485.2260, found 485.2248.

Benzyl (*E*)-1-(Benzo[*d*][1,3]dioxol-6-yl)-3-(dimethyl(phenyl)-silyl)allyl-*N*-hydroxycarbamate (8a). After 3 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 99:1 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **8a** (63 mg, 87%) as a pale yellow oil.

R_f (9:1 hexane−ethyl acetate) = 0.17; ν_{max} (thin film)/cm^{-1} 3355, 2993, 1702, 1504, 1476, 1264, 1028, 823, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.46 (m, 2H), 7.40−7.28 (m, 8H), 6.84 (d, *J* = 1.4 Hz, 1H), 6.79−6.70 (m, 2H), 6.34 (dd, *J* = 18.8, 5.2 Hz, 1H), 6.07 (bs, 1H), 6.03 (dd, *J* = 18.8, 1.5 Hz, 1H), 5.96−5.90 (m, 2H), 5.69 (dd, *J* = 5.0, 1.5 Hz, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.15 (d, *J* = 12.0 Hz, 1H), 0.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 147.6, 147.2, 142.9, 138.1, 135.7, 133.8, 131.9, 131.4, 129.0, 128.5, 128.3, 128.1, 127.8, 122.0, 109.0, 108.1, 101.0, 68.2, 66.1, −2.5, −2.6; HRMS (ES$^+$) Calcd for $C_{26}H_{28}NO_5Si$ $[M + H]^+$ 462.1737, found 462.1721.

Benzyl (*E*)-1-(3,4,5-Trimethoxyphenyl)-3-(dimethyl(phenyl)-silyl)allyl-*N*-hydroxycarbamate (9a). After 1 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 99:1 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **9a** (60 mg, 85%) as a pale yellow oil.

R_f (9:1 hexane−ethyl acetate) = 0.16; ν_{max} (thin film)/cm^{-1} 3345, 2945, 1702, 1593, 1421, 1329, 1129, 833, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.45 (m, 2H), 7.40−7.28 (m, 8H), 7.15 (bs, 1H), 6.51 (s, 2H), 6.37 (dd, *J* = 18.8, 5.5 Hz, 1H), 6.08 (dd, *J* = 18.8, 1.4 Hz, 1H), 5.72 (dd, *J* = 5.0, 1.0 Hz, 1H), 5.25−5.14 (m, 2H), 3.82 (s, 3H), 3.74 (s, 6H), 0.38 (s, 3H), 0.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 142.5, 133.7, 133.5, 132.5, 129.1, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 105.3, 68.2, 67.8, 60.7, 56.0, 55.9, −2.6, −2.6; HRMS (ES$^+$) Calcd for $C_{28}H_{33}NNaO_6Si$ $[M + Na]^+$ 530.1975, found 530.1964.

Benzyl (1*E*,4*E*)-5-(Dimethyl(phenyl)silyl)-1-phenylpenta-1,4-dien-3-yl-*N*-hydroxycarbamate (10a). After 5 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 99:1 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **10a** (63 mg, 83%) as a yellow oil.

R_f (9:1 hexane−ethyl acetate) = 0.27; ν_{max} (thin film)/cm^{-1} 3485, 3026, 2993, 1705, 1507, 1340, 1255, 1108, 1002, 834, 699; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.44 (m, 2H), 7.41−7.27 (m, 13H), 6.61 (dd, *J* = 18.3, 10.0 Hz, 1H), 6.28 (dd, *J* = 15.2, 7.2 Hz, 1H), 6.09 (dd, *J* = 15.2, 1.2 Hz, 1H), 5.99 (d, *J* = 18.3 Hz, 1H), 5.83−5.74 (m, 1H), 5.28−5.15 (m, 3H), 0.36 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 144.4, 137.9, 136.5, 135.6, 133.8, 133.4, 129.6, 129.0, 128.5, 128.5, 128.3, 128.1, 127.9, 127.8, 127.8, 126.6, 68.2, 64.1, −2.6, −2.6; HRMS (ES$^+$) Calcd for $C_{27}H_{30}NO_3Si$ $[M + H]^+$ 444.1995, found 444.1989.

Benzyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(4-chlorophenyl)-allyl-*N*-hydroxy-carbamate (11a). After 12 h, the crude reaction mixture

was analyzed by ^{1}H NMR, indicating a 92:8 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **11a** (63 mg, 84%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.29; ν_{max} (thin film)/cm^{-1} 3205, 2968, 1693, 1489, 1388, 1101, 828, 753; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.47 (m, 2H), 7.40−7.22 (m, 12H), 6.35 (dd, J = 18.8, 5.4 Hz, 1H), 6.03 (dd, J = 18.8, 1.5 Hz, 1H), 5.83 (bs, 1H), 5.73 (dd, J = 5.5, 1.4 Hz, 1H), 5.19 (d, J = 12.2 Hz, 1H), 5.15 (d, J = 12.2 Hz, 1H), 0.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 142.3, 138.0, 136.1, 135.5, 133.8, 133.7, 132.9, 129.8, 129.1, 128.6, 128.5, 128.4, 128.2, 127.8, 68.3, 65.9, −2.6, −2.6; HRMS (ES$^+$) Calcd for $C_{25}H_{27}NO_3SiCl$ [M + H]$^+$ 452.1477, found 452.1489.

***tert*-Butyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(2-methoxy phenyl)-allyl-*N*-hydroxy-carbamate (4b).** After 6 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 96:4 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **4b** (121 mg, 87%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.20; ν_{max} (thin film)/cm^{-1} 3314, 2955, 1706, 1608, 1511, 1295, 1111, 829; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.47 (m, 2H), 7.41 (d, J = 7.5 Hz, 1H), 7.36−7.22 (m, 4H), 6.90 (td, J = 8.2, 7.5 Hz, 2H), 6.38 (bs, 1H), 6.35 (dd, J = 18.8, 4.5 Hz, 1H), 6.14−6.09 (m, 1H), 5.96 (dd, J = 18.8, 1.2 Hz, 1H), 3.80 (s, 3H), 1.40 (s, 9H), 0.35 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 156.5, 143.9, 138.6, 133.8, 130.3, 129.5, 129.2, 128.8, 127.6, 126.5, 120.4, 110.5, 81.5, 60.5, 55.5, 28.2, −2.5, −2.5; HRMS (ES$^+$) Calcd for $C_{23}H_{32}NO_4Si$ [M + H]$^+$ 414.2101, found 414.2115.

Allyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)-allyl-*N*-hydroxycarbamate (4c). After 4 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 96:4 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **4c** (57 mg, 86%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.24; ν_{max} (thin film)/cm^{-1} 3305, 2963, 1699, 1455, 1248, 1103, 825; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.48 (m, 2H), 7.40−7.23 (m, 5H), 6.95 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.33 (dd, J = 18.8, 4.5 Hz, 1H), 6.20 (dd, J = 4.0, 1.0 Hz, 1H), 6.04 (bs, 1H), 6.00 (dd, J = 18.8, 1.4 Hz, 1H), 5.96−5.84 (m, 1H), 5.34−5.16 (m, 2H), 4.66−4.60 (m, 2H), 3.80 (s, 3H), 0.36 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 156.6, 143.3, 138.5, 133.8, 132.4, 130.5, 130.0, 129.2, 128.9, 127.7, 125.8, 120.5, 117.7, 110.6, 66.7, 60.6, 55.5, −2.5, −2.5; HRMS (ES$^+$) Calcd for $C_{22}H_{28}NO_4Si$ [M + H]$^+$ 398.1788, found 398.1829.

Methyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)-allyl-*N*-hydroxycarbamate (4d). After 4 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating an 89:11 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **4d** (63 mg, 82%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.20; ν_{max} (thin film)/cm^{-1} 3247, 2954, 1698, 1457, 1298, 1245, 1112, 827, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.48 (m, 2H), 7.38−7.31 (m, 4H), 7.30−7.26 (m, 1H), 6.97−6.92 (m, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.34 (dd, J = 18.8, 4.4 Hz, 1H), 6.16 (dd, J = 4.5, 1.7 Hz, 1H), 6.07 (s, 1H), 5.99 (dd, J = 18.8, 1.7 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 0.36 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.9, 143.3, 138.5, 133.8, 130.5, 130.0, 129.2, 128.9, 127.7, 125.8, 120.5, 110.7, 60.7, 55.6, 53.2, −2.5, −2.6; HRMS (ES$^+$) Calcd for $C_{20}H_{29}N_2O_4Si$ [M + NH_4]$^+$ 389.1897, found 389.1904.

Phenyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)-allyl-*N*-hydroxycarbamate (4e). After 8 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 92:8 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **4e** (60 mg, 82%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.24; ν_{max} (thin film)/cm^{-1} 3309, 2965, 1702, 1458, 1245, 829; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.50 (m, 2H), 7.39 (dd, J = 7.5, 1.5 Hz, 1H), 7.37−7.28 (m, 6H), 7.22−7.17 (m, 1H), 7.11−7.05 (m, 2H), 6.97 (dd, J = 7.5, 6.5 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.41 (dd, J = 18.8, 4.5 Hz, 1H), 6.33 (dd, J = 4.5, 1.7 Hz, 1H), 6.11 (dd, J = 18.8, 1.5 Hz, 1H), 6.06 (bs, 1H), 3.81 (s, 3H), 0.38 (s, 3H), 0.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 155.0, 151.0, 142.8, 138.4, 133.8, 133.6, 130.4, 129.4, 129.2, 129.0, 127.8, 125.5, 125.4, 121.4, 120.6, 110.8, 61.2, 55.6, −2.5, −2.5; HRMS (ES$^+$) Calcd for $C_{25}H_{31}N_2O_4Si$ [M + NH_4]$^+$ 451.2053, found 451.2041.

***N*-((*E*)-3-(Dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)-allyl-*N*-hydroxybenzamide (4f).** After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 94:6 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **4f** (81 mg, 58%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.21; ν_{max} (thin film)/cm^{-1} 3293, 2965, 1691, 1488, 1360, 1145, 829; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20−8.13 (m, 1H), 7.92−7.77 (m, 2H), 7,75−7.26 (m, 11H), 6,86 (dd, J = 18.2, 1.0 Hz, 1H), 6.45−6.26 (m 3H), 3.70 (s, 3H), 0.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 138.2, 134.3, 133.7, 132.8, 130.9, 130.0, 129.7, 129.0, 128.8, 128.7, 128.4, 128.1, 127.7, 127.5, 126.6, 110.6, 65.7, 54.9, −2.4, −2.6; HRMS (ES$^+$) Calcd for $C_{25}H_{28}NO_3Si$ [M + H]$^+$ 418.1838, found 418.1842.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)-allyl-*N*-hydroxyphenylsulfonamide (4g). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 94:6 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **4g** (88 mg, 58%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.21; ν_{max} (thin film)/cm^{-1} 3290, 2956, 1675, 1490, 1335, 1152, 755; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.78 (m, 2H), 7.58−7.49 (m, 2H), 7.45−7.19 (m, 9H), 6.88−6.77 (m, 2H), 6.21 (dd, J = 18.0, 5.4 Hz, 1H), 5.89 (dd, J = 4.0, 1.0 Hz, 1H), 5.76 (dd, J = 18.0, 1.0 Hz, 1H), 3.78 (s, 3H), 0.23(s, 3H), 0.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 142.4, 138.3, 135.8, 133.7, 133.1, 131.5, 130.0, 129.2, 129.0, 128.9, 128.4, 127.7, 126.3, 120.5, 110.8, 62.6, 55.5, −2.6, −2.9; HRMS (ES$^+$) Calcd for $C_{24}H_{27}NNaO_4SSi$ [M + Na]$^+$ 476.1328, found 476.1338.

(*E*)-3-(Dimethyl(phenyl)silyl)-1-(2-methoxyphenyl)-allyl-*N*-hydroxymethylsulfonamide (4h). After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 96:4 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **4h** (38 mg, 58%) as a colorless oil.

R_f (9:1 hexane−ethyl acetate) = 0.22; ν_{max} (thin film)/cm^{-1} 3297, 2955, 1588, 1440, 1365, 1150, 827; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.43 (m, 3H), 7.41−7.25 (m, 4H), 6.98(d, J = 10.2 Hz, 1H), 7.00−6.85 (m, 2H), 6.49 (dd, J = 18.8, 6.2 Hz, 1H), 6.07 (dd, J = 18.8, 1.2 Hz, 1H), 5.98 (dd, J = 6.2, 1.3 Hz, 1H), 3.83 (s, 3H), 2.67 (s, 3H), 0.35 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 138.9, 133.8, 133.7, 133.0, 130.0, 129.6, 128.9, 127.9, 127.8, 127.8, 102.1, 63.6, 55.7, 24.6, −2.8, 2.8; HRMS (ES$^+$) Calcd for $C_{19}H_{26}NO_4SSi$ [M + H]$^+$ 392.1352, found 392.1348.

***tert*-Butyl (*E*)-3-(Dimethyl(phenyl)silyl)-1-(42-methoxy phenyl)-allyl-*N*-hydroxy-carbamate (5b).** After 12 h, the crude reaction mixture was analyzed by ^{1}H NMR, indicating a 96:4 mixture of *N*- to *O*-allylation products. Column chromatography (9:1 Hexane/EtOAc) isolated *N*-allylated product **5b** (64 mg, 89%) as a yellow oil.

R_f (3:1 hexane−ethyl acetate) = 0.21; IR ν_{max} (thin film)/cm^{-1} 3308,2976, 1706, 1625, 1501, 1053, 911, 806; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.20 (5H, m), 7.09 (1H, t, J = 7.5 Hz), 7.01 (2H, d, J = 7.0 Hz), 6.89 (2H, d, J = 8.5 Hz), 6.27 (1H, dd, J = 18.8, 5.5 Hz), 5.91 (1H, br s), 5.87 (1H, dd, J = 18.8, 1.5 Hz), 5.59 (1H, dd, J = 5.5, 1.3 Hz), 3.73 (3H, s), 1.49 (9H, s), 0.34 (3H, s), 0.33 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.2, 143.1, 139.8, 131.6, 130.1, 129.5, 128.4, 128.1, 124.0, 113.8, 82.5, 66.1, 55.5, 28.4, 26.0, −3.6; HRMS (ES$^+$) Calcd for $C_{23}H_{32}NO_4Si$ [M + H]$^+$ 414.2101, found 414.2101.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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